ISSN 1070-4280, Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 2, pp. 260–267. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © E.S. Kelbysheva, A.P. Pleshkova, S.E. Lyubimov, S.P. Dolgova, N.M. Loim, 2009, published in Zhurnal Organicheskoi Khimii, 2010, Vol. 46, No. 2, pp. 265–267.

Chiral Modification of Polyformyl Compounds of Dendrite Type with Optically Active Primary and Secondary 1,2-Aminoalcohols

E. S. Kelbysheva, A. P. Pleshkova, S. E. Lyubimov, S. P. Dolgova, and N. M. Loim

Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences
Moscow,117813 Russia
e-mail: loim@ineos.ac.ru

Received May 6, 2009

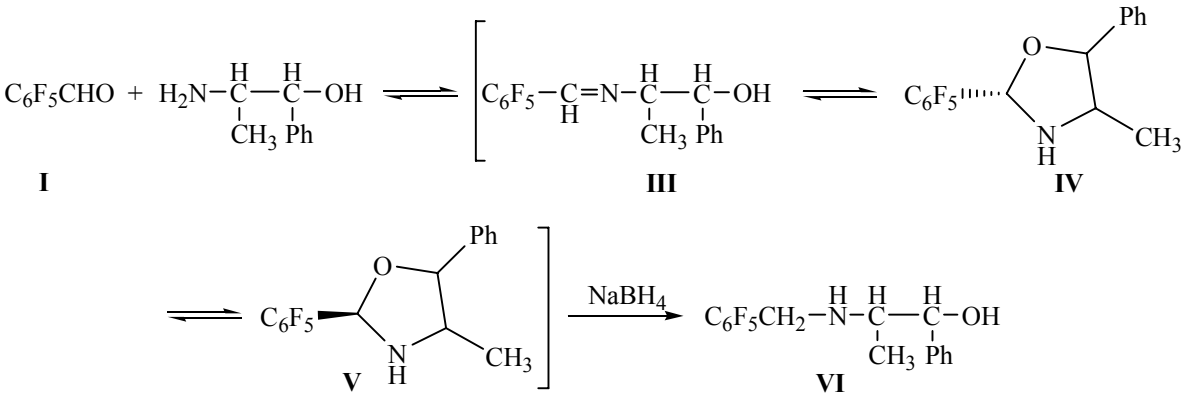
Abstract—Procedures were developed for preparation of optically active dendrones and dendrimers with terminal 1,2-hydroxylimino, 1,2-hydroxylamino and oxazolidinyl groups containing ether bonds in the branches and ester bonds in the backbone of the macromolecule. The compounds described may serve as chiral ligands for asymmetric metallocomplex catclysis.

DOI: 10.1134/S107042801002020X

The theoretical interest and versatile applications of dendrimers promote the research in the field of monodisperse macromolecular compounds of cascade architecture [1–10]. A special place among these compounds belongs to chiral and optically active dendrite molecules providing new opportunities for creating systems of chiral recognition and separation of optically active substances, compounds with nonlinear optic properties, and reagents for reactions of asymmetric synthesis [11–20]. Recently by an example of dendrimers with hydrazidothiophosphate monomer units the promising opportunities were demonstrated of employing the peripheral formyl groups for the preparation of optically active dendrite catalysts [21, 22]. We reported in the previous communication on the synthesis of formyl-containing dendritc molecules of Frische type [23]. In this study we performed a chiral modification of these compounds using optically active 1,2-aminoalcohols leading to the formation of a series of new chiral polyligands of cascade architecture.

By an example of a model reaction of perfluorobenzaldehyde (**I**) with (–)-(1*R*,2*S*)- or (+)-(1*S*,2*R*)-enantiomers of norephedrine we demonstrated that both in the solid phase without solvent or in the benzene or chloroform solutions the corresponding Schiff bases **II** formed quantitatively. According to the ^{1}H NMR spectra the latter substances are present in the solution as

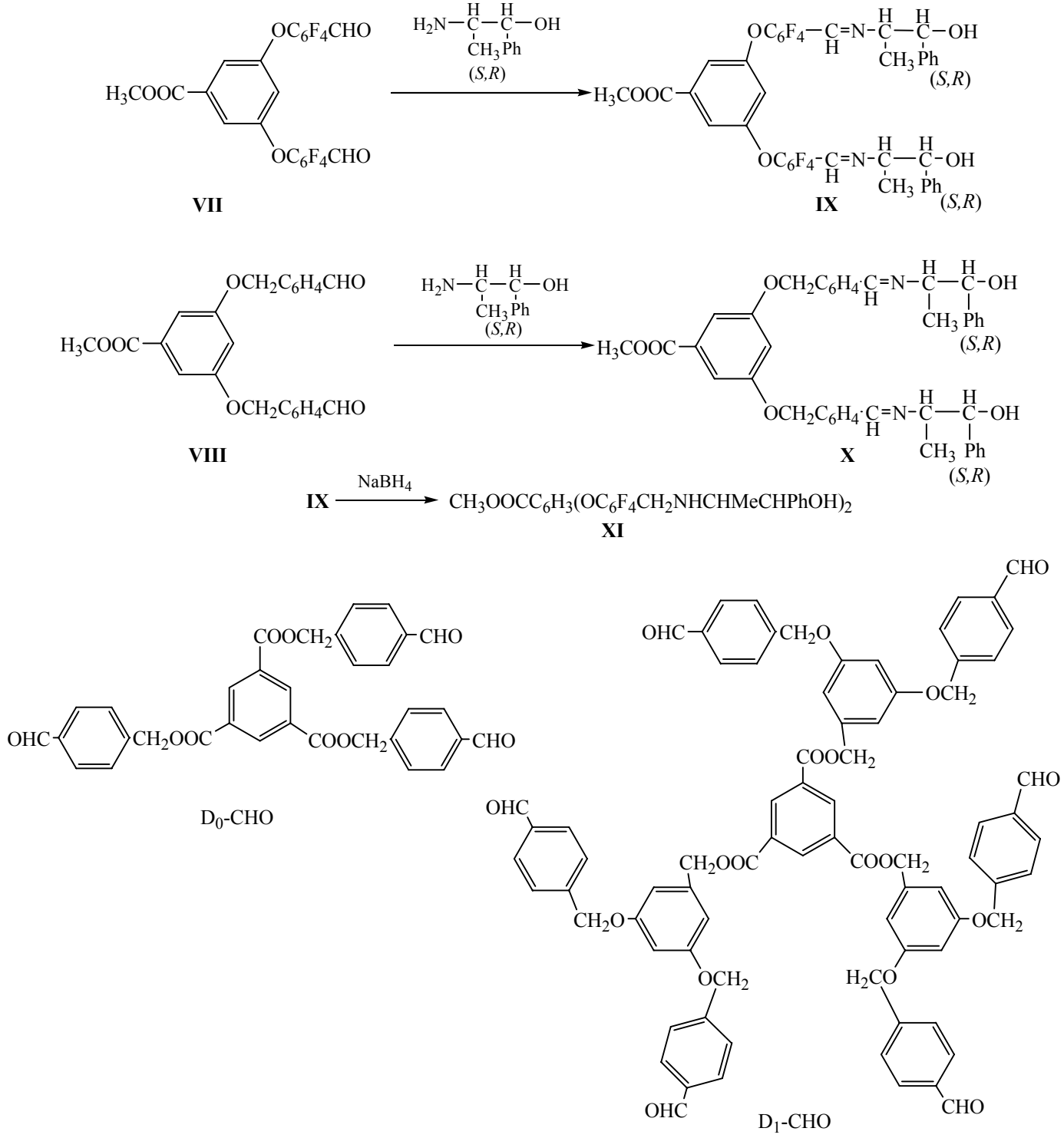
Scheme 1.



260

a mixture of three compounds (Scheme 1): proper imine **III** (open form) and two diastereomeric oxazolidines **IV** and **V** (closed forms of imine). The spectrum in $CDCl_3$ solution contains, in particular, three doublets of CH_3 groups in the region 0.74–1.38 ppm, three overlapping multiplets in the region 3.4–3.7 ppm corresponding to the proton CHMe, and also singlets of protons from the fragment NCHO of diastereomers **IV** and **V** (δ 5.76, 6.28 ppm)

Scheme 2.



and of the proton CH=N of imine **III** (7.97 ppm). The ratio of the three isomeric forms of the condensation product **III**, **IV** and **V** is ~1 : 1 : 1 and depends neither on the reaction conditions nor on the conformation of the initial norephedrine indicating that a fast equilibrium between the forms exists in the solution.

The similar modification of the terminal layer of dendrones **VII** and **VIII** with (+)-norephedrine in solution or in the solid phase also resulted in a quantitative formation of imines **IX** and **X** (Scheme 2) and each among them in solution was present in the form of three isomers: the imine and two diastereomeric oxazolidines.

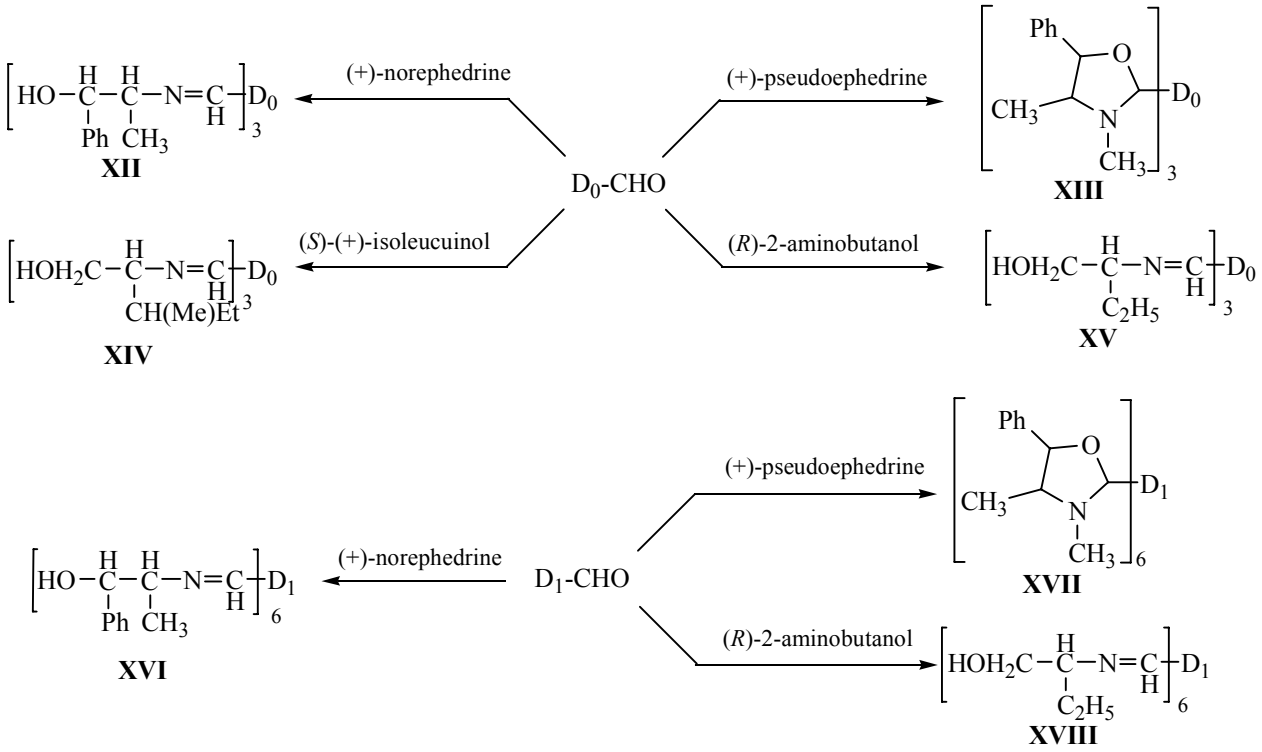
The reduction of 1,2-oxyimines **III** and **IX** with sodium borohydride in methanol furnished the corresponding 1,2-aminoalcohols **VI** and **XI**.

Based on these results we carried out the chiral modification of the peripheral layer of formyldendrimers of the zero (D_0-CHO) and the first (D_1-CHO) generations [23] using (*R*)-2-aminobutanol, (1*S*,2*R*)-norephedrine, (*S*)-isoleucinol, and (1*S*,2*S*)-pseudoephedrine both in the solid phase and in chloroform solution or by boiling the reagents in ethanol in the presence of sodium sulfate (Scheme 3). The yields of the target optically active products in all cases were nearly quantitative (>98%).

At the solid-phase synthesis of dendrimers with the pseudoephedrine in both cases after the completion of the condensation (the absence of the formyl group signal in the ^{1}H NMR spectrum) the oxazolidine fragments in compounds **XIII** and **XVII** exist as two diastereomers at the C^2 center of the heterocycle. In the ^{1}H NMR spectrum of the reaction mixture after 48 h appears a double set of signals for all groups bound to the oxazolidine ring. In particular, in the spectrum of **XVII** two doublets at δ 0.91 and 1.20 ppm are observed and two singlets at 2.35 and 2.15 ppm from the methyl groups in the positions of *4* and *3* of the ring respectively. The relative intensity of the signals of diastereomers essentially depends on the time, and after keeping the reaction mixture over 100 h the thermodynamically less stable diastereomer completely undergoes epimerization into the none stable homochiral stereoisomer of the dendrimer **XVII** with the chemical shifts of the methyl groups 0.91 and 2.35 ppm. Analogous pattern was observed in the reaction of formyldendrimers D_0-CHO and D_1-CHO with the pseudoephedrine in chloroform as solvent.

The chiral modification of formyldendrimers D_0-CHO and D_1-CHO with optically active primary 2-aminoalcohols completes with the formation of Schiff

Scheme 3.

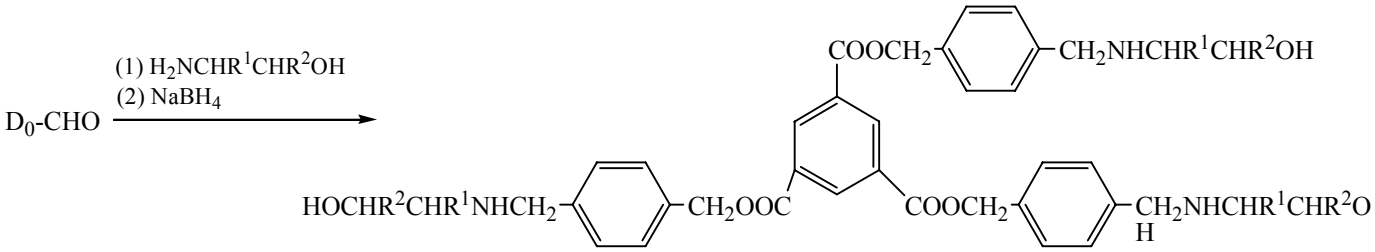


bases at all aldehyde groups As expected, in solutions compounds **XII, XIV–XVI, XVIII** exist in an equilibrium mixture of the open and two closed (oxazolidine) forms of 1,2-hydroxyimine terminal groups with a considerable prevalence of the imine form. In particular, in the spectrum of compound **XII** the intensity of proton singlets of the imine group (δ 8.27 ppm) and of proton signals of OCHN groups of the oxazolidine rings (δ 6.08 and 5.63 ppm) are in the ratio 5:1:2 (see the figure). Therewith the ^{1}H NMR spectra in all cases contain only three sets of signals corresponding to each of the three forms of the terminal groups. Thus the presence in the dendrimer of several peripheral fragments of different nature does not affect the chemical shifts of the terminal groups.

Although the condensation of the reagents in solution and in the solid phase gave the same results, the most efficient procedure proved to be the preparation of the Schiff bases by boiling in ethanol in the presence of sodium sulfate. In these conditions the quantitative yield of products was reached already in 2 h although the initial dendrimers were insoluble in ethanol. Besides by an example of the reaction between D_0-CHO and (1*S*,2*R*)-norephedrine and (*S*)-isoleucinol we showed that this procedure made it possible to carry out the reduction of the dendrimeric iminoalcohols into the aminoalcohols without their isolation (Scheme 4).

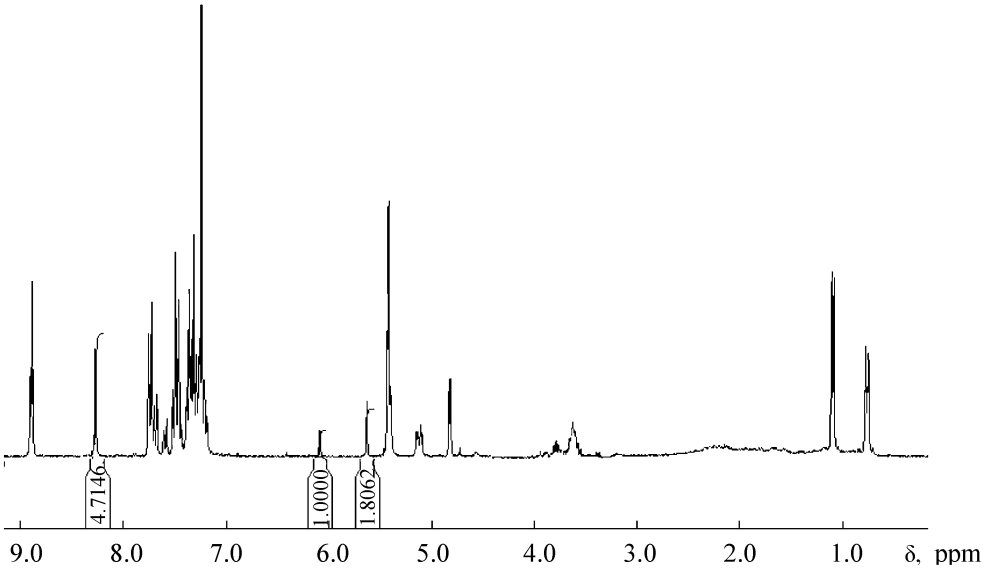
In order to confirm the structure of the above mentioned dendrite compounds and to estimate their molecular weight a comparative investigation was performed of the mass spectra of the formyldendrimers D_0-CHO and D_1-CHO and their derivatives **XII–XV**, **XVII**, and **XVIII**. The ionization was performed by electron impact (EI) or matrix-activated laser desorption-ionozation (MALDI). Although for compounds D_0-CHO, **XII**, **XIV**, and **XV** with the molecular weigh up to 1000 it is possible to obtain EI spectra, the direct information on the molecular mass

Scheme 4.



XIX, XX

R^1 = Me, R^2 = Ph (**XIX**), R^1 = CH(Me)Et, R^2 = H (**XX**).



^{1}H NMR spectrum oof the isomer mixture of compound **XII**.

and structure is contained only in the mass spectrum of D_0-CHO, *m/z* (I_{rel}, %): 564 (10) $[M]^+$, 445 (50) $[M - OCHC_6H_4CH_2]^{+\cdot}$, 429 (80) $[M - OCHC_6H_4CH_2O]^+$, and 119 (95) $[OCHC_6H_4CH_2]^+$. In the other EI spectra only the peaks of fragment ions were observed from the products of the thermal degradation of the initial compound. Unlike that, the application of MALDI in all cases provided informative mass spectra. Therewith among the three tested matrices [2,5-dihydroxybenzoic, 2-cyano-4-hydroxycinnamic, and *trans*-3-(indol-3-yl)acrylic acids] the most generally suitable and efficient was the latter which provided a highly intense peaks in the region of molecular masses and a high signal to noise ratio (≤ 80–102) in the range of masses 700–3000.

The peaks of ions and clusters observed in the MALDI spectra unambiguously confirm both the molecular weight of the dendrite molecules (see EXPERIMENTAL) and their structure. In particular, the comparison of spectra of compounds **XII, XIV, XV, XVIII** and oxazolidine derivatives **XIII** and **XVII** led to the conclusion that in the solid phase 1,2-oxyimines evidently existed in the open and not cyclic form which is registered in the ^{1}H NMR spectra (see above). Actually, in the spectrum of compound **XIII** $[M]^+$ of *m/z* 1005 was observed, and in the spectrum of compound **XVII**, a peak of ion $[M - H]^+$ with *m/z* 2166, their fragmentation occurred through the decomposition of the heterocycle resulting in both cases in the formation of the corresponding ions $[M - PhCHOH]^{+\cdot}$ and $[M - C_{10}H_{14}N]^{+\cdot}$. The pattern in the MALDI spectra of dendrite Schiff bases is another. The characteristic feature of these compounds was the presence of ions $[M + 2H]^+$ (**XII, XIV, XV**) or $[M + H]^{+\cdot}$ (**XVIII**), whose fragmentation involved the cleavage of the N–C bond in the peripheral substituent with the elimination of a neutral molecule of the corresponding oxide and with the formation of ions of dendrite amines.

EXPERIMENTAL

^{1}H, ^{13}C (internal reference the solvent, δ from Me_4Si), and ^{19}F NMR spectra were registered on a spectrometer Bruker WP-200 SY at operating frequencies 200.13, 50.32, and 188.3 MHz respectively. Mass spectra EI were obtained on an instrument MAT 95X at 70 eV, and MALDI spectra, on an instrument Bruker AutoFlex IV with a nitrogen laser, 337 nm. The monitoring of the reaction progress and checking of the products purity was carried out by analytic TLC on Silufol UV-245 plates and by ^{1}H NMR spectra of the samples of reaction mixtures. For column chromatography silica gel 60 (Merck) was used. Optically active aminoalcohols were commercial products of Fluka. Synthesis of compounds **VII** and **VIII** was previously reported [23].

Reactions of aldehydes with optically active 1,2-aminoalcohols. General procedure. *a*. In the solid phase without solvent. The equimolar (with respect to every formyl group) mixture of aldehyde and the chiral aminoalcohol was thoroughly stirred for 24–48 h till the formation of a homogeneous viscous or crystalline substance. The monitoring of the reaction progress was carried out by TLC and by ^{1}H NMR spectra of the samples of reaction mixture. On obtaining solid reaction products they were additionally recrystallized from a mixture hexane–benzene.

b. Liquid-phase interaction. A solution of equimolar (with respect to every formyl group) mixture of aldehyde and the chiral aminoalcohol in benzene was boiled with the use of a Dean-Stark trap for 2–4 h or by stirring the reagents in the chloroform solution at room temperature for 24 h. The solvent was distilled off in a vacuum, and in event of obtaining solid products they were additionally recrystallized from a mixture hexane–benzene.

c. To a dispersion of 3.5 g of anhydrous sodium sulfate in 25 ml of anhydrous EtOH was added 1.8 mmol of dendrimer and 4.83 mmol of (*S*)-aminobutanol or 9.66 mmol of (*S*)-isoleucinol, and the mixture was boiled for 2 h with D_0-CHO or 12 h with D_1-CHO. Then the reaction mixture was cooled to room temperature, the Na_2SO_4 precipitate was filtered off, washed with ethanol, the solvent was distilled off in a vacuum, the residue was recrystallized from a mixture hexane–benzene.

2-Perfluorophenylmethylideneamino-1-phenylpropanol (III). *a*. It was obtained from 0.26 g (1.3 mmol) perfluorobenzaldehyde (**I**) and 0.19 g (1.3 mmol) of (+)-(1*S*,2*R*)- or (–)-(1*R*,2*S*)-enantiomer of norephedrine. Yield 0.43 g (>99%). Oily substance. ^{1}H NMR spectrum of the open form (toluene-d_8), δ, ppm: 1.38 d (3H, CH_3, *J* 6.8 Hz), 2.60 br.s (1H, OH), 3.62 m (1H, $CHCH_3$), 5.20 d (1H, CHOH, *J* 8.2 Hz), 7.19–7.40 m (5H, Ph), 7.97 s (1H, CH=N). Found, %: C 58.54; H 3.65; F 28.92; N 4.22. $C_{16}H_{12}FNO$. Calculated, %: C 58.36; H 3.67; F 29.03; N 4.25.

b. It was obtained from 0.52 g (2.6 mmol) of compound **I** and 0.39 g (2.6 mmol) of norephedrine in 25 ml of benzene. Yield 0.87 g (>99%). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.13 d (3H, CH_3, *J* 6.4 Hz),

3.78 m (1H, $CHCH_3$), 5.02 d (1H, CHOH, *J* 8.5 Hz), 7.2–7.4 m (5H, Ph), 8.29 s (1H, CH=N).

1-Phenyl-2-(perfluorophenylmethylamino)-propanol (VI). To a solution of 1.26 g (3.8 mmol) of compound **III** in 15 ml of MeOH was gradually added under constant stirring at 0°C 0.14 g (3.8 mmol) of sodium borohydride. The reaction mixture was stirred in these conditions for 1 h (TLC monitoring). Then the solvent was evaporated in a vacuum, the residue was dissolved in ethyl acetate and washed with water (2×20 ml). The organic layer was dried with $MgSO_4$, concentrated, the residue was recrystallized from a mixture hexane–ethyl acetate. Yield 1.1 g (61%), mp 115.5–116°C. ^{1}H NMR spectrum (toluene-d_8), δ, ppm: 0.91 d (3H, CH_3, *J* 6.7 Hz), 2.79 m (1H, $CHCH_3$), 3.66 s (2H, CH_2), 4.76 d (1H, CHOH, *J* 7.5 Hz), 7.37–7.48 m (5H, Ph). ^{19}F NMR spectrum (toluene-d_8), δ, ppm: –68.86 m (2F, C_6F_5), –79.70 m (1F, C_6F_5), –86.19...–86.47 m (2F, C_6F_5). Found, %: C 58.01; H 4.23; N 4.46. $C_{16}H_{14}F_5NO$. Calculated, %: C 58.21; H 4.32; N 4.29.

Methyl (3,5-bis[4-(2-hydroxy-2-phenyl-1-methylethyliminomethyl)-2,3,5,6-tetrafluorophenyloxy])benzoate (IX) was obtained from 1.6 g (3.1 mmol) of dialdehyde **VII** and 0.94 g (6.2 mmol) of (+)-norephedrine in 50 ml toluene by method *b*. Yield 2.4 g (>99%), mp 65.5–66°C. ^{1}H NMR spectrum of imine form (toluene-d_8), δ, ppm: 1.27 d (6H, CH_3, *J* 6.6 Hz), 3.68 m (2H, $CHCH_3$), 3.83 s (3H, CH_3O), 4.74 d (2H, CHOH, *J* 8.6 Hz), 5.82 m (1H, C_6H_3), 6.35 m (2H, C_6H_3), 7.19–7.36 m (10H, Ph), 8.31 s (2H, CH=N). ^{19}F NMR spectrum (toluene-d_8), δ, ppm: –63.81ч–63.99 m (4F, C_6F_4), –75.82ч–76.24 m (4F, C_6F_4). Found, %: C 60.97; H 3.86; F 19.32; N 3.52. $C_{40}H_{30}F_8N_2O_6$. Calculated, %: C 61.07; H 3.84; F 19.32; N 3.56.

Yield by method *a* 1.12 g (98%).

Methyl (3,5-bis[4-(1*R*,2*S*)-(2-hydroxy-1-methyl-2-phenylethyliminomethyl)benzyloxy])benzoate (X) was obtained from 0.25 g (0.62 mmol) of compound **VIII** and 0.2 g (1.25 mmol) of (+)-norephedrine by method *b*. Yield 0.44 g (99%). ^{1}H NMR spectrum of the open imine form (toluene-d_8), δ, ppm: 1.22 d (6H, CH_3, *J* 6.4 Hz), 3.65 m (2H, $CHCH_3$), 3.84 s (3H, CH_3OC), 4.45 d (2H, CHOH, *J* 8.1 Hz), 5.17 s (4H, OCH_2), 6.95 m (1H, C_6H_3), 7.14 m (2H, C_6H_3), 7.23–7.35 m (10H, Ph), 7.51–7.70 m (8H, C_6H_4), 8.16 s (2H, CH=N). Found, %: C 75.38; H 6.04; N 3.98. $C_{42}H_{42}N_2O_6$. Calculated, %: C 75.22; H 6.29; N 4.17.

Yield of compound **X** obtained by method *a* from 0.78 g of compound **VIII** and 0.62 g of (+)-norephedrine 1.34 g (>99%).

Methyl (3,5-bis[4-(1*R*,2*S*)-(2-hydroxy-1-methyl-2-phenylethylaminomethyl)-2,3,5,6-tetrafluorophenyloxy])benzoate (XI). At reducing 0.41 g (0.52 mmol) of Schiff base **IX** with 50 mg (1.24 mmol) of sodium borohydride yield 0.37 g (90%). ^{1}H NMR spectrum (toluene-d_8), δ, ppm: 1.02 d (6H, CH_3, *J* 6 Hz), 2.86 m (2H, $CHCH_3$), 3.5–3.7 m (4H, CH_2), 3.85 s (3H, CH_3O), 4.84 d (2H, CHOH, *J* 7.5 Hz), 5.96 s (1H, C_6H_3), 6.36 m (2H, C_6H_3), 7.19–7.28 m (10H, Ph). ^{19}F NMR spectrum (toluene-d_8), ppm: –63.87...–63.99 m (4F, C_6F_4), –75.82...–76.20 m (4F, C_6F_4). Found, %: C 60.64; H 4.46; F 19.28; N 3.59. $C_{40}H_{34}F_8N_2O_6$. Calculated, %: C 60.75; H 4.34; F 19.22; N 3.54.

1,3,5-Tris[4-(1*R*,2*S*)-(2-hydroxy-1-methyl-2-phenylethyliminomethyl)benzyloxycarbonyl]benzene (XII) was obtained by method *b* from 562 mg (1 mmol) of D_0-CHO and 454 mg (3 mmol)of (+)-norephedrine in 50 ml of chloroform. Yield 945 mg (98%), mp 84–85°C (hexane–benzene), $[\alpha]_D^{21}$ –29° (*C* 0.842, DMF). ^{1}H NMR spectrum of predominant open form ($CDCl_3$), δ, ppm: 1.15 d (9H, CH_3, *J* 6.5 Hz), 3.63 m (3H, $CHCH_3$), 4.82 d (3H, CHOH, *J* 5.9 Hz), 5.41 s (6H, CH_2), 7.2–7.4 m (15H, Ph), 7.48 d (6H, C_6H_4, *J* 7.9 Hz) and 7.72 d (6H, C_6H_4, *J* 7.9 Hz), 8.27 s (3H, CH=N), 8.88 s (3H, C_6H_3). Mass spectrum, *m/z*: 965 $[M + 2H]^+$, 831 $[M + 2H - C_9H_{10}O]^+$. Found, %: C 74.65; H 6.19; N 4.41. $C_{60}H_{57}N_3O_9$. Calculated, %: C 74.75; H 5.99; N 4.36.

Yield of compound **XII** by method *a* from 0.78 g of D_0-CHO and 0.6 g of (+)-norephedrine 1.4 g (98%).

1,3,5-Tris[4-(4*S*,5*S*)-(3,4-dimethyl-5-phenyl-1,3-oxazolidin-2-yl)benzyloxycarbonyl]benzene (XIII) was obtained by method *b* from 564 mg (1 mmol) of D_0-CHO and 496 mg (3 mmol) of (+)-pseudoephedrine in 50 ml of chloroform. Yield 987 mg (99%), mp 79–80°C (hexane–benzene), $[\alpha]_D^{21}$ –107° (*C* 0.836, DMF). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.79 d (9H, CH_3CH, *J* 6.4 Hz), 2.19 s (9H, NCH_3), 2.98 m (3H, $CHCH_3$), 4.71 s (3H, NCHO), 5.15 d (3H, CHPh, *J* 7.7 Hz), 5.44 s (6H, OCH_2), 7.20–7.40 m (15H, Ph), 7.52 d (6H, C_6H_4, *J* 8 Hz), 7.68 d (6H, C_6H_4, *J* 8 Hz), 8.92 s (3H, C_6H_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.45 (CH_3), 35.27 (NCH_3), 67.19 (CH_2), 68.82 (CHN), 86.60 (CHO), 99.19 (NCHO), 136.33–126.72 (Ph), 161.79 (CO). Mass spectrum, *m/z*: 1005 $[M]^+$, 898 $[M - PhCHOH]^+$, 857 $[M - C_{10}H_{14}N]^+$. Found, %: C 75.16; H 6.21; N 4.20. $C_{63}H_{63}N_3O_9$. Calculated, %: C 75.20; H 6.31; N 4.18.

Yield of compound **XIII** in the solid-phase synthesis by method *a* from 578 mg of D_0-CHO and 509 mg of (+)-pseudoephedrine 1.09 g (>98%).

1,3,5-Tris[(*S*,*S*)-4-(1-hydroxymethyl-2-methylbutyliminomethyl)benzyloxycarbonyl]benzene (XIV) was obtained by method *c* from 1 g (1.8 mmol) of D_0-CHO and 0.67 g (5.7 mmol) of (+)-(2*S*,3*S*)-isoleucinol in 25 ml of anhydrous ethanol in the presence of 3 g of anhydrous Na_2SO_4. Yield 1.54 g (98%), mp 69–70°C (hexane–benzene), $[\alpha]_D^{21}$ 24° (*c* 0.804, benzene). ^{1}H NMR spectrum of main isomer ($CDCl_3$), δ, ppm: 0.86–0.97 m (18H, CH_3), 1.15 m (3H, CH_2CH_3), 1.26 m (3H, CH_2CH_3), 1.72 m [3H, CH(Mε)Et], 2.93 m (3H, CHN), 3.94 m (3H, CH_2OH), 4.1 m (3H, CH_2OH), 5.42 s (6H, $CH_2C_6H_4$), 7.45 d and 7.78 d (12H, C_6H_4, *J* 7.7 Hz), 8.25 s (3H, CH=N), 8.88 s (3H, C_6H_3). Mass spectrum, *m/z*: 863 $[M + 2H]^+$, 763 $[M + 2H - C_6H_{12}O]^+$. Found, %: C 71.36; H 7.27; N 5.04. $C_{51}H_{63}N_3O_9$. Calculated, %: C 71.05; H 7.37; N 4.87.

1,3,5-Tris[4-(*S*)-(1-hydroxymethylpropylimino)benzyloxycarbonyl]benzene (XV) was obtained by method *b* from 564 mg (1 mmol) of D_0-CHO and 269 mg (3 mmol) of (+)-(*S*)-2-aminobutanol in 50 ml of chloroform. Yield 767 mg (98%), mp 119–120°C (hexane–benzene), $[\alpha]_D^{21}$ 18° (*C* 0.752, DMF). ^{1}H NMR spectrum of main isomer ($CDCl_3$), δ, ppm: 0.92 br.s (9H, CH_3), 1.28 m (6H, CH_2CH_3), 1.69 m (3H, CHN), 3.73 m (6H, CH_2OH), 5.48 s (6H, CH_2), 7.51–7.81 m (12H, C_6H_4), 8.45 s (3H, CH=N), 8.94 s (3H, C_6H_3). Mass spectrum, *m/z*: 779 $[M + 2H]^+$, 707 $[M + 2H - C_4H_8O]^+$. Found, %: C 69.36; H 6.67; N 5.41. $C_{45}H_{51}N_3O_9$. Calculated, %: C 69.48; H 6.61; N 5.40.

1,3,5-Tris{3,5-bis[4-(1*R*,2*S*)-(2-hydroxy-1-methyl-2-phenylethylimino)benzyloxy]benzyloxycarbonyl}benzene (XVI) was obtained by method *b* from 797 mg (0.62 mmol) of D_1-CHO and 562 mg (3.72 mmol) of (+)-norephedrine in 50 ml of chloroform. Yield 1.29 g (98%), mp 111–112°C (hexane–benzene), $[\alpha]_D^{21}$ 2.0° (*C* 1.61, DMF). ^{1}H NMR spectrum of imine form ($CDCl_3$), δ, ppm: 1.20 d (18H, CH_3, *J* 7.6 Hz), 2.58 m (6H, $CHCH_3$), 4.77 d (6H, CHOH, *J* 7.6 Hz), 5.00 s (12H, OCH_2), 5.31 s (6H, $COOCH_2$), 6.53 s (3H, C_6H_3), 6.66 m (6H, C_6H_3), 7.23–7.32 m (30H, Ph), 7.36–7.63 m (24H, C_6H_4), 8.17 s (6H, CH=N), 8.88 s (3H, C_6H_3). Found, %: C 75.98; H 6.32; N 4.12. $C_{132}H_{126}N_6O_{18}$. Calculated, %: C 76.05; H 6.10; N 4.03.

1,3,5-Tris{3,5-bis[4-(4*S*,5*S*)-(3,4-dimethyl-5-phenyl-1,3-oxazolidin-2-yl)benzyloxy]benzyloxycarbonyl}benzene (XVII) was obtained by method *b* from 398 mg (0.3 mmol) of D_1-CHO and 296 mg (1.83 mmol) of (+)-pseudoephedrine in 50 ml of chloroform. Yield 650 mg (99%), mp 108–109°C (hexane–benzene), $[\alpha]_D^{21}$ –14.0° (*C* 0.678, DMF). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.20 d (18H, CH_3, *J* 6.3 Hz), 2.15 s (18H, NCH_3), 2.48 m (6H, $CHCH_3$), 4.75 d (6H, CHPh, *J* 8.3 Hz), 4.92 s (6H, NCHO), 5.01 s (12H, OCH_2), 5.27 s (6H, $COOCH_2$), 6.55 br.s (3H, C_6H_3), 6.63 br.s (6H, C_6H_3), 7.20–7.43 m (30H, Ph and 12H, C_6H_4), 7.55 d (12H, C_6H_4, *J* 8 Hz), 8.90 s (3H, C_6H_3). Mass spectrum, *m/z*: 2166 $[M - H]^+$, 2060 $[M - PhCHOH]^+$, 2019 $[M - C_{10}H_{14}N]^+$. Found, %: C 76.27; H 6.39; N 3.97. $C_{138}H_{138}N_6O_{18}$. Calculated, %: C 76.42; H 6.37; N 3.87.

1,3,5-Tris(3,5-bis{4-[1-(*S*)-hydroxymethylpropylimino]benzyloxy}benzyloxycarbonyl)benzene (XVIII) was obtained by method *c* from 642 mg (0.5 mmol) of D_1-CHO and 267 mg (3 mmol) of (*S*)-2-aminobutanol in 35 ml of anhydrous ethanol in the presence of 5 g of anhydrous sodium sulfate. Yield 0.84 g (98%), mp 142–143°C (hexane–benzene), $[\alpha]_D^{21}$ 2.4° (*C* 0.829, DMF). ^{1}H NMR spectrum of main isomer ($CDCl_3$), δ, ppm: 0.85 br.t (18H, CH_3), 1.15 m (6H, CH_2Me), 1.40 m (6H, CH_2Me), 1.73 m (6H, CHN), 3.8–4.1 m (12H, CH_2OH), 5.01 s (12H, OCH_2), 5.30 s (6H, $COOCH_2$), 6.55 s (3H, C_6H_3), 6.68 m (6H, C_6H_3), 7.28–7.63 m (12H, C_6H_4), 8.51 br.s (6H, CH=N), 9.0 s (3H, C_6H_3). Mass spectrum, *m/z*: 1712 $[M + H]^+$, 1640 $[M - C_4H_8O]^+$. Found, %: C 71.48; H 6.60; N 4.79. $C_{103}H_{114}N_6O_{21}\times H_2CO_3$. Calculated, %: C 71.56; H 6.71; N 4.91.

1,3,5-Tris[4-(1*R*,2*S*)-(2-hydroxy-1-methyl-2-phenylethylaminomethyl)benzyloxycarbonyl]benzene (XIX). To a dispersion of 3 g of anhydrous sodium sulfate in 25 ml of anhydrous EtOH was added 566 mg (1 mmol) of D_0-CHO and 456 mg (3 mmol) of (+)-norephedrine, and the mixture was boiled for 2 h. Then the reaction mixture was cooled to 0°C, and 40 mg (10 mmol) of $NaBH_4$ was added by portions, the mixture was additionally stirred for 1 h and diluted with 100 ml of cold water. The reaction products were extracted into AcOEt, the extract was dried with Na_2SO_4. on filtering the solvent was removed in a vacuum, the residue was crystallized from a mixture hexane–benzene. Yield 941 mg (96%), mp 70–72°C (hexane–benzene), $[\alpha]_D^{21}$ –33° (*C* 0.880, DMF). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.09 d (9H, CH_3, *J* 6.2 Hz), 2.45 m (3H, $CHCH_3$), 4.66 d (3H, CHOH, *J* 7.9 Hz), 4.82 br.s (6H, CH_2N), 5.35 s (6H, CH_2), 7.27–7.34 m (15H, Ph), 7.36 d (6H, C_6H_4,

J 7.9 Hz), 7.62 d (6H, C_6H_4, *J* 7.9 Hz), 8.84 s (3H, C_6H_3). Found, %: C 74.15; H 6.19; N 4.18. $C_{60}H_{63}N_3O_9$. Calculated, %: C 74.28; H 6.55; N 4.33.

1,3,5-Tris[(*S*,*S*)-4-(1-hydroxymethyl-2-methylbutylaminomethyl)benzyloxycarbonyl]benzene (XX) was obtained similarly from 1.2 g (1.8 mmol) of D_0-CHO and 0.67 g (5.7 mmol) of (2*S*,3*S*)-isoleucinol in 25 ml of anhydrous ethanol in the presence of 3 g of anhydrous sodium sulfate. Yield 1.51 g (96%), mp 61–62°C (hexane–benzene), $[\alpha]_D^{21}$ 12° (*c* 0.784, benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (9H, CH_3, *J* 6.3Hz), 1.05 d (9H, CH_3, *J* 7 Hz), 1.42 m (6H, CH_2CH_3), 1.92 m [3H, CH(Mε)Et], 2.83 m (3H, CHN), 3.4 m (3H, CH_2OH), 3.86 m (3H, CH_2OH), 4.80 br.s (6H, CH_2N), 5.50 s (6H, $CH_2C_6H_4$), 7.53–7.66 m (12H, C_6H_4), 8.90 s (3H, C_6H_3). Found, %: C 68.97; H 8.00; N 4.52. $C_{51}H_{69}N_3O_9 \cdot H_2O$. Calculated, %: C 69.13; H 8.08; N 4.74.

The study was carried out under a financial support of the Program of Fundamental Research of the Presidium of the Russian Academy of Sciences "Development of methods of chemical compounds preparation and creation of new materials" P-18.

REFERENCES

1. Soto-Castro, D., Evangelisya-Lara, A., and, Guadarrama, P., *Tetrahedron,* 2006, vol. 62, p. 12116.
2. Gao, C. and Yan, D. *Prog. Polym. Sci*., 2004, vol. 29, p. 183.
3. Beletskaya, I.P. and Chuchuryukin, A.V., *Usp. Khim*., 2000, vol. 69, p. 699.
4. Sharma, A., Desai, A., Ali, R., and Tomalia, D., *J. Chromatography. A.,* 2005, vol. 1081, p. 238.
5. Bystrova, A.V., Parshina, E.V., Tatarinova, E.A., Buzin, M.I., Ozerina, P.A., Ozerin, A.N., and Muzafarov, A.M., *Ros. Nanotekhnologii*, 2007, vol. 2, p. 83.
6. Liang, C. and Frechet, J.M.J.. *Prog. Polym. Sci*., 2005, vol. 30, p. 385.
7. Astruc, D. and Chardac, F. *Chem. Rev*., 2001, vol. 101, p. 2991.
8. Mery, D. and Astruc, D., *Coord. Chem. Rev*., 2006, vol. 250, p. 1965.
9. Kabir, A., Hamlet, C., Newkome, G.R., Yoo, K.S., and Malic, A., *J. Chromatography, A,* 2004, vol. 1034, p. 1.
10. Breslow, R., Wei, S., and Kenesky, C., *Tetrahedron*, 2007, vol. 63, p. 6317.
11. Peerlings, H.W.I., Struijk, M.P., and Meijer, E.W., *Chirality*, 1998, vol. 10, p. 46.
12. Seebach, D., Rheiner, P. B., Greiveldinger, G., Butz, T., and Sellner, H., *Top. Curr. Chem.,* 1998, vol. 197, p. 125.
13. Pugh, V.J., Hu, Q.-S., and Pu, L., *Angew Chem., Int. Ed*., 2000, vol. 39, p. 3638.
14. Kluger, R. and Zhang, J., *J. Am. Chem. Soc*., 2003, vol. 125, p. 6070.
15. Yamagata, M., Kawano, T., Shiba, K., Mori, T., Katayama, Y., and Niidome, T., *Bioorg. Med. Chem. Lett*., 2007, vol. 15, p. 526.
16. Haba, K., Popkov, M., Shamis, M., Lerner, R.A., Barbas, III, C.F., and Shabat, D., *Angew. Chem., Int. Ed*., 2005, vol. 44, p. 716.
17. Kollner, C. and Togni, A., *Canad. J. Chem*., 2001, vol. 79, p. 1762.
18. Imbos, R., Minnaard, A.J., and Feringa, B.L., *J. Chem. Soc., Dalton, Trans*., 2003, p. 2017.
19. Breinbauer, R. and Jacobsen, E.N., *Angew Chem., Int. Ed*., 2000, vol. 41, p. 3123.
20. Tang, W.J., Huang, Y.-Y., He, Y.-M., and Fan, Q.H., *Tetrahedron Asymmetry*, 2006, vol. 17, p. 536.
21. Maraval, V., Pyzowski, J., Caminade, A.-M., and Majoral, J.-P., *J. Org. Chem*., 2003, vol. 68, p. 6043.
22. Laurent, R., Caminade, A.-M., and Majoral, J.-P., *Tetrahedron Lett*., 2005, vol. 46, p. 6503.
23. Loim, N.M. and Kelbysheva, E.S., *Izv. Akad. Nauk, Ser. Khim*., 2004, p. 1995.