Completely Diastereoselective Tricarbonyliron Complexation Reactions of Chiral Dienes

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Complexation of cylic and acyclic dienes, carrying a (1*S*)-(+)-ketopinoxy as the chiral auxiliary, with nonacarbonyldiiron proceeds in a completely diastereoselective fashion to afford diene−iron complexes in moderate yields. When (1*R*)-(−)-ketopinoxy was used as the chiral auxiliary, the opposite enantioisomeric complexes are isolated as a single diastereomer in comparable yield and specific rotation in each case. The stereochemistry of chiral cyclic and acyclic diene−iron complexes is determined by single-crystal X-ray methods.

Due to their abilities to achieve regio- and stereocontrolled bond constructions, (η^4-diene)Fe(CO)$_3$ complexes have been increasingly studied in recent years as synthetic building blocks for the synthesis of biologically active compounds.[1] The bulky tricarbonyl moiety ensures in most cases an extreme diastereoselectivity of reactions at the diene ligand.[2] Therefore, optically pure diene−Fe(CO)$_3$ complexes can be powerful starting materials in the synthesis of enantiomerically pure substances. The methods reported in the literature for the preparation of nonracemic diene−Fe(CO)$_3$ complexes are the classical resolution of racemic mixtures through diastereoisomers,[3] the enzymatic resolution of planar complexes,[4] and the enantioselective complexation of prochiral 1,3-dienes by chiral Fe(CO)$_3$-transfer reagents.[5] Although, some reports described the diastereoselective complexation of enantiomerically pure cyclic and acyclic dienes with tricarbonyliron, low diastereomeric excesses were often obtained.[6] Only few examples showed the completely asymmetric complexation of bulky dienamides[6c] and sulfinyl dienes[6f] and chiral bridged bicyclic dienes[6g] with iron carbonyls. The low diastereoselectivity in most cases may be due to poor steric and/or electronic effects caused by somewhat remote chiral auxiliaries at the diene ligands. In this contribution, we report a facile synthesis of cylic and acyclic dienes carrying a bulky bicyclic skeleton and a keto functionality, which demonstrate the completely facial recognition with iron carbonyls. Moreover, when the opposite form of the chiral dienes was used as the starting substrates, enantioisomeric diene−Fe(CO)$_3$ complexes were prepared as a single diastereomer in each case.

Results and Discussion

As chiral ligands, we decided to investigate (1*S*)-(+)-2-ketopinoxy-1,3-cyclohexadiene derivatives of type **1**. The steric bulky bicyclic compound of **1** possesses a removable chiral auxiliary adjacent to the diene unit and a keto functionality, which may direct the Fe(CO)$_n$ species toward the diene.[7] The synthesis of the chiral diene ligand was carried out as follows. First, (1*S*)-(+)-ketopinic acid (**2**), $[\alpha]^{26}_D$ +64.0° (*c* 1.0, $CHCl_3$) [lit. $[\alpha]^{23}_D$ +58.0° (*c* 1.0, $CHCl_3$)], was prepared from (1*S*)-(+)-10-camphorsulfonic acid [$[\alpha]^{20}_D$ +19.9° (*c* 2.0, H_2O)] in 51% overall yield using the literature procedure.[8] Finally, chiral diene **1** were prepared from 2-cyclohexen-1-one and (1*S*)-(+)-ketopinic acid chloride using the standard coupling method. Thus, treatment of lithium diisopro-

(1) Gigou, A.; Beaucourt, J.-P.; Lellouche, J.-P.; Grée, R. *Tetrahedron Lett.* **1991**, *32*, 635. Franck-Neumann, M.; Colson, P.-J. *Synlett* **1991**, 891. Nunn, K.; Mosset, P.; Grée, R.; Saalfrank, R. W. *J. Org. Chem.* **1992**, *57*, 3359. Tao, C.; Donaldson, W. A. *J. Org. Chem.* **1993**, *58*, 2134.

(2) Pearson, A. J.; Zettler, M. W. *J. Chem. Soc., Chem. Commun.* **1987**, 1243. Laabassi, M.; Grée, R. *Tetrahedron Lett.* **1988**, *29*, 611. Birch, A. J.; Kelly, L. F.; Weerasuria, D. V. *J. Org. Chem.* **1988**, *53*, 278. Pinsard, P.; Lellouche, J.-P.; Beaucourt, J.-P.; Grée, R. *Tetrahedron Lett.* **1990**, *31*, 1140.

(3) Birch, A. J.; Bandara, B. M. R. *Tetrahedron Lett.* **1980**, *21*, 2981. Monpert, A.; Martelli, J.; Grée, R.; Carrié, R. *Tetrahedron Lett.* **1981**, *22*, 1961. Franck-Neumann, M.; Briswalter, C.; Chemla, P.; Martina, D. *Synlett* **1990**, 637. Nakanish, S.; Yamamoto, H.; Otsuji, Y.; Nakazumi, H. *Tetrahedron: Asymmetry* **1993**, *4*, 1969.

(4) Alcock, N. W.; Crout, D. H. G.; Henderson, C. M.; Thomas, S. E. *J. Chem. Soc., Chem. Commun.* **1988**, 746. Howell, J. A. S.; Palin, M. G.; Jaouen, G.; Top, S.; Hafa, H. E.; Cense, J. M. *Tetrahedron: Asymmetry* **1993**, *4*, 1241. Uemura, M.; Nishimura, H.; Yamada, S.; Hayashi, Y.; Nakamura, K.; Ishihara, K.; Ohno, A. *Tetrahedron: Asymmetry* **1994**, *5*, 1673.

(5) Birch, A. J.; Raverty, W. D.; Stephenson, G. R. *Tetrahedron Lett.* **1980**, *21*, 197. Birch, A. J.; Raverty, W. D.; Stephenson, G. R. *Organometallics* **1984**, *3*, 1075. Jenny, T.; Schmid, V. *Chimia* **1993**, *47*, 296. Knölker, H.-J.; Gonser, P. *Synlett* **1992**, 517. Knölker, H.-J.; Gonser, P.; Jones, G. *Synlett* **1994**, 405. Knölker, H.-J.; Hermann H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 341. Maywald, F.; Eilbracht, P. *Synlett* **1996**, 380.

(6) (a) Howard, P. W.; Stephenson, G. R.; Taylor, S. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1603. (b) Howard, P. W.; Stephenson, G. R.; Taylor, S. C. *J. Chem. Soc., Chem. Commun.* **1990**, 1182. (c) Pearson, A. J.; Chang, K.; McConville, D. B.; Youngs, W. J. *Organometallics* **1994**, *13*, 4. (d) Schmalz, H.-G.; Hessler, E.; Bats, J. W.; Dürner, G. *Tetrahedron Lett.* **1994**, *35*, 4543. (e) Ong, C. W.; Huang, C. S.; Chang, T. H. *Organometallics* **1996**, *15*, 4334. (f) Paley, R. S.; Dios, A.; Estroff, L. A.; Lafontaine, J. A.; Montero, C.; McCulley, D. J.; Rubio, M. B.; Ventura, M. P.; Weers, H. L.; Pradilla, R. F.; Castro, S.; Dorado, R.; Morente, M. *J. Org. Chem.* **1997**, *6*, 66326. (g) Salzer, A.; Schmalle, H.; Stauber, R.; Streiff, S. *J. Organomet. Chem.* **1991**, *408*, 403.

(7) Greaves, E. O.; Knox, G. R.; Pauson, P. L. *J. Chem. Soc., Chem. Commun.* **1969**, 1124. Greaves, E. O.; Knox, G. R.; Pauson, P. L.; Toma, S.; Sim, G. R.; Woodhouse, D. I. *J. Chem. Soc., Chem. Commun.* **1971**, 257.

(8) Barlett, P. D.; Knox, L. H. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. 5, p 196. Barlett, P. D.; Knox, L. H. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. 5, p 689.

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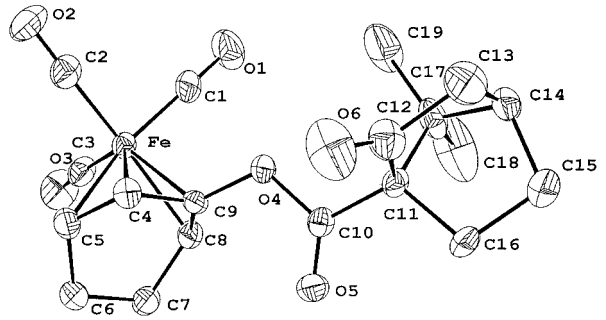
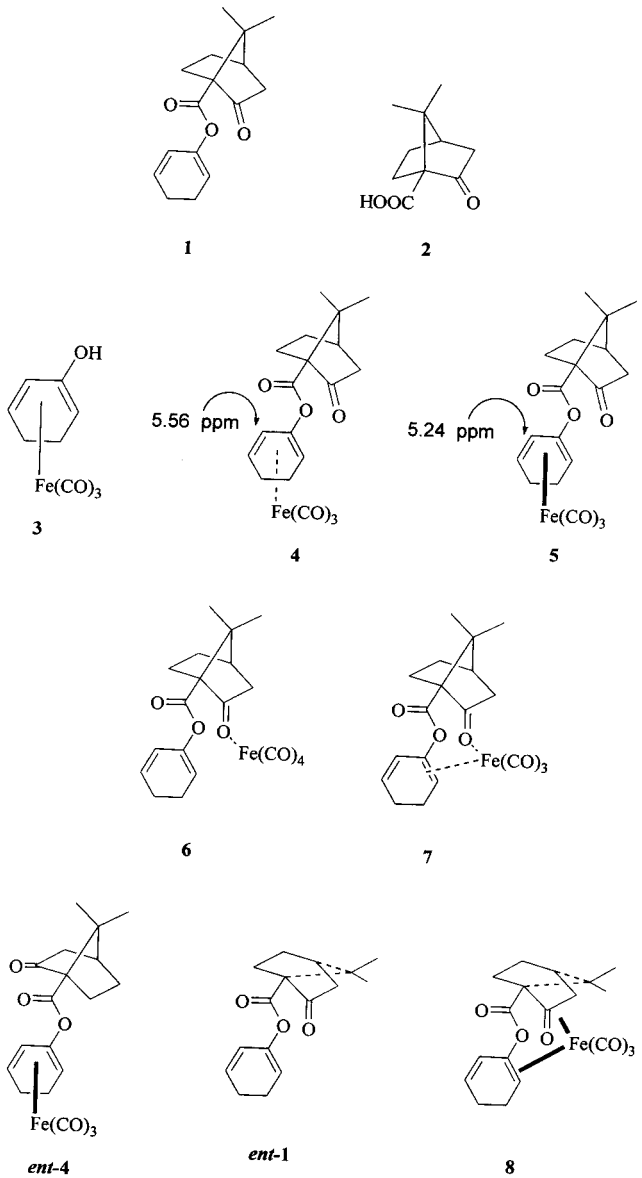


Figure 1. ORTEP drawing of complex **4** (at the 30% probability level). Hydrogen atoms are omitted for clarity.

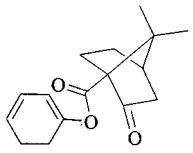
pylamide (LDA) in THF with 1.0 molar equiv of 2-cyclohexen-1-one (1 h, −78 °C) under nitrogen followed by addition of (1*S*)-(+)-ketopinic acid chloride (freshly prepared from (1*S*)-(+)-ketopinic acid, oxalyl chloride, and triethylamine) gave the chiral diene **1** in 74% yield. The preliminary test for the complexation of **1** with $Fe_2(CO)_9$ was conducted in refluxing ether for 6 h under nitrogen. The ^1H NMR spectrum of the crude mixture exhibited three peaks between δ 5.4−6.0 corresponding to the vinyl protons of the starting diene **1** together with a new doublet of doublets centered at δ 5.56, corresponding to the internal vinyl proton of a newly formed diene−$Fe(CO)_3$ complex. This may indicate that only one diastereoisomer was generated during complexation. A trial experiment, in which a racemic complex of **3**[9] was treated with (1*S*)-(+)-ketopinic acid chloride, gave a mixture of diastereoisomeric diene−$Fe(CO)_3$ complexes. ^1H NMR spectroscopy of the crude mixture clearly showed two doublets of doublets centered at δ 5.56 and 5.24, in a ratio of 2:1, assigned to the internal vinyl protons of the diastereoisomeric complexes **4** and **5**, respectively. Encouraged by the result, we proceeded to examine the diastereoselectivity of the complexation reaction of **1** with $Fe_2(CO)_9$. Thus, treatment of **1** with 1.2 molar equiv of $Fe_2(CO)_9$ in refluxing ether under nitrogen for 40 h produced **4** [53%, $[\alpha]^{26}_D$ +15.5° (*c* 1.0, $CHCl_3$)] as a single diastereoisomer after flash column chromatography on silica gel. None of the diastereoisomer **5** was formed, as indicated by the lack of the vinyl proton peak at δ 5.24 in NMR spectroscopy of the crude mixture. The yield of **4**, however, could increase up to 85% when 2.0 molar equiv of $Fe_2(CO)_9$ was used. A single-crystal X-ray structure analysis established the relative stereochemistry within **4** (Figure 1). Since the absolute configuration of (1*S*)-(+)-ketopinic acid is known, the absolute configuration of **4** is as shown and unequivocally confirmed. The stereochemistry of **4** presumably arose from attachment of the keto group with $Fe(CO)_4$ (from dissociation of $Fe_2(CO)_9$ in refluxing ether) at the less sterically hindered bottom face. The reactive electron-deficient intermediate **6** might lose one CO followed by coordination to the electron-rich enol olefin at the bottom side to form the postulated enone−$Fe(CO)_3$ complex **7**. The $Fe(CO)_3$ moiety detached from the keto group followed by recoordination to the pendant olefin on the same face of the diene to furnish diene−$Fe(CO)_3$ complex **4**. It is important to mention that transfer of the $Fe(CO)_3$ moiety from chiral enone−$Fe(CO)_3$ complexes to prochiral dienes in intermolecular fashion gave only modest diastereoselectivities.[6a,b] Therefore, the chiral auxiliary, which allows intramolecular transfer of $Fe(CO)_n$ species, may be critical to ensure the high diastereoselectivity. Moreover, when the opposite form of the chiral diene *ent*-**1** was used as the starting substrate, the enantioisomeric complex *ent*-**4** was obtained as the sole diastereoisomer in comparable yield and specific rotation [49%, $[\alpha]^{26}_D$ −15.64 (*c* 1.0, $CHCl_3$)]. The relative stereochemistry of *ent*-**4** as depicted is confirmed by X-ray diffraction analysis. As mentioned earlier, the iron carbonyl moiety would approach the keto from the less hindered top face followed by coordination to the electron-rich enol olefin to form the enone−$Fe(CO)_3$ intermediate **8**, which led to the formation of *ent*-**4**.



The above strategy can also be applied to diastereoselective synthesis of C-1-substituted (cyclohexa-1,3-diene)$Fe(CO)_3$ complexes. Thus, treatment of 2-cyclohexen-1-one with lithium hexamethyldisilazide (LHMDS) in THF with (1*S*)-(+)-ketopinic acid chloride (1 h, −78 °C) gave the chiral diene **9** in 46% yield as a clear liquid. Complexation of **9** with $Fe_2(CO)_9$, under the same

(9) Yeh, M. C. P.; Sheu, B. A.; Fu, H. W.; Tau, S. I.; Chuang, L. W. *J. Am. Chem.* Soc. **1993**, *115*, 5941.

reaction conditions as described above, produced complex **10** in 68% yield as the sole diastereoisomer isolated after purification by flash column chromatography. The relative stereochemistry of **10** was confirmed by X-ray diffraction analysis and was consistent with the facial selectivities found in the previous cases.



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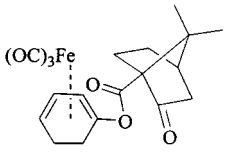

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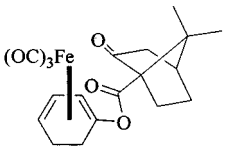
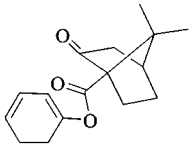


***ent*-10**



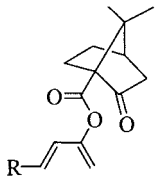
***ent*-9**

Acyclic chiral dienes were prepared in a manner similar to that stated for the cyclic chiral diene **1**. However, chiral dienes obtained from simple enones such as methylvinyl ketone (**11**) and 4-buten-3-one (**12**) were unstable for further comlexation study. Reaction of *trans*-4-phenyl-3-buten-2-one (**13**) and *trans*-5-methyl-3-hexen-2-one (**14**) with (*S*)-ketopinic acid chloride and (*R*)-ketopinic acid chloride produced dienes **15a** (60%), *ent*-**15a** (44%), **15b** (47%), and *ent*-**15b** (64%), respectively, in each case. Chiral dienes **15a**,**b** and *ent*-**15a**,**b** had to be used immediately for the complexation step. The highly diastereoselective complexation of iron carbonyl is also observed with acyclic chiral dienes **15a**,**b** and *ent*-**15a**,**b**. For example, complexation of chiral dienes **15a** and *ent*-**15a** with $Fe_2(CO)_9$ produced enantioisomers **16a** (25%) and *ent*-**16a** (38%), respectively, as the sole diastereoisomer in each case. The low yields for the complexation of chiral acyclic dienes as stated above may due to the instability of the acyclic dienes.

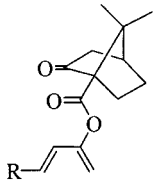
Attempted complexation using an additional methylene group at the diene, for example chiral diene **17**, gave a mixture of diastereoisomers **18** and **19** in a ratio of 1:1.2. The ratio of **18** and **19** was determined by proton (four methyl peaks of the ketopinic moiety at δ 1.16, 1.14, 1.07, and 1.06) and carbon (two ester peaks at δ 169.5 and 169.4) NMR spectra of the crude mixture. Efforts to separate **18** and **19** using flash column chromatography were unsuccessful. On the basis of the above result, a ketopinoxy group directly attaching to the diene is essential for completely diastereoselective complexation with iron carbonyls.

To understand the effect of interconversions on the configuration of the molecular chiral center, optically pure complex **4** was subjected to hydride abstraction (Ph_3CPF_6, 0 °C)[10,11] followed by nucleophilic addition reaction (MeZnI, CuCN, 0 °C).[9] Complex **20** was isolated in 46% yield as the sole diastereoisomer after regular workup and flash column chromatography on silica gel. The X-ray diffraction analysis of **20** (Figure 2) showed that the molecular center of chirality is left unchanged. This result may indicate that no migration occurs of the site of coordination relative to the chiral auxiliary on the ring when the above two reactions are performed under the reaction conditions.

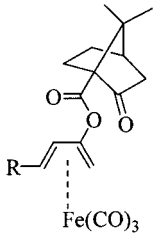
The reaction outlined herein demonstrates that the intramolecular transfer of the $Fe(CO)_3$ moiety from enone to diene can be an effective method for the completely diastereoselective synthesis of chiral (η^4-diene)$Fe(CO)_3$ complexes. Further application of the chiral diene−iron complexes in the synthesis of optically pure organic compounds is currently underway in our laboratories.



15a, R = Ph
15b, R = isopropyl

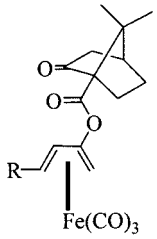


***ent*-15a**, R = Ph
***ent*-15b**, R = isopropyl



16a, R = Ph, $[\alpha]_D^{32}$ 15.15° (*c* 3.3, $CHCl_3$)

16b, R = isopropyl , $[\alpha]_D^{32}$ 15.04° (*c* 0.9, $CHCl_3$)



***ent*-16a**, R = Ph, $[\alpha]_D^{32}$ -14.21° (*c* 3.8, $CHCl_3$)

***ent*-16b**, R = isopropyl , $[\alpha]_D^{32}$ -16.57° (*c* 0.8, $CHCl_3$)

(10) Birch, A. J.; Raverty, W. D.; Stephenson, G. R. *J. Org. Chem.* **1981**, *46*, 5166.
(11) Fischer, E. O.; Fischer, R. D. *Angew. Chem.* **1960**, *72*, 919. Whitesides, T. H.; Arhart, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5296.

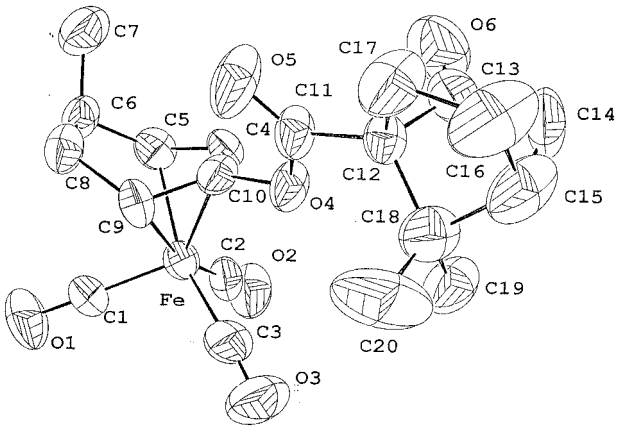
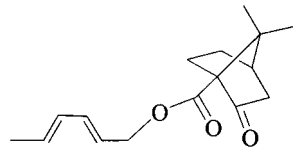


Figure 2. ORTEP drawing of complex **20** (at the 30% probability level). Hydrogen atoms are omitted for clarity.



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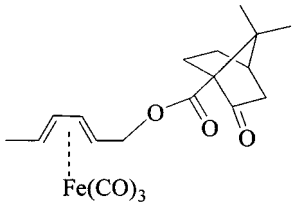

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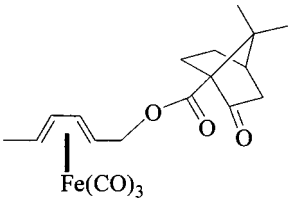

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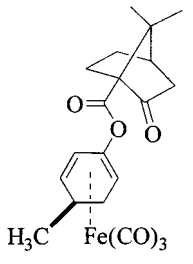

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Experimental Section

All reactions were run under a nitrogen atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Diethyl ether (ether) and tetrahydrofuran (THF) were distilled under nitrogen from a deep blue sodium benzophenone ketyl solution. Methylene chloride was distilled from calcium hydride. (1*S*)-(+)-Ketopinic acid (**2**)[8] and complex **3**[9] were synthesized according to the literature procedures. Flash column chromatography, following the method of Still, was carried out with E. Merck silica gel (Kieselgel 60, 230−400 mesh) using the indicated solvents.[12] Analytical thin-layer chromatography was performed with silica gel 60 F_{254} plastic plates of 0.2 mm thickness from E. Merck. The term "concentration" refers to the removal of solvent with an aspirator pump (Yamato Instrument Company model WP-15) with a Buchi Rotovapor-R. The term "under nitrogen" implies that the apparatus was evacuated (oil pump) and then filled with nitrogen three times. Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. ^{1}H nuclear magnetic resonance (NMR) spectra were obtained with JEOL-EX 400 (400 MHz) and Varian G-200 (200 MHz) spectrometers. The chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or $CHCl_3$ (7.26 ppm) as internal standard. ^{13}C NMR spectra were recorded with JEOL-EX 400 (100.4 MHz) and Varian G-200 (50 MHz) spectrometers with $CDCl_3$ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and are reported as mass/charge (*m*/*e*) with percent relative abundance. High-resolution mass spectra were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer at the Department of Chemistry, Central Instrument Center, Taichung, Taiwan.

General Procedure for Synthesis of Chiral Dienes Bearing a Ketopinoxy Group at the C-2 Position. In a typical procedure, to a solution of (1*S*)-(+)-ketopinic acid (2.82 g, 15.8 mmol) in 30 mL of CH_2Cl_2 at 0 °C was added rapidly, neat, via syringe, oxalyl chloride (2.76 mL, 31.7 mmol) followed by addition of 3.31 mL (23.8 mmol) of triethylamine. The reaction was stirred at 25 °C for 1 h, after which time, the solvent was removed in vacuo. Dried THF (60 mL) was then added to (1*S*)-(+)-ketopinic acid chloride. In a separate flask, to a solution of diisopropylamine (2.44 mL, 17.42 mmol) in 10 mL of THF under nitrogen at −78 °C was added rapidly via syringe a solution of *n*-butyllithium (10.9 mL, 17.42 mmol) in hexane followed by addition of 1.53 mL (15.83 mmol) of 2-cyclohexen-1-one. The reaction was stirred at −78 °C for 1 h. The THF solution of (1*S*)-(+)-ketopinic acid chloride was added via syringe to the above solution at −78 °C. The reaction was stirred at −78 °C for 1 h and at 25 °C for 30 min. The reaction mixture was quenched with saturated ammonium chloride solution via syringe needle and stirred at 25 °C for 30 min. After this time, the reaction mixture was diluted with a mixture of ethyl acetate/hexane (1:2, 100 mL). The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture.

(1′*S*)-(+)-2-Ketopinoxy-1,3-cyclohexadiene (1). The crude mixture obtained from 2-cyclohexen-1-one (15.83 mmol) and (1*S*)-(+)-ketopinic acid chloride (15.83 mmol) was purified via flash column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **1** (3.07 g, 11.8 mmol, 74%) as a colorless oil: $[\alpha]^{24}_D$ +32.9° (*c* 2.02, $CHCl_3$); IR (CH_2Cl_2) 3688, 2956, 1756, 1734, 1685, 1673, 1607, 1389 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (d, J = 8.0 Hz, 1 H), 5.75 (d, J = 12.2 Hz, 1 H), 5.41(m, 1 H), 2.56 (d, J = 16.1 Hz, 1 H), 2.40 (t, J = 12.2 Hz, 1 H), 2.30 (d, J = 8.0 Hz, 2 H), 2.23 (d, J = 8.0 Hz, 2 H), 2.13 (s, 1 H), 2.00 (t, J = 2.0 Hz, 2 H), 1.89 (m, 1 H), 1.84 (d, J = 4.3 Hz, 1 H), 1.20 (s, 3 H), 1.13 (s, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 212.12, 169.65, 146.55, 129.53, 123.87, 111.61, 67.69, 48.97, 43.99, 43.46, 25.70, 25.67, 21.22, 20.60, 20.58, 19.02; MS (20 eV) *m*/*e* 260.2 (M^+, 6), 183.1(4), 165.0 (100), 123.1(11), 95.2 (3); HRMS (EI) *m*/*e* calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1414.

(1′*R*)-(−)-2-Ketopinoxy-1,3-cyclohexadiene (*ent*-1). The crude mixture obtained from 2-cyclohexen-1-one (32.9 mmol) and (1*R*)-(−)-ketopinic acid chloride (32.9 mmol) was purified via flash column chromatography (silica gel, 1:10 ethyl acetate/

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

hexanes) to give ***ent*-1** (5.12 g, 19.7 mmol, 60%) as a colorless oil: $[\alpha]^{23}_D$ −20.35° (*c* 2.0, $CHCl_3$); IR (CH_2Cl_2) 3885, 2361, 1756, 1735, 1605, 1419, 1258, 1254 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.90 (d, J = 9.1 Hz, 1 H), 5.74 (d, J = 10.0 Hz, 1 H), 5.40 (m, 1 H), 2.55 (m, 1 H), 2.40 (m, 2 H), 2.28 (m, 2 H), 2.10 (m, 1 H), 2.00 (m, 2 H), 1.91−1.77 (m, 2 H), 1.48−1.36 (m, 1 H), 1.19 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 212.13, 169.64, 146.55, 129.52, 123.87, 111.60, 67.67, 48.69, 43.98, 43.45, 25.69, 25.66, 21.22, 20.59, 20.57, 19.01; MS (70 eV) *m*/*e* 260.2 (M^+, 18), 210.1 (1), 183.1 (3), 165.0 (100), 123.0 (29), 95.0 (36), 67.1 (21); HRMS (EI) *m*/*e* calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1408.

(1′*S*)-(+)-*trans*-4-Phenyl-2-ketopinoxy-1,3-butadiene (15a). The crude mixture obtained from *trans*-4-phenyl-3-buten-2-one (34.2 mmol) and (1*S*)-(+)-ketopinic acid chloride (34.2 mmol) was purified via flash column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **15a** (6.36 g, 20.5 mmol, 60%) as a yellow oil: $[\alpha]^{24}_D$ + 2.49° (*c* 3.36, $CHCl_3$); IR (CH_2Cl_2) 3066, 2988, 2921, 1715, 1455, 1415, 1363, 1183, 1116, 1025 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.42 (m, 2 H), 7.26 (m, 3 H), 7.02 (d, J = 16.2 Hz, 1 H), 6.66 (d, J = 16.2 Hz, 1 H), 5.12 (d, J = 1.4 Hz, 1 H), 4.95 (d, J = 1.4 Hz, 1 H), 2.54 (m, 2 H), 2.12 (m, 4 H), 1.43 (m, 1 H), 1.26 (s, 3 H), 1.18 (s, 3 H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 210.65, 167.90, 152.19, 136.16, 131.15, 128.51, 128.10, 126.96, 121.68, 105.81, 68.14, 49.25, 44.37, 13.77, 26.40, 26.16, 21.24, 19.63; MS (20 eV) *m*/*e* 310 (2), 181, 165 (100), 131 (52), 77 (3); HRMS (EI) *m*/*e* calcd for $C_{20}H_{22}O_3$ 310.1568, found 310.1596.

(1′*R*)-(−)-*trans*-4-Phenyl-2-ketopinoxy-1,3-butadiene (*ent*-15a). The crude mixture obtained from *trans*-4-phenyl-3-buten-2-one (21.9 mmol) and (1*R*)-ketopinic acid chloride (21.9 mmol) was purified via flash column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give ***ent*-15a** (4.66 g, 15.0 mmol, 44%) as a yellow oil: $[\alpha]^{24}_D$ −2.47° (*c* 2.17, $CHCl_3$); IR (CH_2Cl_2) 3370, 3298, 3031, 2969, 1737, 1669, 1610, 1576, 1449, 1360 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.46 (m, 2 H), 7.32 (m, 3 H), 7.05 (d, J = 16.4 Hz, 1 H), 6.66 (d, J = 16.2 Hz, 1 H), 5.12 (d, J = 1.6 Hz, 1 H), 4.94 (d, J = 1.6 Hz, 1 H), 2.52 (m, 2 H), 2.15 (m, 4 H), 1.42 (m, 1 H), 1.27 (s, 3 H), 1.19 (s, 3 H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 210.65, 167.89, 152.19, 136.16, 131.13, 128.51, 128.08, 126.09, 121.68, 105.81, 68.14, 49.25, 44.37, 43.77, 26.40, 26.16, 21.24, 19.63; MS (70 eV) *m*/*e* 310 (M^+, 15), 238 (14), 210 (11), 165 (100), 131 (72), 77 (4); HRMS (EI) *m*/*e* calcd for $C_{20}H_{22}O_3$ (M^+) 310.1569, found 310.1580.

(1′*S*)-*trans*-5-Methyl-2-ketopinoxy-1,3-hexadiene (15b). The crude mixture obtained from *trans*-5-methyl-3-hexen-2-one (8.9 mmol) and (1*S*)-ketopinic acid chloride (7.4 mmol) was purified via flash column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **15b** (0.97 g, 3.5 mmol, 47%) as a yellow oil: $[\alpha]^{25}_D$ +21.56° (*c* 3.36, $CHCl_3$); IR (CH_2Cl_2) 2964, 1750, 1657, 1612, 1454, 1420, 1391, 1337 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.06 (dd, J = 15.8, 6 Hz, 1 H), 5.92 (dd, J = 15.8, 0.6 Hz, 1 H), 4.91 (d, J = 1.4 Hz, 1 H), 4.77 (d, J = 1.6 Hz, 1 H), 2.61 (m, 2 H), 1.99 (m, 5 H), 1.39 (m, 1 H), 1.24 (s, 3 H), 1.16 (s, 3 H), 1.05 (s, 3 H), 1.02 (s, 3 H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 210.50, 167.78, 152.15, 140.25, 120.61, 103.31, 67.94, 49.14, 44.26, 43.68, 30.38, 26.26, 26.10, 21.64, 21.21, 21.14, 19.54; MS (20 eV) *m*/*e* 277 (5), 276 (28), 275 (16), 165 (100); HRMS (EI) *m*/*e* calcd for $C_{17}H_{24}O_3$ 276.1725, found 276.1728.

(1′*R*)-*trans*-5-Methyl-2-ketopinoxy-1,3-hexadiene (*ent*-15b). The crude mixture obtained from *trans*-5-methyl-3-hexen-2-one (17.1 mmol) and (1*R*)-ketopinic acid chloride (14.2 mmol) was purified via flash column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give ***ent*-15b** (2.51 g, 9.09 mmol, 64%) as a yellow oil: $[\alpha]^{23}_D$ − 26.44° (*c* 3.44, $CHCl_3$); IR (CH_2Cl_2) 2964, 2874, 1750, 1657, 1611, 1419, 1390, 1377 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.06 (dd, J = 15.8, 6 Hz, 1 H), 5.92 (dd, J = 15.8, 0.6 Hz, 1 H), 4.91 (d, J = 1.4 Hz, 1 H), 4.77 (d, J = 1.6 Hz, 1 H), 2.61 (m, 2 H), 1.99 (m, 5 H), 1.39 (m, 1 H), 1.24 (s, 3 H), 1.16 (s, 3 H), 1.05 (s, 3 H), 1.02 (s, 3 H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 210.50, 167.78, 152.15, 140.25, 120.61, 103.31, 67.94, 49.14, 44.26, 43.68, 30.38, 26.26, 26.10, 21.64, 21.21, 21.14, 19.54; MS (20 eV) *m*/*e* 277 (0.11), 276 (0.44), 275 (0.08), 165 (100); HRMS (EI) *m*/*e* calcd for $C_{17}H_{24}O_3$ 276.1725, found 276.1724.

General Procedure for Synthesis of Chiral Dienes Bearing a Ketopinic Acid Ester at the C-1 Position. In a typical procedure, to a solution of (1*S*)-ketopinic acid (2.00 g, 10.99 mmol) in 30 mL of CH_2Cl_2 at 0 °C was added rapidly, neat, via syringe, oxalyl chloride (1.92 mL, 21.98 mmol) followed by addition of 2.30 mL (16.48 mmol) of triethylamine. The reaction was stirred at 25 °C for 1 h, after which time, the solvent was removed in vacuo and dried THF (50 mL) was then added. To a solution of hexamethyldisilylzine (HMDS, 2.55 mL, 12.09 mmol) in 100 mL of THF under nitrogen at −78 °C was added rapidly, via syringe, a solution of *n*-butyllithium (7.6 mL, 12.09 mmol) in hexane (1.6 M) followed by addition of 2.1 mL of hexamethylphosphoramide (HMPA). The reaction mixture was stirred at −78 °C for 20 min. To the above reaction mixture was added 1.07 mL (10.99 mmol) of 2-cyclohexen-1-one. The reaction was stirred at −78 °C for 1 h. The THF solution of the freshly made (1*S*)-ketopinic acid chloride was added via syringe to the above solution at −78 °C. The reaction was stirred at −78 °C for 1 h and 25 °C for 30 min. The solvent was concentrated on a rotary evaporator. The resulting oil was diluted with 20 mL of H_2O and 600 mL of ethyl acetate. The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture.

(1′*S*)-1-Ketopinoxy-1,3-cyclohexadiene (9). The crude mixture obtained from 2-cyclohexen-1-one (10.98 mmol) and (1*S*)-ketopinic acid chloride (10.98 mmol) was purified via flash column chromatography (silica gel, 1:40 ethyl acetate/hexanes) to give **9** (1.32 g, 5.05 mmol, 46%) as a colorless oil: $[\alpha]^{23}_D$ +28.09° (*c* 0.45, $CHCl_3$); IR (CH_2Cl_2) 3688, 2966, 2892, 2833, 1755, 1733, 1665, 1594, 1420, 1318, 1283, 1216, 1138 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.85 (d, J = 8.0 Hz, 1 H), 5.66 (d, J = 8.0 Hz, 2 H), 2.56 (d, J = 16.1 Hz, 1 H), 2.40 (m, 4 H), 2.14−1.96 (m, 4 H), 1.85 (m, 1 H), 1.45 (m, 1 H), 1.20 (s, 3 H), 1.13 (s, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 212.07, 169.28, 149.98, 129.99, 124.27, 123.3, 67.76, 49.04, 43.98, 43.45, 25.68, 25.66, 24.83, 22.96, 20.60, 19.01; MS (20 eV) *m*/*e* 260.2 (M^+, 6), 183.1 (4), 165.1 (100), 123.1 (11), 95.1 (3). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 71.51; H, 7.69.

(1′*R*)-1-Ketopinoxy-1,3-cyclohexadiene (*ent*-9). The crude mixture obtained from 2-cyclohexen-1-one (24.5 mmol) and (*R*)-ketopinic acid chloride (24.5 mmol) was purified via flash column chromatography (silica gel, 1:40 ethyl acetate/hexanes) to give ***ent*-9** (3.31 g, 12.74 mmol, 52%) as a colorless oil: $[\alpha]^{23}_D$ −28.34° (*c* 0.5, $CHCl_3$); IR (CH_2Cl_2) 3885, 2303, 1755, 1733, 1593, 1419, 1256, 1247 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.84−5.82 (m, 1 H), 5.65−5.63 (m, 2 H), 2.59−2.54 (m, 2 H), 2.40 (m, 3 H), 2.14−1.96 (m, 3 H), 1.85 (m, 2 H), 1.46−1.44 (m, 1 H), 1.20 (s, 3 H), 1.13 (s, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 212.1, 169.28, 149.98, 129.99, 124.27, 111.53, 67.76, 49.04, 43.45, 43.98, 25.68, 25.66, 24.83, 22.96, 20.60, 19.01; MS (70 eV) *m*/*e* 260.2 (M^+, 84), 234.2 (5), 183.1 (7), 165.1 (100), 95.1 (4), 69.1 (6); HRMS (EI) *m*/*e* calcd for $C_{16}H_{20}O_3$ (M^+) 260.1412, found 260.0081.

General Procedure for Complexation of Chiral Dienes with $Fe_2(CO)_9$. To a solution of 0.48 g (1.85 mmol) of diene **1** in 10 mL of dried ether was added via spatula 1.01 g (2.78 mmol) of $Fe_2(CO)_9$. The mixture was heated at reflux with stirrng for 40 h. The reaction mixture was then cooled to 25 °C. The solvent was removed on a rotary evaporator to give the crude mixture. It is important to mention that the toxic $Fe(CO)_3$ was produced during use of $Fe_2(CO)_9$ in refluxing ether. Thus, this complexation step should be run in a well-ventilated hood.

(1*R*,2*R*,3*S*,4*S*)-[(1−4-η)-2-(1′*S*)-Ketopinoxy-1,3-cyclohexadiene]tricarbonyliron Complex (4). The crude mixture obtained from diene **1** (0.48 g, 1.85 mmol) and $Fe_2(CO)_9$ (1.01 g, 2.78 mmol) was purified via flash column chromatography (silica gel, 1:40 ethyl acetate/hexanes) to afford complex **4** as a yellow solid (0.39 g, 1.0 mmol, 53%), recrystallization from 1:40 ethyl acetate/hexanes: mp 120−122 °C; $[\alpha]^{26}_D$ +15.50° (*c* 1.0, $CHCl_3$); IR (CH_2Cl_2) 2050, 1977, 1761, 1737, 1618, 1420, 1270 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.56 (d, J = 4.0 Hz, 1 H), 3.42 (m, 1 H), 2.90 (m, 1 H), 2.60 (m, 1 H), 2.40 (m, 1 H), 2.22−1.97 (m, 3 H), 1.86−1.77 (m, 3 H), 1.60−1.55 (m, 2 H), 1.48−1.42 (t, J = 12.1 Hz, 1 H), 1.20 (s, 3 H), 1.14 (s, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 212.41, 170.85, 129.11, 79.89, 67.92, 59.30, 59.14, 51.77, 49.14, 44.11, 43.43, 25.70, 23.92, 22.79, 20.53, 19.03; MS (20 eV) *m*/*e* 372.1 (M^+ − CO, 5), 344.1 (M^+ − 2CO, 83), 316.0 (67), 288.1 (100), 244.0 (9), 229.0 (15), 192.0 (9), 149.9 (10). Anal. Calcd for $C_{19}H_{20}FeO_6$: C, 57.02; H, 5.04. Found: C, 57.17; H, 4.90.

(1*S*,2*S*,3*R*,4*R*)-[(1−4-η)-2-(1′*R*)-Ketopinoxy-1,3-cyclohexadiene]tricarbonyliron Complex (*ent*-4). The crude mixture obtained from diene ***ent*-1** (3.9 g, 15.0 mmol) and $Fe_2(CO)_9$ (9.9 g, 27 mmol) was purified via flash column chromatography (silica gel, 1:40 ethyl acetate/hexanes) to afford complex ***ent*-4** as a yellow solid (2.87 g, 7.2 mmol, 49%): mp 108−111 °C; $[\alpha]^{26}_D$ −15.64° (*c* 1.0, $CHCl_3$); IR (CH_2Cl_2) 3072, 3060, 3051, 2991, 2981, 2050, 1978, 1609, 1445, 1427, 1419, 1280, 1245, 1089 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.48 (d, J = 6.3 Hz, 1 H), 3.35 (m, 1 H), 2.79 (m, 1 H), 2.53−2.48 (m, 1 H), 2.38−2.27 (m, 1 H), 2.08 (m, 1 H), 2.03−1.90 (m, 2 H), 1.85−1.77 (m, 2 H), 1.73−1.65 (m, 1 H), 1.52−1.48 (m, 2 H), 1.41−1.35 (m, 1 H), 1.13 (s, 3 H), 1.07 (s, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 211.34, 170.63, 128.95, 79.87, 67.92, 59.32, 59.14, 51.75, 49.17, 44.13, 43.45, 25.75, 23.97, 22.85, 20.61, 19.11; MS (70 eV) *m*/*e* 372.2 (5), 344.1 (M^+ − 2CO, 74), 316.1 (66), 288.0 (93), 244.1 (17), 229.1 (28), 192.1 (18), 165.1 (100), 121.0 (44); HRMS (EI) *m*/*e* calcd for $C_{19}H_{20}FeO_6$ (M^+ − 2CO) 344.0711, found 344.0706. Anal. Calcd for $C_{19}H_{20}FeO_6$: C, 57.02; H, 5.04. Found: C, 56.51; H, 4.67.

(1*R*,2*R*,3*S*,4*S*)-[(1−4-η)-1-(1′*S*)-Ketopinoxy-1,3-cyclohexadiene]tricarbonyliron Complex (10). The crude mixture obtained from diene **9** (1.19 g, 4.62 mmol) and $Fe_2(CO)_9$ (3.35 g, 9.20 mmol) was purified via flash column chromatography (silica gel, 1:40 ethyl acetate/hexanes) to afford complex **10** as a yellow solid (1.25 g, 3.12 mmol, 68%), recrystallization from 1:40 ethyl acetate/hexanes: mp 104−105 °C; $[\alpha]^{27}_D$ +21.0° (*c* 0.5, $CHCl_3$); IR (CH_2Cl_2) 3688, 3045, 2985, 2052, 1982, 1607, 1420 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.42 (d, J = 4.0 Hz, 1 H), 5.11 (t, J = 4.0 Hz, 1 H), 3.09 (m, 1 H), 2.53 (d, J = 16.0 Hz, 1 H), 2.39−2.33 (m, 1 H), 2.16−1.76 (m, 7 H), 1.70−1.64 (m, 1 H), 1.39 (t, J = 8.0 Hz, 1 H), 1.18 (s, 3 H), 1.09 (s, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 212.19, 169.57, 103.87, 80.52, 68.07, 60.03, 48.96, 44.29, 43.43, 26.42, 25.62, 25.56, 23.30, 20.80, 18.96; MS (20 eV) *m*/*e* 400.0 (M^+, 4), 372.1 (M^+ − CO, 20), 344.1 (M^+ − 2CO, 100), 316.0 (M^+ − 3CO, 95), 288.0 (98), 258.1 (10), 229.0 (12), 162.0 (10), 149.9 (16). Anal. Calcd for $C_{19}H_{20}FeO_6$: C, 57.02; H, 5.04. Found: C, 57.06; H, 5.25.

(2*R*,3*R*,4*S*)-[(1−4-η)-2-(1′*S*)-Ketopinoxy-4-phenyl-1,3-butadiene]tricarbonyliron Complex (16a). The crude mixture obtained from diene **15a** (2.04 g, 6.57 mmol) and $Fe_2(CO)_9$ (12.5 g, 32.9 mmol) was purified via flash column chromatography (silica gel, 1:40 ethyl acetate/hexanes) to afford complex **16a** as a yellow solid (0.81 g, 1.64 mmol, 25%): mp 96−97 °C; $[\alpha]^{32}_D$ +15.15° (*c* 3.3, $CHCl_3$); IR (CH_2Cl_2) 2974, 2053, 1993, 1762, 1740, 1486, 1462, 1312, 1213 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.22 (m, 5 H), 6.174 (d, J = 8.6 Hz, 1 H), 2.53 (m, 2 H), 2.12 (m, 5 H), 1.57 (d, J = 8.6 Hz, 1 H), 1.44 (m, 1 H), 1.25−1.23 (brs, 3 H), 1.19;1.17 (brs, 3 H), 0.95 (d, J = 4.6 Hz, 1 H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 211.37, 211.27, 170.69, 170.47, 140.28, 129.16, 127.06, 126.92, 78.36, 78.21, 67.91, 52.78, 49.02, 43.96, 43.27, 36.74, 36.59, 25.48, 20.45, 18.92; MS (20 eV) *m*/*e* 450 (0.56), 394 (17), 366 (100), 184 (69), 165 (49); HRMS (EI) *m*/*e* calcd for $C_{21}H_{22}FeO_4$ (M^+ − 2CO) 394.0867, found 394.0868. Anal. Calcd for $C_{23}H_{22}FeO_6$: C, 61.35; H, 4.92. Found: C, 61.00; H, 4.74.

(2*S*,3*S*,4*R*)-[(1−4-η)-2-(1′*R*)-Ketopinoxy-4-phenyl-1,3-butadiene]tricarbonyliron Complex (*ent*-16a). The crude mixture obtained from diene ***ent*-15a** (2.50 g, 8.05 mmol) and $Fe_2(CO)_9$ (12.1 g, 32.2 mmol) was purified via flash column chromatography (silica gel, 1:40 ethyl acetate/hexanes) to afford complex **16a** as a yellow solid (1.5 g, 3.05 mmol, 38%): mp 94−95 °C; $[\alpha]^{30}_D$ −14.21° (*c* 3.8, $CHCl_3$); IR (CH_2Cl_2) 3050, 2054, 1986, 1761, 1739, 1420 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.22 (m, 5 H), 6.17 (d, J = 8.4 Hz, 1 H), 2.50 (m, 2 H), 2.06 (m, 5 H), 1.57 (d, J = 8.8 Hz, 1 H), 1.45 (m, 1 H), 1.25−1.22 (brs, 3 H), 1.19−1.17 (brs, 3 H), 0.94 (d, J = 4.6 Hz, 1 H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 209.95, 209.85, 169.72, 169.50, 139.65, 128.66, 126.58, 126.43, 78.44, 78.29, 68.11, 53.20, 53.12, 49.45, 44.53, 44.44, 43.76, 37.28, 26.31, 26.17, 21.20, 19.71; MS (20 eV) *m*/*e* 450 (0.56), 422 (0.8), 394 (18), 366 (100), 184 (10); HRMS (EI) *m*/*e* calcd for $C_{21}H_{22}FeO_4$ (M^+ − 2CO) 394.0867, found 394.0866. Anal. Calcd for $C_{23}H_{22}FeO_6$: C, 61.35; H, 4.92. Found: C, 61.27; H, 4.76.

(2*R*,3*R*,4*R*)-[(1−4-η)-2-(1′*S*)-Ketopinoxy-5-methyl-1,3-hexadiene]tricarbonyliron Complex (16b). The crude mixture obtained from diene **15b** (0.97 g, 3.51 mmol) and $Fe_2(CO)_9$ (1.53 g, 4.2 mmol) was purified via flash column chromatography (silica gel, 1:40 ethyl acetate/hexanes) to afford complex **16b** as a yellow solid (0.29 g, 0.70 mmol, 20%): mp 97−98 °C; $[\alpha]^{25}_D$ +15.04° (*c* 0.9, $CHCl_3$); IR (CH_2Cl_2) 2965, 2051, 1980, 1761, 1739, 1280, 1210, 1092 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.53 (d, J = 7.8 Hz, 1 H), 2.49 (m, 2 H), 1.98 (m, 5 H), 1.50 (m, 2 H), 1.11 (m, 12 H), 0.59 (d, J = 4.4 Hz, 1 H), 0.37 (dd, J = 9.0 Hz, 1 H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 210.14, 210.44, 169.78, 169.55, 126.43, 126.28, 81.86, 81.75, 68.08, 68.03, 64.98, 64.93, 49.49, 49.46, 44.41, 43.80, 43.77, 37.43, 37.25, 33.79, 26.30, 26.22, 26.17, 26.11, 25.81, 24.57, 21.24, 21.18, 19.17; MS (20 eV) *m*/*e* 416 (0.13), 388 (0.88), 360 (11), 322 (100); HRMS (EI) *m*/*e* calcd for $C_{20}H_{25}FeO_6$ (M^+ + 1) 417.1000, found 417.1001.

(2*S*,3*S*,4*S*)-[(1−4-η)-2-(1′*R*)-Ketopinoxy-5-methyl-1,3-hexadiene]tricarbonyliron Complex (*ent*-16b). The crude mixture obtained from diene ***ent*-15b** (1.49 g, 5.4 mmol) and $Fe_2(CO)_9$ (2.94 g, 8.1 mmol) was purified via flash column chromatography (silica gel, 1:40 ethyl acetate/hexanes) to afford complex ***ent*-16b** as a yellow solid (0.33 g, 1.19 mmol, 22%): mp 99−100 °C; $[\alpha]^{23}_D$ −16.57° (*c* 0.8, $CHCl_3$); IR (CH_2Cl_2) 2964, 2051, 1980, 1761, 1739, 1606, 1485, 1462, 1394 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.54 (d, J = 8 Hz, 1 H), 2.47 (m, 2 H), 2.18 (m, 5 H), 1.50 (m, 2 H), 1.12 (m, 12 H), 0.59 (d, J = 4.4 Hz, 1 H), 0.38 (dd, J = 8.8 Hz, 1 H); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 211.55, 211.46, 170.78, 170.56, 126.99, 126.84, 81.88, 81.78, 67.96, 67.91, 64.83, 64.77, 49.12, 44.14, 44.03, 43.39, 43.36, 36.93, 36.75, 33.26, 25.70, 25.62, 25.57, 25.52, 25.19, 23.92, 20.55, 20.50, 19.01; MS (20 eV) *m*/*e* 416 (0.13), 388 (4), 360 (13), 332 (100); HRMS (EI) *m*/*e* calcd for $C_{20}H_{25}FeO_6$ (M^+ − 3CO) 332.10748, found 332.10746. Anal. Calcd for $C_{20}H_{24}FeO_6$: C, 57.71; H, 5.81. Found: C, 57.33; H, 5.56.

(1*R*,2*R*,3*S*,4*S*,5*R*)-[(1−4-η)-2-(1′*S*)-Ketopinoxy-5-methyl-1,3-hexadiene]tricarbonyliron Complex (20). To a solution of triphenylcarbenium hexafluorophosphate (Ph_3CPF_6, 0.324 g, 0.98 mmol) in 5 mL of dried dichloromethane at 0 °C under nitrogen was added rapidly a solution of complex **4** (0.393 g, 0.982 mmol).[10,11] The reaction mixture was stirred at 25 °C for 12 h. The reaction mixture was cooled to 0 °C and diluted with 40 mL of cold ether, and the precipitate was filtered. The yellow solid was washed four times with ether and dried under vacuum to give a cationic salt. (0.48 g, 0.98 mmol, 100%) as a pale yellow powder. A solution of freshly prepared MeCu(ZnI)-CN (2.94 mmol) in 5 mL of THF was added to a stirred suspension of the cation salt in 5 mL of THF at 5 °C under nitrogen. A homogeneous solution was obtained after the reaction mixture was stirred at 25 °C for 2 h. The reaction

was then quenched with saturated ammonium chloride solution at 0 °C and was diluted with 100 mL of ethyl acetate. The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture. The crude mixture was purified via flash column chromatography (silica gel, 1:40 ethyl acetate/hexanes) to afford complex **20** as a yellow solid (0.18 g, 0.45 mmol, 46%), recrystallization from 1:40 ethyl acetate/hexanes: mp 80−83 °C; $[\alpha]^{25}_{D}$ +15.04° (*c* 1.0, $CHCl_3$); IR (CH_2Cl_2) 3687, 2050, 1977, 1607, 1422 cm^{-1}; ^1H NMR(400 MHz, $CDCl_3$) δ 5.51 (d, J = 4.0 Hz, 1 H), 3.22 (m, 1 H), 2.77 (m, 1 H), 2.58 (m, 1 H), 2.43 (t, J = 8.0 Hz, 1 H), 2.15 (m, 1 H), 2.07−1.98 (m, 4 H), 1.88 (m, 1 H), 1.45 (m, 2 H), 1.20 (s, 3 H), 1.15 (s, 3 H), 0.97 (d, J = 4.0 Hz, 3 H); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 212.50, 211.63, 171.04, 129.39, 78.76, 67.95, 58.92, 56.90, 49.16, 44.20, 44.11, 43.49, 43.42, 32.71, 31.88, 31.82, 25.72, 20.57, 19.07; MS (20 eV) *m*/*e* 358.1 (M^+ − 2CO, 100), 330.1 (M^+ − CO, 25), 301.7 (63), 286.1 (86), 164.0 (27). Anal. Calcd for $C_{20}H_{22}FeO_6$: C, 57.99; H, 5.35. Found: C, 57.95; H, 5.45.

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Supporting Information Available: Tables giving crystallographic data, positional parameters, bond lengths and angles, and ORTEP diagrams for **4**, *ent*-**4**, **10**, **16a**, *ent*-**16a**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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