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Free Radical Cyclization Reactions of Alkylsulfonyl and Alkylthio Substituted Aromatic Amide Derivatives

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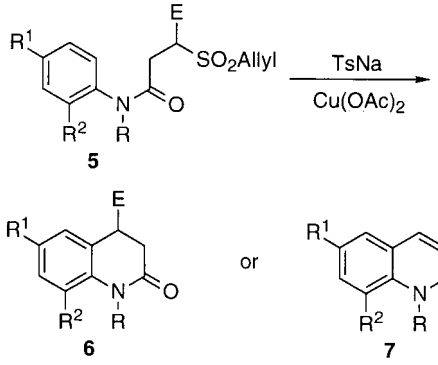
Abstract—Free radical cyclization reactions of alkylsulfonyl and alkylthio substituted aromatic amide derivatives are described. Carbon radicals can be generated efficiently from the sulfonyl radical induced reaction of allylsulfones or the oxidation of carbonyl compounds with manganese(III) acetate. These radicals undergo either 6-membered or 5-membered ring cyclization onto the aromatic ring effectively and provide synthetically useful methods for the syntheses of quinolinones, indolinones and indolinediones.

Introduction

Recently there has been a growing interest in the application of free radical reactions in organic synthesis.[1] Free radical reactions mediated by sulfonyl radicals have been noted by several groups.[2–4] The α-scission of most alkylsulfonyl radicals to generate alkyl radicals is an unfavorable process, but if the alkyl group represents a stabilized radical, the extrusion of sulfur dioxide occurs readily.[5] *p*-Toluenesulfonyl radical can be generated from sodium *p*-toluenesulfinate in aqueous formic acid.[4,6] The alkyl radicals generated from *p*-toluenesulfonyl radical induced reaction of allylsulfones (Scheme 1) can undergo free radical cyclization reaction.[4e] Electrophilic radicals produced from the manganese(III) acetate oxidation of carbonyl compounds undergo efficient addition to a C–C double bonds.[1d–1f,7,8] Compounds containing quinolinone, indolinone and indolinedione represent not only families of biologically active molecules but also precursors of exceeding important classes of compounds, i.e. indoles.[9] This report describes the results of free radical cyclization reactions of alkylsulfonyl and alkylthio substituted aromatic amide derivatives mediated by sodium *p*-toluenesulfinate/copper(II) acetate or manganese(III) acetate.

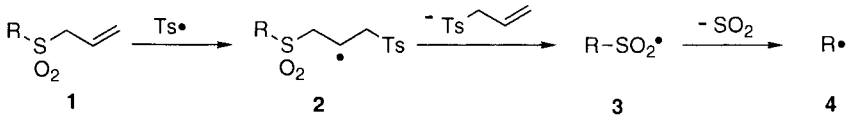
Results and Discussion

We began our studies by examining the reaction behavior of **5a** (Eq. (1)).



(1)

Thus, treatment of **5a** with sodium *p*-toluenesulfinate and copper(II) acetate in 60% aqueous formic acid at 80°C gave **6a** in 53% yield. This free radical addition–cyclization reaction most likely proceeded via the mechanism shown in Scheme 2. Radical **8** generated from **5a** via a similar reaction route shown in Scheme 1 undergoes 6-membered



Scheme 1.

Keywords: free radical cyclization; sulfonyl radical; manganese(III) acetate; aromatic amide derivatives.
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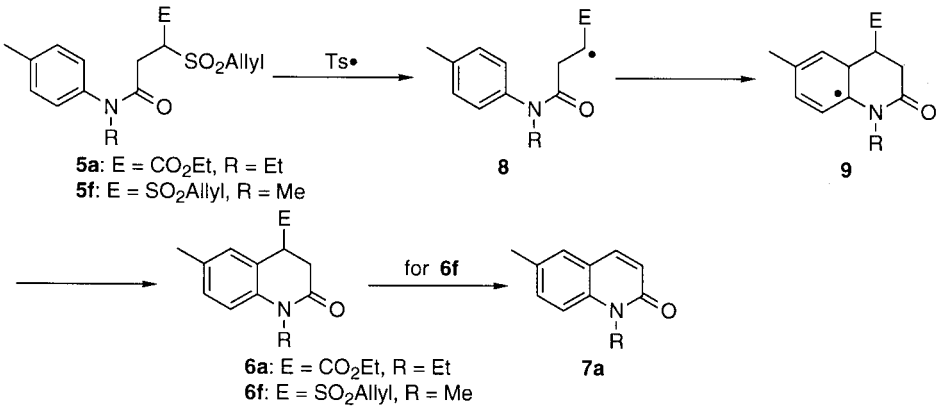
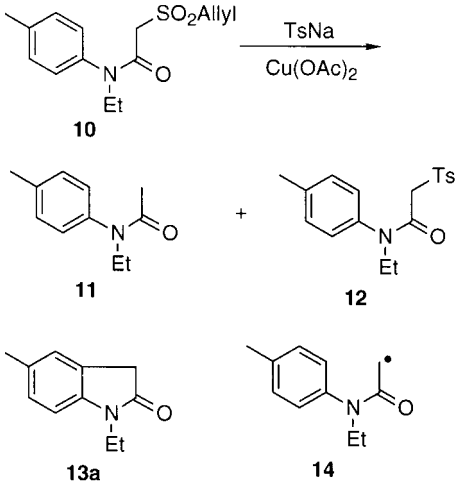


Scheme 2.

Table 1. Sulfonyl radical mediated free radical reactions of β-allylsulfonyl substituted anilides **5**

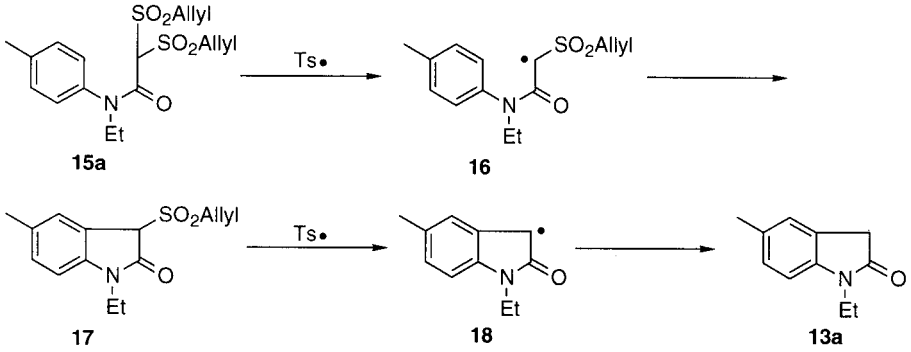
Entry		Substrate				Product (Yield)
		E	R	R^1	R^2	
a	**5a**	CO_2Et	Et	Me	H	**6a** (53%)
b	**5b**	CO_2Et	Et	OMe	H	**6b** (56%)
c	**5c**	CO_2Et	Et	Br	H	**6c** (47%)
d	**5d**	CO_2Et	Et	Cl	H	**6d** (44%)
e	**5e**	CO_2Et	Et	CO_2Et	H	**6e** (49%)
f	**5f**	$AllylSO_2$	Me	Me	H	**7a** (67%)
g	**5g**	$AllylSO_2$	Me	H	H	**7b** (61%)
h	**5h**	$AllylSO_2$	Me	H	Me	**7c** (63%)
I	**5i**	$AllylSO_2$	Me	Cl	H	**7d** (57%)
j	**5j**	$AllylSO_2$	Me	CO_2Me	H	**7e** (55%)
k	**5k**	Ms	Me	Me	H	**7a** (73%)
l	**5l**	Ms	Me	Cl	H	**7d** (64%)

ring cyclization and subsequent oxidation of radical intermediate **9** to give quinolinone **6a**. The scope of this reaction is illustrated in Table 1 (entries a–e). Quinolinone derivatives can be formed effectively by this sulfonyl radical induced reaction in moderate yields. No product derived from *ipso* cyclization can be detected. Similar preference for the 6-membered ring cyclization of aromatic ring has been reported previously.[4d,4e,7,10] With diallylsulfonyl substituted anilide **5f**, quinolinone **7a** was obtained in 67% yield (Table 1, entry f). We believe that this product is produced from the β-elimination of cyclization product **6f**. Other examples are also shown in Table 1 (entries g–l). We also studied the possibilities of 5-membered ring cyclization with **10**. When **10** was treated with sodium *p*-toluenesulfinate and copper(II) acetate, **11** and **12** were obtained in 49 and 26% yields, respectively (Eq. (2)).



(2)

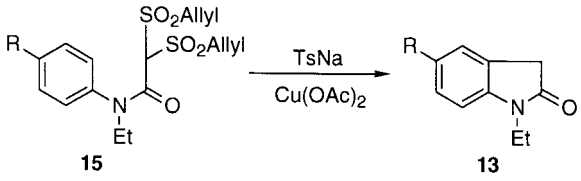
These two products are derived from the hydrogen atom abstraction and coupling reaction with *p*-toluenesulfonyl radical of radical intermediate **14**. No cyclization product **13a** was observed. This result shows that the 6-membered ring cyclization of aromatic ring is easier than that of 5-membered ring process. Similar results have been reported by Citterio.[8a] Since radical **16** is more stable than **14**, we expect that radical **16** can undergo 5-membered ring cyclization effectively. Indeed, when **15a** was treated with sodium *p*-toluenesulfinate and copper(II) acetate, indolinone **13a** was obtained in 49% yield (Eq. (3)).



Scheme 3.

Table 2. Sulfonyl radical mediated free radical reactions of α,α-diallyl-sulfonyl substituted anilides **15**

Entry		Substrate R		Product (Yield)
a	**15a**	Me	–	**13a** (49%)
b	**15a**	Me	Et_3SiH	**13a** (79%)
c	**15a**	Me	Ph_3SiH	**13a** (73%)
d	**15a**	Me	Ph_3CH	**13a** (73%)
e	**15e**	OMe	Et_3SiH	**13b** (69%)
f	**15b**	H	Et_3SiH	**13c** (56%)
g	**15c**	Cl	Et_3SiH	**13d** (47%)
h	**15d**	Br	Et_3SiH	**13e** (52%)
i	**15f**	CO_2Et	Et_3SiH	**13f** (23%)



15 13 (3)

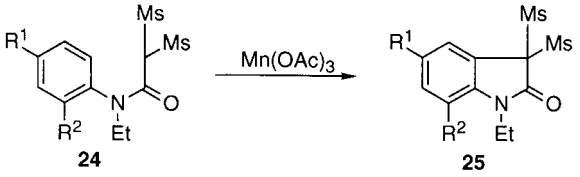
A proposed mechanism for the formation of **13a** is outlined in Scheme 3. Radical **16** generated from **15a** via a similar reaction route shown in Scheme 1 cyclizes onto the aromatic ring to give **17** after oxidation of radical intermediate. Indolinone **17** undergoes further *p*-toluenesulfonyl radical induced reaction to generate radical **18**, which is converted to **13a** by hydrogen atom abstraction from the reaction mixture. To improve the reaction yield, a variety of reagents was added as hydrogen atom source. The results are summarized in Table 2 and triethylsilane gives best yields. Other examples with triethylsilane as hydrogen atom source are also shown in Table 2 (entries e–i). With electron withdrawing groups on benzene ring, it gave lower reaction yield (Table 2, entries g–i). This suggests that the cyclization of electrophilic radical **16** onto the benzene ring with an electron withdrawing group is less favorable.

The manganese(III) acetate initiated oxidative free radical cyclization has been studied by several groups.[7,8] We continue the free radical reaction of alkylsulfonylanilides **19**. The reaction of **19a** with manganese(III) acetate in acetic acid gave **20a** in 88% (Scheme 4). This free radical reaction presumably occurs via the cyclization of radical **21**,

Table 3. Oxidative free radical reactions of β-sulfonyl groups substituted anilides **19**

Entry		Substrate			Product (Yield)
		R	E	R^1	
a	**19a**	4-Cl(C_6H_4)	Ts	Me	**20a** (88%)
b	**19b**	2,4-Cl_2(C_6H_3)	Ts	Me	**20b** (85%)
c	**19c**	C_6H_5	Ms	Br	**20c** (65%)
d	**19d**	Me	Ts	Me	**20d** (62%)
e	**19e**	OEt	Ms	Me	**20e** (53%)
f	**19f**	OEt	Ms	H	**20f** (51%)
g	**19g**	OEt	Ms	Br	**20g** (44%)
h	**19h**	OEt	Ms	CO_2Et	**20h** (42%)
i	**19i**	OEt	Ms	Cl	**20i** (41%)

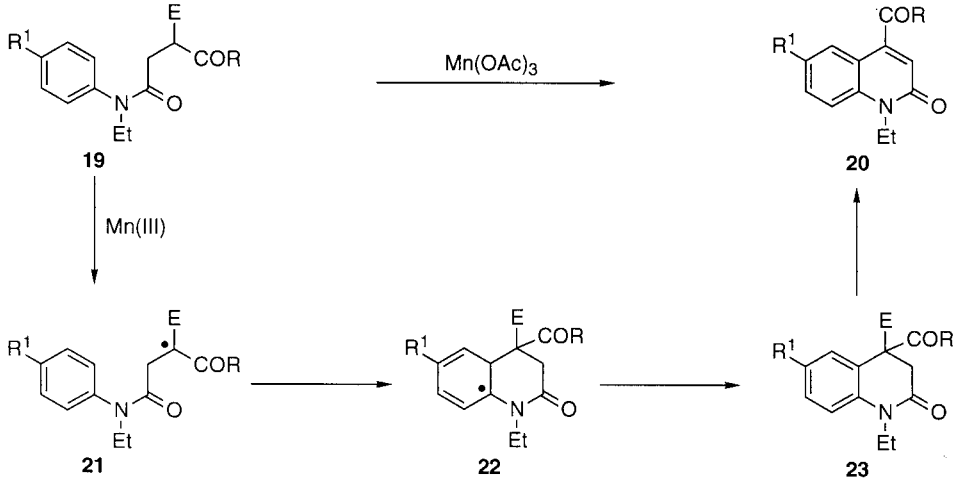
produced from the manganese(III) acetate oxidation of **19a**, followed by oxidation to give **23**. Quinolinone **23** undergoes further β-elimination of *p*-toluenesulfinic acid to produce **20a**. The results of this reaction are summarized in Table 3. It gives lower reaction yield with electron withdrawing group on benzene ring (entries a vs c and e vs h). With R=OEt, this reaction proceeded much slower (40 h) and 4 equiv. of manganese(III) acetate was used. We also studied the possibilities of 5-membered ring cyclization with **24a**. When **24a** was treated with manganese(III) acetate, indolinone **25a** was obtained in 95% yield (Eq. (4)).



24 25 (4)

Indolinone **25a** was formed via a similar reaction shown in Scheme 4. The scope of this reaction is shown in Table 4 and indolinone **25** is synthesized in high yield.

The manganese(III) acetate mediated radical cyclization of α-alkylthioacetamides has been reported recently.[11] We continue this 5-membered ring cyclization with alkylthio-anilide **26a** (Eq. (5)).



Scheme 4.

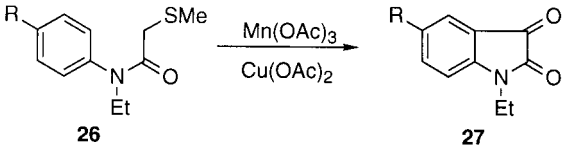
Table 4. Oxidative free radical reactions of α,α-dimethylsulfonyl substituted anilides **24**

Entry		Substrate		Product (Yield)
		R^1	R^2	
a	**24a**	H	H	**25a** (95%)
b	**24b**	Me	H	**25b** (96%)
c	**24c**	Cl	H	**25c** (85%)
d	**24d**	Br	H	**25d** (86%)
e	**24e**	CO_2Et	H	**25e** (85%)
f	**24f**	H	Me	**25f** (94%)
g	**24g**	H	OMe	**25g** (95%)

Table 5. Oxidative free radical reactions of α-methylthio substituted anilides **26**

	Entry	Substrate R	Reaction Time (h)	Product (Yield)
a	**26a**	Me	6	**27a** (89%)
b	**26b**	H	6	**27b** (76%)
c	**26c**	OMe	6	**27c** (67%)
d	**26d**	Br	24	**27d** (36%)[a]
e	**26e**	Cl	24	**27e** (35%)[a]
f	**26f**	CO_2Et	24	**27f** (32%)[a]

[a] Another 3 equiv. of $Mn(OAc)_3$ and 1 equiv. of $Cu(OAc)_2$ was added after heating for 9 h.



26 **27** (5)

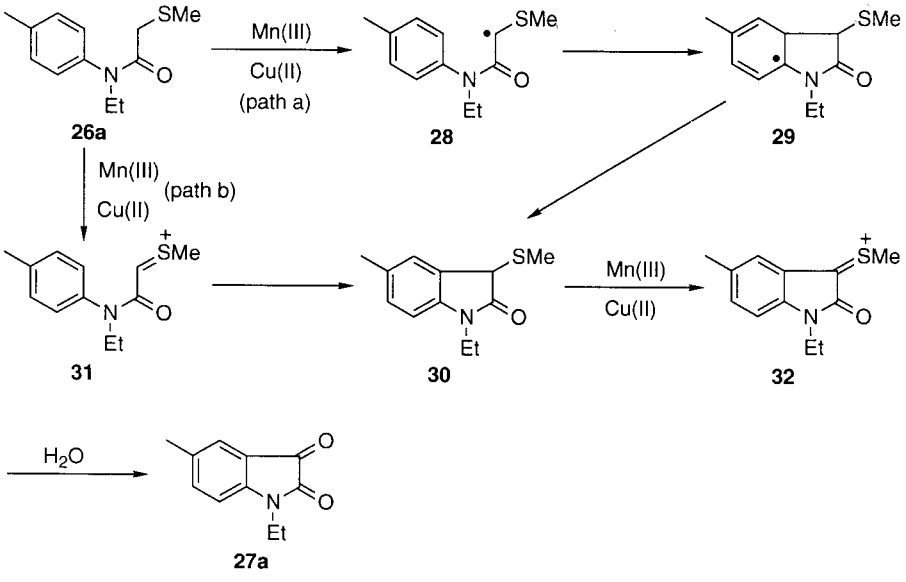
The reaction of **26a** with manganese(III) acetate and copper(II) acetate in acetic acid at 80°C was very sluggish. After heating for 5 days, indolinedione **27a** was isolated in 73% yield. When this reaction was performed in 60% aqueous acetic acid, the starting material was consumed in 54 h to give **27a** in 66% yield. It gave more satisfactory result in 60% aqueous formic acid: **26a** was consumed in 6 h to produce **27a** in 89% yield. The generalities of this reaction are shown in Table 5. Indolinedione **27a** was generated presumably via the reaction route outlined in Scheme 5. The oxidation of manganese(III) acetate of **26a** produced **28**. Radical **28** cyclizes onto the aromatic ring, followed by oxidation of radical intermediate to give **30** (path a). Indolinone 30 undergoes further oxidation and the addition of water to give **27a**. It has been shown that the thionium ion produced via the Pummerer-type reaction undergoes the carbon–carbon bond forming reactions such as the Friedel–Crafts reaction[12] and olefin cyclization.[13] An alternative possibility for the formation of **30** via the electrophilic aromatic substitution reaction of **31** produced by the oxidation of **26a** (path b) cannot be ruled out.

Conclusion

Carbon radicals can be generated efficiently from the *p*-toluenesulfonyl radical induced reaction of allylsulfones or the manganese(III) acetate oxidation of carbonyl compounds. These radicals undergo either 6-membered or 5-membered ring cyclization onto the aromatic ring effectively and provide synthetically useful methods for the syntheses of quinolinones, indolinones and indolinediones. The 6-membered ring cyclization onto the aromatic ring is easier than that of the 5-membered ring process.

Experimental

Melting points were taken with a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were taken with Hitachi 260-30 spectrometer. Nuclear magnetic resonance spectra were recorded on Bruker ADVANCE 300 or Bruker AMX-400 spectrometer. Elemental analyses were performed with a Heraeus CHN-Rapid Analyzer. Mass spectra were recorded with Jeol JMS-SX/SX 102A mass spectrometer. All reactions were carried out under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed by precoated silica gel 60 F-254 plates (0.25 mm thick) of EM Laboratories. The reaction mixture was purified by column chromatography over



26a **28** **29** **31** **30** **32** **27a**

Scheme 5.

EM Laboratories silica gel (230–400 mesh). The spectral data for **13c** and **27b** have been reported.[14]

Typical experimental procedure for the sulfonyl radical mediated reaction of anilide 5

A solution of 148 mg (0.40 mmol) of **5a**, 718 g (4.03 mmol) of sodium *p*-toluenesulfinate and 161 mg (0.81 mmol) of copper(II) acetate in 10 ml of 60% aqueous formic acid was heated at 80°C for 4 h, followed by the addition of 719 mg (4.03 mmol) of sodium *p*-toluenesulfinate and 168 mg (0.84 mmol) copper(II) acetate. The reaction mixture was heated for another 4 h and then diluted with 50 ml of ethyl acetate, washed with three 50 ml portions of aqueous saturated sodium bicarbonate, 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 ethyl acetate–hexane, 1:4) to give 56 mg (53%) of **6a** as a single product.

4-Ethoxycarbonyl-1-ethyl-6-methyl-3,4-dihydro-2(1*H*)-quinolinone 6a. White needles; mp 72–73°C; IR ($CHCl_3$) 2920, 1730, 1665, 1615, 1590, 1505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.15–1.30 (m, 6H, CH_3), 2.31 (s, 3H, CH_3), 2.76 (dd, J=16.0, 6.2 Hz, 1H, CH), 2.96 (dd, J=16.0, 4.4 Hz, 1H, CH), 3.77 (dd, J=6.2, 4.4 Hz, 1H, CH), 3.88–4.07 (m, 2H, NCH_2), 4.07–4.21 (m, 2H, OCH_2), 6.93 (d, J=8.3 Hz, 1H, ArH), 7.07 (s, 1H, ArH), 7.10 (d, J=8.3 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.5(q), 14.0(q), 20.5(q), 34.0(t), 37.0(t), 42.4(d), 61.3(t), 115.0(d), 122.9(s), 129.2(d), 129.3(d), 132.4(s), 136.7(s), 167.4(s), 171.6(s); Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.70; H, 7.29; N, 5.33.

4-Ethoxycarbonyl-1-ethyl-6-methoxy-3,4-dihydro-2(1*H*)-quinolinone 6b. White needles; mp 65–66°C; IR ($CHCl_3$) 2990, 1730, 1670, 1505, 1385 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18–1.26 (m, 6H, CH_3), 2.76 (dd, J=16.0, 6.2 Hz, 1H, CH), 2.97 (dd, J=16.0, 4.3 Hz, 1H, CH), 3.74–3.84 (m, 1H, CH), 3.80 (s, 3H, CH_3), 3.85–4.07 (m, 2H, NCH_2), 4.15 (q, J=6.9 Hz, 2H, OCH_2), 6.83 (s, 1H, ArH), 6.84 (d, J=8.8 Hz, 1H, ArH), 6.97 (d, J=8.8 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.5(q), 14.0(q), 33.9(t), 37.2(t), 42.6(d), 55.6(q), 61.4(t), 113.6(d), 114.6(d), 116.1(d), 124.4(s), 132.6(s), 155.2(s), 167.1(s), 171.4(s); Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.91; N, 5.05. Found: C, 64.95; H, 6.90; N, 5.04.

6-Bromo-4-ethoxycarbonyl-1-ethyl-3,4-dihydro-2(1*H*)-quinolinone 6c. White crystals; mp 53–54°C; IR ($CHCl_3$) 2985, 2925, 1735, 1675, 1595, 1490 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.12–1.37 (m, 6H, CH_3), 2.76 (dd, J=16.1, 6.3 Hz, 1H, CH), 2.99 (dd, J=16.1, 4.1 Hz, 1H, CH), 3.78 (dd, J=6.3, 4.1 Hz, 1H, CH), 3.87–4.05 (m, 2H, NCH_2), 4.09–4.22 (m, 2H, OCH_2), 6.91 (d, J=8.6 Hz, 1H, ArH), 7.40 (d, J=2.3 Hz, 1H, ArH), 7.42 (dd, J=8.6, 2.3 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4(q), 14.0(q), 33.6(t), 37.2(t), 42.0(d), 61.6(t), 115.3(s), 116.7(d), 125.0(s), 131.59(d), 131.62(d), 138.4(s), 167.1(s), 170.9(s); Anal. Calcd for $C_{14}H_{16}BrNO_3$: C, 51.55; H, 4.94; N, 4.29. Found: C, 51.45; H, 4.97; N, 4.28.

6-Chloro-4-ethoxycarbonyl-1-ethyl-3,4-dihydro-2(1*H*)-quinolinone 6d. Pale yellow liquid; IR ($CHCl_3$) 2990, 2940, 1730, 1670, 1600, 1495 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.16–1.28 (m, 6H, CH_3), 2.77 (dd, J=16.1, 6.3 Hz, 1H, CH), 2.99 (dd, J=16.1, 4.2 Hz, 1H, CH), 3.79 (dd, J=6.3, 4.2 Hz, 1H, CH), 3.87–4.07 (m, 2H, NCH_2), 4.07–4.25 (m, 2H, OCH_2) 6.97 (d, J=8.5 Hz, 1H, ArH), 7.26 (s, 1H, ArH), 7.27–7.31 (m, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4(q), 14.0(q), 33.6(t), 37.2(t), 42.1(d), 61.6(t), 116.3(d), 124.7(s), 127.9(s), 128.66(d), 128.74(d), 137.8(s), 167.1(s), 170.9(s); mass spectrum, *m/e* (relative intensity) 281(M^+, 100), 253(2), 209(23), 180(69), 164(30), 117(17), 101(14); exact mass calcd for $C_{14}H_{16}ClNO_3$: *m/e* 281.0819, found *m/e* 281.0817.

4,6-Bis(ethoxycarbonyl)-1-ethyl-3,4-dihydro-2(1*H*)-quinolinone 6e. White powder; mp 90–91°C; IR ($CHCl_3$) 2990, 1730, 1715, 1680, 1615, 1375 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.20–1.28 (m, 6H, CH_3), 1.40 (t, J=7.1 Hz, 3H, CH_3), 2.80 (dd, J=16.1, 6.3 Hz, 1H, CH), 3.04 (dd, J=16.1, 3.9 Hz, 1H, CH), 3.89 (dd, J=6.3, 3.9 Hz, 1H, CH), 3.97–4.09 (m, 2H, NCH_2), 4.11–4.21 (m, 2H, OCH_2), 4.33–4.43 (m, 2H, OCH_2), 7.08 (d, J=8.6 Hz, 1H, ArH), 7.96 (d, J=1.9 Hz, 1H, ArH), 8.00 (dd, J=8.6, 1.9 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4(q), 14.0(q),14.3(q), 33.6(t), 37.3(t), 42.1(d), 60.9(t), 61.5(t), 114.7(d), 122.7(s), 124.7(s), 130.2(d), 130.5(d), 142.9(s), 165.7(s), 167.5(s), 171.1(s); Anal. Calcd for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.39. Found: C, 63.89; H, 6.65; N, 4.39.

1,6-Dimethyl-2(1*H*)-quinolinone 7a. White powder; mp 83–84°C; IR ($CHCl_3$) 3005, 2925, 1650, 1590, 1570, 1465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H, CH_3), 3.70 (s, 3H, NCH_3), 6.68 (d, J=9.5 Hz, 1H, CH), 7.25 (d, J=8.6 Hz, 1H, ArH), 7.31–7.45 (m, 2H, ArH), 7.60 (d, J=9.5 Hz, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.4(q), 29.3(q),114.0(d), 120.6(s), 121.6(d), 128.5(d), 131.6(s), 131.8(d), 138.0(s), 138.7(d), 162.2(s); Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.20; H, 6.39; N, 8.10.

1-Methyl-2(1*H*)-quinolinone 7b. White crystals; mp 74–75°C; IR ($CHCl_3$) 3005, 2925, 1650, 1595, 1455 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H, NCH_3), 6.74 (d, J=9.5 Hz, 1H, CH), 7.25 (t, J=8.2 Hz, 1H, ArH), 7.38 (d, J=8.2 Hz, 1H, ArH), 7.52–7.63 (m, 2H, ArH), 7.69 (d, J=9.5 Hz, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.4(q), 114.1(d), 120.7(s), 121.6(d), 122.2(d), 128.7(d), 130.7(d), 139.0(d), 140.0(s), 162.4(s); Anal. Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.45; H, 5.72; N, 8.84.

1,8-Dimethyl-2(1*H*)-quinolinone 7c. White crystals; mp 85–86°C; IR ($CHCl_3$) 3005, 2930, 1650, 1615, 1585, 1450, 1405 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.73 (s, 3H, CH_3), 3.84 (s, 3H, NCH_3), 6.67 (d, J=9.4 Hz, 1H, CH), 7.12 (t, J=7.7 Hz, 1H, ArH), 7.34 (d, J=7.7 Hz, 1H, ArH), 7.36 (d, J=7.7 Hz, 1H, ArH),7.62 (d, J=9.4 Hz, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.0(q), 36.6(q), 121.1(d), 122.4(d), 122.5(s), 125.0(s), 127.3(d), 135.1(d), 139.9(d), 141.2(s), 164.6(s); Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.28; H, 6.38; N, 8.03.

6-Chloro-1-methyl-2(1*H*)-quinolinone 7d. White needles; mp 149–150°C; IR ($CHCl_3$) 3005, 1655, 1625, 1585, 1565, 1495 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 3H, NCH_3), 6.74 (d, J=9.5 Hz, 1H, CH), 7.30 (d, J=8.8 Hz, 1H, ArH), 7.47–7.56 (m, 2H, ArH), 7.59 (d, J=9.5 Hz, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.5(q), 115.5(d), 121.6(s), 123.0(d), 127.5(s), 127.8(d), 130.5(d), 137.7(d), 138.5(s), 161.9(s); Anal. Calcd for $C_{10}H_8ClNO$: C, 62.03; H, 4.16; N, 7.23. Found: C, 61.97; H, 4.23; N, 7.20.

6-Methoxycarbonyl-1-methyl-2(1*H*)-quinolinone 7e. White crystals; mp 200–201°C; IR ($CHCl_3$) 3005, 2950, 1720, 1660, 1590, 1500 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 3H, NCH_3), 3.96 (s, 3H, OCH_3), 6.75 (d, J=9.5 Hz, 1H, CH), 7.39 (d, J=8.9 Hz, 1H, ArH), 7.72 (d, J=9.5 Hz, 1H, CH), 8.20 (d, J=8.9 Hz, 1H, ArH), 8.26 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.6(q), 52.2(q), 114.1(d), 120.1(s), 122.5(d), 123.9(s), 130.7(d), 131.3(d), 139.0(d), 143.0(s), 162.2(s), 166.1(s); Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.35; H, 5.14; N, 6.52.

Typical experimental procedure for the sulfonyl radical mediated reaction of anilide 15

A solution of 103 mg (0.27 mmol) of **15a**, 463 g (2.60 mmol) of sodium *p*-toluenesulfinate, 105 mg (0.53 mmol) of copper(II) acetate and 68 mg (0.58 mmol) of triethylsilane in 10 ml of 60% aqueous formic acid was heated at 80°C for 4 h, followed by the addition of 464 mg (2.61 mmol) of sodium *p*-toluenesulfinate and 106 mg (0.53 mmol) copper(II) acetate. The reaction mixture was heated for another 3 h and then diluted with 50 ml of ethyl acetate, washed with three 50 ml portions of aqueous saturated sodium bicarbonate, 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 ethyl acetate–hexane, 7:1 then dichloromethane–hexane, 2.5:1) to give 37 mg (79%) of **13a** as a single product.

1-Ethyl-5-methyl-2-indolinone 13a. White crystals; mp 98–99°C; IR ($CHCl_3$) 2990, 2930, 1690, 1625, 1495 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, J=7.2 Hz, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.46 (s, 2H, CH_2), 3.74 (q, J=7.2 Hz, 2H, NCH_2), 6.73 (d, J=8.4 Hz, 1H, ArH), 7.06 (d, J=8.4 Hz, 1H, ArH), 7.07 (s, 1H, ArH); ^{13}C NMR (100.6MHz, $CDCl_3$) δ 12.6(q), 21.0(q), 34.6(t), 35.9(t), 107.9(d), 124.8(s), 125.4(d), 127.9(d), 131.6(s), 141.9(s), 174.6(s); Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.43; H, 7.32; N, 7.65.

1-Ethyl-5-methoxy-2-indolinone 13b. White crystals; mp 75–76°C; IR ($CHCl_3$) 3000, 2935, 1695, 1600, 1495, 1435 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, J=7.2 Hz, 3H, CH_3), 3.49 (s, 2H, CH_2), 3.74 (q, J=7.2 Hz, 2H, NCH_2), 3.79 (s, 3H, OCH_3), 6.74 (d, J=8.5 Hz, 1H, ArH), 6.80 (dd, J=8.5, 2.5 Hz, 1H, ArH), 6.88–6.90 (m, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.6(q), 34.7(t), 36.2(t), 55.8(q), 108.4(d), 112.0(d), 112.1(d), 126.1(s), 137.8(s), 155.6(s), 174.3(s); Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.11; H, 6.92; N, 7.34.

5-Chloro-1-ethyl-2-indolinone 13d. White needles; mp 120–121°C; IR ($CHCl_3$) 2985, 2925, 1615, 1490, 1435 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, J=7.2 Hz, 3H, CH_3), 3.51 (s, 2H, CH_2), 3.75 (q, J=7.2 Hz, 2H, NCH_2), 6.76 (d, J=8.5 Hz, 1H, ArH), 7.25 (d, J=8.5 Hz, 1H, ArH), 7.27 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.5(q), 34.8(t), 35.7(t), 108.9(d), 124.9(d), 126.3(s), 127.4(s), 127.7(d), 142.8(s), 174.0(s); Anal. Calcd for $C_{10}H_{10}ClNO$: C, 61.39; H, 5.15; N, 7.16. Found: C, 61.39; H, 5.25; N, 7.15.

5-Bromo-1-ethyl-2-indolinone 13e. White crystals; mp 107–108°C; IR ($CHCl_3$) 2985, 2930, 1705, 1610, 1485 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, J=7.2 Hz, 3H, CH_3), 3.51 (s, 2H, CH_2), 3.75 (q, J=7.2 Hz, 2H, NCH_2), 6.71 (d, J=7.9 Hz, 1H, ArH), 7.37 (s, 1H, ArH), 7.40 (d, J=7.9 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.5(q), 34.8(t), 35.6(t), 109.5(d), 114.7(s), 126.7(s), 127.7(d), 130.6(d), 143.3(s), 173.9(s); Anal. Calcd for $C_{10}H_{10}BrNO$: C, 50.03; H, 4.20; N, 5.83. Found: C, 50.02; H, 4.38; N, 5.78.

5-Ethoxycarbonyl-1-ethyl-2-indolinone 13f. Colorless liquid; IR ($CHCl_3$) 2990, 2940, 1705, 1620, 1380 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, J=7.3 Hz, 3H, CH_3), 1.39 (t, J=7.2 Hz, 3H, CH_3), 3.56 (s, 2H, CH_2), 3.80 (q, J=7.3 Hz, 2H, NCH_2), 4.37 (q, J=7.2 Hz, 2H, OCH_2), 6.87 (d, J=7.9 Hz, 1H, ArH), 7.93 (s, 1H, ArH), 8.03 (d, J=7.9 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.7(q), 14.4(q), 34.9(t), 35.5(t), 60.9(t), 107.6(d), 124.5(s), 125.7(d), 130.6(d), 148.3(s), 166.4(s), 174.9(s); Mass spectrum, *m/e* (relative intensity) 233(M^+, 100), 218(16), 190(27), 188(78), 160(19), 144(10), 118(33); exact mass calcd for $C_{13}H_{15}NO_3$: *m/e* 233.1052, found *m/e* 233.1043.

Typical experimental procedure for the manganese(III) acetate mediated reaction of anilide 19

A solution of 150 mg (0.31 mmol) of **19a**, 167 mg (0.62 mmol) of manganese(III) acetate in 5 ml of acetic acid was heated at 80°C for 6 h. The reaction mixture was diluted with 50 ml of ethyl acetate, washed with 50 ml of aqueous saturated sodium bisulfite, three 50-ml portions of aqueous saturated sodium bicarbonate, 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 ethyl acetate–hexane, 1:4) to give 89 mg (88%) of **20a** as a single product.

4-(4-Chlorobenzoyl)-1-ethyl-6-methyl-2(1*H*)-quinolinone 20a. Yellow needles; mp 117–118°C; IR ($CHCl_3$) 3005, 2925, 1650, 1585, 1565, 1490 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, J=7.1 Hz, 3H, CH_3), 2.33 (s, 3H, CH_3), 4.41 (q, J=7.1 Hz, 2H, CH_2), 6.66 (s, 1H, CH), 7.30 (d, J=1.7 Hz, 1H, ArH), 7.38 (d, J=8.8 Hz, 1H, ArH), 7.44 (dd, J=8.8, 1.7 Hz, 1H, ArH), 7.47 (d, J=8.6 Hz, 2H, ArH), 7.91 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.7(q), 20.6(q), 37.6(t), 114.5(d), 118.0(s), 120.4(d), 126.6(d), 129.2(d), 131.5(d), 132.1(s), 132.8(d), 134.1(s), 137.4(s), 141.2(s), 146.4(s), 160.4(s), 193.7(s); Anal. Calcd for $C_{19}H_{16}ClNO_2$: C, 70.05; H, 4.95; N, 4.30. Found: C, 69.96; H, 4.92; N, 4.31.

4-(2,4-Dichlorobenzoyl)-1-ethyl-6-methyl-2(1*H*)-quinolinone 20b. Yellow crystals; mp 149–150°C; IR ($CHCl_3$) 3000, 2930, 1645, 1580, 1465, 1375 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.38 (t, J=7.1 Hz, 3H, CH_3), 2.42 (s, 3H, CH_3), 4.38 (q, J=7.1 Hz, 2H, NCH_2), 6.61 (s, 1H, CH), 7.37 (d, J=8.7 Hz, 1H, ArH), 7.38 (dd, J=8.2, 2.1 Hz, 1H, ArH), 7.43–7.52 (m, 2H, ArH), 7.57 (d, J=8.2 Hz, 1H, ArH), 7.83 (d, J=2.1 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.7(q), 20.8(q), 37.7(t), 114.5(d), 117.5(s), 122.9(d), 126.9(d), 127.5(d), 130.7(d), 132.0(d), 132.4(s), 132.7(d), 133.9(s), 135.5(s), 137.6(s), 138.9(s), 145.5(s), 160.6(s), 194.1(s); Anal. Calcd for $C_{19}H_{15}Cl_2NO_2$: C, 63.35; H, 4.20; N, 3.89. Found: C, 63.37; H, 4.21; N, 3.93.

4-Benzoyl-6-bromo-1-ethyl-2(1*H*)-quinolinone 20c. Yellow needles; mp 119–120°C; IR ($CHCl_3$) 3005, 2930, 1660, 1585, 1550, 1450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, J=7.1 Hz, 3H, CH_3), 4.40 (q, J=7.1 Hz, 2H, NCH_2), 6.73 (s, 1H, CH), 7.35 (d, J=9.1 Hz, 1H, ArH), 7.52 (t, J=7.8 Hz, 2H, ArH), 7.63–7.79 (m, 3H, ArH), 7.90–8.01(m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.6(q), 37.8(t), 115.5(s), 116.2(d), 119.8(s), 121.9(d), 128.9(d), 129.5(d), 130.3(d), 134.2(d), 134.7(d), 135.5(s), 138.4(s), 145.7(s), 160.3(s), 194.1(s); Anal. Calcd for $C_{18}H_{14}BrNO_2$: C, 60.69; H, 3.96; N, 3.93. Found: C, 60.63; H, 3.92; N, 3.95.

4-Acetyl-1-ethyl-6-methyl-2(1*H*)-quinolinone 20d. Yellow crystals; mp 140–141°C; IR ($CHCl_3$) 3000, 2925, 1700, 1645, 1580, 1565 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, J=7.1 Hz, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 4.37 (q, J=7.1 Hz, 2H, NCH_2), 6.92 (s, 1H, CH), 7.34 (d, J=8.7, Hz, 1H, ArH), 7.43 (d, J=8.7 Hz, 1H, ArH), 7.79 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.6(q), 20.8(q), 30.1(q), 37.6(t), 114.3(d), 116.8(s), 121.3(d), 126.8(d), 132.2(s), 132.5(d), 137.4(s), 146.1(s), 160.9(s), 201.0(s); Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.35; H, 6.67; N, 6.11.

4-Ethoxycarbonyl-1-ethyl-6-methyl-2(1*H*)-quinolinone 20e. Yellow needles; mp 85–86°C; IR ($CHCl_3$) 2990, 1730, 1665, 1645, 1585, 1255 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (t, J=7.1 Hz, 3H, CH_3), 1.43 (t, J=7.1 Hz, 3H, CH_3), 2.44 (s, 3H, CH_3), 4.37 (q, J=7.1 Hz, 2H, NCH_2), 4.45 (q, J=7.1 Hz, 2H, OCH_2), 7.16 (s, 1H, CH), 7.33 (d, J=8.7 Hz, 1H, ArH), 7.43 (dd, J=8.7, 1.5 Hz, 1H, ArH), 8.13 (d, J=1.5 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.6(q), 14.1(q), 20.8(q), 37.6(t), 61.9(t), 114.2(d), 117.7(d), 124.0(d), 126.9(d), 132.1(s), 132.3(d), 137.3(s), 138.6(s), 160.8(s), 165.6(s); Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.58; H, 6.56; N, 5.34.

4-Ethoxycarbonyl-1-ethyl-2(1*H*)-quinolinone 20f. Yellow crystals; mp 92–93°C; IR ($CHCl_3$) 3000, 1730, 1655, 1590, 1450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, J=7.1 Hz, 3H, CH_3), 1.43 (t, J=7.1 Hz, 3H, CH_3), 4.39 (q, J=7.1 Hz, 2H, NCH_2), 4.45 (q, J=7.1 Hz, 2H, OCH_2), 7.19 (s, 1H, CH), 7.28 (t, J=7.6 Hz, 1H, ArH), 7.43 (d, J=7.6 Hz, 1H, ArH), 7.61 (t, J=7.6 Hz, 1H, ArH), 8.35 (d, J=7.6 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.6(q), 14.1(q), 37.6(t), 61.9(t), 114.3(d), 117.7(s), 122.4(d), 124.1(d), 127.3(d), 131.0(d), 138.8(s), 139.3(s), 160.9(s), 165.4(s); Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.47; H, 6.15; N, 5.78.

6-Bromo-4-ethoxycarbonyl-1-ethyl-2(1*H*)-quinolinone 20g. Yellow needles; mp 142–143°C; IR ($CHCl_3$) 2990, 1730, 1655, 1585, 1430, 1325, 1250 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (t, J=7.1 Hz, 3H, CH_3), 1.43 (t, J=7.1 Hz, 3H, CH_3), 4.35 (q, J=7.1 Hz, 2H, NCH_2), 4.45 (q, J=7.1 Hz, 2H, OCH_2), 7.25 (s, 1H, CH), 7.30 (d, J=9.1 Hz, 1H, ArH), 7.68 (dd, J=9.1, 2.1 Hz, 1H, ArH), 8.59 (d, J=2.1 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.6(q), 14.1(q), 37.8(t), 62.2(t), 115.7(s), 115.9(d), 119.2(s), 125.6(d), 129.8(d), 133.8(d), 137.3(s), 138.3(s), 160.5(s), 164.8(s); Anal. Calcd for $C_{14}H_{14}BrNO_3$: C, 51.87; H, 4.35; N, 4.32. Found: C, 51.82; H, 4.35; N, 4.32.

4,6-Bis(ethoxycarbonyl)-1-ethyl-2(1*H*)-quinolinone 20h. Yellow needles; mp 81–82°C; IR ($CHCl_3$) 2990, 2940, 1715, 1660, 1620, 1590 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.38 (t, J=7.2 Hz, 3H, CH_3), 1.43 (t, J=7.1 Hz, 3H, CH_3), 1.46 (t, J=7.1 Hz, 3H, CH_3), 4.35–4.46 (m, 4H, CH_2), 4.49 (q, J=7.1 Hz, 2H, OCH_2), 7.24 (s, 1H, CH), 7.46 (d, J=9.0 Hz, 1H, ArH), 8.25 (dd, J=9.0, 1.8 Hz, 1H, ArH), 9.05 (d, J=1.8 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.6(q), 14.1(q), 14.3(q), 38.0(t), 61.2(t), 62.2(t), 114.3(d), 117.2(s), 124.5(s), 124.8(d), 129.5(d), 131.7(d), 139.0(s), 142.1(s), 160.9(s), 164.9(s), 165.7(s); Anal. Calcd for $C_{17}H_{19}NO_5$: C, 64.35; H, 6.03; N, 4.41. Found: C, 64.34; H, 6.10; N, 4.46.

6-Chloro-4-ethoxycarbonyl-1-ethyl-2(1*H*)-quinolinone 20i. Yellow needles; mp 133–134°C; IR ($CHCl_3$) 2990, 2925, 1730, 1660, 1590, 1430 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (t, J=7.1 Hz, 3H, CH_3), 1.43 (t, J=7.2 Hz, 3H, CH_3), 4.36 (q, J=7.1 Hz, 2H, NCH_2), 4.45 (q, J=7.2 Hz, 2H, OCH_2), 7.27 (s, 1H, CH), 7.36 (d, J=9.1 Hz, 1H, ArH), 7.56 (dd, J=9.1, 2.4 Hz, 1H, ArH), 8.46 (d, J=2.4 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.6(q), 14.1(q), 37.9(t), 62.2(t), 115.7(d), 118.8(s), 125.7(d), 126.8(d), 128.3(s), 131.1(d), 137.4(s), 137.8(s), 160.5(s), 164.8(s); Anal. Calcd for $C_{14}H_{14}ClNO_3$: C, 60.11; H, 5.04; N, 5.01. Found: C, 60.04; H, 5.01; N, 5.04.

Typical experimental procedure for the manganese(III) acetate mediated reaction of anilide 24

A solution of 156 mg (0.49 mmol) of **24a**, 393 mg (1.47 mmol) of manganese(III) acetate in 5 ml of acetic acid was heated at 80°C for 15 h. The reaction mixture was diluted with 50 ml of ethyl acetate, washed with 50 ml of aqueous saturated sodium bisulfite, three 50-ml portions of aqueous saturated sodium bicarbonate, 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 ethyl acetate–hexane, 1:2.5) to give 147 mg (95%) of **25a** as a single product.

3,3-Bis(methylsulfonyl)-1-ethyl-2-indolinone 25a. White crystals; mp 211–212°C; IR ($CHCl_3$) 3030, 2930, 1725, 1610, 1340 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (t,

J=7.2 Hz, 3H, CH_3), 3.39 (s, 6H, CH_3), 3.85 (q, J=7.2 Hz, 2H, NCH_2), 7.01 (d, J=7.8 Hz, 1H, ArH), 7.25 (t, J=7.8 Hz, 1H, ArH), 7.55 (t, J=7.8 Hz, 1H, ArH), 7.80 (d, J=7.8 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.1(q), 36.2(t), 39.5(q), 87.3(s), 109.9(d), 115.7(s), 123.8(d), 127.7(d), 132.8(d), 144.9(s), 162.7(s); Anal. Calcd for $C_{12}H_{15}NO_5S_2$: C, 45.41; H, 4.76; N, 4.41. Found: C, 45.42; H, 4.75; N, 4.58.

3,3-Bis(methylsulfonyl)-1-ethyl-5-methyl-2-indolinone 25b. White crystals; mp 191–192°C; IR ($CHCl_3$) 3035, 2930, 1720, 1605, 1450 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, J=7.2 Hz, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.37 (s, 6H, CH_3), 3.82 (q, J=7.2 Hz, 2H, NCH_2), 6.90 (d, J=8.0 Hz, 1H, ArH), 7.35 (d, J=8.0 Hz, 1H, ArH), 7.62 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.1(q), 21.1(q), 36.1(t), 39.5(q), 87.3(s), 109.6(d), 115.6(s), 128.3(d), 133.3(d), 133.8(s), 142.3(s), 162.6(s); Anal. Calcd for $C_{13}H_{17}NO_5S_2$: C, 47.12; H, 5.17; N, 4.23. Found: C, 47.17; H, 5.20; N, 4.37.

3,3-Bis(methylsulfonyl)-5-chloro-1-ethyl-2-indolinone 25c. White crystals; mp 212–213°C; IR ($CHCl_3$) 3030, 2930, 1730, 1610, 1485 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, J=7.2 Hz, 3H, CH_3), 3.39 (s, 6H, CH_3), 3.83 (q, J=7.2 Hz, 2H, NCH_2), 6.94 (d, J=8.4 Hz, 1H, ArH), 7.53 (dd, J=8.4, 1.9 Hz, 1H, ArH), 7.79 (d, J=1.9 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.0(q), 36.3(t), 39.6(q), 87.1(s), 110.8(d), 117.2(s), 127.9(d), 129.4(s), 132.8(d), 143.4(s), 162.5(s); Anal. Calcd for $C_{12}H_{14}ClNO_5S_2$: C, 40.97; H, 4.01; N, 3.98. Found: C, 40.91; H, 3.99; N, 4.03.

3,3-Bis(methylsulfonyl)-5-bromo-1-ethyl-2-indolinone 25d. White crystals; mp 228–229°C; IR ($CHCl_3$) 3035, 2925, 1730, 1610, 1480 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, J=7.2 Hz, 3H, CH_3), 3.39 (s, 6H, CH_3), 3.83 (q, J=7.2 Hz, 2H, NCH_2), 6.89 (d, J=8.4 Hz, 1H, ArH), 7.67 (dd, J=8.4, 1.9 Hz, 1H, ArH), 7.92 (d, J=1.9 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.0(q), 36.3(t), 39.6(q), 87.1(s), 111.2(d), 116.4(s), 117.6(s), 130.6(d), 135.7(d), 143.9(s), 162.4(s); Anal. Calcd for $C_{12}H_{14}BrNO_5S_2$: C, 36.37; H, 3.56; N, 3.53. Found: C, 36.15; H, 3.54; N, 3.43.

3,3-Bis(methylsulfonyl)-5-ethoxycarbonyl-1-ethyl-2-indolinone 25e. White crystals; mp 140–141C; IR ($CHCl_3$) 3030, 2930, 1730, 1715, 1610, 1340 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, J=7.2 Hz, 3H, CH_3), 1.40 (t, J=7.1 Hz, 3H, CH_3), 3.44 (s, 6H, CH_3), 3.88 (q, J=7.2 Hz, 2H, NCH_2), 4.40 (q, J=7.1 Hz, 2H, OCH_2), 7.06 (d, J=8.4 Hz, 1H, ArH), 8.28 (d, J=8.4 Hz, 1H, ArH), 8.41 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.1(q), 14.3(q), 36.5(t), 39.6(q), 61.5(t), 87.1(s), 109.5(d), 116.0(s), 126.5(s), 128.5(d), 134.9(d), 148.6(s), 163.0(s), 165.0(s); Anal. Calcd for $C_{15}H_{19}NO_7S_2$: C, 46.26; H, 4.92; N, 3.60. Found: C, 46.15; H, 4.87; N, 3.67.

3,3-Bis(methylsulfonyl)-1-ethyl-7-methyl-2-indolinone 25f. White crystals; mp 180–181°C; IR ($CHCl_3$) 3030, 2930, 1715, 1595, 1465 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, J=7.1 Hz, 3H, CH_3), 2.57 (s, 3H, CH_3), 3.37 (s, 6H, CH_3), 4.07 (q, J=7.1 Hz, 2H, NCH_2), 7.12 (t, J=7.7 Hz, 1H, ArH), 7.29 (d, J=7.7 Hz, 1H, ArH), 7.68 (d, J=7.7 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0(q), 18.9(q), 38.1(t), 39.5(q), 86.8(s), 116.1(s), 121.0(s), 123.6(d), 125.6(d), 136.9(d), 142.9(s), 163.7(s); Anal. Calcd for $C_{13}H_{17}NO_5S_2$: C, 47.12; H, 5.17; N, 4.23. Found: C, 47.10; H, 5.02; N, 4.21.

3,3-Bis(methylsulfonyl)-1-ethyl-7-methoxy-2-indolinone 25g. White crystals; mp 162–163°C; IR ($CHCl_3$) 3015, 2985, 2940, 1715, 1615, 1465 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, J=7.1 Hz, 3H, CH_3), 3.37 (s, 6H, CH_3), 3.92 (s, 3H, OCH_3), 4.10 (q, J=7.1 Hz, 2H, NCH_2), 7.11 (d, J=8.0 Hz, 1H, ArH), 7.18 (t, J=8.0 Hz, 1H, ArH), 7.42 (d, J=8.0 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0(q), 39.0(t), 39.5(q), 56.0(q), 87.3(s), 116.3(d), 116.8(s), 119.8(d), 124.5(d), 133.2(s), 145.5(s), 162.8(s); Anal. Calcd for $C_{13}H_{17}NO_6S_2$: C, 44.95; H, 4.93; N, 4.03. Found: C, 44.96; H, 4.91; N, 3.96.

Typical experimental procedure for the manganese(III) acetate mediated reaction of anilide 26

A solution of 101 mg (0.45 mmol) of **26a**, 601 mg (2.24 mmol) of manganese(III) acetate and 182 mg (0.91 mmol) of copper(II) acetate in 10 ml of 60% formic acid was heated at 80°C for 6 h. The reaction mixture was diluted with 50 ml of ethyl acetate, washed with three 50 ml portions of aqueous saturated sodium bicarbonate, 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 ethyl acetate–hexane, 1:6) to give 96 mg (89%) of **27a** as a single product.

1-Ethyl-5-methyl-2,3-indolinedione 27a. Orange needles; mp 108–109°C; IR ($CHCl_3$) 2925, 1735, 1625, 1600, 1490 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, J=7.2 Hz, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.77 (q, J=7.2 Hz, 2H, NCH_2), 6.81 (d, J=7.7 Hz, 1H, ArH), 7.40 (d, J=7.7 Hz, 1H, ArH), 7.41 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.5(q), 20.6(q), 34.9(t), 109.8(d), 117.6(s), 125.8(d), 133.4(s), 138.7(d), 148.4(s), 157.9(s), 183.9(s); Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.82; H, 5.88; N, 7.38.

1-Ethyl-5-methoxy-2,3-indolinedione 27c. Red plates; mp 102–103°C; IR ($CHCl_3$) 2940, 1735, 1625, 1600, 1490 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, J=7.3 Hz, 3H, CH_3), 3.76 (q, J=7.3 Hz, 2H, NCH_2), 3.81 (s, 3H, OCH_3), 6.82–6.87 (m, 1H, ArH), 7.14 (s, 1H, ArH), 7.12–7.18 (m, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.5(q), 34.9(t), 55.9(q), 109.7(d), 111.0(d), 118.0(s), 124.6(d), 144.4(s), 156.3(s), 157.9(s), 184.0(s); Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.30; H, 5.4; N, 6.86.

5-Bromo-1-ethyl-2,3-indolinedione 27d. Red plates; mp 148–149°C; IR ($CHCl_3$) 2990, 1740, 1610, 1470, 1440 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (t, J=7.3 Hz, 3H, CH_3), 3.78 (q, J=7.3 Hz, 2H, NCH_2), 6.77–6.89 (m, 1H, ArH), 7.66–7.80 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4(q), 35.1(t), 111.7(d), 116.4(s), 118.8(s), 128.3(d), 140.5(d), 149.4(s), 157.1(s), 182.5(s);

Anal. Calcd for $C_{10}H_8BrNO_2$: C, 47.27; H, 3.17; N, 5.51. Found: C, 44.27; H, 3.21; N, 5.52.

5-Chloro-1-ethyl-2,3-indolinedione 27e. Red needles; mp 137–138°C; IR ($CHCl_3$) 3015, 2990, 1745, 1615, 1475 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, J=7.2 Hz, 3H, CH_3), 3.79 (q, J=7.2 Hz, 2H, NCH_2), 6.88 (d, J=8.2 Hz, 1H, ArH), 7.56 (d, J=8.2 Hz, 1H, ArH), 7.58 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4(q), 35.1(t), 111.2(d), 118.4(s), 125.4(d), 129.5(s), 137.7(d), 148.9(s), 157.3(s), 182.7(s); Anal. Calcd for $C_{10}H_8ClNO_2$: C, 57.33; H, 3.85; N, 6.68. Found: C, 57.28; H, 3.92; N, 6.67.

5-Ethoxycarbonyl-1-ethyl-2,3-indolinedione 27f. Orange needles; mp 140–141°C; IR ($CHCl_3$) 2990, 1740, 1715, 1620, 1600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, J=7.2 Hz, 3H, CH_3), 1.40 (t, J=7.1 Hz, 3H, CH_3), 3.84 (q, J=7.2 Hz, 2H, NCH_2), 4.39 (q, J=7.1 Hz, 2H, OCH_2), 6.99 (d, J=8.3 Hz, 1H, ArH), 8.27 (d, J=1.6 Hz, 1H, ArH), 8.33 (dd, J=8.3, 1.6 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.5(q), 14.2(q), 35.3(t), 61.4(t), 109.7(d), 117.2(s), 126.2(s), 126.7(d), 139.9(d), 153.7(s), 157.9(s), 164.9(s), 182.7(s); Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.66. Found: C, 63.16; H, 5.45; N, 5.55.

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