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Reductive Transformations of Schiff Bases in the Synthesis of Functionally Substituted Heteroaromatic Amines

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Abstract—Schiff bases synthesized by condensation of 5- and 6-aminoquinolines, 5-amino-2-methylquinoline, nitroanilines, and pyrimidinylaminoanilines with substituted benzaldehydes and pyridinecarbaldehydes were reduced with sodium tetrahydridoborate in acetic acid to obtain the corresponding *N*-aryl(hetaryl)benzylamines, *N*-(pyridylmethyl)anilines, and *N*-(1,2,3,4-tetrahydroquinolyl)benzylamine derivatives. The reduction of arylhetarylimines with hydrazine hydrate in the presence of Raney nickel involved only the azomethine C=N bond, while the nitrogen-containing heteroaromatic ring remained intact. Under analogous conditions, nitro-substituted Schiff bases and benzyl- and pyridylmethylamines were converted into previously unknown *N*-(aminobenzyl)quinolinamines and aryl(pyridyl)methyl-substituted phenylenediamines.

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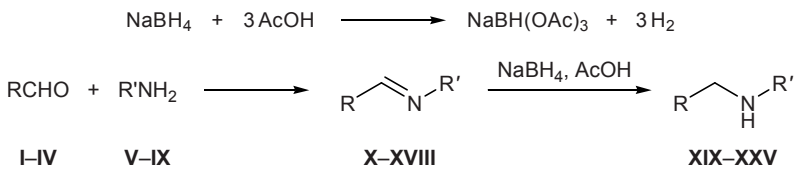
Among a variety of nitrogen-containing heterocyclic compounds, amino derivatives of pyridine, pyrimidine, and quinoline attract considerable interest due to their versatile biological activity and wide application in medicine [1–6]. We previously showed [7] that reductive alkylation of *p*-nitroaniline, 6-aminoquinoline, and *N*-(5-amino-2-methylphenyl)-4-(pyridin-3-yl)pyrimidin-2-amine with methyl 4-formylbenzoate leads to the formation of methoxycarbonyl-substituted *N*-aryl(hetaryl)benzylamines as key intermediates in the synthesis of biomolecules [8].

In the present work we synthesized new functionalized heteroaromatic amines starting from *p*-bromobenzaldehyde (**I**), *m*-nitrobenzaldehyde (**II**), methyl 4-formylbenzoate (**III**), pyridine-3-carbaldehyde (**IV**), on the one hand, and *m*-nitroaniline (**V**), 2-methyl-5-nitroaniline (**VI**), quinolin-5-amine (**VII**), 2-methylquinolin-5-amine (**VIII**), and *N*-[4-(pyridin-3-yl)pyrimidin-2-yl]benzene-1,4-diamine (**IX**), on the other. Compound **IX** is an intermediate in the synthesis of an analog of antileukemic drug Imatinib [8, 9].

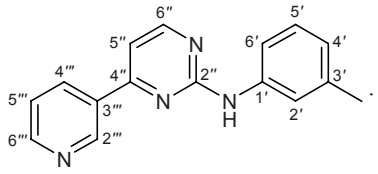
Taking into account our previous results [7], according to which reductive alkylation of primary amines involves intermediate formation of Schiff bases, aldehydes **I**–**IV** were brought into condensation with aromatic and heteroaromatic amines **V**–**IX**. The reactions were carried out by heating equimolar amounts of the reactants in boiling ethanol over a period of 10–30 min, and previously unknown Schiff bases **X**–**XVIII** were isolated in 75–96% yield and were then reduced with sodium tetrahydridoborate in acetic acid (Scheme 1).

The structure of compounds **X**–**XVIII** was confirmed by the IR, NMR, and mass spectra. The IR spectra of **X**–**XVIII** contained an absorption band at 1630–1610 cm^{-1}, which is typical of stretching vibrations of C=N bond. The azomethine CH=N proton resonated in their ^{1}H NMR spectra in the region δ 8.49–8.65 ppm; also, signals from protons in the other molecular fragments were present. The number of signals in the ^{13}C NMR spectra of Schiff bases **X**–**XVIII** was consistent with their structure; the signals were assigned using DEPT pulse sequence. Compounds **X**–**XVIII** displayed molecular ion peaks in the mass spectra. The ^{1}H NMR spectra of *N*-(pyridin-3-ylmethylidene)anilines **XII** and **XIII** were characterized by

Scheme 1.



I, **XIV**, **XXIII**, R = 4-BrC_6H_4; **II**, **XV**, R = 3-$O_2NC_6H_4$; **III**, **X**, **XI**, **XVI**–**XX**, **XXIV**, **XXV**, R = 4-$MeOCOC_6H_4$; **IV**, **XII**, **XIII**, **XXI**, **XXII**, R = pyridin-3-yl; **V**, **X**, **XII**, **XIX**, **XXI**, R′ = 3-$O_2NC_6H_4$; **VI**, **XI**, **XIII**, **XX**, **XXII**, R′ = 2-Me-5-$O_2NC_6H_3$; **VII**, **XIV**–**XVI**, **XXIII**, **XXIV**, R′ = quinolin-5-yl; **VIII**, **XVII**, R′ = 2-methylquinolin-5-yl;

IX, **XVIII**, **XXV**, R′ = 

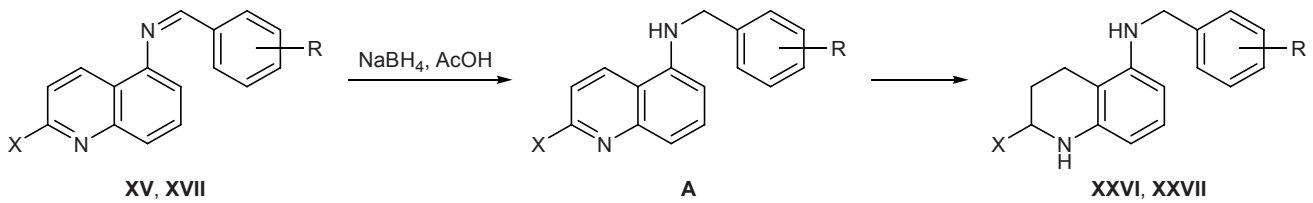
downfield position (δ > 9 ppm) of signal from proton in position *2* of the pyridine ring due to deshielding by the C=N bond.

The reduction of Schiff bases **X**–**XVIII** was performed by stirring a mixture of the substrate, $NaBH_4$, and acetic acid at a ratio of 1:2:6 in benzene at room temperature over a period of 20 h. Sodium triacetoxyhydridoborate generated in that system from $NaBH_4$ and 3 equiv (or excess) acetic acid reduces the protonated C=N bond in Schiff bases **X**–**XIV**, **XVI**, and **XVIII** at room temperature to give the corresponding benzylamines **XIX**–**XXV** in 65–82% yield (Scheme 1). The reduction of 2-methylquinolin-5-amine derivative **XVII** was accompanied by hydrogenation of the pyridine ring with formation of methyl 4-(2-methyl-1,2,3,4-tetrahydroquinolin-5-ylaminomethyl)benzoate (**XXVI**) (Scheme 2). According to published data, the reduction of quinoline with the system $NaBH_4$–AcOH at elevated temperature (50°C) gives *N*-ethyl-1,2,3,4-tetrahydroquinoline as a result of hydrogenation of the nitrogen-containing ring and simultaneous alkylation of the nitrogen atom; here, the alkylating agent is likely to be acetaldehyde generated by self-reduction of $NaBH(OAc)_3$ [10]. The presence of a methyl group in position *2* of the quinoline ring in molecule **XVII** favors its protonation at the endocyclic nitrogen atom and facilitates reduction of the pyridine ring, which occurs together with the reduction of the azomethine bond even at room temperature. The yield of amine **XXVI** was 75% calculated on the initial $NaBH_4$. Neither reduction of acetic acid salts nor N-alkylation of the heterocyclic fragment occurred under the above conditions.

Among Schiff bases **XIV**–**XVI** of the 5-aminoquinoline series, the reduction of only *N*-(*m*-nitrobenzylidene)quinolin-5-amine (**XV**) with sodium tetrahydridoborate in acetic acid gave *N*-(*m*-nitrobenzyl)-1,2,3,4-tetrahydroquinolin-5-amine (**XXVII**). According to the ^1H NMR data, compound **XXVII** was formed as a mixture with quinolin-5-amine **A** at a ratio of 2:1 (Scheme 2). Insofar as amines **XXVII** and **A** were difficult to separate, Schiff base **XV** was reduced with the use of 6 equiv of $NaBH_4$ to ensure complete conversion of intermediate product **A**. In such a way we succeeded in isolating tetrahydroquinoline **XXVII** in 76% yield.

The structure of the reduction products was determined on the basis of their IR, ^1H and ^{13}C NMR, and mass spectra. Unlike initial Schiff bases **X**–**XVIII**, the IR spectra of amines **XIX**–**XXVII** lacked absorption bands assignable to stretching vibrations of azomethine C=N bond, but NH absorption bands were present in

Scheme 2.



XV, **XXVII**, X = H, R = 3-O_2N; **XVII**, **XXVI**, X = Me, R = 4-MeOCO.

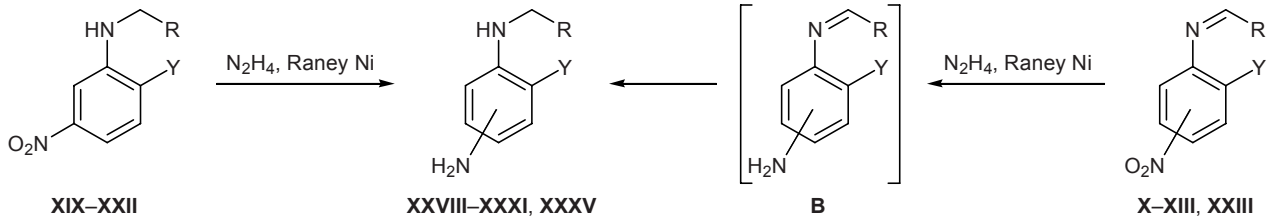
the region 3450–3360 cm^{-1}. The NH proton resonated in the ^1H NMR spectra of **XIX–XXVII** at δ 3.92–6.80 ppm, and signal from the NCH_2 group was located at δ 4.41–4.59 ppm. The corresponding carbon signal appeared in the ^{13}C NMR spectra of **XIX–XXV** at δ_C 48.0–50.0 ppm and was the only signal in that region in the spectra of most amines, except for compounds **XIX**, **XX**, **XXIV**, and **XXV** having a methoxycarbonyl group or other carbon-containing substituent. The ^1H NMR spectra of tetrahydroquinoline derivatives **XXVI** and **XXVII** contained signals in the region δ 1.63–3.44 ppm due to methylene protons in the hydrogenated heteroring, and the NH proton in the heteroring gave a signal at δ 3.80–3.98 ppm. Amines **XXVI** and **XXVII** displayed in the ^{13}C NMR spectra six and four signals, respectively, in the region δ_C 21.5–52.3 ppm. Among these, three signals belong to the endocyclic methylene groups, and one signal (δ_C 46.5–48.0 ppm) originates from the exocyclic methylene group; the other signals belong to carbon-containing substituents.

Molecules of Schiff bases **X–XVIII** and the corresponding reduction products **XIX–XXVII** contain pharmacophoric heterocyclic fragments, bromine atom, and reactive imino, amino, nitro, ester, and other groups. Therefore, these compounds are promising as potential biologically active substances with a broad spectrum of activity, as well as intermediate products for the preparation of new compounds possessing practically important properties. Among numerous reactions involving the above groups, of particular interest are condensations of imines and secondary amines with CH acids, which could lead to polynuclear fused heterocycles having pyridine and quinoline fragments [11–14]. Carboxy group is a precursor of amide bond in biomolecules. Molecules of many medicines contain a nitro group [15] which can be reduced to primary amino group responsible for high chemical and biological potential.

A primary amino group was introduced into molecules of amines **XIX–XXII** via Zinin reaction, i.e., by reduction of compounds **XIX–XXII** with hydrazine hydrate over Raney nickel, as described in [16] for aromatic nitro compounds. For this purpose, hydrazine hydrate was added to a mixture of **XIX–XXII** and the catalyst, and the mixture was heated at 50–60°C for a short time. As a result, we isolated 80–85% of *N*-benzyl- and *N*-(pyridin-3-ylmethyl)benzene-1,3-diamines **XXVIII–XXXI**. The reaction of nitro-substituted Schiff bases **X–XIII** with hydrazine hydrate over Raney nickel was accompanied by reduction of the azomethine bond, and the products were the same diamines (**XXVIII–XXXI**) as those obtained from nitroanilines **XIX–XXII** (Scheme 3). Under analogous conditions, the reduction of *N*-(3-nitrobenzylidene)quinolin-5-amine (**XV**) involved the azomethine C=N bond and the nitro group, while the quinoline ring remained unchanged, and the product was *N*-(3-aminobenzyl)-quinolin-5-amine (**XXXII**) (Scheme 4).

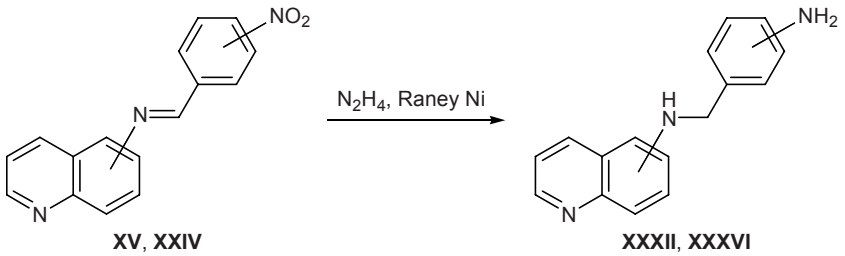
The product structure was confirmed by spectral methods. The primary amino group in molecules **XXVIII–XXXI** gave rise to IR absorption bands in the region 3460–3380 cm^{-1}, stretching vibrations of the secondary N–H bonds had a frequency of 3400–3380 cm^{-1}, and absorption bands in the region 1620–1580 cm^{-1} were assigned to bending vibrations of the amino group. In the ^1H NMR spectra of compounds **XXVIII–XXXI** we observed a singlet from proton in the secondary amino group and broadened two-proton singlets from the primary amino group. The position of these signals was not characteristic, and it depended on the structure of particular compound. It should be noted that signals from aromatic protons in the benzenediamine fragment of **XXVIII–XXXI** were displaced appreciably upfield (by about 1.5 ppm) relative to the corresponding signals of the initial nitro derivatives; the position of signals from the aromatic carbon atoms in the ^{13}C NMR spectra almost did not change.

Scheme 3.



X, **XI**, **XIX**, **XX**, **XXVIII**, **XXIX**, **XXXIII**, **XXXV**, R = 4-$MeOCOC_6H_4$; **XII**, **XIII**, **XXI**, **XXII**, **XXX**, **XXXI**, R = pyridin-3-yl; **X**, **XII**, **XIX**, **XXI**, **XXVIII**, **XXX**, **XXXIII**, **XXXV**, Y = H; **XI**, **XIII**, **XX**, **XXII**, **XXIX**, **XXXI**, Y = Me; **X**, **XII**, **XIX**, **XXI**, Y = 3-O_2N; **XI**, **XIII**, **XX**, **XXII**, Y = 5-O_2N; **XXXIII**, Y = 4-O_2N; **XXVIII**, **XXX**, Y = 3-H_2N; Y = **XXIX**, **XXXI**, 5-H_2N; **XXXV**, Y = 4-H_2N.

Scheme 4.



XV, **XXIV** **XXXII**, **XXXVI**

XV, 5-CH=N, 3-O_2N; **XXIV**, 6-CH=N, 4-O_2N; **XXXII**, 5-$NHCH_2$, 3-H_2N; **XXXVI**, 6-$NHCH_2$, 4-H_2N.

It is known that hydrazine hydrate, which is usually used for selective reduction of nitro group to amino, also reduces nonactivated C=C bond in dicyclopentadiene under analogous conditions [17]. Exocyclic C=N bond in Schiff bases is readily reduced with hydrogen generated *in situ* during aromatization of hydrogenated pyridine ring in the synthesis of azaphenanthrenes from Schiff bases [12, 14]. Taking into account high catalytic activity of Raney nickel, the observed transformation of the C=N bond in the reduction of nitro-substituted Schiff bases with hydrazine hydrate is quite explicable. This reaction deserves specific attention as a one-step procedure for the conversion of nitro imines into diamines.

With a view to determine the scope of the above procedure and the effect of nitro group and its position on the composition of reduction products, we examined reduction with hydrazine hydrate over Raney nickel of Schiff bases **XVI** and **XVIII** having no nitro group. We thus obtained the corresponding secondary amines **XXIV** and **XXV** in high yield (85–92%), as in the reduction of Schiff bases **XVI** and **XVIII** with sodium tetrahydridoborate. No reduction of the heterocyclic fragment was observed. The reaction of Schiff base **XVII** with hydrazine hydrate in the presence of Raney nickel gave benzylamine **A** (Scheme 2), while hydrogenated quinoline derivative **XXVI** was not detected even in trace amount.

Monitoring of the reaction progress by TLC showed formation of intermediate product (obviously, imino amine **B**; Scheme 3) in a few minutes after addition of hydrazine hydrate and the catalyst; the corresponding nitrobenzylamines **XIX**–**XXII** (reduction products of Schiff bases with sodium tetrahydridoborate) were absent in the reaction mixture. These findings indicate that in the reduction with hydrazine hydrate amino-substituted Schiff base **B** is formed initially and that the subsequent hydrogenation of the C=N bond in the latter yields the final diamine.

The system hydrazine hydrate–Raney nickel was also used to reduce methyl 4-(4-nitrophenyliminomethyl)benzoate (**XXXIII**) and *N*-(4-nitrobenzylidene)-quinolin-6-amine (**XXXIV**) which are isomeric to Schiff bases **X** and **XV**; the nitro group in molecules **XXXIII** and **XXXIV** is conjugated with the C=N bond. The reduction products were methyl 4-(4-aminophenylaminomethyl)benzoate (**XXXV**) and *N*-(4-aminobenzyl)quinolin-6-amine (**XXXVI**) (Schemes 3, 4). Their yields (75 and 70%) were comparable with the yields of isomeric compounds **XXVIII** and **XXXV**. These data suggest the absence of mesomeric effect of nitro group in both amine and aldehyde fragments on the reaction course. 5- and 6-Aminoquinoline, pyridine, and pyrimidine rings and carboxy and amide groups remain intact in the reduction with hydrazine hydrate over Raney nickel, but this system readily reduces aldehyde group.

It was also interesting to estimate the probability for decomposition of initial Schiff bases by the action of strong base under the reduction conditions. Decomposition products (up to 20%) were detected in Schiff bases derived from *p*-nitrobenzaldehyde in which the nitro group is conjugated with the reaction center. For example, the reduction of *m*-nitrophenyl derivative **XV** gives up to 15% of quinolin-6-amine. Analogous retro reaction was observed in some cases with the use of less active skeletal catalyst. Therefore, the activity of skeletal catalyst is crucial for decomposition of Schiff bases by the action of strong base, which is concurrent to the reduction of the C=N bond.

We can conclude that variation of reducing agents in the hydrogenation of functionally substituted Schiff bases, including those containing a nitro group, ensures selective synthesis of secondary amines with conservation of the nitro group, benzylamines of the quinoline series with partially hydrogenated heterocyclic fragment, and pyridyl-, pyrimidinyl-, and quinolyl-substituted diamines having both primary and secondary amino groups.

EXPERIMENTAL

The IR spectra were measured in KBr on a Nicolet Protégé-460 spectrometer with Fourier transform. The ^{1}H and ^{13}C NMR spectra were recorded on from solutions in $CDCl_3$ and DMSO-d_6 a Bruker Avance-500 spectrometer at 500 and 125 MHz, respectively, using tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Hewlett–Packard 5890/5972 GC–MS (HP-5MS capillary column, 30 m×0.25 mm, stationary phase 5% of phenylmethylsilicone; injector temperature 250°C). Thin-layer chromatography was performed on Kieselgel 60 F_{254} plates (Merck) using butanol–ethanol–NH_4OH (8 : 1 : 1) and chloroform–methanol (95 : 5) as eluents.

N-[4-(Pyridin-3-yl)pyrimidin-2-yl]benzene-1,3-diamine (**IX**) [7], methyl 4-(4-nitrophenyliminomethyl)benzoate (**XXXIII**) [9], and *N*-(4-nitrophenylmethylidene)quinolin-6-amine (**XXXIV**) [18] were synthesized by known methods.

Schiff bases X–XVIII (*general procedure***).** A solution of equimolar amounts (10 mmol) of aldehyde **I–IV** and amine **V–IX** in 30 ml of ethanol was heated for 10–30 min under reflux. The mixture was cooled, and the precipitate was filtered off and recrystallized from ethanol (**X–XIV**, **XVIII**) or ethanol–benzene (2 : 1) (**XV–XVII**).

Methyl 4-(3-nitrophenyliminomethyl)benzoate (X). Yield 96%, mp 147–148°C. IR spectrum, ν, cm^{-1}: 3060, 3048, 2940, 2850, 1718 (C=O), 1624 (C=N), 1517, 1350 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.95 s (3H, OMe), 7.54 d and 7.57 t (2H, 5′-H, 6′-H, ^3J = 8.1 Hz), 7.99 d (2H, 2-H, 6-H, ^3J = 8.2 Hz), 8.06 s (1H, 2′-H), 8.11 d (1H, 4′-H, ^3J = 8.1 Hz), 8.16 d (2H, 3-H, 5-H, ^3J = 8.2 Hz) 8.55 s (1H, CH=N). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 166.12, 161.15, 152.34, 148.70, 138.84, 132.81, 129.83, 129.76, 128.74, 127.35, 120.66, 115.09, 52.16. Found, %: C 63.14; H 4.21; N 9.73. $C_{15}H_{12}N_2O_4$. Calculated, %: C 63.38; H 4.23; N 9.86.

Methyl 4-(2-methyl-5-nitrophenyliminomethyl)benzoate (XI). Yield 92%, mp 182–183°C. IR spectrum, ν, cm^{-1}: 3070, 3030, 2964, 2920, 1725 (C=O), 1630 (C=N), 1520, 1355 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.46 s (3H, Me), 3.96 s (3H, OMe), 7.38 d (1H, 3′-H, ^3J = 8.2 Hz), 7.82 d (1H, 6′-H, ^4J = 2.8 Hz), 8.00 d (2H, 2-H, 6-H, ^3J = 8.1 Hz), 8.03 d (1H, 4′-H, ^3J = 8.2 Hz), 8.18 d (2H, 3-H, 5-H, ^3J = 8.1 Hz), 8.49 s (1H, CH=N). Found, %: C 64.35; H 4.51; N 9.26. $C_{16}H_{14}N_2O_4$. Calculated, %: C 64.43; H 4.70; N 9.40.

3-Nitro-*N*-(pyridin-3-ylmethylidene)aniline (XII). Yield 82%, mp 95°C. IR spectrum, ν, cm^{-1}: 3090, 3030, 1725 (C=O), 1623 (C=N), 1518, 1355 (NO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.30 t (1H, 5′-H, ^3J = 7.4 Hz), 7.44 d.d (1H, 5-H, ^3J = 8.8, 4.7 Hz), 7.84 d (1H, 2′-H, ^4J = 2.3 Hz), 8.08 d.d (1H, 4′-H, ^3J = 7.4, ^4J = 2.3 Hz), 8.20 d (1H, 6′-H, ^3J = 7.4 Hz), 8.38 d (1H, 6-H, ^3J = 9.0, ^4J = 1.6 Hz), 8.49 s (1H, CH=N), 8.77 d.d (1H, 4-H, ^3J = 4.7, ^4J = 1.4 Hz), 9.14 d (1H, 2-H, ^4J = 1.4 Hz). Mass spectrum: *m*/*z* 227 $[M]^+$. Found, %: C 63.27; H 3.89; N 18.36. $C_{12}H_9N_3O_2$. Calculated, %: C 63.44; H 3.96; N 18.50.

2-Methyl-5-nitro-*N*-(pyridin-3-ylmethylidene)aniline (XIII). Yield 80%, mp 154–155°C. IR spectrum, ν, cm^{-1}: 3065, 3030, 2920, 2850, 1625 (C=N), 1522, 1350 (NO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.47 s (3H, Me), 7.41 d (1H, 3′-H, ^3J = 8.3 Hz), 7.48 d.d (1H, 5-H, ^3J = 9.2, ^4J = 4.8 Hz), 7.84 d (1H, 6′-H, ^4J = 2.3 Hz), 8.04 d.d (1H, 4′-H, ^3J = 8.3, ^4J = 2.3 Hz), 8.33 d.d (1H, 6-H, ^3J = 9.2, ^4J = 1.8 Hz), 8.51 s (1H, CH=N), 8.77 d.d (1H, 4-H, ^3J = 4.8, ^4J = 1.6 Hz), 9.10 d (1H, 2-H, ^4J = 1.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 158.70, 152.59, 151.03, 150.90, 146.94, 140.36, 135.28, 131.21, 130.89, 123.88, 120.76, 112.35, 18.18. Found, %: C 64.68; H 4.41; N 17.25. $C_{13}H_{11}N_{23}O_2$. Calculated, %: C 64.73; H 4.56; N 17.43.

***N*-(4-Bromophenylmethylidene)quinolin-5-amine (XIV).** Yield 85%, mp 108–109°C. IR spectrum, ν, cm^{-1}: 3070, 3055, 1620 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.14 d (1H, 6′-H, ^3J = 7.3 Hz), 7.43 d.d (1H, 3′-H, ^3J = 8.3, 4.2 Hz), 7.65 d (2H, 2-H, 6-H, ^3J = 7.6 Hz), 7.70 t (1H, 7′-H, ^3J = 8.5 Hz), 7.87 d (2H, 3-H, 5-H, ^3J = 7.6 Hz), 8.00 d (1H, 8′-H, ^3J = 8.5 Hz), 8.52 s (1H, CH=N), 8.69 d (1H, 4′-H, J = 8.3 Hz), 8.95 d.d (1H, 2′-H, ^3J = 4.2, ^5J = 1.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 159.42, 150.62, 148.30, 148.26, 134.66, 132.24, 131.88, 130.08, 129.21, 127.12, 126.10, 123.99, 120.57, 112.67. Found, %: C 61.57; H 3.39; Br 25.60; N 8.72. $C_{16}H_{11}BrN_2$. Calculated, %: C 61.74; H 3.54; Br 25.72; N 9.00.

***N*-(3-Nitrophenylmethylidene)quinolin-5-amine (XV).** Yield 80%, mp 157–158°C. IR spectrum, ν, cm^{-1}: 3060, 3040, 1623 (C=N), 1532, 1350 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.16 d (1H, 6′-H, ^3J = 7.3 Hz), 7.42 d.d (1H, 3′-H, ^3J = 8.4, 4.1 Hz), 7.69 m (2H, 5-H, 7′-H), 8.01 d (1H, 8′-H, ^3J = 8.4 Hz), 8.30 d (1H, 6-H, ^3J = 7.6 Hz), 8.34 d (1H, 4-H, ^3J = 8.1 Hz), 8.60 s (1H, CH=N), 8.69 d (1H, 4′-H, ^3J = 8.4 Hz), 8.83 s (1H, 2-H), 8.94 d (1H, 2′-H, ^3J =

4.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 158.07, 151.04, 148.73, 148.53, 147.75, 137.61, 134.39, 132.40, 129.94, 129.38, 128.11, 125.93, 124.31, 123.54, 121.05, 112.96. Found, %: C 69.11; H 3.76; N 14.94. $C_{16}H_{11}N_3O_2$. Calculated, %: C 69.31; H 3.97; N 15.16.

Methyl 4-(quinolin-5-yliminomethyl)benzoate (XVI). Yield 83%, mp 157–158°C. IR spectrum, ν, cm^{-1}: 3040, 3005, 2940, 2858, 1716 (C=O), 1623 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.98 s (3H, OMe), 7.18 d (1H, 6′-H, ^3J = 7.4 Hz), 7.45 d.d (1H, 3′-H, ^3J = 8.4, 4.2 Hz), 7.72 t (1H, 7′-H, ^3J = 7.4 Hz), 8.03 d (1H, 8′-H, ^3J = 7.4 Hz), 8.09 d (2H, 2-H, 6-H, ^3J = 8.2 Hz), 8.19 d (2H, 3-H, 5-H, ^3J = 8.2 Hz), 8.65 s (1H, CH=N), 8.73 d (1H, 4′-H, ^3J = 8.4 Hz), 8.97 d (1H, 2′-H, ^3J = 4.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 167.03, 160.41, 151.46, 149.04, 148.99, 146.49, 140.30, 133.21, 133.10, 130.60, 130.02, 129.42, 128.19, 124.88, 121.47, 113.50, 52.94. Found, %: C 74.25; H 4.71; N 9.53. $C_{18}H_{14}N_2O_2$. Calculated, %: C 74.48; H 4.83; N 9.66.

Methyl 4-(2-methylquinolin-5-yliminomethyl)-benzoate (XVII). Yield 78%, mp 169–170°C. IR spectrum, ν, cm^{-1}: 3055, 3035, 2950, 2850, 1717 (C=O), 1623 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.77 s (3H, Me), 3.97 s (3H, OMe), 7.11 d (1H, 6′-H, ^3J = 7.5 Hz), 7.32 d (1H, 3′-H, ^3J = 7.5 Hz), 7.65 d.d (1H, 7′-H, ^3J = 7.5, 8.5 Hz), 7.93 d (1H, 8′-H, ^3J = 8.5 Hz), 8.08 d (2H, 2-H, 6-H, ^3J = 8.3 Hz), 8.18 d (2H, 3-H, 5-H, ^3J = 8.3 Hz), 8.59 d (1H, 4′-H, ^3J = 8.5 Hz), 8.62 s (1H, CH=N). ^{13}C NMR spectrum, δ_C, ppm: 166.47, 159.62, 159.54, 148.26, 148.15, 139.79, 132.53, 130.00, 129.39, 128.80, 126.90, 122.44, 121.78, 121.34, 112.20, 52.35, 25.34. Found, %: C 74.82; H 5.19; N 9.02. $C_{19}H_{16}N_2O_2$. Calculated, %: C 75.00; H 5.26; N 9.21.

Methyl 4-{3-[4-(pyridin-3-yl)pyrimidin-2-yl-amino]phenyliminomethyl}benzoate (XVIII). Yield 80%, mp 174–175°C. IR spectrum, ν, cm^{-1}: 3302 (NH), 3080, 3030, 2940, 2855, 1718 (C=O), 1610 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.80 s (3H, OMe), 6.97 d (1H, 5′-H, ^3J = 8.0 Hz), 7.21 d (1H, 5″-H, ^3J = 5.1 Hz), 7.43 m (2H, 6′-H, 5‴-H), 7.56 m (2H, 2′-H, 4′-H), 7.71 s (1H, NH), 7.99 d (2H, 2-H, 6-H, ^3J = 8.2 Hz), 8.16 d (2H, 3-H, 5-H, ^3J = 8.2 Hz), 8.36 d (1H, 4‴-H, ^3J = 7.9 Hz), 8.54 d (1H, 6″-H, ^3J = 5.1 Hz), 8.58 s (1H, CH=N), 8.73 d (1H, 6‴-H, ^3J = 4.7 Hz), 9.31 s (1H, 2‴-H). Found, %: C 70.29; H 4.56; N 16.83. $C_{24}H_{19}N_5O_2$. Calculated, %: C 70.42; H 4.65; N 17.11.

Reduction of Schiff bases X–XVIII with sodium tetrahydridoborate. A solution or suspension of 10 mmol of Schiff base **X–XVIII** in 30 ml of benzene was added under stirring at 0°C to a mixture of $NaBH_4$ (20 mmol in the synthesis of compounds **XIX–XXVI** or 60 mmol in the synthesis of **XXVII**), 10 ml of benzene, and glacial acetic acid (60 mmol in the synthesis of **XIX–XXVI** or 360 mmol in the synthesis of **XXVII**). The mixture was stirred for 2 h without external cooling and was left to stand for 20 h at room temperature. The mixture was then treated with 40–50 ml of 20% aqueous sodium hydroxide, and the organic phase was separated, washed with water, and dried over $MgSO_4$. The solvent was distilled off, and the solid residue was recrystallized from ethanol (**XIX–XXII**, **XXVI**, **XXVII**) or toluene (**XXIII–XXV**).

Methyl 4-(3-nitrophenylaminomethyl)benzoate (XIX). Yield 79%, mp 125–126°C. IR spectrum, ν, cm^{-1}: 3410 (NH), 3080, 3060, 2950, 2900, 1720 (C=O), 1620 (δNH), 1540, 1340 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.91 s (3H, OMe), 4.46 d (2H, CH_2, ^3J = 5.8 Hz), 4.52 br.s (1H, NH), 6.85 d.d (1H, 6′-H, ^3J = 8.1, ^4J = 2.3 Hz), 7.25 t (1H, 5′-H, ^3J = 8.1 Hz), 7.41 d (2H, 2-H, 6-H, ^3J = 8.1 Hz), 7.43 br.s (1H, 2′-H), 7.53 d.d (1H, 4′-H, ^3J = 8.1, ^4J = 1.7 Hz), 8.02 d (2H, 3-H, 5-H, ^3J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 167.01, 149.60, 148.63, 143.58, 130.39, 130.09, 129.76, 127.35, 118.93, 112.72, 106.93, 52.40, 47.92. Mass spectrum: *m*/*z* 286 $[M]^+$. Found, %: C 62.80; H 4.83; N 9.54. $C_{15}H_{14}N_2O_4$. Calculated, %: C 62.94; H 4.90; N 9.79.

Methyl 4-(2-methyl-5-nitrophenylaminomethyl)-benzoate (XX). Yield 82%, mp 120–121°C. IR spectrum, ν, cm^{-1}: 3420 (NH), 3100, 3080, 2930, 2860, 1712 (C=O), 1612 (NH), 1530, 1341 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.24 s (3H, Me), 3.90 s (3H, OMe), 4.20 t (1H, NH, ^3J = 5.5 Hz), 4.50 d (2H, CH_2, ^3J = 5.5 Hz), 7.16 d (1H, 3′-H, ^3J = 8.0 Hz), 7.33 d (1H, 6′-H, ^4J = 1.6 Hz), 7.43 d (2H, 2-H, 6-H, ^3J = 8.2 Hz), 7.51 d.d (1H, 4′-H, ^3J = 8.0, ^4J = 1.6 Hz), 8.01 d (2H, 3-H, 5-H, ^3J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 166.47, 147.46, 145.87, 143.04, 129.98, 129.90, 129.43, 129.31, 129.10, 127.00, 112.21, 103.71, 51.87, 47.43, 17.51. Mass spectrum: *m*/*z* 300 $[M]^+$. Found, %: C 63.76; H 5.20; N 9.17. $C_{16}H_{16}N_2O_4$. Calculated, %: C 64.00; H 5.53; N 9.33.

3-Nitro-*N*-(pyridin-3-ylmethyl)aniline (XXI). Yield 80%, mp 143–144°C. IR spectrum, ν, cm^{-1}: 3396 (NH), 3065, 3040, 2920, 2855, 1620 (NH), 1537, 1345 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.48 d (2H, CH_2, ^3J = 5.6 Hz), 5.78 br.s (1H, NH), 6.86 d (1H, 6′-H, ^3J = 7.4 Hz), 7.27 t (1H, 5′-H, ^3J = 7.4 Hz), 7.43 s (1H, 2′-H), 7.50 m (2H, 5-H, 4′-H), 7.94 d (1H, 4-H,

^3J = 7.8 Hz), 8.50 d (1H, 6-H, ^3J = 5.3 Hz), 8.64 s (1H, 2-H). ^{13}C NMR spectrum, δ_C, ppm: 149.35, 148.16, 146.40, 146.31, 146.08, 137.76, 129.77, 125.03, 118.29, 112.28, 106.76, 44.58. Mass spectrum: *m*/*z* 229 $[M]^+$. Found, %: C 62.63; H 4.55; N 18.31. $C_{12}H_{11}N_3O_2$. Calculated, %: C 62.88; H 4.80; N 18.34.

2-Methyl-5-nitro-*N*-(pyridin-3-ylmethyl)aniline (XXII). Yield 78%, mp 117–118°C. IR spectrum, ν, cm^{-1}: 3382 (NH), 3080, 3055, 2940, 2860, 1615 (NH), 1540, 1355 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.42 s (3H, Me), 4.39 d (2H, CH_2, ^3J = 5.0 Hz), 5.68 br.s (1H, NH), 7.38 d (1H, 3′-H, ^3J = 8.1 Hz), 7.49 d.d (1H, 5-H, ^3J = 8.0, 5.6 Hz), 7.76 d (1H, 6′-H, ^4J = 1.9 Hz), 7.96 d.d (1H, 4′-H, ^3J = 8.1, ^4J = 1.9 Hz), 8.01 d (1H, 4-H, ^3J = 8.0 Hz), 8.54 d (1H, 6-H, ^3J = 5.6 Hz), 8.61 d (1H, 2-H, ^4J = 1.9 Hz). Mass spectrum: *m*/*z* 243 $[M]^+$. Found, %: C 63.99; H 5.23; N 17.04. $C_{13}H_{13}N_3O_2$. Calculated, %: C 64.20; H 5.35; N 17.28.

***N*-(4-Bromobenzyl)quinolin-5-amine (XXIII).** Yield 84%, mp 164–165°C. IR spectrum, ν, cm^{-1}: 3410 (NH), 3060, 3035, 2942, 2855, 1618 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.46 d (2H, CH_2, ^3J = 5.5 Hz), 6.34 d (1H, 6′-H, ^3J = 7.6 Hz), 6.70 br.s (1H, NH), 7.25 d (1H, 7′-H, ^3J = 7.6 Hz), 7.30 d (2H, 2-H, 6-H, ^3J = 8.4 Hz), 7.35 d.d (1H, 3′-H, ^3J = 8.5, 4.1 Hz), 7.39 d (1H, 8′-H, ^3J = 7.6 Hz), 7.43 d (2H, 3-H, 5-H, ^3J = 8.4 Hz), 8.59 d (1H, 4′-H, ^3J = 8.5 Hz), 8.78 d (1H, 2′-H, ^3J = 4.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 148.37, 147.79, 142.74, 137.48, 130.09, 129.14, 129.00, 127.67, 119.06, 118.97, 117.78, 115.82, 102.92, 94.70, 45.88. Found, %: C 61.23; H 3.95; Br 25.41; N 8.61. $C_{16}H_{13}BrN_2$. Calculated, %: C 61.34; H 4.15; Br 25.56; N 8.95.

Methyl 4-(quinolin-5-ylaminomethyl)benzoate (XXIV). Yield 72%, mp 108–109°C. IR spectrum, ν, cm^{-1}: 3413 (NH), 3080, 3070, 2936, 2852, 1716 (C=O), 1615 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.89 s (3H, OMe), 4.59 d (2H, CH_2, ^3J = 5.3 Hz), 6.48 d (1H, 6′-H, ^3J = 8.1 Hz), 6.80 br.s (1H, NH), 7.40–7.54 m (5H, 2-H, 6-H, 4′-H, 7′-H, 8′-H), 7.57 t (1H, 3′-H, ^3J = 8.4 Hz), 7.97 d (2H, 3-H, 5-H, ^3J = 8.2 Hz), 8.05 d (1H, 2′-H, ^3J = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 167.27, 166.74, 165.70, 165.63, 163.96, 148.91, 143.68, 143.08, 134.54, 132.27, 128.92, 125.90, 118.76, 116.92, 111.14, 104.85, 95.07, 51.04, 46.37. Found, %: C 73.74; H 5.21; N 9.36. $C_{18}H_{16}N_2O_2$. Calculated, %: C 73.97; H 5.48; N 9.58.

Methyl 4-{3-[4-(pyridin-3-yl)pyrimidin-2-ylamino]phenylaminomethyl}benzoate (XXV). Yield 65%, mp 142–143°C. IR spectrum, ν, cm^{-1}: 3420 (NH), 3360, 3040, 3010, 2923, 2854, 1716 (C=O), 1600 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.92 s (3H, OMe), 4.30 br.s (1H, NH), 4.45 d (2H, CH_2, ^3J = 5.7 Hz), 6.34 d (1H, 5′-H, ^3J = 8.0 Hz), 6.99 d (1H, 6′-H, ^3J = 7.4 Hz), 7.17 m (3H, 2′-H, 4-H, NH), 7.28 d (1H, 5″-H, ^3J = 5.2 Hz), 7.42 d.d (1H, 5‴-H, ^3J = 8.0, ^4J = 4.1 Hz), 7.45 d (2H, 2-H, 6-H, ^3J = 8.1 Hz), 8.18 d (2H, 3-H, 5-H, ^3J = 8.1 Hz), 8.34 d (1H, 4‴-H, ^3J = 8.0 Hz), 8.48 d (1H, 6″-H, ^3J = 5.2 Hz), 8.73 d (1H, 6‴-H, ^3J = 4.1 Hz), 9.28 s (1H, 2‴-H). ^{13}C NMR spectrum, δ_C, ppm: 166.68, 162.19, 160.04, 158.61, 151.16, 148.27, 146.26, 144.65, 140.12, 136.66, 134.87, 134.17, 132.49, 129.46, 128.74, 126.84, 125.03, 123.33, 108.72, 107.91, 107.29, 103.39, 51.81, 47.70. Found, %: C 69.93; H 4.85; N 16.87. $C_{24}H_{21}N_5O_2$. Calculated, %: C 70.07; H 5.11; N 17.03.

Methyl 4-(2-methyl-1,2,3,4-tetrahydroquinolin-5-ylaminomethyl)benzoate (XXVI). Yield 75%, mp 94–95°C. IR spectrum, ν, cm^{-1}: 3410 (NH), 3396, 3070, 3052, 2925, 2915, 2855, 1718 (C=O), 1610 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.20 d (3H, Me), 1.63 m and 2.01 m (2H, 3′-H), 2.48 m (2H, 4′-H), 3.33 m (1H, 2′-H), 3.80 br.s (1H, NH), 3.91 s (3H, OMe), 4.41 s (2H, CH_2), 3.90 br.s (1H, NH), 5.94 d (1H, 6′-H, ^3J = 8.0 Hz), 6.00 d (1H, 8′-H, ^3J = 8.0 Hz), 6.84 t (1H, 7′-H, ^3J = 8.0 Hz), 7.43 d (2H, 2-H, 6-H, ^3J = 8.2 Hz), 8.00 d (2H, 3-H, 5-H, ^3J = 8.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 167.20, 146.14, 145.61, 145.55, 130.12, 129.18, 127.41, 105.58, 105.43, 102.38, 100.45, 52.29, 48.29, 46.51, 30.33, 22.49, 21.54. Found, %: C 73.40; H 6.97; N 8.78. $C_{19}H_{22}N_2O_2$. Calculated, %: C 73.55; H 7.10; N 9.03.

***N*-(3-Nitrobenzyl)-1,2,3,4-tetrahydroquinolin-5-amine (XXVII).** Yield 76%, mp 108–109°C. IR spectrum, ν, cm^{-1}: 3440, 3412 (NH), 3055, 3030, 2923, 2850, 1600 (NH), 1526, 1344 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.04 m (2H, 3′-H), 2.53 m (2H, 4′-H), 3.25 m (2H, 2′-H), 3.98 br.s (1H, NH), 4.47 s (2H, CH_2), 4.92 br.s (1H, NH), 5.88 d (1H, 6′-H, ^3J = 8.1 Hz), 6.03 d (1H, 8′-H, ^3J = 8.1 Hz), 6.64 t (1H, 7′-H, ^3J = 8.1 Hz), 7.49 m (2H, 5-H, 6-H), 8.26 m (2H, 2-H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 149.92, 145.33, 142.09, 140.73, 133.05, 129.86, 129.22, 126.82, 121.80, 119.39, 105.43, 99.88, 47.31, 40.89, 22.01, 21.08. Found, %: C 67.69; H 5.73; N 14.58. $C_{16}H_{17}N_3O_2$. Calculated, %: C 67.84; H 6.01; N 14.84.

Reduction of Schiff bases X–XIII, XV, XVI, XVIII, XXXIII, and XXXIV and nitro-substituted amines XIX–XXII with hydrazine hydrate over Raney nickel (*general procedure*). Schiff base **X**–**XIII**, **XV**, **XVI**, **XVIII**, **XXXIII**, or **XXXIV** or nitro

amine **XIX**–**XXII**, 0.01 mol, was dissolved in 20 ml of ethanol or ethanol (methanol)–tetrahydrofuran (3 : 1), 0.06 g of Raney nickel was added, and 0.04 mol of 80% hydrazine hydrate was then added. The mixture foamed and turned colorless. It was stirred for 25–45 min at 50–60°C and for 1 h at room temperature, and filtered through a layer of celite, the filtrate was evaporated, and the residue was purified by reprecipitation from toluene or ethyl acetate with hexane or by recrystallization from toluene (**XXIV**, **XXV**). Crude 4-aminobenzylquinolin-6-amine (**XXXVI**) was treated with boiling water to remove quinolin-6-amine and dried prior to recrystallization. Analytical samples were obtained through the corresponding hydrochlorides.

Methyl 4-(3-aminophenylaminomethyl)benzoate (XXVIII). Yield 84% (from **X**), 85% (from **XIX**); mp 125–126°C. IR spectrum, ν, cm^{-1}: 3450, 3420, 3380 (NH, NH_2), 3065, 3030, 2840, 2435, 1714 (C=O), 1609 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.75 br.s (2H, NH_2), 4.20 s (3H, OMe), 4.44 br.s (2H, CH_2), 5.94 t (1H, 2′-H, ^4J = 2.1 Hz), 6.12 d.d and 6.15 d.d (1H each, 4′-H, 6′-H, ^3J = 7.8, 2.1 Hz), 7.02 t (1H, 5′-H, ^3J = 7.8 Hz), 7.49 d (2H, 2-H, 6-H, ^3J = 8.1 Hz), 8.08 d (2H, 3-H, 5-H, ^3J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 166.21, 148.71, 147.25, 144.72, 129.86, 129.59, 129.05, 126.76, 104.99, 103.72, 99.19, 60.63, 47.64. Found, %: C 70.22; H 6.09; N 10.63. $C_{15}H_{16}N_2O_2$. Calculated, %: C 70.31; H 6.25; N 10.94.

Methyl 4-(5-amino-2-methylphenylaminomethyl)benzoate (XXIX). Yield 80% (from **XI**), 83% (from **XX**); mp 120–121°C. IR spectrum, ν, cm^{-1}: 3473, 3445, 3380 (NH, NH_2), 3060, 3030, 2920, 2850, 1708 (C=O), 1620 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.07 s (3H, Me), 3.88 s (3H, OMe), 3.30 br.s (2H, NH_2), 4.38 s (2H, CH_2), 3.48 br.s (1H, NH), 5.85 d (1H, 6-H, ^4J = 2.2 Hz), 6.02 d.d (1H, 4-H, ^3J = 8.0, ^4J = 2.2 Hz), 6.82 d (1H, 3′-H, ^3J = 8.0 Hz), 7.4 d (2H, 2-H, 6-H, ^3J = 8.2 Hz), 7.98 d (2H, 3-H, 5-H, ^3J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 166.94, 146.46, 145.70, 145.04, 130.70, 129.93, 128.99, 127.03, 112.36, 104.23, 97.97, 52.06, 47.84, 16.65. Mass spectrum: m/z 270 $[M]^+$. Found, %: C 70.94; H 6.39; N 10.19. $C_{16}H_{18}N_2O_2$. Calculated, %: C 71.11; H 6.67; N 10.37.

***N*-(Pyridin-3-ylmethyl)benzene-1,3-diamine (XXX).** Yield 80% (from **XII**), 84% (from **XXI**); mp 143–144°C. IR spectrum, ν, cm^{-1}: 3460, 3430, 3390 (NH, NH_2), 3065, 3035, 2925, 2845, 1605, 1588 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.31 s (2H, CH_2), 4.00 br.s (3H, NH, NH_2), 5.95 t (1H, 2′-H, ^4J = 2.1 Hz), 6.07 d.d (1H, 4′-H, ^3J = 7.8, ^4J = 2.2 Hz), 6.09 d.d (1H, 6′-H, ^3J = 7.8, ^4J = 2.0 Hz), 6.95 t (1H, 5′-H, ^3J = 7.8 Hz), 7.26 d.d (1H, 5-H, ^3J = 7.9, 4.8 Hz), 7.68 d (1H, 6-H, ^3J = 7.9 Hz), 8.51 d.d (1H, 4-H, ^3J = 4.8, ^4J = 1.6 Hz), 8.60 d (1H, 2-H, ^4J = 1.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 148.98, 148.77, 148.52, 147.54, 135.04, 130.13, 123.49, 105.38, 103.91, 99.45, 45.62. Mass spectrum: m/z 199 $[M]^+$. Found, %: C 72.19; H 6.46; N 20.88. $C_{12}H_{13}N_3$. Calculated, %: C 72.36; H 6.53; N 21.11.

6-Methyl-N^1-(pyridin-3-ylmethyl)benzene-1,3-diamine (XXXI). Yield 83% (from **XIII**), 85% (from **XXII**), mp 143–144°C. IR spectrum, ν, cm^{-1}: 3440, 3380 (NH), 3070, 3040, 2942, 2855, 1600, 1580 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.44 s (3H, Me), 4.48 s (2H, CH_2), 3.78 br.s (3H, NH, NH_2), 5.90 t (1H, 2′-H, ^4J = 1.4 Hz), 6.08 d.d (1H, 4′-H, ^3J = 8.0, 1.4 Hz), 6.82 d (1H, 5′-H, ^3J = 8.0 Hz), 7.23 d.d (1H, 5-H, ^3J = 7.6, 4.5 Hz), 7.70 d (1H, 4-H, ^3J = 7.5 Hz), 8.50 d.d (1H, 6-H, ^3J = 5.0, ^4J = 1.9 Hz), 8.64 d (1H, 2-H, ^4J = 1.9 Hz). Mass spectrum: m/z 213 $[M]^+$. Found, %: C 72.19; H 6.46; N 20.88. $C_{13}H_{15}N_3$. Calculated, %: C 72.36; H 6.53; N 21.11.

***N*-(3-Aminobenzyl)quinolin-5-amine (XXXII).** Yield 78% (from **XV**), mp 108–109°C. IR spectrum, ν, cm^{-1}: 3458, 3420, 3388 (NH), 3065, 3048, 2942, 2855, 1610, 1592 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.22 br.s (2H, NH_2), 3.77 br.s (1H, NH), 4.47 s (2H, CH_2), 5.88 d (1H, 6′-H, ^3J = 8.1 Hz), 6.03 d (1H, 8′-H, ^3J = 8.1 Hz), 7.34 d.d (1H, 3′-H, ^3J = 8.4, 4.1 Hz), 7.49 t (1H, 7′-H, ^3J = 8.1 Hz), 7.56 d (1H, 6-H, ^3J = 8.4 Hz), 8.15 d (1H, 8′-H, ^3J = 7.2 Hz), 8.30 d (1H, 6-H, ^3J = 7.6 Hz), 8.34 d (1H, 4-H, ^3J = 8.1 Hz), 8.69 d (1H, 4′-H, ^3J = 8.4 Hz), 8.86 d.d (1H, 2′-H, ^3J = 4.1, ^4J = 1.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 161.97, 149.90, 148.73, 146.48, 141.98, 134.69, 129.74, 129.38, 129.28, 119.75, 119.51, 119.28, 117.84, 113.36, 109.72, 29.39. Mass spectrum: m/z 249 $[M]^+$. Found, %: C 76.98; H 5.79; N 16.58. $C_{16}H_{15}N_3$. Calculated, %: C 77.11; H 6.02; N 16.87.

Methyl 4-(4-aminophenylaminomethyl)benzoate (XXXV). Yield 75% (from **XXXIII**), mp 125–126°C. IR spectrum, ν, cm^{-1}: 3460, 3410, 3385 (NH), 3080, 3055, 2928, 2852, 1600, 1580 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.90 s (3H, OMe), 4.20 br.s (2H, NH_2), 4.33 s (2H, CH_2), 4.50 br.s (1H, NH), 6.49 d (2H, 2′-H, 6′-H, ^3J = 8.6 Hz), 6.59 d (2H, 3′-H, 5′-H, ^3J = 8.6 Hz), 7.43 d (2H, 2-H, 6-H, ^3J = 8.3 Hz), 7.99 d (2H, 3-H, 5-H, ^3J = 8.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 166.71, 145.16, 140.61, 137.76, 129.58,

128.15, 126.95, 116.56, 114.25, 51.79, 48.76. Mass spectrum: m/z 256 $[M]^+$. Found, %: C 70.15; H 6.05; N 10.84. $C_{15}H_{16}N_2O_2$. Calculated, %: C 70.31; H 6.25; N 10.94.

***N*-(4-Aminobenzyl)quinolin-6-amine (XXXVI).** Yield 78% (from **XXXIV**), mp 108–109°C. IR spectrum, ν, cm^{-1}: 3455, 3400, 3392 (NH), 3065, 3035, 2930, 2848, 1598, 1590 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.98 br.s (3H, NH, NH_2), 4.25 s (2H, CH_2), 6.64 d (2H, 3-H, 5-H, ^3J = 8.1 Hz), 7.14 d (2H, 2-H, 6-H), 7.21 d.d and 7.24 d.d (1H each, 3′-H, 4′-H, ^3J = 5.7, 3.1 Hz), 7.82–7.87 m (3H, 5′-H, 7′-H, 8′-H), 8.62 d.d (1H, 2′-H, ^3J = 8.1, ^3J = 1.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 146.94, 146.23, 144.84, 134.07, 133.99, 130.64, 130.32, 130.28, 129.10, 121.77, 121.57, 121.52, 115.46, 107.57, 103.22, 48.09. Found, %: C 77.03; H 5.81; N 16.63. $C_{16}H_{15}N_3$. Calculated, %: C 77.11; H 6.02; N 16.87.

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