DOI: 10.1002/cjoc.201600429

A Mild and Rapid Synthesis of (*Z*)-*β*-Sulfonyl Enoates from Sodium Sulfinates and Propargyl Esters

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Water-promoted sulfonylation of propargyl esters leading to highly regioselective and stereoselective formation of (*Z*)-*β*-sulfonyl enoates in excellent yields, by a simple, mild, rapid and environmentally benign reaction procedure is reported.

Keywords sodium sulfinates, propargyl esters, green reaction, (*Z*)-*β*-sulfonyl enoates

Introduction

β-Sulfonyl enoates are present in many bioactive molecules and serve as useful building blocks in organic synthesis.[1] The significance of sulfones and the difficulties in their preparation have gained intensive attention (Scheme 1). Traditionally, *β*-sulfonyl enoates were prepared by the reaction of cross-coupling of organostannanes with sulfonyl chlorides,[2] iodosulphonylation-dehydroiodination (Scheme 1a)[3] or imines with ethyl propiolate (Scheme 1b).[4] Recently, a sulfonylation using sodium arylsulfinates of alkyl propiolates leading to (*E*)-*β*-sulfonyl enoates in DMF was reported by Khalili (Scheme 1c).[5] Moreover, a two-step thioconjugate addition-oxidation reaction of ethyl propiolates with numerous types of thiols and *meta*-chloroperbenzoic acids (*m*-CPBA) in the presence of $LiClO_4$ leading to (*Z*)-*β*-sulfonyl enoates was reported (Scheme 1d).[6] However, a majority of them employed a catalyst, an addition agent or a toxic organic solvent and proceeded via two steps. However, these methods present several limitations, such as the use of expensive NHC catalyst, requiring hazardous chemicals and multi-step procedures, occurrence of side reactions, *etc*. In particular, few researches that refer to the mild and rapid synthesis of (*Z*)-*β*-sulfonyl enoates were reported. In consequence, there is still an urgent need for the exploitation of milder and more rapid synthetic method of (*Z*)-*β*-sulfonyl enoates.

Water, as a proton source, is the best solvent for organic synthesis for its natural, inexpensive, and environmentally friendly characteristics.[7] Besides, alkynes, as versatile structural motif, are extensively employed in synthetic sequences.[8] Taking the significance of sulfur-containing organic compounds and related scaffolds into account,[9] and following our interest in functionalization of alkyne,[10] we exploited an efficient sulfonylation of propargyl esters with sodium sulfinates to afford (*Z*)-*β*-sulfonyl enoates via an anion process (Scheme 1e). These conversions can be easily completed in water under green reaction conditions. These transformations did not involve any catalyst, ligand, or organic solvent.

Experimental

Commercially available reagents were of reagent grade (AR grade) and were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silicycle silica gel (200—300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz NMR plus spectrometer using residue solvent peaks as internal standards. Infrared spectra were recorded with IR spectrometer and are reported in reciprocal centimeter (cm^{-1}). High resolution mass spectra were obtained using GCT-TOF instrument with ESI source. Sulfonyl hydrazides and propargyl esters except ethyl propiolate, methyl propiolate were prepared according to literature procedures. Rest of the chemicals were purchased from Sigma Aldrich and Alfa Aesar, and were used without further purification. Solvents were purified by standard methods.

General procedure of 3

A mixture of sodium sulfinate (0.25 mmol),

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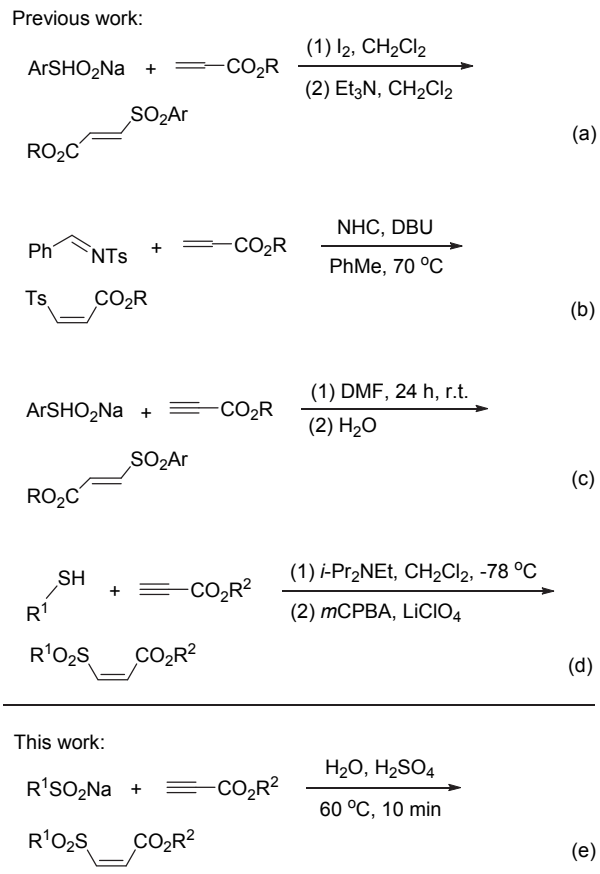
Received July 13, 2016; accepted October 23, 2016; published online December 20, 2016.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201600429 or from the author.

Scheme 1 (a) Iodosulphonylation-dehydroiodination leading to (*E*)-*b*-sulfonyl enoates; (b) imines with ethyl propiolate; (c) sulfonylation using sodium arylsulfinate of alkyl propiolate leading to (*E*)-*b*-sulfonyl enoates; (d) two-step thioconjugate addition-oxidation reaction of ethyl propiolate; (e) catalyst-free sulfonylation of propargyl esters



propargyl esters (0.75 mmol) and 0.025 mmol of H_2SO_4 in water (2 mL) was put into an oil bath at 80 ℃ under magnetic stirring for 10 min under air. After the reaction was complete, the mixture was added 20 mL of water and extracted with EtOAc (3×15 mL) and then the combined organic extract was washed with brine (15 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the corresponding product.

(*Z*)-Ethyl 3-tosylacrylate (3aa) White solid; yield 96% (61.0 mg); m.p. 37 ℃ (Lit. m.p. 36−38 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, J=8.1 Hz, 2H), 7.32 (d, J=8.0 Hz, 2H), 6.45 (ABq, $\Delta\delta_{AB}$=0.04, J_{AB}=12.0 Hz, 2H), 4.32 (q, J=7.1 Hz, 2H), 2.38 (s, 3H), 1.34 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.16, 145.30, 136.60, 135.51, 131.52, 130.06, 128.38, 62.25, 21.79, 14.08. The data meet the literature report.[6]

(*Z*)-Ethyl 3-(phenylsulfonyl)acrylate (3ba) White solid; yield 93% (55.8 mg); m.p. 70 ℃ (Lit. m.p. 69−71 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, J=8.1 Hz, 2H), 7.68−7.58 (m, 1H), 7.54 (t, J=7.6 Hz, 2H), 6.49 (ABq, $\Delta\delta_{AB}$=0.03, J_{AB}=10.0 Hz, 2H), 4.33 (q, J=7.1 Hz, 2H), 1.35 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.20, 139.69, 135.39, 134.28, 132.18, 129.56, 128.45, 62.44, 14.21. The data meet the literature report.[6]

(*Z*)-Ethyl 3-((4-methoxyphenyl)sulfonyl)acrylate (3ca) White solid; yield 98% (66.2 mg); m.p. 76 ℃ (Lit. m.p. 75−77 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, J=8.8 Hz, 2H), 6.99 (d, J=8.8 Hz, 2H), 6.44 (ABq, $\Delta\delta_{AB}$=0.06, J_{AB}=12.0 Hz, 2H), 4.33 (q, J=7.1 Hz, 2H), 3.85 (s, 3H), 1.35 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.30, 164.27, 135.82, 131.03, 130.74, 114.71, 62.26, 55.86, 14.14. The data meet the literature report.[6]

(*Z*)-Ethyl 3-((4-fluorophenyl)sulfonyl)acrylate (3da) White solid; yield 94% (60.6 mg); m.p. 53 ℃ (Lit. m.p. 52−53 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (dd, J=8.8, 5.1 Hz, 2H), 7.25 (d, J=8.1 Hz, 2H), 6.52 (s, 2H), 4.36 (q, J=7.1 Hz, 2H), 1.38 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.45, 164.89, 163.99, 135.63, 135.28, 132.29, 131.42, 131.33, 116.87, 116.65, 62.37, 14.08. The data meet the literature report.[6]

(*Z*)-Ethyl 3-((4-chlorophenyl)sulfonyl)acrylate (3ea) White solid; yield 93% (63.7 mg); m.p. 55 ℃ (Lit. m.p. 54−56 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, J=8.6 Hz, 2H), 7.52 (d, J=8.5 Hz, 2H), 6.50 (s, 2H), 4.34 (q, J=7.3 Hz, 1H), 1.36 (t, J=7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.82, 140.93, 137.98, 135.05, 132.53, 129.81, 129.68, 62.32, 14.00; IR (neat) ν: 2992, 1984, 1794, 1602, 1549, 1347, 1050 cm^{-1}; HRMS calcd for $C_{11}H_{11}ClO_4S$ ($M+Na^+$): 296.9964, found 296.9965.

(*Z*)-Ethyl 3-((4-bromophenyl)sulfonyl)acrylate (3fa) White solid; yield 95% (75.5 mg); m.p. 56 ℃ (Lit. m.p. 55−57 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, J=8.4 Hz, 2H), 7.69 (d, J=8.4 Hz, 2H), 6.50 (s, 2H), 4.34 (q, J=7.1 Hz, 2H), 1.36 (t, J=7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.80, 138.51, 135.01, 132.67, 132.56, 129.84, 129.55, 62.31, 13.99. The data meet the literature report.[6]

(*Z*)-Ethyl 3-(*m*-tolylsulfonyl)acrylate (3ga) Colorless oil; yield 97% (61.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78−7.74 (m, 2H), 7.42 (t, J=4.0 Hz, 2H), 6.48 (ABq, $\Delta\delta_{AB}$=0.03, J_{AB}=10.0 Hz, 2H), 4.33 (q, J=7.1 Hz, 2H), 2.42 (s, 3H), 1.36 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.99, 138.62, 138.26, 134.13, 133.82, 130.65, 128.18, 127.42, 124.31, 61.13, 20.30, 12.96; IR (neat) ν: 1985, 1796, 1601, 1548, 1348, 1051 cm^{-1}; HRMS calcd for $C_{12}H_{14}O_4S$ ($M+Na^+$): 277.0510, found 277.0514.

(*Z*)-Ethyl 3-((3-bromophenyl)sulfonyl)acrylate (3ha) White solid; yield 94% (74.7 mg); m.p. 47 ℃ (Lit. m.p. 47−48 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (t, J=1.9 Hz, 1H), 7.92 (d, J=8.0 Hz, 1H), 7.76 (d, J=8.0 Hz, 1H), 7.43 (t, J=7.9 Hz, 1H), 6.53 (ABq, $\Delta\delta_{AB}$=0.03, J_{AB}=12.0 Hz, 2H), 4.35 (q, J=7.2 Hz, 2H), 1.37 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ: 163.69, 141.35, 137.10, 134.69, 132.93, 131.13, 130.85, 126.83, 123.25, 62.37, 13.98; IR (neat) ν: 2990, 1983, 1795, 1601, 1548, 1346, 1052 cm^{-1}; HRMS calcd for $C_{11}H_{11}BrO_4S$ ($M+Na^+$): 340.9459, found 340.9459.

(*Z*)-Ethyl 3-(*o*-tolylsulfonyl)acrylate (3ia) White solid; yield 95% (60.3 mg); m.p. 56 ℃ (Lit. m.p. 55—56 ℃); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, J=8.0, 1H), 7.50 (t, J=8.0 Hz, 1H), 7.36 (t, J=7.7 Hz, 1H), 7.30 (d, J=7.6 Hz, 1H), 6.58 (d, J=11.7 Hz, 1H), 6.48 (d, J=11.7 Hz, 1H), 4.26 (q, J=7.2 Hz, 2H), 2.63 (s, 3H), 1.31 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.63, 138.53, 137.90, 135.75, 134.11, 132.68, 131.67, 129.86, 126.65, 62.18, 20.40, 14.00; IR (neat) ν: 1984, 1796, 1603, 1549, 1347, 1050 cm^{-1}; HRMS calcd for $C_{12}H_{14}O_4S$ ($M+Na^+$): 277.0510, found 277.0512.

(*Z*)-Ethyl 3-((2-bromophenyl)sulfonyl)acrylate (3ja) White solid; yield 91% (72.3 mg); m.p. 47 ℃ (Lit. m.p. 46—48 ℃); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.19 (dd, J=7.8, 1.8 Hz, 1H), 7.73 (d, J=7.8 Hz, 1H), 7.58—7.43 (m, 2H), 7.06 (d, J=11.6 Hz, 1H), 6.55 (d, J=11.6 Hz, 1H), 4.25 (q, J=7.1 Hz, 2H), 1.30 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.08, 140.25, 136.87, 135.16, 134.91, 132.73, 131.57, 127.89, 120.79, 62.12, 14.01; IR (neat) ν: 2994, 1984, 1796, 1600, 1548, 1348, 1052 cm^{-1}; HRMS calcd for $C_{11}H_{11}BrO_4S$ ($M+Na^+$): 340.9459, found 340.9457.

(*Z*)-Ethyl 3-(mesitylsulfonyl)acrylate (3ka) White solid; yield 99% (69.8 mg); m.p. 67 ℃ (Lit. m.p. 66—68 ℃); ^1H NMR (400 MHz, $CDCl_3$) δ: 6.96 (s, 2H), 6.65 (d, J=11.7 Hz, 1H), 6.41 (d, J=11.7 Hz, 1H), 4.21 (q, J=7.2 Hz, 2H), 2.64 (s, 6H), 2.30 (s, 3H), 1.29 (t, J=7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.50, 143.68, 140.21, 138.15, 133.60, 132.10, 129.45, 61.94, 22.60, 21.03, 13.88; IR (neat) ν: 2996, 1986, 1793, 1605, 1547, 1348, 1052 cm^{-1}; HRMS calcd for $C_{14}H_{18}O_4S$ ($M+Na^+$): 305.0823, found 305.0825.

(*Z*)-Ethyl 3-(naphthalen-2-ylsulfonyl)acrylate (3la) Yellow solid; yield 81% (58.7 mg); m.p. 77 ℃ (Lit. m.p. 76—78 ℃); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.57 (d, J=1.7 Hz, 1H), 8.05—7.90 (m, 4H), 7.66 (dt, J=21.1, 7.1 Hz, 2H), 6.56 (ABq, $\Delta\delta_{AB}$=0.06, J_{AB}=10.0 Hz, 2H), 4.39 (q, J=7.2 Hz, 2H), 1.41 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.01, 136.29, 135.52, 135.17, 132.21, 131.89, 130.23, 129.68, 129.55, 129.50, 128.00, 127.71, 122.73, 62.24, 14.02. The data meet the literature report.[6]

(*Z*)-Ethyl 3-(thiophen-2-ylsulfonyl)acrylate (3ma) White solid; yield 100% (61.5 mg); m.p. 56 ℃ (Lit. m.p. 55—57 ℃); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J=4.0 Hz, 1H), 7.75 (d, J=4.0 Hz, 1H), 7.16 (t, J=4.0 Hz, 1H), 6.63 (d, J=11.5 Hz, 1H), 6.48 (d, J=11.3 Hz, 1H), 4.36 (q, J=7.1 Hz, 2H), 1.38 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.81, 140.70, 135.87, 135.21, 135.14, 131.59, 128.30, 62.35, 14.11. The data meet the literature report.[6]

(*Z*)-Methyl 3-tosylacrylate (3ab) Colorless oil; yield 82% (49.2 mg); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J=8.2 Hz, 2H), 7.36 (d, J=8.0 Hz, 2H), 6.50 (ABq, $\Delta\delta_{AB}$=0.06, J_{AB}=12.0 Hz, 2H), 3.89 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.53, 145.30, 136.42, 135.91, 131.05, 130.02, 128.31, 52.78, 21.72; IR (neat) ν: 1984, 1795, 1601, 1548, 1347, 1050 cm^{-1}; HRMS calcd for $C_{11}H_{12}O_4S$ ($M+Na^+$): 263.0354, found 263.0355.

(*Z*)-Phenyl 3-tosylacrylate (3ac) Yellow solid; yield 76% (57.4 mg); m.p. 86 ℃ (Lit. m.p. 85—87 ℃); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, J=8.1 Hz, 2H), 7.48—7.42 (m, 2H), 7.38—7.28 (m, 5H), 6.67 (ABq, $\Delta\delta_{AB}$=0.03, J_{AB}=12.0 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.79, 150.06, 145.43, 136.21, 130.51, 130.08, 129.62, 128.42, 126.47, 121.56, 21.69; IR (neat) ν: 1984, 1791, 1601, 1549, 1542, 1348, 1052 cm^{-1}; HRMS calcd for $C_{16}H_{14}O_4S$ ($M+Na^+$): 325.0510, found 325.0493.

(*Z*)-Benzyl 3-tosylacrylate (3ad) White solid; yield 75% (59.3 mg); m.p. 103 ℃ (Lit. m.p. 102—103 ℃); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.73 (d, J=8.1 Hz, 2H), 7.40—7.26 (m, 5H), 7.21 (d, J=8.0 Hz, 2H), 6.43 (ABq, $\Delta\delta_{AB}$=0.04, J_{AB}=12.0 Hz, 2H), 5.22 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.89, 145.22, 136.38, 135.86, 134.76, 131.01, 129.94, 128.92, 128.68, 128.65, 128.35, 68.03, 21.70; IR (neat) ν: 2996, 1985, 1794, 1602, 1549, 1541, 1348, 1052 cm^{-1}; HRMS calcd for $C_{17}H_{16}O_4S$ ($M + Na^+$): 339.0667, found 339.0671.

(*Z*)-2-Hydroxyethyl 3-tosylacrylate (3ae) Colorless oil; yield 78% (52.7 mg); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, J=8.1 Hz, 2H), 7.37 (d, J=8.0 Hz, 2H), 6.51 (ABq, $\Delta\delta_{AB}$=0.04, J_{AB}=12.0 Hz, 2H), 4.46 (t, J=4.0 Hz, 2H), 3.94 (t, J=4.3 Hz, 2H), 2.86 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.16, 145.60, 136.03, 135.39, 130.83, 130.18, 128.18, 68.09, 60.69, 21.72; IR (neat) ν: 3362, 2991, 1985, 1794, 1603, 1548, 1348, 1052 cm^{-1}; HRMS calcd for $C_{12}H_{14}O_5S$ ($M+Na^+$): 293.0460, found 293.0456.

(*Z*)-2-(Benzyloxy)ethyl 3-tosylacrylate (3af) White solid; yield 88% (79.2 mg); m.p. 100 ℃ (Lit. m.p. 99—101 ℃); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J=7.9 Hz, 2H), 7.37—7.26 (m, 7H), 6.50 (ABq, $\Delta\delta_{AB}$=0.03, J_{AB}=12.0 Hz, 2H), 4.60 (s, 2H), 4.52—4.45 (m, 2H), 3.81 (dd, J=5.5, 3.9 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.05, 144.17, 136.80, 135.29, 134.51, 130.03, 128.95, 127.41, 127.36, 126.83, 126.74, 72.22, 66.67, 64.05, 20.66; IR (neat) ν: 2994, 1985, 1792, 1604, 1547, 1348, 1051 cm^{-1}; HRMS calcd for $C_{19}H_{20}O_5S$ ($M+Na^+$): 383.0929, found 383.0927.

(*Z*)-2-Bromoethyl 3-tosylacrylate (3ag) White solid; yield 92% (76.4 mg); m.p. 85 ℃ (Lit. m.p. 84—86 ℃); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, J=8.3 Hz, 2H), 7.34 (d, J=8.0 Hz, 2H), 6.49 (ABq, $\Delta\delta_{AB}$=0.04, J_{AB}=12.0 Hz, 2H), 4.58 (t, J=6.3 Hz, 2H), 3.60 (t, J=6.3 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.66, 145.41, 136.16, 135.93, 130.39,

130.06, 128.32, 65.07, 27.85, 21.71; IR (neat) *v*: 2992, 1984, 1793, 1602, 1548, 1348, 1051 cm^{-1}; HRMS calcd for $C_{12}H_{13}BrO_4S$ ($M+Na^+$): 354.9616, found 354.9617.

(*Z*)-2-Methoxy-2-oxoethyl 3-tosylacrylate (3ah) Colorless oil; yield 85% (63.3 mg); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, J=8.0 Hz, 2H), 7.38 (d, J=8.0 Hz, 2H), 6.58 (ABq, $\Delta\delta_{AB}$=0.04, J_{AB}=12.0 Hz, 2H), 4.85 (s, 2H), 3.82 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.52, 162.29, 144.41, 135.70, 129.04, 128.99, 127.41, 60.62, 51.41, 20.71; IR (neat) *v*: 2991, 1984, 1794, 1742, 1602, 1548, 1347, 1051 cm^{-1}; HRMS calcd for $C_{13}H_{14}O_6S$ ($M+Na^+$): 298.0511, found 298.0509.

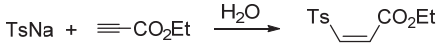
Deuterium generation (*Z*)-ethyl 3-tosylacrylate (4) White solid; yield 96% (61.2 mg); m.p. 37 ℃ (Lit. m.p. 36—38 ℃); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J=7.9 Hz, 2H), 7.36 (d, J=7.9 Hz, 2H), 6.51 (s, 1H), 4.36 (q, J=7.1 Hz, 2H), 2.45 (s, 3H), 1.39 (t, J=7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.02, 144.18, 135.46, 134.37, 128.94, 127.28, 61.14, 20.69, 12.97; IR (neat) *v*: 2994, 1985, 1794, 1602, 1548, 1348, 1051 cm^{-1}; HRMS calcd for $C_{12}H_{13}DO_4S$ ($M+Na^+$): 278.0573, found 278.0574.

Results and Discussion

Firstly, the reaction of sodium 4-methylbenzenesulfinate (**1a**) and ethyl propiolate (**2a**) under air atmosphere in water at room temprature for 12 h (Table 1, Entry 1), gave the desired product (*Z*)-ethyl 3-tosylacrylate (**3aa**) in 11% NMR yield. Subsequently, the temperature was tested and 60 ℃ was the best choice (Entries 1—4). Then, control experiments showed that the quantity of **2a** had a strong influence on the reaction and 3 equivalent of **2a** could improve the yield to 94% (Entries 4—7). We also studied the influence of reaction time, and 1 h had the same yield as 12 h (Entry 6 vs. 8—10). More importantly, when we add 0.1 equivalent of H_2SO_4 to the reaction mixture, the reaction time could be greatly reduced up to 10 min (Entry 10 vs. 11—14) and the yield was higher. We were pleased to find that all of the conditions that we tested resulted in the formation of *Z*-*β*-sulfonyl enoates in high stereoselectivity. Thus, the best conditions for this process comprised ratio (**1a**∶**2a**=1∶3) under air atmosphere in water (2 mL) and 0.1 equivalent of H_2SO_4 at 60 ℃ for 10 min.

We then explored the scope of the reaction (Table 2). First, we tested the scope of aromatic sodium sulfinates and all the corresponding products were obtained in excellent yields. The electronic effect of substituents at the *para* position of the aryl sodium sulfinates was evaluated (**3aa**—**3fa**). The reaction tolerated both electron-donating and electron-withdrawing groups. Aromatic sodium sulfinate with substituents at *meta* (**3ga**—**3ha**) and *ortho* (**3ia**—**3ja)** positions also worked well, although giving slightly lower yields. 2,4,6-Trimethylbenzene sodium sulfinate can also be used as reaction

Table 1 Optimization of the reaction conditions[a]



1a **2a** **3aa**

Entry	Equiv. of **2a**	Temp./℃	Time	Yield[b]/%	*Z*/*E*[b]
1	2	r.t.	12 h	11	6∶1
2	2	40	12 h	35	6∶1
3	2	60	12 h	69	8∶1
4	2	80	12 h	68	8∶1
5	1	60	12 h	36	7∶1
6	3	60	12 h	94	13∶1
7	4	60	12 h	94	13∶1
8	3	60	2 h	94	13∶1
9	3	60	1 h	94	13∶1
10	3	60	30 min	87	13∶1
11[c]	3	60	30 min	96	14∶1
12[d]	3	60	15 min	96	14∶1
13[e]	**3**	**60**	**10 min**	**96**	**14∶1**
14[f]	3	60	5 min	75	14∶1

[a] All reactions were performed with 4-methylbenzenesulfinate (**1a**, 0.25 mmol), water (2 mL), under air. [b] Estimated by ^1H NMR spectroscopy using methylene bromide as an internal reference. [c,d,e] 0.1 equivalent of H_2SO_4 and less time.

substrate, affording the desired product **3ka** in good yield. It is notable that the naphthalene substrate **1l** and the thiophene substrate **1m** can also be transformed into desired products **3la**—**3na** in high yields.

To further exploit the generality of this catalytic reaction, the propargyl esters were also investigated. Propargyl esters generally led to the corresponding products in good yield. Many synthetically important functional groups were readily tolerated, including an alkyl (**3ab**), a phenyl (**3ac**), a benzyl (**3ac**), a free hydroxyl moiety (**3ae**), a protected OH (**3af**), a bromide (**3ag**) and an ester (**3ah**). To our delight, all of the examples in these experiments had excellent stereoselectivity of *Z* configuration (Table 2).

To gain insight into the reaction mechanism, we conducted a series of experiments (Scheme 2). First, when the radical inhibitor TEMPO (2 equiv.) was employed under standard conditions, the reaction afforded **3aa** in 90% yield (Scheme 3a), which implied that the transformation did not proceed via a free-radical pathway.[11] Then, with D_2O (2 mL) as the solvent, the transformation gave a deuterium generation product **4** in 96% yield (Scheme 3b). The deuterium generation experiment implied that the *α*-hydrogen atom of (*Z*)-*β*-sulfonyl enoates resulted from water. Furthermore, the reaction yield of **3aa** reduced to 18% at the basic condition of 1 equiv. of NaOH (Scheme 3c). The alkaline tests indicated that hydronium ions played an important role in the reaction.

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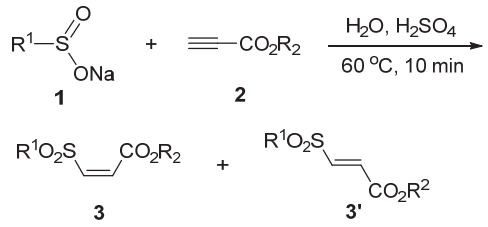
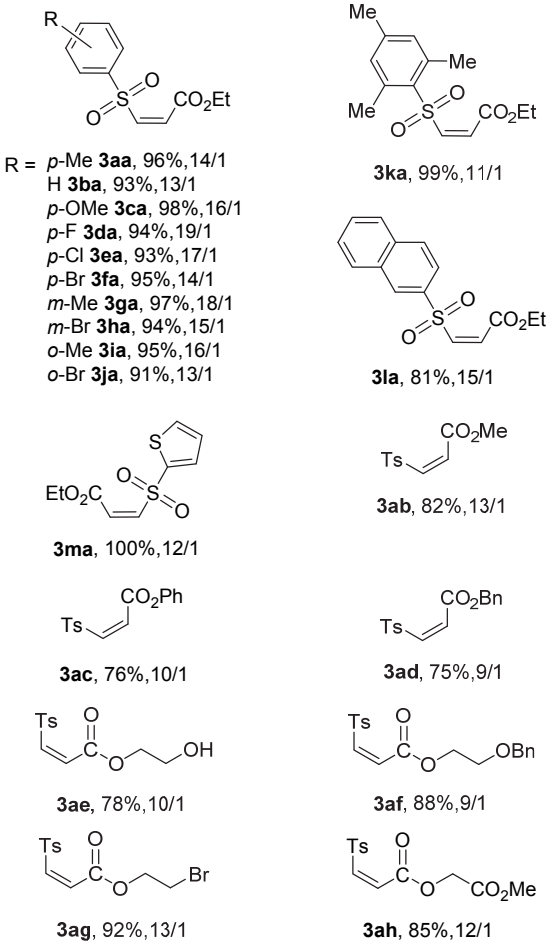
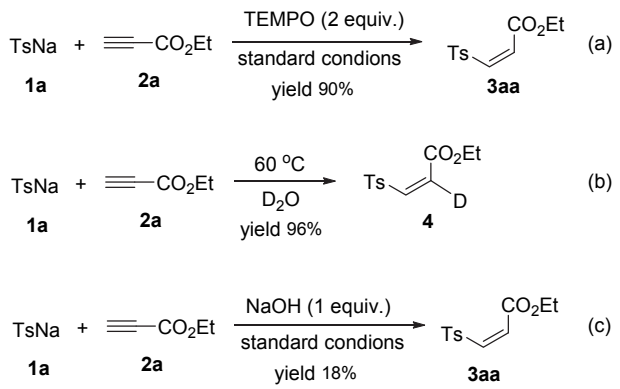
Table 2 Reaction scope[a,b]





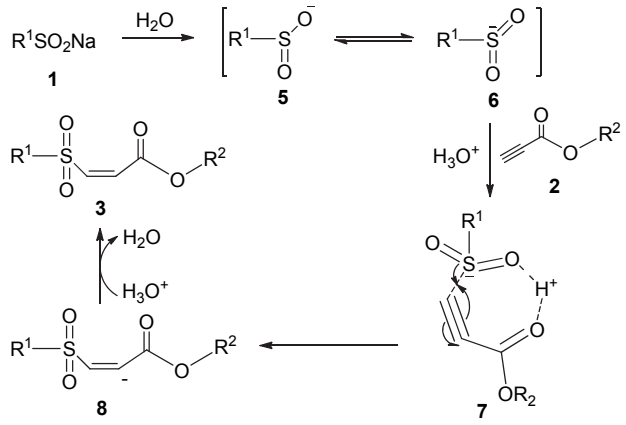
[a] Conditions: **1** (0.25 mmol) and **2** (0.75 mmol) in 2 mL of H_2O, 0.1 equiv. of H_2SO_4, 60 ℃, under air, 10 min. [b] The yields reported for a mixture of isomers after column chromatography.

Scheme 2 Control experiments



On the basis of the results described above and previous reports,[12] a plausible mechanism is proposed in Scheme 3. Firstly, sodium sulfinate is quickly turned into a sulfinyl anion **5**, which can resonate with the sulfur-centered anions **6** in the presence of water. Then, the sulfur-centered anions **6** is selectively added into the propargyl esters **2a** leading to the intermediate **7** in the presence of proton, which can turned into the carbon-centered anions **8**. Finally, the intermediate **8** affords (Z)-*β*-sulfonyl enoate **3aa** by a following proton transfer (PT) from hydrion.

Scheme 3 The proposed mechanism for the reaction



Conclusions

In summary, a simple and rapid regioselective sulfonylation of propargyl esters in water has been developed, giving (*Z*)-*β*-sulfonyl enoates in good yields. The reaction proceeded under mild conditions without any catalyst or organic solvent. A broad range of sodium sulfinates and propargyl esters were tolerated in the reaction, and all the sulfonylation products could be obtained in good yields.

Acknowledgement

This work was supported by the Planned Science and Technology Project of Hunan Province, China (No. 2015WK3003).

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