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MANGANESE(III) ACETATE MEDIATED OXIDATIVE FREE RADICAL REACTIONS BETWEEN INDOLE DERIVATIVES AND 1,3-DICARBONYL COMPOUNDS

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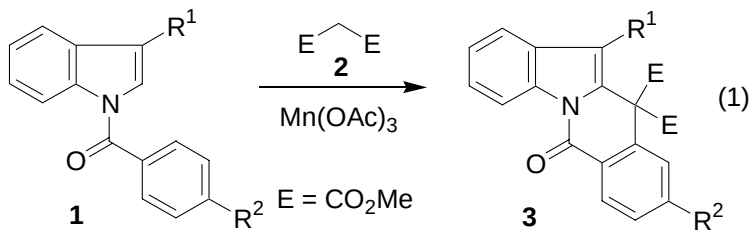
Abstract-Manganese(III) mediated oxidative free radical reactions between indole derivatives and 1,3-dicarbonyl compounds are described. In the presence of dimethyl malonate, the oxidative free radical reaction of 3-unsubstituted indoles resulted in the formation of 2-(3-oxo-2-indolylidene)malonates and these malonates can be prepared in much better yields from corresponding 3-indolecarboxylic acids. On the contrary, the oxidative free radical reaction between 3-unsubstituted indoles and 2,4-pentanedione or ethyl acetoacetate gave furo[3,2-*b*]indoles.

INTRODUCTION

There has been a growing interest in the application of radical reaction in organic synthesis for the last two decades.[1,2] Oxidative methods mediated by metal salts have been explored for the generation of carbon-centered radicals. Among these metal oxidants, manganese(III) acetate and cerium(IV) ammonium nitrate has received most attention. Recent studies have shown that efficient homolytic substitution of aromatic and hereroaromatic substrates can be accomplished using electrophilic carbon-centered radical, which was produced by the metal salts oxidation of 1,3-dicarbonyl compounds.[3,4] Previously, we found that the manganese(III) mediated oxidative free radical reactions between 3-substituted *N*-benzoylindole (**1**) and dimethyl malonate (**2**) produced indolo[1,2-*b*]isoquinoline (**3**)

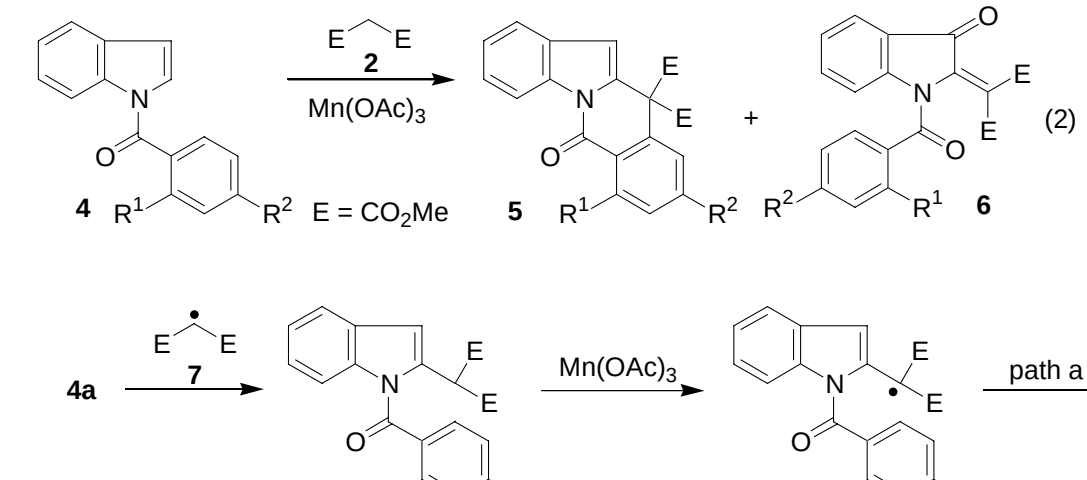


(1)

effectively (Eq. 1).[5] We wish to report here our recent results on the manganese(III) mediated oxidative free radical reactions between *N*-substituted indole derivatives and 1,3-dicarbonyl compounds.

RESULTS AND DISCUSSION

The manganese(III) mediated free radical reaction between 3-unsubstituted *N*-benzoylindole (**4**) and dimethyl malonate (**2**) was first examined (Eq. 2). When indole (**4a**) (R^1 = H, R^2 = OMe) was treated with dimethyl malonate (**2**) and manganese(III) acetate in acetic acid at 80°C, in addition to the expected product (**5a**) (5%), an unexpected product (**6a**) was obtained as the major product (37%) (Table 1, entry 1). Although the mechanistic details of this reaction are unclear, **5a** and **6a** may be formed *via* the reaction route presented in Scheme 1. Manganese(III) oxidation of **2** produces malonyl radical (**7**). This radical intermediate (**7**) adds to the 2-position of **4a** followed by subsequent oxidation to give **8a**. Malonyl radical (**9a**) produced by the manganese(III) oxidation of malonate (**8a**) undergoes either cyclization followed by aromatization to give **5a** (path a) or benzylic oxidation to produce **6a** *via* **11a** (path b). These results demonstrate that the rate of benzylic oxidation (path b) is much faster than that of cyclization (path a). This new benzylic oxidation of **8a** is quite interest and therefore we decided to pursue further this oxidative free radical reaction. Other 3-unsubstituted *N*-benzoylindoles were next examined. With **4b** and **4c** bearing an ortho substituent on the benzoyl group, **6b** and **6c** were generated in 32% and 37% yields, respectively and no **5b** and **5c** could be found (Table 1, entries 2, 3).



Scheme 1

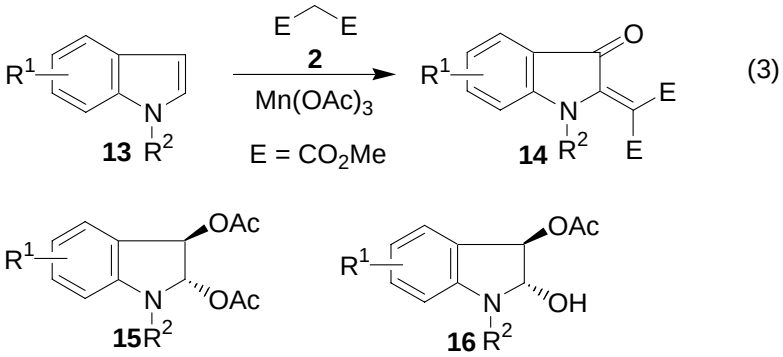


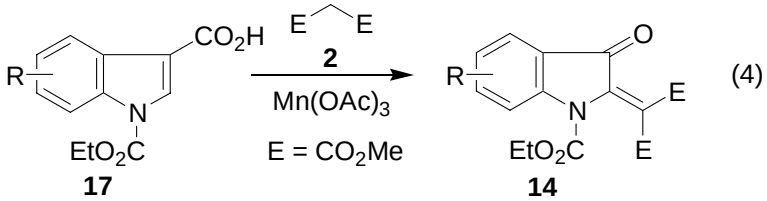
Table 1. Reactions between 3-unsubstituted indole derivatives and dimethyl malonate

entry	indole	reaction time(h)	product(yield(%))
1	**4a**: R^1 = H, R^2 = OMe	6	**5a** (5) **6a** (37)
2	**4b**: R^1 = OMe, R^2 =H	6	**6b** (32)
3	**4c**: R^1 = OMe, R^2 = OMe	6	**6c** (37)
4	**13a**: R^1 = H, R^2 = Mes[a]	12	**14a** (36)
5	**13b**: R^1 = H, R^2 = Ms[b]	6	**14b** (29)
6	**13c**: R^1 = H, R^2 = Ts	7	**14c** (25)
7	**13d**: R^1 = H, R^2 = CO_2Et	3	**14d** (43)
8	**13e**: R^1 = 4-Me, R^2 = Mes[a]	6	**14e** (64)
9	**13f**: R^1 = 4-Me, R^2 = CO_2Et	3	**14f** (74)
10	**13g**: R^1 = 5-Me, R^2 = CO_2Et	3	**14g** (41)
11	**13h**: R^1 = 5-Br, R^2 = CO_2Et	6	**14h** (10)
12	**13i**: R^1 = 4-OMe, R^2 = CO_2Et	3	**14i** (34) **15** (3) **16** (15)

[a] Mes = 2,4,6-trimethylbenzenesulfonyl. [b] Ms = methanesulfonyl.

This manganese(III) mediated reaction was also performed with a variety of *N*-substituted indoles (Eq. 3) and the results are also summarized in Table 1.[6] Reaction of indoles (**13a**), (**13b**) and (**13c**) having a *N*-sulfonyl substituent afforded the corresponding 3-indolones as the only product but without any improvement in reaction yields (entries 4 - 6). However, the reaction of **13d** bearing a weak electron-withdrawing group (R^2 = CO_2Et) gave best result yielding **14d** in 43% yield (entry 7). In order to explore the scope of this reaction, various substituted indoles bearing a *N*-ethoxycarbonyl group were subjected to the similar experimental conditions and **14** was formed in poor to good yield (entries 9 - 12). The position and electron effect of substituent (R^1) on the aryl ring appear to play a major role in this reaction. While **14f** having a 4-methyl group was generated in good yield (74%) (entry 9), **14g** bearing a 5-methyl group was produced in a lower reaction yield (41%) from **13g** (entry 10). With **13h** bearing an electron-withdrawing 5-bromo atom, **14h** was produced in a much lower reaction yield (10%) (entry 11). When **13i** bearing a methoxy group was treated with dimethyl malonate and manganese(III) acetate, in addition to the desired product (**14i**), acetates (**15**) and (**16**) were also obtained (entry 12). Acetates (**15**) and (**16**) were formed presumably *via* the direct manganese(III) oxidation of the indole nucleus.[7] Indeed, treatment of **13i** with manganese(III) acetate in acetic acid at 80°C for 3 h gave **15** and **16** in 30% and

36%, respectively. The structures of **15** and **16** are clearly assigned as *trans* compounds by the analysis of the vicinal coupling constant of the two methine protons (J = 0 Hz) and by the analogy with earlier reported paper.[8] These 3-indolone derivatives and related compounds are the key intermediate for the synthesis of biologically active compounds[9] and have also been used as heterodienes in hetero Diels-Alder reactions.[6a] The poor yield of this manganese(III) mediated free radical reaction between 3-unsubstituted indoles and dimethyl malonate is presumably due to the competing direct manganese(III) oxidation of the indole nucleus. We continued to study this oxidative free radical reaction with 3-indolecarboxylic acid (**17**) (Eq. 4). Reaction of **17a** (R^1 = H, R^2 = CO_2Et) with dimethyl malonate and manganese(III) acetate in acetic acid at 80°C afforded **14d** in 76% yield (Table 2, entry 1). 3-Indolone (**14d**) was produced presumably *via* the benzylic oxidation of **19a**, which was formed from the decarboxylation of **18a**. Malonate (**18a**) was produced from **17a** *via* a similar reaction route (**4a** → → **11a**) shown in Scheme 1. This reaction proceeded slower but gave **14d** in a much better yield when compared to **13d**. A variety of indoles (**17**) was then reacted with dimethyl malonate and manganese(III) acetate and results are also summarized in Table 2 (entries 2-7). In all cases, 3-indolone (**14**) was formed from **17** in a much better reaction yield. 2-Indolone (**21**) can also be obtained from the reaction of 2-indolecarboxylic acid (**20**) with dimethyl malonate and manganese(III) acetate, however, this reaction gave **21** in poor yield (entries 8 and 9).



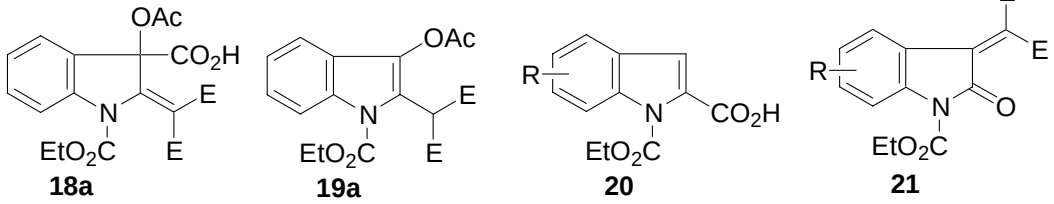
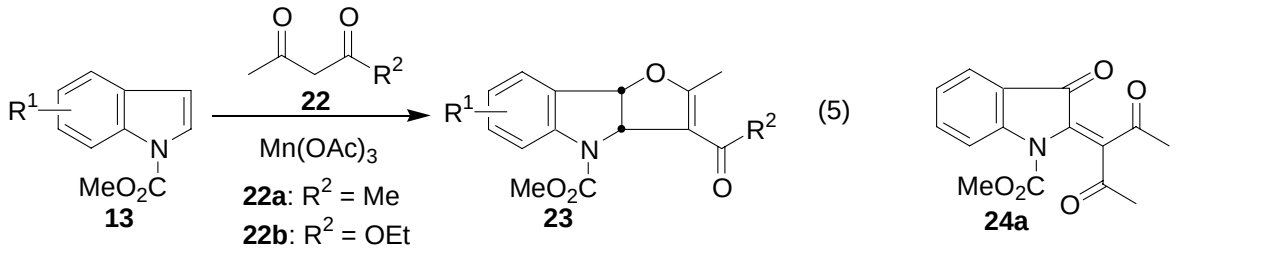
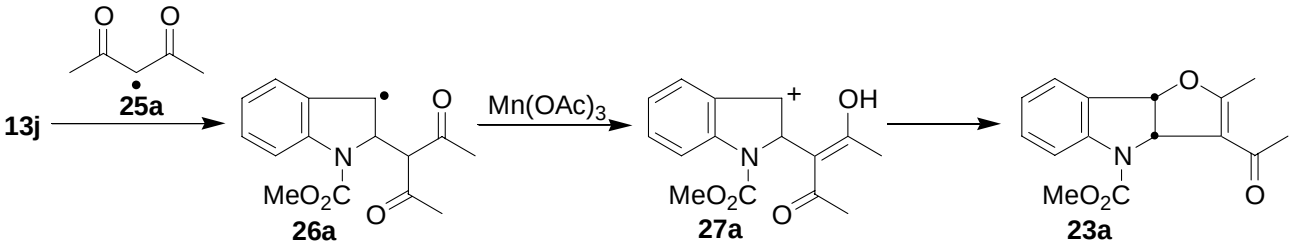


Table 2. Reactions between indolecarboxylic acids and dimethyl malonate

entry	indole	reaction time (h)	product (yield (%))
1	**17a**: R = H	16	**14d** (76)
2	**17b**: R = 5-Me	16	**14g** (91)
3	**17c**: R = 6-Me	16	**14j** (89)
4	**17d**: R = 7-Me	16	**14k**(81)
5	**17e**: R = 5-Br	28	**14h** (69)
6	**17f**: R = 5-Cl	25	**14l** (68)
7	**17g**: R = 5-OMe	10	**14m** (56)
8	**20a**: R = H	23	**21a** (26)
9	**20b**: R = 5-Me	21	**21b** (26)

We next studied the manganese(III) mediated oxidative free radical reaction of indole (**13**) with 2,4-pentanedione (**22a**) or ethyl acetoacetate (**22b**) (Eq. 5). The reaction of indole (**13j**) with 2,4-pentanedione and manganese(III) acetate in acetic acid at 80°C afforded dihydrofuran (**23a**)[10] in 40% yield and no expected **24a** could be found (Table 3, entry 1). The structure of **23a** is clearly assigned as *cis* compounds by the analysis of the vicinal coupling constant of the two methine protons (J = 8.2 Hz) and by the analogy with earlier reported paper.[10e,h] Dihydrofuran (**23a**) was formed presumably *via* the reaction route shown in Scheme 2. 2,4-Pentanedione is first oxidized by manganese(III) acetate to generate α-oxoalkyl radical (**25a**), which then attacks the 2-position of **13j** to give radical (**26a**). Radical adduct (**26a**) now undergoes further oxidation by another manganese(III) acetate to generate cation (**27a**). This cation (**27a**) undergoes electrophilic cyclization to furnish dihydrofuran (**23a**). Analogous results were obtained with other 3-unsubstituted indoles and the results are summarized in Table 3, in all cases, dihydrofuran (**23**) was obtained in modest yield.





Scheme 2

Table 3. Reactions between 3-unsubstituted indoles and 1,3-dicarbonyl compounds

entry	indole	1,3-dicarbonyl compound	reaction time (h)	product (yield (%))
1	**13j**: R^1 = H	**22a**	2	**23a** (40)
2	**13k**: R^1 = 5-Me	**22a**	2	**23b** (47)
3	**13l**: R^1 = 6-Me	**22a**	2	**23c** (41)
4	**13j**: R^1 = H	**22b**	1	**23d** (33)
5	**13k**: R^1 = 5-Me	**22b**	1	**23e** (43)
6	**13l**: R^1 = 6-Me	**22b**	1	**23f** (38)

In conclusion, radical (**7**) and (**25**) generated by the manganese(III) oxidation of 1,3-dicarbonyl compounds undergo efficient addition to the 2-position of 3-unsubstituted indoles. In the presence of dimethyl malonate, this free radical reaction provides a new method for the synthesis of 2-(3-oxo-2-indolylidene)malonates and these malonates can be prepared in much better reaction yields

from corresponding 3-indolecarboxylic acids. On the contrary, the oxidative free radical reaction between 3-unsubstituted indoles and 2,4-pentanedione or ethyl acetoacetate gave furo[3,2-*b*]indoles.

EXPERIMENTAL

Melting points are uncorrected. IR spectra were taken with a Hitachi 260-30 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 or AVANCE 300 spectrometer. Chemical shifts are reported in ppm relative to TMS as internal reference. Elemental analyses were performed with Heraeus CHN-Rapid Analyzer. HRMS were recorded on a JOEL JMS-SX 102 mass spectrometer. Analytical thin-layer chromatography was performed with precoated silica gel 60 F-254 plates (0.25 mm thick) from EM Laboratories and visualized by UV light. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (70-230 mesh).

Typical experimental procedure for the reaction between 3-unsubstituted indoles and dimethyl malonate. A mixture of 151 mg (0.60 mmol) of 1-(4-methoxybenzoyl)indole (**4a**), 324 mg (2.45 mmol) of dimethyl malonate and 1.13 g (4.22 mmol) of manganese(III) acetate in 10 mL of acetic acid was heated at 80°C for 6 h. The reaction mixture was diluted with 100 mL of ethyl acetate, washed with 50 mL of saturated aqueous sodium bisulfite, three 50 mL portions of water, 50 mL of saturated aqueous sodium bicarbonate and then dried with Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on 20 g of silica gel (eluted with 1:4.5 ethyl acetate-hexane and then 1:3.5 ethyl acetate-hexane), followed by crystallization (ethyl acetate-hexane) to give 13 mg (6%) of **5a** and 89 mg (37 %) of **6a**.

Typical experimental procedure for the reaction between indolecarboxylic acids and dimethyl malonate. A mixture of 100 mg (0.43 mmol) of indole-1,3-dicarboxylic acid 1-ethyl ester (**17a**), 227 mg (1.72 mmol) of dimethyl malonate and 805 mg (3.0 mmol) of manganese(III) acetate in 15 mL of acetic acid and 2 mL of ethyl acetate was heated at 80°C for 16 h. After work up as described above, the crude product was purified by column chromatography on 20 g of silica gel using ethyl acetate-hexane (1:4) as eluent, followed by crystallization (ethyl acetate-hexane) to give 108 mg (76%) of **14d**.

9-Methoxy-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11-dicarboxylic acid (5a). white crystals; mp 182-183°C (ethyl acetate-hexane); IR ($CHCl_3$) 3015, 1740, 1690, 1608, 1360 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 3.78 (s, 6H, 2 × OCH_3), 3.92 (s, 3H, OCH_3), 6.89 (s, 1H, ArH), 7.12 (dd, *J* = 8.8, 2.4 Hz, 1H, ArH), 7.18 (d, *J* = 2.4 Hz, 1H, ArH), 7.34 (td, *J* = 7.8, 0.9 Hz, 1H, ArH), 7.42 (td, *J* = 7.8, 0.9 Hz, 1H, ArH), 7.61 (d, *J* = 7.8 Hz, 1H, ArH), 8.41 (d, *J* = 8.8 Hz, 1H, ArH), 8.69 (d, *J* = 7.8 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 53.9 (2 × q), 55.7 (q), 59.3 (q), 109.7 (d), 114.2 (d), 115.4 (d), 116.8 (d), 119.8 (s), 120.7 (d), 124.2 (d), 125.3 (d), 129.0 (s), 131.2 (d + s), 135.2 (s), 135.5 (s), 159.5 (s), 163.4 (s),

168.7 (2 × s); HRMS calcd for $C_{21}H_{17}NO_6$ *m/z* 379.1056, found *m/z* 379.1056.

2-[1-(4-Methoxybenzoyl)-3-oxo-2,3-dihydro-1*H*-2-indolylidene]malonic acid dimethyl ester (6a). yellow crystals; mp 186-187°C (ethyl acetate-hexane); IR ($CHCl_3$) 3010, 1715, 1605, 1465, 1255 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 3.58 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 7.00 (d, *J* = 8.9 Hz, 2H, ArH), 7.02 (d, *J* = 7.7 Hz, 1H, ArH), 7.16 (t, *J* = 7.7 Hz, 1H, ArH), 7.45 (td, *J* = 7.7, 1.2 Hz, 1H, ArH), 7.77 (d, *J* = 7.7 Hz, 1H, ArH), 7.84 (d, *J* = 8.9 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 52.6 (q), 53.3 (q), 55.6 (q), 113.6 (s), 114.3 (3 × d), 121.2 (s), 124.2 (d), 125.4 (d), 125.8 (s), 132.3 (2 × d), 137.2 (d), 139.2 (s), 151.7 (s), 163.1 (s), 164.2 (s), 164.8 (s), 168.6 (s), 184.7 (s); Anal. Calcd for $C_{21}H_{17}NO_7$: C, 63.80; H, 4.33; N, 3.54. Found: C, 63.73; H, 4.42; N, 3.45.

2-[1-(2-Methoxybenzoyl)-3-oxo-2,3-dihydro-1*H*-2-indolylidene]malonic acid dimethyl ester (6b). yellow crystals; mp 167-168°C (ethyl acetate-hexane); IR ($CHCl_3$) 3015, 1715, 1605, 1465, 1295 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 3.56 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 6.90 (d, *J* = 7.6 Hz, 1H, ArH), 7.07 (t, *J* = 7.6 Hz, 1H, ArH), 7.28 (t, *J* = 7.6 Hz, 1H, ArH), 7.49 (td, *J* = 7.8, 1.6 Hz, 1H, ArH), 7.63 (dd, *J* = 7.8, 1.6 Hz, 1H, ArH), 7.66 (t, *J* = 7.8 Hz, 1H, ArH), 7.81 (d, *J* = 7.6 Hz, 1H, ArH), 7.99 (d, *J* = 7.8 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 52.7 (q), 53.1 (q), 55.5 (q), 111.3 (d), 113.2 (s), 116.0 (d), 121.0 (d), 121.83 (s), 121.89 (s), 124.7 (d), 125.0 (d), 132.6 (d), 134.1 (d), 137.6 (d), 141.1 (s), 151.3 (s), 156.0 (s), 163.2 (s), 164.4 (s), 168.1 (s), 185.6 (s); Anal. Calcd for $C_{21}H_{17}NO_7$: C, 63.80; H, 4.33; N, 3.54. Found: C, 63.73; H, 4.39; N, 3.51.

2-[1-(2,4-Dimethoxybenzoyl)-3-oxo-2,3-dihydro-1*H*-2-indolylidene]malonic acid dimethyl ester (6c). yellow crystals; mp 188-189°C (ethyl acetate-hexane); IR ($CHCl_3$) 3015, 1715, 1610, 1465, 1270 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 3.58 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.37 (d, *J* = 2.2 Hz, 1H, ArH), 6.59 (dd, *J* = 7.7, 2.2 Hz, 1H, ArH), 7.25 (t, *J* = 7.9 Hz, 1H, ArH), 7.61 (d, *J* = 7.9 Hz, 1H, ArH), 7.64 (t, *J* = 7.9 Hz, 1H, ArH), 7.79 (d, *J* =7.7 Hz, 1H, ArH), 7.91 (d, *J* = 7.9 Hz, 1H, ArH); ^{13}C NMR (75.4 MHz; $CDCl_3$) δ 52.5 (q), 53.1 (q), 55.5 (q), 55.6 (q), 97.9 (d), 106.2 (d), 112.5 (s), 114.7 (s), 115.5 (d), 121.6 (s), 124.64 (d), 124.69 (d), 134.4 (d), 137.5 (d), 141.3 (s), 151.5 (s), 158.0 (s), 163.3 (s), 164.5 (s), 164.7 (s), 167.6 (s), 185.7 (s); Anal. Calcd for $C_{22}H_{19}NO_8$: C, 62.12; H, 4.50; N, 3.29. Found: C, 62.10; H, 4.52; N, 3.28.

2-[1-(2,4,6-Trimethylbenzenesulfonyl)-3-oxo-2,3-dihydro-1*H*-2-indolylidene]malonic acid dimethyl ester (14a). red powder; mp 165-166°C (ethyl acetate-hexane); IR ($CHCl_3$) 3015, 2955, 1730, 1690, 1615 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 2.21 (s, 3H, CH_3), 2.50 (s, 6H, 2 × CH_3), 3.93 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 6.84 (s, 2H, ArH), 7.12 (d, *J* = 7.6 Hz, 1H, ArH), 7.13 (t, *J* = 7.6 Hz, 1H, ArH), 7.39 (t, *J* = 7.6 Hz, 1H, ArH), 7.67 (d, *J* = 7.6 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 21.0 (q), 22.9 (2 × q), 53.0 (q), 53.4 (q), 115.3 (d), 118.6 (s), 122.1 (s), 125.1 (d), 125.3 (d), 131.2 (s), 132.4 (2 × d), 136.6 (d), 137.4 (s), 140.6 (2 × s), 144.4 (s), 149.2 (s), 163.9 (s), 164.2 (s), 183.5 (s); Anal. Calcd for $C_{22}H_{21}NO_7S$:

C, 59.58; H, 4.77; N, 3.16. Found: C, 59.20; H, 4.96; N, 3.04.

2-(1-Methanesulfonyl-3-oxo-2,3-dihydro-1*H*-2-indolylidene)malonic acid dimethyl ester (14b). yellow crystals; mp 170-171°C (ethyl acetate-hexane); IR ($CHCl_3$) 3030, 2955, 1725, 1600, 1370 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 3.36 (s, 3H, SO_2CH_3), 3.89 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 7.33 (t, *J* = 7.7 Hz, 1H, ArH), 7.62 (d, *J* = 7.7 Hz, 1H, ArH), 7.72 (t, *J* = 7.7 Hz, 1H, ArH), 7.78 (d, *J* = 7.7 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 41.0 (q), 53.3 (q), 53.5 (q), 117.3 (d), 118.9 (s), 123.1 (s), 125.3 (d), 125.9 (d), 135.8 (s), 137.4 (d), 149.9 (s), 163.7 (s), 164.0 (s), 183.4 (s); Anal. Calcd for $C_{14}H_{13}NO_7S$: C, 49.55; H, 3.86; N, 4.13. Found: C, 49.55; H, 3.89; N, 4.11.

2-(3-Oxo-1-*p*-toluenesulfonyl-2,3-dihydro-1*H*-2-indolylidene)malonic acid dimethyl ester (14c). yellow powder; mp 154-155°C (ethyl acetate-hexane); IR ($CHCl_3$) 3015, 2955, 1725, 1600, 1290 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 2.30 (s, 3H, CH_3), 3.972 (s, 3H, OCH_3), 3.977 (s, 3H, OCH_3), 7.12 (d, *J* = 8.1 Hz, 2H, ArH), 7.26 (t, *J* = 7.7 Hz, 1H, ArH), 7.42 (d, *J* = 8.1 Hz, 2H, ArH), 7.55 (d, *J* = 7.7 Hz, 1H, ArH), 7.68 (t, *J* = 7.7 Hz, 1H, ArH), 7.93 (d, *J* = 7.7 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 21.5 (q), 53.3 (q), 53.5 (q), 119.9 (d), 122.7 (d), 124.8 (s), 124.9 (d), 126.9 (d), 127.7 (2 × d), 129.7 (2 × d), 132.1 (s), 137.0 (d), 137.2 (d), 145.7 (s), 150.2 (s), 163.2 (s), 163.7 (s), 184.0 (s); Anal. Calcd for $C_{20}H_{17}NO_7S$: C, 57.82; H, 4.12; N, 3.37. Found: C, 57.85; H, 4.11; N, 3.37.

2-(1-Ethoxycarbonyl-3-oxo-2,3-dihydro-1*H*-2-indolylidene)malonic acid dimethyl ester (14d). yellow powder; mp 110-111°C (ethyl acetate-hexane); IR ($CHCl_3$) 3030, 2955, 1735, 1610, 1470 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.39 (t, *J* = 7.2 Hz, 3H, CH_3), 3.86 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 4.38 (q, *J* = 7.2 Hz, 2H, OCH_2), 7.26 (t, *J* = 7.8 Hz, 1H, ArH), 7.67 (t, *J* = 7.8 Hz, 1H, ArH), 7.76 (d, *J* = 7.8 Hz, 1H, ArH), 7.94 (d, *J* = 7.8 Hz, 1H, ArH); ^{13}C NMR (75.4 MHz; $CDCl_3$) δ 14.1 (q), 52.9 (q), 53.4 (q), 64.1 (t), 116.9 (d), 117.3 (s), 122.2 (s), 124.8 (d), 125.0 (d), 136.6 (s), 137.4 (d), 149.7 (s), 151.0 (s), 163.4 (s), 164.5 (s), 183.8 (s); Anal. Calcd for $C_{16}H_{15}NO_7$: C, 57.66; H, 4.54; N, 4.20. Found: C, 57.51; H, 4.52; N, 4.10.

2-[4-Methyl-1-(2,4,6-trimethylbenzenesulfonyl)-3-oxo-2,3-dihydro-1*H*-2-indolylidene]malonic acid dimethyl ester (14e). yellow crystals; mp 178-179°C (ethyl acetate-hexane); IR ($CHCl_3$) 3030, 2955, 1730, 1595, 1450 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 2.21 (s, 3H, CH_3), 2.50 (s, 6H, 2 × CH_3), 2.55 (s, 3H, CH_3), 3.92 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 6.84 (s, 2H, ArH), 6.86 (d, *J* = 7.8 Hz, 1H, ArH), 6.93 (d, *J* = 7.8 Hz, 1H, ArH), 7.23 (t, *J* = 7.8 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 18.2 (q), 20.9 (q), 22.9 (2 × q), 52.9 (q), 53.4 (q), 112.4 (d), 117.7 (s), 119.8 (s), 127.2 (d), 131.4 (s), 132.4 (2 × d), 135.9 (d), 137.4 (s), 140.5 (2 × s), 141.0 (s), 144.2 (s), 149.5 (s), 164.1 (s), 164.6 (s), 184.1 (s); Anal. Calcd for $C_{23}H_{23}NO_7S$: C, 60.38; H, 5.07; N, 3.06. Found: C, 60.23; H, 5.42; N, 2.78.

2-(1-Ethoxycarbonyl-4-methyl-3-oxo-2,3-dihydro-1*H*-2-indolylidene)malonic acid dimethyl ester

(14f). yellow needles; mp 133-134°C (ethyl acetate-hexane); IR ($CHCl_3$) 3030, 2955, 1730, 1715, 1595 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.38 (t, *J* = 7.2 Hz, 3H, CH_3), 2.62 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 4.36 (q, *J* = 7.2 Hz, 2H, OCH_2), 7.00 (d, *J* = 7.9 Hz, 1H, ArH), 7.49 (t, *J* = 7.9 Hz, 1H, ArH), 7.75 (d, *J* = 7.9 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 14.1 (q), 18.3 (q), 52.8 (q), 53.4 (q), 64.0 (t), 114.0 (d), 116.3 (s), 119.9 (s), 126.9 (d), 136.6 (d), 136.9 (s), 140.8 (s), 150.1 (s), 151.0 (s), 163.6 (s), 164.8 (s), 184.6 (s); Anal. Calcd for $C_{17}H_{17}NO_7$: C, 58.79; H, 4.93; N, 4.03. Found: C, 58.76; H, 4.95; N, 3.97.

2-(1-Ethoxycarbonyl-5-methyl-3-oxo-2,3-dihydro-1*H*-2-indolylidene)malonic acid dimethyl ester (14g). yellow needles; mp 151-152°C (ethyl acetate-hexane); IR ($CHCl_3$) 3030, 2955, 1740, 1490, 1280 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.39 (t, *J* = 7.1 Hz, 3H, CH_3), 2.38 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 4.37 (q, *J* = 7.1 Hz, 2H, OCH_2), 7.46 (dd, *J* = 8.5, 1.6 Hz, 1H, ArH), 7.53 (d, *J* = 1.6 Hz, 1H, ArH), 7.80 (d, *J* = 8.5 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 14.1 (q), 20.7 (q), 52.9 (q), 53.4 (q), 64.0 (t), 116.8 (d), 117.2 (s), 122.3 (s), 124.6 (d), 135.1 (s), 136.8 (s), 138.4 (d), 147.8 (s), 151.0 (s), 163.5 (s), 164.6 (s), 183.9 (s); Anal. Calcd for $C_{17}H_{17}NO_7$: C, 58.79; H, 4.93; N, 4.03. Found: C, 58.77; H, 5.04; N, 3.93.

2-(5-Bromo-1-ethoxycarbonyl-3-oxo-2,3-dihydro-1*H*-2-indolylidene)malonic acid dimethyl ester (14h). yellow crystals; mp 111-112°C (ethyl acetate-hexane); IR ($CHCl_3$) 3015, 1725, 1605, 1325, 1230 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.39 (t, *J* = 7.1 Hz, 3H, CH_3), 3.87 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 4.38 (q, *J* = 7.1 Hz, 2H, OCH_2), 7.75 (dd, *J* = 8.5, 2.2 Hz, 1H, ArH), 7.85 (d, *J* = 8.5 Hz, 1H, ArH), 7.86 (d, *J* = 2.2 Hz, 1H, ArH); ^{13}C NMR (75.4 MHz; $CDCl_3$) δ 14.1 (q), 53.0 (q), 53.5 (q), 64.4 (t), 118.0 (s), 118.2 (s), 118.7 (d), 123.8 (s), 127.4 (d), 136.1 (s), 139.8 (d), 148.4 (s), 150.7 (s), 163.2 (s), 164.1 (s), 182.5 (s); Anal. Calcd for $C_{16}H_{14}NO_7Br$: C, 46.62; H, 3.42; N, 3.40. Found: C, 46.67; H, 3.47; N, 3.36.

2-(1-Ethoxycarbonyl-4-methoxy-3-oxo-2,3-dihydro-1*H*-2-indolylidene)malonic acid dimethyl ester (14i). yellow powder; mp 170-171°C (ethyl acetate-hexane); IR ($CHCl_3$) 3010, 2955, 1735, 1715, 1600 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.36 (t, *J* = 7.1 Hz, 3H, CH_3), 3.83 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 4.33 (q, *J* = 7.1 Hz, 2H, OCH_2), 6.67 (d, *J* = 8.2 Hz, 1H, ArH), 7.46 (d, *J* = 8.2 Hz, 1H, ArH), 7.55 (t, *J* = 8.2 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 14.0 (q), 52.8 (q), 53.3 (q), 56.2 (q), 64.0 (t), 107.1 (d), 108.4 (d), 110.5 (s), 116.0 (s), 137.1 (s), 139.2 (d), 150.7 (s), 150.9 (s), 159.0 (s), 163.6 (s), 164.6 (s), 181.1 (s); Anal. Calcd for $C_{17}H_{17}NO_8$: C, 56.20; H, 4.72; N, 3.86. Found: C, 56.24; H, 4.78; N, 3.79.

2-(1-Ethoxycarbonyl-6-methyl-3-oxo-2,3-dihydro-1*H*-2-indolylidene)malonic acid dimethyl ester (14j). yellow crystals; mp 140-141°C (ethyl acetate-hexane); IR ($CHCl_3$) 1730, 1610, 1270, 1240, 1150 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.38 (t, *J* = 7.2 Hz, 3H, CH_3), 2.48 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3),

3.96 (s, 3H, OCH_3), 4.37 (q, *J* = 7.2 Hz, 2H, OCH_2), 7.06 (d, *J* = 7.8 Hz, 1H, ArH), 7.63 (d, *J* = 7.8 Hz, 1H, ArH), 7.76 (1H, s, ArH); ^{13}C NMR (75.4 MHz; $CDCl_3$) δ 14.1 (q), 22.9 (q), 52.8 (q), 53.3 (q), 64.0 (t), 116.8 (s), 117.2 (d), 119.9 (s), 124.6 (d), 126.1 (d), 137.2 (s), 149.7 (s), 150.1 (s), 151.0 (s), 163.5 (s), 164.6 (s), 183.2 (s); Anal. Calcd for $C_{17}H_{17}NO_7$: C, 58.79; H, 4.93; N, 4.03. Found: C, 58.80; H, 4.96; N, 4.05.

2-(1-Ethoxycarbonyl-7-methyl-3-oxo-2,3-dihydro-1*H*-2-indolylidene)malonic acid dimethyl ester (14k). yellow crystals; mp 164-165°C (ethyl acetate-hexane); IR ($CHCl_3$) 3010, 1725, 1330, 1265, 1175 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.32 (t, *J* = 7.1 Hz, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 4.30 (q, *J* = 7.1 Hz, 2H, OCH_2), 7.26 (t, *J* = 7.5 Hz, 1H, ArH), 7.53 (1H, d, *J* = 7.5 Hz, 1H, ArH), 7.61 (d, *J* = 7.5 Hz, 1H, ArH); ^{13}C NMR (75.4 MHz; $CDCl_3$) δ 14.1 (q), 20.0 (q), 52.9 (q), 53.3 (q), 64.4 (t), 119.2 (s), 122.1 (d), 125.2 (s), 126.3 (d), 130.4 (s), 139.3 (s), 140.0 (d), 149.8 (s), 151.4 (s), 163.4 (s), 164.3 (s), 184.4 (s); Anal. Calcd for $C_{17}H_{17}NO_7$: C, 58.79; H, 4.93; N, 4.03. Found: C, 58.79 H, 4.96; N, 4.07.

2-(5-Chloro-1-ethoxycarbonyl-3-oxo-2,3-dihydro-1*H*-2-indolylidene)malonic acid dimethyl ester (14l). yellow crystals; mp 119-120°C (ethyl acetate-hexane); IR ($CHCl_3$) 1725, 1610, 1465, 1325, 1275 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.39 (t, *J* = 7.1 Hz, 3H, CH_3), 3.87 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 4.38 (q, *J* = 7.1 Hz, 2H, OCH_2), 7.61 (dd, *J* = 8.8, 2.1 Hz, 1H, ArH), 7.70 (d, *J* = 2.1 Hz, 1H, ArH), 7.91 (d, *J* = 8.8 Hz, 1H, ArH); ^{13}C NMR (75.4 MHz; $CDCl_3$) δ 14.1 (q), 53.0 (q), 53.5 (q), 64.4 (t), 118.0 (s), 118.3 (d), 123.4 (s), 124.3 (d), 130.9 (s), 136.2 (s), 137.0 (d), 147.9 (s), 150.7 (s), 163.2 (s), 164.1 (s), 182.7 (s); Anal. Calcd for $C_{16}H_{14}NO_7Cl$: C, 52.26; H, 3.84; N, 3.81. Found: C, 52.32; H, 3.91; N, 3.75.

2-(1-Ethoxycarbonyl-5-methoxy-3-oxo-2,3-dihydro-1*H*-2-indolylidene)malonic acid dimethyl ester (14m). red crystals; mp 99-100°C (ethyl acetate-hexane); IR ($CHCl_3$) 3010, 1735, 1490, 1325, 1270 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.39 (t, *J* = 7.1 Hz, 3H, CH_3), 3.83 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 4.36 (q, *J* = 7.1 Hz, 2H, OCH_2), 7.18 (d, *J* = 2.8 Hz, 1H, ArH), 7.23 (dd, *J* = 9.0, 2.8 Hz, 1H, ArH), 7.84 (d, *J* = 9.0 Hz, 1H, ArH); ^{13}C NMR (75.4 MHz; $CDCl_3$) δ 14.2 (q), 52.9 (q), 53.4 (q), 55.9 (q), 64.0 (t), 106.3 (d), 117.7 (s), 118.4 (d), 123.1 (s), 125.6 (d), 136.9 (s), 144.1 (s), 151.0 (s), 157.2 (s), 163.4 (s), 164.5 (s), 183.8 (s); Anal. Calcd for $C_{17}H_{17}NO_8$: C, 56.20; H, 4.72; N, 3.86. Found: C, 56.22; H, 4.73; N, 3.89.

***trans*-2,3-Diacetoxy-4-methoxy-2,3-dihydroindole-1-carboxylic acid ethyl ester (15).** white crystals; mp 132-133°C (ethyl acetate-hexane); IR ($CHCl_3$) 3010, 2945, 1735, 1615, 1470 cm^{-1}; ^{1}H NMR (300 MHz; $C_2D_2Cl_4$; 80°C) δ 1.32 (t, *J* = 7.2 Hz, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 4.18-4.39 (m, 2H, OCH_2), 6.12 (s, 1H, OCH), 6.61 (d, *J* = 8.3 Hz, 1H, ArH), 6.68 (s, 1H, OCH), 7.34 (t, *J* = 8.3 Hz, 1H, ArH), 7.43 (d, *J* = 8.3 Hz, 1H, ArH); ^{13}C NMR (75.4 MHz; $C_2D_2Cl_4$; 80°C) δ 14.3

(q), 20.6 (2 × q), 55.8 (q), 62.3 (t), 73.8 (d), 87.3 (d), 106.6 (d), 108.2 (d), 113.6 (s), 132.6 (d), 144.8 (s), 152.0 (s), 157.4 (s), 168.4 (s), 169.2 (s); Anal. Calcd for $C_{16}H_{19}NO_7$: C, 56.97; H, 5.68; N, 4.15. Found: C, 57.12; H, 5.78; N, 4.11.

***trans*-3-Acetoxy-2-hydroxy-4-methoxy-2,3-dihydroindole-1-carboxylic acid ethyl ester (16).** white crystals; mp 111-112°C (ethyl acetate-hexane); IR ($CHCl_3$) 3455, 2990, 1730, 1615, 1475 cm^{-1}; ^1H NMR (300 MHz; $C_2D_2Cl_4$; 80°C) δ 1.38 (t, *J* = 7.1 Hz, 3H, CH_3), 2.06 (s, 3H, CH_3), 3.41 (br s, 1H, OH), 3.82 (s, 3H, OCH_3), 4.34 (t, *J* = 7.1 Hz, 2H, OCH_2), 5.67 (d, *J* = 2.8 Hz, 1H, OCH), 6.07 (s, 1H, OCH), 6.54-6.64 (m, 1H, ArH), 7.24-7.35 (m, 2H, ArH); ^{13}C NMR (75.4 MHz; $C_2D_2Cl_4$; 80°C) δ 14.5 (q), 20.8 (q), 55.8 (q), 62.4 (t), 75.4 (d), 88.8 (d), 106.4 (d), 108.0 (d), 113.6 (s), 132.5 (d), 143.9 (s), 152.8 (s), 157.7 (s), 170.0 (s); Anal. Calcd for $C_{14}H_{17}NO_6$: C, 56.94; H, 5.80; N, 4.74. Found: C, 56.94; H, 5.84; N, 4.76.

2-(1-Ethoxycarbonyl-2-oxo-2,3-dihydro-1*H*-3-indolylidene)malonic acid dimethyl ester (21a). yellow crystals; mp 100-101°C (ethyl acetate-hexane); IR ($CHCl_3$) 1735, 1465, 1345, 1295, 1255 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 1.44 (t, *J* = 7.1 Hz, 3H, CH_3), 3.93 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 4.48 (q, *J* = 7.1 Hz, 2H, OCH_2), 7.21 (t, *J* = 7.8 Hz, 1H, ArH), 7.48 (t, *J* = 7.8 Hz, 1H, ArH), 7.98 (d, *J* = 7.8 Hz, 1H, ArH), 8.42 (d, *J* = 7.8 Hz, 1H, ArH); ^{13}C NMR (75.4 MHz; $CDCl_3$) δ 14.2 (q), 53.3 (q), 53.4 (q), 63.8 (t), 115.2 (d), 119.2 (s), 124.9 (d), 128.0 (d), 129.6 (s), 133.0 (s), 133.6 (d), 141.6 (s), 150.2 (s), 163.1 (s), 164.1 (s), 165.5 (s); Anal. Calcd for $C_{16}H_{15}NO_7$: C, 57.66; H, 4.54; N, 4.20. Found: C, 57.53; H, 4.56; N, 4.18.

2-(1-Ethoxycarbonyl-5-methyl-2-oxo-2,3-dihydro-1*H*-3-indolylidene)malonic acid dimethyl ester (21b). orange crystals; mp 129-130°C (ethyl acetate-hexane); IR ($CHCl_3$) 1735, 1485, 1370, 1310, 1270 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 1.44 (t, *J* = 7.1 Hz, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.93 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 4.47 (q, *J* = 7.1 Hz, 2H, OCH_2), 7.28 (d, *J* = 8.2 Hz, 1H, ArH), 7.85 (d, *J* = 8.2 Hz, 1H, ArH), 8.22 (s, 1H, ArH); ^{13}C NMR (75.4 MHz; $CDCl_3$) δ 14.2 (q), 21.2 (q), 53.2 (q), 53.4 (q), 63.7 (t), 114.9 (d), 119.2 (s), 128.3 (d), 129.2 (s), 133.2 (s), 134.3 (d), 134.5 (s), 139.5 (s), 150.2 (s), 163.1 (s), 164.3 (s), 165.6 (s); Anal. Calcd for $C_{17}H_{17}NO_7$: C, 58.79; H, 4.93; N, 4.03. Found: C, 58.77; H, 4.97; N, 4.01.

Typical experimental procedure for the reaction between 3-unsubstituted indoles and 2,4-pentanedione. A mixture of 106 mg (0.61 mmol) of 1-methoxycarbonylindole (**13j**), 243 mg (2.43 mmol) of 2,4-pentanedione and 817 mg (3.05 mmol) of manganese(III) acetate in 10 mL of acetic acid was heated at 80°C for 1 h (the dark brown color of manganese(III) acetate disappeared), followed by the addition of 244 mg (2.44 mmol) of 2,4-pentanedione and 819 mg (3.05 mmol) of manganese(III) acetate. The reaction mixture was heated for another 1 h. After work up as described above, the crude product was purified by column chromatography on 20 g of silica gel (eluted with 1:3 ethyl acetate-hexane) followed by crystallization (ethyl acetate-hexane) to give 65 mg (40 %) of **23a**.

Typical experimental procedure for the reaction between 3-unsubstituted indoles and ethyl acetoacetate. A mixture of 119 mg (0.68 mmol) of 1-methoxycarbonylindole (**14a**), 356 mg (2.74 mmol) of ethyl acetoacetate and 912 mg (3.40 mmol) of manganese(III) acetate in 10 mL of acetic acid was heated at 80°C for 1 h. After work up as described above, the crude product was purified by column chromatography on 20 g of silica gel (eluted with 1:7 ethyl acetate-hexane), followed by crystallization (ethyl acetate-hexane) to give 68 mg (33 %) of **23d**.

3-Acetyl-4-methoxycarbonyl-2-methyl-4,8b-dihydro-3a*H*-furo[3,2-*b*]indole (23a). white needles; mp 113-114°C (ethyl acetate-hexane); IR ($CHCl_3$) 3010, 1705, 1485, 1445, 1385 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 5.91 (d, *J* = 8.2 Hz, 1H, CH), 6.07 (d, *J* = 8.2 Hz, 1H, CH), 7.10 (td, *J* = 7.8, 0.9 Hz, 1H, ArH), 7.37 (td, *J* = 7.8, 1.2 Hz, 1H, ArH), 7.43 (d, *J* = 7.8 Hz, 1H, ArH), 7.74 (d, *J* = 7.8 Hz, 1H, ArH), ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.6 (q), 29.4 (q), 52.8 (q), 68.3 (d), 84.6 (d), 113.8 (s), 116.8 (d), 123.6 (d), 125.8 (d), 128.0 (s), 130.9 (d), 142.1 (s), 153.6 (s), 169.6 (s), 195.9 (s); Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.94; H, 5.51; N, 5.10.

3-Acetyl-4-methoxycarbonyl-2,8-dimethyl-4,8b-dihydro-3a*H*-furo[3,2-*b*]indole (23b). white needles; mp 138-139°C (ethyl acetate-hexane); IR ($CHCl_3$) 3010, 1710, 1600, 1465, 1385 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.12 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 5.88 (d, *J* = 8.3 Hz, 1H, CH), 6.12 (d, *J* = 8.3 Hz, 1H, CH), 6.89 (d, *J* = 7.8 Hz, 1H, ArH), 7.26 (t, *J* = 7.8 Hz, 1H, ArH), 7.57 (d, *J* = 7.8 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.6 (q), 18.1 (q), 29.3 (q), 52.7 (q), 68.1 (d), 84.0 (d), 113.8 (s), 114.0 (d), 124.7 (d), 126.6 (s), 130.9 (d), 136.3 (s), 142.2 (s), 153.6 (s), 169.5 (s), 196.1 (s); Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.88. Found: C, 66.84; H, 6.05; N, 4.94.

3-Acetyl-4-methoxycarbonyl-2,7-dimethyl-4,8b-dihydro-3a*H*-furo[3,2-*b*]indole (23c). white crystals; mp 156-157°C (ethyl acetate-hexane); IR ($CHCl_3$) 3005, 1705, 1595, 1450, 1385 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.13 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 5.90 (d, *J* = 8.2 Hz, 1H, CH), 6.03 (d, *J* = 8.2 Hz, 1H, CH), 7.17 (d, *J* = 8.1 Hz, 1H, ArH), 7.23 (s, 1H, ArH), 7.60 (d, *J* = 8.1 Hz, 1H, ArH); ^{13}C NMR (74.5 MHz, $CDCl_3$) δ 14.7 (q), 20.8 (q), 29.4 (q), 52.7 (q), 68.3 (d), 84.7 (d), 113.8 (s), 116.6 (d), 126.1 (d), 128.1 (s), 131.5 (d), 133.4 (s), 139.8 (s), 153.6 (s), 169.6 (s), 196.0 (s); Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.88. Found: C, 66.73; H, 5.96; N, 4.87.

3-Ethoxycarbonyl-4-methoxycarbonyl-2-methyl-4,8b-dihydro-3a*H*-furo[3,2-*b*]indole (23d). white needles; mp 91-92°C (ethyl acetate-hexane); IR ($CHCl_3$) 3010, 1705, 1640, 1445, 1385 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 4.21 (q, *J* = 7.2 Hz, 2H, OCH_2), 5.95 (d, *J* = 8.4 Hz, 1H, CH), 6.09 (d, *J* = 8.4 Hz, 1H, CH), 7.08 (t, *J* = 7.7 Hz, 1H, ArH), 7.36 (t, *J* = 7.7 Hz, 1H, ArH), 7.40 (d, *J* = 7.7 Hz, 1H, ArH), 7.79 (d, *J* = 7.7 Hz, 1H, ArH); ^{13}C NMR

(75.4 MHz, $CDCl_3$) δ 14.4 (q), 14.5 (q), 52.7 (q), 59.8 (t), 66.9 (d), 84.3 (d), 104.2 (s), 116.8 (d), 123.5 (d), 125.6 (d), 128.4 (s), 130.7 (d), 142.4 (s), 153.7 (s), 165.2 (s), 170.4 (s); Anal. Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.31; H, 5.65; N, 4.59.

3-Ethoxycarbonyl-4-methoxycarbonyl-2,8-dimethyl-4,8b-dihydro-3a*H*-furo[3,2-*b*]indole (23e). white needles; mp 139-140°C (ethyl acetate-hexane); IR ($CHCl_3$) 3010, 1705, 1640, 1465, 1380 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.31 (t, *J* = 7.1 Hz, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 4.21 (q, *J* = 7.1 Hz, 2H, OCH_2), 5.94 (d, *J* = 8.5 Hz, 1H, CH), 6.14 (d, *J* = 8.5 Hz, 1H, CH), 6.88 (d, *J* = 7.8 Hz, 1H, ArH), 7.25 (t, *J* = 7.8 Hz, 1H, ArH), 7.62 (d, *J* = 7.8 Hz, 1H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.37 (q), 14.43 (q), 18.2 (q), 52.6 (q), 59.8 (t), 66.7 (d), 84.0 (d), 104.2 (s), 114.0 (d), 124.7 (d), 126.9 (s), 130.7 (d), 136.3 (s), 142.5 (s), 153.8 (s), 165.3 (s), 170.2 (s); Anal. Calcd for $C_{17}H_{19}NO_5$: C, 64.34; H, 6.03; N, 4.41. Found: C, 64.21; H, 6.03; N, 4.36.

3-Ethoxycarbonyl-4-methoxycarbonyl-2,7-dimethyl-4,8b-dihydro-3a*H*-furo[3,2-*b*]indole (23f). white needles; mp 109-110°C (ethyl acetate-hexane); IR ($CHCl_3$) 3010, 1705, 1495, 1450, 1385 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 1.30 (t, *J* = 7.1 Hz, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 4.20 (q, *J* = 7.1 Hz, 2H, OCH_2), 5.94 (d, *J* = 8.4 Hz, 1H, CH), 6.04 (d, *J* = 8.4 Hz, 1H, CH), 7.16 (d, *J* = 8.3 Hz, 1H, ArH), 7.20 (s, 1H, ArH), 7.65 (d, *J* = 8.3 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.4 (q), 14.5 (q), 20.8 (q), 52.6 (q), 59.8 (t), 67.0 (d), 84.4 (d), 104.2 (s), 116.5 (d), 126.0 (d), 128.5 (s), 131.3 (d), 133.2 (s), 140.0 (s), 153.8 (s), 165.3 (s), 170.3 (s); Anal. Calcd for $C_{17}H_{19}NO_5$: C, 64.34; H, 6.03; N, 4.41. Found: C, 64.06; H, 6.04; N, 4.36.

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