

Dedicated to Professor V.A.Ostrovskii on occasion of his sixtieth birthday

Reactions of Acetylene Ketones in Superacids

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Abstract—Vinyl type cations $\text{ArC}^+=\text{CHCOR}$ generated from acetylene ketones $\text{ArC}\equiv\text{CCOR}$ in superacids HSO_3F and $\text{CF}_3\text{SO}_3\text{H}$ react with diverse benzene derivatives to form alkenylation products, *E*–*Z*-isomers of diarylpropenone structures $\text{Ar}(\text{Ar}')\text{C}=\text{CHCOR}$. The alkenylation of aromatic compounds with acetylene ketones in superacids occurs with the primary *syn*-addition of a hydrogen and an aryl residue to the acetylene bond followed by transformation of the product into *anti*-isomer under the conditions of the reaction.

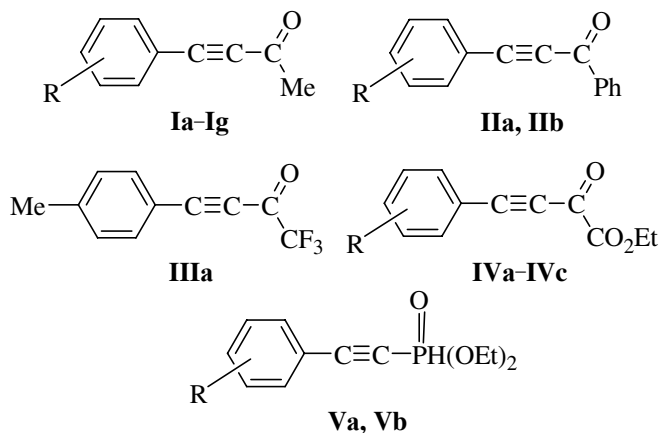
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A special attention paid in the organic chemistry to acetylene ketones is caused by the multitude of their chemical characteristics and transformations [1], and also by their biological action [2]. New opportunities were opened in the chemistry of acetylene derivatives by the application of superacid media (HSO_3F , $\text{CF}_3\text{SO}_3\text{H}$, HF/SbF_5) where the protonation of a triple carbon-carbon bond led to the formation of highly reactive vinyl type carbocations [3–9].

This report concerns the generation in superacids HSO_3F and $\text{CF}_3\text{SO}_3\text{H}$ of vinyl type cations **A** from acetylene ketones **I** (Scheme 1) and the study of ions **A** reaction with benzene derivatives proceeding by the electrophilic substitution mechanism and providing products of aromatic ring alkenylation *E*–*Z*-**B**.

In this study the protonation and reactions in superacids were investigated of the following acetylene

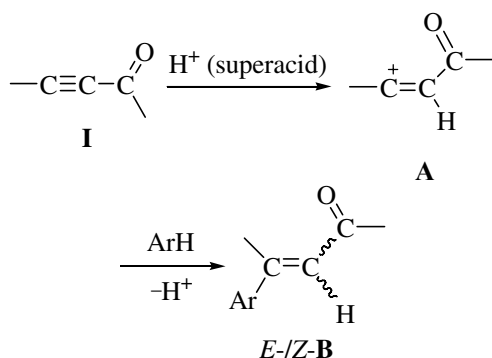
derivatives: 4-arylbut-3-yn-2-ones **Ia–Ig**, 1,3-diarylpropynones **IIa** and **IIb**, 4-(4-methylphenyl)-1,1,1-trifluorobut-3-yn-2-one (**IIIa**), and also of ethyl 4-aryl-2-oxobut-3-ynoates **IVa–IVc** and diethyl (arylethynyl)phosphonates **Va** and **Vb**.



I, R = H (**a**), 4-Me (**b**), 2,4-Me₂ (**c**), 2,4,6-Me₃ (**d**), 2,3,5,6-Me₄ (**e**), Me₅ (**f**), 4-MeO (**g**); **II**, R = 2,4-Me₂ (**a**), 2,4,6-Me₃ (**b**); **IV**, R = 4-Me (**a**), 2,4,6-Me₃ (**b**), 4-MeO (**c**); **V**, R = 2,4,6-Me₃ (**a**), 4-MeO (**b**).

The protonation of 4-phenylbut-3-yn-2-one (**Ia**) studied by ¹H and ¹³C NMR spectroscopy showed that this acetylene ketone in HSO_3F both at –80 and 0°C existed as a stable ion $\text{PhC}\equiv\text{C}-\text{C}(\text{OH})^+\text{Me}$ C O-protonated at the carbonyl group (see EXPERIMENTAL). In HSO_3F even at 0°C cation **C** did not react with benzene, 1-methoxy-4-fluorobenzene, and 1-acetyl-2,3,5,6-tetramethylbenz-

Scheme 1.



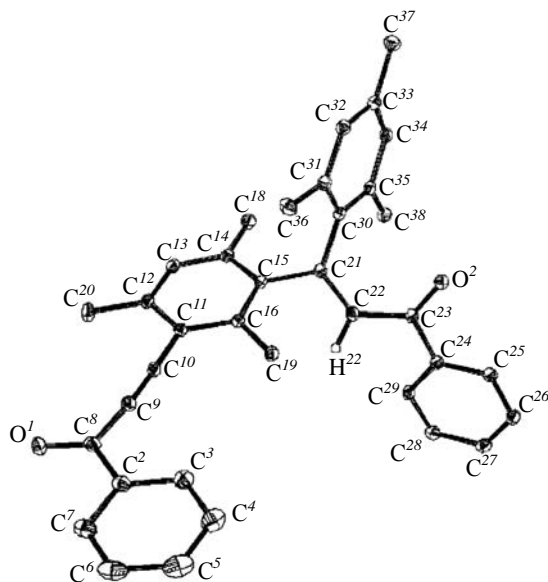


Fig. 1. Molecular structure of *(E)*-3-(2,4,6-trimethylphenyl)-3-[2,4,6-trimethyl-3-(phenylcarbonyl)ethynyl]phenyl]-1-phenylpropanone *E*-(**VIIb**).

ene. In superacids the reactivity is demonstrated by the C-protonated forms of the acetylene carbonyl compounds, vinyl type cations **A** (Scheme 1) [3–5, 9].

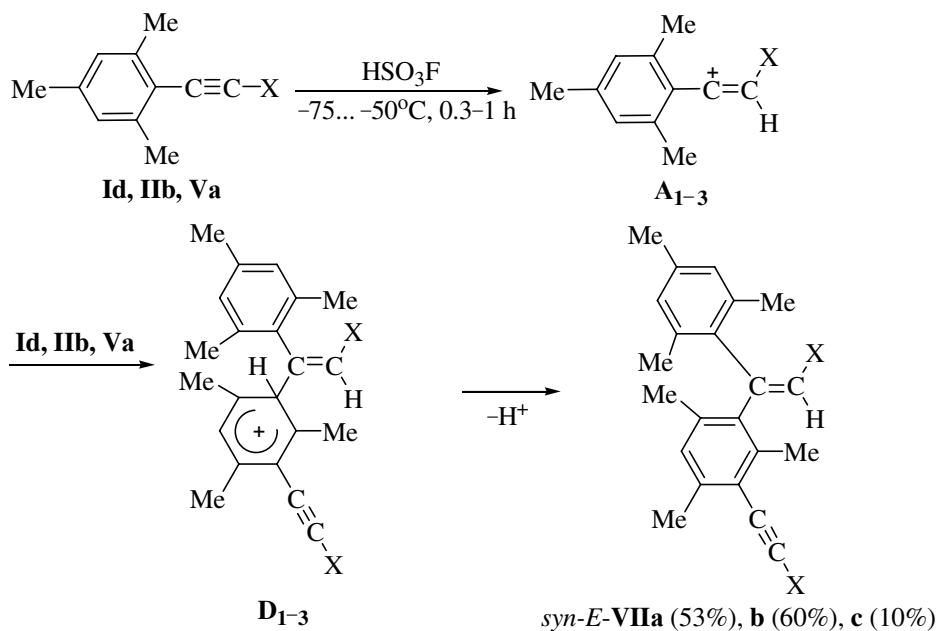
The presence in the aromatic ring of acetylene ketone **Ib** of an electron-donor methyl group increased the basicity of the triple bond $C\equiv C$ and facilitates its

protonation compared to compound **Ia**. In HSO_3F at $-30^\circ C$ ketone **Ib** was protonated at the acetylene atom C^3 and quickly transformed into fluorosulfonate (4-MeC₆H₄)(FO₂SO)C=CHCOMe *Z*-(**VI**) (see EXPERIMENTAL), a product of *anti*-addition of the fluorosulfonic acid to the triple carbon-carbon bond. A similar formation of *anti*-adducts resulting from the isomerization of the primarily arising *syn*-products of fluorosulfonic and trifluoromethanesulfonic acids addition to the acetylene bond of 3-arylpropynic acids derivatives we observed before [9].

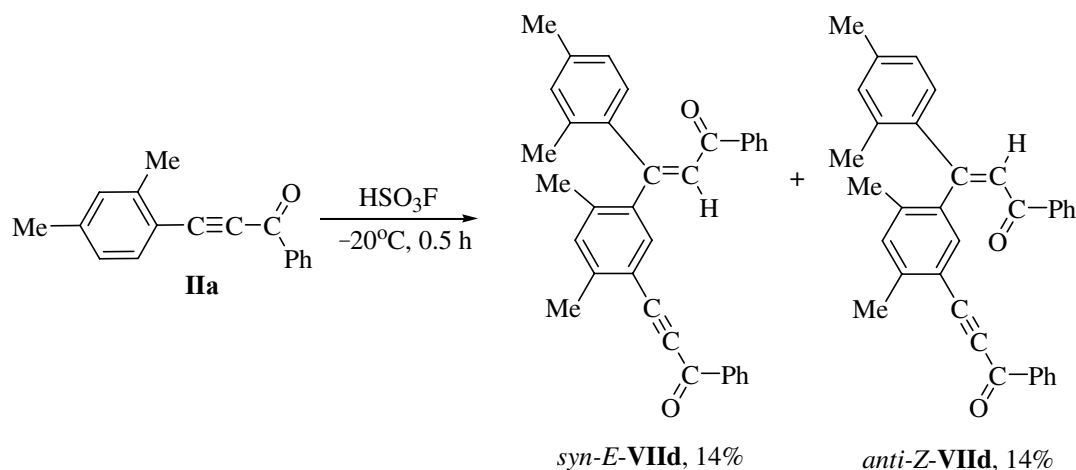
The introduction of two or more methyl groups into the aromatic ring of acetylene compounds **I–V** significantly increases the nucleophilicity of the aromatic π -system. As a result vinyl type cations **A**_{1–3} (Scheme 2) generated in HSO_3F from trimethyl derivatives **Id**, **I Ib**, and **Va** despite the sterical hindrances attacked the aromatic rings of the initial substrates forming dimers *E*-(**VIIa–VIIc**), products of *syn*-addition of hydrogen and aryl moiety to the acetylene bond; in this case fluorosulfonates were not obtained.

X-Ray diffraction analysis demonstrated that compound *E*-**VIIb** possessed a double $C=C$ bond of *E*-configuration. An interesting feature of the *E*-**VIIb** dimer structure is no distortion in its geometric parameters near the sterically overloaded C^{21} atom (Fig. 1). This atom has a traditional planar trigonal surrounding character-

Scheme 2.



Scheme 3.



istic of sp^2 -hybridized carbon atoms. The distances $\text{C}^{21}\text{--}\text{C}^{15}$, $\text{C}^{21}\text{--}\text{C}^{30}$, and $\text{C}^{21}\text{--}\text{C}^{22}$ are 1.509(2), 1.503(2), and 1.350(2) Å respectively and are characteristic of ordinary C–C and double C=C bonds [10]. Aromatic rings at C^{21} atom are virtually perpendicular to each other (92.6 deg), and this position considerably reduces their mutual nonvalence interactions. The molecules of compound *E-VIIb* in the crystal form centrosymmetrical dimers owing to the interaction $\text{O}^1\cdots\text{H}^{22}$ of the neighbor molecules (Fig. 2). The $\text{O}^1\cdots\text{H}^{22}$ distances amount to 2.31(3) Å that is somewhat less than van der Waals contacts $\text{O}\cdots\text{H}$ [11].

On keeping a solution of dimethyl-substituted ketone **IIa** in HSO_3F at -20°C for 0.5 h a mixture was obtained of isomeric dimers *E/Z-VIIId* in 1:1 ratio (Scheme 3).

It should be noted that the triple bond $\text{C}\equiv\text{C}$ in dimers *E/Z-VIIa-VIIId* is inert to protonation by HSO_3F even

at relatively high temperature (-20°C) evidently due to the presence in the structure of these compounds of electron-withdrawing groups $-(\text{Ar})\text{C}=\text{CHX}$ [$\text{X} = \text{COMe}$, COPh , $\text{PO}(\text{OEt})_2$] reducing the basicity of the acetylene bond.

In the presence of alien π -nucleophiles (substituted benzene molecules) ion **A₄** obtained from ketone **IIb** in HSO_3F and $\text{CF}_3\text{SO}_3\text{H}$ at -30°C did not form fluoro-sulfonate *Z-VI* (see above), but reacted with aromatic compounds leading to the formation of alkenylation

Scheme 4.

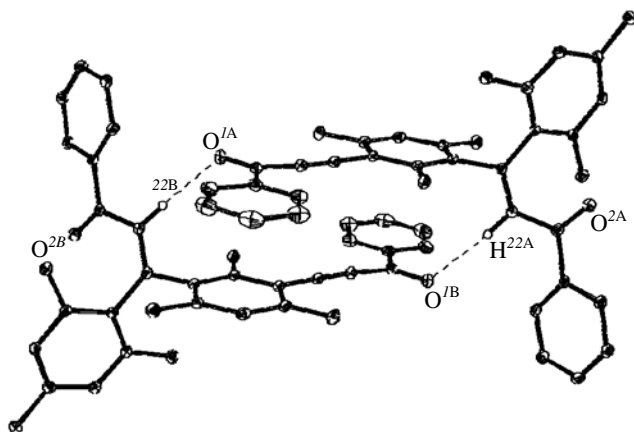
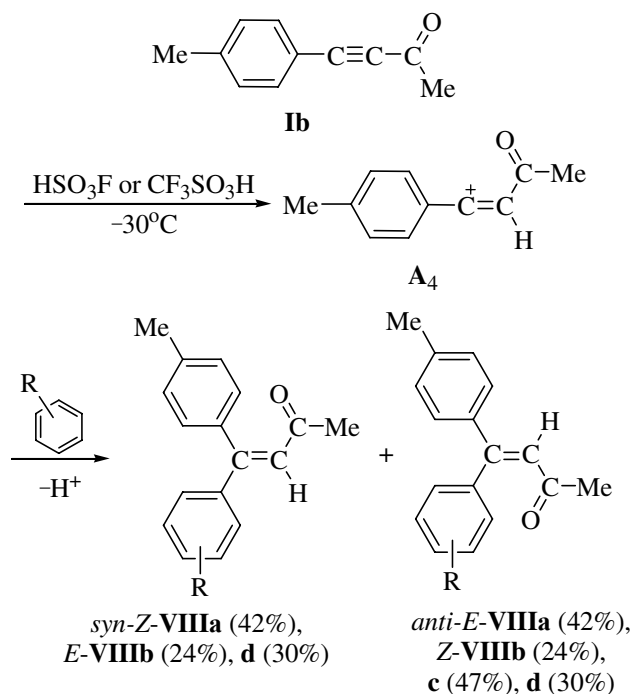


Fig. 2. A fragment of crystal lattice of (*E*)-3-(2,4,6-trimethylphenyl)-3-[2,4,6-trimethyl-3-(phenylcarbonylethynyl)-phenyl]-1-phenylpropenone *E*-(**VIIb**).

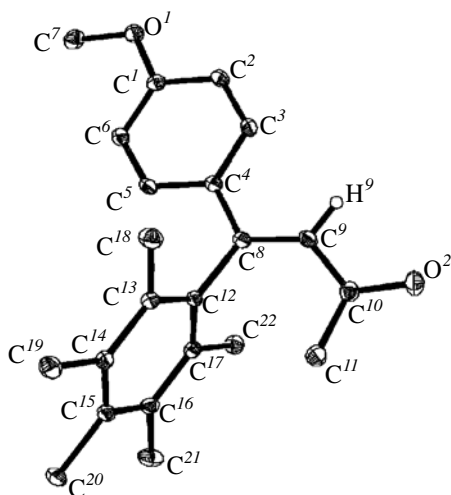


Fig. 3. Molecular structure of (Z)-4-(4-methoxyphenyl)-4-(pentamethylphenyl)but-3-en-2-one Z (**XIVb**).

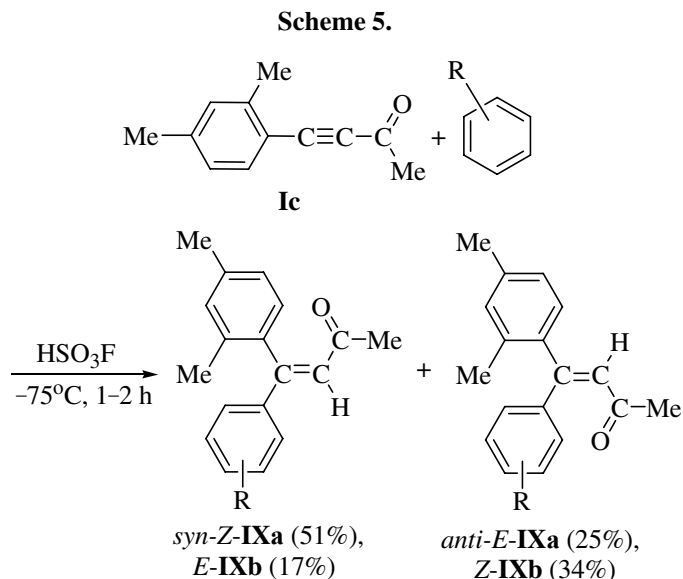
products *E*-/Z-**VIIIa–VIIId** (Scheme 4). We did not enumerate the initial substituted benzenes presented in Schemes 4–14 since their structure was unambiguously determined by the substituents in the aryl fragments of the final alkenylation products $\text{Ar}(\text{Ar}')\text{C}=\text{CHCOR}$.

The precise *E*-/Z-configuration of 4,4-diarylbutenones $\text{Ar}(\text{Ar}')\text{C}=\text{CHCOMe}$ *E*-/Z-**VIIIa–VIIId–XVa–XVd** presented in Schemes 4–10 was established by X-ray diffraction analysis (for compound Z-**XIVb**, Fig. 3) and ^1H NMR spectroscopy. The reference signal used for stereochemical estimation of *E*-/Z-configuration was the resonance of the vinyl proton at the double bond $=\text{C}=\text{CH}-$. The signal of the vinyl protons of *E*-isomers is observed mostly upfield, at δ 6.00–6.53 ppm, and that of Z-isomers downfield, in the region δ 6.46–6.90 ppm (see a similar dependence for related structure in [5, 12, 13]).

The greater number of alkyl substituents and the presence of a strong electron-donor methoxy group at the aromatic ring of arylacetylene ketones $\text{ArC}\equiv\text{CCOMe}$ facilitated the protonation of the triple bond $\text{C}\equiv\text{C}$. Dimethyl-substituted ketones and those with more methyl substituents **Ic–If** and also methoxy derivative **Ig** are protonated in HSO_3F and react with aromatic compounds at lower temperature (-75 ... -50°C) than monomethyl-substituted ketone **Ib** (-30°C , Scheme 4).

Ketone **Ic** in HSO_3F reacted with methoxy-substituted benzenes (Scheme 5) giving mixtures of *E*-/Z-isomers of compounds **IXa** and **IXb** as products of *syn*- and *anti*-addition to the triple bond $\text{C}\equiv\text{C}$.

A stereochemically pure product of *syn*-addition to the acetylene bond, adduct Z-**X**, was obtained by reaction



R = 3,4-MeO₂ (**a**), 2-MeO-5-F (**b**).

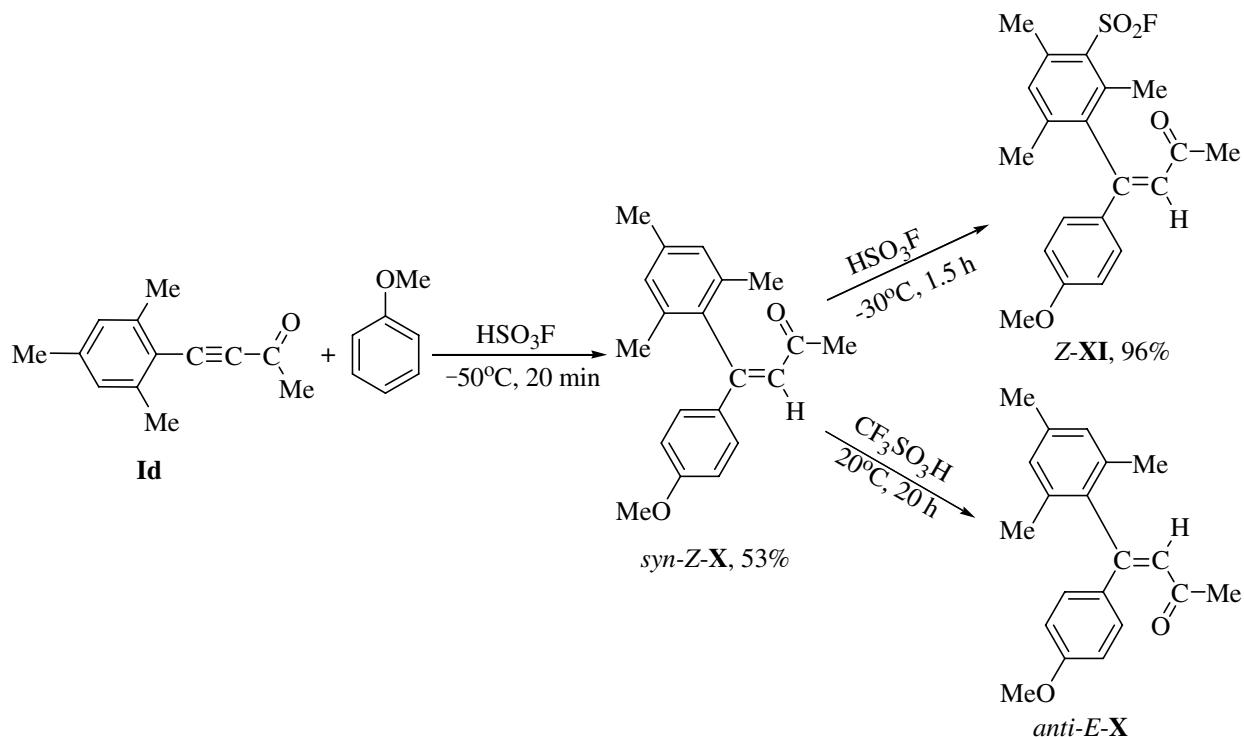
of ketone **Id** with methoxybenzene in HSO_3F at -50°C (Scheme 6). The attempt to carry out isomerization of the isolated individual substance Z-**X** in HSO_3F at a higher temperature (-30°C) resulted in sulfofluorinated product Z-**XI**. A partial isomerization into the *E*-form of compound **X** (see EXPERIMENTAL) succeeded at the use of $\text{CF}_3\text{SO}_3\text{H}$ acid devoid of sulfonation properties (Scheme 6).

We failed to obtain alkenylation product of 1-acetyl-2,3,5,6-tetramethylbenzene with ketone **Id** for the intermediately formed vinyl type cation **A**₁ attacked the aromatic ring of initial compound **Id** giving dimer *E*-**VIIa** (Scheme 2) and did not react with the π -system of the above benzene derivative whose nucleophilicity is reduced by the presence in the structure of the acetyl group.

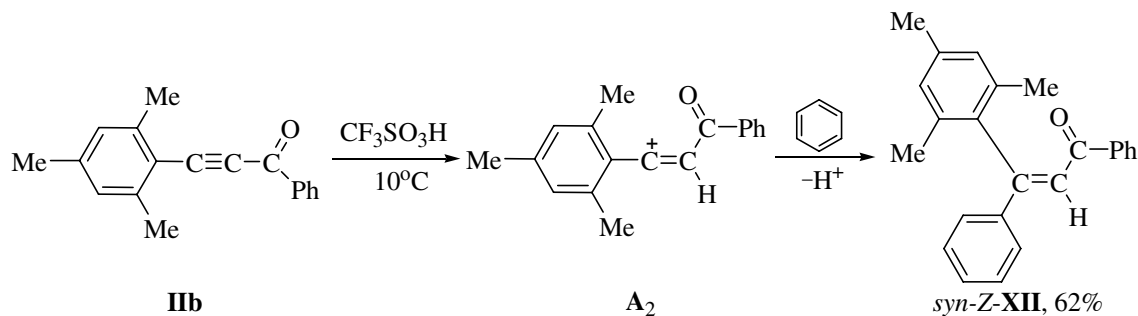
The π -system of a benzene molecule possesses higher π -nucleophilicity than the tetra-substituted aromatic ring of compound **Ib**, and the reaction of benzene with cation **A**₂ gives rise to alkenylation product Z-**XII** (Scheme 7) and not the corresponding dimer *E*-**VIIb** (cf. with Scheme 2).

Acetylene ketones **Ie** and **If**, tetra- and pentamethyl-substituted in the aromatic ring, in HSO_3F (-75°C) and $\text{CF}_3\text{SO}_3\text{H}$ (20°C) in reaction with methoxybenzene and benzene gave stereoselectively only the products of *syn*-addition Z-**XIII**, Z-**XIVa**, and Z-**XIVb** (Schemes 8 and 9). The structure of compound Z-**XIVb** was established by X-ray diffraction analysis (Fig. 3).

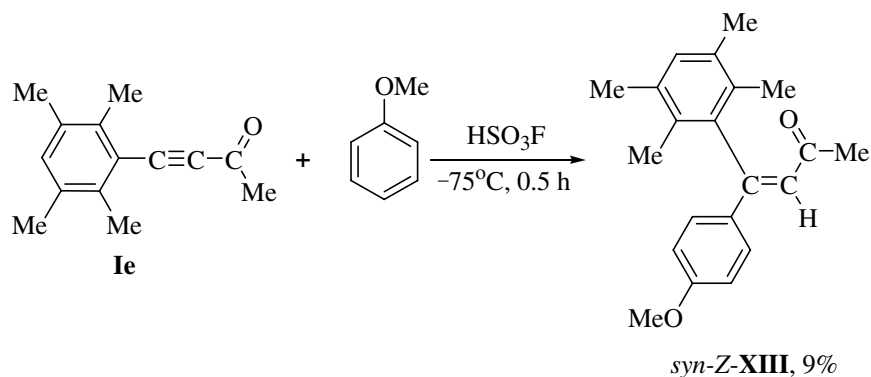
Scheme 6.



Scheme 7.



Scheme 8.



Similar to the structure of *E*-**VIIIb** (Fig. 1) the corresponding olefin atom C^8 in compound **Z-XIVb** possesses planar trigonal surrounding typical of sp^2 -hybridized carbon. The pentamethylphenyl ring is located

nearly normal (92.3°) to the plane of the fragment $\text{C}^{1-11}-\text{O}^{1,2}$ (Fig. 3). Besides in the structure of **Z-XIVb** the dihedral angle between the planes of the fragments $\text{C}^8-\text{C}^9-\text{H}^9$ and $\text{C}^8-\text{C}^4-\text{C}^3$ is 174.9° . Therefore the

vinyl atom H⁹ is located “at the side” of the methoxyphenyl ring in the region of proton deshielding. This proton in the ¹H NMR spectrum gives rise to a downfield signal at δ 6.77 ppm (see EXPERIMENTAL) characteristic of *Z*-isomers of 4,4-diarylbutenones *E*-/*Z*-**VIIIa–VIIId–XVa–XVd** (see above).

Methoxy-substituted ketone **Ig** reacted with benzene in a system CF₃SO₃H–CH₂Cl₂ (–30°C) providing a mixture of isomers *Z*-**XVa** and *E*-**XVb** in a ratio 2:1 in overall yield 98% (Scheme 10). In HSO₃F at –75°C in reaction with sterically hindered substrates compound **Ig** led to the formation of *anti*-addition adducts *Z*-**XVc** and *Z*-**XVd** (Scheme 10).

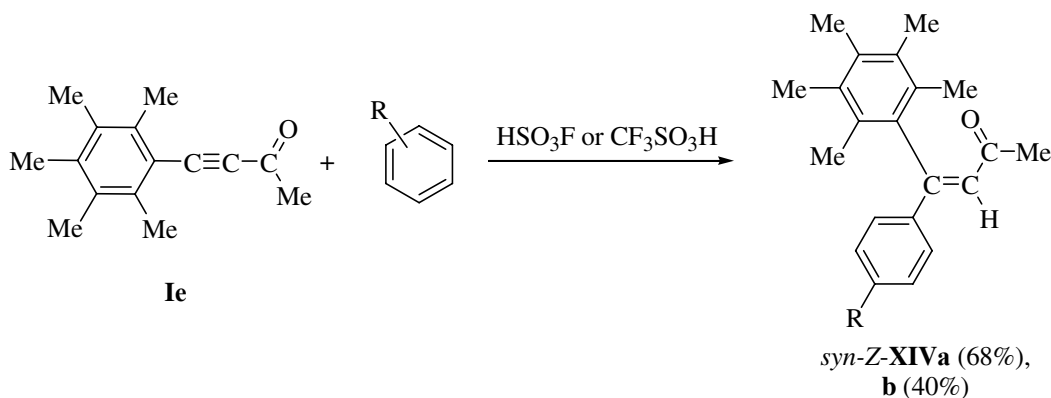
On the other hand the vinyl type cation generated in HSO₃F at –75°C from acetylene ketone **Ig** did not react with the pentamethylbenzene that existed in HSO₃F in a form of arenonium ion [14].

Acetylene derivatives **IVa–IVc** containing both keto and ester groups reacted with methoxybenzene in superacids to give alkenylation products *E*-/*Z*-**XVIa–XVc** (Scheme 11).

On keeping solutions of acetylene compounds **IVa** and **IVc** in HSO₃F in the absence of “alien” aromatic substrates in the reaction mixture followed by treating with hydrochloric acid cooled to –70°C we obtained enol forms **XIXa** and **XIXc** of the corresponding oxoacids **XVIIIa** and **XVIIIc** arising through hydrolysis of the intermediate fluorosulfonates **XVIIa** and **XVIIc** (Scheme 12). The stable existence of these enol forms is characteristic of various aromatic ketoacids [15].

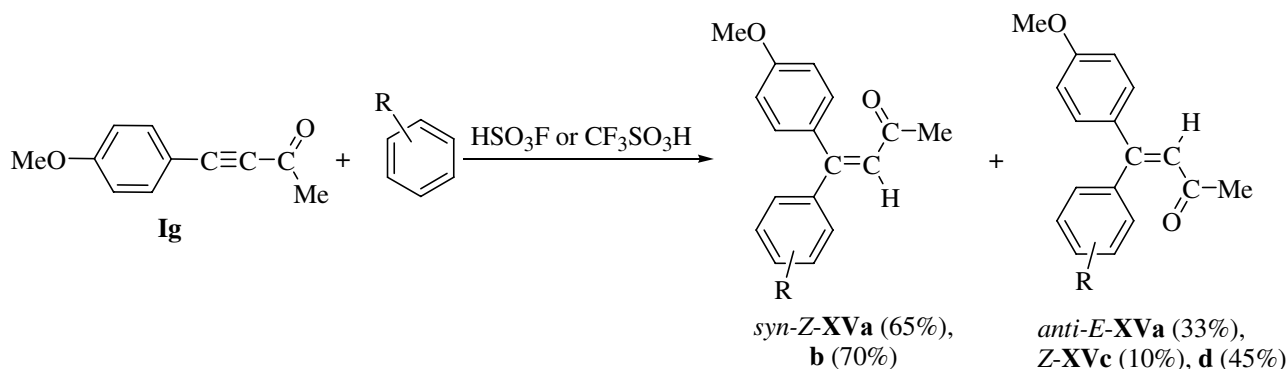
Similar to acetylene carbonyl derivatives **Ib–Ig**, **IIa** and **IIb**, **IVa–IVc** (see also [5]) acetylene phosphonates **Va** and **Vb** reacted with aromatic compounds in

Scheme 9.



R = H (**a**), 4-MeO (**b**).

Scheme 10.



R = H (**a**), 4-MeO (**b**), 4-MeCO-2,3,5,6-Me₄ (**c**), 4-SO₂F-2,3,5,6-Me₄ (**d**).

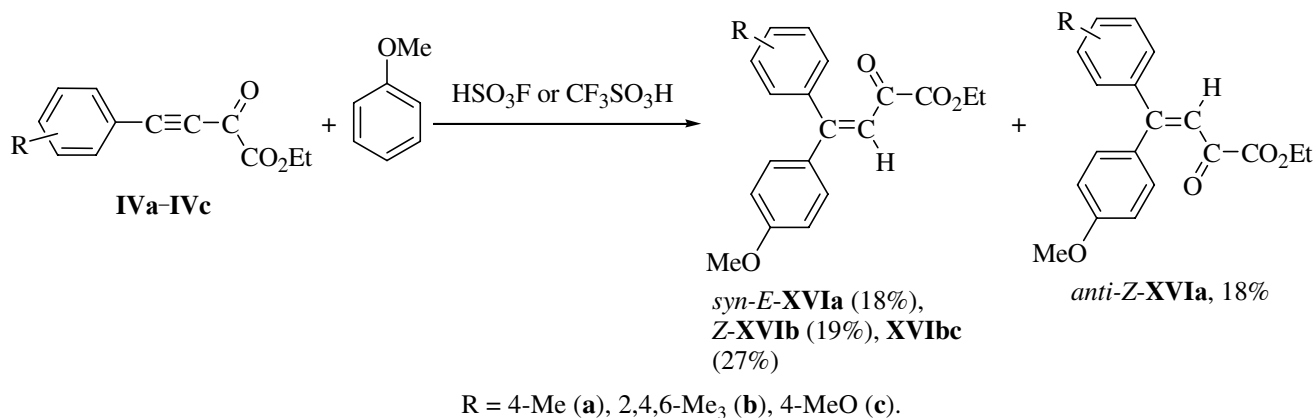
superacids via formation of vinyl type cations **A**_{5,6} (Scheme 13).

Trifluoromethylketone **IIIa** in reaction with 1,4-dimethylbenzene in HSO₃F gave rise to indenol **XXI** (Scheme 14). In this event an additional electrophilic attack occurred of C² atom from the trifluoromethyl-

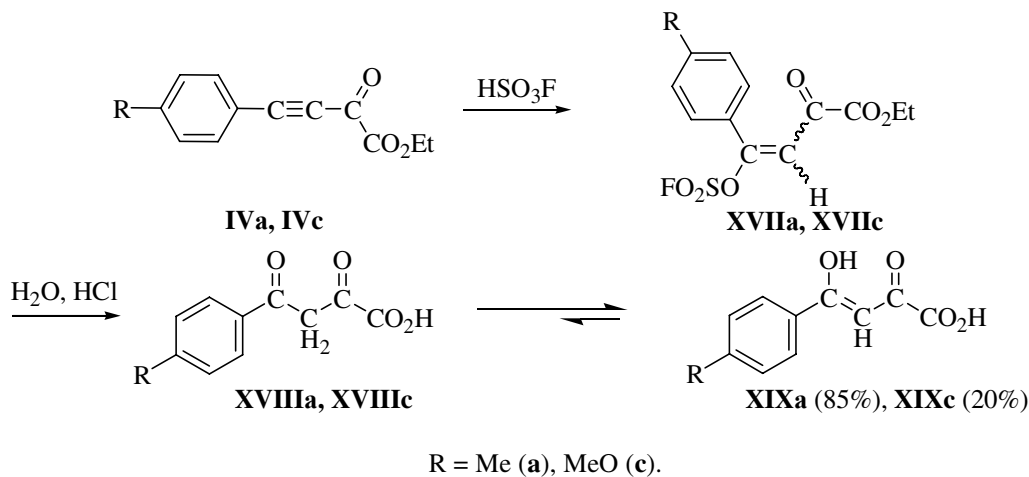
carbonyl group activated by protonation in HSO₃F [16–18] on the aromatic ring of the 1,4-dimethylbenzene.

The characteristic feature of the addition to acetylene bond in superacids at low temperature is the primary formation of adducts originating from the *syn*-addition that under the reaction conditions can isomerize into the

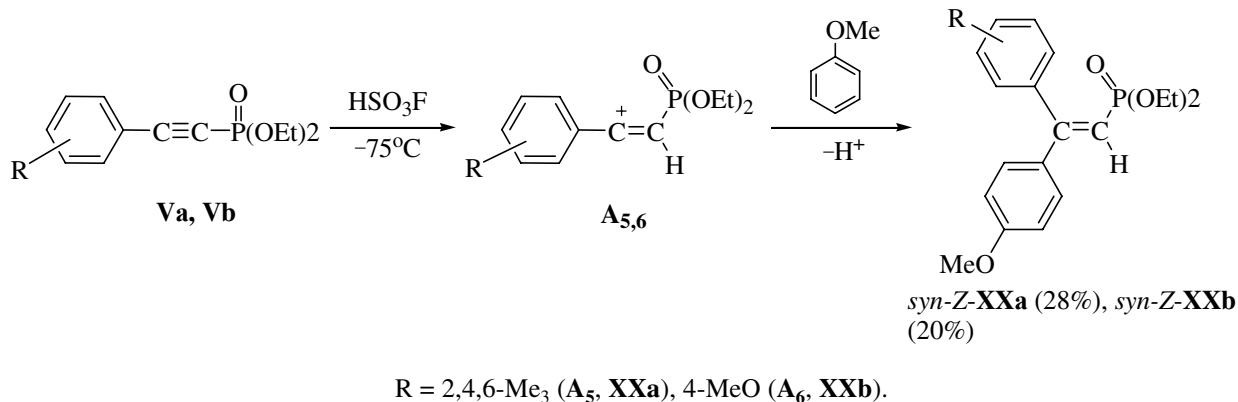
Scheme 11.



Scheme 12.



Scheme 13.



products of *anti*-type [5, 9]. In alkenylation of benzene derivatives in superacids the acetylene ketones first also provide products of *syn*-addition to the triple C≡C bond that convert into *anti*-isomers in superacids at higher temperature as has been demonstrated by an example of isomerization of compound **Z-X** into **E-X** in CF₃SO₃H at 20°C (Scheme 6). The alkenylation at higher temperature in HSO₃F (−30...−20°C) (Scheme 3; **E-/Z-VIIIb** and **E-/Z-VIIIc** in Scheme 4) or in CF₃SO₃H (−30°C) (**E-/Z-XVa** in Scheme 10; **E-/Z-VIIIa** in Scheme 4; **E-/Z-XVIa** in Scheme 11) commonly resulted in the formation of a mixture of *E/Z*-isomers. The presence of three and more methyl groups (with two of them located in the *ortho*-position) in one of the aromatic rings of the final alkenylation products prevented the isomerization of the primarily formed *syn*-adducts into the *anti*-forms (Schemes 1, 6–9) even at relatively high temperature, 10–20°C (compounds **Z-XII** and **Z-XIVa**). On the other hand, the presence in the composition of the final products of methoxy-substituted benzene rings facilitated the isomerization (Schemes 5 and 10).

The findings presented in this study show that vinyl type cations ArC⁺=CHCOR generated in superacids HSO₃F and CF₃SO₃H from arylacetylene ketones ArC≡CCOR (R = Ar, Me, CO₂Et) react efficiently (reaction time 15–120 min, yields up to 98%), regio-selectively and often stereoselectively with benzene derivatives forming diarylpropenone structures Ar(Ar')C=CHCOR.

EXPERIMENTAL

¹H and ¹³C NMR spectra were registered on a spectrometer Bruker AM-500 at operating frequencies 500 and 125.76 MHz respectively from solutions in CDCl₃ and (CD₃)₂SO. As internal references served the residual signals of CHCl₃ (δ 7.25 ppm) and (CD₃)(CD₂H)SO (δ 2.50 ppm) in the ¹H NMR spectra, and the signals of solvents CDCl₃ (δ 77.0 ppm) and (CD₃)₂SO (δ 39.52 ppm) in the ¹³C NMR spectra. IR spectra of compounds solutions in CHCl₃ were recorded on a spectrophotometer Specord 75IR. Mass spectra were taken on MKh-1321 device, ionizing electrons energy 70 eV, direct sample admission into the ion source at 100–120°C. ¹H and ¹³C NMR spectra in HSO₃F were measured on a spectrometer Bruker Avance 400 at operating frequencies 400 and 100 MHz respectively, internal reference CH₂Cl₂, δ_H 5.32, δ_C 53.84 ppm.

In X-ray experiments the sets of reflections intensities were measured on an automatic diffractometer Smart Apex (graphite monochromator, MoK_α radiation, ω-θ scanning). The structures were solved by the direct method and refined by least-squares procedure for F^2_{hkl} in anisotropic approximation for all nonhydrogen atoms. The hydrogen atoms were found from the difference Fourier synthesis and were refined isotropically. All calculations were performed applying software package SHELXTL v. 6.10 [19].

A single crystal of compound **E-VIIIb** of the size 0.28×0.28×0.25 mm for X-ray diffraction study was grown by slow evaporation of the methanol solution of the compound at room temperature within several days. Crystals of C₃₆H₃₂O₂ at 100 K triclinic, *a* 8.5188(7), *b* 12.3964(10), *c* 12.6157(10) Å, α 89.481(2), β 80.585(2), γ 85.958(2)°, *V* 1311.03(18) Å³, *Z* 2, space group P-1, *d*_{calc} 1.258 g/cm³, μ 0.076 mm^{−1}, 1.64 ≤ θ ≤ 29.19°, 9789 reflections were measured, 6833 among them independent (*R*_{int} 0.0184), *R*₁ 0.0597 [*I* > 2σ(*I*)], *wR*₂ 0.1563 (for all reflections).

A single crystal of compound **Z-XIVb** of the size 0.32×0.13×0.12 mm for X-ray diffraction study was grown by slow evaporation of the compound solution in a mixture hexane–ethyl acetate at room temperature within several days. Crystals of C₂₂H₂₆O₂ at 100 K monoclinic, *a* 8.8758(6), *b* 14.5332(9), *c* 14.1883(9) Å, β 101.864(1)°, *V* 1791.1(2) Å³, *Z* 4, space group P2(1)/C, *d*_{calc} 1.196 g/cm³, μ 0.075 mm^{−1}, 2.03 ≤ θ ≤ 26.00°, 10608 reflections were measured, 3511 among them independent (*R*_{int} 0.0213), *R*₁ 0.0422 [*I* > 2σ(*I*)], *wR*₂ 0.1119 (for all reflections).

4-Arylbut-3-yn-2-ones **Ia–Ig** were synthesized by procedure [20]. Preparation and characteristics of 4-phenylbut-3-yn-2-one (**Ia**), 4-(4-methylphenyl)but-3-yn-2-one (**Ib**), 4-(2,4-dimethylphenyl)but-3-yn-2-one (**Ic**), and 4-(4-methoxyphenyl)but-3-yn-2-one (**Ig**) we published before [21].

4-(2,4,6-Trimethylphenyl)but-3-yn-2-one (Id). Yield 60%, mp 35–37°C. ¹H NMR spectrum (CDCl₃), δ, ppm: 2.29 s (3H, CH₃CO), 2.43 s (6H, 2CH₃), 2.46 s (3H, CH₃), 6.89 s (2H_{arom}). Found, %: C 83.75; H 7.43. C₁₃H₁₄O. Calculated, %: C 83.83; H 7.58.

4-(2,3,5,6-Tetramethylphenyl)but-3-yn-2-one (Ie). Yield 25%, mp 93–94°C. ¹H NMR spectrum (CDCl₃), δ, ppm: 2.22 s (6H, 2CH₃), 2.38 s (6H, 2CH₃), 2.48 s (3H, CH₃CO), 7.01 s (1H, H_{arom}). Found, %: C 84.06; H 8.20. C₁₄H₁₆O. Calculated, %: C 83.96; H 8.05.

4-(2,3,4,5,6-Pentamethylphenyl)but-3-yn-2-one (If). Yield 20%, mp 78–80°C. ¹H NMR spectrum

(CDCl₃), δ , ppm: 2.18 s (3H, CH₃), 2.20 s (6H, 2CH₃), 2.45 s (3H, CH₃), 2.47 s (6H, 2CH₃). Found, %: C 84.15; H 8.61. C₁₅H₁₈O. Calculated, %: C 84.07; H 8.47.

1,3-Diarylpropynones **Ila** and **Ilb** were synthesized by procedure [22]. Preparation and characteristics of 3-(2,4,6-trimethylphenyl)-1-phenylpropynone (**Ilb**) we published before [4].

3-(2,4-Dimethylphenyl)-1-phenylpropynone (**Ila**).

Yield 56%, mp 57–59°C. ¹H NMR spectrum (CDCl₃), δ , ppm: 2.36 s (3H, CH₃), 2.55 s (3H, CH₃), 7.04 d (1H_{arom}, *J* 7.8 Hz), 7.10 s (1H_{arom}), 7.51 t (2H_{arom}, *J* 7.6 Hz), 7.54 d (1H_{arom}, *J* 7.8 Hz), 7.61 t (1H_{arom}, *J* 7.6 Hz), 8.22 d (2H_{arom}, *J* 7.6 Hz). Found, %: C 87.18; H 5.90. C₁₇H₁₄O. Calculated, %: C 87.15; H 6.02.

4-(4-Methylphenyl)-1,1,1-trifluorobut-3-yn-2-one (**IIIa**) was obtained as in [23].

Yield 40%, oily substance. ¹H NMR spectrum (CDCl₃), δ , ppm: 2.42 s (3H, Me), 7.25 d (2H_{arom}, *J* 7.9 Hz), 7.56 d (2H_{arom}, *J* 7.9 Hz). Found, %: C 62.25; H 3.30. C₁₁H₇F₃O. Calculated, %: C 62.27; H 3.33. Ethyl 4-aryl-2-oxobut-3-ynoates **IVa–IVc** were prepared by procedure [24].

Ethyl 4-(4-methylphenyl)-2-oxobut-3-ynoate (**IVa**).

Yield 37%, mp 38–40°C. IR spectrum, ν , cm⁻¹: 1680 (C=O), 1725 (C=O), 2190 (C $\equiv$ C). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.41 t (3H, CH₃, *J* 6.9 Hz), 2.40 s (3H, CH₃), 4.39 q (2H, OCH₂, *J* 6.9 Hz), 7.21 d (2H_{arom}, *J* 7.7 Hz), 7.55 d (2H_{arom}, *J* 7.7 Hz). ¹³C NMR spectrum (CDCl₃), δ , ppm: 13.92, 21.80, 63.17, 87.26, 98.87, 115.90, 129.60, 133.84, 142.91, 159.31, 169.50. Found, %: C 72.27; H 5.63. C₁₃H₁₂O₃. Calculated, %: C 72.21; H 5.59.

Ethyl 4-(2,4,6-trimethylphenyl)-2-oxobut-3-ynoate (**IVb**).

Yield 18%, mp 62–64°C. IR spectrum, ν , cm⁻¹: 1680 (C=O), 1730 (C=O), 2180 (C $\equiv$ C). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.41 t (3H, CH₃, *J* 7.3 Hz), 2.31 s (3H, CH₃), 2.49 s (6H, 2CH₃), 4.40 q (2H, OCH₂, *J* 7.3 Hz), 6.92 s (2H_{arom}). ¹³C NMR spectrum (CDCl₃), δ , ppm: 13.96, 20.73, 21.64, 63.07, 95.33, 97.28, 115.97, 128.21, 142.50, 144.10, 159.32, 169.17. Found, %: C 73.80; H 6.63. C₁₅H₁₆O₃. Calculated, %: C 73.75; H 6.60.

Ethyl 4-(4-methoxyphenyl)-2-oxobut-3-ynoate (**IVc**).

Yield 30%, mp 53–55°C. IR spectrum, ν , cm⁻¹: 1680 (C=O), 1730 (C=O), 2180 (C $\equiv$ C). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.37 t (3H, CH₃, *J* 7.1 Hz), 3.81 s (3H, OCH₃), 4.35 q (2H, OCH₂, *J* 7.1 Hz), 6.88 d (2H_{arom}, *J* 8.8 Hz), 7.57 d (2H_{arom}, *J* 8.8 Hz). ¹³C NMR spectrum (CDCl₃), δ , ppm: 13.94 q (CH₃, *J* 127 Hz), 55.47 q (OCH₃, *J* 144 Hz), 63.09 t.q (CH₂, *J* 148, 5 Hz),

87.76 C, 99.71 t (*J* 5 Hz), 110.70 t (*J* 8 Hz), 111.58 d.d (*J* 161, 4 Hz), 136.06 d.d (*J* 163, 7 Hz), 159.44 t (*J* 2.2 Hz), 162.65 m, 169.25 C. Found, %: C 67.30; H 5.36. C₁₃H₁₂O₄. Calculated, %: C 67.23; H 5.21.

The preparation and characteristics of diethyl (2,4,6-trimethylphenylethynyl)phosphonate (**Va**) and diethyl (4-methoxyphenylethynyl) phosphonate (**Vb**) we reported before [25].

Generation of 2-hydroxy-4-phenylbut-3-yn-2-ylum **C** in HSO₃F.

To 0.8 ml of HSO₃F (mp –89°C) frozen in an NMR tube at –110°C (ethanol–liquid nitrogen) was added 30 mg of compound **Ia**. The temperature was raised to –78°C, into the ampule was inserted to the bottom a Teflon capillary of 1 mm internal diameter, and a weak flow of argon was passed through the capillary for 10 min till the formation of a homogeneous solution of ion **C**. The capillary was removed, and 3 mg of CH₂Cl₂ was added. ¹H NMR spectrum (HSO₃F, –80°C), δ , ppm: 3.12 s (3H, Me), 7.68 t (2H^{*m*}, *J* 8.0 Hz), 7.92 t (1H^{*i*}, *J* 8.0 Hz), 8.01 d (2H^{*o*}, *J* 8.0 Hz). ¹H NMR spectrum (HSO₃F, 0°C), δ , ppm: 3.15 s (3H, Me), 7.71 t (2H^{*m*}, *J* 8.0 Hz), 7.95 t (1H^{*i*}, *J* 8.0 Hz), 8.03 d (2H^{*o*}, *J* 8.0 Hz). ¹³C NMR spectrum (HSO₃F, –80°C), δ , ppm: 29.93 (C^{*i*}), 92.40 (C^{*2*}), 116.13 (C^{*3*}), 130.47 (C^{*o*}), 136.75 (C^{*i*}), 138.35 (C^{*m*}), 139.13 (C^{*i*}), 202.82 (C^{*2*}=OH⁺).

Alkenylation of aromatic compounds with arylacetylene derivatives **Ia–Ig–Va**, and **Vb** in superacids HSO₃F and CF₃SO₃H.

To a solution of 0.13–1.00 mmol of aromatic compound in 0.5–2.0 ml of HSO₃F or CF₃SO₃H at –75–20°C while vigorous stirring was gradually added within 10–30 min 0.09–0.47 mmol of arylacetylene derivative **Ia–Ig–Va**, and **Vb**. The reaction mixture was stirred for more 5–90 min and then poured into 15–30 ml of concn. HCl cooled to –70°C. The mixture obtained was warmed to room temperature and extracted with chloroform (3×30 ml). The combined extracts were washed with water, with saturated water solution of NaHCO₃, again with water, dried with Na₂SO₄, the solvent was distilled off in a vacuum of a water-jet pump, and the residue was subjected to column chromatography on silica gel (eluent petroleum ether–ethyl acetate). Yield of the final products **E-/Z-VIIa–VIIId–XXI** was estimated from the weight of the fractions obtained by chromatography.

(Z)-4-(4-Methylphenyl)-4-(fluorosulfonyloxy)but-3-en-2-one **Z-(VI)**

was obtained by keeping a solution of 50 mg (0.31 mmol) of compound **Ib** in 1 ml of HSO₃F at –30°C for 1 h. Yield 65 mg (80%). Oily substance. ¹H NMR spectrum (CDCl₃), δ , ppm: 2.40 s (6H, 2CH₃),

6.47 s (1H, HC=), 7.27 d (2H_{arom}, *J* 7.8 Hz), 7.52 d (1H_{arom}, *J* 7.8 Hz). Mass spectrum: *m/z* 258 [*M*]⁺. Found, %: C 67.30; H 5.36. C₁₁H₁₁FO₄S. Calculated, %: C 51.16; H 4.29. *M* 258.26.

(*E*)-4-[2,4,6-Trimethyl-3-(methylcarbonyl-ethynyl)phenyl]-4-(2,4,6-trimethylphenyl)but-3-en-2-one *E*-(VIIa) was obtained by keeping a solution of 30 mg (0.16 mmol) of compound **Id** in 0.5 ml of HSO₃F at –50°C for 20 min. Yield 32 mg (53%). Oily substance. IR spectrum, *v*, cm^{–1}: 1620 (C=O), 1685 (C=O), 2200 (C≡C). ¹H NMR spectrum (CDCl₃), *δ*, ppm: 1.89 s (3H, Me), 2.07 s (6H, 2Me), 2.42 s (3H, Me), 2.44 s (3H, Me), 6.19 s (1H, HC=), 6.83 s (2H_{arom}), 6.91 br.s (1H_{arom}). Mass spectrum, *m/z* (*I*_{rel}, %): 372 [*M*]⁺ (3), 357 (100), 171 (7), 43 (30). Found, %: C 83.89; H 7.63. C₂₆H₂₈O₂. Calculated, %: C 83.83; H 7.58. *M* 372.51.

(*E*)-3-(2,4,6-Trimethylphenyl)-3-[2,4,6-trimethyl-3-(phenylcarbonylethynyl)phenyl]-1-phenylpropenone *E*-(VIIb) was obtained by keeping a solution of 74 mg (0.3 mmol) of compound **Ib** in 1.5 ml of HSO₃F at –50°C for 0.5 h. Yield 89 mg (60%), mp 182–184°C. IR spectrum, *v*, cm^{–1}: 1620 (C=O), 1650 (C=O), 2180 (C≡C). ¹H NMR spectrum (CDCl₃), *δ*, ppm: 2.08 s (6H, 2CH₃), 2.21 s (6H, 2CH₃), 2.56 s (6H, 2CH₃), 6.75 s (1H, HC=), 6.98 s (1H_{arom}), 7.40 t (2H_{arom}, *J* 7.7 Hz), 7.50 t (3H_{arom}, *J* 7.7 Hz), 7.61 t (1H_{arom}, *J* 7.2 Hz), 7.91 d (2H_{arom}, *J* 7.7 Hz), 8.22 d (2H_{arom}, *J* 7.2 Hz). ¹³C NMR spectrum (CDCl₃), *δ*, ppm: 20.88 q.t (*J* 126.0, 4.6 Hz), 21.10 q.m (*J* 127.0, 4.6 Hz), 21.16 q.m (*J* 125.0, 3.8 Hz), 91.50 s, 95.62 s, 119.36 m, 128.36 d.d (*J* 161.0, 6.7 Hz), 128.59 d.d (*J* 161.0, 7.2 Hz), 129.32 d.m (*J* 155.0, 5.5 Hz), 129.43 d.m (*J* 161.0, 7.2 Hz), 130.63 d.m (*J* 151.0, 5.1 Hz), 132.63 d.m (*J* 152.0, 7.6 Hz), 133.89 d.t (*J* 158.0, 7.2 Hz), 135.09 m, 136.21 d (*J* 4.2 Hz), 137.14 t (*J* 7.2 Hz), 137.37 q (*J* 5.9 Hz), 137.83 t (*J* 7.0 Hz), 138.90 s, 140.37 s, 141.69 d (*J* 4.2 Hz), 142.16 d (*J* 5.0 Hz), 150.69 s, 177.93 s, 191.12 s. Mass spectrum, *m/z* (*I*_{rel}, %): 496 [*M*]⁺ (8), 481 (100), 391 (15), 248 [*M*]⁺⁺ (6), 105 (40), 77 (29). Found, %: C 87.10; H 6.51. C₃₆H₃₂O₂. Calculated, %: C 87.06; H 6.49. *M* 496.24.

(*E*)-2-(2,4,6-Trimethylphenyl)-2-(2,4,6-trimethyl-3-phosphonylethynylphenyl)ethenylphosphonate *E*-(VIIc) was obtained by keeping a solution of 28 mg (0.11 mmol) of compound **Va** in 0.5 ml HSO₃F at –75°C for 1 h. Yield 6 mg (10%). Oily substance. IR spectrum, *v*, cm^{–1}: 2170 (C≡C). ¹H NMR spectrum (CDCl₃), *δ*, ppm: 1.12 t (6H, 2CH₃, *J* 7.1 Hz), 1.39 t (6H, 2CH₃, *J* 7.1 Hz), 2.18 s (3H, Me), 2.23 s (3H, Me), 2.40 s (6H,

2Me), 3.70–3.78 m (2H, CH₂), 3.86–3.94 m (2H, CH₂), 4.21 quintet (4H, 2CH₂, *J* 7.1 Hz), 5.83 d (1H, HC=, *J* 15.2 Hz), 6.79 s (2H_{arom}), 6.89 br.s (1H_{arom}). Mass spectrum, *m/z* (*I*_{rel}, %): 562 [*M* + 2]⁺ (3), 561 [*M* + 1]⁺ (14), 560 [*M*]⁺ (38), 545 (10), 423 (100), 422 (91), 407 (23), 224 (15), 183 (17). Found, %: C 64.30; H 7.59. C₃₀H₄₂O₆P₂. Calculated, %: C 64.27; H 7.55. *M* 560.25.

(*E*)-3-(2,4-Dimethylphenyl)-3-[2,4-dimethyl-5-(phenylcarbonylethynyl)phenyl]-1-phenylpropenone *E*-(VIIId) and (*Z*)-3-(2,4-dimethylphenyl)-3-[2,4-dimethyl-5-(phenylcarbonylethynyl)phenyl]-1-phenylpropenone *Z*-(VIIId) were obtained by keeping a solution of 110 mg (0.47 mmol) of compound **Ia** in 1 ml of HSO₃F at –20°C for 0.5 h. Oily mixture of isomers *E*-VIIId [31 mg (14%)] and *Z*-VIIId [31 mg (14%)].

Compound *E*-VIIId. ¹H NMR spectrum (CDCl₃), *δ*, ppm (extricated from the spectrum of isomers mixture): 2.05 s (3H, CH₃), 2.25 s (3H, CH₃), 2.33 s (3H, CH₃), 2.56 s (3H, CH₃), 7.15 s (1H, HC=), 6.87–7.07 m (H_{arom}), 7.47–7.53 m (H_{arom}), 7.88–7.91 m (H_{arom}).

Compound *Z*-VIIId. ¹H NMR spectrum (CDCl₃), *δ*, ppm (extricated from the spectrum of isomers mixture): 2.14 s (3H, CH₃), 2.30 s (3H, CH₃), 2.32 s (3H, CH₃), 2.52 s (3H, CH₃), 7.32 s (H_{arom}), 7.37–7.43 m (H_{arom}), 7.58–7.63 m (H_{arom}), 8.17–8.21 m (H_{arom}). Mass spectrum (isomers mixture), *m/z* (*I*_{rel}, %): 468 [*M*]⁺ (16), 453 (82), 363 (10), 135 (9), 105 (100), 77 (65). Found, %: C 87.21; H 6.05. C₃₄H₂₈O₂. Calculated, %: C 87.15; H 6.02. *M* 468.21.

(*E*)-(4-Methylphenyl)-4-phenylbut-3-en-2-one *E*-(VIIIa) and (*Z*)-(4-methylphenyl)-4-phenylbut-3-en-2-one *Z*-(VIIIa) were obtained from 30 mg (0.19 mmol) of compound **Ib** and 44 mg (0.57 mmol) of benzene in a mixture of 1 ml of CF₃SO₃H and 0.8 ml of CH₂Cl₂ at –30°C in 0.5 h. Oily mixture of isomers *E*-VIIIa [19 mg (42%)] and *Z*-VIIIa [19 mg (42%)].

Compound *E*-VIIIa. ¹H NMR spectrum (CDCl₃), *δ*, ppm (extricated from the spectrum of isomers mixture): 1.89 s (3H, Me), 2.40 s (3H, Me), 6.53 s (1H, HC=), 7.09–7.41 m (9H_{arom}).

Compound *Z*-VIIIa. ¹H NMR spectrum (CDCl₃), *δ*, ppm (extricated from the spectrum of isomers mixture): 1.85 s (3H, Me), 2.35 s (3H, Me), 6.57 s (1H, HC=), 7.09–7.41 m (9H_{arom}). Mass spectrum (isomers mixture), *m/z* (*I*_{rel}, %): 237 [*M* + 1]⁺ (12), 236 [*M*]⁺ (65), 235 (62), 221 (100), 193 (13), 178 (33), 119 (15), 115 (20), 43 (12). Found, %: C 86.45; H 6.85. C₁₇H₁₆O. Calculated, %: C 86.40; H 6.82. *M* 236.12.

(E)-4-(4-Methylphenyl)-4-(4-methoxyphenyl)but-3-en-2-one E-(VIIIb) and (Z)-4-(4-methylphenyl)-4-(4-methoxyphenyl)but-3-en-2-one Z-(VIIIb) were obtained from 51 mg (0.32 mmol) of compound **Ib** and 68 mg (0.63 mmol) of methoxybenzene in 1 ml of HSO₃F at –30°C in 0.5 h. Oily mixture of isomers *E*-VIIIb [20 mg (24%)] and *Z*-VIIIb [20 mg (24%)].

Compound *E*-VIIIb. ¹H NMR spectrum (CDCl₃), δ, ppm (extricated from the spectrum of isomers mixture): 1.88 s (3H, Me), 2.35 s (3H, Me), 3.85 s (3H, OMe), 6.48 s (1H, HC=), 6.92 d (2H_{arom}, *J* 8.6 Hz), 7.13 d (2H_{arom}, *J* 8.3 Hz), 7.14 d (2H_{arom}, *J* 8.6 Hz), 7.18 d (2H_{arom}, *J* 8.3 Hz).

Compound *Z*-VIIIb. ¹H NMR spectrum (CDCl₃), δ, ppm (extricated from the spectrum of isomers mixture): 1.85 s (3H, Me), 2.40 s (3H, Me), 3.80 s (3H, OMe), 6.50 s (1H, HC=), 6.83 d (2H_{arom}, *J* 8.8 Hz), 7.09 d (2H_{arom}, *J* 8.0 Hz), 7.21 d (2H_{arom}, *J* 8.0 Hz), 7.23 d (2H_{arom}, *J* 8.8 Hz). Mass spectrum (isomers mixture), *m/z* (*I*_{rel}, %): 266 [*M*]⁺ (68), 265 (43), 251 (100), 165 (34), 135 (43), 119 (28), 43 (37). Found, %: C 81.09; H 6.76. C₁₈H₁₈O₂. Calculated, %: C 81.17; H 6.81. *M* 266.13.

(Z)-4-(4-Acetyl-2,3,5,6-tetramethylphenyl)-4-(4-methylphenyl)but-3-en-2-one Z-(VIIIc) was obtained from 51 mg (0.32 mmol) of compound **Ib** and 85 mg (0.48 mmol) of 1-acetyl-2,3,5,6-tetramethylbenzene in 1 ml of HSO₃F at –30°C in 1 h. Yield 50 mg (47%). Oily substance. ¹H NMR spectrum (CDCl₃), δ, ppm: 1.78 s (3H, Me), 1.98 s (6H, 2Me), 2.13 s (6H, 2Me), 2.34 s (3H, Me), 2.51 s (3H, Me), 6.86 s (1H, HC=), 7.12 d (2H_{arom}, *J* 7.7 Hz), 7.20 d (2H_{arom}, *J* 7.7 Hz). Mass spectrum, *m/z* (*I*_{rel}, %): 334 [*M*]⁺ (10), 319 (35), 290 (10), 275 (15), 247 (25), 43 (100). Found, %: C 82.54; H 7.80. C₂₃H₂₆O₂. Calculated, %: C 82.60; H 7.84. *M* 334.19.

(E)-4-(3,4-Dichlorophenyl)-4-(4-methylphenyl)but-3-en-2-one E-(VIIIId) and (Z)-4-(3,4-dichlorophenyl)-4-(4-methylphenyl)but-3-en-2-one Z-(VIIIId) were obtained from 51 mg (0.32 mmol) of compound **Ib** and 94 mg (0.64 mmol) of 1,2-dichlorobenzene in 1 ml of HSO₃F at –30°C in 1.3 h. Oily mixture of isomers *E*-VIIIId [29 mg (30%)] and *Z*-VIIIId [29 mg (30%)]. ¹H NMR spectrum (CDCl₃), δ, ppm (isomers mixture): 1.89 s (3H, Me), 2.06 s (3H, Me), 2.36 s (3H, Me), 2.41 s (3H, Me), 6.48 s (1H, HC=, *E*-VIIIId), 6.61 s (1H, HC=, *Z*-VIIIId), 7.05 d.d (1H_{arom}, *J* 8.2, 1.8 Hz), 7.07 d (2H_{arom}, *J* 7.7 Hz), 7.11 d.d (1H_{arom}, *J* 8.4, 2.1 Hz), 7.15 s (4H_{arom}), 7.22 d (1H_{arom}, *J* 7.7 Hz), 7.28 d (1H_{arom}, *J* 1.8 Hz), 7.34 d (1H_{arom}, *J* 2.1 Hz), 7.38 d (1H_{arom}, *J* 8.4 Hz), 7.46 d (1H_{arom}, *J* 8.2 Hz). Mass spectrum

(70 eV, isomers mixture), *m/z* (*I*_{rel}, %): 308 [*M* + 4]⁺ (3), 306 [*M* + 2]⁺ (17), 304 [*M*]⁺ (24), 291 (61), 289 (100), 226 (20), 191 (18), 189 (21), 119 (25), 115 (14), 91 (12). Mass spectrum (18 eV, isomers mixture), *m/z* (*I*_{rel}, %): 308 [*M* + 4]⁺ (11), 306 [*M* + 2]⁺ (62), 304 [*M*]⁺ (100), 303 (16), 291 (16), 289 (86), 269 (14), 271 (3). Found, %: C 66.96; H 4.65. C₁₇H₁₄Cl₂O. Calculated, %: C 66.90; H 4.62. *M* 304.04.

(E)-4-(2,4-Dimethylphenyl)-4-(3,4-dimethoxyphenyl)but-3-en-2-one E-(IXa) and (Z)-4-(2,4-dimethylphenyl)-4-(3,4-dimethoxyphenyl)but-3-en-2-one Z-(IXa) were obtained from 50 mg (0.29 mmol) of compound **Ic** and 59 mg (0.43 mmol) of 1,2-dimethoxybenzene in 0.6 ml of HSO₃F at –75°C in 1 h. Oily mixture of isomers *E*-IXa [22 mg (25%)] and *Z*-IXa [45 mg (51%)].

Compound *E*-IXa. ¹H NMR spectrum (CDCl₃), δ, ppm (extricated from the spectrum of isomers mixture): 2.01 s (3H, Me), 2.03 s (3H, Me), 2.32 s (3H, Me), 3.78 s (3H, OMe), 3.88 s (3H, OMe), 6.10 s (1H, HC=), 6.73–7.20 m (6H_{arom}).

Compound *Z*-IXa. ¹H NMR spectrum (CDCl₃), δ, ppm (extricated from the spectrum of isomers mixture): 1.74 s (3H, Me), 2.03 s (3H, Me), 2.36 s (3H, Me), 3.82 s (3H, OMe), 3.86 s (3H, OMe), 6.65 s (1H, HC=), 6.73–7.20 m (6H_{arom}). Mass spectrum (isomers mixture), *m/z* (*I*_{rel}, %): 311 [*M* + 1]⁺ (10), 310 [*M*]⁺ (54), 295 (100), 165 (41). Found, %: C 77.45; H 7.22. C₂₀H₂₂O₃. Calculated, %: C 77.39; H 7.14. *M* 310.16.

(E)-4-(2,4-Dimethylphenyl)-4-(2-methoxy-5-fluorophenyl)but-3-en-2-one E-(IXb) and (Z)-4-(2,4-dimethylphenyl)-4-(2-methoxy-5-fluorophenyl)but-3-en-2-one Z-(IXb) were obtained from 50 mg (0.29 mmol) of compound **Ic** and 55 mg (0.44 mmol) of 1-methoxy-4-fluorobenzene in 0.6 ml of HSO₃F at –75°C in 2 h. Oily mixture of isomers *E*-IXb [15 mg (17%)] and *Z*-IXb [30 mg (34%)].

Compound *E*-IXb. ¹H NMR spectrum (CDCl₃), δ, ppm (extricated from the spectrum of isomers mixture): 1.79 s (3H, Me), 2.06 s (3H, Me), 2.34 s (3H, Me), 3.77 s (3H, OMe), 6.74 s (1H, HC=), 6.64–7.05 m (6H_{arom}).

Compound *Z*-IXb. ¹H NMR spectrum (CDCl₃), δ, ppm (extricated from the spectrum of isomers mixture): 2.07 s (3H, Me), 2.10 s (3H, Me), 2.30 s (3H, Me), 3.72 s (3H, OMe), 6.26 s (1H, HC=), 6.64–7.05 m (6H_{arom}). Mass spectrum (isomers mixture), *m/z* (*I*_{rel}, %): 298 [*M*]⁺ (11), 283 (68), 267 (100), 43 (33). Found, %:

C 76.56; H 6.45. $C_{19}H_{19}FO_2$. Calculated, %: C 76.49; H 6.42. *M* 298.14.

(Z)-4-(4-Methoxyphenyl)-4-(2,4,6-trimethylphenyl)but-3-en-2-one Z-(X) was obtained from 30 mg (0.16 mmol) of compound **Id** and 21 mg (0.19 mmol) of methoxybenzene in 0.5 ml HSO_3F at $-50^\circ C$ in 20 min. Yield 25 mg (53%). Oily substance. 1H NMR spectrum ($CDCl_3$), δ , ppm: 1.73 s (3H, Me), 2.03 s (6H, 2Me), 2.33 s (3H, Me), 3.80 s (3H, OMe), 6.76 s (1H, HC=), 6.82 d ($2H_{arom}$, J 8.9 Hz), 6.93 s ($2H_{arom}$), 7.27 d ($2H_{arom}$, J 8.9 Hz). Mass spectrum, m/z (I_{rel} , %): 294 [M]⁺ (57), 279 (100), 250 (66), 173 (29), 147 (29), 135 (23), 43 (57). Found, %: C 81.52; H 7.48. $C_{20}H_{22}O_2$. Calculated, %: C 81.60; H 7.53. *M* 294.16.

(E)-4-(4-Methoxyphenyl)-4-(2,4,6-trimethylphenyl)but-3-en-2-one E-(X) was obtained by keeping a solution of 20 mg (0.07 mmol) of compound **Z-X** in CF_3SO_3H at $20^\circ C$ for 20 h. Yield 10 mg (50%). Oily mixture with initial compound **Z-X** in a ratio 1:1. 1H NMR spectrum ($CDCl_3$), δ , ppm (extricated from the spectrum of isomers mixture): 2.11 s (3H, Me), 2.14 s (6H, 2Me), 2.28 s (3H, Me), 3.80 s (3H, OMe), 6.00 s (1H, HC=), 6.81 d ($2H_{arom}$, J 8.6 Hz), 6.87 s ($2H_{arom}$), 7.15 d ($2H_{arom}$, J 8.6 Hz). Mass spectrum, m/z (I_{rel} , %): 294 [M]⁺ (57), 279 (100), 250 (66), 173 (29), 147 (29), 135 (23), 43 (57). Found, %: C 81.62; H 7.55. $C_{20}H_{22}O_2$. Calculated, %: C 81.60; H 7.53. *M* 294.16.

(Z)-4-(4-Methoxyphenyl)-4-(2,4,6-trimethyl-3-fluorosulfonylphenyl)but-3-en-2-one Z-(XI) was obtained by keeping a solution of 10 mg (0.03 mmol) of compound **Z-X** in 0.5 ml HSO_3F at $-30^\circ C$ for 1.5 h. Yield 12 mg (96%). Oily substance. 1H NMR spectrum ($CDCl_3$), δ , ppm: 2.05 s (3H, Me), 2.07 s (6H, 2Me), 2.40 s (3H, Me), 2.70 s (3H, Me), 3.81 s (3H, OMe), 6.85 d ($2H_{arom}$, J 9.0 Hz), 6.92 s (1H, HC=), 7.14 s ($1H_{arom}$), 7.24 d ($2H_{arom}$, J 9.0 Hz). Mass spectrum, m/z (I_{rel} , %): 376 [M]⁺ (61), 361 (100), 332 (60), 135 (60), 131 (32), 108 (30). Found, %: C 63.80; H 5.37. $C_{20}H_{21}FO_4S$. Calculated, %: C 63.81; H 5.62. *M* 376.11.

(Z)-3-(2,4,6-Trimethylphenyl)-1,3-diphenylpropenone Z-(XII) was obtained from 50 mg (0.2 mmol) of compound **IIb** and 78 mg (1 mmol) of benzene in 2 ml of CF_3SO_3H at $10^\circ C$ in 20 min. Yield 40 mg (62%). Oily substance. IR spectrum, ν , cm^{-1} : 1640 (C=O), 1660 (C=O), 1700 (C $\equiv$ C). 1H NMR spectrum ($CDCl_3$), δ , ppm: 2.04 s (6H, 2CH₃), 2.30 s (3H, CH₃), 6.88 s ($2H_{arom}$), 7.34–7.37 m ($3H_{arom}$), 7.41–7.45 m ($4H_{arom}$), 7.52 t ($1H_{arom}$, J 7.4 Hz), 7.63 s (1H, HC=), 7.95 d ($2H_{arom}$, J 7.4 Hz). Mass spectrum, m/z (I_{rel} , %): 326 [M]⁺ (67),

311 (89), 249 (10), 235 (14), 221 (40), 220 (100), 206 (29), 115 (31), 105 (87), 91 (24), 77 (71). Found, %: C 88.40; H 6.70. $C_{24}H_{22}O$. Calculated, %: C 88.31; H 6.79. *M* 326.17.

(Z)-4-(4-Methoxyphenyl)-4-(2,3,5,6-tetramethylphenyl)but-3-en-2-one Z-(XIII) was obtained from 60 mg (0.3 mmol) of compound **Ie** and 38 mg (0.36 mmol) of methoxybenzene in 1 ml of HSO_3F at $-75^\circ C$ in 0.5 h. Yield 10 mg (9%). Oily substance. 1H NMR spectrum ($CDCl_3$), δ , ppm: 1.65 s (3H, Me), 1.97 s (6H, 2Me), 2.24 s (6H, 2Me), 3.80 s (3H, OMe), 6.78 s (1H, HC=), 6.82 d ($2H_{arom}$, J 8.9 Hz), 7.00 s ($1H_{arom}$), 7.27 d ($2H_{arom}$, J 8.9 Hz). Mass spectrum, m/z (I_{rel} , %): 308 [M]⁺ (56), 293 (100), 264 (95), 246 (27), 187 (27), 157 (22), 43 (62). Found, %: C 81.85; H 7.90. $C_{21}H_{24}O_2$. Calculated, %: C 81.78; H 7.84. *M* 308.18.

(Z)-4-(Pentamethylphenyl)-4-phenylbut-3-en-2-one Z-(XIVa) was obtained from 26 mg (0.12 mmol) of compound **If** and 38 mg (0.36 mmol) of benzene in 1.5 ml of CF_3SO_3H at $20^\circ C$ in 0.75 h. Yield 24 mg (68%), mp $84-85^\circ C$ ($49.2-50.5^\circ C$ [11]). 1H NMR spectrum ($CDCl_3$), δ , ppm: 1.68 s (3H, Me), 2.03 s (6H, 2Me), 2.22 s (6H, 2Me), 2.28 s (3H, Me), 6.82 s (1H, HC=), 7.30–7.35 m ($5H, H_{arom}$).

(Z)-4-(4-Methoxyphenyl)-4-(pentamethylphenyl)but-3-en-2-one Z-(XIVb) was obtained from 30 mg (0.14 mmol) of compound **If** and 18 mg (0.17 mmol) of methoxybenzene in 1 ml of HSO_3F at $-75^\circ C$ in 1.5 h. Yield 18 mg (40%), mp $129-131^\circ C$. 1H NMR spectrum ($CDCl_3$), δ , ppm: 1.64 s (3H, Me), 2.01 s (6H, 2Me), 2.23 s (6H, 2Me), 2.28 s (3H, Me), 3.79 s (3H, OMe), 6.77 s (1H, HC=), 6.82 d ($2H_{arom}$, J 8.9 Hz), 7.29 d ($2H_{arom}$, J 8.9 Hz). Mass spectrum, m/z (I_{rel} , %): 322 [M]⁺ (55), 307 (100), 278 (90), 264 (31), 263 (31), 249 (24), 201 (26), 43 (60). Found, %: C 82.03; H 8.17. $C_{22}H_{26}O_2$. Calculated, %: C 81.95; H 8.13. *M* 322.19.

(E)-4-(4-Methoxyphenyl)-4-phenylbut-3-en-2-one E-(XVa) and (Z)-4-(4-methoxyphenyl)-4-phenylbut-3-en-2-one Z-(XVa) were obtained from 30 mg (0.17 mmol) of compound **Ig** and 27 mg (0.34 mmol) of benzene in a mixture of 1 ml of CF_3SO_3H and 0.5 ml of CH_2Cl_2 at $-30^\circ C$ in 20 min. Oily mixture of isomers **E-(XVa)** [28 mg (65%)] and **Z-(XVa)** [14 mg (33%)].

Compound **E-XVa**. 1H NMR spectrum ($CDCl_3$), δ , ppm (extricated from the spectrum of isomers mixture): 1.83 s (3H, CH₃), 3.81 s (3H, OCH₃), 6.54 s (1H, HC=), 6.80–7.22 m ($9H_{arom}$).

Compound **Z-XVa**. 1H NMR spectrum ($CDCl_3$), δ , ppm (extricated from the spectrum of isomers mixture):

1.91 s (3H, CH₃), 3.85 s (3H, OCH₃), 6.49 s (1H, HC=), 6.80–7.22 m (9H_{arom}). Mass spectrum (isomers mixture), *m/z* (*I*_{rel}, %): 252 [*M*]⁺ (100), 237 (84), 213 (12), 165 (22), 135 (30), 105 (18), 43 (16). Found, %: C 80.90; H 6.32. C₁₇H₁₆O₂. Calculated, %: C 80.93; H 6.39. *M* 252.12.

4,4-Bis(4-methoxyphenyl)but-3-en-2-one (XVb) was obtained from 50 mg (0.29 mmol) of compound **Ig** and 48 mg (0.44 mmol) of methoxybenzene in 1 ml of HSO₃F at –75°C in 1 h. Yield 57 mg (70%), mp 85–86°C. IR spectrum, ν, cm^{–1}: 1650 (C=O). ¹H NMR spectrum (CDCl₃), δ, ppm: 1.86 s (3H, Me), 3.80 s (3H, OMe), 3.84 s (3H, OMe), 6.46 s (1H, HC=), 6.83 d (2H_{arom}, *J* 8.7 Hz), 6.92 d (2H_{arom}, *J* 8.6 Hz), 7.12 d (2H_{arom}, *J* 8.6 Hz), 7.22 d (2H_{arom}, *J* 8.7 Hz). ¹³C NMR spectrum (CDCl₃), δ, ppm: 30.13 q (*J* 127.2 Hz), 55.22 q (*J* 144.1 Hz), 55.27 q (*J* 144.1 Hz), 113.71 d.d (*J* 159.4, 3.8 Hz), 113.71 d.d (*J* 159.4, 3.8 Hz), 125.73 d (*J* 155.6 Hz), 130.05 d.d (*J* 150.1, 7.2 Hz), 131.23 d.d (*J* 150.5, 7.2 Hz), 131.27 quintet (*J* 8.2 Hz), 133.54 quintet (*J* 6.9 Hz), 153.91 s, 160.19 m, 160.79 m, 200.19 q (*J* 5.1 Hz). Mass spectrum, *m/z* (*I*_{rel}, %): 282 [*M*]⁺ (83), 281 (48), 267 (98), 135 (100), 135 (30), 43 (36). Found, %: C 76.62; H 6.45. C₁₈H₁₈O₃. Calculated, %: C 76.57; H 6.43. *M* 282.13.

(Z)-4-(4-Acetyl-2,3,5,6-tetramethylphenyl)-4-(4-methoxyphenyl)but-3-en-2-one Z-(XVc) was obtained from 50 mg (0.29 mmol) of compound **Ig** and 51 mg (0.29 mmol) of 1-acetyl-2,3,5,6-tetramethylbenzene in 1 ml of HSO₃F at –75°C in 20 min. Yield 10 mg (10%). Oily substance. IR spectrum, ν, cm^{–1}: 1620 (C=O), 1690 (C=O). ¹H NMR spectrum (CDCl₃), δ, ppm: 1.77 s (3H, Me), 1.98 s (6H, 2Me), 2.14 s (6H, 2Me), 2.51 s (3H, Me), 3.80 s (3H, OMe), 6.82 s (1H, HC=), 6.83 d (2H_{arom}, *J* 8.9 Hz), 7.25 d (2H_{arom}, *J* 8.9 Hz). Mass spectrum, *m/z* (*I*_{rel}, %): 351 [*M* + 1]⁺ (12), 350 [*M*]⁺ (48), 335 (70), 306 (34), 263 (34), 229 (17), 175 (10), 160 (10), 135 (11), 43 (100). Found, %: C 78.85; H 7.56. C₂₃H₂₆O₃. Calculated, %: C 78.83; H 7.48. *M* 350.19.

(Z)-4-(4-Methoxyphenyl)-4-(2,3,5,6-tetramethyl-4-fluorosulfonylphenyl)but-3-en-2-one Z-(XVd) was obtained from 50 mg (0.29 mmol) of compound **Ig** and 95 mg (0.44 mmol) of 1,2,4,5-tetramethyl-3-fluoro-sulfonylbenzene in 2 ml of HSO₃F at –75°C in 1.5 h. Yield 51 mg (45%). Oily substance. ¹H NMR spectrum (CDCl₃), δ, ppm: 2.03 s (3H, Me), 2.06 s (6H, 2Me), 2.58 s (6H, 2Me), 3.80 s (3H, OMe), 6.86 d (2H_{arom}, *J* 8.9 Hz), 6.90 s (1H, HC=), 7.22 d (2H_{arom}, *J* 8.9 Hz). Mass spectrum, *m/z* (*I*_{rel}, %): 390 [*M*]⁺. Found, %:

C 64.65; H 5.96. C₂₁H₂₃FO₄S. Calculated, %: C 64.60; H 5.94. *M* 390.13.

(E)-Ethyl 4-(4-methylphenyl)-4-(4-methoxyphenyl)-2-oxobut-3-enoate E-(XVIa) and (Z)-ethyl 4-(4-methylphenyl)-4-(4-methoxyphenyl)-2-oxobut-3-enoate Z-(XVIa) were obtained from 22 mg (0.1 mmol) of compound **IVa** and 13 mg (0.12 mmol) of methoxybenzene in 1.5 ml of CF₃SO₃H at –30°C in 15 min. Oily mixture of isomers *E*-**XVIa** [6 mg (18%)] and *Z*-**XVIa** [6 mg (18%)].

Compound *E*-**XVIa**. ¹H NMR spectrum (CDCl₃), δ, ppm (extricated from the spectrum of isomers mixture): 1.18 t (3H, Me, *J* 7.2 Hz), 2.38 s (3H, Me), 3.83 s (3H, OMe), 3.90 q (2H, CH₂, *J* 7.2 Hz), 6.78 s (1H, HC=), 6.89 d (2H_{arom}, *J* 9.0 Hz), 7.17 d (2H_{arom}, *J* 8.3 Hz), 7.18 d (2H_{arom}, *J* 9.0 Hz), 7.24 d (2H_{arom}, *J* 8.3 Hz).

Compound *Z*-**XVIa**. ¹H NMR spectrum (CDCl₃), δ, ppm (extricated from the spectrum of isomers mixture): 1.17 t (3H, Me, *J* 7.2 Hz), 2.39 s (3H, Me), 3.83 s (3H, OMe), 3.86 q (2H, CH₂, *J* 7.2 Hz), 6.82 s (1H, HC=), 6.86 d (2H_{arom}, *J* 8.9 Hz), 7.11 d (2H_{arom}, *J* 8.4 Hz), 7.17 d (2H_{arom}, *J* 8.4 Hz), 7.31 d (2H_{arom}, *J* 8.9 Hz). Mass spectrum (isomers mixture), *m/z* (*I*_{rel}, %): 324 [*M*]⁺ (4), 251 (100), 135 (15), 119 (11). Found, %: C 74.10; H 6.26. C₂₀H₂₀O₄. Calculated, %: C 74.06; H 6.21. *M* 324.14.

(Z)-Ethyl 4-(4-methoxyphenyl)-2-oxobut-4-(2,4,6-trimethylphenyl)-3-enoate Z-(XVIb) was obtained from 29 mg (0.12 mmol) of compound **IVb** and 16 mg (0.15 mmol) of methoxybenzene in 1 ml of HSO₃F at –75°C in 1.5 h. Yield 8 mg (19%). Oily substance. ¹H NMR spectrum (CDCl₃), δ, ppm: 1.19 t (3H, Me, *J* 7.2 Hz), 2.00 s (6H, 2Me), 2.30 s (3H, Me), 3.81 s (3H, OMe), 3.83 q (2H, CH₂, *J* 7.2 Hz), 6.85 d (2H_{arom}, *J* 8.9 Hz), 6.88 s (2H_{arom}), 7.15 s (1H, HC=), 7.34 d (2H_{arom}, *J* 8.6 Hz). Mass spectrum, *m/z* (*I*_{rel}, %): 352 [*M*]⁺ (6), 279 (100), 147 (30), 135 (25), 119 (6), 43 (2). Found, %: C 74.93; H 6.81. C₂₂H₂₄O₄. Calculated, %: C 74.98; H 6.86. *M* 352.17.

Ethyl 4,4-bis(4-methoxyphenyl)-2-oxobut-3-enoate (XVIc) was obtained from 51 mg (0.22 mmol) of compound **IVc** and 24 mg (0.22 mmol) of methoxybenzene in 1 ml HSO₃F at –75°C in 1 h. Yield 20 mg (27%). Oily substance. IR spectrum, ν, cm^{–1}: 1620 (C=O), 1715 (C=O). ¹H NMR spectrum (CDCl₃), δ, ppm: 1.18 t (3H, Me, *J* 7.2 Hz), 3.83 s (3H, OMe), 3.84 s (3H, OMe), 3.90 q (2H, CH₂, *J* 7.2 Hz), 6.77 s (1H, HC=), 6.87 d (2H_{arom}, *J* 8.8 Hz), 6.89 d (2H_{arom}, *J* 8.6 Hz), 7.17 d (2H_{arom}, *J* 8.6 Hz), 7.31 d (2H_{arom}, *J* 8.8 Hz). Mass spectrum, *m/z* (*I*_{rel}, %): 340 [*M*]⁺ (6), 267 (100), 248 (6),

135 (45). Found, %: C 70.65; H 6.05. $C_{20}H_{20}O_5$. Calculated, %: C 70.57; H 5.92. M 340.13.

4-Hydroxy-4-(4-methylphenyl)-2-oxobut-3-enoic acid (XIXa) was obtained by keeping a solution of 50 mg (0.23 mmol) of compound **IVa** in 1 ml HSO_3F at $-50^\circ C$ for 15 min. Yield 40 mg (85%), mp $135-137^\circ C$ (decomp.). 1H NMR spectrum $[(CD_3)_2SO]$, δ , ppm: 2.40 C (3H, Me), 7.08 C (1H, HC=), 7.39 d ($2H_{arom}$, J 8.4 Hz), 7.98 d ($2H_{arom}$, J 8.4 Hz). ^{13}C $[(CD_3)_2SO]$, δ , ppm: 21.3 q.t (J 127.0, 4.3 Hz), 97.7 d (J 169.4 Hz), 128.0 d.d (J 161.4, 6.1 Hz), 129.7 d of quintets (J 160.9, 5.2 Hz), 132.0 t (J 7.1 Hz), 144.9 m, 163.2 d (J 2.2 Hz), 169.7 C, 190.5 m. Mass spectrum, m/z (I_{rel} , %): 206 [M]⁺ (27), 161 (100), 119 (22), 115 (5), 69 (84). Found, %: C 63.89; H 4.91. $C_{11}H_{10}O_4$. Calculated, %: C 64.07; H 4.89. M 206.06.

4-Hydroxy-4-(4-methoxyphenyl)-2-oxobut-3-enoic acid (XIXc) was obtained by keeping a solution of 51 mg (0.22 mmol) of compound **IVc** in 2 ml of CF_3SO_3H at $-30^\circ C$ for 0.5 h followed by the treatment and workup of the reaction mixture analogously to common procedures after alkenylation. Yield 10 mg (20%), mp $180^\circ C$ (decomp.). IR spectrum, ν , cm^{-1} : 1680 (C=O), 3300 (O–H). 1H NMR spectrum $[(CD_3)_2SO]$, δ , ppm: 3.87 s (3H, OMe), 7.06 s (1H, HC=), 7.10 d ($2H_{arom}$, J 8.9 Hz), 8.07 d ($2H_{arom}$, J 8.9 Hz). 1H NMR spectrum ($CDCl_3$), δ , ppm: 3.90 s (3H, OMe), 7.99 d ($2H_{arom}$, J 8.9 Hz), 8.09 s (1H, HC=), 8.99 d ($2H_{arom}$, J 8.9 Hz), 15.40 br.s (2H, OH, COOH). Found, %: C 59.60; H 4.59. $C_{11}H_{10}O_5$. Calculated, %: C 59.46; H 4.54.

(Z)-Diethyl 2-(4-methoxyphenyl)-2-(2,4,6-trimethylphenyl)ethenylphosphonate Z-(XXa) was obtained from 28 mg (0.11 mmol) of compound **Va** and 17 mg (0.16 mmol) of methoxybenzene in 1 ml of HSO_3F at $-75^\circ C$ in 15 min. Yield 11 mg (28%). Oily substance. 1H NMR spectrum ($CDCl_3$), δ , ppm: 1.15 t (6H, $2CH_3$, J 7.0 Hz), 2.10 s (6H, 2Me), 2.29 s (3H, Me), 3.78 s (3H, OMe), 3.85 s (4H, $2CH_2$, J 7.0 Hz), 6.36 d (1H, HC=, J 16.6 Hz), 6.82 d ($2H_{arom}$, J 8.9 Hz), 6.88 s ($2H_{arom}$), 7.23 d ($2H_{arom}$, J 8.9 Hz). Mass spectrum, m/z (I_{rel} , %): 388 [M]⁺ (8), 279 (4), 250 (100), 235 (16), 148 (12). Found, %: C 68.10; H 7.56. $C_{22}H_{29}O_4P$. Calculated, %: C 68.03; H 7.53. M 388.18.

(Z)-Diethyl 2,2-bis(4-methoxyphenyl)ethenylphosphonate Z-(XXb) was obtained from 48 mg (0.18 mmol) of compound **Vb** and 28 mg (0.26 mmol) of methoxybenzene in 1 ml HSO_3F at $-75^\circ C$ in 15 min. Yield 14 mg (20%). Oily substance. 1H NMR spectrum

($CDCl_3$), δ , ppm: 1.14 t (6H, $2CH_3$, J 7.1 Hz), 3.80 s (3H, OMe), 3.83 s (3H, OMe), 3.85–3.94 m (4H, $2CH_2$), 5.99 d (1H, HC=, J 15.6 Hz), 6.82 d ($2H_{arom}$, J 8.7 Hz), 6.89 d ($2H_{arom}$, J 8.6 Hz), 7.22 d ($2H_{arom}$, J 8.7 Hz), 7.32 d ($2H_{arom}$, J 8.6 Hz). Mass spectrum, m/z (I_{rel} , %): 377 [M + 1]⁺ (12), 376 [M]⁺ (44), 319 (10), 266 (13), 240 (100), 225 (94), 160 (15), 135 (19). Found, %: C 63.90; H 6.71. $C_{20}H_{25}O_5P$. Calculated, %: C 63.82; H 6.69. M 376.14.

4,7-Dimethyl-3-(4-methylphenyl)-1-trifluoromethylinden-1-ol (XXI) was obtained from 51 mg (0.24 mmol) of compound **IIIa** and 51 mg (0.48 mmol) of 1,4-dimethylbenzene in 1 ml of HSO_3F at $-50^\circ C$ in 1 h. Yield 8 mg (10%). Oily substance. 1H NMR spectrum ($CDCl_3$), δ , ppm: 2.06 s (3H, Me), 2.33 s (3H, Me), 2.33 s (1H, OH), 6.74 s (1H, HC=), 6.94 d (1H_{arom}, J 7.7 Hz), 7.06 d (1H_{arom}, J 7.7 Hz), 7.11 d (2H_{arom}, J 7.9 Hz), 7.22 d (2H_{arom}, J 7.9 Hz). Mass spectrum, m/z (I_{rel} , %): 318 [M]⁺ (100), 303 (15), 249 (59), 226 (34), 221 (6), 206 (13), 129 (13), 92 (32). Found, %: C 71.73; H 5.41. $C_{19}H_{17}F_3O$. Calculated, %: C 71.69; H 5.38. M 318.12.

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