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Ring closing metathesis and metal-catalyzed cyclopropanation for the preparation of sultone derivatives

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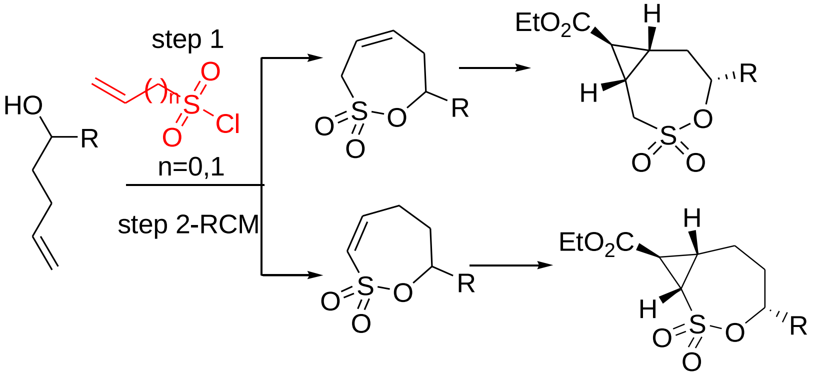
Abstract

Ring closing metathesis (RCM) using Grubbs catalyst 2nd generation as a catalyst was applied to prepare series of novel unsaturated sultones with high yields. Many attempts, were applied for the cyclopropanation of the allylic sultones by Simmon-smith cyclopropanation using diethyl zinc/diiodomethane or Zn-Cu/diiodomethane but in each case the corresponding cyclic adduct was not formed. A novel palladium or preferably rhodium-catalyzed cyclopropanation of unsaturated sultones with ethyl diazoacetate was achieved by the transition metal-catalyzed transfer of a CH-CO_2Et unit. The reaction was applied by a portion-wise addition of ethyl diazoacetate over 6h to a mixture of the sultones and palladium(II) acetate or rhodium(II) acetate dimer under low temperature (0-20 °C). The desired products of the cyclopropanation were achieved in each case, as a single diastereomer with 33- 37% yield in the allylic sultones and 10% for vinylic sultone.



Keywords: Ring closing metathesis (RCM), carbenes generation; sultones, cyclopropanation

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Introduction

Sultones are important scaffolds in organic and bioorganic chemistry with good contribution in the synthesis of different types of heterocycles.[1-6] Additionally, Sultones act as sulfoalkylating agents in organic and natural product synthesis[7,8]. Additionally, several publications have reported several biological activities of the sultones that includes antitumor and antiviral (anti-HIV) activities.[9-12]

On the other hand, a great deal of interest has been focused on the cyclopropanes as they have a wide contribution in the natural products and the biologically active synthetic compounds.[13-16] Furthermore, the ring strain of the σ-bond in the cyclopropane ring make cyclopropane derivatives highly reactive in transition metal catalyzed reactions.

The ring closing metathesis (RCM) and organometallic catalysis using Pd, Rh and Ru compounds are very important tools for organic chemistry and pharmaceutical applications as they used for the preparation of active ingredients in the field of organic chemistry and pharmaceutical industry.[15-22]

From these observations and in continuation of our interest of the chemistry of organo-sulfur heterocycles and sultones chemistry, [22-26] we reported herein an interesting preparation of a series of unsaturated sultones in addition to successful attempts of metal-catalyzed cyclopropanation on the sultone scaffold.

Results and Discussion

In this study, several allylic and vinylic sultones were prepared from the appropriate sulfonate and Subsequent RCM. The unsaturated sulfonates (**3**) were prepared from the reaction of the primary or secondary alkenols (**2a,b**) with allyl sulfonyl chloride (**1**), in the presence of TEA, under low temperature. We apply our modified procedure to obtain high yields of the sulfonates (**3**) via completing the addition process of the reactant under -20 ^{o} C and left the reaction under this temperature for 4 h (Scheme 1).

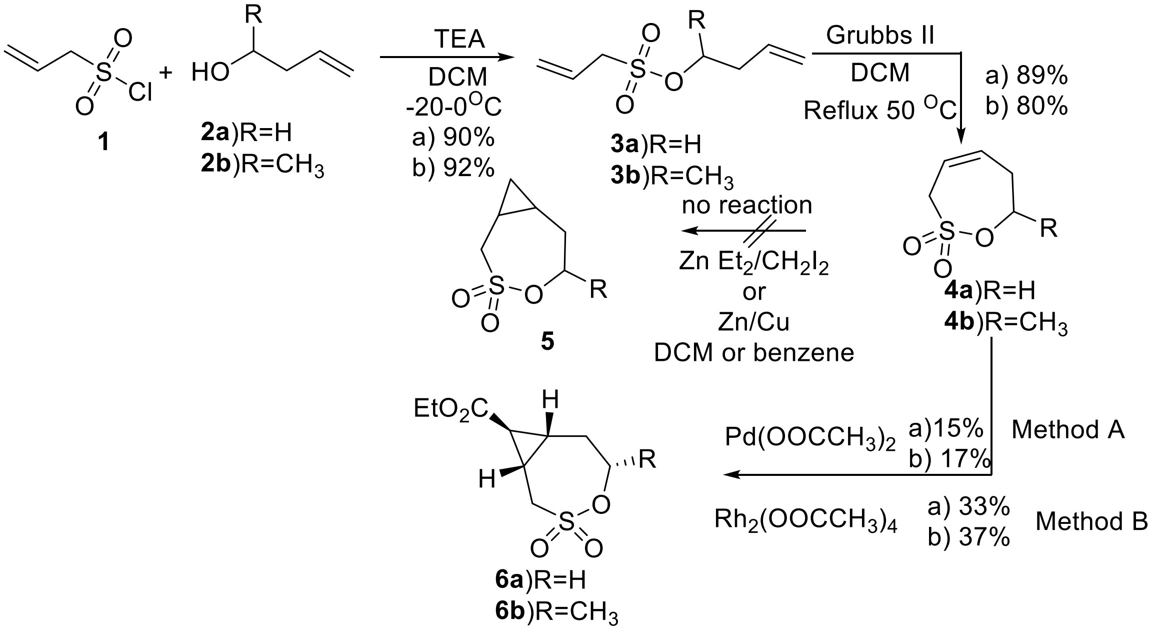
RCM was achieved by portion wise addition of Grubbs catalyst 2nd generation under reflux temperature on a solution of the unsaturated sulfonate **3a** or **3b** to afford the corresponding sultone (**4a,b**). the structures of the sultones (**4a,b**) were confirmed by the elemental analysis and spectral data. The ^{1}H-NMR spectrum of the **4b** revealed doublet signal at 1.35 ppm corresponding to CH_3, multiplets near 5.63, 6.01 ppm for 2 allylic CH. Since there was only a single publication on the intermolecular cyclopropanation of vinylic[27] or allylic sultones prior to our work we decided to investigate this transformation.

Many attempts, in this study, were applied for the cyclopropanation of the sultones **4a,b** by Simmons-Smith cyclopropanation using diethyl zinc/diiodomethane or Zn-Cu/diiodomethane, but in each case the cyclopropanation for the corresponding cyclic adduct was not obtained (Scheme 1).

The successful attempts and the first investigation for the cyclopropanation of the sultones **4a,b** with ethyl diazoacetate to give the desired products as single diastereomers were achieved by palladium(II) acetate or rhodium(II) acetate dimer as a catalyst. The cyclopropanation reaction was achieved via transition metal-catalyzed transfer of a $CH-CO_2Et$ unit under low temperature 0-20 ^{o} C. with continuous and slow addition of ethyl diazoacetate over 6 h.

The yields of the cyclopropanation adducts **6a,b** were 33 and 37 % in the case of rhodium (II) acetate dimer that was higher than the using of palladium(II) acetate with yield 15 and 17%, respectively (Scheme 1).

The structure of the bicyclic compounds **6a,b** were confirmed by the elemental analysis and spectral data. The relative configuration of **6a,b** was assigned by 2D NOESY analysis.The ^{1}H-NMR spectrum of the **6a** revealed signals at 1.25 (CH_3), 1.52-1.62 (2CH), 1.90 (CH), 2.10-2.33 (2CH), 2,33 (CH), 3.01 (CH), 3.81 (CH), 4.10 (CH_2), and 4.95 (CH) ppm.



Scheme 1

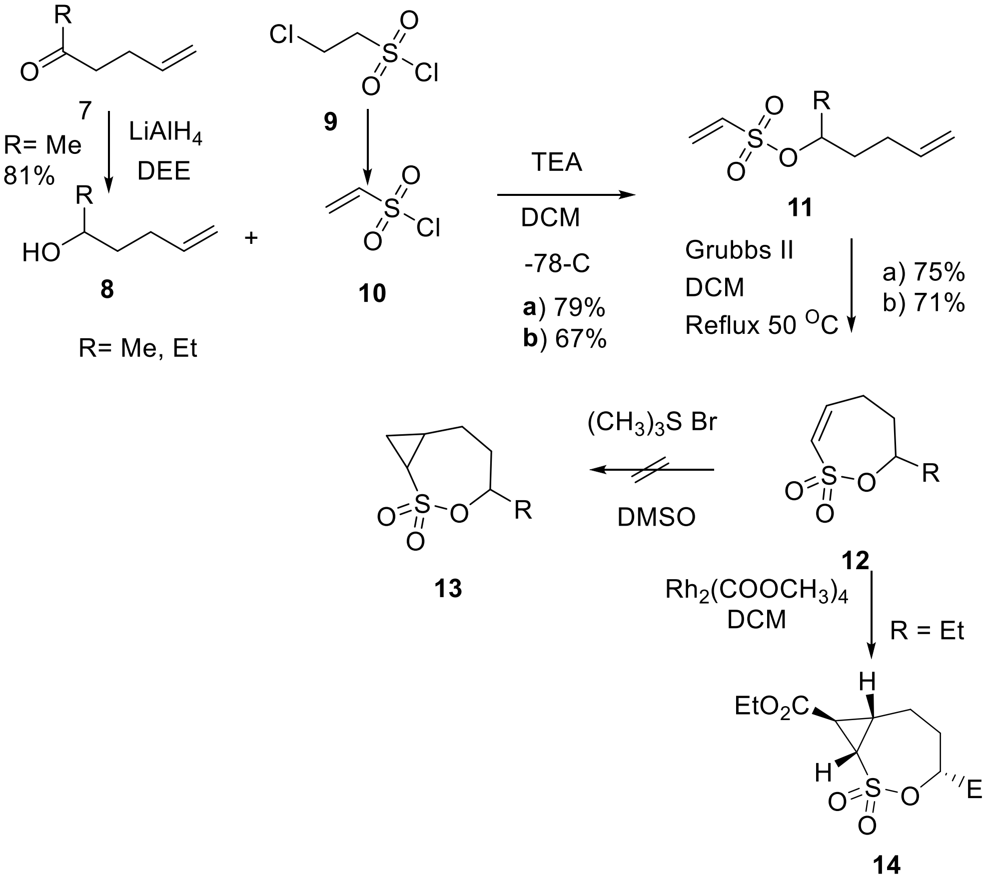
To complete the overall picture for the preparation of novel sultones we have designed the synthetic pathway to prepare new vinyl sultones as presented in scheme 2. Firstly, the secondary allylic alcohols were prepared from the corresponding ketone using $LiAlH_4$. Ethenesulfonyl chloride (**10**) was prepared *in-situ* from the treatment of chloro ethyl sulfonyl chloride (**9**) with TEA under low temperature. The unsaturated sulfonate derivatives (**11**) were readily prepared by esterification of the secondary alcohols (**8**) with the in-situ generated ethenesulfonyl chloride (**10**) in the presence of TEA under low temperature (-40 ° C). The structures of the formed sulfonates were confirmed by elemental analysis and spectral data.

In this study, the second new series of sultones is the vinyl sultones (**12**) prepared by treatment of the freshly prepared vinyl sulfonate (**11**) with Grubbs(II) catalyst that added portion wise under reflux temperature (Scheme 2). The structures of the new vinyl sultones were confirmed by elemental analysis and spectral data. (See the experimental part).

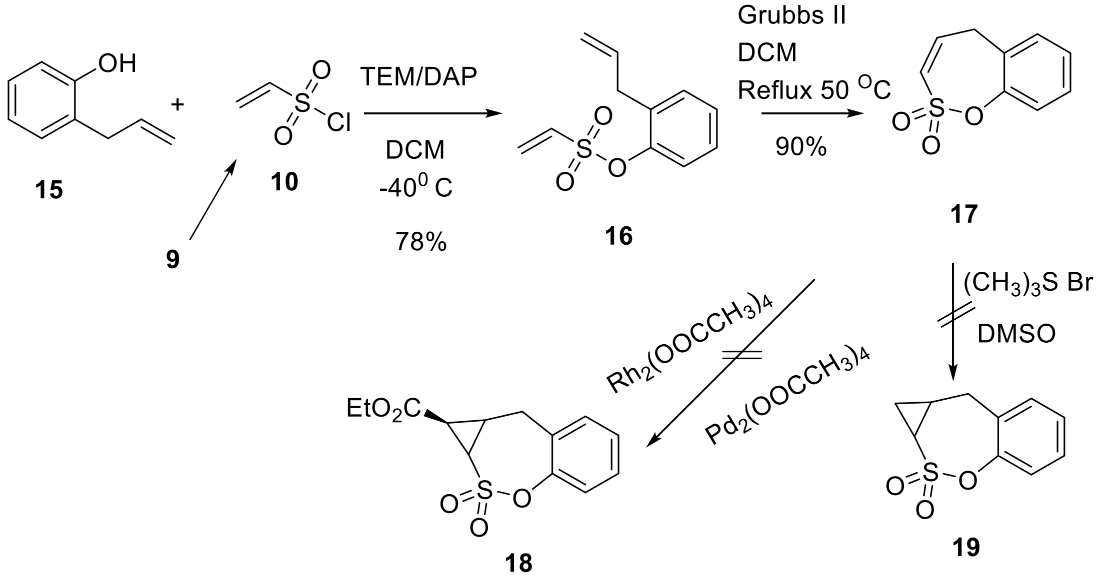
Several attempts were applied for the cyclopropanation of the vinyl sultones **12** using sulfur yields; trimethylsulfonium bromide $(CH_3)_3S^+Br^-$, in the presence of potassium tert-butoxide in DMF but in each case lead to decomposition of the sultones due to the base; potassium tert-butoxide.

Cyclopropanation of the vinyl sultones **12b**, was achieved with very low yield (10%) by treatment with ethyl diazoacetate in the presence of dirhodium(II) tetra acetate as a catalyst under low temperature 0-20 ° C. the cyclopropanation was not achieved by palladium(II) acetate as catalyst (Scheme 2).

The constitution of the bicyclic sultone **14** was confirmed by the elemental analysis and spectral data, while the relative configuration was tentatively assigned in analogy to sultones **6**. The ^{1}H-NMR spectrum of the sultone **14** revealed presence of 3 characteristic bands multiplets near 0.97, 1.15 and 1.70 ppm corresponding to the cyclopropane protons; 6-H, 4-H, and 5-H, respectivly. Two signals that are charactarestic for the ester group were appeared as triplet and quartet at near 1.10 and 4.22 ppm, respectivly.



Scheme 2



Scheme 3

New vinylic sultone constructed on benzene scaffold was obtained by RCM as presented in scheme 3. The first step was the preparation of the unsaturated sulfonate **16** that was readily obtained by esterification of the 2-allylphenol (**15**) with ethenesulfonyl chloride (**10**), in the presence of TEA under low temperature (0-40). The unsaturated sulfonate derivative (**16**) was formed with 78% yield and its structure was confirmed by elemental analysis and spectral data. The vinyl sultone **(17)** was prepared with 90% yield by treatment the sulfonate **16** with Grubbs catalyst 2nd generation under reflux temperature in DCM (Scheme 3).

The ^{1}H-NMR spectrum of the sultone (**17**) revealed bands at 3.72 (m), 6.35 (m) and 6.48 (m) ppm corresponding to CH_2 and 2CH, respectivly. The aromatic protons apperd at 7.21-7.45 ppm.
The structure of the sultone (**17**) was fully confirmed by the X-ray single crystal analysis (Figure 1).

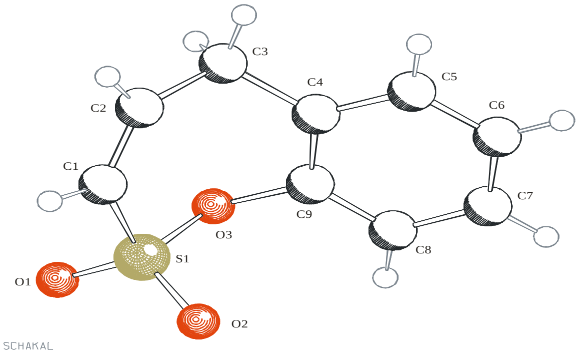


Figure 1: X-ray crystal structure of compound **17**

We have tried to apply the cyclopropanation reaction on the later sultone by different treatments with ethyl diazoacetate in the presence of $Pd(OAc)_2$ or $Rh_2(OAc)_4$ but in each case there was no reaction.

Conclusions

In this study, a novel palladium- or preferably rhodium-catalyzed cyclopropanation of unsaturated sultones with ethyl diazoacetate to give the desired products as a single diastereomer have been achieved. These densely functionalized heterocycles are surely highly interesting intermediates for the preparation of pharmaceutically active compounds. The unsaturated sultones required for these investigations were readily available by esterification of unsaturated alcohols with sulfonyl chlorides and subsequent ruthenium-catalyzed ring-closing metathesis. With a range of novel sultones synthesized in this fashion, we first investigated different conditions for cyclopropanation using the Simmons-Smith methodology and also sulfur ylide chemistry to transfer an un-substituted methylene unit to the alkene moiety of the substrates. Whereas these reactions did not work with the unsaturated sultones at hand, the transition metal-catalyzed transfer of a CH-CO_2Et unit finally succeeded as detailed above. Probably, the cyclopropanation of the vinylic sultones was more difficult than the allylic sultones due to the high electron deficiency of the alkenes of the vinylic sultone. But in case of the allylic sultones where the separation of the sulfonyl group and the olefin by CH_2 group might allow a [2+1] cycloaddition to give the desired cyclopropanes

Experimental Section

General. Infrared spectra were recorded on a THERMONICOLET Avatar 360 instrument using ATR. NMR spectra were recorded on a Bruker AC 300 P (300 MHz ^{1}H, 75 MHz ^{13}C), on a Bruker DRX 500 P (500 MHz ^{1} H, 125 MHz ^{13} C) or on a Bruker AC 600-P (600 MHz ^{1}H, 151 MHz ^{13}C) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using residual proton-containing solvent as internal standard ($CDCl_3$ at 7.26 ppm). Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q (quartet), br (broad). Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Mass spectra were recorded with an Agilent 5973N detector coupled with an Agilent 6890N GC (GC-MS, 70 eV) or else with a Bruker Esquire-LC (direct injection as a methanolic NH_4OAc solution, ESI). HRMS spectra were recorded on a Bruker Daltonic "Impact II" (ESI-TOF). Elemental analysis was performed on a Hekatech EA 3000.

Preparation of prop-2-ene-1-sulfonyl chloride (1). Prop-2-ene-1-sulfonyl chloride (**1**) was prepared by our modification on the reported method[28] as in the following: To a stirred solution of allyl bromide (12.10 g, 0.1mol) in 100 mL distilled water was added Na_2SO_3 (15 g, 0.12mol). The reaction mixture was refluxed for 8h then left to cool to room temperature. The reaction mixture was washed with Et_2O several times and the aqueous layer was evaporated under reduced pressure. The crude product was washed with methanol, filtered off and left to dry to afford (10.2g, 0.07 mol, 71% yield) of sodium allysulfonate. The latter crude product was stirred at zero temperature with 30 mL of $POCl_3$ for 1/2 h then refluxed for 5 h and left to cool to room temperature. 100 mL of THF was then added to the mixture then filtered off and washed several times with dry THF. The filtrate was evaporated carefully on rotavapor and the residue was distilled under vacuum (5 mbar). Allylsulfonyl chloride was separated with boiling point range 37-43 °C as coreless oil (71%).

General procedure for the preparation of but-3-enyl prop-2-ene-1-sulfonate derivatives (3a,b). To a stirred solution of the unsaturated alcohol (**2a,b**) (1.0 equiv.) and dry TEA (1.5 equiv.) in CH_2Cl_2 at low temperature (-20 °C) was added ally sulfonyl chloride (1.2 equiv.) in CH_2Cl_2 drop by drop. The reaction mixture was left to stir under this temperature for 4 h then left to stir for 0.5 h at room temperature. Pentane was then added and the mixture was filtered through Celite. The filtrate was concentrated under reduced pressure and the crud residue was purified by flash chromatography.

General procedure for the preparation of hex-5-en-2-yl ethane sulfonate derivatives (11a,b) and 2-allylphenyl ethenesulfonate (16). A solution of the unsaturated alcohol (**7a,b**) (1.0 equiv.) and dry TEA (1.5 equiv.) in CH_2Cl_2 was stirred at low temperature (-40-0 °C) under inert atmosphere in two necked flask. A solution of 2-chloroethanesulfonyl chloride (1.3-1.5 equiv.) in $CH_2Cl_2$was then added drop by drop. The reaction mixture left to stir under this temperature for 3-7 h. then diluted with pentane and filtered through Celite. The filtrate was concentrated under reduced pressure and the crud residue was purified by flash chromatography.

General procedure for the preparation of sultones 4a,b, 12a,b and 17. To a stirred solution of the sulfonates; **3a**, **3b**, **12a**, **12b** or **16** (1eq) in CH_2Cl_2, in three necked flask under argon atmosphere, was added Grubbs catalyst 2nd generation (0.03-0.05 equiv.) in three portions. The reaction mixture was refluxed with stirring for 5-12 h. the solvent was evaporated under reduced pressure and the solid crude product was purified by column chromatography (silica gel isohexane/ethyl acetate 9/1 or diethyl ether/pentane 1/1) to afford the corresponding sultones **4a**, **4b**, **12a**, **12b** and **17**, respectively.

General procedure for the rhodium catalyzed cyclopropanation using ethyl diazoacetate. To a stirred solution of the sultone **4a**, **4b**, **12a**, **12b** and **17**, respectively (1eq) and the appropriate catalyst; palladium diacetate or rhodium(II) acetate dimer (1-3 mol%) in CH_2Cl_2 under argon atmosphere, was added ethyl diazoacetate (2-3 equiv.) in DCM over 6 h period using syringe pump. The solvent was evaporated under reduced pressure and the solid crude product was purified by column chromatography (silica gel isohexane/ethyl acetate 9/1) to afford the corresponding 3-oxa-2-thiabicyclo[5.1.0]octane 2,2-dioxide.

But-3-enyl prop-2-ene-1-sulfonate (3a). Compound **3a** was prepared according the general procedure from prop-2-ene-1-sulfonyl chloride (**1**) (2.1g, 15 mmol), but-3-en-1-ol (**2a**) (1g, 13.86 mmol) and TEA (2 mL). Colorless oil R*f*: 0.53 (Et_2O/pentane; 1/1)[29] ; Yield (2.44g, 90%). ^1H NMR ($CDCl_3$, 300 MHz): δ_H 2.32-2.48 (m, 2H, CH_2), 3.75 (d, *J* 7.2 Hz, 2 H, CH_2), 4.33 (t, 2H, CH_2), 5.05-5.15 (m, 2H, 2CH), 5.40-5.51 (m, 2H, 2CH), 5.71-5.95 (m, 2H, 2CH).

Pent-4-en-2-yl prop-2-ene-1-sulfonate (3b). Compound **3b** was prepared according the general procedure from prop-2-ene-1-sulfonyl chloride **(1)** (3 g, 21.4 mmol), pent-1-en-2-ol (**2b**) (1.5 g, 17.4 mmol) and TEA (3 mL). Colorless oil R*f*: 0.65 (Et_2O/pentane; 1/1); Yield (3.03 g, 92%). IR (KBr, *v*max, cm^{-1}): 3080, 2982, 2935, 1643,1424, 1336, 1258, 1162, 992, 904. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm)= 1.34 (d, *J* 6.2 Hz, 3 H, CH_3), 2.28–2.47 (m, 2 H, CH_2), 3.73 (d, *J* 7.2 Hz, 2 H, CH_2), 4.72–4.83 (m, 1 H, CH), 5.04–5.13 (m, 2 H, CH_2), 5.33 – 5.43 (m, 2 H, CH_2), 5.63 – 5.91 (m, 2 H, 2CH). ^{13}C NMR (CDCl3, 75 MHz,) (δ ppm): 20.66 (q), 40.95 (t), 55.76 (t), 79.31 (d), 118.98 (t), 124.27 (d), 124.66 (d), 132.28 (d). GC-MS *m/z*(%):190 [M^+] (2), 149 (73) [$C_5H_9SO_3$+], 85 (16) [C_5H_9O+], 69 (100) [C_5H_9+], 68 (37), 67 (37), 53 (11), 45 (7) [C_2H_5O+]. Anal. Calcd for $C_8H_{14}O_3S$ (190.26): C, 50.50; H, 7.42; S, 16.85. Found: C, 50.65; H, 7.68; S, 16.67.

6,7-Dihydro-3*H*-1,2-oxathiepine 2,2-dioxide (4a). Compound **4a** was prepared according the general procedure from but-3-enyl prop-2-ene-1-sulfonate (**3a)** (1.76 g, 10 mmol) and Grubbs catalyst 2nd generation (0.26 g, 0.03 eq) as a colorless crystals (Et_2O/Pentane:1/1); Yield (89%).[28] ^1H NMR ($CDCl_3$, 300 MHz): δ_H 2.55-2.60 (m, 2H, CH_2), 4.11-4.22 (m, 2H, CH_2), 4.51-4.60 (d, 2H, CH_2), 5.75-5.80 (m, 1H, CH), 6.23 (m, 1H, CH).

7-Methyl-6,7-dihydro-3*H*-1,2-oxathiepine 2,2-dioxide (4b). Compound **4b** was prepared according the general procedure from pent-4-en-2-yl prop-2-ene-1-sulfonate (**3b**) (0.95 g, 5 mmol) and Grubbs catalyst 2nd generation (0.13 g, 0.03 eq) as a colorless crystals; yield (0.65 g, 80%); colorless crystals, R*f*: 0.42 (Et_2O/Pentane:1/1). IR (KBr, *v*max, cm^{-1}): 2981, 1453, 1349, 1326, 1154, 1038, 898, 755, 671. ^1H NMR (300 MHz, $CDCl_3$): δ_H 1.35 (d, *J* 6.4 Hz, 3 H, CH3), 2.25–2.37 (m, 1 H, CH), 2.57–2.71 (m, 1 H, CH), 2.73 – 3.83 (m, 1 H, CH), 4.02 – 4.12 (m, 1 H, CH), 4.83 – 4.95 (m, 1 H, CH), 5.63 – 5.74 (m, 1 H, CH), 6.01 – 6.13 (m, 1 H, CH). ^{13}C NMR (75 MHz, $CDCl_3$) (δ ppm): 21.91 (q), 35.84 (t), 50.72 (t), 82.08 (d), 119.73 (d), 133.84 (d). MS *m/z*(%):162 [M^+] (2), 147 (3), 98 (8), 54 (100), 39 (50). Anal. Calcd for $C_6H_{10}O_3S$ (162.20):C, 44.43; H, 6.21 ; S, 19.77. Found:C, 48.48; H, 6,24; S, 19,66.

Ethyl (1*S*,7*S*,8*S*)-4-oxa-3-thiabicyclo[5.1.0]octane-8-carboxylate 3,3-dioxide (6a). Compound **6a** was prepared as colorless low-melting crystals according the general procedure from 6,7-dihydro-3*H*-1,2-oxathiepine 2,2-dioxide (**4a**) (0.148 g, 1 mmol), ethyl diazoacetate (**9**) (0.3 mL of ethyl diazoacetate in 5 mL DCM over 6 h) and 2 mol% of palladium diacetate (method A) (0.004 g) or Rhodium(II) acetate dimer (0.0044g, 1 mol%)(Method B). Yield (A: 0.035 g, 15%, B: 0.077 g, 33%); colorless crystals; mp: 39-40 °C. IR (KBr, v_{max}, cm^{-1}): 2996, 2981, 1712, 1397, 1345, 1151, 963, 891, 860, 729. ^1H NMR ($CDCl_3$, 500 MHz, COSY, NOSY): δ_H 1.25 (t, 3H, CH_3), 1.52-1.62 (m, 2H, 2CH), 1.90 (m, 1H, CH), 2.10-2.33 (m, 2H, 2CH), 2,33 (m, 1H, CH), 3.01 (m, 1H, CH), 3.81 (m, 1H, CH), 4.10 (q, 2H, CH_2), 4.95 (m, 1H, 1-H). ^{13}C NMR ($CDCl_3$, 125 MHz, HSQC, HMBC) δ (ppm): 14.09 (q), 15.89 (d), 23.15 (d), 23.51(d), 48.18 (t), 60.92 (t), 72.14 (t), 170.70 (s, C=O). MS *m/z*(%): 234 [M^+] (8), 206 (13), 189 (58), 155 (20), 126 (75), 79 (81), 67 (100). Anal. Calcd for $C_9H_{14}O_5S$ (234.27): C, 46.14; H, 6.02; S, 13.69. Found: C, 46.21; H, 6.12; S, 13.60.

Ethyl (1S,5S,7S,8S)-5-methyl-4-oxa-3-thiabicyclo[5.1.0]octane-8-carboxylate 3,3-dioxide (6b). Compound **6b** was prepared as colorless low melting colorless crystals according the general procedure from **7-**Methyl-6,7-

dihydro-3*H*-1,2-oxathiepine 2,2-dioxide (**4b**) (0.162 g, 1 mmol), ethyl diazoacetate (**9**) (0.3 mL of ethyl diazoacetate in 5 mL DCM over 6 h) and 2 mol% of palladium(II)acetate (method A) (0.004 g) or 1 mol% of rhodium(II) acetate dimer (method B)(0.0044 g). Yield (A: 0.042 g, 17%, B: 0.092 g, 37%); colorless crystals; mp: 42-43 °C. IR (KBr, v_{max}, cm^{-1}): 2982, 1724, 1367, 1264, 1164, 1024, 919. ^{1}H NMR ($CDCl_3$, 500 MHz, COSY, NOSY): δ_H 1.28 (t, 3H, CH_3), 1.40 (d, 3H, CH_3), 1.42-1.45 (m, 2H, 2CH), 1.75-1.90 (m, 2H, 2CH), 2,33 (m, 1H, CH), 3.01 (m, 1H, CH), 3.81 (m, 1H, CH), 4.20 (q, 2H, CH_2), 4.95 (m, 1H, CH). ^{13}C NMR ($CDCl_3$, 125 MHz, HSQC, HMBC) δ (ppm): 14.16 (q), 17.93 (d), 21.51 (q), 23.70 (d), 31.25 (d), , 37.38 (t) 53.14 (t), 61.16 (t), 81.84 (d), 171.08 (s, C=O). MS *m/z*(%): 248 [M$^+$] (10), 207 (33), 93 (48), 67 (100), 41 (50). Anal. Calcd for $C_{10}H_{16}O_5S$ (248.3): C, 48.37; H, 6.50; S, 12.91. Found: C, 48.41; H, 6.42; S, 12.89.

Hex-5-en-2-yl ethenesulfonate (11a). Compound **11a** was prepared as colorless oil according the general procedure from hex-5-en-2-ol (**8a**) (1.25 g, 12.5 mmol), 2-chloroethanesulfonyl chloride (**9**) (2.14 g, 1.05 equiv.) and 3 mL TEA. Yield (0.148 g, 79%); Colorless oil; R$_f$: 0.73 (EtOAc: Isohexane, 1:4). IR (KBr, v_{max}, cm^{-1}): 3074, 2981, 2938, 1357, 1169, 894, 724. ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H1.48 (d, *J* 6.3 Hz, 3H, CH_3), 1.52-1.78 (m, 2H, CH_2), 2.12-2.21(m, 2H, CH_2), 4.50-4.75 (m, 1H, CH), 4.48-5.15 (m, 2H, 2CH), 5.60-5.80 (m, 1H, CH), 6.0 (d, H, *J* 7.3 Hz CH), 6.33 (d, H, *J* 7.3 Hz CH), 6.55 (m, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 20.75, 29.19, 29.03, 35.68, 80.44, 115.57, 128.95, 133.75, 136.92. MS *m/z*(%):190 [M$^+$] (5), 178 (100), 163 (25). Anal. Calcd for $C_8H_{14}O_3S$ (190.26): C, 50.50; H, 7.42; S, 16.85. Found: C, C, 50.42; H, 7.50; S, 16.76.

Hept-6-en-3-yl ethenesulfonate (11b). Compound **11b** was prepared according the general procedure from hept-6-en-3-ol (**8b**) (1.14 g, 10 mmol), 2-chloroethanesulfonyl chloride (**9**) (2.5 g, 1.5 equiv.) and 4 mL TEA Yield (0.137 g, 67%); Pale yellow oil; R$_f$: 0.58 (Et_2O/Pentane: 1/1). IR (KBr, v_{max}, cm^{-1}): 2968, 2938, 1357, 1162, 985, 755, 723. ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 0.89 (t, 3H, CH_3), 1.60-1.81 (m, 4H, 2CH_2), 2.10-2.38 (m, 2H, CH_2), 4.50-4.61 (m, 1H, CH), 5.0-5.22 (m, 2H, 3CH), 5.6-5.75 (m, 2H, 2CH), 6.10 (d, *J* 7.8 HZ, 1H, CH),´6.31 (d, *J* 7.8 HZ, H, CH), 6.51 5.0 (m, H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 9.11(q), 27.22 (t), 29.03 (t), 34.06 (t), 85 (d), 115.34 (t), 128.71(t), 133.78 (d), 137.06 (d). MS *m/z*(%): 189 [M-CH_3^+] (2), 175 (79; 149 (100); 91(90)[$C_2H_3SO_2^+$]; 55 (95)[$C_4H_7^+$]. Anal. Calcd for $C_9H_{16}O_3S$ (204.28): C, 52.92; H, 7.89; S, 15.69. Found:C, 53.05; H, 7.95; S, 15.72

7-Methyl-6,7-dihydro-5*H*-1,2-oxathiepine 2,2-dioxide (12a). Compound **12a** was prepared according the general procedure from hex-5-en-2-yl ethenesulfonate (**11a**) (0.88 g, 5 mmol), Grubbs catalyst 2nd generation (0.13 g, 0.03 eq) as a colorless crystals; Yield (75%); Pale yellow oil. IR (KBr, v_{max}, cm^{-1}): 3064, 1624, 1332, 1155, 1131, 890, 813, 782, 637. ^{1}H NMR ($CDCl_3$, 600 MHz): δ_H 1.37 (d, *J* 6.2 Hz, 3 H, CH_3), 1.72-2.11 (m, 2H, 2CH-CH_2), 2.32-2.51 (m, 2H, 2CH-CH_2), 4.48 (m, 1H, CH), 6.43-6.51 (m, 2H, 2CH-vinyl). ^{13}C NMR ($CDCl_3$, 151 MHz): 20.89 (q), 25.12 (t), 29.95 (t), 80.70 (d), 129.44 (d), 140.57 (d). MS *m/z*(%):162 [M$^+$] (6), 119 (100), 79 (9.6), 54 (82), 39 (90). Anal. Calcd for $C_6H_{10}O_3S$ (162.20): C, 44.43; H, 6.21 ; S, 19.77. Found: C, 44.48; H, 6,2; S, 19,66.

7-Ethyl-6,7-dihydro-5*H*-1,2-oxathiepine 2,2-dioxide (12b). Compound **12b** was prepared according the general procedure from hept-6-en-3-yl-ethenesulfonate (**11b**) (0.60 g, 2.94 mmol) and Grubbs catalyst 2nd generation (0.078 g, 0.09 mmol, 0.03 equiv.) as a pale yellow oil. Yield (518 mg, 71%); R$_f$: 0.31 (Et_2O/Pentane: 1/1); IR (KBr, v_{max}, cm^{-1}): 2970, 2935, 1335, 1156, 891, 638. ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 0.91 (t, 3H, CH_3), 1.50-1.62 (m, 1H, CH), 1.75-1.92 (m, 2H, 2CH), 2.10-2.20 (m, 1H, CH), 2.51-2.65 (m, 2H, 2CH), 4.52-4.61 (m, H, CH), 6.33-6.51 (m, 2H, 2CH). ^{13}C NMR ($CDCl_3$, 75 MHz; δ ppm): 9.89 (q), 25.07 (t), 27.95 (t), 30.73 (t), 85.59 (d), 131.23 (d), 140.26 (d). MS *m/z*(%):176 [M$^+$] (2), 147 (21) [M-$C_2H_5^+$], 119 (100), 83 (33), 54 (52) [$C_4H_6^+$]. Anal. Calcd for $C_7H_{12}O_3S$ (176.23):C, 47.71; H, 6.86; S, 18.19. Found: C, 47.60; H, 6.57; S, 18.05.

Ethyl (1*S*,4*S*,7*S*,8*R*)-4-ethyl-3-oxa-2-thiabicyclo[5.1.0]octane-8-carboxylate 2,2-dioxide(14). Compound **14** was prepared as colorless low-melting crystals with low yield (10%) according the general procedure from 7-ethyl-6,7-dihydro-5*H*-1,2-oxathiepine-2,2-dioxide (**12b**) (0.176 g, 1 mmol), ethyl diazoacetate (**9**) (0.3 mL of ethyl diazoacetate in 5 mL DCM over 6 h) and (0.0044 g, 1 mol%) rhodium(II) acetate dimer (method B). Yield (A: 0%, B: .026 g, 10%); colorless crystals; mp: 45-47 °C. IR (KBr, v_{max}, cm^{-1}): 2972, 1742, 1334, 1155, 890. ^1H NMR ($CDCl_3$, 500 MHz): δ_H 0.97-1.10 (m, 3H, CH, CH_3), 1.15-1.32 (m, 4H, $2CH_2$), 1.41 (t, 3H, CH_3), 1.70-182 (m, 1H, CH), 2.05-2.21(m, 1H, CH), 2.51-2.62 (m, 2H, CH_2), 4.20-4.29 (m, 2H, CH_2), 4.22-4.32(m, 1H, CH), 4.85-4.98 (m, 1H, 1-H). ^{13}C NMR ($CDCl_3$, 125MHz; δ ppm): 11.22 (q), 14.17 (q), 17.8 (d), 20.90 (d), 25.12 (t), 28.2 (t), 32.59 (t), 61.05 (d), 62.1 (t), 68.20 (d), 189.70 (s). MS *m/z*(%):262 [M^+] (2), 254 (33), 145 (48), 117 (100), 71 (50). Anal. Calcd for $C_{11}H_{18}O_5S$ (262.32): C, 50.36; H, 6.92; S, 12.22. Found: C, 50.16; H, 6.78; S, 12.31.

2-Allylphenyl ethenesulfonate (16). Compound **16** was prepared according the general procedure from 2-allylphenol **(15)** (1.34 g, 10 mmol), chloroethanesulfonyl chloride (**9**) (2.5 g, 1.5 equiv.) and 4 mL of TEA. Yield (1.75 g, 78%); Pale yellow oil R_f: 0.55 (Et_2O/Pentane: 1/1); IR (KBr, v_{max}, cm^{-1}): 3069, 1486, 1368, 1179, 1149, 870, 775, 756. ^1H NMR (300 MHz, $CDCl_3$): δ_H 3.41-352 (m, 2H, CH_2), 5.12-5.23 (m, 2H, =CH_2), 5.92-6.12 (m, 1H, CH), 6.22 (d, 1H, CH), 6.44 (d, 1H, CH), 6.75-6.90 (m, 1H, CH), 7.22-7.41 (m, 4H, 4CH-Ar). ^{13}C NMR (75 MHz, $CDCl_3$; δ ppm): 34.11(CH_2), 116.79 (CH_2), 121.99 (CH), 127.16 (CH), 127.23 (CH), 127.52 (CH), 130.89 (CH), 131.23 (CH_2), 132.58 (CH), 133.02 (CH), 135.42 (CH), 147.53 (CH). MS *m/z* (%): 224 [M^+] (85), 133 (91), 105 (100), 77(51), 51 (20). Anal. Calcd for $C_{11}H_{12}O_3S$(224.27):C, 58.91; H, 5.39; S, 14.30. Found:C, 58.82; H, 5.46; S, 14.32.

5*H*-Benzo[*f*][1,2]oxathiepine 2,2-dioxide (17). Compound **17** was prepared as colorless crystals according to the general procedure from 2-allylphenyl ethenesulfonate (**16**) (0.60 g, 2.67 mmol) and Grubbs catalyst 2nd generation (0.078 g, 0.09 mmol, 0.03 equiv. Yield (0.47 g, 90%); colorless crystals Et_2O/Pentane: 1/1);. IR (KBr, v_{max}, cm^{-1}): 3054, 1613, 1351, 1168, 1147, 878, 767. ^1H NMR ($CDCl_3$, 300 MHz): δ_H 3.72-3.79 (m, 2H, CH_2), 6.35 (m, 1H, CH), 6.48-6.52 (m, 1H, CH), 7.21-7.45 (m, 4H, 4CH-Ar). ^{13}C NMR ($CDCl_3$, δ ppm): 30.99, 123.51, 127.49, 127.64, 129.46, 129.70, 132.03, 137.52, 148.23. MS *m/z*(%):196 [M^+] (26), 131 (100), 103 (26), 77 (22). Anal. Calcd for $C_9H_8O_3S$ (196.22): C, 55.09; H, 4.11; S, 16.34. Found: C, 55.17; H, 3.95; S, 16.46.

Crystal data of compound 17: $C_9H_8O_3S$ M=196.22. a [Å]= 6.7227 (5), b [Å]= 7.2890 (5), c [Å]=9.6408 (7), α [°]=84.431(2), β [°]=85.660(2), γ[°]=63.030 (2), V[Å3]=418.78 (5), T[K]= 100 (2). Figure 1 illustrates the structure as determent. Full data can be obtained on requested from CCDC (CCDC 1867516)

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