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Dedicated to Full Member of the Russian Academy of Sciences M.G. Voronkov on his 90th anniversary

Condensation of 2- and 4- Fluorobenzaldehydes with Vinyl Ethers Derived from Amino Alcohols

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Abstract—2- and 4-Fluorobenzaldehydes reacted with amino alcohol vinyl ethers to give Schiff bases, oxazolidines, and imidazolidines containing a vinyloxy group. The products attract interest as potential biologically active compounds.

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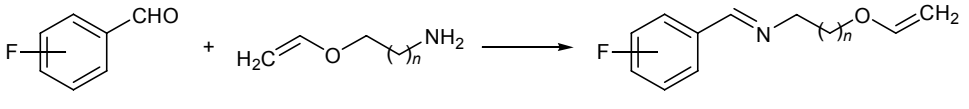
Condensation products of carbonyl compounds with vinyl ethers derived from amino alcohols possess diverse biological activity [1]; biological activity is also intrinsic to organofluorine compounds [2]. Therefore, fluorine-containing carbonyl compounds and amino alcohol vinyl ethers could give rise to biologically active compounds. Aimakov et al. [3] previously reported on the condensation of 4-fluorobenzaldehyde with 2-vinyloxyethanamine [3].

In the present work we examined condensation of 2- and 4-fluorobenzaldehydes **Ia** and **Ib** with various amino alcohol vinyl ethers. The reactions were carried out by keeping equimolar mixtures of the reactants in diethyl ether in the presence of anhydrous potassium carbonate at room temperature over a period of 20 h. The reaction of aldehydes **Ia** and **Ib** with vinyloxyalkanamines **IIa** and **IIb** gave 82–87% of Schiff bases **IIIa**–**IIId** (Scheme 1). The ^{1}H and ^{13}C NMR spectra of compounds **IIIa**–**IIId** contained only one signal from the N=CH proton and carbon atom (δ 8.26–8.64 ppm, δ_C 154.78–161.49 ppm), indicating formation of a single isomer. By analogy with known aliphatic imines [4], Schiff bases **IIIa**–**IIId** were assigned *E* configuration at the double C=N bond.

In the condensation of aldehydes **Ia** and **Ib** with 1-amino-3-(2-vinyloxyethoxy)propan-2-ol (**IV**) containing a hydroxy group in the β-position with respect to primary amino group, Schiff bases **Va** and **Vb** were formed together with stereoisomeric oxazolidines **VIa**, **VIb** and **VIIa**, **VIIb** (Scheme 2). The overall yield of the condensation products was 75–78%.

All condensation products displayed in the IR spectra strong absorption bands in the regions 1641–1647 (C=N) and 1042–1295 cm^{-1} (O–C–N in the oxazolidine ring) [5]. In the ^{1}H NMR spectrum of product mixture **Va**/**VIa**/**VIIa** we observed one signal from N=CH proton (δ 8.62 ppm) and two signals from NCHO protons (δ 5.80 and 5.63 ppm) with an intensity ratio of 1.0:0.08:0.1. The corresponding signals in the ^{1}H NMR spectrum of mixture **Vb**/**VIb**/**VIIb** were located at δ 8.27, 5.66, and 5.34 ppm, and their intensity ratio was 1.0:0.05:0.08. Our results are consistent with the known data according to which tautomeric equilibrium imino alcohol–oxazolidine for imino alco-

Scheme 1.

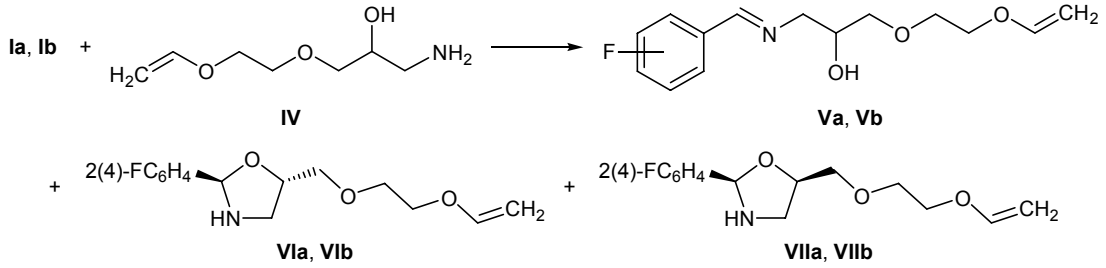


Ia, **Ib** **IIa**, **IIb** **IIIa**–**IIId**

I, 2-F (**a**), 4-F (**b**); **II**, *n* = 1 (**a**), 2 (**b**); **III**, 2-F, *n* = 1 (**a**), 2 (**b**); 4-F, *n* = 1 (**c**), 2 (**d**).

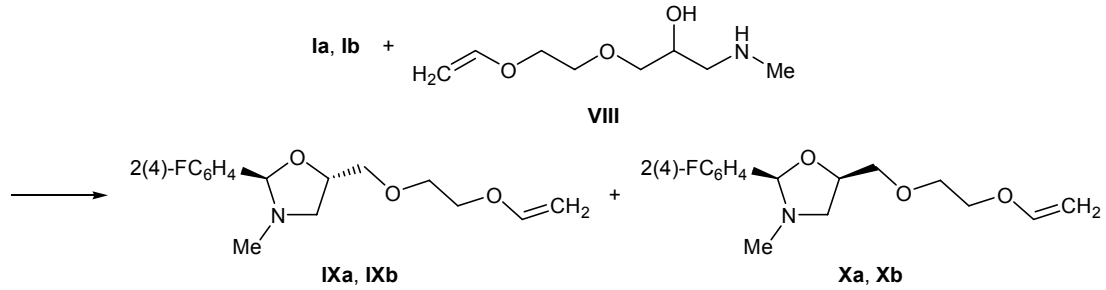
† Deceased.

Scheme 2.



2-F (**a**), 4-F (**b**).

Scheme 3.



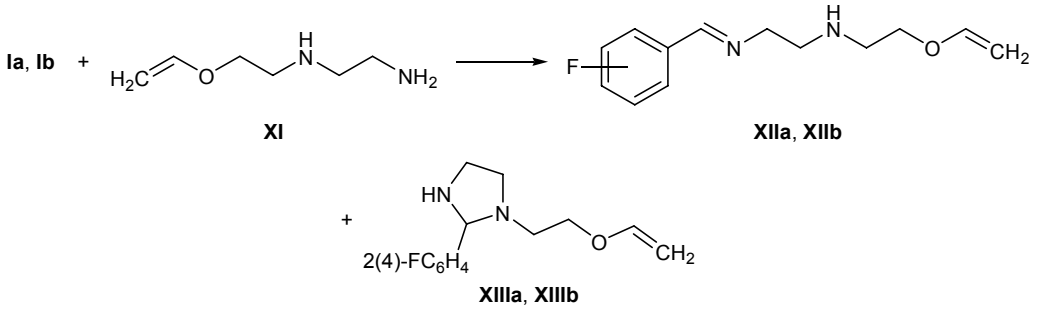
2-F (**a**), 4-F (**b**).

hols obtained from amino alcohols and aromatic aldehydes is usually displaced toward the open-chain structure [6]. Furthermore, it was reported that *N*-aryl-1,3-oxazolidines containing a substituent in the *5*-position exist mainly as *cis* isomers [7]. Therefore, more upfield signals from the NCHO protons were assigned to *cis* isomers **VIIa** and **VIIb**.

The structure of compounds **Va**, **Vb**, **VIa**, **VIb**, **VIIa**, and **VIIb** was also confirmed by the ^{13}C NMR spectra which contained the following signals: 156.45 d (C=N, $^{3}J_{CF}$ = 4.6 Hz, **Va**), 88.16 d (OCHN, $^{3}J_{CF}$ = 3.4 Hz, **VIIa**), 88.25 d (OCHN, $^{3}J_{CF}$ = 2.0 Hz, **VIa**), 161.64 (C=N, **Vb**), 92.15 (OCHN, **VIIb**), 93.16 (OCHN, **VIb**). The OCHN signals were assigned to *trans* and *cis* isomers on the basis of their intensities. Chemical shifts of some protons and carbon nuclei in oxazolidines **VI** and **VII** were not determined because of overlap of the corresponding signals by stronger signals of Schiff bases **V**.

Replacement of the primary amino group in amino alcohol **IV** by secondary amino group makes the formation of Schiff bases impossible. Therefore, the condensation of 1-methylamino-3-(2-vinyloxyethoxy)-propan-2-ol (**VIII**) with aldehydes **Ia** and **Ib** gave mixtures of *trans*/*cis*-isomeric oxazolidines **IXa**/**Xa** and **IXb**/**Xb** in an overall yield of 67–69% (Scheme 3). The formation of two stereoisomers in each case follows from the presence in the ^{1}H and ^{13}C NMR spectra of signals from the OCHN proton and carbon atom of each stereoisomer, δ, δ_C, ppm: **IXa**, 5.06,

Scheme 4.



2-F (**a**), 4-F (**b**).

91.63; **Xa**, 5.10, 91.08; **IXb**, 4.62, 98.07; **Xb**, 4.57, 97.47. Also, well resolved multiplets belonging to the 5-H proton were observed. The chemical shifts of the OC^{5}H proton and carbon nucleus were as follows, δ, δ_C, ppm: **IXa**, 4.33–4.38, 74.90; **Xa**, 4.48–4.54, 76.07; **IXb**, 4.44–4.51, 74.64; **Xb**, 4.29–4.35, 75.78. Signals from all other protons of both stereoisomers were partially or completely overlapped by each other. Therefore, the ratio of stereoisomers was estimated from the intensity of the OCH and NCHO protons; it was 1:0.92 for **Xa**/**IXa** and 1:0.91 for **Xb**/**IXb**. All proton and carbon signals were assigned assuming predominant formation of the *cis* isomer (see above).

By condensation of fluorobenzaldehydes **Ia** and **Ib** with *N*-(2-vinyloxyethyl)ethane-1,2-diamine (**XI**) we obtained mixtures of products containing Schiff bases **XIIa**, **XIIb** and imidazolidines **XIIIa**, **XIIIb** (Scheme 4). The presence of Schiff bases **XIIa** and **XIIb** in the product mixtures was confirmed by IR absorption bands at 1640–1646 cm^{-1} (ν C=N). The ^{1}H and ^{13}C NMR spectra of compounds **XII** and **XIII** contained signals from proton and carbon nucleus in the N=CH (δ 8.30–8.60, δ_C 155.44–155.86 ppm) or NCHN group (δ 4.10–4.65, δ_C 76.26–82.79 ppm). The product ratio was 0.92:1 (**XIIa**/**XIIIa**) and 1.15:1 (**XIIb**/**XIIIb**). Appreciable difference in the ratio of the linear and cyclic condensation products of 2- and 4-fluorobenzaldehydes is likely to be related to different electrophilicities of the C=N carbon atom (due to the presence of a fluorophenyl substituent), which is known to considerably affect the formation of cyclic structure [8].

In the ^{1}H NMR spectra of all compounds synthesized in this work, signals from protons in the vinyloxy group appeared as three doublets of doublets at δ 3.95–3.99 (*cis*-CH=C), 4.12–4.18 (*trans*-CH=C), and 6.42–6.47 ppm (OCH=C); ^2J = 1.7–1.9, $^3J_{cis}$ = 6.2–6.8, $^3J_{trans}$ = 14.0–14.3 Hz; the ^{13}C NMR spectra contained signals at δ_C 86.38–86.55 (=CH) and 151.49–151.63 ppm (OCH=).

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded at 26°C on a Bruker DPX-400 spectrometer at 400.13 and 100.62 MHz, respectively, using $CDCl_3$ as solvent and hexamethyldisiloxane as internal reference. The IR spectra were obtained on a Bruker Vertex-70 spectrometer from thin films.

Condensation of 2- and 4-fluorobenzaldehydes Ia and Ib with amino alcohol vinyl ethers IIa, IIb, IV, VIII, and XI (*general procedure*). A mixture of 0.05 mol of fluorobenzaldehyde **Ia** or **Ib** and 0.11 mol of amine **IIa**, **IIb**, **IV**, **VIII**, or **XI** in 50 ml of diethyl ether was kept for 20 h over anhydrous potassium carbonate. The solvent was distilled off, and the residue was subjected to fractional distillation under reduced pressure.

***N*-[(*E*)-(2-Fluorophenyl)methylidene]-2-(vinyloxy)ethanamine (IIIa).** Yield 86%, bp 82–83°C (3 mm), n_D^{20} = 1.5263. IR spectrum, ν, cm^{-1}: 3117, 3083, 3044, 2929, 2896, 2850, 2759, 1644, 1615, 1583, 1485, 1459, 1386, 1371, 1344, 1321, 1300, 1280, 1233, 1200, 1152, 1100, 1085, 1032, 1005, 984, 962, 912, 863, 817, 802, 760, 702, 621, 537, 460. ^{1}H NMR spectrum, δ, ppm: 3.92 t (2H, NCH_2, ^3J = 5.3 Hz), 3.99–4.05 m (3H, CH_2O, *cis*-CH_2=), 4.24 d.d (1H, *trans*-CH_2=, ^2J = 1.7, $^3J_{trans}$ = 14.4 Hz), 6.49 d.d (1H, =CHO, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.4 Hz), 7.06–7.11 m (5′-H), 7.16–7.20 m (3′-H), 7.38–7.43 m (4′-H), 7.97–8.01 m (6′-H), 8.64 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 60.55 s (CH_2N), 67.28 s (CH_2O), 86.72 s (=CH_2), 115.69 d (C$^{3'}$, $^2J_{CF}$ = 21.5 Hz), 123.68 d (C$^{1'}$, $^2J_{CF}$ = 9.2 Hz), 124.26 d (C$^{5'}$, $^4J_{CF}$ = 3.45 Hz), 127.79 d (C$^{6'}$, $^3J_{CF}$ = 2.7 Hz), 132.28 d (C$^{4'}$, $^3J_{CF}$ = 8.8 Hz), 151.73 s (OCH=), 156.40 d (C=N, $^3J_{CF}$ = 4.6 Hz), 162.24 d (C$^{2'}$, $^1J_{CF}$ = 252.3 Hz). Found, %: C 68.46; H 6.22; F 9.71; N 7.29. $C_{11}H_{12}FNO$. Calculated, %: C 68.38; H 6.26; F 9.83; N 7.25.

***N*-[(*E*)-(2-Fluorophenyl)methylidene]-3-(vinyloxy)propan-1-amine (IIIb).** Yield 87%, bp 105–110°C (4 mm), n_D^{20} = 1.5192. IR spectrum, ν, cm^{-1}: 3117, 3083, 3044, 2937, 2891, 2846, 2759, 1642, 1615, 1582, 1485, 1459, 1380, 1341, 1321, 1300, 1280, 1234, 1197, 1152, 1099, 1075, 1029, 1006, 991, 967, 919, 887, 854, 808, 760, 701, 635, 621, 562, 537, 496. ^{1}H NMR spectrum, δ, ppm: 2.06 q (2H, $CH_2C\mathbf{H}_2CH_2$, ^3J = 6.6 Hz), 3.76 d.t (2H, NCH_2, ^3J = 6.6, ^4J = 1.1 Hz), 3.81 t (2H, CH_2O, ^3J = 6.6 Hz), 4.00 d.d (1H, *cis*-CH_2=, ^2J = 1.9, $^3J_{cis}$ = 6.7 Hz), 4.21 d.d (1H, *trans*-CH_2=, ^2J = 1.9, $^3J_{trans}$ = 14.3 Hz), 6.46 d.d (1H, =CHO, $^3J_{cis}$ = 6.7, $^3J_{trans}$ = 14.3 Hz), 7.06–7.11 m (5′-H), 7.16–7.20 m (3′-H), 7.37–7.43 m (4′-H), 7.95–8.00 m (6′-H), 8.59 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 30.22 s (CH_2), 58.12 s (CH_2N), 65.51 s (CH_2O), 86.42 s (=CH_2), 115.66 d (C$^{3'}$, $^2J_{CF}$ = 21.1 Hz), 123.80 d (C$^{1'}$, $^2J_{CF}$ = 9.2 Hz), 124.22 d (C$^{5'}$, $^4J_{CF}$ = 2.7 Hz), 127.63 d (C$^{6'}$, $^3J_{CF}$ = 2.7 Hz), 132.03 d (C$^{4'}$, $^3J_{CF}$ = 8.4 Hz), 151.76 s (OCH=), 154.78 d (C=N, $^3J_{CF}$ = 4.6 Hz), 162.12 d (C$^{2'}$, $^1J_{CF}$ = 252.3 Hz). Found, %: C 69.50; H 6.86; F 9.10;

N 6.72. $C_{12}H_{14}FNO$. Calculated, %: C 69.55; H 6.81; F 9.17; N 6.76.

***N*-[(*E*)-(4-Fluorophenyl)methylidene]-2-(vinyloxy)ethanamine (IIIc).** Yield 83%, bp 88–90°C (2 mm), n_D^{20} = 1.5242; published data [3]: bp 118–120°C (2.5 mm), n_D^{20} = 1.5270. IR spectrum, ν, cm^{-1}: 3117, 3073, 3056, 3041, 2930, 2875, 2849, 1654, 1647, 1617, 1602, 1509, 1475, 1460, 1441, 1416, 1386, 1370, 1342, 1322, 1295, 1231, 1199, 1152, 1094, 1084, 1035, 1004, 1012, 984, 964, 936, 912, 864, 837, 821, 787, 713, 702, 636, 608, 599, 578, 532, 521, 508, 420. ^{1}H NMR spectrum, δ, ppm: 3.87 t (2H, NCH_2, ^3J = 5.4 Hz), 3.97–4.04 m (3H, CH_2O, *cis*-CH_2=), 4.23 d.d (1H, *trans*-CH_2, ^2J = 2.0, $^3J_{trans}$ = 14.4 Hz), 6.48 d.d (1H, =CHO, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.4 Hz), 7.10 t (2H, 3′-H, 5′-H, J = 8.6 Hz), 7.70–7.79 m (2H, 2′-H, 6′-H), 8.29 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 60.06 s (CH_2N), 67.28 s (CH_2O), 86.66 s (=CH_2), 115.57 d ($C^{3'}$, $C^{5'}$, $^2J_{CF}$ = 21.9 Hz), 130.03 ($C^{2'}$, $C^{6'}$, $^3J_{CF}$ = 8.4 Hz), 132.29 d ($C^{1'}$, $^4J_{CF}$ = 2.3 Hz), 151.67 s (OCH=), 161.49 s (C=N), 162.26 d ($C^{4'}$, $^1J_{CF}$ = 250.7 Hz). Found, %: C 68.43; H 6.20; F 9.77; N 7.22. $C_{11}H_{12}FNO$. Calculated, %: C 68.38; H 6.26; F 9.83; N 7.25.

***N*-[(*E*)-(4-Fluorophenyl)methylidene]-3-(vinyloxy)propan-1-amine (IIId).** Yield 82%, bp 113–115°C (2 mm), n_D^{20} = 1.5177. IR spectrum, ν, cm^{-1}: 3117, 3073, 3041, 2949, 2932, 2874, 2845, 1649, 1616, 1509, 1471, 1457, 1416, 1379, 1339, 1321, 1295, 1231, 1196, 1152, 1093, 1075, 1026, 1011, 992, 971, 923, 888, 860, 835, 822, 797, 713, 702, 636, 619, 600, 577, 523, 514, 386. ^{1}H NMR spectrum, δ, ppm: 2.07 q (3H, CH_2, ^3J = 6.6 Hz), 3.71 t.d (2H, NCH_2, ^3J = 6.6, ^4J = 0.7 Hz), 3.79 t (2H, CH_2O, ^3J = 6.6 Hz), 3.99 d.d (1H, *cis*-CH_2=, ^2J = 1.8, $^3J_{cis}$ = 6.7 Hz), 4.20 d.d (1H, *trans*-CH_2=, ^2J = 1.8, $^3J_{trans}$ = 14.4 Hz), 6.48 d.d (1H, =CHO, $^3J_{cis}$ = 6.7, $^3J_{trans}$ = 14.4 Hz), 7.09 t (2H, 3′-H, 5′-H, ^3J = 8.6 Hz), 7.68–7.76 m (2H, 2′-H, 5′-H), 8.26 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 30.15 s (CH_2), 57.55 s (CH_2N), 65.40 s (CH_2O), 86.36 s (=CH_2), 115.50 d ($C^{3'}$, $C^{5'}$, $^2J_{CF}$ = 21.9 Hz), 129.80 d ($C^{2'}$, $C^{6'}$, $^3J_{CF}$ = 8.8 Hz), 151.69 s (OCH=), 132.45 d ($C^{1'}$, $^4J_{CF}$ = 2.3 Hz), 159.88 s (C=N), 164.11 d ($C^{4'}$, $^1J_{CF}$ = 250.3 Hz). Found, %: C 69.60; H 6.78; F 9.09; N 6.80. $C_{12}H_{14}FNO$. Calculated, %: C 69.55; H 6.81; F 9.17; N 6.76.

1-[(*E*)-(2-Fluorophenyl)methylideneamino]-3-[2-(vinyloxy)ethoxy]propan-2-ol (Va) and 2-(2-fluorophenyl)-5-[2-(vinyloxy)ethoxymethyl]-1,3-oxazolidines VIa and VIIa (*mixture of isomers*). Yield 75%, bp 162–165°C (2 mm), n_D^{20} = 1.5268. IR spectrum, ν, cm^{-1}: 3422, 3117, 3083, 3044, 2919, 2895, 1641, 1614, 1583, 1485, 1459, 1381, 1361, 1322, 1300, 1279, 1234, 1202, 1136, 1100, 1042, 967, 842, 822, 807, 762, 723, 680, 632, 537, 507, 468. ^{1}H NMR spectrum, δ, ppm: **Va**: 2.95 br.s (1H, OH), 3.55–3.86 m (8H, NCH_2, CH_2O), 4.00 d.d (1H, *cis*-CH_2=, ^2J = 2.1, $^3J_{cis}$ = 6.7 Hz), 4.08–4.15 m (1H, C**H**OH), 4.19 d.d (1H, *trans*-CH_2=, ^2J = 2.1, $^3J_{trans}$ = 14.3 Hz), 6.47 d.d (1H, =CHO, $^3J_{cis}$ = 6.7, $^3J_{trans}$ = 14.3 Hz), 7.05 m (1H, 5′-H), 7.15 t (1H, 3′-H, ^3J = 7.6 Hz), 7.36–7.42 m (1H, 4′-H), 7.95 d.t (1H, 6′-H, ^4J = 1.7, ^3J = 7.5 Hz), 8.62 s (1H, CH=N); **VIa**/**VIIa**: 2.14 s (2H, NH), 3.05–3.80 m (8H, NCH_2, CH_2O), 3.98–4.01 m (2H, *cis*-CH_2=), 4.09–4.18 m (4H, *trans*-CH_2=, NCH_2C**H**O), 5.63 s and 5.80 s (1H each, NCHO), 6.46 m (2H, =CHO); 7.02–7.27 m, 7.49 t, 7.55–7.65 m, 7.85 t (8H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: **Va**: 63.98 s (NCH_2), 67.40 s (=CHO**C**H_2), 69.93 (=CHOCH$_2$**C**H_2), 70.14 s (OCH), 73.65 s (OCH**C**H_2O), 86.90 s (=CH_2), 115.84 d ($C^{3'}$, $^2J_{CF}$ = 21.1 Hz), 124.36 d ($C^{1'}$, $^2J_{CF}$ = 3.4 Hz), 127.80 d ($C^{5'}$, $^4J_{CF}$ = 2.3 Hz), 130.18 d ($C^{6'}$, $^3J_{CF}$ = 4.5 Hz), 132.44 d ($C^{4'}$, $^3J_{CF}$ = 8.8 Hz), 151.82 s (OCH=), 156.45 d (C=N, $^3J_{CF}$ = 4.6 Hz), 163.33 ($C^{2'}$, $^1J_{CF}$ = 252.3 Hz); **VIa**/**VIIa**: 49.26 s and 49.84 s (NCH_2), 67.04 s and 67.24 s (=CHO**C**H_2), 69.94 s and 70.02 s (=CHOCH$_2$**C**H_2), 73.19 s and 73.54 s (5-CH_2), 75.02 s and 75.80 s (C^5), 86.68 s and 86.86 s (=CH_2), 88.16 d (C^2, $^3J_{CF}$ = 3.4 Hz), 88.25 d (C^2, $^3J_{CF}$ = 2.0 Hz), 115.52 d and 116.58 d ($C^{3'}$, $^2J_{CF}$ = 21.1 Hz), 124.04 d ($C^{5'}$, $^4J_{CF}$ = 3.5 Hz), 124.24 d ($C^{5'}$, $^4J_{CF}$ = 3.5 Hz), 160.63 d ($C^{2'}$, $^1J_{CF}$ = 248.0 Hz), 160.71 d ($C^{2'}$, $^1J_{CF}$ = 248.4 Hz). Found, %: C 62.83; H 6.89; F 7.18; N 5.12. $C_{14}H_{18}FNO_3$. Calculated, %: C 62.91; H 6.79; F 7.11; N 5.24.

1-[(*E*)-(4-Fluorophenyl)methylideneamino]-3-[2-(vinyloxy)ethoxy]propan-2-ol (Vb) and 2-(4-fluorophenyl)-5-[2-(vinyloxy)ethoxymethyl]-1,3-oxazolidines VIb and VIIb (*mixture of isomers*). Yield 78%, bp 160–162°C (2 mm), n_D^{20} = 1.5253. IR spectrum, ν, cm^{-1}: 3423, 3117, 3073, 2921, 2876, 1647, 1619, 1510, 1453, 1417, 1377, 1360, 1322, 1295, 1231, 1153, 1136, 1094, 1042, 974, 867, 836, 789, 714, 680, 637, 607, 575, 519. ^{1}H NMR spectrum, δ, ppm: **Vb**: 2.63 br.s (1H, OH), 3.54–3.86 m (8H, NCH_2, CH_2O), 4.00 d.d (1H, *cis*-CH_2=, ^2J = 2.1, $^3J_{cis}$ = 6.8 Hz), 4.07–4.12 m (1H, C**H**OH), 4.18 d.d (1H, *trans*-CH_2=, ^2J = 2.1, $^3J_{trans}$ = 14.3 Hz), 6.47 d.d (1H, =CHO, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.3 Hz), 7.07 t (2H, 3′-H, 5′-H, ^3J = 8.6 Hz), 7.69–7.73 m (1H, 2′-H, 6′-H), 8.27 s (1H, CH=N); **VIb**/**VIIb**: 2.63 br.s (2H, NH), 2.96–3.81 m (8H,

NCH_2, CH_2O), 3.99 d.d (2H, *cis*-CH_2=, ^2J = 2.2 Hz), 4.11–4.13 m (2H, 5-H), 4.15 d.d (2H, *trans*-CH_2=, ^2J = 2.2 Hz), 5.34 s and 5.56 s (1H each, 2-H), 6.41–6.51 m (2H, =CHO); 6.98–7.05 m, 7.42–7.52 m, 7.63–7.68 m (8H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: **Vb**: 63.46 s (NCH_2), 67.33 s and 69.89 s (=CHO**C**H_2), 70.09 s (OCH), 73.59 s (5-CH_2), 86.87 s (=CH_2), 115.70 d ($C^{3'}$, $C^{5'}$, $^2J_{CF}$ = 21.8 Hz), 130.13 ($C^{2'}$, $C^{6'}$, $^3J_{CF}$ = 8.4 Hz), 132.32 d ($C^{1'}$, $^3J_{CF}$ = 2.6 Hz), 151.78 s (OCH=), 161.64 s (C=N), 165.40 d ($C^{4'}$, $^1J_{CF}$ = 251.1 Hz); **VIb**/**VIIb**: 48.95 s and 49.69 s (NCH_2), 63.13 s and 63.18 s (=CHO**C**H_2), 67.39 s (5-CH_2), 69.98 s and 70.72 s (=CHOCH_2**C**H_2), 73.19 s and 73.67 s (5-CH_2), 75.23 s and 75.61 s (C^5), 86.33 s and 86.51 s (=CH_2), 92.15 s and 93.16 s (C^2), 115.14 d ($C^{3'}$, $C^{5'}$, $^2J_{CF}$ = 21.2 Hz), 115.22 d ($C^{3'}$, $C^{5'}$, $^2J_{CF}$ = 21.5 Hz), 127.98 d ($C^{2'}$, $C^{6'}$, $^3J_{CF}$ = 8.1 Hz), 128.25 d ($C^{2'}$, $C^{6'}$, $^3J_{CF}$ = 8.4 Hz), 163.49 d ($C^{4'}$, $^1J_{CF}$ = 246.7 Hz), 163.51 d ($C^{4'}$, $^1J_{CF}$ = 246.9 Hz). Found, %: C 62.80; H 6.75; F 7.06; N 5.27. $C_{14}H_{18}FNO_3$. Calculated, %: C 62.91; H 6.79; F 7.11; N 5.24.

2-(2-Fluorophenyl)-3-methyl-5-[2-(vinyloxy)-ethoxymethyl]-1,3-oxazolidines IXa and Xa (*mixture of stereoisomers***).** Yield 67%, bp 142–144°C (2 mm), n_D^{20} = 1.5032. IR spectrum, ν, cm^{-1}: 3117, 3069, 3049, 3021, 2926, 2873, 2807, 2739, 1636, 1618, 1590, 1491, 1457, 1422, 1392, 1365, 1339, 1322, 1297, 1276, 1235, 1203, 1181, 1169, 1133, 1099, 1074, 1057, 1022, 975, 948, 916, 845, 809, 761, 728, 702, 630, 618, 550, 531, 489. ^1H NMR spectrum, δ, ppm: **Xa**: 2.26 s (3H, Me), 2.52–2.57 m and 3.41–3.45 m (1H each, 4-H), 3.61–3.85 m (6H, CH_2O), 3.995 d.d (1H, *cis*-CH_2=, ^2J = 1.9, $^3J_{cis}$ = 6.8 Hz), 4.18 d.d (1H, *trans*-CH_2=, ^2J = 1.9, $^3J_{trans}$ = 14.3 Hz), 4.48–4.54 m (1H, 5-H), 5.10 s (2-H), 6.49 d.d (1H, =CHO, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.3 Hz), 6.99–7.03 m (1H, 5′-H), 7.14 t (1H, 3′-H, $^3J_{trans}$ = 7.5 Hz), 7.28–7.31 m (1H, 4′-H), 7.56–7.62 m (1H, 6′-H); **IXa**: 2.26 s (3H, Me), 2.74–2.78 m and 3.22–3.25 m (1H each, 4-H), 3.61–3.85 m (6H, CH_2O), 3.992 d.d (1H, *cis*-CH_2=, ^2J = 1.9, $^3J_{cis}$ = 6.8 Hz), 4.17 d.d (1H, *trans*-CH_2=, ^2J = 1.9, $^3J_{trans}$ = 14.3 Hz), 4.33–4.38 m (1H, 5-H), 5.06 s (2-H), 6.49 d.d (1H, =CHO, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.3 Hz), 6.99–7.03 m (1H, 5′-H), 7.14 t (1H, 3′-H, $^3J_{trans}$ = 7.5 Hz), 7.28–7.31 m (1H, 4′-H), 7.56–7.62 m (1H, 6′-H). ^{13}C NMR spectrum, δ_C, ppm: **Xa**: 37.46 s (NMe), 57.40 s (NCH_2), 67.25 s (=CHO**C**H_2), 69.92 s (=CHOCH_2**C**H_2), 72.64 (5-CH_2), 76.02 s (C^5), 86.60 s (=CH_2), 91.08 d (C^2, $^3J_{CF}$ = 3.0 Hz), 115.12 d ($C^{3'}$, $^2J_{CF}$ = 21.5 Hz), 124.15 d ($C^{5'}$, $^4J_{CF}$ = 3.1 Hz), 125.71 d ($C^{1'}$, $^2J_{CF}$ = 10.7 Hz), 129.04 d ($C^{6'}$, $^3J_{CF}$ = 3.5 Hz), 130.16 d ($C^{4'}$, $^3J_{CF}$ = 7.7 Hz), 151.67 s (OCH=), 161.39 d ($C^{2'}$, $^1J_{CF}$ = 248.1 Hz); **IXa**: 37.74 s (NMe), 56.80 s (NCH_2), 67.12 s (=CHO**C**H_2), 69.70 s (=CHOCH_2**C**H_2), 73.35 s (5-CH_2), 74.90 s (C^5), 86.58 s (=CH_2), 91.63 d (C^2, $^3J_{CF}$ = 3.0 Hz), 115.19 d ($C^{3'}$, $^2J_{CF}$ = 21.9 Hz), 124.15 d ($C^{5'}$, $^4J_{CF}$ = 3.1 Hz), 125.61 d ($C^{1'}$, $^2J_{CF}$ = 10.7 Hz), 128.84 d ($C^{6'}$, $^3J_{CF}$ = 3.8 Hz), 130.16 d ($C^{4'}$, $^3J_{CF}$ = 7.7 Hz), 151.65 s (OCH=), 161.58 d ($C^{2'}$, $^1J_{CF}$ = 248.4 Hz). Found, %: C 64.11; H 7.24; F 6.58; N 4.82. $C_{15}H_{20}FNO_3$. Calculated, %: C 64.04; H 7.17; F 6.75; N 4.98.

2-(4-Fluorophenyl)-3-methyl-5-[2-(vinyloxy)-ethoxymethyl]-1,3-oxazolidines IXb and Xb (*mixture of stereoisomers***).** Yield 69%, bp 165–167°C (3 mm), n_D^{20} = 1.5003. IR spectrum, ν, cm^{-1}: 3117, 3072, 3054, 2927, 2872, 2796, 2702, 1636, 1607, 1511, 1471, 1456, 1430, 1418, 1375, 1338, 1322, 1293, 1232, 1203, 1170, 1133, 1095, 1075, 1058, 1014, 974, 947, 916, 860, 833, 794, 734, 701, 637, 616, 571, 536, 417. ^1H NMR spectrum, δ, ppm: **Xb**: 2.18 (1H, Me), 2.69–2.73 m and 3.20–3.23 m (1H each, 4-H), 3.58–3.85 m (6H, CH_2O), 3.99 d.d (1H, *cis*-CH_2=, ^2J = 2.1, $^3J_{cis}$ = 6.8 Hz), 4.17 d.d (1H, *trans*-CH_2=, ^2J = 2.1, $^3J_{trans}$ = 14.3 Hz), 4.29–4.35 m (1H, 5-H), 4.57 s (2-H), 6.48 d.d (1H, =CHO, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.3 Hz), 7.04 t (2H, 3′-H, 5′-H, ^3J = 8.7 Hz), 7.39–7.45 m (2H, 2′-H, 6′-H); **IXb**: 2.19 (1H, Me), 2.47–2.52 m and 3.39–3.43 m (1H each, 4-H), 3.58–3.85 m (6H, CH_2O), 3.99 d.d (1H, *cis*-CH_2=, ^2J = 2.1, $^3J_{cis}$ = 6.8 Hz), 4.18 d.d (1H, *trans*-CH_2=, ^2J = 2.1, $^3J_{trans}$ = 14.3 Hz), 4.44–4.51 m (1H, 5-H), 4.62 s (2-H), 6.48 d.d (1H, =CHO, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.3 Hz), 7.04 t (2H, 3′-H, 5′-H, ^3J = 8.7 Hz), 7.39–7.45 m (2H, 2′-H, 6′-H). ^{13}C NMR spectrum, δ_C, ppm: **Xb**: 37.39 s (NMe), 56.83 s (NCH_2), 67.12 s (**C**H_2OCH=), 69.70 s (OCH_2CH_2O), 73.57 s (5-CH_2), 75.78 s (C^5), 86.58 s (=CH_2), 97.47 s (C^2), 115.04 d ($C^{3'}$, $C^{5'}$, $^2J_{CF}$ = 22.5 Hz), 129.58 d ($C^{2'}$, $C^{6'}$, $^3J_{CF}$ = 8.1 Hz), 134.37 s ($C^{1'}$), 151.64 s (OCH=), 163.51 d ($C^{4'}$, $^1J_{CF}$ = 246.9 Hz); **IXb**: 37.56 s (NMe), 57.27 s (NCH_2), 67.27 s (**C**H_2OCH=), 69.90 s (OCH_2CH_2O), 72.68 s (5-CH_2), 74.64 s (C^5), 86.58 s (=CH_2), 98.07 s (C^2), 115.09 d ($C^{3'}$, $C^{5'}$, $^2J_{CF}$ = 22.4 Hz), 129.58 d ($C^{2'}$, $C^{6'}$, $^3J_{CF}$ = 8.1 Hz), 134.37 s ($C^{1'}$), 151.67 s (OCH=), 163.51 d ($C^{4'}$, $^1J_{CF}$ = 246.9 Hz). Found, %: C 64.09; H 7.12; F 6.63; N 4.93. $C_{15}H_{20}FNO_3$. Calculated, %: C 64.04; H 7.17; F 6.75; N 4.98.

N*-[(*E*)-(2-Fluorophenyl)methylidene]-*N*′-[2-(vinyloxy)ethyl]ethane-1,2-diamine (XIIa) and 2-(2-fluorophenyl)-1-[2-(vinyloxy)ethyl]imidazolidine (XIIIa) (mixture of isomers***).** Yield 83%, bp 115–

118°C (2 mm), n_D^{20} = 1.5251. IR spectrum, ν, cm^{-1}: 3116, 3067, 3044, 2933, 2885, 2828, 1640, 1616, 1587, 1486, 1458, 1376, 1338, 1321, 1300, 1279, 1233, 1201, 1182, 1151, 1134, 1151, 1100, 1075, 1031, 999, 964, 947, 912, 890, 814, 760, 729, 701, 622, 601, 558, 530, 470. ^{1}H NMR spectrum, δ, ppm: **XIIa**: 1.80 br.s (1H, NH), 2.95 t (2H, NC**H**$_2$CH$_2$O, ^3J = 5.2 Hz), 3.00 t (2H, =NCH$_2$C**H**$_2$N, ^3J = 5.9 Hz), 3.72 t (2H, =NC**H**$_2$CH$_2$N, ^3J = 5.9 Hz), 3.78 t (2H, OCH$_2$, ^3J = 5.2 Hz), 3.99 d.d (1H, *cis*-CH$_2$=, ^2J = 1.9, $^3J_{cis}$ = 6.7 Hz), 4.18 d.d 1H, *trans*-CH$_2$=, ^2J = 1.9, $^3J_{trans}$ = 14.0 Hz), 6.47 d.d (1H, =CHO, $^3J_{cis}$ = 6.7, $^3J_{trans}$ = 14.0 Hz), 7.02–7.10 m (1H, 5′-H), 7.14–7.19 m (1H, 3′-H), 7.37–7.42 m (1H, 4′-H) 7.99 t (1H, 6′-H, ^3J = 7.4 Hz), 8.64 s (1H, CH=N); **XIIIa**: 1.80 br.s (1H, NH); 2.51–2.61 m, 2.83–2.89 m, 3.11–3.19 m, 3.24–3.32 m, and 3.42–3.48 m (6H, NCH$_2$CH$_2$NCH$_2$); 3.81 t (OCH$_2$, ^3J = 5.2 Hz), 3.97 d.d (1H, *cis*-CH$_2$=, ^2J = 1.9, $^3J_{cis}$ = 6.8 Hz), 4.14 d.d (1H, *trans*-CH$_2$=, ^2J = 1.9, $^3J_{trans}$ = 14.2 Hz), 4.65 s (1H, 2-H), 6.43 d.d (1H, =CHO, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.2 Hz), 7.02–7.10 m (1H, 5′-H), 7.14–7.19 m (1H, 3′-H), 7.26–7.31 m (1H, 4′-H), 7.65 t (1H, 6′-H, ^3J = 7.2 Hz). ^{13}C NMR spectrum, δ$_C$, ppm: **XIIa**: 48.49 s (N**C**H$_2$CH$_2$O), 49.93 s (=NCH$_2$**C**H$_2$NH), 61.54 s (=NCH$_2$), 67.27 s (OCH$_2$), 86.55 s (=CH$_2$), 115.71 d (C$^{3'}$, $^2J_{CF}$ = 21.1 Hz), 123.70 d (C$^{1'}$, $^2J_{CF}$ = 9.2 Hz), 124.25 d (C$^{5'}$, $^4J_{CF}$ = 3.0 Hz), 127.64 d (C$^{6'}$, $^3J_{CF}$ = 2.6 Hz), 132.18 d (C$^{4'}$, $^3J_{CF}$ = 8.4 Hz), 151.72 s (OCH=), 155.44 d (CH=N, $^3J_{CF}$ = 4.1 Hz), 162.16 d (C$^{2'}$, $^2J_{CF}$ = 252.3 Hz); **XIIIa**: 45.03 s (HNCH$_2$), 51.51 (N**C**H$_2$CH$_2$O), 53.22 (HNCH$_2$**C**H$_2$N), 66.93 (CH$_2$O), 76.26 (NCHN), 86.47 (=CH$_2$), 115.43 d (C$^{3'}$, ^2J = 21.9), 124.35 d (C$^{5'}$, ^4J = 3.1 Hz), 127.53 d (C$^{1'}$, ^3J = 11.90 Hz), 128.29 (C$^{6'}$, ^3J = 3.9 Hz), 129.63 (C$^{4'}$, ^3J = 8.0 Hz), 151.63 (OCH=), 161.69 d (C$^{2'}$, $^2J_{CF}$ = 247.3 Hz). Found, %: C 64.71; H 6.87; F 8.46; N 12.51. $C_{12}H_{15}FN_2O$. Calculated, %: C 64.85; H 6.80; F 8.55; N 12.60.

***N*-[(*E*)-(4-Fluorophenyl)methylidene]-*N*′-[2-(vinyloxy)ethyl]ethane-1,2-diamine (XIIb) and 2-(4-fluorophenyl)-1-[2-(vinyloxy)ethyl]imidazolidine (XIIIb) (*mixture of isomers*).** Yield 79%, bp 134–138°C (2 mm), n_D^{20} = 1.5245. IR spectrum, ν, cm^{-1}: 3117, 3070, 3043, 2931, 2883, 2832, 1646, 1616, 1604, 1509, 1460, 1437, 1416, 1367, 1353, 1321, 1294, 1228, 1200, 1153, 1092, 1075, 1015, 999, 965, 947, 912, 835, 822, 786, 772, 714, 635, 599, 569, 543, 519, 463. ^{1}H NMR spectrum, δ, ppm: **XIIb**: 1.67 br.s (1H, NH), 2.93 t (2H, NC**H**$_2$CH$_2$O, ^3J = 5.2 Hz), 2.97 t (2H, =NCH$_2$C**H**$_2$N, ^3J = 5.9 Hz), 3.72 t (2H, =NC**H**$_2$CH$_2$N, ^3J = 5.9 Hz), 3.74 t (2H, OCH$_2$, ^3J = 5.2 Hz), 3.97 d.d (1H, *cis*-CH$_2$=, ^2J = 1.9, $^3J_{cis}$ = 6.6 Hz), 4.16 d.d (1H, *trans*-CH$_2$=, ^2J = 1.8, $^3J_{trans}$ = 14.3 Hz), 6.44 d.d (1H, =CHO, $^3J_{cis}$ = 6.7, $^3J_{trans}$ = 14.3 Hz), 7.07–7.12 m (2H, 3′-H, 5′-H), 7.46–7.75 m (2H, 2′-H, 6′-H), 8.30 s (CH=N); **XIIIb**: 1.67 br.s (1H, NH); 2.48–2.55 m, 2.78–2.84 m, 3.09–3.15 m, 3.25–3.32 m, 3.43–3.48 m (6H, HNCH$_2$CH$_2$NCH$_2$); 3.78 (2H, OCH$_2$, ^3J = 5.2 Hz), 3.95 d.d (1H, *cis*-CH$_2$=, ^2J = 1.7, $^3J_{cis}$ = 6.2 Hz), 4.10 s (1H, NCHN), 4.12 d.d (1H, *trans*-CH$_2$=, ^2J = 1.8, $^3J_{trans}$ = 14.3 Hz), 6.42 d.d (1H, =CHO, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.1 Hz), 7.02–7.06 m (2H, 3′-H, 5′-H), 7.46–7.49 m (2H, 2′-H, 6′-H). ^{13}C NMR spectrum, δ$_C$, ppm: **XIIb**: 48.41 s (=NCH$_2$**C**H$_2$N), 48.91 s (N**C**H$_2$CH$_2$O), 61.00 s (CH$_2$N=), 67.20 s (NCH$_2$**C**H$_2$O), 86.44 s (=CH$_2$), 115.47 d (C$^{3'}$, C$^{5'}$, $^2J_{CF}$ = 22.4 Hz), 129.85 d (C$^{2'}$, C$^{6'}$, ^2J = 8.8 Hz), 132.31 d (C$^{1'}$, ^4J = 3.1 Hz), 151.59 s (OCH=), 160.48 s (C=N), 164.03 d (C$^{4'}$, $^1J_{CF}$ = 250.7 Hz); **XIIIb**: 44.70 s (HN**C**H$_2$CH$_2$N), 51.17 s (N**C**H$_2$CH$_2$O), 53.21 s (N**C**H$_2$CH$_2$NH), 66.86 s (OCH$_2$), 82.79 s (NCHNH), 86.38 s (=CH$_2$), 115.38 d (C$^{3'}$, C$^{5'}$, $^2J_{CF}$ = 22.4 Hz), 129.18 d (C$^{2'}$, C$^{6'}$, $^2J_{CF}$ = 8.1 Hz), 136.11 d (C$^{1'}$, ^4J = 2.2 Hz), 151.49 s (OCH=), 162.64 d (C$^{4'}$, $^1J_{CF}$ = 246.5 Hz). Found, %: C 64.94; H 6.65; F 8.43; N 12.48. $C_{12}H_{15}FN_2O$. Calculated, %: C 64.85; H 6.80; F 8.55; N 12.60.

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