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New method for the synthesis of nitrobiaryls

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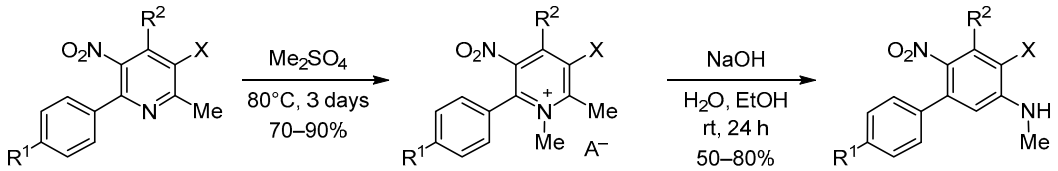


R^1 = H, Cl, Br, Me, OMe; R^2 = H, 2-Fur; X = H, I, NMe_2, Ac, (*cyclo*-Pr)CO, PhCO, 4-MeC_6H_4CO, 4-$MeOC_6H_4CO$, 4-ClC_6H_4CO, 4-BrC_6H_4CO, (1-naphthyl)CO; $A^- = MeSO_4^-$, ClO_4^-, FSO_3^-

Rearrangement of quaternary 6-aryl-2-methyl-3(5)-nitropyridinium salts was used for the synthesis of unsymmetrical nitrobiaryls. The starting nitropyridines were obtained by a three-component one-pot synthesis, two-step Hantzsch synthesis using nitro ketones, and by cyclocondensation of acylpyruvates with enamines derived from nitroacetone and nitroacetophenones.

Keywords: enamines, nitrobiaryls, quaternary pyridinium salts, substituted 3(5)-nitropyridines, Hantzsch synthesis, Kost–Sagitullin rearrangement, one-pot synthesis.

Biaryl motifs form the structural basis for biologically active natural compounds with axial chirality, alkaloids, pharmaceutical agents, monodentate ligands for palladium-catalyzed cross-coupling reactions, chiral bidentate ligands used in catalytic asymmetric synthesis.[1]

Biaryl moiety is also found in the structure of amaryllidaceae alkaloid ismine characterized by cytotoxic activity, natural peptide antibiotics biphenomycins A and B, arylomycins A_2 and B_2, known for their antibacterial activity. Micardis and Diovan (valsartan) are used as antihypertensive drugs. Boscalid is a new generation fungicide with low toxicity that also contains a biaryl group. Also, substituted biaryls with an antitumor activity have been synthesized.[2]

Biphenyl was first obtained by Gattermann in 1890 by treating a solution of benzenediazonium salt with ethanol and copper powder. The classic Ullmann and Gomberg–Bachmann–Hey reactions have only historical value in the original variants, while their more recent modifications have been used for the synthesis of symmetric and asymmetric biaryls. At the same time, the benzidine rearrangement also has maintained its importance as a method for the synthesis of biaryls.[3]

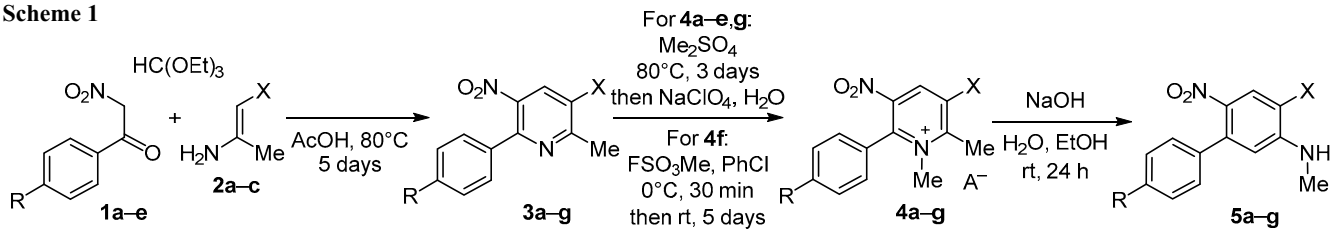
The most common methods for the synthesis of symmetric and asymmetric 2-nitrobiaryls are the Suzuki–Miyaura[4a–i] and Ullmann cross-coupling reactions;[4j–n] decarboxylative Pd-catalyzed cross coupling of *o*-nitrobenzoates with aryl halides (aryl triflates) has been also actively developed;[2g,4o–q] in addition, direct nitration reactions of 4,4'-dihalo- and 4,4'-dimethylbiphenyls have been used for the synthesis of 2-nitrobiaryls,[4r–t] as well as ammonolysis of 10-nitro-6*H*-benzo[*c*]chromen-6-ones has been performed.[4u]

2-Nitrobiaryls serve as starting materials for the synthesis of carbazoles, including natural products, by reductive Cadogan cyclization.[5]

In this work, we present a new method for the synthesis of nitrobiaryls by rearrangement of quaternary nitropyridinium salts (Kost–Sagitullin rearrangement).

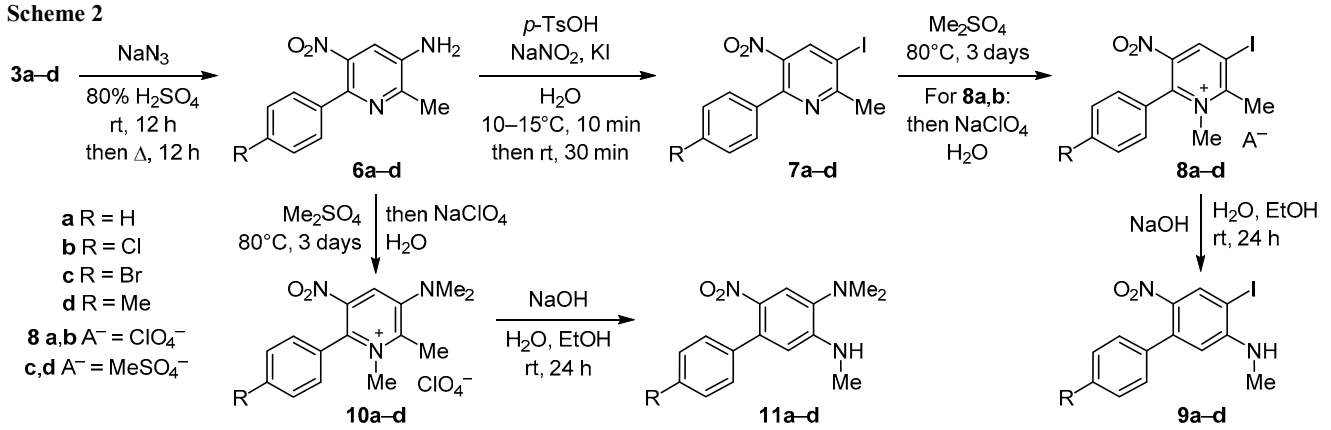
A three-stage synthesis of 2-nitrobiaryls **5a**–**g** is presented in Scheme 1. The starting nitropyridines **3a**–**g** were obtained by a three-component one-pot reaction, the temperature of which was selected depending on the reactivity of nitroacetophenones **1a**–**e** with respect to ethyl orthoformate and enamines **2a**–**c**. The synthesis of pyridines **3a**,**f**,**g** was described by us previously.[6] The quaternary nitropyridinium salts **4a**–**e**,**g** were obtained by heating nitropyridines **3a**–**e**,**g** with an excess of dimethyl sulfate, while the synthesis of pyridinium salt **4f** was effectively achieved by using methyl fluorosulfonate (also known as magic methyl). The rearrangement of pyridinium salt **4a**–**g** by the action of aqueous alcohol solution of sodium hydroxide was achieved at room temperature, with the formation of substituted 2-nitrobiaryls **5a**–**g**. The rearrangement of

Scheme 1



1 a R = H, **b** R = Cl, **c** R = Br, **d** R = Me, **e** R = OMe; **2 a** X = Ac, **b** X = (*cyclo*-Pr)CO, **c** X = COOEt
3–5 a R = H, X = Ac; **b** R = Cl, X = Ac; **c** R = Br, X = Ac; **d** R = Me, X = Ac; **e** R = OMe, X = Ac; **f** R = H, X = (*cyclo*-Pr)CO
3, 4 g R = H, X = COOEt; **5g** R = H, X = COOH; **4 a–e,g** A^- = ClO_4^-, **f** A^- = FSO_3^-

Scheme 2

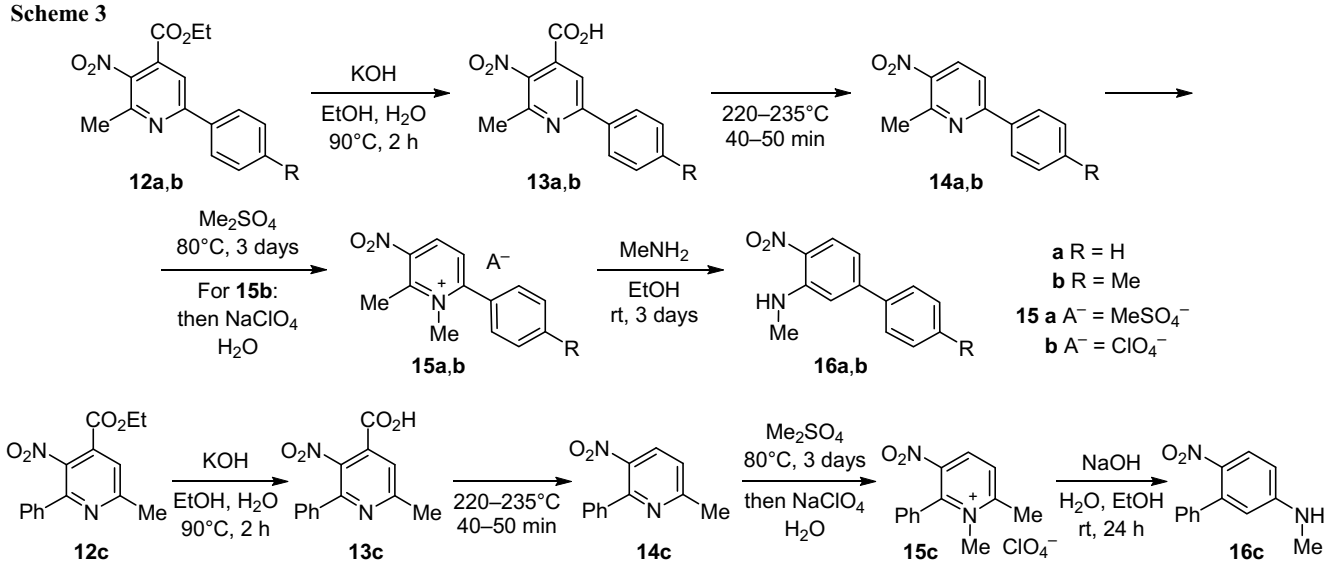


pyridinium salt **4g** (X = COOEt) to biaryl **5g** was accompanied by the hydrolysis of its ester moiety.

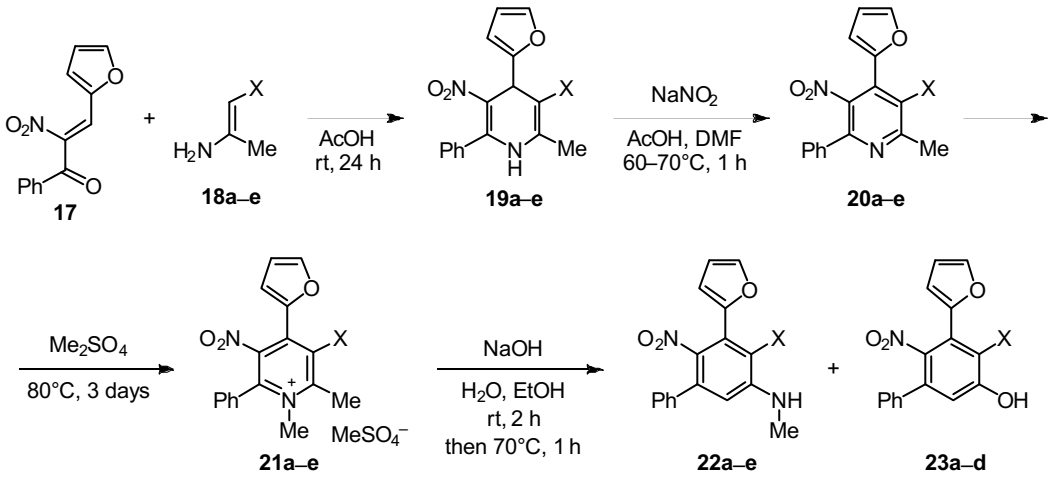
Functional group transformations were used for the synthesis of 3-amino- and 3-iodo-5-nitropyridines **6a**–**d** and **7a**–**d** (Scheme 2). Pyridines **3a**–**d** were transformed into aminopyridines **6a**–**d** by converting the acetyl group into amino group *via* a Schmidt reaction. Diazotation of aminopyridines **6a**–**d** followed by substitution of the diazonium ion with iodine according to known procedures provided 3-iodo-5-nitropyridines **7a**–**d**.[7] The alkylation of 3-amino-5-nitropyridines **6a**–**d** with dimethyl sulfate proceeded at the ring nitrogen and the exocyclic nitrogen atoms with the formation of 3-dimethylamino-5-nitropyridinium salts **10a**–**d**. The rearrangement of pyridinium salts **8a**–**d** and **10a**–**d** in the presence of aqueous alcohol solution of NaOH resulted in the formation of biaryls **9a**–**d** and **11a**–**d** in high yields.

Nitropyridines **12a**–**c** were synthesized by cyclocondensation of aroyl and acetyl pyruvates with enamines of nitroacetone and nitroacetophenone, respectively (Scheme 3).[8] The ester group of pyridine derivatives **12a**–**c** was removed by a hydrolysis reaction followed by a decarboxylation step. The optimum conditions for the rearrangement of pyridinium salts **15a**,**b** involved using an alcohol solution of methylamine as a base, and the yields of biphenyls **16a**,**b** were 50–52%. The rearrangement of salt **15c** under these conditions gave biaryl **16c** at an exceedingly low yield, while the use of an aqueous alcohol solution of NaOH allowed to increase the yield to 25%.

Scheme 3



Scheme 4



a X = 4-MeC_6H_4CO, **b** X = 4-$MeOC_6H_4CO$, **c** X = 4-ClC_6H_4CO, **d** X = 4-BrC_6H_4CO, **e** X = (1-naphthyl)CO

A two stage Hantzsch synthesis was employed for the preparation of 4-furyl-5-nitropyridines **20a**–**e**, starting from nitrochalcone **17** and enamines **18a**–**e**, followed by oxidation of dihydropyridines **19a**–**e** (Scheme 4). The rearrangement of pyridinium salts **21a**–**e** by the action of aqueous alcohol solution of NaOH led to two different biaryls **22a**–**e** and **23a**–**d** at the combined yield of 75–95%. 5-Methylamino-2-nitrobiphenyls **22** were the major products resulting from the rearrangement, while 5-hydroxy-2-nitrobiaryls **23** were present as minor products. Hydroxybiphenyls **23** were formed by aldol-crotonic condensation of the enamine hydrolysis product originating from the open form of pyridinium salt.[9]

Thus, we have developed a new method for the synthesis of nitrobiaryls *via* rearrangement of quaternary nitropyridinium salts. The most highly substituted quaternary pyridinium salts that contained four or five substituents in the pyridine ring gave high yields of the respective biaryls in these rearrangement reactions. This method provides an improved access to nitrobiaryls, which can be used as starting materials for the synthesis of carbazoles and indoles *via* the Cadogan and Bartolly reactions involving the nitro group.

Experimental

IR spectra were recorded on a Simex FT-801 spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance DRX-400 instrument (400 and 100 MHz, respectively) in DMSO-d_6 (compounds **4a**–**g**, **5g**, **8a**–**d**, **10a**–**d**, **13a**–**c**, **15a**–**c**, **21a**–**e**) and in $CDCl_3$ (the rest of the compounds). The solvent signals were used as internal standards (DMSO-d_6: 2.50 ppm for ^{1}H nuclei, 39.5 ppm for ^{13}C nuclei; $CDCl_3$: 7.26 ppm for ^{1}H nuclei, 77.0 ppm for ^{13}C nuclei). ^{13}C NMR spectra were acquired by using the *J*-modulation method. Elemental analysis was performed on a PerkinElmer 2400 Series II CHN elemental analyzer. Melting points were determined on a Boetius hot stage. The reaction progress and purity of the obtained compounds were controlled by a TLC method using Silufol UV-254 plates. Preparative chromatography was performed on Merck 60A silica gel with 0.060–0.200 mm particle size.

Nitroacetophenone (**1a**) was synthesized according to the Gavrilin method from commercially available styrene.[10a] Nitroacetophenones **1b**–**e** were synthesized by the Katritzky method from commercially available benzoic acids.[10b,c] Enamines **2a**–**c** were obtained according to procedures described in publications.[11] The α,β-unsaturated nitro ketone **17** was obtained by reaction of nitroacetophenone with furfural according to a published procedure.[12] Enamines **18a**–**e** were obtained according to procedures described in another publication.[13] Nitropyridines **3a**,**f**,**g** were previously prepared by our group.[6] 3-Nitroisonicotinic esters **12a**–**c** were described in our earlier work.[8]

Synthesis of 6-aryl-2-methyl-5-nitropyridines 3b–e (General method). A solution of nitroacetophenone **1b**–**e** (6 mmol), acetylacetone enamine **2a** (0.6 g, 6 mmol), and $HC(OEt)_3$ (2.7 g, 18 mmol) in AcOH (3 ml) was stirred for 5 days at 80°C. The excess of reactants was removed by distillation at reduced pressure, the residue was refluxed with activated carbon in EtOH (20 ml), and the crystals that precipitated after cooling were filtered off. The product was purified by column chromatography using PhH as eluent, followed by recrystallization from EtOH.

1-[6-(4-Chlorophenyl)-2-methyl-5-nitropyridin-3-yl]-ethanone (3b). Yield 47%, colorless crystals, mp 147–148°C. IR spectrum, ν, cm^{-1}: 1675 (C=O), 1510, 1365 (NO_2). ^{1}H NMR spectrum, δ, ppm: 2.67 (3H, s, 2-CH_3); 2.87 (3H, s, $COCH_3$); 7.42–7.47 (2H, m, H Ar); 7.50–7.55 (2H, m, H Ar); 8.46 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 25.2; 29.3; 129.1; 129.8; 130.9; 133.4; 134.1; 136.8; 143.3; 152.6; 162.0; 197.5. Found, %: C 57.82; H 3.86; N 9.72. $C_{14}H_{11}ClN_2O_3$. Calculated, %: C 57.84; H 3.81; N 9.64.

1-[6-(4-Bromophenyl)-2-methyl-5-nitropyridin-3-yl]-ethanone (3c). Yield 48%, colorless crystals, mp 148–149°C. IR spectrum, ν, cm^{-1}: 1670 (C=O), 1515, 1367 (NO_2). ^{1}H NMR spectrum, δ, ppm: 2.67 (3H, s, 2-CH_3); 2.87 (3H, s, $COCH_3$); 7.43–7.48 (2H, m, H Ar); 7.58–7.62 (2H, m, H Ar); 8.45 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 25.2; 29.3; 125.1; 129.9; 130.9; 132.0; 133.3; 134.6; 143.2; 152.7; 162.0; 197.4. Found, %: C 50.22; H 3.33; N 8.41. $C_{14}H_{11}BrN_2O_3$. Calculated, %: C 50.17; H 3.31; N 8.36.

1-[2-Methyl-6-(4-methylphenyl)-5-nitropyridin-3-yl]-ethanone (3d). Yield 48%, colorless crystals, mp 98–99°C. IR spectrum, ν, cm^{-1}: 1688 (C=O), 1552, 1347 (NO_2). ^1H NMR spectrum, δ, ppm: 2.40 (3H, s, ArC<u>H</u>$_3$); 2.66 (3H, s, 2-CH_3); 2.87 (3H, s, $COCH_3$); 7.25–7.29 (2H, m, H Ar); 7.47–7.52 (2H, m, H Ar); 8.42 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 21.2; 25.2; 29.3; 128.1; 129.1; 130.9; 133.3; 135.2; 137.6; 143.3; 152.7; 161.9; 197.5. Found, %: C 66.70; H 5.28; N 10.37. $C_{15}H_{14}N_2O_3$. Calculated, %: C 66.66; H 5.22; N 10.36.

1-[6-(4-Methoxyphenyl)-2-methyl-5-nitropyridin-3-yl]-ethanone (3e). Yield 26%, colorless crystals, mp 101–102°C. IR spectrum, ν, cm^{-1}: 1674 (C=O), 1530, 1377 (NO_2). ^1H NMR spectrum, δ, ppm: 2.64 (3H, s, 2-CH_3); 2.86 (3H, s, $COCH_3$); 3.85 (3H, s, OCH_3); 6.94–6.99 (2H, m, H Ar); 7.55–7.60 (2H, m, H Ar); 8.39 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 25.3; 29.1; 55.4; 114.3; 121.6; 127.8; 129.8; 130.2; 133.4; 143.0; 153.1; 161.6; 197.5. Found, %: C 62.95; H 5.00; N 9.82. $C_{15}H_{14}N_2O_4$. Calculated, %: C 62.93; H 4.93; N 9.78.

Synthesis of 3-amino-6-aryl-2-methyl-5-nitropyridines 6a–d (General method). A mixture of 3-acetylpyridine **3a**–**d** (6 mmol) and 80% H_2SO_4 (3 ml) was stirred and treated by portionwise addition of NaN_3 (0.43 g, 6.6 mmol). After adding the entire amount of NaN_3, the reaction mixture was stirred at room temperature for 12 h, then ice (12 g) was added and the mixture was refluxed for 12 h, cooled, and neutralized with aqueous ammonia. The precipitate that formed was filtered off and recrystallized from CCl_4.

2-Methyl-5-nitro-6-phenylpyridin-3-amine (6a). Yield 91%, yellow crystals, mp 95–96°C (mp 95–96°C (heptane)[14]).

6-(4-Chlorophenyl)-2-methyl-5-nitropyridin-3-amine (6b). Yield 90%, yellowish-orange crystals, mp 165–166°C. IR spectrum, ν, cm^{-1}: 3505, 3410 (NH_2), 1530, 1360 (NO_2). ^1H NMR spectrum, δ, ppm: 2.49 (3H, s, 2-CH_3); 3.98 (2H, br. s, NH_2); 7.33–7.43 (5H, m, H-4, H Ar). ^{13}C NMR spectrum, δ, ppm: 20.6; 115.7; 128.7; 129.5; 134.7; 135.6; 140.0; 140.5; 144.5; 147.5. Found, %: C 54.70; H 3.86; N 15.99. $C_{12}H_{10}ClN_3O_2$. Calculated, %: C 54.66; H 3.82; N 15.94.

6-(4-Bromophenyl)-2-methyl-5-nitropyridin-3-amine (6c). Yield 90%, yellowish-orange crystals, mp 167–168°C. IR spectrum, ν, cm^{-1}: 3490, 3390 (NH_2), 1535, 1360 (NO_2). ^1H NMR spectrum, δ, ppm: 2.50 (3H, s, 2-CH_3); 3.98 (2H, br. s, NH_2); 7.31–7.36 (2H, m, H Ar); 7.37 (1H, s, H-4); 7.50–7.55 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 20.6; 115.8; 123.0; 129.8; 131.6; 136.1; 140.0; 140.7; 144.6; 147.5. Found, %: C 46.82; H 3.29; N 13.68. $C_{12}H_{10}BrN_3O_2$. Calculated, %: C 46.78; H 3.27; N 13.64.

2-Methyl-6-(4-methylphenyl)-5-nitropyridin-3-amine (6d). Yield 82%, yellowish-orange crystals, mp 120–121°C. IR spectrum, ν, cm^{-1}: 3510, 3420 (NH_2), 1540, 1360 (NO_2). ^1H NMR spectrum, δ, ppm: 2.37 (3H, s, 4'-CH_3); 2.48 (3H, s, 2-CH_3); 3.91 (2H, br. s, NH_2); 7.18–7.23 (2H, m, H Ar); 7.30 (1H, s, H-4); 7.34–7.39 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 20.6; 21.2; 115.7; 127.9; 129.2; 134.1; 138.5; 139.5; 141.8; 144.6; 147.3. Found, %: C 64.22; H 5.42; N 17.31. $C_{13}H_{13}N_3O_2$. Calculated, %: C 64.19; H 5.39; N 17.27.

Synthesis of 6-aryl-3-iodo-2-methyl-5-nitropyridines 7a–d (General method). A mixture of *p*-TsOH·H_2O (1.17 g, 9.0 mmol) in MeCN (12 ml) was treated by the addition of 3-aminopyridine **6a**–**d** (3.0 mmol). The obtained suspension was cooled to 10–15°C and treated by gradually adding a solution of $NaNO_2$ (0.41 g, 6.0 mmol) and KI (1.25 g, 7.5 mmol) in H_2O (1.8 ml). The reaction mixture was stirred with cooling for 10 min, then stirred for 30 min at room temperature, and quenched by pouring into H_2O (50 ml). The mixture was treated by adding 1 M solution of $NaHCO_3$ to pH 9–10 and 2 M solution of $Na_2S_2O_3$ (6 ml). The precipitate that formed was filtered off and recrystallized from petroleum ether (fraction with bp 70–100°C).

3-Iodo-2-methyl-5-nitro-6-phenylpyridine (7a). Yield 93%, colorless crystals, mp 61–62°C. IR spectrum, ν, cm^{-1}: 1535, 1330 (NO_2). ^1H NMR spectrum, δ, ppm: 2.86 (3H, s, 2-CH_3); 7.42–7.48 (3H, m, H Ph); 7.50–7.55 (2H, m, H Ph); 8.48 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 29.0; 92.3; 128.1; 128.7; 129.9; 135.8; 141.7; 143.4; 151.5; 164.2. Found, %: C 42.42; H 2.70; N 8.26. $C_{12}H_{19}IN_2O_2$. Calculated, %: C 42.38; H 2.67; N 8.24.

6-(4-Chlorophenyl)-3-iodo-2-methyl-5-nitropyridine (7b). Yield 92%, colorless crystals, mp 129–130°C. IR spectrum, ν, cm^{-1}: 1530, 1335 (NO_2). ^1H NMR spectrum, δ, ppm: 2.85 (3H, s, 2-CH_3); 7.40–7.43 (2H, m, H Ar); 7.45–7.48 (2H, m, H Ar); 8.49 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 29.0; 92.7; 129.0; 129.5; 134.3; 136.2; 141.9; 143.2; 150.3; 164.5. Found, %: C 38.52; H 2.17; N 7.52. $C_{12}H_8ClIN_2O_2$. Calculated, %: C 38.48; H 2.15; N 7.48.

6-(4-Bromophenyl)-3-iodo-2-methyl-5-nitropyridine (7c). Yield 95%, colorless crystals, mp 129–130°C. IR spectrum, ν, cm^{-1}: 1540, 1340 (NO_2). ^1H NMR spectrum, δ, ppm: 2.85 (3H, s, 2-CH_3); 7.37–7.41 (2H, m, H Ar); 7.55–7.60 (2H, m, H Ar); 8.49 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 29.0; 92.8; 124.5; 129.7; 131.9; 134.7; 141.9; 143.1; 150.4; 164.5. Found, %: C 34.43; H 1.92; N 6.72. $C_{12}H_8BrIN_2O_2$. Calculated, %: C 34.40; H 1.92; N 6.69.

3-Iodo-2-methyl-6-(4-methylphenyl)-5-nitropyridine (7d). Yield 93%, light-yellow crystals, mp 105–106°C. IR spectrum, ν, cm^{-1}: 1540, 1325 (NO_2). ^1H NMR spectrum, δ, ppm: 2.39 (3H, s, 4'-CH_3); 2.84 (3H, s, 2-CH_3); 7.22–7.27 (2H, m, H Ar); 7.40–7.45 (2H, m, H Ar); 8.44 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 21.4; 29.0; 91.8; 128.0; 129.5; 132.9; 140.2; 141.6; 143.4; 151.4; 164.0. Found, %: C 44.11; H 3.15; N 7.95. $C_{13}H_{11}IN_2O_2$. Calculated, %: C 44.09; H 3.13; N 7.91.

Synthesis of 3-nitroisonicotinic acids 13a–c (General method). The appropriate ethyl isonicotinate **12a**–**c** (4 mmol) was added to a solution of KOH (1.12 g, 20 mmol) in EtOH (10 ml) and H_2O (2 ml). The mixture was heated at 90°C for 2 h. The reaction mixture was then cooled and acidified with 10% HCl solution to pH 2–3, the crystals that precipitated were filtered off and recrystallized from 50% AcOH.

2-Methyl-3-nitro-6-phenylisonicotinic acid (13a). Yield 70%, colorless crystals, mp 202–203°C. IR spectrum, ν, cm^{-1}: 3000–2500 (OH), 1708 (C=O), 1535, 1370 (NO_2). ^1H NMR spectrum, δ, ppm: 2.60 (3H, s, 2-CH_3); 7.50–7.55

(3H, m, H Ph); 8.12–8.17 (2H, m, H Ph); 8.20 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 20.6; 117.9; 127.3; 129.0; 130.6; 134.6; 136.2; 143.3; 150.6; 158.0; 164.0. Found, %: C 60.50; H 3.95; N 10.90. $C_{13}H_{10}N_2O_4$. Calculated, %: C 60.47; H 3.90; N 10.85.

2-Methyl-6-(4-methylphenyl)-3-nitroisonicotinic acid (13b). Yield 75%, colorless crystals, mp 196–197°C. IR spectrum, ν, cm^{-1}: 3000–2500 (OH), 1715 (C=O), 1540, 1370 (NO_2). ^{1}H NMR spectrum, δ, ppm: 2.36 (3H, s, 4'-CH_3); 2.58 (3H, s, 2-CH_3); 7.29–7.35 (2H, m, H Ar); 8.01–8.06 (2H, m, H Ar); 8.14 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 20.6; 20.9; 117.4; 127.2; 129.6; 133.5; 135.0; 140.5; 143.1; 150.4; 157.9; 164.1. Found, %: C 61.80; H 4.48; N 10.26. $C_{14}H_{12}N_2O_4$. Calculated, %: C 61.76; H 4.44; N 10.29.

6-Methyl-3-nitro-2-phenylisonicotinic acid (13c). Yield 80%, colorless crystals, mp 212–213°C. IR spectrum, ν, cm^{-1}: 3000–2500 (OH), 1720 (C=O), 1544, 1365 (NO_2). ^{1}H NMR spectrum, δ, ppm: 2.65 (3H, s, 6-CH_3); 7.46–7.53 (5H, m, H Ph); 7.80 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 24.1; 122.2; 127.8; 128.7; 129.8; 133.5; 135.2; 142.3; 150.0; 161.8; 163.9. Found, %: C 60.52; H 3.97; N 10.87. $C_{13}H_{10}N_2O_4$. Calculated, %: C 60.47; H 3.90; N 10.85.

Synthesis of 2(6)-aryl-6(2)-methyl-3-nitropyridines 14a–c (General method). The appropriate isonicotinic acid **13a**–**c** (2.5 mmol) was stirred without solvent and heated at 220–235°C in a thick-walled test tube under a continuous nitrogen stream for 40–50 min. The reaction mixture was cooled and the solid residue was dissolved in benzene, purified by column chromatography (eluent PhH), and recrystallized from petroleum ether (fraction with bp 40–70°C).

2-Methyl-3-nitro-6-phenylpyridine (14a). Yield 55%, colorless crystals, mp 123–124°C. IR spectrum, ν, cm^{-1}: 1565, 1340 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.95 (3H, s, 2-CH_3); 7.47–7.55 (3H, m, H Ph); 7.73 (1H, d, *J* = 8.5, H-5); 8.05–8.11 (2H, m, H Ph); 8.37 (1H, d, *J* = 8.5, H-4). ^{13}C NMR spectrum, δ, ppm: 24.5; 118.1; 127.6; 129.0; 130.5; 133.6; 137.2; 144.1; 154.0; 160.2. Found, %: C 67.32; H 4.75; N 13.12. $C_{12}H_{10}N_2O_2$. Calculated, %: C 67.28; H 4.71; N 13.08.

2-Methyl-6-(4-methylphenyl)-3-nitropyridine (14b). Yield 60%, colorless crystals, mp 126–127°C. IR spectrum, ν, cm^{-1}: 1560, 1330 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.42 (3H, s, 4'-CH_3); 2.94 (3H, s, 2-CH_3); 7.27–7.34 (2H, m, H Ar); 7.69 (1H, d, *J* = 8.5, H-5); 7.94–8.01 (2H, m, H Ar); 8.34 (1H, d, *J* = 8.5, H-4). ^{13}C NMR spectrum, δ, ppm: 21.3; 24.6; 117.7; 127.5; 129.7; 133.5; 134.5; 140.9; 143.8; 153.9; 160.2. Found, %: C 68.45; H 5.34; N 12.31. $C_{13}H_{12}N_2O_2$. Calculated, %: C 68.41; H 5.30; N 12.27.

6-Methyl-3-nitro-2-phenylpyridine (14c). Yield 69%, colorless crystals, mp 60–61°C. IR spectrum, ν, cm^{-1}: 1565, 1345 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.70 (3H, s, 6-CH_3); 7.26 (1H, d, *J* = 8.5, H-5); 7.43–7.48 (3H, m, H Ph); 7.51–7.57 (2H, m, H Ph); 8.06 (1H, d, *J* = 8.5, H-4). ^{13}C NMR spectrum, δ, ppm: 24.8; 121.9; 128.1; 128.6; 129.5; 132.5; 136.7; 144.2; 152.5; 162.1. Found, %: C 67.30; H 4.72; N 13.10. $C_{12}H_{10}N_2O_2$. Calculated, %: C 67.28; H 4.71; N 13.08.

Synthesis of 3-acyl-4-(furan-2-yl)-2-methyl-5-nitro-6-phenyl-1,4-dihydropyridines 19a–e (General method). A solution of 3-(furan-2-yl)-2-nitro-1-phenylprop-2-en-1-one (**17**) (4.86 g, 20 mmol) and enamine **18a**–**e** (20 mmol) in AcOH (15 ml) was stirred at room temperature for 24 h. The crystals that precipitated were filtered off and recrystallized from EtOH.

[4-(Furan-2-yl)-2-methyl-5-nitro-6-phenyl-1,4-dihydropyridin-3-yl](4-methylphenyl)methanone (19a). Yield 60%, yellowish-orange crystals, mp 205–206°C. IR spectrum, ν, cm^{-1}: 3255 (NH), 1636 (C=O), 1500, 1360 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.89 (3H, s, 2-CH_3); 2.40 (3H, s, 4'-CH_3); 5.73 (1H, s, 4-CH); 6.03 (1H, br. s, NH); 6.09 (1H, d, *J* = 2.9, H-3 Fur); 6.24 (1H, dd, *J* = 2.9, *J* = 1.8, H-4 Fur); 7.20–7.25 (2H, m, H Ar); 7.29 (1H, d, *J* = 1.8, H-5 Fur); 7.40–7.52 (5H, m, H Ph); 7.56–7.61 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 18.1; 21.6; 37.3; 106.0; 110.5; 114.3; 122.1; 127.5; 128.8; 129.0; 129.4; 130.2; 134.4; 136.0; 136.3; 141.9; 143.5; 146.3; 154.6; 196.5. Found, %: C 72.03; H 5.05; N 7.08. $C_{24}H_{20}N_2O_4$. Calculated, %: C 71.99; H 5.03; N 7.00.

[4-(Furan-2-yl)-2-methyl-5-nitro-6-phenyl-1,4-dihydropyridin-3-yl](4-methoxyphenyl)methanone (19b). Yield 62%, yellowish-orange crystals, mp 208–209°C. IR spectrum, ν, cm^{-1}: 3256 (NH), 1639 (C=O), 1500, 1355 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.87 (3H, s, 2-CH_3); 3.85 (3H, s, OCH_3); 5.71 (1H, s, 4-CH); 5.96 (1H, br. s, NH); 6.09 (1H, d, *J* = 3.2, H-3 Fur); 6.23 (1H, dd, *J* = 3.2, *J* = 1.5, H-4 Fur); 6.87–6.92 (2H, m, H Ar); 7.28 (1H, d, *J* = 1.5, H-5 Fur); 7.39–7.50 (5H, m, H Ph); 7.66–7.71 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 17.9; 37.5; 55.5; 106.1; 110.6; 114.0; 114.5; 121.9; 127.5; 129.0; 130.2; 131.1; 131.2; 134.5; 135.1; 141.9; 146.5; 154.6; 163.5; 195.4. Found, %: C 69.25; H 4.86; N 6.72. $C_{24}H_{20}N_2O_5$. Calculated, %: C 69.22; H 4.84; N 6.73.

(4-Chlorophenyl)[4-(furan-2-yl)-2-methyl-5-nitro-6-phenyl-1,4-dihydropyridin-3-yl]methanone (19c). Yield 61%, yellowish orange crystals, mp 198–199°C. IR spectrum, ν, cm^{-1}: 3200 (NH), 1642 (C=O), 1485, 1323 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.92 (3H, s, 2-CH_3); 5.71 (1H, s, 4-CH); 5.97 (1H, br. s, NH); 6.09 (1H, d, *J* = 3.3, H-3 Fur); 6.26 (1H, dd, *J* = 3.3, *J* = 1.8, H-4 Fur); 7.29 (1H, d, *J* = 1.8, H-5 Fur); 7.39–7.44 (2H, m, H Ar); 7.46–7.52 (5H, m, H Ph); 7.59–7.63 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 18.3; 37.4; 106.0; 110.6; 114.4; 122.6; 127.9; 128.0; 128.5; 130.0; 131.0; 134.5; 135.9; 136.3; 141.9; 143.0; 145.4; 154.6; 194.7. Found, %: C 65.68; H 4.09; N 6.70. $C_{23}H_{17}ClN_2O_4$. Calculated, %: C 65.64; H 4.07; N 6.66.

(4-Bromophenyl)[4-(furan-2-yl)-2-methyl-5-nitro-6-phenyl)-1,4-dihydropyridin-3-yl]methanone (19d). Yield 65%, yellowish-orange crystals, mp 206–207°C. IR spectrum, ν, cm^{-1}: 3288 (NH), 1640 (C=O), 1493, 1320 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.92 (3H, s, 2-CH_3); 5.71 (1H, s, 4-CH); 5.95 (1H, br. s, NH); 6.09 (1H, d, *J* = 3.1, H-3 Fur); 6.25 (1H, dd, *J* = 3.1, *J* = 1.9, H-4 Fur); 7.29 (1H, d, *J* = 1.9, H-5 Fur); 7.39–7.44 (2H, m, H Ar); 7.46–7.63 (7H, m, H Ar, H Ph). ^{13}C NMR spectrum, δ, ppm:

18.3; 37.4; 106.1; 110.6; 114.9; 122.6; 127.9; 128.1; 128.5; 130.1; 131.0; 134.5; 135.8; 136.4; 141.9; 143.0; 145.5; 154.6; 194.7. Found, %: C 59.40; H 3.71; N 6.07. $C_{23}H_{17}BrN_2O_4$. Calculated, %: C 59.37; H 3.68; N 6.02.

[4-(Furan-2-yl)-2-methyl-5-nitro-6-phenyl-1,4-dihydropyridin-3-yl](1-naphthyl)methanone (19e). Yield 45%, yellowish-orange crystals, mp 207–208°C. IR spectrum, ν, cm^{-1}: 3298 (NH), 1626 (C=O), 1478, 1315 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.78 (3H, s, 2-CH_3); 5.84 (1H, s, 4-CH); 6.09 (1H, d, *J* = 2.8, H-3 Fur); 6.13 (1H, br. s, NH); 6.26–6.28 (1H, m, H-4 Fur); 7.29–7.31 (1H, m, H-5 Fur); 7.37–7.53 (9H, m, H Ar, H Ph); 7.86–7.99 (3H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 18.0; 37.4; 106.0; 110.3; 114.4; 124.3; 127.0; 128.2; 128.9; 129.2; 130.1; 132.4; 134.0; 134.6; 135.7; 141.8; 143.0; 146.0; 154.8; 196.5. Found, %: C 74.33; H 4.66; N 6.49. $C_{27}H_{20}N_2O_4$. Calculated, %: C 74.30; H 4.62; N 6.42.

Synthesis of 3-acyl-4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridines 20a–e (General method). A mixture of the appropriate dihydropyridine **19a**–**e** (10 mmol) and DMF (8 ml) was heated to 60–70°C and treated by the addition of glacial AcOH (8 ml); then $NaNO_2$ (2.07 g, 30 mmol) was added in small portions to the stirred mixture. After the addition of $NaNO_2$ was complete, the reaction mixture was stirred for an additional 1 h at the same temperature, then cooled to room temperature, diluted 4-fold with water, the crystals that precipitated were filtered off and recrystallized from EtOH.

[4-(Furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl]-(4-methylphenyl)methanone (20a). Yield 81%, colorless crystals, mp 127–128°C. IR spectrum, ν, cm^{-1}: 1665 (C=O), 1530, 1350 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.40 (3H, s, 4'-CH_3); 2.51 (3H, s, 2-CH_3); 6.30 (1H, dd, *J* = 3.5, *J* = 1.8, H-4 Fur); 6.61 (1H, dd, *J* = 3.5, *J* = 0.6, H-3 Fur); 7.24–7.25 (2H, m, H Ar); 7.30 (1H, dd, *J* = 1.8, *J* = 0.6, H-5 Fur); 7.46–7.50 (3H, m, H Ph); 7.62–7.66 (2H, m, H Ph); 7.66–7.70 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 21.8; 23.3; 112.3; 114.7; 128.1; 128.8; 129.0; 129.3; 129.7; 130.0; 131.4; 133.6; 135.4; 142.0; 143.4; 145.2; 145.5; 150.8; 157.0; 194.8. Found, %: C 72.38; H 4.58; N 7.09. $C_{24}H_{18}N_2O_4$. Calculated, %: C 72.35; H 4.55; N 7.03.

[4-(Furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl]-(4-methoxyphenyl)methanone (20b). Yield 90%, colorless crystals, mp 149–150°C. IR spectrum, ν, cm^{-1}: 1667 (C=O), 1536, 1340 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.51 (3H, s, 2-CH_3); 3.85 (3H, s, OCH_3); 6.31 (1H, dd, *J* = 3.4, *J* = 1.7, H-4 Fur); 6.61 (1H, dd, *J* = 3.4, *J* = 0.6, H-3 Fur); 6.88–6.92 (2H, m, H Ar); 7.32 (1H, dd, *J* = 1.7, *J* = 0.6, H-5 Fur); 7.45–7.50 (3H, m, H Ph); 7.61–7.66 (2H, m, H Ph); 7.73–7.78 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 23.2; 55.6; 112.2; 114.3; 114.7; 128.1; 128.8; 129.0; 129.1; 130.0; 131.5; 131.7; 135.4; 142.1; 143.5; 145.2; 150.7; 157.0; 164.5; 193.6. Found, %: C 69.59; H 4.40; N 6.80. $C_{24}H_{18}N_2O_5$. Calculated, %: C 69.56; H 4.38; N 6.76.

(4-Chlorophenyl)[4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl]methanone (20c). Yield 80%, colorless crystals, mp 132–133°C. IR spectrum, ν, cm^{-1}: 1663 (C=O), 1530, 1342 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.51 (3H, s, 2-CH_3); 6.32 (1H, dd, *J* = 3.5, *J* = 1.8, H-4 Fur); 6.61 (1H, dd, *J* = 3.5, *J* = 0.7, H-3 Fur); 7.30 (1H, dd, *J* = 1.8, *J* = 0.7, H-5 Fur); 7.38–7.43 (2H, m, H Ar); 7.46–7.51 (3H, m, H Ph); 7.62–7.67 (2H, m, H Ph); 7.69–7.74 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 23.3; 112.5; 114.9; 128.1; 128.9; 129.1; 129.4; 130.2; 130.4; 131.6; 134.4; 135.3; 140.8; 142.0; 143.2; 145.3; 151.1; 157.0; 193.9. Found, %: C 66.00; H 3.65; N 6.73. $C_{23}H_{15}ClN_2O_4$. Calculated, %: C 65.96; H 3.61; N 6.69.

(4-Bromophenyl)[4-(furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl]methanone (20d). Yield 84%, colorless crystals, mp 120–121°C. IR spectrum, ν, cm^{-1}: 1664 (C=O), 1536, 1353 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.51 (3H, s, 2-CH_3); 6.32 (1H, dd, *J* = 3.6, *J* = 1.9, H-4 Fur); 6.62 (1H, dd, *J* = 3.6, *J* = 0.5, H-3 Fur); 7.30 (1H, dd, *J* = 1.9, *J* = 0.5, H-5 Fur); 7.46–7.50 (3H, m, H Ph); 7.56–7.60 (2H, m, H Ar); 7.62–7.67 (4H, m, H Ar, H Ph). ^{13}C NMR spectrum, δ, ppm: 23.3; 112.5; 114.9; 128.1; 128.9; 129.1; 129.7; 130.2; 130.5; 132.4; 134.8; 135.3; 142.0; 143.2; 145.3; 151.1; 157.0; 194.1. Found, %: C 59.66; H 3.30; N 6.09. $C_{23}H_{15}BrN_2O_4$. Calculated, %: C 59.63; H 3.26; N 6.05.

[4-(Furan-2-yl)-2-methyl-5-nitro-6-phenylpyridin-3-yl]-(1-naphthyl)methanone (20e). Yield 78%, colorless crystals, mp 186–187°C. IR spectrum, ν, cm^{-1}: 1660 (C=O), 1530, 1350 (NO_2). ^1H NMR spectrum, δ, ppm: 2.61 (3H, s, 2-CH_3); 6.09–6.18 (1H, m, H-4 Fur); 6.56–6.64 (1H, m, H-3 Fur); 7.05–7.12 (1H, m, H Ar); 7.34–7.42 (1H, m, H-5 Fur); 7.44–7.55 (3H, m, H Ph); 7.57–7.79 (5H, m, H Ar, H Ph); 7.87–7.96 (1H, m, H Ar); 7.97–8.06 (1H, m, H Ar); 9.19–9.27 (1H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 23.4; 112.1; 114.3; 124.3; 125.8; 126.9; 128.1; 128.7; 128.9; 129.1; 130.1; 130.7; 132.3; 132.4; 132.7; 134.1; 134.6; 135.1; 135.4; 142.3; 143.5; 145.5; 150.7; 157.5; 196.6. Found, %: C 74.69; H 4.20; N 6.51. $C_{27}H_{18}N_2O_4$. Calculated, %: C 74.64; H 4.18; N 6.45.

Preparation of quaternary pyridinium salts 4a–e,g, 8a–d, 10a–d, 15a–c, 21a–e (General method). A mixture of the appropriate pyridine **3a**–**e**,**g**, **7a**–**d**, **14a**–**c** or **20a**–**e** (5 mmol) and Me_2SO_4 (1.90 g, 15 mmol) (4.40 g, 35 mmol of Me_2SO_4 was used for 5 mmol of aminopyridine **6a**–**d**) was heated at 80°C for 3 days. The mixture was cooled, washed with anhydrous Et_2O (3×10 ml), and the ether layer was decanted. In the case when the methylsulfate salt failed to crystallize the residue was dissolved in H_2O (5 ml) and treated by the addition of saturated aqueous $NaClO_4$ solution (0.64 g, 5.3 mmol). The pyridinium salts were filtered off, dried, and recrystallized from EtOH.

3-Acetyl-1,2-dimethyl-5-nitro-6-phenylpyridinium perchlorate (4a). Yield 74%, colorless crystals, mp 204–205°C. ^1H NMR spectrum, δ, ppm: 2.77 (3H, s, $COCH_3$); 2.91 (3H, s, 2-CH_3); 3.90 (3H, s, NCH_3); 7.55–7.60 (3H, m, H Ph); 7.66–7.72 (2H, m, H Ph); 9.50 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 19.8; 30.6; 44.8; 127.9; 128.3; 129.5; 131.9; 137.4; 138.5; 146.5; 151.4; 160.0; 197.8. Found, %: C 48.62; H 4.10; N 7.60. $C_{15}H_{15}ClN_2O_7$. Calculated, %: C 48.60; H 4.08; N 7.56.

3-Acetyl-6-(4-chlorophenyl)-1,2-dimethyl-5-nitropyridinium perchlorate (4b). Yield 86%, colorless crystals,

mp 214–215°C. ^{1}H NMR spectrum, δ, ppm: 2.76 (3H, s, $COCH_3$); 2.91 (3H, s, 2-CH_3); 3.90 (3H, s, NCH_3); 7.59–7.64 (2H, m, H Ar); 7.76–7.81 (2H, m, H Ar); 9.50 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 19.8; 30.6; 44.9; 126.7; 129.8; 130.3; 137.0; 137.5; 138.8; 146.4; 150.6; 160.1; 197.7. Found, %: C 44.48; H 3.51; N 6.95. $C_{15}H_{14}Cl_2N_2O_7$. Calculated, %: C 44.46; H 3.48; N 6.91.

3-Acetyl-6-(4-bromophenyl)-1,2-dimethyl-5-nitropyridinium perchlorate (4c). Yield 87%, colorless crystals, mp 226–227°C. ^{1}H NMR spectrum, δ, ppm: 2.76 (3H, s, $COCH_3$); 2.91 (3H, s, 2-CH_3); 3.90 (3H, s, NCH_3); 7.51–7.58 (2H, m, H Ar); 7.89–7.97 (2H, m, H Ar); 9.50 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 19.8; 30.6; 44.9; 125.9; 127.2; 130.5; 132.7; 137.6; 138.8; 146.3; 150.6; 160.1; 197.8. Found, %: C 40.11; H 3.15; N 6.25. $C_{15}H_{14}BrClN_2O_7$. Calculated, %: C 40.07; H 3.14; N 6.23.

3-Acetyl-1,2-dimethyl-6-(4-methylphenyl)-5-nitropyridinium perchlorate (4d). Yield 78%, colorless crystals, mp 194–195°C. ^{1}H NMR spectrum, δ, ppm: 2.43 (3H, s, 4'-CH_3); 2.76 (3H, s, $COCH_3$); 2.90 (3H, s, 2-CH_3); 3.90 (3H, s, NCH_3); 7.44–7.47 (2H, m, H Ar); 7.48–7.51 (2H, m, H Ar); 9.47 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 19.7; 21.0; 30.5; 44.7; 124.9; 128.2; 130.1; 137.2; 138.4; 142.1; 146.6; 151.6; 159.9; 197.7. Found, %: C 49.98; H 4.47; N 7.32. $C_{16}H_{17}ClN_2O_7$. Calculated, %: C 49.95; H 4.45; N 7.28.

3-Acetyl-1,2-dimethyl-6-(4-methoxyphenyl)-5-nitropyridinium perchlorate (4e). Yield 73%, colorless crystals, mp 199–200°C. ^{1}H NMR spectrum, δ, ppm: 2.75 (3H, s, $COCH_3$); 2.89 (3H, s, 2-CH_3); 3.87 (3H, s, OCH_3); 3.92 (3H, s, NCH_3); 7.21–7.26 (2H, m, H Ar); 7.48–7.52 (2H, m, H Ar); 9.45 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 19.8; 30.5; 44.6; 55.5; 115.0; 119.4; 130.2; 137.0; 138.1; 146.8; 151.5; 159.7; 161.7; 197.7. Found, %: C 47.98; H 4.30; N 7.03. $C_{16}H_{17}ClN_2O_8$. Calculated, %: C 47.95; H 4.28; N 6.99.

3-(Ethoxycarbonyl)-1,2-dimethyl-5-nitro-6-phenylpyridinium perchlorate (4g). Yield 87%, colorless crystals, mp 213–214°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.38 (3H, t, *J* = 7.3, $OCH_2C\underline{H}_3$); 3.05 (3H, s, 2-CH_3); 3.91 (3H, s, NCH_3); 4.48 (3H, q, *J* = 7.3, $OC\underline{H}_2CH_3$); 7.54–7.60 (2H, m, H Ph); 7.65–7.72 (3H, m, H Ph); 9.47 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 13.8; 19.9; 45.0; 63.5; 127.9; 128.2; 129.6; 131.5; 132.0; 139.0; 146.5; 152.5; 161.5; 162.5. Found, %: C 47.97; H 4.29; N 7.01. $C_{16}H_{17}ClN_2O_8$. Calculated, %: C 47.95; H 4.28; N 6.99.

3-Iodo-1,2-dimethyl-5-nitro-6-phenylpyridinium perchlorate (8a). Yield 85%, colorless crystals, mp 275–276°C. ^{1}H NMR spectrum, δ, ppm: 3.14 (3H, s, 2-CH_3); 3.93 (3H, s, NCH_3); 7.51–7.56 (2H, m, H Ph); 7.63–7.73 (3H, m, H Ph); 9.64 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 27.2; 46.3; 100.9; 127.9; 128.3; 129.5; 131.9; 146.3; 147.4; 149.7; 162.8. Found, %: C 34.38; H 2.70; N 6.20. $C_{13}H_{12}ClIN_2O_6$. Calculated, %: C 34.35; H 2.66; N 6.16.

6-(4-Chlorophenyl)-3-iodo-1,2-dimethyl-5-nitropyridinium perchlorate (8b). Yield 86%, colorless crystals, mp 252–253°C. ^{1}H NMR spectrum, δ, ppm: 3.15 (3H, s, 2-CH_3); 3.93 (3H, s, NCH_3); 7.54–7.60 (2H, m, H Ar); 7.74–7.80 (2H, m, H Ar); 9.64 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 27.2; 46.5; 101.3; 126.8; 129.8; 130.3; 136.9; 146.1; 147.6; 148.9; 163.0. Found, %: C 31.96; H 2.30; N 5.77. $C_{13}H_{11}Cl_2IN_2O_6$. Calculated, %: C 31.93; H 2.27; N 5.73.

6-(4-Bromophenyl)-3-iodo-1,2-dimethyl-5-nitropyridinium methylsulfate (8c). Yield 93%, colorless crystals, mp 169–170°C. ^{1}H NMR spectrum, δ, ppm: 3.13 (3H, s, 2-CH_3); 3.34 (3H, s, $CH_3SO_4^-$); 3.93 (3H, s, NCH_3); 7.48–7.52 (2H, m, H Ar); 7.87–7.91 (2H, m, H Ar); 9.63 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 27.2; 46.5; 52.8; 101.2; 126.7; 127.2; 130.4; 132.6; 146.1; 147.6; 148.9; 163.1. Found, %: C 30.86; H 2.62; N 5.17. $C_{14}H_{14}BrIN_2O_6S$. Calculated, %: C 30.85; H 2.59; N 5.14.

3-Iodo-1,2-dimethyl-6-(4-methylphenyl)-5-nitropyridinium methylsulfate (8d). Yield 92%, colorless crystals, mp 167–168°C. ^{1}H NMR spectrum, δ, ppm: 3.12 (3H, s, 2-CH_3); 3.39 (3H, s, $CH_3SO_4^-$); 3.93 (3H, s, NCH_3); 7.39–7.49 (4H, m, H Ar); 9.61 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 21.1; 27.2; 46.3; 52.8; 100.7; 125.0; 128.2; 130.0; 142.0; 146.5; 147.1; 149.9; 162.7. Found, %: C 37.55; H 3.60; N 5.85. $C_{15}H_{17}IN_2O_6S$. Calculated, %: C 37.51; H 3.57; N 5.83.

3-(Dimethylamino)-1,2-dimethyl-5-nitro-6-phenylpyridinium perchlorate (10a). Yield 70%, colorless crystals, mp 218–219°C. ^{1}H NMR spectrum, δ, ppm: 2.82 (3H, s, 2-CH_3); 2.93 (6H, s, $N(CH_3)_2$); 3.83 (3H, s, NCH_3); 7.49–7.54 (2H, m, H Ph); 7.61–7.69 (3H, m, H Ph); 8.61 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 17.2; 40.9; 43.2; 124.8; 128.1; 129.1; 129.4; 131.4; 140.4; 147.0; 151.8; 155.4. Found, %: C 48.49; H 4.91; N 11.35. $C_{15}H_{18}ClN_3O_6$. Calculated, %: C 48.46; H 4.88; N 11.30.

6-(4-Chlorophenyl)-3-(dimethylamino)-1,2-dimethyl-5-nitropyridinium perchlorate (10b). Yield 65%, colorless crystals, mp 170–171°C. ^{1}H NMR spectrum, δ, ppm: 2.82 (3H, s, 2-CH_3); 2.93 (6H, s, $N(CH_3)_2$); 3.83 (3H, s, NCH_3); 7.52–7.59 (2H, m, H Ar); 7.70–7.78 (2H, m, H Ar); 8.60 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 19.4; 43.0; 45.1; 124.8; 127.0; 129.6; 131.1; 136.4; 139.4; 146.8; 151.9; 155.5. Found, %: C 44.38; H 4.25; N 10.37. $C_{15}H_{17}Cl_2N_3O_6$. Calculated, %: C 44.35; H 4.22; N 10.34.

6-(4-Bromophenyl)-3-(dimethylamino)-1,2-dimethyl-5-nitropyridinium perchlorate (10c). Yield 70%, colorless crystals, mp 192–193°C. ^{1}H NMR spectrum, δ, ppm: 2.82 (3H, s, 2-CH_3); 2.93 (6H, s, $N(CH_3)_2$); 3.83 (3H, s, NCH_3); 7.45–7.51 (2H, m, H Ar); 7.85–7.91 (2H, m, H Ar); 8.60 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 19.4; 43.0; 45.1; 124.7; 125.3; 127.4; 131.2; 132.5; 139.4; 146.8; 151.9; 155.5. Found, %: C 40.01; H 3.82; N 9.35. $C_{15}H_{17}BrClN_3O_6$. Calculated, %: C 39.98; H 3.80; N 9.32.

3-(Dimethylamino)-1,2-dimethyl-6-(4-methylphenyl)-5-nitropyridinium perchlorate (10d). Yield 60%, colorless crystals, mp 207–208°C. ^{1}H NMR spectrum, δ, ppm: 2.41 (3H, s, 4'-CH_3); 2.80 (3H, s, 2-CH_3); 2.92 (6H, s, $N(CH_3)_2$); 3.83 (3H, s, NCH_3); 7.35–7.40 (2H, m, H Ar); 7.42–7.47 (2H, m, H Ar); 8.60 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 19.3; 21.0; 43.1; 44.9; 124.8; 125.1; 129.0; 130.0; 140.6; 141.5; 147.1; 151.6; 155.3. Found, %: C 49.85; H 5.25; N 10.93. $C_{16}H_{20}ClN_3O_6$. Calculated, %: C 49.81; H 5.23; N 10.89.

1,2-Dimethyl-5-nitro-6-phenylpyridinium methylsulfate (15a). Yield 70%, colorless crystals, mp 176–177°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.93 (3H, s, 2-CH_3); 3.33 (3H, s, $CH_3SO_4^-$); 4.05 (3H, s, NCH_3); 7.64–7.73 (5H, m, H Ph); 8.20 (1H, d, *J* = 8.5, H-5); 9.09 (1H, d, *J* = 8.5, H-4). ^{13}C NMR spectrum, δ, ppm: 18.0; 45.0; 52.8; 127.9; 129.0; 129.3; 131.6; 132.2; 139.0; 148.1; 152.6; 159.7. Found, %: C 49.43; H 4.75; N 8.27. $C_{14}H_{16}N_2O_6S$. Calculated, %: C 49.41; H 4.74; N 8.23.

1,2-Dimethyl-6-(4-methylphenyl)-5-nitropyridinium perchlorate (15b). Yield 75%, colorless crystals, mp 174–175°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.44 (3H, s, 4'-CH_3); 2.92 (3H, s, 2-CH_3); 4.06 (3H, s, NCH_3); 7.48–7.57 (4H, m, H Ar); 8.15 (1H, d, *J* = 8.5, H-5); 9.07 (1H, d, *J* = 8.5, H-4). ^{13}C NMR spectrum, δ, ppm: 18.0; 21.0; 45.0; 127.9; 129.0; 129.3; 129.4; 129.9; 138.9; 148.0; 152.6; 160.0. Found, %: C 49.10; H 4.42; N 8.20. $C_{14}H_{15}ClN_2O_6$. Calculated, %: C 49.06; H 4.41; N 8.17.

1,6-Dimethyl-3-nitro-2-phenylpyridinium perchlorate (15c). Yield 70%, colorless crystals, mp 181–182°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.95 (3H, s, 6-CH_3); 3.83 (3H, s, NCH_3); 7.55–7.59 (2H, m, H Ph); 7.66–7.70 (3H, m, H Ph); 8.39 (1H, d, *J* = 8.5, H-5); 9.14 (1H, d, *J* = 8.5, H-4). ^{13}C NMR spectrum, δ, ppm: 22.1; 43.8; 128.1; 128.4; 129.5; 131.7; 139.0; 147.1; 150.2; 161.7. Found, %: C 47.55; H 4.03; N 8.53. $C_{13}H_{13}ClN_2O_6$. Calculated, %: C 47.50; H 3.99; N 8.52.

4-(Furan-2-yl)-1,2-dimethyl-3-(4-methylbenzoyl)-5-nitro-6-phenylpyridinium methylsulfate (21a). Yield 95%, colorless crystals, mp 229–230°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.41 (3H, s, 4'-CH_3); 2.68 (3H, s, 2-CH_3); 3.36 (3H, s, $CH_3SO_4^-$); 3.87 (3H, s, NCH_3); 6.71 (1H, dd, *J* = 3.7, *J* = 1.4, H-4 Fur); 6.96 (1H, d, *J* = 3.7, H-3 Fur); 7.41–7.46 (2H, m, H Ar); 7.61–7.66 (1H, m, H Ph); 7.67–7.78 (4H, m, H Ph); 7.89–7.94 (2H, m, H Ar); 8.02 (1H, d, *J* = 1.4, H-5 Fur). ^{13}C NMR spectrum, δ, ppm: 20.0; 21.3; 44.1; 52.7; 114.6; 120.5; 127.0; 128.4; 129.5; 129.6; 129.8; 130.2; 131.4; 132.0; 132.2; 134.4; 140.5; 143.2; 147.0; 150.2; 156.2; 191.1. Found, %: C 59.55; H 4.63; N 5.37. $C_{26}H_{24}N_2O_8S$. Calculated, %: C 59.53; H 4.61; N 5.34.

4-(Furan-2-yl)-1,2-dimethyl-3-(4-methoxybenzoyl)-5-nitro-6-phenylpyridinium methylsulfate (21b). Yield 97%, colorless crystals, mp 209–210°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.68 (3H, s, 2-CH_3); 3.37 (3H, s, $CH_3SO_4^-$); 3.87 (3H, s, NCH_3); 3.88 (3H, s, OCH_3); 6.71 (1H, d, *J* = 2.0, H-4 Fur); 6.96 (1H, d, *J* = 3.5, H-3 Fur); 7.08–7.16 (2H, m, H Ar); 7.61–7.79 (5H, m, H Ph); 7.96–8.06 (3H, m, H Ar, H-5 Fur). ^{13}C NMR spectrum, δ, ppm: 20.0; 44.1; 52.7; 55.9; 114.5; 115.0; 120.6; 127.0; 127.3; 128.4; 128.8; 129.4; 129.5; 131.4; 132.3; 134.7; 140.7; 143.3; 150.1; 156.1; 165.2; 189.7. Found, %: C 57.80; H 4.50; N 5.22. $C_{26}H_{24}N_2O_9S$. Calculated, %: C 57.77; H 4.48; N 5.18.

3-(4-Chlorobenzoyl)-4-(furan-2-yl)-1,2-dimethyl-5-nitro-6-phenylpyridinium methylsulfate (21c). Yield 87%, colorless crystals, mp 223–224°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.70 (3H, s, 2-CH_3); 3.38 (3H, s, $CH_3SO_4^-$); 3.89 (3H, s, NCH_3); 6.71 (1H, dd, *J* = 3.9, *J* = 1.8, H-4 Fur); 6.98 (1H, d, *J* = 3.9, H-3 Fur); 7.65–7.78 (7H, m, H Ar, H Ph); 8.00 (1H, d, *J* = 1.8, H-5 Fur); 8.01–8.06 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 19.9; 44.1; 52.6; 114.6; 120.5; 126.8; 128.3; 128.7; 129.3; 129.6; 131.3; 131.5; 132.1; 133.1; 133.8; 140.3; 140.8; 143.2; 150.3; 156.4; 190.4. Found, %: C 55.12; H 3.90; N 5.20. $C_{25}H_{21}ClN_2O_8S$. Calculated, %: C 55.10; H 3.88; N 5.14.

3-(4-Bromobenzoyl)-4-(furan-2-yl)-1,2-dimethyl-5-nitro-6-phenylpyridinium methylsulfate (21d). Yield 85%, colorless crystals, mp 233–234°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.69 (3H, s, 2-CH_3); 3.37 (3H, s, $CH_3SO_4^-$); 3.87 (3H, s, NCH_3); 6.72 (1H, dd, *J* = 3.5, *J* = 1.8, H-4 Fur); 6.98 (1H, dd, *J* = 3.5, *J* = 0.4, H-3 Fur); 7.61–7.77 (5H, m, H Ph); 7.81–7.86 (2H, m, H Ar); 7.93–7.98 (2H, m, H Ar); 8.03 (1H, dd, *J* = 1.8, *J* = 0.4, H-5 Fur). ^{13}C NMR spectrum, δ, ppm: 20.1; 44.2; 52.8; 114.8; 120.7; 127.0; 128.5; 128.9; 129.5; 130.5; 131.4; 131.5; 132.8; 133.3; 133.5; 133.7; 140.4; 143.2; 150.4; 156.5; 190.9. Found, %: C 50.97; H 3.62; N 4.78. $C_{25}H_{21}BrN_2O_8S$. Calculated, %: C 50.94; H 3.59; N 4.75.

4-(Furan-2-yl)-1,2-dimethyl-3-(1-naphthoyl)-5-nitro-6-phenylpyridinium methylsulfate (21e). Yield 89%, colorless crystals, mp 225–226°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.78 (3H, s, 2-CH_3); 3.39 (3H, s, $CH_3SO_4^-$); 3.93 (3H, s, NCH_3); 6.56 (1H, dd, *J* = 3.7, *J* = 1.7, H-4 Fur); 6.98 (1H, d, *J* = 3.7, H-3 Fur); 7.57–7.63 (1H, m, H Ar); 7.71–7.77 (6H, m, H Ar, H Ph); 7.79 (1H, d, *J* = 1.7, H-5 Fur); 7.86–7.91 (1H, m, H Ar); 8.11–8.16 (2H, m, H Ar); 8.32–8.37 (1H, m, H Ar); 9.26–9.30 (1H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 20.0; 44.2; 52.6; 114.2; 119.8; 124.8; 124.9; 126.9; 127.2; 128.6; 129.1; 129.4; 129.7; 129.9; 131.4; 132.1; 133.6; 134.8; 135.7; 136.9; 140.7; 143.4; 150.0; 156.6; 192.5. Found, %: C 62.16; H 4.33; N 5.05. $C_{29}H_{24}N_2O_8S$. Calculated, %: C 62.14; H 4.32; N 5.00.

3-(Cyclopropylcarbonyl)-1,2-dimethyl-5-nitro-6-phenylpyridinium fluorosulfonate (4f). A stirred and cooled (0°C) solution of pyridine derivative **3f** (1.41 g, 5 mmol) in chlorobenzene (15 ml) was treated by dropwise addition of methyl fluorosulfonate (1.71 g, 15 mmol) solution in chlorobenzene (3 ml). The mixture was stirred with cooling for 30 min and then at room temperature for 5 days. The mixture was diluted with Et_2O, the obtained precipitate was filtered off and recrystallized from EtOH. Yield 71%, colorless crystals, mp 172–173°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.30–1.38 (4H, m, CH_2CH_2); 2.62–2.65 (1H, m, CH cyclopropyl); 2.92 (3H, s, 2-CH_3); 3.90 (3H, s, NCH_3); 7.55–7.61 (2H, m, H Ph); 7.66–7.75 (3H, m, H Ph); 9.45 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 14.2; 20.0; 22.4; 44.7; 127.8; 128.3; 129.6; 132.0; 137.1; 139.2; 146.2; 151.3; 159.4; 200.0. Found, %: C 51.55; H 4.35; N 7.10. $C_{17}H_{17}FN_2O_6S$. Calculated, %: C 51.51; H 4.32; N 7.07.

Synthesis of nitrobiphenyls 5a–g, 9a–d, 11a–d, 16c (General method). A suspension of the appropriate pyridinium salt **4a**–**g**, **8a**–**d**, **10a**–**d**, **15c** (1 mmol) in EtOH (4 ml) was treated by the addition of 10% NaOH solution (2 ml). The reaction mixture was stirred at room temperature for 24 h, then diluted with water and neutralized with 50% AcOH solution. The precipitate that formed was filtered off, purified by column chromatography (eluent PhH) and recrystallized from

EtOH (biphenylcarboxylic acid **5g** was purified by re-crystallization from PhMe).

1-[5-(Methylamino)-2-nitrobiphenyl-4-yl]ethanone (5a). Yield 70%, yellow crystals, mp 126–127°C. IR spectrum, ν, cm^{-1}: 3320 (NH), 1630 (C=O), 1560, 1320 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.66 (3H, s, $COCH_3$); 2.97 (3H, d, *J* = 5.1, NHC<u>H</u>$_3$); 6.51 (1H, s, H-6); 7.26–7.33 (2H, m, H Ph); 7.36–7.48 (3H, m, H Ph); 8.63 (1H, s, H-3); 9.44 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 27.7; 29.6; 114.2; 115.3; 127.5; 128.3; 131.6; 134.5; 135.4; 138.7; 144.4; 153.8; 200.0. Found, %: C 66.69; H 5.26; N 10.31. $C_{15}H_{14}N_2O_3$. Calculated, %: C 66.66; H 5.22; N 10.36.

1-[4'-Chloro-5-(methylamino)-2-nitrobiphenyl-4-yl]-ethanone (5b). Yield 68%, yellow crystals, mp 139–140°C. IR spectrum, ν, cm^{-1}: 3290 (NH), 1650 (C=O), 1570, 1325 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.66 (3H, s, $COCH_3$); 2.97 (3H, d, *J* = 5.0, NHC<u>H</u>$_3$); 6.46 (1H, s, H-6); 7.20–7.24 (2H, m, H Ar); 7.36–7.41 (2H, m, H Ar); 8.65 (1H, s, H-3); 9.46 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 27.7; 29.6; 114.1; 115.5; 128.6; 128.9; 131.7; 134.3; 135.1; 137.3; 143.2; 153.8; 200.0. Found, %: C 59.15; H 4.33; N 9.24. $C_{15}H_{13}ClN_2O_3$. Calculated, %: C 59.12; H 4.30; N 9.19.

1-[4'-Bromo-5-(methylamino)-2-nitrobiphenyl-4-yl]-ethanone (5c). Yield 60%, yellow crystals, mp 159–160°C. IR spectrum, ν, cm^{-1}: 3295 (NH), 1655 (C=O), 1565, 1325 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.66 (3H, s, $COCH_3$); 2.97 (3H, d, *J* = 5.0, NHC<u>H</u>$_3$); 6.46 (1H, s, H-6); 7.11–7.21 (2H, m, H Ar); 7.48–7.59 (2H, m, H Ar); 8.65 (1H, s, H-3); 9.46 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 27.7; 29.6; 114.1; 115.5; 122.5; 129.2; 131.5; 131.7; 135.0; 137.8; 143.2; 153.8; 200.0. Found, %: C 51.64; H 3.78; N 8.06. $C_{15}H_{13}BrN_2O_3$. Calculated, %: C 51.60; H 3.75; N 8.02.

1-[4'-Methyl-5-(methylamino)-2-nitrobiphenyl-4-yl]-ethanone (5d). Yield 55%, yellow crystals, mp 155–156°C. IR spectrum, ν, cm^{-1}: 3295 (NH), 1650 (C=O), 1570, 1330 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.41 (3H, s, 4'-CH_3); 2.65 (3H, s, $COCH_3$); 2.97 (3H, d, *J* = 4.5, NHC<u>H</u>$_3$); 6.51 (1H, s, H-6); 7.17–7.25 (4H, m, H Ar); 8.61 (1H, s, H-3); 9.41 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 21.3; 27.7; 29.6; 114.2; 115.3; 127.4; 129.1; 131.6; 135.7; 135.8; 138.2; 144.4; 153.8; 200.0. Found, %: C 67.62; H 5.70; N 9.90. $C_{16}H_{16}N_2O_3$. Calculated, %: C 67.59; H 5.67; N 9.85.

1-[4'-Methoxy-5-(methylamino)-2-nitrobiphenyl-4-yl]-ethanone (5e). Yield 50%, yellow crystals, mp 168–169°C. IR spectrum, ν, cm^{-1}: 3290 (NH), 1650 (C=O), 1570, 1320 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.65 (3H, s, $COCH_3$); 2.97 (3H, d, *J* = 4.5, NHC<u>H</u>$_3$); 3.84 (3H, s, OCH_3); 6.50 (1H, s, H-6); 6.93–6.97 (2H, m, H Ar); 7.21–7.25 (2H, m, H Ar); 8.59 (1H, s, H-3); 9.40 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 27.7; 29.6; 55.3; 113.9; 114.1; 115.2; 128.9; 130.8; 131.6; 135.8; 144.0; 153.8; 159.8; 200.0. Found, %: C 64.05; H 5.39; N 9.38. $C_{16}H_{16}N_2O_4$. Calculated, %: C 63.99; H 5.37; N 9.33.

Cyclopropyl[5-(methylamino)-2-nitro-(1,1'-biphenyl)-4-yl]methanone (5f). Yield 82%, yellow crystals, mp 177–178°C. IR spectrum, ν, cm^{-1}: 3350 (NH), 1650 (C=O), 1550, 1340 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.04–1.11 (2H, m) and 1.18–1.27 (2H, m, CH_2CH_2); 2.66–2.77 (1H, m, CH cyclopropyl); 2.97 (3H, d, *J* = 5.3, NHC<u>H</u>$_3$); 6.51 (1H, s, H-6); 7.27–7.34 (2H, m, H Ph); 7.38–7.47 (3H, m, H Ph); 8.91 (1H, s, H-3); 9.40 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 11.6; 17.3; 29.6; 114.1; 116.0; 127.5; 128.1; 128.3; 130.9; 135.6; 138.9; 144.1; 153.6; 201.3. Found, %: C 68.92; H 5.45; N 9.50. $C_{17}H_{16}N_2O_3$. Calculated, %: C 68.91; H 5.44; N 9.45.

5-(Methylamino)-2-nitrobiphenyl-4-carboxylic acid (5g). Yield 63%, yellow crystals, mp 225–226°C. IR spectrum, ν, cm^{-1}: 3360 (NH), 2900–2300 (OH), 1660 (C=O), 1570, 1330 (NO_2). ^{1}H NMR spectrum, δ, ppm: 2.94 (3H, s, NHC<u>H</u>$_3$); 6.54 (1H, s, H-6); 7.30–7.36 (2H, m, H Ph); 7.38–7.46 (3H, m, H Ph); 8.56 (1H, s, H-3). ^{13}C NMR spectrum, δ, ppm: 29.5; 108.5; 113.8; 127.6; 127.9; 128.2; 130.3; 134.7; 138.6; 143.1; 153.6; 168.3. Found, %: C 61.79; H 4.47; N 10.31. $C_{14}H_{12}N_2O_4$. Calculated, %: C 61.76; H 4.44; N 10.29.

(4-Iodo-6-nitrobiphenyl-3-yl)methylamine (9a). Yield 65%, yellow crystals, mp 120–121°C. IR spectrum, ν, cm^{-1}: 3355 (NH), 1580, 1320 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.96 (3H, d, *J* = 4.9, NHC<u>H</u>$_3$); 4.94 (1H, br. s, NH); 6.32 (1H, s, H-2); 7.26–7.31 (2H, m, H Ph); 7.37–7.44 (3H, m, H Ph); 8.46 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 30.9; 80.8; 110.9; 127.7; 127.9; 128.3; 136.3; 138.0; 139.0; 140.4; 151.3. Found, %: C 44.12; H 3.15; N 7.99. $C_{13}H_{11}IN_2O_2$. Calculated, %: C 44.09; H 3.13; N 7.91.

(4'-Chloro-4-iodo-6-nitrobiphenyl-3-yl)methylamine (9b). Yield 60%, yellow crystals, mp 169–170°C. IR spectrum, ν, cm^{-1}: 3360 (NH), 1575, 1325 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.96 (3H, d, *J* = 5.0, NHC<u>H</u>$_3$); 4.97 (1H, br. s, NH); 6.26 (1H, s, H-2); 7.18–7.23 (2H, m, H Ar); 7.34–7.40 (2H, m, H Ar); 8.48 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 30.9; 81.1; 110.7; 128.6; 129.1; 134.0; 136.5; 137.5; 137.7; 139.3; 151.4. Found, %: C 40.22; H 2.63; N 7.26. $C_{13}H_{10}ClIN_2O_2$. Calculated, %: C 40.18; H 2.59; N 7.21.

(4'-Bromo-4-iodo-6-nitrobiphenyl-3-yl)methylamine (9c). Yield 55%, yellow crystals, mp 186–187°C. IR spectrum, ν, cm^{-1}: 3350 (NH), 1570, 1320 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.96 (3H, d, *J* = 4.9, NHC<u>H</u>$_3$); 4.97 (1H, br. s, NH); 6.25 (1H, s, H-2); 7.12–7.17 (2H, m, H Ar); 7.50–7.55 (2H, m, H Ar); 8.48 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 30.9; 81.1; 110.6; 122.2; 129.4; 131.5; 136.5; 137.6; 138.0; 139.3; 151.4. Found, %: C 36.09; H 2.35; N 6.50. $C_{13}H_{10}BrIN_2O_2$. Calculated, %: C 36.06; H 2.33; N 6.47.

(4-Iodo-4'-methyl-6-nitrobiphenyl-3-yl)methylamine (9d). Yield 50%, yellow crystals, mp 160–161°C. IR spectrum, ν, cm^{-1}: 3350 (NH), 1570, 1330 (NO_2). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.40 (3H, s, 4'-CH_3); 2.95 (3H, d, *J* = 5.1, NHC<u>H</u>$_3$); 4.92 (1H, br. s, NH); 6.31 (1H, s, H-2); 7.15–7.24 (4H, m, H Ar); 8.44 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 21.2; 30.9; 80.5; 111.0; 127.6; 129.1; 136.0; 136.3; 137.8; 138.2; 140.4; 151.2. Found, %: C 45.71; H 3.60; N 7.65. $C_{14}H_{13}IN_2O_2$. Calculated, %: C 45.67; H 3.56; N 7.61.

***N*^{3},*N*^{4},*N*^{4}-trimethyl-6-nitrobiphenyl-3,4-diamine (11a)**. Yield 80%, yellowish-orange crystals, mp 126–127°C.

IR spectrum, ν, cm^{-1}: 3378 (NH), 1520, 1325 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.69 (3H, s, $N(CH_3)_2$); 2.93 (3H, d, *J* = 5.3, NHC<u>H</u>$_3$); 5.39 (1H, br. s, NH); 6.36 (1H, s, H-2); 7.28–7.33 (2H, m, H Ph); 7.35–7.45 (3H, m, H Ph); 7.82 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 30.0; 43.8; 111.0; 117.1; 127.3; 127.9; 128.2; 136.6; 138.5; 140.1; 147.0. Found, %: C 66.46; H 6.36; N 15.56. $C_{15}H_{17}N_3O_2$. Calculated, %: C 66.40; H 6.32; N 15.49.

4'-Chloro-*N*^{3},*N*^{4},*N*^{4}-trimethyl-6-nitrobiphenyl-3,4-diamine (11b). Yield 70%, yellowish-orange crystals, mp 149–150°C. IR spectrum, ν, cm^{-1}: 3368 (NH), 1573, 1325 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.68 (3H, s, $N(CH_3)_2$); 2.92 (3H, d, *J* = 5.3, NHC<u>H</u>$_3$); 5.40 (1H, br. s, NH); 6.29 (1H, s, H-2); 7.18–7.24 (2H, m, H Ar); 7.32–7.39 (2H, m, H Ar); 7.82 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 30.0; 43.7; 105.8; 117.8; 124.4; 125.7; 130.2; 130.3; 132.6; 132.8; 138.0; 146.7. Found, %: C 58.99; H 5.32; N 13.83. $C_{15}H_{16}ClN_3O_2$. Calculated, %: C 58.92; H 5.27; N 13.74.

4'-Bromo-*N*^{3},*N*^{4},*N*^{4}-trimethyl-6-nitrobiphenyl-3,4-diamine (11c). Yield 65%, yellowish-orange crystals, mp 164–165°C. IR spectrum, ν, cm^{-1}: 3387 (NH), 1573, 1320 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.68 (3H, s, $N(CH_3)_2$); 2.92 (3H, d, *J* = 5.3, NHC<u>H</u>$_3$); 5.40 (1H, br. s, NH); 6.28 (1H, s, H-2); 7.12–7.19 (2H, m, H Ar); 7.49–7.54 (2H, m, H Ar); 7.82 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 30.0; 43.7; 110.8; 117.3; 121.5; 129.6; 131.3; 135.5; 136.4; 138.8; 139.2; 148.1. Found, %: C 51.49; H 4.65; N 12.06. $C_{15}H_{16}BrN_3O_2$. Calculated, %: C 51.44; H 4.60; N 12.00.

***N*^{3},*N*^{4},*N*^{4},4'-Tetramethyl-6-nitrobiphenyl-3,4-diamine (11d)**. Yield 75%, yellowish-orange crystals, mp 130–131°C. IR spectrum, ν, cm^{-1}: 3364 (NH), 1567, 1310 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.40 (3H, s, 4'-CH_3); 2.68 (3H, s, $N(CH_3)_2$); 2.92 (3H, d, *J* = 5.2, NHC<u>H</u>$_3$); 5.35 (1H, br. s, NH); 6.34 (1H, s, H-2); 7.17–7.24 (4H, m, H Ar); 7.79 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 21.2; 30.0; 43.8; 111.1; 117.1; 127.8; 128.9; 136.6; 136.8; 137.1; 138.2; 138.4; 147.9. Found, %: C 67.40; H 6.75; N 14.79. $C_{16}H_{19}N_3O_2$. Calculated, %: C 67.35; H 6.71; N 14.73.

***N*-Methyl-6-nitrobiphenyl-3-amine (16c)**. Yield 25%, yellow crystals, mp 120–121°C. IR spectrum, ν, cm^{-1}: 3345 (NH), 1590, 1314 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.90 (3H, d, *J* = 5.1, NHC<u>H</u>$_3$); 4.51 (1H, br. s, NH); 6.37 (1H, d, *J* = 2.8, H-2); 6.50 (1H, dd, *J* = 9.0, *J* = 2.8, H-4); 7.27–7.30 (2H, m, H Ph); 7.35–7.42 (3H, m, H Ph); 8.00 (1H, d, *J* = 9.0, H-5). ^{13}C NMR spectrum, δ, ppm: 30.1; 110.1; 114.1; 127.5; 127.7; 127.8; 128.2; 137.8; 139.6; 140.3; 152.5. Found, %: C 68.46; H 5.35; N 12.32. $C_{13}H_{12}N_2O_2$. Calculated, %: C 68.41; H 5.30; N 12.27.

Synthesis of biphenyls 16a,b (General method). A solution of pyridinium salt **15a**,**b** (1 mmol) in saturated $MeNH_2$ solution in EtOH (20 ml) was stirred at room temperature for 3 days. Ethanol was evaporated at reduced pressure, the residue was purified by column chromatography (eluent $CHCl_3$–EtOAc, 9:1) and recrystallized from EtOH.

***N*-Methyl-4-nitrobiphenyl-3-amine (16a)**. Yield 50%, yellowish-orange crystals, mp 75–76°C. IR spectrum, ν, cm^{-1}: 3396 (NH), 1578, 1343 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.09 (3H, d, *J* = 4.9, NHC<u>H</u>$_3$); 6.87 (1H, dd, *J* = 8.7, *J* = 1.9, H-6); 6.98 (1H, d, *J* = 1.9, H-2); 7.39–7.50 (3H, m, H Ph); 7.57–7.63 (2H, m, H Ph); 8.10 (1H, br. s, NH); 8.23 (1H, d, *J* = 8.7, H-5). ^{13}C NMR spectrum, δ, ppm: 29.7; 111.3; 114.7; 127.3; 127.4; 128.8; 128.9; 131.2; 139.7; 146.5; 149.2. Found, %: C 68.47; H 5.31; N 12.35. $C_{13}H_{12}N_2O_2$. Calculated, %: C 68.41; H 5.30; N 12.27.

***N*,4'-Dimethyl-4-nitrobiphenyl-3-amine (16b)**. Yield 52%, yellowish-orange crystals, mp 96–97°C. IR spectrum, ν, cm^{-1}: 3390 (NH), 1570, 1395 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.41 (3H, s, 4'-CH_3); 3.08 (3H, d, *J* = 4.9, NHC<u>H</u>$_3$); 6.86 (1H, dd, *J* = 8.8, *J* = 1.9, H-6); 6.96 (1H, d, *J* = 1.9, H-2); 7.26–7.30 (2H, m, H Ar); 7.48–7.54 (2H, m, H Ar); 8.10 (1H, br. s, NH); 8.21 (1H, d, *J* = 8.8, H-5). ^{13}C NMR spectrum, δ, ppm: 21.2; 29.7; 110.9; 114.6; 127.2; 127.4; 129.7; 131.0; 136.8; 139.0; 146.5; 149.1. Found, %: C 69.46; H 5.84; N 11.60. $C_{14}H_{14}N_2O_2$. Calculated, %: C 69.41; H 5.82; N 11.56.

Synthesis of furylbiphenyls 22a–e and 23a–d (General method). A suspension of pyridinium salt **21a**–**e** (1 mmol) in EtOH (4 ml) was treated by the addition of 10% aqueous NaOH solution (2 ml). The reaction mixture was stirred at room temperature for 2 h, then heated at 70°C for an additional 1 h, then diluted with water and neutralized with 10% HCl solution. The precipitate that formed was filtered off, the products were separated by column chromatography (eluent $CHCl_3$). The aminobiphenyls **22a**–**e** were recrystallized from EtOH, while the hydroxybiphenyls **23a**–**d** were recrystallized from PhMe.

[3-(Furan-2-yl)-5-(methylamino)-2-nitrobiphenyl-4-yl]-(4-methylphenyl)methanone (22a). Yield 73%, yellow crystals, mp 162–163°C. IR spectrum, ν, cm^{-1}: 3340 (NH), 1656 (C=O), 1530, 1355 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.30 (3H, s, 4'-CH_3); 2.85 (3H, s, NHC<u>H</u>$_3$); 5.62 (1H, br. s, NH); 6.07 (1H, dd, *J* = 3.5, *J* = 1.7, H-4 Fur); 6.30 (1H, dd, *J* = 3.5, *J* = 0.8, H-3 Fur); 6.62 (1H, s, H-6); 7.03–7.08 (2H, m, H Ar); 7.15 (1H, dd, *J* = 1.7, *J* = 0.8, H-5 Fur); 7.41–7.46 (5H, m, H Ph); 7.48–7.52 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 21.6; 30.1; 111.5; 111.7; 113.1; 120.8; 124.5; 127.9; 128.6; 128.7; 128.8; 129.0; 135.0; 137.1; 138.5; 139.2; 143.6; 143.9; 146.0; 148.5; 197.1. Found, %: C 72.86; H 4.94; N 6.85. $C_{25}H_{20}N_2O_4$. Calculated, %: C 72.80; H 4.89; N 6.79.

[3-(Furan-2-yl)-5-hydroxy-2-nitrobiphenyl-4-yl](4-methylphenyl)methanone (23a). Yield 20%, colorless crystals, mp 212–213°C. IR spectrum, ν, cm^{-1}: 3210 (OH), 1644 (C=O), 1531, 1363 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.30 (3H, s, 4'-CH_3); 6.05 (1H, dd, *J* = 3.6, *J* = 1.9, H-4 Fur); 6.35 (1H, dd, *J* = 3.6, *J* = 0.6, H-3 Fur); 7.00–7.06 (2H, m, H Ar); 7.12 (1H, s, H-6); 7.13 (1H, dd, *J* = 1.9, *J* = 0.6, H-5 Fur); 7.41–7.47 (7H, m, H Ar, H Ph); 9.42 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 21.6; 112.0; 113.6; 119.6; 120.4; 124.9; 127.9; 128.7; 128.8; 128.9; 129.3; 134.9; 135.5; 139.7; 142.3; 143.8; 144.2; 145.2; 158.9; 198.3. Found, %: C 72.23; H 4.34; N 3.55. $C_{24}H_{17}NO_5$. Calculated, %: C 72.17; H 4.29; N 3.51.

[3-(Furan-2-yl)-5-(methylamino)-2-nitrobiphenyl-4-yl]-(4-methoxyphenyl)methanone (22b). Yield 71%, yellow

crystals, mp 171–172°C. IR spectrum, ν, cm^{-1}: 3400 (NH), 1640 (C=O), 1550, 1370 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.84 (3H, s, NHC<u>H</u>$_3$); 3.79 (3H, s, OCH_3); 5.45 (1H, br. s, NH); 6.09 (1H, dd, *J* = 3.5, *J* = 1.6, H-4 Fur); 6.32 (1H, dd, *J* = 3.5, *J* = 0.8, H-3 Fur); 6.61 (1H, s, H-6); 6.72–6.77 (2H, m, H Ar); 7.17 (1H, dd, *J* = 1.6, *J* = 0.8, H-5 Fur); 7.41–7.46 (5H, m, H Ph); 7.59–7.63 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 30.2; 55.4; 111.5; 111.6; 112.9; 113.4; 121.2; 124.3; 127.9; 128.6; 128.7; 130.2; 131.4; 137.2; 138.4; 139.2; 143.7; 146.0; 148.3; 163.6; 195.8. Found, %: C 70.12; H 4.75; N 6.50. $C_{25}H_{20}N_2O_5$. Calculated, %: C 70.09; H 4.71; N 6.54.

[3-(Furan-2-yl)-5-hydroxy-2-nitrobiphenyl-4-yl](4-methoxyphenyl)methanone (23b). Yield 15%, colorless crystals, mp 211–212°C. IR spectrum, ν, cm^{-1}: 3194 (OH), 1640 (C=O), 1530, 1360 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.79 (3H, s, OCH_3); 6.08 (1H, dd, *J* = 3.6, *J* = 1.9, H-4 Fur); 6.38 (1H, dd, *J* = 3.6, *J* = 0.8, H-3 Fur); 6.70–6.75 (2H, m, H Ar); 7.11 (1H, s, H-6); 7.15 (1H, dd, *J* = 1.9, *J* = 0.8, H-5 Fur); 7.41–7.47 (5H, m, H Ph); 7.54–7.58 (2H, m, H Ar); 9.23 (1H, br. s, OH). ^{13}C NMR spectrum, δ, ppm: 55.4; 112.0; 113.4; 113.5; 119.5; 120.8; 124.7; 127.9; 128.9; 129.2; 130.0; 131.3; 135.5; 139.4; 142.3; 144.3; 145.3; 158.5; 163.5; 196.8. Found, %: C 69.44; H 4.12; N 3.42. $C_{24}H_{17}NO_6$. Calculated, %: C 69.39; H 4.12; N 3.37.

(4-Chlorophenyl)[3-(furan-2-yl)-5-(methylamino)-2-nitrobiphenyl-4-yl]methanone (22c). Yield 70%, yellow crystals, mp 185–186°C. IR spectrum, ν, cm^{-1}: 3450 (NH), 1660 (C=O), 1525, 1360 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.87 (3H, d, *J* = 3.9, NHC<u>H</u>$_3$); 5.92 (1H, br. s, NH); 6.08 (1H, dd, *J* = 3.6, *J* = 1.9, H-4 Fur); 6.30 (1H, dd, *J* = 3.6, *J* = 0.6, H-3 Fur); 6.65 (1H, s, H-6); 7.16 (1H, dd, *J* = 1.9, *J* = 0.6, H-5 Fur); 7.19–7.23 (2H, m, H Ar); 7.42–7.46 (5H, m, H Ph); 7.47–7.53 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 30.1; 111.8; 112.0; 113.5; 119.4; 124.9; 127.9; 128.3; 128.7; 128.8; 130.0; 136.3; 136.9; 139.0; 139.1; 139.2; 143.8; 145.8; 148.9; 196.3. Found, %: C 66.64; H 3.95; N 6.52. $C_{24}H_{17}ClN_2O_4$. Calculated, %: C 66.59; H 3.96; N 6.47.

(4-Chlorophenyl)[3-(furan-2-yl)-5-hydroxy-2-nitrobiphenyl-4-yl]methanone (23c). Yield 20%, colorless crystals, mp 194–195°C. IR spectrum, ν, cm^{-1}: 3398 (OH), 1640 (C=O), 1525, 1365 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 6.09 (1H, dd, *J* = 3.5, *J* = 1.7, H-4 Fur); 6.38 (1H, dd, *J* = 3.5, *J* = 0.6, H-3 Fur); 7.14 (1H, s, H-6); 7.15 (1H, dd, *J* = 1.7, *J* = 0.6, H-5 Fur); 7.19–7.23 (2H, m, H Ar); 7.40–7.49 (7H, m, H Ar, H Ph); 9.55 (1H, br. s, OH). ^{13}C NMR spectrum, δ, ppm: 112.2; 114.0; 119.5; 119.8; 124.9; 127.9; 128.3; 128.9; 129.4; 129.8; 135.3; 135.8; 139.1; 140.2; 142.4; 144.4; 144.9; 159.2; 197.6. Found, %: C 65.77; H 3.40; N 3.30. $C_{23}H_{14}ClNO_5$. Calculated, %: C 65.80; H 3.36; N 3.34.

(4-Bromophenyl)[3-(furan-2-yl)-5-(methylamino)-2-nitrobiphenyl-4-yl]methanone (22d). Yield 71%, yellow crystals, mp 208–209°C. IR spectrum, ν, cm^{-1}: 3445 (NH), 1660 (C=O), 1525, 1360 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.88 (3H, s, NHC<u>H</u>$_3$); 5.94 (1H, br. s, NH); 6.08 (1H, dd, *J* = 3.5, *J* = 1.7, H-4 Fur); 6.30 (1H, dd, *J* = 3.5, *J* = 0.7, H-3 Fur); 6.65 (1H, s, H-6); 7.16 (1H, dd, *J* = 1.7, *J* = 0.7, H-5 Fur); 7.35–7.42 (4H, m, H Ar); 7.43–7.45 (5H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 30.1; 111.8; 112.1; 113.6; 119.3; 125.0; 127.8; 127.9; 128.8; 129.9; 130.1; 131.3; 136.7; 136.9; 139.1; 143.8; 145.7; 148.9; 196.5. Found, %: C 60.35; H 3.62; N 5.93. $C_{24}H_{17}BrN_2O_4$. Calculated, %: C 60.39; H 3.59; N 5.87.

(4-Bromophenyl)[3-(furan-2-yl)-5-hydroxy-2-nitrobiphenyl-4-yl]methanone (23d). Yield 13%, colorless crystals, mp 210–211°C. IR spectrum, ν, cm^{-1}: 3239 (NH), 1656 (C=O), 1530, 1364 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 6.10 (1H, dd, *J* = 3.1, *J* = 2.0, H-4 Fur); 6.38 (1H, dd, *J* = 3.1, *J* = 0.9, H-3 Fur); 7.14 (1H, s, H-6); 7.15 (1H, dd, *J* = 2.0, *J* = 0.9, H-5 Fur); 7.36–7.40 (4H, m, H Ar); 7.41–7.47 (5H, m, H Ph); 9.57 (1H, br. s, OH). ^{13}C NMR spectrum, δ, ppm: 112.3; 114.0; 119.5; 119.8; 125.0; 127.8; 127.9; 128.9; 129.4; 129.9; 131.3; 135.3; 136.3; 140.3; 142.4; 144.4; 144.9; 159.3; 197.8. Found, %: C 59.48; H 3.05; N 3.08. $C_{23}H_{14}BrNO_5$. Calculated, %: C 59.50; H 3.04; N 3.02.

[3-(Furan-2-yl)-5-(methylamino)-2-nitrobiphenyl-4-yl]-(1-naphthyl)methanone (23e). Yield 87%, yellow crystals, mp 160–161°C. IR spectrum, ν, cm^{-1}: 3400 (NH), 1640 (C=O), 1525, 1360 (NO_2). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.95 (3H, s, NHC<u>H</u>$_3$); 5.65 (1H, dd, *J* = 3.5, *J* = 1.9, H-4 Fur); 6.10 (1H, dd, *J* = 3.5, *J* = 0.8, H-3 Fur); 6.64 (1H, dd, *J* = 1.9, *J* = 0.8, H-5 Fur); 6.71 (1H, s, H-6); 6.72 (1H, br. s, NH); 7.20–7.23 (1H, m, H Ar); 7.30–7.33 (7H, m, H Ar, H Ph); 7.56–7.61 (1H, m, H Ar); 7.75–7.79 (2H, m, H Ar); 8.57–8.61 (1H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 30.1; 111.1; 112.0; 112.1; 120.9; 123.7; 125.6; 126.1; 126.2; 127.5; 127.9; 128.3; 128.7; 128.8; 128.9; 130.4; 132.6; 133.7; 136.2; 137.0; 139.2; 139.6; 144.2; 146.4; 149.9; 199.1. Found, %: C 74.96; H 4.52; N 6.20. $C_{28}H_{20}N_2O_4$. Calculated, %: C 74.99; H 4.50; N 6.25.

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