

Radical Cyclization of *O*-Pentafluorobenzoyloximes Having a (Cyclohexadiene)Fe(CO)$_3$ Moiety

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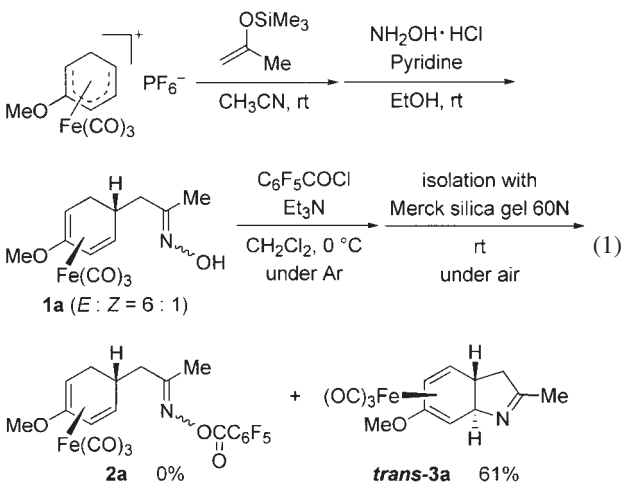
In the presence of atmospheric oxygen, *O*-pentafluorobenzoyloximes having a (2,4-cyclohexadienyl)Fe(CO)$_3$ moiety at the α-position cyclize smoothly to give *trans*-fused [(4,5,6,7-η)-3a,7a-dihydro-3*H*-indole]Fe(CO)$_3$ complexes. The cyclization proceeds via radical chain mechanism initiated by molecular oxygen, in which pentafluorobenzoyloxyl radical plays a role as a chain carrier. Thus obtained *trans*-fused dihydroindole iron complexes readily isomerize to the *cis*-fused isomers on acidic silica gel or under basic conditions. Such isomers are converted to 3a,7a-dihydroindole or indole derivatives by the oxidative removal of the Fe(CO)$_3$ group.

Oxime derivatives are employed as precursors of alkylideneaminyl radicals and their equivalents. Under thermal,[1] photochemical,[2a] oxidative,[3] or reductive[4–8] conditions, or by the treatment with tributylstannane,[2] oxime derivatives having an olefinic or aromatic moiety are converted to a variety of azaheterocycles in radical processes. In addition, oxime derivatives are good radical acceptors; the addition of radicals to the carbon–nitrogen double bond generally occurs at the sp^2 carbon atom, giving aminyl radicals stabilized with oxygen atom.[9–11] As for the addition at the sp^2 nitrogen atom, only one example has been reported by Hatem et al.; this case demonstrates that the intramolecular allyl radical cyclizes at the oxime nitrogen of the *O*-benzoyloxime having phenyl or phosphonate group at the oxime sp^2 carbon.[12] Recently, we have found an example of the radical cyclization at the sp^2 nitrogen of oxime derivatives. That is, *O*-pentafluorobenzoyloximes having a (2,4-cyclohexadienyl)Fe(CO)$_3$ moiety at the α-position cyclize under air to give *trans*-fused dihydroindole derivatives.[13] In this paper are reported the full details of this aerobic cyclization of oxime derivatives.

Results and Discussion

Cyclization of *O*-Pentafluorobenzoyloxime Having a (2,4-Cyclohexadienyl)Fe(CO)$_3$ Moiety at the α-Position. During the course of the study on the intramolecular amino-Heck reactions of olefinic *O*-pentafluorobenzoyloximes,[14] we attempted to prepare *O*-pentafluorobenzoyloxime **2a** having a (2,4-cyclohexadienyl)Fe(CO)$_3$ moiety at the α-position (Eq. 1). Tricarbonyl(η^5-2-methoxycyclohexadienyl)iron hexafluorophosphate was treated with 2-trimethylsiloxypropene and the oximation of the resulting ketone afforded oxime **1a** (*E*:*Z* = 6:1). After the pentaflurobenzoylation of **1a**, the product was isolated with flash column chromatography on Merck silica gel 60N under air. The reaction, however, did not give the desired *O*-pentafluorobenzoyloxime **2a**, but an unexpected *trans*-fused (3a,7a-dihydroindole)Fe(CO)$_3$ complex ***trans*-3a** in 61% yield.



(1)

Although 3a,7a-dihydroindole derivative ***trans*-3a** was obtained in the first experiment, the formation of ***trans*-3a** was not so reproducible: the desired *O*-pentafluorobenzoyloxime **2a** was sometimes isolated instead of ***trans*-3a**. We, therefore, examined the pentafluorobenzoylation and the cyclization of **2a** in detail as follows.

O-Pentafluorobenzoyloxime **2a** was prepared carefully according to the following procedure (Eq. 2). Oxime **1a** (*E*:*Z* = 6:1) was treated with pentafluorobenzoyl chloride and triethylamine for 30 min below 0 °C under argon. After the disappearance of the oxime, the reaction was quenched with ice water. Extraction and the condensation at 0 °C gave a crude product, whose ^{1}H NMR spectrum showed that *O*-pentafluorobenzoyloxime **2a** was formed as a sole product in almost quantitative yield. In fact, purification of the crude **2a** with thin-layer chromatography on Wako gel B-5F below 0 °C gave **2a** almost quantitatively. Since the obtained **2a** gradually colored on standing,[15] the isolated **2a** was immediately submitted for the investigation of the cyclization reaction (Table 1).

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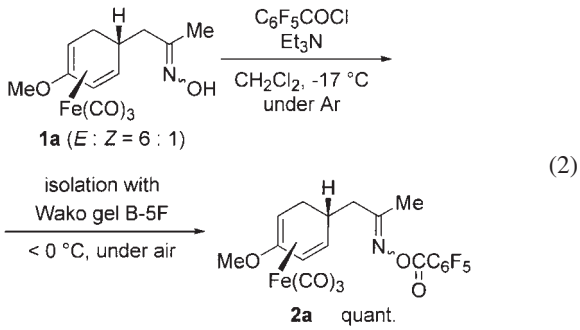
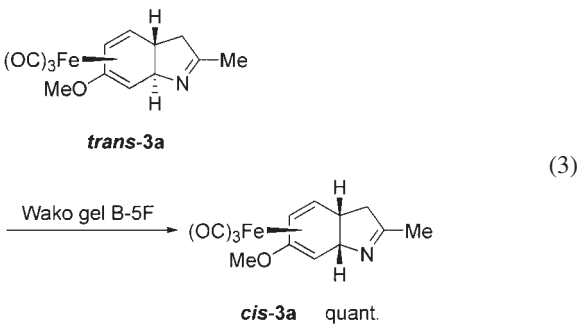


(2)

Firstly, a carefully degassed and sealed NMR tube containing a dichloromethane-d_2 solution of **2a** was prepared, and the reaction was monitored by NMR. Although the NMR tube was heated at 40 °C for 4 h, no reaction was observed (Entry 1). However, when air was introduced into the NMR tube and the tube was heated again at 40 °C, the reaction started after 40 min. The reaction proceeded in the first order to [**2a**] ($k = 9.6 \times 10^{-3}$ s^{-1}) with 4.0 min of the half time, to afford *trans*-fused dihydroindole derivative ***trans*-3a** (Entry 2). Then, the cyclization of **2a** was tried under air. Heating of a dichloromethane solution of **2a** under aerobic atmosphere and the isolation with Merck silica gel 60N gave 77% of ***trans*-3a** with pentafluorobenzoic acid (Entry 3).[16] When 20 mol% of galvinoxyl was added, the cyclization of **2a** did not proceed in refluxing dichloromethane under air for 4 h (Entry 4). The *trans*-fused product ***trans*-3a** was found to isomerize to the *cis*-fused isomer ***cis*-3a** quantitatively on Wako gel B-5F (Eq. 3).

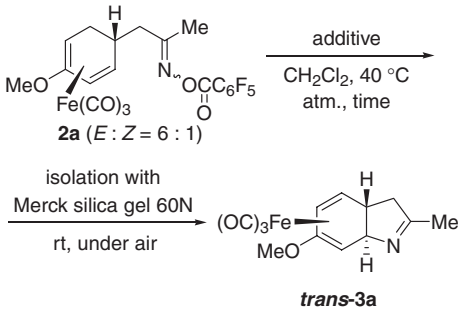


(3)

Thus the cyclization of *O*-pentafluorobenzoyloxime **2a** was effective in dichloromethane at 40 °C under air, and the formation of **3a** in the *O*-pentafluorobenzoylation of oxime **1a** (Eq. 1) was supposed to be intiated by atmospheric oxygen during the isolation. It is noteworthy that the aerobic cyclization of **2a** suddenly began after an induction period and was suppressed by a radical trapping reagent such as galvinoxyl. Therefore, the cyclization of **2a** seems to proceed by a radical chain mechanism initiated by molecular oxygen.[17]

As described above, methyl ketone oxime **1a** (*syn*:*anti* = 1:6) was readily converted to (3a,7a-dihydro-3*H*-indole)-Fe(CO)$_3$ complex ***trans*-3a** by the aerobic cyclization of *O*-pentafluorobenzoyloxime **2a**. Then, the influence of the stereochemistry of oximes was examined by using *syn* and *anti* isomers of phenyl ketone oxime **1b**. As is not the case for oxime **1a**, the isomers of oxime **1b** were separable by choromatography, and *syn* and *anti* **1b** were individually employed for the cyclization (Eq. 4). In this paper, *syn* and *anti* stereochemistry

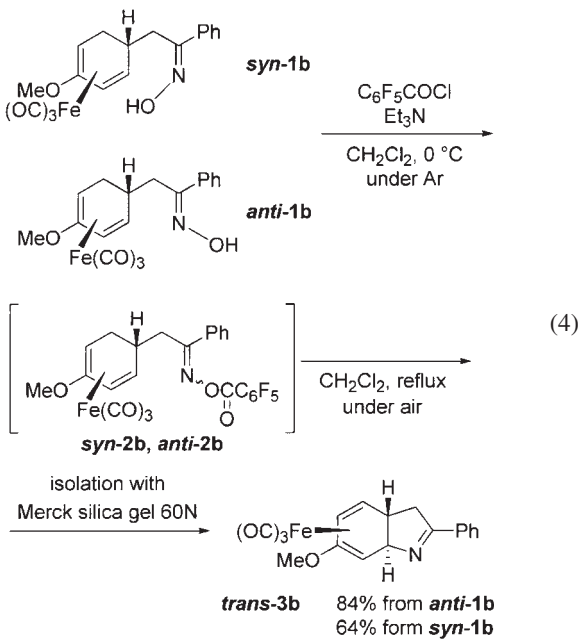
Table 1. Cyclization of *O*-Pentafluorobenzoyloxime **2a**



Entry	Atm.	Time	Additive	Result
1[a)]	degassed	4 h	none	no reaction
2[a)]	air	1.1 h	none	***trans*-3a**[b)]
3	air	0.5 h	none	***trans*-3a** (77%)
4	air	4 h	galvinoxyl (20 mol%)	no reaction

a) Dichloromethane-d_2 was used as a solvent in a sealed NMR tube. b) Yield was not obvious.

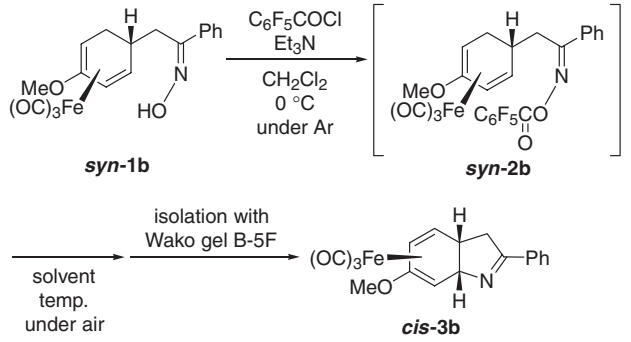
are defined as to whether the hydroxy group orients *syn* or *anti* direction to the (cyclohexadiene)Fe(CO)$_3$ moiety. After the pentafluorobenzoylation of **1b**, the extraction and the condensation at 0 °C gave a crude product. Though the ^{1}H NMR spectrum of the crude product showed the quantitative formation of *O*-pentafluorobenzoyloxime **2b** as a sole product, the isolation of **2b** with chromatography was avoided, because **2b** was so thermally labile that the cyclization to the dihydroindole complex ***trans*-3b** gradually proceeded during the purification. Thus the crude **2b** was immediately dissolved in dichloromethane and heated at reflux under air, and then the product was isolated by Merck silica gel 60N. The cyclization of both ***syn*-2b** and ***anti*-2b** proceeded smoothly in refluxing dichloromethane, and *trans*-fused dihydroindole derivative ***trans*-3b** was obtained in 64% and 84% yield, respectively.



(4)

Several solvents were screened for the aerobic cyclization of ***syn*-2b** (Table 2). Only in dichloromethane did the cyclization

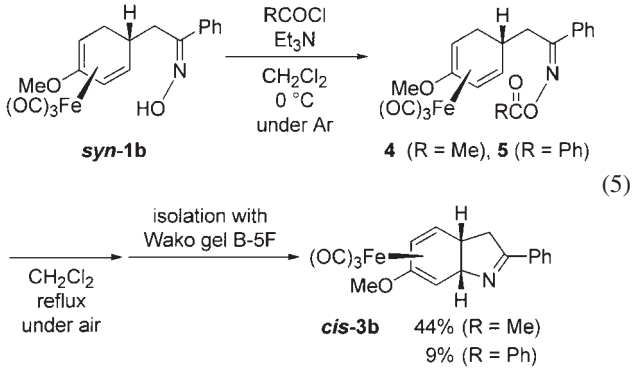
Table 2. Effect of Solvent on the Aerobic Cyclization of ***syn*-2b**



Entry	Solvent	Temp.	***cis*-3b**
1	dichloromethane	40 °C	64%
2	1,2-dichloroethane	75 °C	67%
3	2,2,5,5-tetramethyltetrahydrofuran	85 °C	68%
4	1,4-dioxane	75 °C	28%
5	toluene	70 °C	17%
6	acetonitrile	85 °C	46%

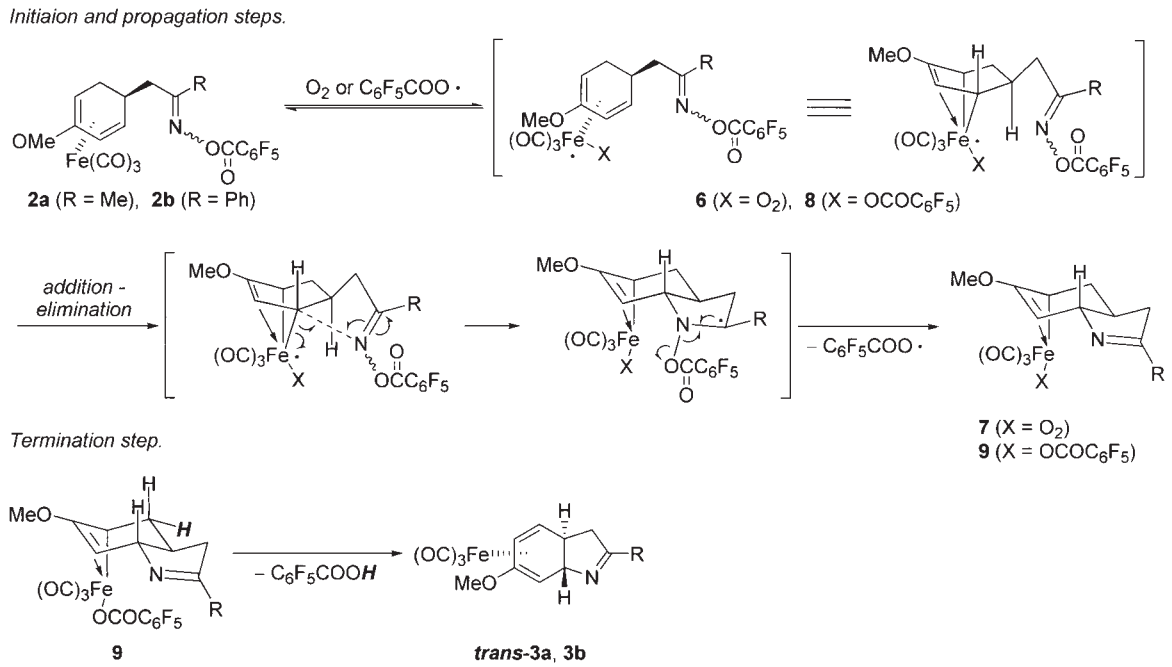
reaction proceed at 40 °C. In 1,2-dichloroethane and 2,2,5,5-tetramethyltetrahydrofuran, the cyclized product ***cis*-3b** was obtained in moderate yield at 75 °C and 85 °C, respectively (Entries 2 and 3). In turn, the reactions in 1,4-dioxane, toluene, and acetonitrile gave low yields of the product even at 70–85 °C (Entries 4 to 6). Thus, dichloromethane is suitable for the cyclization reaction.

The *O*-acyl group on the sp^2 nitrogen atom exhibited a significant influence on the cyclization. The corresponding *O*-acetyl and *O*-benzoyloximes **4** and **5** could be isolated by thin-layer chromatography without the cyclization, and the cyclization proceeded slowly to give dihydroindole derivative ***cis*-3b** in low yields (Eq. 5). In addition, the *O*-methoxycarbonyloxime and *O*-methyloxime as well as the oxime ***syn*-1b** itself were extremely inert and no cyclized product was detected.



(5)

Plausible Mechanism of the Aerobic Cyclization. The cyclization of *O*-pentafluorobenzoyloxime **2a** and **2b** may proceed by a radical chain mechanism initiated by molecular oxygen. Plausible mechanism of the cyclization is shown in Scheme 1. Organotransitionmetal complexes generally have an affinity to molecular oxygen, and the attack of molecular oxygen gives metal-centered radical species.[18] In the initiation step, molecular oxygen reversibly attacks the iron atom of **2** to yield the 19-electron radical species **6**. As reported, 19-electron organometallic complexes having a polyhapto ligand act as 18-electron organometallic complexes having an adjacent carbon-centered radical.[19] For example, one electron-reduction of 18-electron cationic bis(cyclopenadienyl)rhodium complex resulted in the dimerization of the formed 19-elecron organometallic radical at the cyclopentadienyl ring.[19a] Accordingly, the 19-electron diene complex **6** attacks the oxime nitrogen with the cleavage of the carbon–iron bond, releasing pentafluorobenzoyloxyl radical. Thus, the *trans* isomer **7** is obtained steroselectively. The resulting pentafluorobenzoyloxy radical acts as a chain carrier, and causes the propagation step, affording



Scheme 1. Plausible mechanism.

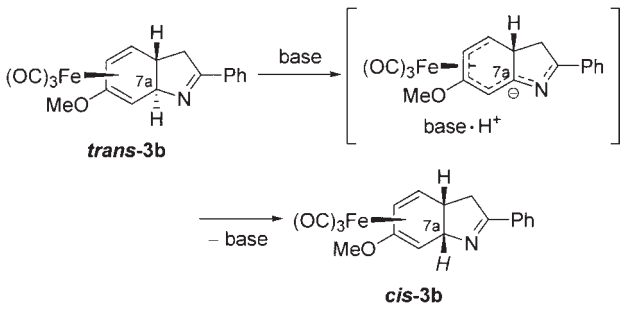
trans-fused bicyclic π-allyliron(II) complex **9** and pentafluorobenzoyloxyl radical. In the termination step, the pentafluorobenzoic acid is eliminated from **9** reductively to form the *trans*-fused (dihydroindole)$Fe(CO)_3$ complex ***trans*-3**.

It is noteworthy that the radical cyclization of the intermediate **6** and **8** proceeds at the oxime nitrogen. The carbon radical generally attacks the oxime derivative at the sp^2 carbon atom, as mentioned in the introduction.[9–11] In the intermediates **6** and **8**, however, the cyclization at the oxime carbon atom is disfavored due to the formation of a four-membered carbocycle. Similar to the suggestion by Hatem et al.,[12] the addition to the nitrogen–carbon double bond may take place at the sp^2 nitrogen atom in this aerobic cyclization of *O*-pentafluorobenzoyloxime **2**.

As explained previously (Eq. 5), *O*-acetyl and benzoyloximes **4** and **5** gave low yields of the dihydroindole derivative ***cis*-3b**. This result indicates that the pentafluorobenzoyloxyl radical serves as a good chain carrier among these acyloxyl radicals. Zao et al. reported that the reaction of 2,5-di-*t*-butyl-1,4-dimethoxybenzene and substituted benzoyl peroxide gives the corresponding 4-*t*-butyl-2,5-dimethoxyphenyl benzoate via the addition of the corresponding benzoyloxyl radical to cation radical of 2,5-di-*t*-butyl-1,4-dimethoxybenzene.[20] As compared to the use of *p*-nitrobenzoyl and *m*-chlorobenzoyl peroxide, the reaction with pentafluorobenzoyl peroxide gave a higher yield of the benzoate, suggesting that pentafluorobenzoyloxyl radical is relatively stable to the decarboxylation.

The solvent effect (Table 2) reflects the function of the pentafluorobenzoyloxyl radical as a chain carrier. In 1,4-dioxane and toluene (Entries 4 and 5), the pentafluorobenzoyloxyl radical readily abstracted hydrogen from the solvent and was quenched before the reaction with unreacted *O*-pentafluorobenzoyloxime. Because it is reported that acyloxyl radicals suffer from the decarboxylation in polar solvents,[25] the cyclization in acetonitrile afforded the product in low yield (Entry 6). Therefore, the use of a less polar solvent having no active hydrogen maintains the stability of the pentafluorobenzoylxoxyl radical to promote the cyclization effectively (Entries 1 to 3).

Isomerization of the *trans*-Fused (Dihydroindole)-$Fe(CO)_3$ Complexes to the *cis* Isomer. The *trans*-fused dihydroindole complex ***trans*-3** readily isomerized to the *cis*-fused isomer ***cis*-3** on acidic silica gel Wako gel B-5F. As described in the preliminary communication,[13] we supposed that the isomerization occurred through cationic (η^5-cyclohexadienyl)-$Fe(CO)_3$ intermediate generated by the heterolytic scission of carbon–nitrogen bond, as reported by Pearson and Knölker et al.[21] No isomerization was observed, however, by the treatment of *trans*-fused dihydroindole complex ***trans*-3b** with carboxylic acids such as pentafluorobenzoic acid and trifluoroacetic acid. Meanwhile, *trans*-fused ***trans*-3b** was found to isomerize quantitaviely to ***cis*-3b** by the treatment with bases such as triethylamine and pyridine. Thus, the isomerization presumably proceeds via the deprotonation of ***trans*-3b** at the 7a-position. Since the dihydroindole ***trans*-3b** is fairly strained, the anionic intermidiate would be converted to the more thermodynamically stable *cis*-fused isomer ***cis*-3b** by the protonation at the 7a-position (Eq. 6). Now the isomerization on Wako gel B-5F is assumed to involve both the *N*-protonation and the successive deprotonation at the 7a-position.



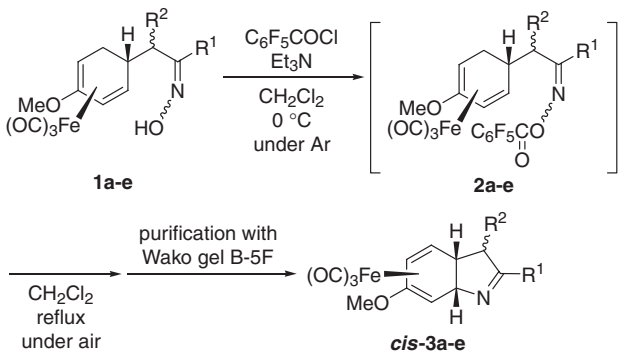
(6)

Synthesis of (3a,7a-Dihydroindole)$Fe(CO)_3$ Complexes. Various ketoximes having a (2,4-cyclohexadienyl)$Fe(CO)_3$ moiety at the α-position were readily converted to (3a,7a-dihydroindole)$Fe(CO)_3$ complexes by the same procedure: the pentafluorobenzoylation and the successive aerobic cyclization of the crude *O*-pentafluorobenzoylketoximes. The cyclized products were isolated by Wako gel B-5F as *cis*-fused (3a,7a-dihydroindole)$Fe(CO)_3$ complexes ***cis*-3a–h** (Tables 3 and 4). In all examples, Beckmann rearrangement products were not detected.

As described earlier, both isomers of oxime **1b** could be cyclized (Table 3, Entries 2 and 3). Even the bulky *t*-butyl ketone oxime **1c** and α-substituted oximes **1d** and **1e** gave moderate yields of dihydroindole derivative ***cis*-3c**, ***cis*-3d**, and ***cis*-3e**, respectively (Table 3, Entries 4 to 6).

In turn, Table 4 exhibits the effect of the substituents on the cyclohexadiene ring. Both the electron-donating and -withdrawing substituents on the diene moiety could be introduced for the cyclization. In the cyclization of ***syn*-1g** and ***syn*-1h** having a substituent at the 5-position of the cyclohexadiene ring, excess use of triethylamine was needed in order to suppress the formation of the regioisomers: 7-substituted-3a,7a-dihydroindole complexes ***cis*-10g** and ***cis*-10h** (Entries 2 and 3). In

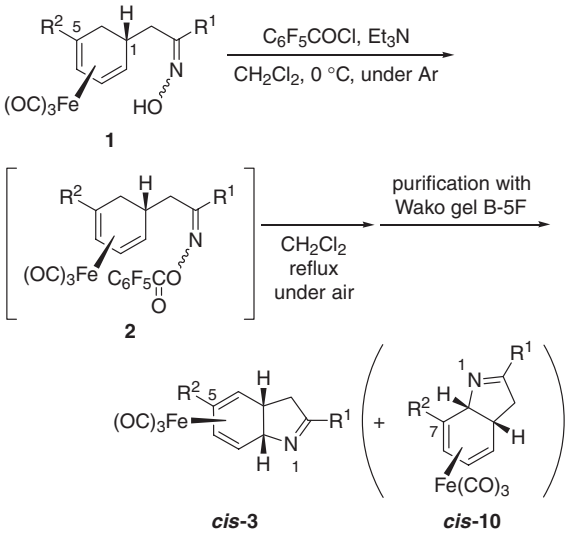
Table 3. Synthesis of (Dihydroindole)$Fe(CO)_3$ Complexes from Oximes **1a–e**



Entry	Substrate	R^1	R^2	***cis*-3**
1	**1a**[a)]	Me	H	77%
2	***anti*-1b**	Ph	H	84%
3	***syn*-1b**	Ph	H	64%
4	***syn*-1c**	*t*-Bu	H	54%
5	***anti*-1d**[b)]	Ph	Me	44%
6	***anti*-1e**[b)]	$-(CH_2)_4-$		57%

a) Isolated as mixture of isomers. b) Single diasteromer. (Relative sterochemistry is not determined.)

Table 4. Synthesis of (Dihydroindole)$Fe(CO)_3$ Complexes from Oximes Having Various (2,4-Cyclohexadienyl)-$Fe(CO)_3$ Moiety



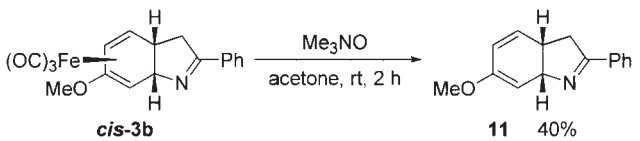
Entry	Oxime	R^1	R^2	*cis*-**3**	*cis*-**10**
1	**1f**[a)]	Me	H	81%	—
2[b)]	*syn*-**1g**	Ph	MeO_2C	60% (15%)	— (27%)
3[b)]	*syn*-**1h**	Ph	Me	58% (43%)	— (13%)

a) Mixture of isomers. b) Excesss of triethylamine was added in the cyclization. Otherwise, both *cis*-**3** and *cis*-**10** were obtained in the yield shown in the parentheses.

these cases, the isomerization of the (diene)$Fe(CO)_3$ moiety of *O*-pentafluorobenzoyloxime was probably promoted by the pentafluorobenzoic acid formed during the reaction, and the subsequent cyclization gave the regioisomers. The role of triethylamine is propably trapping the acid.

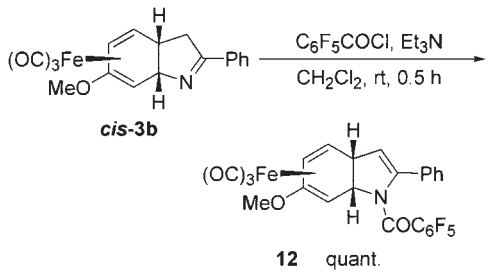
Thus the ketoximes cyclized to give *cis*-fused dihydroindole complexes *cis*-**3a–h**, whereas aldoxime having a (2,4-cyclohexadienyl)$Fe(CO)_3$ at the α-position did not give the cyclized product at all, with the recovery of the corresponding *O*-pentafluorobenzoyloxime.

Transformation of the Cyclized Products into 3a,7a-Dihydroindole and Indole Derivatives. Next, we studied the removal of the $Fe(CO)_3$ group from the cyclized product, *cis*-(3a,7a-dihydroindole)$Fe(CO)_3$ complex *cis*-**3b**. Demetallation of (diene)$Fe(CO)_3$ complex is reported to proceed effecitively by the treatement with amine *N*-oxides and metallic oxidants.[22] When the *cis*-fused cyclized product *cis*-**3b** was treated with cerium(IV) ammonium nitrate and copper(II) chloride in ethanol, the reaction gave a complex mixture without the formation of the desired 3a,7a-dihydroindole **11**. When *cis*-**3b** was oxidized by trimethylamine *N*-oxide in acetone, dihydroindole **11** was obtained, albeit with a low yield of 40% (Eq. 7).



(7)

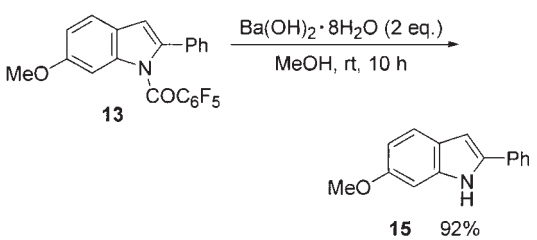
As the low yield of **11** is attributed to the unstability of the imino group of **11** under oxidative conditions,[22a] the imino moiety was protected prior to the oxidation. Due to the steric hindrance around the imine nitrogen, the reaction of *cis*-**3b** with di-*t*-butyl dicarbonate and allyl chloroformate hardly proceeded, and most of the starting material was recovered. Though the acylation of *cis*-**3b** with trifluoroacectic anhydride completed within 2 h, the desired *N*-acyl 3a,7a-dihydroindole complex was obtained only in 41% yield. Surprisingly, the use of bulkier pentafluorobenzoyl chloride resulted in the rapid conversion to *N*-pentafluorobenzoyl 3a,7a-dihydroindole iron complex **12** in quantitative yield (Eq. 8), suggesting that pentafluorobenzoyl chloride is useful for the protection of sterically hindered cyclic imines.



(8)

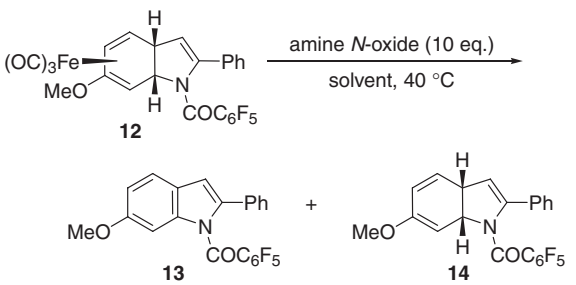
Thus obtained *N*-pentafluorobenzoyl 3a,7a-dihydroindole complex **12** was oxidized with trimethylamine *N*-oxide in dimethylacetamide; the corresponding indole **13** and 3a,7a-dihydronindole **14** were obtained in 36% and 29% yield, repsectively (Table 5, Entry 1). The use of *N*-methylmorpholine *N*-oxide (NMO) improved the yield and the selectivity for the formation of the indole **12** to 72% yield (Table 5, Entry 2). Interestingly, the oxidation in dichloromethane gave 3a,7a-dihydroindole **13** as a major product in 84% yield (Table 5, Entries 3 and 4).[26]

The deprotection on the indole nitrogen of **13** readily proceeded by the treatment with barium hydroxide; 1*H*-indole **15** was obtained in 92% yield (Eq. 9).



(9)

Table 5. Oxidation of **12** with Amine *N*-Oxides



Entry	Amine *N*-oxide	Solvent	**13**	**14**
1	Me_3NO	DMA	36%	29%
2	NMO	DMA	72%	5%
3	NMO	Acetone	24%	73%
4	NMO	CH_2Cl_2	14%	84%

Experimental

General. ^{1}H NMR (500 MHz) spectra were recorded on Bruker DRX 500 and Bruker AVANCE 500 spectrometers in $CDCl_3$ using chloroform (for ^{1}H, $\delta = 7.24$) as an internal standard. ^{13}C NMR (125 MHz) spectra were recorded on Bruker DRX 500 and Bruker AVANCE 500 spectrometers in $CDCl_3$ using chloroform (for ^{13}C, $\delta = 77.0$) as an internal standard. IR spectra were recorded on a Horiba FT 300-S spectrophotometer by ATR method. High-resolution mass spectra were obtained with a JOEL JMS700P mass spectrometer. The melting points were uncorrected. Elemental analyses were carried out at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The Univerisity of Tokyo. Flash column chromatography was performed on Merck silica gel 60N and Kanto Chemical silica gel 60N (sperical, neutral). Preparative thin-layer chromatography was carried out using Wako gel B-5F. Dichloromethane and *N*,*N*-dimethylacetamide were distilled from phosphorus pentoxide and then from calcium hydride, and were stored over molecular sieves 4A. Triethylamine and pyridine were distilled from sodium hydride, and stored over potassium carbonate. Pentafluorobenozyl chloride was purchased form Tokyo Chemical Industry and used after distillation.

Synthesis of Oximes Having a (2,4-Cyclohexadienyl)-Fe(CO)$_3$ Moiety at the α-Position. Oximes having a (2,4-cyclohexadienyl)Fe(CO)$_3$ moiety at the α-position were synthesized by the oximation of the corresponding ketones or aldehyde prepared according to the literature.[23] The experimental procedure is shown below as a typical example for the synthesis of tricarbonyl[*exo*-3-[(2,3,4,5-η)-(4-methoxycyclohexa-2,4-dienyl)]propan-2-one oxime]iron (**1a**).

To a ethanol solution (6 mL) of tricarbonyl[*exo*-2-[(2,3,4,5-η)-(4-methoxycyclohexa-2,4-dienyl)]propan-2-one]iron (305.1 mg, 1 mmol) were added hydroxylamine hydrochloride (104.2 mg, 1.5 mmol) and pyridine (118.6 mg, 1.5 mmol). After the reaction mixture was stirred for 1.5 h at room temperature, the solvent was removed under reduced pressure. The residue was treated with water and aqueous hydrochloric acid, and extracted twice with ethyl acetate. The combined extracts were washed with saturated aqueous solution of sodium hydrogencarbonate, and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the crude product was purified by flash column chromatography (Merck silica gel 60N, ethyl acetate:hexane = 1:7) to afford tricarbonyl[*exo*-2-[(2,3,4,5-η)-(4-methoxycyclohexa-2,4-dienyl)]propan-2-one oxime]iron (**1a**) (312.0 mg, 98%).

Spectral Data for Oximes Having a (2,4-Cyclohexadienyl)-Fe(CO)$_3$ Moiety at the α-Position. Tricarbonyl[*exo*-3-[(2,3,4,5-η)-4-methoxycyclohexa-2,4-dienyl]propan-2-one oxime]iron (1a): *E* and *Z* = 6:1 mixture; Colorless powder; mp 123–124 °C (dec.) (ethyl acetate–hexane); IR (KBr) 3269, 2038, 1979, 1946, 1938, 1487, 1425, 1221 cm^{-1}; ^{1}H NMR δ 1.36 (0.86H, dt, $J = 14.7$, 2.6 Hz), 1.39 (0.14H, m), 1.79 (2.57H, s), 1.80 (0.43H, s), 1.96–2.05 (2.71H, m), 2.15–2.28 (1.29H, m), 2.61 (1H, dd, $J = 6.5$, 3.6 Hz), 3.25–3.28 (1H, m), 3.61 (2.57H, s), 3.63 (0.43H, s), 5.05 (1H, dd, $J = 6.5$, 2.3 Hz), 7.04 (1H, broad s); ^{13}C NMR *E* isomer: δ 13.5, 31.4, 34.6, 45.5, 52.5, 54.1, 54.2, 66.1, 139.8, 157.4, 211.1; *Z* isomer: δ 20.2, 31.5, 34.3, 38.3, 52.5, 54.2, 54.6, 66.4, 139.8, 157.1, 211.1; Anal. Found: C, 48.66; H, 4.71; N, 4.39%. Calcd for $C_{13}H_{15}FeNO_5$: C, 48.63; H, 4.71; N, 4.36%.

Tricarbonyl[*exo*-2-[(2,3,4,5-η)-4-methoxycyclohexa-2,4-dienyl]-1-phenylethan-1-one (*E*)-oxime]iron (*syn*-1b): Colorless powder; mp 135–140 °C (dec.) (dichloromethane–hexane); IR (ZnSe) 3248, 2931, 2036, 1948, 1483, 1423, 1225, 1173, 1024 cm^{-1}; ^{1}H NMR δ 1.42 (1H, dt, $J = 14.6$, 2.5 Hz), 1.94 (1H, ddd, $J = 14.6$, 10.7, 3.8 Hz), 2.23–2.28 (1H, m), 2.56 (1H, dd, $J = 6.5$, 3.5 Hz), 2.68 (1H, dd, $J = 12.9$, 7.5 Hz), 2.73 (1H, dd, $J = 12.9$, 7.5 Hz), 3.23–3.24 (1H, m), 3.59 (3H, s), 4.94 (1H, dd, $J = 6.5$, 2.1 Hz), 7.37–7.38 (3H, m), 7.52–7.54 (2H, m), 8.13 (1H, broad s); ^{13}C NMR δ 31.4, 34.7, 35.0, 52.6, 54.2, 54.6, 66.5, 126.4, 128.6, 129.3, 135.7, 139.7, 158.5, 211.1; Anal. Found: C, 56.35; H, 4.62; N, 3.45%. Calcd for $C_{18}H_{17}FeNO_5$: C, 56.42; H, 4.47; N, 3.66%.

Tricarbonyl[*exo*-2-[(2,3,4,5-η)-4-methoxycyclohexa-2,4-dienyl]-1-phenylethan-1-one (*Z*)-oxime]iron (*anti*-1b): Colorless powder; mp 130 °C (dec.) (dichloromethane–hexane); IR (ZnSe) 3255, 2942, 2038, 1952, 1483, 1458, 1423, 1225, 1024 cm^{-1}; ^{1}H NMR δ 1.42 (1H, dt, $J = 14.6$, 2.7 Hz), 1.94 (1H, ddd, $J = 14.6$, 10.6, 3.8 Hz), 2.23–2.29 (1H, m), 2.56 (1H, dd, $J = 6.5$, 3.5 Hz), 2.68 (1H, dd, $J = 12.9$, 7.5 Hz), 2.74 (1H, dd, $J = 12.9$, 7.4 Hz), 3.23–3.25 (1H, m), 3.59 (3H, s), 4.93 (1H, dd, $J = 6.5$, 2.2 Hz), 7.37–7.39 (3H, m), 7.52–7.54 (2H, m), 8.55 (1H, broad s); ^{13}C NMR δ 31.3, 34.7, 34.7, 45.0, 52.5, 54.1, 54.1, 66.0, 127.6, 128.3, 129.0, 133.0, 139.7, 157.6, 211.0; Anal. Found: C, 56.30; H, 4.56; N, 3.59%. Calcd for $C_{18}H_{17}FeNO_5$: C, 56.42; H, 4.47; N, 3.66%.

Tricarbonyl[*exo*-1-[(2,3,4,5-η)-4-methoxycyclohexa-2,4-dienyl]-3,3-dimethylbutan-2-one (*E*)-oxime]iron (*syn*-1c): Colorless powder; mp 145 °C (dec.) (dichloromethane–hexane); IR (ZnSe) 3255, 2962, 2924, 2035, 1950, 1483, 1460, 1425, 1227, 1173, 1028 cm^{-1}; ^{1}H NMR δ 1.09 (9H, s), 1.42 (1H, dt, $J = 14.6$, 2.7 Hz), 2.03 (1H, ddd, $J = 14.6$, 10.7, 3.8 Hz), 2.14 (1H, dd, $J = 13.1$, 4.8 Hz), 2.29 (1H, dd, $J = 13.1$, 6.6 Hz), 2.48–2.53 (1H, m), 2.65 (1H, dd, $J = 6.5$, 3.4 Hz), 3.27 (1H, m), 3.62 (3H, s), 5.03 (1H, dd, $J = 6.5$, 2.1 Hz), 7.26 (1H, broad s); ^{13}C NMR δ 28.4, 32.2, 35.0, 35.0, 37.5, 52.5, 54.2, 55.5, 66.8, 139.8, 165.6, 211.2; Anal. Found: C, 52.88; H, 5.85; N, 3.59%. Calcd for $C_{16}H_{21}FeNO_5$: C, 52.91; H, 5.83; N, 3.86%.

Tricarbonyl[*exo*-2-[(2,3,4,5-η)-4-methoxycyclohexa-2,4-dienyl]-1-phenylpropan-1-one (*Z*)-oxime]iron (*anti*-1d): Colorless powder; mp 112 °C (dec.) (dichloromethane–hexane); IR (ZnSe) 3234, 2931, 2038, 1954, 1483, 1458, 1423, 1225, 1020 cm^{-1}; ^{1}H NMR δ 1.15 (3H, d, $J = 6.9$ Hz), 1.45 (1H, dt, $J = 14.6$, 2.7 Hz), 2.06 (1H, ddd, $J = 14.6$, 10.3, 3.8 Hz), 2.53–2.58 (1H, m), 2.64 (1H, dd, $J = 6.5$, 3.5 Hz), 2.68 (1H, dq, $J = 10.2$, 6.9 Hz), 3.26–3.27 (1H, m), 3.55 (3H, s), 4.90 (1H, dd, $J = 6.5$, 2.3 Hz), 7.36–7.40 (3H, m), 7.49–7.51 (2H, m), 8.26 (1H, broad s); ^{13}C NMR δ 16.8, 31.4, 39.7, 44.9, 52.1, 53.3, 54.2, 66.8, 127.2, 128.4, 128.9, 136.8, 139.6, 161.9, 211.1; Anal. Found: C, 57.41; H, 5.08; N, 3.53%. Calcd for $C_{19}H_{19}FeNO_5$: C, 57.45; H, 4.82; N, 3.53%.

***anti*-1d** was obtained as a single diastereomer after recrystallization. The relative stereochemistry of the α-position of the oxime moiety was not determined.

Tricarbonyl[*exo*-2-[(2,3,4,5-η)-4-methoxycyclohexa-2,4-dienyl]cyclohexanone (*E*)-oxime]iron (*anti*-1e): Colorless powder; mp 131 °C (dec.) (dichloromethane–hexane); IR (ZnSe) 3290, 3006, 2038, 1952, 1655, 1485, 1425, 1223, 1173, 1022 cm^{-1}; ^{1}H NMR δ 1.41 (1H, dt, $J = 14.8$, 2.7 Hz), 1.45–1.47 (1H, m), 1.56–1.61 (2H, m), 1.65–1.77 (4H, m), 1.96 (1H, ddd, $J = 14.8$, 10.7, 3.9 Hz), 2.25–2.34 (2H, m), 2.40–2.47 (1H, m), 2.76 (1H, dd, $J = 6.5$, 3.6 Hz), 3.24–3.26 (1H, m), 3.60 (3H, s), 5.07 (1H, dd, $J = 6.5$, 2.2 Hz), 8.08 (1H, broad s); ^{13}C NMR δ 23.0, 23.1, 26.2, 30.1, 31.5, 36.3, 50.3, 51.6, 52.9, 54.2, 66.2, 139.8, 162.9, 211.2; Anal. Found: C, 53.13; H, 5.26; N, 3.73%.

Calcd for $C_{19}H_{19}FeNO_5$: C, 53.21; H, 5.30; N, 3.88%.

***anti*-1e** was obtained as a single diastereomer after recystallization. The relative stereochemistry of the α-position of the oxime moiety was not determined.

Tricarbonyl[*exo*-3-[(2,3,4,5-η)-cyclohexa-2,4-dienyl]propan-2-one oxime]iron (1f): *E* and *Z* = 3:1 mixture; Colorless powder; mp 115 °C (dec.) (ethyl acetate–hexane); IR (KBr) 2038, 1972, 1957, 1058, 951 cm^{-1}; ^1H NMR δ 1.24–1.30 (1H, m), 1.80 (2.25H, s), 1.81 (0.75H, s), 1.95–2.07 (2.5H, m), 2.19 (0.25H, dd, J = 12.9, 5.8 Hz), 2.29–2.46 (1.25H, m), 3.01–3.05 (2H, m), 5.27–5.29 (1H, m), 5.35–5.40 (1H, m), 7.35 (1H, broad s); ^{13}C NMR δ 13.5, 20.3, 30.5, 30.6, 34.6, 35.0, 38.4, 45.8, 59.5, 59.6, 65.5, 65.8, 84.3, 84.6, 86.0, 86.1, 157.0, 157.4, 211.9; Anal. Found: C, 49.36; H, 4.49; N, 4.82%. Calcd for $C_{12}H_{13}FeNO_4$: C, 49.51; H, 4.50; N, 4.81%.

Tricarbonyl[methyl (1,2,3,4-η)-5-*exo*-[2-(*E*)-hydroxyimino-2-phenylethyl]cyclohexa-1,3-diene-1-carboxylate]iron (*syn*-1g): Pale-yellow powder; mp 124 °C (dec.) (dichloromethane–hexane); IR (ZnSe) 3384, 2050, 1967, 1704, 1685, 1434, 1265, 1246, 1095, 914, 739, 696, 602, 563 cm^{-1}; ^1H NMR δ 1.19 (1H, dd, J = 15.0, 3.4 Hz), 2.39 (1H, dd, J = 15.0, 10.8 Hz), 2.57–2.62 (1H, m), 2.69 (1H, dd, J = 12.6, 7.9 Hz), 2.78 (1H, dd, J = 12.6, 6.9 Hz), 3.15–3.17 (1H, m), 3.65 (3H, s), 5.26 (1H, dd, J = 6.0, 4.4 Hz), 6.08 (1H, d, J = 4.4 Hz), 7.37–7.38 (3H, m), 7.53–7.54 (2H, m), 7.85 (1H, broad s); ^{13}C NMR δ 29.4, 35.3, 36.2, 51.5, 51.9, 66.5, 84.5, 89.0, 126.3, 128.7, 129.4, 135.4, 157.7, 172.3, 209.7; Anal. Found: C, 55.68; H, 4.15; N, 3.41%. Calcd for $C_{19}H_{17}FeNO_6$: C, 55.50; H, 4.17; N, 3.41%.

Tricarbonyl[*exo*-2-[(2,3,4,5-η)-5-methylcyclohexa-2,4-dienyl]-1-phenylethan-1-one (*E*)-oxime]iron (*syn*-1h): Yellow needle; mp 134 °C (dec.) (dichloromethane–hexane); IR (ZnSe) 3240, 3057, 2914, 2035, 1950, 1442, 931, 758, 609, 565 cm^{-1}; ^1H NMR δ 1.28 (1H, dd, J = 15.2, 3.0 Hz), 2.00 (1H, dd, J = 15.2, 10.6 Hz), 2.49 (1H, ddddd, J = 10.6, 7.7, 7.5, 3.5, 3.0 Hz), 2.65 (1H, dd, J = 12.9, 7.5 Hz), 2.78 (1H, dd, J = 12.9, 7.7 Hz), 2.88 (1H, ddd, J = 6.3, 3.5, 1.1 Hz), 5.05 (1H, dd, J = 6.3, 4.2 Hz), 5.23 (1H, dd, J = 4.2, 1.1 Hz), 7.36–7.39 (3H, m), 7.52–7.56 (2H, m), 8.15 (1H, broad s); ^{13}C NMR δ 23.9, 35.5, 35.6, 36.9, 64.6, 75.8, 80.6, 88.3, 126.4, 128.7, 129.3, 135.6, 158.3, 212.4; Anal. Found: C, 58.65; H, 4.60; N, 3.71%. Calcd for $C_{18}H_{17}FeNO_4$: C, 58.88; H, 4.67; N, 3.81%.

Synthesis of (3a,7a-Dihydroindole)Fe(CO)$_3$ Complexes by the Cyclization of Oximes Having a (2,4-Cyclohexadienyl)-Fe(CO)$_3$ Moiety at the α-Position. When the cyclized product was purified with Merck silica gel 60N, *trans*-fused (3a,7a-dihydro-3*H*-indole)Fe(CO)$_3$ complexes were obtained. In turn, the isolation with Wako gel B-5F afforded the *cis*-fused isomer. The experimental procedure is shown below as a typical example for the synthesis of tricarbonyl[(4,5,6,7-η)-6-methoxy-2-phenyl-3a-*endo*, 7a-*endo*-dihydro-3*H*-indole]iron (***cis*-3b**) from tricarbonyl[*exo*-3-[(2,3,4,5-η)-(4-methoxycyclohexa-2,4-dienyl)]-1-phenylethan-1-one (*E*)-oxime]iron (***syn*-1b**) (Eq. 4 and Table 3, entry 3).

To a solution of tricarbonyl[*exo*-3-[(2,3,4,5-η)-(4-methoxycyclohexa-2,4-dienyl)]-1-phenylethan-1-one (*E*)-oxime]iron (***syn*-1b**) (57 mg, 0.15 mmol) in dichloromethane (0.5 mL) was added triethylamine (24 μL, 0.17 mmol) and then pentafluorobenzoyl chloride (24 μL, 0.17 mmol) at 0 °C. The reaction mixture was stirred at the same temperature for 60 min, and water was added. Below 0 °C, the mixture was extracted twice with dichloromethane, and the combined extracts were washed with water and brine, then dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure with the flask in an ice-water bath, affording crude tricarbonyl[*exo*-3-[(2,3,4,5-η)-(4-methoxycyclohexa-2,4-dienyl)]-1-phenylethan-1-one (*E*)-*O*-pentafluorobenzoyloxime]iron (***syn*-2b**). The *O*-pentafluorobenzoyloxime was immediately dissolved in dichloromethane (2 mL), and heated at reflux temperature under air. After the oxime derivative ***syn*-2b** disappeared, the solvent was removed in vacuo. The crude product was purified with thin-layer chromatography (Wako gel B-5F, ethyl acetate: hexane:triethylamine = 5:1:0.03) to give tricarbonyl[(4,5,6,7-η)-6-methoxy-2-phenyl-3a-*endo*,7a-*endo*-dihydro-3*H*-indole]iron (***cis*-3b**) (35 mg, 64%).

Spectral Data for Isolable *O*-Acyloximes Having a (2,4-Cyclohexadienyl)Fe(CO)$_3$ Moiety at the α-Position. Tricarbonyl[*exo*-3-[(2,3,4,5-η)-4-methoxycyclohexa-2,4-dienyl]propan-2-one *O*-pentafluorobenzoyloxime]iron (2a): *E* and *Z* = 5:1 mixture; Pale yellow oil; IR (KBr) 2939, 2044, 1971, 1651, 1510, 1194 cm^{-1}; ^1H NMR δ 1.34 (0.17H, dt, J = 14.6, 2.6 Hz), 1.44 (0.83H, dt, J = 14.4, 2.2 Hz), 1.97 (2.5H, s), 2.01 (0.83H, ddd, J = 14.4, 10.4, 3.8 Hz), 2.01–2.07 (0.17H, m), 2.04 (0.5H, s), 2.20–2.33 (2.83H, m), 2.39 (0.17H, dd, J = 12.6, 7.8 Hz), 2.54 (0.17H, dd, J = 6.5, 3.3 Hz), 2.57 (0.83H, dd, J = 6.5, 2.8 Hz), 3.26 (0.83H, ddd, J = 3.8, 2.3, 2.2 Hz), 3.25–3.27 (0.17H, m), 3.60 (0.5H, s), 3.62 (2.5H, s), 5.01 (0.17H, dd, J = 6.5, 2.3 Hz), 5.08 (0.83H, dd, J = 6.5, 2.3 Hz); ^{13}C NMR *E* isomer δ 15.6, 31.0, 34.2, 44.9, 52.1, 53.3, 54.1, 65.8, 106.9 (t, J = 13.2 Hz), 137.6 (d complex, J = 242.9 Hz), 139.9, 143.2 (d complex, J = 259.8 Hz), 145.3 (d complex, J = 257.3 Hz), 156.4, 167.7, 210.8; *Z* isomer δ 19.9, 31.2, 34.2, 40.3, 51.8, 53.0, 54.0, 65.6, 106.9 (t, J = 13.2 Hz), 137.6 (d complex, J = 242.9 Hz), 139.9, 143.2 (d complex, J = 259.8 Hz), 145.3 (d complex, J = 257.3 Hz), 156.3, 167.8, 210.8.

Due to the instability on standing even below 0 °C under argon, elemental analysis could not be performed.

Tricarbonyl[*exo*-2-[(2,3,4,5-η)-4-methoxycyclohexa-2,4-dienyl]-1-phenylethan-1-one (*E*)-*O*-acetyloxime]iron (4): Yellow powder; mp 143 °C (dec.) (dichlormethane–hexane); IR (ZnSe) 2970, 2040, 1957, 1739, 1485, 1425, 1365, 1228 cm^{-1}; ^1H NMR δ 1.38 (1H, dt, J = 14.7, 2.7 Hz), 1.98 (1H, ddd, J = 14.7, 10.6, 3.7 Hz), 2.23 (1H, ddddd, J = 13.6, 12.7, 10.6, 3.5, 2.7 Hz), 2.28 (3H, s), 2.48 (1H, dd, J = 3.5, 6.4 Hz), 2.74 (1H, dd, J = 13.6, 7.3 Hz), 2.77 (1H, dd, J = 12.7, 7.3 Hz), 3.26 (1H, ddd, J = 3.7, 2.7, 2.3 Hz), 3.62 (3H, s), 4.94 (1H, dd, J = 6.5, 2.3 Hz), 7.36–7.45 (3H, m), 7.63 (2H, d, J = 7.6 Hz); ^{13}C NMR δ 19.9, 31.7, 34.9, 37.1, 52.1, 53.4, 54.2, 66.1, 127.3, 128.7, 130.6, 134.0, 139.8, 164.6, 169.0, 210.7; HRMS (FAB$^+$) Found: m/z 426.0652, Calcd for $C_{20}H_{20}FeNO_6$: $(M + H)^+$, 426.0640.

Tricarbonyl[*exo*-2-[(2,3,4,5-η)-4-methoxycyclohexa-2,4-dienyl]-1-phenylethan-1-one (*E*)-*O*-benzoyloxime]iron (5): Yellow powder; mp 124 °C (dec.) (dichloromethane–hexane); IR (ZnSe) 2994, 2040, 1955, 1743, 1483, 1448, 1228, 1051, 1022 cm^{-1}; ^1H NMR δ 1.53 (1H, ddd, J = 14.6, 2.7 Hz), 2.05 (1H, ddd, J = 14.6, 10.5, 3.5 Hz), 2.22–2.29 (1H, m), 2.53 (1H, dd, J = 6.5, 3.5 Hz), 2.87–2.95 (2H, m), 3.25–3.27 (1H, m), 3.43 (3H, s), 4.87 (1H, dd, J = 6.5, 2.2 Hz), 7.40–7.46 (3H, m), 7.52 (2H, dd, J = 7.4, 7.1 Hz), 7.63 (1H, t, J = 7.4 Hz), 7.73 (2H, d, J = 6.9 Hz), 8.13 (2H, d, J = 7.1 Hz); ^{13}C NMR δ 31.9, 34.8, 37.3, 52.3, 53.0, 54.1, 65.9, 127.4, 128.7, 128.7, 129.1, 129.6, 130.7, 133.4, 133.6, 139.8, 163.6, 165.7, 210.6.

Spectral Data for (3a,7a-Dihydroindole)Fe(CO)$_3$ Complexes. For ***trans*-3a**, ***cis*-3a**, ***trans*-3b**, and ***cis*-3a**, the stereochemistry was determined by the NOESY experiments (the *trans*-fused isomers: no significant correlation between H^{3a} and H^{7a}, the *cis*-fused isomers: strong correlation between H^{3a} and H^{7a}) (Fig. 1).

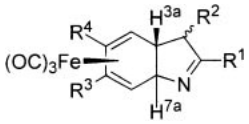


Fig. 1.

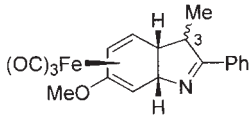


Fig. 2.

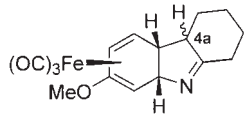


Fig. 3.

Similarly to ***cis*-3a** and ***cis*-3b**, the other (3a,7a-dihydroindole)-$Fe(CO)_3$ complexes were obtained by the isolation with Wako gel B-5F, which suggested that these complexes are *cis*-fused. In addition, due to the instability on standing, elemental analyses could not be performed for the *trans*-fused (3a,7a-dihydroindole)-$Fe(CO)_3$ complexes.

Tricarbonyl[(4,5,6,7-η)-6-methoxy-2-methyl-3a-*endo*,7a-*exo*-dihydro-3*H*-indole]iron (*trans*-3a): Colorless powder; mp 141 °C (ethyl acetate); IR (KBr) 2056, 1981, 1959, 1628, 1493, 1358, 1227, 985 cm^{-1}; ^1H NMR δ 2.23 (3H, s), 2.35 (1H, d, J = 18.0 Hz), 2.68 (1H, dd, J = 6.3, 3.9 Hz), 2.75 (1H, dd, J = 18.0, 10.0 Hz), 2.93–2.95 (1H, m), 3.65 (3H, s), 3.79–3.81 (1H, distorted s), 4.78–4.80 (1H, m), 5.18 (1H, d, J = 6.3 Hz); ^{13}C NMR δ 19.1, 39.3, 46.9, 51.0, 51.9, 55.5, 68.2, 74.8, 140.8, 181.1, 208.0.

Tricarbonyl[(4,5,6,7-η)-6-methoxy-2-methyl-3a-*endo*,7a-*endo*-dihydro-3*H*-indole]iron (*cis*-3a): Yellow plate; mp 105–106 °C (dichlromethane–petroleum ether); IR (KBr) 2040, 2033, 1979, 1643, 1483, 1419, 1255, 1217 cm^{-1}; ^1H NMR δ 1.83 (3H, s), 2.03 (1H, dd, J = 18.0, 3.6 Hz), 2.43 (1H, dd, J = 18.0, 10.0 Hz), 2.65–2.70 (2H, m), 3.60 (3H, s), 3.67 (1H, dd, J = 4.1, 2.1 Hz), 4.47–4.49 (1H, m), 5.08 (1H, dd, J = 6.8, 2.1 Hz); ^{13}C NMR δ 19.7, 39.9, 47.5, 52.6, 54.6, 55.3, 67.3, 78.8, 139.9, 171.3, 210.6; Anal. Found: C, 51.40; H, 4.49; N, 4.70%. Calcd for $C_{13}H_{13}FeNO_4$: C, 51.52; H, 4.32; N, 4.62%.

Tricarbonyl[(4,5,6,7-η)-6-methoxy-2-phenyl-3a-*endo*,7a-*exo*-dihydro-3*H*-indole]iron (*trans*-3b): Colorless powder; mp 139 °C (dec.) (dichloromethane–hexane); IR (ZnSe) 2931, 2038, 1953, 1684, 1597, 1221 cm^{-1}; ^1H NMR δ 2.77–2.80 (2H, m), 3.00–3.04 (1H, m), 3.16 (1H, dd, J = 18.6, 10.6 Hz), 3.63 (3H, s), 3.90–3.94 (1H, m), 5.00–5.06 (1H, m), 5.15 (1H, dd, J = 6.3, 2.0 Hz), 7.45 (2H, dd, J = 7.7, 7.3 Hz), 7.55 (1H, t, J = 7.3 Hz), 7.86 (2H, d, J = 7.7 Hz); ^{13}C NMR δ 38.2, 43.0, 50.9, 52.3, 55.1, 67.7, 75.1, 129.1, 129.2, 130.0, 133.5, 140.3, 173.6, 209.8.

Tricarbonyl[(4,5,6,7-η)-6-methoxy-2-phenyl-3a-*endo*,7a-*endo*-dihydro-3*H*-indole]iron (*cis*-3b): Colorless powder; mp 142 °C (dichloromethane–hexane); IR (ZnSe) 2931, 2038, 1952, 1612, 1483, 1448, 1423, 1225, 1024 cm^{-1}; ^1H NMR δ 2.55 (1H, dt, J = 17.1, 3.2 Hz), 2.80 (1H, dd, J = 6.5, 3.9 Hz), 2.82–2.88 (1H, m), 2.92 (1H, ddd, J = 17.1, 10.5, 1.5 Hz), 3.59 (3H, s), 3.80 (1H, dd, J = 4.2, 2.3 Hz), 4.75–4.88 (1H, m), 5.08 (1H, dd, J = 6.5, 2.3 Hz) 7.37–7.47 (3H, m), 7.73–7.75 (2H, d, J = 6.8 Hz); ^{13}C NMR δ 39.3, 43.7, 54.6, 55.5, 67.3, 79.0, 127.6, 128.3, 130.5, 134.5, 139.9, 168.9, 210.7; Anal. Found: C, 59.01; H, 4.16; N, 3.70%. Calcd for $C_{18}H_{15}FeNO_4$: C, 59.20; H, 4.14; N, 3.84%.

Tricarbonyl[(4,5,6,7-η)-2-(1,1-dimethylethyl)-6-methoxy-3a-*endo*,7a-*endo*-dihydro-3*H*-indole]iron (*cis*-3c): Colorless powder; mp 86 °C (dichloromethane–hexane); IR (ZnSe) 2960, 2038, 1952, 1630, 1485, 1423, 1234 cm^{-1}; ^1H NMR δ 1.05 (9H, s), 2.14 (1H, d, J = 17.9 Hz), 2.49 (1H, dd, J = 10.5, 17.6 Hz), 2.61–2.69 (1H, m), 2.69–2.74 (1H, m), 3.60 (3H, s), 3.72–3.75 (1H, m), 4.50–4.55 (1H, m), 5.06 (1H, d, J = 6.5 Hz); ^{13}C NMR δ 28.0, 35.5, 39.3, 42.3, 53.0, 54.8, 55.3, 67.4, 78.2, 140.1, 180.7, 210.8; Anal. Found: C, 55.67; H, 5.49; N, 3.91%. Calcd for $C_{16}H_{19}FeNO_4$: C, 55.67; H, 5.55; N, 4.06%.

Tricarbonyl[(4,5,6,7-η)-6-methoxy-3-methyl-2-phenyl-3a-*endo*,7a-*endo*-dihydro-3*H*-indole]iron (*cis*-3d): Colorless powder; mp 140 °C (dec.) (dichloromethane–hexane); IR (ZnSe) 2929, 2038, 1950, 1610, 1576, 1485, 1423, 1223, 1018 cm^{-1}; ^1H NMR δ 1.10 (3H, d, J = 7.4 Hz), 2.39 (1H, ddd, J = 8.8, 4.0, 3.3 Hz), 2.84 (1H, dd, J = 6.5, 4.0 Hz), 2.94 (1H, ddq, J = 3.3, 2.4, 7.4 Hz), 3.56 (3H, s), 3.81 (1H, dd, J = 4.4, 2.2 Hz), 4.70 (1H, ddd, J = 8.8, 4.4, 2.4 Hz), 5.07 (1H, dd, J = 6.5, 2.2 Hz), 7.34–7.40 (3H, m), 7.68 (2H, d, J = 7.9 Hz); ^{13}C NMR δ 20.1, 50.0, 50.9, 51.8, 54.6, 55.4, 67.6, 76.4, 128.1, 128.4, 130.2, 133.8, 140.1, 173.1, 210.7; HRMS (FAB$^+$) Found: m/z 380.0559, Calcd for $C_{19}H_{18}FeNO_4$: $(M + H)^+$, 380.0585.

The stereochemistry of the 3-position was not determined (Fig. 2).

Tricarbonyl[(5,6,7,8-η)-7-methoxy-2,3,4,4a,4b-*endo*,8a-*endo*-hexahydro-1*H*-carbazole]iron (*cis*-3e): Yellow oil; IR (ZnSe) 2933, 2040, 1955, 1649, 1485, 1425, 1250, 1215 cm^{-1}; ^1H NMR δ 1.66–1.76 (1H, m), 1.76–1.95 (2H, m), 1.95–2.12 (3H, m), 2.20–2.33 (1H, m), 2.33–2.48 (1H, m), 2.73–2.82 (1H, m), 3.60 (3H, s), 3.64–3.68 (1H, m), 4.40–4.56 (1H, m), 5.13–5.14 (1H, m); ^{13}C NMR δ 25.4, 27.3, 32.2, 34.7, 46.8, 51.5, 54.5, 55.7, 57.5, 67.3, 78.1, 140.0, 177.9, 210.7; HRMS (FAB$^+$) Found: m/z 344.0596, Calcd for $C_{16}H_{18}FeNO_4$: $(M + H)^+$, 344.0585.

The stereochemistry of the 4a-position was not determined (Fig. 3).

Tricarbonyl[(4,5,6,7-η)-2-methyl-3a-*endo*,7a-*endo*-dihydro-3*H*-indole]iron (*cis*-3f): Pale-yellow plates; mp 92–94 °C (dichloromethane–petroleum ether); IR (ZnSe) 2916, 2038, 1950, 1645, 1427, 611, 561 cm^{-1}; ^1H NMR δ 1.85 (3H, s), 2.08 (1H, dd, J = 18.0, 2.9 Hz), 2.48 (1H, dd, J = 18.0, 11.0 Hz), 3.27–3.29 (1H, m), 3.09–3.12 (1H, m), 3.40–3.42 (1H, m), 4.45 (1H, d, J = 8.1 Hz), 5.32 (1H, t, J = 5.3 Hz), 5.39 (1H, t, J = 5.3 Hz); ^{13}C NMR δ 19.7, 40.0, 47.6, 54.4, 62.1, 63.8, 76.9, 85.4, 85.6, 171.4, 211.2; Anal. Found: C, 52.51 H, 4.07; N, 4.98%. Calcd for $C_{12}H_{11}FeNO_3$: C, 52.78; H, 4.06; N, 5.13%.

Tricarbonyl[methyl (4,5,6,7-η)-2-phenyl-3a-*endo*,7a-*endo*-dihydro-3*H*-indole-5-carboxylate] iron (*cis*-3g): Pale-yellow powder; mp 163 °C (dec.) (dichloromethane–petroleum ether); IR (ZnSe) 2052, 1975, 1724, 1614, 1434, 1340, 1265, 1084 cm^{-1}; ^1H NMR δ 2.55 (1H, ddd, J = 17.7, 4.0, 3.0 Hz), 2.98 (1H, dd, J = 17.7, 10.2 Hz), 3.10–3.16 (1H, m), 3.67–3.70 (1H, m), 3.76 (1H, dd, J = 4.0, 1.5 Hz), 3.79 (3H, s), 4.74–4.76 (1H, m), 6.20 (1H, dd, J = 6.7, 1.6 Hz), 7.34–7.40 (3H, m), 7.67–7.68 (2H, m); ^{13}C NMR δ 29.4, 39.3, 43.7, 52.5, 62.8, 63.5, 86.8, 88.9, 127.6, 128.4, 130.8, 134.0, 169.2, 169.7, 209.5.

Tricarbonyl[methyl (4,5,6,7-η)-2-phenyl-3a-*endo*,7a-*endo*-dihydro-3*H*-indole-7-carboxylate] iron (*cis*-10g): Yellow

plates; mp 173–179 °C (dec.) (dichloromethane–petroleum ether); IR (ZnSe) 2950, 2050, 1968, 1704, 1275, 1236, 1085 cm^{-1}; ^1H NMR δ 2.60 (1H, ddd, $J = 17.6$, 3.4, 2.7 Hz), 2.97 (1H, ddd, $J = 17.6$, 10.4, 1.7 Hz), 3.19 (1H, dddd, $J = 10.4$, 9.2, 3.9, 3.4 Hz), 3.31 (1H, ddd, $J = 6.4$, 3.9, 1.4 Hz), 3.79 (3H, s), 5.21 (1H, dddd, $J = 9.2$, 2.7, 1.7, 1.2 Hz), 5.37 (1H, dd, $J = 6.4$, 4.5 Hz), 6.14 (1H, ddd, $J = 4.5$, 1.4, 1.2 Hz), 7.32–7.38 (3H, m), 7.68–7.70 (2H, m); ^{13}C NMR δ 41.4, 44.3, 51.8, 60.3, 64.4, 66.0, 75.0, 85.6, 87.9, 127.7, 128.3, 130.5, 134.1, 169.2, 171.8, 208.9; Anal. Found: C, 57.83; H, 3.90; N, 3.40%. Calcd for $C_{19}H_{15}FeNO_5$: C, 58.04; H, 3.85; N, 3.56%.

Tricarbonyl[(4,5,6,7-η)-5-methyl-2-phenyl-3a-*endo*,7a-*endo*-dihydro-3*H*-indole]iron (*cis*-3h): Pale-yellow needles; mp 143 °C (dec.) (dichloromethane–petroleum ether); IR (ZnSe) 2038, 1955, 1613, 1339, 1019, 758, 690 cm^{-1}; ^1H NMR δ 2.05 (3H, s), 2.51 (1H, ddd, $J = 17.4$, 3.8, 2.8 Hz), 2.94 (1H, ddd, $J = 17.4$, 10.5, 1.6 Hz), 3.03 (1H, dddd, $J = 10.5$, 9.0, 4.0, 3.8 Hz), 3.18 (1H, dd, $J = 4.0$, 1.8 Hz), 3.39 (1H, dd, $J = 6.2$, 4.1 Hz), 4.64 (1H, dddd, $J = 9.0$, 4.1, 2.8, 1.6 Hz), 5.31 (1H, dd, $J = 6.2$, 1.8 Hz), 7.34–7.41 (3H, m), 7.69–7.71 (2H, m); ^{13}C NMR δ 24.9, 40.7, 44.1, 62.2, 78.9, 81.3, 81.9, 88.4, 127.5, 128.3, 130.4, 134.5, 169.7, 211.9; HRMS (FAB$^+$) Found: m/z 350.0465, Calcd for $C_{18}H_{16}FeNO_3$: $(M + H)^+$, 350.0479.

Tricarbonyl[(4,5,6,7-η)-7-methyl-2-phenyl-3a-*endo*,7a-*endo*-dihydro-3*H*-indole]iron (*cis*-10h): Yellow plates; mp 166–168 °C (dec.) (dichloromethane–petroleum ether); IR (ZnSe) 2993, 2905, 2036, 1954, 1613, 1447 cm^{-1}; ^1H NMR δ 1.88 (3H, s), 2.54 (1H, ddd, $J = 17.6$, 3.8, 2.8 Hz), 2.94 (1H, ddd, $J = 17.6$, 10.4, 1.6 Hz), 3.03–3.11 (2H, m), 4.64 (1H, ddd, $J = 9.1$, 2.8, 1.6 Hz), 5.15 (1H, ddd, $J = 6.3$, 4.3, 0.5 Hz), 5.28 (1H, d, $J = 4.3$ Hz), 7.33–7.41 (3H, m), 7.70–7.72 (2H, m); ^{13}C NMR δ 22.8, 40.0, 43.7, 58.7, 66.5, 77.1, 85.4, 103.2, 127.5, 128.4, 130.5, 134.4, 168.9, 211.3; HRMS (FAB$^+$) Found: m/z 350.0465, Calcd for $C_{18}H_{16}FeNO_3$: $(M + H)^+$, 350.0479.

N*-Pentafluorobenzoylation of Tricarbonyl[(4,5,6,7-η)-6-methoxy-2-phenyl-3a-*endo*,7a-*endo*-dihydro-3*H*-indole]iron (*cis*-3b).** To a solution of tricarbonyl[(4,5,6,7-η)-6-methoxy-2-phenyl-3a-*endo*,7a-*endo*-dihydro-3*H*-indole]iron (cis*-3b**) (910 mg, 2.49 mmol) in dichloromethane (10 mL) were added triethylamine (0.420 mL, 2.99 mmol) and then pentafluorobenzoyl chloride (0.390 mL, 2.71 mmol) at 0 °C. The reaction mixture was stirred at the same temperature, then quenched with water and extracted twice with dichloromethane. The combined organic extracts were washed with saturated aqueous sodium hydrogencarbonate and then brine, and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the crude product was purified by thin-layer chromatography (Wako gel B-5F, ethyl acetate:hexane = 1:4) to afford tricarbonyl[(4,5,6,7-η)-6-methoxy-1-pentafluorobenzoyl-2-phenyl-3a-*endo*,7a-*endo*-dihydroindole]iron (**12**) (1.392 g, quant.). Colorless powder; mp 160 °C (dichloromethane–hexane); IR (ZnSe) 2046, 1957, 1647, 1628, 1500, 1487, 1425, 1398, 1381, 1223, 989 cm^{-1}; ^1H NMR δ 2.83 (1H, dd, $J = 6.4$, 4.2 Hz), 3.35 (1H, ddd, $J = 9.8$, 4.2, 1.9 Hz), 3.65 (3H, s), 4.05 (1H, dd, $J = 3.8$, 2.2 Hz), 5.03 (1H, d, $J = 1.9$ Hz), 5.10 (1H, dd, $J = 9.8$, 3.8 Hz), 5.17 (1H, dd, $J = 6.4$, 2.2 Hz), 6.96–7.02 (2H, m), 7.09–7.13 (3H, m); ^{13}C NMR δ 43.6, 49.8, 52.1, 55.1, 65.7, 67.1, 112.4 (d, $J = 20.4$ Hz), 120.5, 127.0, 127.9, 128.7, 131.6, 136.3 (d complex, $J = 249.9$ Hz), 137.0 (d complex, $J = 252.5$ Hz), 138.0, 140.2, 141.3 (d complex, $J = 254.2$ Hz), 141.9 (d complex, $J = 249.5$ Hz), 142.9 (d complex, $J = 243.2$ Hz), 155.1, 210.0; Anal. Found: C, 53.71; H, 2.75; N, 2.44%. Calcd for $C_{25}H_{14}F_5FeNO_5$: C, 53.69; H, 2.52; N, 2.50%.

Oxidation of Tricarbonyl[(4,5,6,7-η)-6-methoxy-1-pentafluorobenzoyl-2-phenyl-3a-*endo*,7a-*endo*-dihydroindole]iron (12) with Amine *N*-Oxide. The experimental procedure is shown below as a typical example for the oxidation with *N*-methylmorphorine *N*-oxide in *N*,*N*-dimethylacetamide.

Anhydrous *N*-methylmorphorine *N*-oxide (284.0 mg, 2.42 mmol) was added to a solution of tricarbonyl[(4,5,6,7-η)-6-methoxy-1-pentafluorobenzoyl-2-phenyl-3a-*endo*,7a-*endo*-dihydroindole]iron (**12**) (106.0 mg, 0.190 mmol) in *N*,*N*-dimethylacetamide (4 mL) at 0 °C. The reaction mixture was stirred at room temperature for 5 h, then passed through a Celite pad. The solvent was removed in vacuo, and the crude product was purified with thin-layer chromatography (Wako gel B-5F, ethyl acetate:hexane = 1:4) to give 6-methoxy-1-pentafluorobenzoyl-2-phenylindole (**13**) (49.9 mg, 72%) and 6-methoxy-1-pentafluorobenzoyl-2-phenyl-*cis*-3a,7a-dihydroindole (**14**) (3.4 mg, 5%).

6-Methoxy-1-pentafluorobenzoyl-2-phenylindole (13): Colorless powder; mp 110–115 °C (dichloromethane–hexane); IR (ZnSe) 2924, 1684, 1655, 1612, 1495, 1371, 1342, 1275, 1219, 991 cm^{-1}; ^1H NMR δ 3.91 (3H, s), 6.57 (1H, s), 7.00 (1H, dd, $J = 2.3$, 8.5 Hz), 7.18–7.25 (5H, m), 7.46 (1H, d, $J = 8.5$ Hz), 8.08 (1H, d, $J = 2.3$ Hz); ^{13}C NMR δ 56.0, 100.6, 112.7 (t, $J = 18.2$ Hz), 112.9, 113.9, 121.2, 123.0, 128.0, 128.4, 128.6, 132.3, 136.8 (d complex, $J = 256.3$ Hz), 137.6, 138.6, 142.3 (d complex, $J = 258.8$ Hz), 143.2 (d complex, $J = 248.8$ Hz), 157.7, 158.9; HRMS (FAB$^+$) Found: m/z 418.0849, Calcd for $C_{22}H_{12}F_5NO_2$: $(M + H)^+$, 418.0866.

6-Methoxy-1-pentafluorobenzoyl-2-phenyl-*cis*-3a,7a-dihydroindole (14): Colorless plates; mp 92–96 °C (dichloromethane–hexane); IR (ZnSe) 2944, 1631, 1498, 1392, 1225, 1130, 989 cm^{-1}; ^1H NMR δ 3.62 (3H, s), 3.96 (1H, ddd, $J = 11.6$, 4.5, 2.3 Hz), 4.96 (1H, dd, $J = 5.0$, 1.7 Hz), 5.22 (1H, d, $J = 2.3$ Hz), 5.74 (1H, dd, $J = 10.0$, 1.7 Hz), 5.79 (1H, dd, $J = 10.0$, 4.5 Hz), 5.96 (1H, d, $J = 11.6$, 3.5 Hz), 7.09–7.13 (5H, m); ^{13}C NMR δ 39.9, 54.5, 62.6, 89.5, 112.7 (t, $J = 18.4$ Hz), 119.0, 122.7, 126.3, 127.2, 127.9, 128.8, 131.6, 136.4 (d complex, $J = 253.4$ Hz), 137.0 (d complex, $J = 252.7$ Hz), 140.7, 141.3 (d complex, $J = 256.8$ Hz), 142.1 (d complex, $J = 253.3$ Hz), 143.1 (d complex, $J = 247.5$ Hz), 153.6, 155.0; Anal. Found: C, 63.10; H, 3.56; N, 3.17%. Calcd for $C_{22}H_{14}F_5NO_2$: C, 63.01; H, 3.37; N, 3.34%.

Transformation of 6-Methoxy-1-pentafluorobenzoyl-2-phenylindole (13) to 6-Methoxy-2-phenylinodle (15). A solution of 6-methoxy-1-pentafluorobenzoyl-2-phenylindole (**13**) (6.1 mg, 0.0145 mmol) in methanol (2 mL) and tetrahydrofuran (2 mL) was treated with lithium hydroxide (25 mg, 1.04 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 10 h, then quenched with water and extracted twice with dichloromethane. The combined organic extracts were washed with saturated aqueous ammonium chloride and then brine, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified with thin-layer chromatography (Wako gel B-5F, ethyl acetate:hexane = 3:1) to afford 6-methoxy-2-phenylindole[24] (**15**) (3.0 mg, 92%). Colorless powder; IR (ZnSe) 3388, 2929, 1734, 1452, 1263, 1159, 1020 cm^{-1}; ^1H NMR δ 3.85 (3H, s), 6.74 (1H, d, $J = 1.7$ Hz), 6.78 (1H, dd, $J = 8.6$, 2.2 Hz), 6.88 (1H, d, $J = 2.2$ Hz), 7.27 (1H, t, $J = 7.4$ Hz), 7.41 (2H, dd, $J = 7.4$, 7.3 Hz), 7.48 (1H, d, $J = 8.6$ Hz), 7.60 (2H, d, $J = 7.3$ Hz), 8.24 (1H, d, $J = 1.7$ Hz); ^{13}C NMR δ 55.6, 94.4, 99.8, 110.2, 121.2, 123.5, 124.7, 127.2, 129.0, 132.5, 136.8, 137.6, 156.7.

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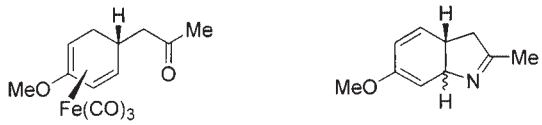

Fig. 4.

17 When radical initiators such as 2,2′-azobis(isobutyronitrile) and benzoyl peroxide were employed for the cyclization of *O*-pentafluorobenzoyloxime **2a**, the cyclized product was obtained in low yield with many by-products.

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