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TETRAHEDRON

Synthesis of Dihydropyrroles by the Intramolecular Addition of Alkylideneaminyl Radicals Generated from *O*-2,4-Dinitrophenyloximes of γ,δ-Unsaturated Ketones

Katsuya Uchiyama, Yujiro Hayashi, and Koichi Narasaka*

Department of Chemistry, School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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Abstract: Alkylideneaminyl radicals are generated from *O*-2,4-dinitrophenyloximes of γ,δ-unsaturated ketones by treatment with NaH and 3,4-methylenedioxyphenol. The resulting radical species successively add to the olefinic moiety intramolecularly to afford dihydropyrroles in the presence of a radical trapping agent. This method is applied for the stereoselective synthesis of xenovenine, a bicyclic 3,5-dialkylpyrrolizidine alkaloid. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Alkylideneaminyl radicals, so called iminyl radicals, have been utilized as reactive intermediates for the synthesis of nitrogen-containing heterocycles.[1-4] For example, 2,3,4-triphenylquinoline or 1,3-diphenylisoquinoline is prepared *via* alkylideneaminyl radicals generated by treatment of 1,2,3,3-tetraphenylpropylideneaminooxyacetic acid or phenyl-(2-styrylphenyl)methyleneaminooxyacetic acid with $K_2S_2O_8$.[2] The thermolysis of 1,5-diphenyl-1,2,5-triazapentadiene generates an alkylideneaminyl radical to give a quinoxaline.[3] In these methods, however, it is hard to find a synthetic application due to the lack of generality and the low product yield.[2,3] Recently, an effective method of generating alkylideneaminyl radical has been reported by the use of radical chain reaction.[1,4] That is, the radical cyclization takes place by treating each of sulphenylimine, *O*-phenylselenomethyloxime, *O*-benzoyloxime, or 1*H*-benzotriazol-1-ylimine of 2-allylcyclohexanone with $(n\text{-Bu})_3SnH$ and 2,2-azobisisobutyronitrile (AIBN) to give 3,3a,4,5,6,7-hexahydro-2-methyl-2*H*-indole.[4]

We have reported a new method for the generation of alkylideneaminyl radicals by one electron reduction of *O*-2,4-dinitrophenyloximes. That is, radicals are generated from *O*-2,4-dinitrophenyloximes of γ,δ-unsaturated ketones by treatment with NaH and 3,4-methylenedioxyphenol, and the resulting radical species successively add to the olefinic moiety intramolecularly to afford cyclic imines.[5] In this report are summarized the full details of this reaction and the application for the stereoselective synthesis of xenovenine.

RESULTS AND DISCUSSION

I. Synthesis of Dihydropyrrole Derivatives.

Recently, we have reported that 2-(3-hydroxyphenyl)ethyl ketone *O*-2,4-dinitrophenyloximes cyclize on the

This paper is dedicated to Professors T. Mukaiyama and D. A. Evans in recognition of their outstanding contributions to the art of organic synthesis.

*E-mail: narasaka@chem.s.u-tokyo.ac.jp Fax: (03) 5800-6891

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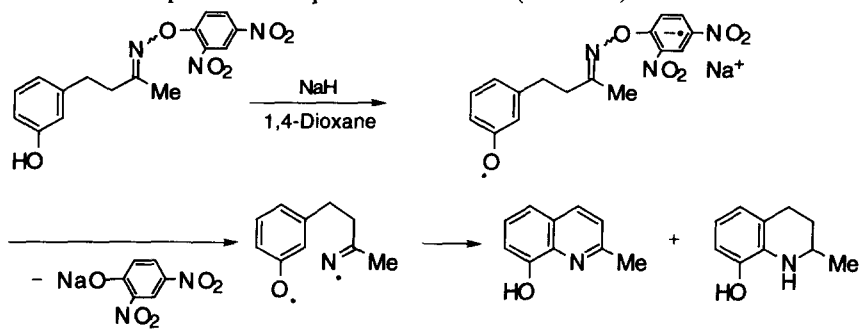
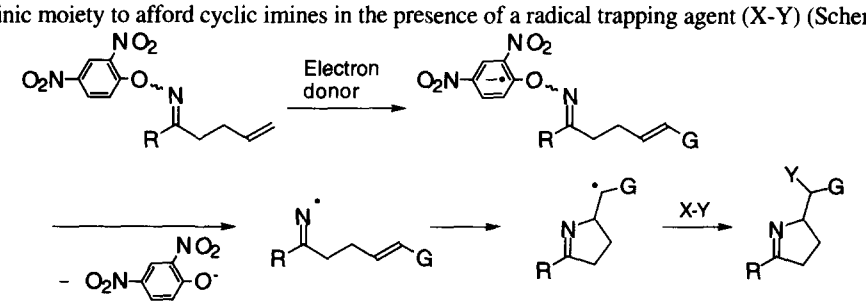
oxime nitrogen atom by treatment with NaH in 1,4-dioxane to afford quinolin-8-ols and their 1,2,3,4-tetrahydro derivatives.[6] This cyclization is initiated by single electron transfer from the phenolate moiety to the 2,4-dinitrophenyl group, and the successive N-O bond cleavage results in the formation of alkylideneaminyl radicals, which are then coupled to afford quinoline derivatives (Scheme 1).[6c]



Scheme 1

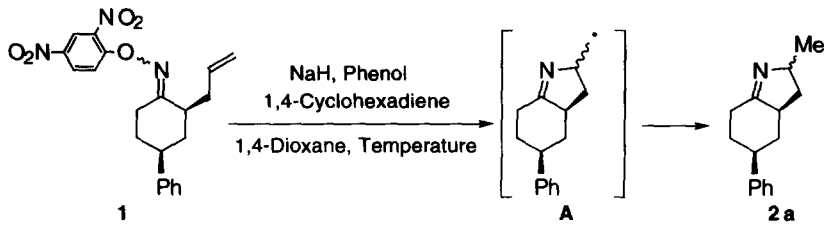
The above-mentioned mechanism suggested us that alkylideneaminyl radicals would be generated from *O*-2,4-dinitrophenyloximes having an olefinic moiety by one electron transfer from an electron donor and add to the olefinic moiety to afford cyclic imines in the presence of a radical trapping agent (X-Y) (Scheme 2).



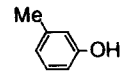
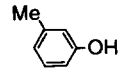
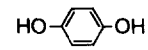
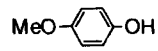
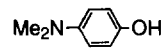
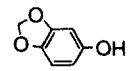
Scheme 2

Based on this assumption, the reaction conditions of cyclization of *cis*-2-allyl-4-phenylcyclohexanone (*E*)-*O*-2,4-dinitrophenyloxime (**1**) were screened (Table 1). When **1** was treated with NaH and *m*-cresol as an electron donating reagent in 1,4-dioxane in the presence of 1,4-cyclohexadiene as a radical trapping agent, 3,3a,4,5,6,7-hexahydro-2-methyl-5-phenyl-2*H*-indole (**2a**) was obtained in 50% yield (Entry 1). The use of 1,4-dioxane degassed by flowing Ar gas improved the yield of **2a** up to 80% (Entry 2). Among several electron-donating agents examined, such as *m*-cresol, *p*-hydroquinone, *p*-methoxyphenol, *p*-*N*,*N*-dimethylaminophenol, and 3,4-methylenedioxyphenol (Entries 2-6), 3,4-methylenedioxyphenol (sesamol, **3**) was found to be a suitable one. That is, treatment of **1** with NaH, sesamol **3**, and 1,4-cyclohexadiene in 1,4-dioxane at 50 °C afforded the hexahydroindole **2a** in 91% yield (Entry 6).

Table 1. Screening of the Reaction Conditions in the Cyclization of Oxime **1**[a)]



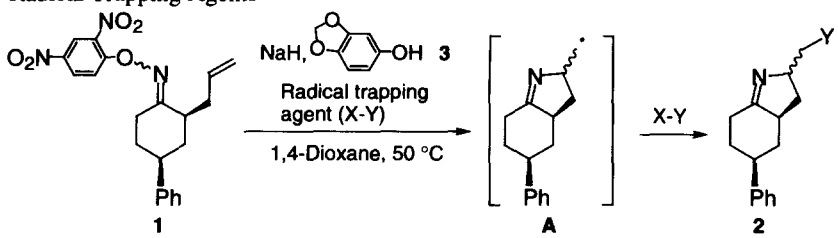
1 **A** **2a**

Entry	Phenol	Temp / °C	Time / h	Yield / %[c)]
1		rt	12	50
2[b)]		50	5	80
3[b)]		50	5	10
4[b)]		50	5	83
5[b)]		50	5	77
6[b)]		50	5	91

a) All reactions were carried out using 10 molar amounts of NaH, an equimolar amount of a phenol, and 10 molar amounts of 1,4-cyclohexadiene. b) 1,4-Dioxane was degassed by flowing Ar. c) Diastereomer ratio=2:1.

Some other radical trapping agents, such as carbon tetrachloride, diphenyl disulphide, and diphenyl diselenide, were also utilized as the radical terminators instead of 1,4-cyclohexadiene, and chloromethyl **2b**, phenylthiomethyl **2c**, and phenylselenomethyl **2d** derivatives were produced in 75%, 70%, and 69% yields, respectively (Table 2). By the method using (*n*-Bu)$_3$SnH and AIBN the cyclized radical intermediate is captured only with the stannane,[1,4] while this method enables the introduction of various functional groups into the cyclized radical intermediate **A** by the use of various radical trapping agents.

Table 2. Cyclization of *O*-2,4-Dinitrophenyloxime**1** in the Presence of Several Radical Trapping Agents[a)]



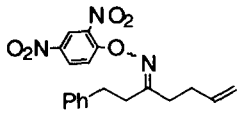
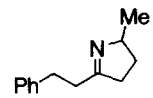
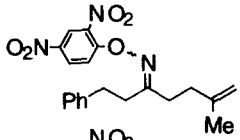
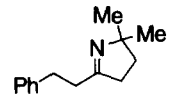
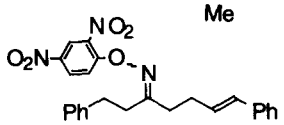
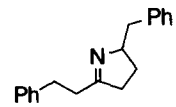
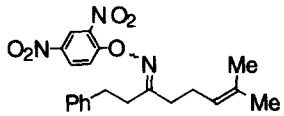
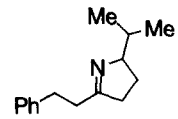
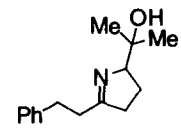
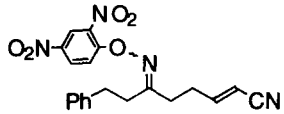
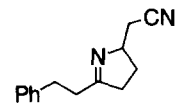
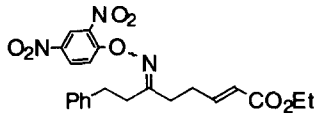
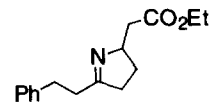
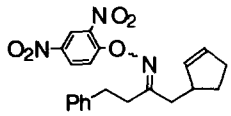
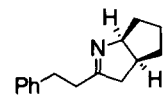
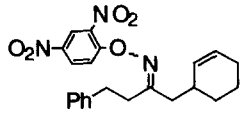
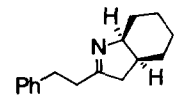
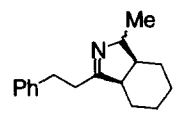
Radical trapping reagent (X-Y)	Time / h	Product **2**[d)] Y	Yield / %	
1,4-Cyclohexadiene[b)]	5	H	91	**2a**
CCl_4[b)]	25	Cl	75[e)]	**2b**
PhSSPh[c)]	10	SPh	70[e)]	**2c**
PhSeSePh[c)]	10	SePh	69[e)]	**2d**

a) All the reactions were carried out using 10 molar amounts of NaH, an equimolar amount of **3**. b) 10 molar amounts of reagent were used. c) 3 molar amounts of reagent were used. d) Diastereomer ratio = 2:1. e) **2a** was afforded as a by-product in about 10% yield.

The cyclization of several γ,δ-unsaturated ketone *O*-2,4-dinitrophenyloximes **4a-i** was investigated in the presence of 1,4-cyclohexadiene under the conditions shown in the footnote of Table 3. In all reactions, 5-*exo* cyclization proceeded selectively, and the corresponding cyclic imines were prepared in good yield. First, the reaction of 1-phenylhept-6-en-3-one *O*-2,4-dinitrophenyloxime (**4a**), a more flexible acyclic compound than the cyclic ketone oxime **1**, afforded 2-methyl-5-phenethyl-3,4-dihydropyrrole (**5a**) in 80% yield (Entry 1). As the reactions of either *E* and *Z* isomer of the oximes **4a** gave **5a** in the same yield, the reaction could be performed by using a mixture of the *E* and *Z* isomers.[6c] The cyclization of oximes of γ,δ-unsaturated ketone having substituted olefinic moieties proceeded smoothly: Each of the substrate with an internal methyl group **4b** or with a terminal phenyl group **4c** cyclized to give the corresponding cyclic imine **5b** or **5c** in 72% or 70% yield (Entries 2,3). The reaction of an oxime having two terminal methyl groups **4d** produced an 5-isopropyl dihydropyrrole **5d** in 27% yield along with a cyclic imine having a hydroxy group **6** in 55% yield (Entry 4). Though the reason of the formation of **6** is still unknown, it is thought that a cyclized radical intermediate is hard to be captured with 1,4-cyclohexadiene due to the steric effect of dimethyl group and is oxidized by sodium 2,4-dinitrophenolate. The reactions of oximes having an electron-withdrawing group such as cyano group **4e** and ethoxycarbonyl group **4f** on the olefinic moiety, many products, including cyclized compounds having sesamol moiety, were generated. As the radicals having electron-withdrawing group is electrophilic, it is supposed that the cyclized radical intermediate reacts with nucleophilic sesamol **3**. Accordingly, **4e** and **4f** were treated with NaH and 1,4-cyclohexadiene in 1,4-dioxane at 80 °C in the absence of sesamol **3**. Though the cyclization reaction proceeded slower than that in the co-existence of **3**, dihydropyrroles **5e** and **5f** were obtained in 86% and 82% yield, respectively (Entry 5,6). Thus, it is revealed that NaH itself has the ability to slowly reduce *O*-2,4-dinitrophenyloximes. A bicyclic imine **5g** was synthesized as a single diastereomer from 2-cyclopentenyl ketone oxime **4g** in 86% yield (Entry 7). Indole

and isoindole structures were constructed: that is, 2-cyclohexenyl ketone oxime **4h** and 2-vinylcyclohexyl ketone oxime **4i** gave hexahydroindole **5h** and hexahydroisoindole **5i** in 85% and 72% yields, respectively (Entries 8,9).

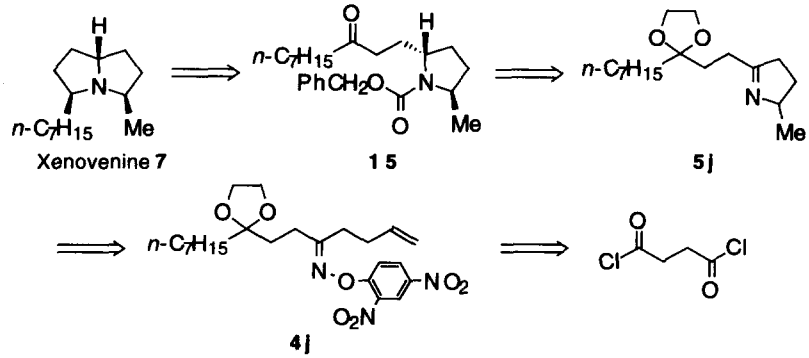
Table 3. Cyclization of several *O*-2,4-Dinitrophenyloxime **4**

Entry	Oxime **4**	Product (Yield / %)			
1[a]		**4a**		**5a** (80)	
2[a]		**4b**		**5b** (72)	
3[a]		**4c**		**5c** (70)	
4[a]		**4d**		**5d** (27)	 **6** (55)
5[b]		**4e**		**5e** (86)	
6[b]		**4f**		**5f** (82)	
7[a]		**4g**		**5g** (86)	
8[a]		**4h**		**5h** (85)	
9[a]		**4i**		**5i** (72)	

a) Reactions were carried out using 10 molar amounts of NaH, an equimolar amount of **3**, and 10 molar amounts of 1,4-cyclohexadiene in 1,4-dioxane at 50 °C for 2-5 h. b) Reactions were carried out using 10 molar amounts of NaH and 10 molar amounts of 1,4-cyclohexadiene in 1,4-dioxane at 80 °C for 24 h. c) Diastereomer ratio = 3:1.

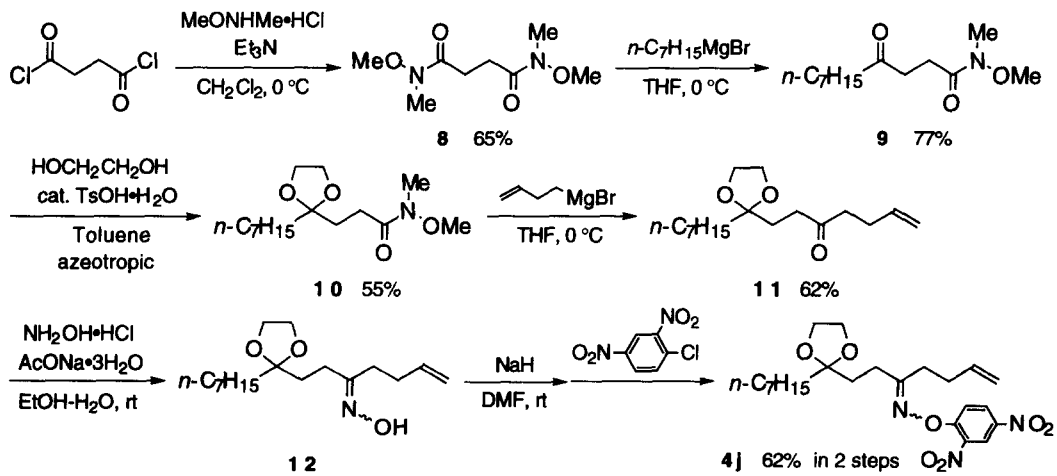
II. Application to the Stereoselective Synthesis of Xenovenine.

Xenovenine ((3*S*,5*R*,8*S*)-3-heptyl-5-methylpyrrolizidine, **7**), which was isolated from the cryptic thief ant *Solenopsis xenovenium*, is the first 3,5-dialkylpyrrolizidine derivative from a natural source[7a] and has been synthesized in racemic form[7] and in optically active form.[8] As the application of the present cyclization reaction, we tried the synthesis of (±)-xenovenine **7** according to the following retrosynthetic scheme; the key steps are the construction of the dihydropyrrole **5j** and the diastereoselective reduction of **5j** to 2,5-*trans* pyrrolidine **15** (Scheme 3).



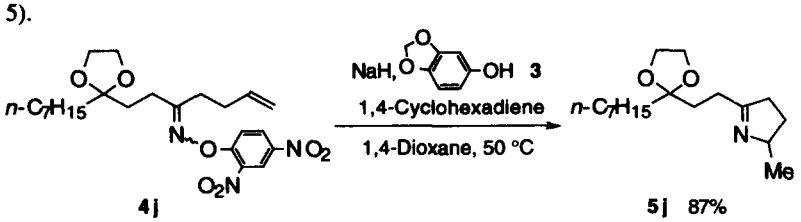
Scheme 3

The cyclization precusor **4j** was prepared as shown in Scheme 4. Reaction of oxalyl chloride and *N,O*-dimethylhydroxylamine hydrochloride gave the Weinreb's amide **8**,[9] which was transformed to β-ketoamide **9** by treatment with an equimolar amount of heptylmagnesium bromide.[10] After the acetalization of the β-ketoamide **9**,[11] the resulting amide **10** was converted to γ,δ-unsaturated ketone oxime **12** by the reaction with 1-butenylmagnesium bromide followed by the oximation with hydroxylamine hydrochloride. Finally, the *O*-2,4-dinitrophenyloxime **4j** was prepared by treatment of the oxime **12** with NaH and 2,4-dinitrochlorobenzene.[12]



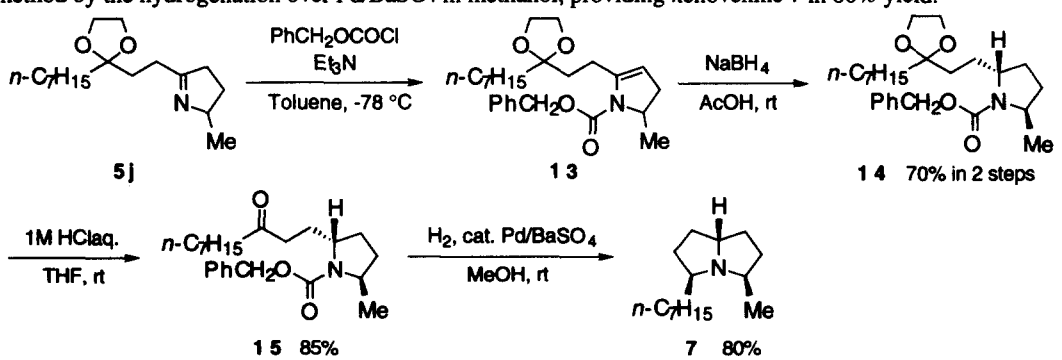
Scheme 4

The cyclization of the oxime **4j**, the first key reaction, successfully proceeded by treatment with NaH, sesamol **3**, and 1,4-cyclohexadiene in 1,4-dioxane at 50 °C, giving the 3,4-dihydro-2*H*-pyrrole **5j** in 87% yield (Scheme 5).



Scheme 5

Then, the stereoselective reduction of **5j**, the second key reaction, was examined. It has been known that the hydrogenation[13c] or the metal hydride-reduction (e.g. DIBAH)[13a] of 2,5-disubstituted 3,4-dihydro-2*H*-pyrrole gives 2,5-*cis*-disubstituted pyrrolidines selectively. In contrast, stereoselective reduction to 2,5-*trans* isomers remains to be established: the $NaBH_4$ reduction in acetic acid afforded the *trans* isomer preferentially, but in only 70:30 ratio.[13a,b] It was found that the dihydropyrrole **5j** could be converted to the 2,5-*trans* pyrrolidine **14** stereoselectively *via* an enecarbamate **13**. That is, **5j** was transformed to **13** by treatment with benzyl chlorocarbonate[14] and successively reduced with $NaBH_4$ in acetic acid to afford a pyrrolidine **14** as a single stereoisomer in 70% yield from **5j**. Deacetalization of **14** gave the known 2,5-*trans*-disubstituted pyrrolidine **15** in 85% yield.[15] The spectral data of **15** are in good agreement with those of the *trans* isomer in the literature.[8c] The final reductive cyclization of **15** was performed according to the literature method by the hydrogenation over Pd/$BaSO_4$ in methanol, providing xenovenine **7** in 80% yield.[8c]



Scheme 6

III. Summary

In summary, a novel method for the generation of alkylideneaminyl radicals has been developed by single electron transfer process. The radical species generated from γ,δ-unsaturated ketone *O*-2,4-dinitrophenyloximes are captured with the olefinic moiety intramolecularly, giving a variety of dihydropyrrole derivatives. This reaction exhibits the synthetic utility as shown in the synthesis of xenovenine.

EXPERIMENTAL

General. All melting points are uncorrected. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on Bruker AM500, Bruker DRX500, and JEOL α-500 spectrometers with $CHCl_3$ (δ=7.24 and 77.0) as an internal standard. IR spectra were measured with a Horiba FT-300S spectrometer. High resolution mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operating at 70 eV. Flash column chromatography was performed on silica gel (Merck Silica gel 60) or alumina gel (Wako Activated Aluminium Oxide) and preparative thin-layer chromatography was carried out using silica gel (Wakogel B-5F) or alumina gel (Merck Aluminiumoxid 60 $PF_{254+366}$). Dehydrated 1,4-dioxane was purchased from Kanto Chemical Co., Inc. and was used as freshly distilled from $LiAlH_4$ under an argon atmosphere, followed by degassed with argon just before use. NaH was purchased in condition of including liquid paraffin from Kanto Chemical Co., Inc. and was washed with distilled petroleum ether under argon, followed by drying under reduced pressure. Dehydrated tetrahydrofuran (THF) was purchased from Kanto Chemical Co., Inc. and dried over MS 4A. CH_2Cl_2 was distilled from P_2O_5, then from CaH_2, and dried over MS 4A. Toluene was distilled and dried over MS 4A. *N,N*-Dimethylformamide (DMF) was distilled under reduced pressure from CaH_2 and dried over MS 4A. Et_3N was freshly distilled from CaH_2. Other commercially available reagents, such as 3,4-methylenedioxyphenol, 1,4-cyclohexadiene, carbon tetrachloride, diphenyl disulphide, and diphenyl diselenide, were used without purification. All reactions were carried out under an argon atmosphere.

Preparation of γ,δ-unsaturated ketone *O*-2,4-Dinitrophenyloximes. Experimental procedures for the preparation of 1-(2-cyclohexenyl)-4-phenylbutan-2-one *O*-2,4-dinitrophenyloxime (**4h**) are shown below as a typical example for the synthesis of γ,δ-unsaturated ketone *O*-2,4-dinitrophenyloximes.

To a THF (15 ml) suspension of NaH (0.24 g, 10.0 mmol) and NaI (1.60 g, 10.7 mmol) was added a THF solution (5 ml) of methyl 3-oxo-5-phenylpentanoate (2.06 g, 10.0 mmol) at room temperature. After the mixture was stirred for 0.5 h at room temperature, a THF solution (5 ml) of 3-bromocyclohexene (1.73 g, 10.7 mmol) was added. After the mixture was stirred for 10 h at room temperature, the reaction mixture was neutralized with saturated aqueous NH_4Cl and organic materials were extracted with Et_2O and dried over $MgSO_4$. After the solvent was removed in vacuo, the crude materials were solved in EtOH (20 ml). To this solution was added 10% aqueous NaOH (20 ml) and the reaction mixture was immediately heated to reflux. After 0.5 h, EtOH was removed in vacuo, and to the reaction mixture was added excess 12 mol dm^{-3} hydrochloric acid. Organic materials were extracted with Et_2O and dried over $MgSO_4$. After the solvent was removed in vacuo, the crude materials were purified by flash column chromatography using silica gel (hexane:AcOEt = 49:1) to give 1-(2-cyclohexenyl)-4-phenylbutan-2-one (1.68 g, 74%).

1-(2-cyclohexenyl)-4-phenylbutan-2-one was converted to the corresponding *O*-2,4-dinitrophenyloxime by the literature procedure.[16]

Spectral Data

(2*S,4*S**)-2-Allyl-4-phenylcyclohexanone (*E*)-*O*-2,4-Dinitrophenyloxime (1)** Yellow needles, Mp 102 °C (hexane-benzene); IR (KBr) 1606, 1522, 1346, 1311 cm^{-1}; ^{1}H NMR: δ = 1.54 (1H, q, J = 12.7 Hz), 1.75 (1H, qd, J = 4.0, 13.1 Hz), 2.09 (1H, td, J = 5.3, 13.9 Hz), 2.17-2.32 (3H, m), 2.57-2.64 (1H, m), 2.72-2.78 (1H, m), 2.90 (1H, tt, J = 3.4, 12.3 Hz), 3.75 (1H, dq, J = 2.5, 14.0 Hz), 5.07 (1H, dd, J = 1.6, 10.3 Hz), 5.10 (1H, dd, J = 1.6, 17.1 Hz), 5.88 (1H, ddt, J = 7.0, 10.3, 17.1 Hz), 7.18-7.23 (3H, m), 7.28-7.32 (2H, m), 7.96 (1H, d, J = 9.4 Hz), 8.42 (1H, dd, J = 2.7, 9.4 Hz), 8.88 (1H, d, J = 2.7 Hz); ^{13}C NMR: δ = 27.5, 33.5, 34.7, 41.0, 43.3, 43.5, 117.0, 117.2, 122.1, 126.7, 128.3, 128.6, 129.4, 136.0, 140.5, 144.6, 157.8, 169.5. Found: C, 63.61; H, 5.44; N, 10.56%. Calcd. for $C_{21}H_{21}N_3O_5$: C, 63.79; H, 5.35; N, 10.63%.

1-Phenylhept-6-en-3-one *O*-2,4-Dinitrophenyloxime (4a) *E*:*Z*=1:1; Yellow oil; IR (KBr) 1604, 1529, 1342, 1309, 1263 cm^{-1}; ^{1}H NMR *E*-isomer: δ = 2.35-2.40 (2H, m), 2.67 (2H, t, J = 7.8 Hz), 2.72 (2H, t, J = 7.8 Hz), 2.97 (2H, t, J = 7.8 Hz), 5.01 (1H, dd, J = 1.5, 10.1 Hz), 5.09 (1H, dd, J = 1.5, 17.1 Hz), 5.82 (1H, ddt, J = 7.0, 10.1, 17.1 Hz), 7.20-7.26 (3H, m), 7.29-7.32 (2H, m), 7.72 (1H, d, J = 9.4 Hz), 8.35 (1H, dd, J = 2.8, 9.4 Hz), 8.86 (1H, d, J = 2.8 Hz); *Z*-isomer: δ = 2.36-2.45 (4H, m), 2.85 (2H, t, J = 7.3 Hz), 2.91 (2H, t, J = 7.3 Hz), 5.04 (1H, dd, J = 1.5, 10.4 Hz), 5.08 (1H, dd, J = 1.5, 17.1 Hz), 5.82 (1H, ddt, J = 6.4, 10.4, 17.1 Hz), 7.13-7.17 (1H, m), 7.22-7.28 (4H, m), 7.87 (1H, d, J = 9.3 Hz), 8.38 (1H, dd, J = 2.7, 9.3 Hz), 8.89 (1H, d, J = 2.7 Hz); ^{13}C NMR *E*-isomer: δ = 29.9, 30.0, 31.9, 35.9, 116.3, 117.3, 122.1, 126.5, 128.6, 128.7, 129.3, 129.4, 136.4, 140.4, 140.6, 157.5, 169.1; *Z*-isomer: δ = 29.7, 32.1, 32.6, 33.9, 116.1, 117.2, 122.1, 126.5, 128.5, 128.6, 129.3, 129.4, 136.6, 140.1, 140.5,

157.6, 169.0. Found: C, 61.58; H, 4.96; N, 11.24%. Calcd. for $C_{19}H_{19}N_3O_5$: C, 61.78; H, 5.18; N, 11.38%.

6-Methyl-1-phenylhept-6-en-3-one *O*-2,4-Dinitrophenyloxime (4b) *E*:*Z*=1:1; Yellow oil; IR (KBr) 1604, 1529, 1473, 1346, 1313, 1268, 876 cm^{-1}; ^1H NMR *E*-isomer: δ = 1.77 (3H, s), 2.30 (2H, t, *J* = 7.6 Hz), 2.71 (2H, t, *J* = 7.6 Hz), 2.72 (2H, t, *J* = 7.6 Hz), 2.97 (2H, t, *J* = 7.6 Hz), 4.74 (1H, s), 4.77 (1H, s), 7.20-7.24 (3H, m), 7.28-7.32 (2H, m), 7.71 (1H, d, *J* = 9.4 Hz), 8.34 (1H, dd, *J* = 2.7, 9.4 Hz), 8.84 (1H, d, *J* = 2.7 Hz); *Z*-isomer: δ = 1.74 (3H, s), 2.31 (2H, t, *J* = 7.8 Hz), 2.46 (2H, t, *J* = 7.8 Hz), 2.84 (2H, t, *J* = 7.8 Hz), 2.92 (2H, t, *J* = 7.8 Hz), 4.71 (1H, s), 4.78 (1H, s), 7.13-7.17 (1H, m), 7.20-7.26 (4H, m), 7.86 (1H, d, *J* = 9.4 Hz), 8.37 (1H, dd, *J* = 2.7, 9.4 Hz), 8.87 (1H, d, *J* = 2.7 Hz); ^{13}C NMR *E*-isomer: δ = 22.0, 28.9, 31.9, 33.7, 35.7, 111.4, 117.2, 122.0, 126.4, 128.3, 128.6, 129.3, 135.8, 140.3, 140.5, 143.8, 157.4, 169.3; *Z*-isomer: δ = 22.3, 32.1, 32.4, 32.7, 33.6, 111.1, 117.2, 122.0, 126.5, 128.4, 128.6, 129.3, 135.8, 140.0, 140.6, 143.8, 157.5, 169.3. Found: C, 62.74; H, 5.58; N, 10.93%. Calcd. for $C_{20}H_{21}N_3O_5$: C, 62.65; H, 5.52; N, 10.96%.

1,7-Diphenylhept-6-en-3-one *O*-2,4-Dinitrophenyloxime (4c) *E*:*Z*=1:1; Yellow oil; IR (KBr) 1604, 1529, 1344, 744 cm^{-1}; ^1H NMR *E*-isomer: δ = 2.51-2.56 (2H, m), 2.74-2.79 (4H, m), 2.99 (2H, t, *J* = 7.7 Hz), 6.14-6.22 (1H, m), 6.38 (1H, d, *J* = 15.8 Hz), 7.21-7.26 (8H, m), 7.28-7.34 (2H, m), 7.64 (1H, d, *J* = 9.4 Hz), 8.27 (1H, dd, *J* = 2.7, 9.4 Hz), 8.81 (1H, d, *J* = 2.7 Hz); *Z*-isomer: δ = 2.50-2.56 (4H, m), 2.87 (2H, t, *J* = 7.6 Hz), 2.95 (2H, t, *J* = 7.6 Hz), 6.16-6.22 (1H, m), 6.44 (1H, d, *J* = 15.7 Hz), 7.15-7.18 (1H, m), 7.22-7.26 (5H, m), 7.28-7.34 (4H, m), 7.84 (1H, d, *J* = 9.3 Hz), 8.29 (1H, dd, *J* = 2.3, 9.3 Hz), 8.86 (1H, d, *J* = 2.3 Hz); ^{13}C NMR *E*-isomer: δ = 29.5, 30.4, 31.8, 35.9, 117.2, 121.9, 126.0, 126.4, 127.2, 127.9, 128.3, 128.4, 129.2, 129.2, 131.6, 135.8, 137.0, 140.0, 140.3, 157.4, 169.0; *Z*-isomer: δ = 29.0, 32.1, 32.6, 34.3, 117.2, 122.0, 126.0, 126.5, 127.4, 128.3, 128.4, 128.6, 129.3, 129.3, 131.5, 135.8, 137.2, 140.0, 140.6, 157.5, 168.9. Found: C, 67.71; H, 5.35; N, 9.18%. Calcd. for $C_{25}H_{23}N_3O_5$: C, 67.41; H, 5.20; N, 9.43%.

7-Methyl-1-phenyloct-6-en-3-one *O*-2,4-Dinitrophenyloxime (4d) *E*:*Z*=1:1; Yellow oil; IR (KBr) 1604, 1531, 1344 cm^{-1}; ^1H NMR *E*-isomer: δ = 1.58 (3H, s), 1.65 (3H, s), 2.30 (2H, q, *J* = 7.4 Hz), 2.59 (2H, t, *J* = 7.8 Hz), 2.71 (2H, t, *J* = 7.8 Hz), 2.96 (2H, t, *J* = 7.4 Hz), 5.12 (1H, t, *J* = 7.4 Hz), 7.20-7.25 (3H, m), 7.28-7.32 (2H, m), 7.70 (1H, d, *J* = 9.4 Hz), 8.34 (1H, dd, *J* = 2.8, 9.4 Hz), 8.85 (1H, d, *J* = 2.8 Hz); *Z*-isomer: δ = 1.62 (3H, s), 1.70 (3H, s), 2.29-2.36 (4H, m), 2.83 (2H, t, *J* = 8.0 Hz), 2.91 (2H, t, *J* = 8.0 Hz), 5.12 (2H, t, *J* = 7.4 Hz), 7.13-7.17 (1H, m), 7.20-7.25 (4H, m), 7.86 (1H, d, *J* = 9.4 Hz), 8.38 (1H, dd, *J* = 2.7, 9.4 Hz), 8.87 (1H, d, *J* = 2.7 Hz); ^{13}C NMR *E*-isomer: δ = 17.6, 24.6, 25.6, 30.4, 31.9, 36.0, 117.2, 122.0, 122.2, 126.4, 128.3, 128.6, 129.2, 129.2, 133.7, 135.9, 140.4, 157.5, 169.5; *Z*-isomer: δ = 17.8, 24.3, 25.7, 32.1, 32.4, 34.6, 117.2, 122.0, 122.3, 126.4, 128.4, 128.5, 129.3, 129.3, 133.3, 135.7, 140.0, 157.6, 169.3. Found: C, 63.46; H, 5.83; N, 10.49%. Calcd. for $C_{21}H_{23}N_3O_5$: C, 63.47; H, 5.83; N, 10.57%.

6-(2,4-Dinitrophenyloxy)imino-8-phenyloct-2-enenitrile (4e) *E*:*Z*=1:1; Yellow needles, mp 117 °C (hexane-benzene); IR (KBr) 2220, 1603, 1525, 1346, 1315, 1273, 879 cm^{-1}; ^1H NMR *E*-isomer: δ = 2.51-2.56 (2H, m), 2.67 (2H, t, *J* = 7.6 Hz), 2.73 (2H, t, *J* = 7.6 Hz), 2.98 (2H, t, *J* = 7.8 Hz), 5.40 (1H, d, *J* = 16.3 Hz), 6.63-6.69 (1H, m), 7.20-7.27 (3H, m), 7.28-7.34 (2H, m), 7.73 (1H, d, *J* = 9.3 Hz), 8.38 (1H, dd, *J* = 2.7, 9.3 Hz), 8.88 (1H, d, *J* = 2.7 Hz); *Z*-isomer: δ = 2.41 (2H, t, *J* = 7.8 Hz), 2.51-2.56 (2H, m), 2.85 (2H, t, *J* = 7.8 Hz), 2.95 (2H, t, *J* = 7.8 Hz) 5.35 (1H, d, *J* = 16.3 Hz), 6.63-6.69 (1H, m), 7.15-7.18 (1H, m), 7.20-7.27 (4H, m), 7.79 (1H, d, *J* = 9.3 Hz), 8.40 (1H, dd, *J* = 2.7, 9.3 Hz), 8.89 (1H, d, *J* = 2.7 Hz); ^{13}C NMR *E*-isomer: δ = 28.9, 29.3, 31.8, 36.0, 101.7, 117.2, 122.1, 126.6, 128.2, 128.7, 129.3, 129.3, 135.8, 140.8, 152.4, 157.1, 167.3; *Z*-isomer: δ = 28.6, 32.0, 32.8, 32.9, 101.1, 116.9, 122.1, 126.7, 128.4, 128.7, 129.3, 129.3, 135.8, 140.8, 153.2, 157.1, 167.6. Found: C, 61.09; H, 4.77; N, 14.14%. Calcd. for $C_{20}H_{18}N_4O_5$: C, 60.91; H, 4.60; N, 14.21%.

Ethyl 6-(2,4-Dinitrophenyloxy)imino-8-phenyloct-2-enate (4f) *E*:*Z*=1:1; Yellow oil; IR (KBr) 1714, 1604, 1531, 1342, 1267 cm^{-1}; ^1H NMR *E*-isomer: δ = 1.24 (3H, t, *J* = 9.4 Hz), 2.52 (2H, q, *J* = 7.8 Hz), 2.71 (2H, t, *J* = 7.8 Hz), 2.72 (2H, t, *J* = 7.8 Hz), 2.97 (2H, t, *J* = 7.8 Hz), 4.13 (2H, q, *J* = 7.2 Hz), 5.85 (1H, d, *J* = 15.6 Hz), 6.92 (1H, dt, *J* = 7.8, 15.6 Hz), 7.19-7.26 (3H, m), 7.29-7.32 (2H, m), 7.72 (1H, d, *J* = 9.3 Hz), 8.35 (1H, dd, *J* = 2.7, 9.3 Hz), 8.87 (1H, d, *J* = 2.7 Hz); *Z*-isomer: δ = 1.28 (3H, t, *J* = 7.2 Hz), 2.45 (2H, t, *J* = 6.6 Hz), 2.52 (2H, q, *J* = 6.6 Hz), 2.84 (2H, t, *J* = 7.8 Hz), 2.93 (2H, t, *J* = 7.8 Hz), 4.18 (2H, q, *J* = 7.2 Hz), 5.86 (1H, d, *J* = 15.7 Hz), 6.93 (1H, dt, *J* = 6.6, 15.7 Hz), 7.13-7.17 (1H, m), 7.20-7.27 (4H, m), 7.82 (1H, d, *J* = 9.4 Hz), 8.37 (1H, dd, *J* = 2.8, 9.4 Hz), 8.87 (1H, d, *J* = 2.8 Hz); ^{13}C NMR *E*-isomer: δ = 14.2, 28.3, 29.1, 31.9, 35.9, 60.3, 117.2, 122.0, 122.2, 126.6, 128.2, 128.6,

129.3, 135.8, 140.0, 140.7, 145.7, 157.2, 166.2, 168.1; *Z*-isomer: δ = 14.2, 27.7, 31.9, 32.7, 33.2, 60.4, 117.2, 122.0, 122.6, 126.6, 128.4, 128.6, 129.3, 135.8, 139.8, 140.7, 146.3, 157.3, 166.2, 168.1. Found: C, 59.62; H, 5.30; N, 9.35%. Calcd. for $C_{22}H_{23}N_3O_7$: C, 59.86; H, 5.25; N, 9.52%.

1-(2-Cyclopentenyl)-4-phenylbutan-2-one *O*-2,4-Dinitrophenyloxime (4g) *E*:*Z*=1:1; Yellow oil; IR (KBr) 1604, 1531, 1473, 1344, 1278 cm^{-1}; ^1H NMR *E*-isomer: δ = 1.52-1.60 (1H, m), 2.07-2.16 (1H, m), 2.29-2.37 (1H, m), 2.42-2.50 (1H, m), 2.62-2.72 (2H, m), 2.79 (2H, t, *J* = 7.8 Hz), 3.02 (2H, t, *J* = 7.8 Hz), 3.11-3.18 (1H, m), 5.63-5.67 (1H, m), 5.80-5.84 (1H, m), 7.20-7.28 (3H, m), 7.28-7.36 (2H, m), 7.76 (1H, d, *J* = 9.4 Hz), 8.39 (1H, dd, *J* = 2.7, 9.4 Hz), 8.89 (1H, d, *J* = 2.7 Hz); *Z*-isomer: δ = 1.50-1.58 (1H, m), 2.13-2.21 (1H, m), 2.30-2.50 (4H, m), 2.85-2.94 (2H, m), 2.94-3.00 (2H, m), 3.10-3.20 (1H, m), 5.70-5.73 (1H, m), 5.83-5.86 (1H, m), 7.16-7.21 (1H, m), 7.24-7.32 (4H, m), 7.92 (1H, d, *J* = 9.4 Hz), 8.43 (1H, dd, *J* = 2.7, 9.4 Hz), 8.93 (1H, d, *J* = 2.7 Hz); ^{13}C NMR *E*-isomer: δ = 29.9, 31.8, 31.9, 36.0, 36.2, 42.7, 117.2, 122.0, 126.4, 128.3, 128.4, 128.6, 129.3, 132.2, 133.1, 135.8, 140.4, 157.5, 168.9; *Z*-isomer: δ = 29.7, 31.9, 32.1, 32.7, 40.5, 42.1, 117.2, 122.1, 126.4, 128.4, 128.5, 128.6, 129.3, 131.9, 133.1, 135.7, 140.0, 157.6, 168.9. Found: C, 63.52; H, 5.31; N, 10.46%. Calcd. for $C_{21}H_{21}N_3O_5$: C, 63.79; H, 5.35; N, 10.63%.

1-(2-Cyclohexenyl)-4-phenylbutan-2-one *O*-2,4-Dinitrophenyloxime (4h) *E*:*Z*=1:1; Yellow oil; IR (KBr) 1604, 1531, 1473, 1344, 1267 cm^{-1}; ^1H NMR *E*-isomer: δ = 1.33-1.43 (1H, m), 1.52-1.63 (1H, m), 1.73-1.87 (2H, m), 1.99-2.09 (2H, m), 2.60-2.68 (3H, m), 2.79 (2H, t, *J* = 7.8 Hz), 3.02 (2H, t, *J* = 7.8 Hz), 5.52-5.58 (1H, m), 5.74-5.80 (1H, m), 7.23-7.30 (3H, m), 7.31-7.37 (2H, m), 7.76 (1H, d, *J* = 9.4 Hz), 8.39 (1H, dd, *J* = 2.7, 9.4 Hz), 8.89 (1H, d, *J* = 2.7 Hz); *Z*-isomer: δ = 1.32-1.40 (1H, m), 1.53-1.67 (1H, m), 1.73-1.81 (1H, m), 1.81-1.89 (1H, m), 2.00-2.10 (2H, m), 2.34 (2H, t, *J* = 7.8 Hz), 2.55-2.61 (1H, m), 2.85-2.95 (2H, m), 2.97 (2H, t, *J* = 7.8 Hz), 5.57-5.63 (1H, m), 5.77-5.83 (1H, m), 7.17-7.22 (1H, m), 7.23-7.33 (4H, m), 7.91 (1H, d, *J* = 9.4 Hz), 8.43 (1H, dd, *J* = 2.7, 9.4 Hz), 8.92 (1H, d, *J* = 2.7 Hz); ^{13}C NMR *E*-isomer: δ = 20.8, 25.0, 28.9, 32.0, 33.0, 36.4, 36.5, 117.2, 122.0, 126.4, 128.3, 128.6, 128.7, 129.2, 129.6, 140.4, 140.5, 157.5, 168.7; *Z*-isomer: δ = 21.0, 25.1, 29.0, 32.1, 32.2, 32.5, 40.6, 117.2, 122.0, 126.4, 128.4, 128.6, 128.7, 129.3, 129.6, 140.1, 140.5, 157.5, 168.7. Found: C, 64.79; H, 5.90; N, 9.96%. Calcd. for $C_{22}H_{23}N_3O_5$: C, 64.54; H, 5.66; N, 10.26%.

3-Phenyl-1-(2-vinylcyclohexyl)-1-propanone *O*-2,4-Dinitrophenyloxime (4i) *E*:*Z*=2:1; Yellow oil; IR (KBr) 1604, 1525, 1471, 1340, 1286 cm^{-1}; ^1H NMR *E*-isomer: δ = 1.25-1.33 (1H, m), 1.45-1.56 (2H, m), 1.58-1.68 (1H, m), 1.68-1.76 (1H, m), 1.76-1.84 (2H, m), 1.84-1.89 (1H, m), 2.45-2.50 (1H, m), 2.51-2.58 (1H, m), 2.67-2.73 (1H, m), 2.85-2.99 (3H, m), 4.98-5.03 (2H, m), 5.93-6.01 (1H, m), 7.12-7.18 (1H, m), 7.25-7.30 (4H, m), 7.83 (1H, d, *J* = 9.4 Hz), 8.37 (1H, dd, *J* = 2.7, 9.4 Hz), 8.86 (1H, d, *J* = 2.7 Hz); *Z*-isomer: δ = 1.35-1.45 (1H, m), 1.45-1.60 (4H, m), 1.60-1.75 (1H, m), 1.80-1.90 (2H, m), 2.58-2.64 (2H, m), 2.83-2.92 (2H, m), 2.92-2.99 (1H, m), 3.47-3.53 (1H, m), 4.96-5.04 (1H, m), 6.11-6.18 (1H, m), 7.18-7.25 (3H, m), 7.25-7.32 (2H, m), 7.75 (1H, d, *J* = 9.4 Hz), 8.35 (1H, dd, *J* = 2.7, 9.4 Hz), 8.88 (1H, d, *J* = 2.7 Hz); ^{13}C NMR *E*-isomer: δ = 21.5, 24.7, 25.3, 31.8, 32.1, 32.3, 41.1, 46.7, 116.0, 117.4, 122.0, 126.4, 128.4, 128.5, 129.3, 135.8, 137.9, 140.4, 140.4, 157.8, 171.2; *Z*-isomer: δ = 20.7, 23.5, 25.9, 31.1, 31.9, 34.0, 41.5, 43.0, 116.7, 117.1, 122.1, 126.2, 128.3, 128.5, 129.3, 135.8, 137.1, 141.2, 157.7, 172.2. Found: C, 65.24; H, 5.99; N, 9.90%. Calcd. for $C_{23}H_{25}N_3O_5$: C, 64.24; H, 5.95; N, 9.92%.

General Procedure for the Synthesis of Dihydropyrroles (Table 2, using 1,4-cyclohexadiene as a radical trapping reagent): To a mixture of NaH (312.6 mg, 13.0 mmol), 3,4-methylenedioxyphenol (**3**) (179.8 mg, 1.30 mmol), and (2*S**,4*S**)-2-allyl-4-phenylcyclohexanone (*E*)-*O*-2,4-dinitrophenyloxime (**1**) (516.2 mg, 1.30 mmol) was added a 1,4-dioxane solution (6.5 ml) of 1,4-cyclohexadiene (0.65 ml) and the mixture was heated to 50 °C. After 5 h, the reaction mixture was quenched by adding H_2O slowly, and organic materials were extracted with AcOEt, and dried over Na_2SO_4. After evaporation of the solvent, the crude products were purified by thin-layer chromatography using alumina gel (hexane:AcOEt = 4:1) to afford 3,3a,4,5,6,7-hexahydro-2-methyl-5-phenyl-2*H*-indole (**2a**) (253.7 mg) in 91% yield.

Spectral Data

3,3a,4,5,6,7-Hexahydro-2-methyl-5-phenyl-2*H*-indole (2a) Two stereoisomers (2:1 ratio) were obtained as an inseparable mixture; yellow oil; IR (neat) 1651, 1495, 1450, 754, 700 cm^{-1}; ^1H NMR δ = 0.97-1.04 (0.66H, m), 1.15 (1H, d, *J* = 6.8 Hz), 1.34 (2H, d, *J* = 6.7 Hz), 1.35-1.43 (1H, m), 1.62-1.78 (1.66H, m), 2.08-2.13 (1H, m), 2.20-2.28 (1H, m), 2.28-2.39 (1.66H, m), 2.72-2.90 (3H, m), 3.86-3.92 (0.66H, m), 4.17-4.22 (0.33H, m), 7.16-7.21 (3H, m), 7.25-7.30 (2H, m); ^{13}C NMR major isomer: δ =

22.8, 31.3, 33.9, 38.7, 42.3, 43.2, 49.0, 66.4, 126.3, 126.7, 128.4, 145.7, 177.1; minor isomer: δ = 22.1, 31.5, 34.4, 36.9, 42.0, 43.4, 47.4, 66.4, 126.3, 126.7, 128.4, 145.6, 177.1. HRMS Found: m/z 213.1516. Calcd. for $C_{15}H_{19}N$ M, 213.1517.

2-Chloromethyl-3,3a,4,5,6,7-hexahydro-2-methyl-5-phenyl-2*H*-indole (2b) Two stereoisomers (2:1 ratio) were separated by silica gel TLC (stereochemistry was not determined); yellow oil; IR (neat) 1653, 1495, 1450, 754, 700 cm^{-1}; ^1H NMR major isomer: δ = 1.36 (1H, dt, J = 8.2, 13.2 Hz), 1.48 (1H, q, J = 12.4 Hz), 1.72 (1H, qd, J = 4.4, 13.2 Hz), 2.10-2.17 (1H, m), 2.24-2.30 (1H, m), 2.31-2.42 (2H, m), 2.76-2.82 (1H, m), 2.82-2.91 (2H, m), 3.75 (1H, dd, J = 4.8, 10.8 Hz), 3.79 (1H, dd, J = 4.6, 10.8 Hz), 4.19-4.27 (1H, m), 7.17-7.21 (3H, m), 7.25-7.31 (2H, m); minor isomer: δ = 1.40 (1H, q, J = 12.4 Hz), 1.64-1.74 (2H, m), 2.09-2.18 (2H, m), 2.24-2.31 (1H, m), 2.39-2.47 (1H, m), 2.76-2.82 (1H, m), 2.82-2.90 (1H, m), 2.90-2.98 (1H, m), 3.64 (1H, dd, J = 5.0, 11.0 Hz), 3.68 (1H, dd, J = 4.0, 11.0 Hz), 4.44-4.49 (1H, m), 7.17-7.21 (3H, m), 7.25-7.31 (2H, m); ^{13}C NMR major isomer: δ = 31.4, 33.5, 34.0, 41.6, 43.0, 48.7, 48.8, 71.8, 126.4, 126.7, 128.5, 145.3, 180.2; minor isomer: δ = 31.3, 32.6, 34.3, 42.2, 43.2, 48.5, 48.8, 71.6, 126.4, 126.7, 128.5, 145.2, 181.3. HRMS Found: m/z 247.1131. Calcd. for $C_{15}H_{18}ClN$ M, 247.1128.

3,3a,4,5,6,7-Hexahydro-5-phenyl-2-phenylthiomethyl-2*H*-indole (2c) Two stereoisomers (2:1 ratio) were separated by silica gel TLC (stereochemistry was not determined); yellow oil; IR (neat) 1649, 1485, 1479, 1446, 744, 698 cm^{-1}; ^1H NMR major isomer: δ = 1.27 (1H, dt, J = 8.6, 13.2 Hz), 1.44 (1H, q, J = 12.4 Hz), 1.70 (1H, qd, J = 4.3, 13.2 Hz), 2.08-2.16 (1H, m), 2.23-2.29 (1H, m), 2.29-2.45 (2H, m), 2.74-2.86 (3H, m), 3.01 (1H, dd, J = 7.9, 13.7 Hz), 3.48 (1H, dd, J = 5.3, 13.7 Hz), 4.05-4.13 (1H, m), 7.13-7.21 (4H, m), 7.23-7.31 (4H, m), 7.35-7.40 (2H, m); minor isomer: δ = 1.39 (1H, q, J = 12.4 Hz), 1.62-1.74 (2H, m), 2.05-2.18 (2H, m), 2.22-2.28 (1H, m), 2.30-2.38 (1H, m), 2.72-2.80 (1H, m), 2.80-2.86 (1H, m), 2.87 (1H, dd, J = 7.9, 12.8 Hz), 2.89-2.97 (1H, m), 3.27 (1H, dd, J = 4.7, 12.8 Hz), 4.31-4.39 (1H, m), 7.13-7.21 (4H, m), 7.23-7.31 (4H, m), 7.35-7.40 (2H, m); ^{13}C NMR major isomer: δ = 31.4, 33.8, 36.1, 40.4, 41.9, 43.0, 48.7, 70.3, 125.8, 126.3, 126.7, 126.8, 128.5, 128.8, 129.1, 136.6, 145.5, 179.0; minor isomer: δ = 31.4, 34.2, 34.3, 39.5, 42.1, 43.3, 48.0, 70.4, 125.9, 126.4, 126.7, 126.8, 128.5, 128.8, 129.1, 136.7, 145.3, 179.8. HRMS Found: m/z 321.1550. Calcd. for $C_{21}H_{23}NS$ M, 321.1551.

3,3a,4,5,6,7-Hexahydro-5-phenyl-2-phenylselenomethyl-2*H*-indole (2d) Two stereoisomers (2:1 ratio) were separated by silica gel TLC (stereochemistry was not determined); yellow oil; IR (neat) 1649, 1495, 1477, 1444, 739, 698 cm^{-1}; ^1H NMR major isomer: δ = 1.23 (1H, dt, J = 8.6, 13.2 Hz), 1.46 (1H, q, J = 12.4 Hz), 1.71 (1H, qd, J = 4.4, 13.2 Hz), 2.08-2.15 (1H, m), 2.23-2.28 (1H, m), 2.28-2.43 (2H, m), 2.72-2.87 (3H, m), 3.07 (1H, dd, J = 7.8, 11.9 Hz), 3.40 (1H, dd, J = 5.4, 11.9 Hz), 4.09-4.17 (1H, m), 7.17-7.24 (6H, m), 7.24-7.32 (2H, m), 7.50-7.55 (2H, m); minor isomer: δ = 1.38 (1H, q, J = 12.4 Hz), 1.61-1.79 (2H, m), 2.08-2.16 (1H, m), 2.20-2.29 (1H, m), 2.32-2.40 (1H, m), 2.70-2.76 (1H, m), 2.80-2.88 (1H, m), 2.88-2.94 (1H, m), 2.94 (1H, dd, J = 7.5, 12.0 Hz), 3.22 (1H, dd, J = 4.9, 12.0 Hz), 4.38-4.46 (1H, m), 7.17-7.24 (6H, m), 7.24-7.32 (2H, m), 7.50-7.55 (2H, m); ^{13}C NMR major isomer: δ = 31.4, 33.9, 34.8, 36.7, 41.9, 43.0, 48.8, 71.0, 126.3, 126.6, 126.7, 128.5, 129.0, 130.6, 132.4, 132.5, 145.5, 178.8; minor isomer: δ = 31.4, 34.2, 34.3, 34.9, 42.1, 43.3, 48.1, 71.1, 126.4, 126.7, 126.8, 128.5, 129.0, 130.5, 132.4, 132.5, 145.4, 179.4. HRMS Found: m/z 369.0994. Calcd. for $C_{21}H_{23}NSe$ M, 369.0996.

3,4-Dihydro-2-methyl-5-phenethyl-2*H*-pyrrole (5a) Yellow oil; IR (neat) 1641, 1602, 1494, 1452, 1317, 752, 700 cm^{-1}; ^1H NMR δ = 1.23 (3H, d, J = 6.8 Hz), 1.30-1.39 (1H, m), 2.02-2.09 (1H, m), 2.41 (1H, ddd, J = 8.7, 8.7, 17.2 Hz), 2.47-2.54 (1H, m), 2.61 (2H, t, J = 7.8 Hz), 2.91 (2H, dt, J = 4.5, 7.8 Hz), 4.01-4.05 (1H, m), 7.15-7.20 (3H, m), 7.24-7.28 (2H, m); ^{13}C NMR δ = 22.0, 30.6, 32.7, 35.3, 37.7, 67.6, 126.0, 128.3, 128.4, 141.4, 176.5. HRMS Found: m/z 187.1343. Calcd. for $C_{13}H_{17}N$ M, 187.1361.

3,4-Dihydro-2,2-dimethyl-5-phenethyl-2*H*-pyrrole (5b) Yellow oil; IR (neat) 1643, 1454, 1365, 750, 700 cm^{-1}; ^1H NMR d = 1.18 (6H, s), 1.65 (2H, t, J = 7.8 Hz), 2.48 (2H, t, J = 7.8 Hz), 2.58 (2H, t, J = 8.0 Hz), 2.89 (2H, t, J = 8.0 Hz), 7.16-7.20 (3H, m), 7.24-7.28 (2H, m); ^{13}C NMR δ = 28.7, 32.9, 35.3, 36.4, 37.6, 72.3, 125.9, 128.3, 128.4, 141.4, 173.8. HRMS Found: m/z 201.1522. Calcd. for $C_{14}H_{19}N$ M, 201.1517.

2-Benzyl-3,4-dihydro-5-phenethyl-2*H*-pyrrole (5c) Yellow oil; IR (neat) 1641, 1495, 1452, 748, 700 cm^{-1}; ^1H NMR δ = 1.53-1.61 (1H, m), 1.88-1.96 (1H, m), 2.34-2.41 (2H, m), 2.62 (1H, dd, J = 8.7,

13.4 Hz), 2.66 (2H, t, J = 8.2 Hz), 2.97 (2H, t, J = 8.2 Hz), 3.20 (1H, dd, J = 4.9, 13.4 Hz), 4.28-4.36 (1H, m), 7.20-7.25 (6H, m), 7.28-7.33 (4H, m); ^{13}C NMR δ = 27.7, 32.7, 35.3, 37.4, 42.3, 73.4, 126.0, 128.2, 128.3, 128.4, 128.4, 129.4, 139.4, 141.4, 177.2. HRMS Found: m/z 263.1680. Calcd. for $C_{19}H_{21}N$ M, 263.1674.

3,4-Dihydro-2-isopropyl-5-phenethyl-2*H*-pyrrole (5d) Yellow oil; IR (neat) 1643, 1495, 1454, 750, 700 cm^{-1}; ^{1}H NMR δ = 0.85 (3H, d, J = 6.8 Hz), 1.00 (3H, d, J = 6.8 Hz), 1.50-1.58 (1H, m), 1.85-1.95 (2H, m), 2.38-2.50 (3H, m), 2.69 (2H, t, J = 8.0 Hz), 2.94 (2H, t, J = 8.0 Hz), 3.80-3.86 (1H, m), 7.18-7.25 (3H, m), 7.28-7.33 (2H, m); ^{13}C NMR δ = 18.0, 19.8, 24.8, 32.9, 35.3, 37.6, 78.3, 126.0, 128.3, 128.4, 141.4, 176.7. HRMS Found: m/z 215.1674. Calcd. for $C_{15}H_{21}N$ M, 215.1674.

3,4-Dihydro-2-(1-hydroxy-1-methylethyl)-5-phenethyl-2*H*-pyrrole (6) Yellow oil; IR (neat) 3390, 1643, 1496, 1456, 1174, 750, 702 cm^{-1}; ^{1}H NMR δ = 1.06 (3H, s), 1.29 (3H, s), 1.61-1.69 (1H, m), 1.88-1.96 (1H, m), 2.43-2.52 (1H, m), 2.52-2.60 (1H, m), 2.67-2.77 (2H, m), 2.90-3.03 (2H, m), 3.90-3.96 (1H, m), 7.19-7.24 (3H, m), 7.28-7.33 (2H, m); ^{13}C NMR δ = 23.7, 24.5, 27.5, 32.5, 35.0, 38.4, 72.3, 81.5, 126.1, 128.3, 128.4, 141.1, 179.0. HRMS Found: m/z 231.1606. Calcd. for $C_{15}H_{21}NO$ M, 231.1623.

2-Cyanomethyl-3,4-dihydro-5-phenethyl-2*H*-pyrrole (5e) Yellow oil; IR (neat) 2247, 1495, 1454, 1423, 1311, 1290, 754, 701 cm^{-1}; ^{1}H NMR δ = 1.67-1.75 (1H, m), 2.18-2.26 (1H, m), 2.52-2.60 (1H, m), 2.62-2.77 (5H, m), 2.92-3.02 (2H, m), 4.25-4.31 (1H, m), 7.18-7.24 (3H, m), 7.28-7.33 (2H, m); ^{13}C NMR d = 24.4, 27.7, 32.5, 35.1, 38.3, 67.9, 117.8, 126.1, 128.2, 128.5, 140.9, 180.1. HRMS Found: m/z 212.1314. Calcd. for $C_{14}H_{16}N_2$ M, 212.1313.

2-Ethoxycarbonylmethyl-3,4-dihydro-5-phenethyl-2*H*-pyrrole (5f) Yellow oil; IR (neat) 1734, 1643, 1495, 1373, 1315, 1261, 1182, 1030, 752, 700 cm^{-1}; ^{1}H NMR δ = 1.29 (3H, t, J = 7.2 Hz), 1.49-1.57 (1H, m), 2.12-2.20 (1H, m), 2.35 (1H, dd, J = 8.7, 15.4 Hz), 2.44-2.60 (2H, m), 2.66 (2H, t, J = 8.0 Hz), 2.82 (1H, dd, J = 5.6, 15.4 Hz), 2.94 (2H, t, J = 8.0 Hz), 4.18 (2H, q, J = 7.2 Hz), 4.35-4.41 (1H, m), 7.19-7.24 (3H, m), 7.28-7.32 (2H, m); ^{13}C NMR δ = 14.2, 28.5, 32.6, 35.3, 37.7, 41.0, 60.3, 68.8, 126.0, 128.2, 128.4, 141.2, 171.9, 177.8. HRMS Found: m/z 259.1592. Calcd. for $C_{16}H_{21}NO_2$ M, 259.1572.

(3a*R,6a*R**)-3a,6a-Dihydro-2-phenethyl-3*H*-cyclopenteno[d]pyrrole (5g)** Yellow oil; IR (neat) 1645, 1495, 1448, 1433, 750, 700 cm^{-1}; ^{1}H NMR δ = 1.22-1.30 (2H, m), 1.42-1.48 (1H, m), 1.62-1.70 (1H, m), 1.71-1.79 (2H, m), 2.15-2.21 (1H, m), 2.55-2.65 (3H, m), 2.70-2.76 (1H, m), 2.84-2.94 (2H, m), 4.48-4.54 (1H, m), 7.15-7.22 (3H, m), 7.27-7.32 (2H, m); ^{13}C NMR δ = 23.9, 32.7, 33.0, 34.7, 34.9, 39.0, 46.6, 78.9, 125.9, 128.2, 128.3, 141.4, 175.7. HRMS Found: m/z 213.1502. Calcd. for $C_{15}H_{19}N$ M, 213.1517. The stereochemistry was determined by the differential NOE experiments (H^{3a} and H^{6a} 8%).

(3a*R,7a*R**)-3a,4,5,6,7,7a-Hexahydro-2-phenethyl-3*H*-indole (5h)** Yellow oil; IR (neat) 1631, 1495, 1450, 1431, 750, 700 cm^{-1}; ^{1}H NMR δ = 1.04-1.11 (1H, m), 1.16-1.28 (1H, m), 1.33-1.43 (3H, m), 1.44-1.52 (1H, m), 1.72-1.82 (2H, m), 2.15-2.20 (2H, m), 2.40-2.47 (1H, m), 2.60-2.67 (2H, m), 2.84-2.96 (2H, m), 3.69-3.75 (1H, m), 7.16-7.23 (3H, m), 7.27-7.32 (2H, m); ^{13}C NMR δ = 21.8, 22.9, 27.4, 28.9, 32.6, 35.9, 36.8, 44.1, 69.1, 125.9, 128.3, 128.3, 141.3, 177.8. HRMS Found: m/z 227.1670. Calcd. for $C_{16}H_{21}N$ M, 227.1674. The stereochemistry was determined by the differential NOE experiments (H^{3a} and H^{7a} 8%).

(3a*R,7a*S**)-3a,4,5,6,7,7a-Hexahydro-1-methyl-2-phenethyl-1*H*-isoindole (5i)** Two stereoisomers (3:1 ratio) were obtained as an inseparable mixture; yellow oil; IR (neat) 1629, 1606, 1495, 1450, 1372, 750, 702 cm^{-1}; ^{1}H NMR δ = 1.20 (2.25H, d, J = 6.7 Hz), 1.21-1.28 (1.50H, m), 1.29 (0.75H, d, J = 7.2 Hz), 1.38-1.50 (2.5H, m), 1.50-1.68 (2H, m), 1.68-1.81 (1.5H, m), 1.90-1.95 (0.5H, m), 2.08-2.16 (0.25H, m), 2.47-2.68 (3.5H, m), 2.85-2.98 (2.25H, m), 3.67-3.73 (0.25H, m), 3.75-3.81 (0.75H, m), 7.17-7.24 (3H, m), 7.26-7.33 (2H, m); ^{13}C NMR major isomer: δ = 19.0, 22.6, 23.8, 25.3, 25.6, 32.5, 33.9, 44.6, 48.0, 68.0, 125.9, 128.3, 128.4, 141.8, 180.1; minor isomer: δ = 15.4, 23.6, 24.0, 24.4, 30.8, 32.6, 33.4, 42.0, 49.8, 67.1, 125.9, 128.3, 128.4, 141.8, 180.1. HRMS Found: m/z 241.1860. Calcd. for $C_{17}H_{23}N$ M, 241.1830.

Synthesis of Xenovenine and its Intermediates

N,N'-Dimethoxy-N,N'-dimethylsuccinamide (8). To a CH_2Cl_2 suspension (500 ml) of *N,O*-dimetthylhydroxylamine hydrochloride (33.60 g, 0.344 mol) and Et_3N (100 ml) was added succinyl chloride (23.67 g, 0.153 mol) slowly at 0 °C (the color of the reaction mixture turned to black). After addition of succinyl chloride, the reaction was left to warm overnight, and quenched with H_2O. The organic materials were extracted with CH_2Cl_2, washed with brine, and dried over $MgSO_4$. After the solvent was removed in vacuo, the crude materials were purified by recrystalization from hexane to yield 19.69 g (63%) of the title compound as a brown needles. Mp 75 °C (haxane); IR (KBr) 1653, 1456, 1425, 1390, 1192, 993 cm^{-1}; ^1H NMR δ = 2.74 (4H, s), 3.15 (6H, s), 3.70 (6H, s); ^{13}C NMR δ = 26.4, 32.2, 61.1, 173.5. Found: C, 46.91; H, 7.73; N, 13.46%. Calcd. for $C_8H_{16}N_2O_4$: C, 47.05; H, 7.90; N, 13.72%.

N-Methoxy-N-methyl-4-oxoundecanamide (9). *n*-$C_7H_{15}MgBr$ (120.0 mmol) was prepared by adding *n*-$C_7H_{15}Br$ (21.50 g, 120.0 mmol) to a THF suspension (80 ml) of Mg (2.92 g, 120.1 mmol) and stirring the reaction mixture for 1 h under refluxing. To a THF solution (500 ml) of **8** (19.69 g, 96.42 mmol) was added a THF solution of *n*-$C_7H_{15}MgBr$ by inverse addition at 0 °C. After stirring for 4 h at 0 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl. The organic materials were extracted with Et_2O, washed with brine, and dried over $MgSO_4$. After the solvent was removed in vacuo, the crude materials were purified by flash column chromatography using silica gel (hexane:AcOEt = 19:1) to yield 19.85 g (77%) of the title compound as a colorless oil. IR (KBr) 1714, 1666, 1464, 1442, 1415, 1383, 1004 cm^{-1}; ^1H NMR δ = 0.83 (3H, t, *J* = 6.7 Hz), 1.17-1.32 (8H, m), 1.50-1.58 (2H, m), 2.43 (2H, t, *J* = 7.5 Hz), 2.65-2.72 (4H, m), 3.13 (3H, s), 3.69 (3H, s); ^{13}C NMR δ = 14.0, 22.5, 23.8, 25.8, 29.0, 29.1, 31.6, 32.2, 36.5, 42.9, 61.1, 173.2, 209.9. HRMS Found: m/z 243.1823. Calcd. for $C_{13}H_{25}NO_3$ M, 243.1834.

N-Methoxy-N-methyl-4,4-methylenedioxyundecanamide (10). To a toluene solution (100 ml) of **9** (19.85 g, 67.3 mmol) was added ethylene glycol (8.36 g, 134.6 mmol) and *p*-toluenesulfonic acid monohydrate (100 mg). The mixture was refluxed for 10 h under the azeotropic conditions using a Dean-Stark condenser, washed with H_2O twice, and dried over $MgSO_4$. After the solvent was removed in vacuo, the crude materials were purified by flash column chromatography using silica gel (hexane:AcOEt = 19:1) to yield 12.71 g (55%) of the title compound as a colorless oil. IR (KBr) 1666, 1462, 1421, 1375, 1178, 1143, 1095 cm^{-1}; ^1H NMR δ = 0.85 (3H, t, *J* = 6.6 Hz), 1.20-1.40 (10H, m), 1.58 (2H, t, *J* = 8.0 Hz), 1.96 (2H, t, *J* = 8.0 Hz), 2.46 (2H, t, *J* = 7.7 Hz), 3.15 (3H, s), 3.66 (3H, s), 3.90-3.95 (4H, m); ^{13}C NMR δ = 14.0, 22.6, 23.7, 26.5, 29.2, 29.8, 31.4, 31.7, 37.2, 61.1, 64.8, 64.9, 65.0, 111.0, 174.2. HRMS Found: m/z 287.2073. Calcd. for $C_{15}H_{29}NO_4$ M, 287.2097.

8,8-Methyleneoxypentadec-1-en-5-one (11). 1-Butenylmagnesium bromide (48.2 mmol) was prepared by adding 1-butenyl bromide (6.50 g, 4.82 mmol) to a THF suspension (30 ml) of Mg (1.20 g, 49.4 mmol) and stirring the reaction mixture for 1 h under refluxing. To a THF solution of 1-butenylmagnesium bromide was added a THF solution (100 ml) of **10** (10.00 g, 32.1 mmol) at 0 °C. After stirring for 4 h at 0 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl. The organic materials were extracted with Et_2O, washed with brine, and dried over $MgSO_4$. After the solvent was removed in vacuo, the crude materials were purified by flash column chromatography using silica gel (hexane:AcOEt = 19:1) to yield 6.15 g (62%) of the title compound as a colorless oil. IR (KBr) 1714, 1462, 1441, 1415, 1357, 1143, 1089, 1047 cm^{-1}; ^1H NMR δ = 0.84 (3H, t, *J* = 6.9 Hz), 1.19-1.34 (10H, m), 1.54 (2H, t, *J* = 7.6 Hz), 1.91 (2H, t, *J* = 7.6 Hz), 2.29 (2H, q, *J* = 6.6 Hz), 2.43 (2H, t, *J* = 7.6 Hz), 2.48 (2H, t, *J* = 7.6 Hz), 3.86-3.90 (4H, m), 4.94 (1H, dd, *J* = 1.5, 10.2 Hz), 4.99 (1H, dd, *J* = 1.5, 17.1 Hz), 5.77 (1H, ddt, *J* = 6.6, 10.2, 17.1 Hz); ^{13}C NMR δ = 14.0, 22.6, 23.8, 27.8, 29.2, 29.8, 30.7, 31.7, 37.2, 37.3, 41.7, 64.9, 64.9, 111.0, 115.1, 137.2, 209.6. Found: C, 72.26; H, 10.84%. Calcd. for $C_{17}H_{30}O_3$: C, 72.30; H, 10.71%.

8,8-Methyleneoxypentadec-1-en-5-one Oxime (12). To an aqueous solution (10 ml) of $NH_2OH{\cdot}HCl$ (0.36 g, 5.17 mmol) and $AcONa{\cdot}3H_2O$ (0.71 g, 5.17 mmol) was added a EtOH solution (10 ml) of **11** (1.33 g, 4.32 mmol). After stirring for 6 h at room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. The organic materials were extracted with AcOEt, washed with brine, and dried over $MgSO_4$. After the solvent was removed in vacuo, the crude materials (1.32 g, slightly yellow oil) were used for the next step without purification. *E*:*Z*=1:1; IR (KBr) 3395, 1643, 1450, 1140, 1092, 1051, 914 cm^{-1}; ^1H NMR δ = 0.80-0.88 (3H, m), 1.19-1.38 (10H, m), 1.54-1.62 (2H, m), 1.78-1.82 (2H, m), 2.20-2.30 (4H, m), 2.35-2.43 (2H, m), 3.86-3.94 (4H, m), 4.94-4.99 (1H, m), 4.99-5.07 (1H, m), 5.75-5.83 (1H, m).

8,8-Methyleneoxypentadec-1-en-5-one O-2,4-Dinitrophenyloxime (4j). To a DMF suspension (5 ml) of NaH (0.12 g, 5.00 mmol) was added a DMF solution (5 ml) of crude **12** (1.32 g, 4.12 mmol). After stirring for 1 h at room temperature, a DMF solution (5 ml) of 2,4-dinitrochlorobenzene (1.01 g, 5.00

mmol) was added to the reaction mixture, and followed by additional stirring overnight. After the reaction mixture was quenched with saturated aqueous NH_4Cl, the organic materials were extracted with AcOEt, washed with brine, and dried over $MgSO_4$. After the solvent was removed in vacuo, the crude materials were purified by flash column chromatography using silica gel (hexane:AcOEt = 19:1) to yield 1.29 g (62% in two steps from **11**) of the title compound as a yellow oil. *E*:*Z*=1:1; *E*-isomer : Yellow oil; IR (KBr) 1606, 1533, 1473, 1344, 1315, 1267, 1140, 922 cm^{-1}; ^1H NMR δ = 0.86 (3H, t, J = 6.9 Hz), 1.20-1.40 (10H, m), 1.61 (2H, t, J = 8.0 Hz), 1.95 (2H, t, J = 8.0 Hz), 2.35 (2H, q, J = 7.5 Hz), 2.46 (2H, t, J = 7.5 Hz), 2.65 (2H, t, J = 7.5 Hz), 3.91-3.98 (4H, m), 5.01 (1H, dd, J = 1.5, 10.1 Hz), 5.08 (1H, dd, J = 1.5, 17.0 Hz), 5.82 (1H, ddt, J = 6.7, 10.1, 17.0 Hz), 7.91 (1H, d, J = 9.4 Hz), 8.39 (1H, dd, J = 2.7, 9.4 Hz), 8.86 (1H, d, J = 2.7 Hz); ^{13}C NMR δ = 14.0, 22.6, 23.9, 28.8, 29.2, 29.8, 29.8, 30.0, 31.8, 32.8, 37.3, 65.1, 65.1, 110.9, 116.1, 117.2, 122.0, 129.3, 136.0, 136.4, 140.5, 157.5, 169.9. Found: C, 59.59; H, 7.03; N, 9.01%. Calcd. for $C_{23}H_{33}N_3O_7$: C, 59.60; H, 7.18; N, 9.07%. *Z*-isomer : Yellow oil; IR (KBr) 1604, 1533, 1473, 1344, 1313, 1279, 1140, 922 cm^{-1}; ^1H NMR δ = 0.85 (3H, t, J = 7.0 Hz), 1.20-1.40 (10H, m), 1.62 (2H, t, J = 8.0 Hz), 1.90 (2H, t, J = 8.0 Hz), 2.39 (2H, q, J = 7.0 Hz), 2.50 (2H, t, J = 8.0 Hz), 2.62 (2H, t, J = 8.0 Hz), 3.93-3.97 (4H, m), 5.04 (1H, dd, J = 1.5, 10.2 Hz), 5.09 (1H, dd, J = 1.5, 17.1 Hz), 5.83 (1H, ddt, J = 6.5, 10.2, 17.1 Hz), 7.89 (1H, d, J = 9.4 Hz), 8.38 (1H, dd, J = 2.7, 9.4 Hz), 8.84 (1H, d, J = 2.7 Hz); ^{13}C NMR δ = 14.0, 22.6, 23.8, 24.8, 29.2, 29.7, 29.8, 31.8, 32.7, 33.5, 37.2, 65.1, 65.1, 110.9, 115.9, 117.3, 122.0, 129.2, 136.0, 136.6, 140.5, 157.5, 169.7. Found: C, 59.63; H, 7.31; N, 9.01%. Calcd. for $C_{23}H_{33}N_3O_7$: C, 59.60; H, 7.18; N, 9.07%.

3,4-Dihydro-2-methyl-5-(3,3-methylenedioxydecyl)-2*H*-pyrrole (5j). To a mixture of NaH (102.9 mg, 4.29 mmol), 3,4-methylenedioxyphenol (**3**) (59.2 mg, 0.429 mmol), and **4j** (209.0 mg, 0.429 mmol) was added a 1,4-dioxane solution (4 ml) of 1,4-cyclohexadiene (0.1 ml) and the mixture was heated to 50 °C. After 5 h, the reaction mixture was quenched by adding H_2O slowly, and the organic materials were extracted with AcOEt, and dried over Na_2SO_4. After the solvent was removed in vacuo, the crude materials were purified by thin-layer chromatography using alumina gel (hexane:AcOEt = 4:1) to yield 113.7 mg (87%) of the title compound as a yellow oil. IR (neat) 1643, 1456, 1323, 1136, 1092, 1047 cm^{-1}; ^1H NMR δ = 0.85 (3H, t, J = 6.9 Hz), 1.20 (3H, d, J = 6.8 Hz), 1.20-1.30 (8H, m), 1.30-1.38 (3H, m), 1.55-1.60 (2H, m), 1.88-1.94 (2H, m), 2.01-2.08 (1H, m), 2.33-2.38 (2H, m), 2.38-2.45 (1H, m), 2.47-2.55 (1H, m), 3.87-3.92 (4H, m), 3.95-4.02 (1H, m); ^{13}C NMR δ = 14.0, 22.0, 22.6, 23.8, 28.1, 29.2, 29.9, 30.6, 31.8, 33.5, 37.5, 37.6, 65.0, 65.1, 67.6, 111.3, 176.7. HRMS Found: m/z 182.1196. Calcd. for $C_{17}H_{31}NO_2$-C_7H_{15} M-C_7H_{15}, 182.1181. HRMS Found: m/z 282.2434. Calcd. for $C_{17}H_{31}NO_2$+H M+H, 282.2433.

***N*-Benzyloxycarbonyl-2,3-dihydro-2-methyl-5-(3,3-methylenedioxydecyl)pyrrole (13).** To a toluene (4 ml) solution of **5j** (295.0 mg, 0.966 mmol) and Et_3N (0.5 ml) was added a 30% toluene solution (1 ml) of benzyloxycarbonyl chloride at -78 °C. The reaction mixture was warmed to room temperature for 2 h, and stirred overnight. A salt of triethylamine hydrochloride was precipitated by diluting with Et_2O (100 ml), removed by filteration. After the solvent was removed in vacuo, the crude materials (433.5 mg, yellow oil) were used for the next step without purification. IR (neat) 1712, 1456, 1404, 1346, 1317, 1288, 1136, 758, 700 cm^{-1}; ^1H NMR δ = 1.14-1.19 (3H, m), 1.20-1.38 (10H, m), 1.48-1.54 (0.5H, m), 1.54-1.64 (2H, m), 1.69-1.77 (0.5H, m), 1.78-1.86 (0.5H, m), 1.86-1.96 (1H, m), 2.28-2.36 (1H, m), 2.50-2.62 (2H, m), 2.67-2.74 (0.5H m), 3.80-3.95 (4H, m), 4.25-4.33 (0.5H, m), 4.33-4.39 (0.5H, m), 4.71 (0.5H, bs), 5.10-5.19 (4H, m), 5.95 (0.5H, bs), 7.27-7.38 (5H, m).

(2*S,5*R**)-*N*-Benzyloxycarbonyl-5-methyl-2-(3,3-methylenedioxydecyl)pyrrolidine (14).** Crude **13** (433.5 mg) was stirred in AcOH (5 ml) at room temperature. $NaBH_4$ (110.0 mg, 2.898 mmol) was added in small portions and the mixture was stirred overnight. The mixture was hydrolyzed with H_2O, saturated with K_2CO_3. The organic materials were extracted with AcOEt, and dried over $MgSO_4$. After the solvent was removed in vacuo, the crude materials were purified by thin-layer chromatography using silica gel (hexane:AcOEt = 4:1) to yield 298.6 mg (70% in two steps from **5j**) of the title compound as a colorless oil. IR (neat) 1701, 1458, 1406, 1350, 1309, 1093 cm^{-1}; ^1H NMR δ = 0.90 (3H, t, J = 6.9 Hz), 1.20-1.45 (13H, m), 1.50-1.72 (6H, m), 1.81-1.98 (2H, m), 1.98-2.10 (2H, m), 3.79-4.16 (6H, m), 5.08-5.21 (2H, m), 7.27-7.39 (5H, m); ^{13}C NMR δ = 14.0, 21.7, 22.0, 22.6, 23.7, 29.2, 29.5, 29.6, 29.8, 31.7, 31.8, 33.6, 37.1, 53.4, 53.8, 57.3, 57.7, 64.8, 64.8, 66.4, 111.5, 127.7, 127.8, 128.3, 137.1, 155.2. Found: C, 71.93; H, 9.56; N, 3.24%. Calcd. for $C_{25}H_{39}NO_4$: C, 71.91; H, 9.41; N, 3.35%.

(2*S,5*R**)-*N*-Benzyloxycarbonyl-5-methyl-2-(3-oxodecyl)pyrrolidine (15).** To a THF solution (5 ml) of **14** (108.1 mg, 0.245 mmol) was added 1 mol dm^{-1} hydrochloric acid (5 ml). After stirring for 1 h at room temperature, the mixture was saturated with K_2CO_3. The organic materials were extracted with AcOEt, and dried over $MgSO_4$. The solvent was removed in vacuo to yield 82.8 mg (85%) of the title

compound as a colorless oil. IR (neat) 1699, 1456, 1406, 1352, 1302, 1097, 698 cm^{-1}; ^1H NMR δ = 0.85 (3H, t, J = 6.9 Hz), 1.14-1.30 (13H, m), 1.40-1.70 (4H, m), 1.80-1.92 (1H, m), 1.92-2.05 (1H, m), 2.20-2.45 (4H, m), 3.80-3.95 (2H, m), 5.04-5.13 (2H, m), 7.24-7.34 (5H, m); ^{13}C NMR δ = 13.9, 21.0, 22.5, 23.7, 27.4, 27.6, 28.9, 29.1, 29.2, 29.8, 31.2, 31.7, 39.6, 42.6, 53.5, 53.7, 57.3, 57.5, 66.5, 127.8, 128.3, 128.4, 137.0, 155.2, 210.7. The spectral data of **15** were in good agreement with those of the literature.[8c]

(3*S,5*R**,8*S**)-3-Heptyl-5-methylpyrrolizidine (Xenovenine, 7).** **15** (93.1 mg, 0.234 mmol) in MeOH (2 ml) was hydrogenated at atmospheric pressure over Pd-$BaSO_4$ (10 mg). After stirring overnight at room temperature, the solution was filtered and the solvent removed in vacuo. The crude materials were purified by thin-layer chromatography using alumina gel (hexane:AcOEt = 9:1) to yield 41.8 mg (80%) of the title compound as a colorless oil. IR (neat) 1460, 1375 cm^{-1}; ^1H NMR δ = 0.84 (3H, t, J = 6.9 Hz), 1.07 (3H, d, J = 6.3 Hz), 1.15-1.30 (11H, m), 1.30-1.53 (5H, m), 1.85-1.97 (4H, m), 2.58 (1H, ddt, J = 6.6, 6.6, 6.6 Hz), 2.73 (1H, ddq, J = 6.2, 6.2, 6.2, 6.2 Hz), 3.56 (1H, dddd, J = 6.9, 6.9, 6.9, 6.9 Hz); ^{13}C NMR δ = 14.1, 21.3, 22.6, 27.2, 29.3, 29.8, 31.5, 31.8, 31.9, 32.3, 34.3, 37.3, 61.9, 65.1, 66.9. HRMS Found: m/z 222.2238. Calcd. for $C_{15}H_{29}N$-H M-H, 222.2222. HRMS Found: m/z 223.2264. Calcd. for $C_{15}H_{29}N$ M, 223.2300. The spectral data of **7** were in good agreement with those of the literature.[7,8]

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