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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 Norland[1], 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, CF_3COONO_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**) (R = 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**) (R = CH_2Ph) 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**) (R = SO_2Ph) with NO_2BF_4 or TFAN afforded an inseparable mixture of **2c**, **3c**, **4c**, and **5c**. (Entries 5, 6) (Table 1)

Scheme 1

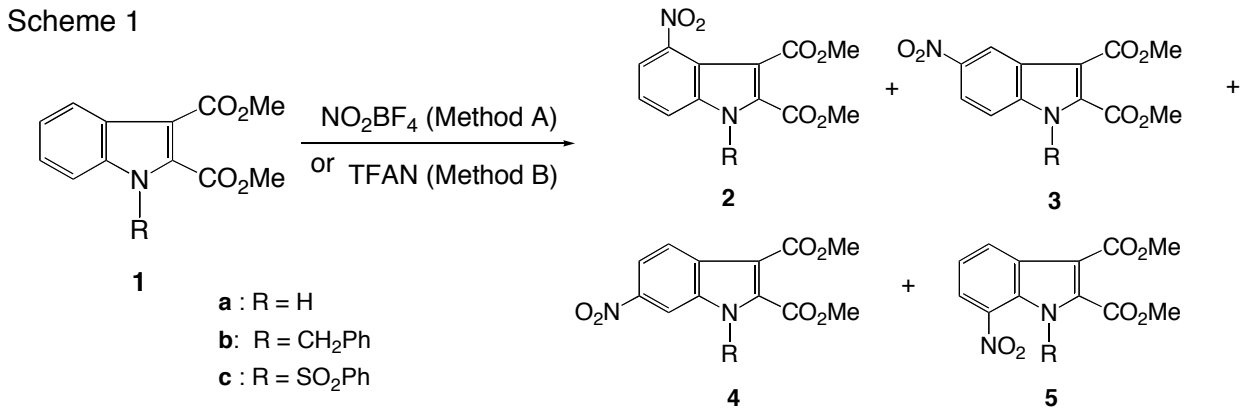


Table 1

					Yield (%)					
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.

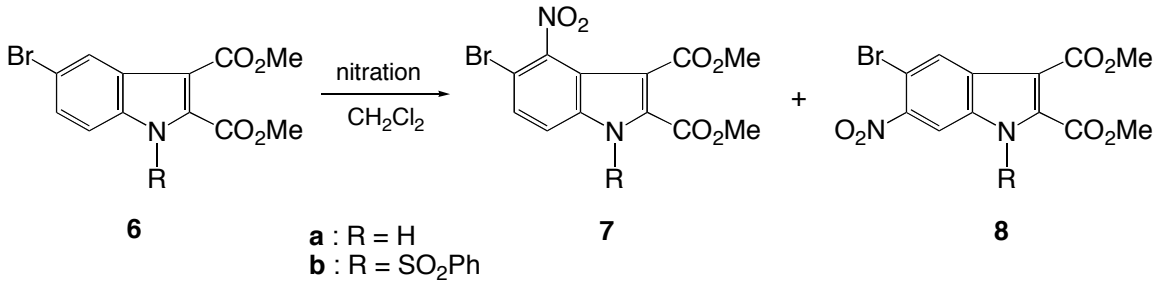
Method A: NO_2BF_4 (2.2 eq) and Sn (IV)Cl_4 (5 eq) in CH_2Cl_2.

Method B: NH_4NO_3 (1.2 eq) and $(CF_3COO)_2O$ (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



6 **7** **8**

a : R = H
b : R = SO_2Ph

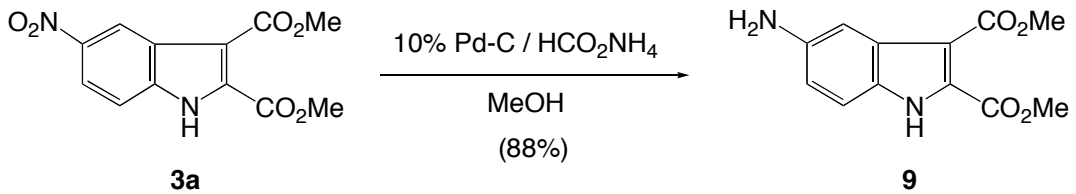
Table 2

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

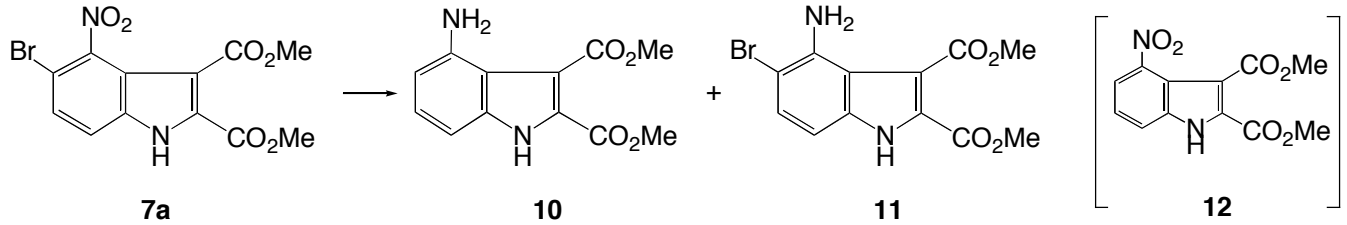


3a **9**

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



7a **10** **11** **12**

Table 3

Entry	Reducing agent	Solvent	Condition		Yield (%) **10**	**11**	Recovered
1	HCO_2NH_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	*n*-Bu_4NBH_4 (3 eq) / $SnCl_2$ (5 eq)	THF	rt	3 d	-	45	42
4	*n*-Bu_4NBH_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 ^{1}H-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 CH_2Cl_2 (1 mL) was added 1M tin (IV) chloride in a CH_2Cl_2 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 $CHCl_3$: MeOH (10 : 1). The extracts were washed with water, dried over Na_2SO_4, 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 nitrate[13] (prepared from ammonium nitrate (1-3 mmol) and trifluoroacetic anhydride (5-10 mmol) in CH_2Cl_2 (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 CH_2Cl_2. The extracts were washed with water, dried over Na_2SO_4, 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 $CHCl_3$. The extracts were washed with water, dried over Na_2SO_4, and concentrated under reduced pressure to afford a residue, which was purified by preparative thin-layer chromatography on silica gel.

Dimethyl 4-Nitroindole-2,3-dicarboxylate (2a); mp 241 °C (MeOH). IR (Nujol) cm^{-1}: 1679, 1519. ^{1}H-NMR ($CDCl_3$) δ: 3.99, 4.05 (6H, s, 2xCO_2CH_3), 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 $C_{12}H_{10}N_2O_6$: 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. ^{1}H-NMR ($CDCl_3$) δ: 4.04 (6H, s, 2xCO_2CH_3), 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 $C_{12}H_{10}N_2O_6$: 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. ^{1}H-NMR (DMSO-d_6) δ: 3.87, 3.95 (6H, s, 2xCO_2CH_3), 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 $C_{12}H_{10}N_2O_6$: 278.0564. Found: 278.0439. *Anal.* Calcd for $C_{12}H_{10}N_2O_6$: 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. ^{1}H-NMR ($CDCl_3$) δ: 4.01, 4.05 (6H, s, 2xCO_2CH_3), 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 $C_{12}H_{10}N_2O_6$: 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 ($CHCl_3$) cm^{-1}: 1724, 1532. ^{1}H-NMR ($CDCl_3$) δ: 3.91, 4.00 (6H, s, 2xCO_2CH_3), 5.85 (2H, s, CH_2), 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. ^{1}H-NMR ($CDCl_3$) δ: 3.94, 3.99 (6H, s, 2xCO_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. ^{1}H-NMR ($CDCl_3$) δ: 3.94, 3.96 (6H, s, 2xCO_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. ^{1}H-NMR ($CDCl_3$) δ: 3.91, 3.99 (6H, s, 2xCO_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. ^{1}H-NMR ($CDCl_3$) δ: 4.01, 4.04 (6H, s, 2xCO_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}H-NMR ($CDCl_3$) δ: 3.69 (2H, br s, NH_2), 3.97 (6H, s, 2xCO_2CH_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 $C_{12}H_{11}O_4N_2Br$: 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}H-NMR ($CDCl_3$) δ: 3.95, 3.96 (6H, s, 2xCO_2CH_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 $C_{12}H_{12}N_2O_4$: 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}H-NMR ($CDCl_3$) δ: 3.95, 3.96 (6H, s, 2xCO_2CH_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 $C_{12}H_{11}N_2O_4Br$: C, 43.94; H, 3.34; N, 8.46. Found: C, 44.06; H, 3.39; N, 8.57.

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