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[4+2] CYCLOADDITIONS OF *o*-THIOQUINONES WITH ALKYNES AND ARYLALKENES: A FACILE SYNTHESIS OF BENZOXATHIINS[#]

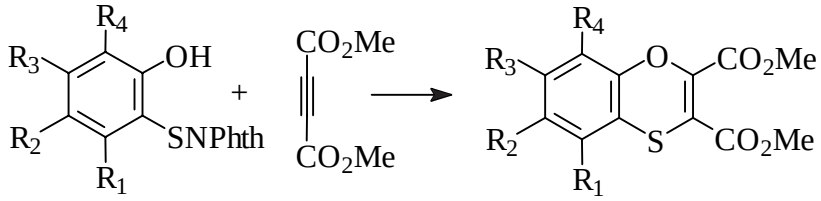
Vijay Nair* and Bini Mathew

Organic Chemistry Division, Regional Research Laboratory (CSIR), Trivandrum-695 019, India
Fax: 91-471-491712; e-mail: gvn@csrrltrd.ren.nic.in

Abstract- *o*-Thioquinones generated *in situ* from *o*-hydroxybenzothiophthalimides underwent facile [4+2] cycloaddition reaction with alkynes and alkenes to afford benzoxathiin derivatives.

The cycloaddition chemistry of *o*-quinones has been the subject of extensive investigations.[1] Our own studies in this area have revealed novel reactivity profiles in the cycloadditions of *o*-quinones with electron rich dienes and fulvenes.[2-8] With the introduction of a facile method for the generation of *o*-thioquinones by Capozzi and co-workers[9-12] and in the context of our general interest in the cycloaddition chemistry of quinones, we have embarked on a systematic investigation in this area. Preliminary results of our studies on the reactions of *o*-thioquinones with heterocyclic dienes[13] and fulvenes[14] have already been reported. The results of our subsequent studies involving alkynes and alkenes are presented in this paper.

N-(2-Hydroxy-5-isopropylphenylthio)phthalimide (**1a**) on treatment with dimethyl acetylenedicarboxylate (DMAD) and pyridine in chloroform at 70 °C afforded the 1,4-benzoxathiin monoadduct (**3a**) in 92% yield. The reaction was found to be applicable to other substituted *o*-thiobenzoquinones and the results are summarized in Scheme 1.



1(a-f) **2** **3(a-f)**

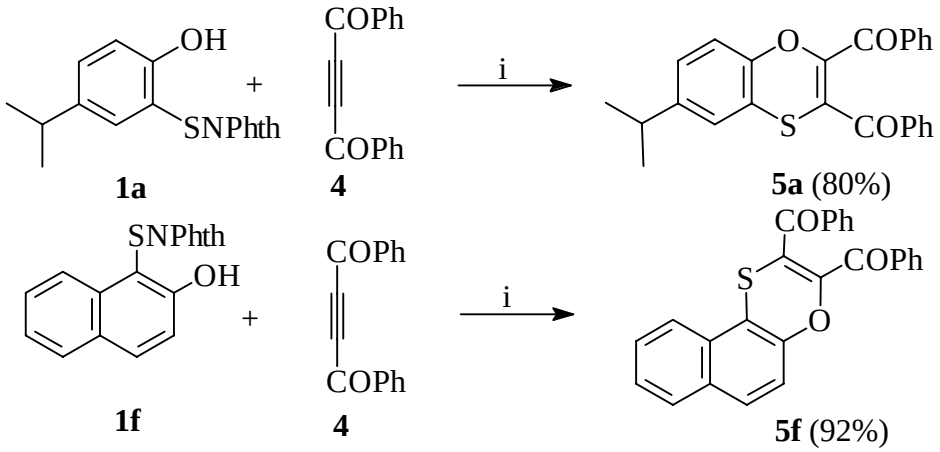
o-Hydroxythiophthalimides	Substituents	Products	Yields(%)[a]
1a	R_1=R_3=R_4=H, R_2=$CHMe_2$	**3a**	92
1b	R_1=R_3=R_4=H, R_2=CMe_3	**3b**	84
1c	R_1=R_3=R_4=H, R_2=OMe	**3c**	86
1d	R_1=R_3=R_4=H, R_2=Me	**3d**	89
1e	R_1 = R_2=R_4=H, R_3=$CHMe_2$	**3e**	73
1f	R_1=R_4=H, R_2-R_3=*o*-Phenylene	**3f**	84

[a]Isolated yield, Reaction conditions: Pyridine, $CHCl_3$, Sealed tube, 70 °C, 15 h

Scheme 1

[#] Dedicated with best wishes to Professor James P. Kutney on the occasion of his 70th birthday.

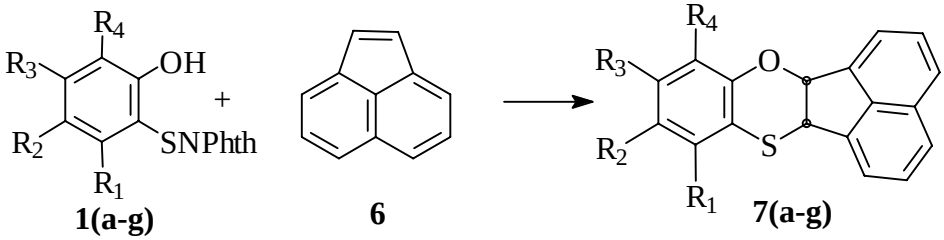
Analogous to the reaction of DMAD, dibenzoyl acetylene (DBA) when treated with 4-isopropyl-2-thiobenzoquinone and 1-thionaphthoquinone in chloroform afforded the corresponding 1,4-oxathiin adducts in good yields (Scheme 2).



i. Pyridine, $CHCl_3$, Sealed tube, 70 °C, 15 h, 80%

Scheme 2

4-Isopropyl-2-thiobenzoquinone on treatment with acenaphthylene in chloroform at 70 °C afforded the 1,4-benzoxathiin adduct (**7a**) in 96% yield. Similar reactions were observed with other *o*-thiobenzoquinones also and the results are summarized in Scheme 3.



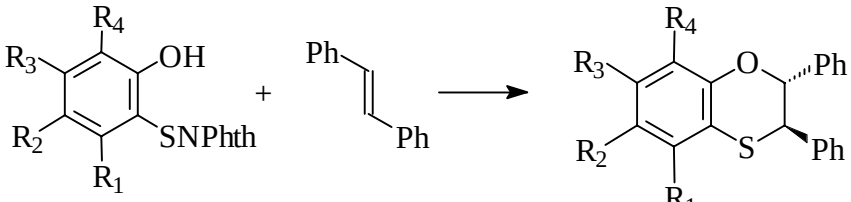
o-Hydroxythiophthalimides	Substituents	Products	Yields(%)[a]
1a	R_1=R_3=R_4=H, R_2=$CHMe_2$	**7a**	96
1b	R_1=R_3=R_4=H, R_2=CMe_3	**7b**	82
1c	R_1=R_3=R_4=H, R_2=OMe	**7c**	91
1d	R_1=R_3=R_4=H, R_2=Me	**7d**	91
1e	R_1 = R_2=R_4=H, R_3=$CHMe_2$	**7e**	86
1f	R_1=R_4=H, R_2-R_3=*o*-Phenylene	**7f**	92
1g	R_2=R_4=H, R_1=R_3=CMe_3	**7g**	85

[a]Isolated yield, Reaction conditions: Pyridine, $CHCl_3$, Sealed tube, 70 °C, 24 h

Scheme 3

4-Isopropyl-2-thiobenzoquinone on treatment with *trans*-stilbene yielded product (**9a**) in 96% yield. The reaction of the other *o*-thiobenzoquinones with *trans*-stilbene also followed the same pathway and the results are summarized in Scheme 4.

When indene was used in place of *trans*-stilbene, with 4-isopropyl-2-thiobenzoquinone we obtained the product (**11a**) regioselectively in 92% yield. We examined the generality of the reaction with other substituted thioquinones and the results are summarized in Scheme 5.

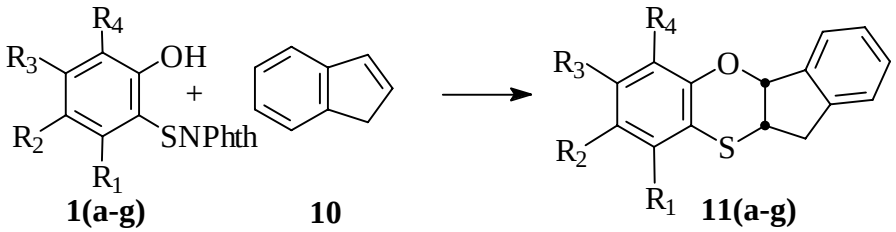


1(a-g) **8** **9(a-g)**

o-Hydroxythiophtalimides	Substituents	Products	Yields(%)[a]
1a	R_1=R_3=R_4=H, R_2=$CHMe_2$	**9a**	96
1b	R_1=R_3=R_4=H, R_2=CMe_3	**9b**	95
1b	R_1=R_3=R_4=H, R_2=OMe	**9c**	86
1d	R_1=R_3=R_4=H, R_2=Me	**9d**	86
1e	R_1 = R_2=R_4=H, R_3=$CHMe_2$	**9e**	60
1f	R_1=R_4=H, R_2-R_3=*o*-Phenylene	**9f**	83
1g	R_2=R_4=H, R_1=R_3=CMe_3	**9g**	87

[a]Isolated yield, Reaction conditions: Pyridine, $CHCl_3$, Sealed tube, 70 °C, 24 h

Scheme 4



1(a-g) **10** **11(a-g)**

o-Hydroxythiophthalimides	Substituents	Products	Yields(%)[a]
1a	R_1=R_3=R_4=H, R_2=$CHMe_2$	**11a**	92
1b	R_1=R_3=R_4=H, R_2=CMe_3	**11b**	91
1c	R_1=R_3=R_4=H, R_2=OMe	**11c**	80
1d	R_1=R_3=R_4=H, R_2=Me	**11d**	92
1e	R_1 = R_2=R_4=H, R_3=$CHMe_2$	**11e**	90
1f	R_1=R_4=H, R_2-R_3=*o*-Phenylene	**11f**	92
1g	R_2=R_4=H, R_1=R_3=CMe_3	**11g**	85

[a]Isolated yield, Reaction conditions: Pyridine, $CHCl_3$, Sealed tube, 70 °C, 16 h

Scheme 5

In order to explain the observed regiochemistry in the above reaction, we have carried out some AM1 calculations using TITAN. The correlation diagram for the reaction of 4-isopropyl-2-thiobenzoquinone with indene is illustrated as an example in Figure 1.

From the correlation diagram in Figure 1, it is evident that the reaction of 4-isopropyl-2-thiobenzoquinone with indene follows inverse electron demand pathway i.e., controlled by LUMO of diene (1a).

It may be noted that on the basis of ^{1}H NMR coupling constants, the relative stereochemistry for **7**, **9** and **11** can be assigned as shown.

In conclusion, our investigations have revealed that the reactions of *o*-thioquinones with different alkynes and alkenes offer a generally efficient and high yield process for the synthesis of 1,4-oxathiins. It is

conceivable that the products of cycloadditions reported herein can potentially undergo a number of interesting transformations.

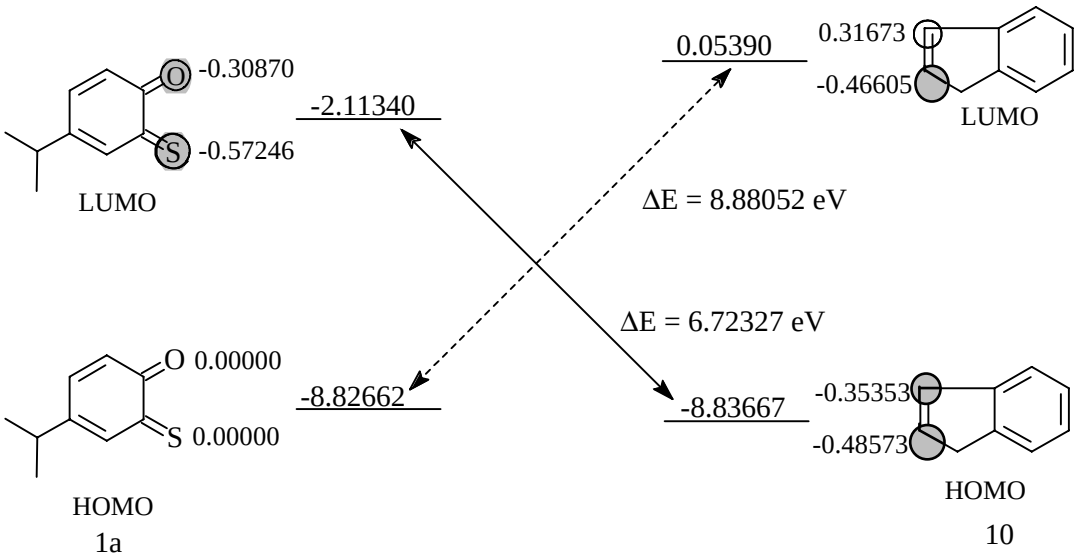


Figure 1

EXPERIMENTAL

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 a Perkin-Elmer model 882 infrared spectrophotometer and Nicolet Impact 400D infrared spectrophotometer, using potassium bromide pellets. NMR spectra were recorded on Bruker-300 spectrometer using chloroform-d3 as solvent. Elemental analyses were done using a Perkin-Elmer 2400 CHN analyzer. High resolution MS were obtained using Finnigan MAT model 8430. Solvents used for experiments were dried and distilled according to literature procedure.

6-(1-Methylethyl)-2,3-bis(carbomethoxy)[1,4]benzoxathiin (**3a**)

A solution of *N*-(2-hydroxy-5-isopropylphenylthio)phthalimide (156 mg, 0.5 mmol), dimethyl acetylenedicarboxylate (85 mg, 0.6 mmol) and pyridine (0.08 mL, 1 mmol) in dry chloroform (2 mL) was taken in a glass tube and sealed under argon atmosphere. The tube was then heated at 70 °C for 15 h. The solvent was removed *in vacuo* and the product subjected to silica gel column chromatography using 5% ethyl acetate in petroleum ether as eluent to afford **3a** (141 mg, 92%) as an yellow viscous liquid. IR (neat) ν_{max}: 780, 945, 1185, 1297, 1634, 1742, 2962 cm^{-1}. ^1H NMR: δ 1.17 (d, J = 6.9 Hz, 6H), 2.76-2.81 (m, 1H), 3.80 (s, 3H), 3.85 (s, 3H), 6.77-6.93 (m, 3H). ^{13}C NMR: δ 23.77, 33.37, 52.83, 116.96, 117.41, 124.51, 126.41, 146.22, 146.98, 148.08, 160.98, 162.66. HRMS calcd for $C_{15}H_{16}O_5S$ 308.0718, found 308.0705.

6-(1,1-Dimethylethyl)-2,3-bis(carbomethoxy)[1,4]benzoxathiin (**3b**)

84%, Yellow viscous liquid. IR (neat) ν_{max}: 831, 1074, 1209, 1263, 1485, 1634, 1748, 2962 cm^{-1}. ^1H NMR: δ 1.85 (s, 9H), 3.73 (s, 3H), 3.78 (s, 3H), 6.72-7.03 (m, 3H). ^{13}C NMR: δ 31.32, 34.57, 52.97, 115.65, 116.83, 117.26, 123.78, 125.60, 146.35, 148.00, 149.51, 161.09, 162.79. HRMS calcd for $C_{16}H_{18}O_5S$ 322.0874, found 322.0868.

6-Methoxy-2,3-bis(carbomethoxy)[1,4]benzoxathiin (**3c**)

86%, Yellow viscous liquid. IR (neat) ν_{max}: 796, 1033, 1270, 1489, 1507, 1726, 2962 cm^{-1}. ^1H NMR: δ 3.65 (s, 3H), 3.75 (s, 3H), 3.78 (s, 3H), 6.38-6.73 (m, 3H). ^{13}C NMR: δ 51.73, 51.89, 54.40, 110.78, 112.25, 112.86, 113.54, 116.32, 117.13, 142.54, 156.39, 160.12, 161.61. HRMS calcd for $C_{13}H_{12}O_6S$ 296.0354, found 296.0341.

6-Methyl-2,3-bis(carbomethoxy)[1,4]benzoxathiin (**3d**)
89%, Yellow viscous liquid. IR (neat) ν_{max}: 789, 1070, 1164, 1278, 1482, 1732, 2956 cm^{-1}. ^1H NMR: δ 2.25 (s, 3H), 3.82 (s, 3H), 3.86 (s, 3H), 6.72-6.82 (m, 3H). ^{13}C NMR: δ 20.79, 52.84, 115.08, 118.36, 126.30, 126.69, 127.15, 127.60, 139.00, 149.99, 160.96, 162.69. HRMS calcd for $C_{13}H_{12}O_5S$ 280.0405, found 280.0415.
7-(1-Methylethyl)-2,3-bis(carbomethoxy)[1,4]benzoxathiin (**3e**)
73%, Yellow viscous liquid. IR (neat) ν_{max}: 798, 1067, 1189, 1256, 1290, 1438, 1634, 1748, 2969 cm^{-1}. ^1H NMR: δ 1.18 (d, J = 6.9 Hz, 6H), 2.78-2.82 (m, 1H), 3.81 (s, 3H), 3.86 (s, 3H), 6.77-6.86 (m, 3H). ^{13}C NMR: δ 23.79, 33.76, 53.06, 111.37, 114.08, 115.92, 124.42, 126.57, 145.94, 150.21, 150.42, 161.16, 162.91. HRMS calcd for $C_{15}H_{16}O_5S$ 308.0718, found 308.0707.
2,3-Bis(carbomethoxy)naphtho[*a*][1,4]benzoxathiin (**3f**)
84%, Yellow viscous liquid. IR (neat) ν_{max}: 811, 1155, 1209, 1276, 1458, 1587, 1647, 1755, 2955 cm^{-1}. ^1H NMR: δ 3.86 (s, 3H), 3.90 (s, 3H), 7.08-7.77 (m, 6H). ^{13}C NMR: δ 51.99, 116.45, 121.88, 124.64, 126.23, 127.27, 127.56, 128.54, 128.90, 129.90, 130.68, 145.80, 146.88, 159.92, 161.66. HRMS calcd for $C_{16}H_{12}O_5S$ 316.3318, found 316.3315.
6-(1-Methylethyl)-2,3-bis(benzoyl)[1,4]benzoxathiin (**5a**)
80%, Yellow crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 80-82 °C). IR (KBr) ν_{max}: 724, 1276, 1485, 1607, 1674, 2975 cm^{-1}. ^1H NMR: δ 1.15 (d, J = 6.9 Hz, 6H), 2.75-2.78 (m, 1H), 6.75-7.81 (m, 13H). ^{13}C NMR: δ 23.48, 33.11, 117.06, 117.66, 124.41, 126.41, 127.86, 128.18, 128.46, 128.57, 129.17, 132.86, 133.07, 133.33, 134.62, 135.15, 135.29, 146.64, 148.47, 148.80, 185.60, 188.74. Anal. Calcd for $C_{25}H_{20}O_3S$: C, 74.98; H, 5.04. Found: C, 74.88; H, 5.02.
2,3-Bis(benzoyl)naphtho[*a*][1,4]benzoxathiin (**5f**)
92%, Yellow crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 118-120 °C). IR (KBr) ν_{max}: 804, 1034, 1276, 1587, 1681, 2969, 3063 cm^{-1}. ^1H NMR: δ 7.19-8.02 (m, 16H). ^{13}C NMR: δ 117.06, 117.66, 123.50, 124.41, 126.41, 127.86, 128.18, 128.46, 128.51, 129.17, 132.82, 132.99, 133.07, 133.23, 134.62, 134.86, 135.15, 135.79, 146.64, 148.47, 148.80, 150.13, 186.60, 187.74. HRMS calcd for $C_{26}H_{16}O_3S$ 408.0820, found 408.0815.
6-(1-Methylethyl)-2,3-dihydroacenaphthene[1,4]benzoxathiin (**7a**)
96%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 125-127 °C). IR (KBr) ν_{max}: 778, 825, 1110, 1222, 1485, 2982 cm^{-1}. ^1H NMR: δ 1.09 (d, J = 6.8 Hz, 6H), 2.67-2.72 (m, 1H), 5.22 (d, J = 7.2 Hz, 1H), 6.22 (d, J = 7.2 Hz, 1H), 6.83 (s, 2H), 6.99 (s, 1H), 7.37-7.66 (m, 6H). ^{13}C NMR: δ 23.83, 23.91, 33.31, 49.66, 84.66, 119.63, 120.16, 121.64, 124.00, 124.30, 125.20, 125.71, 127.21, 128.17, 128.28, 130.59, 137.02, 140.05, 142.20, 143.81, 152.76. HRMS calcd for $C_{21}H_{18}OS$ 318.1078, found 318.1072.
6-(1,1-Dimethylethyl)-2,3-dihydroacenaphthene[1,4]benzoxathiin (**7b**)
82%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 138-140 °C). IR (KBr) ν_{max}: 784, 1034, 1276, 1499, 2942 cm^{-1}. ^1H NMR: δ 1.23 (s, 9H), 5.26 (d, J = 7.0 Hz, 1H), 6.25 (d, J = 7.0 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 7.04 (d, J = 8.2 Hz, 1H), 7.18 (s, 1H), 7.42-7.72 (m, 6H). ^{13}C NMR: δ 31.64, 34.45, 49.89, 84.83, 119.48, 120.38, 121.87, 124.17, 124.26, 124.92, 125.44, 126.40, 128.41, 128.50, 130.88, 137.24, 140.35, 142.38, 146.34, 152.80. Anal. Calcd for $C_{22}H_{20}OS$: C, 79.47; H, 6.06; S, 9.64. Found: C, 79.38; H, 6.01; S, 9.61.
6-Methoxy-2,3-dihydroacenaphthene[1,4]benzoxathiin (**7c**)
91%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 139-141 °C). IR (KBr) ν_{max}: 768, 1197, 1259, 1477, 2927, 3052 cm^{-1}. ^1H NMR: δ 3.57 (s, 3H), 5.22 (d, J = 7.2 Hz, 1H), 6.26 (d, J = 7.2 Hz, 1H), 6.48 (d, J = 2.8 Hz, 1H), 6.65 (d, J = 2.8 Hz, 1H), 6.75 (d, J = 8.7 Hz, 1H), 7.40-7.66 (m, 6H). ^{13}C NMR: δ 49.73, 55.23, 84.81, 113.35, 114.41, 120.25, 120.54, 121.62, 124.01, 125.18, 125.60, 128.14, 128.31, 130.47, 137.16, 139.89, 142.29, 148.22, 155.17. Anal. Calcd for $C_{19}H_{14}O_2S$: C, 74.48; H, 4.60; S, 10.46. Found: C, 74.42; H, 4.61; S, 10.31.

6-Methyl-2,3-dihydroacenaphthene[1,4]benzoxathiin (**7d**)
91%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 140-142 °C). IR (KBr) ν_{max}: 780, 1029, 1265, 1483, 2965, 3033 cm^{-1}. ^1H NMR: δ 2.15 (s, 3H), 5.22 (d, *J* = 7.2 Hz, 1H), 6.27 (d, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 6.71 (s, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 7.38-7.68 (m, 6H). ^{13}C NMR: δ 21.04, 49.77, 84.63, 120.18, 120.75, 121.64, 123.96, 124.20, 125.22, 126.48, 128.15, 128.30, 129.14, 130.49, 137.07, 137.86, 139.93, 142.30, 154.65. Anal. Calcd for $C_{19}H_{14}OS$: C, 78.58; H, 4.86; S, 11.04. Found: C, 78.48; H, 4.69; S, 11.01.
7-(1-Methylethyl)-2,3-dihydroacenaphthene[1,4]benzoxathiin (**7e**)
86%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 115-117 °C). IR (KBr) ν_{max}: 778, 818, 1040, 1357, 1425, 1485, 1566, 1600, 2962 cm^{-1}. ^1H NMR: δ 1.04 (d, *J* = 6.8 Hz, 6H), 2.65-2.69 (m, 1H), 5.17 (d, *J* = 7.1 Hz, 1H), 6.17 (d, *J* = 7.1 Hz, 1H), 6.63 (d, *J* = 1.5 Hz, 1H), 6.75 (s, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 7.33-7.69 (m, 6H). ^{13}C NMR: δ 23.97, 33.88, 50.01, 84.92, 118.25, 120.38, 121.80, 121.85, 124.26, 125.42, 128.38, 128.52, 128.76, 129.34, 130.87, 137.24, 140.29, 142.41, 149.29, 155.20. HRMS calcd for $C_{21}H_{18}OS$ 318.1078, found 318.1072.
2,3-Dihydro-acenaphthenenaphtho[*a*][1,4]benzoxathiin (**7f**)
92%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 165-167 °C). IR (KBr) ν_{max}: 825, 1040, 1108, 1222, 1378, 1499, 1593, 3049 cm^{-1}. ^1H NMR: δ 5.34 (d, *J* = 6.8 Hz, 1H), 6.39 (d, *J* = 6.8 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 1H), 7.20-7.47 (m, 10H), 8.05 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR: δ 49.06, 84.66, 118.82, 119.24, 119.41, 120.67, 122.32, 123.08, 123.50, 124.32, 125.21, 126.36, 127.09, 127.19, 127.38, 129.38, 129.51, 131.64, 136.18, 138.97, 141.07, 152.11. Anal. Calcd for $C_{22}H_{14}OS$: C, 80.95; H, 4.32; S, 9.82. Found: C, 81.00; H, 4.38; S, 9.47.
5,7-Bis(1,1-dimethylethyl)-2,3-dihydroacenaphthene[1,4]benzoxathiin (**7g**)
85%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 156-158 °C). IR (KBr) ν_{max}: 774, 1041, 1253, 1396, 2959, 3033 cm^{-1}. ^1H NMR: δ 1.18 (s, 9H), 1.40 (s, 9H), 5.20 (d, *J* = 7.2 Hz, 1H), 6.24 (d, *J* = 7.2 Hz, 1H), 6.85 (s, 1H), 6.97 (s, 1H), 7.43-7.67 (m, 6H). ^{13}C NMR: δ 30.27, 31.14, 34.56, 36.37, 50.82, 85.08, 115.97, 118.24, 120.50, 121.25, 121.71, 123.91, 125.03, 127.98, 130.61, 137.56, 140.19, 141.48, 149.05, 149.80, 155.82. Anal. Calcd for $C_{26}H_{28}OS$: C, 80.36; H, 7.26; S, 8.25. Found: C, 80.27; H, 7.12; S, 8.47.
2,3-*trans*-Diphenyl-6-(1-methylethyl)-2,3-dihydro[1,4]benzoxathiin (**9a**)
96%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 135-137 °C). IR (KBr) ν_{max}: 760, 815, 1021, 1239, 1318, 1490, 2969 cm^{-1}. ^1H NMR: δ 1.22 (d, *J* = 6.9 Hz, 6H), 2.81-2.85 (m, 1H), 4.37 (d, *J* = 8.9 Hz, 1H), 5.00 (d, *J* = 8.9 Hz, 1H), 6.88-7.14 (m, 13H). ^{13}C NMR: δ 24.06, 33.36, 49.47, 82.07, 118.28, 119.32, 123.52, 123.83, 127.08, 127.83, 127.97, 128.35, 128.90, 136.81, 138.29, 142.14, 150.26. Anal. Calcd for $C_{23}H_{22}OS$: C, 79.74; H, 6.41. Found: C, 79.80; H, 6.38.
2,3-*trans*-Diphenyl-6-(1,1-dimethylethyl)-2,3-dihydro[1,4]benzoxathiin (**9b**)
95%, Colorless crystalline solid, it was recrystallized from dichloromethane-petroleum ether (mp 147-149 °C). IR (KBr) ν_{max}: 811, 1020, 1256, 1499, 2874, 2955 cm^{-1}. ^1H NMR: δ 1.23 (s, 9H), 4.28 (d, *J* = 8.8 Hz, 1H), 4.92 (d, *J* = 8.8 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.95-7.05 (m, 12H). ^{13}C NMR: δ 31.42, 34.20, 49.53, 82.14, 118.01, 118.93, 122.67, 122.91, 127.11, 127.86, 128.01, 128.38, 128.93, 136.83, 138.31, 144.50, 149.99. Anal. Calcd for $C_{24}H_{24}OS$: C, 79.95; H, 6.70; S, 8.89. Found: C, 79.88; H, 6.61; S, 8.88.
2,3-*trans*-Diphenyl-6-methoxy-2,3-dihydro[1,4]benzoxathiin (**9c**)
86%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 148-150 °C). IR (KBr) ν_{max}: 805, 1029, 1259, 1489, 2965 cm^{-1}. ^1H NMR: δ 3.76 (s, 3H), 4.40 (d, *J* = 8.9 Hz, 1H), 4.96 (d, *J* = 8.9 Hz, 1H), 6.57-7.24 (m, 13H). ^{13}C NMR: δ 49.63, 55.58, 82.06, 110.24, 118.97, 119.15, 120.49, 127.10, 127.91, 128.02, 128.40, 128.93, 136.76, 138.31, 146.40, 154.20. Anal. Calcd for $C_{21}H_{18}O_2S$: C, 75.41; H, 5.42; S, 9.58. Found: C, 75.49; H, 5.49; S, 9.69.
2,3-*trans*-Diphenyl-6-methyl-2,3-dihydro[1,4]benzoxathiin (**9d**)
86%, colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 95-97 °C). IR (KBr) ν_{max}: 799, 1023, 1259, 1446, 2965, 3039 cm^{-1}. ^1H NMR: δ 2.29 (s, 3H), 4.34 (d, *J* = 8.9 Hz, 1H),

5.01 (d, J = 8.9 Hz, 1H), 6.72-7.24 (m, 13H). ^{13}C NMR: δ 29.64, 49.27, 81.47, 115.96, 118.94, 122.59, 124.44, 126.14, 127.07, 127.90, 128.37, 128.94, 135.35, 136.90, 138.34, 151.95. Anal. Calcd for $C_{21}H_{18}OS$: C, 79.20; H, 5.69; S, 10.06. Found: C, 79.28; H, 5.61; S, 10.01.

2,3-*trans*-Diphenyl-7-(1-methylethyl)-2,3-dihydro[1,4]benzoxathiin (**9e**)

60%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 125-127 °C). IR (KBr) ν_{max}: 757, 879, 1027, 1297, 1418, 1485, 1566, 2969, 3056 cm^{-1}. ^{1}H NMR: δ 1.22 (d, J = 6.8 Hz, 6H), 2.81-2.86 (m, 1H), 4.37 (d, J = 8.9 Hz, 1H), 5.04 (d, J = 8.9 Hz, 1H), 6.81-7.25 (m, 13H). ^{13}C NMR: δ 24.66, 33.36, 49.47, 82.07, 118.28, 119.32, 123.52, 123.83, 127.08, 127.88, 127.07, 128.35, 128.90, 136.81, 138.29, 142.14, 150.26. Anal. Calcd for $C_{23}H_{22}OS$: C, 79.74; H, 6.41. Found: C, 79.80; H, 6.38.

2,3-*trans*-Diphenyl-2,3-dihydronaphtho[*a*][1,4]benzoxathiin (**9f**)

83%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 170-172 °C). IR (KBr) ν_{max}: 697, 825, 1007, 1229, 1378, 1499, 1607, 2968, 3050 cm^{-1}. ^{1}H NMR: δ 4.34 (d, J = 8.8 Hz, 1H), 5.08 (d, J = 8.8 Hz, 1H), 7.04-7.83 (m, 16H). ^{13}C NMR: δ 48.96, 82.08, 112.89, 119.74, 122.76, 124.23, 125.67, 126.39, 127.26, 128.11, 128.19, 128.26, 128.37, 128.59, 129.09, 129.46, 130.85, 136.98, 138.26, 149.98. HRMS calcd for $C_{24}H_{18}OS$ 354.1078, found 354.1078.

2,3-*trans*-Diphenyl-5,7-bis(1,1-dimethylethyl)-2,3-dihydro[1,4]benzoxathiin (**9g**)

87%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 210-212 °C). IR (KBr) ν_{max}: 742, 1035, 1297, 1452, 1552, 2952 cm^{-1}. ^{1}H NMR: δ 1.30 (s, 9H), 1.51 (s, 9H), 4.26 (d, J = 9.4 Hz, 1H), 5.13 (d, J = 9.4 Hz, 1H), 6.92 (s, 1H), 7.10-7.17 (m, 11H). ^{13}C NMR: δ 29.99, 31.28, 34.55, 36.81, 50.72, 82.78, 104.69, 114.19, 116.47, 117.05, 126.99, 127.84, 128.03, 128.42, 128.90, 137.21, 138.89, 146.45, 147.93. Anal. Calcd for $C_{28}H_{32}OS$: C, 80.72; H, 7.74. Found: C, 80.68; H, 7.71.

6-(1-Methylethyl)-2,3-dihydroindan[*b*][1,4]benzoxathiin (**11a**)

92%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 67-69 °C). IR (KBr) ν_{max}: 764, 831, 1054, 1243, 1492, 2962 cm^{-1}. ^{1}H NMR: δ 1.18 (d, J = 6.9 Hz, 6H), 2.76-2.80 (m, 1H), 3.14-3.16 (m, 1H), 3.28-3.36 (m, 1H), 3.96-3.98 (m, 1H), 5.28 (d, J = 5.3 Hz, 1H), 6.84 (s, 2H), 6.97 (s, 1H), 7.20-7.49 (m, 4H). ^{13}C NMR: δ 24.01, 33.38, 39.37, 42.83, 81.54, 118.84, 120.33, 124.15, 124.83, 125.07, 125.45, 127.13, 129.23, 140.51, 141.86, 142.82, 151.01. HRMS calcd for $C_{18}H_{18}OS$ 282.1078, found 282.1071.

6-(1,1-Dimethylethyl)-2,3-dihydroindan[*b*][1,4]benzoxathiin (**11b**)

91%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 68-70°C). IR (KBr) ν_{max}: 784, 1061, 1115, 1236, 1270, 1492, 2962 cm^{-1}. ^{1}H NMR: δ 1.20 (s, 9H), 3.09-3.11 (m, 1H), 3.24-3.31 (m, 1H), 3.92-3.96 (m, 1H), 5.24 (d, J = 5.3 Hz, 1H), 6.78-7.45 (m, 7H). ^{13}C NMR: δ 31.60, 34.41, 39.56, 43.05, 81.65, 118.73, 119.98, 123.41, 124.34, 125.08, 125.67, 127.37, 129.47, 140.77, 142.09, 145.36, 150.91. HRMS calcd for $C_{19}H_{20}OS$ 296.1234, found 296.1232.

6-Methoxy-2,3-dihydroindan[*b*][1,4]benzoxathiin (**11c**)

80%, Colorless viscous liquid. IR (neat) ν_{max}: 746, 1045, 1214, 1258, 1601, 2837, 2956 cm^{-1}. ^{1}H NMR: δ 3.08-3.15 (m, 1H), 3.28-3.36 (m, 1H), 3.69 (s, 3H), 3.95-3.99 (m, 1H), 5.29 (d, J = 5.4 Hz, 1H), 6.53-7.48 (m, 7H). ^{13}C NMR: δ 39.51, 42.98, 55.37, 82.01, 111.94, 112.17, 119.70, 122.17, 124.74, 125.46, 127.11, 129.21, 140.22, 141.81, 146.91, 154.62. HRMS calcd for $C_{16}H_{14}O_2S$ 270.0714, found 270.0715.

6-Methyl-2,3-dihydroindan[*b*][1,4]benzoxathiin (**11d**)

92%, Colorless viscous liquid. IR (neat) ν_{max}: 796, 1052, 1151, 1251, 1476, 1563, 2912, 2962, 3024 cm^{-1}. ^{1}H NMR: δ 2.23 (s, 3H), 3.04-3.12 (m, 1H), 3.26-3.33 (m, 1H), 3.93-3.99 (m, 1H), 5.35 (d, J = 5.4 Hz, 1H), 6.67-7.48 (m, 7H). ^{13}C NMR: δ 19.67, 39.40, 42.83, 81.16, 116.85, 119.89, 123.39, 124.96, 127.29, 129.37, 136.31, 140.64, 141.92, 153.21. HRMS calcd for $C_{16}H_{14}OS$ 254.0765, found 254.0760.

7-(1-Methylethyl)-2,3-dihydroindan[*b*][1,4]benzoxathiin (**11e**)

90%, Colorless viscous liquid. IR (neat) ν_{max}: 764, 1013, 1074, 1236, 1485, 1573, 2969, 3050 cm^{-1}. ^{1}H NMR: δ 1.09 (d, J = 6.9 Hz, 6H), 2.68-2.73 (m, 1H), 2.99-3.07 (m, 1H), 3.18-3.26 (m, 1H), 3.82-3.86 (m, 1H), 5.21 (d, J = 5.3 Hz, 1H), 6.66-7.43 (m, 7H). ^{13}C NMR: δ 24.02, 33.75, 39.37, 42.85, 81.65, 117.09,

117.46, 120.81, 125.00, 125.54, 127.28, 127.33, 129.37, 140.71, 142.01, 147.46, 153.13. HRMS calcd for $C_{18}H_{18}OS$ 282.1078, found 282.1075.

2,3-Dihydroindan[*b*]naphtho[*a*][1,4]benzoxathiin (**11f**)

92%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp. 118-120 °C). IR (KBr) ν_{max}: 751, 811, 1108, 1229, 1398, 1472, 1613, 2960, 3042 cm^{-1}. ^1H NMR: δ 3.12-3.19 (m, 1H), 3.34-3.42 (m, 1H), 4.04-4.10 (m, 1H), 5.47 (d, J = 5.0 Hz, 1H), 7.11-7.97 (m, 10H). ^{13}C NMR: δ 39.17, 42.29, 81.24, 113.75, 119.98, 122.64, 124.12, 124.98, 125.25, 125.79, 126.10, 127.15, 128.20, 129.25, 129.76, 131.30, 140.73, 141.61, 150.44. HRMS calcd for $C_{19}H_{14}OS$ 290.0765, found 290.0755.

5,7-Bis(1,1-dimethylethyl)-2,3-dihydroindan[*b*][1,4]benzoxathiin (**11g**)

85%, Colorless crystalline solid; recrystallized from dichloromethane-petroleum ether (mp 78-80 °C). IR (KBr) ν_{max}: 789, 1058, 1283, 1489, 1557, 2968 cm^{-1}. ^1H NMR: δ 1.26 (s, 9H), 1.49 (s, 9H), 3.04-3.10 (m, 1H), 3.34-3.42 (m, 1H), 3.97-4.03 (m, 1H), 5.63 (d, J = 6.0 Hz, 1H), 6.90-7.58 (m, 6H). ^{13}C NMR: δ 30.23, 31.25, 34.64, 36.51, 38.60, 44.86, 86.02, 115.22, 117.78, 120.69, 124.49, 125.93, 127.21, 129.11, 140.06, 141.49, 148.56, 149.38, 155.97. HRMS calcd for $C_{23}H_{28}OS$ 352.1860, found 352.1870.

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