ISSN 1070-4280, Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 7, pp. 976–986. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © A.S. Konev, K. Abbaspour Tehrani, A.F. Khlebnikov, M.S. Novikov, J. Magull, 2010, published in Zhurnal Organicheskoi Khimii, 2010, Vol. 46, No. 7, pp. 980–990.

Monofluorinated Aziridines in Asymmetric Synthesis of Chiral Fluorinated Prop-2-yn-1-amines

A. S. Konev[a], K. Abbaspour Tehrani[b], A. F. Khlebnikov[a], M. S. Novikov[a], and J. Magull[c]

[a] *St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*
e-mail: alexander.khlebnikov@pobox.spbu.ru

[b] *Faculty of Sciences, Department of Applied Biological Sciences and Engineering, Laboratory for Organic Chemistry, Vrije Universiteit, Brussel, Belgium*

[c] *Inorganic Chemistry Institute, Georg-August University, Göttingen, D-37077 Germany*

Received May 20, 2009

Abstract—Nonracemic C-fluoroaziridines were synthesized for the first time by reaction of fluorocarbene with *N*-diphenylmethylidene-substituted natural amino acid esters. The products were shown to be used in asymmetric synthesis of chiral fluorinated prop-2-yn-1-amines via one-pot process involving isomerization of 2-fluoroaziridines into α-fluoro imines and subsequent reaction with alkynyldifluoroborane generated *in situ*.

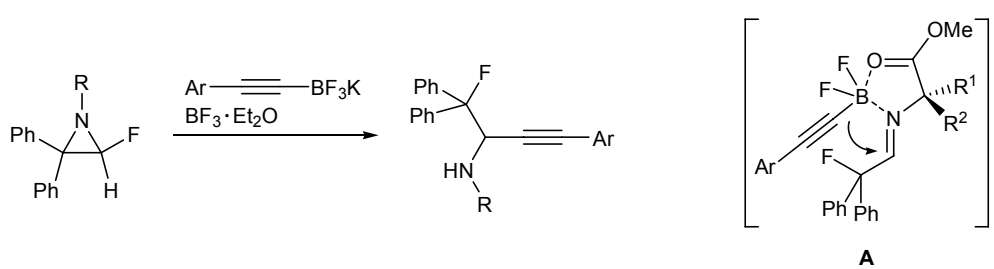
DOI: 10.1134/S1070428010070043

Prop-2-yn-1-amines are widely used as medical agents for the treatment of various diseases [1–10] and as building blocks in the synthesis of polyfunctional nitrogen-containing organic compounds [11–18]. Development of convenient synthetic approaches to chiral prop-2-yn-1-amines [19–25] is an important problem, taking into account that the use of nonracemic drugs is one of the most important lines in modern medicine [26–30].

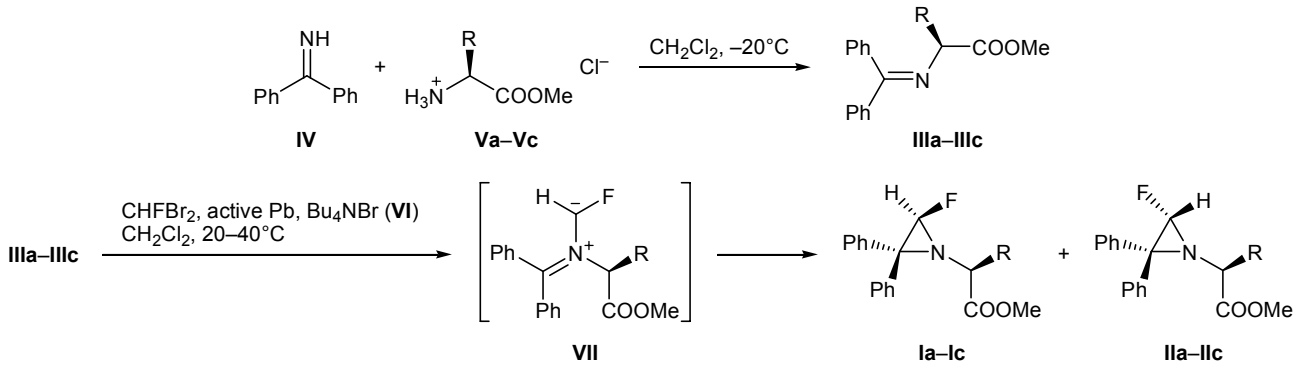
We recently showed that fluorinated prop-2-yn-1-amines can readily be obtained by reaction of potassium arylethynyltrifluoroborates with 3-fluoro-2,2-diphenylaziridine in the presence of boron trifluoride–ether complex (Scheme 1) [31]. It was found that the formation of fluorinated prop-2-yn-1-amines from monofluoroaziridines involves Lewis acid-catalyzed isomerization of 2-fluoroaziridines into α-fluoro imines which then react with alkynyldifluoroborane. Acceleration of the process and reduction in the amount of by-products in the case of substrates containing a methoxycarbonylmethyl group (R = CH_2CO_2Me; **A**, R^1 = R^2 = H) was rationalized assuming formation of intermediate chelate **A** [31]. The formation of cyclic intermediate implies that addition of arylethynyl nucleophile at the C=N bond of substrates with a chiral carbon atom (C* in **A,** $R^1 \neq R^2$) could occur with high diastereoselectivity due to rigidity of the transition state and proximity of the chiral center to the reaction center [32] (Scheme 1).

Therefore, we presumed that the reaction sequence including isomerization of chiral aziridine and subsequent reaction of the imine thus formed with potassium alkynyltrifluoroborate should provide a simple and convenient synthetic route to chiral functionalized prop-2-yn-1-amines. The present article reports on our first results of asymmetric synthesis of fluorinated

Scheme 1.



Scheme 2.



R = Me (**a**), $PhCH_2$ (**b**), (*S*)-MeEtCH (**c**).

prop-2-yn-1-amines from enantiomerically pure imines through chiral fluoroaziridines.

Monofluoroaziridines can be obtained in different ways: by reaction of fluorocarbene with imines [33, 34], by reduction of halofluoroaziridines with Bu_3SnH [35, 36], and by cyclization of β-fluoro-β-bromo(chloro) amines in the presence of bases [37, 38]. The two latter procedures imply basic conditions, so that they are unsuitable for the synthesis of nonracemic compounds derived from amino acids. The procedure proposed by us recently for generation of fluorocarbene via reduction of $CHFBr_2$ with lead [33, 34] makes it possible to synthesize monofluoroaziridines under neutral conditions, avoiding racemization of imines derived from amino acid esters.

Chiral aziridines **I** and **II** were synthesized according to Scheme 2. Enantiomerically pure Schiff bases **III** were prepared as described in [39, 40] from benzophenone imine (**IV**) and amino acid (L-alanine, L-phenylalanine, and L-isoleucine) methyl ester hydrochlorides **Va**–**Vc**. The resulting Schiff bases were brought into reaction with fluorocarbene which was generated by reduction of $CHFBr_2$ with active lead in the presence of tetrabutylammonium bromide (**VI**) under ultrasonic activation [33, 34]. The reaction involved electrophilic attack by fluorocarbene on the lone electron pair on the nitrogen atom in the imine, leading to ylide **VII** which underwent cyclization to aziridines **I** and **II**. In the ^1H and ^{19}F NMR spectra of the reaction mixtures we observed signals from two diastereoisomeric aziridines **I** and **II**. The formation of only two diastereoisomeric products from Schiff base **IIIc** possessing a non-racemizable (3*S*)-chiral center and theoretically racemizable (2*S*)-chiral center indicates the absence of racemization during the process. Diastereoselectivity in the formation of fluoroaziridines and their yields decrease in going from L-alanine to L-isoleucine derivatives (Table 1), i.e., as the size of the R substituent at the chiral center increases. Diastereoisomeric aziridines are not converted into each other during the reaction because of high barrier to opening of the aziridine ring.

In all cases, major isomer **I** was isolated as individual substance, whereas minor isomer **II** was isolated as a mixture with either the major isomer (**Ia**, **Ib**) or the initial Schiff base (**IIIc**). The configuration of aziridine **Ia** was determined by X-ray analysis (Fig. 1), and the configuration of the other aziridines was determined by analysis of their ^1H NMR spectra. The signal from the aziridine proton in major isomers (2*S*,2′*R*)-**Ia**–(2*S*,2′*R*)-**Ic** appeared in a stronger field (δ 4.93–5.42 ppm) relative to the corresponding signal of minor isomers (2*S*,2′*S*)-**IIa**–(2*S*,2′*S*)-**IIc** (δ 5.67–5.73 ppm). As far as we know, fluoroaziridines **I** and

Table 1. Yields and ratios of diastereoisomeric fluoroaziridines **I** and **II** in the reaction mixtures obtained from Schiff bases **III** and fluorocarbene

Schiff base no.	Aziridine no.		R	Ratios of aziridines **I** and **II** in the reaction mixture (^1H NMR data)	Preparative yields of aziridines, % (ratio **I**:**II**)
IIIa	**Ia**	**IIa**	Me	3:1	45% (**Ia**), 6% (**Ia**:**IIa**, 1:1.8)
IIIb	**Ib**	**IIb**	$PhCH_2$	2.3:1	22% (**Ib**), 13% (**Ib**:**IIb**, 1:1.5)
IIIc	**Ic**	**IIc**	(*S*)-Et(Me)CH	1.1:1	6% (**Ic**)

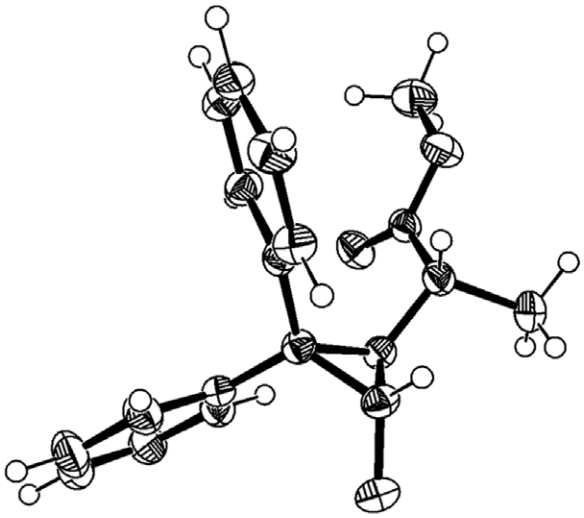


Fig. 1. Structure of the molecule of (2*S*,3′*R*)-2-(3-fluoro-2,2-diphenylaziridin-1-yl)propanoate (**Ia**) according to the X-ray diffraction data.

II represent first examples of chiral nonracemic C-fluoro-substituted aziridines [41, 42]; analogous chiral *C*-chloro- [43] and *C*-bromoaziridines [44] were reported previously.

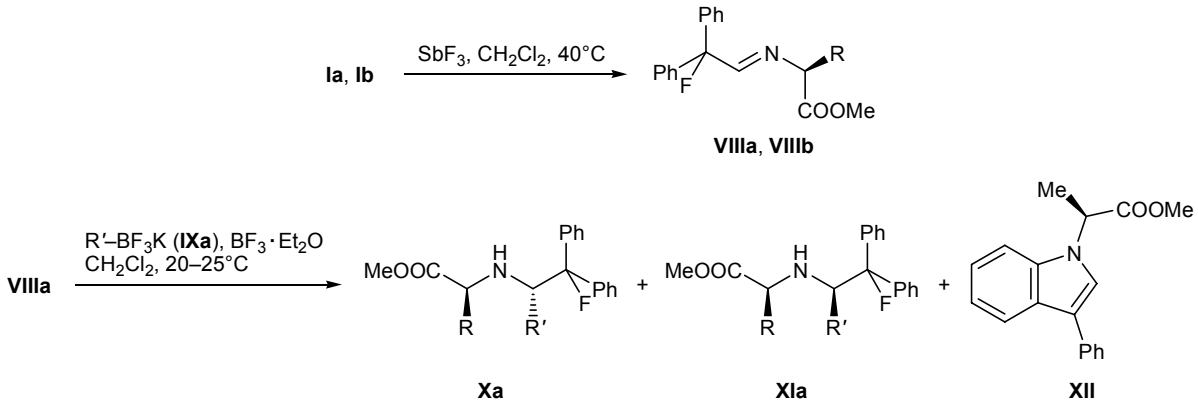
The transformation of aziridines **I** into target fluorinated prop-2-yn-1-amines **X** and **XI** may be accomplished in a stepwise mode or via a one-pot procedure [31]. According to the first approach, aziridine **Ia** was subjected to isomerization into α-fluorinated Schiff base **VIIIa** by the action of SbF_3 as Lewis acid [31, 34, 45]. Analogous isomerization of aziridine **Ib** gave Schiff base **VIIIb** in 94% yield. Imine **VIIIa** was treated (without isolation and purification) with potassium 3-methoxyphenylethynyltrifluoroborate (**IXa**) in methylene chloride at room temperature in the presence of an equimolar amount of boron trifluoride–ether complex to obtain a mixture of diastereoisomeric prop-2-yn-1-amines **Xa** and **XIa** (26%) and indole **XII** (17%) (Scheme 3).

As we showed previously [31], undesirable formation of indole derivative may be minimized by performing isomerization of fluoroaziridines directly in the presence of alkynyltrifluoroborates. In fact, following the second approach, which implied mere treatment of aziridine **Ia** with borate **IXa** in the presence of 1 equiv of $BF_3 \cdot Et_2O$ in CH_2Cl_2 at room temperature, we obtained a mixture of diastereoisomeric amines **Xa** and **XIa** and indole **XII** at a ratio of 5.8 : 1.2 : 1 (^{1}H NMR data). When the reaction was carried out at –20°C, the formation of indole **XII** was suppressed completely, and the products were diastereoisomers **Xa** and **XIa** at a ratio of 5 : 1 (^{1}H NMR). Under analogous conditions, the reaction of aziridine **Ib** with borate **IXa** gave a mixture of diastereoisomeric amines **Xb** and **XIb** at a ratio of 10 : 1 (^{1}H NMR).

Insofar as the transformation of fluoroaziridines **I** and **II** into fluorinated prop-2-yn-1-amines **X** and **XI** involves intermediate formation of α-fluoro imine **VIII** which lacks aziridine chiral center, diastereoisomeric aziridines **I** and **II** could be brought into the reaction without preliminary separation. In order to avoid isomerization of fluoroaziridine into α-fluoro imine **VIII**, the possibility for imination of 2-fluoro-2,2-diphenylacetaldehyde with α-amino acid ester could be considered. Unfortunately, known 2-fluoro-2,2-diphenylacetaldehyde is fairly difficult to synthesize; in addition, this compound is unstable [46].

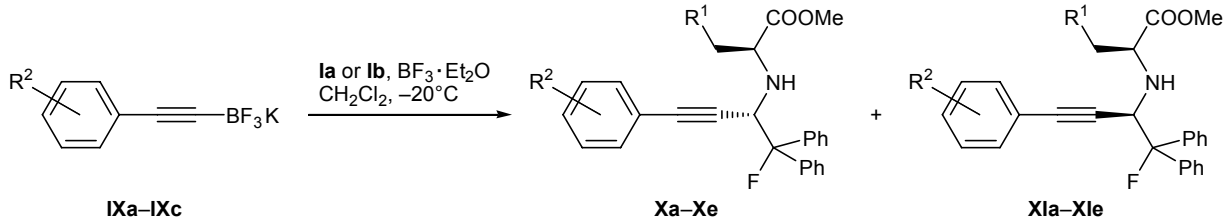
The optimized conditions were applied to synthesize a series of fluorinated prop-2-yn-1-amines **Xa**–**Xe** (Scheme 4, Table 2). These reactions led to the formation of mixtures of only two diastereoisomeric amines

Scheme 3.



R = Me (**a**), $PhCH_2$ (**b**); R′ = 3-$MeOC_6H_4C{\equiv}C$.

Scheme 4.



X and **XI**. The major isomers were isolated as individual substances and fully characterized. According to the ^{1}H, ^{13}C, and ^{19}F NMR spectra, minor isomers **XIa**–**XIe** were always present in the reaction mixtures, but we failed to isolate them pure.

The (2*S*,1′*S*) configuration of amines **Xa**, **Xd**, and **Xe** was proved by X-ray analysis (Fig. 2), and the configuration of **Xb** and **Xc** was determined on the basis of their ^{1}H NMR spectra which characteristically contained a signal from the 1′-H proton at δ 4.44–4.58 ppm (*S*); the corresponding proton in amines **XI** with (*R*)-configuration of the $C^{1'}$ atom resonated in a weaker field (δ 4.70–4.79 ppm).

Scheme 5 rationalizes predominant formation of (2*S*,1′*S*) isomers **X**. The reaction of fluoroaziridines **I** with potassium alkynyltrifluoroborates involves intermediate formation of α-fluoro imines and alkynyldifluoroboranes which are likely to give rise to chelate

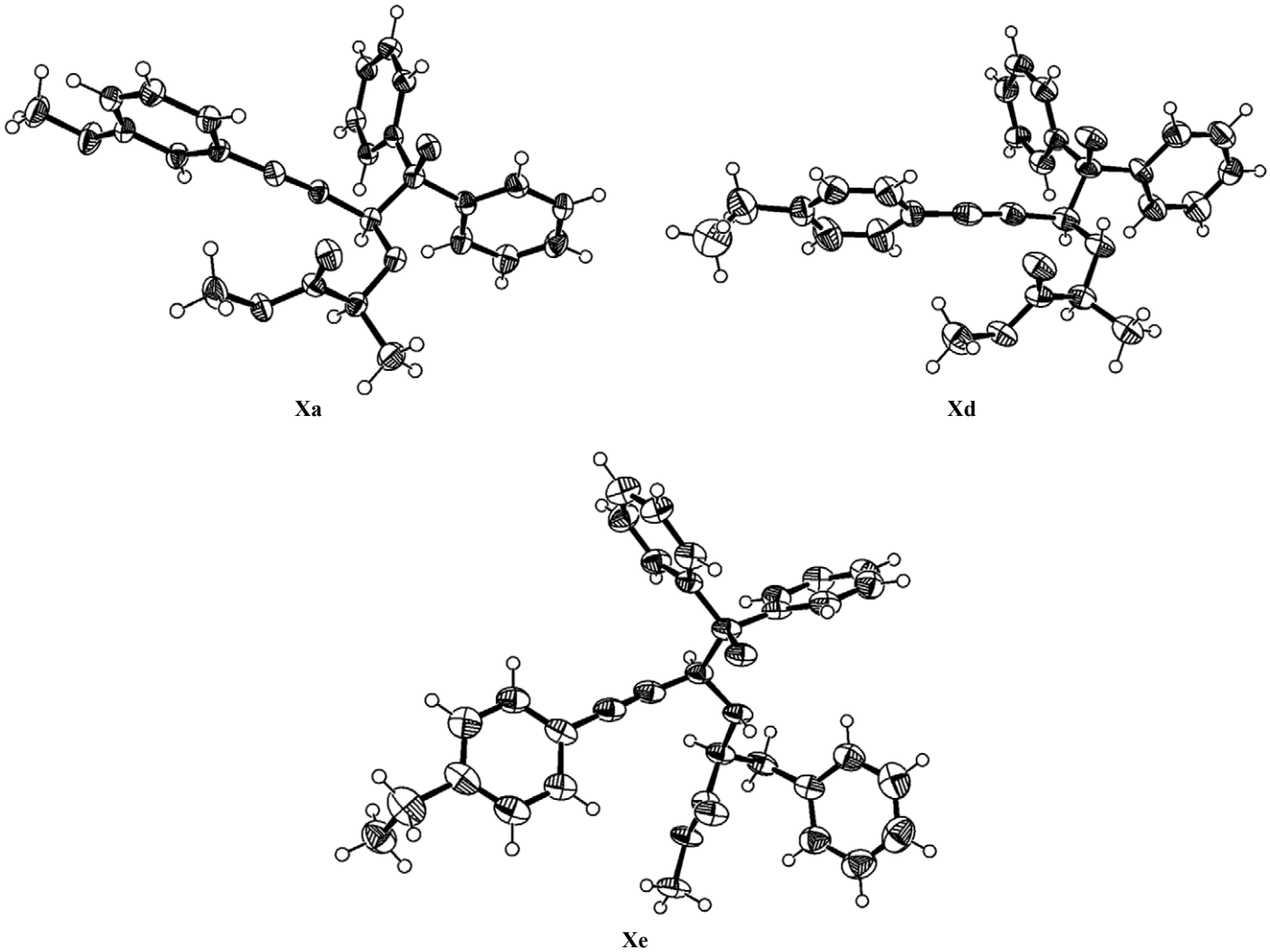
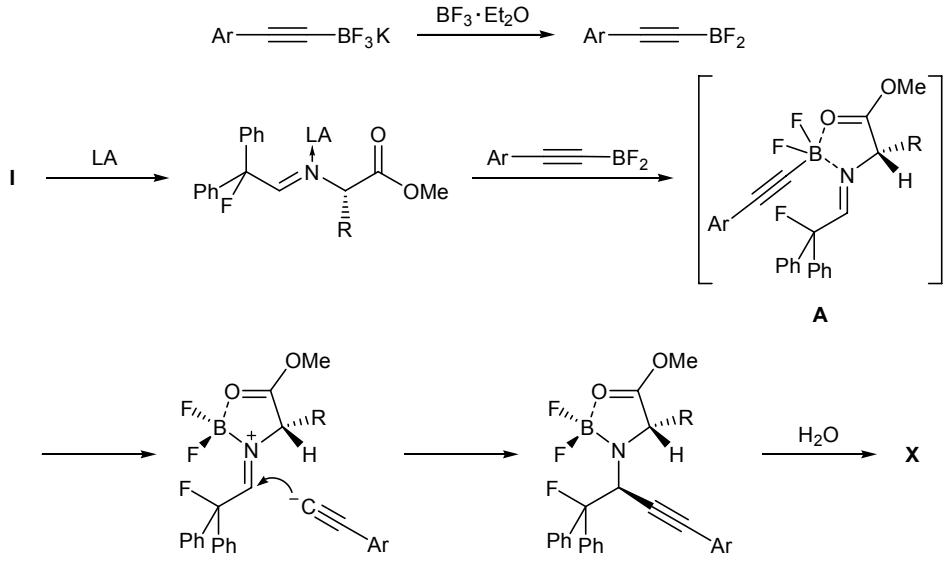


Fig. 2. Structure of the molecules of (2*S*,1′*S*)-2-{3-aryl-1-[fluoro(diphenyl)methyl]prop-2-yn-1-ylamino}propanoates **Xa**, **Xd**, and **Xe**.

Scheme 5.



LA = $BF_3 \cdot OEt_2$ or $ArC{\equiv}CBF_2$.

A. Rigid cyclic structure of intermediate **A** ensures strong differentiation of sides of the C=N bond, so that intramolecular alkynyl group transfer occurs through attack at the less sterically hindered side of the C=N bond in (*S*) isomer **A** and leads to (2*S*,1′*S*) isomer **X**. In keeping with the proposed scheme, the stereoselectivity should increase as the size of the substituent on C^2 increases. In fact, the ratio **X**:**XI** in the reaction mixture changed from 5:1 to 10:1 in going from R^1 = H (**Xa**:**XIa**) to R^1 = Ph (**Xb**:**XIb**).

To conclude, we were the first to synthesize chiral *C*-fluoroaziridines by reaction of fluorocarbene with benzophenone imines derived from chiral amino acid esters. We also demonstrated that chiral *C*-fluoroaziridines can be used in asymmetric synthesis of fluorinated prop-2-yn-1-amines via reaction with potassium arylethynylborates in the presence of boron trifluoride–ether complex.

EXPERIMENTAL

The attenuated total reflectance IR spectra were recorded on an Avatar 370 FTIR spectrometer (Thermo Nicolet), and the IR spectra were measured on a Carl Zeiss UR-20 instrument from solutions in chloroform. The optical rotations were determined on a Perkin–Elmer 241 polarimeter. The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Avance DRX 250 spectrometer at 250, 63, and 235 MHz, respectively, using $CDCl_3$ as solvent. The ^1H and ^{13}C NMR spectra were also obtained on a Bruker DPX-300 instrument at 300 and 75 MHz, respectively. The chemical shifts are given relative to tetramethylsilane (^1H, ^{13}C) or $CFCl_3$ (^{19}F). The mass spectra (electrospray ionization) were obtained on a VGQuattro II mass spectrometer. Silica gel (grain size 0.040–0.063 mm, Merck) was used for flash chromatography. Analytical thin-layer chroma-

Table 2. Asymmetric synthesis of prop-2-yn-1-amines from fluoroaziridines

Aziridine no.	Trifluoroborate no.	Amine no.	R^1	R^2	Yield[a] of **X**+**XI**, % (ratio **X**:**XI**)[b]	Yield of **X**,[a] %
Ia	**IXa**	**Xa**, **XIa**	H	3-MeO	43 (4.7:1)	18
Ib	**IXa**	**Xb**	Ph	3-MeO	35	35
Ia	**IXb**	**Xc**, **XIc**	H	H	30 (4.2:1)	–
Ia	**IXc**	**Xd**, **XId**	H	4-Et	46 (3.4:1)	28
Ib	**IXc**	**Xe**	Ph	4-Et	25	25

[a] Preparative yield.
[b] Ratio of isomers isolated by flash chromatography.

tography was performed on glass plates (Merck) coated with a 0.2-mm layer of silica gel containing a 60F254 ultraviolet indicator. The melting points were measured on a Buchi Melting Point B540 or Boetius apparatus; uncorrected values are given. The elemental compositions were determined on a Hewlett–Packard HP-185B CHN analyzer. Methylene chloride was distilled over calcium hydride; boron trifluoride–ether complex was distilled under reduced pressure prior to use. Tetrabutylammonium bromide (**VI**) was dried in a desiccator over P_2O_5. Dibromofluoromethane [47], Schiff bases **III** [39, 40], potassium trifluoroborates **IX** [48, 49], and active lead [50] were prepared according to known procedures. Commercially available chemicals were used without preliminary purification, unless otherwise stated.

The X-ray diffraction data for compounds **Ia**, **Xa**, **Xd**, and **Xe** were acquired on a STOE IPDS II diffractometer (monochromatized MoK_α irradiation, λ = 0.71073 Å). The complete sets of crystallographic data, as well as CIF files, were deposited to the Cambridge Crystallographic Data Centre (entry nos. CCDC 704880–704882, 705390) and are available from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: *deposit@ccdc.cam.ac.uk*, *http://www.ccdc.cam.ac.uk/deposit*).

Methyl (2*S*,3*S*)-2-(diphenylmethylideneamino)-3-methylpentanoate (IIIc). Yield 53%, colorless crystals, mp 67–69°C, $[\alpha]_D^{25}$ = –158.3° (*c* = 1.03, $CHCl_3$). ^{1}H NMR spectrum (300 MHz), δ, ppm: 0.75–0.95 m (6H, CH_3C), 1.15–1.35 m (1H, CH_2), 1.50–1.70 m (1H, CH_2), 2.05–2.30 m (1H, CHC), 3.74 s (3H, CH_3O), 3.94 d (1H, CHN, *J* = 16.2 Hz), 7.05–7.15 m (2H, H_{arom}), 7.30–7.60 m (6H, H_{arom}), 7.60–7.80 m (2H, H_{arom}). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 11.5 (CH_3), 15.8 (CH_3), 25.2 (CH_2), 39.1 (**C**HC), 51.8 (CH_3O), 70.9 (CHN), 127.9, 128.0, 128.4, 128.5, 128.8, 130.2, 136.4, 139.7, 170.4 (C=N), 172.7 (C=O). Found, %: C 77.80; H 7.68; N 4.65. $C_{20}H_{23}NO_2$. Calculated, %: C 77.64; H 7.49; N 4.53.

Methyl 2-(3-fluoro-2,2-diphenylaziridin-1-yl)-propanoates Ia and IIa. A mixture of 1.006 g (3.8 mmol) of methyl (*S*)-2-(diphenylmethylideneamino)propanoate (**IIIa**), 3.62 g (18.8 mmol) of dibromofluoromethane, 3.12 g (15.1 mmol) of active lead, and 4.87 g (15.1 mmol) of tetrabutylammonium bromide (**VI**) in 15 ml of methylene chloride was subjected to ultrasonic treatment for 59 h at 20–40°C. The mixture was diluted with diethyl ether (30 ml), the organic layer was separated, and the inorganic precipitate was washed thrice with a mixture of 10 ml of methylene chloride and 20 ml of diethyl ether. The organic phase was combined with the washings, washed with water (3 × 40 ml), dried over sodium sulfate, and filtered, and the solvent was removed under reduced pressure. Recrystallization of the residue from diethyl ether gave 503 mg (45%) of methyl (2*S*,3′*R*)-2-(3-fluoro-2,2-diphenylaziridin-1-yl)-propanoate (**Ia**) as colorless crystals with mp 166–168°C, $[\alpha]_D^{25}$ = +160° (*c* = 2.0, CH_2Cl_2). IR spectrum (film), ν, cm^{-1}: 3068, 2980, 2956, 1742 (C=O), 1603, 1496, 1447, 1397, 1300, 1208, 1190, 1175, 1056, 993, 939, 911, 859, 776, 754, 701, 663. ^{1}H NMR spectrum (250 MHz), δ, ppm: 1.53 d (3H, CH_3C, *J* = 7.0 Hz), 2.60 q.d (1H, C**H**CH_3, J_{HH} = 7.0, J_{HF} = 3.9 Hz), 3.68 s (3H, CH_3O), 5.38 d (1H, CHF, *J* = 78.2 Hz), 7.15–7.45 m (8H, H_{arom}), 7.55–7.75 m (2H, H_{arom}). ^{13}C NMR spectrum (63 MHz), δ_C, ppm: 17.3 (**C**H_3C), 51.9 (CH_3O), 56.5 d (CH_3**C**, *J* = 3.6 Hz), 56.9 d (C^3, *J* = 14.0 Hz), 84.8 d (CF, *J* = 244.7 Hz), 127.2, 128.0, 128.5, 128.7, 128.8, 129.9 d (*J* = 2.2 Hz), 134.9 d (*J* = 4.2 Hz), 138.3 d (*J* = 3.6 Hz), 173.0 (C=O). ^{19}F NMR spectrum: δ_F –176.1 ppm, d (*J* = 78.2 Hz). Found, %: C 72.51; H 6.21; N 4.75. $C_{18}H_{18}FNO_2$. Calculated, %: C 72.22; H 6.06; N 4.68. X-Ray diffraction data: $C_{18}H_{18}FNO_2$, *M* 299.33; orthorhombic crystal system, space group $P2_12_12_1$; unit cell parameters: *a* = 8.7709(18), *b* = 12.205(2), *c* = 14.539(3) Å; *V* = 1556.4(5) Å^3; *Z* = 4, *T* = 133(2) K; *F*(000) = 632; d_{calc} = 1.277 mg/m^3; R_{all} = 0.0336, wR_2 = 0.0812; total number of reflections 20106 (2692 independent reflections with R_{int} = 0.0502).

In addition, 67 mg (6%) of a mixture of (2*S*,3′*S*)- and (2*S*,3′*R*)-2-(3-fluoro-2,2-diphenylaziridin-1-yl)-propanoates **Ia** and **IIa** at a ratio of 1.8:1 was isolated as colorless crystals with mp 105–145°C (decomp.).

Methyl (2*S*,3′*S*)-2-(3-fluoro-2,2-diphenylaziridin-1-yl)propanoate (IIa). ^{1}H NMR spectrum (250 MHz), δ, ppm: 1.35 d (3H, CH_3C, *J* = 6.7 Hz), 2.70 q.d (1H, C**H**Me, J_{HH} = 6.7, J_{HF} = 4.0 Hz), 3.77 s (3H, CH_3O), 5.69 d (1H, CHF, *J* = 77.1 Hz), 7.10–7.40 m (10H, H_{arom}). ^{13}C NMR spectrum (63 MHz), δ_C, ppm: 17.6 (**C**H_3C), 52.3 (CH_3O), 55.5 d (C^3, *J* = 14.0 Hz), 55.7 d (**C**HCH_3, *J* = 3.4 Hz), 85.5 d (CHF, *J* = 244.4 Hz), 127.4, 127.99, 128.65, 128.67, 128.85, 130.3 d (*J* = 2.3 Hz), 134.2 d (*J* = 4.1 Hz), 138.1 d (*J* = 3.3 Hz), 172.6 d (*J* = 0.8 Hz). ^{19}F NMR spectrum: δ_F –176.5 ppm, d (*J* = 77.1 Hz).

Methyl 2-(3-fluoro-2,2-diphenylaziridin-1-yl)-3-phenylpropanoates Ib and IIb. A mixture of 2.375 g (6.9 mmol) of methyl (*S*)-2-(diphenylmethylidene-

amino)-3-phenylpropanoate (**IIIb**), 6.37 g (33.2 mmol) of dibromofluoromethane, 5.71 g (27.6 mmol) of active lead, and 8.91 g (27.6 mmol) of quaternary ammonium salt **VI** in 15 ml of methylene chloride was subjected to ultrasonic treatment for 77 h at 20–40°C. The mixture was then treated as described above. By chromatographic purification of the crude product we isolated 573 mg (22%) of methyl (2*S*,3′*R*)-2-(3-fluoro-2,2-diphenylaziridin-1-yl)-3-phenylpropanoate (**Ib**) as colorless crystals with mp 120–121°C, $[\alpha]_D^{25}$ = +166.2° (*c* = 2.0, CH_2Cl_2). IR spectrum (film), ν, cm^{-1}: 3027, 2950, 2864, 1739, 1731 (C=O), 1603, 1493, 1447, 1435, 1401, 1309, 1204, 1175, 1150, 1076, 1037, 1012, 950, 913, 851, 751, 697. ^{1}H NMR spectrum (250 MHz), δ, ppm: 2.79 m (1H, CHN), 3.22 m (2H, CH_2), 3.58 s (3H, CH_3O), 4.93 d (1H, CHF, *J* = 76.8 Hz), 7.00–7.15 m (2H, H_{arom}), 7.15–7.45 m (11H, H_{arom}), 7.45–7.7 m (2H, H_{arom}). ^{13}C NMR spectrum (63 MHz), δ_C, ppm: 39.2 (CH_2), 51.7 (CH_3), 55.0 d (C^3, *J* = 13.8 Hz), 63.3 d (C^2, *J* = 3.9 Hz), 84.8 d (CF, *J* = 244.9 Hz), 126.9, 127.2, 127.9, 128.46, 128.49, 128.5, 128.9, 129.5, 129.9 d (*J* = 2.1 Hz), 134.7 d (*J* = 4.1 Hz), 136.69, 138.2 d (*J* = 3.3 Hz), 171.94 d (C=O, *J* = 1.3 Hz). ^{19}F NMR spectrum: δ_F –175.2 ppm, d (*J* = 76.8 Hz). Found, %: C 76.35; H 5.85; N 3.66. $C_{24}H_{22}FNO_2$. Calculated, %: C 76.78; H 5.91; N 3.73.

In addition, 328 mg (13%) of a mixture of aziridines **Ib** and **IIb** at a ratio of 1:1.5 was isolated.

Methyl (2*S*,3′*S*)-2-(3-fluoro-2,2-diphenylaziridin-1-yl)-3-phenylpropanoate (IIb). ^{1}H NMR spectrum (250 MHz), δ, ppm: 2.92 m (2H, CHN, CH_2), 3.21 m (1H, CH_2), 3.62 s (3H, CH_3O), 5.73 d (1H, CHF, *J* = 77.4 Hz), 6.7–6.9 m (2H, H_{arom}), 7.00–7.50 m (13H, H_{arom}). ^{13}C NMR spectrum (63 MHz), δ_C, ppm: 38.3 (CH_2), 52.1 (CH_3), 56.1 d (C^3, *J* = 14.0 Hz), 62.6 d (C^2, *J* = 3.1 Hz), 84.9 d (CF, *J* = 245.1 Hz), 126.5, 127.5, 127.9, 128.2, 128.75, 128.79, 128.95, 129.2, 130.6 d (*J* = 2.1 Hz), 134.0 d (*J* = 4.1 Hz), 136.72, 137.8 d (*J* = 3.3 Hz), 171.3 d (C=O, *J* = 1.2 Hz). ^{19}F NMR spectrum: δ_F –176.9 ppm, d (*J* = 77.4 Hz).

Methyl 2-(3-fluoro-2,2-diphenylaziridin-1-yl)-3-methylpentanoates Ic and IIc. A mixture of 1.403 g (4.5 mmol) of compound **IIIc**, 4.36 g (22.7 mmol) of dibromofluoromethane, 3.759 g (18.2 mmol) of active lead, and 5.865 g (18.2 mmol) of tetrabutylammonium bromide (**VI**) in 20 ml of methylene chloride was subjected to ultrasonic treatment for 108 h at 20–40°C. A 0.2-ml sample of the reaction mixture was extracted with three portions of a mixture of 0.5 ml of diethyl ether and 0.2 ml of methylene chloride, the extracts were combined and evaporated under reduced pressure, and the residual solvent was removed in a high vacuum. According to the ^{1}H NMR data, the residue contained diastereoisomeric aziridines (2*S*,3*S*,3′*R*)-**Ic** and (2*S*,3*S*,3′*S*)-**IIc** and initial Schiff base **IIIc** at a ratio of 1.1:1.0:5.2. The ratio of compounds **Ic** and **IIc** was 1.2:1 (^{19}F NMR data). The main part of the reaction mixture was treated as described above. Recrystallization of the crude product from hexane–diethyl ether gave 74 mg of aziridine **Ic** as colorless crystals. The filtrate was subjected to chromatography to isolate an additional portion, 23 mg, of **Ic**. Overall yield 97 mg (6%).

Methyl (2*S*,3*S*,3′*R*)-2-(3-fluoro-2,2-diphenylaziridin-1-yl)-3-methylpentanoate (Ic). mp 134–135°C, $[\alpha]_D^{25}$ = +174.8° (*c* = 1.10, $CHCl_3$). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3045, 2970, 2880, 1750 (C=O), 1540, 1500, 1450, 1400, 1310, 1300–1120, 1080, 1040, 1020. ^{1}H NMR spectrum (300 MHz), δ, ppm: 0.92 t (3H, C**H**$_3$CH$_2$, *J* = 7.4 Hz), 1.13 d (3H, C**H**$_3$CH, *J* = 6.9 Hz), 1.41 m (1H, CH_2), 1.56 m (1H, CH_2), 1.97 m (1H, C**H**CH$_3$), 2.55 pseudotriplet (1H, CHN, *J* = 3.3 Hz), 3.57 s (3H, CH_3O), 5.42 d (1H, CHF, *J* = 78 Hz), 7.10–7.25 m (2H, H_{arom}), 7.25–7.45 m (6H, H_{arom}), 7.60–7.70 m (2H, H_{arom}). ^{13}C NMR spectrum (75 MHz), δ_C, ppm: 11.8 (CH_3), 15.7 (CH_3), 25.9 (CH_2), 39.0 (**C**HCH$_3$), 51.3 (CH_3O), 54.8 d (C^2, *J* = 14.0 Hz), 66.2 d (C^2, *J* = 4.0 Hz), 85.9 d (CF, *J* = 244.1 Hz), 127.2, 127.9, 128.4, 129.1, 130.0 d (*J* = 2.2 Hz), 134.9 d (*J* = 4.2 Hz), 138.4 d (*J* = 3.2 Hz), 171.7 (C=O). ^{19}F NMR spectrum: δ_F –172.80 ppm, d (*J* = 78 Hz). Found, %: C 73.94; H 7.07; N 4.22. $C_{21}H_{24}FNO_2$. Calculated, %: C 73.88; H 7.09; N 4.10.

The NMR spectral data for methyl (2*S*,3*S*,3′*S*)-2-(3-fluoro-2,2-diphenylaziridin-1-yl)-3-methylpentanoate (**IIc**) were obtained by analysis of the spectra of a mixture of **IIc** and **IIIc**. ^{1}H NMR spectrum, (250 MHz), δ, ppm: 0.67 t (3H, C**H**$_3$CH$_2$, *J* = 7.3 Hz), 1.11 d (3H, C**H**$_3$CH, *J* = 7.3 Hz), 1.77 m (1H, C**H**CH$_3$), 2.85 pseudotriplet (1H, CHN, *J* = 4.4 Hz), 3.57 (3H, CH_3O), 5.67 d (1H, CHF, *J* = 79 Hz), signals from the CH_2 group and aromatic protons were overlapped by those of the initial Schiff base. ^{19}F NMR spectrum: δ_F –172.75 ppm, d (*J* = 79 Hz).

Methyl (*S*)-2-[(2-fluoro-2,2-diphenylethylidene)-amino]propanoate (VIIIa). A mixture of 10 mg (0.03 mmol) of aziridine **Ia** and 2 mg (0.01 mmol) of antimony(III) fluoride in methylene chloride was heated for 3 h under reflux. The mixture was cooled and filtered from SbF_3, and the filtrate was concen-

trated under reduced pressure. The residue was Schiff base **VIIIa** as an orange oily substance with a purity of ~93% (^{1}H NMR); it was used in further synthesis without additional purification. ^{1}H NMR spectrum (250 MHz), δ, ppm: 1.48 d (3H, CH_3C, J = 6.8 Hz), 3.73 s (3H, CH_3O), 4.14 q (1H, C**H**CH_3, J = 6.8 Hz), 7.0–7.6 m (10H, H_{arom}), 8.15 d (1H, CH=N, J = 10.6 Hz). ^{13}C NMR spectrum (63 MHz), δ_C, ppm: 18.6 (**C**H_3C), 52.1 (CH_3O), 67.0 (CH), 97.9 d (CF, J = 175.9 Hz), 127.1 d (J = 6.9 Hz), 127.2 d (J = 6.7 Hz), 128.19, 128.24, 128.5 d (J = 2.0 Hz), 139.3 d (J = 22.5 Hz), 139.4 d (J = 22.6 Hz), 168.6 d (C=N, J = 32.1 Hz), 172.1 (C=O). ^{19}F NMR spectrum: δ_F –142.0 ppm, d (J = 10.6 Hz).

Methyl (*S*)-2-[(2-fluoro-2,2-diphenylethylidene)-amino]-3-phenylpropanoate (VIIIb). A mixture of 12 mg (0.03 mmol) of aziridine **Ib** and 2 mg (0.01 mmol) of SbF_3 in methylene chloride was heated for 3 h under reflux. The mixture was cooled and filtered from SbF_3, and the filtrate was concentrated under reduced pressure. The orange oily residue was Schiff base **VIIIb** which was sufficiently pure (~94%) for use in further synthesis. ^{1}H NMR spectrum (250 MHz), δ, ppm: 3.05 d.d (1H, CH_2, J = 13.7, 10.0 Hz), 3.28 d.d (1H, CH_2, J = 13.7, 4.0 Hz), 3.67 s (3H, CH_3O), 4.09 d.d (1H, CH, J = 10.0, 4.0 Hz), 6.70–7.60 m (15H, H_{arom}), 7.72 d (1H, CH=N, J = 10.7 Hz). ^{19}F NMR spectrum: δ_F –142.4 ppm, d (J = 10.7 Hz).

Amines Xa–Xe and XIa–XIe (*general procedure*). A mixture of 0.4 mmol of aziridine **Ia** or **Ib** and 0.4 mmol of potassium alkynyltrifluoroborate **IXa**–**IXc** in 8 ml of methylene chloride was cooled to –20°C, a solution of 0.4 mol of $BF_3 \cdot Et_2O$ in 4 ml of methylene chloride was added dropwise under stirring in a nitrogen atmosphere, and the mixture was stirred for 5 h at –20°C and hydrolyzed with 10 ml of water. The organic phase was separated, the aqueous phase was extracted with methylene chloride (3×10 ml), the extracts were combined with the organic phase, dried over Na_2SO_4, and filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane–diethyl ether as eluent.

Methyl (2*S*,1′*S*)- and (2*S*,1′*R*)-2-[1-fluoro(diphenyl)methyl-3-(3-methoxyphenyl)prop-2-yn-1-ylamino]propanoates Xa and XIa. A mixture of amines **Xa** and **XIa** at a ratio of 4.7 : 1 was obtained from 120 mg (0.4 mmol) of aziridine **Ia** and 96 mg (0.4 mmol) of compound **IXa**. Yield 75 mg (43%). Recrystallization of that mixture gave 31 mg (18%) of amine **Xa** as colorless crystals with mp 57–58°C, $[\alpha]_D^{25}$ = +12.8° (c = 1.0, CH_2Cl_2). IR spectrum (film), ν, cm^{-1}: 3340, 3328 (NH), 3058, 2967, 2938, 2835, 1721 (C=O), 1604, 1573, 1483, 1451, 1433, 1372, 1309, 1289, 1198, 1159, 1131, 1050, 970, 877, 852, 781, 757, 742, 703, 689. ^{1}H NMR spectrum (250 MHz), δ, ppm: 1.21 d (3H, CH_3C, J = 6.9 Hz), 2.1 br.s (NH), 3.53 q (1H, CH_3C**H**, J = 6.9 Hz), 3.58 s (3H, $CH_3OC_6H_4$), 3.68 s (3H, CH_3OCO), 4.50 d (1H, CFCH, J = 17.9 Hz), 6.50–6.90 m (3H, H_{arom}), 7.0–7.15 m (1H, H_{arom}), 7.15–7.35 m (6H, H_{arom}), 7.35–7.50 m (2H, H_{arom}), 7.50–7.70 m (2H, H_{arom}). ^{13}C NMR spectrum (63 MHz), δ_C, ppm: 18.5 (**C**H_3CH), 51.9 (CH_3**C**H), 55.2 (CH_3O), 55.3 (CH_3O), 57.0 d (CF**C**H, J = 26.2 Hz), 86.2 d ($C_6H_4C{\equiv}$**C**, J = 5.9 Hz), 87.0 d (C_6H_4**C**≡C, J = 0.9 Hz), 99.7 d (CF, J = 183.6 Hz), 114.7, 116.5, 123.69, 123.99, 126.3 d (J = 8.8 Hz), 126.6 d (J = 7.8 Hz), 127.9 m (6C), 129.2, 140.8 d (J = 23.0 Hz), 141.0 d (J = 22.9 Hz), 159.1, 175.4 (C=O). ^{19}F NMR spectrum: δ_F –151.8 ppm, d (J = 17.9 Hz). Found, %: C 75.27; H 6.17; N 3.28. $C_{27}H_{26}FNO_3$. Calculated, %: C 75.15; H 6.07; N 3.25. X-Ray diffraction data: $C_{27}H_{26}FNO_3$, M 431.49; triclinic crystal system, space group $P1$; unit cell parameters: a = 6.2062(3), b = 8.8691(4), c = 21.3492(11) Å; α = 92.524(4)°, β = 97.993(4)°, γ = 91.494(4)°; V = 1161.97(10) Å^3; Z = 2; T = 133(2) K; $F(000)$ = 456; d_{calc} = 1.233 mg/mm^3; R_{all} = 0.0710, wR_2 = 0.2005; total number of reflections 9920 (7046 independent reflections with R_{int} = 0.0568).

The data for compound **XIa** were derived from the spectra of its mixture with diastereoisomer **Xa**. ^{1}H NMR spectrum (250 MHz), δ, ppm: 1.24 d (3H, CH_3C, J = 7.3 Hz), 2.1 br.s (NH, **Xa** + **XIa**), 3.64 s (3H, C**H**$_3$OC_6H_4), 3.67* s (CH_3OCO), 3.83 q (1H, CH_3C**H**, J = 7.3 Hz), 4.71 d (1H, CFCH, J = 19.5 Hz). ^{13}C NMR spectrum (63 MHz), δ_C, ppm: 19.3 (**C**H_3CH), 51.8 (CH_3**C**H), 55.2* (CH_3O), 55.3* (CH_3O), 56.6 d (CF**C**H, J = 24.8 Hz), 85.6 d ($C_6H_4C{\equiv}$**C**, J = 5.0 Hz), 87.2 d (C_6H_4**C**≡C, J = 0.7 Hz), 99.7* d (CF, J = 183.6 Hz), 114.7*, 116.4* (C_{arom}), 123.68, 124.02, 126.3* d (J = 8.8 Hz), 126.5 d (J = 8.3 Hz), 127.87 d (J = 1.1 Hz), 128.06 d (J = 1.7 Hz), 128.1 d (J = 0.7 Hz), 129.2*, 140.4 d (J = 22.9 Hz), 141.1 d (J = 23.2 Hz), 159.1*, 175.5 (C=O). ^{19}F NMR spectrum: δ_F –154.7 ppm, br.s.

Methyl (2*S*,1′*S*)-2-[1-fluoro(diphenyl)methyl)-3-(3-methoxyphenyl)prop-2-yn-1-ylamino]-3-phenylpropanoate (Xb) was synthesized from 112 mg

* Hereinafter, signals from protons or carbon atoms overlapped by those of the other stereoisomer are marked with an asterisk.

(0.3 mmol) of aziridine **Ib** and 71 mg (0.3 mmol) of compound **IXa**. Yield 53 mg (35%), mp 93–94°C; $[\alpha]_D^{25}$ = +79.1° (*c* = 1.0, CH_2Cl_2). IR spectrum (film), ν, cm^{-1}: 3342 (NH), 3060, 3023, 2941, 1725 (C=O), 1603, 1573, 1479, 1451, 1434, 1288, 1199, 1162, 1040, 998, 966, 873, 779, 754, 737, 701. ^{1}H NMR spectrum (250 MHz), δ, ppm: 2.2 br.s (1H, NH), 2.78 d.d (1H, CH_2, *J* = 13.6, 8.0 Hz), 2.90 d.d (1H, CH_2, *J* = 13.6, 5.5 Hz), 3.57 s (3H, CH_3O), 3.69 d.d (1H, 2-H, *J* = 5.5, 8.0 Hz), 3.75 s (3H, CH_3O), 4.44 d (1H, CFCH, *J* = 18.5 Hz), 6.6–6.9 m (3H, H_{arom}), 7.0–7.5 m (16H, H_{arom}). ^{13}C NMR spectrum (63 MHz), δ_C, ppm: 39.9 (CH_2), 51.8 (C^2), 55.2 (CH_3O), 57.8 d (CF**C**H, *J* = 25.4 Hz), 62.2 (CH_3O), 86.3 d ($C_6H_4C{\equiv}\mathbf{C}$, *J* = 4.9 Hz), 86.9 d ($C_6H_4\mathbf{C}{\equiv}C$, *J* = 0.8 Hz), 99.7 d (CF, *J* = 183.8 Hz), 114.7, 116.4, 123.7, 124.0, 126.1 d (*J* = 8.7 Hz), 126.4, 126.5 d (*J* = 8.1 Hz), 127.8 d (2C, *J* = 1.6 Hz), 127.87 d (4C, *J* = 0.8 Hz), 128.2, 129.1, 129.4, 137.6, 140.6 d (*J* = 23.1 Hz), 141.1 d (*J* = 22.8 Hz), 159.1, 174.8 (C=O). ^{19}F NMR spectrum: δ_F –153.1 ppm, br.s. Found, %: C 78.17; H 6.00; N 2.67. $C_{33}H_{30}FNO_3$. Calculated, %: C 78.08; H 5.96; N 2.76.

Methyl (2*S*,1′*S*)- and (2*S*,1′*R*)-2-[1-fluoro(diphenyl)methyl-3-phenylprop-2-yn-1-ylamino]propanoates Xc and XIc (mixture of diastereoisomers at a ratio of 4.2:1**)** were synthesized from 120 mg (0.4 mmol) of aziridine **Ia** and 83 mg (0.4 mmol) of compound **IXb**. Yield 49 mg (30%), mp 87–88°C. IR spectrum (film), ν, cm^{-1}: 3332 (NH), 3059, 2967, 1741, 1720 (C=O), 1598, 1491, 1451, 1313, 1205, 1158, 1121, 1058, 970, 910.

Compound **Xc**. ^{1}H NMR spectrum (250 MHz), δ, ppm: 1.29 d (3H, C**H**$_3$CH, *J* = 6.9 Hz), 1.70 br.s (NH), 3.61 q (1H, $CH_3C\mathbf{H}$, *J* = 6.9 Hz), 3.65 s (3H, CH_3O), 4.58 d (1H, CFCH, *J* = 17.8 Hz), 7.10–7.70 m (15H, H_{arom}). ^{13}C NMR spectrum (63 MHz), δ_C, ppm: 19.3 (**C**H_3CH), 51.9 ($CH_3\mathbf{C}H$), 55.2 (CH_3O), 57.0 d (CF**C**H, *J* = 26.2 Hz), 86.3 d (PhC≡**C**, *J* = 5.8 Hz), 87.1 d (Ph**C**≡C, *J* = 0.9 Hz), 99.7 d (CF, *J* = 183.7 Hz), 122.7, 126.2 d (*J* = 8.8 Hz), 126.5 d (*J* = 7.8 Hz), 127.84–127.95 m (6C), 128.09, 128.15, 131.5, 140.8 d (*J* = 23.0 Hz), 140.9 d (*J* = 22.7 Hz), 175.3 (C=O). ^{19}F NMR spectrum: δ_F –151.7 ppm, d (*J* = 17.8 Hz). Found, %: C 77.85; H 6.21; N 3.36. $C_{26}H_{24}FNO_2$. Calculated, %: C 77.78; H 6.03; N 3.49.

Compound **XIc**. ^{1}H NMR spectrum (250 MHz), δ, ppm: 1.32 d (3H, C**H**$_3$CH, *J* = 7.0 Hz), 3.72 s (3H, CH_3O), 3.91 q (1H, $CH_3C\mathbf{H}$, *J* = 7.0 Hz), 4.79 d (1H, CFCH, *J* = 19.4 Hz); signals from the NH and aromatic protons were overlapped by the corresponding signals of amine **Xc**. ^{19}F NMR spectrum: δ_F –154.6 ppm, d (*J* = 19.4 Hz).

Methyl (2*S*,1′*S*)- and (2*S*,1′*R*)-2-{3-(4-ethylphenyl)-1-[fluoro(diphenyl)methyl]prop-2-yn-1-ylamino}propanoates Xd and XId (mixture of diastereoisomers at a ratio of 3.4:1**)** were synthesized from 120 mg (0.4 mmol) of aziridine **Ia** and 95 mg (0.4 mmol) of compound **IXc**. Yield 80 mg (46%). Recrystallization of the mixture gave 48 mg (28%) of isomer **Xd** as colorless crystals with mp 103–104°C; $[\alpha]_D^{25}$ = +12.4° (*c* = 0.9, CH_2Cl_2). IR spectrum (film), ν, cm^{-1}: 3332 (NH), 3059, 3027, 2967, 2928, 2864, 1719 (C=O), 1599, 1510, 1495, 1451, 1433, 1372, 1314, 1283, 1206, 1160, 1121, 1058, 970, 908, 832, 796, 741. ^{1}H NMR spectrum (250 MHz), δ, ppm: 1.19 t (3H, C**H**$_3$CH$_2$, *J* = 7.6 Hz), 1.28 d (3H, C**H**$_3$CH, *J* = 6.9 Hz), 2.17 br.s (NH), 2.60 q (2H, $CH_3C\mathbf{H}_2$, *J* = 7.6 Hz), 3.61 q (1H, $CH_3C\mathbf{H}$, *J* = 6.9 Hz), 3.64 s (3H, CH_3O), 4.56 d (1H, CFCH, *J* = 17.5 Hz), 7.06 pseudodoublet (2H, H_{arom}, *J* = 8.3 Hz), 7.15 pseudodoublet (2H, H_{arom}, *J* = 8.3 Hz), 7.20–7.40 m (6H, H_{arom}), 7.40–7.55 m (2H, H_{arom}), 7.55–7.65 m (2H, H_{arom}). ^{13}C NMR spectrum (63 MHz), δ_C, ppm: 15.32 (**C**H_3CH$_2$), 18.5 (**C**H_3CH), 28.7 ($CH_3\mathbf{C}H_2$), 51.9 ($CH_3\mathbf{C}H$), 55.2 (CH_3O), 57.0 d (CF**C**H, *J* = 26.2 Hz), 85.5 d ($C_6H_4C{\equiv}\mathbf{C}$, *J* = 6.0 Hz), 87.2 d ($C_6H_4\mathbf{C}{\equiv}C$, *J* = 0.9 Hz), 99.7 d (CF, *J* = 183.6 Hz), 119.9, 126.3 d (*J* = 8.7 Hz), 126.6 d (*J* = 7.8 Hz), 127.7, 127.87–127.94 m (6C), 131.47, 140.89 d (*J* = 23.0 Hz), 140.93 d (*J* = 23.0 Hz), 144.58, 175.4 (C=O). ^{19}F NMR spectrum: δ_F –151.3 ppm, d (*J* = 17.5 Hz). Found, %: C 78.56; H 6.62; N 3.22. $C_{28}H_{28}FNO_2$. Calculated, %: C 78.30; H 6.57; N 3.26. X-Ray diffraction data: $C_{28}H_{28}FNO_2$, *M* 429.51; monoclinic crystal system, space group $P2_1$; unit cell parameters: *a* = 8.9901(7), *b* = 6.1408(6), *c* = 21.413(2) Å; β = 93.696(7)°; *V* = 1179.65(18) $Å^3$; *Z* = 2; *T* = 133(2) K; *F*(000) = 456; d_{calc} = 1.209 mg× mm^{-3}; R_{all} = 0.1817, wR_2 = 0.1784; total number of reflections 14133 (4562 independent reflections with R_{int} = 0.1661).

The data for amine **XId** were derived from the spectra of its mixture with **Xd**. ^{1}H NMR spectrum (250 MHz), δ, ppm: 1.30 t (3H, CH_3CH_2, *J* = 7.3 Hz), the C**H**$_3$CH signal was overlapped by the C**H**$_3$CH$_2$ signal of **Xd**, 1.55 br.s (NH, **Xd** + **XId**, H_2O], 2.60* q (2H, $CH_3C\mathbf{H}_2$, *J* = 7.3 Hz), 3.72 s (3H, CH_3O), 3.91 q (1H, $CH_3C\mathbf{H}$, *J* = 7.0 Hz), 4.77* d (1H, CFCH, *J* = 19.3 Hz), ^{13}C NMR spectrum (63 MHz), δ_C, ppm: 15.33 (**C**H_3CH$_2$), 19.3 (**C**H_3CH), 28.8* ($CH_3\mathbf{C}H_2$), 51.8 ($CH_3\mathbf{C}H$), 54.0 (CH_3O), 56.7 d (CF**C**H, *J* = 24.9 Hz), 84.9 d ($C_6H_4C{\equiv}\mathbf{C}$, *J* = 5.2 Hz), 87.4 d

(C_6H_4**C**≡C, J = 0.7 Hz), 99.7 d (CF, J = 184.8 Hz), 119.9,* 126.3* (J = 8.6 Hz), 126.5 d (J = 8.2 Hz), 127.7,* 127.83 (3C), 128.01 d (J = 1.8 Hz), 128.06 (2C), 131.49, 140.5 d (J = 22.9 Hz), 141.1 d (J = 23.1 Hz), 144.61, 175.6 (C=O). ^{19}F NMR spectrum: δ_F –154.3 ppm, d (J = 19.3 Hz).

Methyl (2*S*,1′*S*)-2-{3-(4-ethylphenyl)-1-[fluoro(diphenyl)methyl]prop-2-yn-1-ylamino}-3-phenylpropanoate (Xe) was synthesized from 112 mg (0.3 mmol) of aziridine **Ib** and 71 mg (0.3 mmol) of compound **IXc**. Yield 37 mg (25%), mp 133–135°C, $[\alpha]_D^{25}$ = +80.3° (c = 1.0, CH_2Cl_2). IR spectrum (film), ν, cm^{-1}: 3350 (NH), 3059, 3024, 2971, 2931, 2863, 1725 (C=O), 1601, 1494, 1451, 1279, 1198, 1176, 1060, 998, 958, 906, 832, 796, 740, 699. ^{1}H NMR spectrum (250 MHz), δ, ppm: 1.19 t (3H, C**H**$_3$CH$_2$, J = 7.6 Hz), 2.17 br.s (NH), 2.60 q (2H, CH$_3$C**H**$_2$, J = 7.6 Hz), 2.78 d.d (1H, CH$_2$, J = 13.6, 7.9 Hz), 2.89 d.d (1H, CH$_2$, J = 13.6, 5.6 Hz), 3.57 s (3H, CH$_3$O), 3.70 m (1H, C**H**CO$_2$Me), 4.44 d (1H, CFCH, J = 17.9 Hz), 6.90–7.60 m (19H, H$_{arom}$). ^{13}C NMR spectrum (63 MHz), δ_C, ppm: 15.3 (**C**H$_3$CH$_2$), 28.7 (CH$_3$**C**H$_2$), 39.9 (**C**H$_2$Ph), 51.8 (**C**HCO$_2$Me), 57.9 d (CF**C**H, J = 25.5 Hz), 62.3 (CH$_3$O), 85.7 d (C_6H_4C≡**C**, J = 5.1 Hz), 87.1 d (C_6H_4**C**≡C, J = 0.8 Hz), 99.7 d (CF, J = 183.8 Hz), 119.9, 126.1 d (J = 8.7 Hz), 126.4, 126.5 d (J = 8.0 Hz), 127.6, 127.8 d (2C, J = 1.6 Hz), 127.9 (4C), 128.2, 129.4, 131.5, 137.7, 140.7 d (J = 23.1 Hz), 141.1 d (J = 22.8 Hz), 144.5, 174.8 (C=O). ^{19}F NMR spectrum: δ_F –152.8 ppm, d (J = 17.9 Hz). Found, %: C 80.59; H 6.46; N 2.60. $C_{34}H_{32}FNO_2$. Calculated, %: C 80.76; H 6.38; N 2.77. X-Ray diffraction data: $C_{34}H_{32}FNO_2$, M 505.61; monoclinic crystals, space group $P2_1$; unit cell parameters: a = 9.3098(7), b = 5.9421(5), c = 25.298(2) Å; β = 94.239(6)°; V = 1395.7(2) Å^3; Z = 2; T = 133(2) K; F(000) = 536; d_{calc} = 1.203 mg/mm^3; R_{all} = 0.1049, wR_2 = 0.1786; total number of reflections 11713 (5294 independent reflections with R_{int} = 0.1075).

Reaction of Schiff base VIIIa with potassium trifluoro(3-methoxyphenylethynyl)borate (IXa). A mixture of 150 mg (0.5 mmol) of aziridine **Ia** and 9 mg (0.05 mmol) of SbF_3 in 30 ml of methylene chloride was heated for 3 h under reflux. The mixture was filtered from SbF_3, the solvent was removed from the filtrate under reduced pressure, and the residue was dissolved in 10 ml of methylene chloride. Compound **IXa**, 118 mg (0.5 mmol), was added to the resulting solution of Schiff base **VIIIa**, a solution of 71 mg (0.5 mmol) of $BF_3 \cdot Et_2O$ in 1 ml of methylene chloride was then added, and the mixture was stirred for 2 h at room temperature and hydrolyzed with 15 ml of water. The organic phase was separated, the aqueous phase was extracted with methylene chloride (3×6 ml), the extracts were combined with the organic phase, dried over Na_2SO_4, and filtered, the solvent was removed under reduced pressure, and the residue was subjected to flash chromatography on silica gel using hexane–diethyl ether as eluent to isolate 37 mg (17%) of a 6.2:1.0 mixture of diastereoisomeric compounds **Xa** and **XIa** and 37 mg (26%) of indole **XII**.

Methyl (*S*)-2-(3-phenyl-1*H*-indol-1-yl)propanoate (XII). Yellow oily substance. IR spectrum (film), ν, cm^{-1}: 3028, 2950, 1739 (C=O), 1601, 1549, 1461, 1397, 1372, 1305, 1197, 1173, 1099, 1049, 961, 910, 851, 767, 740, 698, 694. ^{1}H NMR spectrum (250 MHz), δ, ppm: 1.86 d (3H, CH$_3$C, J = 7.3 Hz), 3.72 s (CH$_3$O), 5.20 q (1H, CH$_3$C**H**, J = 7.3 Hz), 7.10–7.50 m (7H, H$_{arom}$), 7.60–7.75 m (2H, H$_{arom}$), 7.90–8.00 m (1H, H$_{arom}$). ^{13}C NMR spectrum (63 MHz), δ_C, ppm: 17.6 (**C**H$_3$C), 52.6 (CH$_3$O), 53.5 (CHN), 109.4, 118.1, 120.1, 120.4, 122.3, 122.8, 125.9, 126.4, 127.5, 128.7, 135.3, 136.9, 171.6 (C=O). Mass spectrum, m/z (I_{rel}, %): 281 (16) $[M + 2]^+$, 280 (100) $[M + 1]^+$.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 08-03-00 112) and by the Government of Flanders (Program for Bilateral Collaboration, grant no. 05-03-34811). A.S. Konev is grateful to the St. Petersburg Authorities for financial support.

REFERENCES

1. Dowson, J.H., *J. Neural Transm*., 1987, vol. 23, p. 121.
2. Krishnan, K.R.R., *The American Psychiatric Press Textbook of Psychopharmacology*, Schatzberg, A.F. and Nemeroff, C.B., Eds., Washington, DC: Americal Psychiatric, 1998, 2nd. ed., p. 239.
3. Nies, A. and Robinson, D.S., *Monoamine Oxidase Inhibitors: The State of the Art*, Youdim, M.B.H. and Paykel, E.S., Eds., Chichester: Wiley, 1981, p. 141.
4. Tyrer, P., Gardner, M., Lambourn, J., and Whitford, M., *Monoamine Oxidase Inhibitors: The State of the Art*, Youdim, M.B.H. and Paykel, E.S., Eds., Chichester: Wiley, 1981, p. 149.
5. Baker, G.B., Urichuk, L.J., McKenna, K.F., and Kennedy, S.H., *Cell. Mol. Neurobiol*., 1999, vol. 19, p. 411.
6. Knoll, J., Ecsery, Z., Nievel, J.B., Kelemen, K., and Knoll, B., *Arch. Int. Pharmacodyn. Ther*., 1965, vol. 155, p. 154.
7. Knoll, J., *Monoamine Oxidase: Structure, Function, and Altered Functions*, Singer, T.P., Von Korff, R.W., and Murphy, D.L., Eds., New York: Academic, 1979, p. 431.

8. Ling, L., Urichuk, L.J., Duff Sloley, B., Coutts, R.T., Baker, G.B., Shan, J.J., and Pang, P.K.T., *Bioorg. Med. Chem. Lett*., 2001, vol. 11, p. 2715.
9. D'hooghe, M., Van Brabandt, W., and De Kimpe, N., *J. Org. Chem*., 2004, vol. 69, p. 2703.
10. Salvador, R., Simon, D.Z., and Leonard, L., WO Patent no. 9320804, 1993; *Chem. Abstr*., 1994, vol. 120, no. 216929.
11. Porco, J.A., Jr., Schoenen, F.J., Stout, T.J., Clardy, J., and Schreiber, S.L., *J. Am. Chem. Soc*., 1990, vol. 112, p. 7410.
12. Murai, T., Mutoh, Y., Ohta, Y., and Murakami, M., *J. Am. Chem. Soc*., 2004, vol. 126, p. 5968.
13. Magueur, G., Crousse, B., and Bonnet-Delpon, D., *Tetrahedron Lett*., 2005, vol. 46, p. 2219.
14. Trost, B.M. and Chen, S.-F., *J. Am. Chem. Soc*., 1986, vol. 108, p. 6053.
15. Clive, D.L.J., Cole, D.C., and Tao, Y., *J. Org. Chem*., 1994, vol. 59, p. 1396.
16. Osipov, S.N., Tsouker, P., Hennig, L., and Burger, K., *Tetrahedron*, 2004, vol. 60, p. 271.
17. Semeril, D., Le Notre, J., Bruneau, C., Dixneuf, P., Kolomiets, A.F., and Osipov, S.N., *New J. Chem*., 2001, vol. 25, p. 16.
18. Moroni, M., Koksch, B., Osipov, S.N., Crucianelli, M., Frigerio, M., Bravo, P., and Burger, K., *J. Org. Chem*., 2001, vol. 66, p. 130.
19. Díez, R., Badorrey, R., Díaz-de-Villegas, M.D., and Gálvez, J.A., *Eur. J. Org. Chem*., 2007, p. 2114.
20. Aschwanden, P., Stephenson, C.R.J., and Carreira, E.M., *Org. Lett*., 2006, vol. 8, p. 2437.
21. Bisai, A. and Singh, V.K., *Org. Lett*., 2006, vol. 8, p. 2405.
22. Lo, V.K.-Y., Liu, Y., Wong, M.-K., and Che, C.-M., *Org. Lett*., 2006, vol. 8, p. 1529.
23. Gommermann, N., Koradin, C., Polborn, K., and Knochel, P., *Angew. Chem., Int. Ed*., 2003, vol. 42, p. 5763.
24. Koradin, C., Polborn, K., and Knochel, P., *Angew. Chem., Int. Ed*., 2002, vol. 41, p. 2535.
25. Wei, C. and Li, C.-J., *J. Am. Chem. Soc*., 2002, vol. 124, p. 5638.
26. Caner, H., Groner, E., Levy, L., and Agranat, I., *Drug Discov. Today*, 2004, vol. 4, p. 313.
27. Shimazawa, R., Nagai, N., Toyoshima, S., and Okuda, H., *J. Health Sci*., 2008, vol. 54, p. 23.
28. *Chiral Drugs*, Challener, C.A., Ed., Aldershot, Hampshire, England: Ashgate, 2001.
29. *Chirality in Drug Research*, Francotte, E. and Lindner, W., Eds., Weinheim: Wiley, 2006.
30. *Chirality in Drug Design and Development*, Reddy, I.K. and Mehyar, R., Eds., New York: Marcel Dekker, 2004.
31. Konev, A.S., Stas, S., Novikov, M.S., Khlebnikov, A.F., and Abbaspour Tehrani, K., *Tetrahedron*, 2008, vol. 64, p. 117.
32. Mengel, A. and Reiser, O., *Chem. Rev*., 1999, vol. 99, p. 1191.
33. Konev, A.S., Novikov, M.S., and Khlebnikov, A.F., *Tetrahedron Lett*., 2005, vol. 46, p. 8337.
34. Konev, A.S., Novikov, M.S., and Khlebnikov, A.F., *Russ. J. Org. Chem*., 2007, vol. 43, p. 286.
35. Kostikov, R.R., Khlebnikov, A.F., and Oglobin, K.A., *Dokl. Akad. Nauk SSSR*, 1975, vol. 223, p. 1375.
36. Yamanaka, H., Kikui, J., Teramura, K., and Ando, T., *J. Org. Chem*., 1976, vol. 41, p. 3794.
37. Verniest, G., Colpaert, F., Van Hende, E., and De Kimpe, N., *J. Org. Chem*., 2007, vol. 72, p. 8569.
38. Van Hende, E., Verniest, G., Surmont, R., and De Kimpe, N., *Org. Lett*., 2007, vol. 9, p. 2935.
39. O'Donnell, M.J. and Polt, R.L., *J. Org. Chem*., 1982, vol. 47, p. 2663.
40. Polt, R., Peterson, M.A., and DeYoung, L., *J. Org. Chem*., 1992, vol. 57, p. 5469.
41. Singh, G.S., D'hooghe, M., and De Kimpe, N., *Chem. Rev*., 2007, vol. 107, p. 2080.
42. Konev, A.S. and Khlebnikov, A.F., *Collect. Czech. Chem. Commun*., 2008, vol. 73, p. 1553.
43. Davis, F.A. and Deng, J., *Org. Lett*., 2007, vol. 9, p. 1707.
44. Ziegler, F.E. and Belema, M., *J. Org. Chem*., 1997, vol. 62, p. 1083.
45. Konev, A.S., Novikov, M.S., Khlebnikov, A.F., and Abbaspour Tehrani, K., *J. Fluorine Chem*., 2007, vol. 128, p. 114.
46. Purrington, S.T., Lazaridis, N.V., and Bumgardner, C.L., *Tetrahedron Lett*., 1986, vol. 27, p. 2715.
47. Seyferth, D. and Hopper, S.P., *J. Organomet. Chem*., 1973, vol. 51, p. 77.
48. Molander, G.A., Katona, B.W., and Machrouchi, F., *J. Org. Chem*., 2002, vol. 67, p. 8416.
49. Stas, S. and Abbaspour Tehrani, K., *Tetrahedron*, 2007, vol. 63, p. 8921.
50. Novikov, M.S., Khlebnikov, A.F., Sidorina, E.S., and Kostikov, R.R., *J. Chem. Soc., Perkin Trans. 1*, 2000, p. 231.