Pergamon

TETRAHEDRON

Tetrahedron 58 (2002) 3235–3241

[4+2] Cycloaddition reactions of *o*-thioquinones with pentafulvenes: efficient synthesis of benzoxathiins

Vijay Nair,[a,*] Bini Mathew,[a] Rajeev S. Menon,[a] Saumini Mathew,[a] M. Vairamani[b] and S. Prabhakar[b]

[a]*Organic Chemistry Division, Regional Research Laboratory (CSIR), Trivandrum 695 019, India*
[b]*Analytical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India*

Received 23 August 2001; revised 6 February 2002; accepted 28 February 2002

Abstract—*o*-Thioquinones undergo [4+2] cycloaddition reactions with pentafulvenes leading to 1,4-benzoxathiins. Reactions of 6-styrenylfulvene with *o*-thioquinones also afforded similar products. © 2002 Published by Elsevier Science Ltd.

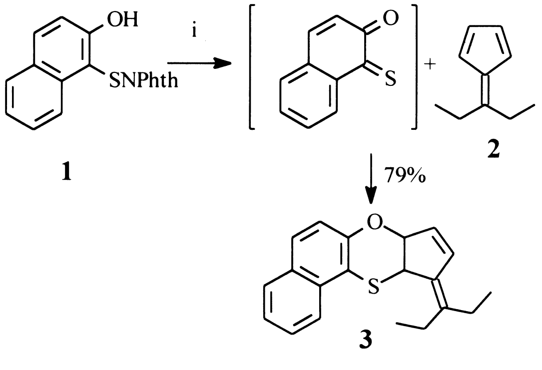
1. Introduction

There has been considerable interest in the cycloaddition reactions of *o*-benzoquinones recently, and their reactivity towards a variety of acyclic and cyclic π-systems has been examined in detail.[1–10] Naturally, during the course of our work in this area, we were intrigued by the reactivity of *o*-thioquinones. It is noteworthy that there has been very little work on these compounds, presumably due to the non-existence of convenient methods for their generation. The introduction of a practical method for the generation of *o*-thioquinones by Capozzi[11] has made these compounds readily accessible. Further, in their limited investigation, Capozzi and co-workers have shown that *o*-thioquinones undergo Diels–Alder reactions with few systems such as styrenes, vinyl ethers and 1,3-butadiene.[12–14] Recently, we have investigated the cycloaddition reactions of *o*-thioquinones with thiophenes and furans, and fulvenes and our preliminary results have been published.[15,16] The details of our extensive investigation of the cycloaddition reactions of *o*-thioquinones with a variety of fulvenes, 6,6-dialkyl, 6,6-cycloalkyl, 6-aryl, 6,6-diaryl and 6-styrenyl, are presented in this paper.

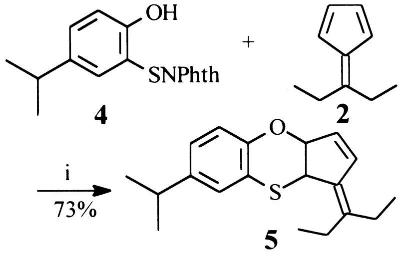
2. Results and discussion

Our studies commenced with the cycloaddition reaction of 1-thionaphthoquinone, generated in situ, with 6,6-diethylfulvene. Thus, 2-hydroxynaphthothiophthalimide on treatment with 6,6-diethylfulvene in presence of pyridine in dry chloroform in a sealed tube (70°C) afforded the product **3** in 79% yield (Scheme 1).

In the ^{1}H NMR spectrum of **3**, the proton adjacent to the sulfur resonated as a doublet at δ 4.29 (J=6.4 Hz) while the proton geminal to oxygen appeared as a doublet at δ 5.54 (J=6.4 Hz). The olefinic protons were observed at δ 6.02 (d, J=5.6 Hz) and 6.55 (d, J=5.6 Hz). The aromatic protons appeared as multiplets centered at δ 7.72. In the ^{13}C NMR spectrum, the CS and CO carbons were visible at δ 47.15



Scheme 1. i. Pyridine, $CHCl_3$, 70°C, sealed tube, 12 h.

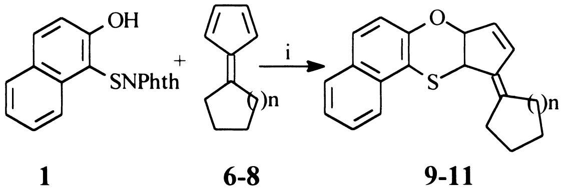


Scheme 2. i. Pyridine, $CHCl_3$, 70°C, sealed tube, 15 h.

Keywords: [4+2] cycloaddition reactions; *o*-thioquinones; pentafulvenes.

[*] Corresponding author. Tel.: +91-471-490406; fax: +91-471-491712; e-mail: gvn@csrrltrd.ren.nic.in

0040–4020/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0040-4020(02)00263-6



Fulvene	n	Product	Yield(%)
6	1	**9**	87
7	2	**10**	91
8	3	**11**	97

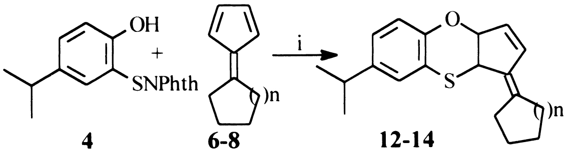
Scheme 3. i. Pyridine, $CHCl_3$, 70°C, sealed tube, 12 h.

and 87.31, respectively. Finally, regiochemistry of the product was confirmed by 2D COSY experiments.

A similar product was also obtained with 4-isopropyl-2-thio-1,2-benzoquinone and this reaction is presented in Scheme 2.

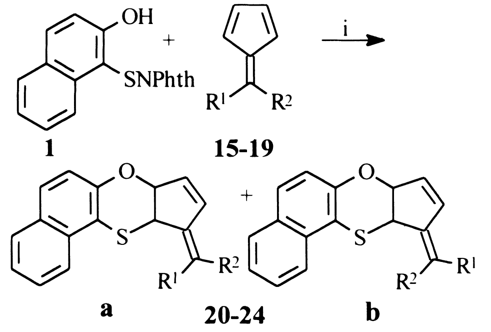
1-Thionaphthoquinone on reaction with 6,6-cycloalkylfulvenes such as 6,6-tetramethylene-, 6,6-pentamethylene-, and 6,6-hexamethylenefulvene afforded 1,4-benzoxathiin adducts in very high yield (Scheme 3).

Similar products were also obtained with 4-isopropyl-2-thio-1,2-benzoquinone and these reactions are presented in Scheme 4.



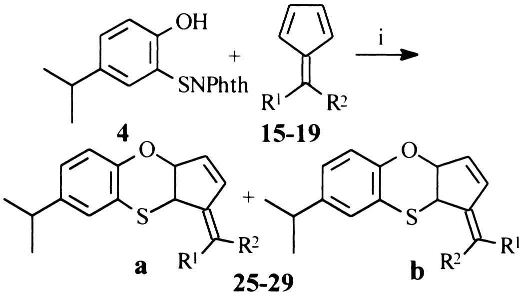
Fulvene	n	Product	Yield(%)
6	1	**12**	61
7	2	**13**	57
8	3	**14**	60

Scheme 4. i. Pyridine, $CHCl_3$, 70°C, sealed tube, 15 h.



Fulvene	Substituents	Products	Yield(%)	a:b
15	$R^1 = R^2 = Ph$	**20**	97	
16	$R^1 = H, R^2 = Ph$	**21**	82	2:1
17	$R^1 = H, R^2 = Ph(OMe)$	**22**	78	1:1
18	$R^1 = CH_3, R^2 = Ph$	**23**	70	1:5
19	$R^1 = H, R^2 = Furyl$	**24**	81	1:1

Scheme 5. i. Pyridine, $CHCl_3$, 70°C, sealed tube, 12 h.



Fulvene	Substituents	Products	Yield(%)	a:b
15	$R^1 = R^2 = Ph$	**25**	72	
16	$R^1 = H, R^2 = Ph$	**26**	82	1:1
17	$R^1 = H, R^2 = Ph(OMe)$	**27**	72	1:2
18	$R^1 = CH_3, R^2 = Ph$	**28**	65	1:5
19	$R^1 = H, R^2 = Furyl$	**29**	82	1:1

Scheme 6. i. Pyridine, $CHCl_3$, 70°C, sealed tube, 15 h.

Arylfulvenes also afforded similar products with 1-thionaphthoquinone (Scheme 5) and 4-isopropyl-2-thio-1,2-benzoquinone (Scheme 6). In the case of unsymmetrical fulvenes, products are inseparable mixtures of *syn* and *anti* isomers. Their composition, however, can be ascertained from the interpretation of the ^1H NMR spectra.

In the ^1H NMR spectrum of **21**, the –CHS– proton appeared as two distinct doublets at δ 4.51 (J=6.7 Hz) and 4.71 (J=6.7 Hz). In the second isomer –CHS– proton is situated very close to the phenyl ring (R^2=Ph) and this proton is slightly shifted to the downfield region. The –CHO– protons appeared as two separate doublets at δ 5.59 (J=6.7 Hz) and 5.72 (J=6.7 Hz). In the ^{13}C NMR spectrum, –CHS– and –CHO– carbons were observed at δ 47.30 and 49.18, and 85.63 and 87.84, respectively. This analogy can be applied to other isomers also.

In order to explain the observed regiochemistry in the above reactions, we have carried out AM1 calculations using PC SPARTAN Graphical Interface Package for Molecular Mechanics and Molecular Orbital Models.[17] The correlation diagram for the reaction of 6,6-diethylfulvene (**2**) with

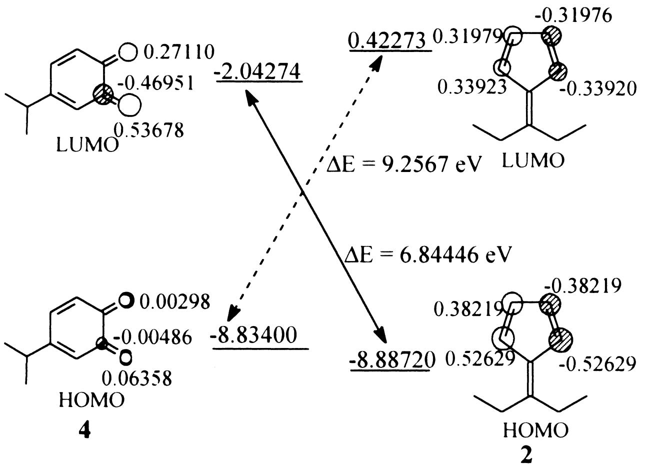
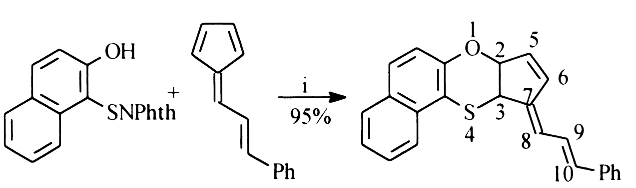


Figure 1.



1 **30** **31**

Scheme 7. i. Pyridine, $CHCl_3$, 70°C, sealed tube, 10 h.

4-isopropyl-2-thio-1,2-benzoquinone (**4**) is illustrated as an example in Fig. 1.

The exclusive formation of [4+2] adduct from 4-isopropyl-2-thio-1,2-benzoquinone and 6,6-diethylfulvene can be explained in terms of the coefficients of the Frontier orbitals at the reacting centers. It is clear from the correlation diagram that the interaction of HOMO(**4**)–LUMO(**2**) is not energetically favored. In contrast, the interaction of HOMO(**2**) with LUMO(**4**) is energetically favorable and therefore it controls the reaction, which can be characterized as a [4+2] cycloaddition reaction with inverse electron demand.

In continuation of the above investigations, we have studied the cycloaddition reactions of 1-thionaphthoquinone with 6-(2-phenylethenyl)fulvene. The latter participated as an efficient dienophile and the 1,4-oxathiin adduct was obtained regioselectively in quantitative yield (Scheme 7).

In the ^{1}H NMR spectrum of **31**, the protons on C-3 and C-2 appeared at δ 4.62 (d, J=6.1 Hz) and 5.66 (d, J=6.1 Hz) respectively. The olefinic protons on C-5 and C-6 resonated as doublets at δ 6.13 (J=5.3 Hz) and 6.39 (J=5.3 Hz) respectively. The signals at δ 6.21 (d, J=11.4 Hz) and 6.55 (d, J=15.4 Hz) can be attributed to C-8 and C-10 protons, respectively. The proton on C-9 resonated along with the aromatic protons and its signal was embedded in the multiplet centered at δ 7.33. The ^{13}C NMR spectrum showed peaks at δ 46.17 and 87.48 which have been assigned to C-3 and C-2 carbons, respectively. It may be noted that other isomeric structure for **31** cannot be categorically ruled out on the basis of spectral data. However, AM1 theoretical calculations[17] lend support to the proposed structure. The correlation diagram for the reaction of 4-isopropyl-2-thiobenzoquinone with 1,3-cyclohexadiene is illustrated in Fig. 2.

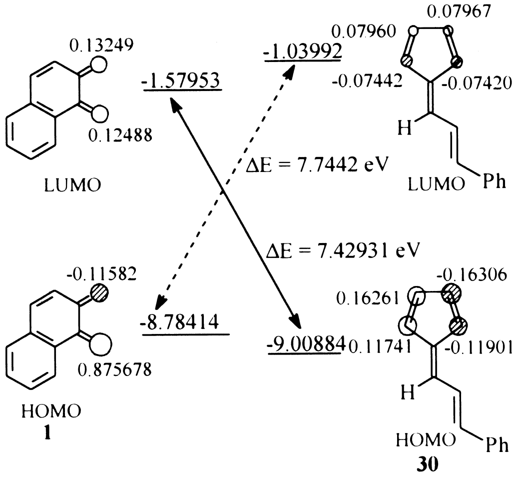
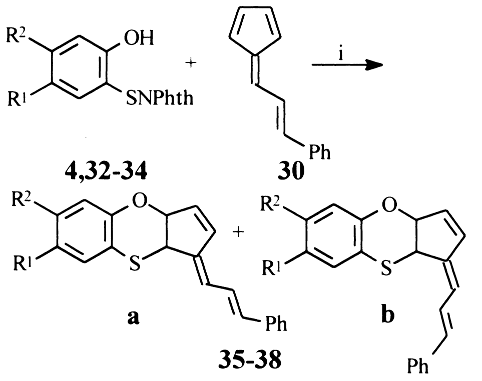


Figure 2.



Thiophthalimides	Substituents	Products	Yield	a:b
4	$R^1 = CHMe_2, R^2 = H$	**35**	58	2:1
32	$R^1 = CMe_3, R^2 = H$	**36**	62	2:1
33	$R^1 = OMe, R^2 = H$	**37**	72	2:1
34	$R^1 = H, R^2 = CHMe_2$	**38**	65	2:1

Scheme 8. i. Pyridine, $CHCl_3$, 70°C, sealed tube, 15 h.

The HOMO(**1**)–LUMO(**30**) interaction is unimportant because of the unsymmetry of the orbital coefficients at the reacting centers. But the orbital coefficients of LUMO(**1**)–HOMO(**30**) show that they are perfectly in match and the reaction proceeds via inverse electron demand pathway.

The fulvene **30** exhibited similar reactivity towards substituted *o*-thiobenzoquinones and the results are summarized in Scheme 8.

In summary, we have unravelled the reactivity of *o*-thioquinones towards various pentafulvenes leading to novel oxathiin adducts. It is noteworthy that the potent biological activities associated with 1,4-oxathiins have drawn attention to the synthesis of compounds incorporating this heterocyclic system.[18–21]

3. Experimental

3.1. General

All reactions were carried out in oven dried glassware under an atmosphere of argon. Melting points were recorded on a Buchi-530 melting point apparatus and are uncorrected. The IR spectra were recorded on Nicolet Impact 400D infrared spectrophotometer, using potassium bromide pellets. NMR spectra were recorded on Bruker-300 spectrometer using chloroform-d3 as solvent. Elemental analysis was done using a Perkin–Elmer 2400 CHN analyzer. High resolution mass spectra were obtained using Finnigan MAT model 8430. Solvents used for experiments were dried and distilled according to literature procedure.

3.1.1. (3a-*cis*)-2,3,3a,11a-Tetrahydro-naphtho[*a*]-1-[(diethyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (3). A solution of 2-hydroxynaphthothiophthalimide (321 mg, 1 mmol), 6,6-diethylfulvene (200 mg, 1.5 mmol) and pyridine (0.16 mL, 2 mmol) in dry chloroform (2 mL) was heated in a sealed tube at 70°C under argon atmosphere for 12 h. The product was purified by silica gel column chromatography to afford **1** (242 mg, 79%) as a pale yellow viscous liquid. IR (neat) $\nu_{\max}$: 811, 1253, 1377, 1458, 1595, 2965, 3058 cm^{-1}. ^{1}H NMR: δ 0.99 (t, J=7.5 Hz, 3H), 1.14 (t, J=7.4 Hz, 3H), 2.16 (q, J=7.4 Hz, 2H), 2.32 (q, J=7.4 Hz, 2H), 4.29 (d, J=6.4 Hz, 1H), 5.54 (d, J=6.4 Hz, 1H), 6.02 (d, J=5.6 Hz, 1H), 6.55 (d, J=5.6 Hz, 1H), 7.17–8.16 (m, 6H). ^{13}C NMR: δ 13.22, 13.64, 24.59, 25.82, 47.15, 87.31, 119.88, 120.40, 123.53, 124.35, 126.19, 127.05, 128.23, 130.14, 132.14, 132.43, 133.37, 136.25, 139.98, 153.81. HRMS calcd for $C_{20}H_{20}OS$ 308.1235, found 308.1227.

3.1.2. (3a-*cis*)-2,3,3a,9a-Tetrahydro-6-(1-methylethyl)-1-[(diethyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (5). 73%, pale yellow viscous liquid. IR (neat) $\nu_{\max}$: 751, 818, 1034, 1229, 1492, 2962 cm^{-1}. ^{1}H NMR: δ 0.92 (t, J=7.5 Hz, 3H), 1.02 (t, J=7.5 Hz, 3H), 1.12 (d, J=6.8 Hz, 6H), 2.05 (q, J=7.5 Hz, 2H), 2.15 (q, J=7.5 Hz, 2H), 2.73–2.77 (m, 1H), 4.24 (d, J=6.5 Hz, 1H), 5.32 (d, J=6.5 Hz, 1H), 5.92 (d, J=5.6 Hz, 1H), 6.50 (d, J=5.6 Hz, 1H), 6.84–7.07 (m, 3H). ^{13}C NMR: δ 12.09, 12.61, 23.04, 23.58, 24.81, 32.55, 46.30, 85.75, 117.78, 124.55, 124.77, 125.87, 131.01, 132.40, 135.33, 138.82, 142.51, 152.84. HRMS calcd for $C_{19}H_{24}OS$ 300.1548, found 300.1546.

3.1.3. (3a-*cis*)-2,3,3a,11a-Tetrahydro-naphtho[*a*]-1-[(cyclopentyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (9). 87%, pale yellow viscous liquid. IR (neat) $\nu_{\max}$: 786, 1228, 1384, 1595, 1614, 2946, 3058 cm^{-1}. ^{1}H NMR: δ 1.69–1.95 (m, 4H), 2.31–2.69 (m, 4H), 4.29 (d, J=6.4 Hz, 1H), 5.56 (d, J=6.4 Hz, 1H), 5.95 (d, J=5.0 Hz, 1H), 6.43 (d, J=5.0 Hz, 1H), 7.91–8.14 (m, 6H). ^{13}C NMR: δ 24.06, 26.48, 26.59, 31.34, 46.96, 87.35, 119.86, 120.54, 123.52, 124.31, 126.13, 127.00, 128.18, 130.15, 131.77, 132.51, 133.87, 134.14, 136.65, 153.98. HRMS calcd for $C_{20}H_{18}OS$ 306.1078, found 306.1064.

3.1.4. (3a-*cis*)-2,3,3a,11a-Tetrahydro-naphtho[*a*]-1-[(cyclohexyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (10). 91%, pale yellow viscous liquid. IR (neat) $\nu_{\max}$: 786, 1017, 1097, 1253, 1465, 1583, 1620, 2934, 2965 cm^{-1}. ^{1}H NMR: δ 1.57–1.63 (m, 6H), 2.21–2.51 (m, 4H), 4.34 (d, J=6.5 Hz, 1H), 5.57 (d, J=6.5 Hz, 1H), 6.02 (d, J=5.6 Hz, 1H), 6.62 (dd, J=1.1, 5.6 Hz, 1H), 7.09–8.17 (m, 6H). ^{13}C NMR: δ 26.49, 27.94, 28.05, 31.56, 32.36, 46.96, 87.35, 119.86, 120.54, 123.52, 124.31, 126.13, 127.00, 128.18, 130.12, 131.77, 132.41, 133.05, 134.14, 136.65, 153.88. HRMS calcd for $C_{21}H_{20}OS$ 320.1235, found 320.1229.

3.1.5. (3a-*cis*)-2,3,3a,11a-Tetrahydro-naphtho[*a*]-1-[(cycloheptyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (11). 97%, pale yellow viscous liquid. IR (neat) $\nu_{\max}$: 792, 1228, 1452, 1589, 2921, 3052 cm^{-1}. ^{1}H NMR: δ 1.53–1.77 (m, 8H), 2.34–2.64 (m, 4H), 4.27 (d, J=6.4 Hz, 1H), 5.53 (d, J=6.4 Hz, 1H), 6.00 (d, J=5.5 Hz, 1H), 6.55 (dd, J=1.4, 5.5 Hz, 1H), 7.17–8.16 (m, 6H). ^{13}C NMR: δ 27.67, 27.88, 28.88, 29.68, 32.16, 33.23, 47.47, 87.39, 119.86, 120.44, 123.54, 124.33, 126.15, 127.00, 128.22, 130.14, 131.80, 132.43, 133.41, 136.69, 137.99, 153.75. HRMS calcd for $C_{22}H_{22}OS$ 334.1391, found 334.1390.

3.1.6. (3a-*cis*)-2,3,3a,9a-Tetrahydro-6-(1-methylethyl)-1-[(cyclopentyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (12). 61%, pale yellow viscous liquid. IR (neat) $\nu_{\max}$: 825, 912, 1020, 1229, 1479, 2955 cm^{-1}. ^{1}H NMR: δ 1.20 (d, J=6.5 Hz, 6H), 1.69–1.79 (m, 4H), 2.27–2.39 (m, 4H), 2.80–2.85 (m, 1H), 4.27 (d, J=6.5 Hz, 1H), 5.42 (d, J=6.5 Hz, 1H), 5.95 (d, J=5.0 Hz, 1H), 6.43 (d, J=5.0 Hz, 1H), 6.91–7.14 (m, 3H). ^{13}C NMR: δ 24.06, 26.48, 26.59, 29.69, 31.34, 33.53, 48.26, 87.06, 118.94, 125.52, 126.91, 130.98, 133.59, 135.03, 135.05, 139.57, 143.63, 153.60. HRMS calcd for $C_{19}H_{22}OS$ 298.1391, found 298.1398.

3.1.7. (3a-*cis*)-2,3,3a,9-Tetrahydro-6-(1-methylethyl)-1-[(cyclohexyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (13). 57%, pale yellow viscous liquid. IR (neat) $\nu_{\max}$: 730, 838, 1027, 1222, 1492, 2948 cm^{-1}. ^{1}H NMR: δ 1.20 (d, J=6.8 Hz, 6H), 1.59–1.63 (m, 6H), 2.22–2.41 (m, 4H), 2.81–2.85 (m, 1H), 4.34 (d, J=6.5 Hz, 1H), 5.40 (d, J=6.5 Hz, 1H), 5.99 (d, J=5.7 Hz, 1H), 6.62 (d, J=5.7 Hz, 1H), 6.92–7.16 (m, 3H). ^{13}C NMR: δ 24.09, 26.54, 28.02, 28.09, 31.62, 32.15, 33.55, 47.15, 86.85, 118.83, 125.60, 125.90, 126.88, 128.78, 133.05, 134.22, 136.59, 143.57, 154.01. HRMS calcd for $C_{20}H_{24}OS$ 312.1548, found 312.1549.

3.1.8. (3a-*cis*)-2,3,3a,9a-Tetrahydro-6-(1-methylethyl)-1-[(cycloheptyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (14). 60%, pale yellow viscous liquid. IR (neat) $\nu_{\max}$: 751, 1027, 1229, 1479, 2921 cm^{-1}. ^{1}H NMR: δ 1.20 (d, J=5.9 Hz, 6H), 1.42–1.72 (m, 8H), 2.35–2.53 (m, 4H), 2.78–2.85 (m, 1H), 4.31 (d, J=6.5 Hz, 1H), 5.41 (d, J=6.5 Hz, 1H), 5.99 (d, J=4.6 Hz, 1H), 6.60 (d, J=4.6 Hz, 1H), 6.92–7.15 (m, 3H). ^{13}C NMR: δ 24.10, 27.65, 27.91, 28.90, 29.71, 33.53, 34.10, 34.56, 47.65, 86.87, 118.80, 124.69, 125.57, 125.77, 131.67, 133.50, 135.56, 137.91, 143.54, 153.77. HRMS calcd for $C_{21}H_{26}OS$ 326.1704, found 326.1689.

3.1.9. (3a-*cis*)-2,3,3a,11a-Tetrahydro-6-naphtho[*a*]-1-[(biphenyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (20). 97%, pale yellow viscous liquid. IR (neat) $\nu_{\max}$: 765, 1033, 1223, 1365, 1449, 1585, 2944 cm^{-1}. ^{1}H NMR: δ 4.57 (d, J=6.5 Hz, 1H), 5.51 (dd, J=1.5, 6.5 Hz, 1H), 6.02 (d, J=5.7 Hz, 1H), 6.44 (d, J=5.7 Hz, 1H), 6.95–7.60 (m, 16H). ^{13}C NMR: δ 48.01, 86.10, 119.96, 120.123, 123.40, 124.45, 126.19, 126.83, 127.29, 127.54, 128.02 (2C), 128.20, 128.31 (2C), 129.66 (2C), 129.86 (2C), 130.23, 132.27, 134.90, 136.31, 137.36, 141.31, 141.58, 141.77, 152.37. HRMS calcd for $C_{28}H_{20}OS$ 404.1235, found 404.1228.

3.1.10. (3a-*cis*)-2,3,3a,11a-Tetrahydro-naphtho[*a*]-1-[phenylmethylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (21). 82%, 2:1 mixture of isomers, pale yellow viscous liquid. IR (neat) $\nu_{\max}$: 792, 1023, 1222, 1390, 1465, 1620, 2959, 3058 cm^{-1}. ^{1}H NMR: δ 4.51 (d, J=6.7 Hz, SCH major isomer, 0.65H), 4.71 (d, J=6.7 Hz, SCH minor isomer, 0.35H), 5.59 (d, J=6.7 Hz, OCH major isomer, 0.65H), 5.72 (d, J=6.7 Hz, OCH minor isomer, 0.35H), 6.12 (d, J=5.4 Hz, minor isomer, 0.35H), 6.25 (d, J=5.4, major isomer, 0.65H), 6.42 (s, minor isomer, 0.35H), 6.44 (d, *J*=5.4 Hz, minor isomer, 0.35H), 6.62 (s, major isomer, 0.65H), 6.87 (d, *J*=5.4 Hz, major isomer, 0.65H), 7.13–8.16 (m, 11H). ^{13}C NMR: δ 47.30, 49.18, 85.63, 87.84, 119.48, 119.77, 120.02, 120.35, 123.54, 124.51, 124.64, 124.78, 126.48, 127.15, 127.40, 128.35, 128.45, 128.66, 128.81, 129.21, 130.42, 132.53, 132.65, 133.70, 134.16, 136.16, 136.75, 137.17, 139.12, 143.95, 144.46, 153.35. HRMS calcd for $C_{22}H_{16}OS$ 328.0922, found 328.0943.

3.1.11. (3a-*cis*)-2,3,3a,11a-Tetrahydro-naphtho[*a*]-1-[(4-methoxyphenyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (22). 78%, 1:1 mixture of isomers, pale yellow viscous liquid. IR (neat) ν_{max}: 798, 1035, 1253, 1464, 1521, 1602, 2965, 3034 cm^{-1}. ^{1}H NMR: δ 3.73 (s, OMe, 1.5H), 3.77 (s, OMe, 1.5H), 4.48 (d, *J*=6.7 Hz, SCH, 0.5H), 4.66 (d, *J*=6.7 Hz, SCH, 0.5H), 5.56 (d, *J*=6.7 Hz, OCH, 0.5H), 5.70 (d, *J*=6.7 Hz, OCH, 0.5H), 6.06 (dd, *J*=1.7, 5.5 Hz, 1st isomer, 0.5H), 6.21 (dd, *J*=1.7, 5.5 Hz, 2nd isomer, 0.5H), 6.35 (s, 1st isomer, 0.5H), 6.54 (s, 2nd isomer, 0.5H), 6.76–6.97 (m, 3H), 7.10–8.16 (m, 8H). ^{13}C NMR: δ 47.35, 49.20, 55.12, 55.17, 85.59, 88.04, 113.86, 114.06, 119.47, 119.78, 119.95, 120.26, 123.47, 123.53, 124.00, 124.27, 124.52, 126.36, 127.25, 128.26, 128.80, 129.51, 129.74, 130.27, 130.32, 130.56, 132.44, 132.56, 134.03, 135.96, 139.17, 141.65, 142.53, 153.18, 153.35, 158.77, 158.92. HRMS calcd for $C_{23}H_{18}O_2S$ 358.1027, found 358.1020.

3.1.12. (3a-*cis*)-2,3,3a,11a-Tetrahydro-naphtho[*a*]-1-[(methylphenyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (23). 70%, 5:1 mixture of isomers, pale yellow viscous liquid. IR (neat) ν_{max}: 782, 1023, 1232, 1398, 1465, 2940, 3058 cm^{-1}. ^{1}H NMR: δ 2.11 (s, Me minor isomer, 0.5H), 2.33 (s, Me major isomer, 2.5H), 4.40 (d, *J*=6.5 Hz, SCH minor isomer, 0.15H), 4.49 (d, *J*=6.5 Hz, SCH major isomer, 0.85H), 5.58 (d, *J*=6.5 Hz, OCH minor isomer, 0.15H), 5.66 (d, *J*=6.5 Hz, OCH major isomer, 0.85H), 6.04 (d, *J*=5.1 Hz, major isomer, 0.85H), 6.11 (d, *J*=5.1 Hz, minor isomer, 0.15H), 6.42 (d, *J*=5.1 Hz, major isomer, 0.85H), 6.68 (d, *J*=5.1 Hz, minor isomer, 0.15H), 7.11–8.22 (m, 11H). ^{13}C NMR: δ 21.65, 22.63, 47.22, 48.22, 86.18, 87.34, 119.80, 119.90, 120.20, 123.32, 123.50, 124.27, 124.45, 126.02, 126.28, 126.39, 126.62, 126.99, 127.09, 127.20, 127.66, 127.97, 128.07, 128.24, 128.30, 130.22, 132.37, 132.48, 133.39, 133.72, 134.14, 135.07, 139.68, 142.34. HRMS calcd for $C_{23}H_{18}OS$ 342.1078, found 342.1081.

3.1.13. (3a-*cis*)-2,3,3a,11a-Tetrahydro-naphtho[*a*]-1-[(furyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (24). 81%, 1:1 mixture of isomers, pale yellow viscous liquid. IR (neat) ν_{max}: 742, 1017, 1216, 1353, 1377, 1458, 1508, 1583, 1620, 2940, 3058 cm^{-1}. ^{1}H NMR: δ 4.51 (d, *J*=6.7 Hz, SCH, 0.5H), 4.97 (d, *J*=6.7 Hz, SCH, 0.5H), 5.62 (d, *J*=6.7 Hz, OCH, 0.5H), 5.84 (d, *J*=6.7 Hz, OCH, 0.5H), 5.99–6.47 (m, 4H), 7.12–8.10 (m, 8H). ^{13}C NMR: δ 47.49, 48.81, 85.56, 86.89, 110.01, 110.71, 111.25, 111.32, 111.76, 119.98, 120.26, 123.34, 123.43, 124.42, 126.13, 126.26, 126.82, 127.27, 128.15, 130.26, 132.28, 132.49, 134.42, 135.73, 138.11, 141.47, 142.23, 142.67, 151.99, 152.12, 152.75. HRMS calcd for $C_{20}H_{14}O_2S$ 318.0714, found 318.0713.

3.1.14. (3a-*cis*)-2,3,3a,9a-Tetrahydro-6-(1-methylethyl)-1-[(biphenyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (25). 72%, pale yellow viscous liquid. IR (neat) ν_{max}: 744, 919, 1034, 1229, 1499, 2975 cm^{-1}. ^{1}H NMR: δ 1.16 (d, *J*=6.8 Hz, 6H), 2.76–2.80 (m, 1H), 4.66 (d, *J*=6.4 Hz, 1H), 5.40 (d, *J*=6.4 Hz, 1H), 6.12 (d, *J*=5.7 Hz, 1H), 6.56 (d, *J*=5.7 Hz, 1H), 6.90–7.37 (m, 13H). ^{13}C NMR: δ 24.01, 24.09, 33.50, 47.73, 85.46, 118.92, 125.18, 125.27, 126.41, 127.28, 127.46, 128.02 (2C), 128.32 (2C), 129.61 (2C), 129.91 (2C), 134.78, 136.43, 137.09, 141.33, 141.71, 142.09, 143.69, 152.33. HRMS calcd for $C_{27}H_{24}OS$ 396.1547, found 396.1552.

3.1.15. (3a-*cis*)-2,3,3a,9a-Tetrahydro-6-(1-methylethyl)-1-[phenylmethylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (26). 82%, 1:1 mixture of isomers, pale yellow viscous liquid. IR (neat) ν_{max}: 737, 912, 1020, 1222, 1485, 2962 cm^{-1}. ^{1}H NMR: δ 1.18 (d, *J*=6.3 Hz, 6H), 2.79–2.83 (m, 1H), 4.46 (d, *J*=6.7 Hz, SCH, 0.5H), 4.72 (d, *J*=6.7 Hz, SCH, 0.5H), 5.45 (d, *J*=6.7 Hz, OCH, 0.5H), 5.52 (d, *J*=6.7 Hz, OCH, 0.5H), 6.23 (d, *J*=5.8 Hz, 1st isomer, 0.5H), 6.32 (d, *J*=5.8 Hz, 2nd isomer, 0.5H), 6.42–6.53 (m, 1H), 6.87–7.49 (m, 9H). ^{13}C NMR: δ 23.99, 24.04, 33.47, 46.93, 48.97, 84.80, 87.00, 118.96, 119.40, 124.20, 124.30, 124.41, 125.67, 127.01, 127.27, 128.26, 128.39, 128.56, 129.03, 133.70, 134.00, 136.08, 136.84, 137.18, 139.08, 143.78, 143.88, 144.36, 144.72, 152.73, 153.04. HRMS calcd for $C_{21}H_{20}OS$ 320.1235, found 320.1226.

3.1.16. (3a-*cis*)-2,3,3a,9a-Tetrahydro-6-(1-methylethyl)-1-[(4-methoxyphenyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (27). 72%, 1:2 mixture of isomers, pale yellow viscous liquid. IR (neat) ν_{max}: 825, 1020, 1175, 1249, 1472, 1499, 1600, 2962 cm^{-1}. ^{1}H NMR: δ 1.19–1.28 (m, 6H), 2.80–2.85 (m, 1H), 3.80 (s, OMe minor isomer, 1H), 3.82 (s, OMe major isomer, 2H), 4.46 (d, *J*=6.5 Hz, SCH minor isomer, 0.35H), 4.70 (d, *J*=6.5 Hz, SCH major isomer, 0.65H), 5.46 (d, *J*=6.5 Hz, OCH minor isomer, 0.35H), 5.59 (d, *J*=6.5 Hz, OCH major isomer, 0.65H), 6.04 (d, *J*=5.9 Hz minor isomer, 0.35H), 6.20 (d, *J*=5.9 Hz major isomer, 0.65H), 6.38–6.47 (m, 1H), 6.86–7.45 (m, 8H). ^{13}C NMR: δ 24.03, 24.08, 33.52, 47.11, 49.13, 55.30, 84.91, 87.32, 113.94, 114.12, 118.98, 123.81, 123.90, 125.66, 125.70, 126.91, 127.01, 128.86, 129.54, 130.49, 132.25, 132.57, 134.02, 136.14, 139.26, 142.21, 142.96, 143.78, 143.88, 152.91, 153.18, 158.80, 158.91. HRMS calcd for $C_{22}H_{22}O_2S$ 350.1340, found 350.1337.

3.1.17. (3a-*cis*)-2,3,3a,9a-Tetrahydro-6-(1-methylethyl)-1-[(methylphenyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (28). 65%, 1:5 mixture of isomers, pale yellow viscous liquid. IR (neat) ν_{max}: 703, 912, 1027, 1074, 1222, 1485, 2962 cm^{-1}. ^{1}H NMR: δ 1.15–1.24 (m, 6H), 2.12 (s, Me minor isomer, 0.5H), 2.24 (s, Me major isomer, 2.5H), 2.76–2.83 (m, 1H), 4.38 (d, *J*=6.2 Hz, SCH minor isomer, 0.15H), 4.46 (d, *J*=6.2 Hz, SCH major isomer, 0.85H), 5.37 (d, *J*=6.2 Hz, OCH minor isomer, 0.15H), 5.50 (d, *J*=6.2 Hz, OCH major isomer, 0.85H), 5.98 (d, *J*=5.3 Hz major isomer, 0.85H), 6.10 (d, *J*=5.3 Hz minor isomer, 0.15H), 6.41 (d, *J*=5.3 Hz, 1H), 6.69–7.36 (m, 8H). ^{13}C NMR: δ 21.51, 23.83, 24.18, 33.22, 47.16, 48.28, 85.46, 86.63, 119.02, 119.20, 125.38, 125.70, 126.31, 126.94, 127.04, 127.74, 128.11, 128.33, 128.43, 130.10, 133.57, 133.92, 134.11, 135.13, 140.06, 142.50, 143.66. HRMS calcd for $C_{22}H_{22}OS$ 334.1391, found 334.1390.

3.1.18. (3a-*cis*)-2,3,3a,9a-Tetrahydro-6-(1-methylethyl)-1-[(furyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (29). 82%, 1:1 mixture of isomers, pale yellow viscous liquid. IR (neat) ν_{max}: 737, 1017, 1222, 1477, 2959 cm^{-1}. ^{1}H NMR: δ 1.18 (d, J=6.8 Hz, 6H), 2.77–2.82 (m, 1H), 4.48 (d, J=6.5 Hz, SCH, 0.5H), 4.90 (d, J=6.5 Hz, SCH, 0.5H), 5.47 (d, J=6.5 Hz, OCH, 0.5H), 5.73 (d, J=6.5 Hz, OCH, 0.5H), 5.95–6.45 (m, 3H), 6.84–7.49 (m, 6H). ^{13}C NMR: δ 23.98, 33.45, 47.19, 48.67, 84.68, 85.98, 109.85, 110.59, 110.91, 111.24, 111.34, 111.71, 119.38, 124.07, 125.03, 125.60, 126.53, 126.93, 134.77, 135.65, 136.08, 138.10, 141.91, 142.22, 142.60, 143.64, 151.89, 152.01, 152.83, 152.90. HRMS calcd for $C_{19}H_{18}O_2S$ 310.1027, found 310.1027.

3.1.19. (3a-*cis*)-2,3,3a,11a-Tetrahydro-naphtho[*a*]-1-[(2-phenylethenyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (31). 95%, pale yellow solid; recrystallized from dichloromethane–petroleum ether (mp 109–111°C). IR (KBr) ν_{max}: 742, 1253, 1358, 1501, 1582, 2965, 3027 cm^{-1}. ^{1}H NMR: δ 4.62 (d, J=6.1 Hz, 1H), 5.66 (d, J=6.1 Hz, 1H), 6.13 (d, J=5.3 Hz, 1H), 6.21 (d, J=11.4 Hz, 1H), 6.39 (d, J=5.3 Hz, 1H), 6.55 (d, J=15.4 Hz, 1H), 7.18–7.49 (m, 9H), 7.63 (d, J=8.7 Hz, 1H), 7.77 (d, J=8.0 Hz, 1H), 8.14 (d, J=8.3 Hz, 1H). ^{13}C NMR: δ 46.17, 87.48, 120.03, 120.13, 123.56, 124.34, 124.55, 125.17, 126.39, 126.59 (2C), 127.40, 127.76, 128.21, 128.65 (2C), 130.31, 132.42, 133.88, 134.23, 137.25, 137.80, 144.82, 153.56. Anal. Calcd for $C_{24}H_{18}OS$: C, 81.33; H, 5.12. Found: C, 81.17; H, 5.15.

3.1.20. (3a-*cis*)-2,3,3a,9a-Tetrahydro-6-(1-methylethyl)-1-[(2-phenylethenyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (35). 58%, 2:1 mixture of isomers, pale yellow viscous liquid. IR (neat) ν_{max}: 712, 1032, 1243, 1492, 2953 cm^{-1}. ^{1}H NMR: δ 1.22–1.27 (m, 6H), 2.89–2.92 (m, 1H), 4.42 (d, J=6.6 Hz, SCH minor isomer, 0.35H), 4.59 (d, J=6.6 Hz, SCH major isomer, 0.65H), 5.52 (d, J=6.6 Hz, OCH 1H), 6.18–7.48 (m, 13H). ^{13}C NMR: 24.12, 24.18, 33.77, 33.98, 46.26, 48.45, 85.34, 86.88, 117.55, 117.85, 121.56, 124.62, 125.12, 126.69, 127.61, 127.82, 128.11, 128.71, 128.88, 128.96, 132.12, 132.86, 133.33, 134.48, 137.74, 148.05, 149.30. HRMS calcd for $C_{23}H_{22}OS$ 346.1391, found 346.1402.

3.1.21. (3a-*cis*)-2,3,3a,9a-Tetrahydro-6-(1,1-dimethylethyl)-1-[(2-phenylethenyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (36). 62%, 2:1 mixture of isomers, pale yellow viscous liquid. IR (neat) ν_{max}: 700, 1042, 1248, 1490, 2959 cm^{-1}. ^{1}H NMR: δ 1.29 (s, 9H), 4.41 (d, J=6.7 Hz, SCH minor isomer, 0.35H), 4.58 (d, J=6.7 Hz, SCH major isomer, 0.65H), 5.47 (d, J=6.8 Hz, OCH 1H), 6.27–7.48 (m, 13H). ^{13}C NMR: 31.54, 31.58, 37.24, 46.15, 47.92, 85.32, 86.73, 118.86, 124.22, 124.76, 124.87, 124.94, 125.35, 126.07, 126.45, 126.73, 127.87, 128.06, 128.52, 128.67, 128.72, 133.43, 133.94, 134.59, 137.75, 148.22, 149.31. HRMS calcd for $C_{24}H_{24}OS$ 360.1548, found 360.1540.

3.1.22. (3a-*cis*)-2,3,3a,9a-Tetrahydro-6-methoxy-1-[(2-phenylethenyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (37). 72%, 2:1 mixture of isomers, pale yellow viscous liquid. IR (neat) ν_{max}: 727, 1047, 1222, 1454, 2953 cm^{-1}. ^{1}H NMR: δ 3.71 (s, OMe minor isomer, 1H), 3.74 (s, OMe major isomer, 2H), 4.39 (d, J=6.8 Hz, SCH minor isomer, 0.35H), 4.56 (d, J=6.7 Hz, SCH major isomer, 0.65H), 5.49 (d, J=6.7 Hz, OCH 1H), 6.06–7.46 (m, 13H). ^{13}C NMR: 46.14, 47.73, 55.52, 55.59, 85.42, 86.89, 110.81, 111.58, 113.78, 113.96, 114.25, 120.10, 120.40, 124.23, 125.28, 126.45, 126.69, 128.52, 128.66, 128.72, 132.89, 133.68, 133.92, 134.46, 134.94, 137.32, 138.03, 145.23, 145.42, 148.46, 149.11. HRMS calcd for $C_{21}H_{18}O_2S$ 334.1028, found 334.1022.

3.1.23. (3a-*cis*)-2,3,3a,9a-Tetrahydro-7-(1-methylethyl)-1-[(2-phenylethenyl)methylene]-1,4-cyclopenta[*b*]-1,4-benzoxathiin (38). 65%, 2:1 mixture of isomers, pale yellow viscous liquid. IR (neat) ν_{max}: 727, 1047, 1232, 1477, 2959 cm^{-1}. ^{1}H NMR: δ 1.20–1.24 (m, 6H), 2.83–2.88 (m, 1H), 4.39 (d, J=6.5 Hz, SCH minor isomer, 0.35H), 4.56 (d, J=6.5 Hz, SCH major isomer, 0.65H), 5.49 (d, J=6.6 Hz, OCH 1H), 6.12–7.46 (m, 13H). ^{13}C NMR: 24.00, 33.65, 33.95, 46.16, 48.30, 85.27, 86.78, 117.55, 117.85, 121.56, 124.62, 125.12, 126.69, 127.61, 127.82, 128.11, 128.71, 128.88, 128.96, 132.12, 132.86, 133.33, 134.48, 137.74, 148.05, 149.30. HRMS calcd for $C_{23}H_{22}OS$ 346.1391, found 346.1377.

Acknowledgements

B. M. and R. S. M. thank CSIR, New Delhi for the award of Research Fellowships.

References

1. For a review of the earlier work, see: Patai, S. *The Chemistry of the Quinonoid Compounds*, Vol. 2; Wiley: New York, 1988 pp 636–645 and references cited therein.
2. Nair, V.; Kumar, S. *Synlett* **1996**, 1143.
3. Nair, V.; Kumar, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1341.
4. Nair, V.; Kumar, S.; Rath, N. P.; Morton, G. O. *Chem. Lett.* **1995**, 383.
5. Nair, V.; Kumar, S.; Williard, P. G. *Tetrahedron Lett.* **1995**, *36*, 1605.
6. Nair, V.; Kumar, S.; Anilkumar, G.; Nair, J. S. *Tetrahedron* **1995**, *51*, 9155.
7. Nair, V.; Kumar, S. *Synth. Commun.* **1996**, *26*, 217.
8. Nair, V.; Kumar, S. *J. Chem. Soc., Perkin Trans. 1* **1996**, 443.
9. Nair, V.; Kumar, S. *Tetrahedron* **1996**, *52*, 4029.
10. Nair, V.; Mathew, B.; Radhakrishnan, K. V.; Rath, N. P. *Tetrahedron* **1999**, *55*, 11017.
11. Capozzi, G.; Menichetti, S.; Nativi, C.; Simonti, M. C. *Tetrahedron Lett.* **1994**, *35*, 9451.
12. Capozzi, G.; Falciani, C.; Menichetti, S.; Nativi, C. *J. Org. Chem.* **1997**, *62*, 2611.
13. Capozzi, G.; Falciani, C.; Menichetti, S.; Nativi, C.; Frank, R. W. *Tetrahedron Lett.* **1995**, *36*, 6755.
14. Capozzi, G.; Falciani, C.; Menichetti, S.; Nativi, C. *Gazz. Chim. Ital.* **1996**, *126*, 227.
15. Nair, V.; Mathew, B.; Radhakrishnan, K. V.; Rath, N. P. *Synlett* **2000**, 61.
16. Nair, V.; Mathew, B. *Tetrahedron Lett.* **2000**, *41*, 6919.

17. AM1 calculations using PC SPARTAN Graphical Interface Package for Molecular Mechanics and Molecular Orbital Models by Wavefunctions Inc. 18401. Von Karman, Suite 370, Irvine, CA, 92612, USA.
18. Breslow, D. S.; Skolnik, H. *Chem. Heterocycl. Compd* **1966**, *21*, 867.
19. Harfenist, M.; Mc Gee, D. P. C.; White, H. L. *J. Med. Chem.* **1991**, *34*, 2931.
20. Melchiorre, L.; Brasili, L.; Giardina, D.; Pigini, M.; Strappaghetti, G. *J. Med. Chem.* **1984**, *27*, 1535.
21. Arnoldi, A.; Bassoli, A.; Caputoi, R.; Merlini, L.; Palumbo, G.; Pedalella, S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1241.