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One-Step Addition of Sulfonic Acids to Acetylene Derivatives: An Alternative and Stereoselective Approach to Vinyl Triflates and Fluorosulfonates

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Dedicated to G. Olah on the occasion of his 80th birthday

Keywords: Superacidic systems / Alkynes / Vinyl triflates / Sulfones / Carbocations

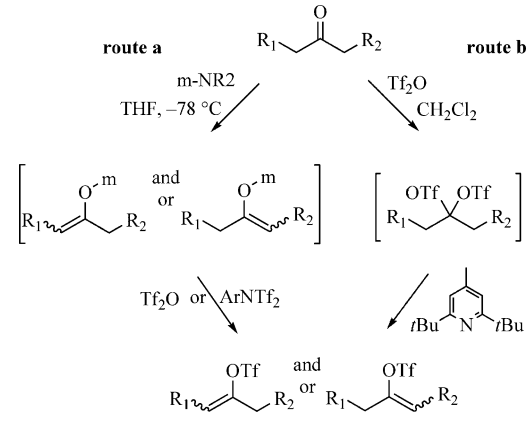
Acetylenic acids and esters as well as acetylenic ketones were efficiently and stereoselectively converted in one step to the corresponding vinyl triflates or fluorosulfonates in triflic or fluorosulfonic acids. Depending on the reaction conditions the *E* or the *Z* isomer can be obtained very conveniently in high isolated yields.

Introduction

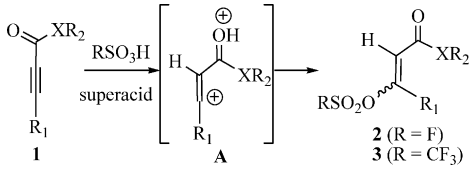
Vinyl triflates are important building blocks in organic synthesis,[1] especially as intermediates for C–C bond formation by Pd-catalyzed coupling reactions.[1–2] Vinyl fluorosulfonates have also been used as precursors for such coupling reactions, although to a much less extent.[3]

Surprisingly enough, only two routes are used to prepare these important intermediates and they are mainly obtained from ketones.[4] Deprotonation of the ketone and further trapping of the so-formed enolate by a triflating agent leads to vinyl triflates (Scheme 1, route a).[1,4,5] They can also be produced by direct triflation of the ketone to yield a *gem*-bis(triflate) intermediate,[6] followed by elimination with a bulky base (Scheme 1, route b).[7] The main problem associated with these methods is the regio- and stereocontrol. In the former method, the regio- and stereoselectivity is due to the first enolization step, whereas in the latter, almost no control can be achieved. It should be noted that side reactions have been reported to occur with these methods.[8]

Expanding the access to vinyl triflates and related reagents, especially through a stereoselective route, is therefore appealing. On the basis of our work on alkyne derivatives[9–10] and from a pioneering investigation,[11] we reasoned that substituted propynones and propynoic acid derivatives **1** could be used as precursors of vinyl triflates or other sulfonates (e.g. **2**, **3**; Scheme 2). Protonation of such compounds in strong acids[12] would regioselectively generate a vinyl cation[13–14] in situ (Scheme 2, **A**), which could be trapped by sulfonic acid to afford the corresponding vinyl sulfonates. Moreover, the resulting dicationic species **A** ex-



Scheme 1. Usual preparation of vinyl triflates (Ar = Ph, pyridine, or 5-chloropyridine).



Scheme 2. Mechanistic hypothesis for an alternative route to vinyl sulfonates (X = O, CH_2).

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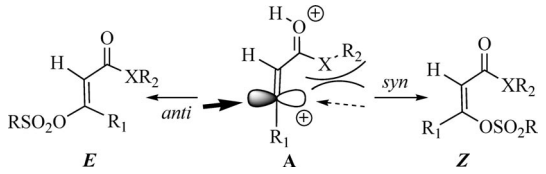
hibits a distinct environment at the vinylic cationic site (Scheme 3). With the protonated carbonyl group on one side, this vinylic cation should be trapped on the other side (*anti* addition), which would lead to the corresponding vinyl sulfonate with *E* stereoselectivity.



Scheme 3. Basis for expected stereoselectivity.

Results and Discussion

To investigate this reaction, we prepared variously substituted propynoic acid derivatives and propynones (Table 1).[15] Upon dissolution in either triflic acid or fluorosulfonic acid at –30 °C, the evolution of the starting materials can easily be monitored by NMR spectroscopy. Disappearance of the spectroscopic signals of the starting material and the appearance of signals for the vinyl sulfonates as well as their relative *E*/*Z* ratio can indeed be easily determined by ^{1}H NMR spectroscopy.

The efficiency of the reaction was first investigated with phenyl-substituted propynoic acid **1a** (Table 1, Entry 1). When **1a** was dissolved in neat fluorosulfonic acid at –80 °C, protonation of the acid group can easily be detected but no further reaction occurred. Upon gradual warming of the reaction mixture, two products were formed. At –40 °C, NMR spectroscopic experiments cleanly showed the disappearance of protonated **1a** and the gradual formation of two series of signals; sharp ^{1}H NMR signals at δ = 6.62 and 6.71 ppm of unequal intensity were assigned to the expected isomeric vinyl fluorosulfonates **2a**. Under these conditions, the isomeric ratio was 90:10, in favor of the *E* fluorosulfonate as demonstrated by the typical shift of the vinylic proton and confirmed by NOE.

In triflic acid, **1a** was also converted into the expected addition product **3a** at low temperature (–30 °C) (Table 1, Entry 2). Interestingly enough, the stereoselectivity was higher under these conditions, probably reflecting larger interactions during the addition of a larger sulfonate.

Similar results were obtained from the corresponding methyl ester **1b** (Table 1, Entries 3–5). Fluorosulfonic acid and triflic acid added to **1b** but at higher temperature (0 °C instead of –30 °C). The expected mixtures of adducts **2b** and **3b** were obtained quantitatively, again in favor of the *E* isomer but with different selectivities. The fluorosulfonic addition was surprisingly less stereoselective (Table 1, Entry 3 vs. 1), whereas the trifluorosulfonic addition was slightly better (Table 1, Entry 4 vs. 2). A preparative version gave the vinyl triflate in high yield and high *E* selectivity without any problem (Table 1, Entry 5). Careful work up allowed isolation of the product in high yields (95%) as a mixture of isomers *without isomerization*, as the same ratio was still observed (Table 1, Entry 5 vs. 4). The corresponding ethyl ester **1c** mostly gave the same results, adducts **2c** and **3c** exhibited the same stereoselection (Table 1, Entries 6 and 7). The stereochemistry of these compounds was determined by NOESY experiments, and spatial correlations were characterized for each isomer (Figure 1).

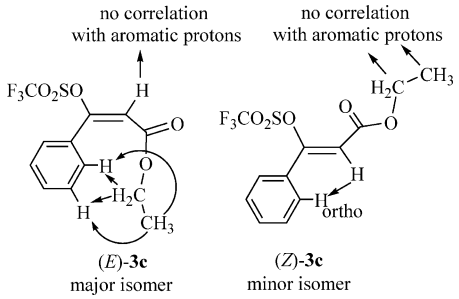


Figure 1. NOESY and ROESY data for the isolated triflates.

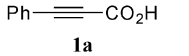
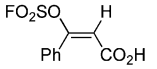
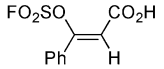
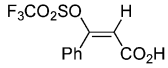
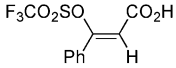
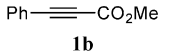
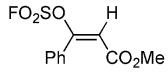
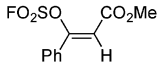
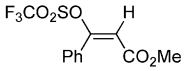
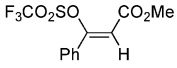
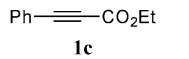
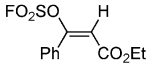
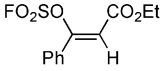
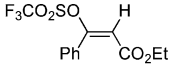
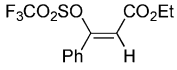
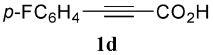
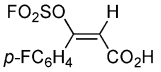
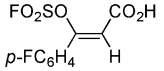
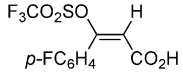
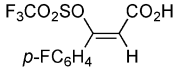
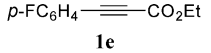
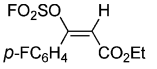
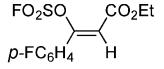
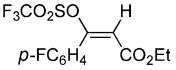
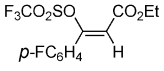
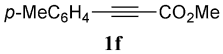
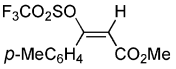
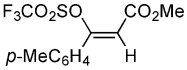
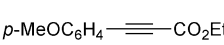
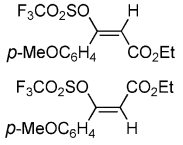
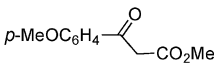
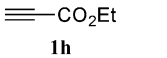
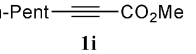
To further look at possible electronic effects and to expand the scope of this method, propynoates bearing aromatic groups of various electron density were also prepared and studied.

para-Fluorophenyl-substituted propiolic acid **1d** reacted similarly to nonsubstituted product **1a**. Both fluorosulfonates and triflates **2d** and **3d** were quantitatively obtained with a similar selectivity for the fluorosulfonate and with a comparable selectivity for the triflate (Table 1, Entries 8 vs. 1 and 9 vs. 2, respectively). Corresponding ester **1e** also yielded expected adducts **2e** and **3e**, and the *E* selectivity was higher for the triflic acid addition (Table 1, Entry 11 vs. 10). It thus seems that an electron-withdrawing group does not interfere much with the sulfonic acid addition across the triple bond.

In sharp contrast, the presence of an electron-donating group on the propynoate system dramatically changed its reactivity. *para*-Methyl-substituted **1f** did not give the expected addition of fluorosulfonic acid, but instead yielded side products. Among them, dimers resulting from self-addition were mostly isolated (Table 1, Entry 12).[16] In triflic acid, the expected addition, however, did occur and afforded expected adducts **3f** with very high *E* stereoselectivity and excellent isolated yield (Table 1, Entry 13). With a more electron-donating methoxy group, **1g** in triflic acid gave expected adduct **3g**, but surprisingly, an equivalent amount of the hydrolysis product, β-keto ester **4g**, was also isolated (Table 1, Entry 14). It seems that more electron-enriched adducts were too sensitive to be isolated and that such vinyl triflates were subsequently hydrolyzed to the corresponding ketones. It is worth noting that unsubstituted or alkyl-substituted ynoates did not react with sulfonic acids (e.g. **1h,i**) and the starting material was recovered quantitatively (Table 1, Entries 15 and 16)

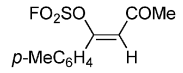
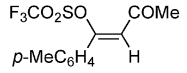
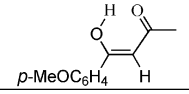
For comparison purposes, the addition reactions of ynones were also studied (Table 2). Hex-3-yn-2-one (**5a**) was used as a standard analog of nonreactive methyl oct-2-ynoate (**1i**), and but-3-yn-2-ones **5b-d** carrying phenyl group of increasing electron-donating properties were used as ana-

Table 1. Synthesis of vinyl fluorosulfonates and vinyl trifluoromethylsulfonates (triflates) by the addition of triflic or fluorosulfonic acid to the triple bond of propynoate derivatives.

	Acetylenic derivative	Reaction conditions	Yields [%]	*E*:*Z* Ratio[a]	Products *E* isomer		*Z* isomer
1	 **1a**	FSO_3H, –40°C, 0.5h	100[a]	90:10		**2a**	
2	**1a**	CF_3SO_3H, –30°C, 0.5h	100[a]	93:7		**3a**	
3	 **1b**	FSO_3H, 0°C, 0.5h	100[a]	78:22		**2b**	
4	**1b**	CF_3SO_3H,	100[a]	95:5		**3b**	
5		0°C, 0.5h	90[b]	95:5			
6	 **1c**	FSO_3H, 0°C, 0.5h	100[a]	79:21		**2c**	
7	**1c**	CF_3SO_3H/ CH_2Cl_2, 0°C, 0.5h	94[b]	94–6		**3c**	
8	 **1d**	FSO_3H, –40°C, 0.5h	100[a]	87:13		**2d**	
9	**1d**	CF_3SO_3H, –30°C, 0.5h	100[a]	85:15		**3d**	
10	 **1e**	FSO_3H, –30°C, 0.5h	100[a]	85:15		**2e**	
11	**1e**	CF_3SO_3H/ CH_2Cl_2, –30°C, 1h	90[b]	91:9		**3e**	
12	 **1f**	FSO_3H, 0°C, 1h	100[a]	–	dimers[16]	–	dimers[16]
13	**1f**	CF_3SO_3H/ CH_2Cl_2, –30°C, 1h	91[a]	96:4		**3f**	
14	 **1g**	CF_3SO_3H/ CH_2Cl_2, –30°C, 0.5h	39(**3g**)/ 42(**4g**)[b]	93:7		**3g**	 **4g**
15	 **1h**	CF_3SO_3H/ CH_2Cl_2, 25 °C, 2 h	0	–	quantitative recovery of the starting material		
16	 **1i**	CF_3SO_3H/ CH_2Cl_2, 25°C, 1.5h		–	quantitative recovery of the starting material		

[a] Yields and *E*/*Z* ratio determined by NMR spectroscopy. [b] Isolated yields.

Table 2. Synthesis of vinyl fluorosulfonates and vinyl trifluoromethylsulfonates (triflates) by the addition of triflic or fluorosulfonic acid to the triple bond of ynone derivatives (isolated yields).

	Acetylenic derivative	Reaction conditions	Yields [%]	*E*:*Z* Ratio	Products
1	Et—≡—COMe **5a**	CF_3SO_3H 50°C, 2h	0	–	quantitative recovery of the starting material
2	Ph—≡—COMe **5b**	CF_3SO_3H 0°C, 2h	0	–	quantitative recovery of the starting material
3	*p*-MeC_6H_4—≡—COMe **5c**	FSO_3H, –30°C, 1h	80	0:100	– **6c** 
4	**5c**	CF_3SO_3H/CH_2Cl_2, 25°C, 15min	87	0:100	– **7c** 
5	*p*-$MeOC_6H_4$—≡—COMe **5d**	CF_3SO_3H, –30°C, 0.5h	91	0:100	– **8d** 

logs of **1b**,**f**,**g**, respectively. As expected from the above-mentioned results, **5a** did not react, but surprisingly, phenyl derivative **5b** also did not react (Table 2, Entries 1 and 2). Only the enriched *para*-methyl- and methoxy-substituted derivatives **5c** and **5d** cleanly gave the expected adducts. Fluorosulfonic and triflic acid treatment of **5c** indeed yielded **6c** and **7c**, respectively, as the exclusive product (Table 2, Entries 3 and 4). For *para*-methoxyphenyl-substituted butyn-2-one **5d**, the triflic acid adduct was not stable enough, and as for its propynoate counterpart **1g**, we could only isolate the hydrolysis product, enol **8d** (Table 2, Entry 5).

Strikingly, these addition products exhibited a completely reverse in stereochemistry in comparison to the ynoate adducts; the *Z* isomer was the exclusive product. NOE spectroscopic experiments allowed the unambiguous assignment of proton signals in these addition products (Figure 2).

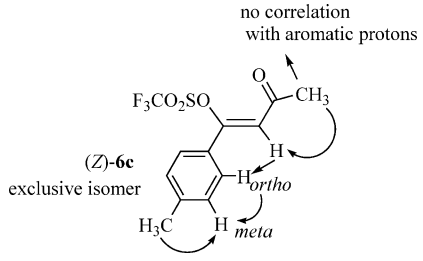


Figure 2. NOESY and ROESY data for isolated triflates.

Moreover, a ROESY experiment allowed us to confirm this stereochemistry and even to estimate the H_{vinyl}–H_{ortho} distance between the vinyl proton and the aromatic *ortho* protons (Figure 2).

According to X-ray literature data, the distance CH_{3Ar}–H_{meta} is around 2.5 Å (e.g. 2.465–2.475 Å in Figure 3).[17] With this distance as a reference, the relative intensities of cross-peak correlations CH_{3Ar}–H_{meta} and H_{vinyl}–H_{ortho} observed in (*Z*)-**6c** suggested a distance H_{vinyl}–H_{ortho} roughly around 3 Å, which is close to the literature data for a *cis* configuration of the vinyl proton and the protons in *ortho* position of the neighboring aromatic ring (e.g. 2.423–2.666 Å in Figure 3), whereas for the *trans* configuration the distance is higher than 3.7 Å (e.g. 3.741–3.809 Å in Figure 3).

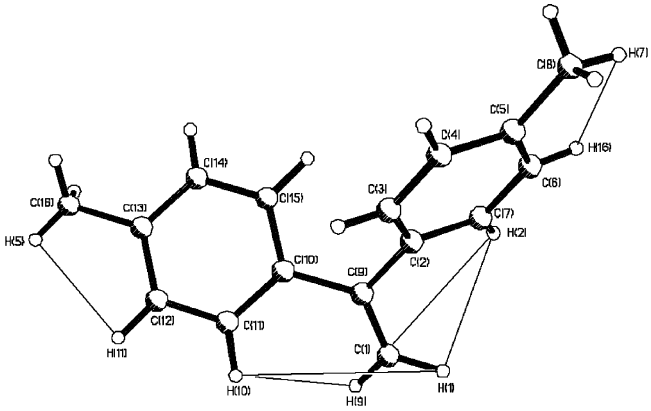
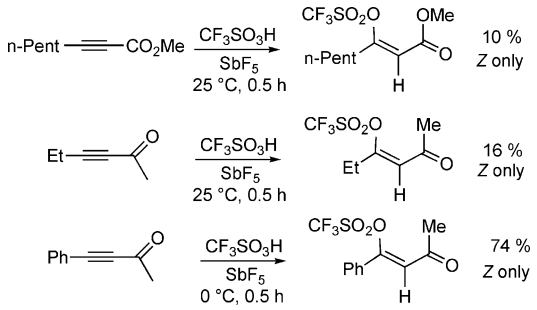


Figure 3. Basis for ROESY correlations and distance estimations. Distances [Å]: H(5)–H(11) 2.475, H(10)–H(9) 2.423, H(2)–H(1) 2.666, H(10)–H(1) 3.741, H(2)–H(9) 3.809.

Discussions and Mechanism

Although ynones seem less reactive than ynoates under the same conditions, some similarities were observed in each series. Unsubstituted or alkyl-substituted derivatives did not reacted with sulfonic acid, whereas an aryl group usually induced fast addition. The results obtained from the ynoates and ynones clearly reflected the reactivity differ-

ences of the triple bond, which can be correlated to the HOMO levels: the more conjugated the substituent, the higher the HOMO.[18] However, under more acidic conditions (mixtures of CF_3SO_3H/SbF_5 having $H_0 \approx -20$), the initially nonreactive ynoates and ynones eventually underwent sulfonic acid additions (Scheme 4). This clearly highlighted the key role of protonation in the reaction mechanism.



Scheme 4. Reactions of ynoates and ynones in a superacidic medium.

Interestingly enough, under such superacidic conditions ($H_0 \approx -20$), the addition stereoselectivity is always in strong favor of the *Z* isomer (the *E* was not detected), whereas in triflic or fluorosulfonic acids, the stereoselectivity seems dependent on the structure: the ynoates give *E* adducts and the ynones give *Z* adducts. These results suggest that adduct equilibration could occur depending on the acidity of the medium.

To address this point, we studied the stability and the possible isomerization of some adducts. We carried out reactions at different temperatures and with prolonged reaction times (Table 3). Such a study could also shed some light on the mechanism of these reactions. Adduct equilibration as well as reversibility of sulfonate addition to conjugated acetylene carbonyl compounds could indeed be envisaged in superacids.

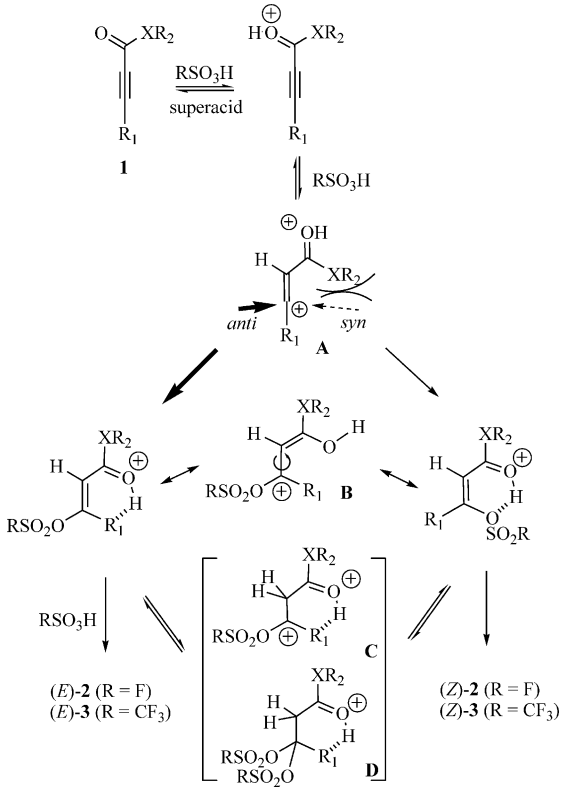
In fluorosulfonic acid, phenylpropynoic acid (**1a**) gave the corresponding vinylic fluorosulfonate, and the *E* isomer was the major adduct (Table 3, Entry 1; *E*/*Z*, 90:10) below –30 °C but at 0 °C, the proportion of *Z* isomer started to increase (Table 3, Entry 2; 76:24). Similar results were obtained with *para*-fluorophenylpropiolic acid (**1d**) (Table 3, Entries 3, 4 vs. 1, 2) as well as with methyl tolylpropynoate (**1f**) and triflic acid (Table 3, Entries 5, 6 vs. 1, 2). Interestingly, after 6 d at –20 °C in triflic acid, the isomer distribution of the **1f** adducts was found to be completely reversed (*E*:*Z*, 9:91). An increase in both the reaction time and the temperature thus plays a key role on the isomeric ratio of sulfonic acid addition. In contrast, *Z* isomers did not evolve further under similar conditions.

It is thus clear that equilibration occurred. These results may be interpreted by kinetic versus thermodynamic considerations. *E* isomers appear as kinetic products that are favored at low temperatures and short reaction times. They would be generated by the addition of the sulfonate group on the less-hindered face of a dicationic intermediate, *anti* to the protonated carbonyl (Scheme 5, **A**). It is worth noting that the stereoselectivity is always better for the triflate

Table 3. Isomerization of vinyl fluorosulfonates and vinyl trifluoromethylsulfonates in triflic or fluorosulfonic acids.

	Acetylenic derivative	Reaction conditions	*E*:*Z* Ratio	Products *E* isomer		*Z* isomer
1	Ph—≡—CO_2H **1a**	FSO_3H, –40°C, 0.5h	90:10	FO_2SO, H, Ph, CO_2H	**2a**	FO_2SO, CO_2H, Ph, H
2	**1a**	FSO_3H, 0°C, 1h	76:24	FO_2SO, H, Ph, CO_2H	**2a**	FO_2SO, CO_2H, Ph, H
3	*p*-FC_6H_4—≡—CO_2H **1d**	FSO_3H, –40°C, 0.5h	87:13	FO_2SO, H, *p*-FC_6H_4, CO_2H	**2d**	FO_2SO, CO_2H, *p*-FC_6H_4, H
4	**1d**	FSO_3H, 0 °C, 0.5h	65:35	FO_2SO, H, *p*-FC_6H_4, CO_2H	**2d**	FO_2SO, CO_2H, *p*-FC_6H_4, H
5	*p*-MeC_6H_4—≡—CO_2Me **1f**	CF_3SO_3H, –30°C, 0.5h	85:15	F_3CO_2SO, H, *p*-MeC_6H_4, CO_2Et	**3f**	F_3CO_2SO, CO_2Et, *p*-MeC_6H_4, H
6	**1f**	CF_3SO_3H, 0°C, 1h	77:23	F_3CO_2SO, H, *p*-MeC_6H_4, CO_2Et	**3f**	F_3CO_2SO, CO_2Et, *p*-MeC_6H_4, H
7	**1f**	CF_3SO_3H, –20°C, 6d	9:91	F_3CO_2SO, H, *p*-MeC_6H_4, CO_2Et	**3f**	F_3CO_2SO, CO_2Et, *p*-MeC_6H_4, H

addition in comparison to the fluorosulfonate addition (Table 1), which is in agreement with what could be expected from the addition of a larger group. Such a stereoselectivity was reported earlier for the fluorosulfonation of propiolic acid and explained by electronic repulsion.[11] Because *Z* isomers are the major product in the case of propynoates after prolonged reaction times, they probably are the more stable compounds.



Scheme 5. Mechanistic proposal for sulfonic acid additions to ynones and ynoates.

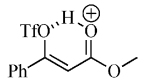
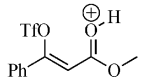
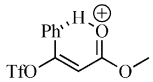
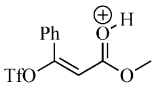
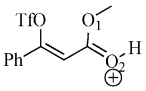
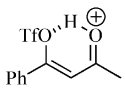
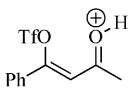
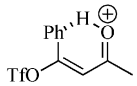
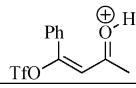
Isomerization from the *E* to the *Z* isomer could be simply envisaged through the mesomeric form **B** in Scheme 5 or possibly through prototropic shift, but such a simple phenomenon would not reflect the reactivity differences observed. Isomerization may rather take place by a further protonation[14] (Scheme 5, **C**) followed by rotation, in agreement with our observations in stronger acidic media (Scheme 4). The addition of a second sulfonate to yield intermediate **D** (Scheme 5) followed by elimination can also be envisaged. Such a *gem*-disulfonate species, analog to **C**, were characterized and are indeed prone to fast elimination;[6] they also were detected in superacid solutions.[11] We thus tried to detect transient species by NMR spectroscopy, either dication **C** or *gem*-bistriflate **D**, but without success. Their lifetimes could render them undetectable on the NMR timescale.

It is worth noting that initial "*anti* addition" to the triple bond followed by isomerization to "*syn* addition" products is known for some reactions of acetylenic compounds in superacids.[19]

Because no intermediate could be detected in the addition to ynones, the isomerization process is probably very fast with vinyl sulfonates derived from ynones and much slower with vinyl sulfonates derived from ynoates.

Accordingly, PM3 calculations[20] on protonated vinyl triflates in the gas phase revealed important differences in stabilities and properties. Table 4 summarizes the calculated results obtained for energy minima (enthalpies of formation) for various geometries and isomers. The protonation of the carbonyl group offers the possibility of an intramolecular hydrogen bond between the newly introduced proton and either the vinylic oxygen atom of the sulfonate group or with the phenyl ring itself. This hydrogen bond significantly participates to the stabilization of these structures (Table 4, Entries 1,3 vs. 2, 4 and 6, 8 vs. 7, 9). As expected, the H–OTf interaction is stronger than the H–Ph interaction, which stabilizes the *Z* isomers more (Table 4, Entry 1 vs. 3 and 6 vs. 8).

Table 4. Thermodynamic stabilities of protonated vinyl triflates esters and ketones calculated at the PM3 level.

Entry	Protonated vinyl triflate	H–OTf / H–Ph distance [Å]	ΔH_f [Kcal^mol^{-1}]
1		1.8414	–117.313
2		–	–109.833
3		2.26	–115.809
4		–	–109.778
5		H1–O1 2.42 H2–O2 2.48	–109.362
6		1.8409	–77.494
7		–	–75.327
8		2.19	–76.128
9		–	–75.062

Calculations also revealed a significant difference in the stabilities between the protonated triflates derived from esters and ketones. Triflyl esters are indeed much more stable than their keto analogs (35–40 kcal mol^{-1} in the gas phase; Table 4, Entries 1–5 vs. 6–9). The relative stability of the protonated vinyl triflate derived from esters may most probably be at the origin of the slower isomerization rate observed in superacids. Furthermore, the comparison of the

free enthalpies of formation between the protonated *E* and *Z* isomers confirms that the *Z* isomers are thermodynamically favored in both the ester and ketone series (Table 4, Entry 1 vs. 3 and 6 vs. 8).

Together, experiments and calculations demonstrate that the stereoselectivity of the compound can be chosen in this synthesis of vinyl fluorosulfonates and triflates. Starting from acetylenic esters, "playing" with the experimental conditions allowed full control over whether the *E* or the *Z* isomer would be formed.

This method offers *a single step* efficient synthesis of the *E* or *Z* isomer of vinyl sulfonates through fluorosulfonic acid addition to acetylenes. Contrary to what was expected with "superacids", the reaction is very convenient, easy to perform, and easily worked up.

Conclusions

We developed an efficient and highly stereoselective method for the synthesis of vinyl sulfonates by the stereoselective addition of sulfonic acids to alkynoic acid derivatives and alkynones. Moreover, the stereoselectivity can be completely reversed from *E* to *Z* by controlling the reaction time and temperature for the ynoates derivatives. Therefore, this *one-pot reaction* offers an easy and innovative alternative to the two-step procedures commonly used to prepare these important intermediates for C–C formations by coupling reactions.

Experimental Section

General Remarks: Phenylpropiolic acid, methyl phenylpropiolate, ethyl phenylpropiolate, ethyl propiolate, 3-hexyn-2-one, and methyl 2-octynoate were purchased from Aldrich and used without further purification. Other starting materials, namely, acids,[10a,15a] esters,[10a,15a] and ketones,[15b] were prepared according to previously reported procedures. The reactions were monitored by thin-layer chromatography carried out on silica plates (silica gel 60 F254, Merck) by using UV light for detection. Column chromatography was performed on silica gel 60 (0.040–0.063 mm, Merck). Melting points (m.p.) were determined with a Bibby-Stenlin Stuart SMP3 melting point apparatus and are uncorrected. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded with a Bruker AC-300 spectrometer at 300, 75, and 300 MHz, respectively. The residual proton solvent peak $CHCl_3$ (δ = 7.26 ppm) for ^{1}H NMR spectra, the signal of $CDCl_3$ (δ = 77.0 ppm) for ^{13}C NMR spectra, and the signal of $CFCl_3$ (δ = 0.0 ppm) for ^{19}F NMR spectra were used as references. NMR experiments in superacids HSO_3F and CF_3SO_3H were performed with a Bruker AC-400 spectrometer at 400 MHz for ^{1}H NMR spectra. ^{1}H NMR spectra in superacids were referenced to the signal of CH_2Cl_2 added as an internal standard (δ = 5.32 ppm). Low- and high-resolution mass spectra were obtained with a Bruker micro-TOF instrument (ESI).

Ethyl 3-(4-Fluorophenyl)propynoate (1e): Prepared by Sonogashira coupling from 1-fluoro-4-iodobenzene and ethyl propiolate according to the literature.[21] Slightly yellow crystals. Yield: 0.98 g (17%). M.p. 54–56 °C (ref.[21] oil). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.33 (t, J = 7.2 Hz, 3 H, OCH_2CH_3), 4.25 (q, J = 7.2 Hz, 2 H, OCH_2CH_3), 7.05 (m, 2 H, Ar), 7.56 (m, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.0 (OCH_2CH_3), 62.1 (OCH_2CH_3), 80.6, 84.9, 115.7 (d, $^{4}J_{C,F}$ = 3.8 Hz, Ar), 116.0 (d, $^{2}J_{C,F}$ = 22.0 Hz, Ar), 135.1 (d, $^{3}J_{C,F}$ = 9.5 Hz, Ar), 153.9 (C=O), 163.86 (d, $^{1}J_{C,F}$ = 252 Hz, Ar) ppm.

Procedure for the Preparation of Vinyl Triflates and Vinyl Fluorosulfonates in NMR Tubes:[10a] **An** NMR tube was loaded with HSO_3F (0.8–1 mL) and cooled down to –78 °C (dry ice/acetone), and the acetylenic compound (5–20 mg) was then added. The temperature was increased up to –40 °C, and a thin Teflon capillary was entered to the bottom of the NMR tube, passing through it a weak flow of argon during 5–10 min to homogenize the solution. The capillary was then removed and CH_2Cl_2 as an internal standard was added. ^{1}H NMR spectra of the in situ obtained vinyl fluorosulfonates were recorded at –40, –30, or 0 °C in the HSO_3F solution. The same procedure was used for the in situ preparation of vinyl triflates from acetylenic compounds in CF_3SO_3H. In this case, the reaction solutions were homogenized at –30 °C, and the ^{1}H NMR spectra of vinyl triflates were taken at –30 or 0 °C.

3-Fluorosulfonyloxy-3-phenyl-2-propenoic Acid (2a): *E* and *Z* isomers were observed in superacid with an *E*:*Z* ratio of 90:10. Protonated **2a**: ^{1}H NMR (400 MHz, FSO_3H, –40 °C): δ = 6.65/6.72 (s, 1 H, *E*/*Z* -CH), 7.67 (m, 2 H, Ph), 7.76 (m, 2 H, Ph), 7.83 (m, 1 H, Ph) ppm.

Methyl 3-Fluorosulfonyloxy-3-phenyl-2-propenoate (2b): *E* and *Z* isomers were observed in superacid with an *E*:*Z* ratio of 78:22. Protonated **2b**: ^{1}H NMR (400 MHz, FSO_3H, 0 °C): δ = 4.34/4.65 (s, O-CH_3) 6.64/6.71 (s, 1 H, *E*/*Z* -CH), 7.65–7.83 (m, 5 H, Ph) ppm.

Ethyl 3-Fluorosulfonyloxy-3-phenyl-2-propenoate (2c): *E* and *Z* isomers were observed in superacid with an *E*:*Z* ratio of 79:21. Protonated **2c**: ^{1}H NMR (400 MHz, FSO_3H, 0 °C): δ = 1.70 (m, 3 H, OCH_2CH_3), 5.12 (m 2 H, OCH_2CH_3) 6.64/6.71 (s, 1 H, *E*/*Z* -CH), 7.64–7.85 (m, 5 H, Ph) ppm.

3-(4-Fluorophenyl)-3-fluorosulfonyloxy-2-propenoic Acid (2d): *E* and *Z* isomers were observed in superacid with an *E*:*Z* ratio of 87:13. Protonated **2d**: ^{1}H NMR (400 MHz, FSO_3H, –40 °C): δ = 6.58/6.65 (s, 1 H, *E*/*Z* -CH), 7.34 (m, 2 H, Ph *Z*+*E*), 7.82 (m, 2 H, Ph *E* isomer), 7.98 (m, 2 H, Ph *Z* isomer) ppm.

Ethyl-3-(4-Fluorophenyl)-3-fluorosulfonyloxy-2-propenoate (2e): *E* and *Z* isomers were observed in superacid with an *E*:*Z* ratio of 87:15. Protonated **2e**: ^{1}H NMR (400 MHz, FSO_3H, –30 °C): δ = 1.73 (m, 3 H, OCH_2CH_3), 5.07 (m, 2 H, OCH_2CH_3) 6.60/6.70 (s, 1 H, *E*/*Z* -CH), 7.65–7.92 (m, 4 H, Ph) ppm.

3-Phenyl-3-trifluoromethylsulfonyloxy-2-propenoic Acid (3a): *E* and *Z* isomers were observed in superacid with an *E*:*Z* ratio of 93:7. Protonated **3a**: ^{1}H NMR (400 MHz, CF_3SO_3H, –30 °C): δ = 6.61/6.70 (s, 1 H, *E*/*Z* -CH), 7.67–7.83 (m, 5 H, Ph) ppm.

3-(4-Fluorophenyl)-3-fluorosulfonyloxy-2-propenoic Acid (3d): *E* and *Z* isomers were observed in superacid with an *E*:*Z* ratio of 85:15. Protonated **3d**: ^{1}H NMR (400 MHz, CF_3SO_3H, –30 °C): δ = 6.52/6.60 (s, 1 H, *E*/*Z* -CH), 7.4 (m, 2 H, Ph *Z*+*E*), 7.8 (m, 2 H, Ph *E* isomer), 8.0 (m, 2 H, Ph *Z* isomer) ppm.

General Preparative Procedure: Fluorosulfonic acid, HSO_3F, or triflic acid, CF_3SO_3H (12.5 mmol), was added dropwise over 5 min to a solution of the acetylenic compound (1.25 mmol) in dichloromethane (10 mL) while stirring vigorously at the temperature shown in Table 1. After stirring for 0.25–1 h (see Table 1), the solution was poured into an ice–water mixture. The aqueous phase was extracted three times with dichloromethane, and the organic layer was washed with saturated $NaHCO_3$, water, and brine and then

dried with Na_2SO_4. After solvent evaporation under reduced pressure, vinyl sulfonates are obtained in pure form. Yields of the pure isolated compounds are given in Table 1.

Preparation of Vinyl Triflates in CF_3SO_3H/SbF_5 Mixtures: Acetylenic compound (0.5 mmol) was added with vigorous stirring to the CF_3SO_3H/SbF_5 mixture (1 mL) with value $H_0 \approx -18$ or –20 at 0 or 25 °C (see Table 2). After 0.5 h stirring, the solution was poured into an ice–water mixture. The aqueous phase was extracted three times with dichloromethane, and the organic layer was washed with saturated $NaHCO_3$, water, and brine and then dried with Na_2SO_4. After solvent evaporation under reduced pressure, vinyl triflates were obtained. Yields of the pure isolated compounds are given in Scheme 4.

3-Phenyl-3-(trifluoromethylsulfonyloxy)propenoic Acid (3a): For the *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.17 (s, 1 H, =CH-), 7.41–7.57 (m, 5H arom.), 9.2 (br. s, 1 H, -COOH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 112.5 (=CH), 118.3 (q, $J_{C,F}$ = 318 Hz, CF_3), 128.4 (C_{Ar}, *meta*-), 129.3 (C_{Ar}, *ortho*-), 130.2 (C_{Ar}, *ipso*-), 132.0 (C_{Ar}, *para*-), 160.8 (=COTf), 168.4 (C=O) ppm. ^{19}F NMR (300 MHz, $CDCl_3$): δ = –74.2 (s, CF_3) ppm. For the *Z* isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.25 (s, 1 H, =CH-), 7.41–7.56 (m, 5 H, arom.), 9.2 (br. s, 1 H, -COOH) ppm. MS: *m*/*z* (%) = 296 (32) $[M]^+$, 231 (23), 149 (8), 105 (13), 102 (100), 77 (17).

Methyl 3-Phenyl-3-trifluoromethylsulfonyloxy-2-propenoate (3b): *E* and *Z* isomers were obtained as a yellow oily mixture in 90% yield (349 mg) with an *E*:*Z* ratio of 95:5. Stereochemical configurations were confirmed by NMR NOESY experiments carried out on the crude mixture. ^{1}H, ^{13}C, and ^{19}F NMR spectroscopic data for the individual isomers were obtained from the spectra of the crude mixture. For the *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.69 (s, 3 H, OCH_3), 6.19 (s, 1 H), 7.41–7.57 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 52.1 (OCH$_3$), 113.1, 118.3 (q, $^1J_{C,F}$ = 318 Hz, CF_3), 128.2, 129.1, 130.4, 131.6, 159.1, 163.8 (C=O) ppm. ^{19}F NMR (300 MHz, $CDCl_3$, 25 °C): δ = –74.2 ppm. For the *Z* isomer: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.84 (s, 3 H, OCH_3), 6.25 (s, 1 H), 7.36–7.58 (m, 5 H, Ph) ppm. MS (ESI+): *m*/*z* (%) = 317 (100) $[M + Li]^+$. HRMS: calcd. for $C_{11}H_9F_3LiO_5S$ $[M + Li]^+$ 317.0283; found 317.0277.

Ethyl 3-Phenyl-3-trifluoromethylsulfonyloxy-2-propenoate (3c): *E* and *Z* isomers were obtained as a yellow oily mixture in 94% yield (381 mg) with an *E*:*Z* ratio of 94:6. Stereochemical configurations were confirmed by NMR NOESY experiments carried out on the crude mixture. ^{1}H, ^{13}C, and ^{19}F NMR spectroscopic data for the individual isomers were obtained from the spectra of the crude mixture. For the *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.92 (t, *J* = 7.1 Hz, 3 H, OCH$_2$CH_3), 4.14 (q, *J* = 7.1 Hz, 2 H, OCH_2CH$_3$), 6.18 (s, 1 H), 7.41–7.57 (m, 5 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 13.8 (OCH$_2$$CH_3$), 61.3 (OCH$_2$$CH_3$), 113.6, 118.3 (q, $^1J_{C,F}$ = 318 Hz, CF_3), 128.2, 129.1, 130.6, 131.6, 159.9, 163.3 (C=O) ppm. ^{19}F NMR (300 MHz, $CDCl_3$, 25 °C): δ = –74.2 ppm. For the *Z* isomer: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.35 (t, *J* = 7.1 Hz, 3 H, OCH$_2$CH_3), 4.32 (q, *J* = 7.1 Hz, 2 H, OCH$_2$$CH_3$), 6.25 (s, 1 H), 7.41–7.57 (m, 5 H, Ph) ppm. MS (ESI+): *m*/*z* (%) = 347 (100) $[M + Na]^+$. HRMS: calcd. for $C_{12}H_{11}F_3NaO_5S$ $[M + Na]^+$ 347.0177; found 347.0171.

Ethyl 3-(4-Fluorophenyl)-3-trifluoromethylsulfonyloxy-2-propenoate (3e): *E* and *Z* isomers were obtained as an orange oily mixture in 90% yield (385 mg) with an *E*:*Z* ratio of 91:9. Stereochemical configurations were confirmed by NMR NOESY experiments carried out on the crude mixture. ^{1}H, ^{13}C, and ^{19}F NMR spectroscopic data for individual isomers were obtained from the spectra of the crude mixture. For the *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.21 (t, *J* = 7.1 Hz, 3 H, OCH$_2$CH_3), 4.15 (q, *J* = 7.1 Hz, 2 H, OCH_2CH$_3$), 6.19 (s, 1 H), 7.13 (m, 2 H, Ar), 7.58 (m, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 13.9 (OCH$_2$$CH_3$), 61.4 (OCH$_2CH_3$), 113.8, 115.6 (d, $^2J_{C,F}$ = 22.2 Hz), 118.3 (q, $^1J_{C,F}$ = 323 Hz, CF_3), 126.7 (d, $^4J_{C,F}$ = 3.1 Hz), 131.7 (d, $^3J_{C,F}$ = 9.0 Hz), 157.9, 163.2 (C=O), 164.4 (d, $^1J_{C,F}$ = 252 Hz) ppm. ^{19}F NMR (300 MHz, $CDCl_3$, 25 °C): δ = –107.1 (1 F, ArF), –74.2 (3 F, SO_2CF_3) ppm. For the *Z* isomer: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.35 (t, *J* = 7.1 Hz, 3 H, OCH$_2$CH_3), 4.31 (q, *J* = 7.1 Hz, 2 H, OCH_2CH$_3$), 6.21 (s, 1 H), 7.10–7.16 (m, 2 H, Ar), 7.56–7.61 (m, 2 H, Ar) ppm. MS (ESI+): *m*/*z* (%) = 349 (100) $[M + Na]^+$. HRMS: calcd. for $C_{12}H_{10}F_4O_5S$ $[M + Li]^+$ 349.0345; found 349.0340.

Methyl 3-(4-Methylphenyl)-3-trifluoromethylsulfonyloxy-2-propenoate (3f): *E* and *Z* isomers were obtained as a yellow oily mixture in 91% yield (368 mg) with an *E*:*Z* ratio of 96:4. Stereochemical configurations were confirmed by NMR NOESY experiments carried out on the crude mixture. ^{1}H, ^{13}C, and ^{19}F NMR spectroscopic data for individual isomers were obtained from the spectra of the crude mixture. For the *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.41 (s, 3 H, OCH$_2$CH_3), 3.70 (s, 3 H, OCH_2CH$_3$), 6.14 (s, 1 H), 7.25 (m, 2 H, Ar), 7.46 (m, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.6 (OCH$_2$$CH_3$), 52.1 (O$CH_2CH_3$), 112.4, 118.3 (q, $^1J_{C,F}$ = 318 Hz, CF_3), 127.6, 129.0, 129.1, 142.4, 159.5, 164.0 (C=O) ppm. ^{19}F NMR (300 MHz, $CDCl_3$, 25 °C): δ = –74.2 ppm. The *Z* isomer was prepared from methyl (*E*)-3-(4-methylphenyl)propynoate (**1f**) after leaving it in pure CF_3SO_3H at –20 °C for 6 d. The reaction mixture was worked up in the general manner described above, and the compound was then recrystallized from MeOH. Brownish solid. M.p. 73–75 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.40 (s, 3 H, OCH$_2$CH_3), 3.83 (s, 3 H, OCH_2CH$_3$), 6.22 (s, 1 H), 7.26 (m, 2 H, Ar), 7.47 (m, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.5 (OCH$_2$$CH_3$), 52.1 (O$CH_2CH_3$), 110.1, 118.3 (q, $^1J_{C,F}$ = 319 Hz, CF_3), 126.5, 128.9, 129.8, 142.6, 155.6, 163.4 (C=O) ppm. ^{19}F NMR (300 MHz, $CDCl_3$, 25 °C): δ = –74.1 ppm. MS (ESI+): *m*/*z* (%) = 347 (100) $[M + Na]^+$. HRMS: calcd. for $C_{12}H_{11}F_3NaO_5S$ $[M + Na]^+$ 347.0177; found 347.0172.

Methyl 3-(4-Methoxyphenyl)-3-trifluoromethylsulfonyloxy-2-propenoate (3g): *E* and *Z* isomers were obtained as an oily mixture in 39% yield (166 mg) with an *E*:*Z* ratio of 93:7. Stereochemical configurations were confirmed by NMR NOESY experiments carried out on the crude mixture. ^{1}H, ^{13}C, and ^{19}F NMR spectroscopic data for individual isomers were obtained from the spectra of the crude mixture. For the *E* isomer: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.79 (s, 3 H), 3.83 (s, 3 H), 6.13 (s, 1 H), 6.93 (m, 2 H, Ar), 7.50 (m, 2 H, Ar) ppm. For the *Z* isomer: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.82 (s, 3 H), 3.85 (s, 3 H), 6.23 (s, 1 H), 6.84 (m, 2 H, Ar), 7.15 (m, 2 H, Ar) ppm. MS (ESI+): *m*/*z* (%) = 363 (100) $[M + Na]^+$. HRMS: calcd. for $C_{12}H_{11}F_3NaO_6S$ $[M + Na]^+$ 363.0126; found 363.0121.

Methyl 3-(4-Methoxyphenyl)-3-oxopropanoate (4g): Was obtained as the major product from methyl 3-(4-methoxyphenyl)propynoate (**1g**) after purification by column chromatography of the crude mixture. Slightly yellow oil (ref.[6] oil). Yield: 109 mg (42%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.75 (s, 3 H), 3.87 (s, 3 H), 3.96 (s, 2 H), 6.94 (m, 2 H, Ar), 7.92 (m, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 45.5, 52.4, 55.5, 114.0, 129.0, 130.9, 164.0, 168.1 (C=O), 190.8 (C=O) ppm. MS (ESI+): *m*/*z* (%) = 215 (100) $[M + Li]^+$. HRMS: calcd. for $C_{11}H_{12}LiO_4$ $[M + Li]^+$ 215.0896; found 215.0890.

(*Z*)-4-Fluorosulfonyloxy-4-(4-methylphenyl)-3-buten-2-one (6c): Yellow oil. Yield: 258 mg (80%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C):

δ = 2.40 (s, 6 H), 6.47 (s, 1 H), 7.27 (m, 2 H, Ar), 7.52 (m, 2 H, Ar) ppm. $C_{11}H_{11}FO_4S$ (258.27): calcd. C 51.16, H 4.29; found C 51.30, H 4.36.

(*Z*)-4-(4-Methylphenyl)-4-trifluoromethylsulfonyloxy-3-buten-2-one (7c): Brownish oil. Yield: 335 mg (87%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.38 (s, 3 H), 2.41 (s, 3 H), 6.48 (s, 1 H), 7.25 (m, 2 H, Ar), 7.48 (m, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.5, 31.7, 116.4, 118.3 (q, $^1J_{C,F}$ = 319 Hz, CF_3), 126.6, 129.8, 133.1, 142.7, 152.6, 194.2 (C=O) ppm. ^{19}F NMR (300 MHz, $CDCl_3$, 25 °C): δ = –74.1 ppm. MS (ESI+): *m*/*z* (%) = 331 (100) $[M + Na]^+$. HRMS: calcd. for $C_{12}H_{11}F_3NaO_4S$ $[M + Na]^+$ 331.0228; found 331.0221.

(*Z*)-4-Hydroxy-4-(4-methoxyphenyl)-3-buten-2-one (8d): Stereochemical configuration was confirmed by NMR NOESY experiments. Slightly yellow crystals. Yield: 218 mg (91%) after column purification. M.p. 52–54 °C (ref.[7] 55–56 °C). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.17 (s, 3 H), 3.87 (s, 3 H), 6.11 (s, 1 H), 6.94 (m, 2 H, Ar), 7.86 (m, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 25.3, 55.4, 95.8, 113.9, 127.5, 129.1, 163.1, 184.1, 196.9 (C=O) ppm.

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