# Diastereoselective Allylations of Enantiopure 3- and 4-Substituted $\eta^4$-(1*Z*)-(Sulfinyldienal)iron(0) Tricarbonyl Complexes

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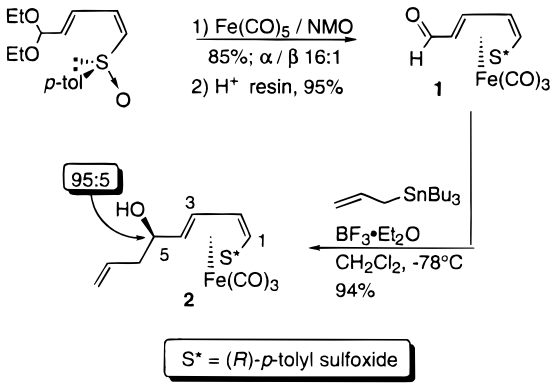
Diastereoselectivity of allylations of enantiopure 3- and 4-substituted $\eta^4$-(1*Z*)-(sulfinyldienal)iron(0) tricarbonyl complexes is dependent on the nature of the alkyl substituent. For 1-sulfinyl-1,3-pentadien-5-al iron complexes (**11a**−**d**), the aldehyde predominately reacts through the s-cis conformer, with diastereoselectivites as high as 95:5 (for homoallylic alcohol **13d**). For 3-formyl-1-sulfinyl-1,3-butadiene iron complexes (**12a**,**b**), the aldehyde predominately reacts through the s-trans conformer (diastereomer ratio for homoallylic alcohol, **14b**, 89:11).



## Introduction

As part of an ongoing project which has sought to utilize the stereodirecting ability of the chiral sulfoxide group[1] in combination with organotransition-metal chemistry,[2] we recently communicated the diastereoselective formation of an $\eta^4$-(1*Z*,3*E*)-(1-sulfinyldiene)iron(0) tricarbonyl complex and the diastereoselective allylation of the derived iron(0) dienal **1** to produce **2** (Scheme 1).[3] The absolute stereochemistry of the new stereocenter of **2** was unambiguously assigned on the basis of X-ray crystallography, which revealed that the major diastereomer was formed as a result of an attack of the nucleophilic allyl stannane upon the aldehyde in its preferred s-cis conformation and along a trajectory anti to the iron tricarbonyl fragment.[4] We were intrigued by the possibility that the presence of an additional substituent at $C_3$ of the diene unit would alter the $C_4$ aldehyde s-cis/s-trans conformational equilibrium and, thus, reduce or even invert the diastereoselectivity of the allylation process. Furthermore, we wondered if the stereochemical control of allylation of an aldehyde at that $C_3$ position would be similarly affected by a substituent a $C_4$. Indeed, we were unaware of a

**Scheme 1**




systematic study of this type involving the comparative diastereoselectivity of nucleophilic reactions along the periphery of iron(0) dienal complexes.[5] Here, we report that the diastereoselectivity of allylations of $\eta^4$-(1*Z*,3*E*)-(3-alkyl-1-sulfinylpentadien-5-al)iron(0) tricarbonyl complexes is highly dependent on the size of the substituent installed at $C_3$ and additionally that diastereoselective allylations of the 3-formyl-4-alkyl analogues are also possible.

## Results and Discussion

**Preparation of Enantiopure Sulfinyl Iron(0) Dienals.** Our planned investigation required the synthesis of analogues of **1** which possessed a functionalized substituent at $C_3$, as well as related sulfinyl iron(0) dienes in which the positions of the substituent and the formyl group were transposed. Preparation of the required sulfinyl iron(0) dienals was achieved by oxida-

(1) For recent reviews, see: (a) *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons: 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) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994.

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

(4) In contrast to the common preference for nucleophilic addition to the s-cis conformation of iron(0) dienals (see ref 5), Iwata has reported an s-trans imine conformational preference in the Lewis-acid-catalyzed addition of organometallic nucleophiles to 1-imino-(*E*,*E*)-iron diene complexes. Takemoto, Y.; Takeuchi, J.; Iwata, C. *Tetrahedron Lett.* **1993**, *34*, 6069−6072.

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

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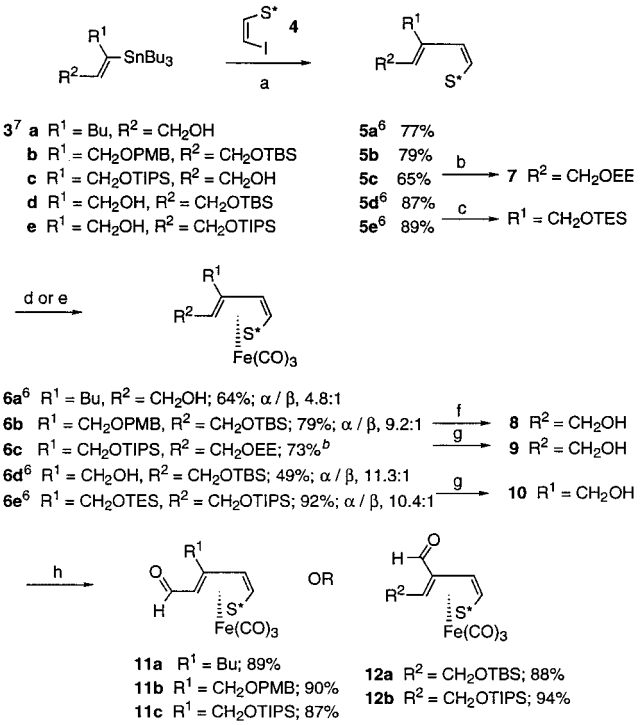
**Scheme 2**[a]

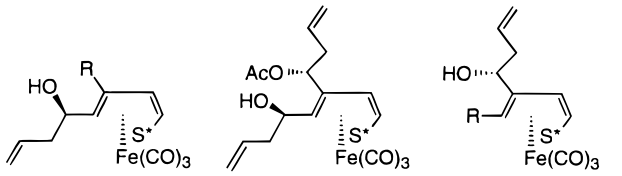



[a] Key: (a) $Pd(CH_3CN)_2Cl_2$ (2-4 mol%), DMF, RT; (b) EVE (10 eq), PPTS, $CH_2Cl_2$, RT, (97%); (c) TESOTf, 2,6-lutidine, $CH_2Cl_2$, RT (75%);[6] (d) For **6a**, **d**: $Fe(CO)_5$, NMO, THF, 0°C to Δ; (e) For **6b**, **c**, **e**: (bda)$Fe(CO)_3$, PhMe, 45°C; (f) TBAF/THF, RT, (93%); (g) HOAc/$H_2O$/THF, 4:1:1 (**9**: RT, 91%; **10**: 0°C, 85%); (h) $SO_3$•pyr, $NEt_3$, DMSO, $CH_2Cl_2$.
[b] α / β ratio not determined.

tion of the corresponding sulfinyl iron(0) dienols, which were each obtained by utilizing our previously reported methodology.[6] Thus, vinyl stannanes **3a**−**e**[7] were prepared and coupled to (*Z*)-2-iodovinyl sulfoxide **4** to provide (1*Z*)-1-sulfinyl dienes **5a**−**e** (Scheme 2).

Our approach to the corresponding sulfinyl diene iron(0) complexes evolved as this study unfolded. In our prior report,[6] we described that diastereoselective complexation of (1*Z*)-1-sulfinyl dienes could be effected with $Fe(CO)_5$ and NMO in modest but acceptable yields. This approach was taken for the synthesis of complexes **6a** and **6d**. To improve the efficiency of the complexation, we began to utilize (bda)$Fe(CO)_3$[8] as the iron tricarbonyl transfer reagent; complex **6b** was first prepared in this manner. Since the use of this reagent was not compatible with alcohol groups, we briefly examined two different protection groups. Sulfinyl diene **5e** was converted into its corresponding triethylsilyl ether in a 75% yield; complex **6e** was then readily obtained. Alternatively, we discovered that sulfinyl diene **5c** could be quantitatively converted to its 1-ethoxyethyl ether derivative **7**; this product was subsequently used without chromatographic purification, thus improving the overall reaction sequence which ultimately afforded sulfinyl iron(0) diene **6c** (Scheme 2). In all cases, the chromatographic separation of the diastereomeric complexes, which were typically formed with a high degree of diastereoselectivity (α/β ratio, ca. 10:1) using (bda)$Fe(CO)_3$, was trivial.

**Chart 1. Major Homoallylic Alcohol Diastereomers Obtained from Allylation of 11 or 12**




With access to an array of sulfinyl iron(0) dienes, conversion to the corresponding sulfinyl iron(0) dienals was straightforward. After selective deprotection where necessary, each sulfinyl iron(0) dienol was oxidized to the corresponding aldehyde **11a**−**c** and **12a**,**b** in excellent yield (Scheme 2).

**Diastereoselective Allylations of Sulfinyl Iron(0) Dienals.** Initial studies were performed with sulfinyl iron dienal **11a**. Treatment of **11a** with allyl tributylstannane and $BF_3$•$Et_2O$ at −78 °C provided homoallylic alcohols **13a** as a chromatographically inseparable mixture of diastereomers in a 65:35 ratio (Chart 1 and Table 1, entry 2). As all efforts to prepare a crystalline derivative of the pure major diastereomer were unsuccessful, we remained unable to unambiguously determine its absolute stereochemistry or to account for the substantially reduced diastereoselectivity of this process as compared to our prior report[3] (Table 1, entry 1). Similarly, allylation of sulfinyl iron dienal **11b** under identical conditions afforded the corresponding alcohols **13b** in a 72:28 diastereomeric ratio (Table 1, entry 3). Although a $^1H$ NMR chemical shift correlation was apparent, an unambiguous stereochemical assignment could not be made. (The major diastereomers of **2**, **13a**, and **13b** each had the more upfield $H_5$ methine and the more downfield $H_1$ absorptions; see Table 1.)

We next investigated the allylation of the related sulfinyl iron dienal **11c**. Homoallylic alcohols **13c** were obtained as an 82:18 ratio of diastereomers (Table 1, entry 4), which were readily separable by chromatography, and thus it became possible to purify the major diastereomer to 100% diastereomeric excess (de). Although neither this diastereomer nor its derivatives[9] could be crystallized in order to make a stereochemical determination by X-ray crystallography, satisfactory crystals of the *minor* homoallylic alcohol diastereomer, **13c(min)**, were ultimately obtained from toluene/hexane at −20 °C. Analysis by X-ray crystallography revealed that the configuration at $C_5$ of the *minor*

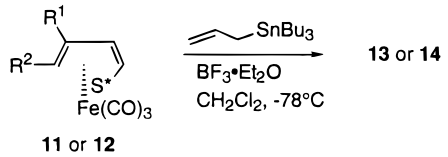
(6) Paley, R. S.; de Dios, A.; Estroff, L. A.; Lafontaine, J. A.; Montero, C.; McCulley, D. J.; Rubio, M. B.; Ventura, M. P.; Weers, H. L.; Fernández de la Pradilla, R.; Castro, S.; Dorado, R.; Morente, M. *J. Org. Chem.* **1997**, *62*, 6326−6343.

(7) Vinyl stannanes **3a** and **3c** were prepared according to the method of Oehlschalger; see: Hutzinger, M. W.; Oehlschalger, A. C. *J. Org. Chem.* **1995**, *60*, 4595−4601. See also: Boukouvalas, J.; Cheng, Y.-X.; Robichaud, J. *J. Org. Chem.* **1998**, *63*, 228−229. Vinyl stannanes **3b**, **3d**, and **3e** were prepared according to the method of Barrett; see: Barrett, A. G. M.; Barta, T. E.; Flygare, J. A. *J. Org. Chem.* **1989**, *54*, 4246−4249.

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

(9) Several derivatives were prepared from the major diastereomer of **13c**, including the corresponding acetate, diol, and diacetate. None could be crystallized.

**Table 1. Allylation of Enantiopure Sulfinyl Iron Complexes**




11 or 12

| | | | | | | | $^1$H NMR data | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $\delta$, $H_1$ (ppm) | | $\delta$, $H_5$ (ppm) | |
| entry | aldehyde | $R^1$ | $R^2$ | alcohol | % yield | d.r.[a] | major | minor | major | minor |
| 1[b] | **1** | H | CHO | **2** | 94 | 95:5 | 3.38 | 3.35 | 3.80 | 3.95 |
| 2 | **11a** | Bu | CHO | **13a** | 84 | 65:35 | 3.39 | 3.30 | 3.86 | 4.03 |
| 3 | **11b** | $CH_2OPMB$ | CHO | **13b** | 93 | 72:28 | 3.37 | 3.30 | 3.90 | 3.98 |
| 4 | **11c** | $CH_2OTIPS$ | CHO | **13c** | 94 | 82:18 | 3.38 | 3.32 | 3.94 | 3.99 |
| 5 | **11d** | c | CHO | **13d** | 90 | 95:5 | 3.45 | 3.35 | 3.95 | 4.20 |
| 6 | **12a** | CHO | $CH_2OTBS$ | **14a** | 88 | 87:13 | 3.39 | 3.43 | d | *d* |
| 7 | **12b** | CHO | $CH_2OTIPS$ | **14b** | 100 | 89:11 | 3.39 | 3.45 | d | *d* |

[a] Diastereomer ratio determined by integration of $^1$H NMR spectra at 400 MHz. [b] See ref 3. [c] $R^1$ = (*R*)−CH(OAc)$CH_2CH$=$CH_2$. [d] See Experimental Section for the methine chemical shift data of **14a** and **14b**. It was not possible to use these absorbances to determine diastereomer ratios.



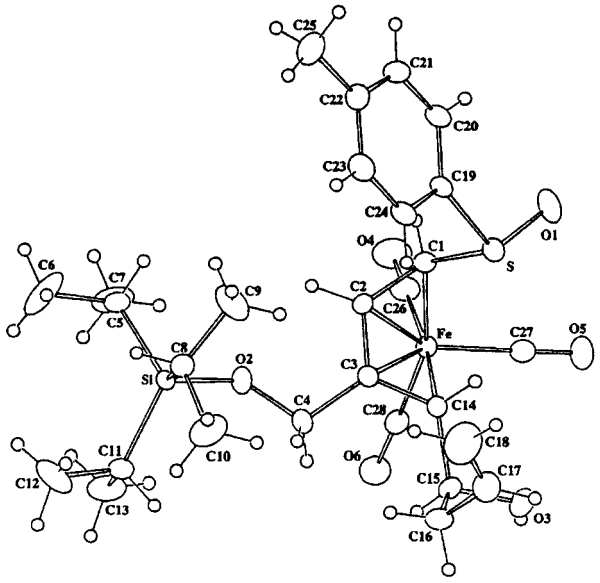



**Figure 1.** Final X-ray structure for **13c(min)**, the minor diastereomer of homoallylic alcohol **13c**.

product was (*S*) (Figure 1). Thus, the stereochemistry of the *major* diastereomer could finally be assigned an (*R*) configuration, which surprisingly corresponded to an attack of the nucleophilic allyl stannane upon the aldehyde in an s-cis conformation (assuming a trajectory which was anti to the iron tricarbonyl fragment). While this finding is in accord with the precedence for nucleophilic additions to aldehydes at the iron(0) diene terminus,[5] the *increasing* selectivity of this process as the steric volume of the $C_3$ substituent increases is contrary to the expectation that the s-trans conformer would be more greatly favored with larger $C_3$ substituents.

Our attention next turned to cases in which the position of the aldehyde and the bulky substituent were transposed, that is, allylation of sulfinyl iron dienals **12a** and **12b** (Table 1, entries 6 and 7). Diastereoselective addition of alkyllithiums (80:20 to 92:8),[10] Grignards (63:37),[10] and zinc−copper reagents (73:27 to 95:5)[11] to $\eta^4$-(2-formyl-1,3-butadiene)iron(0) tricarbonyl complexes have been demonstrated to occur via an s-cis aldehyde conformation; similarly, $LiAlH_4$ reduction of the corresponding methyl ketone has also been shown to proceed preferentially (71:29) via the s-cis conformer.[12] Since allylations of aldehydes **1** and **11a**−**c** were all shown to proceed through an s-trans conformer, regardless of the presence of a substituent at $C_3$, it was unclear how the $C_3$ aldehydes would behave. Allyl stannane addition to **12a** gave the homoallylic alcohols **14a** in an 87:13 diastereomeric ratio; the diastereomers were separable with careful column chromatography, and the major diastereomer could be obtained in nearly homogeneous form (98% de). Allylation of **12b** gave essentially the same result (89:11); fortunately, we were able to crystallize diol **15** (which was obtained from the major diastereomer of **14b** by treatment with TBAF in THF) from $CHCl_3$ in order to obtain an unambiguous stereochemical assignment. X-ray crystallography (Figure 2) revealed that the new stereocenter possessed an (*R*) configuration, indicating that the preferential conformation of the aldehyde must be s-trans. While addition to aldehydes **11a**−**c** favored a conformation which was not dictated by the presence of a $C_3$ substituent, the outcome of addition to aldehydes **12a** and **12b** clearly differed in that it demonstrated that the presence of a substituent at $C_4$ can invert the diastereoselectivity of addition to a $C_3$ aldehyde by causing a conformational change.

The successful allylation of the $C_3$ aldehyde provided an opportunity to study the effect of an even larger $C_3$ substituent upon allylation of a $C_4$ aldehyde. Sulfinyl iron dienal **11d** was obtained after successive acetylation, desilylation, and oxidation of the major diastereomer of **14a**.[13] In this case, allylation of the $C_4$ aldehyde of **11d** was highly diastereoselective, affording the corresponding alcohol in a 95:5 diastereomeric ratio (Table 1, entry 5). X-ray crystallography of the major diastereomer, **13d**, indicated that the new stereocenter

(10) Frank-Neumann, M.; Martina, D.; Heitz, M. P. *J. Organomet. Chem.* **1986**, *301*, 61−77.

(11) Yeh, M.-C. P.; Wang, J.-L.; Ueng, C.-H.; Cheng, S.-J. *Organometallics* **1994**, *13*, 4453−4461.

(12) von Kappes, D.; Gerlach, H.; Zbinden, P.; Dobler, M. *Helv. Chim. Acta* **1990**, *73*, 2136.

(13) The preparation of sulfinyl iron(0) dienal **11d** from alcohol **14a** was carried out as follows: (1) $Ac_2O$/pyr (100%); (2) TBAF/THF (100%); (3) $SO_3$·pyr, DMSO, $NEt_3$, $CH_2Cl_2$ (92%).

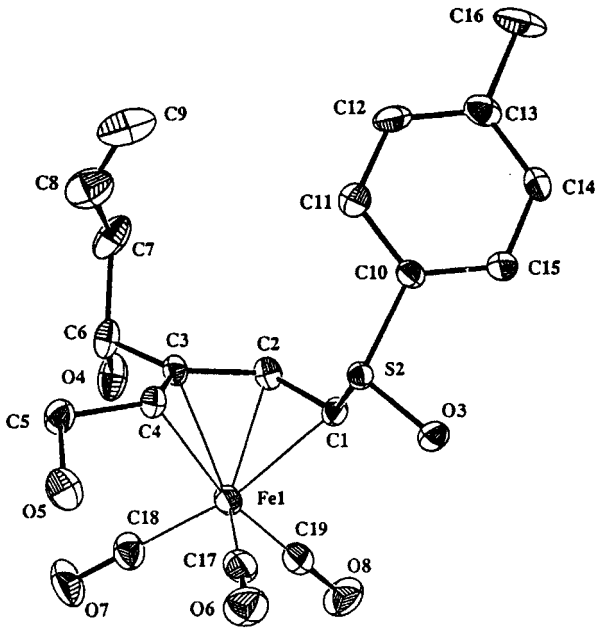



**Figure 2.** Final X-ray structure for the diol, **15**, derived from the major diastereomer of homoallylic alcohol **14b**.

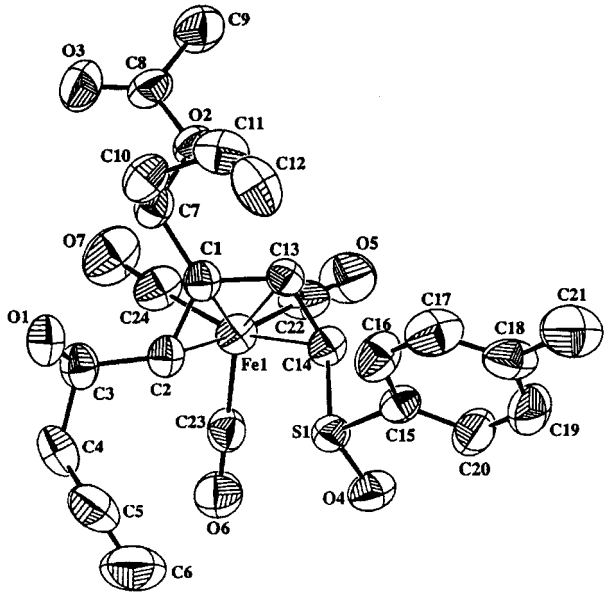



**Figure 3.** Final X-ray structure for the major diastereomer of homoallylic alcohol **13d**.

possessed an (*R*) configuration; addition had again occurred from the s-cis conformation of the aldehyde (Figure 3). While it is likely that the s-trans aldehyde conformer is energetically stabilized with respect to the s-cis conformer of **11d** (true as well for **11**−**c**), approach of the nucleophile to the si face of the s-trans conformer along the Bürgi−Dunitz trajectory[14] must be severely restricted; approach to the re face of the aldehyde is already restricted by the $Fe(CO)_3$ fragment. We speculate that the enhanced diastereoselectivity as the $C_3$ substituent becomes larger is an outcome of the increased likelihood of this substituent occupying a position along this trajectory as it is forced to avoid steric interactions with the $Fe(CO)_3$ fragment as well as with $C_2$ of the diene unit.[15] As the approach to the aldehyde s-trans conformer is increasingly restricted, nucleophilic addition to the s-cis conformer becomes more likely. (An approach which is anti to the $Fe(CO)_3$ fragment would be preferred in either case.) On the other hand, when the aldehyde is positioned at $C_3$ (as in **12a** and **12b**), the absence of a steric interaction with the diene unit apparently allows the $C_4$ substituent to occupy a position which does not hinder a nucleophilic approach to the preferred s-trans conformer, which is anti to the $Fe(CO)_3$ fragment.

In summary, we have demonstrated that highly diastereoselective allylations of enantiopure 3- and 4-substituted $\eta^4$-(1*Z*)-(sulfinyldienal)iron(0) tricarbonyl complexes are possible in some cases. For diene complexes bearing an aldehyde at a terminal position, the aldehyde predominately reacts through the s-cis conformer, whether a substituent is present at the adjacent internal position or not. For diene complexes bearing an aldehyde at the internal position and a silyloxymethylene group at the adjacent terminal position, the aldehyde predominately reacts through the s-trans conformer. Of particular interest is our ability to utilize the chirality of the sulfoxide to ultimately control the formation of one or two new distant chiral centers. Since we are now able to install chirality along the periphery of sulfinyl iron(0) diene complexes, we are currently exploring the elaboration of these compounds into enantiopure carbocycles and heterocycles as well as examining the diastereoselective manipulation of the sulfinyl iron(0) diene. These results will be reported in due course.

## Experimental Section[16]

**Materials.** Vinyl stannanes **3a** and **3c** were prepared according to the method of Oehlschalger;[7] vinyl stannanes **3b**, **3d**, and **3e** were prepared according to the method of Barrett.[7] (−)-Iodovinyl sulfoxide was prepared according to our previously reported method.[6] The $Fe(CO)_3$ transfer reagent (bda)-$Fe(CO)_3$ was prepared according to the literature procedure[8] and stored in the dark in a −20 °C freezer. Unreacted (bda)-$Fe(CO)_3$ was routinely recovered during chromatographic purification of sulfinyl iron(0) diene complexes and was reused. The preparation of sulfinyl dienes **5a**, **5d**, and **5e** as well as sulfinyl iron dienes **6a**, **6d**, and **6e** has already been described.[6]

**4-*tert*-Butyldimethylsilyloxy-1-*p*-methoxybenzyloxy-2-tri-*n*-butylstannylbut-2-ene (3b).** A $CH_2Cl_2$ solution (3 mL) of PMBOC(=NH)$CCl_3$ (726 mg, 2.57 mmol, 3 equiv) was added via cannula to a flask containing vinyl stannane **3d** (421 mg, 0.856 mmol, 1 equiv). PPTS was added (215 mg, 0.856 mmol, 1 equiv) and the solution was stirred for 44 h. It was then diluted with EtOAc (50 mL), and the solution was washed successively with 2 M aqueous HCl (15 mL), water (15 mL), and brine (15 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was chromatographed (silica gel, hexane/EtOAc, 30:1 with 1% $NEt_3$) to afford vinyl stannane **3b** as a clear oil (362 mg, 69%), which was sufficiently pure to use for the Stille coupling to **4**. $^1$H NMR: $\delta$ 0.07 (s, 6H, $(CH_3)_2$Si), 0.76−0.90 (m, 24H, *t*-BuSi and Sn$CH_2CH_2CH_2CH_3$), 1.26 (m, 6H, $SnCH_2CH_2$), 1.33−1.50 (m, 6H, $SnCH_2CH_2CH_2CH_3$), 3.82 (s, 3H, ArO*Me*), 4.15 (partially

(14) (a) Bürgi, H. B.; Dunitz, J. D.; Lehn, J. M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563. (b) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. J. *J. Am. Chem. Soc.* **1973**, *95*, 5065.

(15) The X-ray data for **13c(min)** supports our speculation that this approach is restricted; the bulky OTIPS group is positioned out of the diene plane instead of being coplanar with it (The silicon atom of the TIPS group is positioned 38° above the $O_2-C_3-C_4$ (X-ray numbering) plane).

(16) For general information, see ref 6.

obscured AB system, 2H, $J$ = 17.8 Hz, C$H_2$OPMB), 4.19 (app d, 2H, $J$ = 5.4 Hz, C$H_2$OSi), 4.42 (s, 2H, OC$H_2$Ar), 5.67 (m with tin satellites, 1H, vinylic H), 6.87 (d, 2H, ArH, $J$ = 8.5 Hz), 7.25 (d, 2H, ArH, $J$ = 8.5 Hz). $^{13}$C NMR: $\delta$ −5.1, 10.1, 13.7, 18.3, 25.9, 27.4, 29.1, 55.2, 61.1, 71.2, 72.2, 113.6, 129.4, 130.5, 138.6, 144.7, 159.0. Anal. Calcd for $C_{30}H_{56}O_3SiSn$: C, 58.92; H, 9.23. Found: C, 59.21; H, 9.36.

**($R_s$)-(1*Z*,3*E*)-5-*tert*-Butyldimethylsilyloxy-3-*p*-methoxybenzyloxymethyl-1-*p*-tolylsulfinylpenta-1,3-diene (5b).** To a DMF solution (3.0 mL) of vinyl stannane **3b** (362 mg, 0.592 mmol, 1.2 equiv) and iodovinyl sulfoxide **4** (144 mg, 0.493 mmol, 1.0 equiv) under an argon atmosphere was added Pd($CH_3CN)_2Cl_2$ (5.1 mg, 0.020 mmol, 0.04 equiv). After the mixture was stirred at room temperature for 24 h, the DMF was removed in vacuo. The residue was diluted with EtOAc (30 mL) and washed with a 5% aqueous $NH_4OH$ solution (2 × 10 mL), water (2 × 10 mL), and brine (1 × 10 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo to afford an oil, which was chromatographed (silica gel, hexane/EtOAc, 3:1 to 1:1), providing sulfinyl diene **5b** as a yellow-brown oil (189 mg, 79%). $^1$H NMR: $\delta$ 0.07 (s, 6H, $(CH_3)_2$Si), 0.91 (s, 9H, *t*-BuSi), 2.39 (s, 3H, ArMe), 3.81 (s, 3H, ArO*Me*), 4.27 (partially obscured AB system, 2H, $J$ = 11.8 Hz, C$H_2$OPMB), 4.34 (m, 2H, C$H_2$OSi), 4.44 (s, 2H, OC$H_2$Ar), 6.02 (app t, 1H, $J$ = 5.9, $H_4$), 6.19 (d, 1H, $J$ = 10.6 Hz, $H_1$), 6.54 (d, 1H, $J$ = 10.7 Hz, $H_2$), 6.86 (d, 2H, $J$ = 8.6 Hz, ArH), 7.25 (m, 4H, ArH), 7.55 (d, 2H, $J$ = 8.2 Hz, ArH). $^{13}$C NMR: $\delta$ −5.3, 18.3, 21.3, 25.8, 55.2, 59.7, 65.3, 72.0, 113.8, 124.5, 129.5, 129.7, 129.8, 132.4, 136.1, 137.9, 141.0, 141.4, 141.5, 159.3. IR (neat): 2953, 2929, 2856, 1613, 1514, 1249, 1040, 840 cm$^{-1}$. Anal. Calcd for $C_{27}H_{38}O_4SSi$: C, 66.63; H, 7.87. Found: C, 66.93; H, 8.01.

**($R_s$)-(1*Z*,3*E*)-3-Triisopropylsilyloxymethyl-1-*p*-tolylsulfinylpenta-1,3-dien-5-ol (5c).** To a DMF solution (12.4 mL) of vinyl stannane **3c** (1.319 mg, 2.472 mmol, 1.2 equiv) and iodovinyl sulfoxide **4** (602 mg, 2.060 mmol, 1.0 equiv) under an argon atmosphere was added Pd($CH_3CN)_2Cl_2$ (10.7 mg, 0.041 mmol, 0.02 equiv). After the mixture was stirred at room temperature for 24 h, the DMF was removed in vacuo. The residue was diluted with EtOAc (120 mL) and washed with a 5% aqueous $NH_4OH$ solution (2 × 40 mL), water (2 × 40 mL), and brine (1 × 40 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo to afford an oil, which was chromatographed (silica gel, hexane/EtOAc, 3:1 to 1:1), providing sulfinyl diene **5c** as a golden oil (551 mg, 65%). $^1$H NMR: $\delta$ 1.05−1.20 (m, 21H, OTIPS), 2.21 (app t, 1H, $J$ = 5.9 Hz, OH), 2.42 (s, 3H, Ar$CH_3$), 4.39 (app t, 2H, $J$ = 5.8 Hz, C$H_2$-OH), 4.51 (AB system, 2H, $J$ = 12.9 Hz, C$H_2$OTIPS), 6.06 (t, 1H, $J$ = 6.3 Hz, $H_4$), 6.32 (d, 1H, $J$ = 10.3 Hz, $H_1$), 6.74 (d, 1H, $J$ = 10.4 Hz, $H_2$), 7.32 (d, 2H, $J$ = 8.1 Hz, ArH), 7.56 (d, 2H, $J$ = 8.2 Hz, ArH). $^{13}$C NMR: $\delta$ 11.9, 18.0, 21.4, 59.2, 61.4, 124.6, 130.0, 135.9, 136.4, 127.3, 139.2, 141.3, 141.7. IR (neat): 3388 (br), 2942, 2885, 1463, 1084, 1013, 882, 809 cm$^{-1}$. Anal. Calcd for $C_{22}H_{36}O_3SSi$: C, 64.66; H, 8.88. Found: C, 64.82; H, 9.02.

**($R_s$)-(1*Z*,3*E*)-5-((*R* + *S*)-1-Ethoxy)ethoxy-3-triisopropylsilyloxymethyl-1-*p*-tolylsulfinylpenta-1,3-diene (7).** To a $CH_2Cl_2$ solution (6.7 mL) of sulfinyl dienol **5c** (551 mg, 1.35 mmol, 1.0 equiv) was added ethyl vinyl ether (1.29 mL, 13.5 mmol, 10 equiv) and PPTS (67.8 mg, 0.270 mmol, 0.2 equiv). The solution was stirred for 2 h and was then diluted with EtOAc (100 mL) and washed with 1 M aqueous HCl (30 mL), water (30 mL), and brine (30 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo to afford sulfinyl diene **7**, a mixture of diastereomers, as a light yellow oil (632 mg, 97%), which was not purified further. $^1$H NMR: $\delta$ 1.08−1.16 (m, 21H, OTIPS), 1.22 (t, 3H, $J$ = 7.0 Hz, $CH_2CH_3$), 1.34 (d, 3H, $J$ = 5.4 Hz, CHC$H_3$), 2.41 (s, 3H, Ar$CH_3$), 3.50 (m, 1H, one of $OCH_2$), 3.65 (m, 1H, one of $OCH_2$), 4.30 (m, 2H, $CH_2$-OEE), 4.49 (overlapping AB systems, 2H, $J$ = 12.7 Hz, $CH_2$-OTIPS), 4.77 (overlapping q, 2H, $J$ = 5.4 Hz, C$H$CH$_3$), 5.93 (overlapping t, 1H, $J$ = 6.1 Hz, $H_4$), 6.30 (d, 1H, $J$ = 10.4 Hz, $H_1$), 6.75 (d, 1H, $J$ = 10.3 Hz, $H_2$), 7.30 (d, 2H, $J$ = 8.1 Hz, ArH), 7.56 (d, 2H, $J$ = 8.1 Hz, ArH). $^{13}$C NMR: $\delta$ 11.9, 15.3, 18.0, 19.7, 21.4, 26.8, 27.8, 60.60, 60.63, 60.9, 61.0, 61.1, 99.1, 99.2, 124.6, 129.93, 129.94, 133.2, 136.5, 137.0, 137.1, 138.8, 138.9, 141.1, 141.8. IR (neat): 2940, 2865, 1463, 1383, 1085, 1043, 883, 809 cm$^{-1}$.

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-5-*tert*-Butyldimethylsilyloxy-3-*p*-methoxybenzyloxymethyl-1-*p*-tolylsulfinylpenta-1,3-diene]-iron(0) Tricarbonyl Complex (6b) and Its Minor Diastereomer.** To a toulene solution (4 mL) of sulfinyl diene **5b** (491 mg, 1.01 mmol, 1.0 equiv) was added (bda)Fe$(CO)_3$ (1.16 g, 4.04 mmol, 4.0 equiv); the red-orange solution, under an argon atmosphere, was submerged in a 45 °C oil bath and stirred for 12 h. The solution was cooled to room temperature and filtered through silica gel on a glass frit. After the filter cake was rinsed with EtOAc (250 mL), the filtrate was concentrated in vacuo and the residue was chromatographed (silica gel, hexane/EtOAc, gradient from 9:1 to 2:1) to afford 747 mg of (bda)Fe$(CO)_3$ (86% of the extra 3 equiv) and sulfinyl iron diene **6b**, as a yellow oil (452 mg, 71%). Continued chromatography (1:2 hexane/EtOAc) afforded the minor diastereomer as an impure yellow oil (49.0 mg, 8%). Data for **6b**: $^1$H NMR: $\delta$ 0.09 (s, 6H, $(CH_3)_2$Si), 0.92 (s, 9H, *t*-BuSi), 2.40 (s, 3H, ArMe), 2.83 (app t, 1H, $J$ = 6.7 Hz, $H_4$), 3.36 (d, 1H, $J$ = 7.3 Hz, $H_1$), 3.82 (s, 3H, ArO*Me*), 3.94 (m, 2H, C$H_2$OSi), 4.30 (AB system, 2H, $J$ = 12.9 Hz, C$H_2$OPMB), 4.62 (s, 2H, OC$H_2$-Ar), 5.25 (d, 1H, $J$ = 7.3 Hz, $H_2$), 6.91 (d, 2H, $J$ = 8.6 Hz, ArH), 7.28 (m, 4H, ArH), 7.38 (d, 2H, $J$ = 8.2 Hz, ArH). $^{13}$C NMR: $\delta$ −5.4, −5.3, 14.2, 18.3, 21.0, 21.3, 25.8, 55.2, 60.4, 61.8, 63.2, 67.8, 72.9, 75.3, 76.4, 110.5, 113.9, 114.6, 123.3, 129.3, 129.4, 129.8, 140.7, 145.3, 159.4. IR (neat): 2926, 2852, 2055, 1990, 1510, 1467, 1248, 1082, 1050, 837 cm$^{-1}$. Anal. Calcd for $C_{30}H_{38}O_7FeSSi$: C, 57.50; H, 6.11. Found: C, 57.27; H, 5.98.

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-5-((*R* + *S*)-1-Ethoxy)ethoxy-3-triisopropylsilyloxymethyl-1-*p*-tolylsulfinylpenta-1,3-diene]-iron(0) Tricarbonyl Complex (6c).** To a toulene solution (4 mL) of sulfinyl diene **7** (631.8 mg, 1.314 mmol, 1.0 equiv) was added (bda)Fe$(CO)_3$ (1.501 g, 5.256 mmol, 4.0 equiv); the red-orange solution, under an argon atmosphere, was submerged in a 45 °C oil bath and stirred for 16 h. The solution was cooled to room temperature and filtered through $NEt_3$-washed silica gel on a glass frit. After the filter cake was rinsed with EtOAc (250 mL), the filtrate was concentrated in vacuo and the residue was chromatographed (silica gel, hexane/EtOAc, 9:1 with 1% $NEt_3$ to 7:1 with 1% $NEt_3$) to afford 815 mg of (bda)Fe$(CO)_3$ (72% of the extra 3 equiv) and sulfinyl iron diene **6c**, a mixture of diastereomers due to the 1-ethoxyethyl group, as a yellow oil (595 mg, 73%). $^1$H NMR: $\delta$ 1.10−1.22 (m, 21H, OTIPS), 1.23 (app t, 3H, $J$ = 7.0, 6.4 Hz, $CH_2CH_3$), 1.36 (overlapping d, 3H, $J$ = 5.3 Hz, CHC$H_3$), 2.40 (s, 3H, Ar$CH_3$), 2.83 (m, 1H, $H_4$), 3.42 (overlapping d, 1H, $J$ = 7.4 Hz, $H_1$), 3.54 (m, 1H, one of $OCH_2$), 3.70 (m, 1.5H, one of $OCH_2$ + one-half of ABX system of C$H_2$OEE of one diastereomer), 3.83 (ABX system, 1H, $J$ = 10.9, 8.0, 6.1 Hz, C$H_2$OEE of one diastereomer), 3.96 (one-half of ABX system, 0.5 H, $J$ = 11.1, 6.2 Hz, C$H_2$OEE of one diastereomer), 4.68 (overlapping AB systems, 2H, $J$ = 14.1 Hz, C$H_2$OTIPS), 4.78 (overlapping q, 1H, $J$ = 5.4 Hz, C$H$CH$_3$), 5.37 (d, 1H, $J$ = 6.2 Hz, $H_2$), 7.28 (d, 2H, $J$ = 8.1 Hz, ArH), 7.39 (d, 2H, $J$ = 8.1 Hz). $^{13}$C NMR: $\delta$ 12.8, 16.1, 18.80, 18.81, 20.52, 20.57, 22.2, 58.8, 59.2, 61.7, 61.8, 62.1, 62.2, 64.2, 64.3, 75.56, 75.60, 75.98, 76.05, 100.45, 100.56, 115.2, 115.5, 124.1, 130.7, 141.5, 146.1. IR (neat): 2944, 2865, 2357, 2339, 2061, 1989, 1463, 1384, 1122, 1084, 1052, 883, 809 cm$^{-1}$. Anal. Calcd for $C_{26}H_{44}O_4SSi$: C, 64.95; H, 9.22. Found: C, 64.81; H, 9.39.

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-3-*p*-Methoxybenzyloxymethyl-1-*p*-tolylsulfinylpenta-1,3-dien-5-ol]iron(0) Tricarbonyl Complex (8).** To a THF solution (3.1 mL) of sulfinyl iron diene **6b** (192 mg, 0.306 mmol, 1.0 equiv) was added a 1 M THF solution of TBAF (Aldrich, 0.368 mL, 0.368 mmol, 1.2 equiv).

After the mixture was stirred at room temperature for 2.5 h, the solution was diluted with EtOAc (25 mL), washed with brine (2 × 7 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc, 1:1) to afford sulfinyl iron dienol **8** as a yellow oil (146 mg, 93%). $^1$H NMR: $\delta$ 2.36 (s, 3H, ArH), 2.87 (dd, 1H, $J$ = 8.8, 5.5 Hz, $H_4$), 3.34 (d, 1H, $J$ = 7.3 Hz, $H_1$), 3.79 (s + obscured m, 4H, ArO*Me* + one of C$H_2$OH), 3.90 (br s, 1H, OH), 3.98 (m, 1H, one of C$H_2$OH), 4.38 (partially obscured AB system, 2H, $J$ = 12.7 Hz, C$H_2$OPMB), 4.59 (s, 2H, OC$H_2$Ar), 5.17 (d, 1H, $J$ = 7.3 Hz, $H_2$), 6.88 (d, 2H, $J$ = 8.6 Hz, ArH), 7.20 (d, 2H, $J$ = 8.1 Hz, ArH), 7.26 (d, 2H, $J$ = 8.5 Hz, ArH), 7.30 (d, 2H, $J$ = 8.1 Hz, ArH). $^{13}$C NMR: $\delta$ 21.2, 55.2, 60.9, 62.7, 68.1, 72.8, 74.9, 77.4, 110.6, 113.9, 123.1, 128.9, 129.4, 129.8, 140.9, 144.6, 159.4. IR (neat): 3380 (br), 2931, 2056, 1990, 1611, 1245, 1090, 1034 cm$^{-1}$. Anal. Calcd for $C_{24}H_{24}O_7FeS$: C, 56.26; H, 4.72. Found: C, 56.49; H, 4.93.

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-1-*p*-Tolylsulfinyl-3-*p*-triisopropylsilyloxymethylpenta-1,3-dien-5-ol]iron(0) Tricarbonyl Complex (9).** Sulfinyl diene iron(0) complex **6c** (561 mg, 0.904 mmol) was dissolved in a solution of AcOH/$H_2O$/THF (4:1:1, 5.0 mL) and stirred for 12 h at room temperature. It was then diluted with EtOAc (65 mL) and washed with 1 M aqueous NaOH solution (4 × 20 mL); the combined aqueous washes were extracted with EtOAc (40 mL). The combined organic layers were washed successively with water (2 × 20 mL) and brine (1 × 20 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc, 2:1), yielding the sulfinyl iron dienol complex **9** (452 mg, 91%) as a light yellow foam. $^1$H NMR: $\delta$ 1.08−1.26 (m, 21H, OTIPS), 2.38 (s, 3H, Ar$CH_3$), 2.89 (dd, 1H, $J$ = 9.1, 5.6 Hz, $H_4$), 3.38 (d, 1H, $J$ = 7.3 Hz, $H_1$), 3.48 (m, 1H, OH), 3.83 (m, 1H, one of C$H_2$OH), 4.04 (m, 1H, one of C$H_2$OH), 4.67 (AB system, 2H, $J$ = 13.3 Hz, C$H_2$OTIPS), 5.23 (d, 1H, $J$ = 7.3 Hz), 7.23 (d, 2H, $J$ = 8.0 Hz, ArH), 7.33 (d, 2H, $J$ = 8.2 Hz, ArH). $^{13}$C NMR: $\delta$ 11.9, 17.9, 21.3, 61.2, 62.0, 62.5, 75.0, 76.5, 113.4, 123.2, 129.8, 140.9, 144.9. IR ($CHCl_3$): 3235 (br), 2942, 2865, 2065, 2004, 1465, 1076, 1011, 883 cm$^{-1}$. Anal. Calcd for $C_{25}H_{36}O_6FeSSi$: C, 54.74; H, 6.62. Found: C, 54.51; H, 6.58.

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-3-Hydroxymethyl-1-*p*-tolylsulfinyl-5-triisopropylsilyloxy-1,3-pentadiene]tricarbonyliron(0) Complex (10).** Sulfinyl diene iron(0) complex **6e**[6] (1.369 g, 2.065 mmol) was dissolved in a precooled solution (0 °C) of AcOH/$H_2O$/THF (4:1:1) and stirred for 2 h in a 0 °C refrigerator. It was then diluted with EtOAc (50 mL) and washed successively with 1 M aqueous NaOH (4 × 20 mL), water (2 × 20 mL), and brine (1 × 20 mL); the organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc, 3:1 to 2:1), yielding the sulfinyl iron(0) dienol complex **10** (0.9629 g, 85%) as a yellow solid (mp 108−109.5 °C). $^1$H NMR: $\delta$ 1.11 (m, 21H, OTIPS), 2.41 (s, 3H, ArMe), 2.85 (dd, 1H, $J$ = 10.0, 5.8 Hz, $H_4$), 3.40 (d, 1H, $J$ = 7.2 Hz, $H_1$), 3.95 (ABX system, 2H, $J$ = 11.1, 10.7, 2.8 Hz, C$H_2$OH), 4.20 (ABX system, 2H, $J$ = 11.2, 10.8, 5.8 Hz, C$H_2$OTIPS), 4.68 (dd, 1H, $J$ = 12.7, 2.7 Hz, OH), 5.16 (d, 1H, $J$ = 7.3 Hz, $H_2$), 7.31 (d, 2H, $J$ = 8.1 Hz, ArH), 7.41 (d, 2H, $J$ = 8.2 Hz, ArH). $^{13}$C NMR: $\delta$ 11.8, 17.8, 21.3, 60.6, 62.4, 62.8, 75.4, 78.4, 113.1, 123.1, 129.9, 140.9, 144.7. IR ($CHCl_3$): 3237 (br), 2942, 2865, 2061, 2000, 1462, 1072, 1013, 882 cm$^{-1}$. Anal. Calcd for $C_{25}H_{36}O_6FeSSi$: C, 54.74; H, 6.62. Found: C, 54.98; H, 6.87.

**General Procedure for Formation of Sulfinyl Iron(0) Dienals.** The sulfinyl iron(0) dienol (1 equiv) was dissolved in $CH_2Cl_2$ (3.9 mL/mmol) at room temperature. DMSO (3.9 mL/mmol) was then added to the reaction solution, followed by $NEt_3$ (10 equiv) and $SO_3$·pyr (5 equiv). The solution was stirred at room temperature for 3 h, then diluted with EtOAc (100 mL/mmol) and washed with 2 M HCl (2 × 35 mL/mmol), $H_2O$ (1 × 35 mL/mmol), and brine (1 × 35 mL/mmol). The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting oil was purified via column chromatography (silica gel, hexane/EtOAc mixtures).

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-3-Butyl-1-*p*-tolylsulfinylpenta-1,3-dien-5-al]tricarbonyl iron(0) Complex (11a).** To a solution of alcohol **6a** (0.1694 g, 0.405 mmol) in $CH_2Cl_2$ (1.6 mL) was added DMSO (1.6 mL), $NEt_3$ (0.56 mL, 4.05 mmol, 10 equiv), and $SO_3$·pyr (0.322 g, 2.03 mmol, 5 equiv) according to the general procedure. After column chromatography (silica gel, hexane/EtOAc, 2:1), aldehyde **11a** (0.1504 g, 89%) was obtained as a yellow oil. $^1$H NMR: $\delta$ 0.99 (t, 3H, $J$ = 7.3 Hz, $CH_2CH_3$), 1.42−1.82 (m, 4H, $CH_2CH_2CH_3$), 2.41 (s, 3H, Ar$CH_3$), 2.50 (m, 1H, one of C$H_2$Pr), 2.90 (d, 1H, $J$ = 4.4 Hz, $H_4$), 3.19 (m, 1H, one of C$H_2$Pr), 3.63 (d, 1H, $J$ = 7.3 Hz, $H_1$), 4.99 (d, 1H, $J$ = 7.3 Hz, $H_2$), 7.31 (d, 2H, $J$ = 8.1 Hz, ArH), 7.37 (d, 2H, $J$ = 8.2 Hz, ArH), 9.68 (d, 1H, $J$ = 4.4 Hz, CHO). $^{13}$C NMR: $\delta$ 13.8, 21.4, 22.3, 33.2, 34.4, 56.5, 77.6, 81.3, 117.2, 123.1, 130.1, 141.3, 144.7, 195.0. IR (neat): 2959, 2929, 2872, 2070, 2014, 1987, 1738, 1682, 1493, 1463, 1147, 1083, 1048, 810 cm$^{-1}$. Anal. Calcd for $C_{19}H_{20}O_5FeS$: C, 54.82; H, 4.84. Found: C, 54.98; H, 5.01.

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-3-(4-Methoxybenzyloxymethyl)-1-*p*-tolylsulfinylpenta-1,3-dien-5-al]tricarbonyliron(0) Complex (11b).** To a solution of the alcohol **8** (0.146 g, 0.285 mmol) in $CH_2Cl_2$ (1.1 mL), was added DMSO (1.1 mL), $NEt_3$ (0.40 mL, 2.85 mmol, 10 equiv), and $SO_3$·pyr (0.227 g, 1.43 mmol, 5 equiv) according to the general procedure. After column chromatography (silica gel, hexane/EtOAc, 3:1 to 2:1), aldehyde **11b** (0.131 g, 90%) was obtained as a yellow oil. $^1$H NMR: $\delta$ 2.41 (s, 3H, Ar$CH_3$), 2.93 (d, 1H, $J$ = 3.3 Hz, $H_4$), 3.67 (d, 1H, $J$ = 7.4 Hz, $H_1$), 3.81 (s, 3H, $OCH_3$), 4.62 (app t, 2H, OC$H_2$Ar), 4.74 (AB system, 2H, $J$ = 13.7 Hz, PMBOC$H_2$), 5.49 (d, 1H, $J$ = 7.4 Hz, $H_2$), 6.89 (d, 2H, $J$ = 8.6 Hz, ArH), 7.28 (d, 2H, $J$ = 8.7 Hz, ArH), 7.30 (d, 2H, $J$ = 8.4 Hz, ArH), 7.40 (d, 2H, $J$ = 8.2 Hz, ArH), 9.66 (d, 1H, $J$ = 3.3 Hz, CHO). $^{13}$C NMR: $\delta$ 21.4, 55.0, 55.2, 67.9, 73.2, 76.7, 80.1, 112.4, 113.9, 123.2, 129.1, 129.4, 130.1, 141.3, 144.3, 159.5, 195.1. IR (neat): 2926, 2857, 2072, 2002, 1987, 1682, 1674, 1614, 1515, 1455, 1247, 1082, 1047 cm$^{-1}$. Anal. Calcd for $C_{24}H_{22}O_7FeS$: C, 56.48; H, 4.35. Found: C, 56.61; H, 4.41.

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-1-*p*-Tolylsulfinyl-3-triisopropylsilyloxymethylpenta-1,3-dien-5-al]tricarbonyliron(0) Complex (11c).** To a solution of alcohol **9** (0.105 g, 0.191 mmol) in $CH_2Cl_2$ (0.75 mL) was added DMSO (0.75 mL), $NEt_3$ (0.27 mL, 1.91 mmol, 10 equiv), and $SO_3$·pyr (0.152 g, 0.954 mmol, 5 equiv) according to the general procedure. After column chromatography (silica gel, hexane/EtOAc, 2:1), aldehyde **11c** (0.091 g, 87%) was obtained as a yellow oil. $^1$H NMR: $\delta$ 1.10 (d, 18H, $J$ = 6.7 Hz, Si(CH(C$H_3$)$_2$), 1.20 (m, 3H, SiC$H$(CH$_3$)$_2$), 2.41 (s, 3H, Ar$CH_3$), 2.97 (d, 1H, $J$ = 2.9 Hz, $H_4$), 3.71 (d, 1H, $J$ = 7.5 Hz, $H_1$), 5.06 (AB system, 2H, $J$ = 14.9 Hz, TIPSOC$H_2$), 5.63 (d, 1H, $J$ = 7.4 Hz, $H_2$), 7.31 (d, 2H, $J$ = 8.1 Hz, ArH), 7.41 (d, 2H, $J$ = 8.1 Hz, ArH), 9.69 (d, 1H, $J$ = 3.0 Hz, CHO). $^{13}$C NMR: $\delta$ 11.8, 17.91, 17.93, 21.4, 54.6, 62.1, 78.3, 115.8, 123.2, 130.0, 141.3, 144.4, 194.9. IR (neat): 2943, 2866, 2073, 2015, 1682, 1463, 1113, 1053, 808 cm$^{-1}$. Anal. Calcd for $C_{25}H_{34}O_6FeSSi$: C, 54.94; H, 6.27. Found: C, 55.11; H, 6.06.

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-3-[(*R*)-1-Acetoxybut-3-enyl]-5-hydroxy-1-*p*-tolylsulfinyl-penta-1,3-dien-5-al]tricarbonyliron(0) Complex (11d).** Alcohol **14a** (0.6890 g, 1.17 mmol, 1 equiv) was dissolved in pyridine (11.7 mL), treated with acetic anhydride (1.10 mL, 11.7 mmol, 10 equiv), and stirred overnight. The reaction was diluted with EtOAc (120 mL) and washed with 2 M HCl (2 × 30 mL), $H_2O$ (2 × 30 mL), and brine (30 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting oil was purified by column chromatography (silica gel, hexane/EtOAc, 3:1) to afford the acetate (0.734 g, 99.5%) as a yellow solid (mp 118.5−120 °C). $^1$H NMR: $\delta$ 1.10 (m, 21H, OTIPS), 2.08 (s, 3H, ArMe), 2.75 (m, 2H, one of C$H_2$CHOAc and $H_4$), 2.96 (m, 1H, one of C$H_2$-CHOAc), 3.40 (d, 1H, $J$ = 7.5 Hz, $H_2$), 4.05 (ABX system, 2H, $J$ = 11.6, 8.9, 5.6 Hz, C$H_2$OTIPS), 5.12 (d, 1H, $J$ = 7.5 Hz,

$H_2$), 5.21 (app t, 2H, $J$ = 16.7, 10.7 Hz, $H_{8c}$ and $H_{8t}$), 5.87 (m, 2H, $H_7$ and C*H*OAc), 7.29 (d, 2H, $J$ = 8.2 Hz, ArH), 7.36 (d, 2H, $J$ = 8.2 Hz, ArH). $^{13}$C NMR: $\delta$ 11.9, 18.0, 20.7, 21.4, 41.7, 61.8, 62.1, 69.4, 74.9, 75.8, 112.7, 119.3, 123.2, 129.9, 132.1, 140.9, 145.5, 169.1. IR ($CHCl_3$): 2944, 2866, 2065, 2007, 1742, 1463, 1370, 1216, 1047, 757 cm$^{-1}$.

This acetate (0.734 g, 1.16 mmol, 1 equiv) was dissolved in THF (11.6 mL) and treated with a 1.0 M solution of TBAF in THF (Aldrich, 1.4 mL, 1.40 mmol, 1.2 equiv) and stirred for 1.5 h. The reaction was then diluted with EtOAc (100 mL) and washed wth brine (30 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting oil was purified by chromatography (silica gel, hexane/EtOAc, 1:1) to afford the alcohol (0.5525 g, 100%) as a yellow oil. $^1$H NMR: $\delta$ 2.07 (s, 3H, OAc Me), 2.39 (s, 3H, ArMe), 2.75 (m, 2H, one of C$H_2$CHOAc and $H_4$), 2.92 (m, 1H, one of C$H_2$-CHOAc), 3.38 (d, 1H, $J$ = 7.4 Hz, $H_1$), 3.99 (ABX system, 2H, $J$ = 12.0, 8.9, 5.6 Hz, C$H_2$OH), 5.12 (m, 3H, $H_2$, $H_{8c}$, and $H_{8t}$), 5.85 (m, 2H, $H_7$ and C*H*OAc), 7.23 (d, 2H, $J$ = 8.1 Hz, ArH), 7.28 (d, 2H, $J$ = 8.2 Hz, ArH). $^{13}$C NMR: $\delta$ 14.0, 20.7, 21.3, 41.7, 60.7, 62.3, 69.5, 74.7, 74.9, 112.9, 119.2, 123.1, 129.8, 132.1, 141.1, 144.6, 169.1. IR (neat): 3363 (br), 2931, 2359, 2083, 1990, 1747, 1373, 1230, 1042, 810, 617, 565, 504 cm$^{-1}$.

The alcohol (0.5525 g, 1.164 mmol, 1 equiv) in $CH_2Cl_2$ (4.5 mL) was treated with DMSO (4.5 mL), $NEt_3$ (1.62 mL, 11.64 mmol, 10 equiv), and $SO_3$·pyr (0.926 g, 5.82 mmol, 5 equiv) according to the general procedure. After column chromatography (silica gel, hexane/EtOAc, 4:1), aldehyde **11d** (0.506 g, 92%) was obtained as a yellow oil. $^1$H NMR: $\delta$ 2.13 (s, 3H, OAc Me), 2.43 (s, 3H, ArMe), 2.64 (m, 1H, one of C$H_2$CHOAc), 2.75 (m, 1H, one of C$H_2$CHOAc), 2.87 (d, 1H, $J$ = 2.9 Hz, $H_4$), 3.67 (d, 1H, $J$ = 7.6 Hz, $H_1$), 5.21 (m, 2H, $H_{8c}$ and $H_{8t}$), 5.31 (d, 1H, $J$ = 7.4 Hz, $H_2$), 5.86 (m, 1H, $H_7$), 6.63 (app t, 1H, $J$ = 5.6, 5.5 Hz, C*H*OAc), 7.33 (d, 2H, $J$ = 8.1 Hz, ArH), 7.40 (d, 2H, $J$ = 8.3 Hz, ArH), 9.69 (d, 1H, $J$ = 2.9 Hz, CHO). $^{13}$C NMR: $\delta$ 20.7, 21.4, 41.7, 54.6, 70.2, 77.6, 112.9, 119.7, 123.2, 130.1, 131.8, 141.0, 144.6, 169.5, 194.4. IR (neat): 2926, 2076, 2014, 1746, 1682, 1428, 1372, 1228, 1047, 811, 612, 562 cm$^{-1}$. Anal. Calcd for $C_{21}H_{20}O_7FeS$: C, 53.41; H, 4.27. Found: C, 55.37; H, 4.13.

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-5-*tert*-Butyldimethylsilyloxy-3-formyl-1-*p*-tolylsulfinylpenta-1,3-diene]tricarbonyliron(0) Complex (12a).** To a solution of alcohol **6d** (0.160 g, 0.315 mmol) in $CH_2Cl_2$ (1.3 mL) was added DMSO (1.3 mL), $NEt_3$ (0.44 mL, 3.15 mmol, 10 equiv), and $SO_3$·pyr (0.251 g, 1.58 mmol, 5 equiv) according to the general procedure. After column chromatography (silica gel, hexane/EtOAc, 4:1 to 3:1), aldehyde **12a** (0.140 g, 88%) was obtained as a yellow solid (mp 99−101 °C). $^1$H NMR: $\delta$ 0.10 (s, 6H, $SiCH_3$), 0.91 (s, 9H, $Si(CH_3)_3$), 2.40 (s, 3H, $ArCH_3$), 2.98 (app t, 1H, $J$ = 6.2 Hz), 3.60 (d, 1H, $J$ = 7.6 Hz, $H_1$), 4.18 (ABX system, 2H, $J$ = 13.1, 7.4, 5.1 Hz, $CH_2$-OTBS), 5.50 (d, 1H, $J$ = 7.6 Hz, $H_2$), 7.25 (d, 2H, $J$ = 8.2 Hz, ArH), 7.33 (d, 2H, $J$ = 8.2 Hz, ArH), 9.96 (s, 1H, CHO). $^{13}$C NMR: $\delta$ −5.53, −5.50, 21.3, 25.7, 62.0, 66.3, 79.4, 82.1, 98.7, 123.1, 130.0, 141.2, 192.7. IR ($CHCl_3$): 2930, 2858, 2073, 2021, 1705, 1082, 837 cm$^{-1}$. Anal. Calcd for $C_{22}H_{28}O_6FeSSi$: C, 52.38; H, 5.59. Found: C, 52.57; H, 5.42.

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-3-Formyl-1-*p*-tolylsulfinyl-5-triisopropylsilyloxy-1,3-pentadiene]tricarbonyliron(0) Complex (12b).** To a solution of alcohol **10** (0.926 g, 1.76 mmol) dissolved in $CH_2Cl_2$ (6.9 mL) was added DMSO (6.9 mL), $NEt_3$ (2.45 mL, 17.6 mmol, 10 equiv), and $SO_3$·pyr (1.40 g, 8.78 mmol, 5 equiv) according to the general procedure. After column chromatography (silica gel, hexane/EtOAc, 4:1), aldehyde **12b** (0.9044 g, 94%) was obtained as a yellow solid, mp 106−107.5 °C. $^1$H NMR: $\delta$ 1.10 (m, 21H, OTIPS), 2.40 (s, 3H, ArMe), 3.03 (app t, 1H, $H_4$, $J$ = 6.4, 6.3 Hz), 3.63 (d, 1H, $H_1$, $J$ = 7.6 Hz), 4.30 (ABX system, 2H, $J$ = 13.0, 7.4, 5.4 Hz, C$H_2$-OTIPS), 5.54 (d, 1H, $H_2$, $J$ = 7.4 Hz), 7.30 (d, 2H, ArH, $J$ = 8.1 Hz), 7.36 (d, 2H, ArH, $J$ = 8.2 Hz), 10.02 (s, 1H, aldehyde). $^{13}$C NMR: $\delta$ 12.8, 18.8, 22.2, 63.2, 67.3, 80.4, 82.8, 99.5, 124.0, 130.9, 142.2, 145.5, 193.7. IR ($CHCl_3$): 2944, 2866, 2072, 2021, 1705, 1463, 1216, 1084, 1047, 882, 758, 667, 617 cm$^{-1}$. Anal. Calcd for $C_{25}H_{34}O_6FeSSi$: C, 54.94; H, 6.27. Found: C, 54.81; H, 6.09.

**General Procedure for Synthesis of Homoallylic Alcohols.** The aldehyde (1 equiv) was dissolved in $CH_2Cl_2$ (0.1 M), and the solution was then cooled to −78 °C. Allyltributylstannane (1 equiv) was added dropwise via syringe, followed by dropwise addition of $BF_3$·$Et_2O$ (1 equiv), also via syringe. The solution was stirred for 1 h at −78 °C; a second equivalent of both allyltributylstannane and $BF_3$·$Et_2O$ were then successively added. After another hour of stirring at −78 °C, the reaction was quenched with a saturated aqueous $NaHCO_3$ solution and allowed to warm to room temperature. The solution was then diluted with EtOAc, and the organic layer was washed successively with saturated $NaHCO_3$ and brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The ratio of diastereomers was determined by integration of the $^1$H NMR spectrum of the crude oil. The resulting oil was purified via gradient column chromatography (silica gel, hexane/EtOAc mixtures).

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-3-Butyl-5-(*R*)-hydroxy-1-*p*-tolylsulfinyl-1,3,7-octatriene]-tricarbonyliron(0) Complex (13a) and Its Diastereomer.** Aldehyde **11a** (0.118 g, 0.284 mmol, 1 equiv), dissolved in $CH_2Cl_2$ (2.8 mL), was reacted with allyl tributylstannane (2 × 0.035 mL, total of 0.568 mmol, 2 equiv) and $BF_3$·$Et_2O$ (2 × 0.088 mL, total of 0.568 mmol, 2 equiv) according to the general procedure. The ratio of diastereomers was determined to be 65:35 by integration of the $^1$H NMR spectrum of the crude oil using the $H_1$ and $H_5$ resonances. The diastereomers were inseparable after two successive gradient column chromatographies (silica gel, hexane/EtOAc, 19:1 to 2:1); the diastereomeric alcohols, **13a**, were obtained as a yellow oil (0.107 g, 84%). Partial $^1$H NMR data for the mixture: $\delta$ 1.25 (t, 3H, $J$ = 7.2 Hz), 2.23 (m, 6H, $(CH_2)_3CH_3$), 2.39 (s, 3H, ArMe), 3.28 and 3.36 (two d, total 1H, $J$ = 7.3 Hz, $H_1$), 3.86 and 4.02 (two m, total 1H, $H_5$), 4.83 and 4.90 (d, total 1H, $J$ = 7.3, $H_2$), 5.23 and 5.29 (m, total 2H, $H_8$), 5.81 and 5.93 (m, total 1H, $H_7$), 7.27−7.32 (overlapping doublets, total 4H, $J$ = 8.2 Hz, ArH). Complete characterization was performed on the acetate ($Ac_2O$, pyr) derived from the major isomer since the diastereomeric acetates were chromatographically separable: $^1$HMR $\delta$ 0.97 (t, 3H, $J$ = 7.2 Hz), 1.32−1.57 (m, 3H, three of $(CH_2)_2CH_3$), 1.65−1.75 (m, 1H, one of $(CH_2)_2$-$CH_3$), 2.10 (s, 3H, OAc Me), 2.28 (m, 1H, one of C$H_2(CH_2)_2$-$CH_3$), 2.40 (s, 3H, ArMe), 2.43 (partially obscured m, 1H, one of C$H_2(CH_2)_2CH_3$), 2.56 (m, 1H, one of allylic $CH_2$), 2.69 (d, 1H, $J$ = 9.8 Hz, $H_4$), 2.76 (m, 1H, one of allylic $CH_2$), 3.41 (d, 1H, $J$ = 7.3 Hz, $H_1$), 4.91 (dd, 1H, $J$ = 7.3, 0.7 Hz, $H_2$), 5.25 (m, 3H, $H_5$ and $H_8$), 5.88 (m, 1H, $H_7$), 7.29 (d, 2H, $J$ = 8.2 Hz, ArH), 7.36 (d, 2H, $J$ = 8.2 Hz, ArH). $^{13}$C NMR: $\delta$ 13.9, 21.2, 21.4, 22.6, 33.0, 34.2, 40.0, 61.3, 72.6, 77.2, 78.4, 115.5, 119.4, 123.1, 129.9, 132.3, 140.8, 145.2, 169.7, 206.0. IR (neat): 2955, 2868, 2059, 1982, 1724, 1239, 1054 cm$^{-1}$. Anal. Calcd for $C_{24}H_{28}O_6FeS$: C, 57.61; H, 5.64. Found: C, 57.72; H, 5.79.

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-5-(*R*)-Hydroxy-1-*p*-tolylsulfinyl-3-*p*-methoxybenzyloxymethyl-1,3,7-octatriene]tricarbonyliron(0) Complex (13b) and Its Diastereomer.** Aldehyde **11b** (0.131 g, 0.256 mmol, 1 equiv), dissolved in $CH_2Cl_2$ (2.3 mL), was reacted with allyl tributylstannane (2 × 0.079 mL, total of 0.512 mmol, 2 equiv) and $BF_3$·$Et_2O$ (2 × 0.031 mL, total of 0.512 mmol, 2 equiv) according to the general procedure. The ratio of diastereomers was determined to be 72:28 by integration of the $^1$H NMR spectrum of the crude oil using the $H_1$ and $H_5$ resonances. The diastereomers were inseparable after two successive gradient column chromatographies (silica gel, hexane/EtOAc, 9:1 to 1:1); the diastereomeric alcohols **13b** were obtained as a yellow oil (132 mg, 93%). $^1$H NMR: $\delta$ 2.41 (s, 3H, ArMe), 2.40−2.68 (m, 2H (allylic $CH_2$) + 0.3H (OH from minor diastereomer)), 2.74 and 2.79 (two d, total 1H, $J$ = 9.3 Hz, $H_4$), 3.31 and 3.37 (two d, total 1H, $J$ =

7.4 Hz, $H_1$), 3.49 (d, 0.7H, $J$ = 2.6 Hz, OH from major diastereomer), 3.81 (s, 3H, OMe), 3.90 and 3.98 (m, total 1H, $H_5$), 4.15 (one-half of obscured AB system, 1H, $J$ = 12.1 Hz, one of $CH_2OCH_2Ar$), 4.46−4.66 (m, 3H, $OCH_2Ar$ and one of $CH_2OCH_2Ar$), 5.12 and 5.13 (two d, total 1H, $J$ = 7.3 Hz, $H_2$), 5.19−5.30 (m, 2H, $H_8$), 5.85 and 6.01 (m, total 1H, $H_7$), 6.90 (two d, 2H, $J$ = 8.2 Hz, ArH), 7.25−7.39 (m, 6H, ArH). $^{13}$C NMR: (mixture of diastereomers): $\delta$ 21.3, 41.4, 43.9, 55.22, 66.8, 68.8, 69.5, 69.7, 70.5, 72.8, 72.8, 75.0, 75.9, 79.4, 108.0, 108.8, 113.9, 114.0, 118.7, 119.3, 123.2, 128.4, 129.1, 129.4, 129.6, 129.8, 129.9, 133.7, 140.7, 140.9, 145.07, 145.14, 159.4, 159.6. IR (neat): 3364 (br), 2926, 2862, 2061, 1988, 1611, 1512, 1248, 1082, 1034, 810 cm$^{-1}$. Anal. Calcd for $C_{27}H_{28}O_7FeS$: C, 58.70; H, 5.11. Found: C, 58.86; H, 5.19.

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-5-(*R*)-Hydroxy-1-*p*-tolylsulfinyl-3-triisopropylsilyloxymethyl-1,3,7-octatriene]tricarbonyliron-(0) Complex (13c) and Its Diastereomer (13c(min)).** Aldehyde **11c** (0.536 g, 0.981 mmol, 1 equiv), dissolved in $CH_2Cl_2$ (9.8 mL), was reacted with allyltributylstannane (2 × 0.30 mL, total of 1.96 mmol, 2 equiv) and $BF_3{\cdot}Et_2O$ (2 × 0.12 mL, total of 1.96 mmol, 2 equiv) according to the general procedure. The ratio of diastereomers was determined to be 82:18 by integration of the $^1$H NMR spectrum of the crude oil using the $H_1$ and $H_5$ resonances. The diastereomers were separable via two successive gradient column chromatographies (silica gel, hexane/EtOAc, 19:1 to 4:1) to afford the major diastereomer of homoallylic alcohol **13c** (0.4072 g, 77%) as a yellow oil and its impure minor diastereomer (0.100 g) as a yellow solid. The minor diastereomer, **13c(min)**, was recrystallized from toluene (0.2 mL) and hexane (3 mL) at room temperature. An X-ray structure was then determined from these crystals to determine the absolute stereochemistry of the new stereocenter. Data for **13c**: $^1$H NMR: $\delta$ 1.12 (m, 21H, OTIPS), 2.39 (s, 3H, ArMe), 2.50 (m, 1H, one of $CH_2$CHOH), 2.68 (m, 1H, one of $CH_2$CHOH), 2.78 (d, 1H, $J$ = 9.3 Hz, $H_4$), 3.30 (br s, 1H, O*H*), 3.39 (d, 1H, $J$ = 7.4 Hz, $H_1$), 3.95 (m, 1H, methine), 4.65 (AB system, 2H, $J$ = 12.9 Hz, $CH_2$OTIPS), 5.19 (d, 1H $J$ = 7.4 Hz, $H_2$), 5.25 (d, 1H, $J$ = 10.2 Hz, $H_{8c}$), 5.31 (dd, 1H, $J$ = 16.6, 1.5 Hz, $H_{8t}$), 6.02 (m, 1H, $H_7$), 7.26 (d, 2H, $J$ = 8.1 Hz, ArH), 7.36 (d, 2H, $J$ = 8.2 Hz, ArH). $^{13}$C NMR: $\delta$ 11.8, 17.9, 21.3, 41.6, 63.8, 66.1, 70.5, 75.8, 78.0, 111.9, 119.0, 123.2, 129.8, 133.6, 140.9, 145.2; IR (neat) 3314 (br), 2949, 2863, 2059, 2004, 1467, 1059, 1010, 757, cm$^{-1}$. Anal. Calcd for $C_{28}H_{40}O_6FeSSi$: C, 57.14; H, 6.85. Found: C, 57.23; H, 7.02.

Data for the minor diastereomer, **13c(min)**: $^1$H NMR: $\delta$ 1.12 (m, 21H, OTIPS), 2.09 (m, 1H, OH), 2.40 (s, 3H, ArMe), 2.46 (m, 1H, one of $CH_2$CHOH), 2.63 (m, 1H, one of $CH_2$CHOH), 2.76 (d, 1H, $J$ = 7.0 Hz, $H_4$), 3.34 (d, 1H, $J$ = 7.4 Hz, $H_1$), 4.02 (m, 1H, methine), 4.61 (AB system, 2H, $J$ = 12.9 Hz, $CH_2$OTIPS), 5.25 (m, 3H, $H_2$, $H_{8c}$ and $H_{8t}$), 5.89 (m, 1H, $H_7$), 7.27 (d, 2H, $J$ = 8.0 Hz, ArH), 7.36 (d, 2H, $J$ = 8.1 Hz, ArH). $^{13}$C NMR: $\delta$ 12.6, 18.7, 22.1, 44.7, 63.4, 69.6, 70.3, 75.6, 75.9, 112.0, 120.2, 123.9, 130.5, 134.3, 141.4, 146.3. Anal. Calcd for $C_{28}H_{40}O_6FeSSi$: C, 57.14; H, 6.85. Found: C, 57.18; H, 6.79.

**$\eta$4-α-[($R_s$)-(1*Z*,3*E*)-3-[(*R*)-1-Acetoxybut-3-enyl]-5-(*R*)-hydroxy-1-*p*-tolylsulfinyl-1,3,7-octatriene]tricarbonyl iron (0) complex (13d) and Its Minor Diastereomer.** Aldehyde **11d** (0.255 g, 0.540 mmol, 1 equiv), dissolved in $CH_2Cl_2$ (5.4 mL), was reacted with allyltributylstannane (2 × 0.168 mL; total of 1.08 mmol, 2 equiv) and $BF_3{\cdot}Et_2O$ (2 × 0.066 mL; total of 1.08 mmol, 2 equiv) according to the general procedure. The ratio of diastereomers was determined to be 95:5 by integration of the $^1$H NMR spectrum of the crude oil using the $H_1$ resonances. The diastereomers were separable via two successive gradient column chromatographies (silica gel, hexane/EtOAc, 19:1 to 4:1), yielding the major diastereomer of the homoallylic alcohol **13d** (0.2373 g, 85%) as a yellow oil. The major diastereomer was dissolved in a minimum amount of toluene and recrystallized by diffusion with hexane at room temperature. An X-ray structure was then determined from these crystals. $^1$H NMR: $\delta$ 2.08 (s, 3H, OAc Me), 2.22 (d, 1H, $J$ = 4.3 Hz, OH), 2.41 (s, 3H, ArMe), 2.45 (m, 1H, one of $CH_2$-CHOH), 2.59 (d, 1H, $J$ = 9.4 Hz, $H_4$), 2.75 (m, 2H, one of $CH_2$-CHOH and one of $CH_2$CHOAc), 3.08 (m, 1H, one of $CH_2$-CHOAc), 3.45 (d, 1H, $J$ = 7.5 Hz, $H_1$), 3.95 (m, 1H, C*H*OH), 5.20 (m, 3H, $H_2$, $H_{4c}'$ and $H_{4t}'$), 5.32 (app t, 2H, $J$ = 18.4, 9.6 Hz, $H_{8c}$ and $H_{8t}$), 5.91 (m, 2H, $H_7$ and $H_3'$), 7.29 (d, 2H, $J$ = 8.2 Hz, ArH), 7.37 (d, 2H, $J$ = 8.2 Hz, ArH). $^{13}$C NMR: $\delta$ 21.6, 22.2, 42.7, 43.9, 66.1, 69.7, 70.7, 70.8, 76.6, 114.0, 119.8, 121.0, 124.1, 130.7, 133.4, 134.2, 141.9, 145.7, 170.0. IR ($CHCl_3$): 3347 (br), 3009, 2360, 2064, 2002, 1744, 1221, 1035, 756 cm$^{-1}$. Anal. Calcd for $C_{24}H_{26}O_7FeS$: C, 56.04; H, 5.09. Found: C, 56.09; H, 4.98.

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-5-*tert*-Butyldimethylsilyloxy-3-[(*R*)-1-hydroxybut-3-enyl]-1-*p*-tolylsulfinyl-1,3-pentadiene]-tricarbonyliron(0) Complex (14a) and Its Minor Diastereomer.** Aldehyde **12a** (0.088 g, 0.174 mmol, 1 equiv), dissolved in $CH_2Cl_2$ (1.7 mL), was reacted with allyl tributylstannane (2 × 0.054 mL, total of 0.348 mmol, 2 equiv) and $BF_3{\cdot}Et_2O$ (2 × 0.021 mL, total of 0.348 mmol, 2 equiv) according to the general procedure. The ratio of diastereomers was determined to be 87:13 by integration of the $^1$H NMR spectrum of the crude oil using the $H_1$ resonances. The diastereomeric homoallylic alcohols were separable via two successive gradient column chromatographies (silica gel, hexane/EtOAc, 19:1 to 2:1), yielding **14a** as a yellow oil (0.083 g, 87%, >98% de). $^1$H NMR: $\delta$ 0.11 (s, 6H, $Si(CH_3)_2$), 0.92 (s, 3H, $SiC(CH_3)_3$), 2.38 (s, 3H, ArMe), 2.56 (m, 1H, one of allylic $CH_2$), 2.65 (app t, 1H, $J$ = 7.6, 6.4 Hz, $H_4$), 2.92 (m, 1H, one of allylic $CH_2$), 3.20 (d, 1H, $J$ = 3.6 Hz, OH), 3.35 (d, 1H, $J$ = 7.4 Hz, $H_1$), 3.91 (ABX system, 2H, $J$ = 11.7, 8.4, 5.9 Hz, $CH_2$-OTBS), 4.53 (m, 1H, C*H*OH), 5.24 (m, 3H, $H_2$ and CH=C$H_2$), 6.00 (m, 1H, C*H*=$CH_2$), 7.25 (d, 2H, $J$ = 8.2 Hz, ArH), 7.33 (d, 2H, $J$ = 8.2 Hz). $^{13}$C NMR: $\delta$ −5.4, −5.3, 18.2, 21.3, 25.8, 44.2, 61.3, 61.7, 67.7, 73.4, 75.4, 116.9, 119.0, 123.2, 129.8, 133.5, 140.7, 145.1. IR (neat): 3332 (br), 2904, 2058, 1980, 1643, 1470, 1252, 1049 cm$^{-1}$. Anal. Calcd for $C_{25}H_{34}O_6FeSSi$: C, 54.94; H, 6.27. Found: C, 55.13; H, 6.41.

**$\eta$4-α-[($R_s$)-(1*Z*,3*E*)-3-[(*R*)-1-Hydroxybut-3-enyl]-1-*p*-tolylsulfinyl-5-triisopropylsilyloxy-1,3-pentadiene]tricarbonyliron(0) Complex (14b) and Its Minor Diastereomer.** Aldehyde **12b** (0.341 g, 0.623 mmol, 1 equiv), dissolved in $CH_2Cl_2$ (6.2 mL), was reacted with allyltributylstannane (2 × 0.193 mL, total of 1.25 mmol, 2 equiv) and $BF_3{\cdot}Et_2O$ (2 × 0.077 mL, total of 1.25 mmol, 2 equiv) according to the general procedure. The ratio of diastereomers was determined to be 89:11 by integration of the $^1$H NMR spectrum of the crude oil using the $H_1$ resonances. The diastereomeric homoallylic alcohols were separable via two successive gradient column chromatographies (silica gel, hexane/EtOAc, 19:1 to 4:1), yielding the major diastereomer **14b** (0.3213 g, 86%) as a yellow solid and the minor diastereomer (0.063 g, 14%) also as a yellow solid. Data for **14b**: mp 128−131 °C; $^1$H NMR: $\delta$ 1.09 (m, 21H, OTIPS), 2.39 (s, 3H, ArMe), 2.58 (m, 1H, one of $CH_2$CHOH), 2.62 (d, 1H, $J$ = 3.2 Hz, OH), 2.70 (app t, 1H, $J$ = 8.4, 5.8 Hz, $H_4$), 2.99 (m, 1H, one of $CH_2$CHOH), 3.39 (d, 1H, $J$ = 7.5 Hz, $H_1$), 4.01 (ABX system, 2H, $J$ = 11.6, 11.5, 5.6 Hz, $CH_2$OTIPS), 4.57 (app t, 1H, $J$ = 3.72, 3.68 Hz, C*H*OH), 5.26 (m, 3H, $H_{8c}$, $H_{8t}$ and $H_2$), 5.98 (m, 1H, $H_7$), 7.27 (d, 2H, $J$ = 8.0 Hz, ArH), 7.34 (d, 2H, $J$ = 8.1 Hz, ArH). $^{13}$C NMR: $\delta$ 12.8, 18.8, 22.2, 45.2, 62.5, 62.7, 68.5, 74.4, 76.7, 117.5, 120.3, 124.0, 130.7, 134.4, 141.7, 146.2; IR ($CHCl_3$) 3302 (br), 2943, 2866, 2062, 2001, 1461, 1216, 1065, 1012, 757, 622, 565 cm$^{-1}$. Anal. Calcd for $C_{28}H_{40}O_6FeSSi$: C, 57.14; H, 6.85. Found: C, 57.30; H, 7.01.

Data for the minor diastereomer: $^1$H NMR: $\delta$ 1.25 (m, 21H, OTIPS), 2.40 (s, 3H, ArMe), 2.58 (m, 1H, one of $CH_2$CHOH), 2.65 (dd, 1H, $J$ = 10.2, 5.7 Hz, $H_4$), 2.75 (m, 1H, one of $CH_2$-CHOH), 3.45 (d, 1H, $J$ = 7.4 Hz, $H_1$), 4.09 (app ABX system, 2H, $J$ = 11.3, 10.8, 5.8 Hz, $CH_2$OTIPS), 4.59 (app t, 1H, $J$ = 6.4, 6.8 Hz, C*H*OH), 4.70 (br s, 1H, OH), 5.04 (d, 1H, $J$ = 7.4

**Table 2. Summary of Crystallographic Data for Compounds 13c(min), 13d, and 15**

| complex | **13c(min)** | **13d** | **15** |
|---|---|---|---|
| empirical formula | $C_{28}H_{39}FeO_6SSi$ | $C_{24}H_{23}FeO_7S$ | $C_{19}H_{20}FeO_6S$ |
| fw | 587.59 | 511.33 | 432.26 |
| temp, K | 200 | 293 | 293 |
| wavelength, Å | 1.5418 | 1.5418 | 0.71070 |
| cryst syst | orthorhombic | tetragonal | orthorhombic |
| space group | $P2_12_12_1$ | $P4_3$ | $P2_12_12_1$ |
| unit cell dimens, Å | $a = 13.724(1)$ | $a = 11.3000(10)$ | $a = 10.5979(9)$ |
| | $b = 13.311(1)$ | $b = 11.3000(10)$ | $b = 10.5694(9)$ |
| | $c = 16.789(1)$ | $c = 19.9890(10)$ | $c = 17.834(2)$ |
| vol., Å$^3$ | 3067.0(4) | 2552.4(3) | 1997.6(3) |
| Z | 4 | 4 | 4 |
| density, calcd, mg/m$^3$ | 1.273 | 1.331 | 1.437 |
| abs coeff, mm$^{-1}$ | 11.214 | 5.841 | 0.891 |
| no. of indep reflns | 5197 | 3707 | 3508 |
| refinement method | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ |
| no. of data/params | 5197/350 | 3707/299 | 3508/244 |
| goodness-of-fit on $F^2$ | 0.939 | 1.069 | 1.173 |
| final $R$ indices ($I > 2\sigma(I)$) | R1 = 0.0443, wR2 = 0.0995 | R1 = 0.0676, wR2 = 0.1822 | R1 = 0.0819, wR2 = 0.1798 |
| $R$ indices (all data) | R1 = 0.0500, wR2 = 0.1066 | R1 = 0.0708, wR2 = 0.1925 | R1 = 0.1099, wR2 = 0.2019 |

Hz, $H_2$), 5.14 (d, 1H, $J$ = 10.2 Hz, $H_{8c}$), 5.21 (d, 1H, $J$ = 17.2 Hz, $H_{8t}$), 5.95 (m, 1H, $H_7$), 7.29 (d, 2H, $J$ = 8.2 Hz, ArH), 7.38 (d, 2H, $J$ = 7.8 Hz, ArH).

**$\eta^4$-α-[($R_s$)-(1*Z*,3*E*)-3-[(*R*)-1-Hydroxybut-3-enyl]-1-*p*-tolylsulfinyl-1,3-pentadien-5-ol]tricarbonyliron(0) Complex (15).** Alcohol **14b** (90.7 mg, 0.166 mmol, 1 equiv) was dissolved in THF (1.7 mL) and treated with a 1.0 M THF solution of TBAF (Aldrich, 0.332 mL, 0.332 mmol, 2 equiv). After 45 min, the reaction was diluted with EtOAc (20 mL) and then washed with $H_2O$ (5 mL) and brine (5 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo to yield an orange-yellow oil, which was chromatographed (silica gel, hexane/EtOAc, 3:1 to 1:1) to afford the diol, **15**, as a yellow oil. Crystallization of this oil from $CHCl_3$ gave yellow prisms (mp 144 °C, decomp), which were suitable for analysis by X-ray crystallography (51.1 mg, 72%). $^1$H NMR: $\delta$ 2.07 (d, 1H, $J$ = 3.0 Hz, CHO*H*), 2.33 (app t, 1H, $J$ = 6.4, 4.5 Hz, $CH_2OH$), 2.41 (s, 3H, ArMe), 2.57 (m, 1H, one of allylic $CH_2$), 2.76 (dd, 1H, $J$ = 8.5, 5.9 Hz, $H_4$), 2.97 (m, 1H, one of allylic $CH_2$), 3.43 (d, 1H, $J$ = 7.5 Hz, $H_1$), 3.89 (m, 1H, one of $H_5$), 4.09 (m, 1H, one of $H_5$), 4.55 (m, 1H, C*H*OH), 5.29 (m, 3H, CH=C$H_2$ and $H_2$), 5.98 (m, 1H, C*H*=CH$_2$), 7.28 (d, 2H, $J$ = 8.2 Hz), 7.34 (d, 2H, $J$ = 8.3 Hz). $^{13}$C NMR: (acetone-$d_6$): $\delta$ 21.2, 44.7, 44.8, 60.9, 61.0, 64.9, 68.8, 68.9, 75.0, 77.7, 118.2, 118.5, 124.0, 130.5, 135.3, 141.3, 147.5. Anal. Calcd for $C_{19}H_{20}O_6FeS$: C, 52.79; H, 4.66. Found: C, 52.84; H, 4.72.

**X-ray Structure Determination of 13c(min).** Due to the quality of the sample, data were collected at 200 K from a single crystal (0.27 × 0.38 × 0.53 mm) using a PW1100 four-circle diffractometer. The lattice parameters were refined from 91 reflections (2° < $\theta$ < 40°). Crystal data and other refinement parameters are given in Table 2. Scattering factors and anomalous dispersion corrections were taken from ref 17. The structure was solved by direct methods using *SIR92*[18] and was refined by least-squares analysis using *SHELX93*,[19] with anisotropic thermal parameters for non-H atoms. The positions of the hydrogen atoms were refined as riding on the corresponding C atoms with restraints for the C−H distances, except $H_1$, $H_2$, $H_3$, and $H_{14}$, which were freely isotropically refined. Absorption corrections were performed using *DIFBAS*.[20] Final fractional coordinates and anisotropic thermal parameters of non-hydrogen atoms for complex **13c(min)** are provided in the Supporting Information.

**X-ray Structure Determination of 13d.** Data were collected at room temperature from a single crystal with elongated prismatic shape (0.30 × 0.25 × 0.50 mm) on a CAD4 Enraf-Nonius diffractometer, using graphite-monochromated Cu Kα radiation ($\lambda$ = 1.5418 Å). The lattice parameters were refined from 45 reflections (4° < $\theta$ < 60°). Crystal data and other refinement parameters are given in Table 2. Scattering factors and anomalous dispersion corrections were taken from ref 17. The structure was solved by direct methods using *SIR92*[18] and was refined by least-squares analysis using *SHELX93*,[19] with anisotropic thermal parameters for non-H atoms. The positions of the hydrogen atoms were refined with distance restraints for the C−H and O−H distances. Slight extinction effects were corrected by using *SHELX93*, the extinction coefficient being 0.0038(7). Final fractional coordinates and anisotropic thermal parameters of non-hydrogen atoms for complex **13d** are provided in the Supporting Information.

**X-ray Structure Determination of 15.** Data were collected at room temperature from a single crystal with elongated prismatic shape (0.30 × 0.17 × 0.13 mm) on a CAD4 Enraf-Nonius diffractometer. The lattice parameters were refined from 45 reflections (2° < $\theta$ < 25°). Crystal data and other refinement parameters are given in Table 2. Scattering factors and anomalous dispersion corrections were taken from ref 17. The structure was solved by direct methods using *SIR92*[18] and was refined by least-squares analysis using *SHELX93*,[19] with anisotropic thermal parameters for non-H atoms. Final fractional coordinates and anisotropic thermal parameters of non-hydrogen atoms for complex **15** are provided in the Supporting Information.

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**Supporting Information Available:** Tables of crystal data, positional and thermal parameters, and bond distances and angles for complexes **13c(min)**, **13d**, and **15** (17 pages). Ordering information is given on any masthead page.

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