2-(Trimethylsilyl)ethyl Sulfoxides as a Convenient Source of Sulfenate Anions

Florian Foucoin,[a] Caroline Caupène,[a] Jean-François Lohier,[a] Jana Sopkova de Oliveira Santos,[b] Stéphane Perrio,*[a] Patrick Metzner[a]

[a] Laboratoire de Chimie Moléculaire et Thio-Organique (UMR CNRS 6507), ENSICAEN, Université de Caen-Basse Normandie, 6 Boulevard du Maréchal Juin, 14050 Caen, France
Fax +33(2)31452877; E-mail: perrio@ensicaen.fr

[b] Centre d'Etudes et de Recherche sur le Médicament de Normandie (UPRES EA 3915), Université de Caen Basse-Normandie, 5 Rue Vaubénard, 14032 Caen, France

Received 9 February 2007

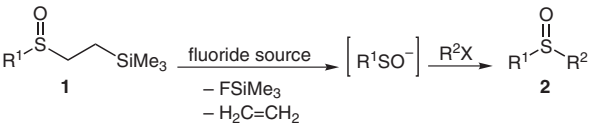
Abstract: The present report describes the novel and smooth generation of sulfenate salts by fluoride-mediated cleavage of 2-(trimethylsilyl)ethyl sulfoxides. Efficiency of the process was elucidated through further reaction with alkyl halides to give stable sulfoxide end products.

Key words: sulfoxides, sulfenate salts, silicon, fluorine, alkylation

Sulfenate salts RSO^- are not common sulfur nucleophiles for the organic chemist, the major contributing factor being a lack of efficient methods for their generation.[1] However, these anions are very attractive as precursors of sulfoxides, sulfenamides, and sulfenic acids and esters. Furthermore, interest in sulfenates has recently been heightened by their identification as key intermediates in some bioorganic transformations.[1,2]

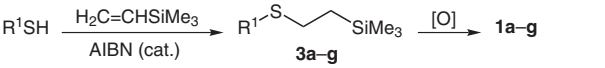
The most relevant routes to sulfenates reported so far consist of *N*-sulfonyloxaziridine-mediated oxidation of thiolates[3] or manipulation of sulfoxides possessing an appropriate functionality. In this context, literature precedents concern the oxidative cleavage of alk-1-ynyl sulfoxides with a palladium(0) catalyst followed by transmetalation with diethylzinc,[4] an addition–elimination methodology with β-sulfinylacrylates,[5] and a retro-Michael reaction initiated by a base from β-sulfinyl esters.[6]

In the early 1990s, Oida mentioned an interesting liberation of a sulfenate species from 2-(trimethylsilyl)ethyl benzenesulfenate according to a fluoride-assisted fragmentation methodology.[7] However, a single example of the generation of the simple benzenesulfenic acid anion is described. These results suggested to us that the analogous sulfoxides **1** could be an alternative and more readily available[8] source of sulfenate anions. An obvious difference during the process is the cleavage of the C–S, instead of the C–O, bond (Scheme 1).[9] Important of note is that the 2-(trimethylsilyl)ethyl (TMSE) group has been used in the past as a practical protecting group for a wide range of functions[10] including sulfur[11] derivatives. The most probable mechanism for the sulfenate formation would involve an initial nucleophilic attack of the fluoride anion on the silicon center, with subsequent elimination of fluorotrimethylsilane and ethene.[12] According to previous mechanistic investigations reported in the literature, maximized delocalization of the Si–C bond electrons into the σ*-orbital of the vicinal C–S bond directly related to conformational considerations should be crucial in the process.[13] Sulfenate quantification could be then ensured by trapping experiments with alkyl halides to give stable sulfoxide derivatives **2** (Scheme 1). The present report outlines the results obtained from this desilylation strategy.

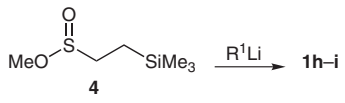


Scheme 1 Sulfenates from 2-(trimethylsilyl)ethyl sulfoxides

Most of the precursors were obtained via the corresponding sulfides **3** (Scheme 2). Regioselective radical addition of aromatic and aliphatic thiols to trimethyl(vinyl)silane in the presence of a catalytic amount of 2,2′-azobis(isobutyronitrile) (1%) afforded 2-(trimethylsilyl)ethyl sulfides **3a–g** in 48–90% yields.[14] Subsequent oxidation with hydrogen peroxide/2,2,2-trifluoroethanol combination[15] or 3-chloroperoxybenzoic acid led to the sulfoxide targets **1a–g** in good yields (80–98%). Ethenic substrate **1h** was directly produced as a mixture of two separable (*Z*)- and (*E*)-diastereomers in an overall 70% yield by reaction of prop-1-enyllithium with methyl 2-(trimethylsilyl)ethanesulfinate (**4**).[16] Similarly, synthesis of alk-1-ynyl substrate **1i** was achieved in 51% yield from the lithium carbanion derived from 3,3-dimethylbut-1-yne.



R^1 = Tol, 4-BrC_6H_4, 4-$F_3CC_6H_4$, 2,6-$Me_2C_6H_3$, 2-naphthyl, 2-pyridyl, *t*-Bu



R^1 = CH=CHMe, C≡C*t*-Bu

Scheme 2 Synthesis of 2-(trimethylsilyl)ethyl sulfoxides **1**

SYNTHESIS 2007, No. 9, pp 1315–1324
Advanced online publication: 18.04.2007
DOI: 10.1055/s-2007-966017; Art ID: P01607SS

Characterization of compounds **1** and **3** by ^{29}Si NMR spectroscopy was systematically investigated.[17] A singlet at δ in the range of 1.48–1.93 was observed in the sulfide series whilst that of the corresponding sulfoxides was significantly shifted to lower field (δ = 3.1–3.42).[18] 4-Bromophenyl derivative **1b** provided crystals suitable for X-ray crystallography.[19] The ORTEP depiction, shown in Figure 1, indicates that the molecule adopts, in the solid state, a staggered conformation in which the trimethylsilyl and sulfinyl units are almost antiperiplanar, with a Si–C8–C7–S dihedral angle value of 175.9°.[20] This is a favorable geometry for the previously suggested σ–σ* interaction between the Si–C8 bonding orbital and the C7–S antibonding orbital. The direct structural effect is a lengthening[21] of the C7–S bond in the order of 0.010 Å, compared to silicon-free analogues (1.825 Å versus 1.815 Å[22] as a standard distance).

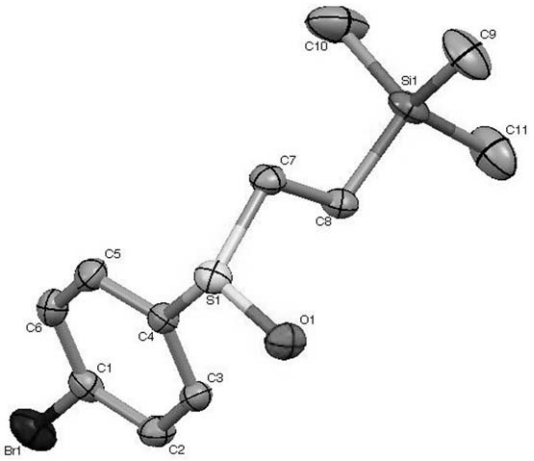


Figure 1 ORTEP diagram of β-silyl sulfoxide **1b** (H atoms not shown)

Silyl sulfoxide **1a** possessing a 4-tolyl group was selected as the prototypical substrate for preliminary investigation of the deprotection conditions and a commercial 1 M tetrabutylammonium fluoride in tetrahydrofuran solution was used as the fluoride source. The protocol we tested first in order to minimize sulfenate degradation, if produced, involves treatment of **1a** in tetrabutylammonium fluoride in tetrahydrofuran in the presence of benzyl bromide. After hydrolysis, solvent evaporation, and standard work-up, purification of the product and especially removal of the ammonium residues were conveniently achieved by column chromatography on silica gel using pentane–ethyl acetate mixtures as eluents. The results are collected in Table 1.

We began our survey by employing a single equivalent of tetrabutylammonium fluoride at room temperature. TLC monitoring revealed after one day the presence of the anticipated benzylic sulfoxide **2aa** but also of unreacted starting material. The reaction was repeated with a twofold excess of tetrabutylammonium fluoride and again the reaction did not attain completion. Purification was however undertaken and product **2aa** was isolated in 52% yield (Table 1, entry 1). Increasing the tetrabutylammonium fluoride loading to three equivalents led to smooth but complete deprotection, and **2aa** was produced in 87% yield (entry 2). A similar yield after only 45 minutes of reaction was obtained by elevating the temperature to 60 °C (entry 3). Furthermore, the amount of tetrabutylammonium fluoride can be reduced to two equivalents at this temperature without any loss of efficiency (entry 4). The use of benzyl chloride as an alternative quench also gave satisfactory results (entry 5). A slightly lower yield of 52% for **2ab** was obtained employing iodomethane (entry 6). Examination of the crude products isolated with the three previous electrophiles revealed the absence of sulfenic ester, which might arise through a competing O-alkylation of the ambident[23] sulfenate. The use of iodoethane likewise led to the corresponding sulfoxide **2ac** in 66% yield (entry 7). Contamination with sulfenate ester was this time observed, but to a small degree only (9%).[24] Both alkylation products were readily separated by purification on a silica gel column. The overall yield for the sequence being 75%, it again demonstrates the efficiency of the intermediate sulfenate formation. A better yield of 84% was reached at room temperature, which also suppresses the formation of the ester byproduct (entry 8). Finally, quantitative deprotection was observed when experiments were performed without initial inclusion of the alkyl halide. However, subsequent electrophilic treatment did not allow the isolation of the final sulfoxide product, instead a complex mixture resulted arising from sulfenate degradation, from which 4-tolyl disulfide, sulfide, and sulfone were identified. These results clearly indicate that above ambient temperatures are tolerated in sulfenate salt chemistry as long as the electrophile is present and if it is sufficiently reactive.

Table 1 Influence of the Reaction Conditions with **1a** (R^1 = Tol) According to Scheme 1

Entry	R^2X (equiv)	TBAF[a] (equiv)	Conditions[b]	Product	Yield[c] (%)
1	BnBr (1.1)	2	r.t., 20 h	**2aa**	52
2	BnBr (1.1)	3	r.t., 4 h	**2aa**	87
3	BnBr (1.1)	3	60 °C, 45 min	**2aa**	85
4	BnBr (1.1)	2	60 °C, 45 min	**2aa**	85
5	BnCl (1.1)	2	60 °C, 45 min	**2aa**	65
6	MeI (1.5)	4	60 °C, 3 h	**2ab**	52
7	EtI (2)	2	60 °C, 105 min	**2ac**	66 (9)[d]
8	EtI (2)	3	r.t., 4 h	**2ac**	84

[a] Commercial 1 M TBAF in THF dried on 4 Å molecular sieves.
[b] Reaction monitored by TLC.
[c] Isolated yields.
[d] The isolated yield of sulfenate ester is shown in parentheses.

2-(Trimethylsilyl)ethoxymethyl sulfoxide **5** was also identified as a potential precursor of sulfenate salts. This compound **5** was prepared by reaction of 4-toluenethiol

with 2-(trimethylsilyl)ethoxymethyl chloride in the presence of triethylamine to give sulfide **6**,[25] followed by oxidation with 3-chloroperoxybenozic acid (Figure 2). Upon treatment with fluoride anions, cleavage should still proceed with evolution of fluorotrimethylsilane and ethene but also of formaldehyde.[26] Reaction of **5** with tetrabutylammonium fluoride (3 equiv) at 60 °C led to disappearance of the starting material within six hours. Unfortunately, the isolated yield of the anticipated benzylic sulfoxide **2aa** did not exceed 21%, the major side product being 4-tolyl disulfide (66% yield).

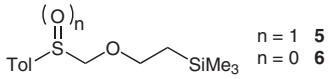


Figure 2

In summary, these preliminary studies revealed that optimal reaction conditions simply involve heating a tetrahydrofuran solution of 2-(trimethylsilyl)ethyl sulfoxides **1** and the electrophile to 60 °C in the presence of tetrabutylammonium fluoride (2 equiv).

The optimized reaction conditions for cleavage/in situ alkylation with benzyl bromide were applicable to several 2-(trimethylsilyl)ethyl sulfoxides as summarized in Table 2. The reactions were monitored by TLC and completed within 20–60 minutes. Various substituents on the benzene ring were compatible, including 4-bromo, 4-(trifluoromethyl), and 2,6-dimethyl groups, furnishing benzylic sulfoxides **2b**–**d** in 69–84% yields (entries 1–3). We have also been able to isolate a naphthyl product **2e** in 86% yield (entry 4). The reaction can be efficiently extended to a heteroaromatic substrate, providing the 2-pyridyl sulfoxide **2f** in 77% yield (entry 5). Worthy of note is that no pyridinium salt, which could result of a competitive alkylation of the nitrogen atom, was detected. Alkynyl 2-(trimethylsilyl)ethyl sulfoxides were also suitable substrates as illustrated with a 66% yield in entry 6. Deprotection was observed with the α,β-unsaturated sulfoxide **1h** but without attaining completion after two hours of reaction. Employing a larger amount of TBAF (4 equiv), disappearance of the starting material was this time observed within 30 minutes and the final sulfoxide product **2h** was isolated in 49% yield with clean retention of the double bond geometry (entry 7).[27] Finally, no fragmentation took place with the aliphatic derivative **1g**, which is quantitatively recovered even after an extended heating or introduction of additional aliquots of tetrabutylammonium fluoride (entry 8).[28] Modification of the conditions including the solvent nature (DMF, toluene, 1,2-dichloroethane, MeCN) and the fluoride source (CsF, CaF_2/KF combination) was then investigated but unfortunately none resulted in the liberation of the desired tertiary sulfenate. Use of potassium *tert*-butoxide and potassium trimethylsiloxide as an alternative desilylation promoter also failed.

Table 2 Benzyl Sulfoxides **2** via Sulfenates According to Scheme 1

Entry	Substrate	R^1	Product[a]	Time[b] (min)	Yield[c] (%)
1	**1b**	4-BrC_6H_4	**2b**	20	84
2	**1c**	4-$F_3CC_6H_4$	**2c**	20	75
3	**1d**	2,6-$Me_2C_6H_3$	**2d**	60	69
4	**1e**	2-naphthyl	**2e**	30	86
5	**1f**	2-pyridyl	**2f**	20	77
6	**1i**	C≡C*t*-Bu	**2i**	30	66
7	**1h**	CH=CHMe	**2h**	30	49[d]
8	**1g**	*t*-Bu	**2g**	270	0

[a] Reaction at 60 °C with commercial 1 M TBAF in THF (2 equiv) and BnBr (1.1 equiv).
[b] Reaction monitored by TLC.
[c] Isolated yields.
[d] Obtained with 4 equiv of TBAF.

In conclusion, we have developed a fluoride-activated strategy towards sulfenate salts using 2-(trimethylsilyl)ethyl sulfoxides as substrates. In situ capture with haloalkanes led to sulfoxides as stable products. Attractive features of the method include the use of stable and readily available materials and reagents, a simple and convenient procedure, and broad scope of the reaction. Furthermore, the sulfinyl moiety being gradually released during the process, it seems particularly well suited to further synthetic applications involving electrophiles less reactive than standard alkyl halides. High yields are obtained for a wide variety of substrates including (het)aryl, alk-1-enyl, and alk-1-ynyl structures. Aliphatic congeners are distinctly more robust and survived under the reaction conditions. Resonance stabilization of the liberated sufenate species probably plays a crucial role for a successful process. Future work will seek to determine conditions or a suitable silicon-containing unit to produce alkanesulfenates and to develop further applications of sulfenic acid anions in organic synthesis.

Anhyd THF and Et_2O were displayed by using an Innovative Technology solvent purification system. All other reagents and solvents were used as received from commercial sources. All reactions were performed in oven-dried glassware, under an atmosphere of N_2. Due to the stench of thiols, all glassware and syringes were washed with bleach after use. The concentrations of organolithium reagents were determined by titration against diphenylacetic acid.[29] Reactions were purified by chromatography column with Merck silica gel Geduran Si 60 (0.040–0.063 nm). TLC was carried out on silica gel 60 F_{254} (1.1 mm, Merck) with spot detection under UV light or through I_2 or $KMnO_4$ oxidation. For Kugelrohr distillation, the temperatures quoted correspond to the oven temperatures. Melting points were obtained on an Electrothermal IA9000 capillary apparatus and are uncorrected. NMR spectra were recorded at room temperature on Bruker DPX 250 or DRX 400 spectrometers. The chemical shifts are calibrated to TMS ($\delta_H = 0.00$) or residual proton and carbon resonance of the solvent $CDCl_3$ ($\delta_H = 7.26$ and $\delta_C = 77.16$). ^{19}F and ^{29}Si chemical shifts are referred to external $CFCl_3$ and TMS, respective-

ly. IR spectra were recorded on a Perkin-Elmer ATR IR instrument. MS spectra were recorded on Varian Saturn 2000 or QTOF Micro Waters instruments. Only peaks of an intensity >10% (except decisive ones) are listed. Elemental analyses were performed with a C, H, N, S, O Thermoquest apparatus.

2-(Trimethylsilyl)ethyl Sulfides 3a–g; General Procedure

A mixture of thiol (1 equiv), trimethyl(vinyl)silane (1.2 equiv), and AIBN (0.01 equiv) was heated at 100 °C in a sealed tube for 20 h. After cooling to r.t. and concentration under reduced pressure, the residue was purified by Kugelrohr distillation to afford sulfide **3**.

1-[(4-Methylphenyl)sulfanyl]-2-(trimethylsilyl)ethane (3a)[8a]

Obtained from 4-toluenethiol (3.73 g, 30.0 mmol) as a colorless oil; yield: 5.94 g (88%); bp 140 °C/9.3 mbar (Lit.[8a] 86–87 °C/0.4 mbar); R_f = 0.25 (pentane).

IR: 2954, 1491, 1248, 1090, 1011, 822, 801 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.00 (s, 9 H), 0.84–0.92 (m, 2 H), 2.30 (s, 3 H), 2.86–2.93 (m, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –1.5, 17.3, 21.3, 30.5, 129.9, 130.1, 133.5, 136.1.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 1.68.

MS (EI): *m/z* (%) = 224 (22) $[M]^+$, 196 (60), 181 (44), 165 (22), 149 (19), 91 (12) $[C_7H_7]^+$, 73 (100) $[SiMe_3]^+$, 45 (25).

1-[(4-Bromophenyl)sulfanyl]-2-(trimethylsilyl)ethane (3b)[30]

Obtained from 4-bromobenzenethiol (1.00 g, 5.29 mmol) as a colorless oil; yield: 1.06 g (69%); bp 115 °C/0.07 mbar; R_f = 0.80 (pentane).

IR: 2952, 1473, 1248, 1091, 1007, 836, 804 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.05 (s, 9 H), 0.88–0.95 (m, 2 H), 2.91–2.98 (m, 2 H), 7.14–7.19 (m, 2 H), 7.38–7.42 (m, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –1.6, 16.9, 29.8, 119.5, 130.6, 132.0, 136.6.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 1.79.

MS (EI): *m/z* (%) = 290 (10) and 288 (10) $[M]^{+}$*, 262 (10) and 260 (10)*, 247 (10) and 245 (30)*, 108 (10), 101 (15), 73 (100) $[SiMe_3]^+$. (*) ^{81}Br and ^{79}Br isotopic pattern.

1-{[4-(Trifluoromethyl)phenyl]sulfanyl}-2-(trimethylsilyl)ethane (3c)

Obtained from 4-(trifluoromethyl)benzenethiol (780 mg, 4.38 mmol) as a colorless oil; yield: 1.08 g (88%); bp 90 °C/0.1 mbar; R_f = 0.87 (pentane).

IR: 2954, 1607, 1324, 1250, 1162, 1120, 1094, 1063, 1013, 821 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.09 (s, 9 H), 0.94–1.01 (m, 2 H), 2.99–3.06 (m, 2 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 7.52 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.4, 16.8, 28.8, 124.6 (q, *J* = 271.5 Hz), 125.9 (q, *J* = 3.8 Hz), 127.4 (q, *J* = 32.5 Hz), 127.5, 143.3.

^{19}F NMR (235.3 MHz, $CDCl_3$): δ = –62.3.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 1.93.

MS (EI): *m/z* (%) = 278 (20) $[M]^+$, 250 (15), 235 (25), 101 (20), 91 (20), 73 (100) $[SiMe_3]^+$.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_{17}F_3SSi$: 278.0772; found: 278.0775.

1-[(2,6-Dimethylphenyl)sulfanyl]-2-(trimethylsilyl)ethane (3d)[8a]

Obtained from 2,6-dimethylbenzenethiol (944 mg, 6.83 mmol) as a colorless oil; yield: 862 mg (53%); bp 90 °C/0.08 mbar (Lit.[8a] 72–74 °C/0.09 mbar); R_f = 0.87 (pentane).

IR: 2952, 2923, 1459, 1248, 856, 836, 767 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = –0.01 (s, 9 H), 0.79–0.87 (m, 2 H), 2.54 (s, 6 H), 2.64–2.72 (m, 2 H), 7.11 (s, 3 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.7, 17.8, 22.3, 31.0, 128.1 (3 Ar–C), 134.1, 143.2.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 1.58.

MS (EI): *m/z* (%) = 238 (20) $[M]^+$, 210 (30), 195 (20), 84 (30), 73 (100) $[SiMe_3]^+$.

1-(2-Naphthylsulfanyl)-2-(trimethylsilyl)ethane (3e)[8a]

Obtained from naphthalene-2-thiol (1.00 g, 6.24 mmol) as a colorless oil; yield: 1.41 g (87%); bp 170 °C/0.08 mbar; R_f = 0.53 (pentane).

IR: 3054, 2951, 1247, 836, 809, 740 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.07 (s, 9 H), 0.88–0.95 (m, 2 H), 2.97–3.04 (m, 2 H), 7.32–7.44 (m, 3 H), 7.64–7.74 (m, 4 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –1.6, 17.0, 29.5, 125.6, 126.5, 126.6, 127.1, 127.4, 127.8, 128.4, 131.7, 133.9, 134.9.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 1.83.

MS (EI): *m/z* (%) = 260 (40) $[M]^+$, 232 (40), 217 (25), 201 (20), 115 (20), 73 (100) $[SiMe_3]^+$.

1-(2-Pyridylsulfanyl)-2-(trimethylsilyl)ethane (3f)

Obtained from pyridine-2-thiol (1.00 g, 9.00 mmol); due to the poor solubility of the substrate in trimethyl(vinyl)silane, toluene (5 mL) was added. The product was obtained as a yellow oil. yield: 915 mg (48%); bp 100 °C/0.08 mbar; R_f = 0.29 (pentane–CH_2Cl_2, 80:20).

IR: 3045, 2953, 1578, 1453, 1413, 1248, 1125, 835, 753 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, 9 H), 0.96–1.01 (m, 2 H), 3.17–3.21 (m, 2 H), 6.96 (ddd, *J* = 1.0, 4.9, 7.4 Hz, 1 H), 7.14 (ddd, *J* = 0.9, 1.0, 8.1 Hz, 1 H), 7.47 (ddd, *J* = 1.8, 7.4, 8.1 Hz, 1 H), 8.42 (ddd, *J* = 0.9, 1.8, 4.9 Hz, 1 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –1.6, 17.0, 26.6, 119.3, 122.2, 136.0, 149.6, 160.2.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 1.80.

MS (ESI): *m/z* (%) = 212 (60) $[M + H]^+$, 184 (100), 168 (20).

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{10}H_{18}NSSi$: 212.0929; found: 212.0919.

1-(*tert*-Butylsulfanyl)-2-(trimethylsilyl)ethane (3g)[8b]

Obtained from *t*-BuSH (3.61 g, 40.0 mmol) as a colorless oil; yield: 6.86 g (90%); bp 60 °C/6.7 mbar; R_f = 0.22 (pentane).

IR: 2955, 2898, 1459, 1363, 1248, 1161, 835 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.02 (s, 9 H), 0.76–0.83 (m, 2 H), 1.32 (s, 9 H), 2.51–2.58 (m, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.6, 17.1, 23.7, 31.1, 42.2.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 1.60.

MS (EI): *m/z* (%) = 190 (1) $[M]^+$, 162 (29), 107 (34), 91 (46), 75 (20), 73 (100) $[SiMe_3]^+$, 57 (33) $[t\text{-Bu}]^+$, 41 (20).

1-{[(4-Methylphenyl)sulfanyl]methoxy}-2-(trimethylsilyl)ethane (6)

Et_3N (1.82 mL, 13.0 mmol, 1.3 equiv) was added dropwise to a soln of 4-toluenethiol (1.24 g, 10 mmol, 1 equiv) and SEMCl (1.96 mL,

11.1 mmol, 1.1 equiv) in anhyd Et_2O (120 mL). The resulting mixture was stirred at r.t. for 2.5 h. After evaporation to dryness and addition of H_2O, the mixture was extracted with CH_2Cl_2 and then washed with H_2O. The combined organic layers were dried ($MgSO_4$) filtered and concentrated under reduced pressure. The crude product was then purified by column chromatography (silica gel, pentane–CH_2Cl_2, 90:10) to afford the anticipated SEM sulfide **6** (2.07 g, 81%) as a colorless oil; R_f = 0.34 (pentane–CH_2Cl_2, 90:10).

IR: 2955, 2901, 1248, 1068, 857, 832, 804 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.01 (s, 9 H), 0.88–0.96 (m, 2 H), 2.31 (s, 3 H), 3.64–3.70 (m, 2 H), 4.94 (s, 2 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 7.34–7.39 (m, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –1.2, 17.9, 21.2, 66.1, 76.2, 129.8, 130.9, 132.7, 136.9.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 0.28.

MS (ESI): *m*/*z* (%) = 277 (60) $[M + Na]^+$, 137 (100).

HRMS (EI): *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{22}NaOSSi$: 277.1058; found: 277.1056.

2-(Trimethylsilyl)ethyl Sulfoxides 1; General Procedures

With Hydrogen Peroxide: To a 2 M soln of sulfide **3** (1 equiv) in 2,2,2-trifluoroethanol, cooled to 0 °C, H_2O_2 (1.2 equiv) was added dropwise. The mixture was stirred at r.t. for 20 h. Solid sodium sulfite (2.1 equiv) was added then the mixture was heated at 50 °C for 30 min. The resulting mixture was filtered on Celite, dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The crude product was then purified by column chromatography (silica gel) to afford pure sulfoxide **1**.

With MCPBA: To a soln of sulfide **3** (1 equiv) in CH_2Cl_2, cooled to 0 °C, a soln of MCPBA (1 equiv) in CH_2Cl_2 was added dropwise. The mixture was stirred for 30 min at 0 °C and washed successively with sat. aq $NaHCO_3$ and H_2O. The organic layer was dried ($MgSO_4$), filtered, and concentrated to dryness. The crude product was purified by column chromatography (silica gel) to afford pure sulfoxide **1**.

1-[(4-Methylphenyl)sulfinyl]-2-(trimethylsilyl)ethane (1a)[9f]

Obtained using the H_2O_2 procedure from sulfide **3a** (5.00 g, 22.3 mmol) as a colorless oil; yield: 4.26 g (80%); R_f = 0.27 (pentane–Et_2O, 60:40).

IR: 2952, 1494, 1248, 1041, 857 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.00 (s, 9 H), 0.76–0.84 (m, 2 H), 2.43 (s, 3 H), 2.63–2.87 (m, 2 H)*, 7.34 (d, *J* = 8.0 Hz, 2 H), 7.49–7.52 (m, 2 H). (*) Upon irradiation of the multiplet at δ = 0.76–0.84, the signal becomes an AB quartet (δ_A = 2.70, δ_B = 2.81, *J* = 13.4 Hz).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.7, 8.2, 21.6, 53.1, 124.5, 130.7, 140.5, 141.5.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 3.20.

^{29}Si NMR (79.5 MHz, THF-d_8): δ = 3.01.

MS (ESI): *m*/*z* (%) = 503 (100) $[2 M + Na]^+$, 263 (82) $[M + Na]^+$, 241 (10) $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{12}H_{20}NaOSSi$: 263.0902; found: 263.0905.

1-[(4-Bromophenyl)sulfinyl]-2-(trimethylsilyl)ethane (1b)

Obtained using the H_2O_2 procedure from sulfide **3b** (1.00 g, 3.46 mmol) as transparent crystals; yield: 974 mg (92%); mp 63–65.5 °C (pentane–CH_2Cl_2); R_f = 0.50 (pentane–EtOAc, 80:20).

IR: 2954, 1465, 1385, 1248, 1042, 1006, 837, 809 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.01 (s, 9 H), 0.70 (dt, *J* = 4.3, 13.8 Hz, 1 H), 0.83 (dt, *J* = 4.2, 13.8 Hz, 1 H), 2.65 (dt, *J* = 4.3, 13.5 Hz, 1 H), 2.81 (dt, *J* = 4.2, 13.5 Hz, 1 H), 7.45–7.48 (m, 2 H), 7.64–7.66 (m, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.8, 7.8, 53.0, 125.4, 126.0, 132.5, 142.8.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 3.34.

MS (ESI): *m*/*z* (%) = 635 (20), 633 (40) and 631 (20) $[2 M + Na]^{+}$*, 613 (20), 611 (40) and 609 (20) $[2 M + H]^{+}$*, 329 (30) and 327 (30) $[M + Na]^{+}$*, 307 (100) and 305 (100) $[M + H]^{+}$*, 279 (10) and 277 (10)*, 189 (30) and 187 (30)*. (*) ^{81}Br and ^{79}Br isotopic pattern.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{18}BrOSSi$: 305.0040; found: 305.0031.

1-{[4-(Trifluoromethyl)phenyl]sulfinyl)}-2-(trimethylsilyl) ethane (1c)

Obtained using the H_2O_2 procedure from sulfide **3c** (1.00 g, 3.59 mmol) as transparent crystals; yield: 965 mg (91%); mp 59–62 °C (pentane–CH_2Cl_2); R_f = 0.20 (pentane–EtOAc, 90:10).

IR: 2956, 2923, 1605, 1321, 1249, 1163, 1125, 1060, 1041, 1011, 827 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = –0.01 (s, 9 H), 0.71 (dt, *J* = 4.2, 13.9 Hz, 1 H), 0.89 (dt, *J* = 4.1, 13.9 Hz, 1 H), 2.68 (dt, *J* = 4.2, 13.6 Hz, 1 H), 2.87 (dt, *J* = 4.1, 13.6 Hz, 1 H), 7.72 and 7.78 (AB, *J* = 8.2 Hz, 4 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.8, 7.8, 53.1, 123.7 (q, *J* = 272.6 Hz), 124.8, 126.2 (q, *J* = 3.6 Hz), 133.0 (q, *J* = 32.9 Hz), 148.2.

^{19}F NMR (235.3 MHz, $CDCl_3$): δ = –62.8.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 3.42.

MS (ESI): *m*/*z* (%) = 611 (35) $[2 M + Na]^+$, 589 (50) $[2 M + H]^+$, 317 (45) $[M + Na]^+$, 295 (100) $[M + H]^+$, 267 (80), 175 (10).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{18}F_3OSSi$: 295.0800; found: 295.0801.

1-[(2,6-Dimethylphenyl)sulfinyl]-2-(trimethylsilyl)ethane (1d)[8a]

Obtained using the H_2O_2 procedure from sulfide **3d** (500 mg, 2.10 mmol) as a white solid; yield: 482 mg (90%); mp 44.5–46.5 °C (Lit.[8a] 42–43 °C); R_f = 0.38 (pentane–EtOAc, 90:10).

IR: 2954, 1246, 1039, 857, 828, 769 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.03 (s, 9 H), 0.64 (dt, *J* = 4.5, 14.0 Hz, 1 H), 1.12 (dt, *J* = 4.0, 14.0 Hz, 1 H), 2.58 (s, 6 H), 2.89 (ddd, *J* = 4.5, 13.0, 14.0 Hz, 1 H), 3.17 (ddd, *J* = 4.0, 13.0, 14.0 Hz, 1 H), 7.05 (d, *J* = 7.6 Hz, 2 H), 7.22 (d-like, *J* = 7.1 Hz, 1 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.8, 10.6, 19.6, 47.8, 130.3, 130.9, 138.1, 138.7.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 3.10.

MS (ESI): *m*/*z* (%) = 531 (85) $[2 M + Na]^+$, 509 (85) $[2 M + H]^+$, 277 (100) $[M + Na]^+$, 255 (85) $[M + H]^+$, 137 (40).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{22}NaOSSi$: 277.1058; found: 277.1057.

2-(2-Naphthylsulfinyl)-1-(trimethylsilyl)ethane (1e)[8a]

Obtained using the H_2O_2 procedure from sulfide **3e** (1.00 g, 3.84 mmol) as a white solid; yield: 944 mg (89%); mp 78–79.5 °C (Lit.[8a] 77–78 °C); R_f = 0.33 (pentane–EtOAc, 80:20).

IR: 2969, 2902, 1245, 1066, 1038, 809 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = –0.02 (s, 9 H), 0.70–0.95 (m, 2 H), 2.77 (dt, *J* = 4.7, 13.2 Hz, 1 H), 2.93 (dt, *J* = 4.7, 13.2 Hz, 1 H), 7.54–7.63 (m, 3 H), 7.90–8.00 (m, 3 H), 8.17 (s, 1 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –1.8, 7.9, 52.6, 120.2, 125.2, 127.4, 127.8, 128.2, 128.7, 129.5, 133.0, 134.5, 140.7.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 3.28.

MS (ESI): *m/z* (%) = 575 (65) $[2 M + Na]^+$, 553 (10) $[2 M + H]^+$, 299 (100) $[M + Na]^+$, 277 (60) $[M + H]^+$, 159 (90).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_{20}NaOSSi$: 299.0902; found: 299.0891.

1-(*tert*-Butylsulfinyl)-2-(trimethylsilyl)ethane (1g)[8b]

Obtained using the H_2O_2 procedure from sulfide **3g** (6.70 g, 35.2 mmol) as a colorless oil; yield: 7.10 g (98%); R_f = 0.20 (CH_2Cl_2–EtOAc, 90:10).

IR: 2954, 2898, 1248, 1036, 838 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 9 H), 0.74–0.82 (m, 1 H), 1.16–1.24 (m, 1 H) signal overlapping with *t*-Bu singlet, 1.24 (s, 9 H), 2.33–2.48 (m, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –1.6, 10.5, 23.2, 41.0, 53.0.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 3.07.

MS (ESI): *m/z* (%) = 435 (45) $[2 M + Na]^+$, 229 (100) $[M + Na]^+$, 207 (10) $[M + H]^+$.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_9H_{22}NaOSSi$: 229.1058; found: 229.1062.

1-(2-Pyridylsulfinyl)-2-(trimethylsilyl)ethane (1f)

Obtained using the MCPBA procedure from sulfide **3f** (600 mg, 2.83 mmol) as a yellow oil; yield: 483 mg (75%); R_f = 0.22 (pentane–EtOAc, 80:20).

IR: 3050, 2953, 1575, 1421, 1248, 1048, 1036, 856, 828 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.02 (s, 9 H), 0.57 (dt, *J* = 4.2, 14.0 Hz, 1 H), 1.05 (dt, *J* = 3.9, 14.0 Hz, 1 H), 2.85 (dt, *J* = 4.2, 13.7 Hz, 1 H), 3.11 (ddd, *J* = 3.9, 13.4, 14.1 Hz, 1 H), 7.36 (ddd, *J* = 1.6, 4.8, 7.1 Hz, 1 H), 7.90–7.98 (m, 2 H), 8.62 (d, *J* = 4.6 Hz, 1 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.8, 7.3, 50.1, 120.6, 124.5, 137.9, 149.7, 164.5.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 3.37.

MS (ESI): *m/z* (%) = 477 (50) $[2 M + H]^+$, 250 (90) $[M + Na]^+$, 228 (85) $[M + H]^+$, 200 (100), 184 (40).

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{10}H_{18}NOSSi$: 228.0878; found: 228.0872.

1-{[(4-Methylphenyl)sulfinyl]methoxy}-2-(trimethylsilyl)ethane (5)

Obtained using the MCPBA procedure from sulfide **6** (1.70 g, 6.69 mmol) as a colorless oil; yield: 1.54 g (85%); R_f = 0.11 (pentane–EtOAc, 90:10).

IR: 2953, 2894, 1248, 1103, 1079, 1041, 857, 833, 808 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.01 (s, 9 H), 0.95–1.02 (m, 2 H), 2.40 (s, 3 H), 3.80–3.88 (m, 2 H), 4.36 and 4.44 (AB, *J* = 10.3 Hz, 2 H), 7.31 (d-like, *J* = 8.0 Hz, 2 H), 7.49–7.53 (m, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –1.2, 18.5, 21.7, 71.4, 92.7, 124.7, 130.2, 138.2, 143.0.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 0.12.

MS (ESI): *m/z* (%) = 563 (40) $[2 M + Na]^+$, 293 (100) $[M + Na]^+$, 271 (10) $[M + H]^+$, 241 (10), 213 (10), 123 (30).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{13}H_{22}NaO_2SSi$: 293.1008; found: 293.1001.

Methyl 2-(Trimethylsilyl)ethanesulfinate (4)[9f]

To a soln of 2-(trimethylsilyl)ethyl sulfoxide **1g** (6.00 g, 29.1 mmol, 1 equiv) in anhyd Et_2O (60 mL) at –78 °C, SO_2Cl_2 (2.57 mL, 32.0 mmol, 1.1 equiv) was added dropwise. The mixture was stirred at –78 °C for 2 h and then allowed to warm slowly to r.t. The mixture was concentrated to dryness and the sulfinyl chloride produced was diluted in anhyd Et_2O (30 mL). The soln was cooled to 0 °C and Et_3N (4.06 mL, 29.1 mmol, 1 equiv) and MeOH (1.29 mL, 32.0 mmol, 1.1 equiv) were added. The mixture was stirred at 0 °C for 1 h. The mixture was hydrolyzed with H_2O (50 mL) and the aqueous layer was extracted with Et_2O (2 × 50 mL). The organic extracts were washed with H_2O (50 mL) and sat. aq NaCl (50 mL) and then dried ($MgSO_4$), filtered, and evaporated to dryness. The crude product was purified by column chromatography (silica gel, pentane–CH_2Cl_2, 40:60) to afford the anticipated product **4** (4.34 g, 83%) as a yellow oil; R_f = 0.29 (pentane–CH_2Cl_2, 40:60). This compound is relatively unstable, even upon storage in the fridge.

IR: 2954, 1459, 1417, 1249, 1127, 994, 852, 830, 680 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.04 (s, 9 H), 0.79–0.92 (m, 2 H), 2.58–2.74 (m, 2 H), 3.77 (s, 3 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.8, 7.3, 52.6, 54.7.

MS (ESI): *m/z* (%) = 203 (60) $[M + Na]^+$, 181 (20) $[M + H]^+$, 165 (100), 153 (20), 151 (50), 107 (20).

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_6H_{17}O_2SSi$: 181.0719; found: 181.0726.

1-(Prop-1-enylsulfinyl)-2-(trimethylsilyl)ethane (1h)

To a soln of 1-bromoprop-1-ene (ratio *E*/*Z* 1:1, 0.12 mL, 1.4 mmol, 1.4 equiv) in anhyd Et_2O (3 mL), cooled to –78 °C, 1.64 M *t*-BuLi in pentane (1.23 mL, 2.0 mmol, 2 equiv) was added dropwise. The mixture was stirred at –78 °C for 1 h and a soln of methyl sulfinate **4** (180 mg, 1.0 mmol, 1 equiv) in anhyd Et_2O (1 mL) was slowly introduced. After 2 h at –78 °C, the mixture was allowed to warm to 0 °C over 1 h and hydrolyzed with H_2O (15 mL). The aqueous layer was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated to dryness. The crude product was then purified by column chromatography (silica gel, CH_2Cl_2–Et_2O, 70:30) to afford a mixture of two separable diastereomeric sulfoxides **1h**.

(*E*)-1h[9f]

Yellow oil; yield: 60 mg (32%); R_f = 0.37 (CH_2Cl_2–Et_2O, 80:20).

IR: 2952, 2915, 1635, 1416, 1248, 1039, 856, 829 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.04 (s, 9 H), 0.75–0.91 (m, 2 H), 1.93 (dd, *J* = 1.6, 6.8 Hz, 3 H), 2.59–2.74 (m, 2 H), 6.17 (dq, *J* = 1.6, 15.1 Hz, 1 H), 6.45 (dq, *J* = 6.8, 15.1 Hz, 1 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.7, 8.2, 18.0, 49.5, 133.3, 137.2.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 3.23.

MS (ESI): *m/z* (%) = 403 (50) $[2 M + Na]^+$, 213 (100) $[M + Na]^+$, 191 (10) $[M + H]^+$, 113 (5).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_8H_{18}NaOSSi$: 213.0745; found: 213.0761.

(*Z*)-1h

Yellow oil; yield: 73 mg (38%); R_f = 0.27 (CH_2Cl_2–Et_2O, 80:20).

IR: 2952, 2899, 1626, 1418, 1248, 1032, 858, 830 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.04 (s, 9 H), 0.73 (dt, *J* = 4.4, 13.9 Hz, 1 H), 0.89 (dt, *J* = 4.3, 13.9 Hz, 1 H), 1.98 (dd, *J* = 1.6, 7.1 Hz, 3 H), 2.63 (ddd, *J* = 4.4, 12.8, 13.8 Hz, 1 H), 2.79 (ddd, *J* = 4.3, 12.8, 13.8 Hz, 1 H), 6.14 (dq, *J* = 1.6, 9.9 Hz, 1 H), 6.32 (dq, *J* = 7.1, 9.9 Hz, 1 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.7, 8.8, 15.6, 49.5, 135.5, 138.5.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 3.19.

MS (ESI): *m/z* (%) = 403 (40) $[2 M + Na]^+$, 213 (100) $[M + Na]^+$, 191 (10) $[M + H]^+$, 113 (5).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_8H_{18}NaOSSi$: 213.0745; found: 213.0734.

1-[(3,3-Dimethylbut-1-ynyl)sulfinyl]-2-(trimethylsilyl)ethane (1i)

To a soln of 3,3-dimethylbut-1-yne (0.92 mL, 7.5 mmol, 1.5 equiv) in anhyd THF (75 mL) at –78 °C, 1.45 M BuLi in hexane (6.9 mL, 10 mmol, 2 equiv) was added dropwise. The mixture was stirred at –78 °C for 2 h and the methyl sulfinate **4** (902 mg, 5.0 mmol, 1 equiv) was introduced. After stirring for 2 h at –78 °C and hydrolysis with sat. aq NH_4Cl (80 mL), the aqueous layer was extracted with EtOAc (2 × 80 mL). The organic layer was washed with sat. aq NaCl (80 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated to dryness. The crude product was then purified by column chromatography (silica gel, pentane–CH_2Cl_2, 30:70) to afford the anticipated sulfoxide **1i** (586 mg, 51%) as a yellow oil. R_f = 0.25 (pentane–CH_2Cl_2, 30:70).

IR: 2970, 2195, 2159, 1249, 1061, 857, 831 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 9 H), 0.99–1.04 (m, 2 H), 1.29 (s, 9 H), 2.91–3.00 (m, 2 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.7, 9.0, 28.6, 30.2, 52.9, 75.9, 112.1.

^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 3.31.

MS (ESI): *m/z* (%) = 483 (700) $[2 M + Na]^+$, 253 (100) $[M + Na]^+$.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{11}H_{22}NaOSSi$: 253.1058; found: 253.1060.

Generation of Sulfenate and In Situ Alkylation To Give Sulfoxides 2; General Procedure

A 1 M soln of TBAF in THF (previously dried on 4 Å molecular sieves) was added to a soln of silyl sulfoxide **1** and the appropriate electrophile in THF (4 mL). The reaction was heated at 60 °C until the reaction is completed according to TLC. The mixture was hydrolyzed with H_2O (15 mL) and THF was removed under vacuum. The aqueous layer was extracted with EtOAc (3 × 15 mL) and the organic layer was washed with sat. aq NaCl (2 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated to dryness. The crude product was then purified by column chromatography (silica gel, pentane–EtOAc mixture) to afford the anticipated sulfoxide **2**.

1-(Benzylsulfinyl)-4-methylbenzene (2aa)[6a]

Obtained by the reaction of sulfoxide **1a** (240 mg, 1.00 mmol, 1 equiv) with BnBr (1.2 mmol, 1.2 equiv) in the presence of TBAF (2.1 equiv) for 45 min as a white solid; yield: 197 mg (85%); mp 139–140 °C (Lit.[6a] 140–141 °C); R_f = 0.26 (pentane–EtOAc, 80:20).

IR: 2928, 1592, 1490, 1046 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 3.98 and 4.10 (AB, *J* = 12.5 Hz, 2 H), 6.94–7.03 (m, 2 H), 7.21–7.30 (m, 7 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4, 63.7, 124.4, 128.2, 128.4, 129.3, 129.5, 130.3, 139.6, 141.6.

MS (CI, isobutane): *m/z* (%) = 271 (2) $[M + C_3H_5]^+$, 269 (2) $[M + C_3H_3]^+$, 231 (100) $[M]^+$, 215 (6).

4-Methyl-1-(methylsulfinyl)benzene (2ab)[6a]

Obtained by the reaction of sulfoxide **1a** (240 mg, 1.00 mmol, 1 equiv) with MeI (1.5 mmol, 1.5 equiv) in the presence of TBAF (4 equiv) for 3 h as a white solid; yield: 81 mg (53%); mp 43–44 °C (cyclohexane) (Lit.[6a] 43–44 °C); R_f = 0.14 (pentane–EtOAc, 60:40).

IR: 2928, 1592, 1490, 1046 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.43 (s, 3 H), 2.71 (s, 3 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.55 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.8, 44.4, 123.9, 130.4, 141.9, 142.9.

MS (EI): *m/z* (%) = 154 (99) $[M]^+$, 139 (100), 138 (42), 91 (29) $[C_7H_7]^+$, 77 (46), 65 (27), 63 (19).

1-(Ethylsulfinyl)-4-methylbenzene (2ac)[6a]

Obtained by the reaction of sulfoxide **1a** (240 mg, 1.00 mmol, 1 equiv) with EtI (1.2 mmol, 1.2 equiv) in the presence of TBAF (3 equiv) at r.t. for 16 h as a yellow oil; yield: 141 mg (84%); R_f = 0.29 (CH_2Cl_2–EtOAc, 80:20).

IR: 3036, 2976, 2932, 2872, 1046 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (t, *J* = 7.5 Hz, 3 H), 2.42 (s, 3 H), 3.22 and 3.28 (AB part of ABX_3, J_{AB} = 13.2 Hz, $J_{AX} = J_{BX}$ = 7.5 Hz, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.50 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 6.0, 21.4, 50.3, 124.2, 129.8, 140.0, 141.4.

MS (EI): *m/z* (%) = 169 (55) $[M]^+$, 152 (25), 140 (100), 92 (45), 91 (37) $[C_7H_7]^+$.

1-(Benzylsulfinyl)-4-bromobenzene (2b)[31]

Obtained by the reaction of sulfoxide **1b** (305 mg, 1.00 mmol, 1 equiv) with BnBr (1.2 mmol, 1.2 equiv) in the presence of TBAF (2.1 equiv) for 20 min as a white solid; yield: 249 mg (84%); mp 141–142.5 °C; R_f = 0.33 (pentane–EtOAc, 80:20).

IR: 3030, 2962, 2910, 1037 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.93 and 4.04 (AB, *J* = 12.6 Hz, 2 H), 6.90–6.95 (m, 2 H), 7.12–7.26 (m, 5 H), 7.48–7.52 (m, 2 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 63.6, 125.8, 126.2, 128.6, 128.7, 130.5, 132.2, 142.0.

MS (ESI): *m/z* (%) = 319 and 317 (80) $[M + Na]^{+}$*, 297 and 295 (100) $[M + H]^{+}$*. (*) ^{81}Br and ^{79}Br isotopic pattern.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{13}H_{11}BrNaOS$: 316.9612; found: 316.9628.

1-(Benzylsulfinyl)-4-(trifluoromethyl)benzene (2c)[32]

Obtained by the reaction of sulfoxide **1c** (294 mg, 1.00 mmol, 1 equiv) with BnBr (1.2 mmol, 1.2 equiv) in the presence of TBAF (2.1 equiv) for 20 min as a white solid; yield: 214 mg (75%); mp 158–160 °C (EtOAc) (Lit.[32] 155–157 °C); R_f = 0.32 (pentane–EtOAc, 80:20).

IR: 2970, 1318, 1153, 1113, 1059, 1038, 1012, 696 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.97 and 4.04 (AB, *J* = 12.7 Hz, 2 H), 6.88–7.91 (m, 2 H), 7.17–7.23 (m, 3 H), 7.39 and 7.60 (AB, *J* = 8.2 Hz, 4 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 63.5, 123.6 (q, *J* = 272.7 Hz), 125.0, 125.9 (q, *J* = 3.8 Hz), 128.5, 128.7, 130.5, 133.2 (q, *J* = 32.8 Hz), 147.3.

^{19}F NMR (235.3 MHz, $CDCl_3$): δ = –62.8.

MS (ESI): *m/z* (%) = 307 (100) $[M + Na]^+$, 285 (20) $[M + H]^+$.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{14}H_{11}NaF_3OS$: 307.0380; found: 307.0380.

1-(Benzylsulfinyl)-2,6-dimethylbenzene (2d)[6a]
Obtained by the reaction of sulfoxide **1d** (254 mg, 1.00 mmol, 1 equiv) with BnBr (1.2 mmol, 1.2 equiv) in the presence of TBAF (2.1 equiv) for 1 h as a white solid; yield: 169 mg (69%); mp 85.5–87 °C (Lit.[6a] 82–84 °C); R_f = 0.26 (pentane–EtOAc, 80:20).

IR: 3057, 2925, 1729, 1456, 1055, 771, 698 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.34 (s, 6 H), 4.37 (s, 2 H), 6.96–7.05 (m, 4 H), 7.18–7.28 (m, 4 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.3, 58.8, 128.4, 128.7, 130.1, 130.2, 130.4, 131.1, 136.8, 139.3.

MS (EI): *m/z* (%) = 244 (4) [M]$^+$, 228 (1), 196 (2), 92 (11), 91 (100) [C_7H_7]$^+$, 77 (6), 65 (15).

HRMS (EI): *m/z* [M]$^+$ calcd for $C_{15}H_{16}OS$: 244.0922; found: 244.0922.

2-(Benzylsulfinyl)naphthalene (2e)[33]
Obtained by the reaction of sulfoxide **1e** (276 mg, 1.00 mmol, 1 equiv) with BnBr (1.2 mmol, 1.2 equiv) in the presence of TBAF (2.1 equiv) for 30 min as a white solid; yield: 230 mg (86%); mp 187–188.5 °C (Lit.[33] 189–190 °C); R_f = 0.24 (pentane–EtOAc, 70:30).

IR: 3030, 2988, 1066, 1039 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.10 and 4.17 (AB, *J* = 12.6 Hz, 2 H), 6.98–7.02 (m, 2 H), 7.19–7.34 (m, 3 H), 7.40–7.44 (m, 1 H), 7.52–7.63 (m, 2 H), 7.76–7.93 (m, 4 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 63.6, 120.3, 125.4, 127.3, 127.9, 128.1, 128.4, 128.6, 129.1, 129.3, 130.5, 132.8, 134.6, 140.0.

MS (ESI): *m/z* (%) = 555 (30) [2 M + Na]$^+$, 289 (100) [M + Na]$^+$, 267 (25) [M + H]$^+$, 159 (10).

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{17}H_{15}OS$: 267.0844; found: 267.0847.

2-(Benzylsulfinyl)pyridine (2f)[34]
Obtained by the reaction of sulfoxide **1f** (227 mg, 1.00 mmol, 1 equiv) with BnBr (1.2 mmol, 1.2 equiv) in the presence of TBAF (2.1 equiv) for 20 min as a white solid; yield: 168 mg (77%); white solid; mp 84–86 °C (pentane–EtOAc) (Lit.[34] 87–88 °C); R_f = 0.22 (pentane–EtOAc, 70:30).

IR: 3030, 2989, 1576, 1454, 1427, 1037, 762, 692 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.07 and 4.37 (AB, *J* = 13.1 Hz, 2 H), 7.00–7.03 (m, 2 H), 7.23–7.27 (m, 3 H), 7.35 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1 H), 7.58–7.62 (m, 1 H), 7.78 (dt, *J* = 7.7, 1.7 Hz, 1 H), 8.66–8.68 (m, 1 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 60.1, 120.8, 124.7, 128.3, 128.4, 129.4, 130.4, 137.8, 149.5, 163.8.

MS (ESI): *m/z* (%) = 457 (15) [2 M + Na]$^+$, 240 (100) [M + Na]$^+$, 218 (100) [M + H]$^+$.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{12}H_{11}NNaOS$: 240.0459; found: 240.0459.

1-(Benzylsulfinyl)prop-1-ene (2h)
Obtained by the reaction of sulfoxide **1h** (ratio *Z*/*E* 80:20, 190 mg, 1.00 mmol, 1 equiv) with BnBr (1.2 mmol, 1.2 equiv) in the presence of TBAF (4 equiv) for 30 min.

(*E*)-2h[35]
White solid; yield: 20 mg (11%); mp 42–43 °C (pentane–EtOAc); R_f = 0.35 (pentane–EtOAc, 30:70).

IR: 3067, 2966, 2913, 1634, 1495, 1435, 1033, 944, 768, 692 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (dd, *J* = 1.5, 6.7 Hz, 3 H), 3.89 and 4.03 (AB, *J* = 12.6 Hz, 2 H), 6.17 (dq, *J* = 1.5, 15.1 Hz, 1 H), 6.33 (dq, *J* = 6.7, 15.1 Hz, 1 H), 7.25–7.27 (m, 2 H), 7.34–7.37 (m, 3 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.9, 60.7, 128.4, 128.8, 129.8, 130.4, 132.8, 137.3.

MS (ESI): *m/z* (%) = 383 (20) [2 M + Na]$^+$, 203 (100) [M + Na]$^+$, 181 (10) [M + H]$^+$, 163 (10), 129 (20), 112 (10), 91 (30).

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{10}H_{12}NaOS$: 203.0507; found: 203.0509.

(*Z*)-2h
White solid; yield: 69 mg (38%); mp 45–47 °C (pentane–EtOAc); R_f = 0.26 (pentane–EtOAc, 30:70).

IR: 3058, 2959, 2919, 1624, 1494, 1434, 1024, 773, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 (dd, *J* = 1.5, 7.0 Hz, 3 H), 3.91 (d, *J* = 12.4 Hz, 1 H), 4.16 (d, *J* = 12.4 Hz, 1 H), 6.09 (dq, *J* = 1.5, 9.9 Hz, 1 H), 6.20 (dq, *J* = 7.0, 9.9 Hz, 1 H), 7.26–7.28 (m, 2 H), 7.32–7.34 (m, 3 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.2, 60.2, 128.4, 128.9, 129.5, 130.5, 134.8, 138.6.

MS (ESI): *m/z* (%) = 383 (50) [2 M + Na]$^+$, 203 (100) [M + Na]$^+$, 181 (40) [M + H]$^+$, 163 (10), 129 (20), 91 (60).

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{10}H_{13}OS$: 181.0687; found: 181.0681.

1-(Benzylsulfinyl)-3,3-dimethylbut-1-yne (2i)[3d]
Obtained from sulfoxide **1i** (230 mg, 1.00 mmol, 1 equiv) and BnBr (1.2 mmol, 1.2 equiv) in the presence of TBAF (2.1 equiv) for 30 min as a yellow oil; yield: 145 mg (66%); R_f = 0.24 (pentane–EtOAc, 90:10).

IR: 3032, 2972, 2160, 1454, 1252, 1060, 768, 700 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.22 (s, 9 H), 4.25 (s, 2 H), 7.32–7.40 (m, 5 H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 28.5, 30.0, 62.9, 75.5, 113.6, 128.7, 128.8, 129.4, 130.7.

MS (EI): *m/z* (%) = 220 (1) [M]$^+$, 91 (100) [C_7H_7]$^+$, 65 (14).

Acknowledgment

We acknowledge financial support from the 'Ministère de la Recherche', CNRS (Centre National de la Recherche Scientifique), the 'Région Basse-Normandie' and the European Union (FEDER funding). We also thank Nicolas Cabrol and Renaud Moucel for the synthesis of starting materials and Dr. Rémi Legay for mass spectrometry measurements and ^{29}Si NMR studies.

References

(1) For a recent review: O'Donnell, J. S.; Schwan, A. L. *J. Sulfur Chem.* **2004**, *25*, 183.
(2) (a) Forman, H. J.; Fukuto, J. M.; Torres, M. *Am. J. Physiol. Cell. Physiol.* **2004**, *287*, C246. (b) Nagahara, N.; Katayama, A. *J. Biol. Chem.* **2005**, *280*, 34569.
(3) (a) Sandrinelli, F.; Perrio, S.; Beslin, P. *J. Org. Chem.* **1997**, *62*, 8626. (b) Sandrinelli, F.; Perrio, S.; Averbuch-Pouchot, M.-T. *Org. Lett.* **2002**, *4*, 3619. (c) Sandrinelli, F.; Fontaine, G.; Perrio, S.; Beslin, P. *J. Org. Chem.* **2004**, *69*, 6916. (d) Sandrinelli, F.; Boudou, C.; Caupène, C.; Averbuch-Pouchot, M.-T.; Perrio, S.; Metzner, P. *Synlett* **2006**, 3289.

(4) (a) Maezaki, N.; Yagi, S.; Ohsawa, S.; Ohishi, H.; Tanaka, T. *Tetrahedron* **2003**, *59*, 9895. (b) Maezaki, N.; Yagi, S.; Yoshigami, R.; Maeda, J.; Suzuki, T.; Ohsawa, S.; Tsukamoto, K.; Tanaka, T. *J. Org. Chem.* **2003**, *68*, 5550. (c) Maezaki, N.; Yagi, S.; Maeda, J.; Yoshigami, R.; Tanaka, T. *Heterocycles* **2004**, *62*, 263.

(5) O'Donnell, J. S.; Schwan, A. L. *Tetrahedron Lett.* **2003**, *44*, 6293.

(6) (a) Caupène, C.; Boudou, C.; Perrio, S.; Metzner, P. *J. Org. Chem.* **2005**, *70*, 2812. (b) Maitro, G.; Prestat, G.; Madec, D.; Poli, G. *J. Org. Chem.* **2006**, *71*, 7449. (c) Maitro, G.; Vogel, S.; Prestat, G.; Madec, D.; Poli, G. *Org. Lett.* **2006**, *8*, 5951.

(7) (a) Oida, T.; Ohnishi, A.; Shimamaki, T.; Hayashi, Y.; Tanimoto, S. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 702. (b) Oida, T.; Nakamura, M.; Takashima, Y.; Hayashi, Y. *Bull. Inst. Chem. Res., Kyoto Univ.* **1992**, *70*, 295.

(8) Benzenesulfenic acid 2-(trimethylsilyl)ethyl ester was prepared by reaction of benzenesulfenyl chloride with 2-(trimethylsilyl)ethyl alcohol. By comparison, the analogous sulfoxides are readily available from commercial compounds according to: (a) Schwan, A. L.; Pippert, M. F. *Tetrahedron: Asymmetry* **1995**, *6*, 131. (b) Schwan, A. L.; Brillon, D.; Dufault, R. *Can. J. Chem.* **1994**, *72*, 325.

(9) The reactivity of more sophisticated β-silyl sulfoxides with TBAF has previously been investigated by the group of Toru, but their attention was focused on the alkene product: (a) Nakamura, S.; Watanabe, Y.; Toru, T. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3403. (b) Nakamura, S.; Takemoto, H.; Ueno, Y.; Toru, T.; Kakumoto, T.; Hagiwara, T. *J. Org. Chem.* **2000**, *65*, 469. (c) Nakamura, S.; Uchiyama, Y.; Ishikawa, S.; Fukinbara, R.; Watanabe, Y.; Toru, T. *Tetrahedron Lett.* **2002**, *43*, 2381. (d) Nakamura, S.; Kusuda, S.; Kawamura, K.; Toru, T. *J. Org. Chem.* **2002**, *67*, 640. (e) Nakamura, S.; Nakayama, J.-i.; Toru, T. *J. Org. Chem.* **2003**, *68*, 5766. Schwan also described a fluoride free deprotection of simple 2-(trimethylsilyl)ethyl sulfoxides by treatment with thionyl chloride to afford sulfinyl chlorides: (f) Schwan, A. L.; Strickler, R. R.; Dunn-Dufault, R.; Brillon, D. *Eur. J. Org. Chem.* **2001**, 1643.

(10) (a) Huttunen, K. M.; Kumpalainen, H.; Leppänen, J.; Rautio, J.; Järvinen, T.; Vepsäläinen, J. *Synlett* **2006**, 701. (b) Fustero, S.; García Sancho, A.; Chiva, G.; Sanz-Cervera, J. F.; del Pozo, C.; Aceña, J. L. *J. Org. Chem.* **2006**, *71*, 3299. (c) Grecian, S. A.; Hadida, S.; Warren, S. D. *Tetrahedron Lett.* **2005**, *46*, 4683. (d) Bottaro, J. C.; Penwell, P. E.; Schmitt, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 9405. (e) Varaprasad, C. V. N. S.; Johnson, F. *Tetrahedron Lett.* **2005**, *46*, 2163. (f) Thakkalapally, A.; Benin, V. *Tetrahedron* **2005**, *61*, 4939.

(11) For a review concerning the 2-(trimethylsilyl)ethyl group in synthesis, see: (a) Chambert, S.; Désiré, J.; Décout, J.-L. *Synthesis* **2002**, 2319. See also for deprotection of sulfides: (b) Flatt, A. K.; Dirk, S. M.; Henderson, J. C.; Shen, D. E.; Su, J.; Reed, M. A.; Tour, J. M. *Tetrahedron* **2003**, *59*, 8555. (c) Chatterji, T.; Kizil, M.; Keerthi, K.; Chowdhury, G.; Pospísil, T.; Gates, K. S. *J. Am. Chem. Soc.* **2003**, *125*, 4996. (d) Hamm, M. L.; Cholera, R.; Hoey, C. L.; Gill, T. J. *Org. Lett.* **2004**, *6*, 3817. (e) Pollack, S. K.; Naciri, J.; Mastrangelo, J.; Patterson, C. H.; Torres, J.; Moore, M.; Shashidhar, R.; Kushmerick, J. G. *Langmuir* **2004**, *20*, 1838. (f) Morales, G. M.; Jiang, P.; Yuan, S.; Lee, Y.; Sanchez, A.; You, W.; Yu, L. *J. Am. Chem. Soc.* **2005**, *127*, 10456. For deprotection of sulfones: (g) Lai, M.-t.; Oh, E.; Shih, Y.; Liu, H.-w. *J. Org. Chem.* **1992**, *57*, 2471. (h) Palmer, J. T.; Fuchs, P. L. *Synth. Commun.* **1988**, *18*, 233. For deprotection of selenothioic acid *S*-esters: (i) Murai, T.; Kamoto, T.; Kato, S. *J. Am. Chem. Soc.* **2000**, *122*, 9850. (j) Niyomura, O.; Sakai, K.; Murai, T.; Kato, S.; Yamaguchi, S.; Tamao, K. *Chem. Lett.* **2001**, 968. (k) Kimura, T.; Murai, T.; Miwa, A.; Kurachi, D.; Yoshikawa, H.; Kato, S. *J. Org. Chem.* **2005**, *70*, 5611. For deprotection of phosphinoselenothioic acid *S*-esters: (l) Kimura, T.; Murai, T. *Chem. Commun.* **2005**, 4077.

(12) (a) Bernhard, W.; Fleming, I. *J. Organomet. Chem.* **1984**, *271*, 281. (b) Jones, S. L.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1153.

(13) Wagner, M.; Kunz, H. *Synlett* **2000**, 400.

(14) (a) Gornowicz, G. A.; Ryan, J. W.; Speier, J. L. *J. Org. Chem.* **1968**, *33*, 2918. (b) Mahadevan, A.; Li, C.; Fuchs, P. L. *Synth. Commun.* **1994**, *24*, 3099. (c) Menichetti, S.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1511.

(15) (a) Bégué, J.-P.; Bonnet-Delpon, D.; Crousse, B. *Synlett* **2004**, 18. (b) Ravikumar, K. S.; Kesavan, V.; Crousse, B.; Bonnet-Delpon, D.; Bégué, J.-P. *Org. Synth.*, Vol. 80; John Wiley & Sons: London, **2003**, 184.

(16) Methyl sulfinate **4** was prepared by oxidative fragmentation of sulfoxide **1g** (R^1 = *t*-Bu) using SO_2Cl_2 to give 2-(trimethylsilyl)ethanesulfinyl chloride,[9f] followed by treatment with MeOH in the presence of Et_3N.

(17) Silicon contains 4.7% ^{29}Si isotope with nuclear spin $I = ½$ and a gyromagnetic ratio $\gamma = -(2\pi)8.46 \times 10^6\ s^{-1}\ T^{-1}$, see for example: Fortis, F.; Barbe, B.; Pétraud, M.; Picard, J.-P. *Chem. Commun.* **1999**, 527.

(18) Similar chemical shifts were observed either in $CDCl_3$ or THF-d_8.

(19) *Crystal structure determination of* **1b**: Single crystals of sulfoxide **1b** suitable for X-ray crystallographic analysis were obtained by slow diffusion of pentane in CH_2Cl_2 soln. X-ray diffraction experiments for monocrystal of **1b** were performed at 150 K with graphite–monochromatized MoK_α radiation on a Bruker-Nonius Kappa CCD area detector diffractometer. Formula $C_{11}H_{17}BrOSSi$, M_r 305.31, crystal system triclinic, space group *P*1, *a* = 6.5653 (3) Å, *b* = 10.1206 (4) Å, *c* = 11.8654 (5) Å, α = 66.082 (2)°, β = 78.256 (3)°, γ = 80.455 (3)°, *V* = 702.54 (5) Å^3, *Z* = 2, density calcd = 1.443 g/cm^3, μ = 3.135 cm^{-1}, *R* = 0.0386, w*R* = 0.0997. Selected bond lengths (Å) and angles(deg): Br1–C1 1.8912 (14), S1–O1 1.4930 (13), S1–C4 1.7924 (13), S1–C7 1.8248 (14), Si1–C8 1.8792 (14), Si1–C9 1.8512 (18), Si1–C10 1.862 (2), Si1–C11 1.862 (2), C7–C8 1.512 (2), O1–S1–C4 106.27 (7), O1–S1–C7 106.60 (7), C4–S1–C7 97.78 (6), C11–Si1–C8 106.90 (8), C9–Si1–C8 109.56 (9), C10–Si1–C8 110.30 (10). Program(s)used to solve structure: SHELXS97. Program(s)used to refine structure: SHELXL97. Software used to prepare material for publication: SHELXL97. Crystallographic data for compound **1b** have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 629340. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; +44 (1223)336408; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

(20) An intramolecular coordination between the oxygen atom of the sulfoxide group and the silicon center was previously detected at low temperature with the analogous electron deficient trifluorosilyl derivatives: Pestunovich, V. A.; Larin, M. F.; Sorokin, M. S.; Albanov, A. I.; Voronkov, M. G. *J. Organomet. Chem.* **1985**, *280*, C17.

(21) Similar structural effects involving the 2-(trimethylsilyl)ethyl system have already been mentioned with carboxylate and sulfenate esters: Green, A. J.; Issa, W.; White, J. M. *Aust. J. Chem.* **1997**, *50*, 927.

(22) See for example: Akazome, M.; Noguchi, M.; Tanaka, O.; Sumikawa, A.; Uchida, T.; Ogura, K. *Tetrahedron* **1997**, *53*, 8315.
(23) (a) Hogg, D. R.; Robertson, A. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1125. (b) Kobayashi, M.; Toriyabe, K. *Sulfur Lett.* **1985**, *3*, 117.
(24) Spectral data are in agreement with those previously reported by us.[6a]
(25) Touaibia, M.; Desjardins, M.-A.; Provençal, A.; Audet, D.; Médard, C.; Morin, M.; Breau, L. *Synthesis* **2004**, 2283.
(26) (a) Lipshutz, B. M.; Pegram, J. J. *Tetrahedron Lett.* **1980**, *21*, 3343. (b) Edwards, M. P.; Doherty, A. M.; Ley, S. V.; Organ, H. M. *Tetrahedron* **1986**, *42*, 3723.
(27) The reaction was carried out with a mixture of both *Z*- and *E*-isomers but also the geometrically pure substrates.
(28) A similar reluctance towards fluoridolysis was also observed with the analogous isopropyl derivative and also in the sulfide series: (a) Anderson, M. B.; Ranasinghe, M. G.; Palmer, J. T.; Fuchs, P. L. *J. Org. Chem.* **1988**, *53*, 3125. (b) Grundberg, H.; Andergran, M.; Nilsson, U. J. *Tetrahedron Lett.* **1999**, *40*, 1811.
(29) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.
(30) Yu, C. J.; Chong, Y.; Kayyem, J. F.; Gozin, M. *J. Org. Chem.* **1999**, *64*, 2070.
(31) Kim, Y. H.; Yoon, C. D. *Synth. Commun.* **1989**, *19*, 1569.
(32) Seago, A.; Houghton, J.; McCague, R.; Foster, A. B.; Coe, P. L.; Falshaw, A. *Biochem. Pharmacol.* **1987**, *36*, 400.
(33) Guo, Y.; Darmanyan, A. P.; Jenks, W. S. *Tetrahedron Lett.* **1997**, *38*, 8619.
(34) Shaw, E.; Bernstein, J.; Losee, K.; Lott, W. A. *J. Am. Chem. Soc.* **1950**, *72*, 4362.
(35) Schwan, A. L.; Lear, Y. *Sulfur Lett.* **2000**, *23*, 111.