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Preparative Synthesis of 4-Hydroxy(Alkyloyloxy, Aryloyloxy)-3-methoxy(ethoxy)phenylmethylene(4-carboxyphenyl)amines

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Abstract—By reactions of vanillin, vanillal, and their esters with 4-aminobenzoic acid in methanol formerly unknown *E*-isomers of azomethines (Schiff's bases) were prepared.

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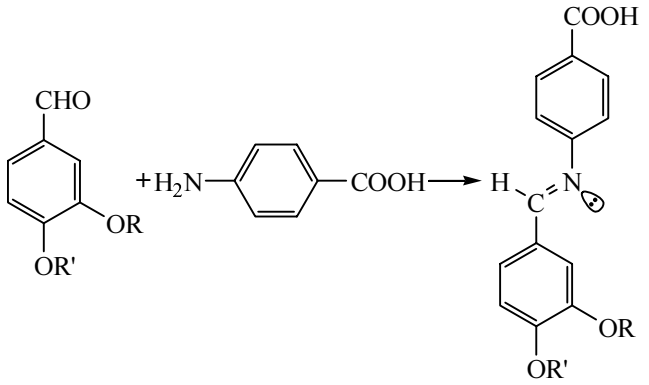
Azomethines (Schiff's bases) are widely used as biologically active compounds, liquid crystals, dyes, luminophors, and polymer stabilizers [1–4]. Based on azomethines efficient drugs were developed exhibiting antidepressant, anticonvulsant, antimicrobial, soponific, psychotropic, nematocidal, antiphlogistic, antitumor, etc. action [5, 6]. Owing to the presence of a polarized C=N heterobond the azomethines are valuable initial products for the synthesis of heterocyclic compounds [7] and β-arylaminoketones, efficient agents of topical anesthesia [8, 9].

In this study we developed a preparative synthesis of previously unknown derivatives of available natural aldehydophenols (vanillin and vanillal) and of their esters **I**. The condensation of vanillin and esters **I** with 4-aminobenzoic acid (**II**) in anhydrous methanol while heating at reflux gave rise to 4-hydroxy(alkyloyloxy, aryloyloxy)-3-methoxy-(ethoxy)phenylmethylene(4-carboxyphenyl)-amines **IIIa–IIIy** and **IVa–IVk**. The reaction was complete within 1.5–2 h, occurred under mild conditions with no catalyst that ensured the retention of the labile ester group. As a result of the process initial compounds **I** and **II** were converted in preparative yields 90–95% into the corresponding azomethines with a reactive carboxy group **IIIa–IIIy** and **IVa–IVk**. It is presumable that the synthesized compounds **IIIa–IIIy** and **IVa–IVk** would prove to be promising for investigating their biological, phototropic, and photochromic activity, spectral characteristics, for preparation therefrom valuable products and optical materials [6], and for further application as accessible synthons in a condensation with CH-acids in order to obtain β-arylaminoketones [8, 9].



I **II** **IIIa –IIIy, IVa –IVk**

III, R = Me, R' = H (**a**), C(O)Me (**b**), C(O)Et (**c**), C(O)Pr-*n* (**d**), C(O)Pr-*i* (**e**), $C(O)(CH_2)_6Me$ (**f**), $C(O)(CH_2)_8Me$ (**g**), $C(O)(CH_2)_{11}Me$ (**h**), $C(O)(CH_2)_{16}Me$ (**i**), $C(O)CH{=}CH_2$ (**j**), $C(O)CMe{=}CH_2$ (**k**), $C(O)(CH_2)_7CH{=}CH(CH_2)_7Me$-*cis* (**l**), $C(O)CH_2C_6H_5$ (**m**), $C(O)CH_2CHMeC_6H_5$ (**n**), $C(O)(CH_2)_2OC_6H_4Me$-4 (**o**), $C(O)C_6H_5$ (**p**), $C(O)C_6H_4Me$-4 (**q**), $C(O)C_6H_4Cl$-2 (**r**), $C(O)C_6H_4Cl$-4 (**s**), $C(O)C_6H_3Cl_2$-2,4 (**t**), $C(O)CH_2OC_6H_3Cl_2$-2,4 (**u**), $C(O)CH_2Br$ (**v**), $C(O)C_6H_4Br$-4 (**w**), $C(O)C_6H_4NO_2$-3 (**x**), 1/2 $[(O)C(CH_2)_2C(O)]$ (**y**); **IV**, R = Et, R^1 = H (**a**), C(O)Me (**b**), C(O)Et (**c**), C(O)Pr-*n* (**d**), C(O)Pr-*i* (**e**), $C(O)CH_2CHMe_2$ (**g**), $C(O)C_6H_5$ (**g**), $C(O)C_6H_4Me$-4 (**h**), $C(O)C_6H_4Cl$-2 (**i**), $C(O)C_6H_4Cl$-4 (**j**), 1/2 $[(O)C(CH_2)_2C(O)]$ (**k**).

The structure of prepared azomethines **IIIa–IIIy** and **IVa–IVk** was confirmed by elemental analysis, IR, UV, ^{1}H NMR spectra, and by titrimetric evaluation of the molecular weight. According to the ^{1}H NMR spectra the azomethines obtained were individual *E*-isomers of 98±1% purity. In the ^{1}H NMR spectra of these compounds the

characteristic signals of the proton HC=N appeared as a singlet at 8.5 ppm. The chemical shift of the proton in the *Z*-isomer is located ususlly by 0.5 ppm downfield due to its occurrence in the deshielding field of the benzene ring from the amino acid part of the molecule [10].

In order to confirm the spatial arrangement of compounds obtained **IIIa–IIIy** and **IVa–IVk** we carried out quantum-chemical calculations of the heat of formation (H_f) for *E*- and *Z*-isomers of compounds **IIIb, IIIp**, **IVb**, and **IVg** in the framework of the semiempirical approximation MNDO-PM3 [11] applying GAMESS [12] software. We performed a total optimization of all bond lengths, bond and dihedral angles in the compounds under investigation. The calculations gave the following values of H_f, kcal mol^{-1}, for *E*-isomers: –136.6 (**IIIb**), –100.8 (**IIIp**), –141.5 (**IVb**), –105.6 (**IVg**); for *Z*-isomers: –136.1 (**IIIb**), –100.3 (**IIIp**), –141.1 (**IVb**), –104.8 (**IVg**). The quantum-chemical calculations revealed that the *E*-configuration is more energetically favorable by 0.4–0.7 kcal mol^{-1} than the *Z*-configuration. The data of the quantum-chemical calculations are well consistent with the X-ray diffraction analysis studies of related compounds [13–15].

EXPERIMENTAL

IR spectra were recorded on a Fourier spectrometer Nicolet Protege-460 from samples pelletized with KBr. UV spectra were measured on a spectrophotometer Specord UV Vis from 1×10^{-4} M solutions in methanol. ^{1}H NMR spectra were registered on a spectrometer Tesla BS-587A (100 MHz) from 5% solutions in $(CD_3)_2SO$, chemical shilts were measured from an internal reference OMTS. The molecular weights were determined by alkalimetric titration of carboxy groups with 0.1 N solution of NaOH in the presence of phenolphthalein as indicator. Vanillin esters **I** were prepared by procedure [16].

4-Hydroxy(alkyloyloxy, aryloyloxy)-3-methoxy-(ethoxy)phenylmethylene(4-carboxyphenyl)-amines IIIa–IIIy and **IVa–IVk (Schiff's bases). General procedure.** In 50–100 ml of anhydrous methanol was dissolved 0.01 mol of vanillin, vanillal, or their ester **I**, and 0.01 m,ol of 4-aminobenzoic acid (**II**) (for compounds **IIIy** and **IVk** 0.02 mol) was added, the solution obtained was heated at reflux for 1.5–2 h and left standing for 20–30 h at 20–23°C. The separated precipitate of azomethines **IIIa–IIIy** and **IVa–IVk** was filtered on a glass frit, washed with a little of methanol, and dried in a vacuum. The obtained compounds **IIIa–IIIy** and **IVa–IVk** were sufficiently pure and did not require recrystallization.

The used methanol was repeatedly applied after distillation through a Vigreux column.

4-Hydroxy-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIa). Yield 94%, mp 208–209°C (from methanol). IR spectrum, ν, cm^{-1}: 1850–3650 (OH), 3071, 3009 (CH_{Ar} and =CH), 2960, 2924, 2852 (CH_{Alk}), 1681, 1660 (C=O), 1630 (C=N), 1584, 1513, 1454, 1430, 1367 (Ar), 1315, 1284, 1218, 1167, 1121, 1026, 973 (CO), 855, 816, 777, 740, 697, 659, 635, 613 (CH_{Ar}). UV spectrum, λ_{max} (ε): 206 (16000), 234 (10000), 295 (11000), 335 (14000). ^{1}H NMR spectrum, δ, ppm: 3.96 s (3H, CH_3O), 6.50 br.s (1H, OH), 6.55–7.95 m (7H, C_6H_3 and C_6H_4), 8.50 s (1H, HC=N), 9.82 s (1H, CO_2H). Found, %: C 66.57; H 5.02; N 4.89. *M* 265.6. $C_{15}H_{13}NO_4$. Calculated, %: C 66.41; H 4.83; N 5.16. *M* 271.3.

4-Acetoxy-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIb). Yield 90%, mp 212–213°C (from methanol). IR spectrum, ν, cm^{-1}: 2000–3620 (OH), 3080, 3010 (CH_{Ar} and =CH), 2975, 2940, 2920, 2890, 2880, 2840, 2800 (CH_{Alk}), 1759, 1681 (C=O), 1629 (C=N), 1600, 1581, 1510, 1464, 1449, 1420, 1369 (Ar), 1315, 1287, 1270, 1219, 1194, 1160, 1114, 1031, 1014, 976, 949 (CO), 873, 860, 834, 774, 756, 699, 673, 640, 609 (CH_{Ar}). UV spectrum, λ_{max} (ε): 205 (23000), 220 (18000), 280 (22000), 295 (22000), 315 (13000). ^{1}H NMR spectrum, δ, ppm: 2.28 s (3H, CH_3COO), 3.88 s (3H, CH_3O), 6.40–8.10 m (7H, C_6H_3 and C_6H_4), 8.53 s (1H, HC=N) , 9.94 s (1H, CO_2H). Found, %: C 65.46; H 5.04; N 4.20. *M* 298.1. $C_{17}H_{15}NO_5$. Calculated, %: C 65.17; H 4.83; N 4.47. *M* 313.3.

4-Propionyloxy-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIc). Yield 92%, mp 184–185°C (from methanol). IR spectrum, ν, cm^{-1}: 2000–3650 (OH), 3075, 3055, 3010 (CH_{Ar} and =CH), 2965, 2939, 2924, 2875, 2851, 2800 (CH_{Alk}), 1757, 1683 (C=O), 1630 (C=N), 1599, 1585, 1504, 1464, 1417, 1367 (Ar), 1315, 1287, 1275, 1216, 1204, 1167, 1138, 1125, 1076, 1033, 1010, 971 (C–O), 891, 865, 823, 804, 774, 748, 698, 661, 612 (CH_{Ar}). UV spectrum, λ_{max} (ε): 206 (24000), 220 (19000), 280 (22000), 295 (22000), 315 (14000). ^{1}H NMR spectrum, δ, ppm: 1.27 t (3H, $\underline{CH_3}CH_2$), 2.54 q (2H, CH_2), 3.88 s (3H, CH_3O), 6.40–8.12 m (7H, C_6H_3 and C_6H_4), 8.52 s (1H, HC=N), 9.93 s (1H, CO_2H). Found, %: C 66.32; H 5.41; N 4.07. *M* 309.6. $C_{18}H_{17}NO_5$. Calculated, %: C 66.05; H 5.23; N 4.28. *M* 327.3.

4-Butyryloxy-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIId). Yield 92%, mp 139–140°C (from methanol). IR spectrum, ν, cm^{-1}: 2100–3650 (OH), 3080, 3069, 3008 (CH_{Ar} and =CH), 2965, 2935, 2877, 2850,

2825, 2800 (CH_{Alk}), 1757, 1676 (C=O), 1633 (C=N), 1589, 1576, 1508, 1466, 1429, 1417, 1380, 1369 (Ar), 1319, 1276, 1218, 1198, 1173, 1149, 1138, 1123, 1104, 1080, 1031, 1012, 975, 966, 945 (CO), 872, 853, 826, 775, 747, 699, 662, 640, 616 (CH_{Ar}). UV spectrum, λ_{max} (ε): 205 (23000), 220 (19000), 280 (22000), 295 (21000), 315 (13000). ^{1}H NMR spectrum, δ, ppm: 1.05 t (3H, CH_3), 1.65 m (2H, CH_2), 2.55 t (2H, CH_2), 3.87 s (3H, CH_3O), 6.42–8.15 m (7H, C_6H_3 and C_6H_4), 8.53 s (1H, HC=N), 9.92 s (1H, CO_2H). Found, %: C 67.11; H 5.80; N 3.83. *M* 325.9. $C_{19}H_{19}NO_5$. Calculated, %: C 66.85; H 5.61; N 4.10. *M* 341.4.

4-Isobutyryloxy-3-methoxyphenylmethylene-(4-carboxyphenyl)amine (IIIe). Yield 90%, mp 168–169°C (from methanol). IR spectrum, ν, cm^{-1}: 2050–3630 (OH), 3080, 3050, 3010 (CH_{Ar} and =CH), 2969, 2933, 2875, 2851, 2830 (CH_{Alk}), 1754, 1677 (C=O), 1631 (C=N), 1589, 1568, 1507, 1466, 1429, 1417, 1385, 1369, 1345 (Ar), 1317, 1276, 1217, 1172, 1152, 1124, 1093, 1028, 980, 965, 945 (CO), 869, 853, 815, 775, 740, 720, 695, 660, 615 (CH_{Ar}). UV spectrum, λ_{max} (ε): 205 (23000), 220 (18000), 280 (22000), 295 (22000), 315 (12000). ^{1}H NMR spectrum, δ, ppm: 1.36 d [6H, $(CH_3)_2C$], 2.90 quintet (1H, CH), 3.88 s (3H, CH_3O), 6.43–8.14 m (7H, C_6H_3 and C_6H_4), 8.52 s (1H, HC=N), 9.93 s (1H, CO_2H). Found, %: C 67.06; H 5.77; N 3.87. *M* 328.3. $C_{19}H_{19}NO_5$. Calculated, %: C 66.85; H 5.61; N 4.10. *M* 341.4.

4-Capryiloyloxy-3-methoxyphenylmethylene-(4-carboxyphenyl)amine (IIIf). Yield 92%, mp 141–142°C (from methanol). IR spectrum, ν, cm^{-1}: 2030–3600 (OH), 3080, 3010 (CH_{Ar} and =CH), 2960, 2920, 2975, 2850, 2820, 2800 (CH_{Alk}), 1757, 1681 (C=O), 1632 (C=N), 1593, 1571, 1505, 1463, 1419, 1380, 1360 (Ar), 1315, 1286, 1222, 1197, 1196, 1169, 1152, 1135, 1112, 1075, 1034, 1010, 980, 945 (CO), 868, 850, 830, 780, 755, 747, 720, 705, 660, 635, 615 (CH_{Ar}). UV spectrum, λ_{max} (ε): 205 (23000), 220 (18000), 280 (22000), 295 (21000), 315 (13000). ^{1}H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3), 1.34 m [8H, $(CH_2)_4$], 1.80 m (2H, CH_2), 2.60 m (2H, CH_2), 3.87 s (3H, CH_3O), 6.45–8.15 m (7H, C_6H_3 and C_6H_4), 8.53 s (1H, HC=N), 9.92 s (1H, CO_2H). Found, %: C 69.84; H 7.03; N 3.23. *M* 384.0. $C_{23}H_{27}NO_5$. Calculated, %: C 69.50; H 6.85; N 3.52. *M* 397.5.

4-Decanoyloxy-3-methoxyphenylmethylene-(4-carboxyphenyl)amine (IIIg). Yield 90%, mp 152–153°C (from methanol). IR spectrum, ν, cm^{-1}: 2100–3540 (OH), 3075, 3050, 3010 (CH_{Ar} and =CH), 2956, 2924, 2853, 2800 (CH_{Alk}), 1749, 1683 (C=O), 1630 (C=N), 1588, 1570, 1507, 1471, 1452, 1417, 1374, 1360 (Ar), 1314, 1276, 1218, 1196, 1170, 1141, 1120, 1076, 1033, 1012, 987, 973, 946 (CO), 871, 855, 839, 808, 790, 777, 746, 722, 700, 660, 636, 616 (CH_{Ar}). UV spectrum, λ_{max} (ε): 205 (22000), 220 (18000), 280 (23000), 295 (21000), 315 (12000). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3), 1.20–1.55 m [12H, $(CH_2)_6$], 1.85 t (2H, CH_2), 2.65 t (2H, CH_2), 3.85 s (3H, CH_3O), 6.44–8.15 m (7H, C_6H_3 and C_6H_4), 8.52 s (1H, HC=N), 9.93 s (1H, CO_2H). Found, %: C 70.88; H 7.49; N 2.95. *M* 418.5. $C_{25}H_{31}NO_5$. Calculated, %: C 70.57; H 7.34; N 3.29. *M* 425.5.

4-Tridecanoyloxy-3-methoxyphenylmethylene-(4-carboxyphenyl)amine (IIIh). Yield 91%, mp 122–123°C (from methanol). IR spectrum, ν, cm^{-1}: 2100–3650 (OH), 3076, 3050, 3015 (CH_{Ar} and =CH), 2949, 2920, 2851, 2790 (CH_{Alk}), 1754, 1680 (C=O), 1627 (C=N), 1602, 1586, 1504, 1471, 1456, 1417, 1372, (Ar), 1318, 1275, 1260, 1231, 1217, 1196, 1173, 1155, 1139, 1117, 1090, 1059, 1034, 1014, 984, 947, 920 (CO), 876, 866, 839, 810, 791, 777, 747, 719, 700, 662, 615 (CH_{Ar}). UV spectrum, λ_{max} (ε): 205 (23000), 220 (19000), 280 (22000), 295 (21000), 315 (13000). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3), 1.32 m [18H, $(CH_2)_9$], 1.77 m (2H, CH_2), 2.64 t (2H, CH_2), 3.84 s (3H, CH_3O), 6.45–8.15 m (7H, C_6H_3 and C_6H_4), 8.54 s (1H, HC=N), 9.93 s (1H, CO_2H). Found, %: C 72.21; H 8.16; N 2.84. *M* 459.2. $C_{28}H_{37}NO_5$. Calculated, %: C 71.92; H 7.98; N 3.00. *M* 467.6.

4-Stearoyloxy-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIi). Yield 90%, mp 33–34°C (from methanol). IR spectrum, ν, cm^{-1}: 2200–3700 (OH), 3080, 3050, 3010 (CH_{Ar} and =CH), 2955, 2918, 2849, 2800 (CH_{Alk}), 1752, 1676 (C=O), 1634 (C=N), 1605, 1590, 1570, 1510, 1470, 1430, 1420, 1375, 1365 (Ar), 1325, 1276, 1225, 1195, 1175, 1150, 1136, 1125, 1115, 1100, 1060, 1032, 1020, 990, 980, 970, 940, 920 (CO), 871, 855, 840, 805, 795, 780, 745, 720, 700, 655, 630, 617 (CH_{Ar}). UV spectrum, λ_{max} (ε): 204 (21000), 220 (18000), 280 (21000), 295 (20000), 315 (11000). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3), 1.10–2.10 m [30H, $(CH_2)_{15}$], 2.70 t (2H, CH_2), 3.87 s (3H, CH_3O), 6.45–8.15 m (7H, C_6H_3 and C_6H_4), 8.54 s (1H, HC=N), 9.92 s (1H, CO_2H). Found, %: C 74.07; H 9.02; N 2.19. *M* 529.8. $C_{33}H_{47}NO_5$. Calculated, %: C 73.71; H 8.81; N 2.60. *M* 537.7.

4-Acryloyloxy-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIj). Yield 90%, mp 160–161°C (from methanol). IR spectrum, ν, cm^{-1}: 2050–3600 (OH), 3090, 3068, 3013 (CH_{Ar} and =CH), 2980, 2945, 2922, 2879, 2850, 2820, 2795 (CH_{Alk}), 1760, 1677 (C=O), 1633 (C=N), 1590, 1570, 1507, 1467, 1429, 1417, 1404, 1369 (Ar), 1318, 1277, 1218, 1198, 1173, 1144, 1117, 1031, 1012, 967, 943

(CO), 899, 872, 853, 793, 775, 746, 698, 672, 615 (CH_{Ar}). UV spectrum, λ_{max} (ε): 206 (25000), 220 (22000), 278 (23000), 295 (21000), 315 (13000). ^{1}H NMR spectrum, δ, ppm: 3.88 s (3H, CH_3O), 5.84–6.88 m (CH=CH_2), 6.50–8.15 m (7H, C_6H_3 and C_6H_4), 8.55 s (1H, HC=N), 9.94 s (1H, CO_2H). Found, %: C 66.82; H 4.74; N 4.16. *M* 320.7. $C_{18}H_{15}NO_5$. Calculated, %: C 66.46; H 4.65; N 4.31. *M* 325.3.

4-Methacryloyloxy-3-methoxyphenylmethylene-(4-carboxyphenyl)amine (IIIk). Yield 92%, mp 204–205°C (from methanol). IR spectrum, ν, cm^{-1}: 2130–3630 (OH), 3080, 3045, 3008 (CH_{Ar} and =CH), 2980, 2930, 2880, 2845, 2830, 2800 (CH_{Alk}), 1731, 1690 (C=O), 1631 (C=N), 1589, 1570, 1509, 1459, 1417, 1376 (Ar), 1320, 1290, 1278, 1219, 1202, 1173, 1153, 1121, 1034, 1012, 980, 945 (CO), 869, 852, 815, 804, 774, 745, 700, 665, 640, 625 (CH_{Ar}). UV spectrum, λ_{max} (ε): 206 (26000), 221 (23000), 277 (23000), 295 (22000), 315 (12000). ^{1}H NMR spectrum, δ, ppm: 2.10 t (3H, CH_3), 3.87 s (3H, CH_3O), 5.80 t (1H, =CH), 6.40 t (1H, =CH), 6.50–8.15 m (7H, C_6H_3 and C_6H_4), 8.54 s (1H, HC=N), 9.93 s (1H, CO_2H). Found, %: C 67.61; H 5.08; N 3.87. *M* 331.4. $C_{19}H_{17}NO_5$. Calculated, %: C 67.25; H 5.05; N 4.13. *M* 339.3.

4-Oleoyloxy-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIl). Yield 90%, mp 111–112°C (from methanol). IR spectrum, ν, cm^{-1}: 2150–3650 (OH), 3076, 3047, 3007 (CH_{Ar} and =CH), 2960, 2924, 2852, 2800 (CH_{Alk}), 1756, 1676 (C=O), 1633 (C=N), 1592, 1508, 1466, 1430, 1416, 1380 (Ar), 1319, 1278, 1220, 1199, 1173, 1150, 1116, 1031, 970, 940 (CO), 880, 860, 840, 780, 745, 735, 720, 700, 660, 640, 615 (CH_{Ar}). UV spectrum, λ_{max} (ε): 205 (25000), 220 (23000), 277 (22000), 295 (22000), 315 (12000). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3), 1.08–2.20 m [22H, $(CH_2)_5$ and $(CH_2)_6$], 2.60 t (2H, CH_2), 3.86 s (3H, CH_3O), 5.40 t [2H, 2(=CH)], 6.45–8.20 m (7H, C_6H_3 and C_6H_4), 8.55 s (1H, HC=N), 9.94 s (1H, CO_2H). Found, %: C 74.23; H 8.62; N 2.38. *M* 527.5. $C_{33}H_{45}NO_5$. Calculated, %: C 73.99; H 8.47; N 2.61. *M* 535.7.

4-Phenylacetoxy-3-methoxyphenylmethylene-(4-carboxyphenyl)amine (IIIm). Yield 90%, mp 157–158°C (from methanol). IR spectrum, ν, cm^{-1}: 2100–3650 (OH), 3100, 3064, 3037, 3006 (CH_{Ar} and =CH), 2960, 2923, 2877, 2853, 2835, 2795 (CH_{Alk}), 1758, 1677 (C=O), 1631 (C=N), 1602, 1590, 1570, 1506, 1499, 1466, 1455, 1429, 1417, 1371, 1348 (Ar), 1317, 1277, 1217, 1197, 1173, 1151, 1134, 1121, 1113, 1032, 1012, 970, 942 (CO), 872, 853, 795, 775, 745, 729, 698, 667, 636, 616 (CH_{Ar}). UV spectrum, λ_{max} (ε): 207 (30000), 220 (22000), 280 (22000), 295 (21000), 315 (12000). ^{1}H NMR spectrum, δ, ppm: 3.82 s (2H, CH_2), 3.89 C (3H, CH_3O), 6.40–8.10 m (12H, C_6H_3, C_6H_4 and C_6H_5), 8.54 s (1H, HC=N), 9.94 s (1H, CO_2H). Found, %: C 71.18; H 5.12; N 3.32. *M* 381.9. $C_{23}H_{19}NO_5$. Calculated, %: C 70.94; H 4.92; N 3.60. *M* 389.4.

4-(2-Phenylbutyryloxy)-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIn). Yield 90%, mp 141–142°C (from methanol). IR spectrum, ν, cm^{-1}: 2050–3650 (OH), 3090, 3070, 3030, 3005 (CH_{Ar} and =CH), 2965, 2930, 2870, 2845, 2830, 2800 (CH_{Alk}), 1759, 1686 (C=O), 1631 (C=N), 1601, 1583, 1508, 1465, 1452, 1419, 1380, 1362 (Ar), 1313, 1277, 1263, 1221, 1197, 1154, 1145, 1120, 1104, 1081, 1057, 1023, 994, 940 (CO), 875, 860, 845, 805, 780, 760, 745, 700, 650, 610 (CH_{Ar}). UV spectrum, λ_{max} (ε): 208 (29000), 220 (21000), 280 (21000), 295 (21000), 315 (11000). ^{1}H NMR spectrum, δ, ppm: 1.44 d (3H, CH_3), 2.90 d (2H, CH_2), 3.40 q (1H, CH), 3.88 s (3H, CH_3O), 6.42–8.12 m (12H, C_6H_3, C_6H_4 and C_6H_5), 8.55 s (1H, HC=N), 9.93 s (1H, CO_2H). Found, %: C 72.26; H 5.78; N 3.14. *M* 394.0. $C_{25}H_{23}NO_5$. Calculated, %: C 71.93; H 5.55; N 3.36. *M* 417.5.

4-[2-(4-Toluyloxy)propionyloxy]-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIo). Yield 94%, mp 213–214°C (from methanol). IR spectrum, ν, cm^{-1}: 2200–3700 (OH), 3100, 3074, 3060, 3040, 3006 (CH_{Ar} and =CH), 2981, 2941, 2921, 2889, 2854, 2800 (CH_{Alk}), 1751, 1689 (C=O), 1629 (C=N), 1603, 1589, 1570, 1509, 1481, 1461, 1417, 1397, 1365 (Ar), 1321, 1278, 1260, 1242, 1222, 1199, 1175, 1161, 1118, 1045, 1032, 971 (CO), 875, 854, 840, 811, 775, 747, 701, 650, 617 (CH_{Ar}). UV spectrum, λ_{max} (ε): 206 (31000), 221 (24000), 280 (23000), 295 (21000), 315 (11000). ^{1}H NMR spectrum, δ, ppm: 2.32 s (3H, CH_3), 3.10 t (2H, CH_2O), 3.89 s (3H, CH_3O), 4.40 t (2H, CH_2C=O), 6.40–8.10 m (11H, C_6H_3 and $2C_6H_4$), 8.54 s (1H, HC=N), 9.94 s (1H, CO_2H). Found, %: C 69.58; H 5.61; N 2.97. *M* 413.9. $C_{25}H_{23}NO_6$. Calculated, %: C 71.93; H 5.55; N 3.36. *M* 417.5.

4-Benzoyloxy-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIp). Yield 92%, mp 226–227°C (from methanol). IR spectrum, ν, cm^{-1}: 2040–3600 (OH), 3090, 3067, 3030, 3006 (CH_{Ar} and =CH), 2969, 2936, 2880, 2850, 2832, 2800 (CH_{Alk}), 1725, 1694 (C=O), 1630 (C=N), 1601, 1587, 1570, 1506, 1467, 1454, 1421, 1378 (Ar), 1318, 1275, 1259, 1220, 1201, 1173, 1153, 1128, 1080, 1965, 1040, 1030, 1012, 1005, 987 (CO), 867, 852, 810, 804, 774, 747, 715, 699, 685, 655, 635, 620 (CH_{Ar}). UV spectrum, λ_{max} (ε): 208 (21000), 241 (21000), 280 (17000), 320 (12000). ^{1}H NMR spectrum, δ, ppm: 3.87 s

(3H, CH_3O), 6.50–8.15 m (12H, C_6H_3, C_6H_4 and C_6H_5), 8.60 s (1H, HC=N), 10.00 s (1H, CO_2H). Found, %: C 70.45; H 4.73; N 3.76. *M* 372.6. $C_{22}H_{17}NO_5$. Calculated, %: C 70.39; H 4.56; N 3.73. *M* 375.4.

4-(4-Methylbenzoyloxy)-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIq). Yield 93%, mp 250–251°C (from methanol). IR spectrum, ν, cm^{-1}: 2040–3550 (OH), 3070, 3954, 3041, 3008 (CH_{Ar} and =CH), 2872, 2850, 2830, 2795 (CH_{Alk}), 1731, 1681 (C=O), 1625 (C=N), 1597, 1573, 1511, 1466, 1445, 1417, 1350 (Ar), 1314, 1280, 1218, 1203, 1160, 1120, 1109, 1070, 1032, 1020, 1010, 970 (CO), 869, 853, 837, 810, 775, 749, 720, 700, 687, 660, 640, 625 (CH_{Ar}). UV spectrum, λ_{max} (ε): 209 (23000), 220 (25000), 253 (28000), 280 (18000), 320 (12000). ^1H NMR spectrum, δ, ppm: 2.46 s (3H, CH_3), 3.88 s (3H, CH_3O), 6.50–8.20 m (11H, C_6H_3 and $2C_6H_4$), 8.60 s (1H, HC=N), 10.00 s (1H, CO_2H). Found, %: C 71.25; H 5.14; N 3.41. *M* 384.1. $C_{23}H_{19}NO_5$. Calculated, %: C 70.94; H 4.92; N 3.60. *M* 389.4.

4-(2-Chlorobenzoyloxy)-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIr). Yield 93%, mp 209–210°C (from methanol). IR spectrum, ν, cm^{-1}: 2000–3640 (OH), 3095, 3067, 3020 (CH_{Ar} and =CH), 2990, 2960, 2923, 2873, 2852, 2800 (CH_{Alk}), 1754, 1677 (C=O), 1629 (C=N), 1602, 1586, 1506, 1465, 1427, 1418, 1372 (Ar), 1319, 1277, 1241, 1218, 1192, 1165, 1152, 1125, 1091, 1082, 1034, 1024, 965 (CO), 875, 856, 809, 776, 748, 706, 696, 665, 650, 617 (CH_{Ar}), 552 (CCl). UV spectrum, λ_{max} (ε): 207 (42000), 220 (26000), 257 (20000), 280 (22000), 295 (22000), 315 (13000). ^1H NMR spectrum, δ, ppm: 3.91 s (3H, CH_3O), 6.50–8.27 m (11H, C_6H_3 and $2C_6H_4$), 8.62 s (1H, HC=N), 10.02 s (1H, CO_2H). Found, %: C 64.82; H 4.16; Cl 8.39; N 3.20. *M* 393.7. $C_{22}H_{16}ClNO_5$. Calculated, %: C 64.48; H 3.93; Cl 8.65; N 3.42. *M* 409.8.

4-(4-Chlorobenzoyloxy)-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIs). Yield 93%, mp 256–257°C (from methanol). IR spectrum, ν, cm^{-1}: 2050–3650 (OH), 3086, 3059, 3010, 3000 (CH_{Ar} and =CH), 2971, 2931, 2880, 2853, 2800 (CH_{Alk}), 1730, 1696 (C=O), 1633 (C=N), 1590, 1509, 1489, 1463, 1452, 1427, 1416, 1372 (Ar), 1313, 1278, 1258, 1217, 1199, 1170, 1151, 1120, 1096, 1076, 1036, 1016, 982 (CO), 868, 848, 773, 749, 712, 699, 680, 660, 637, 620 (CH_{Ar}), 547 (CCl). UV spectrum, λ_{max} (ε): 205 (40000), 220 (26000), 255 (18000), 280 (23000), 295 (20000), 315 (12000). ^1H NMR spectrum, δ, ppm: 3.92 s (3H, CH_3O), 6.45–8.25 m (11H, C_6H_3 and $2C_6H_4$), 8.63 s (1H, HC=N), 10.04 s (1H, CO_2H). Found, %: C 64.87; H 4.10; Cl 8.31; N 3.29 *M* 395.5. $C_{22}H_{16}ClNO_5$. Calculated, %: C 64.48; H 3.93; Cl 8.65; N 3.42. *M* 409.8.

4-(2,4-Dichlorobenzoyloxy)-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIt). Yield 90%, mp 219–220°C (from methanol). IR spectrum, ν, cm^{-1}: 2050–3650 (OH), 3095, 3080, 3040, 3010, 3000 (CH_{Ar} and =CH), 2964, 2927, 2872, 2853, 2800 (CH_{Alk}), 1745, 1711, 1689 (C=O), 1630 (C=N), 1602, 1589, 1508, 1460, 1450, 1429, 1417, 1378 (Ar), 1316, 1280, 1234, 1198, 1170, 1154, 1120, 1089, 1034 (CO), 871, 860, 830, 800, 780, 761, 740, 700, 675, 650, 635, 619 (CH_{Ar}), 550 (CCl). UV spectrum, λ_{max} (ε): 210 (47000), 221 (30000), 257 (24000), 280 (21000), 295 (22000), 310 (12000). ^1H NMR spectrum, δ, ppm: 3.90 s (3H, CH_3O), 6.50–8.50 m (10H, $2C_6H_3$ and C_6H_4), 8.62 s (1H, HC=N), 10.01 s (1H, CO_2H). Found, %: C 59.89; H 3.58; Cl 15.65; N 2.87. *M* 440.2. $C_{22}H_{15}Cl_2NO_5$. Calculated, %: C 59.48; H 3.40; Cl 15.96; N 3.15. *M* 444.3.

4-(2,4-Dichlorophenoxyacetoxy)-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIu). Yield 95%, mp 195–196°C (from methanol). IR spectrum, ν, cm^{-1}: 2030–3630 (OH), 3100, 3080, 3045, 3020, 3000 (CH_{Ar} and =CH), 2990, 2972, 2955, 2921, 2875, 2851, 2830, 2800 (CH_{Alk}), 1774, 1686 (C=O), 1630 (C=N), 1589, 1538, 1508, 1480, 1419, 1392, 1370 (Ar), 1316, 1290, 1278, 1245, 1220, 1195, 1169, 1148, 1118, 1104, 1087, 1074, 1045, 1031, 1015, 960, 940 (CO), 871, 860, 850, 835, 802, 773, 755, 715, 697, 655, 640, 617 (CH_{Ar}), 545, 555 (CCl). UV spectrum, λ_{max} (ε): 205 (42000), 220 (25000), 280 (23000), 295 (21000), 315 (12000). ^1H NMR spectrum, δ, ppm: 3.89 s (3H, CH_3O), 5.00 s (2H, CH_2), 6.45–8.10 m (10H, $2C_6H_3$ and C_6H_4), 8.60 s (1H, HC=N), 9.98 s (1H, CO_2H). Found, %: C 58.64; H 3.77; Cl 14.72; N 2.60. *M* 465.8. $C_{23}H_{17}Cl_2NO_6$. Calculated, %: C 58.24; H 3.61; Cl 14.95; N 2.95. *M* 474.3.

4-Bromoacetoxy-3-methoxyphenylmethylene-(4-carboxyphenyl)amine (IIIv). Yield 90%, mp 205–206°C (from methanol). IR spectrum, ν, cm^{-1}: 2030–3650 (OH), 3100, 3085, 3058, 3040, 3005 (CH_{Ar} and =CH), 2989, 2955, 2922, 2895, 2876, 2853, 2800 (CH_{Alk}), 1768, 1692 (C=O), 1627 (C=N), 1602, 1586, 1575, 1500, 1470, 1451, 1429, 1416, 1406, 1378 (Ar), 1315, 1280, 1257, 1219, 1197, 1185, 1171, 1151, 1113, 1029, 1008, 975 (C–O), 871, 846, 818, 794, 774, 761, 746, 733, 697, 684, 655, 616 (CH_{Ar}), 543 (CBr). UV spectrum, λ_{max} (ε): 207 (25000), 221 (19000), 280 (24000), 295 (24000), 315 (15000). ^1H NMR spectrum, δ, ppm: 3.89 s (3H, CH_3O), 4.40 s (2H, CH_2), 6.40–8.12 m (7H, C_6H_3 and C_6H_4), 8.54 s (1H, HC=N), 9.94 s (1H, CO_2H). Found, %: C 52.29;

H 3.76; Br 19.96; N 3.31. *M* 387.0. $C_{17}H_{14}BrNO_5$. Calculated, %: C 52.06; H 3.60; Br 20.37; N 3.57. *M* 392.2.

4-(4-Bromobenzoyloxy)-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIw). Yield 94%, mp 267–268°C (from methanol). IR spectrum, ν, cm^{-1}: 2000–3640 (OH), 3090, 3065, 3044, 3010 (CH_{Ar} and =CH), 2960, 2934, 2920, 2900, 2870, 2852, 2824, 2795 (CH_{Alk}), 1731, 1670 (C=O), 1632 (C=N), 1604, 1586, 1524, 1504, 1486, 1465, 1424, 1410, 1401 (Ar), 1315, 1293, 1278, 1261, 1220, 1200, 1175, 1155, 1119, 1071, 1050, 1036, 1012, 970 (CO), 897, 876, 847, 804, 777, 752, 730, 704, 681, 658, 637 (CH_{Ar}), 551 (CBr). UV spectrum, λ_{max} (ε): 206 (40000), 220 (28000), 257 (28000), 280 (24000), 295 (22000), 315 (12000). ^{1}H NMR spectrum, δ, ppm: 3.89 s (3H, CH_3O), 6.50–8.20 m (11H, C_6H_3 and $2C_6H_4$), 8.61 s (1H, HC=N), 10.00 s (1H, CO_2H). Found, %: C 58.37; H 3.82; Br 17.14; N 2.81. *M* 442.9. $C_{22}H_{16}BrNO_5$. Calculated, %: C 58.17; H 3.55; Br 17.59; N 3.08. *M* 454.3.

4-(3-Nitrobenzoyloxy)-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIx). Yield 92%, mp 256–257°C (from methanol). IR spectrum, ν, cm^{-1}: 2030–3600 (OH), 3105, 3075, 3050, 3035, 3000 (CH_{Ar} and =CH), 2985, 2975, 2930, 2885, 2850, 2830, 2800 (CH_{Alk}), 1749, 1679 (C=O), 1635 (C=N), 1610, 1594, 1570, 1508, 1481, 1458, 1415, 1380, 1320 (Ar), 1533, 1348 (NO_2), 1314, 1283, 1248, 1219, 1195, 1151, 1118, 1100, 1074, 1054, 1033, 1002, 973 (CO), 872, 862, 815, 801, 770, 730, 713, 701, 655, 620 (CH_{Ar}). UV spectrum, λ_{max} (ε): 205 (28000), 220 (44000), 260 (27000), 280 (24000), 295 (22000), 315 (12000). ^{1}H NMR spectrum, δ, ppm: 3.90 s (3H, CH_3O), 6.50–9.15 m (11H, C_6H_3 and $2C_6H_4$), 8.63 s (1H, HC=N), 10.04 c (1H, CO_2H). Found, %: C 63.08; H 4.01; N 6.30. *M* 417.6. $C_{22}H_{16}N_2O_7$. Calculated, %: C 62.86; H 3.84; N 6.66. *M* 420.4.

4-Succinyloxy-3-methoxyphenylmethylene(4-carboxyphenyl)amine (IIIy). Yield 94%, mp 255–256°C (from methanol). IR spectrum, ν, cm^{-1}: 2030–3650 (OH), 3071, 3000 (CH_{Ar} and =CH), 2970, 2924, 2837, 2851, 2795 (CH_{Alk}), 1760, 1681 (C=O), 1632 (C=N), 1599, 1586, 1507, 1468, 1450, 1419, 1370 (Ar), 1314, 1277, 1220, 1200, 1169, 1152, 1124, 1032, 1013, 968 (CO), 874, 862, 835, 807, 775, 753, 745, 700, 671, 636, 610 (CH_{Ar}). UV spectrum, λ_{max} (ε): 206 (45000), 220 (35000), 280 (43000), 295 (43000), 315 (24000). ^{1}H NMR spectrum, δ, ppm: 3.06 s [4H, $(CH_2)_2$], 3.88 s (6H, $2CH_3O$), 6.40–8.12 m (14H, $2C_6H_3$ and $2C_6H_4$), 8.53 s (2H, 2HC=N), 9.94 s (2H, CO_2H). Found, %: C 65.57; H 4.84; N 4.25. *M* 618.7. $C_{34}H_{28}N_2O_{10}$. Calculated, %: C 65.38; H 4.52; N 4.49. *M* 624.6.

4-Hydroxy-3-ethoxyphenylmethylene(4-carboxyphenyl)amine (IVa). Yield 90%, mp 199–200°C (from methanol). IR spectrum, ν, cm^{-1}: 1830–3550 (OH), 3070, 3051, 3000 (CH_{Ar} and =CH), 2984, 2930, 2897, 2855, 2820, 2800 (CH_{Alk}), 1692 (C=O), 1628 (C=N), 1581, 1523, 1478, 1431, 1419, 1397, 1373 (Ar), 1315, 1294, 1245, 1218, 1168, 1121, 1045, 1018, 992, 976 (CO), 863, 851, 830, 811, 770, 753, 701, 657, 612 (CH_{Ar}). UV spectrum, λ_{max} (ε): 206 (15000), 235 (10000), 295 (11000), 337 (13000). ^{1}H NMR spectrum, δ, ppm: 1.30 t (3H, CH_3), 4.18 q (2H, CH_2), 6.52 br.s (1H, OH), 6.50–7.95 m (7H, C_6H_3 and C_6H_4), 8.50 s (1H, HC=N), 9.80 s (1H, CO_2H). Found, %: C 67.59; H 5.43; N 4.70. *M* 280.7. $C_{16}H_{15}NO_4$. Calculated, %: C 67.36; H 5.30; N 4.91. *M* 285.3.

4-Acetoxy-3-ethoxyphenylmethylene(4-carboxyphenyl)amine (IVb). Yield 90%, mp 144–145°C (from methanol). IR spectrum, ν, cm^{-1}: 2030–3600 (OH), 3073, 3050, 3005 (CH_{Ar} and =CH), 2987, 2935, 2888, 2850, 2810 (CH_{Alk}), 1766, 1683 (C=O), 1629 (C=N), 1599, 1578, 1509, 1470, 1425, 1393, 1366 (Ar), 1316, 1288, 1267, 1218, 1194, 1164, 1115, 1040, 1011, 980 (CO), 862, 837, 774, 763, 720, 700, 675, 640, 615 (CH_{Ar}). UV spectrum, λ_{max} (ε): 205 (22000), 220 (19000), 280 (22000), 295 (21000), 315 (12000). ^{1}H NMR spectrum, δ, ppm: 1.43 t (3H, CH_3), 2.30 s (3H, CH_3COO), 4.13 q (2H, CH_2), 6.40–8.12 m (7H, C_6H_3 and C_6H_4), 8.52 s (1H, HC=N), 9.93 s (1H, CO_2H). Found, %: C 66.32; H 5.43; N 4.07. *M* 316.5. $C_{18}H_{17}NO_5$. Calculated, %: C 66.05; H 5.23; N 4.28. *M* 327.3.

4-Propionyloxy-3-ethoxyphenylmethylene(4-carboxyphenyl)amine (IVc). Yield 93%, mp 175–176°C (from methanol). IR spectrum, ν, cm^{-1}: 2030–3650 (OH), 3074, 3053, 3035, 3010 (CH_{Ar} and =CH), 2982, 2942, 2922, 2900, 2883, 2853, 2800 (CH_{Alk}), 1759, 2684 (C=O), 1629 (C=N), 1600, 1529, 1513, 1476, 1462, 1426, 1398, 1354 (Ar), 1314, 1290, 1270, 1223, 1165, 1144, 1113, 1078, 1041, 1011, 982 (CO), 872, 849, 825, 804, 774, 762, 700, 666, 611 (CH_{Ar}). UV spectrum, λ_{max} (ε): 205 (23000), 220 (20000), 280 (21000), 295 (20000), 315 (11000). ^{1}H NMR spectrum, δ, ppm: 1.37 t (3H, CH_3), 1.42 t (3H, CH_3), 2.68 q (2H, CH_2), 4.15 q (2H, CH_2), 6.40–8.14 m (7H, C_6H_3 and C_6H_4), 8.53 s (1H, HC=N), 9.94 s (1H, CO_2H). Found, %: C 67.09; H 5.87; N 3.84. *M* 330.6. $C_{19}H_{19}NO_5$. Calculated, %: C 66.85; H 5.61; N 4.10. *M* 341.4.

4-Butyryloxy-3-ethoxyphenylmethylene(4-carboxyphenyl)amine (IVd). Yield 93%, mp 168–169°C

(from methanol). IR spectrum, ν, cm^{-1}: 2030–3600 (OH), 3070, 3050, 3020 (CH_{Ar} and =CH), 2980, 2970, 2933, 2900, 2875, 2850, 2830, 2800 (CH_{Alk}), 1758, 1685 (C=O), 1626 (C=N), 1601, 1581, 1514, 1428, 1395 (Ar), 1314, 1288, 1248, 1220, 1190, 1166, 1119, 1085, 1041, 1012, 975 (CO), 869, 846, 808, 775, 763, 753, 696, 664, 613 (CH_{Ar}). UV spectrum, λ_{max} (ε): 205 (22000), 220 (20000), 280 (22000), 295 (22000), 315 (12000). ^{1}H NMR spectrum, δ, ppm: 1.04 t (3H, CH_3), 1.43 t (3H, CH_3), 1.64 m (2H, CH_2), 2.54 t (2H, CH_2), 4.14 q (2H, CH_2), 6.45–8.15 m (7H, C_6H_3 and C_6H_4), 8.52 s (1H, HC=N), 9.94 s (1H, CO_2H). Found, %: C 67.92; H 6.13; N 3.80. *M* 350.4. $C_{20}H_{21}NO_5$. Calculated, %: C 67.59; H 5.96; N 3.94. *M* 355.4.

4-Isobutyryloxy-3-ethoxyphenylmethylene(4-carboxyphenyl)amine (IVe). Yield 90%, mp 191–192°C (from methanol). IR spectrum, ν, cm^{-1}: 2020–3620 (OH), 3075, 3060, 3020, 3000 (CH_{Ar} and =CH), 2980, 2930, 2880, 2850, 2830, 2800 (CH_{Alk}), 1755, 1685 (C=O), 1625 (C=N), 1600, 1586, 1572, 1508, 1469, 1425, 1394, 1367, 1352 (Ar), 1316, 1290, 1275, 1216, 1160, 1124, 1099, 1042, 1011, 975 (CO), 867, 835, 820, 774, 755, 700, 660, 615 (CH_{Ar}). UV spectrum, λ_{max} (ε): 206 (23000), 220 (21000), 280 (22000), 295 (23000), 315 (13000). ^{1}H NMR spectrum, δ, ppm: 1.35 d [6H, $(CH_3)_2C$], 1.44 t (3H, CH_3), 2.92 quintet (1H, CH), 4.14 q (2H, CH_2), 6.45–8.15 m (7H, C_6H_3 and C_6H_4), 8.54 s (1H, HC=N), 9.94 s (1H, CO_2H). Found, %: C 67.90; H 6.10; N 3.88. *M* 352.8. $C_{20}H_{21}NO_5$. Calculated, %: C 67.59; H 5.96; N 3.94. *M* 355.4.

4-Isovaleroyloxy-3-ethoxyphenylmethylene(4-carboxyphenyl)amine (IVf). Yield 90%, mp 156–157°C (from methanol). IR spectrum, ν, cm^{-1}: 2030–3640 (OH), 3085, 3070, 3030, 3005 (CH_{Ar} and =CH), 2965, 2935, 2875, 2855, 2830, 2800 (CH_{Alk}), 1763, 1682 (C=O), 1627 (C=N), 1600, 1587, 1572, 1505, 1427, 1392, 1370 (Ar), 1315, 1288, 1275, 1245, 1215, 1170, 1154, 1119, 1089, 1039, 975 (CO), 870, 854, 830, 800, 775, 745, 730, 700, 655, 630, 620 (CH_{Ar}). UV spectrum, λ_{max} (ε): 205 (21000), 220 (22000), 280 (22000), 295 (23000), 315 (12000). ^{1}H NMR spectrum, δ, ppm: 1.12 d [6H, $(CH_3)_2C$], 1.42 t (3H, CH_3), 1.42–2.90 m (3H, CH and CH_2), 4.12 q (2H, CH_2), 6.45–8.20 m (7H, C_6H_3 and C_6H_4), 8.52 s (1H, HC=N), 9.93 s (1H, CO_2H). Found, %: C 68.63; H 6.44; N 3.50. *M* 355.7. $C_{21}H_{23}NO_5$. Calculated, %: C 68.28; H 6.28; N 3.79. *M* 369.4.

4-Benzoyloxy-3-ethoxyphenylmethylene(4-carboxyphenyl)amine (IVg). Yield 93%, mp 227–228°C (from methanol). IR spectrum, ν, cm^{-1}: 2040–3670 (OH), 3069, 3040, 3007 (CH_{Ar} and =CH), 2984, 2960, 2924, 2876, 2845, 2830, 2800 (CH_{Alk}), 1727, 1693 (C=O), 1632 (C=N), 1603, 1592, 1571, 1509, 1431, 1390, 1380 (Ar), 1317, 1295, 1278, 1261, 1222, 1195, 1161, 1125, 1081, 1064, 1051, 1026, 1015, 990 (CO), 866, 850, 805, 790, 775, 755, 698, 684, 655, 640, 620 (CH_{Ar}). UV spectrum, λ_{max} (ε): 208 (22000), 240 (22000), 280 (17000), 320 (11000). ^{1}H NMR spectrum, δ, ppm: 1.26 t (3H, CH_3), 4.18 q (2H, CH_2), 6.48–8.15 m (12H, C_6H_3, C_6H_4 and C_6H_5), 8.62 s (1H, HC=N), 10.02 s (1H, CO_2H). Found, %: C 71.23; H 5.16; N 3.60. *M* 380.8. $C_{23}H_{19}NO_5$. Calculated, %: C 70.94; H 4.92; N 3.60. *M* 389.4.

4-(4-Methylbenzoyloxy)-3-ethoxyphenylmethylene(4-carboxyphenyl)amine (IVh). Yield 94%, mp 213–214°C (from methanol). IR spectrum, ν, cm^{-1}: 2020–3700 (OH), 3100, 3071, 3040, 3000 (CH_{Ar} and =CH), 2983, 2920, 2879, 2851, 2800 (CH_{Alk}), 1727, 1688 (C=O), 1631 (C=N), 1593, 1511, 1429, 1385 (Ar), 1318, 1276, 1270, 1227, 1202, 1182, 1163, 1128, 1079, 1043, 1020, 990 (CO), 875, 850, 830, 805, 780, 755, 743, 700, 680, 665, 630, 625, 615 (CH_{Ar}). UV spectrum, λ_{max} (ε): 208 (22000), 220 (25000), 253 (27000), 280 (19000), 320 (12000). ^{1}H NMR spectrum, δ, ppm: 1.26 t (3H, CH_3), 2.48 s (3H, CH_3), 4.19 q (2H, CH_2), 6.45–8.12 m (11H, C_6H_3 and $2C_6H_4$), 8.63 s (1H, HC=N), 10.02 s (1H, CO_2H). Found, %: C 71.68; H 5.29; N 3.24. *M* 389.9. $C_{24}H_{21}NO_5$. Calculated, %: C 71.45; H 5.25; N 3.47. *M* 403.4.

4-(2-Chlorobenzoyloxy)-3-ethoxyphenylmethyleneν(4-carboxyphenyl)amine (IVi). Yield 94%, mp 198–199°C (from methanol). IR spectrum, ν, cm^{-1}: 2020–3620 (OH), 3100, 3080, 3070, 3040, 3010 (CH_{Ar} and =CH), 2990, 2989, 2920, 2870, 2800 (CH_{Alk}), 1753, 1675 (C=O), 1630 (C=N), 1597, 1588, 1575, 1503, 1470, 1423, 1400, 1340 (Ar), 1316, 1281, 1260, 1234, 1216, 1189, 1162, 1150, 1134, 1108, 1082, 1024, 963 (CO), 875, 864, 825, 815, 790, 776, 749, 740, 704, 695, 681, 660, 640, 630, 615 (CH_{Ar}), 545 (CCl). UV spectrum, λ_{max} (ε): 208 (43000), 220 (25000), 258 (21000), 280 (22000), 295 (22000), 315 (12000). ^{1}H NMR spectrum, δ, ppm: 1.27 t (3H, CH_3), 4.19 q (2H, CH_2), 6.50–8.28 m (11H, C_6H_3 and $2C_6H_4$), 8.64 s (1H, HC=N), 10.02 s (1H, CO_2H). Found, %: C 65.35; H 4.41; Cl 8.07; N 3.10. *M* 416.2. $C_{23}H_{18}ClNO_5$. Calculated, %: C 65.18; H 4.28; Cl 8.36; N 3.30. *M* 423.9.

4-(4-Chlorobenzoyloxy)-3-ethoxyphenylmethylene(4-carboxyphenyl)amine (IVj). Yield 93%, mp 227–228°C (from methanol). IR spectrum, ν, cm^{-1}: 2000–3630 (OH), 3100, 3090, 3073, 3055, 3020, 3003 (CH_{Ar} and =CH), 2983, 2934, 2900, 2870, 2854, 2800

(CH_{Alk}), 1736, 1693 (C=O), 1630 (C=N), 1591, 1509, 1488, 1432, 1400, 1376 (Ar), 1320, 1283, 1259, 1225, 1205, 1175, 1162, 1123, 1090, 1071, 1042, 1013, 982 (CO), 866, 847, 821, 795, 775, 748, 698, 678, 662, 616 (CH_{Ar}), 549 (CCl). UV spectrum, λ_{max} (ε): 205 (39000), 220 (27000), 255 (19000), 280 (22000), 295 (20000), 315 (13000). ^{1}H NMR spectrum, δ, ppm: 1.28 t (3H, CH_3), 4.20 q (2H, CH_2), 6.42–8.28 m (11H, C_6H_3 and $2C_6H_4$), 8.64 s (1H, HC=N), 10.04 s (1H, CO_2H). Found, %: C 65.38; H 4.37; Cl 8.12; N 3.06. *M* 418.0. $C_{23}H_{18}ClNO_5$. Calculated, %: C 65.18; H 4.28; Cl 8.36; N 3.30. *M* 423.9.

4-Succinyloxy-3-ethoxyphenylmethylene(4-carboxyphenyl)amine (IVk). Yield 90%, mp 247–248°C (from methanol). IR spectrum, ν, cm^{-1}: 2020–3640 (OH), 3071, 3005 (CH_{Ar} and =CH), 2979, 2926, 2872, 2855, 2800 (CH_{Alk}), 1765, 1683 (C=O), 1628 (C=N), 1600, 1588, 1504, 1475, 1431, 1394, 1374 (Ar), 1314, 1274, 1216, 1194, 1166, 1158, 1112, 1039, 1011, 970 (CO), 864, 852, 840, 791, 773, 755, 728, 696, 672, 630, 613 (CH_{Ar}). UV spectrum, λ_{max} (ε): 207 (44000), 220 (35000), 280 (42000), 295 (42000), 315 (23000). ^{1}H NMR spectrum, δ, ppm: 1.25 t (6H, $2CH_3$), 3.06 s [4H, $(CH_2)_2$], 4.19 q (4H, $2CH_2$), 6.42–8.12 m (14H, $2C_6H_3$ and $2C_6H_4$), 8.52 s (2H, 2HC=N), 9.94 s (2H, CO_2H). Found, %: C 66.43; H 5.08; N 4.20. *M* 640.3. $C_{36}H_{32}N_2O_{10}$. Calculated, %: C 66.25; H 4.94; N 4.29. *M* 652.7.

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