

Headline Articles

Synthesis of Pyrrole Derivatives by Palladium-Catalyzed Cyclization of γ,δ-Unsaturated Ketone *O*-Pentafluorobenzoyloximes

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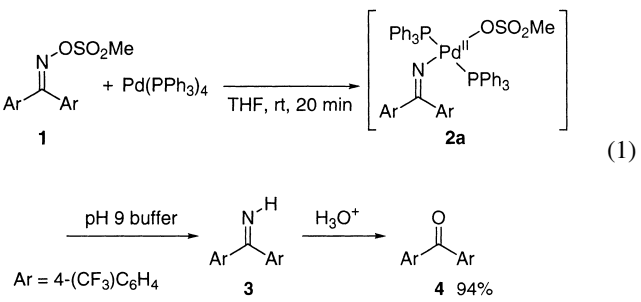
Various pyrrole derivatives are synthesized from γ,δ-unsaturated ketone *O*-pentafluorobenzoyloximes by treatment with catalytic amounts of $Pd(PPh_3)_4$ and triethylamine via alkylideneaminopalladium(II) intermediates generated by oxidative addition of the oximes to the Pd(0) complex.

Though oxime derivatives generally undergo the Beckmann rearrangement,[1–3] there have been reports of some other types of reactions which realize direct intramolecular cyclization on the sp^2 nitrogen atom of oximes with the N–O bond cleavage. One of the typical examples is S_N2-type reaction of oxime derivatives with intramolecular hetero atoms and carbon nucleophiles, affording a variety of nitrogen-heterocycles such as benzoisoxazoles,[4] tetrahydropyrido[1,2-*b*]indazoles,[5] 1,2-benzothiazines,[6] 2,3,7,8-tetrahydrocyclopent[*ij*]isoquinolines,[7] decahydroquinolines,[8] quinolines,[9] and dihydropyrroles.[10] Another representative reaction is the formation of alkylideneaminyl radical species and their equivalents to synthesize phenanthridines,[11] dihydropyrroles,[12–14] and α-carbolines.[15] Transition metal-mediated and -catalyzed cyclizations of oxime have been also reported. Murahashi et al. reported that aminopalladations occurs on γ,δ-unsaturated oximes with the action of an equimolar amount of palladium(II) complex; the successive elimination of the hydroxy group gave pyridines.[16] The palladium(II)-catalyzed cyclization of δ,ε-unsaturated oximes was reported by Grigg et al. to afford cyclic nitrones.[17] Recently, we communicated a new type of synthesis of nitrogen-containing heterocycles by palladium(0)-catalyzed cyclization of olefinic ketone *O*-pentafluorobenzoyloximes via alkylideneaminopalladium species.[18–20] This paper contains full accounts of this catalytic pyrrole synthesis.

Results and Discussion

Reaction of *O*-Methylsulfonyloximes and Palladium(0) Complex. During our study on S_N2-type reaction of oxime derivatives with intermolecular nucleophilic moieties,[21] we expected that low-valent transition metal compounds, good electron donors, would react with oxime derivatives to give oxidative addition compounds, such as alkylideneaminometal species. Accordingly, an equimolar amount reaction of 4,4′-bis(trifluoromethyl)benzophenone *O*-methylsulfonyloxime (**1**) and $Pd(PPh_3)_4$ was examined firstly. After stirring a tetrahydrofuran (THF) solution of the above reagents at room temperature for 20 min, bis[(4-trifluoromethyl)phenyl]methanimine (**3**) was obtained as a crude product after quenching with pH 9 buffer; this was hydrolyzed to benzophenone **4** in 94% overall yield with acidic treatment. The generation of diphenylmethanimine **3** indicated that diarylmethylideneaminopalladium(II) species **2a** was formed by oxidative addition of **1** to $Pd(PPh_3)_4$ (Eq. 1).



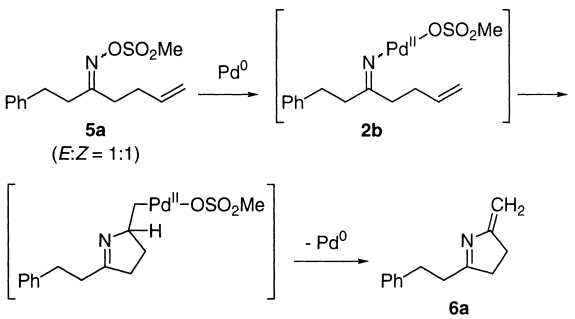
(1)

Trials to isolate the amino complex **2a** have been unsuccessful, so we monitored the reaction of **1** and $Pd(PPh_3)_4$ in CD_2Cl_2 by ^{31}P NMR spectroscopy using 85% H_3PO_4 as an external standard. After 0.5 h at 25 °C, the peak of $Pd(PPh_3)_4$ at 14.5 ppm[22] disappeared and two broad peaks at 29.3 and 34.5 ppm, a singlet peak at 21.9 ppm, and a peak at −5.1 ppm as free PPh_3 were observed. When the reaction mixture were heated to 50 °C, two broad peaks disappeared and only two singlet peaks were observed at 21.2 and −4.3 ppm. Thus, we concluded that *O*-methylsulfonyloxime **1** readily reacts with $Pd(PPh_3)_4$ and some palladium complexes were generated.

Although we could not confirm the formation of alkylideneaminopalladium(II) species **2a** by the NMR study, Pombeiro et

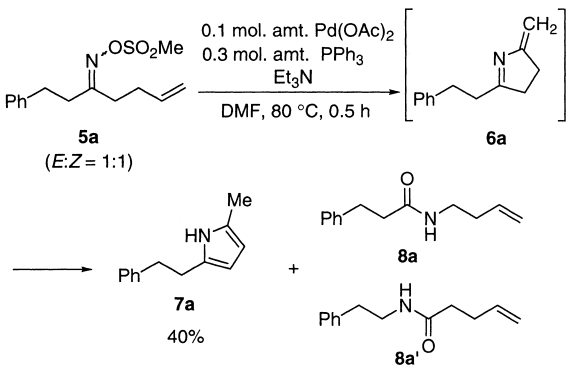
al. recently reported the isolation of an oxidative addition product of acetone oxime to a rhenium(I) complex.[23] In addition, the formation of alkylideneaminopalladium(II) species was also suggested in a recent report on the ring cleavage of cyclobutanone oximes by Uemura et al. with a palladium(0) complex.[24] Accordingly, the reaction of **1** and $Pd(PPh_3)_4$ is likely to afford an oxidative addition species like **2a**. Recently, alkylideneaminopalladium(II) species, which have been utilized scarcely in organic synthesis, have attracted attention as synthetic intermediates. Based on the generation of these species from diphenylmethanimine, palladium-catalyzed amination of aryl halides were reported by Buchwald et al.[25] and Hartwig et al.[26] In contrast to unstable diphenylmethanimine, oxime derivatives are generally stable enough to handle, and the oxidative addition of oximes thus provides another convenient method for generation of alkylideneaminopalladium(II) species.

Then, in order to utilize the alkylideneaminopalladium(II) species in organic synthesis, we examined palladium-catalyzed cyclization of 1-phenyl-6-hepten-3-one *O*-methylsulfonyloxime (**5a**), which is a 1:1 mixture of *E*- and *Z*-forms, expecting that intramolecular amination would proceed similarly to the Heck (Mizoroki–Heck) reaction.[27–29] That is, addition of alkylideneaminopalladium(II) species **2b** generated by the oxidative addition of **5a** to the olefinic moiety and the successive β-hydride elimination would afford 2-methylidene-5-phenethyl-3,4-dihydro-2*H*-pyrrole (**6a**) (Eq. 2).



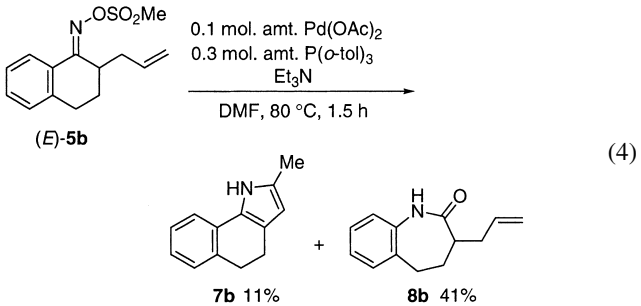
(2)

In fact, after heating a mixture of *O*-methylsulfonyloxime **5a**, triethylamine, and a catalytic amount of $Pd(OAc)_2/PPh_3$ in *N*,*N*-dimethylformamide (DMF) at 80 °C, 2-methyl-5-phenethylpyrrole (**7a**), the aromatization product of the initially formed 3,4-dihydro-2*H*-pyrrole **6a**, was obtained in 40% yield (Eq. 3). The desired amino Heck-type reaction thus occurred, while the Beckmann products **8a** and **8a′** were formed as side



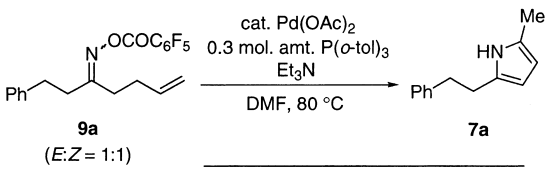
(3)

products. In a similar reaction of 2-allyl-1-tetralone *O*-methylsulfonyloxime (**5b**), the Beckmann product **8b** was obtained as a major product and the desired pyrrole derivative **7b** was formed only in 11% yield (Eq. 4). Though some pyrrole syntheses have been reported by using palladium-mediated and -catalyzed cyclization of alkenes and alkynes containing nitrogen nucleophiles,[30] such as amines[31,32] and hydrazones,[33] the present method is the first example in which using imine equivalent from oximes as nitrogen nucleophiles.



(4)

Synthesis of Pyrrole Derivatives from γ,δ-Unsaturated Ketone *O*-Pentafluorobenzoyloximes. To suppress the Beckmann rearrangement, several *O*-substituted oximes of 1-phenyl-6-hepten-3-one were prepared and submitted to the palladium-catalyzed amino Heck-type cyclization. The cyclization proceeded very slowly in the reactions of *O*-benzoyloxime and *O*-diphenylphosphinoyloxime. Though *O*-trifluoroacetyloxime smoothly reacted, it was hydrolyzed very easily. 1-Phenyl-6-hepten-3-one *O*-pentafluorobenzoyloxime (**9a**) was found to be stable enough for isolation by silica gel column chromatography, and the cyclization proceeded within 1 h to afford pyrrole **7a** in 56% yield without the Beckmann rearrangement. In the absence of palladium catalyst, the cyclization did not occur and the starting material **9a** was recovered (Eq. 5).

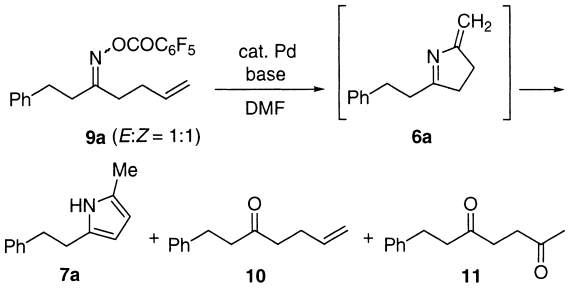


cat. $Pd(OAc)_2$	time	7a	9a
0.1 mol. amt.	1 h	56%	0%
none	4 h	0%	85%

(5)

This amino Heck-type reaction of **9a** was screened under various reaction conditions concerning bases, ligands, and temperature (Table 1). The use of potassium carbonate as a base instead of triethylamine gave pyrrole **7a** in only 13% yield, but gave diketone **11** as a major product in 43% yield (entry 2). Presumably, 3,4-dihydro-2*H*-pyrrole **6a**, a preliminary product of the cyclization, hardly aromatized to pyrrole **7a** under potassium carbonate conditions, and **6a** was hydrolyzed to diketone **11** during work-up. In fact, by addition of triethylamine at 80 °C for 1 h after the palladium-catalyzed cyclization in the presence of potassium carbonate, the yield of

Table 1. The Palladium-Catalyzed Cyclization of **9a**[a)]



Entry	Cat. Pd	Base[b)]	Temp/°C	Time/h	Yield/%[c)]	
					7a	**10**
1	$Pd(PPh_3)_4$	Et_3N	80	1	65	17
2	$Pd(PPh_3)_4$	K_2CO_3	80	1	13[d)]	16
3	$Pd(OAc)_2 + 3PPh_3$	Et_3N	80	1	60	18
4	$Pd(OAc)_2 + 3P(o\text{-tol})_3$	Et_3N	80	1	60	9
5	$Pd(OAc)_2 + 3P(n\text{-Bu})_3$	Et_3N	80	1	47	29
6	$Pd(OAc)_2 + 3P(OPh)_3$	Et_3N	80	1	58[e)]	12
7	$Pd(OAc)_2$ + dppe	Et_3N	80	1	66	11
8	$Pd(OAc)_2$ + dppp	Et_3N	80	1	59	6
9	$Pd(OAc)_2$ + dppb	Et_3N	80	1	58	15
10	$Pd(OAc)_2$	Et_3N	80	1	10[f)]	15
11	$Pd(PPh_3)_4$	Et_3N	50	5	45	27

a) **9a**:cat. Pd = 1.0 : 0.1. The concentration of **9a** was 0.1 mol dm^{-3}. b) 5 molar amounts of Et_3N or 2.5 molar amounts of K_2CO_3 was used. c) Yield was determined by ^1H NMR spectroscopy with anthracene as an internal standard. d) **11** was isolated in 43% yield. e) **9a** was recovered in 20% yield. f) **9a** was recovered in 47% yield.

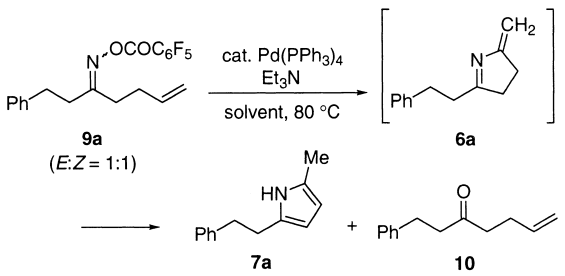
pyrrole **7a** was 54% with a small amount (4%) of diketone **11**.

Without a phosphine ligand, palladium black was deposited (entry 10). The use of phosphine ligand was thus indispensable, and mono and bidentate aryl-phosphines exhibited almost similar effect on the product yield (entries 3,4,7-9). At lower reaction temperature (50 °C), the yield of **7a** decreased (entry 11).

Polar solvents, such as DMF and *N*,*N*-dimethylacetamide (DMA), were found to be more suitable than toluene, acetonitrile, and THF (Table 2, entries 1–5). In almost all cases, ketone **10** was the main side product; it was probably formed by hydrolysis of the initially formed ketimine of **10**. It is noteworthy that the concentration of the mixture considerably influences the product yield and that **7a** was obtained in 81% yield by the reaction at a concentration of 0.02 mol dm^{-3} (entry 6). Based on the above screening, the following experiments were examined by using $Pd(PPh_3)_4$ as a catalyst and triethylamine as a base in DMF at the concentration of 0.02 mol dm^{-3}.

In the reaction of the above phenethyl ketone oxime **9a**, pyrrole **7a** was isolated as a single cyclization product without any particular operation after a common work-up. The reaction of 1-phenyl-4-penten-1-one (*E*)-*O*-pentafluorobenzoyloxime (*E*-**9c**), however, gave a mixture of 2-methylidene-5-phenyl-3,4-dihydro-2*H*-pyrrole (**6c**) and 2-methyl-5-phenylpyrrole (**7c**). To isomerize cyclic imine **6c** to pyrrole **7c**, the crude mixture was treated with 1.5 molar amounts of chlorotrimethylsilane to afford pyrrole **7c** as a sole product (Table 3, entry 1). Stereochemistry of the oxime **9c** did not exhibit any significant influence on the product yield (entries 1 and 2). Therefore, (*E*)- and (*Z*)-alkylideneaminopalladium(II) species seem to readily isomerize under the present reaction conditions. This is a keen

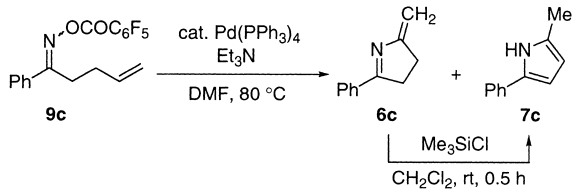
Table 2. Influence of Solvent and Concentration in the Palladium-Catalyzed Cyclization of **9a**[a)]



Entry	Solvent	Conc.[c)]	Time/h	Yield/%[d)]	
				7a	**10**
1	DMF	0.1	1	65	17
2	DMA[b)]	0.1	2	66	19
3	Toluene	0.1	2	42	28
4	MeCN	0.1	3	44	15
5	THF	0.1	2	22	26
6	DMF	0.02	3	81 (72)[e)]	7

a) **9a**:$Pd(PPh_3)_4$:Et_3N = 1.0 : 0.1 : 5.0. b) *N*,*N*-dimethylacetamide. c) The concentration (mol dm^{-3}) of **9a**. d) Yield was determined by ^1H NMR spectroscopy with anthracene as an internal standard. e) Isolated yield is in parentheses.

Table 3. The Palladium-Catalyzed Cyclization of **9c**[a)]



Entry	**9c**	$Pd(PPh_3)_4$/mol amt.	Time/h	Yield/%[c)]
1	(*E*)-**9c**	0.1	1	86
2	(*Z*)-**9c**	0.1	1	83
3	(*E*)-**9c**	0.03	1	82
4	(*E*)-**9c**	0.01[b)]	2	75

a) **9c**:Et_3N = 1.0 : 5.0. The concentration of **9c** was 0.02 mol dm^{-3}. b) PPh_3 (0.04 mol amt.) was added to the reaction mixture. c) Isolated yield.

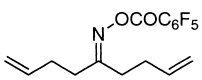
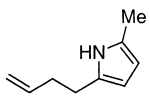
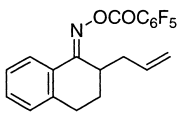
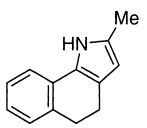
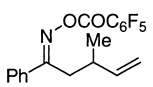
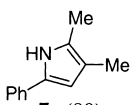
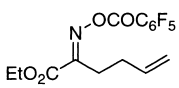
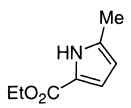
contrast to vinylpalladium species such as (*E*)- and (*Z*)-bromo(styryl)bis(triphenylphosphine)palladium(II), which do not isomerize under the coupling reaction conditions.[34] The cyclization could also be carried out in good yield even by the use of a 0.03 or 0.01 molar amount of $Pd(PPh_3)_4$ (entries 3 and 4).

Zard et al. have reported the synthesis of 2*H*-3,4-dihydropyrroles by the cyclization of γ,δ-unsaturated ketone *O*-pivaloyloximes with nickel(0) metal in acetic acid and 2-propanol,[13b] in which alkylideneaminyl radical is proposed as an intermediate. The present palladium-catalyzed cyclization of (*E*)-**9c** proceeded smoothly even in the presence of radical scavengers such as 1,4-cyclohexadiene and 2,2,6,6-tetramethyl-1-piperidyloxyl (TEMPO) to afford pyrrole **7c** in 84% and 85% yield, respectively. Accordingly, the cyclization does not occur via alkylideneaminyl radical intermediate, but proceeded by intramolecular insertion of the olefinic moiety to aminopalladium species.

The palladium-catalyzed cyclization of *O*-pentafluorobenzoyloximes having a terminal vinyl group proceeded smoothly and the results are listed in Table 4. Like **9a**, bis(homoallyl) ketone oxime **9d** cyclized to pyrrole **7d** in 79% yield without the isomerization procedure with silyl chloride (method A). In the reactions of phenyl and ethoxycarbonyl ketone oximes, the isomerization step with chlorotrimethylsilane was required after the palladium-catalyzed cyclization to obtain pyrroles **7b, 7e**, and **7f** (method B). 2-Allyl-1-tetralone *O*-pentafluorobenzoyloxime (**9b**) was successfully transformed into tricyclic pyrrole **7b** in 89% yield without the Beckmann product (entry 2), whereas the Beckmann rearrangement mainly proceeded in the reaction of the corresponding *O*-methylsulfonyloxime **5b**, as mentioned previously.

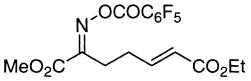
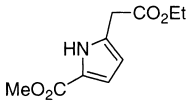
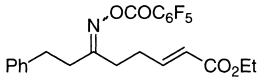
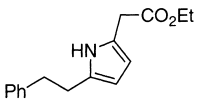
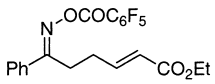
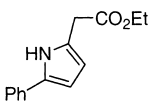
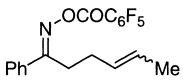
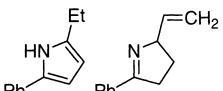
Several disubstituted olefinic ketone *O*-pentafluorobenzoyloximes were cyclized to pyrroles on treatment with the palladium catalyst as described in Table 5. It is well known that electron-deficient alkenes are suitable for the Heck reaction.[28,29] Similar phenomena were also observed in this amino Heck-reaction (entries 1–3). For example, α-keto ester oxime **9g** having ethoxycarbonyl group on the olefinic moiety gave pyrrole **7g** in better yield (78%, entry 1) as compared with the cycliza-

Table 4. Synthesis of Pyrrole Derivatives by Palladium-Catalyzed Cyclization of *O*-Pentafluorobenzoyloximes **9** Having Terminal Vinyl Group[a)]

Entry	Oxime	Method[b)]	Time/h	Product (Yield/%)[c)]
1	 **9d**	A	2	 **7d** (79)
2	 (*E*)-**9b**	B	1	 **7b** (89)
3	 (*E*)-**9e**	B	1	 **7e** (80)
4	 (*E*)-**9f**	B	1	 **7f** (45)

a) Oxime:$Pd(PPh_3)_4$:Et_3N = 1.0 : 0.1 : 5.0. The reaction was conducted in DMF at 80 °C. The concentration of oxime was 0.02 mol dm^{-3}. b) Method A: The isomerization of dihydropyrrole to pyrrole occurred under the palladium-catalyzed cyclization condition. Method B: Dihydropyrrole isomerized to pyrrole by treatment of 1.5 molar amounts of Me_3SiCl in CH_2Cl_2 for 0.5 h after the palladium-catalyzed cyclization. c) Isolated yield.

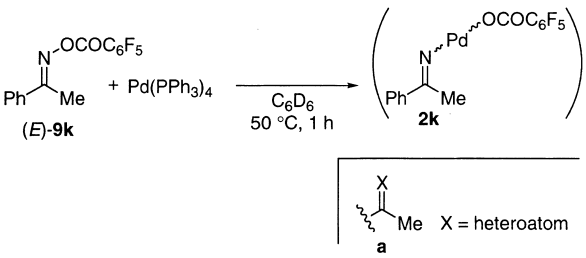
Table 5. Synthesis of Pyrrole Derivatives by Palladium-Catalyzed Cyclization of Disubstituted Olefinic Ketone *O*-Pentafluorobenzoyloximes **9**[a)]

Entry	Oxime	Method[b)]	Time/h	Product (Yield/%)[c)]
1	 (*E*)-**9g**	B	1	 **7g** (78)
2	 **9h** (*E*:*Z* = 3:1)	A	3	 **7h** (75)
3	 (*E*)-**9i**	B	1	 **7i**(88)
4	 (*E*)-**9j** (*E*:*Z* = 2:1)	C	2	 **7j** (65) **12** (8)

a) Oxime:$Pd(PPh_3)_4$:Et_3N = 1.0:0.1:5.0. The reaction was conducted in DMF at 80 °C. The concentration of oxime was 0.02 mol dm^{-3}. b) Method A: The isomerization of dihydropyrrole to pyrrole occurred under the palladium-catalyzed cyclization condition. Method B: Dihydropyrrole isomerized to pyrrole by treatment of 1.5 molar amounts of Me_3SiCl in CH_2Cl_2 for 0.5 h after the palladium-catalyzed cyclization. Method C: Dihydropyrrole isomerized to pyrrole by treatment of SiO_2 in CH_2Cl_2 for 6 h after the palladium-catalyzed cyclization. c) Isolated yield.

tion of vinyl oxime **9f** (Table 4 entry 4). In the cyclization of *O*-pentafluorobenzoyloxime **9j** having a methyl group on olefinic moiety, the formation 3,4-dihydro-2-ethylidene-2*H*-pyrrole **6j** and 2-vinyl-2*H*-3,4-dihydropyrrole **12** was confirmed by ^{1}H NMR spectrum as a mixture after palladium-catalyzed cylization, but 3,4-dihydropyrrole **6j** hardly isomerized by method B to 2-ethylpyrrole **7j**.[18] On the other hand, the isomerization of 3,4-dihydropyrrole **6j** to 2-ethylpyrrole **7j** by treatment with SiO_2 (method C) gave a good result, and 2-ethylpyrrole **7j** and 2-vinyl-2*H*-3,4-dihydropyrrole **12** were obtained in 65% and 8% yield, respectively (entry 4). Dihydropyrrole **12** could not be converted to pyrrole **7j** under these reaction conditions.

On the whole, the transformation of γ,δ-unsaturated ketone *O*-pentafluorobenzoyloximes to pyrrole derivatives has been achieved by using the palladium catalyst, based on the intermediate formation of alkylideneaminopalladium(II) species. The structure of the oxidative addition products of *O*-pentafluorobenzoyloximes of alkyl ketones to $Pd(PPh_3)_4$ is not clear; alkylideneaminopalladium structure or the isomerized-*N*-palladaenamine (aza-allylpalladium) structure.[35] To clarify this, we measured the ^{1}H NMR of the equimolar mixture of acetophenone *O*-pentafluorobenzoyloxime (*E*-**9k**) and $Pd(PPh_3)_4$ in C_6D_6. After 1 h at 50 °C, no peak was observed at olefinic proton region but new methyl peaks were detected at 2.15, 1.81, and 1.64 ppm. Although these new methyl peaks could not be assigned, the result suggested that the reaction products of *E*-**9k** and $Pd(PPh_3)$ had a structure **a** like alkylideneaminopalladium(II) species **2k** (Eq. 6).



(6)

Experimental

General. ^{1}H NMR (500 and 300 MHz) spectra were recorded on Bruker AM 500, Bruker DRX 500, Bruker AVANCE 500, and Bruker DPX 300 spectrometers in $CDCl_3$ [using $CHCl_3$ (for ^{1}H, δ = 7.24) as internal standard] or C_6D_6 [using C_6HD_5 (for ^{1}H, δ = 7.15) as internal standard]. ^{13}C NMR (125 and 75 MHz) spectra were recorded on Bruker AM 500, Bruker DRX 500, Bruker AVANCE 500, and Bruker DPX 300 spectrometers in $CDCl_3$ using $CDCl_3$ (for ^{13}C, δ = 77.00) as internal standard. ^{31}P NMR (121.5 MHz) spectra were recorded on Bruker DPX 300 spectrometer in CD_2Cl_2 using 85% H_3PO_4 (for ^{31}P, δ = 0) as external standard. IR spectra were recorded on a Horiba FT 300-S and Perkin Elmer SPECTRUM 1000 spectrophotometer. High-resolution mass spectra were obtained with a JEOL JMS-SX102A mass

spectrometer. The melting points were uncorrected. Elemental analyses were carried out at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo. Flash column chromatography was performed on silica gel (Merck Silica gel 60, and Kanto Chemical Co., Inc. Silica gel 60N (spherical, neutral)) and Florisil® (Wako Pure Chemical Industries, Ltd.), and preparative thin-layer chromatography was carried out using Wakogel B-5F. *N*,*N*-Dimethylformamide (DMF) was distilled under reduced pressure from CaH_2, and stored over Molecular Sieves 4A under an argon atmosphere. Dichloromethane was distilled from P_2O_5 and then from CaH_2, and was stored over Molecular Sieves 4A. Triethylamine was distilled from NaH and stored over KOH. $Pd(PPh_3)_4$ was purchased from Tokyo Chemical Industry Co., Ltd. and used without purification. Pentafluorobenzoyl chloride was purchased from Tokyo Chemical Industry Co., Ltd. and used without purification. Chlorotrimethylsilane was distilled from CaH_2.

The Reaction of *O*-Methylsulfonyloxime (1) and $Pd(PPh_3)_4$: (Eq. 1): Into a flask containing $Pd(PPh_3)_4$ (289 mg, 0.250 mmol) was added a solution of 4,4′-bis(trifluoromethyl)benzophenone *O*-methylsulfonyloxime (**1**)[21] (103 mg, 0.250 mmol) in THF (2.5 mL) at room temperature under an argon atmosphere. After the reaction mixture was stirred at the same temperature for 20 min, the mixture was quenched with pH 9 buffer at 0 °C. The mixture was extracted twice with ether, and the combined extracts were washed successively with sat. $NaHCO_3$ and brine, and the ether solution was dried over anhydrous magnesium sulfate. The ether was removed in vacuo, and bis(4-trifluoromethylphenyl)methanimine (**3**)[21] was confirmed by ^{1}H NMR spectrum of the crude product. The crude imine was dissolved in acetone (2.5 mL) and water (0.5 mL), and 1 M HCl (1 M = 1.00 mol dm^{-3}, 0.375 mL, 0.375 mmol) was added to the solution. After the resulting solution was stirred at room temperature for 30 min, the reaction was quenched with water. The mixture was extracted twice with ethyl acetate, and the combined extracts were washed successively with sat. $NaHCO_3$ and brine. The ethyl acetate solution was dried over anhydrous sodium sulfate, and the ethyl acetate was removed in vacuo. The crude materials were purified by thin-layer chromatography (silica gel, dichloromethane:hexane = 1:1) to give 4,4′-bis(trifluoromethyl)benzophenone (**4**)[36] (75.0 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (4H, d, J = 8.3 Hz), 7.89 (4H, d, J = 8.3 Hz).

Preparation of γ,δ-Unsaturated Ketone *O*-Methylsulfonyloximes: Experimental procedures for the preparation of γ,δ-unsaturated ketone *O*-methylsulfonyloximes are shown below as a typical example for the synthesis of 1-phenyl-6-hepten-3-one *O*-methylsulfonyloxime (**5a**).

To an ice-methanol cold solution of 1-phenyl-6-hepten-3-one oxime[37] (908 mg, 4.47 mmol) and triethylamine (0.934 mL, 6.70 mmol) in dichloromethane (13 mL) was slowly added a solution of methanesulfonyl chloride (563 mg, 4.91 mmol) in dichloromethane (5 mL), and this mixture was stirred at the same temperature for 2 h. After the reaction was quenched with water, the mixture was extracted twice with dichloromethane. The combined extracts were washed with sat. $NaHCO_3$, and the dichloromethane solution was dried over anhydrous sodium sulfate. The dichloromethane was removed in vacuo, and the crude materials were purified by flash column chromatography (Florisil®, hexane:ethyl acetate = 10:1) at 0 °C to give 1-phenyl-6-hepten-3-one *O*-methylsulfonyloxime (**5a**) (1.17 g, 93%).

Spectral Data for γ,δ-Unsaturated Ketone *O*-Methylsulfonyloximes. 1-Phenyl-6-hepten-3-one *O*-Methylsulfonyloxime (5a): E:Z = 1:1 mixture; Pale yellow oil; IR (KBr) 1644, 1604, 1496, 1455, 1361, 1180, 970, 788, 701, 526 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24-2.35 (3H, m), 2.51 (1H, t, J = 7.8 Hz), 2.64 (1H, t, J = 7.8 Hz), 2.69 (1H, t, J = 7.8 Hz), 2.85 (1H, t, J = 7.8 Hz), 2.90 (1H, t, J = 7.8 Hz), 3.00 (1.5H, s), 3.06 (1.5H, s), 4.98–5.08 (2H, m), 5.70–5.81 (1H, m), 7.15–7.23 (3H, m), 7.25–7.31 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.98, 29.48, 29.63, 31.45, 31.70, 31.78, 33.65, 35.66, 36.25 (overlapped), 115.99, 116.31, 126.39, 126.60, 128.28, 128.29, 128.54, 128.62, 135.95, 126.29, 139.67, 140.08, 169.50, 169.72; FABHRMS Found: *m*/*z* 282.1176. Calcd for $C_{14}H_{20}NO_3S$: M + H, 282.1165.

2-Allyl-1-tetralone (*E*)-*O*-Methylsulfonyloxime (*E*-5b): Pale yellow plates; mp 71–72 °C (isopropyl ether–hexane); IR (KBr) 1640, 1594, 1453, 1417, 1360, 1172, 988, 937, 863, 824, 797, 732, 716, 633, 603, 547, 523, 493 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.88-2.01 (2H, m), 2.24 (1H, dt, J = 13.9, 8.9 Hz), 2.32–2.40 (1H, m), 2.72 (1H, dt, J = 17.1, 4.1 Hz), 2.90–2.99 (1H, m), 3.22 (3H, s), 3.55–3.62 (1H, m), 5.02–5.09 (2H, m), 5.75–5.84 (1H, m), 7.18 (1H, d, J = 7.8 Hz), 7.21 (1H, t, J = 7.8 Hz), 7.36 (1H, t, J = 7.8 Hz), 7.99 (1H, d, J = 7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.04, 24.22, 32.91, 33.43, 36.36, 117.27, 125.55, 126.35, 126.84, 129.02, 131.17, 134.79, 139.78, 165.26; Anal. Found: C, 60.02; H, 5.97; N, 4.74%. Calcd for $C_{14}H_{17}NO_3S$: C, 60.19; H, 6.13; N, 5.01%.

Preparation of γ,δ-Unsaturated Ketone *O*-Pentafluorobenzoyloximes: Experimental procedures for the preparation of γ,δ-unsaturated ketone *O*-pentafluorobenzoyloximes are shown below as a typical example for the synthesis of 1-phenyl-6-hepten-3-one *O*-pentafluorobenzoyloxime (**9a**).

To an ice-cold solution of 1-phenyl-6-hepten-3-one oxime[37] (1.02 g, 5.02 mmol) and triethylamine (0.909 mL, 6.52 mmol) in dichloromethane (15 mL) was slowly added a solution of pentafluorobenzoyl chloride (1.27 g, 5.52 mmol) in dichloromethane (5 mL), and this mixture was stirred at the same temperature for 1 h. After the reaction was quenched with water, the mixture was extracted twice with dichloromethane. The combined extracts were washed with sat. $NaHCO_3$, and the dichloromethane solution was dried over anhydrous sodium sulfate. Solvent was removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel, hexane:ethyl acetate = 9:1) to give 1-phenyl-6-hepten-3-one *O*-pentafluorobenzoyloxime (**9a**) (1.87 g, 94%).

Spectral Data for γ,δ-Unsaturated Ketone *O*-Pentafluorobenzoyloximes. 1-Phenyl-6-hepten-3-one *O*-Pentafluorobenzoyloxime (9a): E:Z = 1:1 mixture; White solid; mp 45–72 °C; IR (KBr) 1760, 1656, 1504, 1454, 1420, 1327, 1198, 1094, 1001, 949, 915, 866, 752, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25–2.42 (3H, m), 2.53 (1H, t, J = 7.8 Hz), 2.67–2.74 (2H, m), 2.85 (1H, t, J = 7.8 Hz), 2.94 (1H, t, J = 7.8 Hz), 4.99–5.08 (2H, m), 5.71–5.83 (1H, m), 7.14 (1H, d, J = 7.6 Hz), 7.17–7.23 (2H, m), 7.24–7.32 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.56, 29.83, 29.92, 31.87, 31.91, 32.11, 33.77, 36.06, 106.85–107.24 (overlapped, m), 115.90, 116.19, 126.33, 126.51, 128.08, 128.24, 128.53, 128.56, 135.99, 136.37, 136.50–136.85 and 138.53–138.89 (overlapped, m d), 139.83, 140.31, 142.09–142.48, 144.10–144.53, and 146.24–146.54 (overlapped, m), 156.45, 156.55, 170.56, 170.73; Anal. Found: C, 60.24; H, 4.13; N, 3.50%. Calcd for $C_{20}H_{16}F_5NO_2$: C, 60.46; H, 4.06; N, 3.53%.

2-Allyl-1-tetralone (*E*)-*O*-Pentafluorobenzoyloxime (*E*-9b): Colorless needles; mp 75–76 °C (hexane); IR (KBr) 1764, 1652, 1526, 1501, 1418, 1323, 1198, 1097, 1004, 926, 866, 772 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.90–2.02 (2H, m), 2.25 (1H, dt, J

= 14.0, 8.9 Hz), 2.32–2.39 (1H, m), 2.73 (1H, dt, J = 16.7, 4.0 Hz), 2.91–3.00 (1H, m), 3.55–3.61 (1H, m), 5.01–5.08 (2H, m), 5.71–5.81 (1H, m), 7.18 (1H, d, J = 7.6 Hz), 7.23 (1H, t, J = 7.6 Hz), 7.36 (1H, t, J = 7.6 Hz), 8.14 (1H, d, J = 7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.20, 24.34, 33.57, 33.73, 106.72–107.24 (m), 117.37, 126.21, 126.56, 127.36, 129.01, 131.29, 134.96, 136.52–136.97 and 138.54–138.96 (m d), 139.95, 142.15–142.54, 144.18–144.61, and 146.22–146.69 (overlapped, m), 156.51, 166.22; Anal. Found: C, 60.46; H, 3.49; N, 3.34%. Calcd for $C_{20}H_{14}F_5NO_2$: C, 60.76; H, 3.57; N, 3.54%.

1-Phenyl-4-penten-1-one (*E*)-*O*-Pentafluorobenzoyloxime (*E*-9c): Colorless crystals; mp 82–84 °C; IR (KBr) 1755, 1655, 1524, 1501, 1418, 1330, 1198, 1002, 922, 890, 773, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.28–2.36 (2H, m), 2.98 (2H, t, J = 7.8 Hz), 4.98–5.05 (2H, m), 5.73–5.83 (1H, m), 7.42 (2H, t, J = 7.2 Hz), 7.48 (1H, t, J = 7.2 Hz), 7.72 (2H, d, J = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.13, 30.62, 107.01–107.15 (m), 116.01, 127.39, 128.74, 131.03, 132.97, 136.01, 136.55–136.97 and 138.54–138.98 (m d), 142.18–142.66, 144.26–144.69, and 146.31–146.68 (overlapped, m), 156.45, 168.10; Anal. Found: C, 58.48; H, 3.32; N, 3.85%. Calcd for $C_{18}H_{12}F_5NO_2$: C, 58.54; H, 3.28; N, 3.79%.

1-Phenyl-4-penten-1-one (*Z*)-*O*-Pentafluorobenzoyloxime (*Z*-9c): Colorless oil; IR (KBr) 1767, 1652, 1505, 1423, 1327, 1197, 1083, 1005, 922, 871, 767, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.23–2.30 (2H, m), 2.83 (2H, t, J = 7.6 Hz), 4.98–5.05 (2H, m), 5.74–5.84 (1H, m), 7.27–7.31 (2H, m), 7.39–7.43 (3H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.02, 34.84, 106.71–107.01 (m), 115.84, 126.86, 128.22, 129.69, 132.12, 136.00, 136.22–136.68 and 138.27–138.65 (m d), 141.89–142.28, 143.87–144.34, and 145.96–146.30 (overlapped, m), 156.48, 168.95; FABHRMS Found: m/z 370.0876. Calcd for $C_{18}H_{13}F_5NO_2$: M + H, 370.0867.

1,8-Nonadien-5-one *O*-Pentafluorobenzoyloxime (9d): White solid; mp < 30 °C; IR (KBr) 1766, 1652, 1525, 1505, 1419, 1327, 1202, 1093, 1004, 919, 867 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25–2.32 (2H, m), 2.33–2.40 (2H, m), 2.46–2.54 (4H, m), 4.99–5.11 (4H, m), 5.71–5.87 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.08, 29.70, 29.83, 33.36, 106.83–107.24 (m), 115.63, 115.87, 135.94, 136.29, 136.38–136.77 and 138.37–138.89 (m d), 141.86–142.39, 144.02–144.41, and 146.10–146.41 (overlapped, m), 156.35, 170.72; Anal. Found: C, 55.21; H, 4.00; N, 4.01%. Calcd for $C_{16}H_{14}F_5NO_2$: C, 55.34; H, 4.06; N, 4.03%.

3-Methyl-1-phenyl-4-penten-1-one (*E*)-*O*-Pentafluorobenzoyloxime (*E*-9e): White powder; mp 69–73 °C; IR (KBr) 1755, 1652, 1526, 1498, 1417, 1328, 1203, 1004, 950, 924, 874, 744, 695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02 (3H, d, J = 6.8 Hz), 2.37–2.52 (1H, m), 2.84–2.99 (2H, m), 4.85–4.95 (2H, m), 5.59–5.73 (1H, m), 7.35–7.52 (3H, m), 7.69 (2H, dd, J = 1.8, 7.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.77, 35.12, 35.96, 106.74–107.39 (m), 113.87, 127.54, 128.70, 130.90, 133.32, 135.75–136.38 and 139.14–139.70 (m d), 141.41–142.10 and 144.78–145.52 (m d), 141.78, 143.47–143.94 and 146.85–147.46 (m d), 156.47, 167.76; Anal. Found: C, 59.35; H, 3.65; N, 3.68%. Calcd for $C_{19}H_{14}F_5NO_2$: C, 59.53; H, 3.68; N, 3.65%.

Ethyl 2-[(*E*)-Pentafluorobenzoyloxyimino]-5-hexenoate (*E*-9f): Colorless oil; IR (KBr) 1779, 1732, 1652, 1505, 1418, 1375, 1326, 1185, 1078, 1006, 901, 767 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.37 (3H, t, J = 7.2 Hz), 2.29–2.36 (2H, m), 2.81 (2H, t, J = 7.6 Hz), 4.36 (2H, q, J = 7.2 Hz), 4.98–5.08 (2H, m), 5.70–5.80 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.83, 27.00, 30.05, 62.78, 105.73–106.12 (m), 116.38, 135.52, 136.55–136.97 and 138.57–138.97 (m d), 142.59–142.96, 144.43–145.07, and 146.58–146.86 (overlapped, m), 155.48, 161.47, 162.19; Anal. Found: C, 49.20; H, 3.24; N, 3.74%. Calcd for $C_{15}H_{12}F_5NO_4$: C, 49.32; H, 3.31; N, 3.83%.

1-Ethyl 7-Methyl (*E*)-6-[(*E*)-Pentafluorobenzoyloxyimino]-2-heptenedioate (*E*-9g): Colorless plates; mp 75–76 °C (hexane); IR (KBr) 1789, 1728, 1652, 1501, 1446, 1326, 1253, 1178, 1126, 1078, 1002, 951, 901, 849, 766 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (3H, t, J = 7.2 Hz), 2.42–2.53 (2H, m), 3.91 (3H, s), 4.14 (2H, q, J = 7.2 Hz), 5.82 (1H, dt, J = 15.6, 1.4 Hz), 6.86 (1H, dt, J = 15.6, 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.70, 25.84, 28.16, 53.10, 59.94, 105.08–105.67 (m), 122.56, 135.61–136.22 and 138.94–139.62 (m d), 141.70–142.41 and 145.11–145.78 (m d), 143.59–144.14 and 146.93–147.53 (m d), 144.86, 154.94, 159.83, 162.25, 165.52; Anal. Found: C, 48.32; H, 3.32; N, 3.09%. Calcd for $C_{17}H_{14}F_5NO_6$: C, 48.24; H, 3.33; N, 3.31%.

Ethyl (*E*)-6-(Pentafluorobenzoyloxyimino)-8-phenyl-2-octenoate (9h): E:Z = 3:1 mixture; White solid; mp 41–55 °C; IR (KBr) 1757, 1714, 1651, 1494, 1453, 1416, 1368, 1326, 1254, 1190, 1090, 1033, 1000, 942, 865, 772, 716 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *E*-isomer: δ 1.26 (3H, t, J = 7.1 Hz), 2.37–2.44 (2H, m), 2.57 (2H, t, J = 7.4 Hz), 2.67–2.74 (2H, m), 2.94 (2H, t, J = 7.7 Hz), 4.16 (2H, q, J = 7.1 Hz), 5.80 (1H, dt, J = 15.6, 1.4 Hz), 6.85 (1H, dt, J = 15.6, 6.9 Hz), 7.17–7.23 (3H, m), 7.24–7.31 (2H, m); *Z*-isomer: δ 1.27 (3H, t, J = 7.1 Hz), 2.37–2.44 (2H, m), 2.45–2.52 (2H, m), 2.67–2.74 (2H, m), 2.85 (2H, t, J = 7.7 Hz), 4.17 (2H, q, J = 7.1 Hz), 5.81 (1H, dt, J = 15.7, 1.5 Hz), 6.88 (1H, dt, J = 15.7, 6.4 Hz), 7.13 (2H, d, J = 7.6 Hz), 7.17–7.23 (1H, m), 7.24–7.31 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) *E*-isomer: δ 13.77, 27.88, 28.44, 31.73, 35.72, 60.00, 106.48–106.70 (m), 122.37, 126.05, 127.96, 128.22, 136.23–136.65 and 138.23–138.67 (m d), 139.90, 141.86–142.31, 143.90–144.24, and 145.96–146.35 (overlapped, m), 145.36, 156.00, 165.63, 169.49; *Z*-isomer: δ 13.81, 27.63, 31.63, 31.96, 32.79, 59.93, 106.48–106.70 (m), 122.15, 126.25, 127.83, 128.27, 136.23–136.65 and 138.23-138.67 (m d), 139.43, 141.86–142.31, 143.90–144.24, and 145.96–146.35 (overlapped, m), 146.04, 156.00, 165.83, 169.49; Anal. Found: C, 58.85; H, 4.37; N, 2.96%. Calcd for $C_{23}H_{20}F_5NO_4$: C, 58.85; H, 4.29; N, 2.98%.

Ethyl (*E*)-6-[(*E*)-Pentafluorobenzoyloxyimino]-6-phenyl-2-hexenoate (*E*-9i): Colorless crystals; mp 93–95 °C; IR (KBr) 1760, 1716, 1652, 1528, 1494, 1324, 1284, 1196, 895, 769, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (3H, t, J = 7.2 Hz), 2.42–2.50 (2H, m), 3.04 (2H, t, J = 7.7 Hz), 4.15 (2H, q, J = 7.2 Hz), 5.81 (1H, dt, J = 15.6, 1.4 Hz), 6.89 (1H, dt, J = 15.6, 6.9 Hz), 7.43 (2H, dt, J = 1.5, 7.2 Hz), 7.49 (1H, dt, J = 1.5, 7.2 Hz), 7.71 (2H, dd, J = 1.5, 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.03, 27.09, 28.92, 60.25, 106.52–106.83 (m), 122.58, 127.28, 128.83, 131.22, 132.49, 136.55–136.93 and 138.56–138.93 (m d), 142.25–142.66, 144.27–144.70, and 146.31–146.68 (overlapped, m), 145.51, 156.18, 165.93, 167.05; Anal. Found: C, 57.02; H, 3.63; N, 2.95%. Calcd for $C_{21}H_{16}F_5NO_4$: C, 57.15; H, 3.65; N, 3.17%.

1-Phenyl-4-hexen-1-one (*E*)-*O*-Pentafluorobenzoyloxime (*E*-9j): E:Z = 2:1 mixture; White solid; mp 59–70 °C; IR (KBr) 1754, 1653, 1607, 1525, 1498, 1466, 1444, 1324, 1200, 1097, 1040, 1002, 971, 951, 888, 774, 745, 695, 627 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (1H, dd, J = 0.9, 6.8 Hz), 1.60 (2H, dd, J = 1.0, 6.0 Hz), 2.20–2.27 (1.33H, m), 2.28–2.36 (0.67H, m), 2.88–2.96 (2H, m), 5.31–5.52 (2H, m), 7.36–7.50 (3H, m), 7.67–7.76 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.45, 17.65, 24.05, 28.45, 28.85, 29.59, 106.82–107.51 (m, overlapped), 125.65, 126.81, 127.40 (overlapped), 127.60, 128.60,

128.69, 128.71, 130.93, 130.98, 133.03, 133.10, 136.52–136.94 and 138.52–138.94 (overlapped, m d), 142.12–142.55, 144.23–144.62, and 146.24–146.67 (overlapped, m), 156.50 (overlapped), 168.30, 168.32; Anal. Found: C, 59.32; H, 3.75; N, 3.35%. Calcd for $C_{19}H_{14}F_5NO_2$: C, 59.53; H, 3.68; N, 3.65%.

Typical Procedure for the Synthesis of Pyrroles. (Method A). (Table 4, entry 1): Into a flask containing $Pd(PPh_3)_4$ (119 mg, 0.103 mmol) was added a solution of 1,8-nonadien-5-one *O*-pentafluorobenzoyloxime (**9d**) (358 mg, 1.03 mmol) in DMF (51 mL) and triethylamine (0.718 mL, 5.15 mmol) under an argon atmosphere, and the mixture was heated to 80 °C for 2 h. The mixture was quenched with water at 0 °C, and organic materials were extracted twice with ether. The combined extracts were washed successively with water and with brine two times, and the ether solution was dried over anhydrous magnesium sulfate. The ether was removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel, hexane:ethyl acetate = 15:1) to give 2-(3-butenyl)-5-methylpyrrole (**7d**) (110 mg, 79%).

Typical Procedure for the Synthesis of Pyrroles. (Method B). (Table 4, entry 2): Into a flask containing $Pd(PPh_3)_4$ (68.7 mg, 0.0595 mmol) was added a solution of 2-allyl-1-tetralone (*E*)-*O*-pentafluorobenzoyloxime (*E*-**9b**) (235 mg, 0.594 mmol) in DMF (30 mL) and triethylamine (0.414 mL, 2.97 mmol) under an argon atmosphere, and the mixture was heated to 80 °C for 1 h. The mixture was quenched with water at 0 °C, and organic materials were extracted twice with ether. The combined extracts were washed successively with water and with brine two times, and the ether solution was dried over anhydrous magnesium sulfate. The ether was removed in vacuo, and the crude products were dissolved in dichloromethane (12 mL) under an argon atmosphere, then chlorotrimethylsilane (0.113 mL, 0.892 mmol) was added to the solution. After the resulting solution was stirred at room temperature for 30 min, the mixture was neutralized with sat. $NaHCO_3$ at 0 °C. Organic materials were extracted twice with dichloromethane, and the dichloromethane solution was dried over anhydrous sodium sulfate. The dichloromethane was removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel, hexane:ethyl acetate = 9:1) to give 2-methyl-4,5-dihydro-1*H*-benz[*g*]indole (**7b**) (97.2 mg, 89%).

2-Ethyl-5-phenylpyrrole (7j) and 3,4-Dihydro-5-phenyl-2-vinyl-2*H*-pyrrole (12) (Method C). (Table 5, entry 4): Into a flask containing $Pd(PPh_3)_4$ (108 mg, 0.0934 mmol) was added a solution of 1-phenyl-4-hexen-1-one (*E*)-*O*-pentafluorobenzoyloxime (*E*-**9j**) (358 mg, 0.934 mmol) in DMF (47 mL) and triethylamine (0.651 mL, 4.67 mmol) under an argon atmosphere, and the mixture was heated to 80 °C for 2 h. The mixture was quenched with water at 0 °C, and organic materials were extracted twice with ether. The combined extracts were washed successively with water and with brine two times, and the ether solution was dried over anhydrous magnesium sulfate. The ether was removed in vacuo, and the crude products were dissolved in dichloromethane (9.3 mL) under an argon atmosphere, and silica gel (1.8 g) was added to the solution. After the resulting solution was stirred at room temperature for 6 h, silica gel was filtered off. The filtrate was removed in vacuo, and the crude materials were purified by flash column chromatography (silica gel, hexane:ethyl acetate = 15:1) to give 2-ethyl-5-phenylpyrrole (**7j**) (104 mg, 65%) and 3,4-dihydro-5-phenyl-2-vinyl-2*H*-pyrrole (**12**) (12.9 mg, 8%), respectively.

Spectral Data. 2-Methyl-5-phenethylpyrrole (7a):[38] Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.20 (3H, s), 2.83–2.95 (4H, m), 5.76 (1H, dd, J = 2.9, 2.9 Hz), 5.81 (1H, dd, J = 2.9, 2.9 Hz), 7.17–7.23 (3H, m), 7.29 (2H, d, J = 7.4 Hz), 7.45 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.88, 29.63, 36.17, 105.10, 105.57, 125.99, 126.06, 128.33, 128.35, 130.50, 141.70.

2-Methyl-4,5-dihydro-1*H*-benz[*g*]indole (7b): Colorless crystals; mp 93–95 °C (hexane); IR (KBr) 3420, 1610, 1588, 1509, 1442, 1404, 1287, 1251, 1158, 789, 758, 731, 695, 637, 493 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.31 (3H, s), 2.67 (2H, t, J = 7.6 Hz), 2.89 (2H, t, J = 7.6 Hz), 5.79 (1H, d, J = 1.6 Hz), 6.99 (1H, dt, J = 1.1, 7.4 Hz), 7.06 (1H, d, J = 7.4 Hz), 7.11–7.17 (2H, m), 7.95 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.28, 21.83, 30.05, 106.22, 117.54, 120.80, 124.34, 126.36, 126.42, 128.19, 128.62, 129.44, 134.31; Anal. Found: C, 85.32; H, 7.28; N, 7.54%. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64%.

2-Methyl-5-phenylpyrrole (7c):[39] Pale yellow crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (3H, s), 5.94 (1H, dd, J = 3.0, 3.0 Hz), 6.39 (1H, dd, J = 3.0, 3.0 Hz), 7.15 (1H, t, J = 7.5 Hz), 7.32 (2H, t, J = 7.5 Hz), 7.41 (2H, d, J = 7.5 Hz), 8.09 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.15, 106.14, 107.90, 123.30, 125.61, 128.78, 129.02, 130.74, 132.91.

2-(3-Butenyl)-5-methylpyrrole (7d): Pale yellow oil; IR (KBr) 3372, 1640, 1593, 1514, 1402, 1183, 1038, 994, 913, 767, 666 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.23 (3H, s), 2.33–2.40 (2H, m), 2.65 (2H, t, J = 7.6 Hz), 4.99–5.12 (2H, m), 5.75 (1H, dd, J = 2.9, 2.9 Hz), 5.78 (1H, dd, J = 2.9, 2.9 Hz), 5.84–5.94 (1H, m), 7.62 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.89, 27.04, 33.73, 104.94, 105.50, 115.06, 126.03, 130.58, 138.15; HRMS Found: *m*/*z* 135.1031. Calcd for $C_9H_{13}N$: M, 135.1049.

2,3-Dimethyl-5-phenylpyrrole (7e):[40] Colorless crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.03 (3H, s), 2.22 (3H, s), 6.26 (1H, d, J = 2.7 Hz), 7.12 (1H, t, J = 7.8 Hz), 7.30 (2H, t, J = 7.8 Hz), 7.38 (2H, d, J = 7.8 Hz), 7.91 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.90, 11.09, 107.75, 116.20, 123.15, 125.16, 125.40, 128.74, 129.27, 132.95.

Ethyl 5-Methylpyrrole-2-carboxylate (7f):[41] Pale yellow crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (3H, t, J = 7.1 Hz), 2.29 (3H, s), 4.27 (2H, q, J = 7.1 Hz), 5.93 (1H, dd, J = 3.0, 3.0 Hz), 6.79 (1H, dd, J = 3.0, 3.0 Hz), 8.81 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.10, 14.46, 60.04, 108.82, 116.04, 121.30, 133.89, 161.40.

Ethyl 5-Methoxycarbonyl-2-pyrroleacetate (7g): Pale yellow plates; mp 70–72 °C (hexane); IR (KBr) 3307, 1739, 1680, 1497, 1449, 1332, 1275, 1239, 1178, 1042, 1002, 801, 778 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (3H, t, J = 7.1 Hz), 3.66 (2H, s), 3.82 (3H, s), 4.18 (2H, q, J = 7.1 Hz), 6.05 (1H, dd, J = 2.8, 3.5 Hz), 6.81 (1H, dd, J = 2.8, 3.5 Hz), 9.53 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.07, 33.26, 51.33, 61.34, 109.82, 115.69, 122.27, 129.20, 161.46, 170.04; Anal. Found: C, 56.64; H, 6.02; N, 6.40%. Calcd for $C_{10}H_{13}NO_4$: C, 56.86; H, 6.20; N, 6.63%.

Ethyl 5-Phenethyl-2-pyrroleacetate (7h): Pale yellow solid; mp < 30 °C; IR (KBr) 3374, 1731, 1592, 1498, 1454, 1370, 1256, 1188, 1031, 765, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (3H, t, J = 7.1 Hz), 2.85–2.95 (4H, m), 3.59 (2H, s), 4.15 (2H, q, J = 7.1 Hz), 5.83 (1H, dd, J = 2.8, 2.8 Hz), 5.88 (1H, dd, J = 2.8, 2.8 Hz), 7.16–7.22 (3H, m), 7.28 (2H, t, J = 7.6 Hz), 8.29 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.12, 29.72, 33.34, 36.05, 60.99, 105.11, 107.17, 121.80, 126.00, 128.33, 128.37, 132.03, 141.57, 171.31; FABHRMS Found: *m*/*z* 258.1487. Calcd for $C_{16}H_{20}NO_2$: M + H, 258.1495.

Ethyl 5-Phenyl-2-pyrroleacetate (7i):[42] Colorless crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29 (3H, t, J = 7.1 Hz), 3.70 (2H, s), 4.19 (2H, q, J = 7.1 Hz), 6.05 (1H, dd, J = 3.0, 3.0 Hz), 6.40

(1H, dd, J = 3.0, 3.0 Hz), 7.17 (1H, t, J = 7.6 Hz), 7.33 (2H, t, J = 7.6 Hz), 7.45 (2H, d, J = 7.6 Hz), 8.99 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.11, 33.30, 61.20, 105.79, 109.09, 123.58, 124.48, 125.94, 128.75, 132.07, 132.68, 171.18.

2-Ethyl-5-phenylpyrrole (7j):[39] Colorless crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (3H, t, J = 7.6 Hz), 2.67 (2H, q, J = 7.6 Hz), 5.70 (1H, dd, J = 3.0, 3.0 Hz), 6.40 (1H, dd, J = 3.0, 3.0 Hz), 7.15 (1H, t, J = 7.6 Hz), 7.32 (2H, t, J = 7.6 Hz), 7.42 (2H, d, J = 7.6 Hz), 8.10 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.58, 20.98, 105.97, 106.21, 123.37, 125.64, 128.78, 130.57, 132.97, 135.60.

3,4-Dihydro-5-phenyl-2-vinyl-2*H*-pyrrole (12): Pale yellow oil; IR (KBr) 1688, 1643, 1614, 1576, 1499, 1449, 1341, 1268, 1026, 992, 920, 763, 693, 558 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.73–1.82 (1H, m), 2.24–2.32 (1H, m), 2.86–2.95 (1H, m), 2.99–3.08 (1H, m), 4.69–4.75 (2H, m), 5.11 (1H, dt, J = 10.3, 1.4 Hz), 5.25 (1H, dt, J = 17.1, 1.4 Hz), 5.98 (1H, ddd, J = 6.7, 10.3, 17.1 Hz), 7.34–7.46 (3H, m), 7.86 (2H, dd, J = 1.5, 7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.17, 35.01, 74.83, 114.60, 127.76, 128.38, 130.50, 134.43, 140.12, 173.27; FABHRMS Found: m/z 172.1108. Calcd for $C_{12}H_{14}N$: M + H, 172.1127.

Acetophenone (*E*)-*O*-Pentafluorobenzoyloxime (*E*-9k): White powder; IR (KBr) 1766, 1649, 1500, 1332, 1203, 995, 885, 694 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.46 (3H, s), 7.42–7.46 (2H, m), 7.47–7.51 (1H, m), 7.77–7.80 (2H, m); ^{1}H NMR (500 MHz, C_6D_6) δ 1.90 (3H, s), 6.97–7.05 (2H, m), 7.06–7.09 (1H, m), 7.57–7.60 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.9, 107.1 (m), 127.2, 128.7, 131.1, 134.0, 136.9 (m), 138.9 (m), 142.4 (m), 144.5 (m), 146.5 (m), 156.4, 165.0; Anal. Found: C, 54.67; H, 2.64; N, 4.26%. Calcd for $C_{15}H_{18}F_5NO_2$: C, 54.72; H, 2.45; N, 4.25%.

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