Regioselective Synthesis of Quinolin-8-ols and 1,2,3,4-Tetrahydroquinolin-8-ols by the Cyclization of 2-(3-Hydroxyphenyl)ethyl Ketone *O*-2,4-Dinitrophenyloximes

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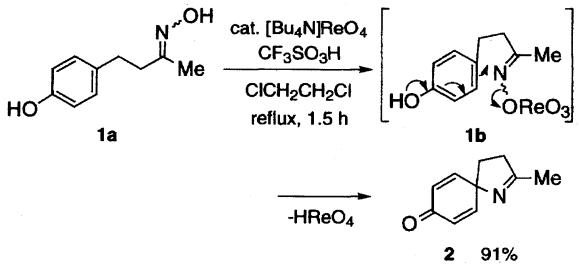
Cyclization of 2-(3-hydroxyphenyl)ethyl ketone *O*-2,4-dinitrophenyloximes proceeds on the oxime nitrogen atom by the treatment with NaH and then with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and acetic acid to yield quinolin-8-ols regioselectively. The reaction in the presence of $Na[BH_3(CN)]$ affords 1,2,3,4-tetrahydroquinolin-8-ols. The present cyclization proceeds via alkylideneaminyl radical intermediates generated by the single electron transfer between 3-hydroxyphenyl and 2,4-dinitrophenyl moieties.

The Beckmann rearrangement is one of the well-known reactions of oxime derivatives,[1] and the resulting *N*-substituted nitrilium ions have been widely utilized as synthetic intermediates for the preparation of nitrogen-containing heterocycles,[2—4] whereas only several examples have been reported for the substitution type reaction on sp^2 nitrogen atom of oximes.[3—8] Though, in some of them, nitrogen–carbon bond formation is realized, these reactions have not been well generalized as synthetic tools.[4—6]

Recently, we have reported that quinolines and azaspirotrienones can be synthesized by the cyclization of phenethyl ketone oximes by the use of a catalytic amount of tetrabutylammonium perrhenate ($[Bu_4N]ReO_4$) and trifluoromethanesulfonic acid (CF_3SO_3H).[9] For example, 4-(4-hydroxyphenyl)butan-2-one oxime (**1a**) cyclized, giving an 1-azaspirotrienone **2** in 91% yield without a Beckmann rearrangement product as shown in Eq. 1. In this reaction, the oxime **1a** is thought to be converted to a perrhenic acid ester **1b** and a nucleophilic attack of the phenyl group occurs on the sp^2 nitrogen atom. Recent ab initio MP2 calculations revealed that the intramolecular cyclization reaction of the protonated 2-(4-hydroxyphenyl)ethyl ketone oxime **1a** to the 1-azaspirotrienone **2** proceeds via S_N2 reaction on sp^2 nitrogen atom with an activation energy comparable to that of the Beckmann rearrangement.[10]

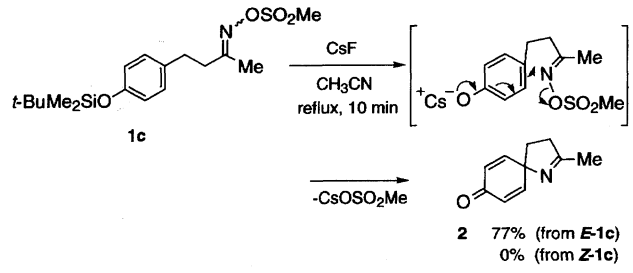


(1)

Further investigations toward the cyclization of phenethyl ketone oximes realized the regioselective synthesis of quinolin-8-ols and 1,2,3,4-tetrahydroquinolin-8-ols from 2-(3-hydroxyphenyl)ethyl ketone *O*-2,4-dinitrophenyloximes, and the preliminary results have been reported briefly.[11] In this paper, full accounts of this cyclization reaction will be discussed with the mechanistic study.

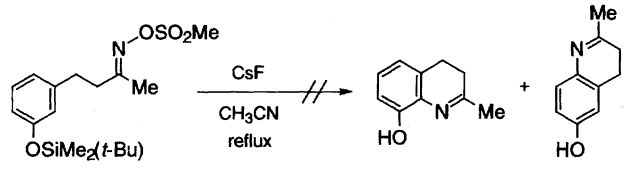
Results and Discussion

Synthesis of Quinolin-8-ol Derivatives. As described in Eq. 1, transformation of the 2-(4-hydroxyphenyl)ethyl ketone oxime **1a** to the 1-azaspirotrienone **2** proceeded under the rhenium-catalyzed acidic conditions. A similar cyclization was also observed by employing an *O*-methylsulfonyloxime. That is, when (*E*)-4-(4-*t*-butyldimethylsiloxyphenyl)butan-2-one *O*-methylsulfonyloxime (***E*-1c**) was treated with cesium fluoride in refluxing acetonitrile, the spiro compound **2** was obtained in 77% yield, while the *Z*-isomer ***Z*-1c** did not give the spiro compound **2** (Eq. 2).



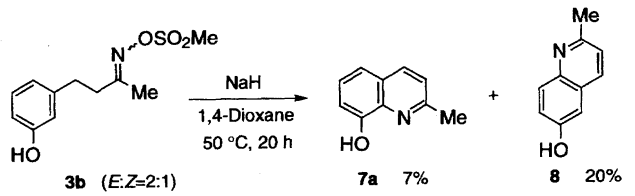
(2)

Although the above method was expected to promote the cyclization of the *meta*-siloxy isomer of **1c**, (*E*)-4-(3-*t*-butyldimethylsiloxyphenyl)butan-2-one *O*-methylsulfonyloxime (***E*-3a**), to give 3,4-dihydro-2-methylquinolin-8-ol (**4**) and the 6-hydroxy isomer **5** (Eq. 3), the reaction did not occur and only the desilylated compound **3b** was given under the above reaction conditions.



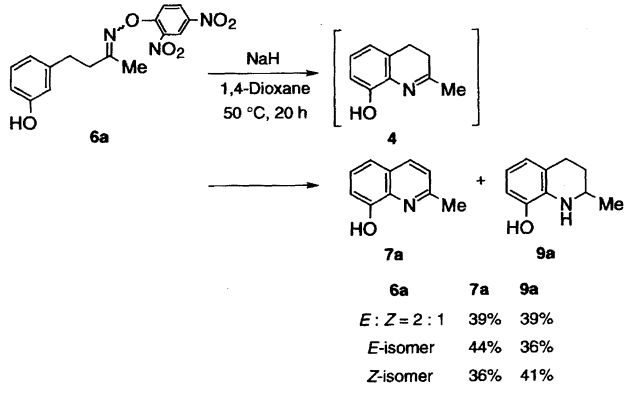
(3)

In order to achieve the cyclization of 2-(3-hydroxyphenyl)-ethyl ketone oximes, various *O*-substituted oxime derivatives such as *O*-methylsulfonyl, *O*-2-chlorobenzoyl, *O*-2,6-dichlorobenzoyl, and *O*-2,4-dinitrophenyl oximes, **3b**, **3c**, **3d**, and **6a**, were treated with NaH in 1,4-dioxane. Neither **3c** nor **3d** cyclized, while the *O*-methylsulfonyloxime **3b** cyclized but in low yields to 2-methylquinolin-6- and -8-ols (**7a** and **8**), which were air-oxidized products of the initially formed 3,4-dihydroquinolines **4** and **5** (Eq. 4).



(4)

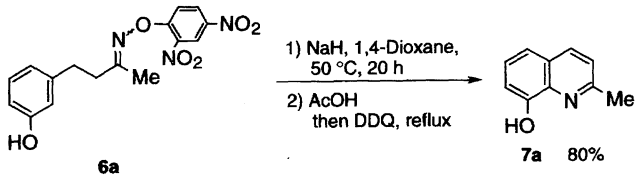
The quinoline **7a** and the 1,2,3,4-tetrahydroquinoline **9a**, which were disproportionated products from the 3,4-dihydroquinoline **4**, were obtained in good yield, when the *O*-2,4-dinitrophenyloxime **6a** was treated with NaH in 1,4-dioxane at 50 °C.[12] In this reaction, the quinolin-8-ol derivatives **7a** and **9a** were obtained regioselectively and the 6-hydroxy isomer **8**, which was the major product in the cyclization of the *O*-methylsulfonyloxime **3b** (Eq. 4), was not detected at all. Interestingly, both of the *E* and *Z*-isomers cyclized to give the quinolines **7a** and **9a** in almost the same yield. Monitoring the progress of each reaction of *E*-**6a** and *Z*-**6a** by ^{1}H NMR spectroscopy suggested that each reaction proceeded with almost the same reaction rate (Eq. 5).



6a	7a	9a
E : *Z* = 2 : 1	39%	39%
E-isomer	44%	36%
Z-isomer	36%	41%

(5)

In order to obtain the quinoline **7a** as a sole product, transformation of the 1,2,3,4-tetrahydroquinoline **9a** to **7a** was examined, and the 1,2,3,4-tetrahydroquinoline **9a** was found to be oxidized quantitatively to **7a** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). Accordingly, a one-pot synthesis of the quinoline **7a** was realized as follows: After the reaction of **6a** with NaH in 1,4-dioxane, excess NaH was quenched with acetic acid. Successive treatment of the reaction mixture with a 0.5 molar amount of DDQ gave the quinoline **7a** in 80% yield from **6a** without a detectable amount of the 1,2,3,4-tetrahydroquinoline **9a** (Eq. 6).[13]



(6)

As listed in Table 1, by applying this one-pot procedure, various *O*-2,4-dinitrophenyloximes of 2-(3-hydroxyphenyl)ethyl ketones **6b**—**g** cyclized to provide quinolin-8-ols **7b**—**g** in moderate to good yield. It is noteworthy that, in all cases, none of the regioisomers such as quinolin-8-ols nor the Beckmann rearrangement products could be detected at all. The stereochemistry of oximes exhibited no influence on the product yield in the same manner as Eq. 5: That is, both of the *E*-isomer of **6a** and a 2 : 1 mixture of the *E* and *Z*-isomers were converted to the cyclized product **7a** in the same yield (80%) (Entries 1 and 2). Accordingly, separation of stereoisomers of oximes is not required from the synthetic point of view. An alkenyl quinoline **7d** was prepared in 60% yield (Entry 5). The reaction of a 2-(3-hydroxyphenyl)propyl ketone oxime **6e** gave a 2,4-disubstituted quinoline **7e** in 74% yield (Entry 6). Though it has been known that the Beckmann rearrangement readily proceeds in case of the reaction of α-substituted phenethyl ketone oxime such as 4-(3,4-methylenedioxyphenyl)-3-methylbutan-2-one oxime,[9a,9c] a 3-substituted quinoline **7f** was obtained in 72% yield from an α-substituted *O*-2,4-dinitrophenyloxime **6f** without the Beckmann rearrangement (Entry 7). The reaction of an oxime **6g** having bromo substituent gave 5-bromo-2-methylquinolin-8-ol (**7g**) in 90% yield (Entry 8).

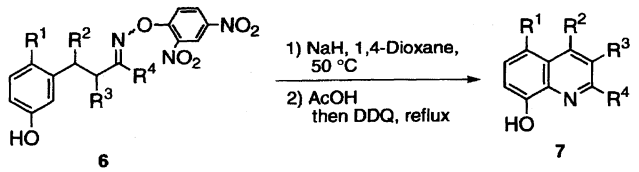


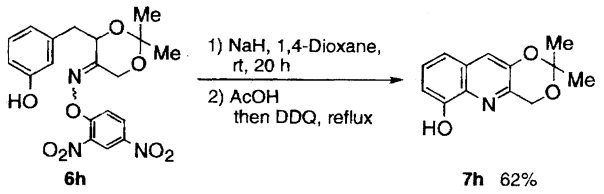
Table 1. Preparation of Quinolines **7** from *O*-2,4-Dinitrophenyloximes **6**

Entry	Oxime **6**	R^1	R^2	R^3	R^4	Yield/%	
1	**6a**[a]	H	H	H	Me	**7a**	80
2	**6a**[b]	H	H	H	Me	**7a**	80
3	**6b**[c]	H	H	H	Et	**7b**	75
4	**6c**[b]	H	H	H	*i*-Pr	**7c**	84
5	**6d**[c]	H	H	H	CH=CHPh	**7d**	60
6	**6e**[b]	H	Me	H	Me	**7e**	74
7	**6f**[b]	H	H	Me	Et	**7f**	72
8	**6g**[b]	Br	H	H	Me	**7g**	90

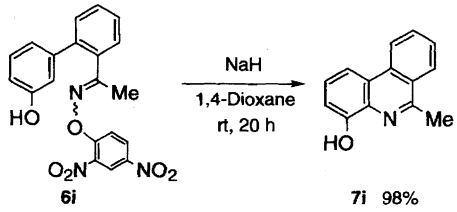
a) *E*-Isomer was employed. b) A mixture of *E* and *Z*-isomers of **6** (*E* : *Z* = 2 : 1) was employed. c) A mixture of *E* and *Z*-isomers of **6** (*E* : *Z* = 1 : 1) was employed.

Various *O*-2,4-dinitrophenyloximes derived from ketones are thus smoothly cyclized to quinolines, however, the reaction of an aldoxime, 3-(3-hydroxyphenyl)propanal *O*-2,4-dinitrophenyloxime, gave 3-(3-hydroxyphenyl)propiononitrile by the Beckmann fragmentation reaction.

Tricyclic derivatives were constructed regioselectively by the present method. An *O*-2,4-dinitrophenyloxime of 1,3-dioxan-5-one **6h** was converted to a 4*H*-1,3-dioxino[5,4-*b*]quinoline **7h** in 62% yield (Eq. 7). Phenanthridin-4-ol **7i** was also prepared in 98% yield by treating an acetophenone oxime derivative **6i** with NaH at room temperature (Eq. 8). Though the Beckmann rearrangement of aryl ketone oxime derivatives is generally a facile reaction, no Beckmann rearrangement product was formed in this reaction.



6h **7h** 62% (7)

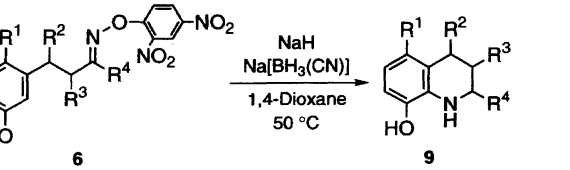


6i **7i** 98% (8)

Synthesis of 1,2,3,4-Tetrahydroquinolin-8-ol Derivatives. In the cyclization reaction of 4-(3-hydroxyphenyl)-butan-2-one *O*-2,4-dinitrophenyloxime (**6a**), the 3,4-dihydroquinoline **4** was generated as the preliminary product (Eq. 5). If this 3,4-dihydroquinoline **4** could be reduced prior to the disproportionation, the 1,2,3,4-tetrahydroquinoline **9a** would be provided. Thus, the cyclization of **6a** was attempted in the coexistence of a reducing reagent. Among several reducing reagents examined, sodium cyanoborohydride (Na[BH_3(CN)]) was found to be a suitable one. By the use of sodium borohydride, zinc borohydride, sodium triacetoxyborohydride, lithium tri-*t*-butoxyaluminum hydride as reducing reagents, the 1,2,3,4-tetrahydroquinoline **9a** was obtained in less than 30% yield. When the oxime **6a** was treated with NaH and Na[BH_3(CN)] in 1,4-dioxane at 50 °C, the 2-methyl-1,2,3,4-tetrahydroquinolin-8-ol (**9a**) was obtained in 78% yield without forming the quinoline **7a** and the Beckmann rearrangement product (Table 2, Entry 1).

The results of this reductive cyclization of several 2-(3-hydroxyphenyl)ethyl ketone *O*-2,4-dinitrophenyloxime derivatives **6** are listed in Table 2. In all reactions, 1,2,3,4-tetrahydroquinolin-8-ol derivatives **9** were obtained regioselectively without forming quinolines.

This cyclization reaction was successfully applied as follows to prepare tricyclic derivatives. *cis*-2-(3-Hydroxyphenyl)cyclohexyl methyl ketone *O*-2,4-dinitrophenyloxime **6j** cyclized at room temperature within 5 h to afford an octahydrophenanthridine **9j** in 86% yield without forming a stereoisomer (Eq. 9). The reaction of the corresponding *trans*-substituted cyclohexyl derivative **6k** proceeded more slowly (17 h at room temperature) as compared to that of the *cis*-isomer **6j**, giving a phenanthridine derivative **9k** in 52% yield with an aromatized product **7k** in 12% yield (Eq. 10).

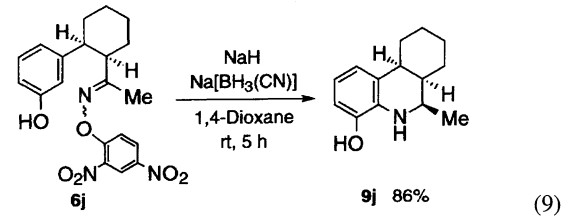


6 **9**

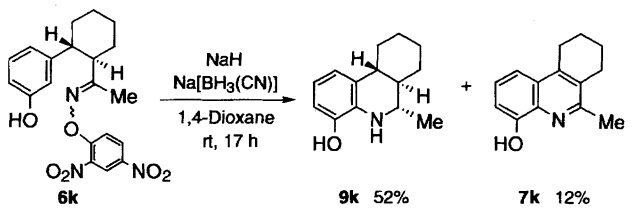
Table 2. Preparation of 1,2,3,4-Tetrahydroquinolines **9** from *O*-2,4-Dinitrophenyloximes **6**

Entry	Oxime **6**[b]	R^1	R^2	R^3	R^4	Yield/%	
1	**6a**	H	H	H	Me	**9a**	78
2	**6c**	H	H	H	*i*-Pr	**9c**	83
3	**6d**	H	H	H	CH=CHPh	**9d**	64
4[a]	**6e**	H	Me	H	Me	**9e**	83[d]
5[a]	**6f**	H	H	Me	Et	**9f**	71[e]
6	**6f**[c]	H	H	Me	Et	**9f**	70[e]
7	**6g**	Br	H	H	Me	**9g**	92

a) Reactions were carried out at room temperature. b) *E*-isomer was employed unless otherwise noted. c) A mixture of *E* and *Z*-isomers of **6** (*E*:*Z* = 2:1) was employed. d) *cis*:*trans* = 5:1. e) Diastereomer ratio = 1.8:1

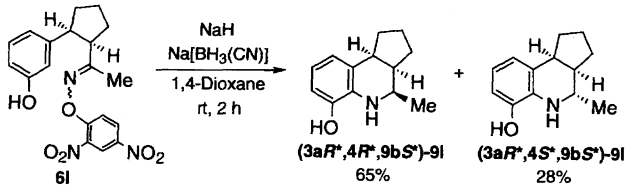


6j **9j** 86% (9)



6k **9k** 52% **7k** 12% (10)

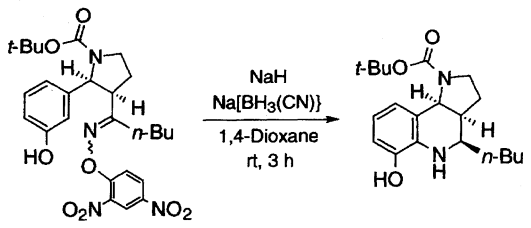
In addition, by the cyclization of a cyclopentyl ketone *O*-2,4-dinitrophenyloxime **6l**, hexahydrocyclopenta[*c*]quinolines (**3a***R**,**4***R**,**9b***S**)-**9l** and (**3a***R**,**4***S**,**9b***S**)-**9l** were afforded in a 93% total yield in a 2.3:1 diastereomer ratio (Eq. 11).



6l (**3a***R**,**4***R**,**9b***S**)-**9l** 65% (**3a***R**,**4***S**,**9b***S**)-**9l** 28% (11)

A hexahydropyrroloquinoline was synthesized by the cyclization of an *O*-2,4-dinitrophenyloxime having 2,3-*cis*-disubstituted pyrrolidine moiety **6m**, yielding a hexahydropyrrolo[3,2-*c*]quinoline **9m** in 93% yield as a single

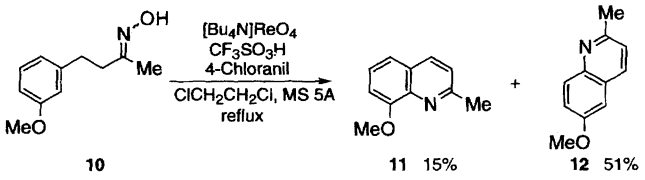
diastereoisomer (Eq. 12).



6m **9m** 93% (12)

The Reaction Mechanism. As mentioned in the introduction, the cyclization of phenethyl ketone oximes with $[Bu_4N]ReO_4$ and CF_3SO_3H is supposed to proceed by the intramolecular S_N2 substitution on sp^2 nitrogen atom of oximes. The present cyclization reaction, however, is not well elucidated by S_N2 mechanism due to the following phenomena.

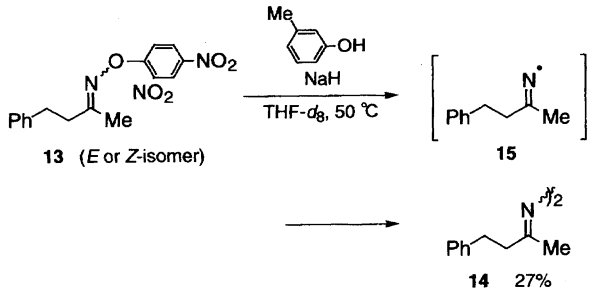
As reported previously, the $[Bu_4N]ReO_4$ and CF_3SO_3H catalyzed reaction of 4-(3-methoxyphenyl)butan-2-one oxime (**10**) gave two regioisomers, 8-methoxy- and 6-methoxy-2-methylquinolines (**11** and **12**) (Eq. 13),[9a,9c] whereas the present cyclization of the *O*-2,4-dinitrophenyloxime **6a** afforded the quinolin-8-ol **7a** selectively without forming the 6-hydroxy isomer.



10 **11** 15% **12** 51% (13)

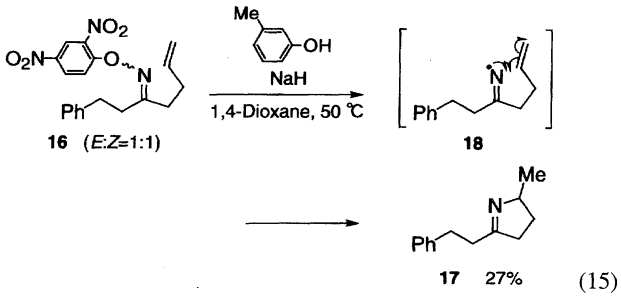
In the presence of CF_3SO_3H, the *E*/*Z* isomerization of oximes occurs so rapidly that both stereoisomers of **1a** smoothly cyclized by treatment with $[Bu_4N]ReO_4$ and CF_3SO_3H (Eq. 1).[9,10] In the reaction of 4-(4-*t*-butyldimethylsiloxyphenyl)butan-2-one *O*-methylsulfonyloxime (**1c**) with CsF, in which the *E*/*Z* isomerization of the oximes does not occur, the *E*-isomer ***E*-1c** was readily converted to **2**, while the *Z*-isomer did not cyclize to the azaspirotrienone **2** (Eq. 2). In contrast, both of the *E* and *Z*-isomers of *O*-2,4-dinitrophenyloxime **6a** cyclized by treating with NaH to give the quinolines **7a** and **9a** (Eq. 5).

Isomerization of the *O*-2,4-dinitrophenyloxime was examined by employing 4-phenylbutan-2-one *O*-2,4-dinitrophenyloxime (**13**), which has a phenyl group instead of a 3-hydroxyphenyl group to prevent the cyclization. The *E* or *Z*-isomer of **13**, *m*-cresol, and NaH was monitored by ^1H NMR spectroscopy. This experiment revealed that the isomerization of these oximes hardly occurred under the reaction conditions, but an unexpected product, 4-phenylbutan-2-one azine (**14**), was obtained in 27% yield. The formation of the azine **14** was thought to be formed by the dimerization of an alkylideneaminyl radical **15** (Eq. 14).[14]



13 (*E* or *Z*-isomer) **15** **14** 27% (14)

Generation of the aminyl radical **15** in the above experiment was confirmed by the intramolecular radical trap experiment. When 1-phenylhept-6-en-3-one *O*-2,4-dinitrophenyloxime (**16**), an oxime having an olefinic moiety, was treated with *m*-cresol and NaH, 2-methyl-5-(1-phenylethyl)-3,4-dihydro-2*H*-pyrrole (**17**), which is the cyclization product of an alkylideneaminyl radical **18**,[15] was obtained in 27% yield (Eq. 15).

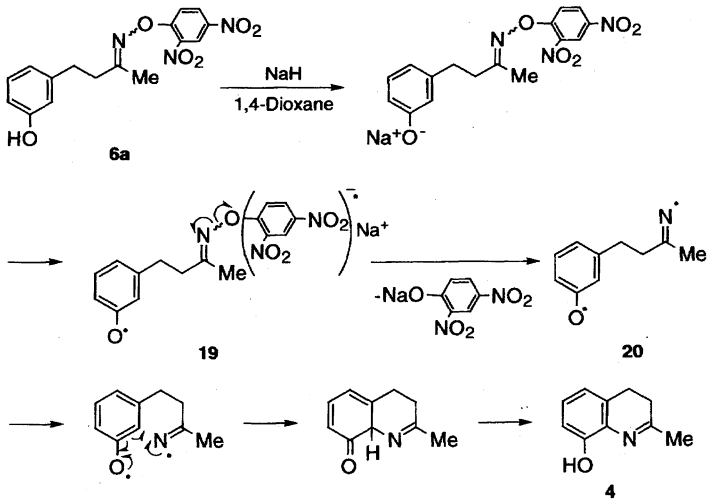


16 (*E*:*Z*=1:1) **18** **17** 27% (15)

Thus, it strongly suggested that the cyclization of 2-(3-hydroxyphenyl)ethyl ketone *O*-2,4-dinitrophenyloximes **6** does not proceed by S_N2 reaction on the sp^2 nitrogen atom but by radical coupling via alkylideneaminyl radical intermediates as shown in Scheme 1. Firstly, treatment of the oxime **6a** with NaH gives a sodium phenolate intermediate, in which intramolecular electron transfer occurs from the phenolate moiety to the dinitrophenyl group to generate an anion radical intermediate **19**. The nitrogen–oxygen bond of the oxime moiety cleaves to provide an alkylideneaminyl radical **20** and sodium 2,4-dinitrophenolate. The intramolecular coupling of the biradical intermediate **20** and the successive isomerization give the 3,4-dihydroquinolin-8-ol **4**.

Summary

Many synthetic methods have been developed for the preparation of quinolines[2a] and 1,2,3,4-tetrahydroquinolines[2a,16] due to the interesting biological properties of quinoline and tetrahydroquinoline alkaloids. Most of the synthetic methods are based on the derivation from aniline derivatives,[2a] and as for the synthesis of tetrahydroquinolines, reduction of the corresponding quinoline derivatives is mainly employed.[16] Only a few methods have been reported for the construction of quinoline and tetrahydroquinoline skeleton by the formation of N–C(8a) bond as a key step. For example, in the cases of quinoline synthesis, oxidative cyclization of 2-(3-aminopropyl)benzene-1,4-diol with $K_2[Fe(CN)_6]$[17] and alkylideneaminyl radical cyclization of



Scheme 1. The mechanism of the cyclization of dinitrophenyloxime **6a**.

(1,2,3,3-tetraphenylpropylideneaminooxy)acetic acid with $K_2S_2O_8$.[18] In the cases of tetrahydroquinoline synthesis, the electrophilic amination of *N*-acetoxy-3-phenylpropanamide with $FeCl_3$[19] and the aminyl radical cyclization of *N*-chloro-*N*-methyl-3-phenylpropylamine with $FeSO_4$ have been reported.[20] The present method would provide an efficient method for construction of quinoline framework by the formation of N–C(8a) bond starting from oxime derivatives. It is also noteworthy from a synthetic point of view that the present cyclization has a wide generality to prepare quinolin-8-ols and 1,2,3,4-tetrahydroquinolin-8-ols having various substituents.

Mechanistically, the reaction proceeds via alkylideneaminyl radical intermediates generated by single electron transfer between the two aryl moieties. Recently, alkylideneaminyl radicals have been utilized as reactive intermediates in organic synthesis.[14,21–23] For instance, the reaction of alkylideneaminooxyacetic acid with $K_2S_2O_8$,[18] and the cyclization of each of *O*-phenylselenomethyloxime, sulfenylimine, benzoyloxime, and 1*H*-benzotriazol-1-ylimine of 2-(prop-2-enyl)cyclohexanone is promoted by $(n\text{-Bu})_3SnH$, giving 3,3a,4,5,6,7-hexahydro-2-methyl-2*H*-indole.[21,22]

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) and preparative thin-layer chromatography was carried out using Wakogel B-5F. Dehydrated 1,4-dioxane was purchased from Kanto Chemical Co., Inc. and was used as freshly distilled from $LiAlH_4$ under an argon atmosphere. 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. DDQ was recrystallized from benzene and dried under reduced pressure. AcOH was purchased from Takahashi Pure Chemical Co. and used without purification. $Na[BH_3(CN)]$ was purchased from Kanto Chemical Co., Inc. and used without purification. *m*-Cresol was purified by distillation under reduced pressure. All reactions were carried out under an argon atmosphere unless otherwise noted.

Preparation of 2,4-Dinitrophenyloximes. Experimental procedures for the preparation of 4-(3-hydroxyphenyl)butan-2-one are shown below as a typical example for the synthesis of phenethyl ketone derivatives.

To an ethanol solution (100 ml) of 3-hydroxybenzaldehyde (17.0 g, 0.140 mol) and acetone (40.4 g, 0.696 mol) was added 10% aqueous sodium hydroxide (100 ml) at 0 °C. After the mixture was stirred for 2 h at 0 °C, the solution was neutralized by adding 1 mol dm^{-3} hydrochloric acid. The organic materials were extracted with ethyl acetate and the combined extracts were washed with brine and dried over $MgSO_4$. After the solvent was removed in vacuo, the crude materials were purified by flash column chromatography (hexane : ethyl acetate = 2 : 1) to give 4-(3-hydroxyphenyl)but-3-en-2-one (22.0 g, 97%). Under a hydrogen atmosphere, an ethanol (100 ml) solution of 4-(3-hydroxyphenyl)but-3-en-2-one (22.0 g, 0.136 mmol) was added to an ethanol suspension (50 ml) of 10% Pd/C. After the mixture was stirred at room tenperature for 1 h, the mixture was filtered through a short pad of Celite to remove Pd/C. After the solvent was removed in vacuo, the crude materials were purified by flash column chromatography (hexane : ethyl acetate = 3 : 1) to give 4-(3-hydroxyphenyl)butan-2-one (20.8 g, 95%).

4-(3-Hydroxyphenyl)butan-2-one was converted to the corresponding *O*-2,4-dinitrophenyloxime by the literature procedure.[24]

Spectral Data for 2,4-Dinitrophenyloximes of Phenethyl Ketone Derivatives. 4-(3-Hydroxyphenyl)butan-2-one (*E*)-*O*-2,4-Dinitrophenyloxime (*E*-6a): Yellow needles, Mp 110 °C (hexane–benzene); IR (KBr) 3487, 1606, 1523, 1342 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.17 (3H, s), 2.70 (2H, t, J = 7.7 Hz), 2.90 (2H, t, J = 7.7 Hz), 4.90 (1H, bs), 6.67—6.70 (2H, m), 6.74 (1H, d, J = 7.8 Hz), 7.16 (1H, t, J = 7.8 Hz), 7.75 (1H, d, J = 9.4 Hz), 8.35 (1H, dd, J = 2.7, 9.4 Hz), 8.84 (1H, d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 16.1, 31.8, 36.9, 113.2, 115.2, 117.3, 119.7, 121.9, 129.2, 129.5, 135.8, 140.3, 141.7, 156.6, 157.3, 166.5. Found: C, 55.36; H, 4.55; N, 12.13%. Calcd for $C_{16}H_{15}N_3O_6$: C, 55.65; H, 4.38; N, 12.17%.

4-(3-Hydroxyphenyl)butan-2-one (*Z*)-*O*-2,4-Dinitrophenyloxime (*Z*-6a): Yellow needles, Mp 118 °C (hexane–benzene); IR

(KBr) 3427, 1604, 1527, 1344 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.03 (3H, s), 2.85—2.87 (4H, m), 5.05 (1H, bs), 6.62 (1H, dd, J = 2.3, 7.6 Hz), 6.73 (1H, d, J = 2.3 Hz), 6.76 (1H, d, J = 7.6 Hz), 7.10 (1H, t, J = 7.6 Hz), 7.87 (1H, d, J = 9.4 Hz), 8.37 (1H, dd, J = 2.7, 9.4 Hz), 8.86 (1H, d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 20.1, 31.7, 33.1, 113.5, 115.3, 117.1, 120.7, 122.1, 129.3, 129.8, 135.8, 140.4, 141.8, 155.8, 157.4, 167.1. Found: C, 55.39; H, 4.64; N, 12.47%. Calcd for $C_{16}H_{15}N_3O_6$: C, 55.65; H, 4.38; N, 12.17%.

1-(3-Hydroxyphenyl)pentan-3-one (*E*)-*O*-2,4-Dinitrophenyloxime (*E*-6b): Yellow needles, Mp 70 °C (hexane–benzene); IR (KBr) 3282, 1606, 1529, 1348 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.19 (3H, t, J = 7.7 Hz), 2.59 (2H, q, J = 7.7 Hz), 2.70 (2H, t, J = 7.7 Hz), 2.91 (2H, t, J = 7.7 Hz), 4.97 (1H, bs), 6.68 (1H, dd, J = 2.3, 7.8 Hz), 6.71 (1H, d, J = 2.3 Hz), 6.78 (1H, d, J = 7.8 Hz), 7.16 (1H, d, J = 7.8 Hz), 7.74 (1H, d, J = 9.4 Hz), 8.35 (1H, dd, J = 2.8, 9.4 Hz), 8.84 (1H, d, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 10.3, 23.7, 31.7, 35.1, 113.8, 115.3, 117.3, 120.7, 122.0, 129.3, 129.8, 135.8, 140.5, 142.4, 155.8, 157.6, 170.7. Found: C, 56.87; H, 4.79; N, 11.76%. Calcd for $C_{17}H_{17}N_3O_6$: C, 56.82; H, 4.77; N, 11.69%.

1-(3-Hydroxyphenyl)pentan-3-one (*Z*)-*O*-2,4-Dinitrophenyloxime (*Z*-6b): Yellow needles, Mp 130 °C (hexane–benzene); IR (KBr) 3479, 1604, 1527, 1344 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.19 (3H, t, J = 7.4 Hz), 2.37 (2H, q, J = 7.4 Hz), 2.78—2.87 (4H, m), 5.34 (1H, bs), 6.63 (1H, dd, J = 2.2, 7.8 Hz), 6.75 (1H, d, J = 2.2 Hz), 6.77 (1H, d, J = 7.8 Hz), 7.11 (1H, d, J = 7.8 Hz), 7.89 (1H, d, J = 9.4 Hz), 8.37 (1H, dd, J = 2.7, 9.4 Hz), 8.86 (1H, d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 10.3, 28.0, 32.0, 32.2, 113.5, 115.3, 117.2, 120.7, 122.1, 129.4, 129.8, 135.7, 140.4, 141.9, 155.8, 157.6, 170.5. Found: C, 57.11; H, 4.94; N, 11.75%. Calcd for $C_{17}H_{17}N_3O_6$: C, 56.82; H, 4.77; N, 11.69%.

1-(3-Hydroxyphenyl)-4-methylpentan-3-one (*E*)-*O*-2,4-Dinitrophenyloxime (*E*-6c): Yellow needles, Mp 138 °C (hexane–benzene); IR (KBr) 3478, 1604, 1527, 1344 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.12 (6H, d, J = 6.9 Hz), 2.65 (1H, sept, J = 6.9 Hz), 2.76 (2H, t, J = 8.0 Hz), 2.86 (2H, t, J = 8.0 Hz), 5.40 (1H, bs), 6.65 (1H, dd, J = 2.2, 7.7 Hz), 6.78 (1H, d, J = 2.2 Hz), 6.79 (1H, d, J = 7.7 Hz), 7.12 (1H, d, J = 7.7 Hz), 7.90 (1H, d, J = 9.4 Hz), 8.38 (1H, dd, J = 2.8, 9.4 Hz), 8.87 (1H, d, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 19.8, 31.3, 32.3, 34.5, 113.5, 115.3, 117.3, 120.8, 122.1, 129.4, 129.8, 135.7, 140.4, 142.3, 155.8, 157.7, 173.3. Found: C, 57.80; H, 5.18; N, 11.25%. Calcd for $C_{18}H_{19}N_3O_6$: C, 57.91; H, 5.13; N, 11.25%.

1-(3-Hydroxyphenyl)-4-methylpentan-3-one (*Z*)-*O*-2,4-Dinitrophenyloxime (*Z*-6c): Yellow needles, Mp 95 °C (hexane–benzene); IR (KBr) 3440, 1606, 1525, 1344 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.16 (6H, d, J = 7.0 Hz), 2.67 (2H, t, J = 7.7 Hz), 2.93 (2H, t, J = 7.7 Hz), 3.57 (1H, sept, J = 7.0 Hz), 4.97 (1H, bs), 6.68 (1H, dd, J = 2.5, 7.8 Hz), 6.72 (1H, d, J = 2.5 Hz), 6.80 (1H, d, J = 7.8 Hz), 7.17 (1H, d, J = 7.8 Hz), 7.75 (1H, d, J = 9.4 Hz), 8.36 (1H, dd, J = 2.8, 9.4 Hz), 8.84 (1H, d, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 19.0, 29.1, 31.5, 31.7, 113.2, 115.3, 117.3, 120.7, 122.0, 129.3, 129.8, 135.9, 140.5, 142.9, 155.8, 157.6, 173.1. Found: C, 57.72; H, 5.09; N, 11.27%. Calcd for $C_{18}H_{19}N_3O_6$: C, 57.91; H, 5.13; N, 11.25%.

5-(3-Hydroxyphenyl)-1-phenylpent-1-en-3-one (*E*)-*O*-2,4-Dinitrophenyloxime (*E*-6d): Yellow needles, Mp 168 °C (hexane–benzene); IR (KBr) 3390, 1604, 1527, 1340 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.89—2.92 (4H, m), 6.60 (1H, dd, J = 1.5, 8.0 Hz), 6.65 (1H, d, J = 1.5 Hz), 6.66 (1H, d, J = 8.0 Hz), 7.05 (1H, t, J = 8.0 Hz), 7.10 (1H, d, J = 16.7 Hz), 7.28—7.33 (3H, m), 7.49—7.51 (2H, m), 7.57 (1H, d, J = 16.7 Hz), 7.71 (1H, d, J = 9.4 Hz), 8.30 (1H, dd, J = 2.8, 9.4 Hz), 8.81 (1H, d, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 31.9, 33.1, 113.2, 115.3, 115.7, 117.2, 119.7, 122.1, 127.9, 128.2, 128.9, 129.5, 130.2, 135.1, 135.5, 140.4, 140.5, 142.2, 156.9, 157.4, 162.3. Found: C, 63.80; H, 4.65; N, 9.38%. Calcd for $C_{23}H_{19}N_3O_6$: C, 63.74; H, 4.42; N, 9.70%.

5-(3-Hydroxyphenyl)-1-phenylpent-1-en-3-one (*Z*)-*O*-2,4-Dinitrophenyloxime (*Z*-6d): Yellow needles, Mp 150 °C (hexane–benzene); IR (KBr) 3465, 1604, 1527, 1344 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.81 (2H, t, J = 8.0 Hz), 3.05 (2H, t, J = 8.0 Hz), 6.52 (1H, dd, J = 1.5, 7.8 Hz), 6.69 (1H, d, J = 1.5 Hz), 6.70 (1H, d, J = 7.8 Hz), 6.78 (1H, d, J = 16.5 Hz), 7.01 (1H, t, J = 7.8 Hz), 7.08 (1H, d, J = 16.5 Hz), 7.25—7.34 (3H, m), 7.42—7.45 (2H, m), 7.89 (1H, d, J = 9.4 Hz), 8.35 (1H, dd, J = 2.7, 9.4 Hz), 8.83 (1H, d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 28.7, 33.1, 113.3, 115.3, 117.2, 119.9, 121.7, 122.1, 127.3, 128.9, 129.4, 129.5, 129.6, 135.3, 135.7, 138.3, 140.7, 141.8, 156.8, 157.2, 166.2. Found: C, 63.40; H, 4.50; N, 9.57%. Calcd for $C_{23}H_{19}N_3O_6$: C, 63.74; H, 4.42; N, 9.70%.

4-(3-Hydroxyphenyl)pentan-2-one *O*-2,4-Dinitrophenyloxime (6e): $E:Z$ = 2 : 1 mixture; Yellow needles, Mp 105 °C (hexane–benzene); IR (KBr) 3579, 1608, 1525, 1342 cm^{-1}; ^1H NMR ($CDCl_3$) *E*-isomer: δ = 1.30—1.32 (3H, m), 2.09 (3H, s), 2.58—2.63 (1H, m), 2.65—2.70 (1H, m), 3.07—3.14 (1H, m), 4.85 (1H, bs), 6.67 (1H, dd, J = 2.0, 7.8 Hz), 6.71 (1H, d, J = 2.0 Hz), 6.79 (1H, d, J = 7.8 Hz), 7.16 (1H, t, J = 7.8 Hz), 7.61 (1H, d, J = 9.4 Hz), 8.32 (1H, dd, J = 2.6, 9.4 Hz), 8.82 (1H, d, J = 2.6 Hz); *Z*-isomer: δ = 1.33—1.35 (3H, m), 1.88 (3H, s), 2.78—2.82 (1H, m), 2.86—2.90 (1H, m), 3.10—3.17 (1H, m), 4.78 (1H, bs), 6.60 (1H, dd, J = 2.4, 7.8 Hz), 6.71 (1H, d, J = 2.4 Hz), 6.77 (1H, d, J = 7.8 Hz), 7.09 (1H, t, J = 7.8 Hz), 7.82 (1H, d, J = 9.4 Hz), 8.36 (1H, dd, J = 2.7, 9.4 Hz), 8.87 (1H, d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) *E*-isomer: δ = 16.2, 22.1, 37.0, 43.5, 113.5, 113.8, 117.4, 119.3, 122.0, 129.4, 129.8, 135.7, 140.3, 147.4, 155.8, 157.5, 166.2; *Z*-isomer: δ = 20.4, 21.9, 37.3, 39.7, 113.6, 113.7, 117.1, 119.3, 122.1, 129.4, 129.7, 135.6, 140.4, 146.8, 155.7, 157.4, 166.8. Found: C, 56.57; H, 4.72; N, 11.67%. Calcd for $C_{17}H_{17}N_3O_6$: C, 56.82; H, 4.77; N, 11.69%.

1-(3-Hydroxyphenyl)-2-methylpentan-3-one *O*-2,4-Dinitrophenyloxime (6f): $E:Z$ = 1 : 1 mixture; Yellow needles, Mp 132 °C (hexane–benzene); IR (KBr) 3496, 1603, 1520, 1345 cm^{-1}; ^1H NMR ($CDCl_3$) *E*-isomer: δ = 1.18—1.22 (6H, m), 2.46—2.57 (2H, m), 2.66—2.70 (1H, m), 2.84—2.89 (1H, m), 2.92—2.97 (1H, m), 4.92 (1H, bs), 6.66—6.69 (2H, m), 6.73 (1H, d, J = 7.6 Hz), 7.14 (1H, t, J = 7.6 Hz), 7.69 (1H, d, J = 9.4 Hz), 8.34 (1H, dd, J = 2.6, 9.4 Hz), 8.84 (1H, d, J = 2.6 Hz); *Z*-isomer: δ = 1.15—1.29 (6H, m), 2.30—2.44 (2H, m), 2.69—2.74 (1H, m), 2.77—2.82 (1H, m), 3.71—3.79 (1H, m), 4.92 (1H, bs), 6.58 (1H, dd, J = 2.0, 7.6 Hz), 6.67 (1H, d, J = 2.0 Hz), 6.71 (1H, d, J = 7.6 Hz), 7.06 (1H, t, J = 7.6 Hz), 7.82 (1H, d, J = 9.4 Hz), 8.36 (1H, dd, J = 2.7, 9.4 Hz), 8.85 (1H, d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) *E*-isomer: δ = 10.7, 17.7, 22.5, 40.1, 40.9, 113.4, 115.9, 117.3, 121.4, 122.0, 129.3, 129.6, 135.9, 140.4, 141.2, 155.7, 157.7, 174.3; *Z*-isomer: δ = 10.1, 16.4, 24.5, 36.3, 39.5, 113.4, 115.7, 117.1, 121.4, 121.9, 128.3, 129.3, 129.6, 136.0, 140.5, 155.6, 157.6, 173.2. Found: C, 58.04; H, 5.04; N, 10.95%. Calcd for $C_{18}H_{19}N_3O_6$: C, 57.91; H, 5.13; N, 11.25%.

4-(2-Bromo-5-hydroxyphenyl)butan-2-one (*E*)-*O*-2,4-Dinitrophenyloxime (*E*-6g): Yellow needles, Mp 146 °C (hexane–benzene); IR (KBr) 3566, 1604, 1523, 1344 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.21 (3H, s), 2.69 (2H, t, J = 7.8 Hz), 2.99 (2H, t, J = 7.8 Hz), 4.82 (1H, bs), 6.60 (1H, dd, J = 2.9, 9.6 Hz), 6.75 (1H, d, J = 2.9 Hz), 7.38 (1H, d, J = 9.6 Hz), 7.83 (1H, d, J = 9.4 Hz), 8.38 (1H, dd, J = 2.7, 9.4 Hz), 8.86 (1H, d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 16.4, 32.8, 35.6, 114.7, 115.5, 117.3, 122.0, 129.2, 129.3, 133.8, 136.2, 140.7, 140.8, 155.1, 157.4, 166.1. Found: C,

45.32; H, 3.44; Br, 18.78; N, 9.96%. Calcd for $C_{13}H_{14}BrN_3O_6$: C, 45.30; H, 3.33; Br, 18.84; N, 9.91%.

4-(2-Bromo-5-hydroxyphenyl)butan-2-one (*Z*)-*O*-2,4-Dinitrophenyloxime (*Z*-6g): Yellow needles, Mp 164 °C (hexane–benzene); IR (KBr) 3461, 1604, 1522, 1340 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.10 (3H, s), 2.83 (2H, t, J = 8.0 Hz), 2.97 (2H, t, J = 8.0 Hz), 5.25 (1H, bs), 6.56 (1H, dd, J = 3.0, 8.5 Hz), 6.86 (1H, d, J = 3.0 Hz), 7.32 (1H, d, J = 8.5 Hz), 7.91 (1H, d, J = 9.4 Hz), 8.40 (1H, dd, J = 2.8, 9.4 Hz), 8.88 (1H, d, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 20.0, 31.4, 32.0, 113.0, 115.5, 117.2, 117.3, 122.0, 129.4, 133.3, 135.4, 140.0, 140.4, 156.5, 157.4, 167.1. Found: C, 45.42; H, 3.42; Br, 18.77; N, 9.92%. Calcd for $C_{16}H_{14}BrN_3O_6$: C, 45.30; H, 3.33; Br, 18.84; N, 9.91%.

4-(3-Hydroxyphenyl)methyl-2,2-dimethyl-1,3-dioxan-5-one (*E*)-*O*-2,4-Dinitrophenyloxime (*E*-6h): Yellow needles, Mp 140 °C (hexane–benzene); IR (KBr) 3456, 1604, 1531, 1346, 1223 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.33 (3H, s), 1.40 (3H, s), 2.94 (1H, dd, J = 8.4, 14.6 Hz), 3.28 (1H, dd, J = 4.0, 14.6 Hz), 4.62 (1H, dd, J = 1.5, 18.0 Hz), 4.74 (1H, ddd, J = 1.5, 4.0, 8.4 Hz), 4.89 (1H, d, J = 18.0 Hz), 4.90 (1H, bs), 6.70 (1H, dd, J = 2.2, 7.8 Hz), 6.80 (1H, d, J = 2.2 Hz), 6.87 (1H, d, J = 7.8 Hz), 7.17 (1H, t, J = 7.8 Hz), 7.77 (1H, d, J = 9.3 Hz), 8.40 (1H, dd, J = 2.8, 9.3 Hz), 8.87 (1H, d, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 24.0, 24.1, 36.3, 58.6, 69.4, 101.5, 113.5, 116.3, 117.1, 121.7, 122.1, 128.3, 129.4, 129.5, 139.2, 141.1, 155.5, 156.9, 167.8. Found: C, 54.78; H, 4.61; N, 10.01%. Calcd for $C_{20}H_{15}N_3O_6$: C, 54.68; H, 4.59; N, 10.07%.

1-[2-(3-Hydroxyphenyl)phenyl]ethan-1-one (*E*)-*O*-2,4-Dinitrophenyloxime (*E*-6i): Yellow needles, Mp 170 °C (hexane–benzene); IR (KBr) 3502, 1601, 1529, 1344, 1315 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.11 (3H, s), 4.95 (1H, bs), 6.82 (1H, dd, J = 2.8, 7.8 Hz), 6.85 (1H, d, J = 2.8 Hz), 6.90 (1H, d, J = 7.8 Hz), 7.26 (1H, t, J = 7.8 Hz), 7.41—7.45 (2H, m), 7.48—7.54 (2H, m), 7.67 (1H, d, J = 9.4 Hz), 8.34 (1H, dd, J = 2.8, 9.4 Hz), 8.86 (1H, d, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 18.1, 114.5, 115.8, 117.5, 120.4, 121.9, 127.4, 129.1, 129.3, 129.7, 130.1, 130.6, 134.0, 135.9, 140.6, 141.1, 142.1, 157.0, 157.4, 167.1. Found: C, 60.79; H, 3.98; N, 10.71%. Calcd for $C_{20}H_{15}N_3O_6$: C, 61.07; H, 3.84; N, 10.68%.

(1*R,2*S**)-(±)-2-(3-Hydroxyphenyl)cyclohexyl Methyl Ketone (*E*)-*O*-2,4-Dinitrophenyloxime (*E*-6j):** Yellow oil; IR (KBr) 3523, 2937, 1531, 1346, 1284 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.54—1.80 (2H, m), 1.81 (3H, s), 1.84—1.89 (4H, m), 2.02—2.03 (1H, m), 2.04—2.16 (1H, m), 3.01—3.04 (2H, m), 6.76 (1H, s), 6.79 (1H, d, J = 7.8 Hz), 7.09 (1H, t, J = 7.7 Hz), 7.54 (1H, d, J = 9.3 Hz), 8.33 (1H, dd, J = 2.7, 9.3 Hz), 8.77 (1H, d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 17.7, 22.9, 25.1, 27.2, 28.4, 41.4, 47.6, 113.0, 114.6, 117.0, 117.5, 119.8, 121.9, 129.3, 129.8, 140.4, 146.0, 155.4, 157.5, 168.8. HRMS Found: *m/z* 400.1493. Calcd for $C_{20}H_{21}N_3O_6$: M, 400.1509.

(1*R,2*R**)-(±)-2-(3-Hydroxyphenyl)cyclohexyl Methyl Ketone (*E*)-*O*-2,4-Dinitrophenyloxime (*E*-6k):** Yellow oil; IR (KBr) 3460, 1604, 1531, 1344 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.41—1.52 (2H, m), 1.87—1.95 (2H, m), 1.97 (3H, s), 2.67—2.72 (2H, m), 4.73 (1H, bs), 6.60 (1H, dd, J = 2.55, 8.0 Hz), 6.66 (1H, s), 6.73 (1H, d, J = 7.7 Hz), 7.11 (1H, d, J = 7.8 Hz), 7.90 (1H, d, J = 9.4 Hz), 8.28 (1H, dd, J = 2.8, 9.4 Hz), 8.79 (1H, d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 13.7, 25.6, 26.8, 30.8, 34.3, 46.9, 49.3, 113.4, 114.2, 117.4, 119.8, 121.9, 129.2, 129.7, 140.3, 146.4, 150.2, 155.8, 157.4, 169.7. HRMS Found: *m/z* 400.1493. Calcd for $C_{20}H_{21}N_3O_6$: M, 400.1509.

(1*R,2*S**)-(±)-2-(3-Hydroxyphenyl)cyclopentyl Methyl Ketone (*E*)-*O*-2,4-Dinitrophenyloxime (*E*-6l):** Yellow oil; IR (KBr) 3426, 2952, 1604, 1529, 1346 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.74 (3H, s), 2.00—2.04 (4H, m), 2.12—2.19 (2H, m), 3.21 (1H, q, J = 7.8 Hz), 3.47 (1H, q, J = 7.7 Hz), 4.67 (1H, bs), 6.61 (1H, dd, J = 2.4, 7.9 Hz), 6.73 (1H, d, J = 7.7 Hz), 7.10 (1H, d, J = 7.9 Hz), 7.57 (1H, d, J = 9.3 Hz), 8.33 (1H, dd, J = 2.7, 9.4 Hz), 8.81 (1H, d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 14.1, 24.0, 28.6, 31.4, 48.3, 50.8, 113.3, 115.0, 117.4, 120.3, 121.9, 129.2, 129.4, 135.7, 140.2, 144.1, 155.7, 157.5, 168.7. HRMS Found: *m/z* 386.1335. Calcd for $C_{19}H_{19}N_3O_6$: M, 386.1352.

(2*R,3*S**)-(±)-1-*t*-Butoxycarbonyl-2-(3-hydroxyphenyl)-pyrrolidin-3-yl Butyl Ketone (*E*)-*O*-2,4-Dinitrophenyloxime (*E*-6m):** Yellow oil; IR (KBr) 2954, 1693, 1490, 1394 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.92 (3H, t, J = 7.3 Hz), 1.19 (9H, s), 1.36—1.40 (2H, m), 1.50—1.53 (2H, m), 2.02—2.07 (2H, m), 2.48—2.55 (2H, m), 3.88 (1H, t, J = 9.9 Hz), 5.05 (1H, J = 7.9 Hz), 6.57 (1H, d, J = 6.9 Hz), 6.62 (1H, s), 6.64 (1H, d, J = 8.2 Hz), 7.07 (1H, t, J = 7.7 Hz), 7.19 (1H, d, J = 7.7 Hz), 8.26 (1H, d, J = 6.8 Hz), 8.79 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 13.7, 20.2, 23.0, 28.2, 29.6, 29.7, 31.3, 45.6, 48.8, 63.4, 113.1, 114.6, 117.4, 118.9, 121.8, 129.2, 129.5, 135.8, 140.6, 142.3, 156.4, 157.2, 168.0. HRMS Found: *m/z* 529.2328. Calcd for $C_{26}H_{32}N_4O_8$: M, 529.2298.

4-Phenylbutan-2-one (*E*)-*O*-2,4-Dinitrophenyloxime (*E*-13): Yellow needles, Mp 79 °C (hexane–benzene); IR (KBr) 1606, 1522, 1342, 1261, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.18 (3H, s), 2.72 (2H, t, J = 7.8 Hz), 2.96 (2H, t, J = 7.8 Hz), 7.21—7.23 (3H, m), 7.29—7.33 (2H, m), 7.72 (1H, d, J = 9.4 Hz), 8.33 (1H, dd, J = 2.7, 9.4 Hz), 8.82 (1H, d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 16.3, 32.0, 37.2, 117.3, 122.0, 126.5, 128.3, 128.6, 129.3, 135.8, 140.2, 140.5, 157.4, 166.5. Found: C, 58.41; H, 4.61; N, 12.82%. Calcd for $C_{16}H_{15}N_3O_5$: C, 58.36; H, 4.59; N, 12.76%.

4-Phenylbutan-2-one (*Z*)-*O*-2,4-Dinitrophenyloxime (*Z*-13): Yellow needles, Mp 107 °C (hexane–benzene); IR (KBr) 1604, 1523, 1340, 1271, 1138 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.02 (3H, s), 2.87—2.93 (4H, m), 7.13—7.16 (1H, m), 7.22—7.25 (4H, m), 7.86 (1H, d, J = 9.3 Hz), 8.35 (1H, dd, J = 2.7, 9.3 Hz), 8.85 (1H, d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 20.1, 31.9, 33.2, 117.1, 122.0, 126.4, 128.4, 128.6, 129.3, 135.7, 139.9, 140.4, 157.4, 167.1. Found: C, 58.59; H, 4.71; N, 12.70%. Calcd for $C_{16}H_{15}N_3O_5$: C, 58.36; H, 4.59; N, 12.76%.

1-Phenylhept-6-en-3-one *O*-2,4-Dinitrophenyloxime (16): *E*:*Z* = 1:1 mixture; Yellow oil; IR (KBr) 1604, 1529, 1342, 1309, 1263 cm^{-1}; ^1H NMR ($CDCl_3$) *E*-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); *Z*-isomer: δ = 2.40—2.35 (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); ^{13}C NMR ($CDCl_3$) *E*-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; *Z*-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. 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%.

General Procedure for the Synthesis of Quinolines. (Table 2, Entry 1): To a 1,4-dioxane (5 ml) suspension of NaH (240.1 mg, 10.0 mmol) was added a 1,4-dioxane solution (15 ml) of 4-(3-hydroxyphenyl)butan-2-one *O*-2,4-dinitrophenyloxime (**6a**) (345.3 mg, 1.0 mmol) and the mixture was heated to 50 °C. After 20 h, the reaction mixture was acidified by AcOH (1 ml), followed by the

addition of a 1,4-dioxane solution (5 ml) of DDQ (113.5 mg, 0.5 mmol) and the mixture was immediately heated to reflux. After 2 h, the reaction mixture was neutralized with saturated aqueous sodium hydrogencarbonate and organic materials were extracted with ethyl acetate and dried over sodium sulfate. After evaporation of the solvent, the crude products were purified by thin-layer chromatography (hexane : ethyl acetate = 1 : 1) to afford 2-methylquinolin-8-ol (**7a**) (127.3 mg, 0.80 mmol) in 80% yield.

7a:[25] Colorless needles, Mp 73 °C (hexane–benzene) (lit, 73—73.5 °C); IR (KBr) 3415, 1508, 1469, 1252 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.71 (3H, s), 7.12 (1H, d, J = 7.9 Hz), 7.26 (1H, d, J = 7.9 Hz), 7.28 (1H, d, J = 8.4 Hz), 7.36 (1H, t, J = 7.9 Hz), 8.01 (1H, d, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ = 24.9, 109.8, 117.5, 122.7, 126.5, 126.6, 136.1, 137.7, 151.7, 156.9.

The spectral data were in good agreement with those of the authentic sample purchased from Tokyo Chemical Industry Co., Inc.

Spectral Data. **2-Ethylquinolin-8-ol (7b):**[26] Colorless needles, Mp 194 °C (hexane–benzene) (lit, 194.5—196.5 °C); IR (KBr) 3390, 2972, 1508, 1468, 1244 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.39 (3H, t, J = 7.6 Hz), 2.98 (2H, q, J = 7.6 Hz), 7.12 (1H, d, J = 8.0 Hz), 7.26 (1H, d, J = 8.0 Hz), 7.30 (1H, d, J = 8.4 Hz), 7.36 (1H, t, J = 8.0 Hz), 8.03 (1H, d, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ = 13.3, 31.6, 109.7, 117.5, 121.8, 126.6, 126.8, 136.2, 137.6, 151.8, 161.9.

2-Isopropylquinolin-8-ol (7c):[27] Colorless needles, Mp 89 °C (hexane–benzene) (lit, 89—91 °C); IR (KBr) 3228, 2964, 1504, 1458, 1196 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.38 (6H, d, J = 6.9 Hz), 3.22 (1H, sept, J = 6.9 Hz), 7.13 (1H, d, J = 7.9 Hz), 7.26 (1H, d, J = 7.9 Hz), 7.33 (1H, d, J = 8.5 Hz), 7.36 (1H, t, J = 7.9 Hz), 8.04 (1H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ = 22.4, 36.5, 109.6, 117.5, 120.7, 126.7, 126.9, 136.3, 137.4, 151.9, 165.3.

2-Styrylquinolin-8-ol (7d):[28] Colorless needles, Mp 103 °C (hexane–benzene) (lit, 104—105 °C); IR (KBr) 3402, 1506, 1441, 1333, 1254 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.16 (1H, d, J = 8.0 Hz), 7.27 (1H, d, J = 8.0 Hz), 7.31—7.35 (2H, m), 7.36—7.42 (3H, m), 7.59—7.63 (3H, m), 7.69 (1H, d, J = 16.3 Hz), 8.08 (1H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ = 110.1, 117.7, 120.3, 127.2, 127.3, 127.5, 128.1, 128.6, 128.7, 128.8, 134.3, 136.4, 138.0, 152.1, 153.6.

2,4-Dimethylquinolin-8-ol (7e):[25a] Colorless needles, Mp 62 °C (hexane–benzene) (lit, 64 °C); IR (KBr) 3446, 1511, 1463, 1248 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.65 (3H, s), 2.67 (3H, s), 7.08 (1H, dd, J = 1.2, 7.9 Hz), 7.31 (1H, s), 7.42 (1H, t, J = 7.9 Hz), 7.48 (1H, dd, J = 1.2, 7.9 Hz); ^{13}C NMR ($CDCl_3$) δ = 18.5, 24.7, 110.2, 114.6, 124.0, 127.1, 127.6, 138.4, 145.7, 153.3, 157.3.

2-Ethyl-3-methylquinolin-8-ol (7f):[28] Colorless needles, Mp 46 °C (hexane–benzene) (lit, 46—47 °C); IR (KBr) 3325, 1495, 1452, 1188 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.39 (3H, t, J = 7.4 Hz), 2.45 (3H, s), 2.94 (2H, q, J = 7.4 Hz), 7.05 (1H, d, J = 7.9 Hz), 7.19 (1H, d, J = 7.9 Hz), 7.33 (1H, t, J = 7.9 Hz), 7.80 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 11.8, 18.9, 28.6, 108.6, 116.8, 126.6, 127.3, 130.5, 135.4, 136.3, 151.8, 160.6.

5-Bromo-2-methylquinolin-8-ol (7g):[29] Colorless needles, Mp 69 °C (hexane–benzene) (lit, 67 °C); IR (KBr) 3375, 1500, 1390, 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.73 (3H, s), 7.01 (1H, d, J = 8.2 Hz), 7.38 (1H, d, J = 8.6 Hz), 7.60 (1H, d, J = 8.2 Hz), 8.31 (1H, d, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ = 24.7, 109.6, 110.5, 123.8, 125.7, 129.9, 135.7, 138.3, 151.5, 157.6.

2,2-Dimethyl-4*H*-1,3-dioxano[5,4-*b*]quinolin-6-ol (7h): Colorless needles, Mp 70 °C (hexane–benzene); IR (KBr) 3375, 1500, 1360, 1284, 1128 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.61 (6H, s), 5.05 (2H, s), 6.99 (1H, d, J = 8.0 Hz), 7.18 (1H, d, J = 8.0 Hz), 7.34 (1H, t, J = 8.0 Hz), 7.87 (1H, s); ^{13}C NMR ($CDCl_3$) δ = 24.8, 63.3, 100.7, 107.9, 116.9, 119.5, 127.9, 129.3, 133.2, 142.5, 146.9, 151.7. Found: C, 67.33; H, 5.58; N, 6.04%. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06%.

6-Methylphenanthridin-4-ol (7i): Colorless needles, Mp 85 °C (hexane–benzene); IR (KBr) 3390, 1581, 1483, 1338, 1236 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.00 (3H, s), 7.20 (1H, d, J = 7.8 Hz), 7.49 (1H, t, J = 8.2 Hz), 7.68 (1H, t, J = 7.8 Hz), 7.82 (1H, t, J = 7.8 Hz), 7.96 (1H, d, J = 7.8 Hz), 8.19 (1H, d, J = 8.2 Hz), 8.56 (1H, d, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ = 23.1, 110.5, 112.4, 122.8, 124.1, 126.4, 126.7, 127.2, 127.4, 130.6, 132.5, 132.7, 152.5, 156.7. Found: C, 80.42; H, 5.43; N, 6.92%. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69%.

General Procedure for the Synthesis of 1,2,3,4-Tetrahydroquinolines. (Table 2, Entry 1): To a 1,4-dioxane (10 ml) suspension of NaH (240.1 mg, 10.0 mmol) and $Na[BH_3(CN)]$ (314.2 mg, 5.0 mmol) was added a 1,4-dioxane solution (10 ml) of 4-(3-hydroxyphenyl)butan-2-one *O*-2,4-dinitrophenyloxime (**6a**) (345.3 mg, 1.0 mmol) at room temperature. After the mixture was stirred for 10 h at 50 °C, the reaction mixture was quenched by adding 1 mol dm^{-3} HCl solution until the reaction mixture became acidic (pH 1). After being stirred for 0.5 h, the reaction mixture was neutralized with aqueous sodium hydrogencarbonate and organic materials were extracted with ethyl acetate and dried over sodium sulfate. After evaporation of the solvent, the crude products were purified by thin-layer chromatography (Silica gel, hexane : ethyl acetate = 4 : 1) to afford 2-methyl-1,2,3,4-tetrahydroquinolin-8-ol (**9a**) (127.3 mg, 0.78 mmol) in 78% yield.

Spectral Data. ^1H and ^{13}C NMR spectra of **9a**—**n** were too broad to determine the stereochemistry. Accordingly, all tetrahydroquinolines **9a**—**n** were converted to *t*-butyldimethylsilyl ether **9a′**—**n′** by the literature procedure,[30] and each spectrum was measured.

8-*t*-Butyldimethylsiloxy-2-methyl-1,2,3,4-tetrahydroquinoline (9a′): Colorless oil; IR (KBr) 3426, 2933, 1486, 1259, 836 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.21 (6H, s), 0.99 (9H, s), 1.20 (3H, d, J = 6.2 Hz), 1.52—1.58 (1H, m), 1.89—1.92 (1H, m), 2.69—2.71 (1H, m), 2.78—2.81 (1H, m), 3.35—3.40 (1H, m), 6.42 (1H, t, J = 7.7 Hz), 6.53 (1H, d, J = 7.7 Hz), 6.59 (1H, d, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ = −4.3, 22.5, 25.8, 25.9, 26.4, 30.2, 115.3, 115.4, 121.6, 132.9, 141.4. HRMS Found: *m/z* 277.1823. Calcd for $C_{16}H_{27}NOSi$: M, 277.1862.

8-*t*-Butyldimethylsiloxy-2-isopropyl-1,2,3,4-tetrahydroquinoline (9c′): Colorless oil; IR (KBr) 2956, 1494, 1257, 835 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.21 (3H, s), 0.22 (3H, s), 0.97 (6H, t, J = 7.1 Hz), 0.99 (9H, s), 1.64—1.74 (2H, m), 2.68—2.74 (1H, m), 2.76—2.82 (1H, m), 2.97—3.01 (1H, m), 4.13 (1H, bs), 6.41 (1H, t, J = 7.7 Hz), 6.53 (1H, d, J = 7.7 Hz), 6.59 (1H, d, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ = −4.4, −4.3, 18.3, 18.6, 25.0, 25.8, 26.6, 32.7, 56.9, 115.1, 115.2, 121.7, 121.8, 128.8, 136.9, 141.5. HRMS Found: *m/z* 305.2171. Calcd for $C_{18}H_{31}NOSi$: M, 305.2175.

8-*t*-Butyldimethylsiloxy-2-styryl-1,2,3,4-tetrahydroquinoline (9d′): Colorless oil; IR (KBr) 3421, 1587, 1492, 1257, 966, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.23 (3H, s), 0.24 (3H, s), 0.99 (9H, s), 1.81—1.83 (1H, m), 2.04—2.08 (1H, m), 2.74—2.83 (1H, m), 4.01 (1H, bs), 4.21 (1H, bs), 6.28 (1H, dd, J = 6.7, 15.8 Hz), 6.47 (1H, t, J = 7.7 Hz), 6.57—6.62 (3H, m), 7.18—7.23 (1H, m), 7.30 (2H, t, J = 7.5 Hz), 7.36 (2H, d, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ = −4.2, −4.1, 18.2, 18.3, 25.9, 28.6, 29.4, 50.4, 115.5, 115.8, 121.9, 126.4, 127.1, 128.5, 128.6, 129.8, 130.6, 132.5, 135.9. HRMS Found: *m/z* 365.2149. Calcd for $C_{23}H_{31}NOSi$: M, 365.2176.

(2R^*,4S^*)-(±)-8-*t*-Butyldimethylsiloxy-2,4-dimethyl-1,2,3,4-tetrahydroquinoline (9e′): Colorless oil; IR (KBr) 3421, 1587, 1492, 1257, 966, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.21 (6H, s), 0.99 (9H, s), 1.19 (3H, d, J = 6.3 Hz), 1.29 (3H, d, J = 6.8 Hz), 1.90 (1H, dq, J = 2.6, 12.6 Hz), 2.92—2.96 (1H, m), 3.40 (1H, bs), 3.99 (1H, bs), 6.47 (1H, t, J = 7.8 Hz), 6.55 (1H, d J = 7.5 Hz), 6.76 (1H, d, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ = −4.4, −4.3, 18.2, 20.3, 22.7, 25.8, 30.9, 40.9, 46.8, 115.4, 119.5, 121.7, 126.7, 136.6, 141.4. HRMS Found: *m/z* 291.1985. Calcd for $C_{17}H_{29}NOSi$: M, 291.2018.

The stereochemistry was determined by the observation of NOE between H^2 and H^4 protons of the major isomer of **9e′** (Chart 1).

8-*t*-Butyldimethylsiloxy-2-ethyl-3-methyl-1,2,3,4-tetrahydroquinoline (9f′): Diastereomer ratio = 1.8 : 1; Colorless oil; IR (KBr) 2958, 2929, 1494, 1255, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$) major isomer: δ = 0.21 (6H, s), 0.98 (3H, t, J = 9.2 Hz), 1.00 (9H, s), 1.40—1.49 (1H, m), 1.65—1.72 (1H, m), 1.74—1.78 (1H, m), 2.44 (1H, dd, J = 9.8, 16.3 Hz), 2.73 (1H, dd, J = 5.0, 8.7 Hz), 2.83 (1H, dt, J = 3.4, 8.1 Hz), 4.17 (1H, bs), 6.42 (1H, t, J = 7.7 Hz), 6.54 (1H, d, J = 7.7 Hz), 6.58 (1H, d, J = 7.4 Hz); minor isomer: δ = 0.19 (3H, s), 0.21 (3H, s), 0.87 (1H, d, J = 6.9 Hz), 1.00 (9H, s), 1.42—1.53 (2H, m), 2.07 (1H, m), 2.44 (1H, dd, J = 5.0, 11.1 Hz), 2.91 (1H, dd, J = 6.3, 16.1 Hz), 3.14 (1H, s), 4.11 (1H, s), 6.19 (1H, t, J = 7.7 Hz), 6.54 (1H, d J = 7.6 Hz), 6.59 (1H, d, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) major isomer: δ = −4.3, 9.4, 18.3, 25.8, 26.8, 33.7, 34.7, 58.0, 115.1, 115.2, 121.4, 121.7, 136.2, 141.2; minor isomer: δ = −4.4, −4.3, 10.6, 13.9, 18.2, 24.8, 25.9, 29.2, 34.4, 55.9, 115.2, 115.3, 120.7, 122.6, 135.9, 141.2. HRMS Found: *m/z* 305.2110. Calcd for $C_{18}H_{31}NOSi$: M, 305.2175.

5-Bromo-8-*t*-butyldimethylsiloxy-2-methyl-1,2,3,4-tetrahydroquinoline (9g′): Colorless oil; IR (KBr) 2931, 1486, 1259, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.19 (6H, s), 0.98 (9H, s), 1.20 (3H, d, J = 6.2 Hz), 1.51—1.58 (1H, m), 1.94—1.96 (1H, m), 2.61—2.68 (1H, m), 3.29—3.31 (1H, m), 4.07 (1H, bs), 6.42 (1H, d J = 8.4 Hz), 6.67 (1H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ = −4.3, 18.2, 22.2, 25.8, 27.5, 29.9, 46.1, 116.4, 116.9, 118.5, 120.5, 138.4, 140.5. HRMS Found: *m/z* 357.0976. Calcd for $C_{16}H_{26}BrNOSi$: M, 357.0948.

(6R^*,6aR^*,10aS^*)-(±)-4-*t*-Butyldimethylsiloxy-6-methyl-5,6,6a,7,8,9,10,10a-octahydrophenantridine (9j′): Colorless oil; IR (KBr) 2929, 2856, 1494, 1259, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.18 (3H, s), 0.19 (3H, s), 0.99 (9H, s), 1.54—1.66 (1H, m), 2.37 (1H, dt, J = 2.6, 13.8 Hz), 3.15 (1H, d, J = 4.2 Hz), 3.50—3.53 (1H, m), 3.87 (1H, bs), 6.47 (1H, t, J = 7.7 Hz), 6.56 (1H, d, J = 7.6 Hz), 6.80 (1H, d, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ = −4.4, −4.3, 18.9, 20.3, 20.9, 25.9, 26.0, 26.1, 28.9, 37.3, 39.4, 50.2, 115.2, 115.4, 119.7, 122.4, 137.0, 140.9. HRMS Found: *m/z* 331.2329. Calcd for $C_{20}H_{33}NOSi$: M, 331.2333.

The stereochemistry was determined by the differential NOE experiments (H^6 and H^{6a} 6.4%, H^6 and H^{10a} 6.5%) (Chart 2).

(6S^*,6aR^*,10aR^*)-(±)-4-*t*-Butyldimethylsiloxy-6-methyl-5,6,6a,7,8,9,10,10a-octahydrophenantridine (9k′): Colorless oil; IR (KBr) 2929, 2856, 1493, 1255, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.20 (3H, s), 0.21 (3H, s), 1.00 (9H, s), 1.17 (3H, d, J = 6.2 Hz), 1.82 (3H, t, J = 8.01 Hz), 1.88 (1H, d, J = 13.5 Hz), 1.95 (1H, d, J = 10.9 Hz), 2.34—2.41 (1H, m), 3.11 (1H, dq, J = 6.2, 9.6 Hz), 3.97 (1H, bs), 6.45 (1H, t, J = 7.8 Hz), 6.56 (1H, d, J = 7.7 Hz), 6.76 (1H, d, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ = −4.3, 18.2, 20.7, 25.8, 25.9, 26.0, 29.2, 30.1, 40.7, 43.7, 51.7, 114.8, 115.3, 118.0, 125.4, 135.9, 140.6. HRMS Found: *m/z* 331.2329. Calcd for $C_{20}H_{33}NOSi$: M, 331.2333.

Chart 1.

Chart 2.

The coupling constant between H^6 and H^{6a} (J_{H6-H6a} = 9.6 Hz) suggested the stereochemistry as shown in **9k′** (Chart 3).

(±)-6-*t*-Butyldimethylsiloxy-4-methyl-2,3,3a,4,5,9b-hexahydro-1*H*-cyclopenta[*c*]quinoline (9l′) (3aR^*,4R^*,9bS^*)-9l′ : (3aR^*,4S^*,9bS^*)-9l′ = 2.3 : 1; Colorless oil; IR (KBr) 2898, 1587, 782, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$) (3aR^*,4R^*,9bS^*)-isomer: δ = 0.18 (3H, s), 0.19 (3H, s), 0.99 (9H,s), 1.16 (3H, d, J = 6.5 Hz), 1.45—1.53 (1H, m), 1.67—1.73 (1H, m), 2.00—2.08 (1H, m), 2.18—2.42 (1H, m), 3.26—3.30 (1H, m), 3.35—3.40 (1H, m), 3.84 (1H, bs), 5.49—6.53 (2H, m), 6.69—6.71 (1H, m); (3aR^*,4S^*,9bS^*)-isomer: δ = 0.21 (6H, s), 0.99 (9H, s), 1.18 (3H, d, J = 6.2 Hz), 1.48—1.51 (2H, m), 1.60—1.68 (2H, m), 1.88—1.96 (1H, m), 2.15—2.20 (1H, m), 2.65—2.70 (1H, m), 2.90—2.95 (1H, m), 4.13 (1H, bs), 5.48—6.54 (2H, m), 6.74 (1H, d, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) (3aR^*,4R^*,9bS^*)-isomer: δ = −4.4, −4.3, 18.3, 20.3, 23.6, 23.7, 25.9, 35.0, 40.6, 45.1, 47.9, 114.9, 116.5, 121.7, 127.5, 137.6, 141.5; (3aR^*,4S^*,9bS^*)-isomer: δ = −4.4, −4.3, 20.3, 24.1, 25.8, 29.0, 35.5, 41.0, 43.2, 49.0, 116.2, 118.5, 122.1, 127.1, 136.6, 141.6. HRMS Found: *m/z* 317.2162. Calcd for $C_{19}H_{31}NOSi$: M, 317.2176.

The stereochemistry of the major isomer **9l′** was determined by the differential NOE experiments (H^2 and H^3 7.4%, H^2 and H^4 3.2%) (Chart 4).

1-*t*-Butoxycarbonyl-4-butyl-6-*t*-butyldimethylsiloxy-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline (9m′): Colorless oil; IR (KBr) 2931, 1693, 1392, 1257 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.20 (6H, s), 0.91 (3H, t, J = 6.7 Hz), 1.03 (9H, s), 1.04—1.23 (2H, m), 1.35—1.36 (2H, m), 1.37 (4.5H, s), 1.42 (4.5H, s), 1.43 (2H, bs), 1.47—1.60 (1H, m), 1.79—1.94 (1H, m), 2.34—2.36 (1H, m), 3.23—3.30 (1.5H, m), 3.32—3.38 (1H, m), 3.45—3.49 (0.5H, m), 4.10 (1H, d, J = 6.9 Hz), 5.10 (0.5H, d, J = 7.0 Hz), 5.20 (0.5H, d, J = 7.3 Hz), 6.50—6.53 (1H, m), 6.56—6.58 (1H, m), 7.11 (0.5H, d, J = 7.5 Hz), 7.26 (0.5H, d, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ = −4.4, −4.3, 14.1, 18.2, 21.4, 22.7, 25.8, 28.2, 28.6, 28.7, 33.9, 41.6, 45.2, 50.9, 56.0, 116.0, 116.9, 122.2, 123.0, 136.0, 141.1,

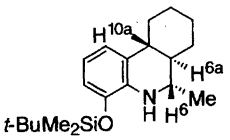


Chart 3.

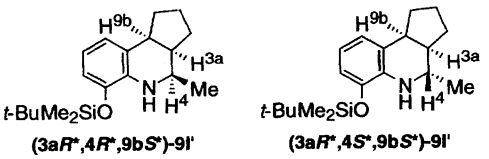


Chart 4.

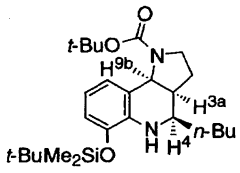


Chart 5.

156.1. HRMS Found: *m/z* 460.3126. Calcd for $C_{26}H_{44}N_2O_3Si$: M, 460.3121.

The stereochemistry of the major isomer **9m′** was determined by the differential NOE experiments (H^2 and H^3 8.6%, H^3 and H^4 12.5%) (Chart 5).

General Procedure for the Reaction of *O*-2,4-Dinitrophenyloximes with *m*-Cresol and NaH. (Eq. 14): To a 1,4-dioxane (2 ml) suspension of NaH (57.8 mg, 2.4 mmol) was added a 1,4-dioxane solution (2 ml) of 1-phenylhept-6-en-3-one *O*-2,4-dinitrophenyloxime (**16**) (89.1 mg, 0.24 mmol) and the mixture was heated to 50 °C. After 5 h, the reaction mixture was neutralized with saturated aqueous ammonium chloride and organic materials were extracted with ethyl acetate and dried over sodium sulfate. After evaporation of the solvent, the crude products were purified by thin-layer chromatography (hexane : ethyl acetate = 1 : 1) to afford 2-methyl-5-phenethyl-3,4-dihydro-2*H*-pyrrole (**17**) (12.3 mg, 0.066 mmol) in 27% yield.

17: Yellow oil; IR (neat) 1641, 1602, 1494, 1452, 1317, 752, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 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 ($CDCl_3$) 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.

Spectral Data. 4-Phenylbutan-2-one Azine (14): Colorless oil; IR (neat) 1641, 1495, 1450, 1363, 748, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.66 (6H, s), 2.59 (4H, t, J = 7.9 Hz), 2.91 (4H, t, J = 7.9 Hz), 7.15—7.28 (10H, m); ^{13}C NMR ($CDCl_3$) δ = 17.0, 32.6, 40.4, 126.2, 128.4, 128.5, 141.5, 160.6. HRMS Found: *m/z* 292.1950. Calcd for $C_{20}H_{24}N_2$: M, 292.1939.

The spectral data were in good agreement with those of the authentic sample which was prepared from 4-phenylbutan-2-one and hydrazine hydrate by the literature procedure.[31]

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13) A 0.5 molar amount of DDQ is enough to obtain **7a** in good yield probably because generated 2,4-dinitrophenol acts as an oxidant in this reaction. On the other hand, when an equimolar amount of DDQ was used, the yield of the quinoline **7a** decreased to 49% owing to the overoxidation of quinoline **7a**.

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