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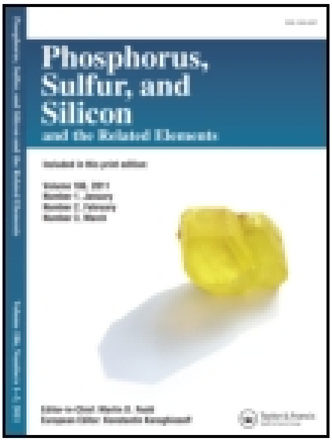

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Bifunctionalized Allenes. Part VIII. An Efficient and Varied Method for the Synthesis of 2-Sulfonylated Alka-2,3-Dienoates

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Accepted author version posted online: 10 Aug 2012.Published online: 05 Jul 2013.

To cite this article: Ivaylo K. Ivanov & Valerij Ch. Christov (2013) Bifunctionalized Allenes. Part VIII. An Efficient and Varied Method for the Synthesis of 2-Sulfonylated Alka-2,3-Dienoates, Phosphorus, Sulfur, and Silicon and the Related Elements, 188:7, 913-919, DOI: 10.1080/10426507.2012.718299

To link to this article: http://dx.doi.org/10.1080/10426507.2012.718299

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Phosphorus, Sulfur, and Silicon, 188:913–919, 2013

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2012.718299

BIFUNCTIONALIZED ALLENES. PART VIII. AN EFFICIENT AND VARIED METHOD FOR THE SYNTHESIS OF 2-SULFONYLATED ALKA-2,3-DIENOATES

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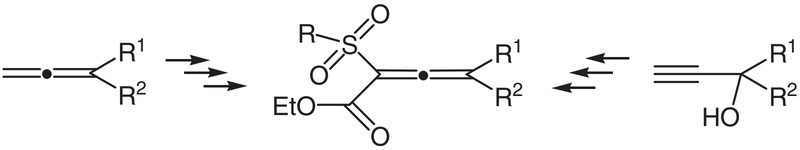
GRAPHICAL ABSTRACT



Abstract *An efficient and varied method for the synthesis of 2-sulfonylated alka-2,3-dienoates by intermediate formation of allenecarboxylates, allenyl sulfones, and propargyl sulfinates using the relatively high acidity of the hydrogen atom at the allenic C-1 atom and the [2,3]-sigmatropic rearrangement is described.*

Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.*

Keywords 2-Sulfonylated alka-2,3-dienoates; allenecarboxylates; allenyl sulfones; synthesis

INTRODUCTION

Allenes are unique compounds in organic chemistry by virtue of their adjacent, orthogonal π-bonds. Synthesis and use of allene derivatives have been expanded in preparative organic chemistry in the past three decades. The presence of two π electron clouds separated by a single sp hybridized carbon atom is the identifying structural characteristic of allenes, and it is this unique structural and electronic arrangement that is responsible for the extraordinary reactivity profile displayed by allenic compounds.[1]

Functionalized allenes have attracted a growing attention because of their versatility as key building blocks for organic synthesis. Functionalized allenes could be potentially involved in a number of transformations due to their high reactivity. Their main synthetic

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Received 20 June 2012; accepted 1 August 2012.

Support from the Research Fund of the Konstantin Preslavsky University of Shumen (Projects Nos. RD-05-137/2011 and RD-05-247/2012) is acknowledged. Special thanks to MSc Boris Prodanov and MSc Radost Nikolova for the technical help in the chromatographical separations.

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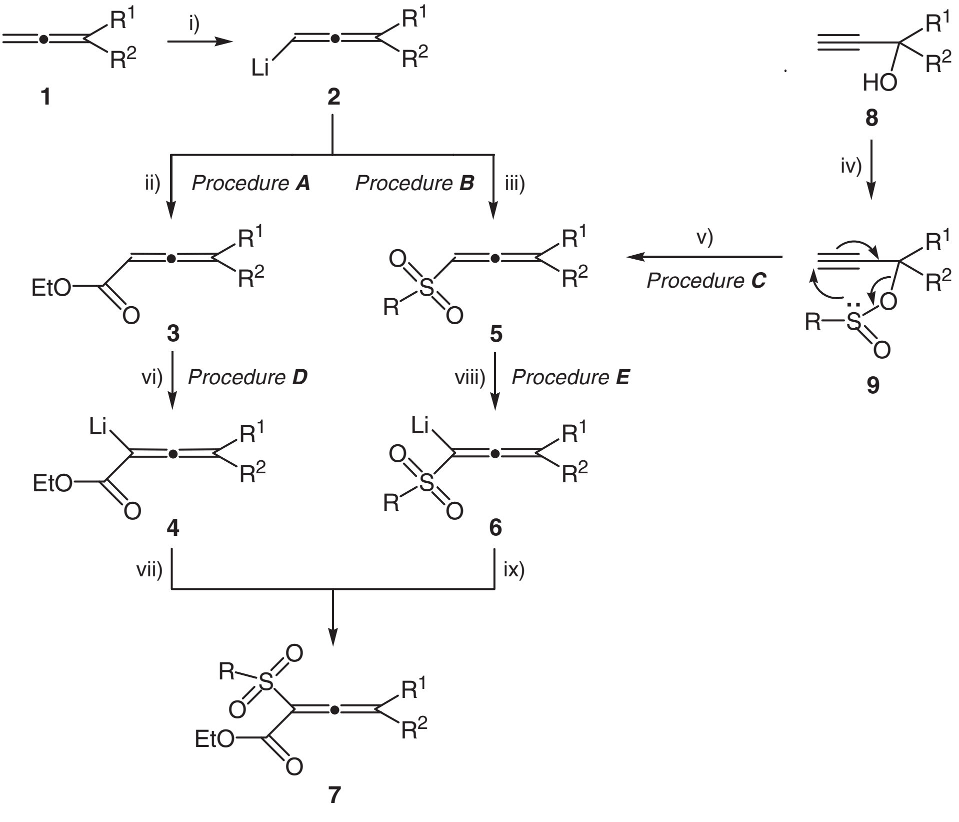
application is presently based on their ability to undergo function assisted lithiation and subsequent reactions with various electrophiles.[2–4]

Reaction of propargyl alcohols with sulfinyl chlorides is a convenient method for the preparation of propargyl sulfinates, which usually undergo [2,3]-sigmatropic rearrangement to allenyl sulfones.[5] An alternative route starts from methyl 4-hydroxy-2-alkynoate that enables the preparation of sulfonyl-substituted[6] allenecarboxylates.

As a part of our research program on the chemistry of the bifunctionalized allenes, we required a convenient method to introduce the sulfonyl group in the α-position to the ester group of the allenecarboxylates or the ester group in the α-position to the sulfonyl group of the allenyl sulfones. In continuation of our previous reports on the synthesis[7a,7b,7g] and electrophilic cyclization reactions[7a–7f] of bifunctionalized allenes, we have found an efficient and varied method for the synthesis of 2-sulfonylated alka-2,3-dienoates by intermediate formation of allenecarboxylates and allenyl sulfones.

RESULTS AND DISCUSSION

The method for the synthesis of the 2-sulfonylated alka-2,3-dienoates **7** consists of the following experimental procedures according to the reaction sequence outlined in Scheme 1.



Scheme 1 An efficient and varied method for synthesis of the 2-sulfonylated alka-2,3-dienoates **7** by intermediate formation of the allenecarboxylates **3**, the allenyl sulfones **5**, and the propargyl sulfinates **9**.

Table 1 Synthesis of the allenecarboxylates **3**, the allenyl sulfones **5**, and the 2-sulfonylated allenecarboxylates **7** according to Scheme 1

					Yields[a] (%), according to procedure no.				
Entry	R	R[1]	R[2]	Allene	**A**	**B**	**C**[b]	**D**	**E**
1	Me	Me	Me	**3a**, **5a**, **7a** [c]	67	69	49	64	70
2	Me	-$(CH_2)_5$-		**3b**, **5b**, **7b** [c]	65	71	52	64	64
3	Me	Me	Ph	**3c**, **5c**, **7c**	66	69	—	58	67
4	CCl_3	Me	Me	**3a**, **5d**, **7d** [c]	67	70	—	50	61
5	CCl_3	-$(CH_2)_5$-		**3b**, **5e**, **7e**	65	74	51	—	66
6	Ph	Me	Me	**3a**, **5f**, **7f**	67	—	49	57	63
7	Ph	-$(CH_2)_5$-		**3b**, **5g**, **7g**	65	70	47	65	61
8	Me_3SiO	Me	Me	**3a**, **7h**	67	—	—	60	—
9	Me_3SiO	-$(CH_2)_5$-		**3b**, **7i**	65	—	—	62	—
10	Me_3SiO	Me	Ph	**3c**, **7j**	66	—	—	59	—

[a] Isolated yields by chromatographical purification on silica gel.

[b] Overall yields without isolation of the alkynes **9**.

[c] Compounds **7a**, **7b**, and **7d** have been described in our earlier article.[7g]

Procedure A: Reaction of the lithio compounds **2**, in situ generated from alka-1,2-diene **1** and *n*-BuLi in tetrahydrofuran (THF) at −60°C, with ethyl chloroformate leads to formation of the expected allenecarboxylates **3a–b**, that were isolated by column chromatography as pale yellow oils in 65–67% yield after a conventional workup (see Table 1).

Reagents and conditions:

i) BuLi, THF, −60°C, 1 h, −20°C, 1 h;
ii) *Procedure **A***: $ClCO_2Et$, THF, −60°C to r.t., 1 h;
iii) *Procedure **B***: RSO_2Cl (R = Me, CCl_3, Ph), THF, −60°C to r.t., 2 h;
iv) *Procedure **C***: RS(O)Cl (R = Me, CCl_3, Ph), Et_3N, ether, −60°C, 1 h, r.t., 3 h;
v) [2,3]-sigmatropic rearrangement, toluene, reflux, 3 h;
vi) *Procedure **D***: BuLi, THF, −60°C, 1 h;
vii) RSO_2Cl, (R = Me, CCl_3, Ph, Me_3SiO), THF, −60°C to r.t., 2 h;
viii) *Procedure **E***: BuLi, THF, −60°C, 1 h;
ix) $ClCO_2Et$, THF, −60°C to r.t., 2 h;

Procedure B: The allenyl sulfones **5** are readily available by the reaction of the lithiated alka-1,2-diene **2**, prepared in situ according to ***Procedure A***, with methane-, trichloromethane-, or benzene-sulfonyl chloride in 69–74% isolated yield by chromatographical purification on silica gel.

Procedure C: Another strategy for the synthesis of the allenyl sulfones **5**, using our experience on the preparation of the vinyl allenyl sulfones,[8] relies on the well-precedented [2,3]-sigmatropic rearrangement of propargylic sulfinates to allenyl sulfones.[5] The starting materials in the synthesis of the allenyl sulfones **5** are the appropriate α-alkynols **8**, which react with methane-, trichloromethane-, or benzene-sulfinyl chloride in the presence of triethyl amine. Reflux of the intermediate formed propargyl sulfinates **9** (which may be or not be isolated) in toluene provokes a [2,3]-sigmatropic rearrangement to the expected allenyl sulfones **5**, which were purified by column chromatography on silica gel with 47–52% overall yield.

Procedure D: We found that the allenecarboxylates **3a–c**, prepared according to ***Procedure A***, can smoothly be deprotonated at α-position by *n*-BuLi in THF. The in situ resulting lithio compounds **4** can react with methane-, trichloromethane-, benzene-, or trimethylsilyloxy-sulfonyl chloride to give the pure 2-alkane(benzene)sulfonyl-allenoates **7a**–**g** or 2-trimethylsilyloxysulfonyl-allenoates **7h**–**j** in 50–65% yield after column chromatographically purification. Compounds **7a**, **7b**, and **7d** have been described in our earlier article.[7g]

Procedure E: The synthesized allenyl sulfones **5**, according to ***Procedure B*** or ***Procedure C***, undergo in situ lithiation at the α-carbon in treatment with *n*-BuLi and subsequent reaction with ethyl chloroformate to produce the desired 2-alkane(benzene)sulfonyl-allenoates **7a**–**g**, which after a conventional workup were isolated by column chromatography as light yellow oils in 61–70% yield.

In conclusion, a convenient, efficient, and varied method for the synthesis of a new family of 1,1-diacceptor-substituted allenes—namely 2-sulfonylated allenecarboxylates, derived by intermediate formation of allenecarboxylates, allenyl sulfones, and propargyl sulfinates applying the relatively high acidity of the hydrogen atom at the allenic C-1 atom and the [2,3]-sigmatropic rearrangement—has been explored. Further investigations on this potentially important synthetic methodology are currently in progress. At the same time, the synthetic application of the prepared 2-sulfonyl-functionalized allenecarboxylates for the synthesis of different heterocyclic compounds is now under investigation as a part of our general synthetic strategy for investigation of the score and limitations of the electrophilic cyclization reactions of bifunctionalized allenes. Results of these investigations will be reported in due course.

EXPERIMENTAL

Synthesis of the Allenecarboxylates 3 According to Procedure A

To a solution of *n*-BuLi (1.6 M in hexane, 6.25 mL, 10 mmol) in THF (70 mL) was added, dropwise with stirring over 15 min, a solution of alka-1,2-diene **1** (11 mmol) in THF (20 mL) at −60°C. The reaction mixture was stirred at this temperature for 1 h, the cooling bath was removed and the reaction mixture was allowed to warm up to −20°C and stirred at that temperature for 1 h, which was followed by the dropwise addition of a solution of chloroformate (1.09 g, 10 mmol) in 20 mL of THF at −60°C. After the addition was completed, the mixture was warmed to r.t. and stirred for 1 h. Then the mixture was quenched with 2N HCl, extracted with Et_2O, washed with sat. NaCl, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on column (silica gel, Kieselgel Merck 60 F_{254}) using a mixture of hexane and EtOAc as an eluent to give the pure allenoates **3a–c**.

According to **Procedure A**, the 1-ethenylidencyclohexane **1b** (1.19 g, 11 mmol) was converted by lithiation with BuLi and following reaction with chloroformate into *ethyl 3-cyclohexyliden-2-propenoate* **3b**. Yield: 1.17 g (65%, 6.5 mmol); light yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.20$ (t, $J = 7.2$ Hz, 3H, $MeCH_2O$), 1.30–2.43 (m, 10H, cyclohexylidene), 4.04 (q, $J = 7.2$ Hz, 2H, $MeCH_2O$), 5.37 (s, 1H, =CH). ^{13}C NMR ($CDCl_3$, 62.9 MHz): $\delta = 14.8$ (CH_3), 24.1 (CH_2), 26.4 (CH_2), 33.0 (CH_2), 61.2 (CH_2), 90.3 (CH), 102.3 (C), 168.5 (C), 207.6 (C). IR (film): 1712 (C=O), 1954 (C=C=C). Anal. Calcd. for $C_{11}H_{16}O_2$ (180.24): C, 73.29; H, 8.95. Found: C, 73.35; H, 8.87.

Synthesis of the Allenyl Sulfones 5 According to Procedure B

To lithiated allene **2**, generated in situ by **Procedure A**, was added, dropwise with stirring, a solution of methane-, trichloromethane-, or benzene-sulfonyl chloride (10 mmol) in 30 mL of THF at −60°C. After the addition was completed, the mixture was warmed to r.t. and stirred for 2 h. Then the mixture was quenched with 2N HCl, extracted with Et_2O, washed with sat. NaCl, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on column (silica gel, Kieselgel Merck 60 F_{254}) using a mixture of hexane and EtOAc as an eluent to give the pure allenyl sulfones **5a**–**g**.

According to **Procedure B**, the 3-methylbuta-1,2-diene **1a** (0.749 g, 10 mmol) was converted by lithiation with BuLi and following reaction with trichloromethane-sulfonyl chloride (2.18 g, 10 mmol) into the *3-methyl-buta-1,2-dienyl trichloromethyl sulfone* **5d**. Yield: 1.75 g (70%, 7.0 mmol); yellow oil. ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 1.71$ (d, $J = 2.7$ Hz, 6H, 2Me), 6.24 (d, $J = 2.7$ Hz, 1H, =CH). ^{13}C NMR ($CDCl_3$, 62.9 MHz): $\delta =$ 21.7 (CH_3), 102.8 (C), 106.5 (CH), 107.8 (C), 205.6 (C). IR (film): 1122, 1338 (SO_2), 1957 (C=C=C). Anal. Calcd. for $C_6H_7O_2SCl_3$ (249.53): C, 28.88; H, 2.83; S, 12.85. Found: C, 28.93; H, 2.88; S, 12.91.

Synthesis of the Allenyl Sulfones 5 According to Procedure C

To a solution of α-alkynol **8** (10 mmol) and triethylamine (1.21 g, 12 mmol) in dry ether (50 mL) at −60°C was added, dropwise with stirring, a solution of freshly distilled or recrystallized methane-, trichloromethane-, or benzene-sulfinyl chloride (10 mmol) in the same solvent (20 mL). The reaction mixture was stirred for 1 h at the same temperature and for 3 h at r.t. and then washed with water, 2N HCl, extracted with Et_2O. The extract was washed with sat. NaCl, and dried over anhydrous Na_2SO_4. Evaporation yielded the crude product **9**, which was dissolved in dried toluene (10 mL) and refluxed for 3 h. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (Kieselgel Merck 60 F_{254}) (eluent: EtOAc-heptane) to yield the pure allenyl sulfones **5a**–**g**.

According to **Procedure C**, the *methyl 3-methyl-buta-1,2-dienyl sulfone* **5a** (yield: 0.72 g, 49%, 4.9 mmol) was prepared in a one-pot reaction via [2,3]-sigmatropic rearrangement of the 2-methanesulfinyloxy-2-methylbut-3-yn **9a**, obtained from 2-methylbut-3-yn-2-ol **8a** (0.84 g, 10 mmol) and methane-sulfinyl chloride (0.99 g, 10 mmol) in the presence of triethylamine. Spectroscopic properties of **5a** were fully in accord with those reported above (**Procedure B**).

Synthesis of the 2-sulfonylated Allenecarboxylates 7 According to Procedure D

To a solution of *n*-BuLi (1.6 M in hexane, 3.13 mL, 5 mmol) in THF (20 mL) was added, dropwise with stirring over 20 min, a solution of allenecarboxylate **3** (5.5 mmol) in THF (10 mL) at −60°C. The reaction mixture was stirred at this temperature for 1 h, which was followed by the dropwise addition of a solution of methane-, trichloromethane-, benzene-, or trimethylsilyloxy-sulfonyl chloride (5 mmol) in 10 mL of THF at −60°C. After the addition was completed, the mixture was warmed to r.t. and stirred for 2 h. Then the mixture was quenched with 2N HCl, extracted with Et_2O, washed with sat. NaCl, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on column (silica gel, Kieselgel Merck 60 F_{254}) using a mixture of hexane and EtOAc as eluent to give the pure 2-sulfonylated allenoates **7a–j**.

According to **Procedure D**, the *ethyl 2-methanesulfonyl-4-phenyl-penta-2,3-dienoate* **7c** (yield: 0.81 g, 58%, 2.89 mmol) was prepared by lithiation of ethyl 4-phenylpenta-2,3-dienoate **3c** (1.11 g, 5.5 mmol) with BuLi and following reaction with methane-sulfonyl chloride (0.57 g, 5 mmol). Light yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.42 (t, J = 7.1 Hz, 3H, $MeCH_2O$), 2.07 (s, 3H, Me), 2.98 (s, 3H, $MeSO_2$), 4.31 (q, J = 7.1 Hz, 3H, $MeCH_2O$), 7.04–7.59 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 14.0 (CH_3), 18.2 (CH_3), 41.2 (CH_3), 62.0 (CH_2), 97.4 (C), 109.1 (C), 128.0–139.2 (Ph), 162.5 (C), 214.8 (C). IR (film): 1126, 1340 (SO_2), 1717 (C=O), 1955 (C=C=C). Anal. Calcd. for $C_9H_{14}O_4S$ (280.34): C, 59.98; H, 5.75; S, 11.44. Found: C, 60.04; H, 5.71; S, 11.49.

According to **Procedure D**, the *ethyl 3-cyclohexylidene-trimethylsilyloxysulfonyl-prop-2-enoate* **7i** (yield: 1.03 g, 62%, 3.1 mmol) was prepared by lithiation of the ethyl 3-cyclohexyliden-2-propenoate **3b** (0.99 g, 5.5 mmol) with BuLi and following reaction with trimethylsilyloxy-sulfonyl chloride (2.23 g, 5 mmol). Light yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.32 (s, 9H, Me_3SiO), 1.31 (t, J = 7.0 Hz, 3H, Me), 1.42–2.36 (m, 10H, cyclohexyliden), 5.01 (q, J = 7.0 Hz, 2H, $MeCH_2O$). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 6.6 (CH_3), 14.8 (CH_3), 24.0 (CH_2), 26.4 (CH_2), 30.1 (CH_2), 58.3 (CH_2), 91.1 (C), 103.5 (C), 163.2 (C), 207.3 (C). IR (film): 1142, 1338 (SO_2), 1956 (C=C=C). Anal. Calcd. for $C_{14}H_{24}O_5SSi$ (332.49): C, 50.57; H, 7.28; S, 9.64. Found: C, 50.70; H, 7.19; S, 9.72.

Synthesis of the 2-Sulfonylated Allenecarboxylates 7 According to Procedure E

To a solution of *n*-BuLi (1.6 M in hexane, 3.13 mL, 5 mmol) in THF (20 mL) was added, dropwise with stirring over 20 min, a solution of allenyl sulfone **5** (5.5 mmol) in THF (10 mL) at −60°C. The reaction mixture was stirred at this temperature for 1 h, which was followed by the dropwise addition of a solution of chloroformate (0.55 g, 5 mmol) in 10 mL of THF at −60°C. After the addition was completed, the mixture was warmed to r.t. and stirred for 2 h. Then the mixture was quenched with 2N HCl, extracted with Et_2O, washed with sat. NaCl, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on column (silica gel, Kieselgel Merck 60 F_{254}) using a mixture of hexane and EtOAc as eluent to give the pure 2-sulfonylated allenoates **7a–g**.

According to **Procedure E**, the *ethyl 3-cyclohexylidene-2-trichloromethanesulfonyl-prop-2-enoate* **7e** (yield: 1.19 g, 66%, 3.3 mmol) was prepared by lithiation of the 2-cyclohexyliden-ethenyl trichloromethyl sulfone **5e** (1.64 g, 5.5 mmol) with BuLi and following reaction with chloroformate. Light yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.41 (t, J = 7.0 Hz, 3H, Me), 1.35–2.40 (m, 10H, cyclohexylidene), 4.29 (q, J = 7.0 Hz, 2H, $MeCH_2O$). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 15.2 (CH_3), 23.9 (CH_2), 26.0 (CH_2), 33.3 (CH_2), 62.4 (CH_2), 91.2 (C), 106.3 (C), 110.4 (C), 155.7 (C), 212.6 (C). IR (film): 1132, 1337 (SO_2), 1722 (C=O), 1955 (C=C=C). Anal. Calcd. for $C_{12}H_{15}O_4SCl_3$ (361.67): C, 39.85; H, 4.18; S, 8.87. Found: C, 39.95; H, 4.28; S, 8.83.

Supplemental materials available. Method of analysis, starting materials, and full spectroscopic and characterization data including ^{1}H and ^{13}C NMR and IR spectral data and elemental analyses for all new compounds and literature references to these data for known compounds is listed.

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