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Simple and practical one-step synthesis of new 1,3-dienic δ-sultones from terminal alkynes and some synthetic applications of these compounds

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Simple and practical one-step synthesis of new 1,3-dienic δ-sultones from terminal alkynes and some synthetic applications of these compounds

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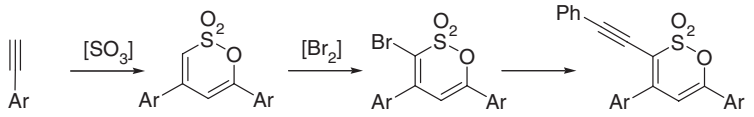
1,3-Dienic δ-sultones 4,6-diaryl-[1,2]oxathiine 2,2-dioxides were synthesized via a one-step reaction of arylalkynes with dioxane sulfotrioxide. The reactivity of various alkynes in this reaction was investigated. The resulting sultones were brominated with Br_2 or *N*-bromosuccinimide regioselectively α to sulfur and subsequently coupled with phenylacetylene using Sonogashira conditions.



Keywords: alkynes; dioxane sulfotrioxide; δ-sultones; bromination; Sonogashira coupling

1. Introduction

Sultones are important heterocyclic compounds in organic synthesis (*1*, *2*) and medicinal chemistry (*3*). Recently developed powerful methodologies for the generation of these cyclic sulfonates include the intramolecular Diels–Alder reaction (*4*), ring closing metathesis (*5*), Pd-catalyzed intramolecular coupling reaction (*6*), Rh-catalyzed C–H insertion (*7*), and Rh-catalyzed carbene cyclization cycloaddition cascade (*8*). However, a general method for the synthesis of 1,3-dienic δ-sultones has not been described yet. We have previously investigated a simple synthesis of the 1,3-dienic δ-sultone 4,6-diphenyl-[1,2]oxathiine 2,2-dioxide using a novel reaction of phenylacetylene with sulfuric acid or dioxane sulfotrioxide (*9*, *10*) and also a practical synthesis of 1,2-diketones via oxidation of 1,2-diaryl substituted alkynes with dioxane sulfotrioxide under similar conditions

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[#]X-ray diffraction analysis.

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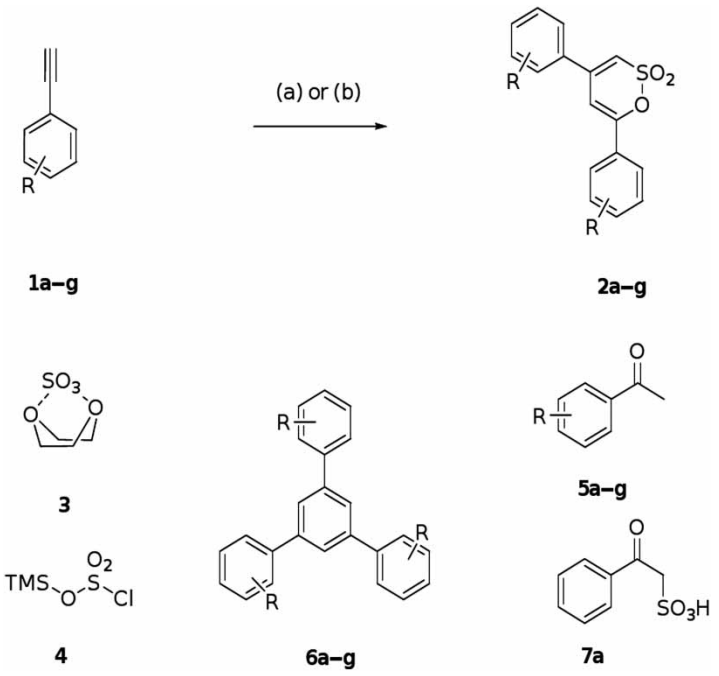

Figure 1. Synthesis of sultones **2a**–**2g** from arylalkynes **1a**–**1g**. Reaction conditions: (a) dioxane sulfotrioxide **3** (1 equiv.), dioxane/$CHCl_3$, 1:1 (v/v) (Table 1); (b) trimethylsilyl chlorosulfonate **4** (1 equiv.), addition of **4** over 5 min (Table 2).

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(*11*). Here we communicate a further study on the one-step heterocyclization of arylalkynes with sulfur trioxide to give new 4,6-diaryl substituted 1,3-dienic δ-sultones as well as some synthetic applications of these compounds.

2. Results and discussion

We found earlier that treatment of phenylacetylene **1a** with dioxane sulfotrioxide (*12*) gave a better yield of sultone **2a** as compared to the reaction with sulfuric acid and oleum (*10*). Therefore, dioxane sulfotrioxide was used in further experiments. In order to determine the scope of the reaction and to achieve a better understanding of its pathway, sulfonation of a series of substituted phenylacetylenes was undertaken. The influence of substituents on the reactivity of the substrate and on the yields of the products was investigated. Gratifyingly, our method to synthesize sultone

Table 1. Synthesis of 1,3-dienic δ-sultones from alkynes **1a**–**1h** and dioxane sulfotrioxide **3** in dioxane/$CHCl_3$ 1:1 (v/v).

Substrate	R	T	Reaction time (h)	Product (yield, %)
1a	H	Reflux	3.5	**2a** (40)
1b	*p*-Me	Reflux	4.5	**2b** (38)
1c	*p*-Cl	Reflux	4.5	**2c** (38)
1d	*m*-Cl	0 °C to rt	60	**2d** (40)
1e	*p*-MeO	0 °C to rt	7.5[a]	**2e** (8)
1g	*p*-Ph	Reflux	4	**2g** (13)
1h	*p*-NO_2	0 °C to rt or reflux	4–22	**2h** (0)

Note: [a]Addition of a solution of **3** in dioxane/$CHCl_3$ 1:1 (v/v) at 0 °C over 3 h.

Table 2. Synthesis of 1,3-dienic δ-sultones from alkynes **1a**–**1h** and trimethylsilyl chlorosulfonate **4** in dioxane/$CHCl_3$ 1:1 (v/v).

Substrate	R	T	Reaction time (h)	Product (yield, %)
1a	H	0 °C to rt	24	**2a** (34)
1b	*p*-Me	0 °C to rt	48	**2b** (47)
1c	*p*-Cl	0 °C to rt	24	**2c** (38)
1d	*m*-Cl	0 °C to rt	60	**2d** (14)
1e	*p*-MeO	−78 °C to rt	66	**2e** (45)[a]
1f	*o*-MeO	−78 °C to rt	66	**2f** (28)[b]
1g	*p*−Ph	Reflux	4	**2g** (38)
1h	*p*-NO_2	0 °C to rt or reflux	4–22	**2h** (0)

Notes: [a]Reaction in $CHCl_3$/dioxane/CH_2Cl_2 1:3:3 (v/v/v).
[b]Reaction in dioxane/CH_2Cl_2 1:2 (v/v).

2a from alkyne **1a** with dioxane sulfotrioxide **3** at reflux could easily be extended to the conversion of alkynes **1b** and **1c** to sultones **2b** and **2c**, respectively, whereas the transformation of **1d** to **2d** proceeded best at lower temperature (Figure 1, Table 1).

Acetophenones **5a**–**5g** (ca. 5%), 1,3,5-triarylbenzenes **6a**–**6g** (5–10%), and unidentified compounds of high polarity were also isolated by flash chromatography from the reaction mixture as by-products of the sulfonation of **1a**–**1g**. The 1,3,5-substitution of **6a**–**6g** was confirmed by NMR analysis of all products and by X-ray diffraction analysis of **6b**.[1] Sulfonic acid **7a** (ca. 7%) was additionally obtained from the product mixture derived from **1a**.

Methoxy derivatives **1e** and **1f** could not be converted into the corresponding sultones **2e** and **2f** under these conditions due to the higher reactivity of these substrates. On the other hand, a decrease in the reaction temperature to 0 °C and slower addition of the solution of **3** to the solution of **1e** resulted in the formation of sultone **2e** in 8% yield. Apparently, electron-rich arylalkynes need lower temperatures for conversion to sultones **2**. However, further decrease in the reaction temperature below 0 °C was not possible due to the insolubility of dioxane sulfotrioxide **3** in the cold solvent. The 4-phenyl derivative **1g** showed a rather low reactivity with dioxane sulfotrioxide **3** (13% of **2g** with 87% conversion of starting alkyne). Unfortunately, 4-nitrophenylacetylene **1h** could not be converted into sultone **2h**. At 0 °C, alkyne **1h** was recovered, whereas an increased temperature resulted in decomposition of **1h**.

In another series of experiments, liquid trimethylsilyl chlorosulfonate (**4**) in dioxane/chloroform solution was used instead of **3**. It is well known that **4** can be used as an equivalent of SO_3 (*13*). Slow addition of **4** to the substrate and dioxane caused formation of **3** *in situ* at low temperature and thus, ensured mild reaction conditions excluding areas with high concentration of SO_3. With this SO_3 source, sultones **2a**–**2d** were synthesized from the corresponding alkynes **1a**–**1d** in 14–47% yields (Figure 1, Table 2). Slow addition of **4** to a solution of **1e** in dioxane/chloroform/dichloromethane at −78 °C allowed the preparation of sultone **2e** in 45% yield. Here, dichloromethane was added as a co-solvent to avoid solidification of the reaction mixture at low temperature. Under similar conditions, alkyne **1f** was also converted into sultone **2f**, albeit in a lower yield of 28%, probably due to the steric hindrance caused by the *o*-methoxy group. Sultones **2e** and **2f** were unstable to air, but could be safely stored in a chloroform solution. The biphenyl alkyne **1g** reacted rather reluctantly with **4** at rt (7% of **2g** with 46% conversion of starting compound), but at reflux sultone **2g** was formed in 38% yield. Similar to the reaction of **1h** with **3**, no sultone formation was noted after treatment of this electron-deficient substrate with reagent **4**.

The proposed mechanism of this heterocyclization is shown in Figure 2. We presume that alkyne **1** is first sulfonated with SO_3 to afford a highly reactive β-sultone existing in the cyclic **I** and zwitterionic **II** form. Subsequent addition of a further equivalent of alkyne **1** to this β-sultone then gives the stable δ-sultone **2**. In conclusion, a range of monosubstituted arylalkynes **1a**–**1h** were investigated in a heterocyclization reaction with SO_3 to give δ-sultones. The reactivity of

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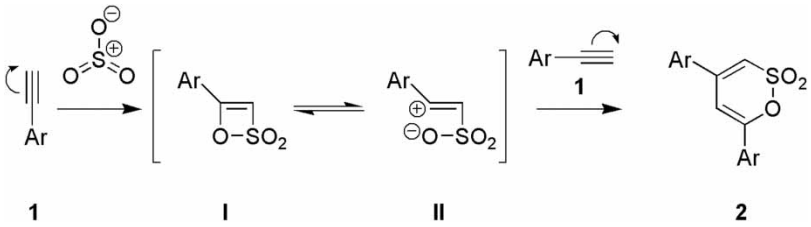

Figure 2. Proposed mechanism of the heterocyclization of alkynes to give δ-sultones.

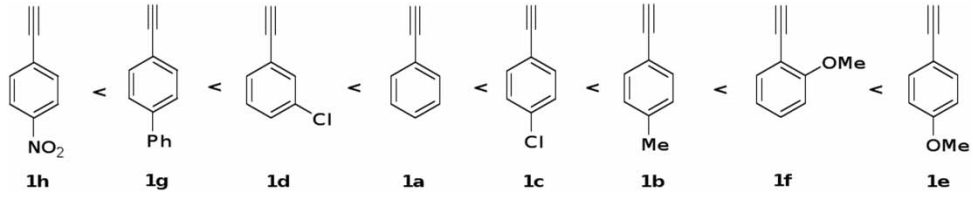

Figure 3. Relative reactivity of compounds **1a**–**1h** in the reaction with SO_3 sources **3** and **4** based on the M and I effects of the substituents.

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3 and **4** toward the alkynes investigated is similar, but not identical. The relative reactivity of these compounds toward the SO_3 sources **3** and **4** is depicted in Figure 3. Alkynes **1a**–**1d** and **1g** react readily with sulfonating agents **3** and **4** at room temperature or above, while the electron-rich methoxy derivatives **1e** and **1f** only give the desired products in decent yields at very low temperatures using **4** as the SO_3 source. Due to the presence of the electron-withdrawing nitro group in the *para* position of the phenyl ring, acetylene **1h** neither gave a sultone with **3** or **4**.

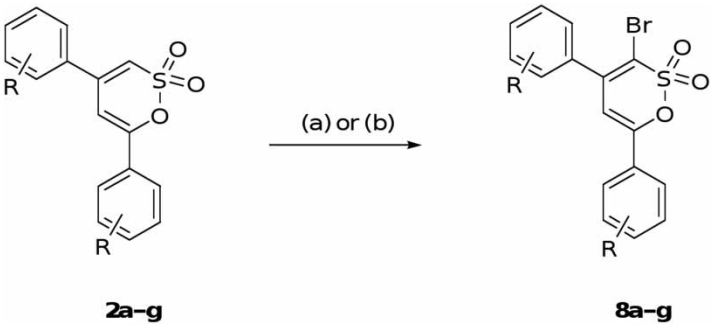

Figure 4. Bromination of δ-sultones **2a**–**2g**. Reaction conditions: (a) Br_2 (1.5 equiv.), $CHCl_3$, reflux; (b) NBS (1.05 equiv.), $CHCl_3$, rt.

Table 3. Bromination of δ-sultones **2a**–**2g** with Br_2 or NBS

Substrate	R	Bromine source	Reaction time (min)	Product (yield, %)
2a	H	Br_2	90	**8a** (95)
2b	*p*-Me	Br_2	45	**8b** (97)
2c	*p*-Cl	Br_2	120	**8c** (96)
2d	*m*-Cl	Br_2	60	**8d** (98)
2e	*p*-MeO[a]	NBS	60	**8e** (95)
2f	*o*-MeO[a]	NBS	60	**8f** (74)
2g	*p*−Ph	Br_2	45	**8g** (70)

Note: [a]Reaction at rt.

These results underpin an electrophilic attack at the alkyne moiety in the course of this sultone generating reaction.

In the next part of our studies, we investigated some synthetic applications of the new 1,3-dienic δ-sultones. These investigations commenced with bromination of sultone **2a**, which is readily available (*9*). The reaction of δ-sultone **2a** was carried out at 60 °C in chloroform with one or more equivalents of bromine. The regioselectivity of this overall vinylic substitution process can readily be rationalized. Only attack of a positive bromine source at the carbon α to sulfur in **2a** generates a highly delocalized carbenium ion, which in turn undergoes elimination of a proton to afford product **8a**. To our delight, we observed an almost quantitative yield and virtually no side products, also using an excess of Br_2. Further investigation of this bromination reaction led

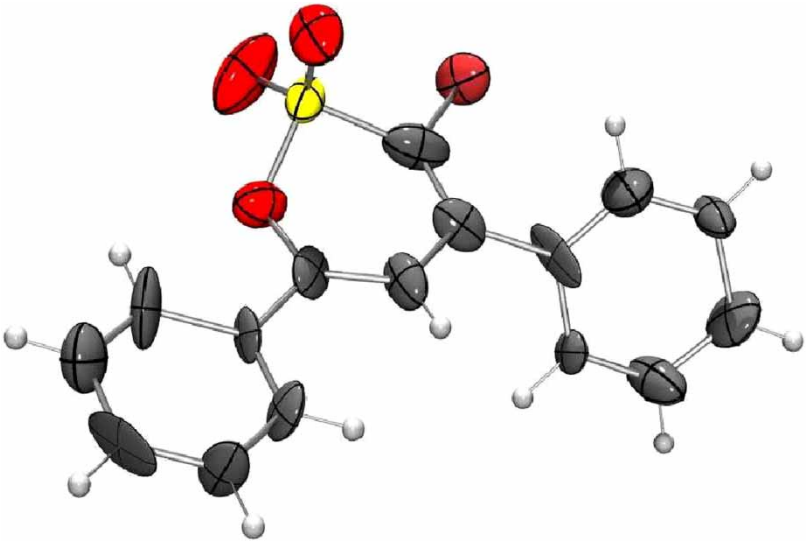

Figure 5. X-ray diffraction analysis of **8a**.

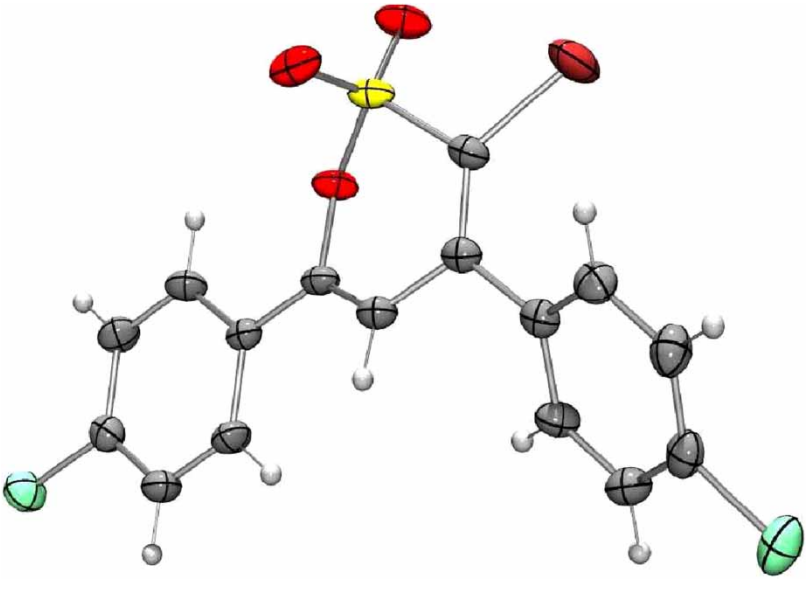

Figure 6. X-ray diffraction analysis of **8c**.

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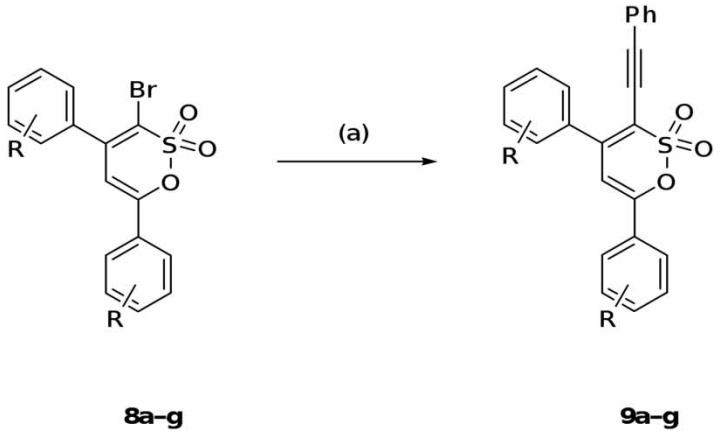

Figure 7. Sonogashira coupling of bromo sultones **8a**–**8g** with phenylacetylene **1a**. Reaction conditions: (a) **1a** (2 equiv.), $PdCl_2$, PPh_3, CuI, THF/Et_3N, 2:1 (v/v), reflux.

Table 4. Sonogashira coupling of bromo sultones **8a**–**8g** with phenylacetylene **1a**.

Substrate	R	Reaction time (h)	Product (yield, %)
8a	H	17.5	**9a** (90)
8b	*p*-Me	19	**9b** (55)
8c	*p*-Cl	19	**9c** (65)
8d	*m*-Cl	18.5	**9d** (70)
8e	*p*-MeO	24	**9e** (98)
8f	*o*-MeO	18	**9f** (98)
8g	*p*−Ph	19	**9g** (69)

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to a general method for functionalization of 1,3-dienic δ-sultones **2**. To this end, sultones **2b**–**2d** and **2g** were treated with bromine to give the corresponding bromo sultones **8b**–**8d** and **8g**, respectively, in 70–98% yield with complete regioselectivity (Figure 4, Table 3). The structure of products **8** was confirmed by spectroscopic data and X-ray diffraction analysis of bromo sultones **8a** (Figure 5) and **8c** (Figure 6).[1] Methoxy-activated sultones **2e** and **2f** gave mixtures of more highly brominated unstable products with bromine. Fortunately, products **8e** and **8f** were readily available by treatment of **2e** or **2f** with 1 equiv. of *N*-bromosuccinimide (NBS) at room temperature in 95 and 74% yield, respectively. In contrast to the starting material **2f**, the brominated compound **8f** was stable when exposed to air.

Bromo sultones **8a**–**8g** are useful substrates for further functionalizations. Thus, subsequent treatment of these compounds with phenylacetylene under Sonogashira conditions provided the internal alkynes **9a**–**9g** in high yields (Figure 7, Table 4).

3. Conclusion

In summary, we have established a new method to synthesize 1,3-dienic δ-sultones, based on earlier work (*9, 10*). The scope was expanded to include various substituents at the phenyl residue. We optimized the reaction conditions, especially temperature and SO_3 source, by adjusting them for each substrate individually. All sultones were generated in moderate yields up to 47%, however, in a single operation. Furthermore, we have shown that these sultones could be functionalized with complete regioselectivity in excellent yields. Bromination only occurred at the carbon atom adjacent to the sulfur atom, and a subsequent Sonogashira coupling with phenylacetylene was carried out in good yields.

4. Experimental

4.1. *General*

All reactions requiring exclusion of moisture were run under argon using flame-dried glassware. Solvents were dried by distillation from Na (dioxane), P_2O_5 ($CHCl_3$), or by passing through activated alumina (CH_2Cl_2). Solvent mixtures are reported as v/v ratios. All commercially available compounds were used as received unless stated otherwise. Starting alkynes were synthesized from the corresponding aryl bromides by two-step procedures via Sonogashira coupling with 2-methyl-3-butyn-2-ol (*14*) with subsequent cleavage using anhydrous KOH and 18-crown-6 in benzene for the retro Favorski reaction (*15*) (alkynes **1b**, **1c**, **1e**–**1h**) or with ethynyltrimethylsilane with subsequent cleavage using KOH in methanol/diethyl ether (*16*) (alkyne **1d**). Sulfur (VI) oxide was distilled from 60% oleum or a P_2O_5/H_2SO_4 mixture (1:2, mol/mol) and converted into dioxane sulfotrioxide by a known method (*12*). Flash chromatography: Merck silica gel 60 (40–63 μm). Thin-layer chromatography: Merck silica gel 60 F_{254} plates with UV visualization of the spots. Melting points: Kleinfeld Labortechnik Electrothermal IA 9100 apparatus. ^{1}H and ^{13}C NMR: Bruker DRX-500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, $CDCl_3$, δ (ppm), calibrated to the residual resonance of the solvent) or else Bruker AC-300 (^{1}H: 300 MHz, ^{13}C: 75.4 MHz, $CDCl_3$, δ (ppm), calibrated to the residual resonance of the solvent), s = singlet, d = doublet, t = triplet, m = multiplet, psd = pseudo-doublet. Mass spectra: Hewlett Packard 5890 GC coupled with a Hewlett Packard 5972 detector and Agilent 6890N GC coupled with an Agilent 5973N detector (GC/MS, m/z, 70 eV), or else Hewlett Packard 1100 – Bruker EsquireIon Trap (ESI/APCI, m/z, 10–50 V). FT-IR spectra: Nicolet 205 and Nicolet Avatar 360 spectrometer (ν, cm^{-1}). X-ray diffraction analysis: Nonius Kappa CCD diffractometer equipped with a molybdenum fine-focus sealed tube.

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4.2. *Preparation of sultones 2a–2d and 2g from arylalkynes 1a–1d and 1g with dioxane sulfotrioxide 3* (*general procedure 1*)

The arylalkyne **1a**–**1d** or **1g** (2.5 mmol) was dissolved in a $CHCl_3$/dioxane mixture (4 mL, 1:1) in a 10-mL flask at rt. Dioxane sulfotrioxide **3** (0.420 g, 2.5 mmol) was added, and the mixture was stirred under reaction conditions as shown in Table 1. After cooling to rt, the reaction mixture was filtered through a silica gel layer (2 cm) eluting with ethyl acetate. The volatiles were removed in vacuo, and the products were purified by column chromatography with pentane/ethyl acetate.

4.3. *Preparation of sultones 2a–2d and 2g from arylalkynes 1a–1d and 1g with trimethylsilyl chlorosulfonate 4* (*general procedure 2*)

The arylalkyne **1a**–**1d** or **1g** (2.5 mmol) was dissolved in a $CHCl_3$/dioxane mixture (6 mL, 1:1) in a 10-mL flask and cooled to 0 °C. Trimethylsilyl chlorosulfonate **4** (0.472 g, 2.5 mmol) was added dropwise at this temperature. Then the cooling bath was removed, and the mixture was stirred under reaction conditions as shown in Table 2. The resulting mixture was filtered at rt through a silica gel layer (2 cm) eluting with ethyl acetate. The volatiles were removed in vacuo, and the products were purified by column chromatography with pentane/ethyl acetate.

4.4. *Preparation of sultones 2e and 2f from arylalkynes 1e and 1f* (*general procedure 3*)

The methoxyphenylethyne **1e** or **1d** (2.5 mmol) was dissolved in CH_2Cl_2 (10 mL) in a 50-mL flask at rt. Dioxane (7 mL) and $CHCl_3$ (3 mL) were added, and the solution was cooled to −78 °C.

Trimethylsilyl chlorosulfonate **4** (0.472 g, 2.5 mmol) dissolved in 1:1 dioxane/CH_2Cl_2 (1 mL) was added to the alkyne solution dropwise over 30 min at −78 °C. The resulting mixture was stirred for 3 h at this temperature and warmed slowly to rt. After stirring for 60 h, the reaction mixture was filtered through a silica gel layer (ca. 3 cm) eluting with ethyl acetate. The volatiles were removed in vacuo, and the products were purified by column chromatography with pentane/ethyl acetate.

4.4.1. *4,6-Diphenyl-[1,2]-oxathiine 2,2-dioxide* (***2a***)

Column chromatography with pentane/ethyl acetate (5:1). Yield: see Tables 1 and 2. Pale yellow crystalline compound, m.p. 158 °C. $R_f = 0.32$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 6.73 (s, 1H), 6.79 (s, 1H), 7.46–7.62 (m, 8H), 7.79–7.83 (m, 2H). ^{13}C NMR: 102.23 (CH), 113.12 (CH), 125.09 (2 CH), 126.81 (2 CH), 129.00 (2 CH), 129.30 (2 CH), 130.78 (CH), 130.90 (C), 131.43 (CH), 135.56 (C), 147.65 (C), 156.51 (C). MS (ESI): 285 $[M+H]^+$, 302 $[M+NH_4]^+$. IR: 528, 562, 582, 605, 682, 727, 754, 790, 855, 932, 1005, 1041, 1076, 1164, 1224, 1251, 1281, 1345, 1398, 1420, 1450, 1494, 1541, 1578, 1627, 1652, 1696, 1735, 3069, 3093. Elemental analysis: calc. for $C_{16}H_{12}O_3S$: C 67.59, H 4.25, S 11.18; found: C 67.77, H 4.17, S 11.19. For X-ray crystallographic data, see our previous work (*17*).

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4.4.2. *4,6-Ditolyl-[1,2]-oxathiine 2,2-dioxide* (***2b***)

Column chromatography with pentane/ethyl acetate (5:1). Yield: see Tables 1 and 2. Pale yellow solid, m.p. 189 °C. $R_f = 0.37$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 2.40 (s, 6H), 6.65 (s, 1H), 6.67 (s, 1H), 7.24–7.29 (m, 4H), 7.44 (psd, $J = 9.0$ Hz, 2H), 7.68 (psd, $J = 9.0$ Hz, 2H). ^{13}C NMR: 21.32 (CH_3), 21.48 (CH_3), 101.37 (CH), 111.80 (CH), 125.84 (2 CH), 126.86 (2 CH), 128.19 (C), 129.66 (2 CH), 129.92 (2 CH), 132.67 (C), 141.20 (C), 141.98 (C), 147.61 (C), 156.56 (C). MS (ESI): 313 $[M+H]^+$, 642 $[2M+NH_4]^+$. IR: 544, 591, 639, 670, 707, 743, 771, 794, 820, 861, 929, 1004, 1020, 1047, 1126, 1156, 1187, 1230, 1250, 1292, 1345, 1414, 1450, 1510, 1536, 1570, 1621, 2921, 3076. Elemental analysis: calc. for $C_{18}H_{16}O_3S$: C 69.21, H 5.16, S 10.26; found: C 69.95, H 5.17, S 10.84.

4.4.3. *4,6-Di(4-chlorphenyl)-[1,2]-oxathiine 2,2-dioxide* (***2c***)

Column chromatography with pentane/ethyl acetate (5:1). Yield: see Tables 1 and 2. Pale yellow solid, m.p. 200 °C. $R_f = 0.29$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 6.66 (s, 1H), 6.73 (s, 1H), 7.45–7.49 (m, 6H), 7.74 (psd, $J = 9.0$ Hz, 2H). ^{13}C NMR: 102.11 (CH), 113.61 (CH), 127.17 (2 CH), 128.12 (2 CH), 129.22 (C), 129.41 (2 CH), 129.66 (2 CH), 133.80 (C), 137.25 (C), 137.90 (C), 146.41 (C), 155.78 (C). MS (ESI): 353 $[M+H]^+$, 370 $[M+NH_4]^+$, 391 $[M+K]^+$, 727 [2M+Na]. IR: 537, 570, 595, 630, 673, 706, 722 749, 775, 828, 861, 929, 1004, 1048, 1091, 1121, 1159, 1223, 1251, 1288, 1349, 1407, 1459, 1487, 1532, 1560, 1590, 1620, 1912, 2959, 3078. Elemental analysis: calc. for $C_{16}H_{10}Cl_2O_3S$: C 54.41, H 2.85, S 9.08; found: C 53.72, H 2.91, S 8.51.

4.4.4. *4,6-Di(3-chlorphenyl)-[1,2]-oxathiine 2,2-dioxide* (***2d***)

Column chromatography with pentane/ethyl acetate (5:1). Yield: see Tables 1 and 2. Pale yellow solid, m.p. 137–138 °C. $R_f = 0.34$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 6.69 (s, 1H), 6.76 (s, 1H), 7.40–7.54 (m, 6H), 7.69 (d, $J = 7.5$ Hz, 1H), 7.78 (s, 1H). ^{13}C NMR: 102.67 (CH), 114.56 (CH), 124.01 (CH), 124.99 (CH), 125.90 (CH), 126.95 (CH), 130.33 (CH), 130.65 (CH), 130.91

(CH), 131.53 (CH), 132.39 (C), 135.28 (C), 135.44 (C), 137.00 (C), 146.08 (C), 155.34 (C). MS (ESI): 353 $[M+H]^+$, 370 $[M+NH_4]^+$, 727 $[2M+Na]^+$. IR: 548, 560, 587, 649, 666, 689, 747, 777, 806, 823, 851, 882, 933, 1044, 1083, 1165, 1228, 1255, 1274, 1356, 1422, 1473, 1535, 1563, 1620, 1653, 1697, 1733, 3064, 3091. Elemental analysis: calc. for $C_{16}H_{10}Cl_2O_3S$: C 54.41, H 2.85, S 9.08; found: C 54.41, H 3.16, S 7.75.

4.4.5. *4,6-Di(4-methoxyphenyl)-[1,2]-oxathiine 2,2-dioxide* (***2e***)

Column chromatography with pentane/ethyl acetate (3:1). Yield: see Tables 1 and 2. Pale yellow solid, m.p. 162–163 °C (decomp.). Slowly decomposes on the air at rt with the building of pink products. $R_f = 0.34$ (pentane/ethyl acetate, 3:1). ^{1}H NMR: 3.87 (s, 6H), 6.60 (s, 2H), 6.97–7.01 (m, 4H), 7.51 (psd, $J = 9.0$ Hz, 2H), 7.75 (psd, $J = 9.0$ Hz, 2H). ^{13}C NMR: 55.47 (CH_3), 55.49 (CH_3), 100.40 (CH), 110.22 (CH), 114.41 (2 CH), 114.61 (2 CH), 123.49 (C), 127.72 (2 CH), 127.84 (C), 128.33 (2 CH), 147.39 (C), 156.38 (C), 161.71 (C), 162.17 (C). MS (ESI): 345 $[M+H]^+$, 362 $[M+NH_4]^+$, 361 $[M+OH]^-$, 705 $[2M+OH]^-$.

4.4.6. *4,6-Di(2-methoxyphenyl)-[1,2]-oxathiine 2,2-dioxide* (***2f***)

Column chromatography with pentane/ethyl acetate (3:1). Yield: see Tables 1 and 2. Yellow solid, m.p. 127–128 °C. $R_f = 0.32$ (pentane/ethyl acetate, 3:1). ^{1}H NMR: 3.88 (s, 3H), 3.92 (s, 3H), 6.80 (s, 1H), 6.97–7.10 (m, 4H), 7.15 (s, 1H), 7.37–7.46 (m, 3H), 7.82 (d, $J = 7.8$ Hz, 1H). ^{13}C NMR: 55.62 (CH_3), 55.69 (CH_3), 109.33 (CH), 111.41 (CH), 111.59 (CH), 116.08 (CH), 120.03 (C), 120.86 (CH), 120.98 (CH), 125.06 (C), 129.00 (CH), 129.70 (CH), 131.44 (CH), 131.81 (CH), 145.50 (C), 151.41 (C), 157.11 (C), 157.55 (C). MS (ESI): 345 $[M+H]^+$, 362 $[M+NH_4]^+$, 706 $[2\ M+NH_4]^+$. IR: 548, 565, 587, 600, 613, 672, 707, 731, 747, 777, 808, 830, 856, 926, 994, 1019, 1055, 1127, 1157, 1184,1206, 1242, 1272, 1299, 1341, 1432, 1458, 1486, 1532, 1575, 1598, 1623, 2839, 2945, 2998, 3127. Elemental analysis: calc. for $C_{18}H_{16}O_5S$: C 62.78, H 4.68, S 9.81; found: C 61.58, H 4.63, S 8.88.

4.4.7. *4,6-Di(biphenyl-4-yl)-[1,2]-oxathiine 2,2-dioxide* (***2g***)

Column chromatography with pentane/ethyl acetate (10:1). Yield: see Tables 1 and 2. Yellow solid, m.p. 213 °C. $R_f = 0.32$. ^{1}H NMR: 6.78 (s, 1H), 6.83 (s, 1H), 7.41–7.52 (m, 6H), 7.63–7.67 (m, 6H), 7.71–7.75 (m, 4H), 7.90 (psd, $J = 7.4$ Hz, 2H). ^{13}C NMR: 101.97 (CH), 112.70 (CH), 126.40 (2 CH), 127.14 (4 CH), 127.32 (2 CH), 127.63 (2 CH), 127.94 (2 CH), 128.15 (CH), 128.22 (CH), 129.00 (2 CH), 129.01 (2 CH), 129.69 (C), 134.29 (C), 139.67 (C), 139.70 (C), 143.75 (C), 144.23 (C), 147.26 (C), 156.38 (C). MS (ESI): 437 $[M+H]^+$. IR: 568, 603, 635, 694, 747, 761, 834, 863, 933, 1003, 1049, 1074, 1161, 1226, 1291, 1340, 1408, 1484, 1515, 1535, 1560, 1600, 1623, 1697, 1724, 2850, 2922, 3026, 3078. Elemental analysis: calc. for $C_{28}H_{20}O_3S$: C 77.04, H 4.62, S 7.35; found: C 76.67, H 4.16, S 7.15.

4.4.8. *1,3,5-Tritolylbenzene* (***6b***)

Yield 5% by the general procedure 1. Yellow solid. $R_f = 0.85$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 2.42 (s, 9H), 7.16–7.98 (m, 15H). ^{13}C NMR: 21.78 (3 CH_3), 127.84 (6 CH), 129.31 (6 CH), 130.19 (6 CH), 137.89, (3 C), 139.06 (3 C), 142.83 (3 C). MS (GC–MS): 348 (100) $[M]^+$.

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4.5. *Bromination of sultones 2a–2d and 2g* (*general procedure 4*)

Sultone **2a**–**2d** or **2g** (0.5 mmol) was dissolved in $CHCl_3$ (15 mL) in a two-necked flask equipped with a water condenser. Bromine (0.75 mmol, 1.5 equiv.) was added, and the reaction mixture was stirred at 65 °C bath temperature. HBr gas was removed from the reaction mixture by a gentle argon flow. After 1 h, the reaction mixture was cooled, and the volatiles were removed in vacuo. The residue was dissolved in ethyl acetate, filtered through a 2-cm silica gel layer, and the solvent was removed in vacuo.

4.5.1. *3-Bromo-4,6-diphenyl-[1,2]-oxathiine 2,2-dioxide* (***8a***)

Yield: see Table 3. Pale yellow solid, m.p. 144–145 °C. $R_f = 0.34$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 6.50 (s, 1H), 7.44–7.55 (m, 8H), 7.73–7.76 (m, 2H). ^{13}C NMR: 105.62 (CH), 108.61 (C), 125.63 (2 CH), 128.03 (2 CH), 128.85 (2 CH), 129.06 (2 CH), 129.92 (CH), 130.12 (C), 131.47 (CH), 136.16 (C), 145.96 (C), 154.03 (C). MS (ESI): 380 $[M+NH_4]^+$. IR: 556, 609, 626, 676, 695, 753, 788, 804, 856, 888, 919, 957, 1014, 1038, 1072, 1100, 1187, 1236, 1287, 1372, 1419, 1447, 1473, 1485, 1493, 1621, 1654, 1697, 1733, 2922, 3004, 3031, 3087. Elemental analysis: calc. for $C_{16}H_{11}BrO_3S$: C 52.91, H 3.05, S 8.83; found: C 52.82, H 2.80, S 9.01. X-ray: Figure 5.[1]

4.5.2. *3-Bromo-4,6-ditolyl-[1,2]-oxathiine 2,2-dioxide* (***8b***)

Yield: see Table 3. Pale brown solid, m.p. 145–146 °C. $R_f = 0.39$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 2.41 (s, 3H), 2.43 (s, 3H), 6.44 (s, 1H), 7.25–7.32 (m, 4H), 7.38 (psd, $J = 8.3$ Hz, 2H), 7.63 (psd, $J = 8.3$ Hz, 2H). ^{13}C NMR: 21.41 (CH_3), 21.52 (CH_3), 104.97 (CH), 107.51 (C), 125.61 (2 CH), 127.43 (C), 128.04 (2 CH), 129.46 (2 CH), 129.77 (2 CH), 133.55 (C), 140.19 (C), 142.13 (C), 146.10 (C), 154.16 (C). MS (ESI): 391 $[M+H]^+$; 408 $[M+NH_4]^+$. IR: 561, 588, 616, 643, 699, 741, 782, 813, 894, 958, 1011, 1030, 1099, 1123, 1175, 1192, 1273, 1312, 1369, 1409, 1502, 1540, 1753, 1606, 1623, 1684, 1734, 1916, 2857, 2920, 2956, 3033. Elemental analysis: calc. for $C_{18}H_{15}BrO_3S$: C 55.25, H 3.86, S 8.29; found: C 54.87, H 3.35, S 8.99.

4.5.3. *3-Bromo-4,6-di(4-chlorphenyl)-[1,2]-oxathiine 2,2-dioxide* (***8c***)

Yield: see Table 3. Dark yellow solid, m.p. 149 °C. $R_f = 0.32$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 6.42 (s, 1H), 7.40–7.50 (m, 6H), 7.67 (psd, $J = 8.6$ Hz, 2H). ^{13}C NMR: 105.49 (CH), 109.38 (C), 126.90 (2 CH), 128.49 (C),129.26 (2 CH), 129.49 (4 CH), 134.31 (C), 136.29 (C), 137.94 (C), 144.78 (C), 153.30 (C). MS (ESI): 448/450/452 $[M+NH_4]^+$. IR: 684, 725, 755, 777, 845, 880, 946, 996, 1014, 1077, 1098, 1163, 1182, 1238, 1290, 1380, 1426, 1459, 1476, 1507, 1568, 1592, 1645, 1674, 1704, 1869, 2009, 2030, 2056, 2851, 2927, 2981, 3064, 3296. Elemental analysis: calc. for $C_{16}H_9BrCl_2O_3S$: C 44.47, H 2.10, S 7.42; found: C 44.12, H 1.93, S 7.05. X-ray: Figure 6.[1]

4.5.4. *3-Bromo-4,6-di(3-chlorphenyl)-[1,2]-oxathiine 2,2-dioxide* (***8d***)

Yield: see Table 3. Pale brown solid, m.p. 146–147 °C. $R_f = 0.37$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 6.45 (s, 1H), 7.34–7.50 (m, 6H), 7.62 (d, $J = 7.5$ Hz, 1H), 7.71 (s, 1H). ^{13}C NMR: 106.01 (CH), 110.33 (C), 123.75 (CH), 125.64 (CH), 126.26 (CH), 128.06 (CH), 130.19 (CH), 130.31 (CH), 130.42 (CH), 131.59 (CH), 131.72 (C), 134.99 (C), 135.40 (C), 137.49 (C), 144.39 (C), 152.90 (C). MS (ESI): 448/450/452 $[M+NH_4]^+$. IR: 536, 557, 585, 615, 656, 691, 736, 786, 852, 880, 899, 914, 960, 1038, 1078, 1191, 1238, 1276, 1320, 1378, 1421, 1473, 1564, 1592,

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1621, 1697, 2924, 3080. Elemental analysis: calc. for $C_{16}H_9BrCl_2O_3S$: C 44.47, H 2.10, S 7.42; found: C 44.14, H 2.30, S 7.12.

4.5.5. *4,6-Di(biphenyl-4-yl)-3-brom-[1,2]-oxathiine 2,2-dioxide* (***8g***)

Yield: see Table 3. Yellow solid, m.p. 166 °C. $R_f = 0.40$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 6.57 (s, 1H), 7.37–7.52 (m, 6H), 7.56–7.74 (m, 10H), 7.83 (psd, $J = 8.0$ Hz, 2H). ^{13}C NMR: 105.45 (CH), 108.33 (C), 126.12 (2 CH), 127.09 (2 CH), 127.15 (2 CH), 127.47 (2 CH), 127.66 (2 CH), 128.04 (CH), 128.24 (CH), 128.64 (2 CH), 128.90 (C), 128.98 (4 CH), 134.94 (C), 139.55 (C), 139.86 (C), 142.86 (C), 144.26 (C), 145.70 (C), 153.91 (C). MS (ESI): 517 $[M+H]^+$, 534 $[M+NH_4]^+$, 539 $[M+Na]^+$. IR: 539, 564, 580, 638, 693, 729, 763, 788, 829, 893, 959, 1004, 1035, 1076, 1099, 1118, 1187, 1239, 1278, 1331, 1376, 1420, 1458, 1485, 1516, 1557, 1624, 1731, 1924, 2853, 2926, 3031, 3064. Elemental analysis: calc. for $C_{28}H_{19}BrO_3S$: C 65.25, H 3.72, S 6.22, found: C 65.27, H 3.52, S 5.96.

4.5.6. *Bromination of sultones **2e** and **2f*** (*general procedure 5*)

Sultone **2e** or **2f** (0.1 mmol) was dissolved in $CHCl_3$ (15 mL). NBS (0.019 g, 0.105 mmol) was added, and the reaction mixture was stirred at rt. After 1 h, the volatiles were removed in vacuo. The residue was dissolved in ethyl acetate and filtered through a 2-cm silica gel layer. The solvent was removed in vacuo, and the products were purified by column chromatography with pentane/ethyl acetate (3:1).

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4.5.7. *3-Bromo-4,6-di(4-methoxyphenyl)-[1,2]-oxathiine 2,2-dioxide* (***8e***)

Yield: see Table 3. Pale yellow solid, m.p. 127–128 °C. Slowly decomposed when exposed to air at rt with formation of pink products. $R_f = 0.38$ (pentane/ethyl acetate, 3:1). ^{1}H NMR: 3.86 (s, 3H), 3.87 (s, 3H), 6.35 (s, 1H), 6.94–7.01 (m, 4H), 7.44 (psd, $J = 9.0$ Hz, 2H), 7.67 (psd, $J = 9.0$ Hz, 2H). ^{13}C NMR: 55.38 (CH_3), 55.47 (CH_3), 104.03 (CH), 105.89 (C), 114.06 (2 CH), 114.47 (2 CH), 122.53 (C), 126.91 (2 CH), 129.79 (2 CH), 133.71 (C), 145.87 (C), 153.89 (C), 160.71 (C), 162.19 (C). MS (ESI): 423 $[M+H]^+$.

4.5.8. *3-Bromo-4,6-di(2-methoxyphenyl)-[1,2]-oxathiine 2,2-dioxide* (***8f***)

Yield: see Table 3. Pale brown solid, m.p. 142–143 °C. $R_f = 0.35$ (pentane/ethyl acetate, 3:1). ^{1}H NMR: 3.97 (s, 6H), 7.00 (s, 1H), 7.05–7.17 (m, 4H), 7.36–7.40 (m, 1H), 7.49–7.58 (m, 2H), 7.92 (dd, $J = 7.9$ and 1.7 Hz, 1H). ^{13}C NMR: 55.62 (CH_3), 55.65 (CH_3), 110.08 (C), 111.21 (CH), 111.42 (CH), 111.48 (CH), 119.19 (C), 120.64 (CH), 120.89 (CH), 125.53 (C), 128.63 (CH), 129.51 (CH), 131.06 (CH), 132.02 (CH), 144.75 (C), 150.07 (C), 156.09 (C), 157.47 (C). MS (ESI): 423 $[M+H]^+$, 440 $[M+NH_4]^+$, 864 $[2M+NH_4]^+$. IR: 528, 574, 612, 652, 683, 747, 784, 806, 835, 852, 896, 956, 1008, 1045, 1084, 1122, 1186, 1245, 1289, 1370, 1433, 1458, 1473, 1490, 1529, 1611, 1632, 1729, 2839, 2966, 3015, 3117. Elemental analysis: calc. for $C_{18}H_{15}BrO_5S$: C 51.08, H 3.57, S 7.58; found: 50.89, H 3.32, S 7.32.

4.6. *Sonogashira coupling of bromo sultones 8a–8f* (*general procedure 6*)

Starting sultone **8a**–**8f** (0.2 mmol) was dissolved in THF (4 mL) and triethylamine (2 mL) in a two-necked flask equipped with a water condenser. Phenylacetylene **1a** (0.4 mmol) and triphenylphosphine (0.025 mmol) were added, and the reaction mixture was stirred at rt. After 5 min,

$PdCl_2$ and CuI (both 0.01 mmol) were added, and the reaction mixture was heated at 77 °C bath temperature. After 24 h, the volatiles were removed in vacuo. The residue was dissolved in ethyl acetate and filtered through a 2-cm silica gel layer. The solvent was removed in vacuo, and the products were purified by column chromatography with pentane/ethyl acetate (3:1).

4.6.1. *4,6-Diphenyl-3-(phenylethynyl)-1,2-oxathiine 2,2-dioxide* (***9a***)

Yield: see Table 4. Dark yellow solid, m.p. 125–126 °C. $R_f = 0.30$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 6.64 (s, 1H), 7.12–7.17 (m, 2H), 7.23–7.45 (m, 10H), 7.65–7.71 (m, 3H). ^{13}C NMR: 73.89 (C), 81.53 (C), 102.10 (C), 105.32 (CH), 121.74 (C), 125.76 (CH), 128.41 (3 CH), 128.44 (CH), 128.51 (CH), 128.55 (CH), 128.98 (CH), 129.19 (CH), 130.68 (C), 131.68 (CH), 132.46 (3 CH), 133.75 (CH), 133.96 (CH), 135.80 (C), 147.21 (C), 154.89 (C). MS (ESI): 385 $[M+H]^+$, 402 $[M+NH_4]^+$, 407 $[M+Na]^+$, 786 $[2M+NH_4]^+$, 791 $[2M+Na]^+$. IR: 541. 571, 585, 647, 662, 682, 702, 748, 766, 826, 865, 908, 926, 1006, 1033, 1075, 1123, 1186, 1238, 1282, 1319, 1369, 1397, 1449, 1478, 1494, 1515, 1613, 1697, 1733, 2186, 3025, 3059. Elemental analysis: calc. for $C_{24}H_{16}O_3S$: C 74.98, H 4.19, S 8.34; found: C 75.05, H 4.12, S 8.10.

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4.6.2. *4,6-Ditolyl-3-(phenylethynyl)-1,2-oxathiine 2,2-dioxide* (***9b***)

Yield: see Table 4. Yellow solid, m.p. 65 °C. $R_f = 0.35$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 2.34 (s, 3H), 2.37 (s, 3H), 6.59 (s, 1H), 7.18–7.28 (m, 7H), 7.37–7.38 (m, 2H), 7.57–7.62 (m, 4H). ^{13}C NMR: 21.49 (CH_3), 21.54 (CH_3), 79.93 (C), 101.67 (C), 104.59 (CH), 112.95 (C), 122.02 (C), 125.77 (2 CH), 128.03 (C), 128.38 (2 CH), 128.50 (2 CH), 129.27 (3 CH), 129.76 (2 CH), 131.65 (2 CH), 133.01 (C), 140.78 (C), 142.13 (C), 147.35 (C), 155.05 (C). MS (ESI): 413 $[M+H]^+$, 430 $[M+NH_4]^+$. IR: 593, 640, 688, 754, 814, 910, 1004, 1022, 1115, 1180, 1240, 1318, 1371, 1419, 1440, 1457, 1485, 1509, 1558, 1608, 1655, 1733, 2192, 2863, 2921, 3026, 3058. Elemental analysis: calc. for $C_{26}H_{20}O_3S$: C 75.70, H 4.89, S 7.77; found: C 75.45, H 5.02, S 7.42.

4.6.3. *4,6-Di(4-Chlorphenyl)-3-(phenylethynyl)-1,2-oxathiine 2,2-dioxide* (***9c***)

Yield: see Table 4. Dark yellow solid, m.p. 90–92 °C. $R_f = 0.31$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 6.62 (s, 1H), 7.31–7.52 (m, 9H), 7.71 (psd, $J = 8.7$ Hz, 4H). ^{13}C NMR: 79.29 (C), 103.08 (C), 105.19 (CH), 114.57 (C), 121.47 (C), 127.00 (2 CH), 128.51 (2 CH), 128.98 (2 CH), 129.05 (C), 129.44 (2 CH), 129.75 (CH), 129.89 (2 CH), 131.76 (2 CH),134.07 (C), 136.63 (C), 137.87 (C), 145.60 (C), 154.04 (C). MS (ESI): 470 $[M+NH_4]^+$. IR: 552, 581, 605, 631, 687, 752, 781, 822, 907, 1007, 1088, 1121, 1182, 1233, 1373, 1401, 1459, 1485, 1530, 1590, 1621, 1907, 2189, 2853, 2922, 3079. Elemental analysis: calc. for $C_{24}H_{14}Cl_2O_3S$: C 63.59, H 3.11, S 7.07; found: C 63.88, H 3.33, S 6.85.

4.6.4. *4,6-Di(3-Chlorphenyl)-3-(phenylethynyl)-1,2-oxathiine 2,2-dioxide* (***9d***)

Yield: see Table 4. Dark yellow solid, m.p. 43–44 °C. $R_f = 0.31$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 6.68 (s, 1H), 7.35–7.53 (m, 9H), 7.59–7.63 (m, 1H), 7.66–7.71 (m, 1H), 7.76–7.79 (m, 2H). ^{13}C NMR: 79.14 (C), 103.69 (C), 105.70 (CH), 115.44 (C), 121.35 (C), 123.84 (CH), 125.72 (CH), 126.63 (CH), 128.51 (2 CH), 128.60 (CH), 129.82 (CH), 130.01 (CH), 130.36 (CH), 130.49 (CH), 131.47 (CH), 131.83 (2 CH), 132.27 (C), 134.70 (C), 135.35 (C), 137.14 (C), 145.04 (C), 153.59 (C). MS (ESI): 453 $[M+H]^+$, 470 $[M+NH_4]^+$. IR: 528, 574, 592, 643, 683, 754, 779, 857, 884, 924, 997, 1012, 1079, 1098, 1126, 1168, 1235, 1300, 1375, 1422, 1479, 1507, 1523,

1593, 1619, 1652, 1686, 1732, 2190, 2921, 3066. Elemental analysis: calc. for $C_{24}H_{14}Cl_2O_3S$: C 63.59, H 3.11, S 7.07; found: C 63.90, H 3.42, S 6.84.

4.6.5. *4,6-Di(4-methoxyphenyl)-3-(phenylethynyl)-1,2-oxathiine 2,2-dioxide* (***9e***)

Yield: see Table 4. Dark yellow oil, $R_f = 0.31$ (pentane/ethyl acetate, 3:1). ^{1}H NMR: 3.87 (s, 3H), 3.88 (s, 3H), 6.58 (s, 1H), 6.95–7.04 (m, 4H), 7.30–7.36 (m, 3H), 7.42–7.46 (m, 2H), 7.74 (m, 4H). ^{13}C NMR: 55.40 (CH_3), 55.47 (CH_3), 80.14 (C), 101.18 (C), 103.51 (CH), 111.43 (C), 113.89 (2 CH), 114.47 (2 CH), 122.09 (C), 123.22 (C), 127.62 (2 CH), 128.09 (C), 128.34 (2 CH), 129.13 (CH), 130.24 (2 CH), 131.53 (2 CH), 147.21 (C), 154.86 (C), 161.24 (C), 162.23 (C). MS (ESI): 445 $[M+H]^+$, 462 $[M+NH_4]^+$, 906 $[2M+NH_4]^+$, 911 $[2M+Na]^+$. IR: 536, 582, 687, 755, 798, 909, 1024, 1076, 1172, 1228, 1255, 1308, 1369, 1455, 1484, 1509, 1538, 1558, 1571, 1600, 1734, 2192, 2840, 2924, 2961.

4.6.6. *4,6-Di(2-Methoxyphenyl)-3-(phenylethynyl)-1,2-oxathiine 2,2-dioxide* (***9f***)

Yield: see Table 4. Yellow oil, $R_f = 0.32$ (pentane/ethyl acetate, 3:1). ^{1}H NMR: 3.96 (s, 3H), 3.98 (s, 3H), 7.05–7.20 (m, 4H), 7.28 (s, 1H), 7.35–7.45 (m, 5H), 7.48–7.58 (m, 2H), 7.66 (dd, $J = 7.7$ and 1.7 Hz, 1H), 7.95 (dd, $J = 7.7$ and 1.7 Hz, 1H). ^{13}C NMR: 55.55 (CH_3), 55.62 (CH_3), 77.95 (C), 101.58 (C), 110.41 (2 CH), 111.71 (CH), 115.43 (C), 119.74 (C), 120.30 (CH), 120.89 (CH), 122.09 (C), 125.21 (C), 128.27 (2 CH), 128.78 (CH), 129.08 (CH), 130.06 (CH), 131.27 (CH), 131.58 (2 CH), 131.97 (CH), 146.87 (C), 150.53 (C), 156.89 (C), 157.56 (C). MS (ESI): 445 $[M+H]^+$, 462 $[M+NH_4]^+$, 906 $[2\ M+NH_4]^+$, 911 $[2\ M+Na]^+$. IR: 592, 642, 689, 751, 810, 837, 912, 991, 1021, 1049, 1121, 1183, 1247, 1290, 1369, 1396, 1420, 1434, 1458, 1474, 1485, 1528, 1598, 1630, 2194, 2838, 2937, 3068.

4.6.7. *4,6-Di-(Biphenyl-4-yl)-3-(phenylethinyl)-[1,2]-oxathiine 2,2-dioxide* (***9g***)

Yield: see Table 4. Yellow solid, m.p. 189 °C. $R_f = 0.30$ (pentane/ethyl acetate, 5:1). ^{1}H NMR: 6.81 (s, 1H), 7.35–7.37 (m, 3H), 7.42–7.52 (m, 8H), 7.64–7.78 (m, 8H), 7.87–7.91 (m, 4H). ^{13}C NMR: 79.87 (C), 102.42 (C), 105.11 (CH), 113.70 (C), 121.85 (C), 126.27 (2 CH), 127.12 (2 CH), 127.18 (2 CH), 127.22 (2 CH), 127.65 (2 CH), 128.06 (CH), 128.24 (CH), 128.44 (2 CH), 128.98 (4 CH), 129.09 (2 CH), 129.45 (CH), 129.49 (CH), 131.71 (2 CH), 134.65 (C), 139.61 (C), 139.94 (C), 143.24 (C), 144.21 (C), 146.77 (C), 154.74 (C). MS (ESI): 537 $[M+H]^+$, 554 $[M+NH_4]^+$, 559 $[M+Na]^+$. IR: 545, 583, 632, 684, 725, 748, 761, 783, 836, 907, 1000, 1025, 1114, 1190, 1238, 1298, 1346, 1375, 1396, 1456, 1483, 1512, 1600, 2181, 2845, 2922, 3028, 3057. Elemental analysis: calc. for $C_{36}H_{24}O_3S$: C 80.57 H 4.51 S 5.98 found: C 80.21 H 4.44 S 5.83.

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Note

1. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 776086 (**6b**), CCDC 776085 (**8a**), CCDC 776084 (**8c**).

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