Supporting Information

Facile Synthesis of Polycyclic Indole Derivatives: The Generation and Reaction of Tungsten-Containing Azomethine Ylides

Hiroyuki Kusama, Jun Takaya, and Nobuharu Iwasawa*

Department of Chemistry, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152-8551, Japan

General. All operations were performed under an argon atmosphere. ^1H and ^{13}C -NMR spectra were recorded on a Bruker DRX-500 (500 MHz for ^1H and 125 MHz for ^{13}C) or a JEOL Lambda-400 (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer in CDCl_3 (99.8% atom enriched, Acros Co., Ltd.). Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual CHCl_3 (δ_{H} 7.26) for ^1H spectra and CDCl_3 for ^{13}C (δ_{C} 77.0). IR spectra were recorded on a IR-810 or a FT/IR-460 plus (JASCO Co., Ltd.). Photoirradiation was performed with a 250W super high-pressure mercury lamp (USHIO INC.). Silica Gel 60 (Kanto Chemical Co., Inc.) or Aluminum oxide 90 active neutral (activity I) (0.063-0.200 mm, Merck) was used for flash column chromatography. Merck Kieselgel 60 F_{254} (0.25 mm thickness, coated on glass 20_20 cm^2) plate was used for thin layer chromatography (TLC), and Wakogel B-5F coated on glass in a thickness of 0.7 mm was used for preparative TLC. THF was freshly distilled from benzophenone ketyl, and all other solvents were distilled according to the usual procedures and stored over Molecular Sieves. High resolution mass analyses (FAB) were performed on a JEOL JMS-700 mass spectrometer using NBA as matrix. Elemental analyses were performed on a Perkin-Elmer 2400 instrument.

General Experimental Procedures

General procedure for the preparation of aldimines derived from 2-(1-alkynyl)anilines and benzaldehyde (1a, 15a-c) :

(E)-N-benzylidene-2-ethynylaniline (1a)

To a stirred mixture of *o*-ethynylaniline (310 mg, 2.6 mmol) and MS5A (4.7 g) in toluene (4.0 mL) was added benzaldehyde (0.27 mL, 2.7 mmol) at room temperature. After 6 days, the reaction mixture was filtered through short pad of Celite and the filtrate was concentrated under reduced pressure. The resulting residue was purified by bulb-to-bulb distillation to give **1a** (400 mg, 74%) as a single isomer. The geometry was confirmed to be *E* by the observation of an NOE between the aldimine proton and the aromatic proton on 6-position.

IR (neat) 3061, 2103, 1632 cm^{-1}

MS (FAB⁺), *m/z* (relative intensity, %) 206 ($[\text{M}+1]^+$, 100), 205 (M^+ , 67).

^1H -NMR (400 MHz) δ = 3.21 (s, 1H), 7.04 (d, J = 8.0 Hz, 1H), 7.14-7.18 (m, 1H), 7.35-7.39 (m, 1H), 7.47-7.51 (m, 3H), 7.56 (d, J = 7.6 Hz, 1H), 7.94-7.96 (m, 2H), 8.46 (s, 1H).

^{13}C -NMR (100 MHz) δ = 81.2, 81.3, 115.1, 119.4, 125.1, 128.7, 129.0, 129.7, 131.6, 133.6, 135.9, 154.5, 162.1.

Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{N}$: C, 87.77; H, 5.40; N, 6.82. Found: C, 88.04; H, 5.64; N, 6.64.

Other aldimine derivatives (**15a-c**) were prepared according to the above procedure, but in the case of **15c**, the crude product was used without further purification.

(E)-N-benzylidene-2-(1-pentynyl)aniline (15a)

The geometry was confirmed to be *E* by the observation of an NOE between the aldimine proton and the aromatic proton on 6-position.

IR (neat) 3062, 2962, 2230, 1632 cm^{-1}

MS (FAB⁺), *m/z* (relative intensity, %) 248 ($[\text{M}+1]^+$, 100), 247 (M^+ , 56), 218 (11).

^1H -NMR (400 MHz) δ = 0.96 (t, J = 7.3 Hz, 3H), 1.51-1.57 (m, 2H), 2.36 (t, J = 7.1 Hz, 2H), 7.02 (dd, J = 7.8, 1.1 Hz, 1H), 7.11 (ddd, J = 7.8, 7.8, 1.1 Hz, 1H), 7.28 (ddd, J = 7.8, 7.8, 1.5 Hz, 1H), 7.45-7.50 (m, 4H), 7.92-7.94 (m, 2H), 8.46 (s, 1H).

^{13}C -NMR (100 MHz) δ = 13.4, 21.6, 22.1, 78.3, 94.7, 116.8, 119.5, 125.0, 128.4, 128.6, 128.9, 131.4, 132.9, 136.2, 153.8, 161.8.

Anal. Calcd for C₁₈H₁₇N: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.33; H, 7.18; N, 5.60.

(E)-N-benzylidene-2-(1-propynyl)aniline (15b)

The geometry was confirmed to be *E* by the observation of an NOE between the aldimine proton and the aromatic proton on 6-position.

IR (neat) 3061, 2913, 2237, 1630 cm⁻¹

MS (FAB⁺), *m/z* (relative intensity, %) 220 ([M+1]⁺, 100), 119 (M⁺, 29).

¹H-NMR (400 MHz) δ = 2.03 (s, 3H), 7.01 (brd, *J* = 7.8 Hz, 1H), 7.12 (ddd, *J* = 7.8, 7.8, 1.5 Hz, 1H), 7.29 (ddd, *J* = 7.8, 7.8, 1.5 Hz, 1H), 7.45-7.51 (m, 4H), 7.93-7.96 (m, 2H), 8.46 (s, 1H).

¹³C-NMR (100 MHz) δ = 4.6, 77.3, 90.2, 117.0, 119.4, 125.6, 128.4, 128.7, 128.9, 131.4, 133.0, 136.2, 153.7, 161.8.

HRMS Calcd for C₁₆H₁₃N, M 219.1048. Found *m/z* 219.1037.

(E)-N-benzylidene-2-(2-phenylethynyl)aniline (15c)

The geometry was confirmed to be *E* by the observation of an NOE between the aldimine proton and the aromatic proton on 6-position.

IR (neat) 3060, 1633, 1493 cm⁻¹

MS (FAB⁺), *m/z* (relative intensity, %) 282 ([M+1]⁺, 100), 281 (M⁺, 33), 204 (11).

¹H-NMR (400 MHz) δ = 7.09 (brd, *J* = 8.0 Hz, 1H), 7.19 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.25-7.30 (m, 3H), 7.36 (ddd, *J* = 7.8, 7.8, 1.5 Hz, 1H), 7.40-7.43 (m, 2H), 7.49-7.52 (m, 3H), 7.60 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.97-8.00 (m, 2H), 8.55 (s, 1H).

¹³C-NMR (100 MHz) δ = 87.3, 93.6, 116.1, 119.7, 123.5, 125.1, 128.1, 128.2, 128.8, 128.9, 129.2, 131.4, 131.6, 132.8, 136.1, 153.8, 162.1.

HRMS Calcd for C₂₁H₁₅N, M 281.1204. Found *m/z* 281.1176.

Preparation of imide derivatives (1b, c) :

(E)-Ethyl N-(2-ethynylphenyl)formimidate (1b)

A mixture of *o*-ethynylaniline (240 mg, 2.1 mmol), triethyl orthoformate (4.0 mL, 24 mmol), *p*-toluenesulfonic acid (8.5 mg, 0.045 mmol) and MS4A (1.8 g) in benzene (4.0 mL) was heated under reflux for 12 h, and was filtered through a short pad of Celite. The filtrate was concentrated under reduced pressure, and the resulting residue was purified by bulb-to-bulb distillation to give the imide (1b) (320 mg, 86%). The geometry was confirmed to be *E* by the observation of an NOE between the formimidic proton and the aromatic proton on 6-position.

IR (neat) 2981, 2104, 1647 cm⁻¹

MS (FAB⁺), *m/z* (relative intensity, %) 174 ([M+1]⁺, 100), 173 (M⁺, 47), 128 (45).

¹H-NMR (400 MHz) δ = 1.40 (t, *J* = 7.1 Hz, 3H), 3.19 (s, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 6.88 (brd, *J* = 7.8 Hz, 1H), 7.05 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.28 (ddd, *J* = 7.8, 7.8, 1.5 Hz, 1H), 7.48 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.72 (s, 1H).

¹³C-NMR (100 MHz) δ = 14.1, 62.6, 80.6, 81.5, 115.4, 121.1, 123.8, 129.6, 133.4, 150.2, 155.7.

Anal. Calcd for C₁₁H₁₁NO: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.19; H, 6.31; N, 8.00.

(Z)-Methyl N-(2-ethynylphenyl)acetimidate (1c)

The reaction of *o*-ethynylaniline and trimethyl orthoacetate was conducted under the similar reaction conditions described above and the crude mixture was purified by column chromatography (Aluminum oxide 90 active neutral) to give the title compound 1c in 82% yield. The geometry was assigned to be *Z* by the observation of an NOE of its ethyl ester analogue (between the methylene proton of ethyl ester and the aromatic proton on 6-position).

IR (neat) 2946, 2104, 1677 cm⁻¹

MS (FAB⁺), *m/z* (relative intensity, %) 173 (M⁺, 100), 149 (30), 142 (52), 101 (37).

¹H-NMR (400 MHz) δ = 1.82 (s, 3H), 3.13 (s, 1H), 3.84 (s, 3H), 6.77-6.79 (m, 1H), 6.99 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.27 (ddd, *J* = 7.8, 7.8, 1.4 Hz, 1H), 7.46 (dd, *J* = 7.8, 1.2 Hz, 1H).

¹³C-NMR (100 MHz) δ = 16.4, 53.5, 80.2, 81.3, 114.0, 121.2, 122.7, 129.6, 133.2, 151.2, 162.2.

Anal. Calcd for C₁₁H₁₁NO: C, 76.28; H, 6.40; N, 8.09. Found: C, 75.98; H, 6.35; N, 7.80.

General procedure for tungsten-catalyzed reaction of imine derivatives with ketene silyl acetal 3 :

A mixture of an imine derivative (0.10 mmol), ketene silyl acetal 3 (0.20 mmol) and tungstenhexacarbonyl (0.010 mmol) in toluene (5.0 ml) was irradiated with a 250W super high-pressure mercury lamp (USHIO INC.) at room temperature. After disappearance of the starting material, triphenylphosphine (0.010 mmol) was added to deactivate the

tungsten complex. 1N HCl aq. was added and the reaction mixture was extracted with ethyl acetate. Organic layer was dried with magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (hexane-ethyl acetate=3:1-5:1) to afford a polycyclic indole derivative.

3-Phenyl-2,3-dihydropyrrolo[1,2-*a*]indol-1-one (5a)

IR (neat) 3057, 2922, 1707, 1539 cm^{-1}

MS (FAB⁺), *m/z* (relative intensity, %) 247 (*M*⁺, 93), 143 (100), 115 (45).

¹H-NMR (400 MHz) δ = 3.06 (dd, *J* = 18.8, 3.9 Hz, 1H), 3.67 (dd, *J* = 18.8, 8.1 Hz, 1H), 5.72 (dd, *J* = 8.1, 3.9 Hz, 1H), 6.92-6.95 (m, 1H), 7.11-7.21 (m, 5H), 7.33-7.38 (m, 3H), 7.77-7.80 (m, 1H).

¹³C-NMR (100 MHz) δ = 50.2, 57.1, 99.1, 111.7, 121.5, 124.1, 125.2, 126.0, 128.5, 129.2, 132.4, 134.8, 136.2, 139.9, 192.0.

Anal. Calcd for C₁₇H₁₃NO: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.47; H, 5.19; N, 5.52.

3-Ethoxy-2,3-dihydropyrrolo[1,2-*a*]indol-1-one (5b)

Irradiated for 3 h (for 100 mol% of W(CO)₆) or 24 h (for 10 mol% of W(CO)₆).

IR (neat) 2978, 2928, 1718, 1543 cm^{-1}

MS (FAB⁺), *m/z* (relative intensity, %) 216 ([*M*+1]⁺, 100), 215 (*M*⁺, 70), 170 (29).

¹H-NMR (400 MHz) δ = 1.21 (t, *J* = 7.1 Hz, 3H), 3.10 (dd, *J* = 18.7, 1.6 Hz, 1H), 3.38 (dq, *J* = 9.0, 7.1 Hz, 1H), 3.40 (dd, *J* = 18.7, 6.2 Hz, 1H), 3.69 (dq, *J* = 9.0, 7.1 Hz, 1H), 6.20 (dd, *J* = 6.2, 1.6 Hz, 1H), 7.01 (d, *J* = 0.7 Hz, 1H), 7.23 (ddd, *J* = 8.2, 7.1, 0.9 Hz, 1H), 7.40 (ddd, *J* = 8.5, 7.1, 0.9 Hz, 1H), 7.58 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.77 (brd, *J* = 8.2 Hz, 1H).

¹³C-NMR (100 MHz) δ = 15.1, 46.7, 61.6, 82.2, 100.0, 111.6, 122.0, 124.2, 125.8, 132.6, 135.1, 135.7, 190.8.

Anal. Calcd for C₁₃H₁₃NO₂: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.25; H, 6.36; N, 6.23.

3-Methoxy-3-methyl-2,3-dihydropyrrolo[1,2-*a*]indol-1-one (5c)

Irradiated for 2h.

IR (neat) 3056, 2990, 1715, 1542 cm^{-1}

MS (FAB⁺), *m/z* (relative intensity, %) 216 ([*M*+1]⁺, 100), 215 (*M*⁺, 80), 184 (59), 144 (34), 99 (35).

¹H-NMR (400 MHz) δ = 1.99 (s, 3H), 2.94, (s, 3H), 3.10 (d, *J* = 19.3 Hz, 1H), 3.36 (d, *J* = 19.3 Hz, 1H), 7.00 (s, 1H), 7.23 (brdd, *J* = 8.4, 8.4 Hz, 1H), 7.41 (brdd, *J* = 8.4, 8.4 Hz, 1H), 7.64 (brd, *J* = 8.4 Hz, 1H), 7.79 (brd, *J* = 8.4 Hz, 1H).

¹³C-NMR (100 MHz) δ = 26.9, 49.9, 50.0, 90.0, 99.5, 112.6, 121.9, 124.3, 125.9, 132.7, 134.0, 136.9, 190.5.

Anal. Calcd for C₁₃H₁₃NO₂: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.51; H, 6.16; N, 6.26.

General procedure for tungsten-catalyzed reaction of imine derivatives with other electron-rich alkenes 7-10 :

To a mixture of an alkene (0.20 mmol) and tungstenhexacarbonyl (0.010 mmol) in toluene (4.0 ml) was added a solution of an imine derivative (0.10 mmol) in toluene (1.0 ml) over 1~2 h under photo-irradiation (a 250W super high-pressure mercury lamp (USHIO INC.)) at room temperature. The reaction mixture was further irradiated until disappearance of the starting material was confirmed by TLC. Triphenylphosphine (0.010 mmol) was added to deactivate the tungsten complex and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (hexane-ethyl acetate=3:1-10:1, or benzene-hexane=2:1) to afford polycyclic indole derivatives.

1-*t*-Butoxy-3-phenyl-2,3-dihydropyrrolo[1,2-*a*]indole (11)

Imine **1a** was added over 2 h and the mixture was further irradiated for 1 h.

11 was obtained as a 86:14 mixture of *cis* and *trans* isomers. The stereochemistry of the minor product was determined to be *trans* by the observed NOE shown below. Therefore, the major product was assigned to be the corresponding *cis* isomer.

cis-11 (major product)

IR (neat) 2973, 1454, 1363 cm^{-1}

MS (FAB⁺), *m/z* (relative intensity, %) 305 (*M*⁺, 100), 232 (53).

¹H-NMR (400 MHz) δ = 1.35 (s, 9H), 2.47 (ddd, *J* = 13.4, 7.3, 6.1 Hz, 1H), 3.27 (ddd, *J* = 13.4, 7.6, 7.6 Hz, 1H), 5.22-5.27 (m, 2H), 6.37 (s, 1H), 6.67 (brd, *J* = 8.3 Hz, 1H), 6.91 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.01 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H), 7.30-7.37 (m, 5H), 7.58 (brd, *J* = 8.0 Hz, 1H).

^{13}C -NMR (100 MHz) δ = 28.6, 48.9, 59.9, 67.7, 74.3, 93.9, 110.5, 119.4, 120.6, 121.0, 127.0, 127.9, 128.7, 132.1, 133.3, 140.7, 145.8.

HRMS Calcd for $\text{C}_{21}\text{H}_{23}\text{NO}$, M 305.1780. Found m/z 305.1778.

***trans*-11 (minor product)**

IR (neat) 2973, 1454, 1364 cm^{-1}

MS (FAB $^+$), m/z (relative intensity, %) 306 ($[\text{M}+1]^+$, 50), 305 (M^+ , 100), 232 (41)

^1H -NMR (400 MHz) δ = 1.34 (s, 9H), 2.77 (ddd, J = 13.2, 7.1, 5.5 Hz, 1H), 2.96 (ddd, J = 13.2, 7.8, 4.2 Hz, 1H), 5.30 (dd, J = 7.1, 4.2 Hz, 1H), 5.62 (dd, J = 7.8, 5.5 Hz, 1H), 6.39 (s, 1H), 6.74 (d, J = 8.2 Hz, 1H), 6.95 (dd, J = 8.2, 8.2 Hz, 1H), 7.03 (dd, J = 8.2, 8.2 Hz, 1H), 7.07-7.09 (m, 2H), 7.29-7.35 (m, 3H), 7.60 (d, J = 8.2 Hz, 1H).

^{13}C -NMR (100 MHz) δ = 28.5, 49.6, 59.4, 66.9, 74.4, 94.2, 110.6, 119.4, 120.8, 121.0, 126.2, 127.7, 128.9, 132.2, 133.3, 141.3, 145.8.

HRMS Calcd for $\text{C}_{21}\text{H}_{23}\text{NO}$, M 305.1780. Found m/z 305.1756.

Scheme 1

In the reaction of **1a** and **7**, 2:1 cycloadduct **19** and another 2:1 cycloadduct **20** were obtained as by-products.

Product 19

The structure and its stereochemistry were assigned as above by comparison with the similar product obtained by reaction of *p*-bromophenyl substituted aldimine, whose structure was confirmed by X-ray analysis.

IR (neat) 3155, 1470, 1383 cm^{-1}

MS (FAB $^+$), m/z (relative intensity, %) 511 ($[\text{M}+1]^+$, 75), 510 (M^+ , 100), 453 (19), 410 (16), 321 (16), 206 (18).

^1H -NMR (500 MHz) δ = 0.93 (s, 9H), 2.31 (ddd, J = 13.4, 5.5, 3.7 Hz, 1H), 3.11 (ddd, J = 13.4, 7.9, 4.8 Hz, 1H), 4.40 (dd, J = 4.8, 3.7 Hz, 1H), 4.91 (d, J = 2.6 Hz, 1H), 5.04 (dd, J = 7.9, 5.5 Hz, 1H), 5.46 (d, J = 7.5 Hz, 1H), 5.63 (d, J = 2.6 Hz, 1H), 6.47 (s, 1H), 6.65 (brdd, J = 7.5, 7.5 Hz, 1H), 6.69 (brdd, J = 7.5, 7.5 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.99 (brdd, J = 8.0, 8.0 Hz, 1H), 7.06 (brdd, J = 8.0, 8.0 Hz, 1H), 7.16 (d, J = 7.2 Hz, 2H), 7.25-7.42 (m, 9H), 7.62 (d, J = 8.0 Hz, 1H).

^{13}C -NMR (125 MHz) δ = 28.2, 44.1, 61.1, 61.6, 67.7, 74.5, 74.9, 83.0, 91.7, 110.9, 112.1, 118.2, 119.7, 120.95, 120.97, 123.6, 126.1, 127.4, 127.5, 127.7, 127.9, 128.9, 129.8, 132.2, 133.3, 133.6, 139.2, 141.6, 147.4, 149.0.

HRMS Calcd for $\text{C}_{36}\text{H}_{34}\text{N}_2\text{O}$, M 510.2671. Found m/z 510.2646.

Product 20

The spectral data of another 2:1 cycloadduct **20** are as follows. At present we cannot conclude its exact structure (possibly a stereo- or structural-isomer of **19**).

IR (neat) 3029, 2971, 1603, 1479, 1454 cm^{-1}

MS (FAB $^+$), m/z (relative intensity, %) 511 ($[\text{M}+1]^+$, 81), 510 (M^+ , 100), 453 (24), 206 (24).

^1H -NMR (in CD_3CN , at 333K, 500 MHz, 2H missing) δ = 1.14 (s, 9H), 2.13 (ddd, J = 13.5, 8.4, 5.8 Hz, 1H), 2.92 (ddd, J = 13.5, 6.6, 5.9 Hz, 1H), 4.62 (dd, J = 5.9, 5.8 Hz, 1H), 5.07 (dd, J = 8.4, 6.6 Hz, 1H), 5.25 (d, J = 8.1 Hz, 1H), 5.36 (d, J = 8.6 Hz, 1H), 5.97-5.98 (m, 2H), 6.14 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 6.37-6.41 (m, 1H), 6.52 (d, J = 0.8 Hz, 1H), 6.62-6.64 (m, 1H), 6.88 (ddd, J = 8.2, 8.2, 1.2 Hz, 1H), 6.99 (ddd, J = 8.2, 8.2, 1.2 Hz, 1H), 7.10-7.22 (b, 2H), 7.16-7.20 (m, 1H), 7.25-7.30 (m, 3H), 7.38-7.40 (m, 2H), 7.57-7.59 (m, 1H).

^{13}C -NMR (100 MHz) δ = 28.4, 42.8, 57.3, 63.7, 64.8, 74.4, 76.8, 81.9, 91.7, 111.2, 113.9, 118.3, 119.5, 120.4, 120.9, 126.2, 126.5, 127.6, 127.8, 127.9, 128.0, 128.5 (b, 1C), 129.7, 130.0, 132.0, 133.9, 137.1, 138.1, 148.9, 149.5.

HRMS Calcd for $\text{C}_{36}\text{H}_{34}\text{N}_2\text{O}$, M 510.2671. Found m/z 510.2688.

1-Methoxy-1-methyl-3-phenyl-2,3-dihydropyrrolo[1,2-*a*]indole (12)

Imine **1a** was added over 1 h and the mixture was further irradiated for 2 h for the reaction using 100 mol% of W(CO)₆.

Imine **1a** was added over 2 h and the mixture was further irradiated for 1 h for the reaction using 10 mol% of W(CO)₆.

The product was obtained as a mixture of two diastereomers, and the major isomer was determined to be (1*S**,3*R**)-isomer by the observed NOE shown below. Therefore, the other isomer was assigned to be the corresponding (1*S**,3*S**)-isomer.

IR (neat) 2976, 2934, 1453, 1225, 1093, 1071 cm⁻¹

MS (FAB⁺), *m/z* (relative intensity, %) 278 ([M+1]⁺, 45), 277 (M⁺, 100), 246 (77).

(1*S**,3*R**)-12

¹H-NMR (400 MHz) ; (1*S**,3*S**)-12 δ = 1.69 (s, 3H), 2.78 (dd, *J* = 13.7, 5.5 Hz, 1H), 2.99 (dd, *J* = 13.7, 8.3 Hz, 1H), 3.32 (s, 3H), 5.36 (dd, *J* = 8.3, 5.5 Hz, 1H), 6.42 (s, 1H), 6.80 (brd, *J* = 8.3 Hz, 1H), 7.00 (ddd, *J* = 8.3, 8.3, 1.2 Hz, 1H), 7.07 (brdd, *J* = 8.3, 8.3 Hz, 1H), 7.28-7.38 (m, 5H), 7.63 (brd, *J* = 8.3 Hz, 1H). ; (1*S**,3*R**)-12 δ = 1.76 (s, 3H), 2.53 (dd, *J* = 13.9, 8.3 Hz, 1H), 3.16 (dd, *J* = 13.9, 6.8 Hz, 1H), 3.22 (s, 3H), 5.57 (dd, *J* = 8.3, 6.8 Hz, 1H), 6.45 (s, 1H), 6.60 (brd, *J* = 8.3 Hz, 1H), 6.95 (ddd, *J* = 8.3, 8.3, 1.2 Hz, 1H), 7.05 (ddd, *J* = 8.3, 8.3, 1.0 Hz, 1H), 7.19-7.21 (m, 2H), 7.35-7.36 (m, 3H), 7.63 (brd, *J* = 8.3 Hz, 1H).

¹³C-NMR (100 MHz) ; (1*S**,3*S**)-12 δ = 25.1, 51.26, 51.34, 59.4, 79.3, 93.7, 110.7, 119.7, 121.09, 121.12, 126.5, 127.8, 128.8, 132.4, 132.8, 140.9, 145.7. ; (1*S**,3*R**)-12 δ = 23.2, 51.0, 54.5, 60.4, 78.6, 94.1, 110.9, 119.4, 121.1, 121.2, 126.7, 128.1, 128.9, 132.1, 132.5, 140.2, 145.0.

Anal. Calcd for C₁₉H₁₉NO: C, 82.28; H, 6.90; N, 5.05. Found: C, 81.99; H, 6.74; N, 4.77.

3a-(Morpholin-4-yl)-10-phenyl-1,2,3,3a,10,10a-hexahydrocyclopenta[*c*]pyrrolo[1,2-*a*]indole (13)

Imine **1a** was added over 1 h and the mixture was further irradiated for 1 h for the reaction using 100 mol% of W(CO)₆.

Imine **1a** was added over 1 h and the mixture was further irradiated for 13 h for the reaction using 10 mol% of W(CO)₆.

The stereochemistry of the minor isomer was determined to be (3*aR**,10*S**,10*aS**) by the observation of an NOE between the methine proton adjacent to the nitrogen and the methine proton on the ring junction. Therefore, the major product was assigned to be the corresponding (3*aR**,10*R**,10*aS**) isomer.

(3*aR**,10*R**,10*aS**)-13 (major product)

IR (neat) 2956, 2857, 1453 cm⁻¹

MS (FAB⁺), *m/z* (relative intensity, %) 358 (M⁺, 39), 315 (100), 272 (42).

¹H-NMR (400 MHz) δ = 1.41-1.52 (m, 1H), 1.85-1.88 (m, 1H), 2.00-2.08 (m, 3H), 2.27 (dd, *J* = 12.0, 5.9 Hz, 1H), 2.52-2.68 (m, 4H), 3.04-3.06 (m, 1H), 3.67-3.73 (m, 4H), 4.92 (d, *J* = 4.4 Hz, 1H), 6.33 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.09 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.23-7.26 (m, 2H), 7.33-7.38 (m, 3H), 7.63 (d, *J* = 8.0 Hz, 1H)

¹³C-NMR (100 MHz) δ = 25.2, 33.8, 39.4, 49.3, 60.2, 67.2, 67.6, 77.3, 93.9, 110.9, 119.7, 120.5, 120.8, 125.7, 127.6, 128.8, 132.5, 133.6, 141.1, 146.5.

Anal. Calcd for C₂₄H₂₆N₂O: C, 80.41; H, 7.31; N, 7.81. Found: C, 80.12; H, 7.34; N, 7.71.

(3*aR**,10*S**,10*aS**)-13 (minor product)

IR (neat) 2955, 2855, 1452 cm⁻¹

MS (FAB⁺), *m/z* (relative intensity, %) 358 (M⁺, 12), 315 (16), 272 (100), 244 (18), 149 (37).

¹H-NMR (400 MHz) δ = 1.20-1.36 (m, 2H), 1.54-1.65 (m, 2H), 2.00 (ddd, *J* = 12.1, 12.1, 5.4 Hz, 1H), 2.36 (dd, *J* = 12.1, 5.6 Hz, 1H), 2.39-2.53 (brs, 2H), 2.72-2.76 (m, 2H), 3.40 (dd, *J* = 8.7, 8.7 Hz, 1H), 3.68-3.73 (m, 2H), 3.76-3.80 (m, 2H), 5.67 (d, *J* = 8.7 Hz, 1H), 6.34 (s, 1H), 6.62 (d, *J* = 8.2 Hz, 1H), 6.67-6.82 (br, 2H), 6.93 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.06 (dd, *J* = 7.9, 7.1 Hz, 1H), 7.20-7.50 (br, 2H), 7.33 (dd, *J* = 7.1, 7.1 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H)

¹³C-NMR (125 MHz, at 333K) δ = 26.2, 28.8, 38.3, 48.9, 55.8, 64.9, 67.3, 77.2, 93.7, 111.6, 119.6, 120.4, 120.9, 127.6, 127.8, 128.5, 132.1, 133.5, 137.7, 145.8.

HRMS Calcd for C₂₄H₂₆N₂O: 358.2045. Found 358.2054.

2-Phenyl-2*H*-3,3a,10,10a-tetrahydrofuro[2,3-*c*]pyrrolo[1,2-*a*]indol-2-one (14)

Imine **1a** was added over 1 h and the mixture was further irradiated for 9 h for the reaction using 100 mol% of W(CO)₆.

Imine **1a** was added over 1 h and the mixture was further irradiated for 11 h for the reaction using 10 mol% of $W(CO)_6$. The stereochemistry of the major isomer was determined to be (3aS*,10S*,10aS*) by the observation of an NOE between the methine proton adjacent to the nitrogen and the methine proton on the ring junction. Therefore, the minor product was assigned to be the corresponding (3aS*,10R*,10aS*) isomer.

(3aS*,10S*,10aS*)-14 (major product)

IR (neat) 3055, 2987, 1789, 1421 cm^{-1}

MS (FAB⁺), m/z (relative intensity, %) 290 ([M+1]⁺, 82), 289 (M⁺, 100).

¹H-NMR (400 MHz) δ = 2.92 (dd, J = 17.9, 1.6 Hz, 1H), 3.03 (dd, J = 17.9, 8.8 Hz, 1H), 4.25 (dddd, J = 8.8, 5.9, 1.6, 1.6 Hz, 1H), 5.32 (d, J = 5.9 Hz, 1H), 5.76 (s, 1H), 6.39-6.40 (m, 1H), 6.96-7.00 (m, 3H), 7.08 (ddd, J = 7.1, 7.1, 1.5 Hz, 1H), 7.11 (ddd, J = 7.1, 7.1, 1.2 Hz, 1H), 7.31-7.34 (m, 3H), 7.61-7.63 (m, 1H).

¹³C-NMR (100 MHz) δ = 34.5, 36.8, 65.7, 93.2, 94.5, 110.3, 120.2, 121.0, 121.8, 125.8, 128.7, 129.3, 132.0, 133.3, 136.8, 143.4, 174.6.

Anal. Calcd for C₁₉H₁₅NO₂: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.76; H, 5.07; N, 4.58.

(3aS*,10R*,10aS*)-14 (minor product)

IR (neat) 2919, 1780, 1454 cm^{-1}

MS (FAB⁺), m/z (relative intensity, %) 290 ([M+1]⁺, 69), 289 (M⁺, 100).

¹H-NMR (400 MHz) δ = 2.95 (dd, J = 18.1, 2.6 Hz, 1H), 3.10 (dd, J = 18.1, 9.7 Hz, 1H), 4.24 (dddd, J = 9.7, 6.3, 2.6, 1.2 Hz, 1H), 5.57 (dd, J = 6.3, 5.3 Hz, 1H), 5.60 (d, J = 5.3 Hz, 1H), 6.38-6.39 (m, 1H), 6.58 (dd, J = 8.3, 1.0 Hz, 1H), 6.96 (ddd, J = 8.3, 8.3, 1.0 Hz, 1H), 7.07 (ddd, J = 8.3, 8.3, 1.0 Hz, 1H), 7.19-7.30 (br, 2H), 7.39-7.41 (m, 3H), 7.59 (brd, J = 8.3 Hz, 1H).

¹³C-NMR (100 MHz) δ = 35.2, 37.8, 65.2, 87.4, 94.9, 111.1, 120.2, 121.0, 121.4, 128.5, 128.6, 128.9, 132.2, 132.8, 133.5, 143.2, 174.5.

HRMS Calcd for C₁₉H₁₅NO₂: 289.1103. Found 289.1092.

1-*t*-Butoxy-3-phenyl-9-propyl-2,3-dihydropyrrolo[1,2-*a*]indole (17a)

Imine **15a** was added over 1 h and the mixture was further irradiated for 11 h.

The stereochemistry of the products was determined by the observation of NOEs as shown below.

***cis*-17a (minor)**

IR (neat) 3049, 2972, 2930, 2869, 1456, 1363 cm^{-1}

MS (FAB⁺), m/z (relative intensity, %) 348 ([M+1]⁺, 39), 347 (M⁺, 100), 318 (18), 274 (19).

¹H-NMR (400 MHz) δ = 0.99 (t, J = 7.6 Hz, 3H), 1.32 (s, 9H), 1.65-1.80 (m, 2H), 2.43 (ddd, J = 13.2, 7.3, 5.5 Hz, 1H), 2.81 (t, J = 7.6 Hz, 2H), 3.27 (ddd, J = 13.2, 7.3, 7.3 Hz, 1H), 5.17 (dd, J = 7.3, 7.3 Hz, 1H), 5.29 (dd, J = 7.3, 5.5 Hz, 1H), 6.63 (brd, J = 8.1 Hz, 1H), 6.88 (ddd, J = 8.1, 8.1, 1.0 Hz, 1H), 6.98 (ddd, J = 8.1, 8.1, 1.0 Hz, 1H), 7.28-7.37 (m, 5H), 7.54 (brd, J = 8.1 Hz, 1H).

¹³C-NMR (100 MHz) δ = 14.3, 24.5, 25.8, 28.8, 50.0, 59.8, 67.6, 74.3, 108.6, 110.4, 118.6, 119.2, 120.4, 127.0, 127.8, 128.7, 131.9, 133.1, 141.0, 141.1.

HRMS Calcd for C₂₄H₂₉NO: 347.2249. Found 347.2273.

***trans*-17a (major)**

IR (neat) 2971, 1456, 1363 cm^{-1}

MS (FAB⁺), m/z (relative intensity, %) 348 ([M+1]⁺, 45), 347 (M⁺, 100), 318 (18), 274 (30).

¹H-NMR (500 MHz) δ = 1.01 (t, J = 7.4 Hz, 3H), 1.34 (s, 9H), 1.72-1.80 (m, 2H), 2.75 (ddd, J = 13.3, 6.8, 5.4 Hz, 1H), 2.78-2.86 (m, 2H), 2.95 (ddd, J = 13.3, 7.9, 3.6 Hz, 1H), 5.36 (dd, J = 6.8, 3.6 Hz, 1H), 5.56 (dd, J = 7.9, 5.4 Hz, 1H), 6.69 (ddd, J = 8.1, 1.0, 0.8 Hz, 1H), 6.92 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H), 7.01 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 7.05-7.09 (m, 2H), 7.26-7.33 (m, 3H), 7.57 (ddd, J = 8.0, 1.0, 0.8 Hz, 1H).

¹³C-NMR (125 MHz) δ = 14.3, 24.5, 26.1, 28.7, 50.5, 59.2, 66.9, 74.4, 108.7, 110.4, 118.6, 119.3, 120.6, 126.2, 127.6, 128.8, 132.1, 133.1, 141.0, 141.8.

Anal. Calcd for C₂₄H₂₉NO: C, 82.95; H, 8.41; N, 4.03. Found: C, 82.67; H, 8.35; N, 3.75.

6-*t*-Butoxy-4-phenyl-2-propyl-5,6-dihydro-4H-pyrrolo[3,2-*ij*]quinoline (18a)

major-18a

Stereochemistry of the products (**major**, **minor-18a**) was not determined.

IR (neat) 3059, 2967, 1449 cm⁻¹

MS (FAB⁺), m/z (relative intensity, %) 348 ([M+1]⁺, 47), 347 (M⁺, 100), 274 (28).

¹H-NMR (400 MHz) δ = 0.87 (t, J = 7.3 Hz, 3H), 1.06 (s, 9H), 1.56-1.66 (m, 2H), 2.32 (t, J = 7.8 Hz, 2H), 2.53 (ddd, J = 13.9, 5.4, 3.9 Hz, 1H), 2.66 (ddd, J = 13.9, 4.9, 4.9 Hz, 1H), 4.90-4.92 (m, 1H), 5.51-5.54 (m, 1H), 6.30 (d, J = 0.8 Hz, 1H), 6.92 (d, J = 7.6 Hz, 2H), 7.01-7.02 (m, 1H), 7.07 (dd, J = 7.6, 7.6 Hz, 1H), 7.16-7.25 (m, 3H), 7.47 (d, J = 7.6 Hz, 1H).

¹³C-NMR (100 MHz) δ = 13.9, 21.6, 28.2, 28.7, 40.6, 55.0, 64.3, 73.7, 99.2, 118.0, 118.5, 119.5, 123.3, 126.2, 126.4, 126.6, 128.1, 134.5, 141.1, 143.2.

HRMS Calcd for C₂₄H₂₉NO: 347.2249. Found 347.2230.

minor-18a

IR (neat) 2966, 2928, 1449 cm⁻¹

MS (FAB⁺), m/z (relative intensity, %) 348 ([M+1]⁺, 49), 347 (M⁺, 100), 274 (32).

¹H-NMR (500 MHz) δ = 0.90 (t, J = 7.3 Hz, 3H), 1.20 (s, 9H), 1.58-1.69 (m, 2H), 2.40-2.56 (m, 4H), 4.61 (dd, J = 10.8, 4.8 Hz, 1H), 5.51 (dd, J = 4.5, 3.5 Hz, 1H), 6.29 (s, 1H), 6.78-6.80 (m, 2H), 7.07-7.11 (m, 2H), 7.20-7.28 (m, 3H), 7.44-7.46 (m, 1H).

¹³C-NMR (100 MHz) δ = 13.9, 21.5, 28.0, 28.4, 39.4, 55.1, 63.0, 74.4, 99.0, 116.0, 117.8, 119.6, 124.9, 125.2, 125.7, 127.3, 128.6, 134.3, 140.0, 142.2.

HRMS Calcd for C₂₄H₂₉NO: 347.2249. Found 347.2230.

1-*t*-Butoxy-9-methyl-3-phenyl-2,3-dihydropyrrolo[1,2-*a*]indole (17b)

Imine **15b** was added over 1 h and the mixture was further irradiated for 1 h.

The stereochemistry of the products was determined by the observation of NOEs as shown below.

cis-17b (minor)

IR (neat) 3050, 2973, 2930, 2869, 1456, 1362 cm⁻¹

MS (FAB⁺), m/z (relative intensity, %) 320 ([M+1]⁺, 33), 319 (M⁺, 100), 262 (8), 246 (34).

¹H-NMR (400 MHz) δ = 1.36 (s, 9H), 2.39 (s, 3H), 2.45 (ddd, J = 13.4, 7.3, 5.6 Hz, 1H), 3.29 (ddd, J = 13.4, 7.3, 7.3, 1H), 5.19 (dd, J = 7.3, 7.3 Hz, 1H), 5.31 (dd, J = 7.3, 5.6 Hz, 1H), 6.66 (brd, J = 8.3 Hz, 1H), 6.92 (ddd, J = 8.3, 7.1, 1.2 Hz, 1H), 7.02 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H), 7.30-7.38 (m, 5H), 7.53 (brd, J = 8.0 Hz, 1H).

¹³C-NMR (100 MHz) δ = 8.2, 28.7, 50.0, 59.7, 67.5, 74.4, 103.0, 110.2, 118.7, 118.9, 120.6, 126.9, 127.8, 128.7, 131.9, 133.6, 140.8, 141.1.

Anal. Calcd for C₂₂H₂₅NO: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.54; H, 8.12; N, 4.21.

trans-17b (major)

IR (neat) 3051, 2973, 2930, 1456, 1362 cm⁻¹

MS (FAB⁺), m/z (relative intensity, %) 320 ([M+1]⁺, 52), 319 (M⁺, 100), 262 (11), 246 (44).

¹H-NMR (400 MHz) δ = 1.35 (s, 9H), 2.39 (s, 3H), 2.74 (ddd, J = 13.4, 6.7, 5.6 Hz, 1H), 2.94 (ddd, J = 13.4, 7.7, 3.5, 1H), 5.35 (dd, J = 6.7, 3.5 Hz, 1H), 5.56 (dd, J = 7.7, 5.6 Hz, 1H), 6.68 (ddd, J = 8.3, 1.2, 1.2 Hz, 1H), 6.93 (ddd, J = 8.3, 7.1, 1.2 Hz, 1H), 7.02 (ddd, J = 8.0, 7.1, 1.2 Hz, 1H), 7.07-7.10 (m, 2H), 7.27-7.34 (m, 3H), 7.54 (ddd, J = 8.0, 1.2, 1.2 Hz, 1H).

¹³C-NMR (100 MHz) δ = 8.5, 28.6, 50.5, 59.2, 66.7, 74.4, 103.0, 110.3, 118.6, 119.0, 120.7, 126.2, 127.6, 128.8, 132.0, 133.6, 140.8, 141.6.

Anal. Calcd for C₂₂H₂₅NO: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.61; H, 8.12; N, 4.10.

1-*t*-Butoxy-3,9-diphenyl-2,3-dihydropyrrolo[1,2-*a*]indole (17c)

Imine **15c** was added over 1 h and the mixture was further irradiated for 11 h.

The stereochemistry of the products was determined by the observation of NOEs as shown below.

cis-17c (major)

IR (neat) 3054, 2974, 1604, 1456, 1364 cm⁻¹

MS (FAB⁺), m/z (relative intensity, %) 382 ([M+1]⁺, 37), 381 (M⁺, 100), 324 (7), 308 (28).

¹H-NMR (400 MHz) δ = 1.19 (s, 9H), 2.57 (ddd, J = 13.6, 6.1, 4.9 Hz, 1H), 3.32 (ddd, J = 13.6, 7.4, 7.4, 1H), 5.30 (dd, J = 7.4, 6.1 Hz, 1H), 5.38 (dd, J = 7.4, 4.9 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H), 6.99 (dd, J = 8.3, 8.3 Hz, 1H), 7.07 (dd, J = 8.3, 8.3 Hz, 1H), 7.27-7.47 (m, 8H), 7.75-7.78 (m, 3H).

¹³C-NMR (100 MHz) δ = 28.8, 49.3, 60.0, 68.0, 74.7, 110.6, 110.7, 119.9, 120.0, 121.3, 125.7, 127.1, 127.9, 128.0, 128.8, 129.9, 131.8, 132.1, 135.0, 141.0, 141.5.

Anal. Calcd for C₂₇H₂₇NO: C, 85.00; H, 7.13; N, 3.67. Found: C, 84.85; H, 7.20; N, 3.41.

trans-17c (minor)

IR (neat) 3052, 2974, 1603, 1455, 1365 cm⁻¹

MS (FAB⁺), m/z (relative intensity, %) 382 ([M+1]⁺, 47), 381 (M⁺, 100), 324 (8), 308 (46).

¹H-NMR (400 MHz) δ = 1.19 (s, 9H), 2.77 (ddd, J = 13.3, 6.8, 6.4 Hz, 1H), 3.03 (ddd, J = 13.3, 7.2, 2.8, 1H), 5.46 (dd, J = 6.4, 2.8 Hz, 1H), 5.67 (dd, J = 7.2, 6.8 Hz, 1H), 6.71 (d, J = 8.3 Hz, 1H), 6.97-7.01 (m, 1H), 7.05-7.09 (m, 1H), 7.17-7.20 (m, 2H), 7.28-7.38 (m, 4H), 7.45 (dd, J = 7.6, 7.6 Hz, 2H), 7.73-7.75 (m, 2H), 7.78 (d, J = 8.1 Hz, 1H).

¹³C-NMR (100 MHz) δ = 28.7, 50.3, 59.7, 67.2, 74.6, 110.6, 110.8, 119.7, 120.0, 121.3, 125.8, 126.5, 127.9, 128.1, 128.9, 129.7, 131.8, 132.1, 135.1, 140.8, 141.5.

Anal. Calcd for C₂₇H₂₇NO: C, 85.00; H, 7.13; N, 3.67. Found: C, 84.84; H, 7.37; N, 3.41.

6-*t*-Butoxy-2,4-diphenyl-5,6-dihydro-4*H*-pyrrolo[3,2-*i*]quinoline (18c)

Stereochemistry of the products (**major**, **minor-18c**) was not determined.

major-18c

IR (neat) 2968, 2925, 1449 cm⁻¹

MS (FAB⁺), m/z (relative intensity, %) 382 ([M+1]⁺, 51), 381 (M⁺, 100).

¹H-NMR (400 MHz) δ = 1.12 (s, 9H), 2.51-2.65 (m, 2H), 2.61 (ddd, J = 13.8, 5.4, 5.4, 1H), 4.97 (dd, J = 5.4, 4.0 Hz, 1H), 5.72 (dd, J = 5.4, 5.4 Hz, 1H), 6.62 (s, 1H), 6.79 (d, J = 6.9 Hz, 2H), 7.04-7.20 (m, 7H), 7.25-7.27 (m, 3H), 7.57 (dd, J = 6.8, 2.0 Hz, 1H).

¹³C-NMR (100 MHz) δ = 28.3, 41.2, 56.0, 64.3, 73.8, 102.4, 119.1, 119.2, 120.2, 124.4, 126.25, 126.33, 126.4, 127.4, 127.9, 128.0, 128.7, 133.0, 135.4, 140.6, 143.6.

HRMS Calcd for C₂₇H₂₇NO: 381.2093. Found 381.2097.

minor-18c

IR (neat) 2924, 1447 cm⁻¹

MS (FAB⁺), m/z (relative intensity, %) 382 ([M+1]⁺, 53), 381 (M⁺, 100).

^1H -NMR (500 MHz) δ = 1.19 (s, 9H), 2.44 (ddd, J = 12.8, 10.9, 4.6 Hz, 1H), 2.53 (ddd, J = 12.8, 4.5, 2.9, 1H), 4.63 (dd, J = 10.9, 4.5 Hz, 1H), 5.63 (dd, J = 4.6, 2.9 Hz, 1H), 6.65 (s, 1H), 6.85 (brd, J = 7.5 Hz, 2H), 7.14-7.20 (m, 2H), 7.22-7.31 (m, 8H), 7.55 (brd, J = 7.5 Hz, 1H).

^{13}C -NMR (125 MHz) δ = 28.4, 39.4, 56.2, 63.1, 74.5, 102.1, 117.2, 118.6, 120.2, 125.2, 125.8, 125.9, 127.3, 127.7, 128.4, 128.7, 128.8, 132.5, 135.4, 139.9, 143.0.

HRMS Calcd for $\text{C}_{27}\text{H}_{27}\text{NO}$: 381.2093. Found 381.2111.