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**NITRATION OF DIMETHYL 1-SUBSTITUTED
INDOLE-2,3-DICARBOXYLATES: SYNTHESIS OF NITRO-
AND AMINOINDOLE DERIVATIVES**

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Abstract – The treatment of dimethyl indole-2,3-dicarboxylate with nitronium tetrafluoroborate in the presence of tin (IV) chloride produced dimethyl 5-nitroindole-2,3-dicarboxylate as the major product. In a similar manner, the dimethyl 1-benzyl- and 1-benzenesulfonylindole-2,3-dicarboxylates provided a mixture of the corresponding 4-nitro-, 5-nitro-, 6-nitro- and 7-nitroindole derivatives. However, dimethyl 5-bromoindole-2,3-dicarboxylate gave dimethyl 5-bromo-4-nitroindole-2,3-dicarboxylate as the sole product, which was converted to dimethyl 4-aminoindole-2,3-dicarboxylate.

The nitration of indoles is one of the useful reactions for introducing the nitrogen atom directly into indole rings, but indoles having an electron-donating group are unstable under the usual nitration conditions and also undergo undesirable oxidation and polymerization. However, indoles possessing an electron-withdrawing group such as acyl or ester group are relatively stable under severe nitration conditions. The aromatic nitro group is a useful functional group, which could be converted into various groups *via* an amino group by reduction. The nitration of ethyl indole-2-carboxylate afforded 4-nitroindole derivative in low yield as reported by Norland¹, and from methyl indole-3-carboxylate, a mixture of methyl 4-nitroindole-3-carboxylate (30%) and ethyl 6-nitroindole-3-carboxylate (30%) was obtained by Nakatsuka.² Ottoni showed that 3-acetyl-5-nitroindole was obtained at low temperature by the nitration of 3-acetylindole with nitronium tetrafluoroborate (NO_2BF_4), but at 60° C, 3-acetyl-6-nitroindole was isolated as the sole product.³ Tobinaga reported the synthesis of chuangxinmycin from 3-acetyl-4-nitroindole, which was prepared by the nitration of 3-acetylindole in the presence of metal in low yield.⁴ We reported that dimethyl indole-2,3-dicarboxylates and indole-2,3-dicarboxylic anhydrides were useful synthons for the synthesis of pratosine,⁵ hippadine,⁵ murrayaquinone-A,⁶ ellipticine,⁷⁻⁹ olivacine,¹⁰ and caulersin.¹¹ Recently, we showed the selective bromination of the dimethyl indole-2,3-dicarboxylates and the synthesis of the dimethyl 5-bromo-,

6-bromo-, and 5,6-dibromoindole-2,3-dicarboxylates because many bromoindole alkaloids have been isolated from various sources.¹² In this study, we examine the nitration of the dimethyl 1-substituted indole-2,3-dicarboxylates (**1**) using NO_2BF_4 and trifluoroacetyl nitrate (TFAN, $\text{CF}_3\text{COONO}_2$)¹³ to enhance their utility as a synthon for the synthesis of the indole alkaloids.

The reaction of dimethyl indole-2,3-dicarboxylate (**1a**) ($\text{R} = \text{H}$) with NO_2BF_4 in the presence of tin (IV) chloride in dichloromethane at -20°C gave dimethyl 5-nitroindole-2,3-dicarboxylate (**3a**) in 79% yield as a major product with a mixture of dimethyl 6-nitro- (**4a**) and 7-nitroindole-2,3-dicarboxylate (**5a**), in 4% and 13% yields, respectively, but with TFAN, **1a** gave a mixture of dimethyl 4-nitroindole-2,3-dicarboxylate (**2a**), **3a**, **4a**, and **5a** in 9%, 30%, 13%, and 9% yields, respectively. (Entries 1, 2) The nitration of dimethyl 1-benzylindole-2,3-dicarboxylate (**1b**) ($\text{R} = \text{CH}_2\text{Ph}$) with NO_2BF_4 resulted in a complex mixture, but with TFAN, a mixture of **2b**, **3b**, and **4b** was obtained. (Entries 3, 4) The treatment of dimethyl 1-benzenesulfonylindole-2,3-dicarboxylate (**1c**) ($\text{R} = \text{SO}_2\text{Ph}$) with NO_2BF_4 or TFAN afforded an inseparable mixture of **2c**, **3c**, **4c**, and **5c**. (Entries 5, 6) (Table 1)

Scheme 1

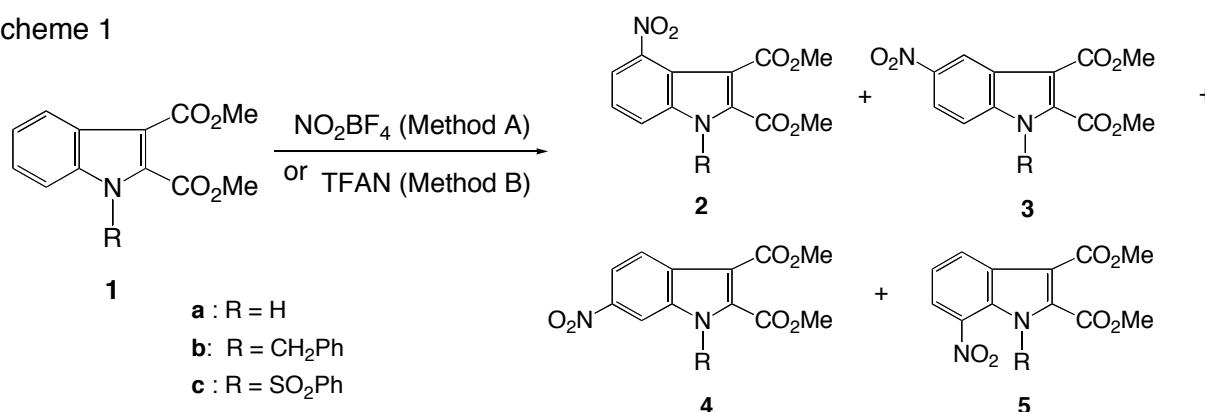


Table 1

Entry	1	Method	Condition	2	3	4	5	1	Total
1	a	A	-20°C 5 h	-	79	4	13	-	99
2	a	B	-78°C 0.5 h	9	30	13	9	23	84
3	b	A	rt 3 h	-	-	-	-	-	-
4	b	B	-78°C 2 h	16	35	19	-	16	86
5 ¹⁾	c	A	rt 8 h	16	26	26	-	-	68
6 ¹⁾	c	B	-78°C 3 h	30	28	24	15	-	97

1) SO_2Ph derivatives (**2c**, **3c**, **4c**, **5c**) were isolated as NH derivatives (**2a**, **3a**, **4a**, **5a**) by treatment with tetrabutylammonium fluoride.

Method A: NO_2BF_4 (2.2 eq) and Sn(IV)Cl_4 (5 eq) in CH_2Cl_2 .

Method B: NH_4NO_3 (1.2 eq) and $(\text{CF}_3\text{COO})_2\text{O}$ (10eq) in CH_2Cl_2 .

We also examined the nitration of the dimethyl 5-bromoindole-2,3-dicarboxylates (**6a** and **6b**) because **6a** and **6b** were easily obtained by the bromination of dimethyl indole-2,3-dicarboxylate (**1a**) and (**1b**),

respectively.¹² A complex mixture was obtained from the reaction of dimethyl 5-bromoindole-2,3-dicarboxylate (**6a**) ($R = H$) with TFAN, but dimethyl 5-bromo-4-nitroindole-2,3-dicarboxylate (**7a**) was isolated as the sole product in 83% yield by treatment with NO_2BF_4 . (Entries 1, 2) However, the treatment of **6b** with TFAN provided an inseparable mixture of dimethyl 5-bromo-4-nitro- (**7b**) and 5-bromo-4-nitroindole-2,3-dicarboxylate (**8b**), which were isolated as **7a** and **8a** by treatment of tetrabutylammonium fluoride in 60% and 35% yields, respectively. (Entry 3) (Table 2)

Scheme 2

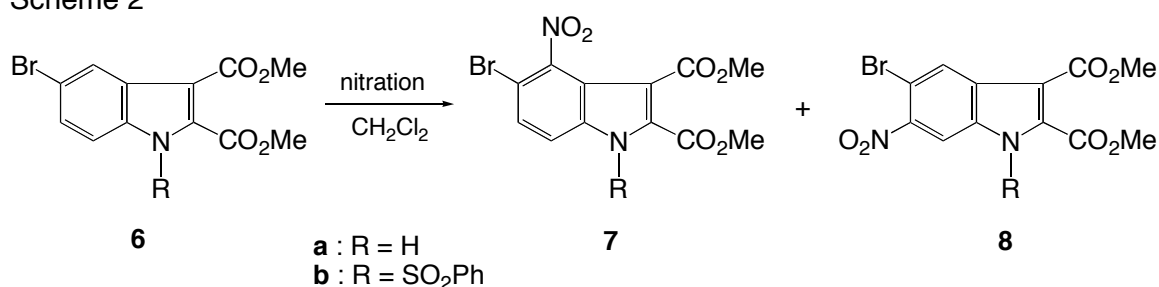


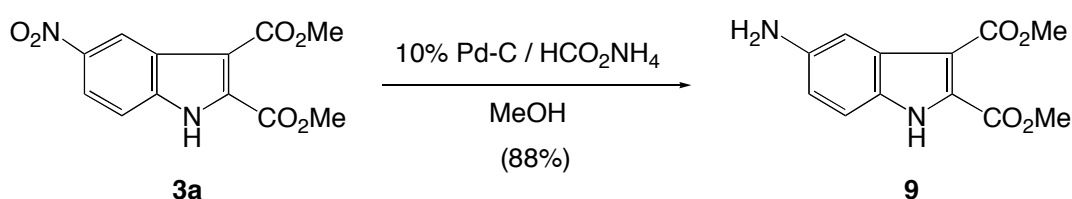
Table 2

Entry	6	R	Nitrating agent	Condition	Yield(%)	
					7	8
1	a	H	TFAN (3 eq)	-20 °C 0.5 h	-	-
2	a	H	NO_2BF_4 (2.2 eq)	0°C 0.5 h	83	-
3 ¹⁾	b	SO_2Ph	TFAN (3 eq)	-20 °C 0.5 h	60	35

1) SO_2Ph derivatives (**7b** and **8b**) were isolated as NH derivatives (**7a** and **8a**) by treatment with tetrabutylammonium fluoride.

Finally, we examined the conversion of the nitro group in dimethyl 5-nitroindole-2,3-dicarboxylate (**3a**) and dimethyl 5-bromo-4-nitroindole-2,3-dicarboxylate (**7a**) to an amino group in them. (**3a**) was treated with ammonium formate in the presence of 10% Pd-C in hot MeOH to give a corresponding dimethyl 5-aminoindole-2,3-dicarboxylate (**9**) in 88% yield. (Scheme 3)

Scheme 3



The reduction of **7a** with ammonium formate in the presence of 10% Pd-C in hot MeOH provided dimethyl 4-aminoindole-2,3-dicarboxylate (**10**) in 85% yield, but dimethyl 5-bromo-4-aminoindole-2,3-dicarboxylate (**11**) was not isolated. (Entry 1) The treatment of **7a** with sodium borohydride in the

presence of tin (II) chloride resulted in a low yield. (Entry 2) However, **7a** was treated with tetra-*n*-butylammonium borohydride (3 eq) in the presence of tin (II) chloride in tetrahydrofuran to give dimethyl 4-amino-5-bromoindole-2,3-dicarboxylate (**11**) in 45% yield and **7a** was also recovered in 42% yield, but in the presence of excess tetra-*n*-butylammonium borohydride (6 eq), a mixture of **10** and **11** was obtained in 42% and 58% yields, respectively. (Entries 3, 4) (Scheme 4) (Table 3)

Scheme 4

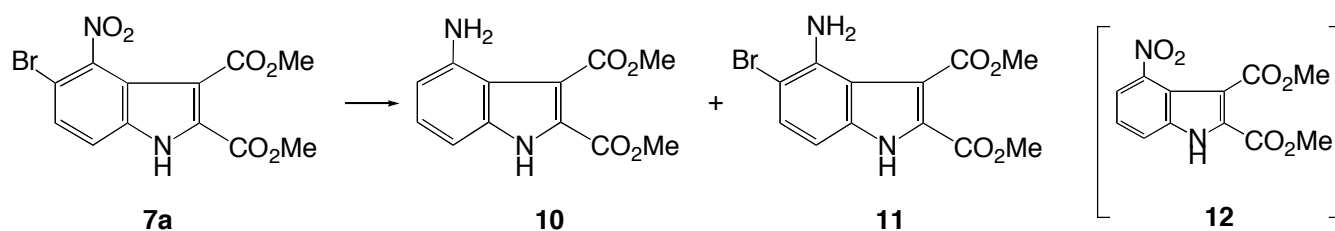


Table 3

Entry	Reducing agent	Solvent	Condition	Yield (%)		
				10	11	Recovered
1	HCO ₂ NH ₄ (3 eq) / 10% Pd-C	MeOH	reflux 2 h	85	-	-
2	NaBH ₄ (1.5 eq) / SnCl ₂ (5 eq)	MeOH	reflux 9 h	30	-	-
3	<i>n</i> -Bu ₄ NBH ₄ (3 eq) / SnCl ₂ (5 eq)	THF	rt 3 d	-	45	42
4	<i>n</i> -Bu ₄ NBH ₄ (6 eq) / SnCl ₂ (5 eq)	THF	rt 10 min	42	58	-

EXPERIMENTAL

Melting points were determined using a Yanagimoto micromelting point apparatus and are uncorrected. The ¹H-NMR spectra were determined by a JEOL JNM-GSX 270 spectrometer using tetramethylsilane as the internal standard. The IR spectra were recorded using a JASCO FT/IR-7000 spectrophotometer. The high MS were recorded by a JOEL JMS-HX100 spectrometer. Column chromatography was performed on E. Merck silica gel 60 (70-230 mesh or 230-400 mesh).

Nitration of Dimethyl Indole-2,3-dicarboxylates (**1**): General Procedure

By Using Nitronium Tetrafluoroborate (Method A)

To a mixture of dimethyl indole-2,3-dicarboxylates (**1**) (1 mmol) in CH₂Cl₂ (1 mL) was added 1M tin (IV) chloride in a CH₂Cl₂ solution, then the nitronium tetrafluoroborate (1–3 mmol) and the reaction mixture was stirred at rt. Water was added to the mixture and the mixture was extracted with CHCl₃ : MeOH (10 : 1). The extracts were washed with water, dried over Na₂SO₄, and concentrated under reduced pressure to afford a residue, which was purified by preparative thin-layer chromatography on silica gel (*n*-hexane : AcOEt = 3 : 1 - 2 : 3) to give the dimethyl 4-nitro- (**2**), 5-nitro (**3**), 6-nitro- (**4**), and

7-nitroindole-2,3-dicarboxylate (**5**). These reaction conditions and results are shown in Tables 1 and 2.

Using Trifluoroacetyl Nitrate (TFAN) (Method B)

The dimethyl indole-2,3-dicarboxylates (**1**) (1 mmol) were added to trifluoroacetyl nitrate¹³ (prepared from ammonium nitrate (1-3 mmol) and trifluoroacetic anhydride (5-10 mmol) in CH₂Cl₂ (1 mL)), stirring for 1 h at rt) and the mixture was stirred. The reaction mixture was added to water and the mixture was extracted with CH₂Cl₂. The extracts were washed with water, dried over Na₂SO₄, and concentrated under reduced pressure to afford a residue, which was purified by preparative thin-layer chromatography on silica gel (*n*-hexane : AcOEt = 3 : 1 - 2 : 3) to give the dimethyl 4-nitro- (**2**), 5-nitro (**3**), 6-nitro- (**4**), and 7-nitroindole-2,3-dicarboxylate (**5**). These reaction conditions and results are shown in Table 1 and 2.

Debenzensulfonylation of Dimethyl 1-Benzenesulfonylnitroindole-2,3-dicarboxylates (**2c**, **3c**, **4c**, **5c**) and Dimethyl 1-Benzenesulfonyl-5-bromo-nitroindole-2,3-dicarboxylates (**7**, **8**) : General Procedure for Preparation of Dimethyl Nitroindole-2,3-dicarboxylates

To a solution of an inseparable mixture of dimethyl nitroindole-2,3-dicarboxylates (**2c**, **3c**, **4c**, **5c**) (40 mg, 0.1 mmol) in THF (1 mL), a 1.0 M solution of tetrabutylammonium fluoride in THF (0.1 mL, 0.1 mmol) was added at -20 °C, and the mixture was stirred for 30 min. The reaction mixture was neutralized with 1% hydrochloric acid, and the aqueous mixture was extracted with CHCl₃. The extracts were washed with water, dried over Na₂SO₄, and concentrated under reduced pressure to afford a residue, which was purified by preparative thin-layer chromatography on silica gel.

Dimethyl 4-Nitroindole-2,3-dicarboxylate (2a); mp 241 °C (MeOH). IR (Nujol) cm⁻¹: 1679, 1519. ¹H-NMR (CDCl₃) δ: 3.99, 4.05 (6H, s, 2xCO₂CH₃), 7.60 (1H, t, *J* = 8 Hz, H-6), 7.78 (1H, d, *J* = 8.5 Hz, H-7), 8.05 (1H, d, *J* = 8.5 Hz, H-5), 9.30 (1H, br s, H-1). *Anal.* Calcd for C₁₂H₁₀N₂O₆: C, 51.80; H, 3.62; N, 10.07. Found: C, 51.70; H, 3.70; N, 10.11.

Dimethyl 5-Nitroindole-2,3-dicarboxylate (3a); mp 213-214 °C (MeOH). IR (Nujol) cm⁻¹: 1737, 1525. ¹H-NMR (CDCl₃) δ: 4.04 (6H, s, 2xCO₂CH₃), 7.54 (1H, d, *J* = 9 Hz, H-7), 8.27 (1H, dd, *J* = 9, 2 Hz, H-6), 9.02 (1H, d, *J* = 2 Hz, H-4), 9.64 (1H, br s, H-1). *Anal.* Calcd for C₁₂H₁₀N₂O₆: C, 51.80; H, 3.62; N, 10.07. Found: C, 51.89; H, 3.67; N, 10.10.

Dimethyl 6-Nitroindole-2,3-dicarboxylate (4a); mp 214 °C (MeOH). IR (Nujol) cm⁻¹: 1678, 1518. ¹H-NMR (DMSO-*d*₆) δ: 3.87, 3.95 (6H, s, 2xCO₂CH₃), 8.07 (1H, dd, *J* = 8, 1.5 Hz, H-5), 8.12 (1H, d, *J* = 8 Hz, H-4), 8.38 (1H, d, *J* = 1.5 Hz, H-7), 13.30 (1H, br s, H-1). HRMS (EI) *m/z*: Calcd for C₁₂H₁₀N₂O₆: 278.0564. Found: 278.0439. *Anal.* Calcd for C₁₂H₁₀N₂O₆: C, 51.80; H, 3.62; N, 10.07. Found: C, 51.82; H, 3.60; N, 10.16.

Dimethyl 7-Nitroindole-2,3-dicarboxylate (5a); mp 120 °C (*n*-hexane). IR (Nujol) cm⁻¹: 1707, 1544. ¹H-NMR (CDCl₃) δ: 4.01, 4.05 (6H, s, 2xCO₂CH₃), 7.41 (1H, d, *J* = 8 Hz, H-5), 8.34 (1H, dd, *J* = 8, 1 Hz, H-6 or H-4), 8.47 (1H, d, *J* = 8 Hz, H-4 or H-6), 10.60 (1H, br s, H-1). *Anal.* Calcd for C₁₂H₁₀N₂O₆: C, 51.80; H, 3.62; N, 10.07. Found: C, 51.86; H, 3.67; N, 10.13.

Dimethyl 1-Benzyl-4-nitroindole-2,3-dicarboxylate (2b); mp 114 °C (EtOH). IR (CHCl₃) cm⁻¹: 1724, 1532. ¹H-NMR (CDCl₃) δ: 3.91, 4.00 (6H, s, 2xCO₂CH₃), 5.85 (2H, s, CH₂), 7.00-7.08 (2H, m, arom), 7.23-7.32 (3H, m, arom), 7.42 (1H, t, *J* = 8 Hz, H-6), 7.69 (1H, d, *J* = 8 Hz, H-7 or 5), 8.11 (1H, d, *J* = 8

Hz, H-5 or 7). *Anal.* Calcd for $C_{19}H_{16}N_2O_6$: C, 61.95; H, 4.38; N, 7.61. Found: C, 61.89; H, 4.43; N, 7.61.

Dimethyl 1-Benzyl-5-nitroindole-2,3-dicarboxylate (3b); mp 147 °C (AcOEt). IR ($CHCl_3$) cm^{-1} : 1714, 1524. 1H -NMR ($CDCl_3$) δ : 3.94, 3.99 (6H, s, $2 \times CO_2CH_3$), 5.48 (2H, s, CH_2), 7.07-7.13 (2H, m, arom), 7.28-7.33 (3H, m, arom), 7.38 (1H, d, $J = 9$ Hz, H-7), 8.18 (1H, dd, $J = 9, 2$ Hz, H-6), 9.07 (1H, d, $J = 2$ Hz, H-4). *Anal.* Calcd for $C_{19}H_{16}N_2O_6$: C, 61.95; H, 4.38; N, 7.61. Found: C, 61.91; H, 4.39; N, 7.60.

Dimethyl 1-Benzyl-6-nitroindole-2,3-dicarboxylate (4b); mp 167 °C (AcOEt). IR ($CHCl_3$) cm^{-1} : 1713, 1522. 1H -NMR ($CDCl_3$) δ : 3.94, 3.96 (6H, s, $2 \times CO_2CH_3$), 5.50 (2H, s, CH_2), 7.10-7.16 (2H, m, arom), 7.28-7.34 (3H, m, arom), 8.16 (1H, dd, $J = 9, 2$ Hz, H-5), 8.27 (1H, d, $J = 9$ Hz, H-4), 8.29 (1H, d, $J = 2$ Hz, H-7). *Anal.* Calcd for $C_{19}H_{16}N_2O_6$: C, 61.95; H, 4.38; N, 7.61. Found: C, 62.10; H, 4.39; N, 7.63.

Dimethyl 5-Bromo-4-nitroindole-2,3-dicarboxylate (7a); mp 230-232 °C (MeOH). IR ($CHCl_3$) cm^{-1} : 1719, 1543. 1H -NMR ($CDCl_3$) δ : 3.91, 3.99 (6H, s, $2 \times CO_2CH_3$), 7.48 (1H, d, $J = 9$ Hz, H-6 or H-7), 7.61 (1H, d, $J = 9$ Hz, H-7 or H-6), 9.48 (1H, br s, H-1). *Anal.* Calcd for $C_{12}H_9N_2O_6Br$: C, 40.36; H, 2.54; N, 7.85. Found: C, 40.26; H, 2.59; N, 7.90.

Dimethyl 5-Bromo-6-nitroindole-2,3-dicarboxylate (8a); mp 224-226 °C (MeOH). IR ($CHCl_3$) cm^{-1} : 1716. 1H -NMR ($CDCl_3$) δ : 4.01, 4.04 (6H, s, $2 \times CO_2CH_3$), 8.04 (1H, s, H-4 or H-7), 8.47 (1H, s, H-7 or H-4). *Anal.* Calcd for $C_{12}H_9N_2O_6Br$: C, 40.36; H, 2.54; N, 7.85. Found: C, 40.37; H, 2.55; N, 7.87.

Preparation of Dimethyl 5-Aminoindole-2,3-dicarboxylate (9), Dimethyl 4-Aminoindole-2,3-dicarboxylate (10), and Dimethyl 5-Bromo-4-aminoindole-2,3-dicarboxylate (11) by Reduction of Dimethyl Nitroindole-2,3-dicarboxylate (3a and 7a): General Procedure

a) Using Ammonium Formate in the Presence of 10% Pd/C

A mixture of dimethyl 5-bromo-4-nitroindole-2,3-dicarboxylate (**3a**) (56 mg, 0.2 mmol), ammonium formate (76 mg, 1.2 mmol), and 10% Pd/C (6 mg) in MeOH (2 mL) was refluxed for 2 h. The catalyst was removed by filtration through Cerite, then the filtrate was evaporated. The residue was purified by preparative thin-layer chromatography (*n*-hexane : AcOEt = 1 : 1) to give dimethyl 5-aminoindole-2,3-dicarboxylate (**9**) (44 mg, 88%) as a yellow solid. These reaction conditions and results are shown in Table 3.

b) Using Sodium Borohydride or Tetrabutylammonium Borohydride

A suspension of dimethyl 5-bromo-4-nitroindole-2,3-dicarboxylate (**7a**) (36 mg, 0.1 mmol), tin (II) chloride ($SnCl_2 \cdot 2H_2O$), sodium borohydride or tetrabutylammonium borohydride in MeOH or THF (1 mL) was stirred or refluxed. Water was added to the reaction mixture and the mixture was extracted with $CHCl_3$. The extracts were washed with water, dried over Na_2SO_4 , and concentrated under reduced pressure to afford a residue, which was purified by chromatography on silica gel (*n*-hexane : AcOEt = 1 : 1) to afford dimethyl 4-amino-indole-2,3-dicarboxylate (**10**) and dimethyl 5-bromo-4-aminoindole-2,3-dicarboxylate (**11**). These reaction conditions and results are shown in Table 3.

Dimethyl 5-Aminoindole-2,3-dicarboxylate (9); mp 74-77 °C (*n*-hexane- CH_2Cl_2). IR ($CHCl_3$) cm^{-1} :

3403, 3318, 1716, 1683. $^1\text{H-NMR}$ (CDCl_3) δ : 3.69 (2H, br s, NH_2), 3.97 (6H, s, $2\times\text{CO}_2\text{CH}_3$), 6.83 (1H, dd, $J = 8, 1.5$ Hz, H-6), 7.23 (1H, d, $J = 8$ Hz, H-7), 7.33 (1H, d, $J = 1.5$ Hz, H-6), 9.08 (1H, br s, H-1). HRMS (FAB) m/z : Calcd for $\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}_2\text{Br}$: 325.9902. Found: 325.9883.

Dimethyl 4-Aminoindole-2,3-dicarboxylate (10); mp 128-130 °C (*n*-hexane-ether). IR (CHCl_3) cm^{-1} : 3449, 3360, 1730, 1698. $^1\text{H-NMR}$ (CDCl_3) δ : 3.95, 3.96 (6H, s, $2\times\text{CO}_2\text{CH}_3$), 5.49 (2H, br s, NH_2), 6.66 (1H, d, $J = 9$ Hz, H-6 or H-7), 7.37 (1H, d, $J = 9$ Hz, H-7 or H-6), 8.97 (1H, br s, H-1). *Anal.* Calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_4$: C, 58.06; H, 4.87; N, 11.29. Found: C, 57.96; H, 4.85; N, 11.17.

Dimethyl 4-Amino-5-bromoindole-2,3-dicarboxylate (11); mp 172-173 °C (MeOH). IR (KCl) cm^{-1} : 3445, 3303, 1698. $^1\text{H-NMR}$ (CDCl_3) δ : 3.95, 3.96 (6H, s, $2\times\text{CO}_2\text{CH}_3$), 5.49 (2H, br s, NH_2), 6.66 (1H, d, $J = 9$ Hz, H-6 or H-7), 7.37 (1H, d, $J = 9$ Hz, H-7 or H-6), 8.97 (1H, br s, H-1). *Anal.* Calcd for $\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_4\text{Br}$: C, 43.94; H, 3.34; N, 8.46. Found: C, 44.06; H, 3.39; N, 8.57.

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