Excellent Chiral Introduction by Diene Iron-Tricarbonyl Moiety. III[1]: Asymmetric Synthesis of Hydroxyethylidene Dipeptide Isostere Using a Diastereoselective 1,2-Nucleophilic Addition of Organocerium Reagents into a 1-Azatriene $Fe(CO)_3$ Complex

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Received December 11, 1995; accepted January 23, 1996

A 1-iminobutadiene-iron tricarbonyl [$Fe(CO)_3$] complex (1) reacts with various organometallic nucleophiles in a stereoselective manner, and especially, by use of organocerium reagents, only single secondary amine complexes (2) were obtained in good yields. Application of this methodology was demonstrated in the asymmetric synthesis of hydroxyethylidene dipeptide isostere from the chiral starting material *N*-{(2*R*)-(2*E*)-tricarbonyl[2-5-η-2,4-pentadienylidene]iron} benzylamine (1b).

Key words 1,2-nucleophilic addition; 1-azatriene iron-tricarbonyl complex; organocerium reagent; 1,4-functionalization; iodocyclocarbamation; hydroxyethylidene dipeptide isostere

The diastereoselective addition of organometallic reagents to the C=N double bond of chiral imines offers an attractive approach for the asymmetric synthesis of chiral amine.[2] Thus far, numerous stereoselective nucleophilic additions into the chiral imines derived from 1-phenylethylamine[3] and amino acid derivatives[4,5] as a chiral auxiliary have been reported.

In connection with our program aimed at the development of a highly stereoselective reaction mediated by a diene iron tricarbonyl complex, which can be easily removed by oxidative decomplexation, converted to various functional groups, and expected to induce high stereoselectivity,[6] we investigated the diastereoselective nucleophilic addition of several organometallics to an 1-iminodiene complex (**1**).

Recently, acyclic and functionalized diene-iron tricarbonyl complexes have been demonstrated to be valuable intermediates in organic synthesis to construct stereogenic centers utilizing the chirality of an iron tricarbonyl moiety.[6] Concerning the stereoselectivity of the 1,2-nucleophilic additions to the C=O double bond, it has been manifested that organometallic reagents react with dienone iron tricarbonyl complexes stereoselectively,[7] but those reagents generally offer a diastereomixture of secondary alcohols in reaction with dienal complexes.[8] On the other hand, there have been no reports on the stereoselectivity of the nucleophilic addition of organometallics into the 1-imino-diene complex (**1**). The point of this work is to determine whether such addition to imine complexes occurs stereoselectively or not. In addition, the resulting amine complex (**2**) and its decomplexed product (**3**) seem to be versatile intermediates for the synthesis of several alkaloids bearing a diene moiety such as clavepictin B[9] and for the subsequent transformation utilizing a diene moiety such as an electrophile-mediated cyclization reaction and Diels-Alder reaction[10] (Chart 1). If stereo- and regiocontrolled β-hydroxylation of the acyclic diene moiety can be achieved by intramolecular iodocarbamation reaction, this methodology would be very effective for the synthesis of biologically active α,β-amino alcohol

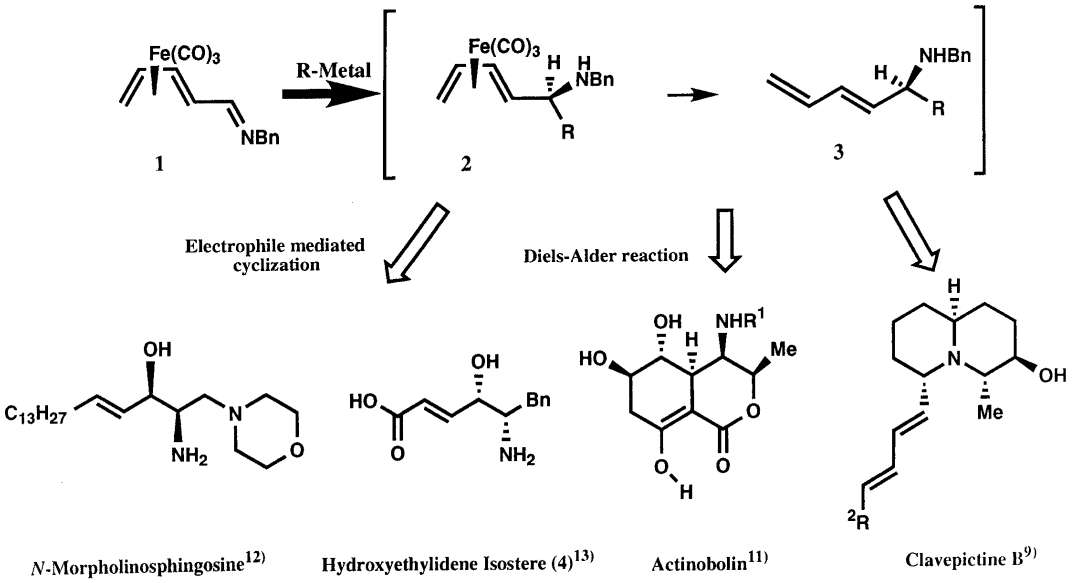

Chart 1

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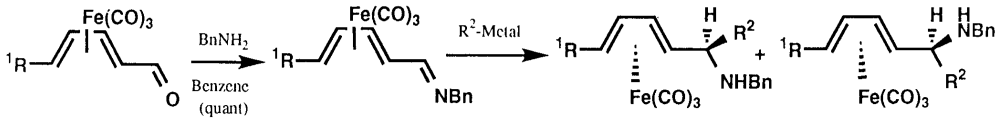
bearing a C=C double bond such as sphingosine derivatives,[12] and hydroxyethylidene dipeptide isostere[13] (Chart 1). In this paper, we report the stereoselective nucleophilic addition of organocerium reagents ($RCeCl_2$ or $RMgX\text{-}CeCl_3$) to the 1-imino-diene complex (**1**), resulting in (1*RS*,2*SR*)-amine complexes (**2**), as well as its application to the asymmetric synthesis of a hydroxyethylidene dipeptide isostere (**4**) by the use of intramolecular iodocarbamation cyclization as a key step.[14]

Results and Discussion

Racemic 1-imino-diene complexes (**1a**[6g] and **1b**) were prepared by the condensation of known dienal complexes[15] and benzylamine in the presence of molecular sieves 4A in benzene at room temperature. The results of the 1,2-nucleophilic addition of several organometallics to **1a, b** are summarized in Table 1. Whereas the reaction of **1a** with organolithium, Grignard reagent and aluminumate complex gave *ψ-endo* **2a** and *ψ-endo* **2b** in a highly diastereoselective manner, respectively, these reagents are not suitable for the aimed reaction because of the low chemical yield (entries 2—4). Therefore, we next examined the reaction of **1a** with none-basic organometallic reagents. Diallylcuprate reagent[16] reacted with **1a** smoothly in tetrahydrofuran (THF) at −78 °C to afford a separable epimeric mixture of *ψ-endo* **2b** and *ψ-exo* **2b** in moderate yield and stereoselectivity (entry 5). On the other hand, treatment of **1a** with *n*-butylcerium reagent,[17a] prepared *in situ* from *n*-butyllithium and cerium(III) chloride ($CeCl_3$) at −78 °C for 30 min, provided the alkylated secondary amine complex (*ψ-endo* **2a**) not only in good yield (74%) but also with excellent diastereoselectivity (entry 6). Similarly, the exposure of methyl- and phenyl-cerium reagents as nucleophiles to **1a, b** provided the corresponding amine complexes (**2c—e**) in good yields and in a highly stereoselective manner, respectively (entries 7—9). It is worthy to note that the organocerium reagents can be replaced by the mixing system[17b] prepared from the corresponding Grignard reagents (5 eq) and $CeCl_3$ (5 eq) without loss of stereoselectivity (entries 10—13). However, a switch in metal species from cerium to ytterbium decreased the chemical yield (entry 14). Therefore, the most successful organometallic reagents in the nucleophilic attack to the imine complexes were usually organocerium derivatives. The diastereomeric purity of **2a—f** (entries 2—4, 6—14) was determined by their 500 MHz ^{1}H-NMR spectra. The stereochemistries of the secondary amines (*ψ-endo* **2b** and *ψ-exo* **2b**) were predicted from *Rf* values according to Lillya's method,[18a] which had been applied to secondary alcohols. They proposed that since the hydroxy group of the *ψ-endo* isomer is sterically shielded by a $Fe(CO)_3$ moiety, the *Rf* value of the *ψ-endo* isomer is higher than that of the *ψ-exo* isomer. We applied this method to the secondary amine complexes (*ψ-endo* **2b** and *ψ-exo* **2b**).[18b] We estimated that the major product (less polar) was a *ψ-endo* isomer from the *Rf* values of the products (*ψ-endo* **2b**; *Rf* 0.30, *ψ-exo* **2b**; *Rf* 0.15, AcOEt : hexane = 1 : 10). Those of the other secondary amine complexes (**2a, c—f**) were estimated, as shown in Table 1, from a mechanistic analogy of **2b**.

In order to definitely determine the relative configurations of the resultant secondary amines, we planned the asymmetric synthesis of the hydoxyethylidene dipeptide isostere (**4**). The hydroxyethylidene dipeptide isostere (**4**) first reported by Hanson and Lindberg is an interesting dipeptide analog which was designed to restrict conformational flexibility and to be susceptible to an attack of

Table 1. Diastereoselective Addition of Organometallic Reagents to 1-Iminodiene-iron Complex (**1**)



1a, b
1a: R^1 = Me, **1b**: R^1 = H

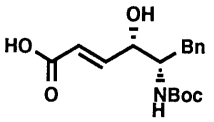
Ψ-endo **2a—f** *Ψ-exo* **2b**
2a: R^1 = Me, R^2 = *n*-Bu, **2b**: R^1 = Me, R^2 = allyl,
2c: R^1 = Me, R^2 = Me, **2d**: R^1 = Me, R^2 = Ph,
2e: R^1 = H, R^2 = Me, **2f**: R^1 = H, R^2 = Ph

Entry	Substrate	R^2-Metal	Product	Yield (%)[a] (*Ψ-endo* : *Ψ-exo*)	de[b] (%)
1	**1a**	*n*-BuLi	—	0 : 0	—
2	**1a**	*n*-BuLi, BBr_3	**2a**	46 : 0[c]	100
3	**1a**	(allyl)MgBr	**2b**	40 : 0[c]	100
4	**1a**	(allyl)$AlEt_3$MgBr	**2b**	30 : 0[c]	100
5	**1a**	$(allyl)_2CuMgBr \cdot BF_3$	**2b**	46 : 16	48
6	**1a**	*n*-$BuCeCl_2$	**2a**	74 : 0	100
7	**1a**	$MeCeCl_2$	**2c**	69 : 0	100
8	**1b**	$MeCeCl_2$	**2e**	62 : 0	100
9	**1a**	$PhCeCl_2$	**2d**	57 : 0	100
10	**1a**	MeMgBr, $CeCl_3$	**2c**	70 : 0	100
11	**1a**	PhMgBr, $CeCl_3$	**2d**	95 : 0	100
12	**1b**	PhMgBr, $CeCl_3$	**2f**	80 : 0	100
13	**1a**	(allyl)MgBr, $CeCl_3$	**2b**	79 : 0	100
14	**1a**	(allyl)MgBr, $YbCl_3$	**2b**	41 : 0[c]	100

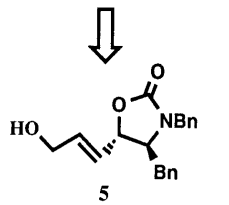
a) Isolated yields. *b*) Determined by 500 MHz ^{1}H-NMR spectra. *c*) Recovery of the starting material (30—51%) as an aldehyde after SiO_2 column.

enzyme nucleophiles such as cysteine thiol.[13] Moreover, it is not only incorporated in renin inhibitor but is also a key intermediate in the synthesis of *trans* alkene dipeptide isosteres, which are important components of peptidomimetic analogs of enkephalin, substance P and protein kinase inhibitor.[19]

The retrosynthetic analysis is illustrated in Chart 2. In turn, the synthetic precursor (**5**) of **4** can be easily derived from **6** by the iodocyclocarbamation reaction, recently developed by us[20] for regio- and stereocontrolled 1,4-functionalization of an acyclic 1,3-diene system. Furthermore, **6** can be available from **2g** by oxidative decomplexation and protection of the amino group. Employing the stereoselective 1,2-nucleophilic addition reaction described above, **2g** would be synthesized from the chiral imine complex (**1b**).



Hydroxyethylidene Isostere (**4**)



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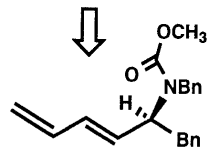

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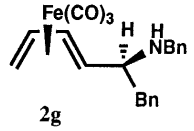
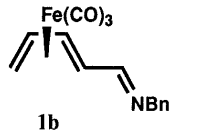


2g



1b

Chart 2

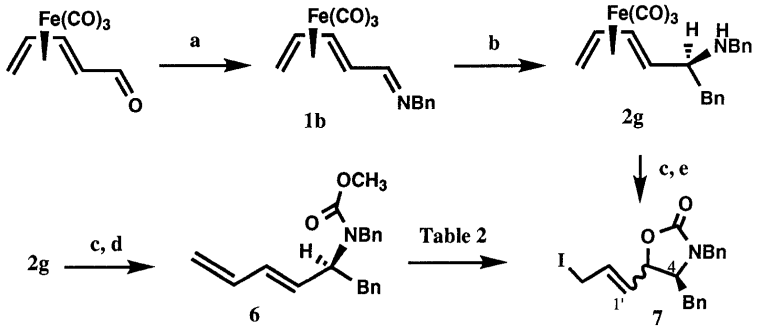
A chiral imine complex (**1b**) was synthesized from a known chiral pentadienal complex[6a] in the same manner as racemates (**1b**) (Chart 3). The exposure of **1b** on the diastereoselective nucleophilic addition of benzylcerium reagents gave rise to the desired amine complex (**2g**) as a single isomer in high yield. We investigated the stereoselective introduction of the β-hydroxy group into **2g** by the intramolecular iodocarbamation of the methyl carbamate (**6**). The requisite carbamate (**6**) was prepared from **2g** by the following sequence: protection of the amino group with methyl chloroformate and then decomplexation of the iron complex with ammonium cerium(IV) nitrate (CAN) in MeOH at $-40\,^{\circ}C$.

The result of the intramolecular iodocarbamation of **6** is shown in Table 2. The reaction of **6** with *N*-iodosuccinimide (NIS) and iodonium dicollidine perchlorate $[I(coll)_2ClO_4]$[21] proceeded regioselectively, but the desired oxazolidinone (**7**) could not be obtained in a stereoselective manner (entries 1 and 2). On the other hand, the reaction of **6** with iodine (I_2) in CH_2Cl_2 at room temperature gave rise to **7** stereoselectively (entry 3), and furthermore, the addition of potassium iodine (KI) to the reaction mixture promoted the reaction rate to afford **7** in 86% yield (entry 4). The diastereomeric ratio of **7** was estimated by 500 MHz ^{1}H-NMR spectra (*trans*/*cis* = 97/3), and the relative stereochemistry of the major isomer (**7**) was determined to be *trans* by the nuclear Overhauser effect (NOE) enhancement between C4-H and C1′-H.

Table 2. Iodocyclocarbamation of **6**[a]

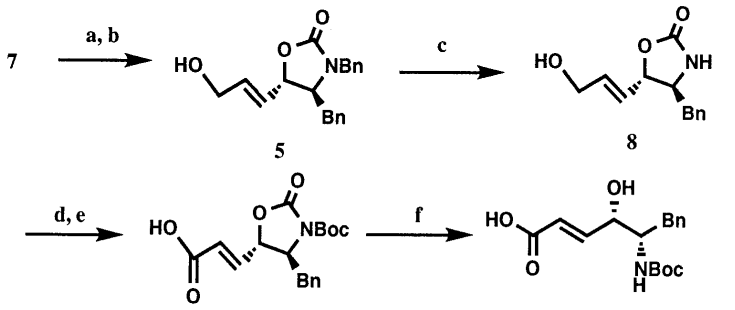
Entry	Reagents	Yield (%)	*trans*-**7** : *cis*-**7**[b]
1	NIS	10	50 : 50
2	$I(coll)_2ClO_4$	20	60 : 40
3	I_2	43	92 : 8
4	I_2, KI	86	97 : 3

a) The reactions were carried out in CH_2Cl_2 at room temperature. *b*) Determined by 500 MHz ^{1}H-NMR.



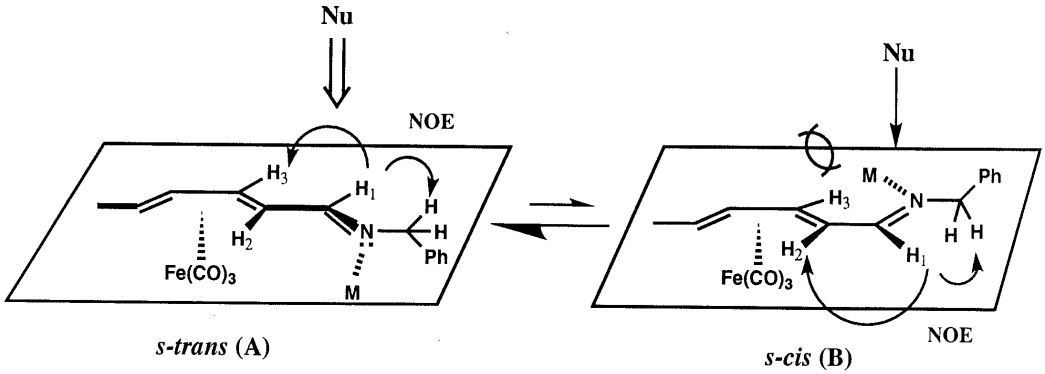
a) $BnNH_2$, MS4A, Benzene, r.t. (quant.); b) BnMgCl, $CeCl_3$, THF, −30°C (90%); c) $ClCO_2CH_3$, K_2CO_3, CH_2Cl_2, r.t., (98%); d) CAN, CH_3CN, −40°C, (91%); e) I_2, KI, CH_2Cl_2, r.t. (90%)

Chart 3



a) AgOAc, DMF, AcOH, r.t.; b) 1.0 M $NaOH_{aq.}$, MeOH, r.t., (94%, 2steps); c) Li, NH_3, THF, −78°C, (94%); d) Jones reagent, acetone, r.t., (84%); e) $(Boc)_2O$, DMAP, Et_3N, THF, r.t., (74%); f) $CsCO_3$, MeOH, r.t. (78%)

Chart 4



M = BBr_3, $CeCl_3$, $YbCl_3$, RMgBr, $RCeCl_2$, $(RAlEt_3)MgBr$

Fig. 1

Moreover, as it was known that the $Fe(CO)_3$ moiety can be removed by treatment with I_2,[22] we investigated the one-pot iodocyclocarbamation from the diene iron complex (**2g**). As expected, the reaction of **2g** with I_2-KI proceeded smoothly to afford **7** in an improved yield without loss of stereoselectivity (Chart 3).

Subsequently, an inseparable mixture of **7** was converted to the alcohol (**5**), namely acetoxylation of **7** with silver acetate was followed by hydrolysis with sodium hydroxide to afford a mixture of *trans*- and *cis*-**5**, from which *trans*-**5** could be separated by recrystallization from isopropyl ether ($^iPr_2O$) (Chart 4). Birch reduction of the isolated alcohol (**5**) gave rise to the debenzyl compound (**8**) in 94% yield. Successive treatment of **8** by Jones oxidation and protection with di-*tert*-butyl dicarbonate gave the acid (**9**), which was converted to the desired hydroxyethyliden dipeptide isostere (**4**) in 78% yield by subjection with cesium carbonate in MeOH. The specific rotation of **4**, $[\alpha]_D^{25}$ −98.2° (c=0.185, MeOH) [lit. $[\alpha]_D^{25}$ −100° (c=0.64, MeOH) for 4*S*,5*S*],[15a] confirms our assignment of an (*S*) configuration at C5 in **4**. Therefore, the stereochemistries of *ψ-endo* **2a**—**f** were determined as shown in Table 1. Here we have achieved the asymmetric synthesis of the hydroxyethylidene dipeptide isostere (**4**) using a diastereoselective 1,2-nucleophilic addition of organocerium reagents into **1b**.

From the stereochemical outcome of the major products, the nucleophilic addition to the imine complexes (**1a, b**) should be explained as follows. Observation of NOE enhancement from the H_1 proton to two olefinic protons (H_2, H_3) and a benzyl proton in **1a** reveals that the imine complex (**1a**) exists as an equilibrium mixture of both conformers (A and B) bearing an (*E*)-imine form, respectively. However, in cases using Lewis acidic organometallic reagents (organoaluminum, organomagnesium, and organocerium derivatives) and also in the presence of Lewis acids such as BBr_3, $CeCl_3$, and $YbCl_3$, the coordinated complex of conformer A by Lewis acid would be more stable than that of conformer B because of the severe steric hindrance between Lewis acid and H_3 in the latter case (Fig. 1). Therefore, nucleophiles attack from the opposite side of the bulky tricarbonyl iron unit in the coordinated conformer A to yield *ψ-endo* **2** stereoselectively. On the other hand, diallylcuprate reagent, of which stereoselective nucleophilic addition to chiral imines proceeded without coordination to the nitrogen atom,[23] adds to the C=N double bond of both conformers (A and B) from the upper side, resulting in the diastereomixture of *ψ-endo* **2b** and *ψ-exo* **2b**.

In conclusion, considering of the perfect diastereoselectivity, our method might be one of the best tools to synthesize optically active natural products containing a nitrogen atom. In practice, this method was applicated to the asymmetric synthesis of hydroxyethylidene dipeptide isostere.

Experimental

All melting points were determined using a Yanagimoto MP-21 melting point apparatus and are uncorrected. 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.

(1*RS*,2*SR*,5*RS*)-(2*E*,4*E*)-Tricarbonyl[2-5-η-*N*-benzyl-1-butyl-2,4-hexadienylamine]iron (ψ-*endo* 2a) Table 1, entry 2; Boron tribromide (29.9 μl, 0.317 mmol) was added to a solution of **1a** (34.3 mg, 0.105 mmol) in toluene (1 ml) at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 30 min. The mixture was allowed to cool to −78 °C. A solution of *n*-butyllithium (0.328 ml, 1.6 M) in *n*-hexane was added to the mixture at −78 °C. The mixture was stirred at −78 °C for 15 min, and then the reaction was quenched with 10% NaOH 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 = 10 : 1) to give ψ-*endo* **2a** (17.6 mg, 46%) as a yellow oil and (2*E*,4*E*)-tricarbonyl[2-5-η-hexadienal]iron (8.2 mg, 32%). ^{1}H-NMR ($CDCl_3$) δ: 0.92 (t, 3H, J = 7.1 Hz, C4′-H), 1.13 (m, 2H, C2-H and C5-H), 1.26—1.77 (m, 7H, C1′-H, C2′-H, C3′-H and NH), 1.40 (d, 3H, J = 6.0 Hz, C6-H), 2.36 (m, 1H, C1-H), 3.71 (d, 1H, J = 12.6 Hz, PhCH$_a$), 3.83 (d, 1H, J = 12.6 Hz, PhCH$_b$), 5.04 (dd, 1H, J = 5.0, 8.6 Hz, C3-H or C4-H), 5.12 (dd, 1H, J = 5.0, 8.8 Hz, C3-H or C4-H), 7.23—7.36 (m, 5H, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 14.1(C4′), 19.1 (C6), 23.0 (C3′), 27.8 (C2′), 36.1 (C1′), 52.0 (PhCH$_2$), 58.2 (C5), 61.6 (C1), 69.1 (C2), 82.2 (C3), 84.9 (C4), 126.9 (Ar), 128.1 (Ar), 128.4 (Ar), 140.4 (Ar-quarternary), 212.3 (CO). IR ($CHCl_3$): 3200—3300, 2960, 2940, 2100 (CO), 1980 (CO), 1450 cm^{-1}. MS *m/z* (%): 383 (M^+, 0.63), 299 (100), 186 (28). HRMS Calcd for $C_{20}H_{25}FeNO_3$: 383.1184. Found: 383.1191.

(1*RS*,2*SR*,5*RS*)-(2*E*,4*E*)-Tricarbonyl[2-5-η-1-allyl-*N*-benzyl-2,4-hexadienylamine]iron (ψ-*endo* 2b) Table 1, entry 3: A solution of allylmagnesium bromide (0.148 mmol, 1.75 M) in Et_2O was added to a solution of **1a** (27.4 mg, 0.0843 mmol) in Et_2O (1 ml) at −78 °C under a nitrogen atmosphere. The mixture was allowed to warm to −30 °C. The mixture was stirred at −30 °C for 1 h, and then the reaction was quenched with water. 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 = 10 : 1) to give ψ-*endo* **2b** (12.3 mg, 40%) and (2*E*,4*E*)-tricarbonyl[2-5-η-hexadienal]iron (5.9 mg, 30%).

Table 1, entry 4: A solution of allylmagnesium bromide (0.311 mmol, 1.0 M) in Et_2O was added to a solution of Et_3Al (0.340 ml, 0.91 M) in *n*-hexane at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 30 min. A solution of **1a** (20.2 mg, 0.0622 mmol) in THF (1 ml) was added to the mixture at −78 °C for 3 h. The mixture was allowed to warm to 0 °C for 5 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 ψ-*endo* **2b** (6.8 mg, 30%) and (2*E*,4*E*)-tricarbonyl-[2-5-η-hexadienal]iron (7.5 mg, 51%).

Table 1, entry 14: Anhydrous $YbCl_3$ (94.3 mg, 0.317 mmol) was placed in a two-necked flask and heated at 140 °C under 0.1 mmHg for 4 h. While the flask was still hot, argon gas was introduced. The flask was cooled in an ice-bath and THF (1 ml) was introduced *via* a syringe. The flask was then placed in an ultrasonic bath (Bransonic B2200) at room temperature for 1 h. The resulting white slurry was then cooled to 0 °C, a solution of allylmagnesium bromide in Et_2O (0.317 ml, 1.0 M) was added to the mixture at −78 °C. The mixture was stirred at 0 °C for 5 min. The mixture was cooled to −78 °C, and then a solution of **1a** (21.5 mg, 0.0662 mmol) in THF (1 ml) was added to the mixture. The resulting 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 ψ-*endo* **2b** (10.0 mg, 41%) as a yellow oil and (2*E*,4*E*)-tricarbonyl[2-5-η-hexadienal]iron (5.0 mg, 32%). ^{1}H-NMR ($CDCl_3$) δ: 1.07 (dd, 1H, J = 8.5, 8.5 Hz, C2-H), 1.13 (qd, 1H, J = 6.4, 9.0 Hz, C5-H), 1.40 (d, 3H, J = 6.4 Hz, C6-H), 1.49 (br s, 1H, NH), 2.26 (m, 1H, C1′-H$_a$), 2.43 (m, 2H, C1′-H$_b$ and C1-H), 3.77 (d, 1H, J = 12.4 Hz, PhCH$_a$), 3.85 (d, 1H, J = 12.4 Hz, PhCH$_b$), 5.04 (dd, 1H, J = 5.1, 9.0 Hz, C4-H), 5.09 (m, 3H, C3′-H and C3-H), 5.83 (m, 1H, C2′-H), 7.25—7.35 (m, 5H, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 19.0 (C6), 41.2 (C1′), 52.0 (PhCH$_2$), 58.2 (C5), 61.2 (C1), 67.8 (C2), 82.0 (C3), 85.1 (C4), 117.7 (C3′), 127.0 (Ar), 128.1 (Ar), 134.8 (C2′), 140.2 (Ar-quarternary), 212.2 (CO). IR ($CHCl_3$): 3500—3300 (NH), 3100—2900, 2050 (CO), 1980 (CO) cm^{-1}. MS *m/z* (%): 367 (M^+, 0.13), 283 (100), 186 (20). HRMS Calcd for $C_{17}H_{21}FeNO$: 311.0972. Found: 311.0987. CIMS *m/z* (%): 368.0 ($M^+ + 1$, 26), 69.0(100).

(1*RS*,2*SR*,5*RS*)-(2*E*,4*E*)-Tricarbonyl[2-5-η-1-allyl-*N*-benzyl-2,4-hexadienylamine]iron (ψ-*endo* 2b) and (1*RS*,2*RS*,5*SR*)-(2*E*,4*E*)-Tricarbonyl[(2-5-η-1-allyl-*N*-benzyl-2,4-hexadienyl-amine]iron (ψ-*exo* 2b) Table 1, entry 5: A solution of allylmagnesium bromide (0.293 ml, 1.75 M) in Et_2O was added to a suspension of CuI (48.9 mg, 0.257 mmol) in THF (1 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. $BF_3 \cdot Et_2O$ (94.8 μl, 0.771 mmol) was added to the mixture at −78 °C. The mixture was stirred at −78 °C for 10 min. A solution of **1a** (27.8 mg, 0.0855 mmol) in THF (1 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 ψ-*endo* **2b** (14.4 mg, 46%) and ψ-*exo* **2b** (4.9 mg, 16%) as a yellow oil. ψ-*exo* **2b**; ^{1}H-NMR ($CDCl_3$) δ: 0.92 (dd, 1H, J = 8.6, 8.6 Hz, C2-H), 1.21 (qd, 1H, J = 6.4, 8.3 Hz, C5-H), 1.25 (br s, 1H, NH), 1.41 (d, 3H, J = 6.4 Hz, C6-H), 2.27 (ddd, 1H, J = 8.3, 8.3, 12.9 Hz, C1′-H$_a$), 2.37 (ddd, 1H, J = 3.4, 8.8, 12.9 Hz, C1′-H$_b$), 2.50 (m, 1H, C1-H), 3.72 (d, 1H, J = 13.0 Hz, PhCH$_a$), 3.94 (d, 1H, J = 13.0 Hz, PhCH$_b$), 5.04 (dd, 1H, J = 5.1, 8.6 Hz, C3-H), 5.07 (dd, 1H, J = 5.1, 8.3 Hz, C4-H), 5.13 (d, 1H, J = 11.1 Hz, C3′-H$_a$), 5.18 (d, 1H, J = 20.1 Hz, C3′-H$_b$), 5.82 (m, 1H, C2′-H), 7.24—7.32 (m, 5H, Ar-H). IR ($CHCl_3$): 3500—3100 (NH), 3100—2900, 2050 (CO), 1980 (CO), 1450 cm^{-1}. MS *m/z* (%): 367 (M^+, 0.050), 283 (100), 186 (24). HRMS Calcd for $C_{19}H_{21}FeNO_3$: 367.0868. Found: 367.0852.

General Procedure for the Reaction of 1a, b with Organocerium Reagents; (1*RS*,2*SR*,5*RS*)-(2*E*,4*E*)-Tricarbonyl[2-5-η-*N*-benzyl-1-methyl-2,4-hexadienylamine]iron (ψ-*endo* 2c) as an Example Method A: Table 1, entry 7: Anhydrous cerium chloride (113 mg, 0.458 mmol) was placed in a two-necked flask and heated at 140 °C under 0.1 mmHg for 4 h. While the flask was still hot, argon gas was introduced. The flask was cooled in an ice-bath, and THF (2 ml) was introduced *via* syringe. The flask was then placed in an ultrasonic bath (Bransonic B2200) at room temperature for 1 h. The resulting white slurry was then cooled to −78 °C, a solution of methyllithium in Et_2O (0.380 ml, 1.2 M) was added to the mixture at −78 °C, and then the mixture was stirred at −78 °C for 30 min. A solution of **1a** (29.8 mg, 0.0917 mmol) in THF (0.5 ml) was added to the mixture at −78 °C, and then the mixture was stirred at −78 °C for 1 h. 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 ψ-*endo* **2c** (21.5 mg, 69%).

Method B: Table 1, entry 10: The white slurry prepared from anhydrous $CeCl_3$ (116 mg, 0.473 mmol) was then cooled to −30 °C. A solution of methylmagnesium bromide in THF (0.473 ml, 1.0 M) was added to the mixture at −30 °C, and then the mixture was stirred at −30 °C for 30 min. A solution of **1a** (30.8 mg, 0.0948 mmol) in THF (0.5 ml) was added to the mixture at −30 °C, and then the mixture was stirred at −30 °C for 1 h. 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 ψ-*endo* **2c** (22.8 mg, 70%) as a yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.10—1.16 (m, 2H,

C2-H and C5-H), 1.24 (d, 3H, J=6.0 Hz, C1-Me), 1.39 (d, 3H, J=6.0 Hz, C6-H), 2.51 (qd, 1H, J=6.0, 8.3 Hz, C1-H), 3.69 (d, 1H, J=13.0 Hz, PhCH_a), 3.85 (d, 1H, J=13.0 Hz, PhCH_b), 5.04 (dd, 1H, J=5.1, 8.5 Hz, C3-H or C4-H), 5.08 (dd, 1H, J=5.1, 8.6 Hz, C3-H or C4-H), 7.24—7.33 (m, 5H, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 19.1 (C1-Me), 23.1 (C6), 51.9 (PhCH$_2$), 56.8 (C1), 58.2 (C5), 70.0 (C2), 81.4 (C3), 85.5 (C4), 127.0 (Ar), 128.0 (Ar), 128.5 (Ar), 140.1 (Ar-quarternary), 212.3 (CO). IR ($CHCl_3$): 3200—3500 (OH), 2900—3000, 2050 (CO), 1990 (CO), 1250 cm^{-1}. MS m/z (%): 341 (M^+, 0.40), 257 (100). HRMS Calcd for $C_{17}H_{19}FeNO_3$: 341.0711. Found: 341.0706.

(1*RS*,2*SR*,5*RS*)-(2*E*,4*E*)-Tricarbonyl[2-5-η-*N*-benzyl-1-butyl-2,4-hexadienylamine]iron (ψ-*endo* 2a) Table 1, entry 6: ψ-*endo* **2a** was obtained from **1a** (39.0 mg, 0.120 mmol) in 74% yield (34.0 mg) using *n*-butylcerium reagent (method A).

(1*RS*,2*SR*)-(2*E*,4*E*)-Tricarbonyl[2-5-η-*N*-benzyl-1-methyl-2,4-pentadienylamine]iron (ψ-*endo* 2e) Table 1, entry 8: ψ-*endo* **2e** was obtained from **1b** (192 mg, 0.619 mmol) in 62% yield (125 mg) using methylcerium reagent (method A) as a yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 0.32 (dd, 1H, J=2.1, 9.0 Hz, C5-H$_c$), 1.16 (dd, 1H, J=8.1, 8.1 Hz, C2-H), 1.28 (d, 3H, J=6.4 Hz, C1-Me), 1.63 (br s, 1H, NH), 1.76 (dd, 1H, J=2.1, 6.8 Hz, C5-H$_t$), 2.60 (qd, 1H, J=6.4, 8.1 Hz, C1-H), 3.74 (d, 1H, J=13.0 Hz, PhCH_a), 3.89 (d, 1H, J=13.0 Hz, PhCH_b), 5.27 (m, 2H, C3-H and C4-H), 7.34 (m, 5H, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 23.1 (C1-Me), 40.2 (C5), 51.7 (PhCH$_2$), 56.6 (C1), 71.1 (C2), 81.6 (C4), 85.7 (C3), 126.9 (Ar), 128.0 (Ar), 128.4 (Ar), 140.0 (Ar-quarternary), 211.5 (CO). IR (KBr): 3030, 2968, 2044 (CO), 1975 (CO) cm^{-1}. MS m/z (%): 327 (M^+, 0.69), 243 (100), 161 (71). *Anal.* Calcd for $C_{16}H_{17}FeNO_3$: C, 58.74; H, 5.24; N, 4.28. Found: C, 58.59; H, 5.32; N, 4.44.

(1*RS*,2*SR*,5*RS*)-(2*E*,4*E*)-Tricarbonyl[2-5-η-*N*-benzyl-1-phenyl-2,4-hexadienylamine]iron (ψ-*endo* 2d) Table 1, entry 9: ψ-*endo* **2d** was obtained from **1a** (30.2 mg, 0.0929 mmol) in 57% yield (21.2 mg) using phenylcerium reagent (method A).

Table 1, entry 11: ψ-*endo* **2d** was obtained from **1a** (29.5 mg, 0.0908 mmol) in 95% yield (34.7 mg) using phenylcerium reagent (method B) as a yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.15 (qd, 1H, J=6.4, 8.6 Hz, C5-H), 1.27 (dd, 1H, J=9.0, 9.0 Hz, C2-H), 1.36 (d, 3H, J=6.4 Hz, C6-H), 3.34 (d, 1H, J=9.0 Hz, C1-H), 3.47 (d, 1H, J=13.5 Hz, PhCH_a), 3.60 (d, 1H, J=13.5 Hz, PhCH_b), 4.98 (dd, 1H, J=4.8, 8.6 Hz, C4-H), 5.09 (dd, 1H, J=4.8, 9.0 Hz, C3-H), 7.21—7.38 (m, 10H, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 19.0 (C6), 51.7 (PhCH$_2$), 58.4 (C5), 66.8 (C1), 69.2 (C2), 81.4 (C3), 85.9 (C4), 126.8 (Ar), 126.9 (Ar), 127.4 (Ar), 128.0 (Ar), 128.3 (Ar), 128.8 (Ar), 140.2 (Ar-quarternary), 144.5 (Ar-quarternary), 212.0 (CO). IR (KBr): 3028, 2924, 2040 (CO), 1979 (CO), 1601, 1493 cm^{-1}. MS m/z (%): 403 (M^+, 0.30), 319 (100), 214 (43). HRMS Calcd for $C_{22}H_{21}FeNO_3$: 403.0868. Found: 403.0855.

(1*RS*,2*SR*)-(2*E*,4*E*)-Tricarbonyl[2-5-η-*N*-benzyl-1-phenyl-2,4-pentadienylamine]iron (ψ-*endo* 2f) Table 1, entry 12: ψ-*endo* **2f** was obtained from **1b** (83.1 mg, 0.267 mmol) in 80% yield (83.8 mg) using phenylcerium reagent (method B) as yellow crystals. mp 58.0—59.0 °C (*n*-hexane). ^{1}H-NMR ($CDCl_3$) δ: 0.31 (dd, 1H, J=1.7, 9.4 Hz, C5-H$_c$), 1.30 (dd, 1H, J=8.5, 8.5 Hz, C2-H), 1.55 (br s, 1H, NH), 1.75 (dd, 1H, J=1.7, 6.8 Hz, C5-H$_t$), 3.40 (d, 1H, J=8.5 Hz, C1-H), 3.47 (d, 1H, J=13.3 Hz, PhCH_a), 3.64 (d, 1H, J=13.3 Hz, PhCH_b), 5.18 (ddd, 1H, J=4.3, 6.8, 9.4 Hz, C4-H), 5.26 (dd, 1H, J=4.3, 8.5 Hz, C3-H), 7.21—7.38 (m, 10H, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 40.5 (C5), 51.6 (PhCH$_2$), 66.7 (C1), 70.2 (C2), 82.2 (C4), 85.8 (C3), 126.9 (Ar), 127.0 (Ar), 127.5 (Ar), 128.0 (Ar), 128.4 (Ar), 128.8 (Ar), 140.1 (Ar-quarternary), 144.3 (Ar-quarternary), 211.4 (CO). IR (KBr): 3028, 2926, 2854, 2044 (CO), 1965 (CO), 1600 cm^{-1}. MS m/z (%): 361 (M^+ − CO, 0.80), 305 (100), 260 (41). *Anal.* Calcd for $C_{21}H_{19}FeNO_3$: C, 64.80; H, 4.92; N, 3.60 Found: C, 64.80; H, 5.17; N, 3.56.

(1*RS*,2*SR*,5*RS*)-(2*E*,4*E*)-Tricarbonyl[2-5-η-*N*-benzyl-1-allyl-2,4-hexadienylamine]iron (ψ-*endo* 2b) Table 1, entry 13: ψ-*endo* **2b** was obtained from **1a** (29.9 mg, 0.0920 mmol) in 79% yield (27.4 mg) using allylcerium reagent (method B).

***N*-{(2*R*)-(2*E*)-Tricarbonyl[2-5-η-2,4-pentadienylidene]iron}benzylamine (1b)** A mixture of (2*R*)-(2*E*)-tricarbonyl[2-5-η-2,4-pentadienal]iron (636 mg, 2.86 mmol), prepared according to the reported procedure,[6a] benzylamine (0.310 ml, 2.86 mmol), molecular sieve 4A (650 mg), and dry benzene (10 ml) was stirred at room temperature for 1.5 h. The concentration of the reaction mixture *in vacuo* gave the desired product (**1b**) (890 mg, 100%) as a yellow oil $[\alpha]_D^{26}$ +28.3° (c=1.09, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.68 (dd, 1H, J=2.7, 9.2 Hz, C5-H$_c$), 1.69 (dd, 1H, J=7.7, 7.7 Hz, C2-H), 1.96 (dd, 1H, J=2.7, 6.8 Hz, C5-H$_t$), 4.54 (s, 2H, PhCH$_2$), 5.37 (ddd, 1H, J=4.7, 6.8, 9.2 Hz, C4-H), 5.75 (dd, 1H, J=4.7, 7.7 Hz, C3-H), 7.23—7.35 (m, 5H, Ar-H), 7.54 (d, 1H, J=7.7 Hz, C1-H). ^{13}C-NMR ($CDCl_3$) δ: 40.5 (C5), 56.7 (C2), 64.3 (PhCH$_2$), 83.4 (C4), 85.8 (C3), 126.5 (Ar), 127.5 (Ar), 128.1 (Ar), 138.7 (Ar-quarternary), 164.3 (C1), 209.9 (CO). IR (KBr): 3062, 3030, 2830, 2052 (CO), 1979 (CO), 1639 (C=N), 1452 cm^{-1}. MS m/z (%): 283 (M^+ − CO, 2.8), 255 (52), 227 (100). HRMS Calcd for $C_{15}H_{13}FeNO_3$: 311.0243. Found: 311.0228.

(1*S*,2*R*)-(2*E*)-Tricarbonyl[2-5-η-1,*N*-dibenzyl-2,4-pentadienyl-amine]-iron (2g) This was prepared by adding the chiral imine (**1b**) (890 mg, 2.86 mmol) to benzylcerium reagent using method B to give **2g** (1.04 g, 90%) as a yellow oil. $[\alpha]_D^{26}$ +40.1° (c=1.01, $CHCl_3$). ^{1}H-NMR (C_6D_6) δ: −0.13 (d, 1H, J=8.6 Hz, C5-H$_c$), 0.78 (dd, 1H, J=8.6, 8.6 Hz, C2-H), 1.15 (br s, 1H, NH), 1.24 (d, 1H, J=6.0 Hz, C5-H$_t$), 2.42 (dd, 1H, J=7.7, 12.8 Hz, PhCH_aC), 2.52 (ddd, 1H, J=5.1, 7.7, 8.6 Hz, C1-H), 2.84 (dd, 1H, J=5.1, 12.8 Hz, PhCH_bC), 3.73 (d, 1H, J=12.8 Hz, PhCH_aN), 3.76 (d, 1H, J=12.8 Hz, PhCH_bN), 4.40 (m, 2H, C3-H and C4-H), 6.95 (d, 2H, J=6.8 Hz, Ar-H), 7.06—7.16 (m, 4H, Ar-H), 7.22 (dd, 2H, J=7.7, 7.7 Hz, Ar-H), 7.37 (d, 2H, J=7.7 Hz, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 40.2 (C5), 43.2 (PhCH$_2$C), 52.1 (PhCH$_2$N), 63.5 (C1), 68.7 (C2), 81.0 (C4), 86.4 (C3), 126.3 (Ar), 127.0 (Ar), 128.0 (Ar), 128.3 (Ar), 128.4 (Ar), 129.7 (Ar), 138.4 (Ar-quarternary), 140.0 (Ar-quarternary), 211.5 (CO). IR (KBr): 3336, (NH) 3028, 2926, 2042 (CO), 1979 (CO), 1597 cm^{-1}. MS m/z (%): 347 (M^+ − 2CO, 14), 320 (23), 319 (100), 228 (39). *Anal.* Calcd for $C_{22}H_{21}FeNO_3$: C, 65.53; H, 5.25; N, 3.47. Found: C, 65.78; H, 5.35; N, 3.44.

(1*S*)-(2*E*)-1,*N*-Dibenzyl-*N*-carbomethoxy-2,4-pentadienylamine (6) Methyl chloroformate (0.51 ml, 6.65 mmol) was added to a solution of **2g** (1.03 g, 2.56 mmol) and K_2CO_3 (1.32 g, 9.58 mmol) in CH_2Cl_2 (35 ml) at 0 °C under a nitrogen atmosphere. The mixture was allowed to warm to room temperature and stirred at room temperature for 3 h. The reaction was quenched with water. The resulting mixture was extracted with CH_2Cl_2. 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 the carbamate (1.15 g, 98%). CAN (620 mg, 1.13 mmol) was added to a solution of the carbamate (174 mg, 0.377 mmol) in CH_3CN (5 ml) at −40 °C under a nitrogen atmosphere. The mixture was stirred at −40 °C for 1 h. The reaction was quenched with saturated $NaHCO_3$ solution. The resulting mixture was extracted with AcOEt. 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 = 20 : 1) to give **6** (110 mg, 91%) as a colorless oil. $[\alpha]_D^{24}$ −20.1° (c=1.53, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 2.86—3.08 (m, 2H), 3.68 (s, 3H, COOMe), 4.19—4.49 (m, 3H), 5.04 (d, 1H, J=10.3 Hz, C5-H), 5.10 (d, 1H, J=17.1 Hz, C5-H), 5.81 (m, 1H, C2-H), 5.94 (dd, 1H, J=10.3, 15.4 Hz, C3-H), 6.22 (ddd, 1H, J=10.3, 10.3, 17.1 Hz, C4-H), 7.17—7.27 (m, 10H, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 39.0 (PhCH$_2$), 49.6 (PhCH$_2$), 52.4 (Me), 61.0 (C1), 117.4 (C5), 126.2, 126.9, 127.3, 127.7, 128.2, 129.1, 132.0, 132.6, 136.2, 138.1 (Ar-quarternary), 138.4 (Ar-quarternary), 156.5 (C=O). IR (KBr): 3028, 2860, 1701 (C=O), 1603 cm^{-1}. MS m/z (%): 322 (M^+ + 1, 1.0), 231 (100). *Anal.* Calcd for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.56; H, 7.20; N, 4.37.

(4*S*,5*S*)-3,4-Dibenzyl-5-[(*E*)-3-iodopropenyl]oxazolidin-2-one and (4*S*,5*R*)-3,4-Dibenzyl-5-[(*E*)-3-iodopropenyl]oxazolidin-2-one (7) Method A: A mixture of **6** (104 mg, 0.325 mmol), I_2 (248 mg, 0.976 mmol), KI (80.9 mg, 0.488 mmol), and CH_2Cl_2 (5 ml) was stirred at room temperature for 12 h. The resulting mixture was extracted with AcOEt. The extract was washed with saturated $Na_2S_2O_3$ solution, water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 5 : 1) to give **7** (118 mg, 84%).

Method B: A mixture of the carbamate iron complex of **2g** (1.00 g, 2.1 mmol), I_2 (2.20 g, 8.68 mmol), KI (0.720 g, 4.34 mmol) and CH_2Cl_2 (35 ml) was stirred at room temperature for 36 h. The resulting mixture was extracted with AcOEt. The extract was washed with saturated $Na_2S_2O_3$ solution, water and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 3 : 1) to give **7** (848 mg, 90%) as a yellow oil. $[\alpha]_D^{26}$ −80.5° (c=0.995, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 2.68 (dd, 97/100 × 1H, J=8.8, 13.8 Hz, PhCH_a), 2.75 (dd, 3/100 × 1H, J=7.9, 14.4 Hz, PhCH_a), 2.94 (dd, 3/100 × 1H, J=6.4, 14.4 Hz, PhCH_b), 3.09 (dd, 97/100 × 1H, J=4.7, 13.8 Hz, PhCH_b), 3.44 (ddd, 97/100 × 1H, J=4.7, 5.6, 8.8 Hz, C4-H),

3.64 (dd, 97/100 × 1H, J=9.4, 15.4 Hz, C3′-H_a), 3.66 (dd, 97/100 × 1H, J=9.4, 15.4 Hz, C3′-H_b), 3.77 (d, 3/100 × 1H, J=15.4 Hz, PhC$\underline{H}_a$N), 3.84 (d, 3/100 × 2H, J=8.1 Hz, C3′-H), 3.96 (ddd, 3/100 × 1H, J=6.4, 6.8, 7.9 Hz, C4-H), 4.07 (d, 97/100 × 1H, J=15.2 Hz, PhC$\underline{H}_a$N), 4.58 (dd, 97/100 × 1H, J=5.6, 5.6 Hz, C5-H), 4.87 (d, total 1H, J=15.2 Hz, PhC$\underline{H}_b$N), 5.14 (dd, 3/100 × 1H, J=6.8, 6.8 Hz, C5-H), 5.26 (dd, 97/100 × 1H, J=5.6, 15.0 Hz, C1′-H), 5.67 (dd, 3/100 × 1H, J=6.8, 15.0 Hz, C1′-H), 5.74 (ddd, 97/100 × 1H, J=9.4, 9.4, 15.0 Hz, C2′-H), 6.04 (td, 3/100 × 1H, J=8.1, 15.0 Hz, C2′-H), 7.03—7.37 (m, 10H, Ar-H). ^{13}C-NMR ($CDCl_3$) major δ: 2.6 (C3′), 38.1 (Ph$\underline{C}H_2$C), 46.1 (Ph$\underline{C}H_2$N), 60.4 (C4), 77.0 (C5), 127.2 (Ar), 127.8 (Ar), 128.8 (Ar), 129.0 (C1′), 131.1 (C2′), 134.9 (Ar-quarternary), 135.4 (Ar-quarternary), 157.1 (C=O). IR (KBr): 3030, 2927, 1751 (C=O), 1495 cm^{-1}. MS m/z (%): 433 (M^+, 0.040), 342 (68), 91 (100). *Anal.* Calcd for $C_{20}H_{20}INO_2$: C, 55.44; H, 4.65; N, 3.23. Found: C, 55.50; H, 4.71; N, 3.20.

(4*S*,5*S*)-3,4-Dibenzyl-5-[(*E*)-3-hydroxy-1-propenyl]oxazolidin-2-one (5) Silver acetate (392 mg, 2.35 mmol) was added to a solution of **7** (848 mg, 1.96 mmol) in DMF–AcOH (1 : 1, 20 ml) at room temperature. The mixture was stirred at room temperature for 1.5 h. The mixture was diluted 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 = 3 : 1) to give the acetate (653 mg, 91%). A solution of NaOH (5.37 ml, 1 N) was added to a solution of the acetate (653 mg, 1.79 mmol) in 25% aqueous MeOH (15 ml) at room temperature. The mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated NH_4Cl 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 recrystallization from $^iPr_2O$ to give **5** (421 mg, 73%) as colorless crystals. mp 111—112 °C ($^iPr_2O$). $[\alpha]_D^{25}$ −75.8° (c=1.00, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.17 (t, 1H, J=6.0 Hz, O$\underline{H}$), 2.69 (dd, 1H, J=8.6, 13.7 Hz, PhC$\underline{H}_a$C), 3.10 (dd, 1H, J=4.7, 13.7 Hz, PhC$\underline{H}_b$C), 3.48 (m, 1H, C4-H), 3.96 (dd, 2H, J=6.0, 6.0 Hz, C3′-H), 4.06 (d, 1H, J=15.0 Hz, PhC$\underline{H}_a$N), 4.59 (dd, 1H, J=6.0, 6.0 Hz, C5-H), 4.86 (d, 1H, J=15.0 Hz, PhC$\underline{H}_b$N), 5.34 (dd, 1H, J=6.0, 15.4 Hz, C1′-H), 5.61 (td, 1H, J=6.0, 15.4 Hz, C2′-H), 7.05 (d, 2H, J=6.8 Hz, Ar-H), 7.20—7.36 (m, 8H, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 38.2 (Ph$\underline{C}H_2$C), 46.2 (Ph$\underline{C}H_2$N), 60.7 (C4), 61.6 (C3′), 78.4 (C5), 125.8 (C1′), 127.0 (Ar), 127.8 (Ar), 127.9 (Ar), 128.6 (Ar), 128.7 (Ar), 129.2 (Ar), 133.9 (C2′), 135.2 (Ar-quarternary), 135.5 (Ar-quarternary), 157.7 (C=O). IR (KBr): 3431 (OH), 3030, 2926, 1743 (C=O), 1443 cm^{-1}. MS m/z (%): 232 (M^+ − Bn, 99), 91 (100). HRMS Calcd for $C_{13}H_{14}NO_3$ (M^+ − Bn): 232.0971. Found: 232.0971. CIMS m/z (%): 324.0 (M^+ + 1, 100).

(4*S*,5*S*)-4-Benzyl-5-[(*E*)-3-hydroxy-1-propenyl]oxazolidin-2-one (8) Lithium (11.0 mg, 1.59 mmol) was added to liquid NH_3 (5 ml) at −78 °C, and the mixture was stirred for 10 min under a nitrogen atmosphere. A solution of **5** (50.3 mg, 0.156 mmol) in THF (1 ml) was added to the resulting solution, and the whole was stirred for 10 min. The reaction was quenched with NH_4Cl, and then the mixture was allowed to warm to room temperature to remove the NH_3. The residue was extracted with AcOEt. The extract was washed with water and brine, dried, and then concentrated *in vacuo*. The residue was purified by preparative TLC to give **8** (34.3 mg, 94%) as colorless crystals. mp 97.5—99.5 °C (benzene). $[\alpha]_D^{25}$ −60.4° (c=0.505, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 2.82 (dd, 1H, J=8.8, 13.7 Hz, PhC$\underline{H}_a$C), 2.94 (dd, 1H, J=5.1, 13.7 Hz, PhC$\underline{H}_b$C), 3.78 (m, 1H, C4-H), 4.18 (d, 2H, J=4.3 Hz, C3′-H), 4.73 (dd, 1H, J=6.8, 6.8 Hz, C5-H), 5.01 (br s, 1H, N$\underline{H}$), 5.76 (dd, 1H, J=6.8, 15.4 Hz, C1′-H), 5.94 (td, 1H, J=4.3, 15.4 Hz, C2′-H), 7.18 (d, 2H, J=7.3 Hz, Ar-H), 7.28—7.36 (m, 3H, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 40.5 (Ph$\underline{C}H_2$), 59.5 (C4), 61.8 (C3′), 81.6 (C5), 125.7 (C1′), 127.1 (Ar), 128.8 (Ar), 129.1 (Ar), 134.6 (C2′), 135.8 (Ar-quarternary), 158.8 (C=O). IR (KBr): 3282 (OH), 3028, 2924, 1751 (C=O), 1456 cm^{-1}. MS m/z (%): 234 (M^+ + 1, 1.9), 142 (100), 70 (99). *Anal.* Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00 Found: C, 67.01; H, 6.47; N, 5.88.

(4*S*,5*S*)-4-Benzyl-3-(*tert*-butyloxy)carbonyl-2-oxooxazolidin-5-(*E*)-propenoic Acid (9) Jones reagent (0.140 ml, 2.7 M) was added to a solution of 8 (44.0 mg, 0.189 mmol) in acetone (2 ml) at room temperature. The mixture was stirred at room temperature for 15 min. The reaction was quenched with isopropanol and the whole mixture was concentrated *in vacuo*. The residue thus obtained was diluted with AcOEt. The organic layer was washed with brine, dried, and then concentrated *in vacuo*. The residue was purified by preparative TLC to give the carboxylic acid (39.0 mg, 84%) as colorless crystals. mp 66.0—68.0 °C (AcOEt–hexane). $[\alpha]_D^{29}$ −54.6° (c=0.980, MeOH). ^{1}H-NMR ($CDCl_3$) δ: 2.95 (m, 2H, PhC$\underline{H}_2$), 3.84 (m, 1H, C4-H), 4.90 (dd, 1H, J=5.1, 6.0 Hz, C5-H), 5.46 (br s, 1H, N$\underline{H}$), 6.08 (d, 1H, J=15.8 Hz, C2′-H), 6.81 (dd, 1H, J=5.1, 15.8 Hz, C1′-H), 7.19 (d, 2H, J=7.3 Hz, Ar-H), 7.29—7.38 (m, 3H, Ar-H). ^{13}C-NMR (CD_3OD) δ: 41.6 (Ph$\underline{C}H_2$), 60.0 (C4), 80.3 (C5), 124.0 (C2′), 128.1 (Ar), 129.7 (Ar), 130.5 (Ar), 136.9 (Ar-quarternary), 143.9 (C1′), 160.4 (CO), 168.7 (COOH). IR (KBr): 3032 (OH), 2922, 1753 (C=O), 1732 (C=O), 1390 cm^{-1}. MS m/z (%): 247 (M^+, 0.43), 156 (38), 92 (100). HRMS Calcd for $C_{13}H_{13}NO_4$: 247.0845. Found: 247.0850.

Et_3N (29.3 μl, 0.210 mmol) was added to a solution of the acid (17.4 mg, 0.0704 mmol) in THF (2 ml) at room temperature, and then the mixture was stirred at room temperature for 1 h. Di-*tert*-butyl dicarbonate (53.7 mg, 0.247 mmol) and 4-dimethylaminopyridine (1.7 mg, 0.014 mmol) was added to the mixture at room temperature, and then the mixture was stirred at 60 °C for 12 h. The reaction was quenched with 0.1 N HCl 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 preparative TLC (MeOH : $CHCl_3$ = 1 : 5) to give **9** (17.9 mg, 74%) as colorless crystals. mp 89.0—91.5 °C (AcOEt–hexane). $[\alpha]_D^{28}$ −28.9° (c=1.56, MeOH). ^{1}H-NMR (CD_3OD) δ: 1.56 (s, 9H, C$\underline{Me}_3$), 3.05 (dd, 1H, J=7.9, 13.4 Hz, PhC$\underline{H}_a$), 3.26 (dd, 1H, J=3.9, 13.4 Hz, PhC$\underline{H}_b$), 4.36 (m, 1H, C4-H), 4.96 (m, 1H, C5-H), 5.83 (d, 1H, J=15.5 Hz, C2′-H), 6.63 (dd, 1H, J=5.3, 15.5 Hz, C1′-H), 7.25—7.36(m, 5H, Ar-H). ^{13}C-NMR (CD_3OD) δ: 28.2 (C$\underline{Me}_3$), 39.4 (Ph$\underline{C}H_2$), 62.0 (C4), 77.0 (C5), 85.8 ($\underline{C}Me_3$), 125.7 (C2′), 128.5 (Ar), 130.0 (Ar), 130.8 (Ar), 136.2 (Ar-quarternary), 142.3 (C1′), 150.7 (CO), 153.6 (CO), 169.3 (COOH). IR (KBr): 2931, 1801 (C=O), 1722 (C=O), 1371 cm^{-1}. MS m/z (%): 347 (M^+, 0.51), 186 (17), 156 (42), 155 (41), 92 (100). HRMS Calcd for $C_{18}H_{21}NO_6$: 347.1369. Found: 347.1371.

(4*S*,5*S*)-(*E*)-5-Amino-*N*-[(*tert*-butyloxy)carbonyl]-4-hydroxy-6-phenyl-2-hexenoic Acid (4) $CsCO_3$ (33.6 mg, 0.103 mmol) was added to a solution of **9** (17.9 mg, 0.0515 mmol) in MeOH (3 ml) at room temperature, and then the mixture was stirred at room temperature for 24 h. The reaction was quenched with 0.1 N HCl 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 preparative TLC (MeOH : $CHCl_3$ = 1 : 5) to give **4** (12.9 mg, 78%) as colorless crystals. mp 147—149 °C (MeOH–H_2O). $[\alpha]_D^{25}$ −98.2° (c=0.185, MeOH). ^{1}H-NMR (CD_3OD) δ: 1.33 (s, 9H, C$\underline{Me}_3$), 2.68 (dd, 1H, J=9.4, 13.7 Hz, C6-H), 2.93 (dd, 1H, J=6.0, 13.7 Hz, C6-H), 3.63 (br s, 61/100 × 1H, O$\underline{H}$), 3.88 (m, 1H, C5-H), 4.28 (m, 1H, C4-H), 6.04 (d, 1H, J=15.0 Hz, C2-H), 6.35 (d, 61/100 × 1H, J=9.8 Hz, N$\underline{H}$), 6.92 (dd, 1H, J=4.3, 15.0 Hz, C3-H), 7.25 (m, 5H, Ar-H). IR (KBr): 3373 (OH), 2926, 1697 (C=O) cm^{-1}, MS m/z (%): 248 (M^+ − ^{t}BuO, 3.0), 220 (21), 164 (65), 130 (39), 120 (100). HRMS Calcd for $C_{13}H_{14}NO_4$ (M^+ − ^{t}BuO): 248.0921. Found: 248.0915. CIMS m/z (%): 322.0 (M^+ + 1, 3.8), 266.0 (100).

Acknowledgement The present work was partially supported by the Takeda Chemical Industries, Ltd. Foundation and by a Grant-in-Aid for Scientific Research on the Priority Area of Reactive Organometallics No. 05236101 from the Ministry of Education, Science, Sports and Culture.

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