Synthesis of ellipticine by reaction of 1-(4-methoxybenzyl)indole-2,3-dicarboxylic anhydride with (3-bromo-4-pyridyl)-triisopropoxytitanium

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Reaction of 1-benzyl- and 1-(4-methoxybenzyl)indole-2,3-dicarboxylic anhydride with (3-bromo-4-pyridyl)triisopropoxytitanium gave the corresponding 2-acylindole-3-carboxylic acids as the sole product. Deprotection of the 1-(4-methoxybenzyl) group of the 2-acylindole-3-carboxylic acid was performed by treatment with perchloric acid in acetic acid to afford 2-(3-bromoisonicotinoyl)indole, which was converted to ellipticine.

Ellipticine, 5,11-dimethyl-6*H*-pyrido[4,3-*b*]carbazole, has potent antitumor activity[1] and many useful methods for its synthesis have been developed.[2] In a previous paper we described the synthesis of ellipticine,[3] but in this synthesis debenzylation of the 1-benzyl-2-(3-bromoisonicotinoyl)indole resulted in low yield. However, recently, we have shown that the 4-methoxybenzyl and 3,4-dimethoxybenzyl groups are suitable for the protection of the nitrogen in an indole and deprotection of the 4-methoxybenzyl and 3,4-dimethoxybenzyl groups was performed by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or trifluoroacetic acid depending on the substituents of the indoles.[4] In this paper we report the detailed synthesis of ellipticine by the reaction of 1-benzyl-[3,5] and 1-(4-methoxybenzyl)indole-2,3-dicarboxylic anhydride (**1** and **10**) with (3-bromo-4-pyridyl)triisopropoxytitanium.

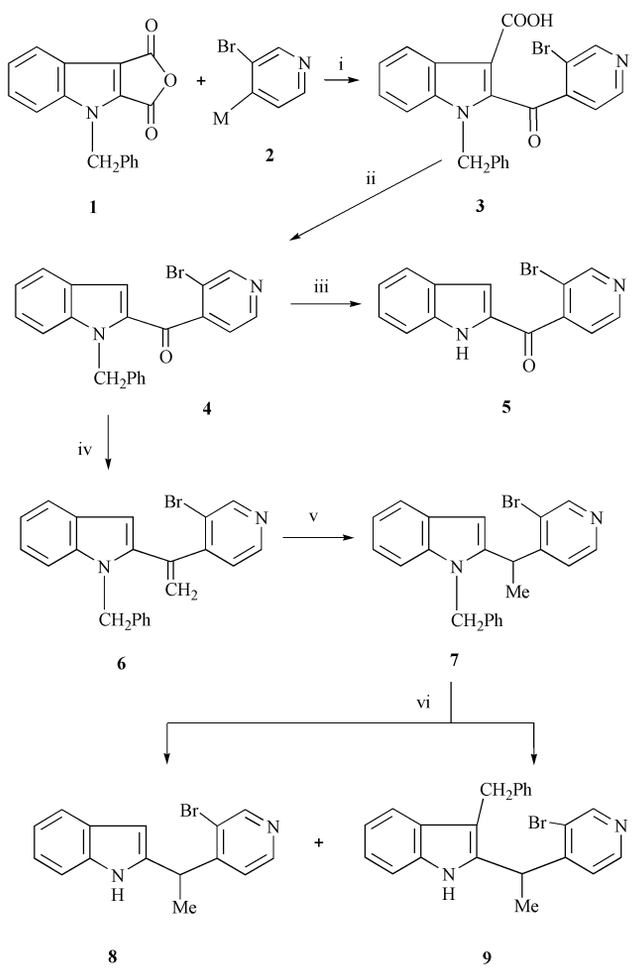
Results and discussion

Reaction of 1-benzylindole-2,3-dicarboxylic anhydride **1**[6] with 3-bromo-4-lithiopyridine (**2**, M = Li) in THF at −96 °C gave 1-benzyl-2-(3-bromoisonicotinoyl)indole-3-carboxylic acid **3** in 42% yield (Scheme 1).[5] Many attempts to obtain **3** under various conditions were less than satisfactory (Table 1 entry 1, 2). However, treatment of **1** with (3-bromo-4-pyridyl)triisopropoxytitanium (**2**, M = Ti(OPr-*i*)$_3$)[7] afforded **3** in 86% yield (Table 1, entry 3, 4).

Debenzylation of the carboxylic acid **3** by treatment with $AlCl_3$ and anisole[8] resulted in recovery of **3**. However, after removal of the carboxy group from **3** with 20% hydrochloric acid in acetic acid, debenzylation of the 1-benzyl-2-(3-bromoisonicotinoyl)indole **4** was performed by treatment of $AlCl_3$ and anisole to give 2-(3-bromoisonicotinoyl)indole **5** in 42% yield, but the yield was still low.

Table 1 Reaction of the anhydride **1** with 4-metalated 3-bromopyridine **2**

Entry	M	**2** (equiv.)	Yield of **3** (%)
1	Li	1.2	42
2	Li	2.0	25
3	Ti(OPr-*i*)$_3$	1.2	60
4	Ti(OPr-*i*)$_3$	2.0	86



Scheme 1 *Reagents and conditions*: i. **2**, in THF, −96 °C; ii, 20% $HClO_4$ in AcOH, reflux (94%); iii, $AlCl_3$ in anisole, 100 °C (42%); iv, $Ph_3P{=}CH_2$ in THF (66%); v, PtO_2 in EtOH (83%); vi, $AlCl_3$ in anisole, 100 °C **8** (28%) and **9** (27%).

Finally, we examined the effect of the 2-substituents on the indole ring on the reactivity of 1-benzyl-2-(4-pyridylmethyl)-indole derivative **7** compared with that of the 2-acylindole **5**. Compound **5** was changed to **7** by treatment with methylenetriphenylphosphorane ($Ph_3P{=}CH_2$), followed by catalytic

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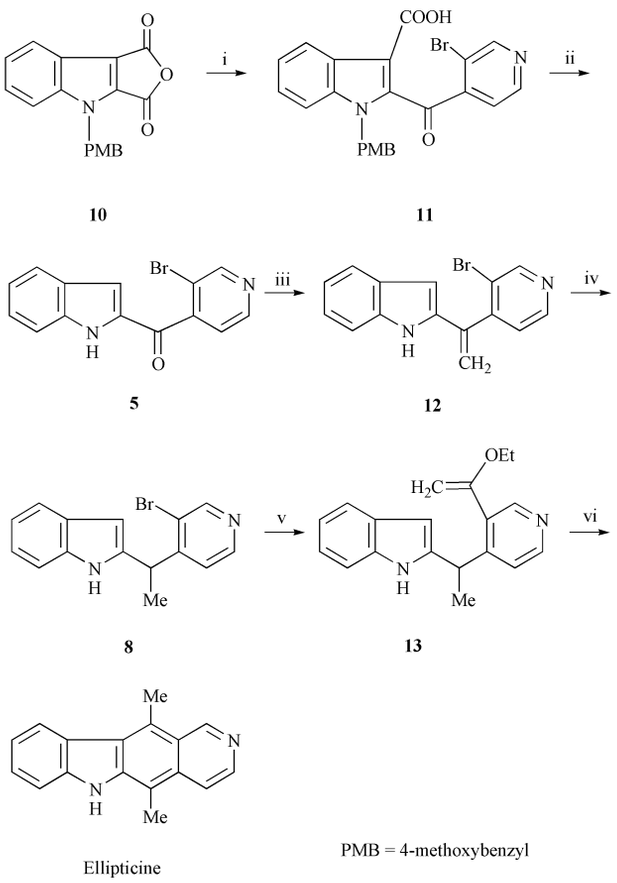
hydrogenation. Compound **7** was treated with $AlCl_3$ and anisole at 100 °C to afford a mixture of the debenzylated product **8** and 3-benzyl derivative **9** in 28 and 27% yields, respectively. These results show that debenzylation of **3**, **4**, and **7** was difficult. Therefore, we investigated the utility of the 4-methoxybenzyl group as a protecting group of an indole nitrogen in the synthesis of ellipticine.

1-(4-Methoxybenzyl)indole-2,3-dicarboxylic anhydride **10** was reacted with (3-bromo-4-pyridyl)triisopropoxytitanium (**2**, M = Ti(OPr-*i*)$_3$) in THF at −96 °C to provide 1-(4-methoxybenzyl)-2-(3-bromoisonicotinoyl)indole-3-carboxylic acid **11** in 61% yield (Scheme 2). Removal of both the 4-methoxybenzyl and carboxy groups was performed by treatment with 20% perchloric acid in acetic acid to provide **5** in 81% yield.



Scheme 2 *Reagents and conditions*: i. **2** (M = Ti(OPr-*i*)$_3$) in THF, −96 °C (61%); ii, 20% $HClO_4$ in AcOH, reflux (81%); iii, $Ph_3P{=}CH_2$ in THF (63%); iv, PtO_2 in EtOH (73%); v, (ethoxyvinyl)tributyltin in toluene, reflux (97%); vi, 10% HCl in THF, rt (87%).

In a similar conversion to **7** from **4**, **5** was converted to **8** by treatment with methylenetriphenylphosphorane ($Ph_3P{=}CH_2$), followed by catalytic hydrogenation. Treatment of **8** with (1-ethoxyvinyl)tributyltin in the presence of tetrakis(triphenylphosphine)palladium(0) in refluxing toluene gave the corresponding ethoxyvinyl derivative **13**, which was converted to ellipticine[9,10] in 87% yield by treatment with 10% hydrochloric acid.

Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. The ^{1}H-NMR spectra were determined on a JEOL JNM-GSX 270 spectrometer using tetramethylsilane as an internal standard and $CDCl_3$ as solvent and *J* values are given in Hz. The IR spectra were recorded with a JASCO FT/IR-7000 spectrophotometer. The high resolution MS were recorded on a JEOL JMS-HX100 spectrometer. Column chromatography was performed on E. Merck silica gel 60 (70–230 mesh or 230–400 mesh). Tetrahydrofuran (THF) was distilled from sodium and benzophenone prior to use. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride prior to use.

1-Benzyl-2-(3-bromoisonicotinoyl)indole 4

A suspension of 1-benzyl-2-(3-bromoisonicotinoyl)indole-3-carboxylic acid **3**[5] (435 mg, 1.0 mmol) in 20% perchloric acid (10 cm^3) and acetic acid (5 cm^3) was refluxed for 3 h. The reaction mixture was neutralized by addition of saturated sodium hydrogen carbonate solution and extracted with $CHCl_3$. The combined extracts were washed with water and dried over Na_2SO_4, then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane : AcOEt = 10 : 1) to give 1-benzyl-2-(3-bromoisonicotinoyl)indole **4** (368 mg, 94%), mp 103–104 °C (from *n*-hexane); ν_{max}(Nujol)/cm^{-1} 1652; δ_H ($CDCl_3$) 5.97 (2H, s, C*H*$_2$Ph), 6.87 (1H, d, *J* 1, 3-H), 7.12–7.48 (9H, m, Ar), 7.65 (1H, dt, *J* 8, 1, 4-H), 8.66 (1H, d, *J* 5, 6′-H), 8.83 (1H, s, 2′-H) (Calcd. for $C_{21}H_{15}BrN_2O$: C, 64.46; H, 3.86; N, 7.16. Found: C, 64.36; H, 4.06; N, 7.17%).

2-(3-Bromoisonicotinoyl)indole 5

A mixture of 1-benzyl-2-(3-bromoisonicotinoyl)indole **4** (587 mg, 1.5 mmol) and aluminium(III) chloride (998 mg, 7.5 mmol) in anisole (15 cm^3) was stirred for 1.5 h at 100 °C. Aluminium(III) chloride (599 mg, 4.5 mmol) was added to the mixture and the mixture was stirred for another 2.5 h at 100 °C. The reaction mixture was neutralized by addition of saturated sodium hydrogen carbonate solution and extracted with $CHCl_3$. The combined extracts were washed with water and dried over Na_2SO_4, then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2–AcOEt = 10 : 1) to give 2-(3-bromoisonicotinoyl)-indole **5** (188 mg, 42%), mp 220–221 °C (from MeOH); ν_{max}($CHCl_3$)/cm^{-1} 3454, 1643; δ_H ($CDCl_3$) 6.88 (1H, dd, *J* 2.5, 1, 3-H), 7.18 (1H, ddd, *J* 8, 7, 1, 5-H), 7.42 (1H, ddd, *J* 8, 7, 1, 6-H), 7.42 (1H, d, *J* 5, 5′-H), 7.49 (1H, dd, *J* 8, 1, 7-H), 7.68 (1H, dd, *J* 8, 1, 4-H), 8.69 (1H, d, *J* 5, 6′-H), 8.89 (1H, s, 2′-H), 9.23 (1H, br s, NH) (Calcd. for $C_{14}H_9BrN_2O$: C, 55.84; H, 3.01; N, 9.30. Found: C, 55.80; H, 3.14; N, 9.24%).

From 11

Using a procedure similar to that described for the preparation of **4**, **5** (17 mg, 81%) was obtained from 1-(4-methoxybenzyl)-2-(3-bromoisonicotinoyl)indole-3-carboxylic acid **11** (33 mg, 0.07 mmol).

1-(1-Benzyl-2-indolyl)-1-(3-bromo-4-pyridyl)ethene 6

A solution of 1-benzyl-2-(3-bromoisonicotinoyl)indole **4** (391 mg, 1 mmol) in THF (1.5 cm^3) was added to a solution of methylenetriphenylphosphorane [prepared from methyltriphenylphosphonium bromide (430 mg, 1.2 mmol) and 1.56 M *n*-butyllithium in *n*-hexane solution (5.8 cm^3, 9 mmol) for 30 min at rt] in THF (2.5 cm^3) at 0 °C and the mixture was stirred for 22 h under argon. The reaction mixture was acidified with 10% hydrochloric acid and extracted with CH_2Cl_2. The organic extracts were washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (*n*-hexane–AcOEt = 10 : 1) to give 1-(1-benzyl-2-indolyl)-1-(3-bromo-4-pyridyl)ethene **6** (258 mg, 66%), mp 102–103 °C (from *n*-hexane); δ_H ($CDCl_3$) 5.38 (2H, s, C*H*$_2$Ph), 5.51 (1H, s, vinyl), 5.63 (1H, s, vinyl), 6.35 (1H, s, 3-H), 6.96–7.35 (9H, m, Ar), 7.56–7.64 (1H, m, 4-H), 8.43 (1H, d, *J* 5, 6′-H), 8.66 (1H, s, 2′-H) (Calcd. for $C_{22}H_{17}BrN_2$: C, 67.88; H, 4.40; N, 7.20. Found: C, 67.79; H, 4.50; N, 7.18%).

1-(1-Benzyl-2-indolyl)-1-(3-bromo-4-pyridyl)ethane 7 and 1-(1-benzyl-2-indolyl)-1-(4-pyridyl)ethane

A suspension of 1-(1-benzyl-2-indolyl)-1-(3-bromo-4-pyridyl)-ethene **6** (389 mg, 1 mmol) and PtO_2 (45 mg) in AcOEt (20 cm^3) was stirred for 8 h under hydrogen. The catalyst was removed by filtration through Celite and the filtrate was evaporated off. The residue was purified by column chromatography (*n*-hexane–AcOEt = 4 : 1) to yield 1-(1-benzyl-2-indolyl)-1-(3-bromo-4-pyridyl)ethane **7** (326 mg, 83%) as an oil; δ_H ($CDCl_3$) 1.61 (3H, d, *J* 7, $CHCH_3$), 4.53 (1H, q, *J* 7, $CHCH_3$), 4.89 (1H, d, *J* 17, CH_2Ph), 5.16 (1H, d, *J* 17, CH_2Ph), 6.68 (1H, s, 3-H), 6.75–6.83 (2H, m, Ar), 6.85 (1H, d, *J* 5, 5′-H), 7.08–7.72 (6H, m, Ar), 7.65–7.72 (1H, m, 4-H), 8.19 (1H, d, *J* 5, 6′-H), 8.57 (1H, s, 2′-H) (HRMS *m*/*z* Calcd. for $C_{22}H_{19}BrN_2$: *M*, 390.0732. Found: M^+, 390.0755). 1-(1-Benzyl-2-indolyl)-1-(4-pyridyl)ethane (4.5 mg, 10%) as an oil; δ_H ($CDCl_3$) 1.64 (3H, d, *J* 7, $CHCH_3$), 4.06 (1H, q, *J* 7, $CHCH_3$), 4.89 (1H, d, *J* 17, CH_2Ph), 5.21 (1H, d, *J* 17, CH_2Ph), 6.62 (1H, s, 3-H), 6.76–6.84 (2H, m, Ar), 7.02 (2H, d, *J* 5, 3′-H and 5′-H), 7.09–7.24 (6H, m, Ar), 7.63–7.71 (1H, m, 4-H), 8.44 (2H, d, *J* 5, 2′-H and 6′-H) (HRMS *m*/*z* Calcd. for $C_{22}H_{20}N_2$: *M*, 312.1626. Found: M^+, 312.1629).

1-(2-Indolyl)-1-(3-bromo-4-pyridyl)ethane 8 and 1-(3-benzyl-2-indolyl)-1-(3-bromo-4-pyridyl)ethane 9

Using a procedure similar to that described for the preparation of **5**, 1-(2-indolyl)-1-(3-bromo-4-pyridyl)ethane **8** (8 mg, 28%) and 1-(3-benzyl-2-indolyl)-1-(3-bromo-4-pyridyl)ethane **9** (11 mg, 27%) were obtained from 1-(1-benzyl-2-indolyl)-1-(3-bromo-4-pyridyl)ethane **7** (39 mg, 0.1 mmol).

8: mp 117–119 °C (from *n*-hexane–AcOEt); ν_{max}($CHCl_3$)/cm^{-1} 3464; δ_H ($CDCl_3$) 1.69 (3H, d, *J* 7, $CHCH_3$), 4.68 (1H, q, *J* 7, $CHCH_3$), 6.47–6.50 (1H, m, 3-H), 7.00 (1H, d, *J* 5, 5′-H), 7.06–7.30 (3H, m, Ar), 7.56–7.62 (1H, m, 4-H), 7.98 (1H, br s, NH), 8.34 (1H, d, *J* 5, 6′-H), 8.69 (1H, s, 2′-H) (HRMS *m*/*z* Calcd. for $C_{15}H_{13}BrN_2$: *M*, 300.0262. Found: M^+, 300.0267).

9: oil; ν_{max}($CHCl_3$)/cm^{-1} 3436; δ_H ($CDCl_3$) 1.64 (3H, d, *J* 7, $CHCH_3$), 4.02 (2H, s, $-CH_2Ph$), 4.75 (1H, q, *J* 7, $CHCH_3$), 7.00–7.22 (8H, m, Ar), 7.35 (1H, d, *J* 8.5, 7-H), 7.44 (1H, d, *J* 8, 4-H), 7.94 (1H, s, NH), 8.32 (1H, d, *J* 5, 6′-H), 8.61 (1H, s, 2′-H) (HRMS *m*/*z* Calcd. for $C_{22}H_{19}BrN_2$: *M*, 390.0732. Found: M^+, 390.0733).

1-(4-Methoxybenzyl)indole-2,3-dicarboxylic anhydride 10

To a suspension of sodium hydride (1.20 g, 60% assay, 30 mmol) in *N*,*N*-dimethylformamide (6 cm^3) was added indole-2,3-dicarboxylic acid (1.23 g, 6 mmol), then 4-methoxybenzyl chloride (2.44 cm^3, 18 mmol) at 0 °C. After the mixture was stirred for 24 h at room temperature, the mixture was poured into water and washed with Et_2O. The aqueous layer was acidified (pH = 1) with concentrated hydrochloric acid to give a precipitate, which was collected by filtration to afford 1-(4-methoxybenzyl)indole-2,3-dicarboxylic acid (1.35 g, 69%).

A suspension of 1-(4-methoxybenzyl)indole-2,3-dicarboxylic acid (650 mg, 2 mmol) and trifluoroacetic anhydride (0.85 cm^3, 6 mmol) in CH_2Cl_2 (20 cm^3) was stirred for 4 h at room temperature. The reaction mixture was evaporated off to afford a solid, which was washed with *n*-hexane–$CHCl_3$ (3 : 1) to give 1-(4-methoxybenzyl)indole-2,3-dicarboxylic anhydride **10** (473 mg, 77%), mp 177–179 °C (from THF); ν_{max}(Nujol)/cm^{-1} 1825, 1766; δ_H (DMSO-d_6) 3.69 (3H, s, OMe), 5.81 (2H, s, CH_2Ph), 6.82 (2H, d, *J* 9, 2′-H and 6′-H), 7.09 (2H, d, *J* 9, 3′-H and 5′-H), 7.15–7.28 (2H, m, Ar), 7.50 (1H, d, *J* 8.5, 7-H), 8.28 (1H, d, *J* 8.5, 4-H) (HRMS *m*/*z* Calcd. for $C_{18}H_{13}NO_4$: *M*, 307.0845. Found: M^+, 307.0823).

1-(4-Methoxybenzyl)-2-(3-bromoisonicotinoyl)indole-3-carboxylic acid 11

To a solution of 3-bromo-4-lithiopyridine [prepared from 3-bromopyridine (0.23 cm^3, 2.4 mmol), diisopropylamine (0.34 cm^3, 2.4 mmol), and 1.56 M *n*-butyllithium in *n*-hexane solution (1.6 cm^3, 2.4 mmol) in THF (5 cm^3) at room temperature] was added 1.0 M chlorotitanium triisopropoxide in *n*-hexane solution (2.4 cm^3, 2.4 mmol) at −96 °C. A solution of 1-(4-methoxybenzyl)indole-2,3-dicarboxylic anhydride **10** (368 mg, 1.2 mmol) in THF (5 cm^3) was added to the dark suspension at −96 °C and the mixture was stirred for 1 h. The reaction mixture was quenched by addition of 10% hydrochloric acid and extracted with $CHCl_3$. The combined extracts were washed with water and dried over Na_2SO_4, then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel ($CHCl_3$–MeOH = 20 : 1) to give **11** (343 mg, 61%), mp 232–233 °C (from acetone); ν_{max}(Nujol)/cm^{-1} 1679; δ_H (DMSO-d_6) 3.68 (3H, s, OMe), 5.50 (2H, s, CH_2Ph), 6.78–6.84 (2H, m, Ar), 7.04–7.12 (2H, m, Ar), 7.17 (1H, d, *J* 5, 5′-H), 7.31 (1H, ddd, *J* 8, 6.5, 1.5, 5-H), 7.41 (1H, ddd, *J* 8, 6.5, 1.5, 6-H), 7.72 (1H, d, *J* 8, H-7), 8.03–8.08 (1H, m, 4-H), 8.53 (1H, d, *J* 5, 6′-H), 8.83 (1H, s, 2′-H) (Calcd. for $C_{23}H_{17}BrN_2O_4$: C, 59.40; H, 3.68; N, 6.02. Found: C, 59.29; H, 3.81; N, 5.91%) (HRMS *m*/*z* Calcd. for $C_{23}H_{17}BrN_2O_4$: *M*, 464.0372. Found: M^+, 464.0397).

1-(2-Indolyl)-1-(3-bromo-4-pyridyl)ethene 12

A solution of 2-(3-bromoisonicotinoyl)indole **5** (60 mg, 0.2 mmol) in THF (1.5 cm^3) was added to a solution of methylenetriphenylphosphorane [prepared from methyltriphenylphosphonium bromide (157 mg, 0.44 mmol) and 1.56 M *n*-butyllithium in *n*-hexane solution (0.28 cm^3, 0.44 mmol) for 30 min at rt] in THF (1 cm^3) at 0 °C and the mixture was stirred for 18 h under argon. The reaction mixture was acidified with 10% hydrochloric acid and extracted with CH_2Cl_2. The organic extracts were washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (CH_2Cl_2–AcOEt = 50 : 1) to give 1-(2-indolyl)-1-(3-bromo-4-pyridyl)ethene **12** (38 mg, 63%), mp 171–172 °C (from MeOH); ν_{max}($CHCl_3$)/cm^{-1} 3472; δ_H ($CDCl_3$) 5.26 (1H, s, one of CH_2), 5.26 (1H, s, one of CH_2), 6.16 (1H, d, *J* 2, 3-H), 7.08 (1H, ddd, *J* 8, 7, 1, 5-H), 7.21 (1H, ddd, *J* 8.5, 7, 1.5, 6-H), 7.32 (1H, dd, *J* 5, 0.5, 5′-H), 7.36 (1H, dd, *J* 8.5, 1, 7-H), 7.52 (1H, br d, *J* 8, 4-H), 8.31 (1H, br s, NH), 8.58 (1H, d, *J* 5, 6′-H), 8.81 (1H, d, *J* 0.5, 2′-H) (Calcd. for $C_{15}H_{11}BrN_2$: C, 60.22; H, 3.71; N, 9.37. Found: C, 60.16; H, 3.86; N, 9.24%).

1-(2-Indolyl)-1-(3-bromo-4-pyridyl)ethane 8

A suspension of 1-(2-indolyl)-1-(3-bromo-4-pyridyl)ethene **12** (60 mg, 0.2 mmol) and PtO_2 (9 mg) in AcOEt (4 cm^3) was stirred for 8 h under hydrogen. The catalyst was removed by filtration through Celite and the filtrate was evaporated off. The residue was purified by column chromatography (CH_2Cl_2–AcOEt = 20 : 1) to yield 1-(2-indolyl)-1-(3-bromo-4-pyridyl)-ethane **8** (44 mg, 73%).

1-(2-Indolyl)-1-[3-(1-ethoxyvinyl)-4-pyridyl]ethane 13

A solution of 1-(2-indolyl)-1-(3-bromo-4-pyridyl)ethane **8** (36 mg, 0.12 mmol), (1-ethoxyvinyl)tributyltin (0.061 cm^3, 0.18 mmol), and tetrakis(triphenylphosphine)palladium(0) (3 mg, 0.0024 mmol) in toluene (2 cm^3) was refluxed for 1 h under argon. The insoluble material was filtered off and the filtrate was concentrated to give a residue, which was purified by column chromatography (*n*-hexane–AcOEt = 5 : 1) to yield 1-(2-indolyl)-1-[3-(1-ethoxyvinyl)-4-pyridyl]ethane **13** (34 mg, 97%) as an oil; ν_{max}($CHCl_3$)/cm^{-1} 3426; δ_H ($CDCl_3$) 1.47 (3H, t, *J* 7, OCH_2CH_3), 1.70 (3H, d, *J* 7, $=CHCH_3$), 4.04 (2H, q, *J* 7, OCH_2CH_3), 4.41 (1H, d, *J* 2.5, vinyl), 4.48 (1H, q, *J* 7, $=CHCH_3$), 4.52 (1H, d, *J* 2.5, vinyl), 6.46–6.49 (1H, m, 3-H), 7.02–7.21 (4H, m, Ar), 7.55–7.61 (1H, m, 4-H), 8.41 (1H, d, *J* 5, 6′-H), 8.41 (1H, br, NH), 8.55 (1H, s, 2′-H) (HRMS *m*/*z* Calcd. for $C_{19}H_{20}N_2O$: *M*, 292.1576. Found: M^+, 292.1602).

Ellipticine

A solution of 1-(2-indolyl)-1-[3-(1-ethoxyvinyl)-4-pyridyl]-ethane **13** (29 mg, 0.1 mmol) and 10% hydrochloric acid (0.2 cm^3) in THF (0.8 cm^3) was stirred for 16 h at rt. The reaction mixture was neutralized by addition of 5% sodium hydrogen carbonate solution and extracted with $CHCl_3$–MeOH (10 : 1). The organic extracts were washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (CH_2Cl_2–AcOEt = 40 : 1) to give ellipticine (22 mg, 87%), mp >300 °C (from MeOH) [lit.[9] 312–314 °C (dec.)]. δ_H (DMSO-d_6) 2.80 (3H, s, CH_3), 3.27 (3H, s, CH_3), 7.22–7.33 (1H, m, Ar), 7.49–7.61 (2H, m, Ar), 7.91 (1H, d, *J* 6, 4-H), 8.36 (1H, d, *J* 8, 10-H), 8.43 (1H, d, *J* 6, 3-H), 9.69 (1H, s, 1-H), 11.25 (1H, s, NH) (HRMS *m/z* Calcd. for $C_{17}H_{14}N_2$: *M*, 246.1157. Found: M^+, 246.1185).

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