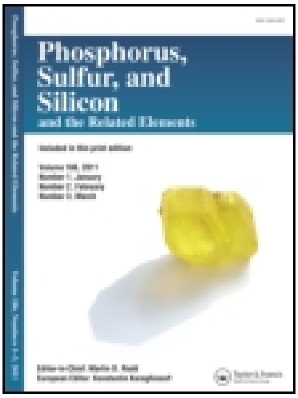

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Thionation of Chalcone and Aurone Derivatives by Lawesson's Reagent

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To cite this article: Eman Elhefny (2013): Thionation of Chalcone and Aurone Derivatives by Lawesson's Reagent, Phosphorus, Sulfur, and Silicon and the Related Elements, 188:6, 804-811

To link to this article: http://dx.doi.org/10.1080/10426507.2012.704457

Phosphorus, Sulfur, and Silicon, 188:804–811, 2013

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2012.704457

THIONATION OF CHALCONE AND AURONE DERIVATIVES BY LAWESSON'S REAGENT

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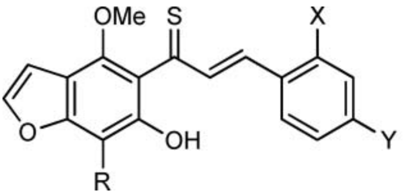
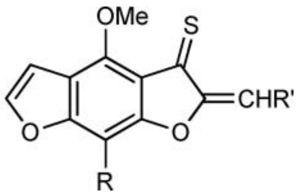
GRAPHICAL ABSTRACT





Abstract *The reaction of Lawesson's reagent (LR **5**) with chalcones (**4a–h**) and aurones (**12a–h**) proceeds in refluxing toluene to give the respective benzofuranylprop-2-en-1-thiones (**8a–h**) and benzodifuran-3-thiones (**13a–h**). Correct elemental analyses and spectroscopic data were obtained for the new compounds.*

Keywords Lawesson reagent; chalcones; aurones

INTRODUCTION

It has been reported[1,2] that condensation of visnaginone (**2a**) and khelleinone (**2b**) with *p*-chlorobenzaldehyde, *p*-methoxybenzaldehyde, 2,4-dimethoxybenzaldehyde, and *p*-nitrobenzaldehyde yields the respective chalcones (**4a–h**).[3,4] Compounds **2a** and **2b** are essentially prepared by the alkaline hydrolysis of visnagin (**1a**) and khaellin (**1b**), respectively (Scheme 1).

Chalcones and several of their derivatives inhibit the voltage-gated potassium channel, which constitutes a promising new target for the treatment of T-cell-mediated autoimmune diseases, such as sclerosis.[5] Besides their well-known biological activity, they are used as precursors for the synthesis of many heterocyclic compounds, such as pyrazoles, pyrazolines, and flavones.[6,7]

In the course of our continuing studies on the chemistry of chalcones,[7] it was of interest to investigate the reaction of the prop-2-en-1-one derivatives (**4a–h**) toward Lawesson's reagent (LR **5**). Aromatic ketones react with **5** to give, in most cases, the corresponding thioketones.[8–11] The chemistry of Lawesson's reagent **5** (LR **5**) and related reagents has

Received 22 August 2011; accepted 6 June 2012.

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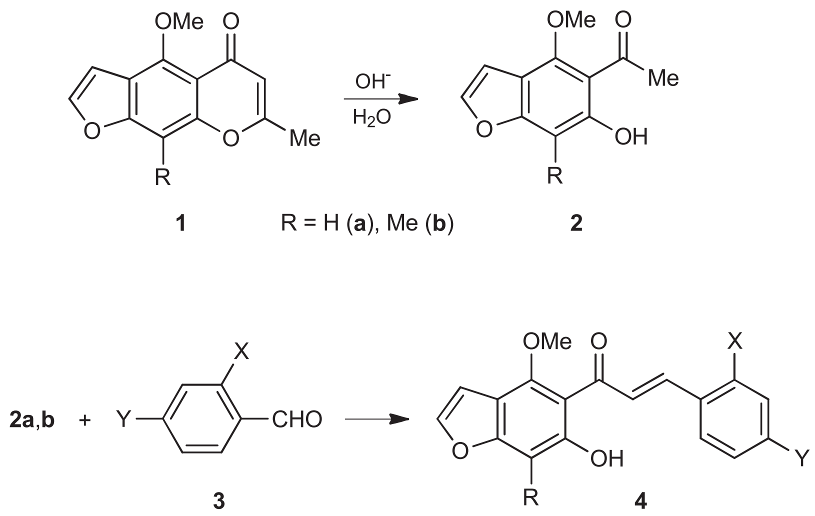


	X	Y
a	H	Cl
b	OMe	H
c	OMe	OMe
d	OMe	NO_2

	R	X	Y
a	H	H	Cl
b	H	H	OMe
c	H	OMe	OMe
d	H	H	NO_2
e	OMe	H	Cl
f	OMe	H	OMe
g	OMe	OMe	OMe
h	OMe	H	NO_2

Scheme 1

been reviewed by several groups of investigators,[12–14] taking into consideration that their main use is the thionation of carbonyl compounds, such as ketones,[15–17] carboxamides,[18] esters,[19] enaminones,[20] lactams,[21] and γ, δ-lactones.[22]

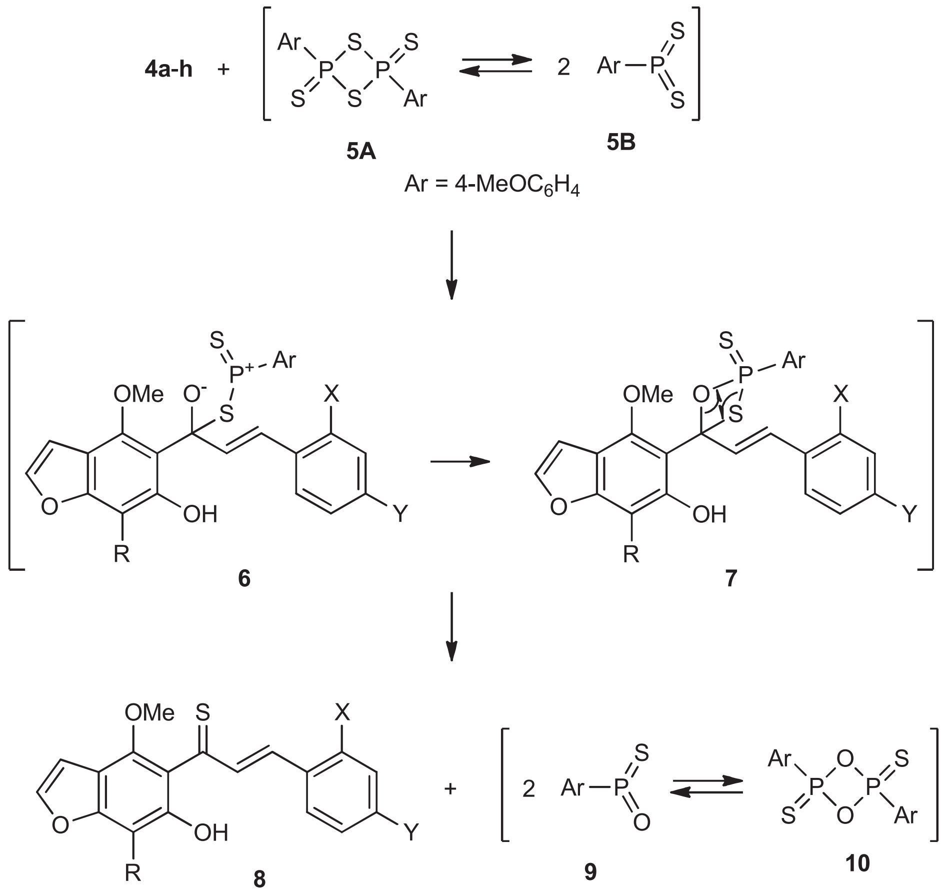
RESULTS AND DISCUSSION

It has been now found that chalcones **4a–h** react with LR **5** in 1:1 molar ratios in refluxing dry toluene to give crystalline compounds, for which the (3-aryl-1-benzofuran-5-yl)propen-1-thione structures **8a–h** were assigned (Scheme 2).

Compounds **8a–h** are chromatographically pure and readily soluble in 90% aqueous NaOH. It is worth to mention that, the reaction of **2a**,**b** with the same reagent **5**, on the other hand, gives the cyclic 1,2-oxaphosphinanes **11a**,**b**, respectively[23] (Figure 1).

A possible mechanism of formation of compounds **8** is depicted in Scheme 2. Initial nucleophilic attack by LR in its monomer form **5B** on the carbonyl carbon atom in **4** can give the betaine intermediate **6**, which cyclizes to form the transient species **7**. From these species the oxa thio phosphorane **9** is eliminated yielding the final thioketones **8**. Dimerization of **9** yields the dioxoanalogue **10**[24] of LR **5**.

Satisfactory micro-analytical and spectroscopic data were obtained for compounds **8a–h**. Thus, the IR spectrum (KBr) of **8a**, taken as an example, showed the presence of the thiocarbonyl band at 1345 cm^{-1}. The strong carbonyl band present in the spectrum of

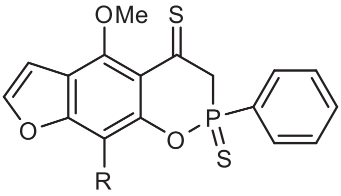


	R	X	Y
a	H	H	Cl
b	H	H	OMe
c	H	OMe	OMe
d	H	H	NO_2
e	OMe	H	Cl
f	OMe	H	OMe
g	OMe	OMe	OMe
h	OMe	H	NO_2

Scheme 2

chalcone **4a** at 1730 cm^{-1} was absent in the spectrum of **8a**. Its mass spectrum (MS) showed an ion peak at *m*/*e* = 328.5 [M^+]. Its ^{1}H NMR spectrum [dimethylsulfoxide (DMSO)-d_6] showed signals at $\delta = 3.88$ (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 6.60 (s, 1H, olefinic-H), 7.20 (s, 1H, olefinic-H), 7.60 (s, 1H, furane); 7.18 (s, 1H, furane), 7.90 (d, $J = 9.2$ Hz, 2H, aromtic-H), 8.18 (d, $J = 9.2$ Hz, 2H, aromtic-H), 12.66 (s, 1H, OH, exchangeable with D_2O).

The aurones **12a–h** were prepared according to an established procedure by oxidation of the chalcones **4a–h** with hydrogen peroxide.[4] Compounds **12a–h** were allowed to react

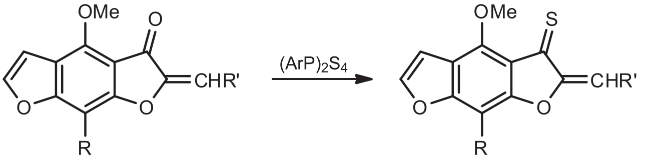


11

R = H (**a**), OMe (**b**)

Figure 1 Cyclic 1,2-oxaphosphinone structures 11a,b.

with LR **5** in boiling toluene to give the corresponding benzo[1,2-*b*:5,4-*b*]difuran-3-thiones **13a**–**h** (Scheme 3). Compatible elemental analyses and spectroscopic measurements were obtained for the isolated thioketones **13a**–**h** (see experimental section).



12a-h **13a-h**

	R	R'
a	H	4-ClC_6H_4
b	H	4-$MeOC_6H_4$
c	H	2,5-$(MeO)_2C_6H_3$
d	H	4-$NO_2C_6H_4$
e	OMe	4-ClC_6H_4
f	OMe	4-$MeOC_6H_4$
g	OMe	2,5-$(MeO)_2C_6H_3$
h	OMe	4-$NO_2C_6H_4$

Scheme 3

Satisfactory micro-analytical and spectroscopic measurements were obtained for compounds **13a**–**h**. The IR spectrum (KBr, cm^{-1}) of **13a**, taken as an example, shows characteristic bands at 3415 cm^{-1} (OH), 3295 cm^{-1} (C—H), 3280–3270 cm^{-1} (aliphatic protons), and 1345 cm^{-1} (C=S). Its MS shows an ion peak at $m/e = 342.5$ [M^+]. The proton spectrum further supports the structure of **13a** (see Experimental section).

CONCLUSIONS

In summary, we report a study on the thionation of chalcones and aurones using LR. Benzofuranylprop-2-en-1-thiones **8a**–**h** and benzodifuran-3-thiones **13a**–**h** were obtained in high yields of 96–98% and 65–80%, respectively.

EXPERIMENTAL

Synthetic Methods, Analytical, and Spectral Data

Melting points (mp) were determined with an electrothermal apparatus (Buchi 535) in an open capillary tube and are uncorrected. The IR spectra were recorded in KBr pellets with a PA-9721 IR spectrophotometer. The ^1H NMR spectra were obtained with a Varian EM-390 spectrometer in $CDCl_3$ as solvent using tetramethylsilane (TMS) as internal reference. Chemical shifts (δ) are given in ppm. The MS were recorded with Kratos (70 eV) Ms

Equipment. The elemental analyses were carried out by the micro-analytical unit at the National Research Centre, Giza, Egypt.

All reactions were monitored by thin layer chromatography (TLC) carried out on 0.2 mm silica gel 60 F-254 (Merck) plates using UV light (254 and 366 nm) for detection. Column chromatography was carried out on a Baker silica gel powder (60–200 mesh).

Synthesis of Compounds 8a–h: General Procedure

To a suspension of **4a**–**h** (0.01 mol) in dry toluene (30 mL) LR (0.404 g, 0.001 mol) was added. The reaction mixture was stirred at refluxing temperature until no more of the starting materials were detected by TLC. The solvent was evaporated under vacuum and the remaining solids were treated with the proper solvent for crystallization.

1-(6-Hydroxy-4-methoxy-1-benzofuran-5-yl)-3-(2-methoxy-4-chlorophenyl)2,4-dienyl)propene thione (8a). Yield 97%, mp 113 °C, brown crystals (from benzene). MS, *m/z*: (344.5, 20.5%). IR (KBr), ν (cm^{-1}): 3425 (OH), 3290 (CH, aromatic), 2885 (CH, aliphatic), 1345 (C=S). ^{1}H NMR (270 MHz, CDCl$_3$, TMS): δ = 3.88 (s, 3H, OCH$_3$), 6.60 (s, 1H, olefinic-H), 7.20 (s, 1H, olefinic-H), 6.60 (s, 1H, furane-H), 7.18 (s, 1H, furane-H), 7.18 (m, 2H, arom-H), 7.80 (m, 2H, arom-H), 12.66 (s, 1H, OH, exchangeable with D$_2$O). Anal. calcd. for $C_{18}H_{13}ClO_3S$: C 62.70, H 3.80, S 9.30%. Found: C 62.69, H 3.77, S 9.31%.

1-(6-Hydroxy-4-methoxy-1-benzofuran-5-yl)-3-(2,4-dimethoxyphenyl-2,4-dienyl)propene-1-thione (8b). Yield 98%, mp 127 °C (MeOH). MS, *m/z*: (340, 21%). IR (KBr), ν (cm^{-1}): 3445 (OH), 3292 (CH, aromatic), 2885 (CH, aliphatic), 1351 (C=S). ^{1}H NMR (270 MHz, CDCl$_3$, TMS): δ = 3.88 (s, 3H, OCH$_3$); 6.60 (s, 1H, olefinic-H); 7.20 (s, 1H, olefinic-H); 6.60 (s, 1H, furane-H); 7.18 (s, 1H, furane-H); 6.66 (m, 2H, arom-H); 7.70 (m, 2H, arom-H); 12.66 (s, 1H, OH, exchangeable with D$_2$O). Anal. calcd. for $C_{19}H_{16}O_4S$: C 67.04, H 4.74, S, 9.42%. Found: C 67.20, H 4.79, S 9.41%.

1-(6-Hydroxy-4-methoxy-1-benzofuran-5-yl)-3-(2-methoxy-2,4-dienyl)propene-1-thione (8c). Yield 98%, mp 145 °C, orange crystals (from benzene). MS, *m/z*: (370, 22.8%). IR (KBr), ν (cm^{-1}): 3445 (OH), 3290 (CH, aromatic), 2885 (CH, aliphatic), 1345 (C=S). ^{1}H NMR (270 MHz, CDCl$_3$, TMS): δ = 3.88 (s, 3H, OCH$_3$), 4.00 (s, 3H, OCH$_3$), 6.60 (s, 1H, olefinic-H), 7.20 (s, 1H, olefinic-H); 6.60 (s, 1H, furane-H), 7.18 (s, 1H, furane-H), 7.18 (m, 2H, arom-H), 7.80 (m, 2H, arom-H), 12.66 (s, 1H, OH, exchangeable with D$_2$O). Anal. calcd. for $C_{20}H_{18}O_5S$: C 64.85, H, 4.85, S 8.66%. Found: C 64.86, H 4.86, S 8.64%.

1-(6-Hydroxy-4-methoxy-1-benzofuran-5-yl)-3-(2-methoxy-4-nitrophenyl-2,4-dienyl)propene thione (8d). Yield 98%, mp 220 °C, reddish crystals (from benzene). MS, *m/z*: (355, 66%). IR (KBr), ν (cm^{-1}): 3425 (OH), 3290 (CH, aromatic), 2885 (CH, aliphatic), 1345 (C=S). ^{1}H NMR (270 MHz, CDCl$_3$, TMS): δ = 3.88 (s, 3H, OCH$_3$), 4.00 (s, 3H, OCH$_3$), 4.10 (s, 3H, OCH$_3$), 6.60 (s, 1H, olefinic-H), 7.20 (s, 1H, olefinic-H), 6.60 (s, 1H, furane-H), 7.18 (s, 1H, furane-H), 7.18 (m, 2H, arom-H), 7.80 (d, 2H, arom-H), 12.66 (s, 1H, OH, D$_2$O exchangeable). Anal. calcd. for $C_{18}H_{13}NO_5S$: C 60.85, H 3.66, N 3.94, S 9.02%. Found: C 60.84, H 3.69, N 3.93, S, 9.01%.

(2E)-3-(4-Chlorophenyl)-1-(6-hydroxy-4-methoxy-1-benzofuran-5-yl)prop-2-ene-1-thione (8e). Yield 99%, mp 120 °C, yellow crystals (from MeOH). MS, *m/z*: (374.5, 24.2%). IR (KBr), ν (cm^{-1}): 3405 (OH), 3290–3285 (CH, aromatic), 2995–2880 (CH, aliphatic), 1345 (C=S). ^{1}H NMR (270 MHz, CDCl$_3$, TMS): δ = 3.88 (s, 3H, OCH$_3$), 4.00 (s, 3H, OCH$_3$), 6.60 (s, 1H, olefinic-H), 7.20 (s, 1H, olefinic-H), 7.60

(s, 1H, furane-H), 7.18 (s, 1H, furane-H), 7.90 (m, 2H, arom-H), 8.18 (m, 2H, arom-H), 12.66 (s, 1H, OH, D_2O exchangeable). Anal. calcd. for $C_{19}H_{15}ClO_4S$: C 60.88, H 4.03, S, 8.54%. Found: C 60.88, H 4.00, S 8.55%.

(2E)-1-(6-Hydroxy-4,7-dimethoxy-1-benzofuran-5-yl)-3-(4-methoxyphenyl)prop-2-ene-1-thione (8f). Yield 98%, mp 100 °C, yellow crystals (from MeOH). MS, *m/z*: (370, 30.2%). IR (KBr), ν (cm^{-1}): 3415 (OH), 3290–3280 (CH, aromatic), 2885–2870 (CH, aliphatic), 1345 (C=S). ^1H NMR (270 MHz, $CDCl_3$, TMS): $\delta = 3.50$ (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 6.60 (s, 1H, olefinic-H), 7.20 (s, 1H, olefinic-H), 6.60 (s, 1H, furane-H), 7.18 (s, 1H, furane-H), 6.80 (m, 2H, arom-H), 7.40 (m, 2H, arom-H), 12.00 (s, 1H, OH, D_2O exchangeable). Anal. calcd. for $C_{20}H_{18}O_5S$: C 64.86, H 4.86, S 8.66%. Found: C 64.85, H 4.90, S 8.64%.

1-(6-Hydroxy-4,7-dimethoxy-1-benzofuran-5-yl)-3-(4-dimethoxyphenyl) prop-2-ene-1-thione (8g). Yield 98%, mp 115 °C, orange crystals (from benzene). MS, *m/z*: (401, 60.3%). IR (KBr), ν (cm^{-1}): 3425 (OH), 3285 (CH, aromatic), 2885 (CH, aliphatic), 1345 (C=S). ^1H NMR (270 MHz, $CDCl_3$, TMS): $\delta = 3.88$ (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 4.14 (s, 3H, OCH_3), 6.60 (s, 1H, olefinic-H), 7.20 (s, 1H, olefinic-H), 6.60 (s, 1H, furane-H), 7.18 (s, 1H, furane-H), 7.18 (m, 2H, arom-H), 7.80 (m, 2H, arom-H), 12.60 (s, 1H, OH, D_2O exchangeable). Anal. calcd. for $C_{21}H_{21}O_6S$: C 62.84, H 5.23, S 7.98%. Found: C 62.83, H 5.27, S, 7.99%.

1-(6-Hydroxy-4,7-dimethoxy-1-benzofuran-5-yl)-3-(4-nitrophenyl)prop-2-ene-1-thione (8h). Yield 98%, mp 175 °C, yellow crystals (from MeOH/benzene). MS, *m/z*: (385, 21.0%). IR (KBr), ν (cm^{-1}): 3435 (OH), 3290 (CH, aromatic), 2885 (CH, aliphatic), 1351 (C=S). ^1H NMR (270 MHz, $CDCl_3$, TMS): $\delta = 3.88$ (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 6.60 (s, 1H, olefinic-H), 7.20 (s, 1H, olefinic-H), 6.60 (s, 1H, furane-H), 7.18 (s, 1H, furane-H), 7.18 (m, 2H, arom-H), 7.80 (m, 2H, arom-H), 12.66 (s, 1H, OH, D_2O exchangeable). Anal. calcd. for $C_{19}H_{15}NO_6S$: C 59.22, H 3.89, N 3.63, S 8.31%. Found: C 59.21, H 3.92, N, 3.63, S 8.32%.

Synthesis of Compounds 13a–h: General Procedure

To a suspension of aurones **12a–h** (0.01 mol) in dry toluene (30 mL) LR (0.005 mol) was added. The reaction mixture was refluxed for 22 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered and the solvent was evaporated in vacuo. The resulting residue was applied to a column by packing slurry of silica gel in *n*-hexane. Ethyl acetate/petroleum ether (4: 6, v/v) was used as an eluent.

2-(3-Chloro-benzylidene)-4-methoxy-benzo[1,2-b;5,4-b]difurane-3-thione (13a). Yield 60%, mp 198 °C, yellow crystals. MS, *m/z*: (342.5, 18.15%). IR (KBr), ν (cm^{-1}): 3415 (OH), 3295 (CH), 3280–3270 (CH, aliphatic), 1345 (C=S). ^1H NMR (270 MHz, DMSO-d_6, TMS): $\delta = 4.16$ (s, 3H, OCH_3), 4.21 (s, 3H, OCH_3), 7.80 (s, 1H, $C\underline{H}R$), 6.80 (m, 1H, furane-H), 7.30 (m, 1H, furane-H), 6.70 (d, 2H, arom-H), 7.50 (d, 2H, arom-H), 12.66 (s, 1H, OH, D_2O exchangeable). Anal. calcd. for $C_{18}H_{11}ClO_3S$: C 63.07, H 3.21, S 9.34%. Found: C 63.30, H 3.23, S 9.35%.

4-Methoxy-2-(3-methoxy-benzylidene)-benzo[1,2-b;5,4-b]difurane-3-thione (13b). Yield 70%, mp 210 °C, yellow crystals. MS, *m/z*: (338, 30.2%). IR (KBr), ν (cm^{-1}): 3415 (OH), 3295 (CH), 3280–3270 (CH, aliphatic), 1345(C=S). ^1H NMR (270 MHz, DMSO-d_6, TMS): $\delta = 4.16$ (s, 3H, OCH_3), 4.21 (s, 3H, OCH_3), 7.80 (s, 1H, $C\underline{H}R$), 6.80 (m, 1H, furane-H), 7.30 (m, 1H, furane-H), 6.70 (m, 2H, arom-H), 7.50 (m, 2H, arom-H), 12.66 (s, 1H, OH, D_2O exchangeable). Anal. calcd. for $C_{19}H_{14}O_4S$: C 67.45, H 4.14, S 9.48%. Found: C 67.44, H 4.17, S 9.46%.

2-(3,5-Dimethoxy-benzylidene)-4-methoxy-benzo[1,2-b;5,4-b′]difurane-3-thione (13c). Yield 70%, mp 200 °C, brown crystals. MS, *m/z*: (368, 60.1%). IR (KBr), ν (cm^{-1}): 3415 (OH), 3295 (CH), 3280–3270 (CH-aliphatic), 1345 (C=S). ^1H NMR (270 MHz, DMSO-d_6, TMS): $\delta = 4.16$ (s, 3H, OCH_3), 4.21 (s, 3H, OCH_3), 7.80 (s, 1H, $C\underline{H}R$), 6.80 (m, 1H, furane-H), 7.30 (m, 1H, furane-H), 6.70 (m, 2H, arom-H), 7.50 (m, 2H, arom-H), 12.66 (s, 1H, OH, D_2O exchangeable). Anal. calcd. for $C_{20}H_{16}O_5S$: C 65.22, H 4.34, S 8.70%. Found: C 65.20, H 4.38, S 8.69%.

4-Methoxy-2-(3-methoxy-5-nitro-benzylidene)-benzo[1,2-b;5,4-b′]difurane-3-thione (13d). Yield 80%, mp 290 °C, brownish crystals. MS, *m/z*: (353, 24.14%). IR (KBr), ν (cm^{-1}): 3415 (OH), 3295 (CH), 3280–3270 (CH-aliphatic), 1345 (C=S). ^1H NMR (270 MHz, DMSO-d_6, TMS): $\delta = 4.16$ (s, 3H, OCH_3), 4.21 (s, 3H, OCH_3), 7.80 (s, 1H, $C\underline{H}R$), 6.80 (m, 1H, furane-H), 7.30 (m, 1H, furane-H), 6.70 (m, 2H, arom-H), 7.50 (m, 2H, arom-H), 12.66 (s, 1H, OH, D_2O exchangeable). Anal. calcd. for $C_{18}H_{11}NO_5S$: C 61.19, H 3.11, N 3.96, S 9.07%. Found: C 61.18, H 3.12, N 3.96, S 9.06%.

2-(3-Chloro-benzylidene)-4,8-dimethoxy-benzo[1,2-b;5,4-b′]difurane-3-thione (13e). Yield 60%, mp 215 °C, brown crystals. MS, *m/z*: (372.5, 10.12%). IR (KBr), ν (cm^{-1}): 3415 (OH), 3295 (CH), 3280–3270 (CH, aliphatic), 1345 (C=S). ^1H NMR (270 MHz, DMSO-d_6, TMS): $\delta = 4.16$ (s, 3H, OCH_3), 4.21 (s, 3H, OCH_3), 7.80 (s, 1H, $C\underline{H}R$), 6.80 (m, 1H, furane-H), 7.30 (m, 1H, furane-H), 6.70 (m, 2H, arom-H), 7.50 (m, 2H, arom-H), 12.66 (s, 1H, OH, D_2O exchangeable). Anal. calcd. for $C_{19}H_{13}ClO_4S$: C 61.20, H 3.49, S 8.60%. Found: C 60.21, H, 3.48, S, 8.59%.

4,8-Dimethoxy-2-(3-methoxy-benzylidene)-benzo[1,2-b;5,4-b′]difurane-3-thione (13f). Yield 65%, mp 165 °C, orange crystals. MS, *m/z*: (368, 17.44%). IR (KBr), ν (cm^{-1}): 3415 (OH), 3295 (CH), 3280–3270 (CH, aliphatic), 1345 (C=S). ^1H NMR (270 MHz, DMSO-d_6, TMS): $\delta = 4.16$ (s, 3H, OCH_3), 4.21 (s, 3H, OCH_3), 7.80 (s, 1H, $C\underline{H}R$), 6.80 (m, 1H, furane-H), 7.30 (m, 1H, furane-H), 6.70 (m, 2H, arom-H), 7.50 (m, 2H, arom-H), 12.66 (s, 1H, OH, D_2O exchangeable). Anal. calcd. for $C_{20}H_{16}O_5S$: C 65.22, H 4.35, S 8.69%. Found: C, 65.20, H 3.38, S 8.70%.

2-(3,5-Dimethoxy-benzylidene)-4,8-dimethoxy-benzo-[1,2-b;5,4-b′]difurane-3-thione (13g). Yield 60%, mp 205 °C, brownish crystals. MS, *m/z*: (398, 55.6%). IR (KBr), ν (cm^{-1}): 3415 (OH), 3295 (CH), 3280–3270 (CH, aliphatic), 1345 (C=S). ^1H NMR (270 MHz, DMSO-d_6, TMS): $\delta = 4.16$ (s, 3H, OCH_3), 4.21 (s, 3H, OCH_3), 7.80 (s, 1H, $C\underline{H}R$), 6.80 (m, 1H, furane-H), 7.30 (m, 1H, furane-H), 6.70 (m, 2H, arom-H), 7.50 (m, 2H, arom-H), 12.66 (s, 1H, OH, D_2O exchangeable). Anal. calcd. for $C_{21}H_{18}O_6S$: C 63.32, H 4.52, S 8.04%. Found: C 63.30, H 4.55, S 8.05%.

4,8-Dimethoxy-2-(3-methoxy-5-nitro-benzylidene)-benzo[1,2-b;5,4-b′]difurane-3-thione (13h). Yield 75%, mp 315 °C, orange crystals. MS, *m/z*: (382, 60.1%). IR (KBr), ν (cm^{-1}): 3415 (OH), 3295 (CH), 3280–3270 (CH, aliphatic), 1345 (C=S). ^1H NMR (270 MHz, DMSO-d_6, TMS): $\delta = 4.16$ (s, 3H, OCH_3), 4.21 (s, 3H, OCH_3), 7.80 (s, 1H, $C\underline{H}R$), 6.80 (m, 1H, furane-H), 7.30 (m, 1H, furane-H), 6.70 (m, 2H, arom-H), 7.50 (m, 2H, arom-H), 12.66 (s, 1H, OH, D_2O exchangeable). Anal. calcd. for $C_{19}H_{12}NO_6S$: C 59.53, H 3.39, N 3.65, S 8.36%. Found: C 59.52, H 3.42, N 3.65, S 8.38%.

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