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Synthesis of dihydrofuro- and *C*-alkenylated naphthoquinones catalyzed by manganese(III) acetate

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The easily synthesis of dihydrofuronaphthoquinones and *C*-alkenylated naphthoquinones has been investigated through the radical oxidative cyclization of 2-hydroxy-1,4-naphthoquinones and thiophene or furan substituted alkenes catalyzed by manganese(III) acetate. The corresponding heteroaryl substituted dihydrofurans and naphthoquinones have been isolated in good yields.

Introduction

Free radical reactions by using transition metal salts, such as manganese, cerium and cobalt, for the formation of carbon-carbon bonds have become more and more important in organic syntheses during the last decades, mainly because of their selective, specific, and mild reaction facilities.[1] One of the well-known examples of this application is the manganese(III) acetate mediated free radical reaction. This reaction has emerged as an important synthetic method for the formation of highly functionalized products such as furans,[2] dihydrofurans,[3] lactones,[4] lactams,[5] and natural products.[6]

Compounds containing the quinone moiety represents an important class of biologically active molecules which are widespread in nature.[7] Many natural and synthetic naphthoquinones are known as potential antitumor,[8] tripanocidal,[9] molluscicidal,[10] leishmanicidal,[11] antibacterial[12] and antitubercular[13] agents.

Dihydrofuro- and *C*-alkenylated naphthoquinones have recently gained considerable interest due to their useful application in the synthesis of a huge variety of valuable compounds.[1,15] The present study reports the easily synthesis of these compounds by using $Mn(OAc)_3$ as catalyst.

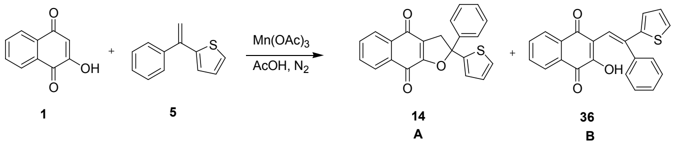
On the basis of these considerations, in the present contribution we have evaluated the possibility to develop the reaction between 2-hydroxy-1,4-naphthoquinones **(1-4)** and hetereoaromatic substituted alkenes (**5-13**) in the presence of $Mn(OAc)_3$ as catalyst and in acetic acid as medium.

Results and discussion

In order to find the best reaction conditions, at first we have analyzed three parameters, namely the reagent molar ratio, the reaction temperature and the reaction time, by using 2-hydroxy-1,4-naphthoquinone **1** and 2-(1-phenylethenyl)thiophene **5** as model reagents. Concerning the first parameter examined, after having performed the reaction with different **1** / **5** / $Mn(OAc)_3$ molar ratios in acetic acid for 10 minutes at 65°C, the best yield in product **14** (77%) was obtained by using 1 / 1.25 / 2.5 molar ratio.

Then the variation of the yield with respect to reaction temperature and time was studied (Table 1); the best result in term of yield and selectivity in dihydrofuronaphthoquinone **14** was obtained at 65 °C for 5 minutes (Table 1, entry 2). A further increase of the temperature (up to 95 °C) or of the reaction time (up to 60 minutes) resulted in lower yield and selectivity values (Table 1, entries 7-9 and 3-5 respectively).

Table 1. The experimental results of the reactions between **1** and **5** catalyzed by $Mn(OAc)_3$.

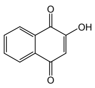
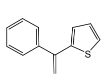
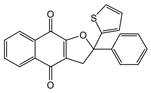
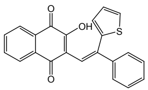
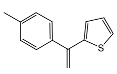
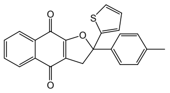
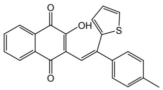
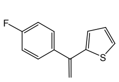
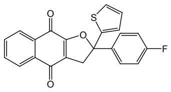
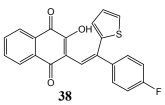
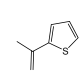
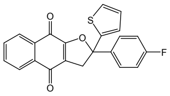
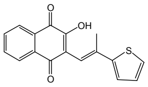


Entry	Time (min)	Temperature (°C)	Yield (%)	
			14	**36**
1	1	65	74	-
2	5	65	76	-
3	10	65	77	9
4	20	65	71	11
5	60	65	70	18
6	1440	65	1	60
7	5	75	75	-
8	5	85	73	-
9	5	95	73	-
10	120	75	30	32
11	120	85	17	46
12	120	95	-	57

Interestingly, by carrying out the reaction at 65 °C for longer reaction times (24 hours), the *C*-alkenylated naphthoquinone **36**, deriving from dihydrofuronaphthoquinone **14**, was formed in 60% yield with and 98% selectivity (Table 1, entry 6). The same good result can be obtained by increasing the temperature to 95 °C and by decreasing the reaction time to 2 hours (Table 1, entry 12).

By using 2-hydroxy-1,4-naphthoquinone **1** the process was then extended to various 1,1-disubstitued alkenes **5-8** by carrying out the reaction in acetic acid in the presence of $Mn(OAc)_3$ at 65 °C for 10 minutes; results are shown in Table 2.

Table 2. The results of 10 minutes reactions of **1** with **5-8** catalyzed by $Mn(OAc)_3$ at 65°C in AcOH.

2-Hydroxy naphthoquinone	Alkene	Products		Yield, % **A***(**B***)
		cyclization **A**	elimination **B**	
 1	 5	 14	 36	77 (9)
	 6	 15	 37	86 (10)
	 7	 16	 38	89 (9)
	 8	 17	 39	51 (11)

*Yields were determined from the results of 10 minutes reaction.

Under these conditions dihydrofuronaphthoquinones **14-17** were isolated in good yields (up to 89%) in a very short reaction time. The highest yields were observed by using electronrich 1,1-disubstituted alkenes, probably because the stability of carbocation intermediate is increased by the presence of electrondonating substituents. The yields of products **36-39** were lower (9-11%), but they can be increased up to ~75 % by increasing the reaction time to 24 hours (Table 3). Interestingly, ^{1}H NMR spectra of products **36-39** showed that they are obtained as cis-trans (*Z-E*) mixtures except for product **39** that was obtained as a single E isomer; this is probably due to the larger size of the thiophene group with respect to the methyl one.

Table 3. Results of the reaction reactions of **1** with **5-8** catalyzed by $Mn(OAc)_3$ at 65°C in AcOH for 24 hours.

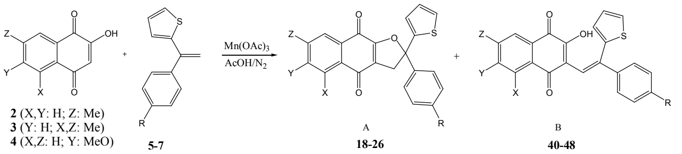
Entry	2-Hydroxy naphthoquinone	Alkene	Time (h)	**A**(%)	**B**(%)	**B** *Z-E* ratio
1	1	5	24	**14**(<1)	**36**(60)	1/2.7
2	1	6	24	**15**(<1)	**37**(75)	1/2.2
3	1	7	24	**16**(<1)	**38**(74)	1/3.1
4	1	8	24	**17**(<1)	**39**(29)	-

#Calculated from ^{1}H NMR spectra

The reaction was also extended to various 2-hydroxy-1,4-naphthoquinones **2-4** with 1,1-disubstituted alkenes **5-7** (Table 4). After 5 minutes the dihydrofuronaphthoquinones **18-26** are the sole reaction products and can be isolated in 64-86% yield; the best results are gained when a fluorine atom is present on the aromatic ring of the alkene.

By performing the reaction for 24 hours, the corresponding *C*-alkenylated naphthoquinones **40-48** can also be isolated in 47-80% yield and <99% selectivity.

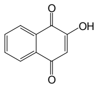
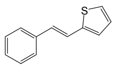
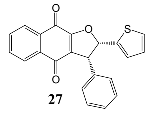
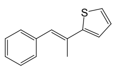
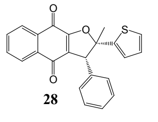
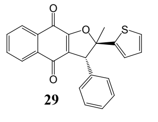
Table 4. The reactions of **5-7** with **2-4** catalyzed by $Mn(OAc)_3$.



Entry	X	Y	Z	R	Time (min)	**A**(%)	**B**(%)	**B** *Z-E* ratio
1	H	H	Me	H	5	**18**(66)	-	-
2	Me	H	Me	H	5	**19**(64)	-	-
3	H	MeO	H	H	5	**20**(72)	-	-
4	H	H	Me	Me	5	**21**(73)	-	-
5	Me	H	Me	Me	5	**22**(69)	-	-
6	H	MeO	H	Me	5	**23**(81)	-	-
7	H	H	Me	F	5	**24**(79)	-	-
8	Me	H	Me	F	5	**25**(73)	-	-
9	H	MeO	H	F	5	**26**(86)	-	-
10	H	H	Me	H	24h	**18**(<1)	**40**(47)	1/2.3
11	Me	H	Me	H	24h	**19**(<1)	**41**(57)	1/2.5
12	H	MeO	H	H	24h	**20**(<1)	**42**(69)	1/2
13	H	H	Me	Me	24h	**21**(<1)	**43**(49)	1/2.2
14	Me	H	Me	Me	24h	**22**(<1)	**44**(60)	1/2.3
15	H	MeO	H	Me	24h	**23**(<1)	**45**(77)	1/2
16	H	H	Me	F	24h	**24**(<1)	**46**(70)	1/3
17	Me	H	Me	F	24h	**25**(<1)	**47**(69)	1/3
18	H	MeO	H	F	24h	**26**(<1)	**48**(80)	1/3

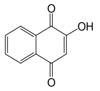
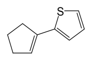
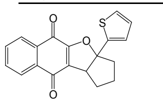
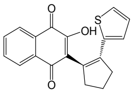
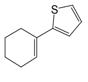
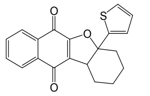
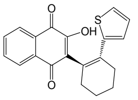
2-Hydroxy-1,4-naphthoquinone (**1**) was also reacted with 2-[(*E*)-2-phenylethenyl]thiophene (**9**) and only dihydrofuran product **27** was obtained in 56% yield (Table 5). From the coupling constant value between H4 and H5 (*J*= 6.0 Hz) it was deduced that the phenyl and 2-thienyl moieties are in the *cis* configuration in the 4,5-dihydro-4-phenyl-5-(2-thienyl)furan.[17] On the contrary, two different dihydrofurans were obtained by reaction of 2-hydroxy-1,4-naphthoquinone (**1**) with 2-(1-methyl-2-phenyl-vinyl)-thiophene (**10**) (Table 5); in this case too the alkenylnaphtoquinone was not isolated. The determination of dihydrofuran structures (**28, 29**) was realized by HSQC measurement: the proton at ~5 ppm was determined to be on C(4). This indicates that the phenyl group is on C(4) and the 2-thienyl and methyl groups are on C(5) of the dihydrofuran moiety.

Table 5. The reactions of **1** with **9-10** catalyzed by $Mn(OAc)_3$ at 65° C in AcOH.

2-Hydroxy naphthoquinone	Alkene	Product	Yield, % **A***
		cyclization **A**	
 1	 9	 27	56
	 10	 28  29	37, 13

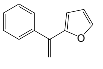
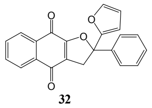
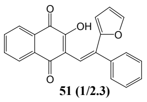
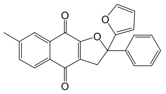
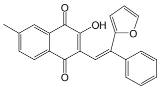
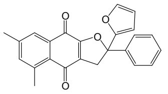
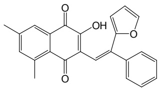
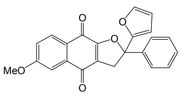
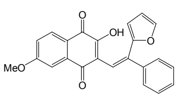
Substituted cyclic alkenes **11** and **12** were also utilized in the reaction with 2-hydroxy-1,4-naphthoquinone **1**. In this case dihydronaphtoquinones **30** and **31** and alkenylnaphtoquinones **49** and **50**) were isolated as single *trans* isomers (Table 6).

Table 6. The reactions of **1** with **11-12** catalyzed by Mn(OAc)$_3$ at 65°C in AcOH.

2-Hydroxy naphthoquinone	Alkene	Product		Yield, % **A** (**B**)
		cyclization **A**	elimination **B**	
 **1**	 **11**	 **30**	 **49**	**37 (12)**
	 **12**	 **31**	 **50**	**52 (3)**

In order to evaluate the influence on the yield of the presence of thiophene and furane rings on the alkene moiety, the reactions between 2-hydroxy-1,4-naphthoquinones **1-4** and 2-(1-phenylvinyl)furane **13** were performed. Dihydrofurans **32-35** were obtained in moderate yields (54-62%), whereas alkenylnaphthoquinones **51-54** were formed as a isomeric mixture (~1/2.5) in >50% yield. In must be underlined that the yields obtained with the thiophene substituted alkenes are higher than those obtained with the furan substituted ones.

Table 7. The reactions of 2-(1phenylvinyl)furane (**13**) with **1-4** catalyzed Mn(OAc)$_3$ in different rection times.

Alkene	2-Hydroxy naphthoquinone	Products		Yield, % **A*** (**B**$^\#$)
		cyclization **A**	*elimination* **B** (*E/Z* ratio)	
 **13**	1	 **32**	 **51 (1/2.3)**	**62 (55)**
	2	 **33**	 **52 (1/2.2)**	**57 (50)**
	3	 **34**	 **53 (1/2.7)**	**54 (53)**
	4	 **35**	 **54 (1/2.4)**	**59 (57)**

*Yields for compounds **A** (**32-35)** were calculated from the results of 10 minutes reaction. $^\#$Yields for compounds **B** (**51-54)** were calculated from the results of 24 hours reaction.

On the basis of the above reported results, a plausible mechanism for the formation of dihydrofuran and elimination products is shown in Scheme 1. According to this mechanism, the reaction of 2-hydroxy-1,4-naphthoquinone **1** with alkene **2** catalyzed by Mn(OAc)$_3$ produces a carbon-radical **X**. This radical **X** is in turn oxidized to the carbocation **Y** by one equivalent of Mn(OAc)$_3$, followed by cyclization and proton elimination to give dihydrofuronaphtho-4,9-diones **A**. Concerning the formation of 3-alkenyl-2-hydroxy-1,4-naphthoquinone **B**, it can be obtained either through H$^+$ elimination from carbocation **Y** or by ring opening of dihydrofuronaphtho-4,9-diones **A** and then H$^+$ elimination.

Dihydrofuronaphthoquinone is the sole product at beginning of the reactions (ca. 5 min.); however *C*-alkenylated product is formed at prolonged reaction times and at high temperatures. Therefore the formation of dihydrofuronaphthoquinones is an equilibrium: by increasing reaction temperature and time, the equilibrium can be shifted through the formation of the *C*-alkenylated product.

Finally, it must be underlined that in a previous work,[15] only the dihydrofuran product was obtained as a result of the reaction of **1** with 1,1-diphenyl ethylene; indeed in the present work both dihydrofuran and *C*-alkenylated (elimination) products were synthesized in the reactions of **1-4** with heteroaromatic substituted alkenes (**5-13**). On the basis of ^{1}H NMR spectra of cyclization products **A,** it has been possible to identify a *cis-trans* isomeric mixture; one of these isomers was finally confirmed by X-ray crystallography and an ORTEP view is reported in Figure 1 together with the atomic labeling scheme and a list of the most important bond distances and angles.

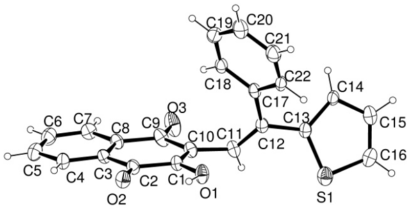


Figure 1. ORTEP view of compound **36** together with the atomic labeling scheme. Ellipsoids are drawn at their 50% probability level. Most important bond distances (Å) and angles (°): C1-O1 1.336(2), C2-O2 1.221(2), C9-O3 1.202(3), C10-C11 1.477(3), C11-C12 1.318(3), C12-C17 1.510(3), C12-C13 1.511(3); C12-C11-C10 127.4(2), C11-C12-C17124.32(19),C11-C12-C13 120.4(2), C17-C12-C13 115.20(17). Cambridge Crystallographic Data Centre the deposition number CCDC 883886.

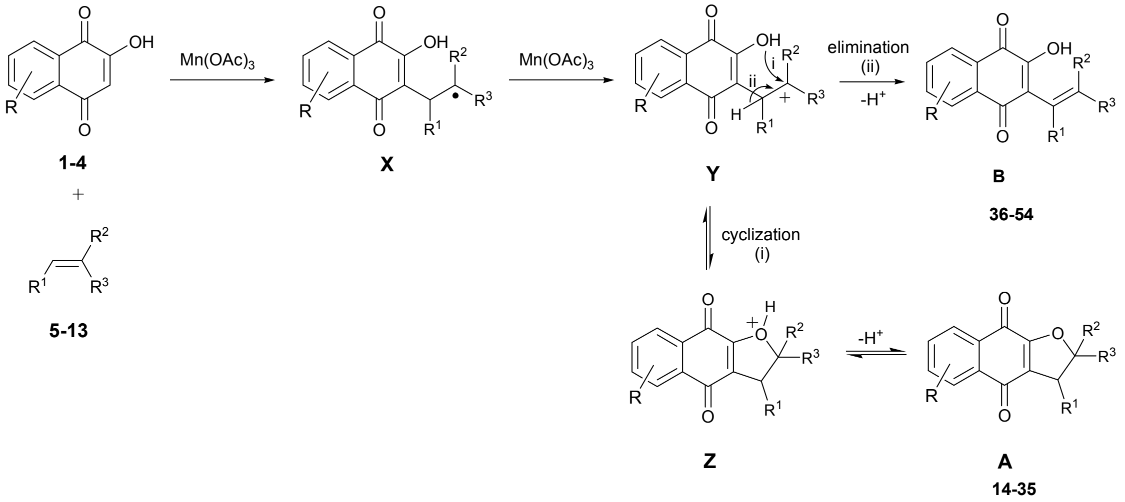
In the molecular structure of compound **36** the alkenyl group defined by atoms C10, C11, H11, C12, C13, C17 is planar. The mean planes of the phenylic, thiophenic and naphtoquinone substituents form dihedral angles of 44.15(4)°, 38.34(4)° and 70.50(5)° respectively with the alkenyl mean plane. In the crystal packing of compound **36**, two molecules are linked by hydrogen bonds between the hydroxylic and the quinonic oxygen atoms forming a dimer. In particular the O1···O2 distance is 2.900(4) Å and O1-H1···O2 angle is 148.11(3)°.

Conclusions

We have described a simple, convenient and efficient preparation of polyfunctionalized dihydrofuronaphtho-4,9-diones (**14-35**) and 3-alkenyl-2-hydroxy-1,4-naphthoquinones (**36-54**). The simplicity of the procedure, the mildness of the reaction conditions and the good yields represent significant improvement. Effects of temperature, reaction time and substituent over product formation were studied, and complementary studies are in progress in order to explain different product formation and to extend the reaction to other substrates.

Experimental

2-Hydroxy-1,4-naphthoquinone **1** is an available commercial product and has been used in high purity. 2-Hydroxy-1,4-naphthoquinone derivatives **2-4** are synthesized using suitable starting materials.[18,19] The conjugated alkenes **5-13** were prepared by dehydration reaction from the carbinole formed by



Scheme 1. The mechanism for formation of cyclization and C-alkylated products.

Grignard reaction of arylmagnesium bromide and suitable carbonyl compounds.[20] 2-Isopropenylthiophene **8** was prepared by reaction of triphenylphosphoniummethyl bromide and 2-acetylthiophene in NaH/THF.[21] All conjugated alkenes were freshly prepared before use in the radical cyclization reactions. Radical reactions were performed at 1:1.25:2.5 molar ratio [naphthoquinone:alkene:Mn(OAc)$_3$] under nitrogen atmosphere in AcOH. All compounds were purified by column chromatography or preparative TLC and were characterized by IR, ^{1}H - ^{13}C NMR, mass spectra and microanalyses.

Melting points were determined on an electrothermal capillary melting point apparatus. IR spectra (KBr disc, CHCl$_3$) were obtained with a Matson 1000 FT-IR in the 400–4000 cm^{-1} range with 4 cm^{-1} resolution. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX-400 MHz and Varian Mercury-400 High performance Digital FT-NMR spectrophotometers. Mass spectra were measured on a Waters 2695 Alliance Micromass ZQ (ESI$^+$) LC/MS and Agilent Technologies 6890 N Network GC System spectrophotometer. Elemental analyses were performed on a VarioEL III CHNS instrument. Thin layer chromatography (TLC) was performed on Merck aluminium-packed silica gel plates. Purification of the products was performed by column chromatography on silica gel (Merck silica gel 60, 40–63 µm) or preparative TLC on silica gel of Merck (PF$_{254–366nm}$).

Reaction of naphthoquinones with alkenes catalyzed by Mn(OAc)$_3$: General procedure.

A solution of Mn(OAc)$_3$ (0.67 g, 2.5 mmol) in 10 mL of glacial AcOH was heated under N$_2$ at 80 °C, until dissolution. Then the solution was cooled to 65 °C, and a solution of 1,4-naphthoquinone (1 mmol) and alkene (1.25 mmol) in AcOH (5 mL) was added. The reaction was completed at 10 minutes (or 24 hours). Then, distilled water (20 mL) was added, and the mixture was extracted with CHCl$_3$ (3x20 mL). The combined organic phases were neutralized with sat. NaHCO$_3$, dried (anhy. Na$_2$SO$_4$) and evaporated. Crude products were purified by column chromatography on silica gel with hexane/EtOAc 5:1 as eluent.

2-Phenyl-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (14). Yellow solid; mp 172-173 °C; IR (KBr, cm^{-1}): 3110, 3004, 2910, 1680 (C=O), 1651(C=O), 1627, 1200 (C-O-C), 952, 717; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.11 (dd, *J* = 7.6 and 1.6 Hz, 1H), 8.07 (dd, *J* = 7.6 and 1.6 Hz, 1H), 7.72 (td, *J* = 7.6 and 1.6 Hz, 1H), 7.68 (td, *J* = 7.6 and 1.6 Hz, 1H), 7.30 (dd, *J* = 6.8 and 1.6 Hz, 2H), 7.37 (m, 3H), 7.32 (dd, *J* = 5.2 and 1.2 Hz, 1H), 6.97 (dd, *J* = 3.6 and 1.2 Hz, 1H), 6.95 (dd, *J* = 5.2 and 3.6 Hz, 1H), 4.07 (d, *J* = 17.2 Hz, 1H), 3.84 (d, *J* = 17.2 Hz, 1H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 182.3, 177.8, 158.4, 147.5, 143.5, 134.4, 133.3, 133.2, 131.9, 128.9, 128.7, 127.1, 127.0, 126.8, 126.6, 126.3, 125.6, 123.6, 94.1, 43.5; LC/MS (ESI, m/z): 359.07 (MH$^+$, 100). Anal. Calcd for $C_{22}H_{14}O_3S$: C,73.72; H, 3.94; S, 8.95. Found: C, 73.82; H, 4.01; S, 8.92.

2-Hydroxy-3-[(*E* and *Z*)-2-phenyl-2-(2-thiophenyl)ethenyl] naphthalene-1,4-dione (36). Red solid; mp 185-186 °C; IR (KBr, cm^{-1}): 3359, 2917, 1654 (C=O), 1646 (C=O), 1277 (C-O-C), 1027, 958, 698; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.02 (d, *J* = 7.2 Hz, 2H) [8.08 (dd, *J* = 7.6 and 1.6 Hz, 2H)], 7.73 (td, *J* = 7.6 and 1.2 Hz, 1H) [7,69- 7.78 (m, 2H)], 7.66 (td, *J* = 7.6 and 1.6 Hz, 1H), 7.48 (dd, *J* = 7.6 and 2.0 Hz, 1H), 7.37 (dd, *J* = 4.8 and 1.6 Hz, 1H), 7.25-7.31 (m, 4H), 6.99 (dd, *J* = 4.8 and 3.6 Hz, 1H), 6.92 (dd, *J* = 3.6 and 1.2 Hz, 1H) [6.93 (dd, *J* = 3.6 and 0.8 Hz, 1H)], 6.88 (s, 1H) [6.61 (s, 1H)], LC/MS, (ESI, m/z): 359.25 (MH$^+$,100). Anal. Calcd for $C_{22}H_{14}O_3S$: C,73.72; H, 3.94; S, 8.95. Found: C, 73.55; H, 4.07; S, 9.03.

2-(4-Methylphenyl)-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (15). Yellow solid; mp 165-166 °C; IR (KBr, cm^{-1}): 3098, 2972, 1679 (C=O), 1657(C=O), 1638, 1201 (C-O-C), 955, 703; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.10 (dd, *J* = 7.6 and 1.6 Hz, 1H), 8.06 (dd, *J* = 7.6 and 1.6 Hz, 1H), 7.72 (td, *J* = 7.6 and 1.6 Hz, 1H), 7.68 (td, *J* = 7.6 and 1.6 Hz, 1H), 7.41 (d, *J* = 8 Hz, 2H), 7.31 (dd, *J* = 4.8 and 1.2 Hz, 1H), 7.19 (d, *J* = 8 Hz, 2H), 6.97 (dd, *J* = 3.6 and 1.2 Hz, 1H), 6.94 (dd, *J* = 4.8 and 3.6 Hz, 1H), 4.03 (d, *J* = 17.2 Hz, 1H), 3.82 (d, *J* = 17.2 Hz, 1H), 2.35 (s, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 182.4, 177.8, 158.4, 147.7, 140.5, 138.6, 134.4, 133.3, 133.2, 131.9, 129.4, 127.0, 126.7, 126.6, 126.3, 125.6, 123.7, 94.1, 43.4, 21.3; GC/MS (m/z, %): 372.1 (M$^+$, 100). Anal. Calcd for $C_{23}H_{16}O_3S$: C,74.17; H, 4.33; S, 8.61. Found: C, 74.14; H, 4.30; S, 8.56.

2-Hydroxy-3-[(*E(and)Z*)-2-(4-methylphenyl-2-(2-thiophenyl) ethenyl]naphthalene-1,4-dione (37). Red solid; mp 192-194 °C; IR (KBr, cm^{-1}): 3340, 2986, 1657 (C=O), 1652(C=O), 1375, 1274 (C-O-C), 1022, 728, 666; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.04 (t, *J* = 7.6 Hz, 2H) [8.07 (d, *J* = 7.6 Hz, 1H), 8.09 (d, *J* = 7.6 Hz, 1H)], 7.74 (t, *J* = 7.6 Hz, 1H) [7,69- 7.77 (m, 2H)], 7.68 (t, *J* = 7.6 Hz, 1H), [7.37 (d, *J* = 8.0 Hz, 2H)], 7.30 (d, *J* = 4.8 Hz, 1H) [7,27 (d, *J* = 3.6 Hz, 1H)], 7.20 (d, *J* = 8.0 Hz, 2H), [7.17 (d, *J* = 8.0 Hz, 2H)], 7.06 (d, *J* = 8.0 Hz, 2H), 6.99 (dd, *J* = 4.8 ve 3.6 Hz, 1H), 6.95 (d, *J* = 3.6 Hz, 1H) [6.93 (d, *J* = 3.6 Hz, 1H)], 6.85 (s, 1H) [6.60 (s, 1H)], 2.32 (s, 3H) [2.40 (s, 3H)]; GC/MS (m/z, %): 372.1 (M$^+$, 100). Anal. Calcd for $C_{23}H_{16}O_3S$: C,74.17; H, 4.33; S, 8.61. Found: C, 74.29; H, 4.26; S, 8.73.

2-(4-Flourophenyl)-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (16). Yellow solid; mp 160-161 °C; IR (KBr, cm^{-1}): 3098, 3066, 1678 (C=O), 1655(C=O), 1638, 1582, 1204 (C-O-C), 956, 713; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.10 (dd, *J* = 7.6 and 1.6 Hz, 1H), 8.06 (dd, *J* = 7.6 and 1.6 Hz, 1H), 7.72 (td, *J* = 7.6 and 1.6 Hz, 1H), 7.68 (td, *J* = 7.6 and 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.8 and 4.8 and 1.6 Hz, 2H), 7.33 (dd, *J* = 4.8 and 1.6 Hz, 1H), 7.07 (t, *J* = 8.8 Hz, 2H), 6.94-6.97 (m, 2H), 4.05 (d, *J* = 17.2 Hz, 1H), 3.78 (d, *J* = 17.2 Hz, 1H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 182.3, 177.7, 164.0, 161.6, 158.2, 147.3, 139.3, 134.4, 133.3, 131.9-133.2 (C$_{ipso}$, i, J= 126.5 Hz), 127.6 (C$_{meta}$, i, J= 8.4 Hz), 127.2, 127.1, 126.8, 126.6, 123.5, 115.7 (C$_{orto}$, i, J= 21.4 Hz), 93.6, 43.5; GC/MS, (m/z, %) : 376.0 (M$^+$, 100).). Anal. Calcd for $C_{22}H_{13}FO_3S$: C,70.20; H, 3.48; S, 8.52. Found: C, 70.17; H, 3.46; S, 8.48.

2-[(*E(and)Z*)-2-(4-flourophenyl)-2-(2-thiophenyl)ethenyl]-3-hydroxynaphthalene-1,4-dione (38). Red solid; mp 207-208 °C; IR (KBr, cm^{-1}): 3357, 3077, 2915, 1657 (C=O), 1590, 1276 (C-O-C), 1043, 730; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H) [8.08 (t, *J* = 8.4 Hz, 2H)], 7.74 (t, *J* = 7.6 Hz. 1H), 7.67 (t, *J* = 7.6 Hz. 1H) [7,65- 7.77 (m, 2H)], [7.44 (td, *J* = 8.8 and 2.0 Hz, 2H)], 7.29 (m, 3H+[1H]), [7.05 (t, *J* = 8.8 Hz, 2H)], 6.90-7.00 (m, 5H+[3H]), 6.86 (s, 1H) [6.55 (s, 1H)]; GC/MS, (m/z, %) : 376.0 (M$^+$, 100).). Anal. Calcd for $C_{22}H_{13}FO_3S$: C,70.20; H, 3.48; S, 8.52. Found: C, 70.11; H, 3.48; S, 8.47.

2-Methyl-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (17). Yellow solid; mp 178-179 °C; IR (KBr, cm^{-1}): 3098, 2982, 1679 (C=O), 1644(C=O), 1626, 1204 (C-O-C), 955, 722; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.11 (dd, *J* = 6.0 and 1.6 Hz, 1H), 8.08 (dd, *J* = 6.0 and 1.6 Hz, 1H), 7.73 (td, *J* = 7.6 and 1.6 Hz, 1H), 7.69 (td, *J* = 7.6 and 1.6 Hz, 1H), 7.31 (dd, *J* = 5.2 and 1.2 Hz, 1H), 7.12 (dd, *J* = 3.6 and 1.2 Hz, 1H), 6.99 (dd, *J* = 5.2 and 3.6 Hz, 1H), 3.62 (d, *J* = 17.2 Hz, 1H), 3.37 (d, *J* = 17.2 Hz, 1H), 1.99 (s, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 182.3, 177.9, 158.3, 147.3, 134.2, 133.1, 131.7, 127.2, 127.0, 126.4, 126.1, 125.8, 124.2, 123.2, 91.4, 42.2, 29.3; GC/MS (m/z, %): 296.1 (M$^+$, 100). Anal. Calcd for $C_{17}H_{12}O_3S$: C, 68.90; H, 4.08; S, 10.82. Found: C, 68.82; H, 4.11; S, 10.89

2-hydroxy-3-[(1*E*)-2-(2-thiophenyl)prop-1-en-1-yl]naphthalene-1,4-dione (39). Red solid; mp 144-145 °C; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.02 (dd, *J* = 7.6 and 1.6 Hz, 1H), 7.99 (dd, *J* = 7.6 and 1.6 Hz, 1H), 7.84 (td, *J* = 7.6 and 1.6 Hz, 1H), 7.80 (td, *J* = 7.6 and 1.6 Hz, 1H), 7.46 (dd, *J* = 5.2 and 0.8 Hz, 1H), 7.25 (dd, *J* = 3.6 and 0.8 Hz, 1H), 7.07 (dd, *J* = 5.2 and 3.6 Hz, 1H), 6.56 (d, *J* = 1.2 Hz, 1H), 1.98 (d, *J* = 1.2 Hz, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 184.6, 181.5, 151.4, 147.1, 137.8, 135.3, 133.4, 133.2, 129.8, 127.7, 127.2, 126.4, 125.5, 124.7, 120.5, 114.5, 19.9; GC/MS (m/z, %): 296.1 (M$^+$, 61). Anal. Calcd for $C_{17}H_{12}O_3S$: C,68.90; H, 4.08; S, 10.82. Found: C, 68.81; H, 4.10; S, 10.86.

7-Methyl-2-phenyl-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (18). Yellow solid; mp 176-177 °C; IR (KBr, cm^{-1}): 3029, 2980, 1676 (C=O), 1657 (C=O), 1643, 1246 (C-O-C), 984, 728; ^{1}H-NMR (400 MHz, DMSO-D^6) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 1.2 Hz, 1H), 7.50-7.55 (m, 3H), 7.34-7.42 (m, 3H), 7.31 (dd, *J* = 4.8 and 1.2 Hz, 1H), 6.98 (dd, *J* = 3.6 and 1.2 Hz, 1H), 6.95 (dd, *J* = 4.8 and 3.6 Hz, 1H), 4.06 (d, *J* = 17.6 Hz, 1H), 3.82 (d, *J* = 17.6 Hz, 1H), 3.19 (s, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 182.4, 178.1, 158.3, 147.6, 144.4, 143.6, 134.9, 131.8, 130.9, 128.8, 128.6, 127.2, 127.1, 127.0, 126.8, 21.9, 126.5, 125.6, 123.5, 93.9, 43.5; LC-MS (ESI, m/z) 373.35 (MH$^+$, 56). Anal. Calcd for $C_{23}H_{16}O_3S$: C, 74.17; H, 4.33; S, 8.61. Found: C, 74.06; H, 4.26; S, 8.59.

3-hydroxy-6-methyl-2-[(*E(and)Z*)-2-phenyl-2-(2-thiophenyl)] naphthalene-1,4-dione (40). Red solid; mp 148-151 °C; IR (KBr, cm^{-1}): 3350, 3061, 1653 (C=O), 1642 (C=O), 1597, 1299 (C-O-C), 917, 748; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H) [8.08 (d, *J* = 7.6 and 1.6 Hz, 2H)], 7.80 (s,1H) [7,88 (s, 1H)], 7.50 (d, *J* = 7.6 Hz, 1H) [7.54 (d, *J* = 7.6 Hz, 1H)], 7.23-7.47 (m, 5H), 6.97 (dd, *J* = 5.2 and 3.6 Hz, 1H), 6.92 (dd, *J* = 3.6 and 1.2 Hz, 1H), 6.86 (s, 1H) [6.60 (s, 1H)], 2.45 (s, 3H) [2.48 (s, 3H)]; LC-MS (ESI, m/z) 373.35 (MH$^+$, 18). Anal. Calcd for $C_{23}H_{16}O_3S$: C, 74.17; H, 4.33; S, 8.61. Found: C, 74.19; H, 4.32; S, 8.59.

5,7-Dimethyl-2-phenyl-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (19). Yellow solid; mp 169-170 °C; IR (KBr, cm^{-1}): 3071, 2996, 1673 (C=O), 1646 (C=O), 1601, 1232 (C-O-C), 1054, 717; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.85 (s, 1H), 7.54 (dd, *J* = 8.0 and 1.6 Hz, 2H), 7.33-7.40 (m, 3H), 7.30 (dd, *J* = 5.2 and 1.2 Hz, 1H), 7.28 (s,1H), 6.97 (dd, *J* = 3.6 and 1.2 Hz, 1H), 6.93 (dd, *J* = 5.2 and 3.6 Hz, 1H), 4.02 (d, *J* = 17.6 Hz, 1H), 3.79 (d, *J* = 17.6 Hz, 1H), 2.70 (s, 3H), 2.41(s, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 184.8, 178.2, 156.8, 147.7, 143.7, 143.1, 141.4, 139.3, 133.5, 128.7, 128.6, 128.0, 127.1, 126.9, 126.7, 126.4, 125.7, 124.9, 93.6, 43.9, 22.9, 21.6; LC/MS, (ESI, m/z) : 387.48 (MH$^+$, 100). Anal. Calcd for $C_{24}H_{18}O_3S$: C,74.59; H, 4.69; S, 8.30. Found: C, 74.53; H, 4.65; S, 8.33.

5,7-dimethyl-2-hydroxy-3-[(*E(and)Z*)-2-phenyl-2-(2-thiophenyl) ethenyl]naphthalene-1,4-dione (41). Red solid; mp 176-177 °C; IR (KBr, cm^{-1}): 3371, 2992, 1657 (C=O), 1654 (C=O), 1630; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.75 (s, 1H) [7.82 (s, 1H)], [7.48 (m, 2H)], 7.23-7.36 (m, 6H), 7.11 (s, 1H), 6.98 (dd, *J* = 5.2 and 3.6 Hz, 1H), 6.90-6.93 (m, 1H), 6.90 (s, 1H) [6.64 (s, 1H)], [2.42 (s, 3H), 2.45 (s, 3H)], 2.39 (s, 3H), 2.38 (s, 3H); LC/MS, (ESI, m/z) : 387.48 (MH$^+$, 60). Anal. Calcd for $C_{24}H_{18}O_3S$: C,74.59; H, 4.69; S, 8.30. Found: C, 74.60; H, 4.75; S, 8.32.

6-Methoxy-2-phenyl-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (20).Yellow solid; mp 168-169 °C; IR (KBr, cm^{-1}): 3096, 2938, 1668 (C=O), 1656 (C=O), 1584, 1247 (C-O-C), 965, 698; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.53-7.55 (m, 3H), 7.34-7.41 (m, 3H), 7.32 (dd, *J* = 4.8 and 1.2 Hz, 1H), 7.12 (d, *J* = 8.4 ve 2.8 Hz, 1H), 6.98 (dd, *J* = 3.6 and 1.2 Hz, 1H), 6.95 (dd, *J* = 4.8 and 3.6 Hz, 1H), 4.05 (d, *J* = 17.6 Hz, 1H), 3.94 (s, 3H), 3.82 (d, *J* = 17.6 Hz, 1H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 182.2, 176.9, 164.8, 158.9, 147.5, 143.6, 135.7, 129.2, 128.8, 128.6, 127.1, 127.0, 126.9, 125.6, 125.2, 122.9, 118.8, 110.9, 94.1, 56.2, 43.5; GC-MS (m/z, %) 388.1 (M$^+$, 100). Anal. Calcd for $C_{23}H_{16}O_4S$: C,71.12; H, 4.15; S, 8.25. Found: C, 71.34; H, 4.07 S, 8.31.

2-Hydroxy-6-methoxy-3-[(*E(and)Z*)-2-phenyl-(2-thiophenyl) ethenyl]naphthalene-1,4-dione (42). Red solid; mp 171-174 °C; IR (KBr, cm^{-1}): 3335, 3065, 2944, 1646 (C=O), 1588, 1309, 1248 (C-O-C), 700; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 1H) [8.01 (d, *J* = 8.4 Hz, 1H)], 7.58 (s, 1H), 7.46 (d, *J* = 2.8 Hz, 1H) [7.51 (d, *J* = 2.8 Hz, 1H)], 7.23-7.37 (m, 5H), 7.08 (dd, *J* = 8.8 and 2.8 Hz, 1H) [7.12 (dd, *J* = 8.4 and 2.4 Hz, 1H)], 6.97 (dd, *J* = 5.2 and 4.0 Hz, 1H), 6.93 (m, 1H), 6.90 (dd, *J* = 3.6 and 1.2 Hz, 1H), 6.84 (s, 1H) [6.57 (s, 1H)], 3.92 (s, 3H) [3.93 (s, 3H)]; GC-MS (m/z, %) 388 (M$^+$, 100). Anal. Calcd for $C_{23}H_{16}O_4S$: C,71.12; H, 4.15; S, 8.25. Found: C, 71.09; H, 4.07; S, 8.28.

7-Methyl-2-(4-Methylphenyl)-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (21). Yellow solid; mp 169-170 °C; IR (KBr, cm^{-1}): 3066, 2921, 1677 (C=O), 1655 (C=O), 1643, 1240 (C-O-C), 984, 714; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J*= 8.0 Hz, 1H), 7.90 (s, 1H), 7.50 (d, *J*= 8.0 Hz, 1H), 7.41 (d, *J*= 8.0 Hz, 2H), 7.30 (d, *J*= 4.8, 1H), 7.19 (d, *J*= 8.0 Hz, 2H), 6.96-6.94 (m, 2H), 4.02 (d, *J*= 17.6 Hz, 1H), 3.80 (d, *J*= 17.6 Hz, 1H), 2.47 (s, 3H), 2.36 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 182.5, 178.2, 158.3, 147.8, 144.3, 140.6, 138.5, 134.9, 131.8, 130.9, 129.4, 127.2, 127.0, 126.7, 126.5, 125.6, 123.6, 94.0, 43.4, 21.9, 21.3; LC-MS (ESI, m/z): 387.39 (M$^+$+H, 15), 409.34 (M + Na$^+$, 100), 450.36 (M + Na$^+$ + CH_3CN, 51). Anal. Calcd for $C_{24}H_{18}O_3S$: C,74.59; H, 4.69; S, 8.30. Found: C, 74.64; H, 4.62; S, 8.32.

3-hydroxy-6-methyl-2-[(*E(and)Z*)-2-(4-methylphenyl-(2-thiophenyl)ethenyl]naphthalene-1,4-dione (43). Red solid; mp 173-176 °C; IR (KBr, cm^{-1}): 3350, 3019, 1651 (C=O), 1599, 1352 (C-O-C), 739; ^{1}H-NMR (400 MHz, $CDCl_3$) δ [7.99 (d, *J*= 8.0 Hz, 1H)] 7.96 (d, *J*= 8.0 Hz, 1H), 7.95 (s, 1H), 7.79 (d, *J*= 8.4 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H) [7.52 (d, *J* = 8.0 Hz, 1H)], [7.50 (dd, *J*= 4.0 and 1.2 Hz, 1H)], 7.32 (dd, *J*= 5.2 and 1.2 Hz, 1H), 7.25 (d, *J*= 8.4 Hz, 2H), [7.21 (d, *J*= 8.4 Hz, 2H), 7.12 (d, *J*= 8.4 Hz, 2H)], 6.92 (dd, *J*= 5.2 and 4.0 Hz, 1H) [7.05 (dd, *J*= 5.2 and 4.0 Hz, 1H)], 6.90 (s, 1H) [7.01 (s, 1H)], 6.82 (dd, *J*= 3.2 and 1.2 Hz, 1H), 2.49 (s, 3H) [2.34 (s, 3H), 2.37 (s, 3H)], 1.84 (s, 3H); LC-MS (ESI, m/z): 387.56 (M$^+$+H, 13), 409.53 (M + Na$^+$, 100), 450.42 (M + Na$^+$ + CH_3CN, 50).). Anal. Calcd for $C_{24}H_{18}O_3S$: C,74.59; H, 4.69; S, 8.30. Found: C, 74.63; H, 4.71; S, 8.31.

5,7-Dimethyl-2-(4-Methylphenyl)-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (22). Yellow solid; mp 155-156 °C; IR (KBr, cm^{-1}): 2918, 1674 (C=O), 1644 (C=O), 1636, 1270 (C-O-C), 1052, 982, 714; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.41 (d, *J*= 8.0 Hz, 2H), 7.29 (d, *J*= 5.2 Hz, 1H), 7.27 (s, 1H), 7.18 (d, *J*= 8.0 Hz, 2H), 6.92-6.97 (m, 2H), 4.00 (d, *J*= 17.6 Hz, 1H), 3.77 (d, *J*= 17.6 Hz, 1H), 2.69 (s, 3H), 2.40 (s, 3H), 2.35 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.9, 178.3, 156.9, 148.0, 143.1, 141.4, 140.8, 139.3, 138.4, 133.5, 129.4, 128.0, 127.0, 126.9, 126.6, 126.4, 125.6, 125.0, 93.7, 43.8, 22.9, 21.6, 21.4; LC/MS, (ESI, m/z) : 401.99 (M+H$^+$, 12), 423.90 (M+Na$^+$, 15), 464 (M+Na$^+$ + CH3CN, 100). Anal. Calcd for $C_{25}H_{20}O_3S$: C,74.98; H, 5.03; S, 8.01. Found: C, 74.93; H, 5.06; S, 7.99.

5,7-Dimethyl-2-hydroxy-3-[(*E(and)Z*)-2-(4-methylphenyl)-(2-thiophenyl)ethenyl] naphthalene-1,4-dione (44). Red solid; mp 178-180 °C; IR (KBr, cm^{-1}): 3349, 2918, 1649 (C=O), 1598, 1293 (C-O-C), 1089, 727; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H) [7.81 (s, 1H)], [7.37 (d, *J*= 7.6 Hz, 2H)], 7.25-7.30 (m, 2H+[2*H*]), 7.19 (d, *J*= 7.6 Hz, 2H), 7.04 (d, *J*= 7.6 Hz, 2H) [7.15 (d, *J*= 8.0 Hz, 2H)], 6.91-6.98 (m, 2H+[2H]), 6.86 (s, 1H) [6.62 (s, 1H)], 2.39 (s, 3H) [2.41 (s, 3H), 2.43 (s, 3H)], 2.37 (s, 3H+[3H]), 2.31 (s, 3H); LC/MS, (ESI, m/z) : 401.53 (M+H$^+$, 50), 423.41 (M+Na$^+$, 30), 464.53 (M+Na$^+$ + CH3CN, 100). Anal. Calcd for $C_{25}H_{20}O_3S$: C,74.98; H, 5.03; S, 8.01. Found: C, 74.87; H, 5.02; S, 8.01.

6-Methoxy-2-(4-Methylphenyl)-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (23). Yellow solid; mp 215-216 °C; IR (KBr, cm^{-1}): 3029, 2976, 1670 (C=O), 1590, 1246 (C-O-C), 967, 699; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J*= 8.8 Hz, 1H), 7.52 (d, *J*= 2.8 Hz, 1H), 7.41 (d, *J*= 8.0 Hz, 2H), 7.30 (dd, *J* = 5.2 and 1.2 Hz, 1H), 7.19 (d, *J*= 8.0 Hz, 2H), 7.10 (d, *J*= 8.8 and 2.8 Hz, 1H), 6.97 (dd, *J* = 3.6 and 1.2 Hz, 1H), 6.94 (dd, *J*= 5.2 and 3.6 Hz, 1H), 4.02 (d, *J*= 17.6 Hz, 1H), 3.93 (s, 3H), 3.80 (d, *J*= 17.6 Hz, 1H), 2.35 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 182.2, 176.9, 164.8, 158.9, 147.7, 140.6, 138.5, 135.6, 129.4, 129.2, 127.0, 126.7, 125.6, 125.2, 123.0, 118.8, 110.8, 94.2, 56.2, 43.4, 21.3; LC-MS (ESI, m/z) 403.84 (M+H$^+$, 100). Anal. Calcd for $C_{24}H_{18}O_4S$: C,71.62; H, 4.51; S, 7.97. Found: C, 71.76; H, 4.53; S, 7.94.

2-hydroxy-6-methoxy-3-[(*E(and)Z*)-2-(4-methylphenyl)-(2-thiophenyl)ethenyl]naphthalene-1,4-dione (45). Red solid; mp 205-208 °C; IR (KBr, cm^{-1}): 3333, 3079, 2975, 1649 (C=O), 1589, 1248 (C-O-C), 819; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J*= 8.8 Hz, 1H) [8.02 (d, *J*= 8.4 Hz, 1H)], 7.48 (d, *J*= 2.4 Hz, 1H) [7.51 (d, *J*= 2.4 Hz, 1H)], [7.35 (d, *J*= 8.0 Hz, 2H)], 7.32 (s, 1H, OH) [7.15 (s, 1H, OH)], [7.28 (dd, *J*= 4.8 and 1.2 Hz, 1H),7.24 (dd, *J*= 4.8 and 2.0 Hz, 1H)], 7.18 (d, *J*= 8.0 Hz, 2H), 7.09 (dd, *J*= 8.8 and 2.8 Hz, 1H) [7.13 (dd, *J*= 8.8 and 2.8 Hz, 1H)], 7.06 (d, *J*= 8.4 Hz, 2H), 6.98 (dd, *J*= 5.2 and 3.6 Hz, 1H), 6.92-6.94 (m, 2H), 6.80 (s, 1H) [6.55 (s, 1H)], 3.93 (s, 3H) [3.94 (s, 3H)], 2.32 (s, 3H) [2.39 (s, 3H)]; LC-MS (ES+, m/z) 403.53 (M+H$^+$, 100). Anal. Calcd for $C_{24}H_{18}O_4S$: C,71.62; H, 4.51; S, 7.97. Found: C, 71.61; H, 4.49; S, 7.96

2-(4-Fluorophenyl)-7-methyl-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (24). Yellow solid; mp 174-175 °C; IR (KBr, cm^{-1}): 3090, 2921, 1676 (C=O), 1656 (C=O), 1642, 1240 (C-O-C), 984, 712; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J*= 8.0 Hz, 1H), 7.90 (s, 1H), 7.50 (m, 3H), 7.32 (dd, *J*= 4.8 and 1.6, 1H), 7.08 (t, *J*= 8.8 Hz, 2H), 6.94-6.98 (m, 2H), 4.04 (d, *J*= 17.2 Hz, 1H), 3.78 (d, *J*= 17.2 Hz, 1H), 2.48 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 182.3, 178.0, 164.0, 161.5, 158.1, 147.3, 144.5, 139.4 (C_{para}, i, J= 3.2 Hz), 135.0, 131.8, 130.9, 127.6 (C_{meta}, i, J= 8.4 Hz), 127.3, 127.2, 127.1, 126.8, 126.5, 123.4, 115.7 (C_{orto}, i, J= 21.8 Hz), 93.5, 43.5, 21.9; LC/MS, (ESI, m/z) : 391.34 (M$^+$+H, 100), 413.32 (M + Na$^+$, 37), 454.33 (M + Na$^+$ + CH_3CN, 100). Anal. Calcd for $C_{23}H_{15}FO_3S$: C,70.75; H, 3.87; S, 8.21. Found: C, 70.80; H, 3.91 S, 8.22.

2-[(*E(and)Z*)-2-(4-fluorophenyl)-2-(2-thiophenyl)ethenyl]-3-hydroxy-6-methylnaphthalene-1,4-dione (46). Red solid; mp 186-188 °C; IR (KBr, cm^{-1}): 3346, 3067, 1650 (C=O), 1598, 1298 (C-O-C), 851, 717; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J*= 8.0 Hz, 1H) [7.95 (d, *J*= 8.0 Hz, 1H)], 7.82 (d, *J*= 0.8 Hz, 1H) [7,88 (d, *J*= 0.8 Hz, 1H)], 7.52 (dd, *J*= 7.6 and 0.8 Hz, 1H) [7.55 (dd, *J*= 7.6 and 0.8 Hz, 1H)], [7.44 (m, 2H), 7.40 (s, 1H)], 7.23-7.31 (m, 4H + [3H]) 6.98 (dd, *J*= 5.2 and 3.6 Hz, 1H), 6.94 (td, *J*= 8.0 and 1.6 Hz, 2H) [7.05 (t, *J*= 8.8 Hz, 2H)], 6.89 (dd, *J*= 3.6 and 1.2 Hz, 1H), 6.85 (s, 1H) [6.55 (s, 1H)], 2.46 (s, 3H) [2.48 (s, 3H)]; LC/MS, (ESI, m/z) : 391.35 (M$^+$+H, 60), 413.30 (M + Na$^+$, 20), 454.34 (M + Na$^+$ + CH_3CN, 10). Anal. Calcd for $C_{23}H_{15}FO_3S$: C,70.75; H, 3.87; S, 8.21. Found: C, 70.82; H, 3.94; S, 8.21.

5,7-Dimethyl-2-(4-fluorophenyl)-2-(2-thiophenyl)-2,3-dihydro-naphtho[2,3-*b*]furan-4,9-dione (25). Yellow solid; mp 162-163 °C; IR (KBr, cm^{-1}): 3099, 2969, 1680 (C=O), 1648 (C=O), 1600, 1223 (C-O-C), 836, 716; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J*= 1.6 Hz, 1H), 7.51 (m, 2H), 7.32 (dd, *J*= 4.4 and 1.6 Hz, 1H), 7.29 (d, *J*= 1.6 Hz, 1H), 7.07 (td, *J*= 8.8 and 1.0 Hz, 2H), 6.94-6.98 (m, 2H), 4.02 (d, *J*= 17.6 Hz, 1H), 3.75 (d, *J*= 17.6 Hz, 1H), 2.70 (s, 3H), 2.42 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 184.8, 178.2, 164.0, 161.5, 156.7, 147.5, 143.3, 141.5, 139.5 (C_{para}, i, J= 3.2 Hz), 139.4, 133.5, 128.0, 127.7 (C_{meta}, i, J= 8.3 Hz), 127.2, 127.1, 126.8, 126.4, 124.9, 115.7 (C_{orto}, i, J= 21.2 Hz), 93.2, 44.0, 23.0, 21.6; LC/MS, (ESI, m/z) : 405.34 (M+H$^+$, 100), 427.31 (M+Na$^+$, 20), 468.32 (M+Na$^+$ + CH_3CN, 95). Anal. Calcd for $C_{24}H_{17}FO_3S$: C,71.27; H, 4.24; S, 7.93. Found: C, 71.34; H, 4.20; S, 7.90.

3-[(*E(and)Z*)-2-(4-fluorophenyl)-(2-thiophenyl)ethenyl]-2-hydroxy-5,7-dimethyl-naphthalene -1,4-dione (47). Red solid; mp 179-182 °C; IR (KBr, cm^{-1}): 3350, 2920, 1648 (C=O), 1597, 1337, 1091 (C-O-C), 705; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J*= 1.6Hz, 1H) [7.82 (d, *J*= 1.2Hz, 1H)], [7.45 (dd, *J*= 8.8 and 5.2 Hz, 2H)], 7.26-7.32 (m, 4H+[4H]), 7.14 (s, 1H), 6.98 (dd, *J*= 5.2 and 3.6 Hz, 1H), 6.94 (td, *J*= 8.8 and 2.4 Hz, 1H) [7.04 (td, *J*= 8.8 and 2.4 Hz, 2H)], 6.90-6.93 (m, 1H), 6.88 (s, 1H) [6.59 (s, 1H)], 2.45 (s, 3H) [2.42 (s, 3H), 2.45 (s, 3H)], 2.40 (s, 3H); LC/MS, (ESI, m/z) : 405.45 (M+H$^+$, 100). Anal. Calcd for $C_{24}H_{17}FO_3S$: C,71.27; H, 4.24; S, 7.93. Found: C, 71.33; H, 4.32; S, 7.96.

2-(4-Fluorofenil)-6-methoxy-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (26). Yellow solid; mp 170-171 °C; IR (KBr, cm^{-1}): 3077, 2944, 1671 (C=O), 1654 (C=O),1583, 1246 (C-O-C), 948, 714; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J*= 8.8 Hz, 1H), 7.53 (d, *J*= 2.4 Hz, 1H), 7.50 (ddd, *J*= 8.4 and 5.2 and 2.0 Hz, 2H), 7.32 (dd, *J*= 5.2 and 1.6 Hz, 1H), 7.11 (dd, *J*= 8.8 and 2.4 Hz, 1H), 7.07 (td, *J*= 8.4 and 2.0 Hz, 2H), 6.94-6.98 (s, 2H), 4.04 (d, *J*= 17.2 Hz, 1H), 3.94 (s, 3H), 3.77 (d, *J*= 17.2 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 182.1, 176.8, 164.8, 162.5 (C_{ipso}, i, *J*= 246.1 Hz), 158.8, 147.3, 139.4 (C_{para}, i, *J*= 3.11Hz), 135.6, 129.2, 127.6 (C_{meta}, i, *J*= 8.4 Hz), 127.2, 127.1, 126.8, 125.2, 122.8, 118.8, 115.7 (C_{orto}, i, *J*= 21.3 Hz), 110.9, 93.7, 56.2, 43.5; LC-MS (ESI, m/z) 407.46 (M+H$^+$, 98), 429.57 (M+Na$^+$, 35), 470.22 (M+Na$^+$ + CH3CN, 100). Anal. Calcd for $C_{23}H_{15}FO_4S$: C,67.97; H, 3.72; S, 7.89. Found: C, 68.04; H, 3.64; S, 7.93.

3-[(*E(and)Z*)-2-(4-fluorophenyl)-2-(2-thiophenyl)ethenyl]-2-hydroxy-6-methoxy naphthalene-1,4-dione (48). Red solid; mp 176-178 °C; IR (KBr, cm^{-1}): 3325, 3069, 2918, 1656 (C=O), 1589, 1248 (C-O-C), 973, 701; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J*= 8.8 Hz, 1H) [8.02 (d, *J*= 8.0 Hz, 1H)], 7.47 (d, *J*= 2.8 Hz, 1H) [7.51 (d, *J*= 2.4 Hz, 1H)], 7.38 (s, 1H, OH) [7.57 (s, 1H, OH)], [7.42 (ddd, *J*= 8.8 and 6.4 and 2.4 Hz, 2H)], 7.28-7.30 (m, 3H), 7.11 (dd, *J*= 8.4 and 2.8 Hz, H-7) [7.12 (dd, *J*= 8.8 and 2.8 Hz, 1H)], 7.00 (dd, *J*= 4.8 and 3.6 Hz, 1H), 6.95 (td, *J*= 8.4 and 1.0 Hz, 2H) [7.06 (td, *J*= 8.4 and 1.0 Hz, 2H)], 6.89 (dd, *J*= 3.6 and 1.2 Hz, 1H), 6.82 (s, 1H) [6.52 (s, 1H)], 3.93 (s, 3H) [3.94 (s, 3H)]; LC-MS (ESI, m/z) 407.37 (M+H$^+$, 100). Anal. Calcd for $C_{23}H_{15}FO_4S$: C,67.97; H, 3.72; S, 7.89. Found: C, 67.93; H, 3.78; S, 7.87.

3-Phenyl-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (27). Yellow solid; mp 164-165 °C; IR (KBr, cm^{-1}): 3029, 2928, 1679 (C=O), 1651 (C=O), 1592, 1193 (C-O-C), 964, 719; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J*= 6.4 and 2.4 Hz, 1H), 8.01 (dd, *J*= 6.4 and 2.4 Hz, 1H), 7.68-7.72 (m, 2H), 7.30-7.39 (m, 6H), 7.16 (dd, *J*= 3.6 and 0.8 Hz, 1H), 7.02 (dd, *J*= 4.8 and 3.6 Hz, 1H), 6.01 (d, *J*= 6.0 Hz, 1H), 4.87 (d, *J*= 6.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 181.7, 178.3, 159.1, 141.3, 139.8, 134.6, 133.3, 131.9, 129.4, 128.2, 127.6, 127.4, 127.0, 126.6, 126.5, 126.0, 90.8, 55.4; LC/MS, (ESI, m/z) : 359.02 (M+H$^+$,100). Anal. Calcd for $C_{22}H_{14}O_3S$: C,73.72; H, 3.94; S, 8.95. Found: C, 73.83; H, 3.89; S, 8.88.

2-Methyl-3-phenyl-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (28). Yellow solid; mp 178-170 °C; IR (KBr, cm^{-1}): 3091, 2981, 1681 (C=O), 1651(C=O), 1361, 1209 (C-O-C), 962, 728; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.15 (m, 1H), 8.00 (m, 1H), 7.70 (m, 2H), 7.32-7.39 (m, 3H), 7.29 (dd, *J*= 5.2 and 1.2 Hz, 1H), 7.20 (d, *J*= 6.4 Hz, 2H), 7.15 (dd, *J*= 3.6 and 1.2 Hz, 1H), 6.99 (dd, *J*= 5.2 and 3.6 Hz, 1H), 4.98 (s,1H), 1.48 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 181.8, 178.4, 159.4, 149.5, 136.2, 134.6, 133.4, 131.9, 129.1, 128.9, 128.4, 127.3, 126.7, 126.6, 125.9, 125.5, 123.8, 94.9, 58.5, 26.1; GC-MS (m/z, %) 372.2 (M$^+$, 100). Anal. Calcd for $C_{23}H_{16}O_3S$: C,74.17; H, 4.33; S, 8.61. Found: C, 74.18; H, 4.22; S, 8.63.

2-Methyl-3-phenyl-2-(2-thiophenyl)-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (29). Yellow solid; mp 144-145 °C; IR (KBr, cm^{-1}): 3065, 2975, 1684 (C=O), 1660 (C=O), 1635, 1225 (C-O-C), 964, 699; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.19 (m, 1H), 8.01 (m, 1H), 7.73 (m, 2H), 7.08 (m, 3H), 7.01 (d, *J*= 5.2 Hz, 1H), 6.91 (m, 2H), 6.69 (dd, *J*= 5.2 and 4.0 Hz, 1H), 6.59 (d, *J*= 4.0 Hz, 1H), 4.66 (s, 1H), 2.07 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 181.9, 178.4, 159.1, 143.2, 136.7, 134.6, 133.4, 133.3, 131.9, 128.7, 128.3, 127.7, 126.7, 126.6, 126.3, 125.2, 125.1, 96.4, 59.1, 30.8; GC-MS (m/z, %) 372.2 (M$^+$, 100). Anal. Calcd for $C_{23}H_{16}O_3S$: C,74.17; H, 4.33; S, 8.61. Found: C, 74.10; H, 4.32; S, 8.67.

3a-(2-thiophenyl)-2,3,3a,10b-tetrahydro-1*H*-cyclopenta[*b*] naphtho[2,3-*d*]furan-5,10-dione (30). Yellow solid; mp 174-175 °C; IR (KBr, cm^{-1}): 3095, 2963, 1680 (C=O), 1645 (C=O), 1628, 1208 (C-O-C), 968, 710; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.09 (t, *J*= 8.0 Hz, 2H), 7.73 (td, *J*= 7.6 and 1.6 Hz, 1H), 7.70 (td, *J*= 7.6 and 1.6 Hz, 1H), 7.30 (d, *J*= 4.8 Hz, 1H), 7.10 (d, *J*= 3.2 Hz, 1H), 6.99 (dd, *J*= 4.8 and 3.2 Hz, 1H), 4.06 (dd, *J*= 8.8 and 1.6 Hz, 1H), 2.73 (dd, *J*= 14.4 and 6.0 Hz, 1H), 2.20 (m, 3H), 1.96 (m, 1H), 1.81 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 182.5, 178.0, 159.0, 145.7, 134.4, 133.4, 133.2, 131.9, 127.3, 126.6, 126.3, 125.9, 124.3, 102.2, 53.3, 42.6, 33.1, 25.2; GC-MS (m/z, %) 322.0 (M$^+$, 100). Anal. Calcd for $C_{19}H_{14}O_3S$: C,70.79; H, 4.38; S, 9.95. Found: C, 70.65; H, 4.41; S, 9.90.

2-Hydroxy-3-[2-(2-thiophenyl)cyclopent-1en-1-yl]naphthalene-1,4-dione (49). Red solid; mp 188-189 °C; IR (KBr, cm^{-1}): 3370, 3073, 2997, 1667 (C=O), 1639 (C=O), 1592, 1275 (C-O-C), 725; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.15 (m, 2H), 7.80 (td, *J*= 7.6 and 1.2 Hz, 1H), 7.74 (td, *J*= 7.6 and 1.2 Hz, 1H), 7.45 (s, 1H, OH), 7.09 (d, *J*= 4.8 Hz, 1H), 6.97 (d, *J*= 3.6 Hz, 1H), 6.91 (dd, *J*= 4.8 and 3.6 Hz, 1H), 3.04 (s, 2H), 2.82 (m, 2H), 2.16 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 183.4, 181.3, 153.4, 139.5, 136.3, 135.4, 133.6, 133.3, 129.7, 127.5, 127.4, 126.9, 126.5, 125.9, 125.6, 122.0, 38.5, 37.3, 22.9; GC/MS, (m/z, %): 322.0 (M$^+$, 45). Anal. Calcd for $C_{19}H_{14}O_3S$: C,70.79; H, 4.38; S, 9.95. Found: C, 70.90; H, 4.26; S, 10.03.

4a-(2-thiophenyl)-1,2,3,4,4a,11b-hexahydrobenzo[*b*]nafto[2,3-*d*]furan-6,11-dione (31). Yellow solid; mp 114-115 °C; IR (KBr, cm^{-1}): 3089, 3029, 2934, 1679 (C=O), 1651 (C=O), 1633, 1192 (C-O-C), 964, 719; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.02 (t, *J*= 8.0 Hz, 2H), 7.72 (td, *J*= 7.6 and 1.6 Hz, 1H), 7.67 (td, *J*= 7.6 and 1.6 Hz, 1H), 7.28 (dd, *J*= 5.2 and 0.8 Hz, 1H), 7.15 (dd, *J*= 3.6 and 0.8 Hz, 1H), 6.98 (dd, *J*= 5.2 and 3.6 Hz, 1H), 3.86 (t, *J*= 6.4 Hz, 1H), 2.39

(m, 1H), 2.22 (m, 1H), 2.05 (m, 2H), 1.62 (m, 4H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 182.7, 178.4, 159.0, 147.8, 134.4, 133.4, 133.2, 131.8, 127.9, 127.1, 126.1, 126.2, 125.6, 124.5, 93.2, 47.1, 34.3, 25.2, 19.6, 19.4; GC/MS, (m/z, %): 336 (M$^+$, 100). Anal. Calcd for $C_{20}H_{16}O_3S$: C,71.41; H, 4.79; S, 9.53. Found: C, 71.39; H, 4.72; S, 9.65.

2-Hydroxy-3-[2-(2-thiophenyl)cyclohex-1-en-1-yl]naphthalene-1,4-dione (50). Red solid; mp 172-174 °C; IR (KBr, cm^{-1}): 3350, 2931, 1662 (C=O), 1646 (C=O), 1635, 1265 (C-O-C), 720; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.10 (d, *J*= 7.2 Hz, 2H), 7.77 (t, *J*= 7.6 Hz, 1H), 7.71 (t, *J*= 7.6 Hz, 1H), 7.01 (d, *J*= 4.4 Hz, 1H), 6.92 (d, *J*= 3.6 Hz, 1H), 6.82 (dd, *J*= 4.8 and 3.6 Hz, 1H), 2.60-2.64 (m, 2H), 2.29-2.31 (m, 2H), 1.79-1.92 (m, 4H); LC/MS (ESI, m/z) : 337.38 (MH$^+$, 85). Anal. Calcd for $C_{20}H_{16}O_3S$: C,71.41; H, 4.79; S, 9.53. Found: C, 71.32; H, 4.85; S, 9.44.

2-(2-furyl)-2-phenyl-2,3-dihydronafto[2,3-*b*]furan-4,9-dione (32). Yellow solid; mp 148-149 °C; IR (KBr, cm^{-1}): 3022, 2928, 1677 (C=O), 1633 (C=O), 1593, 1253 (C-O-C), 955, 757; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.12 (dd, *J*= 7.2 and 1.6 Hz, 1H), 8.07 (dd, *J*= 7.2 and 1.6 Hz, 1H), 7.72 (td, *J*= 7.2 and 1.6 Hz, 1H), 7.69 (td, *J*= 7.2 and 1.6 Hz, 1H), 7.51-7.54 (m, 2H), 7.35-7.43 (m, 4H), 6.31 (dd, *J*= 3.2 and 2.0 Hz, 1H), 6.11 (d, *J*= 2.8 Hz, 1H), 4.13 (d, *J*= 17.2 Hz, 1H), 3.64 (d, *J*= 17.2 Hz, 1H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 182.4, 177.9, 158.6, 154.1, 144.1, 141.5, 134.4, 133.3, 133.2, 131.9, 128.8, 126.6, 126.3, 125.8, 123.7, 110.8, 110.7, 91.4, 40.2; LC/MS, (ESI, m/z): 343.41 (M+H$^+$, 100). Anal. Calcd for $C_{22}H_{14}O_4$: C,77.18; H, 4.12. Found: C, 77.23; H, 4.10.

2-[(*E(and)Z*)-2-(2-furanyl)-2-phenylethenyl]-3-hydroxy naphthalene-1,4-dione (51). Black solid; mp 126-129 °C; IR (KBr, cm^{-1}): 3348, 3047, 1647 (C=O), 1590, 1331 (C-O-C), 724; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.00 (dd, *J*= 7.6 and 1.6 Hz, 2H) [8.08 (td, *J*= 7.6 and 1.6 Hz, 2H)], 7.66-7.76 (m, 1H+[2H]), 7.63 (td, *J*= 7.6 and 1.6 Hz, 1H), 7.49-7.51 (m, 2H+[2H]), 7.23-7.34 (m, 4H+[4H]), 7.03 (s, 1H) [6.48 (s, 1H)], 6.38 (m, 1H+[1H]), 6.15 (d, *J*= 3.6 Hz, 1H) [6.30 (d, *J*= 3.2 Hz, 1H)]; LC/MS, (ESI, m/z): 343.55 (M+H$^+$, 12), 365.44 (M+Na$^+$, 24), 406.45 (M+Na$^+$+CH$_3$CN, 100). Anal. Calcd for $C_{22}H_{14}O_4$: C,77.18; H, 4.12. Found: C, 77.34 H, 4.08.

2-(2-furyl)-7-methyl-2-phenyl-2,3-dihydronafto[2,3-*b*]furan-4,9-dione (33). Yellow solid; mp 188-189 °C; IR (KBr, cm^{-1}): 3004, 2984, 1669 (C=O), 1656 (C=O), 1591, 1240 (C-O-C), 954, 741; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.95 (d, *J*= 7.6 Hz, 1H), 7.90 (s, 1H), 7.49-7.53 (m, 3H), 7.36-7.43 (m, 4H), 6.31 (m, 1H), 6.11 (d, *J*= 2.8 Hz, 1H), 4.11 (d, *J*= 17.2 Hz, 1H), 3.62 (d, *J*= 17.2 Hz, 1H), 2.47 (s, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 182.2, 177.9, 158.2, 153.9, 144.1, 143.8, 141.3, 134.7, 131.5, 130.7, 128.5, 126.9, 126.2, 125.5, 123.4, 110.5, 110.4, 91.1, 40.0, 21.6; LC/MS, (ESI, m/z) 357.5 (M+H$^+$, 20), 379.5 (M+Na$^+$, 30), 420.5 (M+Na$^+$+ CH$_3$CN, 100). Anal. Calcd for $C_{23}H_{16}O_4$: C,77.52; H, 4.53. Found: C, 77.57; H, 4.53.

2-[(*E(and)Z*)-2-(2-furanyl)-2-phenylethenyl]-3-hydroxy-6-methylnaphthalene-1,4-dione (52). Black solid; mp 128-131 °C; IR (KBr, cm^{-1}): 3331, 3066, 1645 (C=O), 1588, 1254 (C-O-C), 754; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.90 (d, *J*= 7.6 Hz, 1H) [7.97 (d, *J*= 8.0 Hz, 1H)], 7.80 (s, 1H) [7.89 (s, 1H)], 7.49-7.54 (m, 3H+[3H]), 7.24-7.38 (m, 4H+[4H]), 7.18 (s, 1H+[1H], OH), 7.02 (s, 1H) [6.48 (s, 1H)], 6.37-6.40 (m, 1H+[1H]), 6.15 (d, *J*= 2.8 Hz, 1H) [6.30 (d, *J*= 3.6 Hz, 1H)], 2.45 (s, 3H) [2.49 (s, 3H)]; LC/MS, (ESI, m/z): 357.5 (M+H, 10), 379.5 (M+Na, 37), 420.5 (M+Na+CH$_3$CN, 100). Anal. Calcd for $C_{23}H_{16}O_4$: C,77.52; H, 4.53. Found: C, 77.48; H, 4.59.

5,7-Dimethyl-2-(2-furyl)-2-phenyl-2,3-dihydronafto[2,3-*b*]furan-4,9-dione (34). Yellow solid; mp 155-156 °C; IR (KBr, cm^{-1}): 3029, 2971, 1672 (C=O), 1651 (C=O), 1599, 1242 (C-O-C), 758; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.84 (d, *J*= 1.6 Hz, 1H),7.51-7.53 (m, 2H), 7.42 (dd, *J*= 2.0 and 0.8 Hz, 1H), 7.34-7.41 (m, 3H), 7.27 (s, 1H), 6.30 (dd, *J*= 3.2 and 2.0 Hz, 1H), 6.12 (dd, *J*= 2.8 and 0.8 Hz, 1H), 4.08 (d, *J*= 17.2 Hz, 1H), 3.58 (d, *J*= 17.2 Hz, 1H), 2.69 (s, 3H), 2.40 (s, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 184.9, 178.3, 157.0, 154.3, 144.0, 143.1, 141.7, 141.4, 139.3, 133.5, 128.7, 128.6, 128.0, 126.3, 125.8, 125.0, 110.7, 110.6, 91.0, 40.6, 23.0, 21.6; LC/MS, (ESI, m/z): 371.5 (M+H$^+$, 48), 393.7 (M+Na$^+$, 36), 434.6 (M+Na$^+$+CH$_3$CN, 100). Anal. Calcd for $C_{24}H_{18}O_4$: C,77.82; H, 4.90. Found: C, 77.71; H, 4.91.

3-[(*E(and)Z*)-2-(2-furanyl)-2-phenylethenyl]-2-hydroxy-5,7-dimethylnaphthalene-1,4-dione (53). Black solid; mp 112-115 °C; IR (KBr, cm^{-1}): 3352, 3059, 2927, 1646 (C=O), 1640, 1334, 1091 (C-O-C), 756; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.74 (s, 1H) [7.83 (s, 1H)], 7,47- 7.51 (m, 2H+[2H]), 7.24-7.37 (m, 5H+[4H]), [7.15 (s, 1H)], 7.06 (s, 1H) [6.50 (s, 1H)], 6.39 (m, 1H+[1H]), 6.17 (d, *J*= 3.2 Hz, 1H) [6.30 (d, *J*= 3.6 Hz, 1H)], 2.38 (s, 3H), 2.37 (s, 3H) [2.43 (s, 3H), 2.54 (s, 3H)]; LC/MS, (ESI, m/z): 371.5 (MH$^+$, 35), 393.6 (M+Na, 40), 434.5 (M+Na+CH$_3$CN, 100). Anal. Calcd for $C_{24}H_{18}O_4$: C,77.82; H, 4.90. Found: C, 77.69; H, 4.99.

2-(2-Furyl)-6-methoxy-2-phenyl-2,3-dihydronafto[2,3-*b*]furan-4,9-dione (35). Yellow solid; mp 171-172 °C; IR (KBr, cm^{-1}): 3107, 2918, 1677 (C=O), 1659 (C=O), 1597, 1229 (C-O-C), 984, 753; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.03 (d, *J*= 8.8 Hz, 1H), 7.51-7.53 (m, 3H), 7.36-7.43 (m, 4H), 7.10 (dd, *J*= 8.8 and 2.8 Hz, 1H), 6.31 (dd, *J* = 3.2 and 2.0 Hz, 1H), 6.11 (d, *J*= 3.2 Hz, 1H), 4.10 (d, *J*= 17.2 Hz, 1H), 3.93 (s, 3H), 3.60 (d, *J*= 17.2 Hz, 1H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 182.2, 176.9, 164.8, 159.1, 154.1, 144.1, 141.6, 135.6, 129.1, 128.7, 125.8, 125.2, 123.0, 118.7, 110.8, 110.7, 91.5, 56.2, 40.2; LC/MS, (ESI, m/z) 373.4 (M+H$^+$, 100). Anal. Calcd for $C_{23}H_{16}O_4$: C,74.19; H, 4.33. Found: C, 74.25; H, 4.34.

3-[(*E(and)Z*)-2-(2-furanyl)-2-phenylethenyl]-2-hydroxy-6-methoxynaphthalene-1,4-dione (54). Black solid; mp 146-149 °C; IR (KBr, cm^{-1}): 3349, 1645 (C=O), 1598, 1336, 917, 747; ^{1}H-NMR (400 MHz, CDCl$_3$) δ 7.95 (d, *J*= 8.8 Hz, 1H) [8.04 (d, *J*= 8.8 Hz, 1H)], 7.49-7.51 (m, 2H+[2H]), 7.46 (d, *J*= 2.8 Hz, 1H) [7.54 (d, *J*= 2.8 Hz, 1H)], 7.25-7.39 (m, 4H+[4H]), 7.08 (dd, *J*= 8.8 and 2.8 Hz, 1H) [7.14 (dd, *J*= 8.8 and 2.8 Hz, 1H)], 6.99 (s, 1H) [6.46 (s, 1H)], 6.40 (m, 1H+[1H]), 6.14 (d, *J*= 3.2 Hz, 1H) [6.29 (d, *J*= 3.2 Hz, 1H)], 3.92 (s, 3H) [3.94 (s, 3H)]; LC/MS, (ESI, m/z): 373.4 (M+H$^+$, 20), 395.5 (M+Na$^+$, 37), 436.5 (M+Na$^+$+CH$_3$CN, 100).). Anal. Calcd for $C_{23}H_{16}O_4$: C,74.19; H, 4.33. Found: C, 74.29; H, 4.22.

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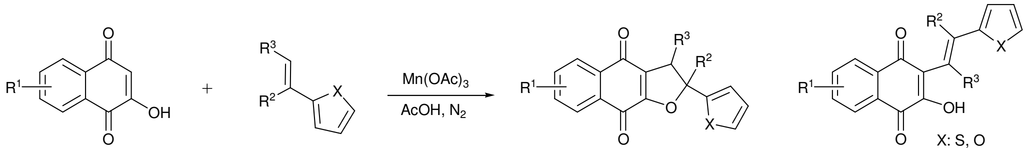
GRAPHİCAL ABSTRACT



1 **2** **3** **4**

X: S, O
R^1: H, Me, MeO
R^2: Me, Ph, 4-MePh, 4-FPh
cylopentene, cyclohekzene
R^3: H, Me, Ph