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N-[(*E*)-3-Alkoxy-4-hydroxy(alkoxy, alkanoyloxy, aroyloxy)-benzylidene]-4-phenoxyanilines

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Abstract—Condensation of 4-phenoxyaniline with benzaldehydes of the vanillin series in methanol gave the corresponding Schiff bases, *N*-[(*E*)-3-alkoxy-4-hydroxy(alkoxy, alkanoyloxy, aroyloxy)benzylidene]-4-phenoxyanilines.

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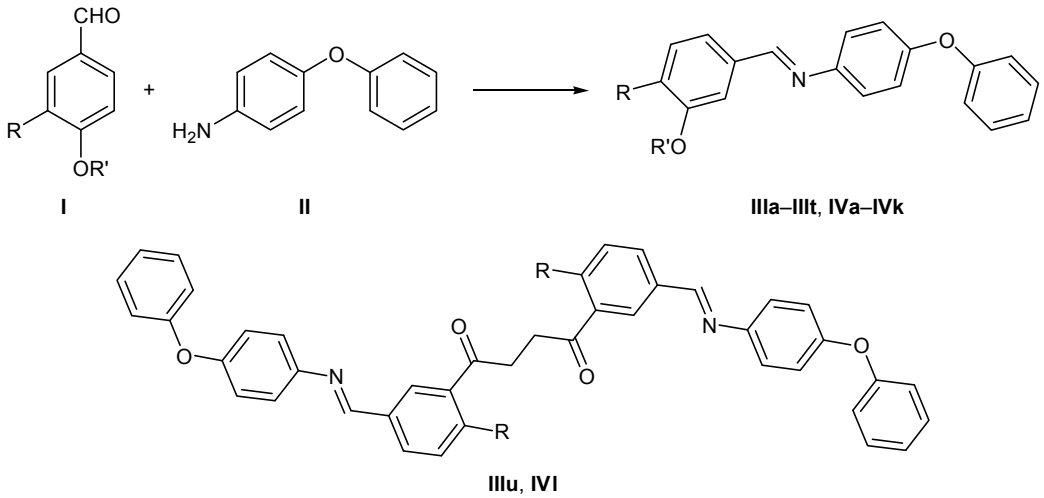
We previously reported on the synthesis of Schiff bases of the vanillin series and their film-forming properties and sensitivity to heat and light [1–3]. The synthesized compounds turned out to be promising as materials for the preparation of nanofilms and nanomaterials based thereon [4–6].

The goal of the present work was to develop a preparative procedure for the synthesis of new aromatic Schiff bases containing hydroxy, ether, and ester groups, as well as carborane fragments. By condensation of vanillin (4-hydroxy-3-methoxybenzaldehyde), vanillal (3-ethoxy-4-hydroxybenzaldehyde), and ethers and esters derived therefrom with 4-phenoxyaniline (**II**) in boiling anhydrous methanol we obtained the corresponding aromatic Schiff bases **IIIa**–**IIIu** and **IVa**–**IVl** in 84–90% yield. The reactions were complete in 10–15 min under mild conditions in the absence of a catalyst, which favored conservation of labile ester groups. According to the ^{1}H NMR data, the purity of the isolated compounds was 96±1%.

Compounds **IIIa**–**IIIu** and **IVa**–**IVl** are colorless or slightly colored crystalline or glassy substances. They

Scheme 1.



III, R = H, R′ = Me (**a**); R = MeO, R′ = H (**b**), Me (**c**), MeC(O) (**d**), EtC(O) (**e**), PrC(O) (**f**), $Me_2CHC(O)$ (**g**), $Me(CH_2)_6C(O)$ (**h**), $Me(CH_2)_8C(O)$ (**i**), $Me(CH_2)_{16}C(O)$ (**j**), $H_2C{=}C(Me)C(O)$ (**k**), $PhCH_2C(O)$ (**l**), $PhCH(Me)CH_2C(O)$ (**m**), PhC(O) (**n**), 2,4-$Cl_2C_6H_3C(O)$ (**o**), 4-$BrC_6H_4C(O)$ (**p**), 3-$O_2NC_6H_4C(O)$ (**q**), MeOC(O) (**r**), EtOC(O) (**s**), 1,2-$C_2B_{10}H_{11}$-1-C(O) (**t**); R = MeO (**u**); **IV**, R = EtO, 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**), 1,2-$C_2B_{10}H_{11}$-1-C(O) (**k**); R = EtO (**l**).

contained no impurities of the initial reactants, and no additional purification was necessary. The structure of **IIIa**–**IIIu** and **IVa**–**IVl** was proved by their elemental analyses, IR and ^{1}H NMR spectra, and determination of the molecular weight by cryoscopy. Protons in the HC=N group of **IIIa**–**IIIu** and **IVa**–**IVl** gave a singlet at δ 8.41–8.51 ppm in the ^{1}H NMR spectra, which is typical of Schiff bases with *E* configuration of the double C=N bond [7].

The *E* configuration of these compounds was also confirmed by quantum-chemical calculations of heats of formation (H_f) of *E* and *Z* isomers of Schiff bases **IIIa**, **IIIc**, **IIId**, **IVa**, **IVc**, and **IVd**. The calculations were performed in terms of MNDO PM3 semiempirical approximation [8, 9] using GAMESS software [10] with complete optimization of geometric parameters (bond lengths, bond angles, and dihedral angles). The following values of H_f (kcal/mol) were obtained for the *E* isomers (the corresponding values for the *Z* isomers are given in parentheses): **IIIa**, 27.2 (28.0); **IIIc**, –7.1 (–6.3); **IIId**, –49.3 (–47.8); **IVa**, –18.9 (–18.2); **IVc**), –55.9 (–55.5); **IVd**, –60.1 (–59.6). Thus the *E* isomers are more energetically favorable (by 0.4–1.5 kcal/mol) than their *Z* isomers, which is consistent with the data reported previously for structurally related compounds [3, 4]. The calculated energy barrier to the *E*–*Z* transformation was 6–8 kcal/mol; this value is lower by 3–5 kcal/mol than the energy barrier to the *E*–*Z* transformation of Schiff bases derived from biphenyl-4-amine [2]. Computer simulation of the thermal *E*–*Z* isomerization of Schiff bases **IIIa**, **IIIc**, **IIId**, **IVa**, **IVc**, and **IVd** showed that stretching and bending vibrations of the phenoxyphenyl group provide the main contribution to the reduction of the energy barrier [11].

EXPERIMENTAL

The IR spectra were measured on a Nicolet Protégé-460 spetrophotometer with Fourier transform from samples prepared as KBr pellets. The ^{1}H NMR spectra were recorded on a Tesla BS-587A instrument at 100 MHz from 5% solutions in $CDCl_3$ using tetramethylsilane as internal reference. The elemental compositions were determined with an accuracy of ±0.1% on an Elementar Vario EL-III CHNOS analyzer. The molecular weights were determined by cryoscopy in benzene.

Initial vanillin and vanillal esters **I** were synthesized according to the procedures described in [12–15]; 4-phenoxyaniline (**II**) was commercial product of analytical grade (purity 99%), mp 83–84°C.

***N*-[(*E*)-3-Alkoxy-4-hydroxy(alkoxy, alkanoyloxy, aroyloxy)benzylidene]-4-phenoxyanilines IIIa–IIIt and IVa–IVk (*general procedure*).** A solution of 5 mmol of aldehyde **I** and 5 mmol of 4-phenoxyaniline (**II**) in 30 ml of anhydrous methanol was heated for 15 min under reflux. The hot solution was filtered through a folded filter paper, and the filtrate was cooled and kept for 10–15 h at 5°C. The precipitate was filtered off through a glass filter or separated by decanting, washed with a small amount of methanol, and dried in air.

Bis{2-alkoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]phenyl} succinates IIIu and IVl (*general procedure*). A solution of 5 mmol of bis(4-formyl-2-methoxyphenyl) succinate or bis(2-ethoxy-4-formylphenyl) succinate and 10 mmol of 4-phenoxyaniline (**II**) in 30 ml of anhydrous methanol was heated for 15 min under reflux. The hot solution was filtered through a folded filter paper, and the filtrate was cooled and kept for 10–15 h at 5°C. The precipitate was filtered off through a glass filter, washed with a small amount of methanol, and dried in air.

***N*-[(*E*)-4-Methoxybenzylidene]-4-phenoxyaniline (IIIa).** Yield 88%, mp 105–106°C. IR spectrum, ν, cm^{-1}: 3080, 3061, 3035, 3020, 3008 (C–H_{arom}); 2962, 2945, 2922, 2879, 2845, 2844 (C–H_{aliph}); 1622 (C=N); 1606, 1588, 1575, 1509, 1500, 1491, 1417 (C=C_{arom}); 1280, 1264, 1251, 1190, 1181, 1168, 1105, 1076, 1030 (C–O); 872, 852, 826, 816, 785, 765, 745, 693 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 3.88 s (3H, Me), 6.90–7.95 m (13H, H_{arom}), 8.42 s (1H, CH=N). Found, %: C 79.48; H 5.72; N 4.28. *M* 291.5. $C_{20}H_{17}NO_2$. Calculated, %: C 79.19; H 5.65; N 4.62. *M* 303.4.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenol (IIIb). Yield 90%, mp 77–78°C. IR spectrum, ν, cm^{-1}: 3500 (OH); 3080, 3063, 3035, 3020, 3003 (C–H_{arom}); 2980, 2065, 2939, 2920, 2913, 2860, 2840 (C–H_{aliph}); 1624 (C=N); 1593, 1518, 1511, 1500, 1488, 1467, 1453, 1428 (C=C_{arom}); 1289, 1236, 1209, 1180, 1152, 1121, 1099, 1071, 1027, 1012 (C–O); 867, 852, 841, 823, 787, 753, 727, 711, 693, 613 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 3.95 s (3H, Me), 6.05 br.s (1H, OH), 6.80–7.75 m (12H, H_{arom}), 8.38 s (1H, CH=N). Found, %: C 75.53; H 5.48; N 3.97. *M* 311.2. $C_{20}H_{17}NO_3$. Calculated, %: C 75.22; H 5.37; N 4.39. *M* 319.4.

***N*-[(*E*)-3,4-Dimethoxybenzylidene]-4-phenoxyaniline (IIIc).** Yield 90%, mp 107–108°C. IR spectrum, ν, cm^{-1}: 3095, 3080, 3062, 3040, 3022, 3014

($C–H_{arom}$); 2975, 2936, 2920, 2910, 2890, 2870, 2846, 2835 ($C–H_{aliph}$); 1624 (C=N); 1596, 1588, 1582, 1516, 1498, 1488, 1463, 1448, 1417 ($C=C_{arom}$); 1274, 1238, 1210, 1140, 1099, 1070, 1019 (C–O); 865, 850, 825, 810, 806, 796, 778, 755, 735, 694, 616 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 3.96 s (3H, 3-OMe), 4.00 s (3H, 4-OMe), 6.80–7.75 m (12H, H_{arom}), 8.40 s (1H, CH=N). Found, %: C 75.87; H 5.79; N 3.95. *M* 326.0. $C_{21}H_{19}NO_3$. Calculated, %: C 75.66; H 5.74; N 4.20. *M* 333.4.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl acetate (IIId). Yield 85%, glassy substance. IR spectrum, ν, cm^{-1}: 3080, 3065, 3038, 3010 ($C–H_{arom}$); 2968, 2939, 2922, 2873, 2844, 2833 ($C–H_{aliph}$); 1766 (C=O); 1626 (C=N); 1589, 1506, 1499, 1488, 1465, 1418, 1369 ($C=C_{arom}$); 1277, 1239, 1213, 1195, 1151, 1120, 1033, 1010 (C–O); 904, 858, 837, 790, 756, 693, 660, 620 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 2.34 s (3H, Me), 3.95 s (3H, MeO), 6.80–7.70 m (12H, H_{arom}), 8.42 s (1H, CH=N). Found, %: C 73.42; H 5.43; N 3.54. *M* 347.9. $C_{22}H_{19}NO_4$. Calculated, %: C 73.12; H 5.30; N 3.88. *M* 361.4.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl propanoate (IIIe). Yield 88%, glassy substance. IR spectrum, ν, cm^{-1}: 3080, 3066, 3038, 3009 ($C–H_{arom}$); 2981, 2941, 2919, 2879, 2848, 2830 ($C–H_{aliph}$); 1764 (C=O); 1627 (C=N); 1589, 1504, 1499, 1488, 1464, 1418, 1369 ($C=C_{arom}$); 1276, 1239, 1213, 1195, 1135, 1074, 1033 (C–O); 880, 858, 837, 790, 760, 740, 693, 620 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.28 t (3H, Me), 2.54 q (2H, CH_2), 3.94 s (3H, MeO), 6.80–7.70 m (12H, H_{arom}), 8.42 s (1H, CH=N). Found, %: C 73.82; H 5.77; N 3.32. *M* 361.5. $C_{23}H_{21}NO_4$. Calculated, %: C 73.58; H 5.64; N 3.73. *M* 375.4.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl butanoate (IIIf). Yield 87%, glassy substance. IR spectrum, ν, cm^{-1}: 3080, 3066, 3038, 3008 ($C–H_{arom}$); 2966, 2936, 2875, 2850, 2828 ($C–H_{aliph}$); 1763 (C=O); 1627 (C=N); 1589, 1506, 1488, 1465, 1417, 1370 ($C=C_{arom}$); 1277, 1240, 1214, 1197, 1147, 1122, 1100, 1070, 1033 (C–O); 857, 837, 790, 755, 693, 620 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.05 t (3H, Me), 1.64 m (2H, MeC**H**$_2$), 2.54 t [2H, $CH_2C(O)$], 3.94 s (3H, MeO), 6.80–7.70 m (12H, H_{arom}), 8.42 s (1H, CH=N). Found, %: C 74.29; H 6.05; N 3.23. *M* 376.1. $C_{24}H_{23}NO_4$. Calculated, %: C 74.02; H 5.95; N 3.60. *M* 389.5.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl 2-methylpropanoate (IIIg). Yield 89%, glassy substance. IR spectrum, ν, cm^{-1}: 3080, 3064, 3039, 3008 ($C–H_{arom}$); 2975, 2937, 2875, 2849, 2827 ($C–H_{aliph}$); 1761 (C=O); 1628 (C=N); 1589, 1505, 1488, 1468, 1417, 1370 ($C=C_{arom}$); 1276, 1239, 1214, 1199, 1150, 1123, 1094, 1035 (C–O); 865, 838, 790, 755, 693, 620 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.37 d (6H, **Me**$_2$CH), 2.88 m (1H, CH), 3.94 s (3H, MeO), 6.80–7.70 m (12H, H_{arom}), 8.43 s (1H, CH=N). Found, %: C 74.38; H 6.11; N 3.28. *M* 379.3. $C_{24}H_{23}NO_4$. Calculated, %: C 74.02; H 5.95; N 3.60. *M* 389.5.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl octanoate (IIIh). Yield 90%, glassy substance. IR spectrum, ν, cm^{-1}: 3080, 3065, 3039, 3008 ($C–H_{arom}$); 2954, 2928, 2870, 2856 ($C–H_{aliph}$); 1764 (C=O); 1628 (C=N); 1589, 1505, 1488, 1465, 1417, 1371 ($C=C_{arom}$); 1276, 1240, 1214, 1197, 1139, 1121, 1102, 1034 (C–O); 875, 857, 840, 790, 755, 740, 725, 692 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.94 t (3H, Me), 1.34 m (8H, CH_2), 1.80 m (2H, MeC**H**$_2$), 2.58 t [2H, $CH_2C(O)$], 3.94 s (3H, MeO), 6.80–7.70 m (12H, H_{arom}), 8.43 s (1H, CH=N). Found, %: C 75.85; H 7.10; N 2.84. *M* 437.0. $C_{28}H_{31}NO_4$. Calculated, %: C 75.48; H 7.01; N 3.14. *M* 445.6.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl decanoate (IIIi). Yield 90%, glassy substance. IR spectrum, ν, cm^{-1}: 3080, 3065, 3039, 3005 ($C–H_{arom}$); 2953, 2926, 2870, 2854 ($C–H_{aliph}$); 1764 (C=O); 1628 (C=N); 1589, 1505, 1488, 1465, 1417, 1370 ($C=C_{arom}$); 1276, 1240, 1214, 1198, 1138, 1121, 1111, 1034 (C–O); 875, 857, 838, 790, 756, 740, 725, 693 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.91 t (3H, Me), 1.20–1.54 m (12H, CH_2), 1.84 m (2H, MeC**H**$_2$), 2.64 t [2H, $CH_2C(O)$], 3.94 s (3H, MeO), 6.80–7.70 m (12H, H_{arom}), 8.43 s (1H, CH=N). Found, %: C 76.34; H 7.66; N 2.61. *M* 461.4. $C_{30}H_{35}NO_4$. Calculated, %: C 76.08; H 7.45; N 2.96. *M* 473.6.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl octadecanoate (IIIj). Yield 90%, mp 42–43°C. IR spectrum, ν, cm^{-1}: 3080, 3066, 3039, 3004 ($C–H_{arom}$); 2956, 2915, 2873, 2849 ($C–H_{aliph}$); 1759 (C=O); 1627 (C=N); 1589, 1509, 1499, 1489, 1471, 1417, 1370 ($C=C_{arom}$); 1277, 1242, 1214, 1198, 1138, 1121, 1106, 1031 (C–O); 875, 854, 837, 790, 757, 740, 722, 692 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, Me), 1.10–2.12 m (30H, CH_2), 2.68 t [2H, $CH_2C(O)$], 3.94 s (3H, MeO), 6.80–7.70 m (12H, H_{arom}), 8.43 s (1H, CH=N). Found, %: C 78.23; H 8.86; N 2.02. *M* 569.5. $C_{38}H_{51}NO_4$. Calculated, %: C 77.91; H 8.77; N 2.39. *M* 585.8.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl 2-methylprop-2-enoate (IIIk). Yield 84%, mp 126–127°C. IR spectrum, ν, cm^{-1}: 3100, 3085, 3055, 3045, 3017 (=CH_2, C–H_{arom}); 2982, 2970, 2930, 2885, 2850, 2835 (C–H_{aliph}); 1730 (C=O); 1683 (C=C); 1627 (C=N); 1598, 1584, 1503, 1492, 1477, 1461, 1419, 1376 (C=C_{arom}); 1274, 1231, 1212, 1199, 1151, 1124, 1099, 1031 (C–O); 873, 860, 838, 820, 803, 775, 762, 743, 715, 698, 645, 618, 603 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 2.10 s (3H, Me), 3.94 s (3H, MeO), 5.80 s and 6.41 s (1H each, =CH_2), 6.80–7.75 m (12H, H_{arom}), 8.45 s (1H, CH=N). Found, %: C 73.97; H 5.83; N 3.25. *M* 360.4. $C_{23}H_{21}NO_4$. Calculated, %: C 73.58; H 5.64; N 3.73. *M* 375.4.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl phenylacetate (IIIl). Yield 85%, glassy substance. IR spectrum, ν, cm^{-1}: 3092, 3063, 3033, 3010 (C–H_{arom}); 2966, 2936, 2921, 2874, 2848, 2830 (C–H_{aliph}); 1763 (C=O); 1626 (C=N); 1589, 1510, 1499, 1488, 1464, 1455, 1417, 1371 (C=C_{arom}); 1277, 1239, 1214, 1199, 1152, 1119, 1074, 1032 (C–O); 860, 840, 791, 755, 729, 694, 660, 650, 620 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 3.82 s (2H, CH_2), 3.94 s (3H, MeO), 6.80–7.75 m (17H, H_{arom}), 8.45 s (1H, CH=N). Found, %: C 77.19; H 5.48; N 2.92. *M* 422.8. $C_{28}H_{23}NO_4$. Calculated, %: C 76.87; H 5.30; N 3.20. *M* 437.5.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl 3-phenylbutanoate (IIIm). Yield 87%, glassy material. IR spectrum, ν, cm^{-1}: 3086, 3075, 3028, 3004 (C–H_{arom}); 2965, 2934, 2878, 2855, 2830 (C–H_{aliph}); 1761 (C=O); 1627 (C=N); 1589, 1505, 1500, 1488, 1464, 1454, 1417, 1369 (C=C_{arom}); 1277, 1239, 1214, 1198, 1149, 1131, 1981, 1033 (C–O); 880, 857, 838, 790, 758, 745, 700, 622 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.45 d (3H, Me), 2.92 d (2H, CH_2), 3.40 q (1H, CH), 3.94 s (3H, MeO), 6.80–7.74 m (17H, H_{arom}), 8.45 s (1H, CH=N). Found, %: C 77.82; H 5.96; N 2.75. *M* 451.6. $C_{30}H_{27}NO_4$. Calculated, %: C 77.40; H 5.85; N 3.01. *M* 465.5.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl benzoate (IIIn). Yield 84%, mp 112–113°C. IR spectrum, ν, cm^{-1}: 3070, 3030, 3010 (C–H_{arom}); 2970, 2945, 2925, 2884, 2850, 2830 (C–H_{aliph}); 1743 (C=O); 1629 (C=N); 1593, 1506, 1487, 1465, 1450, 1416, 1370 (C=C_{arom}); 1278, 1255, 1233, 1212, 1195, 1151, 1121, 1080, 1061, 1035, 1024 (C–O); 871, 844, 810, 790, 760, 740, 710, 692, 680, 619 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 3.94 s (3H, MeO), 6.70–8.20 m (17H, H_{arom}), 8.49 s (1H, CH=N). Found, %: C 76.91; H 5.15; N 3.03. *M* 409.7. $C_{27}H_{21}NO_4$. Calculated, %: C 76.58; H 5.00; N 3.31. *M* 423.5.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl 2,4-dichlorobenzoate (IIIo). Yield 88%, mp 92–93°C. IR spectrum, ν, cm^{-1}: 3095, 3075, 3060, 3045, 3020 (C–H_{arom}); 2974, 2940, 2925, 2876, 2850, 2830 (C–H_{aliph}); 1721 (C=O); 1629 (C=N); 1589, 1506, 1488, 1460, 1455, 1417, 1377 (C=C_{arom}); 1279, 1240, 1214, 1195, 1151, 1140, 1123, 1104, 1075, 1032 (C–O); 880, 862, 855, 832, 796, 780, 761, 755, 740, 720, 695, 675, 622 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 3.95 s (3H, MeO), 6.70–8.50 m (15H, H_{arom}), 8.50 s (1H, CH=N). Found, %: C 65.98; H 4.47; Cl 13.88; N 2.50. *M* 480.3. $C_{27}H_{19}Cl_2NO_4$. Calculated, %: C 65.60; H 4.28; Cl 14.34; N 2.83. *M* 494.4.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl 4-bromobenzoate (IIIp). Yield 87%, mp 118–119°C. IR spectrum, ν, cm^{-1}: 3095, 3082, 3060, 3040, 3030, 3011 (C–H_{arom}); 2970, 2940, 2922, 2870, 2860, 2845, 2835 (C–H_{aliph}); 1739 (C=O); 1629 (C=N); 1588, 1510, 1496, 1481, 1460, 1420, 1395 (C=C_{arom}); 1294, 1262, 1239, 1214, 1202, 1161, 1113, 1072, 1031, 1010 (C–O); 866, 845, 820, 810, 751, 695, 676, 620 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 3.95 s (3H, MeO), 6.70–8.20 m (16H, H_{arom}), 8.51 s (1H, CH=N). Found, %: C 64.93; H 4.19; Br 15.45; N 2.34. *M* 492.6. $C_{27}H_{20}BrNO_4$. Calculated, %: C 64.55; H 4.01; Br 15.91; N 2.79. *M* 502.4.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl 3-nitrobenzoate (IIIq). Yield 86%, mp 119–120°C. IR spectrum, ν, cm^{-1}: 3110, 3100, 3090, 3070, 3050, 3040, 3010 (C–H_{arom}); 2978, 2940, 2925, 2880, 2845, 2830 (C–H_{aliph}); 1742 (C=O); 1630 (C=N); 1620, 1590, 1586, 1506, 1500, 1488, 1466, 1440, 1418, 1370 (C=C_{arom}); 1539, 1352 (NO_2); 1283, 1252, 1232, 1211, 1197, 1150, 1121, 1110, 1100, 1080, 1035 (C–O); 865, 857, 840, 825, 815, 775, 755, 714, 705, 690, 655, 620 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 3.94 (3H, MeO), 6.70–9.15 m (16H, H_{arom}), 8.49 s (1H, CH=N). Found, %: C 69.68; H 4.47; N 5.60. *M* 455.3. $C_{27}H_{20}N_2O_6$. Calculated, %: C 69.23; H 4.30; N 5.98. *M* 468.5.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl methyl carbonate (IIIr). Yield 84%, mp 83–84°C. IR spectrum, ν, cm^{-1}: 3090, 3080, 3070, 3060, 3016, 3002 (C–H_{arom}); 2978, 2953, 2940, 2920, 2880, 2840, 2830 (C–H_{aliph}); 1764 (C=O); 1628 (C=N); 1597, 1587, 1508, 1490, 1485, 1465, 1440, 1417, 1373 (C=C_{arom}); 1275, 1265, 1256, 1235, 1213, 1194, 1151, 1119, 1103, 1056, 1034 (C–O); 871, 858, 830, 800,

776, 758, 730, 720, 694, 650, 620 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 3.94 (3H, 3-MeO), 3.97 s [3H, 4-MeOC(O)], 6.85–7.75 m (12H, H_{arom}), 8.44 s (1H, CH=N). Found, %: C 70.35; H 5.21; N 3.28. *M* 367.7. $C_{22}H_{19}NO_5$. Calculated, %: C 70.02; H 5.07; N 3.71. *M* 377.4.

Ethyl 2-methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]phenyl carbonate (IIIs). Yield 85%, mp 73–74°C. IR spectrum, ν, cm^{-1}: 3070, 3060, 3040, 3008 (C–H_{arom}); 2985, 2960, 2928, 2900, 2880, 2850, 2830 (C–H_{aliph}); 1756 (C=O); 1626 (C=N); 1589, 1510, 1499, 1489, 1441, 1430, 1385 (C=C_{arom}); 1279, 1244, 1215, 1200, 1162, 1123, 1063, 1045 (C–O); 880, 860, 840, 822, 790, 786, 747, 691, 621 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.45 t (3H, Me), 3.93 s (3H, MeO), 4.18 q (2H, CH_2), 6.85–7.72 m (12H, H_{arom}), 8.43 s (1H, CH=N). Found, %: C 70.89; H 5.62; N 3.19. *M* 376.2. $C_{23}H_{21}NO_5$. Calculated, %: C 70.58; H 5.41; N 3.58. *M* 391.4.

2-Methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]phenyl 1,3-dicarbadodecaborane-1-carboxylate (IIIt). Yield 84%, mp 120–121°C. IR spectrum, ν, cm^{-1}: 3080, 3062, 3045, 3015 (C–H_{arom}, C–H_{carb}); 2967, 2929, 2880, 2845 (C–H_{aliph}); 2606 (B–H); 1745 (C=O); 1630 (C=N); 1589, 1505, 1488, 1464, 1417, 1384 (C=C_{arom}); 1325, 1279, 1242, 1218, 1193, 1167, 1147, 1125, 1029 (C–O); 876, 855, 840, 820, 790, 750, 740, 690, 630, 610 (δC–H_{arom}, δC–$H_{carb.}$). ^{1}H NMR spectrum, δ, ppm: 3.12 br.s (1H, CH, carborane), 3.94 s (3H, MeO), 6.70–7.80 (12H, H_{arom}), 8.42 s (1H, CH=N). Found, %: C 56.83; H 5.74; B 21.68; N 2.42. *M* 473.6. $C_{23}H_{27}B_{10}NO_4$. Calculated, %: C 56.43; H 5.56; B 22.08; N 2.86. *M* 489.6.

Bis{2-methoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]phenyl} succinate (IIIu). Yield 87%, mp 161–162°C. IR spectrum, ν, cm^{-1}: 3090, 3080, 3060, 3040, 3015 (C–H_{arom}); 2970, 2944, 2934, 2900, 2870, 2845, 2830 (C–H_{aliph}); 1748 (C=O); 1626 (C=N); 1598, 1588, 1504, 1489, 1468, 1417, 1372 (C=C_{arom}); 1273, 1243, 1211, 1194, 1166, 1150, 1117, 1034 (C–O); 873, 863, 838, 818, 790, 780, 751, 740, 685, 675, 620 (C–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 3.07 s (4H, CH_2), 3.94 s (6H, MeO), 6.80–7.70 m (24H, H_{arom}), 8.43 s (2H, CH=N). Found, %: C 73.58; H 5.24; N 3.50. *M* 706.5. $C_{44}H_{36}N_2O_8$. Calculated, %: C 73.32; H 5.03; N 3.89. *M* 720.8.

2-Ethoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]phenol (IVa). Yield 89%, mp 63–64°C. IR spectrum, ν, cm^{-1}: 3350 (O–H); 3080, 3065, 3035, 3004 (C–H_{arom}); 2980, 2065, 2934, 2910, 2878, 2847 (C–H_{aliph}); 1621 (C=N); 1593, 1519, 1512, 1505, 1488, 1440, 1399, 1385 (C=C_{arom}); 1287, 1249, 1201, 1163, 1123, 1111, 1071, 1043 (C–O); 866, 858, 837, 830, 815, 787, 780, 746, 711, 691, 614 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.48 t (3H, Me), 4.22 q (2H, CH_2O), 6.05 br.s (1H, OH), 6.85–7.70 m (12H, H_{arom}), 8.36 s (1H, CH=N). Found, %: C 75.94; H 5.85; N 3.94. *M* 320.6. $C_{21}H_{19}NO_3$. Calculated, %: C 75.66; H 5.74; N 4.20. *M* 333.4.

***N*-[(*E*)-3-Ethoxy-4-methoxybenzylidene]-4-phenoxyaniline (IVb).** Yield 89%, mp 93–94°C. IR spectrum, ν, cm^{-1}: 3090, 3070, 3060, 3040, 3017, 3001 (C–H_{arom}); 2985, 2970, 2924, 2871, 2840 (C–H_{aliph}); 1622 (C=N); 1592, 1587, 1577, 1512, 1501, 1487, 1433, 1385 (C=C_{arom}); 1269, 1234, 1207, 1190, 1164, 1138, 1111, 1026 (C–O); 868, 834, 820, 805, 788, 773, 740, 730, 691, 616 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.52 t (3H, Me), 3.95 s (3H, MeO), 4.26 q (2H, CH_2O), 6.70–7.65 m (12H, H_{arom}), 8.39 s (1H, CH=N). Found, %: C 76.45; H 6.23; N 3.74. *M* 334.7. $C_{22}H_{21}NO_3$. Calculated, %: C 76.06; H 6.09; N 4.03. *M* 347.4.

2-Ethoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]phenyl acetate (IVc). Yield 90%, glassy substance. IR spectrum, ν, cm^{-1}: 3080, 3065, 3039, 3012 (C–H_{arom}); 2981, 2934, 2900, 2881, 2845 (C–H_{aliph}); 1766 (C=O); 1626 (C=N); 1589, 1509, 1499, 1488, 1440, 1394, 1369 (C=C_{arom}); 1278, 1240, 1210, 1163, 1120, 1041, 1010 (C–O); 873, 857, 836, 790, 753, 693, 670, 620 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.43 t (3H, C**H**$_3$CH$_2$), 2.34 s (3H, Me), 4.14 q (2H, CH_2O), 6.70–7.70 m (12H, H_{arom}), 8.43 s (1H, CH=N). Found, %: C 73.90; H 5.76; N 3.37. *M* 362.8. $C_{23}H_{21}NO_4$. Calculated, %: C 73.58; H 5.64; N 3.73. *M* 375.4.

2-Ethoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]phenyl propanoate (IVd). Yield 87%, glassy substance. IR spectrum, ν, cm^{-1}: 3080, 3065, 3039, 3009 (C–H_{arom}); 2981, 2940, 2900, 2881, 2830 (C–H_{aliph}); 1764 (C=O); 1627 (C=N); 1588, 1500, 1488, 1431, 1394 (C=C_{arom}); 1275, 1240, 1213, 1161, 1136, 1121, 1074, 1042 (C–O); 885, 874, 857, 838, 790, 755, 693, 620 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.38 t [3H, C**H**$_3$CH$_2$C(O)], 1.43 t (3H, C**H**$_3$CH$_2$O), 2.68 q [2H, CH_2C(O)], 4.14 q (2H, CH_2O), 6.70–7.70 m (12H, H_{arom}), 8.43 s (1H, CH=N). Found, %: C 74.43; H 6.11; N 3.35. *M* 370.9. $C_{24}H_{23}NO_4$. Calculated, %: C 74.02; H 5.95; N 3.60. *M* 389.5.

2-Ethoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]phenyl butanoate (IVe). Yield 84%, glassy substance. IR spectrum, ν, cm^{-1}: 3080, 3065, 3039, 3008

($C–H_{arom}$); 2975, 2934, 2900, 2875, 2830 ($C–H_{aliph}$); 1763 (C=O); 1627 (C=N); 1589, 1505, 1500, 1487, 1431, 1390, 1368 ($C=C_{arom}$); 1276, 1240, 1213, 1161, 1143, 1120, 1075, 1042 (C–O); 878, 856, 837, 790, 755, 693, 620 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.03 t [3H, **Me**$(CH_2)_2$], 1.44 t (3H, **Me**CH_2O), 1.64 m (2H, Me**C**$\mathbf{H}_2$$CH_2$), 2.54 t [2H, $CH_2C(O)$], 4.14 q (2H, CH_2O), 6.70–7.70 m (12H, H_{arom}), 8.43 s (1H, CH=N). Found, %: C 74.72; H 6.25; N 3.12. *M* 391.0. $C_{25}H_{25}NO_4$. Calculated, %: C 74.42; H 6.25; N 3.47. *M* 403.5.

2-Ethoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl 2-methylpropanoate (IVf). Yield 86%, mp 87–88°C. IR spectrum, ν, cm^{-1}: 3090, 3070, 3061, 3052, 3017 ($C–H_{arom}$); 2982, 2970, 2934, 2895, 2884, 2873, 2840, 2827 ($C–H_{aliph}$); 1755 (C=O); 1629 (C=N); 1600, 1589, 1581, 1510, 1500, 1493, 1480, 1465, 1432, 1415, 1390, 1380, 1368 ($C=C_{arom}$); 1285, 1270, 1239, 1213, 1167, 1118, 1099, 1040 (C–O); 880, 863, 837, 794, 778, 745, 735, 702, 655, 645, 619 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.37 d (6H, Me_2C), 1.42 t (3H, Me), 2.88 m (1H, CH), 4.18 q (2H, CH_2O), 6.80–7.72 m (12H, H_{arom}), 8.43 s (1H, CH=N). Found, %: C 74.83; H 6.34; N 3.06. *M* 393.4. $C_{25}H_{25}NO_4$. Calculated, %: C 74.42; H 6.25; N 3.47. *M* 403.5.

2-Ethoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl 3-methylbutanoate (IVg). Yield 84%, mp 47–48°C. IR spectrum, ν, cm^{-1}: 3090, 3065, 3039, 3010 ($C–H_{arom}$); 2980, 2962, 2934, 2900, 2873, 2815 ($C–H_{aliph}$); 1762 (C=O); 1627 (C=N); 1589, 1505, 1500, 1488, 1431, 1393, 1369 ($C=C_{arom}$); 1290, 1275, 1240, 1213, 1197, 1160, 1153, 1120, 1099, 1042 (C–O); 876, 857, 838, 790, 755, 695, 621 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.13 d (6H, Me_2C), 1.42 t (3H, Me), 1.43–2.90 m (3H, CH, CH_2), 4.14 q (2H, CH_2O), 6.70–7.70 m (12H, H_{arom}), 8.43 s (1H, CH=N). Found, %: C 75.08; H 6.74; N 3.04. *M* 409.5. $C_{26}H_{27}NO_4$. Calculated, %: C 74.80; H 6.52; N 3.35. *M* 417.5.

2-Ethoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl 4-methylbenzoate (IVh). Yield 85%, mp 80–81°C. IR spectrum, ν, cm^{-1}: 3090, 3070, 3040, 3009 ($C–H_{arom}$); 2980, 2970, 2924, 2900, 2878, 2848, 2820 ($C–H_{aliph}$); 1733 (C=O); 1626 (C=N); 1611, 1587, 1498, 1488, 1430, 1390, 1370 ($C=C_{arom}$); 1269, 1260, 1243, 1212, 1196, 1172, 1161, 1118, 1070, 1042, 1018 (C–O); 873, 855, 837, 790, 780, 750, 744, 691, 625 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.34 t (3H, C$\mathbf{H}_3$$CH_2$), 2.48 s (3H, C$\mathbf{H}_3$$C_6H_4$), 4.18 q (2H, CH_2O), 6.70–8.25 m (16H, H_{arom}), 8.49 s (1H, CH=N). Found, %: C 77.46; H 5.70; N 2.74. *M* 438.8. $C_{29}H_{25}NO_4$. Calculated, %: C 77.14; H 5.58; N 3.10. *M* 451.5.

2-Ethoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl methyl carbonate (IVi). Yield 84%, mp 72–73°C. IR spectrum, ν, cm^{-1}: 3090, 3080, 3064, 3035, 3004 ($C–H_{arom}$); 2990, 2977, 2965, 2939, 2920, 2880, 2844, 2830 ($C–H_{aliph}$); 1758 (C=O); 1627 (C=N); 1597, 1587, 1508, 1490, 1484, 1465, 1416, 1385, 1371 ($C=C_{arom}$); 1277, 1252, 1236, 1214, 1200, 1197, 1151, 1120, 1097, 1056, 1034 (C–O); 869, 855, 835, 817, 794, 777, 760, 750, 740, 715, 695, 645, 635, 619 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.42 t (3H, C$\mathbf{H}_3$$CH_2$), 3.97 s (3H, MeO), 4.14 q (2H, CH_2O), 6.80–7.75 m (12H, H_{arom}), 8.44 s (1H, CH=N). Found, %: C 70.86; H 5.53; N 3.32. *M* 380.2. $C_{23}H_{21}NO_5$. Calculated, %: C 70.58; H 5.41; N 3.58. *M* 391.4.

2-Ethoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl ethyl carbonate (IVj). Yield 83%, glassy substance. IR spectrum, ν, cm^{-1}: 3090, 3078, 3040, 3015 ($C–H_{arom}$); 2982, 2937, 2901, 2876, 2822 ($C–H_{aliph}$); 1765 (C=O); 1628 (C=N); 1589, 1507, 1499, 1488, 1432, 1394, 1369 ($C=C_{arom}$); 1279, 1244, 1215, 1200, 1163, 1122, 1097, 1055, 1043 (C–O); 874, 857, 837, 815, 790, 776, 755, 693, 619 (δC–H_{arom}). ^{1}H NMR spectrum, δ, ppm: 1.20–1.70 m (6H, Me), 4.00–4.50 m (4H, CH_2O), 6.80–7.75 m (12H, H_{arom}), 8.43 s (1H, CH=N). Found, %: C 71.45; H 5.89; N 3.30. *M* 382.8. $C_{24}H_{23}NO_5$. Calculated, %: C 71.10; H 5.72; N 3.45. *M* 405.4.

2-Ethoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]-phenyl 1,3-dicarbadodecaborane-1-carboxylate (IVk). Yield 88%, mp 132–133°C. IR spectrum, ν, cm^{-1}: 3090, 3061, 3045, 3005 ($C–H_{arom}$, $C–H_{carb}$); 2979, 2961, 2931, 2897, 2884, 2860, 2830 ($C–H_{aliph}$); 2608 (B–H); 1758 (C=O); 1625 (C=N); 1589, 1508, 1488, 1456, 1424, 1388 ($C=C_{arom}$); 1290, 1237, 1212, 1190, 1160, 1115, 1105, 1036 (C–O); 869, 828, 796, 770, 728, 718, 691, 630, 619 (δC–H_{arom}, δC–H_{carb}). ^{1}H NMR spectrum, δ, ppm: 1.45 t (3H, Me), 3.12 br.s (1H, CH, carborane), 4.18 q (2H, CH_2O), 6.65–7.75 m (12H, H_{arom}), 8.42 s (1H, CH=N). Found, %: C 57.73; H 5.89; B 21.07; N 2.54. *M* 488.5. $C_{24}H_{29}B_{10}NO_4$. Calculated, %: C 57.24; H 5.80; B 21.47; N 2.78. *M* 503.6.

Bis{2-ethoxy-4-[(*E*)-4-phenoxyphenyliminomethyl]phenyl} succinate (IVl). Yield 85%, mp 155–156°C. IR spectrum, ν, cm^{-1}: 3070, 3060, 3040, 3004 ($C–H_{arom}$); 2975, 2929, 2895, 2880, 2850, 2830 ($C–H_{aliph}$); 1758 (C=O); 1630 (C=N); 1600, 1589, 1510, 1499, 1487, 1426, 1395 ($C=C_{arom}$); 1287, 1266, 1235, 1214, 1198, 1161, 1124, 1116, 1040 (C–O); 860, 840, 815, 793, 780, 740, 693, 665, 620 (δC–H_{arom}). ^{1}H NMR

spectrum, δ, ppm: 1.44 t (6H, C**H**$_3$CH$_2$), 3.07 s [4H, (CH$_2$)$_2$], 4.14 q (4H, CH$_2$O), 6.80–7.70 m (24H, H$_{arom}$), 8.43 s (2H, 2CH=N). Found, %: C 74.01; H 5.39; N 3.51. *M* 735.7. $C_{46}H_{40}N_2O_8$. Calculated, %: C 73.78; H 5.38; N 3.74. *M* 748.8.

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