DOI: 10.1002/ejoc.200900926

A Cascade Approach to Captodative Trifluoromethylated Enamines or Vinylogous Guanidinium Salts: Aromatic Substituents as Switches of Reaction Direction

Alexander Yu. Rulev,*[a] Vasiliy M. Muzalevskiy,[b] Evgeniy V. Kondrashov,[a] Igor A. Ushakov,[a] Aleksey V. Shastin,[c] Elizabeth S. Balenkova,[b] Günter Haufe,[d] and Valentine G. Nenajdenko*[b]

Keywords: Amines / Nucleophilic substitution / Domino reactions

β-Halo-β-(trifluoromethyl)styrenes readily react with a variety of nitrogen nucleophiles bearing primary amino groups to afford either the captodative trifluoromethylated enamines or vinylogous guanidinium salts in a selective fashion depending on the electronic natures of the aromatic substituents.

Introduction

The significant progress in synthetic fluorine chemistry over recent decades is well documented.[1] The presence of fluorine atoms in a molecule is known often to induce unusual chemical, physical and biological properties. As a consequence, much attention has been devoted to the development of synthetic routes to various classes of fluorinated compounds. Among these, trifluoromethylated enamines have attracted increasing attention from organic chemists. They have found numerous applications in the construction of new fluorine-containing biologically active compounds and analogues of natural products.[2] *gem*-Amino(trifluoromethyl)olefins are of great theoretical, synthetic and pharmacological interest as distinctive captodative systems each bearing a strongly electron-donating amino function and a highly electronegative trifluoromethyl group at the same carbon atom of the double bond.

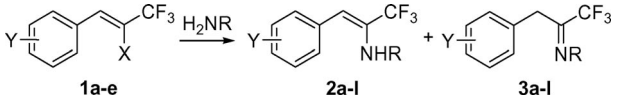
It is no surprise that different efforts to prepare α-polyfluoroalkyl-containing enamines have been undertaken, including Wittig reactions with trifluoroacetamides,[3,4] treatment of amines with perfluoroalkyl ketones,[5] additions of amines to trifluoromethylacetylenes[6] and direct trifluoromethylation of pyrrolidinones.[7] A simple method for the preparation of fluoroalkyl β-enaminophosphonates from alkylphosphonates and perfluoroalkyl nitriles has also been reported.[8] The most straightforward route to captodative (trifluoromethyl)-aminoalkenes is through the substitution of an appropriate leaving group in the corresponding alkene by an amino function. In general, nucleophilic vinylic substitution is an important synthetic tool for the preparation of compounds containing heteroatom-substituted carbon–carbon double bonds.[9] Previously this methodology has been successfully applied to the synthesis of various captodative aminoalkenes containing carbonyl, formyl or alkoxycarbonyl functions.[10] Similar approaches using α-halo (trifluoromethyl) olefins have been reported only infrequently. Some *gem*-perfluoroalkylated enamines have been prepared by treatment of β-halo- or β-alkoxy-substituted β-(trifluoromethyl)styrenes with lithium alkylamides.[11] Very recently, we have developed an efficient method of synthesis of α-trifluoromethylated aminoalkenes by treatment of β-halo-β-(trifluoromethyl)styrenes with secondary amines.[12] The starting alkenes can be prepared very easily by a novel general method for catalytic olefination of carbonyl compounds.[13] As a part of our research program relating to the synthesis of novel captodative aminoalkenes and understanding of the particularities of their chemical behaviour, we have now examined reactions between the same styrenes and primary amines. Here we describe our synthetic efforts to achieve captodative amino(trifluoromethyl)alkenes bearing secondary amino groups.

[a] A. E. Favorsky Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,
1, Favorsky Str., Irkutsk 664033, Russia
Fax: +7-3952-419346
E-mail: rulev@irioch.irk.ru
[b] Moscow State University, Department of Chemistry,
Leninskie Gory, Moscow 119992, Russia
Fax: +7-495-9328846
E-mail: nen@acylium.chem.msu.ru
[c] Institute of Problems of Chemical Physics,
Chernogolovka, Moscow Region 142432, Russia
[d] Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster,
48149 Münster, Germany
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900926.

Results and Discussion

The β-halogen-β-(trifluoromethyl)styrenes **1a**–**l** (see Tables 1 and 2, below), including the parent compound **1l** and derivatives bearing either electron-withdrawing or electron-donating groups on their benzene rings, were used in reactions with primary amines. It was found that the structural peculiarities of substrates **1** have a dramatic influence on the pathways of the transformations, summarized in Tables 1 and 2, below.

Initially we focused on styrenes bearing electron-withdrawing groups, because they had previously displayed higher activities in reactions with secondary amines.[12] The target enamines **2** were successfully obtained from the styrenes **1a**–**e** containing strong acceptors such as NO_2 in their aromatic rings. The reactions between these olefins and a wide range of nitrogen nucleophiles bearing primary amino groups could be performed under diverse experimental conditions (from some minutes to two days, from room temperature to reflux, without solvent or in THF, dioxane or alcohol), exclusively providing mixtures of the corresponding enamines **2** and azomethines **3**, which could easily be separated by column chromatography (Scheme 1, Table 1).



Scheme 1. Reactions between primary amines and styrenes **1a**–**e**.

Generally, the position of the nitro substituent in the aryl group or the nature of the vinylic halogen atom (Br or Cl) in the initial substrate **1**, as well as the steric and electronic effects of the substituent on the nitrogen atom of the aliphatic amine, have just a small influence on the yields and stereoselectivities. The best results were achieved when basic primary amines were used as nucleophiles (Table 1, Entries 1–12). It should be noted that decreased nucleophilicity resulted in reaction failure with aromatic amines (Table 1, Entries 13, 14). Thus, when the styrene **1d** was treated with an excess of aniline, only the signals of the unchanged starting materials were detectable by NMR spectroscopy even after prolonged heating of the reaction mixture in dioxane at reflux and starting material was recovered almost quantitatively after usual workup.

In all reactions studied, the enamines **2** were formed as mixtures of *Z* and *E* isomers. The stereoselectivities of the overall transformations were high; by ^{1}H NMR spectroscopy the *Z* double bond geometry was seen to be strongly favoured in most cases, by up to 9:1. The *Z* configurations were assigned to the major isomers of **2** by application of ^{1}H–^{1}H 2D homonuclear NOESY (Figure 1). In the spectrum of the major isomer of the enamine **2a**, for example, there are NOE peaks between the signal of the olefinic proton and the *ortho*-protons of the aromatic ring only. In contrast, the NOESY spectrum of the minor isomer has cross-peaks of the olefinic proton both with the H-2 aromatic protons and with the protons of a CH_2 group of the cyclohexyl moiety. As in cases both of normal enamines and of captodative carbonyl-bearing enamines,[10] the signal for the olefinic proton of an *E* isomer is always observed at lower frequency.

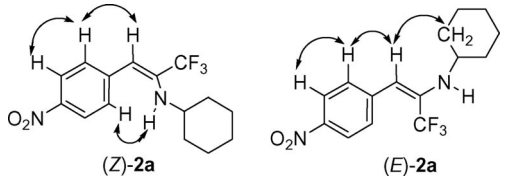


Figure 1. Main NOESY correlations for enamine **2a**.

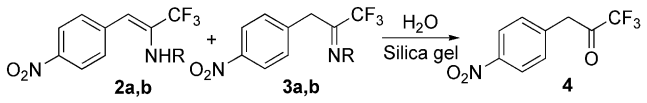
It should be noted that enamines **2** are slowly transformed into their tautomers **3** (Scheme 1). Thus, low-intensity signals for compound **3a** were observed in the proton spectra of enamine **2a** after a week in $CDCl_3$ solution at ambient temperature.

Table 1. Reactions between primary amines and styrenes **1a**–**e**.

Entry	Styrene	Y	X	Amine R	Conditions	Product	*Z*/*E* ratio in **2**	Yield (%)[a]
1	**1a**	4-NO_2	Br	*c*Hex	THF, reflux, 8 h	**2a**	88:12	75
						3a		11
2	**1a**	4-NO_2	Br	*s*Bu	EtOH, reflux, 8 h	**2b**	90:10	29
						3b		45
3	**1b**	4-NO_2	Cl	Me	MeOH, room temp., 1 d	**2c** + **3c** (1:3)	52:48	85
4	**1b**	4-NO_2	Cl	*i*Pr	neat, room temp., 2 d	**2d** + **3d** (1:0.9)	88:12	88
5	**1b**	4-NO_2	Cl	$Ph(CH_2)_2$	neat, room temp., 1.5 d	**2e** + **3e** (1:4)	80:20	90
6	**1b**	4-NO_2	Cl	(*S*)-PhCHMe	neat, 120 °C, 18 h	**2f** + **3f** (1:1)	76:24	63
7	**1b**	4-NO_2	Cl	$(MeO)_2CHCHMe$	neat, 120 °C, 6 h	**2g** + **3g** (1:0.5)	91:9	80
8	**1c**	3-NO_2	Cl	*c*Hex	THF, reflux, 7 h	**2h** + **3h** (1:1.4)	90:10	71
9	**1c**	3-NO_2	Cl	*s*Bu	EtOH, reflux, 8 h	**3i**	91:9	20[b]
10	**1d**	2-NO_2	Br	*c*Hex	neat, room temp., 6 h	**2j** + **3j** (1:1.1)	88:12	97
11	**1d**	2-NO_2	Br	*s*Bu	dioxane, reflux, 3 h	**2k** + **3k** (1:1.5)	90:10	96
12	**1 e**	2-NO_2	Cl	*i*Pr	neat, room temp., 6 h	**2l** + **3l** (1:0.9)	88:12	96
13	**1b**	4-NO_2	Cl	4-$MeOC_6H_4$	THF, reflux, 2 h	–	–	0
14	**1d**	2-NO_2	Br	Ph	dioxane, reflux, 6 h	–	–	0

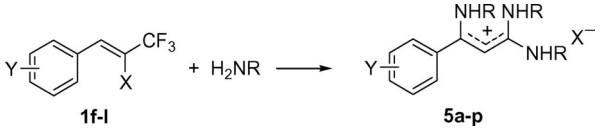
[a] Isolated yield. [b] 30% yield of starting material was recovered; if the reaction was carried out in THF at reflux for 15 h more than 80% of the initial styrene **1c** was recovered.

The enamine or azomethine moieties in compounds **2** or **3** are easily hydrolyzed to give the corresponding carbonyl derivatives. The accompanying hydrolysis reaction begins during silica gel column chromatography. For this reason the yields of the purified target compounds decreased slightly, and sometimes the corresponding ketones **4** (Scheme 2) were formed simultaneously. Thus, during purification of enamines **2a** and **2b** and azomethines **3a** and **3b** small quantities (up to 3–5%) of ketone **4** were isolated.



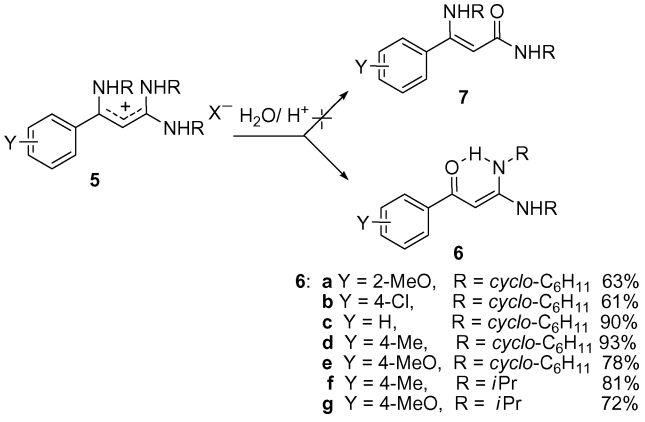
Scheme 2. Hydrolysis of derivatives **2a**, **2b**, **3a** and **3b**.

Surprisingly, in reactions between primary amines and styrenes lacking acceptor-substituted aromatic rings, neither the expected captodative enamines **2** nor their isomers **3** were obtained. In contrast to styrenes **1a**–**e**, the analogues **1f**–**k**, bearing functional groups such as Me, OMe, and Cl, underwent unusual transformations on treatment with primary aliphatic amines, leading to the triamino derivatives **5a**–**m** in moderate to high yields, independently of the substituent position in the aromatic ring (Scheme 3, Table 2). The parent unsubstituted styrene **1l** is also a suitable substrate, affording the products **5n**–**p** in good yields.



Scheme 3. Reactions between primary amines and styrenes **1f**–**l**.

The derivatives **5** thus obtained are useful precursors of push-pull aminoenones **6**. In fact, the compounds **5** were easily hydrolyzed with dilute HCl to give the ketones **6a**–**g** in good yields. Aminoenones of this type can be versatile intermediates for the synthesis of various heterocycles (Scheme 4).[14] Additionally, these transformations provided direct chemical evidence for the structures of the unusual salts **5**. It should be noted that the alternative structure represented by the isomeric amides **7** was excluded by additional NMR spectroscopic experiments. That is, there are significant differences in the chemical shifts of the NH protons in the ^{1}H NMR spectrum of the hydrolysis product of compound **5a** (4.12 and 11.39 ppm), due to intramolecular hydrogen bond formation. Moreover, the low-frequency chemical shift of the α-carbon atom (δ = 80.33 ppm), together with the high-frequency shift of the β-carbon atom (δ = 159.21 ppm) of the obtained product, suggest the presence of an extremely polar carbon–carbon double bond: the difference [$\Delta\delta = \delta(C_\beta) - \delta(C_\alpha)$] amounts to +79 ppm and is comparable to those observed for simple push-pull aminoenones (65–70 ppm).[15] Finally, the chemical shift of the carbonyl group (183.50 ppm) provides an additional argument for the structure of ketone **6a**. The structure of this compound was also confirmed by careful analysis of 2D NMR spectra (NOESY, HSQC, HMBC).



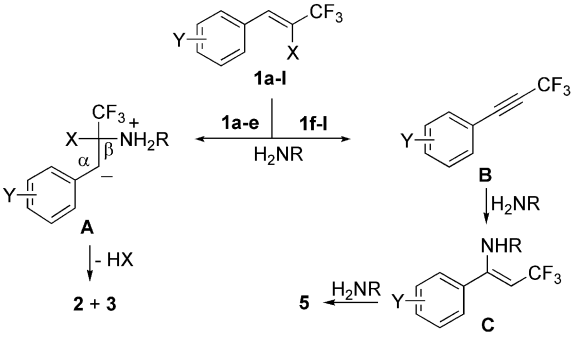
Scheme 4. Hydrolysis of derivatives **5** to afford compounds **6**.

Table 2. Reactions between primary amines and styrenes **1f**–**l**.

Entry	Styrene	Y	X	Amine R	Conditions	Product	Yield (%)[a]
1	**1f**	4-Cl	Br	*c*Hex	neat, reflux, 1 h	**5a**	64
2	**1f**	4-Cl	Br	*i*Pr	neat, 80 °C, 5 h	**5b**	63
3	**1f**	4-Cl	Br	$(MeO)_2CHCHMe$	neat, 120 °C, 4 h	**5c**	39
4	**1g**	4-Cl	Cl	*i*Pr	neat, 120 °C, 18 h	**5d**	34
5	**1g**	4-Cl	Cl	*c*Hex	diglyme, reflux, 8 h	**5e**	20[b]
6	**1h**	4-Me	Br	*c*Hex	neat, reflux, 3 h	**5f**	85
7	**1h**	4-Me	Br	*i*Pr	neat, 120 °C, 4 h	**5g**	92
8	**1i**	4-MeO	Br	*s*Bu	neat, reflux, 8 h	**5h**	61
9	**1i**	4-MeO	Br	*i*Pr	neat, 120 °C, 4 h	**5i**	81
10	**1i**	4-MeO	Br	*c*Hex	dioxane, reflux, 7 h	**5j**	65
11	**1j**	3-MeO	Br	*c*Hex	dioxane, reflux, 7 h	**5k**	59
12	**1k**	2-MeO	Br	*c*Hex	neat, reflux, 7 h	**5l**	72
13	**1k**	2-MeO	Br	*s*Bu	neat, reflux, 3 h	**5m**	69
14	**1l**	H	Br	*i*Pr	neat, 120 °C, 6 h	**5n**	85
15	**1l**	H	Br	*c*Hex	THF, reflux, 7 h	**5o**	88
16	**1l**	H	Br	Bn	EtOH, reflux, 6 h	**5p**	61

[a] Isolated yields. [b] 50% yield of the starting material was recovered. No reaction occurred when THF or dioxane were used as solvents.

Although the data currently available do not yet allow the assignment of detailed mechanisms for the formation of compounds **2**, **3** and **5** in the reactions between styrenes **1** and primary amines, the results obtained can be explained in terms of the general domino transformations shown in Scheme 5 as the most probable hypothesis.

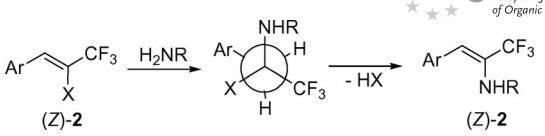


Scheme 5. Possible mechanisms for the formation of compounds **2**, **3** and **5**.

A principal reason for the different reaction directions in the nucleophilic substitutions of **1a**–**e** and **1f**–**l** would appear to be the stabilities of the intermediate zwitterions **A** (stabilized by the acceptor substituents) in the cases of the alkenes **1a**–**e** (addition/elimination)[16] and the impossibility of such a direction in the cases of the olefins **1f**–**l**, for which initial HX elimination with intermediate formation of acetylenes **B** and subsequent nucleophilic addition (elimination/addition) would seem to be the most favourable reaction pathway. From the mechanistic point of view, the key steps of the substitution of the halogen atoms in styrenes **1a**–**e** would seem to be β-addition of the primary amines to the carbon–carbon double bond and subsequent elimination of the hydrogen halide: *Ad – E*. It should be underlined that the presence of an aromatic ring bearing an electron-withdrawing group should stabilize the β adduct **A**. The dehydrohalogenation of this intermediate by the amine leads directly to the enamine **2** and its tautomer **3**.

Evidence in support of this hypothesis (i.e., β-addition instead of α-addition) was obtained by stereochemical analysis of the reaction. The geometries of the styrenes **1a** and **2a** were elucidated by comparison of the vicinal coupling constants between the carbon atom of the CF_3 group and the olefinic proton ($^3J_{H,CF}$ = 5.5 Hz for both compounds **1a** and **2a**).[17,18] Taking into account that the major isomer of the enamine **2a** has the *Z* configuration, we concluded that the initial styrene **1a** would have the same geometry. The preservation of the configuration can be easily explained in terms of a preferable *anti*-elimination of HX (Scheme 6). Moreover, no alternative intermediate, such as a diamino derivative, has been detected (cf. ref.[19]).

The preference for the pathway involving an initial direct β-addition of the primary amine to the double bond of the starting styrene **1a** and subsequent dehydrohalogenation resulting in the formation of enamine **2a** was confirmed by RHF-MP2 quantum chemical calculations at the MP2/6–311+dp level with use of styrenes bearing either electron-withdrawing (NO_2) or electron-donating (Me) substituents, as well as the unsubstituted parent compound, as models, together with methylamine. Full optimization of the geometries of the molecules was performed, as well as calculation of the total energies corresponding to these optimized geometries. Calculations were carried out for the isolated molecules of the model compounds (in vacuo) with replacement of the complex amino fragment with the methylamine moiety as a simplification. The calculations were performed for all possible conformers of the final products of methylamine addition at the α (group 1) or β (group 2) positions of the styrenes. For each group the most stable conformers and their energies were chosen and compared with each other. In all cases, the formation of β adducts was preferred over that of the α adducts by 5–6 kcal mol^{-1}. The corresponding calculated structures and their energies are listed in the Table in the Supporting Information.



Scheme 6. Formation of compounds (*Z*)-**2**.

In contrast, the styrenes **1f**–**l**, lacking electron-withdrawing substituted aromatic rings, react with primary amines by an alternative pathway through an elimination/addition sequence to give the enamines **C**. The intermediate acetylene derivatives **B** were detected by NMR and GC-MS. When the product mixture resulting from the reaction between the styrene **1i** and *sec*-butylamine was applied to column chromatography, two fractions were obtained: the major one was the product **5h**, whereas the minor one contained a mixture of the initial substrate **1i** and an unknown compound. Careful analysis of the 1D (^{1}H, ^{13}C) and 2D (HMBC, COSY) NMR spectra of the latter fraction confirmed the presence of alkyne **B** (Y = 4-MeO) in the mixture. The ^{13}C NMR spectrum contains two quadruplets at δ = 74.9 ppm (J = 52.1 Hz) and δ = 87.3 ppm (J = 6.4 Hz) attributable to the acetylenic carbon atoms, together with a quadruplet for the CF_3 group (δ = 120.9 ppm, J = 231 Hz). The signals for the aromatic moiety were observed at δ = 114.5, 126.3, 130.2 and 161.8 ppm. The presence of a molecular ion of *m*/*z* 200 in the mass spectrum also confirmed the structure of alkyne **B** (Y = MeO). Amines add to alkyne **B**, leading directly to enamines **C**, which undergo succeeding transformations as we have described previously,[12] so this hypothetical scheme provides a convenient explanation for the selectivity of the formation either of the enamines **2** or of the salts **5**.

Conclusions

In summary, we have demonstrated that vinylic substitution of *gem*-trifluoromethylated haloalkenes with primary amines is a valuable synthetic tool for the preparation of

captodative amino(trifluoromethyl)alkenes. However, the synthesis of the target enamines is strongly limited by the natures of the substituents on the aromatic rings, which can be regarded as switches of the reaction direction: whereas styrenes bearing electron-withdrawing groups led exclusively to the target enamines **2** (or their tautomers **3**), their analogues containing electron-donating substituents in their aromatic rings (or without substituents) underwent previously unprecedented[12] transformations into the amidinium salts **5**.

Experimental Section

General Remarks: ^{1}H, ^{13}C, ^{15}N and ^{19}F NMR spectra were recorded with Bruker ARX 300, Bruker AMX 400 and Bruker AVANCE 400 MHz spectrometers with solutions in $CDCl_3$, [D_6]-DMSO or $(CD_3)_2CO$. Chemical shifts (δ) in ppm are reported with use of the residual chloroform (7.25 for ^{1}H and 77.20 for ^{13}C), DMSO (2.50 for ^{1}H and 29.90, 39.50 for ^{13}C) or acetone (2.09 for ^{1}H and 29.90, 206.70 for ^{13}C) as internal references. The coupling constants (J) are given in Hertz (Hz). The concerted application of ^{1}H–^{1}H 2D COSY[20] and NOESY[21] homonuclear experiments as well as ^{1}H–^{13}C 2D HSQC[22] and HMBC[23] heteronuclear experiments was used for the distinction of the carbon and proton resonances in all cases. The IR spectra were recorded with a Bruker Vertex 70 FT-IR spectrometer and with a portable Varian 3100 diamond ATR/FT-IR spectrometer. The GC/MS analyses were performed with a Shimadzu GCMS-QP5050A instrument (EI, 70 eV). ESI-MS spectra were measured with a MicroTof Bruker Daltonics instrument. The silica gel used for flash chromatography was 230–400 mesh. All reagents were of reagent grade and were either used as such or distilled prior to use. All the solvents were dried by standard procedures and freshly distilled prior to use. The β-chloro- and β-bromo-β-(trifluoromethyl)styrenes **1a**–**l** were prepared as reported previously.[13b,13h] The quantum chemical calculations were carried out at the MP2/6–311+dp level with use of the PC GAMESS/Firefly QC package.[24]

General Procedure for Reactions between the β-Chloro- and β-Bromo-β-Trifluoromethylstyrenes 1a–e and Primary Amines: The appropriate styrene (**1a**–**e**, 1–1.5 mmol) and the amine [10–15 mmol; in this case methylamine in methanol (8 M) was used], either in the solvent given or without solvent, were maintained at room temperature or reflux or were heated in a sealed glass tube with a Young tap. Excess amine and solvent were evaporated off at reduced pressure and the residue was purified by column chromatography [silica gel, CH_2Cl_2/pentane (2:1) or Et_2O/hexane (1:2)]. The enamines **2a** and **2b** and the azomethines **3a** and **3b** were separated on silica gel, with Et_2O/hexane (1:7) as eluent. In the NMR spectra of some mixtures of the (*Z*,*E*)-enamines **2** and the azomethines **3** only the most characteristic signals are given for minor components.

***N*-[1,1,1-Trifluoro-3-(4-nitrophenyl)prop-2-en-2-yl]cyclohexanamine (2a):** Yellow solid; m.p. 77 °C; yield 235 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$): *Z* isomer: δ = 0.95–1.90 (m, 10 H, CH_2 cyclohexyl), 2.95 (s, 1 H, NH), 3.45 (m, 1 H, CH cyclohexyl), 5.92 (s, 1 H, CH=), 7.49 (d, J = 8.6 Hz, 2 H, CH_{Ar}), 8.17 (d, J = 8.6 Hz, 2 H, CH_{Ar}) ppm. *E* isomer: δ = 0.95–1.90 (m, 10 H, CH_2 cyclohexyl), 3.18–3.30 (m, 1 H, CH cyclohexyl), 5.55 (s, 1 H, CH=), 7.32 (d, J = 8.6 Hz, 2 H, CH_{Ar}), 8.10 (d, J = 8.6 Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): *Z* isomer: δ = 25.0, 25.6, 34.0 (CH_2), 54.0 (CH), 104.1 (q, J = 5.0 Hz, CH=), 122.1 (q, J = 275.7 Hz, CF_3), 123.9 (C-3,5), 129.1 (C-2,6), 135.6 (q, J = 33 Hz, =C–N), 142.7 (C-1), 146.0 (C-4) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): *Z* isomer: δ = –69.3 ppm. *E* isomer: δ = –63.2 ppm. ^{15}N NMR (40.6 MHz, $CDCl_3$): *Z* isomer: δ = –302.5 (NH), –10.8 (NO_2) ppm. IR (KBr): $\tilde{\nu}$ = 1633, 3372 cm^{-1}. MS (EI): *m*/*z* (%) = 314 (5) $[M]^+$, 178 (28), 83 (83), 55 (100). $C_{15}H_{17}F_3N_2O_2$ (314.303): calcd. C 57.32, H 5.45, N 8.91; found C 57.51, H 5.60, N 9.22.

***N*-[2,2,2-Trifluoro-1-(4-nitrobenzyl)ethylidene]cyclohexylamine (3a):** Oil; yield 11%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10–1.80 (m, 10 H, CH_2 cyclohexyl), 3.48 (m, 1 H, CH cyclohexyl), 3.87 (s, 2 H, CH_2), 7.31 (d, J = 8.6 Hz, 2 H, CH_{Ar}), 8.17 (d, J = 8.6 Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.2, 25.4, 32.9 (CH_2), 32.7 ($ArCH_2$), 60.9 (CH), 119.9 (q, J = 279.5 Hz, CF_3), 124.3 (C-3,5), 129.3 (C-2,6), 142.4 (C-1), 147.2 (C-4), 153.0 (q, J = 33 Hz, C=N) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –71.9 ppm. IR (KBr): $\tilde{\nu}$ = 1600 cm^{-1}. MS (EI): *m*/*z* (%) = 314 (12) $[M]^+$, 232 (26), 83 (46), 55 (100). $C_{15}H_{17}F_3N_2O_2$ (314.303): calcd. C 57.32, H 5.45, N 8.91; found C 57.61, H 5.24, N 8.68.

1,1,1-Trifluoro-3-(4-nitrobenzyl)acetone (4): Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.13 (s, 2 H, CH_2), 7.39 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 8.21 (d, J = 8.8 Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 43.3 (Ar-CH_2), 115.2 (q, J = 286 Hz, CF_3), 124.2 (C-3,5), 130.9 (C-2,6), 137.8 (C-1), 147.9 (C-4), 186.9 (q, J = 38 Hz, C=N) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –78.5 ppm. MS (EI): *m*/*z* (%) = 233 (17) $[M]^+$, 164 (24), 136 (77), 78 (100).

***N*-[2-(4-Nitrophenyl)-1-(trifluoromethyl)ethenyl]-2-butylamine (2b):** Yellow solid; m.p. 71 °C; yield 125 mg (29%). ^{1}H NMR (400 MHz, $CDCl_3$): *Z* isomer: δ = 0.84 (t, J = 7.3 Hz, 3 H, CH_3), 1.01 (d, J = 6.2 Hz, 3 H, CH_3), 1.30–1.50 (m, 2 H, CH_2), 3.15 (m, 1 H, NH), 3.38 (m, 1 H, CH), 5.92 (s, 1 H, CH=), 7.48 (d, J = 8.6 Hz, 2 H, CH_{Ar}), 8.17 (d, J = 8.6 Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.2 (CH_3CH_2), 20.6 (CH_3CH), 30.3 (CH_2CH_3), 52.0 (CH), 103.6 (q, J = 5.0 Hz, CH=), 122.1 (q, J = 276.0 Hz, CF_3), 123.9 (C-3,5), 129.1 (C-2,6), 135.7 (q, J = 33 Hz, =C–N), 142.7 (C-1), 146.0 (C-4) ppm. ^{15}N NMR (40.6 MHz, $CDCl_3$): *Z* isomer: δ = –302.7 (NH), –11.8 (NO_2) ppm. IR (KBr): $\tilde{\nu}$ = 1627, 3379 cm^{-1}. MS (EI): *m*/*z* (%) = 288 $[M]^+$ (14), 259 (48), 198 (31), 57 (74). 41 (100%). $C_{13}H_{15}F_3N_2O_2$ (288.266): calcd. C 54.17, H 5.24; found C 53.94, H 5.30.

***N*-[2,2,2-Trifluoro-1-(4-nitrobenzyl)ethylidene]-2-butylamine (3b):** Oil; yield 194 mg (45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.70–1.20 (m, 6 H, CH_3), 1.45–1.60 (m, 2 H, CH_2), 3.56 (m, 1 H, CH), 3.84 (A-part of the AB system, J = 16 Hz, 1 H, Ar-CH_2), 3.90 (B-part of the AB system, J = 16 Hz, 1 H, Ar-CH_2), 7.31 (d, J = 8.6 Hz, 2 H, CH_{Ar}), 8.16 (d, J = 8.6 Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.7 (CH_3CH_2), 20.6 (CH_3CH), 30.3 (CH_2CH_3), 32.8 ($ArCH_2$), 58.4 (CH), 119.9 (q, J = 279.5 Hz, CF_3), 124.2 (C-3,5), 129.4 (C-2,6), 142.3 (C-1), 147.2 (C-4), 153.6 (q, J = 33 Hz, C=N) ppm. ^{15}N NMR (40.6 MHz, $CDCl_3$): δ = –19.4 (C=N), –12.1 (NO_2) ppm. IR (KBr): $\tilde{\nu}$ = 1599 cm^{-1}. MS (EI): *m*/*z* (%) = 288 $[M]^+$ (7), 259 (15), 57 (93), 41 (100%). $C_{13}H_{15}F_3N_2O_2$ (288.266): calcd. C 54.17, H 5.24; found C 53.77, H 5.44.

Mixture of (*Z*,*E*)-Enamine 2c and Azomethine 3c: Yellow-orange solid; yield 209 mg (85%).

3,3,3-Trifluoro-*N*-methyl-1-(4-nitrophenyl)prop-1-en-2-amine (2c): ^{1}H NMR (300 MHz, $CDCl_3$): *Z* isomer: δ = 2.72 (d, J = 5.2 Hz, 3 H, Me), 5.91 (s, 1 H, CH=), 7.46 (d, J = 8.8 Hz, 2 H, Ar) ppm. *E* isomer: δ = 2.35 (d, J = 5.0 Hz, 3 H, Me), 5.47 (s, 1 H, CH=), 8.12

(d, J = 8.3 Hz, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *Z* isomer: δ = 30.3 (Me), 101.3 (q, J = 6.1 Hz, CH=), 123.6 (C-3,5), 129.0 (C-2,6), 142.4 (C-1) ppm. *E* isomer: δ = 33.7 (Me), 98.9 (q, J = 2.2 Hz, CH=), 123.3 (C-3,5), 128.9 (q, J = 2.6 Hz, C-2,6), 143.1 (C-1) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): *Z* isomer: δ = –68.7 ppm. *E* isomer: δ = –63.2 ppm.

***N*-[1,1,1-Trifluoro-3-(4-nitrophenyl)propan-2-ylidene]methanamine (3c):** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.42 (s, 3 H, Me), 3.96 (s, 2 H, CH_2), 7.35 (d, J = 8.7 Hz, 2 H, Ar), 8.21 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.3 (CH_2), 39.6 (Me), 119.6 (q, J = 278.7 Hz, CF_3), 124.2 (C-3,5), 129.1 (C-2,6), 141.2 (C-1), 147.1 (C-4), 157.2 (q, J = 32.9 Hz, *C*-CF_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –72.6 ppm. ESI-MS (*m*/*z*): calcd. for $C_{10}H_9F_3N_2O_2Na$ $[M]^+$ 269.0514; found 269.0508. $C_{10}H_9F_3N_2O_2$ (246.186): calcd. C 48.79, H 3.68, N 10.38; found C 48.74, H 3.45, N 10.33.

Mixture of (*Z*,*E*)-Enamine 2d and Azomethine 3d: Yellow solid; yield 241 mg (88%).

3,3,3-Trifluoro-*N*-isopropyl-1-(4-nitrophenyl)prop-1-en-2-amine (2d): ^{1}H NMR (300 MHz, $CDCl_3$): *Z* isomer: δ = 1.10 (d, J = 6.0 Hz, 6 H, Me), 3.31–3.43 (m, 2 H, CH, NH), 5.99 (s, 1 H, CH=), 7.54 (d, J = 8.7 Hz, 2 H, Ar), 8.20 (d, J = 8.7 Hz, 2 H, Ar) ppm. *E* isomer: δ = 1.28 (d, J = 6.2 Hz, 6 H, Me), 3.52–3.63 (m, 1 H), 5.53 (s, 1 H, s, CH=), 8.10 (d, J = 8.9 Hz, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *Z* isomer: δ = 22.8 (Me), 46.6 (CH), 104.3 (q, J = 5.0 Hz, CH=), 119.8 (q, J = 279.4 Hz, CF_3), 123.6 (C-3,5), 128.9 (C-2,6), 135.5 (q, J = 30.1 Hz, *C*-CF_3), 142.1 (C-1), 145.8 (C-4) ppm. *E* isomer: δ = 21.7 (Me), 44.2 (CH), 98.9 (q, J = 2.2 Hz, CH=), 123.3 (C-3,5), 128.8 (C-2,6), 143.2 (C-1) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): *Z* isomer: δ = –69.7 ppm. *E* isomer: δ = –63.2 ppm.

***N*-[1,1,1-Trifluoro-3-(4-nitrophenyl)propan-2-ylidene]propan-2-amine (3d):** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (d, J = 6.2 Hz, 6 H, Me), 3.88 (sept, J = 6.2 Hz, 1 H, CH), 3.94 (s, 2 H, CH_2), 7.37 (d, J = 8.9 Hz, 2 H, Ar), 8.20 (d, J = 8.9 Hz, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.0 (Me), 32.4 (CH_2), 52.4 (CH), 121.9 (q, J = 275.9 Hz, CF_3), 124.1 (C-3,5), 129.1 (C-2,6), 142.5 (C-1), 147.0 (C-4), 152.8 (q, J = 32.8 Hz, *C*-CF_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –72.1 ppm. ESI-MS (*m*/*z*): calcd. for $C_{12}H_{13}F_3N_2O_2Na$ $[M]^+$ 297.0827; found 297.0821. $C_{12}H_{13}F_3N_2O_2$ (274.239): calcd. C 52.56, H 4.78, N 10.21; found C 52.63, H 4.82, N 10.07.

Mixture of (*Z*,*E*)-Enamine 2e and Azomethine 3e: Yellow oil; yield 302 mg (90%).

3,3,3-Trifluoro-1-(4-nitrophenyl)-*N*-phenethylprop-1-en-2-amine (2e): ^{1}H NMR (300 MHz, $CDCl_3$): *Z* isomer: δ = 2.79 (t, J = 6.8 Hz, 2 H, CH_2), 3.24 (q, J = 6.5 Hz, 2 H, CH_2), 5.91 (s, 1 H, CH=), 8.07 (d, J = 8.9 Hz, 2 H, Ar) ppm. *E* isomer: δ = 2.97 (t, J = 7.1 Hz, 2 H, CH_2), 3.34 (q, J = 6.5 Hz, 2 H, CH_2), 5.54 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *Z* isomer: δ = 34.5, 47.2, 103.0 (q, J = 5.5 Hz, CH=), 123.8 (C-3,5, 4-$NO_2C_6H_4$), 126.9 (CH, Ph), 128.8 (CH, Ph), 128.9 (C-2,6, 4-$NO_2C_6H_4$), 136.2 (q, J = 30.1 Hz, *C*-CF_3), 138.0 (C-1, Ph), 142.2 (C-1, 4-$NO_2C_6H_4$), 145.7 (C-4, 4-$NO_2C_6H_4$) ppm. *E* isomer: δ = 44.9 (CH), 123.7 (C-3,5, 4-$NO_2C_6H_4$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): *Z* isomer: δ = –68.2 ppm. *E* isomer: δ = –63.1 ppm.

***N*-[1,1,1-Trifluoro-3-(4-nitrophenyl)propan-2-ylidene]-2-phenylethanamine (3e):** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.04 (t, J = 6.9 Hz, 2 H, CH_2), 3.65 (s, 2 H, CH_2), 3.78 (td, J = 6.9, 1.6 Hz, 2 H, CH_2), 7.07 (d, J = 8.8 Hz, 2 H, Ar), 7.10–7.17 (m, 2 H), 7.21–7.33 (m, 3 H), 8.06 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.6 (4-$NO_2C_6H_4CH_2$), 36.2 (CH_2Ph), 54.0 (NCH_2), 119.7 (q, J = 279.5 Hz, CF_3), 124.1 (C-3,5, 4-$NO_2C_6H_4$), 126.7 (CH, Ph), 128.6 (CH, Ph), 129.0 (CH, Ph), 129.1 (C-2,6, 4-$NO_2C_6H_4$), 139.0 (C-1, Ph), 141.4 (C-1, 4-$NO_2C_6H_4$), 147.0 (C-4, 4-$NO_2C_6H_4$), 156.0 (q, J = 32.7 Hz, *C*-CF_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –72.0 ppm. ESI-MS (*m*/*z*): calcd. for $C_{17}H_{15}F_3N_2O_2Na$ $[M]^+$ 359.0983; found 359.0984.

Mixture of (*Z*,*E*)-Enamine 2f and Azomethine 3f: Yellow oil; yield 212 mg (63%).

3,3,3-Trifluoro-1-(4-nitrophenyl)-*N*-(1-phenylethyl)prop-1-en-2-amine (2f): ^{1}H NMR (300 MHz, $CDCl_3$): *Z* isomer: δ = 1.42 (d, J = 6.7 Hz, 3 H, Me), 4.30 (quint, J = 6.7 Hz, 1 H, CH), 5.92 (s, 1 H, CH=), 7.17–7.36 (m, 7 H, Ar), 8.12 (d, J = 8.9 Hz, 2 H, Ar) ppm. *E* isomer: δ = 1.55 (d, J = 6.5 Hz, 3 H, Me), 5.32 (s, 1 H, CH=), 8.02 (d, J = 8.9 Hz, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *Z* isomer: δ = 23.5 (Me), 54.4 (CH), 104.4 (q, J = 4.8 Hz, CH=), 121.9 (q, J = 275.9 Hz, CF_3), 123.4 (C-3,5, 4-$NO_2C_6H_4$), 125.8 (CH, Ph), 127.5 (CH, Ph), 128.6 (CH, Ph), 129.3 (C-2,6, 4-$NO_2C_6H_4$), 134.5 (q, J = 30.3 Hz, *C*-CF_3), 142.3 (C-1, 4-$NO_2C_6H_4$), 142.7 (C-1, Ph), 146.0 (C-4, 4-$NO_2C_6H_4$) ppm. *E* isomer: δ = 24.6 (Me), 53.5 (CH), 101.8 (q, J = 2.2 Hz, CH=), 123.2 (C-3,5, 4-$NO_2C_6H_4$), 125.6 (CH, Ph), 129.0 (C-2,6, 4-$NO_2C_6H_4$), 134.2 (q, J = 30.9 Hz, *C*-CF_3), 142.6 (C-1, Ph), 142.9 (C-1, 4-$NO_2C_6H_4$), 145.6 (C-4, 4-$NO_2C_6H_4$) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): *Z* isomer: δ = –69.2 ppm. *E* isomer: δ = –62.9 ppm.

***N*-[1,1,1-Trifluoro-3-(4-nitrophenyl)propan-2-ylidene]-1-phenylethanamine (3f):** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.49 (d, J = 6.5 Hz, 3 H, Me), 3.90 (A-part of the AB system, J = 16.1 Hz, 1 H), 4.00 (B-part of the AB system, J = 16.1 Hz, 1 H), 4.78 (q, J = 6.5 Hz, 1 H, CH), 6.92–6.98 (m, 1 H, Ph), 7.18–7.37 (m, 6 H, Ar), 8.10 (d, J = 8.9 Hz, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.8 (Me), 32.9 (CH_2), 60.9 (CH), 119.8 (q, J = 279.4 Hz, CF_3), 124.1 (C-3,5, 4-$NO_2C_6H_4$), 126.4 (CH, Ph), 127.6 (CH, Ph), 128.8 (CH, Ph), 129.2 (C-2,6, 4-$NO_2C_6H_4$), 141.6 (C-1, 4-$NO_2C_6H_4$), 143.1 (C-1, Ph), 147.0 (C-4, 4-$NO_2C_6H_4$), 153.9 (q, J = 32.9 Hz, *C*-CF_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –71.9 ppm. ESI-MS (*m*/*z*): calcd. for $C_{17}H_{15}F_3N_2O_2Na$ $[M]^+$ 359.0983; found 359.0978.

Mixture of (*Z*,*E*)-Enamine 2g and Azomethine 3g: Yellow oil; yield 267 mg (80%).

3,3,3-Trifluoro-*N*-(1,1-dimethoxypropan-2-yl)-1-(4-nitrophenyl)prop-1-en-2-amine (2g): ^{1}H NMR (300 MHz, $CDCl_3$): *Z* isomer: δ = 1.07 (d, J = 6.6 Hz, 3 H, Me), 3.41 (s, 3 H, OMe), 3.45 (s, 3 H, OMe), 4.06 (m, 1 H, CH), 4.16 (d, J = 2.9 Hz, 1 H, CH), 5.96 (s, 1 H, CH=), 7.58 (d, J = 8.8 Hz, 2 H, Ar), 8.19 (d, J = 8.8 Hz, 2 H, Ar) ppm. *E* isomer: δ = 1.16 (d, J = 6.5 Hz, 3 H, Me), 3.49 (s, 3 H, MeO), 3.50 (s, 3 H, MeO), 4.32 (d, J = 4.1 Hz, 1 H, CH), 5.61 (s, 1 H, CH=), 7.36 (d, J = 8.9 Hz, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *Z* isomer: δ = 14.9 (Me), 51.9 (*C*HMe), 56.3, 56.4 (OMe), 103.8 (q, J = 5.3 Hz, CH=), 106.8 [*C*H(OMe)$_2$], 121.8 (q, J = 275.8 Hz, CF_3), 123.8 (C-3,5), 128.8 (C-2,6), 135.6 (q, J = 30.1 Hz, *C*-CF_3), 142.3 (C-1), 145.9 (C-4) ppm. *E* isomer: δ = 13.9 (Me), 50.5 (CH), 55.6 (MeO), 56.2 (MeO), 106.1 [*C*H(MeO)$_2$], 123.3 (C-3,5), 128.9 (C-2,6, Ar) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): *Z* isomer: δ = –68.3 ppm. *E* isomer: δ = –63.1 ppm.

***N*-[1,1,1-Trifluoro-3-(4-nitrophenyl)propan-2-ylidene]-1,1-dimethoxypropan-2-amine (3g):** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (d, J = 6.4 Hz, 3 H, Me), 3.43 (s, 3 H, MeO), 3.44 (s, 3 H, MeO), 3.82 (sept, J = 6.5 Hz, 1 H, CH), 3.93 (s, 2 H, CH_2), 4.36 (d, J = 6.9 Hz, 1 H, CH), 7.41 (d, J = 8.8 Hz, 2 H, Ar), 8.19 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.6 (Me), 32.8 (CH_2), 54.9, 56.9 (OMe), 60.2 (*C*HMe), 107.7 [*C*H(OMe)$_2$], 119.7 (q, J = 279.7 Hz, CF_3), 124.0 (C-3,5), 129.4 (C-2,6), 141.7 (C-1), 147.1 (C-

4), 155.5 (q, J = 32.5 Hz, C-CF_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –71.8 ppm. ESI-MS (m/z): calcd. for $C_{14}H_{17}F_3N_2O_4Na$ $[M]^+$ 357.1038; found 357.1039. $C_{14}H_{17}F_3N_2O_4$ (334.291): calcd. C 50.30, H 5.13, N 8.38; found C 50.32, H 5.20, N 8.30.

Mixture of (*Z*,*E*)-Enamine 2h and Azomethine 3h: Yellow-orange oil; yield 223 mg (71%).

***N*-[2-(3-Nitrophenyl)-1-(trifluoromethyl)ethenyl]cyclohexanamine (2h):** ^{1}H NMR (400 MHz, $CDCl_3$): *Z* isomer: δ = 0.95–1.89 (m, 10 H, CH_2), 2.90 (m, 1 H, C*H*NH), 3.30 (d, J = 9.7 Hz, 1 H, NH), 5.96 (s, 1 H, CH=), 7.49 (m, 1 H, 5-H), 7.65 (m, 1 H, 6-H), 8.04 (m, 1 H, 4-H), 8.31 (s, 1 H, 2-H) ppm. *E* isomer: δ = 1.06–2.07 (m, 10 H, CH_2), 3.15 (m, 1 H, C*H*NH), 3.71 (br. s, 1 H, NH), 5.51 (s, 1 H, CH=), 7.40 (m, 1 H, 5-H), 7.48 (m, 1 H, 6-H), 7.97 (m, 1 H, 4-H), 8.03 (s, 1 H, 2-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): *Z* isomer: δ = 24.9, 25.5, 33.9 (CH_2), 53.9 (CH–NH), 104.6 (q, J = 5 Hz, CH=), 121.6 (C-2), 122.0 (q, J = 275 Hz, CF_3), 123.1 (C-4), 129.3 (C-6), 134.6 (C-5), 134.9 (q, J = 30 Hz, C-CF_3), 137.1 (C-1), 148.4 (C-3) ppm. *E* isomer: δ = 24.2, 25.9, 31.7 (CH_2), 51.5 (CH–NH), 98.4 (CH=), 120.7 (C-2), 123.2 (C-4), 128.3 (C-6), 134.7 (C-5), 137.7 (C-1), 148.1 (C-3) ppm. ^{15}N NMR (40.6 MHz, $CDCl_3$): *Z* isomer: δ = –303.6 (NH), –9.5 (NO_2) ppm. *E* isomer: δ = –297.1 (NH), –9.7 (NO_2) ppm. MS (EI): m/z (%)= 314 (17) $[M]^+$, 271 (11), 232 (17), 184 (22), 83 (68), 55 (100).

***N*-[2,2,2-Trifluoro-1-(3-nitrobenzyl)ethylidene]cyclohexanamine (3h):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23–1.77 (m, 10 H, CH_2), 3.54 (m, 1 H, CHN=C), 3.89 (s, 2 H, ArCH_2), 7.49–7.56 (m, 2 H, 4,5-H), 8.04 (s, 1 H, 2-H), 8.12 (m, 1 H, 6-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.2, 25.3, 32.3 (CH_2), 32.7 (Ar*C*H_2), 60.8 (*C*HN=C), 119.9 (q, J = 279.5 Hz, CF_3), 122.1, 123.2, 129.7, 134.1 (CH_{Ar}), 136.8 (C-1), 148.7 (C-3), 153.1 (q, J = 32.3 Hz, C-CF_3) ppm. ^{15}N NMR (40.6 MHz, $CDCl_3$): δ = –19.4 (C=N), –12.1 (NO_2) ppm. IR (film): $\tilde{\nu}$ = 1617, 1676 cm^{-1}. MS (EI): m/z (%) = 314 (15) $[M]^+$, 271 (8), 232 (12), 185 (15), 178 (42), 163 (10), 136 (17), 83 (73), 55 (100). $C_{15}H_{17}F_3N_2O_2$ (314.303): calcd. C 57.32, H 5.45; found C 57.84, H 5.24.

***N*-[2,2,2-Trifluoro-1-(3-nitrobenzyl)ethylidene]butan-2-amine (3i):** Yellow oil; yield 60 mg (20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79 (t, J = 7.4 Hz, 3 H, CH_2*Me*), 1.13 (d, J = 6.2 Hz, 3 H, CH*Me*), 1.51–1.62 (m, 2 H, CH*C*H_2), 3.62 (m, 1 H, CHN=C), 3.86 (A-part of the AB system, J = 15.6 Hz, 1 H), 3.91 (B-part of the AB system, J = 15.6 Hz, 1 H), 7.48–7.53 (m, 2 H, 5,6-H), 8.05 (s, 1 H, 2-H), 8.12 (m, 1 H, 4-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.7 (CH_2*Me*), 20.7 (CH*Me*), 30.3 (*C*H_2Me), 32.4 (Ar*C*H_2), 58.3 (*C*H–C=N), 119.8 (q, J = 279.5 Hz, CF_3), 122.3, 123.3, 130.0, 134.4 (CH_{Ar}), 136.7 (C-1), 148.6 (C-3), 153.6 (q, J = 32.5 Hz, C-CF_3) ppm. MS (EI): m/z (%) = 288 (17) $[M]^+$, 259 (85), 163 (74), 136 (28), 90 (38), 57 (100).

Mixture of (*Z*,*E*)-Enamine 2j and Azomethine 3j: Yellow oil; yield 305 mg (97%).

***N*-[2-(2-Nitrophenyl)-1-(trifluoromethyl)ethenyl]cyclohexanamine (2j):** ^{1}H NMR (400 MHz, $CDCl_3$): *Z* isomer: δ = 0.80–1.80 (m, 10 H, CH_2), 2.69 (m, 1 H, C*H*NH), 3.20 (d, J = 9.0 Hz, 1 H, NH), 6.18 (s, 1 H, CH=), 7.37 (m, 1 H, 4-H), 7.56 (m, 1 H, 5-H), 7.61 (m, 1 H, 6-H), 7.99 (m, 1 H, 3-H) ppm. *E* isomer: δ = 0.80–1.80 (m, 10 H, CH_2), 3.18 (m, 1 H, C*H*NH), 3.63 (br. s, 1 H, NH), 5.83 (s, 1 H, CH=), 7.95 (m, 1 H, 3-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): *Z* isomer: δ = 24.8, 25.5, 33.4 (CH_2), 53.6 (CHNH), 101.0 (q, J = 5.4 Hz, CH=), 122.1 (q, J = 275.6 Hz, CF_3), 124.8 (C-3), 127.8 (C-4), 130.6 (C-1), 130.9 (C-6), 132.8 (C-5), 134.2 (q, J = 30.3 Hz, C-CF_3), 147.9 (C-2) ppm. *E* isomer: δ = 23.8, 25.9, 32.3 (CH_2), 51.5 (CHNH), 96.8 (q, J = 2 Hz, CH=), 124.4 (C-3), 148.2 (C-2) ppm. ^{15}N NMR (40.6 MHz, $CDCl_3$): *Z* isomer: δ = –306.4 (NH), –12.1 (NO_2) ppm. *E* isomer: δ = –299.1 (NH), –10.1 (NO_2) ppm.

***N*-[2,2,2-Trifluoro-1-(2-nitrobenzyl)ethylidene]cyclohexanamine (3j):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.8–1.8 (m, 10 H, CH_2), 3.41 (m, 1 H, C*H*N=C), 4.12 (s, 2 H, ArCH_2), 7.45 (m, 1 H, 4-H), 7.20 (m, 1 H, 6-H), 7.58 (m, 1 H, 5-H), 8.05 (m, 1 H, 3-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.1, 25.3 (CH_2), 30.2 (Ar*C*H_2), 32.7 (CH_2), 60.5 (*C*H–C=N), 119.8 (q, J = 279.5 Hz, CF_3), 125.5 (C-3), 128.5 (C-4), 129.7 (C-6), 131.2 (C-1), 133.7 (C-5), 148.7 (C-2), 152.7 (q, J = 32.2 Hz, C-CF_3) ppm. ^{15}N NMR (40.6 MHz, $CDCl_3$): δ = –19.4 (C=N), –11.4 (NO_2) ppm. MS (EI): m/z (%) = 314 (0.6) $[M]^+$, 232 (3), 215 (12), 163 (6), 120 (16), 92 (22), 83 (41), 55 (100). $C_{15}H_{17}F_3N_2O_2$ (314.303): calcd. C 57.32, H 5.45; found C 57.22, H 5.57.

Mixture of (*Z*,*E*)-Enamine 2k and Azomethine 3k: Light brown oil; yield 277 mg (96%).

***N*-[2-(2-Nitrophenyl)-1-(trifluoromethyl)ethenyl]butan-2-amine (2k):** ^{1}H NMR (400 MHz, $CDCl_3$): *Z* isomer: δ = 0.73 (t, J = 7.4 Hz, 3 H, CH_2*Me*), 0.93 (d, J = 6.2 Hz, 3 H, CH*Me*), 1.24 (m, 2 H, CHCH_2), 2.88 (m, 1 H, C*H*NH), 3.13 (d, J = 9.3 Hz, 1 H, NH), 6.17 (s, 1 H, CH=), 7.22 (m, 1 H, 6-H), 7.37 (m, 1 H, 4-H), 7.57 (m, 1 H, 5-H), 7.99 (m, 1 H, 3-H) ppm. *E* isomer: δ = 0.64 (t, J = 7.5 Hz, 3 H, CH_2*Me*), 0.97 (d, J = 7.4 Hz, 3 H, CH*Me*), 1.34 (m, 2 H, CHCH_2), 3.29 (m, 1 H, C*H*NH), 3.71 (br. s, 1 H, NH), 5.80 (s, 1 H, CH=), 7.94 (m, 1 H, 3-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): *Z* isomer: δ = 10.0 (CH_2*Me*), 20.1 (CH*Me*), 29.8 (*C*H_2Me), 51.9 (*C*HNH), 100.8 (q, J = 5.4 Hz, CH=), 122.1 (q, J = 275.5 Hz, CF_3), 124.8 (C-3), 127.8 (C-4), 130.8 (C-1), 131.3 (C-6), 132.8 (C-5), 134.6 (q, J = 29.9 Hz, C-CF_3), 147.9 (C-2) ppm. *E* isomer: δ = 10.1 (CH_2*Me*), 19.1 (CH*Me*), 28.7 (*C*H_2Me), 49.8 (*C*HNH), 96.8 (CH=), 148.3 (C-2) ppm.

***N*-[2,2,2-Trifluoro-1-(2-nitrobenzyl)ethylidene]butan-2-amine (3k):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (t, J = 7.4 Hz, 3 H, CH_2*Me*), 1.13 (d, J = 6.2 Hz, 3 H, CH*Me*), 1.58 (m, 2 H, CHCH_2), 3.50 (m, 1 H, C*H*N=C), 4.08 (A-part of the AB system, J = 17.2 Hz, 1 H), 4.18 (B-part of the AB system, J = 17.2 Hz, 1 H), 7.22 (m, 1 H, 6-H), 7.45 (m, 1 H, 4-H), 7.58 (m, 1 H, 5-H), 8.04 (m, 1 H, 3-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 10.7 (CH_2*Me*), 20.4 (CH*Me*), 30.3 (*C*H_2Me), 30.3 (Ar*C*H_2), 58.2 (*C*H–N=C), 119.7 (q, J = 279.5 Hz, CF_3), 125.5 (C-3), 128.5 (C-4), 129.6 (C-1), 130.6 (C-6), 133.6 (C-5), 148.7 (C-2), 153.4 (q, J = 32.2 Hz, C-CF_3) ppm. IR (film): $\tilde{\nu}$ = 1661, 3402 cm^{-1}. MS (EI): m/z (%) = 288 (6) $[M]^+$, 259 (20), 232 (11), 215 (74), 163 (19), 120 (49), 92 (78), 57 (100). $C_{13}H_{15}F_3N_2O_2$ (288.261): calcd. C 54.16, H 5.24; found C 54.15, H 5.25.

Mixture of (*Z*,*E*)-Enamine 2l and Azomethine 3l: Yellow oil; yield 263 mg (96%).

3,3,3-Trifluoro-*N*-isopropyl-1-(2-nitrophenyl)prop-1-en-2-amine (2l): ^{1}H NMR (300 MHz, $CDCl_3$): *Z* isomer: δ = 0.99 (d, J = 6.0 Hz, 6 H, Me), 3.03–3.20 (m, 2 H, CH, NH), 6.22 (s, 1 H, CH=), 7.48 (td, J = 7.6, 1.4 Hz, 1 H, Ar), 7.65 (td, J = 7.6, 1.4 Hz, 1 H, Ar), 8.02 (dd, J = 7.6, 1.0 Hz, 1 H, Ar) ppm. *E* isomer: δ = 1.28 (d, J = 6.1 Hz, 6 H, Me), 5.83 (s, 1 H, CH=), 7.97 (dd, J = 8.2, 1.4 Hz, 1 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *Z* isomer: δ = 22.8 (Me), 46.5 (CH), 101.7 (q, J = 5.4 Hz, CH=), 119.7 (q, J = 279.4 Hz, CF_3), 124.8 (C-3), 127.8 (C-4), 130.4 (C-1), 130.8 (C-6), 132.8 (C-5), 134.4 (q, J = 30.1 Hz, C-CF_3), 147.8 (C-2) ppm. *E* isomer: δ = 22.0 (Me), 44.1 (CH), 124.3 (C-3), 127.3 (C-4), 132.4 (C-5) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): *Z* isomer: δ = –69.8 ppm. *E* isomer: δ = –62.8 ppm.

***N*-[1,1,1-Trifluoro-3-(2-nitrophenyl)propan-2-ylidene]propan-2-amine (3l):** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (d, J = 6.1 Hz, 6 H, Me), 3.78 (sept, J = 6.1 Hz, 1 H, CH), 4.15 (s, 2 H, CH_2), 7.21 (d, J = 7.6 Hz, 1 H, Ar), 7.40 (td, J = 7.6, 1.2 Hz, 1 H, Ar), 7.59 (td, J = 7.6, 1.2 Hz, 1 H, Ar), 8.09 (dd, J = 7.6, 1.3 Hz, 1 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.8 (Me), 30.2 (CH_2), 52.3 (CH), 121.9 (q, J = 275.4 Hz, CF_3), 125.6 (C-3), 128.5 (C-4), 129.6 (C-1), 131.1 (C-6), 133.7 (C-5), 148.5 (C-2), 152.7 (q, J = 32.2 Hz, *C*-CF_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –72.0 ppm. ESI-MS (*m*/*z*): calcd. for $C_{12}H_{13}F_3N_2O_2Na$ $[M]^+$ 297.0827; found 297.0821. $C_{12}H_{13}F_3N_2O_2$ (274.239): calcd. C 52.56, H 4.78, N 10.21; found C 52.52, H 4.77, N 10.04.

General Procedure for the Synthesis of Vinylogous Guanidinium Salts 5a–p: The appropriate styrene (**1f**–**l**, 1–1.5 mmol) and the amine (10–15 mmol) were heated either at reflux or in a sealed glass tube with a Young tap. The product obtained (**5a**–**p**) was purified by column chromatography [silica gel, CH_2Cl_2/CH_3OH (9:1) or $CHCl_3$/MeOH (9:1)].

***N*-[1,3-Bis(cyclohexylamino)-3-(4-chlorophenyl)prop-2-enylidene]cyclohexanaminium Bromide (5a):** Light yellow solid; m.p. 137 °C; yield 502 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80–2.00 (br. m, 30 H), 3.00–3.50 (br. s, 3 H), 4.41 (br. s, 1 H), 5.13 (br. s, 1 H), 7.10–7.40 (m, 4 H), 8.31 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 24.8, 25.3, 31.8, 32.4, 32.9 (CH_2), 52.7, 54.4 (NCH), 80.6 (Ar–C=*C*H), 129.2 (C-3,5), 129.6 (C-2,6), 134.1 (C-1), 136.7 (C-4), 156.5 (Ar–*C*=CH), 162.5 (N–C–N) ppm. IR (KBr): $\tilde{\nu}$ = 1567, 1602, 3205, 3422 cm^{-1}. $C_{27}H_{41}BrClN_3 \cdot H_2O$: calcd. C 59.94, H 8.01; found C 59.67; H 7.71.

***N*-[1,3-Bis(isopropylamino)-3-(4-chlorophenyl)prop-2-enylidene]-propan-2-aminium Bromide (5b):** Pale brown crystals; m.p. 116–118 °C; yield 253 mg (63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84–1.28 (br. s, 12 H), 1.28–1.39 (br. s, 6 H), 1.65–1.75 (br. s, 1 H), 3.50–3.86 (br. s, 3 H), 4.38–4.61 (br. s, 1 H), 7.31 (d, J = 8.3 Hz, 2 H, Ar), 7.44 (d, J = 8.3 Hz, 2 H, Ar), 7.89–9.13 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8, 22.3 (CH_3), 45.6, 46.7 (CH), 81.7 (Ar–C=*C*H), 129.2 (C-3,5), 129.8 (C-2,6), 133.9 (C-1), 136.5 (C-4), 157.2 (Ar–*C*=CH), 162.1 (N–C–N) ppm. ESI-MS (*m*/*z*) calcd. for $C_{18}H_{29}ClN_3^+$ $[M]^+$: 322.2050; found 322.2045.

***N*-{3-(4-Chlorophenyl)-1-[(1,1-dimethoxyethyl)amino]-3-[(2,2-dimethoxy-1-methylethyl)amino]prop-2-enylidene}-1,1-dimethoxypropan-2-aminium Bromide (5c):** Brown sticky oil; yield 223 mg (39%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.53–0.79 (br. s, 3 H, Me), 1.16–1.46 (m, 6 H, Me), 2.46–2.68 (br. s, 1 H), 3.21–3.61 (m, 18 H, MeO), 4.34–4.51 (br. s, 1 H), 4.51–4.68 (br. s, 1 H), 4.82–5.38 (br. s, 1 H), 7.41 (d, J = 8.6 Hz, 2 H, Ar), 7.48 (d, J = 8.6 Hz, 2 H, Ar), 7.60–7.92 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4, 15.4, 16.3, 16.8, 51.8, 53.0, 55.5, 56.6, 56.8, 57.1, 57.3, 80.6 (Ar–C=*C*H), 129.2 (CH), 130.2 (CH), 134.9, 136.5, 160.1 (Ar–*C*=CH), 162.5 (N–C–N) ppm. ESI-MS (*m*/*z*) calcd. for $C_{24}H_{41}ClN_3O_6^+$ $[M]^+$: 502.2684; found 502.2686.

***N*-[1,3-Bis(isopropylamino)-3-(4-chlorophenyl)prop-2-enylidene]-propan-2-aminium Chloride (5d):** Pale brown crystals; m.p. 103–105 °C; yield 120 mg (34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.71–1.26 (br. s, 12 H), 1.26–1.40 (br. s, 6 H), 2.01–2.21 (br. s, 1 H), 3.43–3.95 (br. s, 3 H), 4.44–4.57 (br. s, 1 H), 4.64–5.04 (br. s, 1 H), 7.32 (d, J = 8.0 Hz, 2 H, Ar), 7.42 (d, J = 8.0 Hz, 2 H, Ar), 8.41–9.28 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8, 22.4 (CH_3), 45.4, 46.7 (CH), 81.8 (Ar–C=*C*H), 129.3 (C-3,5), 129.6 (C-2,6), 134.1 (C-1), 136.7 (C-4), 156.7 (Ar–*C*=CH), 162.4 (N–C–N) ppm. ESI-MS (*m*/*z*) calcd. for $C_{18}H_{29}ClN_3^+$ $[M]^+$: 322.2050; found 322.2045.

***N*-[1,3-Bis(cyclohexylamino)-3-(4-chlorophenyl)prop-2-enylidene]cyclohexanaminium Chloride (5e):** Light yellow solid; m.p. 221–224 °C; yield 96 mg (20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90–2.10 (m, 30 H, CH_2), 3.30 (br. m, 3 H, C*H*NH), 4.31–5.03 (4 × br. s, 2 H, NH, CH=C), 7.31 (d, J = 8.2 Hz, 2 H, 3,5-H), 7.40 (d, J = 8.2 Hz, 2 H, 2,6-H), 8.34 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.7, 24.9, 25.0, 31.9, 32.5, 33.1 (CH_2), 52.8 (CH–N), 53.8 (CH–N), 54.4 (CH–N), 78.4 (Ar–C=*C*H), 129.6 (C-2,3,5,6), 134.2 (C-1), 137.0 (C-4), 156.5 (br. s, Ar–*C*=CH), 159.6 (br. s, N–C–N) ppm. IR (KBr): $\tilde{\nu}$ = 1531, 1573, 1605, 3332, 3382 cm^{-1}. MS (EI): *m*/*z* (%) (direct input, relative intensity) = 438 (3) $[M - HCl]^+$, 358 (10), 261 (5), 222 (10), 179 (10), 139 (17), 98 (33), 83 (40), 59 (72), 55 (92), 44 (100). $C_{27}H_{41}Cl_2N_3 \cdot H_2O$ (496.555): calcd. C 65.31, H 8.73, Cl 14.28; found C 65.11, H 8.98, Cl 13.93.

***N*-[1,3-Bis(cyclohexylamino)-3-(4-methylphenyl)prop-2-enylidene]cyclohexanaminium Bromide (5f):** Light yellow solid; m.p. 245–247 °C; yield 430 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80–2.00 (br. m, 30 H), 2.33 (s, 3 H), 3.22 (br. s, 3 H), 3.32 (br. s, 1 H), 3.42 (br. s, 2 H), 4.65 (br. s, 1 H), 6.82 (br. s, 1 H), 7.10–7.40 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0 (CH_3), 24.3, 24.7, 25.2, 31.8, 32.7, 32.8 (CH_2), 52.2, 54.1 (NCH), 80.6 (Ar–C=*C*H), 127.7 (C-3,5), 129.6 (C-2,6), 132.6 (C-1), 140.9 (C-4), 158.9 (Ar–*C*=CH), 162.5 (N–C–N) ppm. IR (KBr): $\tilde{\nu}$ = 1567, 1596, 3202, 3409 cm^{-1}. $C_{28}H_{44}BrN_3$ (502.59): calcd. C 66.92, H 8.82, N 8.36; found C 66.88, H 8.62, N 8.36.

***N*-[1,3-Bis(isopropylamino)-3-(4-methylphenyl)prop-2-enylidene]-propan-2-aminium Bromide (5g):** Brownish sticky oil; yield 350 mg (92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.70–1.24 (br. s, 12 H), 1.24–1.39 (br. s, 6 H), 2.39 (s, 3 H, Me), 3.55–4.06 (br. s, 3 H), 4.45–4.63 (br. s, 1 H), 4.73–5.04 (br. s, 1 H), 7.24 (br. s, 4H Ar), 7.70–8.67 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1 (4-*Me*C_6H_4-), 21.8, 22.1 (CH_3), 45.2, 46.4 (CH), 75.4 (Ar–C=*C*H), 127.9 (C-3,5), 129.6 (C-2,6), 132.3 (C-1), 140.7 (C-4), 158.7 (Ar–*C*=CH), 162.2 (N–C–N) ppm. ESI-MS (*m*/*z*) calcd. for $C_{19}H_{32}N_3^+$ $[M]^+$: 302.2596; found 302.2591. $C_{19}H_{32}BrN_3 \cdot 1/3\,H_2O$: calcd. C 58.76, H 8.48, N 10.82; found C 58.79, H 8.25, N 10.49.

***N*-[1,3-Bis(*sec*-butylamino)-3-(4-methoxyphenyl)prop-2-enylidene]-butan-2-aminium Bromide (5h):** Colourless solid; yield 405 mg (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.50–1.60 (br. m, 24 H), 3.15 (br. s, 1 H), 3.54 (s, 3 H), 4.11 (br. s, 1 H), 4.86 (br. s, 1 H), 6.65 (d, J = 8.2 Hz, 2 H), 7.04 (d, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.1 (*C*$H_3$$CH_2$), 19.1, 19.5 (*C*$H_3$CH), 28.4, 29.1 ($CH_3$*C*$H_2$), 50.7 (NCH), 55.1 ($OCH_3$), 77.4 (Ar–C=*C*H), 114.1 (C-3,5), 127.2 (C-1), 129.2 (C-2,6), 158.1 (Ar–*C*=CH), 161.2 (N–C–N), 163.01 (C-4) ppm. IR (KBr): $\tilde{\nu}$ = 1570, 1609, 3222, 3413 cm^{-1}. This compound was passed through a short column (silica gel) and was used without additional purification.

***N*-[1,3-Bis(isopropylamino)-3-(4-methoxyphenyl)prop-2-enylidene]-propan-2-aminium Bromide (5i):** Pale brown crystals; m.p. 96–98 °C; yield 321 mg (81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.67–1.24 (br. s, 12 H), 1.24–1.45 (br. s, 6 H), 2.09–2.37 (br. s, 1 H), 3.51–4.03 (br. s, 2 H), 3.84 (s, 3 H, MeO), 4.41–4.59 (br. s, 1 H), 4.65–5.01 (br. s, 1 H), 6.96 (d, J = 8.6 Hz, 2 H), 7.30 (d, J = 8.6 Hz, 2 H), 7.81–8.73 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8, 22.2 (CH_3), 45.3, 46.5 (CH), 55.4 (MeO), 74.9 (Ar–C=*C*H), 114.4 (C-3,5), 127.3 (C-1), 129.6 (C-2,6), 158.5 (Ar–*C*=CH), 159.3 (N–C–N), 161.3 (C-4) ppm. ESI-MS (*m*/*z*) calcd. for $C_{19}H_{32}N_3O^+$ $[M]^+$: 318.2545; found 318.2540. $C_{19}H_{32}BrN_3O$ (398.39): calcd. C 57.28, H 8.10, N 10.55; found C 57.08, H 8.01, N 10.17.

***N*-[1,3-Bis(cyclohexylamino)-3-(4-methoxyphenyl)prop-2-enylidene]-cyclohexanaminium Bromide (5j):** Colourless solid; m.p. 230–

233 °C; yield 337 mg (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95–2.10 (m, 30 H, CH_2), 3.05–3.40 (3 × br. m, 3 H, C*H*NH), 3.80 (s, 3 H, CH_3), 4.38 (br. s, 1 H), 6.89 (d, J = 8.4 Hz, 2 H, 3,5-H), 7.22 (d, J = 8.4 Hz, 2 H, 2,6-H), 8.45 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.7, 24.8, 24.9, 25.0, 25.6, 32.1, 32.7, 33.1, 34.3 (CH_2), 52.6 (CHN), 54.0 (br. s, CHN), 55.7 (OMe), 77.6 (Ar–C=*C*H), 114.8 (C-3,5), 129.6 (C-2,6), 158.0 (Ar–*C*=CH), 161.6 (C-4), 163.3 (N–C–N) ppm. IR (KBr): $\tilde{\nu}$ = 1509, 1570, 1609, 3221, 3416 cm^{-1}. MS (EI): *m*/*z* (direct input, relative intensity) = 438 (2.4) [M – HBr]$^+$, 354 (8), 339 (2), 257 (2), 216 (3), 175 (5), 134 (15), 82 (7), 55 (19), 40 (100). $C_{28}H_{44}BrN_3O$ (518.573): calcd. C 64.85, H 8.55; found C 64.89, H 8.45.

***N*-[1,3-Bis(cyclohexylamino)-3-(3-methoxyphenyl)prop-2-enylidene]-cyclohexanaminium Bromide (5k):** Light yellow solid; m.p. 243–245 °C; yield 306 mg (59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90–2.10 (m, 30 H, CH_2), 3.13–3.46 (3 × br. s, 3 H, CHN), 3.82 (s, 3 H, OMe), 4.25–4.90 (2 × br. s, 2 H, NH, CH=C), 6.84–7.00 (m, 3 H, 2,4,6-H), 7.33 (m, 1 H, 5-H), 8.50 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.4, 24.6, 24.8, 25.3, 31.9, 32.4, 32.9 (CH_2), 52.3 (CHN), 55.5 (CHN), 113.6 (C-2), 116.0 (C-4), 119.8 (C-6), 130.4 (C-5), 136.8 (C-1), 157.4 (Ar–C=CH), 159.9 (C-3), 162.3 (N–C–N) ppm. IR (KBr): $\tilde{\nu}$ = 1451, 1531, 1570, 1599, 1649, 3220, 3412 cm^{-1}. MS (EI): *m*/*z* (direct input, relative intensity) = 438 (1.3) [M – HBr]$^+$, 354 (4), 238 (5), 175 (7), 134 (9), 83 (39), 56 (51), 44 (100). $C_{28}H_{44}BrN_3O{\cdot}H_2O$ (536.60): calcd. C 62.67, H 8.64; found C 62.58, H 8.59.

***N*-[1,3-Bis(cyclohexylamino)-3-(2-methoxyphenyl)prop-2-enylidene]-cyclohexanaminium Bromide (5l):** Colourless solid; m.p. 134 °C; yield 374 mg (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90–1.90 (br. m, 31 H), 3.14 (br. s, 1 H), 3.54 (br. s, 1 H), 3.72 (s, 3 H), 4.58 (br. s, 1 H), 6.70–7.40 (br. m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 24.7, 24.8, 25.0, 32.1, 32.5 (CH_2), 52.5 (NCH), 55.9 (OCH_3), 81.2 (Ar–C=*C*H), 111.9 (C-3), 121.5 (C-5), 124.5 (C-1), 129.8 (C-6), 131.9 (C-4), 154.8 (Ar–*C*=CH), 156.2 (C-2), 156.3 (N–C–N) ppm. IR (KBr): $\tilde{\nu}$ = 1568, 1606, 3211, 3412 cm^{-1}. $C_{28}H_{44}BrN_3O{\cdot}H_2O$ (536.60): calcd. C 62.67, H 8.64; found C 62.25, H 8.27.

***N*-[1,3-Bis(*sec*-butylamino)-3-(2-methoxyphenyl)prop-2-enylidene]-butan-2-aminium Bromide (5m):** Colourless hygroscopic solid; yield 394 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.50–1.70 (br. m, 24 H), 3.22 (br. s, 1 H), 3.58 (br. s, 1 H), 3.72 (s, 3 H), 4.64 (br. s, 1 H), 6.70–7.40 (br. m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.9, 10.2 (CH_3CH_2), 19.2, 19.8 (CH_3CH), 28.4, 28.8 (CH_3CH_2), 50.6 (NCH), 55.3 (OCH_3), 79.9 (Ar–C=*C*H), 111.3 (C-3), 121.1 (C-5), 123.8 (C-1), 129.3 (C-6), 131.5 (C-4), 154.4 (Ar–*C*=CH), 155.5 (C-2), 159.3 (N–C–N) ppm. IR (KBr): $\tilde{\nu}$ = 1564, 1600, 3202, 3407 cm^{-1}. $C_{22}H_{38}BrN_3O{\cdot}H_2O$ (458.49): calcd. C 57.63, H 8.79; found C 57.60, H 8.72.

***N*-[1,3-Bis(isopropylamino)-3-phenylprop-2-enylidene]propan-2-aminium Bromide (5n):** Pale brown crystals; m.p. 86–88 °C; yield 312 mg (85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80–1.27 (br. s, 12 H), 1.27–1.38 (br. s, 6 H), 1.99–2.35 (br. s, 1 H), 3.77–4.10 (br. s, 3 H), 4.44–4.68 (br. s, 1 H), 4.72–5.13 (br. s, 1 H), 7.31–7.39 (m, 2 H), 7.40–7.55 (m, 2 H), 7.71–8.98 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8, 22.1 (CH_3), 45.3, 46.5 (CH), 75.8 (Ar–C=*C*H), 128.0, 129.1, 130.4 (CH_{Ar}), 135.3 (C-1), 158.6 (Ar–*C*=CH), 159.3 (N–C–N) ppm. ESI-MS: *m*/*z* calcd. for $C_{18}H_{30}N_3^+$ [M]$^+$: 288.2440; found 288.2434. $C_{18}H_{30}BrN_3$ (368.36): calcd. C 58.69, H 8.21, N 11.41; found C 58.56, H 8.43, N 11.11.

***N*-[1,3-Bis(cyclohexylamino)-3-phenylprop-2-enylidene]cyclohexanaminium Bromide (5o):** Colourless solid; m.p. 231–234 °C; yield 430 mg (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80–2.10 (m, 30 H, CH_2), 3.15–3.63 (3 × br. s, 3 H, CHN), 4.33–5.15 (2 × br. s, 2 H, CH=C, NH), 7.39 (br. d, 5 H, Ph), 8.29 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 24.8, 25.3, 31.9, 32.3, 32.9, 34.1 (CH_2), 52.6, 53.5, 54.2 (CHN), 77.9 (*C*H=C), 128.0 (C-2,6), 129.2 (C-3,5), 130.6 (C-4), 135.7 (C-1), 158.0 (br. s, *C*=CH), 162.5 (N–C–N) ppm. IR (KBr): $\tilde{\nu}$ = 1450, 1529, 1568, 1609, 3221, 3420 cm^{-1}. MS (EI): *m*/*z* (%) (direct input, relative intensity) = 407 (10) [M – HBr]$^+$, 324 (34), 309 (8), 227 (10), 186 (8), 145 (24), 104 (47), 55 (100), 44 (51). $C_{27}H_{42}BrN_3$ (488.547): calcd. C 66.38, H 8.67; found C 66.11, H 8.50.

***N*-[1,3-Bis(benzylamino)-3-phenylprop-2-enylidene]phenylmethanaminium Bromide (5p):** Light brown solid; m.p. 158–161 °C; yield 312 mg (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.11–4.89 (br. m, 7 H, CH_2, CH=C), 6.70 (br. s, 1 H, NH), 7.09–7.27 (m, 20 H, Ph), 9.06 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 47.9 (br. s, CH_2), 77.4 (C=*C*H), 127.3, 127.7, 127.8, 128.3, 128.7, 128.9, 129.4 (CH_{Ar}), 130.9, 134.6, 136.6 (C-1), 160.7 (*C*=CH), 161.7 (N–C–N) ppm. IR (KBr): $\tilde{\nu}$ = 1524, 1565, 1615, 3234, 3415 cm^{-1}. MS (EI): *m*/*z* (%) (direct input, relative intensity) = 431 (0.3) [M – HBr]$^+$, 354 (<1), 340 (1), 235 (1), 193 (1), 159 (1), 130 (2), 106 (9), 91 (89), 65 (18), 40 (100). $C_{30}H_{30}BrN_3$ (512.483): calcd. C 70.21, H 5.90; found C 69.94, H 6.07.

General Procedure for the Synthesis of Aminoenones 6: A concentrated aqueous solution of HCl (10 mL) was added to the appropriate salt **5** (1 mmol) and the mixture was stirred with heating for 3–6 h. Volatiles were then removed in vacuo, and the residue was treated with saturated $NaHCO_3$ solution (5 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined extract was dried with $CaCl_2$, solvent was evaporated, and the residue was purified by column chromatography [silica gel, $CHCl_3$/MeOH (9:1)].

3,3-Bis(cyclohexylamino)-1-(2-methoxyphenyl)prop-2-en-1-one (6a): Colourless solid; m.p. 219 °C; yield 225 mg (63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20–2.15 (br. m, 20 H), 3.15–3.45 (br. m, 2 H), 3.83 (s, 3 H), 4.12 (br. s, 1 H), 5.18 (br. s, 1 H), 6.87 (d, J = 8.2 Hz, 1 H), 6.93 (m, 1 H), 7.25 (m, 1 H), 7.61 (d, J = 8.2 Hz, 1 H), 11.39 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 24.9, 25.6, 29.8, 32.9, 33.6 (CH_2), 49.1, 51.0 (NCH), 55.8 (OCH_3), 80.3 (CH=), 111.3 (C-3), 120.4 (C-5), 129.6 (C-4), 129.8 (C-6), 132.9 (C-1), 156.8 (C-2), 159.2 (N–C–N), 183.5 (C=O) ppm. ^{15}N NMR (40.6 MHz, $CDCl_3$): δ = –285.9, –276.6 (NH) ppm. IR (KBr): $\tilde{\nu}$ = 1582, 1601, 3261 cm^{-1}. MS (EI): *m*/*z* (%)= 356 (11) [M]$^+$, 135 (78), 55 (85), 40 (100). $C_{22}H_{32}N_2O_2{\cdot}H_2O$ (374.53): calcd. C 70.55, H 9.15; found C 70.93, H 8.88.

1-(4-Chlorophenyl)-3,3-bis(cyclohexylamino)prop-2-en-1-one (6b): Colourless solid; m.p. 167 °C; yield 220 mg (61%). ^{1}H NMR [400 MHz, $(CD_3)_2CO$]: δ = 1.60–2.70 (br. m, 20 H), 4.05–4.25 (br. m, 2 H), 5.92 (br. s, 1 H), 6.22 (br. s, 1 H), 7.92 (d, J = 6.2 Hz, 2 H), 8.42 (d, J = 6.2 Hz, 2 H), 12.29 (s, 1 H) ppm. ^{13}C NMR [100 MHz, $(CD_3)_2CO$]: δ = 25.2, 26.1, 26.6, 33.9, 34.3 (CH_2), 49.2, 52.4 (NCH), 76.0 (CH=), 128.9 (C-3,5), 129.2 (C-2,6), 135.5 (C-1), 142.5 (C-4), 160.9 (N–C–N), 181.9 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1580, 1605, 3284 cm^{-1}. MS (EI): *m*/*z* (%) = 360 (12) [M]$^+$, 197 (20), 139 (56), 55 (100). $C_{21}H_{29}ClN_2O{\cdot}H_2O$ (378.95): calcd. C 66.56, H 8.25; found C 66.88, H 8.07.

3,3-Bis(cyclohexylamino)-1-phenylprop-2-en-1-one (6c): Colourless solid; m.p. 210 °C; yield 294 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22–2.10 (m, 20 H, CH_2), 3.28 (m, 1 H, C*H*NH), 3.42 (m, 1 H, C*H*NH), 4.22 (d, J = 6.1 Hz, 1 H, NH), 5.23 (s, 1 H, CH=), 7.36 (m, 3 H, 3,4,5-H), 7.82 (m, 2 H, 2,6-H), 11.54 (d, J = 6.1 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.4, 24.8, 25.6, 32.9, 33.7 (CH_2), 49.0 (NCH), 51.0 (NCH), 75.6 (C=*C*H), 126.6 (C-3,5), 128.0 (C-2,6), 129.4 (C-4), 142.4 (C-1),

159.5 (*C*=CH), 183.9 (C=O) ppm. IR (KBr): ṽ = 1573, 1582, 3262 cm^{-1}. MS (EI): *m*/*z* (direct input, relative intensity) = 326 (5) [M]$^+$, 243 (4), 227 (5), 163 (19), 146 (12), 105 (66), 77 (43), 55 (96), 41 (100). $C_{21}H_{30}N_2O$ (326.476): calcd. C 77.26, H 9.26; found C 77.54, H 9.08.

3,3-Bis(cyclohexylamino)-1-(4-methylphenyl)prop-2-en-1-one (6d): Solid; m.p. 149 °C; yield 317 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15–2.10 (m, 20 H, CH_2 cyclohexyl), 2.34 (s, 3 H, CH_3), 3.26 (m, 1 H, C*H*NH), 3.40 (m, 1 H, C*H*NH), 4.27 (d, *J* = 6.9 Hz, 1 H, NH), 5.19 (s, 1 H, CH=), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.70 (d, *J* = 8.0 Hz, 2 H), 11.49 (d, *J* = 7.0 Hz, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.3 (CH_3), 24.3, 24.8, 25.5, 32.8, 33.5 (CH_2), 48.8, 50.9 (CH), 75.2 (CH=), 126.4 (C-3,5), 128.6 (C-2,6), 139.3 (C-4), 139.5 (C-1), 159.3 (N–C–N), 183.6 (C=O) ppm. IR (KBr): ṽ = 1582, 1606, 2929, 3197, 3269 cm^{-1}. $C_{22}H_{32}N_2O$ (340.504): calcd. C 77.60, H 9.47; found C 77.48, H 9.42.

3,3-Bis(cyclohexylamino)-1-(4-methoxyphenyl)prop-2-en-1-one (6e): Solid; m.p. 165 °C; yield 278 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20–2.10 (m, 20 H, CH_2 cyclohexyl), 3.25 (m, 1 H, C*H*NH), 3.38 (m, 1 H, C*H*NH), 4.27 (d, *J* = 6.7 Hz, 1 H, NH), 5.16 (s, 1 H, CH=), 6.85 (d, *J* = 8.8 Hz, 2 H), 7.76 (d, *J* = 8.8 Hz, 2 H), 11.44 (d, *J* = 6.8 Hz, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.3, 24.8, 25.5, 29.7, 32.8, 33.5 (CH_2), 48.8, 50.9 (CH), 55.21 (CH_3), 74.7 (CH=), 113.1 (C-3,5), 128.0 (C-2,6), 134.8 (C-1), 159.3 (N–C–N), 160.6 (C-4), 183.0 (C=O) ppm. IR (KBr): ṽ = 1584, 1603, 2928, 3190, 3268 cm^{-1}. $C_{22}H_{32}N_2O_2$ (356.502): calcd. C 74.12, H 9.05; found C 73.93, H 8.96.

3,3-Bis(isopropylamino)-1-(4-methylphenyl)prop-2-en-1-one (6f): Pale brown powder; m.p. 184–185 °C; yield 211 mg (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (br. s, 12 H, CH_3), 2.35 (s, 3 H, CH_3), 3.61 (m, 1 H, C*H*NH), 3.78 (m, 1 H, C*H*NH), 4.36 (br. s, 1 H, NH), 5.21 (s, 1 H, CH=), 7.17 (s, 2 H, Ar), 7.71 (s, 2 H, Ar), 11.37 (br. s, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.3 (4-*C*H$_3$C$_6$H$_4$), 23.0, 23.2 [CH(*C*H$_3$)$_2$], 43.9, 41.8 (CH), 75.3 (CH=), 126.4 (C-3,5), 128.6 (C-2,6), 139.4 (C-4, C-1), 159.6 (N–C–N), 183.6 (C=O) ppm. $C_{16}H_{24}N_2O$ (260.375): calcd. C 73.81, H 9.29; found C 74.08, H 9.38.

3,3-Bis(isopropylamino)-1-(4-methoxyphenyl)prop-2-en-1-one (6g): Pale brown powder; m.p. 171–172 °C; yield 199 mg (72%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.17 (br. s, 12 H, CH_3), 3.70–3.96 (m, 5 H, CH_3O, 2 × C*H*NH), 5.15 (s, 1 H, CH=), 6.07 (br. s, 1 H, NH), 6.89 (d, *J* = 7.2 Hz, 2 H), 7.71 (d, *J* = 7.2 Hz, 2 H), 11.29 (d, *J* = 6.8 Hz, 1 H, NH) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]DMSO): δ = 23.1, 23.4 [CH(*C*H$_3$)$_2$], 41.3, 43.7 (CH), 55.5 (CH_3O), 74.0 (CH=), 113.5 (C-3,5), 128.1 (C-2,6), 135.2 (C-1), 159.8 (N–C–N), 160.6 (C-4), 181.1 (C=O) ppm. $C_{16}H_{24}N_2O_2$ (276.374): calcd. C 69.53, H 8.75; found C 69.75, H 8.87.

Supporting Information (see footnote on the first page of this article):

Acknowledgments

This project was supported by the Deutsche Forschungsgemeinschaft (DFG) through grant Gz: 436 RUS 113/858/0-1 and by the Russian Foundation for Basic Research (grant nos. 08-03-00736-a, RFBR-DFG 07-03-91562-NNIO_a and 08-03-00067-a).

[1] a) R. E. Banks, B. E. Smart, J. C. Tatlow (Eds.), *Organofluorine Chemistry. Principles and Commercial Applications*, Plenum Press, New York, **1994**; b) M. Howe-Grant, *Fluorine Chemistry: A Comprehensive Treatment*, John Wiley & Sons, New York, **1995**; c) T. Hiyama, *Organofluorine Compounds. Chemistry and Applications*, Springer, Berlin, **2000**; d) R. D. Chambers, *Fluorine in Organic Chemistry*, Blackwell, Oxford, **2004**; e) P. Kirsch, *Modern Fluoroorganic Chemistry: Synthesis Reactivity, Applications*, Wiley-VCH, Weinheim, **2004**; f) M. Shimizu, T. Hiyama, *Angew. Chem. Int. Ed.* **2005**, *44*, 214–231; g) K. Uneyama, *Organofluorine Chemistry*, Blackwell, Oxford, **2006**.

[2] a) K. Uneyama, O. Morimoto, F. Yamashita, *Tetrahedron Lett.* **1989**, *30*, 4821–4824; b) I. I. Gerus, M. G. Gorbunova, V. P. Kukhar, *J. Fluorine Chem.* **1994**, *69*, 195–198; c) W. Cen, Y. Ni, V. Shen, *J. Fluorine Chem.* **1995**, *73*, 161–164; d) M. A. Kurykia, I. M. Volpin, L. S. German, *J. Fluorine Chem.* **1996**, *80*, 9–12; e) A. V. Sanin, V. G. Nenajdenko, K. I. Smolko, D. I. Denisenko, E. S. Balenkova, *Synthesis* **1998**, 842–846; f) J. P. Bégué, D. Bonnet-Delpon, D. Bouvet, M. H. Rock, *J. Chem. Soc. Perkin Trans. 1* **1998**, 1797–1800; g) H. Moon, T. Uegaki, T. Konno, T. Ishihara, H. Yamanaka, *Tetrahedron Lett.* **1999**, *40*, 2985–2988; h) B. Jiang, F. Zhang, W. Xiong, *Tetrahedron* **2002**, *58*, 265–270.

[3] J. P. Bégué, D. Bonnet-Delpon, D. Mesureur, G. Née, S. Wu, *J. Org. Chem.* **1992**, *57*, 3807–3814.

[4] J. P. Bégué, D. Mesureur, *Synthesis* **1989**, 309–312.

[5] a) V. A. Soloshonok, T. Ono, *Synlett* **1996**, 919–921; b) P. Bravo, M. Crucianelli, M. Zanda, *Tetrahedron Lett.* **1995**, *36*, 3043–3046.

[6] W. Cen, Y. Ni, Y. Shen, *J. Fluorine Chem.* **1995**, *73*, 161–164.

[7] H. Bürger, T. Dittmar, G. Pawelke, *J. Fluorine Chem.* **1995**, *70*, 89–93.

[8] F. Palacios, A. M. O. de Retana, S. Pascual, J. Oyarzabal, *J. Org. Chem.* **2004**, *69*, 8767–8774.

[9] C. F. Bernasconi, Z. Rappoport, *Acc. Chem. Res.* **2009**, *42*, in press. DOI: 10.1021/ar900048q.

[10] A. Yu. Rulev, *Usp. Khim.* **2002**, *71*, 225–254; A. Yu. Rulev, *Russ. Chem. Rev.* **2002**, *71*, 195–221.

[11] a) B. Jiang, F. Zhang, W. Xiong, *Tetrahedron* **2002**, *58*, 261–264; b) W. Dmowski, *J. Fluorine Chem.* **1984**, *26*, 379–394.

[12] V. M. Muzalevskiy, V. G. Nenajdenko, A. Yu. Rulev, I. A. Ushakov, G. V. Romanenko, A. V. Shastin, E. S. Balenkova, G. Haufe, *Tetrahedron* **2009**, *65*, 6991–7000.

[13] For key publications, see: a) A. V. Shastin, V. N. Korotchenko, V. G. Nenajdenko, E. S. Balenkova, *Tetrahedron* **2000**, *56*, 6557–6563; b) V. N. Korotchenko, A. V. Shastin, V. G. Nenajdenko, E. S. Balenkova, *Tetrahedron* **2001**, *57*, 7519–7527; c) V. N. Korotchenko, A. V. Shastin, V. G. Nenajdenko, E. S. Balenkova, *J. Chem. Soc. Perkin Trans. 1* **2002**, 883–887; d) V. N. Korotchenko, V. G. Nenajdenko, A. V. Shastin, E. S. Balenkova, *Org. Biomol. Chem.* **2003**, *1*, 1906–1908; e) V. G. Nenajdenko, A. V. Shastin, V. N. Korotchenko, G. N. Varseev, E. S. Balenkova, *Eur. J. Org. Chem.* **2003**, 302–308; f) V. G. Nenajdenko, G. N. Varseev, V. N. Korotchenko, A. V. Shastin, E. S. Balenkova, *J. Fluorine Chem.* **2004**, *125*, 1339–1345; g) V. G. Nenajdenko, V. N. Korotchenko, A. V. Shastin, E. S. Balenkova, *Russ. Chem. Bull.* **2004**, *53*, 1034–1064; h) V. G. Nenajdenko, G. N. Varseev, A. V. Shastin, E. S. Balenkova, *J. Fluorine Chem.* **2005**, *126*, 907–913; i) V. M. Muzalevskiy, V. G. Nenajdenko, A. V. Shastin, E. S. Balenkova, G. Haufe, *Synthesis* **2009**, 2249–2259.

[14] U. Kuckländer, *Enaminones as Synthons*, in: *The Chemistry of Enamines* (Ed.: Z. Rappoport.), Wiley, New York, **1994**, pp. 523–636.

[15] J. L. Chiara, A. Gomez-Sanchez, *NMR Spectra*, in: *The Chemistry of Enamines* (Ed.: Z. Rappoport), Wiley, New York, **1994**, pp. 279–404.

[16] Z. Rappoport, *Acc. Chem. Res.* **1992**, *25*, 474–479.

[17] A. A. Bothner-By, S. Castellano, H. Günther, *J. Am. Chem. Soc.* **1965**, *87*, 2439–2442.

[18] S. Andreades, *J. Am. Chem. Soc.* **1962**, *84*, 864–865.

[19] A. Yu. Rulev, *Usp. Khim.* **1998**, *67*, 317–332; *Russ. Chem. Rev.* **1998**, *67*, 279–293.

[20] K. Nagayama, A. Kumar, K. Wüthrich, R. R. Ernst, *J. Magn. Reson.* **1980**, *40*, 321–334.
[21] J. Jeener, B. H. Meier, P. Bachmann, R. R. Ernst, *J. Chem. Phys.* **1979**, *71*, 4546–4553.
[22] A. Bax, S. Subramanian, *J. Magn. Reson.* **1986**, *67*, 565–569.
[23] A. Bax, M. F. Summers, *J. Am. Chem. Soc.* **1986**, *108*, 2093–2094.
[24] A. A. Granovsky, PC GAMESS/Firefly version 7.1.F. www.http://classic.chem.msu.su/gran/gamess/index.html.

Received: August 14, 2009
Published Online: November 17, 2009

