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Solvent-Dependent Reactions for the Synthesis of β-Keto-Benzo-δ-Sultone Scaffolds via DBU-Catalyzed O-Sulfonylation/Intramolecular Baylis–Hillman/1,3-H Shift or Dehydration Tandem Sequences

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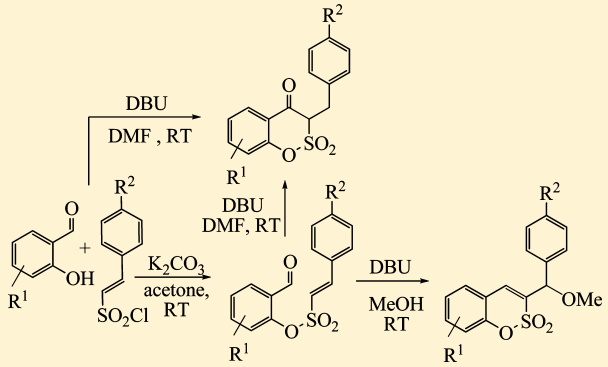
Supporting Information

ABSTRACT: We have developed a solvent-dependent method for the synthesis of novel benzo-δ-sultone scaffolds. A variety of benzylbenzo[*e*][1,2]oxathiin-4(3*H*)-one-2,2-dioxides were obtained in high yields in DMF using a one-pot, DBU-catalyzed condensation of 2-hydroxybenzaldehydes with a number of (*E*)-2-phenylethenesulfonyl chlorides. On the other hand, the initially prepared 2-formylphenyl-(*E*)-2-phenylethenesulfonate derivatives underwent DBU-catalyzed reactions to a series of 3-[methoxy-(phenyl)methyl]benzo[*e*][1,2]oxathiine-2,2-dioxides in moderate to good yields in MeOH. These reactions presumably proceed via DBU-catalyzed O-sulfonylation/intramolecular Baylis–Hillman/1,3-H shift or dehydration tandem sequences, respectively.



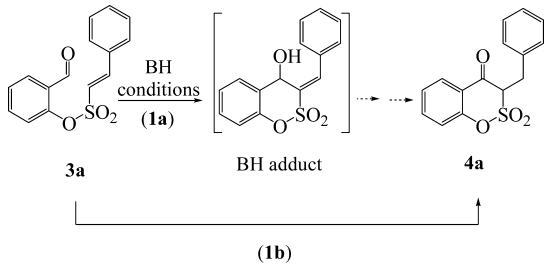
INTRODUCTION

A base-catalyzed reaction of carbon electrophiles with the activated alkenes (alkynes) or electron-deficient Michael-accepting components, known as Baylis–Hillman (BH) reaction, is an efficient process going cleanly under very mild conditions, affording a highly functionalized adduct.[1] Considerable progress has been achieved in developing effective catalysts such as DBU,[2] DABCO,[3] DMAP,[4] PR_3,[5] Et_3N,[6] quinuclidine,[7] and imidazole.[8] The BH reaction was discovered in 1972.[9] Recent attention has been focused on the intramolecular versions of the BH reaction.[10] Such reactions in principle can provide carbocyclic or heterocyclic compounds in different ring sizes with functionality.[11]

The internal esters of hydroxy sulfonic acids or sulfur analogues of lactones, which are called sultones, constitute a class of heterocyclic compounds whose chemistry continues to be of interest.[12] The biological activities of sultones consist of skin sensitization[13] and antiviral activities.[14] Sultones are considered as sulfoalkylating agents due to their easy reaction with a variety of nucleophiles for the synthesis of alkylsulfonic acids.[15] Traditionally, sultone synthesis has relied on classical cyclization protocols such as elimination reaction of the corresponding hydroxy sulfonic acid derivatives,[16] treatment of diazotized amino sulfonic acids and esters with powdered copper,[17] and intramolecular Diels–Alder reaction of vinylsulfonic acid esters.[18] A number of transition-metal-catalyzed processes and indirect methods to sultones have also recently been reported.[19] Sultones are known as valuable heterocyclic intermediates that offer novel possibilities for stereoselective transformations. For example, δ-sultones obtained via rhodium-catalyzed reaction of sulfonate ester derivatives have undergone reductive and oxidative reactions that make possible excision of the $-SO_3-$ moiety.[19a] On the other hand, the β-iodo-α,β-unsaturated γ-sultones were found to show dual behavior with soft or hard nucleophiles.[20]

Recently reported discovery of a new family of non-nucleoside anti-HCMV and anti-VZV agents based upon the β-keto-γ-sultone template[21] prompted us to explore the synthesis of β-keto-δ-sultone template as the structurally related analogue. To achieve this goal, we initially prepared the bifunctional 2-formylphenyl-(*E*)-2-phenylethenesulfonates (**3a**) (Scheme 1a). We then examined the possibility of doing intramolecular BH reaction on **3a** to obtain the corresponding BH adduct as the precursor for the preparation of the desired β-keto-δ-sultone (**4a**). The preliminary results of our investigation showed that **4a** has remarkably been generated after subjecting **3a** to the BH conditions (Scheme 1b). Details of the serendipitous formation of β-keto-benzo-δ-sultones via an one-pot reaction is described in this presentation.

Scheme 1. (1a) Proposed Procedure for the Synthesis of β-Keto-δ-sultone, (1b) Direct Transformation of 3a into 4a



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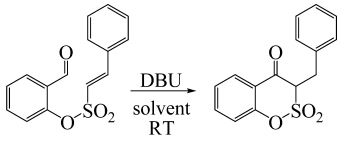
RESULTS AND DISCUSSION

Vinyl sulfonate **3a**, prepared via condensation of aldehyde **1a** with (*E*)-2-phenylethenesulfonyl chloride (**2a**)[22] (vide infra), served for our early exploration of intramolecular BH chemistry (Scheme 2, Table 1). Compared to other solvents that afford the cyclic adduct **4a** in 10−35% yields within 120 h (entries 1−6, Table 1), **4a** was obtained in 40% yield in DMF, upon addition of DBU (50 mol %) (entry 7, Table 1). Changing the amount of solvent from 10 to 3 mL drastically reduced the reaction time to 6 h (entry 8, Table 1). Increasing the DBU amount from 50 to 100 mol % was found to increase the yield of **4a** to 65% (entry 9, Table 1). It was discovered that reaction proceeds to completion within 48 h, affording **4a** in 89% yield (entry 10, Table 1). An excess of DBU was found to have no effect on the increasing yield of **4a**, although reaction time was decreased to 6 h (entry 11, Table 1). It has recently been reported that the BH reaction is second order in aldeyde.[23] Therefore, the effect of decreasing amount of solvent on rate enhancement is rationalized. Although the BH reactions have been found to be efficient by stoichiometric amount of base,[23] rate enhancement upon addition of 200 mol % of DBU may be interpreted perhaps by shifting away from the activated alkene toward the corresponding sulfonate anion as the initial equilibrium is established (see Scheme 4). That the reaction proceeds efficiently in DMF may be due to unique solvation of the polar transition state in this solvent.

Scheme 2. Product 4a Obtained via DBU-Catalyzed BH Reaction of 3a



3a **4a**

Table 1. Effect of Solvent on the Formation of 4a

entry	solvent (mL)	time (h)	yield (%)[a]
1	H_2O (10)	120	10
2	$PhCH_3$ (10)	120	20
3	MeCN (10)	120	35
4	CH_2Cl_2 (10)	120	15
5	1,4-dioxane (10)	120	11
6	Et_2O (10)	120	11
7	DMF (10)	120	42
8	DMF (3)	6	45
9	DMF (3)[b]	6	65
10	DMF (3)[b]	48	89
11	DMF (3)[c]	6	89

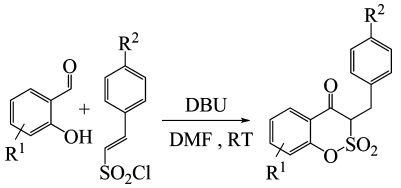
[a]Isolated yields. [b]100 mol % of DBU was used. [c]200 mol % of DBU was used.

Utilization of DABCO, imidazole, 1,2,4-triazole, triethylamine, DMAP, and a tertiary phosphine such as Ph_3P, which are commonly employed in the traditional BH coupling, was ineffective at promoting cyclization of sulfonate **3a**. Therefore, DBU was used as the efficient base in the next steps.

Our later studies revealed that **4a** could be prepared if aldehyde **1a** and (*E*)-phenylethenesulfonyl chloride (**2a**) were reacted with DBU (300 mol %) in a one-pot reaction in DMF at room temperature. Therefore, the implication of 2-formylphenyl-(*E*)-2- phenylethenesulfonate **3a** in the initial reaction is confirmed.

This new method was applied to a range of substrates with different substitution patterns of the aromatic rings (Scheme 3, Table 2). The structures of **4a−n** were deduced by elemental analysis, MS, IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. For example, part of the ^{1}H NMR spectrum of, for example, **4a** exhibited two doublet of doublets at δ 3.56 (1H, J = 14.7, 5.6 Hz) and 3.62 (1H, J = 14.7, 7.0 Hz) due to Ph−CH_2 and one doublet of doublets at δ 4.54 (1H, J = 6.8, 5.8 Hz) for CHC═O groups, respectively. The ^{1}H-decoupled ^{13}C NMR spectrum of **4a** showed 13 distinct signals, including a characteristic signal at δ 185.3 due to C═O group, in agreement with the proposed structure.

Scheme 3. Product 4a−o Obtained via DBU-Catalyzed Reaction of 1a−e with 2a−d



1a-e **2a-d** **4a-o**

Table 2. Results Obtained for the Formation of 4a−o

entry	R^1	R^2	time (min)	product	yield (%)[a]
1	H	H	360	**4a**	89
2	6-OMe	H	660	**4b**	90
3	5-OMe	H	1080	**4c**	88
4	4-Br	H	300	**4d**	88
5	H	4-Me	210	**4e**	85
6	6-OMe	4-Me	210	**4f**	85
7	4-Br	4-Me	220	**4g**	87
8	H	4-Br	100	**4h**	84
9	6-OMe	4-Br	140	**4i**	85
10	4-Br	4-Br	20	**4j**	84
11	H	4-Cl	150	**4k**	83
12	6-OMe	4-Cl	180	**4l**	87
13	4-Br	4-Cl	40	**4m**	89
14	4-Cl	H	300	**4n**	88
15	4-NO_2	H	300	**4o**	

[a]Isolated yield.

The proposed mechanism for the DBU-catalyzed intramolecular BH reaction is illustrated in Scheme 4. The in situ generated **3a** from condensation of **1a** with **2a** undergoes the nucleophilic addition of the DBU at the β position to form the sulfonate anion **I**. Subsequent addition of DBU-associated sulfonate anion **I** to the aldehyde group affords the intermediate **II**. The generated alcohol **III** in the next step is transformed into ketone **4a** perhaps by a DBU-catalyzed 1,3-H shift. The rate-determining step (RDS) of the Baylis−Hillman reaction involves an aldol-type reaction between the zwitterionic enolate and an aldehyde (Scheme 4).[24] The stabilization of the intermediate β-ammonium enolate through conjugation seems to be a more likely explanation for the origin of the increased reactivity of DBU (Figure 1).[25] The higher basicity of DBU as a sterically hindred base with lower pK_a[26] in comparison to DABCO,[26] imidazole,[27] 1,2,4-triazole,[28] triethylamine,[27] DMAP,[29] and Ph_3P[27] may not also be overlooked.

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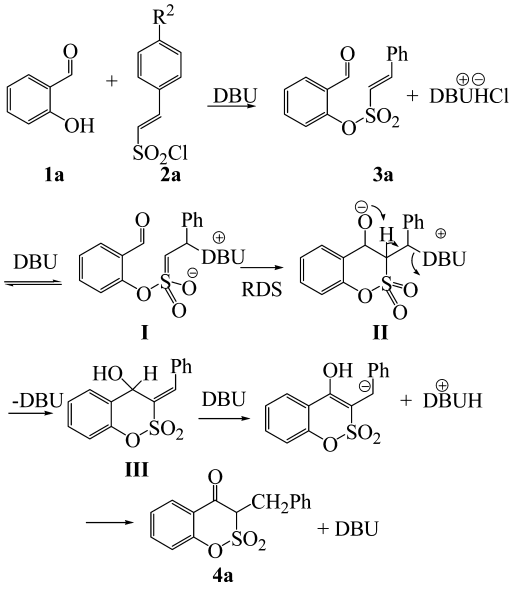
Scheme 4. Suggested Mechanism for the Formation of 4a



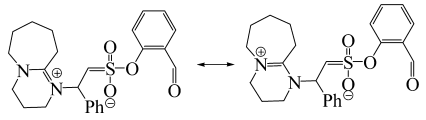


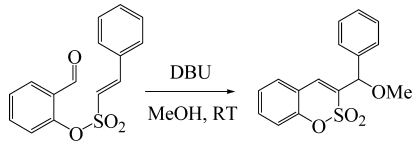
Figure 1. Stabilization of the β-ammonium enolate through conjugation.

Therefore, in this specific case, the basicity of DBU is more important than its steric hindrance.

The results indicated in Table 2 support the suggested mechanism. The increasing equilibrium concentration of enolate **I**, as well as the cyclization rate of **I** to **II**, is expected to increase by electron-withdrawing substituents present at either phenyl rings. Notably, either unsubstituted aldehydes or phenylethenesulfonyl chlorides and those bearing electron-withdrawing halides on the aromatic rings readily afford the corresponding benzo-δ-sultone (entries 1, 4, 8, 11, and 14). In the case of **4j** and **4m**, in which both components bearing electron-withdrawing halides, reactions are surprisingly fast (entries 10 and 13). The aldehyde **4c** bearing a strong electron-donating substituent at the para-position proceeds more sluggishly (entry 3). In addition, benzo-δ-sultones have been formed from reaction of meta-electron-donating substituted aldehydes with unsubstituted or para-electron-donating substituted (*E*)-2-phenylethenesulfonyl chlorides in moderate times (entries 2, 5, and 6). Finally, no reaction progress was observed with 2-hydroxy-5-nitrobenzaldehyde (**1f**) (entry 15). To explore further insight into this reaction, we initially prepared the 2-formyl-4-nitrophenyl (*E*)-2-phenylethenesulfonate (**3l**) (vide infra). When subjected to BH conditions, **3l** failed to show any progress toward the formation of the desired product. Instead, a salt-like product with no movement on the TLC plate was found to have been formed. Consumption of the starting aldehyde **3l** along with the formation of a salt product are telltales that **3l** has been engaged in an unwanted reaction. Although there are several reports in literature on the base-catalyzed BH reaction of nitrophenylaldehydes with different Michael acceptors,[30] the inability of **1f** to show similar BH reactivity remains to be resolved. Further investigation on this subject is currently underway in our laboratory.

Surprisingly, when reaction of **3a** was carried out in MeOH, 3-[methoxy(phenyl)methyl]benzo[*e*][1,2]oxathiine-2,2-dioxides (**5a**) was identified as the sole product (Scheme 5). To our

Scheme 5. DBU-Catalyzed Reaction of 3a to 5a in MeOH



delight, reaction of **3a** either with MeOH/K_2CO_3 or MeOH/NaOMe solutions also afforded product **5a**. To further explore the scope of this reaction, vinyl sulfonates **3b–l** were prepared and subjected to DBU-catalyzed BH reaction in MeOH (Scheme 6, Table 3). As seen, a range of electron-donating

Scheme 6. Results Obtained for the Formation of 5a–l

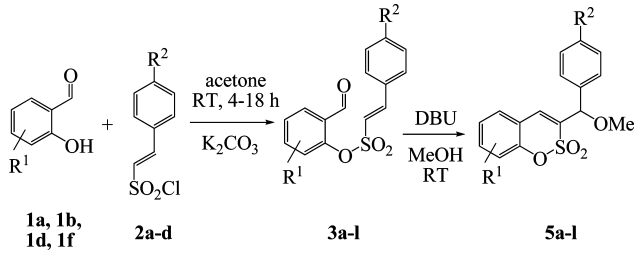


Table 3. Results Obtained for the Formation of 3a–l and 5a–l

entry	R^1	R^2	vinyl sulfonate	yield (%)	time (h)	product	yield (%)[a]
1	H	H	**3a**	96	24	**5a**	53
2	6-OMe	H	**3b**	95	36	**5b**	48
3	4-Br	H	**3c**	96	28	**5c**	55
4	H	4-Me	**3d**	97	58	**5d**	40
5	4-Br	4-Me	**3e**	96	72	**5e**	36
6	H	4-Br	**3f**	95	12	**5f**	65
7	6-OMe	4-Br	**3g**	95	30	**5g**	56
8	4-Br	4-Br	**3h**	94	24	**5h**	54
9	H	4-Cl	**3i**	95	22	**5i**	60
10	6-OMe	4-Cl	**3j**	96	48	**5j**	54
11	4-Br	4-Cl	**3k**	95	72	**5k**	44
12	4-NO_2	H	**3l**	95	72	**5l**	15

[a]Isolated yield.

or electron-withdrawing substituents in either phenyl rings are tolerated. The structures of **5a–l** were deduced by elemental analysis, MS, IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. For example, part of the ^{1}H NMR spectrum of, for example, **5a** exhibited two singlets at δ 5.39 (1H), and 3.49 (3H) due to PhCH and MeO groups, respectively. The ^{1}H-decoupled ^{13}C NMR spectrum of **5a** showed 14 distinct signals, in agreement with the proposed structure.

The suggested mechanism for the formation of **5a** is shown in Scheme 7a. The in situ generated MeO^- via acid–base reaction with DBU promotes the intramolecular BH reaction, affording intermediates **I** and **II**. The latter is easily transformed into **5a** through dehydration rather than the traditional reaction to BH adduct. The pseudoaromatic character, if any, of **5a** may

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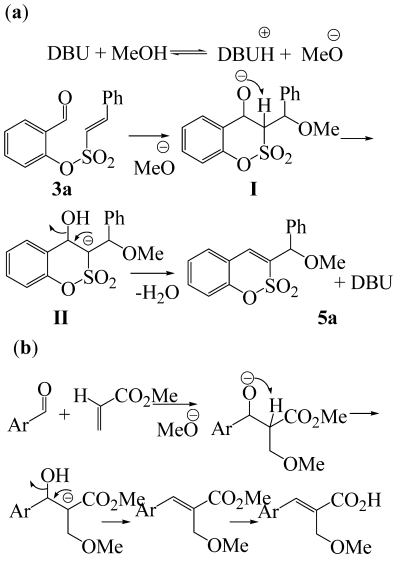
be the driving force for this process. This mechanism was proposed on the basis of the previously reported work by Ciganek, who showed that NaOMe in THF could mediate the coupling of methyl acrylate with aromatic aldehydes.[31] The reactions produced α-methoxymethylcinnamic acids (after hydrolysis) with moderate yields via Baylis–Hillman-type reactions (Scheme 7b).

Scheme 7. (a) Suggested Mechanism for the Formation of 5a in MeOH, (b) Previously Suggested Mechanism of MeO^--Mediated Coupling of Methyl Acrylate with an Aldehyde



Notably, the vinyl sulfonate **3l** containing a nitro group meta to the aldehyde position has proceeded sluggishly to the corresponding adduct **5l** during 72 h (Table 3, entry 12). The formation of **5l** from **3l** in MeOH although with low efficiency is interesting since **3l** failed to show any reactivity in DMF (vide supra).

In conclusion, a number of solvent-dependent BH reactions were carried out in this work for the synthesis of novel benzo-δ-sultone scaffolds. Whereas the one-pot, DBU-catalyzed condensation of 2-hydroxybenzaldehydes with a number of (*E*)-2-phenylethenesulfonyl chlorides exhibit 3-benzylbenzo[*e*]-[1,2]oxathiin-4(3*H*)-one, 2,2-dioxides in high yields in DMF, reactions of the initially prepared 2-formylphenyl-(*E*)-2-phenylethenesulfonate derivatives with DBU afford 3-[methoxy-(phenyl)methyl]benzo[*e*][1,2]oxathiine-2,2-dioxides in moderate to good yields in MeOH. These new structures broaden the benzo-δ-scaffolds that are accessible through intramolecular BH reactions, and many of them may represent interesting pharmacophores. To the best of our knowledge, no method of using an intramolecular BH reaction in the synthesis of β-keto-benzo-δ-sultone scaffolds via tandem sequences is found in literature.

EXPERIMENTAL SECTION

General Information. ^{1}H NMR, ^{13}C NMR, NOESY, HMBC, MS, and elemental analysis were measured with conventional spectrometers. All solvents were purified and dried by following standard procedures unless otherwise stated.

Synthesis of 2-Formylphenyl-(*E*)-2-phenylethenesulfonate Derivatives 3. General procedure: K_2CO_3 (0.69 g, 5 mmol) was added to a solution of 2-hydroxybenzaldehyde (**1a**) (0.61 g, 5 mmol) and (*E*)-2-phenylethenesulfonyl chloride (**2a**) (1.01 g, 5 mmol) in acetone (30 mL). The mixture was stirred for 4 h at rt. The solvent was evaporated under reduce pressure and the residue poured into the water (30 mL). The mixture was extracted with CH_2Cl_2 (30 mL) and the organic phase dried over Na_2SO_4. The solvent was then evaporated under reduced pressure, and the crude product was recrystallized from C_2H_5OH to afford **3a**.

*2-Formylphenyl-(E)-2-phenylethenesulfonate (**3a**):* White solid (1380 mg, 96%); mp 59–62 °C; IR (KBr) ν_{max} 3059, 2885, 1690 (C═O); 1604, 1361 ($-SO_2$), 1147 ($-SO_2$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (1H, s, CHO), 7.96 (1H, d, J = 7.6 Hz, Ar), 7.66 (1H, t, J = 7.62 Hz, Ar), 7.63 (1H, d, J = 15.5 Hz, C═CHAr), 7.53–7.44 (7H, m, Ar), 7.00 (1H, d, J = 15.5 Hz, SO_2CH═C) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.3 (C═O), 151.1, 147.8, 135.9, 132.6, 130.0, 129.8, 129.7, 129.6, 129.2, 128.1, 124.2, 120.3 (C–Ar) ppm; m/z (EI, 70 eV) 287 (10, $M^+ - 1$), 167 (88), 120 (25), 103 (100), 77 (36%). Anal. Calcd for $C_{15}H_{12}O_4S$: C, 62.32; H, 4.12. Found: C, 62.49; H, 4.20%.

*2-Formyl-6-methoxyphenyl-(E)-2-phenylethenesulfonate (**3b**):* White solid (1510 mg, 95%); mp 96–98 °C; IR (KBr) ν_{max} 3065, 2898, 1690 (C═O), 1614, 1576, 1362 ($-SO_2$), 1144 ($-SO_2$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.41 (1H, s, CHO), 7.55 (1H, d, J = 15.6 Hz, C═CHAr), 7.56–7.45 (6H, m, Ar), 7.37 (1H, t, J = 7.9 Hz, Ar), 7.21 (1H, d, J = 8.2 Hz, Ar), 7.07 (1H, d, J = 15.6 Hz, SO_2CH═C), 3.82 (3H, s, MeO) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.7 (C═O), 152.0, 146.0, 140.8, 132.2, 131.8, 129.9, 129.7, 128.1, 128.4, 121.6, 120.4, 118.6 (C–Ar), 56.9 (OCH_3) ppm; m/z (EI, 70 eV) 301 (1, $M^+ - 1$), 167 (83), 151 (53), 103 (100), 77 (42%). Anal. Calcd for $C_{16}H_{14}O_5S$: C, 60.29; H, 4.38. Found: C, 60.37; H, 4.43%.

*2-Formyl-4-bromophenyl-(E)-2-phenylethenesulfonate (**3c**):* White solid (1755 mg, 96%); mp 69–70 °C; IR (KBr) ν_{max} 3064, 2877, 1693 (C═O), 1607, 1380 ($-SO_2$), 1165 ($-SO_2$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (1H, s, CHO), 8.07 (1H, s, Ar), 7.75 (1H, d, J = 8.7 Hz, Ar), 7.63 (1H, d, J = 15.5 Hz, C═CHAr), 7.54–7.46 (5H, m, Ar), 7.33 (1H, d, J = 8.7 Hz, Ar), 6.94 (1H, d, J = 15.5 Hz, SO_2CH═C) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.9 (C═O), 149.9, 148.4, 138.6, 132.8, 132.5, 131.6, 131.0, 129.8, 129.3, 126.0, 121.8, 119.8 (C–Ar) ppm; m/z (EI, 70 eV) 367 (1, $M^+ + 1$), 200 (8), 167 (90), 103 (100), 77 (29%). Anal. Calcd for $C_{15}H_{11}BrO_4S$: C, 49.01; H, 3.00. Found: C, 49.06; H, 3.02%.

*(E)-2-Formylphenyl-2-p-tolylethenesulfonate (**3d**):* White solid (1465 mg, 97%); mp 58–60 °C; %; IR (KBr) ν_{max} 3058, 1690 (C═O), 1601, 1346 ($-SO_2$), 1148 ($-SO_2$), 854, 776 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.38 (1H, s, CHO), 7.94 (1H, dd, J = 7.5, 1.4 Hz, Ar), 7.66 (1H, dd, J = 7.8, 1.6 Hz, Ar), 7.58 (1H, d, J = 15.4 Hz, C═CHAr), 7.46 (2H, t, J = 8.2 Hz, Ar), 7.41 (2H, d, J = 8.0 Hz, Ar), 7.27 (2H, d, J = 7.9 Hz, Ar), 6.90 (1H, d, J = 15.4 Hz, SO_2CH═C), 2.43 (3H, s, CH3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.3 (C═O), 151.2, 147.9, 143.5, 135.8, 130.5, 130.0, 129.8, 129.3, 129.1, 128.0, 124.2, 118.9 (C–Ar), 22.1 (CH3) ppm; m/z (EI, 70 eV) 301 (22, $M^+ - 1$), 285 (17), 181 (75), 118 (100), 91 (29%). Anal. Calcd for $C_{16}H_{14}O_4S$: C, 63.48; H, 4.51. Found: C, 63.56; H, 4.67%.

*(E)-4-Bromo-2-formylphenyl-2-p-tolylethenesulfonate (**3e**):* Yellow solid (1825 mg, 96%); mp 97–99 °C; IR (KBr) ν_{max} 3070, 1683 (C═O), 1599, 1340 ($-SO_2$), 1149 ($-SO_2$), 834, 787 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.29 (1H, s, CHO), 8.07 (1H, d, J = 2.5 Hz, Ar), 7.75 (1H, dd, J = 8.7, 2.5 Hz, Ar), 7.60 (1H, d, J = 15.4 Hz, C═CHAr), 7.42 (2H, d, J = 8.0 Hz, Ar), 7.33 (1H, d, J = 8.8 Hz, Ar), 7.28 (2H, d, J = 8.1 Hz, Ar), 6.87 (1H, d, J = 15.4 Hz, SO_2CH═C), 2.44 (3H, s, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.9 (C═O), 150.1, 148.5, 143.8, 138.5, 132.4, 131.1, 130.5, 129.4, 128.9, 126.0, 121.8, 118.4 (C–Ar), 22.1 (CH_3) ppm; m/z (EI, 70 eV) 380 (1, M^+), 376 (6), 281 (26), 181 (100), 117 (99%). Anal. Calcd for $C_{16}H_{13}BrO_4S$: C, 50.38; H, 3.40. Found: C, 50.41; H, 3.44%.

*(E)-2-Formylphenyl-2-(4-bromophenyl)ethenesulfonate (**3f**):* White solid (1740 mg, 95%); mp 101–104 °C; IR (KBr) ν_{max} 3054, 2894, 1690 (C═O), 1676, 1601, 1341 ($-SO_2$), 1161 ($-SO_2$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.35 (1H, s, CHO), 7.97 (1H, t, J = 7.7 Hz, Ar), 7.68 (1H, t, J = 7.8 Hz, Ar), 7.61 (2H, d, J = 8.4 Hz, Ar), 7.55 (1H, d, J = 15.5 Hz, C═CHAr), 7.48 (1H, t, J = 7.5 Hz, Ar), 7.45 (1H, d, J = 8.2 Hz, Ar), 7.39 (2H, d, J = 8.4 Hz, Ar), 6.98 (1H, d, J =

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15.5 Hz, SO_2CH=C) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.3 (C=O), 150.9, 146.3, 135.9, 133.1, 130.7, 130.5, 130.1, 129.7, 128.2, 127.3, 124.3, 121.1 (C−Ar) ppm; *m*/*z* (EI, 70 eV) 369 (2, M^+ + 2), 367 (3, M^+), 247 (54), 183 (94), 120 (60), 102 (100%). Anal. Calcd for $C_{15}H_{11}BrO_4S$: C, 48.98; H, 3.03. Found: C, 49.06; H, 3.02%.

*(E)-2-Formyl-6-methoxyphenyl-2-(4-bromophenyl)-ethenesulfonate (**3g**):* White solid (1885 mg, 95%); mp 124−126 °C; IR (KBr) ν_{max} 3077, 1693 (C=O), 1481, 1351 (−SO_2), 1142 (−SO_2), 1063, 857 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.39 (1H, s, CHO), 7.61 (2H, d, *J* = 8.3 Hz, Ar), 7.55 (1H, d, *J* = 7.8 Hz, Ar), 7.48 (1H, d, *J* = 15.5 Hz, C=CHAr), 7.22 (1H, d, *J* = 8.2 Hz, Ar), 7.41−7.37 (3H, m, Ar), 7.07 (1H, d, *J* = 15.5 Hz, SO_2CH=C), 3.86 (3H, s, OCH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.6 (C=O), 152.6, 144.5, 140.6, 133.1, 131.7, 131.1, 130.3, 128.5, 126.8, 122.4, 120.6, 118.7 (C−Ar), 60.0 (OCH_3) ppm; *m*/*z* (EI, 70 eV) 398 (5, M^+ + 2), 396 (6, M^+), 247 (71), 181 (72), 151 (100), 102 (85%) . Anal. Calcd for $C_{16}H_{13}BrO_5S$: C, 49.33; H, 3.27. Found: C, 49.38; H, 3.30%.

*(E)-4-Bromo-2-formylphenyl-2-(4-bromophenyl)ethenesulfonate (**3h**):* White solid (2095 mg, 94%); mp 133−135 °C; IR (KBr) ν_{max} 3063, 1691 (C=O), 1467, 1371 (−SO_2), 1156 (−SO_2), 845, 742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.27 (1H, s, CHO), 8.07 (1H, d, *J* = 2.1 Hz, Ar), 7.77 (1H, dd, *J* = 8.7, 2.1 Hz, Ar), 7.62 (2H, d, *J* = 8.2 Hz, Ar), 7.58 (1H, d, *J* = 15.5 Hz, C=CHAr), 7.40 (2H, d, *J* = 8.2 Hz, Ar), 7.33 (1H, d, *J* = 8.7 Hz, Ar), 6.95 (1H, d, *J* = 15.5 Hz, SO_2CH=C) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.8 (C=O), 149.7, 146.9, 138.6, 138.2, 132.8, 131.0, 130.6, 130.5, 127.5, 126.0, 122.0, 120.6 (C−Ar) ppm; *m*/*z* (EI, 70 eV) 447 (1, M^+ + 2), 445 (1, M^+), 247 (90), 183 (84), 102 (100), 63 (28%). Anal. Calcd for $C_{15}H_{10}Br_2O_4S$: C, 40.35; H, 2.18. Found: C, 40.38; H, 2.26%.

*(E)-2-Formylphenyl-2-(4-chlorophenyl)ethenesulfonate (**3i**):* Yellow solid (1525 mg, 95%); mp 113−116 °C; IR (KBr) ν_{max} 3058, 2887, 1691 (C=O), 1595, 1350 (−SO_2), 1176 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.35 (1H, s, CHO), 7.97 (1H, d, *J* = 6.7 Hz, Ar), 7.96 (1H, t, *J* = 6.6 Hz, Ar), 7.57 (1H, d, *J* = 15.5 Hz, C=CHAr), 7.48−7.44 (6H, m, Ar), 6.96 (1H, d, *J* = 15.5 Hz, SO_2CH=C) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.3 (C=O), 150.9, 146.3, 138.8, 135.9, 130.4, 130.3, 130.2, 130.1, 129.8, 128.2, 124.3, 120.9 (C−Ar) ppm; *m*/*z* (EI, 70 eV) 324 (1, M^+ + 2), 322 (3, M^+), 201 (74), 137 (100), 120 (41), 102 (54%). Anal. Calcd for $C_{15}H_{11}ClO_4S$: C, 55.76; H, 3.38. Found: C, 55.82; H, 3.44%.

*(E)-2-Formyl-6-methoxyphenyl-2-(4-chlorophenyl)-ethenesulfonate (**3j**):* White solid (1690 mg, 96%); mp 118−120 °C; IR (KBr) ν_{max} 3071, 1695 (C=O), 1372 (−SO_2), 1147 (−SO_2), 1060, 854 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.39 (1H, s, CHO), 7.55 (1H, dd, *J* = 7.8, 1.4 Hz, Ar), 7.49 (1H, d, *J* = 15.4 Hz, C=CHAr), 7.38 (1H, t, *J* = 8.1 Hz, Ar), 7.46−7.43 (4H, m, Ar), 7.22 (1H, dd, *J* = 8.2, 1.4 Hz, Ar), 7.05 (1H, d, *J* = 15.5 Hz, SO_2CH=C), 3.86 (3H, s, OCH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.6 (C=O), 152.6, 144.4, 140.6, 138.4, 131.7, 130.7, 130.2, 130.1, 128.5, 122.3, 120.6, 118.7 (C−Ar), 56.9 (OCH_3) ppm; *m*/*z* (EI, 70 eV) 354 (1, M^+ + 2), 352 (3, M^+), 201 (66), 151 (62), 137 (74), 102 (49), 49 (100%). Anal. Calcd for $C_{16}H_{13}ClO_5S$: C, 54.39; H, 3.52. Found: C, 54.47; H, 3.71%.

*(E)-4-Bromo-2-formylphenyl-2-(4-chlorophenyl)ethenesulfonate (**3k**).* Yellow solid (1905 mg, 95%); mp 118−120 °C; IR (KBr) ν_{max} 3092, 1691 (C=O), 1446, 1371 (−SO_2), 1156 (−SO_2), 832, 742 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.27 (1H, s, CHO), 8.07 (1H, d, *J* = 2.5 Hz, Ar), 7.71 (1H, dd, *J* = 8.7, 2.5 Hz, Ar), 7.59 (1H, d, *J* = 15.5 Hz, C=CHAr), 7.49−7.44 (4H, m, Ar), 7.33 (1H, d, *J* = 8.7 Hz, Ar), 6.94 (1H, d, *J* = 15.5 Hz, SO_2CH=C) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.9 (C=O), 149.8, 146.8, 139.1, 138.6, 132.8, 131.0, 130.5, 130.2, 130.1, 126.0, 122.0, 120.5 (C−Ar) ppm; *m*/*z* (EI, 70 eV) 401 (2, M^+), 201 (100), 137 (89), 102 (48), 63 (21%). Anal. Calcd for $C_{15}H_{10}BrClO_4S$: C, 44.81; H, 2.36. Found: C, 44.85; H, 2.51%.

*2-Formyl-4-nitrophenyl-(E)-2-phenylethenesulfonate (**3l**):* Cream solid (1580 mg, 95%); mp 104−107 °C; IR (KBr) ν_{max} 3062, 2896, 1693 (C=O), 1609, 1344 (−SO_2), 1162 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (1H, s, CHO), 8.79 (1H, s, Ar), 8.50 (1H, d, *J* = 7.9 Hz, Ar), 7.71 (1H, d, *J* = 15.4 Hz, C=CHAr), 7.67−7.48 (6H, m, Ar), 7.02 (1H, d, *J* = 15.4 Hz, SO_2CH=C) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.1 (C=O), 154.7, 149.2, 146.9, 133.2, 131.3, 130.3, 130.1, 129.9, 129.5, 125.4, 125.6, 119.5 (C−Ar) ppm; *m*/*z* (EI, 70 eV) 334 (10, M^+ + 1), 316 (53), 273 (100), 183 (27), 151 (49%). Anal. Calcd for $C_{15}H_{11}NO_6S$: C, 54.00; H, 3.29; N, 4.14. Found: C, 54.05; H, 3.33; N, 4.20%.

Synthesis of 3-Benzylbenzo[*e*][1,2]oxathiin-4(3*H*)-one-2,2-dioxide Derivatives 4. General procedure: To a stirring solution of DBU (0.453 g, 300 mol %) in DMF (3 mL) were added 2-hydroxybenzaldehyde (**1a**) (0.122 g, 1 mmol) and (*E*)-2-phenylethenesulfonyl chloride (**2a**) (0.202 g, 1 mmol) at room temperature. The progress of the reaction was followed by TLC. After completion, CH_2Cl_2 (20 mL) and H_2O (20 mL) were added and the mixture was neutralized with diluted HCl. The organic phase was separated, and aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, eluent: 1:2, *n*-hexane/CH_2Cl_2) to afford the ketone **4a**.

*3-Benzylbenzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4a**):* White solid (256 mg, 89%); mp 106−108 °C; IR (KBr) ν_{max} 1694 (C=O), 1374 (−SO_2); 1146 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (1H, dd, *J* = 7.9, 1.6 Hz), 7.73 (1H, ddd, *J* = 8.3, 7.6, 1.6 Hz, Ar), 7.42 (1H, t, *J* = 7.6 Hz, Ar), 7.36−7.28 (6H, m, Ar), 4.54 (1H, dd, *J* = 6.8, 5.8 Hz, CHC=O), 3.62 (1H, dd, *J* = 14.7, 7.0 Hz, Ph−CHH), 3.56 (1H, dd, *J* = 14.7, 5.6 Hz, Ph−CHH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.3 (C=O), 153.9, 137.7, 135.6, 129.8, 129.7, 129.2, 128.0, 126.9, 120.9, 119.7 (C−Ar), 72.0 (CH), 31.8 (CH_2) ppm; *m*/*z* (EI, 70 eV) 288 (2, M^+), 224 (100), 207 (11), 147 (53), 91 (38%). Anal. Calcd for $C_{15}H_{12}O_4S$: C, 62.48; H, 4.00 Found: C, 62.49; H, 4.20%.

*3-Benzyl-8-methoxybenzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4b**):* White solid (286 mg, 90%); mp 112−114 °C; IR (KBr) ν_{max} 1681 (C=O), 1368 (−SO_2); 1150 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (1H, d, *J* = 8.8 Hz, Ar), 7.36−7.29 (5H, m, Ar), 6.92 (1H, dd, *J* = 8.8, 2.0 Hz, Ar), 6.72 (1H, d, *J* = 2.0 Hz, Ar), 4.49 (1H, t, *J* = 6.2 Hz, CHC=O), 3.92 (3H, s, OCH_3), 3.61 (1H, dd, *J* = 14.7, 6.7 Hz, Ph−CHH), 3.51 (1H, dd, *J* 14.7, 5.8 Hz, Ph−CHH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.9 (C=O), 167.2, 155.7, 135.8, 131.4, 129.7, 129.2, 127.9, 114.1, 103.9 (C−Ar), 71.5 (CH), 56.7 (OCH_3), 31.9 (CH_2) ppm; *m*/*z* (EI, 70 eV) 318 (0.5, M^+), 254 (100), 177 (53), 150 (35), 91 (25%). Anal. Calcd for $C_{16}H_{14}O_5S$: C, 60.40; H, 4.31. Found: C, 60.37; H, 4.43%.

*3-Benzyl-7-methoxybenzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4c**):* White solid (280 mg, 88%); mp 91−93 °C; IR (KBr) ν_{max} 1681 (C=O), 1368 (−SO_2); 1150 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (1H, d, *J* = 8.8 Hz, Ar), 7.36−7.29 (5H, m, Ar), 6.91 (1H, dd, *J* = 8.8, 2.0 Hz, Ar), 6.72 (1H, d, *J* = 2.0 Hz, Ar), 4.48 (1H, t, *J* = 6.3 Hz, CHC=O), 3.92 (3H, s, OCH_3), 3.61 (1H, dd, *J* = 14.7, 6.7 Hz, Ph−CHH), 3.51 (1H, dd, *J* = 14.7, 5.8 Hz, Ph−CHH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.9 (C=O), 167.2, 155.7, 135.9, 131.4, 129.7, 129.2, 127.9, 114.1, 104.0 (C−Ar), 71.5 (CH), 56.7 (OCH_3), 32.0 (CH_2) ppm; *m*/*z* (EI, 70 eV) 318 (1, M^+), 254 (100), 177 (53), 150 (40), 91 (21%). Anal. Calcd for $C_{16}H_{14}O_5S$: C, 60.34; H, 4.32. Found: C, 60.37; H, 4.43%.

*3-Benzyl-6-bromobenzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4d**):* Yellow solid (322 mg, 88%); mp 118−120 °C; IR (KBr) ν_{max} 1692 (C=O), 1386 (−SO_2); 1165 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (1H, d, *J* = 2.4 Hz, Ar), 7.81 (1H, dd, *J* = 8.7, 2.5 Hz, Ar), 7.36−7.29 (5H, m, Ar), 7.18 (1H, d, *J* = 8.7 Hz, Ar), 4.54 (1H, t, *J* = 6.3 Hz, CHC=O), 3.59 (1H, dd, *J* = 14.7, 6.9 Hz, Ph−CHH), 3.54 (1H, dd, *J* = 14.8, 5.8 Hz, Ph−CHH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.3 (C=O), 152.7, 140.3, 135.2, 132.2, 129.7, 129.3, 128.1, 122.2, 121.6, 120.1 (C−Ar), 71.9 (CH), 31.9 (CH_2) ppm; *m*/*z* (EI, 70 eV) 368 (2, M^+ + 2), 366 (2, M^+), 304 (92), 302 (83), 200 (63), 91 (100%). Anal. Calcd for $C_{15}H_{11}BrO_4S$: C, 49.20; H, 2.81. Found: C, 49.06; H, 3.02%.

*3-(4-Methylbenzyl)benzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4e**):* White solid (257 mg, 85%); mp 149−151 °C; IR (KBr) ν_{max} 1705 (C=O), 1371 (−SO_2); 1165 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.1 (1H, dd, *J* = 7.9, 1.6 Hz, Ar), 7.73 (1H, dt, *J* = 8.4,

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1.6 Hz, Ar), 7.42 (1H, dt, J = 7.9, 0.6 Hz, Ar), 7.29 (1H, d, J = 8.3 Hz, Ar), 7.19 (2H, d, J = 8.0 Hz, Ar), 7.15 (2H, d, J = 8.0 Hz, Ar), 4.52 (1H, dd, J = 6.8, 6.0 Hz, CHC═O), 3.58−3.51 (2H, m, CH_2), 2.35 (3H, s, CH_3), ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.4 (C═O), 153.9, 137.7, 137.6, 132.4, 129.9, 129.7, 129.6, 126.8, 120.9, 119.7 (C−Ar), 72.2 (CH), 31.6 (CH_2), 21.5 (CH_3) ppm; m/z (EI, 70 eV) 302 (15, M^+), 237 (100), 147 (52), 118 (67), 105 (58%) . Anal. Calcd for $C_{16}H_{14}O_4S$: C, 63.20; H, 4.63. Found: C, 63.56; H, 4.67%.

*8-Methoxy-3-(4-methylbenzyl)benzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4f**):* White solid (286 mg, 86%); mp 128−130 °C; IR (KBr) ν_{max} 1703 (C═O), 1368 (−SO_2); 1153 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (1H, dd, J = 7.6, 1.4 Hz, Ar), 7.32 (1H, t, J = 8.0 Hz, Ar), 7.28 (1H, d, J = 6.5 Hz, Ar), 7.19 (2H, d, J = 8.0 Hz, Ar), 7.15 (2H, d, J = 7.9 Hz, Ar), 4.50 (1H, t, J = 6.5, CHC═O), 3.99 (3H, s, OCH_3), 3.52 (2H, d, J = 6.5 Hz, CH_2), 2.35 (3H, s, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.6 (C═O), 149.8, 143.2, 137.6, 132.5, 129.9, 129.5, 126.6, 121.8, 120.2, 119.7 (C−Ar), 72.1 (CH), 57.1 (OCH_3), 31.6 (CH_2), 21.5 (CH_3) ppm; m/z (EI, 70 eV) 332 (8, M^+), 268 (81), 150 (92), 122 (71), 105 (100%). Anal. Calcd for $C_{17}H_{16}O_5S$: C, 61.50; H, 4.66. Found: C, 61.43; H, 4.85%.

*6-Bromo-3-(4-methylbenzyl)benzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4g**):* White solid (370 mg, 87%); mp 129−131 °C; IR (KBr) ν_{max} 1684 (C═O), 1387 (−SO_2); 1173 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (1H, d, J = 2.4 Hz, Ar), 7.82 (1H, dd, J = 8.7, 2.4 Hz, Ar), 7.19−7.14 (5H, m, Ar), 4.51 (1H, t, J = 6.4, CHC═O), 3.52 (2H, d, J = 6.4 Hz, CH_2), 2.35 (3H, s, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.3 (C═O), 152.8, 140.2, 137.8, 133.0, 132.0, 130.0, 129.5, 122.2, 121.6, 120.0 (C−Ar), 72.0 (CH), 31.7 (CH_2), 21.5 (CH_3) ppm; m/z (EI, 70 eV) 382 (8, M^+ + 2), 380 (8, M^+), 317 (37), 118 (100), 105 (73), 77 (23%). Anal. Calcd for $C_{16}H_{13}BrO_4S$: C, 50.40; H, 3.21. Found: C, 50.41; H, 3.44%.

*3-(4-Bromobenzyl)benzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4h**):* White solid (307 mg, 84%); mp 147−149 °C; IR (KBr) ν_{max} 1697 (C═O), 1376 (−SO_2); 1170 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (1H, dd, J = 7.9, 1.7 Hz, Ar), 7.75 (1H, ddd, J = 8.2, 7.5, 1.7 Hz, Ar), 7.47 (2H, d, J = 8.4 Hz, Ar), 7.43 (1H, dt, J = 8.3, 1.0 Hz, Ar), 7.30 (1H, dt, J = 4.7, 0.6 Hz, Ar), 7.21 (2H, d, J = 10.7 Hz, Ar), 4.50 (1H, dd, J = 6.8, 5.7 Hz, CHC═O), 3.59 (1H, dd, J = 14.8, 6.8 Hz, Ph−CHH), 3.49 (1H, dd, J = 14.8, 5.7 Hz, Ph−CHH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.1 (C═O), 153.9, 137.8, 134.6, 132.3, 131.5, 129.8, 127.0, 122.1, 120.9, 119.8 (C−Ar), 71.7 (CH), 31.1 (CH_2) ppm; m/z (EI, 70 eV) 368 (6, M^+ + 2), 366 (6, M^+), 303 (83), 147 (100), 120 (96), 92 (82%). Anal. Calcd for $C_{15}H_{11}BrO_4S$: C, 48.95; H, 2.72. Found: C, 49.06; H, 3.02%.

*3-(4-Bromobenzyl)-8-methoxybenzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4i**):* Yellow solid (340 mg, 85%); mp 163−165 °C; IR (KBr) ν_{max} 1700 (C═O), 1386 (−SO_2); 1151 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (1H, dd, J = 7.7, 1.7 Hz, Ar), 7.46 (2H, d, J = 8.4 Hz, Ar), 7.33 (1H, t, J = 7.9 Hz, Ar), 7.30 (1H, dd, J = 8.1, 1.6 Hz, Ar), 7.20 (2H, d, J = 8.4 Hz, Ar), 4.48 (1H, dd, J = 6.9, 5.8 Hz, CHC═O), 3.97 (3H, s, OCH3), 3.56 (1H, dd, J = 14.8, 7.0 Hz, Ph−CHH), 3.49 (1H, dd, J = 14.8, 5.7 Hz, Ph−CHH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.4 (C═O), 149.8, 143.7, 134.7, 132.3, 131.5, 126.7, 122.0, 121.8, 120.2, 119.9 (C−Ar), 71.7 (CH), 57.1 (OCH_3), 31.2 (CH_2), ppm; m/z (EI, 70 eV) 398 (7, M^+ + 2), 396 (7, M^+), 334 (33), 169 (34), 150 (100), 122 (67%). Anal. Calcd for $C_{16}H_{13}BrO_5S$: C, 48.40; H, 3.26. Found: C, 48.38; H, 3.30%.

*6-Bromo-3-(4-bromobenzyl)benzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4j**):* White solid (375 mg, 84%); mp 174−175 °C; IR (KBr) ν_{max} 1695 (C═O), 1374 (−SO_2); 1157 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (1H, d, J = 2.3 Hz, Ar), 7.83 (1H, dd, J = 8.7, 2.4 Hz, Ar), 7.47 (2H, d, J = 8.2 Hz, Ar), 7.19 (3H, d, J = 8.4 Hz, Ar), 4.50 (1H, t, J = 6.2 Hz, CHC═O), 3.57 (1H, dd, J = 14.9, 6.8 Hz, Ph−CHH), 3.49 (1H, dd, J = 14.8, 5.6 Hz, Ph−CHH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.1 (C═O), 152.8, 140.3, 134.2, 132.4, 132.2, 131.4, 122.3, 122.2, 121.6, 120.2 (C−Ar), 71.6 (CH), 31.1 (CH_2) ppm; m/z (EI, 70 eV) 446 (6, M^+ + 2), 444 (4, M^+), 200 (86), 171 (67), 77 (59), 63 (100%). Anal. Calcd for $C_{15}H_{10}Br_2O_4S$: C, 40.51; H, 2.08. Found: C, 40.38; H, 2.26%.

*3-(4-Chlorobenzyl)benzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4k**):* White solid (267 mg, 83%); mp 149−151 °C; IR (KBr) ν_{max} 1697 (C═O), 1377 (−SO_2); 1169 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (1H, dd, J = 7.9, 1.5 Hz, Ar), 7.74 (1H, dt, J = 8.6, 1.6 Hz, Ar), 7.43 (1H, t, J = 7.3 Hz, Ar), 7.32−7.25 (5H, m, Ar), 4.52 (1H, dd, J = 6.5, 5.9 Hz, CHC═O), 3.60 (1H, dd, J = 14.8, 6.8 Hz, Ph−CHH), 3.50 (1H, dd, J = 14.8, 5.7 Hz, Ph−CHH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.2 (C═O), 153.9, 137.8, 134.1, 134.0, 131.1, 129.8, 129.4, 127.0, 120.8, 119.8 (C−Ar), 71.8 (CH), 31.0 (CH_2) ppm; m/z (EI, 70 eV) 324 (2, M^+ + 2), 322 (7, M^+), 257 (100), 147 (87), 120 (87), 92 (68%). Anal. Calcd for $C_{15}H_{11}ClO_4S$: C, 55.71; H, 3.31. Found: C, 55.82; H, 3.44%.

*3-(4-Chlorobenzyl)-8-methoxybenzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4l**):* White solid (306 mg, 87%); mp 154−156 °C; IR (KBr) ν_{max} 1686 (C═O), 1377 (−SO_2); 1152 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (1H, dd, J = 7.7, 1.5 Hz, Ar), 7.34 (2H, d, J = 8.0 Hz, Ar), 7.32−7.28 (2H, m, Ar), 7.26 (2H, d, J = 8.4 Hz, Ar), 4.49 (1H, dd, J = 6.7, 5.8 Hz, CHC═O), 3.58 (1H, dd, J = 14.8, 7.0 Hz, Ph−CHH), 3.51 (1H, dd, J = 14.8, 5.7 Hz, Ph−CHH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.5 (C═O), 149.8, 143.7, 134.1, 133.9, 131.1, 129.4, 126.7, 121.8, 120.2, 119.9 (C−Ar), 71.7 (CH), 57.1 (OCH_3), 31.1 (CH_2) ppm; m/z (EI, 70 eV) 354 (2, M^+ + 2), 352 (7, M^+), 288 (42), 150 (89), 91 (44), 69 (100%). Anal. Calcd for $C_{16}H_{13}ClO_5S$: C, 54.55; H, 3.54. Found: C, 54.47; H, 3.71%.

*6-Bromo-3-(4-chlorobenzyl)benzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4m**):* Yellow solid (356 mg, 89%); mp 166−168 °C; IR (KBr) ν_{max} 1694 (C═O), 1375 (−SO_2); 1158 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (1H, d, J = 2.4 Hz, Ar), 7.83 (1H, dd, J = 8.7, 2.4 Hz, Ar), 7.32 (2H, d, J = 8.4 Hz, Ar), 7.25 (2H, d, J = 8.4 Hz, Ar), 7.18 (1H, d, J = 8.7 Hz, Ar), 4.50 (1H, t, J = 6.3 Hz, CHC═O), 3.58 (1H, dd, J = 14.9, 8.8 Hz, Ph−CHH), 3.50 (1H, dd, J = 14.9, 5.0 Hz, Ph−CHH), ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.1 (C═O), 152.8, 140.5, 133.7, 132.2, 131.1, 129.4, 122.2, 121.6, 120.2 (C−Ar), 71.7 (CH), 31.0 (CH_2) ppm; m/z (EI, 70 eV) 402 (11, M^+ + 2), 400 (8, M^+), 338 (100), 200 (63), 138 (32), 125 (58%). Anal. Calcd for $C_{15}H_{10}BrClO_4S$: C, 44.80; H, 2.18. Found: C, 44.85; H, 2.51%.

*3-Benzyl-6-chlorobenzo[e][1,2]oxathiin-4(3H)-one-2,2-dioxide (**4n**):* White solid (283 mg, 88%); mp 128−130 °C; IR (KBr) ν_{max} 1694 (C═O), 1386 (−SO_2); 1165 (−SO_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (1H, s, Ar), 7.66 (1H, d, J = 8.2 Hz, Ar), 7.34−7.23 (6H, m, Ar), 4.54 (1H, br, CHC═O), 3.57 (2H, br, CH_2) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.4 (C═O), 152.2, 137.4, 135.2, 132.8, 129.7, 129.3, 129.1, 128.1, 121.9, 121.4 (C−Ar), 71.8 (CH), 31.9 (CH_2) ppm; m/z (EI, 70 eV) 324 (1, M^+ + 2), 322 (3, M^+), 258 (100), 181 (62), 154 (79), 91 (92%). Anal. Calcd for $C_{15}H_{11}ClO_4S$: C, 55.51; H, 3.22. Found: C, 55.82; H, 3.44%.

Synthesis of 3-[Methoxy(phenyl)methyl]benzo[*e*][1,2]-oxathiine-2,2-dioxide Derivatives 5. General procedure: To a stirring solution of DBU (0.076 g, 50 mol %) in MeOH (10 mL) was added 2-formylphenyl-(*E*)-2-phenylethenesulfonate (**3a**) (0.288 g, 1 mmol) at room temperature. The progress of the reaction was followed by TLC. After completion, the solvent was removed under reduced pressure and H_2O (30 mL) and CH_2Cl_2 (30 mL) were added. The two phases were separated, and the organic phase was washed with a solution of Na_2CO_3 (5%, 3 × 15 mL). The organic phase was then dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, eluent: 1:2, *n*-hexane/CH_2Cl_2) to afford 3-[methoxy(phenyl)methyl]-benzo[*e*][1,2]oxathiine-2,2-dioxide (**5a**).

*3-[Methoxy(phenyl)methyl]benzo[e][1,2]oxathiine-2,2-dioxide (**5a**):* White solid (160 mg, 53%); mp 114−116 °C; IR (KBr) ν_{max} 1365 (−SO_2), 1171 (−SO_2), 1096, 905, 762 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51−7.43 (6H, m, Ar), 7.35 (1H, d, J = 6.7 Hz, Ar), 7.29 (1H, d, J = 4.9 Hz, Ar), 7.27 (1H, s, Ar), 6.82 (1H, s, C═CH), 5.39 (1H, s, ArCH), 3.49 (3H, s, OCH_3) ppm; ^{13}C NMR (125 MHz, CDCl3) δ 151.4, 138.5, 136.8, 132.1, 131.9, 129.9, 129.5, 129.3, 128.1, 126.3, 120.5, 119.1 (C−Ar), 80.2 (C−OMe), 58.2 (OCH_3), ppm; m/z (EI, 70 eV) 302 (3, M^+), 238 (24), 207 (100), 178 (16), 77 (5%). Anal. Calcd for $C_{16}H_{14}O_4S$: C, 63.60; H, 4.44. Found: C, 63.56; H, 4.67%.

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*8-Methoxy-3-[methoxy(phenyl)methyl]benzo[e][1,2]oxathiine-2,2-dioxide (**5b**):* White solid (159 mg, 48%); mp 126−128 °C; IR (KBr) ν_{max} 1480, 1362 (−SO_2), 1163 (−SO_2), 1100 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51−7.41 (5H, m, Ar), 7.20 (1H, t, J = 8.0 Hz, Ar), 7.04 (1H, d, J = 7.5 Hz, Ar), 6.91 (1H, dd, J = 7.6, 0.8 Ar), 6.76 (1H, d, J = 1.2 Hz, C═CH), 5.39 (1H, s, ArCH), 3.94 (3H, s, OCH_3), 3.48 (3H, s, OCH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 140.8, 138.8, 136.8, 132.1, 129.5, 129.3, 128.1, 126.2, 121.4, 121.2, 115.2 (C−Ar), 80.2 (C−OMe), 58.1 (OCH_3), 56.9 (OCH_3) ppm; m/z (EI, 70 eV) 332 (31, M^+), 268 (7), 237 (100), 194 (14), 77 (12%). Anal. Calcd for $C_{17}H_{16}O_5S$: C, 61.63; H, 4.84. Found: C, 61.43; H, 4.85%.

*6-Bromo-3-[methoxy(phenyl)methyl]benzo[e][1,2]oxathiine-2,2-dioxide (**5c**):* White solid (209 mg, 55%); mp 135−137 °C; IR (KBr) ν_{max} 1473, 1366 (−SO_2), 1169 (−SO_2), 1091, 822, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (1H, dd, J = 8.7, 2.3 Hz, Ar), 7.42−7.50 (6H, m, Ar), 7.17 (1H, d, J = 8.7 Hz, Ar), 6.72 (1H, d, J = 1.1 Hz, C═CH), 5.38 (1H, d, J = 1.3 Hz, ArCH), 3.48 (3H, s, OCH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 140.0, 136.4, 134.8, 132.3, 130.5, 129.7, 129.4, 128.1, 122.1, 120.8, 119.1 (C−Ar), 80.2 (C−OMe), 58.2 (OCH_3) ppm; m/z (EI, 70 eV) 382 (3, M^+ + 2), 380 (3, M^+), 316 (19), 287 (100), 205 (19), 121 (28%). Anal. Calcd for $C_{16}H_{13}BrO_4S$: C, 50.29; H, 3.38. Found: C, 50.41; H, 3.44%.

*3-[Methoxy(p-tolyl)methyl]benzo[e][1,2]oxathiine-2,2-dioxide (**5d**):* White solid (127 mg, 40%); mp 114−116 °C; IR (KBr) ν_{max} 2926, 1368 (−SO_2), 1168 (−SO_2), 1115, 909, 815, 758 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (1H, dt, J = 7.8, 1.5 Hz, Ar), 7.39 (2H, d, J = 8.0 Hz, Ar), 7.35 (1H, d, J = 7.5 Hz, Ar), 7.29−7.26 (4H, m, Ar), 6.84 (1H, s, C═CH), 5.36 (1H, s, ArCH), 3.47 (3H, s, OCH_3), 2.43 (3H, s, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 139.4, 138.7, 133.7, 132.1, 131.7, 130.0, 129.9, 128.1, 126.3, 120.5, 119.0 (C−Ar), 80.1 (C−OMe), 58.0 (OCH_3), 21.7 (CH_3) ppm; m/z (EI, 70 eV) 316 (14, M^+), 285 (21), 252 (75), 221 (100), 178 (55), 135 (54), 91 (21%). Anal. Calcd for $C_{17}H_{16}O_4S$: C, 64.47; H, 5.02. Found: C, 64.54; H, 5.10%.

*6-Bromo-3-(methoxy-p-tolylmethyl)-benzo[e][1,2]oxathiine-2,2-dioxide (**5e**):* White solid (142 mg, 36%); mp 116−118 °C; IR (KBr) ν_{max} 2924, 1368 (−SO_2), 1166 (−SO_2), 1089, 819, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (1H, dd, J = 8.7, 2.3 Hz, Ar), 7.50 (1H, d, J = 2.3 Hz, Ar), 7.36 (2H, d, J = 8.0 Hz, Ar), 7.16 (1H, d, J = 8.7 Hz, Ar), 6.73 (1H, s, C═CH), 5.34 (1H, s, ArCH), 3.46 (3H, s, OCH_3), 2.42 (3H, s, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 139.6, 138.7, 133.3, 132.3, 131.5, 130.3, 130.1, 128.1, 122.2, 120.8, 119.0 (C−Ar), 80.0 (C−OMe), 58.0 (OCH_3), 21.7 (CH_3) ppm; m/z (EI, 70 eV) 396 (4, M^+ + 2), 394 (4, M^+), 330 (24), 299 (100), 205 (22), 135(41), 91 (32%). Anal. Calcd for $C_{17}H_{15}BrO_4S$: C, 51.55; H, 3.69. Found: C, 51.66; H, 3.83%.

*3-[(4-Bromophenyl)methoxymethyl]benzo[e][1,2]oxathiine-2,2-dioxide (**5f**):* White solid (247 mg, 65%); mp 119−121 °C; IR (KBr) ν_{max} 2925, 1369 (−SO_2), 1171 (−SO_2), 1071, 815, 758 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (2H, d, J = 8.4, Hz, Ar), 7.47 (1H, dt, J = 8.5, 1.5 Hz, Ar), 7.40−7.37 (3H, m, Ar), 7.32−7.27 (2H, m, Ar), 6.87 (1H, s, C═CH), 5.34 (1H, s, ArCH), 3.47 (3H, s, OCH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 137.9, 136.1, 132.5, 132.3, 131.9, 129.9, 129.7, 126.4, 123.6, 120.4, 119.1 (C−Ar), 79.5 (C−OMe), 58.2 (OCH_3) ppm; m/z (EI, 70 eV) 382 (3, M^+ + 2), 380 (4, M^+), 316 (15), 285 (100), 205 (79), 161(35), 89 (30%). Anal. Calcd for $C_{16}H_{13}BrO_4S$: C, 50.49; H, 3.25. Found: C, 50.41; H, 3.44%.

*3-[(4-Bromophenyl)methoxymethyl]-8-methoxybenzo[e][1,2]-oxathiine-2,2-dioxide (**5g**):* White solid (230 mg, 56%); mp 167−169 °C; IR (KBr) ν_{max} 2927, 1364 (−SO_2), 1156 (−SO_2), 1069, 873, 722 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (2H, d, J = 8.4 Hz, Ar), 7.38 (2H, d, J = 8.4 Hz, Ar), 7.22 (1H, t, J = 8.0 Hz, Ar), 7.06 (1H, dd, J = 7.8, 1.1 Hz, Ar), 6.94 (1H, dd, J = 7.8, 1.1 Hz, Ar), 6.82 (1H, s, C═CH), 5.34 (1H, s, ArCH), 3.95 (3H, s, $ArOCH_3$), 3.47 (3H, s, OCH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 138.2, 136.1, 132.6, 132.5, 132.0, 129.7, 126.4, 123.5, 121,3, 121.2, 115.3 (C−Ar), 79.6 (C−OMe), 58.2 (OCH_3), 56.9 ($ArOCH_3$) ppm; m/z (EI, 70 eV) 412 (9, M^+ + 2), 410 (9, M^+), 315 (100), 236 (15), 199 (14), 165(18), 152 (18%). Anal. Calcd for $C_{17}H_{15}BrO_5S$: C, 49.68; H, 3.57. Found: C, 49.65; H, 3.68%.

*6-Bromo-3-[(4-bromophenyl)methoxymethyl]benzo[e][1,2]-oxathiine-2,2-dioxide (**5h**):* White solid (248 mg, 54%); mp 145−147 °C; IR (KBr) ν_{max} 2927, 1370 (−SO_2), 1165 (−SO_2), 1073, 819 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (2H, d, J = 8.3 Hz, Ar), 7.56 (1H, dd, J = 8.7, 2.2 Hz, Ar), 7.53 (1H, d, J = 2.1 Hz, Ar), 7.36 (2H, d, J = 8.6, Hz, Ar), 6.80 (1H, s, C═CH), 5.33 (1H, s, ArCH), 3.47 (3H, s, OCH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 139.3, 135.7, 134.9, 132.6, 132.4, 130.5, 129.7, 123.8, 122.0, 120.8, 119.2 (C−Ar), 79.5 (C−OMe), 58.2 (OCH_3) ppm; m/z (EI, 70 eV) 460 (5, M^+ + 2), 458 (3, M^+), 396 (16), 365 (100), 285 (32), 199(44), 176 (64%). Anal. Calcd for $C_{16}H_{12}Br_2O_4S$: C, 41.72; H, 2.58. Found: C, 41.76; H, 2.63%.

*3-[(4-Chlorophenyl)methoxymethyl]benzo[e][1,2]oxathiine-2,2-dioxide (**5i**):* White solid (202 mg, 60%); mp 118−120 °C; IR (KBr) ν_{max} 2946, 1370 (−SO_2), 1168 (−SO_2), 1087, 814, 755 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.48−7.43 (5H, m, Ar), 7.38 (1H, dd, J = 7.7, 1.5 Hz, Ar), 7.31−7.26 (2H, m, Ar), 6.90 (1H, s, C═CH), 5.36 (1H, s, ArCH), 3.48 (3H, s, OCH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 138.0, 135.6, 132.3, 131.9, 130.0, 129.6, 129.4, 129.3, 126.5, 120.4, 119.1 (C−Ar), 79.6 (C−OMe), 58.2 (OCH_3) ppm; m/z (EI, 70 eV) 338 (1, M^+ + 2), 336 (3, M^+), 305 (7), 272 (20), 257 (18), 241(100), 205 (18%). Anal. Calcd for $C_{16}H_{13}ClO_4S$: C, 56.99; H, 3.73. Found: C, 57.06; H, 3.89%.

*3-[(4-Chlorophenyl)methoxymethyl]-8-methoxybenzo[e][1,2]-oxathiine-2,2-dioxide (**5j**):* White solid (198 mg, 54%); mp 149−151 °C; IR (KBr) ν_{max} 2928, 1365 (−SO_2), 1157 (−SO_2), 1084, 873, 722 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (4H, br, Ar), 7.22 (1H, t, J = 8.0 Hz, Ar), 7.06 (1H, d, J = 7.8 Hz, Ar), 6.94 (1H, d, J = 7.7 Hz, Ar), 6.83 (1H, s, C═CH), 5.36 (1H, s, ArCH), 3.95 (3H, s, $ArOCH_3$), 3.47 (3H, s, OCH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 138.3, 135.6, 135.3, 132.0, 129.8, 129.6, 129.4, 126.4, 121.3, 121,2, 115.3 (C−Ar), 79.5 (C−OMe), 58.2 (OCH_3), 56.9 ($ArOCH_3$) ppm; m/z (EI, 70 eV) 368 (5, M^+ + 2), 366 (15, M^+), 271 (100), 265 (13), 241 (38), 165(15), 155 (19%). Anal. Calcd for $C_{17}H_{15}ClO_5S$: C, 55.58; H, 4.09. Found: C, 55.66; H, 4.12%.

*6-Bromo-3-[(4-chlorophenyl)(methoxy)methyl]benzo[e][1,2]-oxathiine-2,2-dioxide (**5k**):* White solid (182 mg, 44%); mp 173−175 °C; IR (KBr) ν_{max} 1473, 1368 (−SO_2), 1168 (−SO_2), 1090, 823 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56−7.43 (6H, m, Ar), 7.16 (1H, d, J = 8.5 Hz, Ar), 6.80 (1H, s, C═CH), 5.34 (1H, s, ArCH), 3.47 (3H, s, OCH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 139.4, 135.6, 135.2, 134.9, 132.4, 130.5, 129.7, 129.4, 122.0, 120.8, 119.2 (C−Ar), 79.5 (C−OMe), 58.2 (OCH_3) ppm; m/z (EI, 70 eV) 416 (6, M^+ + 2), 414 (5, M^+), 352 (25), 321 (100), 205 (13), 155 (24%). Anal. Calcd for $C_{16}H_{12}BrClO_4S$: C, 46.21; H, 2.79. Found: C, 46.23; H, 2.91%.

*3-[Methoxy(phenyl)methyl]-6-nitrobenzo[e][1,2]oxathiine-2,2-dioxide (**5l**):* Yellow oil (53 mg, 15%); IR (KBr) ν_{max} 3069, 1342 (−SO_2), 1157 (−SO_2), 986, 826, 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (1H, d, J = 15.5 Hz, Ar), 7.55−7.36 (6H, m, Ar), 7.75 (1H, d, J = 15.5 Hz, Ar), 3.90 (1H, s, C═CH), 3.88 (3H, s, OCH_3), 3.30 (1H, s, ArCH) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 139.0, 132.3, 132.1, 130.2, 129.6, 129.4, 129.2, 129.0, 127.0, 120.6, 119.4 (C−Ar), 78.8 (C−OMe), 56.6 (OCH_3) ppm; m/z (EI, 70 eV) 348 (2, M^+), 181 (33), 167 (61), 103 (100), 77 (41%). Anal. Calcd for $C_{16}H_{13}NO_6S$: C, 55.28; H, 3.68; N, 3.95. Found: C, 55.33; H, 3.77; N, 4.03%.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H NMR and ^{13}C NMR spectra of all compounds, plus NOESY and HMBC of **4h** and **5g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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