Oxidative Fragmentations of 2-(Trimethylsilyl)ethyl Sulfoxides − Routes to Alkane-, Arene-, and Highly Substituted 1-Alkenesulfinyl Chlorides

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Dedicated to Professor Gord Lange on the occasion of his retirement

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The preparation of a collection of alkyl, aryl, and 1-alkenyl 2-(trimethylsilyl)ethyl sulfoxides is outlined, using mostly vinyltrimethylsilane or 2-(trimethylsilyl)ethanesulfenyl chloride (**5**) as key starting materials. The 2-(trimethylsilyl)ethyl group can be cleaved from many of the sulfoxides under oxidative fragmentation conditions using sulfuryl chloride and the reaction represents a new protocol for sulfinyl chloride synthesis. The method is suitable for most alkane- and arenesulfinyl chlorides (**3**), but is limited to highly substituted vinylic sulfinyl chlorides. 1-Alkenyl 2-(trimethylsilyl)ethyl sulfoxides with reduced double bond substitution (**6**, **7**, **11**) succumb to reactions involving chlorination of the double bond. The β-effect of silicon is invoked to explain the ability of the 2-(trimethylsilyl)ethyl group to induce C–S bond scission under the oxidative cleavage reaction conditions. A mechanism is offered to account for the role played by the β-silicon atom of the 2-(trimethylsilyl)ethyl group. Indeed, the silicon atom is self-sacrificial in that it diverts the course of the reaction from the usual α-carbon chlorination mode to one of oxidative cleavage, whereby the 2-(trimethylsilyl)ethyl group is lost. The overall reaction calls upon the ability of silicon atoms to donate electron density by hyperconjugation.

The sulfinyl chloride unit is one of the fundamental building blocks of organosulfur chemistry.[1] It is not only the ultimate starting unit for many sulfinic acid derivatives,[2] but also for a number of sulfonyl-containing functionalities.[3−6] Sulfinyl chlorides remain one of the key starting points in the preparation of enantioenriched sulfoxides through the intermediacy of chiral sulfinic esters[1,7,8] and amides.[9,10] An extension of that chiral sulfinate chemistry ties to the burgeoning field of asymmetric sulfinimine chemistry and the synthetic diversity that it offers.[11,12]

Many preparations of sulfinyl chlorides involve oxidations of a sulfur atom.[1,13] That atom may belong to a thiol, disulfide or thiolacetate and the resulting sulfinyl chloride must be separated from acidic by-products or otherwise treated in the presence of those by-products. A less common protocol entails starting with a sulfoxide and effecting C−S bond cleavage by way of oxidative fragmentation conditions (Scheme 1). Such a method circumvents the acidic conditions of older procedures and provides a sulfinyl chloride readily available for further functionalization. In this regard, the phthalimidomethyl[14,15] and *tert*-butyl[16] groups have proved useful for the generation of a number of alkane- and arenesulfinyl chlorides or their derivatives. The method is also useful for the generation of 1-alkenesulfinyl chlorides when the group to be severed is a *p*-methoxybenzyl or benzhydryl group.[17]

X = H, Ac, SR; G = removable alkyl group (see text)

Scheme 1

2-(Trimethylsilyl)ethyl sulfur functionalities play a variety of roles in organic chemistry.[18,19] Vinylic and acetylenic 2-(trimethylsilyl)ethyl sulfides are particularly useful as a source of α,β-unsaturated thiolates,[20−24] while Toru et al. have shown that lithiated 2-(trimethylsilyl)ethyl sulfoxides serve as viable vinyl anion synthons.[25] Fuchs and coworkers employed alkyl 2-(trimethylsilyl)ethyl sulfides as agents for the selective formation of β-thioglycosides.[26] Weinreb et al. have shown that 2-(trimethylsilyl)ethylsulfonyl chloride is an excellent reagent for the sulfonyl-based protection of primary and secondary amines. The amines are readily released through the use of fluoride.[27]

In addition to the characteristics that promote the useful chemistry described above, the 2-(trimethylsilyl)ethyl group also has electron-donating properties not unlike those of phthalimidomethyl and *tert*-butyl and, as such, could enhance the fragmentation reaction pathway of sulfoxides upon treatment with a positive chlorine equivalent. To that end, this paper outlines the successful use of 2-(trimethylsilyl)ethyl sulfoxides for the generation of a wide range of sulfinyl chlorides including the first collection of highly functionalized vinylsulfinyl chlorides.[28−30]

Results and Discussion

Alkane- and Arenesulfinyl Chlorides

The 2-(trimethylsilyl)ethyl sulfoxides **2** used for the various Pummerer-like treatments described herein were pre-

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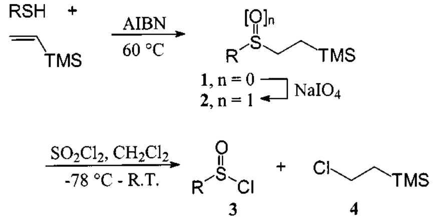
pared by $NaIO_4$ oxidation of the corresponding sulfides **1**. Sulfides **1** were obtained through radical addition of a thiol to trimethyl(vinyl)silane as described previously by us[31] and others.[26,32] The overall approach to sulfoxides **2** is indicated in the first two steps of Scheme 2, with the yields presented in Table 1.[31,33] Although treatment of simple alkyl-bearing sulfoxides with sulfuryl chloride would be expected to afford the product of α-chlorination,[34,35] it was quickly discovered that the 2-(trimethylsilyl)ethyl group induced a different behavior. The reaction of sulfuryl chloride with both aryl and alkyl 2-(trimethylsilyl)ethyl sulfoxides afforded sulfinyl chlorides, resulting from C−S bond cleavage on the side bearing the silicon atom (Scheme 2). The products were identified by their boiling points and through spectroscopic means. Most diagnostic was the S=O stretch of the products in their IR spectra. This band was typically in the 1160−1143 cm^{-1} range, which is higher than that of the starting sulfoxide by ca. 110 cm^{-1}. When the reactions were performed on a preparative scale, the products were distilled (***CAUTION!***) where possible and good yields of the sulfinyl chloride were usually obtained (Table 1). Exceptions include those systems bearing smaller (propyl) groups opposite the 2-(trimethylsilyl)ethyl moiety. This is due to a co-product of the reaction, 2-(trimethylsilyl)ethyl chloride (**4**).



Scheme 2

2-(Trimethylsilyl)ethyl chloride (**4**) was formed in 10−40% yield as evidenced by viewing the ^1H NMR spectrum of the crude reaction mixture. Compound **4** has a boiling point similar to the products with a smaller alkyl group, such as **3g−i**, and in those cases separation through distillation was difficult even though the crude mixtures indicated an 80−85% yield of sulfinyl chloride. The yield of 64% for **3h** is still substantially higher than the 21% reported previously.[36] All sulfinyl compounds can be treated without purification due to the comparativly low reactivity of the coproduct **4**.

This preparative route to sulfinyl chlorides is valuable since a 2-(trimethylsilyl)ethyl-protected sulfur atom can be carried through several steps before eventual liberation as a sulfinyl chloride. The 2-(trimethylsilyl)ethyl sulfides are particularly stable toward acid, base and heat and the corresponding sulfoxides, though more reactive, also possess some of these qualities. Furthermore, the reaction mixture is devoid of HCl and AcCl, which are acidic by-products of some preparations of sulfinyl chlorides.[1]

1-Alkenesulfinyl Chlorides

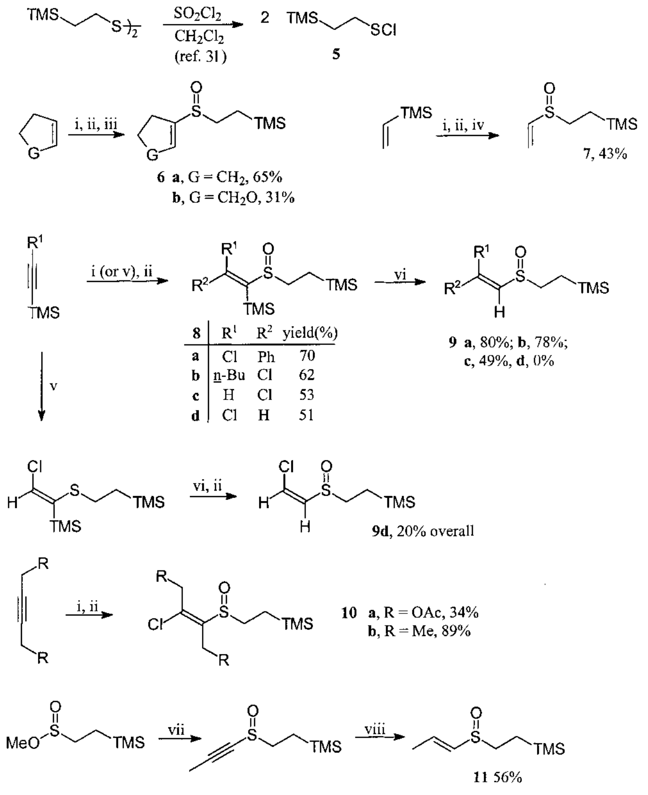
The oxidative fragmentation method is to this point the only published protocol for the generation of a family of 1-alkenesulfinyl chlorides.[17] It was reported that *p*-methoxybenzyl and diphenylmethyl groups could be oxidatively cleaved from the sulfinyl unit, offering a collection of monosubstituted ethenesulfinic acid derivatives. As discovered above, the 2-(trimethylsilyl)ethyl functionality also promotes fragmentation and, accordingly, a number of sulfoxides were prepared for evaluation as precursors to sulfinyl chlorides.

2-(Trimethylsilyl)ethanesulfenyl chloride (**5**)[31] was chosen as a starting material since it is readily available from bis[2-(trimethylsilyl)ethyl] disulfide, and it would allow rapid introduction of the 2-(trimethylsilyl)ethyl group and a chloride functionality onto an unsaturated substrate. Depending on the substrate(s) chosen, there is adequate opportunity to create highly substituted ethenesulfinyl entities, thereby fashioning a protocol that is complementary to the existing 1-alkenesulfinyl chloride preparation.[17]

Table 1. Preparation of 2-(trimethylsilyl)ethyl sulfoxides **2** and their oxidative fragmentation to sulfinyl chlorides **3** (Scheme 1)

Entry		R	Yields of pure material		
			Sulfides **1**[a]	Sulfoxides **2**[a]	Sulfinyl chlorides **3**
1	**a**	Ph	84	98	90
2	**b**	*p*-MeC_6H_4	87[b]	98	94
3	**c**	*p*-ClC_6H_4	82	80	92
4	**d**	*m*-$MeOC_6H_4$	88	87	83[c][d]
5	**e**	2-naphthyl	92[b]	90	80[c][e]
6	**f**	$PhCH_2$	87[b]	98	94
7	**g**	*i*Pr	85	95	59
8	**h**	allyl	81[f]	86	64
9	**i**	*n*Pr	80	95	61
10	**j**	$TMS(CH_2)_2$	85[b]	99[b]	68[g]
11	**k**	*c*-C_6H_{11}	89[b]	95	96
12	**l**	*n*-$C_{12}H_{23}$	93[c]	94	100[c]
13	**m**	$EtOC(O)CH_2$	83	91	0

[a] Compounds were purified by either flash chromatography, recrystallization or distillation. − [b] This yield has been reported previously by our group; see refs.[31,33] − [c] Crude yield reported. − [d] Derivatized for isolation and identification. − [e] Decomposition occurred during purification by distillation. − [f] Sulfide **1h** was prepared by the reaction of $TMS(CH_2)_2SH$ and allyl bromide. − [g] Since this work was performed, we have reported an improved synthesis of **3j** through the reaction of *tert*-butyl 2-(trimethylsilyl)ethyl sulfoxide with SO_2Cl_2 in ether; see ref.[31]



i: **5**, CH_2Cl_2, -78 °C; ii: MCPBA, CH_2Cl_2, -78 °C; iii: NaI, DBU, 80 °C, THF; iv: TBAF
v: **5**, CH_2Cl_2, O °C; vi: K_2CO_3, MeOH; vii: $MeC{\equiv}C^-Li^+$, THF; viii: LAH, diethyl ether.

Scheme 3

Scheme 3 shows several reaction equations outlining the synthesis of the starting materials prepared for this section of the study. The addition of 2-(trimethylsilyl)ethanesulfenyl chloride (**5**) across the double bond of cyclopentene and dihydropyran afforded the expected β-chlorosulfide adducts, which were treated with base to eliminate readily HCl and create, after oxidation, sulfoxides **6**. Sulfenyl chloride **5** was also added across trimethyl(vinyl)silane in a regioselective manner; subsequent oxidation and fluoride-induced elimination of TMSCl supplied vinyl sulfoxide **7**.

The use of trimethylsilyl-substituted alkynes offered direct preparation of vinylsulfur compounds without the need for an elimination step and offered a single adduct due to the directing effects of the silyl unit.[37,38] Sulfoxides **8b−c** were prepared by employing this protocol; the *trans* mode of addition arises from the reactions of sulfenyl chlorides with alkynes.[39] Chemoselective protiodesilylation of **8a−c** was readily achieved and furnished sulfoxides **9a−c**. It was found that performing the addition of **5** to trimethylsilylacetylene at higher temperature preferentially yielded the opposite geometric isomer **8d**. However, **8d** decomposed under various protiodesilylation conditions. Sulfoxide **9d** was eventually obtained by chemoselective protiodesilylation *prior to* oxidation. The coupling constants in the ^{1}H NMR spectra of **9c** and **9d** validated the initial assignments of the modes of addition of sulfenyl chloride **5**. Further support can be found through the appearance of the proton signals of the methylene groups that are attached to the double bond in **8b** and **9b**. They each exhibit AB character with a substantial difference in chemical shift, which is induced by the asymmetry of the proximate *cis*-sulfinyl unit. In previous observations,[17] methylene units *trans* to a sulfinyl group experience only small or nonexistent anisotropic effects.

Compounds **8a** and **9a** have been assigned the (*Z*) geometry based on evidence related here and later in the paper. Application of the alkene additivity rule to **9a** was not considered immediately helpful, since the actual ^{1}H NMR chemical shift of the lone vinylic H falls about halfway between predicted values for the (*E*) and (*Z*) isomers. However, the additivity rule predicts higher δ values than experimentally found for (*E*)- and (*Z*)-2-phenylethenyl sulfoxides previously prepared in our laboratory. Making a correction then favors the geometry indicated for **9a**. Also when the sulfide formed by addition of **5** to phenyl(trimethylsilyl)acetylene was heated, no geometry change occurred, suggesting that the more thermodynamic isomer was the one already isolated. To explain the isolation of the thermodynamically favored *cis* adduct of **5** with the alkyne, it is suggested that the addition mechanism does not involve the intermediacy of a thiirenium ion. Rather, due to the relative energetics of each mode of carbocation stabilization, we submit that the combination of the silicon β-effect[40−42] and benzylic stabilization can override the geometry-directing effects of the bridging sulfur atom.[43] A related precedent is available: The finding that Br_2 adds across (*E*)-2-(trimethylsilyl)styrene to afford the *syn* adduct and not the usual *anti* product indicates that the strength the silicon β-effect and benzylic stabilization can overcome the bridging bromonium ion.[44,45]

Without the directing effects of a TMS group, compound **5** also presents a lone adduct upon reaction with symmetric alkynes. Thus, addition of **5** to such acetylenes and subsequent *m*-CPBA oxidation provided unsaturated sulfoxides **10**. Finally, (*E*)-propenyl 2-(trimethylsilyl)ethyl sulfoxide (**11**) was prepared by addition of 1-propynyllithium[46] to methyl 2-(trimethylsilyl)ethanesulfinate and reduction of the triple bond.

The various vinylic sulfoxides **6−11** were exposed to SO_2Cl_2 to generate the sulfinyl chlorides. In those instances where sulfinyl chloride was present (TLC), an IR spectrum was obtained and the acid chloride was quenched with K_2CO_3 and either cyclohexanol or 3-phenylpropanol. Isolation of the resulting sulfinate ester facilitated full characterization to confidently ascertain the structure of the sulfinyl chloride.[17] Table 2 indicates the results from all oxidative fragmentation attempts.

The more substituted congeners, including **8a**,**b**/**9a**,**b**/**10a**,**b**, gave clean fragmentation and the capture reactions provided α,β-unsaturated sulfinate esters **13a**,**b**/**14a**,**b**/**15a**,**b** in 52−87% yield (Figure 1), comparable to those obtained through oxidative fragmentation reactions of other vinylic sulfoxides.[17] Sulfoxides **6a** and **7** reacted with the oxidant, but not in the manner expected: No C−S fragmentation was detected and a Pummerer-like addition occurred instead. Substrate **6b** did not offer any isolable product. Com-

Table 2. Oxidative fragmentation attempts of vinylic 2-(trimethylsilyl)ethyl sulfoxides (see Figure 1)

Entry	Starting sulfoxide	Product(s)[a]	Yield[b]	S=O stretch[c]
1	**7**	**12a**	45%	–
2	**6a**	**12b**	79%	–
3	**6b**	no products obtained	–	–
4	**8a**	**13a**[d]	87%	1153
5	**8b**	**13b**	59%	1149
6	**8c**	**13d**	52%	1138
7	**8d**	**13d**	57%	1139
8	**9a**	**14a**[d]	65%	1154
9	**9b**	**14b**	67%	1154
10	**9c**[e]	**14c**	33%	–
11	**9c**	**14c**	57%	1133
12	**9d**[e]	**14c**	34%	–
13	**9d**	**14c**	32%	–
		14d	27%	1154
14	**10a**	**15a**[d]	53%	1156
15	**10b**	**15b**[d]	78%	1153
16	**11**	**16**	27%	1145[f]

[a] Conditions involve 1.2 equiv. of SO_2Cl_2 unless otherwise stated. Sulfinyl chlorides, if present, were captured by the addition of $Ph(CH_2)_3OH$ [i.e., Z = $(CH_2)_3Ph$] unless otherwise stated. – [b] Yield of chromatographed material. – [c] The S=O stretch (in cm^{-1}) of the intermediary sulfinyl chloride is reported when measurable. – [d] Sulfinyl chlorides were captured with cyclohexanol (Z = c-C_6H_{11}). – [e] 0.7 equiv. of SO_2Cl_2 was employed. – [f] It is unknown whether the sulfinyl chloride associated with this IR stretching frequency is unsaturated or dichlorinated.

pounds **8c**,**d** both afforded the same reaction product, assigned the structure of **13d** after protiodesilylation and measurement of the ^1H NMR coupling constant of the (*Z*)-vinylic hydrogen atoms. ^1H NMR analysis of the fragmentation mixtures in the cases of **8c**,**d** revealed that isomerization most likely took place prior to sulfinyl chloride formation.

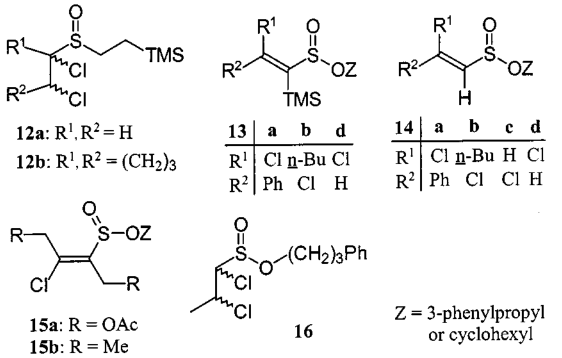


Figure 1. Products of oxidative fragmentations of vinylic 2-(trimethylsilyl)ethyl sulfoxides (see Table 2)

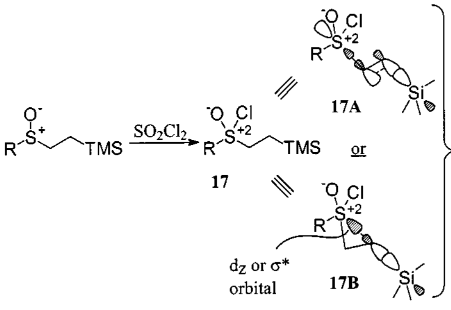
The observation of double bond isomerization during sulfinyl chloride formation prompted a reexamination of compounds **13a**,**b**/**14a**,**b**/**15a**,**b**. Those compounds with methylene groups (*Z*) to the sulfinyl unit (**13b**/**14b**/**15a**,**b**) again exhibited noteworthy magnetic anisotropy upon ^1H NMR analysis of the hydrogen atoms in that methylene group. To confirm the structures assigned to **13a** and **14a**, **13a** was first converted into **14a** through protiodesilylation to confirm that each compound contained the same relative placement of the sulfur atom and the chlorine atom. A comparison of the ^1H NMR chemical shifts of the vinylic hydrogen atoms of sulfinate **14a**, sulfoxide **9a** and the intermediary sulfinyl chloride was then performed. The trend of increasing incremental chemical shifts in the order of sulfoxide < sulfinate < sulfinyl chloride is consistent with that already established,[17] and indicates that double bond isomerization had not occurred.

The fragmentation chemistry of sulfoxides **9c**,**d** (Entries 10–13) had to be performed carefully as too much sulfuryl chloride lowered the yield. The best yields were obtained using 0.7 equiv. of SO_2Cl_2, although **9d**, with the (*Z*)-Cl group showed a tendency to isomerize to its (*Z*) isomer *after* formation of the sulfinyl chloride. The behavior of **11** proved unique. IR and TLC analysis indicated sulfinyl chloride formation, although the eventual product had been doubly chlorinated. NMR experiments could not determine whether the chlorination occurred before or after a successful fragmentation.

Mechanism

The literature generally favors the formation of a chlorosulfoxonium ion (**17**, Scheme 4) upon the reaction of a sulfoxide with chlorine or a chlorine surrogate such as SO_2Cl_2. With many alkyl substituents, an α-deprotonation reaction occurs and consequent reactions afford an α-chlorosulfoxide. Clearly in the case of the 2-(trimethylsilyl)ethyl group, the chlorosulfoxonium ion follows an alternative pathway. The evidence suggests that for chlorosulfoxonium ions bearing 2-(trimethylsilyl)ethyl groups, carbon–sulfur bond cleavage is the preferred fate. That cleavage is presumably brought on by the electron-donating influence of the silicon atom.

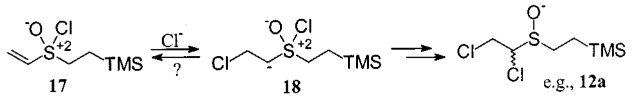
It is suggested that the silicon atom imparts electron density toward the cationic sulfur atom. Reasonable modes of stabilization are shown in Scheme 4. Mode A invokes a hyperconjugative stabilization action of a β-silicon atom[37,47] where electron donation from the C–Si σ bond to the C–S σ* anti-bonding orbital weakens the C–S bond. Stabilization mode B involves percaudal or γ-stabilization[48–50] whereby there is direct electron donation from the σ lobe of the Si–C bond to an available lobe on the cationic sulfur.



Scheme 4

That sulfur orbital may be a sulfur d orbital or a σ* orbital of the S−O or S−Cl bond. Based on solvolysis rate enhancement data, which balances β- and γ-stabilization against model compounds,[37,47] mode A would be predicted to be the more likely of the two options. Furthermore, an experimental preference for intermediate **17A** can be found by analysis of the fragmentation reactions mixtures. One piece of evidence that points towards the involvement of **17A** is that TMSCH$_2$CH$_2$Cl accompanied sulfinyl chloride in each fragmentation. This material may be formed by chloride attack of an intermediate with a weakened C−S bond such as in **17A**, or by capture of the 2-(trimethylsilyl)ethyl cation upon its spontaneous release from **17A**. On the other hand, it is difficult to envision a method for the release of the 2-(trimethylsilyl)ethyl unit from intermediate **17B**. On the basis of this analysis, we suggest that silicon offers stabilization to the sulfur cation as shown for **17A** and that mode of interaction induces chloride attack *at* the α-carbon atom in preference to deprotonation of the α-carbon atom, the typical recourse for chlorosulfoxonium ions.[34,35]

The above mechanism is suitable for the entries indicated in Table 1 and for the alkenesulfinyl chloride formation represented in Table 2. The occurrence of the dichlorination products of Table 2 can be readily explained by nucleophilic attack at the chlorosulfoxonium stage or later. The positively charged sulfur atom of **17** enhances the electrophilic character of the double bond and offers the chloride ion another option for attack. Hence, a Michael addition followed by Pummerer-like chemistry completes the formation of the doubly chlorinated compounds (Scheme 5). The data suggests that those substrates with fewer double-bond substituents are more prone to attack, while more substituted double bonds favor C−S bond cleavage.



Scheme 5

The mechanism presented in Scheme 5 can also account for the isomerizations observed for compounds **8d** and **9d**. It is feasible that the formation of intermediate **18** is reversible and, if so, there is opportunity for C−C single bond rotation and hence isomerization as the double-bonded compound is regenerated. In the instances of **8d** and **9d**, Michael additions are presumably occurring, but loss of one of the two possible chlorides prevails over subsequent "Pummerer steps". The fragmentation reaction eventually affords the sulfinyl chloride.

There is a clear preference for the isomer **8d** to isomerize to the (*E*) isomer. It is suggested herein that the *trans* disposition of silicon and halogen atoms about a double bond is thermodynamically favored over the alternative. Figure 2 depicts the opportunity for significant σ(Si−C) to σ* (C−Cl) donation that is expected to be present in any (*E*)-1-chloro-2-silylalkene. Such an interaction offers a stabilizing advantage over the opposite double bond geometry.

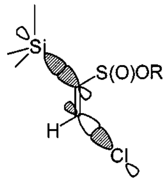


Figure 2. A stabilizing orbital interaction in (*E*)-2-silyl-1-alkenyl chlorides

Conclusions

The 2-(trimethylsilyl)ethyl group can be cleaved from alkyl, aryl, and selected 1-alkenyl 2-(trimethylsilyl)ethyl sulfoxides under oxidative fragmentation conditions and represents a new preparation of sulfinyl chlorides. The reaction is generally straightforward for alkane- and arenesulfinyl chlorides, but for a successful 1-alkenesulfinyl chloride synthesis using this protocol, there must be a high degree of substitution on the double bond of the substrates. In this regard, the method is complementary to the only other synthetic approach to 1-alkenesulfinyl chlorides, which has been shown to be suitable for a family of un- and monosubstituted systems.[17] The various examples presented permit the claim that the fragmentation protocol is one of the most broadly applicable sulfinyl chloride syntheses available.

A mechanism is offered to account for the role played by the β-silicon atom of the 2-(trimethylsilyl)ethyl group. Indeed, the silicon atom is self-sacrificial in that it diverts the course of the reaction from the usual α-carbon chlorination mode to one of oxidative cleavage, whereby the 2-(trimethylsilyl)ethyl group is lost. The overall reaction invokes the ability of silicon atoms to donate electron density by hyperconjugation.

Experimental Section

Our general experimental methods have been reported previously.[17,31,33] SO$_2$Cl$_2$ was employed either neat or as a 1 M solution in CH$_2$Cl$_2$. Older bottles were discarded before complete consumption of the contents.

General Synthesis of Sulfides 1a−g, i−m: The thiol and trimethyl(vinyl)silane (1.2 equiv.) were combined under nitrogen in the absence of solvent. Azobisisobutyronitrile (AIBN) (ca. $^1/_{40}$ equiv.) was added and the mixture was refluxed for 2−24 h and was monitored by GC. Upon completion, the mixture was fractionally distilled or chromatographed to afford pure sulfide. The syntheses of sulfides **1a**,[32] **b**, **e**, **f**, **k**,[33] **g**,[26] and **j**[31] by this method have been reported previously. The following sulfides have not been reported.

4-Chlorophenyl 2-(Trimethylsilyl)ethyl Sulfide (1c): M.p. 45.5−46 °C. − ^{1}H NMR (200 MHz): δ = 7.23 (s, 4 H), 2.90 (m, 2 H), 0.86 (m, 2 H), 0.03 (s, 9 H). − ^{13}C NMR (50.3 MHz): δ = 135.68, 131.54, 130.24, 128.88, 29.82, 16.74, −1.79. − MS (EI); *m*/*z* (%): 244 (2).

3-Methoxyphenyl 2-(Trimethylsilyl)ethyl Sulfide (1d): ^{1}H NMR (200 MHz): δ = 7.21 (m, 1 H), 6.87 (m, 2 H), 6.71 (m, 1 H), 3.80 (s, 3 H), 2.96 (m, 2 H), 0.95 (m, 2 H), 0.05 (s, 9 H). − ^{13}C NMR (50.3 MHz): δ = 160.00, 138.81, 129.72, 120.93, 114.16, 111.26, 55.10, 29.09, 16.59, −2.02. − MS (EI); *m*/*z* (%): 240 (13).

***n*-Propyl 2-(Trimethylsilyl)ethyl Sulfide (1i):** B.p. 96−98 °C (20 Torr). − ^{1}H NMR (200 MHz): δ = 2.44 (m, 2 H), 2.39 (t, *J* = 7.3 Hz, 2 H), 1.50 (hextet, *J* = 7.3 Hz, 2 H), 0.88 (t, *J* = 7.3 Hz, 3 H), 0.75 (m, 2 H). − ^{13}C NMR (50.3 MHz): δ = 33.73, 27.26, 22.69, 17.14, 13.35, −1.94. − MS (EI); *m*/*z* (%): 176 (4).

***n*-Dodecyl 2-(Trimethylsilyl)ethyl Sulfide (1j):** ^{1}H NMR (400 MHz): δ = 2.52 (m, 2 H), 2.49 (t, *J* = 7.3 Hz, 2 H), 1.56 (m, 2 H), 1.35 (m, 2 H), 1.24 [s (br.), 16 H], 0.86 (t, *J* = 7.4 Hz, 3 H), 0.84 (m, 2 H), 0.00 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 31.9, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 27.5, 22.7, 17.4, 14.1, −1.8. − GCMS; *m*/*z* (%): 302 (5).

Ethyl 2-[2-(Trimethylsilyl)ethylthio]acetate (1m): B.p. 64−65 °C (0.3 Torr). − ^{1}H NMR (200 MHz): δ = 4.10 (d, *J* = 7.2 Hz, 2 H), 3.14 (s, 2 H), 2.60 (m, 2 H), 1.20 (t, *J* = 7.2 Hz, 3 H), 0.79 (m, 2 H), −0.05 (s, 9 H). − ^{13}C NMR (50.3 MHz): δ = 170.18, 60.74, 33.10, 28.00, 16.38, 13.88, −2.11. − MS (EI); *m*/*z* (%): 220 (2).

Synthesis of Allyl 2-(Trimethylsilyl)ethyl Sulfide (1h): To *S*-[2-(trimethylsilyl)ethyl] thioacetate (9.40 g, 53.4 mmol) in MeOH (40 mL) was added methanolic KOH solution (9.4 g KOH in 100 mL MeOH) under nitrogen. The solution was stirred for 1.5 h after which allyl bromide (6.46 g, 53.4 mmol) in MeOH (35 mL) was added. After 20 min of stirring, NH_4Cl (aq.) was added and the mixture was extracted with light petroleum ether (3 × 30 mL). The combined extracts were dried, concentrated, and distilled to afford pure sulfide **1h** (4.54 g, 81%), b.p. 50−50.5 °C (3 Torr). − ^{1}H NMR (200 MHz): δ = 5.77 (m, 1 H), 5.09−5.00 (m, 2 H), 3.12 (d, *J* = 7.2 Hz, 2 H), 2.47 (m, 2 H), 0.82 (m, 2 H), 0.03 (s, 9 H). − ^{13}C NMR (50.3 MHz): δ = 134.4, 116.3, 34.3, 26.0, 16.9, −1.8. − MS (EI); *m*/*z* (%): 174 (8).

General Synthesis of Sulfoxides 2a−l: To a flask containing a cooled (0 °C) mixture of 2-(trimethylsilyl)ethyl sulfide (4.0−6.0 g, 17.7−26.6 mmol), MeOH (60−100 mL) and water (25−50 mL), was added solid $NaIO_4$ (17.7−26.6 mmol) in small portions. The ice bath was removed after 30 min and the solution was stirred for 3−12 h. Most of the methanol was removed under reduced pressure (aspirator). The inorganic solid was removed by suction filtration through Celite^{TM} and was washed with CH_2Cl_2 (2 × 10 mL). The filtrate was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried with $MgSO_4$, filtered, concentrated (aspirator), and chromatographed on silica gel (EtOAc/hexanes) to afford analytically pure sulfoxide. Sulfoxide **2j**, prepared by this method, has been reported.[31]

Phenyl 2-(Trimethylsilyl)ethyl Sulfoxide (2a): The reaction of sulfide **1a** (4.32 g, 17.7 mmol) with $NaIO_4$ (3.95 g, 17.7 mmol) afforded sulfoxide **2a**[32] (4.51 g, 98%) after chromatography.

4-Methylphenyl 2-(Trimethylsilyl)ethyl Sulfoxide (2b): The reaction of 4-methylphenyl sulfide (**1b**) (7.32 g, 32.7 mmol) with $NaIO_4$ (7.77 g, 32.7 mmol) afforded sulfoxide **2b**[25] (7.68 g, 98%) after chromatography.

4-Chlorophenyl 2-(Trimethylsilyl)ethyl Sulfoxide (2c): The reaction of sulfide **1c** (4.32 g, 17.7 mmol) with $NaIO_4$ (3.95 g, 17.7 mmol) afforded sulfoxide **2c** (4.51 g, 98%) as a solid after chromatography, m.p. 44.5−45 °C (hexanes/EtOAc). − ^{1}H NMR (200 MHz): δ = 7.52 (d, *J* = 8.2 Hz, 2 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 2.75 (m, 2 H), 0.85 (m, 2 H), 0.01 (s, 9 H). − ^{13}C NMR (50.3 MHz): δ = 142.0, 137.0, 129.4, 125.6, 52.9, 7.6, −2.0. − IR (film): 1042 (S=O) cm^{-1}. − MS (CI); *m*/*z* (%): 261 (6) [(M + H)$^+$]. − $C_{11}H_{17}ClOSSi$ (260.9): calcd. C 50.65, H 6.57; found C 50.90, H 6.79.

3-Methoxyphenyl 2-(Trimethylsilyl)ethyl Sulfoxide (2d): The reaction of sulfide **1d** (5.56 g, 23.1 mmol) with $NaIO_4$ (4.95 g, 23.1 mmol) afforded sulfoxide **2d** (5.17 g, 87%) as an oil after chromatography. − ^{1}H NMR (400 MHz): δ = 7.40 (t, *J* = 7.9 Hz, 1 H), 7.20 (m, 1 H), 7.09 (m, 1 H), 7.01 (m, 1 H), 3.87 (s, 3 H), 2.81 (dt, *J* = 13.0, 4.8 Hz, 1 H), 0.89−0.74 (m, 2 H), −3.42 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 160.3, 145.1, 130.0, 117.2, 116.2, 108.6, 55.5, 52.9, 8.0, −1.9. − MS (CI, NH_3); *m*/*z* (%): 257 (100) [(M + H)$^+$]. − $C_{12}H_{20}O_2SSi$ (256.4): calcd. C 56.21, H 7.86; found C 56.06, H 8.02.

2-Naphthyl 2-(Trimethylsilyl)ethyl Sulfoxide (2e): The reaction of sulfide **1e** (2.60 g, 10.0 mmol) with $NaIO_4$ (2.14 g, 10.0 mmol) afforded sulfoxide **2e**[33] (2.28 g, 90%) after recrystallization.

Benzyl 2-(Trimethylsilyl)ethyl Sulfoxide (2f): The reaction of sulfide **1f** (5.11 g, 22.8 mmol) with $NaIO_4$ (4.87 g, 22.8 mmol) afforded sulfoxide **2f**[33] (5.45 g, 98%) after chromatography.

2-Propyl 2-(Trimethylsilyl)ethyl Sulfoxide (2g): The reaction of sulfide **1g** (5.06 g, 28.7 mmol) with $NaIO_4$ (6.14 g, 28.7 mmol) afforded sulfoxide **2g** (5.25 g, 95%) as an oil after chromatography. − ^{1}H NMR (400 MHz): δ = 2.75 (sept, *J* = 7.0 Hz, 1 H), 2.65−2.50 (m, 2 H), 1.28 (d, *J* = 7.0 Hz, 3 H), 1.26 (d, *J* = 7.0 Hz, 2 H), 1.00 (dt, *J* = 4.7, 13.6 Hz, 1 H), 0.79 (dt, *J* = 4.9, 13.6 Hz, 1 H), 0.04 (s, 9 H). − ^{13}C NMR (50.3 MHz): δ = 48.6, 43.7, 16.1, 14.2, 8.4, −2.1. − IR (film): 1032 (S=O) cm^{-1}. − MS (CI); *m*/*z* (%): 193 (22) [(M + H)$^+$]. − $C_{12}H_{20}OSSi$ (240.4): calcd. C 49.94, H 10.78; found C 49.86, H 10.26.

Allyl 2-(Trimethylsilyl)ethyl Sulfoxide (2h): The reaction of sulfide **1h** (5.10 g, 29.3 mmol) with $NaIO_4$ (6.26 g, 29.3 mmol) afforded sulfoxide **2h** (4.80 g, 86%) as an oil after chromatography. − ^{1}H NMR (200 MHz): δ = 5.88 (m, 1 H), 5.46−5.32 (m, 2 H), 3.45 (m, 2 H), 2.68 (m, 2 H), 0.89 (m, 2 H), 0.07 (s, 9 H). − ^{13}C NMR (50.3 MHz): δ = 125.7, 122.8, 54.2, 45.7, 8.1, −2.2. − IR (film): 1039 (S=O) cm^{-1}. − MS (CI); *m*/*z* (%): 190 (0.5), 162 (55), 101 (58), 91 (33), 75 (37), 74 (37), 73 (100).

1-Propyl 2-(Trimethylsilyl)ethyl Sulfoxide (2i): The reaction of sulfide **1i** (5.19 g, 29.4 mmol) with $NaIO_4$ (6.30 g, 29.4 mmol) afforded sulfoxide **2i** (5.36 g, 95%) as an oil after chromatography. − ^{1}H NMR (200 MHz): δ = 2.70−2.54 (m, 4 H), 1.81 (m, 2 H), 1.08 (t, *J* = 7.3 Hz, 3 H), 0.99 (ddd, *J* = 14.1, 12.9, 5.5 Hz, 1 H), 0.81 (ddd, *J* = 14.1, 12.5, 5.9 Hz, 1 H). − ^{13}C NMR (50.3 MHz): δ = 52.0, 46.3, 15.1, 12.3, 7.4, −1.8. − IR (film): 1028 (S=O) cm^{-1}. − MS (CI); *m*/*z* (%): 231 (28) [(M + H)$^+$]. − $C_{12}H_{20}OSSi$ (240.4): calcd. C 49.94, H 10.78; found C 50.12, H 10.61.

Cyclohexyl 2-(Trimethylsilyl)ethyl Sulfoxide (2k): The reaction of sulfide **1k** (5.30 g, 24.5 mmol) with $NaIO_4$ (5.24 g, 24.5 mmol) afforded sulfoxide **2k**[33] (5.15 g, 95%) after chromatography.

1-Dodecyl 2-(Trimethylsilyl)ethyl Sulfoxide (2l): The reaction of sulfide **1l** (5.35 g, 17.8 mmol) with $NaIO_4$ (3.80 g, 17.8 mmol) afforded sulfoxide **2l** (5.25 g, 94%) as a white solid after chromatography, m.p. 42−43 °C [petroleum ether (boiling range 60−80 °C)/EtOAc]. − ^{1}H NMR (400 MHz): δ = 2.68−2.62 (m, 4 H), 1.75 (m, 2 H), 1.44 (m, 2 H), 1.24 [s (br.), 16 H], 0.97 (dt, J = 13.8, 5.1 Hz, 1 H), 0.88 (t, J = 6.9 Hz, 3 H), 0.80 (dt, J = 13.8, 5.1 Hz, 1 H), 0.05 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 51.4, 47.6, 31.9, 29.6 (2 C), 29.5, 29.3, 29.3, 29.2, 28.9, 22.64, 22.61, 14.1, 8.6, −1.9. − IR (film): 1041 (S=O) cm^{-1}. − MS (EI); m/z (%): 303 (1.6) [(M + H)$^+$]. − $C_{15}H_{36}OSSi$ (292.6): calcd. C 64.08, H 12.02; found C 63.74, H 12.40.

Ethyl 2-[2-(Trimethylsilyl)ethylsulfinyl]acetate (1m): The reaction of sulfide **1m** (6.08 g, 27.6 mmol) with $NaIO_4$ (5.90 g, 27.6 mmol) afforded sulfoxide **2m** (5.90 g, 91%) as a white solid after chromatography. − ^{1}H NMR (200 MHz): δ = 4.17 (q, J = 7.2 Hz, 2 H), 3.62 (s, 2 H), 2.79 (m, 2 H), 1.14 (t, J = 7.2 Hz, 3 H), 0.82 (m, 2 H), 0.01 (s, 9 H). − ^{13}C NMR (50.3 MHz): δ = 165.0, 61.8, 54.6, 28.0, 13.9, 8.0, −2.1. − IR (film): 1732 (C=O), 1041 (S=O) cm^{-1}. − MS (CI); m/z (%): 237 (14) [(M + H)$^+$], 209 (38), 192 (23), 137 (22), 135 (24), 120 (35), 101 (30), 91 (39), 85 (37), 75 (31), 73 (100).

General Method for the Synthesis of Sulfinyl Chlorides 3a−k: To a stirred solution of sulfoxide **2** (9−21 mmol) in CH_2Cl_2 (15−35 mL) at −78 °C was added SO_2Cl_2 (neat, 1.2 equiv.) by syringe. The solution was stirred at −78 °C for 0.5 h and then at room temp. for 3 h. The CH_2Cl_2 was removed in vacuo to afford the crude sulfinyl chloride. The material was distilled where possible or characterized after further concentration.

CAUTION! The distillations should be performed with extreme care and with the appropriate safety equipment in place. Explosions are very possible.

Benzenesulfinyl Chloride (3a): The reaction of sulfoxide **2a** (4.17 g, 18.4 mmol) with SO_2Cl_2 (2.98 g, 22.1 mmol) afforded sulfinyl chloride **3a** (2.83 g, 90%) after distillation, b.p. 62−63 °C (0.04 Torr), ref.[51] b.p. 71−73 °C (1.5 Torr).

4-Methylbenzenesulfinyl Chloride (3b): The reaction of sulfoxide **2b** (4.09 g, 17.0 mmol) with SO_2Cl_2 (2.75 g, 20.4 mmol) afforded sulfinyl chloride **3b** (2.78 g, 94%) after distillation, b.p. 79−80 °C (0.01 Torr), ref.[52] b.p. 79 °C (0.012 Torr).

4-Chlorobenzenesulfinyl Chloride (3c): The reaction of sulfoxide **2c** (4.00 g, 15.3 mmol) with SO_2Cl_2 (2.48 g, 18.4 mmol) afforded sulfinyl chloride **3c**[14,15] (1.83 g, 92%) after distillation, b.p. 68−69 °C (0.04 Torr).

3-Methoxybenzenesulfinyl Chloride (3d): The reaction of sulfoxide **2d** (2.15 g, 8.39 mmol) with SO_2Cl_2 (1.36 g, 10.1 mmol) afforded 1.33 g (83%) of sulfinyl chloride **3d**, as determined from a mixture containing **3d** and 2-(trimethylsilyl)ethyl chloride. − ^{1}H NMR (400 MHz): δ = 7.46 (t, J = 7.9 Hz, 1 H), 7.38 (m, 2 H), 7.01 (d, J = 7.9 Hz, 1 H), 3.86 (s, 3 H). − ^{13}C NMR (100.6 MHz): δ = 160.2, 146.6, 130.3, 120.3, 115.8, 107.68, 55.6. − IR (film): 1152 (S=O) cm^{-1}. − For full characterization, a sample of **3d** generated from sulfoxide **2d** (608 mg, 2.37 mmol) and SO_2Cl_2 (384 mg, 2.84 mmol) was treated with 3-phenylpropanol (436 mg, 3.20 mmol) and K_2CO_3 (9.49 mmol) to afford, after chromatography (EtOAc/hexanes, 10:90), 472 mg (68% overall) of 3-phenylpropyl 3-methoxybenzenesulfinate. − ^{1}H NMR (400 MHz): δ = 7.44 (m, 1 H), 7.28−7.24 (m, 4 H), 7.20−7.12 (m, 3 H), 7.07 (m 1 H), 4.06 (dt, J = 6.4, 9.9 Hz, 1 H), 3.87 (s, 3 H), 3.63 (dt, J = 6.4, 9.9 Hz, 1 H), 2.67 (t, J = 7.6 Hz, 2 H), 1.95 (dt, J = 6.4, 7.6 Hz, 2 H). − ^{13}C NMR (100.6 MHz): δ = 160.1, 145.9, 140.9, 130.1, 128.4 (2 C), 126.0, 118.6, 117.5, 109.4, 63.7, 55.5, 31.8, 31.3. − IR (film): 1132 (S=O) cm^{-1}. − $C_{16}H_{18}O_3S$ (290.4): calcd. C 66.18, H 6.25; found C 66.18, H 6.08.

2-Naphthalenesulfinyl Chloride (3e): The reaction of sulfoxide **2e** (2.72 g, 9.84 mmol) with SO_2Cl_2 (1.60 g, 11.8 mmol) afforded crude sulfinyl chloride **3e**.[14,15] Estimated yield 80%; substantial decomposition occurred during distillation, b.p. 134−138 °C (0.04 Torr).

Phenylmethanesulfinyl Chloride (3f): The reaction of sulfoxide **2f** (4.15 g, 17.4 mmol) with SO_2Cl_2 (2.81 g, 20.8 mmol) afforded sulfinyl chloride **3f**[14,15] (2.83 g, 94%) after distillation, b.p. 84−88 °C (0.01 Torr).

2-Propanesulfinyl Chloride (3g): The reaction of sulfoxide **2g** (3.82 g, 19.9 mmol) with SO_2Cl_2 (3.22 g, 23.8 mmol) afforded sulfinyl chloride **3g** (1.49 g, 59%) after distillation, b.p. 22−23 °C (1.0 Torr), ref.[36] b.p. 68−72 °C (20 Torr).

2-Propenesulfinyl Chloride (3h): The reaction of sulfoxide **2h** (4.00 g, 21.1 mmol) with SO_2Cl_2 (3.40 g, 25.2 mmol) afforded sulfinyl chloride **3h** (1.68 g, 64%) after distillation, b.p. 54−56 °C (6 Torr), ref.[53] b.p. 77 °C (36 Torr).

1-Propanesulfinyl Chloride (3i): The reaction of sulfoxide **2i** (4.28 g, 22.3 mmol) with SO_2Cl_2 (3.60 g, 26.7 mmol) afforded sulfinyl chloride **3i** (1.71 g, 61%) after distillation, b.p. 22−23 °C (1.0 mm), ref.[53] b.p. 66 °C (12 Torr).

2-(Trimethylsilyl)ethanesulfinyl Chloride (3j): The reaction of sulfoxide **2j** (4.44 g, 17.8 mmol) with SO_2Cl_2 (2.62 g, 19.5 mmol) afforded sulfinyl chloride **3j**[31] (2.23 g, 68%) after distillation, during which some decomposition occurred, b.p. 59−60 °C (0.25 Torr).

Cyclohexanesulfinyl Chloride (3k): The reaction of sulfoxide **2k** (4.39 g, 18.9 mmol) with SO_2Cl_2 (3.06 g, 22.7 mmol) afforded sulfinyl chloride **3k** (3.02 g, 96%) after distillation, b.p. 62−64 °C (0.07 Torr), ref.[54] b.p. 87 °C (0.7 Torr).

1-Dodecanesulfinyl Chloride (3l): On a smaller scale, the reaction of sulfoxide **2l** (700 mg, 2.22 mmol) with SO_2Cl_2 (358 mg, 2.65 mmol) afforded crude sulfinyl chloride **3l**[51] (610 mg, 100%).

Preparation of 1-Alkenyl 2-(Trimethylsilyl)ethyl Sulfoxides

Preparation of 1-Cyclopentenyl 2-(Trimethylsilyl)ethyl Sulfoxide (6a): A solution of 2-(trimethylsilyl)ethyl disulfide (3.00 g, 11.3 mmol) and cyclopentene (1.68 g, 24.8 mmol) was prepared in dry CH_2Cl_2 (30 mL) and cooled to −78 °C under N_2. SO_2Cl_2 (1.53 g, 11.3 mmol) was added to the reaction mixture by syringe. The mixture was warmed to room temp., stirred overnight, and concentrated to afford the crude β-chlorosulfide. A sample of the crude sulfide (5.26 g, 22.2 mmol) was dissolved in CH_2Cl_2 and the solution was cooled to −78 °C. A dried solution of m-CPBA (5.50 g, 22.2 mmol) in CH_2Cl_2 was introduced dropwise and the mixture was allowed to warm up overnight. Workup was carried out by impinging the solution with ammonia and filtering the resulting solid.[55] After concentration of the filtrate, the residue was subjected to flash chromatography on silica gel (hexanes/EtOAc, 3:1 then 0:1) to afford the β-chlorosulfoxide. To a solution of the purified β-chlorosulfoxide (1.23 g, 4.87 mmol) in THF (20 mL) at room temp. was added DBU (1.63 g, 10.7 mmol) and NaI (1.60 g, 10.7 mmol). The mixture was stirred for 20 h at 75 °C and, after cooling, the solvent was removed. Flash chromatography on silica gel (hexanes/EtOAc, 4:1 then 1:1) of the residue afforded pure sulfoxide **6a** (742 mg, 65%, 3 steps). − ^{1}H NMR (400 MHz): δ = 6.31 [s (br.), 1 H], 2.60 (m, 2 H), 2.44 (m, 4 H), 1.99 (m, 2 H), 0.75−0.61

(m, 2 H), −0.05 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 145.0, 138.1, 46.5, 32.5, 28.4, 23.3, 7.9, −2.1. − IR (film): 1037 (S=O) cm^{-1}. − MS (EI); *m/z* (%): 188 (24) [(M − 28)$^+$], 91 (9), 75 (20), 74 (13), 73 (100), 67 (13). − $C_{10}H_{20}OSSi$ (216.4): calcd. C 55.50, H 9.31; found C 55.39, H 9.22.

Preparation of 3-Dihydropyranyl 2-(Trimethylsilyl)ethyl Sulfoxide (6b): A solution of 2-(trimethylsilyl)ethyl disulfide (4.00 g, 15.0 mmol) and dihydropyran (3.4 g, 40 mmol) was prepared in dry CH_2Cl_2 (50 mL) and cooled to −78 °C under N_2. SO_2Cl_2 (2.03 g, 15.0 mmol) was added to the reaction mixture by syringe. The mixture was warmed to room temp. over 3.5 h and was re-cooled to −78 °C. DBU (5.23 g, 35.0) was then added. The mixture was stirred for 16 h and water (50 mL) and light petroleum ether (50 mL) were added. The organic layer was washed with 5% citric acid solution and was dried with Na_2SO_4. The mixture was filtered, concentrated, and the crude product purified by flash chromatography on silica gel (hexanes/EtOAc, 8:1). A sample of the purified sulfide (4.20 g, 19.4 mmol) was dissolved in CH_2Cl_2 and the solution was cooled to −78 °C. A dried solution of *m*-CPBA (6.14 g, 19.6 mmol) in CH_2Cl_2 was introduced dropwise and the mixture was allowed to warm up overnight. Workup was achieved by impinging the solution with ammonia and filtering off the resulting solid.[55] After concentration of the filtrate, the residue was subjected to flash chromatography on silica gel (hexanes/EtOAc, 8:1 then 0:1) to afford sulfoxide **6b** (1.83 g, 31%, 2 steps). − ^{1}H NMR (400 MHz): δ = 6.99 (s, 1 H), 4.17 (m, 1 H), 3.93, (m, 1 H), 2.79−2.58 (m, 2 H), 2.49 (m, 1 H), 2.03−1.91 (m, 3 H), 0.75 (m, 1 H), 0.49 (m, 1 H), 0.00 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 151.0, 114.9, 66.9, 45.7, 21.3, 13.9, 9.7, −2.0. − IR (film): 1634 (C=C), 1030 (S=O) cm^{-1}. − MS (EI); *m/z* (%): 216 (4) [M$^+$], 204 (12), 75 (12), 73 (100). − $C_{10}H_{20}O_2SSi$ (232.4): calcd. C 51.68, H 8.67; found C 51.89, H 8.44.

Preparation of Ethenyl 2-(Trimethylsilyl)ethyl Sulfoxide (7): A solution of 2-(trimethylsilyl)ethyl disulfide (1.24 g, 4.66 mmol) was prepared in dry CH_2Cl_2 (30 mL) and was cooled to −78 °C under N_2. SO_2Cl_2 (5.25 mL, 1 M solution in CH_2Cl_2, 5.25 mmol) was added to the mixture by syringe. The mixture was stirred for 15 min at −78 °C and trimethyl(vinyl)silane (0.932 mg, 9.32 mmol) was added. The mixture was stirred until the reaction was complete by TLC and/or GC analysis. A solution of *m*-CPBA (2.20 g, 9.32 mmol) in CH_2Cl_2 (30 mL) was added dropwise. The mixture was stirred 1.5 h and was filtered through a bed of Celite†. The filtrate was re-cooled to −78 °C and TBAF (12 mL, 1 M in THF, 12 mmol) was added dropwise. The cooling bath was removed and the solution was stirred for 12 h. The solution was washed with water (15 mL), saturated aqueous Na_2CO_3 (2 × 20 mL), dilute aqueous HCl (2 × 10 mL), and brine. The mixture was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography (EtOAc/hexane) afforded sulfoxide **7** (706 mg, 43%, 3 steps) as an oil. − ^{1}H NMR (400 MHz): δ = 6.53 (dd, *J* = 16.5, 9.8 Hz, 1 H), 6.04 (dd, *J* = 16.5, 0.8 Hz, 1 H), 5.94 (dd, *J* = 9.8, 0.8 Hz, 1 H), 2.75 (m, 1 H), 2.56 (m, 1 H), 0.83 (m, 2 H), 0.01 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 140.0, 122.3, 48.8, 7.31, −2.0. − IR (film): 1049 (S=O) cm^{-1}. − MS (CI, CH_4); *m/z* (%): 177 (10) [(M + H)$^+$], 161 (25), 149 (62), 148 (30), 147 (35), 133 (54), 117 (24), 101 (82), 85 (36), 74 (24), 73 (100). − $C_7H_{16}OSSi$ (176.3): calcd. C 47.68, H 9.14; found C 47.56, H 9.11.

General Method for the Synthesis of Chloroalkenyl 2-(Trimethylsilyl)-ethyl Sulfoxides Using Sulfenyl Chloride 5: A solution of 2-(trimethylsilyl)ethyl disulfide (1 equiv.) was prepared in dry CH_2Cl_2 (10 mL/mmol) and cooled to −78 °C under N_2. SO_2Cl_2 (1.2 equiv., 1 M solution in CH_2Cl_2) was added to the mixture by syringe. The mixture was stirred for 15 min at −78 °C and the alkyne (2 equiv.) was added. The mixture was stirred until the reaction was complete by TLC and/or GC analysis and was concentrated under reduced pressure. A solution of the crude sulfide in CH_2Cl_2 (2.5 mL/mmol) was cooled to −78 °C and a solution of *m*-CPBA (1 equiv.) in CH_2Cl_2 (4 mL/mmol) was added dropwise. The mixture was stirred for 3−4 h until the reaction was complete by TLC and was filtered through a bed of Celite™. The solution was washed (3 × 100 mL) with Na_2CO_3, brine, dried with $MgSO_4$, filtered, and concentrated. The sulfoxide was isolated using flash chromatography through silica gel with EtOAc/hexanes. Sulfoxide yields were calculated from the disulfide. In some instances, the oxidant was added directly to the product of the electrophilic addition without prior concentration.

(*Z*)-2-Chloro-2-phenyl-1-(trimethylsilyl)ethenyl 2-(Trimethylsilyl)-ethyl Sulfoxide (8a): 2-(Trimethylsilyl)ethyl disulfide (1.22 g, 4.59 mmol) in dry CH_2Cl_2 (40 mL) was treated with SO_2Cl_2 (5.96 mL, 5.96 mmol) followed by the addition of 1-trimethylsilyl-2-phenylacetylene (1.60 g, 9.17 mmol). The crude sulfide was concentrated under reduced pressure and oxidized with *m*-CPBA (2.21 g, 7.80 mmol) in CH_2Cl_2 (40 mL). Sulfoxide **8a** (2.67 g, 70%, 2 steps) was isolated as a solid after flash chromatography (EtOAc/hexanes), m.p. 61−63 °C (EtOAc/hexanes). − ^{1}H NMR (400 MHz): δ = 7.50−7.47 (m, 3 H), 7.36−7.32 (m, 2 H), 2.60 (m, 1 H), 2.40 (m, 1 H), 0.82 (dt, *J* = 14.0, 4.0 Hz, 1 H), 0.57 (dt, *J* = 14.0, 4.0 Hz, 1 H), 0.51 (s, 9 H), 0.00 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 152.7, 150.5, 130.5, 129.4, 128.9, 128.2, 47.0, 9.8, 1.2, 0.0. − IR (CH_2Cl_2): 1050 (S=O) cm^{-1}. − MS (CI, NH_3); *m/z* (%): 359 (14) [(M + H)$^+$], 241 (13), 177 (15), 175 (48), 134 (13), 103 (21), 93 (24), 91 (100), 75 (26), 61 (37), 59 (17), 57 (43), 56 (17). − $C_{16}H_{27}ClOSSi_2$ (359.1): calcd. C 53.52, H 7.58; found C 53.95, H 7.72.

(*E*)-2-Butyl-2-chloro-1-(trimethylsilyl)ethenyl 2-(Trimethylsilyl)ethyl Sulfoxide (8b): 2-(Trimethylsilyl)ethyl disulfide (1.04 g, 3.91 mmol) in dry CH_2Cl_2 (40 mL) was treated with SO_2Cl_2 (5.08 mL, 5.08 mmol) followed by the addition of 1-(trimethylsilyl)hexyne (1.20 g, 7.82 mmol). The crude sulfide was concentrated under reduced pressure and oxidized with *m*-CPBA (2.10 g, 7.41 mmol) in CH_2Cl_2 (40 mL). Sulfoxide **8b** (1.59 g, 60%, 2 steps) was isolated as an oil after flash chromatography (20% EtOAc/hexanes). − ^{1}H NMR (400 MHz): δ = 2.83 (dt, *J* = 13.8, 4.0 Hz, 1 H), 2.71 (dt, *J* = 13.8, 4.0 Hz, 1 H), 2.74−2.42 (m, 2 H), 1.71 (m, 1 H), 1.58−1.32 (m, 3 H), 0.93 (m, 3 H), 0.59 (dt, *J* = 13.8, 4.0 Hz, 1 H), 0.31 (s, 9 H), 0.04 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 155.6, 146.3, 48.6, 31.1, 26.0, 23.2, 13.7, 10.6, 0.94, −1.9. − IR (film): 1093 (S=O) cm^{-1}. − MS (EI); *m/z* (%): 310 [M$^+$ (4), 275 (8), 196 (11), 147 (37), 101 (25), 93 (26), 85 (46), 74 (48), 73 (39), 72 (100), 69 (33), 36 (46). − $C_{14}H_{31}ClOSSi_2$ (339.1): calcd. C 49.59, H 9.21; found C 49.50, H 9.00.

(*E*)-2-Chloro-1-(trimethylsilyl)ethenyl 2-(Trimethylsilyl)ethyl Sulfoxide (8c): 2-(Trimethylsilyl)ethyl disulfide (1.01 g, 3.79 mmol) in dry CH_2Cl_2 (40 mL) was treated with SO_2Cl_2 (4.93 mL, 4.93 mmol) followed by the addition of (trimethylsilyl)acetylene (1.07 mL, 7.58 mmol). The crude sulfide was concentrated under reduced pressure and oxidized with *m*-CPBA (2.26 g, 7.98 mmol) in CH_2Cl_2 (40 mL). Sulfoxide **8c** (1.14 g, 53%, 2 steps) was isolated as an oil after flash chromatography (10% EtOAc/hexanes). − ^{1}H NMR (400 MHz): δ = 7.00 (s, 1 H), 2.80 (m, 1 H), 2.65 (m, 1 H), 0.87 (dt, *J* = 13.9, 4.3 Hz, 1 H), 0.71 (dt, *J* = 13.9, 4.3 Hz, 1 H), 0.32 (s, 9 H), 0.04 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 153.2, 145.6, 50.3, 8.9, −0.19, −2.0. − IR (film): 1045 (S=O) cm^{-1}. − MS (CI, NH_3); *m/z* (%): 283 (74) [(M + H)$^+$], 219 (19), 165 (13), 147 (29), 105 (100), 101 (18), 91 (34), 73 (27), 65 (71). − $C_{10}H_{23}ClOSSi_2$ (283.0): calcd. C 42.45, H 8.19; found C 42.59, H 8.21.

(*Z*)-2-Chloro-1-(trimethylsilyl)ethenyl 2-(Trimethylsilyl)ethyl Sulfoxide (8d): 2-(Trimethylsilyl)ethyl disulfide (430 mg, 1.62 mmol) in dry CH_2Cl_2 (40 mL) was treated with SO_2Cl_2 (2.83 mL, 2.83 mmol). The mixture was warmed to room temperature and (trimethylsilyl)acetylene (456 µL, 3.23 mmol) was added. The crude sulfide was concentrated under reduced pressure and oxidized with *m*-CPBA (837 mg, 2.96 mmol) in CH_2Cl_2 (40 mL). Sulfoxide **8d** (466 mg, 51%, 2 steps) was isolated as a solid after flash chromatography (EtOAc/hexanes, 1:10), m.p. 36−39 °C (EtOAc/hexanes). − ^1H NMR (400 MHz): δ = 6.58 (s, 1 H), 2.82 (m, 2 H), 1.05−0.95 (m, 2 H), 0.24 (s, 9 H), 0.05 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 148.1, 143.9, 48.9, 8.6, −1.9, −2.7. − IR ($CDCl_3$): 1043 (S=O) cm^{-1}. − MS (CI, NH_3); *m/z* (%): 283 (33) [$(M + H)^+$], 91 (13), 90 (100), 74 (10), 73 (21). − $C_{10}H_{23}ClOSSi_2$ (283.0): calcd. C 42.44, H 8.49; found C 42.55, H 7.94.

(*E*)-1,4-Bis(acetoxy)-3-chloro-2-but-2-enyl 2-(Trimethylsilyl)ethyl Sulfoxide (10a): A stirred mixture of 2-(trimethylsilyl)ethyl disulfide (3.00 g, 11.3 mmol) and (*E*)-butyne-1,4-diyl diacetate (4.60 g, 27.1 mmol) in dry CH_2Cl_2 (50 mL) at −78 °C was treated with SO_2Cl_2 (1.68 g, 12.4 mmol). The mixture was allowed to warm up to room temp. overnight, concentrated and subjected to silica gel flash chromatography (EtOAc/hexanes) to afford 3.40 g of sulfide. To a stirred solution of the sulfide (1.88 g) in CH_2Cl_2 (100 mL) at −78 °C was added *m*-CPBA (1.25 g, 5.30 mmol) in CH_2Cl_2 (100 mL) and the mixture was allowed to warm up to room temp. overnight. Filtration through Celite™, concentration and silica gel flash chromatography (EtOAc/hexanes) afforded sulfoxide **10a** (1.67 g, 34%, 2 steps). − ^1H NMR (400 MHz): δ = 5.03 (AB q, *J* = 12.5 Hz, 2 H), 5.00 (AB q, *J* = 13.0 Hz, 2 H), 2.93 (ddd, *J* = 14.3, 12.9, 4.2 Hz, 1 H), 2.78 (ddd, *J* = 14.3, 12.8, 4.2 Hz, 1 H), 2.11 (s, 3 H), 2.06 (s, 3 H), 0.89 (dt, *J* = 13.8, 4.2 Hz, 1 H), 0.66 (dt, *J* = 13.8, 4.2 Hz, 1 H), 0.04 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 169.9 (2 C), 140.8, 139.9, 62.4, 55.3, 49.3, 20.7, 20.5, 9.5, −2.0. − IR (film): 1748 (C=O), 1031 (S=O) cm^{-1}. − MS (EI); *m/z* (%): 326 (1.6) [$(M - 28)^+$], 194 (31), 149 (14), 146 (13), 134 (23), 117 (43), 101 (17), 85 (55), 75 (55), 74 (29), 73 (77), 56 (55). − $C_{13}H_{23}ClO_5SSi$ (354.9): calcd. C 43.99, H 6.53; found C 43.72, H 6.43.

(*E*)-4-Chloro-3-hex-3-enyl 2-(Trimethylsilyl)ethyl Sulfoxide (10b): A stirred mixture of 2-(trimethylsilyl)ethyl disulfide (3.50 g, 13.1 mmol) and 3-hexyne (4.48 g, 54.5 mmol) in dry CH_2Cl_2 (50 mL) at −78 °C was treated with SO_2Cl_2 (1.84 g, 13.7 mmol). The mixture was allowed to warm up to room temp. over 4 h and was then concentrated to afford the crude sulfide. To a stirred solution of the crude sulfide (5.85 g) in CH_2Cl_2 (135 mL) at −78 °C was added *m*-CPBA (5.73 g, 24.2 mmol) in CH_2Cl_2 (85 mL) and the mixture was allowed to warm up to room temp. over 6 h. Filtration through Celite™, concentration and silica gel flash chromatography (EtOAc/hexanes) afforded sulfoxide **10b** (5.67 g, 89%, 2 steps). − ^1H NMR (200 MHz): δ = 2.82−2.32 (m, 6 H), 1.12 (t, *J* = 7.4 Hz, 3 H), 1.10 (t, *J* = 7.4 Hz, 3 H), 0.83 (dt, *J* = 13.9, 4.4 Hz, 1 H), 0.55 (dt, *J* = 13.9, 4.4 Hz, 1 H), −2.25 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 143.8, 140.1, 48.4, 29.3 18.4, 13.6, 12.7, 9.8, −2.0. − IR (film): 1625 (C=C), 1049 (S=O) cm^{-1}. − MS (EI); *m/z* (%): 238 (22) [$(M - 28)^+$], 101 (16), 85 (39), 75 (27), 74 (26), 73 (100), 59 (44). − $C_{11}H_{23}ClOSSi$ (266.9): calcd. C 49.50, H 8.69; found C 49.73, H 8.43.

(*E*)-2-Methylethenyl 2-(Trimethylsilyl)ethyl Sulfoxide (11): A solution of 1-bromo-1-propene (700 µL, 8.05 mmol) in dry THF was cooled to −78 °C under N_2. *n*BuLi (4.72 mL, 11.8 mmol) was added dropwise and the mixture was stirred for 2 h at −78 °C. *tert*-Butyl 2-(trimethylsilyl)ethanesulfinate (966 mg, 5.37 mmol) was added and the solution was stirred until the reaction was complete by TLC analysis (1−2 h). The reaction was quenched with NH_4Cl (aq.) and the organic layer was separated. The aqueous layer was extracted with EtOAc and the organic layers combined. The organic layer was then washed with NH_4Cl (3 × 50 mL), brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. 1-Propynyl 2-(trimethylsilyl)ethyl sulfoxide (612 mg, 61%) was isolated as an oil after flash chromatography (25% EtOAc/hexanes). − ^1H NMR (400 MHz): δ = 2.95 (m, 2 H), 2.09 (s, 3 H), 1.01 (m, 2 H), 0.06 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 101.1, 76.4, 52.5, 8.6, 4.8, −1.9. − IR (film): 2192, 1032 (S=O) cm^{-1}. − To 1-propynyl 2-(trimethylsilyl)ethyl sulfoxide (732 mg, 3.89 mmol) in THF (10 mL) was added DIBAL (4.7 mL, 4.67 mmol, 1 M solution in heptanes) dropwise at −78 °C under N_2. After 1 h, the reaction was quenched with NH_4Cl. The organic layer was separated, washed with brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Sulfoxide **11** (676 mg, 91%) was isolated as an oil after flash chromatography (25% EtOAc/hexanes). − ^1H NMR (400 MHz): δ = 6.44 (dq, *J* = 15.0, 6.8 Hz, 1 H), 6.16 (dq, *J* = 15.0, 1.4 Hz, 1 H), 2.65 (m, 2 H), 1.92 (dd, *J* = 6.8, 1.4 Hz, 3 H), 0.82 (m, 2 H), 0.03 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 137.1, 133.0, 49.3, 17.9, 8.0, −1.9. − IR (film): 1635 (C=C), 1051 (S=O) cm^{-1}. − MS (EI); *m/z* (%): 162 (11) [$(M - 28)^+$], 101 (6), 75 (16), 75 (10), 73 (100). − $C_8H_{18}OSSi$ (190.4): calcd. C 50.47, H 9.53; found C 50.61, H 9.67

General Method for the Desilylation of 1-Alkenyl 2-(Trimethylsilyl)-ethyl Sulfoxides: The trimethyl(vinyl)silane group was removed by preparing a solution of the silylated sulfoxide **8** in MeOH (5 mL/mmol) followed by the immediate addition of K_2CO_3 (1−5.5 equiv.). The reaction mixture was stirred for 1 h then filtered and concentrated under reduced pressure. The desilylated product was isolated using flash chromatography through silica gel with EtOAc/hexanes as the eluent.

(*Z*)-2-Chloro-2-phenylethenyl 2-(Trimethylsilyl)ethyl Sulfoxide (9a): Sulfoxide **8a** (520 mg, 1.45 mmol) was treated with K_2CO_3 (200 mg, 1.45 mmol) in methanol to afford sulfoxide **9a** (333 mg, 80%) as an oil after chromatography (10% EtOAc/hexanes). − ^1H NMR (400 MHz): δ = 7.49 (m, 3 H), 7.39 (m, 2 H), 6.81 (s, 1 H), 2.70 (dt, *J* = 14.0, 4.0 Hz, 1 H), 2.30 (dt, *J* = 14.0, 4.0 Hz, 1 H), 0.96 (dt, *J* = 14.0, 4.2 Hz, 1 H), 0.73 (dt, *J* = 14.0, 4.2 Hz, 1 H), 0.00 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 143.5, 129.8, 129.6, 129.0, 128.3, 122.7, 46.2, 5.5, 0.0. − IR (film): 1627 (C=C), 1063 (S=O) cm^{-1}. − MS (CI, NH_3); *m/z* (%): 287 (33) [$(M + H)^+$], 171 (37), 169 (100), 151 (28), 101 (25), 91 (65), 73 (39). − $C_{13}H_{19}ClOSSi$ (286.9): calcd. C 54.42, H 6.68; found C 54.22, H 6.46.

(*E*)-2-Chloro-1-hex-1-enyl 2-(Trimethylsilyl)ethyl Sulfoxide (9b): Sulfoxide **8b** (538 mg, 1.59 mmol) was treated with K_2CO_3 (1.21 g, 8.74 mmol) in methanol to afford sulfoxide **9b** (331 mg, 78%) as an oil after chromatography (EtOAc/hexanes). − ^1H NMR (400 MHz): δ = 6.61 (s, 1 H), 2.81 (dt, *J* = 13.6, 4.0 Hz, 1 H), 2.59 (dt, *J* = 13.6, 4.0 Hz, 1 H), 2.49 (ddd, *J* = 14.6, 8.8, 6.4 Hz, 1 H), 2.09 (ddd, *J* = 14.6, 8.8, 6.4 Hz, 1 H), 1.57−1.50 (m, 2 H), 1.39 (sext, *J* = 7.4 Hz, 2 H), 0.93 (t, *J* = 7.4 Hz, 3 H), 0.86 (dt, *J* = 13.8, 4.4 Hz, 1 H), 0.73 (dt, *J* = 13.8, 4.4 Hz, 1 H), 0.04 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 144.8, 122.8, 47.5, 29.5, 25.7, 22.5, 13.5, 6.9, −2.0. − IR (film): 1621 (C=C), 1050 (S=O) cm^{-1}. − MS (EI); *m/z* (%): 238 (9), 196 (17), 124 (11), 101 (34), 85 (45), 75 (34), 74 (32), 73 (100), 59 (40). − $C_{11}H_{23}ClOSSi$ (266.9): calcd. C 49.50, H 8.69; found C 49.71, H 8.57.

(*E*)-2-Chloroethenyl 2-(Trimethylsilyl)ethyl Sulfoxide (9c): Sulfoxide **8c** (571 mg, 2.02 mmol) was treated with K_2CO_3 (280 mg, 2.02 mmol) in methanol to afford sulfoxide **9c** (206 mg, 49%) as an oil after chromatography (EtOAc/hexanes). − ^{1}H NMR (400 MHz): δ = 6.80 (d, *J* = 13.2 Hz, 1 H), 6.62 (d, *J* = 13.2 Hz, 1 H), 2.75 (m, 2 H), 0.86 (m, 2 H), 0.05 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 134.8, 128.3, 49.7, 7.6, −1.9. − IR (film): 1050 (S=O) cm^{-1}. − MS (CI, NH_3); *m*/*z* (%): 283 (76) [(M + TMS)$^+$], 211 (9) [(M + H)$^+$], 167 (17), 149 (29), 147 (29), 102 (10), 101 (87), 93 (16), 75 (19), 74 (15), 73 (100). − $C_7H_{15}ClOSSi$ (210.8): calcd. C 39.89, H 7.17; found C 39.00, H 7.18.

(*Z*)-2-Chloroethenyl 2-(Trimethylsilyl)ethyl Sulfoxide (8d): A solution of 2-(trimethylsilyl)ethyl disulfide (553 mg, 2.08 mmol) in dry CH_2Cl_2 (40 mL) was cooled to −78 °C and treated with SO_2Cl_2 (2.49 mL, 2.49 mmol) followed, after 15 min, by the addition of (trimethylsilyl)acetylene (590 μL, 4.15 mmol). The crude sulfide was concentrated under reduced pressure then redissolved in MeOH (10 mL) and treated with K_2CO_3 (390 mg, 2.82 mmol) at room temp. After 1 h the reaction mixture was filtered and concentrated under reduced pressure. The crude sulfide was oxidized with *m*-CPBA (445 mg, 2.32 mmol) in CH_2Cl_2 (40 mL) at −78 °C to afford sulfoxide **9d** (172 mg, 20%) as an oil after flash chromatography. − ^{1}H NMR (400 MHz): δ = 6.63 (d, *J* = 7.0 Hz, 1 H), 6.47 (d, *J* = 7.0 Hz, 1 H), 2.85−2.30 (m, 2 H), 0.94−0.79 (m, 2 H), −0.03 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 138.0, 127.2, 49.3, 8.4, −1.9. − IR (film): 1043 (S=O) cm^{-1}. − MS (CI, NH_3); *m*/*z* (%): 211 (15) [(M + H)$^+$], 91 (10), 90 (100), 73 (18). − $C_7H_{15}ClOSSi$ (210.8): calcd. C 39.89, H 7.17; found C 39.68, H 6.99.

General Method for the Oxidative Fragmentation of 1-Alkenyl 2-(Trimethylsilyl)ethyl Sulfoxides: A solution of 1-alkenyl 2-(trimethylsilyl)ethyl sulfoxide (1.0 equiv.) was prepared in dry CH_2Cl_2 (10 mL) and cooled to −78 °C under N_2. SO_2Cl_2 (usually 1.2 equiv., as a 1 M solution in CH_2Cl_2) was added by syringe. The mixture was stirred for 10 min, then allowed to warm up to room temp. over 60 min and a sample (500−900 μL) was taken for IR analysis. Upon cooling to −78 °C, 3-phenyl-1-propanol or cyclohexanol (0.9−1.0 equiv.) was added followed by the immediate addition of K_2CO_3 (2.5 to 4 equiv.). The reaction mixture was stirred for 10 min and then allowed to warm up slowly to room temperature over 2−3 h. When the reaction was complete by TLC analysis, the reaction mixture was filtered through a bed of Celite^{TM} and concentrated under reduced pressure. The vinylic sulfinate was isolated by flash chromatography on silica gel with EtOAc/hexanes as the eluent. Sulfinate yields were calculated with alcohol as the limiting reagent. In cases where TLC did not indicate a sulfinyl chloride, the workup was performed without addition of alcohol or K_2CO_3.

Fragmentation Attempt of Ethenyl 2-(Trimethylsilyl)ethyl Sulfoxide (7): The reaction of sulfoxide **7** (136 mg, 0.77 mmol) with SO_2Cl_2 (1.2 mL, 0.96 mmol) provided 1,2-dichloroethyl 2-(trimethylsilyl)ethyl sulfoxide (**12a**, 86 mg, 45%) as an inseparable 14:1 mixture of diastereomers. − Major isomer: ^{1}H NMR (400 MHz): δ = 4.71 (dd, *J* = 8.9, 6.1 Hz, 1 H), 4.10 (dd, *J* = 11.9, 8.9 Hz, 1 H), 3.91 (dd, *J* = 11.9, 6.1 Hz, 1 H), 2.90 (dt, *J* = 13.4, 4.3 Hz, 1 H), 2.78 (dt, *J* = 13.4, 4.3 Hz, 1 H), 0.93 (dt, *J* = 13.8, 4.8 Hz, 1 H), 0.63 (dt, *J* = 13.8, 4.8 Hz, 1 H), −0.04 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 71.7, 45.8, 42.3, 9.1, −2.1. − IR (film): 2951, 1251, 1053, 849 cm^{-1}. − MS (CI, CH_4); *m*/*z* (%): 321 (12) [(M + TMS for ^{37}Cl)$^+$], 319 (15) [(M + TMS for ^{35}Cl)$^+$], 247 (15) [(M + H for ^{35}Cl)$^+$], 185 (37), 183 (65), 149 (28), 101 (76), 93 (18), 85 (18), 75 (54), 74 (38), 73 (100). − $C_7H_{16}Cl_2OSSi$ (247.3): calcd. C 34.00, H 6.52; found C 33.90, H 6.66.

Fragmentation Attempt of 1-Cyclopentenyl 2-(Trimethylsilyl)ethyl Sulfoxide (6a): The reaction of sulfoxide **6a** (193 mg, 0.89 mmol) with SO_2Cl_2 (1.2 mL, 1.11 mmol) provided 1,2-dichlorocyclopentyl 2-(trimethylsilyl)ethyl sulfoxide (**12b**, 202 mg, 79%) as an inseparable 1.67:1 mixture of isomers. − Major isomer: ^{1}H NMR (400 MHz): δ = 4.44 (dd, *J* = 5.0, 3.0 Hz, 1 H), 2.93−2.73 (m, 3 H), 2.67−2.60 (m, 1 H), 2.48−2.41 (m, 1 H), 2.21−2.00 (m, 3 H), 1.19 (m, 1 H), 0.83 (m, 1 H), 0.07 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 91.3, 66.8, 44.1, 36.6, 35.5, 20.9, 9.3, −1.9. − Minor isomer: ^{13}C NMR (100.6 MHz): δ = 94.5, 67.4, 44.9, 33.8, 33.1, 21.1, 9.6, −1.9. − Mixture of isomers: IR (film): 1994, 1953, 1419, 1247, 1098, 1053, 861, 845 cm^{-1}. − MS (CI, CH_4); *m*/*z* (%): 359 (100) [(M + TMS for ^{37}Cl)$^+$], 361 (15) [(M + TMS for ^{35}Cl)$^+$], 287 (11) [(M + H for ^{35}Cl)$^+$], 225 (29), 223 (72), 101 (45), 73 (77). − $C_{10}H_{20}Cl_2OSSi$ (287.3): calcd. C 41.80, H 7.02; found C 41.75, H 6.96.

Fragmentation Attempt of 2-Dihydropyranyl 2-(Trimethylsilyl)ethyl Sulfoxide (6b): The reaction of sulfoxide **6b** (251 mg, 1.08 mmol) with SO_2Cl_2 (1.3 mL, 1.3 mmol) provided no evidence of sulfinyl chloride and no isolable product after the addition of methanol.

Synthesis of Cyclohexyl (*E*)-2-Chloro-2-phenyl-1-(trimethylsilyl)-ethenesulfinate (13a): The reaction of sulfoxide **8a** (317 mg, 0.88 mmol) with SO_2Cl_2 (1.2 mL, 1.15 mmol) provided the sulfinyl chloride (S=O stretch 1153 cm^{-1}). Addition of cyclohexanol (100 μL, 0.84 mmol) and K_2CO_3 (306 mg, 2.21 mmol) afforded sulfinate ester **13a** as a pair of rotational isomers (273 mg, 87%) as an oil after flash chromatography (8% EtOAc/hexanes). − ^{1}H NMR (400 MHz): δ = 7.48−7.43 (m, 3 H), 7.35−7.32 (m, 2 H), 4.27 (m, 1 H, major isomer), 4.19 (m, 1 H, minor isomer), 2.11 (m, 1 H), 1.85−1.47 (m, 5 H), 1.45−1.26 (m, 4 H), 0.41 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ(major isomer) = 130.3, 129.2, 128.6, 128.8, 77.9, 33.4, 32.9, 25.1, 23.5, 0.77; δ(minor isomer, signals that can be observed) = 78.7, 33.5, 33.0. − IR (film): 3056, 2937, 2859, 1414, 1369, 1266, 1252, 1135, 961, 845 cm^{-1}. − MS (CI, NH_3); *m*/*z* (%): 429 (19) [(M + TMS)$^+$], 357 (100) [(M + H)$^+$], 303 (17), 277 (28), 275 (64), 257 (14), 175 (31), 121 (38), 83 (18), 73 (15). − $C_{17}H_{25}ClO_2SSi$ (357.0): calcd. C 57.20, H 7.06; found C 56.97, H 6.92.

Synthesis of 3-Phenylpropyl (*E*)-2-Butyl-2-chloro-1-(trimethylsilyl)-ethenesulfinate (13b): The reaction of sulfoxide **8b** (279 mg, 0.82 mmol) with SO_2Cl_2 (1.07 mL, 1.07 mmol) provided the sulfinyl chloride (S=O stretch 1149 cm^{-1}). Addition of 3-phenyl-1-propanol (100 μL, 0.74 mmol) and K_2CO_3 (456 mg, 3.30 mmol) afforded sulfinate ester **13b** (168 mg, 59%) as an oil after flash chromatography (EtOAc/hexanes, 7:93). − ^{1}H NMR (400 Hz): δ = 7.31−7.28 (m, 2 H), 7.22−7.17 (m, 3 H), 3.99 (t of AB q, *J* = 10.0, 6.4 Hz, 2 H), 2.77−2.69 (m, 3 H), 2.60 (ddd, *J* = 13.3, 10.0, 6.0 Hz, 1 H), 2.06−1.99 (m, 2 H), 1.68−1.58 (m, 2 H), 1.43 (sext, *J* = 7.2 Hz, 2 H), 0.95 (t, *J* = 7.2 Hz, 3 H), 0.34 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 159.9, 148.0, 140.8, 128.5, 128.4, 126.1, 67.2, 31.9, 31.7, 30.9, 25.5, 23.1, 12.8, 0.8. − IR (film): 3027, 2957, 2932, 2872, 1497, 1466, 1455, 1252, 1139, 1042, 1010 cm^{-1}. − MS (EI); *m*/*z* (%): 372 (2, M$^+$), 357 (10), 239 (17), 139 (17), 119 (44), 118 (76), 117 (17), 105 (17), 95 (15), 93 (21), 92 (18), 91 (86), 81 (20), 79 (20), 77 (17), 75 (18), 74 (19), 73 (100), 65 (18). − $C_{17}H_{29}ClOSSi$ (345.0): calcd. C 59.18, H 8.47; found C 58.97, H 8.57.

Synthesis of 3-Phenylpropyl (*E*)-2-Chloro-1-(trimethylsilyl)ethenesulfinate (13d): The reaction of sulfoxide **8c** (448 mg, 1.59 mmol) with SO_2Cl_2 (1.91 mL, 1.91 mmol) provided the sulfinyl chloride

(S=O stretch 1138 cm^{-1}). Addition of 3-phenyl-1-propanol (194 μL, 1.43 mmol) and K_2CO_3 (880 mg, 6.37 mmol) afforded sulfinate ester **13d** (238 mg, 52%) as an oil after flash chromatography (7% EtOAc/hexanes). − ^{1}H NMR (400 MHz): δ = 7.21−7.16 (m, 2 H), 7.12−7.08 (m, 3 H), 6.59 (s, 1 H), 4.00 (t of AB q, *J* = 10.0, 6.4 Hz, 2 H), 2.64 (t, *J* = 7.2 Hz, 2 H), 1.99−1.91 (m, 2 H), 0.16 (s, 9 H). − ^{13}C NMR (100.6 MHz): δ = 149.8, 144.8, 140.8, 128.4 (2 C), 126.0, 66.7, 31.7, 31.5, −2.7. − IR (film): 3027, 3004, 2956, 1604, 1568, 1497, 1455, 1382, 1252, 1188, 1124, 1121, 1006, 920 cm^{-1}. − MS (EI); *m/z* (%): 317 (14) [M$^+$], 119 (55), 118 (84), 117 (36), 105 (28), 104 (17), 103 (30), 91 (100), 83 (25), 79 (25), 78 (22), 77 (31), 75 (22), 74 (23), 73 (88), 65 (38), 63 (17), 51 (18). − $C_{14}H_{21}ClO_2SSi$ (316.9): calcd. C 53.06, H 6.68; found C 52.87, H 6.67. − The reaction of sulfoxide **13d** (223 mg, 0.79 mmol) with SO_2Cl_2 (0.950 mL, 0.95 mmol) provided the sulfinyl chloride (S=O stretch 1139 cm^{-1}). Addition of 3-phenyl-1-propanol (100 μL, 0.75 mmol) and K_2CO_3 (438 mg, 3.17 mmol) afforded sulfinate ester **13d** (137 mg, 57%) as an oil after flash chromatography (7% EtOAc/hexanes).

Synthesis of Cyclohexyl (*Z*)-2-Chloro-2-phenylethenesulfinate (14a): The reaction of sulfoxide **9a** (182 mg, 0.63 mmol) with SO_2Cl_2 (760 μL, 0.76 mmol) provided the sulfinyl chloride (S=O stretch 1154 cm^{-1}). Addition of cyclohexanol (57 mg, 0.57 mmol) and K_2CO_3 (351 mg, 2.53 mmol) afforded sulfinate ester **14a** (117 mg, 65%) as an oil after flash chromatography (10% EtOAc/hexanes). − ^{1}H NMR (400 MHz): δ = 7.46−7.36 (m, 5 H), 7.14 (s, 1 H), 4.21 (m, 1 H), 1.80 (m, 1 H), 1.63 (m, 2 H), 1.47 (m, 3 H), 1.21 (m, 4 H). − ^{13}C NMR (100.6 MHz): δ = 148.1, 129.8, 129.2, 128.9, 128.6, 126.5, 79.4, 33.3, 32.9, 24.9, 23.5, 23.3. − IR (film): 3063, 3033, 3005, 2959, 2911, 2836, 1610, 1513, 1455, 1303, 1251, 1178, 1032, 909 cm^{-1}. − MS (EI); *m/z* (%): 284 (3) [M$^+$], 205 (41), 204 (20), 203 (90), 185 (21), 139 (33), 138 (32), 137 (77), 102 (100), 101 (28), 83 (97), 77 (21), 67 (21), 55 (85), 51 (20). − $C_{14}H_{17}ClO_2S$ (284.8): calcd. C 59.04, H 6.02; found C 58.83, H 5.92.

Synthesis of 3-Phenylpropyl (*E*)-2-Butyl-2-chloroethenesulfinate (14b): The reaction of sulfoxide **9b** (116 mg, 0.43 mmol) with SO_2Cl_2 (521 μL, 0.52 mmol) provided the sulfinyl chloride (S=O stretch 1154 cm^{-1}). Addition of 3-phenyl-1-propanol (59.3 μL, 0.44 mmol) and K_2CO_3 (152 mg, 1.10 mmol) afforded sulfinate ester **14b** (87 mg, 67%) as an oil after flash chromatography (7% EtOAc/hexanes). − ^{1}H NMR (400 MHz): δ = 7.35−7.30 (m, 2 H), 7.26−7.21 (m, 3 H), 6.90 (s, 1 H), 3.95 (t of AB q, *J* = 9.8, 6.4 Hz, 2 H), 2.75 (t, *J* = 7.6 Hz, 2 H), 2.62−2.54 (m, 1 H), 2.42−2.34 (m, 1 H), 2.08−2.01 (m, 2 H), 1.64−1.57 (m, 2 H), 1.44 (sext, *J* = 7.4 Hz, 2 H), 0.98 (t, *J* = 7.4 Hz, 3 H). − ^{13}C NMR (100.6 MHz): δ = 148.3, 140.8, 128.5, 128.4, 126.8, 126.1, 64.9, 31.9, 31.4, 29.6, 25.4, 22.6, 13.7. − IR (film): 3027, 2957, 2932, 2873, 2863, 1625, 1601, 1466, 1454, 1139, 1007 cm^{-1}. − MS (CI, NH_3); *m/z* (%): 301 (32) [(M + H)$^+$], 183 (29), 165 (25), 119 (100), 118 (45), 117 (26), 91 (79), 81 (21), 57 (25), 59 (45). − $C_{15}H_{21}ClO_2S$ (300.8): calcd. C 59.89, H 7.04; found C 59.70, H 6.94.

Synthesis of 3-Phenylpropyl (*E*)-2-Chloroethenesulfinate (14c): The reaction of sulfoxide **9c** (200 mg, 0.95 mmol) with SO_2Cl_2 (670 μL, 0.67 mmol) provided sulfinyl chloride (S=O stretch 1133 cm^{-1}). Addition of 3-phenyl-1-propanol (120 μL, 0.91 mmol) and K_2CO_3 (331 mg, 2.39 mmol) afforded sulfinate ester **14c** (133 mg, 57%) as an oil after flash chromatography (7% EtOAc/hexanes). − ^{1}H NMR (400 MHz): δ = 7.32−7.29 (m, 2 H), 7.23−7.18 (m, 3 H), 6.97 (d, *J* = 13.2 Hz, 1 H), 6.68 (d, *J* = 13.2 Hz, 1 H), 4.01 (t of AB q, *J* = 10.0, 6.4 Hz, 1 H), 2.73 (t, *J* = 7.6 Hz, 2 H), 2.03 (m, 2 H). − ^{13}C NMR (100.6 MHz): δ = 140.7, 137.9, 132.3, 128.5, 128.4, 126.1, 65.0, 31.8, 31.3. − IR (film): 3062, 3027, 2950, 2886, 1603, 1581, 1497, 1454, 1168, 1125, 1004, 901, 834, 772 cm^{-1}. − MS (CI, NH_3); *m/z* (%): 183 (2), 119 (14), 118 (27), 105 (7), 92 (5), 91 (100), 77 (14), 65 (10). − $C_{11}H_{13}ClO_2S$ (244.7): calcd. C 53.98, H 5.35; found C 53.70, H 5.09.

Synthesis of 3-Phenylpropyl (*Z*)-2-Chloroethenesulfinate (14d): The reaction of sulfoxide **9d** (383 mg, 2.04 mmol) with SO_2Cl_2 (1.28 mL, 1.28 mmol) provided the sulfinyl chloride (S=O stretch 1154 cm^{-1}). Addition of 3-phenyl-1-propanol (280 μL, 2.04 mmol) and K_2CO_3 (704 mg, 5.09 mmol) afforded sulfinate ester **14c** (143 mg, 32%, from sulfoxide) as an oil and **14d** (123 mg, 27%, from sulfoxide) as an oil that could not be completely purified using flash chromatography (7% EtOAc/hexanes). − **14d**: ^{1}H NMR (400 MHz): δ = 7.22−7.16 (m, 2 H), 7.12−7.08 (m, 3 H), 6.64 (d, *J* = 7.0 Hz, 1 H), 6.53 (d, *J* = 7.0 Hz, 1 H), 4.06 (m, 1 H), 3.95 (m, 1 H), 2.64 (t, *J* = 7.2 Hz, 2 H), 1.99−1.92 (m, 2 H). − ^{13}C NMR (100.6 MHz): δ = 140.7, 139.9, 128.4 (2 C), 128.2, 126.1, 66.6, 31.7, 31.5. − IR (film): 3085, 3028, 2951, 2884, 1574, 1497, 1454, 1249, 1151, 1006 cm^{-1}. MS (EI); *m/z* (%): 245 [18, (M$^+$ for ^{35}Cl)], 119 (30), 118 (97), 117 (29), 91 (100), 73 (15). − HRMS (EI), calcd. for $C_{11}H_{14}{}^{35}ClO_2S$: 245.0403; found 245.0403. − The reaction of sulfoxide **9d** (153 mg, 0.73 mmol) with SO_2Cl_2 (0.770 mL, 0.77 mmol) provided the sulfinyl chloride. Addition of 3-phenyl-1-propanol (100 μL, 0.77 mmol) and K_2CO_3 (406 mg, 2.94 mmol) afforded the *trans* isomer of the sulfinate ester **14c** (60 mg, 34%, from the sulfoxide) as an oil (7% EtOAc/hexanes).

Synthesis of Cyclohexyl (*E*)-1,4-Bis(acetoxy)-3-chloro-2-but-2-enesulfinate (15a): The reaction of sulfoxide **10a** (245 mg, 0.69 mmol) with SO_2Cl_2 (0.83 mL, 0.83 mmol) provided the sulfinyl chloride (S=O stretch 1156 cm^{-1}). Addition of cyclohexanol (75 mg, 0.75 mmol) and K_2CO_3 (207.mg, 1.50 mmol) afforded sulfinate ester **15a** (130 mg, 53%) after flash chromatography (10% EtOAc/hexanes) and several water washes of the chromatographic fractions, which also contained cyclohexanol. − ^{1}H NMR (400 MHz): δ = 5.04 (s, 2 H), 5.02 (AB q, *J* = 12.6 Hz, 2 H), 4.28 (m, 1 H), 2.13 (s, 3 H), 2.07 (s, 3 H), 1.92 (m, 2 H), 1.73 (m, 2 H), 1.51 (m, 1.52) 1.49−1.24 (m, 2 H). − ^{13}C NMR (100.6 MHz): δ = 170.3, 169.9, 144.1, 141.9, 79.3, 62.0, 55.7, 33.5, 33.0, 25.0, 23.6, 23.6, 20.6, 20.5. − IR (film): 2938, 2859, 1748, 1633, 1448, 1376, 1224, 1143, 1032 cm^{-1}. − MS (EI); *m/z* (%): 253 (1) [(M − $C_6H_{11}O$) + H]$^+$, 211 (19), 146 (59), 111 (49), 104 (81), 92 (47), 91 (61), 86 (60), 85 (64), 84 (100), 60 (35), 52 (89). − $C_{14}H_{21}ClO_6S$ (352.8): calcd. C 47.66, H 6.00; found C 47.42, H 5.81.

Synthesis of Cyclohexyl (*E*)-4-Chloro-3-hex-3-enesulfinate (15b): The reaction of sulfoxide **10b** (128 mg, 0.48 mmol) with SO_2Cl_2 (0.60 mL, 0.60 mmol) provided the sulfinyl chloride (S=O stretch 1153 cm^{-1}). Addition of cyclohexanol (35 mg, 0.35 mmol) and K_2CO_3 (249 mg, 1.80 mmol) afforded sulfinate ester **15b** (99 mg, 78%) after flash chromatography (7% EtOAc/hexanes). − ^{1}H NMR (400 MHz): δ = 4.21 (m, 1 H), 2.79−2.61 (m, 3 H), 2.54−2.45 (m, 1 H), 1.93 (m, 2 H), 1.74 (m, 2 H), 1.58−1.50 (m, 2 H), 1.39−1.24 (m, 2 H), 1.20 (t, *J* = 7.5 Hz, 3 H), 1.17 (t, *J* = 7.6 Hz, 3 H). − ^{13}C NMR (100.6 MHz): δ = 145.4, 144.9, 78.1, 33.7, 33.0, 28.9, 25.1, 23.7, 23.6, 18.3, 13.4, 12.7. − IR (film): 2977, 2935, 2859, 1630, 1454, 1371, 1141, 934 cm^{-1}. − MS (EI); *m/z* (%): 264 (2, M$^+$), 185 (29), 183 (78), 167 (18), 165 (16), 83 (100), 82 (21), 81 (25), 67 (31), 55 (64). − $C_{12}H_{21}ClO_2S$ (264.8): calcd. C 54.43, H 7.99; found C 54.19, H 8.08.

Synthesis of 3-Phenylpropyl 1,2-Dichloropropanesulfinate (16): The reaction of sulfoxide **11** (132 mg, 0.69 mmol) with SO_2Cl_2 (902 μL, 0.90 mmol) provided sulfinyl chloride (S=O stretch 1145 cm^{-1}). Addition of 3-phenyl-1-propanol (89 μL, 0.66 mmol) and K_2CO_3

(192 mg, 1.39 mmol) afforded sulfinate ester **16** (52 mg, 27%) as an oil after flash chromatography (15% EtOAc/hexanes). − ^{1}H NMR (400 MHz): δ = 7.27−7.24 (m, 2 H), 7.21−7.14 (m, 3 H), 4.59−4.54 (m, 2 H), 4.14−4.08 (m, 2 H), 2.71 (t, *J* = 7.2 Hz, 2 H), 2.06−1.99 (m, 2 H), 1.66−1.61 (m, 3 H). − ^{13}C NMR (100.6 MHz): δ = 140.5, 128.5, 128.4, 126.2, 81.5, 69.2, 54.5, 31.6, 31.5, 20.5. − IR (film): 3027, 2953, 2867, 1604, 1497, 1497, 1464, 1455, 1383, 1249, 1136, 1051, 1016 cm^{-1}. − HRMS (EI), Calcd. for $C_{12}H_{17}{}^{35}Cl_2O_2S$: 295.0323; found 295.0308.

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