PREPARATION OF ALKYL-SUBSTITUTED INDOLES IN THE BENZENE PORTION. Part 2

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Abstract ——— General Procedure for synthesizing alkylindoles (14) was developed by cyclization of 12 in i-PrOH using H_2SO_4 as a catalyst to 1-tosylindoles (13), whose protecting group was reductively cleaved with Mg in MeOH. 7-t-Alkylindoles (23 and 24) were synthesized by removal of the tosyl group of 26 and 35 in advance, followed by treatment of the resulting 34 and 36 with *p*-TsOH in refluxing C_6H_6.

In the preceding paper,[1] *we reported an acid-catalyzed cyclization of* 4-(1-methoxycarbonyl-2-pyrrolyl)-2-butenone derivatives (1) to readily form 1-methoxycarbonylindoles (4)(X=COOMe) in very good yields. This implies that any hydroxy-carbonyl compound having the related structure of either 2 or 3 would behave similarly in an acidic condition to yield 4. Judging from the extremely electron-rich character of the pyrrole ring, the sulfonyl group would also be substituted for methoxycarbonyl as the group protecting the pyrrole nitrogen atom. Here we describe that readily accessible, variously alkylated 3-(1,3-dioxolan-2-yl)-1-(1-*p*-toluenesulfonyl-2-pyrrolyl)propanols (12) are suitable substrates for synthesizing indole derivatives (13) with alkyl groups in the benzene portion. The same system was previously reported by Loozen and co-workers[2] for obtaining naphthalene, benzo[*b*]thiophen, and benzimidazole derivatives. Indole synthesis was once the subject of their investigation but it was reported to be unsuccessful, probably due to the unstable nature of both the starting pyrroles and the produced indoles. They did not use the protecting groups at the nitrogen atoms.[2c]

As preliminary experiments, we synthesized simple pyrrole derivatives (8a, 8b, and 8c) bearing methoxycarbonyl, methanesulfonyl, and *p*-toluenesulfonyl (Tosyl) groups, from 5 and 6,[3] and submitted one of these, 8a to the treatment with $SnCl_4$ in CH_2Cl_2

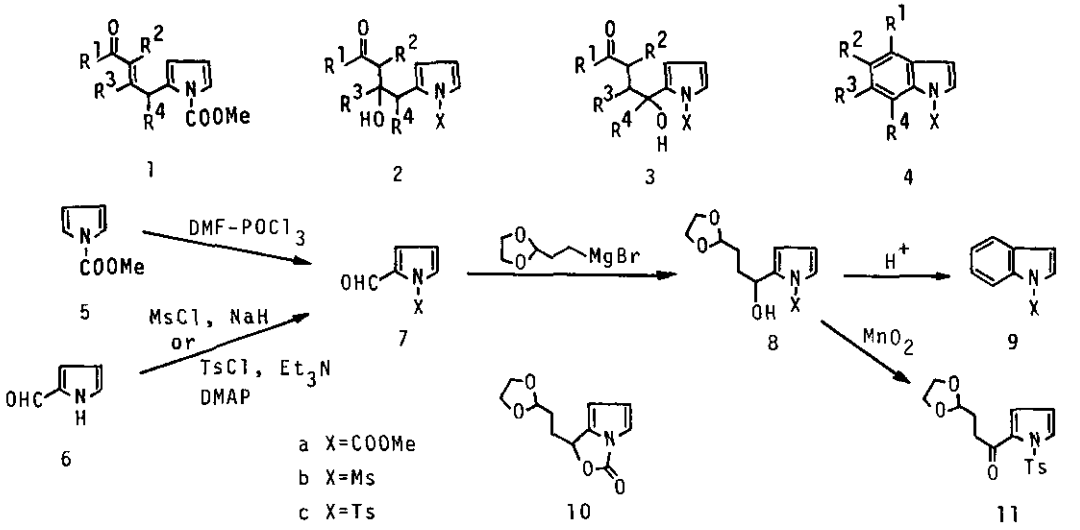

Chart 1

and *p*-TsOH in refluxing C_6H_6 (Chart 1). Both were successful conditions for our previous alkylindole synthesis.[1,4] But the results were quite disappointing and only the latter afforded 1-methoxycarbonylindole (9a) in 15% yield. Eventually Loozen's condition (10% H_2SO_4 in refluxing MeOH) gave good results and 9a, 9b, and 9c were obtained from 8a, 8b, and 8c in 68%, 85%, and 82% yields respectively. Among these three series, the COOMe group was inferior in producing a by-product (10) during the Grignard reaction, and the tosyl group was superior to the mesyl in the cleavage step of the resulting sulfonylindoles. Therefore we decided compounds expressed by the structure (12) to be suitable for our improved indole synthesis. The compound (12b) was prepared from the tosylpyrrole derivative (8) by way of 11 (MnO_2, 76% yield), followed by the EtMgBr treatment (99% yield)(Chart 2). The indole synthesis from 12b was re-examined using H_2SO_4 as a catalyst in various kinds of solvents (Table 1). Refluxing in isopropanol containing 6% H_2SO_4 was the best way to obtaining 7-ethyl-1-tosylindole (13b). Grignard reaction of 11 or the base-catalyzed α-alkylation of 11, followed by $NaBH_4$ reduction afforded the variously substituted compounds (12a, 12c, 12d, 12e, 12f, 12g, and 12h). Furthermore, 2-formyl-1-tosylpyrrole (7c) was treated with 2-(2-methyl-1,3-dioxolan-2-yl)ethylmagnesium bromide to give 12i, and all of these were subjected to the indole formation reaction. 1-Tosylindoles were obtained in fair to good yield (Table 1), accompanied by the occasional formation of by-products (15, 16, and 17). 4-Methylindole derivative (13i) was converted to an aldehyde (19)[5] and an ester (21)[5a,6] for the starting materials of the indole alkaloid synthesis.[5a,7] Although the tosyl group

of 13 was conventionally cleaved with $LiAlH_4$[6a] or by alkaline hydrolysis,[6a] we found a milder and chemoselective method, *i.e.*, stirring a MeOH solution of 13 with *ca.* a 15-fold amount of Mg at room temperature. Table 1 shows the results of this new technique, affording alkylindoles (14) in excellent yields. 6-(3-Methyl-2-butenyl)indole (14h) was identical with the sample of the preceding paper.

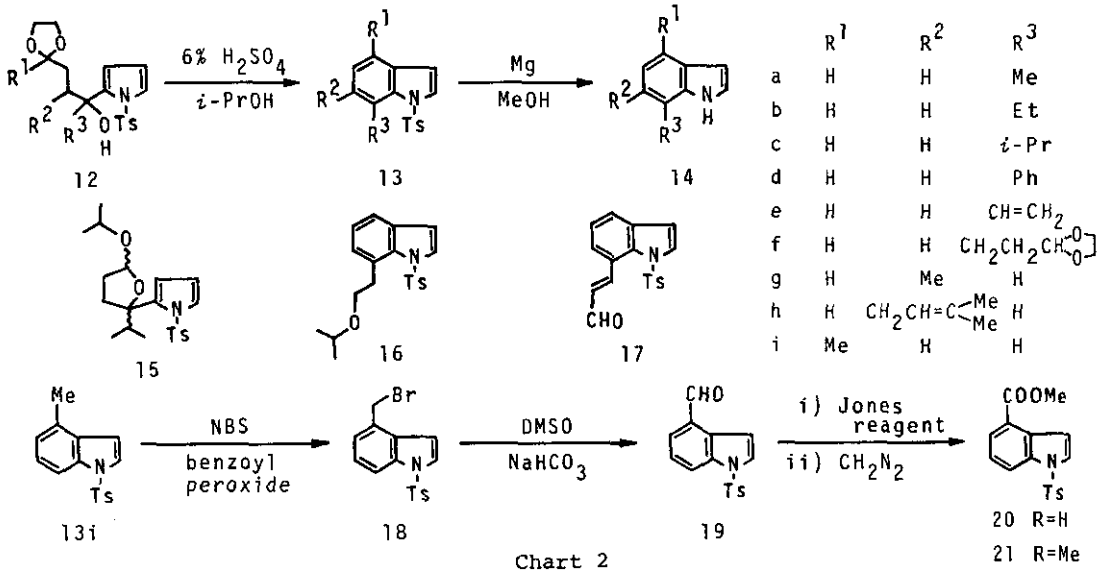

Chart 2

	R¹	R²	R³
a	H	H	Me
b	H	H	Et
c	H	H	*i*-Pr
d	H	H	Ph
e	H	H	CH=CH₂
f	H	H	CH_2CH_2CH(O, O)
g	H	Me	H
h	H	$CH_2CH=C$(Me, Me)	H
i	Me	H	H

Table 1. Synthesis of Alkylindole Derivatives by Treatment of 1-Tosylpyrrole Derivatives with 6% H_2SO_4 in Refluxing Solvents

Starting Material	Solvent	Reaction Time	1-Tosylindole Yield %	Alkylindole Yield %
12a	i-PrOH	15 min	13a 75	14a 98
12b	MeOH-H_2O (1:2)	20 min	13b 64	14b 95
	t-BuOH-H_2O (1:2)	15 min	62	
	DME-H_2O (1:2)	20 min	38	
	MeOH	15 min	70	
	i-PrOH	15 min	75	
12c	i-PrOH	15 min	13c 55 with 15 31	14c 93
12d	i-PrOH	20 min	13d 70	14d 99
12e	i-PrOH	15 min	13e 45 with 16 11	14e 90
12f	i-PrOH	15 min	13f 44 with 17 15	
12g	i-PrOH	15 min	13g 88	14g 98
12h	i-PrOH	10 min	13h 25	14h 92
12i	i-PrOH	3.5 h	13i 58	14i 95

Aiming at the total synthesis of teleocidins A-1 and A-2 (22),[8] we next investigated the preparation of 7-t-alkylindole derivatives (23 and 24) (Chart 3). A Grignard reagent produced *in situ* from Mg and 3-methyl-2-butenyl halide was reported to react with a ketone compound to yield a 1,1-dimethyl-2-propenyl-carbinol derivative (25).[9] This was smoothly applied to the acylpyrrole (11), and 26 was prepared in 83% yield. However, when 26 was submitted to the above indole synthesis, the only compound isolated was 27, probably formed by an acid-catalyzed rearrangement of 28, followed by cyclization of 29 to the tetrahydrofuran ring. The dihydro derivative (30) also resisted the indole formation, and instead, 31 and 32 were obtained in 47% and 18% yields. The latter compound was considered to be derived from an interme-

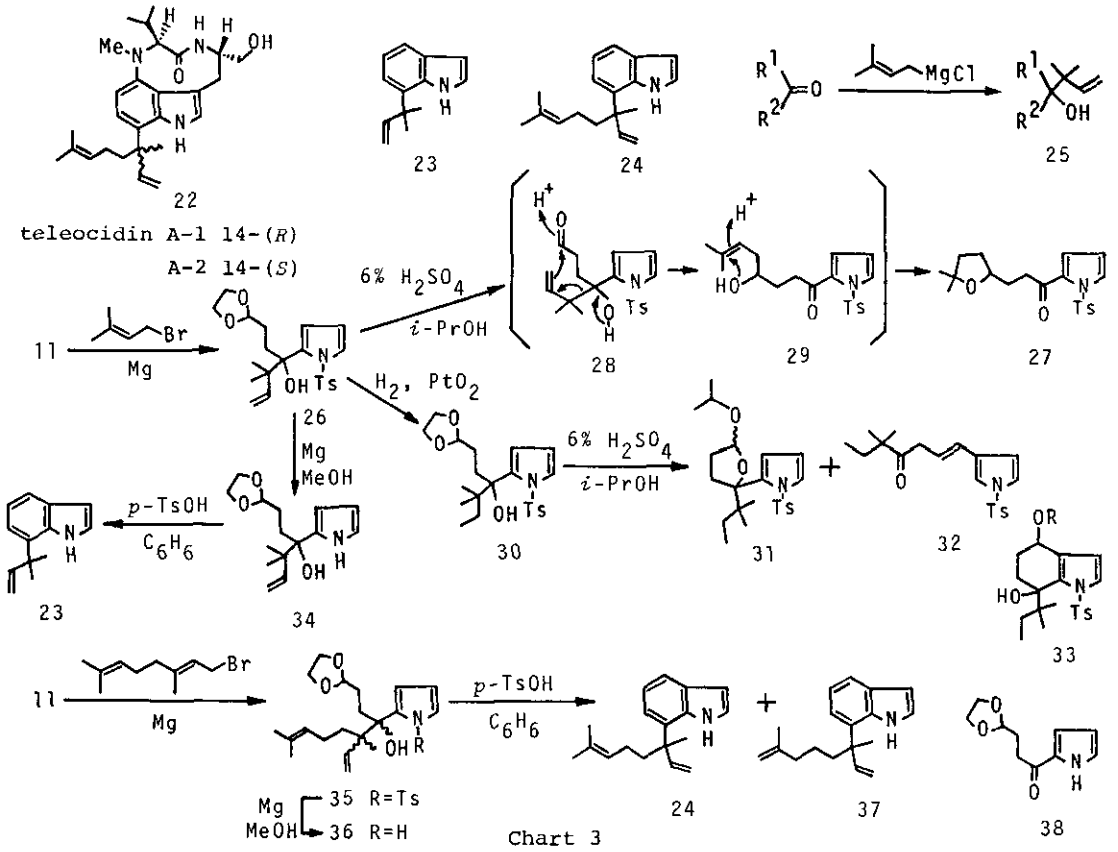

Chart 3

diate (33) to the indole aromatization, which opened the ring by the retro-Friedel-Crafts mechanism. This was probably due to the steric hindrance between the tosyl and tertiary alkyl groups. To release this congestion, the tosyl group was removed by our method with Mg in MeOH at room temperature for 2 h to give 34 in 92% yield. Using alkaline hydrolysis, 5% KOH in DME-H_2O (4:1) at about 50°C for 2 h, 34 was

obtained in only 11% yield, together with the recovery of 26 in 60% yield. A relatively stable compound (34) was briefly refluxed in C_6H_6 in the presence of a catalytic amount of *p*-TsOH. The desired 7-(1,1-dimethyl-2-propenyl)indole (23) was produced in 84% yield.

Analogously, the Grignard reaction with 11 was carried out using *E*-3,7-dimethyl-2,6-octadienyl (geranyl) bromide. Concomitant cleavage of the tosyl group occurred partially from both 11 and the product (35) by the attack of an excess of the Grignard reagent, so that 35 was converted to 36 without purification and all of 36 was treated as above with *p*-TsOH. The indole derivative (24) having the teleocidin A side chain was obtained in 46% yield, calculated from 11, accompanied by 38 in 12% yield. GCMS data revealed that 24 contains about 7% of an inseparable double bond isomer (37).

In conclusion, 7-t-alkylindoles were synthesized from detosylated substances such as 34 and 36 by the *p*-TsOH catalysis in boiling C_6H_6. Reflux of 12 in 6% H_2SO_4 containing isopropanol was effective for the other indoles carrying alkyl groups in the benzene portion. The detosylated compound obtained from 12b was very unstable and afforded a complex mixture when treated with *p*-TsOH.

EXPERIMENTAL

For the general description of instruments and others, refer to that in the preceding paper. HRMS were determined on a JEOL JMS-DX-300 spectrometer.

Preparation of 2-Formyl-1-methoxycarbonylpyrrole (7a)

To a solution of the Vilsmeier reagent prepared from DMF (15.0 ml) and $POCl_3$ (9.78 g) in C_6H_6 (20 ml) at 0°C for 10 min, a solution of 1-methoxycarbonylpyrrole (5) (2.64 g) in C_6H_6 (10 ml) was added. The mixture was stirred at 0°C for 1 h; 30°C, 10 min; and 60-63°C, 1 h, and it was poured into sat. $NaHCO_3$-H_2O. The whole was shaken with Et_2O, and usual work-up, followed by column chromatography [hexane-EtOAc (3:1)] afforded 7a (2.91 g, 90%), slightly yellow oil. Ms *m/z*: 153 (M^+). Ir (film) cm^{-1}: 1760, 1667. Nmr ($CDCl_3$) δ: 4.02 (3H, s), 6.28 (1H, dd, J=3.5, 3.5 Hz), 7.15 (1H, dd, J=3.5, 1.5 Hz), 7.43 (1H, dd, J=3.5, 1.5 Hz), 10.28 (1H, s).

Preparation of 2-Formyl-1-methanesulfonylpyrrole (7b)

To a solution of 2-formylpyrrole (6) (202 mg) in THF (5 ml), 50% NaH (112 mg) was added and the mixture was stirred at -20°C for 10 min under N_2 atmosphere. It was cooled at -44°C and to this was added MsCl (0.17 ml) in THF (2 ml). The mixture was stirred for 15 min and quenched by addition of sat. NH_4Cl-H_2O. Extraction with CH_2Cl_2, followed by usual work-up and PTLC [hexane-EtOAc (3:1)] gave 7b (344 mg, 94%), colorless oil. Ms *m/z*: 173 (M^+). Ir (film) cm^{-1}: 1672. Nmr ($CDCl_3$) δ: 3.59 (3H, s), 6.39 (1H, dd, J=3.5, 3.5 Hz), 7.20 (1H, dd, J=3.5, 1.5 Hz), 7.57 (1H, ddd, J=3.5, 1.5, 1 Hz), 9.69 (1H, d, J=1 Hz).

Preparation of 2-Formyl-1-p-toluenesulfonylpyrrole (7c)

A solution of 6 (279 mg), *p*-TsCl (733 mg), Et_3N (1.0 ml), and dimethylaminopyridine

(30 mg) in CH_2Cl_2 (4 ml) was stirred at room teperature for 14 h. Addition of sat. $NaHCO_3$-H_2O, extraction with CH_2Cl_2, usual work-up, and column chromatography [hexane-CH_2Cl_2 (1:1)] afforded 7c (670 mg, 92%), colorless prisms, mp 95-96°C (CH_2Cl_2-hexane). Anal. Calcd for $C_{12}H_{11}NO_3S$: C, 57.81; H, 4.45; N, 5.62. Found: C, 57.97; H, 4.35; N, 5.68. Ms *m/z*: 249 (M^+). Ir (KBr) cm^{-1}: 1659, 1591. Nmr ($CDCl_3$) δ: 2.37, (3H, s), 6.37 (1H, dd, J=3.5, 3.5 Hz), 7.12 (1H, dd, J=3.5, 1.5 Hz), 7.29 and 7.80 (A_2B_2, J=8 Hz), 7.61 (1H, dd, J=3.5, 1.5 Hz), 9.99 (1H, s).

An Example for the Conversion of 7 to 8

A solution of 7c (141 mg) in THF (3 ml) was treated at -20°C for 15 min under N_2 atmosphere with the reagent (1.50 ml), prepared from Mg (90 mg) and 2-(1,3-dioxolan-2-yl)ethyl bromide (0.60 ml) in THF (3.4 ml). Addition of sat. NH_4Cl-H_2O, followed by extraction with CH_2Cl_2, usual work-up, and PTLC [hexane-EtOAc (2:1)] afforded 8c (195 mg, 98%), colorless syrup. HRMS Calcd for $C_{17}H_{21}NO_5S$: 351.1141. Found: 351.1147. Nmr ($CDCl_3$) δ: 2.37 (3H, s), 3.12 (1H, d, J=4.5 Hz, exchangeable with D_2O), 3.65-4.05 (4H, m), 4.90 (1H, t, J=5.5 Hz by addition of D_2O), 4.83 (1H, t, J=4.5 Hz), 6.19 (1H, dd, J=3.5, 3.5 Hz), 6.19-6.33 (1H, m), 7.26 (1H, dd, J=3.5, 2 Hz), 7.26 and 7.65 (A_2B_2, J=8 Hz).

8a (28%) and 10 (39%) from 7a. 8a: Colorless syrup. Ms *m/z*: 255 (M^+). Ir (film) cm^{-1}: 3490, 1742. Nmr ($CDCl_3$) δ: 3.63-4.06 (4H, m), 3.93 (3H, s), 4.78-5.04 (2H, m), 6.07 (1H, dd, J=3.5, 3.5 Hz), 6.14-6.26 (1H, m), 7.15 (1H, dd, J=3.5, 2 Hz).

10: Colorless prisms, mp 58.5-59.5°C (hexane-Et_2O). Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87; N, 6.28. Found: C, 59.07; H, 5.95; N, 6.38. Ms *m/z*: 223 (M^+). Ir (KBr) cm^{-1}: 1785. Nmr ($CDCl_3$) δ: 3.68-4.07 (4H, m), 4.87 (1H, t, J=4 Hz), 5.49 (1H, br t, J=6 Hz), 5.99 (1H, ddd, J=3, 1.5, 1 Hz), 6.39 (1H, dd, J=3,3 Hz), 6.99 (1H, dd, J=3, 1 Hz).

8b, 98% from 7b. Colorless needles, mp 90-91°C (hexane-CH_2Cl_2). Anal. Calcd for $C_{11}H_{17}NO_5S$: C, 47.98; H, 6.22; N, 5.09. Found: C, 47.94; H, 6.19; N, 5.01. Ms *m/z*: 275 (M^+). Nmr ($CDCl_3$) δ: 3.18 (1H, d, J=6 Hz, exchangeable with D_2O), 3.30 (3H, s), 3.71-4.10 (4H, m), 4.92 (1H, t, J=4 Hz), 5.06 (1H, dt, J=6, 6 Hz), 6.19 (1H, dd, J=3.5, 3.5 Hz), 6.24-6.36 (1H, m), 7.11 (1H, dd, J=3.5, 2 Hz).

An Example for the Conversion of 8 to 1-Substituted Indoles (9)

To a heating (100°C) solution of 10% H_2SO_4-H_2O (5 ml), 8c (63 mg) in MeOH (2.5 ml) was added dropwise and the mixture was refluxed for 20 min. H_2O was added, the mixture was extracted with CH_2Cl_2, and the extract was washed with sat. $NaHCO_3$-H_2O. Usual work-up and PTLC [hexane-EtOAc (6:1)] gave 9c[6a] (40 mg, 82%), colorless needles, mp 85-86°C (hexane-CH_2Cl_2).

Oxidation of 8c to 11

A mixture of 8c (552 mg) and MnO_2 (2.055 g) in C_6H_6 (15 ml) was stirred under reflux for 3 h. Inorganic material was filtered off and evaporation of the filtrate and CH_2Cl_2 washing afforded a crystalline mass (509 mg), which was purified by PTLC [hexane-EtOAc (3:1)] and recrystallization from hexane-Et_2O to give 11 (415 mg, 76%), colorless needles, mp 66-67°C. Anal. Calcd for $C_{17}H_{19}NO_5S$: C, 58.44; H, 5.48; N, 4.01. Found: C, 58.30; H, 5.38; N, 4.12. Ms *m/z*: 349 (M^+). Ir (KBr) cm^{-1}: 1680. Nmr ($CDCl_3$) δ: 1.96 (2H, dt, J=4.5, 7.5 Hz), 2.40 (3H, s), 2.81 (2H, t, J=7.5 Hz), 3.66-4.04 (4H, m), 4.86 (1H, t, J=4.5 Hz), 6.29 (1H, dd, J=3.5, 3.5 Hz), 7.04 (1H, dd, J=3.5, 1.5 Hz), 7.27 and 7.87 (A_2B_2, J=8 Hz), 7.75 (1H, dd, J=3.5, 1.5 Hz).

Preparation of 12a-f and 12i

The Grignard reaction was carried out in the similar way to the preparation of 8 from 7.

12a, 99% from 11. Colorless oil. HRMS Calcd for $C_{18}H_{23}NO_5S$: 365.1294. Found: 365.1273. Nmr ($CDCl_3$) δ: 1.56 (3H, s), 2.36 (3H, s), 3.65-4.05 (4H, m), 4.13 (1H, s, exchangeable with D_2O), 4.74 (1H, dd, J=4.5, 4.5 Hz), 6.06-6.23 (2H, m), *ca.* 7.12-7.28 (1H, m), 7.20 and 7.61 (A_2B_2, J=8.5 Hz).

12b, 99% from 11. Colorless syrup. HRMS Calcd for $C_{19}H_{25}NO_5S$: 379.1451. Found: 379.1440. Nmr ($CDCl_3$) δ: 0.69 (3H, t, J=7.5 Hz), 2.37 (3H, s), 3.67-4.04 (4H, m), 4.06 (1H, s, exchangeable with D_2O), 4.77 (1H, dd, J=4.5, 4.5 Hz), 6.17 (2H, d, J= 2.5 Hz), ca. 7.21-7.33 (1H, m), 7.21 and 7.63 (A_2B_2, J=8 Hz).

12c, 74% from 11. Colorless syrup. HRMS Calcd for $C_{20}H_{27}NO_5S$: 393.1610. Found: 393.1618. Nmr ($CDCl_3$) δ: 0.76 (3H, d, J=7 Hz), 0.87 (3H, d, J=7 Hz), 1.34-1.67 (2H, m), 1.70-2.06 (2H, m), 2.27 (1H, qq, J=7, 7 Hz), 2.36 (3H, s), 3.64-4.01 (4H, m), 4.01 (1H, s, exchangeable with D_2O), 4.73 (1H, dd, J=4.5, 4.5 Hz), 6.14 (1H, dd, J=3.5, 2 Hz), 6.18 (1H, dd, J=3.5, 3.5 Hz), 7.21 and 7.61 (A_2B_2, J=8.5 Hz), 7.28 (1H, dd, J=3.5, 2 Hz).

12d,92% from 11. Colorless prisms, mp 122-123.5°C (CH_2Cl_2-MeOH). Anal. Calcd for $C_{23}H_{25}NO_5S$: *C, 64.61; H, 5.89; N, 3.28. Found: C, 64.59; H, 5.94; N, 3.26.* Ms *m/z*: 427 (M^+). Nmr ($CDCl_3$) δ: 2.27 (3H, s), 3.58-3.97 (4H, m), 4.74 (1H, dd, J=4, 4 Hz), 5.03 (1H, s, exchangeable with D_2O), 6.23 (1H, dd, J= 3.5, 3.5 Hz), 6.50 (1H, dd, J=3.5, 2 Hz), 6.83 and 6.90 (A_2B_2, J=8.5 Hz), 7.04 (5H, s), 7.25 (1H, dd, J=3.5, 2 Hz).

12e, 87% from 11. Colorless oil. HRMS Calcd for $C_{19}H_{23}NO_5S$: 377.1297 Found: 377.1308. Nmr ($CDCl_3$) δ: 2.38 (3H, s), 3.67-4.04 (4H, m), 4.45 (1H, s, exchangeable with D_2O), 4.85 (1H, dd, J=4.5, 4.5 Hz), 5.00 (1H, dd, J=10.5, 2.5 Hz), 5.04 (1H, dd, J=17, 2.5 Hz), 5.89 (1H, dd, J=17, 10.5 Hz), 6.17 (1H, dd, J=3.5, 3.5 Hz), 6.29 (1H, dd, J=3.5, 2 Hz), 7.11-7.32 (3H, m), 7.60 (2H, $\underline{A}_2B_2$, J=8.5 Hz).

12f, 97% from 11. Colorless oil. HRMS Calcd for $C_{22}H_{29}NO_7S$: 451.1662. Found: 451.1640. Nmr ($CDCl_3$) δ: 2.33 (3H, s), 4.17 (1H, s, exchangeable with D_2O), 4.71 (2H, dd, J=4.5, 4.5), 6.08-6.26 (2H, m), 7.19-7.34 (1H, m), 7.19 and 7.59 (A_2B_2, J=8.5 Hz).

12i, 91% from 7c. Colorless oil. Ms *m/z*: 365 (M^+). Nmr ($CDCl_3$) δ: 1.24 (3H, s), 2.35 (3H, s), 3.23 (1H, br. s, exchangeable with D_2O), 3.85 (4H, s), 4.90 (1H, br t, J=6 Hz), 6.19 (1H, dd, J=3.5, 3.5 Hz), 6.28 (1H, dd, J=3.5, 2 Hz), 7.24 and 7.66 (A_2B_2, J=8.5 Hz), 7.25 (1H, dd, 3.5, 2 Hz).

Preparation of 12g from 11

To a solution of 11 (80 mg) and MeI (0.14 ml) in THF (3 ml), t-BuOK (51 mg) was added at -78°C under N_2 atmosphere, and the mixture was stirred at -78--55°C for 2.5 h. Addition of sat. NH_4Cl-H_2O, followed by extraction with CH_2Cl_2, usual work-up, and PTLC [hexane-EtOAc (4:1) and then hexane-EtOAc (3:1)] afforded α-methylated ketone compound (69 mg, 83%), colorless syrup, ms *m/z*: 363 (M^+), ir (film) cm^{-1}: 1678, nmr ($CDCl_3$) δ: 1.09 (3H, d, J=7 Hz), 1.59 (1H, ddd, J=14, 5, 5 Hz), 2.12 (1H, ddd, J=14, 7.5, 5 Hz), 2.38 (3H, s), 3.10-3.54 (1H, m), 3.59-3.96 (4H, m), 4.71 (1H, dd, J=5, 5 Hz), 6.31 (1H, dd, J=3.5, 3.5 Hz), 7.09 (1H, dd, J=3.5, 1.5 Hz), 7.28 and 7.88 (A_2B_2, J=8.5 Hz), 7.76 (1H, dd, J=3.5, 1.5 Hz); and enol methyl ether

compound (3 mg, 4%), colorless syrup, ms *m/z*: 363 (M^+), ir (film) cm^{-1}: 1663, nmr ($CDCl_3$) δ: 2.37 (3H, s), 2.50 (2H, dd, J=7, 5 Hz), 3.18 (3H, s), 3.72-4.10 (4H, m), 4.59 (1H, t, J=7 Hz), 4.89 (1H, t, J=5 Hz), 6.20 (2H, d, J=2.5 Hz), 7.21 and 7.73 (A_2B_2, J=8.5 Hz), 7.34 (1H, dd, J=2.5, 2.5 Hz). To a solution of the α-methylated ketone compound (65 mg) in EtOH (2 ml) was added $NaBH_4$ (20 mg) and the mixture was warmed at 60°C for 2.5 h. Addition of sat. NH_4Cl-H_2O, followed by extraction with CH_2Cl_2, usual work-up, and PTLC (CH_2Cl_2) affoded 12g (61 mg, 93%), colorless syrup as a diastereomeric mixture (1:1). Ms *m/z*: 365 (M^+). Nmr ($CDCl_3$) δ: 0.78 and 0.96 (3H, d each, J=6.5 Hz), 2.37 (3H, s), 2.58-3.12 (1H, br s, exchangeable with D_2O), 4.94 (1H, t, J=4.5 Hz).

Preparation of 12h from 11

Similar treatment of 11 (80 mg) with 3-methyl-2-butenyl bromide (0.16 ml) and t-BuOK (71 mg) afforded α-alkylated ketone compound (54 mg, 56%), colorless syrup, ms *m/z*: 417 (M^+), ir (film) cm^{-1}: 1680, nmr ($CDCl_3$) δ: 1.47 (3H, s), 1.58 (3H, s), 2.40 (3H, s), 3.57-3.94 (4H, m), 4.67 (1H, dd, J=5.5, 4 Hz), 4.92 (1H, dd, J=7, 7 Hz), 6.31 (1H, dd, J=3.5, 3.5 Hz), 7.08 (1H, dd, J=3.5, 1.5 Hz), 7.28 and 7.88 (A_2B_2, J=8.5 Hz), 7.79 (1H, dd, J=3.5, 1.5 Hz); and enol alkyl ether (17 mg, 18%), colorless syrup, ir (film) cm^{-1}: 1668, nmr δ: 1.50 (3H, s), 1.68 (3H, s), 2.39 (3H, s), 2.54 (2H, dd, J=7, 5 Hz), 3.71-4.11 (6H, m), 4.66 (1H, t, J=7 Hz), 4.89 (1H, t, J=5 Hz), 5.19 (1H, br t, J=6.5 Hz), 6.20 (2H, d, J=3 Hz), 7.21 and 7.75 (A_2B_2, J=8.5 Hz), 7.35 (1H, dd, J=3, 3 Hz). α-Alkylated ketone compound (51 mg) was reduced with $NaBH_4$ (12 mg) in EtOH (2 ml) to give 12h(32 mg, 62%), colorless oil as a diastereomeric mixture, ms *m/z*: 419 (M^+), nmr ($CDCl_3$) δ: 1.55 (3H, s), 1.67 (3H, s), 2.38 (3H, s), 2.84 and 3.17 (1H, br s each, exchangeable with D_2O), 4.90 (1H, t, J=5 Hz), 6.24 (1H, dd, J=3.5, 3.5 Hz), 7.26 and 7.67 (A_2B_2, J=8.5 Hz); and the recovery of the starting ketone (6 mg, 12%).

Conversion of 12 to 13

Preparation of 7-ethyl-1-tosylindole (13b) is shown as a typical example. To a refluxing solution of 95% H_2SO_4 (0.4 ml) in i-PrOH (3.6 ml), 12b (34 mg) in i-PrOH (2.0 ml) was added dropwise and the mixture was refluxed with stirring for 15 min. After cooling, it was extracted with CH_2Cl_2, the extract was washed with sat. $NaHCO_3$, and treated as usual. Purification by PTLC [hexane-EtOAc (9:1)] yielded 13b (20 mg, 75%), colorless syrup. HRMS Calcd for $C_{17}H_{17}NO_2S$: 299.0978. Found: 299.0968. Nmr ($CDCl_3$) δ: 1.10 (3H, t, J=7.5 Hz), 2.30 (3H, s), 3.05 (2H, q, J=7.5 Hz), 6.63 (1H, d, J=4 Hz), 7.49 (2H, $\underline{A}_2B_2$, J=8 Hz), 7.72 (1H, d, J=4 Hz).

13a: Colorless oil. HRMS Calcd for $C_{16}H_{15}NO_2S$: 285.0821. Found: 285.0778. Nmr ($CDCl_3$) δ: 2.26 (3H, s), 2.53 (3H, s), 6.60 (1H, d, J=4 Hz), 7.24-7.40 (1H, m), 7.48 (2H, $\underline{A}_2B_2$, J=8.5 Hz), 7.72 (1H, d, J=4 Hz).

13c: Colorless syrup. HRMS Calcd for $C_{18}H_{19}NO_2S$: 313.1136. Found: 313.1126. Nmr ($CDCl_3$) δ: 1.03 (6H, d, J=7 Hz), 2.32 (3H, s), 3.95 (1H, septet, J=7 Hz), 6.62 (1H, d, J=3.5 Hz), 7.17 and 7.47 (A_2B_2, J=8.5 Hz), 7.74 (1H, d, J=3.5 Hz). 15: Colorless prisms, mp 153-154°C (hexane-CH_2Cl_2). Anal. Calcd for $C_{21}H_{29}NO_4S$: C, 64.42; H, 7.47; N, 3.58. Found: C, 64.31; H, 7.49; N, 3.67. Ms *m/z*: 391 (M^+). Nmr ($CDCl_3$) δ: 0.76 (3H, d, J=7 Hz), 0.86 (3H, d, J=7 Hz), 0.92 (3H, d, J=6 Hz), 1.13 (3H, d, J=6 Hz), 1.39-1.69 (2H, m), 1.87-2.21 (2H, m), 2.39 (3H, s), 2.69 (1H, qq, J=7, 7 Hz), 3.68 (1H, qq, J=6, 6 Hz), 3.86-3.99 (1H, m), 6.06-6.23 (2H, m), 7.22 and 7.46

(A_2B_2, J=8.5 Hz), *ca.* 7.38-7.54 (1H, m).
13d: Colorless needles, mp 139-140°C (MeOH). Anal. Calcd for $C_{21}H_{17}NO_2S$: C, 72.60; H, 4.93; N, 4.03. Found : C, 72.31; H, 5.12; N, 4.10. Ms *m/z*: 347 (M^+). Nmr ($CDCl_3$) δ: 2.29 (3H, s), 6.67 (1H, d, J=4 Hz), 7.21 (5H, s), 7.44 (1H, dd, J= 7.5, 1.5 Hz), 7.67 (1H, d, J=4 Hz).
13e: Colorless prisms, mp 86-87°C (hexane-CH_2Cl_2). Anal. Calcd for $C_{17}H_{15}NO_2S$: C, 68.66; H, 5.08; N, 4.71. Found: C, 68.33; H, 5.02; N, 4.83. Ms *m/z*: 297 (M^+). Ir (KBr) cm^{-1}: 1625. Nmr ($CDCl_3$) δ: 2.30 (3H, s), 5.17 (1H, dd, J=10.5, 1.5 Hz), 5.41 (1H, dd, J=17, 1.5 Hz), 6.64 (1H, d, J=4 Hz), 7.10 and 7.51 (A_2B_2, J=8.5 Hz), 7.63 (1H, dd, J=17, 10.5 Hz), 7.73 (1H, d, J=4 Hz). 16: Colorless syrup. HRMS Calcd for $C_{20}H_{23}NO_3S$: 357.1399. Found: 357.1419. Nmr ($CDCl_3$) δ: 1.08 (6H, d, J=6 Hz), 2.34 (3H, s), 6.65 (1H, d, J=4 Hz), 7.17 and 7.53 (A_2B_2, J=8.5 Hz), 7.73 (1H, d, J=4 Hz).
12f: Isolated as an aldehyde after treatment with 5% HCl in THF-H_2O (1:1) at 20°C for 2 h. Colorless syrup. *HRMS Calcd for* $C_{18}H_{17}NO_3S$: 327.0929. Found: 327.0911. Ir ($CHCl_3$) cm^{-1}: 1729. Nmr ($CDCl_3$) δ: 2.34 (3H, s), 2.75 (2H, br t, J=7.5 Hz), 3.31 (2H, t, J=7.5 Hz), 6.66 (1H, d, J=4 Hz), 7.38 (1H, dd, J=7, 2 Hz), 7.49 (2H, A_2B_2, J=8.5 Hz), 7.73 (1H, d, J=4 Hz), 9.74 (1H, t, J=1 Hz). 17: Colorless syrup. HRMS Calcd for $C_{18}H_{15}NO_3S$: 325.0772. Found: 325.0784. Ir ($CHCl_3$) cm^{-1}: 1680, 1628. Nmr ($CDCl_3$) δ: 2.31 (3H, s), 6.42 (1H, dd, J=16, 8 Hz), 6.72 (1H, d, J=4 Hz), 7.13 and 7.43 (A_2B_2, J=8.5 Hz), *ca.* 7.30-7.57 (2H, m), 7.57 (1H, dd, J=7, 2 Hz), 7.78 (1H, d, J=4 Hz), 8.58 (1H, d, J=16 Hz), 9.74 (1H, d, J=8 Hz).
13g: Colorless syrup. Ms *m/z*: 285 (M^+). Nmr ($CDCl_3$) δ: 2.26 (3H s), 2.45 (3H, s), 6.55 (1H, d, J=4 Hz), 7.00 (1H, d, J=8 Hz), 7.13 and 7.72 (A_2B_2, J=8.5 Hz), 7.35 (1H, d, J=8 Hz), 7.45 (1H, d, J=4 Hz), 7.80 (1H, br s).
13h: Colorless syrup. Ms *m/z*: 339 (M^+). Ir (film) cm^{-1}: 1615. Nmr ($CDCl_3$) δ: 1.74 (3H, br s), 1.77 (3H, br s), 2.33 (3H, s), 3.45 (2H, d, J=7 Hz), 5.35 (1H, br t, J=7 Hz), 6.58 (1H, d, J=4 Hz), 7.04 (1H, dd, J=8, 1 Hz), 7.20 and 7.75 (A_2B_2, J=8.5 Hz), 7.40 (1H, d, J=8 Hz), 7.48 (1H, d, J=4 Hz), 7.80 (1H, s).
13i: Colorless prisms, mp 107-108°C (hexane-CH_2Cl_2). Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.34; H, 5.30; N, 4.91. Found: C, 67.32; H, 5.34; N, 4.90. Ms *m/z*: 285 (M^+). Nmr ($CDCl_3$) δ: 2.26 (3H, s), 2.43 (3H, s), 6.64 (1H, d, J=3.5 Hz), 6.98 (1H, d, J= 7.5 Hz), *ca.* 7.06-7.29 (1H, m), 7.15 and 7.73 (A_2B_2, J=8.5 Hz), 7.54 (1H, d, J=3.5 Hz), 7.73-7.91 (1H, m).

NBS Oxidation of 13i

A solution of 4-methyl-1-tosylindole (13i)(44 mg), NBS (30 mg), and benzoyl peroxide (10 mg) in CCl_4 (3 ml) was refluxed with stirring for 40 min. Addition of sat. $NaHCO_3$-H_2O, followed by extraction with CH_2Cl_2, usual work-up, and PTLC [hexane-EtOAc (9:1)] afforded 18 (45 mg, 80%), colorless prisms, mp 132-133°C (Et_2O). Anal. Calcd for $C_{16}H_{14}BrNO_2S$: C, 52.75; H, 3.87; N, 3.85. Found: C, 52.91; H, 3.80; N, 3.75. Ms *m/z*: 365, 363 (M^+). Nmr ($CDCl_3$) δ: 2.29 (3H, s), 4.66 (2H, s), 6.80 (1H, d, J=4 Hz), 7.09-7.37 (2H, m), 7.18 and 7.75 (A_2B_2, J=8.5 Hz), 7.64 (1H, d, J=4 Hz), 7.84-8.07 (1H, m).

Preparation of 4-Formyl-1-tosylindole (19) from 18

A mixture of 18 (25 mg) and $NaHCO_3$ (50 mg) in DMSO (1.5 ml)was heated at 82-85°C for 30 min under N_2 atmosphere. Addition of sat. $NaHCO_3$-H_2O, followed by extraction with Et_2O, usual work-up, and PTLC [hexane-CH_2Cl_2 (1:1)] gave 19[5a] (17 mg, 83%), colorless prisms, mp 144-145°C (hexane-C_6H_6)(lit., mp 142°C).

Conversion of 19 to Methyl 1-Tosylindolyl-4-carboxylate (21)

A solution of 19 (72 mg) in acetone (2 ml) was treated with Jones reagent (0.2 ml) at 0°C for 1 h. After addition of MeOH (2 ml) at 0°C, Et_2O solution of CH_2N_2 was slowly added. Sat. $NaHCO_3$-H_2O was added and the mixture was extracted with Et_2O. Filtration followed by usual work-up and PTLC [hexane-CH_2Cl_2 (1:1)] gave 21[5a] (75 mg, 95%), colorless prisms, mp 147-148°C (CH_2Cl_2-MeOH)(lit., mp 145-146°C).

Reductive Deprotection of 13 to Alkylindoles (14)

Preparation of 7-methylindole (14a) is shown as a typical example. Mg (51 mg) was added to a solution of 13a (40 mg) in MeOH (3 ml) and the mixture was stirred at 22°C for 2 h. Addition of sat. NH_4Cl-H_2O, followed by extraction with CH_2Cl_2, usual work-up, and PTLC [hexane-EtOAc (14:1)] gave 14a[10] (18 mg, 98%), colorless scales, mp 82.5-83°C (hexane)(lit., mp 85°C).

Alkylindoles (14b, 14g, 14h, and 14i) were already reported.[1,4]

14c: Colorless oil. HRMS Calcd for $C_{11}H_{13}N$: 159.1048. Found: 159.1056. Nmr ($CDCl_3$) δ: 1.38 (6H, d, J=7 Hz), 3.21 (1H, septet, J=7 Hz), 6.52 (1H, dd, J=3.5, 2 Hz), 6.97-7.23 (3H, m), 7.37-7.60 (1H, m), 8.08 (1H, br s).

14d: Colorless prisms, mp 57.5-58°C (cyclohexane). Ms *m/z*: 193 (M^+). Nmr ($CDCl_3$) δ: 6.57 (1H, dd, J=3.5, 2.5 Hz), 7.08 (1H, dd, J=3.5, 2 Hz), *ca.* 7.08-7.29 (2H, m), 8.03 (1H, br s).

14e: Colorless oil. Ms *m/z*: 143 (M^+). Ir (film) cm^{-1}: 3440, 1633. Nmr ($CDCl_3$) δ: 5.39 (1H, dd, J=11.5, 1.5 Hz), 5.75 (1H, dd, J=17.5, 1.5 Hz), 6.55 (1H, dd, J=3.5, 2 Hz), 6.97 (1H, dd, J=17.5, 11.5 Hz), 7.57 (1H, br d, J=7.5 Hz), 8.37 (1H, br s). Picrate, mp 124-125°C (hexane-C_6H_6). Anal. Calcd for $C_{10}H_9N \cdot C_6H_3N_3O_7$: C, 51.61; H, 3.25; N, 15.05. Found: C, 51.62; H, 3.34; N, 14.85.

Preparation of 26 from 11

To a cooled solution (-20°C) of 11 (60 mg) and Mg (41 mg) in THF (4 ml) was added 3-methyl-2-butenyl bromide (0.10 ml) and the mixture was stirred for 20 min under N_2 atmosphere. The reaction mixture was quenched with sat. NH_4Cl-H_2O and it was extracted with CH_2Cl_2. Usual work-up followed by PTLC [hexane-EtOAc (4:1)] gave 26 (60 mg, 83%), colorless oil. HRMS Calcd for $C_{22}H_{29}NO_5S$: 419.1764. Found: 419.1752. Ir (film) cm^{-1}: 1635. Nmr ($CDCl_3$) δ: 0.96 (3H, s), 1.00 (3H, s), 1.76 (2H, dd, J=7.5, 7.5 Hz), 2.35 (3H, s), 3.56-3.91 (4H, m), 4.40 (1H, s, exchangeable with D_2O), 4.53 (1H, dd, J=5, 5 Hz), 4.94 (1H, dd, J=17, 1.5 Hz), 5.01 (1H, dd, J=11, 1.5 Hz), 5.85 (1H, dd, J=17, 11 Hz), 5.97 (1H, dd, J=3.5, 2Hz), 6.21 (1H, dd, J=3.5, 3.5 Hz), 7.18 and 7.54 (A_2B_2, J=8.5 Hz), 7.43 (1H, dd, J=3.5, 2 Hz).

Acid Treatment of 26 to Form 27

6% H_2SO_4 treatment of 26 (29 mg) as above afforded 27 (15 mg, 58%), colorless prisms, mp 103-104°C (hexane-CH_2Cl_2). Anal. Calcd for $C_{20}H_{25}NO_4S$: C, 63.97; H, 6.71; N, 3.73. Found: C, 64.08; H, 6.65; N, 3.77. Ms *m/z*: 375 (M^+). Ir (KBr) cm^{-1}: 1685. Nmr ($CDCl_3$) δ: 1.19 (6H, s), 2.40 (3H, s), 3.88 (1H, dddd, J=6, 6, 6, 6 Hz), 6.27 (1H, dd, J=3.5, 3.5 Hz), 7.04 (1H, dd, J=3.5, 1.5 Hz), 7.27 and 7.85 (A_2B_2, J=8.5 Hz), 7.73 (1H, dd, J=3.5, 1.5 Hz).

Catalytic Hydrogenation of 26 to 30

A solution of 26 (45 mg) in MeOH (3 ml) was hydrogenated over PtO_2 (2 mg) for 10 min at atmospheric pressure. The catalyst was removed by filtration, the filtrate was evaporated *in vacuo*, and the residue was purified by PTLC [hexane-EtOAc (4:1)] to give 30 (44 mg, 97%), colorless oil. Ms *m/z*: 350 ($M^+ - \cdot CMe_2Et$). Nmr ($CDCl_3$) δ:

0.75 (3H, t, J=6.5 Hz), 0.83 (6H, s), 1.77 (2H, t, J=8 Hz), 2.36 (3H, s), 3.57-3.92 (4H, m), 4.35 (1H, s, exchangeable with D_2O), 4.54 (1H, t, J=4.5 Hz), 5.99 (1H dd, J=3.5, 2 Hz), 6.22 (1H, dd, J=3.5, 3.5 Hz), 7.21 and 7.56 (A_2B_2, J=8.5 Hz), 7.44 (1H, dd, J=3.5, 2 Hz).

Acid Treatment of 30 to Form 31 and 32

6% H_2SO_4 treatment of 30 (51 mg) as above afforded 31 (24 mg, 47%) and 32 (8 mg, 18%). 31: Colorless prisms, mp 126-127°C (hexane-CH_2Cl_2). Anal. Calcd for $C_{23}H_{33}NO_4S$: C, 65.84; H, 7.93; N, 3.34. Found: C, 65.80; H, 7.92; N, 3.34. Ms *m/z*: 360 (M^+- i-PrO·). Nmr ($CDCl_3$) δ: 0.70 (3H, t, J=7.5 Hz), 0.78 (6H, s), 0.98 (3H, d, J=6.5 Hz), 1.12 (3H, d, J=6.5 Hz), 2.42 (3H, s), 3.74 (1H, qq, J=6.5, 6.5 Hz), 3.78-3.93 (1H, m), 6.13 (1H, dd, J=3.5, 2.5 Hz), 6.23 (1H, dd, J=3.5, 3.5 Hz), 7.24 and 7.44 (A_2B_2, J=8.5 Hz), 7.61 (1H, dd, J=3.5, 2.5 Hz). 32: Colorless oil. Ms *m/z*: 359 (M^+). Ir (film) cm^{-1}: 1705, 1640. Nmr ($CDCl_3$) δ: 0.77 (3H, t, J=7.5 Hz), 1.11 (6H, s), 1.57 (2H, q, J=7.5 Hz), 2.37 (3H, s), 3.33 (2H, dd, J=7, 1.5 Hz), 6.01 (1H, dt, J=16, 7 Hz), 6.17 (1H, dd, J=3.5, 3.5 Hz), 6.28-6.40 (1H, m), 6.83 (1H, br. d, J=16 Hz), 7.12-7.32 (1H, m), 7.23 and 7.64 (A_2B_2, J=8.5 Hz).

Reductive Deprotection 26 to Form 34

Applying the above procedure, 26 (24 mg) was deprotected with Mg (21 mg) to 34 (14 mg, 92%), colorless oil after purification by PTLC [hexane-EtOAc (4:1)]. Ms *m/z*: 247 (M^+-H_2O). Ir ($CHCl_3$) cm^{-1}: 1633. Nmr ($CDCl_3$) δ: 0.93 (3H, s), 1.02 (3H, s), 3.11 (1H, s, exchangeable with D_2O), 3.68-4.06 (4H, m), 4.81 (1H, dd, J=4, 4 Hz), 5.04 (1H, dd, J=17, 1.5 Hz), 5.07 (1H, dd, J=11.5, 1.5 Hz), 5.74-5.92 (1H, m), 6.03 (1H, dd, J=17, 11.5 Hz), 6.05-6.23 (1H, m), 6.56-6.70 (1H, m), 8.61 (1H, br s).

Preparation of 7-(1,1-Dimethyl-2-propenyl)indole (23)

A solution of 34 (12 mg) and *p*-TsOH·H_2O (2.5 mg) in C_6H_6 (2 ml) was refluxed with stirring for 5 min. Addition of sat. $NaHCO_3$-H_2O, followed by extraction with CH_2Cl_2, usual work-up, and PTLC [hexane-CH_2Cl_2 (8:1)] afforded 23 (7 mg, 84%), colorless oil. HRMS Calcd for $C_{13}H_{15}N$: 185.1203. Found: 185.1187. Nmr ($CDCl_3$) δ: 1.53 (6H, s), 5.20 (1H, dd, J=10, 1.5 Hz), 5.30 (1H, dd, J=17.5, 1.5 Hz), 6.25 (1H, dd, J=17.5, 10 Hz), 6.51 (1H, dd, J=3.5, 2 Hz), 7.41-7.66 (1H, m), 8.55 (1H, br s).

Preparation of 7-(3,7-Dimethyl-1,6-octadien-3-yl)indole (24)

According to the method for 26, 11 (60 mg) was treated with Mg (41 mg) and geranyl bromide (0.16 ml) in THF (4 ml) at 0°C for 1 h to give 35 (65 mg), 36 (7 mg), and 38 (4 mg, 12%) after PTLC [hexane-EtOAc (5:1)]. Deprotection of 35 (65 mg) with Mg (48 mg) in MeOH (3 ml) afforded further crop (49 mg) of 36. The combined 36 in C_6H_6 (4 ml) was refluxed with *p*-TsOH·H_2O (5 mg) for 3 min under N_2 atmosphere. Work-up as above followed by PTLC [hexane-CH_2Cl_2 (13:1)] provided 24 (20 mg, 46% from 11) as colorless oil. 24 containing 7% 37: GC-HRMS Calcd for $C_{18}H_{23}N$: 253.1828. Found for 24: 253.1826; for 37: 253.1825. Ir ($CHCl_3$) cm^{-1}: 3490, 1634. Nmr of 24 ($CDCl_3$) δ: 1.43 (3H, br s), 1.48 (3H, s), 1.62 (3H, br s), 4.93-5.17 (1H, m), 5.25 (1H, dd, J=10, 1.5 Hz), 5.26 (1H, dd, J=17.5, 1.5 Hz), 6.24 (1H, dd, J=17.5, 10 Hz), 6.49 (1H, dd, J=3.5, 2.5 Hz), 7.41-7.65 (1H, m), 8.57 (1H, br s). Nmr of 37 δ: 4.57 (1H, br s), 4.67 (1H, br s). 38: Colorless syrup. Ms *m/z*: 195 (M^+). Ir ($CHCl_3$) cm^{-1}: 1640. Nmr ($CDCl_3$) δ: 2.08 (2H, dt, J=4.5, 7.5 Hz), 2.90 (2H, t, J=7.5 Hz), 3.70-4.08 (4H, m), 4.96 (1H, t, J=4.5 Hz), 9.19-9.88 (1H, br s, exchangeable with D_2O).

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