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Synthesis of *N*-[4-Hydroxy(alkoxy, acyloxy)-3-alkoxybenzylidene]-1-(1-adamantyl)ethanamines from 1-(1-Adamantyl)ethanamine Hydrochloride (Rimantadine)

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Abstract—Reactions of 1-(1-adamantyl)ethanamine with vanillin, vanillal, veratraldehyde, 3-ethoxy-4-methoxybenzaldehyde, and 4-formyl-2-methoxy(ethoxy)phenyl esters gave previously unknown Schiff bases containing an adamantane fragment.

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Adamantane derivatives most of which are nitrogen-containing compounds constitute one of the main groups of antiviral agents [1]. In particular, 1-(1-adamantyl)ethanamine hydrochloride (Rimantadine) is the most potent among anti-influenza drugs [2–4]. Much effort is put to the development of convenient methods of synthesis of adamantane derivatives containing pharmacophoric fragments with the goal of searching for new biologically active substances [5–7].

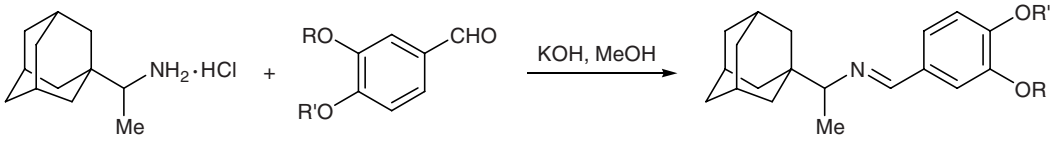
The present study was aimed at synthesizing new Schiff bases on the basis of commercially available 1-(1-adamantyl)ethanamine hydrochloride (**I**, Rimantadine) and substituted aromatic aldehydes **II**, such as vanillin and its derivatives (vanillal, veratraldehyde, 3-ethoxy-4-methoxybenzaldehyde, and specially prepared esters derived from vanillin and vanillal and carboxylic acids) [8–11]. 1-(1-Adamantyl)ethanamine hydrochloride was converted into the corresponding base by treatment with solid potassium hydroxide in anhydrous ethanol in the presence of phenolphthalein as indicator and was brought into condensation with aldehydes **II** on heating in boiling anhydrous ethanol. The reaction was complete in 5–10 min, and mild conditions of the process (no catalyst, pH ~7) ensured conservation of the ester groups that are sensitive to hydrolysis and alcoholysis. The yields of Schiff bases **IIIa**–**IIIt** and **IVa**–**IVj** were 80–92% (Scheme 1).

The structure of compounds **IIIa**–**IIIt** and **IVa**–**IVj** was confirmed by the analytical data, determination of their molecular weight by cryoscopy, and ^{1}H NMR, IR, and UV spectra. According to the ^{1}H NMR data, Schiff bases **IIIa**–**IIIt** and **IVa**–**IVj** were isolated as pure *E* isomers [12, 13] containing 97±1% of the main substance.

EXPERIMENTAL

The IR spectra were recorded on a Nicolet Protege-460 spectrometer with Fourier transform from samples prepared as thin films or KBr pellets. The UV spectra

Scheme 1.



I **II** **IIIa–IIIt, IVa–IVj**

III, R = Me, R′ = H (**a**), Me (**b**), MeC(O) (**c**), EtC(O) (**d**), PrC(O) (**e**), $Me_2CHC(O)$ (**f**), $Me(CH_2)_6C(O)$ (**g**), $Me(CH_2)_8C(O)$ (**h**), $Me(CH_2)_{16}C(O)$ (**i**), $H_2C{=}C(Me)C(O)$ (**j**), $PhCH_2C(O)$ (**k**), $PhCH(Me)CH_2C(O)$ (**l**), PhC(O) (**m**), 4-$MeC_6H_4C(O)$ (**n**), 4-$ClC_6H_4C(O)$ (**o**), 2,4-$Cl_2C_6H_3C(O)$ (**p**), 4-$BrC_6H_4C(O)$ (**q**), 3-$O_2NC_6H_4C(O)$ (**r**), MeOC(O) (**s**), EtOC(O) (**t**); **IV**, R = Et, R′ = H (**a**), Me (**b**), MeC(O) (**c**), EtC(O) (**d**), PrC(O) (**e**), $Me_2CHC(O)$ (**f**), $Me_2CHCH_2C(O)$ (**g**), 4-$MeC_6H_4C(O)$ (**h**), MeOC(O) (**i**), EtOC(O) (**j**).

were measured on a Specord UV-Vis spectrophotometer from 1×10^{-4} M solutions in ethanol. The ^{1}H NMR spectra were obtained on a Tesla BS-587A instrument (100 MHz) from 5% solutions in $CDCl_3$ using TMS as internal reference. The molecular weights were determined by cryoscopy in benzene.

General procedure for the synthesis of *N*-[4-hydroxy(alkoxy, acyloxy)-3-alkoxybenzylidene]-1-(1-adamantyl)ethanamines IIIa–IIIt and IVa–IVj. 1-(1-Adamantyl)ethanamine hydrochloride (**I**), 0.002 mol, was dissolved in 20 ml of anhydrous ethanol, ~0.002 mol of 90% solid potassium hydroxide and 0.1 mg of phenolphthalein (indicator) were added, the mixture was heated for 10–15 min under reflux, and excess alkali was neutralized by adding a few drops (1–2) of glacial acetic acid until the crimson color disappeared. The corresponding aldehyde **II**, 0.002 mol, was then added in one portion, and the mixture was heated for 5–10 min under reflux and filtered while hot to separate KCl. The filtrate was left to stand for 20–30 h at 5–10°C. Schiff bases **IIIa**–**IIIt** and **IVa**–**IVj** separated from the solution as crystalline or oily substances. The products were separated by filtration or decanting, washed with a small amount of 40% aqueous ethanol, and dried under reduced pressure. Compounds **IIIa**–**IIIt** and **IVa**–**IVj** were sufficiently pure, and no additional purification was required.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenol (IIIa). Yield 90%, vitreous substance. IR spectrum, ν, cm^{-1}: 3450 (OH); 3060, 3009 (=C–H, C–H_{arom}); 2973, 2930, 2903, 2847 (C–H_{aliph}); 1642 (C=N); 1593, 1514, 1452, 1360 (C–C_{arom}); 1283, 1239, 1155, 1124, 1033 (C–O); 870, 850, 820, 780, 740 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 208 (11), 225 (10), 270 (10), 300 (6). ^{1}H NMR spectrum, δ, ppm: 1.12 d (3H, Me), 1.40–2.10 m (15H, Ad), 2.82 q (1H, CH), 3.96 s (3H, MeO), 6.80 br.s (1H, OH), 6.84–7.45 m (3H, C_6H_3), 8.09 s (1H, HC=N). Found, %: C 77.08; H 8.83; N 4.45. *M* 304.6. $C_{20}H_{27}NO_2$. Calculated, %: C 76.64; H 8.68; N 4.67. *M* 313.4.

1-(1-Adamantyl)-*N*-(3,4-dimethoxybenzylidene]-ethanamine (IIIb). Yield 89%, vitreous substance. IR spectrum, ν, cm^{-1}: 3080, 3004 (=C–H, C–H_{arom}); 2964, 2935, 2903, 2846 (C–H_{aliph}); 1643 (C=N); 1601, 1586, 1513, 1464, 1451, 1419, 1360 (C–C_{arom}); 1268, 1237, 1159, 1139, 1028 (C–O); 873, 854, 812, 752 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 208 (12), 225 (11), 270 (10), 304 (6). ^{1}H NMR spectrum, δ, ppm: 1.13 d (3H, Me), 1.52–2.22 m (15H, Ad), 2.84 q (1H, CH), 3.92 s and 3.96 s (3H each, MeO), 6.80–7.45 m (3H, C_6H_3), 8.11 s (1H, HC=N). Found, %: C 77.24; H 9.12; N 3.90. *M* 318.1. $C_{21}H_{29}NO_2$. Calculated, %: C 77.03; H 8.93; N 4.28. *M* 327.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl acetate (IIIc). Yield 83%, mp 112–113°C (from ethanol). IR spectrum, ν, cm^{-1}: 3080, 3045, 3003 (=C–H, C–H_{arom}); 2977, 2940, 2900, 2846 (CH_{aliph}); 1767 (C=O); 1641 (C=N); 1601, 1590, 1509, 1450, 1413, 1366 (C–C_{arom}); 1287, 1270, 1207, 1190, 1157, 1108, 1033, 1004 (C–O); 900, 875, 846, 815, 785, 760 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 209 (13), 221 (13), 255 (10), 300 (4). ^{1}H NMR spectrum, δ, ppm: 1.13 d (3H, Me), 1.54–2.12 m (15H, Ad), 2.32 s (3H, Me), 2.82 q (1H, CH), 3.90 s (3H, MeO), 6.95–7.50 m (3H, C_6H_3), 8.13 s (1H, HC=N). Found, %: C 74.51; H 8.35; N 3.55. *M* 348.3. $C_{22}H_{29}NO_3$. Calculated, %: C 74.33; H 8.22; N 3.94. *M* 355.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl propionate (IIId). Yield 88%, vitreous substance. IR spectrum, ν, cm^{-1}: 3070, 3004 (=C–H, C–H_{arom}); 2978, 2904, 2847 (C–H_{aliph}); 1766 (C=O); 1645 (C=N); 1601, 1509, 1463, 1452, 1417, 1359 (C–C_{arom}); 1273, 1195, 1139, 1077, 1035 (C–O); 885, 825, 813, 782, 754 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 208 (13), 222 (13), 255 (10), 302 (4). ^{1}H NMR spectrum, δ, ppm: 1.13 d (3H, Me), 1.26 t (3H, Me), 1.50–2.12 m (15H, Ad), 2.55–3.00 m (4H, CH, CH_2), 3.90 s (3H, MeO), 6.96–7.50 m (3H, C_6H_3), 8.16 s (1H, HC=N). Found, %: C 75.07; H 8.63; N 3.51. *M* 357.8. $C_{23}H_{31}NO_3$. Calculated, %: C 74.76; H 8.46; N 3.79. *M* 369.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl butyrate (IIIe). Yield 87%, mp 66–67°C (from ethanol). IR spectrum, ν, cm^{-1}: 3072, 3005 (=C–H, C–H_{arom}); 2966, 2940, 2907, 2847 (C–H_{aliph}); 1766 (C=O); 1646 (C=N); 1601, 1514, 1465, 1450, 1417, 1375 (C–C_{arom}); 1288, 1269, 1185, 1138, 1111, 1034 (C–O); 883, 832, 812, 785, 744 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 208 (12), 221 (13), 254 (10), 301(4). ^{1}H NMR spectrum, δ, ppm: 0.95–1.15 m (6H, Me), 1.45–2.15 m (17H, CH_2, Ad), 2.61 t (2H, CH_2), 2.88 q (1H, CH), 3.90 s (3H, MeO), 6.96–7.50 m (3H, C_6H_3), 8.16 s (1H, HC=N). Found, %: C 75.39; H 8.75; N 3.42. *M* 373.2. $C_{24}H_{33}NO_3$. Calculated, %: C 75.16; H 8.67; N 3.65. *M* 383.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl isobutyrate (IIIf). Yield 90%, vitreous substance. IR spectrum, ν, cm^{-1}: 3070, 3004 (=C–H, C–H_{arom}); 2974, 2934, 2904, 2847 (C–H_{aliph}); 1764 (C=O); 1645 (C=N); 1601, 1504, 1467, 1453, 1418,

1386 (C–C_{arom}); 1272, 1199, 1180, 1153, 1122, 1092, 1036 (C–O); 864, 820, 781, 750, 730 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε×10^{-3}): 208 (13), 222 (13), 255 (10), 302 (4). ^{1}H NMR spectrum, δ, ppm: 1.14 d (3H, Me), 1.37 d (6H, Me_2C), 1.55–2.25 m (15H, Ad), 2.70–3.07 m (2H, CH), 3.89 s (3H, MeO), 6.92–7.55 m (3H, C_6H_3), 8.13 s (1H, HC=N). Found, %: C 75.28; H 8.70; N 3.57. *M* 375.0. $C_{24}H_{33}NO_3$. Calculated, %: C 75.16; H 8.67; N 3.65. *M* 383.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl octanoate (IIIg). Yield 87%, vitreous substance. IR spectrum, ν, cm^{-1}: 3075, 3003 (=C–H, C–H_{arom}); 2970, 2932, 2905, 2848 (C–H_{aliph}); 1766 (C=O); 1646 (C=N); 1601, 1509, 1465, 1452, 1417, 1378 (C–C_{arom}); 1273, 1197, 1142, 1120, 1036 (C–O); 875, 840, 828, 780, 759, 725 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε×10^{-3}): 209 (13), 222 (13), 254 (10), 302 (4). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, Me), 1.80 d (3H, Me), 1.30–2.15 m [25H, $(CH_2)_5$, Ad], 2.62 t (2H, CH_2), 2.79 q (1H, CH), 3.89 s (3H, MeO), 6.95–7.50 m (3H, C_6H_3), 8.16 s (1H, HC=N). Found, %: C 76.86; H 9.54; N 2.99. *M* 421.7. $C_{28}H_{41}NO_3$. Calculated, %: C 76.50; H 9.40; N 3.19. *M* 439.6.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl decanoate (IIIh). Yield 86%, vitreous substance. IR spectrum, ν, cm^{-1}: 3074, 3003 (=C–H, C–H_{arom}); 2960, 2924, 2906, 2849 (C–H_{aliph}); 1766 (C=O); 1646 (C=N); 1601, 1509, 1465, 1453, 1417, 1377 (C–C_{arom}); 1273, 1197, 1139, 1094, 1036 (C–O); 877, 845, 837, 785, 760, 720 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε×10^{-3}): 209 (13), 222 (13), 254 (10), 302 (4). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, Me), 1.78 d (3H, Me), 1.30–2.15 m [29H, $(CH_2)_7$, Ad], 2.63 t (2H, CH_2), 2.78 q (1H, CH), 3.89 s (3H, MeO), 6.95–7.50 m (3H, C_6H_3), 8.16 s (1H, HC=N). Found, %: C 77.32; H 9.87; N 2.68. *M* 449.5. $C_{30}H_{45}NO_3$. Calculated, %: C 77.04; H 9.70; N 2.99. *M* 467.7.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl octadecanoate (IIIi). Yield 80%, vitreous substance. IR spectrum, ν, cm^{-1}: 3075, 3003 (=C–H, C–H_{arom}); 2955, 2922, 2850 (C–H_{aliph}); 1766 (C=O); 1644 (C=N); 1600, 1507, 1465, 1455, 1416, 1380 (C–C_{arom}); 1273, 1197, 1151, 1137, 1114, 1040 (C–O); 875, 845, 835, 815, 785, 755, 720 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε×10^{-3}): 209 (12), 222 (12), 254 (10), 304 (4). ^{1}H NMR spectrum, δ, ppm: 0.91 t (3H, Me), 1.80 d (3H, Me), 1.28–2.20 m [45H, $(CH_2)_{15}$, Ad], 2.64 t (2H, CH_2), 2.79 q (1H, CH), 3.89 s (3H, MeO), 6.95–7.52 m (3H, C_6H_3), 8.17 s (1H, HC=N). Found, %: C 80.06; H 10.82; N 2.23. *M* 560.3. $C_{38}H_{61}NO_3$. Calculated, %: C 78.71; H 10.60; N 2.42. *M* 579.9.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl methacrylate (IIIj). Yield 80%, vitreous substance. IR spectrum, ν, cm^{-1}: 3100, 3080, 3040, 3020 (=C–H, C–H_{arom}); 2966, 2940, 2904, 2847 (C–H_{aliph}); 1741 (C=O); 1645 (C=N); 1600, 1504, 1464, 1452, 1417, 1379 (C–C_{arom}); 1290, 1272, 1201, 1126, 1035 (C–O); 880, 820, 780, 745, 730 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε×10^{-3}): 208 (16), 221 (16), 255 (11), 302 (4). ^{1}H NMR spectrum, δ, ppm: 1.30 d (3H, Me), 1.50–2.10 m (18H, Me, Ad), 2.82 q (1H, CH), 3.90 s (3H, MeO), 5.76 m and 6.40 m (1H each, $=CH_2$), 6.95–7.50 m (3H, C_6H_3), 8.14 s (1H, HC=N). Found, %: C 75.78; H 8.38; N 3.41. *M* 369.2. $C_{24}H_{31}NO_3$. Calculated, %: C 75.56; H 8.19; N 3.67. *M* 381.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl phenylacetate (IIIk). Yield 80%, vitreous substance. IR spectrum, ν, cm^{-1}: 3090, 3085, 3040, 2004 (=C–H, C–H_{arom}); 2966, 2935, 2903, 2846 (C–H_{aliph}); 1765 (C=O); 1645 (C=N); 1601, 1508, 1464, 1454, 1417, 1380 (C–C_{arom}); 1274, 1234, 1197, 1154, 1119, 1033 (C–O); 900, 872, 840, 828, 785, 760, 730, 702 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε×10^{-3}): 210 (20), 220 (14), 256 (10), 303 (4). ^{1}H NMR spectrum, δ, ppm: 1.31 d (3H, Me), 1.52–2.14 m (15H, Ad), 2.84 q (1H, CH), 3.82 s (2H, CH_2), 3.90 s (3H, MeO), 6.98–7.55 m (8H, H_{arom}), 8.20 s (1H, HC=N). Found, %: C 78.21; H 7.75; N 3.14. *M* 419.0. $C_{28}H_{33}NO_3$. Calculated, %: C 77.93; H 7.71; N 3.25. *M* 431.6.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl 3-phenylbutanoate (IIIl). Yield 83%, vitreous substance. IR spectrum, ν, cm^{-1}: 3090, 3080, 3042, 2004 (=C–H, C–H_{arom}); 2966, 2937, 2904, 2846 (C–H_{aliph}); 1763 (C=O); 1645 (C=N); 1601, 1508, 1464, 1452, 1417, 1379 (C–C_{arom}); 1274, 1197, 1155, 1132, 1035 (C–O); 876, 835, 765, 740, 700 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε×10^{-3}): 210 (20), 220 (14), 256 (9), 302 (4). ^{1}H NMR spectrum, δ, ppm: 1.31 d (3H, Me), 1.42 d (3H, Me), 1.54–2.14 m (15H, Ad), 2.65–3.15 m (3H, CH, CH_2), 3.43 m (1H, CH), 3.90 s (3H, MeO), 7.00–7.55 m (8H, H_{arom}), 8.20 s (1H, HC=N). Found, %: C 78.81; H 8.32; N 2.88. *M* 444.7. $C_{30}H_{37}NO_3$. Calculated, %: C 78.40; H 8.11; N 3.05. *M* 459.6.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl benzoate (IIIm). Yield 90%, mp 132–133°C (from ethanol). IR spectrum, ν, cm^{-1}: 3095,

3080, 3060, 3002 (=C–H, C–H_{arom}); 2980, 2965, 2935, 2916, 2885, 2848, 2812 (C–H_{aliph}); 1746 (C=O); 1642 (C=N); 1601, 1569, 1514, 1469, 1447, 1417, 1380 (C–C_{arom}); 1294, 1271, 1241, 1194, 1161, 1110, 1092, 1033 (C–O); 864, 815, 780, 765, 750, 740, 708 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 208 (33), 220 (21), 255 (16), 298 (6). ^{1}H NMR spectrum, δ, ppm: 1.32 d (3H, Me), 1.52–2.14 m (15H, Ad), 2.84 q (1H, CH), 3.90 s (3H, MeO), 7.15–8.20 m (8H, H_{arom}), 8.21 s (1H, HC=N). Found, %: C 77.84; H 7.56; N 3.18. *M* 409.3. $C_{27}H_{31}NO_3$. Calculated, %: C 77.68; H 7.48; N 3.35. *M* 417.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl 4-methylbenzoate (IIIn). Yield 91%, mp 126–127°C (from ethanol). IR spectrum, ν, cm^{-1}: 3090, 3078, 3040, 3012 (=C–H, C–H_{arom}); 2977, 2935, 2901, 2845 (C–H_{aliph}); 1731 (C=O); 1645 (C=N); 1612, 1603, 1514, 1445, 1420, 1395 (C–C_{arom}); 1293, 1269, 1202, 1165, 1115, 1076, 1067, 1040, 1019 (C–O); 875, 835, 830, 815, 790, 748, 720 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 208 (34), 222 (20), 255 (24), 300 (5). ^{1}H NMR spectrum, δ, ppm: 1.32 d (3H, Me), 1.50–2.14 m (15H, Ad), 2.45 s (3H, Me), 2.84 q (1H, CH), 3.90 s (3H, MeO), 7.10–8.12 m (7H, H_{arom}), 8.21 s (1H, HC=N). Found, %: C 78.12; H 7.80; N 3.09. *M* 420.5. $C_{28}H_{33}NO_3$. Calculated, %: C 77.93; H 7.71; N 3.25. *M* 431.6.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl 4-chlorobenzoate (IIIo). Yield 86%, mp 110–111°C (from ethanol). IR spectrum, ν, cm^{-1}: 3090, 3080, 3040, 3002 (=C–H, C–H_{arom}); 2972, 2937, 2902, 2846, 2814 (C–H_{aliph}); 1732 (C=O); 1645 (C=N); 1602, 1593, 1515, 1488, 1466, 1446, 1401, 1372 (C–C_{arom}); 1294, 1266, 1195, 1160, 1109, 1071, 1033, 1014 (C–O); 870, 852, 814, 776, 754, 740, 714, 685 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 208 (34), 220 (24), 254 (25), 300 (5). ^{1}H NMR spectrum, δ, ppm: 1.32 d (3H, Me), 1.54–2.16 m (15H, Ad), 2.84 q (1H, CH), 3.90 s (3H, MeO), 7.14–8.24 m (7H, H_{arom}), 8.22 s (1H, HC=N). Found, %: C 71.96; H 6.84; Cl 7.49; N 2.88. *M* 438.1. $C_{27}H_{30}ClNO_3$. Calculated, %: C 71.75; H 6.69; Cl 7.84; N 3.10. *M* 452.0.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl 2,4-dichlorobenzoate (IIIp). Yield 86%, mp 130–131°C (from ethanol). IR spectrum, ν, cm^{-1}: 3090, 3080, 3003 (=C–H, C–H_{arom}); 2970, 2935, 2903, 2845, 2820 (C–H_{aliph}); 1753 (C=O); 1644 (C=N); 1600, 1582, 1556, 1513, 1467, 1446, 1375 (C–C_{arom}); 1292, 1196, 1161, 1148, 1108, 1085, 1032 (C–O); 868, 840, 830, 815, 785, 775, 761, 730, 678 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 210 (38), 223 (30), 254 (16), 300 (6). ^{1}H NMR spectrum, δ, ppm: 1.32 d (3H, Me), 1.55–2.16 m (15H, Ad), 2.85 q (1H, CH), 3.90 s (3H, MeO), 7.11–8.48 m (6H, H_{arom}), 8.23 s (1H, HC=N). Found, %: C 66.91; H 6.12; Cl 14.18; N 2.50. *M* 471.2. $C_{27}H_{39}Cl_2NO_3$. Calculated, %: C 66.67; H 6.01; Cl 14.58; N 2.88. *M* 486.4.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl 4-bromobenzoate (IIIq). Yield 92%, mp 133–134°C (from ethanol). IR spectrum, ν, cm^{-1}: 3090, 3065, 3040, 3003 (=C–H, C–H_{arom}); 2980, 2930, 2902, 2843, 2813 (C–H_{aliph}); 1740 (C=O); 1646 (C=N); 1602, 1590, 1514, 1448, 1420, 1399, 1375 (C–C_{arom}); 1293, 1265, 1202, 1158, 1108, 1071, 1032, 1011 (C–O); 869, 850, 820, 800, 780, 760, 749, 730, 681 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 207 (38), 223 (28), 254 (24), 300 (6). ^{1}H NMR spectrum, δ, ppm: 1.32 d (3H, Me), 1.53–2.16 m (15H, Ad), 2.84 q (1H, CH), 3.90 s (3H, MeO), 7.18–8.24 m (7H, H_{arom}), 8.22 s (1H, HC=N). Found, %: C 65.57; H 6.20; Br 15.86; N 2.52. *M* 478.3. $C_{27}H_{30}BrNO_3$. Calculated, %: C 65.32; H 6.09; Br 16.10; N 2.82. *M* 496.4.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl 3-nitrobenzoate (IIIr). Yield 84%, mp 152–153°C (from ethanol). IR spectrum, ν, cm^{-1}: 3090, 3040, 3004 (=C–H, C–H_{arom}); 2990, 2980, 2930, 2906, 2846, 2815 (C–H_{aliph}); 1742 (C=O); 1646 (C=N); 1620, 1604, 1592, 1512, 1469, 1450, 1442, 1420, 1373 (C–C_{arom}); 1530, 1346 (NO_2); 1290, 1259, 1196, 1157, 1116, 1027 (C–O); 863, 812, 785, 770, 716, 703 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 205 (37), 220 (38), 260 (19), 300 (7). ^{1}H NMR spectrum, δ, ppm: 1.15 d (3H, Me), 1.55–2.15 m (15H, Ad), 2.79 q (1H, CH), 3.90 s (3H, MeO), 7.05–9.10 m (7H, H_{arom}), 8.19 s (1H, HC=N). Found, %: C 70.32; H 6.58; N 5.98. *M* 451.7. $C_{27}H_{30}N_2O_5$. Calculated, %: C 70.11; H 6.54; N 6.06. *M* 462.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl methyl carbonate (IIIs). Yield 85%, mp 101–102°C (from ethanol). IR spectrum, ν, cm^{-1}: 3080, 3040, 3003 (=C–H, C–H_{arom}); 2975, 2940, 2900, 2846 (C–H_{aliph}); 1774 (C=O); 1643 (C=N); 1602, 1513, 1449, 1414, 1374 (C–C_{arom}); 1292, 1254, 1198, 1164, 1113, 1092, 1059, 1033 (C–O); 880, 850, 840, 820, 776, 740 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 208 (13), 222 (13), 255 (10), 302 (4). ^{1}H NMR spectrum, δ, ppm: 1.13 d (3H, Me), 1.52–2.12 m (15H, Ad), 2.74 q (1H, CH), 3.90 s (6H, MeO), 6.90–7.50 m (3H, H_{arom}), 8.10 s (1H, HC=N). Found, %: C 71.38; H 7.95; N 3.52. *M* 362.8. $C_{22}H_{29}NO_4$. Calculated, %: C 71.13; H 7.87; N 3.77. *M* 371.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-methoxyphenyl ethyl carbonate (IIIt). Yield 86%, mp 74–75°C (from ethanol). IR spectrum, ν, cm^{-1}: 3080, 3060, 3040, 3005 (=C–H, C–H_{arom}); 2979, 2968, 2908, 2848 (C–H_{aliph}); 1765 (C=O); 1646 (C=N); 1604, 1591, 1517, 1467, 1450, 1419, 1369 (C–C_{arom}); 1302, 1262, 1210, 1166, 1112, 1092, 1064, 1033 (C–O); 878, 830, 819, 785, 773, 760 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 208 (13), 220 (13), 255 (10), 302 (4). ^{1}H NMR spectrum, δ, ppm: 1.13 d (3H, Me), 1.30 t (3H, Me), 1.54–2.12 m (15H, Ad), 2.74 q (1H, CH), 3.90 s (3H, MeO), 4.30 q (2H, CH_2), 6.90–7.52 m (3H, C_6H_3), 8.10 s (1H, HC=N). Found, %: C 71.85; H 8.21; N 3.41. *M* 373.0. $C_{23}H_{31}NO_4$. Calculated, %: C 71.66; H 8.10; N 3.63. *M* 385.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-ethoxyphenol (IVa). Yield 86%, mp 58–59°C (from ethanol). IR spectrum, ν, cm^{-1}: 3410 (OH); 3060, 3008 (=C–H, C–H_{arom}); 2976, 2930, 2902, 2845 (C–H_{aliph}); 1643 (C=N); 1593, 1514, 1440, 1360 (C–C_{arom}); 1280, 1238, 1187, 1154, 1124, 1040 (C–O); 870, 823, 814, 780, 740 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 208 (11), 224 (10), 270 (10), 300 (6). ^{1}H NMR spectrum, δ, ppm: 1.12 d (3H, Me), 1.60 t (3H, Me), 1.50–2.15 m (15H, Ad), 2.80 q (1H, CH), 4.22 q (2H, CH_2), 6.70 br.s (1H, OH), 6.80–7.50 m (3H, C_6H_3), 8.11 s (1H, HC=N). Found, %: C 77.24; H 9.12; N 4.06. *M* 319.5. $C_{21}H_{29}NO_2$. Calculated, %: C 77.03; H 8.93; N 4.28. *M* 327.5.

1-(1-Adamantyl)-*N*-(3-ethoxy-4-methoxybenzylidene)ethanamine (IVb). Yield 89%, vitreous substance. IR spectrum, ν, cm^{-1}: 3078, 3040, 3005 (=C–H, C–H_{arom}); 2977, 2937, 2903, 2846 (C–H_{aliph}); 1642 (C=N); 1601, 1585, 1513, 1441, 1390, 1360 (C–C_{arom}); 1265, 1236, 1167, 1138, 1092, 1031 (C–O); 873, 811, 773, 763 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 208 (12), 224 (11), 270 (10), 305 (6). ^{1}H NMR spectrum, δ, ppm: 1.12 d (3H, Me), 1.50 t (3H, Me), 1.51–2.05 m (15H, Ad), 2.69 q (1H, CH), 3.91 s (3H, MeO), 4.16 q (2H, CH_2), 6.80–7.45 m (3H, C_6H_3), 8.09 s (1H, HC=N). Found, %: C 77.65; H 9.16; N 3.87. *M* 329.7. $C_{22}H_{31}NO_2$. Calculated, %: C 77.38; H 9.15; N 4.10. *M* 341.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-ethoxyphenyl acetate (IVc). Yield 88%, vitreous substance. IR spectrum, ν, cm^{-1}: 3070, 3040, 3009 (=C–H, C–H_{arom}); 2978, 2937, 2903, 2846 (C–H_{aliph}); 1768 (C=O); 1644 (C=N); 1601, 1592, 1510, 1440, 1368 (C–C_{arom}); 1275, 1197, 1164, 1120, 1042 (C–O); 901, 875, 842, 815, 790, 770, 760 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 209 (12), 222 (13), 254 (10), 300 (5). ^{1}H NMR spectrum, δ, ppm: 1.12 d (3H, Me), 1.48 t (3H, Me), 1.52–2.15 m (15H, Ad), 2.32 s (3H, Me), 2.83 q (1H, CH), 4.15 q (2H, CH_2), 6.92–7.52 m (3H, C_6H_3), 8.13 s (1H, HC=N). Found, %: C 74.96; H 8.53; N 3.50. *M* 355.2. $C_{23}H_{31}NO_3$. Calculated, %: C 74.76; H 8.46; N 3.79. *M* 369.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-ethoxyphenyl propionate (VId). Yield 89%, vitreous substance. IR spectrum, ν, cm^{-1}: 3070, 3045, 3005 (=C–H, C–H_{arom}); 2979, 2945, 2904, 2847 (C–H_{aliph}); 1768 (C=O); 1645 (C=N); 1601, 1508, 1448, 1431, 1392, 1360 (C–C_{arom}); 1272, 1182, 1138, 1121, 1077, 1043 (C–O); 885, 826, 817, 790, 770, 755 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 207 (12), 222 (13), 254 (10), 301 (5). ^{1}H NMR spectrum, δ, ppm: 1.05–1.55 m (9H, 3Me), 1.50–2.08 m (15H, Ad), 2.45–2.95 m (3H, CH, CH_2), 4.12 q (2H, CH_2), 6.94–7.48 m (3H, C_6H_3), 8.13 s (1H, HC=N). Found, %: C 75.31; H 8.75; N 3.30. *M* 369.9. $C_{24}H_{33}NO_3$. Calculated, %: C 75.16; H 8.67; N 3.65. *M* 383.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-ethoxyphenyl butyrate (VIe). Yield 85%, vitreous substance. IR spectrum, ν, cm^{-1}: 3080, 3040, 3010 (=C–H, C–H_{arom}); 2968, 2929, 2904, 2847 (C–H_{aliph}); 1766 (C=O); 1645 (C=N); 1601, 1588, 1507, 1448, 1431, 1382 (C–C_{arom}); 1272, 1146, 1120, 1092, 1042 (C–O); 876, 831, 790, 775, 758, 740 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 207 (12), 223 (12), 254 (10), 302 (5). ^{1}H NMR spectrum, δ, ppm: 0.85–1.55 m (9H, Me), 1.40–2.09 m (17H, CH_2, Ad), 2.25–2.90 m (3H, CH, CH_2), 4.12 q (2H, CH_2), 6.90–7.50 m (3H, C_6H_3), 8.11 s (1H, HC=N). Found, %: C 75.72; H 8.97; N 3.28. *M* 386.5. $C_{25}H_{35}NO_3$. Calculated, %: C 75.53; H 8.87; N 3.52. *M* 397.6.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-ethoxyphenyl isobutyrate (VIf). Yield 84%, vitreous substance. IR spectrum, ν, cm^{-1}: 3080, 3040, 3010 (=C–H, C–H_{arom}); 2978, 2930, 2904, 2847 (C–H_{aliph}); 1746 (C=O); 1645 (C=N); 1601, 1590, 1505, 1469, 1449, 1431, 1387 (C–C_{arom}); 1272, 1163 1121, 1092, 1042 (C–O); 864, 814, 790, 780, 764, 745 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 209 (13), 221 (13), 255 (10), 300 (4). ^{1}H NMR spectrum, δ, ppm: 0.92 d (3H, Me), 1.24 d (6H, Me_2C), 1.47 t (3H, Me), 1.55–2.10 m (15H, Ad), 2.75–3.00 m (2H, CH), 4.12 q (2H, CH_2), 6.92–7.50 m (3H, C_6H_3), 8.14 s (1H, HC=N). Found, %: C 75.66; H 8.87; N 3.31. *M* 384.8. $C_{25}H_{35}NO_3$. Calculated, %: C 75.53; H 8.87; N 3.52. *M* 397.6.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-ethoxyphenyl 3-methylbutanoate (VIg). Yield 84%, vitreous

substance. IR spectrum, ν, cm^{-1}: 3075, 3040, 3008 (=C–H, C–H_{arom}); 2975, 2963, 2940, 2904, 2847 (C–H_{aliph}); 1764 (C=O); 1645 (C=N); 1602, 1507, 1450, 1430, 1361 (C–C_{arom}); 1288, 1272, 1150, 1120, 1092, 1043 (C–O); 875, 830, 790, 770, 755, 740 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 209 (12), 222 (13), 254 (10), 300 (5). ^{1}H NMR spectrum, δ, ppm: 0.93 d (3H, Me), 1.08 d (6H, Me_2C), 1.48 t (3H, Me), 1.55–2.16 m (17H, CH_2, Ad), 2.60–3.10 m (2H, CH), 4.12 q (2H, CH_2), 6.90–7.50 m (3H, C_6H_3), 8.14 s (1H, HC=N). Found, %: C 76.10; H 9.22; N 3.04. *M* 397.6. $C_{26}H_{37}NO_3$. Calculated, %: C 75.87; H 9.06; N 3.40. *M* 411.6.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-ethoxyphenyl 4-methylbenzoate (IVh). Yield 91%, mp 122–123°C (from ethanol). IR spectrum, ν, cm^{-1}: 3090, 3078, 3040, 3012 (=C–H, C–H_{arom}); 2977, 2935, 2901, 2845 (C–H_{aliph}); 1731 (C=O); 1645 (C=N); 1612, 1603, 1514, 1445, 1420, 1395 (C–C_{arom}); 1293, 1269, 1202, 1165, 1115, 1076, 1067, 1040, 1019 (C–O); 875, 835, 830, 815, 790, 748, 720 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 208 (33), 223 (20), 254 (24), 300 (5). ^{1}H NMR spectrum, δ, ppm: 1.32 d (3H, Me), 1.49 t (3H, Me), 1.50–2.14 m (15H, Ad), 2.45 s (3H, Me), 2.84 q (1H, CH), 4.14 q (2H, CH_2), 7.10–8.12 m (7H, H_{arom}), 8.21 s (1H, HC=N). Found, %: C 78.35; H 8.13; N 2.85. *M* 431.6. $C_{29}H_{35}NO_3$. Calculated, %: C 78.17; H 7.92; N 3.14. *M* 445.6.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-ethoxyphenyl methyl carbonate (IVi). Yield 87%, vitreous substance. IR spectrum, ν, cm^{-1}: 3075, 3055, 3012 (=C–H, C–H_{arom}); 2979, 2035, 2903, 2847 (C–H_{aliph}); 1771 (C=O); 1644 (C=N); 1602, 1593, 1511, 1440, 1380 (C–C_{arom}); 1276, 1256, 1206, 1168, 1122, 1090, 1065, 1042 (C–O); 880, 812, 776, 760, 740 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 209 (13), 222 (13), 254 (10), 302 (4). ^{1}H NMR spectrum, δ, ppm: 1.13 d (3H, Me), 1.47 t (3H, Me), 1.47–2.15 m (15H, Ad), 2.86 q (1H, CH), 3.90 s (3H, MeO), 4.15 q (2H, CH_2), 6.90–7.55 m (3H, C_6H_3), 8.12 s (1H, HC=N). Found, %: C 71.94; H 8.18; N 3.37. *M* 376.8. $C_{23}H_{31}NO_4$. Calculated, %: C 71.66; H 8.10; N 3.63. *M* 385.5.

4-[1-(1-Adamantyl)ethyliminomethyl]-2-ethoxyphenyl ethyl carbonate (IVj). Yield 85%, mp 102–103°C (from ethanol). IR spectrum, ν, cm^{-1}: 3075, 3060, 3015 (=C–H, C–H_{arom}); 2986, 2971, 2940, 2930, 2909, 2895, 2847, 2820 (C–H_{aliph}); 1760 (C=O); 1646 (C=N); 1601, 1591, 1515, 1477, 1448, 1421, 1398, 1368 (C–C_{arom}); 1307, 1293, 1260, 1207, 1170, 1116, 1063, 1039 (C–O); 878, 840, 820, 805, 790, 777, 765 (δC–H_{arom}). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-3}$): 208 (12), 221 (13), 254 (10), 301 (4). ^{1}H NMR spectrum, δ, ppm: 1.25–1.55 m (9H, Me), 1.45–2.15 m (15H, Ad), 2.85 q (1H, CH), 3.95–4.50 m (4H, CH_2), 6.90–7.50 m (3H, C_6H_3), 8.12 s (1H, HC=N). Found, %: C 72.46; H 8.45; N 3.17. *M* 387.1. $C_{24}H_{33}NO_4$. Calculated, %: C 72.15; H 8.32; N 3.51. *M* 399.5.

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