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Hetero Diels–Alder reactions of *o*-thioquinones with cyclic dienes: an efficient synthesis of novel heterocyclic compounds

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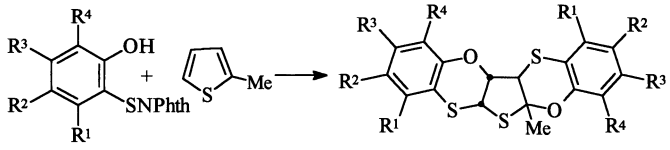
Abstract—*o*-Thioquinones undergo facile hetero Diels–Alder reactions with cyclic dienes leading to novel heterocyclic compounds.

The Diels–Alder reaction, being one of the most powerful carbon–carbon bond forming processes has been the subject of extensive research during the past few decades.[1,2] In this context, *o*-quinones have received considerable attention due to the exceptionally versatile reactivity of these compounds as carbodiene, heterodiene and dienophile.[3–10] Recent work in our own laboratory has exposed some novel reactivity patterns of *o*-quinones in cycloaddition reactions with a variety of substrates.[11–17] As a logical extension of this work we became interested in the systematic investigation of the corresponding thioanalogue. Access to variety of thioquinones by a recently reported method by Capozzi and coworkers[18–21] has permitted a detailed study of their Diels–Alder reactions. We were particularly interested in the cycloadditions of *o*-thioquinones with cyclic dienes.[22,23] In an earlier communication,[22] we reported the [4+2] cycloaddition reactions of *o*-thioquinones with heterocyclic dienes. The details of our studies involving carbocyclic and heterocyclic dienes are disclosed here.

1. Results and discussion

The initial experiment involving the reaction of 4-isopropyl-2-thio-1,2-benzoquinone, generated in situ from **1a**, with 2-methylthiophene afforded 1,4-oxathiin diadduct **3a** in



1(a-e) 2 3(a-e)

o-Hydroxyphenylthiophthalimides	Substituents	Products	Yields*
1a	R^1=R^3=R^4=H, R^2=$CHMe_2$	3a	70%
1b	R^1=R^3=R^4=H, R^2=CMe_3	3b	70%
1c	R^1=R^3=R^4=H, R^2=Me	3c	93%
1d	R^2=R^4=H, R^1=R^3=CMe_3	3d	85%
1e	R^3=R^4=H, R^1-R^2=*o*-Phenylene	3e	78%

Scheme 1. *Isolated yield. *Reaction conditions*: Pyridine, $CHCl_3$, sealed tube, 70°C, 24 h.

Keywords: Diels–Alder reactions; *o*-quinone; dienes.
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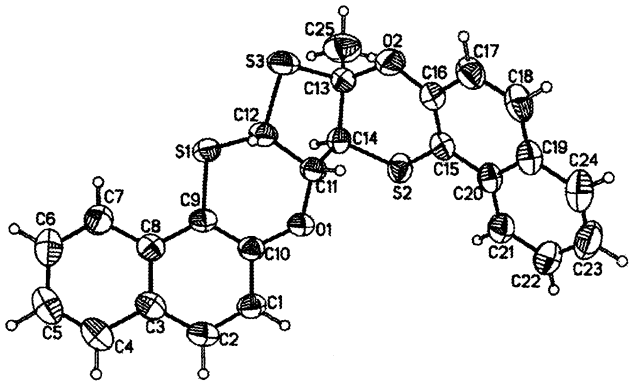


Figure 1. X-Ray structure of **3e**.

70% yield. Similar reactivity pattern was observed with different substituted *o*-thiobenzoquinones and Scheme 1 summarizes the results of our investigation.

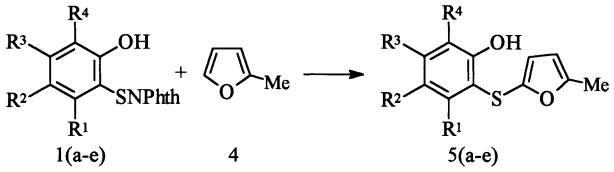
In the ^{1}H NMR spectrum of **3a**, the SCH proton on the benzoxathiin ring appeared at δ 3.87 (J=8.6 Hz) as a doublet. The SCHS proton appeared as a doublet at δ 4.64 (J=5.0 Hz) whereas the OCH proton resonated as a double doublet at δ 4.68 (J=5.1, 3.4 Hz). Examination of the ^{13}C NMR spectrum showed the presence of four deshielded sp^3 carbon signals at δ 52.73, 80.98, 44.02 and 91.91 and these are assigned to the carbon atoms of the oxathiin ring viz., S–CH–S, O–CH, S–CH and O–CMe–S carbons, respectively. Finally the structure was determined unambiguously by single crystal X-ray analysis of product **3e** (Fig. 1).

Interestingly, the reaction of 2-methylfuran with 4-isopropylthioquinone afforded phenol derivative **5a** in 74% yield. Similar results were obtained with substituted *o*-thiobenzoquinones and the results are summarized in Scheme 2.

The IR spectrum of **5a** showed –OH absorption at 3474 cm^{-1}. In the ^{1}H NMR spectrum, the furan protons presented two separate doublets at δ 5.90 (J=2.8 Hz) and 6.45 (J=2.8 Hz), respectively. The –OH proton resonated at δ 6.49 (exchangeable by D_2O).

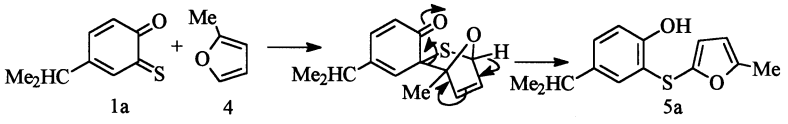
A mechanistic rationalization for the formation of the product may be presented as shown (Scheme 3).

Alternatively, an ene type reaction (Scheme 4) can account for the formation of **5a**.

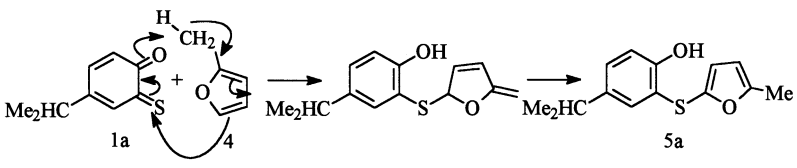


o-Hydroxyphenylthiophthalimides	Substituents	Products	Yields*
1a	R^1=R^3=R^4=H, R^2=CHMe$_2$	5a	74%
1b	R^1=R^3=R^4=H, R^2=CMe$_3$	5b	86%
1c	R^1=R^3=R^4=H, R^2=Me	5c	92%
1d	R^2=R^4=H, R^1=R^3=CMe$_3$	5d	88%
1e	R^3=R^4=H, R^1-R^2=*o*-Phenylene	5e	78%

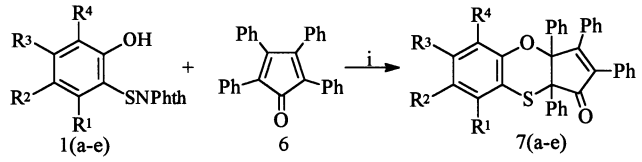
Scheme 2. *Isolated yield. *Reaction conditions*: Pyridine, $CHCl_3$, sealed tube, 70°C, 24 h.



Scheme 3.



Scheme 4.



o-Hydroxyphenylthiophthalimides	Substituents	Products	Yields*
1a	R^1=R^3=R^4=H, R^2=$CHMe_2$	7a	100%
1b	R^1=R^3=R^4=H, R^2=CMe_3	7b	99%
1c	R^1=R^3=R^4=H, R^2=Me	7c	90%
1d	R^2=R^4=H, R^1=R^3=CMe_3	7d	95%
1e	R^3=R^4=H, R^1-R^2=*o*-Phenylene	7e	100%

Scheme 5. *Isolated yield. *Reaction conditions*: Pyridine, $CHCl_3$, sealed tube, 70°C, 24 h.

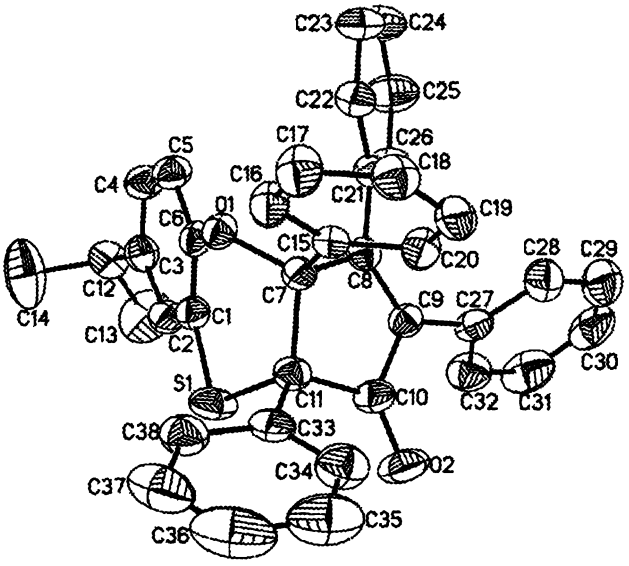


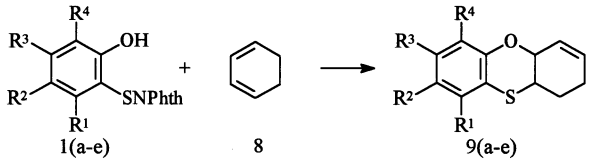
Figure 2. X-Ray structure of **7a**.

The reaction of 4-isopropyl-2-thiobenzoquinone and the electron deficient diene tetracyclone afforded **7a** in 100% yield. Other substituted thiobenzoquinones also readily underwent similar Diels–Alder reactions to form 1,4-benzoxathiin adducts and the results are summarized in Scheme 5.

The IR spectrum of **7a** exhibited carbonyl absorption at 1721 cm^{-1}, typical of cyclopentenones. The ^{13}C NMR spectrum showed the carbonyl carbon at δ 197.39, characteristic of the α,β-unsaturated ketone. The OCPh and SCPh carbons of the benzoxathiin were discernible at δ 95.72 and 70.50, respectively. Final proof for the structure was obtained by single crystal X-ray analysis of **7a** (Fig. 2).

The reaction of 1,3-cyclohexadiene and 4-isopropyl-2-thiobenzoquinone gave rise to the benzoxathiin **9a** regioselectively in 71% yield. The reaction was found to be applicable to other substituted *o*-thiobenzoquinones and the results are summarized in Scheme 6.

In the ^1H NMR spectrum of **9a**, the methylenic protons



o-Hydroxyphenylthiophthalimides	Substituents	Products	Yields*
1a	R^1=R^3=R^4=H, R^2=$CHMe_2$	9a	71%
1b	R^1=R^3=R^4=H, R^2=CMe_3	9b	84%
1c	R^1=R^3=R^4=H, R^2=Me	9c	92%
1d	R^2=R^4=H, R^1=R^3=CMe_3	9d	51%
1e	R^3=R^4=H, R^1-R^2=*o*-Phenylene	9e	79%

Scheme 6. *Isolated yield. *Reaction conditions*: Pyridine, $CHCl_3$, sealed tube, 70°C, 15 h.

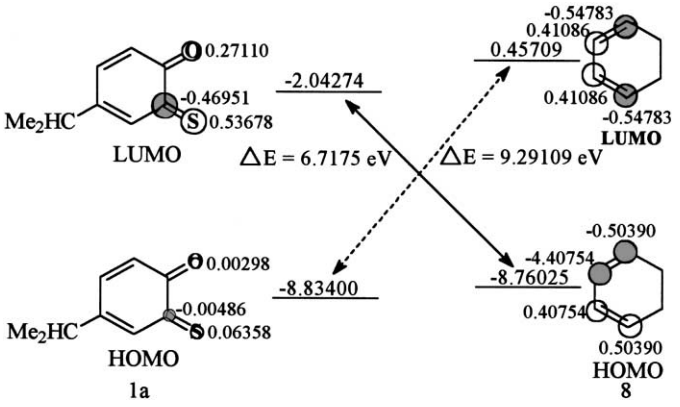
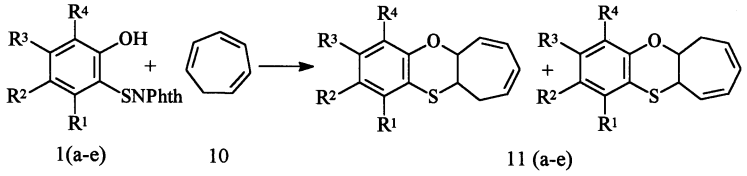


Figure 3.



o-Hydroxyphenylthiophthalimides	Substituents	Products	Yields*
1a	$R^1=R^3=R^4=H$, $R^2=CHMe_2$	11a	62%, 2:1
1b	$R^1=R^3=R^4=H$, $R^2=CMe_3$	11b	84%, 1:1
1c	$R^1=R^3=R^4=H$, $R^2=Me$	11c	89%, 1:1
1d	$R^2=R^4=H$, $R^1=R^3=CMe_3$	11d	79%, 2:1
1e	$R^3=R^4=H$, R^1-R^2=*o*-Phenylene	11e	84%, 1:1

Scheme 7. *Isolated yield. *Reaction conditions*: Pyridine, $CHCl_3$, sealed tube, 70°C, 14 h.

resonated as a multiplet centered at δ 2.10. The –SCH proton resonated as a multiplet in the region δ 3.33–3.37. A broad singlet at δ 4.39 was assigned to the –OCH proton. The olefinic protons resonated as multiplets centered at δ 5.95. In the ^{13}C NMR spectrum, the SCH and OCH carbons were visible at δ 38.35 and 69.08, respectively. It may be noted that regioisomeric structure for **9a** cannot be categorically ruled out on the basis of spectral data. However, AM1 theoretical calculations[24] lend support to the proposed regiochemistry of **9a**. The correlation diagram for the reaction of 4-isopropyl-2-thiobenzoquinone with 1,3-cyclohexadiene is illustrated in Fig. 3.

The HOMO(1a)–LUMO(8) interaction is unimportant because the unsymmetry of the orbital coefficients at the reacting centers. But the orbital coefficients of LUMO(1a)–HOMO(8) show that they are perfectly in match and the reaction proceeds via an inverse electron demand pathway.

2-Hydroxy-5-isopropylphenylthiophthalimide on treatment with 1,3,5-cycloheptatriene in presence of pyridine at 70°C in chloroform produced **11a** as an inseparable mixture of regioisomers in 62% yield. Similar reactivity pattern was exhibited by different substituted *o*-thioquinones towards 1,3,5-cycloheptatriene and the results are summarized in Scheme 7.

In the ^1H NMR spectrum of **11a,** the SCH proton appeared as two distinct multiplets centered at δ 3.46 and 4.16 and the OCH proton resonated as separate multiplets centered at δ 4.77 and 4.88. The olefinic protons appeared as a multiplet centered at δ 5.82. In the ^{13}C NMR spectrum, the peaks at δ 39.91 and 43.52 can be attributed to SCH carbon and the signals at δ 74.49 and 75.30 can be assigned to OCH carbon. The regioisomeric ratio of the adducts was determined by integrating SCH and OCH proton signals.

In conclusion, we have obtained some novel results for the reaction of *o*-thioquinones with carbocyclic and heterocyclic dienes. The reaction of *o*-thioquinones with carbocyclic dienes such as tetracyclone and 1,3-cyclohexadiene, heterocyclic diene such as 2-methyl thiophene and also 1,3,5-cycloheptatriene afforded 1,4-oxathiins. But in the case of 2-methylfuran, *o*-thioquinone acts as a dienophile and furan as a diene resulting in the formation of substituted phenols. 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.[25–28]

2. Experimental

2.1. 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 were 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-d as solvent. Elemental analyses were 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.

2.1.1. 1a-Methyl-1a,4a,1a′,4a′-tetrahydrothiophene[*b*]-bis[7-(1-methylethyl)]-1,4-benzoxathiin (3a). 2-Hydroxy-5-isopropylphenylthiophthalimide (156 mg, 0.5 mmol) and 2-methylthiophene (74 mg, 0.75 mmol) were dissolved in chloroform (2 mL) in a Schlenk glass tube in presence of pyridine (0.08 mL, 1 mmol) and heated at 70°C for 24 h. The solvent was removed in vacuo and the residue after silica gel column chromatography afforded the benzoxathiin derivative **3a** (75 mg, 70%) as a colorless viscous liquid. IR (neat) ν_{max}: 825, 1088, 1236, 1492, 2962 cm^{-1}. ^1H NMR: δ 1.18–1.24 (m, 12H), 1.95 (s, 3H), 2.79–2.85 (m, 2H), 3.87 (d, J=8.6 Hz, 1H), 4.64 (d, J=5.0 Hz, 1H), 4.68 (dd, J=5.0, 8.6 Hz, 1H), 6.84–7.01 (m, 6H). ^{13}C NMR: δ 22.98, 28.30, 28.67, 32.35, 32.47, 44.02, 52.73, 80.98, 91.91, 117.42, 117.85, 118.02, 118.92, 124.26, 124.48, 125.00, 127.59, 142.24, 143.12, 147.10, 148.16. HRMS calcd for $C_{23}H_{26}O_2S_3$ 430.1094, found 430.1088.

2.1.2. 1a-Methyl-1a,4a,1a′,4a′-tetrahydrothiophene[*b*]-bis-[7-(1,1-dimethylethyl)]-1,4-benzoxathiin (3b). 3b (70%), colorless crystalline solid; recrystallized from CH_2Cl_2–petroleum ether (mp 145–147°C). IR (KBr) ν_{max}: 798, 1094, 1270, 1492, 2969 cm^{-1}. ^1H NMR: δ 1.19 (s, 9H), 1.24 (s, 9H), 1.89 (s, 3H), 3.79 (d, J=8.8 Hz, 1H), 4.54 (d, J=5.0 Hz, 1H), 4.62 (dd, J=5.0, 8.8 Hz, 1H), 6.76–7.19 (m, 6H). ^{13}C NMR: δ 29.54, 31.60, 34.45, 34.58, 45.05, 53.85, 81.90, 92.83, 118.11, 118.48, 118.71, 119.73, 124.41, 124.66 (2C), 125.11, 145.60, 146.50, 148.05, 149.07. Anal. Calcd for $C_{25}H_{30}O_2S_3$: C, 65.46; H, 6.59; S, 20.97. Found: C, 65.67; H, 6.61; S, 20.93.

2.1.3. 1a-Methyl-1a,4a,1a′,4a′-tetrahydrothiophene[*b*]-bis-(7-methyl)-1,4-benzoxathiin (3c). 3c (93%), colorless viscous liquid. IR (neat) ν_{max}: 802, 1083, 1145, 1258, 1451, 1482, 1570, 2930, 2974 cm^{-1}. ^1H NMR: δ 1.96 (s, 3H), 1.98 (s, 3H), 2.24 (s, 3H), 3.87 (d, J=8.6 Hz, 1H), 4.58 (d, J=5.8 Hz, 1H), 4.67 (dd, J=5.8, 8.6 Hz, 1H), 6.72–7.18 (m, 6H). ^{13}C NMR: δ 29.64, 30.14 (2C), 44.98, 53.79, 81.13, 93.44, 116.58, 119.49, 120.77, 123.33, 124.31, 125.95, 128.23, 137.37, 137.52, 149.92, 151.29, 151.34. HRMS calcd for $C_{19}H_{18}O_2S_3$ 374.0468, found 374.0461.

2.1.4. 1a-Methyl-1a,4a,1a′,4a′-tetrahydrothiophene[*b*]-bis-[6,8-bis(1,1-dimethylethyl)]-1,4-benzoxathiin (3d). 3d (85%), colorless crystalline solid; recrystallized from dichloromethane–petroleum ether (mp 175–177°C). IR (KBr)ν_{max}: 805, 1067, 1291, 1397, 1465, 1596, 2959 cm^{-1}. ^1H NMR: δ 1.26 (s, 9H), 1.29 (s, 9H), 1.43 (s, 9H), 1.59 (s, 9H), 2.10 (s, 3H), 4.05 (d, J=8.9 Hz, 1H), 4.19 (d, J=5.6 Hz, 1H), 4.45 (dd, J=5.6, 8.9 Hz, 1H), 6.79 (d, J=1.5 Hz, 1H), 6.85 (d, J=1.5 Hz, 1H), 7.04 (s, 1H), 7.18 (s, 1H). ^{13}C NMR: δ 30.33, 30.41, 30.74, 31.31, 31.39, 34.71, 34.87, 36.58, 36.69, 48.22, 57.60, 83.86, 97.07, 114.78, 116.23, 117.69, 118.33, 118.65 (2C), 119.33, 148.36, 149.89, 150.00, 150.42, 153.62. Anal. Calcd for $C_{33}H_{46}O_2S_3$: C, 69.42; H, 8.12; S, 16.84. Found: C, 68.98; H, 8.03; S, 16.81.

2.1.5. 1a-Methyl-1a,4a,1a′,4a′-tetrahydrothiophene[*b*]-bis-(naphth[2,3-*b*])-1,4-oxathiin (3e). 3e (78%), colorless crystalline solid; recrystallized from dichloromethane–petroleum ether (mp 174–176°C). IR (KBr) ν_{max}: 764, 825, 1074, 1222, 1378, 1506, 1587, 2928, 3049 cm^{-1}. ^1H NMR: δ 2.02 (s, 3H), 4.12 (d, J=9.1 Hz, 1H), 4.61 (d, J=5.0 Hz, 1H), 4.81 (dd, J=5.0, 9.1 Hz, 1H), 7.11–8.08 (m, 12H). ^{13}C NMR: δ 28.92, 44.50, 53.39, 81.44, 92.09, 112.30, 112.65, 119.65, 120.35, 122.54, 123.02, 124.48, 124.77, 126.52, 126.62, 127.03 (2C), 128.20, 128.34, 129.72, 130.20, 131.02, 131.57, 148.35, 148.95. Anal. Calcd for $C_{25}H_{18}O_2S_3$: C, 67.23; H, 4.06. Found: C, 67.38; H, 3.99. Crystal data for **3e**: $C_{25}H_{18}O_2S_3$, FW 446.57, 0.33×0.24×0.20 mm, triclinic, space group $P1$, unit cell dimensions: a=8.7088(2) Å, α=102.275°; b=10.3190(2) Å, β=90.490°; c=11.7724(2) Å, γ=101.434°. R indices (all data) $R1$=0.0502, $wR2$=0.0991. volume, Z=1011.82(3) $Å^3$, 2. D_{calc}=1.466 mg m^{-3}, $F(000)$=464. Absorption coefficient 0.387 mm^{-1}; reflections collected 15715 (Sheldrick, G. M., Siemens, Analytical X-ray Division, Madison, WI, 1995).

2.1.6. 4-(1-Methylethyl)-2-[(4-methyl-2-furyl)thio]phenol (5a). 5a (74%), colorless viscous liquid. IR (neat) ν_{max}: 783, 1195, 1220, 1320, 1476, 1588, 2923, 2968, 3474 cm^{-1}. ^1H NMR: δ 1.18 (d, J=6.8 Hz, 6H), 2.24 (s, 3H), 2.77–2.82 (m, 1H), 5.90 (d, J=2.8 Hz, 1H), 6.45 (d, J=2.8 Hz, 1H), 6.49 (s, 1H), 6.85–7.31 (m, 3H). ^{13}C NMR: δ 13.87, 24.04, 33.12, 107.84, 115.38, 118.03 (2C), 129.25, 132.35, 141.18, 141.34, 154.20, 155.67. HRMS calcd for $C_{14}H_{16}O_2S$ 248.0871, found 248.0875.

2.1.7. 4-(1,1-Dimethylethyl)-2-[(4-methyl-2-furyl)thio]-phenol (5b). 5b (86%), colorless viscous liquid. IR (neat) ν_{max}: 789, 827, 1014, 1189, 1258, 1482, 2968, 3474 cm^{-1}. ^1H NMR: δ 1.27 (s, 9H), 2.25 (s, 3H), 5.91 (d, J=2.8 Hz, 1H), 6.46 (d, J=2.8 Hz, 1H), 6.48 (s, 1H), 6.86 (d, J=8.5 Hz, 1H), 7.23 (d, J=2.2 Hz, 1H), 7.47 (d, J=2.2 Hz, 1H). ^{13}C NMR: δ 13.98, 31.48, 34.17, 107.93, 115.16, 117.94, 118.09, 128.48, 131.49, 141.47, 143.67, 153.99, 155.77. HRMS calcd for $C_{15}H_{18}O_2S$ 262.1027, found 262.1023.

2.1.8. 4-Methyl-2-[(4-methyl-2-furyl)thio]phenol (5c). 5c (92%), colorless viscous liquid. IR (neat) ν_{max}: 783, 1026, 1158, 1245, 1326, 1445, 1482, 1563, 1613, 2956, 3461 cm^{-1}. ^1H NMR: δ 2.24 (s, 3H), 2.27 (s, 3H), 5.89 (d, J=2.9 Hz, 1H), 6.42 (d, J=2.9 Hz, 1H), 6.57 (s, 1H), 6.63 (d, J=7.6 Hz, 1H), 6.76 (s, 1H), 7.34 (d, J=7.6 Hz, 1H). ^{13}C NMR: δ 13.98, 21.43, 107.90, 115.34, 116.21, 117.79, 121.89, 134.84, 141.78, 142.01, 155.68, 156.22. HRMS calcd for $C_{12}H_{12}O_2S$ 220.0558, found 220.0560.

2.1.9. 4-Bis(1,1-dimethylethyl)-2-[(4-methyl-2-furyl)-thio]phenol (5d). 5d (85%), colorless viscous liquid. IR (neat) ν_{max}: 789, 1014, 1270, 1407, 1557, 2968, 3455 cm^{-1}. ^1H NMR: δ 1.28 (s, 9H), 1.56 (s, 9H), 2.26 (s, 3H), 5.89 (d, J=2.8 Hz, 1H), 6.31 (d, J=2.8 Hz, 1H), 6.91–6.99 (m, 3H). ^{13}C NMR: δ 13.96, 31.55, 31.77, 36.30, 37.48, 107.75, 111.05, 113.84, 116.02, 116.07, 142.38, 152.56, 154.00, 154.82, 158.21. HRMS calcd for $C_{19}H_{26}O_2S$ 275.1469, found 275.1474.

2.1.10. 1-[(4-Methyl-2-furyl)thio]-2-naphthol (5e). 5e (86%), colorless viscous liquid. IR (neat) ν_{max}: 821, 1014, 1120, 1195, 1258, 1395, 1507, 2937, 2974, 3417 cm^{-1}. ^1H NMR: δ 2.21 (s, 3H), 5.85 (d, J=2.8 Hz, 1H), 6.47 (d, J=2.8 Hz, 1H), 7.22–8.54 (m, 7H). ^{13}C NMR: δ 14.00, 107.82, 110.38, 117.11, 117.65, 123.60, 124.67, 127.56, 128.49, 129.42, 132.22, 134.95, 141.20, 155.39, 156.13. HRMS calcd for $C_{15}H_{12}O_2S$ 256.0558, found 256.0565.

2.1.11. 1a,4a-Dihydro-1a,2,3,4a-tetraphenyl-7-(1-methylethyl)-4*H*-cyclopenta[*b*]1,4-benzoxathiin-4-one (7a). 7a (100%), yellow crystalline solid; recrystallized from dichloromethane–methanol (mp 199–201°C). IR (KBr) ν_{max}: 803, 1142, 1243, 1337, 1449, 1613, 1721, 2969, 3070 cm^{-1}. ^1H NMR: δ 1.13 (d, J=6.5 Hz, 6H), 2.76–2.79 (m, 1H), 6.13 (d, J=8.2 Hz, 1H), 6.57 (s, 1H), 6.73 (d, J=7.9 Hz, 1H), 6.93–7.45 (m, 20H). ^{13}C NMR: δ 23.80, 24.20, 33.50, 70.50, 95.72, 120.31, 124.04, 124.45, 124.90, 126.91, 127.24, 127.35, 127.73, 128.01, 128.40, 128.64, 129.15, 129.52, 129.93, 130.62, 132.22, 136.16, 138.71, 144.76, 150.53, 161.29, 197.39. Anal. Calcd for $C_{38}H_{30}O_2S$: C, 82.87; H, 5.49. Found: C, 82.81; H, 5.42. Crystal data for **7a**: $C_{38}H_{30}O_2S$, FW 550.68, 0.33×0.28×0.22 mm, monoclinic, space group $P2_1/n$, unit cell dimensions: a=10.5208(2) Å, α=90°; b=16.3602(3) Å, β=95.763°; c=17.3232(3) Å, γ=90°. R indices (all data) $R1$=0.0777, $wR2$=0.1520. volume, Z=2966.64.7(9) $Å^3$, 4; D_{calc}=1.233 mg m^{-3}. $F(000)$=1160. Absorption coefficient 0.142 mm^{-1}; reflections collected 64030 (Sheldrick, G. M., Siemens, Analytical X-ray Division, Madison, WI, 1995).

2.1.12. 1a,4a-Dihydro-1a,2,3,4a-tetraphenyl-7-(1,1-dimethylethyl)-4*H*-cyclopenta[*b*]1,4-benzoxathiin-4-one (7b). 7b (99%), yellow crystalline solid; recrystallized from dichloromethane–methanol (mp 215–217°C). IR (KBr) ν_{max}: 798, 1034, 1108, 1270, 1499, 1715, 2969 cm^{-1}. ^1H NMR: δ 1.14 (s, 9H), 6.02 (d, J=8.4 Hz, 1H), 6.61–7.36 (m, 22H). ^{13}C NMR: δ 31.53, 34.55, 70.51, 95.56, 120.13, 123.23, 123.83, 124.05, 127.04, 127.31, 127.43, 127.81, 128.50, 129.59, 130.11, 130.77, 132.45, 136.31, 138.95, 142.32, 147.05, 150.44, 161.06, 196.78. Anal. Calcd for $C_{39}H_{32}O_2S$: C, 82.95; H, 5.72. Found: C, 82.84; H, 5.69.

2.1.13. 1a,4a-Dihydro-1a,2,3,4a-tetraphenyl-7-methyl-4*H*-cyclopenta[*b*]1,4-benzoxathiin-4-one (7c). 7c (90%), crystalline yellow solid; recrystallized from dichloromethane–methanol (mp 188–190°C). IR (KBr) ν_{max}: 693, 749, 1054, 1141, 1340, 1440, 1489, 1695, 2952, 3052 cm^{-1}. ^1H NMR: δ 1.95 (s, 3H), 6.68–7.45 (m, 23H). ^{13}C NMR: δ 20.66, 68.20, 95.08, 118.01, 121.44, 124.63, 124.88, 125.75, 126.43, 126.85, 127.10, 127.23, 127.53, 127.60, 127.94, 128.28, 128.84, 129.09, 129.70, 129.87, 130.48, 136.80, 142.35, 152.45, 196.89. Anal. Calcd for $C_{36}H_{26}O_2S$: C, 82.73; H, 5.02. Found: C, 82.93; H, 5.09.

2.1.14. 1a,4a-Dihydro-1a,2,3,4a-tetraphenyl-6,8-bis(1,1-dimethylethyl)-4*H*-cyclopenta[*b*]1,4-benzoxathiin-4-one (7d). 7d (95%), yellow crystalline solid; recrystallized from dichloromethane–methanol (mp 223–225°C). IR (KBr) ν_{max}: 687, 761, 1203, 1340, 1402, 1440, 1489, 1701, 2959, 3058 cm^{-1}. ^1H NMR: δ 1.00 (s, 9H), 1.50 (s, 9H), 6.14 (s, 1H), 6.70–7.51 (m, 21H). ^{13}C NMR: δ 30.33, 31.00, 34.40, 36.53, 72.08, 95.07, 116.34, 118.88, 121.02, 126.85, 127.17, 127.28, 127.41, 127.70, 127.87, 128.23, 128.41, 129.14, 129.87, 130.63, 132.52, 136.26, 138.83, 142.90, 147.88, 149.19, 153.75, 198.27. Anal. Calcd for $C_{43}H_{40}O_2S$: C, 83.18; H, 6.49. Found: C, 83.35; H, 6.72.

2.1.15. 8a,11a-Dihydro-8a,10,11,11a-tetraphenyl-9*H*-cyclopenta[*e*]naphth[2,3-*b*]-1,4-oxathiin-9-one (7e). 7e (100%), yellow crystalline solid; recrystallized from dichloromethane–methanol (mp 225–227°C). IR (KBr) ν_{max}: 717, 1155, 1236, 1337, 1452, 1499, 1593, 1715, 3056 cm^{-1}. ^1H NMR: δ 6.37 (d, J=8.8 Hz, 1H), 6.67 (d, J=7.5 Hz, 2H), 6.90–7.49 (m, 21H), 7.63 (d, J=7.9 Hz, 1H), 8.05 (d, J=8.2 Hz, 1H). ^{13}C NMR: δ 70.00, 96.05, 120.19, 122.90, 125.08, 126.17, 126.58, 126.79, 127.18, 127.32, 127.69, 128.02, 128.27, 128.48, 129.07, 129.61, 129.80, 129.90, 130.15, 130.35, 130.51, 131.83, 136.10, 138.64, 142.00, 150.46, 160.63, 196.15. HRMS calcd for $C_{39}H_{26}O_2S$ 558.1638, found 558.1653.

2.1.16. 1a,4,5,5a-Tetrahydro-8-isopropyldibenz-1,4-oxathiin (9a). 9a (71%), colorless viscous liquid. IR (neat) ν_{max}: 831, 946, 993, 1243, 1499, 2975, 3050 cm^{-1}. ^1H NMR: δ 1.18 (d, J=6.9 Hz, 6H), 1.98–2.29 (m, 4H), 2.74–2.83 (m, 1H), 3.33–3.37 (m, 1H), 4.39 (brs, 1H), 5.92–5.98 (m, 2H), 6.73–6.85 (m, 3H). ^{13}C NMR: δ 24.01, 25.61, 26.40, 33.33, 38.35, 69.08, 117.72, 118.21, 123.10, 123.91, 125.59, 132.60, 142.31, 149.14. HRMS calcd for $C_{15}H_{18}OS$ 246.1078, found 246.1076.

2.1.17. 1a,4,5,5a-Tetrahydro-8-(1,1-dimethylethyl)dibenz-1,4-oxathiin (9b). 9b (84%), colorless viscous liquid. IR (neat) ν_{max}: 784, 885, 987, 1081, 1249, 1492, 2969 cm^{-1}. ^1H NMR: δ 1.19 (s, 9H), 1.88–2.23 (m, 4H), 3.26–3.30 (m, 1H), 4.33 (brs, 1H), 5.86–5.94 (m, 2H), 6.68–6.93 (m, 3H). ^{13}C NMR: δ 25.87, 26.63, 31.61, 34.35, 38.59, 69.30, 117.44, 118.15, 122.41, 123.20, 125.92, 132.75, 144.80, 149.06. HRMS calcd for $C_{16}H_{20}OS$ 260.1234, found 260.1231.

2.1.18. 1a,4,5,5a-Tetrahydro-8-methyl-dibenz-1,4-oxathiin (9c). 9c (92%), colorless viscous liquid. IR (neat) ν_{max}: 789, 854, 1084, 1160, 1249, 1290, 1455, 1478, 1561, 2927 cm^{-1}. ^1H NMR: δ 1.93–2.36 (m, 7H), 3.33–3.37 (m, 1H), 4.39–4.43 (m, 1H), 5.92–5.98 (m, 2H), 6.65–6.91 (m, 3H). ^{13}C NMR: δ 25.53, 26.31, 26.56, 38.34, 68.64, 115.67, 118.97, 122.83, 125.61, 126.18, 132.49, 134.88, 150.89. HRMS calcd for $C_{13}H_{14}OS$ 218.0765, found 218.0766.

2.1.19. 1a,4,5,5a-Tetrahydro-7,9-bis(1,1-dimethylethyl)-dibenz-1,4-oxathiin (9d). 9d (51%), colorless crystalline solid; recrystallized from dichloromethane–petroleum

ether (mp 65–67°C). IR (KBr) ν_{max}: 805, 867, 1054, 1290, 1396, 1552, 2952, 3033 cm^{-1}. ^1H NMR: δ 1.27 (s, 9H), 1.48 (s, 9H), 1.91–2.30 (m, 4H), 3.37–3.42 (m, 1H), 4.38 (brs, 1H), 5.90–6.00 (m, 2H), 6.81 (s, 1H), 7.04 (s, 1H). ^{13}C NMR: δ 25.07, 26.29, 29.91, 31.16, 34.43, 36.64, 39.94, 69.91, 114.21, 115.60, 117.47, 125.58, 132.34, 146.27, 147.36, 153.19. Anal. Calcd for $C_{20}H_{28}OS$: C, 75.89; H, 8.89; S, 10.13. Found: C, 75.47; H, 8.89; S, 10.05.

2.1.20. 8a,9,10,12a-Tetrahydronaphtho[2,3-*b*]benz-1,4-oxathiin (9e). 9e (79%), colorless crystalline solid; recrystallized from CH_2Cl_2–petroleum ether (mp 85–87°C). IR (KBr) ν_{max}: 764, 804, 1020, 1054, 1236, 1391, 1465, 1607, 2921, 3043 cm^{-1}. ^1H NMR: δ 1.92–2.25 (m, 4H), 3.39–3.44 (m, 1H), 4.48 (brs, 1H), 5.88–5.97 (m, 2H), 6.96–7.78 (m, 6H). ^{13}C NMR: δ 25.88, 26.52, 37.79, 69.19, 111.12, 119.92, 122.59, 124.17, 125.32, 125.92, 126.25, 128.45, 129.78, 130.95, 132.94, 148.42. HRMS calcd for $C_{16}H_{14}OS$ 254.0757, found 254.0765.

2.1.21. 6a,11a-Dihydro-4-(1-methylethyl)-7*H*-cyclohepta-[*b*]benz-1,4-oxathiin and 6a,11a-dihydro-4-(1-methylethyl)-11*H*-cyclohepta[*b*]benz-1,4-oxathiin (11a). 11a (62%, 2:1 mixture of regioisomers), colorless viscous liquid. IR (neat) ν_{max}: 690, 825, 1034, 1229, 1499, 2969, 3050 cm^{-1}. ^1H NMR: δ 1.17 (d, J=6.8 Hz, 6H), 2.58–2.98 (m, 3H), 3.44–3.48 (m), 4.14–4.17 (m) 4.75–4.79 (m), 4.86–4.89 (m), 5.67–5.97 (m, 4H), 6.74–6.83 (m, 3H). ^{13}C NMR: δ 24.07, 33.36, 33.66, 33.87, 39.91, 43.52, 74.49, 75.30, 114.96, 117.46, 118.33, 118.75, 123.68, 124.35, 124.87, 127.74, 128.52, 132.85, 142.03, 142.32, 147.67, 147.85. HRMS calcd for $C_{16}H_{18}OS$ 258.1078, found 258.1082.

2.1.22. 6a,11a-Dihydro-4-(1,1-dimethylethyl)-7*H*-cyclohepta[*b*]benz-1,4-oxathiin and 6a,11a-dihydro-4-(1,1-dimethylethyl)-11*H*-cyclohepta[*b*]benz-1,4-oxathiin (11b). 11b (84%, 1:1 mixture of regioisomers), colorless viscous liquid. IR (neat) ν_{max}: 690, 818, 1034, 1270, 1485, 2975, 3050 cm^{-1}. ^1H NMR: δ 1.19 (s, 9H), 2.54–2.94 (m, 2H), 3.40–3.45 (m), 4.10–4.14 (m), 4.70–4.74 (m), 4.82–4.86 (m), 5.65–5.95 (m, 4H), 6.64–6.94 (m, 3H). ^{13}C NMR: δ 29.87, 31.58, 31.76, 33.85, 40.13, 43.78, 74.71, 75.51, 118.22, 118.33, 122.72, 122.84, 122.99, 123.41, 123.47, 124.11, 125.05, 125.15, 127.96, 128.49, 128.68, 133.04, 144.87, 147.55. HRMS calcd for $C_{17}H_{20}OS$ 272.1234, found 272.1239.

2.1.23. 6a,11a-Dihydro-4-methyl-7*H*-cyclohepta[*b*]benz-1,4-oxathiin and 6a,11a-dihydro-4-methyl-11*H*-cyclohepta[*b*]benz-1,4-oxathiin (11c). 11c (89%, 1:1 mixture of regioisomers), colorless viscous liquid. IR (neat) ν_{max}: 799, 1029, 1159, 1253, 1477, 2965, 3033 cm^{-1}. ^1H NMR: δ 2.24 (s, 3H), 2.42–3.20 (m, 2H), 3.46–3.50 (m), 4.15–4.17 (m), 4.78–4.81 (m), 4.90–4.93 (m), 5.68–6.04 (m, 4H), 6.63–6.88 (m, 3H). ^{13}C NMR: δ 20.99, 33.60, 33.95, 39.74, 43.45, 75.49, 76.57, 119.10, 122.70, 122.96, 124.94, 125.02, 125.91, 127.24, 127.80, 128.32, 128.60, 128.68, 129.76, 132.92, 135.54, 136.00, 149.36, 149.71. HRMS calcd for $C_{14}H_{14}OS$ 230.0765, found 230.0765.

2.1.24. 6a,11a-Dihydro-3,5-bis(1,1-dimethylethyl)-7*H*-cyclohepta[*b*]benz-1,4-oxathiin and 6a,11a-dihydro-3,5-bis(1,1-dimethylethyl)-11*H*-cyclohepta[*b*]benz-1,4-oxathiin(11d). 11d (79%, 2:1 mixture of regioisomers), colorless viscous liquid. IR (neat) ν_{max}: 789, 1033, 1264, 1401, 1463, 1551, 1601, 2962, 3050 cm^{-1}. ^1H NMR: δ 1.25–1.46 (m, 18H), 2.53–2.58 (m, 1H), 3.09–3.18 (m, 1H), 3.41–3.44 (m), 4.00–4.04 (m), 4.75–4.79 (m), 4.80–4.84 (m), 5.55–6.17 (m, 4H), 6.49–6.99 (m, 2H). ^{13}C NMR: δ 29.90, 30.09, 31.22, 33.07, 33.94, 36.66, 45.80, 75.38, 75.76, 104.70, 105.93, 114.03, 116.56, 116.81, 123.59, 125.37, 125.42, 127.97, 129.23, 129.76, 131.22, 148.34, 151.12. HRMS calcd for $C_{21}H_{28}OS$ 328.1860, found 328.1867.

2.1.25. 1a,6a-Dihydronaphtho[2,3-*b*]-6*H*-cyclohepta[*e*]-1,4-oxathiin and 1a,6a-dihydro-2*H*-cyclohepta[*e*]-naphtho[2,3-*b*]-1,4-oxathiin (11e). 11e (84%, 1:1 mixture of regioisomers), colorless viscous liquid. IR (neat) ν_{max}: 811, 1047, 1222, 1270, 1391, 1465, 1512, 1607, 2969 cm^{-1}. ^1H NMR: δ 2.57–2.87 (m, 2H), 3.55–3.59 (m), 4.19–4.21 (m), 4.83–4.86 (m), 4.96–4.99 (m), 5.80–5.94 (m, 4H), 6.95–7.70 (m, 6H). ^{13}C NMR: δ 32.46, 32.88, 38.16, 42.07, 73.18, 74.21, 118.69, 118.86, 121.16, 121.41, 122.86, 123.02, 123.89, 124.39, 124.67, 124.96, 125.11, 125.16, 126.82, 127.14, 127.20, 127.52, 131.88, 145.60, 146.40. HRMS calcd for $C_{17}H_{14}OS$ 266.0765, found 266.0757.

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