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Asymmetric Synthesis of (Diene)Fe(CO)$_3$ Complexes by a Catalytic Enantioselective Alkylation Using Dialkylzincs

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Abstract:
The reaction of *meso*-(2,4-hexadien-1,6-dial)Fe(CO)$_3$ complex **1** with several alkylzincs in the presence of 50 mol% of (*S*)-(+)-diphenyl(1-methylpyrrolidin-2-yl)methanol **6a** proceeded with high enantiotopic group- and diastereotopic face-selectivity to give (2*R*,6*S*)-alcohol complexes **2a-c** as major products, except in the case with dimethylzinc (>90% de and >98% ee). On the other hand, the methylation of **1** with Me_2Zn proceeded with high enantioselectivity by adding 1.8 equiv. of Ti(O*i*-Pr)$_4$ in the presence of 3 mol% of (*S*,*S*)-1,2-bis(trifluoromethylsulfonamide)cyclohexane **9a** (82% de, 96% ee). The enantioselective alkylation was also applied to the kinetic resolution of racemic (sorbic aldehyde)Fe(CO)$_3$ complex **10**. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords Aldehydes; Alkylation; Asymmetric induction; Iron and compounds

1. Introduction

Chiral (diene)Fe(CO)$_3$ complexes have been used as chiral synthons in asymmetric synthesis to prepare natural products.[1-5] The availability of these complexes as single enantiomers usually depends on the resolution method, such as recrystallization or column chromatographic separation of derived diastereomers.[6,7] Recently, however, more elegant methods, involving stereoselective Fe(CO)$_3$ complexation of chiral and achiral dienes and desymmetrization of *meso*-(diene)Fe(CO)$_3$ complexes, have been developed. The former can be divided into two categories: auxiliary-directed diastereoselective complexation[8-12] of chiral dienes and reagent-controlled

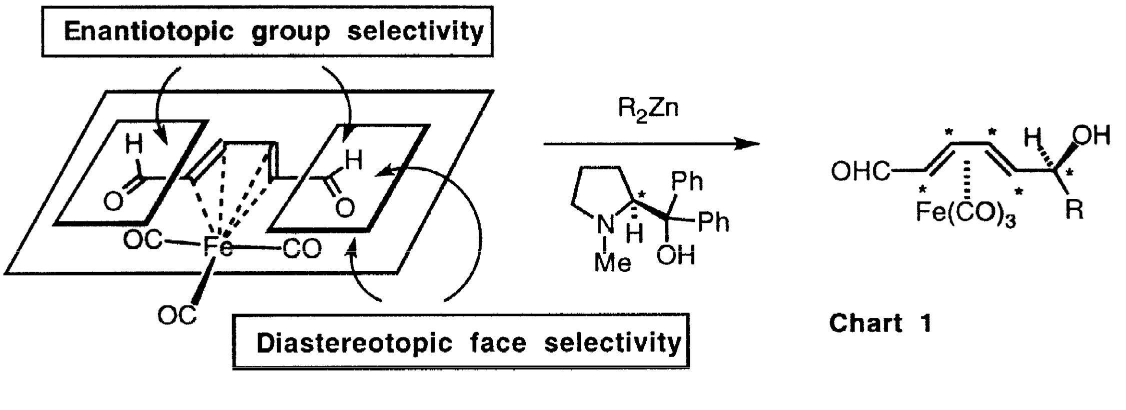

Chart 1

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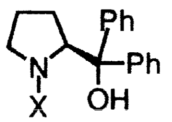
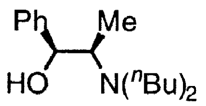


6a : X = Me
6b : X = H
6c : X = CH_2CMe_3



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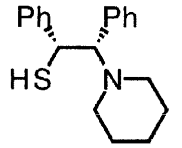

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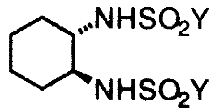

9a : Y = CF_3
9b : Y = CH_3
9c : Y =

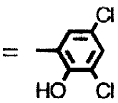

Chart 2

enantioselective complexation[13-17] of achiral dienes. In the latter case, bifunctional *meso*-(diene)$Fe(CO)_3$ complexes would be ideal and useful starting materialsfor asymmetric synthesis of natural products, since $Fe(CO)_3$ complexation of *meso*-dienes does not give diastereoisomers, and two-directional functionalization[18] using the $Fe(CO)_3$ chirality is possible. Despite the synthetic versatility of *meso*-complexes, there have been only two reports concerning differentiation of the enantiotopic functionality: biochemical reduction,[15] and acetylation[16] and allylboration using a stoichiometric amount of a chiral reagent.[17]

We recently reported a more efficient approach,[19] i.e., the catalytic enantioselective alkylation[20,21] of *meso*-(dienal)$Fe(CO)_3$ complex **1** with dialkyl zincs. Our method is the first example of construction of contiguous five stereogenic centers, involving a (diene)$Fe(CO)_3$ complex and a secondary alcohol, at the same time by the catalytic enantioselective alkylation of **1** (Chart 1), while the reaction of metallocenecarboxaldehydes with alkylzinc reagents in the presence of a catalytic amount of chiral β-aminoalcohols had been successfully conducted to introduce the stereogenic center of chiral secondary alcohols.[22] We report here the details of the highly enantiotopic group- and diastereotopic face-selective alkylation of *meso*-(dienal)$Fe(CO)_3$ complex **1** with dialkylzincs in the presence of various chiral ligands as well as the kinetic resolution of racemic (sorbic aldehyde)$Fe(CO)_3$ complex **10** by the catalytic enantioselective alkylation.

2. Results and discussion

2.1 The catalytic enantioselective alkylation of 1 with dialkylzincs using various chiral ligands.

We initiated this study on **1** with diethylzinc in the presence of a known catalyst [(*S*)-(1-methylpyrrolidin-2-yl)diphenylmethanol (**6a**)][23] (Chart 2) under typical conditions. A solution of **1** in toluene was allowed to react with 2.5 equiv. of Et_2Zn (1 M solution in hexane) at 0 ℃ under a nitrogen atmosphere in the presence of 10 mol % of **6a**. The reaction was not complete in 4 h, and gave rise to mono-alkylated adducts **2a** and **3a** along with dialkylated ketone **4**, mono-alkylated alcohol **5**, and the starting material **1** (entry 1 in Table 1). The desired mono-alkylated adducts **2a** and **3a** could be easily separated by SiO_2 column chromatography with $CHCl_3$/MeOH=30/1 and their relative configurations were deduced from their *Rf*-values according to Lillya's empirical rule,[24] that is, major polar product **2a** and less polar product **3a** were assigned to be ψ-exo and ψ-endo adducts, respectively. The diastereomeric ratio of **2a** and **3a** was very high (de >95%). The enantiomeric purity of the major product **2a** was determined to be 94% ee by ^{19}F-NMR analysis of the (+)- and (-)-MTPA derivatives from **2a**. The reaction with 0.5 equiv. of the chiral catalyst **6a** for 1 h led to the best result, giving **2a** in good yield (78%) and with higher ee (>95%) (entry 2), and the addition of more than 0.5 equiv. of **6a** did not further improve results. An increase in the reaction time so that all of the starting material would be consumed did not give improved results, irrespective of reaction temperature (entries 3 and 4). In addition, neither ether nor dichloromethane gave better results than the mixture of hexane and toluene (entries 5 and 6). The use of other

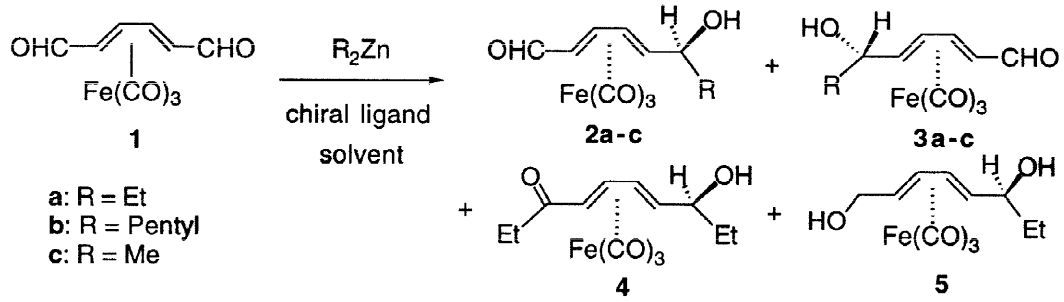

Table 1

The catalytic asymmetric alkylation of a meso $Fe(CO)_3$ complex **1** with dialkylzincs in the presence of several chiral ligands **6a-c**, **7** and **8**[a]

Entry	R_2Zn	Ligand (eq.)	Solvent[b]	Time (hr)	Yield[c] (%) 2	3	4	5	1	Ee of **2**[d] (%)
1	Et	**6a** (0.1)	T - H (4:1)	4	59	1	7	1	9	94
2	Et	**6a** (0.5)	T - H (4:1)	1	78	3	2	3	9	>98
3	Et	**6a** (0.5)	T - H (4:1)	2	53	2	14	24	2	96
4	Et	**6a** (0.5)	T - H (5:1)	5[e]	68	2	2	6	19	>98
5	Et	**6a** (0.5)	M - H (3:1)	5	53	4	-	trace	28	>98
6	Et	**6a** (0.5)	E - H (5:1)	3	29	2	-	-	52	>98
7	Et	**6b** (0.5)	T - H (4:1)	2	59	3	1	3	29	96
8	Et	**6c** (0.5)	T - H (4:1)	1	48	5	trace	-	34	70
9	Et	**7** (0.5)	T - H (4:1)	1	65	4	10	4	10	[f]
10	Et	**8** (0.5)	T - H (4:1)	3	31	7	-	-	30	[f]
11	Pentyl	**6a** (0.5)	T	1.5	82	4	-	-	6	>98
12	Pentyl	**6a** (0.5)	M - T (3:1)	5	29	1	-	-	39	>98
13	Pentyl	**6a** (0.5)	TFT	2	62	3	-	-	23	75
14	Me	**6a** (0.5)	T - H (4:1)	2	17	2	-	-	57	86
15	Me	**6a** (0.5)	M - H (3:1)	5	9	9	-	-	81	76

[a] Reactions were carried out at 0 °C in the presence of 2.5 equiv. of dialkylzinc except entry 4. [b] T = toluene, H = *n*-hexane, M = dichloromethane, E = Ether, TFT = trifluorotoluene. [c] Isolated yield. [d] Determined by ^{1}H-NMR and ^{19}F-NMR analysis of the MTPA derivative of **2a-c**. [e] The reaction was carried out at -20 °C. [f] Not detemined.

catalysts such as aminoalcohols **6b**,[25] **6c**, and **7**[26] and aminothiol **8**,[27] (Chart 2) gave **2a** and **3a** with lower diastereo- and enantio-selectivity (entries 7-10). Without the chiral ligand, the reaction did not proceed, leading to recovery of the starting material **1**.

We next investigated the enantiotopic group-selective alkylations with other dialkylzincs under the optimized conditions. The reaction of **1** with dipentylzinc in toluene proceeded similarly as that with diethylzinc to give **2b** in 82% yield with high diastereo- and enantioselectivity (entry 11). In this case, neither ketone **4b** nor diol **5b** was detected in the reaction mixture, regardless of the reaction time and the equivalence of dialkylzinc. In order to examine the effect of dipole moment of the solvents on the stereoselectivity, we carried out the reaction in more polar solvents such as dichloromethane and trifluoromethyltoluene to compare with toluene (entries 12 and 13). It is revealed that both the reaction rate and stereoselectivity decrease as the dipole moment of the solvent increases. On the other hand, methylation of **1** with dimethylzinc under similar conditions proceeded much more slowly than pentylation, and the methyl adduct was obtained in low yield even with prolonged reaction time and in more polar solvents (entries 14 and 15). Thus, the mono-alkylation of **1** with Et_2Zn and $(n\text{-Pentyl})_2Zn$ has been achieved with high enantioselectivity and good diastereoselectivity except for methylation by using the chiral ligand **6a**.

2.2 *The catalytic enantioselective methylation of 1 with Me_2Zn and $Ti(Oi\text{-}Pr)_4$ using the chiral ligand 9a*

To improve the chemical yield and ee in the methylation of **1**, we examined several conditions of the catalytic enantioselective alkylation. After many experiments, we found that the chemical yield was dramatically increased by adding titanium isopropoxide to the reaction mixture in the presence of (*S*,*S*)-1,2-bis(trifluoromethylsulfonamide)cyclohexane **9a** (Chart 2) as a chiral ligand according to Kobayashi's method[28] (Table 2). In addition, a chiral ligand and equivalences both of Me_2Zn and $Ti(Oi\text{-}Pr)_4$ were important to attain high enantiotopic group-selectivity (entries 1-4). Namely, the addition of more than 2 equiv. of both Me_2Zn and $Ti(Oi\text{-}Pr)_4$ decreased the chemical yield and stereoselectivity due to production of dialkylated adducts (entry 1). The reaction of **1** with 1.8 equiv. of Me_2Zn and 1.8 equiv. of $Ti(Oi\text{-}Pr)_4$ in the presence of **9a** (3 mol%) gave the desired product **2c** in 71% yield with good stereoselectivity (82% de, 96% ee: entry 2). Moreover, with the intention of improving the enantiotopic group-selectivity, the reaction with other reported chiral ligands (Chart 2) was investigated. The methylsulfonamide derivative **9b**,[28] a more basic chiral ligand, has less catalytic activity compared with **9a**, affording **2c** in low yield and with poor stereoselectivity (entry 3). Although the 3,5-dichloro-2-hydroxybenzenesulfonamide derivative **9c**,[29] a tetradentate chiral ligand, induced good group-selectivity comparable to **9a**, the yield of **2c** was poor even with a 20 mol% of **9c** (entry 4). In any event, the reaction of **1** with Me_2Zn (1.8 equiv.) and $Ti(Oi\text{-}Pr)_4$ (1.8 equiv.) using **9a** (3 mol%) was revealed to be the optimal reaction conditions for the catalytic enantioselective methylation of **1**.

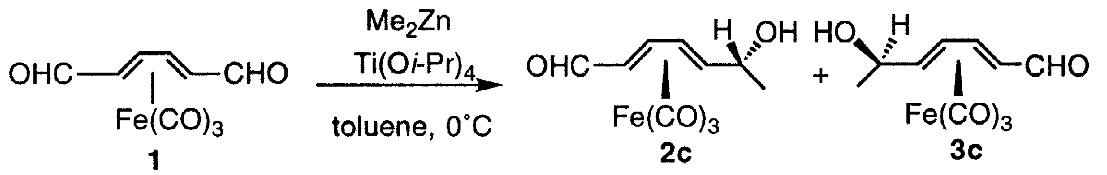

Table 2.
The catalytic asymmetric methylation of **1** with dimethylzinc using chiral ligands **9a-c**[a]

Entry	Ligand (mol%)	Me_2Zn (equiv.)	$Ti(Oi\text{-}Pr)_4$ (equiv.)	Time (h)	Yield[b] (%) 2	3	1	Ee[c] of **2c** (%)
1	**9a** (4.5)	2.6	2.6	4	51	8	6	88
2	**9a** (3)	1.8	1.8	1.5	71	7	12	96
3	**9b** (3)	1.8	1.8	2	33	9	43	54
4	**9c** (20)	1.8	1.4	2	34	5	57	87

[a] Reactions were carried out at 0 °C with Me_2Zn and $Ti(Oi\text{-}Pr)_4$ in the presence of **9a-c**. [b] Isolated yield. [c] Determined by ^{1}H-NMR and ^{19}F-NMR analysis of the MTPA derivatives of **2c**.

2.3 *Determination of the absolute configurations of the alkylated adducts 2a-c and 3a-c.*

The absolute configurations of the ψ-exo adducts **2a-c** and ψ–endo adducts **3a-c** were predicted from their circular dichroism (CD) spectra according to the empirical rule,[30] which suggests that the sign of the CD maximum at around 400 nm wavelength attributable to d-d transitions should be related to the absolute configuration of (diene)$Fe(CO)_3$ complexes bearing a carbonyl substituent directly linked at either or both terminal position of the dienes (Chart 3). For example, if the left substituent R^1 is a chromophore in compound **I** in Chart 3, a strong positive band should be exhibited at around 400 nm in the CD spectrum. On the contrary, if the right substituent R^2 is a chromophore, a strong negative band should be exhibited at around 400 nm in the CD spectrum. By adapting this empirical rule to our compounds **2-4**, **2a** ($\Delta\varepsilon$ +2.4) and **3a** ($\Delta\varepsilon$ −2.3) were assigned to (2*R*,6*S*)- and (2*S*,6*S*)-isomers, respectively, and the ketone **4** ($\Delta\varepsilon$ +2.6) was also assigned to a

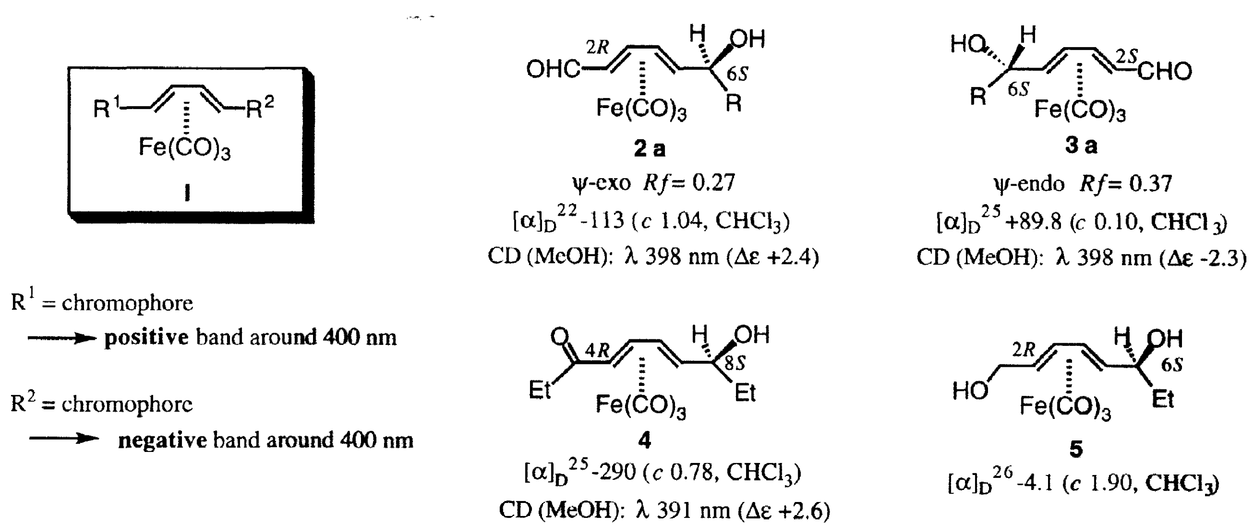

Chart 3. Determination of the absolute configurations of **2a**, **3a**, **4**, and **5** from their $[\alpha]_D$ and CD spectra

(4*R*)-isomer. Furthermore, the absolute configuration of the diol **5** ($[\alpha]_D^{25}$ −4.1) could be determined to be a (2*R*,6*S*)-isomer by the chemical transformation of **2a** into **5** ($[\alpha]_D^{26}$ −6.3) with sodium borohydride and comparison of their optical rotations. Similarly, the absolute configurations of the remaining products **2b-c** and **3b-c** were assigned to (2*R*,6*S*)- and (2*S*,6*S*)-isomers, respectively, as **2a** and **3a**.

*2.4 The kinetic resolution of the racemic (sorbic aldehyde)Fe(CO)$_2$L complexes (**10**, **14** and **15**) by the catalytic enantioselective ethylation with Et$_2$Zn and **6a**.*

The kinetic resolution of racemic $Fe(CO)_3$ complexes is a useful alternative method for the asymmetric synthesis of the (diene)$Fe(CO)_3$ complexes. Although, thus far, several methods such as biochemical transformation[15,16] and asymmetric allylboration[17,31] of (dienal)$Fe(CO)_3$ complexes have been reported, ee's of the recovered starting materials and products were usually variable depending on the conversion of the starting material and, therefore, development of efficient and reliable methods is desired. Then, we initiated this study anticipating that the high enantiotopic group-selectivity of the enantioselective alkylation of **1** with Et_2Zn and **6a** can be applied to intermolecular differentiation of the racemic (sorbic aldehyde)$Fe(CO)_3$ complex **10** (Chart 4). In the presence of **6a** (0.2 equiv.), *rac*-**10** was treated with Et_2Zn (1.0 equiv.) in a similar manner as **1** to give (−)-**11** (36%) and (+)-**12** (7%) with recovery of (−)-**10** [40%, $[\alpha]_D^{28}$ −82 (*c* 0.78, $CHCl_3$): ref.[15] $[\alpha]_D$ −112 (*c* 1, $CHCl_3$)] (entry 1 in Table 3). Under these conditions, ethylation of (+)-**10** proceeded preferentially, and the selectivity factor $s = k_{(+)\text{-}10}/k_{(-)\text{-}10}$ was calculated to be *ca.* 5. Significantly, ee's of the major and minor products (−)-**11** and (+)-**12** were determined to be >95% ee by the Mosher ester technique, while that of the recovered starting material was not satisfactory. In order to improve the ee of the recovered starting material, we carried out the reaction of *rac*-**10** with 2.0 equiv. of Et_2Zn, resulting in the improved optical purity of (−)-**10** [22%, $[\alpha]_D^{28}$ −114 (*c* 0.73, $CHCl_3$)] as well as an increase of chemical yield of (−)-**11**(38%) without decrease of the ee (>95% ee) (entry 2). An additional increase of the chiral ligand **6a** (0.4 equiv.) had no effect on the ee of the recovered starting material and products, but the chemical yields of (−)-**11** and **10** were improved (entry 3). Based on these results, both the matched- and mismatched- double asymmetric ethylations of (+)-**10** and (−)-**10** with **6a** provided the enantiomerically pure alcohols (−)-**11** and (+)-**12**, respectively, irrespective of the reaction conditions. The absolute configurations of (−)-**11** and (+)-**12** were determined by the comparison of $[\alpha]_D$ with the known compounds (4*S*)-**13** [ref.[32] $[\alpha]_D$ +416 (*c* 0.7, CH_2Cl_2)] as follows. The oxidation of (−)-**11** with *n*-PrMgCl and 1,1'-(azodicarbonyl)dipiperidine[33] gave rise to the corresponding ketone (+)-**13** [$[\alpha]_D^{28}$ +407 (*c* 0.61, CH_2Cl_2)], which indicates that the configuration of (−)-**11** is (3*S*,4*S*). Similarly, (+)-**12** was assigned to be (3*S*,4*R*)-isomer from the $[\alpha]_D$ of (−)-**13** [$[\alpha]_D^{28}$ −404 (*c* 0.54, CH_2Cl_2)], which was derived from (+)-**12** in the same manner as (−)-**11**.

We next carried out the enantioselective alkylation of the (sorbic aldehyde)-$Fe(CO)_2$(triphenylphosphine)[34] and -$Fe(CO)_2$(trimethylphosphite) complexes **14** and **15** to investigate the effect of tricarbonyl ligands on the stereoselectivity. Unfortunately, the alkylation of these complexes did not proceed owing to the bulkiness of the ligand and/or the strong electron-donation from the $Fe(CO)_2L$ groups to the aldehyde and led to the recovery of the starting materials.

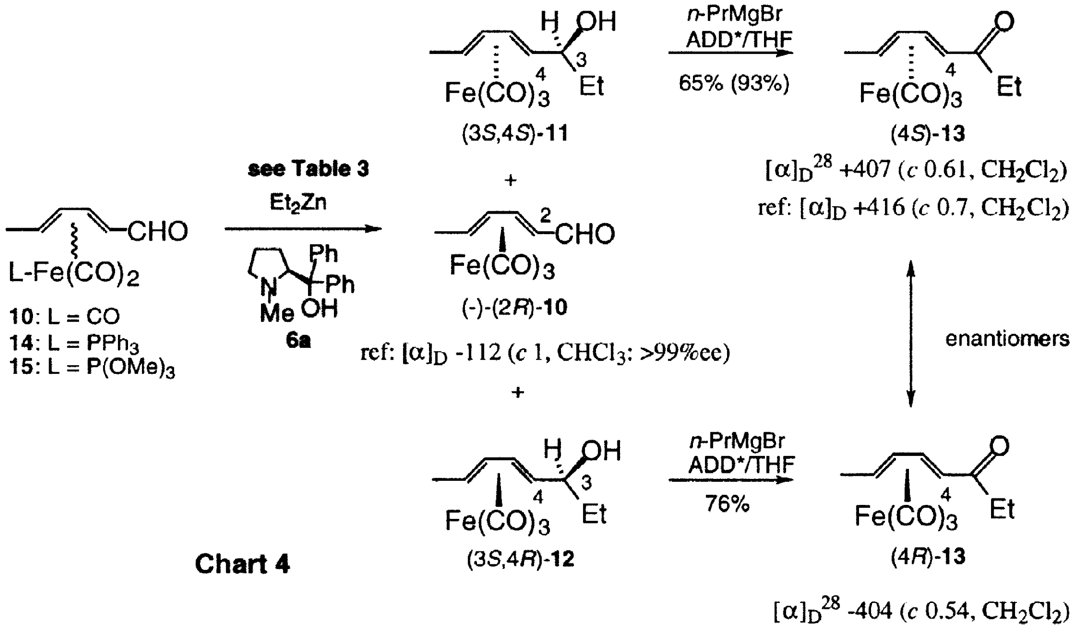

Chart 4

Table 3.
The kinetic resolution of the racemic $Fe(CO)_3$ complex **10** by the catalytic asymmetric alkylation with Et_2Zn and **6a**[a]

Entry	Reaction Conditions		Yield[b] (%)			$[\alpha]_D$[c]		
	Et_2Zn (eq.)	**6a** (eq.)	**11**	**12**	**10**	**11**	**12**	**10**
1	1.0	0.2	36	7	40	-19.2	17.4	-82
2	2.0	0.2	38	11	22	-19.6	22.4	-114
3	2.0	0.4	46	10	41	-20.8	23.1	-111

[a] Reactions were carried out at 0 °C in the presence of Et_2Zn and **6a**. [b] Isolated yield. [c] $[\alpha]_D$ were taken in $CHCl_3$.

2.5 The postulated reaction mechanism of the enantiotopic group-differentiating alkylation with dialkylzinc.

Based on the reported reaction mechanism[20,21] of the catalytic asymmetric alkylation of aldehydes with diethylzinc and chiral ligand **6a**, the high enantioselectivity (*S*-alcohol selectivity) of the alkylated products **2**, **3**, **11** and **12** can be easily explained by the normal transition-state model generated from R_2Zn, **1** (or **10**), and **6a** in a ratio of 2/1/1. Although the high enantiotopic group-selectivity (2*R* vs 2*S*) is a very interesting phenomenum, it is difficult to explain why **2** (or **11**) should be produced as a major product, but not **3** (or **12**). Indeed, from the mechanistic studies, we speculated that the differentiating reaction of the two enantiotopic functional groups of **1** was attributable to the four transition-state models (TS-model **A-D**) in Chart 5. Initially, we expected that the catalytic asymmetric alkylation of **1** would give rise to the ψ–endo adduct (2*S*,6*S*)-**3** as a major product *via* the TS-model **C**, where **1** adopts the energetically most stable *s-trans* conformation and, furthermore, dialkylzinc attacks the aldehyde group from the opposite direction to the $Fe(CO)_3$ group of **1**. On the contrary, the ψ-exo adducts (2*R*,6*S*)-**2** were obtained with high stereoselectivity. Judging from the observed selectivity, the TS-model **A** and **B** should be the most plausible transition-state model among the TS-models **A-D**. Although the TS-model **A** and **B** were interconvertible with each other *via* the rotation of the C1-C2 bond, the TS-model **A** seems to be more stable due to the dipole-dipole interaction[35] of the $Fe(CO)_3$ moiety with dialkylzinc. This interaction can be observed in the TS-model **A** and **D**, but in the latter case, these two functional groups are located too close to interact each dipole moment ideally owing to the severe steric hindrance. Consequently, only TS-model **A** would become an energetically predominant pathway to give the (2*R*,6*S*)-**2** with high enantiotopic group-selectivity. In fact, the replacement of the solvent from toluene (molecular dipole moment: μ = 0.38) to the morepolar solvents such as dichloromethane (μ = 1.69) and trifluoromethyltoluene (μ = 2.56) decreased the reaction rate, resulting in poor chemical yield and low enantiotopic group-selectivity (entries 11-13, Table 1). In the case of **10**, a similar TS-model **A** (X = Me) would become an energetically predominant pathway to give (-)-**11** as a major product with poorer enantiotopic group-selectivity (**11** vs **12**). The decrease of the selectivity may also be explained by the dipole-dipole interaction, that is, since the iron atom of **10**, being a weaker π-acid, seems to be less polarized than that of **1**, a strong π-acid with two electron-withdrawing groups, the dipole-dipole interaction between the iron and dialkylzinc would become weaker in the TS-model **A** of **10**. These facts indicate that the dipole-dipole interaction between the iron carbonyl moiety and dialkylzinc plays a crucial role to obtain acceptable chemical yield and high enantiotopic group-selectivity.

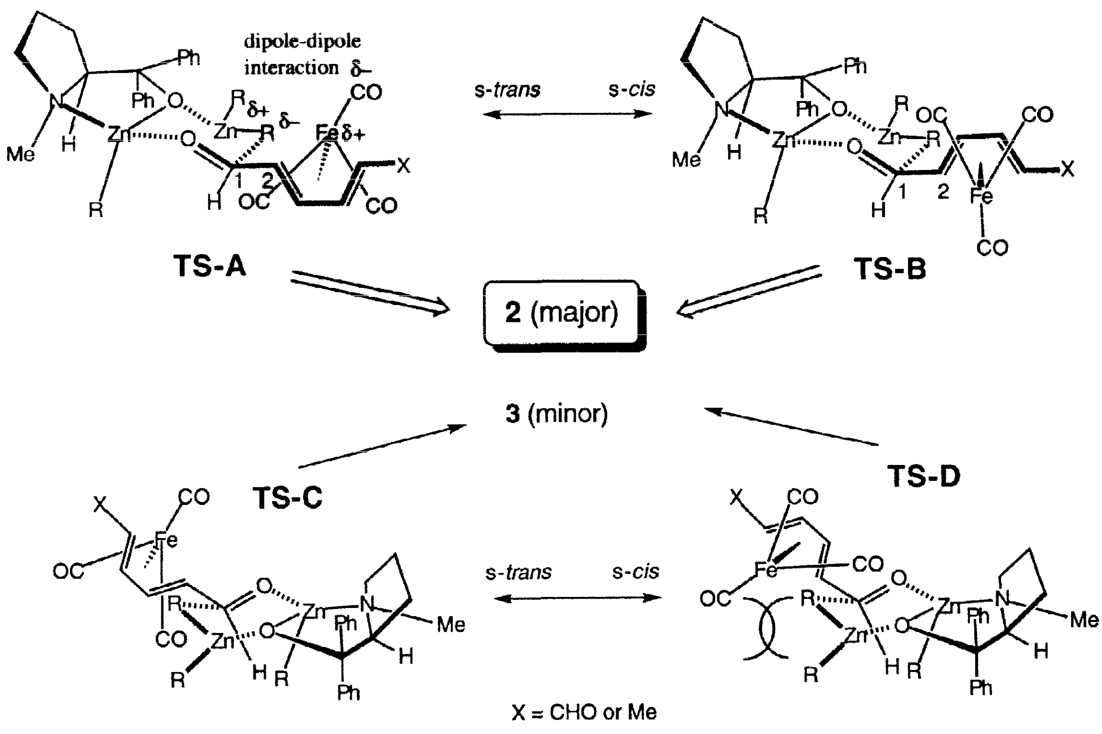

Chart 5. The postulated reaction mechanism of the enantiotopic group-selective alkylation of **1** and **10** with dialkylzinc and **6a**

3. Conclusion

In summary, we have achieved the first catalytic asymmetric synthesis of the $Fe(CO)_3$ complexes bearing an aldehyde group **2a-c** by the enantiotopic group-selective alkylation of the *meso*-(dienal) $Fe(CO)_3$ complex **1** with several dialkylzincs and the chiral ligands **6a** and **9a**. This method was applied to the kinetic resolution of *rac*-(sorbic aldehyde)$Fe(CO)_3$ complex **10**, giving the mono-alkylated complex **11** and starting material **10** with high enantioselectivity. In terms of the mild conditions, operational simplicity, and high stereoselectivity, this catalytic asymmetric alkylation is revealed to be very useful for the synthesis of chiral $Fe(CO)_3$ complexes. In addition, these obtained products **2a-c**, possessing aldehyde and alcohol groups, are versatile synthetic intermediates for the asymmetric synthesis of natural products. Further synthetic studies using **2a-c** are underway in our laboratories.

4. Experimental

General: Melting points are uncorrected. IR spectra were obtained using a Horiba FT-210 spectrometer. ^1H NMR spectra were obtained using a JEOL JNM-GX-500 (500MHz) spectrometer. ^{13}C NMR spectra were obtained using a JEOL JNM-EX-270 (67.8MHz) spectrometer. Optical rotations were measured with a JASCO DIP-360 polarimeter. Mass spectra (MS) were measured with a Shimadzu GCMS-QP-1000 spectrometer. High resolution mass spectra (HRMS) were measured with a JEOL JMS-D300 spectrometer. Circular dichroism spectra (CD) were obtained using a JASCO J-720W spectropolarimeter. A 1.0 M solution of diethylzinc and dimethylzinc in hexane was purchased from Kanto Chemicals, and dipentylzinc was prepared according to the literature.[36] Column chromatography was carried out using Merck Kieselgel 60. Toluene was distilled from sodium benzophenone ketyl radical under argon. Dichloromethane was freshly distilled from calcium hydride. Dry ether and THF were obtained from Kanto Chemicals.

(*S*)-(–)-[*N*-(2',2'-Dimethylpropyl)pyrrolidin-2-yl)]diphenylmethanol (6c) To a stirred solution of **6b** (500 mg, 2.00 mmol) in dry ether (10 ml) was added pivaloyl chloride (0.36 ml, 3.00 mmol) at room temperature under a nitrogen atmosphere. After 2 h, 3-(dimethylamino)propylamine (0.37 ml, 3.00 mmol) was added and the mixture was stirred for additional 20 min. AcOEt was added and the organic phase was succesively washed with a saturated $NaHCO_3$ solution, water, a 1 M HCl solution, and brine. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. $LiAlH_4$ (151 mg, 4.00 mmol) was slowly added to a solution of the residue in dry THF (7 ml) at 0 °C, and the resulting suspension was heated under reflux for 2 h. After the cooled mixture was quenched with a 1 M HCl solution, the mixture was adjusted to pH 10 by adding an aqueous NaOH solution, and the precipitate was filtered through a pad of Celite. The filtrate was extracted with Et_2O three times and the combined extracts were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was recrystallized from hexane to give **6c** (380 mg, 59%) as colorless crystals. **6c**: mp 113-117 °C (hexane). $[\alpha]_D^{22}$ –53.1 (c = 1.07, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 0.74 (s, 9H, ^tBu), 1.50-1.74 (m, 4H, $C\underline{H}_2C\underline{H}_2CH$), 2.11 (d, 1H, J = 12.8 Hz, $C\underline{H}_2{}^tBu$), 2.15 (d, 1H, J = 12.8 Hz, $C\underline{H}_2{}^tBu$), 2.46 (td, 1H, J = 7.7, 10.3 Hz, CH_2N), 3.20 (td, 1H, J = 6.0, 10.3 Hz, CH_2N), 3.98 (dd, 1H, J = 6.4, 7.3 Hz, CHN), 5.16 (br, 1H, OH), 7.10-7.69 (m, 10H, Ar-H). ^{13}C NMR ($CDCl_3$) δ: 25.0 ($\underline{C}H_2CH_2CH$), 28.7 ($C(\underline{C}H_3)_3$), 29.1 ($\underline{C}H_2CH$), 32.1 ($\underline{C}(CH_3)_3$), 58.3 ($N\underline{C}H_2CH$), 69.7 ($\underline{C}H_2{}^tBu$), 73.1 (CHN), 77.2 (C1), 125.2 (Ar), 125.9 (Ar), 126.1 (Ar), 126.2 (Ar), 127.7 (Ar), 127.9 (Ar), 147.1 (Ar), 147.9 (Ar). IR (KBr): 3286 (OH), 2956, 1383, 1448 (Ar) cm^{-1}. MS m/z (%): 308 (M^+-Me, 3.1), 266 (M^+- ^tBu, 4.6), 246 (M^+-Ph, 4.2), 140 (M^+-$C(OH)Ph_2$, 100), 70 (100). *Anal* Calcd for $C_{22}H_{29}NO$: C, 81.69; H,9.04; N, 4.33. Found: C, 81.58; H,8.90; N, 4.30.

(2*R*,5*S*,6*S*,2*E*,4*E*)-Tricarbonyliron[(η^4-2-5)-6-hydroxyocta-2,4-dienal] (2a), (2*S*,5*R*,6*S*,2*E*,4*E*)-Tricarbonyliron[(η^4-2-5)-6-hydroxyocta-2,4-dienal] (3a) and (4*R*,7*S*,8*S*,4*E*,6*E*)-Tricarbonyliron[(η^4-4-7)-8-hydroxydeca-4,6-dien-3-one] (4) General procedure (entries 1-10 in Table 1) for the catalytic asymmetric alkylation of **1** using the chiral ligands **6a-c**: (entry 2 in Table 1): To a stirred solution of **1** (100 mg, 0.400 mmol) and **6a** (53.4 mg, 0.200 mmol) in dry toluene (4 ml) was added dropwise a 1.0 M solution of Et_2Zn in hexane (1.0 ml, 1.00 mmol) at 0 °C under a nitrogen atmosphere. After 1 h, a 1 M HCl solution was added to the reaction mixture, and the resulting mixture was extracted with AcOEt. The extract was washed with brine, dried over $MgSO_4$, and then concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, $CHCl_3$/Acetone = 30/1) to give **1** (8.9 mg, 9%), **3a** (3.7 mg, 3%), **4** (2.1 mg, 2%), **2a** (87.2 mg, 78%), and **5** (3.4 mg, 3%). **2a**; yellow crystals: mp 44-45 °C (hexane/benzene). $[\alpha]_D^{22}$ −113.3 (*c* = 1.04, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 1.03 (t, 3H, *J* = 7.2 Hz, C8-H), 1.36 (dd, 1H, *J* = 4.3, 7.7 Hz, C2-H), 1.58 (m, 2H, C5-H, C7-H), 1.65 (d, 1H, *J* = 5.1 Hz, OH), 1.76 (ddq, 1H, *J* = 3.7, 7.2, 13.7 Hz, C7-H), 3.58-3.63 (m, 1H C6-H), 5.59 (dd, 1H, *J* = 5.1, 8.6 Hz, C4-H), 5.84 (dd, 1H, *J* = 5.1, 7.7 Hz, C3-H), 9.32 (d, 1H, *J* = 4.3 Hz, C1-H). ^{13}C NMR ($CDCl_3$) δ: 9.6 (C8), 31.8 (C7), 54.6 (C2), 68.0 (C5), 73.9 (C6), 82.2 (C3), 86.4 (C4), 196.4 (C1), 208.5 (CO). IR (KBr): 3392 (OH), 2967, 2059 (CO), 1986 (CO), 1677 (C=O) cm^{-1}. MS *m/z* (%): 280 (M^+, 0.8), 252 (M^+-CO, 1.1), 224 (M^+-2CO, 2.9), 196 (M^+-3CO, 4.2), 95 (100). HRMS Calcd for $C_{11}H_{12}FeO_5$: 280.0035. Found: 280.0040. CD (*c* = 0.0247, MeOH) λ 397.5 nm (Δε +2.38), 352.5 (−2.43), 324.0 (+1.58), 273.5 (−6.70). **3a**; a yellow oil: $[\alpha]_D^{25}$ +89.8 (*c* = 0.10, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 1.03 (t, 3H, *J* = 7.3 Hz, C8-H), 1.24 (dd, 1H, *J* = 4.3, 8.6 Hz, C2-H), 1.57 (d, 1H, *J* = 5.7 Hz, OH), 1.58-1.68 (m, 3H, C5-H, C7-H), 3.59-3.65 (m, 1H, C6-H), 5.50 (dd, 1H, *J* = 5.1, 8.6 Hz, C3-H), 5.83 (dd, 1H, *J* = 5.1, 7.7 Hz, C4-H), 9.32 (d, 1H, *J* = 4.3 Hz, C1-H). IR (KBr): 3400 (OH), 2925, 2059 (CO), 1992 (CO), 1677 (C=O) cm^{-1}. MS *m/z* (%): 280 (M^+, 1.0), 252 (M^+-CO, 1.8), 224 (M^+-2CO, 5.2), 196 (M^+-3CO, 8.3), 95 (100). HRMS Calcd for $C_{11}H_{12}FeO_5$: 280.0033. Found: 280.0028. CD (*c* = 0.017, MeOH) λ 398.0 nm (Δε −2.34), 352.0 (+2.58), 323.5 (−2.06). **4**; a yellow oil: $[\alpha]_D^{25}$ −289.6 (*c* = 0.78, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 1.02 (t, 3H, *J* = 7.7 Hz, C1-H), 1.09 (t, 3H, *J* = 7.7 Hz, C10-H), 1.30 (d, 1H, *J* = 8.2 Hz, C4-H), 1.40 (dd, 1H, *J* = 8.1, 8.6 Hz, C7-H), 1.55-1.60 (m, 1H, C9-H),1.62 (d, 1H, *J* = 5.1 Hz, OH), 1.72-1.80 (m, 1H, C9-H), 2.41 (dq, 1H, *J* = 7.7, 16.2 Hz, C2-H), 2.42 (dq, 1H, *J* = 7.7, 16.2 Hz, C2-H), 3.51-3.55 (m, 1H, C8-H), 5.52 (dd, 1H, *J* = 5.1, 8.6 Hz, C6-H), 5.87 (dd, 1H, *J* = 5.1, 8.2 Hz, C5-H). ^{13}C NMR ($CDCl_3$) δ: 8.6 (C1), 9.7 (C10) 31.7 (C9), 35.7 (C2), 53.4 (C4), 66.8 (C7), 74.4 (C8), 82.4 (C5), 85.9 (C6), 206.3 (C3). IR (KBr): 3444 (OH), 2975, 2056 (CO), 1998 (CO), 1670 (C=O) cm^{-1}. MS *m/z* (%): 308 (M^+, 4.9), 280 (M^+-CO, 7.6), 252 (M^+-2CO, 26), 224 (M^+-3CO, 54), 152 (100) 95 (100), 57 (100). HRMS Calcd for $C_{13}H_{16}FeO_5$: 308.0346. Found: 308.0342. CD (*c* = 0.0612, MeOH) λ 390.5 nm (Δε +2.65), 336.0 (−6.81). **5**; a yellow oil: $[\alpha]_D^{26}$ −4.10 (*c* = 1.90, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 1.00 (t, 3H, *J* = 7.5 Hz, C8-H), 1.13 (dd, 1H, *J* = 7.7, 7.7 Hz, C5-H), 1.18-1.27 (m, 1H, C2-H), 1.49-1.50 (m, 1H, C7-H), 1.65 (br s, 2H, OH), 1.73 (ddq, 1H, *J* = 3.4, 7.5, 13.7 Hz, C7-H), 3.44 (ddd, 1H, *J* = 3.4, 7.7, 7.7 Hz, C6-H), 3.67 (dd, 1H, *J* = 7.7, 12.0 Hz, C1-H), 3.75 (dd, 1H, *J* = 5.1, 12.0 Hz, C1-H), 5.23 (dd, 1H, *J* = 4.8, 7.3 Hz, C3-H), 5.34 (dd, 1H, *J* = 4.8, 7.7 Hz, C4-H). ^{13}C NMR ($CDCl_3$) δ: 9.8 (C8), 31.4 (C7), 60.8 (C2), 64.3 (C1), 65.4 (C5), 75.2 (C6), 83.9 (C4), 84.1 (C3), 211.1 (CO). IR (KBr): 3332 (OH), 2879, 2048 (CO), 1965 (CO) cm^{-1}. MS *m/z* (%): 282 (M^+, 2.1), 254 (M^+-CO, 4.8), 226 (M^+-2CO, 5.8), 79 (100). HRMS Calcd for $C_{11}H_{14}FeO_5$: 282.0190. Found: 282.0213.

(2*R*,5*S*,6*S*,2*E*,4*E*)-Tricarbonyliron[(η^4-2-5)-2,4-octadiene-1,6-diol] (5) To a solution of **2a** (26.0 mg, 0.093 mmol) in MeOH (1 ml) was added $NaBH_4$ (3.5 mg, 0.093 mmol) at room temperature. After 15 min, the solvent was removed under reduced pressure and the residue was diluted with AcOEt. The organic phase was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (SiO_2, hexane/AcOEt = 1/1) to give **5** (20.4 mg, 78%); $[\alpha]_D^{26}$ −6.26 (*c* = 1.02,

$CHCl_3$).

(2*R*,5*S*,6*S*,2*E*,4*E*)-Tricarbonyliron[(η^4-2-5)-6-hydroxyundeca-2,4-dienal] (2b) and (2*S*,5*R*, 6*S*, 2*E*, 4*E*)-Tricarbonyliron[(η^4-2-5)-6-hydroxyundeca-2,4-dienal] (3b) (Entry 11 in Table 1): To a stirred solution of **1** (1.00 g, 4.00 mmol) and **6a** (534 mg, 2.00 mmol) in dry toluene (36 ml) was added dropwise a 1.0 M solution of $(n\text{-}C_5H_{11})_2Zn$ (10 ml, 10 mmol) in toluene at 0 °C under a nitrogen atmosphere. After the same workup of the reaction mixture as for **2a** and **3a**, the residue was purified by column chromatography (SiO_2, $CHCl_3$/Acetone = 20/1) to give **3b** (46 mg, 4%), **1** (55 mg, 6%), and **2b** (1.06 g, 82%). **2b**; a yellow oil: $[\alpha]_D^{25}$ −91.2 (*c* = 1.96, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 0.91 (t, 3H, *J* = 6.8 Hz, C11-H), 1.30-1.39 (m, 6H, C8, 9, 10-H), 1.46-1.53 (m, 1H, C2-H), 1.56-1.61 (m, 2H, C5-H, OH), 1.46-1.53 (m, 2H, C7-H), 3.66 (m, 1H, C6-H), 5.58 (dd, 1H, *J* = 5.1, 8.6 Hz, C4-H), 5.84 (dd, 1H, *J* = 5.1, 8.6 Hz, C3-H), 9.31 (d, 1H, *J* = 4.3 Hz, C1-H). ^{13}C NMR ($CDCl_3$) δ: 14.0 (C11), 22.5 (C10), 25.0 (C9), 31.5 (C8), 38.6 (C7), 54.7 (C2), 68.3 (C5), 72.7 (C6), 82.0 (C3), 86.3 (C4), 196.3 (C1), 208.3 (CO). IR (KBr): 3437 (OH), 2933, 2060 (CO), 1986 (CO), 1676 (C=O), 1406, 623, 561 cm^{-1}. MS *m/z* (%): 322 (M$^+$, 0.4), 294 (M$^+$-CO, 0.4), 266 (M$^+$-2CO, 1.1), 238 (M$^+$-3CO, 4.2), 220 (100). *Anal* Calcd for $C_{14}H_{18}FeO_5$: C, 52.19; H, 5.63. Found: C, 51.97; H, 5.63. CD (*c* = 0.0179, MeOH) λ 396.0 nm (Δε +1.98), 352.0 (−1.98), 323.0 (+1.26), 272.5 (−8.43). **3b**; a yellow oil: $[\alpha]_D^{20}$ +76.5 (*c* = 0.53, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 0.91 (t, 3H, *J* = 7.3 Hz, C11-H), 1.24 (ddd, 1H, *J* = 1.2, 4.3, 7.9 Hz, C2-H), 1.30-1.36 (m, 6H, C8, 9, 10-H), 1.36-1.50 (m, 1H, C5-H), 1.56-1.63 (m, 3H, C7-H, OH), 3.70 (ddd, 1H, *J* = 4.3, 6.1, 12.2 Hz, C6-H), 5.49 (dd, 1H, *J* = 4.9, 8.5 Hz, C4-H), 5.83 (ddd, 1H, *J* = 1.2, 4.9, 7.9 Hz, C3-H), 9.31 (d, 1H, *J* = 4.3 Hz, C1-H). ^{13}C NMR ($CDCl_3$) δ: 14.0 (C11), 22.5 (C10), 25.0 (C9), 31.6 (C8), 40.5 (C7), 54.6 (C2), 71.3 (C5), 72.8 (C6), 81.2 (C3), 85.4 (C4), 196.1 (C1), 207.9 (CO). IR (KBr): 3431 (OH), 2931, 2060 (CO), 1992 (CO), 1678 (C=O), 1454, 1134, 611, 599 cm^{-1}. MS *m/z* (%): 266 (M$^+$-2CO, 6.3), 238 (M$^+$-3CO, 13), 220 (53), 81 (89), 67(100). HRMS Calcd for $C_{12}H_{15}FeO_5$ (M$^+$-2CO): 266.0605. Found: 266.0627. CD (*c* = 0.023, MeOH) λ 396.5 nm (Δε -1.17), 352.5 (1.31), 324.0 (−0.96).

(2*R*, 5*S*, 6*S*, 2*E*, 4*E*)-Tricarbonyliron[(η^4-2-5)-6-hydroxyhepta-2,4-dienal] (2c) and (2*S*, 5*R*, 6*S*, 2*E*, 4*E*)-Tricarbonyliron[(η^4-2-5)-6-hydroxyhepta-2,4-dienal] (3c) (Entry 14 in Table 1): To a stirred solution of **1** (30.0 mg, 0.120 mmol) and **6a** (16.0 mg, 0.060 mmol) in dry toluene (1.2 ml) was added dropwise a 1.0 M solution of Me_2Zn (0.30 ml, 0.30 mmol) in hexane at 0 °C under a nitrogen atmosphere. After the same workup of the reaction mixture as for **2a** and **3a**, the residue was purified by column chromatography (SiO_2, $CHCl_3$/Acetone = 30/1) to give **1** (17.2 mg, 57%), **3c** (0.8 mg, 2 %), and **2c** (5.0 mg, 17%). **2c**; yellow crystals: mp 72-73 °C (hexane/benzene). $[\alpha]_D^{27}$ −126.0 (*c* = 0.47, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 1.34 (dd, 1H, *J* = 4.3, 8.1 Hz, C2-H), 1.42 (d, 3H, *J* = 6.0 Hz, C7-H), 1.51-1.54 (m, 1H, C5-H), 1.64 (d, 1H, *J* = 4.3 Hz, OH), 3.78 (m, 1H, C6-H), 5.55 (dd, 1H, *J* = 4.7, 9.0 Hz, C4-H), 5.84 (dd, 1H, *J* = 4.7, 8.1 Hz, C3-H), 9.32 (d, 1H, *J* = 4.3 Hz, C1-H). ^{13}C NMR ($CDCl_3$) δ: 25.7 (C7), 54.9 (C2), 68.8 (C5), 69.6 (C6), 82.4 (C3), 86.6 (C4), 196.2 (C1), 207.2 (CO). IR (KBr): 3398 (OH), 2973, 2059 (CO), 1988 (CO), 1673 (C=O) cm^{-1}. MS *m/z* (%): 238 (M$^+$-CO, 8.5), 210 (M$^+$-2CO, 19), 182 (M$^+$-3CO, 32), 81 (100). *Anal* Calcd for $C_{10}H_{10}FeO_5$: C, 45.15; H, 3.79. Found: C, 45.17; H,3.77. CD (*c* = 0.0148, MeOH) λ 394.0 nm (Δε +1.88), 352 (−1.80), 323.5 (+1.52). **3c**; a yellow oil: $[\alpha]_D^{27}$ +58.0 (*c* = 0.22, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 1.23 (dd, 1H, *J* = 4.3, 8.5 Hz, C2-H), 1.41 (d, 3H, *J* = 6.0 Hz, C7-H), 1.47 (d, 1H, *J* = 3.4 Hz, OH), 1.62 (dd, 1H, *J* = 6.0, 8.6 Hz, C5-H), 3.97-4.01 (m, 1H, C6-H), 5.49 (dd, 1H, *J* = 5.1, 8.6 Hz, C4-H), 5.84 (dd, 1H, *J* = 5.1, 8.5 Hz, C3-H), 9.32 (d, 1H, *J* = 4.3 Hz, C1-H). ^{13}C NMR ($CDCl_3$) δ: 26.5 (C7), 54.5 (C2), 68.4 (C5), 72.5 (C6), 81.1 (C3), 85.0 (C4), 196.0 (C1), 208.4 (CO). IR (KBr): 3453 (OH), 2973, 2057 (CO), 1996 (CO), 1678 (C=O) cm^{-1}. MS *m/z* (%): 266 (M$^+$, 5.4), 238 (M$^+$-CO, 7.2), 210 (M$^+$-2CO, 16), 182 (M$^+$-3CO, 21), 81 (100). HRMS Calcd for $C_{10}H_{10}FeO_5$: 265.9877. Found: 265.9890.

General procedure (entries 1-4 in Table 2) for the catalytic asymmetric alkylation of **1** using the chiral ligands

9a-c: (entry 2 in Table 2): A solution of **9a** (226.8 mg, 0.600 mmol) and $Ti(Oi\text{-}Pr)_4$ (10.7 ml, 36.0 mmol) in dry toluene (50 ml) was stirred at 50 °C for 30 min under a nitrogen atmosphere. After the mixture was cooled to −78 °C, a 1.0 M solution of Me_2Zn (36 ml, 36 mmol) in hexane and a solution of **1** (5.0 g, 20.0 mmol) in dry toluene (90 ml) were successively added to the reaction mixture. The resulting mixture was allowed to warm slowly to 0 °C and stirried at 0 °C for 1 h. After being quenched with a 2 M aqueous HCl solution (80 ml), the mixture was extracted with AcOEt. The extract was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (SiO_2, $CHCl_3$/Acetone = 20/1 to 10/1) to give **1** (0.59g, 12%), **3c** (0.37g, 7%), and **2c** (3.82g, 71%).

(3*S*,4*S*,4*E*,6*E*)-Tricarbonyliron[(η^4-4-7)-4,6-octadien-3-ol] (11) and (3*S*,4*R*,4*E*,6*E*)-Tricarbonyliron[(η^4-4-7)-4,6-octadien-3-ol] (12) General procedure (Entry 2 in Table 3): To a stirred solution of **1** (300 mg, 1.27 mmol) and **6a** (68.0 mg, 0.254 mmol) in dry toluene (6 ml) was added dropwise a 1.02 M solution of Et_2Zn (2.5 ml, 2.54 mmol) in hexane at −20 °C under an argon atmosphere. The resulting mixture was allowed to warm slowly to 0 °C and stirred at 0 °C for 2 h. After being quenched with a 1 M HCl solution (2 ml), the mixture was extracted with hexane/AcOEt (5/1). The extract was washed with 1 M HCl solution, water, and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexane/AcOEt = 10/1) to give **12** (38.6 mg, 11%), **10** (66.2 mg, 22%), and **11** (129.1 mg, 38%). **11**; a yellow oil: $[\alpha]_D^{27}$ −19.6 (c = 1.05, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 0.94-1.02 (m, 4H, C1-H_3 and C4-H), 1.23 (m, 1H, C7-H), 1.42 (d, 3H, J = 6.2 Hz, C8-H), 1.44-1.62 (m, 2H, C2-Ha and OH), 1.73 (m, 1H, C2-Hb), 3.36 (m, 1H, C3-H), 5.06 (dd, 1H, J = 5.1, 8.4 Hz, C6-H), 5.23 (dd, 1H, J = 5.1, 8.1 Hz, C5-H). MS *m/z* (%): 266 (M^+, 33), 249 (M^+-OH, 100), 238 (M^+-CO, 48), 221 (M^+-OH-CO, 40), 210 (M^+-2CO, 48), 193 (M^+-OH-2CO, 71), 182 (M^+-3CO, 23). *Anal* Calcd for $C_{11}H_{14}FeO_4$: C, 49.66; H, 5.30. Found: C, 49.36; H, 5.39. **12**; a yellow oil: $[\alpha]_D^{29}$ +22.4 (c = 0.67, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 0.97 (t, 3H, J = 7.3 Hz, C1-H), 1.03 (dd, 1H, J = 7.6, 7.6 Hz, C4-H), 1.14 (m, 1H, C7-H), 1.36 (d, 1H, J = 3.5 Hz, OH), 1.42 (d, 3H, J = 6.2 Hz, C8-H), 1.44-1.70 (m, 2H, C2-H), 3.37 (m, 1H, C3-H), 5.06 (dd,1H, J = 5.1, 8.6 Hz, C6-H), 5.15 (dd, 1H, J = 5.1, 8.4 Hz, C5-H). MS *m/z* (%): 266 (M^+, 31), 249 (M^+-OH, 60), 238 (M^+-CO, 67), 210 (M^+-2CO, 67), 193 (M^+-OH-2CO, 40), 182 (M^+-3CO, 31), 109 (M^+-OH-$Fe(CO)_3$, 100). *Anal* Calcd for $C_{11}H_{14}FeO_4$: C, 49.66; H, 5.30. Found: C, 49.74; H, 5.35.

(4*S*,4*E*,6*E*)-Tricarbonyliron[(η^4-4-7)-4,6-octadien-3-one] (+)-(13) To a stirred solution of **11** (83.8 mg, 0.315 mmol) in dry THF (2 ml) was added slowly a 0.96 M solution of *n*-propylmagnesium bromide (0.36 ml, 0.347 mmol) in THF at 0 °C under an argon atmosphere. After 15 min, 1,1'-(azodicarbonyl)-dipiperidine (159 mg, 0.630 mmol) was added at once to the reaction mixture at 0 °C, and then the mixture was stirred at 0 °C for 30 min. After quenched with brine, the mixture was extracted with ether. The extract was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was diluted with a mixture of hexane and AcOEt (1/1) and the suspension was filtered through a pad of silica gel. The filtrate was concentrated *in vacuo* and the resulting residue was purified by column chromatography (SiO_2, hexane/AcOEt = 5/1) to give (+)-**13** (53.7 mg, 65%) and **11** (25.7 mg, 31%). (+)-**13**; yellow crystals: $[\alpha]_D^{28}$ +407 (c = 0.61, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ: 1.08 (t, 3H, J = 7.4 Hz, C1-H), 1.24 (d, 1H, J = 8.1 Hz, C4-H), 1.47 (d, 3H, J = 5.7 Hz, C8-H), 1.53 (m, 1H, C7-H), 2.39 (m, 2H, C2-H), 5.25 (dd, 1H, J = 4.9, 7.8 Hz, C6-H), 5.80 (dd, 1H, J = 4.9, 8.1 Hz, C5-H). MS *m/z* (%): 265 (M^++1, 100), 236 (M^+-CO, 38), 208 (M^+-2CO, 69), 180 (M^+-3CO, 42). HRMS Calcd for $C_{11}H_{13}FeO_4$: 265.0164. Found: 265.0170.

(4*R*,4*E*,6*E*)-Tricarbonyliron[(η^4-4-7)-4,6-octadien-3-one] (−)-13 The ketone (−)-**13** (9.1 mg, 76 %) was synthesized from **12** (12.0 mg, 0.045 mmol) by the same procedure as (+)-**13**. (−)-**13**; yellow crystals: $[\alpha]_D^{28}$ −404 (c = 0.54, CH_2Cl_2).

(2*R*,5*S*,6*S*,2*E*,4*E*)-Tricarbonyliron[(η^4-2-5)-6-hydroxyocta-2,4-dienyl] (*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetate General procedure for synthesis of MTPA derivatives of **2a-c:** To a solution of **2a** (11.8 mg, 0.042 mmol) in MeOH (0.5 ml) was added $NaBH_4$ (1.6 mg, 0.042 mmol) at room temperature. After 5 min, the solvent was removed under reduced pressure, and the residue was diluted with AcOEt. The organic phase was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. To a solution of the residue in CH_2Cl_2 (0.75 ml) were added (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (MTPA-Cl) (8.6 μl, 0.046 mmol), Et_3N (6.4 μl, 0.046 mmol) and DMAP (1.4 mg, 0.012 mmol). After being stirred for 30 min, the mixture was concentrated *in vacuo*. The residue was purified by preparative TLC (SiO_2, hexane/AcOEt = 2/1), giving (*R*)-MTPA derivative of **2a** (11.2 mg, 53%). a yellow oil : ^{1}H NMR ($CDCl_3$) δ: 1.00 (t, 3H, *J* = 7.3 Hz, C8-H), 1.06 (td, 1H, *J* = 5.8, 8.5 Hz, C2-H), 1.18 (dd, 1H, *J* = 7.7, 7.7 Hz, C5-H), 1.57 (br s, 1H, OH), 1.49-1.72 (m, 2H, C7-H), 3.46 (dt, 1H, *J* = 3.4, 7.7 Hz, C6-H), 3.55 (s, 3H, OMe), 4.28 (dd, 1H, *J* = 9.0, 11.5 Hz, C1-H), 4.37 (dd, 1H, *J* = 5.8, 11.5 Hz, C1-H), 5.30 (dd, 1H, *J* = 5.1, 7.7 Hz, C4-H), 5.35 (dd, 1H, *J* = 5.1, 8.5 Hz, C3-H), 7.39-7.51 (m, 5H, Ar-H). IR (KBr): 2996, 2051 (CO), 1984 (CO), 1970 (CO), 1747 (C=O), 1170 (CF_3) cm^{-1}. MS *m/z* (%): 414 (M^+-3CO, 43), 396 (90), 189 (52), 108 (100), 79 (100). HRMS Calcd for $C_{18}H_{21}F_3FeO_4$ (M^+-3CO): 414.0741. Found: 414.0732.

(2*R*,5*S*,6*S*,2*E*,4*E*)-Tricarbonyliron[(η^4-2-5)-6-hydroxyocta-2,4-dienyl] (*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetate (*S*)-MTPA derivative of **2a** (16.4 mg, 67%) was synthesized from **2a** (13.8 mg, 0.049 mmol), (*S*)-MTPA-Cl (10.0 μl, 0.054 mmol), Et_3N (7.5 μl, 0.054 mmol) and DMAP (1.6 mg, 0.013 mmol) by the same procedure as (*R*)-MTPA derivative of **2a**. a yellow oil : ^{1}H NMR ($CDCl_3$) δ: 1.00 (t, 3H, *J* = 7.7 Hz, C8-H), 0.98-1.05 (m, 1H, C2-H), 1.18 (dd, 1H, *J* = 7.7, 8.1 Hz, C5-H), 1.57 (br s, 1H, OH), 1.51-1.58 (m, 1H, C7-H), 1.72 (dq, 1H, *J* = 3.4, 7.7 Hz, C7-H), 3.44-3.49 (m, 1H, C6-H), 3.55 (s, 3H, OMe), 4.27 (dd, 1H, *J* = 9.0, 11.5 Hz, C1-H), 4.39 (dd, 1H, *J* = 5.6, 11.5 Hz, C1-H), 5.33 (dd, 1H, *J* = 5.1, 7.7 Hz, C4-H), 5.37 (dd, 1H, *J* = 5.1, 8.5 Hz, C3-H), 7.39-7.41 (m, 3H, Ar-H), 7.51 (m, 2H, Ar-H). IR (KBr): 3700 (OH), 2052 (CO), 1983 (CO), 1747 (C=O), 1170 (CF_3) cm^{-1}. MS *m/z* (%): 414 (M^+-3CO, 14), 396 (27), 189 (50), 108 (100). HRMS Calcd for $C_{18}H_{21}F_3FeO_4$ (M^+-3CO): 414.0741. Found: 414.0743.

(2*R*,5*S*,6*S*,2*E*,4*E*)-Tricarbonyliron[(η^4-2-5)-6-hydroxyundea-2,4-dienyl] (*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetate (*R*)-MTPA derivative of **2b** (7.6 mg, 68%) was synthesized from **2b** (6.7 mg, 0.022 mmol), (*R*)-MTPA-Cl (5.8 μl, 0.030 mmol), and DMAP (2.5 mg, 0.021 mmol) by the same procedure as (*R*)-MTPA derivative of **2a**. a yellow oil : ^{1}H NMR ($CDCl_3$) δ: 0.90 (m, 3H, C11-H), 1.06 (m, 1H, C5-H), 1.19 (m, 1H, C2-H), 1.26-1.50 (m, 6H, C8, 9, 10-H), 1.51-1.53 (m, 2H, C7-H, OH), 1.60-1.67 (m, 1H, C7-H), 3.50 (m, 1H, C6-H), 3.55 (s, 3H, OMe), 4.28 (dd, 1H, *J* = 8.5, 11.6 Hz, C1-H), 4.37 (dd, 1H, *J* = 5.5, 11.6 Hz, C1-H), 5.29 (dd, 1H, *J* = 4.9, 7.9 Hz, C3-H), 5.35 (dd, 1H, *J* = 4.9, 8.5 Hz, C4-H), 7.40 (m, 3H, Ar-H), 7.50 (m, 2H, Ar-H). IR (KBr): 3348 (OH), 2933, 2052 (CO), 1984 (CO), 1742 (C=O), 1170 (CF_3) cm^{-1}. MS *m/z* (%): 457 (M^++1-3CO, 2), 439 (6), 189 (17), 79 (100). HRMS Calcd for $C_{21}H_{27}F_3FeO_4$ (M^+-3CO): 456.1210. Found: 456.1200.

(2*R*,5*S*,6*S*,2*E*,4*E*)-Tricarbonyliron[(η^4-2-5)-6-hydroxyundea-2,4-dienyl] (*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetate (*S*)-MTPA derivative of **2b** (4.3 mg, 72%) was synthesized from **2b** (3.6 mg, 0.011 mmol)), (*S*)-MTPA-Cl (2.3 μl, 0.012 mmol), and DMAP (1.6 mg, 0.013 mmol) by the same procedure as (*R*)-MTPA derivative of **2a**. a yellow oil : ^{1}H NMR ($CDCl_3$) δ: 0.90 (t, 3H, *J* = 7.3 Hz, C11-H), 1.06 (m, 1H, C5-H), 1.19 (m, 1H, C2-H), 1.31-1.56 (m, 7H, C8, 9, 10-H, OH), 1.60-1.68 (m, 2H, C7-H), 3.52 (ddd, 1H, *J* = 3.1, 7.9, 7.9 Hz, C6-H), 3.56 (s, 3H, OMe), 4.27 (dd, 1H, *J* = 8.5, 11.6 Hz, C1-H), 4.39 (dd, 1H, *J* = 5.5, 11.6 Hz, C1-H), 5.33 (dd, 1H, *J* = 4.9, 7.3 Hz, C3-H), 5.36 (dd, 1H, *J* = 4.9, 7.9 Hz, C4-H), 7.40 (m, 3H, Ar-H), 7.51 (m, 2H, Ar-H),. IR (KBr): 3403 (OH), 2922, 2052 (CO), 1986 (CO), 1747 (C=O), 1171 (CF_3) cm^{-1}. MS *m/z* (%): 457 (M^++1-3CO, 4.3), 439 (11), 150 (100). HRMS Calcd for $C_{21}H_{27}F_3FeO_4$ (M^+-3CO): 456.1210. Found: 456.1793.

(2*R*,5*S*,6*S*,2*E*,4*E*)-Tricarbonyliron[(η^4-2-5)-6-hydroxyhepta-2,4-dienyl] (*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetate (*R*)-MTPA derivative of **2c** (4.8 mg, 52%) was synthesized from **2c**

(5.0 mg, 0.019 mmol), (*R*)-MTPA-Cl (4.6 μl, 0.025 mmol), Et_3N (4.0 μl, 0.025 mmol) and DMAP (0.2 mg, 0.003 mmol) by the same procedure as (*R*)-MTPA derivative of **2a**. a yellow oil : ^{1}H NMR ($CDCl_3$) δ: 1.09 (td, 1H, *J* = 6.0, 8.6 Hz, C2-H), 1.14 (dd, 1H, *J* = 8.1, 8.1 Hz, C5-H), 1.36 (t, 3H, *J* = 6.0 Hz, C7-H), 1.49 (d, 1H, *J* = 6.8 Hz, OH), 3.55 (s, 3H, OMe), 3.63-3.68 (m, 1H, C6-H), 4.29 (dd, 1H, *J* = 8.6, 12.0 Hz, C1-H), 4.37 (dd, 1H, *J* = 5.1, 12.0 Hz, C1-H), 5.28-5.33 (m, 2H, C3, 4-H), 7.38-7.51 (m, 5H, Ar-H). IR (KBr): 2797, 2054 (CO), 1984 (CO), 1747 (C=O), 1170 (CF_3) cm^{-1}. MS *m/z* (%): 400 (M^+-3CO, 15), 382 (18), 189 (13), 94 (100), 79 (52). HRMS Calcd for $C_{17}H_{19}F_3FeO_4$ (M^+-3CO): 400.0584. Found: 400.0583.

(2*R*,5*S*,6*S*,2*E*,4*E*)-Tricarbonyliron[(η^4-2-5)-6-hydroxyhepta-2,4-dienyl] (*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetate (*S*)-MTPA derivative of **2c** (6.6 mg, 73%) was synthesized from **2c** (7.7 mg, 0.019 mmol), (*S*)-MTPA-Cl (8.1 μl, 0.044 mmol), Et_3N (6.1 μl, 0.044 mmol) and DMAP (0.4 mg, 0.004 mmol) by the same procedure as (*R*)-MTPA derivative of **2a**. a yellow oil : ^{1}H NMR ($CDCl_3$) δ: 1.04-1.08 (m, 1H, C2-H), 1.18 (dd, 1H, *J* = 7.0, 7.7 Hz, C5-H), 1.36 (t, 3H, *J* = 7.7 Hz, C7-H), 1.57 (br s, 1H, OH), 3.55 (s, 3H, OMe), 3.66 (dq, 1H, *J* = 6.4, 7.0 Hz, C6-H), 4.27 (dd, 1H, *J* = 9.0, 11.9 Hz, C1-H), 4.39 (dd, 1H, *J* = 5.1, 11.9 Hz, C1-H), 5.33 (m, 2H, C3, 4-H), 7.37-7.56 (m, 5H, Ar-H). IR (KBr): 3300 (OH), 2052 (CO), 1986 (CO), 1747 (C=O), 1170 (CF_3) cm^{-1}. MS *m/z* (%): 400 (M^+-3CO, 8.2), 189 (13), 94 (100), 79 (52). HRMS Calcd for $C_{17}H_{19}F_3FeO_4$ (M^+-3CO): 400.0584. Found: 400.0587.

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