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Synthesis of Chiral Azomethines Starting from L-Valine Methyl Ester Hydrochloride and Substituted Benzaldehydes of Vanillin Series

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Abstract—A preparative method of synthesis of chiral azomethines was developed consisting in the reaction of L-valine methyl ester hydrochloride reaction with substituted benzaldehydes of vanillin series.

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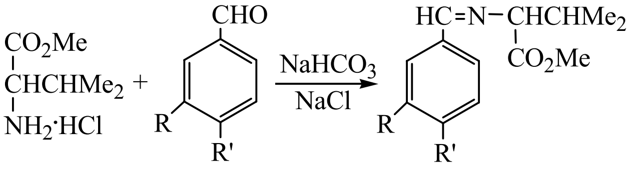
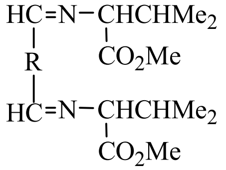
L-Valine methyl ester hydrochloride (**I**) may serve as a con-venient and available synthon for the synthesis of chiral nitrogen-containing organic compounds [1–3]. Many among the derivatives of natural amino acids derivatives , in particular, of N-[*O*-(C)-carboranyl]alanine, exhibit high antibacterial and antitumor action [4].

The condensation of L-valine methyl ester hydrochloride (**I**) with substituted benzaldehydes **II** in the presence of sodium hydrogen carbonate (at the stoichiometric reagents ratio 1 : 1 : 1) afforded new chiral alkylaromatic azomethines (Schiff bases) containing ether and ester groups **IIIa–IIIx, IVa–IVn, V, VIa, VIb**. The condensation was carried out at boiling the mixture of initial reagents in anhydrous methanol for 30–45 min. Chiral alkylaromatic azomethines **IIIa–IIIx, IVa–IVn, V, VIa, VIb** were obtained in preparative yields 78–89%.



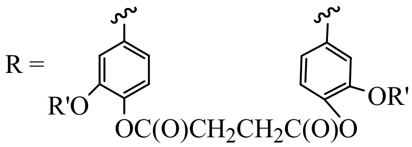
I **II** **IIIa–IIIx, IVa–IVn**

III, R = R’ = H (**a**); R = H, R' = MeO (**b**); R = MeO, R' = HO (**c**), MeO (**d**), MeC(O)O (**e**), EtC(O)O (**f**), PrC(O)O (**g**), $Me_2CHC(O)O$ (**h**), BuC(O)O (**i**), $Me_2CHCH_2C(O)O$ (**j**), $Me(CH_2)_6C(O)O$ (**k**), $Me(CH_2)_8C(O)O$ (**l**), $Me(CH_2)_{16}C(O)O$ (**m**), $H_2C=C(Me)C(O)O$ (**n**), $C_6H_5CH(Me)CH_2C(O)O$ (**o**), $C_6H_5C(O)O$ (**p**), 2,4-$Cl_2C_6H_3C(O)O$ (**q**), 4-$BrC_6H_4C(O)O$ (**r**), 3-$O_2NC_6H_4C(O)O$ (**s**), MeOC(O)O (**t**), EtOC(O)O (**u**), 1-AdC(O)O (**v**), *o*-$HCB_{10}H_{10}CC(O)O$ (**w**), *m*-$HCB_{10}H_{10}CC(O)O$ (**x**); **IV**, R = EtO, R’ = HO (**a**), MeO (**b**), MeC(O)O (**c**), EtC(O)O (**d**), PrC(O)O (**e**), $Me_2CHC(O)O$ (**f**), BuC(O)O (**g**), $Me_2CHCH_2C(O)O$ (**h**), 4-$MeC_6H_4C(O)O$ (**i**), MeOC(O)O (**j**), EtOC(O)O (**k**), 1-AdC(O)O (**l**), *o*-$HCB_{10}H_{10}CC(O)O$ (**m**), *m*-$HCB_{10}H_{10}CC(O)O$ (**n**).



V, VIa, VIb

R = 4,4'-$C_6H_4C_6H_4$ (**V**);



R' = Me (**VIa**), Et (**VIb**).

The obtained azomethines **IIIa–IIIx, IVa–IVn, V, VIa, VIb** are colorless or weakly colored thick oily fluids or crystalline substances, they do not require additional purification and are free of impurities of the initial compounds. The composition and structure of azomethines

IIIa–IIIx, IVa–IVn, V, VIa, VIb were proved by IR, UV, ^{1}H NMR spectra, elemental analysis, and cryoscopic measurement of the molecular weight. According to ^{1}H NMR spectra the purity of compounds obtained reached 94 ± 2%.

In the IR spectra of azomethines **IIIa–IIIx, IVa–IVn, V, VIa, VIb** the following characteristic absorption bands were observed, ν, cm^{-1}: 3080–3000, 870–620 (CH_{arom}), 2995–2825 (CH_{aliph}), 1770–1739 ($C{=}O_{ester}$) (**IIIe–IIIx, IVc–IVn, VIa, VIb**); 1643–1637 (C=N), 1607–1417 ($C{=}C_{arom}$), 1270–1033 (C–O) cm^{-1}. In the IR spectrum of compound **IIIs** the presence of NO_2 group was confirmed by the characteristic absorption bands in the region 1531 and 1348 cm^{-1}. In the IR spectra of carborane-containing azomethines **IIIw, IIIx, IVv, IVn** the absorption bands of $C–H_{carborane}$ appeared at 3070 (**IIIw, IVm**) and 3032 (**IIIx, IVn**); of B–H, at 2680–2660 cm^{-1}.

In the UV spectra of compounds **IIIe–IIIx, IVc–IVn, VIa, VIb** characteristic absorption maxima are observed at λ_{max}, nm (e): 208 (13000), 220 (13000), 254 (9000), 300 (400) due to the presence in these molecules of the fragments of methyl (*E,S*)-2-(4-acyloxy-3-alkoxybenzylideneamino)-3-methybutyrate.

The ^{1}H NMR spectra of azomethines **IIIa–IIIx, IVa–IVn, V, VIa, VIb** contain the signals of protons from Me_2C group as two doublets in the region 0.80–1.10 ppm, signals of CH_{aliph} as two multiplets in the region 2.15–2.60 and 3.30–3.70 ppm, signals of CO_2Me as a singlet in the range 3.65–3.75 ppm. In the ^{1}H NMR spectra of azomethines **IIIb–IIIx, IVb, VIa** the signals of MeO group appear as a singlet in the range 3.74–3.80 ppm, in the spectra of compounds **IVa–IVn, VIb** the protons of EtO groups give rise to a triplet in the range 0.90–1.30 ppm (Me) and a quartet at 3.80–4.20 ppm (CH_2). The signals of the aromatic protons in the spectra of compounds **IIIa–IIIx, IVa–IVn, V, VIa, VIb** are observed in the region 6.80–7.50 ppm, the protons of the azomethine group HC=N appear as a singlet in the region 8.11– 8.22 ppm characteristic of (*E*)- azomethines [5].

In the IR, UV, and ^{1}H NMR spectra of azomethines **IIIa–IIIx, IVa–IVn, V, VIa, VIb** the appropriate absorption bands and proton signals prove the presence of the structural fragments of ester groups [6].

EXPERIMENTAL

IR spectra of compounds were recorded on FTIR spectrophotometer Nicolet Protege-460 from thin films or in KBr pellets, UV spectra, on spectrophotometer Specord UV Vis from 1×10^{-4} M solution of compounds in methanol, ^{1}H NMR spectra were registered on a spectrometer Tesla BS-587A (100 MHz) from 5% solutions in deuterochloroform or DMSO-d_6, intertnal reference TMS. The specific rotation was measured on a CM-2 instrument from 5% solutions of substances in methanol. Elemental analyses were carried out on a C,H,N,O,S-analyzer Elementar Vario EL-III, accuracy of the measurements 0.1%. The molecular weights were determined by cryoscopy in benzene.

L-Valine methyl ester hydrochloride (**I**) used in the research was of "pure for analysis" grade (purity 98%), mp 171–172°C, $[\alpha]_D^{20}$ +23.4°. Vanillin and vanillal esters **II** were obtained by procedures [7–12].

Chiral alkylaromatic azomethins containing ether and ester groups IIIa–IIIx, IVa–IVn. A mixture of 5 mmol of L-valine methyl ester hydrochloride (**I**), 5 mmol of substituted benzaldehyde **II**, and 5 mmol of sodium hydrogen carbonate in 39 ml of anhydrous methanol was boiled for 30–45 min. The hot solution was filtered through a folded paper filter, the solvent was removed in a vacuum. Azomethines **IIIa–IIIx, IVa–IVn** were dissolved in 10 ml of anhydrous ethyl ether, the solution was filtered through a folded paper filter, the solvent was removed in a vacuum. The final purification was performed by column chromatography on neutral aluminum oxide, 40–100 μm, II grade Brockmann activity, eluent dichloromethane.

Methyl (*E,S*)-2-benzylideneamino-3-methylbutyrate (IIIa). Yield 84%, d_{20}^{20} 1.2630, n_D^{20} 1.5212, $[\alpha]_D^{20}$ –41.1°. Found, %: C 71.54; H 7.88; N 6.12. *M* 210.4. $C_{13}H_{17}NO_2$. Calculated, %: C 71.21; H 7.81; N 6.39. *M* 219.3.

Methyl (*E,S*)-3-methyl-2-(4-methoxybenzylideneamino)-butyrate (IIIb). Yield 88%, d_{20}^{20} 1.2801, n_D^{20} 1.5296, $[\alpha]_D^{20}$ –50.4°. Found, %: C 67.59; H 7.83; N 5.36. *M* 235.2. $C_{14}H_{19}NO_3$. Calculated, %: C 67.45; H 7.68; N 5.62. *M* 249.3.

Methyl (*E,S*)-2-(4-hydroxy-3-methoxy-benzylideneamino)-3-methylbutyrate (IIIc). Yield 78%, d_{20}^{20} 1.2864, n_D^{20} 1.5568, $[\alpha]_D^{20}$ –38.5°. Found, %: C 63.52; H 7.29; N 4.93. *M* 252.7. $C_{14}H_{19}NO_4$. Calculated, %: C 63.38; H 7.22; N 5.28. *M* 265.3.

Methyl (*E,S*)-2-(3,4-dimethoxybenzylideneamino)-3-methylbutyrate (IIId). Yield 89%, d_{20}^{20} 1.2814, n_D^{20} 1.5338, $[\alpha]_D^{20}$ –36.8°. Found, %: C 64.80; H 7.64;

N 4.85. *M* 270.5. $C_{15}H_{21}NO_4$. Calculated, %: C 64.50; H 7.58; N 5.01. *M* 279.3.

Methyl (*E*,*S*)-2-(4-acetyloxy-3-methoxybenzylideneamino)-3-methylbutyrate (IIIe). Yield 85%, d_{20}^{20} 1.2410, n_D^{20} 1.5192, $[\alpha]_D^{20}$ –32.7°. Found, %: C 62.53; H 6.89; N 4.56. *M* 299.6. $C_{16}H_{21}NO_5$. Calculated, %: C 62.53; H 6.89; N 4.56. *M* 307.3.

Methyl (*E*,*S*)-3-methyl-2-(3-methoxy-4-propionyloxybenzylideneamino)butyrate (IIIf). Yield 88%, d_{20}^{20} 1.2365, n_D^{20} 1.5198, $[\alpha]_D^{20}$ –31.0°. Found, %: C 63.86; H 7.35; N 4.07. *M* 314.8. $C_{17}H_{23}NO_5$. Calculated, %: C 63.54; H 7.21; N 4.36. *M* 321.4.

Methyl (*E*,*S*)-2-(4-butyryloxy-3-methoxybenzylideneamino)-3-methylbutyrate (IIIg). Yield 88%, d_{20}^{20} 1.2280, n_D^{20} 1.5084, $[\alpha]_D^{20}$ –27.2°. Found, %: C 64.72; H 7.68; N 3.85. *M* 321.0. $C_{18}H_{25}NO_5$. Calculated, %: C 64.46; H 7.51; N 4.18. *M* 335.4.

Methyl (*E*,*S*)-2-(4-isobutyryloxy-3-methoxybenzylidene-amino)-3-methylbutyrate (IIIh). Yield 82%, d_{20}^{20} 1.2212, n_D^{20} 1.4988, $[\alpha]_D^{20}$ –25.9°. Found, %: C 64.58; H 7.60; N 3.89. *M* 322.4. $C_{18}H_{25}NO_5$. Calculated, %: C 64.46; H 7.51; N 4.18. *M* 335.4.

Methyl (*E*,*S*)-2-(4-valeroyloxy-3-methoxybenzylideneamino)-3-methylbutyrate (IIIi). Yield 85%, d_{20}^{20} 1.1840, n_D^{20} 1.5125, $[\alpha]_D^{20}$ –24.6°. Found, %: C 65.70; H 7.85; N 3.80. *M* 334.3. $C_{19}H_{27}NO_5$. Calculated, %: C 65.31; H 7.79; N 4.01. *M* 349.4.

Methyl (*E*,*S*)-2-(4-isovaleroyloxy-3-methoxybenz-ylideneamino)-3-methylbutyrate (IIIj). Yield 84%, d_{20}^{20} 1.1748, n_D^{20} 1.4926, $[\alpha]_D^{20}$ –25.2°. Found, %: C 65.76; H 7.92; N 3.82. *M* 335.1. $C_{19}H_{27}NO_5$. Calculated, %: C 65.31; H 7.79; N 4.01. *M* 349.4.

Methyl (*E*,*S*)-2-(4-capryloyloxy-3-methoxybenzylideneamino)-3-methylbutyrate (IIIk). Yield 81%, d_{20}^{20} 1.1730, n_D^{20} 1.4944, $[\alpha]_D^{20}$ –22.3°. Found, %: C 67.12; H 8.34; N 3.46. *M* 368.2. $C_{21}H_{31}NO_5$. Calculated, %: C 66.82; H 8.28; N 3.71. *M* 377.5.

Methyl (*E*,*S*)-2-(4-decanoyloxy-3-methoxybenzylideneamino)-3-methylbutyrate (IIIl). Yield 83%, d_{20}^{20} 1.1645, n_D^{20} 1.4972, $[\alpha]_D^{20}$ –21.7°. Found, %: C 68.37; H 8.82; N 3.18. *M* 389.5. $C_{23}H_{35}NO_5$. Calculated, %: C 68.12; H 8.70; N 3.45. *M* 405.5.

Methyl (*E*,*S*)-3-methyl-2-(3-methoxy-4-stearoyloxy-benzylideneamino)butyrate (IIIm). Yield 80%, mp 37–38°C (methanol), $[\alpha]_D^{20}$ –17.4°. Found, %: C 72.23; H 10.07; N 2.49. *M* 501.6. $C_{31}H_{51}NO_5$. Calculated, %: C 71.91; H 9.93; N 2.71. *M* 517.7.

Methyl (*E*,*S*)-2-(4-methacryloyloxy-3-methoxybenzylideneamino)-3-methylbutyrate (IIIn). Yield 84%, d_{20}^{20} 1.210, n_D^{20} 1.5130, [$[\alpha]_D^{20}$ –30.3°. Found, %: C 65.14; H 7.08; N 4.13. *M* 324.8. $C_{18}H_{23}NO_5$. Calculated, %: C 64.85; H 6.95; N 4.20. *M* 333.4.

Methyl (*E*,*S*)-3-methyl-2-[3-methoxy-4-(3-phenyl-butyryloxy)benzylideneamino]-butyrate (IIIo). Yield 84%, d_{20}^{20} 1.2303, n_D^{20} 1.5352, $[\alpha]_D^{20}$ –21.8°. Found, %: C 70.26; H 7.25; N 3.06. *M* 401.2. $C_{24}H_{29}NO_5$. Calculated, %: C 70.05; H 7.10; N 3.40. *M* 411.5.

Methyl (*E*,*S*)-2-(4-benzoyloxy-3-methoxybenzylideneamino)-3-methylbutyrate (IIIp). Yield 89%, d_{20}^{20} 1.2415, n_D^{20} 1.5512, $[\alpha]_D^{20}$ –25.3°. Found, %: C 68.47; H 6.38; N 3.37. *M* 355.7. $C_{21}H_{23}NO_5$. Calculated, %: C 68.28; H 6.28; N 3.79. *M* 369.4.

Methyl (*E*,*S*)-2-[4-(2,4-dichlorobenzoyloxy)-3-methoxy-benzylideneamino]-3-methylbutyrate (IIIq). Yield 83%, d_{20}^{20} 1.3419, n_D^{20} 1.5578, $[\alpha]_D^{20}$ –20.6°. Found, %: C 57.84; H 4.82; Cl 15.85; N 2.93. *M* 419.1. $C_{21}H_{21}Cl_2NO_5$. Calculated, %: C 57.55; H 4.83; Cl 16.18; N 3.20. *M* 438.3.

Methyl (*E*,*S*)-2-[4-(4-bromobenzoyloxy)-3-methoxy-benzylideneamino]-3-methyl-butyrate (IIIr). Yield 85%, d_{20}^{20} 1.3503, n_D^{20} 1.5668, $[\alpha]_D^{20}$ –21.4°. Found, %: C 56.61; H 5.07; Br 17.36; N 2.90. *M* 425.8. $C_{21}H_{22}BrNO_5$. Calculated, %: C 56.26; H 4.95; Br 17.82; N 3.12. *M* 448.3.

Methyl (*E*,*S*)-3-methyl-2-[-3-methoxy-4-(3-nitrobenzoyl-oxy)benzylideneamino]butyrate (IIIs). Yield 80%, mp 73–74°C, $[\alpha]_D^{20}$ –19.7°. Found, %: C 61.11; H 5.38; N 6.43. *M* 402.6. $C_{21}H_{22}N_2O_7$. Calculated, %: C 60.86; H 5.35; N 6.76. *M* 414.4.

Methyl (*E*,*S*)-3-methyl-2-(4-methoxycarbonyloxy-3-methoxybenzylideneamino)butyrate (IIIt). Yield 79%, d_{20}^{20} 1.2246, n_D^{20} 1.5065, $[\alpha]_D^{20}$ –32.5°. Found, %: C 59.84; H 6.70; N 4.02. *M* 316.5. $C_{16}H_{21}NO_6$. Calculated, %: C 59.43; H 6.55; N 4.33; *M* 323.3.

Methyl (*E*,*S*)-3-methyl-2-(-3-methoxy-4-ethoxycarbonyloxybenzylideneamino)butyrate (IIIu). Yield 82%, d_{20}^{20} 1.2204, n_D^{20} 1.5048, $[\alpha]_D^{20}$ –30.4°. Found, %: C 60.88; H 6.94; N 3.81. *M* 322.0. $C_{17}H_{23}NO_6$. Calculated, %: C 60.52; H 6.87; N 4.15. *M* 337.4.

Methyl (*E*,*S*)-2-[4-(1-adamantanemethanoyloxy)-

3-methoxybenzylideneamino]-3-methylbutyrate (IIIv). Yield 88%, mp 60–61°C, $[\alpha]_D^{20}$ –26.6°. Found, %: C 70.56; H 7.99; N 2.97. *M* 412.5. $C_{25}H_{33}NO_5$. Calculated, %: C 70.23; H 7.78; N 3.28. *M* 427.5.

Methyl (*E*,*S*)-2-[4-(*O*-carborane-C-methanoyloxy)-3-methoxybenzylideneamino]-3-methylbutyrate (IIIw). Yield 83%, mp 76–77°C, $[\alpha]_D^{20}$ –21.7°. Found, %: C 48.25; H 4.52; B 25.12; N 2.93. *M* 405.6. $C_{17}H_{19}B_{10}NO_5$. Calculated, %: C 47.99; H 4.50; B 25.41; N 3.29. *M* 425.4.

Methyl (*E*,*S*)-2-[4-(*μ*-carborane-C-methanoyloxy)-3-methoxybenzylideneamino]-3-methylbutyrate (IIIx). Yield 80%, mp 85–86°C, $[\alpha]_D^{20}$ –22.5 $[\alpha]_D^{20}$. Found, %: C 48.34; H 4.59; B 25.02; N 2.98. *M* 410.2. $C_{17}H_{19}B_{10}NO_5$. Calculated, %: C47.99; H 4.50; B 25.41; N 3.29. *M* 425.4.

Methyl (*E*,*S*)-2-(4-hydroxy-3-ethoxy-benzylideneamino)-3-methylbutyrate (IVa). Yield 80%, d_{20}^{20} 1.2835, n_D^{20} 1.5362, $[\alpha]_D^{20}$ –36.5°. Found, %: C 64.57; H 7.66; N 4.82. *M* 265.4. $C_{15}H_{21}NO_4$. Calculated, %: C 64.50; H 7.58; N 5.01. *M* 279.3.

Methyl (*E*,*S*)-3-methyl-2-(4-methoxy-3-ethoxybenzylideneamino)butyrate (IVb). Yield 83%, d_{20}^{20} 1.2663, n_D^{20} 1.5255, $[\alpha]_D^{20}$ –38.1°. Found, %: C 65.70; H 8.00; N 4.34. *M* 281.4. $C_{16}H_{23}NO_4$. Calculated, %: C 65.51; H 7.90; N 4.77. *M* 293.4.

Methyl (*E*,*S*)-2-(4-acetyloxy-3-ethoxybenzylideneamino)-3-methylbutyrate (IVc). Yield 88%, d_{20}^{20} 1.2370, n_D^{20} 1.5208, $[\alpha]_D^{20}$ –37.2°. Found, %: C 63.80; H 7.32; N 4.02. *M* 313.2. $C_{17}H_{23}NO_5$. Calculated, %: C 63.54; H 7.21; N 4.36. *M* 321.4.

Methyl (*E*,*S*)-3-methyl-2-(4-propionyloxy-3-oxybenzylideneamino)butyrate (IVd). Yield 87%, d_{20}^{20} 1.2342, n_D^{20} 1.5036, $[\alpha]_D^{20}$ –36.8°. Found, %: C 64.67; H 7.68; N 3.95. *M* 362.3. $C_{18}H_{25}NO_5$. Calculated, %: C 64.46; H 7.51; N 4.18. *M* 335.4.

Methyl (*E*,*S*)-2-(4-butyryloxy-3-ethoxybenzylideneamino)-3-methylbutyrate (IVe). Yield 82%, d_{20}^{20} 1.2235, n_D^{20} 1.5070, $[\alpha]_D^{20}$ –34.0°. Found, %: C 65.67; H 7.86; N 3.83. *M* 335.3. $C_{19}H_{27}NO_5$. Calculated, %: C 65.31; H 7.79; N 4.01. *M* 349.4.

Methyl (*E*,*S*)-2-(4-isobutyryloxy-3-ethoxybenzylidene-amino)-3-methylbutyrate (IVf). Yield 86%, d_{20}^{20} 1.2206, n_D^{20} 1.5012, $[\alpha]_D{}^{20}$ –27.5°. Found, %: C 65.63; H 7.82; N 3.80. *M* 339.4. $C_{19}H_{27}NO_5$. Calculated, %: C 65.31; H 7.79; N 4.01. *M* 349.4.

Methyl (*E*,*S*)-2-(4-valeroyloxy-3-ethoxybenzylidene-amino)-3-methylbutyrate (IVg). Yield 86%, d_{20}^{20} 1.1817, n_D^{20} 1.5170, $[\alpha]_D^{20}$ –25.6°. Found, %: C 66.36; H 8.27; N 3.61. *M* 349.5. $C_{20}H_{29}NO_5$. Calculated, %: C 66.09; H 8.04; N 3.85. *M* 363.4.

Methyl (*E*,*S*)-2-(4-isovaleroyloxy-3-ethoxybenzylidene-amino)-3-methylbutyrate (IVh). Yield 85%, d_{20}^{20} 1.1714, n_D^{20} 1.5028, $[\alpha]_D^{20}$ –24.8°. Found, %: C 66.31; H 8.20; N 3.52. *M* 351.6. $C_{20}H_{29}NO_5$. Calculated, %: C 66.09; H 8.04; N 3.85. *M* 363.4.

Methyl (*E*,*S*)-3-methyl-2-[4-(4-methyl-benzoyloxy)-3-ethoxybenzylideneamino]butyrate (IVi). Yield 85%, d_{20}^{20} 1.2226, n_D^{20} 1.5490, $[\alpha]_D^{20}$ –20.3°. Found, %: C 69.64; H 6.97; N 3.19. *M* 385.8. $C_{23}H_{27}NO_5$. Calculated, %: C 69.50; H 6.85; N 3.52. *M* 397.5.

Methyl (*E*,*S*)-2-{[4-(methoxycarbonyl)oxy]-3-ethoxybenzylideneamino}-3-methylbutyrate (IVj). Yield 80%, d_{20}^{20} 1.2208, n_D^{20} 1.5090, $[\alpha]_D^{20}$ –34.8°. Found, %: C 60.80; H 6.99; N 3.92. *M* 328.3. $C_{17}H_{23}NO_6$. Calculated, %: C 60.52; H 6.87; N 4.15. *M* 337.4.

Methyl (*E*,*S*)-3-methyl-2-(3-ethoxy-4-ethoxycarbonyl-oxybenzylideneamino)butyrate (IVk). Yield 82%, d_{20}^{20} 1.2168, n_D^{20} 1.5060, $[\alpha]_D^{20}$ –32.5°. Found, %: C 61.87; H 7.23; N 3.76. *M* 337.4. $C_{18}H_{25}NO_6$. Calculated, %: C 61.52; H 7.17; N 3.99. *M* 351.4.

Methyl (*E*,*S*)-2-[4-(1-adamantanemethanoyloxy)-3-ethoxybenzylideneamino]-3-methylbutyrate (IVl). Yield 86%, d_{20}^{20} 1.2658, n_D^{20} 1.5280, $[\alpha]_D^{20}$ –21.0°. Found, %: C 70.93; H 8.13; N 2.90. *M* 428.7. $C_{26}H_{35}NO_5$. Calculated, %: C 70.72; H 7.99; N 3.17. *M* 441.6.

Methyl (*E*,*S*)-2-[4-(*O*-carborane-C-methanoyloxy)-3-ethoxybenzylideneamino]-3-methylbutyrate (IVm). Yield 80%, mp 70–71°C, $[\alpha]_D^{20}$ –19.7°. Found, %: C 49.46; H 5.06; B 24.18; N 2.90. *M* 418.7. $C_{18}H_{21}B_{10}NO_5$. Calculated, %: C 49.19; H 4.82; B 24.60; N 3.19. *M* 439.5.

Methyl (*E*,*S*)-2-[4-(*m*-carborane-C-methanoyloxy)-3-ethoxybenzylideneamino]-3-methylbutyrate (IVn). Yield 81%, mp 79–80°C, $[\alpha]_D^{20}$ –19.1°. Found, %: C 49.50; H 5.03; B 24.11; N 2.92. *M* 422.3. $C_{18}H_{21}B_{10}NO_5$. Calculated, %: C 49.19; H 4.82; B 24.60; N 3.19. *M* 439.5.

Diazomethines V, VIa, VIb were obtained and isolated analogously to compounds **IIIa–IIIx, IVa–IVn**. A mixture of 10 mmol of compound I, 5 of dialdehyde, and 10 mmol of sodium hydrogen carbonate in 50 ml of anhydrous methanol was boiled for 45 min.

Dimethyl (*S*,*S*)-2,2'-{biphenyl-4,4'-diylbis[(*E*)-

methylidenenitrilo]}-3,3'-dimethyldibutanoate (V). Yield 84%, mp 124–125°C, $[\alpha]_D^{20}$ –62.6°. Found, %: C 71.69; H 7.52; N 6.14. *M* 415.9. $C_{26}H_{32}N_2O_4$. Calculated, %: C 71.53; H 7.39; N 6.42. *M* 436.5.

Di[2-methoxy-4-(*E*,*S*)-(2-methyl-1-methoxy-carbonyl-propyliminomethyl)phenyl]succinate (VIa). Yield 87%, mp 67–68°C, $[\alpha]_D^{20}$ –40.3°. Found, %: C 62.95; H 6.59; N 4.18. *M* 598.2. $C_{32}H_{40}N_2O_{10}$. Calculated, %: C 62.73; H 6.58; N 4.57. *M* 612.7.

Di[4-(*E*,*S*)-(2-methyl-1-methoxycarbonyl-propyliminomethyl)-2-ethoxyphenyl]succinate (VIb). Yield 83%, mp 62–63°C, $[\alpha]_D^{20}$ –39.1°. Found, %: C 64.16; H 7.08; N 4.05. *M* 618.5. $C_{34}H_{44}N_2O_{10}$. Calculated, %: C 63.74; H 6.92; N 4.37. *M* 640.7.

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