

Diastereoselective Alkylation of (Diene-Aldehyde)Fe(CO)₃ Complexes with Functionalized Zinc-Copper Reagents NuCu(CN)ZnI

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Addition of functionalized zinc-copper reagents to the title complexes proceeds in a highly diastereoselective fashion to afford dienol complexes. The relative configurations of adducts **3d** were determined by single X-ray diffraction analysis.

INTRODUCTION

The use of (diene-aldehyde)Fe(CO)₃ complexes for the diastereoselective generation of hydroxy functionalities adjacent to a conjugated diene is well documented.² Lithium,³ magnesium,⁴ allylborane⁵ and allylindium⁶ organometallics are known to react with complex **1** to provide diastereomeric isomers **3** (ψ -*exo*, more polar) and **4** (ψ -*endo*, less polar)⁷ with **3** as the major adducts. However, with titanium and aluminium reagents the reactions proceed with an inversion of the diastereoselectivity.² Reports of the addition of organocopper derivatives to **1** and **2** are lacking. In our preliminary investigations, the reaction of dimethylcuprate [(CH₃)₂CuLi] with complex **2** led by reductive coupling to complex **8** as the major product in 46% yield. Here we report that the recently developed functionalized zinc-copper reagents **7** [NuCu(CN)ZnI, Nu may contain important functional groups such as an ester, nitrile, acetoxy, allyl or benzyl group]⁸ react in the presence of Lewis acid with complexes **1** and **2** to give dienol complexes **3-6** in good yields in a highly diastereoselective fashion. Dienol complexes such as **3-6** may prove of special interest as substrates for intramolecular cyclizations.⁹

RESULTS AND DISCUSSION

In a typical experiment, treatment of a THF (tetrahydrofuran) solution of the highly functionalized zinc-copper reagent EtO₂C(CH₂)₃Cu(CN)ZnI (**7b**) (4.0 equiv) and BF₃·OEt₂ (3.0 equiv) with complex **1** in THF (-78 °C, 10 h, under nitrogen),^{8a,b} followed by treatment with saturated aqueous ammonium chloride, extraction by diethyl ether and flash-column chromatography on silica gel afforded in 79% overall yield **3b** (more polar) and **4b** (less polar) in the ratio 86:14 (entry 2, Table 1). The diastereomeric ratio (dr) values of the respective diastereomeric complexes **3** and **4** were determined directly on the crude adducts by means of integration of the appropriate, characteristic ¹H NMR signals. Results of the addition of functionalized zinc-copper reagents to complexes **1** and **2** are shown in Table 1. The stereochemical assignments for **3** and **4** as *exo* and *endo* isomers respectively were based on the chemical shifts of the hydroxy protons (for example, δ 2.47 ppm for **3b** and δ 1.75 ppm for **4b**), which are consistent with those reported in the literature.^{4a} Rigorous proof of the structure of **3d** was accomplished by X-ray diffraction analysis (Fig. 1). The *exo* isomers, having small R_f values on silica gel, are the major adducts from the addition and the diastereoselectivity is

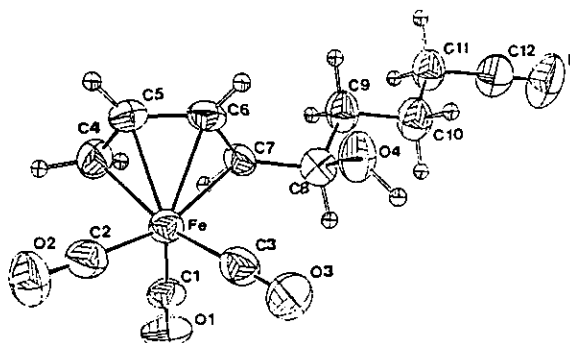
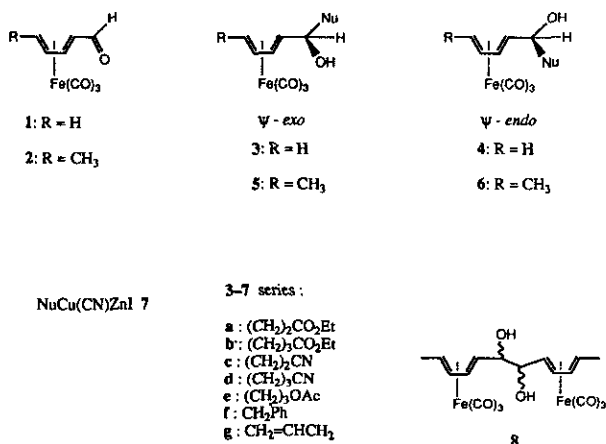


Fig. 1. ORTEP representation of the structure of **3d**.

Table 1. Diastereoselective Formation of Complexes 3-6 by Addition of NuCu(CN)ZnI 7 to (Diene-Aldehyde)Fe(CO)₃ Complex 1 and 2^a

Entry	Complex	NuCu(CN)ZnI 7	Lewis Acid	dr/%		Yield/% ^b
				ψ - <i>exo</i> / ψ - <i>endo</i>		
1	1	Nu=(CH ₂) ₂ CO ₂ Et 7a	BF ₃ ·OEt ₂	3a : 4a = 78 : 22		77
2	1	Nu=(CH ₂) ₃ CO ₂ Et 7b	BF ₃ ·OEt ₂	3b : 4b = 86 : 14		79
3	1	Nu=(CH ₂) ₂ CN 7c	BF ₃ ·OEt ₂	3c : 4c = 82 : 18		59
4	1	Nu=(CH ₂) ₃ CN 7d	BF ₃ ·OEt ₂	3d : 4d = 80 : 20		64
5	1	Nu=(CH ₂) ₃ OAc 7e	BF ₃ ·OEt ₂	3e : 4e = 86 : 14		61
6	1	Nu=CH ₂ Ph 7f	BF ₃ ·OEt ₂	3f : 4f = 93 : 7		71 ^c
7	2	7a	BF ₃ ·OEt ₂	5a : 6a = 77 : 23		88
8	2	7b	BF ₃ ·OEt ₂	5b : 6b = 81 : 19		77
9	2	7b	TiCl ₄	5b : 6b = 16 : 84		84
10	2	7b	AlCl ₃	5b : 6b = 43 : 57		17
11	2	7c	BF ₃ ·OEt ₂	5c : 6c = 79 : 21		47
12	2	7d	BF ₃ ·OEt ₂	5d : 6d = 85 : 15		69
13	2	7e	BF ₃ ·OEt ₂	5e : 6e = 84 : 16		84
14	2	7f	BF ₃ ·OEt ₂	5f : 6f = 92 : 8		92 ^c
15	2	7f	TiCl ₄	5f : 6f = 14 : 86		92 ^c
16	2	PhCH ₂ ZnBr 9	BF ₃ ·OEt ₂	5f : 6f = 93 : 7		56 ^c
17	2	CH ₂ =CHCH ₂ ZnBr 10	BF ₃ ·OEt ₂	5g : 6g = 72 : 28		82 ^c
18	2	7f	none	5f : 6f = 79 : 21		60

^a All reagents were stirred under an atmosphere of nitrogen at -78 °C for 10 h.

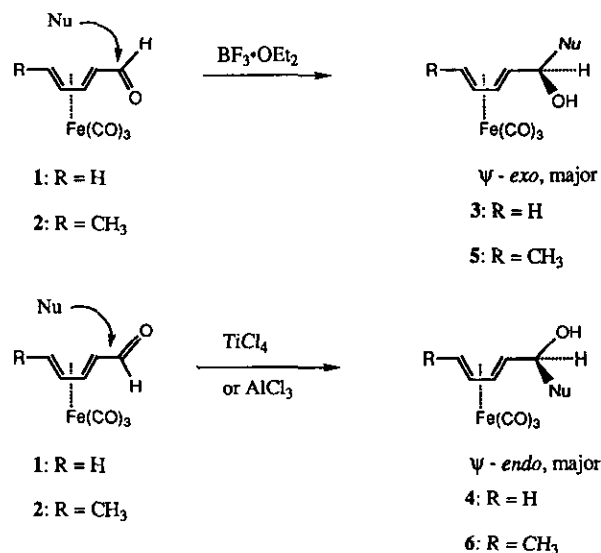
^b All indicated yields were isolated yields. Satisfactory spectral data (IR, ¹H and ¹³C NMR, and high-resolution mass spectra) were obtained for all compounds.

^c The reagents were stirred under an atmosphere of nitrogen at -78 °C for 6 h.

consistent with the reaction of complex 1 with lithium reagents. Moreover, the selectivity is not altered when the reactive benzylic zinc-copper species reacts with complex 2 with or without BF₃·OEt₂ (entries 14, 18).¹⁰ Thus, the favor *s-cis* conformer (at -78 °C) of complex 1 may not be influenced by BF₃·OEt₂.² Based on the above assumptions, addition of the functionalized zinc-copper species on the opposite face of the iron carbonyl moiety to the *s-cis* conformer (as shown in Scheme I) would give 3 as the major adduct. However, varied selectivities were obtained when reactions were performed in TiCl₄ or AlCl₃ (entries 9, 10, 15, Table 1), which agrees with the reaction of lithium reagents with 1 in TiCl₄ or AlCl₃.² The reason is unclear. TiCl₄ or AlCl₃ may shift the equilibrium to favor the *s-trans* conformers.¹¹ Thus, nucleophilic additions of the zinc-copper reagents to the *s-trans* conformers would lead to ψ -*endo* 4 as the major adducts (Scheme I). Both benzylic and allylic zinc reagents are capable of addition without CuCN (entries 16, 17, Table 1) and benzylic zinc and benzylic zinc-copper reagents (entries 6, 14, 16, Table 1) give the highest dr values (93 : 7).

In summary, we have shown that the alkylation of (diene-aldehyde)Fe(CO)₃ complexes with functionalized zinc-copper reagents give dienol complexes in highly diastereoselective fashion.

Scheme I



Further applications involving intramolecular addition of the ester enolate of complex 3a and 3b to the pendant (η^4 -diene)Fe(CO)₃ moiety are in progress in our laboratory.

EXPERIMENTAL SECTION

Spectra

¹H nuclear magnetic resonance (NMR) spectra were obtained with JEOL-EX 400 (400 MHz), Bruker AC-300 (300 MHz), and Bruker AC-200 (200 MHz) spectrometers. The chemical shifts are reported on the scale in ppm with either tetramethylsilane (0.00 ppm) or CHCl₃ (7.26 ppm) as internal standards. ¹³C NMR spectra were recorded with JEOL-EX 400 (100.4 MHz) and Bruker AC 200 (50.2 MHz) spectrometers with CDCl₃ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO FT/IR-5300 spectrometer. Mass spectra were measured on a JEOL JMS-D 100 spectrometer at an ionization energy 20 eV and are reported as mass/charge (m/z) with per cent relative abundance. High-resolution mass-spectra (HRMS) data were obtained on an AEI MS-9 double-focusing mass spectrometer and JEOL JMS SX/SX-102A instrument in the department of chemistry of National Chung-Hsing University, Central Instrument Center, Taichung.

Chromatography

Flash-column chromatography, following the method of Still,¹² was carried out with silica gel (Merck, Kieselgel 60, 230-400 mesh) using the indicated solvents. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 F₂₅₄ plastic plates of 0.2-mm thickness (Merck, Germany). Spots on the TLC plate were made visual with UV light or sulfuric acid (1%) and *p*-anisaldehyde (1%) in ethanol.

Reagents and Solvents

Tetrahydrofuran (THF) and diethyl ether (ether) were distilled under nitrogen from benzophenone ketyl immediately before use. Benzyl bromide, allyl bromide, BF₃·OEt₂ and 2,4-hexadienal (Aldrich) were distilled before use. Titanium tetrachloride and aluminum trichloride (Janssen) were used without further purification. Zinc powder (purity > 99.9%), 1,2-dibromoethane and chlorotrimethylsilane (Merck) were used without purification. Diironnonacarbonyl was obtained by photolysis of ironpentacarbonyl in benzene and acetic acid according to the literature procedure.¹³

General Procedure I: Preparation of Functionalized Iodides

Sodium iodide (2.5 equiv) was placed in a spherical flask (250 mL) equipped with a refluxing condenser and a magnetic stirrer. Dried acetone (100 mL) was added to the

reaction mixture, followed by addition of equimolar proportions of the corresponding functionalized chloride. The mixture was stirred for 12 h to give a pale yellow solution. The reaction mixture was diluted with EtOAc/hexane (1/3) and the precipitate was filtered. The resultant solution was washed with water (3 × 150 mL), saturated aqueous sodium chloride solution (3 × 150 mL), dried over anhydrous magnesium sulfate (20 g), and then concentrated on a rotary evaporator. The residue was distilled under reduced pressure to give a colorless liquid. The functionalized iodides were stored under nitrogen over a bed of copper powder (1.0 g) at 0 °C for a long period.

General Procedure II: Preparation of Functionalized Zinc-Copper Reagents⁸

In a three-neck spherical flask (100 mL) equipped with an additional funnel, a thermometer, a nitrogen outlet and a magnetic stirrer was placed zinc (1.7 g, 26 mmol, Merck, 99.9% purity). The system was flushed three times with nitrogen. Tetrahydrofuran (2 mL) was admitted by syringe through the additional funnel, followed by addition of 1,2-dibromoethane (0.2 mL). The reaction mixture was heated to 65 °C with a hot air blower for a minute and cooled to 25 °C. The processes were repeated twice. Chlorotrimethylsilane (0.2 mL) was then added to the reaction mixture at 25 °C. After stirring at 25 °C for 30 min, a solution of the functionalized iodides (25 mmol) in THF (10 mL) was added dropwise to keep the temperature below 35 °C. After the addition was complete, the reaction mixture was stirred at 35-40 °C for an additional 12 h (at room temperature for ethyl 3-iodopropionate and 3-iodopropionitrile and at 0 °C for 2 h in the case of benzyl bromide). Generally little zinc (100 mg) remained in the mixture. A solution of CuCN (1.98 g, 22 mmol) and LiCl (1.9 g, 44 mmol, predried under reduced pressure at 150 °C for 1 h) in THF (22 mL) was cooled to -78 °C. The zinc solution prepared above was admitted by syringe slowly into the CuCN/LiCl solution. The reaction mixture was stirred at 0 °C for 30 min and was ready to use.

General Procedure III: Reaction of the Functionalized Zinc-Copper Reagents with (Diene-Aldehyde)Fe(CO)₃ Complexes

The functionalized zinc-copper reagents (4.0 mol proportions) and Lewis acid (3.0 mol proportions) were added via syringe to the solution of aldehyde **1** or **2** in THF (7 mL) at -78 °C under nitrogen. The reaction mixture was allowed to stir at -78 °C for 10 h. The reaction mixture was then quenched with saturated aqueous ammonium chloride solution and was diluted with a solution of mixture (100 mL) of

EtOAc/hexanes (1/2). The resultant solution was washed with water (100 mL \times 3), and brine (100 mL \times 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture.

(4R*,5R*)-[(5-8- η)-Ethyl 4-hydroxy-*trans*-5,7-octadienoate]tricarbonyliron complex (3a)

The crude mixture obtained from addition of the corresponding zinc-copper reagent (4.0 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (3.0 mmol) to aldehyde **1** (200 mg, 0.9 mmol) was purified via flash-column chromatography (silica gel, 1:15 ethyl acetate/hexanes) to give **3a** (176 mg, 60%) and **4a** (46 mg, 17%), both as yellow oils. **3a**: IR (CH_2Cl_2) 3601, 3431, 3065, 2988, 2051, 1983, 1728, 1444, 1377, 1298, 1205, 1059 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.43 (*dd*, $J = 8.3, 4.9$ Hz, 1 H), 5.29 (*ddd*, $J = 9.3, 7.8, 4.9$ Hz, 1 H), 4.13 (*q*, $J = 7.3$ Hz, 2 H), 3.49 (*m*, 1 H), 2.97 (*br*, 1 H), 2.48 (*t*, $J = 6.8$ Hz, 2 H), 2.02 (*m*, 1 H), 1.82 (*m*, 1 H), 1.80 (*dd*, $J = 7.8, 2.4$ Hz, 1 H), 1.25 (*t*, $J = 7.3$ Hz, 3 H), 0.97 (*dd*, $J = 8.3, 7.8$ Hz, 1 H), 0.39 (*dd*, $J = 9.3, 2.4$ Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl_3) δ 211.2, 174.1, 86.3, 82.5, 73.0, 65.3, 60.6, 40.3, 33.2, 30.6, 14.0; MS (20 eV) m/z (rel intensity) 324 (M^+ , 1), 296 (3), 268 (31), 240 (100), 222 (35), 194 (80), 160 (21), 148 (85), 134 (80), 122 (65), 79 (20); HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{16}\text{O}_4\text{Fe}$ ($\text{M}^+ - 2\text{CO}$) 268.0398, found 268.0402.

(4S*,5R*)-[(5-8- η)-Ethyl 4-hydroxy-*trans*-5,7-octadienoate]tricarbonyliron complex (4a)

IR (CH_2Cl_2) 3602, 3430, 2988, 2051, 1977, 1728, 1377, 1350, 1271, 1180, 1064 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.36 (*dd*, $J = 8.3, 4.9$ Hz, 1 H), 5.26 (*ddd*, $J = 9.3, 7.8, 4.9$ Hz, 1 H), 4.14 (*q*, $J = 7.3$ Hz, 2 H), 3.59 (*m*, 1 H), 2.48 (*t*, $J = 6.8$ Hz, 2 H), 2.09 (*br*, 1 H), 1.90 (*m*, 2 H), 1.78 (*dd*, $J = 7.8, 2.4$ Hz, 1 H), 1.26 (*t*, $J = 7.3$ Hz, 3 H), 1.03 (*dd*, $J = 8.3, 7.8$ Hz, 1 H), 0.30 (*dd*, $J = 9.3, 2.4$ Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl_3) δ 211.3, 173.8, 84.9, 81.5, 73.1, 68.9, 60.6, 40.2, 34.6, 30.9, 14.1; MS (20 eV) m/z (rel intensity) 324 (M^+ , 1), 296 (4), 268 (34), 240 (100), 222 (31), 194 (80), 160 (24), 132 (31), 122 (63), 79 (21); HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{16}\text{O}_4\text{Fe}$ ($\text{M}^+ - 2\text{CO}$) 268.0398, found 268.0406.

(5R*,6R*)-[(6-9- η)-Ethyl 5-hydroxy-*trans*-6,8-nonadienoate]tricarbonyliron complex (3b)

The crude mixture obtained from addition of the corresponding zinc-copper reagent (7.0 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (5.0 mmol) to aldehyde **1** (380 mg, 1.7 mmol) was purified via flash-column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **3b** (287 mg, 68%) and **4b** (45 mg,

11%), both as yellow oils. **3b**: IR (CH_2Cl_2) 3606, 3468, 3072, 3064, 2940, 2050, 1976, 1727, 1420, 1375, 1244, 1193, 1071 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.43 (*dd*, $J = 8.3, 4.9$ Hz, 1 H), 5.26 (*ddd*, $J = 9.3, 7.8, 4.9$ Hz, 1 H), 4.13 (*q*, $J = 7.3$ Hz, 2 H), 3.45 (*m*, 1 H), 2.47 (*br*, 1 H), 2.35 (*t*, $J = 7.3$ Hz, 2 H), 1.80 (*dd*, $J = 7.8, 2.4$ Hz, 1 H), 1.71 (*m*, 2 H), 1.58 (*m*, 2 H), 1.26 (*t*, $J = 7.3$ Hz, 3 H), 1.01 (*dd*, $J = 8.3, 7.8$ Hz, 1 H), 0.38 (*dd*, $J = 9.3, 2.4$ Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl_3) δ 211.3, 173.9, 86.5, 82.5, 73.2, 65.7, 60.4, 40.4, 37.9, 33.8, 20.6, 14.1; MS (20 eV) m/z (rel intensity) 338 (M^+ , 1), 310 (3), 282 (23), 254 (100), 236 (20), 208 (28), 184 (25), 134 (36), 83 (23); HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{18}\text{O}_3\text{Fe}$ ($\text{M}^+ - 3\text{CO}$) 254.0605, found 254.0593.

(5S*,6R*)-[(6-9- η)-Ethyl 5-hydroxy-*trans*-6,8-nonadienoate]tricarbonyliron complex (4b)

IR (CH_2Cl_2) 3604, 3470, 3070, 3064, 2984, 2048, 1974, 1729, 1411, 1376, 1283, 1241, 1184 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.34 (*dd*, $J = 8.3, 4.9$ Hz, 1 H), 5.26 (*ddd*, $J = 9.3, 7.8, 4.9$ Hz, 1 H), 4.13 (*q*, $J = 7.3$ Hz, 2 H), 3.52 (*m*, 1 H), 2.34 (*t*, $J = 7.8$ Hz, 2 H), 1.78 (*dd*, $J = 7.8, 2.4$ Hz, 1 H), 1.76 (*m*, 2 H), 1.75 (*br*, 1 H), 1.59 (*m*, 2 H), 1.25 (*t*, $J = 7.3$ Hz, 3 H), 1.05 (*dd*, $J = 8.3, 7.8$ Hz, 1 H), 0.30 (*dd*, $J = 9.3, 2.4$ Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl_3) δ 211.4, 173.6, 85.0, 81.5, 73.3, 69.3, 60.4, 40.2, 39.2, 34.0, 21.1, 14.2; MS (20 eV) m/z (rel intensity) 338 (M^+ , 1), 310 (2), 282 (20), 254 (100), 236 (12), 208 (19), 174 (23), 134 (23); HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{18}\text{O}_3\text{Fe}$ ($\text{M}^+ - 3\text{CO}$) 254.0605, found 254.0589.

(4R*,5R*)-[(5-8- η)-4-Hydroxy-*trans*-5,7-octadieneni-*trile*]tricarbonyliron complex (3c)

The crude mixture obtained from addition of the corresponding zinc-copper reagent (4.0 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (3.0 mmol) to aldehyde **1** (200 mg, 0.9 mmol) was purified via flash-column chromatography (silica gel, 1:5 ethyl acetate/hexanes) to give **3c** (125 mg, 50%) and **4c** (22 mg, 9%), both as yellow oils. **3c**: IR (CH_2Cl_2) 3601, 3478, 3054, 2936, 2249, 2049, 1993, 1609, 1478, 1387, 1283, 1173, 1061 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.42 (*dd*, $J = 8.3, 4.9$ Hz, 1 H), 5.30 (*ddd*, $J = 9.3, 7.8, 4.9$ Hz, 1 H), 3.56 (*m*, 1 H), 2.52 (*t*, $J = 6.8$ Hz, 2 H), 2.03 (*m*, 1 H), 1.85 (*dd*, $J = 7.8, 2.4$ Hz, 1 H), 1.83 (*m*, 1 H), 0.90 (*dd*, $J = 8.3, 7.8$ Hz, 1 H), 0.42 (*dd*, $J = 9.3, 2.4$ Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl_3) δ 210.8, 119.5, 86.1, 83.1, 72.2, 63.7, 40.9, 33.7, 13.8; MS (20 eV) m/z (rel intensity) 277 (M^+ , 1), 249 (13), 221 (61), 193 (100), 175 (11), 153 (16), 135 (11), 111 (13), 79 (11); HRMS (EI) m/z calcd for $\text{C}_8\text{H}_{11}\text{ONFe}$ ($\text{M}^+ - 3\text{CO}$) 193.0190, found 193.0191.

(4*S,5*R**)-[(5-8-η)-4-Hydroxy-trans-5,7-octadienenitrile]tricarbonyliron complex (4c)**

IR (CH₂Cl₂) 3607, 3410, 3052, 2930, 2247, 2051, 1985, 1607, 1441, 1379, 1275, 1127, 1065 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.34 (*m*, 2 H), 3.63 (*m*, 1 H), 2.53 (*t*, *J* = 6.8 Hz, 2 H), 1.90 (*m*, 2 H), 1.85 (*dd*, *J* = 7.8, 2.4 Hz, 1 H), 0.98 (*dd*, *J* = 8.3, 7.8 Hz, 1 H), 0.35 (*dd*, *J* = 9.3, 2.4 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 210.8, 119.4, 84.7, 82.1, 72.0, 67.2, 40.7, 34.8, 13.9; MS (20 eV) *m/z* (rel intensity) 277 (M⁺, 3), 249 (16), 221(70), 193 (100), 175 (15), 153 (23), 135 (15), 111 (19), 79 (18); HRMS (EI) *m/z* calcd for C₈H₁₁ONFe (M⁺ - 3CO) 193.0190, found 193.0193.

(5*R,6*R**)-[(6-9-η)-5-Hydroxy-trans-6,8-nonadienenitrile]tricarbonyliron complex (3d)**

The crude mixture obtained from addition of the corresponding zinc-copper reagent (4.0 mmol) and BF₃·OEt₂ (3.0 mmol) to aldehyde **1** (200 mg, 0.9 mmol) was purified via flash-column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **3d** (138 mg, 53%) and **4d** (30 mg, 11%), both as yellow oils. **3d**: mp 75-76 °C (hexane/dichloromethane); IR (CH₂Cl₂) 3601, 3486, 3049, 2940, 2249, 2051, 1983, 1456, 1386, 1263, 1120, 1069 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.42 (*dd*, *J* = 8.3, 4.9 Hz, 1 H), 5.31 (*ddd*, *J* = 9.3, 7.8, 4.9 Hz, 1 H), 3.50 (*m*, 1 H), 2.41 (*t*, *J* = 6.8 Hz, 2 H), 1.84 (*m*, 1 H), 1.82 (*m*, 2 H), 1.72 (*dd*, *J* = 7.8, 2.4 Hz, 1 H), 1.67 (*m*, 1 H), 0.96 (*dd*, *J* = 8.3, 7.8 Hz, 1 H), 0.41 (*dd*, *J* = 9.3, 2.4 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.1, 119.6, 86.3, 82.7, 72.9, 65.0, 40.6, 37.0, 21.6, 16.8; MS (20 eV) *m/z* (rel intensity) 291 (M⁺, 1), 263 (3), 235 (36), 207 (100), 189 (21), 187 (33), 134 (21), 127 (85), 126 (45), 96 (55); HRMS (EI) *m/z* calcd for C₉H₁₃ONFe (M⁺ - 3CO) 207.0343, found 207.0350.

(5*S,6*R**)-[(6-9-η)-5-Hydroxy-trans-6,8-nonadienenitrile]tricarbonyliron complex (4d)**

IR (CH₂Cl₂) 3605, 3491, 3067, 2939, 2249, 2049, 1987, 1458, 1381, 1265, 1124, 1061 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.31 (*m*, 2 H), 3.52 (*m*, 1 H), 2.41 (*t*, *J* = 6.8 Hz, 2 H), 1.82 (*m*, 2 H), 1.72 (*m*, 1 H), 1.71 (*m*, 2 H), 1.03 (*dd*, *J* = 8.3, 7.8 Hz, 1 H), 0.33 (*dd*, *J* = 9.3, 2.4 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.2, 119.5, 84.8, 81.8, 73.2, 68.7, 40.5, 38.4, 21.9, 17.1; MS (20 eV) *m/z* (rel intensity) 291 (M⁺, 1), 263 (4), 235 (30), 207 (100), 189 (19), 187 (29), 134 (17), 127 (65), 126 (34), 96 (15); HRMS (EI) *m/z* calcd for C₉H₁₃ONFe (M⁺ - 3CO) 207.0343, found 207.0347.

(4*R,5*R**)-[(5-8-η)-1-Acetoxy-4-hydroxy-trans-5,7-octadiene]tricarbonyliron complex (3e)**

The crude mixture obtained from addition of the corresponding zinc-copper reagent (4.0 mmol) and BF₃·OEt₂ (3.0 mmol) to aldehyde **1** (230 mg, 1.04 mmol) was purified via flash-column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **3e** (177 mg, 53%) and **4e** (23 mg, 8%), both as yellow oils. **3e**: IR (CH₂Cl₂) 3601, 3437, 3057, 2961, 2051, 1975, 1734, 1437, 1389, 1244, 1042 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.42 (*dd*, *J* = 8.3, 4.9 Hz, 1 H), 5.30 (*ddd*, *J* = 8.8, 7.8, 4.9 Hz, 1 H), 4.12 (*t*, *J* = 6.4 Hz, 2 H), 3.50 (*m*, 1 H), 2.05 (*s*, 3 H), 1.99 (*br*, 1 H), 1.81 (*m*, 1 H), 1.77 (*m*, 3 H), 1.61 (*m*, 1 H), 1.00 (*dd*, *J* = 8.3, 7.8 Hz, 1 H), 0.40 (*dd*, *J* = 8.8, 2.9 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.2, 171.3, 86.4, 82.5, 73.1, 65.6, 64.1, 40.4, 34.6, 24.5, 20.8; MS (20 eV) *m/z* (rel intensity) 324 (M⁺, 1), 296 (2), 268 (26), 240 (100), 222 (4), 180 (97), 136 (35), 97 (14), 79 (55); HRMS (EI) *m/z* calcd for C₁₁H₁₆O₄Fe (M⁺ - 2CO) 268.0398, found 268.0399.

(4*S,5*R**)-[(5-8-η)-1-Acetoxy-4-hydroxy-trans-5,7-octadiene]tricarbonyliron complex (4e)**

IR (CH₂Cl₂) 3603, 3437, 3067, 2959, 2049, 1971, 1734, 1437, 1389, 1244, 1039 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.33 (*dd*, *J* = 8.3, 4.9 Hz, 1 H), 5.26 (*ddd*, *J* = 8.8, 7.8, 4.9 Hz, 1 H), 4.10 (*t*, *J* = 6.4 Hz, 2 H), 3.53 (*m*, 1 H), 2.05 (*s*, 3 H), 1.80 (*dd*, *J* = 7.8, 2.9 Hz, 1 H), 1.76 (*m*, 2 H), 1.64 (*m*, 2 H), 1.05 (*dd*, *J* = 8.3, 7.8 Hz, 1 H), 0.32 (*dd*, *J* = 8.8, 2.9 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.2, 171.1, 85.0, 81.6, 73.5, 69.1, 64.2, 40.3, 36.2, 25.1, 20.9; MS (20 eV) *m/z* (rel intensity) 324 (M⁺, 1), 296 (2), 268 (28), 240 (100), 222 (3), 180 (97), 136 (35), 97 (16), 79 (59); HRMS (EI) *m/z* calcd for C₁₁H₁₆O₄Fe (M⁺ - 2CO) 268.0398, found 268.0396.

(2*R,3*R**)-[(3-6-η)-2-Hydroxy-1-phenyl-trans-3,5-hexadiene]tricarbonyliron complex (3f)**

The crude mixture obtained from addition of the corresponding zinc-copper reagent (4.0 mmol) and BF₃·OEt₂ (3.0 mmol) to aldehyde **1** (160 mg, 0.72 mmol) was purified via flash-column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give **3f** (150 mg, 66%) and **4f** (12 mg, 5%), both as yellow oils. **3f**: IR (CH₂Cl₂) 3594, 3455, 3030, 2924, 2045, 1983, 1605, 1495, 1454, 1383, 1205, 1117, 1053, 872, 806 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.19 (*m*, 5 H), 5.40 (*dd*, *J* = 8.3, 4.9 Hz, 1 H), 5.25 (*ddd*, *J* = 9.3, 6.8, 4.9 Hz, 1 H), 3.61 (*m*, 1 H), 3.05 (*dd*, *J* = 13.7, 2.4

Hz, 1 H), 2.67 (*dd*, $J = 13.7, 10.3$ Hz, 1 H), 1.89 (*br*, 1 H), 1.80 (*dd*, $J = 6.8, 1.5$ Hz, 1 H), 1.04 (*dd*, $J = 8.3, 7.8$ Hz, 1 H), 0.40 (*dd*, $J = 9.3, 1.5$ Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl_3) δ 211.4, 137.8, 129.3, 128.6, 126.7, 86.5, 82.6, 74.6, 64.7, 45.4, 40.4; MS (20 eV) m/z (rel intensity) 314 (M^+ , 10), 286 (6), 258 (60), 230 (90), 212 (92), 194 (35), 148 (42), 138 (100), 134 (65), 91 (38); HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{OFe}$ ($M^+ - 3\text{CO}$) 230.0394, found 230.0390.

(2*S,3*R**)-[(3-6- η)-2-Hydroxy-1-phenyl-*trans*-3,5-hexadiene]tricarbonyliron complex (4f)**

IR (CH_2Cl_2) 3598, 3409, 3050, 2928, 2049, 1979, 1690, 1605, 1495, 1454, 1381, 1206, 1120, 874, 730 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.21 (*m*, 5 H), 5.19 (*m*, 2 H), 3.75 (*m*, 1 H), 2.86 (*m*, 2 H), 1.77 (*dd*, $J = 6.8, 2.4$ Hz, 1 H), 1.08 (*dd*, $J = 8.3, 7.8$ Hz, 1 H), 0.31 (*dd*, $J = 9.3, 2.4$ Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl_3) δ 211.5, 137.5, 129.5, 128.6, 126.7, 85.0, 81.5, 74.8, 68.0, 46.6, 40.1; MS (20 eV) m/z (rel intensity) 314 (M^+ , 5), 286 (14), 258 (64), 230 (87), 212 (86), 194 (33), 148 (49), 138 (100), 134 (89), 91 (60); HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{OFe}$ ($M^+ - 3\text{CO}$) 230.0394, found 230.0392.

(4*R,5*R**,8*S**)-[(5-8- η)-Ethyl 4-hydroxy-*trans*-5,7-nonadienoate]tricarbonyliron complex (5a)**

The crude mixture obtained from addition of the corresponding zinc-copper reagent (4.0 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (3.0 mmol) to aldehyde **2** (250 mg, 1.06 mmol) was purified via flash-column chromatography (silica gel, 1:15 ethyl acetate/hexanes) to give **5a** (245 mg, 68%) and **6a** (69 mg, 20%), both as yellow oils. **5a**: IR (CH_2Cl_2) 3603, 3428, 3051, 2992, 2045, 1973, 1728, 1445, 1379, 1244, 1184, 1032 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.23 (*dd*, $J = 8.3, 4.9$ Hz, 1 H), 5.06 (*dd*, $J = 8.3, 4.9$ Hz, 1 H), 4.12 (*q*, $J = 7.3$ Hz, 2 H), 3.42 (*m*, 1 H), 3.06 (*br*, 1 H), 2.47 (*t*, $J = 7.3$ Hz, 2 H), 1.99 (*m*, 1 H), 1.81 (*m*, 1 H), 1.41 (*d*, $J = 5.9$ Hz, 3 H), 1.25 (*t*, $J = 7.3$ Hz, 3 H), 1.23 (*m*, 1 H), 0.93 (*dd*, $J = 8.3, 7.8$ Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl_3) δ 211.8, 174.1, 86.3, 82.1, 73.2, 64.1, 60.5, 58.2, 33.1, 30.6, 19.0, 14.0; MS (20 eV) m/z (rel intensity) 338 (M^+ , 1), 310 (2), 282 (24), 254 (29), 236 (63), 208 (100), 162 (41), 148 (36), 134 (87), 122 (27); HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{18}\text{O}_3\text{Fe}$ ($M^+ - 3\text{CO}$) 254.0605, found 254.0611.

(4*S,5*R**,8*S**)-[(5-8- η)-Ethyl 4-hydroxy-*trans*-5,7-nonadienoate]tricarbonyliron complex (6a)**

IR (CH_2Cl_2) 3601, 3432, 3050, 2982, 2043, 1971, 1728, 1443, 1379, 1289, 1181, 1032 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.16 (*dd*, $J = 8.3, 4.9$ Hz, 1 H), 5.06 (*dd*, $J =$

8.3, 4.9 Hz, 1 H), 4.13 (*q*, $J = 7.3$ Hz, 2 H), 3.52 (*m*, 1 H), 2.46 (*t*, $J = 7.3$ Hz, 2 H), 2.02 (*br*, 1 H), 1.86 (*m*, 2 H), 1.41 (*d*, $J = 6.4$ Hz, 3 H), 1.25 (*t*, $J = 7.3$ Hz, 3 H), 1.14 (*m*, 1 H), 1.00 (*dd*, $J = 8.3, 7.8$ Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl_3) δ 211.8, 173.8, 85.4, 80.5, 73.1, 67.1, 60.5, 58.1, 34.5, 30.8, 19.0, 14.1; MS (20 eV) m/z (rel intensity) 338 (M^+ , 1), 310 (3), 282 (34), 254 (48), 236 (100), 208 (42), 188 (28), 162 (64), 148 (56), 134 (90), 122 (38); HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{18}\text{O}_3\text{Fe}$ ($M^+ - 3\text{CO}$) 254.0605, found 254.0601.

(5*R,6*R**,9*S**)-[(6-9- η)-Ethyl 5-hydroxy-*trans*-6,8-decadienoate]tricarbonyliron complex (5b)**

The crude mixture obtained from addition of the corresponding zinc-copper reagent (4.0 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (3.0 mmol) to aldehyde **2** (200 mg, 0.85 mmol) was purified via flash-column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **5b** (188 mg, 63%) and **6b** (42 mg, 14%), both as yellow oils. **5b**: IR (CH_2Cl_2) 3601, 3468, 3067, 2982, 2042, 1983, 1728, 1444, 1379, 1298, 1188, 1032 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.23 (*dd*, $J = 8.3, 4.9$ Hz, 1 H), 5.06 (*dd*, $J = 8.3, 4.9$ Hz, 1 H), 4.13 (*q*, $J = 7.3$ Hz, 2 H), 3.38 (*m*, 1 H), 2.34 (*t*, $J = 7.3$ Hz, 2 H), 1.81 (*m*, 1 H), 1.76 (*m*, 2 H), 1.56 (*m*, 1 H), 1.41 (*d*, $J = 6.3$ Hz, 3 H), 1.26 (*t*, $J = 7.3$ Hz, 3 H), 1.24 (*m*, 1 H), 0.96 (*dd*, $J = 8.3, 7.8$ Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl_3) δ 211.9, 173.8, 86.3, 82.2, 73.4, 64.5, 60.3, 58.3, 37.7, 33.7, 20.7, 19.0, 14.1; MS (20 eV) m/z (rel intensity) 352 (M^+ , 1), 324 (3), 296 (26), 268 (44), 250 (100), 222 (45), 206 (15), 174 (24), 148 (33), 134 (48); HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{20}\text{O}_3\text{Fe}$ ($M^+ - 3\text{CO}$) 268.0762, found 268.0767.

(5*S,6*R**,9*S**)-[(6-9- η)-Ethyl 5-hydroxy-*trans*-6,8-decadienoate]tricarbonyliron complex (6b)**

IR (CH_2Cl_2) 3603, 3487, 3065, 2932, 2043, 1971, 1728, 1445, 1377, 1298, 1186, 1032 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.14 (*dd*, $J = 8.3, 4.9$ Hz, 1 H), 5.05 (*dd*, $J = 8.3, 4.9$ Hz, 1 H), 4.13 (*q*, $J = 7.3$ Hz, 2 H), 3.45 (*m*, 1 H), 2.34 (*t*, $J = 7.3$ Hz, 2 H), 1.76 (*m*, 1 H), 1.69 (*m*, 2 H), 1.60 (*m*, 1 H), 1.41 (*d*, $J = 5.9$ Hz, 3 H), 1.26 (*t*, $J = 7.3$ Hz, 3 H), 1.14 (*dd*, $J = 8.3, 5.9$ Hz, 1 H), 1.02 (*dd*, $J = 8.3, 7.8$ Hz, 1 H); ^{13}C NMR (100.4 MHz, CDCl_3) δ 212.0, 173.5, 85.3, 80.7, 73.4, 68.2, 60.3, 58.1, 39.1, 34.0, 21.1, 19.0, 14.2; MS (20 eV) m/z (rel intensity) 352 (M^+ , 1), 324 (5), 296 (33), 268 (51), 250 (100), 222 (68), 206 (12), 174 (17), 148 (20), 134 (33); HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{20}\text{O}_3\text{Fe}$ ($M^+ - 3\text{CO}$) 268.0762, found 268.0766.

(a) Using TiCl_4

The crude mixture obtained from addition of the corre-

sponding zinc-copper reagent (4.0 mmol) and TiCl₄ (3.0 mmol) to aldehyde **2** (210 mg, 0.89 mmol) was purified via flash-column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **5b** (46 mg, 15%) and **6b** (216 mg, 69%), both as yellow oils.

(b) Using AlCl₃

The crude mixture obtained from addition of the corresponding zinc-copper reagent (4.0 mmol) and AlCl₃ (3.0 mmol) to aldehyde **2** (210 mg, 0.89 mmol) was purified via flash-column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **5b** (25 mg, 8%) and **6b** (27 mg, 9%), both as yellow oils.

(4R*,5R*,8S*)-[(5-8-η)-4-Hydroxy-trans-5,trans-7-nonadienenitrile]tricarbonyliron complex (5c)

The crude mixture obtained from addition of the corresponding zinc-copper reagent (4.0 mmol) and BF₃·OEt₂ (3.0 mmol) to aldehyde **2** (200 mg, 0.85 mmol) was purified via flash-column chromatography (silica gel, 1:5 ethyl acetate/hexanes) to give **5c** (96 mg, 38%) and **6c** (22 mg, 9%), both as yellow oils. **5c**: IR (CH₂Cl₂) 3601, 3482, 3052, 2932, 2249, 2047, 1968, 1607, 1441, 1381, 1217, 1113, 1059 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.21 (*dd*, *J* = 8.3, 4.9 Hz, 1 H), 5.09 (*dd*, *J* = 8.8, 4.9 Hz, 1 H), 3.47 (*m*, 1 H), 2.50 (*t*, *J* = 6.8 Hz, 2 H), 2.00 (*m*, 1 H), 1.82 (*m*, 1 H), 1.43 (*d*, *J* = 6.4 Hz, 3 H), 1.27 (*m*, 1 H), 0.85 (*dd*, *J* = 8.3, 7.8 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.5, 119.6, 86.8, 81.7, 72.3, 62.5, 58.9, 33.5, 19.1, 13.8; MS (20 eV) *m/z* (rel intensity) 291 (M⁺, 2), 263 (12), 235 (68), 207 (90), 189 (100), 167 (17), 149 (15), 134 (25), 113 (50), 93 (18); HRMS (EI) *m/z* calcd for C₉H₁₃ONFe (M⁺ - 3CO) 207.0343, found 207.0348.

(4S*,5R*,8S*)-[(5-8-η)-4-Hydroxy-trans-5,trans-7-nonadienenitrile]tricarbonyliron complex (6c)

IR (CH₂Cl₂) 3601, 3405, 3057, 2930, 2247, 2047, 1968, 1616, 1443, 1381, 1287, 1119, 1063 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.13 (*m*, 2 H), 3.54 (*m*, 1 H), 2.51 (*t*, *J* = 6.8 Hz, 2 H), 1.88 (*m*, 2 H), 1.43 (*d*, *J* = 6.3 Hz, 3 H), 1.21 (*m*, 1 H), 0.94 (*dd*, *J* = 8.3, 7.8 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.4, 119.4, 85.8, 80.3, 72.0, 66.0, 58.7, 34.6, 18.9, 13.8; MS (20 eV) *m/z* (rel intensity) 291 (M⁺, 1), 263 (8), 235 (54), 207 (74), 189 (100), 167 (44), 149 (49), 134 (27), 113 (78), 93 (14); HRMS (EI) *m/z* calcd for C₉H₁₃ONFe (M⁺ - 3CO) 207.0343, found 207.0351.

(5R*,6R*,9S*)-[(6-9-η)-5-Hydroxy-trans-6,trans-8-decadienenitrile]tricarbonyliron complex (5d)

The crude mixture obtained from addition of the corre-

sponding zinc-copper reagent (4.0 mmol) and BF₃·OEt₂ (3.0 mmol) to aldehyde **2** (200 mg, 0.85 mmol) was purified via flash-column chromatography (silica gel, 1:5 ethyl acetate/hexanes) to give **5d** (151 mg, 58%) and **6d** (30 mg, 11%), both as yellow oils. **5d**: IR (CH₂Cl₂) 3601, 3488, 3059, 2922, 2250, 2045, 1970, 1441, 1381, 1251, 1113, 1032 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.20 (*dd*, *J* = 8.3, 4.9 Hz, 1 H), 5.07 (*dd*, *J* = 8.8, 4.9 Hz, 1 H), 3.42 (*m*, 1 H), 2.39 (*t*, *J* = 6.8 Hz, 2 H), 1.83 (*m*, 2 H), 1.69 (*m*, 1 H), 1.64 (*m*, 1 H), 1.42 (*d*, *J* = 5.9 Hz, 3 H), 1.25 (*m*, 1 H), 0.91 (*dd*, *J* = 8.3, 7.8 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.7, 119.6, 86.6, 81.9, 73.3, 68.7, 58.7, 37.0, 21.7, 19.0, 16.9; MS (20 eV) *m/z* (rel intensity) 305 (M⁺, 1), 277 (3), 249 (35), 221(25), 203 (100), 200 (24), 134 (70), 125 (29), 79 (16); HRMS (EI) *m/z* calcd for C₁₀H₁₅ONFe (M⁺ - 3CO) 221.0503, found 221.0506.

(5S*,6R*,9S*)-[(6-9-η)-5-Hydroxy-trans-6,trans-8-decadienenitrile]tricarbonyliron complex (6d)

IR (CH₂Cl₂) 3601, 3410, 3048, 2926, 2250, 2043, 1968, 1439, 1381, 1244, 1117, 1032 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.10 (*m*, 2 H), 3.47 (*m*, 1 H), 2.40 (*t*, *J* = 6.8 Hz, 2 H), 1.84 (*m*, 2 H), 1.70 (*m*, 2 H), 1.43 (*t*, *J* = 6.4 Hz, 3 H), 1.21 (*m*, 1 H), 0.99 (*dd*, *J* = 8.3, 7.8 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.7, 119.4, 85.6, 80.5, 73.3, 67.4, 58.6, 38.2, 21.9, 18.9, 17.0; MS (20 eV) *m/z* (rel intensity) 305 (M⁺, 1), 277 (3), 249 (30), 221(20), 203 (100), 200 (20), 134 (58), 125 (23), 79 (13); HRMS (EI) *m/z* calcd for C₁₀H₁₅ONFe (M⁺ - 3CO) 221.0503, found 221.0509.

(4R*,5R*,8S*)-[(5-8-η)-1-Acetoxy-4-hydroxy-trans-5,trans-7-nonadiene]tricarbonyliron complex (5e)

The crude mixture obtained from addition of the corresponding zinc-copper reagent (4.0 mmol) and BF₃·OEt₂ (3.0 mmol) to aldehyde **2** (210 mg, 0.89 mmol) was purified via flash-column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **5e** (223 mg, 74%) and **6e** (30 mg, 10%), both as yellow oils. **5e**: IR (CH₂Cl₂) 3601, 3435, 3049, 2962, 2043, 1964, 1734, 1443, 1383, 1271, 1119, 1040 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.22 (*dd*, *J* = 8.3, 4.9 Hz, 1 H), 5.07 (*dd*, *J* = 8.8, 4.9 Hz, 1 H), 4.10 (*m*, 2 H), 3.43 (*m*, 1 H), 2.05 (*s*, 3 H), 1.94 (*br*, 1 H), 1.80 (*m*, 1 H), 1.76 (*m*, 2 H), 1.59 (*m*, 1 H), 1.42 (*d*, *J* = 6.4 Hz, 3 H), 1.24 (*m*, 1 H), 0.96 (*dd*, *J* = 8.3, 7.8 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.8, 171.3, 86.3, 82.1, 73.2, 64.5, 64.1, 58.2, 34.4, 24.5, 20.7, 18.9; MS (20 eV) *m/z* (rel intensity) 338 (M⁺, 1), 310 (5), 282 (33), 254 (50), 236 (100), 194 (45), 148 (35), 134 (36), 93 (28), 83 (80), 79 (69), 71(5); HRMS (EI) *m/z* calcd for C₁₁H₁₈O₃Fe (M⁺ - 3CO) 254.0605,

found 254.0604.

(4*S,5*R**,8*S**)-[(5-8- η)-1-Acetoxy-4-hydroxy-*trans*-5,*trans*-7-nonadiene]tricarbonyliron complex (6e)**

IR (CH₂Cl₂) 3603, 3437, 3051, 2988, 2043, 1970, 1734, 1443, 1381, 1240, 1171, 1034 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.14 (*dd*, *J* = 8.3, 4.9 Hz, 1 H), 5.07 (*dd*, *J* = 8.8, 4.9 Hz, 1 H), 4.09 (*m*, 2 H), 3.45 (*m*, 1 H), 2.05 (*s*, 3 H), 1.78 (*m*, 2 H), 1.64 (*m*, 2 H), 1.42 (*d*, *J* = 6.4 Hz, 3 H), 1.16 (*m*, 1 H), 1.02 (*dd*, *J* = 8.3, 7.8 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 212.0, 171.1, 85.4, 80.7, 73.5, 68.1, 64.3, 58.3, 36.1, 25.1, 20.9, 19.0; MS (20 eV) *m/z* (rel intensity) 338 (M⁺, 1), 310 (3), 282 (38), 254 (52), 236 (100), 194 (38), 148 (33), 134 (43), 93 (19), 83 (67), 79 (67), 71 (57); HRMS (EI) *m/z* calcd for C₁₂H₁₈O₄Fe (M⁺ - 2CO) 282.0555, found 282.0559.

(2*R,3*R**,6*S**)-[(3-6- η)-2-Hydroxy-1-phenyl-*trans*-3,*trans*-5-heptadiene]tricarbonyliron complex (5f)**

The crude mixture obtained from addition of the corresponding zinc-copper reagent (4.0 mmol) and BF₃·OEt₂ (3.0 mmol) to aldehyde 2 (200 mg, 0.85 mmol) was purified via flash-column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give 5f (236 mg, 85%) and 6f (20 mg, 7%), both as yellow oils. 5f: IR (CH₂Cl₂) 3596, 3455, 3030, 2922, 2045, 1975, 1605, 1495, 1453, 1381, 1238, 1103, 1047, 995, 849 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.19 (*m*, 5 H), 5.19 (*dd*, *J* = 8.3, 5.4 Hz, 1 H), 5.04 (*dd*, *J* = 9.3, 5.4 Hz, 1 H), 3.53 (*m*, 1 H), 3.03 (*dd*, *J* = 13.7, 2.9 Hz, 1 H), 2.64 (*dd*, *J* = 13.7, 9.8 Hz, 1 H), 1.94 (*br*, 1 H), 1.42 (*d*, *J* = 6.4 Hz, 3 H), 1.24 (*m*, 1 H), 0.99 (*dd*, *J* = 8.3, 7.8 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 212.0, 137.9, 129.3, 128.6, 126.7, 86.5, 82.2, 74.9, 63.5, 58.4, 45.1, 19.1; MS (20 eV) *m/z* (rel intensity) 328 (M⁺, 4), 300 (2), 272 (17), 244 (100), 226 (62), 171 (24), 165 (18), 149 (26), 129 (15), 91 (56), 81 (12); HRMS (EI) *m/z* calcd for C₁₃H₁₆OFe (M⁺ - 3CO) 244.0551, found 244.0555.

(2*S,3*R**,6*S**)-[(3-6- η)-2-Hydroxy-1-phenyl-*trans*-3,*trans*-5-heptadiene]tricarbonyliron complex (6f)**

IR (CH₂Cl₂) 3596, 3378, 3030, 2924, 2043, 1968, 1667, 1604, 1495, 1453, 1381, 1246, 1113, 1032, 909, 876, 787 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.16 (*m*, 5 H), 4.96 (*dd*, *J* = 8.3, 4.9 Hz, 1 H), 4.90 (*dd*, *J* = 8.3, 4.9 Hz, 1 H), 3.63 (*m*, 1 H), 2.81 (*d*, *J* = 6.8 Hz, 2 H), 1.55 (*br*, 1 H), 1.37 (*d*, *J* = 6.3 Hz, 3 H), 1.10 (*m*, 1 H), 1.00 (*dd*, *J* = 8.3, 7.8 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 212.2, 137.6, 129.5, 128.8, 126.7, 85.3, 80.8, 74.9, 66.9, 57.9, 46.4, 19.0; MS (20 eV) *m/z* (rel intensity) 328 (M⁺, 2), 300 (2), 272 (15), 244

(76), 226 (39), 171(45), 165 (33), 129 (27), 91 (100), 81 (23); HRMS (EI) *m/z* calcd for C₁₃H₁₆OFe (M⁺ - 3CO) 244.0551, found 244.0547.

(a) Using TiCl₄

The crude mixture obtained from addition of the corresponding zinc-copper reagent (4.0 mmol) and TiCl₄ (3.0 mmol) to aldehyde 2 (200 mg, 0.85 mmol) was purified via flash-column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give 5f (32 mg, 11%) and 6f (225 mg, 81%), both as yellow oils.

(b) Reaction with PhCH₂ZnBr (9)

The crude mixture obtained from addition of the corresponding zinc reagent (4.0 mmol) and BF₃·OEt₂ (3.0 mmol) to aldehyde 2 (200 mg, 0.85 mmol) was purified via flash-column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give 5f (145 mg, 52%) and 6f (10 mg, 4%), both as yellow oils.

(4*R,5*R**,8*S**)-[(5-8- η)-4-Hydroxy-*trans*-5,*trans*-7-nona-1,5,7-triene]tricarbonyliron complex (5g)**

The crude mixture obtained from addition of the corresponding zinc reagent (4.0 mmol) and BF₃·OEt₂ (3.0 mmol) to aldehyde 2 (200 mg, 0.85 mmol) was purified via flash-column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give 5g (128 mg, 54%) and 6g (66 mg, 28%), both as yellow oils. 5g: IR (CH₂Cl₂) 3598, 3081, 2920, 2041, 1971, 1640, 1439, 1381, 1215, 1125, 1032, 924, 878 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.86 (*m*, 1 H), 5.25 (*dd*, *J* = 8.3, 4.9 Hz, 1 H), 5.20 (*dd*, *J* = 16.0, 4.4 Hz, 1 H), 5.17 (*s*, 1 H), 5.07 (*dd*, *J* = 8.8, 4.9 Hz, 1 H), 3.46 (*m*, 1 H), 2.50 (*m*, 1 H), 2.25 (*m*, 1 H), 1.96 (*br*, 1 H), 1.42 (*d*, *J* = 5.9 Hz, 3 H), 1.25 (*m*, 1 H), 0.95 (*dd*, *J* = 8.3, 7.8 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 211.9, 134.0, 118.9, 86.5, 82.2, 72.9, 63.3, 58.3, 43.0, 19.1; MS (20 eV) *m/z* (rel intensity) 278 (M⁺, 1), 250 (19), 222 (59), 194 (82), 176 (77), 148 (29), 135 (100), 121 (17), 105 (18), 97 (24), 91(18), 79 (25), 77 (11); HRMS (EI) *m/z* calcd for C₉H₁₄OFe (M⁺ - 3CO) 194.0394, found 194.0399.

(4*S,5*R**,8*S**)-[(5-8- η)-4-Hydroxy-*trans*-5,*trans*-7-nona-1,5,7-triene]tricarbonyliron complex (6g)**

IR (CH₂Cl₂) 3599, 3055, 2919, 2041, 1952, 1640, 1439, 1381, 1277, 1213, 1122, 1032, 925, 868 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.81 (*m*, 1 H), 5.14 (*m*, 3 H), 5.05 (*dd*, *J* = 8.8, 4.9 Hz, 1 H), 3.53 (*m*, 1 H), 2.31 (*m*, 2 H), 1.69 (*br*, 1 H), 1.41 (*d*, *J* = 6.3 Hz, 3 H), 1.13 (*m*, 1 H), 1.01 (*dd*, *J* = 8.8, 7.3 Hz, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 212.0, 134.1, 118.5, 85.3, 80.6, 72.7, 67.2, 57.8, 44.4, 19.0; MS (20 eV) *m/z* (rel intensity) 278 (M⁺, 1), 250 (26), 222 (71), 194

(100), 176 (98), 148 (39), 135 (46), 121 (48), 105 (34), 97 (58), 91(47), 79 (60), 77 (29); HRMS (EI) m/z calcd for C₆H₁₄OFe (M⁺ - 3CO) 194.0394, found 194.0399.

Reaction of Aldehyde 2 with PhCH₂Cu(CN)ZnBr (7f) without Lewis Acid

The crude mixture obtained from addition of the corresponding zinc-copper reagent (4.0 mmol) to aldehyde 2 (230 mg, 1.0 mmol) was purified via flash-column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give 5f (155 mg, 47%) and 6f (42 mg, 13%), both as yellow oils.

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Key Words

Diastereoselective alkylation; (Diene-aldehyde)Fe(CO)₃ complex; Functionalized zinc-copper reagents; Diastereomeric ratio.

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