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## ONE-POT SYNTHESIS OF 1-ARYLINDOLE-3-CARBOXYLATES FROM 2-(2-ISOCYANOPHENYL)ACETATES

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**Abstract** - An efficient method for the preparation of 1-arylindole-3-carboxylates under mild conditions has been developed. Thus, cyclization of ethyl 2-(2-isocyanophenyl)acetates using sodium hydride at room temperature was followed by 1-arylation of the resulting ethyl 1-sodioindole-3-carboxylates with fluoro(di)nitrobenzenes to give ethyl 1-(di)nitrophenylindole-3-carboxylates in generally good yields. This method also allows preparation of 1,1'-(4,6-dinitro-1,3-phenylene)diindole derivatives by using 1,3-difluoro-4,6-dinitrobenzene.

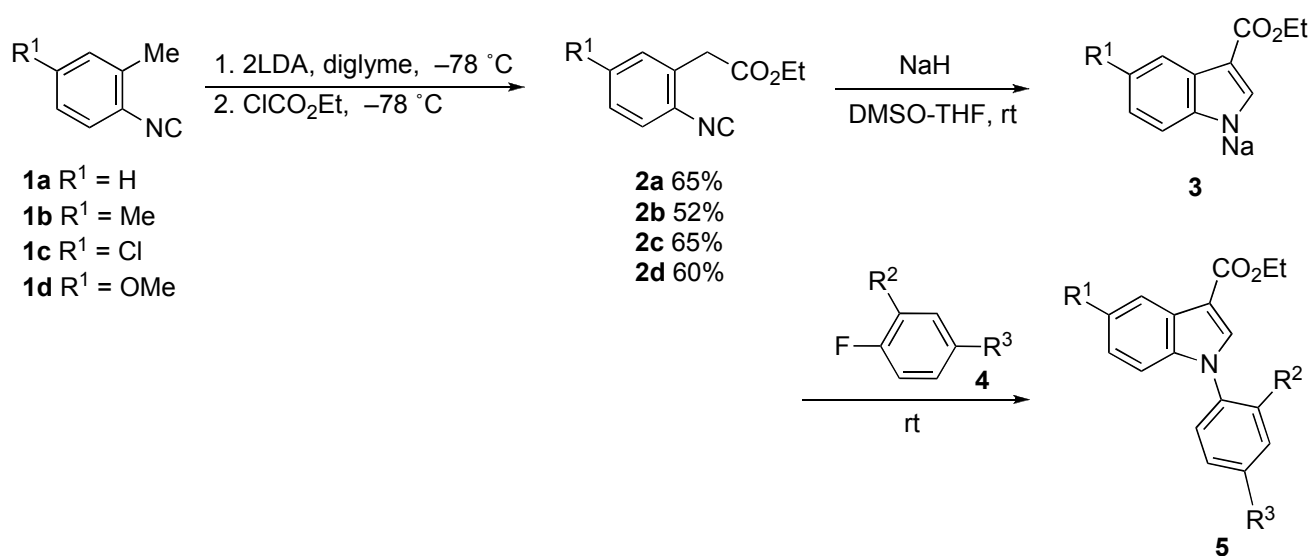
## INTRODUCTION

2-(Lithiomethyl)phenyl isocyanides have been used as intermediates in syntheses of a number of indole derivatives and related heterocycles by reactions with various electrophiles followed by cyclization.<sup>1</sup> Methyl 2-(2-isocyanophenyl)acetate, which could be prepared by reacting 2-(lithiomethyl)phenyl isocyanide with methyl chloroformate,<sup>2</sup> was elaborated to the preparation of methyl indole-3-carboxylate and methyl 3-alkyl-3*H*-indole-3-carboxylates by copper(I) oxide-catalyzed cyclization.<sup>3</sup> However, any other elaborations of 2-(2-isocyanophenyl)acetates have not been reported so far. In this report, we describe a facile one-pot procedure for the synthesis of ethyl 1-arylindole-3-carboxylates by cyclization of ethyl 2-(2-isocyanophenyl)acetates followed by 1-arylation with fluoro(di)nitrobenzenes under mild conditions. Indole-3-carboxylates are synthetically as well as medicinally important heterocyclic compounds,<sup>4</sup> and so, several methods for their preparation have been recently reported.<sup>5</sup> However, only a few methods have been reported for the synthesis of 1-aryl derivatives involving construction of the pyrrole moiety.<sup>6</sup> Most of syntheses of 1-arylindole-3-carboxylates have been based on the copper-catalyzed coupling reactions between indole-3-carboxylates and halobenzenes at higher temperature.<sup>7</sup>

## RESULTS AND DISCUSSION

The one-pot conversion of ethyl 2-(2-isocyanophenyl)acetates (**2**), which were easily prepared from

2-methylphenyl isocyanides (**1**) on a successive treatment with lithium diisopropylamide (LDA) and ethyl chloroformate according to the procedure reported by Ito et al,<sup>1,2</sup> into ethyl 1-(2-[or 4-]nitro- or 2,4-dinitrophenyl)indole-3-carboxylates (**5**) was conducted as illustrated in Scheme 1. Thus, compounds (**2**) were treated with sodium hydride in dimethyl sulfoxide (DMSO)–THF at room temperature. The cyclization proceeded slowly (for about 3 h) to generate the corresponding ethyl 1-sodioindole-3-carboxylates (**3**). Subsequent 2-(or 4-)nitro- or 2,4-dinitro-phenylation was achieved by adding 1-fluoro-2-(or 4-)nitro- or 1-fluoro-2,4-dinitro-benzenes (**4**) to give, after usual workup followed by purification by preparative TLC on silica gel, the desired 1-arylindole-3-carboxylates (**5**). The results are summarized in Table 1. From these results it can be seen that the 1-arylation reactions generally proceeded very smoothly (within 30 min) and cleanly to give the desired products (**5**) in fair to good yields.<sup>8</sup> When the sequence was carried out using 1-fluoro-2,4-dinitrobenzene, the dinitroarylation completed immediately (within 5 min) to give the corresponding ethyl 1-(2,4-dinitrophenyl)indole-3-carboxylates (**5d, g, i, and j**) in good yields (Entries 4, 7, 9, and 10).<sup>9</sup>



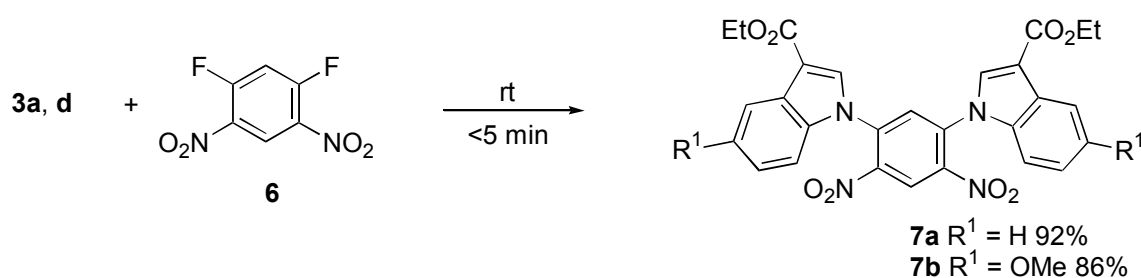
Scheme 1

Table 1. Preparation of 1-Arylindole-3-carboxylates (**5**)

Entry	<b>2</b>	<b>4</b>	Time/min	<b>5</b> (Yield/%) <sup>a</sup>
1	<b>2a</b>	<b>4a</b> (R <sup>2</sup> = NO <sub>2</sub> , R <sup>3</sup> = H)	10	<b>5a</b> (84)
2	<b>2a</b>	<b>4b</b> (R <sup>2</sup> = NO <sub>2</sub> , R <sup>3</sup> = Me)	10	<b>5b</b> (82)
3	<b>2a</b>	<b>4c</b> (R <sup>2</sup> = H, R <sup>3</sup> = NO <sub>2</sub> )	30	<b>5c</b> (80)
4	<b>2a</b>	<b>4d</b> (R <sup>2</sup> = R <sup>3</sup> = NO <sub>2</sub> )	<5	<b>5d</b> (91)
5	<b>2b</b>	<b>4a</b>	10	<b>5e</b> (76)
6	<b>2b</b>	<b>4c</b>	30	<b>5f</b> (76)
7	<b>2b</b>	<b>4d</b>	<5	<b>5g</b> (84)
8	<b>2c</b>	<b>4a</b>	10	<b>5h</b> (86)
9	<b>2c</b>	<b>4d</b>	<5	<b>5i</b> (90)
10	<b>2d</b>	<b>4d</b>	<5	<b>5j</b> (91)

<sup>a</sup>Yields are of purified products.

We next examined the possibility of the synthesis of 1,1'-(4,6-dinitro-1,3-phenylene)diindole derivatives **7** as an application of the present cyclization-arylation sequence. As shown in Scheme 2, when 1-sodioindole-3-carboxylates (**3**) were treated with 1,3-difluoro-4,6-dinitrobenzene (**6**) (2:1 molar ratio) under the same conditions as described for the preparation of 1-arylindole-3-carboxylates (**5**), the arylation reaction also proceeded very smoothly to lead to the formation of the corresponding desired products (**7**) in good-to-excellent yields. To the best of our knowledge, this type of (phenylene)diindoles are unknown in the literature.



**Scheme 2**

Unfortunately, however, it should be noted that the use of 2-fluorobenzonitrile instead of fluoro(di)nitrobenzenes in the 1-arylation step using **2a** resulted in the formation of an intractable mixture of products, from which no more than a trace amount of the desired ethyl 1-(2-cyanophenyl)indole-3-carboxylates was obtained. This may be due to lability of the cyano function under the reaction conditions.

In conclusion, 2-(2-isocyanophenyl)acetates have been utilized for the one-pot synthesis of 1-[(di)nitrophenyl]indole-3-carboxylates. Notable advantages of the present synthesis include: i) simplicity of the procedure, ii) milder reaction conditions, iii) readily availability of the starting materials, and iv) good yields of products. This procedure has been applied to the synthesis of 1,1'-(1,3-phenylene)diindole derivatives. Further elaboration of 2-(2-isocyanophenyl)acetates to the preparation of other types of heterocycles is currently being pursued in our laboratory.

## EXPERIMENTAL

The melting points were determined on a Laboratory Devices MEL-TEMP II melting-point apparatus and are uncorrected. The IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer.  $^1\text{H}$  NMR spectra were determined using  $\text{SiMe}_4$  as an internal reference in  $\text{CDCl}_3$  with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz.  $^{13}\text{C}$  NMR spectra were determined using  $\text{SiMe}_4$  as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz in  $\text{CDCl}_3$ . Low- and high-resolution mass spectra (EI, 70 eV) were recorded on a JEOL JMS-AX505 HA spectrometer. Thin-layer

chromatography (TLC) was carried out using Merck Kieselgel 60 PF<sub>254</sub>. Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All of the solvents used were dried over the appropriate drying agents and distilled under argon prior to use.

**Starting Materials.** 2-Methylphenyl isocyanides (**1**) were prepared by a modification<sup>1</sup> of Ugi's Method.<sup>10</sup> All other chemicals used in this study were commercially available.

**Typical Procedure for the Preparation of 2-(2-Isocyanophenyl)acetates (2). Ethyl 2-(2-Isocyanophenyl)acetate (2a).** To a stirred deep-red solution of 2-lithiomethylphenyl isocyanide, which was generated in situ by treating **1a** (1.2 g, 10 mmol) with 2 molar amount of LDA in diglyme (25 mL) at –78 °C, was added ethyl chloroformate (1.1 g, 10 mmol) dropwise. The color of the solution immediately turned into light red. Saturated aqueous NH<sub>4</sub>Cl (30 mL) was added, and organic materials were extracted with Et<sub>2</sub>O three times (30 mL each). The combined extracted was washed with water five times and then brine once, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (1:5 THF–hexane) to give **2** (1.2 g, 65%); pale-yellow needles; mp 45–46 °C (hexane); IR (KBr) 2122, 1732 cm<sup>–1</sup>; <sup>1</sup>H NMR δ 1.28 (t, *J* = 7.3 Hz, 3H), 3.80 (s, 2H), 4.20 (q, *J* = 7.3 Hz, 2H), 7.32 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.34–7.42 (m, 3H). Anal. Calcd for C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.68; H, 6.00; N, 7.25.

**Ethyl 2-(2-Isocyano-5-methylphenyl)acetate (2b):** a yellow oil; *R<sub>f</sub>* 0.40 (1:7 THF–hexane); IR (neat) 2120, 1737 cm<sup>–1</sup>; <sup>1</sup>H NMR δ 1.29 (t, *J* = 7.3 Hz, 3H), 2.36 (s, 3H), 3.75 (s, 2H), 4.20 (q, *J* = 7.3 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.14 (s, 1H), 7.28 (d, *J* = 7.8 Hz, 1H); MS *m/z* 203 (M<sup>+</sup>, 100). HR-MS. Calcd for C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub>: M, 203.0946. Found: *m/z* 203.0958.

**Ethyl 2-(5-Chloro-2-isocyanophenyl)acetate (2c):** a yellow oil; *R<sub>f</sub>* 0.29 (1:7 THF–hexane); IR (neat) 2122, 1738 cm<sup>–1</sup>; <sup>1</sup>H NMR δ 1.29 (t, *J* = 7.3 Hz, 3H), 3.76 (s, 2H), 4.21 (q, *J* = 7.3 Hz, 2H), 7.30 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.36 (d, *J* = 1.8 Hz, 1H); MS *m/z* 223 (M<sup>+</sup>, 100). HR-MS. Calcd for C<sub>11</sub>H<sub>10</sub>ClNO<sub>2</sub>: M, 223.0400. Found: *m/z* 223.0391.

**Ethyl 2-(2-Isocyano-5-methoxyphenyl)acetate (2d):** a yellow oil; *R<sub>f</sub>* 0.20 (1:7 Et<sub>2</sub>O–hexane); IR (neat) 2118, 1738 cm<sup>–1</sup>; <sup>1</sup>H NMR δ 1.28 (t, *J* = 7.3 Hz, 3H), 3.75 (s, 2H), 3.82 (s, 3H), 4.20 (q, *J* = 7.3 Hz, 2H), 6.80 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.85 (d, *J* = 2.7 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 1H); MS *m/z* 219 (M<sup>+</sup>, 100). HR-MS. Calcd for C<sub>12</sub>H<sub>13</sub>NO<sub>3</sub>: M, 219.0895. Found: *m/z* 219.0912.

**Typical Procedure for the Preparation 1-Arylindole-3-carboxylates (5) and (7). Ethyl 1-(2-Nitrophenyl)indole-3-carboxylate (5a).** To a stirred suspension of NaH (60% in oil; 21 mg, 0.53 mmol) in DMSO–THF (1:1 v/v, 2 mL) at rt was added a solution of **2** (0.10 g, 0.53 mmol) in THF (1 mL) dropwise; the mixture was stirred at the same temperature for 3 h. 1-Fluoro-2-nitrobenzene (**4a**) (75 mg, 0.53 mmol) was added, and stirring was continued for an additional 10 min. Saturated aqueous NH<sub>4</sub>Cl (10 mL) was added, and organic materials were extracted with AcOEt three times (10 mL each). The combined extracted was washed with water three times and then brine once, and dried over

anhydrous  $\text{Na}_2\text{SO}_4$ . After evaporation of the solvent, the residue was purified by preparative TLC on silica gel (1:3 THF–hexane) to give **5a** (0.14 g, 84%); a yellow solid; mp 110–111 °C (hexane– $\text{CH}_2\text{Cl}_2$ ); IR (KBr) 1692, 1528, 1346  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.44 (t,  $J = 7.3$  Hz, 3H), 4.42 (q,  $J = 7.3$  Hz, 2H), 7.06 (d,  $J = 7.8$  Hz, 1H), 7.25 (td,  $J = 7.3, 1.4$  Hz, 1H), 7.33 (ddd,  $J = 7.8, 7.3, 0.9$  Hz, 1H), 7.59 (dd,  $J = 7.8, 1.4$  Hz, 1H), 7.69 (ddd,  $J = 7.8, 7.3, 1.4$  Hz, 1H), 7.81 (ddd,  $J = 7.8, 7.3, 1.4$  Hz, 1H), 7.90 (s, 1H), 8.13 (dd,  $J = 7.8, 1.4$  Hz, 1H), 8.25 (d,  $J = 7.3$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  14.50, 60.05, 109.79, 110.80, 122.11, 122.80, 123.95, 125.79, 126.44, 129.69, 130.12, 131.64, 134.10 (two overlapped C's), 137.42, 146.19, 164.69; MS  $m/z$  310 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_4$ : C, 65.80; H, 4.55; N, 9.03. Found: C, 65.74; H, 4.35; N, 8.87.

**Ethyl 1-(4-Methyl-2-nitrophenyl)indole-3-carboxylate (5b)**: a yellow solid; mp 144–145 °C (hexane– $\text{CH}_2\text{Cl}_2$ ); IR (KBr) 1699, 1539, 1348  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.43 (t,  $J = 7.3$  Hz, 3H), 2.57 (s, 3H), 4.41 (q,  $J = 7.3$  Hz, 2H), 7.03 (d,  $J = 8.2$  Hz, 1H), 7.24 (ddd,  $J = 8.2, 7.3, 1.4$  Hz, 1H), 7.31 (ddd,  $J = 7.8, 7.3, 0.9$  Hz, 1H), 7.44 (d,  $J = 7.8$  Hz, 1H), 7.59 (ddd,  $J = 7.8, 1.4$  Hz, 1H), 7.88 (s, 1H), 7.93 (s, 1H), 8.24 (d,  $J = 7.8$  Hz, 1H); MS  $m/z$  324 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4$ : C, 66.66; H, 4.97; N, 8.64. Found: C, 66.68; H, 5.08; N, 8.39.

**Ethyl 1-(4-Nitrophenyl)indole-3-carboxylate (5c)**: pale-yellow needles; mp 150–152 °C (hexane– $\text{CH}_2\text{Cl}_2$ ); IR (KBr) 1686, 1545, 1346  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.45 (t,  $J = 7.3$  Hz, 3H), 4.44 (q,  $J = 7.3$  Hz, 2H), 7.35–7.40 (m, 2H), 7.58 (d,  $J = 7.3$  Hz, 1H), 7.74 (d,  $J = 9.2$  Hz, 2H), 8.07 (s, 1H), 8.29 (dd,  $J = 7.3, 1.4$  Hz, 1H), 8.45 (d,  $J = 9.2$  Hz, 2H); MS  $m/z$  310 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_4$ : C, 65.80; H, 4.55; N, 9.03. Found: C, 65.74; H, 4.72; N, 9.24.

**Ethyl 1-(2,4-Dinitrophenyl)indole-3-carboxylate (5d)**: a yellow solid; mp 165–167 °C (hexane– $\text{CH}_2\text{Cl}_2$ ); IR (KBr) 1697, 1543, 1344  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.44 (t,  $J = 7.3$  Hz, 3H), 4.43 (q,  $J = 7.3$  Hz, 2H), 7.10 (d,  $J = 8.2$  Hz, 1H), 7.32 (ddd,  $J = 8.2, 7.3, 1.4$  Hz, 1H), 7.38 (ddd,  $J = 8.2, 7.3, 0.9$  Hz, 1H), 7.86 (d,  $J = 8.7$  Hz, 1H), 7.88 (s, 1H), 8.28 (d,  $J = 8.2$  Hz, 1H), 8.65 (dd,  $J = 8.7, 2.3$  Hz, 1H), 8.98 (d,  $J = 2.3$  Hz, 1H); MS  $m/z$  355 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_6$ : C, 57.47; H, 3.69; N, 11.83. Found: C, 56.43; H, 3.56; N, 11.44

**Ethyl 5-Methyl-1-(2-nitrophenyl)indole-3-carboxylate (5e)**: a yellow oil;  $R_f$  0.39 (1:4 THF–hexane); IR (neat) 1699, 1533, 1350  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.43 (t,  $J = 7.3$  Hz, 3H), 2.49 (s, 3H), 4.41 (q,  $J = 7.3$  Hz, 2H), 6.94 (d,  $J = 8.2$  Hz, 1H), 7.07 (dd,  $J = 8.2, 1.4$  Hz, 1H), 7.58 (dd,  $J = 8.2, 1.4$  Hz, 1H), 7.67 (ddd,  $J = 8.2, 7.3, 1.4$  Hz, 1H), 7.80 (ddd,  $J = 8.2, 7.3, 1.4$  Hz, 1H), 7.85 (s, 1H), 8.05 (s, 1H), 8.11 (dd,  $J = 8.2, 1.4$  Hz, 1H); MS  $m/z$  324 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4$ : C, 66.66; H, 4.97; N, 8.64. Found: C, 66.64; H, 4.94; N, 8.64.

**Ethyl 5-Methyl-1-(4-nitrophenyl)indole-3-carboxylate (5f)**: a yellow solid; mp 165–167 °C (hexane– $\text{CH}_2\text{Cl}_2$ ); IR (KBr) 1684, 1549, 1342  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.45 (t,  $J = 7.3$  Hz, 3H), 2.52 (s, 3H), 4.43 (q,  $J = 7.3$  Hz, 2H), 7.18 (d,  $J = 8.2$  Hz, 1H), 7.47 (d,  $J = 8.2$  Hz, 1H), 7.72 (d,  $J = 8.7$  Hz, 2H), 8.02

(s, 1H), 8.08 (s, 1H), 8.44 (d,  $J = 8.7$  Hz, 2H); MS  $m/z$  324 ( $M^+$ , 100). Anal. Calcd for  $C_{18}H_{16}N_2O_4$ : C, 66.66; H, 4.97; N, 8.64. Found: C, 66.39; H, 4.90; N, 8.41.

**Ethyl 1-(2,4-Dinitrophenyl)-5-methylindole-3-carboxylate (5g):** a yellow solid; mp 132–134 °C (hexane–CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 1678, 1541, 1346 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.44 (t,  $J = 7.3$  Hz, 3H), 2.50 (s, 3H), 4.43 (q,  $J = 7.3$  Hz, 2H), 6.99 (d,  $J = 8.2$  Hz, 1H), 7.12 (d,  $J = 8.2$  Hz, 1H), 7.83 (s, 1H), 7.84 (d,  $J = 8.7$  Hz, 1H), 8.07 (s, 1H), 8.63 (dd,  $J = 8.7, 2.7$  Hz, 1H), 8.97 (d,  $J = 2.7$  Hz, 1H); <sup>13</sup>C NMR  $\delta$  14.51, 21.52, 60.34, 109.07, 112.44, 121.84, 122.33, 126.24, 127.12, 128.39, 130.52, 132.94, 133.49, 134.97, 137.02, 145.21, 146.54, 164.25; MS  $m/z$  369 ( $M^+$ , 100). Anal. Calcd for  $C_{18}H_{15}N_3O_6$ : C, 58.54; H, 4.09; N, 11.38. Found: C, 58.66; H, 4.17; N, 11.07.

**Ethyl 5-Chloro-1-(2-nitrophenyl)indole-3-carboxylate (5h):** a yellow solid; mp 128–130 °C (hexane–CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 1690, 1535, 1364 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.44 (t,  $J = 7.3$  Hz, 3H), 4.42 (q,  $J = 7.3$  Hz, 2H), 6.96 (d,  $J = 8.7$  Hz, 1H), 7.21 (dd,  $J = 8.7, 2.3$  Hz, 1H), 7.57 (d,  $J = 7.8$  Hz, 1H), 7.71 (ddd,  $J = 7.8, 7.3, 1.4$  Hz, 1H), 7.82 (ddd,  $J = 7.8, 7.3, 1.4$  Hz, 1H), 7.90 (s, 1H), 8.14 (d,  $J = 7.8$  Hz, 1H), 8.23 (d,  $J = 2.3$  Hz, 1H); MS  $m/z$  344 ( $M^+$ , 100). Anal. Calcd for  $C_{17}H_{13}ClN_2O_4$ : C, 59.23; H, 3.80; N, 8.13. Found: C, 59.22; H, 3.83; N, 7.84.

**Ethyl 5-Chloro-1-(2,4-dinitrophenyl)indole-3-carboxylate (5i):** an orange solid; mp 182–183 °C (hexane–CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 1607, 1535, 1366 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.46 (t,  $J = 7.3$  Hz, 3H), 4.44 (q,  $J = 7.3$  Hz, 2H), 7.00 (d,  $J = 9.2$  Hz, 1H), 7.27 (dd,  $J = 9.2, 1.8$  Hz, 1H), 7.85 (d,  $J = 8.7$  Hz, 1H), 7.88 (s, 1H), 8.26 (d,  $J = 1.8$  Hz, 1H), 8.67 (dd,  $J = 8.7, 2.7$  Hz, 1H), 8.99 (d,  $J = 2.7$  Hz, 1H); MS  $m/z$  389 ( $M^+$ , 100). Anal. Calcd for  $C_{17}H_{12}ClN_3O_6$ : C, 52.39; H, 3.10; N, 10.78. Found: C, 52.34; H, 3.20; N, 10.68.

**Ethyl 1-(2,4-Dinitrophenyl)-5-methoxyindole-3-carboxylate (5j):** an orange solid; mp 190–191 °C (hexane–THF); IR (KBr) 1682, 1607, 1541, 1346 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.43 (t,  $J = 7.3$  Hz, 3H), 3.91 (s, 3H), 4.42 (q,  $J = 7.3$  Hz, 2H), 6.93 (dd,  $J = 8.7, 2.3$  Hz, 1H), 7.00 (d,  $J = 8.7$  Hz, 1H), 7.75 (d,  $J = 2.3$  Hz, 1H), 7.81 (s, 1H), 7.85 (d,  $J = 8.7$  Hz, 1H), 8.63 (dd,  $J = 8.7, 2.3$  Hz, 1H), 8.96 (d,  $J = 2.3$  Hz, 1H); MS  $m/z$  385 ( $M^+$ , 100). Anal. Calcd for  $C_{18}H_{15}N_2O_7$ : C, 56.11; H, 3.92; N, 10.91. Found: C, 56.07; H, 4.02; N, 10.85.

**Ethyl 1-[2,4-Dinitrophenyl-5-(3-ethoxycarbonylindol-1-yl)]indole-3-carboxylate (7a):** an orange-yellow solid; mp 103–105 °C (hexane–CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 1699, 1539, 1339 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.44 (t,  $J = 7.3$  Hz, 6H), 4.43 (q,  $J = 7.3$  Hz, 4H), 7.18 (d,  $J = 8.2$  Hz, 2H), 7.36 (ddd,  $J = 8.2, 7.3, 1.4$  Hz, 2H), 7.40 (ddd,  $J = 7.8, 7.3, 1.4$  Hz, 2H), 7.90 (s, 2H), 7.91 (s, 1H), 8.28 (d,  $J = 7.8$  Hz, 2H), 8.95 (s, 1H); <sup>13</sup>C NMR  $\delta$  14.45, 60.49, 109.24, 113.40, 122.84, 123.92, 124.85, 125.05, 126.86, 130.15, 132.73, 136.45, 136.59, 143.15, 163.93; MS  $m/z$  542 ( $M^+$ , 100). Anal. Calcd for  $C_{28}H_{22}N_4O_8$ : C, 61.99; H, 4.09; N, 10.33. Found: C, 61.66; H, 4.36; N, 10.06.

**Ethyl 1-[2,4-Dinitrophenyl-5-(3-ethoxycarbonyl-5-methoxyindol-1-yl)]-5-methoxyindole-3-carboxylate (7b):** a yellow solid; mp 212–214 °C (hexane–CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 1695, 1616, 1541, 1346

cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.43 (t, *J* = 7.3 Hz, 6H), 3.91 (s, 6H), 4.42 (q, *J* = 7.3 Hz, 4H), 6.97 (dd, *J* = 8.7, 2.7 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 2.7 Hz, 2H), 7.84 (s, 2H), 7.88 (s, 1H), 8.90 (s, 1H); MS *m/z* 602 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>30</sub>H<sub>26</sub>N<sub>4</sub>O<sub>10</sub>: C, 59.80; H, 4.35; N, 9.30. Found: C, 59.68; H, 4.40; N, 9.13.

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