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Excellent Chiral Introduction by Diene Iron-Tricarbonyl Moiety. II[1]: A Formal Synthesis of (+)- and (−)-Frontalin Using a Diastereoselective 1,2-Nucleophilic Addition of Organometallics into a (*Z*)-Dienone $Fe(CO)_3$ Complex

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A nucleophilic addition of alkyllithiums to the (*Z*)-dienone iron-tricarbonyl [$Fe(CO)_3$] complex (3) gave the (*Z*)-dienol complex (4) exclusively, while the reaction of 3 with alkylmagnesium bromide or trialkylaluminum provided the (*E*)-dienol complex (2) *via* the isomerization of 3 to the (*E*)-dienone complex (1). Application of this methodology was demonstrated in a formal synthesis of both (+)- and (−)-frontalin from the same chiral starting material, {(2*S*,5*S*)-(2*E*,4*Z*)-tricarbonyl[2-5-*η*-11-chloro-2,4-undecadien-6-one]iron} (8).

Key words 1,2-nucleophilic addition; *Z*-dienone iron-tricarbonyl complex; organometallic; olefin isomerization; frontalin; formal synthesis

Much attention has been focused on the highly stereocontrolled addition of organometallics to acyclic ketones bearing a chiral auxiliary.[2] Several groups have attained such diastereoselective nucleophilic additions to chiral open-chain α-ketoaldehyde derivatives, such as α-keto-1,3-oxathiane,[3] α-ketoaminal[4] and α-ketoacetal,[5] by taking advantage of chiral aldehyde equivalents; furthermore, the reactions have been successfully applied to asymmetric syntheses of natural products such as frontalin,[3d,4c] malyngolide,[4d] and mevalolactone[3c,5b] (Fig. 1). There still remains, however, the important problem of how to obtain all possible diastereomers in a highly stereoselective manner from the same starting materials, which would be extremely useful in organic synthesis.[6] Thus far, little methodology has been developed for obtaining different stereoisomers in regard to nucleophilic addition to chiral ketones.[7] By simply changing the metal species of nucleophiles, Fujisawa and Utimoto succeeded in reversing the diastereoselectivity of the organometallic addition to the chiral 2-acyl-oxazolidine[7d] and 2- acyl-1,3-oxathianes,[7a] independently.

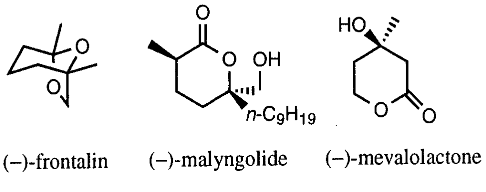

Fig. 1

In order to attain this goal by a different methodology, we were interested in the diastereoselective nucleophilic addition of a dienone iron complex with organometallics. Acyclic and functionalized diene-iron tricarbonyl complexes have been proven to be valuable intermediates in organic synthesis due to the highly efficient protecting and stereodirecting properties of the $Fe(CO)_3$ moiety.[8] Concerning the 1,2-asymmetric induction using $Fe(CO)_3$ chirality, Neumann has reported that the reaction of *E*-dienone complexes (**1**) with alkyllithiums resulted in the exclusive formation of an alcohol complex (**2**).[9] However, there have been few reports on the stereoselective nucleophilic addition of *Z*-dienone iron complex (**3**),[10] which isomerizes easily to the *E*-dienone complex (**1**) in the presence of an acid and base.[11]

If the nucleophilic addition of a *Z*-dienone iron complex (**3**) would give a tertiary alcohol (**4**) stereoselectively, we could obtain the antipodal alcohol of **2**, which is obtained from **1**. This means that both enantiomers (A and B) of the tertiary alcohols can be synthesized from the same starting materials (**3**) (Chart 1). Then, that situation stimulated us to investigate the following subjects: (i) the nucleophilic addition of **3** to give **4**, and (ii) the possibility

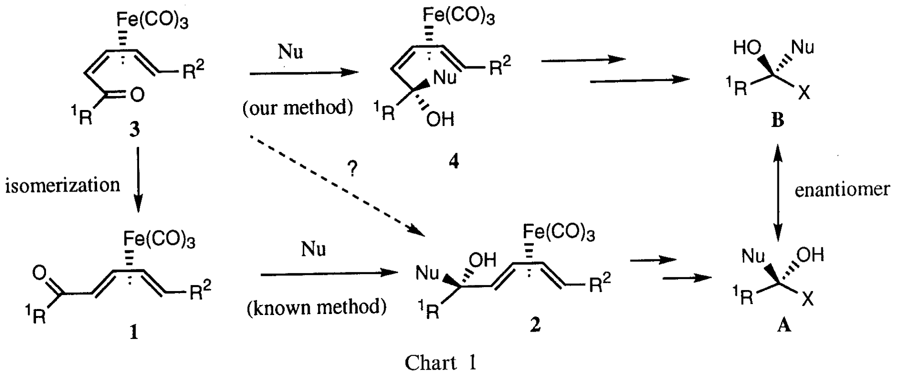

Chart 1

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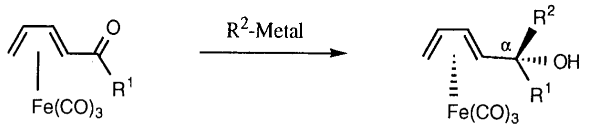
of a one-pot transformation of **3** to **2** *via* **1**. Herein, we report the novel reactions of **3** which afford different diastereomers (**2** and **4**) depending on the organometallics employed, along with a formal synthesis of (+)- and (−)- frontalin.[12]

Results and Discussion

The *E*- and *Z*-dienone complexes (**1a, b** and **3a, b**) were prepared by the known method.[13] First, we examined the nucleophilic addition to the racemic (*E*)-dienone complexes (**1a, b**) with several organometallics other than alkyllithiums (Table 1). All reactions of **1a** with Grignard reagents, triethylaluminum (Et_3Al), and diallylcuprate reagent afforded tertiary alcohol complexes (**2a**—**d**) in 69—87% yields as a single diastereomer, respectively (entries 5—9). These products (**2a**—**d**) were identical with the single ones observed with organolithiums reported by Neumann[9] (entries 1—4). Unfortunately, since we could not succeed in reversing diastereoselectivity by changing the metal species of the nucleophiles, we synthesized the diastereomer (**2d**) of **2a** by the reaction of **1b** with MeLi to determine the precise diastereomeric ratio of the addition products (**2a** and **2d**). Their ^{1}H-NMR spectra [Cα-methyl proton of **2a** and **2d** (for **2a**: δ 1.35; for **2d**: δ 1.30)] revealed that the diastereomeric purity of **2a** and **2d** was very high, respectively. Similarly, the purity of **2b** and **2c** was also determined by 500 MHz ^{1}H-NMR. The stereochemistries of **2a**—**d** were estimated by reference to Franck-Neumann's report.[9]

We next investigated the reactivity of **3a, b** with the above mentioned organometals. The representative results are shown in Table 2, from which the unique characters of **3a, b** compared with **1a, b** were revealed, in addition to the high stereoselectivity observed in all of the entries.

Table 1. Diastereoselective Addition of Organometallic Reagents to *E*-Dienone Complex (**1**)



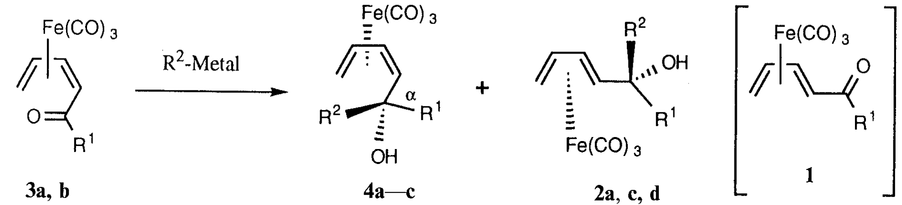
1a, b
a: R^1 = Me
b: R^1 = *n*-Bu

2a—**d**
a: R^1 = Me, R^2 = *n*-Bu; **b**: R^1 = Me, R^2 = allyl;
c: R^1 = Me, R^2 = Et; **d**: R^1 = *n*-Bu, R^2 = Me

Entry	Substrate	R^2-Metal	Product	Yield (%)	de (%)
1[a]	**1a**	*n*-BuLi	**2a**	78	100
2[b]	**1a**	EtLi	**2c**	64	100
3[a]	**1a**	(allyl)Li	**2b**	63	100
4[a]	**1b**	MeLi	**2d**	98	100
5[a]	**1a**	*n*-BuMgBr	**2a**	76	100
6[a]	**1a**	(allyl)MgBr	**2b**	69	100
7[a]	**1b**	MeMgBr	**2d**	85	100
8[c]	**1a**	Et_3Al	**2c**	73	100
9[a]	**1a**	$(allyl)_2CuMgBr \cdot BF_3$	**2b**	87	100

a) The reactions were carried out in tetrahydrofuran (THF) at −78 °C. *b*) The reaction was carried out in toluene at −78 °C. *c*) The reaction was carried out in benzene at room temperature.

Table 2. Diastereoselective Addition of Organometallic Reagents to *Z*-Dienone Complex (**3**)



3a, b
3a: R^1 = Me
3b: R^1 = *n*-Bu

4a—**c**
4a: R^1 = Me, R^2 = *n*-Bu
4b: R^1 = Me, R^2 = allyl
4c: R^1 = *n*-Bu, R^2 = Me

2a, c, d
2a: R^1 = Me, R^2 = *n*-Bu
2c: R^1 = Me, R^2 = Et
2d: R^1 = *n*-Bu, R^2 = Me

Entry	Substrate	R^2-Metal	Product	Yield (%) (**4**:**2**)	de (%)
1[a]	**3a**	*n*-BuLi	**4a**	51: 0	100
2[a]	**3a**	(allyl)MgBr	**4b**	53: 0	100
3[a]	**3a**	$(allyl)_2CuMgBr \cdot BF_3$	**4b**	63: 0	100
4[a]	**3b**	MeLi	**4c**	96: 0	100
5[b]	**3a**	Et_3Al	**2c**	0:81	100
6[a]	**3a**	*n*-BuMgBr	**2a**	0:97	100
7[a]	**3b**	MeMgBr	**2d**	0:89	100

a) The reactions were carried out in THF at −78 °C. *b*) The reaction was carried out in benzene at room temperature.

Namely, the addition of organolithium and (allyl)$_2$Cu-MgBr·BF$_3$ into **3a, b** occurred very quickly to give normal addition products (**4a**—**c**)$^{14)}$ as a sole product, respectively (entries 1, 3 and 4). However, similar treatment of **3a** with Et$_3$Al produced **2c**, which was obtained by the reaction of **1a** with Et$_3$Al, as a single product (entry 5). Furthermore, in the cases of Grignard reagents (entries 2, 6 and 7), the related reactions gave unpredictable results; that is, either **2a, d** or **4b** was obtained stereoselectively according to the difference of nucleophiles (R^2) of the reagents. Such an abnormal outcome may be attributed to the Lewis acidity of the organometallic reagents, which promotes an initial Z to E isomerization of the starting materials (**3a, b**). In practice, treatment of the Z-dienone complex (**3b**) with Me$_3$Al in benzene at room temperature gave rise to the E-dienone complex (**1b**) in 68% yield as a sole product.$^{15)}$ The diastereomeric ratio of the addition products (**4a** and **4c**) was determined by ^{1}H-NMR [Cα-methyl proton of **4a** and **4c** (for **4a**: δ 1.32; for **4c**: δ 1.09)] in the same manner as **2a** and **2d**. The purity of **4b** and **2c** was also determined by 500 MHz ^{1}H-NMR.

In order to determine the relative configurations of the resultant tertiary alcohols, we planned the asymmetric syntheses of (+)- and (−)-frontalin starting from a chiral diene Fe(CO)$_3$ complex.

Frontalin$^{16)}$ is known to be an aggregation pheromone of the southern pine beetle, *Dendorctonus frontalis*, and of the western pine bark beetle, *Dendroctonus brevicomis*. Several enantioselective syntheses of frontalin have been reported (sharpless asymmetric epoxidation of allylic alcohol,$^{17)}$ Baker's yeast mediated transformation,$^{18)}$ and the use of a chiral auxiliary$^{3d,4c,19)}$). Although frontalin contains two asymmetric centers, only the stereochemistry of C1 needs to be specifically addressed in the planning stage of the frontalin synthesis, since the correct configuration of C5 is dictated by that of C1 during the formation of the bicyclic ketal system. Thus, 2-methyl-6-heptene-1,2-diol (**5**) was reported to be an excellent building block for the synthesis of frontalin.$^{17c,e,18c,e)}$ A retrosynthetic analysis was illustrated in Chart 2. In turn, (R)- and (S)-**5** can be obtained from chiral tertiary alcohols (**6** and **7**) by oxidative decomplexation and cleavage of a carbon-carbon double bond, respectively. As described above, the stereoselective 1,2-nucleophilic addition of a methyl group onto **8** would provide both desired products (**6** and **7**) in a highly stereoselective manner by switching the organometallic reagent as a nucleophile.

For this purpose, a chiral Z-dienone complex (**8**) was prepared from a known chiral pentadiene iron tricarbonyl complex (**9**)$^{20)}$ by the Friedel–Crafts reaction. As expected, the diastereoselective addition of CH$_3$Li to **8** yielded the desired Z-tertiary alcohol complex (**6**) in 86% yield. The optically active tertiary dienol (**10**) was accessible from **6** in 98% yield by decomplexation with ammonium cerium-(IV) nitrate (CAN). Sequential ozonolysis and hydride-reduction of **10** gave (R)-**11** in 79% yield, which was followed by elimination with potassium *tert*-butoxide (^{t}BuOK) in dimethyl sulfoxide (DMSO)$^{21)}$ to afford the desired product [(R)-**5**] (Chart 3). The specific rotation of (R)-**5**, $[\alpha]_D^{25}$ +2.38° (c=0.405, CHCl$_3$) [lit. $[\alpha]_D^{25}$ −2.6° (c=1.4, CHCl$_3$) for (S)-**5**$^{18c)}$], confirms our assignment (R) of absolute configuration at C2 in (R)-5. Therefore,

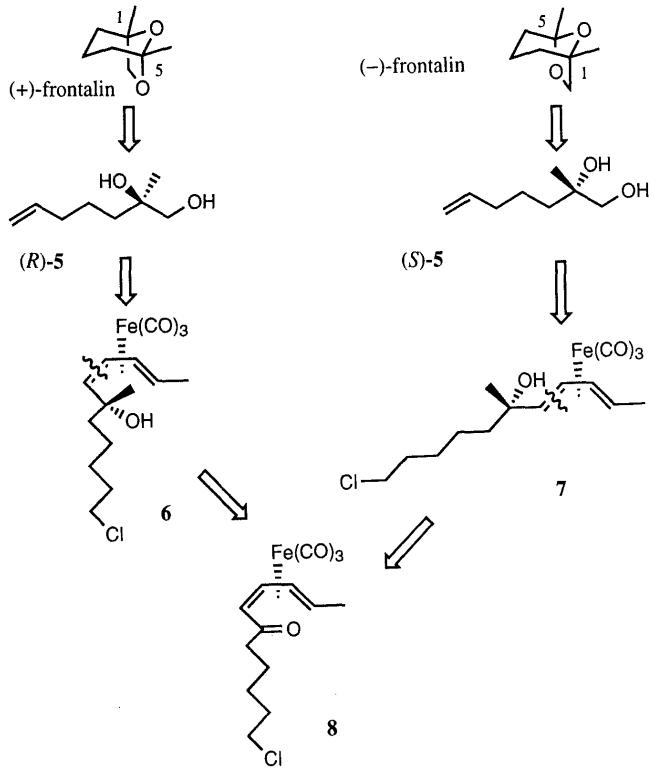


Chart 2

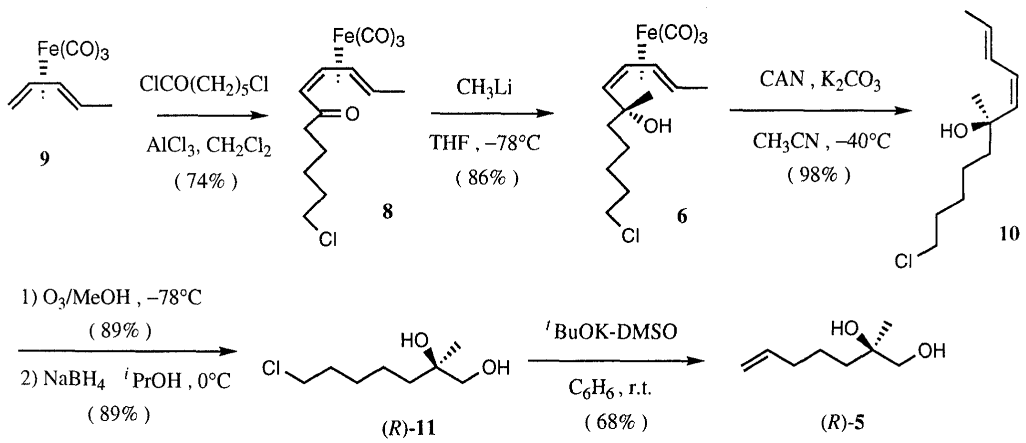


Chart 3

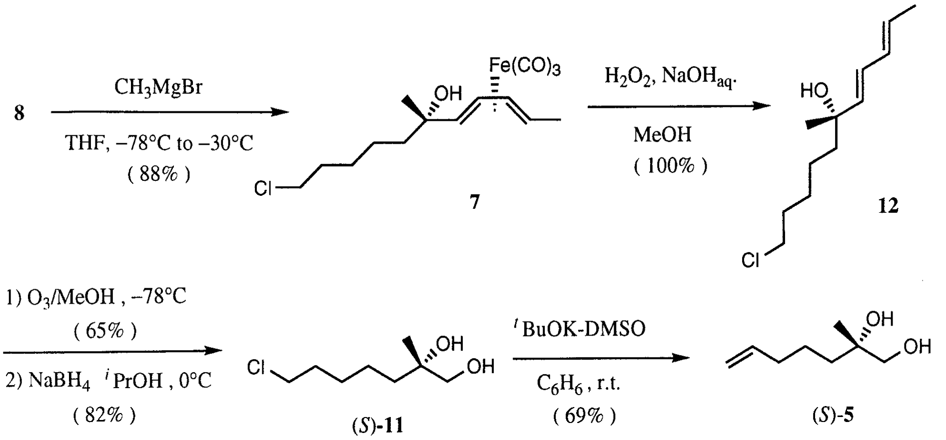


Chart 4

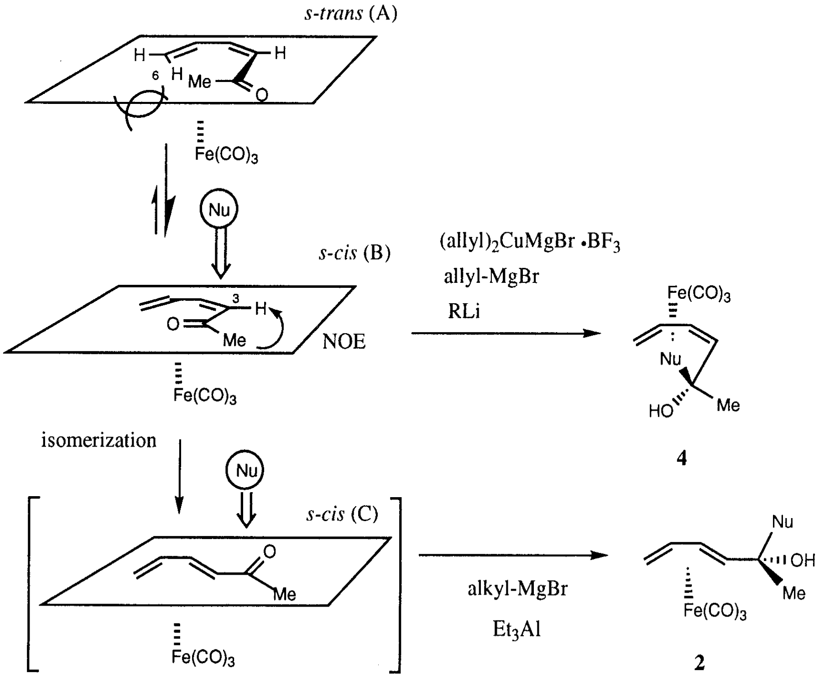


Fig. 2. Reaction Mechanism of Organometallic Addition to *E*- and *Z*-Dienone Complexes

the stereochemistries of **4a**—**c** were determined as shown in Table 2.

An *E*-tertiary alcohol complex (**7**) was obtained by the diastereoselective reaction of **8** with CH_3MgBr in 88% yield. Unfortunately, decomplexation of **7** with CAN gave the optical active tertiary dienol (**12**) only in low yield, whereas the reaction of **7** with H_2O_2 in MeOH[22] increase the yield of **12** to 100%. Similarly, ozonolysis and reduction of **12** with $NaBH_4$ gave (*S*)-**11**, which was followed by elimination with ^{t}BuOK in DMSO to afford the desired product [(*S*)-**5**] (Chart 4). The specific rotation of (*S*)-**5**, $[\alpha]_D^{24}$ $-2.55°$ ($c=0.185$, $CHCl_3$) [lit. $[\alpha]_D^{25}$ $-2.6°$ ($c=1.4$, $CHCl_3$) for (*S*)-**5**[18c]], confirms our assignment (*S*) of absolute configuration at C2 in (*S*)-**5**. Therefore, the stereochemistries of **2a**—**d** were determined as shown in Tables 1, 2. Herein, we have achieved a formal synthesis of (+)- and (−)-frontalin from a sole chiral *Z*-dienone complex (**8**), by which we could determine the relative configuration of the nucleophilic addition adducts (**2** and **4**).

Such high diastereoselectivity could be explained as follows (Fig. 2). From the nuclear Overhauser effect (NOE) enhancement between C3-H and Me, the *s-cis* conformer (B) would be more stable than the *s-trans* one (A) due to severe steric hindrance between C6-H and Me in the latter case. Therefore, when the non-Lewis acidic and strong nucleophiles, such as allylmagnesium bromide and diallylcuprate, are employed, nucleophiles attack from the opposite side of the bulky tricarbonyl iron unit in the *s-cis* conformer (B) to yield **4** stereoselectively. On the other hand, when the Lewis acidic and weak nucleophiles such as alkylmagnesium reagents and Et_3Al are used, isomerization of the *Z*-dienone complex (**3**) to the *E*-dienone complex (**1**) occurs, and then nucleophiles similarly attack from the opposite side of the bulky tricarbonyl iron unit in the more stable *s-cis* conformer (C) to yield **2** stereoselectively.

In conclusion, we have succeeded in synthesizing both diastereomers (**2** and **4**) of the tertiary alcohols from the *Z*-dienone complex (**3**) with perfect stereoselectivity by simply changing organometallic reagents. Furthermore, this method has been applied to the synthesis of both enantiomers of frontalin from the sole chiral *Z*-dienone complex (**8**).

Experimental

Measurements of optical rotations were carried out using a JASCO DIP-360 digital polarimeter. IR spectral measurements were performed with a Hitachi 260-10 IR spectrometer as a $CHCl_3$ solution of the sample, or a Horiba FT-210 IR spectrometer as a neat sample on KBr by the diffuse reflection measurement method. ^{1}H-NMR spectra were measured with a JEOL JNM-GX500 spectrometer (500 MHz). ^{13}C-NMR spectra were measured with a JEOL JNM-EX270 spectrometer (67.8 MHz). All signals are expressed as ppm downfield from tetramethylsilane, used as an internal standard (δ value). The following abbreviations are used: singlet (s), doublet (d), triplet (t), multiplet (m), broad (br). Mass spectra (MS) were taken with a Shimadzu QP-1000 GCMS spectrometer, and high-resolution mass spectra (HRMS) and chemical ionization mass spectra (CIMS) were measured with a JEOL JMS-D300 mass spectrometer. Unless otherwise noted, all reactions were performed using anhydrous solvents. Merck Kieselgel 60 was used as an adsorbent for column chromatography. All extracts were dried over anhydrous $MgSO_4$.

(*Z*)-Tricarbonyl[1-4-*η*-1,3-nonadien-5-one]iron (3b) Valeryl chloride (97.3 μl, 0.820 mmol) was added to a suspension of $AlCl_3$ (109 mg, 0.820 mmol) in CH_2Cl_2 (1.5 ml) at 0 °C for 20 min. A solution of tricarbonyl[1-4-*η*-butadiene]iron[23] (145 mg, 0.745 mmol) in CH_2Cl_2 (0.5 ml) was added to the mixture at room temperature. The mixture was stirred at room temperature for 10 min. The reaction was quenched with a saturated NH_3 solution. The resulting mixture was extracted with $CHCl_3$. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 10 : 1) to give **3b** (148 mg, 72%) as a yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 0.90 (t, 3H, J = 7.5 Hz, C9-H), 1.30 (m, 2H), 1.39 (dd, 1H, J = 1.7, 9.8 Hz, C1-H_c), 1.51 (m, 2H), 2.22 (dd, 1H, J = 1.7, 7.7 Hz, C1-H_t), 2.39 (m, 2H, C6-H), 3.14 (d, 1H, J = 6.4 Hz, C4-H), 5.38 (dd, 1H, J = 5.6, 6.4 Hz, C3-H), 5.54 (ddd, 1H, J = 5.6, 7.7, 9.8 Hz, C2-H). ^{13}C-NMR ($CDCl_3$) δ: 13.8 (C9), 22.4 (C8), 27.0 (C7), 42.1 (C6), 45.3 (C1), 56.2 (C4), 85.6 (C3), 93.5 (C2), 205.1 (C5), 209.3 (CO). IR (KBr): 2962, 2060 (CO), 1988 (CO), 1668 (C=O) cm^{-1}. MS *m*/*z* (%): 278 (M^+, 0.9), 250 (12), 222 (40), 194 (100). HRMS Calcd for $C_{12}H_{14}FeO_4$: 278.0241. Found: 278.0241.

(*E*)-Tricarbonyl[1-4-*η*-1,3-nonadien-5-one]iron (1b) Sodium methoxide (237 mg, 4.39 mmol) was added to a solution of **3b** (203 mg, 0.732 mmol) in MeOH (8 ml) at 0 °C. The mixture was allowed to warm to room temperature. The mixture was stirred at room temperature for 7 h, and then the reaction was quenched with water. The resulting mixture was extracted with Et_2O. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 10 : 1) to give **1b** (186 mg, 91%) as a yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 0.69 (dd, 1H, J = 1.5, 9.4 Hz, C1-H_c), 0.92 (t, 3H, J = 7.3 Hz, C9-H), 1.24 (d, 1H, J = 8.1 Hz, C4-H), 1.33 and 1.58 (m, each 2H, C7-H and C8-H), 2.01 (dd, 1H, J = 1.5, 6.8 Hz, C1-H_t), 2.39 (m, 2H, C6-H), 5.44 (ddd, 1H, J = 4.7, 6.8, 9.4 Hz, C2-H), 5.98 (dd, 1H, J = 4.7, 8.1 Hz, C3-H). ^{13}C-NMR ($CDCl_3$) δ: 13.7 (C9), 22.3 (C8), 26.6 (C7), 41.1 (C1), 42.3 (C6), 54.3 (C4), 84.9 (C2), 85.9 (C3), 205.4 (C5), 209.4 (CO). IR (KBr): 2960, 2058 (CO), 1988 (CO), 1676 (C=O) cm^{-1}. MS *m*/*z* (%): 278 (M^+, 5.5), 250 (14), 222 (36), 194 (100). HRMS Calcd for $C_{12}H_{14}FeO_4$: 278.0241. Found: 278.0241.

(4*RS*,5*RS*)-(*E*)-Tricarbonyl[1-4-*η*-5-methyl-1,3-nonadien-5-ol]iron (2a) Experimental procedure for entries 1 and 5 of Table 1 and entry 6 of Table 2 will be described.

a) Table 1, entry 1: A solution of *n*-butyllithium (0.230 ml, 1.6 M) in *n*-hexane was added to a solution of **1a** (17.5 mg, 0.0742 mmol) in THF (1 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred for 10 min at −78 °C, and then the reaction was quenched with saturated NH_4Cl solution. The resulting mixture was extracted with AcOEt. The extract was washed with saturated NH_4Cl solution, water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 20 : 1) to give **2a** (16.9 mg, 78%)

b) Table 1, entry 5: A solution of *n*-butylmagnesium bromide (0.760 ml, 0.90 M) in THF was added to a solution of **1a** (32.3 mg, 0.137 mmol) in THF (1 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 15 min, and then the reaction was quenched with water. The resulting mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 10 : 1) to give **2a** (30.7 mg, 76%).

c) Table 2, entry 6: A solution of *n*-butylmagnesium bromide (0.590 ml, 0.90 M) in THF was added to a solution of **3a** (25.0 mg, 0.106 mmol) in THF (1 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 15 min, and then the reaction was quenched with water. The resulting mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 10 : 1) to give **2a** (30.1 mg, 97%) as a yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 0.19 (dd, 1H, J = 2.4, 9.2 Hz, C1-H_c), 0.90 (t, 3H, J = 7.1 Hz, C9-H), 1.07 (d, 1H, J = 9.0 Hz, C4-H), 1.12 (s, 1H, O$\underline{H}$), 1.26—1.36 (m, 4H), 1.35 (s, 3H, C5-$\underline{Me}$), 1.50—1.57 (m, 2H), 1.70 (dd, 1H, J = 2.4, 6.4 Hz, C1-H_t), 5.23 (ddd, 1H, J = 5.1, 6.4, 9.2 Hz, C2-H), 5.50 (dd, 1H, J = 5.1, 9.0 Hz, C3-H). ^{13}C-NMR ($CDCl_3$) δ: 14.0 (C9), 23.0 (C8), 26.3 (C7), 31.9 (C5-$\underline{Me}$), 39.2 (C6), 45.1 (C1), 72.8 (C5), 75.4 (C4), 79.4 (C2), 84.3 (C3), 212.2 (CO). IR (KBr): 3624 (OH), 2960, 2864, 2044 (CO), 1975 (CO), 1468, 1375 cm^{-1}. MS *m*/*z* (%): 294 (M^+, 5.0), 210 (44), 192 (100), 136 (33), 79 (96). HRMS Calcd for $C_{13}H_{18}FeO_4$: 294.0552. Found: 294.0552.

(4*RS*,5*RS*)-(*E*)-Tricarbonyl[5-8-*η*-4-methyl-1,5,7-octatrien-4-ol]iron (2b) Experimental procedure for entries 3, 6 and 9 of Table 1 will be described.

a) Table 1, entry 3: A solution of *n*-butyllithium (0.230 ml, 1.70 M) in *n*-hexane was added to a solution of allyltributyltin (127 mg, 0.384 mmol) in THF (1 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 30 min, and then a solution of **1a** (30.1 mg, 0.128 mmol) was added to the mixture at −78 °C. The mixture was stirred for 20 min at −78 °C, and then the reaction was quenched with water. The resulting mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 20 : 1) to give **2b** (22.3 mg, 63%).

b) Table 1, entry 6: A solution of allylmagnesium bromide (0.170 ml, 1.0 M) in THF was added to a solution of **1a** (33.4 mg, 0.142 mmol) in THF (1 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 15 min, and then the reaction was quenched with water. The resulting mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 15 : 1) to give **2b** (27.1 mg, 69%).

c) Table 1, entry 9: A solution of allylmagnesium bromide (0.840 ml, 1.0 M) in Et_2O was added to a suspension of CuI (80.2 mg, 0.421 mmol) in THF (1.5 ml) at −30 °C under a nitrogen atmosphere. The mixture was stirred at −30 °C for 20 min. The mixture was allowed to cool to −78 °C. $BF_3 \cdot Et_2O$ (52.0 μl, 0.423 mmol) was added to the mixture at −78 °C. The mixture was stirred at −78 °C for 10 min. A solution of **1a** (33.1 mg, 0.144 mmol) in THF (0.5 ml) was added to the mixture at −78 °C. The mixture was stirred at −78 °C for 30 min, and then the reaction was quenched with 10% NaOH solution. The resulting mixture was extracted with AcOEt. The extract was washed with water, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 15 : 1) to give **2b** (34.0 mg, 87%) as a yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 0.18 (dd, 1H, J = 2.6, 9.4 Hz, C8-H_c), 1.05 (d, 1H, J = 9.0 Hz, C5-H), 1.35 (s, 3H, C4-$\underline{Me}$), 1.46 (s, 1H, O$\underline{H}$), 1.70 (dd, 1H, J = 2.6, 6.8 Hz, C8-H_t), 2.31 (d, 2H, J = 7.7 Hz, C3-H), 5.11 (d, 1H, J = 17.1 Hz, C1-H_a), 5.19 (d, 1H, J = 10.3 Hz, C1-H_b), 5.23 (ddd, 1H, J = 5.8, 6.8, 9.4 Hz, C7-H), 5.45 (dd, 1H, J = 5.8, 9.0 Hz, C6-H), 5.86 (tdd, 1H, J = 7.7, 10.3, 17.1 Hz, C2-H). ^{13}C-NMR ($CDCl_3$) δ: 31.3 (C4-$\underline{Me}$), 39.2 (C3), 49.6 (C8), 72.0 (C4), 74.6 (C5), 79.7 (C7), 84.1 (C6), 119.6 (C1), 133.4 (C2), 211.9 (CO). IR ($CHCl_3$): 3600 (OH), 2900—3020, 2050 (CO), 1990 (CO), 1250 cm^{-1}. MS *m*/*z* (%) : 278 (M^+, 1.0), 250 (9), 222 (25), 194 (33), 120 (61), 105 (96), 91 (100). HRMS Calcd for $C_{12}H_{14}FeO_4$: 278.0242. Found: 278.0249.

(3*RS*,4*RS*)-(*E*)-Tricarbonyl[4-7-*η*-3-methyl-4,6-heptadien-3-ol]iron (2c) Experimental procedure for entries 2 and 8 of Table 1 and entry 5 of Table 2 will be described.

a) Table 1, entry 2: A solution of ethyllithium (1.20 ml, 0.52 M) in Et_2O was added to a solution of **1a** (29.0 mg, 0.120 mmol) in toluene (2 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 10 min, and then the reaction was quenched with saturated

NH$_4$Cl solution. The resulting mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 10 : 1) to give **2c** (20.5 mg, 64%).

b) Table 1, entry 8: A solution of triethylaluminum (0.460 ml, 0.91 M) in *n*-hexane was added to a solution of **1a** (32.9 mg, 0.139 mmol) in benzene (2 ml) at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 1 h, and then the reaction was quenched with saturated NH$_4$Cl solution. The resulting mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 10 : 1) to give **2c** (19.9 mg, 73%).

c) Table 2, entry 5: A solution of triethylaluminum (0.410 ml, 0.91 M) in *n*-hexane was added to a solution of **3a** (17.6 mg, 0.0746 mmol) in benzene (1 ml) at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 4 h, and then the reaction was quenched with saturated NH$_4$Cl solution. The resulting mixture was extracted with AcOEt. The extract was washed with saturated NH$_4$Cl solution, water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 15 : 1) to give **2c** (16.2 mg, 81%) as a yellow oil. ^{1}H-NMR (CDCl$_3$) δ: 0.18 (dd, 1H, J = 2.6, 9.4 Hz, C7-H$_c$), 0.93 (dd, 3H, J = 7.3, 7.3 Hz, C1-H), 1.05 (d, 1H, J = 8.6 Hz, C4-H), 1.35 (s, 3H, C3-Me), 1.55 (qd, 1H, J = 7.3, 13.7 Hz, C2-H$_a$), 1.60 (qd, 1H, J = 7.3, 13.7 Hz, C2-H$_b$), 1.70 (dd, 1H, J = 2.6, 6.8 Hz, C7-H$_t$), 5.23 (ddd, 1H, J = 5.1, 6.8, 9.4 Hz, C6-H), 5.50 (dd, 1H, J = 5.1, 8.6 Hz, C5-H). ^{13}C-NMR (CDCl$_3$) δ: 8.5 (C1), 31.5 (C3-Me), 37.8 (C2), 39.2 (C7), 72.9 (C3), 74.9 (C4), 79.4 (C6), 84.4 (C5), 212.2 (CO). IR (CHCl$_3$): 3600 (OH), 2980—3100, 2050 (CO), 1980 (CO) cm^{-1}. MS *m/z* (%): 266 (M$^+$, 11), 238 (31), 210 (31), 182 (37), 164 (100), 93 (59), 79 (90). *Anal.* Calcd for C$_{11}$H$_{14}$FeO$_4$: C, 49.65; H, 5.30 Found: C, 49.83; H, 5.38.

(4*RS*,5*SR*)-(*E*)-Tricarbonyl[1-4-η-5-methyl-1,3-nonadien-5-ol]iron (2d) The experimental procedure for entries 4 and 7 of Table 1 and entry 7 of Table 2 will be described.

a) Table 1, entry 4: A solution of methyllithium (0.250 ml, 1.0 M) in Et$_2$O was added to a solution of **1b** (24.4 mg, 0.0878 mmol) in THF (1 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 20 min, and then allowed to warm to −30 °C. The mixture was stirred at −30 °C for 30 min, and then the reaction was quenched with water. The resulting mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 10 : 1) to give **2d** (25.3 mg, 98%).

b) Table 1, entry 7: A solution of methylmagnesium bromide (0.350 ml, 0.90 M) in THF was added to a solution of **1b** (29.4 mg, 0.106 mmol) in THF (1 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 30 min, and then the reaction was quenched with water. The resulting mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 10 : 1) to give **2d** (26.4 mg, 85%).

c) Table 2, entry 7: A solution of methylmagnesium bromide (0.216 ml, 0.96 M) in THF was added to a solution of **3b** (23.1 mg, 0.0831 mmol) in THF (1 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 15 min, and then allowed to warm to −30 °C. The mixture was stirred at −30 °C for 30 min, and then the reaction was quenched with saturated NH$_4$Cl solution. The resulting mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 10 : 1) to give **2d** (21.7 mg, 89%), as a yellow oil. ^{1}H-NMR (CDCl$_3$) δ: 0.20 (dd, 1H, J = 1.4, 9.2 Hz, C1-H$_c$), 0.94 (t, 3H, J = 6.8 Hz, C9-H), 1.16 (d, 1H, J = 9.0 Hz, C4-H), 1.30 (s, 3H, C5-Me), 1.36 (m, 4H), 1.63 (m, 3H), 1.70 (dd, 1H, J = 1.4, 5.8 Hz, C1-H$_t$), 5.24 (ddd, 1H, J = 5.1, 5.8, 9.2 Hz, C2-H), 5.54 (dd, 1H, J = 5.1, 9.0 Hz, C3-H). ^{13}C-NMR (CDCl$_3$) δ: 14.0 (C9), 23.1 (C8), 26.4 (C7), 29.6 (C5-Me), 39.2 (C6), 46.0 (C1), 73.0 (C5), 76.0 (C4), 79.9 (C2), 84.0 (C3), 212.2 (CO). IR (CHCl$_3$): 3620 (OH), 2900—3000, 2050 (CO), 1980 (CO) cm^{-1}. MS *m/z* (%): 294 (M$^+$, 3.0), 276 (4.0), 266 (18), 238 (23), 210 (33), 192 (100). HRMS Calcd for C$_{13}$H$_{18}$FeO$_4$: 294.0555. Found: 294.0556.

(4*RS*,5*RS*)-(*Z*)-Tricarbonyl[1-4-η-5-methyl-1,3-nonadien-5-ol]iron (4a) A solution of *n*-butyllithium (0.100 ml, 1.6 M) in *n*-hexane was added to a solution of **3a** (25.7 mg, 0.109 mmol) in THF (1 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 5 min, and then the reaction was quenched with saturated NH$_4$Cl solution. The resulting mixture was extracted with AcOEt. The extract was washed with saturated NH$_4$Cl solution, water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 20 : 1) to give **4a** (16.5 mg, 51%) as a yellow oil. ^{1}H-NMR (CDCl$_3$) δ: 0.90 (t, 3H, J = 6.8 Hz, C9-H), 1.22—1.43 (m, 7H), 1.32 (s, 3H, C5-Me), 1.91 (d, 1H, J = 7.7 Hz, C1-H$_t$), 2.63 (d, 1H, J = 8.5 Hz, C4-H), 2.93 (d, 1H, J = 9.8 Hz, C1-H$_c$), 5.19 (dd, 1H, J = 5.0, 8.5 Hz, C3-H), 5.58 (ddd, 1H, J = 5.0, 7.7, 9.8 Hz, C2-H). ^{13}C-NMR (CDCl$_3$) δ: 14.1 (C9), 23.0 (C8), 26.6 (C7), 31.2 (C5-Me), 43.0 (C1), 47.9 (C6), 69.9 (C4), 75.4 (C5), 83.5 (C3), 95.6 (C2), 211.3 (CO). IR (CHCl$_3$): 3600 (OH), 2900—3000, 2050 (CO), 1980 (CO) cm^{-1}. MS *m/z* (%): 294 (M$^+$, 3.0), 266 (14), 238 (23), 210 (34), 192 (100). HRMS Calcd for C$_{13}$H$_{18}$FeO$_4$: 294.0555. Found: 294.0571.

(4*RS*,5*RS*)-(*Z*)-Tricarbonyl[5-8-η-4-methyl-1,5,7-octatrien-4-ol]iron (4b) The experimental procedure for entries 2 and 3 of Table 2 will be described.

a) Table 2, entry 2: A solution of allylmagnesium bromide (0.270 ml, 2.0 M) in Et$_2$O was added to a solution of **3a** (25.8 mg, 0.109 mmol) in THF (1 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 20 min, and then the reaction was quenched with saturated NH$_4$Cl solution. The resulting mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 10 : 1) to give **4b** (16.0 mg, 53%).

b) Table 2, entry 3: A solution of allylmagnesium bromide (0.786 ml, 1.0 M) in Et$_2$O was added to a suspension of CuI (74.8 mg, 0.393 mmol) in THF (1.5 ml) at −30 °C under a nitrogen atmosphere. The mixture was stirred at −30 °C for 20 min. The mixture was allowed to cool to −78 °C. BF$_3$·Et$_2$O (48.3 μl, 0.393 mmol) was added to the mixture at −78 °C. The mixture was stirred at −78 °C for 10 min. A solution of **3a** (30.9 mg, 0.131 mmol) in THF (0.5 ml) was added to the mixture at −78 °C. The mixture was stirred at −78 °C for 30 min, and then the reaction was quenched with 10% NaOH solution. The resulting mixture was extracted with AcOEt. The extract was washed with water, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 15 : 1) to give **4b** (22.8 mg, 63%) as a yellow oil. ^{1}H-NMR (C$_6$D$_6$) δ: 1.05 (s, 3H, C4-Me), 1.61 (ddd, 1H, J = 1.4, 1.4, 7.7 Hz, C8-H$_t$), 1.79 (m, 2H, C3-H), 2.25 (d, 1H, J = 8.5 Hz, C5-H), 3.07 (ddd, 1H, J = 1.4, 1.4, 9.8 Hz, C8-H$_c$), 4.54 (m, 1H, C6-H), 4.81 (m, 1H, C1-H$_a$), 4.94 (m, 2H, C1-H$_b$ and C7-H), 5.52 (m, 1H, C2-H). ^{13}C-NMR (CDCl$_3$) δ: 30.9 (C4-Me), 42.8 (C8), 52.4 (C3), 69.1 (C5), 74.8 (C4), 83.2 (C6), 95.7 (C7), 119.6 (C1), 133.9 (C2), 211.2 (CO). IR (KBr): 2978, 2931, 2046 (CO), 1971 (CO), 1375 cm^{-1}. MS *m/z* (%): 278 (M$^+$, 0.39), 222 (36), 194 (100), 148 (59). HRMS Calcd for C$_{12}$H$_{14}$FeO$_4$: 278.0242. Found : 278.0242.

(4*RS*,5*SR*)-(*Z*)-Tricarbonyl[1-4-η-5-methyl-1,3-nonadien-5-ol]iron (4c) A solution of methyllithium (0.160 ml, 1.2 M) in Et$_2$O was added to a solution of **3b** (26.9 mg, 0.0968 mmol) in THF (1 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 5 min, and then the reaction was quenched with saturated NH$_4$Cl solution. The resulting mixture was extracted with AcOEt. The extract was washed with saturated NH$_4$Cl solution, water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 20 : 1) to give **4c** (20.1 mg, 96%) as a yellow oil. ^{1}H-NMR (CDCl$_3$) δ: 0.94 (t, 3H, J = 7.1 Hz, C9-H), 1.09 (s, 3H, C5-Me), 1.16 (s, 1H, OH), 1.26—1.56 (m, 6H), 1.96 (d, 1H, J = 8.1 Hz, C1-H$_t$), 2.69 (d, 1H, J = 8.6 Hz, C4-H), 2.94 (d, 1H, J = 9.8 Hz, C1-H$_c$), 5.20 (dd, 1H, J = 4.7, 8.6 Hz, C3-H), 5.61 (ddd, 1H, J = 4.7, 8.1, 9.8 Hz, C2-H). ^{13}C-NMR (CDCl$_3$) δ: 14.0 (C9), 23.0 (C8), 26.2 (C7), 33.5 (C5-Me), 43.7 (C1), 46.6 (C6), 69.9 (C4), 74.5 (C5), 84.1 (C3), 95.9 (C2), 211.3 (CO). IR (CHCl$_3$): 3600 (OH), 2900—3000, 2050 (CO), 1990 (CO) cm^{-1}. MS *m/z* (%): 294 (M$^+$, 1.0), 266 (10), 238 (41), 210 (37), 192 (100), 148 (49). HRMS Calcd for C$_{13}$H$_{18}$FeO$_4$: 294.0551. Found: 294.0544.

(2*S*,5*S*)-(2*E*,4*Z*)-Tricarbonyl[2-5-η-11-chloro-2,4-undecadien-6-one]iron (8) A solution of 6-chloroheptanoyl chloride (1.63 g, 9.62 mmol) in CH$_2$Cl$_2$ (1 ml) was added to a suspension of AlCl$_3$ (1.28 g, 9.62 mmol) in CH$_2$Cl$_2$ (19 ml) at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 20 min. A solution of the iron complex (**9**)[20] (1.00 g, 4.81 mmol) in CH$_2$Cl$_2$ (1 ml) was added to the mixture at room temperature. The mixture was stirred at room temperature for 10 min. The reaction was quenched with saturated NH$_3$ solution at −40 °C. The resulting mixture was extracted with CHCl$_3$. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 15 : 1) to give **8** (1.21 g, 74%) as a yellow oil. $[\alpha]_D^{32}$ +607° (c=1.43, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.43—1.46 (m, 2H), 1.53 (d, 3H, J=6.0 Hz, C1-H), 1.54—1.61 (m, 2H), 1.75—1.80 (m, 2H, C10-H), 2.22 (qd, 1H, J=6.0, 9.4 Hz, C2-H), 2.36 (ddd, 1H, J=6.0, 6.8, 15.4 Hz, C7-H$_a$), 2.46 (ddd, 1H, J=6.0, 6.8, 15.4 Hz, C7-H$_b$), 3.01 (d, 1H, J=6.0 Hz, C5-H), 3.53 (t, 2H, J=6.4 Hz, C11-H), 5.22 (dd, 1H, J=6.0, 6.0 Hz, C4-H), 5.36 (dd, 1H, J=6.0, 9.4 Hz, C3-H). ^{13}C-NMR ($CDCl_3$) δ: 20.1 (C1), 24.2 (C9), 26.7 (C8), 32.5 (C10), 42.1 (C7), 44.9 (C11), 56.0 (C5), 64.1 (C2), 81.1 (C4), 96.9 (C3), 205.2 (C6), 210.1 (CO). IR (KBr): 2947, 2866, 2052 (CO), 1975 (CO), 1666 (C=O), 1429 cm^{-1}. MS m/z (%): 340 (M$^+$, 0.072), 284 (13), 256 (41), 220 (100). HRMS Calcd for $C_{14}H_{17}ClFeO_4$: 340.0165. Found: 340.0168.

(2*S*,5*S*,6*R*)-(2*E*,4*Z*)-Tricarbonyl[2-5-η-11-chloro-6-methyl-2,4-undecadien-6-ol]iron (6) A solution of methyllithium (4.40 ml, 0.70 M) in Et$_2$O was added to a solution of **8** (604 mg, 1.77 mmol) in THF (23 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 5 min, and then the reaction was quenched with water. The resulting mixture was extracted with Et$_2$O. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 15 : 1) to give **6** (545 mg, 86%) as a yellow oil. $[\alpha]_D^{30}$ +14.1° (c=1.22, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.10 (s, 3H, C6-$\underline{\mathrm{Me}}$), 1.39—1.57 (m, 7H), 1.45 (d, 3H, J=6.0 Hz, C1-H), 1.82 (m, 2H, C10-H), 2.56 (d, 1H, J=8.6 Hz, C5-H), 3.56 (t, 2H, J=6.6 Hz, C11-H), 3.77 (qd, 1H, J=6.0, 9.8 Hz, C2-H), 5.00 (dd, 1H, J=5.1, 8.6 Hz, C4-H), 5.38 (dd, 1H, J=5.1, 9.8 Hz, C3-H). ^{13}C-NMR ($CDCl_3$) δ: 19.8 (C1), 23.3 (C9), 27.2 (C8), 32.5 (C10), 33.3 (C6-$\underline{\mathrm{Me}}$), 44.9 (C11), 46.7 (C7), 61.1 (C2), 69.7 (C5), 74.4 (C6), 79.3(C4), 99.2 (C3), 211.9 (CO). IR (KBr): 3608 (OH), 3084, 2937, 2040 (CO), 1956 (CO), 1450, 1375 cm^{-1}. MS m/z (%) : 356 (M$^+$, 0.090), 282 (30), 256 (41), 254 (100), 214 (69). *Anal.* Calcd for $C_{15}H_{21}ClFeO_4$: C, 50.52; H, 5.94. Found: C, 50.72; H, 5.95.

(*R*)-(2*E*,4*Z*)-11-Chloro-6-methyl-2,4-undecadien-6-ol (10) A suspension of CAN (1.28 g, 2.33 mmol) in CH_3CN (5 ml) was added to a mixture of **6** (277 mg, 0.776 mmol), K_2CO_3 (1.07 g, 7.78 mmol) and CH_3CN (10 ml) at −40 °C under a nitrogen atmosphere for 10 min, and then the reaction was quenched with saturated $NaHCO_3$ solution. The mixture was extracted with Et$_2$O. The extract was washed with saturated $NaHCO_3$ solution, water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 10 : 1) to give **10** (164 mg, 98%) as a colorless oil. $[\alpha]_D^{31}$ −33.2° (c=0.670, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.36 (s, 3H, C6-$\underline{\mathrm{Me}}$), 1.37—1.62 (m, 8H), 1.76—1.81 (m, 1H, O$\underline{\mathrm{H}}$), 1.78 (d, 3H, J=6.0 Hz, C1-H), 3.53 (t, 2H, J= 6.8 Hz, C11-H), 5.25 (d, 1H, J=12.0 Hz, C5-H), 5.67 (qd, 1H, J=6.0, 14.8 Hz, C2-H), 5.92 (dd, 1H, J=11.4, 12.0 Hz, C4-H), 6.85 (dd, 1H, J=11.4, 14.8 Hz, C3-H). ^{13}C-NMR ($CDCl_3$) δ: 18.6 (C1), 23.7 (C9), 27.6 (C8), 30.0 (C6-$\underline{\mathrm{Me}}$), 32.9 (C10), 44.0 (C7), 45.3 (C11), 74.7 (C6), 128.2 (C4), 129.8 (C2), 132.0 (C5), 134.3 (C3). IR (KBr): 3566 (OH), 2937, 2860, 1651 (C=C), 1454, 1371 cm^{-1}. MS m/z (%): 216 (M$^+$, 2.9), 111 (100). HRMS Calcd for $C_{12}H_{21}ClO$: 216.1282. Found: 216.1283.

(*R*)-7-Chloro-2-methyl-1,2-heptanediol [(*R*)-(11)] Ozone (generated by passing O_2 through an ozonizer) was bubbled through a solution of **10** (149 mg, 0.686 mmol) in MeOH (19 ml) at −78 °C for 10 min. After flushing the solution with argon gas to remove excess O_3, Me_2S (1.5 ml) was added to the solution. The mixture was allowed to warm to 0 °C. The mixture was concentrated *in vacuo*, and then the residue was purified by column chromatography (hexane : AcOEt = 1 : 3) to give the product (109 mg, 89%) as a colorless oil. $[\alpha]_D^{33}$ −1.46° (c=1.16, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.31 (s, 3H, C2-$\underline{\mathrm{Me}}$), 1.43—1.45 (m, 4H), 1.67—1.78 (m, 4H), 3.12 (s, 1H, O$\underline{\mathrm{H}}$), 3.52 (t, 2H, J=6.8 Hz, C7-H), 9.51 (s, 1H, C$\underline{\mathrm{H}}$O). ^{13}C-NMR ($CDCl_3$) δ: 22.4 (C5), 22.6 (C2-$\underline{\mathrm{Me}}$), 27.0 (C4), 32.3 (C6), 36.9 (C3), 44.8 (C7), 77.8 (C2), 203.7 (CO). IR (KBr): 3379 (OH), 2935, 2862, 1732 (C=O), 1460 cm^{-1}. MS m/z (%): 149 (M$^+$−HCO, 11), 111 (100).

Sodium borohydride (80.5 mg, 2.13 mmol) was added to a solution of the product (94.9 mg, 0.532 mmol) in isopropanol (^{i}PrOH, 18 ml) at 0 °C, and the mixture was stirred at the same temperature for 2 h, then the reaction was quenched with water. The mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 1 : 5) to give (*R*)-(**11**) (85.6 mg, 89%) as a colorless oil. $[\alpha]_D^{30}$ ≈0° (c=0.485, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.17 (s, 3H, C2-$\underline{\mathrm{Me}}$), 1.38—1.52 (m, 6H), 1.77—1.83 (m, 2H), 3.42 (d, 1H, J=10.9 Hz, C1-H$_a$), 3.47 (d, 1H, J=10.9 Hz, C1-H$_b$), 3.54 (t, 2H, J=6.6 Hz, C7-H). ^{13}C-NMR ($CDCl_3$) δ: 23.3 (C5), 23.5 (C2-$\underline{\mathrm{Me}}$), 27.7 (C4), 32.8 (C6), 38.8 (C3), 45.3 (C7), 70.0 (C1), 73.2 (C2). IR (KBr): 3396 (OH), 2939, 2866 cm^{-1}. MS m/z (%): 165 (M$^+$−Me, 4.5), 149 (58), 75 (100). HRMS Calcd for $C_7H_{14}ClO_2$ (M$^+$−Me): 165.0682. Found: 165.0685. CIMS m/z (%): 181.0 (M$^+$, 0.5), 163.0 (100).

(*R*)-2-Methyl-6-heptene-1,2-diol [(*R*)-(5)] A solution of ^{t}BuOK (1.2 ml, 1.0 M) in DMSO was added to a solution of (*R*)-(**11**) (53.0 mg, 0.293 mmol) in benzene (1 ml) at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 4 h, and then the reaction was quenched with 0.1 N HCl. The mixture was extracted with Et$_2$O. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : Et$_2$O = 1 : 8) to give (*R*)-(**5**) (29.7 mg, 68%) as a colorless oil. $[\alpha]_D^{25}$ +2.38° (c=0.405, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.18 (s, 3H, C2-$\underline{\mathrm{Me}}$), 1.43—1.49 (m, 4H), 1.78 (br s, 2H, O$\underline{\mathrm{H}}$), 2.08 (td, 2H, J=6.8, 6.8 Hz, C5-H), 3.42 (d, 1H, J=11.1 Hz, C1-H$_a$), 3.48 (dd, 1H, J=1.7, 11.1 Hz, C1-H$_b$), 4.97 (dd, 1H, J=1.1, 9.8 Hz, C7-H$_a$), 5.02 (dd, 1H, J=1.1, 17.1 Hz, C7-H$_b$), 5.80 (tdd, J=6.8, 9.8, 17.1 Hz, 1H, C6-H). ^{13}C-NMR ($CDCl_3$) δ: 23.0 (C4), 23.2 (C2-$\underline{\mathrm{Me}}$), 34.2 (C5), 38.1 (C3), 69.7 (C1), 73.0 (C2), 114.8 (C7), 138.5 (C6). IR (KBr): 3398 (OH), 2935, 1641 (C=C), 1464 cm^{-1}. MS m/z (%): 129 (M$^+$−Me, 0.50), 113 (56), 95 (48), 75 (100). HRMS Calcd. for $C_7H_{13}O$ (M$^+$−CH_2OH): 113.0967. Found: 113.0970. CIMS m/z (%): 145.0 (M$^+$+1, 3.2), 109.0 (100).

(2*S*,5*R*,6*S*)-(2*E*,4*E*)-Tricarbonyl[2-5-η-11-chloro-6-methyl-2,4-undecadien-6-ol]iron (7) A solution of methylmagnesium bromide (3.60 ml, 0.40 M) in THF was added to a solution of **8** (60.9 mg, 0.179 mmol) in THF (5 ml) at −78 °C under a nitrogen atmosphere. The resulting mixture was stirred at −78 °C for 30 min, and then allowed to warm to −30 °C. The mixture was stirred at −30 °C for 2 h, and then the reaction was quenched with water. The resulting mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 10 : 1) to give **7** (55.8 mg, 88%) as a yellow oil. $[\alpha]_D^{27}$ +12.7° (c=0.935, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.04 (qd, 1H, J=6.4, 9.0 Hz, C2-H), 1.09 (d, 1H, J=8.5 Hz, C5-H), 1.28 (s, 3H, C6-$\underline{\mathrm{Me}}$), 1.41 (d, 3H, J=6.4 Hz, C1-H), 1.47—1.55 (m, 7H), 1.82 (m, 2H, C10-H), 3.55 (t, 2H, J=6.6 Hz, C11-H), 5.03 (dd, 1H, J=5.1, 9.0 Hz, C3-H), 5.34 (dd, 1H, J=5.1, 8.5 Hz, C4-H). ^{13}C-NMR ($CDCl_3$) δ: 19.1 (C1), 23.6 (C9), 27.3 (C8), 29.7 (C6-$\underline{\mathrm{Me}}$), 32.5 (C10), 45.0 (C11), 45.9 (C7), 57.1 (C2), 72.8 (C6), 74.5 (C5), 79.5 (C4), 83.9 (C3), 212.7 (CO). IR (KBr): 3496 (OH), 2941, 2862, 2038 (CO), 1965 (CO), 1444 cm^{-1}. MS m/z (%): 356 (M$^+$, 2.7), 300 (78), 272 (100), 254 (95). HRMS Calcd for $C_{15}H_{21}ClFeO_4$: 356.0478. Found: 356.0489.

(*S*)-(2*E*,4*E*)-11-Chloro-6-methyl-2,4-undecadien-6-ol (12) A solution of NaOH (99.8 mg, 2.50 mmol) in H_2O (3 ml) was added to a mixture of **7** (67.4 mg, 0.189 mmol), 30% H_2O_2 solution (3.38 ml) and MeOH (5 ml) at 0 °C. The resulting mixture was allowed to warm to room temperature. The mixture was stirred at room temperature for 30 min, then extracted with Et$_2$O. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 10 : 1) to give **12** (40.8 mg, 100%) as a colorless oil. $[\alpha]_D^{23}$ +2.47° (c=0.550, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.29 (s, 3H, C6-$\underline{\mathrm{Me}}$), 1.30—1.56 (m, 7H), 1.74—1.80 (m, 2H, C10-H), 1.76 (dd, 3H, J=1.7, 6.8 Hz, C1-H), 3.52 (t, 2H, J=6.8 Hz, C11-H), 5.61 (d, 1H, J=15.4 Hz, C5-H), 5.70 (qd, 1H, J=6.8, 15.0 Hz, C2-H), 6.04 (ddd, 1H, J=1.7, 10.3, 15.4 Hz, C4-H), 6.17 (dd, 1H, J=10.3, 15.0 Hz, C3-H). ^{13}C-NMR ($CDCl_3$) δ: 18.1 (C1), 23.3 (C9), 27.2 (C8), 28.1 (C6-$\underline{\mathrm{Me}}$), 32.5 (C10), 42.5 (C7), 45.0 (C11), 72.8 (C6), 127.6 (C4), 129.3 (C2), 130.9 (C3), 137.4 (C5). IR (KBr): 3527 (OH), 3018, 2937 cm^{-1}. MS m/z (%): 216 (M$^+$, 7.8), 149 (16), 111 (100). HRMS Calcd for $C_{12}H_{21}ClO$: 216.1282. Found: 216.1284.

(*S*)-7-Chloro-2-methyl-1,2-heptanediol [(*S*)-(11)] (*S*)-(**11**) was obtained from **12** (43.6 mg, 0.201 mmol) in 53% yield (19.5 mg) using the same method as described for (*R*)-(**11**). $[\alpha]_D^{25}$ ≈0° (c=0.815, $CHCl_3$).

(*S*)-2-Methyl-6-heptene-1,2-diol [(*S*)-(5)] (*S*)-(**5**) was obtained from (*S*)-(**11**) (12.2 mg, 0.0675 mmol) in 69% yield (6.7 mg) using the same method as described for (*R*)-(**5**). $[\alpha]_D^{24}$ −2.55° (c=0.185, $CHCl_3$).

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