Tetrahedron 64 (2008) 6334–6340

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

New method of alkenylation of anilines by acetylene compounds in the superacid HSO_3F

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ARTICLE INFO

Article history:
Received 25 January 2008
Received in revised form 7 April 2008
Accepted 24 April 2008
Available online 29 April 2008

Keywords:
Arene alkenylation
Friedel–Crafts reactions
Acetylene compounds
Anilines
Superacids
Fluorosulfonic acid

ABSTRACT

Vinyl cations, generated by protonation of the triple bond of α,β-alkynylcarbonyl compounds in the superacid HSO_3F, react efficiently with arylammonium (anilinium) ions at low temperatures −75 and −30 °C in 30–75 min with the formation of Friedel–Crafts-type products of anilinium ring alkenylation in 14–62% yields. Regio- and stereoselectivity of such electrophilic aromatic substitution has been studied in detail.

1. Introduction

Arylamines (anilines) are widely used for industrial production of dyes, pharma-, and agrochemicals. In organic chemistry, anilines are objects of special interest for the preparation of various heterocyclic compounds.[1,2]

The classical syntheses of arylamines bearing alkenyl (vinyl) substituents in the aromatic ring are based on the Heck reaction.[3,4] Recently, new methods of alkenyl substituted anilines have been developed with the use of Grignard reagents.[5,6]

In this paper, we present a new synthesis of vinyl-substituted anilines on the basis of alkenylation of aniline rings by acetylene compounds in the superacid HSO_3F. This study is based on our work on the chemistry of alkynes in superacids,[7–14] in particular on the alkenylation of arenes,[8,11,12] and on other studies on acetylene chemistry in superacids.[15–19]

The superacid HSO_3F is a unique medium for generating vinyl cations **A** by the protonation of the triple bond of acetylene compounds **1** (Scheme 1).[7–19] Arylamines exist in superacids in the form of arylammonium (anilinium) ions **B**[20] (Scheme 1). Electrophilic aromatic substitution with a participation of these cations **A** and **B** results in the formation of arenium dication **C**. Deprotonation of the latter gives vinyl-substituted arylammonium ion **D**, which finally leads to alkenylation product (*E*/*Z*)-**2** after quenching of the superacidic reaction mixture with aqueous $NaHCO_3$.

Vinyl cations **A** containing electron-withdrawing groups X=CO_2R, COR are considered as strong (or super-) electrophilic species[17–19,21,22] due to the additional electrophilic activation of the vinyl cationic center by the electron-withdrawing groups X solvated in the superacids.[8,9,13,14] The cations **A** are sufficiently electrophilic to attack such deactivated π-nucleophiles as aromatic systems of arylammonium ions **B** (Scheme 1).

2. Results and discussion

Simply dissolution of arylamine in HSO_3F at low temperature, and consequent addition of acetylene compound **1** to the obtained arylamonium ion **B** solution followed by the final basic quenching of the reaction mixture affords compound **2** (Scheme 1). The reaction conditions (amount of reagents, temperature, and time) for the alkenylation of arylamonium ions by acetylene compounds **1a–c** in HSO_3F with the formation of products **2a–o** are given in Table 1. Reaction temperature (Table 1) was chosen according to the temperature at which the acetylene substrates **1a–c** undergo protonation in superacids. In HSO_3F, acetylene esters **1a**,**b** form reactive vinyl cations **A** at −75 and −30 °C, respectively;[11,13,14] and ketone **1c** gives vinyl cation at −30 °C.[12–14]

As it has been shown before,[11,12] the addition of a proton and an aryl moiety to alkynes proceeds in a *syn*-fashion in superacids at low temperature (−75 to −50 °C). At higher temperature (−30 to 20 °C)

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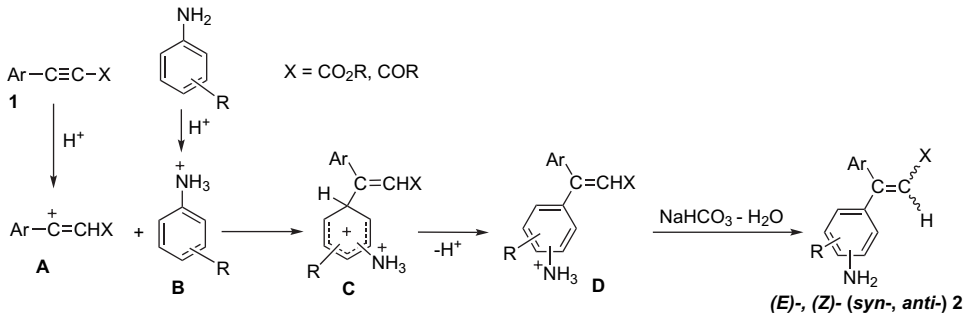
doi:10.1016/j.tet.2008.04.092



Scheme 1.

in superacids, the *syn*-adducts are isomerized into their *anti*-analogues. In this study, we have observed the same regularity for the compounds **2a**–**o**. Thus, individually isolated (*E*)-isomer **2l** (entry 10) was transformed into (*Z*)-**2l** in HSO_3F at −30 °C (Scheme 2).

The *E*/*Z*-configuration of the alkenylation products **2a**–**o** was determined by ^1H NMR spectroscopy. Similarly to our previous X-ray and NMR investigations of 3,3-diarylpropenone systems,[11,12] in this study, we used a signal of vinyl proton of compounds (*E*/*Z*)-**2a**–**o** as a stereochemical reference point to make an assignment of *E*/*Z*-configuration. The vinyl proton signal of the *E*-isomers of 3,3-diarylpropenoates **2a**–**c**,**e**–**g**,**i**–**l**,**n**,**o** (resonance at δ 5.82–6.28 ppm) are up-field shifted compared to the corresponding signal for their *Z*-isomers **2b**,**c**,**l** (resonance at δ 6.38–6.60 ppm) and to the vinyl proton signal for the *Z*-isomers of 4,4-diarylbut-3-en-2-ones **2d**,**h**,**m** (resonance at δ 6.63–6.80 ppm) (see Section 4).[11,12]

Additional proof for stereochemical configuration of the compound (*E*)-**2g** has been provided by a ROESY experiment, which reveals strong correlation between the vinyl proton (δ 5.82 ppm) and two methyl substituents (δ 2.05 and 2.06 ppm) in aniline ring (Fig. 1). This type of correlation is only possible for the *E*-isomer due to the spatial closeness of these proton groups. Also confirmation of the *E*-configuration is the absence of any correlation between the vinyl proton and aromatic *ortho*-protons in the *para*-tolyl ring.[23]

The electron-withdrawing ammonium group, NH_3^+, deactivates the aromatic π-system of ion **B** (Scheme 1) in electrophilic substitution. Thus, *N*-protonated forms of aniline and *N*,*N*-dimethylaniline do not react with vinyl cations generated from the compounds **1b**,**c** in HSO_3F at −30 °C; no alkenylation products are formed. In these cases, the initial acetylenes **1b**,**c** react with HSO_3F and afford the corresponding vinyl fluorosulfonates.[14]

The presence of only one methyl group in the aniline ring permits reaction of the corresponding arylammonium ions with vinyl cations. *ortho*- and *para*-Methyl substituted anilines give compounds (*E*/*Z*)-**2a**,**b** (entries 1 and 2) as products of the regioselective substitution into *meta*-position to electron-acceptor group NH_3^+. The same position selectivity has been observed in the trifluoromethylation and bromination of these mono-methyl-substituted anilines in the superacidic system HF–SbF_5.[24,25]

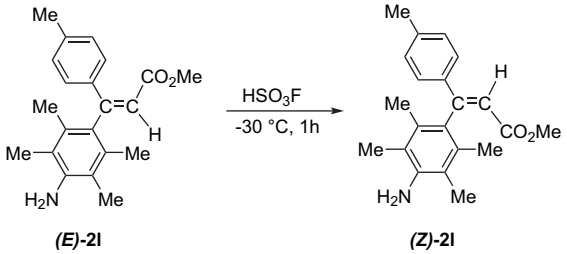
Substitution in the 2-methylphenylammonium ion goes selectively at the position 5, leading solely to the product (*E*)-**2a** (entry 1). ^1H NMR spectrum of the compound (*E*)-**2a** reveals the typical set of signals corresponding to a proton spin system of 1,2,4-trisubstituted benzene (aniline ring in the structure (*E*)-**2a**). These signals are two doublets at δ 6.55 and 6.99 ppm with coupling constants *J* 1.7 and 7.8 Hz, respectively, and the doublet of doublets at δ 6.67 ppm with the same constants *J* 7.8 and 1.7 Hz (see Section 4). In case of alternative substitution at position 3 (also *meta*-position to group NH_3^+) in the 2-methylphenylammonium ion, the aniline ring in the formed alkenylation product should be 1,2,3-trisubstituted benzene, which shows a rather complex proton spectrum, but that does not take place indeed.

Alkenylation of the 2,4-dimethylphenylammonium ion by compounds **1a**,**c** proceeds selectively at the position 5 of arylammonium ring (entries 3 and 4). Acetylene ester **1a** forms a mixture of stereoisomers (*E*/*Z*)-**2c** (entry 3), but ketone **1c** gives only the isomerized compound (*Z*)-**2d** (entry 4).[26]

The 3,4-dimethylphenylammonium ion gives two alkenylation products (*E*)-**2e** and (*E*)-**2f** as a result of substitution at the positions 6 and 5 of the arylammonium ring, respectively, in reaction with ester **1a** (entry 5). Identification of compounds (*E*)-**2e** and (*E*)-**2f** has been done on the basis of their ^1H NMR spectra. Thus, the proton spectrum of isomer (*E*)-**2f** contains two doublets at δ 6.39 and 6.51 ppm with constant *J* 2.3 Hz that corresponds to two aromatic *meta*-protons in the positions 2 and 4 of the aniline ring. On the contrary, two singlets of aniline ring *para*-protons of compound (*E*)-**2e** appear at δ 6.43 and 6.83 ppm in ^1H NMR spectrum (see Section 4).

Vinyl cations, generated from acetylenes **1a**–**c**, are sufficiently active to attack sterically protected arylammonium substrates (entries 6–11) bearing even a bulky *tert*-butyl group (entry 8). Ketone **1c** forms products of *anti*-addition to the triple bond (*Z*)-**2h**,**m** (entries 7 and 11). Acetylene esters **1a**,**b** lead to the formation of *syn*-addition products (*E*)-**2g**,**i**–**l** (entries 6 and 8–10).[26]

The 2,4,5-trimethylphenylammonium ion is attacked at both available positions of its aromatic ring giving two alkenylation products (*E*)-**2j** and (*E*)-**2k** (entry 9). The latter is substitution product into *ortho*-position to ammonium group despite its electron-withdrawing character; it is also substitution into *ortho*-position to



Scheme 2.

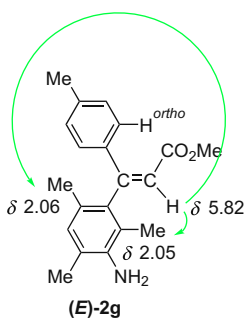


Figure 1. ROESY data for compound (*E*)-**2g** (green arrows show correlations).

Table 1
Reaction conditions and products of alkenylation of arylammonium ions by acetylene compounds in HSO_3F

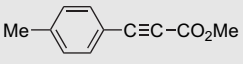
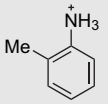
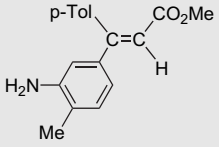
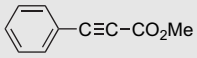
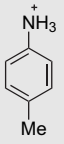
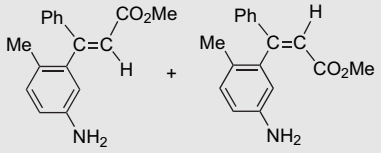
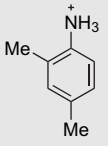
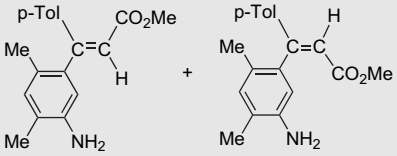
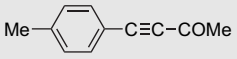
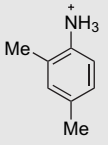
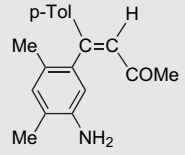
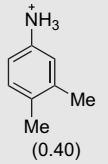
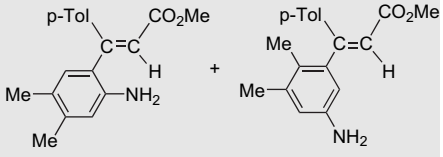
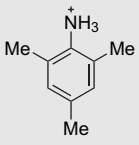
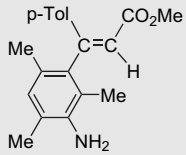
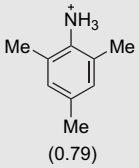
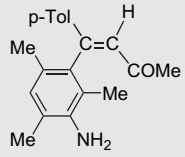
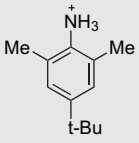
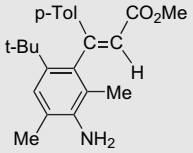
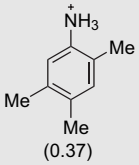
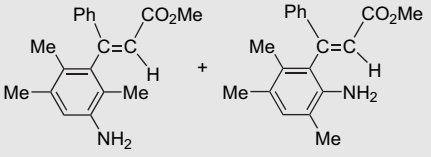
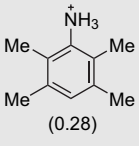
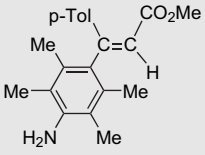
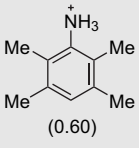
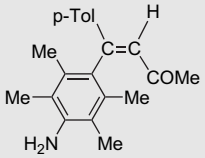
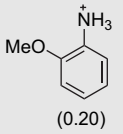
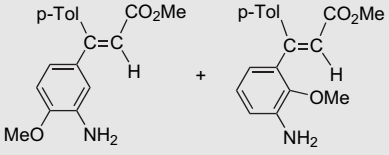
Entry	Acetylene compound, number (amount, mmol)	Arylammonium ion (amount, mmol)	Reaction conditions			Alkenylation product, number (yield, %)
			HSO_3F, ml	Temperature, °C	Time, min	
1	 **1a** (0.17)	 (0.23)	1	−75	60	 **(*E*)-2a** (17)
2	 **1b** (0.31)	 (0.77)	1	−30	30	 **(*E*)-2b** (12) (***Z***)-**2b** (2)
3	**1a** (0.17)	 (0.17)	1	−75	60	 **(*E*)-2c** (24) **(*Z*)-2c** (13)
4	 **1c** (0.32)	 (0.64)	1	−30	60	 **(*Z*)-2d** (56)
5	**1a** (0.20)	 (0.40)	1	−75	45	 **(*E*)-2e** (34) **(*E*)-2f** (7)
6	**1a** (0.09)	 (0.79)	0.7	−75	60	 **(*E*)-2g** (38)
7	**1c** (0.32)	 (0.79)	1	−30	75	 **(*Z*)-2h** (44)

Table 1 (*continued*)

Entry	Acetylene compound, number (amount, mmol)	Arylammonium ion (amount, mmol)	Reaction conditions			Alkenylation product, number (yield, %)
			HSO_3F, ml	Temperature, °C	Time, min	
8	**1a** (0.13)	 (0.13)	0.7	−75	60	 **(*E*)-2i** (34)
9	**1b** (0.31)	 (0.37)	1	−30	60	 **(*E*)-2j** (30) + **(*E*)-2k** (18)
10	**1a** (0.23)	 (0.28)	1	−75	60	 **(*E*)-2l** (25)
11	**1c** (0.32)	 (0.60)	1	−30	60	 **(*Z*)-2m** (31)
12	**1a** (0.16)	 (0.20)	1	−75	60	 **(*E*)-2n** (45) + **(*E*)-2o** (17)

methyl group. In this case the electron-donating methyl groups in the anilinium ion rule the electrophilic substitution.

It is worth noting the unusual chromatographic behavior of compounds (*E*)-**2e** and (*E*)-**2k** (entries 5 and 9). They have lower retention parameters in column chromatography on silica gel (higher R_f values in TLC) than their isomers (*E*)-**2f** and (*E*)-**2j** respectively and even than initial anilines. Most likely, it is caused by sterical shielding of the *ortho*-amino group in the structures (*E*)-**2e** and (*E*)-**2k**.

2-Methoxy-substituted anilinium ion gives two alkenylation products (*E*)-**2n**,**o** (entry 12) as a result of substitution into the *para*- and *ortho*-position relatively to the methoxy group. In this reaction, at low temperature, −75 °C, only the products resulting from overall *syn*-addition to the acetylene bond of compound **1a** are formed (entry 12).

Yields of alkenylation products (*E*/*Z*)-**2a**–**o** are quite moderate in a range of 14–62%. The lowest yields in 14 and 17% have been obtained at the transformations of mono-methyl-substituted anilines (entries 1 and 2). Di-, tri- and tetramethyl-anilines, which are more reactive in aromatic electrophilic substitution, afford reaction products in higher yields, 25–56% (entries 3–11). The highest yield, 62% totally for two isomers, has been reached by the alkenylation of the activated 2-methoxy-substituted aniline (entry 12).

All amount of the starting acetylenes **1a**–**c** has been completely consumed under the reaction conditions for all examples shown in Table 1. The formation of reaction products in modest yields in HSO_3F can be explained by secondary reactions of the obtained compounds (*E*/*Z*)-**2a**–**o**, which are enones with conjugated carbon–carbon double and carbonyl bonds. These enone structures undergo various transformations in superacids.[27] Apart from that, in HSO_3F, the fluorosulfonation of aromatic rings of the products (*E*/*Z*)-**2a**–**o** may take place decreasing the yields.[12]

3. Conclusion

A new simple regio- and stereoselective synthesis of alkenyl-(vinyl-)substituted anilines has been developed on the basis of Friedel–Crafts-type alkenylation of alkyl- and methoxy-substituted

anilines by vinyl cations, generated from acetylene compounds in the superacid HSO_3F at low temperature −75 or −30 °C.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectra were recorded on Brucker AM-500 NMR spectrometer (working frequencies 500 and 125 MHz, respectively) in $CDCl_3$ solutions. The residual proton–solvent peak of $CDCl_3$ (δ 7.25 ppm) for ^1H NMR spectra, the signal of $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR spectra were used as internal references. Mass spectra (electron impact, ionization energy 70 eV) were measured on a machine MKh-1321. IR spectra of compounds in $CHCl_3$ solutions were recorded on Specord 75 IR spectrometer. IR spectra of compounds in KBr pressed tablets were recorded on FSM 1201 IR spectrometer. Analytical thin-layer chromatography (TLC) was performed using *Silufol* silica gel UV-254 plates. Preparative separation of reaction mixtures was carried out by column chromatography on silica gel Chemapol 60/100. Chromatography eluent: hexanes/ethyl acetate.

4.2. Starting materials

Synthesis and properties of methyl-3-(4-methylphenyl)propiolate **1a**, methyl-3-phenylpropiolate **1b**, and 4-(4-methylphenyl)but-3-yn-2-one **1c** were previously published.[12,28] Arylamines are commercially available substances.

4.3. General alkenylation procedure

Arylamine (0.1–0.79 mmol) was added to cooled HSO_3F (0.7–1.0 ml) at the temperature of −75 or −30 °C with vigorous magnetic stirring. After complete dissolving of arylamine in HSO_3F at the above-mentioned temperature, acetylene compound (0.09–0.32 mmol, 0.4–1 equiv) was also added. Reaction mixture was stirred at the temperature of −75 or −30 °C for 30–75 min (see Table 1). Then the mixture was quenched with a cooled (−75 °C) concentrated aqueous HCl (~10 ml). CAUTION: very vigorous decomposition of HSO_3F into H_2SO_4 and HF. The resulting mixture was diluted with water (~100 ml). Products were extracted with $CHCl_3$ (3×50 ml). Combined extracts were subsequently washed with H_2O (~50 ml), saturated aqueous $NaHCO_3$ (~30 ml), H_2O (~30 ml), and dried over Na_2SO_4. After solvent evaporation under the reduced pressure, the reaction products were finally isolated by column chromatography on silica gel.

4.4. Characterization of the products

*4.4.1. (E)-Methyl-3-(3-amino-4-methylphenyl)-3-(4-methylphenyl)propenoate (E)-**2a***

Compound (*E*)-**2a** was obtained from 2-methylphenylamine (24 mg, 0.23 mmol) and acetylene **1a** (30 mg, 0.17 mmol) in HSO_3F (1 ml) at −75 °C in 60 min in 8 mg (17%) according to the general alkenylation procedure. Slightly yellow oily compound. R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. IR ν_{max} (KBr) 3415, 3375, 1717, 1618 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 2.15 (s, 3H, Me), 2.38 (s, 3H, Me), 3.59 (br s, 2H, NH_2), 3.60 (s, 3H, OMe), 6.28 (s, 1H, =CH–), 6.55 (d, $1H_{arom.}$, *J* 1.7=Hz), 6.67 (dd, $1H_{arom.}$, *J*=7.8, 1.7 Hz), 6.99 (d, $1H_{arom.}$, *J*=7.8 Hz), 7.09 (d, $2H_{arom.}$, *J*=8.0 Hz), 7.17 (d, $2H_{arom.}$, *J*=8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) 17.15, 21.36, 51.08, 114.83, 115.40, 118.81, 124.00, 128.45, 129.13, 130.33, 137.84, 140.02, 144.36, 157.65, 166.60. MS, *m*/*z* (I_{rel}, %): 281 (M^+, 100), 266 (3), 250 (28). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.60; H, 7.15; N, 4.87.

*4.4.2. (E)-Methyl-3-(5-amino-2-methylphenyl)-3-phenylpropenoate (E)-**2b** and (Z)-methyl-3-(5-amino-2-methylphenyl)-3-phenylpropenoate (Z)-**2b***

Compounds (*E*)-**2b** and (*Z*)-**2b** were obtained as oily inseparable mixture of isomers from 4-methylphenylamine (83 mg, 0.77 mmol) and acetylene **1b** (50 mg, 0.31 mmol) in HSO_3F (1 ml) at −30 °C in 30 min in 11 mg (12%) for (*E*)-**2b**, and 1.5 mg (2%) for (*Z*)-**2b** according to the general alkenylation procedure. IR (for mixture) ν_{max} (KBr) 3450, 3362, 1722, 1610 cm^{-1}. (***E***)-**2b** R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. ^1H NMR (500 MHz, $CDCl_3$) (from the spectrum of mixture) 1.94 (s, 3H, Me), 3.64 (s, 3H, OMe), 3.58 (br s, 2H, NH_2), 5.98 (s, 1H, =CH–), 6.54 (d, $1H_{arom.}$, *J*=2.5 Hz), 6.59 (dd, $1H_{arom.}$, *J*=8.1, 2.5 Hz), 6.92 (d, $1H_{arom.}$, *J*=8.1 Hz), 7.23–7.30 (m, $5H_{arom.}$). (*Z*)-**2b** R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. ^1H NMR (500 MHz, $CDCl_3$) (from the spectrum of mixture) 1.95 (s, 3H, Me), 3.60 (s, 3H, OMe), 3.58 (br s, 2H, NH_2), 6.41 (d, $1H_{arom.}$, *J*=2.5 Hz), 6.48 (s, 1H, =CH–), 6.63 (dd, $1H_{arom.}$, *J*=8.1, 2.5 Hz), 7.02 (d, $1H_{arom.}$, *J*=8.1 Hz), 7.23–7.30 (m, $5H_{arom.}$). MS (for mixture), *m*/*z* (I_{rel}, %): 267 (M^+, 100), 236 (33), 207 (56), 206 (47), 197 (47), 130 (33), 115 (28). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.47; H, 6.30; N, 5.43.

*4.4.3. (E)-Methyl-3-(5-amino-2,4-dimethylphenyl)-3-(4-methylphenyl)propenoate (E)-**2c** and (Z)-methyl-3-(5-amino-2,4-dimethylphenyl)-3-(4-methylphenyl)propenoate (Z)-**2c***

Compounds (*E*)-**2c** and (*Z*)-**2c** were obtained as oily inseparable mixture of isomers from 2,4-dimethylphenylamine (21 mg, 0.17 mmol) and acetylene **1a** (30 mg, 0.17 mmol) in HSO_3F (1 ml) at −75 °C in 60 min in 13 mg (24%) for (*E*)-**2c**, and 6 mg (13%) for (*Z*)-**2c** according to the general alkenylation procedure. IR (for mixture) ν_{max} (KBr) 3450, 3373, 1720, 1621 cm^{-1}. (*E*)-**2c** R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. ^1H NMR (500 MHz, $CDCl_3$) (from the spectrum of mixture) 1.93 (s, 3H, Me), 2.14 (s, 3H, Me), 2.34 (s, 3H, Me), 3.47 (s, 2H, NH_2), 3.65 (s, 3H, OMe), 5.93 (s, 1H, =CH–), 6.51 (s, $1H_{arom.}$), 6.82 (s, $1H_{arom.}$), 7.09 (d, $2H_{arom.}$, *J*=8.0 Hz), 7.14 (d, $2H_{arom.}$, *J*=8.0 Hz). (*Z*)-**2c** R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. ^1H NMR (500 MHz, $CDCl_3$) (from the spectrum of mixture) 1.94 (s, 3H, Me), 2.17 (s, 3H, Me), 2.34 (s, 3H, Me), 3.60 (s, 3H, OMe), 3.69 (s, 2H, NH_2), 6.38 (s, $1H_{arom.}$), 6.45 (s, 1H, =CH–), 6.92 (s, $1H_{arom.}$), 7.10 (d, $2H_{arom.}$, *J*=7.8 Hz), 7.23 (d, $2H_{arom.}$, *J*=7.8 Hz). MS (for mixture), *m*/*z* (I_{rel}, %): 295 (M^+, 100), 280 (9), 264 (26), 235 (22), 221 (38), 147.5 (M^{++}, 5). Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.41; H, 7.05; N, 4.73.

*4.4.4. (Z)-4-(5-Amino-2,4-dimethylphenyl)-4-(4-methylphenyl)-but-3-en-2-one (Z)-**2d***

Compound (*Z*)-**2d** was obtained from 2,4-dimethylphenylamine (77 mg, 0.64 mmol) and acetylene **1c** (50 mg, 0.32 mmol) in HSO_3F (1 ml) at −30 °C in 60 min in 49 mg (56%) according to the general alkenylation procedure. Yellow oily compound. R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. IR ν_{max} (KBr) 3470, 3363, 1655, 1594 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 1.80 (s, 3H, Me), 1.93 (s, 3H, Me), 2.19 (s, 3H, Me), 2.33 (s, 3H, Me), 3.55 (br s, 2H, NH_2), 6.43 (s, $1H_{arom.}$), 6.63 (s, 1H, =CH–), 6.93 (s, $1H_{arom.}$), 7.10 (d, $2H_{arom.}$, *J*=8.3 Hz), 7.22 (d, $2H_{arom.}$, *J*=8.3 Hz). MS, *m*/*z* (I_{rel}, %): 279 (M^+, 53), 264 (100), 236 (30), 221 (20). Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.61; H, 8.02; N, 4.93.

*4.4.5. (E)-Methyl-3-(2-amino-4,5-dimethylphenyl)-3-(4-methylphenyl)propenoate (E)-**2e***

Compound (*E*)-**2e** was obtained from 3,4-dimethylphenylamine (49 mg, 0.4 mmol) and acetylene **1a** (35 mg, 0.2 mmol) in HSO_3F (1 ml) at −75 °C in 45 min in 20 mg (34%) according to the general alkenylation procedure. White solid. Mp 200 °C (decomposition). R_f [30% hexanes/ethyl acetate (8.5:1 v/v)]. IR ν_{max} (KBr) 3462, 3373, 1720, 1621 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 2.13 (s, 3H, Me), 2.17 (s,

3H, Me), 2.35 (s, 3H, Me), 3.42 (br s, 2H, NH_2), 3.64 (s, 3H, OMe), 6.10 (s, 1H, =CH–), 6.43 (s, $1H_{arom.}$), 6.83 (s, $1H_{arom.}$), 7.14 (d, $2H_{arom.}$, J=8.0 Hz), 7.21 (d, $2H_{arom.}$, J=8.0 Hz). MS, m/z (I_{rel}, %): 295 (M^+, 59), 264 (70), 263 (88), 248 (26), 236 (100), 222 (23). Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.21; H, 7.17; N, 4.82.

4.4.6. (E)-Methyl-3-(5-amino-2,3-dimethylphenyl)-3-(4-methylphenyl)propenoate (E)-**2f**

Compound (*E*)-**2f** was obtained from 3,4-dimethylphenylamine (49 mg, 0.4 mmol) and acetylene **1a** (35 mg, 0.2 mmol) in HSO_3F (1 ml) at −75 °C in 45 min in 4 mg (7%) according to the general alkenylation procedure. Slightly yellow oily compound. R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. IR ν_{max} (KBr) 3453, 3368, 1723, 1618 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 1.89 (s, 3H, Me), 2.15 (s, 3H, Me), 2.32 (s, 3H, Me), 3.65 (s, 5H, OMe, NH_2), 5.91 (s, 1H, =CH–), 6.39 (d, $1H_{arom.}$, J=2.3 Hz), 6.51 (d, $1H_{arom.}$, J=2.3 Hz), 7.09 (d, $2H_{arom.}$, J=8.0 Hz), 7.14 (d, $2H_{arom.}$, J=8.0 Hz). MS, m/z (I_{rel}, %): 295 (M^+, 100), 280 (14), 264 (25), 236 (35), 221 (39). Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.08; H, 7.45; N, 4.76.

4.4.7. (E)-Methyl-3-(3-amino-2,4,6-trimethylphenyl)-3-(4-methylphenyl)propenoate (E)-**2g**

Compound (*E*)-**2g** was obtained from 2,4,6-trimethylphenylamine (14 mg, 0.1 mmol) and acetylene **1a** (15 mg, 0.09 mmol) in HSO_3F (0.7 ml) at −75 °C in 60 min in 10 mg (38%) according to the general alkenylation procedure. Colorless oily compound. R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. IR ν_{max} (KBr) 3460, 3393, 1717, 1616 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 2.05 (s, 3H, Me), 2.06 (s, 3H, Me), 2.16 (s, 3H, Me), 2.31 (s, 3H, Me), 3.51 (br s, 2H, NH_2), 3.68 (s, 3H, OMe), 5.82 (s, 1H, =CH–), 6.79 (s, $1H_{arom.}$), 7.06 (d, $2H_{arom.}$, J=8.1 Hz), 7.15 (d, $2H_{arom.}$, J=8.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) 14.73, 17.57, 19.53, 21.27, 51.22, 119.15, 121.32, 124.63, 127.02, 128.33, 129.12, 129.51, 134.90, 138.57, 140.24, 140.63, 155.67, 167.16. MS, m/z (I_{rel}, %): 309 (M^+, 100), 278 (7), 249 (13), 234 (25), 221 (14). Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.48; H, 7.47; N, 4.53.

4.4.8. (Z)-4-(3-Amino-2,4,6-trimethylphenyl)-4-(4-methylphenyl)-but-3-en-2-one (Z)-**2h**

Compound (*Z*)-**2h** was obtained from 2,4,6-trimethylphenylamine (106 mg, 0.79 mmol) and acetylene **1c** (50 mg, 0.32 mmol) in HSO_3F (1 ml) at −30 °C in 75 min in 41 mg (44%) according to the general alkenylation procedure. Slightly yellow oily compound. R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. IR ν_{max} ($CHCl_3$) 3400, 3300, 1630, 1590 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 1.72 (s, 3H, Me), 1.94 (s, 3H, Me), 1.95 (s, 3H, Me), 2.21 (s, 3H, Me), 2.33 (s, 3H, Me), 3.56 (br s, 2H, NH_2), 6.80 (s, 1H, =CH–), 6.86 (s, $1H_{arom.}$), 7.10 (d, $2H_{arom.}$, J=8.1 Hz), 7.24 (d, $2H_{arom.}$, J=8.1 Hz). MS, m/z (I_{rel}, %): 293 (M^+, 100), 278 (96), 263 (10), 234 (31), 220 (21). Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.90; H, 7.68; N, 4.71.

4.4.9. (E)-Methyl-3-(6-tert-butyl-3-amino-2,4-dimethylphenyl)-3-(4-methylphenyl)propenoate (E)-**2i**

Compound (*E*)-**2i** was obtained from 4-*tert*-butyl-2,6-dimethylphenylamine (22 mg, 0.13 mmol) and acetylene **1a** (22 mg, 0.13 mmol) in HSO_3F (0.75 ml) at −75 °C in 60 min in 15 mg (34%) according to the general alkenylation procedure. Slightly yellow oily compound. R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. IR ν_{max} (KBr) 3460, 3393, 1717, 1616 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 1.22 (s, 9H, CMe_3), 2.00 (s, 3H, Me), 2.22 (s, 3H, Me), 2.31 (s, 3H, Me), 3.60 (br s, 2H, NH_2), 3.72 (s, 3H, OMe), 5.86 (s, 1H, =CH–), 7.05 (d, $2H_{arom.}$, J=8.3 Hz), 7.13 (s, $1H_{arom.}$), 7.20 (d, $2H_{arom.}$, J=8.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) 15.05, 18.07, 21.24, 33.09, 36.19, 51.35, 119.97, 120.46, 121.12, 127.32, 128.37, 130.04, 135.12, 137.29, 138.55, 138.87, 140.35, 155.31, 167.71. MS, m/z (I_{rel}, %): 351 (M^+, 100), 336 (83), 304 (17), 294 (14), 276 (34), 262 (43). Anal. Calcd for $C_{23}H_{29}NO_2$: C, 78.59; H, 8.32; N, 3.99. Found: C, 78.65; H, 8.27; N, 4.01.

4.4.10. (E)-Methyl-3-(3-amino-2,5,6-trimethylphenyl)-3-phenylpropenoate (E)-**2j**

Compound (*E*)-**2j** was obtained from 2,4,5-trimethylphenylamine (50 mg, 0.37 mmol) and acetylene **1b** (50 mg, 0.31 mmol) in HSO_3F (1 ml) at −30 °C in 60 min in 38 mg (30%) according to the general alkenylation procedure. White solid. Mp 126–128 °C. R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. IR ν_{max} (KBr) 3490, 3393, 1719, 1618 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 2.02 (s, 3H, Me), 2.03 (s, 3H, Me), 2.17 (s, 3H, Me), 3.48 (br s, 2H, NH_2), 3.68 (s, 3H, OMe), 5.87 (s, 1H, =CH–), 6.53 (s, $1H_{arom.}$), 7.27 (m, $5H_{arom.}$). MS, m/z (I_{rel}, %): 295 (M^+, 100), 264 (10), 248 (11), 236 (29), 220 (42), 134 (23). Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.35; H, 7.21; N, 4.69.

4.4.11. (E)-Methyl-3-(2-amino-3,5,6-trimethylphenyl)-3-phenylpropenoate (E)-**2k**

Compound (*E*)-**2k** was obtained from 2,4,5-trimethylphenylamine (50 mg, 0.37 mmol) and acetylene **1b** (50 mg, 0.31 mmol) in HSO_3F (1 ml) at −30 °C in 60 min in 22 mg (18%) according to the general alkenylation procedure. White solid. Mp 98–100 °C. R_f [30% hexanes/ethyl acetate (8.5:1 v/v)]. IR ν_{max} (KBr) 3485, 3388, 1720, 1616 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 2.04 (s, 3H, Me), 2.13 (s, 3H, Me), 2.15 (s, 3H, Me), 3.57 (br s, 2H, NH_2), 3.68 (s, 3H, OMe), 6.03 (s, 1H, =CH–), 6.86 (s, $1H_{arom.}$), 7.29–7.30 (m, $3H_{arom.}$), 7.35–7.37 (m, $2H_{arom.}$). MS, m/z (I_{rel}, %): 295 (M^+, 70), 264 (29), 248 (8), 236 (100), 221 (29). Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.30; H, 7.28; N, 4.74.

4.4.12. (E)-Methyl-3-(4-amino-2,3,5,6-tetramethylphenyl)-3-(4-methylphenyl)propenoate (E)-**2l**

Compound (*E*)-**2l** was obtained from 2,3,5,6-tetramethylphenylamine (41 mg, 0.28 mmol) and acetylene **1a** (50 mg, 0.31 mmol) in HSO_3F (1 ml) at −75 °C in 60 min in 19 mg (25%) according to the general alkenylation procedure. White solid. Mp 197–199 °C. R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. IR ν_{max} (KBr) 3485, 3390, 1720, 1615 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 2.09 (s, 6H, 2Me), 2.13 (s, 6H, 2Me), 2.31 (s, 3H, Me), 3.62 (br s, 2H, NH_2), 3.67 (s, 3H, OMe), 5.82 (s, 1H, =CH–), 7.06 (d, $2H_{arom.}$, J=7.5 Hz), 7.15 (d, $2H_{arom.}$, J=7.5 Hz). MS, m/z (I_{rel}, %): 323 (M^+, 100), 308 (24), 292 (12), 250 (47), 235 (52), 161.5 (M^{++}, 10). Anal. Calcd for $C_{21}H_{25}NO_2$: C, 77.98; H, 7.79; N, 4.33. Found: C, 78.01; H, 7.70; N, 4.35.

4.4.13. (Z)-Methyl-3-(4-amino-2,3,5,6-tetramethylphenyl)-3-(4-methylphenyl)propenoate (Z)-**2l**

Compound (*Z*)-**2l** was obtained under the stirring of solution of compound (*E*)-**2l** (15 mg, 0.05 mmol) in HSO_3F (0.8 ml) at −30 °C in 60 min in 13 mg (87%) with a quenching of the reaction mixture according to the general alkenylation procedure. Colorless oily compound. R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. IR ν_{max} (KBr) 3480, 3380, 177, 1610 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 1.97 (s, 6H, 2Me), 2.10 (s, 6H, 2Me), 2.33 (s, 3H, Me), 3.58 (s, 5H, OMe, NH_2), 6.60 (s, 1H, =CH–), 7.09 (d, $2H_{arom.}$, J=8.3 Hz), 7.23 (d, $2H_{arom.}$, J=8.3 Hz). Anal. Calcd for $C_{21}H_{25}NO_2$: C, 77.98; H, 7.79; N, 4.33. Found: C, 77.88; H, 7.85; N, 4.38.

4.4.14. (Z)-4-(4-Amino-2,3,5,6-tetramethylphenyl)-4-(4-methylphenyl)but-3-en-2-one (Z)-**2m**

Compound (*Z*)-**2m** was obtained from 2,3,5,6-tetramethylphenylamine (89 mg, 0.60 mmol) and acetylene **1c** (50 mg, 0.32 mmol) in HSO_3F (1 ml) at −30 °C in 60 min in 30 mg (31%) according to the general alkenylation procedure. Slightly yellow oily compound. R_f [20% hexanes/ethyl acetate (8.5:1 v/v)]. IR ν_{max} (KBr) 3480, 3387, 1647, 1593 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) 1.65 (s, 3H, Me), 2.00 (s,

6H, 2Me), 2.12 (s, 6H, 2Me), 2.33 (s, 3H, Me), 3.70 (br s, 2H, NH_2), 6.80 (s, 1H, =CH–), 7.10 (d, 2H$_{arom.}$, J=8.2 Hz), 7.24 (d, 2H$_{arom}$, J=8.2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) 13.45, 17.38, 21.19, 29.18, 118.42, 127.29, 127.89, 128.77, 129.33, 129.40, 131.03, 139.66, 142.43, 154.95, 200.54. MS, m/z (I_{rel}, %): 307 (M^+, 100), 292 (98), 264 (33), 248 (27), 234 (22). Anal. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C, 82.28; H, 8.21; N, 4.48.

4.4.15. (*E*)-Methyl-3-(3-amino-4-methoxyphenyl)-3-(4-methylphenyl)propenoate (*E*)-**2n**

Compound (*E*)-**2n** was obtained from 2-methoxyphenylamine (25 mg, 0.2 mmol) and acetylene **1a** (28 mg, 0.16 mmol) in HSO_3F (1 ml) at −75 °C in 60 min in 22 mg (45%) according to the general alkenylation procedure. Yellow oily compound. R_f [10% hexanes/ethyl acetate (8.5:1 v/v)]. IR ν_{max} (KBr) 3470, 3375, 1719, 1605 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) 2.34 (s, 3H, Me), 3.62 (s, 3H, OMe), 3.77 (br s, 2H, NH_2), 3.87 (s, 3H, OMe), 6.22 (s, 1H, =CH–), 6.54 (d, 1H$_{arom.}$, J=2.0 Hz), 6.62 (dd, 1H$_{arom.}$, J=8.2, 2.0 Hz), 6.78 (d, 1H$_{arom.}$, J=8.2 Hz), 7.11 (d, 2H$_{arom.}$, J=8.1 Hz), 7.20 (d, 2H$_{arom.}$, J=8.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) 21.33, 51.20, 55.52, 109.80, 114.71, 119.55, 125.85, 128.92, 129.64, 133.83, 135.91, 136.37, 138.54, 148.60, 154.65, 167.10. MS, m/z (I_{rel}, %): 297 (M^+, 100), 282 (29), 266 (12), 222 (16), 194 (11). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.70; H, 6.41; N, 4.65.

4.4.16. (*E*)-Methyl-3-(3-amino-2-methoxyphenyl)-3-(4-methylphenyl)propenoate (*E*)-**2o**

Compound (*E*)-**2o** was obtained as oily inseparable mixture with compound (*E*)-**2n** from 2-methoxyphenylamine (25 mg, 0.2 mmol) and acetylene **1a** (28 mg, 0.16 mmol) in HSO_3F (1 ml) at −75 °C in 60 min in 8 mg (17%) according to the general alkenylation procedure. R_f [15% hexanes/ethyl acetate (8.5:1 v/v)]. ^{1}H NMR (500 MHz, $CDCl_3$) (from the spectrum of mixture) 2.38 (s, 3H, Me), 3.59 (s, 3H, OMe), 3.76 (br s, 2H, NH_2), 3.85 (s, 3H, OMe), 6.24 (s, 1H, =CH–), 6.64–6.71 (m, 3H$_{arom.}$), 7.08 (d, 2H$_{arom.}$, J=7.9 Hz), 7.17 (d, 2H$_{arom.}$, J=7.9 Hz). MS (for mixture), m/z (I_{rel}, %): 297 (M^+, 100), 282 (29), 266 (12), 222 (16), 194 (11). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.70; H, 6.41; N, 4.65.

Acknowledgements

The authors thank the Government of the city of Saint-Petersburg for financial support of this work.

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