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Transformations of Conjugated Enynones in the Superacid CF_3SO_3H. Synthesis of Butadienyl Triflates, Indanones, and Indenes

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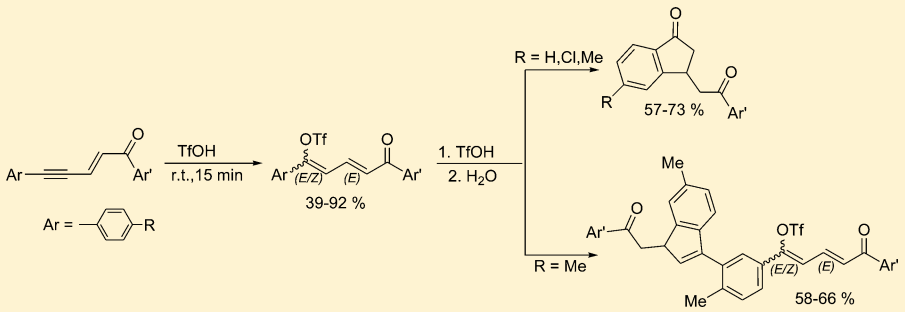
Supporting Information



ABSTRACT: Conjugated 1,5-diarylpent-2-en-4-yn-1-ones add the superacid CF_3SO_3H to the acetylenic bond with formation of the corresponding butadienyl triflates. Under superacidic reaction conditions, these triflates are transformed into indanone or indene derivatives depending on which substituents on the aromatic ring are conjugated with the butadiene fragment. In a less acidic system (10% vol pyridine in CF_3SO_3H) only the formation of butadienyl triflates takes place. Cationic reaction intermediates were studied by means of NMR and DFT calculations.

INTRODUCTION

Conjugated enynones, containing carbon−carbon double and triple bonds along with a carbonyl group, are an important class of multifunctional reagents. They possess a high reactivity toward nucleophilic agents and take part in dipolar cycloaddition. In particular, 1,5-substituted pent-2-en-4-yn-1-ones **1** (Figure 1) add easily N-[1−3] and S-[4−6] nucleophiles with formation of adducts to the carbon−carbon double or triple bonds. Enynones **1** were explored in the synthesis of various heterocycles, such as furanes,[7−19] 1,2,3-triazoles,[20] pyrazols,[21,22] aziridines (which may be consequently transformed into pyrroles),[23] and carbocycles through intermediate generation of pyrylium ions,[24,25] etc. (Figure 1).

Surprisingly, to the best of our knowledge there are only two examples of electrophilic addition to enynones **1** made in 1960. These are bromination carried out by Petrov and co-workers[26] and cyclization into pyrylium ions in H_2SO_4 and $HClO_4$ conducted by Stetter and Reischl.[27]

Based on our current research on the electrophilic activation of alkynes[28−31] and alkenes[32−34] in Brønsted and Lewis (super)acids, we undertook this study on the transformation of 1,5-diarylpent-2-en-4-yn-1-ones **1a−j** bearing various donor and acceptor substituents on aryl rings (Figure 2) under the

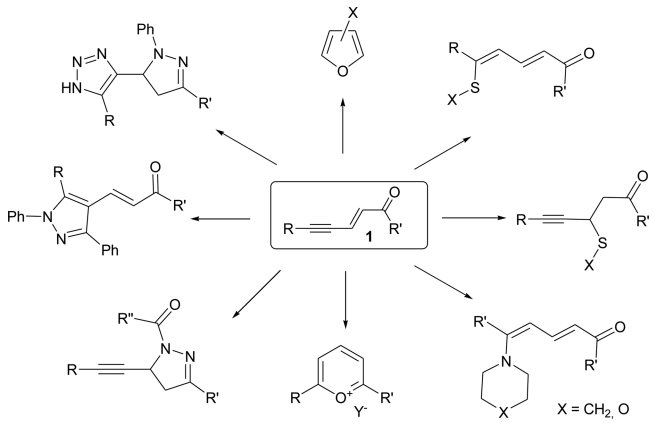


Figure 1. Conjugated enynones **1** and some of their valuable synthetic transformations (selected data from refs 1−27).

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action of acidic reagents. We expected to generate highly reactive electrophilic species under protonation of conjugated enynones in Brønsted superacids.

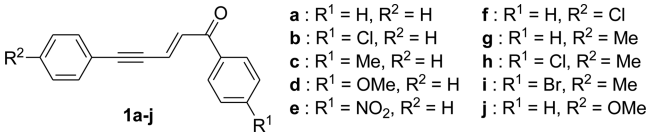


Figure 2. Starting 1,5-diarylpent-2-en-4-yn-1-ones **1a–j** used in this study.

RESULTS AND DISCUSSION

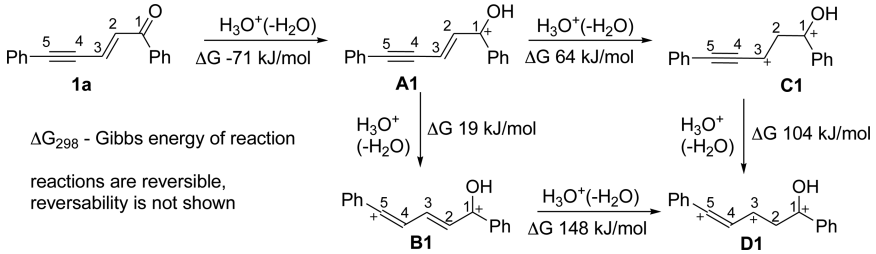
At the beginning we considered possible ways of protonation of pent-2-en-4-yn-1-ones **1**. Thus, protonation of 1,5-diphenylpent-2-en-4-yn-1-one **1a** may proceed in several consecutive steps (Table 1). A first proton is bonded to the more basic carbonyl oxygen that affords cation **A1**. Then, protonation of the carbon–carbon triple or double bonds may occur leading to species **B1** or **C1**, respectively, which in turn may be protonated to trication **D**. Calculations of Gibbs free energies of these protonation reactions showed that the formation of cation **A** is energetically favorable with ΔG_{298} −71 kJ/mol (see reaction ΔG_{298} values in the scheme in Table 1). The second protonation, which leads to species **B1** and **C1**, is unfavorable, but the formation of cation **B1** is less unfavorable. So, the second protonation should rather take place on the triple bond than on the double one for such conjugated enynones. Finally, trication **D1** is very high in energy (see big positive ΔG_{298} values of the corresponding reactions).

To estimate the electronic properties of the reaction intermediates, we performed DFT calculations of species **A1**, **B1**, **C1**, and **D1** derived from starting enynone **1a** (Table 1). Charge distribution, contribution of atomic orbital into LUMO, and global electrophilicity indices ω[35,36] were calculated. Compared to cation **A1**, dication **B1** and **C1** have higher values of electrophilicity indices, and they may be considered as strong electrophiles.[37,38] The comparison of the charge distributions in species **A1**, **B1**, **C1** reveals that carbon C^5 bears a large part of the positive charge (Table 1). Among these three species, dication **B1** has the largest charge on C^5 (0.46 e). Apart from that, this carbon in **B1** gives the highest contribution (31%) in LUMO. These data show a coincidence of charge and orbital control in the reactivity of carbon C^5 in species **B1**. Thus, both calculated thermodynamic parameters (ΔG_{298} of reactions) and electronic characteristics (Table 1) indicate that dications **B**, with an electrophilic center on carbon C^5, are probably the main reactive species derived from enynones **1** under protonation. The formation of trications **D** is unlikely due to thermodynamic reason.

Then we carried out preparative reactions of enynone **1a** in the superacid CF_3SO_3H (triflic acid, TfOH) and under the action of other acids (Table 2). In TfOH at room temperature or at −35 °C just for 15 min, the formation of isomeric butadienyl triflates (2*E*,4*Z*)- and (2*E*,4*E*)-**2a**, as products of TfOH addition to the acetylenic bond, was observed (entries 1, 2). This reveals that, most probably, the intermediate species in this reaction is dication **B1** in accord with DFT calculations (Table 1). On increasing reaction time to 2 h, one more reaction product, indanone **3a**, was detected in a yield of 11% (entry 3). Further increasing the reaction time to 60 h gave **3a** in a higher yield of 79% along with a small amount (12%) of triflates **2a** (entry 4). This indanone **3a** solely became a product at higher reaction temperature 65 °C in TfOH for 5 h (entry 6). Increasing the temperature up to 120 °C for 4 h led to a dramatic decrease of the yield of **3a** (27%, entry 7). Apart from that, individually isolated isomeric triflates **2a** were converted into **3a** in TfOH. The data obtained prove that triflate **2a** is formed first, and then one is transformed into indanone **3a**. The use of other Brønsted (H_2SO_4, CF_3CO_2H) or Lewis ($AlCl_3$) acids did not give compounds **2a** and **3a** (entries 9–11). The weaker acid CF_3CO_2H did not activate this reaction (entry 8) as only protonation of carbonyl oxygen takes place affording cation **A1** (Table 1), which is not reactive.

Then reactions of enynones **1b–e**, bearing a phenyl ring (R^2 = H) at the acetylenic bond and various substituents R^1 in the aroyl group, and **1f**, having R^1 = H and R^2 = Cl, were conducted in TfOH (Table 3). Analogously to the transformation of **1a** (Table 2), one may regulate the formation of triflates **2** and indanones **3** by varying the reaction conditions. For a short reaction time 0.3–1 h, the main reaction products were triflates **2** (Table 3, entries 1, 2, 5, 6, 9, 12, 14). Increasing reaction time (entries 8, 10, 11, 13) or temperature (entry 4)

Table 1. Selected Electronic Characteristics (DFT Calculations) of Cations A, B, C, D Derived from Protonation of Enynone 1a and Calculated Gibbs Energies ΔG_{298} of Protonation Reactions



cation	E_{HOMO}, eV	E_{LUMO}, eV	ω,[a] eV	$q(C^1)$,[b] e	$q(C^3)$,[b] e	$q(C^5)$,[b] e	$k(C^1)_{LUMO}$,[c] %	$k(C^3)_{LUMO}$,[c] %	$k(C^5)_{LUMO}$,[c] %
A1	−6.92	−4.03	5.2	0.54	0.01	0.20	11	9	6
B1	−7.95	−4.65	6.0	0.58	−0.03	**0.46**	2	3	**31**
C1	−8.08	−4.98	6.9	0.65	0.04	0.28	9	14	12
D1	−8.21	−5.91	10.8	0.64	0.28	0.62	2	19	15

[a]Global electrophilicity index $\omega = (E_{HOMO} + E_{LUMO})\ 2/8(E_{LUMO} - E_{HOMO})$. [b]Natural charges. [c]Contribution of atomic orbital into the molecular orbital.

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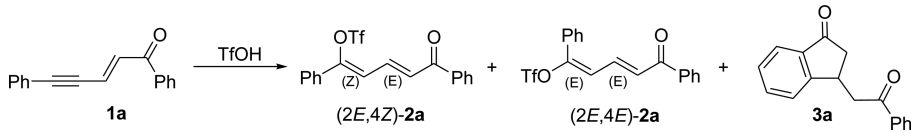
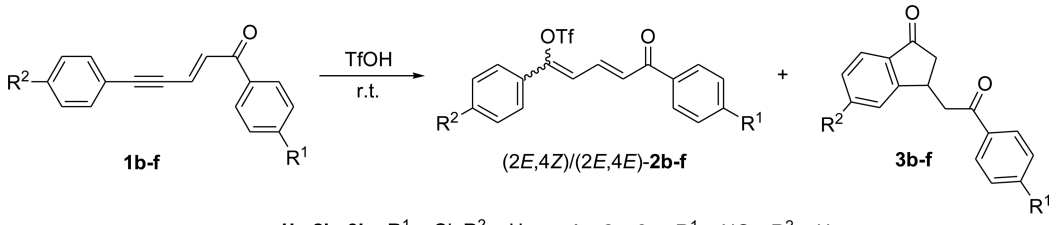
Table 2. Transformations of Enynone 1a under the Action of Acids



	reaction conditions			reaction products[a]		
				triflate **2a**		
entry	acid	temp,°C	time, h	ratio of isomers (2E,4Z)/(2E,4E)	yield, %	indanone **3a**, yield, %
1	TfOH	r.t.	0.25	1.7/1	95	–
2	TfOH	−35	0.25	1.2/1	84	–
3	TfOH	r.t.	2	4.1/1	81	11
4	TfOH	r.t.	60	2.1/1	12	79
5	TfOH	65	1	3.8/1	51	27
6	TfOH	65	5		–	78 (64)
7	TfOH	120	4		–	27
8	CF_3CO_2H	r.t.	1		–[b]	–
9	H_2SO_4	r.t.	1	complex mixture		
10	H_2SO_4	r.t.	60	complex mixture		
11	$AlCl_3$[c]	r.t.	60	complex mixture		

[a]Yields in crude reaction mixtures, and yield after chromagraphic isolation is given in parentheses. [b]Starting enynone **1a** was quantitatively recovered after the reaction. [c]3 equiv of $AlCl_3$ was explored in solution in anhydrous dichloromethane.

Table 3. Transformations of Enynones 1b–f into Triflates 2b–f and Indanones 3b–f in TfOH



1b, 2b, 3b : R^1 = Cl, R^2 = H **1e, 2e, 3e** : R^1 = NO_2, R^2 = H
1c, 2c, 3c : R^1 = Me, R^2 = H **1f, 2f, 3f** : R^1 = H, R^2 = Cl
1d, 2d, 3d : R^1 = OMe, R^2 = H

			reaction products[a]				
			triflate **2**			indanone **3**	
entry	starting enynone, no.	reaction time, h	no.	ratio of isomers (2E,4Z)/(2E,4E)	yield, %	no.	yield, %
1	**1b**	1	**2b**	3.2/1	90	**3b**	2
2	**1b**	12	**2b**	3.6/1	79	**3b**	12
3	**1b**	60	**2b**	3.6/1	35	**3b**	58
4	**1b**	5[b]			-	**3b**	69 (57)
5	**1c**	0.3	**2c**	1.9/1	87	**3c**	3
6	**1c**	1	**2c**	3.4/1	83	**3c**	7
7	**1c**	12	**2c**	2.5/1	31	**3c**	53
8	**1c**	60	**2c**		-	**3c**	88 (73)
9	**1d**	1	**2d**	2.3/1	63	**3d**	33
10	**1d**	36	**2d**		-	**3d**	77 (60)
11	**1d**	60	**2d**		-	**3d**	79
12	**1e**	1	**2e**		97	**3e**	-
13	**1e**	60	**2e**		-	**3e**	37
14	**1f**	0.5	**2f**	2/1	97	**3f**	0
15	**1f**	60	**2f**	2.7/1	90	**3f**	8 (6)
16	**1f**	12[c]		complex mixture			

[a]Reactions were carried out at room temperature. Yields in crude reaction mixtures, and yields after chromagraphic isolation are given in parentheses. [b]Reaction was carried out at 65 °C. [c]Reaction was carried out at 80 °C.

led to the exclusive formation of indanones **3**. Under the formation of indanones **3**, cyclization in the aryl ring adjacent to the triple bond takes place, but the presence of electron-withdrawing substituents R^2 on this ring makes it difficult. Thus, for **1f** (with R^2 = Cl) the yield of indanone **3f** was very low (8%) after 60 h at room temperature (entry 15). An increase in temperature up to 80 °C resulted in the formation of a complex mixture of products (entry 16).

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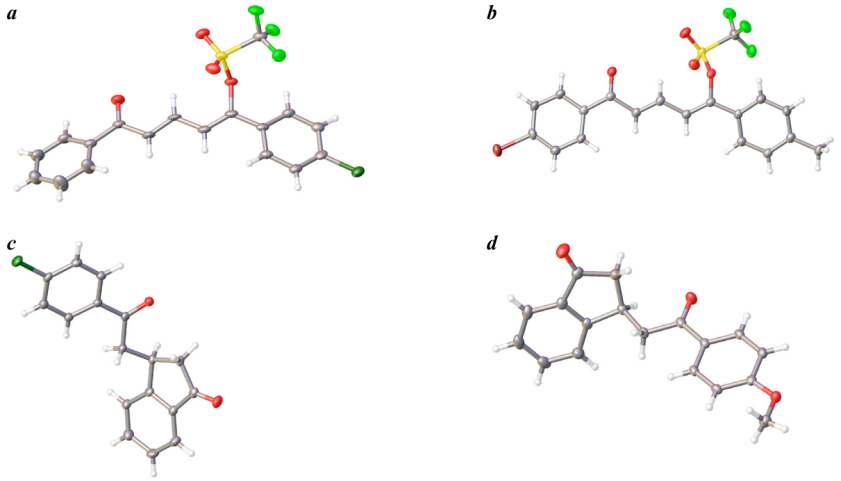

Figure 3. Molecular structures of (2*E*,4*Z*)-**2f** (a), (2*E*,4*Z*)-**2i** (b), **3b** (c), and **3d** (d) (ellipsoid contours of probability levels are 50%).

The structures of indanones **3b,d** were confirmed by X-ray data (Figure 3c,d). The stereochemistry of triflates **2** was determined by NOESY correlations (Figure 4) and X-ray

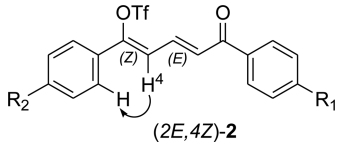

Figure 4. Selected NOESY correlation (arrow) for triflates (2*E*,4*Z*)-**2** proving the *Z*-configuration for the double bond C^4═C^5.

analysis of selected isomers (2*E*,4*Z*)-**2f**, (2*E*,4*Z*)-**2i** (Figure 3a,b). The *E*-configuration of the C^2═C^3 double bond for triflates **2** was additionally confirmed by the high value of the spin−spin coupling constant between the vinyl protons H^2 and H^3 $^3J \sim 15$ Hz in ^{1}H NMR. It should be noted that compound **2** was formed mainly as a 4*Z*-isomer (Tables 2, 3, and 6) as a result of the *anti*-addition of proton and triflate counterion to the acetylenic bond of enynones **1**. Previously we observed the same stereochemistry for the addition of superacids TfOH or FSO_3H to acetylene carboxylic acids, their esters, and acetylenic ketones, which gave, at first, products from *syn*-addition of superacids to the triple bond followed by isomerization into *anti*-isomers.[28,39,40]

A plausible reaction mechanism for the formation of compounds **2** and **3** is shown in Scheme 1. The reaction of dication **B** with the triflate ion gives the O-protonated form of butadienyl triflate **E**, which upon hydrolysis affords triflate **2**. Cation **E**, with a carbocationic center at C^3 on the resonance form **E′**, may undergo cyclization into cation **F**. Under the superacidic reaction conditions, the latter is protonated with a formation of stable cation **G**. And finally, upon quenching with water cation **G** affords indanone **3**. The formation of species **G** was proven by generation of cation **G1** from enynone **1a** in TfOH at room temperature after keeping the reaction solution for 60 h and was monitored by ^{1}H and ^{13}C NMR (see selected ^{1}H and ^{13}C NMR signals for species **G1** in Scheme 1). The

Scheme 1. Plausible Reaction Mechanism of Transformation of Enynone 1 into Triflate 2, and Indanone 3, and Selected ^{1}H, ^{13}C NMR Data for Cation G1, Generated from 1a in TfOH

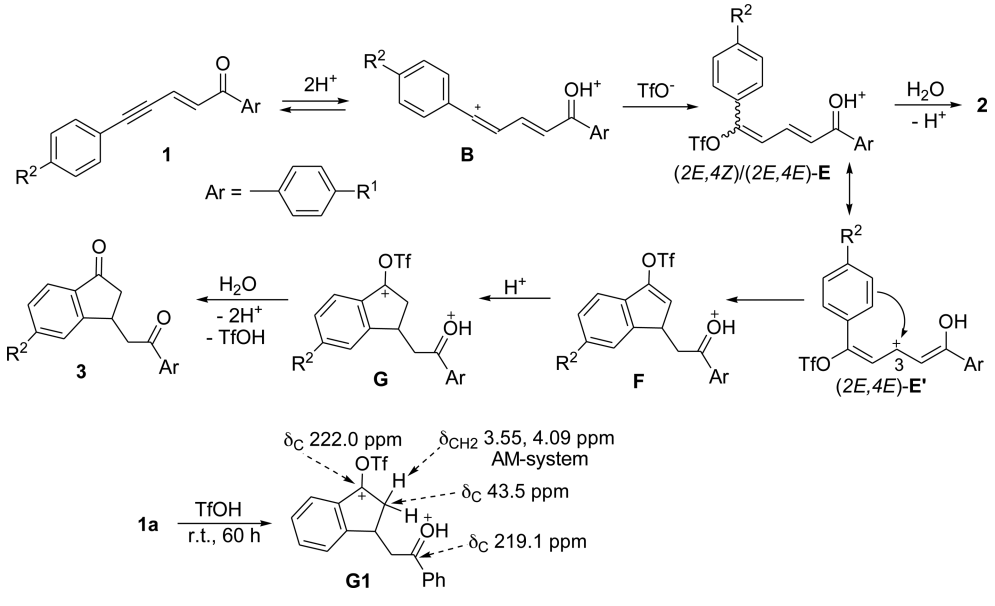

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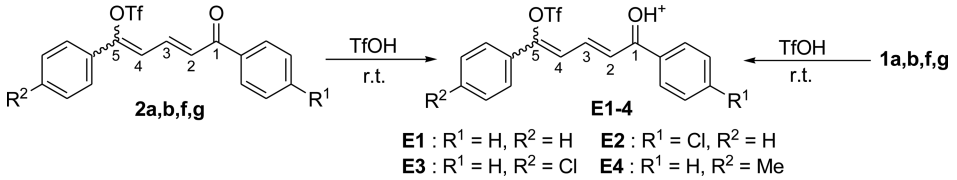
Table 4. Selected ^{1}H, ^{13}C, ^{19}F NMR Data for Enynones 2a,b,f,g and Their O-Protonated Forms E1−E4, Respectively



	^{1}H NMR, δ_H, ppm (J_{H-H}, Hz)		^{13}C NMR, δ_C, ppm			
triflates **2**[a] and cations **E**[b]	H^3 (doublet of doublets)	H^4 (doublet)	C^1	C^3	C^5	^{19}F NMR, δ_F, ppm
(2*E*,4*Z*)-**2a**	7.73 (*J* 15.1, 11.4 Hz)	6.72 (*J* 11.4 Hz)	190.1	135.1	151.3	−73.07
(2*E*,4*Z*)-**E1**	8.72 (*J* 14.4, 11.8 Hz)	7.42 (*J* 11.8 Hz)	199.4	163.4	158.8	−73.55
(2*E*,4*E*)-**2a**	7.53 (*J* 15.0, 11.7 Hz)	6.66 (*J* 11.7, 0.4 Hz)	189.3	137.0	154.2	−73.75
(2*E*,4*E*)-**E1**	8.46 (*J* 14.5, 11.8 Hz)	7.16 (*J* 11.8 Hz)	198.3	167.8	162.3	−74.68
(2*E*,4*Z*)-**2b**	7.73 (*J* 15.1, 11.4 Hz)	6.71 (*J* 11.4 Hz)	188.8	135.5	151.5	−73.03
(2*E*,4*Z*)-**E2**	8.69 (*J* 14.3, 11.8 Hz)	7.42 (*J* 11.8 Hz)	197.3	163.5	158.4	−73.48
(2*E*,4*E*)-**2b**	7.53 (*J* 14.9, 11.7 Hz)	6.65 (*J* 11.7 Hz)	188.0	137.6	154.5	−73.74
(2*E*,4*E*)-**E2**	8.44 (*J* 14.5, 11.8 Hz)	7.16 (*J* 11.8 Hz)	196.1	168.0	161.9	−74.69
(2*E*,4*Z*)-**2f**	7.70 (*J* 15.1, 11.3 Hz)	6.70 (*J* 11.3 Hz)	190.0	134.7	150.0	−72.98
(2*E*,4*Z*)-**E3**	8.68 (*J* 14.4, 11.8 Hz)	7.40 (*J* 11.8 Hz)	199.4	161.6	158.2	−73.58
(2*E*,4*E*)-**2f**	7.46 (*J* 15.0, 11.6 Hz)	6.66 (*J* 11.6 Hz)	189.2	136.4	152.8	−73.64
(2*E*,4*E*)-**E3**	8.41 (*J* 14.6, 11.8 Hz)	7.16 (*J* 11.8 Hz)	198.1	165.9	160.7	−74.65
(2*E*,4*Z*)-**2g**	7.72 (*J* 15.1, 11.4 Hz)	6.67 (*J* 11.4 Hz)	190.3	135.4	151.6	−73.08
(2*E*,4*Z*)-**E4**	8.72 (*J* 14.3, 11.9 Hz)	7.40 (*J* 11.9 Hz)	198.3	159.4	164.2	−73.97

[a]NMR spectra of **2a,b,f,g** were recorded in $CDCl_3$ at room temperature. [b]NMR spectra of **E1−E4** were recorded in TfOH at room temperature.

Scheme 2. Plausible Reaction Mechanism of Formation of "Dimeric" Compounds 4a−c from Enynones 1g−i and Selected ^{1}H, ^{13}C NMR Data for Cation J1, Generated from (2*E*,4*Z*)-4a in TfOH

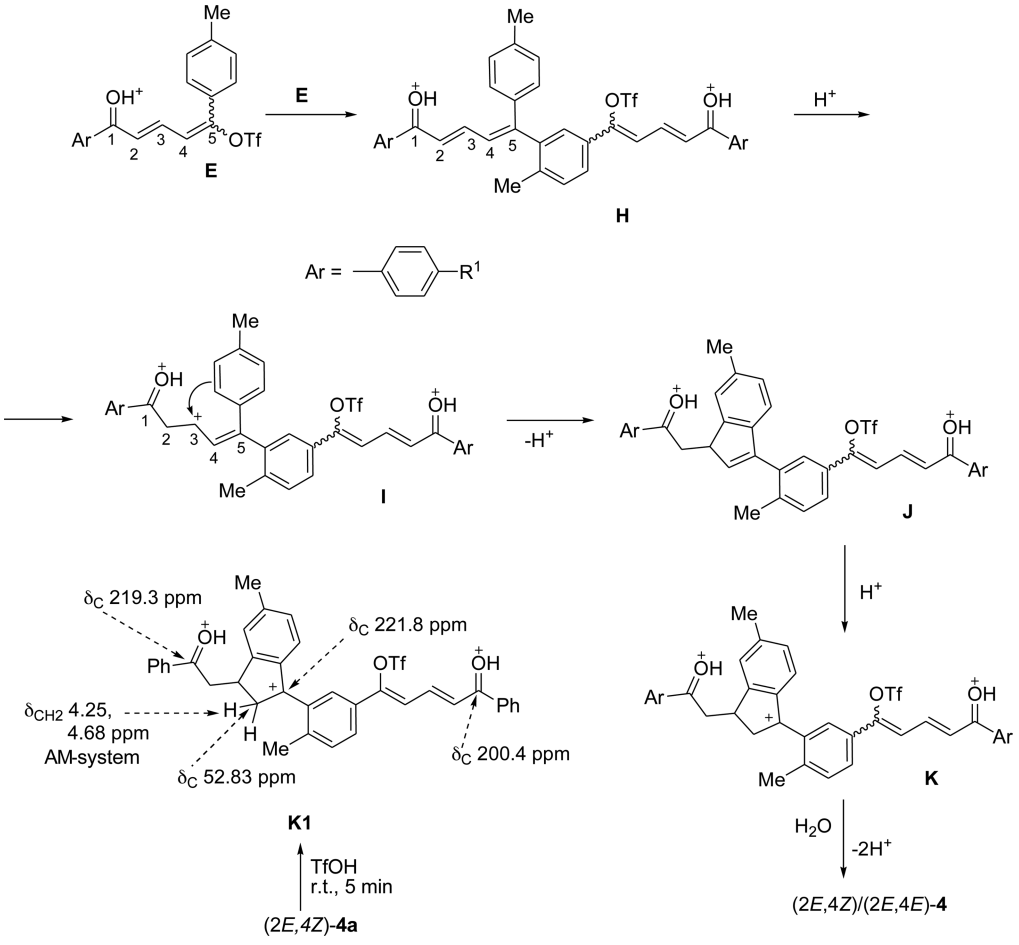


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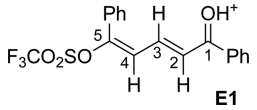
Table 5. Selected Electronic Characteristics (DFT Calculations) of Cation (2*E*,4*E*)-E1 Derived from O-Protonation of Triflate (2*E*,4*E*)-2a

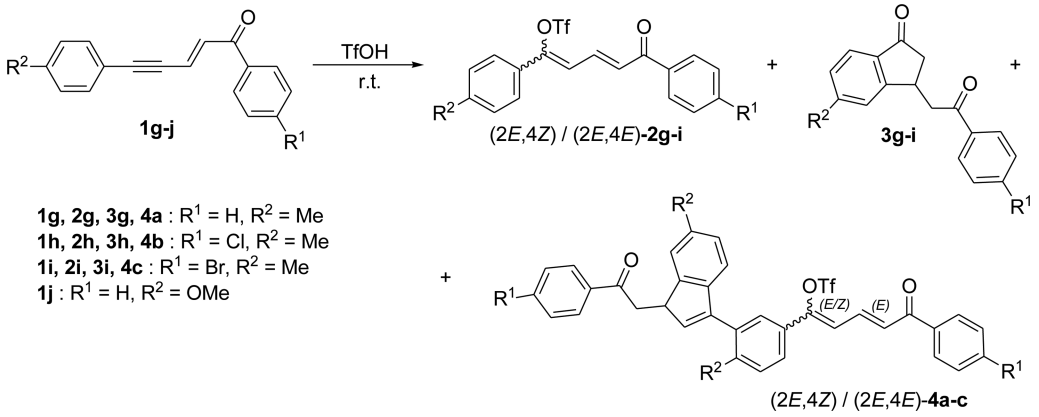


E1

E_{HOMO}, eV	E_{LUMO}, eV	ω,[a] eV	$q(C^1)$,[b] e	$q(C^3)$,[b] e	$q(C^5)$,[b] e	$k(C^1)_{LUMO}$,[c] %	$k(C^3)_{LUMO}$,[c] %	$k(C^5)_{LUMO}$,[c] %
−7.04	−4.03	5.1	0.55	−0.03	0.42	12.1	12.3	4.5

[a]Global electrophilicity index $\omega = (E_{HOMO} + E_{LUMO})\ 2/8(E_{LUMO} - E_{HOMO})$. [b]Natural charges. [c]Contribution of atomic orbital into the molecular orbital.

Table 6. Transformations of Enynones 1g−i into Triflates 2g−i, Indanones 3g−i, and Dimers 4a−c in TfOH



				reaction products[a]							
				triflate **2**			indanone **3**		dimers **4**		
entry[a]	starting enynone, no.	time, h	concentration of **1**	no.	ratio of isomers (2*E*,4*Z*)/(2*E*,4*E*)	yield, %	no.	yield, %	no.	ratio of isomers (2*E*,4*Z*)/(2*E*,4*E*)	yield, %
1	**1g**	1	0.1	**2g**	3.2/1	54	**3g**	12	**4a**	2/1	32
2	**1g**	60	0.1	**2g**		–	**3g**	50	**4a**	3.3/1	46
3	**1g**	12	0.025	**2g**		–	**3g**	63	**4a**	2.4/1	33
4	**1g**	12	0.05	**2g**		–	**3g**	55(40)	**4a**	3.3/1	42
5	**1g**	12	0.4	**2g**		–	**3g**	15	**4a**	4.4/1	80(66)
6	**1g**	0.3	0.05	**2g**	4.5/1	70	**3g**	5	**4a**	1.6/1	19
7	**1g**	0.25[b]	0.05	**2g**	1.9/1	80	**3g**	2	**4a**	1.1/1	10
8	**1g**	0.17	0.05	**2g**	4.8/1	75		−5	**4a**	1.3/1	17
9	**1h**	60	0.1	**2h**		–	**3h**	35	**4b**	3.9/1	59
10	**1h**	12	0.05	**2h**		–	**3h**	55(39)	**4b**	3/1	38
11	**1h**	12	0.4	**2h**		–	**3h**	15	**4b**	4.8/1	78(59)
12	**1i**	60	0.1	**2i**		–	**3i**	32	**4c**	3.5/1	55
13	**1i**	12	0.05	**2i**		–	**3i**	50(36)	**4c**	3.4/1	41
14	**1i**	12	0.4	**2i**		–	**3i**	15	**4c**	4.9/1	79(58)
15	**1j**	36	0.1				complex mixture				
16	**1j**	12	0.05				complex mixture				

[a]Reactions were carried out at room temperature. Yields in crude reaction mixtures and yields after chromagraphic isolation are given in parentheses. [b]Reaction was carried out at 0 °C.

exact assignment of NMR signals for **G1** and other species (see **E1**−**E4** in Table 4 and **K1** in Scheme 2) was done based on HMBC and HSQC spectra (see SI).

Both (2*E*,4*Z*)- and (2*E*,4*E*)-isomers of **2** lead to the formation of indanone **3**. Individually isolated triflates (2*E*,4*Z*)-**2a** and (2*E*,4*E*)-**2a** were separately subjected to reaction in TfOH at room temperature for 60 h and gave the same indanone **3a**. This reveals that an equilibrium between the 4*Z*- and 4*E*-isomers of triflates **2** is established in the superacid, most probably through the intermediate formation of vinyl cation **B** (see Scheme 1), since the 4*E*-isomer has the more favorable configuration for cyclization.

We undertook a special NMR study on the generation of cations **E** from enynones **1** or triflates **2** in TfOH. Species **E** is formed immediately upon dissolving either **1** or **2** in TfOH at room temperature. Table 4 contains selected ^{1}H, ^{13}C, and ^{19}F NMR data of triflates (2*E*,4*Z*)/(2*E*,4*E*)-**2a,b,f,g** in $CDCl_3$ and of their O-protonated forms **E1**−**E4** in TfOH, respectively. The comparison of spectra of cations **E1**−**E4** and their neutral precursors **2a,b,f,g** shows that the signals of carbonyl carbon C^1 and carbon C^5 in ^{13}C NMR are around 9 and 7−13 ppm downfield shifted, respectively, when protonated (see the corresponding differences in chemical shifts in Table 4). More striking is the behavior of the C^3 signal which is about 24−31

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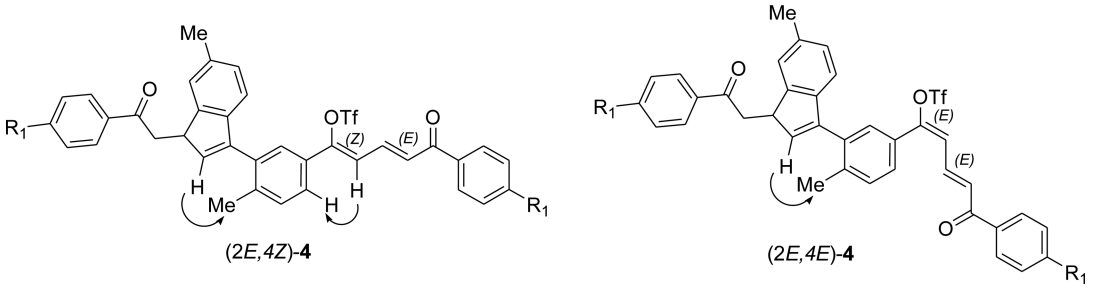
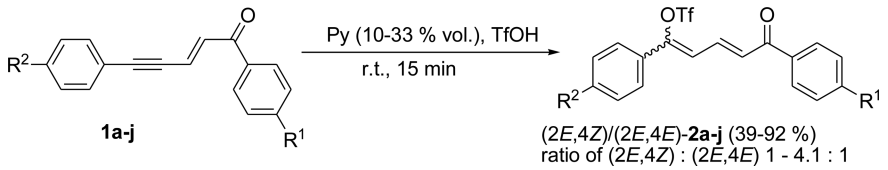


Figure 5. Selected NOESY correlations (arrows) for isomeric indenes (2*E*,4*Z*)/(2*E*,4*E*)-**4** proving their structures and the stereochemistry of the double bond C^4═C^5.

Scheme 3. Quantitative Formation of Triflates 2a−j from Enynones 1a−j in the System Pyridine-TfOH



ppm downfield shifted upon protonation. In ^{1}H NMR, proton ^{3}H shows a big downfield shift of around 1 ppm, while the signal of proton ^{4}H is about 0.5−0.7 ppm downfield shifted on the protonated form. This reveals that the positive charge in species **E** is substantially delocalized on carbon C^3, making this carbon an electrophilic center, which explains the intramolecular electrophilic aromatic substitution and the formation of indanones (Scheme 1).

Contrary to NMR data (Table 4), DFT calculations of cation **E1** do not show any substantial positive charge delocalization into carbon C^3, which would even bear a little negative charge −0.03 e (Table 5). But C^3 has a bigger contribution (12.3%) of atomic orbital in the LUMO compared to the other possible reactive center carbon C^5 (4.5%). Thus, according to NMR data (Table 4), the reactivity of carbon C^3 in O-protonated triflates **E** (Scheme 1) may be explained by charge factor, but DFT calculations (Table 5) reveal orbital contribution into the reactivity of C^3.

In the case of enynones **1g−i** bearing an electron-donating methyl group on the aryl ring conjugated with the acetylenic bond (R^2 = Me), one more reaction pathway was observed. Apart from triflates **2g−i** and indanones **3g−i**, the formation of "dimeric" structures **4a−c** was detected (Table 6). For **1g** and short reaction times (0.17−1 h), the main reaction products were isomeric triflates (2*E*,4*Z*)/(2*E*,4*E*)-**2g** (entries 1, 6−8), which were further converted into indanone **3g** and compounds (2*E*,4*Z*)/(2*E*,4*E*)-**4a** by increasing time until 12−60 h (entries 2−5). The same was observed for enynones **1h,i**, which gave indanones **3h,i** and indenes (2*E*,4*Z*)/(2*E*,4*E*)-**4b,c** (entries 9, 12). Analogous to triflates **2** (Tables 2, 3, and 6), the main diastereoisomers of compounds **4a−c** were the (2*E*,4*Z*), as *anti*-addition products of TfOH to the triple bond. The formation of "dimers" **4a−c** strongly depends on the concentration of starting materials **1g−i** in TfOH. Increasing concentration leads to an increase of the yield of indenes **4** (up to 80%) and to a decrease of the yield of indanones **3** (down to 15%, follow yields in entries 3−5 for **1g**, entries 10, 11 for **1h**, and entries 13, 14 for **1i** at the same reaction time and temperature). The reactions of formation of compounds **3** and **4** are concurrent processes. Increase of concentration of enynone **1** contributes to the predominance of the intermolecular reaction affording "dimers" **4**. Surprisingly, the methoxy-substituted enynone **1j** (R^2 = MeO) in TfOH gave only mixture of oligomers (entries 15, 16). The exact structures and stereochemistry of indenes (2*E*,4*Z*)/(2*E*,4*E*)-**4a−c** were confirmed by NOESY correlations (Figure 5).

The plausible mechanism of formation of compounds **4** is presented in Scheme 2. The intermolecular substitution on the tolyl ring of O-protonated triflate **E** by the carbon C^5 of another species **E** gives cation **H**. This substitution takes place in the *ortho*-position relative to the methyl substituent as confirmed by the NOESY correlation observed between the methyl substituent and the vinylic proton on the indene fragment in both (2*E*,4*Z*) and (2*E*,4*E*)-**4** (Figure 5). Cation **H** is then protonated at C^2 of the butadiene system leading to cation **I**, which undergoes a cyclization on the tolyl ring via C^3 to give cation **J**. This species, in turn, is protonated in TfOH with formation of the stable cation **K**. The cation **K1** was independently generated from (2*E*,4*E*)-**4a** in TfOH at room temperature and characterized by ^{1}H and ^{13}C NMR (see Scheme 2). Finally hydrolysis of the reaction mixture gives compounds **4**. It should be mentioned that triflate **2g** gives stable O-protonated form **E4** (Table 4), and no protonation occurs on carbons of butadiene system.

An alternative way of formation of indenes **4** may be the initial formation of cations **G** (see Scheme 1) followed by its Friedel−Crafts reaction with species **E** leading to cations **K** (Scheme 2).

It should be noted that in the ^{1}H NMR spectra of cations **G1** and **K1** (see Schemes 1 and 2), the diastereotopic methylene protons adjacent to the carbocationic center give large germinal coupling constants of 22.4 and 24.2 Hz, respectively, (see Experimental Section and SI), due to the strong π-acceptor character of the cationic center.

Formations of compounds **3** and **4** are concurrent reactions depending on both reaction conditions (see dependence on the concentration of starting materials **1** in Table 6) and electronic properties of cations **E** (see NMR data in Table 4 and DFT calculations in Table 5). The cyclization into indanone **3** goes through carbon C^3 in species **E** (Scheme 1), while carbon C^5 takes part in the intermolecular key-stage of dimerization leading to intermediate **H** (Scheme 2). Comparison of charge

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and orbital distribution in cation **E1** (DFT calculation, Table 5) shows that C^5 has a rather large positive charge (0.42 e), but small orbital contribution into the LUMO. So, reactivity of this carbon may be mainly explained in terms of charge control. Furthermore, enynones **1g−i** have a donating methyl group (R^2 = Me) on the aryl ring adjacent to the triple bond, that increases the π-nucleophilicity of this ring and facilitates the intermolecular electrophilic attack in the intermediate species derived from **1g−i** (Scheme 2), contrary to enynones **1a−f** (R^2 = H, Cl) which do not give "dimers" due to their nonactivated aryl rings (Tables 2, 3).

We also found the best conditions for the solely formation of triflates **2a−j**, as initial products of addition of TfOH to the acetylenic bond of enynones **1a−j**. We discovered that the use of pyridine in amount of 10−33% vol in TfOH decreases acidity and allows to obtain only triflates **2a−j** (Scheme 3) with no consequent formation of compounds **3** or **4**, even for long reaction times. Analogously to previously investigated vinyl triflates,[39,40] the ratio of isomers **2a−j** depends on reaction temperature and time (see Experimental Section).

(*E*,*Z*)-Isomers of both triflates **2** and indenes **4** were separated by flash column chromatography and characterized as individually isolated compounds. There is only one exception for isomeric triflates **2j** having R^2 = MeO, which are unstable at room temperature and are decomposed on silica gel (see Experimental Section). Once isolated, triflates **2** and **4** are sensitive to light and to acidic conditions that lead to isomerization. Yields of indanones **3** and compounds **4** are decreased upon chromatographic isolation on silica gel (see Tables 2, 3, and 6 and Experimental Section).

It should be noted that vinyl triflates are in great demand for organic synthesis of cross-couplings and other reactions.[28,39−43] Concerning indanones, much effort is given to their synthesis[44−48] due to the biological activity of these compounds.[49,50]

CONCLUSIONS

In conclusion, we have studied reactions of 1,5-diarylpent-2-en-4-yn-1-ones in the superacid CF_3SO_3H proceeding with initial addition of CF_3SO_3H to acetylenic bond that gives butadienyl triflates. Under superacidic reaction conditions, these triflates are further cyclized into indanones or afford "dimeric" compounds depending on substituents in the aryl ring conjugated with the butadiene system. Reaction intermediates and mechanisms were studied by means of NMR and DFT calculations.

EXPERIMENTAL SECTION

The NMR spectra of solutions of compounds in $CDCl_3$ and cations in the superacid TfOH were recorded at 400, 376, and 101 MHz for ^1H, ^{19}F, and ^{13}C NMR, respectively, at room temperature. The residual proton-solvent peak $CDCl_3$ (δ 7.26 ppm) for ^1H NMR spectra and the carbon signal of $CDCl_3$ (δ 77.16 ppm) for ^{13}C NMR spectra were used as references. ^{19}F NMR spectra were indirectly referred to the signal of $CFCl_3$ (δ 0.0 ppm). NMR spectra in TfOH were referenced to the signal of CH_2Cl_2 added as internal standard: δ 5.30 ppm for ^1H NMR spectra and δ 53.52 ppm for ^{13}C NMR spectra. IR spectra of compounds were taken in dichloromethane solutions. HRMS was carried out for ESI-QTOF mode. Chromato-mass-spectrometry data were obtained at capillary column (30 m × 0.32 mm), thickness of the stationary phase 1.25 μm. The preparative reactions were monitored by thin-layer chromatography carried out on silica gel plates using UV light for detection. Preparative flash column chromatography was performed on silica gel.

X-ray Analysis. A suitable crystals were selected and studied on the diffractometer for X-ray analysis. The crystals were kept at 100(2) K during data collection. Using Olex2[51] the structure was solved with the ShelXS[52] structure solution program using direct methods and refined with the ShelXL refinement package using least squares minimization. CCDC 1437437 (2*E*,4*Z*-**2f**), CCDC 1437438 (2*E*,4*Z*-**2i**), CCDC 1437435 (**3b**), and CCDC 1437436 (**3d**) contain the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.htmL or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

DFT Calculations. All computations were carried out at the DFT/HF hybrid level of theory using Becke's three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP) by using GAUSSIAN 2003 program packages.[53] The geometries optimization were performed using the 6-311+G(2d,2p) basis set (standard 6-311 basis set added with polarization (d, p) and diffuse functions). Optimizations were performed on all degrees of freedom, and solvent-phase optimized structures were verified as true minima with no imaginary frequencies. The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima and to estimate the thermodynamic parameters. Gibbs free energies were calculated for 25 °C. Solvent-phase calculations used the polarizable continuum model (PCM).

We used commercially available solvents (petroleum ether, dichloromethane, ethyl acetate, diethyl ether) and CF_3SO_3H, which were redistilled before use.

Starting 1,5-Diarylpent-2-en-4-yn-1-ones 1a−j. The title compounds were obtained in yields of 40−89% according to known procedure.[54] Compounds **1a−d,g,h** were characterized by ourselves (A.A.G.) previously.[54]

*(E)-1-(4-Nitrophenyl)-5-phenylpent-2-en-4-yn-1-one (**1e**).* Yellow solid, mp 127−129 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 8.8 Hz, 2H), 7.55−7.50 (m, 2H), 7.42−7.35 (m, 3H), 7.39 (d, J = 15.4 Hz, 1H), 7.18 (d, J = 15.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.5, 150.4, 142.2, 132.3, 132.2, 129.9, 129.6, 128.7, 127.3, 124.1, 122.1, 101.4, 87.7. IR (CH_2Cl_2, cm^{-1}) ν 2197 (w, C≡C stretch), 1667 (m, C═O stretch), 1582 (s, C═C stretch), 1530 (s, N−O asymmetric stretch), 1348 (m, N−O symmetric stretch). HRMS (ESI) m/z calcd for $C_{17}H_{12}NO_3$ $[M + H]^+$ 278.0812, found 278.0810.

*(E)-5-(4-Chlorophenyl)-1-phenylpent-2-en-4-yn-1-one (**1f**).* Yellow solid, mp 93−95 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01−7.97 (m, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.45 (dm, J = 8.7 Hz, 2H), 7.44 (d, J = 15.4 Hz, 1H), 7.35 (dm, J = 8.5 Hz, 2H), 7.11 (d, J = 15.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9, 137.3, 135.7, 133.6, 133.42, 133.38, 129.1, 128.9, 128.7, 124.8, 120.9, 98.0, 88.8. IR (CH_2Cl_2, cm^{-1}) ν 2199 (w, C≡C stretch),1661 (m, C═O stretch), 1582 (s, C═C stretch). HRMS (ESI) m/z calcd for $C_{17}H_{12}ClO$ $[M + H]^+$ 267.0571, found 267.0578 ; $C_{17}H_{11}ClNaO$ $[M + Na]^+$ 289.0391, found 289.0399.

*(E)-1-(4-Bromophenyl)-5-(4-methylphenyl)pent-2-en-4-yn-1-one (**1i**).* Yellow solid, mp 128−130 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (dm, J = 8.6 Hz, 2H), 7.64 (dm, J = 8.6 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 15.4 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 15.4 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 140.2, 136.2, 132.19, 132.18, 132.15, 130.2, 129.5, 128.5, 126.1, 119.2, 100.6, 87.5, 21.8. IR (CH_2Cl_2, cm^{-1}) ν 2195 (m, C≡C stretch),1659 (m, C═O stretch), 1589 (s, C═C stretch). HRMS (ESI) m/z calcd for $C_{18}H_{14}$ ^{79}BrO $[M + H]^+$ 325.0223, found 325.0209 ; $C_{18}H_{13}$ $^{79}BrNaO$ $[M + Na]^+$ 347.0042, found 347.0029.

*(E)-5-(4-Methoxyphenyl)-1-phenylpent-2-en-4-yn-1-one (**1j**).* Yellow solid, mp 102−104 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02−7.97 (m, 2H), 7.62−7.56 (m, 1H), 7.52−7.47 (m, 2H), 7.47 (dm, J = 8.9 Hz, 2H), 7.40 (d, J = 15.5 Hz, 1H), 7.14 (d, J = 15.5 Hz, 1H), 6.89 (dm, J = 8.9 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1, 160.7, 137.6, 133.9, 133.2, 132.3, 128.8, 128.7, 125.7, 114.5, 114.4, 100.3, 87.3, 55.5. IR (CH_2Cl_2, cm^{-1}) ν 2193 (m, C≡C

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stretch),1659 (m, C=O stretch), 1582 (s, C=C stretch). HRMS (ESI) m/z calcd for $C_{18}H_{15}O_2$ $[M + H]^+$ 263.1067, found 263.1069 ; $C_{18}H_{14}NaO_2$ $[M + Na]^+$ 285.0886, found 285.0891.

General Procedure for the Transformation of Enynones 1 into Triflates 2 and Indanones 3 in TfOH. A 0.2 mmol portion of starting enynone **1** was added portionwise to 2 mL of TfOH, and the solution was stirred at definite conditions (reaction temperature and time are indicated in Tables 2, 3, and 6). Running the reaction for 0.25−1 h leads to the formation of triflates **2** mainly, and for enynones **1a**−**i**, running the reaction for 12−60 h gives indanones **3a**−**i** (Tables 2, 3, and 6). The reaction mixture was then diluted with 4 mL of chloroform, cooled to 0 °C, and quenched by dropwise addition of cold water (4 mL). The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed first with water and then with a diluted solution of $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. Reaction products were isolated by flash column chromatography on silica gel (previously deactivated with triethylamine). Yields of compounds **2**, **3**, and **4** depend on reaction conditions (time, temperature, concentration of starting enynones) as shown in Tables 2, 3, and 6.

General Procedure for the Transfrormation of Enynones 1a−i into Dienyl Triflates 2a−i in the System Pyridine-TfOH. A 0.3 mmol portion of starting enynone **1** was added portionwise to a solution of pyridine (0.3 mL, 10% vol) in triflic acid (2.7 mL), and the solution was stirred 15 min at room temperature. The reaction was then diluted with 6 mL of chloroform, cooled to 0 °C, and quenched by dropwise addition of cold water (6 mL). The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed first with water and then with a diluted solution of $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. Reaction products were isolated by flash column chromatography on silica gel (previously deactivated with triethylamine). For all products, the (2*E*,4*E*)-isomer was obtained first, followed by the more polar (2*E*,4*Z*)-isomer. Triflates (2*E*,4*Z*), (2*E*,4*E*)-**2j** were obtained with the use of 33% vol of pyridine.

*(2E,4E)-1,5-Diphenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2a**).* The title compound was obtained from enynone **1a** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 10:1, R_f 0.36, yield 48 mg, 42%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.93 (m, 2H), 7.62−7.57 (m, 1H), 7.57−7.46 (m, 8H), 7.29 (dd, J = 15.0, 0.5 Hz, 1H), 6.66 (dd, J = 11.7, 0.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3, 154.2, 137.6, 137.0, 133.4, 131.4, 131.1, 130.0, 129.19, 129.16, 128.9, 128.6, 120.9, 118.6 (q, J = 320.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.75 (s). IR (CH_2Cl_2, cm^{-1}) ν 1665 (s, C=O stretch), 1603 (s, C=C stretch). HRMS (ESI) m/z calcd for $C_{18}H_{14}F_3O_4S$ $[M + H]^+$ 383.0559, found 383.0568 ; $C_{18}H_{13}F_3NaO_4S$ $[M + Na]^+$ 405.0379, found 405.0389.

*(2E,4Z)-1,5-Diphenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2a**).* The title compound was obtained from enynone **1a** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 10:1, R_f 0.23, yield 57 mg, 50%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.93 (m, 2H), 7.73 (dd, J = 15.1, 11.4 Hz, 1H), 7.65−7.56 (m, 3H), 7.53−7.43 (m, 5H), 7.18 (d, J = 15.1 Hz, 1H), 6.72 (d, J = 11.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 151.3, 137.6, 135.1, 133.2, 132.7, 131.1, 129.9, 129.2, 128.8, 128.7, 126.1, 119.1, 118.6 (q, J = 320.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.07 (s). IR (CH_2Cl_2, cm^{-1}) ν 1665 (s, C=O stretch), 1603 (s, C=C stretch), 1589 (s, C=C stretch). HRMS (ESI) m/z calcd for $C_{18}H_{14}F_3O_4S$ $[M + H]^+$ 383.0559, found 383.0567 ; $C_{18}H_{13}F_3NaO_4S$ $[M + Na]^+$ 405.0379, found 405.0395.

*(2E,4E)-1-(4-Chlorophenyl)-5-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2b**).* The title compound was obtained from enynone **1b** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 14:1, R_f 0.37, yield 55 mg, 44%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dm, J = 8.6 Hz, 2H), 7.53 (dd, J = 14.9, 11.7 Hz, 1H), 7.54−7.49 (m, 5H), 7.46 (dm, J = 8.6 Hz, 2H), 7.24 (d, J = 15.2 Hz, 1H), 6.65 (d, J = 11.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 154.5, 139.9, 137.6, 135.9, 131.5, 131.0, 130.0, 129.31, 129.22, 129.19, 129.18, 120.8, 118.5 (q, J = 320.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.74 (s). IR (CH_2Cl_2, cm^{-1}) ν 1665 (s, C=O stretch), 1593 (s, C=C stretch). HRMS (ESI) m/z calcd for $C_{18}H_{13}ClF_3O_4S$ $[M + H]^+$ 417.0170, found 417.0173 ; $C_{18}H_{12}ClF_3NaO_4S$ $[M + Na]^+$ 438.9989, found 438.9994.

*(2E,4Z)-1-(4-Chlorophenyl)-5-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2b**).* The title compound was obtained from enynone **1b** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 14:1, R_f 0.2, yield 51 mg, 41%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dm, J = 8.5 Hz, 2H), 7.73 (dd, J = 15.1, 11.4 Hz, 1H), 7.63−7.58 (m, 2H), 7.50−7.44 (m, 5H), 7.13 (d, J = 15.1 Hz, 1H), 6.71 (d, J = 11.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 151.5, 139.7, 135.9, 135.5, 132.6, 131.2, 130.1, 129.23, 129.19 (2C), 126.2, 119.0, 118.6 (q, J = 320.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.03 (s). IR (CH_2Cl_2, cm^{-1}) ν 1667 (s, C=O stretch), 1593 (s, C=C stretch). HRMS (ESI) m/z calcd for $C_{18}H_{13}ClF_3O_4S$ $[M + H]^+$ 417.0170, found 417.0177 ; $C_{18}H_{12}ClF_3NaO_4S$ $[M + Na]^+$ 438.9989, found 438.9997.

*(2E,4E)-1-(4-Methylphenyl)-5-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2c**).* The title compound was obtained from enynone **1c** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 14:1, R_f 0.32, yield 50 mg, 42%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 2H), 7.55−7.46 (m, 6H), 7.32−7.27 (m, 3H), 6.65 (d, J = 11.6 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 154.0, 144.4, 136.6, 135.0, 131.4, 131.1, 130.1, 129.6, 129.19 (s), 129.15, 128.8, 121.0, 118.6 (q, J = 320.6 Hz), 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.76 (s). IR (CH_2Cl_2, cm^{-1}) ν 1663 (s, C=O stretch), 1609 (s, C=C stretch). HRMS (ESI) m/z calcd for $C_{19}H_{16}F_3O_4S$ $[M + H]^+$ 397.0716, found 397.0731 ; $C_{19}H_{15}F_3NaO_4S$ $[M + Na]^+$ 419.0535, found 419.0550.

*(2E,4Z)-1-(4-Methylphenyl)-5-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2c**).* The title compound was obtained from enynone **1c** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 14:1, R_f 0.19, yield 56 mg, 47%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 2H), 7.72 (dd, J = 15.1, 11.4 Hz, 1H), 7.63−7.59 (m, 2H), 7.48−7.44 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 15.1 Hz, 1H), 6.71 (d, J = 11.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5, 151.1, 144.2, 135.1, 134.6, 132.8, 131.1, 129.9, 129.6, 129.2, 128.9, 126.1, 119.2, 118.6 (q, J = 320.7 Hz), 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.07 (s). IR (CH_2Cl_2, cm^{-1}) ν 1663 (s, C=O stretch), 1609 (s, C=C stretch), 1589 (s, C=C stretch). HRMS (ESI) m/z calcd for $C_{19}H_{16}F_3O_4S$ $[M + H]^+$ 397.0716, found 397.0723 ; $C_{19}H_{15}F_3NaO_4S$ $[M + Na]^+$ 419.0535, found 419.0545.

*(2E,4E)-1-(4-Methoxyphenyl)-5-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2d**).* The title compound was obtained from enynone **1d** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 6:1, R_f 0.27, yield 42 mg, 34%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dm, J = 8.9 Hz, 2H), 7.55−7.46 (m, 6H), 7.29 (d, J = 15.0 Hz, 1H), 6.97 (dm, J = 8.9 Hz, 2H), 6.65 (d, J = 11.6 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.6, 163.9, 153.9, 136.2, 131.3, 131.1, 131.0, 130.5, 130.0, 129.18, 129.14, 121.1, 118.6 (q, J = 320.7 Hz), 114.1, 55.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.77 (s). IR (CH_2Cl_2, cm^{-1}) ν 1661 (s, C=O stretch), 1603 (s, C=C stretch), 1171 (s, C−O stretch). HRMS (ESI) m/z calcd for $C_{19}H_{16}F_3O_5S$ $[M + H]^+$ 413.0665, found 413.0681 ; $C_{19}H_{15}F_3NaO_5S$ $[M + Na]^+$ 435.0484, found 435.0500.

*(2E,4Z)-1-(4-Methoxyphenyl)-5-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2d**).* The title compound was obtained from enynone **1d** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 6:1, R_f 0.18, yield 71 mg, 57%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dm, J = 8.9 Hz, 2H), 7.72 (dd, J = 15.0, 11.4 Hz, 1H), 7.63−7.58 (m, 2H), 7.47−7.43 (m, 3H), 7.20 (d, J = 15.0 Hz, 1H), 6.97 (dm, J = 8.9 Hz, 2H), 6.70 (dd, J = 11.4, 0.6 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 163.8, 150.9, 134.2, 132.8, 131.04, 130.99, 130.6, 129.8, 129.2, 126.1, 119.3, 118.6 (q, J = 320.7 Hz), 114.1, 55.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.07 (s). IR (CH_2Cl_2, cm^{-1}) ν 1661 (s, C=O stretch), 1603 (s, C=C stretch), 1173 (s, C−O

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J. Org. Chem. 2016, 81, 1967−1980

stretch). HRMS (ESI) m/z calcd for $C_{19}H_{16}F_3O_5S$ $[M + H]^+$ 413.0665, found 413.0672 ; $C_{19}H_{15}F_3NaO_5S$ $[M + Na]^+$ 435.0484, found 435.0489.

*(2E,4E)-1-(4-Nitrophenyl)-5-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2e**).* The title compound was obtained from enynone **1e** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 6:1, R_f 0.38, yield 10 mg, 8%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dm, J = 8.8 Hz, 2H), 8.10 (dm, J = 8.8 Hz, 2H), 7.57 (dd, J = 14.9, 11.7 Hz, 1H), 7.56−7.50 (m, 5H), 7.25 (d, J = 14.9 Hz, 1H), 6.67 (d, J = 11.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.8, 155.4, 150.5, 142.2, 139.1, 131.8, 130.9, 129.5, 129.3 (2C), 128.8, 124.1, 120.5, 118.5 (q, J = 320.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.69 (s). IR (CH_2Cl_2, cm^{-1}) ν 1670 (m, C═O stretch), 1603 (s, C═C stretch), 1530 (s, N−O asymmetric stretch), 1348 (m, N−O symmetric stretch). HRMS (ESI) m/z calcd for $C_{18}H_{13}F_3NO_6S$ $[M + H]^+$ 428.0410, found 428.0432 ; $C_{18}H_{12}F_3NNaO_6S$ $[M + Na]^+$ 450.0230, found 450.0247.

*(2E,4Z)-1-(4-Nitrophenyl)-5-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2e**).* The title compound was obtained from enynone **1e** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 6:1, R_f 0.2, yield 40 mg, 31%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (dm, J = 8.8 Hz, 2H), 8.09 (dm, J = 8.8 Hz, 2H), 7.75 (dd, J = 15.1, 11.4 Hz, 1H), 7.64−7.59 (m, 2H), 7.52−7.44 (m, 3H), 7.13 (d, J = 15.1 Hz, 1H), 6.75 (d, J = 11.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 152.2, 150.4, 142.3, 136.9, 132.3, 131.5, 129.6, 129.3, 128.8, 126.2, 124.1, 118.7, 118.5 (q, J = 320.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −72.97 (s). IR (CH_2Cl_2, cm^{-1}) ν 1670 (s, C═O stretch), 1603 (s, C═C stretch), 1587 (s, C═C stretch), 1530 (s, N−O asymmetric stretch), 1350 (s, N−O symmetric stretch). HRMS (ESI) m/z calcd for $C_{18}H_{13}F_3NO_6S$ $[M + H]^+$ 428.0410, found 428.0431 ; $C_{18}H_{12}F_3NNaO_6S$ $[M + Na]^+$ 450.0230, found 450.0243.

*(2E,4E)-5-(4-Chlorophenyl)-1-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2f**).* The title compound was obtained from enynone **1f** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 9:1, R_f 0.46, yield 38 mg, 30%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.94 (m, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.53−7.44 (m, 6H), 7.46 (dd, J = 15.0, 11.6 Hz, 1H), 7.31 (d, J = 15.0 Hz, 1H), 6.66 (d, J = 11.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.2, 152.8, 137.8, 137.5, 136.4, 133.5, 130.44, 130.38, 129.61, 129.54, 128.9, 128.6, 121.5, 118.5 (q, J = 320.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.64 (s). IR (CH_2Cl_2, cm^{-1}) ν 1665 (m, C═O stretch), 1601 (m, C═C stretch). HRMS (ESI) m/z calcd for $C_{18}H_{13}ClF_3O_4S$ $[M + H]^+$ 417.0170, found 417.0184 ; $C_{18}H_{12}ClF_3NaO_4S$ $[M + Na]^+$ 438.9989, found 439.0006.

*(2E,4Z)-5-(4-Chlorophenyl)-1-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2f**).* The title compound was obtained from enynone **1f** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 9:1, R_f 0.28, yield 56 mg, 45%). Brownish solid, mp 85−77 °C. Single crystal suitable for X-ray diffraction was obtained by slow evaporation of a diluted solution of (2*E*,4*Z*)-**2f** in dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.93 (m, 2H), 7.70 (dd, J = 15.1, 11.3 Hz, 1H), 7.62−7.57 (m, 1H), 7.54 (dm, J = 8.7 Hz, 2H), 7.54−7.46 (m, 2H), 7.43 (dm, J = 8.7 Hz, 2H), 7.19 (d, J = 15.1 Hz, 1H), 6.70 (d, J = 11.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0, 150.0, 137.5, 137.3, 134.7, 133.3, 131.2, 130.2, 129.6, 128.9, 128.7, 127.4, 119.6, 118.5 (q, J = 320.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −72.98 (s). IR (CH_2Cl_2, cm^{-1}) ν 1665 (m, C═O stretch), 1587 (s, C═C stretch). HRMS (ESI) m/z calcd for $C_{18}H_{13}ClF_3O_4S$ $[M + H]^+$ 417.0170, found 417.0187 ; $C_{18}H_{12}ClF_3NaO_4S$ $[M + Na]^+$ 438.9989, found 438.9997.

*(2E,4E)-5-(4-Methylphenyl)-1-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2g**).* The title compound was obtained from enynone **1g** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 10:1, R_f 0.36, yield 31 mg, 26%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.94 (m, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.57−7.46 (m, 3H), 7.41 (d, J = 8.2 Hz, 2H), 7.32−7.24 (m, 3H), 6.60 (d, J = 11.7 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.4, 154.7, 142.1, 137.7, 137.4, 133.4, 129.9, 129.5, 129.1, 128.9, 128.6, 128.3, 120.3, 118.6 (q, J = 320.7 Hz), 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.78 (s). IR (CH_2Cl_2, cm^{-1}) ν 1663 (m, C═O stretch), 1601 (m, C═C stretch), 1587 (m, C═C stretch). HRMS (ESI) m/z calcd for $C_{19}H_{16}F_3O_4S$ $[M + H]^+$ 397.0716, found 397.0721 ; $C_{19}H_{15}F_3NaO_4S$ $[M + Na]^+$ 419.0535, found 419.0542.

*(2E,4Z)-5-(4-Methylphenyl)-1-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2g**).* The title compound was obtained from enynone **1g** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 10:1, R_f 0.21, yield 50 mg, 42%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.93 (m, 2H), 7.72 (dd, J = 15.1, 11.4 Hz, 1H), 7.62−7.57 (m, 1H), 7.53−7.47 (m, 4H), 7.26 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 15.1 Hz, 1H), 6.67 (d, J = 11.4 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.3, 151.6, 141.8, 137.7, 135.4, 133.2, 129.94, 129.92, 129.4, 128.8, 128.7, 126.1, 118.6 (q, J = 320.6 Hz), 118.2, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.08 (s). IR (CH_2Cl_2, cm^{-1}) ν 1663 (m, C═O stretch), 1601 (s, C═C stretch), 1589 (s, C═C stretch). HRMS (ESI) m/z calcd for $C_{19}H_{16}F_3O_4S$ $[M + H]^+$ 397.0716, found 397.0723 ; $C_{19}H_{15}F_3NaO_4S$ $[M + Na]^+$ 419.0535, found 419.0549.

*(2E,4E)-1-(4-Chlorophenyl)-5-(4-methylphenyl)-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2h**).* The title compound was obtained from enynone **1h** and was isolated by flash column chromatography (petroleum ether/dichloromethane 2:1, R_f 0.26, yield 39 mg, 30%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dm, J = 8.6 Hz, 2H), 7.53 (dd, J = 15.0, 11.7 Hz, 1H), 7.47 (dm, J = 8.6 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 15.0 Hz, 1H), 6.59 (d, J = 11.7 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.1, 155.0, 142.2, 139.9, 138.0, 136.0, 129.99, 129.91, 129.23, 129.15, 128.9, 128.2, 120.1, 118.6 (q, J = 320.7 Hz), 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.77 (s). IR (CH_2Cl_2, cm^{-1}) ν 1665 (m, C═O stretch), 1595 (s, C═C stretch). HRMS (ESI) m/z calcd for $C_{19}H_{15}ClF_3O_4S$ $[M + H]^+$ 431.0326, found 431.0328.

*(2E,4Z)-1-(4-Chlorophenyl)-5-(4-methylphenyl)-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2h**).* The title compound was obtained from enynone **1h** and was isolated by flash column chromatography (petroleum ether/dichloromethane 2:1, R_f 0.16, yield 57 mg, 44%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.5 Hz, 2H), 7.72 (dd, J = 15.1, 11.4 Hz, 1H), 7.50 (br d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.26 (br d, J = 8.1 Hz, 2H), 7.10 (d, J = 15.1 Hz, 1H), 6.67 (d, J = 11.4 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9, 151.8, 141.9, 139.7, 136.0, 135.8, 130.1, 130.0, 129.8, 129.2, 128.8, 126.1, 118.6 (q, J = 320.6 Hz), 118.0, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.04 (s). IR (CH_2Cl_2, cm^{-1}) ν 1665 (m, C═O stretch), 1593 (s, C═C stretch). HRMS (ESI) m/z calcd for $C_{19}H_{15}ClF_3O_4S$ $[M + H]^+$ 431.0326, found 431.0334.

*(2E,4E)-1-(4-Bromophenyl)-5-(4-methylphenyl)-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2i**).* The title compound was obtained from enynone **1i** and was isolated by flash column chromatography (petroleum ether/dichloromethane 2:1, R_f 0.24 yield 43 mg, 30%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dm, J = 8.6 Hz, 2H), 7.63 (dm, J = 8.6 Hz, 2H), 7.53 (dd, J = 15.0, 11.7 Hz, 1H), 7.41 (br d, J = 8.2 Hz, 2H), 7.30 (br d, J = 8.0 Hz, 2H), 7.21 (d, J = 15.0 Hz, 1H), 6.59 (d, J = 11.7 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3, 155.0, 142.2, 138.0, 136.4, 132.2, 130.1, 129.9, 129.2, 128.9, 128.6, 128.2, 120.1, 118.6 (q, J = 320.7 Hz), 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.76 (s). IR (CH_2Cl_2, cm^{-1}) ν 1665 (s, C═O stretch), 1593 (s, C═C stretch). HRMS (ESI) m/z calcd for $C_{19}H_{15}{}^{81}BrF_3O_4S$ $[M + H]^+$ 476.9800, found 476.9807 ; $C_{18}H_{14}{}^{81}BrF_3NaO_4S$ $[M + Na]^+$ 498.9621, found 498.9628.

*(2E,4Z)-1-(4-Bromophenyl)-5-(4-methylphenyl)-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2i**).* The title compound was obtained from enynone **1i** and was isolated by flash column chromatography (petroleum ether/dichloromethane 2:1, R_f 0.19, yield 61 mg, 43%). Brownish solid, mp 85−87 °C. Single crystal suitable for X-ray diffraction was obtained by slow evaporation of a diluted solution of (2*E*,4*Z*)-**2i** in dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dm, J = 8.6 Hz, 2H), 7.72 (dd, J = 15.1, 11.4 Hz, 1H), 7.64 (dm, J = 8.6 Hz, 2H), 7.50 (br d, J = 8.3 Hz, 2H), 7.26 (br d, J = 8.0 Hz, 2H), 7.10 (d, J = 15.1 Hz, 1H), 6.67 (d, J = 11.4 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.0, 151.9, 141.9, 136.4,

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135.8, 132.2, 130.2, 130.0, 129.8, 128.7, 128.4, 126.1, 118.6 (q, J = 320.6 Hz), 118.0, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.04 (s). IR (CH_2Cl_2, cm^{-1}) ν 1665 (s, C═O stretch), 1591 (s, C═C stretch). HRMS (ESI) m/z calcd for $C_{19}H_{15}$ $^{81}BrF_3O_4S$ $[M + H]^+$ 476.9800, found 476.9811 ; $C_{19}H_{14}$ $^{79}BrF_3NaO_4S$ $[M + Na]^+$ 496.9640, found 496.9656.

*(2E,4E)-5-(4-Methoxyphenyl)-1-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2j**).* The title compound was obtained as minor isomer from enynone **1j** using a solution of 33% vol of pyridine in TfOH as reaction solvent and could not be isolated by flash column chromatography on silica gel. ^{1}H and ^{19}F NMR spectra were recorded on the crude reaction mixture and showed a yield of 49% of both isomers and in a ratio of 4.8:1. ^{1}H NMR (400 MHz, $CDCl_3$, from the spectrum of mixture of isomers) δ 8.01−7.97 (m, 2H), 7.74−7.44 (m, 6H), 7.39 (d, J = 15.5 Hz, 1H), 6.89 (dm, J = 8.9 Hz, 2H), 6.56 (d, J = 11.6 Hz, 1H), 3.84 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$, from the spectrum of mixture of isomers) δ −73.81 (s). HRMS (ESI) m/z calcd for $C_{19}H_{15}F_3NaO_5S$ $[M + Na]^+$ 435.0484, found 435.0479 (for the mixture of isomers).

*(2E,4Z)-5-(4-Methoxyphenyl)-1-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**2j**).* The title compound was obtained as major isomer from enynone **1j** using a solution of 33% of pyridine in TfOH as reaction solvent and could not be isolated by flash column chromatography on silica gel. ^{1}H and ^{19}F NMR spectra were recorded on the crude reaction mixture and showed a yield of 49% of both isomers in a ratio of 4.8:1. ^{1}H NMR (400 MHz, $CDCl_3$, from the spectrum of mixture of isomers) δ 7.97−7.93 (m, 2H), 7.71 (dd, J = 15.1, 11.4 Hz, 1H), 7.61−7.56 (m, 1H), 7.56 (dm, J = 8.9 Hz, 2H), 7.52−7.47 (m, 2H), 7.13 (d, J = 15.2 Hz, 1H), 6.96 (dm, J = 8.9 Hz, 2H), 6.61 (d, J = 11.4 Hz, 1H), 3.86 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$, from the spectrum of mixture of isomers) δ −73.09 (s). HRMS (ESI) m/z calcd for $C_{19}H_{15}F_3NaO_5S$ $[M + Na]^+$ 435.0484, found 435.0479 (for the mixture of isomers).

*3-(2-Oxo-2-phenylethyl)indan-1-one (**3a**).* The title compound was obtained from enynone **1a** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 6:1, R_f 0.3, yield 32 mg, 64%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.95 (m, 2H), 7.78 (d, J = 7.7 Hz, 1H), 7.64−7.56 (m, 2H), 7.54 (d, J = 7.7 Hz, 1H), 7.51−7.45 (m, 2H), 7.41 (t, J = 7.4 Hz, 1H), 4.12−4.02 (m, 1H), 3.56 (dd, J = 17.7, 4.8 Hz, 1H), 3.26 (dd, J = 17.7, 9.1 Hz, 1H), 3.12 (dd, J = 19.3, 7.7 Hz, 1H), 2.37 (dd, J = 19.3, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8, 198.2, 157.7, 137.1, 136.7, 135.0, 133.6, 128.9, 128.2, 128.1, 125.8, 123.9, 45.4, 44.2, 33.8. IR (KBr, cm^{-1}) ν 1711 (s, C═O stretch), 1684 (s, C═O stretch). HRMS (ESI) m/z calcd for $C_{17}H_{15}O_2$ $[M + H]^+$ 251.1067, found 251.1076 ; $C_{17}H_{14}NaO_2$ $[M + Na]^+$ 273.0886, found 273.0903.

*3-(2-(4-Chlorophenyl)-2-oxoethyl)indan-1-one (**3b**).* The title compound was obtained from enynone **1b** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 7:1, R_f 0.3, yield 33 mg, 57%). Yellowish solid, mp 108−110 °C. Single crystal suitable for X-ray diffraction was obtained by slow evaporation of a diluted solution of **3b** in diethyl ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dm, J = 8.6 Hz, 2H), 7.78 (d, J = 7.7 Hz, 1H), 7.64−7.58 (m, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.45 (dm, J = 8.7 Hz, 2H), 7.47−7.39 (m, 1H), 4.10−4.01 (m, 1H), 3.53 (dd, J = 17.8, 4.8 Hz, 1H), 3.22 (dd, J = 17.8, 9.0 Hz, 1H), 3.12 (dd, J = 19.3, 7.7 Hz, 1H), 2.35 (dd, J = 19.3, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 197.0, 157.5, 140.2, 137.1, 135.06, 135.04, 129.6, 129.2, 128.1, 125.7, 124.0, 45.4, 44.1, 33.8. IR (KBr, cm^{-1}) ν 1713 (s, C═O stretch), 1686 (m, C═O stretch). HRMS (ESI) m/z calcd for $C_{17}H_{14}ClO_2$ $[M + H]^+$ 285.0677, found 285.0686.

*3-(2-(4-Methylphenyl)-2-oxoethyl)indan-1-one (**3c**).* The title compound was obtained from enynone **1c** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 7:1, R_f 0.3, yield 39 mg, 73%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 7.6 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.29−7.24 (m, 2H), 4.11−4.02 (m, 1H), 3.53 (dd, J = 17.6, 4.8 Hz, 1H), 3.22 (dd, J = 17.6, 9.1 Hz, 1H), 3.11 (dd, J = 19.3, 7.6 Hz, 1H), 2.42 (s, 3H), 2.36 (dd, J = 19.4, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.9, 197.8, 157.9, 144.5, 137.1, 135.0, 134.3, 129.6, 128.3, 128.0, 125.8, 123.9, 45.3, 44.2, 33.9, 21.8. IR (KBr, cm^{-1}) ν 1713 (s, C═O stretch), 1682 (m, C═O stretch). HRMS (ESI) m/z calcd for $C_{18}H_{17}O_2$ $[M + H]^+$ 265.1223, found 265.1247.

*3-(2-(4-Methoxyphenyl)-2-oxoethyl)indan-1-one (**3d**).* The title compound was obtained from enynone **1d** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 4:1, R_f 0.3, yield 34 mg, 60%). Brown solid, mp 124−126 °C. Single crystal suitable for X-ray diffraction was obtained by slow evaporation of a diluted solution of **3d** in diethyl ether/dichloromethane 3:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dm, J = 8.9 Hz, 2H), 7.77 (d, J = 7.7 Hz, 1H), 7.64−7.58 (m, 1H), 7.53 (d, J = 7.3 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 6.94 (dm, J = 8.9 Hz, 2H), 4.11−4.03 (m, 1H), 3.87 (s, 3H), 3.50 (dd, J = 17.4, 4.9 Hz, 1H), 3.20 (dd, J = 17.4, 9.1 Hz, 1H), 3.11 (dd, J = 19.4, 7.6 Hz, 1H), 2.37 (dd, J = 19.4, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0, 196.7, 163.9, 157.9, 137.1, 135.0, 130.5, 129.9, 128.0, 125.8, 123.9, 114.0, 55.7, 45.0, 44.2, 34.0. IR (KBr, cm^{-1}) ν 1713 (s, C═O stretch), 1676 (m, C═O stretch). HRMS (ESI) m/z calcd for $C_{18}H_{17}O_3$ $[M + H]^+$ 281.1172, found 281.1180 ; $C_{18}H_{16}NaO_3$ $[M + Na]^+$ 303.0992, found 303.1003.

*3-(2-(4-Nitrophenyl)-2-oxoethyl)indan-1-one (**3e**).* The title compound was obtained from enynone **1e** and was isolated by flash column chromatography (petroleum ether/ethyl acetate 4:1, R_f 0.3, yield 22 mg, 37%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dm, J = 8.9 Hz, 2H), 8.12 (dm, J = 8.9 Hz, 2H), 7.78 (d, J = 7.7 Hz, 1H), 7.66−7.60 (m, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H), 4.13−4.03 (m, 1H), 3.62 (dd, J = 18.1, 4.7 Hz, 1H), 3.31 (dd, J = 18.1, 9.0 Hz, 1H), 3.15 (dd, J = 19.3, 7.7 Hz, 1H), 2.36 (dd, J = 19.3, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.3, 196.7, 157.0, 150.7, 141.0, 137.1, 135.2, 129.2, 128.3, 125.6, 124.15, 124.06, 45.9, 44.0, 33.6. IR (KBr, cm^{-1}) ν 1709 (s, C═O stretch), 1686 (m, C═O stretch), 1520 (s, N−O asymmetric stretch), 1348 (m, N−O symmetric stretch). HRMS (ESI) m/z calcd for $C_{17}H_{14}NO_4$ $[M + H]^+$ 296.0917, found 296.0925 ; $C_{17}H_{13}NNaO_4$ $[M + Na]^+$ 318.0737, found 318.0746.

*5-Chloro-3-(2-oxo-2-phenylethyl)indan-1-one (**3f**).* The title compound was obtained from enynone **1e** and was isolated by flash column chromatography (petroleum ether/ethyl acetate/dichloromethane 8:1:1, R_f 0.24, yield 9 mg, 6%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.95 (m, 2H), 7.70 (d, J = 8.2 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.53 (br s, 1H), 7.52−7.46 (m, 2H), 7.39 (dd, J = 8.2, 1.3 Hz, 1H), 4.10−4.01 (m, 1H), 3.55 (dd, J = 17.9, 5.0 Hz, 1H), 3.28 (dd, J = 17.9, 8.8 Hz, 1H), 3.14 (dd, J = 19.4, 7.7 Hz, 1H), 2.39 (dd, J = 19.4, 3.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 197.8, 159.2, 141.6, 136.6, 135.6, 133.8, 128.96, 128.88, 128.2, 126.2, 125.1, 45.1, 44.2, 33.6. IR (CH_2Cl_2, cm^{-1}) ν 1715 (s, C═O stretch), 1686 (s, C═O stretch). HRMS (ESI) m/z calcd for $C_{17}H_{14}ClO_2$ $[M + H]^+$ 285.0677, found 285.0679 ; $C_{17}H_{13}ClNaO_2$ $[M + Na]^+$ 307.0496, found 307.0513.

*5-Methyl-3-(2-oxo-2-phenylethyl)indan-1-one (**3g**).* The title compound was obtained from enynone **1g** and was isolated by flash column chromatography (petroleum ether/ethyl acetate/chloroform 9:1:1, R_f 0.2, yield 21 mg, 40%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.95 (m, 2H), 7.67 (d, J = 7.8 Hz, 1H), 7.62−7.56 (m, 1H), 7.51−7.45 (m, 2H), 7.32 (br s, 1H), 7.22 (br d, J = 7.8 Hz, 1H), 4.06−3.97 (m, 1H), 3.56 (dd, J = 17.7, 4.8 Hz, 1H), 3.24 (dd, J = 17.7, 9.1 Hz, 1H), 3.11 (dd, J = 19.3, 7.6 Hz, 1H), 2.45 (s, 3H), 2.35 (dd, J = 19.3, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.4, 198.3, 158.3, 146.3, 136.8, 134.8, 133.6, 129.3, 128.9, 128.2, 126.1, 123.8, 45.5, 44.4, 33.6, 22.3. IR ($CHCl_3$, cm^{-1}) ν 1703 (s, C═O stretch), 1688 (s, C═O stretch). HRMS (ESI) m/z calcd for $C_{18}H_{17}O_2$ $[M + H]^+$ 265.1223, found 265.1225 ; $C_{18}H_{16}NaO_2$ $[M + Na]^+$ 287.1043, found 287.1055.

*5-Methyl-3-(2-oxo-2-(4-chlorophenyl)ethyl)indan-1-one (**3h**).* The title compound was obtained from enynone **1h** and was isolated by flash column chromatography (petroleum ether/ethyl acetate/chloroform 9:1:1, R_f 0.19, yield 23 mg, 39%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dm, J = 8.6 Hz, 2H), 7.66 (d, J = 7.8 Hz, 1H), 7.45 (dm, J = 8.6 Hz, 2H), 7.30 (br s, 1H), 7.22 (br d, J = 7.8 Hz, 1H), 4.04−3.95 (m, 1H), 3.52 (dd, J = 17.8, 4.7 Hz, 1H), 3.20 (dd, J =

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J. Org. Chem. 2016, 81, 1967−1980

17.8, 9.1 Hz, 1H), 3.10 (dd, J = 19.2, 7.7 Hz, 1H), 2.45 (s, 3H), 2.33 (dd, J = 19.2, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.2, 197.0, 158.0, 146.3, 140.1, 135.1, 134.8, 129.6, 129.4, 129.2, 126.0, 123.8, 45.5, 44.3, 33.6, 22.3. IR (KBr, cm^{-1}) ν 1700 (s, C=O stretch), 1680 (s, C=O stretch). HRMS (ESI) m/z calcd for $C_{18}H_{16}ClO_2$ $[M + H]^+$ 299.0833, found 299.0841 ; $C_{18}H_{15}ClNaO_2$ $[M + Na]^+$ 321.0653, found 321.0662.

*3-(2-(4-Bromophenyl)-2-oxo-ethyl)-5-methylindan-1-one (**3i**).* The title compound was obtained from enynone **1i** and was isolated by flash column chromatography (petroleum ether/ethyl acetate/chloroform 9:1:1, R_f 0.2, yield 25 mg, 36%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dm, J = 8.6 Hz, 2H), 7.67 (d, J = 7.8 Hz, 1H), 7.62 (dm, J = 8.6 Hz, 2H), 7.30 (br s, 1H), 7.22 (br d, J = 7.8 Hz, 1H), 4.04−3.95 (m, 1H), 3.51 (dd, J = 17.8, 4.7 Hz, 1H), 3.19 (dd, J = 17.8, 9.1 Hz, 1H), 3.10 (dd, J = 19.2, 7.7 Hz, 1H), 2.44 (s, 3H), 2.32 (dd, J = 19.2, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.2, 197.2, 158.0, 146.3, 135.5, 134.8, 132.2, 129.7, 129.4, 128.9, 126.0, 123.8, 45.4, 44.3, 33.5, 22.3. IR (KBr, cm^{-1}) ν 1703 (s, C=O stretch), 1679 (s, C=O stretch). HRMS (ESI) m/z calcd for $C_{18}H_{16}$ $^{79}BrO_2$ $[M + H]^+$ 343.0328, found 343.0320 ; $C_{18}H_{15}$ $^{79}BrNaO_2$ $[M + Na]^+$ 365.0148, found 365.0148.

General Procedure for Transformation of Enynones 1g−i into "Dimeric" Compounds 4a−c in TfOH. A 0.5 mmol portion of enynone **1** was added portionwise to 1.25 mL of TfOH, and the solution was stirred at room temperature during 12 h. The reaction mixture was then diluted with 3 mL of chloroform, cooled to 0 °C, and quenched by dropwise addition of cold water (3 mL). The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed first with water and then with a diluted solution of $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. Reaction products were isolated by flash column chromatography on silica gel (previously deactivated with triethylamine) allowed to obtained first the (2*E*,4*E*)-isomer, followed by the more polar (2*E*,4*Z*)-isomer. See other reaction conditions in Table 6.

*(2E,4E)-5-(4-Methyl-3-(6-methyl-1-(2-oxo-2-phenylethyl)-1H-inden-3-yl)phenyl)-1-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**4a**).* The title compound was obtained from enynone **1g** and was isolated by flash column chromatography (dichloromethane/petroleum ether 3:2, R_f 0.2−0.25 ; then petroleum ether/ethyl acetate 11:1, R_f 0.28, yield 39 mg, 12%). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−7.99 (m, 2H), 7.98−7.92 (m, 2H), 7.61−7.53 (m, 3H), 7.51−7.40 (m, 7H), 7.33 (br s, 1H), 7.25 (d, J = 15.0 Hz, 1H), 7.12 (br d, J = 7.7 Hz, 1H), 7.03 (d, J = 7.7 Hz, 1H), 6.62 (d, J = 11.7 Hz, 1H), 6.46 (d, J = 1.9 Hz, 1H), 4.34−4.28 (m, 1H), 3.51 (dd, J = 17.5, 6.2 Hz, 1H), 3.22 (dd, J = 17.5, 8.5 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 189.4, 154.4, 147.7, 142.7, 141.6, 140.6, 137.7, 137.4, 137.0, 136.7, 136.5, 135.5, 133.4, 133.3, 131.2, 129.9, 129.7, 128.86, 128.83, 128.59, 128.57, 128.37, 128.32 (2C), 128.0, 124.5, 120.6, 118.6 (q, J = 320.8 Hz), 44.9, 40.8, 21.6, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.68 (s). IR (CH_2Cl_2, cm^{-1}) ν 1686 (s, C=O stretch), 1665 (s, C=O stretch), 1601 (s, C=C stretch). HRMS (ESI) m/z calcd for $C_{37}H_{30}F_3O_5S$ $[M + H]^+$ 643.1761, found 643.1782 ; $C_{37}H_{29}F_3NaO_5S$ $[M + Na]^+$ 665.1580, found 665.1598.

*(2E,4Z)-5-(4-Methyl-3-(6-methyl-1-(2-oxo-2-phenylethyl)-1H-inden-3-yl)phenyl)-1-phenyl-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**4a**).* The title compound was obtained from enynone **1g** and was isolated by flash column chromatography (dichloromethane/petroleum ether 3:2, R_f 0.2−0.25 ; then petroleum ether/ethyl acetate 9:1, R_f 0.2, yield 174 mg, 54%). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−8.00 (m, 2H), 7.99−7.92 (m, 2H), 7.72 (dd, J = 15.1, 11.4 Hz, 1H), 7.63−7.56 (m, 2H), 7.55−7.46 (m, 6H), 7.39−7.34 (m, 2H), 7.15 (d, J = 15.1 Hz, 1H), 7.12 (d, J = 7.7 Hz, 1H), 6.98 (d, J = 7.7 Hz, 1H), 6.70 (d, J = 11.4 Hz, 1H), 6.48 (d, J = 2.0 Hz, 1H), 4.36−4.27 (m, 1H), 3.56 (dd, J = 17.6, 6.0 Hz, 1H), 3.21 (dd, J = 17.6, 8.8 Hz, 1H), 2.42 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 190.2, 151.3, 147.7, 143.2, 141.6, 140.3, 137.7, 137.0, 136.7, 136.5, 135.6, 135.3, 133.5, 133.2, 131.2, 130.2, 129.5, 128.86, 128.82, 128.7, 128.3, 127.8, 127.0, 125.2, 124.5, 120.5, 118.6 (q, J = 320.7 Hz), 118.4, 44.9, 40.8, 21.6, 20.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −72.98 (s). IR (CH_2Cl_2, cm^{-1}) ν 1686 (s, C=O stretch), 1665 (s, C=O stretch), 1601 (s, C=C stretch), 1589 (s, C=C stretch). HRMS (ESI) m/z calcd for $C_{37}H_{30}F_3O_5S$ $[M + H]^+$ 643.1761, found 643.1766 ; $C_{37}H_{29}F_3NaO_5S$ $[M + Na]^+$ 665.1580, found 665.1581.

*(2E,4E)-1-(4-Chlorophenyl)-5-(4-methyl-3-(6-methyl-1-(2-oxo-2-(4-chlorophenyl)ethyl)-1H-inden-3-yl)phenyl)-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**4b**).* The title compound was obtained from enynone **1h** and was isolated by flash column chromatography (petroleum ether/dichloromethane 3:2, R_f 0.2−0.25 ; then petroleum ether/ethyl acetate 19:1, R_f 0.2, yield 39 mg, 11%). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.57 (dd, J = 15.0, 11.7 Hz, 1H), 7.47−7.39 (m, 7H), 7.31 (br s, 1H), 7.20 (d, J = 15.0 Hz, 1H), 7.12 (br d, J = 7.7 Hz, 1H), 7.03 (d, J = 7.7 Hz, 1H), 6.61 (d, J = 11.7 Hz, 1H), 6.45 (d, J = 1.8 Hz, 1H), 4.33−4.25 (m, 1H), 3.47 (dd, J = 17.6, 6.2 Hz, 1H), 3.18 (dd, J = 17.6, 8.4 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 188.1, 154.7, 147.5, 142.9, 141.6, 140.7, 139.93, 139.84, 137.9, 136.50, 136.48, 136.0, 135.6, 135.3, 131.2, 129.97, 129.90, 129.7, 129.22, 129.16, 129.05, 128.5, 128.4, 128.0, 124.5, 120.6, 120.4, 118.6 (q, J = 320.8 Hz), 44.8, 40.8, 21.6, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.67 (s). IR (CH_2Cl_2, cm^{-1}) ν 1690 (m, C=O stretch), 1665 (m, C=O stretch), 1591 (s, C=C stretch). HRMS (ESI) m/z calcd for $C_{37}H_{28}Cl_2F_3O_5S$ $[M + H]^+$ 711.0981, found 711.0976 ; $C_{37}H_{27}Cl_2F_3NaO_5S$ $[M + Na]^+$ 733.0801, found 733.0827.

*(2E,4Z)-1-(4-Chlorophenyl)-5-(4-methyl-3-(6-methyl-1-(2-oxo-2-(4-chlorophenyl)ethyl)-1H-inden-3-yl)phenyl)-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**4b**).* The title compound was obtained from enynone **1h** and was isolated by flash column chromatography (petroleum ether/dichloromethane 3:2, R_f 0.2−0.25 ; then petroleum ether/ethyl acetate 12:1, R_f 0.2, yield 171 mg, 48%). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dm, J = 8.6 Hz, 2H), 7.89 (dm, J = 8.6 Hz, 2H), 7.72 (dd, J = 15.0, 11.4 Hz, 1H), 7.54−7.50 (m, 2H), 7.47 (dm, J = 8.6 Hz, 2H), 7.46 (dm, J = 8.6 Hz, 2H), 7.37 (d, J = 8.7 Hz, 1H), 7.33 (br s, 1H), 7.11 (br d, J = 7.5 Hz, 1H), 7.10 (d, J = 15.0 Hz, 2H), 6.97 (d, J = 7.7 Hz, 1H), 6.69 (d, J = 11.4 Hz, 1H), 6.45 (d, J = 2.0 Hz, 1H), 4.33−4.24 (m, 1H), 3.52 (dd, J = 17.6, 5.9 Hz, 1H), 3.16 (dd, J = 17.6, 8.7 Hz, 1H), 2.41 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 188.8, 151.6, 147.5, 143.3, 141.6, 140.4, 140.0, 139.7, 136.6, 136.2, 136.0, 135.6 (2C), 135.2, 131.2, 130.13, 130.06, 129.7, 129.18, 129.16, 128.8, 127.9, 127.0, 125.3, 124.5, 120.5, 118.6 (q, J = 320.8 Hz), 118.3, 44.8, 40.8, 21.6, 20.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −72.95 (s). IR (CH_2Cl_2, cm^{-1}) ν 1688 (m, C=O stretch), 1665 (m, C=O stretch), 1591 (s, C=C stretch). HRMS (ESI) m/z calcd for $C_{37}H_{28}Cl_2F_3O_5S$ $[M + H]^+$ 711.0981, found 711.1014 ; $C_{37}H_{27}Cl_2F_3NaO_5S$ $[M + Na]^+$ 733.0801, found 733.0854.

*(2E,4E)-1-(4-Bromophenyl)-5-(4-methyl-3-(6-methyl-1-(2-oxo-2-(4-bromophenyl)ethyl)-1H-inden-3-yl)phenyl)-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**4c**).* The title compound was obtained from enynone **1i** and was isolated by flash column chromatography (petroleum ether/dichloromethane 1:1, R_f 0.16−0.2 ; then petroleum ether/ethyl acetate 14:1, R_f 0.29, yield 44 mg, 11%). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dm, J = 8.6 Hz, 2H), 7.81 (dm, J = 8.6 Hz, 2H), 7.64−7.59 (m, 4H), 7.58 (dd, J = 15.0, 11.7 Hz, 1H), 7.44−7.40 (m, 3H), 7.31 (br s, 1H), 7.20 (dd, J = 15.0, 0.5 Hz, 1H), 7.12 (br d, J = 7.7 Hz, 1H), 7.03 (d, J = 7.7 Hz, 1H), 6.61 (dd, J = 11.7, 0.4 Hz, 1H), 6.45 (d, J = 2.0 Hz, 1H), 4.32−4.25 (m, 1H), 3.47 (dd, J = 17.6, 6.2 Hz, 1H), 3.17 (dd, J = 17.6, 8.4 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 188.2, 154.8, 147.5, 142.9, 141.6, 140.7, 137.9, 136.5, 136.4, 135.7, 135.6, 132.21, 132.15, 131.2, 130.2, 130.1, 129.9, 129.83, 129.81, 129.0, 128.7, 128.5, 128.4, 128.0, 124.5, 120.6, 120.4, 118.6 (q, J = 320.8 Hz), 44.8, 40.8, 21.6, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.67 (s). IR (CH_2Cl_2, cm^{-1}) ν 1686 (m, C=O stretch), 1665 (m, C=O stretch), 1587 (s, C=C stretch). HRMS (ESI) m/z calcd for $C_{37}H_{28}$ $^{79}Br_2F_3O_5S$ $[M + H]^+$ 798.9971, found 798.9965 ; $C_{37}H_{27}$ $^{79}Br_2F_3NaO_5S$ $[M + Na]^+$ 820.9790, found 820.9784.

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J. Org. Chem. 2016, 81, 1967−1980

*(2E,4Z)-1-(4-Bromophenyl)-5-(4-methyl-3-(6-methyl-1-(2-oxo-2-(4-bromophenyl)ethyl)-1H-inden-3-yl)phenyl)-5-(trifluoromethylsulfonyloxy)penta-2,4-dien-1-one (**4c**).* The title compound was obtained from enynone **1i** and was isolated by flash column chromatography (petroleum ether/dichloromethane 1:1, R_f 0.16−0.2 ; then petroleum ether/ethyl acetate 11:1, R_f 0.22, yield 188 mg, 47%). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.72 (dd, J = 15.0, 11.4 Hz, 1H), 7.63 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.54−7.50 (m, 2H), 7.37 (d, J = 8.7 Hz, 1H), 7.33 (br s, 1H), 7.14−7.06 (m, 2H), 6.97 (d, J = 7.7 Hz, 1H), 6.69 (d, J = 11.4 Hz, 1H), 6.45 (d, J = 1.8 Hz, 1H), 4.33−4.24 (m, 1H), 3.52 (dd, J = 17.6, 5.9 Hz, 1H), 3.15 (dd, J = 17.6, 8.7 Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7, 189.0, 151.6, 147.5, 143.3, 141.6, 140.4, 136.6, 136.4, 136.2, 135.72, 135.66, 135.63, 132.19, 132.17, 131.2, 130.2 (2C), 129.8, 128.77, 128.74, 128.4, 127.9, 127.0, 125.3, 124.5, 120.5, 118.6 (q, J = 320.9 Hz), 118.3, 44.8, 40.8, 21.6, 20.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ −72.93 (s). IR (CH_2Cl_2, cm^{-1}) ν 1686 (m, C═O stretch), 1665 (m, C═O stretch), 1587 (s, C═C stretch). HRMS (ESI) m/z calcd for $C_{37}H_{28}$ ^{79}Br $^{81}BrF_3O_5S$ $[M + H]^+$ 800.9954, found 800.9909 ; $C_{37}H_{27}$ ^{79}Br $^{81}BrF_3NaO_5S$ $[M + Na]^+$ 822.9773, found 822.9776.

NMR Data of Cations E1−E4, G1, and K1 in TfOH. *O-Protonated Form (2E,4Z)-**E1** of Triflate (2E,4Z)-**2a**.* ^{1}H NMR (400 MHz, TfOH) δ 8.83 (dd, J = 14.4, 11.9 Hz, 1H), 8.39 (d, J = 7.8 Hz, 2H), 8.25 (t, J = 7.6 Hz, 1H), 8.03 (d, J = 7.8 Hz, 2H), 7.96 (t, J = 7.9 Hz, 2H), 7.87−7.81 (m, 1H), 7.76−7.66 (m, 3H), 7.53 (d, J = 11.8 Hz, 1H). ^{13}C NMR (101 MHz, TfOH) δ 199.4, 163.4, 158.8, 142.8, 135.9, 133.9, 131.9, 131.7, 130.9, 130.6, 129.0, 123.9, 119.9. ^{19}F NMR (376 MHz, TfOH) δ −73.55 (s).

*O-Protonated Form (2E,4Z)-**E2** of Triflate (2E,4Z)-**2b**.* ^{1}H NMR (400 MHz, TfOH) δ 8.69 (dd, J = 14.3, 11.8 Hz, 1H), 8.25 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 7.8 Hz, 2H), 7.83 (d, J = 8.7 Hz, 2H), 7.75−7.69 (m, 1H), 7.63 (t, J = 7.7 Hz, 2H), 7.55 (d, J = 14.4 Hz, 1H), 7.42 (d, J = 11.8 Hz, 1H). ^{13}C NMR (101 MHz, TfOH) δ 197.3, 163.5, 158.4, 151.3, 136.0, 135.1, 132.2, 131.8, 131.4, 130.6, 129.1, 129.0, 120.0. ^{19}F NMR (376 MHz, TfOH) δ −73.48 (s).

*O-Protonated Form (2E,4Z)-**E3** of Triflate (2E,4Z)-**2f**.* ^{1}H NMR ^{1}H NMR (400 MHz, TfOH) δ 8.68 (dd, J = 14.4, 11.8 Hz, 1H), 8.29 (d, J = 8.1 Hz, 2H), 8.16 (t, J = 7.4 Hz, 1H), 7.89−7.82 (m, 4H), 7.67−7.56 (m, 3H), 7.40 (d, J = 11.8 Hz, 1H). ^{13}C NMR (101 MHz, TfOH) δ 199.4, 161.6, 158.2, 142.9, 142.8, 133.9, 132.4, 131.7, 131.0, 130.8, 130.4, 130.1, 120.1. ^{19}F NMR (376 MHz, TfOH) δ −73.58 (s).

*O-Protonated Form (2E,4Z)-**E4** of Triflate (2E,4Z)-**2g**.* ^{1}H NMR (400 MHz, TfOH) δ 8.72 (dd, J = 14.3, 11.9 Hz, 1H), 8.24 (d, J = 7.8 Hz, 2H), 8.14−8.06 (m, 1H), 7.91−7.78 (m, 4H), 7.52 (d, J = 14.4 Hz, 1H), 7.46 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 11.9 Hz, 1H), 2.52 (s, 3H). ^{19}F NMR (376 MHz, TfOH) δ −73.97 (s).

Cation **G1** was generated from **1a** in TfOH at room temperature for 60 h. ^{1}H NMR (400 MHz, TfOH) δ 8.59−7.77 (m, 9H), 4.60−4.52 (m, 1H), 4.47 (dd, J = 18.4, 4.3 Hz, 1H), 4.21 (dd, J = 18.4, 9.2 Hz, 1H), 4.09 (dd, J = 22.4, 5.4 Hz, 1H), 3.55 (d, J = 22.4 Hz, 1H). ^{13}C NMR (101 MHz, TfOH) δ 222.0, 219.1, 167.0, 148.1, 147.4, 136.0, 133.0, 132.4, 131.3, 129.7, 129.4, 128.2, 43.5, 42.0, 38.8. ^{19}F NMR (376 MHz, TfOH) δ −73.65 (s).

Cation **K1** was generated from (2*E*,4*Z*)-**4a** in TfOH at room temperature for 5 min. ^{1}H NMR (400 MHz, TfOH) δ 8.64 (dd, J = 14.6, 11.5 Hz, 1H), 8.59 (d, J = 8.2 Hz, 2H), 8.42−8.27 (m, 3H), 8.33 (d, J = 8.5 Hz, 2H), 8.20 (t, J = 7.4 Hz, 1H), 8.10 (s, 1H), 8.09 (s, 1H), 8.02−7.82 (m, 6H), 7.67 (d, J = 14.6 Hz, 1H), 7.47 (d, J = 11.5 Hz, 1H), 4.78−4.57 (m, 3H), 4.32 (dd, J = 19.2, 8.9 Hz, 1H), 4.25 (d, J = 24.2 Hz, 1H), 2.96 (s, 3H), 2.82 (s, 3H). ^{13}C NMR (101 MHz, TfOH) δ 221.8 (C), 219.3 (C), 200.4 (C), 175.8 (C), 175.0 (C), 158.0 (C), 155.9 (CH), 149.0 (C), 147.2 (CH), 143.7 (CH), 142.7 (C), 139.5 (CH), 136.8 (CH), 136.5 (CH), 136.0 (CH), 135.7 (CH), 134.7 (CH), 134.4 (CH), 132.3 (CH), 132.0 (C), 131.8 (CH), 130.6 (C), 130.2 (CH), 129.6 (C), 125.6 (CH), 121.4 (CH), 52.8 (CH_2), 43.0 (CH), 41.6 (CH_2), 25.4 (CH_3), 22.3 (CH_3). ^{19}F NMR (376 MHz, TfOH) δ −73.38 (s).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02785.

Crystallographic data (CIF)
Crystallographic data (CIF)
Crystallographic data (CIF)
Crystallographic data (CIF)
^{1}H, ^{13}C, and ^{19}F spectra of compounds and cations, X-ray data, computational details (PDF)

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Notes

The authors declare no competing financial interest.

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