ChemPubSoc Europe

DOI: 10.1002/ejoc.201700423

EurJOC European Journal of Organic Chemistry

Full Paper

Superelectrophilic Activation

Brønsted Acid Promoted Cyclization of Cross-Conjugated Enynones into Dihydropyran-4-ones

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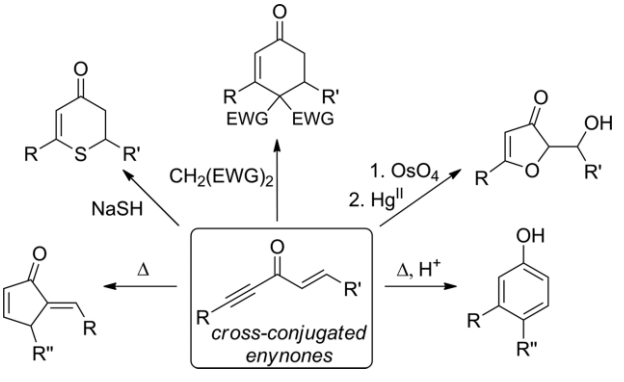
Abstract: In triflic acid or sulfuric acid, diaryl-substituted cross-conjugated enynones undergo addition of the acid to the carbon–carbon triple bond to afford the corresponding vinyl triflates or sulfates. The vinyl triflates are stable under aqueous workup, whereas the vinyl sulfates are hydrolyzed to α,β-unsaturated 1,3-diketones (existing as conjugated enol forms). Extended reaction times lead to cyclization into dihydropyran-4-ones with yields of up to 95 %. The protonated forms of the vinyl triflates or sulfates in triflic and sulfuric acid, respectively, are studied as reactive intermediates by NMR spectroscopy. Plausible reaction mechanisms for the formation of dihydropyran-4-ones are discussed.

Introduction

Superelectrophilic activation makes it possible to form cationic species of enhanced reactivity, and this requires their relative stabilization, typically by delocalization of the positive charge over conjugated systems.[1] We have shown recently that diaryl-substituted conjugated enynones, in particular 1,5-diarylpent-2-en-4-yne-1-ones, are suitable structures for access to vinyl triflates, indanones, and indenes under superelectrophilic activation.[2] Clearly, the reactivity of an enynone depends on the relative positions of the three functional groups (C=O, C=C, and C≡C), and we decided to study the behavior of systems in which the carbonyl group is cross-conjugated between the double and the triple bonds (i.e., cross-conjugated enynones). The protonation of these basic centers may lead to the formation of highly reactive multicentered electrophilic species.

In organic synthesis, cross-conjugated enynones are precursors of different cyclization products through two types of reactions, that is, electrocyclization upon enolization, which leads to methylenecyclopentenones[3] or phenols[4] depending on the reaction conditions, and double Michael additions in the presence of soft nucleophiles such as sulfides[5] or activated methylene compounds[6] to give the corresponding unsaturated six-membered dihydrothiopyran-4-one and cyclohex-2-enone rings (Scheme 1). Analogously, the double addition of water (or an oxygenated equivalent), which would give the dihydropyran-4-one core has not yet been described, probably because the hardness of oxygen does not favor conjugate additions. An intramolecular conjugate addition of OH can take place after the selective dihydroxylation of the double bond but leads to furanone derivatives instead of pyran-4-ones in this case (Scheme 1).[7]



Scheme 1. Synthetic transformations of cross-conjugated enynones towards cyclization products (data from refs.[3–7]).

The main goal of this work was to study the transformations of 1,5-diaryl-substituted cross-conjugated enynones of type **1**, namely, 1,5-diarylpent-1-en-4-yn-3-ones, under conditions of electrophilic activation by Brønsted or Lewis acids. We show that the cyclization of such species into dihydropyran-4-ones occurs in sulfuric acid and trifluoromethanesulfonic acid (triflic acid, CF_3SO_3H, TfOH) and that the water equivalent is provided by the dehydration of the acid. Compounds **1** are first converted into vinyl sulfate of triflate intermediates through the

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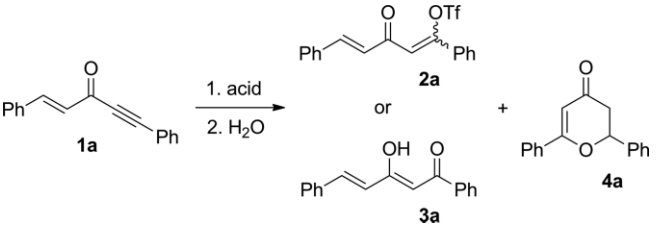
addition of the acid to the triple bond and are further cyclized into 2,6-diaryl-substituted dihydropyran-4-ones, for which the oxygen atom is provided by the acid. A mechanistic study reveals that the cyclization might involve the two types of reactions mentioned above, that is, Michael addition and oxa-6π electrocyclization.

Results and Discussion

The diphenyl-substituted enynone **1a** was selected as a model to explore the reactivity in the presence of different acids (Table 1). The Brønsted acids CF_3CO_2H and aqueous HCl as well as the Lewis acid $AlCl_3$ are not strong enough to activate **1a**, as the starting material was recovered unreacted in each case (Table 1, Entries 1, 2, and 15). In the presence of $AlBr_3$, **1a** becomes electrophilic enough, but the reaction affords only a complex mixture of condensation products in the absence of a suitable nucleophile (Table 1, Entry 16). More interesting results were obtained for H_2SO_4 and TfOH, which are strong enough to activate **1a**, and the presence of the weakly nucleophilic conjugate base allows a nucleophilic addition to the triple bond. Thus, in TfOH, **1a** was converted into both the (1*Z*,4*E*) and the (1*E*,4*E*) isomers of the vinyl triflate **2a** by the addition of TfOH (Table 1, Entries 6–13). The stereochemical (*E*,*Z*) configurations of triflates **2** were determined by NOESY experiments [see also the X-ray structure of (1*Z*,4*E*)-**2b** in Figure 1]. In sulfuric acid, the corresponding vinyl sulfate was hydrolyzed during the aqueous workup to form the α,β-unsaturated 1,3-diketone **3a** (Table 1, Entry 3), which is depicted in its predominant tautomeric form.[8]

After extended reaction times, the vinyl sulfate and triflate are both converted into dihydropyran-4-one **4a**. This transformation is more efficient in H_2SO_4, and almost complete conversion was observed after 60 h at room temperature (Table 1, Entry 4), whereas **4a** was obtained in only 31 % yield under the same conditions in TfOH (Table 1, Entry 13). The increase of temperature did not accelerate the rate of formation of **4a** in TfOH but led to a complex mixture of products (Table 1, Entry 14), owing to the relative instability of triflate **2a**. Interestingly, the 1,3-diketone **3a** (product obtained from **1a** in H_2SO_4 after aqueous workup) was observed in TfOH together with **4a** (Table 1, Entries 12 and 13). In this case, it is assumed to be the product of the ring-opening of **4a** by reversible oxa-6π electrocyclization.[9]

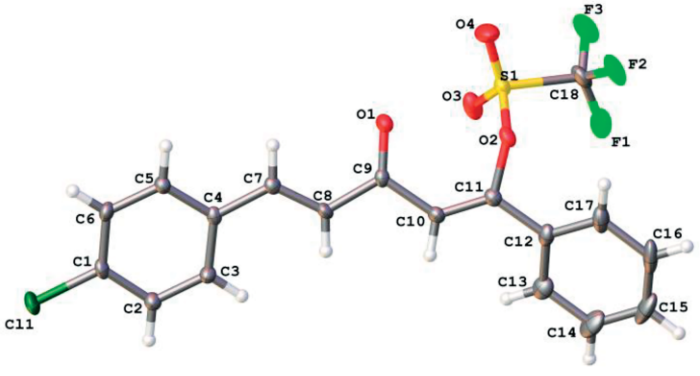
Table 1. Transformations of enynone **1a** in the presence of different Brønsted and Lewis acids.[a]



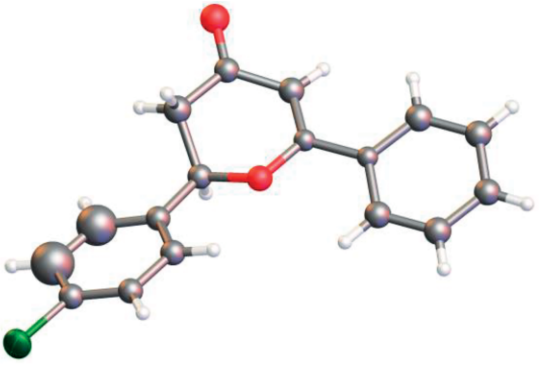
Entry	Acid[b]	*T* [°C]	*t* [h]	Reaction products[c] 2a [%]	Ratio (1*Z*,4*E*)/(1*E*,4*E*)	3a [%]	4a [%]
1	CF_3CO_2H	r.t.	15	quantitative recovery of starting material			
2	HCl(aq.)	r.t.	15	quantitative recovery of starting material			
3	H_2SO_4	r.t.	1	–	–	81	10
4	H_2SO_4	r.t.	60	–	–	4	93
5	H_2SO_4	60	24	mixture of sulfonated dihydropyran-4-ones			
6	TfOH	–38	0.5	12	1:2	0	0
7	TfOH	0	0.5	91	1.7:1	0	0
8	TfOH	0	1	95	4.7:1	0	0
9	TfOH	r.t.	0.25	94	4.6:1	0	0
10	TfOH	r.t.	1	98	8.4:1	0	0
11	TfOH	r.t.	2	95	7.5:1	0	traces
12	TfOH	r.t.	20	84	6.5:1	traces	13
13	TfOH	r.t.	60	65	6.7:1	3	31
14	TfOH	60	12	complex mixture			
15	$AlCl_3$[d]	r.t.	2	quantitative recovery of starting material			
16	$AlBr_3$[d]	r.t.	0.5	complex mixture			

[a] Reactions performed with 0.1 mol L^{-1} of enynone **1a**. [b] The indicated acid was used as the reaction solvent. [c] The yields and ratios were determined by NMR spectroscopic analysis of the crude reaction mixtures. [d] The acid (5 equiv.) in anhydrous dichloromethane as the reaction solvent.

The variations of the ratio of the (*E*/*Z*) isomers of **2a** with temperature and reaction time indicate that the addition of TfOH seems to give the (1*E*) isomer initially by *syn* addition, and this isomer is then transformed into the more stable (1*Z*) isomer, and (1*Z*,4*E*)/(1*E*,4*E*) ratios of up to 8.4:1 were observed after 1 h at room temperature (compare Table 1, Entries 6–11). Although the main isomer (1*Z*,4*E*)-**2a** could be isolated by flash



(1*Z*,4*E*)-**2b**

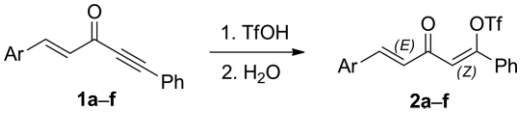


4b

Figure 1. Molecular structures of (1*Z*,4*E*)-**2b** (CCDC-1530422) and **4b** (CCDC-1530422); the ellipsoids show probability levels of 50 %.

column chromatography with silica gel and was relatively stable, the minor isomer (1*E*,4*E*) returned to the starting enynone **1a** through the spontaneous elimination of TfOH. Therefore, we decided to prepare different triflate derivatives from enynones **1b**–**1f** by optimizing the formation of the (1*Z*,4*E*) isomers (Table 2). Vinyl triflates are synthetically interesting,[10] and the results in Table 2 show the effects on the reactivity of enynones **1** owing to the presence of electron-donating and -withdrawing substituents on the aryl ring conjugated with the double bond.

Table 2. Transformation of enynones **1a**–**1f** into vinyl triflates (1*Z*,4*E*)-**2a**–**2f** in TfOH.[a]



1a–f **2a–f**

Entry	Enynone	Ar	*T* [°C]	*t* [h]	Triflate (1*Z*,4*E*)-**2**	Yield [%][b]	Ratio (1*Z*,4*E*)/(1*E*/4*E*)[c]
1	**1a**	Ph	r.t.	1	**2a**	81	8.4:1
2	**1b**	*p*-Cl-C_6H_4	r.t.	1	**2b**	73	6.5:1
3[d]	**1c**	*p*-NO_2-C_6H_4	r.t.	3	**2c**	61	6.5:1
4	**1d**	*p*-Me-C_6H_4	r.t.	1	**2d**	66	4.6:1
5	**1e**	*p*-OMe-C_6H_4	0	0.5	**2e**	76	8: 1
6	**1f**	3,4-$(OMe)_2$-C_6H_3	0	0.5	**2f**	78	4.8:1

[a] Reactions performed with 0.1 mol L^{-1} of enynone in TfOH as the reaction solvent. [b] Yield of isolated product. [c] Ratios determined from the crude reaction mixtures by ^{19}F or ^1H NMR spectroscopic analysis. [d] 0.025 mol L^{-1} of enynone **1c**.

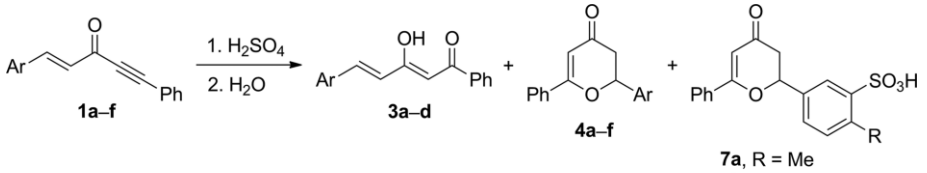
The reactivity depends directly on the stability and the ease of formation of the cationic intermediates, which in turn depends on the nature of the substituents on the conjugated aryl ring. Thus, although enynones **1b** and **1d** (Ar = *p*-Cl-C_6H_4 and *p*-Me-C_6H_4, respectively; Table 2, Entries 2 and 4) did not show significant differences in reactivity, **1c** (Ar = *p*-NO_2-C_6H_4; Table 2, Entry 3) gave the vinyl triflate **2c** with a slower reaction rate, owing to the presence of the strongly electron-withdrawing NO_2 group at the *para* position. This not only affects the reaction rate but also increases the electrophilicity of the cationic intermediates that lead to competing condensation reactions, although these can be limited by lowering the initial concentration of **1c**. In contrast, the methoxy groups at the *para* positions of enynones **1e** and **1f** (Table 2, Entries 5 and 6) allows faster conversions into the corresponding vinyl triflates, which could be readily obtained at 0 °C. As expected, the presence of a second methoxy substituent at the *meta* position for enynone **1f** did not significantly affect the reactivity (compare Table 2, Entries 5 and 6), as the *meta* position is not involved in the delocalization of the positive charge.

The different ratios of *E*/*Z* isomers observed in Table 2 are difficult to rationalize as they depend on two factors: (1) the relative stabilities of both isomers and (2) the spontaneous conversion of the (1*E*) isomer into the starting enynone. The two features may be diversely affected by the nature of a given substituent on the aryl ring.

It is worth noting that the extension of the conjugated system through the insertion of an additional double bond has a negative effect on the formation of the vinyl triflates: dienynone **5** gives the very unstable triflate **6**, which could not be obtained in triflic acid, even at low temperatures. However, it could be stabilized by lowering the acidity of the reaction medium with pyridine as a non-nucleophilic organic cosolvent. The best result was obtained for a 20 % volume of pyridine, and 34 % of the (1*Z*) isomer was isolated after 18 h at room temperature (Scheme 2). The minor (1*E*) isomer could not be identified.

Similar differences in reactivity were observed in sulfuric acid (see Table 3) regarding both the addition of H_2SO_4 (leading to

Table 3. Transformation of enynones **1a**–**1f** into 1,3-diketones **3** and dihydropyran-4-ones **4** and **7** in H_2SO_4.[a]

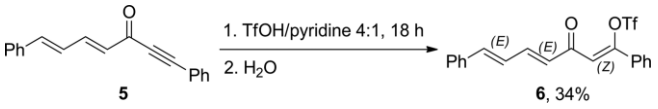


1a–f **3a–d** **4a–f**

7a, R = Me
7b, R = OMe

Entry	Enynone	Ar	*T* [°C]	*t* [h]	Main product, yield [%][b]
1	**1a**	Ph	r.t.	1	**3a**, 72
2	**1a**	Ph	r.t.	60	**4a**, 95
3	**1b**	*p*-Cl-C_6H_4	r.t.	2.5	**3b**, 82
4	**1b**	*p*-Cl-C_6H_4	r.t.	96	**4b**, 89
5	**1c**	*p*-NO_2-C_6H_4	r.t.	18	**3c**, 92
6	**1c**	*p*-NO_2-C_6H_4	65	36	**4c**, 80
7	**1d**	*p*-Me-C_6H_4	0	4	**3d**, 28
8	**1d**	*p*-Me-C_6H_4	r.t.	1.5	**4d**, 72
9	**1d**	*p*-Me-C_6H_4	r.t.	60	**7a**, 68[c]
10	**1e**	*p*-OMe-C_6H_4	0	1.5	**4e**, 43
11	**1e**	*p*-OMe-C_6H_4	0 to r.t.	12	**7b**, 77[c]
12	**1f**	3,4-$(OMe)_2$-C_6H_3	0	2	**4f**, 22

[a] All reactions were performed with 0.1 mol L^{-1} of enynone in H_2SO_4 as the reaction solvent. [b] Yield of isolated product. [c] The product was not isolated, and the yield was determined by ^1H NMR spectroscopic analysis of the crude reaction mixture in H_2SO_4.



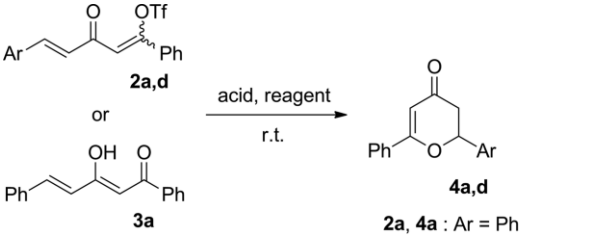
Scheme 2. Transformation of dienynone **5** into the vinyl triflate **6**.

1,3-diketones **3**) and the cyclization into dihydropyran-4-ones **4** (see the X-ray structure of **4b** in Figure 1). For example, the conversion of enynone **1c** containing the nitro group into the corresponding dihydropyran-4-one **4c** required a reaction temperature of 65 °C (Table 3, Entry 6), whereas the same reaction for enynones with methoxy substituents (**1e** and **1f**) was rather fast at 0 °C (Table 3, Entries 10 and 12). In the latter case, the cyclizations were so fast that we observed only traces of the corresponding diketones, which, therefore, could not be isolated.

After the cyclization in H_2SO_4, the presence of activating groups on the Ar ring at the 2-position of the dihydropyran-4-one scaffold leads to further sulfonation reactions, which are responsible for the decreased yields of **4d**–**4f**. The sulfonated products were not stable after workup and gave ring-opening and fragmentation products. However, the sulfonated derivatives **7a** (Ar = *p*-Me-C_6H_4) and **7b** (Ar = *p*-OMe-C_6H_4) were stable as O-protonated forms in the reaction medium H_2SO_4 and could be characterized by NMR spectroscopy and HRMS (see Exp. Sect.), which revealed selective sulfonation at the *meta* position of the 2-aryl ring. This selectivity can mostly be explained by the presence of an activating substituent, but the protonation of the carbonyl group also deactivates the conjugated 6-phenyl ring by delocalization of the positive charge. This was shown by comparative NMR spectroscopy studies of dihydropyran-4-ones **4a** and **4b**, first in the H_2SO_4 reaction medium (i.e., the protonated species **D1** and **D2**) and then for isolated compounds in $CDCl_3$ (see Scheme 3). In the ^{13}C NMR spectra, the deshielding ($\Delta\delta_C$ = 20 ppm) of the C^6 atoms (δ_C = 190 ppm) in protonated species **D1** and **D2**, compared with the same atoms in neutral precursors **4a** and **4b** (δ_C = 170 ppm), reveals a substantial positive-charge delocalization from the protonated carbonyl group into the Ph–C^6=C^5H moiety. Analogously, a deshielding of 0.9 ppm is observed for H^5 in the ^1H NMR spectrum.

To understand the reaction mechanism and to find conditions that would avoid the sulfonation, we wanted to determine the reason why the cyclization into dihydropyran-4-ones seemed to proceed more readily through the vinyl sulfates in H_2SO_4 than through the triflates in TfOH. As mentioned above, the triflate **2a** gives only 31 % yield of **4a** after 60 h in TfOH (see Table 1, Entry 13). However, interestingly, when **2a** is dissolved in H_2SO_4 under the same conditions, **4a** is obtained in 80 % yield (Table 4, Entry 1). The presence of 10 % volume of H_2SO_4 in TfOH was enough to accelerate the cyclization, and **4a** was obtained in more than 50 % yield after 24 h (Table 4, Entry 4), even though the main products after full conversion were sulfonated dihydropyran-4-ones (Table 4, Entry 5) owing to the enhanced sulfonation properties of H_2SO_4 when dissolved and partially protonated in TfOH. In contrast, the presence of water did not show any positive effect, and the presence of H_2O_2, which forms peroxytriflic acid CF_3SO_4H in TfOH,[11] led to a complex mixture of oxidation products (Table 4, Entries 2 and 3).

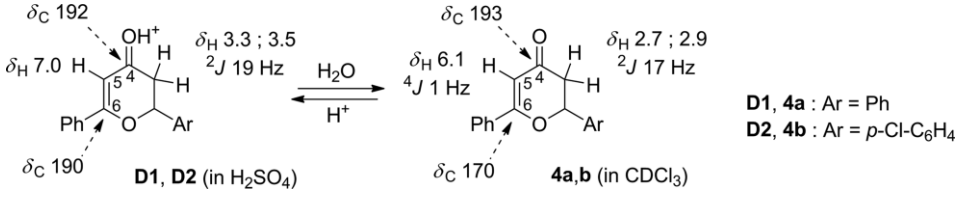
Table 4. Screening of different conditions for the cyclization of triflates **2** and 1,3-diketones **3** into dihydropyran-4-ones **4**.



Entry	Starting material[a]	Acid[b]	Reagent[c]	*T* [h]	Product Yield [%][d]
1	**2a**	H_2SO_4	none	60	**4a**, 80
2	**2a**	TfOH	H_2O	60	**4a**, 28
3	**2a**	TfOH	H_2O_2	2	complex mixture
4	**2a**	TfOH	H_2SO_4	24	**4a**, >50
5	**2a**	TfOH	H_2SO_4	48	sulfonated dihydropyran-4-ones
6	**2a**	TfOH	H_3PO_4	24	**4a**, 15
7	**2a**	TfOH	CF_3CO_2H	24	**4a**, 15
8	**2a**	TfOH	HNO_3	24	complex mixture
9	**2a**	TfOH	$HClO_4$	5	complex mixture
10	**2a**	TfOH	HSO_3Cl	48	**4a**, >50
11	**2d**	TfOH	HSO_3Cl	16	**4d**, traces + **7a**, main product
12	**2a**	TfOH	HSO_3F	48	complex mixture
13	**3a**	H_2SO_4	none	24	**4a**, 96
14	**3a**	TfOH	none	1.5	**4a**, 96

[a] 0.1 mol L^{-1} of starting material, vinyl triflates **2a** and **2d** were generated in situ from the corresponding enynones **1a** and **1d** before the addition of the reagent. [b] Reaction solvent. [c] 10 % volume in solution in TfOH. [d] Yields determined by ^1H NMR spectroscopic analysis of the crude reaction mixtures.

The above observations led us to explore the effects of other Brønsted acids on the cyclization in TfOH. The Brønsted acids are presented in Table 4 in the order of their increasing acid



Scheme 3. NMR spectroscopy studies of dihydropyran-4-ones **4a** and **4b** in H_2SO_4 and in $CDCl_3$; the protonation of the carbonyl group in H_2SO_4 and the positive-charge delocalization are shown (chemical shifts δ are given in ppm).

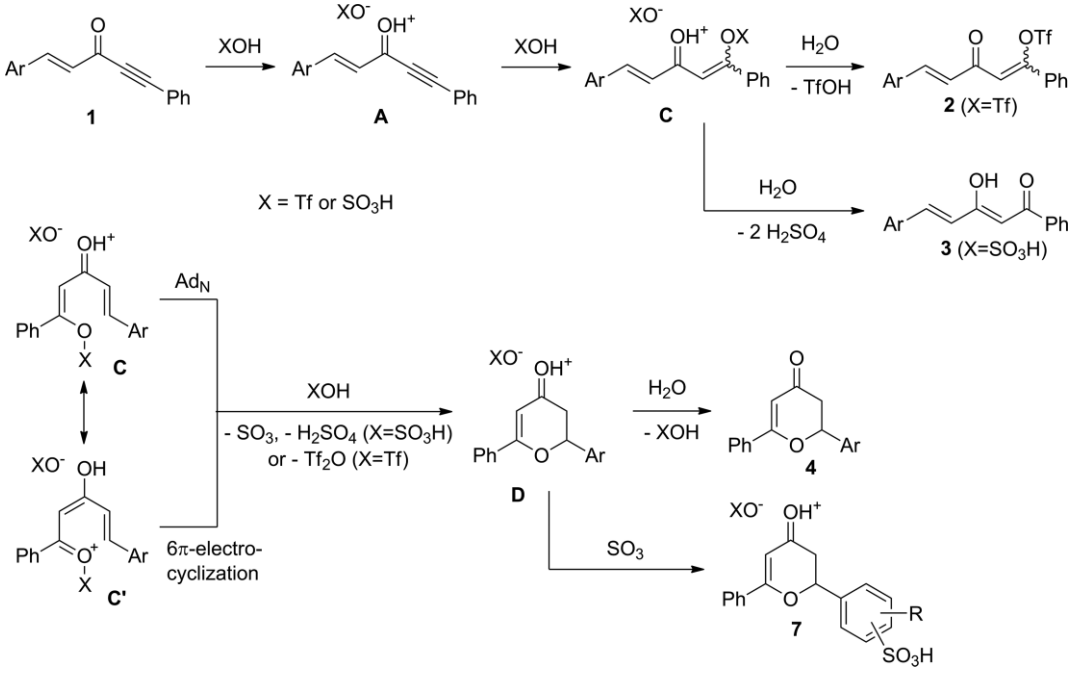
strength (Table 4, Entries 6–12). The weakest H_3PO_4 and CF_3CO_2H did not show any effect on the cyclization rate, and the strong oxidizing agents $HClO_4$ and HNO_3 led to complex mixtures of products. A complex mixture was also observed with HSO_3F (Table 4, Entry 12) but may be explained in this case by an enhanced electrophilic activation owing to the stronger acid strength of HSO_3F (Hammett acidity function, H_0 = –15.1) compared with that of TfOH (H_0 = –14.1).[12] Only HSO_3Cl (H_0 = –13.8) had a positive effect on the cyclization rate, and more than 50 % conversion of **2a** into **4a** was observed after 48 h (Table 4, Entry 10). However, HSO_3Cl is also a powerful sulfonating agent and leads again to sulfonated products, as shown for **4d** (Ar = *p*-Me-C_6H_4; Table 4, Entry 11).

To understand the reaction mechanism, the point to consider is the analogous cyclization of 1,3-diketones **3**. Under the same conditions, they are converted into dihydropyran-4-ones faster than the corresponding vinyl sulfates and triflates; for example, a complete conversion of **3a** into **4a** is achieved after 24 h in H_2SO_4 and 90 min in TfOH (Table 4, Entries 13 and 14). α,β-Unsaturated 1,3-diketones can be considered as hydrated derivatives of conjugated enynones, and their cyclization in acidic media has already been described.[13] The authors proposed a mechanism involving either an intramolecular conjugated nucleophilic addition of the protonated enol or a 6π electrocyclization of its tautomeric form. In agreement with this supposition, we propose the same mechanism in Scheme 4 by considering the protonated vinyl sulfates (X = SO_3H) and triflates (X = Tf), drawn as mesomeric forms **C** and **C′**, as structural derivatives of α,β-unsaturated 1,3-diketones with X different from H. See also the relatively close synthesis of pyran-4-ones from 2,5-enynones and cross-conjugated diynones.[14]

According to this mechanism, the cyclization of **C** into **D** occurs with the oxygen atom initially provided by the acid XOH and, therefore, requires the elimination of "X^{+}" (i.e. SO_3H^+ or Tf^+). The ease of elimination directly affects the cyclization rate: although $^{+}SO_3H$ can easily leave as SO_3 and a proton, the Tf^+ group is probably derived as triflic anhydride (Tf_2O) in a slower reaction; therefore, the cyclization is more difficult in TfOH. The derivatization of Tf^+ is easier in the presence of more nucleophilic species such as H_2SO_4 or HSO_3Cl, and this results in the faster conversion of **2a** into **4a** observed in Table 4. For HSO_3Cl, we assume the formation of the mixed anhydride $TfOSO_2Cl$.[15] It should be mentioned that H_3PO_4 and CF_3CO_2H, which are supposed to be the most nucleophilic acids in Table 4, are actually fully protonated in TfOH and, therefore, ineffective.

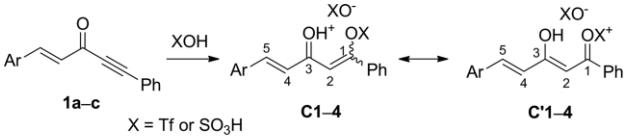
An NMR spectroscopy study of the vinyl triflates and sulfates **C1**–**C4** in TfOH and H_2SO_4, presented in Table 5, reveals that the real structures of these cationic species, between the resonance structures **C** or **C′**, seem to depend on the X group and acidic medium XOH. For X = Tf (species **C1** and **C2**, Table 5, Entries 1–4), two (*E*/*Z*) isomers were observed in each case with structures similar to the resonance form **C** rather than **C′**. Species **C1** and **C2** are the O-protonated forms of triflates **2a** and **2b**, respectively, with chemical shifts of δ = 190.6–194.3 ppm for the carbonyl carbon atom C^3 in their ^{13}C NMR spectra. The protonation of the carbonyl group is additionally supported by the large ^1H and ^{13}C NMR chemical shifts of H^5 and C^5 of δ = 8.77–8.93 ppm and δ = 166.6–169.0 ppm, respectively, which indicate a charge delocalization into the Ar–C^5H=C^4H fragment. Similar chemical shifts of ca. 167.6–172.3 ppm are observed for the C^1 atoms next to the OTf group.

In contrast, for X = SO_3H (species **C3** and **C4**; Table 5, Entries 5 and 6), the C^1 atom has larger ^{13}C NMR chemical shifts of 184.9–188.0 ppm and is now slightly more deshielded than C^3 (δ = 182.6–183.4 ppm), whereas H^5 and C^5 have smaller ^1H and ^{13}C NMR chemical shifts of 7.99–8.14 and 130.3–147.7 ppm,



Scheme 4. Plausible reaction mechanism for the transformation of enynones **1** into triflates **2**, 1,3-diketones **3**, and dihydropyran-4-ones **4** and **7**.

Table 5. Selected ^{1}H and ^{13}C NMR spectroscopic data of species **C1**–**C4** generated from enynones **1a**–**1c** in TfOH or H_2SO_4.[a]



C1 (from **1a** in TfOH): Ar = Ph, X = Tf
C2 (from **1b** in TfOH): Ar = *p*-Cl-C_6H_4, X = Tf
C3 (from **1b** in H_2SO_4): Ar = *p*-Cl-C_6H_4, X = SO_3H
C4 (from **1c** in H_2SO_4): Ar = *p*-NO_2-C_6H_4, X = SO_3H

		^{1}H NMR, δ_H [ppm]			^{13}C NMR, δ_C [ppm]				
Entry	Cation	H^2 (s)	H^4 (d)	H^5 (d)	C^1	C^2	C^3	C^4	C^5
1	(1*Z*,4*E*)-**C1**	7.47	7.56 (J = 15.4 Hz)	8.93 (J = 15.4 Hz)	167.6	109.9	190.6	120.8	169.0
2	(1*E*,4*E*)-**C1**[b]	7.09	7.18 (J = 15.1 Hz)	8.85 (J = 15.1 Hz)	171.8	113.8	194.0	119.9	169.0
3	(1*Z*,4*E*)-**C2**	7.45	7.51 (J = 15.4 Hz)	8.86 (J = 15.4 Hz)	168.0	110.0	190.6	121.1	166.7
4	(1*E*,4*E*)-**C2**[b]	7.08	7.11 (J = 15.1 Hz)	8.77 (J = 15.1 Hz)	172.3	113.7	194.3	120.2	166.6
5	**C3**	6.60	6.86 (J = 15.8 Hz)	7.99 (J = 15.8 Hz)	184.9	97.9	183.4	119.3	130.3
6	**C4**	6.87	7.18 (J = 16.0 Hz)	8.14 (J = 16.0 Hz)	188.0	99.1	182.6	124.3	147.7

[a] The ^{1}H and ^{13}C NMR spectra were recorded with samples in TfOH or H_2SO_4 at room temperature and referenced relative to the CH_2Cl_2 ^{1}H and ^{13}C signals at δ = 5.30 and 53.52 ppm, respectively. [b] Minor isomer in mixture of (*E*/*Z*) isomers, δ_C determined from ^{1}H–^{13}C HSQC and HMBC spectra.

respectively. This shows that the delocalization of the positive charge is mainly over atoms C^1 and C^3; as only single isomers of **C3** and **C4** were observed, one may assume that the structures of such vinyl sulfates are closer to the mesomeric form **C′** . If the triflates and sulfates have different structures, then one may suppose that they also have different cyclization mechanisms, that is, intramolecular nucleophilic addition for triflates (structure **C**) and oxa-6π electrocyclization for sulfates (structure **C′**).

It should be emphasized that **2** and **3** are derivatives of hemicurcuminoids, which are used widely for the preparation of many practically valuable and biologically active compounds.[16] Concerning dihydropyran-4-ones **4**, such motifs are well represented in natural and bioactive products.[17] For these reasons, several methods have been developed for their synthesis, such as the hetero-Diels–Alder reaction,[18] transition-metal-catalyzed cyclizations of β-hydroxy enones[19] or ynones,[20] and acid-catalyzed cyclizations of 5-hydroxy-1,3-diketones[21] or other carbonyl compounds.[22]

Conclusions

We have described the behavior of diaryl-substituted cross-conjugated enynones under electrophilic activation in TfOH or H_2SO_4 and showed that they are efficient precursors of vinyl triflates, vinyl sulfates, α,β-unsaturated 1,3-diketones, and dihydropyran-4-ones. The different cationic intermediates of these reactions have been studied by NMR spectroscopy. We have shown that the initial products of the additions of acids to the triple bonds of these enynones, vinyl triflates and sulfates, could be considered as particular derivatives of α,β-unsaturated 1,3-diketones with a similar reactivity under acidic conditions that leads finally to the formation of dihydropyran-4-ones. This work extends the relevance of cross-conjugated enynones as intermediates in the synthesis of carbocyclic and heterocyclic compounds.

Experimental Section

General Experimental Methods: All reagents and solvents were used directly as purchased or purified according to standard procedures when necessary. Analytical thin-layer chromatography was performed with commercial silica gel plates, visualized with short-wavelength UV light (254 nm), and stained with a *p*-anisaldehyde solution in EtOH/H_2SO_4 with subsequent heating. Flash column chromatography was performed with silica gel 60 and mixtures of petroleum ether and ethyl acetate or chloroform. The NMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Bruker AVANCE III 400 (400, 376 and 100 MHz for ^{1}H, ^{19}F, and ^{13}C NMR spectra, respectively) spectrometer at 25 °C. The residual proton solvent peak (δ = 7.26 ppm) for ^{1}H NMR spectra and the carbon signal of $CDCl_3$ (δ = 77.16 ppm) for ^{13}C NMR spectra were used as references. The ^{19}F NMR spectra were indirectly referenced to the signal of $CFCl_3$ (δ = 0.0 ppm). The ^{1}H and ^{13}C NMR spectra of cations in TfOH and H_2SO_4 were referenced relative to the signal of CH_2Cl_2 added as an internal standard at δ_H = 5.30 ppm and δ_C = 53.52 ppm. Splitting patterns are designated as: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, and m = multiplet. The IR spectra were recorded with samples in CH_2Cl_2 or $CHCl_3$ solutions or as KBr pellets with a Shimadzu IR Affinity-1 spectrometer in the wavenumber region 400–4000 cm^{-1} with a resolution of 4 cm^{-1}, Happ–Genzel apodization, and 20 scans. The HRMS was performed with Bruker maXis HRMS-ESI-QTOF and Varian 902-MS MALDI mass spectrometers.

X-ray Analysis: Suitable crystals of (1*Z*,4*E*)-**2b** and **4b** were studied with an Agilent Technologies (Oxford Diffraction) "Supernova" diffractometer and were kept at 293(2) and 100.01(10) K, respectively, during data collection. Within Olex2,[23] the structure was solved with the SHELXS[24] structure solution program by direct methods and refined with the SHELXL[25] refinement package through least-squares minimization.

CCDC 1530422 [for (1*Z*,4*E*)-**2b**] and 1530422 (for **4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Starting materials: Compounds **1a**–1**f** and **5** were synthesized according to the literature procedures.[26,29]

(*E*)-1,5-Diphenylpent-1-en-4-yn-3-one (1a): Colorless solid, m.p. 72–73 °C. The compound has already been prepared and characterized.[27,28]

(*E*)-1-(4-Chlorophenyl)-5-phenylpent-1-en-4-yn-3-one (1b): Yellowish solid, m.p. 113–115 °C. This compound has already been prepared and partially characterized.[28,29] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 16.1 Hz, 1 H), 7.68–7.62 (m, 2 H), 7.54 (d, J = 8.5 Hz, 2 H), 7.51–7.46 (m, 1 H), 7.45–7.39 (m, 4 H), 6.84 (d, J = 16.1 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.0, 146.7, 137.3, 133.1, 132.7, 130.8, 129.9, 129.6, 129.1, 128.8, 120.3, 91.9, 86.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2212 (m), 1628 (s), 1612 (s) cm^{-1}. HRMS (MALDI): calcd. for $C_{17}H_{12}ClO$ $[M + H]^+$ 267.0571; found 267.0580.

(*E*)-1-(4-Nitrophenyl)-5-phenylpent-1-en-4-yn-3-one (1c): Colorless solid, m.p. 187–188 °C. This compound has already been prepared and partially characterized.[29] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (dm, J = 8.8 Hz, 2 H), 7.90 (d, J = 16.2 Hz, 1 H), 7.76 (dm, J = 8.8 Hz, 2 H), 7.69–7.63 (m, 2 H), 7.53–7.48 (m, 1 H), 7.47–7.41 (m, 2 H), 6.96 (d, J = 16.2 Hz, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 177.4, 149.1, 144.4, 140.3, 133.2, 132.0, 131.1, 129.3, 128.9, 124.4, 119.9, 92.8, 86.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2210 (m), 1632 (s), 1612 (s), 1518 (s), 1344 (s) cm^{-1}. HRMS (MALDI): calcd. for $C_{17}H_{12}NO_3$ $[M + H]^+$ 278.0812; found 278.0798.

(*E*)-1-(4-Methylphenyl)-5-phenylpent-1-en-4-yn-3-one (1d): Yellowish solid, m.p. 61–62 °C. This compound has already been prepared and partially characterized.[29,30] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 16.1 Hz, 1 H), 7.68–7.63 (m, 2 H), 7.51 (d, J = 8.1 Hz, 2 H), 7.51–7.45 (m, 1 H), 7.44–7.39 (m, 2 H), 7.24 (d, J = 8.0 Hz, 2 H), 6.84 (d, J = 16.1 Hz, 1 H), 2.40 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.4, 148.6, 142.0, 133.1, 131.5, 130.7, 130.0, 128.9, 128.8, 127.8, 120.5, 91.5, 86.8, 21.7 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2214 (m), 1630 (s), 1606 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{14}NaO$ $[M + Na]^+$ 269.0937; found 269.0926.

(*E*)-1-(4-Methoxyphenyl)-5-phenylpent-1-en-4-yn-3-one (1e): Yellowish solid, m.p. 107–109 °C. This compound has already been prepared and partially characterized.[28,29] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 16.0 Hz, 1 H), 7.67–7.63 (m, 2 H), 7.56 (dm, J = 8.8 Hz, 2 H), 7.50–7.44 (m, 1 H), 7.44–7.38 (m, 2 H), 6.95 (dm, J = 8.8 Hz, 2 H), 6.77 (d, J = 16.0 Hz, 1 H), 3.86 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.4, 162.4, 148.4, 133.0, 130.7, 130.6, 128.8, 127.0, 126.6, 120.6, 114.7, 91.2, 86.9, 55.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2210 (m), 1624 (s), 1598 (m), 1571 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{14}NaO_2$ $[M + Na]^+$ 285.2923; found 285.2926.

(*E*)-1-(3,4-Dimethoxyphenyl)-5-phenylpent-1-en-4-yn-3-one (1f): Yellowish solid, m.p. 127–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 16.0 Hz, 1 H), 7.68–7.63 (m, 2 H), 7.50–7.44 (m, 1 H), 7.44–7.38 (m, 2 H), 7.20 (dd, J = 8.3, 2.0 Hz, 1 H), 7.11 (d, J = 2.0 Hz, 1 H), 6.91 (d, J = 8.3 Hz, 1 H), 6.77 (d, J = 16.0 Hz, 1 H), 3.94 (s, 6 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.2, 152.2, 149.6, 148.5, 133.0, 130.6, 128.8, 127.2, 126.8, 123.9, 120.5, 111.3, 110.2, 91.3, 86.9, 56.18, 56.11 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2213 (m), 1626 (s), 1596 (s), 1512 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{17}O_3$ $[M + H]^+$ 293.1172; found 293.1154; calcd for $C_{19}H_{16}NaO_3$ $[M + Na]^+$ 315.0992; found 315.0990.

(4*E*,6*E*)-1,7-Diphenylhepta-4,6-dien-1-yn-3-one (5): Yellowish solid, m.p. 66–67 °C. This compound has already been prepared and characterized.[31]

General Procedure for the Transformation of Enynones 1a–1f into Vinyl Triflates 2a–2f, 1,3-Diketones 3a–3d, and Dihydropyran-4-ones 4a–4f: Enynone **1** (0.2 mmol) was added to the indicated acid (TfOH or H_2SO_4, 2 mL), and the solution was stirred at the indicated temperature for the indicated reaction time (see Tables 1, 2, and 3). The reaction mixture was then diluted with chloroform (4 mL), cooled to 0 °C, and quenched under vigorous stirring by the dropwise addition of an excess volume of cold water. The organic layer was separated, and the aqueous layer was extracted again with chloroform. The combined organic layers were washed with a diluted solution of $NaHCO_3$, dried with Na_2SO_4, and concentrated under reduced pressure. The reaction products were isolated by flash column chromatography with silica gel. For triflates **2**, the crude reaction mixtures were first analyzed by ^{1}H and ^{19}F NMR spectroscopy to determine the ratios of (1*Z*,4*E*)/(1*E*,4*E*) isomers and to identify the minor isomers (1*E*,4*E*), which were unstable and not isolated. The main (1*Z*,4*E*) isomers were isolated and protected from light and acids.

(1*Z*,4*E*)-1,5-Diphenyl-1-(trifluoromethylsulfonyloxy)penta-1,4-dien-3-one (2a): The title compound was prepared from enynone **1a** in TfOH (room temp., 1 h) and isolated by flash column chromatography (petroleum ether/EtOAc, 9:1, 62 mg, 81 % yield). Yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 16.0 Hz, 1 H), 7.68–7.63 (m, 2 H), 7.62–7.56 (m, 2 H), 7.56–7.51 (m, 1 H), 7.51–7.46 (m, 2 H), 7.44–7.40 (m, 3 H), 6.94 (d, J = 16.0 Hz, 1 H), 6.78 (s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.9, 153.5, 145.2, 134.3, 132.3, 131.9, 131.2, 129.24, 129.19, 128.8, 126.8, 126.5, 118.4 (q, J = 320.6 Hz), 117.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.76 ppm. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 1682 (m), 1665 (m), 1626 (s), 1140 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{14}F_3O_4S$ $[M + H]^+$ 383.0559; found 383.0519; calcd. for $C_{18}H_{13}F_3NaO_4S$ $[M + Na]^+$ 405.0379; found 405.0368.

(1*E*,4*E*)-1,5-Diphenyl-1-(trifluoromethylsulfonyloxy)penta-1,4-dien-3-one (2a): The title compound was identified in the crude reaction mixture as a minor isomer of (1*Z*,4*E*)-**2a**; (1*Z*,4*E*)/(1*E*,4*E*) ratio 8.4:1. ^{1}H NMR (400 MHz, $CDCl_3$, selected signals): δ = 6.604 (s, 1 H), 6.596 (d, J = 16.0 Hz, 1 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.68 ppm.

(1*Z*,4*E*)-5-(4-Chlorophenyl)-1-phenyl-1-(trifluoromethylsulfonyloxy)penta-1,4-dien-3-one (2b): The title compound was prepared from enynone **1b** in TfOH (room temp., 1 h) and isolated by flash column chromatography (petroleum ether/EtOAc, 9:1, 61 mg, 73 % yield). Yellowish solid. Single crystals suitable for X-ray diffraction analysis were obtained by the slow evaporation of a dilute solution in dichloromethane, m.p. 110–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 15.9 Hz, 1 H), 7.68–7.62 (m, 2 H), 7.56–7.45 (m, 5 H), 7.39 (d, J = 8.5 Hz, 2 H), 6.90 (d, J = 15.9 Hz, 1 H), 6.76 (s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.6, 153.7, 143.7, 137.2, 132.9, 132.2, 132.0, 129.9, 129.5, 129.3, 126.78, 126.77, 118.4 (q, J = 320.7 Hz), 117.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.73 ppm. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1665 (m), 1624 (s), 1595 (m), 1138 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{13}ClF_3O_4S$ $[M + H]^+$ 417.0170; found 417.0161; calcd. for $C_{18}H_{12}ClF_3NaO_4S$ $[M + Na]^+$ 438.9989; found 438.9983.

(1*E*,4*E*)-5-(4-Chlorophenyl)-1-phenyl-1-(trifluoromethylsulfonyloxy)penta-1,4-dien-3-one (2b): The title compound was identified in the crude reaction mixture as a minor isomer of (1*Z*,4*E*)-**2b**; (1*Z*,4*E*)/(1*E*,4*E*) ratio 6.5:1. ^{1}H NMR (400 MHz, $CDCl_3$, selected signals): δ = 6.58 (s, 1 H), 6.54 (d, J = 16.0 Hz, 1 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.67 ppm.

(1*Z*,4*E*)-5-(4-Nitrophenyl)-1-phenyl-1-(trifluoromethylsulfonyloxy)penta-1,4-dien-3-one (2c): The title compound was prepared from enynone **1c** in TfOH (8 mL, room temp., 3 h) and isolated by flash column chromatography (petroleum ether/EtOAc, 6:1, 52 mg, 61 % yield). Brownish solid, m.p. 131–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (dm, J = 8.8 Hz, 2 H), 7.77 (d, J = 15.7 Hz, 1 H), 7.74 (dm, J = 8.7 Hz, 2 H), 7.69–7.64 (m, 2 H), 7.59–7.53 (m, 1 H), 7.53–7.47 (m, 2 H), 7.05 (d, J = 15.9 Hz, 1 H), 6.78 (s, 1 H) ppm. ^{13}C NMR

(101 MHz, $CDCl_3$): δ = 185.2, 154.4, 149.0, 141.8, 140.5, 132.3, 132.0, 129.7, 129.34, 129.27, 126.8, 124.4, 118.4 (q, J = 320.6 Hz), 117.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.61 ppm. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 1669 (w), 1627 (s), 1609 (m), 1525 (s), 1347 (s), 1139 (s) cm^{-1}. HRMS (MALDI): calcd. for $C_{18}H_{13}F_3NO_6S$ $[M + H]^+$ 428.0410; found 428.0403.

(1*E*,4*E*)-5-(4-Nitrophenyl)-1-phenyl-1-(trifluoromethylsulfonyloxy)penta-1,4-dien-3-one (2c): The title compound was identified in the crude reaction mixture as a minor isomer of (1*Z*,4*E*)-**2c**; (1*Z*,4*E*)/(1*E*,4*E*) ratio 6.5:1. ^1H NMR (400 MHz, $CDCl_3$, selected signals): δ = 8.20 (dm, J = 8.8 Hz, 2 H), 7.99–7.95 (m, 2 H), 6.61 (d, J = 15.9 Hz, 1 H), 6.60 (s, 1 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.62 ppm.

(1*Z*,4*E*)-5-(4-Methylphenyl)-1-phenyl-1-(trifluoromethylsulfonyloxy)penta-1,4-dien-3-one (2d): The title compound was prepared from enynone **1d** in TfOH (room temp., 1 h) and isolated by flash column chromatography (petroleum ether/EtOAc, 9:1, 52 mg, 66 % yield). Brownish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, J = 15.9 Hz, 1 H), 7.68–7.63 (m, 2 H), 7.56–7.45 (m, 5 H), 7.22 (d, J = 8.0 Hz, 2 H), 6.90 (d, J = 15.9 Hz, 1 H), 6.77 (s, 1 H), 2.39 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.9, 153.3, 145.4, 141.9, 132.4, 131.9, 131.7, 130.0, 129.2, 128.8, 126.8, 125.6, 118.4 (q, J = 320.6 Hz), 117.4, 21.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.79 ppm. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1662 (w), 1623 (s), 1596 (m), 1138 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{16}F_3O_4S$ $[M + H]^+$ 397.0716; found 397.0715; calcd. for $C_{19}H_{15}F_3NaO_4S$ $[M + Na]^+$ 419.0535; found 419.0536.

(1*E*,4*E*)-5-(4-Methylphenyl)-1-phenyl-1-(trifluoromethylsulfonyloxy)penta-1,4-dien-3-one (2d): The title compound was identified in the crude reaction mixture as a minor isomer of (1*Z*,4*E*)-**2d**; (1*Z*,4*E*)/(1*E*,4*E*) ratio 4.6:1. ^1H NMR (400 MHz, $CDCl_3$, selected signals): δ = 7.30 (d, J = 8.0 Hz, 2 H), 7.17 (d, J = 8.0 Hz, 2 H), 6.60 (s, 1 H), 6.56 (d, J = 16.0 Hz, 1 H), 2.37 (s, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.69 ppm.

(1*Z*,4*E*)-5-(4-Methoxyphenyl)-1-phenyl-1-(trifluoromethylsulfonyloxy)penta-1,4-dien-3-one (2e): The title compound was prepared from enynone **1e** in TfOH (0 °C, 30 min) and isolated by flash column chromatography (petroleum ether/EtOAc, 5:1, 63 mg, 76 % yield). Brownish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 15.9 Hz, 1 H), 7.67–7.62 (m, 2 H), 7.55 (dm, J = 8.8 Hz, 2 H), 7.55–7.45 (m, 3 H), 6.93 (dm, J = 8.8 Hz, 2 H), 6.82 (d, J = 15.9 Hz, 1 H), 6.75 (s, 1 H), 3.86 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.8, 162.3, 153.2, 145.2, 132.5, 131.8, 130.7, 129.2, 127.1, 126.8, 124.3, 118.4 (q, J = 320.6 Hz), 117.6, 114.7, 55.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.82 ppm. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1661 (w), 1623 (s), 1596 (s), 1171 (s), 1138 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{16}F_3O_5S$ $[M + H]^+$ 413.0665; found 413.0660; calcd. for $C_{19}H_{15}F_3NaO_5S$ $[M + Na]^+$ 435.0484; found 435.0483.

(1*E*,4*E*)-5-(4-Methoxyphenyl)-1-phenyl-1-(trifluoromethylsulfonyloxy)penta-1,4-dien-3-one (2e): The title compound was identified in the crude reaction mixture as a minor isomer of (1*Z*,4*E*)-**2e**; (1*Z*,4*E*)/(1*E*,4*E*) ratio 8:1. ^1H NMR (400 MHz, $CDCl_3$, selected signals): δ = 6.59 (s, 1 H), 6.49 (d, J = 16.0 Hz, 1 H), 3.83 (s, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.70 ppm.

(1*Z*,4*E*)-5-(3,4-Dimethoxyphenyl)-1-phenyl-1-(trifluoromethylsulfonyloxy)penta-1,4-dien-3-one (2f): The title compound was prepared from enynone **1e** in TfOH (0 °C, 30 min) and isolated by flash column chromatography (petroleum ether/EtOAc, 3:1, 69 mg, 78 % yield). Brownish oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, J = 15.8 Hz, 1 H), 7.67–7.62 (m, 2 H), 7.56–7.50 (m, 1 H), 7.50–7.44 (m, 2 H), 7.19 (dd, J = 8.3, 1.9 Hz, 1 H), 7.12 (d, J = 1.9 Hz, 1 H), 6.89 (d, J = 8.3 Hz, 1 H), 6.83 (d, J = 15.8 Hz, 1 H), 6.77 (s, 1 H), 3.93 (s, 6 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 185.8, 153.2, 152.2, 149.5, 145.6, 132.4, 131.9, 129.2, 127.4, 126.8, 124.4, 124.1, 118.4 (q, J = 320.5 Hz), 117.5, 111.3, 110.1, 56.2, 56.1 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.78 ppm. IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 1660 (w), 1622 (s), 1593 (m), 1512 (s), 1266 (s), 1139 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{18}F_3O_6S$ $[M + H]^+$ 443.0776; found 443.0769; calcd. for $C_{20}H_{17}F_3NaO_6S$ $[M + Na]^+$ 465.0596; found 465.0587.

(1*E*,4*E*)-5-(3,4-Dimethoxyphenyl)-1-phenyl-1-(trifluoromethylsulfonyloxy)penta-1,4-dien-3-one (2f): The title compound was identified in the crude reaction mixture as a minor isomer of (1*Z*,4*E*)-**2f**; (1*Z*,4*E*)/(1*E*,4*E*) ratio 4.8:1. ^1H NMR (400 MHz, $CDCl_3$, selected signals): δ = 7.03 (dd, J = 8.3, 2.0 Hz, 1 H), 6.60 (s, 1 H), 6.47 (d, J = 15.9 Hz, 1 H), 3.91 (s, 3 H), 3.86 (s, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.70 ppm.

(2*Z*,4*E*)-3-Hydroxy-1,5-diphenylpenta-2,4-dien-1-one (3a): The title compound was prepared from enynone **1a** in H_2SO_4 (room temp., 1 h) and isolated by flash column chromatography (petroleum ether/$CHCl_3$, 2:1, 36 mg, 72 % yield). Yellowish solid, m.p. 111–112 °C. The compound has already been prepared and characterized.[13]

(2*Z*,4*E*)-5-(4-Chlorophenyl)-3-hydroxy-1-phenylpenta-2,4-dien-1-one (3b): The title compound was prepared from enynone **1b** in H_2SO_4 (room temp., 2.5 h) and isolated by flash column chromatography (petroleum ether/$CHCl_3$, 3:1, 47 mg, 82 % yield). Yellowish solid, m.p. 126–127 °C. The compound has already been prepared and characterized.[32] ^1H NMR (400 MHz, $CDCl_3$): δ = 16.10 (s, 1 H), 7.98–7.93 (m, 2 H), 7.63 (d, J = 15.8 Hz, 1 H), 7.59–7.53 (m, 1 H), 7.52–7.45 (m, 4 H), 7.37 (dm, J = 8.5 Hz, 2 H), 6.62 (d, J = 15.8 Hz, 1 H), 6.34 (s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 189.8, 178.9, 138.6, 136.4, 136.0, 133.7, 132.8, 129.35, 129.27, 128.8, 127.5, 124.0, 98.0 ppm.

(2*Z*,4*E*)-3-Hydroxy-5-(4-nitrophenyl)-1-phenylpenta-2,4-dien-1-one (3c): The title compound was prepared from enynone **1c** in H_2SO_4 (room temp., 18 h) and isolated by flash column chromatography (petroleum ether/$CHCl_3$, 1:1, 54 mg, 92 % yield). Yellowish solid, m.p. 147–148 °C. The compound has already been prepared and partially characterized.[33] ^1H NMR (400 MHz, $CDCl_3$): δ = 15.89 (s, 1 H), 8.26 (d, J = 8.8 Hz, 2 H), 8.00–7.94 (m, 2 H), 7.73–7.66 (m, 3 H), 7.61–7.55 (m, 1 H), 7.53–7.46 (m, 2 H), 6.76 (d, J = 15.9 Hz, 1 H), 6.40 (s, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.1, 176.8, 148.3, 141.5, 136.7, 136.3, 133.2, 128.9, 128.6, 127.7, 127.6, 124.4, 98.9 ppm.

(2*Z*,4*E*)-3-Hydroxy-1-phenyl-5-*p*-tolylpenta-2,4-dien-1-one (3d): The title compound was prepared from enynone **1d** in H_2SO_4 (0 °C, 4 h) and isolated by flash column chromatography (petroleum ether/$CHCl_3$, 3:2, 15 mg, 28 % yield). Yellowish solid, m.p. 117–118 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 16.21 (s, 1 H), 7.99–7.92 (m, 2 H), 7.68 (d, J = 15.8 Hz, 1 H), 7.58–7.52 (m, 1 H), 7.52–7.45 (m, 4 H), 7.21 (d, J = 8.0 Hz, 2 H), 6.62 (d, J = 15.8 Hz, 1 H), 6.34 (s, 1 H), 2.39 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 189.1, 180.2, 140.6, 140.3, 136.5, 132.6, 132.5, 129.8, 128.8, 128.2, 127.5, 122.5, 97.6, 21.6 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1630 (s), 1595 (s), 1506 (vs), 1464 (s), 1167 (s) cm^{-1}. HRMS (MALDI): calcd. for $C_{18}H_{17}O_2$ $[M + H]^+$ 265.1223; found 265.1217.

2,3-Dihydro-2,6-diphenylpyran-4-one (4a): The title compound was prepared from enynone **1a** in H_2SO_4 (room temp., 60 h) and isolated by flash column chromatography (petroleum ether/EtOAc, 4:1, 48 mg, 95 % yield). Colorless solid, m.p. 94–95 °C. The compound has already been prepared and characterized.[21d,34] ^1H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.76 (m, 2 H), 7.53–7.39 (m, 8 H), 6.13 (d, J = 0.8 Hz, 1 H), 5.59 (dd, J = 14.1, 3.4 Hz, 1 H), 2.96 (dd, J =

16.9, 14.1 Hz, 1 H), 2.75 (ddd, *J* = 16.9, 3.4, 0.9 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.0, 170.4, 138.5, 132.7, 131.9, 129.01, 128.99, 128.9, 126.8, 126.3, 102.5, 81.2, 43.1 ppm.

2-(4-Chlorophenyl)-2,3-dihydro-6-phenylpyran-4-one (4b): The title compound was prepared from enynone **1b** in H_2SO_4 (room temp., 96 h) and isolated by flash column chromatography (petroleum ether/EtOAc, 9:1, 51 mg, 89 % yield). Single crystals suitable for X-ray diffraction analysis were obtained by the slow evaporation of a dilute solution in heptanes, m.p. 87–88 °C (lit.[21d] m.p. 90–92 °C). The compound has already been prepared and characterized.[21d] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.74 (m, 2 H), 7.53–7.48 (m, 1 H), 7.47–7.40 (m, 6 H), 6.13 (d, *J* = 0.9 Hz, 1 H), 5.56 (dd, *J* = 13.9, 3.5 Hz, 1 H), 2.91 (dd, *J* = 16.8, 13.9 Hz, 1 H), 2.73 (ddd, *J* = 16.8, 3.5, 0.9 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.5, 170.3, 136.9, 134.9, 132.6, 132.0, 129.2, 128.9, 127.7, 126.8, 102.6, 80.4, 43.0 ppm.

2,3-Dihydro-2-(4-nitrophenyl)-6-phenylpyran-4-one (4c): The title compound was prepared from enynone **1c** in H_2SO_4 (65 °C, 36 h) and isolated by flash column chromatography (petroleum ether/EtOAc, 4:1, 47 mg, 80 % yield). Yellowish solid, m.p. 117–118 °C. The compound has already been prepared and characterized.[21d] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (dm, *J* = 8.8 Hz, 2 H), 7.81–7.75 (m, 2 H), 7.69 (dm, *J* = 8.7 Hz, 2 H), 7.56–7.50 (m, 1 H), 7.49–7.43 (m, 2 H), 6.16 (s, 1 H), 5.71 (dd, *J* = 13.5, 3.9 Hz, 1 H), 2.90 (dd, *J* = 16.8, 13.5 Hz, 1 H), 2.80 (dd, *J* = 16.8, 3.9 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.6, 170.0, 148.2, 145.4, 132.2 (2 C), 129.0, 127.0, 126.8, 124.3, 102.8, 79.9, 43.0 ppm.

2,3-Dihydro-2-(4-methylphenyl)-6-phenylpyran-4-one (4d): The title compound was prepared from enynone **1d** in H_2SO_4 (room temp., 90 min) and isolated by flash column chromatography (petroleum ether/EtOAc, 5:1, 38 mg, 72 % yield). Yellowish solid, m.p. 74–75 °C. The compound has already been prepared and characterized.[21d] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.75 (m, 2 H), 7.52–7.46 (m, 1 H), 7.46–7.37 (m, 4 H), 7.26 (d, *J* = 7.9 Hz, 2 H), 6.12 (s, 1 H), 5.55 (dd, *J* = 14.1, 3.3 Hz, 1 H), 2.96 (dd, *J* = 16.9, 14.1 Hz, 1 H), 2.72 (dd, *J* = 16.9, 3.3 Hz, 1 H), 2.40 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.2, 170.5, 138.9, 135.5, 132.8, 131.9, 129.6, 128.8, 126.8, 126.4, 102.4, 81.1, 43.0, 21.3 ppm.

2,3-Dihydro-2-(4-methoxyphenyl)-6-phenylpyran-4-one (4e): The title compound was prepared from enynone **1e** in H_2SO_4 (0 °C, 90 min) and isolated by flash column chromatography (petroleum ether/EtOAc, 4:1, 24 mg, 43 % yield). Yellowish solid, m.p. 93–94 °C. The compound has already been prepared and characterized.[21d] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.73 (m, 2 H), 7.51–7.46 (m, 1 H), 7.45–7.39 (m, 4 H), 6.98 (dm, *J* = 8.8 Hz, 2 H), 6.14 (d, *J* = 0.9 Hz, 1 H), 5.56 (dd, *J* = 14.1, 3.3 Hz, 1 H), 3.85 (s, 3 H), 2.97 (dd, *J* = 16.8, 14.1 Hz, 1 H), 2.74 (ddd, *J* = 16.8, 3.3, 0.9 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.3, 170.5, 160.2, 132.8, 131.9, 130.4, 128.8, 128.0, 126.8, 114.4, 102.4, 81.0, 55.5, 42.9 ppm.

2,3-Dihydro-2-(3,4-dimethoxyphenyl)-6-phenylpyran-4-one (4f): The title compound was prepared from enynone **1f** in H_2SO_4 (0 °C, 2 h) and isolated by flash column chromatography (petroleum ether/EtOAc, 3:1, 14 mg, 22 % yield). Yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81–7.74 (m, 2 H), 7.52–7.47 (m, 1 H), 7.46–7.40 (m, 2 H), 7.04 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.02 (d, *J* = 1.8 Hz, 1 H), 6.93 (d, *J* = 8.2 Hz, 1 H), 6.12 (s, 1 H), 5.52 (dd, *J* = 14.1, 3.2 Hz, 1 H), 3.921 (s, 3 H), 3.917 (s, 3 H), 2.98 (dd, *J* = 16.8, 14.1 Hz, 1 H), 2.72 (dd, *J* = 16.8, 3.2 Hz, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 193.2, 170.5, 149.7, 149.4, 132.8, 131.9, 130.9, 128.9, 126.8, 119.2, 111.3, 109.7, 102.5, 81.2, 56.17, 56.15, 43.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2926 (s), 1665 (s), 1570 (s), 1518 (s), 1375 (s), 1327 (m), 1267 (s), 1138 (m) cm^{-1}. HRMS (MALDI): calcd. for $C_{19}H_{19}O_4$ [M + H]$^+$ 311.1278; found 311.1285.

(1*Z*,4*E*,6*E*)-1,7-Diphenyl-1-(trifluoromethylsulfonyloxy)hepta-1,4,6-trien-3-one (6): Enynone **5** (26 mg, 0.1 mmol) was added to a solution of pyridine (0.2 mL) in TfOH (0.8 mL), and the resultant solution was stirred at room temperature for 18 h. The reaction mixture was then diluted with chloroform (2 mL), cooled to 0 °C, and quenched under vigorous stirring by the dropwise addition of an excess of cold water. The organic layer was separated, and the aqueous layer was extracted again with chloroform. The combined organic layers were washed first with water and then with a diluted solution of $NaHCO_3$, dried with Na_2SO_4, and concentrated under reduced pressure. The title compound was isolated by flash column chromatography with silica gel (petroleum ether/EtOAc, 10:1, 14 mg, 34 % yield) and then protected from light and acids. Dark red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.62 (m, 2 H), 7.53 (dd, *J* = 15.2, 10.6 Hz, 1 H), 7.56–7.45 (m, 5 H), 7.41–7.33 (m, 3 H), 7.04 (d, *J* = 15.5 Hz, 1 H), 6.94 (dd, *J* = 15.5, 10.6 Hz, 1 H), 6.71 (s, 1 H), 6.48 (d, *J* = 15.2 Hz, 1 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 185.8, 153.3, 145.2, 143.3, 136.0, 132.4, 131.9, 129.9, 129.7, 129.2, 129.1, 127.6, 126.8, 126.6, 118.4 (q, *J* = 320.6 Hz), 117.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –73.80 ppm. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 1662 (w), 1621 (s), 1582 (m), 1423 (s), 1140 (s) cm^{-1}. HRMS (MALDI): calcd. for $C_{20}H_{16}F_3O_4S$ [M + H]$^+$ 409.0716; found 409.0722.

5-(3,4-Dihydro-4-oxo-6-phenyl-2*H*-pyran-2-yl)-2-methylbenzenesulfonic Acid (7a): Enynone **1d** (25 mg, 0.1 mmol) was dissolved in H_2SO_4 (1 mL), and the solution was stirred at room temperature for 60 h. The title compound was identified as the O-protonated form by NMR spectroscopy and HRMS analysis of the reaction mixture (68 % yield, determined by ^{1}H NMR spectroscopy). ^{1}H NMR (400 MHz, H_2SO_4): δ = 8.17 (s, 1 H), 8.11 (d, *J* = 8.0 Hz, 2 H), 7.89 (t, *J* = 7.5 Hz, 1 H), 7.85 (d, *J* = 8.1 Hz, 1 H), 7.70–7.60 (m, 3 H), 7.05 (s, 1 H), 6.08 (dd, *J* = 15.3, 4.5 Hz, 1 H), 3.55 (dd, *J* = 18.8, 15.7 Hz, 1 H), 3.35 (dd, *J* = 18.9, 4.4 Hz, 1 H), 2.75 (s, 3 H) ppm. ^{13}C NMR (101 MHz, H_2SO_4): δ = 191.9, 189.9, 140.6, 139.1, 134.6, 134.2, 132.9, 132.7, 130.5, 129.8, 128.4, 126.7, 98.3, 81.8, 34.1, 19.3 ppm. HRMS (MALDI): calcd. for $C_{18}H_{17}O_5S$ [M + H]$^+$ 345.0791; found 345.0798.

5-(3,4-Dihydro-4-oxo-6-phenyl-2*H*-pyran-2-yl)-2-methoxybenzenesulfonic Acid (7b): Enynone **1e** (26 mg, 0.1 mmol) was dissolved in H_2SO_4 (1 mL) at 0 °C, and the solution was stirred overnight as it warmed slowly to room temperature. The title compound was identified as the O-protonated form by NMR spectroscopy and HRMS analysis of the reaction mixture (77 % yield, determined by ^{1}H NMR spectroscopy). ^{1}H NMR (400 MHz, H_2SO_4): δ = 8.10 (d, *J* = 7.9 Hz, 2 H), 8.08 (d, *J* = 2.1 Hz, 1 H), 7.96 (dd, *J* = 8.9, 1.9 Hz, 1 H), 7.89 (t, *J* = 7.5 Hz, 1 H), 7.64 (t, *J* = 7.9 Hz, 2 H), 7.40 (d, *J* = 9.0 Hz, 1 H), 7.04 (s, 1 H), 6.03 (dd, *J* = 15.4, 4.3 Hz, 1 H), 4.11 (s, 3 H), 3.57 (dd, *J* = 18.8, 15.8 Hz, 1 H), 3.32 (dd, *J* = 18.9, 4.3 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, H_2SO_4): δ = 191.9, 189.9, 158.2, 139.1, 135.8, 130.5, 129.8, 128.4, 128.2, 126.6, 123.5, 114.2, 98.3, 81.8, 56.9, 34.0 ppm. HRMS (MALDI): calcd. for $C_{18}H_{17}O_6S$ [M + H]$^+$ 361.0746; found 361.0736.

NMR Spectroscopic Data of Cations C1–C4 and D1–D2

(1*Z*,4*E*)-C1: Generated from a solution of enynone **1a** (23 mg, 0.1 mmol) in TfOH (1 mL) stirred for 1 h at room temperature and identified by NMR spectroscopic analysis of the reaction mixture; (1*Z*,4*E*)/(1*E*,4*E*) ratio 10.3:1. ^{1}H NMR (400 MHz, TfOH): δ = 8.93 (d, *J* = 15.4 Hz, 1 H), 8.08 (d, *J* = 7.7 Hz, 2 H), 8.02 (d, *J* = 7.8 Hz, 2 H), 7.91 (t, *J* = 7.5 Hz, 1 H), 7.85 (t, *J* = 7.4 Hz, 1 H), 7.75–7.66 (m, 4 H), 7.56 (d, *J* = 15.4 Hz, 1 H), 7.47 (s, 1 H) ppm. ^{13}C NMR (101 MHz, TfOH):

δ = 190.6, 169.0, 167.6, 140.4, 137.4, 134.9, 134.2, 132.1, 131.3, 130.9, 129.9, 120.8, 109.9 ppm. ^{19}F NMR (376 MHz, TfOH): δ = –73.70 (s) ppm.

(1*E*,4*E*)-C1: Identified as a minor isomer in a mixture with (1*Z*,4*E*)-**C1**. ^{1}H NMR (400 MHz, TfOH, selected signals): δ = 8.85 (d, *J* = 15.1 Hz, 1 H), 7.18 (d, *J* = 15.1 Hz, 1 H), 7.09 (s, 1 H) ppm. ^{13}C NMR (101 MHz, TfOH, selected signals): δ = 194.0, 171.8, 169.0, 119.9, 113.8 ppm. ^{19}F NMR (376 MHz, TfOH): δ = –74.42 (s) ppm.

(1*Z*,4*E*)-C2: Generated from a solution of enynone **1b** (27 mg, 0.1 mmol) in TfOH (1 mL) stirred for 1 h at room temperature and identified by NMR spectroscopic analysis of the reaction mixture; (1*Z*,4*E*)/(1*E*,4*E*) ratio 10.3:1. ^{1}H NMR (400 MHz, TfOH): δ = 8.86 (d, *J* = 15.4 Hz, 1 H), 8.06–7.96 (m, 4 H), 7.86 (t, *J* = 7.4 Hz, 1 H), 7.74–7.65 (m, 4 H), 7.51 (d, *J* = 15.4 Hz, 1 H), 7.45 (s, 1 H) ppm. ^{13}C NMR (101 MHz, TfOH): δ = 190.6, 168.0, 166.7, 147.9, 137.6, 135.6, 132.6, 132.1, 131.9, 130.9, 130.0, 121.1, 110.0 ppm. ^{19}F NMR (376 MHz, TfOH): δ = –73.66 (s) ppm.

(1*E*,4*E*)-C2: Identified as a minor isomer in a mixture with (1*Z*,4*E*)-**C2**. ^{1}H NMR (400 MHz, TfOH, selected signals): δ = 8.77 (d, *J* = 15.1 Hz, 1 H), 7.11 (d, *J* = 15.1 Hz, 1 H), 7.08 (s, 1 H) ppm. ^{13}C NMR (101 MHz, TfOH, selected signals): δ = 194.3, 172.3, 166.6, 120.2, 113.7 ppm. ^{19}F NMR (376 MHz, TfOH): δ = –74.39 (s) ppm.

C3: Generated from a solution of enynone **1b** (27 mg, 0.1 mmol) in H_2SO_4 (1 mL) stirred for 2.5 h at room temperature and identified by NMR spectroscopic analysis of the reaction mixture. ^{1}H NMR (400 MHz, H_2SO_4): δ = 7.99 (d, *J* = 15.8 Hz, 1 H), 7.95 (d, *J* = 7.9 Hz, 2 H), 7.79 (t, *J* = 7.5 Hz, 1 H), 7.63–7.54 (m, 4 H), 7.37 (d, *J* = 8.3 Hz, 2 H), 6.86 (d, *J* = 15.8 Hz, 1 H), 6.60 (s, 1 H) ppm. ^{13}C NMR (101 MHz, H_2SO_4): δ = 184.9, 183.4, 151.8, 140.5, 137.5, 131.4, 130.3, 130.0, 129.8 (2 C), 129.1, 119.3, 97.9 ppm.

C4: Generated from a solution of enynone **1c** (28 mg, 0.1 mmol) in H_2SO_4 (1 mL) stirred for 18 h at room temperature and identified by NMR spectroscopic analysis of the reaction mixture. ^{1}H NMR (400 MHz, H_2SO_4): δ = 8.39 (d, *J* = 8.8 Hz, 2 H), 8.14 (d, *J* = 16.0 Hz, 1 H), 8.09 (d, *J* = 7.9 Hz, 2 H), 7.94 (d, *J* = 8.8 Hz, 2 H), 7.88 (t, *J* = 7.5 Hz, 1 H), 7.67 (t, *J* = 7.8 Hz, 2 H), 7.18 (d, *J* = 16.0 Hz, 1 H), 6.87 (s, 1 H) ppm. ^{13}C NMR (101 MHz, H_2SO_4): δ = 188.0, 182.6, 148.2, 147.7, 140.6, 138.5, 130.7, 129.9, 129.8 (2 C), 125.0, 124.3, 99.1 ppm.

D1: Generated from a solution of enynone **1a** (23 mg, 0.1 mmol) in H_2SO_4 (1 mL) stirred for 60 h at room temperature and identified by NMR spectroscopic analysis of the reaction mixture. ^{1}H NMR (400 MHz, H_2SO_4): δ = 8.04 (d, *J* = 7.8 Hz, 2 H), 7.85 (t, *J* = 7.3 Hz, 1 H), 7.60 (t, *J* = 7.9 Hz, 2 H), 7.53 (s, 5 H), 6.98 (s, 1 H), 5.96 (dd, *J* = 15.0, 4.6 Hz, 1 H), 3.50 (dd, *J* = 19.1, 15.2 Hz, 1 H), 3.26 (dd, *J* = 19.1, 4.6 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, H_2SO_4): δ = 192.0, 190.0, 138.8, 133.5, 130.4, 130.3, 129.7, 129.2, 128.6, 126.5, 98.1, 83.4, 34.0 ppm.

D2: Generated from a solution of enynone **1b** (27 mg, 0.1 mmol) in H_2SO_4 (1 mL) stirred for 96 h at room temperature and identified by NMR spectroscopic analysis of the reaction mixture. ^{1}H NMR (400 MHz, H_2SO_4): δ = 8.06 (d, *J* = 7.9 Hz, 2 H), 7.87 (t, *J* = 7.5 Hz, 1 H), 7.61 (t, *J* = 7.9 Hz, 2 H), 7.51–7.42 (m, 4 H), 7.00 (s, 1 H), 5.96 (dd, *J* = 15.2, 4.6 Hz, 1 H), 3.48 (dd, *J* = 19.0, 15.2 Hz, 1 H), 3.28 (dd, *J* = 19.0, 4.6 Hz, 1 H) ppm. ^{13}C NMR (101 MHz, H_2SO_4): δ = 191.9, 189.9, 138.9, 136.1, 132.1, 130.4, 129.8, 129.3, 128.5, 127.9, 98.1, 82.6, 34.0 ppm.

Acknowledgments

This work was supported by Saint Petersburg State University, Saint Petersburg, Russia (grant no. 12.40.515.2017). Spectral studies were performed at the Center for Magnetic Resonance, the Center for Chemical Analysis and Materials Research, and the Research Center for X-ray Diffraction Studies of Saint Petersburg State University, Saint Petersburg, Russia.

Keywords: Carbocations · Cyclization · Enones · Enynes · Superacidic systems

[1] G. A. Olah, D. A. Klumpp, *Superelectrophiles and Their Chemistry*, Wiley, Hoboken, **2008**.
[2] a) S. Saulnier, A. A. Golovanov, A. Y. Ivanov, I. A. Boyarskaya, A. V. Vasilyev, *J. Org. Chem.* **2016**, *81*, 1967–1980; b) S. Saulnier, A. A. Golovanov, A. V. Vasilyev, *RSC Adv.* **2016**, *6*, 103546–103555.
[3] a) P. A. Jacobi, L. M. Armacost, J. I. Kravitz, M. J. Martinelli, H. G. Selnick, *Tetrahedron Lett.* **1988**, *29*, 6865–6868; b) P. A. Jacobi, L. M. Armacost, J. I. Kravitz, M. J. Martinelli, *Tetrahedron Lett.* **1988**, *29*, 6869–6872; c) P. A. Jacobi, L. M. Armacost, H. L. Brielmann, R. O. Cann, J. I. Kravitz, M. J. Martinelli, *J. Org. Chem.* **1994**, *59*, 5292–5304; d) P. A. Jacobi, H. L. Brielmann, R. O. Cann, *J. Org. Chem.* **1994**, *59*, 5305–5316.
[4] a) P. A. Jacobi, J. I. Kravitz, *Tetrahedron Lett.* **1988**, *29*, 6873–6876; b) P. A. Jacobi, J. I. Kravitz, W. Zheng, *J. Org. Chem.* **1995**, *60*, 376–385.
[5] a) A. Rosiak, J. Christoffers, *Tetrahedron Lett.* **2006**, *47*, 5095–5097; b) A. Rosiak, R. M. Müller, J. Christoffers, *Monatsh. Chem.* **2007**, *138*, 13–26.
[6] G. Stork, M. Tomasz, *J. Am. Chem. Soc.* **1964**, *86*, 471–478.
[7] a) C. M. Marson, E. Edaan, J. M. Morrell, S. J. Coles, M. B. Hursthouse, D. T. Davies, *Chem. Commun.* **2007**, 2494–2496; b) M. Ostovar, C. M. Marson, *Tetrahedron* **2013**, *69*, 6639–6647.
[8] F. Jiménez-Cruz, L. Fragoza Mar, J. L. García-Gutierrez, *J. Mol. Struct.* **2013**, *1034*, 43–50.
[9] C. M. Beaudry, J. P. Malerich, D. Trauner, *Chem. Rev.* **2005**, *105*, 4757–4778.
[10] a) K. Ritter, *Synthesis* **1993**, 735–762; b) S. Chassaing, S. Specklin, J.-M. Weibel, P. Pale, *Tetrahedron* **2012**, *68*, 7245–7263; c) N. V. Zyk, O. V. Denisko, N. S. Zefirov, *Russ. J. Org. Chem.* **1994**, *30*, 461–479; d) A. V. Vasilyev, *Russ. Chem. Rev.* **2013**, *82*, 187–204.
[11] A. T. Nielsen, R. L. Atkins, W. P. Norris, *J. Org. Chem.* **1980**, *45*, 2341–2347.
[12] G. A. Olah, G. K. S. Prakash, A. Molnár, J. Sommer, *Superacid Chemistry*, 2nd ed., Wiley, Hoboken, **2009**.
[13] F. K. MacDonald, D. J. Burnell, *J. Org. Chem.* **2009**, *74*, 6973–6979.
[14] a) F. Yang, K.-G. Ji, S.-C. Zhao, S. Ali, Y.-Y. Ye, X.-Y. Liu, Y.-M. Liang, *Chem. Eur. J.* **2012**, *18*, 6470–6474; b) Y. F. Qiu, F. Yang, Z.-H. Qiu, M.-J. Zhong, L.-J. Wang, Y.-Y. Ye, B. Song, Y.-M. Liang, *J. Org. Chem.* **2013**, *78*, 12018–12028.
[15] K. K. Johri, Y. Katsuhara, D. D. Desmarteau, *J. Fluorine Chem.* **1982**, *19*, 227–242.
[16] a) E. Kim, A. Felouat, Z. Zaborova, J.-C. Ribierre, J. W. Weon, S. Senatore, C. Matthews, P.-F. Lenne, C. Baffert, A. Karapetyan, M. Giorgi, D. Jacquemin, M. Ponce-Vargas, B. Le Guennic, F. Fages, A. D'Aléo, *Org. Biomol. Chem.* **2016**, *14*, 1311–1324; b) C. I. Nieto, M. P. Cabildo, M. P. Cornago, D. Sanz, R. M. Claramunt, I. Alkorta, J. Elguero, J. A. García, A. Lopez, D. Acuna-Castroviejo, *J. Mol. Struct.* **2015**, *1100*, 518–529; c) S. W. Leong, S. M. M. Faudzi, F. Abas, M. F. F. M. Aluwi, K. Rullah, L. K. Wai, M. N. A. Bahary, S. Ahmad, C. L. Tham, K. Shaari, *Molecules* **2014**, *19*, 16058–16081; d) J. P. A. Ferreira, V. L. M. Silva, J. Elguero, A. M. S. Silva, *Tetrahedron* **2013**, *69*, 9701–9709; e) P. Cornago, P. Cabildo, D. Sanz, R. M. Claramunt, M. C. Torralba, M. R. Torres, J. Elguero, *Eur. J. Org. Chem.* **2013**, 6043–6054; f) D. Sharma, S. Kumar, J. K. Makrandi, *Green Chem. Lett. Rev.* **2009**, *2*, 53–55.
[17] a) J. Zheng, L. Lin, K. Fu, Y. Zhang, X. Liu, X. Feng, *Chem. Eur. J.* **2014**, *20*, 14493–14498; b) I. Larrosa, P. Romea, F. Urpi, *Tetrahedron* **2008**, *64*, 2683–2723; c) P. A. Clarke, S. Santos, *Eur. J. Org. Chem.* **2006**, 2045–2053.
[18] a) S. Danishefsky, J. F. Kerwin Jr., S. Kobayashi, *J. Am. Chem. Soc.* **1982**, *104*, 358–360; b) T. Tanemitsu, Y. Asajima, T. Shibata, M. Miyazaki, K. Nagata, T. Itoh, *Heterocycles* **2011**, *83*, 2525–2534; c) S. Miesowicz, W. Chaladaj, J. Jurczak, *Synlett* **2010**, 1421–1425; d) P. C. B. Page, P. H. Williams, E. W. Collington, H. Finch, *J. Chem. Soc., Chem. Commun.* **1987**, 756–757.
[19] a) M. Reiter, S. Ropp, V. Gouverneur, *Org. Lett.* **2004**, *6*, 91–94; M. Reiter, H. Turner, R. Mills-Webb, V. Gouverneur, *J. Org. Chem.* **2005**, *70*, 8478–

8485; b) I. S. Youg, M. W. Haley, A. Tam, S. A. Tymonko, Z. Xu, R. L. Hanson, A. Goswami, *Org. Process Res. Dev.* **2015**, *19*, 1360–1368.
[20] a) C. Wang, C. J. Forsyth, *Org. Lett.* **2006**, *8*, 2997–3000; b) M. Schuler, F. Silva, C. Bobbio, A. Tessier, V. Gouverneur, *Angew. Chem. Int. Ed.* **2008**, *47*, 7927–7930; *Angew. Chem.* **2008**, *120*, 8045; c) H. Fuwa, S. Matsukida, M. Sasaki, *Synlett* **2010**, 1239–1242; d) H. Fuwa, K. Mizunuma, S. Matsukida, M. Sasaki, *Tetrahedron* **2011**, *67*, 4995–5010; e) W.-Y. Huang, T. Nishikawa, A. Nakazaki, *ACS Omega* **2017**, *2*, 487–495.
[21] a) B. Gao, Z. Yu, Z. Fu, X. Feng, *Tetrahedron Lett.* **2006**, *47*, 1537–1539; b) C. Yu, F. Zheng, H. Ye, W. Zhong, *Tetrahedron* **2009**, *65*, 10016–10021; c) R. Ahmad, R. Ahmad Khera, A. Villinger, P. Langer, *Tetrahedron Lett.* **2009**, *50*, 3020–3022; d) R. Ahmad Khera, R. Ahmad, I. Ullah, O. U. R. Abid, O. Fatunsin, M. Sher, A. Villinger, P. Langer, *Helv. Chim. Acta* **2010**, *93*, 1705–1715.
[22] a) Z. Lian, Q. Y. Zhao, Y. Wei, M. Shi, *Eur. J. Org. Chem.* **2012**, 3338–3341; b) P. A. Clarke, P. B. Sellars, N. Mistry, *Tetrahedron Lett.* **2011**, *52*, 3654–3656; c) R. A. Khera, M. Hussain, R. Ahmad, A. Saeed, A. Villinger, C. Fischer, P. Langer, *J. Fluorine Chem.* **2010**, *131*, 892–897; d) N. I. Totah, D. Chen, *Tetrahedron Lett.* **1998**, *39*, 213–216; e) A. P. Kozikowski, C.-S. Lit, *J. Org. Chem.* **1985**, *50*, 778–785.
[23] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
[24] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[25] G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3–8.
[26] E. D. Voronova, A. A. Golovanov, K. Yu. Suponitsky, I. V. Fedyanin, A. V. Vologzhanina, *Cryst. Growth Des.* **2016**, *16*, 3859–3869.
[27] a) K. G. Migliorese, Y. Tanaka, S. I. Miller, *J. Org. Chem.* **1974**, *39*, 739–747; b) D. A. Alonso, C. Nájera, M. C. Pacheco, *J. Org. Chem.* **2004**, *69*, 1615–1619.
[28] F. Gao, Y. Huang, *Adv. Synth. Catal.* **2014**, *356*, 2422–2428.
[29] N. V. Utekhina, N. V. Korzhova, V. M. Kazantseva, Yu. N. Surov, V. D. Orlov, S. P. Korshunov, *Russ. J. Gen. Chem.* **1988**, *58*, 612–616.
[30] H. Yuan, Y. Shen, S. Yu, L. Shan, Q. Sun, W. Zhang, *Synth. Commun.* **2013**, *43*, 2817–2823.
[31] M. Hari Babu, V. Dwivedi, R. Kant, M. Sridhar Reddy, *Angew. Chem. Int. Ed.* **2015**, *54*, 3783–3786; *Angew. Chem.* **2015**, *127*, 3854.
[32] A. R. Thomas, W. G. Shuler, E. A. Smith, S. S. Carlisle, S. L. Knick, A. J. Puciaty, C. R. Metz, D. G. VanDerveer, C. D. McMillen, W. T. Pennington, C. F. Beam, *J. Chem. Crystallogr.* **2013**, *43*, 629–635.
[33] M. Paul, P. Venugopalan, K. Krishnankutty, *Asian J. Chem.* **2002**, *14*, 1335–1340.
[34] H. Wang, B. J. Shuhler, M. Xian, *J. Org. Chem.* **2007**, *72*, 4280–4283.

Received: March 24, 2017