One-Pot, Three-Component Synthesis of Open-Chain, Polyfunctional Sulfones

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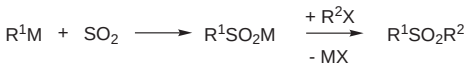
Abstract: Silyl enol ethers of esters, ketones, as well as allylstannane and allylsilanes react with sulfur dioxide activated with *t*-$BuMe_2SiOSO_2CF_3$ to give silyl sulfinates that can be reacted in the same pot with a variety of electrophiles generating the corresponding polyfunctional sulfones. The silyl sulfinate intermediates are formed via ene-reactions following probably concerted mechanisms.

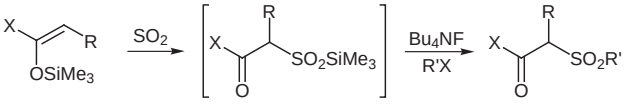
Keywords: ene-reaction, enoxysilanes, sulfinates, sulfones

A great number of efficient methods are available for the synthesis of open-chain sulfones.[1] Functional sulfones containing allylic or/and carbonyl functions are relatively rare. Their preparation has relied on the multiple-step approaches including the oxidation of sulfide intermediates,[1,2] the nucleophilic displacements of sulfuryl chlorides[1,3] and the electrophilic reaction of sulfinate salts.[1,4] Other methods have used the sulfinate sulfone rearrangement[1,5] and the radical addition of α-haloalkanesulfonyl bromides to alkenes.[1,6] One-pot, three component methods that combine sulfur dioxide with two organic reagents have been proposed. They include low yielded radical processes,[1] metal-catalyzed addition to olefins,[7] reduction of SO_2 into sulfur dioxide radical anion and its subsequent reaction with allyl halides or Michael acceptors leading to symmetrical sulfones in most cases.[1,8] The most versatile method condenses first SO_2 with Grignard or lithium organo-reagents giving the corresponding sulfinate salts that react, in a second step, with appropriate electrophiles[1] according to Equation 1.



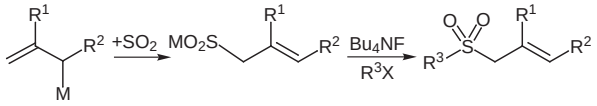
Equation 1

This method cannot be applied to systems bearing carbonyl functions. We report here that silyl sulfinates obtained by the ene-reaction of SO_2 with silyl enol ethers derived from esters[9] and ketones can be reacted without purification with electrophiles to generate open-chain, polyfunctional sulfones in one-pot operations (Equation 2).[10–12]



Equation 2

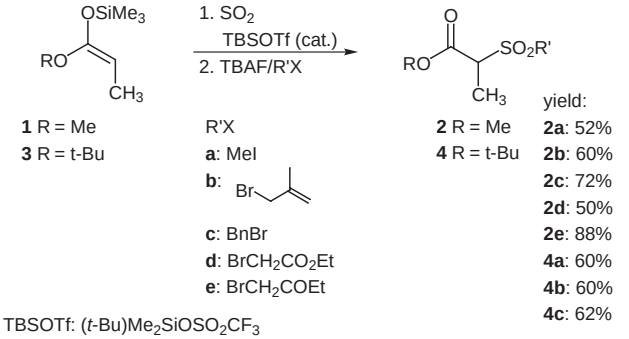
The method can be applied also to allylstannane and allylsilanes that can be condensed with SO_2 and organic electrophiles giving non-symmetrical, open-chain allylic sulfones (Equation 3).[13]



Equation 3

In a typical experiment enoxysilane **1** (1 equiv) was added slowly to an anhydrous solution of SO_2 (10 equiv) and CH_2Cl_2 containing *t*-$BuMe_2SiOSO_2CF_3$ (0.05 equiv) at –78 °C. After 30 minutes, the excess of SO_2 was removed by distillation (0.01 Torr, –78 °C). Addition of 1 M solution of Bu_4NF in THF (1 equiv) and electrophiles **a**–**e** (2.5 equiv) gave a mixture that was allowed to reach 20 °C in a few hours. Usual workup and flash chromatography on silica gel provided the corresponding pure sulfones **2a**–**e** in good yields (52–72%). Similar results were obtained from the silyl enol ether **3** with electrophiles **a**–**c** that produced sulfones **4a**–**c** in good yields (Scheme 1).

We have found that the ene-reaction of SO_2 with **1** could also be catalyzed by $(CF_3SO_2)_2NH$ instead of *t*-$BuMe_2SiOSO_2CF_3$, giving an intermediate silyl sufinate **5** that reacted with Bu_4NF and 2-methylprop-2-enyl bromide (**b**) giving **2b** in 60% yield.



Scheme 1

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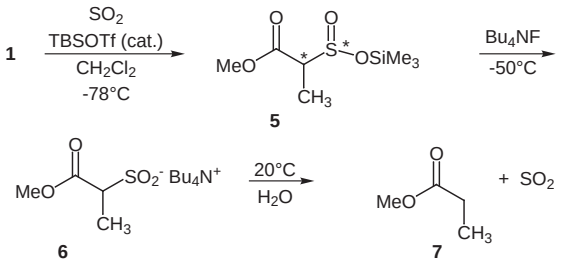
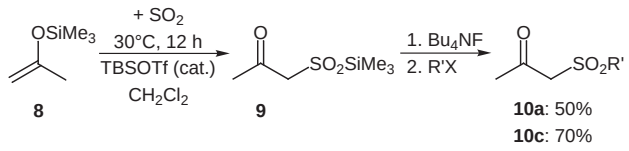
When the reaction of **1** with SO_2 catalyzed by *t*-Bu-$Me_2SiOSO_2CF_3$ was followed by ^1H and ^{13}C NMR, it was over at –78 °C in less than 10 minutes, giving a 3:4 mixture of two diastereomeric silyl sulfinates **5**. In the absence of the Lewis acid catalyst the ene-reaction **1** + SO_2 → **5** did not occur (Equation 4).



Equation 4

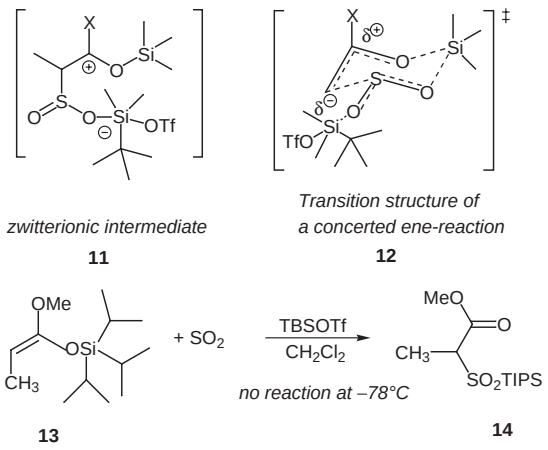
Desilylation of **5** by Bu_4NF (or with pyridine·HF) occurred in about 1 hour at –50 °C. In CD_2Cl_2 containing one equivalent of Bu_4N^+ or $pyrH^+$, the desulfination of the sulfinate **6** was over in a few hours at 20 °C, giving methyl propanoate (**7**).

The silyl enol ether **8** derived from acetone also underwent the ene-reaction with SO_2 under the promotion with *t*-$BuMe_2SiOSO_2CF_3$ (0.1 equiv). The reaction was much slower than with enol ethers **1** and **3**. It requires heating to 30 °C for 12 hours (instead of –78 °C for **1**,**3**). The intermediate silyl sulfinate **9** so obtained was desilylated at –40 °C with Bu_4NF and then reacted with electrophiles such as MeI (**a**) and BnBr (**c**) giving sulfones **10a** and **10c** in 50 and 70% yield, respectively (Scheme 2).[14]



Scheme 2

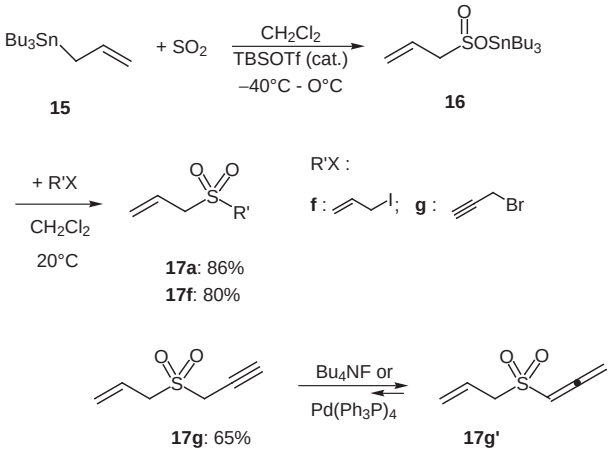
The much lower reactivity of **8** compared with **1** and **3** toward the Lewis acid promoted ene-reaction of SO_2 can be interpreted in terms of a mechanism involving either the zwitterionic intermediates of type **11** or a one-step process in which **11** is only a limiting structure of the transition state (Scheme 3). We have found that the silyl enol ether **13** is much less reactive than **1** toward SO_2. This suggests that the oxygen–silicon bond is formed partially during the rate-determining step of the silyl enol ene-reaction, thus indicating that the rate determining step for the reaction **13** + SO_2 → **14** is not the formation of a zwitterion of type **11** in which the S=O bond ignores the silyloxy moiety.



Scheme 3

The bulky TIPS makes the S=Osilicium interaction in the transition structure **12** more difficult than the less bulky Me_3Si group.

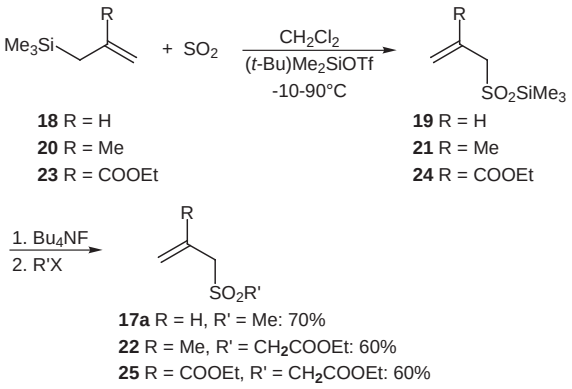
Allyl(tributyl)tin (**15**) is known[15] to undergo the ene-reaction with SO_2 providing tributyltin prop-2-ene-1-sulfinate (**16**). In the presence of *t*-$BuMe_2SiOSO_2CF_3$ (0.1 equiv) the reaction took about 12 hours at –40 °C to completion (or 20 min at 0 °C). Without destannylation **16** reacted with methyl iodide (**a**), allyl idodide (**f**) and propargyl bromide (**g**) to give sulfones **17a**,**f** and **17g** in 86, 80 and 65% yield, respectively. In the presence of Bu_4NF or $Pd(PPh_3)_4$ **17g** was equilibrated with **17g'** (Scheme 4).[16]



Scheme 4

To our knowledge, allylsilanes have not been reported to undergo the ene-reaction with SO_2. We have found that allyl(trimethyl)silane **18** reacts with SO_2 more slowly than allyl(tributyl)stannane (**15**). The reaction requires activation by *t*-$BuMe_2SiOSO_2CF_3$ (1 equiv) and 12 hours at 40 °C to be completed. It gives the silyl sulfinate **19**, which was not isolated but reacted with Bu_4NF and MeI to provide sulfone **17a** in 70% yield. Desilylation of **19** by Bu_4NF was required for the sulfone formation as **19** would not react with MeI directly.

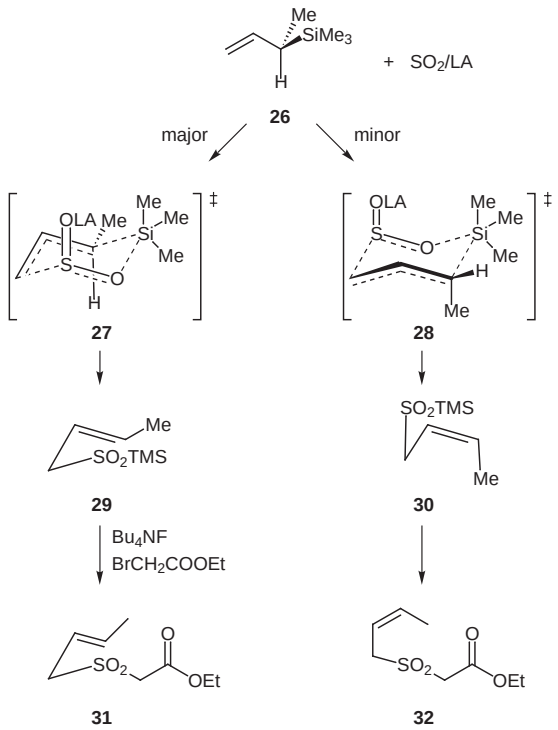
We have explored also the reactions of SO_2 with derivatives **20** and **23** (Scheme 5). None of these compounds did react with SO_2 alone, except for their polymerization into polysulfones. In the presence of one equivalent of *t*-Bu-$Me_2SiOSO_2CF_3$, **20** reacts slowly already at –10 °C to generate silyl sulfinate **21**. Reaction was complete after 12 hours at 30 °C. Sulfinate **21** was not isolated but desilylated with one equivalent of Bu_4NF and reacted with ethyl bromoacetate to give sulfone **22** in 60% yield. The ethoxycarbonyl derivative **23** also reacted with SO_2 and *t*-Bu-$Me_2SiOSO_2CF_3$, but at higher temperature (90 °C, 12 h), giving intermediate sulfinate **24** that was not isolated but desilylated with Bu_4NF and alkylated with ethyl bromoacetate to produce diester **25** in 45% yield.



Scheme 5

The observation, that the 2-methyl substitution of allyltrimethylsilane accelerates its Lewis acid promoted ene-reaction with SO_2, can be explained by a mechanism involving the formation of a zwitterionic intermediate of type **11** in its rate detemining step, or by a concerted mechanism in which **11** is only a limiting structure of its transition state **12** (Scheme 3). This interpretation is confirmed by the stereoselective ene-reaction of SO_2 with (but-3-en-2-yl)trimethylsilane (**26**)[17] that gave, after desilylation and alkylation with ethyl bromoacetate, a 4:1 mixture of (*E*)- and (*Z*)-alkene **31** and **32** (Scheme 6). The transition structure **27** adopting a pseudo-equatorial methyl substituent at the center adjacent to the silyl group is preferred over the alternative transition structure **28** placing this methyl substituent in a pseudo-axial position.[18]

In conclusion,the ene-reaction of sulfur dioxide with enoxysilanes derived from esters is a known reaction[9] that had never been exploited. We have found that the enoxysilanes derived from ketones can also undergo the ene-reaction with SO_2 in the presence of *t*-Bu$Me_2SiOSO_2CF_3$ as promotor. The silyl sulfinates so obtained can be desilylated by Bu_4NF and reacted with all kinds of electrophiles generating polyfunctional sulfones in one-pot operations. The ene-reation of SO_2 with allylstannane is a known reaction that now has been extended to the allylsilanes, giving sulfinic intermediates that can be also alkylated.



Scheme 6

The following reactivity sequence has been observed for the ene-reaction of SO_2 promoted by *t*-Bu-$Me_2SiOSO_2CF_3$: silyl ethers from esters > silyl ethers from ketones ≈ allystannane > allylsilanes. The reaction rate depends on electronic and steric factors. A one-step, concerted mechanism in which the oxygen–sulfur bond is formed simultaneously with the carbon–sulfur bond best explain the results (substituent effects on the rate, stereochemistry). Alternatively, formation of zwitterion intermediates preceding the transfer of the silyl group in the rate determining step could represent an alternative mechanism.

All solvents were distilled prior to use: THF and Et_2O from Na and benzophenone; DMF, CH_2Cl_2, and toluene from P_2O_5. Light petroleum ether used refers to the fraction boiling at 40–60 °C. Solutions after reactions and extractions were evaporated in a rotatory evaporator under reduced pressure. Liquid/solid flash chromatography (FC): columns of silica gel (0.040–0.63 μm, Merck No.9385 silica gel 60, 240–400 mesh). TLC for reaction monitoring: Merck silica gel $60F_{254}$ plates; detection by UV light. Pancaldi reagent [$(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O], or $KMnO_4$. Reagents were from Fluka or Aldrich and used without purification. Mps are uncorrected; Tottoli (Büchi SMP-20) apparatus. IR Spectra: Perkin-Elmer-1420 or Beckman –IR 4230 spectrometer. ^1H NMR Spectra: Bruker-DPX-400, or Bruker-ARX-400 spectrometer; δ(H) in ppm relative to internal Me_4Si (0.00 ppm) or to the solvent's residual ^1H signal [$CHCl_3$, δ(H) 7.27; C_6HD_5, δ(H) 7.16; CHD_2COCD_3, δ(H) 1.95; CD_2HCN, δ(H) 2.50; CHD_2SOCD_3, δ(H) 2.50, CH_2OD, δ(H) 3.31] as internal reference, all ^1H signal assignments were confirmed by double irradiation experiments or by 2D COSY-DQF or COSY-45 spectra. ^{13}C NMR Spectra: same instruments as above (101.61 MHz); δ(C) in ppm relative to internal Me_4Si (0.00 ppm) or to solvent's C-signal [$CDCl_3$, δ(C) 77.0; C_6D_6, δ(C) 128.4;

$(CD_3)_2CO$, δ(C) 29.8; CD_3CN, δ(C) 1.3; $(CD_3)_2SO$, δ(C) 39.5; CD_3OD, δ(C) 49.2] as internal reference; coupling constants *J* in Hz (± 0.5 Hz). MS: Nermag R-10-10C, chemical ionization (NH_3) mode *m*/*z* (amu) [% relative base peak (100%)]. Elemental analyses: Ilse Beetz, D-96301 Kronach, Germany.

Products **15**,**18** (Fluka, AG, Buchs, Switzerland) and **20** (ABCR, Karlsruhe, Germany) are commercially available.

Three-Component Synthesis of Polyfunctional Sulfones; General Procedure

t-$BuMe_2SiOSO_2CF_3$ (0.14 mmol, 0.05 equiv) in anhyd CH_2Cl_2 (2 mL) was degassed by freeze-thaw cycles on the vacuum line. SO_2 (1.2 mL, 27.4 mmol, 10 equiv), dried by reaction with I_2 and quinoline (Karl-Fischer process), was transferred on the vacuum line to the CH_2Cl_2 solution frozen at –196 °C. The mixture was allowed to melt and to warm to –78 °C. After 30 min at this temperature the enoxysilanes **1**, **3**, **8**, **13**, allylstannane **15** or the anhyd allylsilanes **18**, **20**, **23**, **29** (2.74 mmol, 1 equiv) in anhyd CH_2Cl_2 (2 mL) were added slowly. The mixture was stirred at –78 °C for 2–5 h (**1**,**3**), at 30 °C for 12 h (**8**, **18**, **20**, **29**) or at 90 °C for 12 h (**23**) in a sealed tube. After cooling to –78 °C, the excess of SO_2 and the solvent were evaporated under reduced pressure (0.001 Torr) to dryness (ca. 1 h). A 1 M solution of Bu_4NF in THF (2.74 mL, 2.74 mmol, 1 equiv) and electrophiles **a**–**e** (6.85 mmol, 2.5 equiv) were added under Argon. The mixture was stirred at this temperature for 1 h, then at –40 °C for 1 h, and gradually allowed to reach 20 °C in about 10 h. After the addition of H_2O (20 mL), and neutralization with $NaHCO_3$, the mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with brine (20 mL), dried ($MgSO_4$) and the solvent eliminated under reduced pressure with a reflux. The residue was purified by FC.

Sulfones **2a**,[19] **10a**,[20] **10c**,[21] **17a**,[22] **17f**,[23] **17g**,[16] **17g'**,[16] showed spectral data identical to those reported for these compounds.

Methyl 2-(Methylsulfonyl)propanoate (2a)[15]

Purification by FC (light petroleum ether–EtOAc, 3:2, R_f 0.32); colorless solid (52%); mp 65.5–66.5 °C.

Methyl 2-[(2-Methylprop-2-enyl)sulfonyl]propanoate (2b)

Purification by FC (light petroleum ether–EtOAc, 4:1, R_f 0.20); colorless oil (60%).

IR (film): 3550, 2955, 1745, 1455, 1380, 1320, 1065, 915, 860, 680 cm^{-1}.

UV (MeCN): λ_{max} = 200 nm (ε = 2090).

^1H NMR (400 MHz, $CDCl_3$): δ = 5.16 (2 s, 2 H, H-3'), 3.92 (d, 1 H, ^2J = 13.0 Hz, H-1'), 3.80 (q, 1 H, ^3J = 8.6 Hz, H-2), 3.50 (d, 1 H, ^2J = 13.0 Hz, H-1'), 3.32 (s, 3 H, CH_3O), 1.88 (s, 3 H, CH_3-C2'), 1.48 (d, 3 H, ^3J = 8.6 Hz, H-3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.4 (s, C=O), 120.8 [t, ^1J(C,H) = 153 Hz, C3'], 60.2 [d, ^1J(C,H) = 149 Hz, C2], 51.9 [q, ^1J(C,H) = 152 Hz, CH_3O], 30.43 [t, ^1J(C,H) = 125 Hz, C1'], 22.4 [q, ^1J(C,H) = 126 Hz, C3], 9.5 [q, ^1J(C,H) = 131 Hz, CH_3-C2'].

CI-MS (NH_3): *m*/*z* = 224 (100, $[M + 18]^+$), 207 (13, $[M + 1]^+$).

Anal. Calcd for $C_8H_{14}O_4S$ (206.3): C, 46.60; H, 6.80. Found: C, 46.58; H, 6.84.

Methyl 2-(Benzylsulfonyl)propanoate (2c)

Purification by FC (light petroleum ether–EtOAc, 7:3, R_f 0.40); colorless oil (72%).

IR (film): 3545, 2955, 1745, 1455, 1320, 1065, 1010, 860, 795, 775, 735, 670 cm^{-1}.

UV (MeCN): λ_{max} = 219 nm (ε = 4730).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.48 and 7.11 (m, 5 H), 4.48 and 4.10 (2 d, 2 H, ^2J = 15 Hz, CH_2Ph), 3.61 (q, 1 H, ^3J = 8.2 Hz, H-2), 3.31 (s, 3 H, CH_3O), 1.30 (d, 3 H, ^3J = 8.2 Hz, H-3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 166.0 (s, C=O), 158.0 (m, C_{arom}), 60.6 [d, ^1J(C,H) = 157 Hz, C2], 59.2 (t, ^1J(C,H) = 159 Hz, $CH_2C_6H_5$], 9.8 [q, ^1J(C,H) = 145 Hz, C3].

CI-MS (NH_3): *m*/*z* = 260 (100, $[M + 18]^+$), 243 (25, $[M + 1]^+$), 91 (89, $C_7H_7^+$).

Anal. Calcd for $C_{11}H_{14}O_4S$ (242.3): C, 54.48; H, 5.82. Found: C, 54.52; H, 5.88.

Methyl 2-(Ethoxycarbonylmethylsulfonyl)propanoate (2d)

Purification by FC (light petroleum ether–EtOAc, 7:2, R_f 0.33); colorless oil (50%).

IR (film): 2990, 2960, 1745, 1330, 1275, 1140, 1025, 910, 860, 735 cm^{-1}.

UV (MeCN): λ_{max} = 200 nm (ε = 2100).

^1H NMR (400 MHz, $CDCl_3$): δ = 4.52 (q, 1 H, ^3J = 8.6 Hz, H-2), 4.43 and 3.80 (2 d, 2 H, ^2J = 17 Hz, CH_2SO_2), 3.95 (m, 2 H, CH_2O), 3.30 (s, 3 H, CH_3O), 1.51 (d, 3 H, ^3J = 8.6 Hz, H-3), 0.97 (t, 3 H, ^3J = 8.6, CH_2CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.0 (s, C=O), 163.6 (s, C=O), 63.3 [t, ^1J(C,H) = 158 Hz, C1'], 63.2 (d, ^1J(C,H) = 162 Hz, C2], 58.2 [t, ^1J(C,H) = 167 Hz, C3']), 52.9 [q, ^1J(C,H) = 157 Hz, CH_3O], 13.9 [q, ^1J(C,H) = 156 Hz, C3], 9.3 (q, ^1J(C,H) = 162 Hz, CH_2CH_3].

CI-MS (NH_3): *m*/*z* = 256 (100, $[M + 18]^+$), 239 (30, $[M + 1]^+$).

Anal. Calcd for $C_8H_{14}O_6S$ (238.3): C, 40.33; H, 5.92. Found: C, 40.36; H, 5.88.

Methyl 2-(2-Oxobutylsulfonyl)propanoate (2e)

Purification by FC (light petroleum ether–EtOAc, 2:1, R_f 0.30); yellow oil (88%).

IR (film): 2930, 2180, 1720, 1440, 1300, 1125, 875 cm^{-1}.

UV (MeCN): λ_{max} = 197 nm (ε = 1800).

^1H NMR (400 MHz, $CDCl_3$): δ = 4.28 (q, 1 H, ^3J = 8.7 Hz, H-2), 4.19 and 3.65 (2 d, 2 H, ^2J = 17.4 Hz, H-1'), 3.25 (s, 3 H, CH_3O), 2.11 (m, 2 H, H-3'), 1.40 (d, 3 H, ^3J = 8.7 Hz, H-3), 0.85 (t, 3 H, ^3J = 8.7 Hz, H-4').

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 199.2 and 166.6 (2 s, 2 C=O), 62.9 [d, ^1J(C,H) = 160 Hz, C2], 61.2 [t, ^1J(C,H) = 169 Hz, C1'], 53 [q, ^1J(C,H) = 151 Hz, CH_3O], 37.6 [t, ^1J(C,H) = 162 Hz, C3'], 9.4 [q, ^1J(C,H) = 151 Hz, C3)], 9.3 [q, ^1J(C,H) = 151 Hz, C4'].

CI-MS (NH_3): *m*/*z* = 240 (100, $[M + 18]^+$), 223 (50, $[M + 1]^+$).

Anal. Calcd for $C_8H_{14}O_5S$ (222.3): C, 43.23; H, 6.35. Found: C, 43.27; H, 6.38.

tert-Butyl 2-(Methylsulfonyl)propanoate (4a)

Purification by FC (light petroleum ether–EtOAc, 7:2, R_f 0.37); white crystals (60%);

mp 87.6–88.4 °C.

IR (KBr): 3500, 2925, 1725, 1305, 1135 cm^{-1}.

UV (MeCN): λ_{max} = 192 nm (ε = 2100).

^1H NMR (400 MHz, $CDCl_3$): δ = 3.44 (q, 1 H, ^3J = 6.5 Hz, H-2), 2.5 (s, 3 H, H-1'), 1.42 (s, 9 H, *t*-C_4H_9), 1.35 (d, 3 H, ^3J = 6.5 Hz, H-3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 161.8 (s, C=O), 83.2 (s), 65.5 [d, ^1J(C,H) = 162 Hz, C2], 38.4 [q, ^1J(C,H) = 155 Hz, C1'], 27.9 [q, ^1J(C,H) = 167 Hz, *t*-C_4H_9], 11.6 [q, ^1J(C,H) = 154 Hz, C3].

CI-MS (NH_3): *m*/*z* = 226 (100, $[M + 18]^+$), 209 (3, $[M + 1]^+$).

Anal. Calcd for $C_8H_{16}O_4S$ (208.3): C, 46.13; H, 7.74. Found: C, 46.39; H, 7.80.

***tert*-Butyl 2-[(2-Methylprop-2-enyl)sulfonyl]propanoate (4b)**
Purification by FC (light petroleum ether–EtOAc, 85:15, R_f 0.28); colorless oil (60%).

IR (film): 3610, 3020, 2930, 1640, 1425, 135, 1135, 940, 885, 765 cm^{-1}.

UV (MeCN): λ_{max} = 196 nm (ε = 1930).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.20 and 5.08 (2 s, 2 H, H-3'), 4.02 and 3.55 (AB, 2 H, H-1'), 3.82 (q, 1 H, ^3J = 6.4 Hz, H-2), 2.0 (br s, 3 H, CH_3-C2'), 1.60 (d, 3 H, ^3J = 6.4 Hz, H-3), 1.52 (s, 9 H, *t*-C_4H_9).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 166.1 (s, C=O), 120.8 [t, ^1J(C,H) = 161 Hz, C3'], 83.2 (s), 62.6 [d, ^1J(C,H) = 161 Hz, C2], 60.4 [t, ^1J(C,H) = 167 Hz, C1'], 28.6 (q, ^1J(C,H) = 152 Hz, *t*-C_4H_9], 11.0 [q, ^1J(C,H) = 168 Hz, C3], 25.8 [q, ^1J(C,H) = 157 Hz, CH_3-C2'].

CI-MS (NH_3): *m*/*z* = 266 (100, $[M + 18]^+$), 249 (20, $[M + 1]^+$).

Anal. Calcd for $C_{11}H_{20}O_4S$ (248.3): C, 53.15; H, 8.05. Found: C, 53.25; H, 7.99.

***tert*-Butyl 2-(Benzylsulfonyl)propanoate (4c)**
Purification by FC (light petroleum ether–EtOAc, 7:3, R_f 0.63); colorless oil (62%).

IR (film): 2980, 1740, 1320, 1120, 840, 795 cm^{-1}.

UV (MeCN): λ_{max} = 197 nm (ε = 2660), 216 nm (2200).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 and 7.20 (m, 5 H), 4.52 and 4.12 (2 d, 2 H, ^2J = 13.0 Hz, H-1'), 4.05 (q, 1 H, ^3J = 6.9 Hz, H-2), 1.46 (s, 9 H, *t*-C_4H_9), 1.37 (d, 3 H, ^3J = 6.9 Hz, H-3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 166.1 (s, C=O), 127.0 (m, $C_{ar\text{-}om}$), 83.0 (s), 61.7 [d, ^1J(C,H) = 161 Hz, C2], 57.7 [t, ^1J(C,H) = 166 Hz, C1'], 28.0 [q, ^1J(C,H) = 178 Hz, *t*-C_4H_9), 10.0 [q, ^1J(C,H) = 168 Hz, C3].

CI-MS (NH_3): *m*/*z* = 302 (100, $[M + 18]^+$), 285 (13, $[M + 1]^+$), 91 (64, $C_7H_7^+$).

Anal. Calcd for $C_{14}H_{20}O_4S$ (284.4): C, 59.07; H, 7.03. Found: C, 59.15; H, 6.94.

Ethyl [(2-Methylprop-2-enyl)sulfonyl]acetate (22)
Purification by FC (light petroleum ether–EtOAc, 7:3, R_f 0.33); yellow oil with a sweet smell (60%).

IR (film): 3640, 2985, 2360, 1740, 1645, 1450, 1325, 1120, 1025, 915 cm^{-1}.

UV (MeCN): λ_{max} = 216 nm (ε = 1356).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.3 (2 s, 2 H, H-3'), 4.31 (q, 2 H, ^3J = 7.0 Hz, CH_2CH$_3$), 4.18 (s, 2 H, H-1'), 3.98 (s, 2 H, H-2), 2.10 (s, 3 H, CH_3-C2'), 1.38 (t, 3 H, *J* = 7.0 Hz, CH_2CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 163.1 (s, C=O), 134.1 (s, C2'), 121.3 [t, ^1J(C,H) = 187 Hz, C3'], 62.7 [t, ^1J(C,H) = 178 Hz, CH_2CH_3), 61.6 [t, ^1J(C,H) = 169 Hz, C1'], 54.9 [t, ^1J(C,H) = 162 Hz, C2], 22.8 [q, ^1J(C,H) = 156 Hz, C2'], 13.9 (q, ^1J(C,H) = 168 Hz, CH_2CH_3).

CI-MS (NH_3): *m*/*z* = 224 (100, $[M + 18]^+$), 207 (18, $[M + 1]^+$).

Anal. Calcd for $C_8H_{14}O_4S$ (206.2): C, 46.56; H, 6.79. Found: C, 46.57; H, 6.81.

Ethyl 2{[(2-Ethoxy-2-oxethyl)sulfonyl]methyl}acrylate (25)
Purification by FC (light petroleum ether–EtOAc, 6:4, R_f 0.45); colorless oil (60%).

IR (film): 3415, 2965, 2395, 1635, 1370, 1330, 1265, 1100, 1025 cm^{-1}.

UV (MeCN): λ_{max} = 195 nm (ε = 1715).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.57 (s, 1 H, H-1), 6.00 (s, 1 H, H-1), 4.28 (m, 4 H, CH_2CH$_3$), 3.95 [d, 1 H, ^2J(C,H) = 10.9 Hz, H-3), 3.88 (d, 1 H, ^2J(C,H) = 12 Hz, H-1'], 3.80 [d, 1 H, ^2J(C,H) = 10.9 Hz, H-3], 3.62 [d, 1 H, ^2J(C,H) = 12 Hz, H-1'], 1.36 (m, 6 H, CH_2CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 172.1 (s, C=O), 166.0 (s, C=O acrylate), 138.3 (s, C2), 129.0 [t, ^1J(C,H) = 198 Hz, C1], 62.3 [t, ^1J(C,H) = 174 Hz, CH_2CH_3), 55.6 [t, ^1J(C,H) = 167 Hz, C3], 52.7 [t, ^1J(C,H) = 171 Hz, C1'], 15.07 [q, ^1J(C,H) = 182 Hz, CH_2CH_3).

CI-MS (NH_3): *m*/*z* = 282 (100, $[M + 18]^+$, 265 (16, $[M + 1]^+$).

Anal. Calcd for $C_{10}H_{16}O_6S$ (264.3): C, 45.45; H, 6.06. Found: C, 45.40; H, 6.13.

Ethyl [(*E*)- and (*Z*)-But-2-enylsulfonyl]acetate (34 and 35) (4:1 Mixture)
Purification by FC (light petroleum ether–EtOAc, 3:1, R_f 0.40); yellow oil (74%).

IR (film): 2985, 2943, 1739, 1398, 1325, 1141, 1109, 1025, 9711,667 cm^{-1}.

UV (MeCN): λ_{max} = 192 nm (ε = 1823).

CI-MS (NH_3): *m*/*z* = 224 (100, $[M + 18]^+$, 207 (5, $[M + 1]^+$).

Anal. Calcd for $C_8H_{14}O_4S$ (264.29): C, 46.64; H, 6.85. Found: C, 46.61; H, 6.84.

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^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.65 (dq, 1 H, ^3J = 8.9, ^4J = 1.8 Hz, H-2), 5.43 (dtq, 1 H, ^3J = 8.9, ^3J = 6.9, ^3J = 8.0 Hz, H-3), 3.93 (t, 2 H, ^3J = 8.3 Hz, CH_2CH$_3$), 3.67 (d, 2 H, ^3J = 6.9 Hz, H-4), 3.58 (br s, 2 H, H-1'), 1.44 (d, 3 H, ^3J = 8.0 Hz, H-1), 0.96 (t, 3 H, ^3J = 8.3, CH_2CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 163.2 (s, C=O), 136.1 [d, ^1J(C,H) = 160 Hz, C3), 117.3 [t, ^1J(C,H) = 176 Hz, C2], 61.8 [t, ^1J(C,H) = 175 Hz, C1'], 56.8 [t, ^1J(C,H) = 180 Hz, CH_2CH_3], 54.8 [t, ^1J(C,H) = 180 Hz, C4], 17.7 [q, ^1J(C,H) = 159 Hz, C1], 13.5 [q, ^1J(C,H) = 161 Hz, CH_2CH_3).

35
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.65 (dq, 1 H, ^3J = 8.9, ^3J = 1.8 Hz, H-2), 5.43 (dtq, 1 H, ^3J = 8.9, ^3J = 6.9, ^3J = 8.0 Hz, H-3), 3.93 (t, 2 H, ^3J = 8.3 Hz, CH_2CH$_3$), 3.78 (d, 2 H, ^3J = 6.9 Hz, H-4), 3.58 (br s, 2 H, H-1'), 1.55 (d, 3 H, ^3J = 8.0 Hz, H-1), 096 (t, 3 H, ^3J = 8.3 Hz, CH_2CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 163.2 (s, C=O), 131.3 [d, ^1J(C,H) = 160 Hz, C3], 115.9 [t, ^1J(C,H) = 176 Hz, C2], 55.2 [t, ^1J(C,H) = 175 Hz, C1'], 50.0 (t, ^1J(C,H) = 180 Hz, CH_2CH_3], 47.9 [t, ^1J(C,H) = 180 Hz, C4], 17.7 [q, ^1J(C,H) = 159 Hz, C1], 12.8 [q, ^1J(C,H) = 161 Hz, CH_2CH_3).

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