Oxidative arylamination of 1,3-dinitrobenzene and 3-nitropyridine under anaerobic conditions: the dual role of the nitroarenes

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Abstract

1,3-Dinitrobenzene and 3-nitropyridine react with lithium arylamides under anaerobic conditions to produce *N*-aryl-2,4-dinitroanilines and *N*-aryl-5-nitropyridin-2-amines, respectively, in 8-42% yields.

Keywords: Nucleophilic aromatic substitution of hydrogen, oxidative arylamination, 1,3-dinitrobenzene, 3-nitropyridine, *N*-aryl-2,4-dinitroanilines, *N*-aryl-5-nitropyridin-2-amines

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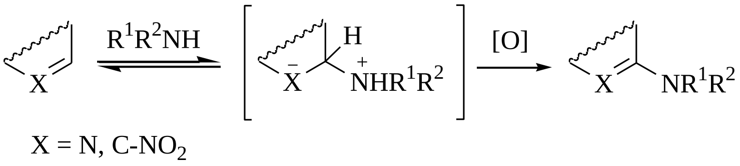
Introduction

The importance of aromatic and heteroaromatic amines is generally known[1]. The most common method for their preparation is nucleophilic aromatic substitution of halide or other nucleofugal groups under conventional[2] or catalytic conditions[3]. In cases of electron-deficient substrates, such as azines and nitroarenes, the nucleophilic aromatic substitution of hydrogen (S_N^H),[4] including its oxidative[5] and vicarious[6] versions, is an attractive alternative to the above methods. This methodology does not require any preliminary introduction of a classical leaving group into an aromatic substrate and need not expensive catalysts or ligands. Mechanistically, the oxidative S_N^H-amination consists of σ^H-adduct formation and its subsequent oxidative rearomatization (Scheme 1).



Scheme 1. Oxidative amination of azines and nitroarenes.

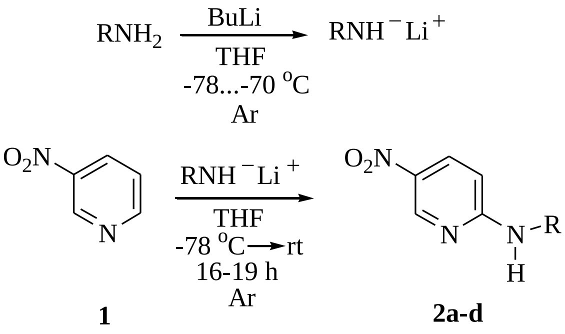
In the presence of $KMnO_4$ electron-deficient azines and nitroarenes can be smoothly aminated by potassium amide in a liquid ammonia or liquid ammonia itself.[5a] In our previous reports we have shown that an alkylamine/$AgPy_2MnO_4$ system is very efficient for the oxidative alkylamination of fused azines,[5b] 3-nitropyridine[5c], 1,3-dinitrobenzene and nitronaphthalenes[5d]. In the course of this study, we have been interested in the S_N^H-arylamination of aromatic substrates. Unfortunately, the oxidative amination and alkylamination procedure is not suitable for arylamination because of the low nucleophilicity and high sensitivity arylamines towards oxidation. This is why S_N^H-arylamination reactions are still rare. The majority of these are intramolecular and are performed using mild oxidants such as sulfur, chloranil, nitrobenzene.[7] In some cases, oxidation of σ^H-complexes with the oxygen in air was observed.[8] When nitroarenes were used as substrates, the NO_2 group itself was often found to be an acceptor of hydride ion.[9] Similarly, for the amination of azaheterocycles, the ring C=N bond can intercept hydride ion.[8b]

To date, only a few intermolecular oxidative arylamination reactions have been reported. 5-azacinnoline,[10] 3-X-1,2,4-triazines (X = SMe, SBu^t, OMe)[11] and 2-X-3-nitropyridines (X = H, Cl)[12] were found to be suitable substrates. In all cases, the reaction was carried out with anilines[10] or hetarylamines[10-12] in the presence of a strong base. Thus, to be performed the reaction needs metal arylamide as a nucleophile. Interaction of 5-azacinnoline with arylamines demanded 20 days for completion with crucial access to the air. Arylamination of 1,2,4-triazines proceeded without external oxidant under an inert atmosphere. Obviously, the substrate itself served here as a hydride ion acceptor. 3-Nitropyridines reacted with 2-, 3- or 4-aminopyridines in the presence of LiHMDS (or LDA) in THF without isolation of the reaction mixture from the air oxygen. The use of nitrobenzene as a co-solvent has been shown to improve the yield of the arylamination product. Here we wish to report on the direct arylamination of 3-nitropyridine and 1,3-dinitrobenzene by reacting with lithium aryl(hetaryl)amides under anaerobic conditions.

Results and Discussion

Note, for arylamination of 3-nitropyridines[12], 2-, 3- or 4-aminopyridines were solely used as nucleophiles. Checking the feasibility of a similar approach for other aryl- and hetarylamides was our initial goal. We have also yet to answer if this reaction is possible under anaerobic conditions.

At first, we studied reaction of 3-nitropyridine **1** with 2-aminopyridine under modified experimental procedure (Scheme 2, Table 1). Lithium arylamide was prepared by treating 2-aminopyridine (1.1 mmol) with butyl lithium (1.2 mmol, 1.6M solution in hexane) in anhydrous THF at –78 to -70 °C under argon. Solution of 3-nitropyridine **1** (1 mmol) in THF was subsequently added. The reaction mixture was stirred for 16-19 h with gradual warming to room temperature. After extraction and flash column chromatography 5-nitro-*N*-(pyridin-2-yl)pyridin-2-amine **2a** was obtained in 19% yields (Table 1, Entry 1). Increased amounts of 2-aminopyridine and BuLi led to **2a** in higher yields (Table 1, Entries 2-4). The use of 1.6 equiv of arylamine and 1.7 equiv of BuLi was optimal and gave an even better yield of **2a** compared with the published[11] procedure. Upon arylamination of **1** with quinolin-2-amine or aniline similar results were observed (Table 1, Entries 10,11,13,14). The corresponding *N*-aryl-5-nitropyridin-2-amines **2b** and **2c** were obtained in 34-37% yields. The procedure was also suitable for amination of **1** with phenylamidine yielding compound **2d** (Table 1, Entry 16).

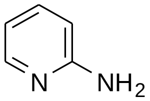
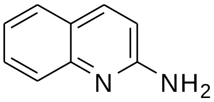
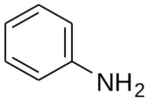
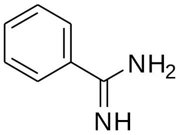


Scheme 2. Synthesis of *N*-aryl-5-nitropyridin-2-amines **2a-d**.

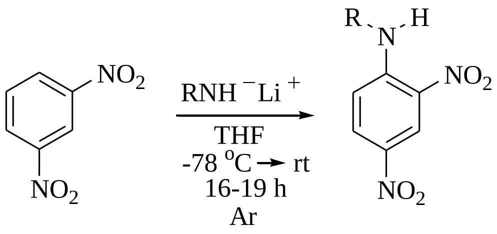
The use of nitrobenzene as a co-solvent, as has been shown[12], improves the yield of the arylamination product due to its ability to accept a hydride ion from σ^H-adduct and thus, facilitate the rearomatization step. To check this observation, we carried out the reaction of 3-nitropyridine **1** with 2-aminopyridine using nitrobenzene as an additive. Indeed, this additive provided higher yields of **2a** (Table 1, Entries 5-7). The use of 1.1 equiv of nitrobenzene was found to be optimal. Addition of nitrobenzene assisted also the reaction of **1** with phenylamidine (Table 1, Entry 17). At the same time, its influence on the reactions with other aryl(hetaryl)amines was not essential (Table 1, Entries 12 and 15).

To verify the hypothesis of oxidation with nitrobenzene, we carried out the reaction of **1** with 2-aminopyridine in the presence of 1,2- or 1,3-dinitrobenzene as soon as their oxidative ability is certainly higher. However, 1,2-dinitrobenzene additive gave less yield of **2a** (Table 1, Entry 8) than in the reference experiment with nitrobenzene (Table 1, Entry 6). Interestingly, when the reaction of 3-nitropyridine **1** with 2-aminopyridine was carried out in the presence of 1,3-dinitrobenzene **3**, the arylamino derivatives **2a** and **4a** were obtained in 13 and 28% yields, respectively (Table 1, Entry 9). This indicated that 1,3-dinitrobenzene is more reactive towards amides comparing with 3-nitropyridine.

Table 1. Synthesis of *N*-aryl-5-nitropyridin-2-amines **2a-d**

Entry	Amine	Equiv of amine	Equiv of BuLi	Additive	Equiv of additive	Product	Yield (%)
1		1.1	1.2	-	-	**2a**	19
2		1.3	1.4	-	-	**2a**	29
3		1.6	1.7	-	-	**2a**	41
4		2.0	2.2	-	-	**2a**	39
5		1.3	1.4	$PhNO_2$	1.1	**2a**	41
6		1.6	1.7	$PhNO_2$	1.1	**2a**	52
7		1.6	1.7	$PhNO_2$	2.0	**2a**	44
8		1.6	1.7	1,2-$C_6H_4(NO_2)_2$	1.1	**2a**	46
9		1.6	1.7	1,3-$C_6H_4(NO_2)_2$	1.1	**2a** **4a**	13 28
10		1.3	1.4	-	-	**2b**	27
11		1.6	1.7	-	-	**2b**	34
12		1.6	1.7	$PhNO_2$	1.1	**2b**	33
13		1.3	1.4	-	-	**2c**	38
14		1.6	1.7	-	-	**2c**	37
15		1.6	1.7	$PhNO_2$	1.1	**2c**	39
16		1.6	1.7	-	-	**2d**	22
17		1.6	1.7	$PhNO_2$	1.1	**2d**	33

As a second part of our work, we examined the arylamination of 1,3-dinitrobenzene **3** using the optimized reaction conditions developed for **1**. The results are collected in Scheme 3 and Table 2.



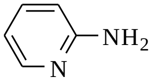
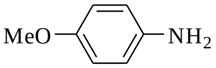
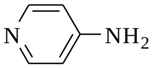
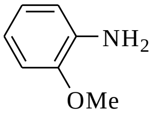
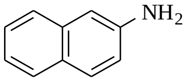
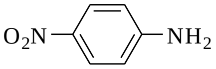
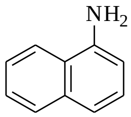
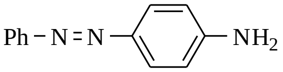
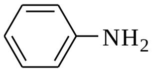
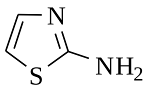
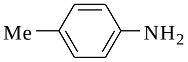
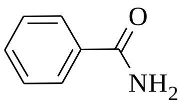
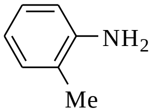
3 **4a-m**

Scheme 3. Synthesis of *N*-aryl-2,4-dinitroanilines **4a-m**.

As shown in Table 2, the nature of the arylamine affects the reaction. Evidently, if the NH-acidity of arylamine is high, the corresponding N-anion is formed easier. On the other hand, the greater the NH-acidity of arylamine, the lower the nucleophilicity of the corresponding N-anion. The steric accessibility of the N-nucleophilic center should be also taken into account. The sum of these factors is responsible for yields of the arylamination products **4**. Indeed, as it follows from Table 2 and data on the NH-acidity of arylamines, the highest yields of **4** were obtained upon using of 2- and 4-aminopyridines having middle pK_a values (Table 2, Entries 1,2). The presence of a substituent in the position *ortho* to the amino group of arylamine makes difficult the nucleophilic attack and, perhaps, oxidation of the arylamino-σ^H-complex. That is why compounds **4g** and **4i** were obtained in low yields (Table 2, Entries 7,9). The greater steric hindrance of the *peri*-amino group may cause reduction in the yield switching from **4c** to **4d** (Table 2, Entries 3,4).

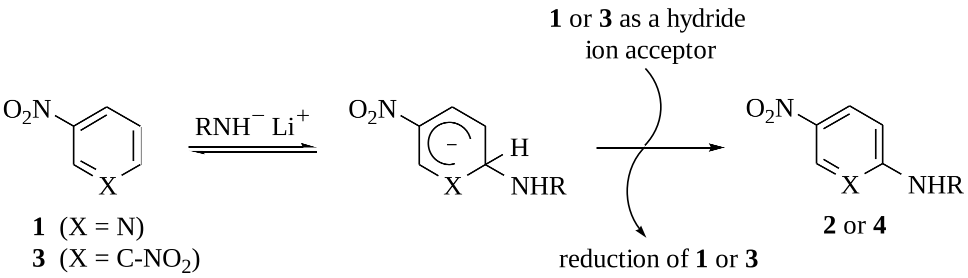
The developed procedure was also suitable for amination of **3** with benzamide yielding compound **4m** (Table 2, Entry 13).

Table 2. Synthesis of N-aryl-2,4-dinitroanilines **4a-m**

Entry	Amine (pK_a)[a]	Product	Yield (%)	Entry	Amine (pK_a)[a]	Product	Yield (%)
1	 (27.7)	**4a**	41	8		**4h**	28
2	 (26.5)	**4b**	42	9		**4i**	9
3		**4c**	39	10	 (20.9)	**4j**	20
4		**4d**	31	11		**4k**	16
5	 (30.6)	**4e**	32	12		**4l** **5**	5 8
6	 (31.0)	**4f**	34	13		**4m**	12
7		**4g**	8				

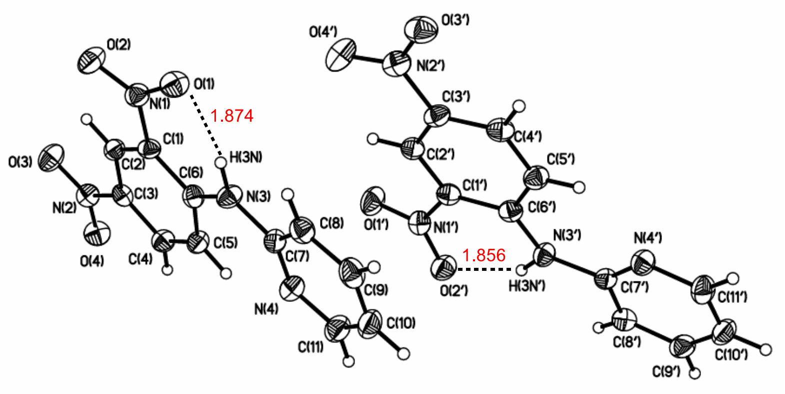
[a]NH-Acidity in DMSO.[13]

It should be mentioned that the reactions of 3-nitropyridine and 1,3-dinitrobenzene with aryl(hetaryl)amides were carried out under anaerobic conditions. Thus, one can conclude that the substrate itself acts here as the oxidant accepting a hydride ion from anionic σ^H-complex (Scheme 4). That is why the yields of the arylamination products **2** and **4** did not exceed 42%. In addition, when 2-aminothiazole was used as a nucleophile, the arylamino derivative **4l** was obtained together with 3-nitroaniline **5** (the reduction product of **3**) (Table 2, Entry 12).

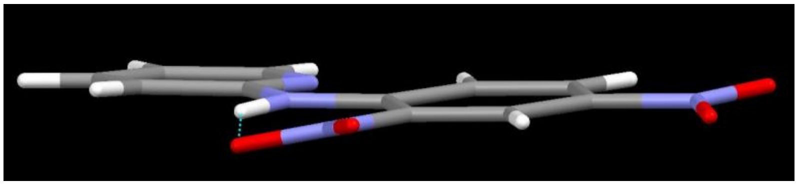


Scheme 4. Mechanism of the compounds **2** and **4** formation.

The structures of compounds **2** and **4** were characterized by UV, IR, ^{1}H NMR, ^{13}C NMR, mass spectroscopy and in two cases (compounds **4a** and **4k**) single crystal X-ray diffraction analysis. The X-ray data indicate the presence of intramolecular hydrogen bond of the N-H….O type with the length range 1.856-1.898 Å (Figures 1A and 2). Interestingly, the six-membered cycle of **4a** closed by intramolecular hydrogen bond is not planar: the dihedral angle between the O-N-O and H-N-C planes is ~12^o (Figure 1B). Molecule **4k** adopts a spiral-like shape: the dihedral angle between the planes of the neighbouring benzene rings is ~33-35^o (Figure 2).



A – ORTEP plots for X-ray crystal structure of **4a** with crystallographic numbering scheme (two independent molecules in the unit cell; the length of intramolecular hydrogen bond is marked in red)



B – view on the molecule **4a**, showing that the cycle closed by intramolecular hydrogen bond is not planar (C – grey, N – blue, O – red, H – white)

Figure 1. The X-ray crystal structure of **4a**.

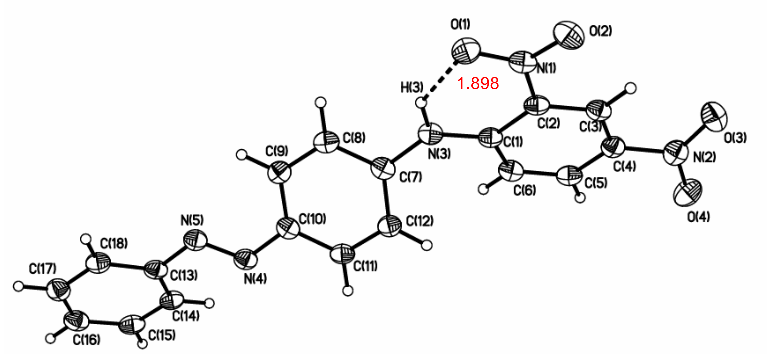


Figure 2. The X-ray crystal structure of **4k** (the length of intramolecular hydrogen bond is marked in red).

Conclusions

In the present paper we have shown that *N*-aryl-2,4-dinitroanilines and *N*-aryl-5-nitropyridin-2-amines may be easily obtained from 1,3-dinitrobenzene and 3-nitropyridine, respectively, through oxidative nucleophilic substitution of hydrogen, using the metal amides of a range of aryl(hetaryl)amines as reactants. The reaction proceeds under anaerobic conditions. The nitroarene plays the dual role in this reaction acting as the substrate and oxidizing agent.

Experimental Section

General. ^{1}H NMR spectra were obtained on a Bruker DPX-250 (250 MHz) and Bruker Avance 400 (400 MHz) spectrometers. ^{13}C NMR spectra were recorded on a Bruker DPX-250 (62.9 MHz) and Bruker Avance 400 (100 MHz) spectrometers. ^{1}H and ^{13}C NMR chemical shifts are in parts per million relative to Me_4Si. Coupling constants are in Hertz. IR spectra were recorded on a Varian Excalibur 3100 FT-IR and Cary 50 Probe spectrometers using Nujol. UV spectra were registered on a FSM-1201 spectrophotometer with $CHCl_3$ as a solvent. Mass spectra were measured on a Finnigan MAT INCOS 50 spectrometer. CHN analysis was accomplished by combustion analysis (Dumas and Pregl method). Melting points were determined in glass capillaries using a PTP device and are uncorrected. Column chromatography was performed on silica gel 60 (70-200 mesh; Merck). All commercial reagents (3-nitropyridine, 1,3-dinitrobenzene, aryl- and hetarylamines, BuLi, THF) were purchased from Acros and Aldrich and used without additional purification.

Crystallographic data for **4a** and **4k** (atomic coordinates, bond lengths, bond angles and thermal parameters) have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition number CCDC 815054 (**4a**) and CCDC815055(**4k**).

^{1}H and ^{13}C NMR spectra of all **2** and **4** as well as crystallographic data for **4a** and **4k** are available as supporting information.

General procedure for the synthesis of *N*-aryl-5-nitropyridin-2-amines (2a-d)

Lithium arylamide was prepared by treating arylamine (1.6 mmol) with butyl lithium (1.7 mmol, 1.6M solution in hexane) in anhydrous THF (4 mL) at -78…-70 °C under argon. Solution of 3-nitropyridine **1** (124 mg, 1 mmol) in THF (1 mL) was added dropwise. The resulting mixture was stirred for 16-19 h with gradual warming to room temperature. The reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate (5 x 10 mL). The organic extract was dried over $MgSO_4$, concentrated and purified by silica gel chromatography using dichloromethane/methanol (100 : 1) mixture as the eluent. The bright yellow fraction was collected. Subsequent recrystallization of the crude product from heptane or toluene gave **2** in the yield pointed in Table 1.

5-Nitro-*N*-(pyridin-2-yl)pyridin-2-amine (2a). Yellow needles, mp 200-201 °C (heptane), ref.[14] 196-197.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.16 (dd, *J* = 2.8, 0.6 Hz, 1H, 6-H), 8.40 (dd, *J* = 9.3, 2.8 Hz, 1H, 4-H), 8.37 (ddd, *J* = 5.0, 1.9, 0.8 Hz, 1H, 6′-H), 7.89 (d, *J* = 9.3 Hz, 1H, 3-H), 7.87 (br s, 1H, NH), 7.72 (ddd, *J* = 8.3, 7.3, 1.9 Hz, 1H, 4′-H), 7.49 (dm, *J* = 8.3 Hz, 1H, 3′-H), 7.03 (ddd, *J* = 5.0, 7.3, 0.9 Hz, 1H, 5′-H). ^{13}C NMR (DMSO-D_6, 100 MHz) δ 158.4, 153.4, 148.1, 145.8, 138.6, 137.6, 133.6, 118.6, 113.8, 111.0. IR: 3269 (N-H), 1496 and 1331 cm^{-1} (NO_2). UV, λ_{max} (lg ε): 290 sh (2.56), 362 (3.31), end absorption up to 443 nm. MS, *m/z* (I ≥ 10%): 216 (100) $[M]^+$, 215 (77), 170 (23), 169 (39) $[M\text{-}HNO_2]^+$, 79 (16), 78 (71), 52 (13), 51 (21). Anal. Calcd for $C_{10}H_8N_4O_2$: C, 55.55; H, 3.73; N, 25.91%. Found: C, 55.39; H, 4.04; N, 25.72%.

***N*-(5-Nitropyridin-2-yl)quinolin-2-amine (2b).** Yellow powder, mp 235-237 °C (toluene). ^{1}H NMR (DMSO-D_6, 400 MHz): δ 9.16 (dd, *J* = 2.8, 0.5 Hz, 1H, 6′-H), 8.66 (d, *J* = 9.3 Hz, 1H, 3′-H), 8.55 (dd, *J* = 9.3, 2.8 Hz, 1H, 4′-H), 8.29 (d, *J* = 8.9 Hz, 1H, 4-H), 7.84-7.88 (m, 3H, 5-H, 8-H and NH), 7.70 (ddd, *J* = 7.0, 8.4, 1.5 Hz, 1H, 6-H), 7.68 (d, *J* = 8.9 Hz, 1H, 3-H), 7.46 (ddd, *J* = 7.0, 8.0, 1.1 Hz, 1H, 7-H). ^{13}C NMR (DMSO-D_6, 100 MHz): δ 158.2, 152.6, 146.7, 145.6, 138.5, 138.2, 134.0, 130.4, 128.2, 127.4, 125.2, 124.9, 115.0, 111.6. IR: 3356 (N-H), 1495 and 1327 cm^{-1} (NO_2). UV, λ_{max} (lg ε): 300 (2.86), 328 (2.97), 370 (3.44), end absorption up to 480 nm. MS, *m/z* (I ≥ 10%): 266 (75) $[M]^+$, 265 (63), 220 (24), 219 (41) $[M-HNO_2]^+$, 129 (25), 128 (100), 110 (14), 102 (12), 101 (29), 77 (17), 51 (15). Anal. Calcd for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04%. Found: C, 62.87; H, 4.03; N, 21.36%.

5-Nitro-*N*-phenylpyridin-2-amine (2c). Yellow needles, mp 135-136 ºC (heptane), ref.[15] 135 ºC. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 9.08 (d, *J* = 2.7 Hz, 1H, 6-H), 8.24 (dd, *J* = 9.3, 2.7 Hz, 1H, 4-H), 7.34-7.45 (m, 4H, Ph and NH), 7.19-7.30 (m, 2H, Ph), 6.77 (dd, *J* = 9.3, 0.5 Hz, 1H, 3-H). IR: 3237 (N-H), 1505 and 1335 cm^{-1} (NO_2). UV, λ_{max} (lg ε): 366 (3.30), end absorption up to 474 nm. MS, *m/z* (I ≥ 10%): 215 (89) $[M]^+$, 214 (100), 169 (18), 168 (71) $[M-HNO_2]^+$, 142 (14), 115 (25), 84 (12), 78 (16), 77 (58), 65 (24), 51 (37). Anal. Calcd for $C_{11}H_9N_3O_2$: C, 61.39; H, 4.22; N, 19.53%. Found: C, 61.64; H, 4.30; N, 19.32%.

***N*-(5-Nitropyridin-2-yl)benzimidamide (2d).** Yellow needles, decomp. >185 ºC (heptane). ^{1}H NMR (DMSO-D$_6$, 400 MHz): δ 10.69 (br s, 1H, NH), 9.21 (dd, *J* = 2.9, 0.5 Hz, 1H, 6′-H), 8.37 (dd, *J* = 9.0, 2.9 Hz, 1H, 4′-H), 7.96 (m, 2H, Ph), 7.47-7.55 (m, 3H, Ph), 7.30 (d, *J* = 9.0 Hz, 1H, 3′-H), 6.35 (br s, 1H, NH). ^{13}C NMR (DMSO-D$_6$, 100 MHz): δ 166.9, 160.8, 143.9, 137.9, 135.3, 132.3, 131.3, 128.2, 127.7, 121.1. IR: 3326 and 3162 (N-H), 1519 and 1337 cm^{-1} (NO_2). UV, λ_{max} (lg ε): 266 (4.06), 314 (4.40), 376 sh (3.57), end absorption up to 436 nm. MS, *m/z* (I ≥ 10%): 242 (36) $[M]^+$, 241 (100), 195 (33) $[M-HNO_2]^+$, 194 (14), 104 (78), 77 (66), 66 (15), 51 (28). Anal. Calcd for $C_{12}H_{10}N_4O_2$: C, 59.50; H, 4.16; N, 23.13%. Found: C, 59.22; H, 4.41; N, 22.86%.

General procedure for the synthesis of 2,4-dinitro-*N*-arylanilines (4a-m)

Lithium arylamide was prepared by treating arylamine (1.6 mmol) with butyl lithium (1.7 mmol, 1.6M solution in hexane) in anhydrous THF (8 mL) at -78…-70 ºC under argon. Solution of 1,3-dinitrobenzene **3** (168 mg, 1 mmol) in THF (2 mL) was added dropwise. The resulting mixture was stirred for 16-19 h with gradual warming to room temperature. The reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate (5 x 15 mL). The organic extract was dried over MgSO$_4$, concentrated and purified by silica gel chromatography using the next mixtures as the eluent: dichloromethane/hexane (10:1) for **4a-d,f**; dichloromethane/hexane (5:1) for **4g,i,k,m**; dichloromethane for **4h,j**; diethyl ether/hexane (1:1) for **4e**; hexane/ethyl acetate (3:1) for **4l**. From the first colorless fraction 1,3-dinitrobenzene was recovered (from the reaction with *o*-toluidine – 87 mg, *p*-anisidine – 47 mg, *o*-anisidine – 102 mg, *p*-nitroaniline – 72 mg, 4-aminoazobenzene – 58 mg). The bright yellow fraction was collected. Subsequent recrystallization of the crude product from heptane gave **4** in the yield pointed in Table 2.

***N*-(2,4-Dinitrophenyl)pyridin-2-amine (4a)**. Orange needles, mp 154-156 ºC (heptane), ref.[16] 155 ºC. ^{1}H NMR (DMSO-D$_6$, 250 MHz): δ 10.34 (br s, 1H, NH), 8.79 (s, 1H, 3′-H), 8.29-8.46 (m, 2H, 3-H, 5′-H and 6-H), 7.82 (m, 1H, 4-H), 7.26 (d, *J* = 7.9 Hz, 1H, 6′-H), 7.19 (m, 1H, 5-H). ^{13}C NMR (DMSO-D$_6$, 62.9 MHz): δ 153.2, 148.2, 142.7, 139.6, 139.3, 135.8, 129.9, 123.2, 121.7, 120.1, 115.8. IR: 3304 (N-H), 1514, 1494, 1335 and 1296 cm^{-1} (NO_2). UV, λ_{max} (lg ε): 355 (4.13), end absorption up to 511 nm. MS, *m/z* (I ≥ 10%): 260 (5) $[M]^+$, 214 (31) $[M-NO_2]^+$, 168 (54) [M-2NO$_2$]$^+$, 140 (10), 88 (12), 74 (40), 67 (12), 63 (53), 51 (100), 46 (90), 39 (63). Anal. Calcd for $C_{11}H_8N_4O_4$: C, 50.77; H, 3.10; N, 21.53%. Found: C, 50.99; H, 3.25; N, 21.27%.

***N*-(2,4-Dinitrophenyl)pyridin-4-amine (4b).** Bright yellow needles, mp 198-200 °C (heptane). ^{1}H NMR (DMSO-D$_6$, 250 MHz): δ 9.98 (br s, 1H, NH), 8.84 (d, *J* = 2.7 Hz, 1H, 3′-H), 8.51 (m, 2H, 2-H and 6-H), 8.31 (dd, *J* = 9.4, 2.7 Hz, 1H, 5′-H), 7.59 (d, *J* = 9.4 Hz, 1H, 6′-H), 7.32 (br d, *J* = 5.9 Hz, 2H, 3-H and 5-H). ^{13}C NMR (CDCl$_3$, 62.9 MHz): δ 151.7, 147.0, 144.1, 139.5, 135.7, 130.4, 123.9, 120.1, 117.1. IR: 3325 (N-H), 1514 and 1336 cm^{-1} (NO$_2$). UV, λ_{max} (lg ε): 325 (4.13), 351 (4.11), end absorption up to 471 nm. MS, *m/z* (I ≥ 10%): 260 (65) [M]$^+$, 197 (10), 191 (10), 184 (10), 168 (35) [M-2NO$_2$]$^+$, 155 (22), 140 (57), 130 (22), 114 (47), 102 (12), 93 (11), 88 (29), 78 (70), 63 (47), 51 (100), 46 (25), 39 (27). Anal. Calcd for $C_{11}H_8N_4O_4$: C, 50.77; H, 3.10; N, 21.53%. Found: C, 51.04; H, 3.38; N, 21.42%.

***N*-(2,4-Dinitrophenyl)naphthalen-2-amine (4c).** Orange needles, mp 171-173 °C (heptane), ref.[17] 173 °C. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 10.11 (br s, 1H, NH), 9.14 (d, *J* = 2.5 Hz, 1H, 3′-H), 8.13 (dd, *J* = 9.5, 2.2 Hz, 1H, 5′-H), 7.96 (d, *J* = 8.5 Hz, 1H, 4-H), 7.83-7.90 (m, 2H, naphthalene), 7.76 (d, *J* = 1.3 Hz, 1H, 1-H), 7.51-7.58 (m, 2H, naphthalene), 7.37 (dd, *J* = 8.5, 2.2 Hz, 1H, 3-H), 7.21 (d, *J* = 9.5 Hz, 1H, 6′-H). ^{13}C NMR (CDCl$_3$, 62.9 MHz): δ 147.4, 137.9, 134.5, 134.3, 132.6, 131.7, 130.8, 130.3, 128.3, 128.1, 127.7, 127.2, 124.5, 123.9, 123.8, 116.6. IR: 3309 (N-H), 1513, 1347 and 1328 cm^{-1} (NO$_2$). UV, λ_{max} (lg ε): 355 (3.89), end absorption up to 521 nm. MS, *m/z* (I ≥ 10%): 309 (100) [M]$^+$, 262 (10), 246 (23), 217 (76) [M-2NO$_2$]$^+$, 216 (80), 204 (24), 189 (57), 163 (13), 152 (10), 139 (14), 127 (58), 115 (58), 109 (16), 102 (16), 94 (18), 89 (15), 77 (37), 63 (48), 51 (19), 46 (17), 44 (19), 38 (16). Anal. Calcd for $C_{16}H_{11}N_3O_4$: C, 62.14; H, 3.58; N, 13.59%. Found: C, 61.79; H, 3.90; N, 13.21%.

***N*-(2,4-Dinitrophenyl)naphthalen-1-amine (4d)**. Orange crystals, mp 190-191 °C (heptane), ref.[18] 190-191 °C. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 10.17 (br s, 1H, NH), 9.23 (d, *J* = 2.7 Hz, 1H, 3′-H), 8.06 (dd, *J* = 9.5, 2.7 Hz, 1H, 5′-H), 7.92-7.99 (m, 2H, naphthalene), 7.83-7.87 (m, 1H, naphthalene), 7.47-7.62 (m, 4H, naphthalene), 6.77 (d, *J* = 9.5 Hz, 1H, 6′-H). ^{13}C NMR (DMSO-D$_6$, 62.9 MHz): δ 149.0, 136.9, 135.2, 134.7, 131.7, 130.7, 130.5, 129.4, 129.2, 128.0, 127.7, 127.1, 126.2, 124.3, 123.5, 117.8. IR: 3313 (N-H), 1519 and 1334 cm^{-1} (NO$_2$). UV, λ_{max} (lg ε): 348 (4.12), end absorption up to 506 nm. MS, *m/z* (I ≥ 10%): 309 (33) [M]$^+$, 229 (10), 216 (100), 204 (25), 189 (41), 163 (14), 153(15), 139 (11), 127 (56), 115 (43), 107 (13), 101 (16), 89 (14), 77 (35), 63 (98), 52 (35), 46 (82), 39 (30). Anal. Calcd for $C_{16}H_{11}N_3O_4$: C, 62.14; H, 3.58; N, 13.59%. Found: C, 62.50; H, 3.92; N, 13.32%.

2,4-Dinitro-*N*-phenylaniline (4e). Orange-red needles, mp 157-159 °C (heptane), ref.[18] 153-155 °C. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 9.96 (br s, 1H, NH), 9.15 (d, *J* = 2.5 Hz, 1H, 3-H), 8.15 (dd, *J* = 9.5, 2.5 Hz, 1H, 5-H), 7.46-7.53 (m, 2H, Ph), 7.24-7.40 (m, 3H, Ph), 7.15 (d, *J* = 9.5 Hz, 1H, 6-H). ^{13}C NMR (CDCl$_3$, 62.9 MHz): δ 147.5, 137.8, 137.1, 131.5, 130.7, 130.3, 128.2, 125.9, 124.5, 116.5. IR: 3319 (N-H), 1518, 1495 and 1336 cm^{-1} (NO$_2$). UV, λ_{max} (lg ε): 355 (4.07), end absorption up to 530 nm. MS, *m/z* (I ≥ 10%): 259 (100) [M]$^+$, 196 (16), 182 (12), 167 (58) [M-2NO$_2$]$^+$, 154 (19), 139 (41), 128 (11), 113 (10), 97 (13), 89 (12), 83 (16), 77 (61), 69 (28), 63

(34), 57 (52), 51 (64), 46 (49), 43 (89), 38 (14). Anal. Calcd for $C_{12}H_9N_3O_4$: C, 55.60; H, 3.50; N, 16.21%. Found: C, 55.84; H, 3.17; N, 15.98%.

2,4-Dinitro-*N*-*p*-tolylaniline (4f). Orange needles, mp 133-135 °C (heptane), ref.[18] 134-135 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 9.91 (br s, 1H, NH), 9.14 (d, *J* = 2.5 Hz, 1H, 3-H), 8.12 (dd, *J* = 9.5, 2.5 Hz, 1H, 5-H), 7.07-7.30 (m, 5H, *p*-Tol and 6-H), 2.40 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 147.9, 138.3, 137.6, 134.4, 131.3, 131.2, 130.3, 126.0, 124.5, 116.5, 21.5. IR: 3311 (N-H), 1519, 1337 and 1318 cm^{-1} (NO_2). UV, λ_{max} (lg ε): 355 (4.19), end absorption up to 513 nm. MS, *m/z* (I ≥ 10%): 273 (100) [M]$^+$, 226 (11), 210 (11), 180 (93) [M-2NO$_2$-H]$^+$, 152 (17), 139 (13), 91 (18), 77 (16), 65 (20), 51 (11), 46 (16), 39 (14). Anal. Calcd for $C_{13}H_{11}N_3O_4$: C, 57.14; H, 4.06; N, 15.38%. Found: C, 56.86; H, 4.23; N, 15.65%.

2,4-Dinitro-*N*-*o*-tolylaniline (4g). Orange needles, mp 124-126 °C (heptane), ref.[18] 125-126 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 9.81 (br s, 1H, NH), 9.19 (d, *J* = 2.7 Hz, 1H, 3-H), 8.13 (dd, *J* = 9.5, 2.7 Hz, 1H, 5-H), 7.23-7.40 (m, 4H, *o*-Tol), 6.81 (d, *J* = 9.5 Hz, 1H, 6-H), 2.25 (s, 3H, Me). ^{13}C NMR (DMSO-D$_6$, 62.9 MHz): δ 148.1, 137.0, 136.7, 136.1, 132.2, 131.2, 130.8, 128.9, 128.4, 128.2, 124.3, 117.2, 18.2. IR: 3330 (N-H), 1515, 1497 and 1340 cm^{-1} (NO_2). UV, λ_{max} (lg ε): 348 (4.20), end absorption up to 500 nm. MS, *m/z* (I ≥ 10%): 273 (37) [M]$^+$, 180 (100) [M-2NO$_2$-H]$^+$, 152 (39), 139 (20), 128 (15), 115 (10), 91 (38), 77 (48), 65 (74), 51 (38), 46 (92), 39 (60). Anal. Calcd for $C_{13}H_{11}N_3O_4$: C, 57.14; H, 4.06; N, 15.38%. Found: C, 57.41; H, 4.33; N, 15.12%.

***N*-(4-Methoxyphenyl)-2,4-dinitroaniline (4h)**. Orange-red needles, mp 139-141 °C (heptane), ref.[18] 139-140 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 9.85 (br s, 1H, NH), 9.16 (d, *J* = 2.6 Hz, 1H, 3-H), 8.12 (dd, *J* = 9.6, 2.6 Hz, 1H, 5-H), 7.20 (d, *J* = 9.0 Hz, 2H, 3′-H and 5′-H), 6.99 (m, 3H, 6-H, 2′-H and 6′-H), 3.85 (s, 3H, OMe). ^{13}C NMR (DMSO-D$_6$, 62.9 MHz): δ 159.1, 148.4, 136.8, 131.4, 131.0, 130.6, 128.6, 124.3, 117.6, 115.8, 56.3. IR: 3314-3341 (N-H), 1520, 1511, 1335 and 1320 cm^{-1} (NO_2). UV, λ_{max} (lg ε): 274 (3.75), 356 (4.09), end absorption up to 526 nm. MS, *m/z* (I ≥ 10%): 289 (100) [M]$^+$, 274 (21), 242 (14), 227 (14), 209 (17), 197 (11) [M-2NO$_2$]$^+$, 196 (11), 182 (54), 154 (64), 126 (34), 123 (37), 92 (14), 77 (29), 63 (43), 51 (21), 46 (22). Anal. Calcd for $C_{13}H_{11}N_3O_5$: C, 53.98; H, 3.83; N, 14.53%. Found: C, 54.29; H, 3.63; N, 14.25%.

***N*-(2-Methoxyphenyl)-2,4-dinitroaniline (4i).** Orange-red needles, mp 165-166 °C (heptane), ref.[19] 167-168 °C (ethanol). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 9.86 (br s, 1H, NH), 9.16 (d, *J* = 2.5 Hz, 1H, 3-H), 8.15 (dd, *J* = 9.6, 2.5 Hz, 1H, 5-H), 7.26-7.38 (m, 2H, 3′-H and 6′-H), 7.09 (d, *J* = 9.6 Hz, 1H, 6-H), 6.98-7.07 (m, 2H, 4′-H and 5′-H), 3.85 (s, 3H, OMe). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 153.9, 147.2, 137.7, 131.8, 130.0, 128.9, 125.9, 125.8, 124.4, 121.5, 116.7, 112.5, 56.2. IR: 3312 (N-H), 1521, 1499, 1337 and 1303 cm^{-1} (NO_2). UV, λ_{max} (lg ε): 262 (3.58), 272 (3.81), 362 (4.11), end absorption up to 531 nm. MS, *m/z* (I ≥ 10%): 289 (100) [M]$^+$, 257 (16), 227 (14), 182 (16), 154 (17), 127 (12), 77 (26), 63 (32), 51 (24), 39 (17). Anal. Calcd for $C_{13}H_{11}N_3O_5$: C, 53.98; H, 3.83; N, 14.53%. Found: C, 53.72; H, 3.50; N, 14.81%.

2,4-Dinitro-*N*-(4-nitrophenyl)aniline (4j). Yellow needles, mp 185-187 °C (heptane), ref.[20] 186-186.7 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 10.04 (br s, 1H, NH), 9.19 (d, *J* = 2.5 Hz, 1H, 3-H), 8.27-8.38 (m, 3H, 3′-H, 5′-H and 5-H), 7.41-7.49 (m, 3H, 2′-H, 6′-H and 6-H). ^{13}C NMR

(DMSO-D_6, 62.9 MHz): δ 146.2, 144.4, 139.6, 135.7, 130.4, 126.2, 123.9, 123.4, 123.3, 120.3. IR: 3308 (N-H), 1515 and 1334 cm^{-1} (NO_2). UV, λ_{max} (lg ε): 274 (4.17), 360 (4.36), end absorption up to 490 nm. MS, *m/z* ($I \geq 5\%$): 304 (100) $[M]^+$, 274 (12), 241 (5), 182 (9), 166 (16), 154 (9), 139 (20), 76 (5), 63 (11). Anal. Calcd for $C_{12}H_8N_4O_6$: C, 47.38; H, 2.65; N, 18.42%. Found: C, 47.09; H, 2.54; N, 18.23%.

2,4-Dinitro-*N*-(4-(phenyldiazenyl)phenyl)aniline (4k). Red needles, mp 174-176 °C (heptane), ref.[21]. ^1H NMR ($CDCl_3$, 250 MHz): δ 10.06 (br s, 1H, NH), 9.19 (d, *J* = 2.2 Hz, 1H, 3-H), 8.23 (dd, *J* = 9.5, 2.2 Hz, 1H, 5-H), 8.04 (d, *J* = 8.5 Hz, 2H, 3′-H and 5′-H), 7.93 (m, 2H, Ph), 7.52 (m, 3H, Ph), 7.45 (d, *J* = 8.5 Hz, 2H, 2′-H and 6′-H), 7.35 (d, *J* = 9.5 Hz, 1H, 6-H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 152.9, 151.5, 146.5, 139.4, 138.4, 132.3, 131.9, 130.5, 129.6, 125.5, 125.1, 124.5, 123.4, 116.7. IR: 3299 (N-H), 1514 and 1340 cm^{-1} (NO_2). UV, λ_{max} (lg ε): 368 (4.26), end absorption up to 552 nm. MS, *m/z* ($I \geq 10\%$): 363 (16) $[M]^+$, 258 (26), 139 (14), 105 (13), 92 (18), 77 (98), 63 (21), 51 (47), 39 (12). Anal. Calcd for $C_{18}H_{13}N_5O_4$: C, 59.50; H, 3.61; N, 19.28%. Found: C, 59.58; H, 3.44; N, 19.56%.

***N*-(2,4-Dinitrophenyl)thiazol-2-amine (4l)**. Orange crystals, mp 153-155 °C (heptane). ^1H NMR (DMSO-D_6, 250 MHz): δ 11.0 (br s, 1H, NH), 8.80 (d, *J* = 2.8 Hz, 1H, 3′-H), 8.59 (d, *J* = 9.5 Hz, 1H, 6′-H), 8.45 (dd, *J* = 9.5, 2.5 Hz, 1H, 5′-H), 7.50 (d, *J* = 3.8 Hz, 1H, 5-H), 7.36 (d, *J* = 3.8 Hz, 1H, 4-H). ^{13}C NMR (DMSO-D_6, 62.9 MHz): δ 161.9, 142.1, 139.8, 135.6(1), 135.6(0), 130.3, 123.0, 120.8, 115.9. IR: 3293 (N-H), 1519, 1504, 1338 and 1311 cm^{-1} (NO_2). UV, λ_{max} (lg ε): 266 (4.06), 356 (4.20), end absorption up to 518 nm. MS, *m/z* ($I \geq 10\%$): 266 (100) $[M]^+$, 249 (31), 220 (18) $[M-NO_2]^+$, 193 (50), 174 (31), $[M-2NO_2]^+$, 129 (11), 103 (14), 100 (24), 75 (33), 63 (43), 58 (84), 50 (19), 45 (72), 40 (20). Anal. Calcd for $C_9H_6N_4O_4S$: C, 40.60; H, 2.27; N, 21.04; S, 12.04%. Found: C, 40.25; H, 2.03; N, 21.36; S, 11.70%.

***N*-(2,4-Dinitrophenyl)benzamide (4m).** Yellow needles, mp 194-196 °C (heptane). ^1H NMR (DMSO-D_6, 250 MHz): δ 11.23 (br s, 1H, NH), 8.76 (d, *J* = 2.3 Hz, 1H, 3′-H), 8.60 (dd, *J* = 9.1, 2.3 Hz, 1H, 5′-H), 8.14 (d, *J* = 9.1 Hz, 1H, 6′-H), 7.99 (d, *J* = 7.5 Hz, 2H, 2-H and 6-H), 7.59-7.73 (m, 3H, 3-H, 4-H and 5-H). ^{13}C NMR (DMSO-D_6, 62.9 MHz): δ 166.4, 143.7, 141.8, 138.2, 133.8, 133.7, 129.7, 129.5, 128.8, 126.4, 122.1. IR: 3102-3132 (N-H), 1699 (C=O), 1339 cm^{-1} (NO_2). UV, λ_{max} (lg ε): 304 (4.57), end absorption up to 434 nm. MS, *m/z* ($I \geq 5\%$): 287 (7) $[M]^+$, 105 (100), 77 (50), 51 (14). Anal. Calcd for $C_{13}H_9N_3O_5$: C, 54.36; H, 3.16; N, 14.63%. Found: C, 54.08; H, 3.33; N, 14.39%.

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