Novel cycloadditions of *ortho*-thioquinones with acyclic dienes: expeditious synthesis of 1,4-benzooxathiines

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ortho-Thioquinones generated *in situ* from *N*-(*o*-hydroxyphenylsulfanyl)phthalimides easily undergo [4 + 2] cycloaddition reaction with acyclic dienes to afford novel heterocyclic compounds.

Introduction

The cycloadditions of *o*-benzoquinones have attracted the attention of a number of research groups.[1] Our own investigations in this area have uncovered novel reactivity profiles of these interesting compounds.[2–4] In contrast, there has been very little work on the cycloadditions of *ortho*-thioquinones, largely due to the nonexistence of suitable methods for the synthesis of these compounds. The situation, however, changed with the introduction of a convenient method for the synthesis of *ortho*-thioquinones and the investigation of some cycloadditions of the latter by Capozzi *et al.*[5–8] Very recently we have reported the cycloaddition reactions of *ortho*-thioquinones with heterocyclic dienes[9] and fulvenes.[10] In this context, it was of interest to examine the reactivity of *ortho*-thioquinones towards acyclic dienes. The results of our investigations indicating a remarkable reactivity difference between 2,6-dimethylocta-2,4,6-triene (alloocimene) **2**, 2-methylpenta-1,3-diene **6** and 2,4-dimethylpenta-1,3-diene **9** are presented here.

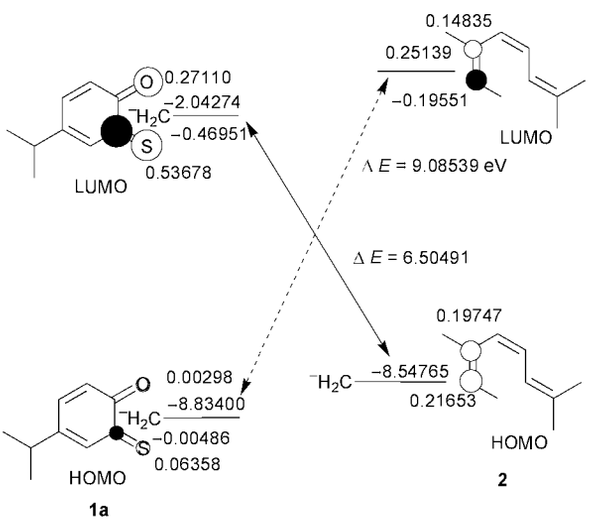
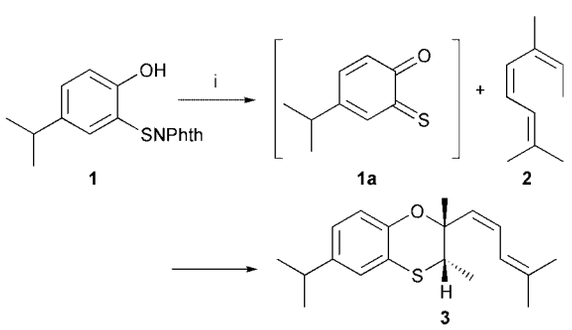


Fig. 1

Results and discussion

Initially our studies were focused on the cycloaddition reaction of 4-isopropyl-2-thio-1,2-benzoquinone **1a**, generated *in situ*, with alloocimene. *N*-(2-Hydroxy-5-isopropylphenylsulfanyl)-phthalimide **1** on treatment with alloocimene **2** in the presence of pyridine in dry chloroform in a sealed tube (70 °C) afforded the product **3** in 100% yield (Scheme 1). The ^{1}H NMR spectrum



Scheme 1 *Reagents, conditions, and yield*: i. Pyridine, $CHCl_3$, 70 °C, sealed tube, 10 h, 100%.

of **3** showed a quartet at δ 3.03 (J = 6.9 Hz) assigned to the SCH proton in the benzooxathiine ring. Evidently the addition took place at the 6,7-olefinic bond of alloocimene; the quartet at δ 3.03 is diagnostic for a product resulting from this mode of addition. The three olefinic protons appeared at δ 5.53 (d, J = 15.2 Hz), 5.71 (d, J = 10.7 Hz) and 6.36 (dd, J = 11.0, 15.2 Hz). The ^{13}C signals for SC and OC carbons in the benzooxathiine ring appeared at δ_C 40.48 and 75.48, respectively.

In order to explain the observed mode of cycloadditions and periselectivity in the above reaction, we have carried out AM1 calculations using the PC SPARTAN Graphical Interface Package for Molecular Mechanics and Molecular Orbital Models.[11] The correlation diagram for the reaction of 4-isopropyl-2-thio-1,2-benzoquinone **1a** with alloocimene **2** is illustrated in Fig. 1. From the correlation diagram in Fig. 1, it is evident that the reaction of 4-isopropyl-2-thio-1,2-benzoquinone **1a** with alloocimene **2** follows an inverse-electron-demand pathway, *i.e.*, it is controlled by the LUMO of diene **1a**. The sign and size of the orbital coefficients at the reacting centers show that the HOMO(**1a**)–LUMO(**2**) interaction is unimportant since it is not symmetry allowed.

The reaction took a similar course with other substituted 2-thio-1,2-benzoquinones and the results are summarized in Scheme 2.

The reaction of 4-isopropyl-2-thio-1,2-benzoquinone **1a** with 2-methylpenta-1,3-diene **6** gave rise to the benzoxathiine derivative **7** in 56% yield (Scheme 3). The ^{1}H NMR spectrum of **7** showed the two protons adjacent to sulfur appearing as a

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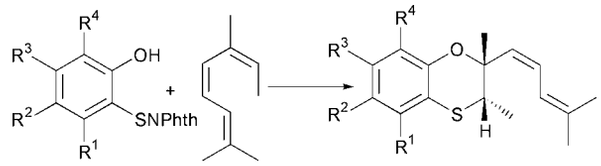
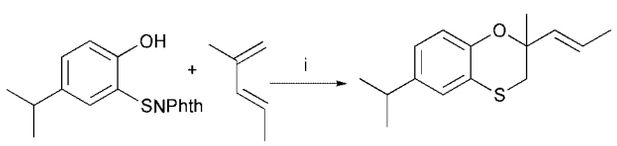


4(a-d) 2 5(a-d)

Thioquinone precursor	Substituents	Products	Yields (%)
4a	$R^1=R^3=R^4=H$, $R^2=CMe_3$	**5a**	93
4b	$R^1=R^3=R^4=H$, $R^2=OMe$	**5b**	94
4c	$R^1=R^3=R^4=H$, $R^2=Me$	**5c**	94
4d	$R^2=R^4=H$, $R^1=R^3=CMe_3$	**5d**	100

Scheme 2 *Reagents and conditions*: pyridine, $CHCl_3$, sealed tube, 70 °C, 10 h.

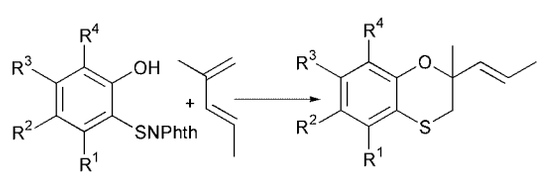


1 6 7

Scheme 3 *Reagents, conditions, and yield*: pyridine, $CHCl_3$, 70 °C, sealed tube, 15 h, 56%.

singlet at δ 2.83. In the ^{13}C NMR spectrum, the carbons attached to oxygen and sulfur appeared at δ_C 73.32 and 34.77, respectively.

The reaction was found to be applicable to other 2-thio-1,2-benzoquinones also, and the results are summarized in Scheme 4.

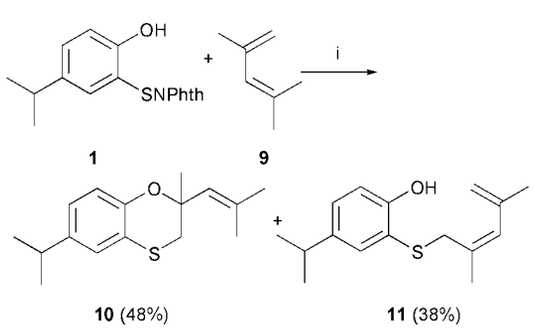


4(a-d) 6 8(a-d)

Thioquinone precursor	Substituents	Products	Yields (%)
4a	$R^1=R^3=R^4=H$, $R^2=CMe_3$	**8a**	77
4b	$R^1=R^3=R^4=H$, $R^2=OMe$	**8b**	68
4c	$R^1=R^3=R^4=H$, $R^2=Me$	**8c**	40
4d	$R^2=R^4=H$, $R^1=R^3=CMe_3$	**8d**	54

Scheme 4 *Reagents and conditions*: pyridine, $CHCl_3$, sealed tube, 70 °C, 15 h.

The reaction of 4-isopropyl-2-thio-1,2-benzoquinone **1a** with 2,4-dimethylpenta-1,3-diene **9** afforded products **10** and **11** in 86% combined yield (Scheme 5). In the ^1H NMR spectrum of **10**, the methylene protons adjacent to sulfur resonated as a

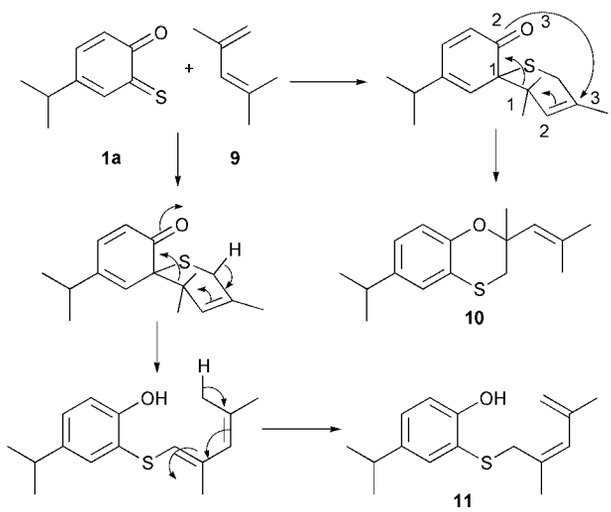


1 9 **10** (48%) **11** (38%)

Scheme 5 *Reagents and conditions*: pyridine, $CHCl_3$, 70 °C, sealed tube, 12 h.

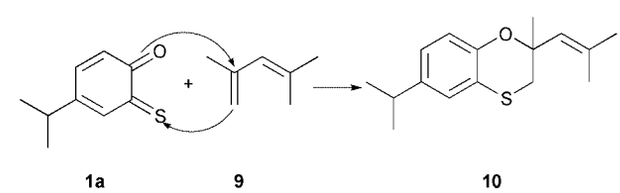
multiplet centered at δ 2.77. The olefinic proton resonated as a singlet at δ 5.28. In the ^{13}C NMR spectrum, the methylene carbon was visible at δ_C 35.81 and the quaternary carbon adjacent to oxygen appeared at δ_C 73.29. The IR spectrum of **11** showed characteristic hydroxylic absorption at 3411 cm^{-1}. In the ^1H NMR spectrum, the methylene protons adjacent to sulfur resonated as a singlet at δ 3.24. The olefinic protons resonated as singlets at δ 4.67, 4.90 and 5.28. The OH proton was visible at δ 6.48 (exchangeable by D_2O). In the ^{13}C NMR spectrum, the methylene carbon near to sulfur appeared at δ_C 47.34.

The probable pathways leading to the formation of the products, illustrated for the reaction of **1a** and **9**, are outlined in Scheme 6.[6]



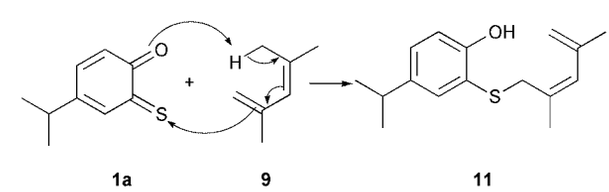
Scheme 6

It may be noted that a hetero-Diels–Alder reaction involving the *ortho*-thioquinone as the 4π component can also account for the formation of **10** (Scheme 7).



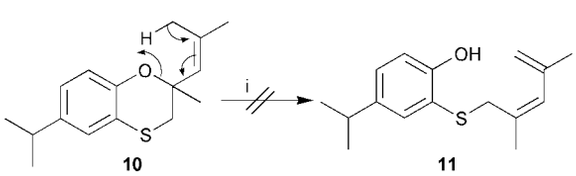
Scheme 7

Similarly, an ene-type reaction (Scheme 8) can account for the formation of **11**.[12]

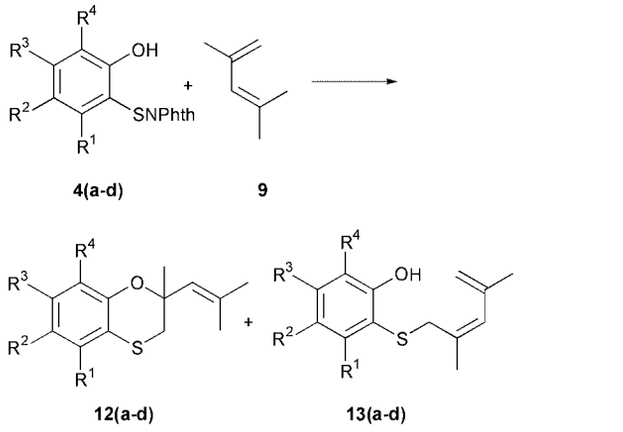


Scheme 8

Although less probable, a pathway invoking stepwise reaction leading to the observed product **11** also cannot be ruled out. In order to confirm this possibility, the product **10** was heated at 70 °C in $CHCl_3$ for 12 hours; however, it did not lead to the product **11** (Scheme 9).



Scheme 9 *Conditions*: $CHCl_3$, sealed tube, 70 °C, 12 h.



Thioquinone precursor	Substituents	Products	Yields (%)
4a	R^1=R^3=R^4=H, R^2=CMe_3	**12a, 13a**	45, 36
4b	R^1=R^3=R^4=H, R^2=OMe	**12b, 13b**	56, 32
4c	R^1=R^3=R^4=H, R^2=Me	**12c, 13c**	57, 30
4d	R^2=R^4=H, R^1=R^3=CMe_3	**12d, 13d**	42, 39

Scheme 10 *Conditions*: pyridine, $CHCl_3$, sealed tube, 70 °C, 12 h.

Similar results were obtained with various substituted *o*-thiobenzoquinones and these are presented in Scheme 10.

Conclusions

In conclusion, our investigations have revealed that the reactions of *ortho*-thioquinones with 2,4-dimethylpenta-1,3-diene, 2-methylpenta-1,3-diene and allocimene proceed *via* different pathways. It is noteworthy that the potent biological activities associated with 1,4-oxathiines have drawn attention to the synthesis of compounds incorporating this heterocyclic systems.[13–16]

Experimental

All reactions were carried out in oven-dried glassware under an atmosphere of argon. The melting point of compound **5d** was recorded on a Buchi-530 melting point apparatus and was uncorrected. IR spectra were recorded on a Perkin-Elmer model 882 infrared spectrophotometer and a Nicolet Impact 400D infrared spectrophotometer, using potassium bromide pellets. NMR spectra were recorded on a Bruker-300 spectrometer using chloroform-d as solvent. High-resolution mass spectra were obtained using a Finnigan MAT model 8430. Elemental analysis was done using a Perkin-Elmer 2400 CHN analyzer. Solvents used for experiments were dried and distilled according to the literature procedure. Petroluem ether refers to the fraction of distillation range 60–80 °C.

2,3-*trans*-Dimethyl-2-(4-methylpenta-1,3-dienyl)-2,3-dihydro-6-(1-methylethyl)-1,4-benzooxathiine 3

N-(2-Hydroxy-5-isopropylphenylsulfanyl)phthalimide **1** (156 mg, 0.5 mmol), alloocimene **2** (136 mg, 1 mmol), pyridine (0.08 mL, 1 mmol) and dry chloroform (2 mL) were placed in a glass tube, which was sealed under argon atmosphere. The tube was then heated at 70 °C for 10 h. The solvent was removed *in vacuo* and the product subjected to silica gel (100–200 mesh) column chromatography using petroleum ether as eluent to afford compound **3** (151 mg, 100%) as a colorless, viscous liquid; IR (neat) ν_{max} 804, 1034, 1094, 1270, 1482, 2962, 3042 cm^{-1}; ^1H NMR: δ 1.11 (d, *J* 6.8 Hz, 6H), 1.20 (d, *J* 6.8 Hz, 3H), 1.34 (s, 3H), 1.63 (s, 3H), 1.68 (s, 3H), 2.67–2.72 (m, 1H), 3.03 (q, *J* 6.9 Hz, 1H), 5.53 (d, *J* 15.2 Hz, 1H), 5.71 (d, *J* 10.7 Hz, 1H), 6.36 (dd, *J* 11.0, 15.2 Hz, 1H), 6.70–6.75 (m, 3H); ^{13}C NMR δ 15.73, 17.30, 20.03, 23.04, 24.99, 32.22, 40.48, 75.48, 116.01, 117.48, 122.58, 123.29, 123.63, 125.39, 131.65, 135.07, 140.17, 147.01 (HRMS Calc. for $C_{19}H_{26}OS$: *M*, 302.1696. Found: M^+, 302.1704).

2,3-*trans*-Dimethyl-2-(4-methylpenta-1,3-dienyl)-2,3-dihydro-6-(1,1-dimethylethyl)-1,4-benzoxathiine 5a

Obtained in 93% yield as a colorless, viscous liquid; IR (neat) ν_{max} 791, 1023, 1108, 1263, 1384, 1492, 2969 cm^{-1}; ^1H NMR δ 1.19–1.23 (m, 12H), 1.34 (s, 3H), 1.64 (s, 3H), 1.69 (s, 3H), 3.03 (q, *J* 6.9 Hz, 1H), 5.53 (d, *J* 15.2 Hz, 1H), 5.72 (d, *J* 10.6 Hz, 1H), 6.36 (dd, *J* 10.9, 15.2 Hz, 1H), 6.71 (d, *J* 8.3 Hz, 1H), 6.89–6.94 (m, 2H); ^{13}C NMR δ 15.73, 17.30, 20.01, 25.00, 30.39, 33.02, 40.54, 75.46, 115.55, 117.19, 121.71, 122.31, 123.44, 125.42, 131.66, 135.11, 142.48, 146.75 (HRMS Calc. for $C_{20}H_{28}OS$: *M*, 316.1846. Found: M^+, 316.1860).

2,3-*trans*-Dimethyl-2-(4-methylpenta-1,3-dienyl)-2,3-dihydro-6-methoxy-1,4-benzoxathiine 5b

Obtained in 94% yield as a colorless, viscous liquid; IR (neat) ν_{max} 802, 1034, 1220, 1258, 1376, 1451, 1495, 2962 cm^{-1}; ^1H NMR δ 1.27 (d, *J* 6.9 Hz, 3H), 1.39 (s, 3H), 1.71 (s, 3H), 1.75 (s, 3H), 3.09 (q, *J* 6.9 Hz, 1H), 3.71 (s, 3H), 5.58 (d, *J* 15.2 Hz, 1H), 5.77 (d, *J* 10.9 Hz, 1H), 6.41 (dd, *J* 10.9, 15.2 Hz, 1H), 6.51–6.57 (m, 2H), 6.77 (d, *J* 8.7 Hz, 1H); ^{13}C NMR δ 15.78, 17.32, 20.28, 24.98, 40.32, 54.42, 75.44, 109.62, 111.18, 117.17, 118.36, 123.47, 125.37, 131.58, 135.03, 142.98, 152.59 (HRMS Calc. for $C_{17}H_{22}O_2S$: *M*, 290.1331. Found: M^+, 290.1340).

2,3-*trans*-2,3,6-Trimethyl-2-(4-methylpenta-1,3-dienyl)-2,3-dihydro-1,4-benzooxathiine 5c

Obtained in 94% yield as a colorless, viscous liquid; IR (neat) ν_{max} 789, 1020, 1264, 1295, 1382, 1489, 1557, 2924, 2980 cm^{-1}; ^1H NMR δ 1.26 (d, *J* 6.9 Hz, 3H), 1.40 (s, 3H), 1.72 (s, 3H), 1.76 (s, 3H), 2.24 (s, 3H), 3.08 (q, *J* 6.9 Hz, 1H), 5.60 (d, *J* 15.2 Hz, 1H), 5.79 (d, *J* 10.6 Hz, 1H), 6.43 (dd, *J* 10.6, 15.2 Hz, 1H), 6.61–6.87 (m, 3H); ^{13}C NMR δ 16.67, 18.32, 20.88, 21.06, 25.98, 41.27, 76.82, 115.32, 118.21, 120.90, 123.52, 125.36, 125.50, 131.71, 134.16, 134.95, 148.85 (HRMS Calc. for $C_{17}H_{22}OS$: *M*, 274.1388. Found: M^+, 274.1391).

2,3-*trans*-Dimethyl-2-(4-methylpenta-1,3-dienyl)-2,3-dihydro-5,7-bis(1,1-dimethylethyl)-1,4-benzooxathiine 5d

Obtained in 100% yield as a colorless, crystalline solid, mp 110–112 °C; IR (KBr) ν_{max} 805, 998, 1035, 1110, 1272, 1309, 1402, 1545, 2971 cm^{-1}; ^1H NMR δ 1.28 (2s, 12H), 1.44–1.48 (m, 12H), 1.76 (s, 3H), 1.78 (s, 3H), 3.05 (q, *J* 6.8 Hz, 1H), 5.61 (d, *J* 15.2 Hz, 1H), 5.81 (d, *J* 10.4 Hz, 1H), 6.51 (dd, *J* 11.0, 15.1 Hz, 1H), 6.80 (s, 1H), 6.99 (s, 1H); ^{13}C NMR δ 16.24, 18.45, 19.78, 26.11, 29.75, 30.07, 31.38, 36.76, 42.75, 77.62, 114.66, 115.47, 116.45, 124.65, 126.65, 133.15, 136.14, 146.22, 147.73, 151.25 (Calc. for $C_{24}H_{36}OS$: C, 77.36; H, 9.74. Found: C, 77.41; H, 9.68%).

2-Methyl-2-(prop-1-enyl)-2,3-dihydro-6-(1-methylethyl)-1,4-benzooxathiine 7

Obtained in 56% yield as a colorless, viscous liquid; IR (neat) ν_{max} 864, 952, 1070, 1270, 1457, 1489, 2968 cm^{-1}; ^1H NMR δ 1.18 (d, *J* 6.8 Hz, 6H), 1.47 (s, 3H), 1.68 (d, *J* 6.2 Hz, 3H), 2.75–2.79 (m, 1H), 2.80–2.83 (m, 2H), 5.55 (d, *J* 15.5 Hz, 1H), 5.67–5.78 (m, 1H), 6.73–6.85 (m, 3H); ^{13}C NMR δ 17.90, 24.16, 26.35, 33.33, 34.77, 73.32, 118.75, 123.97, 124.79, 125.62, 133.72 (2C), 141.16, 148.63.

2-Methyl-2-(prop-1-enyl)-2,3-dihydro-6-(1,1-dimethylethyl)-1,4-benzooxathiine 8a

Obtained in 77% yield as a colorless, viscous liquid; IR (neat) ν_{max} 821, 864, 952, 1270, 1370, 1389, 1489, 2862, 2962 cm^{-1};

^{1}H NMR δ 1.26 (s, 9H), 1.47 (s, 3H), 1.68 (d, J 5.9 Hz, 3H), 2.83–2.89 (m, 2H), 5.55 (d, J 15.4 Hz, 1H), 5.67–5.76 (m, 1H), 6.74–6.77 (m, 1H), 6.98–7.01 (m, 2H); ^{13}C NMR δ 17.87, 26.31, 31.47, 34.10, 34.79, 73.34, 118.42, 123.04, 123.81, 125.59, 133.71 (2C), 143.44, 148.34 (HRMS Calc. for $C_{16}H_{22}OS$: M, 2624.1391. Found: M^+, 262.1394).

2-Methyl-2-(prop-1-enyl)-2,3-dihydro-6-methoxy-1,4-benzooxathiine 8b

Obtained in 68% yield as a colorless, viscous liquid; IR (neat) ν_{max} 805, 830, 960, 1048, 1216, 1259, 1489, 2934, 2977 cm^{-1}; ^{1}H NMR δ 1.43 (s, 3H), 1.64 (d, J 5.8 Hz, 3H), 2.81–2.83 (m, 2H), 3.69 (s, 3H), 5.51 (d, J 15.6 Hz, 1H), 5.63–5.72 (m, 1H), 6.51–6.54 (m, 2H), 6.70–6.73 (m, 1H); ^{13}C NMR δ 17.88, 26.34, 34.70, 55.54, 73.07, 111.01, 112.52, 117.01, 119.60, 125.71, 133.51, 144.58, 153.53.

2,6-Dimethyl-2-(prop-1-enyl)-2,3-dihydro-1,4-benzooxathiine 8c

Obtained in 40% yield as a colorless, viscous liquid; IR (neat) ν_{max} 805, 1066, 1159, 1297, 1458, 1483, 2859, 2921 cm^{-1}; ^{1}H NMR δ 1.45 (s, 3H), 1.65 (d, J 6.2 Hz, 3H), 2.22 (s, 3H), 2.81–2.85 (m, 2H), 5.52 (d, J 15.4 Hz, 1H), 5.64–5.75 (m, 1H), 6.59–6.69 (m, 2H), 6.86–6.88 (m, 1H); ^{13}C NMR δ 17.87, 26.41, 29.95, 34.69, 73.49, 112.91, 119.19, 121.89, 125.62, 126.98, 133.65, 135.60, 150.43 (HRMS Calc. for $C_{13}H_{16}OS$: M, 220.0921. Found: M^+, 220.0914).

2-Methyl-2-(prop-1-enyl)-2,3-dihydro-5,7-bis(1,1-dimethylethyl)-1,4-benzooxathiine 8d

Obtained in 54% yield as a colorless, viscous liquid; IR (neat) ν_{max} 796, 1045, 1270, 1301, 1408, 1551, 2962 cm^{-1}; ^{1}H NMR δ 1.25 (s, 9H), 1.45 (s, 9H), 1.48 (s, 3H), 1.68 (d, J 6.0 Hz, 3H), 2.74–2.76 (m, 2H), 5.58 (d, J 15.4 Hz, 1H), 5.69–5.78 (m, 1H), 6.76 (s, 1H), 6.98 (s, 1H); ^{13}C NMR δ 17.77, 26.02, 30.053, 31.27, 34.48, 36.41, 36.66, 75.01, 114.44, 116.36, 125.10, 134.41 (2C), 146.77, 148.04, 152.03 (HRMS Calc. for $C_{20}H_{30}OS$: M, 318.2017. Found: M^+, 318.2006).

2-Methyl-2-(2-methylprop-1-enyl)-2,3-dihydro-6-(1-methylethyl)-1,4-benzooxathiine 10

Obtained in 48% yield as a colorless, viscous liquid; IR (neat) ν_{max} 804, 1064, 1226, 1264, 1451, 1489, 2930, 2968 cm^{-1}; ^{1}H NMR δ 1.18 (d, J 6.6 Hz, 6H), 1.55 (s, 3H), 1.67 (s, 3H), 1.80 (s, 3H), 2.74–2.90 (m, 3H), 5.28 (s, 1H), 6.69–6.85 (m, 3H); ^{13}C NMR δ 18.87, 24.23, 27.20, 27.43, 33.41, 35.81, 73.29, 116.09, 118.72, 123.77, 124.69, 126.90, 136.96, 141.24, 148.59 (HRMS Calc. for $C_{16}H_{22}OS$: M, 262.1391. Found: M^+, 262.1398).

4-(1-Methylethyl)-2-(2,4-dimethylpenta-2,4-dienylsulfanyl)-phenol 11

Obtained in 38% yield as a colorless, viscous liquid; IR (neat) ν_{max} 814, 896, 1014, 1189, 1226, 1476, 2962, 3411 cm^{-1}; ^{1}H NMR δ 1.17 (d, J 6.3 Hz, 6H), 1.67 (s, 3H), 1.92 (s, 3H), 2.76–2.81 (m, 1H), 3.24 (s, 2H), 4.67 (s, 1H), 4.90 (s, 1H), 5.28 (s, 1H), 6.48 (s, 1H), 6.85 (d, J 8.2 Hz, 1H), 7.06–7.16 (m, 2H); ^{13}C NMR δ 16.92, 23.31, 24.32, 33.38, 47.34, 114.49, 115.34, 117.93, 129.32, 131.42, 131.52, 134.18, 140.88, 141.27, 155.34 (HRMS Calc. for $C_{16}H_{22}OS$: M, 262.1391. Found: M^+, 262.1390).

2-Methyl-2-(2-methylprop-1-enyl)-2,3-dihydro-6-(1,1-dimethylethyl)-1,4-benzooxathiine 12a

Obtained in 45% yield as a colorless, viscous liquid; IR (neat) ν_{max} 864, 939, 1083, 1145, 1226, 1264, 1376, 1489, 2930, 2968 cm^{-1}; ^{1}H NMR δ 1.26 (s, 9H), 1.55 (s, 3H), 1.67 (s, 3H), 1.80 (s, 3H), 2.84–2.85 (m, 2H), 5.28 (s, 1H), 6.70 (d, J 8.3 Hz, 1H), 6.96–6.99 (m, 2H); ^{13}C NMR δ 17.69, 26.04, 26.23, 30.40, 33.01, 34.64, 72.16, 114.42, 117.25, 121.70, 122.57, 125.78, 135.75, 142.36, 147.14 (HRMS Calc. for $C_{17}H_{24}OS$: M, 276.1545. Found: M^+, 276.1547).

4-(1,1-Dimethylethyl)-2-(2,4-dimethylpenta-2,4-dienylsulfanyl)-phenol 13a

Obtained in 36% yield as a colorless, viscous liquid; IR (neat) ν_{max} 821, 1020, 1176, 1258, 1364, 1476, 2962, 3424 cm^{-1}; ^{1}H NMR δ 1.25 (s, 9H), 1.67 (s, 3H), 1.93 (s, 3H), 3.25 (s, 2H), 4.66 (s, 1H), 4.89 (s, 1H), 5.29 (s, 1H), 6.48 (s, 1H), 6.85 (d, J 8.4 Hz, 1H), 7.23–7.31 (m, 2H); ^{13}C NMR δ 16.85, 23.23, 31.53, 34.10, 47.30, 114.10, 115.36, 117.51, 128.26, 131.30, 131.44, 133.10, 141.15, 143.14, 154.90 (HRMS Calc. for $C_{17}H_{24}OS$: M, 276.1545. Found: M^+, 276.1540).

2-Methyl-2-(2-methylprop-1-enyl)-2,3-dihydro-6-methoxy-1,4-benzooxathiine 12b

Obtained in 56% yield as a colorless, viscous liquid; IR (neat) ν_{max} 796, 852, 939, 1058, 1208, 1258, 1370, 1485, 2924, 2980 cm^{-1}; ^{1}H NMR δ 1.54 (s, 3H), 1.65 (s, 3H), 1.78 (s, 3H), 2.75–2.91 (m, 2H), 3.70 (s, 3H), 5.25 (s, 1H), 6.50–6.53 (m, 2H), 6.67 (d, J 9.5 Hz, 1H); ^{13}C NMR δ 18.72, 27.03, 27.35, 35.86, 55.42, 72.97, 110.82, 112.18, 117.28, 119.43, 126.55, 136.87, 144.46, 153.59 (HRMS Calc. for $C_{14}H_{18}O_2S$: M, 250.1027. Found: M^+, 250.1031).

4-Methoxy-2-(2,4-dimethylpenta-2,4-dienylsulfanyl)phenol 13b

Obtained in 32% yield as a colorless, viscous liquid; IR (neat) ν_{max} 811, 1029, 1054, 1216, 1259, 1483, 2934, 2971, 3431 cm^{-1}; ^{1}H NMR δ 1.66 (s, 3H), 1.93 (s, 3H), 3.24 (s, 2H), 3.70 (s, 3H), 4.67 (s, 1H), 4.90 (s, 1H), 5.29 (s, 1H), 6.23 (s, 1H), 6.76–6.92 (m, 3H); ^{13}C NMR δ 16.78, 23.19, 47.20, 55.77, 114.53, 115.07, 115.19, 117.51, 120.50, 131.31, 131.46, 141.20, 151.48, 152.90 [HRMS Calc. for $C_{14}H_{18}O_2S$: M, 250.1027. Found: ($M^+ - CH_2$), 236.1035 (OMe changed to OH)].

2,6-Dimethyl-2-(2-methylprop-1-enyl)-2,3-dihydro-1,4-benzooxathiine 12c

Obtained in 57% yield as a colorless, viscous liquid; IR (neat) ν_{max} 796, 1064, 1233, 1370, 1451, 1489, 1557, 2930, 2980 cm^{-1}; ^{1}H NMR δ 1.55 (s, 3H), 1.66 (s, 3H), 1.80 (s, 3H), 2.22 (s, 3H), 2.82–2.87 (m, 2H), 5.28 (s, 1H), 6.61–6.63 (m, 2H), 6.87 (d, J 9.5 Hz, 1H); ^{13}C NMR δ 17.71, 19.88, 25.97, 26.20, 34.51, 72.23, 111.99, 115.32, 118.24, 120.84, 123.33, 125.67, 134.16, 149.19 (HRMS Calc. for $C_{14}H_{18}OS$: M, 234.1072. Found: M^+, 234.1078).

4-Methyl-2-(2,4-dimethylpenta-2,4-dienylsulfanyl)phenol 13c

Obtained in 30% yield as a colorless, viscous liquid; IR (neat) ν_{max} 799, 1153, 1446, 1483, 2921, 2965, 3413 cm^{-1}; ^{1}H NMR δ 1.67 (s, 3H), 1.91 (s, 3H), 2.29 (s, 3H), 3.20 (s, 2H), 4.74 (s, 1H), 4.91 (s, 1H), 5.27 (s, 1H), 6.58–7.25 (m, 4H); ^{13}C NMR δ 16.80, 23.24, 26.94, 47.42, 114.46, 115.08, 121.42, 121.62, 131.34, 136.01, 136.39, 141.28, 141.74, 157.16 (HRMS Calc. for $C_{14}H_{18}OS$: M, 234.1072. Found: M^+, 234.1068).

2-Methyl-2-(2-methylprop-1-enyl)-2,3-dihydro-5,7-bis(1,1-dimethylethyl)-1,4-benzooxathiine 12d

Obtained in 42% yield as a colorless, viscous liquid; IR (neat) ν_{max} 789, 1070, 1258, 1307, 1389, 1457, 1557, 1601, 2868, 2968 cm^{-1}; ^{1}H NMR δ 1.24 (s, 9H), 1.45 (s, 9H), 1.54 (s, 3H), 1.66 (s, 3H), 1.78 (s, 3H), 2.80 (s, 2H), 5.29 (s, 1H), 6.69 (s, 1H), 6.96 (s, 1H); ^{13}C NMR δ 18.86, 27.02, 27.28, 29.64, 29.98, 31.26, 36.51, 36.67, 73.56, 114.55, 116.32, 127.66, 136.06 (2C), 146.26, 147.46, 151.34 (HRMS Calc. for $C_{21}H_{32}OS$: M, 332.2173. Found: M^+, 332.2161).

3,5-Bis(1,1-dimethylethyl)-2-(2,4-dimethylpenta-2,4-dienyl-sulfanyl)phenol 13d

Obtained in 39% yield as a colorless, viscous liquid; IR (neat) ν_{max} 795, 864, 1226, 1307, 1407, 1463, 1607, 2868, 2968, 3355 cm^{-1}; ^1H NMR δ 1.29 (s, 9H), 1.48 (s, 9H), 1.80 (s, 3H), 1.97 (s, 3H), 3.25 (s, 2H), 4.78 (s, 1H), 4.98 (s, 1H), 5.70 (s, 1H), 6.91 (d, *J* 1.8 Hz, 1H), 6.98 (d, *J* 1.8 Hz, 1H), 7.32 (s, 1H); ^{13}C NMR δ 14.10, 22.63, 31.16, 31.57, 34.95, 37.34, 48.14, 109.93, 114.21, 115.53, 131.23, 131.91, 132.27, 141.13, 153.23, 153.38, 158.01 (HRMS Calc. for $C_{21}H_{32}OS$: *M*, 332.2173. Found: M^+, 332.2169).

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