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Synthesis of Schiff Bases from Biphenyl-4-amine and Vanillin, Vanillal, and Their Esters

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Abstract—Reactions of vanillin, vanillal, and esters derived therefrom with biphenyl-4-amine in anhydrous methanol gave previously unknown Schiff bases containing ether and ester moieties.

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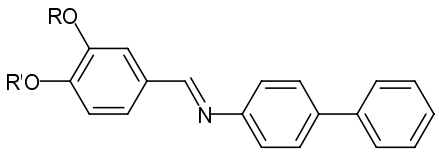
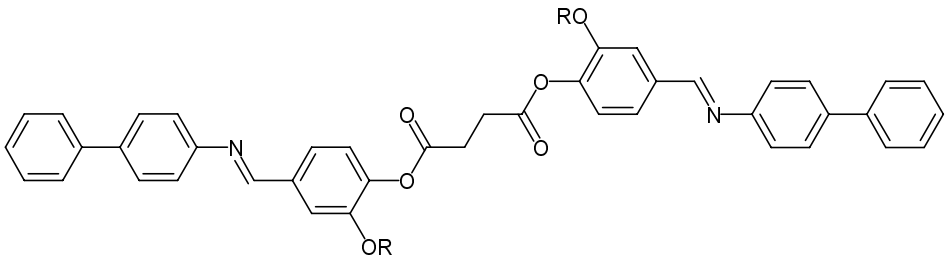
Natural aromatic hydroxy aldehydes, vanillin and vanillal (3-methoxy- and 3-ethoxy-4-hydroxybenzaldehydes), as well as esters derived therefrom, may be used as accessible source of aromatic structural fragments containing ether and ester moieties for purposeful synthesis of various biologically active compounds, drugs, liquid crystals, dyes, and luminophores [1–5].

The present article reports on the synthesis of new Schiff bases by condensation of vanillin, vanillal, and the corresponding esters with biphenyl-4-amine in boiling anhydrous methanol. The reactions were complete in 0.5–1 h, and Schiff bases **I**–**XXXIV** were obtained in 90–95% yield. The product structure was confirmed by the analytical data, molecular weight determination by cryoscopy, and ^{1}H NMR, IR, and UV spectra. According to the ^{1}H NMR data, the purity of compounds **I**–**XXXIV** was 98±1% and they were individual *E* isomers. The HC=N signal appeared in the ^{1}H NMR spectra as a singlet at 8.4 ppm.

Schiff bases **I**–**XXXIV** possess a mesogenic biphenyl fragment and attract interest as potential liquid crystals [6–8]. Among these, the most promising are long-chain esters **VI**–**IX** and **XI**. We also plan to examine biological activity of these compounds.



I–**XXIII**, **XXV**–**XXXIII**



XXIV, **XXXIV**

I–**XXIV**, R = Me; **XXV**–**XXXIV**, R = Et; **I**, **XXV**, R' = H; **II**, **XXVI**, R' = MeCO; **III**, **XXVII**, R' = $MeCH_2CO$; **IV**, **XXVIII**, R' = $Me(CH_2)_2CO$; **V**, **XXIX**, R' = Me_2CHCO; **VI**, R' = $Me(CH_2)_6CO$; **VII**, R' = $Me(CH_2)_8CO$; **VIII**, R' = $Me(CH_2)_{11}CO$; **IX**, R' = $Me(CH_2)_{16}CO$; **X**, R' = CH_2=C(Me)CO; **XI**, R' = *cis*-$Me(CH_2)_7CH$=$CH(CH_2)_7CO$; **XII**, R' = $PhCH_2CO$; **XIII**, R' = $PhCH(Me)CH_2CO$; **XIV**, R' = 4-$MeC_6H_4O(CH_2)_2CO$; **XV**, **XXXI**, R' = PhCO; **XVI**, **XXXII**, R' = 4-MeC_6H_4CO; **XVII**, R' = 4-ClC_6H_4CO; **XVIII**, R' = 2,4-$Cl_2C_6H_3CO$; **XIX**, R' = 2,4-$Cl_2C_6H_3OCH$-$_2CO$; **XX**, R' = $BrCH_2CO$; **XXI**, R' = PhCHBrCHBrCO; **XXII**, R' = 4-BrC_6H_4CO; **XXIII**, R' = 3-$O_2NC_6H_4CO$; **XXX**, R = Me_2CHCH_2CO; **XXXIII**, R' = 2-ClC_6H_4CO.

EXPERIMENTAL

The IR spectra were recorded on a Nicolet Protege-460 Fourier-transform spectrometer from samples prepared as KBr pellets. The UV spectra were measured on a Specord UV-Vis spectrophotometer from solution in methanol with a concentration of 1×10^{-4} M. The ^{1}H NMR spectra were obtained on a Tesla BS-587A instrument (100 MHz) from 5% solutions in $CDCl_3$ containing octamethylcyclotetrasiloxane as internal reference. The molecular weights were determined by cryoscopy in benzene. Initial vanillin and vanillal esters were synthesized according to the procedures described in [4, 9, 10].

Schiff bases I–XXXIV (*general procedure*). Biphenyl-4-amine, 0.01 mol, was added to a solution of 0.01 mol of the corresponding aldehyde (0.005 mol in the synthesis of compounds **XXIV** and **XXXIV**) in 50 ml of anhydrous methanol. The mixture was heated for 0.5–1 h under reflux and was left to stand for 20–30 h at 20–23°C. The precipitate was filtered off through a glass filter, washed with a small amount of methanol, and dried under reduced pressure. Compounds **I**–**XXXIV** thus isolated were sufficiently pure, and no additional purification by recrystallization was necessary. The solvent may be reused after distillation through a Vigreaux column.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenol (I). Yield 93%, mp 193–194°C. IR spectrum, ν, cm^{-1}: 3420 (OH); 3090, 3060, 3040, 3030 3008 (C–H_{arom}, =C–H); 1624 (C=N); 1587, 1516, 1483, 1462, 1453, 1427, 1381 (C–C_{arom}); 870, 840, 826, 763, 754, 728, 718, 694, 635, 620, 615 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (20000), 238 (8000), 280 (8000), 338 (13000). ^{1}H NMR spectrum, δ, ppm: 4.02 s (3H, Me), 6.20 br.s (1H, OH), 7.15–7.75 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.41 s (1H, HC=N). Found, %: C 79.38; H 5.70; N 4.41. *M* 290.7. $C_{20}H_{17}NO_2$. Calculated, %: C 79.19; H 5.65; N 4.62. *M* 303.4.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl acetate (II). Yield 94%, mp 136–137°C. IR spectrum, ν, cm^{-1}: 3085, 3065, 3023, 3002 (C–H_{arom}, =C–H); 1766 (C=O); 1626 (C=N); 1600, 1583, 1505, 1484, 1465, 1450, 1417, 1366 (C–C_{arom}); 872, 860, 846, 765, 750, 722, 691, 662, 630, 600 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (19000), 270 (10000), 320 (9000). ^{1}H NMR spectrum, δ, ppm: 2.28 s (3H, Me), 3.88 s (3H, MeO), 7.00–7.70 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.39 s (1H, HC=N). Found, %: C 76.72; H 5.68; N 3.91. *M* 337.2. $C_{22}H_{19}NO_3$. Calculated, %: C 76.50; H 5.54; N 4.06. *M* 345.4.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl propionate (III). Yield 93%, mp 103–103°C. IR spectrum, ν, cm^{-1}: 3085, 3060, 3025, 3001 (C–H_{arom}, =C–H); 1759 (C=O); 1628 (C=N); 1599, 1581, 1512, 1484, 1464, 1449, 1415, 1355, 1317 (C–C_{arom}); 875, 840, 830, 805, 763, 720, 690, 620 (C–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (20000), 270 (10000), 319 (9000). ^{1}H NMR spectrum, δ, ppm: 1.28 t (3H, Me), 2.54 q (2H, CH_2), 3.88 s (3H, MeO), 7.00–7.70 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.39 s (1H, HC=N). Found, %: C 77.02; H 5.96; N 3.70. *M* 350.9. $C_{23}H_{21}NO_3$. Calculated, %: C 76.86; H 5.89; N 3.90. *M* 359.4.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl butanoate (IV). Yield 94%, mp 114–115°C. IR spectrum, ν, cm^{-1}: 3080, 3070, 3060, 3030, 3000 (C–H_{arom}, =CH); 1756 (C=O); 1626 (C=N); 1600, 1582, 1503, 1482, 1465, 1451, 1416, 1370 (C–C_{arom}); 867, 846, 800, 771, 760, 724, 699, 635, 618 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 205 (19000), 270 (10000), 320 (9000). ^{1}H NMR spectrum, δ, ppm: 1.04 t (3H, Me), 1.66 m (2H, CH_2), 2.56 t (2H, CH_2CO), 3.87 s (3H, MeO), 7.00–7.75 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.39 s (1H, HC=N). Found, %: C 77.34; H 6.35; N 3.58. *M* 361.1. $C_{24}H_{23}NO_3$. Calculated, %: C 77.19; H 6.21; N 3.75. *M* 373.5.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl 2-methylpropionate (V). Yield 94%, mp 97–98°C. IR spectrum, ν, cm^{-1}: 3085, 3060, 3025, 3002 (C–H_{arom}, =CH); 1762 (C=O); 1628 (C=N); 1594, 1503, 1483, 1458, 1416, 1369, 1315 (C–C_{arom}); 862, 840, 825, 767, 755, 730, 698, 640, 615 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (19000), 270 (10000), 320 (9000). ^{1}H NMR spectrum, δ, ppm: 1.27 d (6H, Me_2C), 2.80 quint (1H, CH), 3.86 s (3H, MeO), 7.00–7.72 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.39 s (1H, HC=N). Found, %: C 77.39; H 6.30; N 3.51. *M* 364.3. $C_{24}H_{23}NO_3$. Calculated, %: C 77.19; H 6.21; N 3.75. *M* 373.5.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl octanoate (VI). Yield 92%, mp 72–73°C. IR spectrum, ν, cm^{-1}: 3080, 3070, 3025, 3003 (C–H_{arom}, =CH); 1760 (C=O); 1626 (C=N); 1600, 1586, 1513, 1490, 1466, 1417, 1377, 1320 (C–C_{arom}); 875, 845, 764, 730, 697, 630, 620 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (20000), 270 (10000), 320 (10000). ^{1}H NMR spectrum, δ, ppm: 0.94 t (3H, Me), 1.20–1.50 m (8H, CH_2), 1.78 t (2H, CH_2), 2.62 t (2H, CH_2CO), 3.86 s (3H, MeO), 7.02–7.70 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.39 s (1H, HC=N). Found, %: C 77.39; H 7.38; N 2.97. *M* 418.8. $C_{28}H_{31}NO_3$. Calculated, %: C 78.29; H 7.27; N 3.26. *M* 429.6.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl nonanoate (VII). Yield 95%, mp 93–94°C. IR spectrum, ν, cm^{-1}: 3090, 3080, 3065, 3030, 3002 (C–H_{arom}, =CH); 1757 (C=O); 1628 (C=N); 1600, 1578, 1509, 1484, 1464, 1414, 1385, 1320 (C–C_{arom}); 875, 865, 840, 766, 730, 690, 640, 615 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 205 (19000), 270 (10000), 322 (9000). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, Me), 1.12–1.55 m (12H, CH_2), 1.78 t (2H, CH_2), 2.58 t (2H, CH_2CO), 3.87 s (3H, MeO), 7.00–7.74 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.40 s (1H, HC=N). Found, %: C 79.10; H 7.84; N 2.88. *M* 447.2. $C_{30}H_{35}NO_3$. Calculated, %: C 78.74; H 7.71; N 3.06. *M* 457.6.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl tridecanoate (VIII). Yield 90%, mp 77–78°C. IR spectrum, ν, cm^{-1}: 3090, 3075, 3035, 3003 (C–H_{arom}, =C–H); 1763 (C=O); 1629 (C=N); 1600, 1580, 1508, 1477, 1467, 1413, 1380, 1320 (C–C_{arom}); 877, 855, 840, 767, 722, 690, 635, 612 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (19000), 268 (10000), 320 (9000). ^{1}H NMR spectrum, δ, ppm: 0.87 t (3H, Me), 1.15–1.52 m (18H, CH_2), 1.72 t (2H, CH_2), 2.58 t (2H, CH_2CO), 3.86 s (3H, MeO), 7.00–7.75 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.40 s (1H, HC=N). Found, %: C 79.55; H 8.56; N 2.63. *M* 486.5. $C_{33}H_{41}NO_3$. Calculated, %: C 79.32; H 8.27; N 2.80. *M* 499.7.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl octadecanoate (IX). Yield 94%, mp 83–84°C. IR spectrum, ν, cm^{-1}: 3085, 3070, 3030, 3003 (C–H_{arom}, =C–H); 1760 (C=O); 1627 (C=N); 1600, 1586, 1507, 1485, 1468, 1417, 1372, 1315 (C–C_{arom}); 875, 860, 844, 764, 721, 692, 617 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (19000), 270 (10000), 320 (8000). ^{1}H NMR spectrum, δ, ppm: 0.82 t (3H, Me), 1.05–1.45 m (28H, CH_2), 1.70 t (2H, CH_2), 2.52 t (2H, CH_2CO), 3.86 s (3H, MeO), 6.98–7.65 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.38 s (1H, HC=N). Found, %: C 80.36; H 9.17; N 2.21. *M* 540.5. $C_{38}H_{51}NO_3$. Calculated, %: C 80.10; H 9.02; N 2.46. *M* 569.8.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl 2-methylprop-2-enoate (X). Yield 94%, mp 76–77°C. IR spectrum, ν, cm^{-1}: 3085, 3070, 3030, 3002 (C–H_{arom}, =CH); 1731 (C=O); 1665 (C=C); 1627 (C=N); 1600, 1587, 1504, 1483, 1451, 1440, 1416, 1380, 1317 (C–C_{arom}); 880, 870, 840, 830, 810, 767, 760, 730, 695, 635, 623 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 206 (25000), 222 (16000), 267 (12000), 315 (10000). ^{1}H NMR spectrum, δ, ppm: 2.03 s (3H, Me), 3.86 s (3H, MeO), 5.72 s (1H, =CH), 6.35 s (1H, =CH), 7.05–7.75 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.43 s (1H, HC=N). Found, %: C 77.92; H 5.84; N 3.51. *M* 362.0. $C_{24}H_{21}NO_3$. Calculated, %: C 77.61; H 5.70; N 3.77. *M* 371.4.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl (9*Z*)-nonadec-9-enoate (XI). Yield 90%, mp 63–64°C. IR spectrum, ν, cm^{-1}: 3080, 3070, 3030, 3003 (C–H_{arom}, =C–H); 1763 (C=O); 1660 (C=C); 1630 (C=N); 1600, 1580, 1507, 1484, 1465, 1417, 1375, 1320 (C–C_{arom}); 880, 865, 840, 766, 730, 695, 640, 620 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 206 (24000), 221 (16000), 268 (12000), 315 (10000). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, Me), 1.07–2.15 m (26H, CH_2), 2.62 t (2H, CH_2), 3.86 s (3H, MeO), 5.40 t (2H, =CH), 7.95–7.65 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.40 s (1H, HC=N). Found, %: C 80.57; H 8.93; N 2.24. *M* 543.1. $C_{38}H_{49}NO_3$. Calculated, %: C 80.38; H 8.70; N 2.47. *M* 567.8.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl 2-phenylacetate (XII). Yield 90%, mp 107–108°C. IR spectrum, ν, cm^{-1}: 3080, 3070, 3025, 3005 (C–H_{arom}, =CH); 1759 (C=O); 1632 (C=N); 1590, 1504, 1483, 1459, 1414, 1375, 1310 (C–C_{arom}); 875, 850, 800, 775, 770, 760, 735, 725, 696, 650, 620 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 209 (26000), 220 (15000), 270 (11000), 320 (10000). ^{1}H NMR spectrum, δ, ppm: 3.80 s (2H, CH_2), 3.85 s (3H, MeO), 6.95–7.70 m (17H, C_6H_3, C_6H_4, C_6H_5), 8.40 s (1H, HC=N). Found, %: C 79.92; H 5.54; N 3.04. *M* 407.6. $C_{28}H_{23}NO_3$. Calculated, %: C 79.79; H 5.50; N 3.32. *M* 421.5.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl 3-phenylbutanoate (XIII). Yield 91%, mp 116–117°C. IR spectrum, ν, cm^{-1}: 3085, 3065, 3020 (C–H_{arom}, =C–H); 1746 (C=O); 1632 (C=N); 1593, 1506, 1483, 1461, 1449, 1414, 1367, 1320 (C–C_{arom}); 868, 855, 847, 820, 760, 754, 730, 697, 634, 635, 620 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 209 (27000), 220 (14000), 272 (11000), 320 (10000). ^{1}H NMR spectrum, δ, ppm: 1.38 d (3H, Me), 2.82 d (2H, CH_2), 3.35 q (1H, CH), 3.82 s (3H, MeO), 7.00–7.65 m (17H, C_6H_3, C_6H_4, C_6H_5), 8.40 s (1H, HC=N). Found, %: C 80.43; H 6.12; N 2.89. *M* 436.9. $C_{30}H_{27}NO_3$. Calculated, %: C 80.15; H 6.05; N 3.12. *M* 449.5.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl 3-(4-methylphenoxy)propionate (XIV). Yield 93%, mp 132–133°C. IR spectrum, ν, cm^{-1}: 3080, 3065, 3027, 3000 (C–H_{arom}, =C–H); 1753 (C=O); 1627 (C=N); 1601, 1590, 1509, 1487, 1463, 1417, 1400, 1392, 1365, 1322 (C–C_{arom}); 875, 863, 843, 830, 810, 766, 754, 740, 724, 691, 619 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (27000), 220 (20000), 270

(10000), 320 (10000). ^{1}H NMR spectrum, δ, ppm: 2.29 s (3H, Me), 3.06 t (2H, CH_2O), 3.86 s (3H, MeO), 4.36 t (2H, CH_2), 6.60–7.60 m (16H, C_6H_3, C_6H_4, C_6H_5), 8.40 s (1H, HC=N). Found, %: C 77.74; H 5.93; N 2.82. *M* 451.3. $C_{30}H_{27}NO_4$. Calculated, %: C 77.40; H 5.85; N 3.01. *M* 465.5.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl benzoate (XV). Yield 95%, mp 131–132°C. IR spectrum, ν, cm^{-1}: 3090, 3080, 3055, 3025, 3003 (C–H_{arom}, =C–H); 1755 (C=O); 1632 (C=N); 1589, 1503, 1480, 1460, 1440, 1430, 1415, 1375, 1318 (C–C_{arom}); 875, 840, 805, 771, 742, 725, 695, 640, 618 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (34000), 220 (28000), 262 (20000), 320 (12000). ^{1}H NMR spectrum, δ, ppm: 3.89 s (3H, MeO), 7.15–8.10 m (17H, C_6H_3, C_6H_4, C_6H_5), 8.42 s (1H, HC=N). Found, %: C 79.95; H 5.31; N 3.20. *M* 392.4. $C_{27}H_{21}NO_3$. Calculated, %: C 79.59; H 5.19; N 3.44. *M* 407.5.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl 4-methylbenzoate (XVI). Yield 93%, mp 161–162°C. IR spectrum, ν, cm^{-1}: 3077, 3060, 3040, 3010 (C–H_{arom}, =C–H); 1741 (C=O); 1627 (C=N); 1605, 1591, 1503, 1480, 1463, 1416, 1376, 1317 (C–C_{arom}); 872, 865, 837, 770, 747, 725, 700, 685, 635, 620 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 207 (36000), 222 (18000), 252 (20000), 270 (12000), 320 (10000). ^{1}H NMR spectrum, δ, ppm: 2.39 s (3H, Me), 3.85 s (3H, MeO), 7.10–8.10 m (16H, C_6H_3, C_6H_4, C_6H_5), 8.42 s (1H, HC=N). Found, %: C 80.03; H 5.57; N 3.06. *M* 309.1. $C_{28}H_{23}NO_3$. Calculated, %: C 79.79; H 5.50; N 3.32. *M* 421.5.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl 4-chlorobenzoate (XVII). Yield 92%, mp 171–172°C. IR spectrum, ν, cm^{-1}: 3085, 3075, 3050, 3035, 3015 (C–H_{arom}, =C–H); 1742 (C=O); 1629 (C=N); 1600, 1590, 1583, 1510, 1482, 1465, 1445, 1420, 1400, 1355, 1317 (C–C_{arom}); 879, 860, 845, 825, 763, 753, 730, 696, 635, 615 (δC–H_{arom}); 525 (C–Cl). UV spectrum, λ_{max}, nm (ε): 204 (36000), 221 (24000), 265 (17000), 320 (11000). ^{1}H NMR spectrum, δ, ppm: 3.89 s (3H, MeO), 7.10–8.30 m (16H, C_6H_3, C_6H_4, C_6H_5), 8.44 s (1H, HC=N). Found, %: C 73.61; H 4.66; Cl 7.86; N 2.87. *M* 430.7. $C_{27}H_{20}ClNO_3$. Calculated, %: C 73.38; H 4.56; Cl 8.02; N 3.17. *M* 441.9.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl 2,4-dichlorobenzoate (XVIII). Yield 94%, mp 145–146°C. IR spectrum, ν, cm^{-1}: 3091, 3080, 3060, 3024, 3002 (C–H_{arom}, =C–H); 1755 (C=O); 1626 (C=N); 1586, 1560, 1504, 1481, 1462, 1419, 1375, 1317 (C–C_{arom}); 870, 863, 845, 830, 805, 785, 767, 756, 730, 696, 670, 620 (δC–H_{arom}); 530, 560 (C–Cl). UV spectrum, λ_{max}, nm (ε): 210 (42000), 260 (18000), 320 (10000). ^{1}H NMR spectrum, δ, ppm: 3.90 s (3H, MeO), 7.02–8.50 m (15H, C_6H_3, C_6H_4, C_6H_5), 8.44 s (1H, HC=N). Found, %: C 68.23; H 4.14; Cl 14.57; N 2.80. *M* 468.2. $C_{27}H_{19}Cl_2NO_3$. Calculated, %: C 68.08; H 4.02; Cl 14.88; N 2.94. *M* 476.4.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl 2-(2,4-dichlorophenoxy)acetate (XIX). Yield 93%, mp 167–168°C. IR spectrum, ν, cm^{-1}: 3090, 3080, 3025, 3000 (C–H_{arom}, =C–H); 1784 (C=O); 1629 (C=N); 1590, 1506, 1484, 1460, 1449, 1425, 1415, 1391, 1377, 1320 (C–C_{arom}); 870, 841, 801, 775, 769, 754, 740, 730, 690, 655, 620, 605 (δC–H_{arom}); 540, 555 (C–Cl). UV spectrum, λ_{max}, nm (ε): 205 (40000), 224 (20000), 270 (11000), 320 (10000). ^{1}H NMR spectrum, δ, ppm: 3.88 s (3H, MeO), 4.98 s (2H, CH_2), 6.88–7.60 m (15H, C_6H_3, C_6H_4, C_6H_5), 8.41 s (1H, HC=N). Found, %: C 66.59; H 4.32; Cl 13.68; N 2.51. *M* 489.6. $C_{28}H_{21}Cl_2NO_4$. Calculated, %: C 66.41; H 4.18; Cl 14.00; N 2.77. *M* 506.4.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl 2-bromoacetate (XX). Yield 93%, mp 112–113°C. IR spectrum, ν, cm^{-1}: 3090, 3075, 3030, 3010 (C–H_{arom}, =C–H); 1786 (C=O); 1629 (C=N); 1506, 1484, 1464, 1440, 1425, 1417, 1360, 1313 (C–C_{arom}); 870, 845, 835, 815, 764, 755, 725, 690, 635, 615 (δC–H_{arom}); 550 (C–Br). UV spectrum, λ_{max}, nm (ε): 204 (21000), 270 (11000), 320 (10000). ^{1}H NMR spectrum, δ, ppm: 3.87 s (3H, MeO), 4.30 s (2H, CH_2), 7.05–7.80 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.40 s (1H, HC=N). Found, %: C 62.43; H 4.42; Br 18.34; N 3.07. *M* 409.5. $C_{22}H_{18}BrNO_3$. Calculated, %: C 62.28; H 4.28; Br 18.83; N 3.30. *M* 424.3.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl 2,3-dibromo-3-phenylpropionate (XXI). Yield 90%, mp 107–108°C. IR spectrum, ν, cm^{-1}: 3090, 3075, 3030, 3005 (C–H_{arom}, =C–H); 1726 (C=O); 1629 (C=N); 1591, 1504, 1483, 1454, 1417, 1380, 1320 (C–C_{arom}); 862, 835, 805, 759, 725, 691, 645, 620, 605 (δC–H_{arom}); 540 (C–Br). UV spectrum, λ_{max}, nm (ε): 208 (28000), 220 (15000), 270 (11000), 320 (10000). ^{1}H NMR spectrum, δ, ppm: 2.23 d (1H, CH), 3.92 s (3H, MeO), 4.80–5.58 m (1H, CH), 7.12–7.75 m (17H, C_6H_3, C_6H_4, C_6H_5), 8.42 s (1H, HC=N). Found, %: C 58.93; H 4.06; Br 26.59; N 2.17. *M* 580.0. $C_{29}H_{23}Br_2NO_3$. Calculated, %: C 58.71; H 3.91; Br 26.93; N 2.36. *M* 593.3.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl 4-bromobenzoate (XXII). Yield 93%, mp 167–168°C.

IR spectrum, ν, cm^{-1}: 3095, 3085, 3070, 3030 (C–H_{arom}, =C–H); 1740 (C=O); 1630 (C=N); 1586, 1509, 1482, 1464, 1450, 1420, 1400, 1365, 1318 (C–C_{arom}); 877, 842, 820, 780, 762, 750, 730, 696, 680, 635, 612 (δC–H_{arom}); 542 (C–Br). UV spectrum, λ_{max}, nm (ε): 205 (35000), 265 (30000), 320 (12000). ^{1}H NMR spectrum, δ, ppm: 3.89 s (3H, MeO), 7.18–8.10 m (16H, C_6H_3, C_6H_4, C_6H_5), 8.44 s (1H, HC=N). Found, %: C 66.86; H 4.23; Br 16.17; N 3.60. *M* 472.2. $C_{27}H_{20}BrNO_3$. Calculated, %: C 66.68; H 4.14; Br 16.43; N 2.88. *M* 486.3.

4-(Biphenyl-4-yliminomethyl)-2-methoxyphenyl 3-nitrobenzoate (XXIII). Yield 94%, mp 135–136°C. IR spectrum, ν, cm^{-1}: 3100, 3090, 3080, 3060, 3035, 3000 (C–H_{arom}, =C–H); 1756 (C=O); 1629 (C=N); 1591, 1506, 1481, 1463, 1451, 1414, 1375, 1321 (C–C_{arom}); 1535, 1347 (NO_2); 870, 860, 845, 812, 770, 755, 740, 712, 690, 650, 630, 618 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 205 (30000), 222 (42000), 260 (20000), 320 (12000). ^{1}H NMR spectrum, δ, ppm: 3.87 s (3H, MeO); 7.15–7.80 m, 8.35–8.55 m, and 8.90–9.05 m (16H, C_6H_3, C_6H_4, C_6H_5); 8.44 s (1H, HC=N). Found, %: C 71.94; H 4.58; N 5.92. *M* 441.7. $C_{27}H_{20}N_2O_5$. Calculated, %: C 71.67; H 4.46; N 6.19. *M* 452.5.

Bis[4-(biphenyl-4-yliminomethyl)-2-methoxyphenyl] succinate (XXIV). Yield 92%, mp 212–213°C. IR spectrum, ν, cm^{-1}: 3090, 3080, 3070, 3040, 3010 (C–H_{arom}, =C–H); 1757 (C=O); 1628 (C=N); 1600, 1580, 1509, 1485, 1465, 1450, 1417, 1350, 1318 (C–C_{arom}); 880, 870, 845, 830, 800, 766, 735, 695, 660, 612 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (38000), 270 (20000), 320 (19000). ^{1}H NMR spectrum, δ, ppm: 3.05 s (4H, (CH_2), 3.88 s (6H, MeO), 7.10–7.50 m (24H, C_6H_3, C_6H_4, C_6H_5), 8.39 s (2H, HC=N). Found, %: C 76.94; H 5.38; N 3.84. *M* 672.3. $C_{44}H_{36}N_2O_6$. Calculated, %: C 76.73; H 5.27; N 4.07. *M* 688.8.

4-(Biphenyl-4-yliminomethyl)-2-ethoxyphenol (XXV). Yield 93%, mp 153–154°C. IR spectrum, ν, cm^{-1}: 3427 (OH); 3090, 3040, 3030 (C–H_{arom}, =C–H); 1628 (C=N); 1578, 1519, 1439, 1400, 1388 (C–C_{arom}); 880, 838, 830, 764, 720, 690, 630, 613 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (20000), 237 (8000), 280 (8000), 337 (12000). ^{1}H NMR spectrum, δ, ppm: 1.44 t (3H, Me), 4.21 q (2H, CH_2), 7.10–7.62 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.36 s (1H, HC=N). Found, %: C 79.75; H 6.14; N 4.19. *M* 308.6. $C_{21}H_{19}NO_2$. Calculated, %: C 79.47; H 6.03; N 4.41. *M* 317.4.

4-(Biphenyl-4-yliminomethyl)-2-ethoxyphenyl acetate (XXVI). Yield 90%, mp 88–89°C. IR spectrum, ν, cm^{-1}: 3080, 3055, 3027 (C–H_{arom}, =C–H); 1767 (C=O); 1627 (C=N); 1600, 1583, 1504, 1482, 1504, 1482, 1430, 1394, 1368, 1318 (C–C_{arom}); 867, 860, 845, 766, 735, 695, 660, 620 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (18000), 270 (10000), 320 (9000). ^{1}H NMR spectrum, δ, ppm: 1.36 t (3H, Me), 2.26 s (3H, MeCO), 4.11 q (2H, CH_2), 7.02–7.70 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.37 s (1H, HC=N). Found, %: C 77.08; H 6.04; N 3.61. *M* 347.9. $C_{23}H_{21}NO_3$. Calculated, %: C 76.86; H 5.89; N 3.90. *M* 359.4.

4-(Biphenyl-4-yliminomethyl)-2-ethoxyphenyl propionate (XXVII). Yield 91%, mp 92–93°C. IR spectrum, ν, cm^{-1}: 3090, 3060, 3040, 3024, 3001 (C–H_{arom}, =C–H); 1764 (C=O); 1627 (C=N); 1592, 1504, 1484, 1470, 1440, 1431, 1393, 1370, 1364, 1320 (C–C_{arom}); 880, 842, 830, 770, 760, 727, 698, 640, 620 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 205 (19000), 270 (11000), 320 (9000). ^{1}H NMR spectrum, δ, ppm: 1.37 t (3H, Me), 1.43 t (3H, Me), 2.67 q (2H, CH_2), 4.12 q (2H, CH_2), 7.04–7.72 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.37 s (1H, HC=N). Found, %: C 77.42; H 6.28; N 3.74. *M* 365.0. $C_{24}H_{23}NO_3$. Calculated, %: C 77.19; H 6.21; N 3.75. *M* 373.5.

4-(Biphenyl-4-yliminomethyl)-2-ethoxyphenyl butanoate (XXVIII). Yield 90%, mp 92–93°C. IR spectrum, ν, cm^{-1}: 3085, 3065, 3040, 3025, 3002 (C–H_{arom}, =C–H); 1757 (C=O); 1626 (C=N); 1588, 1504, 1484, 1460, 1430, 1393, 1360, 1320 (C–C_{arom}); 865, 843, 804, 769, 761, 735, 698, 640, 620 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (20000), 270 (10000), 320 (9000). ^{1}H NMR spectrum, δ, ppm: 0.98 t (3H, Me), 1.36 t (3H, Me), 1.76 q (2H, CH_2), 2.53 t (2H, CH_2), 4.12 q (2H, CH_2), 6.95–7.65 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.38 s (1H, HC=N). Found, %: C 77.78; H 6.63; N 3.30. *M* 370.2. $C_{25}H_{25}NO_3$. Calculated, %: C 77.49; H 6.50; N 3.61. *M* 387.5.

4-(Biphenyl-4-yliminomethyl)-2-ethoxyphenyl 2-methylpropanoate (XXIX). Yield 92%, mp 112–113°C. IR spectrum, ν, cm^{-1}: 3090, 3080, 3045, 3030, 3003 (C–H_{arom}, =C–H); 1762 (C=O); 1631 (C=N); 1595, 1594, 1484, 1470, 1440, 1430, 1393, 1370, 1340, 1315 (C–C_{arom}); 866, 860, 840, 830, 820, 770, 760, 735, 698, 640, 620 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (18000), 270 (10000), 320 (9000). ^{1}H NMR spectrum, δ, ppm: 1.15–1.45 m (9H, Me), 2.82 quint (1H, CH), 4.08 q (2H, CH_2), 6.97–7.65 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.38 s (1H, HC=N). Found, %: C 77.83; H 6.65; N 3.34. *M* 371.6. $C_{25}H_{25}NO_3$. Calculated, %: C 77.49; H 6.50; N 3.61. *M* 387.5.

4-(Biphenyl-4-yliminomethyl)-2-ethoxyphenyl 3-methylbutanoate (XXX). Yield 93%, mp 87–88°C. IR spectrum, ν, cm^{-1}: 3090, 3066, 3045, 3029 (C–H_{arom}, =C–H); 1750 (C=O); 1626 (C=N); 1600, 1580, 1505, 1483, 1470, 1450, 1428, 1393, 1356, 1320 (C–C_{arom}); 863, 842, 763, 725, 695, 635, 616 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 205 (19000), 270 (11000), 320 (10000). ^{1}H NMR spectrum, δ, ppm: 1.13 d (6H, Me_2C), 1.43 t (3H, Me), 1.44–2.92 m (3H, CH, CH_2), 4.10 q (2H, CH_2), 6.95–7.65 m (12H, C_6H_3, C_6H_4, C_6H_5), 8.38 s (1H, HC=N). Found, %: C 78.06; H 6.93; N 3.20. *M* 388.3. $C_{26}H_{27}NO_3$. Calculated, %: C 77.78; H 6.78; N 3.49. *M* 401.5.

4-(Biphenyl-4-yliminomethyl)-2-ethoxyphenyl benzoate (XXXI). Yield 93%, mp 142–143°C. IR spectrum, ν, cm^{-1}: 3090, 3075, 3040 (C–H_{arom}, =C–H); 1736 (C=O); 1629 (C=N); 1586, 1506, 1485, 1440, 1429, 1390, 1380, 1320 (C–C_{arom}); 885, 870, 840, 825, 777, 770, 730, 707, 695, 676, 620 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (35000), 220 (27000), 264 (20000), 320 (11000). ^{1}H NMR spectrum, δ, ppm: 1.27 t (3H, Me), 4.14 q (2H, CH_2), 7.15–7.75 m and 8.05–8.25 m (17H, C_6H_3, C_6H_4, C_6H_5), 8.41 s (1H, HC=N). Found, %: C 80.12; H 5.54; N 3.04. *M* 413.5. $C_{28}H_{23}NO_3$. Calculated, %: C 79.79; H 5.50; N 3.32. *M* 421.5.

4-(Biphenyl-4-yliminomethyl)-2-ethoxyphenyl 4-methylbenzoate (XXXII). Yield 95%, mp 151–152°C. IR spectrum, ν, cm^{-1}: 3090, 3080, 3070, 3037, 3002 (C–H_{arom}, =C–H); 1734 (C=O); 1625 (C=N); 1612, 1588, 1505, 1485, 1430, 1395, 1378, 1312 (C–C_{arom}); 872, 840, 790, 770, 760, 746, 723, 687, 635, 620 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 208 (35000), 221 (18000), 250 (20000), 270 (11000), 320 (10000). ^{1}H NMR spectrum, δ, ppm: 1.27 t (3H, Me), 2.39 s (3H, Me), 4.14 q (2H, CH_2), 7.12–7.65 m and 7.95–8.07 m (16H, C_6H_3, C_6H_4, C_6H_5), 8.43 s (1H, HC=N). Found, %: C 80.27; H 5.93; N 2.96. *M* 422.8. $C_{29}H_{25}NO_3$. Calculated, %: C 79.98; H 5.79; N 3.22. *M* 435.5.

4-(Biphenyl-4-yliminomethyl)-2-ethoxyphenyl 2-chlorobenzoate (XXXIII). Yield 94%, mp 123–124°C. IR spectrum, ν, cm^{-1}: 3090, 3080, 3040 (C–H_{arom}, =C–H); 1741 (C=O); 1627 (C=N); 1600, 1586, 1505, 1480, 1470, 1430, 1395, 1380, 1312 (C–C_{arom}); 878, 840, 800, 768, 757, 725, 701, 640, 615 (δC–H_{arom}); 520 (C–Cl). UV spectrum, λ_{max}, nm (ε): 207 (28000), 220 (20000), 265 (15000), 320 (11000). ^{1}H NMR spectrum, δ, ppm: 1.33 t (3H, Me), 4.16 q (2H, CH_2), 7.12–7.63 m and 7.95–8.15 m (16H, C_6H_3, C_6H_4, C_6H_5), 8.44 s (1H, HC=N). Found, %: C 73.99; H 5.03; Cl 7.41; N 2.90. *M* 442.6. $C_{28}H_{22}ClNO_3$. Calculated, %: C 73.76; H 4.86; Cl 7.78; N 3.07. *M* 455.9.

Bis[4-(biphenyl-4-yliminomethyl)-2-ethoxyphenyl] succinate (XXXIV). Yield 93%, mp 183–184°C. IR spectrum, ν, cm^{-1}: 3080, 3040 (C–H_{arom}, =C–H); 1759 (C=O); 1630 (C=N); 1600, 1585, 1506, 1485, 1430, 1395, 1375, 1325 (C–C_{arom}); 870, 860, 840, 805, 770, 730, 695, 665, 620 (δC–H_{arom}). UV spectrum, λ_{max}, nm (ε): 204 (37000), 270 (20000), 320 (18000). ^{1}H NMR spectrum, δ, ppm: 1.36 t (6H, Me), 3.05 s (4H, CH_2CH_2), 4.12 q (4H, OCH_2), 7.10–7.52 m (24H, C_6H_3, C_6H_4, C_6H_5), 8.38 s (2H, 2HC=N). Found, %: C 77.23; H 5.74; N 3.65. *M* 687.8. $C_{46}H_{40}N_2O_6$. Calculated, %: C 77.08; H 5.62; N 3.91. *M* 716.8.

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