Fischer Indolization of N^{α}-Alkyl-2-allylphenylhydrazones

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Fischer indolization of the hydrazones of 8-allyl-1-amino-1,2,3,4-tetrahydroquinoline and related compounds was investigated. Fischer indolization induced Cope rearrangement of the allyl group and acid-catalyzed intramolecular cycloaddition between the hydrazonyl group and the vinyl group. The base treatment of the latter reaction product caused eliminative ring-opening of the adduct and led to the formation of an indoline skeleton bearing a 2-ketoalkyl group at the C-2 position.

Keywords Fischer indolization; intramolecular 2-acetonylindoline; hydrazone; 4*H*-pyrrolo[3,2,1-*ij*]quinoline; 1*H*-pyrazolo[1,5-*a*]indole; Stevens rearrangement

We have reported the intramolecular polar cycloaddition of 2-allylphenylhydrazones for the construction of pyrazolo[1,5-*a*]indoles under Fischer indolization reaction conditions.1) We have also reported the acid-catalyzed *N*-Claisen rearrangement of 1-allyl-8-(1-ethyl-2-propenyl)-THQ (THQ: 1,2,3,4-tetrahydroquinoline), resulting in the displacement of the 8-substituent by the allyl group and the rearrangement of the 8-substituent to the C-6 position.2) Fusco and Sannicolo have summarized the novel reactions of *ortho*-substituted phenylhydrazones under Fischer indolization conditions,3) for instance, the migration of the 8-methyl group of the hydrazones of 1-amino-THQ derivatives to either C-74) or C-5.5) On the basis of these observations, we became interested in the chemical behavior of the hydrazone derivatives **1** of 8-allyl-1-amino-THQ under Fischer indolization conditions, because this reaction could allow either a convenient preparation of indole derivatives bearing a 6-allyl group or a new type of polar cycloaddition which could lead to novel heterocyclic compounds directly or indirectly. In this paper we would like to report our findings.

Fischer Indolization of the Hydrazones 1a and 1b 8-Allyl-1-amino-THQ was prepared by the Hofmann rearrangement of the 1-carbamoyl derivative, which was readily derived from 8-allyl-THQ6) and sodium isocyanate.7) The condensation of 8-allyl-1-amino-THQ with the corresponding ketones yielded the hydrazones **1**. In Chart 1 the preferred isomers are shown. The geometries of the hydrazones **1** were determined by examination of the infrared (IR) absorption and nuclear magnetic resonance (NMR) spectrum. For instance, the carbonyl absorption of the *E* isomer of **1c** in the IR spectrum appeared at lower frequency (1711 cm^{-1} in CCl_4; 1704 cm^{-1} neat) than that of the *Z* isomer (1729 cm^{-1}) because of more effective participation of lone-pair electrons on N(1) in resonance with the ester carbonyl group.8) The *E* geometry of **1b** was similarly determined from its carbonyl absorption (1704 cm^{-1} neat). The involvement of N(1) in the resonance of the hydrazonyl group is the reason why 2-C of the *E* isomer of **1c** resonated at lower magnetic field (δ 53.8 ppm) than that of *Z* isomer (δ 52.9 ppm) in the ^{13}C-NMR spectra. In the ^{1}H-NMR spectra of **1c**, 2-H on THQ (triplet-like multiplet) was subject to the anisotropic effect of the phenyl group on the hydrazonyl group. The 2-H signal of the *Z* isomer (δ 3.66) was seen at lower magnetic field than that of the *E* isomer (δ 3.15 ppm) because the phenyl group of the *Z* isomer is on the opposite side of the hydrazonyl group and that of the *E* isomer is close to 2-H. In the ^{1}H-NMR spectrum of **1d**, the chemical shift of 2-H (δ 3.68 ppm) was in good accord with the value expected for the *E* isomer in which the phenyl group is on the opposite side of the hydrazonyl moiety and 2-H is beyond the range of the anisotropic effect of the phenyl group. A similar argument was used to assign the stereochemistry of **1e** (δ 3.54 ppm), which has no phenyl group on the hydrazonyl group. The *E* isomers of both **1d** and **1e** are the more stable ones. The chemical shift of 2-H for **1b** also supports *E* configuration of **1b** as assigned from the IR spectrum, *vide supra*. The hydrazone **1a** was treated with 10% sulfuric acid in ethanol at refluxing temperature (Fischer indolization)

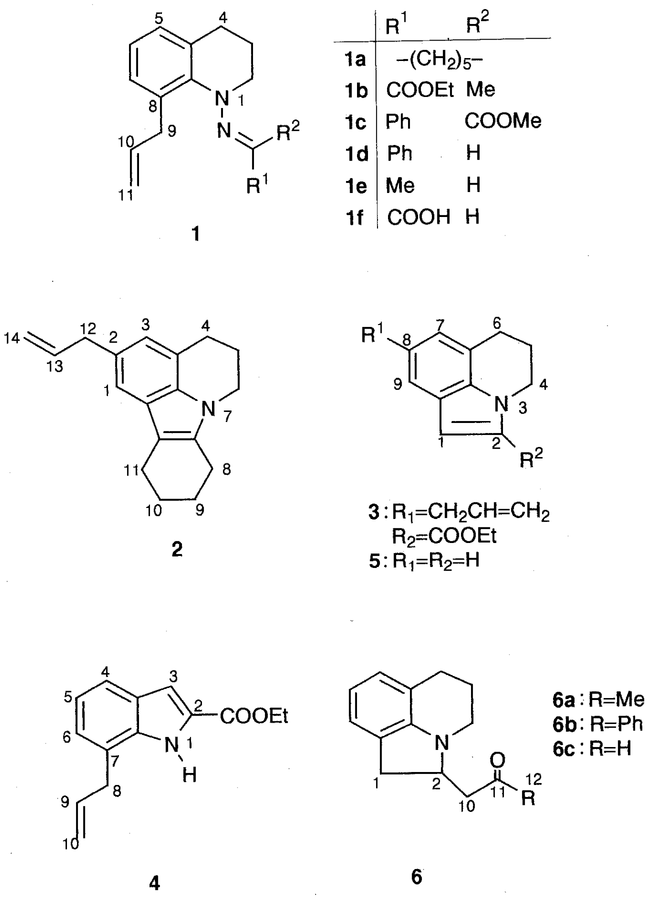
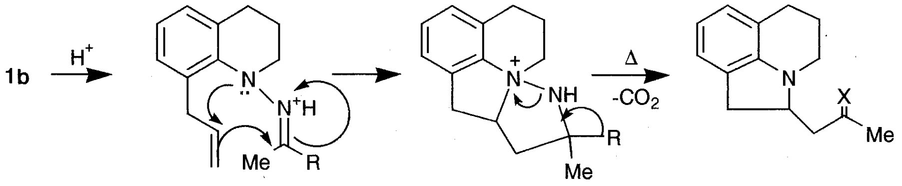


Chart 1



7a: R=COOEt
7b: R=COO$^-$

X=NH
6a: X=O

Chart 2

and the usual work-up gave two indole derivatives, **2** (65.3%) and 8-allyl-THQ (2.5%). The 8-allyl group of **1a** rearranged to C-6 during Fischer indolization. The position of the allyl group was supported by the presence of two singlet signals due to aromatic protons at δ 6.70 and 7.10 ppm in the ^{1}H-NMR spectrum. When **1b** was subjected to the same reaction, the indoles **3** (13.7%) and **4** (0.2%) were obtained. The position of the allyl group in **3** was similarly deduced from the ^{1}H-NMR spectrum and confirmed by the transformation into 8-allyllilolidine (lilolidine; 1,2,5,6-tetrahydro-4*H*-prrolo[3,2,1-*ij*]quinoline)[9] through consecutive reactions of hydrolysis, decarboxylation and reduction (see Experimental). The structure of the trace product **4** was deduced from its ^{1}H-NMR spectra. A similar product has been reported in Fischer indolization of ethyl acetoacetate hydrazones of a similar type of compound.[10] The structure of **4** was confirmed by the independent preparation of **4** from indoline-2-carboxylic acid ester by successive *N*-allylation, *N*-Claisen rearrangement, dehydrogenation and ester-exchange reactions (see Experimental). Since the combined yield from the organic extracts was poor, the basic aqueous layer was evaporated and the residue was extracted with chloroform. The extract was chromatographed repeatedly and 5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (1,2-dehydrolilolidine **5**) (2.8%)[11] and 2-acetonyllilolidine (**6a**) (2.0%) were isolated. The product **5** was reduced with sodium cyanoborohydride in acetic acid into lilolidine. The composition of **6a** was indicated by high-resolution mass spectrometry (HRMS) ($C_{14}H_{17}NO$ Calcd: 215.1308; Found: 215.1299). Detailed comparisons of the ^{13}C-NMR spectra of **6a** with those of 2-methyllilolidine[12] allowed us to assign the skeleton of this product. The presence of methyl ketone as shown by the IR (ν_{max} 1714 cm^{-1}) and ^{1}H-NMR spectra (δ 2.11, 3H, s) led us to postulate the structure **6** for this ketone product. The reaction mechanism for the formation of **6a** from **1b** was of interest, and is proposed to be as shown in Chart 2. The protonated hydrazone cyclizes intramolecularly with the allyl group to give the tetracyclic ion **7a**. We have reported this type of cyclization of 2-allylphenylhydrazone.[1] Hydrolysis of the ester and warming of the carboxylate **7b** permits decarboxylative ring opening to the imine of **6a**, X=NH, which can be readily hydrolyzed into **6a**, X=O.

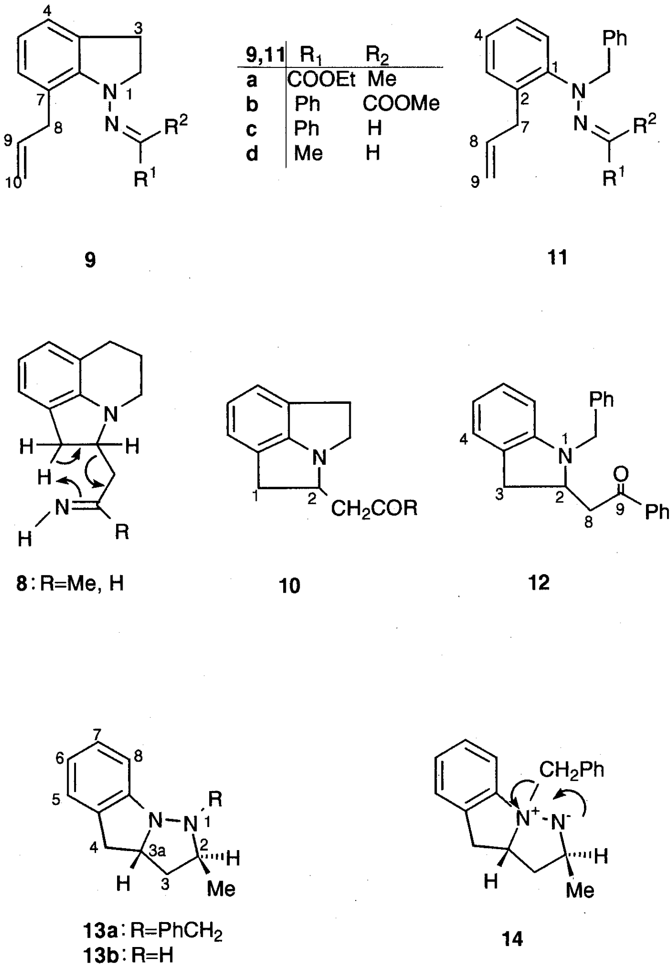
The Preparation of 6 from the Hydrazone 1 by One-Pot Reaction We looked for reaction conditions favoring the above reaction pathway and found that treatment of the initial adduct with strong base opens the ring of the cycloadduct, as shown for **7**, and leads to the formation of **6**. Thus, after Fischer indolization, 30% potassium hydroxide solution was added to the reaction mixture to make about 10% solution of potassium hydroxide and this strongly basic solution was refluxed for 2 h. These two procedures, the acid-catalyzed intramolecular cycloaddition and the base-catalyzed ring-opening of the cycloadduct, were carried out in one pot. By this one-pot procedure the yield of **6a** was improved to 48%. This procedure was applied to the other hydrazones **1c**—**f** and the results are summarized in Table I.

Table I. Preparation of **6** from **1**

Starting material	Products	Yields (%)
1b	**6a**	48
1c	**6b**	65
1d	**6b**	47
1e	—	—
1f	**5**	37

The hydrazones **1c** and **1d** gave the same product **6b**. In the case of **1e**, no product was isolated. The reaction of **1f**, which was prepared *in situ*, did not give **6c** but provided **5** in 37% yield. The formation of **5** from **1b**, *vide supra*, and **1f** can be rationalized in terms of a fragmentation reaction as shown for the imine **8**, R=Me, H. The key step in the formation of **6** is the ring-opening reaction of the initial cycloaddition product, so the presence of a readily removable substituent such as carboxylate or an acidic proton (R in **7**) seems to be essential for the success of this transformation.

One-Pot Reaction of the Hydrazones 9 and 11 When this one-pot method was applied to the hydrazone with the indoline skeleton **9**, the reaction became complex and no cyclization product **10** was obtained. This complication may be due to the high strain energy of the intermediate with three consecutively condensed five-membered rings which is formed by intramolecular cycloaddition as described for **7**, although the skeleton of **10**, 1,2-dihydropyrrolo[3,2,1-*ki*]indole, has been synthesized by Fischer indolization.[13] Then the one-pot reaction was applied to the hydrazones **11** which have no such strain in the reaction intermediate. Although the one-pot reaction of **11a** and **11b** did not give the expected product, the hydrazone **11c** gave the oily product **12** (21.3%), the structure of which was deduced from the HRMS ($C_{23}H_{21}NO$ Calcd: 327.1622; Found: 327.1643) and IR (ν_{max} 1684 cm^{-1}) spectra. Detailed comparisons of the ^{1}H- and ^{13}C-NMR spectra with those of indoline derivatives allowed us to assign the skeleton of the product **12**. When the hydrazone **11d** was subjected to the same reaction, the cyclized pro-



9,11	R_1	R_2
a	COOEt	Me
b	Ph	COOMe
c	Ph	H
d	Me	H

Chart 3

duct was obtained, on one occasion, in 76.7% yield. This product has the same molecular composition as the starting hydrazone ($C_{18}H_{20}N_2$ Calcd: 264.1625; Found: 264.1590) and no carbonyl or NH absorption in the IR spectrum. Detailed investigation of its ^{1}H- and ^{13}C-NMR spectra suggested the presence of the saturated pyrazolo[1,5-*a*]indole nucleus[1] and we assigned the structure **13a** for this product. The reaction pathway leading to **13a** involves migration of the benzyl group from quaternary nitrogen to anionic nitrogen as shown in **14**, *i.e.*, Stevens rearrangement.[14] The product **13a** was eventually shown to be identical with the benzylated product derived from 2-methyl-2,3,3a,4-tetrahydro-1*H*-pyrazolo[1,5-*a*]indole (**13b**), which was obtained by the intramolecular cycloaddition of acetaldehyde 2-allylphenylhydrazone.[1] In conclusion we have found a novel method to construct the indoline nucleus with a 2-ketoalkyl group at the C-2 position,[13] starting from N^{α}-alkyl-2-allylphenylhydrazone analogues. It is noteworthy that N^{α}-benzyl-2-allylphenylhydrazone could be a useful starting material for the preparation of 1-protected pyrazolo[1,5-*a*]indoles.

Experimental[16]

8-Allyl-1-amino-1,2,3,4-tetrahydroquinoline 1) Sodium isocyanate (85%, 3.21 g, 42 mmol) was added to a suspension of 8-allyl-THQ hydrochloride (4.40 g, 21 mmol) in acetonitrile (60 ml). After stirring for 1.5 h, trifluoroacetic acid (1.62 ml, 21 mmol) was added to the reaction mixture and stirring was resumed for 4 h. The reaction mixture was evaporated and the residue was basified with aqueous sodium hydrogen carbonate. Extraction of the basic solution with dichloromethane (three times) and washing of the extracts with aqueous sodium hydrogen carbonate once and with saturated brine twice gave, after usual work-up, a yellow solid (4.49 g), which was recrystallized from cyclohexane to give 8-allyl-1-carbamoyl-1,2,3,4-tetrahydroquinoline (4.30 g, 94.8%), mp 94.5—95.0 °C. HRMS Calcd for $C_{13}H_{16}N_2O$: 216.1261. Found: 216.1238. MS *m*/*z*: 216 (M^+, 20), 199 (25), 172 (100), 144 (30), 130 (13). IR (KBr): 3457, 3284, 3203, 1631, 1403, 775 cm^{-1}. ^{1}H-NMR δ: 1.75—2.19 (2H, br, H-3), 2.64 (2H, br t, $J=6.5$ Hz, H-4), 2.88 (1H, br, NH), 3.45 (2H, br, H-2), 4.52 (1H, br, NH), 4.83 (2H, br, H-9), 5.03 and 5.10 (2H, each m, H-11), 5.89 (1H, tdd, $J=6.7, 9.3, 17.5$ Hz, H-10), 7.04—7.15 (3H, m, Ar-H). ^{13}C-NMR δ: 24.3 (C-3), 26.4 (C-4), 35.3 (C-9), 42.5 (C-2), 116.2 (C-11), 126.5 (d), 126.6 (d), 128.2 (d), 135.7 (s), 136.4 (d), 136.9 (s), 138.3 (s), 157.9 (s, CO). *Anal.* Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.17; H, 7.52, N, 12.89.

2) The above urea compound (10.0 g, 46.2 mmol) was dissolved in ethanol (250 ml) and the solution was cooled with ice-water. Under vigorous stirring, a mixture of 1.8 N sodium hypochlorite (52 ml, 94 mmol) and 2.5 N sodium hydroxide was introduced and the resulting solution was stirred at room temperature for 1.5 h, then warmed at 70 °C for 1 h. The reaction mixture was diluted with water (200 ml), acidified with 2 N hydrochloric acid and basified with sodium carbonate. After saturation with sodium chloride, the solution was extracted with ether three times. The crude product (8.00 g) was chromatographed on silica gel with a mixture of dichloromethane and ethyl acetate to give 8-allyl-1-amino-1,2,3,4-tetrahydroquinoline as an oil (7.71 g, 88.6%). MS *m*/*z*: 173 (M^+, 100), 172 (72), 170 (21), 168 (24), 158 (41), 154 (32), 145 (31), 144 (38), 130 (35). IR (neat): 3336, 3072, 3002, 2932, 1637, 1600, 1451, 913, 768 cm^{-1}. ^{1}H-NMR δ: 1.84 (2H, m, H-3), 2.77 (2H, t, $J=6.5$ Hz, H-4), 3.25 (2H, t, $J=5.3$ Hz, H-2), 3.54 (2H, s, NH_2), 3.56 (2H, d, $J=6.3$ Hz, H-9), 5.06, 5.11 and 5.15 (2H, each m, H-11), 6.07 (1H, tdd, $J=6.3, 10.2, 16.8$ Hz, H-10), 6.91 (1H, m, 6-H), 6.97 (1H, d, $J=7.3$ Hz, 5-H), 7.03 (1H, dd, $J=2.4, 6.8$ Hz). ^{13}C-NMR δ: 16.2 (C-3), 27.6 (C-4), 35.4 (C-9), 55.6 (C-2), 115.6 (C-10), 123.4 (C-6), 127.7 (d), 127.9 (d), 128.6 (s), 135.1 (s), 147.1 (s). Hydrobromide, mp 182 °C (dec.). IR (KBr): 2850, 2670, 1638, 1590, 1563, 1528, 913, 772 cm^{-1}. *Anal.* Calcd for $C_{12}H_{17}BrN_2$: C, 53.54; H, 6.37; N, 10.41. Found: C, 53.52; H, 6.47; N, 10.35.

Preparation of the Hydrazones 1 General Procedure: 8-Allyl-1-amino-THQ (10 mmol) was dissolved in 60% acetic acid (20 ml) and a ketone (12 mmol) was added to this solution. The reaction mixture was stirred at room temperature for 1 h, then water (60 ml) was added and the solution was extracted with ether three times. The organic extract was washed successively with aqueous sodium hydrogen carbonate twice and brine three times. The crude product was purified by column chromatography on silica gel. **1a**: syrup (41%). MS *m*/*z*: 268 (M^+, 13), 170 (100). IR ($CHCl_3$): 1703, 1618, 1448, 1000, 910 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.60—2.10 (8H, m), 2.35 (2H, m, $CH_2-C=N$), 2.70 (2H, m, $CH_2-C=N$), 2.86 (2H, t, $J=6$ Hz, H-4), 3.13 (2H, m, H-2), 3.22 (2H, d, $J=6$ Hz, H-9), 4.90 and 5.15 (2H, each m, H-11), 6.00 (1H, tdd, $J=6, 9, 17$ Hz, H-10), 6.97 (3H, s, Ar-H). **1b**: syrup (93%). HRMS Calcd for $C_{17}H_{22}N_2O_2$: 286.1680. Found: 286.1711. MS *m*/*z*: 286 (M^+, 11), 213 (26), 170 (100), 144 (17), 130 (6). IR (neat): 3073, 1704, 1577, 1459, 1303, 1146 cm^{-1}. ^{1}H-NMR δ: 1.31 (3H, t, $J=7.1$ Hz, $C\underline{H}_3CH_2O$), 1.91 (2H, br quintet, $J=6.2$ Hz, H-3), 2.23 (3H, s, $CH_3-C=N$), 2.79 (2H, br t, $J=6.5$ Hz, H-4), 3.18 (2H, d, $J=6.6$ Hz, H-9), 3.57 (2H, t, $J=5.5$ Hz, H-2), 4.29 (2H, q, $J=7.1$ Hz, $OC\underline{H}_2CH_3$), 4.96–5.07 (2H, m, H-11), 5.94 (1H, tdd, $J=6.7, 10.0, 16.8$ Hz, H-10), 6.90—7.06 (3H, m, Ar-H). ^{13}C-NMR δ: 14.2 (q), 17.0 (q), 22.7 (C-3), 27.5 (C-4), 36.7 (C-9), 53.1 (C-2), 61.4 (t), 115.1 (C-11), 124.3 (d), 126.7 (d), 128.5 (d), 130.7 (s), 135.5 (s), 137.8 (d), 143.8 (s), 146.5 (s), 165.6 (s). **1c**: *Z* isomer, yellow syrup (35.5%). HRMS Calcd for $C_{21}H_{22}N_2O_2$: 334.1680. Found: 334.1694. MS *m*/*z*: 334 (M^+, 11), 275 (15), 170 (100), 144 (11). IR (CCl_4): 3064, 1729, 1446, 1216, 1148 cm^{-1}. ^{1}H-NMR δ: 2.00 (2H, m, H-3), 2.71 (2H, br t, $J=6.2$ Hz, H-4), 3.38 (2H, d, $J=6.8$ Hz, H-9), 3.66 (2H, br t, $J=6.2$ Hz, H-2), 3.79 (3H, s, $COOCH_3$), 4.94—5.05 (2H, m, H-11), 5.89 (1H, tdd, $J=6.7, 9.9, 16.8$ Hz, H-10), 6.93—7.11 (3H, m, Ar-H), 7.28—7.34 (3H, m, Ar-H), 7.51—7.56 (2H, m, Ar-H). ^{13}C-NMR δ: 24.0 (C-3), 27.3 (C-4), 36.3 (C-9), 52.1 (q), 52.9 (C-2), 115.5 (C-11), 124.5 (C-6), 125.9 (d × 2), 126.1 (d), 128.3 (d × 2), 128.5 (d × 2), 132.4 (s), 135.2 (s), 135.4 (s), 137.7 (d), 139.0 (s), 142.8 (s), 167.1 (s, CO). *E* isomer, yellow syrup (41.8%). HRMS Calcd for $C_{21}H_{22}N_2O_2$: 334.1680. Found: 334.1704. MS *m*/*z*: 334 (M^+, 8), 275 (16), 170 (100), 144 (12). IR (CCl_4) cm^{-1}: 1711, 1435, 1271, 1145. IR (neat): 1704 cm^{-1}. ^{1}H-NMR δ: 1.76 (2H, m, H-3), 2.58 (2H, br t, $J=6.1$ Hz, H-4), 3.15 (2H, br t, $J=6.3$ Hz, H-2), 3.57 (2H, d, $J=6.4$ Hz, H-9), 3.78 (3H, s,

$COOCH_3$), 5.03—5.12 (2H, m, H-11), 6.08 (1H, tdd, *J*=6.6, 9.5, 17.6 Hz, H-10), 6.85—7.10 (3H, m, Ar-H), 7.28—7.38 (5H, m, Ar-H). ^{13}C-NMR δ: 24.6 (C-3), 27.2 (C-4), 37.1 (C-9), 52.3 (q), 53.8 (C-2), 115.2 (C-11), 124.5 (C-6), 125.9 (C-5), 127.7 (d × 2), 128.2 (d), 129.4 (d × 2), 129.5 (d), 132.4 (s), 132.8 (s), 134.3 (s), 135.8 (s), 138.0 (d), 142.5 (s), 166.5 (s, CO). The *E* isomer isomerized readily to the *Z* isomer to form a mixture of isomers. **1d**: pale yellow syrup (69%). HRMS Calcd for $C_{19}H_{20}N_2$: 276.1625. Found: 276.1606. MS *m/z*: 276 (M^+, 10), 172 (14), 171 (23), 170 (100), 157 (9), 156 (9), 144 (10). IR (neat): 3059, 1637, 1587, 1558, 1478, 1455, 1171, 915, 754, 694 cm^{-1}. ^{1}H-NMR δ: 2.02 (2H, m, H-3), 2.69 (2H, br t, *J*=6.3 Hz, H-4), 3.56 (2H, d, *J*=6.6 Hz, H-9), 3.68 (2H, br t, *J*=6 Hz, H-2), 4.99—5.10 (2H, m, H-11), 5.98 (1H, tdd, *J*=6.6, 10.4, 17.0 Hz, H-10), 6.93—7.65 (8H, m, Ar-H). ^{13}C-NMR δ: 22.8 (C-3), 27.7 (C-4), 36.9 (C-9), 49.1 (C-2), 115.4 (C-11), 123.3 (d), 125.8 (d × 2), 126.6 (d), 127.5 (d), 128.4 (d × 2), 128.8 (d), 130.9 (s), 133.0 (d), 133.4 (s), 136.6 (s), 137.9 (d), 140.8 (s). **1e**: pale yellow oil (86.9%). HRMS Calcd for $C_{14}H_{18}N_2$: 214.1469. Found: 214.1450. MS *m/z*: 214 (M^+, 23), 172 (22), 171 (20), 170 (100), 144 (23), 130 (9). IR (neat): 3073, 1637, 1593, 1456, 1290, 910, 769 cm^{-1}. ^{1}H-NMR δ: 1.89 (2H, m, H-3), 1.92 (3H, d, *J*=5.1 Hz, $C\underline{H}_3$–CH=N), 2.70 (2H, br t, *J*=6.6 Hz, H-4), 3.31 (2H, d, *J*=6.6 Hz, H-9), 3.54 (2H, br t, *J*=5.7 Hz, H-2), 5.01—5.12 (2H, m, H-11), 5.97 (1H, tdd, *J*=6.7, 10.0, 16.9 Hz, H-10), 6.53 (1H, q, *J*=5.2 Hz, N=C$\underline{H}$–Me), 6.95—7.08 (3H, m, Ar–H). ^{13}C-NMR δ: 18.6 (q), 20.9 (C-3), 27.2 (C-4), 36.2 (C-9), 49.9 (C-2), 115.3 (C-11), 123.9 (d), 127.7 (d), 127.3 (d), 130.8 (s), 135.1 (d), 135.1 (s), 137.9 (d), 140.7 (s).

Fischer Indolization of the Hydrazone 1a A solution of **1a** (268 mg, 1 mmol) and 10% sulfuric acid in ethanol (4 ml) was refluxed for 3 h. The reaction mixture was diluted with water (10 ml), basified with sodium carbonate then extracted with ether three times. The extract (247 mg) was purified by chromatography (silica gel, benzene) to give 8-allyl-THQ (4.3 mg, 2.5%) and 2-allyl-5,6,8,9,10,11-hexahydro-4*H*-pyrido[3,2,1-*jk*]carbazole (**2**) (164 mg, 65.3%) as colorless plates, mp 74.0—76.0 °C (EtOH). IR (KBr): 3080, 1640, 1430, 903 cm^{-1}. ^{1}H-NMR δ: 1.90 (4H, m, H-9 + H-10), 2.18 (2H, m, H-5), 2.70 (4H, m, H-8 + H-11), 2.93 (2H, t, *J*=6 Hz, H-4), 3.47 (2H, d, *J*=6 Hz, H-12), 3.93 (2H, t, *J*=5.5 Hz, H-6), 4.92 and 5.17 (2H, each m, H-14), 6.08 (1H, tdd, *J*=6, 9, 17 Hz, H-13), 6.70 (1H, s, H-3), 7.10 (1H, s, H-1). *Anal.* Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.41; N, 5.57. Found: C, 86.17; H, 8.51; N, 5.34.

Fischer Indolization of the Hydrazone 1b The hydrazone **1b** (1.025 g, 3.6 mmol) was reacted in 10% sulfuric acid in ethanol (20 ml) for 3.5 h. Dilution with water (10 ml), basification and extraction of the reaction mixture gave the crude product A (169 mg). The basic aqueous layer was evaporated. The residue was dissolved in methanol and the solution was filtered to remove the insoluble material. The filtrate was evaporated and the residue was triturated with chloroform. The soluble part was evaporated to give the crude product B (1.237 g). Chromatography of the crude product A provided the indoles **3** (133 mg, 13.7%) and **4** (1.8 mg, 0.2%). No other product was obtained in a pure state. The products **3** and **4** were also obtained by the reaction with acetic acid, *vide infra*. 8-Allyl-2-ethoxycarbonyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (**3**), mp 29.0—29.5 °C (hexane). MS *m/z*: 269 (M^+, 100), 240 (25), 229 (14), 196 (51), 173 (94). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ε): 213 (4.39), 241 (4.47), 290 (sh), 300 (4.36), 325 (sh). IR (KBr): 3075, 1706, 1637, 1218, 745 cm^{-1}. ^{1}H-NMR δ: 1.38 (3H, t, *J*=7 Hz, $C\underline{H}_3CH_2O$), 2.18 (2H, m, H-5), 2.93 (2H, t, *J*=6 Hz, H-6), 3.45 (2H, d, *J*=6.5 Hz, H-10), 4.37 (2H, q, *J*=7Hz, $OC\underline{H}_2Me$), 4.53 (2H, t, *J*=5 Hz, H-4), 4.95—5.18 (1H, m, H-12), 6.05 (1H, tdd, *J*=6.5, 9.0, 17.5 Hz, H-11), 6.88 (1H, br s, H-7), 7.15 (2H, s, H-1), 7.28 (1H, br s, H-9). 7-Allyl-2-ethoxycarbonylindole (**4**), mp 95.0—95.5 °C (petroleum ether). MS *m/z*: 229 (M^+, 100), 183, 155. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ε): 233 (4.56), 293 (4.47). IR (KBr): 3355, 1695, 1638, 1200 cm^{-1}. ^{1}H-NMR δ: 1.37 (3H, t, *J*=7.1 Hz, $C\underline{H}_3CH_2O$), 3.67 (2H, d, *J*=6.4 Hz, H-8), 4.36 (2H, q, *J*=7.1 Hz, $OC\underline{H}_2Me$), 5.09 (1H, qd, *J*=1.7, 10.3 Hz, H-10), 5.14 (1H, qd, *J*=1.7, 17.1 Hz, H-11), 6.09 (1H, tdd, *J*=6.6, 10.3, 17.1 Hz, H-9), 7.07 (1H, t, *J*=7.1 Hz, H-5), 7.13 (1H, dd, *J*=1.9, 7.1 Hz, H-6), 7.18 (1H, d, *J*=1.9 Hz, H-3), 7.55 (1H, dd, *J*=1.9, 7.1 Hz, H-4), 9.75 (1H, br, NH). The crude product B was chromatographed (silica gel, chloroform) and separated into three fractions. The first eluate contained the unspecified product A. The second fraction contained another unspecified product B, colorless needles, mp 108—114 °C (dec.) (methanol–acetone). The third fraction was obtained by evaporation of the methanol eluate. This fraction was treated with benzene to crystallize the unspecified product C (19 mg), colorless needles, mp 118—119 °C (methanol–acetone). The soluble part was crystallized from petroleum ether and the ketone **6a** (19 mg), mp 66—69 °C was isolated. The crude product B obtained by the similar reaction of **1b** (0.573 g) was acetylated with pyridine and acetic anhydride and chromatographed to obtain three fractions. The sublimation of the first eluate at 105 °C (28 mmHg) gave 5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (**5**) (8.8 mg, 2.8%), mp 85.5—86.0 °C.[11] The second fraction was a complex mixture. The third fraction, the methanol eluate, was chromatographed again on alumina to isolate the unspecified products A (76 mg) and B (11 mg). The hydrazone **1b** (1.08 g) in acetic acid (16 ml) was warmed at 90 °C for 3 h. The reaction mixture was diluted with water and extracted to give the product (233 mg). The aqueous layer was concentrated and the residual solution was extracted with ethyl acetate to give the product (107 mg). Both products were combined and chromatographed to give the indole **3** (197 mg, 18.3%) as the first fraction and the second eluate (25 mg) which was purified by flash column chromatography to give the indole **4** (9.6 mg, 1.1%).

Transformation of the Ester 3 into 8-Allyllilolidine[9] 1) The ester **3** (366 mg) was dissolved in a mixture of potassium hydroxide (1.0 g), water (5 ml) and ethanol (15 ml) and the solution was refluxed for 5 h under nitrogen. The reaction mixture was concentrated and acidified, and the resulting crystals were collected. The filtrate was extracted with ethyl acetate. The combined yield of the acid was 319 mg (97%). 8-Allyl-2-carboxy-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline, mp 205.5—206.0 °C (dec.) (acetone–hexane). IR (KBr): 2600, 1665, 1245, 917, 757 cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 2.19 (2H, m, H-5), 2.93 (2H, t, *J*=6.1 Hz, H-6), 3.42 (2H, d, *J*=6.6 Hz, H-10), 4.52 (2H, t, *J*=5.7 Hz, H-4), 4.99 (1H, m, H-12), 5.09 (1H, d, *J*=17.1 Hz, H-12), 6.00 (1H, tdd, *J*=6.6, 10.2, 17.1 Hz, H-11), 6.86 (1H, br s, H-7), 7.11 (1H, s, H-1), 7.25 (1H, br s, H-9).

2) The acid (149 mg) was gradually heated to 210 °C and kept at this temperature for 0.5 h. Sublimation of the reaction product at 210 °C (17 mmHg) and chromatographic purification of the sublimation residue yielded 8-allyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline as an oil (110 mg, 95%). MS *m/z*: 197 (M^+, 100), 196 (64), 170 (19), 168 (10). IR ($CHCl_3$): 3070, 1638, 1498, 1330, 915 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 2.17 (2H, m, H-5), 2.95 (2H, t, *J*=6 Hz, H-6), 3.53 (2H, d, *J*=6.5 Hz, H-10), 4.15 (2H, t, *J*=5.5 Hz, H-4), 5.01, 5.18 and 5.30 (2H, each m, H-12), 6.10 (1H, tdd, *J*=6.5, 9.5, 17 Hz, H-11), 6.38 (1H, d, *J*=3 Hz, H-1), 6.78 (1H, s, H-7), 7.03 (1H, d, *J*=3 Hz, H-2), 7.28 (1H, s, 9-H).

3) This indole (113 mg) and sodium cyanoborohydride (108 mg) were dissolved in methanol (5 ml). Under vigorous stirring, a drop of methyl orange solution was added, then 2 N hydrochloric acid in methanol was introduced so as to keep the solution acidic. When the solution remained acidic, it was stirred overnight. The reaction mixture was evaporated and the residue was basified with 1 N sodium hydroxide and extracted. The product (107 mg, 94%) was identical with authentic 8-allyl-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline[9] according to IR and ^{1}H-NMR spectral comparisons. This amine was transformed into the picrate (132 mg), mp 140.0—141.0 °C and identified form the IR spectrum.

Preparation of 7-Allyl-2-ethoxycarbonylindole (4) 1) A mixture of methyl indoline-2-carboxylate (4.70 g, 26.5 mmol), allyl bromide (4.80 g, 39.8 mmol) and potassium carbonate (2.23 g, 26.5 mmol) in acetonitrile (130 ml) was stirred at room temperature for 2 d. The reaction mixture was evaporated and the residue was diluted with water and extracted with ether. The crude product was purified by column chromatography (silica gel, dichloromethane) to give methyl 1-allylindoline-2-carboxylate as a liquid (4.3 g, 75%). MS *m/z*: 217 (M^+, 17), 152 (100), 143 (4), 130 (8), 117 (38), 84 (17). IR (neat): 1751, 1608, 1486, 1203, 995, 923, 746 cm^{-1}. ^{1}H-NMR δ: 3.13 (1H, dd, *J*=8.9, 15.7 Hz, H-3), 3.35 (1H, dd, *J*=10.1, 15.7 Hz, H-3), 3.75 (3H, s, $COOCH_3$), 3.66—3.97 (2H, m, $NC\underline{H}_2CH=$), 4.26 (1H, dd, *J*=8.9, 10.1 Hz, H-2), 5.15—5.30 (2H, m, $\underline{H}_2C=CH$), 5.25—5.95 (1H, m, $H_2C=C\underline{H}CH_2$), 6.51 (1H, d, *J*=7.8 Hz, H-7), 6.66 (1H, t, *J*=7.4 Hz, H-5), 7.02 (1H, d, *J*=6.8 Hz, H-4), 7.06 (1H, t, *J*=7.5 Hz, H-6). ^{13}C-NMR δ: 33.4 (C-3), 50.7 (t), 52.0 (q), 64.8 (C-2), 107.4 (C-7), 117.8 (t), 118.1 (C-5), 124.0 (C-6), 126.8 (s), 127.6 (C-4), 133.0 (d), 150.7 (s), 173.2 (s, CO).

2) Boron trifluoride etherate (0.79 ml, 6.4 mmol) was slowly introduced into a mixture of the above ester (1.40 g, 6.4 mmol) and hydroquinone (0.07 g) at 0 °C with exclusion of moisture. Then the reaction mixture was heated at 160 °C for 1.2 h. Aqueous potassium carbonate was added to the reaction mixture while hot, then the solution was extracted with ether after it had cooled. The crude product was flash-chromatographed to give three fractions: methyl 7-allyl-1-methylindoline-2-carboxylate as the first fraction (oil, 0.4 g, 28%), an impure fraction and methyl 7-allylindoline-2-carboxylate as the third fraction (oil, 0.2 g, 14%). The impure fraction was methylated with a mixture of 35% formalin, sodium cyanoborohydride and acetic acid in acetonitrile. Chromatography of the product gave the same compound as from the first fraction and 5-allyl-2-methoxycarbonylindole as a solid. ^{1}H-NMR δ: 3.64 (2H, d, *J*=6.3 Hz, $C\underline{H}_2CH=$),

3.93 (3H, s, $COOCH_3$), 5.16—5.28 (2H, m, $\underline{H}_2C=CH$), 6.06 (1H, tdd, J=6.3, 10.2, 16.8 Hz, $CH_2C\underline{H}=CH_2$), 7.11 (1H, d, J=6.8 Hz, H-7), 7.12 (1H, d, J=2.2 Hz, H-4), 7.21 (1H, d, J=1.9 Hz, H-3), 7.51 (1H, dd, J=2.2, 6.8 Hz, H-6). ^{13}C-NMR δ: 36.2 (t), 52.0 (q), 109.2 (C-3), 116.8 (t), 120.9 (C-6), 121.1 (C-4), 123.0 (s), 125.2 (C-7), 127.0 (C-5), 127.6 (s), 135.9 (d), 136.3 (s), 162.4 (s, CO). Methyl 7-allyl-1-methylindoline-2-carboxylate: MS *m/z*: 231 (M$^+$, 20), 172 (100), 131 (30). IR ($CHCl_3$): 1743, 1457 cm^{-1}. ^{1}H-NMR δ: 2.97 (3H, s, $COOCH_3$), 3.07 (1H, dd, J=9.2, 15.8 Hz, H-3), 3.37 (1H, dd, J=10.2, 15.8 Hz, H-3), 3.46 (2H, d, J=5.8 Hz, H-8), 3.77 (3H, s, NCH_3), 3.96 (1H, dd, J=9.2, 10.2 Hz, H-2), 4.97—5.14 (2H, m, $\underline{H}_2C=CH$), 6.03 (1H, tdd, J=5.8, 10.2, 16.8 Hz, $H_2C=C\underline{H}CH_2$), 6.70 (1H, t, J=7.3 Hz, H-5), 6.88 (1H, d, J=8.3 Hz, H-4), 6.93 (1H, br d, J=8.3 Hz, H-6). ^{13}C-NMR δ: 33.1 (C-3), 36.2 (t), 40.2 (q), 52.1 (q), 69.2 (C-2), 116.0 (t), 119.8 (C-5), 121.9 (s), 122.3 (C-6), 128.6 (s), 130.5 (C-4), 137.4 (d), 149.9 (s), 173.5 (s, CO). Methyl 7-allylindoline-2-carboxylate: IR ($CHCl_3$): 3357, 3364, 1708, 1441, 1000, 922 cm^{-1}. ^{1}H-NMR δ: 3.30 (2H, br d, J=6.3 Hz, $C\underline{H}_2CH=$), 3.31—3.39 (2H, m, H-3), 3.73 (3H, s, $COOCH_3$), 4.37 (1H, dd, J=6.3, 9.2 Hz, H-2), 5.16 (br s), 5.07—5.11 (2H, m, $\underline{H}_2C=CH$), 5.85—6.05 (1H, m, $CH_2C\underline{H}=CH_2$), 6.72 (1H, t, J=7.4 Hz, H-5), 6.89 (1H, br d, J=7.5 Hz, H-4), 6.98 (1H, br d, J=7.3 Hz, H-6). ^{13}C-NMR δ: 33.8 (C-3), 36.2 (t), 52.4 (q), 59.7 (C-2), 116.0 (t), 119.8 (C-5), 121.3 (s), 122.57 (C-6), 126.7 (s), 128.1 (C-4), 135.8 (d), 148.74 (s), 174.6 (s, CO).

3) A mixture of methyl 7-allylindoline-2-carboxylate (188 mg, 0.8 mmol) and dichlorodicyano-*p*-benzoquinone (237 mg, 1 mmol) in benzene (17 ml) was stirred overnight at room temperature. The reaction mixture was evaporated and the residue was dissolved in dichloromethane and chromatographed to give 7-allyl-2-methoxycarbonylindole, mp 241—242 °C (cyclohexane). HRMS Calcd for $C_{13}H_{13}NO_2$: 215.0946. Found: 215.0964. MS *m/z*: 215 (M$^+$, 83), 182 (23), 156 (44), 155 (100), 154 (72), 123 (47), 115 (28). IR (KBr): 3328, 1703, 1538, 1444, 1289, 1255, 1210, 997, 910, 826, 785, 753, 741 cm^{-1}. ^{1}H-NMR δ: 3.65 (2H, d, J=6.3 Hz, $C\underline{H}_2CH=$), 3.93 (3H, s, $COOCH_3$), 5.16—5.28 (2H, m, $\underline{H}_2C=CH$), 6.06 (1H, tdd, J=6.3, 10.2, 16.8 Hz, $CH_2C\underline{H}=CH_2$), 7.09 (1H, t, J=7.1 Hz, H-5), 7.12—7.16 (1H, m, H-6), 7.22 (1H, d, J=1.9 Hz, H-3), 7.57 (1H, dd, J=2.0, 6.8 Hz, H-4), 8.88 (1H, br s, NH). ^{13}C-NMR δ: 36.3 (t), 52.0 (q), 109.1 (C-3), 116.8 (t), 120.9 (C-4), 121.1 (C-5), 123.0 (s), 125.2 (C-6), 126.9 (C-7), 127.6 (s), 135.8 (d), 136.3 (s), 162.4 (s).

4) The methyl ester (59 mg, 0.28 mmol) was treated with sodium ethoxide in ethanol and the mixture was stirred overnight. After gradual concentration to half volume, the solution was evaporated under reduced pressure. The residue was acidified with 1 N hydrochloric acid then basified with sodium carbonate. Extraction with ether gave the product (3 mg), which was identified as the ethyl ester **4** from its ^{1}H-NMR spectrum. The basic aqueous layer was acidified and extracted to afford 7-allylindole-2-carboxylic acid (35 mg), mp 168.5—169.5 °C (isopropyl ether). MS *m/z*: 201 (M$^+$, 30), 183 (11), 156 (27), 155 (41), 154 (40), 128 (32), 115 (17), 43 (100). IR (KBr): 3423, 3090—2400, 1680, 1640, 1542, 1247, 934, 820, 748 cm^{-1}. ^{1}H-NMR (CD_3OD) δ: 3.66 (2H, d, J=6.3 Hz, $C\underline{H}_2CH=$), 5.05—5.16 (2H, m, $\underline{H}_2C=CH$), 6.08 (1H, tdd, J=6.3, 10.2, 16.8 Hz, $CH_2C\underline{H}=CH_2$), 7.01 (1H, t, J=7.0 Hz, H-5), 7.05—7.09 (1H, m, H-6), 7.18 (1H, d, J=1.4 Hz, H-3), 7.49 (1H, dd, J=2.2, 6.8 Hz, H-4). ^{13}C-NMR δ: 36.2 (t), 110.1 (C-3), 116.2 (t), 121.3 (C-4), 121.6 (C-5), 125.2 (s), 125.6 (C-6), 128.9 (s), 129.2 (s), 137.6 (d), 137.9 (s), 165.1 (s, CO).

Typical One-Pot Reaction for the Preparation of 6a from the Hydrazone 1b A solution of the hydrazone **1b** (50 mg, 1.7 mmol) and 10% sulfuric acid in ethanol (10 ml) was refluxed at 110 °C (bath temperature) for 1 h. After the solution had cooled, 30% potassium hydroxide (10 ml) was added and the resulting solution was refluxed for 2 h. The reaction mixture was evaporated and the residue was extracted in a Soxlet apparatus to give the extract (304 mg), which was chromatographed (silica gel, dichloromethane) to give 2-acetonyl-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (**6a**), mp 69.0 °C (petroleum ether). HRMS Calcd for $C_{14}H_{17}NO$: 215.1308. Found: 215.1299. MS *m/z*: 215 (M$^+$, 18), 158 (100), 130 (25). IR (KBr): 3048, 2840, 1714, 1600, 1481, 1457, 1372, 1340, 1139, 759 cm^{-1}. ^{1}H-NMR δ: 2.06 (2H, m, H-5), 2.11 (3H, s, H-12), 2.55 (1H, dd, J=10.3, 16.7 Hz, H-10), 2.66 (2H, br t, J=6.6 Hz, H-6), 2.98 (1H, dd, J=4.5, 16.7 Hz, H-10), 3.11—3.23 (2H, m, H-4), 3.73 (1H, dtd, J=4.5, 8.1, 10.3 Hz, H-2), 6.60 (1H, t, J=7.3 Hz, H-8), 6.80 (1H, d, J=7.3 Hz, H-7), 6.88 (1H, d, J=7.3 Hz, H-9). ^{13}C-NMR δ: 23.1 (C-5), 23.9 (C-6), 30.8 (C-12), 35.8 (C-1), 45.2 (t), 47.2 (t), 62.5 (C-2), 118.5 (d), 119.3 (s), 121.7 (d), 126.2 (d), 127.3 (d), 149.2 (s), 207.3 (s).

2-(1,2,5,6-Tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolyl)acetophenone (6b) Syrup. HRMS Calcd for $C_{19}H_{19}NO$: 277.1466. Found: 277.1484. MS *m/z*: 277 (M$^+$, 10), 159 (13), 158 (100), 157 (24), 156 (9), 130 (17). IR (neat): 3051, 2839, 1685, 1600, 1482, 1210, 753 cm^{-1}. ^{1}H-NMR δ: 2.06 (2H, m, H-5), 2.56—2.77 (4H, m, H-1 + H-6), 3.13—3.33 (3H, m, H-4 + H-10), 3.52 (1H, dd, J=4.2, 16.8 Hz, H-10), 3.96 (1H, m, H-2), 6.61 (1H, t, J=7.1 Hz, H-8), 6.82 (d, J=7.6 Hz, Ar-H), 6.89 (1H, d, J=7.3 Hz, H-7), 7.42—7.62 (3H, m, Ar-H), 7.98 (2H, d, J=8.1 Hz, H-9). ^{13}C-NMR δ: 23.1 (C-5), 23.9 (C-6), 36.1 (C-1), 42.4 (t), 45.3 (t), 63.0 (C-2), 118.5 (d), 119.3 (s), 121.7 (d), 126.2 (d), 127.4 (s), 128.0 (d×2), 128.6 (d×2), 133.2 (d), 137.0 (s), 149.3 (s), 198.7 (s).

***In Situ* Preparation of 1f and Its One-Pot Reaction** 8-Allyl-1-amino-THQ (500 mg, 2.7 mmol) and glyoxylic acid monohydrate (300 mg, 3.3 mmol) were dissolved in 0.2% sulfuric acid in ethanol (5 ml) and the mixture was stirred at room temperature for 2 h. Then sulfuric acid (0.24 ml) was slowly added and the acidic solution was refluxed at 120 °C (bath temperature) for 4 h. After the solution had cooled, 30% potassium hydroxide (5 ml) was added and the basic solution was refluxed for 4 h. Work-up and purification as described above gave 5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (**5**) (155 mg, 37%), which was identified from its ^{1}H-NMR spectrum.

Preparation of the Hydrazone 11 1) A mixture of *N*-allyl-*N*-benzylaniline (10.0 g, 44.8 mmol), *p*-benzoquinone (0.5 g) and boron trifluoride etherate (12.70 g, 90 mmol) was gradually heated up to 170 °C and the volatile fraction was removed under exclusion of moisture. The reaction was continued at 170 °C for 2 h. After the reaction mixture had cooled, water and 30% sodium hydroxide were added and the resulting solution was extracted with ether. The crude product (10.5 g) was chromatographed to give *N*-benzyl-2-allylaniline as a colorless oil (94.7%). HRMS: Calcd for $C_{16}H_{17}N$: 223.1360. Found: 223.1349. MS *m/z*: 223 (M$^+$, 35), 221 (29), 220 (90), 206 (13), 144 (17), 132 (72), 117 (27), 91 (100). IR (neat): 3438, 3063, 3030, 2843, 1634, 1604, 1586, 1510, 1452, 1323, 1259, 916, 749, 698 cm^{-1}. ^{1}H-NMR δ: 3.30 (2H, d, J=6.1 Hz, allylic CH_2), 4.12 (1H, br s, NH), 4.32 (2H, s, benzylic CH_2), 5.02—5.22 (2H, m, $\underline{H}_2C=CH$), 5.95 (1H, tdd, J=6.2, 10.4, 16.5 Hz, $CH_2=C\underline{H}CH_2$), 6.61 (1H, d, J=8.1 Hz, Ar-H), 6.70 (1H, dt, J=1.0, 10.7 Hz, Ar-H), 7.03—7.16 (2H, m, Ar-H), 7.16—7.34 (5H, m, Ar-H). ^{13}C-NMR δ: 36.5 (t), 46.1 (t), 110.7 (d), 116.3 (t), 117.4 (d), 123.5 (s), 127.1 (d), 127.3 (d×2), 127.6 (d), 128.5 (d×2), 129.8 (d), 135.9 (d), 139.4 (s), 146.1 (s).

2) This amine was subjected to the same reaction as described for the preparation of **1**. *N*-Benzyl-*N*-carbamoyl-2-allylaniline (79.5%), mp 106.0—106.5 °C, was transformed to the *N*-amino compound, which was coupled with ketones to give the hydrazones **11**. *N*-Amino-*N*-benzyl-2-allylaniline, red syrup (94.0%). MS *m/z*: 223 (7), 221 (15), 220 (15), 179 (4), 146 (7), 144 (6), 132 (19), 130 (19), 118 (32), 91 (100). IR (neat): 3337, 3063, 3029, 2827, 1637, 1603, 1489, 1452, 913, 887, 762, 737, 699 cm^{-1}. ^{1}H-NMR δ: 3.34 (2H, s, NH_2), 3.63 (2H, d, J=6.4 Hz, allylic CH_2), 4.11 (2H, s, benzylic CH_2), 5.05—5.15 (2H, m, $\underline{H}_2C=CH$), 6.05 (1H, tdd, J=6.6, 9.5, 17.8 Hz, $CH_2C\underline{H}=CH_2$), 7.03—7.41 (9H, m, Ar-H). ^{13}C-NMR δ: 35.1 (t), 64.9 (t), 115.7 (t), 119.5 (d), 124.3 (d), 126.8 (d), 127.4 (d), 138.5 (d×2), 128.7 (d×2), 130.1 (d), 134.1 (s), 137.6 (s), 137.7 (d), 151.5 (s).

11a: Yellow syrup (94.9%). MS *m/z*: 336 (M$^+$, 4), 263 (4), 245 (72), 222 (11), 220 (10), 171 (15), 131 (23), 130 (100), 91 (49). IR (neat): 3064, 3029, 2979, 1703, 1639, 1574, 1307, 1142, 728 cm^{-1}. ^{1}H-NMR δ: 1.34 (3H, t, J=7.2 Hz, $C\underline{H}_3CH_2O$), 1.42 (3H, s, $CH_3C=N$), 3.38 (2H, d, J=6.6 Hz, H-7), 4.26 (2H, q, $OC\underline{H}_2Me$), 4.66 (2H, s, benzylic CH_2), 5.02—5.12 (2H, m, H-9), 5.85 (1H, tdd, J=6.6, 10.6, 17.1 Hz, H-8), 6.76 (1H, dd, J=1.2, 7.8 Hz, H-6), 7.04 (1H, ddd, J=1.8, 7.3, 7.8 Hz, H-5), 7.14 (1H, ddd, J=1.2, 7.3, 7.6 Hz, H-4), 7.23 (1H, dd, J=1.8, 7.6 Hz, H-3), 7.23—7.32 (5H, m, Ar-H). ^{13}C-NMR δ: 14.3 (q), 15.6 (q), 35.1 (t), 61.1 (t), 64.9 (t), 116.7 (t), 126.4 (d), 126.7 (d×2), 127.3 (d), 128.0 (d×2), 129.4 (d×2), 130.1 (d), 135.7 (s), 136.0 (d), 137.4 (s), 139.5 (s), 147.2 (s), 165.8 (s).

11b: *Z*-Isomer: syrup (72.2%). HRMS Calcd for $C_{25}H_{24}N_2O_2$ 384.1835. Found: 384.1814. MS *m/z*: 384 (M$^+$, 13), 325 (17), 293 (55), 261 (52), 220 (27), 130 (100), 91 (71). IR (neat): 3057, 3032, 2856, 1724, 1639, 1224, 1054, 928, 728 cm^{-1}. ^{1}H-NMR δ: 3.11 (3H, s, $COOCH_3$), 3.42 (2H, d, J=6.6 Hz, H-7), 4.69 (2H, s, benzylic CH_2), 5.04—5.14 (2H, m, H-9), 5.92 (1H, tdd, J=6.6, 10.7, 16.4 Hz, H-8), 6.74—7.53 (14H, Ar-H). ^{13}C-NMR δ: 35.2 (t), 51.1 (q), 64.6 (t), 116.6 (t), 125.4 (d×2), 126.7 (d), 127.3 (d×2), 127.8 (d), 128.1 (d×3), 128.3 (d×2), 129.2 (d×2), 129.6 (d), 135.3 (s), 136.5 (d), 137.5 (s), 137.7 (s), 144.8 (s), 165.6 (s). *E*-Isomer: syrup (26.7%). HRMS Calcd for $C_{25}H_{24}N_2O_2$: 384.1835. Found: 384.1853. MS *m/z*: 384 (M$^+$, 4), 325 (6), 293 (18), 261 (16), 222 (21), 220 (20), 132 (44), 130 (97), 105 (79), 91 (100). IR (neat): 3062, 3029, 2948, 1708, 1639, 1299, 1214, 1138, 726, 699 cm^{-1}. ^{1}H-NMR δ: 3.09 (2H, d, J=6.6 Hz, H-7), 3.78 (3H, s, $COOCH_3$), 4.77 (2H, s, benzylic CH_2), 4.94—5.09 (2H, m, H-9), 5.68 (1H, tdd, J=6.5, 10.1, 16.7 Hz, H-8), 6.50—7.32 (14H, Ar-H). ^{13}C-NMR δ: 35.4 (t), 52.3 (q), 64.7 (t), 116.6 (t), 126.3 (d), 126.5 (s), 126.9 (d $\times$ 2), 127.3 (d $\times$ 2), 127.5 (d), 128.2 (d $\times$ 2), 128.9 (d $\times$ 2), 129.0 (d $\times$ 2), 129.4 (d), 130.3 (d), 133.9 (s), 135.5 (s), 136.2 (d), 137.1 (s), 144.9 (s), 166.1 (s). The *E*-isomer isomerizes in solution to form a mixture of isomers.

11c: Colorless crystals (74.6%), mp 52.0—52.5 °C (hexane). HRMS Calcd for $C_{23}H_{22}N_2$: 326.1782. Found: 326.1820. MS *m*/*z*: 326 (M$^+$, 8), 235 (100), 222 (24), 220 (14), 130 (57), 91 (48). IR (KBr): 3061, 2856, 1641, 1589, 1561, 1348, 1129, 949, 755, 693 cm^{-1}. ^{1}H-NMR δ: 3.34 (2H, d, J = 6.6 Hz, H-7), 4.86 (2H, s, benzylic CH_2), 4.94—5.04 (2H, m, H-9), 5.82 (1H, tdd, J = 6.6, 10.5, 17.1 Hz, H-8), 6.95 (1H, s, CH = N), 6.97—7.50 (14H, Ar-H). ^{13}C-NMR δ: 35.5 (t), 60.1 (t), 116.0 (t), 125.7 (d $\times$ 2), 126.5 (d), 126.9 (d), 127.1 (d), 127.3 (d), 127.5 (d), 128.1 (d $\times$ 2), 128.3 (d $\times$ 4), 130.3 (d), 133.7 (d), 136.6 (s), 136.9 (s), 137.6 (s), 137.7 (s), 144.4 (s).

11d: The reaction to prepare this hydrazone in 60% acetic acid yielded only a complex mixture. Thus the following procedure was employed. A mixture of *N*-amino-*N*-benzyl-2-allylaniline (500 mg, 2.1 mmol) and 90% acetaldehyde (0.26 ml, 4.2 mmol) in ethanol (5 ml) was stirred at room temperature for 5 min then the mixture was evaporated without heating. The residue was chromatographed to give **11d** (90.9%) as a pale yellow oil. MS *m*/*z*: 174 (40), 149 (10), 132 (24), 131 (66), 126 (24), 91 (100). IR (neat): 3421 (br), 3063, 3029, 2848, 1638, 1598, 1489, 1453, 915, 762, 727, 699 cm^{-1}. ^{1}H-NMR δ: 1.83 (3H, d, J = 5.1 Hz, $C\underline{H}_3CH=$), 3.32 (2H, d, J = 6.6 Hz, H-7), 4.66 (2H, s, benzylic CH_2), 4.91—5.03 (2H, m, H-9), 5.80 (1H, tdd, J = 6.7, 10.6, 17.2 Hz, H-8), 6.37 (1H, q, J = 5.3 Hz, $N=C\underline{H}Me$), 7.06—7.33 (9H, m, Ar-H). ^{13}C-NMR δ: 18.6 (q), 35.2 (t), 59.9 (t), 115.7 (t), 125.7 (d), 126.3 (d), 126.8 (d), 127.4 (d), 128.0 (d $\times$ 2), 128.2 (d $\times$ 2), 130.0 (d), 135.1 (d), 137.2 (d), 137.6 (s), 138.0 (s), 145.9 (s).

2-(*N*-Benzylindolinyl)acetophenone (12) Colorless syrup (21.3%). HRMS Calcd for $C_{23}H_{21}NO$: 327.1622. Found: 327.1643. MS *m*/*z*: 327 (M$^+$, 5), 208 (31), 173 (94), 132 (29), 130 (16), 91 (100). IR (neat): 3028, 2848, 1684, 1606, 1484, 1452, 1367, 1266, 1209, 751, 697 cm^{-1}. ^{1}H-NMR δ: 2.71 (1H, dd, J = 8.1, 15.9 Hz, H-3), 3.15 (1H, dd, J = 9.3, 16.8 Hz, H-8), 3.40 (1H, dd, J = 3.7, 16.8 Hz, H-8), 3.44 (1H, dd, J = 8.8, 15.9 Hz, H-3), 4.24 (1H, dq, J = 3.7, 8.7 Hz, H-2), 4.30 and 4.36 (2H, each d, J = 16.6 Hz, benzylic CH_2), 6.37 (1H, d, J = 7.8 Hz, H-7), 6.65 (1H, dt, J = 0.7, 7.3 Hz, Ar-H), 6.97—7.57 (10H, m, Ar-H), 7.80—7.85 (2H, m, Ar-H). ^{13}C-NMR δ: 36.0 (C-3), 43.4 (C-8), 51.9 (benzylic C), 61.4 (C-2), 107.0 (C-7), 117.8 (C-5), 124.3 (C-6), 127.0 (C-4), 127.2 (d $\times$ 2), 127.4 (d), 127.9 (d $\times$ 2), 128.3 (s), 128.5 (d $\times$ 4), 133.1 (d), 136.8 (s), 138.9 (s), 152.0 (s), 198.6 (s).

(2*SR*,3a*SR*)-1-Benzyl-2-methyl-2,3,3a,4-tetrahydro-1*H*-pyrazolo[2,3-*a*]indole (13a) Syrup (76.7%). HRMS Calcd for $C_{18}H_{20}N_2$: 264.1625. Found: 264.1590. MS *m*/*z*: 264 (M$^+$, 6), 174 (26), 173 (100), 132 (58), 130 (33). IR (neat): 3027, 2937, 1604, 1594, 1477, 1459, 1265, 763, 734, 698 cm^{-1}. ^{1}H-NMR δ: 1.23 (3H, d, J = 6.6 Hz, H-9), 1.82 (1H, ddd, J = 3.9, 7.3, 12.6 Hz, H-3), 2.09 (1H, ddd, J = 9.7, 10.6, 12.6 Hz, H-3), 2.95 (1H, dd, J = 2.7, 16.1 Hz, H-4), 3.17 (1H, dd, J = 9.0, 16.1 Hz, H-4), 3.22 (1H, qdd, J = 6.6, 7.3, 9.7 Hz, H-2), 3.55 and 3.92 (2H, each d, J = 12.9 Hz, benzylic CH_2), 4.30 (1H, dddd, J = 2.7, 3.9, 9.0, 9.7 Hz, H-3a), 6.5—7.5 (9H, m, Ar-H).

Decoupling Experiment: Irradiation at δ 4.30 changed the couplings of the following signals: δ 1.82, dd, J = 7.3, 12.5 Hz; δ 2.09, dd, J = 10.6, 12.6 Hz; 2.95, d, J = 16 Hz; δ 3.17, d, J = 16.1 Hz. ^{13}C-NMR δ: 15.7 (C-10), 35.9 (C-4), 41.6 (C-3), 53.2 (benzylic C), 57.8 (C-2), 61.2 (C-3a), 114.4 (C-8), 121.5 (C-6), 124.2 (C-5), 126.5 (d), 127.4 (C-7), 128.0 (d $\times$ 2), 128.9 (d $\times$ 2), 129.1 (C-4a), 140.3 (s), 152.7 (C-8a).

Transformation of 13b into 13a The amine **13b** (100 mg, 0.6 mmol) was allowed to react with benzoyl chloride (0.135 ml, 1.2 mmol) and triethylamine (0.4 ml) in dichloromethane overnight to give the *N*-benzoyl product, which was dissolved in dry THF (5 ml) and dropped into a solution of lithium aluminum hydride (45 mg, 1.2 mmol) in dry ether (10 ml). The resulting mixture was stirred at room temperature for 3 h, then worked up. The crude product was purified by chromatography to give **13a** (110 mg, 72.3%), which was identical with the specimen obtained by the one-pot reaction of **11d** on the basis of comparisons of ^{1}H- and ^{13}C-NMR spectra.

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