Studies in sigmatropic rearrangement: synthesis of 3,11a-dimethyl-6a,11a-dihydro-1H,6H-pyran[3',4':5,6]thiopyran[4,3-b][1]benzofuran-1-one


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Dedicated to Professor (Mrs.) A. Chatterjee on her 85th birthday
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Abstract
Thermal rearrangement of 4-aryloxymethyl-7-methylthiopyrano-[3,2-c]pyran-5-ones 6a-f afforded a number of hitherto unreported benzofuro[3,2-c]-6a,11a-dihydro-3,11a-dimethylthiopyranopyran-1-one 15a-e in good yields (60-67%) along with the exocyclic derivatives 16d,e,f as minor products (10-15%). Compounds 6a-f were in turn synthesized in 72-85% yields by the thermal rearrangement of 4-(4'-aryloxybut-2'-ynylthio)-6-methylpyran-2-ones 5a-f. Compounds 5a-f were obtained in (50-55%) yields by the phase-transfer catalyzed alkylation of 4-mercapto-6-methyl-2-pyrone 3 with 1-aryloxy-4-chlorobut-2-yne 4a-f.

Keywords: Regioselective synthesis, [3,3] sigmatropic rearrangement, sulfur heterocycles, phase-transfer catalysis, 1-aryloxy-4-chlorobut-2-yne, Claisen rearrangement

Introduction

4-Hydroxy-6-methyl-2-pyrene (triacetic acid lactone) 1 is a natural product of polyketide origin. Many naturally occurring compounds contain the basic structural unit of 4-hydroxy(or methoxy)-6-alkyl-2-pyrene. Some of these compounds possess biogenetically plausible groups at C-3 or C-5 or both. Elasnin, isolated from Steptromices sp., for example, is a specific inhibitor of human leukocyte elastase, an enzyme involved in inflammatory processes such as pulmonary emphysema. As a logical extension, many more simple pyrones structurally related to elasnin have been synthesized and evaluated as inhibitors of several elastases. Some 4-hydroxy-2-pyrones are known to display the properties of anticoagulant agents. In a continuation of our work on the synthesis of bioactive heterocycles by the application of sigmatropic rearrangements, we recently published the synthesis of fused thienopyrone heterocyclic systems. We, then, became interested to find the influence of different substituents in the
benzene nucleus of our substrate 4-aryloxymethyl-7-methylthiopyran[3,2-c]pyran-5-ones, **6a-f** on the course of the rearrangement.

The starting materials for this investigation, 4-(4'-aryloxybut-2'-ynylthio)-6-methylpyran-2-ones **5a-f** were synthesized from 4-mercapto-6-methylpyran-2-ones and 1-aryloxy-4-chlorobut-2-yne by our earlier published procedure. (Scheme 1)

**Results and Discussion**

Substrates **5a-f** contain a propargyl vinyl sulfide moiety as well as aryl propargyl ether segment. Compounds with this structural feature offer an excellent scope for the study of competition between oxy-and thio-Claisen rearrangements as well as the synthesis of new heterocycles through [3,3] Sigmatropic rearrangements.

![Scheme 1](image-url)
Occurrence of [3,3] Sigmatropic rearrangement at the vinyl propargyl sulfide segment of compounds 5a-f may lead to polyheterocycles 6-8 while that at aryl propargyl ether part may generate polyheterocycles 9-11.

With this end in view, substrate 5a was refluxed in chlorobenzene (131-132°C) and the isolated product was shown to be compound 6a from its elemental analysis and spectroscopic data. The $^1$H-NMR of compound 6a showed a two-proton doublet at $\delta$ 3.34 ($J$ 6Hz) assignable to two C$_2$-H, a two-proton triplet centered at $\delta$ 5.96 owing to C$_3$-H due to ($J$ 6Hz), a two-proton broad singlet at $\delta$ 5.01 owing to –CH$_2$OAr, a one-proton singlet at $\delta$ 6.01 due to C$_8$-H, a three proton singlet at $\delta$ 2.22 assignable to C$_7$-CH$_3$ and two two-proton doublets at $\delta$ 6.79 ($J$ 9Hz) and $\delta$ 6.86 ($J$ 9Hz) owing to four aromatic protons.

The $^{13}$C-NMR spectrum of compound 6a also strongly supported its structure. The $^{13}$C chemical shift of compound 6a was assigned by DEPT experiments. Multiplicity was also ascertained by DEPT experiment. Substrates 5b-f were similarly treated to obtained compounds 6b-f.

Scheme 2
Mechanistic rationalization of the formation of 6 from 5 involves a [3,3] sigmatropic rearrangement at the vinyl propargyl sulfide segment of 5 leading to an allenyl intermediate 12. Intermediate 12 may undergo tautomerization to furnish 13. A [1,5]H shift in 13 may give 14 which, on 6π electrocyclic ring-closure, can afford compound 6 (Scheme 2).

All the six substrates 5a-f afforded thiopyranopyrone derivatives 6a-f exclusively despite the possibility of the formation of other polyheterocycles 7-11. A lesser energy requirement for the sigmatropic rearrangement in vinyl propargyl systems9 compared to that in aryl propargyl moieties10 might be responsible for this excellent regioselectivity.

Presence of an aryl allyl ether segment in compound 6 may enable it to undergo a thermal [3,3] sigmatropic rearrangement. When compound 6a was subjected to thermal rearrangement in refluxing o-dichlorobenzene (179-181°C), the isolated product was shown to be compound 15a from its elemental analysis and spectral data. Product 15a was also obtained when the sulfide 5a was refluxed in o-dichlorobenzene for 12h.

The ¹H-NMR of compound 15a showed three one proton doublet of doublets at δ 2.80 (J 9.9,13.5Hz), 3.01 (J 3.9,13.5Hz) and 3.41 (J 3.9,9.9 Hz) indicating the presence of two C₆-H and one C₆a-H. This structure of compound 15a was further confirmed by its ¹³C-NMR spectrum.

Fused furanothiopyran derivatives 15a,b,c were obtained as the sole products from the rearrangement of compounds 6a,b,c. Compounds 6d,e, however, afforded a mixture of 15d,e and the exo-cyclic derivatives 16d,e. Compound 6f gave only the exo-cyclic product 16f (Scheme 3). Formation of compound 15 and 16 from 6 can be mechanistically interpreted as outlined in (Scheme 4).

Scheme 3

Compound 6 may undergo [3,3] sigmatropic rearrangement at the aryl allyl ether part to produce intermediate 17. Tautomerization of 17 may afford 18, which, on ‘5-exo’ ring closure, should furnish compound 15. Compound 16 can be obtained through a [1,3] prototropic rearrangement in compound 6.
Presence of different substituents in the benzene nucleus of compound 6 thus brings about a change in the mode of the rearrangement. However the role of some substituents in the formation of exocyclic derivatives 16de,f is not clear. Here it is noteworthy that in the synthesis of pyranopyrone derivatives from 4-(4'-aryloxybut-2'-ynyl)-6-methyl-2-pyrones, only exocyclic products corresponding to 8 were obtained\textsuperscript{11}. Synthesis of pyridinopyrone heterocycles from 4-(N-4'-aryloxybut-2'-ynyl)-N-methylamino-6-methyl-2-pyrones also afforded chiefly the exocyclic products along with the endocyclic compounds as minor products corresponding to 6 only in three cases.\textsuperscript{12} In the present instance, all the substrate 5a-f afforded the endocyclic derivatives 6a-f.

**Conclusions**

In conclusion, thermal sigmatropic rearrangement has been successfully utilised as an efficient tool for the synthesis of fused furanothiopyran heterocyclic ring systems with moderate regioselectivity. Presence of various substituents in the benzene ring of compound 6 alters the
course of rearrangement in spite of their seemingly remote distance from the site of rearrangement.

**Experimental Section**

**General Procedures.** Melting points were determined in an open capillary and are uncorrected. IR spectra were recorded on a Perkin-Elmer L 120-000A spectrometer (ν<sub>max</sub> in cm<sup>-1</sup>) using samples as neat liquids and solid samples were recorded in KBr disks and UV absorption spectra were recorded in EtOH on a Shimadzu UV-2401PC spectrophotometer (λ<sub>max</sub> in nm).<sup>1</sup>H NMR (300 MHz, 500 MHz) and<sup>13</sup>C NMR (75.5 MHz, 125.7 MHz) spectra were recorded on a Bruker DPX-300 and Bruker DPX-500 spectrometer in CDCl<sub>3</sub> (chemical shift in δ) with TMS as internal standard. Elemental analyses and mass spectra were recorded on a JEOL JMS600 instrument. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded at Indian Institute of Chemical Biology, Kolkata and Bose Institute, Kolkata. Silica gel [(60-120 mesh), Spectrochem, India] was used for chromatographic separation. Silica gel G[E-Merck (India)] was used for TLC. Petroleum ether refers to the fraction boiling between 60ºC and 80ºC.

**Synthesis of 4-mercapto-6-methylpyran-2-one 3**

This compound was synthesized by our earlier published procedure.<sup>8</sup>

**General procedure for the synthesis of compounds 5a-f**

These compounds were synthesized following a similar procedure published earlier.<sup>8</sup>

**4-[4-(4'-Methoxyphenoxynbut-2-ynylthio)]-6-methyl-2-pyrene (5a).** Yield 53%; mp. 76-78 ºC; λ<sub>max</sub> 230, 268, 291 nm; IR (KBr)ν<sub>max</sub> : 1715, 1635, 1506, 1221 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ 2.19 (s, 3H, C<sub>6</sub>-CH<sub>3</sub>), 3.66 (s, 2H, -SCH<sub>2</sub>), 3.77 (s, 3H, -OCH<sub>3</sub>), 4.63 (s, 2H, -OCH<sub>2</sub>), 5.82 (s, 1H, C<sub>3</sub>-H), 5.92 (s, 1H, C<sub>5</sub>-H), 6.81-6.88 (m, 4H, ArH); MS m/z 316 (M<sup>+</sup>). Anal Calcd. For C<sub>17</sub>H<sub>16</sub>O<sub>4</sub>S: C, 64.54; H, 5.09. Found: C, 64.42; H, 5.21%.

**4-[4-(3',5'-Dimethylphenoxybut-2-ynylthio)]-6-methyl-2-pyrene (5b).** Yield 55%; mp. 82-84 º C; λ<sub>max</sub> 230, 268, 302 nm; IR (KBr)ν<sub>max</sub> : 1717, 1635, 1501, 1221 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 2.19 (s, 3H, C<sub>6</sub>-C<sub>6</sub>-CH<sub>3</sub>), 2.28 (s, 6H, -C<sub>6</sub>-CH<sub>3</sub>), 3.67 (s, 2H, -SCH<sub>2</sub>), 4.65 (s, 2H, -OCH<sub>2</sub>), 5.83 (s, 1H, C<sub>3</sub>-H), 5.93 (s, 1H, C<sub>5</sub>-H), 6.55-6.62 (m, 3H, ArH); MS m/z 314 (M<sup>+</sup>). Anal Calcd. For C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>S: C, 68.77; H, 5.77. Found: C, 68.62; H, 5.76 %.

**4-[4-(2',4'-Dimethylphenoxybut-2-ynylthio)]-6-methyl-2-pyrene (5c).** Yield 55%; mp. 80-82 º C; λ<sub>max</sub> 230, 268, 302 nm; IR (KBr)ν<sub>max</sub> : 1716, 1635, 1506, 1221 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ 2.19 (s, 3H, C<sub>6</sub>-CH<sub>3</sub>), 2.24 (s, 3H, -CH<sub>3</sub>), 2.27 (s, 3H, -CH<sub>3</sub>), 3.67 (s, 2H, -SCH<sub>2</sub>), 4.65 (s, 2H, -OCH<sub>2</sub>), 5.83 (s, 1H, C<sub>3</sub>-H), 5.93 (s, 1H, C<sub>5</sub>-H), 6.55-6.62 (m, 3H, ArH); MS m/z 314 (M<sup>+</sup>). Anal Calcd. For C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>S: C, 68.77; H, 5.77. Found: C, 68.62; H, 5.54 %.

**4-(4-Phenoxybut-2-ynylthio)-6-methyl-2-pyrene (5d).** Yield 52% mp. 78-80 º C; λ<sub>max</sub> 220, 269, 302 nm; IR (KBr)ν<sub>max</sub> : 1700, 1610, 1475, 1220 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 2.19 (s,
3H, C₆-CH₃), 3.67 (s, 2H, -SCH₂), 4.69 (s, 2H, -OCH₂), 5.82 (s, 1H, C₃-H), 5.94 (s, 1H, C₅-H), 6.91-7.31 (m, 5H, ArH); MS m/z 286 (M⁺) Anal Calcd. For C₁₀H₁₄O₃S C, 67.11; H, 4.93. Found: C, 67.32; H, 4.98 %

4-[4-(4'-Methylphenoxybut-2-ynylthio)]-6-methyl-2-pyrones (5e). Yield 50%, mp. 71-72 °C; λ max 222, 270, 302 nm; IR (KBr) ν max : 1700, 1620, 1485, 1220 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz): δ 2.19 (s, 3H, -CH₃), 2.28 (s, 3H, -CH₃), 3.66 (s, 2H, -SCH₂), 4.66 (s, 2H, -OCH₂), 5.82 (s, 1H, C₃-H), 5.93 (s, 1H, C₅-H), 6.81 (d, J 9Hz, 2H, ArH), 7.06 (d, J 9Hz, 2H, ArH); MS m/z 300 (M'). Anal Calcd. For C₁₇H₁₆O₅S C, 67.98; H, 5.37 Found: C, 68.11; H, 5.48 %

4-[4-(4'-Chlorophenoxybut-2-ynylthio)]-6-methyl-2-pyrones (5f). Yield 52%, mp. 76-78 °C; λ max 224, 271, 303 nm; IR (KBr) ν max : 1700, 1620, 1480, 1215 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz): δ 2.20 (s, 3H, C₆-CH₃), 3.66 (s, 2H, -SCH₂), 4.67 (s, 2H, -OCH₂), 5.81 (s, 1H, C₃-H), 5.91 (s, 1H, C₅-H), 6.84 (d, J 9Hz, 2H, ArH), 7.21 (d, J 9Hz, 2H, ArH); MS m/z 320, 322 (M'). Anal Calcd. For C₁₇H₁₃ClO₃S C, 59.91; H, 4.08 Found: C, 60.12; H, 4.26 %

**General procedure for the synthesis of 4-aryloxymethyl-7-methyl thiopyran[3,2-c]pyran-5-ones 6a-f**

Compounds 5a-f (200 mg) were refluxed in chlorobenzene (3 ml) for 5 h. The reaction mixture was then cooled and directly subjected to column chromatography over silica gel. Chlorobenzene was eluted out with petroleum ether. Compounds 6a-f were obtained when the column was eluted with benzene-petroleum ether (3:1). These compounds 6a-f were recrystallised from chloroform-petroleum ether.

**Compound (6a).** Yield 80%; mp. 96-98 °C; λ max: 232, 278, 301 nm; IR (KBr) ν max: 1705, 1626, 1507, 1229 cm⁻¹; ¹H-NMR (CDCl₃, 500 MHz): δ 2.22 (s, 3H, C₇-CH₃), 3.34 (d, J 6 Hz, 2H, C₂-H), 3.75 (s, 3H, -OCH₃), 5.01 (brs, 2H, -CH₂OAr), 5.96 (t, J 6 Hz, 1H, C₃-H), 6.01 (s, 1H, C₈-H), 6.79 (d, J 9Hz, 2H, ArH), 6.86 (d, J 9Hz, 2H, ArH); ¹³C-NMR (CDCl₃, 125.7 MHz): δ 20.03 (C₇-CH₃), 25.07(C₂), 56.11 (C₄-OCH₃), 69.55 (CH₂OAr), 105.16 (C₈), 114.51 (C₄a), 114.74 (C₃), 114.96 (C₃', C₆'), 116.59 (C₃', C₅'), 134.57 (C₄), 153.16 (C₆a), 154.36 (C₄''), 155.24 (C₁'), 159.16 (C₇), 159.64 (C₈); m/z 316 (M⁺); Anal Calcd. For C₁₇H₁₆O₄S C, 64.54; H, 5.09. Found C, 64.34; H, 5.01 %.

**Compound (6b).** Yield 83%; mp. 120-122 °C; λ max: 248, 302 nm; IR (KBr) ν max: 1708, 1633, 1500, 1255 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz): δ 2.22 (s, 3H, -CH₃), 2.27 (s, 6H, -CH₃), 3.34 (d, J 6 Hz, 2H, C₂-H), 5.02 (brs, 2H, -CH₂OAr), 5.97 (t, J 6 Hz, 1H, C₃-H), 6.02 (s, 1H, C₈-H), 6.57 (m, 3H, ArH); ¹³C-NMR (CDCl₃, 75.5 MHz): δ 19.57 (C₇-CH₃), 21.39 (C₃'-CH₃,C₅'-CH₃), 24.61 (C₂), 56.11 (C₄'-OCH₃), 67.94 (-CH₂OAr), 104.73 (C₈), 112.69 (C₂'', C₆'), 114.03 (C₃), 115.39 (C₄a), 122.58 (C₄''), 133.97 (C₄), 139.03 (C₃', C₅'), 154.78 (C₈a), 158.53 (C₁'), 158.75 (C₇), 159.14 (C₈); MS m/z 314 (M⁺); Anal Calcd. For C₁₈H₁₈O₅S C, 68.77; H, 5.77. Found C, 68.59; H, 5.57 %.

**Compound (6c).** Yield 85%; mp. 116-118 °C; λ max: 223 , 248, 302 nm; IR (KBr) ν max: 1710, 1644, 1533, 1268 cm⁻¹; ¹H-NMR (CDCl₃, 500 MHz): δ 2.22 (s, 3H, -CH₃), 2.27 (s, 6H, CH₃),
3.35 (d, J 6 Hz, 2H, C2-H), 5.02 (brs, 2H, -CH2OAr), 5.98 (t, J 6 Hz, 1H, C3-H), 6.02 (s, 1H, C6-H), 6.57-6.59 (m, 3H, ArH), m/z 314 (M+); Anal Calcd. For C18H18O3S: C, 68.77; H, 5.77. Found C, 68.65; H, 5.53 %.

**Compound (6d).** Yield 72%; gummy mass; λmax: 222, 247, 299 nm; IR (KBr) νmax: 1690, 1620, 1490, 1250 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) : δ 2.22 (s, 3H, C7-CH3), 3.34 (d, J 6 Hz, 2H, C2-H), 5.07 (brs, 2H, -CH2OAr), 5.98 (t, J 6 Hz,1H, C3-H), 6.02 (s, 1H, C6-H), 6.90-7.32 (m, 5H, ArH); MS m/z 286 (M+); Anal Calcd. For C16H14O3S: C, 67.11; H, 4.93. Found C, 67.36; H, 5.09%.

**Compound (6e).** Yield 73%; mp. 97-99 °C; λmax: 224, 246, 304 nm; IR (KBr) νmax: 1690, 1620, 1490, 1270 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) : δ 2.22 (s, 3H, -CH3), 2.27 (s, 3H, CH3), 3.33 (d, J 6 Hz, 2H, C2-H), 5.03 (brs, 2H, -CH2OAr), 5.97 (t, J 6 Hz, 1H, C3-H), 6.01 (s, 1H, C6-H), 6.82 (d, J 9Hz, 2H, ArH), 7.04 (d, J 9Hz, 2H, ArH); MS m/z 300 (M+); Anal Calcd. For C17H16O3S : C, 67.98; H, 5.37. Found C, 68.19; H, 5.47 %.

**Compound (6f).** Yield 80%; mp. 108-109 °C; λmax: 221, 247, 302 nm; IR (KBr) νmax: 1690, 1630, 1485, 1255 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz) : δ 2.23 (s, 3H, C7-CH3), 3.34 (d, J 6 Hz, 2H, C2-H), 5.04 (brs, 2H, -CH2OAr), 5.94 (t, J 6 Hz,1H, C3-H), 6.02 (s, 1H, C6-H), 6.84 (d, J 9Hz, 2H, ArH), 7.19 (d, J 9Hz, 2H, ArH); MS m/z 320, 322 (M+); Anal Calcd. For C16H13ClO3S : C, 59.91; H, 4.08. Found C, 60.15; H, 4.19 %.

**General procedure for the synthesis of 3,11a-dimethyl-6a,11a-dihydro-1H,6H-pyra |||:
1H, C₆-H), 3.28 (dd, J 3.9, 9.9 Hz, 1H, C₆a-H), 5.88 (s, 1H, C₄-H), 6.54-6.62 (m, 2H, ArH), 13C-NMR (CDCl₃, 75.5 MHz): δ 18.13 (C₃-CH₃), 19.40(C₁₁a-CH₃), 21.52 (C₉-CH₃), 23.38 (C₇-CH₃), 28.04 (C₆), 49.93 (C₆a), 83.67 (C₁₁a), 104.76 (C₄), 109.45 (C₁₀), 122.99 (C₉), 116.12 (C₆b), 124.22 (C₁₁b), 133.94 (C₇), 139.38 (C₉), 154.02 (C₄), 157.01 (C₁₀a), 158.94 (C₃), 159.53 (C₁); MS m/z 314 (M⁺); Anal Calcd. for C₁₃H₁₈O₃S: C, 68.77; H, 5.77. Found C, 68.64; H, 5.58%.

**Compound (15c).** Yield 67%; mp. 106-108 °C; λ max: 205, 233, nm; IR (KBr) ν max: 1704, 1643, 1439, 1222 cm⁻¹; ¹H-NMR (CDCl₃, 500 MHz): δ 2.20 (s, 3H, -CH₃), 2.27 (s, 3H, -CH₃), 2.31 (s, 3H, -CH₃), 1.70 (s, 3H, C₁₁a-CH₃), 2.60 (dd, J 9.9, 13.5 Hz, 1H, C₆-H), 2.90 (dd, J 3.9, 13.5 Hz, 1H, C₆-H), 2.32 (dd, J 3.9, 9.9 Hz, 1H, C₆a-H), 5.88 (s, 1H, C₄-H), 6.54-6.62 (m, 2H, ArH); MS m/z 314 (M⁺); Anal Calcd. for C₁₃H₁₈O₃S: C, 68.77; H, 5.77. Found C, 68.59; H, 5.52%.

**Compound (15d).** Yield 60%; Gummy mass; λ max: 211, 255, nm; IR (KBr) ν max: 1690, 1620, 1430, 1240 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz): δ 2.18 (s, 3H, C₃-CH₃), 1.81 (s, 3H, C₁₁a-CH₃), 2.81 (dd, J 9.9, 13.5 Hz, 1H, C₆-H), 3.02 (dd, J 3.9, 13.5 Hz, 1H, C₆-H), 3.48 (dd, J 3.9, 9.9 Hz, 1H, C₆a-H), 5.82 (s, 1H, C₄-H), 6.93-7.39 (m, 4H, ArH); MS m/z 286 (M⁺); Anal Calcd. for C₁₆H₁₄O₃S: C, 67.11; H, 4.93. Found C, 67.28; H, 5.02%.

**Compound (15e).** Yield 63%; mp. 130-131 °C; UV(EtOH) λ max: 211, 254, nm; IR (KBr) ν max: 1690, 1620, 1450, 1240 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz): δ 2.17 (s, 3H, -CH₃), 2.23 (s, 3H, -CH₃), 1.79 (s, 3H, C₁₁a-CH₃), 2.76 (dd, J 9.9, 13.5 Hz, 1H, C₆-H), 2.98 (dd, J 3.9, 13.5 Hz, 1H, C₆-H), 3.40 (dd, J 3.9, 9.9 Hz, 1H, C₆a-H), 5.82 (s, 1H, C₄-H), 6.82-6.84 (m, 1H, ArH), 6.96-7.02 (m, 2H, ArH), MS m/z 300 (M⁺); Anal Calcd. for C₁₇H₁₆O₃S: C, 67.98; H, 5.37. Found C, 68.16; H, 5.22%.

**Compound (16d).** Yield 10%; mp. 88-89 °C; UV(EtOH) λ max: 213, 260, nm; IR (KBr) ν max: 1690, 1620, 1450, 1230 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz): δ 2.19 (s, 3H, -CH₃), 2.99 (t, J 6 Hz, 2H, -CH₂), 3.05 (t, J 6 Hz, 2H, -CH₂), 5.85 (s, 1H, C₅-H), 7.05-7.34 (m, 5H, ArH), 8.20 (s, 1H, C=CHOAr); MS m/z 286 (M⁺); Anal Calcd. for C₁₄H₁₄O₃S: C, 67.11; H, 4.93. Found C, 67.27; H, 4.78%.

**Compound (16e).** Yield 12%; mp. 92-93 °C; UV(EtOH) λ max: 213, 259, nm; IR (KBr) ν max: 1690, 1620, 1450, 1230 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz): δ 2.18 (s, 3H, -CH₃), 2.31 (s, 3H, -CH₃), 3.01 (t, J 6 Hz, 2H, -CH₂), 3.04 (t, J 6 Hz, 2H, -CH₂), 5.84 (s, 1H, C₅-H), 6.89-6.99 (m, 2H, ArH), 7.03-7.11 (m, 2H, ArH), 8.16 (s, 1H, C=CHOAr); MS m/z 300 (M⁺); Anal Calcd. for C₁₅H₁₆O₃S: C, 67.98; H, 5.37. Found C, 68.17; H, 5.13%.

**Compound (16f).** Yield 15%; Gummy mass; UV(EtOH) λ max: 213, 259, nm; IR (KBr) ν max: 1690, 1620, 1450, 1230 cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz): δ 2.19 (s, 3H, -CH₃), 2.98 (t, J 6 Hz, 2H, -CH₂), 3.05 (t, J 6 Hz, 2H, -CH₂), 5.86 (s, 1H, C₅-H), 6.93-7.05 (m, 2H, ArH), 7.14-7.33 (m, 2H, ArH), 8.14 (s, 1H, C=CHOAr); MS m/z 320, 322 (M⁺); Anal Calcd. for C₁₆H₁₃ClO₃S: C, 59.91; H, 4.08. Found C, 59.82; H, 4.22%.
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References


