Synthetic studies in sulfur heterocycles. One-pot synthesis of "thioaurones" and their conversion into [1]benzothieno[3,2-*b*]pyrans *via* tandem reactions

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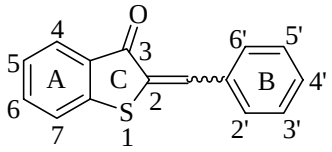
Abstract

Thioaurones were prepared one pot in high yield by the treatment of *N*,*N*-diethyl-2-(methylsulfanyl)arylamides with LDA and an aromatic aldehyde through directed *ortho*-metalation. Heating the thioaurones derived from cinnamaldehyde above 200 ºC resulted in [1]benzothieno[3,2-*b*]pyrans. Treatment of *N*,*N*-diethyl-2-(methylsulfanyl)benzamide and crotonaldehyde gave 4-(methylsulfanyl)benzothieno[3,2,-*b*]pyran *via* conjugate nucleophilic addition and ring closure in one pot. A possible mechanistic pathway is discussed.

Keywords: Thioaurone, electrocyclic ring closure, [1,3] H shift, tandem reaction

Introduction

The derivatives of 2-benzylidinebenzo[*b*]thiophen-3(2*H*)-one (**1**) are known as thioaurones which was first introduced by O'Sullivan [1] in 1977.



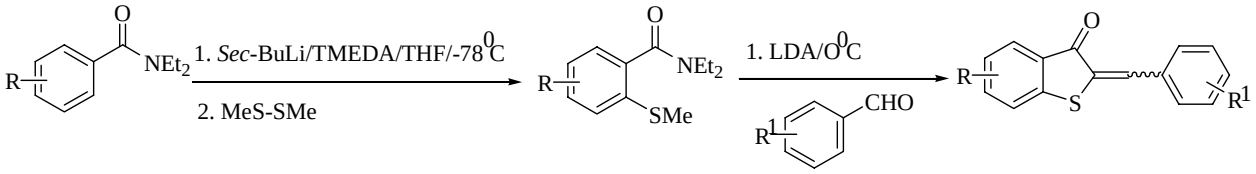
1

Even synthesis of thioaurone was achieved almost one century ago,[2,3] they are relatively little known. Thioaurones are interesting molecule because of their diverse uses such as thioindigo-like dyes[4-17] and photochromic materias. Mention have been made of their application in photoresponsive devices and photoswitchable biomolecules.[18-22] Despite, the growing interest in aurones as potential medicinal agent [23] will probably result in similar interest

in the thio analogs. In addition, these compounds can be used as aqueous jet-printing ink[24] and as auxiliary thermometer packaging. Although these compounds are known for quite some time but a more expedient synthetic route than the previously reported one,[25-30] to this class of compounds was needed in their manifold uses. Recently Cabiddu[24] and his co-workers reported formation of thioindoxyls from commercially available ethyl-2-methylsulfanylbenzoates. Its limitation is the absence of any substitution in the benzene ring of thioaurone because commercially available starting material used by the authors imposed this constraint. Our approach (Scheme 1) could do away with such constraints. The yields are good to excellent (Table 1). When thioaurones **3a**, **3d**, **3n**, **3s**, **3u** were heated in a silicone oil bath at 210 ^{0}C (bath temperature) for 6-7 hrs, a brown mass were obtained in each case which after purification afforded colorless crystalline (except **5e**) [1]Benzothieno[3,2,-*b*]pyrans (Scheme 2).

Result and Discussion

The great utility of directed *ortho*-metalation reaction in organic synthesis is well documented.[31-33] In our preliminary communication[34] we reported the synthesis of thioaurones. We prepared *N*,*N*-diethylarylamide from different substituted benzoic acids and introduced methylsulfanyl group *ortho*-to the -CONEt$_2$ using directed *ortho*-metalation.



2 **3 (a-v**

Scheme 1

This *N*,*N*-diethyl-2-methylsulfanylarylamide was treated with LDA at O^{0}C under argon atmosphere and after a brief interval, a solution of aromatic aldehyde in tetrahydrofuran was added to the reaction mixture which was kept at O^{0}C. Usual acidic workup[35] afforded the thioaurones (**3a-3v**) and were crystallized from ethylacetate-hexane. The yields (Table 1) were good to excellent. The most plausible mechanistic pathway (Fig-1) involves the deprotonation of the methyl sulfanyl group by LDA forming a thioindoxyl intermediate which under basic condition immediately reacts with aldehyde followed by dehydration afforded the product. It is important to note that thioaurone may exist as two isomer, *E* and *Z*. (Fig 2).

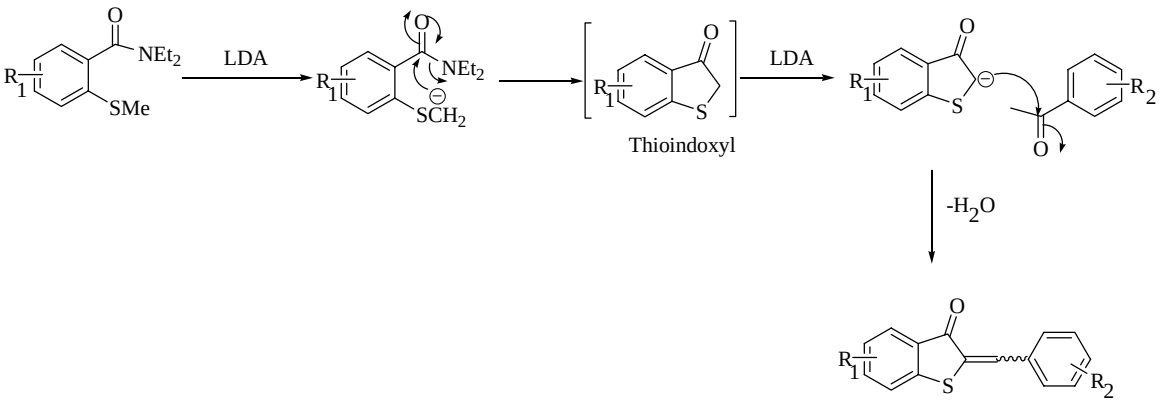
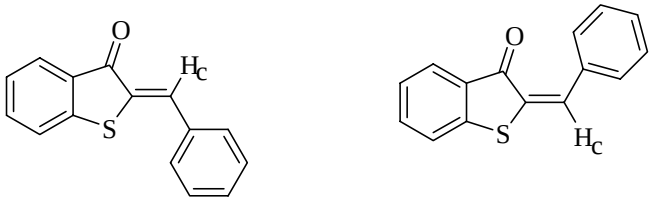


Figure 1



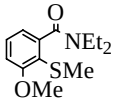
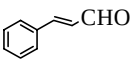
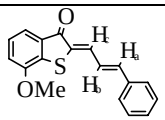
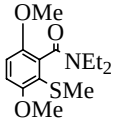
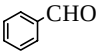
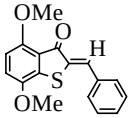
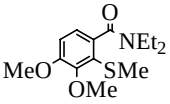
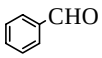
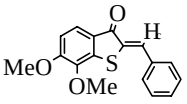
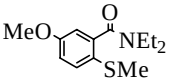
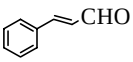
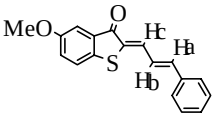
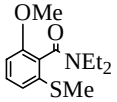
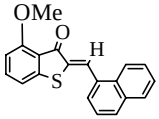
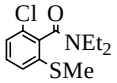
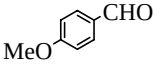
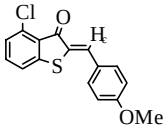
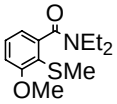
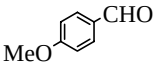
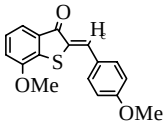
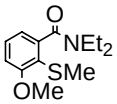
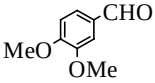
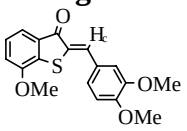
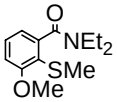
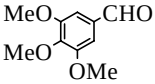
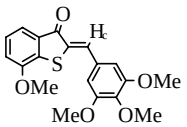
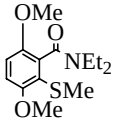
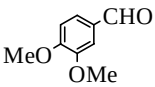
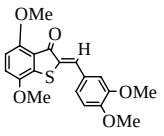
1. *Z*(trans) **1.** *E* (cis)

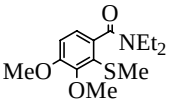
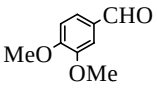
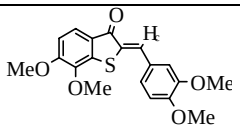
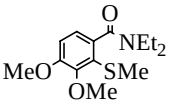
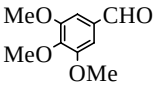
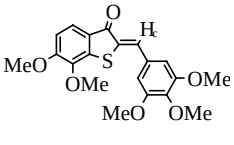
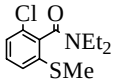
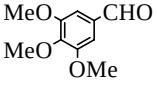
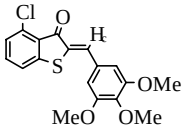
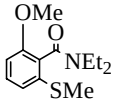
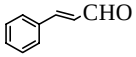
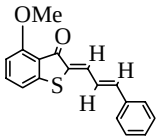
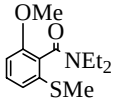
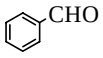
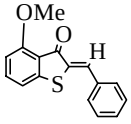
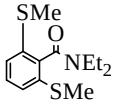
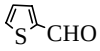
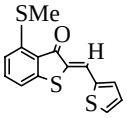
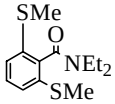
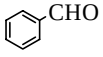
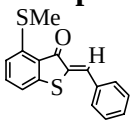
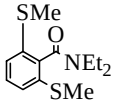
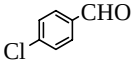
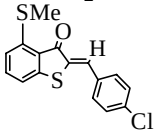
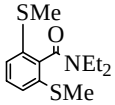
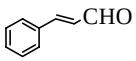
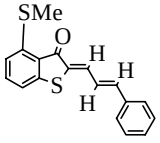
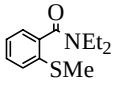
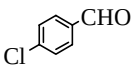
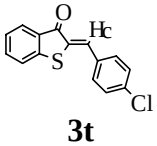
Figure 2

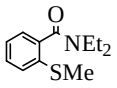
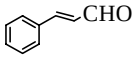
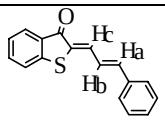
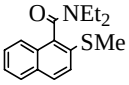
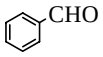
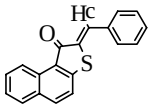
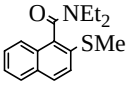
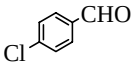
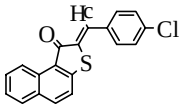
The *Z* isomer is thermodynamically more stable than the *E* isomer[20] and therefore it can be assumed that all thioaurones with undetermined stereochemistry of the double bond are most probably *Z* isomer. The unstable *E* isomer can be prepared by irradiation of the *Z* form with sunlight[36] or UV/VIS light.[1,20-22] The equilibrium formed upon irradiation is unstable and in darkness the *Z* isomer is formed again.

The two isomers can be distinguished based on their NMR studies. The α-hydrogen (H_c) to the exocyclic double bond appears in the range of δ 7.87-7.97 ppm for Z isomer while for *E* isomer it appears in δ 7.50-7.65 ppm range.[1,20] The chemical shift values in the ^{1}H NMR of our products clearly indicate that all the thioaurones we obtained were *Z*. In ^{13}C NMR spectra, the carbonyl group itself in *E* isomer appears 5 ppm down field in comparison to *Z*[1] isomer. The yield reported in Table-1 is the isolated yield of compounds after purification. GC/MS analysis reveled the isolated products to be pure. Intrigued by Tang's[37] observation of an equilibrium between *Z* and *E* isomers in polar solvents, such as methanol, we dissolved pure sample of a *Z* isomer in ethanol and subjected to HPLC analysis which indicates the presence of *Z* isomer ≥ 99% with traces of *E* isomer. All the compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR and elemental analysis.

Table 1. One pot synthesis of diversely substituted thioaurones

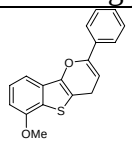
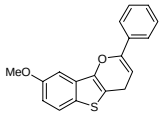
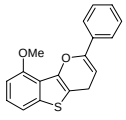
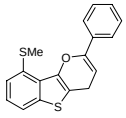
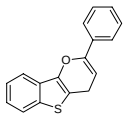
Entry	2-methylsulfanyl aryl amide	Aldehyde	Product	Yield
1			 **3a**	83%
2			 **3b**	89%
3			 **3c**	94%
4			 **3d**	74%
5			 **3e**	69%
6			 **3f**	78%
7			 **3g**	84%
8			 **3h**	93%
9			 **3i**	95%
10			 **3j**	89%

11			 **3k**	94%
12			 **3l**	93%
13			 **3m**	94%
14			 **3n**	86%
15			 **3o**	76%
16			 **3p**	92%
17			 **3q**	78%
18			 **3r**	80%
19			 **3s**	78%
20			 **3t**	79%

21			 **3u**	75%
22			 **3v**	82%
23			 **3w**	93%

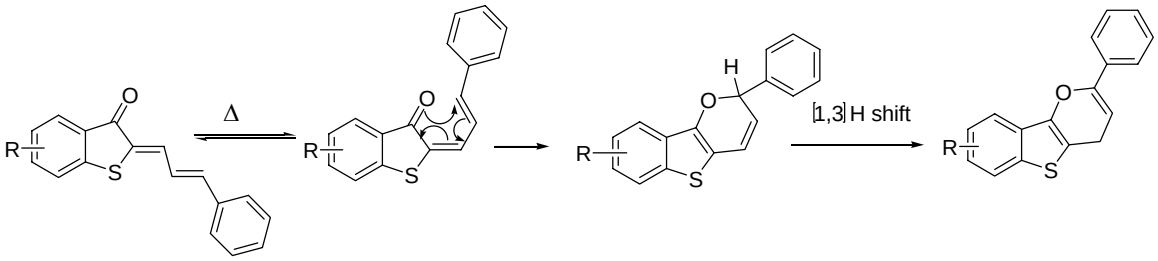
Now when the thioaurones **3a**, **3d**, **3n**, **3s**, **3u**, derived from cinnamaldehyde were heated in a silicon oil bath at 210 ^{0} C for 7 hours, a brown mass was obtained in which the carbonyl peaks were absent in the IR spectra. In the proton NMR spectra a two proton multiplet was present for all the compounds at δ= 2.88 to 3.22 ppm. The aromatic region showed the presence of six proton multiplet and three doublet of doublets. On the basis of spectroscopic and analytical data, the resulting compounds were assigned the structure [1]benzothieno[3,2,-*b*]pyrans. The yields are mediocre (Table 2).

Table 2. Synthesis of [1]benzothieno[3,2,-*b*]pyrans

Entry	Thioaurone	Heating product	Yield
1	**3a**	 **4a**	78%
2	**3d**	 **4b**	65%
3	**3n**	 **4c**	73%
4	**3s**	 **4d**	69%
5	**3u**	 **4e**	68%

In the ^{13}C NMR, signals due to methyl and methylene carbons were present in appropriate places. The signals due to C-2 in each case appears around δ=186 ppm. This considerable down field shift is explained by its attachment to the ring oxygen atom, phenyl ring and the double bond.

The possible mechanism consists of electrocyclic ring closure (of cisoid conformation) and [1,3]hydrogen shift in tandem as shown in scheme 2.

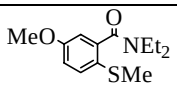
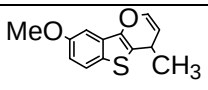
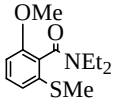
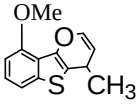
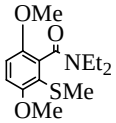
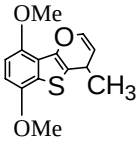
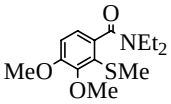
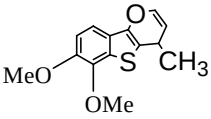
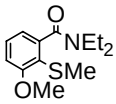
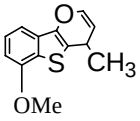


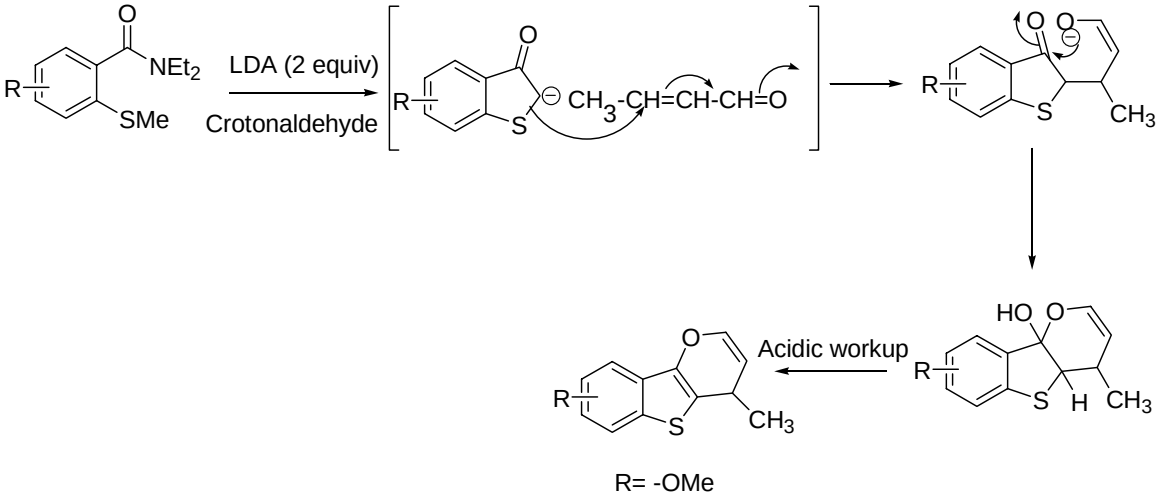
Scheme 2

It is interesting to note that when *N,N*-diethyl-2-methylsulfanyl benzamides were treated with LDA and crotonaldehyde, a reddish brown gummy products were obtained which upon repeated choromatography afforded thick liquid products. The NMR spectra does not match with[1]benzothieno[3,2,-*b*]pyrans as it shows three-proton signals at δ=3.89 ppm and 1.61 ppm as singlet and doublet respectively. The same products (Table 3) were obtained with other 2-methylsulfanylbenzamides. On the basis of analytical and spectral data, these compounds were assigned as 4-methyl[1]Benzothieno[3,2,-*b*]pyrans (**5**). The most plausible mechanistic pathway involves (Scheme 3) the formation of thioindoxyl, conjugate nucleophilic addition and ring closure.

In summary, we have shown above a new approach towards the synthesis of a wide variety of thioaurones and their successful application for the synthesis of [1]benzothieno[3,2,-*b*]pyrans which is not otherwise possible by the methods described in the literature and their formation in one pot is particularly convenient.

Table 3. Synthesis of 4-methyl[1]benzothieno[3,2,-*b*]pyrans

Entry	Benzamide	Product	Yield
1		 **5a**	40%
2		 **5b**	45%
3		 **5c**	43%
4		 **5d**	50%
5		 **5e**	56%



Scheme 3

Experimental Section

General Procedures. Melting points were taken on a Mel-Temp capillary apparatus and are uncorrected with respect to stem correction. ^{1}H and ^{13}C NMR spectra were recorded on a 400

MHz Bruker ADVANCE DRX-400 Multinuclear NMR spectrometer. Chemical shifts are reported in reference to TMS as internal standard. IR spectra was recorded on a Perkin-elmer 881 Spectrometer (ν in cm^{-1}). Elemental analysis were obtained from SMU Analytical Service Laboratories. HPLC analysis were carried out on a Waters Delta prep 4000 instrument equipped with a Whelk-01 (25 cm x 4.6) column (purchased from Regis Technologies, Inc.) and UV detector at 254 nm. The eluent, hexane/isopropanol (70/30, v/v) was run at flow rate of 1 mL/min. GC/MS was performed on HP 7673 Automatic Sampler Instrument.

Experimental Procedure

To a vigorously stirred solution of LDA (2.5 equiv) and dry THF (10 mL) at O ^{0}C kept under argon, a solution of *N*,*N*-diethyl-2-(methylsulfanyl)benzamide (1 gm, 4.0 mmol) was added through a needle syringe system. Stirring was continued for 20 minutes at the same temperature. To this mixture, a solution of aldehyde (6.0 mmol) in dry THF (5 mL) was slowly added at the same temperature and stirring was continued for another 1 hr. The resultant mixture was then allowed to warm to room temperature and poured into water (100 mL). The pH was adjusted to 4-5 by addition of 10% aq HCl. Organic layer was separated and aqueous layer was extracted with ether (3 X100 mL). The combined organic layer was washed with water, dried (Na_2SO_4) and removal of solvent afforded the crude product which was purified by crystallization (ethyl acetate-hexane). All the compounds reported below were prepared in the same way.

7-Methoxy-2-(3-phenylallylidene)benzo[*b*]thiophen-3(2*H*)-one (3a). Yellowish fluffy solid; m.p. 152-153 ^{0}C; IR (KBr)$\nu_{C=0}$ 1635 cm;$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 (3H, s, -OMe), 6.97 (1H, dd, *J*=7.9, 8.1 Hz, aromatic), 7.1 (1H, d, *J*=15.4 Hz, H_b), 7.38 (1H, dd, J_1=7.9, J_2=8.1 Hz, aromatic), 7.45-7.41(4H, m, aromatic), 7.61 (1H, s, H_c), 7.67-7.64 (2H, m, aromatic), 7.93 (1H, d, *J*=15.4 Hz, H_a); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.6, 109.5, 116.4, 122.9, 126.6, 129.1, 129.4, 131.3, 132.6, 133.0, 134.8, 144.6, 154.8, 165.2, 186.4; *Anal*. Calcd. for $C_{18}H_{14}O_2S$, C, 73.40; H, 4.76. Found C, 73.50; H, 4.80%.

2-Benzylidene-4,7-dimethoxy-benzo[*b*]thiophene-3-one (3b). Pale yellow solid; m.p. 109-111 ^{0}C; IR(KBr)$\nu_{C=0}$ 1690 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (3H, s, -OMe), 3.95 (3H, s, -OMe), 6.62 (1H, d, *J*=7.8 Hz, aromatic), 6.79 (1H, d, *J* =7.8 Hz, aromatic), 7.12-7.21 (3H, m, aromatic), 7.31 (2H, dd, J_1=2.5 Hz, J_2=7.8 Hz, aromatic), 7.85 (1H, s, H_c); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.5, 55.6, 111.9, 119.2, 121.5, 124.3, 125.7 126.2, 126.5, 127.3, 127.9, 128.1, 134.5, 140.1, 155.3, 155.8, 187.3; *Anal.* Calcd. for $C_{17}H_{14}O_3S$, C, 68.44; H, 4.73. Found C, 68.50; H, 4.71%.

2-Benzylidene-6,7-dimethoxy-benzo[*b*]thiophene-3-one (3c). Yellow solid; m.p. 111-113 ^{0}C; IR.(KBr)$\nu_{C=0}$ 1689 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (3H, s, -OMe), 3.95 (3H, s, -OMe), 6.69 (1H, d, *J* =7.8 Hz, aromatic), 7.10-7.14 (2H, m, aromatic), 7.21-7.30 (4H, m, aromatic), 7.91 (1H, s, H_c); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 55.9, 111.3, 119.1, 120.1, 121.5, 122.9, 125.7, 127.9, 126.3, 126.5, 127.5, 128.4, 130.3, 140.1, 186.9; *Anal.* Calcd. for $C_{17}H_{14}O_3S$, C, 68.44; H, 4.73. Found C, 68.48; H, 4.78%.

5-Methoxy-2-(3-phenyl-allylidene)-benzo[*b*]thiophene-3-one (3d). Yellowish solid; m.p. 146-147 ^{0}C, IR (KBr)$\nu_{C=0}$ 1639.4 cm;$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (3H, s, -OMe), 6.95 (1H, d, *J*=15.5 Hz, H_b), 7.12 (1H, dd, *J*=2.4, 8.8 Hz, aromatic), 7.30 (1H, d, *J*=2.4 Hz, aromatic), 7.37-7.35 (4H, m, aromatic), 7.52 (1H, s, H_c), 7.55-7.59 (2H, m, aromatic), 7.80 (1H, d, *J*=15.5 Hz, H_a); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.0, 109.3, 115.1, 122.1, 122.8, 124.5, 129.1, 129.4, 131.3, 131.8, 132.7, 134.8, 144.6, 158.1, 164.4, 186.3; *Anal.* Calcd. for $C_{18}H_{14}O_2S$, C, 73.40, H, 4.76. Found C, 73.5; H, 4.75%.

4-Methoxy-2-napthalen-1-ylmethylene-benzo[b]thiophene-3-one (3e). Reddish yellow solid; m.p. 139-140 ^{0}C; IR. (KBr)$\nu_{C=0}$ 1676 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (3H, s, OMe), 7.31-7.60 (4H, m, aromatic), 7.82 (2H, d, *J*=8.0 Hz, aromatic), 7.83 (1H, s, H_c), 8.00 (1H, d, *J*=8.0 Hz, aromatic), 8.33 (1H, dd, *J*=1.5 Hz, J_2= 7.8 Hz, aromatic), 9.01 (1H, dd, J_1=7.8 Hz, J_2=8.0 Hz, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.3, 105.4, 115.7, 124.8, 125.8, 126.3, 126.8, 127.8, 128.5, 128.8, 129.1, 131.8, 132.1, 132.2, 134.3, 135.0, 173.7, 194.0; *Anal.* Calcd. for $C_{20}H_{14}O_2CS$, C, 75.47, H, 4.4. Found C, 75.48; H, 4.51%.

4-Chloro-2-(4-methoxy-benzyledene)-benzo[*b*]thiophen-3-one (3f). Yellowish solid; m.p. 141-142^{0}C; IR. (KBr)$\nu_{C=0}$ 1674 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (3H, s, -OMe), 7.01 (2H, d, *J*=8.0 Hz, aromatic), 7.37 (1H, dd, *J*=1.5 Hz, J_2= 7.6 Hz, aromatic), 7.40 (1H, dd, *J*=7.6, J_2= 7.6 Hz, aromatic), 7.6 (1H, dd, *J*=1.5 Hz, J_2= 7.6 Hz, aromatic), 7.87 (1H, s, H_c), 8.05 (2H, d, *J*=8.0 Hz, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 110.0, 114.1, 114.5, 121.9, 126.9, 127.1, 130.3, 130.8, 131.1, 132.1, 132.7, 142.9, 163.8, 165.9, 190.5; *Anal*. Calcd. for $C_{16}H_{11}O_2ClS$, C, 63.47; H, 3.63. Found C, 63.5; H, 3.65%.

7-Methoxy-2-(4-methoxybenzylidene)-benzo[*b*]thiophene-3-one (3g). Fibrous yellow crystal; m.p. 105-106 ^{0}C; IR.(KBr)$\nu_{C=0}$ 1697 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (3H, s, -OMe), 3.94 (s, 3H, -OMe), 6.89 (1H, dd, J_1=7.9 Hz, J_2=7.8 Hz aromatic), 6.95 (2H, d, *J*=8.0 Hz, aromatic), 7.32 (1H, dd, *J*=7.9 Hz, J_2=7.8 Hz, aromatic), 7.60 (1H, dd, *J*=7.9 Hz, aromatic), 7.87 (1H, s, H_c), 8.06 (2H, d, *J*=8.0 Hz, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 55.9, 109.3, 110.1, 114.4, 114.7, 116.4, 121.5, 126.4, 131.0, 131.3, 132.4, 154.6, 163.7, 165.7, 191.2; *Anal.* Calcd. for $C_{17}H_{14}O_3S$, C, 68.44; H, 4.73. Found C, 68.45; H, 4.77%.

2-(3,4-Dimethoxy-benzylidene)-7-methoxy-benzo[*b*]thiophene-3-one (3h). Yellowish solid; m.p. 113-115 ^{0}C; IR(KBr)$\nu_{C=0}$ 1696 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (3H, s, -OMe), 3.89 (6H, s, -OMe × 2), 6.65 (1H, dd, *J* =7.8, 8.0 Hz, aromatic), 6.71 (1H, d, *J* =2.5 Hz, aromatic), 6.76 (1H, dd, *J* =2.5 Hz, J_2=7.8 Hz, aromatic), 6.90 (1H, d, *J* =7.8 Hz, aromatic), 7.12-7.23 (m, 2H, aromatic), 7.93 (1H, s, H_c); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 56.3, 56.5, 111.9, 114.3, 119.5, 119.8, 120.3, 122.9, 125.8, 126.3, 127.9, 138.1, 140.0, 149.3, 150.1, 162.9, 190.0; *Anal.* Calcd. for $C_{18}H_{16}O_4S$, C, 65.84; H, 4.91. Found C, 65.84; H, 4.92%.

7-Methoxy-2-(3,4,5-trimethoxy-benzylidene)-benzo[*b*]thiophene-3-one (3i). Brown solid; m.p. 130-131 ^{0}C. I.R.(KBr)$\nu_{C=0}$ 1694 cm;$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (6H, s, -OMe X2), 3.81 (3H, s, -OMe), 3.89 (3H, s, -OMe), 6.61 (2H, s, aromatic), 6.85 (1H, d, *J* =7.8 Hz, aromatic), 7.13-7.25 (2H, m, aromatic), 7.95 (1H, s, H_c); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 56.3, 56.5, 56.9, 106.1, 106.7, 119.3, 120.1, 122.5, 125.9, 127.3, 129.3, 138.3, 139.9, 150.1,

151.1, 153.5, 163.1, 189.9; *Anal.* Calcd. for $C_{19}H_{18}O_5S$, C, 63.67; H, 5.06. Found C, 63.69; H, 5.05%.

2-(3,4-Dimethoxy-benzylidene)-4,7-dimethoxy-benzo[*b*]thiophene-3-one (3j). White crystal; m.p. 115-117 ^{0}C; IR(KBr)$\nu_{C=0}$ 1693 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (3H, s, -OMe), 3.93 (3H, s, -OMe), 3.98 (6H, s, -OMe X 2), 6.61 (1H, d, *J*=2.3 Hz, aromatic), 6.65 (1H, d, *J*= 7.8 Hz, aromatic), 6.78 (1H, dd, J_1 =2.3 Hz, J_2=7.8 Hz, aromatic), 6.93 (2H, d, *J* =7.8 Hz, aromatic), 7.89 (1H, s, H_c); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 56.0, 56.3, 56.9, 111.9, 112.8, 115.3, 119.3, 120.1, 121.3, 124.0, 125.9, 127.3, 139.1, 147.5, 148.1, 155.5, 155.8, 189.1. *Anal.* Calcd. for $C_{19}H_{18}O_5S$, C, 63.67; H, 5.06. Found C, 63.68; H, 5.07%.

2-(3,4-Dimethoxy-benzylidene)-6,7-dimethoxy-benzo[*b*]thiophene-3-one (3k). Brownish solid; m.p. 111-112 ^{0}C; IR (KBr)$\nu_{C=0}$ 1697 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (6H, s, -OMe X 2), 3.89 (6H, s, -OMe X 2), 6.61 (1H, d, *J* =7.8 Hz, aromatic), 6.63 (1H, d, *J*=7.8 Hz, aromatic), 6.71 (1H, d, *J*=2.5 Hz, aromatic), 6.78 (1H, dd, *J*=2.5 Hz, J_2=7.8 Hz, aromatic), 7.10 (1H, d, *J*=7.8 Hz, aromatic), 7.97 (1H, s, H_c); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 56.3, 56.9, 56.8, 112.4, 112.9, 115.0, 119.5, 123.1, 125.9, 128.1, 130.7, 139.1, 146.5, 147.5, 148.8, 153.5, 190.1; *Anal.* Calcd. for $C_{19}H_{18}O_5S$, C, 63.67; H, 5.06. Found C, 63.68; H, 5.09%.

6,7-Dimethoxy-2-(3,4,5-trimethoxy-benzylidene)-benzo[*b*]thiophene-3-one (3l). Yellowish solid; m.p. 151-152 ^{0}C; IR (KBr)$\nu_{C=0}$ 1696 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (6H, s, -OMe X 2), 3.81 (3H, s, -OMe), 3.89 (6H, s, -OMe X 2), 6.63 (2H, s, aromatic), 6.91 (1H, d, *J* =7.8 Hz, aromatic), 7.25 (1H, d, *J* =7.8 Hz, aromatic), 7.90 (s, 1H, H_c); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 55.9, 56.3, 56.6, 106.1, 106.5, 112.3, 120.5, 123.5, 125.3, 129.1, 130.7, 139.3, 153.7, 155.7, 155.9, 163.1, 163.5, 191.0; *Anal.* Calcd. for $C_{20}H_{20}O_6S$, C, 61.84; H, 5.19. Found C, 61.83; H, 5.18%.

4-Chloro-2-(3,4,5-trimethoxy-benzyylidene)-benzo[*b*]thiophene-3-one (3m). Yellowish needle; m.p. 117-118 ^{0}C; IR(KBr)$\nu_{C=0}$ 1678 cm;$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (3H, s, -OMe), 3.95 (6H, s, -OMe), 6.32 (2H, s, aromatic), 7.21-7.25 (m, 2H, aromatic), 7.32 (1H, dd, J_1 =7.8 Hz, J_2=8.0 Hz, aromatic), 7.89 (1H, s, H_c); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 56.3, 56.6, 106.1, 106.6, 125.6, 126.5, 126.9, 129.5, 135.5, 135.9, 136.0, 137.8, 140.1, 155.5, 156.2, 161.1, 190.0.; *Anal.* Calcd. for $C_{18}H_{15}ClO_4S$, C, 59.59; H, 4.17. Found C, 59.58; H, 4.17%.

4-Methoxy-2-(3-phenyl-allylidine)benzo[*b*]thiophene-3-one (3n). Red solid; m.p. 180-182^{0}C; IR (KBr)$\nu_{C=0}$ 1649 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (3H, s, -OMe), 6.71 (1H, d, *J* =8.2 Hz, aromatic), 6.90-7.09{3H, m, (H_b + 2H aromatic)}, 7.29-7.40 {3H, m, (H_c + 2H aromatic)}, 7.43-7.60 {4H, m, (H_a + 3H aromatic)}; ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.2, 96.4, 107.9, 116.4, 124.6, 127.8, 128.0, 129.1, 129.2, 129.7, 132.0, 133.3, 136.5, 136.5, 142.9, 147.7, 160.9, 186.4; *Anal.* Calcd. for $C_{18}H_{14}O_2S$, C, 73.44; H, 4.79. Found C, 73.53; H, 4.85%.

2-Benzylidene-4-methoxy-benzo[*b*]thiophene-3-one (3o). Yellow crystalline solid; m.p. 160-161^{0}C, IR (KBr)$\nu_{C=0}$1680 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (3H, s, -OMe), 6.76 (1H, d, *J*=8.2 Hz, aromatic) 7.07 (1H, d, *J*=7.7 Hz, aromatic), 7.38-7.53(4H, m, aromatic), 7.68-7.71 (2H, m, aromatic), 7.88 (1H, s, H_c); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.3, 108.3, 116.3, 118.9,

119.3, 129.3, 130.1, 130.6, 131.2, 131.5, 132.6, 134.8, 136.9, 148.7, 161.2, 187.1; *Anal*. Calcd. for $C_{16}H_{12}O_2S$, C, 71.62, H, 4.51. Found, C, 71.65; H, 4.52%.

2-Methylsulfanyl-2-thiophen-2-ylmethylene-benzo[*b*]thiophene-3-one (3p). Yellow solid**;** m.p.166-168 ^{0}C; IR (KBr)$\nu_{C=0}$ 1666 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (3H, s, -SMe), 7.04 (1H, d, *J*=7.9 Hz, aromatic), 7.16-7.24 (2H, m, aromatic), 7.42-7.48 (2H, m, aromatic), 7.63 (1H, d, *J*=4.9 Hz, aromatic), 8.05 (1H, s, H_c); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 119.3, 120.3, 125.6, 128.9, 130.7, 131.6, 132.7, 133.5, 134.6, 139.6, 145.5, 169.7, 188.1; *Anal*. Calcd. for $C_{14}H_{10}OS_3$, C, 57.90; H, 3.47. Found C, 57.91; H, 3.52%.

2-Benzylidene-4-methylsulfanyl-benzo[*b*]thiophene-3-one (3q). Red solid; m.p. 173-175 ^{0}C; IR (KBr)$\nu_{C=0}$ 1679 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (3H, s, -SMe), 7.03 (1H, d, J=7.6 Hz, aromatic), 7.19 (1H, d, J=7.6 Hz, aromatic), 7.38-7.48 (4H, m, aromatic), 7.65-7.68 (2H, m, aromatic), 7.87 (1H, s, H_c); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 118.7, 119.9, 124.3, 125.6, 128.2, 128.2, 131.1, 131.7, 132.8, 134.4, 145.4, 147.1, 160.7, 187.3; Anal. Calcd. for $C_{16}H_{12}OS_2$, C, 67.57; H, 4.25. Found C, 67.56; H, 4.26%.

2-(4-Chlorobenzylidene)-4-methylsulfanyl-benzo[*b*]thiophene-3-one (3r). Yellow crystalline solid; m.p. 213-215 ^{0}C; IR (KBr)$\nu_{C=0}$ 1678 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54 (3H, s, -SMe), 7.06 (1H, d, *J*=7.7 Hz, aromatic), 7.21 (1H, d, *J*=7.7 Hz, aromatic), 7.42-7.49 (3H, m, aromatic), 7.59 -7.62 (2H, m, aromatic), 7.81 (1H, s, H_c); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 118.7, 119.9, 121.3, 124.5, 125.6, 129.2, 130.2, 131.1, 131.8, 132.8, 134.4, 145.4, 147.1, 160.1, 188.7; *Anal*. Calcd. for $C_{16}H_{11}ClOS_2$, C, 60.27; H, 3.48. Found C, 60.39; H, 3.53%.

4-Methylsulfanyl-2-(3-phenyl-allylidene)benzo[*b*]thiophene-3-one (3s). Red solid; m.p. 210-212 ^{0}C; IR (KBr)$\nu_{C=0}$1655 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (3H, s, -SMe), 6.97-7.19 {4H, m, (H_b + 2H aromatic)}, 7.35-7.47 {4H, m, H_c+ 3H aromatic)}, 7.52-7.62 {3H, m, (H_a + 3H aromatic)}; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 119.2, 119.5, 120.0, 124.6, 127.8, 127.9, 128.2, 129.2, 129.8, 132.5, 132.8, 136.4, 143.3, 145.3, 146.9, 160.0, 187.9; *Anal*. Calcd. for $C_{18}H_{14}OS_2$, C, 60.27; H, 3.48. Found, C, 60.39; H, 3.53%.

2-(4-Chlorobenzylidene)benzo[*b*]thiophen-3-one (3t). Yellow solid; m.p.162-165 ^{0}C; IR (KBr)$\nu_{C=0}$1678 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (1H, d, *J*=7.7 Hz, aromatic), 7.43-7.51(3H, m, aromatic), 7.56-7.64 (3H, m, aromatic), 7.89 (1H, s, H_c), 7.95 (1H, d, *J*=7.7 Hz, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.3, 126.1, 127.5, 129.2, 129.6, 130,6, 131.1, 132.4, 132.7, 133.1, 133.3, 135.8, 136.5, 146.1, 188.8; Anal. Calcd. for $C_{15}H_9ClOS$, C, 66.05; H, 3.33. Found C, 66.07; H, 3.37%.

2-(3-Phenyl-allylidine)benzo[*b*]thiophene-3-one (3u). Reddish solid; m.p.138-140 ^{0}C; IR (KBr)$\nu_{C=0}$1662 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 -7.13 {m, 2H, (H_b+ 1H aromatic)}, 7.25-7.55 {8H, m, (H_c+ 7H aromatic)}, 7.58 (1H, d, J=7.9 Hz, aromatic), 7.69 (1H, d, J=15 Hz, H_a); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.3, 124.6, 125.7, 127.1, 127.9, 127.98, 128.2, 129.3, 129.7, 130.0, 132.0, 133.3, 135.4, 136.3, 143.9, 145.6, 188.8; Anal. Calcd. for $C_{17}H_{12}OS$, C, 77.24; H, 4.58. Found C, 77.26; H, 4.58%.

2-Benzylidine naptho[2,1-*b*]thiophen-1-one (3v). Yellowish solid; m.p.186-188 ^{0}C; IR (KBr)$\nu_{C=0}$ 1678 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.55 (5H, m, aromatic), 7.67-7.75

(3H, m, aromatic), 7.86 (1H, d, *J*=8.0 Hz, aromatic), 7.98-8.02 {2H, m (H_c + aromatic)}, 9.37 (1H, d, *J*=8.0 Hz, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.9, 123.5, 126.7, 128.8, 129.0, 129.4, 130.0, 130.5, 131.1, 131.3, 131.7, 132.1, 134.4, 134.7, 136.6, 144.7, 150.5, 189.3; *Anal*. Calcd. for $C_{19}H_{12}OS$, C, 79.14; H, 4.19, Found C, 79.19; H, 4.20%.

2-(4-Chlorobenzylidene)naptho[2,1-*b*]thiophen-1-one (3w). Yellowish solid; m.p. 216-218 ^{0}C; IR (KBr)$\nu_{C=0}$ 1680 cm.$^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.56 (4H, m, aromatic), 7.65-7.74 (3H, m, aromatic), 7.87 (1H, d, *J*=8.0 Hz, aromatic), 7.95 (1H, s, H_c), 8.03 (1H, d, *J*=8.0 Hz, aromatic), 9.35 (1H, d, *J*=8.0 Hz, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.9, 123.5, 123.7, 126.8, 128.9, 129.7, 129.9, 130.2, 131.6, 131.7, 132.1, 132.5, 132.8, 133.2, 136.5, 136.8, 150.1, 189.2; *Anal*. Calcd. for $C_{19}H_{11}ClOS$, C, 70.69; H, 3.43, Found C, 70.71; H, 3.44%.

General procedure for the synthesis of 2-Phenyl-4H-benzo[4,5]thieno[3,2-*b*]pyran

Thioaurones derived from cinnamaldehyde were taken in a small rb fitted with a reflux condencer and were heated in a silicone oil bath at 210 ^{0}C (bath temperature) for 6-7 hrs under argon atmosphere. After cooling, the residue was dissolved in small portion of dichloromethane and was subjected to SiO_2 choromatographic purification [eluant: EtOAc: light petroleum (3:17, v/v)]

6-Methoxyphenyl-4*H*-benzo[4,5]thieno[3,2-*b*]pyran (4a). Colorless needle shaped crystal, mp-194-195 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88-3.22 (2H, m), 4.00 (3H, s, -OMe), 5.70 (1H, dd, *J*=3.3, 3.4 Hz), 6.93 (1H, dd, *J* =7.8, 8.5 Hz), 7.35 (1H, dd, *J* =7.8, 8.5 Hz), 7.42-7.55 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.4, 56.2, 83.2, 109.1, 115.8, 116.1, 126.6, 126.7, 129.3, 129.4, 130.7, 132.0, 138.4, 155.1, 161.5, 186.8. *Anal*. Calcd. for $C_{18}H_{14}O_2S$, C, 73.40; H, 4.76, Found C, 73.50; H, 4.8%.

8-Methoxyphenyl-4*H*-benzo[4,5]thieno[3,2-*b*]pyran (4b). Colorless solid, mp-207 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80-3.18 (2H, m), 3.78 (3H, s, -OMe), 5.67 (1H, dd, *J* =3.2, 3.3 Hz), 7.10 (1H, dd, *J* =2.5, 8.8 Hz), 7.22-7.50 (7H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.4, 56.0, 83.4, 104.0, 121.3, 124.9, 126.9, 129.3, 129.4, 129.5, 131.8, 134.0, 138.3, 158.1, 186.7. *Anal*. Calcd. for $C_{18}H_{14}O_2S$, C, 73.40; H, 4.76, Found C, 73.52; H, 4.83%.

9-Methoxyphenyl-4*H*-benzo[4,5]thieno[3,2-*b*]pyran (4c). Separated as needle shaped white crystal. mp-198-199 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.89-3.3 (2H, m), 3.99 (3H, s), 5.69 (1H, dd, *J* =3.3, 3.4 Hz), 6.91 (1H, dd, *J* =2.5, 7.8 Hz), 7.39 (1H, dd, *J* =7.8, 8.5 Hz), 7.41-7.56 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.5, 56.3, 83.4, 109.1, 115.9, 116.1, 126.3, 126.5, 129.5, 130.1, 130.7, 132.0, 138.5, 155.3, 161.6, 186.5. *Anal*. Calcd. for $C_{18}H_{14}O_2S$, C, 73.44; H, 4.79, Found C, 73.45; H, 4.73%.

9-Methylsulfanyl-4*H*-benzo[4,5]thieno[3,2-*b*]pyran (4d). Separated as yellowish solid. mp-200-201 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (3H, s, -SMe), 2.81-3.21 (2H, m, -CH_2-), 5.69 (1H, dd, *J* =3.3, 3.4 Hz), 7.13 (1H, dd, *J* =7.5, 8.0 Hz), 7.20-7.25 (3H, m), .31-7.60 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5, 44.3, 83.5, 109.3, 115.1, 116.3, 126.3, 126.6, 129.3, 129.4, 130.7, 130.9, 132.0, 137.5, 160.5, 187.4. *Anal*. Calcd. for $C_{18}H_{14}OS_2$, C, 69.64; H, 4.55, Found C, 69.65; H, 4.53%.

2-Phenyl-4*H*-benzo[4,5]thieno[3,2-*b*]pyran (4e). Separated as colorless gummy liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.9-3.3 (2H, m, -CH_2), 5.51 (1H, dd, J =3.4, 3.5 Hz), 7.14-7.21 (3H, m), 7.30-7.31 (4H, m), 7.43-7.65 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.9, 83.4, 111.3, 123.8, 124.3, 124.5, 126.1, 126.3, 127.3, 128.4, 132.3, 135.5, 137.5, 154.7, 186.9. Anal. Calcd. for $C_{17}H_{12}OS$, C, 77.24; H, 4.58, Found C, 77.28; H, 4.60%.

General procedure for the synthesis of 4-Methyl-4H-benzo[4,5]thieno[3,2-b]pyran. Prepared in the same way as 4.1.1. except crotonaldehyde was used instead of aromatic aldehyde.

8-Methoxy-4-methyl-4*H*-benzo[4,5]thieno[3,2-*b*]pyran (5a). Yellowish gummy liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ1.61 (3H, d, *J*= 6.4 Hz, -CH_3), 2.60-2.80 (1H, m), 3.89 (3H, s, -OMe), 4.84-4.88 (1H, m), 6.21 (1H, d, *J* =8.9 Hz), 6.99 (1H, dd, *J* =2.1, 8.8 Hz), 7.19 (1H, dd, *J* =2.1, 8.8 Hz), 7.75 (1H, dd, *J* =7.8, 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 29.2, 56.1, 108.9, 111.9, 122.5, 124.5, 125.7, 132.1, 133.8, 134.7, 140.2, 154.6. *Anal.* Calcd. for $C_{18}H_{12}O_2S$, C, 67.24; H, 5.17, Found C, 67.30; H, 5.40%.

9-Methoxy-4-methyl-4*H*-benzo[4,5]thieno[3,2-*b*]pyran (5b). Separated as yellowish gummy liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (3H, d, *J*= 6.3 Hz, -CH_3), 2.61-2.83 (1H, m), 3.78 (3H, s), 4.85-4.89 (1H, m), 6.20 (1H, d, *J* =8.5 Hz), 6.81 (1H, dd, *J* = 2.5, 8.5 Hz), 7.20 (1H, dd, *J* =2.5, 8.5 Hz), 7.68 (1H, dd, *J* =7.8, 8.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 29.3, 55.6, 108.3, 111.5, 122.3, 124.3, 125.6, 132.1, 133.3, 134.5, 140.1, 155.3. *Anal.* Calcd. for $C_{13}H_{12}O_2S$, C, 67.21; H, 5.21, Found C, 67.30; H, 5.20%.

6,9-Dimethoxy-4-methyl-4*H*-benzo[4,5]thieno[3,2-*b*]pyran (5c). Separated as yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (3H, d, *J*= 6.4 Hz, -CH_3), 2.63-2.83 (1H, m), 3.79 (3H, s), 3.81 (3H, s), 4.86-4.89 (1H, m), 6.19 (1H, d, *J* =8.5 Hz), 6.71 (1H, d, *J* =8.5 Hz), 6.78 (1H, d, *J*= 8.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 29.1, 55.3, 56.0, 108.9, 110.1, 111.3, 118.1, 124.3, 140.3, 148.1, 149.6, 154.7. *Anal.* Calcd. for $C_{14}H_{14}O_3S$, C, 64.10; H, 5.38, Found C, 64.10; H, 5.40%.

6,7-Dimethoxy-4-methyl-4*H*-benzo[4,5]thieno[3,2-*b*]pyran (5d). Separated as low melting solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ1.61 (3H, d, *J*= 6.2 Hz, -CH_3), 2.61-2.81 (1H, m), 3.86 (3H, s), 3.89 (3H, s), 4.85-4.89 (1H, m), 6.20 (1H, d, *J* =8.9 Hz), 6.72 (1H, d, *J* =8.5 Hz), 6.79 (1H, d, *J* = 8.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 29.3, 56.1, 56.2, 108.5, 110.3, 111.9, 117.3, 124.5, 140.1, 141.7, 143.5, 154.6. *Anal.* Calcd. for $C_{14}H_{14}O_3S$, C, 64.10; H, 5.38, Found C, 64.11; H, 5.39%.

6-Methoxy-4-methyl-4*H*-benzo[4,5]thieno[3,2-*b*]pyran (5e). Separated as colorless gummy liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (3H, d, *J*= 6.3 Hz, -CH_3), 2.63-2.84 (1H, m), 3.79 (3H, s), 4.85-4.89 (1H, m), 6.18 (1H, d, *J* =8.9 Hz), 6.80 (1H, dd, *J* =2.3, 8.0 Hz), 7.21-7.30 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9, 29.3, 55.6, 108.3, 110.0, 111.5, 116.5, 117.1, 123.5, 125.5, 133.5, 140.1, 155.3. *Anal.* Calcd. for $C_{13}H_{12}O_2S$, C, 67.24; H, 5.17, Found C, 67.21; H, 5.21%.

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