MANGANESE(III) ACETATE INITIATED OXIDATIVE FREE RADICAL REACTION BETWEEN BENZOYLINDOLES AND DIMETHYL MALONATE[1]

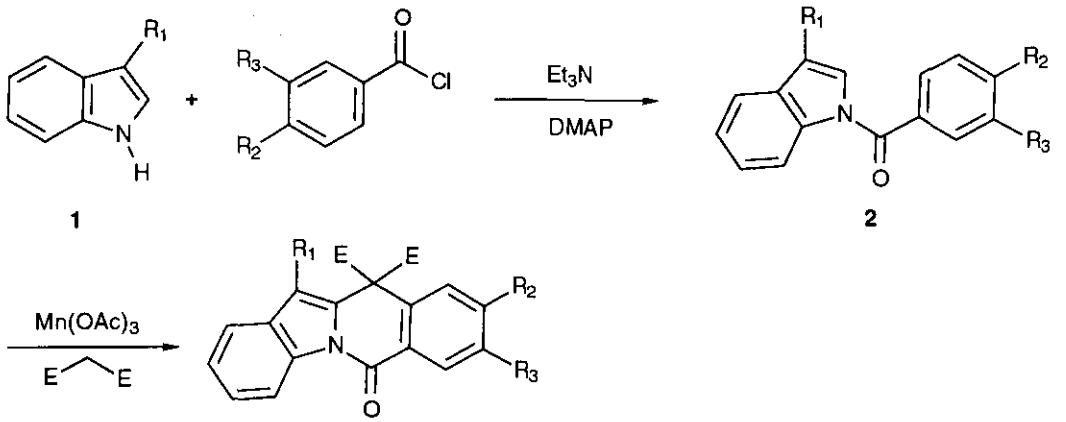
Sheow-Fong Wang and Che-Ping Chuang*

Department of Chemistry, National Cheng Kung University, Tainan, Taiwan, 70101, R.O.C.

Abstract - A free radical reaction between benzoylindoles and dimethyl malonate initiated by manganese(III) acetate is described. This free radical reaction provides a new method for the synthesis of indolo[1,2-*b*]isoquinolines and benzo[*b*]carbazoles. With meta substituent on benzoyl group, this reaction shows unusual high regioselectivity.

The carbon-centered radical initiated reaction is currently being used in organic synthesis as a valuable method for C-C bond formation.[2] Electrophilic radicals produced from the manganese(III) acetate oxidation of 1,3-dicarbonyl compounds undergo efficient addition to a C-C double bond.[3,4] The free radical addition of a carbon radical to aryl and heteroaryl rings has been reported.[5,6] We report here our results of manganese(III) initiated oxidative free radical reaction between benzoylindoles and dimethyl malonate.

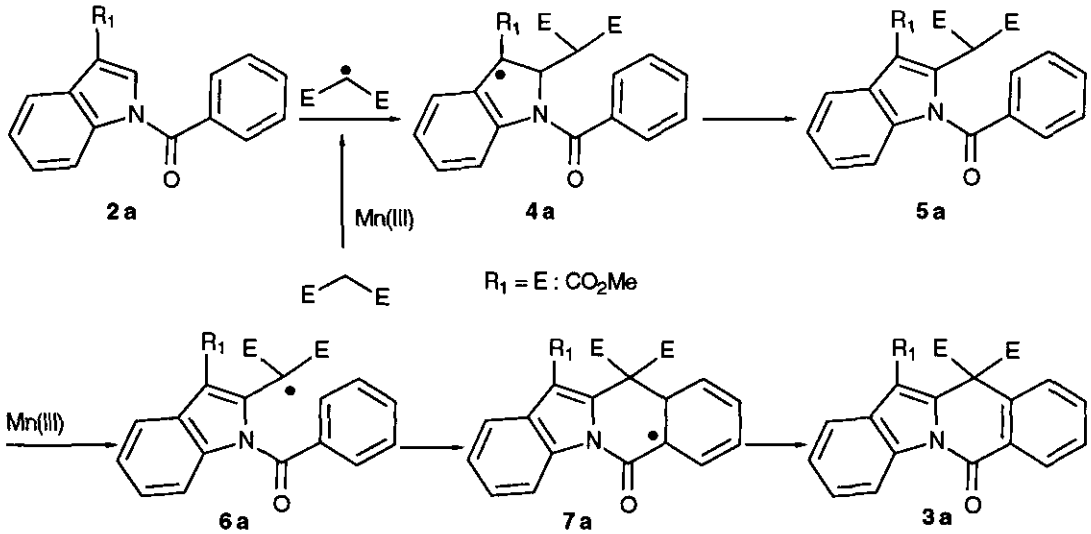
We began our studies with the reaction shown in Scheme 1. 1-Benzoylindoles (**2**) were prepared from indoles (**1**) and benzoyl chloride in the presence of triethylamine and dimethylaminopyridine. Thus, treatment of **2a** and dimethyl malonate with manganese(III) acetate in glacial acetic acid at 80 °C gave **3a** in 83% yield. The generalities of this reaction are shown in Table 1 (Entries a - i). With R_1=CO_2Me, it gave best results (Entries a, b and c). The results illustrate that this oxidative free radical reaction of indoles



Scheme 1

Table 1: The Free Radical Reaction between 1-Benzoylindoles (**2**) and Dimethyl Malonate

Entry		Substrate			Product
		R_1	R_2	R_3	(Yield)
a	**2a**	CO_2Me	H	H	**3a**(83%)
b	**2b**	CO_2Me	OMe	H	**3b**(74%)
c	**2c**	CO_2Me	Ph	H	**3c**(81%)
d	**2d**	CN	H	H	**3d**(59%)
e	**2e**	CN	Me	H	**3e**(57%)
f	**2f**	CN	OMe	H	**3f**(62%)
g	**2g**	COMe	H	H	**3g**(48%)
h	**2h**	COMe	Me	H	**3h**(52%)
i	**2i**	COMe	Ph	H	**3i**(42%)
j	**2j**	CN	H	Me	**3j**(72%)
k	**2k**	CO_2Me	H	Me	**3k**(80%)
l	**2l**	COMe	H	Me	**3l**(57%)
m	**2m**	CN	H	Cl	**3m**(59%)
n	**2n**	CO_2Me	H	Cl	**3n**(82%)
o	**2o**	COMe	H	Cl	**3o**(49%)
p	**2p**	CN	H	Br	**3p**(65%)
q	**2q**	CO_2Me	H	Br	**3q**(84%)



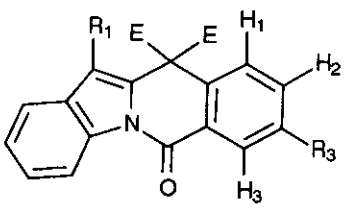
Scheme 2

(**2**) proceeds efficiently for the formation of isoquinolines (**3**).

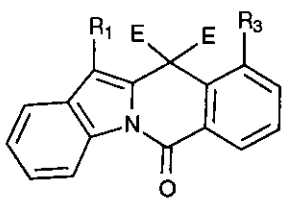
A possible mechanism for this free radical annulation reaction is shown in Scheme 2. Initiation occurs with the manganese(III) acetate oxidation of dimethyl malonate followed by addition and oxidation to produce

malonate (**5a**). Malonyl radical (**6a**) produced by the manganese(III) oxidation of malonate (**5a**) undergoes intramolecular cyclization and oxidation to give **3a**.

With meta substituent on benzoyl group, the regioselectivity of this reaction was also examined. Presumably, two possible products (**3**) and (**8**) could be obtained. When **2j** was treated with dimethyl malonate and manganese(III) acetate surprisingly only one product **3j** was isolated in 72% yield and no trace of **8j** could be found. The structure of **3j** was determined by the ^{1}H NMR spectral analysis. The ^{1}H NMR spectrum clearly shows three signals at δ 7.58 (dd, J=8.2, 1.4 Hz), δ 7.65 (d, J=8.2 Hz) and δ 8.22 (d, J=1.4 Hz) corresponding to the aromatic protons on benzoyl group. Examples are summarized in Table 1 (Entries j - q). In all cases, only one product was obtained. The ^{1}H NMR spectral data are listed in Table 2. This high regioselectivity can be ascribed to the steric effect between tertiary malonyl radical (**9**) and substituent R3.



3j - 3q



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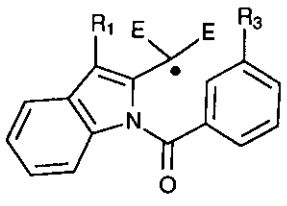

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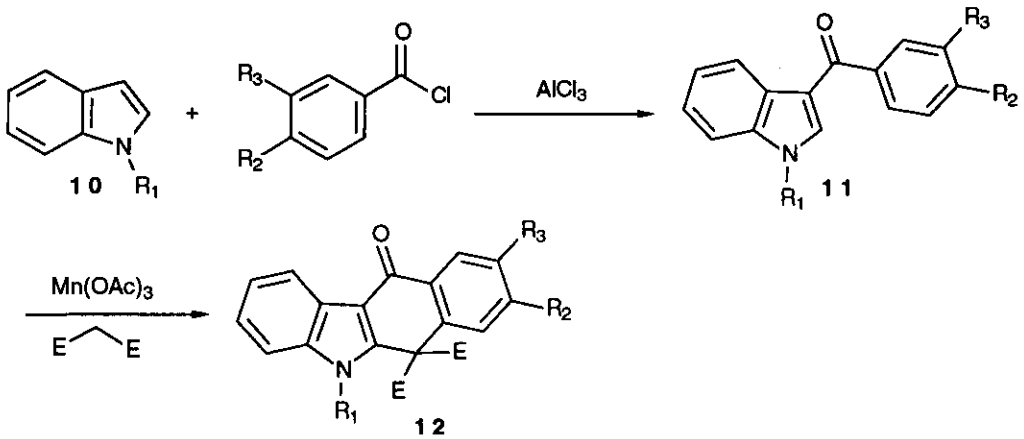
Table 2: The ^{1}H NMR Spectral Data of Isoquinolines (**3**)

Entry		Substrate		H_1	H_2	H_3
		R_1	R_3			
a	**3j**	CN	Me	7.65(d, J=8.2 Hz)	7.58(dd, J=8.2, 1.4 Hz)	8.22(d, J=1.4 Hz)
b	**3k**	CO_2Me	Me	8.04(d, J=8.2 Hz)	7.45-7.59(m)	8.28(br s)
c	**3l**	COMe	Me	8.14(d, J=8.2 Hz)	7.48-7.56(m)	8.27(br s)
d	**3m**	CN	Cl	7.70-7.76(m)		8.37-8.40(m)
e	**3n**	CO_2Me	Cl	8.13(d, J=8.7 Hz)	7.68(dd, J=8.7, 2.4 Hz)	8.44(d, J=2.4 Hz)
f	**3o**	COMe	Cl	8.22(d, J=8.6 Hz)	7.68(dd, J=8.6, 2.4 Hz)	8.43(d, J=2.4 Hz)
g	**3p**	CN	Br	7.64(d, J=8.5 Hz)	7.88(dd, J=8.5, 2.2 Hz)	8.56(d, J=2.2 Hz)
h	**3q**	CO_2Me	Br	8.06(d, J=8.6 Hz)	7.83(dd, J=8.6, 2.3 Hz)	8.60(d, J=2.3 Hz)

We also studied this manganese(III) initiated free radical reaction with 3-benzoylindoles (**11**). 3-Benzoylindoles (**11**) were prepared from the Friedel-Crafts reaction of **10** with benzoyl chloride in the presence of aluminum chloride.[7] The reaction of **11a** with dimethyl malonate and manganese(III) acetate under the same condition as the reactions above resulted in the formation of **12a** in 43% yield. Other examples of this reaction were shown in Table 3. Lower yields were observed than in the corresponding reactions of 1-benzoylindoles (**2**). This reaction gave better results with R_1=Ms. This reaction presumably

proceeds *via* similar mechanism shown in Scheme 2. The regioselectivity of this reaction with meta substituted 3-benzoylindoles (**11**) was also studied. The results are also summarized in Table 3 (Entries i - n). In all cases, only one product was obtained. The NMR spectral for protons on benzoyl group are listed in Table 4.



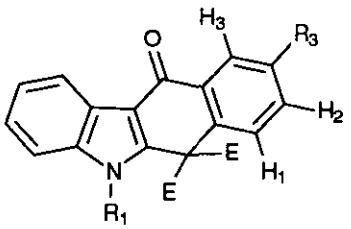
Scheme 3

Table 3: The Free Radical Reaction between 3-Benzoylindoles (**11**) and Dimethyl Malonate

Entry		Substrate			Product
		R_1	R_2	R_3	(Yield)
a	**11a**	Me	H	H	**12a**(43%)
b	**11b**	Ms	H	H	**12b**(54%)
c	**11c**	Me	Me	H	**12c**(40%)
d	**11d**	Ms	Me	H	**12d**(69%)
e	**11e**	Me	Cl	H	**12e**(27%)
f	**11f**	Ms	Cl	H	**12f**(36%)
g	**11g**	Ms	Br	H	**12g**(41%)
h	**11h**	Ms	OMe	H	**12h**(52%)
i	**11i**	Me	H	Me	**12i**(54%)
j	**11j**	Ms	H	Me	**12j**(56%)
k	**11k**	Me	H	Cl	**12k**(52%)
l	**11l**	Ms	H	Cl	**12l**(53%)
m	**11m**	Me	H	Br	**12m**(41%)
n	**11n**	Ms	H	Br	**12n**(72%)

In conclusion, the malonyl radical produced by the manganese(III) acetate oxidation undergoes addition followed by cyclization effectively with benzoylindoles. This oxidative free radical reaction provides a novel method for the synthesis indolo[1,2-*b*]isoquinolines and benzo[*b*]carbazoles from readily available

benzoylindoles and dimethyl malonate. With meta substituent on benzoyl group, this reaction shows unusual high regioselectivity.



12i - 12n

Table 4: The ^{1}H NMR Spectral Data for Benzo[*b*]carbazoles (**12**)

Entry		Substrate R_1	R_3	H_1	H_2	H_3
a	**12i**	Me	Me	7.68(d, J=8.1 Hz)	7.37-7.47(m)	8.25(br s)
b	**12j**	Ms	Me	8.32(d, J=8.3 Hz)	7.49(dm, J=8.3 Hz)	8.20(br s)
c	**12k**	Me	Cl	7.74(d, J=8.5 Hz)	7.56(dd, J=8.5, 2.4 Hz)	8.40(d, J=2.4 Hz)
d	**12l**	Ms	Cl	8.42(d, J=8.7 Hz)	7.64(dd, J=8.7, 2.4 Hz)	8.36(d, J=2.4 Hz)
e	**12m**	Me	Br	7.67(d, J=8.5 Hz)	7.72(dd, J=8.5, 2.2 Hz)	8.56(d, J=2.2 Hz)
f	**12n**	Ms	Br	8.34(d, J=8.7 Hz)	7.79(dd, J=8.7, 2.3 Hz)	8.52(d, J=2.3 Hz)

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were recorded on Bruker Ac-200 or Bruker AMX-400 spectrometer. Elemental analyses were performed with a Heraeus CHN-Rapid Analyzer. All reactions were carried out under a nitrogen atmosphere. Analytical thin layer chromatography was performed by precoated silica gel 60 F-254 plates (0.25 mm thick) of EM Laboratories and visualized either by UV or by spraying with 5% phosphomolybdic acid in ethanol following by heating. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (230-400 Mesh).

Typical experimental procedure: A solution of 130 mg (0.47 mmol) of **2a**, 255 mg (1.93 mmol) of dimethyl malonate and 749 mg (2.79 mmol) of manganese(III) acetate dihydrate in 10 mL of glacial acetic acid was heated in an 80 ^{o}C oil bath for 24 h. The reaction mixture was diluted with 100 mL of ethyl acetate, washed with 50 mL of saturated aqueous sodium bisulfite, three 25-mL portions of water, dried (Na_2SO_4) and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with dichloromethane-hexane, 3:1) followed by recrystallization (chloroform-hexane) to give 158 mg (83%) of **3a** .

6-Oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11,12-tricarboxylic acid trimethyl ester (3a): mp 248-249 ^{o}C; IR ($CHCl_3$) 3030, 2950, 1780, 1705, 1365, 1330, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.61 (s, 6H, OCH_3), 3.95 (s, 3H, OCH_3), 7.44-7.54 (m, 2H, ArH), 7.62 (td, J=

7.7, 0.7 Hz, 1H, ArH), 7.73 (td, J= 7.7, 1.3 Hz, 1H, ArH), 8.18 (dd, J= 7.7, 0.7 Hz, 1H, ArH), 8.21-8.26 (m, 1H, ArH), 8.48 (dd, J= 7.7, 1.3 Hz, 1H, ArH), 8.75-8.85 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 51.4(q), 53.6(q), 57.5(s), 111.4(s), 116.9(d), 121.5(d), 125.2(s), 125.4(d), 125.9(d), 126.8(s), 127.8(d), 129.3(d), 129.5(d), 133.1(s), 134.3(d), 134.6(s), 139.5(s), 159.7(s), 164.7(s), 166.3(s); Anal. Calcd for $C_{22}H_{17}NO_7$: C, 64.86; H, 4.21; N, 3.44. Found: C, 64.89; H, 4.24; N, 3.41.

9-Methoxy-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11,12-tricarboxylic acid trimethyl ester (3b): mp 246-247 °C; IR ($CHCl_3$) 3030, 2955, 1780, 1700, 1610, 1455, 1365, 1330, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.61 (s, 6H, OCH_3), 3.94 (s, 6H, OCH_3), 7.11 (dd, J= 8.8, 2.5 Hz, 1H, ArH), 7.43-7.51 (m, 2H, ArH), 7.64 (d, J= 2.5 Hz, 1H, ArH), 8.22 (dm, J= 6.6 Hz, 1H, ArH), 8.40 (d, J= 8.8 Hz, 1H, ArH), 8.81 (dm, J= 7.9 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 51.4(q), 53.6(q), 55.9(q), 57.4(s), 110.9(s), 112.1(d), 116.2(d), 116.9(d), 118.0(s), 121.5(d), 125.2(d), 125.8(d), 126.8(s), 131.5(d), 134.6(s), 135.3(s), 139.8(s), 159.6(s), 164.3(s), 164.7(s), 166.3(s); Anal. Calcd for $C_{23}H_{19}NO_8$: C, 63.16; H, 4.38; N, 3.20. Found: C, 63.16; H, 4.36; N, 3.24.

6-Oxo-9-phenyl-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11,12-tricarboxylic acid trimethyl ester (3c): mp 233-234 °C; IR ($CHCl_3$) 3030, 2955, 1785, 1700, 1610, 1455, 1365, 1330, 1290 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.62 (s, 6H, OCH_3), 3.96 (s, 3H, OCH_3), 7.40-7.53 (m, 5H, ArH), 7.68 (dm, J= 7.7 Hz, 2H, ArH), 7.83 (dm, J= 8.2 Hz, 1H, ArH), 8.25 (dm, J= 6.3 Hz, 1H, ArH), 8.40 (br s, 1H, ArH), 8.52 (dm, J= 8.2 Hz, 1H, ArH), 8.83 (dm, J= 7.6 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 51.4(q), 53.6(q), 57.5(s), 111.3(s), 116.9(d), 121.5(d), 123.8(s), 125.4(d), 125.9(d), 126.0(d), 126.9(s), 127.4(d), 128.1(d), 128.8(d), 129.0(d), 129.8(d), 133.5(s), 134.6(s), 138.7(s), 139.5(s), 147.1(s), 159.6(s), 164.6(s), 166.3(s); Anal. Calcd for $C_{28}H_{21}NO_7$: C, 69.56; H, 4.38; N, 2.90. Found: C, 69.30; H, 4.48; N, 2.71.

12-Cyano-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11-dicarboxylic acid dimethyl ester (3d): mp 195-196 °C; IR ($CHCl_3$) 3025, 2960, 2230, 1750, 1710, 1455, 1360, 1330, 1230 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.88 (s, 6H, OCH_3), 7.44-7.55 (m, 2H, ArH), 7.61-7.69 (m, 1H, ArH), 7.74-7.82 (m, 3H, ArH), 8.42 (dm, J= 8.1 Hz, 1H, ArH), 8.67 (dm, J= 7.2 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 54.3(q), 59.5(s), 95.3(s), 113.1(s), 117.0(d), 119.3(d), 125.5(s), 125.7(d), 127.1(d), 127.6(s), 128.6(d), 129.2(d), 129.8(d), 133.0(s), 133.7(s), 134.3(d), 138.2(s), 159.2(s), 166.4(s); Anal. Calcd for $C_{21}H_{14}N_2O_5$: C, 67.38; H, 3.77; N, 7.48. Found: C, 67.33; H, 3.76; N, 7.48.

12-Cyano-9-methyl-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11-dicarboxylic acid dimethyl ester (3e): mp 207-209 °C; IR ($CHCl_3$) 3030, 2960, 2230, 1745, 1710, 1455, 1360, 1330, 1230 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.52 (s, 3H, CH_3), 3.89 (s, 6H, OCH_3), 7.42-7.57 (m, 4H, ArH), 7.78 (d, J= 7.7 Hz, 1H, ArH), 8.31 (d, J= 8.0 Hz, 1H, ArH), 8.68 (d, J= 7.7 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 22.0(q), 54.3(q), 59.5(s), 95.0(s), 113.2(s), 117.1(d), 119.3(d), 123.0(s), 125.6(d), 127.0(d), 127.6(s), 128.9(d), 129.3(d), 130.9(d), 133.0(s), 133.8(s), 138.4(s), 145.7(s), 159.2(s), 166.6(s); Anal. Calcd for $C_{22}H_{16}N_2O_5$: C, 68.04; H, 4.15; N, 7.21. Found: C, 68.05; H, 4.10; N, 7.26.

12-Cyano-9-methoxy-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11-dicarboxylic acid dimethyl ester (3f): mp 200-201 °C; IR ($CHCl_3$) 3010, 2955, 2230, 1745, 1705, 1610, 1455,

1355, 1330, 1275, 1245 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.88 (s, 6H, OCH_3), 3.91 (s, 3H, OCH_3), 7.13 (dm, J= 8.8 Hz, 1H, ArH), 7.18-7.21 (m, 1H, ArH), 7.43-7.53 (m, 2H, ArH), 7.77 (dm, J= 7.8 Hz, 1H, ArH), 8.35 (dm, J= 8.8 Hz, 1H, ArH), 8.66 (dm, J= 8.6 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 54.4(q), 55.8(q), 59.6(s), 94.9(s), 113.2(s), 113.6(d), 115.8(d), 117.0(d), 118.2(s), 119.2(d), 125.5(d), 127.0(d), 127.5(s), 131.6(d), 133.7(s), 135.1(s), 138.3(s), 158.9(s), 164.3(s), 166.4(s); Anal. Calcd for $C_{22}H_{16}N_2O_6$: C, 65.35; H, 3.99; N, 6.93. Found: C, 65.28; H, 3.92; N, 6.90.

12-Acetyl-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11-dicarboxylic acid dimethyl ester (3g): mp 213°C (decomp); IR ($CHCl_3$) 3030, 1780, 1760, 1705, 1455, 1350, 1330 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.76 (s, 3H, CH_3), 3.59 (s, 6H, OCH_3), 7.47-7.54 (m, 2H, ArH), 7.60 (td, J= 7.8, 1.1 Hz, 1H, ArH), 7.71 (td, J= 7.8, 1.5 Hz, 1H, ArH), 7.94-8.01 (m, 1H, ArH), 8.25 (dd, J= 7.8, 1.1 Hz, 1H, ArH), 8.45 (dd, J= 7.8, 1.5 Hz, 1H, ArH), 8.86-8.93 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 31.2(q), 53.4(q), 58.0(s), 117.6(d), 118.9(s), 120.2(d), 125.2(s), 125.4(d), 125.6(d), 126.4(s), 128.1(d), 129.1(d), 129.5(d), 133.0(s), 134.4(d), 135.0(s), 159.9(s), 165.9(s), 195.6(s); Anal. Calcd for $C_{22}H_{17}NO_6$: C, 67.52; H, 4.38; N, 3.58. Found: C, 67.58; H, 4.35; N, 3.56.

12-Acetyl-9-methyl-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11-dicarboxylic acid dimethyl ester (3h): mp 240 °C (decomp); IR ($CHCl_3$) 3030, 1780, 1760, 1705, 1530, 1455, 1350, 1330 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.49 (s, 3H, CH_3), 2.76 (s, 3H, CH_3), 3.58 (s, 6H, OCH_3), 7.40 (dm, J= 8.0 Hz, 1H, ArH), 7.46-7.53 (m, 2H, ArH), 7.95-8.01 (m, 1H, ArH), 8.03 (br s, 1H, ArH), 8.33 (d, J= 8.0 Hz, 1H, ArH), 8.87-8.93 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 22.0(q), 31.2(q), 53.3(q), 57.8(s), 117.5(d), 118.6(s), 120.1(d), 122.6(s), 125.2(d), 125.4(d), 126.3(s), 128.1(d), 129.1(d), 130.6(d), 132.9(s), 135.0(s), 140.1(s), 145.8(s), 160.0(s), 165.9(s), 195.5(s); Anal. Calcd for $C_{23}H_{19}NO_6$: C, 68.14; H, 4.72; N, 3.45. Found: C, 68.09; H, 4.64; N, 3.44.

12-Acetyl-6-oxo-9-phenyl-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11-dicarboxylic acid dimethyl ester (3i): mp 206 °C (decomp.); IR ($CHCl_3$) 3030, 1780, 1760, 1705, 1610, 1455, 1350, 1330 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.79 (s, 3H, CH_3), 3.61 (s, 6H, OCH_3), 7.40-7.55 (m, 5H, ArH), 7.68 (dm, J= 6.8 Hz, 2H, ArH), 7.83 (dd, J= 8.4, 1.7 Hz, 1H, ArH), 7.98-8.03 (m, 1H, ArH), 8.50 (d, J= 1.7 Hz, 1H, ArH), 8.51 (d, J= 8.4 Hz, 1H, ArH), 8.90-8.97 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 31.2(q), 53.5(q), 57.4(s), 117.6(d), 118.9(s), 120.2(d), 123.8(s), 125.4(d), 125.6(d), 126.4(d), 127.4(d), 128.1(d), 128.8(d), 129.0(d), 129.7(d), 133.5(s), 135.0(s), 138.8(s), 140.0(s), 147.2(s), 159.8(s), 165.9(s), 195.6(s); Anal. Calcd for $C_{28}H_{21}NO_6$: C, 71.94; H, 4.53; N, 3.00. Found: C, 71.65; H, 4.49; N, 2.93.

12-Cyano-8-methyl-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11-dicarboxylic acid dimethyl ester (3j): mp 215-216 °C; IR ($CHCl_3$) 3030, 2955, 2230, 1750, 1710, 1455, 1355, 1325, 1230, 1210 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.49 (s, 3H, CH_3), 3.88 (s, 6H, OCH_3), 7.45-7.55 (m, 2H, ArH), 7.58 (dd, J= 8.2, 1.4 Hz, 1H, ArH), 7.65 (d, J= 8.2 Hz, 1H, ArH), 7.78 (dm, J= 8.0 Hz, 1H, ArH), 8.22 (d, J= 1.4 Hz, 1H, ArH), 8.66 (d, J= 8.0 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.0(q), 54.3(q), 59.3(s), 95.2(s), 113.1(s), 117.0(d), 119.3(d), 125.2(s), 125.6(d), 127.0(d), 127.6(s), 128.5(d), 129.4(d), 130.1(s), 133.7(s), 135.3(d), 138.4(s), 140.2(s), 159.4(s),

166.6(s); Anal. Calcd for $C_{22}H_{16}N_2O_5$: C, 68.04; H, 4.15; N, 7.21. Found: C, 68.05; H, 4.20; N, 7.32.

8-Methyl-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11,12-tricarboxylic acid trimethyl ester (3k): mp 244-245 °C; IR ($CHCl_3$) 3030, 2955, 1780, 1755, 1700, 1450, 1360, 1330, 1290, 1230, 1180, 1150 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.49 (s, 3H, CH_3), 3.60 (s, 6H, OCH_3), 3.95 (s, 3H, OCH_3), 7.45-7.59 (m, 3H, ArH), 8.04 (d, J= 8.2 Hz, 1H, ArH), 8.17-8.27 (m, 1H, ArH), 8.28 (br s, 1H, ArH), 8.80-8.87 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.0(q), 51.5(q), 53.5(q), 57.2(s), 111.2(s), 116.9(d), 121.5(d), 124.9(s), 125.4(d), 125.9(d), 126.9(s), 127.7(d), 129.4(d), 130.3(s), 134.6(s), 135.3(d), 139.7(s), 139.9(s), 159.9(s), 164.8(s), 166.4(s); Anal. Calcd for $C_{23}H_{19}NO_7$: C, 65.56; H, 4.54; N, 3.32. Found: C, 65.51; H, 4.51; N, 3.43.

12-Acetyl-8-methyl-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11-dicarboxylic acid dimethyl ester (3l): mp 227 °C (decomp.); IR ($CHCl_3$) 3010, 2955, 1780, 1755, 1705, 1530, 1450, 1350, 1330, 1180 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.48 (s, 3H, CH_3), 2.77 (s, 3H, CH_3), 3.60 (s, 6H, OCH_3), 7.48-7.56 (m, 3H, ArH), 7.97-8.03 (m, 1H, ArH), 8.14 (d, J= 8.2 Hz, 1H, ArH), 8.27 (br s, 1H, ArH), 8.88-8.95 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.0(q), 31.3(q), 53.4(q), 57.6(s), 117.5(d), 118.7(s), 120.1(d), 124.9(s), 125.3(d), 125.5(d), 126.3(s), 127.9(d), 129.2(d), 130.1(s), 135.0(s), 135.4(d), 139.8(s), 140.1(s), 160.1(s), 166.0(s), 195.5(s); Anal. Calcd for $C_{23}H_{19}NO_6$: C, 68.14; H, 4.72; N, 3.45. Found: C, 68.11; H, 4.67; N, 3.48.

8-Chloro-12-cyano-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11-dicarboxylic acid dimethyl ester (3m): mp 224-225 °C; IR ($CHCl_3$) 3020, 2955, 2230, 1745, 1715, 1455, 1360, 1330, 1255, 1230 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.89 (s, 6H, OCH_3), 7.48-7.58 (m, 2H, ArH), 7.70-7.76 (m, 2H, ArH), 7.80 (dm, J= 7.4 Hz, 1H, ArH), 8.37-8.40 (m, 1H, ArH), 8.65 (dd, J= 7.4, 1.2 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 54.6(q), 59.2(s), 95.9(s), 113.0(s), 117.1(d), 119.5(d), 126.0(d), 127.0(s), 127.4(d), 127.6(s), 129.0(d), 130.3(d), 131.2(s), 133.7(s), 134.4(d), 136.5(s), 137.6(s), 158.1(s), 166.2(s); Anal. Calcd for $C_{21}H_{13}N_2O_5Cl$: C, 61.70; H, 3.21; N, 6.85. Found: C, 61.69; H, 3.24; N, 6.81.

8-Chloro-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11,12-tricarboxylic acid trimethyl ester (3n): mp 247 °C (decomp); IR ($CHCl_3$) 3030, 2955, 1780, 1755, 1705, 1365, 1330, 1280, 1230, 1180, 1150 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.62 (s, 6H, OCH_3), 3.96 (s, 3H, OCH_3), 7.46-7.55 (m, 2H, ArH), 7.68 (dd, J= 8.7, 2.4 Hz, 1H, ArH), 8.13 (d, J= 8.7 Hz, 1H, ArH), 8.20-8.24 (m, 1H, ArH), 8.44 (d, J= 2.4 Hz, 1H, ArH), 8.76-8.80 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 51.6(q), 53.8(q), 57.3(s), 111.9(s), 116.9(d), 121.7(d), 125.7(d), 126.2(d), 126.80(s), 126.83(s), 129.0(d), 129.6(d), 131.4(s), 134.4(d), 134.6(s), 136.3(s), 139.0(s), 158.6(s), 164.7(s), 166.0(s); Anal. Calcd for $C_{22}H_{16}NO_7Cl$: C, 59.81; H, 3.65; N, 3.17. Found: C, 59.92; H, 3.62; N, 3.07.

12-Acetyl-8-chloro-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11-dicarboxylic acid dimethyl ester (3o): mp 239 °C (decomp); IR ($CHCl_3$) 3010, 2955, 1780, 1760, 1710, 1455, 1370, 1350, 1330, 1230 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.78 (s, 3H, CH_3), 3.61 (s, 6H, OCH_3), 7.51-7.58 (m, 2H, ArH), 7.68 (dd, J= 8.6, 2.4 Hz, 1H, ArH), 7.97-8.03 (m, 1H, ArH), 8.22 (d, J= 8.6 Hz, 1H, ArH), 8.43 (d, J= 2.4 Hz, 1H, ArH), 8.85-8.92 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz)

δ 31.3(q), 53.6(q), 57.7(s), 117.5(d), 119.2(s), 120.3(d), 125.6(d), 125.8(d), 126.3(s), 126.7(s), 128.7(d), 129.8(d), 131.3(s), 134.4(d), 134.9(s), 136.2(s), 139.2(s), 158.8(s), 165.6(s), 195.6(s); Anal. Calcd for $C_{22}H_{16}NO_6Cl$: C, 62.05; H, 3.79; N, 3.29. Found: C, 61.96; H, 3.86; N, 3.35.

8-Bromo-12-cyano-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11-dicarboxylic acid dimethyl ester (3p): mp 235-236 °C; IR ($CHCl_3$) 3010, 2955, 2230, 1750, 1715, 1455, 1355, 1330, 1225 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.88 (s, 6H, OCH_3), 7.50-7.60 (m, 2H, ArH), 7.64 (d, J= 8.5 Hz, 1H, ArH), 7.80 (dm, J= 8.0 Hz, 1H, ArH), 7.88 (dd, J= 8.5, 2.2 Hz, 1H, ArH), 8.56 (d, J= 2.2 Hz, 1H, ArH), 8.67 (d, J= 7.8 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 54.6(q), 59.3(s), 95.9(s), 113.0(s), 117.1(d), 119.5(d), 124.5(s), 126.1(d), 127.2(s), 127.4(d), 127.6(s), 130.4(d), 131.8(s), 132.0(d), 133.7(s), 137.3(d), 137.6(s), 158.0(s), 166.2(s); Anal. Calcd for $C_{21}H_{13}N_2O_5Br$: C, 55.65; H, 2.89; N, 6.18. Found: C, 55.59; H, 2.92; N, 6.25.

8-Bromo-6-oxo-6,11-dihydroindolo[1,2-*b*]isoquinoline-11,11,12-tricarboxylic acid *trimethyl ester (3q)*: mp 248-249 °C; IR ($CHCl_3$) 3035, 2955, 1780, 1760, 1700, 1455, 1365, 1330, 1280, 1150 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.62 (s, 6H, OCH_3), 3.95 (s, 3H, OCH_3), 7.47-7.55 (m, 2H, ArH), 7.83 (dd, J= 8.6, 2.3 Hz, 1H, ArH), 8.06 (d, J= 8.6 Hz, 1H, ArH), 8.20-8.25 (m, 1H, ArH), 8.60 (d, J= 2.3 Hz, 1H, ArH), 8.77-8.81 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 51.6(q), 53.8(q), 57.3(s), 111.8(s), 116.9(d), 121.6(d), 124.2(s), 125.6(d), 126.1(d), 126.8(s), 126.9(s), 129.6(d), 131.86(s), 131.94(d), 134.5(s), 137.2(d), 138.9(s), 158.4(s), 164.7(s), 165.9(s); Anal. Calcd for $C_{22}H_{16}NO_7Br$: C, 54.34; H, 3.32; N, 2.88. Found: C, 54.43; H, 3.39; N, 2.72.

5-Methyl-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12a): mp 233-234 °C; IR ($CHCl_3$) 3010, 2955, 1765, 1645, 1475, 1235 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.67 (s, 6H, OCH_3), 3.84 (s, 3H, NCH_3), 7.34-7.50 (m, 3H, ArH), 7.52-7.70 (m, 2H, ArH), 7.76-7.88 (m, 1H, ArH), 8.40-8.50 (m, 1H, ArH), 8.50-8.62 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 31.5(q), 53.9(q), 58.6(s), 109.7(d), 112.9(s), 122.4(d), 123.1(d), 124.1(s), 124.4(d), 126.9(d), 127.6(d), 129.1(d), 131.8(d), 132.3(s), 134.3(s), 138.5(s), 142.0(s), 167.6(s), 179.5(s); Anal. Calcd for $C_{21}H_{17}NO_5$: C, 69.41; H, 4.72; N, 3.85. Found: C, 69.34; H, 4.73; N, 3.85.

5-Methanesulfonyl-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12b): mp 270 °C (decomp.); IR ($CHCl_3$) 3035, 2955, 1785, 1760, 1720, 1660, 1370, 1250, 1220, 1175 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.36 (s, 3H, SO_2CH_3), 3.75 (s, 6H, OCH_3), 7.51-7.59 (m, 2H, ArH), 7.61 (td, J= 7.7, 1.1 Hz, 1H, ArH), 7.67-7.74 (m, 1H, ArH), 7.94-8.00 (m, 1H, ArH), 8.41 (dd, J= 7.7, 1.6 Hz, 1H, ArH), 8.46 (dd, J= 7.7, 1.1 Hz, 1H, ArH), 8.63-8.70 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 40.6(q), 53.9(q), 58.4(s), 112.8(d), 117.3(s), 123.3(d), 125.2(d), 125.4(s), 126.76(d), 126.83(d), 128.7(d), 129.4(d), 131.1(s), 133.1(d), 133.5(s), 135.7(s), 144.1(s), 166.7(s), 180.6(s); Anal. Calcd for $C_{21}H_{17}NO_7S$: C, 59.01; H, 4.01; N, 3.28. Found: C, 59.08; H, 3.99; N, 3.28.

5,8-Dimethyl-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12c): mp 270 °C (decomp); IR ($CHCl_3$) 3010, 2955, 1765, 1640, 1610, 1470, 1450, 1210 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.47 (s, 3H, CH_3), 3.68 (s, 6H, OCH_3), 3.83 (s, 3H, NCH_3), 7.34-7.50 (m, 4H, ArH), 7.58 (s, 1H, ArH), 8.33 (d, J= 8.0 Hz, 1H, ArH), 8.50-8.60 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.8(q), 31.4(q), 53.9(q), 58.4(s), 109.7(d), 112.9(s), 122.5(d), 123.0(d),

124.2(s), 124.4(d), 126.9(d), 127.9(d), 130.0(s), 130.2(d), 134.3(s), 138.4(s), 142.0(s), 142.6(s), 167.7(s), 179.7(s); Anal. Calcd for $C_{22}H_{19}NO_5$: C, 70.02; H, 5.07; N, 3.71. Found: C, 70.04; H, 5.05; N, 3.75.

5-Methanesulfonyl-8-methyl-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12d): mp 267 °C (decomp); IR ($CHCl_3$) 3030, 2955, 1785, 1760, 1725, 1660, 1610, 1455, 1430, 1370, 1250, 1170 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.51 (s, 3H, CH_3), 3.34 (s, 3H, SO_2CH_3), 3.74 (s, 6H, OCH_3), 7.41 (dd, J= 8.4, 0.9 Hz, 1H, ArH), 7.46-7.60 (m, 2H, ArH), 7.89-8.00 (m, 1H, ArH), 8.23 (d, J= 0.9 Hz, 1H, ArH), 8.29 (d, J= 8.4 Hz, 1H, ArH), 8.59-8.71 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.1(q), 40.5(q), 53.8(q), 58.3(s), 112.8(d), 117.3(s), 123.3(d), 125.1(d), 125.4(s), 126.6(d), 126.8(d), 128.8(s), 128.9(d), 130.4(d), 133.6(s), 135.7(s), 144.0(s), 144.1(s), 166.7(s), 180.5(s); Anal. Calcd for $C_{22}H_{19}NO_7S$: C, 59.86; H, 4.34; N, 3.17. Found: C, 59.76; H, 4.42; N, 3.09.

8-Chloro-5-methyl-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12e): mp 261 °C (decomp); IR ($CHCl_3$) 3010, 2955, 1765, 1745, 1645, 1590, 1470, 1450, 1225 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.73 (s, 6H, OCH_3), 3.84 (s, 3H, NCH_3), 7.35-7.49 (m, 3H, ArH), 7.57 (dd, J= 8.5, 2.0 Hz, 1H, ArH), 7.79 (d, J= 2.0 Hz, 1H, ArH), 8.38 (d, J= 8.5 Hz, 1H, ArH), 8.47-8.58 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 31.7(q), 54.2(q), 58.6(s), 109.8(d), 112.8(s), 122.5(d), 123.3(d), 124.0(s), 124.7(d), 127.7(d), 128.4(d), 129.6(d), 131.0(s), 135.8(s), 138.2(s), 138.6(s), 141.7(s), 167.2(s), 178.4(s); Anal. Calcd for $C_{21}H_{16}NO_5Cl$: C, 63.40; H, 4.05; N, 3.52. Found: C, 63.39; H, 4.09; N, 3.43.

8-Chloro-5-methanesulfonyl-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12f): mp 282 °C (decomp); IR ($CHCl_3$) 3030, 2955, 1785, 1760, 1720, 1660, 1430, 1370, 1250, 1175 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.36 (s, 3H, SO_2CH_3), 3.78 (s, 6H, OCH_3), 7.45-7.63 (m, 3H, ArH), 7.88-8.02 (m, 1H, ArH), 8.34 (d, J= 8.5 Hz, 1H, ArH), 8.45 (d, J= 2.0 Hz, 1H, ArH), 8.58-8.71 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 40.6(q), 54.1(q), 58.4(s), 112.8(d), 117.1(s), 123.3(d), 125.2(s), 125.3(d), 126.9(d), 128.3(d), 128.8(d), 129.6(s), 130.0(d), 135.0(s), 135.7(s), 139.6(s), 143.7(s), 166.3(s), 179.5(s); Anal. Calcd for $C_{21}H_{16}NO_7ClS$: C, 54.61; H, 3.49; N, 3.03. Found: C, 54.54; H, 3.43; N, 3.02.

8-Bromo-5-methanesulfonyl-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12g): mp 282 °C (decomp); IR ($CHCl_3$) 3030, 2955, 1785, 1760, 1730, 1660, 1585, 1425, 1370, 1250, 1175 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.36 (s, 3H, SO_2CH_3), 3.78 (s, 6H, OCH_3), 7.47-7.62 (m, 2H, ArH), 7.75 (dd, J= 8.4, 1.8 Hz, 1H, ArH), 7.88-8.02 (m, 1H, ArH), 8.26 (d, J= 8.4 Hz, 1H, ArH), 8.61 (d, J= 1.8 Hz, 1H, ArH), 8.58-8.71 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 40.6(q), 54.1(q), 58.3(s), 112.8(d), 117.1(s), 123.3(d), 125.2(s), 125.3(d), 126.9(d), 128.2(s), 128.3(d), 130.0(s), 131.6(d), 133.0(d), 135.0(s), 135.7(s), 143.7(s), 166.3(s), 179.7(s); Anal. Calcd for $C_{21}H_{16}NO_7BrS$: C, 49.82; H, 3.18; N, 2.77. Found: C, 49.89; H, 3.21; N, 2.70.

5-Methanesulfonyl-8-methoxy-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12h): mp 294 °C (decomp); IR ($CHCl_3$) 3010, 2955, 1780, 1760, 1720, 1650, 1605, 1435, 1370, 1260, 1170 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.34 (s, 3H, SO_2CH_3), 3.75 (s,

6H, OCH_3), 3.94 (s, 3H, OCH_3), 7.11 (dd, J= 8.8, 2.5 Hz, 1H, ArH), 7.44-7.59 (m, 2H, ArH), 7.87-8.00 (m, 1H, ArH), 7.96 (d, J= 2.5 Hz, 1H, ArH), 8.35 (d, J= 8.8 Hz, 1H, ArH), 8.60-8.71 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 40.5(q), 53.8(q), 55.7(q), 58.4(s), 112.8(d), 113.6(d), 115.5(d), 117.2(s), 123.4(d), 124.5(s), 125.1(d), 125.5(s), 126.6(d), 128.9(d), 135.7(s), 143.6(s), 163.2(s), 166.7(s), 180.0(s); Anal. Calcd for $C_{22}H_{19}NO_8S$: C, 57.76; H, 4.19; N, 3.06. Found: C, 57.73; H, 4.17; N, 2.99.

5,9-Dimethyl-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12i): mp 255 °C (decomp); IR ($CHCl_3$) 3010, 2955, 1760, 1645, 1610, 1470, 1450, 1435, 1230 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.48 (s, 3H, CH_3), 3.68 (s, 6H, OCH_3), 3.83 (s, 3H, NCH_3), 7.37-7.47 (m, 4H, ArH), 7.68 (d, J= 8.1 Hz, 1H, ArH), 8.25 (br s, 1H, ArH), 8.52-8.58 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.1(q), 31.5(q), 53.8(q), 58.3(s), 109.7(d), 113.0(s), 122.5(d), 123.0(d), 124.1(s), 124.4(d), 127.1(d), 127.6(d), 131.5(s), 132.1(s), 132.7(d), 138.4(s), 139.2(s), 142.1(s), 167.7(s), 179.8(s); Anal. Calcd for $C_{22}H_{19}NO_5$: C, 70.02; H, 5.07; N, 3.71. Found: C, 70.03; H, 5.02; N, 3.75.

5-Methanesulfonyl-9-methyl-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12j): mp 270 °C (decomp); IR ($CHCl_3$) 3015, 2955, 1780, 1760, 1720, 1660, 1430, 1370, 1250, 1215, 1175 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.48 (s, 3H, CH_3), 3.35 (s, 3H, SO_2CH_3), 3.74 (s, 6H, OCH_3), 7.49 (dm, J= 8.3 Hz, 1H, ArH), 7.50-7.60 (m, 2H, ArH), 7.93-7.99 (m, 1H, ArH), 8.20 (br s, 1H, ArH), 8.32 (d, J= 8.3 Hz, 1H, ArH), 8.64-8.70 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.0(q), 40.5(q), 53.8(q), 58.2(s), 112.8(d), 117.4(s), 123.4(d), 125.1(d), 125.5(s), 126.7(d), 127.0(d), 128.6(d), 130.8(s), 130.9(s), 134.0(d), 135.7(s), 139.7(s), 144.2(s), 166.8(s), 180.8(s); Anal. Calcd for $C_{22}H_{19}NO_7S$: C, 59.86; H, 4.34; N, 3.17. Found: C, 59.80; H, 4.32; N, 3.17.

9-Chloro-5-methyl-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12k): mp 254-255 °C; IR ($CHCl_3$) 3010, 2955, 1765, 1650, 1530, 1475, 1450, 1435, 1210 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.70 (s, 6H, OCH_3), 3.85 (s, 3H, NCH_3), 7.36-7.47 (m, 3H, ArH), 7.56 (dd, J= 8.5, 2.4 Hz, 1H, ArH), 7.74 (d, J= 8.5 Hz, 1H, ArH), 8.40 (d, J= 2.4 Hz, 1H, ArH), 8.53 (dm, J= 7.7 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 31.7(q), 54.1(q), 58.5(s), 109.8(d), 112.8(s), 122.5(d), 123.3(d), 124.0(s), 124.7(d), 126.9(d), 129.3(d), 131.8(d), 132.5(s), 134.0(s), 135.9(s), 138.6(s), 142.0(s), 167.3(s), 178.1(s); Anal. Calcd for $C_{21}H_{16}NO_5Cl$: C, 63.40; H, 4.05; N, 3.52. Found: C, 63.40; H, 4.16; N, 3.28.

9-Chloro-5-methanesulfonyl-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12l): mp 290 °C (decomp); IR ($CHCl_3$) 3030, 2955, 1780, 1760, 1730, 1665, 1430, 1370, 1245, 1175 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.36 (s, 3H, SO_2CH_3), 3.75 (s, 6H, OCH_3), 7.51-7.59 (m, 2H, ArH), 7.64 (dd, J= 8.7, 2.4 Hz, 1H, ArH), 7.92-7.98 (m, 1H, ArH), 8.36 (d, J= 2.4 Hz, 1H, ArH), 8.42 (d, J= 8.7 Hz, 1H, ArH), 8.62-8.67 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 40.6(q), 54.0(q), 58.3(s), 112.9(d), 117.2(s), 123.4(d), 125.2(s), 125.3(d), 126.6(d), 127.0(d), 130.4(d), 131.7(s), 132.6(s), 132.9(d), 135.8(s), 136.4(s), 144.1(s), 166.4(s), 179.3(s); Anal. Calcd for $C_{21}H_{16}NO_7ClS$: C, 54.61; H, 3.49; N, 3.03. Found: C, 54.62; H, 3.51; N, 2.99.

9-Bromo-5-methyl-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12m): mp 261-262 °C; IR ($CHCl_3$) 3010, 2955, 1765, 1645, 1470, 1450, 1435, 1230 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.70 (s, 6H, OCH_3), 3.85 (s, 3H, NCH_3), 7.40-7.50 (m, 3H, ArH), 7.67 (d, J= 8.5 Hz, 1H, ArH), 7.72 (dd, J= 8.5, 2.2 Hz, 1H, ArH), 8.51-8.55 (m, 1H, ArH), 8.56 (d, J= 2.2 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 31.7(q), 54.1(q), 58.5(s), 109.8(d), 112.8(s), 122.5(d), 123.3(d), 123.98(s), 124.02(s), 124.7(d), 129.5(d), 129.9(d), 133.0(s), 134.1(s), 134.7(d), 138.6(s), 141.9(s), 167.2(s), 177.9(s); Anal. Calcd for $C_{21}H_{16}NO_5Br$: C, 57.03; H, 3.65; N, 3.17. Found: C, 57.02; H, 3.62; N, 3.14.

9-Bromo-5-methanesulfonyl-11-oxo-6,11-dihydrobenzo[*b*]carbazole-6,6-dicarboxylic acid dimethyl ester (12n): mp 295 °C (decomp); IR ($CHCl_3$) 3030, 2955, 1780, 1760, 1730, 1660, 1430, 1370, 1245, 1175 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.36 (s, 3H, SO_2CH_3), 3.75 (s, 6H, OCH_3), 7.51-7.59 (m, 2H, ArH), 7.79 (dd, J= 8.7, 2.3 Hz, 1H, ArH), 7.93-7.98 (m, 1H, ArH), 8.34 (d, J= 8.7 Hz, 1H, ArH), 8.52 (d, J= 2.3 Hz, 1H, ArH), 8.62-8.67 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 40.6(q), 54.0(q), 58.3(s), 112.9(d), 117.1(s), 123.4(d), 124.5(s), 125.2(s), 125.3(d), 127.0(d), 129.7(d), 130.6(d), 132.2(s), 132.7(s), 135.7(s), 135.9(d), 144.0(s), 166.4(s), 179.2(s); Anal. Calcd for $C_{21}H_{16}NO_7BrS$: C, 49.82; H, 3.18; N, 2.77. Found: C, 49.82; H, 3.13; N, 2.67.

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