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Oxidative free radical reactions between 2-benzyl-1,4-naphthoquinones and β-dicarbonyl compounds

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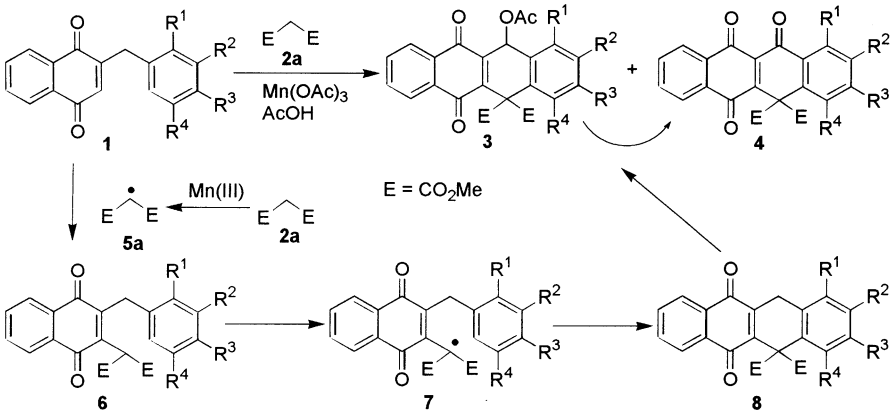
Abstract—Oxidative free radical reactions between 2-benzyl-1,4-naphthoquinones and β-dicarbonyl compounds are described. Electrophilic carbon-centered radicals produced by the manganese(III) acetate or cerium(IV) ammonium nitrate oxidation of β-dicarbonyl compounds undergo efficient addition to a C–C double bond of quinone ring. This free radical reaction provides a novel method for the synthesis of naphthacene-5,12-diones. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Free radical reactions have become increasingly important in organic synthesis in the last two decades.[1] Compounds containing the quinone group represent an important class of biologically active molecules that are widespread in nature.[2,3] The oxidative addition of an electrophilic carbon-centered radical to alkenes mediated by metal salts has received considerable attention in the organic synthesis for the construction of carbon–carbon bonds. Among these, manganese(III) acetate and cerium(IV) ammonium nitrate have been used most efficiently.[1d–f,4,5] These reactions can be performed intermolecularly and intramolecularly. The free radical reaction of 1,4-naphthoquinones has been reported.[5c–h,6] We found that oxidative free radical reactions of 2-anilino-1,4-naphthoquinones with β-dicarbonyl compounds produced benzo[*b*]acridine-6,11-diones and benzo[*f*]indole-4,9-diones effectively.[5d,h] We describe here our results on the oxidative free radical reactions between 2-benzyl-1,4-naphthoquinones and β-dicarbonyl compounds.

2. Results and discussion

We began our studies with the manganese(III) mediated reaction shown in Scheme 1. When 2-benzyl-1,4-naphthoquinone (**1a**) was treated with dimethyl malonate (**2a**) and manganese(III) acetate in acetic acid at 70°C, **3a** and **4a** were obtained in 29 and 2% yields, respectively (Table 1, entry 1). A possible mechanism for this reaction is shown in Scheme 1. Initiation occurs with the manganese(III) acetate oxidation of **2a** to produce radical **5a**. This radical intermediate **5a** undergoes intermolecular addition to the



Scheme 1.

Keywords: manganese(III) acetate; cerium(IV) ammonium nitrate; oxidative; free radical; 2-benzyl-1,4-naphthoquinone.
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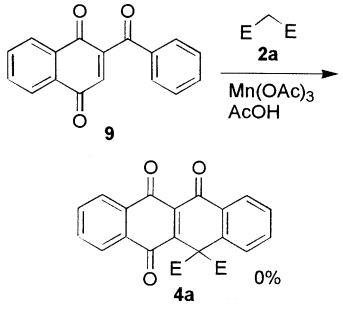
Table 1. Manganese(III) mediated free radical reactions of 2-benzyl-1,4-naphthoquinone **1**

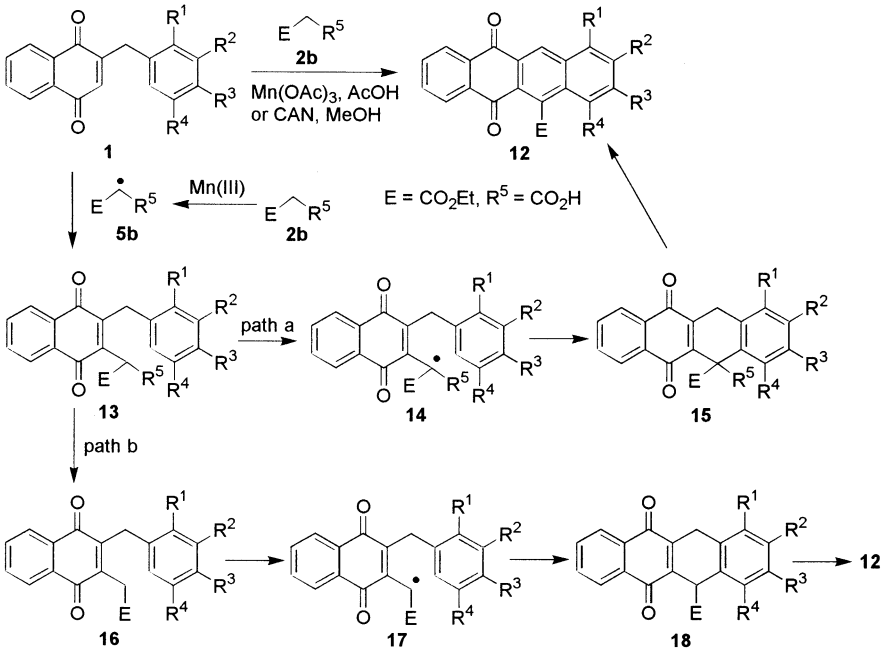
Entry	Quinone	β-Dicarbonyl compound	Conversion (%)	Product (yield (%))	
1	**1a**: R^1=H, R^2=H, R^3=H, R^4=H	**2a**	100	**3a** (29)	**4a** (2)
2		**2b**	80	**12a** (33)	
3	**1b**: R^1=H, R^2=H, R^3=Me, R^4=H	**2a**	100	**3b** (35)	**4b** (7)
4		**2b**	80	**12b** (36)	
5	**1c**: R^1=Me, R^2=H, R^3=H, R^4=H	**2a**	100	**3c** (54)	**4c** (5)
6		**2b**	77	**12c** (56)	
7	**1d**: R^1=H, R^2=H, R^3=OMe, R^4=H	**2a**	100	**3d**[a]	**4d** (45)
8		**2b**	76	**12d** (19)	
9		**2b**	89	**12d** (12)	
10	**1e**: R^1=H, R^2=Me, R^3=H, R^4=Me	**2a**	100	**3e** (31)	**4e** (1)
11		**2b**	70	**12e** (41)	
12	**1f**: R^1=Me, R^2=H, R^3=Me, R^4=H	**2b**	76	**12f** (67)	
13		**2b**	93	**12f** (58)	
14	**1g**: R^1=H, R^2=H, R^3=Br, R^4=H	**2a**	100	**3g** (9)	**4g** (2)
15		**2b**	76	**12g** (51)	
16	**1h**: R^1=H, R^2=H, R^3=Cl, R^4=H	**2a**	100	**3h** (6)	**4h** (2)
17		**2b**	89	**12h** (43)	

[a] **3d** cannot be isolated from the reaction mixture.

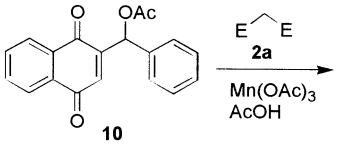
quinone ring followed by oxidation to give **6a**, which was oxidized by manganese(III) acetate to generate radical **7a**. This radical **7a** undergoes further intramolecular cyclization followed by aromatization to give **8a**. Quinone **8a** undergoes benzylic oxidation to produce **3a**, which can also be oxidized further to generate **4a**. It is probable that **3a** and **4a** are generated via the manganese(III) mediated reaction of **9**, **10** and **11a**, which are derived from the benzylic oxidation of **1a**. When **9**, **10** and **11a** were treated with manganese(III) acetate under similar conditions, **3a** and **4a** were obtained in poor yield (Eqs. (1)–(3)).

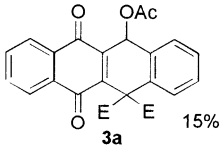


(1)

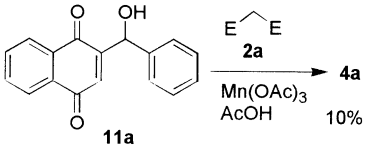


Scheme 2.





(2)



(3)

Based on these results, we believe that the mechanism shown in Scheme 1 is the main route for the formation of **3a** and **4a**. The results of this manganese(III) mediated reaction are summarized in Table 1. Quinone **3** is the major product except in entry 7 (R^1=R^2=R^4=H, R^3=OMe). This is presumably due to the electron donating effect of the methoxy group and the rate of benzylic oxidation of **3d** increases. With an electron-withdrawing group on the benzene ring, the yield of this reaction is reduced substantially (entries 14 and 16).[7] These results can be rationalized by the consideration that the electron deficiency of radical intermediate **7** makes the rate of intramolecular cyclization to the benzene ring with an electron-withdrawing group much slower. It is known that β-ketoacids undergo decarboxylation to give ketones. We believed that quinone **15** will also undergo decarboxylation followed by aromatization to give **12** (Scheme 2). When quinone **1a** was treated with ethyl malonate (**2b**) and manganese(III) acetate under similar conditions, **12a** was obtained in 33% yield (Table 1, entry 2). The scope of this reaction is also illustrated in Table 1. In all cases, this reaction does not go to completion and the yield of product decreases after prolonged heating (entries 8, 12 vs 9, 13). This can be attributed to the competing benzylic oxidation of starting material. Quinone **12a** was generated either via the decarboxylation followed by aromatization of **15a** (path a), which was formed via a similar reaction route shown in Scheme 1 or the intramolecular cyclization followed by aromatization of radical intermediate **17a** (path b), which was produced by the decarboxylation and oxidation of **13a** (Scheme 2). In contrast to the results of the reaction between **1** and dimethyl malonate (**2a**), the reaction yields are not affected by the electronic effect of the substituents on the benzene ring. Based on these results, path b is the most likely reaction route for the formation of **12a**.

The cerium(IV) mediated oxidative free radical reaction has been reported.[1d,e] We have continued to study this oxidative free radical reaction with cerium(IV) ammonium nitrate. When 2-benzyl-1,4-naphthoquinone (**1a**) was treated with dimethyl malonate (**2a**) and cerium(IV) ammonium nitrate in methanol at 60°C, **19a** was obtained in 59% yield (Eq. (4)).

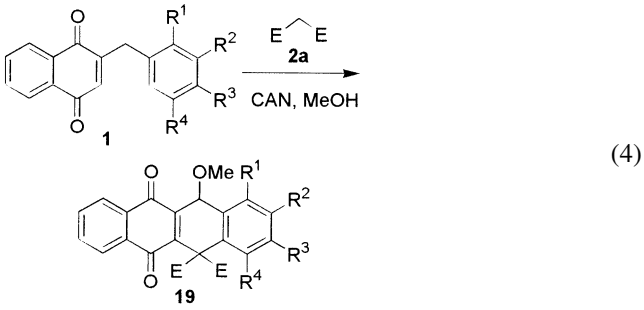
Table 2. Cerium(IV) mediated free radical reactions of 2-benzyl-1,4-naphthoquinone **1**

Entry	Quinone	β-Dicarbonyl compound	Conversion (%)	Product (yield (%))
1	**1a**: R^1=H, R^2=H, R^3=H, R^4=H	**2a**	100	**19a** (59)
2		**2b**	87	**12a** (30)
3		**2c**	100	**12a** (29)
4	**1b**: R^1=H, R^2=H, R^3=Me, R^4=H	**2a**	100	**19b** (51)
5		**2b**	92	**12b** (19)
6		**2c**	100	**12b** (30)
7	**1c**: R^1=Me, R^2=H, R^3=H, R^4=H	**2a**[a]	100	**19c** (43)
8		**2b**	87	**12c** (43)
9		**2c**	100	**12c** (33)
10	**1d**: R^1=H, R^2=H, R^3=OMe, R^4=H	**2a**	100	**19d** (24)
11		**2b**	90	**12d** (7)
12		**2c**	100	**12d** (20)
13	**1e**: R^1=H, R^2=Me, R^3=H, R^4=Me	**2a**	100	**19e** (43)
14		**2b**	84	**12e** (20)
15		**2c**	100	**12e** (32)
16	**1f**: R^1=Me, R^2=H, R^3=Me, R^4=H	**2b**	74	**12f** (43)
17		**2c**	100	**12f** (35)
18	**1g**: R^1=H, R^2=H, R^3=Br, R^4=H	**2b**	91	**12g** (47)
19		**2c**	100	**12g** (38)
20	**1h**: R^1=H, R^2=H, R^3=Cl, R^4=H	**2a**[a]	100	**19h** (56)
21		**2b**	92	**12h** (43)
22		**2c**	100	**12h** (39)
23	**1i**: R^1=Br, R^2=H, R^3=H, R^4=H	**2b**	83	**12i** (47)
24		**2c**	100	**12i** (29)
25	**1j**: R^1=Cl, R^2=H, R^3=H, R^4=H	**2a**[a]	100	**19j** (40)
26		**2b**	87	**12j** (45)
27		**2c**	100	**12j** (32)
28	**1k**: R^1=Cl, R^2=H, R^3=Cl, R^4=H	**2b**	75	**12k** (52)
29		**2c**	100	**12k** (25)
30	**1l**: R^1=Me, R^2=H, R^3=Br, R^4=H	**2b**	79	**12l** (53)
31		**2c**	100	**12l** (31)

[a] This reaction was performed with diethyl malonate.

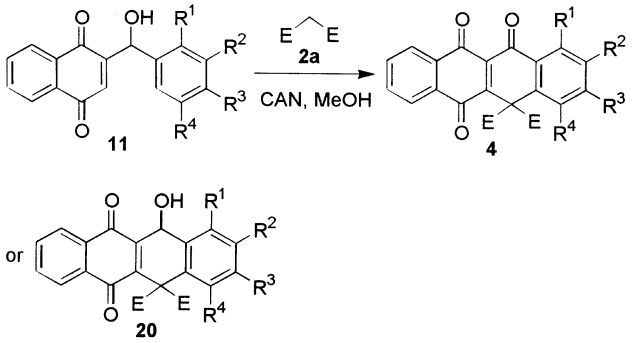
Table 3. Free radical reactions of 2-(α-hydroxybenzyl)-1,4-naphthoquinone **11**

Entry	Quinone	Metal salt	Product (yield (%))
1	**11a**: R^1=H, R^2=H, R^3=H, R^4=H	$Mn(OAc)_3$	**4a** (10)
2	**11b**: R^1=H, R^2=H, R^3=Me, R^4=H	$Mn(OAc)_3$	**4b** (12)
3		CAN	**4b** (47)
4	**11c**: R^1=Me, R^2=H, R^3=H, R^4=H	$Mn(OAc)_3$	**4c** (16)
5		CAN	**20c** (63)
6	**11d**: R^1=H, R^2=H, R^3=OMe, R^4=H	$Mn(OAc)_3$	**4d** (1)
7		CAN	**4d** (17)
8	**11e**: R^1=H, R^2=Me, R^3=H, R^4=Me	$Mn(OAc)_3$	**4e** (7)
9		CAN	**4e** (35)
10	**11f**: R^1=H, R^2=H, R^3=Br, R^4=H	CAN	**4f** (52)
11	**11g**: R^1=H, R^2=H, R^3=Cl, R^4=H	CAN	**4g** (57)
12	**11h**: R^1=Me, R^2=H, R^3=Br, R^4=H	CAN	**20h** (65)
13	**11i**: R^1=Br, R^2=H, R^3=H, R^4=OMe	CAN	**20i** (61)



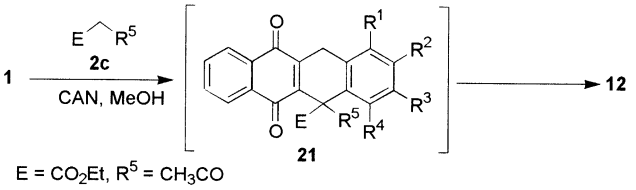
(4)

Quinone **19a** was formed via a similar reaction route shown in Scheme 1. The results of this reaction are summarized in Table 2. This reaction proceeded at a much faster reaction rate (60°C, 5 h) than that performed with manganese(III) acetate. Even though the manganese(III) mediated reaction between 2-(α-hydroxybenzyl)-1,4-naphthoquinone **11b** and dimethyl malonate (**2a**) gave **4b** in rather poor yield (Table 3, entry 2), we also performed this reaction with cerium(IV) ammonium nitrate. To our surprise, **4b** was obtained in much better yield (47%) from **11b** (Eq. (5)).



(5)

Other examples are shown in Table 3. With *ortho* substituent on the benzene ring, quinone **20** was obtained and no **4** could be found (entries 5,12 and 13). This can be rationalized by consideration that the steric effect of the ortho substituent makes the rate of benzylic oxidation of **4** much slower. The oxidative free radical reaction of 2-benzyl-1,4-naphoquinone (**1a**) with ethyl malonate (**2b**) and cerium(IV) ammonium nitrate under similar conditions gave **12a** (Scheme 2). The results of this reaction are also summarized in Table 2. In most cases, it gave similar results to those performed with manganese(III) acetate. Cerium(IV) mediated free radical reaction of **1** with ethyl acetoacetate (**2c**) was next examined. Treatment of **1a** with ethyl acetoacetate (**2c**) and cerium(IV) ammonium nitrate gave **12a** in 29% yield (Eq. (6)).



(6)

Other examples are also shown in Table 2. Reactions generally proceeded to completion within less than 5 h. It is probable that **12** was formed via retro Claisen condensation followed by aromatization of **21**, which was produced via a similar route shown in Scheme 1.[8]

In conclusion, radical **5**, generated by the oxidation of β-dicarbonyl compounds with manganese(III) acetate or cerium(IV) ammonium nitrate, undergoes efficient addition to the C–C double bond of 2-benzyl-1,4-naphthoquinones. It proceeded much faster with cerium(IV) ammonium nitrate. This free radical reaction provides a novel method for the synthesis of naphthacene-5,12-diones from readily available 2-benzyl-1,4-naphthoquinones and β-dicarbonyl compounds.

3. Experimental

3.1. General considerations

Melting points are uncorrected. The NMR spectra were recorded on a Brucker AVANCE-300, AMX-400 or AVANCE-600 spectrometer. Chemical shifts are reported in ppm relative to TMS as internal reference. Analytical thin layer chromatography was performed with precoated silica gel 60 F-254 plates (0.25 mm thick) from EM Laboratories and visualized either by UV or by spraying with 5% phosphomolybdic acid in ethanol followed by heating. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (70–230 mesh).

Typical experimental procedure for the reaction mediated by manganese(III) acetate. A solution of 200 mg (0.81 mmol) of 2-benzyl-1,4-naphthoquinone (**1a**),

429 mg (3.25 mmol) of dimethyl malonate (**2a**), and 1.30 g (4.85 mmol) of manganese(III) acetate in 10 mL of acetic acid was heated at 70°C for 41 h (the dark brown color of manganese(III) acetate disappeared), followed by the addition of 437 mg (3.30 mmol) of dimethyl malonate and 1.30 g (4.85 mmol) of manganese(III) acetate. The reaction mixture was heated for another 31 h and then diluted with 100 mL of ethyl acetate, washed with 50 mL of saturated aqueous sodium bisulfite, three 50 mL portions of water, and three 50 mL portions of aqueous saturated sodium bicarbonate, dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with 2:1 dichloromethane–hexane) followed by recrystallization (hexane–ethyl acetate) to give 58 mg (29%) of **4a** followed by 5 mg (2%) of **3a**.

Typical experimental procedure for the reaction mediated by CAN. To a solution of 120 mg (0.48 mmol) of 2-benzyl-1,4-naphthoquinone (**1a**) in 10 ml of methanol and 2 ml of chloroform heated at 60°C was added 639 mg (4.84 mmol) of dimethyl malonate (**2a**), and 3.98 g (7.26 mmol) of CAN in three portions for every 2 h periods. The reaction mixture was heated for another hour. After workup as described above, the residue was chromatographed over 20 g of silica gel (eluted with 1:3 ethyl acetate–hexanes) followed by recrystallization (hexanes–ethyl acetate) to give 116 mg (59%) of **19a**.

3.1.1. 12-Acetoxyl-5,5-dimethoxycarbonyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (3a). Orange crystals; mp 210–211°C; IR ($CHCl_3$) 3015, 1740, 1670, 1435, 1290 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 3H, $COCH_3$), 3.715 (s, 3H, OCH_3), 3.718 (s, 3H, OCH_3), 7.37 (s, 1H, OCH), 7.40–7.49 (m, 2H, ArH), 7.68–7.76 (m, 2H, ArH), 7.77–7.85 (m, 2H, ArH), 8.15–8.22 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.9(q), 53.3(q), 53.7(q), 58.3(s), 63.1(d), 126.7(d), 127.1(d), 128.0(d), 129.2(d), 129.5(d), 130.2(d), 131.1(s), 131.67(s), 131.70(s), 132.2(s), 134.2(d), 134.4(d), 139.4(s), 144.4(s), 167.0(s), 168.5(s), 169.8(s), 182.4(s), 183.1(s); Anal. Calcd for $C_{24}H_{18}O_8$: C, 66.36; H, 4.18. Found: C, 66.28; H, 4.26.

3.1.2. 12-Acetoxyl-5,5-dimethoxycarbonyl-3-methyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (3b). Yellow crystals; mp 204–205°C; IR ($CHCl_3$) 3020, 2955, 1740, 1670, 1295 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 3H, $COCH_3$), 2.40 (s, 3H, CH_3), 3.71 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 7.24 (d, J=7.8 Hz, 1H, ArH), 7.34 (s, 1H, OCH), 7.51 (s, 1H, ArH), 7.62 (d, J=7.8 Hz, 1H, ArH), 7.76–7.87 (m, 2H, ArH), 8.13–8.25 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.9(q), 21.4(q), 53.3(q), 53.6(q), 58.1(s), 63.0(d), 126.7(d), 127.1(d), 128.16(d), 128.2(s), 130.1(d), 130.2(d), 131.7(s), 131.9(s), 134.2(d), 134.4(d), 139.4(s), 139.8(s), 144.4(s), 167.1(s), 168.5(s), 168.9(s), 182.5(s), 183.3(s); Anal. Calcd for $C_{25}H_{20}O_8$: C, 66.95; H, 4.50. Found: C, 66.93; H, 4.49.

3.1.3. 12-Acetoxyl-5,5-dimethoxycarbonyl-1-methyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (3c). Yellow crystals; mp 148–150°C; IR ($CHCl_3$) 3015, 2955, 1745, 1675, 1235 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.87 (s, 3H, $COCH_3$), 2.59 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 7.27 (d, J=8.7 Hz, 1H, ArH), 7.32–7.42 (m, 2H, ArH), 7.44 (s, 1H, OCH), 7.76–7.84 (m, 2H, ArH), 8.13–8.24 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.8(q), 20.8(q), 53.3(q), 53.8(q), 60.1(s), 61.4(d), 126.5(d), 126.8(d), 127.1(d), 129.3(d), 129.7(s), 131.1(d), 131.6(s), 131.8(s), 134.2(d), 134.3(d), 134.9(s), 137.6(s), 141.2(s), 145.1(s), 167.4(s), 168.9(s), 169.7(s), 182.2(s), 182.8(s); Anal. Calcd for $C_{25}H_{20}O_8$: C, 66.93; H, 4.49. Found: C, 67.08; H, 4.89.

3.1.4. 12-Acetoxyl-5,5-dimethoxycarbonyl-2,4-dimethyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (3e). Yellow powder; mp 193–194°C; IR ($CHCl_3$) 3020, 1740, 1675, 1285, 1235 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.87 (s, 3H, $COCH_3$), 2.32 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 3.74 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 7.10 (s, 1H, ArH), 7.26(s, 1H, ArH), 7.39 (s, 1H, OCH), 7.74–7.83 (m, 2H, ArH), 8.11–8.21 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.7(q), 20.9(q), 21.0(q), 53.3(q), 53.7(q), 59.8(s), 64.5(d), 126.5(d), 127.3(d), 129.4(d), 130.8(s), 131.2(s), 132.2(s), 134.2(d), 134.3(d), 135.1(d), 138.4(s), 138.6(s), 141.0(s), 146.5(s), 167.7(s), 169.4(s), 170.3(s), 182.0(s), 182.9(s); Anal. Calcd for $C_{26}H_{22}O_8$: C, 67.53; H, 4.79. Found: C, 67.26; H, 4.95.

3.1.5. 12-Acetoxyl-3-bromo-5,5-dimethoxycarbonyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (3g). Yellow powder; mp 213–214°C; IR ($CHCl_3$) 3030, 2955, 1740, 1675, 1595, 1295 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 3H, $COCH_3$), 3.74 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 7.30 (s, 1H, OCH), 7.56 (dd, J=8.3, 1.8 Hz, 1H, ArH), 7.62 (d, J=8.3 Hz, 1H, ArH), 7.79–7.84 (m, 2H, ArH), 7.85 (d, J=1.8 Hz, 1H, ArH), 8.15–8.23 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.8(q), 53.6(q), 53.9(q), 58.1(s), 62.6(d), 123.8(d), 126.7(d), 127.2(d), 130.1(s), 130.9(d), 131.58(s), 131.63(s), 131.7(d), 132.5(d), 134.2(s), 134.3(d), 134.5(d), 139.0(s), 143.9(s), 166.6(s), 168.1(s), 169.8(s), 182.2(s), 182.9(s); Anal. Calcd for $C_{24}H_{17}BrO_8$: C, 56.16; H, 3.34. Found: C, 55.90; H, 3.46.

3.1.6. 12-Acetoxyl-3-chloro-5,5-dimethoxycarbonyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (3h). Yellow powder; mp 197–198°C; IR ($CHCl_3$) 3030, 2955, 1740, 1675, 1295 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 3H, $COCH_3$), 3.74 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 7.31 (s, 1H, OCH), 7.40(dd, J=8.4, 2.0 Hz, 1H, ArH), 7.69 (d, J=8.4 Hz, 1H, ArH), 7.70 (d, J=2.0 Hz, 1H, ArH), 7.79–7.87 (m, 2H, ArH), 8.15–8.24 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.9(q), 53.6(q), 53.9(q), 58.2(s), 62.6(d), 126.8(d), 127.2(d), 128.1(d), 129.6(d), 131.56(d), 131.59(s), 131.64(s), 134.0(s), 134.3(d), 134.5(d), 135.7(s), 139.1(s), 144.0(s), 166.6(s), 168.1(s), 169.8(s), 182.2(s), 182.9(s); Anal. Calcd for $C_{24}H_{17}ClO_8$: C, 61.48; H, 3.65. Found: C, 61.46; H, 3.69.

3.1.7. 5,5-Dimethoxycarbonyl-5,6,11,12-tetrahydro-6,11,12-trioxo-naphthacene (4a). Red crystals; mp 243–244°C; IR ($CHCl_3$) 3020, 1785, 1700, 1675, 1285 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 6H, OCH_3), 7.60 (td, J=7.7, 1.0 Hz, 1H, ArH), 7.71 (td, J=7.7, 1.0 Hz, 1H, ArH), 7.82 (td, J=7.5, 1.1 Hz, 1H, ArH), 7.88 (td, J=7.5, 1.1 Hz, 1H, ArH), 8.02 (d, J=7.7, 1.0 Hz, 1H, ArH), 8.14 (dd, J=7.7, 1.0 Hz, 1H, ArH), 8.19–8.26 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 53.8(q), 56.3(s), 126.7(d),

127.1(d), 127.5(d), 127.7(d), 129.7(d), 131.05(s), 131.14(s), 132.4(s), 133.7(s), 134.0(d), 134.1(d), 135.3(d), 148.3(s), 166.0(s), 181.6(s), 182.1(s), 185.4(s); Anal. Calcd for $C_{22}H_{14}O_7$: C, 67.69; H, 3.62. Found: C, 67.66; H, 3.65.

3.1.8. 5,5-Dimethoxycarbonyl-3-methyl-5,6,11,12-tetrahydro-6,11,12-trioxo-naphthacene (4b). Red crystals; mp 250–251°C; IR ($CHCl_3$) 3030, 1785, 1745, 1695, 1280 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.49 (s, 3H, CH_3) 3.65(s, 6H, OCH_3), 7.39 (d, J=8.1 Hz, 1H, ArH), 7.76–7.83 (m, 2H, ArH), 7.88 (t, J=7.3 Hz, 1H, ArH), 8.06–8.14 (m, 2H, ArH), 8.22 (d, J=7.3 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.0(q), 53.8(q), 58.8(s), 126.6(d), 127.0(d), 127.5(d), 127.8(d), 128.8(s), 130.8(d), 131.0(s), 131.1(s), 132.4(s), 133.6(s), 134.0(d), 135.3(d), 145.5(s), 148.2(s), 166.0(s), 181.76(s), 181.84(s), 185.5(s); Anal. Calcd for $C_{23}H_{16}O_7$: C, 68.32; H, 3.99. Found: C, 68.36; H, 3.98.

3.1.9. 5,5-Dimethoxycarbonyl-1-methyl-5,6,11,12-tetrahydro-6,11,12-trioxo-naphthacene (4c). Red crystals; mp 242–243°C; IR ($CHCl_3$) 3030, 1780, 1675, 1595, 1285 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.75 (s, 3H, CH_3) 3.68 (s, 6H, OCH_3), 7.37 (d, J=7.8 Hz, 1H, ArH), 7.54 (t, J=7.8 Hz, 1H, ArH), 7.75 (d, J=7.8 Hz, 1H, ArH), 7.78–7.90 (m, 2H, ArH), 8.14 (d, J=7.5 Hz, 1H, ArH), 8.22 (d, J=7.5 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.2(q), 53.8(q), 57.1(s), 125.6(d), 126.7(d), 127.0(d), 130.0(s), 131.2(s), 132.3(s), 132.98(d), 133.02(d), 134.1(d), 135.2(d), 141.1(s), 145.6(s), 166.5(s), 181.4(s), 184.1(s), 184.9(s); exact mass calcd for $C_{23}H_{16}O_7$ *m/e* 404.0896, found *m/e* 404.0895.

3.1.10. 3-Methoxy-5,5-dimethoxycarbonyl-5,6,11,12-tetrahydro-6,11,12-trioxo-naphthacene (4d). Red crystals; mp 263–264°C; IR ($CHCl_3$) 3030, 1785, 1690, 1600, 1285 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 6H, OCH_3), 3.94 (s, 3H, OCH_3) 7.10 (dd, J=8.8, 2.5 Hz, 1H, ArH), 7.47 (d, J=2.5 Hz, 1H, ArH), 7.81 (td, J=7.5, 1.3 Hz, 1H, ArH), 7.88 (td, J=7.5, 1.3 Hz, 1H, ArH), 8.12 (dd, J=7.5, 1.3 Hz, 1H, ArH), 8.18 (d, J=8.8 Hz, 1H, ArH), 8.21 (dd, J=7.5, 1.3 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 53.7(q), 55.8(q), 56.2(s), 111.3(d), 116.5(d), 124.6(s), 126.5(d), 127.0(d), 130.1(d), 130.9(s), 131.0(s), 132.5(s), 133.9(d), 135.3(d), 135.8(s), 148.0(s), 164.1(s), 165.9(s), 180.8(s), 181.8(s), 185.5(s); Anal. Calcd for $C_{23}H_{16}O_8$: C, 65.72; H, 3.84. Found: C, 65.78; H, 3.85.

3.1.11. 5,5-Dimethoxycarbonyl-2,4-dimethyl-5,6,11,12-tetrahydro-6,11,12-trioxo-naphthacene (4e). Red crystals; mp 230–231°C; IR ($CHCl_3$) 3035, 1740, 1695, 1365, 1285 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H, CH_3) 2.58 (s, 3H, CH_3) 3.73(s, 6H, OCH_3), 7.35 (s, 1H, ArH), 7.77–7.91 (m, 2H, ArH), 7.87 (s, 1H, ArH), 8.12 (dd, J=7.6, 1.2 Hz, 1H, ArH) 8.18 (dd, J=7.6, 1.2 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.7(q), 20.8(q), 53.7(q), 57.7(s), 126.4(d), 126.7(d), 126.8(d), 130.8(s), 131.5(s), 131.9(s), 132.7(s), 132.9(s), 134.1(d), 135.0(d), 138.3(s), 139.2(s), 139.5(d), 148.0(s), 166.7(s), 181.3(s), 183.3(s), 184.8(s); Anal. Calcd for $C_{24}H_{18}O_7$: C, 68.90; H, 4.34. Found: C, 68.84; H, 4.45.

3.1.12. 3-Bromo-5,5-dimethoxycarbonyl-5,6,11,12-tetrahydro-6,11,12-trioxo-naphthacene (4g). Red needles; mp 272–273°C; IR ($CHCl_3$) 3035, 1790, 1700, 1590, 1285 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 6H, OCH_3), 7.72 (dd, J=8.4, 1.8 Hz, 1H, ArH), 7.82 (td, J=7.6, 1.1 Hz, 1H, ArH), 7.88 (td, J=7.6, 1.1 Hz, 1H, ArH), 8.06 (d, J=8.4 Hz, 1H, ArH), 8.12 (dd, J=7.6, 1.1 Hz, 1H, ArH), 8.17 (d, J=1.8 Hz, 1H, ArH) 8.21 (dd, J=7.6, 1.1 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 54.1(q), 56.0(s), 126.8(d), 127.1(d), 129.3(d), 129.7(s), 129.8(s), 130.4(d), 130.7(s), 130.9(s), 132.3(s), 133.3(d), 134.1(d), 135.0(s), 135.5(d), 148.1(s), 165.5(s), 181.3(s), 181.4(s), 185.1(s); Anal. Calcd for $C_{22}H_{13}BrO_7$: C, 56.31; H, 2.79. Found: C, 56.23; H, 3.02.

3.1.13. 3-Chloro-5,5-dimethoxycarbonyl-5,6,11,12-tetrahydro-6,11,12-trioxo-naphthacene (4h). Red crystals; mp 266–267°C; IR ($CHCl_3$) 3030, 1790, 1695, 1595, 1285 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 6H, OCH_3), 7.55 (dd, J=8.5, 1.9 Hz, 1H, ArH), 7.81 (td, J=7.5, 1.0 Hz, 1H, ArH), 7.88 (td, J=7.5, 1.0 Hz, 1H, ArH), 8.00 (d, J=1.9 Hz, 1H, ArH), 8.09–8.18 (m, 2H, ArH), 8.20 (dd, J=7.5, 1.0 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 54.0(q), 56.0(s), 126.7(d), 127.0(d), 127.4(d), 129.2(d), 129.4(s), 130.3(d), 130.7(s), 130.9(s), 132.2(s), 134.1(d), 135.0(s), 135.5(d), 140.9(s), 148.1(s), 165.5(s), 181.1(s), 181.4(s), 185.1(s); Anal. Calcd for $C_{22}H_{13}ClO_7$: C, 62.20; H, 3.08. Found: C, 62.06; H, 3.24.

3.1.14. 5-Ethoxycarbonyl-6,11-dihydro-6,11-dioxo-naphthacene (12a). Orange needles; mp 226–227°C; IR ($CHCl_3$) 3010, 1730, 1680, 1280, 1240 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.53 (t, J=7.2 Hz, 3H, CH_3), 4.73 (q, J=7.2 Hz, 2H, OCH_2), 7.70–7.76 (m, 2H, ArH), 7.79–7.84 (m, 2H, ArH), 7.97 (d, J=8.4 Hz, 1H, ArH), 8.12 (d, J=7.8 Hz, 1H, ArH), 8.33–8.39 (m, 2H, ArH), 8.93 (s, 1H, ArH); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 14.1(q), 62.3(t), 125.9(s), 126.7(d), 127.4(d), 127.7(d), 129.3(s), 129.7(d), 130.4(d), 130.8(d), 131.9(s), 133.9(s), 134.2(s), 134.4(d), 134.9(s), 135.0(s), 169.1(s), 182.2(s), 182.3(s); Anal. Calcd for $C_{21}H_{14}O_4$: C, 76.36; H, 4.27. Found: C, 76.43; H, 4.29.

3.1.15. 5-Ethoxycarbonyl-3-methyl-6,11-dihydro-6,11-dioxo-naphthacene (12b). Yellow needles; mp 258–260°C; IR ($CHCl_3$) 3010, 1725, 1675, 1330, 1270 $cm-^1$; ^1H NMR (600 MHz, $CDCl_3$) δ 1.54 (t, J=7.2 Hz, 3H, CH_3), 2.56 (s, 3H, CH_3), 4.74 (q, J=7.2 Hz, 2H, OCH_2), 7.52 (d, J=8.4 Hz, 1H, ArH), 7.70 (s, 1H, ArH), 7.78–7.83 (m, 2H, ArH), 8.00 (d, J=8.4 Hz, 1H, ArH), 8.31–8.37 (m, 2H, ArH), 8.86 (s, 1H, ArH); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 14.1(q), 22.2(q), 62.2(t), 125.6(d), 126.0(s), 127.4(d), 127.7(d), 128.5(s), 130.2(d), 130.6(d), 132.1(d), 132.2(s), 133.2(s), 133.9(s), 134.1(s), 134.2(d), 134.3(d), 141.2(s), 169.3(s), 182.29(s), 182.33(s); Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.59; H, 4.78.

3.1.16. 5-Ethoxycarbonyl-1-methyl-6,11-dihydro-6,11-dioxo-naphthacene (12c). Yellow needles; mp 275–276°C; IR ($CHCl_3$) 2985, 1730, 1675, 1280, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.52 (t, J=7.2 Hz, 3H,

CH_3), 2.86 (s, 3H, CH_3), 4.72 (q, J=7.2 Hz, 2H, OCH_2), 7.54 (d, J=7.5 Hz, 1H, ArH), 7.62 (t, J=7.5 Hz, 1H, ArH), 7.78–7.89 (m, 3H, ArH), 8.31–8.41 (m, 2H, ArH), 9.12 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1(q), 19.7(q), 62.3(t), 124.9(d), 125.5(s), 127.2(d), 127.4(d), 127.7(d), 128.7(s), 130.3(d), 130.5(d), 132.3(s), 133.9(s), 134.2(s), 134.3(s), 134.4(d), 135.3(s), 137.6(s), 169.4(s), 182.3(s), 182.5(s); Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.71; H, 4.76.

3.1.17. 5-Ethoxycarbonyl-3-methoxy-6,11-dihydro-6,11-dioxo-naphthacene (12d). Yellow needles; mp 239–240°C; IR ($CHCl_3$) 3010, 1730, 1675, 1620, 1585, 1240 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.53 (t, J=6.9 Hz, 3H, CH_3), 3.96 (s, 3H, OCH_3), 4.72 (q, J=6.9 Hz, 2H, OCH_2), 7.18 (d, J=2.1 Hz, 1H, ArH), 7.35 (dd, J=9.0, 2.1 Hz, 1H, ArH), 7.79–7.84 (m, 2H, ArH), 8.02 (d, J=9.0 Hz, 1H, ArH), 8.31–8.39 (m, 2H, ArH), 8.85 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3(q), 55.6(q), 62.2(t), 104.4(d), 123.0(d), 126.5(s), 127.4(d), 127.7(d), 130.5(s), 130.6(d), 132.0(d), 133.0(s), 133.8(s), 133.9(s), 134.1(s), 134.2(d), 134.4(d), 161.1(s), 169.5(s), 182.3(s), 182.6(s); Anal. Calcd for $C_{22}H_{16}O_5$: C, 73.33; H, 4.48. Found: C, 73.19; H, 4.57.

3.1.18. 5-Ethoxycarbonyl-2,4-dimethyl-6,11-dihydro-6,11-dioxo-naphthacene (12e). Yellow needles; mp 299–300°C; IR ($CHCl_3$) 2990, 1730, 1675, 1375, 1280 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (t, J=7.3 Hz, 3H, CH_3), 2.50 (s, 3H, CH_3), 2.78 (s, 3H, CH_3), 4.81–4.55 (m, 2H, OCH_2), 7.36 (s, 1H, ArH), 7.74 (s, 1H, ArH), 7.77–7.84 (m, 2H, ArH), 8.30–8.38 (m, 2H, ArH), 8.82 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8(q), 21.4(q), 21.5(q), 62.2(t), 126.3(s), 127.1(d), 127.9(d), 128.9(d), 129.4(s), 131.6(d), 133.6(s), 134.1(d), 134.3(d), 134.8(s), 136.3(d), 136.6(s), 136.8(s), 139.8(s), 171.2(s), 182.50(s), 182.54(s); Anal. Calcd for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found: C, 76.75; H, 5.20.

3.1.19. 5-Ethoxycarbonyl-1,3-dimethyl-6,11-dihydro-6,11-dioxo-naphthacene (12f). Yellow needles; mp 289–290°C; IR ($CHCl_3$) 3010, 1725, 1675, 1280, 1260 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (t, J=7.1 Hz, 3H, CH_3), 2.53 (s, 3H, CH_3), 2.83 (s, 3H, CH_3), 4.73 (q, J=7.1 Hz, 2H, OCH_2), 7.40 (s, 1H, ArH), 7.57 (s, 1H, ArH), 7.78–7.86 (m, 2H, ArH), 8.31–8.41 (m, 2H, ArH), 9.08 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.2(q), 19.6(q), 22.2(q), 62.2(t), 123.9(d), 125.7(s), 127.0(d), 127.4(d), 127.7(d), 128.1(s), 132.72(s), 132.75(s), 133.0(d), 134.0(s), 134.27(d), 134.33(d), 134.6(s), 137.4(s), 140.9(s), 169.7(s), 182.4(s), 182.6(s); Anal. Calcd for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found: C, 76.99; H, 5.07.

3.1.20. 3-Bromo-5-ethoxycarbonyl-6,11-dihydro-6,11-dioxo-naphthacene (12g). Yellow needles; mp 231–232°C; IR ($CHCl_3$) 2990, 1730, 1680, 1325, 1280 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.53 (t, J=7.2 Hz, 3H, CH_3), 4.73 (q, J=7.2 Hz, 2H, OCH_2), 7.78 (dd, J=8.7, 1.6 Hz, 1H, ArH), 7.81–7.85 (m, 2H, ArH), 7.98 (d, J=8.7 Hz, 1H, ArH), 8.10 (d, J=1.6 Hz, 1H, ArH), 8.32–8.38 (m, 2H, ArH), 8.88 (s, 1H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.1(q), 62.6(t), 125.4(s), 126.8(s), 127.5(d), 127.8(d), 129.0(d), 129.6(s), 130.6(d), 131.7(d), 132.9(s), 133.2(s), 133.3(d), 133.7(s), 133.9(s), 134.1(s), 134.5(d), 134.6(d), 168.6(s), 181.9(s), 182.0(s); Anal. Calcd for $C_{21}H_{13}BrO_4$: C, 61.63; H, 3.20. Found: C, 61.56; H, 3.47.

3.1.21. 3-Chloro-5-ethoxycarbonyl-6,11-dihydro-6,11-dioxo-naphthacene (12h). Yellow crystals; mp 252–253°C; IR ($CHCl_3$) 3010, 1730, 1675, 1325, 1280 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (t, J=7.2 Hz, 3H, CH_3), 4.74 (q, J=7.2 Hz, 2H, OCH_2), 7.61 (dd, J=8.8, 1.7 Hz, 1H, ArH), 7.79–7.85 (m, 2H, ArH), 7.89 (d, J=1.7 Hz, 1H, ArH), 8.03 (d, J=8.8 Hz, 1H, ArH), 8.29–8.36 (m, 2H, ArH), 8.85 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1(q), 62.5(t), 125.6(d), 126.7(s), 127.4(d), 127.7(d), 129.3(s), 130.5(d), 130.7(d), 131.7(d), 132.4(s), 132.9(s), 133.6(s), 133.8(s), 133.9(s), 134.48(d), 134.52(d), 136.8(s), 168.6(s), 181.8(s), 181.9(s); Anal. Calcd for $C_{21}H_{13}ClO_4$: C, 69.15; H, 3.59. Found: C, 69.08; H, 3.62.

3.1.22. 1-Bromo-5-ethoxycarbonyl-6,11-dihydro-6,11-dioxo-naphthacene (12i). Orange crystals; mp 243–244°C; IR ($CHCl_3$) 3010, 1730, 1680, 1280, 1255 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (t, J=7.2 Hz, 3H, CH_3), 4.72 (q, J=7.2 Hz, 2H, OCH_2), 7.58 (t, J=7.9 Hz, 1H, ArH), 7.80–7.89 (m, 2H, ArH), 7.94 (d, J=7.9 Hz, 1H, ArH), 8.02 (d, J=7.9 Hz, 1H, ArH), 8.31–8.37 (m, 1H, ArH), 8.37–8.44 (m, 1H, ArH), 9.35 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1(q), 62.5(t), 125.4(s), 126.49(d), 126.51(s), 127.6(d), 127.8(d), 130.2(d), 130.5(d), 133.2(s), 133.7(d), 133.8(s), 134.0(s), 134.5(d), 134.6(d), 135.3(s), 168.7(s), 181.88(s), 181.92(s); Anal. Calcd for $C_{21}H_{13}BrO_4$: C, 61.63; H, 3.20. Found: C, 61.49; H, 3.19.

3.1.23. 1-Chloro-5-ethoxycarbonyl-6,11-dihydro-6,11-dioxo-naphthacene (12j). Yellow crystals; mp 250–251°C; IR ($CHCl_3$) 3010, 1730, 1680, 1280, 1255 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (t, J=7.2 Hz, 3H, CH_3), 4.72 (q, J=7.2 Hz, 2H, OCH_2), 7.66 (t, J=8.0 Hz, 1H, ArH), 7.79–7.95 (m, 4H, ArH), 8.31–8.45 (m, 2H, ArH), 9.39 (s, 1H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.1(q), 62.5(t), 125.8(d), 126.6(s), 127.57(d), 127.60(d), 127.8(d), 129.9(d), 130.0(s), 130.2(d), 132.6(s), 133.1(s), 133.8(s), 134.0(s), 134.5(d), 134.6(d), 134.8(s), 135.3(s), 168.7(s), 181.9(s), 182.0(s); Anal. Calcd for $C_{21}H_{13}ClO_4$: C, 69.15; H, 3.59. Found: C, 68.98; H, 3.67.

3.1.24. 1,3-Dichloro-5-ethoxycarbonyl-6,11-dihydro-6,11-dioxo-naphthacene (12k). Yellow crystals; mp 243–244°C; IR ($CHCl_3$) 2990, 1730, 1680, 1280, 1250 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (t, J=7.2 Hz, 3H, CH_3), 4.72 (q, J=7.2 Hz, 2H, OCH_2), 7.77 (d, J=2.0 Hz, 1H, ArH), 7.81–7.88 (m, 3H, ArH), 8.30–8.41 (m, 2H, ArH), 9.30 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1(q), 62.7(t), 124.7(d), 127.4(d), 127.5(s), 127.6(d), 127.8(d), 130.1(s), 130.5(d), 130.9(s), 133.2(s), 133.6(s), 133.9(s), 134.3(s), 134.6(d), 134.7(d), 135.7(s), 136.0(s), 168.2(s), 181.5(s), 181.7(s); Anal. Calcd for $C_{21}H_{12}Cl_2O_4$: C, 63.18; H, 3.03. Found: C, 63.12; H, 3.12.

3.1.25. 3-Bromo-5-ethoxycarbonyl-1-methyl-6,11-dihydro-6,11-dioxo-naphthacene (12l). Yellow needles; mp

292–293°C; IR ($CHCl_3$) 1730, 1675, 1325, 1280 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.52 (t, J=7.2 Hz, 3H, CH_3), 2.85 (s, 3H, CH_3), 4.72 (q, J=7.2 Hz, 2H, OCH_2), 7.66 (s, 1H, ArH), 7.80–7.88 (m, 2H, ArH), 7.96 (s, 1H, ArH), 8.31–8.42 (m, 2H, ArH), 9.08 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1(q), 19.5(q), 62.5(t), 125.2(s), 126.5(s), 127.07(d), 127.13(d), 127.5(d), 127.8(d), 129.1(s), 132.9(s), 133.3(s), 133.7(s), 133.8(s), 134.1(s), 134.3(s), 134.5(d), 134.6(d), 139.5(s), 168.9(s), 182.1(s), 182.3(s); Anal. Calcd for $C_{22}H_{15}BrO_4$: C, 62.43; H, 3.57. Found: C, 62.24; H, 3.57.

3.1.26. 12-Methoxy-5,5-dimethoxycarbonyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (19a). Yellow crystals; mp 218–219°C; IR ($CHCl_3$) 2990, 1730, 1670, 1375, 1250 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.23 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 5.69 (s, 1H, OCH), 7.41–7.50 (m, 2H, ArH), 7.50–7.57 (m, 1H, ArH), 7.57–7.65 (m, 1H, ArH), 7.75–7.83 (m, 2H, ArH), 8.13–8.24 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 53.3(q), 53.7(q), 56.1(q), 59.1(s), 70.2 (d), 126.7(d), 127.1(d), 128.50(d), 128.54(d), 129.2(d), 129.4(d), 131.7(s), 131.9(s), 132.1(s), 133.4(s), 134.16(d), 134.23(d), 142.0(s), 144.0(s), 167.4(s), 169.4(s), 183.15(s), 183.20(s); Anal. Calcd for $C_{23}H_{18}O_7$: C, 67.96; H, 4.47. Found: C, 67.85; H, 4.65.

3.1.27. 12-Methoxy-5,5-dimethoxycarbonyl-3-methyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (19b). Yellow crystals; mp 207–209°C; IR ($CHCl_3$) 2950, 1740, 1670, 1600, 1295 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H, CH_3), 3.21 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 5.67 (s, 1H, OCH), 7.21–7.31 (m, 1H, ArH), 7.38–7.48 (m, 2H, ArH), 7.73–7.86 (m, 2H, ArH), 8.10–8.25 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.4(q), 53.2(q), 53.6(q), 55.8(q), 58.9(s), 69.8 (d), 126.6(d), 127.0(d), 128.7(d), 129.0(s), 129.2(d), 129.4(d), 131.7(s), 131.8(s), 133.0(s), 134.1(d), 134.2(d), 139.2(s), 141.9(s), 143.8(s), 167.4(s), 169.3(s), 183.17(s), 183.20(s); Anal. Calcd for $C_{24}H_{20}O_7$: C, 68.40; H, 5.02. Found: C, 68.12; H, 4.93.

3.1.28. 5,5-Diethoxycarbonyl-12-methoxy-1-methyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (19c). Yellow crystals; mp 167–168°C; IR ($CHCl_3$) 2985, 2930, 1735, 1670, 1295 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, J=7.2 Hz, 3H, CH_3), 1.16 (t, J=7.4 Hz, 3H, CH_3), 2.58 (s, 3H, CH_3), 3.09 (s, 3H, OCH_3), 4.08–4.31 (m, 4H, OCH_2), 6.13 (s, 1H, OCH), 7.27 (d, J=7.7 Hz, 1H, ArH), 7.33 (t, J=7.7 Hz, 1H, ArH), 7.52 (d, J=7.7 Hz, 1H, ArH), 7.76–7.85 (m, 2H, ArH), 8.13–8.25(m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7(q), 19.4(q), 54.7(q), 59.4(s), 62.3(t), 62.5(t), 66.0(d), 126.1 (d), 126.7(d), 126.8(d), 128.6(d), 130.4(s), 130.7(d), 131.6(s), 131.8(s), 133.5(s), 134.1(d), 137.7(s), 141.3(s), 144.7(s), 166.9(s), 168.8(s), 183.0(s), 183.6(s); Anal. Calcd for $C_{26}H_{24}O_7$: C, 69.62; H, 5.40. Found: C, 69.35; H, 5.38.

3.1.29. 3,12-Dimethoxy-5,5-dimethoxycarbonyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (19d). Orange crystals; mp 196–198°C; IR ($CHCl_3$) 2955, 2925, 1735, 1670, 1245 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.19 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 5.67 (s, 1H, OCH), 6.98 (dd, J=8.4, 2.4 Hz, 1H, ArH), 7.16 (d, J=2.4 Hz, 1H, ArH), 7.46 (d, J=8.4 Hz, 1H, ArH), 7.75–7.83 (m, 2H, ArH), 8.12–8.23 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 53.3(q), 53.7(q), 55.5(q), 55.6(q), 59.0(s), 69.6(d), 113.6(d), 114.6(d), 124.3(s), 126.7(d), 127.0(d), 130.5(d), 131.7(s), 131.8(s), 134.1(d), 134.2(d), 134.4(s), 142.0(s), 143.7(s), 160.0(s), 167.2(s), 169.2(s), 183.2 (s); Anal. Calcd for $C_{24}H_{20}O_8$: C, 66.04; H, 4.62. Found: C, 65.91; H, 4.77.

3.1.30. 12-Methoxy-5,5-dimethoxycarbonyl-2,4-dimethyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (19e). Orange crystals; mp 172–173°C; IR ($CHCl_3$) 3010, 2960, 1735, 1670, 1285 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 3.17 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 5.51 (s, 1H, OCH), 7.10 (s, 1H, ArH), 7.13 (s, 1H, ArH), 7.74–7.81 (m, 2H, ArH), 8.12–8.19 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.6(q), 20.8(q), 53.2(q), 53.6(q), 56.4(q), 60.0(s), 71.4(d), 126.3(d), 127.2(d), 128.2(d), 131.1(s), 131.2(s), 132.2(s), 133.5(s), 134.0(d), 134.2(d), 134.5(d), 137.8(s), 138.7(s), 143.5(s), 145.8(s), 167.9(s), 170.9(s), 182.9(s), 183.0(s); Anal. Calcd for $C_{25}H_{22}O_7$: C, 69.10; H, 5.11. Found: C, 68.94; H, 5.18.

3.1.31. 3-Chloro-5,5-diethoxycarbonyl-12-methoxy-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (19h). Yellow crystals; mp 187–188°C; IR ($CHCl_3$) 2990, 1735, 1670, 1600, 1290 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, J=7.0 Hz, 3H, CH_3), 1.19 (t, J=7.0 Hz, 3H, CH_3), 3.19 (s, 3H, OCH_3), 4.16 (q, J=7.0 Hz, 2H, OCH_2), 4.21–4.34 (m, 2H, OCH_2), 5.69 (s, 1H, OCH), 7.41 (dd, J=1.9, 8.2 Hz, 1H, ArH), 7.48 (d, J=8.2 Hz, 1H, ArH), 7.66 (d, J=1.9 Hz, 1H, ArH), 7.76–7.85 (m, 2H, ArH), 8.12–8.25(m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.69(q), 13.73(q), 55.7(q), 59.1(s), 62.6(t), 62.8(t), 69.5(d), 126.7 (d), 127.0(d), 128.6(d), 128.8(d), 130.5(d), 130.6(s), 131.6(s), 131.8(s), 134.2(d), 135.0(s), 135.2(s), 141.2(s), 143.7(s), 166.2(s), 168.3(s), 182.9(s), 183.1(s); Anal. Calcd for $C_{25}H_{21}ClO_7$: C, 64.09; H, 4.52. Found: C, 63.99; H, 4.68.

3.1.32. 1-Chloro-5,5-diethoxycarbonyl-12-methoxy-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (19j). Yellow crystals; mp 143–145°C; IR ($CHCl_3$) 2990, 1740, 1670, 1595, 1295 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.44 (t, J=7.2 Hz, 3H, CH_3), 1.18 (t, J=7.3 Hz, 3H, CH_3), 3.33 (s, 3H, OCH_3), 4.08–4.34 (m, 4H, OCH_2), 6.26 (s, 1H, OCH), 7.37 (t, J=7.9 Hz, 1H, ArH), 7.49 (d, J=7.9 Hz, 1H, ArH), 7.51 (d, J=7.9 Hz, 1H, ArH), 7.76–7.85 (m, 2H, ArH), 8.12–8.27(m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.67(q), 13.72(q), 57.3(q), 59.3(s), 62.5(t), 62.8(t), 66.5(d), 126.7 (d), 126.9(d), 127.3(d), 129.56(d), 129.60(d), 131.0(s), 131.5(s), 131.8(s), 134.2(d), 134.6(s), 136.2(s), 141.6(s), 144.0(s), 166.4(s), 168.8(s), 182.8(s), 183.1(s); Anal. Calcd for $C_{25}H_{21}ClO_7$: C, 64.09; H, 4.52. Found: C, 64.02; H, 4.69.

3.1.33. 12-Hydroxy-5,5-dimethoxycarbonyl-1-methyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (20c). Yellow powder; mp 258–260°C; IR ($CHCl_3$) 3510, 2990, 1765, 1730, 1250 cm^{-1}; ^1H NMR (600 MHz, DMSO) δ 2.52 (s, 3H, CH_3), 3.54 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 5.89 (s, 1H, OH), 6.02 (s, 1H, OCH), 7.26–7.34

(m, 3H, ArH), 7.91–7.98 (m, 2H, ArH), 8.07–8.11 (m, 1H, ArH), 8.11–8.14 (m, 1H, ArH); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 18.8(q), 53.0(q), 53.5(q), 57.5(d), 58.5(s), 125.7(d), 126.4(d), 126.7(d), 128.1(d), 130.5(d), 131.2(s), 131.5(s), 132.2(s), 133.6(s), 134.9(d), 135.1(d), 137.3(s), 140.9(s), 143.3(s), 167.0(s), 169.0(s), 182.9(s), 183.4(s); Anal. Calcd for $C_{23}H_{18}O_7$: C, 67.96; H, 4.47. Found: C, 67.87; H, 4.50.

3.1.34. 3-Bromo-12-hydroxy-5,5-dimethoxycarbonyl-1-methyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (20h). Yellow powder; mp 274–276°C; IR ($CHCl_3$) 3520, 2955, 1775, 1735, 1670, 1295 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 3H, CH_3), 2.88 (d, J=5.8 Hz, 1H, OH) 3.69 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 6.09 (d, J=5.8 Hz, 1H, OCH), 7.44 (s, 1H, ArH), 7.78 (s, 1H, ArH), 7.79–7.86 (m, 2H, ArH), 8.12–8.18 (m, 1H, ArH), 8.18–8.25 (m, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.3(q), 53.5(q), 54.0(q), 57.4(s), 60.0(d), 123.0(s), 126.7(d), 127.1(d), 128.1(d), 130.2(s), 131.65(s), 131.74(s), 132.7(s), 134.4(d), 134.5(d), 140.9(s), 140.99(s), 141.04(s), 167.1(s), 168.0(s), 183.6(s), 184.7(s); Anal. Calcd for $C_{23}H_{17}BrO_7$: C, 57.02; H, 3.54. Found: C, 56.80; H, 3.63.

3.1.35. 1-Bromo-12-hydroxy-4-Methoxy-5,5-dimethoxycarbonyl-5,6,11,12-tetrahydro-6,11-dioxo-naphthacene (20i). Yellow crystals; mp 252–254°C; IR ($CHCl_3$) 3585, 2955, 1735, 1675, 1290 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (d, J=5.1 Hz, 1H, OH), 3.69 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 6.42 (d, J=5.1 Hz, 1H, OCH), 6.91 (d, J=8.8 Hz, 1H, ArH), 7.63 (d, J=8.8 Hz, 1H, ArH), 7.73–7.82 (m, 2H, ArH), 8.11–8.19 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 53.2(q), 53.9(q), 57.1(q), 57.9(s), 62.6(d), 114.7(d), 115.8(s), 126.1(s), 126.4(d), 127.2(d), 131.2(s), 132.2(s), 134.1(d), 134.3(d), 134.6(s), 142.7(s), 143.5(s), 157.2(s), 167.6(s), 170.0(s), 182.7(s), 183.2(s); Anal. Calcd for $C_{23}H_{17}BrO_8$: C, 55.20; H, 3.43. Found: C, 55.04; H, 3.41.

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