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Dedicated to Full Member of the Russian Academy of Sciences N.S. Zefirov on His 70th Anniversary

Reactions of Vinyl Type Carbocations Generated in Fluorosulfonic Acid with Benzene Derivatives. New Synthesis of Alkyl 3,3-Diarylpropenoates

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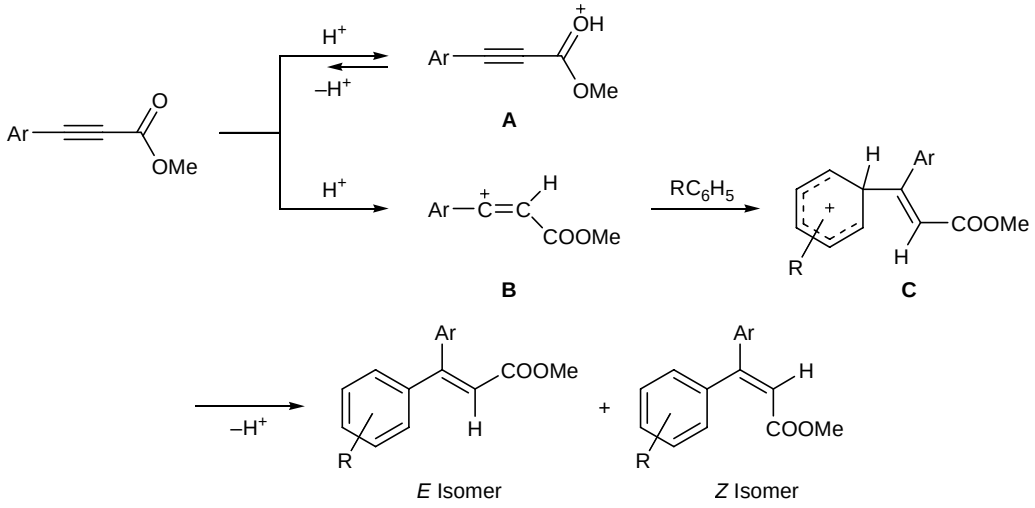
Abstract—Vinyl type carbocations $ArC^+=CHX$ [X = CO_2H, CO_2Alk, C≡N, $P(O)(OAlk)_2$] generated from alkyl 3-arylpropynoates and related compounds in fluorosulfonic acid at –75 to –20°C react with various benzene derivatives, following the mechanism of electrophilic substitution of hydrogen. A new procedure for the synthesis of alkyl 3,3-diarylpropenoates having various substituents in the aryl fragments has been developed on the basis of protonation of the triple bond in alkyl 3-arylpropynoates.

Acetylenic compounds and products of their various transformations are widely used in the preparation of practically important substances, materials, and compositions; therefore, theoretical, synthetic, and applied aspects of the reactivity of these compounds are continuously and extensively studied [1]. A new line in the chemistry of alkynes is alkenylation of arenes with acetylene derivatives in the presence of Lewis acids, such as $Sc(OTf)_3$ and $Hf(OTf)_4$ [2], or catalysts based on palladium(II) complexes [3].

While studying transformations of acetylenic compounds in superacids [4–10] we have revealed a key reaction based on protonation of the triple bond in acetylene derivative to give vinyl type carbocation which then reacts with appropriate aromatic substrate [6–8]. It seems to be reasonable to estimate the synthetic potential of this new reaction and its scope upon variation of donor–acceptor properties of substituents in the acetylenic and aromatic components. Scheme 1 illustrates the reaction mechanism which involves

Scheme 1.



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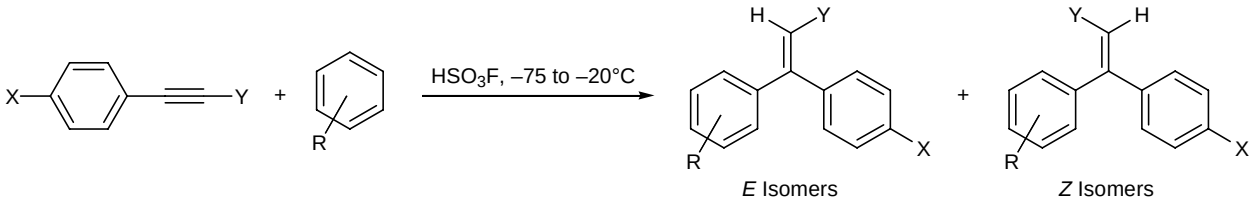
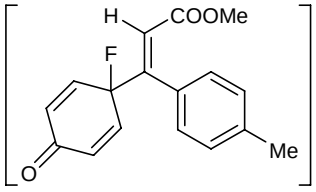
Scheme 2.

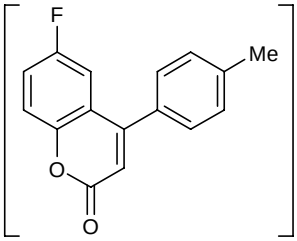


I–VIII **IX**, **Xa–Xl**, **XIa–XIh**, **XIIa–XIIc**, **XIIIa**, **XIIIb**, **XIVa**, **XIVb** **XVa–XVc**, **XVIa**, **XVIb**

I, **IX**, X = MeO, Y = CO_2Me, R = 4-MeO (**a**); **II**, **X**, X = Me, Y = CO_2Me, R = 2,3,5,6-Me_4 (**a_1**), 2,3,5,6-Me_4(MeOCOCH=CTol-4) (**a_2**), 2-Me-5-MeOCOC≡C (**b_1**), 2-MeOCOC≡C-5-Me (**b_2**), 2,3,5,6-Me_4-4-NC CH_2 (**c**), 2,3,5,6-Me_4-4-NC (**d**), 2,3,5,6-Me_4-4-MeCO (**e**), 2,3,5,6-Me_4-4-FSO_2 (**f**), 2,4,6-Me_3-3-O_2N (**g**), 3-F-4-MeO (**h**), 2-EtO-5-Br (**i**), 3,4-$(MeO)_2$ (**j**), 2-MeO-5-F (**k_1**); **III**, **XI**, X = H, Y = CO_2Me, R = H (**a**), 4-*t*-Bu (**b**), 2,4-Me_2 (**c**), 2,3-Me_2 (**d_1**), 3,4-Me_2 (**d_2**), 2,5-Me_2 (**e**), 2,4,5-Me_3 (**f**), 2,3,5,6-Me_4-4-H_2N (**g**), 2-MeO-5-F (**h**); **IV**, **XII**, X = F, Y = CO_2Me, R = 2,3,5,6-Me_4-4-FSO_2 (**a**), 3,4-Cl_2 (**b**), 2,5-$(MeO)_2$ (**c**); **V**, **XIII**, X = I, Y = CO_2Et, R = 2,3,5,6-Me_4-4-MeCO (**a**); X = 3-O_2N-4-MeO, Y = CO_2Et, R = 2,3,5,6-Me_4-4-MeCO (**b**); **VI**, **XIV**, X = H, Y = CO_2H, R = 2,3,5,6-Me_4 (**a**), 2,3,5,6-Me_4-4-MeCO (**b**); **VII**, **XV**, X = H, Y = CN, R = 2,3,5,6-Me_4-4-FSO_2 (**a**), X = 4-Cl, Y = 4-NCC_6H_4, R = 2,3,5,6-Me_4-4-MeCO (**b**); X = H, Y = 4-$MeOCOC_6H_4$, R = 2,3,5,6-Me_4-4-MeCO (**c**); **VIII**, **XVI**, X = H, Y = P(O)$(OEt)_2$, R = 2,3,5,6-Me_4-4-FSO_2 (**a**), 3,4-$(MeO)_2$ (**b**).



E-**Xk**$_2$

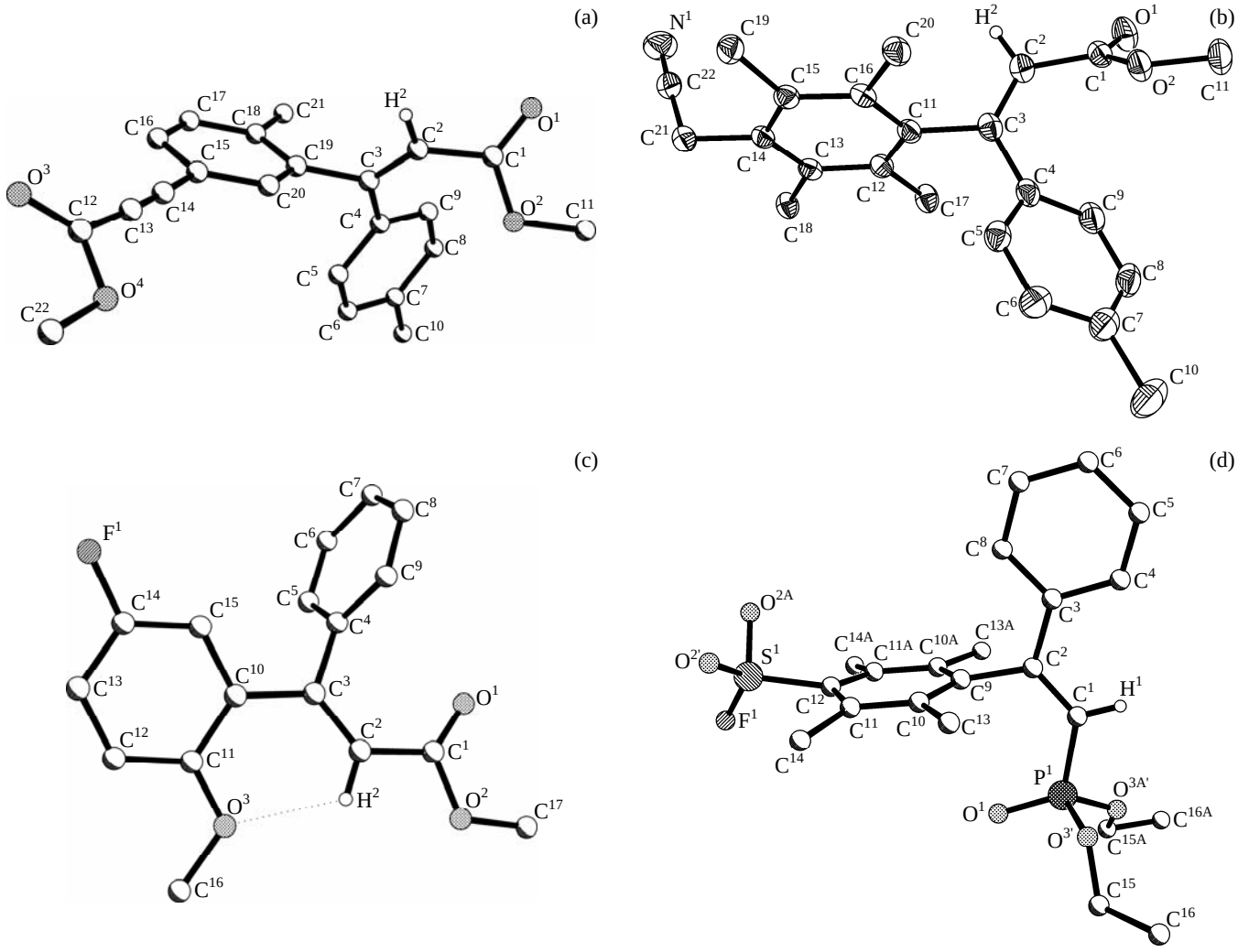


XI$_1$

equilibrium protonation of methyl 3-arylpropynoate at the carbonyl oxygen atom with formation of a fairly stable cation **A** (O-protonation) [9]. Slow protonation of carbon atom at the triple bond leads to reactive ion **B** (C-protonation) which reacts with appropriate aromatic substrate to afford arenium ion **C**. Deprotonation of the latter yields methyl (*E*)- or/and (*Z*)-3,3-diarylpropenoates.

The set of the examined acetylenic (compounds **I**–**VIII**) and aromatic substrates is shown in Scheme 2; no special numbering was used for aromatic substrates, for their structure unambiguously follows from the structure of the corresponding alkenylation products. The experimental conditions were selected with account taken of the reactivity of type **B** carbocations and arene nucleophilicity. The configuration (*E* or *Z*) of products **IX**–**XVI** was determined on the basis of the ^{1}H NMR data (see Experimental) and the X-ray diffraction data for compounds *E*-**Xb$_1$**, *E*-**Xc**, *E*-**XIi**, and *Z*-**XVIa** (see figure). The *E* isomers of **IX**–**XVI** characteristically showed in the ^{1}H NMR spectra a signal at δ δ 5.32–6.30 ppm from the vinyl =CH– proton, while the corresponding signal of the *Z* isomers was located in a weaker field (δ 6.28–6.66 ppm), in keeping with published data [3]. The maximal difference in the chemical shifts of that proton between the *Z* and *E* isomers, $\Delta\delta = \delta_Z - \delta_E$ = 0.78–0.89 ppm, was observed for compounds **Xa$_1$**, **Xf**, **XIVa**, and **XVIa** with sterically loaded aromatic fragments due to magnetically anisotropic properties of the latter. According to the X-ray diffraction data for compound *E*-**Xc**, the dihedral angle between the $C^{11}C^{12}C^{13}$ and $C^3C^2H^2$ planes is 97.6°, so that the vinyl proton appears above the plane of the tetramethyl-substituted benzene ring. In the ^{1}H NMR spectrum of *E*-**Xc**, the H^2 signal is located at δ 5.79 ppm. For comparison, the corresponding proton in structure *Z*-**XVIa** (see figure) resides at the side of the phenyl ring (in the deshielded region), and it resonates in a weaker field (δ 6.53 ppm; cf. δ 5.66 ppm for *E*-**XVIa**).

By analogy with the previously described addition of superacids (HSO_3F and CF_3SO_3H) to 3-arylpropynoic acid derivatives [9], the reactions of acetylenic compounds examined in the present work (Scheme 2) occur as *syn* addition of proton and aryl residue at the triple bond, yielding at –75°C mainly *E* isomers of **IX**–**XVI**. Above –50°C, the *E* isomers are converted into the corresponding *Z* isomers (*anti*-addition products).



Structure of molecules (a) *E*-**Xb$_1$**, (b) *E*-**Xc**, (c) *E*-**XIi**, and (d) *Z*-**XVIa** according to the X-ray diffraction data (hydrogen atoms, except for vinylic, are not shown).

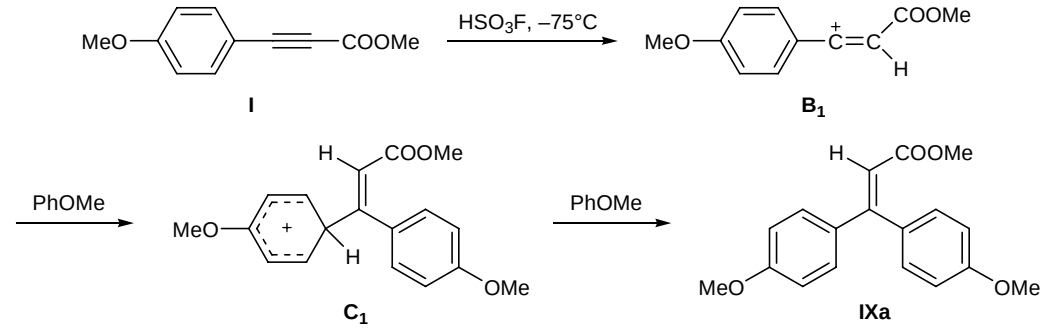
For example, compound *Z*-**Xf** was obtained by keeping a solution of its isomer *E*-**Xf** in fluorosulfonic acid for 1 h at –30°C.

Various aromatic compounds are capable of reacting with carbocations **B** (Schemes 1, 2): unsubstituted benzene, alkylbenzenes, and methoxybenzenes. Ions **B** also effectively react with deactivated compounds (with reduced π-nucleophilicity), e.g., 1,2-dichlorobenzene, and 2,4,6-trimethylnitrobenzoene, as well as with sterically hindered aromatic substrates, such as 1-acetyl-2,3,5,6-tetramethylbenzene, 2,3,5,6-tetramethylbenzonitrile, etc. (see Experimental). Less nucleophilic systems like methyl 4-methoxybenzoate and 4-methylnitrobenzene failed to produce alkenylation products in reactions with compounds **II** and **IV**.

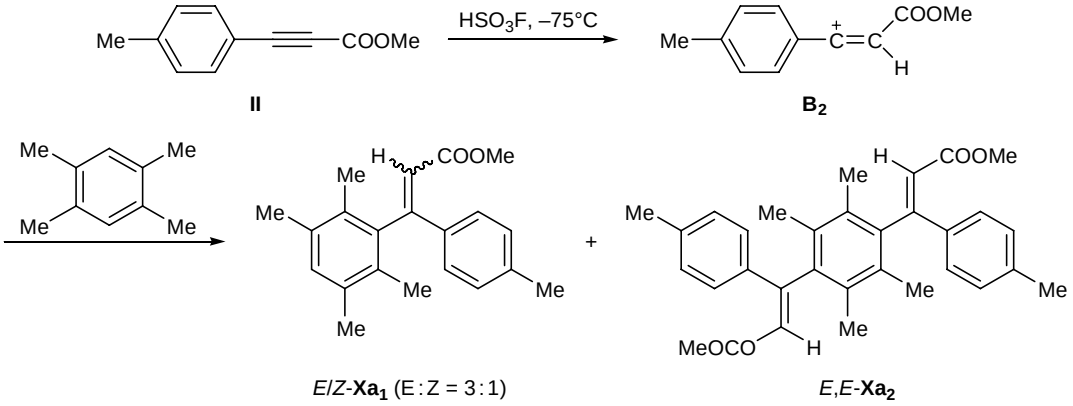
Let us consider particular reactions of vinyl type cations **B** with various benzene derivatives. Dissolution of ester **I** in HSO_3F in the presence of anisole gave 3,3-diarylpropenoate **IXa** in a good yield. Compound **IXa** is the product of regioselective attack of cation **B$_1$** at the *para* position with respect to the methoxy group (Scheme 3). The reaction with 1,2,4,5-tetramethylbenzene (durene) gives a mixture of mono- and bis-alkylation products. This aromatic substrate in HSO_3F exists mainly as arenium ion [10]; however, just neutral 1,2,4,5-tetramethylbenzene species (which are present in a small concentration) react with cation **B$_2$** generated from methyl 3-(4-methylphenyl)propynoate (**II**). Monoadduct *E*-**Xa$_1$** reacts with **B$_2$** to give *E*,*E*-**Xa$_2$** (Scheme 4). The two steps in the synthesis of bis-adduct *E*,*E*-**Xa$_2$** are stereoselective, but the monoadduct undergoes partial isomerization.

When a solution of acetylenic compound **II** in HSO_3F was kept at –75°C in the absence of aromatic

Scheme 3.

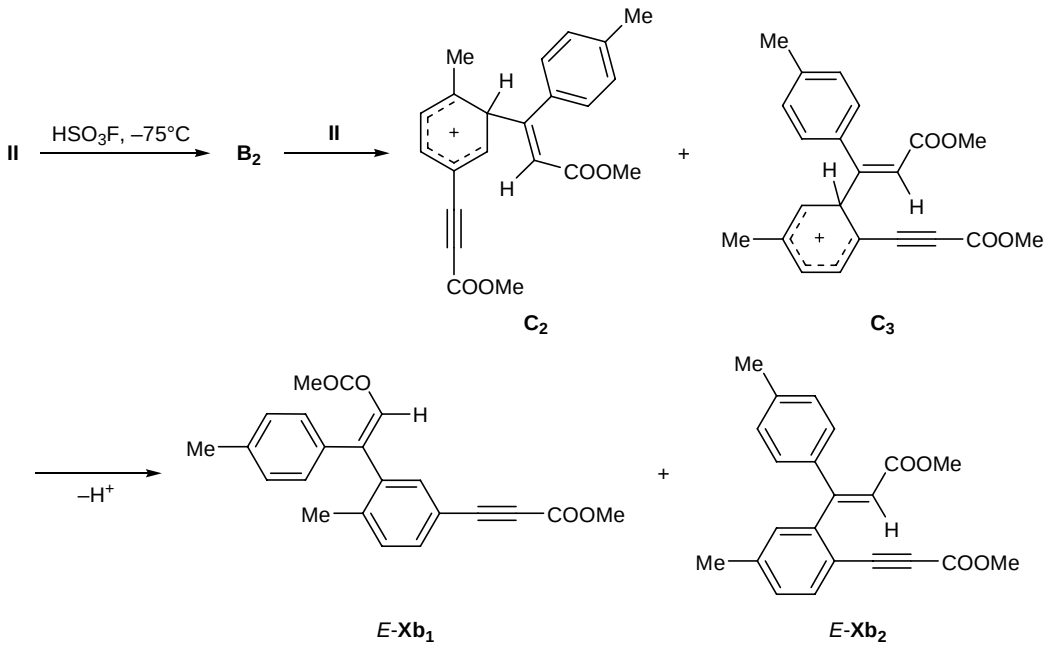


Scheme 4.

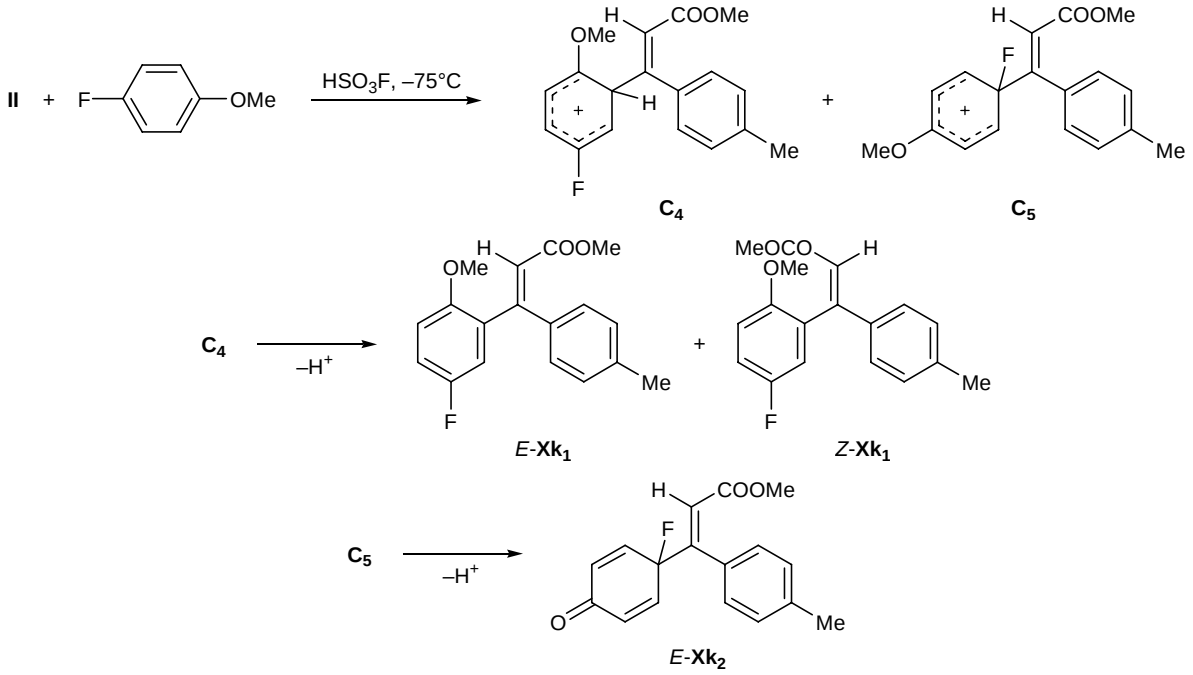


substrate, cation $\mathbf{B_2}$ stereoselectively attacked the tolyl fragment in initial compound **II** to produce arenium ions $\mathbf{C_2}$ and $\mathbf{C_3}$. After deprotonation, final regioisomeric products *E*-$\mathbf{Xb_1}$ and *E*-$\mathbf{Xb_2}$ were isolated (Scheme 5). The structure of *E*-$\mathbf{Xb_1}$ was proved by X-ray analysis (see figure). The relative inertness of the triple bond in compounds *E*-$\mathbf{Xb_1}$ and *E*-$\mathbf{Xb_2}$ to HSO_3F may be rationalized in terms of reduced basicity of the acetylenic carbon atoms due to electron-withdrawing effect of the C(Ar)=$CHCO_2Me$ group.

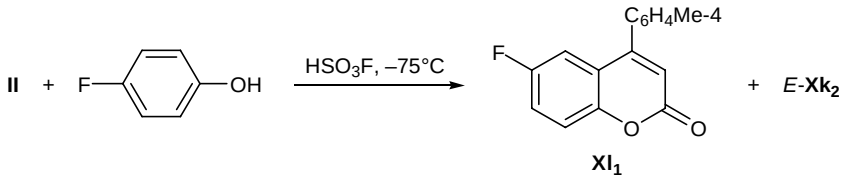
Scheme 5.



Scheme 6.



Scheme 7.



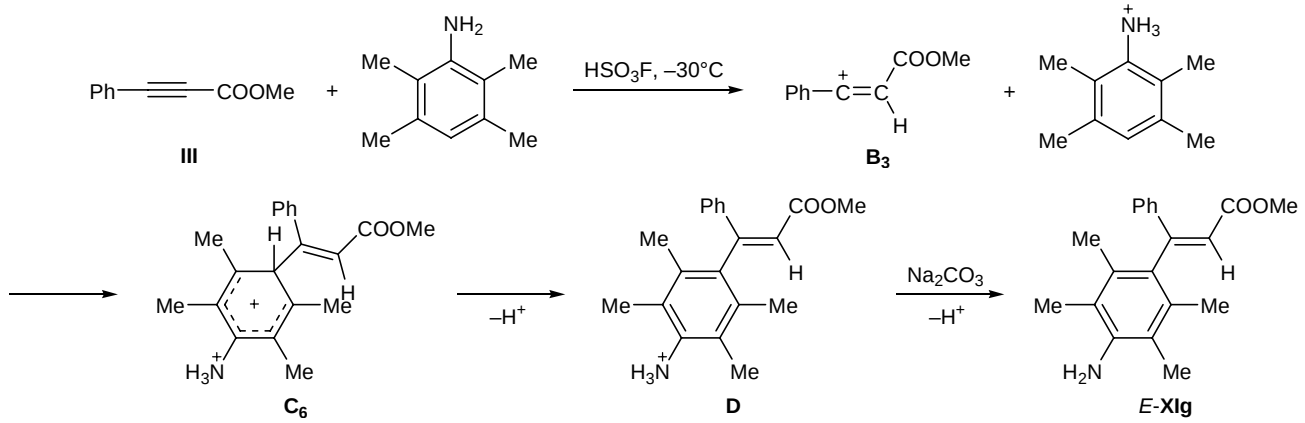
Scheme 6 shows the transformations of ester **II** in reaction with *p*-fluoroanisole. Here, different nucleophilic centers in *p*-fluoroanisole are involved in formation of new covalent bond. Apart from conventional electrophilic substitution of hydrogen, *ipso* attack on the carbon atom attached to fluorine leads to intermediate arenium ion $\mathbf{C_5}$ which undergoes demethylation to give *E*-$\mathbf{Xk_2}$. Under analogous conditions, the reaction of methyl 3-(4-methylphenyl)propynoate (**II**) with *p*-fluorophenol resulted in formation of compound *E*-$\mathbf{Xk_2}$ and intramolecular cyclization product, substituted coumarin $\mathbf{Xl_1}$ (Scheme 7).

2,3,5,6-Tetramethylaniline in fluorosulfonic acid is completely protonated at the nitrogen atom, and it exists exclusively as arylammonium ion [11] (Scheme 8). Therefore, further transformations of ester **III** involve ion $\mathbf{B_3}$ and 2,3,5,6-tetramethylphenylammonium ion, giving rise to "exotic" doubly charged arenium ion $\mathbf{C_6}$ whose deprotonation yields arylammonium ion **D**. The final product (compound *E*-**XIh**) was isolated from the reaction mixture by treatment with a solution of sodium carbonate.

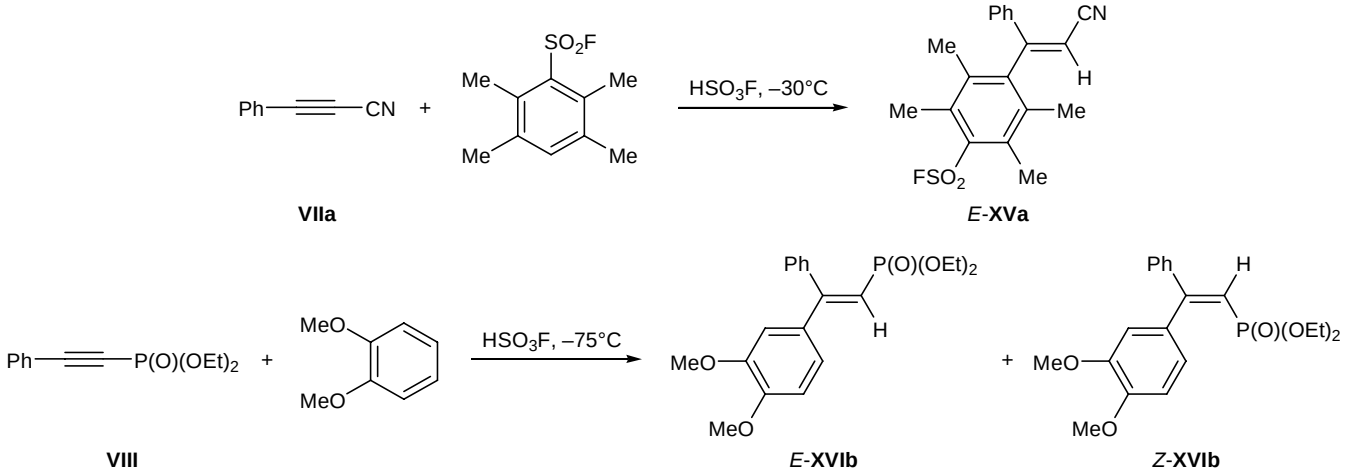
Apart from 3-arylpropynoic acids and their esters **I**–**VI**, other structurally related compounds were brought into reactions with aromatic substrates in HSO_3F. Nitrile **VIIa** and phosphonate **VIII** reacted, respectively, with 2,3,5,6-tetramethylbenzenesulfonyl fluoride and 1,2-dimethoxybenzene to afford the corresponding alkenylation products *E*-**XVa** and *E/Z*-**XVIb** (Scheme 9). Likewise, triarylethenes *Z*-**XVb** and *Z*-**XVc** were obtained by reaction of diarylacetylenes **VIIb** and **VIIc** with 2,3,5,6-tetramethylacetophenone (Scheme 10).

To conclude, we have developed a new procedure for the synthesis of alkyl 3,3-diarylpropenoates and related compounds having various substituents in the aryl fragments. Systematic study of reactions of vinyl type cations generated in HSO_3F with various benzene derivatives has been performed for the first time. A multistep mechanism has been proposed for these reactions. It implies protonation of the triple bond in acetylenic compound to give vinyl type carbocation, followed by addition of aromatic substrate and deprotonation of the arenium ion thus formed.

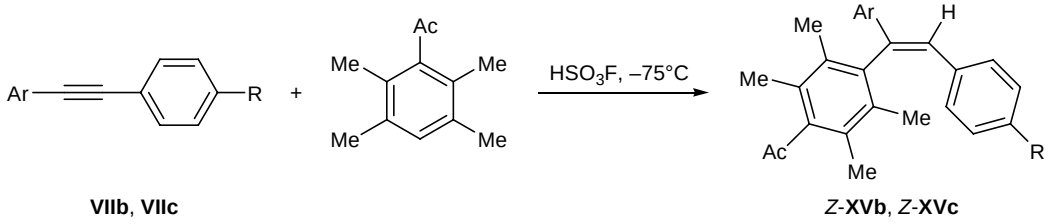
Scheme 8.



Scheme 9.



Scheme 10.



Ar = 4-ClC_6H_4, R = CN (**b**); Ar = Ph, R = MeOCO (**c**).

EXPERIMENTAL

The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker AM-500 spectrometer at 500, 125.76, and 470.7 MHz, respectively, using $CDCl_3$ as solvent. The chemical shifts were measured relative to the solvent signals (^1H: $CHCl_3$, δ 7.25 ppm; ^{13}C: $CDCl_3$, δ_C 77.0 ppm) or $CFCl_3$ (^{19}F: δ_F 0.0 ppm). The IR spectra were obtained on a Specord 75IR spectrometer from solutions in $CHCl_3$. The mass spectra were run on an MKh-1321 instrument. The molecular weights were determined from the high-resolution mass spectra recorded on a Finnigan MAT 8200 spectrometer.

X-Ray analysis of single crystals of compounds *E*-**Xb$_1$**, *E*-**Xc**, *E*-**XIi**, and *Z*-**XVIa** was performed on a Smart APEX automatic diffractometer (MoK_α irradiation, graphite monochromator, ω–θ scanning). The structures were solved by the direct method and were refined with respect to F^2_{hkl} by the least-squares procedure in anisotropic approximation for all non-hydrogen

atoms. Hydrogen atoms were localized by the Fourier difference synthesis, and their positions were refined in isotropic approximation. All calculations were performed with the use of SHELXTL 6.10 software package [12].

The synthesis and properties of acetylene derivatives, methyl 3-(4-methoxyphenyl)propynoate (**I**), methyl 3-(4-methylphenyl)propynoate (**II**), methyl 3-phenylpropynoate (**III**), methyl 3-(4-fluorophenyl)-propynoate (**IV**), ethyl 3-(4-iodophenyl)propynoate (**Va**), ethyl 3-(4-methoxy-3-nitrophenyl)propynoate (**Vb**), 3-phenylpropynoic acid (**VI**), and 3-phenylpropynenitrile (**VIIa**), were reported in [8, 9]. 4-(4-Chlorophenylethynyl)benzonitrile (**VIIb**) and methyl 4-phenylethynylbenzoate (**VIIc**) were described in [13]; and diethyl phenylethynylphosphonate (**VIII**) was synthesized according to [14].

General procedure for reactions of acetylene derivatives I–VIII with aromatic compounds in fluorosulfonic acid. A solution of 0.15–1.12 mmol of aromatic compound in 0.5–1.5 ml of fluorosulfonic acid was cooled to –75 to –20°C, and 0.1–0.5 mmol of acetylene derivative **I–VIII** was slowly added (over a period of 10–30 min) under vigorous stirring. The mixture was stirred for 5–60 min, poured into 15–30 ml of concentrated hydrochloric acid cooled to –60°C, and treated with chloroform (3×30 ml). The combined extracts were washed in succession with water, a saturated aqueous solution of $NaHCO_3$, and water again, dried over Na_2SO_4, and evaporated under reduced pressure (water-jet pump). The residue was subjected to chromatographic separation on silica gel using petroleum ether–ethyl acetate as eluent. The yields of compounds *E*/*Z*-**IX**–**XVI** are given for the products isolated by chromatography.

Methyl 3,3-bis(4-methoxyphenyl)propenoate (IX) was obtained from 32 mg (0.17 mmol) of compound **I** and 80 mg (0.74 mol) of anisole in 1 ml of HSO_3F at –75°C (reaction time 30 min). Yield 27 mg (54%), oily substance. ^{1}H NMR spectrum, δ, ppm: 3.62 s (3H, OMe), 3.81 s (3H, OMe), 3.84 s (3H, OMe), 6.22 s (1H, HC=), 6.83 d (2H, H_{arom}, J = 8.8 Hz), 6.90 d (2H, H_{arom}, J = 8.6 Hz), 7.14 d (2H, H_{arom}, J = 8.6 Hz), 7.23 d (2H, H_{arom}, J = 8.8 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 298 (100) $[M]^+$, 267 (47) $[M - OMe]^+$, 240 (13), 239 (10), 225 (17), 153 (11), 152 (11), 135 (53). Found, %: C 72.31; H 6.19. $C_{18}H_{18}O_4$. Calculated, %: C 72.47; H 6.08. *M* 298.33.

Methyl (*E*)-3-(2,3,5,6-tetramethylphenyl)-3-(4-tolyl)propenoate (*E*-Xa$_1$) was obtained (together with compounds *Z*-**Xa$_1$** and *E*,*E*-**Xa$_2$**) from 96 mg (0.50 mmol) of compound **II** and 70 mg (0.50 mmol) of 1,2,4,5-tetramethylbenzene in 1.5 ml of HSO_3F at –75°C (reaction time 40 min). Chromatographic separation gave 15 mg (10%) of an oily product (a mixture with **II** and *Z*-**Xa$_1$**). ^{1}H NMR spectrum (from the spectrum of the mixture), δ, ppm: 2.09 s (6H, Me), 2.21 s (6H, Me), 2.31 s (3H, Me), 3.69 s (3H, OMe), 5.82 s (1H, HC=), 6.93 s (1H, H_{arom}), 7.06 d (2H, H_{arom}, J = 8.1 Hz), 7.16 d (2H, H_{arom}, J = 8.0 Hz).

Methyl (*Z*)-3-(2,3,5,6-tetramethylphenyl)-3-(4-tolyl)propenoate (*Z*-Xa$_1$) was obtained (together with *E*-**Xa$_1$** and *E*,*E*-**Xa$_2$**) from 96 mg (0.50 mmol) of compound **II** and 70 mg (0.50 mmol) of 1,2,4,5-tetramethylbenzene in 1.5 ml of HSO_3F at –75°C (reaction time 40 min). Chromatographic separation gave 5 mg (3%) of an oily product (a mixture with **II** and *E*-**Xa$_1$**). ^{1}H NMR spectrum (from the spectrum of the mixture), δ, ppm: 2.23 s (6H, Me), 2.31 s (6H, Me), 2.33 s (3H, Me), 3.57 s (3H, OMe), 6.61 s (1H, HC=), 6.96 s (1H, H_{arom}), 7.11 d (2H, H_{arom}, J = 8.2 Hz), 7.22 d (2H, H_{arom}, J = 8.2 Hz).

(*E*,*E*)-1,4-Bis[2-methoxycarbonyl-1-(4-tolyl)-ethenyl]-2,3,5,6-tetramethylbenzene (*E*,*E*-Xa$_2$) was obtained (together with compounds *E*-**Xa$_1$** and *Z*-**Xa$_1$**) from 96 mg (0.50 mmol) of compound **II** and 70 mg (0.50 mmol) of 1,2,4,5-tetramethylbenzene in 1.5 ml of HSO_3F at –75°C (reaction time 40 min). Yield 55 mg (22%), mp 218–220°C. ^{1}H NMR spectrum ($CDCl_3$, a mixture of two atropoisomers, *syn*:*anti* = 1:1), δ, ppm: 2.11 s (12H, Me), 2.13 s (12H, Me), 2.32 s (6H, Me), 2.33 s (6H, Me), 3.69 s (6H, OMe), 3.69 s (6H, OMe), 5.82 s (2H, HC=), 5.85 s (2H, HC=), 7.09 d (4H, H_{arom}, J = 8.2 Hz), 7.10 d (4H, H_{arom}, J = 8.2 Hz), 7.16 d (4H, H_{arom}, J = 8.2 Hz), 7.18 d (4H, H_{arom}, J = 8.2 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 482 (100) $[M]^+$, 467 (18) $[M - Me]^+$, 450 (42), 435 (36), 408 (24), 391 (15), 377 (15), 375 (12), 363 (14), 335 (11), 319 (12), 275 (11), 247 (12), 241 (12), 175 (12), 119 (18), 105 (11), 91 (11), 59 (14). Found, %: C 79.36; H 7.00. $C_{32}H_{34}O_4$. Calculated, %: C 79.64; H 7.10. *M* 482.61.

Methyl (*E*)-3-(5-methoxycarbonylethynyl-2-methylphenyl)-3-(4-tolyl)propenoate (*E*-Xb$_1$) was obtained (together with *E*-**Xb$_2$**) by keeping a solution of 50 mg (0.29 mmol) of compound **II** in 1 ml of HSO_3F for 45 min at –75°C. Yield 64 mg (64%). Compound *E*-**Xb$_1$** was described previously [6].

Methyl (*E*)-3-(2-methoxycarbonylethynyl-5-methylphenyl)-3-(4-tolyl)propenoate (*E*-Xb$_2$) was obtained (together with *E*-**Xb$_1$**) by keeping a solution

of 50 mg (0.29 mmol) of compound **II** in 1 ml of HSO_3F for 45 min at –75°C. Yield 11 mg (11%). Compound *E*-**Xb$_2$** was described previously [6].

Methyl (*E*)-3-(4-cyanomethyl-2,3,5,6-tetramethylphenyl)-3-(4-tolyl)propenoate (*E*-Xc) was obtained from 30 mg (0.17 mmol) of compound **II** and 33 mg (0.19 mmol) of 2-(2,3,5,6-tetramethylphenyl)-acetonitrile in 0.6 ml of HSO_3F at –75°C (reaction time 45 min). Yield 44 mg (75%). Compound *E*-**Xc** was described previously [6].

Methyl (*E*)-3-(4-cyano-2,3,5,6-tetramethylphenyl)-3-(4-tolyl)propenoate (*E*-Xd) was obtained from 30 mg (0.17 mmol) of compound **II** and 32 mg (0.20 mmol) of 2,3,5,6-tetramethylbenzonitrile in 0.6 ml of HSO_3F at –75°C (reaction time 45 min). Yield 15 mg (26%), mp 115–118°C. IR spectrum, ν, cm^{-1}: 1610 (C=C), 1720 (C=O), 2220 (C≡N). ^{1}H NMR spectrum, δ, ppm: 2.14 (6H, Me), 2.32 s (3H, Me), 2.46 s (6H, Me), 3.70 s (3H, OMe), 5.76 s (1H, HC=), 7.09 d (2H, H_{arom}, J = 8.3 Hz), 7.12 d (2H, H_{arom}, J = 8.3 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 333 (69) $[M]^+$, 318 (23) $[M - Me]^+$, 302 (23) $[M - OMe]^+$, 286 (35), 273 (100), 259 (78), 245 (27), 244 (24), 228 (17), 182 (12), 119 (13), 115 (17), 105 (12), 91 (14), 59 (12). Found, %: C 79.51; H 6.87. $C_{22}H_{23}NO_2$. Calculated, %: C 79.25; H 6.95. *M* 333.42.

Methyl (*E*)-3-(4-acetyl-2,3,5,6-tetramethylphenyl)-3-(4-tolyl)propenoate (*E*-Xe) was obtained from 30 mg (0.17 mmol) of compound **II** and 33 mg (0.19 mmol) of 2,3,5,6-tetramethylacetophenone in 0.6 ml HSO_3F at –75°C (reaction time 50 min). Yield 20 mg (33%), mp 116–118°C. IR spectrum, ν, cm^{-1}: 1350, 1435, 1515, 1620, 1695 (C=O), 1725 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.10 s (12H, Me), 2.32 s (3H), 2.48 s (3H, Me), 3.69 s (3H, OMe), 5.79 s (1H, HC=), 7.08 d (2H, H_{arom}, J = 8.0 Hz), 7.14 d (2H, H_{arom}, J = 8.0 Hz). Found, %: C 78.62; H 7.57. $C_{23}H_{26}O_3$. Calculated, %: C 78.83; H 7.48. *M* 350.45.

Methyl (*E*)-3-(4-fluorosulfonyl-2,3,5,6-tetramethylphenyl)-3-(4-tolyl)propenoate (*E*-Xf) was obtained from 30 mg (0.17 mmol) of compound **II** and 41 mg (0.19 mmol) 2,3,5,6-tetramethylbenzenesulfonyl fluoride in 1.5 ml of HSO_3F at –75°C (reaction time 45 min). Yield 25 mg (38%). Compound *E*-**Xf** was described previously in [6].

Methyl (*Z*)-3-(4-fluorosulfonyl-2,3,5,6-tetramethylphenyl)-3-(4-tolyl)propenoate (*Z*-Xf), 7 mg (10%), was obtained together with isomer *E*-**Xf**, 33 mg (50%), from 30 mg (0.17 mmol) of compound **II** and 41 mg (0.19 mmol) of 2,3,5,6-tetramethylbenzenesulfonyl fluoride in 1.0 ml of HSO_3F at –50°C (reaction time 15 min). Compound *Z*-**Xf** was also formed in quantitative yield by keeping a solution of 30 mg (0.08 mmol) of isomer *E*-**Xf** in 0.5 ml of HSO_3F for 60 min at –30°C. Oily substance. ^{1}H NMR spectrum, δ, ppm: 2.06 s (6H, Me), 2.35 s (3H, Me), 2.59 d (6H, Me, J_{HF} = 2.0 Hz), 3.60 s (3H, OMe), 6.66 s (1H, HC=), 7.15 s (1H, H_{arom}). Found, %: C 64.97; H 6.12. $C_{21}H_{23}FO_4S$. Calculated, %: C 64.60; H 5.94. *M* 390.47.

Methyl (*E*)-3-(4-tolyl)-3-(2,4,6-trimethyl-3-nitrophenyl)propenoate (*E*-Xg) was obtained from 60 mg (0.34 mmol) of compound **II** and 62 mg (0.39 mmol) of 1,3,5-tetramethyl-2-nitrobenzene in 1.2 ml of HSO_3F at –75°C (reaction time 45 min). Yield 18 mg (9%), mp 83–85°C. ^{1}H NMR spectrum, δ, ppm: 2.13 s (3H, Me), 2.19 s (3H, Me), 2.27 s (3H, Me), 2.33 s (3H, Me), 3.70 s (3H, OMe), 5.83 s (1H, HC=), 6.99 s (1H, H_{arom}), 7.09 d (2H, H_{arom}, J = 7.9 Hz), 7.12 d (2H, H_{arom}, J = 7.9 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 339 (43) $[M]^+$, 332 (71) $[M - OH]^+$, 308 $[M - OMe]^+$, 290 (100), 262 (18), 248 (14), 233 (22), 219 (22), 202 (28), 174 (15), 119 (25), 91 (14). Found, %: C 70.54; H 6.20. $C_{20}H_{21}NO_4$. Calculated, %: C 70.78; H 6.24. *M* 339.39.

Methyl (*E*)-3-(3-fluoro-4-methoxyphenyl)-3-(4-tolyl)propenoate (*E*-Xh) and methyl (*Z*)-3-(3-fluoro-4-methoxyphenyl)-3-(4-tolyl)propenoate (*Z*-Xh) were obtained as an oily mixture of *E* and *Z* isomers at a ratio of 2:1 [*E*-**Xh**, 18 mg (35%); *Z*-**Xh**, 9 mg (17%)] from 30 mg (0.17 mmol) of compound **II** and 101 mg (0.80 mmol) of 1-fluoro-2-methoxybenzene in 0.6 ml of HSO_3F at –75°C (reaction time 45 min). ^{1}H NMR spectrum (recorded for isomer mixture), δ, ppm: *E*-**Xh**: 2.39 s (3H, Me), 3.61 s (3H, OMe), 3.89 s (3H, OMe), 6.26 s (1H, HC=), 6.72–7.23 m (7H, H_{arom}); *Z*-**Xh**: 2.36 s (3H, Me), 3.63 s (3H, OMe), 3.92 s (3H, OMe), 6.28 s (1H, HC=), 6.72–7.23 m (7H, H_{arom}). Mass spectrum (*E*/*Z*), *m*/*z* (I_{rel}, %): 300 (100) $[M]^+$, 269 (71) $[M - OMe]^+$, 242 (14), 241 (16), 226 (10), 183 (16), 153 (23), 119 (22). Found, %: C 72.30; H 5.50. $C_{18}H_{17}FO_3$. Calculated, %: C 71.99; H 5.71. *M* 300.32.

Methyl (*E*)-3-(5-bromo-2-ethoxyphenyl)-3-(4-tolyl)propenoate (*E*-Xi) was obtained from 30 mg (0.17 mmol) of compound **II** and 140 mg (0.70 mmol) of 1-bromo-4-ethoxybenzene in 0.6 ml HSO_3F at –75°C (reaction time 40 min). Yield 29 mg (45%), mp 99–100°C. ^{1}H NMR spectrum, δ, ppm: 1.06 t (3H, J = 7.0 Hz), 2.34 s (3H, Me), 3.63 s (3H, OMe), 3.79 q (2H, CH_2, J = 7.0 Hz), 6.15 s (1H, HC=), 6.70 d (1H,

H_{arom}, J = 8.7 Hz), 7.10 s (4H, H_{arom}), 7.30 d (1H, H_{arom}, J = 2.4 Hz), 7.36 d (1H, H_{arom}, J = 2.3 Hz), 7.36 d.d (1H, H_{arom}, J = 8.7, 2.3 Hz). Mass spectrum, m/z (I_{rel}, %): 376 (35) $[M + 2]^+$, 374 (34) $[M]^+$, 331 (21), 329 (21) $[M - OEt]^+$, 317 (11), 315 (14), 303 (45), 301 (47), 300 (27), 288 (27), 286 (27), 222 (100), 208 (15), 207 (18), 179 (30), 178 (36), 165 (18), 152 (15), 89 (11), 59 (18). Found, %: C 60.63; H 5.06. $C_{19}H_{19}BrO_3$. Calculated, %: C 60.81; H 5.10. *M* 375.26.

Methyl (*E*)-3-(3,4-dimethoxyphenyl)-3-(4-tolyl)-propenoate (*E*-Xj) was obtained from 30 mg (0.17 mmol) of compound **II** and 100 mg (0.72 mmol) of 1,2-dimethoxybenzene in 0.6 ml of HSO_3F at –75°C (reaction time 45 min). Yield 9 mg (17%), mp 98–101°C. ^{1}H NMR spectrum, δ, ppm: 2.39 s (3H, Me), 3.61 s (3H, OMe), 3.88 s (3H, OMe), 6.27 s (1H, HC=), 6.77 d (1H, H_{arom}, J = 8.4 Hz), 6.80 d.d (1H, H_{arom}, J = 8.4, 2.0 Hz), 6.88 d (1H, H_{arom}, J = 2.0 Hz), 7.10 d (2H, H_{arom}, J = 7.9 Hz), 7.18 d (2H, H_{arom}, J = 7.9 Hz). Mass spectrum, m/z (I_{rel}, %): 312 (100) $[M]^+$, 281 (28) $[M - OMe]^+$, 265 (5), 254 (7), 165 (22), 119 (14). Found, %: C 72.90; H 6.40. $C_{19}H_{20}O_4$. Calculated, %: C 73.06; H 6.45. *M* 312.36.

Methyl (*E*)-3-(5-fluoro-2-methoxyphenyl)-3-(4-tolyl)propenoate (*E*-Xk$_1$) was obtained (together with compounds *Z*-**Xk$_1$** and *E*-**Xk$_2$**) from 60 mg (0.34 mmol) of compound **II** and 222 mg (1.76 mmol) of 1-fluoro-4-methoxybenzene in 1.2 ml of HSO_3F at –75°C (reaction time 40 min). Yield 18 mg (18%), mp 79–82°C. ^{1}H NMR spectrum, δ, ppm: 2.35 s (3H, Me), 3.62 s (3H, OMe), 3.64 s (3H, OMe), 6.25 s (1H, HC=), 6.79–6.84 m (2H, H_{arom}), 6.97 t.d (1H, H_{arom}, J = 8.4, 3.0 Hz), 7.09 d (2H, H_{arom}, J = 8.2 Hz), 7.12 d (2H, H_{arom}, J = 8.2 Hz). ^{19}F NMR spectrum: δ_F –120.45 ppm, m. Mass spectrum, m/z (I_{rel}, %): 300 (49) $[M]^+$, 269 $[M - OMe]^+$, 227 (34), 226 (30), 199 (21), 196 (13), 183 (16), 119 (10), 105 (16). Found, %: C 71.88; N 5.60. $C_{18}H_{17}FO_3$. Calculated, %: C 71.99; H 5.71. *M* 300.32.

Methyl (*Z*)-3-(5-fluoro-2-methoxyphenyl)-3-(4-tolyl)propenoate (*Z*-Xk$_1$) was obtained (together with *E*-**Xk$_1$** and *E*-**Xk$_2$**) from 60 mg (0.34 mmol) of compound **II** and 222 mg (1.76 mmol) of 1-fluoro-4-methoxybenzene in 1.2 ml of HSO_3F at –75°C (reaction time 40 min). Yield 10 mg (10%), mp 86–89°C. ^{1}H NMR spectrum, δ, ppm: 2.34 s (3H, Me), 3.60 s (3H, OMe), 3.66 s (3H, OMe), 6.45 s (1H, HC=), 6.77 d.d (1H, H_{arom}, J = 8.5, 3.2 Hz), 6.87 d.d (1H, H_{arom}, J = 9.1, 4.3 Hz), 7.03 t.d (1H, H_{arom}, J = 8.4, 3.2 Hz), 7.11 d (2H, H_{arom}, J = 8.2 Hz), 7.20 d (2H, H_{arom}, J = 8.2 Hz). ^{19}F NMR spectrum: δ_F –120.83 ppm, m. Mass spectrum, m/z (I_{rel}, %): 300 (41) $[M]^+$, 269 (100) $[M - OMe]^+$, 227 (28), 199 (15), 183 (11), 105 (10). Found, %: C 71.69; H 5.82. $C_{18}H_{17}FO_3$. Calculated, %: C 71.99; H 5.71. *M* 300.32.

Methyl (*E*)-3-(1-fluoro-4-oxo-2,5-cyclohexadienyl)-3-(4-tolyl)propenoate (*E*-Xk$_2$), 20 mg (21%), was obtained together with *E*-**Xk$_1$** and *Z*-**Xk$_1$** from 60 mg (0.34 mmol) of compound **II** and 222 mg (1.76 mmol) of 1-fluoro-4-methoxybenzene in 1.2 ml of HSO_3F at –75°C (reaction time 40 min). It was also isolated in an amount of 56 mg (68%) (together with *E*-**Xl$_1$**) in the reaction of 50 mg (0.29 mmol) of compound **II** and 36 mg (0.32 mmol) of 4-fluorophenol in 1.0 ml of HSO_3F at –75°C (reaction time 60 min). Oily substance. IR spectrum, ν, cm^{-1}: 1065, 1165, 1610, 1625, 1675, 1690, 1725 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.31 s (3H, Me), 3.55 (3H, OMe), 6.19 d (2H, HC=, J = 10.0 Hz), 6.48 s (1H, HC=), 6.80 d.d (2H, HC=, J = 10.0, 7.0 Hz), 6.89 d (2H, H_{arom}, J = 8.1 Hz), 7.08 d (2H, H_{arom}, J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.24 q (J = 126.8 Hz), 51.54 q (J = 147.1 Hz), 89.16 d ($^1J_{CF}$ = 176.3 Hz), 120.05 d.d (J = 164.0, $^3J_{CF}$ = 11.0 Hz), 128.02 d.d (J = 158.6, 6.5 Hz), 128.53 d.q (J = 158.6, 5.0 Hz), 130.48 d.d.d (J = 168.3, 3.4, $^3J_{CF}$ = 8.2 Hz), 130.52 d ($^3J_{CF}$ = 2.7 Hz), 138.42 s (J = 6.5 Hz), 142.72 d.d.d (J = 167.8, 5.1, $^2J_{CF}$ = 22.4 Hz), 153.05 d.q [J = 4.0, $^2J_{CF}$ = 20.8 Hz), 165.21 m (J = 3 Hz), 184.01 d ($^4J_{CF}$ = 5.5 Hz). ^{19}F NMR spectrum: δ_F –145.73 ppm. Mass spectrum, m/z (I_{rel}, %): 286 (6) $[M]^+$, 268 (3) $[M - H_2O]^+$, 227 (10), 207 (10), 199 (12), 183 (15), 176 (15), 175 (100), 119 (23), 116 (31), 115 (45), 91 (29), 59 (22), 53 (10). Found: m/z 286.1041 $[M]^+$. $C_{17}H_{15}FO_3$. Calculated: *M* 286.1005.

6-Fluoro-4-(4-tolyl)-2*H*-chromen-2-one (Xl$_1$) was obtained (together with compound *E*-**Xk$_2$**) from 50 mg (0.29 mmol) of compound **II** and 36 mg (0.32 mmol) of 4-fluorophenol in 1.0 ml of HSO_3F at –75°C (reaction time 60 min). Yield 7 mg (9%), mp 181–183°C. IR spectrum, ν, cm^{-1}: 700, 740, 1065, 1120, 1440, 1680, 1695, 1730. ^{1}H NMR spectrum, δ, ppm: 2.45 s (3H, Me), 6.40 s (1H, HC=), 7.21 d.d (1H, H_{arom}, J = 9.0, 2.9 Hz), 7.25 t.d (1H, H_{arom}, J = 8.3, 2.9 Hz), 7.37 d.d (1H, H_{arom}, J = 9.0, 5.6 Hz). ^{19}F NMR spectrum: δ_F –113.80 ppm. Found: m/z 254.0751 $[M]^+$. $C_{16}H_{11}FO_2$. Calculated: *M* 254.0743.

Methyl 3,3-diphenylpropenoate (XIa) was obtained from 50 mg (0.31 mmol) of compound **III** and 87 mg (1.12 mmol) of benzene in 1.0 ml of HSO_3F at

–30°C (reaction time 30 min). Yield 60 mg (82%), oily substance. ^{1}H NMR spectrum, δ, ppm: 3.62 s (3H, OMe), 6.39 s (1H, HC=), 7.20–7.45 m (10H, H_{arom}). Found: *m*/*z* 238.1007 $[M]^+$. $C_{16}H_{14}O_2$. Calculated: *M* 238.0994.

Methyl (*Z*)-3-(4-*tert*-butylphenyl)-3-phenylpropenoate (*Z*-XIb) was obtained from 50 mg (0.31 mmol) of compound **III** and 87 mg (0.65 mmol) of *tert*-butylbenzene in 1.0 ml of HSO_3F at –30°C (reaction time 30 min). Yield 73 mg (80%), oily substance. ^{1}H NMR spectrum, δ, ppm: 1.36 s (9H, *t*-Bu), 3.63 s (3H, OMe), 6.39 s (1H, HC=), 7.12–7.45 m (9H, H_{arom}). Found: *m*/*z* 294.1632 $[M]^+$. $C_{20}H_{22}O_2$. Calculated: *M* 294.1620.

Methyl (*Z*)-3-(2,4-dimethylphenyl)-3-phenylpropenoate (*Z*-XIc) was obtained from 50 mg (0.31 mmol) of compound **III** and 87 mg (0.82 mmol) of 1,3-dimethylbenzene in 1.0 ml of HSO_3F at –30°C (reaction time 30 min). Yield 63 mg (76%), oily substance. ^{1}H NMR spectrum, δ, ppm: 2.03 s (3H, Me), 2.36 s (3H, Me), 3.61 s (3H, OMe), 6.51 s (1H, HC=), 6.90–7.40 m (8H, H_{arom}). Found: *m*/*z* 266.1281 $[M]^+$. $C_{18}H_{18}O_2$. Calculated: *M* 266.1307.

Methyl (*Z*)-3-(2,3-dimethylphenyl)-3-phenylpropenoate (*Z*-XId$_1$) and methyl (*E*,*Z*)-3-(3,4-dimethylphenyl)-3-phenylpropenoate (*E*,*Z*-XId$_2$) were obtained from 50 mg (0.31 mmol) of compound **III** and 87 mg (0.82 mmol) of 1,2-dimethylbenzene in 1.0 ml of HSO_3F at –30°C (reaction time 30 min). Oily isomer mixture: *Z*-**XId$_1$**, 34 mg (41%); *E*-**XId$_2$**, 14 mg (17%); *Z*-**XId$_2$**, 14 mg (17%). ^{1}H NMR spectrum (isomer mixture), δ, ppm: 2.01 s (3H, Me), 2.24 s (3H, Me), 2.26 s (3H, Me), 2.27 (3H, Me), 2.31 s (3H, Me), 2.32 s (3H, Me), 3.60 s (3H, OMe), 3.60 s (3H, OMe), 3.64 s (3H, OMe), 6.32 s (1H, HC=), 6.36 s (1H, HC=), 6.54 s (1H, HC=), 6.75–7.40 m (24H, H_{arom}). Found (isomer mixture): *m*/*z* 266.1281 $[M]^+$. $C_{18}H_{18}O_2$. Calculated: *M* 266.1307.

Methyl (*Z*)-3-(2,5-dimethylphenyl)-3-phenylpropenoate (*Z*-XIe) was obtained from 50 mg (0.31 mmol) of compound **III** and 87 mg (0.82 mmol) of 1,4-dimethylbenzene in 1.0 ml of HSO_3F at –30°C (reaction time 30 min). Yield 78 mg (95%), oily substance. ^{1}H NMR spectrum, δ, ppm: 2.06 s (3H, Me), 2.33 s (3H, Me), 3.61 s (3H, OMe), 6.53 s (1H, HC=), 6.87 d (1H, H_{arom}, *J* = 1.5 Hz), 7.10 d.d (1H, H_{arom}, *J* = 7.7, 1.5 Hz), 7.14 d (1H, H_{arom}, *J* = 7.7 Hz), 7.30–7.38 m (5H, H_{arom}). Found: *m*/*z* 266.1336 $[M]^+$. $C_{18}H_{18}O_2$. Calculated: *M* 266.1307.

Methyl (*Z*)-3-phenyl-3-(2,3,5-trimethylphenyl)-propenoate (*Z*-XIf$_1$) and methyl (*Z*)-3-phenyl-3-(2,4,5-trimethylphenyl)propenoate (*Z*-XIf$_2$) were obtained from 50 mg (0.31 mmol) of compound **III** and 61 mg (0.51 mmol) of 1,2,4-trimethylbenzene in 1.0 ml of HSO_3F at –30°C (reaction time 30 min). Oily isomer mixture: *Z*-**XIf$_1$**, 19 mg (22%); *Z*-**XIf$_2$**, 19 mg (22%). ^{1}H NMR spectrum (isomer mixture), δ, ppm: 1.96 s (3H, Me), 2.02 s (3H, Me), 2.22 s (3H, Me), 2.26 s (3H, Me), 2.27 s (3H, Me), 2.28 s (3H, Me), 3.60 s (3H, OMe), 3.61 s (3H, OMe), 6.49 s (1H, HC=), 6.51 s (1H, HC=), 6.71 s (1H, H_{arom}), 6.80 s (1H, H_{arom}), 6.98 s (1H, H_{arom}), 7.01 s (1H, H_{arom}), 7.28–7.36 m (10H, H_{arom}). Found (isomer mixture): *m*/*z* 280.1471 $[M]^+$. $C_{19}H_{20}O_2$. Calculated: *M* 280.1463.

Methyl (*E*)-3-(4-amino-2,3,5,6-tetramethylphenyl)-3-phenylpropenoate (*E*-XIg) was obtained from 50 mg (0.31 mmol) of compound **III** and 46 mg (0.31 mmol) of 2,3,5,6-tetramethylaniline in 1.0 ml of HSO_3F at –30°C (reaction time 30 min). Yield 14 mg (15%), mp 187–189°C. ^{1}H NMR spectrum, δ, ppm: 2.09 s (6H, Me), 2.14 s (6H, Me), 3.66 s (3H, OMe), 5.87 s (1H, HC=), 7.24–7.28 m (5H, H_{arom}). Found: *m*/*z* 309.1805 $[M]^+$. $C_{20}H_{23}NO_2$. Calculated: *M* 309.1729.

Methyl (*E*)-3-(5-fluoro-2-methoxyphenyl)-3-phenylpropenoate (*E*-XIh) was obtained (together with *Z*-**XIh**) from 50 mg (0.31 mmol) of compound **III** and 111 mg (0.88 mmol) of 1-fluoro-4-methoxybenzene in 1.0 ml of HSO_3F at –50°C (reaction time 60 min). Yield 12 mg (13%), mp 79–82°C. ^{1}H NMR spectrum, δ, ppm: 3.61 s (3H, OMe), 3.62 s (3H, OMe), 6.30 s (1H, HC=), 6.79–6.84 m (2H, H_{arom}), 6.98 t.d (1H, H_{arom}, *J* = 8.4, 3.1 Hz), 7.19–7.22 m (2H, H_{arom}), 7.29–7.33 m (3H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 286 (30) $[M]^+$, 255 (100) $[M - OMe]^+$, 239 (10), 212 (48), 196 (13), 183 (87), 165 (18), 157 (17), 149 (13), 133 (10), 115 (10), 107 (20), 105 (13), 91 (43), 77 (28), 63 (23), 59 (27), 51 (33). Found, %: C 71.50; H 5.37. $C_{17}H_{15}FO_3$. Calculated, %: C 71.32; H 5.28. *M* 286.30.

Methyl (*Z*)-3-(5-fluoro-2-methoxyphenyl)-3-phenylpropenoate (*Z*-XIh) was obtained (together with *E*-**XIh**) from 50 mg (0.31 mmol) of compound **III** and 111 mg (0.88 mmol) of 1-fluoro-4-methoxybenzene in 1.0 ml of HSO_3F at –50°C (reaction time 60 min). Yield 13 mg (15%), mp 86–89°C. ^{1}H NMR spectrum, δ, ppm: 3.61 s (3H, OMe), 3.66 s (3H, OMe), 6.46 s (1H, HC=), 6.79 d.d (1H, H_{arom}, *J* = 8.4, 3.1 Hz), 6.88 d.d (1H, H_{arom}, *J* = 9.0, 4.4 Hz), 7.04 t.d (1H, H_{arom}, *J* = 8.5, 3.1 Hz), 7.29–7.35 m (5H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 286 (13) $[M]^+$, 255 (63) $[M - OMe]^+$, 231 (10), 212 (45), 199 (13), 196 (14),

183 (100), 170 (16), 165 (22), 157 (22), 153 (34), 107 (20), 105 (23), 91 (28), 77 (40), 63 (20), 59 (22). Found, %: C 71.45; H 5.41. $C_{17}H_{15}FO_3$. Calculated, %: C 71.32l; H 5.28. *M* 286.30.

Methyl (*E*)-3-(4-fluorophenyl)-3-(4-fluorosulfonyl-2,3,5,6-tetramethylphenyl)propenoate (*E*-XIIa) was obtained from 30 mg (0.17 mmol) of compound **IV** and 56 mg (0.26 mmol) of 2,3,5,6-tetramethylbenzenesulfonyl fluoride in 0.5 ml of HSO_3F at –30°C (reaction time 60 min). Yield 46 mg (68%), mp 101–103°C. ^{1}H NMR spectrum, δ, ppm: 2.21 s (6H, Me), 2.58 d (6H, Me, J_{HF} = 2.2 Hz), 3.72 s (3H, OMe), 5.81 s (1H, HC=), 7.00 t (2H, H_{arom}, *J* = 8.7 Hz), 7.24 d.d (2H, H_{arom}, *J* = 8.4, 5.4 Hz). ^{19}F NMR spectrum: δ_F 72.89 ppm, m (1F, FO_2S, *J* = 2.5 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 394 (59) $[M]^+$, 379 (22) $[M - Me]^+$, 363 (22) $[M - OMe]^+$, 334 (100), 320 (33), 310 (24), 252 (37), 251 (63), 237 (35), 221 (22), 119 (17), 115 (15), 59 (30). Found, %: C 60.68; H 5.13. $C_{20}H_{20}F_2O_4S$. Calculated, %: C 60.90; H 5.11. *M* 394.43.

Methyl (*E*)-3-(3,4-dichlorophenyl)-3-(4-fluorophenyl)propenoate (*E*-XIIb) and methyl (*Z*)-3-(3,4-dichlorophenyl)-3-(4-fluorophenyl)propenoate (*Z*-XIIb) were obtained from 30 mg (0.17 mmol) of compound **IV** and 50 mg (0.34 mmol) of 1,2-dichlorobenzene in 0.5 ml of HSO_3F at –30°C (reaction time 60 min). Oily isomer mixture: *E*-**XIIb**, 10 mg (19%); *Z*-**XIIb**, 9 mg (17%). ^{1}H NMR spectrum (isomer mixture), δ, ppm: 3.63 s (3H, OMe), 3.64 s (3H, OMe), 6.32 s (1H, HC=), 6.33 s (1H, HC=), 7.01–7.54 m (14H, H_{arom}). Mass spectrum (isomer mixture), *m*/*z* (I_{rel}, %): 328 (5) $[M + 4]^+$, 326 (32) $[M + 2]^+$, 324 (48) $[M]^+$, 297 (7), 295 (45), 293 (67) $[M - OMe]^+$, 230 (57), 194 (50), 167 (35), 149 (100), 123 (38). Found, %: C 58.67; H 3.26. $C_{16}H_{11}Cl_2FO_2$. Calculated, %: C 59.10; H 3.41. *M* 325.16.

Methyl (*Z*)-3-(2,5-dimethoxyphenyl)-3-(4-fluorophenyl)propenoate (*Z*-XIIc) was obtained from 30 mg (0.17 mmol) of compound **IV** and 36 mg (0.26 mmol) of 1,4-dimethoxybenzene in 0.6 ml of HSO_3F at –30°C (reaction time 30 min). Yield 25 mg (47%), oily substance. ^{1}H NMR spectrum, δ, ppm: 3.60 s (3H, OMe), 3.63 s (3H, OMe), 3.74 s (3H, OMe), 6.39 s (1H, HC=), 6.60 d (1H, H_{arom}, *J* = 1.5 Hz), 6.86–6.90 m (2H, H_{arom}), 6.98 t (2H, H_{arom}, *J* = 8.6 Hz), 7.30 d.d (2H, H_{arom}, *J* = 8.7, 5.4 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 316 (75) $[M]^+$, 285 (100) $[M - OMe]^+$, 270 (10), 242 (15), 171 (10), 170 (10), 149 (10), 124 (27), 123 (16), 109 (32), 81 (11). Found, %: C 68.26; H 5.51. $C_{18}H_{17}FO_4$. Calculated, %: C 68.35; H 5.42. *M* 316.32.

Ethyl (*E*)-3-(4-acetyl-2,3,5,6-tetramethylphenyl)-3-(4-iodophenyl)propenoate (*E*-XIIIa) was obtained from 60 mg (0.20 mmol) of compound **Va** and 52 mg (0.30 mmol) of 2,3,5,6-tetramethylacetophenone in 1.2 ml of HSO_3F at –50°C (reaction time 60 min). Yield 12 mg (12%), oily substance. ^{1}H NMR spectrum, δ, ppm: 1.24 t (3H, Me, *J* = 7.1 Hz), 2.10 s (12H, Me), 2.47 s (3H, Me), 4.16 q (2H, OCH_2, *J* = 7.1 Hz), 5.84 s (1H, HC=) 6.99 d (2H, H_{arom}, *J* = 8.3 Hz), 7.60 d (2H, H_{arom}, *J* = 8.3 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 476 (67) $[M]^+$, 461 (97) $[M - Me]^+$, 431 (11) $[M - OEt]^+$, 429 (14), 414 (14), 402 (17), 359 (12), 233 (10), 217 (19), 203 (22), 202 (22), 175 (15.5), 43 (100). Found, %: C 57.70; H 5.30. $C_{23}H_{25}IO_3$. Calculated, %: C 57.99; H 5.29. *M* 476.35.

Ethyl (*E*)-3-(4-acetyl-2,3,5,6-tetramethylphenyl)-3-(4-methoxy-3-nitrophenyl)propenoate (*E*-XIIIb) and ethyl (*Z*)-3-(4-acetyl-2,3,5,6-tetramethylphenyl)-3-(4-methoxy-3-nitrophenyl)propenoate *Z*-(XIIIb) were obtained from 30 mg (0.12 mmol) of compound **Vb** and 50 mg (0.28 mmol) of 2,3,5,6-tetramethylacetophenone in 0.6 ml of HSO_3F at –20°C (reaction time 60 min). Oily isomer mixture: *E*-**XIIIb**, 15 mg (29%); *Z*-**XIIIb**, 8 mg (15%). IR spectrum, ν, cm^{-1}: 1015, 1180, 1280, 1350, 1525, 1615, 1690 (C=O), 1715 (C=O). ^{1}H NMR spectrum, δ, ppm: *E*-**XIIIb**: 1.24 t (3H, Me, *J* = 7.1 Hz), 2.09 s (6H, Me), 2.10 s (6H, Me), 2.48 s (3H, Me), 4.18 q (2H, OCH_2, *J* = 7.1 Hz), 5.85 s (1H, HC=) 6.98 d (1H, H_{arom}, *J* = 8.8 Hz), 7.48 d.d (1H, H_{arom}, *J* = 8.6, 2.0 Hz), 7.79 d (1H, H_{arom}, *J* = 2.0 Hz); *Z*-**XIIIb**: 1.07 t (3H, *J* = 7.1 Hz), 1.95 s (6H, Me), 2.12 s (6H, Me), 2.50 s (3H, Me), 3.95 s (3H, OMe), 4.01 q (2H, CH_2, *J* = 7.1 Hz), 6.61 s (1H, HC=), 6.98 d (1H, H_{arom}, *J* = 8.9 Hz), 7.31 d.d (1H, H_{arom}, *J* = 8.5, 2.0 Hz), 7.91 d (1H, H_{arom}, *J* = 2.0 Hz). Found, %: C 67.50; H 6.35. $C_{24}H_{27}NO_6$. Calculated, %: C 67.75; H 6.40. *M* 425.47.

(*E*)-3-Phenyl-3-(2,3,5,6-tetramethylphenyl)-propenoic acid (*E*-XIVa) and (*Z*)-3-phenyl-3-(2,3,5,6-tetramethylphenyl)propenoic acid (*Z*-XIVa) were obtained from 30 mg (0.21 mmol) of compound **VI** and 110 mg (0.82 mmol) of 1,2,4,5-tetramethylbenzene in 0.5 ml of HSO_3F at –30°C (reaction time 30 min). *E*/*Z* Ratio 1:1. Yield of *E*-**XIVa** 11 mg (19%), mp 210–212°C (isomer mixture). Yield of *Z*-**XIVa** 29 mg (49%), mp 205–208°C. ^{1}H NMR spectrum, δ, ppm: *E*-**XIVa**: 2.09 s (6H, Me), 2.21 s (6H, Me), 5.86 s (1H, HC=), 6.95 s (1H, H_{arom}), 7.26–7.36 m (5H, H_{arom}), 10.0 br.s (1H, COOH); *Z*-**XIVa**: 1.95 s (6H, Me), 2.23 s (6H, Me), 6.64 s (1H, HC=), 6.99 s (1H, H_{arom}), 7.26–7.36 m (5H, H_{arom}), 9.0 br.s

(1H, COOH). Mass spectrum (isomer mixture), *m*/*z* (I_{rel}, %): 280 (100) $[M]^+$, 265 (47) $[M - Me]^+$, 247 (10), 234 (27), 220 (44), 219 (51), 206 (46), 189 (12), 143 (10), 133 (15), 115 (20), 96 (14), 95 (14), 91 (17), 77 (12), 44 (15). Found, %: isomer mixture: C 81.35; H 7.23; *Z*-**XIVa**: C 81.31; H 7.26. $C_{19}H_{20}O_2$. Calculated, %: C 81.40; H 7.19. *M* 280.36.

(*E*)-3-(4-Acetyl-2,3,5,6-tetramethylphenyl)-3-phenylpropenoic acid (*E*-XIVb) was obtained from 30 mg (0.21 mmol) of compound **VI** and 50 mg (0.28 mmol) of 2,3,5,6-tetramethylacetophenone in 0.6 ml of HSO_3F at –30°C (reaction time 30 min). Yield 18 mg (27%), mp 240–243°C. ^{1}H NMR spectrum, δ, ppm: 2.10 s (6H, Me), 2.11 s (6H, Me), 5.86 s (1H, HC=), 6.99 s (1H, H_{arom}), 7.27–7.32 m (5H, H_{arom}), 10.2 br.s (1H, COOH). Mass spectrum, *m*/*z* (I_{rel}, %): 322 (38) $[M]^+$, 307 (100) $[M - Me]^+$, 261 (5), 234 (6), 233 (6), 220 (9), 219 (10), 203 (9), 115 (6), 43 (19). Found, %: C 78.10; H 7.00. $C_{21}H_{22}O_3$. Calculated, %: C 78.23; H 6.88. *M* 322.40.

(*E*)-3-(4-Fluorosulfonyl-2,3,5,6-tetramethylphenyl)-3-phenylpropenonitrile (*E*-XVa) was obtained from 20 mg (0.16 mmol) of compound **VIIa** and 52 mg (0.24 mmol) of 2,3,5,6-tetramethylbenzenesulfonyl fluoride in 0.5 ml of HSO_3F at –30°C (reaction time 90 min). Yield 12 mg (22%), mp 180–183°C. IR spectrum, ν, cm^{-1}: 1060, 1380, 1410, 2220 (C≡N). ^{1}H NMR spectrum, δ, ppm: 2.15 s (6H, Me), 2.58 d (6H, Me, $^5J_{HF}$ = 2.2 Hz), 5.32 s (1H, HC=), 7.40–7.48 m (3H, H_{arom}), 7.56 d (2H, H_{arom}, *J* = 8.0 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 343 (75) $[M]^+$, 328 (44) $[M - Me]^+$, 259 (100), 244 (58), 233 (19), 230 (14), 220 (14), 217 (19), 203 (19), 202 (22), 115 (17), 108 (14), 101 (18), 91 (15), 77 (17), 51 (11), 39 (14). Found, %: C 66.41; H 5.26. $C_{19}H_{18}FNO_2S$. Calculated, %: C 66.45; H 5.28. *M* 343.42.

(*Z*)-4-[2-(4-Acetyl-2,3,5,6-tetramethylphenyl)-2-(4-chlorophenyl)ethenyl]benzonitrile (*Z*-XVb) was obtained from 30 mg (0.13 mmol) of compound **VIIb** and 44 mg (0.25 mmol) of 2,3,5,6-tetramethylacetophenone in 1.0 ml of HSO_3F at –75°C (reaction time 15 min). Yield 22 mg (40%), mp 201–205°C. IR spectrum, ν, cm^{-1}: 1350, 1415, 1485, 1600, 1690 (C=O), 2235 (C≡N). ^{1}H NMR spectrum, δ, ppm: 2.12 s (6H, Me), 2.15 s (6H, Me), 2.49 s (3H, Me), 6.46 s (1H, HC=), 6.99 d (2H, H_{arom}, *J* = 8.4 Hz), 7.15 d (2H, H_{arom}, *J* = 8.4 Hz), 7.27 d (2H, H_{arom}, *J* = 8.1 Hz), 7.52 d (2H, H_{arom}, *J* = 8.1 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 415 (23) $[M + 2]$, 413 (60) $[M]^+$, 400 (38), 399 (38), 398 (100) $[M - Me]^+$, 355 (10), 297 (10), 153 (10), 43 (48). Found, %: C 78.27; H 5.87. $C_{27}H_{24}ClNO$. Calculated, %: C 78.34; H 5.84. *M* 413.94.

Methyl (*Z*)-4-[2-(4-Acetyl-2,3,5,6-tetramethylphenyl)-2-phenylethenyl]benzoate (*Z*-XVc) was obtained from 50 mg (0.21 mmol) of compound **VIIc** and 74 mg (0.42 mmol) of 2,3,5,6-tetramethylacetophenone in 1.0 ml of HSO_3F at –75°C (reaction time 15 min). Yield 10 mg (12%), mp 170–172°C. ^{1}H NMR spectrum, δ, ppm: 2.13 s (6H, Me), 2.19 s (6H, Me), 2.49 s (3H, Me), 3.90 s (3H, MeO), 6.47 s (1H, HC=), 7.07–7.34 m (7H, H_{arom}), 7.88 d (2H, H_{arom}, *J* = 8.2 Hz). Found, %: C 81.39; H 6.80. $C_{28}H_{28}O_3$. Calculated, %: C 81.52; H 6.84. *M* 412.20.

Diethyl (*E*)-[2-(4-fluorosulfonyl-2,3,5,6-tetramethylphenyl)-2-phenylethenyl]phosphonate (*E*-XVIa) and diethyl (*Z*)-[2-(4-fluorosulfonyl-2,3,5,6-tetramethylphenyl)-2-phenylethenyl]phosphonate (*Z*-XVIa) were obtained from 50 mg (0.21 mmol) of compound **VIII** and 50 mg (0.23 mmol) of 2,3,5,6-tetramethylbenzenesulfonyl fluoride in 1.0 ml of HSO_3F at –30°C (reaction time 60 min). Yield of *E*-**XVIa** 6 mg (6%). ^{1}H NMR spectrum (from the spectrum of isomer mixture), δ, ppm: 1.14 t (6H, Me, *J* = 7.0 Hz), 2.22 s (6H, Me), 2.57 d (6H, Me, J_{HF} = 1.9 Hz), 4.18–4.25 m (4H, OCH_2), 5.66 d (1H, HC=, $^2J_{HP}$ = 14.7 Hz), 7.23–7.40 m (5H, H_{arom}). Found (for isomer mixture), %: C 58.76; H 6.53. $C_{22}H_{28}FO_5PS$. Calculated, %: C 58.14; H 6.21. *M* 454.49. Yield of *Z*-**XVIa** 50 mg (52%), mp 150–157°C. ^{1}H NMR spectrum, δ, ppm: 1.14 t (6H, Me, *J* = 7.0 Hz), 2.14 s (6H, Me), 2.60 d (6H, Me, J_{HF} = 1.9 Hz), 3.73–3.91 m (4H, OCH_2), 6.53 d (1H, HC=, $^2J_{HP}$ = 15.3 Hz), 7.23–7.27 m (2H, H_{arom}), 7.31–7.40 m (3H, H_{arom}). Mass spectrum (isomer mixture), *m*/*z* (I_{rel}, %): 454 (23) $[M]^+$, 370 (10), 316 (100) $[M - P(O)(OEt)_2]^+$, 301 (10), 233 (47), 217 (18), 203 (16), 139 (33), 138 (67), 111 (49), 81 (18). Found, %: C 57.84; H 6.13. $C_{22}H_{28}FO_5PS$. Calculated, %: C 58.14; H 6.21. *M* 454.49.

Diethyl (*E*)-[2-(3,4-dimethoxyphenyl)-2-phenylethenyl]phosphonate (*E*-XVIb) and diethyl (*Z*)-[2-(3,4-dimethoxyphenyl)-2-phenylethenyl]phosphonate (*Z*-XVIb) were obtained from 50 mg (0.21 mmol) of compound **VIII** and 58 mg (0.42 mmol) of 1,2-dimethoxybenzene in 1.0 ml of HSO_3F at –30°C (reaction time 30 min). Yield of *E*-**XVIb** 22 mg (28%). ^{1}H NMR spectrum (from the spectrum of isomer mixture), δ, ppm: 1.11 t (6H, Me, *J* = 7.1 Hz), 3.80 s (6H, OMe), 3.83–3.94 m (4H, OCH_2), 6.11 d (1H, HC=, $^2J_{HP}$ = 15.3 Hz), 6.75–

6.77 m (2H, H_{arom}), 6.84 s (1H, H_{arom}), 7.33–7.38 m (5H, H_{arom}). Found (mixture of isomers), %: C 63.41; H 6.50. $C_{20}H_{25}O_5P$. Calculated, %: C 63.82; H 6.69. *M* 376.38. Yield of *Z*-**XVIb** 22 mg (28%). ^{1}H NMR spectrum (from the spectrum of isomer mixture), δ, ppm: 1.14 t (6H, Me, J = 7.1 Hz), 3.80 s (6H, OMe), 3.83–3.94 m (4H, OCH_2), 6.04 d (1H, HC=, $^2J_{HP}$ = 15.5 Hz), 6.85 d (1H, H_{arom}, J = 8.3 Hz), 6.91 d.d (1H, H_{arom}, J = 8.3, 2.0 Hz), 7.03 d (1H, H_{arom}, J = 2.0 Hz), 7.27–7.32 m (5H, H_{arom}).

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