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Reactions of alkyl 4-hydroxybut-2-ynoates with arenes under superelectrophilic activation with triflic acid or HUSY zeolite: alternative propargylation or allenylation of arenes, and synthesis of furan-2-ones

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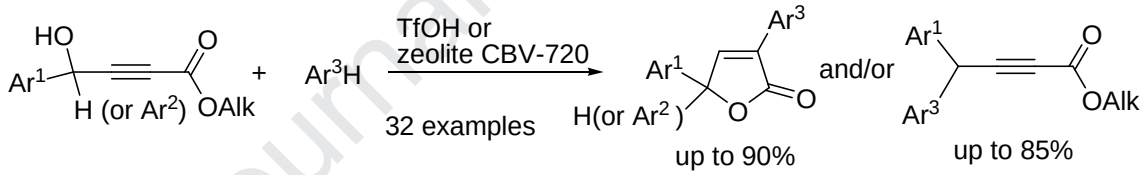
Tel.: 07 812 670 93 52; fax: 07 812 670 93 90

Keywords:
4-hydroxybut-2-ynoates; furan-2-one; propargylation; triflic acid; zeolites

Graphical Abstract



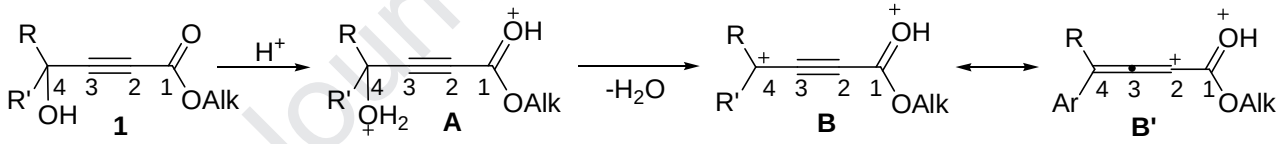
Abstract

Reactions of alkyl 4-aryl(or 4,4-diaryl)-4-hydroxybut-2-ynoates [Ar(H or Ar')(OH)C^4–C^3≡C^2–CO_2Alk] with arenes under the action of triflic acid TfOH or HUSY zeolite result in the formation of two main compounds, aryl substituted furan-2-ones or products of propargylation of electron rich arenes. Key reactive intermediates in these transformations are the corresponding O,O-diprotonated forms of starting butynoates, Ar(H or Ar')($^+OH_2$)C^4–C^3≡C^2– C(=O^+H)(OAlk), dehydration of which gives rise to mesomeric propargyl-allenyl cations Ar(H or Ar')(OH)$^4C^+$–C^3≡C^2–C(=O^+H)(OAlk) ↔ Ar(H or Ar')(OH)^{4}C=C^3=$^2C^+$–C(=O^+H)(OAlk), having two electrophilic centers on the carbons C4 and C2 respectively. Reactions of these species with arenes at C4 lead to products of arene propargylation, alternatively, reactions at C2 result in allenylation of arenes, followed by further transformation into furan-2-ones. Using quantum chemical calculations by the DFT method, it has been shown that the reactivity of such propargyl-allenyl cations is mainly explained by orbital factors. Plausible reaction mechanism is discussed.

Introduction

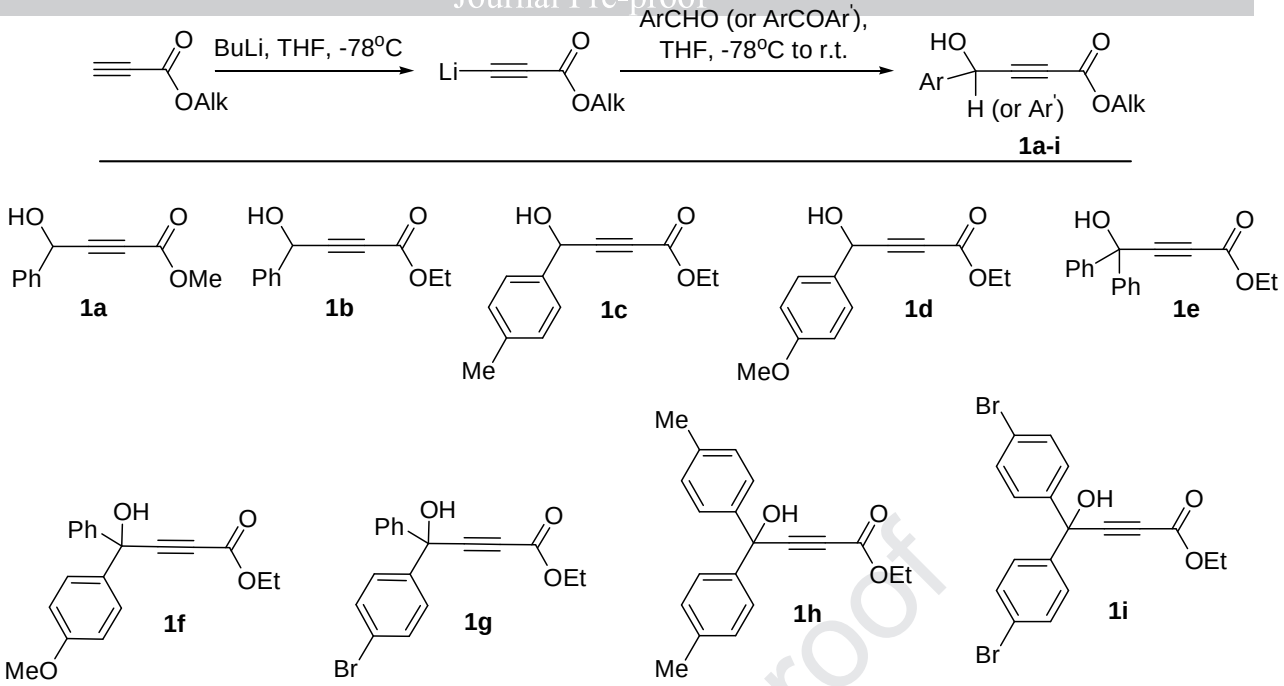
Esters of 4-hydroxybut-2-ynoic acid (alkyl 4-hydroxybut-2-ynoates) are promising building blocks in organic synthesis. The presence of three important functional groups, such as, acetylene bond conjugated with ester substituent and hydroxyl group of the propargyl type, in the structure of these compounds allows involving them in many useful synthetic transformations. They take part in cycloaddition[1,2] and addition of nucleophiles to the acetylene bond,[3-5] Meyer-Schuster rearrangement of propargyl fragment,[6-8] Ritter reaction onto the hydroxyl carbon,[9] cyclization into furans,[10,11] and metal catalyzed transformation into furan-2-ones.[12-14]

Based on our works on superelectrophilic activation of acetylene compounds,[15] we undertook a special study on transformations of alkyl 4-hydroxybut-2-ynoates under the action of various acids. Protonation of these substrates in Brønsted superacids may proceed with a formation of O,O-diprotonated species **A**, at the beginning.[16,17] Then dehydration of cations **A** may give rise to mesomeric propargyl-allenyl cations **B**↔**B'**, which have two electrophilic centers on the carbons C2 and C4 and, consequently, may possess a dual reactivity. These species **A** and **B** may take part in interaction with nucleophiles, such as aromatic molecules.



Scheme 1. Protonation of alkyl 4-hydroxybut-2-ynoates in Brønsted acid leading to cations **A** and **B**.

The main goal of this work was a study of reactions of alkyl 4-hydroxybut-2-ynoates **1** with arenes under the electrophilic activation conditions with Brønsted and Lewis strong acids, or acidic zeolites. The synthesis of starting butynoates **1a-I**, bearing one or two aryl rings with various substituents, is shown in Scheme 2.



Scheme 2. Synthesis of alkyl 4-hydroxybut-2-ynoates **1a-l** used in this study.

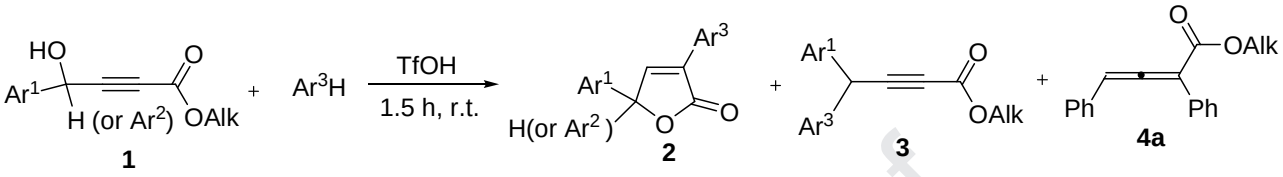
Results and discussion

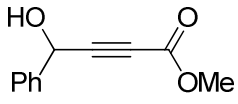
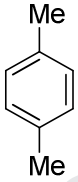
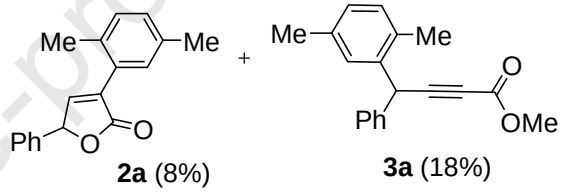
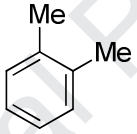
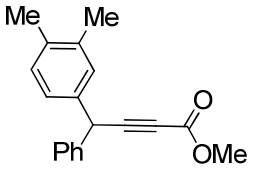
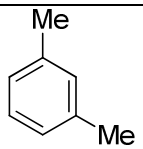
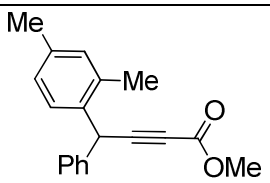
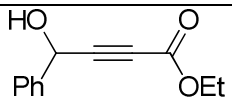
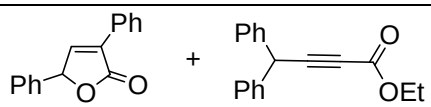
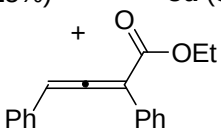
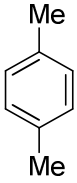
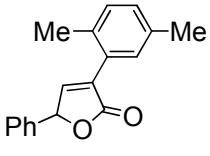
Reactions of alkyl butynoates **1** with arenes in TfOH at room temperature for 1.5 h are shown in Table 1. The main reaction products are furan-2-ones **2** obtained in yields up to 90%. Benzene, and its methylated and halogenated derivatives have been successfully involved in this reaction. However, reactions of butynoates **1** with such donating arenes, as anisole (methoxybenzene) and veratrole (1,2-dimethoxybenzene), in TfOH led to complex mixtures of reaction products. Apart from that, monoaryl substituted butynoates **1c,d** bearing donating aryl ring gave oligomeric compounds in reactions with benzene and other arenes. Contrary to that, diaryl substituted butynoates **1e-i** formed the corresponding furanones **2d-p** (entries 8-20, Table 1) in good yields, mainly. Most probably, furanones **2** having one or two donating aryl rings in the position 5 are unstable in TfOH and undergo oligomerization under superacidic conditions. Indication of that is the low yields of compounds **2k,l** obtained from 5,5-bis-(4-methylphenyl) butynoate **1h** (entries 15, 16). Structures of some furanones, **2d-f,m,o,p** were confirmed by X-ray analysis (see Table 1).

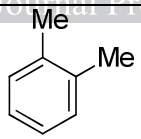
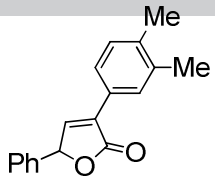
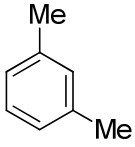
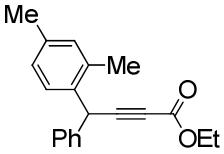
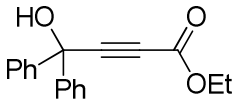
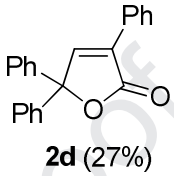
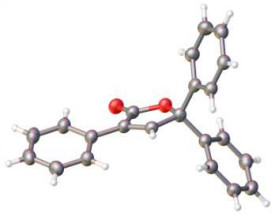
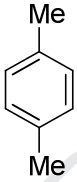
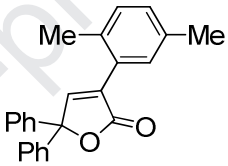
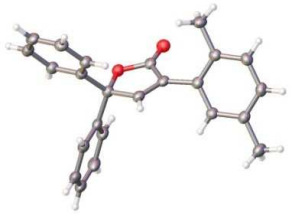
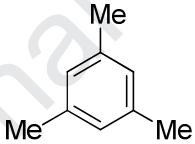
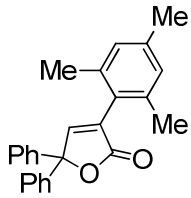
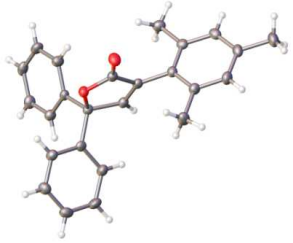
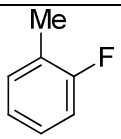
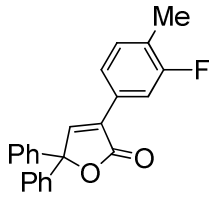
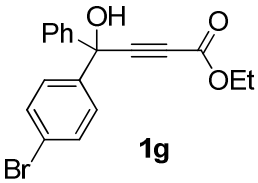
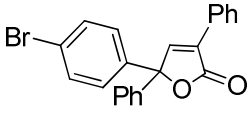
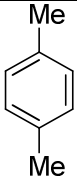
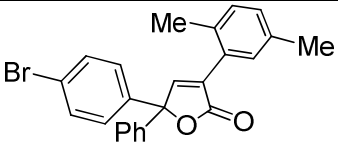
Apart from furanones **2**, other compounds were obtained in this reaction. Thus, monoarylated butynoates **1a,b** gave rise to products of propargylation of arenes **3a-e** (entries 1-4, 7) and allene **4a** (entry 4). The formation of compounds **3** and **4** may be explained by a generation and reactivity of various cationic species derived from starting butynoates **1** under acidic conditions (see Scheme 1, and discussion on reaction mechanism below).

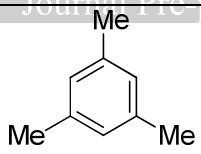
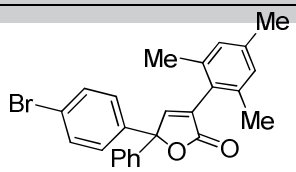
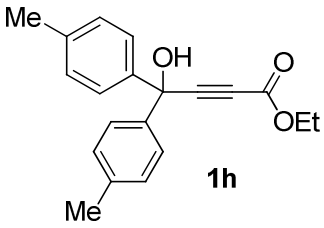
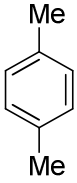
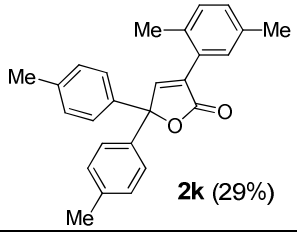
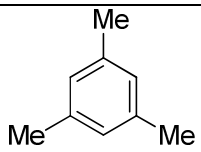
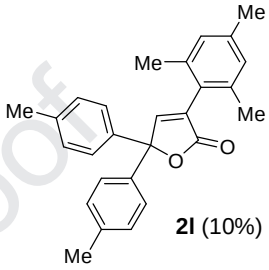
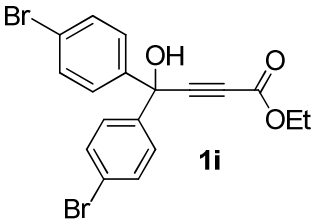
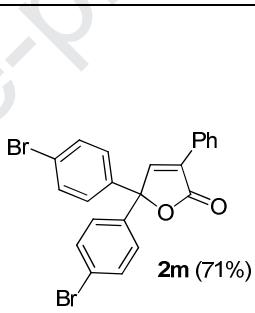
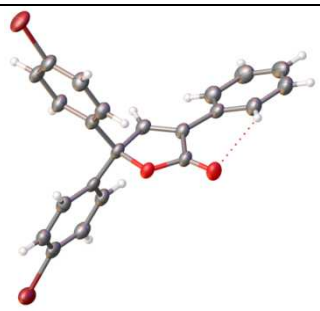
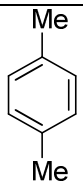
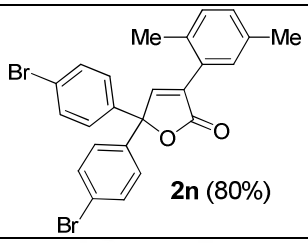
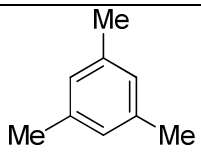
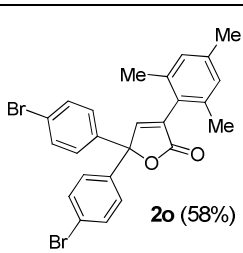
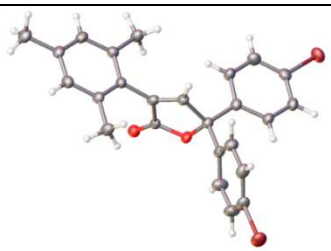
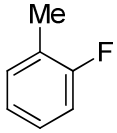
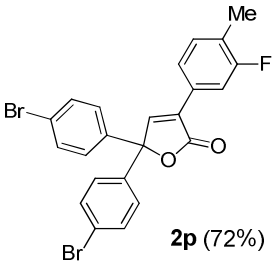
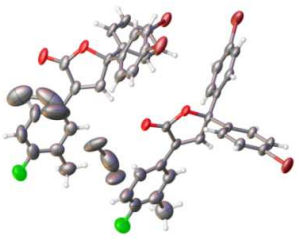
It should be mentioned that other acids were not efficient in this reaction. Thus, interaction of butynoates **1** with benzene under the action of H_2SO_4 or AlX_3 (X = Cl, Br) resulted in the formation of complex mixtures of oligomeric compounds.

Table 1. Reactions of alkyl 4-hydroxybut-2-ynoates **1** with arenes in TfOH at room temperature for 1.5 h leading to compounds **2**, **3**, and **4** (for X-ray structures of **2d-f,m,o,p** ellipsoid contour of probability levels are 50%).



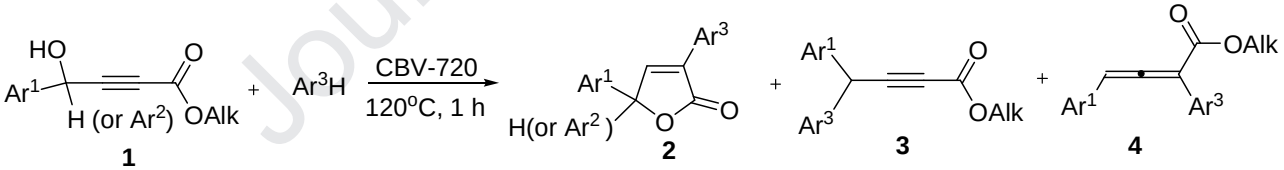
Entry	Starting compounds		Reaction products, yields (%)
	Butynoates, **1**	Arenes, Ar^3H	
1	 **1a**		 **2a** (8%) **3a** (18%)
2	**1a**		 **3b** (47%)
3	**1a**		 **3c** (54%)
4	 **1b**		 **2b** (25%) **3d** (30%)  **4a** (30%)
5	**1b**		 **2a** (90%)

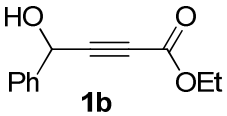
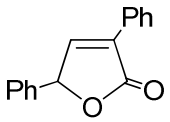
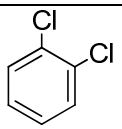
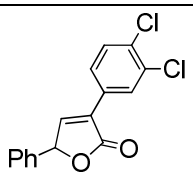
6	**1b**		 **2c** (15%)
7	**1b**		 **3e** (85%)
8	 **1e**		 **2d** (27%)  X-ray of **2d**
9	**1e**		 **2e** (73%)  X-ray of **2e**
10	**1e**		 **2f** (79%)  X-ray of **2f**
11	**1e**		 **2g** (20%)
12	 **1g**		 **2h** (58%)
13	**1g**		 **2i** (75%)

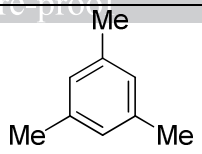
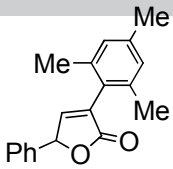
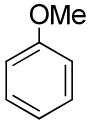
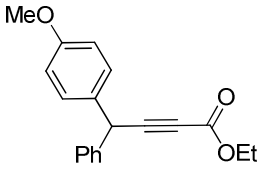
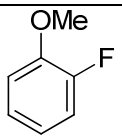
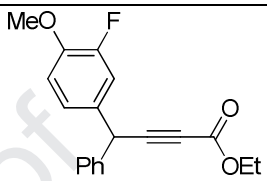
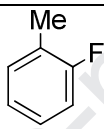
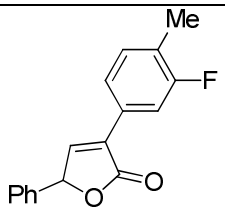
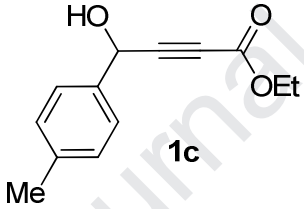
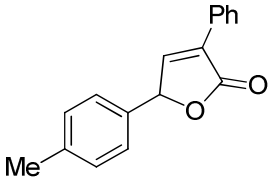
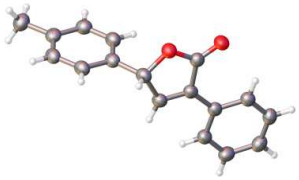
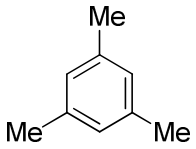
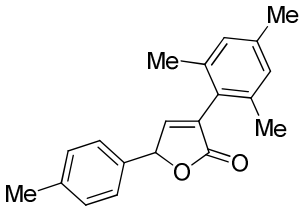
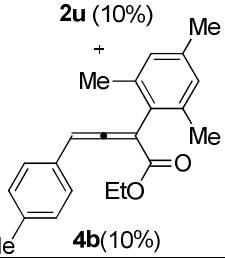
14	**1g**		 **2j** (74%)
15	 **1h**		 **2k** (29%)
16	**1h**		 **2l** (10%)
17	 **1i**		 **2m** (71%)  X-ray of **2m**
18	**1i**		 **2n** (80%)
19	**1i**		 **2o** (58%)  X-ray of **2o**
20	**1i**		 **2p** (72%)  X-ray of **2p**

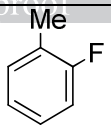
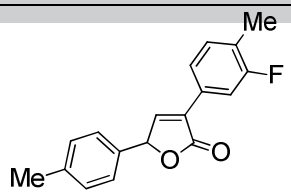
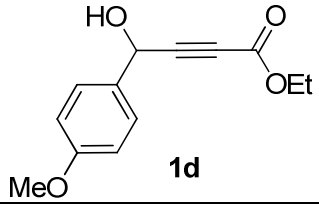
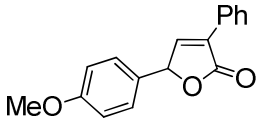
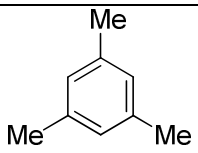
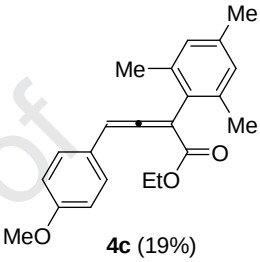
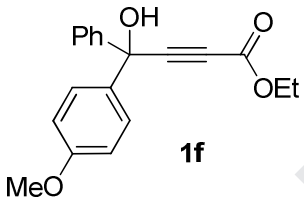
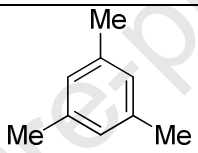
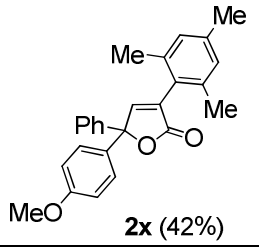
Then, reactions of butynoates **1** with arenes were studied under the action of acidic HUSY zeolite CBV-720 in glass high pressure tube at 120°C for 1 h (Table 2). Zeolites are considered as "green" reagents in organic synthesis, they act as effective acidic promoters and catalysts in many reactions.[18] Analogously to TfOH (Table 1), the main products in the zeolite-promoted reactions were furanones **2** (Table 2, see X-ray structure for **2t**). However, there are some differences in reactions under the action of these two acidic reagents, TfOH and zeolite CBV-720. Monoaryl substituted butynoates **1c,d** having donating aryl groups led to furanones **2t-w** with the zeolite (entries 7-10, Table 2), contrary to the same reactions in TfOH. Therefore, the zeolite is more tolerant to the structures of such 5-monoaryl substituted furanones **2t-w** in comparison with TfOH. On the other hand, surprisingly, reactions of diarylated butynoates **1e-i** with various arenes furnished oligomeric compounds! For these substrates, we were able to obtain only compound **2x** in the reaction of butynoates **1f** with mesitylene (entry 12). Contrary to TfOH (*vide supra*), reactions of butynoate **1b** with anisole and 2-fluoroanisole led to arene propargylation products **3f,g** (entries 4, 5). Also, in some cases, allenes **4b,c** were isolated (entries 8, 11). However, in general, the yields of target furanones **2** and esters **3** (Table 2) are less with the zeolite compared to the reactions in TfOH (Table 1).

Table 2. Reactions of alkyl 4-hydroxybut-2-ynoates **1** with arenes under the action of acidic HUSY zeolite CBV-720 at 120°C for 1 h in glass high pressure tube leading to compounds **2**, **3**, and **4** (for X-ray structure of **2t** ellipsoid contour of probability levels are 50%).

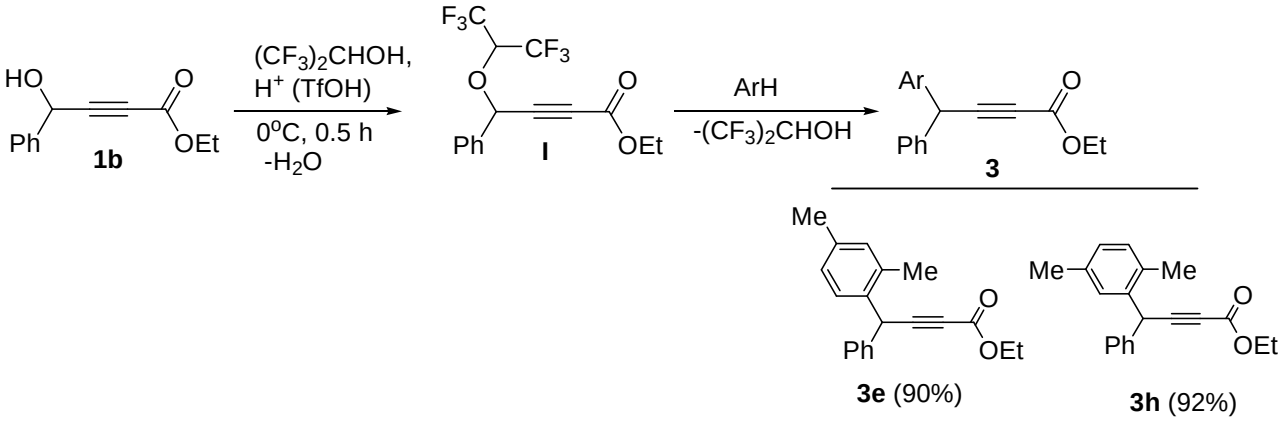


Entry	Starting compounds		Reaction products, yields (%)
	Butynoates, **1**	Arenes, Ar^3H	
1	 **1b**		 **2b** (15%)
2	**1b**		 **2q** (36%)

3	**1b**		 **2r** (10%)
4	**1b**		 **3f** (30%)
5	**1b**		 **3g** (28%)
6	**1b**		 **2s** (9%)
7	 **1c**		 **2t** (27%)  X-Ray of **2t**
8	**1c**		 **2u** (10%) +  **4b**(10%)

9	**1c**		 **2v** (52%)
10	 **1d**		 **2w** (35%)
11	**1d**		 **4c** (19%)
12	 **1f**		 **2x** (42%)

Additionally, we carried out the propargylation of *meta*- and *para*-xylenes by 4-hydroxybutynoate **1b** in hexafluoroisopropanol (HFIP) with catalytic amount of TfOH, that led to esters **3e,h** in high yields (Scheme 3). HFIP is widely used in activation of alcohols in Friedel-Crafts alkylation of electron rich arenes.[19] This reaction proceeds through an intermediate formation of HFIP-ether **I**, followed by arene propargylation. It should be mentioned that the reaction did not proceed without Brønsted acid.



Scheme 3. Propargylation of *meta*- and *para*-xylenes by 4-hydroxybutynoate **1b** in the system hexafluoroisopropanol (HFIP)-TfOH leading to compounds **3e,h**.

Summarizing all the data obtained on reactions of butynoates **1** with arenes under the electrophilic activation conditions (Tables 1, 2), one may propose the following plausible reaction mechanism in Brønsted superacid (Scheme 4). Protonation of oxygen atoms of carbonyl and hydroxyl groups in TfOH gives rise to species **A**, which may react with arenes by electrophilic center at the carbon C4 in S_{N2} way leading to propargylation products **3**. Dehydration of species **A** results in the formation of mesomeric propargyl-allenyl cations **B**↔**B'**, possessing two reactive centers, carbons C4 and C2, correspondingly. Interaction of arenes with carbon C4 of species **B** leads to compound **3**. On the other hand, reaction at C2 gives products of allenylation of arenes, O-protonated forms of allenes **C**, which form allenes **4** upon hydrolysis of reaction mixtures. Species **C** may undergo consequent protonation on the central carbon of the allene system with formation of allyl cations **D**. The latter is cyclized into species **E**, which are finally transformed into furanones **2**.

Similar reaction mechanism should be realized with acidic zeolite, which has Brønsted and Lewis acidic centers. Protonation or coordination of basic centers (oxygen atoms and unsaturated carbon-carbon bonds) of substrates **1** with the zeolite acidic centers give rise to the corresponding reactive cationic species.

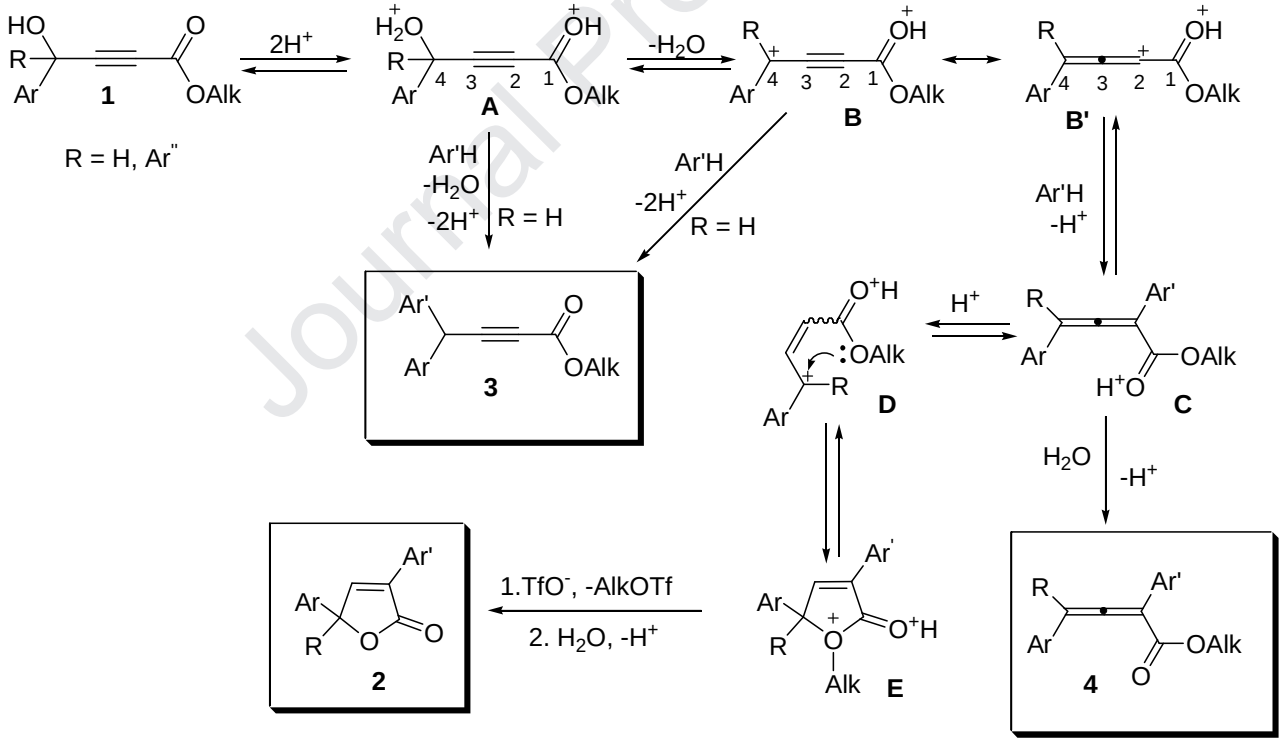
Based on the proposed mechanism (Scheme 4), some features of this reaction could be explained. Thus, diarylsubstituted butynoates **1e-i** did not give products of propargylation **3** (see Table 1). It happens, probably, due to spatial reason, since interaction of cations **A** or **B** (having aryl ring R) with arene molecule should lead to the formation of sterically hindered triarylmethyl fragment, that is unfavorable. Propargylation products are mainly formed with electron rich arenes, such as xylenes (Table 1) or anisole and 2-fluoroanisole (Table 2), that, probably, shows participation of species **A** in this reaction. Allenes **4**, laying on a way of formation of compounds **2**, were isolated as intermediate compounds, when unstable furanones **2** were oligomerized under the acidic reaction conditions.

Some other results of the studied reactions may be rationalized as well. There is a different reactivity for methyl ester **1a** and ethyl ester **1b** (compare entries 2 and 6, Table 1). Taking into account a reversibility of electrophilic process stages (Scheme 4), the formation of furanone **2c** from ethyl ester **1b** may be explained by easy transformation of the corresponding species **E** with Alk = Et into furanone **2c** (entry 6, Table 1). Since, for cationoid transition state, an elimination of ethyltriflate EtOTf from this species **E** should proceed easier, than in the case of species **E** having Alk = Me, which is formed from methyl ester **1a**. For the latter, the corresponding species **E** may undergo back conversion into cation **B**, which finally gives alkyne **3b** (entry 2, Table 1).

Apart from that, there are different results for the reactions of butynoate **1a** with two aromatic substrates *para*-xylene and benzene (entries 1 and 4, Table 1) having various nucleophilicity. In the latter case, the formation of allene **4a** was observed (entry 4, Table 1). Such allenes lie in the

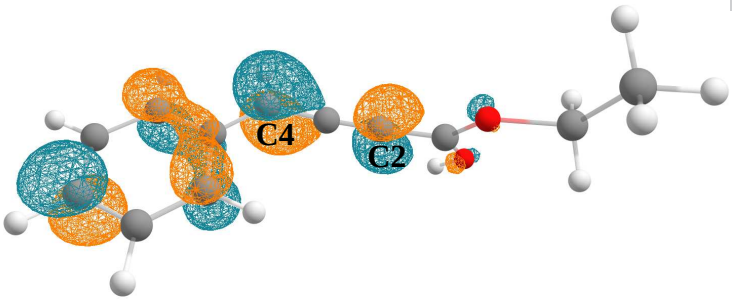
reaction pathway (see species **C** in Scheme 4). Benzene is less π-nucleophilic compared to *para*-xylene, consequently, reactions of intermediate cationic species with benzene run slower, and for the reaction time 1.5 h, one could detect the formation of allene **4a** (entry 4, Table 1). More active *para*-xylene reacts faster with cationic species finally giving furanone **2a** and alkyne **3a** (entry 1, Table 1).

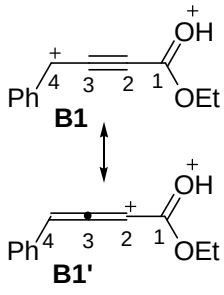
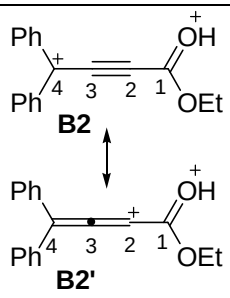
To estimate electronic and electrophilic properties of intermediate species of this reaction we carried out quantum chemical calculations (DFT method) for cations **B1**↔**B1'** and **B2**↔**B2'** derived from butynones **1b** and **1e**, correspondingly (Table 3). Charge distribution, contribution of atomic orbital into LUMO and global electrophilicity indices ω[20,21] were calculated. Cations **B1** and **B2** are rather strong electrophiles, since they have high values of electrophilicity indices ω 30.28 и 29.49 eV, respectively. It is noteworthy that carbons C2 and C4 do not bear a big positive charge. The positive charge is mainly localized on the carbonyl carbon C1 and in phenyl rings. However, atoms C2 and C4 give a substantial atomic orbital contributions into LUMO (see also view of LUMO for **B1** in Table 3). Thus, the electrophilic reactivity of atoms C2 and C4 is mainly ruled by orbital factors, rather than charge ones.



Scheme 4. Plausible Brønsted superacid-promoted mechanism of reaction of butynoates **1** with arenes leading to compounds **2**, **3, 4**.

Table 3. Selected electronic characteristics (DFT calculations) of cations **B1**↔**B1'** and **B2**↔**B2'**, derived from butynones **1b** and **1e**, correspondingly. View of LUMO of species **B1**↔**B1'** showing large contributions of atomic orbitals on the carbon C2 and C4 into LUMO.



Cation	E_{HOMO}, eV	E_{LUMO}, eV	ω,[a] eV	$q(C^1)$,[b] e	$q(C^2)$,[b] e	$q(C^4)$,[b] e	$k(C^2)_{LUMO}$,[c] %	$k(C^4)_{LUMO}$,[c] %
 **B1** ↔ **B1'**	-15.11	-12.06	30.28	0.82	-0.013	-0.013	16.0	31.2
 **B2** ↔ **B2'**	-13.67	-11.08	29.49	0.83	-0.06	0.08	10.3	19.5

[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.

Thus, one of the main results of the present work is a novel metal free synthesis of aryl substituted furan-2-ones. It should be specially emphasized that preparation of furan-2-ones is an actual goal of organic chemistry, since these compounds possess a broad range of biological activities.[22] The main methods of synthesis of these furan derivatives are mainly based on metal-catalyzed transformations of alkynes[12-14,23-29] and metal- or acid-promoted reactions of alkenes.[30-43]

Conclusion

We have developed a novel synthesis of aryl substituted furan-2-ones based on reactions of alkyl 4-aryl(or 4,4-diaryl)-4-hydroxybut-2-ynoates with arenes under the action of triflic acid TfOH or acidic zeolite CBV-720. It has been found that in order to obtain the corresponding furan-2-ones from alkyl 4,4-diaryl-substituted 4-hydroxybut-2-ynoates better to use TfOH. On the other hand, for the synthesis of furan-2-ones from alkyl 4-aryl-substituted 4-hydroxybut-2-ynoates one should take

the zeolite. Apart from furan-2-ones, these reactions give alternative products of propargylation of donating arenes.

Experimental part

The NMR spectra of solutions of compounds in $CDCl_3$ were recorded on Bruker AVANCE III 400 (at 400, 376 and 100 MHz for ^1H, ^{19}F and ^{13}C NMR spectra respectively) spectrometer at 25°C. The residual proton-solvent peak $CDCl_3$ (δ 7.26 ppm) for ^1H NMR spectra and the carbon signal of $CDCl_3$ (δ 77.0 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). HRMS (ESI-TOF) was carried out at instruments Bruker maXis-ESI-QTOF Mass Spectrometer. IR spectra of compounds were taken with Bruker spectrometer. The preparative reactions were monitored by thin-layer chromatography carried out on silica gel plates (Alugram SIL G/UV-254), using UV light for detection. Preparative TLC was performed on silica gel Chemapol L 5/40 with petroleum ether-ethyl acetate mixture eluation. HUSY zeolite CBV-720 was purchased from the company Zeolist Int.

X-ray diffraction study. A suitable crystal was selected and studied on the diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2[44] the structure was solved with the ShelXS[45] structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. CCDC 1919234 – (**2d),** CCDC 1919237 – (**2e**), CCDC 1919238 – (**2f**), CCDC 1919240 – (**2m**), CCDC 1919241 – (**2o**), CCDC 1919242 – (**2p**), CCDC 1919243 – (**2t**) 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: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

DFT calculations. All computations were carried out at the DFT level of theory using functional B3LYP by using GAUSSIAN 2009 program packages.[46] The geometries optimization were performed using the B3LYP basis set (standard 6-311 basis set added with polarization (d, p) and diffuse functions). Optimizations were performed on all degrees of freedom and gas-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. Atomic charges and contributions in LUMO for species **B1, B2** were obtained using NBO analysis.

Starting alkyl 4-hydroxybutynoates **1a-i** were obtained according the literature procedure.[42]

General procedure for the synthesis of starting butynoates 1a-i. Solution of BuLi in hexanes (6.4 mmol, 4 mL, 1.6 M concentration) was added dropwise for 5 min to a solution of ethyl (or methyl) propynoate (3.3 mmol) in THF (10 mL) at –78°C with vigorous magnetic stirring.

After 10 min the corresponding aromatic aldehyde or benzophenon (3.2 mmol) was added at –78°C. Reaction mixture was slowly heated to room temperature for 2 h. Then mixture was treated with saturated aqueous solution of NH_4Cl (4 mL), extracted with EtOAc (3 × 10 mL). The combined extracts were dried with Na_2SO_4. After evaporation of the solvent under the reduced pressure, reaction product was isolated by preparative TLC using petroleum ether – ethyl acetate mixture (4 : 1 vol.) as an eluent.

*Methyl 4-hydroxy-4-phenylbut-2-ynoate (**1a**)*.[47] Yield of 75%. Yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 3.50 t (1H), 3.76 s (3H), 5.52 s (1H), 7.32 – 7.40 m (3H), 7.47 – 7.50 m (2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 52.9, 64.1, 87.0, 126.7, 128.8, 128.8, 128.9, 138.6, 153.9. IR (KBr), cm^{-1}: 1717 (C=O), 2239 (C≡C), 3429 (O-H). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{11}H_{10}NaO_3$ 213.0522, found 213.0522.

*Ethyl 4-hydroxy-4-phenylbut-2-ynoate (**1b**)*.[47] Yield of 75%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.30 t (3H, *J* 7 Hz), 2.88 s (1H, OH), 4.24 q (2H, *J* 7 Hz), 5.56 s (1H), 7.35 – 7.41 m (3H), 7.50 – 7.52 m (2H).

*Ethyl 4-hydroxy-(4-methylphenyl)but-2-ynoate (**1c**)*.[47] Yield of 95%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.31 t (3H, *J* 7.1 Hz), 2.36 s (3H), 4.24 q (2H, *J* 7.1 Hz), 5.53 s (1H), 7.1 d (2H, *J* 8.0 Hz), 7.4 d (2H, *J* 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 13.9, 21.1, 62.2, 64.1, 77.8, 86.2, 126.6, 129.5, 135.7, 138.8, 153.3. IR (KBr), cm^{-1}: 1712 (C=O), 2235 (C≡C), 3397 (O-H). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{13}H_{14}NaO_3$ 241.0835, found 241.0836.

*Ethyl 4-hydroxy-4-(4-methoxyphenyl)but-2-ynoate (**1d**)*.[47] Yield of 48%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 1.31 t (3H, *J* 7.14 Hz), 4.18 s (1H), 4.81 s (3H), 4.24 q (2H, *J* 7.13 Hz), 5.51 s (1H), 6.91 d (2H, *J* 8.8 Hz), 7.44 d (2H, *J* 8.8 Hz).

*Ethyl 4-hydroxy-4,4-diphenylbut-2-ynoate (**1e**).* Yield of 60%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 1.32 t (3H, *J* 7.1 Hz), 2.88 s (1H, OH), 4.25 q (2H, *J* 7.1 Hz), 7.28 – 7.37 m (6H), 7.57 – 7.59 m (4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 14.0, 62.3, 74.4, 78.6, 88.6, 126.1, 128.2, 128.5, 143.2, 153.5. IR (KBr), cm^{-1}: 1698 (C=O), 2238 (C≡C), 3441 (O-H). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{18}H_{16}NaO_3$ 303.0992, found 303.0992.

*Ethyl 4-hydroxy-4-(4-methoxyphenyl)-4-phenylbut-2-ynoate (**1f**).* Yield of 70%. Yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 1.33 t (3H, *J* 7.1 Hz), 3.26 s (1H, OH), 3.80 s (3H), 4.27 q (2H, *J* 7.1 Hz), 6.86-6.90 m (2H), 7.32-7.39 m (3H), 7.48-7.50 m (2H), 7.58-7.60 m (2H).IR (KBr), cm^{-1}: 1711 (C=O), 2233 (C≡C), 3434 (O-H). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{19}H_{18}NaO_4$ 333.1097, found 333.1092.

*Ethyl 4-(4-bromophenyl)-4-hydroxy-4-phenylbut-2-ynoate (**1g**).* Yield of 30%. Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 1.31 t (3H, *J* 7.1 Hz), 3.31 s (1H, OH), 4.25 q (2H, *J* 7.1 Hz), 7.31 – 7.35 m (3H), 7.42 – 7.48 m (4H), 7.53 – 7.55 m (2H). ^{13}CNMR (100 MHz, $CDCl_3$) δ, ppm:

14.0, 62.4, 74.0, 78.9, 87.8, 122.4, 126.0, 127.9, 128.5, 128.6, 131.6, 142.3, 142.7, 153.3. IR (KBr), cm^{-1}: 1712 (C=O), 2235 (C≡C), 3434 (O-H). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{18}H_{15}BrNaO_3$ 381.0097, found 381.0097.

*Ethyl 4-hydroxy-4,4-di(4-methylphenyl)but-2-ynoate (**1h**).* Yield of 40%. Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 0.93 t (3H, *J* 7.1 Hz), 2.34 s (6H), 3.11 m (1H, OH), 4.25 q (2H, *J* 7.1 Hz), 7.15 d (4H, *J* 8.2 Hz), 7.45 d (4H, *J* 8.2 Hz).^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm:14.1, 21.1, 62.2, 74.1, 78.4, 90.1, 126.0, 129.1, 138.0, 140.6, 153.6. IR (KBr), cm^{-1}: 1713 (C=O), 2234 (C≡C), 3430 (O-H). HRMS (ESI) m/z: $[M+Na]^+$calcd. for$C_{20}H_{20}NaO_3$331.1305, found 331.1305.

*Ethyl 4,4-di(4-bromophenyl)-4-hydroxybut-2-ynoate (**1i**).* Yield of 45%. Orange oil.^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm:1.31 t (3H, *J* 7 Hz), 3.54 s (1H, OH), 4.24 q (2H, *J* 7 Hz), 7.38 – 7.41 m (4H), 7.45 – 7.47 m (4H). ^{13}CNMR (100 MHz, $CDCl_3$) δ, ppm: 14.0, 62.6, 73.5, 79.0, 87.2, 122.7, 127.7, 131.7, 141.9, 153.2. IR (KBr), cm^{-1}: 1713 (C=O), 2236 (C≡C). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{18}H_{14}Br_2NaO_3$ 458.9202, found 458.9202.

General procedure for reaction of butynoates 1 with arenes in TfOH. Synthesis of compounds 2, 3, 4 (Table 1). TfOH (0.1 mL) was added to a solution of butynoate **1** (0.16 mmol) in arene (1mL) at room temperature with vigorous magnetic stirring. Reaction mixture was stirred at room temperature for 1.5 h. Then the reaction mixture was poured into water (10 mL), extracted with CH_2Cl_2 (3 × 10 mL). Combined extracts were washed with saturated aqueous solution of $NaHCO_3$ (2 ×10 mL), water (10 mL), dried with Na_2SO_4. Organic solvents were distilled off under the reduced pressure, reaction products were isolated by preparative TLC using petroleum ether – ethyl acetate mixture (9 : 1 vol.) as an eluent. Yields of compounds **2**, **3** and **4** are presented in Table 1.

General procedure for reaction of butynoates 1 with arenes under the action of acidic zeolite HUSY (CBV-720). Synthesis of compounds 2, 3, 4 (Table 2).

A mixture of butynoate **1** (0.15 mmol), 5 mL of arene and 250 mg of HUSY zeolite CBV-720 (commercially available material), which was pre-calcinated at 400-450°C for 2 h, was heated in the high pressure glass tube at 120°C for 1 h with vigorous magnetic stirring. Then, the reaction mixture was cooled down to room temperature. The zeolite was filtered off on a glass filter and washed several times with CH_2Cl_2 (3 × 10 mL). Organic solutions were combined and were distilled off under the reduced pressure. Reaction products were isolated by preparative TLC using petroleum ether – ethyl acetate mixture (9 : 1 vol.) as an eluent. Yields of compounds **2**, **3** and **4** are presented in Table 2.

Procedure for reaction of butynoate 1b with xylenes in hexafluoroisopropanol (HFIP) with a catalytic amount of TfOH. Synthesis of compounds 3e,h (Scheme 3). Butynoate **1b** (0.15 mmol) was added to mixture of arene (0.05 mL) with HFIP (0.1 mL) and TfOH (catalytic amount)

at 0°C. The mixture was magnetically stirred 0.5 h at this temperature. Then the reaction mixture was poured into water (10 mL), extracted with $CHCl_3$ (3 × 10 mL). The combined extracts were washed with saturated aqueous solution of $NaHCO_3$ (2 ×10 mL), water (10 mL), dried with Na_2SO_4. Evaporation of organic solvent under the reduced pressure gave pure reaction products **3e** (yield of 90%) or **3h** (yield of 92%).

*3-(2,5-Dimethylphenyl)-5-phenylfuran-2(5H)-one (**2a**).* Yellow oil. ^{1}H NMR(400 MHz, $CDCl_3$)δ, ppm: 2.33 s (3H), 2.34 s (3H), 6.07 d (1H, *J* 1.7 Hz), 7.12 d (1H, *J* 7.6 Hz), 7.16 d (1H, *J* 7.9 Hz), 7.23 s (1H), 7.36dd (2H, *J* 1.7 Hz *J* 7.6 Hz), 7.40 d (1H, *J* 1.7 Hz), 7.41 – 7.46 m (3H).^{13}CNMR(100 MHz, $CDCl_3$) δ, ppm: 20.0, 20.9, 29.7, 82.1, 126.6, 129.0, 129.1, 129.3, 130.0, 130.1, 130.6, 133.0, 133.5, 135.0, 135.5, 150.6. IR (KBr), cm^{-1}: 1766 (C=O). HRMS (ESI) m/z: $[M+Na]^+$calcd. for $C_{18}H_{16}NaO_2$ 287.1043, found 287.1043.

*3,5-Diphenylfuran-2(5H)-one (**2b**).* Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 6.06 d (1H, *J* 1.8 Hz), 7.33-7.35 m (2H), 7.40-7.44 m (6H), 7.63 d (1H, *J* 1.8 Hz), 7.89-7.91 m (2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 29.7, 81.6, 126.6, 127.2, 128.7, 129.1, 129.3, 129.3, 129.5, 134.8, 147.3, 171.7. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{16}H_{12}NaO_2$ 259.0730, found 259.0733.

*3-(3,4-Dimethylphenyl)-5-phenylfuran-2(5H)-one (**2c**).* Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.29 s (3H), 2.30 s (3H), 5.75 d (1H, *J* 1.6 Hz), 6.81 – 7.22 m (9H), 7.59 d (1H,*J* 1.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 21.0, 21.9, 83.2, 127.7, 128.3, 128.8, 129.4, 130.2, 130.4, 131.0, 131.2, 131.6, 134.1, 134.5, 136.5, 150.5, 170. HRMS (ESI) m/z: $[M+Na]^+$calcd. for $C_{18}H_{16}NaO_2$ 287.1043, found 287.1045.

*3,5,5-Triphenylfuran-2(5H)-one (**2d**).* Colorless solid, mp147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 7.34 – 7.43 m (13H), 7.90 – 7.92 m (2H), 8.03 s (1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 89.1, 126.7, 127.3, 128.6, 128.7, 128.8, 129.3, 129.6, 129.8, 139.8, 150.3, 170.8. IR (KBr), cm^{-1}: 1755 (C=O). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{22}H_{16}NaO_2$ 335.1043, found 335.1043.

*3-(2,5-Dimethylphenyl)-5,5-diphenylfuran-2(5H)-one (**2e**).* Colorless solid, mp140°C.^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.31 s (3H), 2.33 s (3H), 7.11dd (1H, *J* 1.4 Hz, *J* 7.9 Hz), 7.15 d (1H, *J* 7.9 Hz), 7.23 s (1H), 7.34 – 7.43 m (10H), 7.82 s (1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 20.0, 20.8, 89.8, 126.7, 128.6, 128.8, 128.9, 130.0, 130.2, 130.6, 131.7, 133.5, 135.5, 139.9, 153.9, 171.3. IR (KBr), cm^{-1}: 1762 (C=O). HRMS (ESI) m/z: $[M+Na]^+$calcd. for $C_{24}H_{20}NaO_2$ 363.1356, found 363.1356.

*3-(1,3,5-Trimethylphenyl)-5,5-diphenylfuran-2(5H)-one (**2f**).* Colorless solid, mp130°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.14 s (6H), 2.29 s (3H), 6.91 s (2H), 7.38 – 7.41 m (10H), 7.73 s (1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 20.3, 21.1, 90.4, 126.0, 126.7, 128.5, 128.6, 128.8, 131.7, 136.7, 138.6, 140.0, 155.2, 171.4. IR (KBr), cm^{-1}: 1762 (C=O). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{25}H_{22}NaO_2$ 377.1512, found 377.1512.

*3-(3-Fluoro-4-methylphenyl)-5,5-diphenylfuran-2(5H)-one (**2g**).* Colorless solid, mp108°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.31 d (3H, *J* 2.0 Hz), 7.04 t (1H, *J* 8.9 Hz), 7.34 – 7.39 m (10H), 7.71 – 7.77 m (2H), 7.97 s (1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 14.5 d (*J* 3.5 Hz), 89.1, 115.4 d (*J* 3.7 Hz), 125.1 d (*J* 3.7 Hz), 125.4 d (*J* 4.9 Hz), 126.6 d (*J* 4.9 Hz), 126.7, 128.6, 128.8, 128.9, 130.6 d (*J* 5.4 Hz), 139.8, 149.7, 162.1 d (*J* 284.9 Hz), 170.8. ^{19}F NMR (376 MHz, $CDCl_3$)δ, ppm: -115.08. IR (KBr), cm^{-1}: 1757 (C=O). HRMS (ESI) m/z: $[M+Na]^+$calcd. for$C_{23}H_{17}FNaO_2$ 367.1105, found 367.1105.

*5-(4-Bromophenyl)-3,5-diphenylfuran-2(5H)-one (**2h**).* Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 7.25 – 7.27 m (2H), 7.35 – 7.38 m (5H), 7.41 – 7.43 m (2H), 7.49 – 7.52 m (3H), 7.89 – 7.91 m (2H), 7.98 c (1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 88.6, 122.9, 126.6, 127.3, 128.4, 128.8, 128.8, 128.9, 129.7, 130.1, 130.1, 130.2, 131.9, 138.9, 139.3, 149.6. IR (KBr), cm^{-1}: 1762 (C=O). HRMS (ESI) m/z: $[M+Na]^+$ calcd. For $C_{22}H_{15}BrNaO_2$ 413.0148, found 413.0148.

*5-(4-Bromophenyl)-3-(2,5-dimethylphenyl)-5-phenylfuran-2(5H)-one (**2i**).* Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.29 c (3H), 2.33 c (3H), 7.10 – 7.16 m (2H), 7.20 c (1H), 7.27 – 7.30 m (2H), 7.40 – 7.41 m (5H), 7.51 – 7.54 m (2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 20.0, 20.8, 89.2, 122.9, 126.6, 128.3, 128.7, 128.8, 128.9, 130.1, 130.1, 130.6, 132.0, 132.0, 133.5, 135.5, 139.1, 139.4, 135.2, 171.0. IR (KBr), cm^{-1}: 1765 (C=O). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{24}H_{19}BrNaO_2$ 419.0641, found 419.0641.

*5-(4-Bromophenyl)-3-(1,3,5-trimethylphenyl)-5-phenylfuran-2(5H)-one (**2j**).* Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.11 c (3H), 2.13 c (3H), 2.29 c (3H), 6.91 c (2H), 7.27 – 7.29 m (2H), 7.35 – 7.42 m (5H), 7.51 – 7.55 m (2H), 7.68 c (1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 20.3, 21.1, 89.8, 122.9, 125.8, 126.6, 128.3, 128.5, 128.9, 128.9, 132.0, 136.6, 136.7, 138.7, 139.2, 139.5, 154.6, 171.1. IR (KBr), cm^{-1}: 1764 (C=O). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{25}H_{21}BrNaO$ 2433.0798, found 433.0798.

*5-Bis(4-methylphenyl)-3-(2,5-dimethylphenyl)-5-phenylfuran-2(5H)-one **(2k)**.* Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.29 c (3H), 2.32 c (3H), 3.36 c (3H), 7.09 d (1H, *J* 7.7 Hz), 7.14 d (1H, *J* 7.8 Hz), 7.18 d (5H, *J* 8.3 Hz), 7.27 d (4H + $CDCl_3$, *J* 8.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 20.0, 20.8, 21.1, 89.7, 126.6, 129.1, 129.4, 129.8, 130.2, 130.5, 131.4, 133.5, 135.4, 137.1, 38.4, 154.2, 171.5. IR (KBr), cm^{-1}: 1761 (C=O). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{26}H_{24}NaO$ 2369.1849, found369.1849.

*5-Bis(4-methylphenyl)-3-(1,3,5-trimethylphenyl)-5-phenylfuran-2(5H)-one **(2l)**.* Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.14 s (3H), 2.28 c (2H), 2.37 c (3H), 2.45 c (6H), 6.90 c (1H), 7.19 d (2H, *J* 8.0 Hz), 7.28 d (4H, *J* 8.0 Hz), 7.71 d (4H, *J* 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 20.3, 21.1, 21.6, 126.6, 128.4, 128.9, 129.4, 130.2, 135.3, 136.8, 137.2, 138.4, 142.9, 155.5,

196.3. IR (KBr), cm^{-1}: 1763 (C=O), 2922 (C=C). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{27}H_{26}NaO$ 2405.1825, found 405.1825.

*5-Bis(4-bromophenyl)-3-phenylfuran-2(5H)-one (**2m**).* Orange solid, mp130°C. ^1H NMR (400 MHz, $CDCl_3$) δ, ppm: 7.24 d (4H, *J* 8.6 Hz), 7.42 – 7.45 m (3H), 7.51 d (4H, *J* = 8.60 Hz), 7.88 – 7.90 m (2H), 7.93 c (1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 88.1, 123.2, 127.3, 128.3, 128.8, 129.9, 130.4, 132.1, 138.4, 148.9, 170.2. IR (KBr), cm^{-1}: 1762 (C=O). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{22}H_{14}Br_2NaO_2$ 490.9253, found 490.9253.

*5-Bis(4-bromophenyl)-3-(2,5-dimethylphenyl)furan-2(5H)-one (**2n**).* Orange oil. ^1H NMR(400 MHz, $CDCl_3$)δ, ppm: 2.28 c (3H), 2.33 c (3H), 7.11 – 7.16 m (2H), 7.19 c (1H), 7.25 d (4H, *J* 8.6 Hz), 7.53 d (4H, *J* 8.6 Hz), 7.72 c (1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 20.0, 20.8, 88.6, 123.2, 128.3, 128.4, 130.1, 130.2, 130.7, 132.1, 132.3, 133.4, 135.6, 138.5, 152.6, 170.7. IR (KBr), cm^{-1}: 1763 (C=O). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{24}H_{18}Br_2NaO_2$ 518.9566, found 518.9566.

*5-Bis(4-bromophenyl)-3-(1,3,5-trimethylphenyl)furan-2(5H)-one (**2o**).* Yellow solid, mp180°C. ^1H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.10 c (6H), 2.29 c (3H), 6.91 c (2H), 7.23 – 7.26 m (4H), 7.52 – 7.55 m (4H), 7.64 c (1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 20.3, 21.1, 89.2, 123.2, 125.5, 128.2, 128.6, 132.1, 132.4, 136.6, 138.6, 138.8, 153.9, 170.8. IR (KBr), cm^{-1}: 1764 (C=O). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{25}H_{20}Br_2NaO_2$ 532.9772, found 532.9772.

*5-Bis(4-bromophenyl)-3-(3-fluoro-4-methylphenyl)furan-2(5H)-one(**2p**).* Yellow solid, mp100°C. ^1H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.31 d (3H, *J* 1.5 Hz), 7.05 t (1H, *J* 8.9 Hz), 7.22 – 7.24 m (4H), 7.50 – 7.52 m (4H), 7.69 – 7.75 m (2H), 7.86 c (1H). ^{13}C NMR(100 MHz, $CDCl_3$) δ, ppm: 14.6 (*J* 3.3 Hz), 88.2, 115.5 (*J* 22.9 Hz), 123.2, 124.6 (*J* 3.8 Hz), 125.5 (*J* 17.8 Hz), 167.7 (*J* 8.4 Hz), 128.3, 129.6, 130.6 (*J* 5.6 Hz), 132.1, 138.3, 148.4, 162.3 (*J* 249.6 Hz), 170.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ, ppm: -114.32. IR (KBr), cm^{-1}: 1760 (C=O). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{23}H_{15}Br_2FNaO_2$ 522.9315, found 522.9315.

*3-(3,4-Dichlorophenyl)-5-phenylfuran-2(5H)-one (**2q**).* Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ, ppm: 6.05 d (1H, *J* 1.6 Hz), 7.31 – 7.33 m (2H), 7.40 – 7.44 m (3H), 7.50 – 7.52 m (1H), 7.68 d (1H, *J* 2.0 Hz), 7.77 – 7.79 m (1H), 8.04 d (1H, *J* 2.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 81.6, 126.4, 126.5, 129.0, 129.0, 129.1, 129.2, 129.5, 130.7, 133.1, 133.8, 134.2, 148.4, 171.0. IR (KBr), cm^{-1}: 1757 (C=O) HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{16}H_{10}Cl_2NaO_2$ 326.9950, found 326.9950.

*3-(1,3,5-Trimethylphenyl)-5-phenylfuran-2(5H)-one(**2r**).* Brown oil. ^1H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.21 c (3H), 2.22 c (3H), 2.30 c (3H), 6.12 d (1H, *J* 1.5 Hz), 6.93 c (1H), 6.94 c (1H), 7.31 d (1H, *J* 1.5 Hz), 7.36 – 7.38 m (2H), 7.41 – 7.44 m (3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 20.3, 20.5, 21.1, 82.7, 126.2, 126.6, 128.5, 128.5, 129.2, 129.3, 132.9, 135.0, 136.6, 136.6,

138.6, 151.9, 172.2. IR (KBr), cm^{-1}: 1762 (C=O). HRMS (ESI) m/z: $[M+Na]^+$calcd. for$C_{19}H_{18}NaO_2$ 310.1199, found 310.1199.

*3-(3-Fluoro-4-methylphenyl)-5-phenylfuran-2(5H)-one (**2s**).* Yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.32 d (3H, *J* 2.3 Hz), 6.02 c (1H), 7.05 t (1H), 7.32 – 7.34 m (2H), 7.38 – 7.43 m (3H), 7.56 d (1H, *J* 7.6 Hz), 7.69 – 7.72 m (1H), 7.75 – 7.77 m (1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 14.6, 81.5, 115.4 d (*J* 22.7 Hz), 125.4 d (*J* 17.7 Hz), 126.5 d (*J* 8.5 Hz), 126.6, 129.1, 129.3, 129.4, 130.2, 130.5 d (*J* 5.5 Hz), 134.8, 146.7 d (*J* 1.4 Hz), 162.1 d (*J* 248.8 Hz), 171.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ, ppm: - 115.16. IR (KBr), cm^{-1}: 1759 (C=O). HRMS (ESI) m/z: $[M+Na]^+$calcd. for $C_{17}H_{13}FNaO_2$ 291.0792, found 291.0793.

*5-(4-Methylphenyl)-3-phenylfuran-2(5H)-one (**2t**).* Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.37 c (3H), 5.99 d (1H, *J* 1.8 Hz), 7.22 c (4H), 7.40-7.45 m (3H), 7.60 d (1H, *J* 1.8 Hz), 7.89-7.91 m (2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 21.2, 81.5, 126.7, 127.2, 128.7, 129.4, 129.5, 129.7, 131.0, 131.8, 139.3, 147.4, 171.8. IR (KBr), cm^{-1}: 1758 (C=O). HRMS (ESI) m/z: $[M+Na]^+$calcd. for$C_{17}H_{14}NaO_2$ 273.0886, found 273.0886.

*5-(4-Methylphenyl)-3-(1,3,5-Trimethylphenyl)furan-2(5H)-one (**2u**).* Yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.21 c (6H), 2.30 c (3H), 2.38 c (3H), 6.08 d (1H, *J* 1.7 Hz,), 6.93 c (2H), 7.25 c (4H), 7.29 d (1H, *J* 1.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 20.3, 20.5, 21.1, 21.2, 82.7, 113.0, 126.3, 126.6, 128.5, 129.8, 131.9, 131.9, 132.8, 136.6, 138.5, 139.3, 152.1, 172.3. IR (KBr), cm^{-1}: 1759 (C=O). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{20}H_{20}NaO_2$ 315.1356, found 315.1356.

*3-(3-Fluoro-4-methylphenyl)-5-(4-methylphenyl)furan-2(5H)-one (**2v**).* Colorless oil.^1H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.31 d (3H, *J* 1.8 Hz), 2.38 c (3H), 5.98 d (1H, *J* 1.9 Hz), 7.05 t (1H), 7.21 c (4H), 7.54 d (1H, *J* 1.9 Hz), 7.68 – 7.72 m (1H), 7.75 – 7.77 m (1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 14.6 d (*J* 3.6 Hz), 21.2, 81.5, 115.4 d (*J* 22.9 Hz), 125.4 d (*J* 17.7 Hz), 126.5 d (*J* 8.2 Hz), 126.6, 129.7, 130.1, 130.5 d (*J* 5.5 Hz), 131.7, 139.4, 146.8 d (*J* 1.3 Hz), 147.4, 162.0 d (*J* 284.4 Hz), 171.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ, ppm: -115.26.IR (KBr), cm^{-1}: 1754 (C=O). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{18}H_{15}FNaO_2$ 305.0948, found 305.0948.

*5-(4-Methoxyphenyl)-3-phenylfuran-2(5H)-one (**2w**).* Brown oil. ^1HNMR (400 MHz, $CDCl_3$) δ, ppm: 3.82 c (3H), 5.98 d (1H, *J* 1.7 Hz), 6.91-6.94 m (2H), 7.24 c (2H), 7.41 – 7.46 m (3H), 7.60 d (1H, *J* 1.93 Hz), 7.90-7.92 m (2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 29.7, 55.4, 81.4, 113.7, 114.5, 126.6, 127.2, 128.3, 128.7, 129.4, 129.5, 130.4, 131.2, 147.2, 160.4, 171.7. IR (KBr), cm^{-1}: 1758 (C=O). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{17}H_{14}NaO_3$ 289.0835, found 289.0835.

*5-(4-Methoxyphenyl)-3-(1,3,5-trimethylphenyl)-5-phenylfuran-2(5H)-one (**2x**).* Yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.11 c (3H), 2.17 c (3H), 2.29 c (3H), 3.82 c (3H), 6.90 – 6.92 m (4H), 7.30 d (2H, *J* 8.8 Hz,), 7.35 – 7.40 m (5H), 7.68 c (1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm:

20.3, 20.4, 21.1, 55.3, 90.3, 114.1, 126.1, 126.6, 128.2, 128.5, 128.8, 131.4, 132.0, 136.7, 136.8, 138.5, 140.2, 155.4, 159.7, 171.5. IR (KBr), cm^{-1}: 1761 (C=O). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{26}H_{24}NaO_3$407.1618, found 407.1618.

*Methyl 4-(2,5-dimethylphenyl)-4-phenylbut-2-ynoate (**3a**).* Yellow oil .^{1}HNMR (400 MHz, $CDCl_3$) δ, ppm: 2.23 c (3H), 2.32 c (3H), 3.78 c (3H), 5.27 c (1H), 7.00 – 7.06 m (2H), 7.19 c (1H), 7.23 – 7.34 m (5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 19.1, 21.1, 40.0, 52.6, 76.25, 88.7, 127.2, 127.9, 128.4, 128.7, 129.4, 130.8, 132.7, 136.0, 136.8, 138.6, 154.2. IR (KBr), cm^{-1}: 1716 (C=O), 2234 (C≡C). HRMS (ESI) m/z: $[M+Na]^+$calcd. For $C_{19}H_{18}NaO_2$ 301.1199, found 301.1199.

*Methyl 4-(3,4-dimethylphenyl)-4-phenylbut-2-ynoate (**3b**).* Yellow oil. ^{1}HNMR (400 MHz, $CDCl_3$) δ, ppm: 2.23 c (3H), 2.24 c (3H), 3.78 c (3H), 5.07 c (1H), 7.08 – 7.10 m (3H), 7.30 – 7-34 m (2H), 7.35 – 3.37 m (3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 19.4, 19.8, 42.6, 52.6, 76.4, 88.9, 125.2, 127.3, 127.8, 128.8, 129.1, 130.1, 135.8, 136.8, 137.1, 139.7, 154.2. IR (KBr), cm^{-1}: 1716 (C=O), 2236 (C≡C). HRMS (ESI) m/z: $[M+Na]^+$calcd. For $C_{19}H_{18}NaO_2$ 301.1199, found 301.1199.

*Methyl 4-(3,5-dimethylphenyl)-4-phenylbut-2-ynoate (**3c**).* Yellow oil. ^{1}HNMR (400 MHz, $CDCl_3$) δ, ppm: 2.24 c (3H), 2.31 c (3H), 3.77 c (3H), 5.26 c (1H), 6.99 c (1H), 7.03 d (1H, *J* 8.0 Hz), 7.28 – 7.33 m (6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 19.5, 20.9, 39.8, 52.6, 76.2, 88.7, 127.2, 127.2, 127.9, 128.7, 128.7, 131.7, 134.2, 135.7, 137.4, 138.7, 154.2. IR (KBr), cm^{-1}: 1719 (C=O), 2924 (C≡C). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{19}H_{18}NaO_2$ 301.1200, found 301.1199.

*Ethyl 4,4-diphenylbut-2-ynoate(**3d**).* Yellow oil.^{1}HNMR(400 MHz, $CDCl_3$) δ, ppm: 1.36 t (3H, *J* 7.1 Hz), 4.29 q (2H, *J* 7.1 Hz), 5.17 s (1H), 7.26-7.41 m (10H). ^{13}CNMR (100 MHz, $CDCl_3$) δ, ppm: 14.0, 42.9, 62.0, 81.6, 88.0, 126.6, 127.2, 127.4, 127.9, 139.4, 147.3, 153.8. HRMS(ESI) m/z: $[M+Na]^+$calcd. for $C_{18}H_{16}NaO_2$ 287.1035, found 287.1035.

*Ethyl 4-(3,5-dimethylphenyl)-4-phenylbut-2-ynoate (**3e**).* Yellow oil .^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 1.33 t (3H, *J* 7.2 Hz), 2.27 c (3H), 2.33 c (3H), 4.25 q (2H, *J* 7.2 Hz), 5.29 c (1H), 6.97-7.10 m (3H), 7.23-7.38 m (6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 14.1, 19.5, 20.9, 39.7, 61.9б 76.5, 88.3, 127.2, 127.2, 127.9, 128.7, 128.8, 131.7, 134.3, 135.7, 137.3, 138.7, 153.8.IR (KBr), cm^{-1}: 1710 (C=O), 2231 (C≡C). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{20}H_{20}NaO_2$ 315.1352, found 315.1352.

*Ethyl 4-(4-methoxyphenyl)-4-phenylbut-2-ynoate (**3f**).* Orange oil. ^{1}HNMR (400 MHz, $CDCl_3$) δ, ppm: 1.33 t (3H), 3.80 s (3H), 4.25 q (2H), 5.10 s (1H), 6.87 d (2H, *J* 8.7 Hz), 7.27 d (2H, *J* 8.7 Hz), 7.27 s (1H), 7.31 – 7.36 m (4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 14.1, 42.2, 55.3, 62.0, 76.7, 88.3, 114.2, 127.3, 127.8, 128.8, 129.0, 131.6, 139.8, 156.8, 158.9. IR (KBr), cm^{-1}: 1708 (C=O), 2232 (C≡C). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{19}H_{18}NaO_3$ 317.1148, found 317.1148.

*Ethyl 4-(3-fluoro-4-methoxyphenyl)-4-phenylbut-2-ynoate (**3g**).* Orange oil. ^{1}HNMR (400 MHz, $CDCl_3$) δ, ppm: 1.33 t (3H, *J* 7.1 Hz), 3.88 s (3H), 4.26 q (2H, *J* 7.1 Hz), 5.07 s (1H), 6.92 t (1H, *J* 8.6 Hz), 7.04 – 7.09 m (2H), 7.27 s (1H), 7.34 – 7.35 m (4H). ^{13}CNMR (100 MHz, $CDCl_3$) δ, ppm: 14.0, 42.1, 56.3, 62.1, 77.2, 87.4, 113.6 d (*J* 1.8 Hz), 115.8 d (*J* 19.7 Hz), 123.5 d (*J* 3.7 Hz), 127.6, 127.8, 128.9, 132.4 d (*J* 5.7 Hz), 139.1, 147.0 d (*J* 10.6 Hz), 152.4 d (*J* 253.9 Hz), 153.6. ^{19}FNMR($CDCl_3$, 376 MHz)δ, ppm: - 133.98.IR (KBr), cm^{-1}: 1082 (C-F), 1708 (C=O), 2235 (C≡C). HRMS(ESI) m/z: $[M+Na]^+$ calcd. for $C_{19}H_{17}FNaO_3$ 335.1054, found 335.1054.

*Ethyl 4-(2,5-dimethylphenyl)-4-phenylbut-2-ynoate (**3h**).* Yellow oil. ^{1}HNMR (400 MHz, $CDCl_3$) δ, ppm: 1.27 t (3H, *J* 7.1 Hz), 2.19 c (3H), 2.28 c (3H), 4.19 q (2H, *J* 7.2 Hz), 5.23 c (1H), 7.17 – 7.33 m (8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 14.2, 40.0, 61.9, 82.1, 88.2, 127.2, 127.5, 127.9, 128.4, 128.7, 129.1, 129.5, 129.9, 130.2, 130.8, 138.6, 150.7, 153.8. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{20}H_{20}NaO_2$ 315.1355, found 315.1356.

*Ethyl 2,4-diphenylbut-2-diynoate (**4a**).*^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 1.34 t (3H,*J* 7.1 Hz), 4.27 q (2H, *J* 7.1 Hz), 6.06 c (1H), 7.26-7.41 m (10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 14.0, 42.9, 62.0, 81.6, 88.0, 128.7, 128.8, 129.1, 129.3, 139.4, 147.3, 153.8, 212.0. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{18}H_{16}NaO_2$ 287.1035, found 287.1035.

*Ethyl 2-(1,3,5-trimethylphenyl) -4-(4-methylphenyl)but-2-diynoate (**4b**).* Yellow oil. ^{1}HNMR (400 MHz, $CDCl_3$) δ, ppm: 1.28 t (3H, *J* 7.1 Hz), 2.27 s (3H), 2.28 s (6H), 2.34 s (3H), 4.26 q (2H, *J* 7.1 Hz), 6.56 s (1H), 6.89 s (2H), 7.14 d (2H, *J* 8.0 Hz), 7.22 d (2H, *J* 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 14.3, 20.6, 21.0, 21.3, 61.3, 96.9, 103.7, 127.6, 128.4, 128.9, 129.4, 129.5, 136.7, 137.5, 137.7, 165.8, 212.7. IR (KBr), cm^{-1}: 1735 (C=O), 2956 (C=C). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{22}H_{24}NaO_2$ 343.1669, found 343.1669.

*Ethyl 2-(1,3,5-trimethylphenyl)-4-(4-methoxyphenyl)but-2-diynoate (**4c**).* Yellow oil. ^{1}HNMR (400 MHz, $CDCl_3$) δ, ppm: 1.28 t (3H, *J* 7.1 Hz), 2.27 s (3H), 2.28 s (6H), 3.80 s (3H), 4.26 q (2H, *J* 7.1 Hz), 6.55 s (1H), 6.87 d (2H, *J* 8.7 Hz), 6.89 s (2H), 7.26 d (2H, *J* 8.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 14.3, 20.6, 21.0, 55.3, 61.3, 96.6, 103.7, 113.0, 114.3, 124.1, 128.4, 128.8, 129.5, 136.6, 137.5, 159.4, 165.8, 212.5. IR (KBr), cm^{-1}: 1714 (C=O), 2922 (C=C). HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{22}H_{24}NaO_3$ 359.1618, found 359.1618.

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Highlights

- Metal-free synthesis of furan-2-ones
- Superelctrophilic activation of 4-hydroxybut-2-ynoates with Bronsted superacids and acidic zeolites
- Reaction mechanism of electrophilic transformations of 4-hydroxybut-2-ynoates with arenes into furan-2-ones