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Diastereoselective Intramolecular Pinacol Couplings of Sulfinyl Iron(0) Diene Complexes

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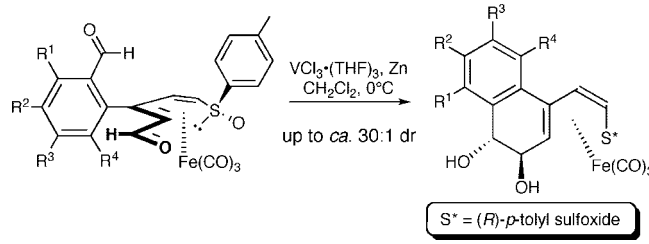

3-(2-Formylaryl)-1-sulfinyl-(1*Z*,3*E*)-pentadien-5-al iron tricarbonyl complexes were prepared to examine the feasibility and diastereoselectivity of intramolecular pinacol couplings on such substrates. It was found that the pinacol coupling, promoted by $VCl_3 \cdot (THF)_3$/Zn, proceeded in good yield and with high diastereoselectivity (>23:1 dr), provided the 2-formylaryl unit remained unsubstituted at the aryl C3 position (*ortho* to the formyl group). In these latter cases the pinacol coupling was diastereorandom. A 3-formyl-4-(2-formylaryl)-1-sulfinyl-(1*Z*,3*E*)-butadiene iron tricarbonyl complex also underwent diastereoselective pinacol coupling (22:1 dr). 3-(3-Formylindolyl)-1-sulfinyl-(1*Z*,3*E*)-pentadien-5-al iron tricarbonyl complexes were also prepared, though pinacol coupling of these substrates proceeded in, at best, modest yield for two of the four examples tested. All cases described herein represent the first intramolecular pinacol couplings performed on the periphery of an iron(0) diene tricarbonyl complex.

Introduction

Diastereoselective transformations of the organic ligand of transition metal complexes are among the fundamental methodological tactics of modern synthesis. The most commonly encountered examples involve manipulations of η^6-arene $Cr(CO)_3$ complexes,[1] η^4-diene $Fe(CO)_3$ complexes,[2] substituted ferrocenes,[3] and η^3-allyl complexes.[4] As a result of our interest in developing new synthetic methods that utilize enantiomerically pure transition metal complexes with organic ligands, we have previously described the diastereoselective complexation[5] of enantiopure 1-(1*Z*)-sulfinyldienes, **1**, that afford the corresponding η^4-diene $Fe(CO)_3$ complexes, **2** (Scheme 1).[6] Furthermore, we have reported that more functionalized complexes, exemplified by **3**, can be prepared and diastereoselectively transformed creating new stereocenters along the periphery of the iron(0) diene complex.[7] Spurred on by Uemura's report[8] of diastereoselective intramolecular pinacol couplings of η^6-arene $Cr(CO)_3$ complexes (Scheme 2), we chose to investigate if this methodology could be successfully extended to appropriately functionalized sulfinyl iron(0) diene complexes.

We were aware of only a single instance of an iron(0) diene complex being used as the stereodirecting group in a pinacol coupling: an intermolecular dimerization of an enantiopure

* Corresponding author.

(1) (a) Rosillo, M.; Domínguez, G.; Pérez-Castells, J. *Chem. Soc. Rev.* **2007**, *36*, 1589–1604. (b) Pape, A. R.; Kaliappan, K. P.; Kündig, E. P. *Chem. Rev.* **2000**, *100*, 2917–2940. (c) Rose-Munch, F.; Rose, E. *Curr. Org. Chem.* **1999**, *3*, 445–467. (d) Semmelhack, M. F. *In Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; *Vol. 12*, p. 979. (e) Davies, S. G.; McCarthy, T. D. *In Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; *Vol. 12*, p. 1039.

(2) (a) Knölker, H.-J. *In Transition Metals For Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 2004; *Vol. 1*, pp. 585–599. (b) Knölker, H.-J.; Braier, A.; Bröcher, D. J.; Cämmerer, S.; Fröhner, W.; Gonser, P.; Hermann, H.; Herzberg, D.; Reddy, K. R.; Rohde, G. *Pure Appl. Chem.* **2001**, *73*, 1075–1086. (c) Knölker, H.-J. *Chem. Soc. Rev.* **1999**, *28*, 151–157. (d) Donaldson, W. A. *Curr. Org. Chem.* **2000**, *4*, 837–868. (e) Gfee, R.; Lellouche, J. P. *In Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, U.K., 1995; *Vol. 4*, pp. 129−273. (f) Donaldson, W. A. *In Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; *Vol. 12*, pp. 623−635. (g) Pearson, A. J. *In Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; *Vol. 12*, p. 637. (h) Pearson, A. J. *Iron Compounds in Organic Synthesis*; Academic Press: London, U.K., 1994.

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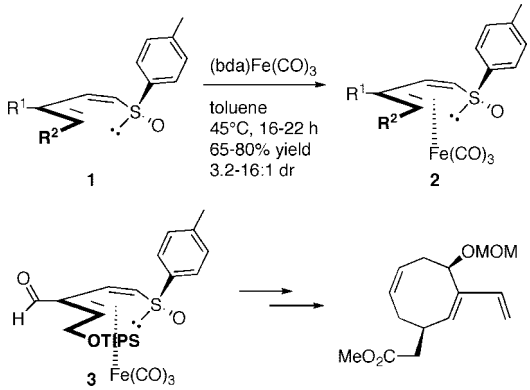
SCHEME 1



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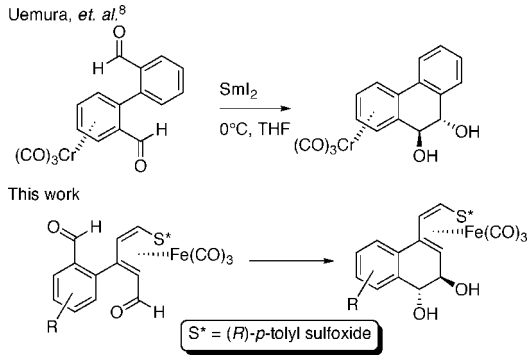
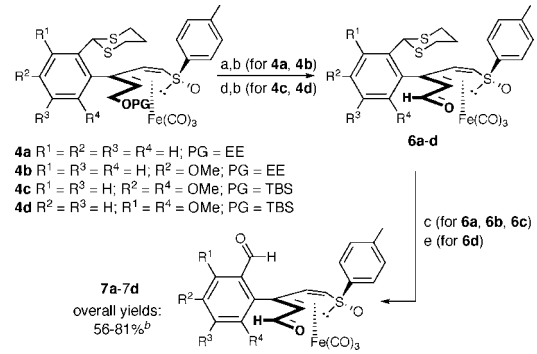


iron(0) dienal complex proceeding through a ketyl−radical intermediate.[9] In fact, there appear to be only two other examples in which any type of radical intermediate has been generated along the diene periphery in η^4-diene $Fe(CO)_3$ complexes.[10] Thus, as compared to the related η^6-arene $Cr(CO)_3$ complexes, where the chemistry of radicals formed at the adjacent benzylic position is well studied and synthetically useful,[11] radical chemistry at allylic positions of η^4-diene $Fe(CO)_3$ complexes remains quite underdeveloped. Herein, we report the initial findings of our ongoing study.

Results and Discussion

Our prior communication described the synthesis of the enantiopure sulfinyl iron(0) diene complexes, **4a**−**d**, required as precursors for the examination of the feasibility of the pinacol

SCHEME 3[a]



[a] Reagents and conditions: (a) 2M aq HCl/EtOAc (1:1). (b) SO_3·pyr, NEt_3, DMSO/CH_2Cl_2 (1:1). (c) $Hg(ClO_4)_2$, $CaCO_3$, THF/H_2O (2:1). (d) TBAF, THF. (e) $PhI(O_2CCF_3)$, $NaHCO_3$, CH_3CN/H_2O (85:15). See supporting information for details.

couplings.[12] For each complex the stereochemical assignment for the position of the $Fe(CO)_3$ fragment, relative to the sulfoxide stereocenter, was made on the basis of the X-ray crystallographic and ^1H NMR spectroscopic precedence established for this class of compounds.[13] Conversion of complexes **4a**−**d** into dialdehydes, **7a**−**d**, via alcohols **5a**−**d** and dithianyl aldehydes **6a**−**d**, was accomplished using straightforward functional group manipulations (Scheme 3). Several details are noteworthy: First, although complexes **4b**−**d** were readily separated from their corresponding minor β-facial diastereomers, the facial diastereomers of complex **4a** were inseparable. Rather than undertake a tedious chromatographic separation of the diastereomers, this mixture was carried through subsequent steps until the preparation of dialdehyde **7a**, when the minor isomer was easily removed. Second, the more sterically demanding η^4-dienol $Fe(CO)_3$ complexes **5c** and **5d**, which possess axial chirality in addition to planar chirality, showed some erosion of stereochemical fidelity upon oxidation to the corresponding η^4-dienal $Fe(CO)_3$ complexes **6c** and **6d**. Dithianyl aldehyde **6c** was obtained as a 9:1 diastereomeric mixture, and dithianyl aldehyde **6d** was obtained as a ca. 30:1 mixture of diastereomers. We have assigned these diastereomeric contaminants to be atropisomers, as a result of rotation about the aryl−iron(0) diene bond, made possible by the reduced size of the allylic functionality (formyl vs CH_2OH). This process is minimized in **6d** because the dithiane unit is effectively larger due to the presence of the *ortho*-methoxy group (which diminishes the dithiane's conformational mobility). Conversion of the diastereomeric mixture

(3) (a) Atkinson, R. C. J.; Gibson, V. C.; Long, N. J. *Chem. Soc. Rev.* **2004**, *33*, 313–328. (b) Sutcliffe, O. B.; Bryce, M. R. *Tetrahedron: Asymmetry* **2003**, *14*, 2297–2325. (c) Richards, C. J.; Locke, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377–2407. (d) *Ferrocenes*; Togni, A., Hayashi, T., Eds.; *VCH*: Weinheim, Germany, 1995.

(4) (a) Garnier, E. C.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2008**, *130*, 7449–7458, and references therein. (b) Cox, L. R.; Ley, S. V. *Chem. Soc. Rev.* **1998**, *27*, 301–314. (c) Ley, S. V.; Cox, L. R.; Meek, G. *Chem. Rev.* **1996**, *96*, 423–442.

(5) Paley, R. S. *Chem. Rev.* **2002**, *102*, 1493–1523.

(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) Paley, R. S.; Estroff, L. A.; Gauguet, J.-M.; Hunt, D. K.; Newlin, R. C. *Org. Lett.* **2000**, *2*, 365–368.

(8) Taniguchi, N.; Hata, T.; Uemura, M. *Angew. Chem., Int. Ed.* **1999**, *9*, 1232–1235.

(9) Taniguchi, N.; Uemura, M. *Tetrahedron* **1998**, *54*, 12775–12788.

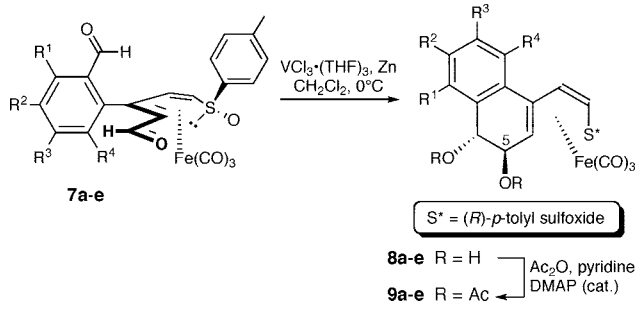
(10) (a) Wei, L. L.; Lai, M. C.; Ong, C. W. *Tetrahedron Lett.* **2000**, *41*, 3407–3410. (b) Hwang, W.-S.; Liao, R.-L.; Ong, C. W. *Polyhedron* **1989**, *8*, 479.

(11) References 8, 9, and: (a) Byers, J. H.; Janson, N. J. *Org. Lett.* **2006**, *8*, 3453–3455. (b) Merlic, C. A.; Walsh, J. C. *J. Org. Chem.* **2001**, *66*, 2265–2274. (c) Merlic, C. A.; Hietbrink, B. N.; Houk, K. N. *J. Org. Chem.* **2001**, *66*, 6738–6744. (d) Merlic, C. A.; Miller, M. M.; Hietbrink, B. N.; Houk, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 4904–4918. (e) Merlic, C. A.; Walsh, J. C.; Tantillo, D. J.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 3596–3606. (f) Schmalz, H.-G.; de Koning, C. B.; Bernicke, D.; Siegel, S.; Pfletschinger, A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1620–1623. (g) Merlic, C. A.; Walsh, J. C. *Tetrahedron Lett.* **1998**, *39*, 2083–2086. (h) Taniguchi, N.; Uemura, M. *Tetrahedron Lett.* **1997**, *38*, 7199–7202. (i) Taniguchi, N.; Kaneta, N.; Uemura, M. *J. Org. Chem.* **1996**, *61*, 6088–6089. (j) Schmalz, H.-G.; Siegel, S.; Bats, J. W. *Angew. Chem., Int. Ed.* **1995**, *34*, 2383–2385. (k) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1989**, *54*, 2904–2910.

(12) Paley, R. S.; Liu, J. M.; Lichtenstein, B. R.; Knoedler, V. L.; Sanan, T. T.; Adams, D. J.; Fernandez, J.; Rablen, P. R. *Org. Lett.* **2003**, *5*, 309–312.

(13) ^1H NMR: the chemical shift of the proton β to the sulfoxide was used to assign the facial stereochemistry of the $Fe(CO)_3$ fragment. See the Supporting Information for ref 12. X-ray: (a) Paley, R. S.; Estroff, L. A.; McCulley, D. J.; Martínez-Cruz, L. A.; Jiménez Sánchez, A.; Cano, F. H. *Organometallics* **1998**, *17*, 1841–1849. (b) Paley, R. S.; Rubio, M. B.; Fernández de la Pradilla, R.; Dorado, R.; Hundal née Sood, G.; Martínez-Ripoll, M. *Organometallics* **1996**, *15*, 4672–4674.

TABLE 1. Intramolecular Pinacol Coupling of 3-(2-Formylaryl)-1-sulfinyl-(1*Z*,3*E*)-Pentadien-5-al Iron Tricarbonyl Complexes, 7a-e



dial	R^1	R^2	R^3	R^4	% yield, **8a-e**	% yield, **9a-e**	dr (*trans*/*cis*)[a]
7a	H	H	H	H	67	91	ca. 30:1
7b	H	OMe	H	H	67	91	27:1
7c	H	OMe	H	OMe	76	96	23:1
7d	OMe	H	H	OMe	84	92	1:1.1
7e	Me	OMe	H	H	74	85	1:1.5

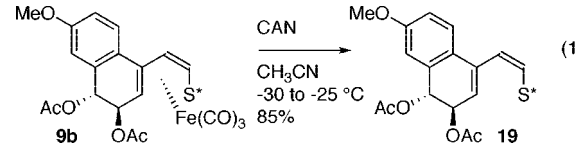
[a] Determined by integration of the ^{1}H NMR spectrum.

of **6c** into dialdehyde **7c** resulted in the formation of a single compound, presumably because atropisomerism is no longer possible. However, the more sterically demanding dialdehyde **7d** was obtained as a 98.4:1.6 diastereomeric mixture. This mixture was used in subsequent steps.

We were then delighted to discover that pinacol couplings of dialdehydes **7a**−**c** could be readily effected by treatment with Pedersen's reagent, $[V_2Cl_3(THF)_6]_2(Zn_2Cl_6)$, prepared in situ by treating $VCl_3 \cdot (THF)_3$ with Zn dust.[14] Diols **8a**−**c** were obtained with excellent diastereoselectivities (Table 1: conversion of the diols into the corresponding diacetates **9a**−**c** facilitated ^{1}H NMR analysis). In the absence of our ability to crystallize any of these compounds, we relied on a combination of precedence and careful comparisons to ^{1}H NMR spectroscopic data, of related compounds, to assign the stereochemistry of the new stereocenters of the pinacol products. By analogy to Uemura's example,[8] as well as to many other known diastereoselective conversions in iron(0) diene complex chemistry,[2] the stereochemistry of the C5 acetates was assigned as *anti* to the $Fe(CO)_3$ fragment for each complex. The relative stereochemistry of the major diastereomeric diacetates was assigned as *trans*, again by analogy to the Uemura coupling, but also by the support of ample ^{1}H NMR spectroscopic data of related compounds. For example, the oxygenated dihydronaphthalenes **10a**−**c** reported by Lautens[15] provide a useful comparison. The *trans* stereochemistry of the substituents gave ^{1}H NMR coupling constants in the range of 10.3−11.0 Hz, which compares favorably to the corresponding values of 10.7−11.2 Hz observed in the spectra of the major diastereomers of **9a**−**c** (Table 2). Additionally, Suzuki reported broadening of the H5 and H6 signals at ambient temperatures for the related dioxygenated dihydrophenanthrenes. We did not observe such broadening, but the **9a**–**c** coupling constants are also consistent with those observed by Suzuki at low temperature for conformers with substituents in a *trans* diequatorial relationship (J = 10.8 and 11.5 Hz).[16]

Though pinacol diacetates **9a**−**c** were obtained with high diastereoselectivity, conversion of dialdehyde **7d** into diol **8d** exhibited a striking loss of diastereoselectivity. The reaction proceeded in a diastereorandom manner. We assigned the *trans* isomer of the corresponding diacetate (**9d**) to be the compound with the J_{H5-H6} coupling constant of 2.7 Hz. This is in accord with the assignments made by Lautens for dihydronaphthalenes **10d**−**g**, which are compounds with a substituent *ortho* to the benzylic alcohol (i.e., $R^1 \neq H$).[15] A similar coupling constant of 3.5 Hz was also measured in a related dioxygenated dihydrobenz[*a*]anthracene, as reported by Suzuki.[17] Our assignment is also supported by chemical shift data. In our series (**9a**–**e**) the chemical shift of H6 is consistently 0.08−0.15 ppm more downfield for the *trans* diastereomer (Table 2). To evaluate whether the lack of selectivity in the pinacol coupling was due to a bidentate coordination of the vanadium atom to the formyl and *ortho*-methoxy substituents or to a steric effect, the related substrate **7e** was prepared from the known 6-iodo-3-methoxy-2-methylbenzaldehyde (Scheme 4).[18] Pinacol coupling of dialdehyde **7e** was also diastereorandom, suggesting a steric origin for the loss of selectivity, as well as a limitation of this methodology. We attribute this to a destabilization of the conformer (**A**, Figure 1) that would lead to the *trans* diastereomer. Equilibration to conformer **B** provides a pathway to the *cis* isomer via the vanadium(III) ketyl. That two diastereomeric diols are formed and not four suggests that the ketyl formed adjacent to the iron(0) diene system is configurationally stable. While it is possible that this configurational stability is a result of an interaction between the ketyl p-orbital and the appropriate d-orbital of the electron-rich iron atom, it is also likely that the rotation about the C4−C5 bond is simply minimized as a result of its steric environment. That is, it is expected that the s-*trans* conformer of the aldehyde would be favored over the s-*cis* conformer, and that this preference would be maintained during the conversion to the corresponding ketyl. This is a situation similar to one described by Merlic in a related η^6-arene $Cr(CO)_3$ complex,[11b] where it was concluded that steric effects play the dominant role because of theoretical and experimental evidence that the chromium tricarbonyl fragment does not significantly stabilize adjacent radicals. It is possible that this argument also pertains to radicals adjacent to iron(0) diene complexes with a similar substitution pattern.

That the $Fe(CO)_3$ fragment can be removed to reveal the 1-sulfinyl diene unit without aromatization of the ring created by the pinacol coupling was established by careful treatment of diacetate **9b** with CAN at low temperature to produce **19** (eq 1) as a 16:1 diastereomeric mixture.[19]



We have also endeavored to extend this methodology to include indole systems, where we envisioned attaching a

(14) (a) Konradi, A. W.; Pedersen, S. F. *J. Org. Chem.* **1992**, *57*, 28–32. (b) Freudenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 8014–8016.

(15) Lautens, M.; Schmid, G. A.; Chau, A. *J. Org. Chem.* **2002**, *67*, 8043–8053.

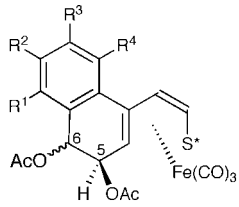
(16) (a) Ohmori, K.; Kitamura, M.; Ishikawa, Y.; Kato, H.; Oorui, M.; Suzuki, K. *Tetrahedron Lett.* **2002**, *43*, 7023–7026. (b) Ohmori, K.; Kitamura, M.; Suzuki, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 1226–1229.

(17) Ohmori, K.; Mori, K.; Ishikawa, Y.; Tsuruta, H.; Kuwahara, S.; Harada, N.; Suzuki, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 3167–3171.

(18) Kende, A. S.; Curran, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1857–1864.

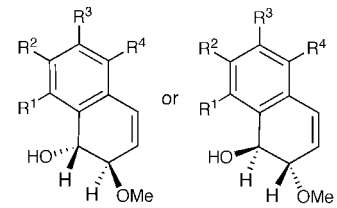
(19) Similar treatment of diol **8b** produced the corresponding sulfinyl diene in substantially poorer yield.

TABLE 2. ^{1}H NMR Data Including Comparison of Coupling Constants: Pinacol Diacetates (9a−e) vs Dihydronaphthalenes (Lautens,[15] 10a−g)



9a-e

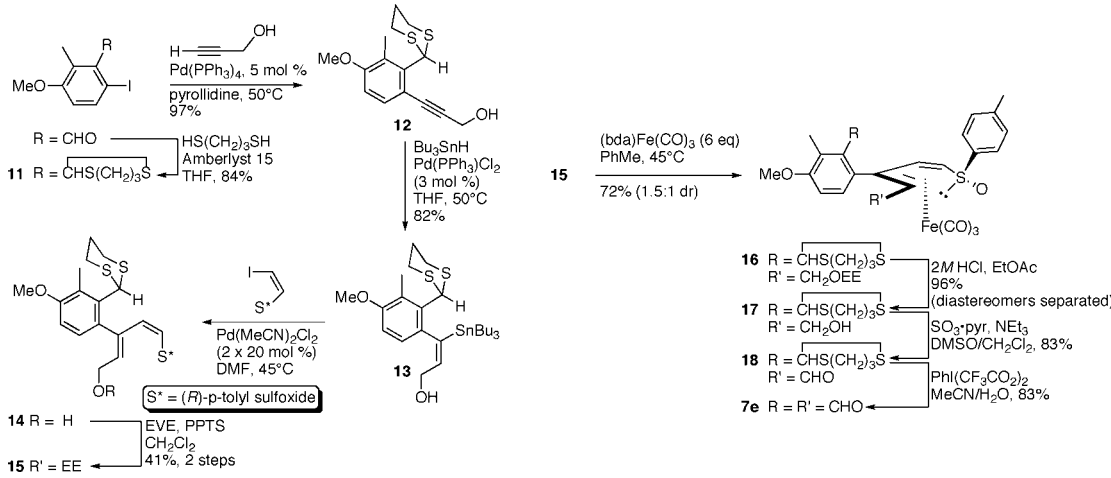
	R^1	R^2	R^3	R^4	trans $J_{H_5\text{-}H_6}$ (Hz)	cis $J_{H_5\text{-}H_6}$ (Hz)	trans δ_{H_6} (ppm)	cis δ_{H_6} (ppm)
9a	H	H	H	H	10.7	3.0	6.53	6.44
9b	H	OMe	H	H	10.8	2.9	6.48	6.40
9c	H	OMe	H	OMe	11.2	2.9	6.17	6.09
9d	OMe	H	H	OMe	2.7	6.5	6.64	6.49
9e	Me	OMe	H	H	2.9	2.3	6.40	6.27



10a-c **10d-g**

	R^1	R^2	R^3	R^4	J_{trans}, Hz
10a	H	OMe	H	H	10.3
10b	H	Br	H	H	10.6
10c	H	H	Ac	H	11.0
10d	OMe	H	Cl	H	2.7
10e	OMe	H	H	Cl	2.5
10f	OMe	H	H	Ac	2.5
10g	Me	H	H	H	1.9

SCHEME 4



potential nucleophilic tether to the indole nitrogen for eventual intramolecular attack on the corresponding decomplexed sulfinyl diene or compounds derived from it. While this latter goal has not yet been realized, we have prepared a series of pinacol precursors and have examined the intramolecular pinacol coupling of each of them. The synthesis of complexes **20a** and **20b** was previously reported.[12] The conversion of each of these to dialdehydes **23a** and **23b** is shown in Scheme 5. More elaborate *N*-alkylated complexes **23c** and **23d** have also been prepared. The synthetic routes to these compounds are depicted in Schemes 6 and 7.

These reaction sequences feature a number of noteworthy details. Indeed Schemes 6 and 7 feature the most highly functionalized sulfinyl diene iron(0) tricarbonyl complexes that we have prepared to date. First, it was necessary to assemble the *N*-alkyl-2-alkynylindole **26** (Scheme 6) in the order presented. The Stille coupling (as well as the related Sonogashira coupling) on the hindered *N*-alkyl-2-bromo-3-dithianylindole

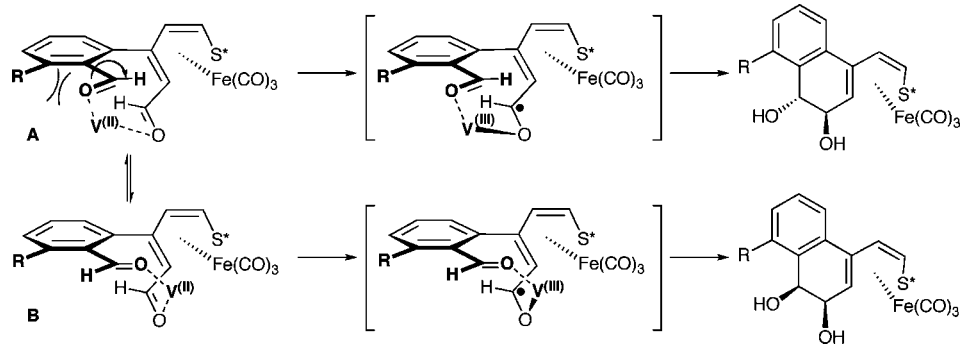
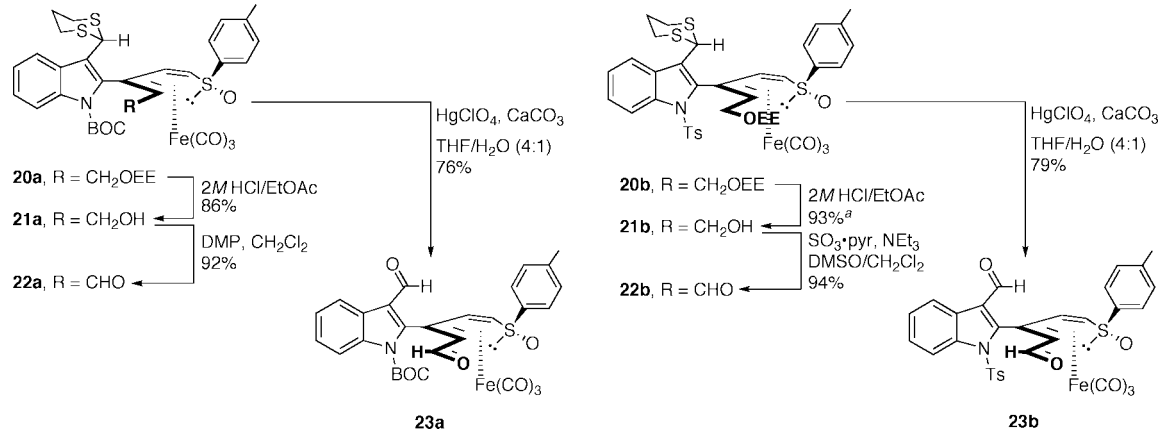


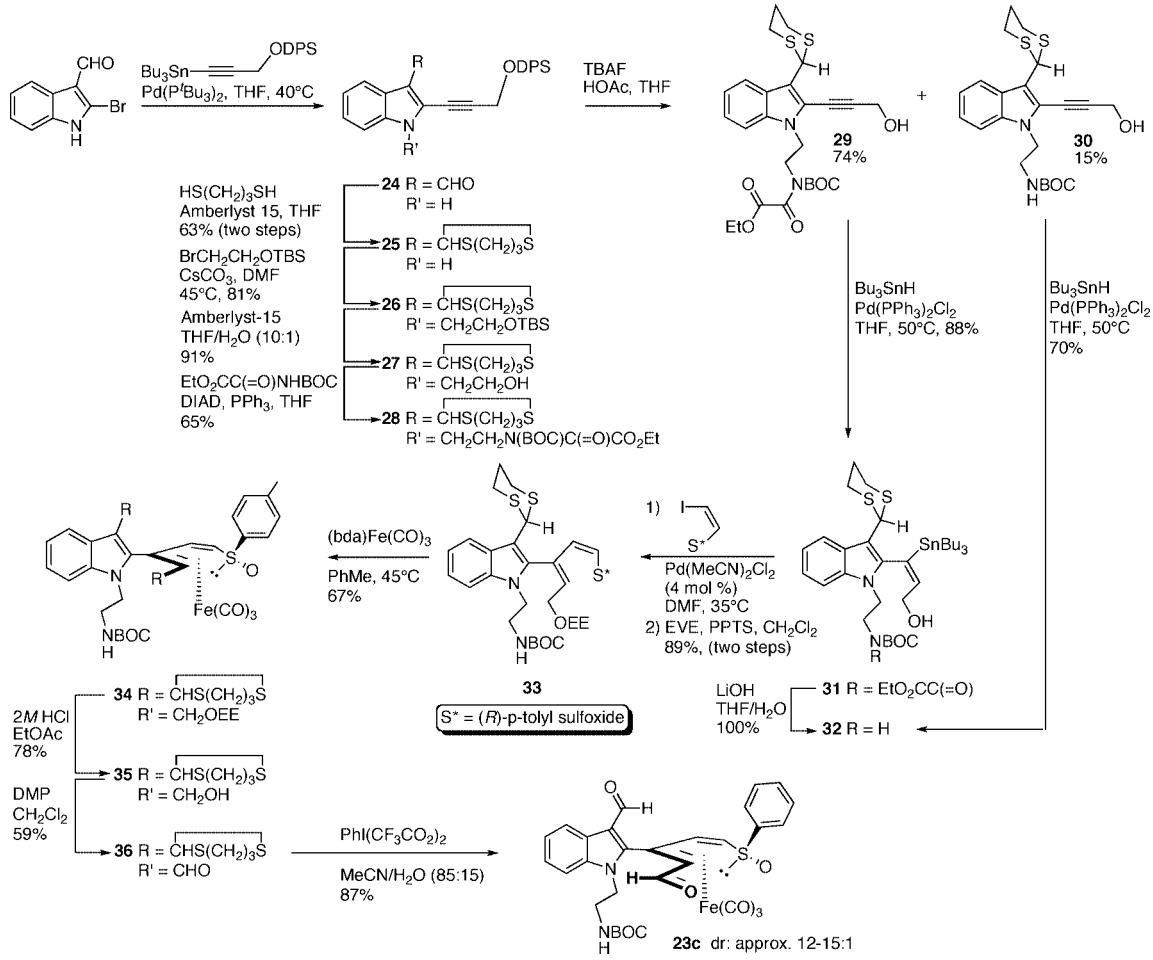
FIGURE 1. Loss of diastereoselectivity during pinacol couplings.

SCHEME 5



[a] This yield represents the combined yield for the hydrolysis of the diastereomeric complexes, **20b**. The diastereomeric alcohols were separable, and yield of the depicted diastereomer, **21b**, was 71%.

SCHEME 6

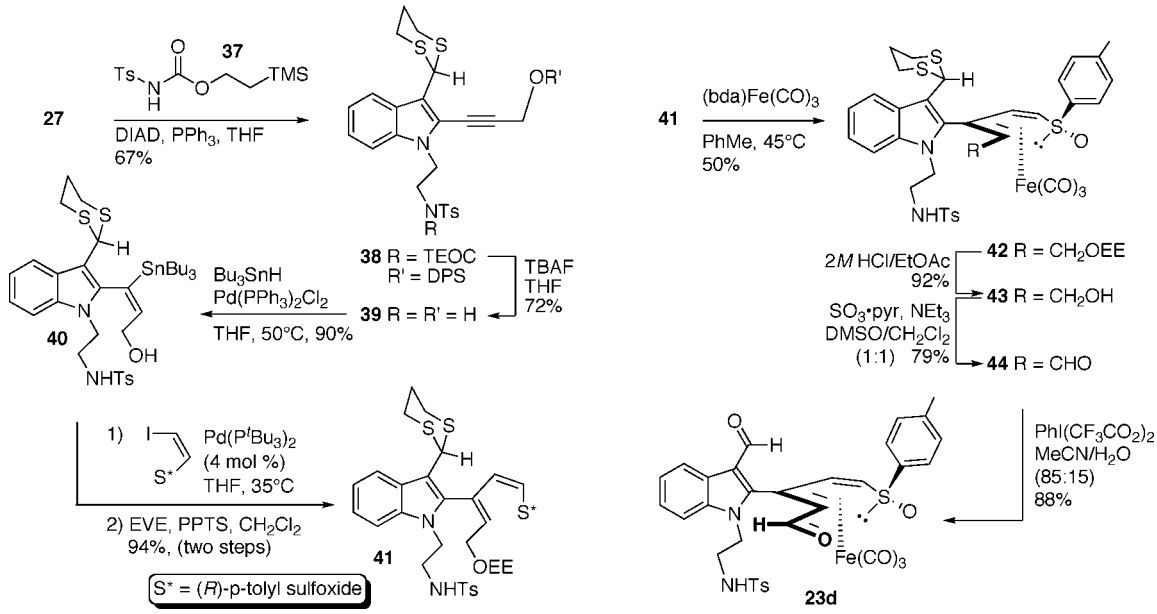


was not successful, and we were unable to prepare the *N*-alkyl-2-bromo-3-formylindole from our 2-bromo-3-formylindole starting material.[20] Second, after selective deprotection of the TBS ether to produce **27**, Mitsunobu chemistry was used to install a protected primary amine (the intended future intramolecular nucleophile). For **28** (Scheme 6) the commercially available *N*-BOC ethyl oxamate[21] was employed, while synthesis of **38** (Scheme 7) featured the use of the previously unknown TEOC-protected *p*-toluenesulfonamide **37**.[22] This later enabled the sulfonamido nitrogen and the propargylic oxygen atoms to be deprotected at the same time in order to produce **39** using conditions which were compatible with the vinyl stannane functionality. Third, the palladium-catalyzed hydrostannylation

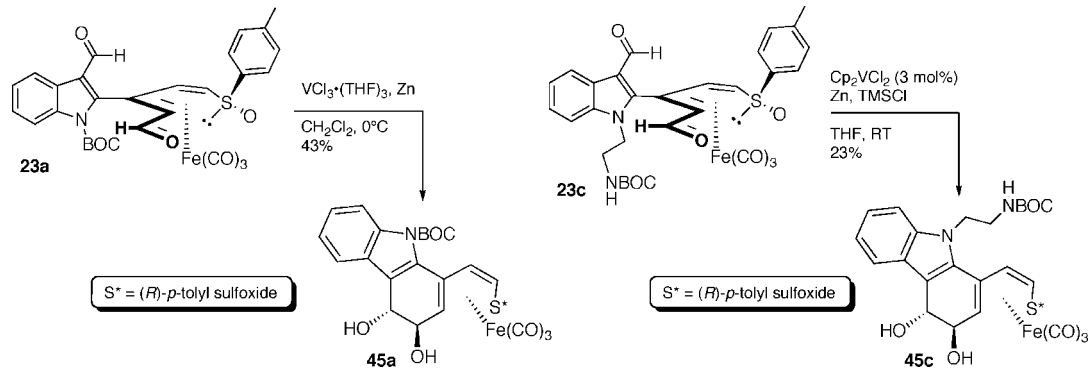
(20) Gilchrist, T. L.; Kemmitt, P. D.; Germain, A. L. *Tetrahedron* **1997**, *53*, 4447–4456.

(21) The Mitsunobu reaction of *N*-BOC ethyl oxamate has been described: Berrée, F.; Michelot, G.; Le Corre, M. *Tetrahedron Lett.* **1998**, *39*, 8275–8276.

SCHEME 7



SCHEME 8



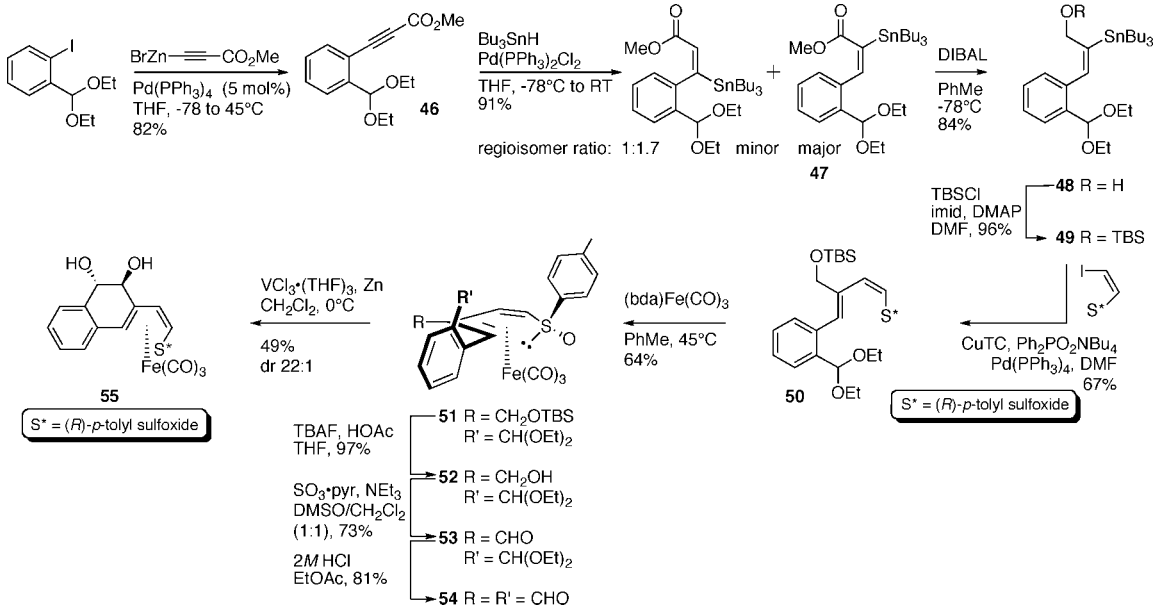
of each of the 3-dithianyl-2-alkynylindoles proceeded with the same high level of regioselectivity observed in the analogous *ortho*-substituted benzene derivatives.[23] Fourth, Stille coupling of the atropisomeric (but racemic) vinyl stannane **32** (Scheme 6) gave the corresponding sulfinyl diene, **33**, as a ca. 3.3:1 mixture of diastereomers (atropisomers). This appeared to be an equilibrium mixture, since TLC showed that solutions of each of the chromatographically separated atropisomeric sulfinyl dienes become the same mixture upon standing. Stille coupling with vinyl stannane **40** (Scheme 7) gave a similar (4:1) atropisomeric mixture. Finally, complexation to provide the corresponding sulfinyl iron(0) diene complexes proceeded with a degree of dynamic kinetic resolution, as observed in related systems.[12] For the BOC-protected series (Scheme 6), evaluation of the diastereomer ratio by ^{1}H NMR integration was difficult. At least three of the four possible diastereomers were observed, and the analysis was further complicated by diastereomers resulting from the presence of the stereocenter of the EE protecting group. Our estimate is that the major diastereomer of complex **34**, which led to dialdehyde **23c**, is formed in a ca. 5:1 ratio. Purification to a single diastereomer was carried out following hydrolysis of the EE group. However, the ^{1}H NMR spectra of this series of complexes remained complicated, possibly as a result of rotamers due to the BOC group. For the Ts-protected series (Scheme 7), iron(0) diene complex **43** could be purified to >95% purity after hydrolysis of the EE group. The diastereomeric ratio of the complexation itself, which gave **42**, was again difficult to evaluate. The major diastereomer obtained after chromatography (a yield of 50% is cited in Scheme 7) could not be rigorously purified from minor diastereomers. However, after processing **42** into **23d**, the ^{1}H NMR spectrum of the latter compound revealed only a trace of a diastereomeric impurity.

Despite the significant effort put forth to prepare dialdehydes **23a**−**d**, a reliable and high-yielding set of conditions for the intramolecular pinacol coupling in this indole series has, unfortunately, not yet been found (Scheme 8). For example, the conversion of **23a** into diol **45a** using Pedersen's method[14] has, thus far, only been achieved in a modest 43% yield, though it is reassuring to observe that a single diastereomer was obtained in the process (assigned as *trans*, $J_{H5-H6} = 7.9$ Hz, for the corresponding diacetate). Unfortunately, substantial decomposition occurred during the reaction, and unreacted dialdehyde was neither observed or recovered. Similarly, diol **45c** (*trans*, $J_{H5-H6} = 8.0$ Hz, for the corresponding diacetate) was obtained

(22) See the Supporting Information for the procedure for the synthesis of **37**.

(23) (a) Rubin, M.; Trofimov, A.; Gevorgyan, V. *J. Am. Chem. Soc.* **2005**, *127*, 10243–10249. (b) Alami, M.; Liron, F.; Gervais, M.; Peyrat, J. F.; Brion, J. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 1578–1580. (c) Liron, F.; Le Garrec, P.; Alami, M. *Synlett* **1999**, 246–248.

SCHEME 9



in a 23% yield using the method of Hirao.[24] It remains unclear if the ca. 5.5:1 ratio of peaks in the ^{1}H NMR spectrum represents a diastereomeric mixture or is a result of rotamers about the N−BOC bond. We have been unable to prepare pinacol coupling products from substrates **23b** or **23d**.

Finally, we examined the pinacol coupling of a substrate where the positions of the aldehyde and the *o*-formyl aryl group had been transposed. The preparation of the requisite dialdehyde pinacol precursor also afforded us the opportunity to re-evaluate the protecting group scheme used in the previously described sequences. Our choice of the dithiane had not been arbitrary, as we had been unable to carry out Stille couplings of aryl vinyl stannanes possessing an *ortho* substituent unless a benzylic sulfur atom was present.[12] Presumably this was a result of a favorable interaction between the palladium and sulfur atoms that accelerated the key Stille transmetalation step.[25] Unfortunately, the use of the dithiane group also led to a reduced diastereofacial selectivity in the $Fe(CO)_3$ complexation step. We believe this latter outcome was a result of heteroatom delivery[5] of the $Fe(CO)_3$ fragment from a dithiane sulfur atom that could be positioned either above or below the diene plane. This would bring the metal fragment toward the diene along competing trajectories, somewhat removed from the directing influence of the sulfoxide, and these trajectories likely possessed transition states that were close in energy. With our intention to transpose the groups along the diene periphery, it was logical to set aside the dithiane protecting group in favor of an acetal. This group would seem less likely to participate in the undesired heteroatom delivery and would be strategically effective, if we could solve the potential difficulties presented by a Stille coupling that would no longer benefit from the sulfur−palladium interaction. Indeed, we had already encountered a situation that pointed to the challenges inherent in effecting the synthesis of this family of aryl-substituted sulfinyl dienes. Diene **14** (Scheme 4) could only be prepared in modest yield because of a sluggish Stille coupling. In this case, the high degree of substitution on the aromatic ring presumably prevented the dithiane group from adopting a conformation that would allow the beneficial sulfur−palladium interaction to take place.

With this challenge in mind, the diethyl acetal of *o*-iodobenzaldehyde was chosen as the starting point of the sequence. Negishi coupling[26] afforded the aryl alkynyl ester **46**. Palladium-catalyzed hydrostannylation of this substrate at room temperature resulted in the formation of regioisomers in a 1:1 ratio, as the electronic bias of hydride addition to the alkynyl ester[27] could not overcome the intrinsic regiochemical preference dictated by the *ortho* substituent.[23] The maximum yield of the desired regioisomer **47** was obtained by starting the hydrostannylation at −78 °C and allowing the reaction mixture to warm to room temperature slowly. A 1.7:1 ratio of regioisomers was obtained, and the isomers were readily separated by chromatography. After reduction and protection of the resulting alcohol, sulfinyl diene **50** *could be obtained in good yield by using the Stille coupling conditions* recently extolled by Fürstner.[28] Complexation of this sulfinyl diene gave complex **51** with, as expected an acetal rather than a dithiane, a high degree of diastereofacial selectivity (>10:1). Routine functional group manipulation led to the dialdehyde pinacol precursor **54**, and the pinacol coupling was successfully accomplished to produce diol **55** in a moderate yield (49%), but with high diastereoselectivity (22:1). The *trans* stereochemical assignment of corresponding diacetate (major isomer: $J = 2.3$ Hz; minor isomer: $J = 4.2$ Hz) was based on the precedence established by the analogous transformations described above.

Conclusions

In conclusion, we have reported the first intramolecular pinacol couplings performed on the periphery of an iron(0) diene

(24) Hirao, T.; Ogawa, A.; Asahara, M.; Muguruma, Y.; Sakurai, H. *Org. Syn.* **2005**, *81*, 26–28. Diol **45c** could not be prepared using Pedersen's method. .

(25) (a) Espinet, P.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *36*, 4704–4734. (b) Itami, K.; Kamei, T.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, *123*, 8773–8779. (c) Crisp, G. T.; Gebauer, M. G. *Tetrahedron Lett.* **1995**, *36*, 3389–3392. (d) Vedejs, E.; Haight, A. R.; Moss, W. O. *J. Am. Chem. Soc.* **1992**, *114*, 6556–6558.

(26) Anastasia, L.; Negishi, E. *Org. Lett.* **2001**, *3*, 3111–3113.

(27) Smith, N. D.; Mancuso, J.; Lautens, M. *Chem. Rev.* **2000**, *100*, 3257–3282, and references therein.

(28) Fürstner, A.; Funel, J.-A.; Tremblay, M.; Bouchez, L. C.; Nevado, C.; Waser, M.; Ackerstaff, J.; Stimson, C. C. *Chem. Commun.* **2008**, 2873–2875.

tricarbonyl complex. The transformation is highly diastereoselective, but not without limitations, as substitution *ortho* to the aromatic formyl group results in a complete loss of diastereoselectivity. Also, attempts to extend the methodology to indole systems were only partially successful, as the pinacol coupling proceeded in low to moderate yields in the best cases and failed completely in others. The pinacol coupling precursors were the most functionality-rich 1-sulfinyl diene iron(0) tricarbonyl complexes we have prepared to date. As a consequence of developing the synthetic routes to prepare them, a number of other discoveries were made: (a) the importance of using the Fürstner modification of the Stille reaction for the preparation of a hindered 1-sulfinyl diene, (b) the use of a new Mitsunobu nucleophile (**37**), (c) the observation that 3-substituted 2-alkynylindoles undergo highly regioselective palladium-catalyzed hydrostannylations, and (d) that it is possible to exert some control over the regioselectivity of the hydrostannylation of an alkyne (**46**) with conflicting regiochemically directing groups. Furthermore, we gained useful insight about the atropisomeric stability of 3-aryl-1-sulfinyl iron(0) tricarbonyl complexes **4**−**7**. We are continuing to explore other diastereoselective transformations of sulfinyl iron(0) diene complexes, as well as the chemistry of the decomplexed sulfinyl dienes. These results will be reported in due course.

Experimental Section

Representative Reaction Sequence for Preparation of Sulfinyl Dienes, the Corresponding Iron(0) Diene Complexes, Pinacol Coupling Precursors, and Products. Alkynyl Ester 46. Diisopropylamine (0.259 mL, 1.85 mmol, 1.3 equiv) was dissolved in THF (2 mL) in a flame-dried Schlenk flask under an argon atmosphere. This solution was cooled to 0 °C, and n-BuLi (1.13 mL of a 1.6 M solution in hexanes, 1.81 mmol, 1.27 equiv) was added via syringe. After stirring for 15 min, the solution was cooled to −78 °C, and methyl propiolate (0.165 mL, 1.85 mmol, 1.3 equiv) was added via syringe. After stirring 15 min, a freshly prepared solution of $ZnBr_2$ (417 mg, 1.85 mmol, 1.3 equiv) in THF (1 mL) was added via cannula. After stirring an additional 15 min, a solution of *o*-iodobenzaldehyde diethyl acetal (435.8 mg, 1.42 mmol, 1.0 equiv) in THF (1 mL) was added via cannula, followed by $Pd(PPh_3)_4$ (82.3 mg, 0.0712 mmol, 0.05 equiv). The reaction was stirred at −78 °C for 30 min, was warmed to 0 °C over 1 h, was placed in a 45 °C oil bath, and was stirred at that temperature for 20 h. After this time the solvent was removed on the rotary evaporator, and the residue was dissolved in toluene (containing 3% NEt_3 by volume) and was filtered through a bed of silica gel on a glass frit filter using 4:1 hexanes/ethyl acetate (with 1% NEt_3 by volume) as the eluant. The filtrate was concentrated on the rotary evaporator to a brown oil that was chromatographed (silica gel, 19:1 hexanes/ethyl acetate with 1% NEt_3) to afford aryl alkyne **46** as a clear oil (305.5 mg, 82%). ^{1}H NMR (400 MHz) δ 1.28 (t, 6H, J = 7.1 Hz), 3.63 (m, 2H), 3.77 (m, 2H), 3.87 (s, 3H), 5.76 (s, 1H), 7.35 (td, 1H, J = 7.6, 1.3 Hz), 7.50 (td, 1H, J = 7.6, 1.1 Hz), 7.60 (dd, 1H, J = 7.6, 1.2 Hz), 7.70 (dd, 1H, J = 7.6, 1.2 Hz); ^{13}C NMR (100 MHz) δ 15.2, 52.8, 63.2, 84.2, 84.5, 100.5, 118.3, 126.3, 128.4, 130.9, 133.7, 142.9, 154.4; IR (neat) 2978, 2881, 2223, 1715, 1435, 1299, 1207, 1176, 1061, 764 cm^{-1}. HRMS (M + Na^+) calculated for $C_{15}H_{18}O_4Na$ 285.1097, found 285.1101.

Vinyl Stannane 47 (and Minor Regioisomer). Alkyne **46** (292.5 mg, 1.115 mmol) was dissolved in THF (11.2 mL) under an argon atmosphere. $Pd(PPh_3)_2Cl_2$ (23.5 mg, 0.0335 mmol, 3 mol%) was added and the solution was cooled to −78 °C. Bu_3SnH (0.600 mL, 2.23 mmol, 2 equiv) was added dropwise via syringe, and the reaction was allowed to slowly warm to room temperature overnight. At this time the solvent was removed on the rotary evaporator. A ^{1}H NMR spectrum of the crude material revealed a 1.7:1 ratio of regioisomers in favor of the desired vinyl stannane **47**. The crude material was chromatographed (silica, 40:1 hexanes/EtOAc with 1% NEt_3) to give vinyl stannane **47** (374 mg, 61%) as a clear oil. Fractions containing the minor isomer were pooled, concentrated, and subjected to a second chromatography to afford the regioisomeric vinyl stannne as a clear oil (185 mg, 30%). Data for the major regioisomer (**47**): ^{1}H NMR (400 MHz) δ 0.93 (t, 9H, J = 7.3 Hz), 1.09 (m, 6H), 1.24 (t, 6H, J = 7.0 Hz), 1.39 (m, 6H), 1.58 (m, 6H), 3.52 (m, 2H), 3.56 (s, 3H), 3.64 (m, 2H), 5.55 (s, 1H), 7.22 (s with tin satellites, 1H, J_{SnH} = 24.6 Hz), 7.21−7.30 (m, 3H), 7.59 (d, 1H, J = 8.1 Hz); ^{13}C NMR (100 MHz) δ 10.6, 13.7, 15.2, 27.3, 28.9, 51.1, 61.6, 100.3, 126.3, 127.6, 128.1, 136.0, 137.0, 140.2, 143.2, 173.1; IR (neat) 2957, 2929, 2872, 1701, 1458, 1341, 1217, 1197, 1175, 1117, 1057, 760 cm^{-1}. HRMS exact mass calculated for [M + Na]$^+$ 577.2310, found 577.2310. Data for the minor regioisomer: ^{1}H NMR (400 MHz) δ 0.88 (t, 9H, J = 7.3 Hz), 0.92 (m, 6H), 1.14 (t, 6H, J = 7.0 Hz), 1.2 (m, 6H), 1.43 (m, 6H), 3.35 (m, 1H), 3.48 (m, 2H), 3.52 (s, 3H), 3.70 (m, 1H), 5.29 (s, 1H), 6.22 (s with tin satellites, 1H, J_{SnH} = 28.0 Hz), 6.80 (m, 1H), 7.18 (m, 1H), 7.27 (m, 1H), 7.59 (dd, 1H, J = 7.8, 1.2 Hz); ^{13}C NMR (100 MHz) δ 10.4, 13.6, 15.0, 15.2, 27.3, 28.8, 50.9, 59.9, 62.2, 99.6, 123.7, 124.9, 126.2, 127.9, 128.6, 131.8, 143.9, 163.9, 169.5; IR (neat) 2957, 2928, 2872, 2854, 1732, 1713, 1464, 1351, 1263, 1192, 1161, 1053, 753 cm^{-1}. HRMS (M + Na^+) calculated for $C_{27}H_{46}O_4NaSn$ 577.2310, found 577.2309.

Vinyl Stannane 48. Ester **47** (374.1 mg, 0.6761 mmol, 1 equiv) was dissolved in toluene (6.8 mL) under an argon atmosphere, and this solution was cooled to −78 °C. DIBAL (0.253 mL, 1.420 mmol, 2.1 equiv) was added via syringe. The solution was stirred at −78 °C for 2 h, and the temperature was slowly raised to 0 °C over 30 min. The reaction was quenched by addition of saturated aq sodium potassium tartrate (6 mL). The mixture was vigorously stirred for 15 min at room temperature, diluted with EtOAc (40 mL) and H_2O (6 mL), and poured into a separatory funnel. The organic layer was separated and the aqueous layer was extracted with EtOAc (15 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated on the rotary evaporator. The residue was chromatographed (30:1 hexanes/EtOAc with 1% NEt_3) to afford alcohol **48** as a clear oil (299.3 mg, 84%). ^{1}H NMR (400 MHz) δ 0.92 (t, 9H, J = 7.3 Hz), 1.04 (m, 6H), 1.24 (t, 6H, J = 7.0 Hz), 1.39 (m, 6H), 1.61 (m, 6H), 1.80 (br t, 1H, J = 5.0 Hz), 3.50−3.70 (m, 4H), 4.31 (br d with tin satellites, 2H, J_{HH} = 3.3 Hz, J_{SnH} = 20.8 Hz), 5.54 (s, 1H), 6.86 (t with tin satellites, 1H, J_{HH} = 1.4 Hz, J_{SnH} = 34.0 Hz), 7.03 (m, 1H), 7.29 (m, 2H), 7.63 (m, 1H); ^{13}C NMR (100 MHz) δ 10.3, 13.7, 15.2, 27.4, 29.3, 29.7, 61.7, 64.2, 100.1, 126.3, 126.8, 127.9, 129.1, 135.9, 136.6, 137.3, 151.1; IR (neat) 3485 (br), 2956, 2925, 1456, 1375, 1116, 1057, 762 cm^{-1}. HRMS (M + Na^+) calculated for $C_{26}H_{46}O_3NaSn$ 549.2361, found 549.2359.

Vinyl Stannane 49. Alcohol **48** (261.5 mg, 0.4978 mmol, 1 equiv) was dissolved in DMF under an inert argon atmosphere. Imidazole (67.8 mg, 0.9955 mmol, 2.0 equiv), DMAP (12 mg, 0.100 mmol, 0.2 equiv), and TBSCl (93.8 mg, 0.622 mmol, 1.25 equiv) were added consecutively. After 24 h the solution was diluted with Et_2O (100 mL) and saturated aq $NaHCO_3$ solution (30 mL) and this was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with Et_2O (30 mL). The organic layers were combined and washed with brine (30 mL), dried ($MgSO_4$), filtered, and concentrated on the rotary evaporator. The residue was purified by column chromatography (hexanes with 1% NEt_3) to afford silyl ether **49** as a clear oil (306 mg, 96%). ^{1}H NMR (400 MHz) δ 0.01 (s, 6H), 0.87 (s, 9H), 0.93 (t, 9H, J = 7.3 Hz), 0.99 (m, 6H), 1.24 (t, 6H, J = 7.0 Hz), 1.38 (m, 6H), 1.58 (m, 6H), 3.51 (m, 2H), 3.66 (m, 2H), 4.40 (d with tin satellites, 2H, J_{HH} = 2.1 Hz, J_{SnH} = 18.2 Hz), 5.52 (s, 1H), 6.79 (t with tin satellites, 1H, J_{HH} = 2.0 Hz, J_{SnH} = 35.3 Hz), 7.02 (m, 1H), 7.27 (m, 2H), 7.64 (m, 1H); ^{13}C NMR (100 MHz) δ −5.3, 10.5, 13.8, 15.2, 18.5, 26.1, 27.5, 29.3, 62.2, 65.3, 100.2, 126.0, 126.8, 127.8,

128.9, 134.6, 136.2, 137.3, 152.2; IR (neat) 2956, 2928, 2856, 1464, 1252, 1117, 1055, 837, 779 cm^{-1}. HRMS ($M + Na^+$) calculated for $C_{32}H_{60}O_3NaSiSn$ 663.3226, found 663.3239.

Sulfinyl Diene 50. A Schlenk flask equipped with a stir bar was charged with vinyl stannane **49** (302.1 mg, 0.4723 mmol, 1 equiv), evacuated, and brought into the glovebox where it was dissolved in anhydrous DMF (4.7 mL). The iodovinylsulfoxide[6] (138 mg, 0.472 mmol, 1 equiv) was added to the stirred solution, followed by CuTC (94.6 mg, 0.496 mmol, 1.05 equiv), $Ph_2PO_2NBu_4$ (228 mg, 0.496 mmol, 1.05 equiv), and $Pd(PPh_3)_4$ (54.6 mg, 0.0472 mmol, 0.10 equiv). The flask was sealed, brought out of the glovebox, and the contents were stirred at room temperature for 3 h. H_2O (5 mL) was added, and the mixture was stirred for 15 min, when it was further diluted with Et_2O (40 mL) and H_2O (5 mL) and transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with Et_2O (10 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated on the rotary evaporator to give a brown oil whichwas placed on a vacuum pump overnight to remove DMF. The residue was chromatographed twice (first, 3:1 hexanes/EtOAc; second, 4:1 to 3.5:1 hexanes/EtOAc) to afford sulfinyl diene **50** as a pale yellow-orange oil (163.5 mg, 67%). ^1H NMR (400 MHz) δ 0.02 (s, 6H), 0.88 (s, 9H), 1.20 (overlapping triplets, 6H, $J = 7.0$ Hz), 2.43 (s, 3H), 3.56 (m, 4H), 4.34 (one of AB system, 1H, $J = 11.7$ Hz), 4.44 (one of AB system, 1H, $J = 11.7$ Hz), 5.59 (s, 1H), 6.37 (d, 1H, $J = 10.5$ Hz), 6.86 (dd, 1H, $J = 10.4$, 1.2 Hz), 7.13 (s, 1H), 7.28−7.39 (m, 5H), 7.67 (m, 3H); ^{13}C NMR (100 MHz) δ −5.3, 15.2, 18.3, 21.4, 25.9, 60.9, 61.4, 61.5, 99.7, 124.7, 126.6, 128.0, 129.7, 129.9, 134.7, 136.4, 137.3, 139.1, 141.0; IR (neat) 2955, 2929, 2883, 2857, 1471, 1254, 1082, 1046, 839, 777 cm^{-1}. HRMS ($M + Na^+$) calculated for $C_{29}H_{42}O_4NaSSi$ 537.2465, found 537.2468.

Sulfinyl Diene Iron(0) Tricarbonyl Complex 51. (bda)$Fe(CO)_3$ (450 mg, 1.573 mmol, 5 equiv) was added to a toluene (3.1 mL) solution of sulfinyl diene **50** (162.0 mg, 0.3147 mmol) under an Ar atmosphere. The flask was sealed and submerged in a 45 °C oil bath. The reaction was stirred for 21 h, at which time the flask was removed from the bath, and the contents were cooled to room temperature. The solution was filtered through NEt_3-treated silica gel on a glass-fritted filter. The silica gel was washed with ample EtOAc. The filtrate was evaporated, and the residue was chromatographed (silica, 9:1 hexanes/EtOAc with 1% NEt_3) to afford sulfinyl iron complex **51** (131.8 mg, 64%) as a yellow oil and recovered (bda)$Fe(CO)_3$ (223 mg, 62% of the excess 4 equiv). ^1H NMR (400 MHz) δ 0.04 (s, 3H), 0.06 (s, 3H), 0.91 (s, 9H), 1.24 (m, 6H), 2.44 (s, 3H), 3.48 (d, 1H, $J = 7.5$ Hz), 3.51−3.62 (m, 3H), 3.71 (m, 1H), 4.07 (s, 1H), 4.13 (one of AB system, 1H, $J = 13.4$ Hz), 4.62 (one of AB system, 1H, $J = 13.4$ Hz), 5.27 (d, 1H, $J = 7.4$ Hz), 5.63 (s, 1H), 7.33 (m, 5H), 7.52 (d, 2H, $J = 8.1$ Hz), 7.63 (d, 1H, $J = 5.0$ Hz); ^{13}C NMR (100 MHz) δ −5.7, −5.5, 15.1, 15.2, 18.1, 21.4, 25.7, 61.2, 62.1, 62.3, 66.7, 72.8, 101.1, 114.5, 123.4, 127.3, 128.5, 129.9, 130.5, 135.1, 138.5, 140.7, 145.9; IR (neat) 2956, 2930, 2859, 2056, 1996, 1464, 1373, 1254, 1106, 1052, 839, 779 cm^{-1}. HRMS ($M + Na^+$) calculated for $C_{32}H_{42}O_7NaSSi^{56}Fe$ 677.1662, found 677.1668.

Sulfinyl Dienol Iron(0) Tricarbonyl Complex 52. Silyl ether **51** (115.6 mg, 0.177 mmol, 1 equiv) was dissolved in THF (1.8 mL). Acetic acid (14 μL, 0.25 mmol, 1.4 equiv) was added via syringe, followed by a 1.0 M TBAF solution in THF (0.247 mL, 0.247 mmol, 1.4 equiv). After 70 min this solution was diluted with EtOAc (40 mL), transferred to a separatory funnel, and washed successively with saturated aq $NaHCO_3$ (10 mL) and brine (10 mL). After drying ($MgSO_4$), filtration, and concentration of the organic layer by rotary evaporation, the residue obtained was purified by chromatography (4:1 hexanes/EtOAc with 1% NEt_3 to 2:1 hexanes/EtOAc with 1% NEt_3) to afford alcohol **52** as a yellow oil (93.0 mg, 97%). ^1H NMR (400 MHz) δ 1.26 (overlapping triplets, 6H, $J = 7.0$ Hz), 2.44 (s, 3H), 3.52 (d, 1H, $J = 7.3$ Hz), 3.52−3.61 (m, 2H), 3.67−3.77 (m + broadened one of ABX system, 3H), 4.01 (broadened one of ABX system, 1H, $J = 11.6$, 9.1 Hz), 4.22 (s, 1H), 4.25 (s, 1H), 5.21 (d, 1H, $J = 7.3$ Hz), 5.60 (s, 1H), 7.29−7.41 (m, 5H), 7.51 (d, 2H, $J = 8.2$ Hz), 7.57 (dd, 1H, $J = 6.8$, 2.0 Hz); ^{13}C NMR (100 MHz) δ 15.0, 21.4, 62.3, 62.5, 63.7, 69.6, 74.4, 77.5, 102.1, 111.9, 123.3, 127.7, 127.8, 129.1, 130.0, 131.8, 134.2, 138.1, 140.9, 145.2; IR ($CHCl_3$) 3342 (br), 2978, 2929, 2877, 2059, 1990, 1451, 1117, 1049, 811 cm^{-1}. HRMS ($M + Na^+$) calculated for $C_{26}H_{28}O_7NaS^{56}Fe$ 563.0797, found 563.0794.

Sulfinyl Dienal Iron(0) Tricarbonyl Complex 53. Alcohol **52** (93.0 mg, 0.172 mmol, 1 equiv) was dissolved in CH_2Cl_2 (0.67 mL) and DMSO (0.67 mL) under an argon atmosphere. NEt_3 (0.24 mL, 1.72 mmol, 10 equiv) was added, followed by SO_3·pyr (134 mg, 0.861 mmol, 5 eq), and this solution was stirred at room temperature for 4.5 h. It was then diluted with EtOAc (35 mL), washed with a 1M aq HCl solution (2 × 10 mL) and brine (2 × 10 mL), dried ($MgSO_4$), filtered, and concentrated on the rotary evaporator. The residue was purified by chromatography (5:1 hexanes/EtOAc with 1% NEt_3) to afford aldehyde **53** as a yellow oil (67.6 mg, 73%). ^1H NMR (400 MHz) δ 1.17 (t, 3H, $J = 7.0$ Hz), 1.24 (t, 3H, $J = 7.0$ Hz), 2.43 (s, 3H), 3.46−3.76 (series of multiplets, 4H), 3.67 (d, 1H, $J = 7.7$ Hz), 4.44 (s, 1H), 5.50 (s, 1H), 5.68 (d, 1H, $J = 7.7$ Hz), 7.32 (m, 3H), 7.39 (m, 2H), 7.51 (m, 3H), 9.65 (s, 1H); ^{13}C NMR (100 MHz) δ 14.97, 15.02, 21.4, 62.5, 63.4, 67.8, 74.6, 79.6, 100.3, 103.4, 123.2, 127.95, 128.03, 128.9, 130.0, 132.4, 133.3, 138.4, 141.3, 145.1, 192.2, 207.3 (CO); IR ($CHCl_3$) 2977, 2874, 2064, 2007, 1709, 1053, 757 cm^{-1}. HRMS ($M + Na^+$) calculated for $C_{26}H_{26}O_7NaS^{56}Fe$ 561.0641, found 561.0625.

Sulfinyl Dienal Iron(0) Tricarbonyl Complex (Pinacol Coupling Precursor) 54. Acetal **53** (65.6 mg, 0.122 mmol) was dissolved in EtOAc (1 mL). A 2 M aq solution of HCl (1 mL) was added, and the reaction was stirred at room temperature for 4 h. At this time it was diluted with EtOAc (30 mL) and transferred to a separatory funnel, and the small aqueous layer was removed. The organic layer was washed successively with a saturated aq $NaHCO_3$ solution (2 × 7 mL) and brine (1 × 7 mL), was dried ($MgSO_4$), filtered, and concentrated on the rotary evaporator. The residue was chromatographed (2:1 hexanes/EtOAc) to afford dialdehyde **54** as an orange oil that solidified on the vacuum pump (45.7 mg, 81%). ^1H NMR (400 MHz) δ 2.45 (s, 3H), 3.79 (d, 1H, $J = 7.8$ Hz), 4.43 (s, 1H), 5.62 (dd, 1H, $J = 7.8$, 0.8 Hz), 7.37 (d, 2H, $J = 8.3$ Hz), 7.49 (d, 1H, $J = 7.5$ Hz), 7.58 (d, 2H, $J = 8.3$ Hz), 7.65 (m, 2H), 7.87 (dd, 1H, $J = 7.4$, 1.6 Hz), 9.67 (s, 1H), 10.18 (d, 1H, $J = 0.3$ Hz); ^{13}C NMR (100 MHz) δ 21.5, 66.5, 80.8, 99.7, 123.3, 128.5, 130.2, 134.02, 134.05, 134.9, 135.6, 136.5, 141.4, 144.8, 191.3, 193.0, 206.9 (CO); IR ($CHCl_3$) 3017, 2850, 2742, 2067, 2005, 1705, 1699, 1047 cm^{-1}. HRMS ($M + H^+$) calculated for $C_{22}H_{17}O_6S^{56}Fe$ 465.0090, found 465.0085.

Pinacol Coupling Product (55) and Corresponding Diacetate. In the glovebox, $VCl_3(THF)_3$ (56 mg, 0.151 mmol, 2.8 equiv) was placed in a Schlenk flask. In the fumehood under an argon atmosphere this was dissolved in CH_2Cl_2 (1.0 mL), and zinc dust (6.2 mg, 0.094 mmol, 1.75 equiv) was added. The red solution turned brown-green after ca. 5 min. The solution was stirred for a total of 30 min, when it was cooled to 0 °C. A 0 °C CH_2Cl_2 (1.0 mL) solution of dialdehyde **54** (25 mg, 0.054 mmol, 1 equiv) was added via cannula, and after 15 min the reaction was quenched with 5% aq sodium tartrate solution (2 mL). This mixture was stirred vigorously for 1 h, was diluted with CH_2Cl_2 (10 mL) and more 5% aq sodium tartrate solution (10 mL), and was transferred to a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (1 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The residue was chromatographed (silica, 1.5:1 to 1:1, hexanes/EtOAc) to give diol **55** (12.3 mg, 49%) as a yellow oil that was fully characterized as the corresponding diacetate. ^1H NMR (400 MHz) δ 2.40 (s, 3H), 3.49 (d, 1H, $J = 7.2$ Hz), 4.21 (br m, 1H), 4.36 (s, 1H), 4.66 (br d, 1H, $J = 9.6$ Hz), 4.94 (br d, 1H, $J = 8.9$ Hz), 5.90 (d, 1H, $J = 7.1$ Hz), 7.25−7.31 (m, 5H), 7.43 (d, 2H, $J = 8.1$ Hz), 7.48 (d, 1H, $J = 7.6$ Hz), 7.56 (d, 1H, $J = 5.9$ Hz); ^{13}C NMR (100

MHz) δ 21.4, 58.4, 73.6, 74.0, 74.5, 111.4, 123.4, 124.8, 127.4, 128.4, 128.7, 130.1, 135.2, 141.2, 144.2.

The diol was dissolved in pyridine (0.3 mL). Acetic anhydride (0.049 mL, 0.523 mmol, 20 equiv) and DMAP (1.6 mg, 13.1 μmol, 0.5 equiv) were added, and the solution was stirred overnight. The reaction was diluted with EtOAc (20 mL), and this solution was washed with 1 M aq HCl solution (2 $\times$ 5 mL), H_2O (1 $\times$ 5 mL), and brine (2 $\times$ 5 mL). After drying ($MgSO_4$), filtration, and concentration, the residue obtained was chromatographed (silica, 2:1 hexanes/EtOAc) to give the diacetate (12.4 mg, 86%) as a yellow oil. The ^{1}H NMR spectrum revealed a 22:1 diastereomeric mixture. Major isomer: ^{1}H NMR (400 MHz) δ 2.11 (s, 3H), 2.18 (s, 3H), 2.42 (s, 3H), 3.48 (d, 1H, J = 7.3 Hz), 4.18 (s, 1H), 5.52 (dd, 1H, J = 7.4, 1.0 Hz), 5.79 (d, 1H, J = 2.3 Hz), 6.18 (d, 1H, J = 2.3 Hz), 7.28−7.40 (m, 7H), 7.46 (dd, 1H, J = 7.1, 2.3 Hz); ^{13}C NMR (100 MHz) δ 21.1, 21.4, 56.5, 69.3, 71.6, 74.3, 80.6, 103.2, 123.1, 126.5, 128.0, 128.6, 128.8, 130.0, 130.1, 131.0, 136.7, 141.2, 144.8, 169.5, 169.8, 207.0 (CO); IR ($CHCl_3$) 2995, 2926, 2062, 2000, 1743, 1492, 1370, 1217, 1047, 1024 cm^{-1}. HRMS (M + H$^+$) calculated for $C_{26}H_{23}O_8S^{56}Fe$ 551.0458, found 551.0452.

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Supporting Information Available: Full experimental procedures, spectra data, and copies of the ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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