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Palladium-Catalyzed Regio- and Stereoselective Hydrosulfonation of Propiolate Esters

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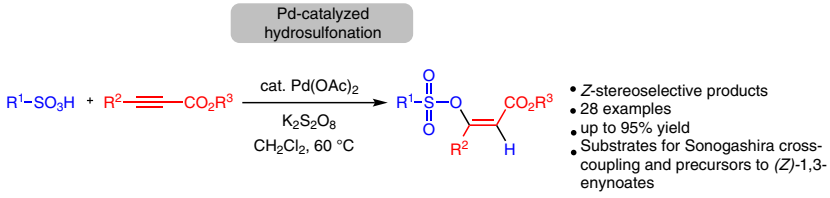

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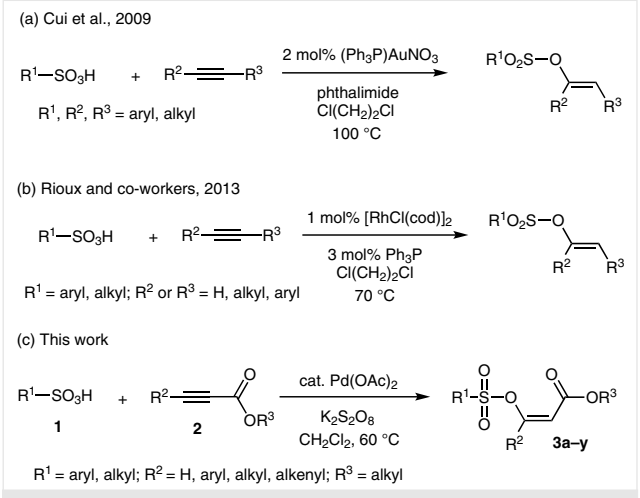
Abstract An efficient palladium-catalyzed addition reaction of alkyl- and arylsulfonic acids to propiolate esters to yield alkenyl sulfonates is demonstrated. The formation of alkenyl sulfonates is highly regio- and stereoselective with favorable yields of up to 95%, and two of the alkenyl sulfonates are utilized for a Sonogashira cross-coupling reaction to produce (*Z*)-1,3-enynoates.

Key words palladium, sulfonic acid, propiolate, regioselective, stereoselective, alkenyl sulfonate, Sonogashira cross-coupling

Transition-metal-catalyzed reactions are powerful synthetic tools for molecular functionalization and functional group transformations.[1] Alkynes often have been the incorporated units for developing acyclic/cyclic structures for use in pharmaceutical and material science applications.[2] In this context, metal-catalyzed nucleophilic addition to alkynes has been a reliable tool for synthesizing alkenyl compounds.[3] In particular, the Pd catalysis associated with alkynes has efficiently expanded access to various molecular scaffolds.[4] In addition, the evolved gold-catalyzed nucleophilic addition with alkynes is another approach for scaffold synthesis because of the acidic nature of gold.[5] Transition metals, such as gold,[6] palladium,[7] silver,[8] ruthenium,[9] and mercury,[10] catalyze the addition of weak acid nucleophiles, such as sulfonic acids, carboxylic acids or alcohols, to alkynes through an O-attack to produce compounds with an enol ether moiety. Alkenyl sulfonates are substantial building blocks for polymer syntheses[11] and metal-catalyzed coupling reagents.[12] Although alkenyl sulfonates can be prepared through robust stoichiometric tosylation of β-keto esters with TsCl and appropriate bases,[13] metal-catalyzed synthesis of alkenyl sulfonates with regio- and stereoselective control is challenging. Previous approaches relied on cationic gold to achieve hydrosulfonation of alkynes. Cui et al. demonstrated an efficient gold-catalyzed Markovnikov addition of aryl/methanesulfonic acids to aryl/alkylacetylenes with phthalimide as an additive in 1,2-dichloroethane at 100 °C, providing stereo- and regioselective access to substituted vinyl sulfonates in favorable yields (Scheme 1, a).[14] In addition, Rioux and co-workers demonstrated a ligand-controlled rhodium-catalyzed addition of aryl/alkylsulfonic acids to arylacetylenes in 1,2-dichloroethane at 70 °C (Scheme 1, b).[15] However, the developed methods are limited to aryl- or alkylacetylenes and are not applicable to propiolates, likely due to known reactivity of propiolates with liberated phosphines from metal complexes.[16] Other metal-free methods by superacid-catalyzed addition of triflic or fluorosulfonic acid to electron-poor alkynes provided vinyl triflates or fluorosulfonates.[17]



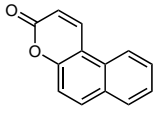
Scheme 1 Reactivity of (a), (b) aryl/alkylacetylenes, and (c) propiolates toward metal-catalyzed aryl/alkylsulfonic acid addition

Our recent study in *anti*-Michael addition of phosphines with propiolate esters inspired us to prepare conjugated alkynoates.[18] Previous methods for synthesizing alkyl (*Z*)-5-phenylpent-2-en-4-ynoates entails using relatively labile alkyl (*Z*)-2-iodoacrylates as substrates in a Sonogashira coupling reaction. Our interest in developing another surrogate intermediate without using labile iodo substrates prompted us to evaluate the effectiveness of using alkenyl sulfonates prepared from a metal-catalyzed anti-Markovnikov addition of arylsulfonic acids to propiolate esters. In lieu of gold-catalysis, herein we present a new, general, cost-effective, and phosphine-free method for synthesizing alkyl (*Z*)-β-arylsulfonate-substituted α,β-unsaturated carboxylate esters by Pd-catalysis in high stereo- and regioselectivity and favorable yields (Scheme 1, c). Two of the obtained alkenyl sulfonates can be efficient substrates for a Sonogashira cross-coupling reaction to provide conjugated (*Z*)-1,3-enynoates in favorable yields.

We first investigated the optimal reaction conditions with *p*-toluenesulfonic acid (**1a**, PTSA) and methyl propiolate (**2a**) as substrates under various catalysts, oxidants, solvents, and temperatures (Table 1). Initially, the reaction performed with 1 equivalent of **1a** (0.15 mmol), 3 equivalents of **2a**, 5 mol% of $Pd(OAc)_2$, and 3 equivalents of $K_2S_2O_8$ as oxidants in dichloromethane/trifluoroacetic acid (5 mL:0.1 mL) at 50 °C for 24 hours exclusively afforded (*Z*)-**3a** in a 48% yield (Table 1, entry 1). When the reaction time was extended to 40 hours, the yield decreased to 44 % (entry 2). Doubling the molar amounts of PTSA decreased the yield markedly to 13% (entry 3). Furthermore, elevating the reaction temperature to 60 or 70 °C produced a mixture of *Z*- and *E*-isomers (1:1) in an overall 31% yield (entry 4), but provided only the *E*-isomer **3a′** in a poor yield at 80 °C (entry 5, 12%). Notably, only trace amounts of products were observed in 1,4-dioxane/TFA at 100 °C (entry 6). In addition, increasing the loading of TFA deteriorated the performance of yields (entry 7). We next found that the reaction also proceeded without TFA as an additive (entry 8).

A similar loss of stereoselectivity was observed at an elevated temperature (Table 1, entry 9). Unexpectedly, the reaction yields were largely improved while the amounts of **2a** (entries 10, 11) were increased – a 92% yield was achieved with 6 equivalents of **2a** (entry 11). This observed reaction required $Pd(OAc)_2$ as a catalyst because a control experiment in the absence of catalyst produced no (*Z*)-**3a** (entry 12). The present reaction became less efficient with other oxidants such as $KHSO_5$ and $Cu(OAc)_2$ (entries 13–15). However, reaction with *p*-benzoquinone as an oxidant produced an 84% yield (entry 16). We also used 2.5 mol% of $Pd(OAc)_2$ as a catalyst and obtained an 83% yield of (*Z*)-**3a** (entry 17). Finally, using other metal catalysts, such as $PdCl_2(PPh_3)_2$, $Co(acac)_2$, $Co(OAc)_2$, $Mn(OAc)_3$, and Ag_2O (entries 18–22), revealed that only $PdCl_2(PPh_3)_2$ can catalyze to produce an 18% yield of (*Z*)-**3a** (entry 18). It is noteworthy that without the oxidant $K_2S_2O_8$, the reaction produced only 56% of product (entry 23). Our attempts at using other catalysts, such as AgOAc, AgOTf, $AgNO_3$, $PdCl_2$, CuOAc, and $AuCl_3$ (entries 24–29) revealed that only the reaction with $AuCl_3$ gave noticeable yield and regioselectivity – 34% with a *Z*/*E* ratio of 38:62.

Under the optimized conditions, the reaction scope of sulfonic acid addition to alkynes was examined next (Scheme 2). First, we noted that reactions with electron-donating arylsulfonic acids **1a**–**e** and methyl propiolate (**2a**) produced favorable yields, and those with ethyl propiolate (**2b**) provided only slightly lower yields of (*Z*)-**3** (Scheme 2, entries 1–10, 65–93%). Steric hindrance from the *ortho*-methyl moiety of arylsulfonic acids, as well as the ethyl moiety of the propiolate **2b**, lowered the yield by approximately 10%. The isolated products **3a**–**j** were all highly regio- and stereoselective with a *Z*-configuration, corroborated with crystallographic analysis.[19] The addition of electron-withdrawing 4-chlorophenylsulfonic acid was evaluated next by using this catalysis and found that (*Z*)-**3k**,**l** were formed in 74–75% yields (entries 11, 12). However, more electron-deficient 2,4-dinitrobenzenesulfonic acid resulted in poor yields (entry 13, 17%). An addition of 2- and 1-naphthalenesulfonic acids to alkynes was then carried out (entries 14–16), and gave the alkenyl sulfonates (*Z*)-**3n**–**p** in 56–82% yields; it was noteworthy that 1-naphthalenesulfonic acid performed relatively poorly because of the steric effect (entry 16). However, we could not produce the corresponding alkenyl sulfonates while using the 2-naphthyl propiolate (**2c**) as a substrate; only 3*H*-naphtho[2,1-*b*]pyran-3-one (**A**) (Figure 1) was isolated in 31–33% yield through cyclization (entries 17, 18).[20]



A

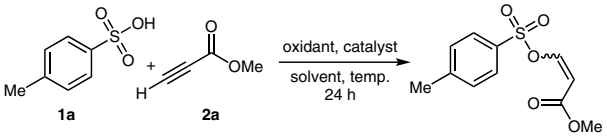
Figure 1 Structure of product **A**

Next, the chemical reactivity of alkylsulfonic acids – methanesulfonic and ethanesulfonic acids – was tested, which showed that the hydrosulfonation produced moderate to favorable yields (Scheme 2, entries 19–21, 66–86%). The reaction with trifluoromethanesulfonic acid as a nucleophile did not produce corresponding product **3s′**. This is likely due to the presence of strong electron-withdrawing trifluoromethyl moiety. Furthermore, longer carbon-chain internal alkynes were also reactive, but relatively less reactive than shorter ones. Products **3v** and **3w** were obtained in 51% and 31% yield, respectively, for *p*-tolylsulfonation and methanesulfonation to methyl 2-hexynoate (entries 22, 23). However, the chemical reactivity with the short internal alkyne, ethyl 2-butynoate, was superior; 95% of *p*-tolylsulfonation product **3x** was isolated (entry 24). In the case of ethyl 3-phenylpropynoate and dimethyl acetylenedicar-

boxylate, no corresponding addition products were observed (entries 25, 26). Finally, we found that other nucleophiles, ethanol, 2,4-dimethylbenzoic acid, and 4-methylbenzenesulfonamide, did not work under the standard conditions (entries 27–29). In short, the examples with electron-withdrawing functionality on sulfonic acids gave lower yields, such as 2,4-dinitrophenyl substitution (entry 13), and that with electron-donating moiety gave better yields, such as ethyl substitution (entry 21).

We further noted that these isolated alkenyl sulfonates **3** can undergo a Sonogashira cross-coupling reaction[21] with arylacetylenes catalyzed by $Pd(PPh_3)_4$. A previously report-

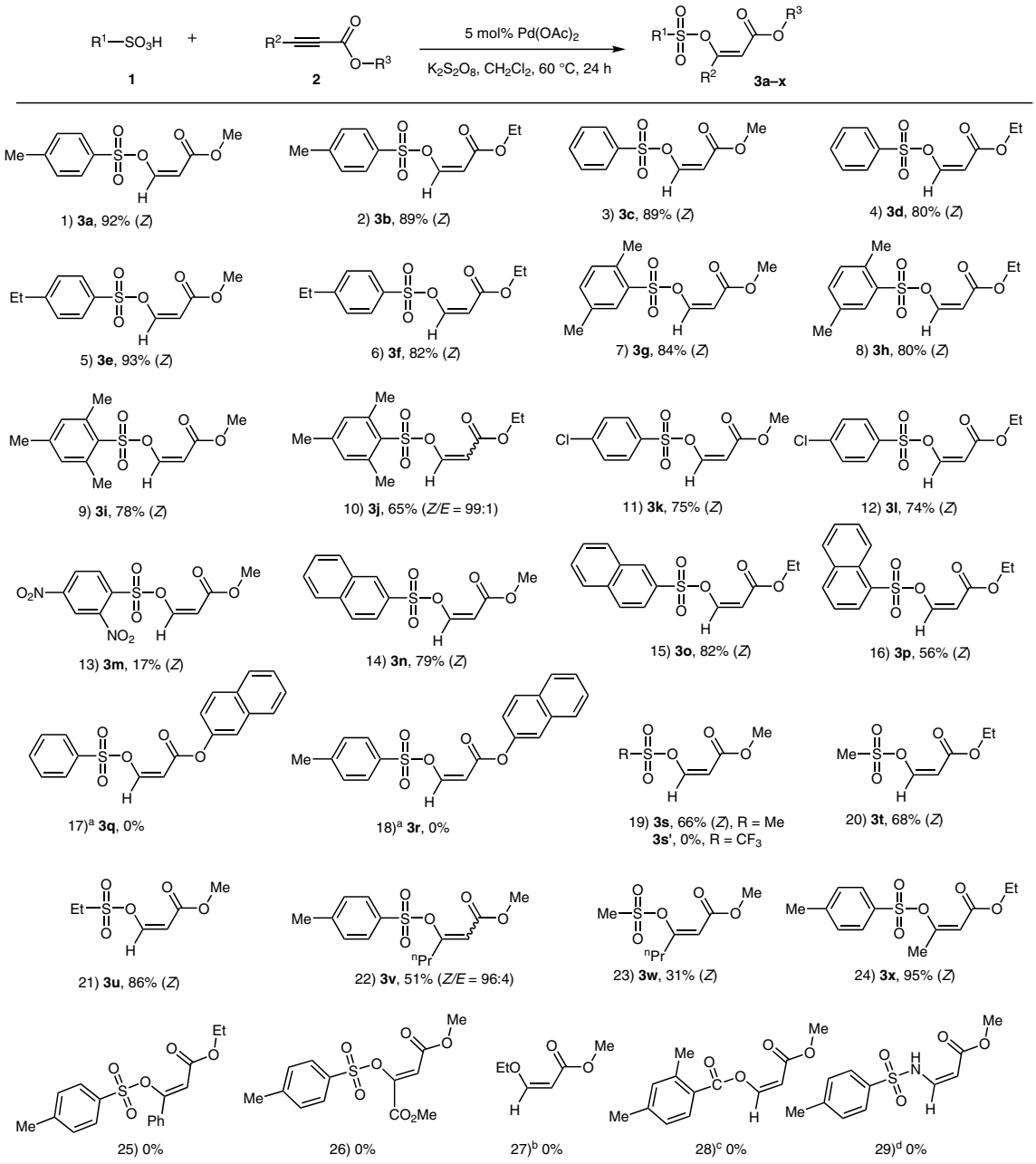
Table 1 Optimization of the Reaction Conditions[a]



Entry	**2a** (equiv)	Oxidant	Catalyst	Solvent (mL)	Temp (°C)	Yield (%)[b] of **3a**	Ratio *Z*/*E*
1	3	$K_2S_2O_8$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2/TFA (5:0.1)	50	48	100:0
2[c]	3	$K_2S_2O_8$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2/TFA (5:0.1)	50	44	100:0
3[d]	3	$K_2S_2O_8$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2/TFA (5:0.1)	50	13	100:0
4	3	$K_2S_2O_8$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2/TFA (5:0.1)	60 or 70	31	1:1
5	3	$K_2S_2O_8$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2/TFA (5:0.1)	80	12	0:100
6	3	$K_2S_2O_8$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	1,4-dioxane/TFA (5:0.1)	100	trace	–
7	3	$K_2S_2O_8$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2/TFA (5:1)	60	9	100:0
8	3	$K_2S_2O_8$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2 (5)	60	52	100:0
9	3	$K_2S_2O_8$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2 (5)	70	39	54:46
10	4	$K_2S_2O_8$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2 (5)	60	78	100:0
11	6	$K_2S_2O_8$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2 (5)	60	92	100:0
12	6	$K_2S_2O_8$ (3 equiv)	none	CH_2Cl_2 (5)	60	0	–
13	6	$KHSO_5$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2 (5)	60	48	100:0
14	3	$KHSO_5$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2 (5)	70	31	100:0
15	6	$Cu(OAc)_2$ (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2 (5)	60	0	–
16	6	*p*-benzoquinone (3 equiv)	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2 (5)	60	84	100:0
17	6	$K_2S_2O_8$ (1.5 equiv)	$Pd(OAc)_2$ (2.5 mol%)	CH_2Cl_2 (5)	60	83	100:0
18	6	$K_2S_2O_8$ (3 equiv)	$PdCl_2(PPh_3)_2$ (10 mol%)	CH_2Cl_2 (5)	60	18	100:0
19	6	$K_2S_2O_8$ (3 equiv)	$Co(acac)_2$ (10 mol%)	CH_2Cl_2 (5)	60	ND	–
20	6	$K_2S_2O_8$ (3 equiv)	$Co(OAc)_2$ (10 mol%)	CH_2Cl_2 (5)	60	ND	–
21	6	$K_2S_2O_8$ (3 equiv)	$Mn(OAc)_3$ (10 mol%)	CH_2Cl_2 (5)	60	ND	–
22	6	$K_2S_2O_8$ (3 equiv)	Ag_2O (10 mol%)	CH_2Cl_2 (5)	60	ND	–
23	6	none	$Pd(OAc)_2$ (5 mol%)	CH_2Cl_2 (5)	60	56	100:0
24	6	$K_2S_2O_8$ (3 equiv)	AgOAc (5 mol%)	CH_2Cl_2 (5)	60	6	100:0
25	6	$K_2S_2O_8$ (3 equiv)	AgOTf (5 mol%)	CH_2Cl_2 (5)	60	13	100:0
26	6	$K_2S_2O_8$ (3 equiv)	$AgNO_3$ (10 mol%)	CH_2Cl_2 (5)	60	11	100:0
27	6	$K_2S_2O_8$ (3 equiv)	$PdCl_2$ (5 mol%)	CH_2Cl_2 (5)	60	25	100:0
28	6	$K_2S_2O_8$ (3 equiv)	CuOAc (5 mol%)	CH_2Cl_2 (5)	60	9	100:0
29	6	$K_2S_2O_8$ (3 equiv)	$AuCl_3$ (5 mol%)	CH_2Cl_2 (5)	60	34	38:62

[a] Reaction conditions: PTSA (0.15 mmol, 1 equiv), **2a**, oxidant, catalyst, under N_2 for 24 h, unless otherwise noted.
[b] Yields were determined by ^1H NMR analysis using mesitylene as an internal standard. ND: Not detected.
[c] Reaction time: 40 h.
[d] Reaction was carried out with 0.30 mmol of PTSA.

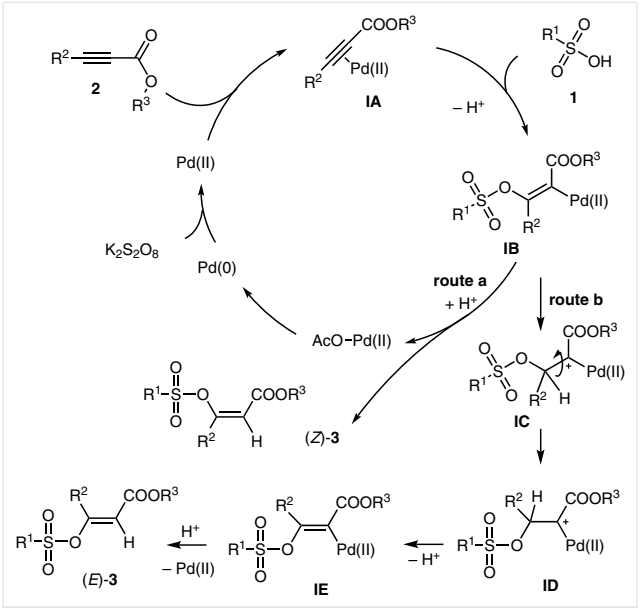
ed condition was used, which worked effectively with trisubstituted alkenes having an OTs group.[13] Because of the relatively higher reactivity of our prepared disubstituted alkenyl sulfonates, a new condition was optimized, as shown in Table S1 (Supporting Information). Alkyl (*Z*)-5-phenylpent-2-en-4-ynoates (**5**)[22] were obtained in favorable yields with 4-chlorophenyl-substituted sulfonate **3k** and arylacetylenes **4** under Pd(0) catalysis in a combination of solvents, THF/*i*-Pr_2NEt (4:1.5), at 90 °C for 24 hours (Table S2). This cross-coupling reaction can also be expanded to substrate **3x**, producing β-methyl-substituted enynoate **5b** in 79% yield (Table S2, entry 2).



Scheme 2 Hydrosulfonation of substituted alkynoates. *Reagents and conditions*: The reactions of entries 1–26 were performed using 0.15 mmol of sulfonic acid **1**, 0.90 mmol of alkyne **2**, 0.45 mmol of $K_2S_2O_8$, and 0.0075 mmol of $Pd(OAc)_2$ in CH_2Cl_2 (5 mL) at 60 °C for 24 h under N_2. [a] Product **A** was isolated in 31% in entry 17, and 33% in entry 18. [b] EtOH was used instead of **1**. [c] 2,4-Dimethylbenzoic acid was used instead of **1**. [d] 4-Methylbenzenesulfonamide was used instead of **1**.

The studied Pd-catalyzed hydrosulfonation reaction can also be extended to enynedioate **2i** to produce β-arylsulfonated dienedioates **3y**,**z** and **3aa**–**ad** in 47% to 89% yields (Table 2). Instead of using 5 mol% of metal catalysts, hydrosulfonation of **2i** demanded for 10 mol% of $Pd(OAc)_2$ to achieve comparable yields under the same reaction time and temperature, likely due to relatively poor reactivity of **2i**. This hydrosulfonation tolerated aryl- and alkylsulfonic acids, and took place regioselectively at β(γ′)-carbon, which is likely due to pre-coordination of alkynyl moiety to Pd(II) that enabled β(γ′)-carbon more electrophilic toward nucleophilic attack. It is noteworthy that phosphines[18] and amines[23] underwent addition at the α(δ′)-carbon of **2i**, but Gilman reagents[18f] and the present studied hydrosulfonation reaction proceeded with β(γ′)-addition.

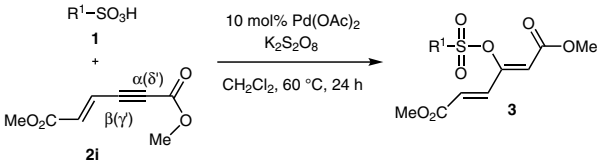
Scheme 3 displays the proposed reaction mechanism. First, alkynoates **2** coordinate with the Pd(II) to form intermediate **IA**. The OH group of sulfonic acids undergoes a nucleophilic attack at the β-position of intermediate **IA** in an antiperiplanar fashion to produce intermediate **IB** after the loss of a proton. Protonation of intermediate **IB** provides the (*Z*)-**3** (route **a**). In route **b**, protonation on the sulfonated carbon of intermediate **IB** allows a C–C bond rotation on intermediate **IC** and furnishes (*E*)-**3** on protonation of **IE**. Route **b** is relatively less plausible because a cation is next to an ester moiety in higher energy intermediate **IC**. This rationale accounts for the *Z*-stereoselective hydrosulfonation of propiolate esters. The Pd(II) species may be possibly reduced to Pd(0) during the reaction course through other slow-rate pathway,[24] thus rendering loss of active Pd(II) species. The oxidant $K_2S_2O_8$ was used to reoxidize Pd(0) to produce Pd(II) and thus complete the catalytic cycle.



Scheme 3 Proposed catalytic cycle

In conclusion, we have successfully demonstrated an effective methodology for the highly regio- and stereoselective syntheses of alkenyl sulfonates through Pd(II)-catalyzed aryl/alkylsulfonic acid addition to electron-deficient alkynoates. The alkenyl sulfonates can undergo a Sonogashira-type cross-coupling reaction with arylacetylenes by Pd(0)-catalysis to yield conjugated 1,3-enynoates (Supporting Information).

Table 2 Hydrosulfonation of Enynedioates[a]



Entry	R^1	Product	Yield (%)	*Z*/*E*
1	Ph **1b**	**3y**	79	*Z*
2	4-MeC_6H_4 **1a**	**3z**	89	*Z*
3	4-EtC_6H_4 **1c**	**3aa**	81	*Z*
4	2,5-$Me_2C_6H_3$ **1d**	**3ab**	76	*Z*
5	2,4,6-$Me_3C_6H_2$ **1e**	**3ac**	47	*Z*
6	Et **1k**	**3ad**[19]	71	*Z*

[a] Reactions were performed using 0.25 mmol of sulfonic acid **1**, 1.0 mmol of enynedioate **2**, 0.25 mmol of $K_2S_2O_8$, and 0.025 mmol of $Pd(OAc)_2$ in CH_2Cl_2 (4 mL) under N_2.

All reactions were carried out under N_2, unless otherwise mentioned. All the obtained products were characterized by ^1H NMR, ^{13}C NMR, mass spectrometry, and IR spectroscopy. Melting points were measured on an Electrothermal MEL-TEMP melting point apparatus. IR spectra were recorded on a Bruker spectrophotometer. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker-300 MHz spectrometer and chemical shifts were reported in parts per million (ppm, δ) with $CHCl_3$ as a reference. Standard abbreviations are used to describe proton coupling patterns; coupling constants *J* are quoted in Hz. ^{13}C NMR data were acquired at 75 or 100 MHz. $Pd(OAc)_2$, trifluoroacetic acid (TFA), alkyl or arylsulfonic acids, methyl or ethyl propiolates, and other reagents or chemicals were used as purchased without further purification.

Alkenyl Sulfonates 3a–x; General Procedure

To a pressure-affordable thick-wall glass tube containing aryl/alkylsulfonic acid **1** (0.15 mmol), alkyne **2** (0.90 mmol), $Pd(OAc)_2$ (1.7 mg, 0.0075 mmol), and $K_2S_2O_8$ (122 mg, 0.45 mmol) were added anhyd CH_2Cl_2 (5 mL). The tube was sealed with an O-ring and a teflon cap. The mixture was then stirred at 60 °C for 24 h. Upon completion of the reaction, CH_2Cl_2 was removed under reduced pressure. Elution with CH_2Cl_2/hexanes (2:1) gave the desired product (*Z*)-**3**.

Methyl (*Z*)-3-(Tosyloxy)acrylate (3a)

Yield: 35 mg (92%); white solid; mp 73–74 °C; R_f = 0.28 (CH_2Cl_2/hexanes, 5:1).

FT-IR (KBr): 2956, 2924, 2851, 1727, 1662, 1596, 1380, 1285, 1260, 1194, 1169, 1054, 936, 829, 809, 707, 692, 692, 597, 551 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.4 Hz, 2 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 6.95 (d, *J* = 7.0 Hz, 1 H), 5.32 (d, *J* = 7.0 Hz, 1 H), 3.68 (s, 3 H), 2.46 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2, 146.0, 144.6, 132.3, 130.1, 128.0, 105.8, 51.6, 21.7.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{11}H_{12}O_5S$: 256.0405; found: 256.0394.

Methyl (*E*)-3-(Tosyloxy)acrylate (3a'); Table 1, entry 5

Yield: 7 mg (18%); colorless liquid; R_f = 0.4 (hexanes/EtOAc, 5:1).

FT-IR (KBr): 3001, 2953, 2922, 2853, 1724, 1648, 1545, 1517, 1388, 1315, 1284, 1190, 1078, 936, 812, 787, 698, 548 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.3 Hz, 2 H), 7.69 (d, *J* = 12.2 Hz, 1 H), 7.39 (d, *J* = 8.3 Hz, 2 H), 5.69 (d, *J* = 12.2 Hz, 1 H), 3.72 (s, 3 H), 2.48 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.0, 150.9, 146.7, 132.3, 130.7, 128.5, 108.7, 52.2, 22.2.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{11}H_{12}O_5S$: 256.0405; found: 256.0408.

Ethyl (*Z*)-3-(Tosyloxy)acrylate (3b)

Yield: 36 mg (89%); white solid; mp 71–72 °C; R_f = 0.38 (CH_2Cl_2/hexanes, 2:1).

FT-IR (KBr): 2994, 2929, 2909, 1725, 1659, 1410, 1387, 1374, 1201, 1167, 1201, 1055, 1028, 942, 903, 838, 810, 709, 694, 665, 593, 553, 521 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.3 Hz, 2 H), 7.37 (d, *J* = 8.3 Hz, 2 H), 6.94 (d, *J* = 7.0 Hz, 1 H), 5.31 (d, *J* = 7.0 Hz, 1 H), 4.13 (q, *J* = 7.2 Hz, 2 H), 2.46 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.8, 145.9, 144.4, 132.3, 130.1, 128.0, 106.3, 60.5, 21.7, 14.1.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{12}H_{14}O_5S$: 270.0562; found: 270.0562.

Methyl (*Z*)-3-(Phenylsulfonyloxy)acrylate (3c)

Yield: 32 mg (89%); colorless liquid; R_f = 0.31 (CH_2Cl_2/hexanes, 2:1).

FT-IR (KBr): 3078, 3008, 2955, 1730, 1660, 1450, 1381, 1286, 1259, 1193, 1171, 1049, 994, 935, 829, 757, 735, 688, 603, 580 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 7.2 Hz, 2 H), 7.69–7.72 (m, 1 H), 7.57–7.60 (m, 2 H), 6.97 (d, *J* = 7.0 Hz, 1 H), 5.35 (d, *J* = 7.0 Hz, 1 H), 3.68 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6, 145.0, 135.7, 135.1, 129.9, 128.4, 106.5, 52.1.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{10}H_{10}O_5S$: 242.0249; found: 242.0250.

Ethyl (*Z*)-3-(Phenylsulfonyloxy)acrylate (3d)

Yield: 31 mg (80%); colorless liquid; R_f = 0.33 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 3096, 3077, 2985, 2940, 2907, 1726, 1660, 1450, 1385, 1194, 1176, 1048, 943, 842, 736, 688, 600, 580 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 7.9 Hz, 2 H), 7.68–7.72 (m, 1 H), 7.57–7.62 (m, 2 H), 6.96 (d, *J* = 6.9 Hz, 1 H), 5.34 (d, *J* = 6.9 Hz, 1 H), 4.13 (q, *J* = 7.2 Hz, 2 H), 1.23 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.7, 144.2, 135.3, 134.6, 129.5, 127.9, 106.6, 60.5, 14.1.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{11}H_{12}O_5S$: 256.0405; found: 256.0401.

Methyl (*Z*)-3-(4-Ethylphenylsulfonyloxy)acrylate (3e)

Yield: 38 mg (93%); colorless liquid; R_f = 0.38 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 2969, 2921, 2852, 1732, 1661, 1439, 1381, 1283, 1262, 1195, 1169, 1050, 997, 935, 873, 829, 693, 655, 599, 564, 533 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.4 Hz, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 6.96 (d, *J* = 7.0 Hz, 1 H), 5.32 (d, *J* = 7.0 Hz, 1 H), 3.68 (s, 3 H), 2.75 (q, *J* = 7.6 Hz, 2 H), 1.28 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2, 152.0, 144.7, 132.4, 128.9, 128.1, 105.7, 51.6, 28.9, 14.9.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{12}H_{14}O_5S$: 270.0562; found: 270.0559.

Ethyl (*Z*)-3-(4-Ethylphenylsulfonyloxy)acrylate (3f)

Yield: 35 mg (82%); colorless liquid; R_f = 0.53 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 2974, 2935, 2877, 1729, 1660, 1412, 1384, 1196, 1177, 1050, 942, 840, 696, 656, 596, 562 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.4 Hz, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 6.95 (d, *J* = 7.0 Hz, 1 H), 5.31 (d, *J* = 7.0 Hz, 1 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 2.75 (q, *J* = 7.6 Hz, 2 H), 1.21–1.30 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.8, 152.0, 144.4, 132.5, 128.9, 128.1, 106.3, 60.5, 29.0, 14.9, 14.1.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{13}H_{16}O_5S$: 284.0718; found: 284.0717.

Methyl (*Z*)-3-(2,5-Dimethylphenylsulfonyloxy)acrylate (3g)

Yield: 34 mg (84%); white solid; mp 77–78 °C; R_f = 0.33 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 3071, 2955, 2929, 2862, 1723, 1655, 1366, 1269, 1205, 1175, 1054, 947, 890, 824, 711, 601 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.79 (s, 1 H), 7.37 (d, *J* = 7.7 Hz, 1 H), 7.27 (d, *J* = 7.7 Hz, 1 H), 6.96 (d, *J* = 7.0 Hz, 1 H), 5.30 (d, *J* = 7.0 Hz, 1 H), 3.71 (s, 3 H), 2.70 (s, 3 H), 2.39 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2, 144.6, 136.3, 136.0, 135.3, 133.5, 132.7, 129.8, 104.9, 51.5, 20.7, 19.6.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{12}H_{14}O_5S$: 270.0562; found: 270.0560.

Ethyl (*Z*)-3-(2,5-Dimethylphenylsulfonyloxy)acrylate (3h)

Yield: 34 mg (80%); white solid; mp 62–63 °C; R_f = 0.28 (CH_2Cl_2/hexanes, 2:1).

FT-IR (KBr): 3074, 2984, 2926, 1717, 1657, 1367, 1264, 1204, 1178, 1052, 955, 834, 713, 594 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.79 (s, 1 H), 7.36 (d, *J* = 7.8 Hz, 1 H), 7.27 (d, *J* = 7.8 Hz, 1 H), 6.95 (d, *J* = 7.0 Hz, 1 H), 5.28 (d, *J* = 7.0 Hz, 1 H), 4.19 (q, *J* = 7.1 Hz, 2 H), 2.39 (s, 3 H), 2.70 (s, 3 H), 1.26 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.8, 144.3, 136.3, 136.0, 135.3, 133.5, 132.7, 129.8, 105.3, 60.5, 20.7, 19.7, 14.1.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{13}H_{17}O_5S$: 285.0797; found: 285.0789.

Methyl (*Z*)-3-(Mesitylsulfonyloxy)acrylate (3i)

Yield: 33 mg (78%); white solid; mp 72–73 °C; R_f = 0.5 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 3081, 3030, 2994, 2952, 2854, 1730, 1659, 1605, 1440, 1370, 1281, 1262, 1192, 1165, 1052, 998, 932, 854, 823, 692, 658, 601, 575, 538 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.00 (s, 2H), 6.96 (d, *J* = 7.1 Hz, 1H), 5.28 (d, *J* = 7.1 Hz), 3.71 (s, 3H), 2.69 (s, 6H), 2.32 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.3, 144.5, 140.3, 131.8, 130.1, 104.5, 51.5, 22.4, 21.0 ppm.

HRMS (EI^+): *m*/*z* [M^+] calcd for $C_{13}H_{16}O_5S$: 284.0718; found: 253.0534 (M – 31; $C_{12}H_{13}O_4S$).

Ethyl (*Z*)-3-(Mesitylsulfonyloxy)acrylate (3j)

Yield: 29 mg (65%) (*Z*/*E* = 99:1); white solid; R_f = 0.53 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 3103, 2990, 2943, 2909, 1728, 1657, 1603, 1566, 1386, 1369, 1266, 1199, 1161, 1097, 1028, 943, 899, 834, 811, 738, 717, 700, 661, 594, 575, 540 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.00 (s, 2 H), 6.94 (d, *J* = 7.1 Hz, 1 H), 5.26 (d, *J* = 7.1 Hz, 1 H), 4.17 (q, *J* = 7.2 Hz, 2 H), 2.69 (s, 6 H), 2.32 (s, 3 H), 1.26 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.0, 144.4, 144.2, 140.3, 131.9, 130.2, 104.9, 60.5, 22.5, 21.1, 14.1.

HRMS (EI^+): *m*/*z* [M^+] calcd for $C_{14}H_{18}O_5S$: 298.0875; found: 298.0858.

Methyl (*Z*)-3-(4-Chlorophenylsulfonyloxy)acrylate (3k)

Yield: 31 mg (75%); white solid; mp 62–63 °C; R_f = 0.48 (CH_2Cl_2/hexanes, 2:1).

FT-IR (KBr): 3099, 3012, 2960, 2925, 2853, 1726, 1658, 1387, 1193, 1170, 1091, 1049, 933, 822, 808, 706, 687, 620, 594, 526 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.8 Hz, 2 H), 7.57 (d, *J* = 8.8 Hz, 2 H), 6.95 (d, *J* = 6.9 Hz), 5.38 (d, *J* = 6.9 Hz, 1 H), 3.68 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.9, 144.2, 141.5, 133.7, 129.8, 129.4, 106.6, 51.6.

HRMS (EI^+): *m*/*z* [M^+] calcd for $C_{10}H_9ClO_5S$: 275.9859; found: 275.9860.

Ethyl (*Z*)-3-(4-Chlorophenylsulfonyloxy)acrylate (3l)

Yield: 32 mg (74%); white solid; mp 72–73 °C; R_f = 0.48 (CH_2Cl_2/hexanes, 2:1).

FT-IR (KBr): 3100, 2991, 1722, 1657, 1391, 1274, 1204, 1172, 1094, 1051, 1028, 945, 903, 823, 809, 766, 706, 694, 631, 588, 521 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.8 Hz, 2 H), 7.56 (d, *J* = 8.8 Hz, 2 H), 6.94 (d, *J* = 6.9 Hz, 1 H), 5.37 (d, *J* = 6.9 Hz, 1 H), 4.14 (q, *J* = 7.2 Hz, 2 H), 1.24 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.4, 144.0, 141.4, 133.7, 129.8, 129.3, 107.0, 60.5, 14.0.

HRMS (EI^+): *m*/*z* [M^+] calcd for $C_{11}H_{11}ClO_5S$: 290.0016; found: 290.0012.

Methyl (*Z*)-3-(2,4-Dinitrophenylsulfonyloxy)acrylate (3m)

Yield: 8.5 mg (17%); white solid; mp 87–88 °C: R_f = 0.33 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 3109, 2957, 2921, 2850, 1737, 1660, 1544, 1443, 1350, 1166, 1037, 991, 938, 829, 751, 696, 618, 588 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 2.0 Hz, 1 H), 8.55–8.65 (m, 2 H), 7.04 (d, *J* = 6.8 Hz, 1 H), 5.54 (d, *J* = 6.8 Hz, 1 H), 3.72 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.7, 150.7, 148.2, 143.3, 134.3, 133.2, 127.4, 120.7, 107.1, 51.9.

HRMS (EI^+): *m*/*z* [M^+] calcd for $C_{10}H_8N_2O_9S$: 331.9951; found: 300.9756 (M – 31, $C_9H_5N_2O_8S$).

Methyl (*Z*)-3-(Naphthalen-2-ylsulfonyloxy)acrylate (3n)

Yield: 35 mg (79%); colorless liquid; R_f = 0.43 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 3081, 3009, 2953, 2924, 2853, 1730, 1660, 1438, 1381, 1184, 1184, 1169, 1050, 933, 862, 816, 751, 695, 656, 617, 590, 550 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.54 (s, 1 H), 7.89–8.03 (m, 4 H), 7.62–7.73 (m, 2 H), 7.02 (d, *J* = 7.0 Hz, 1 H), 5.33 (d, *J* = 7.0 Hz, 1 H), 3.65 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.1, 144.6, 135.5, 131.9, 131.7, 130.0, 129.9, 129.8, 129.4, 128.0(2C), 122.1, 105.9, 51.5.

HRMS (EI^+): *m*/*z* [M^+] calcd for $C_{14}H_{12}O_5S$: 292.0405; found: 292.0400.

Ethyl (*Z*)-3-(Naphthalen-2-ylsulfonyloxy)acrylate (3o)

Yield: 37.6 mg (82%); colorless liquid; R_f = 0.4 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 3080, 2984, 2937, 2906, 1726, 1658, 1384, 1271, 1174, 1048, 1020, 950, 861, 816, 751, 699, 655, 617, 550 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.53 (s, 1 H), 7.89–8.03 (m, 4 H), 7.62–7.73 (m, 2 H), 7.01 (d, *J* = 7.0 Hz, 1 H), 5.33 (d, *J* = 7.0 Hz, 1 H), 4.11 (q, *J* = 7.2 Hz, 2 H), 1.20 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.6, 144.4, 135.5, 131.9, 131.7, 130.0, 129.9, 129.8, 129.4, 128.0(2C), 122.1, 106.4, 60.5, 14.0.

HRMS (EI^+): *m*/*z* [M^+] calcd for $C_{15}H_{14}O_5S$: 306.0562; found: 306.0568.

Ethyl (*Z*)-3-(Naphthalen-1-ylsulfonyloxy)acrylate (3p)

Yield: 25.7 mg (56%); colorless liquid; R_f = 0.38 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 3083, 2983, 2933, 1726, 1659, 1509, 1378, 1273, 1174, 1048, 979, 941, 842, 805, 770, 698, 586, 503 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.69 (d, *J* = 8.6 Hz, 1 H), 8.31 (dd, *J* = 1.1, 7.4 Hz, 1 H), 8.17 (d, *J* = 8.3 Hz, 1 H), 7.78–8.03 (m, 1 H), 7.55–7.78 (m, 3 H), 6.95 (d, *J* = 7.0 Hz, 1 H), 5.24 (d, *J* = 7.0 Hz, 1 H), 4.08 (q, *J* = 7.2 Hz, 2 H), 1.16 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.7, 143.9, 136.3, 130.8, 130.3, 129.0, 128.8, 128.2, 128.0, 127.5, 124.8, 123.9, 106.1, 60.5, 14.0.

HRMS (EI^+): *m*/*z* [M^+] calcd for $C_{15}H_{14}O_5S$: 306.0562; found: 306.0561.

Methyl (*Z*)-3-(Methylsulfonyloxy)acrylate (3s)

Yield: 17.8 mg (66%); colorless liquid; *Rf* = 0.2 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 3006, 2957, 2851, 1729, 1436, 1317, 1294, 1256, 1070, 990, 822, 754 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.98 (d, *J* = 6.9 Hz, 1 H), 5.45 (d, *J* = 6.9 Hz, 1 H), 3.73 (s, 3 H), 3.19 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2, 144.2, 106.3, 51.7, 38.6.

HRMS (EI^+): *m*/*z* [M^+] calcd for $C_5H_8O_5S$: 180.0092; found: 180.0099.

Ethyl (*Z*)-3-(Methylsulfonyloxy)acrylate (3t)

Yield: 20 mg (68%); colorless liquid; R_f = 0.3 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 3086, 3030, 2987, 2939, 2909, 1726, 1660, 1407, 1374, 1257, 1167, 1054, 1023, 971, 944, 900, 844, 795, 685, 579, 525 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.98 (d, *J* = 6.9 Hz, 1 H), 5.47 (d, *J* = 6.9 Hz, 1 H), 4.21 (q, *J* = 7.1 Hz, 2 H), 3.21 (s, 3 H), 1.29 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2, 144.4, 107.3, 61.1, 39.0, 14.6.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_6H_{10}O_5S$: 194.0249; found: 148.9902 (M – 45, $C_4H_5O_4S$).

Methyl (*Z*)-3-(Ethylsulfonyloxy)acrylate (3u)

Yield: 25 mg (86%); colorless liquid; R_f = 0.23 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 3085, 2989, 2954, 2852, 1729, 1659, 1440, 1398, 1370, 1283, 1244, 1201, 1164, 1067, 1042, 997, 936, 870, 829, 782, 747, 674, 539 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.01 (d, *J* = 6.9 Hz, 1 H), 5.40 (d, *J* = 6.9 Hz, 1 H), 3.73 (s, 3 H), 3.31 (q, *J* = 7.4 Hz, 2 H), 1.49 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.3, 144.6, 105.2, 51.6, 46.7, 8.0.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_6H_{10}O_5S$: 194.0249; found: 194.0243.

Methyl (*Z*)-3-(Tosyloxy)hex-2-enoate (3v)

Yield: 22.7 mg (51%); colorless liquid; R_f = 0.35 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 3094, 3073, 2966, 2877, 1736, 1672, 1598, 1460, 1374, 1380, 1289, 1205, 1174, 1136, 1091, 1018, 934, 815, 767, 710, 692, 972, 633, 551, 524 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.3 Hz, 2 H), 7.36 (d, *J* = 8.3 Hz, 2 H), 5.53 (s, 1 H), 3.59 (s, 3 H), 2.60 (s, 3 H), 2.36 (t, *J* = 7.5 Hz, 2 H), 1.51–1.61 (m, 2 H), 0.90 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.9, 160.4, 145.8, 133.9, 130.1, 128.8, 110.5, 51.8, 37.5, 22.1, 20.0, 13.6.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{14}H_{18}O_5S$: 298.0875; found: 298.0882.

Methyl (*Z*)-3-(Methylsulfonyloxy)hex-2-enoate (3w)

Yield: 10.3 mg (31%); colorless liquid; R_f = 0.33 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 2964, 2938, 2878, 2850, 1730, 1671, 1520, 1464, 1436, 1358, 1229, 1210, 1168, 1018, 975, 938, 914, 888, 793, 631, 523 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.62 (s, 1 H), 3.72 (s, 3 H), 3.33 (s, 3 H), 2.45 (t, *J* = 7.4 Hz, 2 H), 1.60–1.71 (m, 2 H), 0.97 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6, 160.9, 109.2, 51.5, 39.6, 37.9, 19.4, 13.2.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_8H_{14}O_5S$: 222.0562; found: 222.0558.

Ethyl (*Z*)-3-(Tosyloxy)but-2-enoate (3x)

Yield: 40.5 mg (95%); colorless liquid; R_f = 0.4 (hexanes/EtOAc, 2:1).

FT-IR (KBr): 3073, 2984, 2929, 1729, 1676, 1598, 1445, 1372, 1303, 1277, 1211, 1175, 1366, 1093, 1048, 1018, 924, 859, 816, 762, 711, 692, 655, 606, 553 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.1 Hz, 2 H), 7.28 (d, *J* = 8.1 Hz, 2 H), 5.42 (s, 1 H), 3.98 (q, *J* = 7.1 Hz, 2 H), 2.38 (s, 3 H), 2.03 (s, 3 H), 1.13 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.3, 156.6, 145.8, 133.8, 130.1, 128.7, 111.2, 60.7, 22.1, 22.0, 14.5.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{13}H_{16}O_5S$: 284.0718; found: 284.0711.

Dialkyl (2*Z*,4*E*)-3-(Aryl/Alkylsulfonyloxy)hexa-2,4-dienedioates 3y,z and 3aa–ad

To a pressure-affordable thick-wall glass tube containing aryl/alkylsulfonic acid **1** (0.25 mmol), enyndioate **2i** (168 mg, 1.00 mmol), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and $K_2S_2O_8$ (68 mg, 0.25 mmol) were added anhyd CH_2Cl_2 (4 mL) under N_2. The tube was sealed with an O-ring and a teflon cap. The mixture was then stirred at 60 °C for 24 h. Upon completion of the reaction, CH_2Cl_2 was removed under reduced pressure. Elution with hexanes/EtOAc (4:1) gave the respective desired products **3y**,**z** and **3aa**–**ad**.

Dimethyl (2*Z*,4*E*)-3-(Phenylsulfonyloxy)hexa-2,4-dienedioate (3y)

Yield: 64 mg (79%); white solid; mp 96–77 °C; R_f = 0.3 (hexanes/EtOAc, 4:1).

FT-IR (KBr): 3071, 3004, 2953, 2919, 2850, 1722, 1620, 1434, 1384, 1280, 1222, 1176, 1091, 939, 853, 738, 687, 608, 670, 522 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98–8.01 (m, 2 H), 7.68–7.73 (m, 1 H), 7.56–7.61 (m, 2 H), 7.04 (d, *J* = 15.5 Hz, 1 H), 6.09 (d, *J* = 15.5 Hz, 1 H), 5.99 (s, 1 H), 3.72 (s, 3 H), 3.66 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.5, 163.0, 150.9, 137.2, 135.9, 134.6, 129.3, 128.4, 126.3, 118.0, 52.1, 51.9.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{14}H_{14}O_7S$: 326.0460; found: 326.0462.

Dimethyl (2*Z*,4*E*)-3-[(4-Methylphenyl)sulfonyloxy]hexa-2,4-dienedioate (3z)

Yield: 76 mg (89%); white solid; mp 94–95 °C; R_f = 0.25 (hexanes/EtOAc, 4:1).

FT-IR (KBr): 3068, 2992, 2948, 1730, 1618, 1434, 1384, 1309, 1281, 1227, 1173, 991, 934, 900, 760, 686, 666, 598, 542, 522 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.02 (d, *J* = 15.6 Hz, 1 H), 6.06 (d, *J* = 15.6 Hz, 1 H), 5.97 (s, 1 H), 3.70 (s, 3 H), 3.64 (s, 3 H), 2.43 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.5, 163.0, 150.9, 145.9, 137.2, 132.7, 129.8, 128.4, 126.1, 118.0, 52.0, 51.8, 21.6.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{15}H_{16}O_7S$: 340.0617; found: 340.0612.

Dimethyl (2*Z*,4*E*)-3-[(4-Ethylphenyl)sulfonyloxy]hexa-2,4-dienedioate (3aa)

Yield: 72 mg (81%); white solid; mp 92–93 °C; R_f = 0.25 (hexanes/EtOAc, 4:1).

FT-IR (KBr): 3434, 3072, 2955, 2850, 1724, 1620, 1436, 1386, 1282, 1223, 1176, 1093, 1009, 975, 940, 840, 761, 681, 604, 561, 532 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.4 Hz, 2 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 7.02 (d, *J* = 15.6 Hz, 1 H), 6.03 (d, *J* = 15.6 Hz, 1 H), 5.98 (s, 1 H), 3.70 (s, 3 H), 3.66 (s, 3 H), 2.73 (q, *J* = 7.8 Hz, 2 H), 1.24 (t, *J* = 7.8 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.6, 163.2, 152.1, 151.0, 137.2, 133.1, 128.8, 128.6, 126.2, 118.1, 52.1, 51.9, 29.0, 15.1.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{16}H_{18}O_7S$: 354.0773; found: 354.0775.

Dimethyl (2*Z*,4*E*)-3-[(2,5-Dimethylphenyl)sulfonyloxy]hexa-2,4-dienedioate (3ab)

Yield: 67 mg (76%); yellow liquid; R_f = 0.25 (hexanes/EtOAc, 4:1).

FT-IR (KBr): 3069, 2998, 2954, 2847, 1725, 1620, 1493, 1369, 1282, 1222, 1178, 1031, 975, 938, 856, 764, 707, 638, 585, 553, 491 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (s, 1 H), 7.32 (d, *J* = 7.7 Hz, 1 H), 7.25 (d, *J* = 7.7 Hz, 1 H), 7.03 (d, *J* = 15.6 Hz, 1 H), 6.06 (d, *J* = 15.6 Hz, 1 H), 5.95 (s, 1 H), 3.69 (s, 3 H), 3.51 (s, 3 H), 2.68 (s, 3 H), 2.32 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3, 162.8, 150.8, 137.5, 136.2, 135.3, 134.9, 134.8, 132.5, 129.6, 125.7, 117.7, 51.8, 51.5, 20.4, 20.0.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{16}H_{18}O_7S$: 354.0773; found: 354.0777.

Dimethyl (2*Z*,4*E*)-3-(Mesitylsulfonyloxy)hexa-2,4-dienedioate (3ac)

Yield: 43 mg (47%); white solid; mp 110–111 °C; R_f = 0.35 (hexanes/EtOAc, 4:1).

FT-IR (KBr): 3074, 2985, 2952, 2926, 2852, 1725, 1620, 1437, 1374, 1281, 1222, 1175, 1033, 974, 939, 855, 762, 726, 683, 604, 537 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.07 (d, *J* = 15.6 Hz, 1 H), 7.00 (s, 2 H), 6.12 (d, *J* = 15.6 Hz, 1 H), 5.96 (s, 1 H), 3.72 (s, 3 H), 3.53 (s, 3 H), 2.63 (s, 6 H), 2.31 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.6, 163.1, 151.3, 144.0, 139.8, 137.9, 132.3, 131.8, 126.0, 117.8, 52.0, 51.7, 22.8, 21.0.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{17}H_{20}O_7S$: 368.0930; found: 368.0927.

Diphenyl (2*Z*,4*E*)-3-(Ethylsulfonyloxy)hexa-2,4-dienedioate (3ad)

Yield: 49 mg (71%); white solid; mp 98–100 °C; R_f = 0.28 (hexanes/EtOAc, 4:1).

FT-IR (KBr): 3073, 2993, 2949, 2844, 1717, 1614, 1436, 1356, 1313, 1288, 1221, 1171, 996, 938, 904, 872, 789, 760, 685, 592, 533, 458 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.15 (d, *J* = 15.6 Hz, 1 H), 6.65 (d, *J* = 15.6 Hz, 1 H), 5.99 (s, 1 H), 3.77 (s, 3 H), 3.74 (s, 3 H), 3.61 (q, *J* = 7.5 Hz, 2 H), 1.56 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 163.2, 152.0, 137.9, 127.4, 116.6, 52.1, 51.9, 47.9, 8.1.

HRMS (EI$^+$): *m*/*z* [M$^+$] calcd for $C_{10}H_{14}O_7S$: 278.0460; found: 278.0458.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588501. Scanned photocopies of NMR ($CDCl_3$) spectral data for all new compounds and X-ray crystallographic (CIF) data of compounds **3a**, **3g**, **3k**, and **3ad** are included.

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