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A two-step oxidative aromatic substitution of hydrogen as a convenient way to 2-nitrodiarylamines

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ABSTRACT

A method for the synthesis of differently substituted 2-nitrodiarylamines via nucleophilic substitution of hydrogen in nitroarenes is described. In the two-step procedure, the first step omits classical substitution of halogens in starting nitroarenes and occurs efficiently at the position *ortho* to the activating group. Subsequent oxidation of the 2-nitrosoanilines so formed is accomplished with a cheap and environmentally friendly reagent, sodium perborate, under mild conditions. In exceptional cases of the amine-substituted nitrosoanilines, more selective oxidant (IBX) is required.

1. Introduction

2-Nitrodiarylamines play an important role in organic synthesis as intermediates in numerous syntheses of a variety of polynitrogen heterocyclic compounds. In addition, they are important in bio-organic as well as material chemistry, and some of them have been reported to exhibit biological activity themselves (Fig. 1). Even the simplest 2-nitrodiphenylamine was found to be capable of some inhibition of amyloid fibril formation.[1] Diversely substituted derivatives of general formula **A** act as fungicides,[2] **B** exhibits anti-HIV and cytotoxic activity[3] and **C** shows inhibitory effect on AKR1C3 enzyme.[4]

Despite the above applications, the number of convenient methods for the synthesis of these compounds is rather limited. The most popular one is substitution of halogens (fluorine or chlorine) with an appropriate arylamine according to the S_NAr scheme, carried out under basic conditions[3,5] which can be moderated by the use of microwave irradiation.[5c] Other good leaving groups in that reaction, for instance NO_2, are less common.[6] Substitution of poorer nucleofuges such as Br, I or $OSO_2C_4F_9$,[7] usually required Pd-based catalysts in the Buchwald-Hartwig reaction.[8] Pd- or Cu catalyzed cross-coupling reactions were used also for *N*-arylation of unsubstituted *ortho*-nitroanilines.[9] Occasionally, decarboxylative substitution of COOH group[10] and Smiles/Chapman rearrangement[11] leading to *o*-nitrodiarylamines were reported. The most common methods require starting nitroarenes *ortho* substituted with halogens or other functional groups wasted during the substitution process, the use of metal catalysts, and often harsh reaction conditions. Reported environmentally oriented methods apparently could not avoid all of those problems.[5d]

A valuable alternative for the S_NAr substitution of halogens is nucleophilic aromatic substitution of hydrogen that can be accomplished by means of various routes.[12] The most regarded, and of broader application in synthesis are vicarious (VNS) and oxidative (ONSH) nucleophilic substitution of hydrogen. Both VNS[13] and ONSH[14] were used successfully for the amination of nitroarenes. However, while substitution of hydrogen with an unsubstituted amino group by both methods is rather easy and quite general as regards the nitroarene, *N*-arylamination is much more restricted. An oxidative process was found to be effective mainly for relatively electron-poor, reactive nitroarenes such as nitropyridine, nitronaphthalene or 2,4-dinitrobezene derivatives.[14] Intermolecular oxidative arylamination of mononitrobenzene was reported but only *para* hydrogen can be substituted that way.[15] The same limitation was found for the VNS arylamination of nitrobenzene derivatives with *N*-arylsulfenamides.[13a] Low nucleophilicity of the arylamine nucleophile and in certain cases steric hindrance, can be responsible for preferred *para* addition to the aromatic ring. Furthermore, the competing *ortho* addition often leads to some undesired processes. One example is the well-known Wohl-Aue

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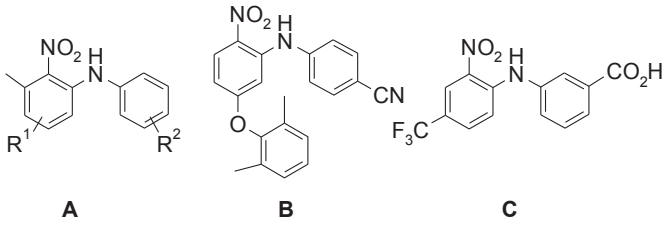


Fig. 1. Biologically active derivatives of 2-nitrodiarylamine.

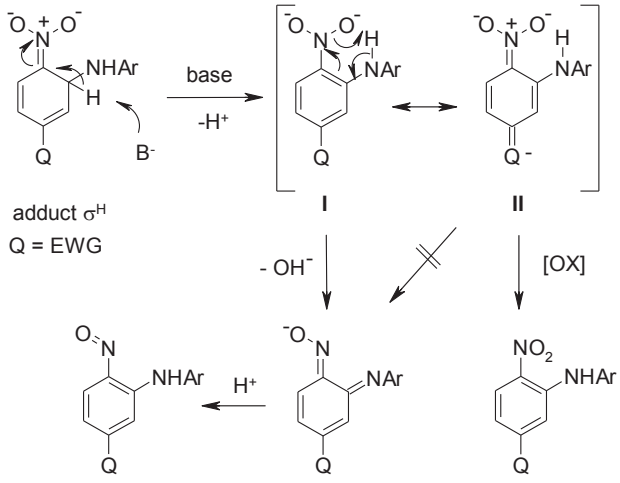
condensation of nitroarenes with aniline anions furnishing phenazines.[16] The crucial step of this process comprises substitution of the *ortho* hydrogen atom with concurrent reduction of the nitro group, hence, the formation of intermediate *ortho*-nitrosodiphenylamine which undergo fast cyclization to the condensed system.[16c]

In the course of our studies on the nucleophilic substitution of hydrogen in nitroarenes we found that when the anilide anion was generated by *t*-BuOK in THF or DMF at low temperature and was reacted with nitroarenes, the reaction provided *N*-aryl-2-nitrosoanilines,[17] compounds for the synthesis of which there were no usable methods until that time.[18] That is, by application of properly selected conditions the Wohl-Aue condensation could be halted after its first step, and the *ortho*-arylamination of the nitroarenes was achieved, although at the expense of the nitro group being reduced.

Despite a broad scope of nitroarenes and arylamines which successfully form *N*-aryl-2-nitrosoanilines,[17,19] in several cases, the reaction does not occur selectively. The main products are accompanied with some amount of the corresponding 2-nitrodiarylamines, apparently formed in the competitive oxidative substitution reaction. It seemed to be of interest to examine this undesired process and to try to employ it for the practical synthesis of 2-nitrodiarylamines by nucleophilic substitution of hydrogen.

2. Results and discussion

Under the standard, anaerobic reaction conditions used for the formation of *N*-aryl-2-nitrosoanilines the spontaneous oxidative process appeared to be rather exceptional, and restricted to the relatively electron-poor reactants collected in Table 1. In certain



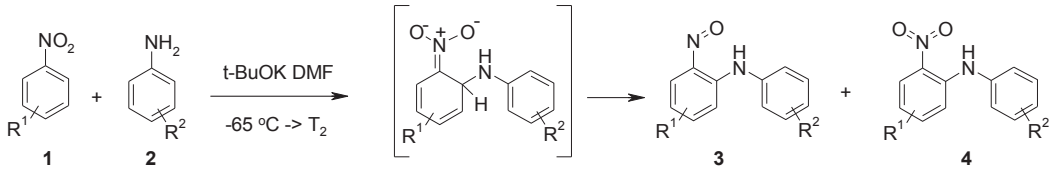
Scheme 1. Two possible routes of transformation of the σH-adducts under basic conditions.

cases, however, the nitroanilines **4** are the only isolable products (entries 5–7). These observations appear to be in accord with the proposed mechanism of the reaction,[17b] involving base-promoted deprotonation of the σ-adduct to create a dianionic form susceptible for both intramolecular elimination of water and oxidation by the starting nitroarene as an oxidant (Scheme 1).

The electron-withdrawing substituents present in both reactants apparently favor the latter process. Scheme 1 shows how the electron-withdrawing group Q conjugates with a lone pair of the nitro group (mesomeric structure **II**) which hinders intramolecular elimination of OH^-. Consequently, formation of a nitroso group is obstructed and there is a chance for the oxidative process.

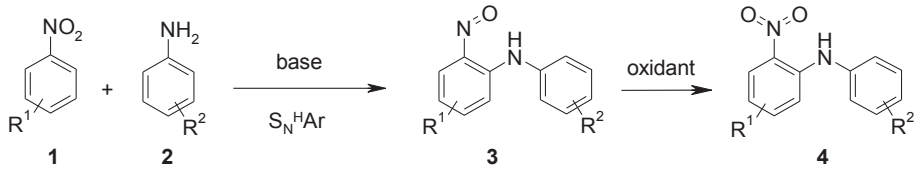
In accord with such understanding is an observation that *N*-methylaniline which lacks a suitable *N*-hydrogen atom is not susceptible to the intramolecular dehydration, and it reacted with nitroarenes giving products of ONSH exclusively, in yields dependent on the excess of the nitroarene used.[17b] Poor nucleophilicity of the arylamine anion (e.g. 4-cyanoaniline) is, supposedly, responsible for the unfavorable equilibrium constant of the σ^H-adduct formation, and consequently, for the relatively high concentration of the unbound starting nitroarene playing the role of an oxidant. In both cases, the use of larger excess of the nitroarene favors the

Table 1
The S_N^HAr reactions of electron-poor nitroarenes and anilines.



Entry	R1[a]	R2[a]	T2	3, Yield,[b] %		4, Yield,[b] %	
1	4-Cl	4-CN	−65 °C	**3a**	52 (27)[c]	**4a**	8 (31)[c]
2	4-Cl	2-CN	r.t.	**3b**	40	**4b**	20
3	2-Br-4-Cl	2-Br-4-Cl	−65 °C	**3c**	29	**4c**	41
4	4-CF_3	4-Cl	−65 °C	**3d**	18	**4d**	22
5	4-CF_3	4-CN	r.t.	**3e**	–	**4e**	56
6	4-CN	4-CN	r.t.	**3f**	–	**4f**	60
7	4-CN	4-Cl	−65 °C	**3g**	–	**4g**	40

[a] Numbering refers to the positions in the starting nitroarene and aniline.
[b] Isolated yields.
[c] In parentheses shown the yields of the reaction with 2 equiv. of **1**.



Scheme 2. Two-step synthesis of *o*-nitrodiarylamines via nucleophilic substitution of hydrogen.

oxidation and the yields of the corresponding nitroanilines **4** are significantly higher (Table 1, entry 1).

In order to direct the reaction of less electrophilic nitroarenes towards the oxidative process, several modifications of the reaction conditions were attempted, such as addition of external oxidants, changes of the solvent and temperature of the reaction. They were not successful, however, resulting in the formation of complex mixtures of products of chemo- and regio-unselective processes.[20] Since the main goal was to develop a simple, economical and environmental friendly protocol for the synthesis of 2-nitrodiarylamines from simple nitroarenes, we turned towards a two-step approach which comprises substitution of *ortho* hydrogen in nitroarenes with arylamines furnishing *N*-aryl-2-nitrosoanilines, followed by subsequent oxidation of the latter (Scheme 2).

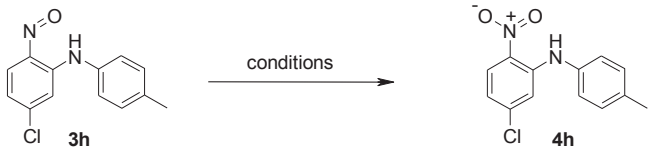
Oxidation of aromatic nitroso compounds to nitro compounds, a process known for over a century, can be achieved by several oxidizing agents which have been reviewed.[21] In fact, the reaction is of limited value in the synthesis of nitroaromatic compounds, because the latter are generally more readily available. It should be mentioned, however, that nitrosation of electron-rich aromatic rings followed by oxidation of the intermediate nitroso compounds with nitrous acid,[22] $K_3Fe(CN)_6$[23] was applied, instead of non-selective or low-yielding direct nitration, for the synthesis of some nitroarenes. For this aim to be achieved, catalytic oxidation by H_2O_2 in the presence of nitric acid,[24] CH_3ReO_3,[25] CrO_3[26] or $(NH_4)_6Mo_7O_{24}$[27] was also used successfully. A few examples of the occasional oxidation of *N*-substituted 2-nitrosoanilines using hydrogen peroxide under acidic[18a] or basic[18b,c] conditions as well as by *m*-CPBA[28] have been reported as a proof for the structure of the corresponding nitroso compounds.

Searching for a more general and efficient oxidation method, applicable for 2-nitrosoanilines, several experiments with the model nitrosoaniline **3h** were performed (Table 2).

Although a number of oxidizing systems gave reasonable yields of **4a**, we selected the relatively cheap and environmental friendly sodium perborate tetrahydrate which in subsequent experiments was found to be a convenient and efficient oxidant for a broad set of 2-nitrosoanilines **3** (Table 3). Sodium perborate is known as a versatile reagent usable for oxidation of different functional groups such as amines, sulfides, ketones, hydroquinones, but only one example of the oxidation of nitrosobenzene to nitrobenzene has been reported.[29] In the case of *N*-aryl-2-nitrosoanilines, possessing both reactive function, i.e. nitroso group and arylamino substituent, the oxidant was found to be selective enough, so that the amine nitrogen remained unaffected and the desired *N*-aryl-2-nitroanilines were obtained in high yields.

The reaction gave satisfactory results for nitrosoanilines **3** variously substituted with moderate electron-withdrawing and electron-donating groups in both aromatic rings, and was tolerant towards sensitive bromides and iodides. However, poor results were obtained in the oxidation of *N*-aryl-2-nitrosoanilines bearing additional 5-alkylamino or 5-dialkylamino groups in the nitrosoaromatic ring. The reactions produced multi-component mixtures, apparently as a result of unselective oxidation, involving not only a nitroso group, but also the alkylamino substituent. For such special type of nitrosoanilines a more selective oxidant was required. After some research, positive results were obtained with 2-iodoxybenzoic acid (IBX), the oxidant rather ineffective in the attempted oxidation of the model nitrosoaniline (Table 1). The oxidation of appropriate *N*-aryl-2-nitrosoanilines **5a-f** with IBX

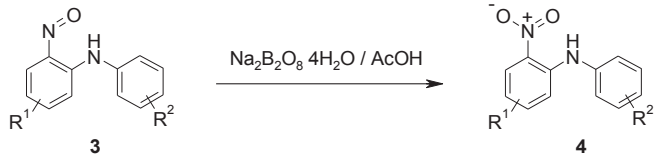
Table 2
Oxidation of nitrosoaniline **3h** under various conditions.



Entry	Oxidant	Catalyst (mol %)	Solvent	Temperature	Time,[a] h	Yield,[b] %
1	H_2O_2	NaOH (excess)	MeOH	r.t.	3	35
2	H_2O_2	–	AcOH	r.t.	24	46
3	H_2O_2	CrO_3 (30)	EtOH	60 °C	3	76
4	H_2O_2	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (30)	MeOH	60 °C	6	77
5	H_2O_2	$Na_2WO_4\cdot 2H_2O$ (15)	DCM[c]	r.t.	48[d]	traces
6	$Na_2BO_3\cdot 4H_2O$	–	AcOH	40 °C	2	99
7	*m*-CPBA	–	CH_2Cl_2	r.t	0.1	74
8	IBX[e]	-	DMSO	r.t or 40 °C	24	no reaction
9	IBX[e]	–	DMSO	110 °C	4	decomp.

[a] Reactions carried out until apparent disappearance of **3h** by tlc.
[b] Yields based on quantitative GC analyses.
[c] Vigorously stirred two-phase system.
[d] No conversion of **3h** was observed by tlc.
[e] 2-Iodoxybenzoic acid.

Table 3
Oxidation of nitrosoanilines **3h-x** with sodium perborate tetrahydrate.



Entry	R^1	R^2	3	Temp. °C	Time, h	4	Yield %[a]
1	5-Cl	4′-Me	**3h**	45	2	**4h**	92
2	5-F	4′-Me	**3i**	45	1	**4i**	64
3	5-F	2′,6′-Me_2	**3j**	45	1.5	**4j**	85
4	5-Cl	2′-I	**3k**	45	1.5	**4k**	98
5	5-OMe	4′-Br	**3l**	45	3	**4l**	90
6	4-CF_3	4′-Cl	**3m**	55	1	**4m**	98
7	4-CF_3	5′-Cl-2′-OMe	**3n**	55	2	**4n**	98
8	3,5-Cl_2	4′-Cl	**3o**	85	3	**4o**	56
9	5-Cl	4′-Cl	**3p**	45	2	**4p**	95
10	H	4′-OMe	**3q**	45	0.5	**4q**	84
11	5-Cl	2′-F	**3r**	45	0.5	**4r**	50
12	H	2′-Cl	**3s**	45	2	**4s**	74
13	5-Cl	2′-*t*-Bu	**3t**	45	1.5	**4t**	86
14	5-OMe	2′-*t*-Bu	**3u**	45	1.5	**4u**	96
15	5-Cl	2′-I-4′-Me	**3v**	45	10	**4v**	69
16	5-OMe	4′-Me	**3w**	45	2	**4w**	75
17	5-F	4′-Cl	**3x**	45	4	**4x**	95

[a] Isolated yield.

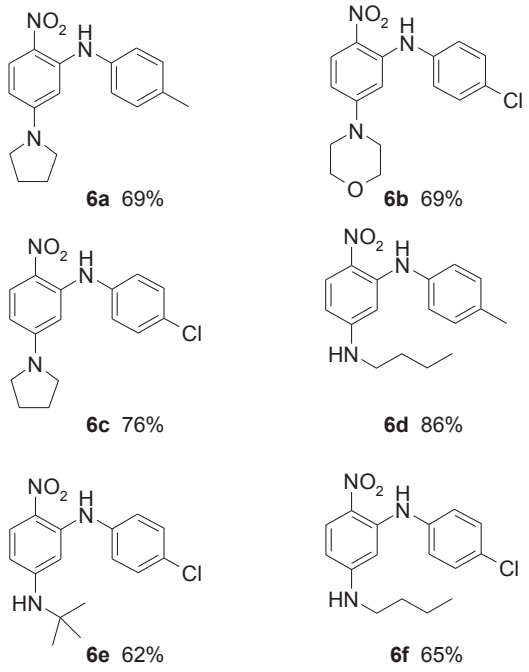


Fig. 2. Nitroanilines 6a-f obtained by oxidation of corresponding 5-amino-2-nitrosoanilines 5a-f.

(DMSO, room temperature, 20 h) gave nitroanilines **6a-f** collected in Fig. 2.

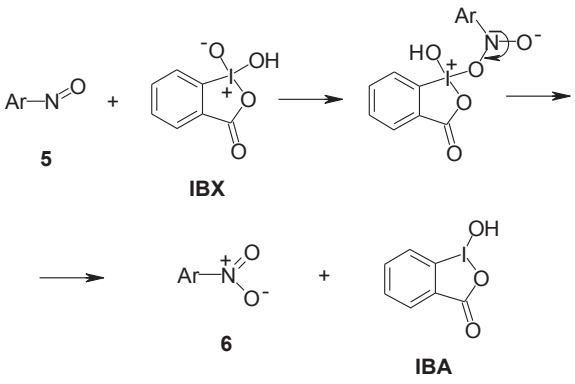
To our best knowledge, this versatile reagent[30] has never been used for oxidation of nitroso compounds, while the oxidation of arylamine[31] and anilide[32] groups have been reported. Thus, the selectivity of IBX in the oxidation of **5**, having three different nitrogen groups, might be a serious concern. In both reports, however, it was stated that an arylamine moiety substituted with strong EWG groups, such as nitro group, remained resistant towards this oxidant. Extensive mechanistic investigations led to the conclusion that several reactions of IBX, including oxidation of amines, are initiated by single electron transfer (SET) from the substrate to IBX to form a radical cation, a process which presumably is prevented by strong EWG. It is reasonable to assume, that a nitroso group should also prevent the undesired oxidation of the amine nitrogen atoms in the starting 5-amino-2-nitrosoanilines, and in the same way, the resulting nitro group prevents the product from undergoing undesired subsequent oxidation.

A nitroso group is often considered as an aza-analogue of a carbonyl group of aldehydes, and indeed, it shows similar reactivity and undergoes similar reactions, such as nucleophilic addition and condensation, reduction and oxidation with most typical redox reagents. In this respect, however, oxidation with IBX seems different. This oxidant is known for efficient oxidation of a broad range of alcohols to the corresponding carbonyl compounds, which in the case of primary alcohols are aldehydes. Further oxidation of aldehydes to carboxylic acids is very rare, however, and requires special conditions such as the additional presence of hydroxylic nucleophile[33] or a solvent-free system at elevated temperature.[34] Contrary to that, the nitroso group of nitrosoanilines **5a-f** is oxidized readily under very mild conditions (DMSO, ambient temperature) and the yields are reasonable.

A possible mechanism of the IBX oxidation of nitrosoarenes may be analogous to the ionic mechanism proposed for the oxidation of aldehydes,[34] except that it involves a lone electron pair of the nitrogen atom in the step of elimination of IBA (2-iodosobenzoic acid), making the whole process much easier (Scheme 3).

3. Conclusion

The developed two-step method for the synthesis of differently substituted 2-nitrodiarylamines engages nucleophilic substitution of hydrogen in nitroarenes followed by oxidation of the 2-nitrosoanilines so formed, with a cheap and environmentally friendly reagent. The first step omits classical substitution of halogens in the starting nitroarenes, occurs efficiently at the position *ortho* to the activating group, and potential leaving groups *para* (F, Cl, OR) or *ortho* (Cl, OR) to the nitro group remain unaffected. The oxidation step, which can be carried out with the crude product from the first step, occurs under mild conditions with sodium perborate tetrahydrate and only in exceptional cases of the amine-substituted compounds requires a special, more selective oxidant (IBX). The above features make the method a valuable alternative to the popular methods based on the S_NAr reaction.



Scheme 3. Proposed mechanistic scheme for the oxidation nitrosoanilines 5 with IBX.

4. Experimental section

4.1. General

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 500 instruments at 298 K. Chemical shifts are expressed in ppm referred to TMS (^{1}H NMR at 500 MHz,^{13}C NMR at 125 MHz), coupling constants in Hertz. Mass spectra (EI, 70 eV and ESI in MeOH) were obtained on an AutoSpec Premier and an API 365 spectrometers. IR spectra were recorded on a JASCO FT/IR-6200 apparatus. GC analyses were performed on a Hewlett Packard HP6890 GC system with HP5 column and FID (carrier gas – helium). Silica gel Merck 60 (230–400 mesh) was used for column chromatography. THF was distilled from sodium/benzophenone ketyl prior to use. DMF was dried over CaH_2, distilled and stored over molecular sieves.

Following nitrosoanilines were obtained and described previously: **3h, 3p, 3w**[17a]; **3i** [34a]; **3j**, **3l**, **3o**, **3x** [17b]; **3k**, **3v**[19c]; **3m**, **3n**[19d]; **3q**[19e]; **3r**, **3s**[19f]; **3t**[19g]; **5b, c, f**[19h]; **5e**[19b].

4.2. Reactions of electron-poor nitroarenes and anilines (Table 1)

To a cooled solution of *t*-BuOK (6 mmol, 672 mg) in DMF (12 mL) was added dropwise at −65 °C a solution of aniline **1** (2 mmol), then nitroarene **2** (2 mmol) in DMF (2 mL each). The mixture was stirred at this temperature for 20–60 min or, in a few cases, the cooling bath was removed and the mixture was allowed to reach room temperature (see Table 1). The reaction mixture was then poured into a concentrated NH_4Cl solution (ca. 50 mL) and extracted with EtOAc. The extract was washed thoroughly with water and brine, and dried with Na_2SO_4. After evaporation, the crude product was subjected to column chromatography (SiO_2, hexane/AcOEt, hexane/CH_2Cl_2 or hexane/toluene) to isolate **3** and/or **4**.

4.3. Characterization of N-aryl-2-nitrosoanilines 3a-d and nitroanilines 4a-g (Table 1)

4.3.1. 5-Chloro-N-(4-cyanophenyl)-2-nitrosoaniline (**3a**)

Red solid; mp 205–206 °C; IR (KBr): 3296, 3095, 2921, 2224, 1594, 1552, 1507, 1458, 1336, 1264, 1157, 1107, 1078, 941, 818, 795, 567 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09 (dd, J = 2.0, 8.7 Hz, 1 H), 7.31 (d, J = 2.0 Hz, 1 H), 7.38–7.42 (m, 2 H), 7.71–7.74 (m, 2 H), 8.56 (br s, 1 H), 11.42 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 108.9, 114.4, 118.3, 120.4, 123.3, 132.5, 133.9, 137.7, 141.7, 145.1, 155.1; MS (EI, 70 eV): m/z (%) 257 (M^+, 22), 240 (100), 226 (46), 192 (47), 164 (19); HRMS (EI) m/z $[M]^+$ calcd for $C_{13}H_8N_3O^{35}Cl$: 257.0356; found: 257.0356.

4.3.2. 5-Chloro-N-(2-cyanophenyl)-2-nitrosoaniline (**3b**)

Dark solid; mp 128–129 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.02–7.12 (m, 2 H); 7.37 (ddd, J = 1.2, 7.9, 9.1 Hz, 1 H); 7.56 (d, J = 7.9 Hz, 1 H), 7.67 (ddd, J = 1.2, 7.9, 9.1 Hz, 1 H); 7.75 (dd, J = 1.2, 7.9 Hz, 1 H), 8.58 (br s, 1 H), 11.4 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 108.6, 114.4, 115.9, 120.3, 124.9, 126.4, 134.0, 134.1, 140.4; 144.8; 155.0; MS (ESI, MeOH): m/z = 258 $[M+H]^+$; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{13}H_9N_3O^{35}Cl$: 258.0434; found: 258.0426.

4.3.3. 3-Bromo-5-chloro-N-(2-bromo-4-chlorophenyl)-2-nitrosoaniline (**3c**)

Dark solid; mp 128–134 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.79 (d, J = 2.0 Hz, 1 H), 7.30 (d, J = 8.4 Hz, 1 H), 7.36–7.41 (m, 2 H), 7.72 (d, J = 2.0 Hz, 1 H), 12.28 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 114.4, 120.7, 123.7, 127.8, 128.3, 128.9, 132.3, 133.6, 133.66, 133.71, 138.5, 144.8, 151.2; MS (EI, 70 eV): m/z (%) = 426 (4), 424 (6), 422 (M^+ 4), 347 (56), 345 (100), 343 (73); HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{12}H_6N_2O^{35}Cl_2^{79}Br_2Na$: 444.8122; found: 444.8110.

4.3.4. N-(4-Chlorophenyl)-2-nitroso-5-trifluoromethylaniline (**3d**)

Dark solid; mp 84–85 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18–7.28 (m, 3 H), 7.33 (s, 1 H), 7.4–7.56 (m, 2 H), 8.88 (d, J = 6.9 Hz, 1 H), 11.56 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 113.3 (q, J_{CF} = 4.2 Hz), 114.1 (q, J_{CF} = 3.3 Hz), 122.9 (q, J_{CF} = 274 Hz), 126.0, 130.2, 132.5, 134.9, 137.8 (q, J_{CF} = 32.7 Hz), 148.9, 155.7; MS (ESI, MeOH): m/z = 301 $[M+H]^+$; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{11}H_9N_2O^{35}ClF_3$: 301.1496; found: 301.1490.

4.3.5. 5-Chloro-N-(4-cyanophenyl)-2-nitroaniline (**4a**)

Orange needles; mp 234 °C (lit.[35] 221–224 °C); IR (KBr): 3322, 3114, 3097, 2225, 1599, 1563, 1502, 1483, 1336, 1251, 1066, 936, 836, 747, 552 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.16 (dd, J = 2.0, 8.9, 1 H), 7.4 (d, J = 8.9, 2 H), 7.78 (d, J = 8.9, 2 H), 7.45 (d, J = 2.2, 1 H), 8.14 (d, J = 8.9, 1 H), 9.48 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 104.5, 119.1, 119.2, 120.3, 121.1, 128.2, 133.7, 136.1, 139.1, 140.0, 144.8; MS (EI, 70 eV): m/z (%) 275 (41), 273 (M^+, 100), 256 (15), 239 (38), 228 (27); HRMS (EI): m/z $[M]^+$ calcd for $C_{13}H_8N_3O_2^{35}Cl$: 273.0305; found: 273.0304.

4.3.6. 5-Chloro-N-(2-cyanophenyl)-2-nitroaniline (**4b**)

Orange crystals; mp 140–141 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.90 (dd, J = 2.0, 9.1, 1 H); 7.14 (d, J = 2.0 Hz, 1 H), 7.34 (dd, J = 8.2, 7.7 Hz, 1 H); 7.67 (ddd, J = 8.2, 8.2, 1.4 Hz, 1 H); 7.75 (dd, J = 1.4, 7.7 Hz, 1 H), 7.51 (d, J = 8.2 Hz, 1 H), 8.21 (d, J = 9.1 Hz, 1 H), 9.67 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 108.4, 115.9, 116.0, 120.0, 123.9, 125.9, 128.2, 133.1, 134.1, 134.2; 141.4; 141.5; 142.4; MS (EI, 70 eV): m/z (%) 273 (100), 241 (11), 239 (28), 228 (23), 192 (58); HRMS (EI): m/z $[M]^+$ calcd for $C_{13}H_8N_3O_2^{35}Cl$: 273.0305; found: 273.0302.

4.3.7. 3-Bromo-5-chloro-N-(2-bromo-4-chlorophenyl)-2-nitroaniline (**4c**)

Yellow crystals; mp 167–168 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.82 (dd, J = 9.2, 2.1 Hz, 1 H), 6.99 (d, J = 2.1 Hz, 1 H), 7.37–7.38 (m, 2 H), 7.72–7.73 (m, 1 H), 8.18 (d, J = 9.2 Hz, 1 H), 9.44 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 115.2, 119.0, 120.4, 126.0128.2, 128.8, 132.0, 132.4, 133.6, 135.6, 142.3, 142.5; MS (EI, 70 eV): m/z (%) = 444 (4), 442 (11), 440 (13), 438 (M^+ 5), 364 (45), 362 (100), 360 (62); HRMS (EI): m/z $[M]^+$ calcd for $C_{12}H_6N_2O_2^{35}Cl_2^{79}Br_2$: 437.8173; found: 437.8175.

4.3.8. N-(4-Chlorophenyl)-2-nitro-5-trifluoromethylaniline (**4d**)

Orange crystals; mp 161 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.01 (dd, J = 1.5, 8.8 Hz, 1 H), 7.21–7.25 (m, 2H), 7.38 (d, J = 0.7 Hz, 1 H), 7.42–7.45 (m, 2 H), 8.32 (d, J = 8.8 Hz, 1 H), 9.45 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 113.2, (q, J_{CF} = 4.0 Hz), 113.8 (q, J_{CF} = 3.5 Hz), 122.7 (q, J_{CF} = 273 Hz), 125.9, 127.8, 130.3, 132.0, 134.6, 136.3, 137.0 (q, J_{CF} = 33.2 Hz), 142.6; MS (EI, 70 eV): m/z (%) = 316 (100), 284 (10), 282 (25), 269 (41); HRMS (EI): m/z $[M]^+$ calcd for $C_{13}H_8N_2O_2^{35}ClF_3$: 316.0226; found: 316.0236.

4.3.9. N-(4-Cyanophenyl)-2-nitro-5-trifluoromethylaniline (**4e**)

Yellow crystals; mp 93–94 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18 (dd, J = 1.7, 8.7 Hz, 1 H), 7.34–7.38 (m, 2 H), 7.65 (br s, 1 H), 7.71–7.75 (m, 2 H), 8.35 (d, J = 8.7 Hz, 1 H), 9.50 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 108.4, 114.2 (q, J_{CF} = 4.0 Hz), 115.9 (q, J_{CF} = 3.5 Hz), 118.3, 122.0, 122.6 (q, J_{CF} = 273 Hz), 128.0, 134.1, 136.5, 137.0 (q, J_{CF} = 33 Hz), 140.0, 142.6; MS (EI, 70 eV): m/z (%) = 307 (45), 273 (100), 260 (21), 240 (2); HRMS (EI): m/z $[M]^+$ calcd for $C_{14}H_8N_3O_2F_3$: 307.0569; found: 307.0576.

4.3.10. 5-Cyano-N-(4-cyanophenyl)-2-nitroaniline (**4f**)

Orange solid; mp 139–140 °C; IR (KBr): 3297, 3111, 2224, 1600, 1584, 1564, 1504, 1483, 1338, 1254, 1064, 842, 663 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 7.36–7.40 (m, 2H), 7.53 (dd, J = 1.5, 8.5 Hz, 1 H), 7.75–7.79 (m, 2 H), 7.94 (d, J = 1.5 Hz, 1 H), 8.22 (d, J = 8.5 Hz, 1 H), 9.45 (s, 1 H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 104.7, 117.6, 117.7, 119.6, 120.2, 124.5, 125.6, 127.8, 134.2, 138.1, 140.8, 145.5; MS (EI, 70 eV): m/z (%) = 264 (100), 247 (14), 230 (22), 219 (17); HRMS (EI): m/z $[M]^+$ calcd for $C_{14}H_8N_4O_2$: 264.0647; found: 264.0644.

4.3.11. N-(4-Chlorophenyl)-5-cyano-2-nitroaniline (**4g**)

Orange solid; mp 133 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.01 (dd, J = 1.5, 8.5 Hz, 1 H), 7.18–7.24 (m, 2 H), 7.38 (d, J = 1.5 Hz, 1 H), 7.42–7.5 (m, 2 H), 8.30 (d, J = 8.5 Hz, 1 H), 9.41 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 117.0, 119.1, 119.5, 120.3, 126.3, 127.8, 130.5, 132.6, 134.8, 135.8, 142.8; MS (EI, 70 eV): m/z (%) = 253 (58), 237 (26), 236 (100), 222 (40); HRMS (EI): m/z $[M]^+$ calcd for $C_{14}H_{11}N_3O_2$: 253.0851; found: 253.0855.

4.4. Preparation of nitrosoaniline 3u

To a cooled solution of *t*-BuOK (6 mmol, 672 mg) in DMF (12 mL) was added dropwise at −65 °C a solution of 2-*t*-butylaniline (298 mg, 2 mmol), then *p*-nitroaanisole (274 mg, 2 mmol) in DMF (2 mL each). The mixture was stirred at this temperature for 60 min. The reaction mixture was then poured into a concentrated NH_4Cl solution (ca. 50 mL) and extracted with EtOAc. The extract was washed thoroughly with water and brine, and dried with Na_2SO_4. After evaporation, the crude product was subjected to column chromatography (SiO_2, hexane/toluene) to isolate **3u**, 432 mg (76% yield).

4.4.1. N-(2-t-Butylphenyl)-5-methoxy-2-nitrosoaniline (**3u**)

Dark green crystals; mp 75–76 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.37 (s, 9 H), 3.71 (s, 3 H), 5.97 (d, J = 2.2 Hz, 1 H), 6.55 (dd, J = 9.2, 2.2 Hz, 1 H), 7.18–7.30 (m, 3 H), 7.52 (dd, J = 7.8, 1.0 Hz, 1 H), 8.52 (d, J = 9.2 Hz, 1 H), 13.2 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.6, 35.0, 55.8, 94.2, 109.2, 127.0, 127.5, 127.7, 129.3, 135.1, 139.0, 142.3, 146.3, 154.0, 167.0; MS (ESI): m/z $[M+H]^+$ = 285; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{21}N_2O_2$: 285.1603; found: 285.1605.

4.5. Preparation of nitrosoanilines 5a and 5d. General procedure[19h]

To a solution of 5-fluoro-*N*-(4-methylphenyl)-2-nitrosoaniline **3i** (0.5 mmol) in MeCN (10 mL) was added appropriate amine (2.5 mmol) and the mixture was stirred at ambient temperature for 1 h. After the reaction was complete the mixture was poured into water and extracted three times with AcOEt. The combined extracts were washed with water, brine and the solvent was evaporated. The crude product was pure enough to use in the oxidation reaction.

4.6. Characterization of new N-aryl-2-nitrosoanilines 5

4.6.1. N-(4-Methylphenyl)-2-nitroso-5-(pyrrolidin-1-yl)aniline (**5a**)

Yield 95%; Dark green solid; mp 161–164 °C; IR (KBr): 2966, 2867, 1625, 1496, 1314, 1136, 911, 804, 663, 503 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.98–2.03 (m, 4 H), 2.35 (s, 3 H), 3.2–3.6 (m, 4 H), 5.87 (d, J = 2.4 Hz, 1 H), 6.35 (dd, J = 9.5, 2.4 Hz, 1 H), 8.10 (d, J = 9.5 Hz, 1 H), 13.12 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.0, 25.2, 48.2, 89.1, 107.6, 124.4, 130.0, 135.2, 135.3, 139.8, 141.8, 151.9, 153.4; MS(EI): m/z (%) 281 (M^+, 67), 267 (83), 264 (100), 250 (42); HRMS(EI): m/z $[M]^+$ calcd for $C_{17}H_{19}N_3O$: 281.1528; found: 281.1533.

4.6.2. 5-n-Butylamino-N-(4-methylphenyl)-2-nitrosoaniline (**5d**)

Yield 97%; Dark reddish solid; mp 112–114 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.4 Hz, 3 H), 1.34–1.42 (m, 2 H), 1.56–1.63 (m, 2 H),2.35 (s, 3 H), 3.10–3.16 (m, 2 H), 5.35 (br s, 1 H), 5.91 (d, J = 2.2 Hz, 1 H), 6.27 (dd, J = 9.2, 1.5 Hz, 1 H), 7.14–7.20 (m, 4 H), 8.02 (d, J = 9.2 Hz, 1 H), 13.42 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7, 20.1, 21.0, 31.0, 42.9, 87.6, 109.7, 124.6, 130.0, 135.0, 135.6, 140.8, 141.4, 152.0, 155.5; MS(EI): m/z (%) 283 (M^+, 56), 266 (100), 226 (58), 209 (54); HRMS(EI): m/z $[M]^+$ calcd for $C_{17}H_{21}N_3O$: 283.1685; found: 283.1685.

4.7. Oxidation of N-aryl-2-nitrosoanilines 3 with sodium perborate. Synthesis of 2-nitrodiarylamines 4 (Table 3); general procedure

To a solution of nitrosoaniline **3** (1.0 mmol) in AcOH (8 mL) was added $NaBO_3 \cdot 4H_2O$ (460 g, 3.0 mmol) and the mixture was stirred at the temperature and for the time specified in Table 1. The reaction mixture was then poured into water (ca. 100 mL) and extracted with EtOAc (3 × 30 mL). The combined extract was washed with water (3 × 100 mL), brine, and dried with Na_2SO_4. After evaporation the crude product was purified by column chromatography (SiO_2, hexane/EtOAc).

4.8. Characterization of 2-nitrodiarylamines 4 (Table 3)

4.8.1. 5-Chloro-2-nitro-N-(4-methylphenyl)-aniline (**4h**)

Red solid; mp 126–127 °C (lit[36] 125–126 °C); IR (KBr): 3332, 3112, 3032, 2919, 1605, 1565, 1511, 1483, 1336, 1246, 931, 784, 529 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 6.68 (dd, J = 9.2, 2.1 Hz, 1 H), 7.07 (d, J = 2.1 Hz, 1 H), 7.14–7.17 (m, 2 H), 7.24–7.27 (m, 2 H), 8.14 (d, J = 9.2 Hz, 1 H), 9.49 (broad s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.04, 115.10, 117.52, 125.17, 128.06, 130.56, 131.20, 135.08, 136.55, 142.46, 144.47; MS(EI): m/z (%) 262 (M^+, 100), 228 (44), 215 (39), 180 (37), 181 (36); HRMS(EI): m/z $[M]^+$ calcd for $C_{13}H_{11}N_2O_2^{35}Cl$: 262.0509; found: 262.0507.

4.8.2. 5-Fluoro-2-nitro-N-(4-methylphenyl)-aniline (**4i**)

Orange crystals; mp 125–128 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 6.44 (ddd, J = 9.5, 2.6 Hz, J_{HF} = 7.1 Hz, 1 H), 6.72 (dd, J = 2.6 Hz, J_{HF} = 11.5 Hz, 1 H), 7.14–7.17 (m, 2 H), 7.23–7.27 (m, 2 H), 8.24 (dd, J = 9.5 Hz, J_{HF} = 6.12 Hz, 1 H), 9.58 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.0, 101.2 (d, J_{CF} = 27.6 Hz), 105.6 (d, J_{CF} = 24.6 Hz), 125.2, 129.5, 129.7 (d, J_{CF} = 12.0 Hz), 130.5, 135.2, 136.6, 146.1 (d, J_{CF} = 13.3 Hz), 167.2 (d, J_{CF} = 254.6 Hz); MS(EI): m/z (%) 246 (M^+, 100), 212 (40), 198 (46), 185 (31); HRMS(EI): m/z $[M]^+$ calcd for $C_{13}H_{11}N_2O_2F$: 246.0805; found: 246.0809.

4.8.3. 5-Fluoro-N-(2,6-dimethylphenyl)-2-nitroaniline (**4j**)

Yellow crystals; mp 90–91 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 6.00 (dd, J = 2.6 Hz, J_{HF} = 11.3 Hz, 1 H), 6.42 (ddd, J = 9.6, 2.6 Hz, J_{HF} = 7.1 Hz, 1 H), 7.17–7.24 (m, 3 H), 8.27 (dd, J = 9.6 Hz, J_{HF} = 6.1 Hz, 1 H), 9.28 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.1, 100.3 (d, J_{CF} = 27.6 Hz), 105.2 (d, J_{CF} = 24.8 Hz), 128.1, 128.9, 129.8 (d, J_{CF} = 12.0 Hz), 134.8, 136.5, 146.7 (d, J_{CF} = 13.3 Hz), 167.7 (d, J_{CF} = 254.6 Hz), one signal missing; MS(EI): m/z (%) 260 (M^+, 100), 212 (68), 198 (38); HRMS(EI): m/z $[M]^+$ calcd for $C_{14}H_{13}N_2O_2F$: 260.0961; found: 260.0971.

4.8.4. 5-Chloro-N-(2-iodophenyl)-2-nitroaniline (**4k**)

Orange crystals; mp 130–132 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.78 (dd, J = 9.2, 2.2 Hz, 1 H), 6.93 (d, J = 2.2 Hz, 1 H), 7.00–7.05 (m, 1 H), 7.41 (dd, J = 8.0, 1.5 Hz, 1 H), 7.42–7.46 (m, 1 H), 7.97 (dd, J = 8.0, 1.2 Hz, 1 H), 8.19 (d, J = 9.2 Hz, 1 H), 9.46 (br s, 1 H); ^{13}C NMR

(125 MHz, $CDCl_3$): δ = 96.9, 115.2, 118.5, 125.8, 128.1, 128.1, 129.6, 131.9, 139.9, 140.4, 142.5, 143.0; MS(EI): *m/z* (%) 376 (41), 374 (M^+, 100), 230 (44), 202 (50), 201 (54), 166 (54); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{12}H_8N_2O_2I$: 373.9319; found: 373.9329.

*4.8.5. N-(4-Bromophenyl)-5-methoxy-2-nitroaniline (**4l**)*

Orange crystals; mp 147–150 °C (lit.[37] 149 °C); ^1H NMR (500 MHz, $CDCl_3$): δ = 3.76 (s, 3 H), 6.37 (dd, *J* = 9.5, 2.6 Hz, 1 H), 6.52 (d, *J* = 2.6 Hz, 1 H), 7.16–7.20 (m, 2 H), 7.52–7.56 (m, 2 H), 8.19 (d, *J* = 9.5 Hz, 1 H), 9.66 (broad s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.7, 97.5, 106.7, 118.7, 126.1, 127.7, 129.1, 132.9, 137.8, 144.93, 165.6; MS(EI): *m/z* (%) 324 (99), 322 (M^+, 100), 290 (24), 288 (24), 226 (26), 197 (39), 154 (45); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{13}H_{11}N_2O_3^{79}Br$: 321.9953; found: 321.9940.

*4.8.6. N-(4-chlorophenyl)-4-trifluoromethylo-2-nitroaniline (**4m**)*

Orange crystals; mp 83–85 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 8.8 Hz, 1 H), 7.22–7.27 (m, 3 H), 7.42–7.45 (m, 2 H), 7.56 (dd, *J* = 8.8, 1.6 Hz, 1 H), 8.51 (s, 1 H), 9.63 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 116.4, 119.8 (q, J_{CF} = 34.7 Hz), 123.3 (q, J_{CF} = 272 Hz), 124.8 (q, J_{CF} = 4.6 Hz), 126.5, 130.2, 131.9 (q, J_{CF} = 3.0 Hz), 131.9, 132.4, 136.1, 144.9.

MS (EI) *m/z* (%) = 318 (44), 317 (26), 316 (M^+, 100), 297 (14), 282 (30), 269 (44), 235 (42), 201 (17); HRMS (EI): *m/z* $[M]^+$ calcd for $C_{13}H_8N_2O_2^{35}ClF_3$: 316.0226, found: 316.0224.

*4.8.7. N-(5-Chloro-2-methoxyphenyl)-2-nitro-4-trifluoromethylaniline (**4n**)*

Orange crystals; mp 138–143 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.87 (s, 3 H), 6.94 (d, *J* = 8.8 Hz, 1 H), 7.21 (dd, *J* = 8.8, 2.5 Hz, 1 H), 7.25 (d, *J* = 8.8 Hz, 1 H), 7.36 (d, *J* = 2.5 Hz, 1 H), 7.60 (dd, *J* = 9.1, 2.0 Hz, 1 H), 8.51 (d, *J* = 1.1 Hz, 1 H), 9.59 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 56.0, 112.7, 116.7, 120.0 (q, J_{CF} = 34.3 Hz), 123.3 (q, J_{CF} = 271 Hz), 123.8, 124.7 (q, J_{CF} = 3.7 Hz), 125.6, 126.5, 127.7, 131.7 (q, J_{CF} = 2.9 Hz), 132.8, 143.9, 151.5; MS(EI): *m/z* (%) 348 (49), 346 (M^+, 100), 285 (57), 222 (27); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{14}H_{10}N_2O_3^{35}ClF_3$: 346.0332; found: 346.0323.

*4.8.8. 3,5-Dichloro-N-(2-Chlorophenyl)-2-nitroaniline (**4o**)*

Orange crystals; mp 99–102 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.94 (d, *J* = 2.2 Hz, 1 H), 7.02 (d, *J* = 2.2 Hz, 1 H), 7.10–7.13 (m, 2 H), 7.35–7.39 (m, 2 H), 7.44 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 114.7, 121.2, 124.3, 129.7, 130.1, 130.9, 135.7, 137.1, 138.7, 141.3; MS(EI): *m/z* (%) 320 (40), 318 (98), 316 (M^+, 100), 284 (39), 282 (39), 271 (56), 269 (50), 237 (56), 235 (80); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{12}H_7N_2O_2^{35}Cl_3$: 315.9573; found: 315.9587.

*4.8.9. 5-Chloro-N-(4-chlorophenyl)-2-nitroaniline (**4p**)*

Orange crystals; mp 158–159 °C (lit.[17b] 158–159 °C); ^1H NMR (500 MHz, $CDCl_3$): δ = 6.75 (dd, *J* = 9.3, 2.0 Hz, 1 H), 7.08 (d, *J* = 2.0 Hz, 1 H), 7.20–7.24 (m, 2 H), 7.41–7.44 (m, 2 H), 8.16 (d, *J* = 9.3 Hz, 1 H), 9.46 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 115.1, 118.3, 126.1, 128.2, 130.1, 131.7, 131.8, 136.5, 142.6, 143.5; MS(EI): *m/z* (%) 284 (73), 282 (M^+, 100), 248 (42), 235 (38), 201 (49); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{12}H_8N_2O_2^{35}Cl_2$: 281.9963; found: 281.9961.

*4.8.10. N-(4-Methoxyphenyl)-2-nitroaniline (**4q**)*

Orange crystals; mp 82–85 °C (lit[2] 78–79 °C, lit[5c] 83–86 °C); ^1H NMR (500 MHz, $CDCl_3$): δ = 3.84 (s, 3 H), 6.71 (ddd, *J* = 8.7, 7.0, 1.2 Hz, 1 H), 6.94–6.98 (m, 2 H), 7.00 (dd, *J* = 8.7, 1.2 Hz, 1 H), 7.18–7.22 (m, 2 H), 7.32 (ddd, *J* = 8.7, 7.0, 1.5 Hz, 1 H), 8.19 (dd, *J* = 8.7, 1.5 Hz, 1 H), 9.41 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.5, 115.0, 115.7, 116.7, 126.6, 127.1, 131.2, 132.5, 135.7, 144.5, 157.9; MS(EI): *m/z* (%) 244 (M^+, 100), 229 (51), 210 (26), 182 (36), 154 (44); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{13}H_{12}N_2O_3$: 244.0848; found: 244.0847.

*4.8.11. 5-Chloro-N-(2-fluorophenyl)-2-nitroaniline (**4r**)*

Yellow crystals; mp 138–140 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.78 (dd, *J* = 9.1, 2.2 Hz, 1 H), 6.97–6.99 (m, 1 H), 7.21–7.32 (m, 3 H), 7.36–7.41 (m, 1 H), 8.17 (d, *J* = 9.1 Hz, 1 H), 9.35 (broad s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.2, 117.0 (d, J_{CF} = 19.5 Hz), 118.4, 125.0 (d, J_{CF} = 4.0 Hz), 125.7 (J_{CF} = 12.0 Hz), 127.3 (d, J_{CF} = 7.4 Hz), 128.0, 132.0, 142.5, 143.2, 156.9 (d, J_{CF} = 247.8 Hz), one signal missing; MS(EI): *m/z* (%) 268 (46), 266 (M^+, 100), 232 (45), 219 (49), 185 (46); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{12}H_8N_2O_2^{35}ClF$: 266.0258; found: 266.0261.

*4.8.12. N-(2-Chlorophenyl)-2-nitroaniline (**4s**)*

Orange crystals; mp 111–115 °C [lit.[38] 112–113 °C (benzene)]; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.83–6.88 (m, 1 H), 7.13–7.19 (m 1 H), 7.27–7.32 (m, 1 H), 7.38–7.43 (m, 1 H), 7.47 (dd, *J* = 8.0, 1.3 Hz, 1 H), 7.51 (dd, *J* = 8.0, 1.6 Hz, 1 H), 8.22 (dd, *J* = 8.6, 1.7 Hz, 1 H), 9.47 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 116.2, 118.4, 124.4, 126.1, 126.7, 127.5, 128.7, 130.6, 134.3, 135.6, 136.2, 141.5; MS(EI): *m/z* (%) 248 (M^+, 100), 201 (54), 167 (68); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{12}H_9N_2O_2^{35}Cl$: 248.0353; found: 248.0348.

*4.8.13. N-(2-t-Butylphenyl)-5-chloro-2-nitroaniline (**4t**)*

Orange crystals; mp 139–140 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.40 (s, 9 H), 6.67 (dd, *J* = 9.1, 2.2 Hz, 1 H), 6.76 (d, *J* = 2.1 Hz, 1 H), 7.18–7.21 (m, 1 H), 7.29–7.32 (m, 2 H), 7.53–7.56 (m, 1 H), 8.16, (d, *J* = 9.1 Hz), 9.6 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.6, 35.1, 115.4, 117.2, 127.5, 127.6, 127.9, 128.0, 129.3, 131.2, 136.3, 142.6, 145.2, 149.9; MS(EI): *m/z* (%) 306 (42), 304 (M^+, 85), 228 (100); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{16}H_{17}N_2O_2^{35}Cl$: 304.0979; found: 304.0982.

*4.8.14. N-(2-t-Butylphenyl)-5-methoxy-2-nitroaniline (**4u**)*

Orange crystals; mp 87–90 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.40 (s, 9H), 3.67 (s, 3 H), 6.12 (d, *J* = 2.7 Hz, 1 H), 6.29 (dd, *J* = 9.5, 2.7 Hz, 1 H), 7.22–7.28 (m, 3 H), 7.51–7.55 (m, 1 H), 8.19 (d, *J* = 9.5 Hz, 1 H), 9.81 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.6, 35.1, 55.6, 97.6, 106.0, 127.2, 127.2, 127.7, 129.0, 129.5, 136.9, 146.9, 147.1, 165.6, one signal missing; MS(EI): *m/z* (%) 300 (M^+, 85), 224 (100); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{17}H_{20}N_2O_3$: 300.1474; found: 300.1470.

*4.8.15. 5-Chloro-N-(2-iodo-4-methylphenyl)-2-nitroaniline (**4v**)*

Yellow crystals; mp 147–149 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 6.74 (dd, *J* = 8.9, 2.0 Hz, 1 H), 6.82 (d, *J* = 2 Hz, 1 H), 7.25 (d, *J* = 8.5 Hz, 2 H), 7.80 (s, 1 H), 8.17 (d, *J* = 8.5 Hz, 1 H), 9.39 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.5, 97.4, 115.1, 118.1, 126.2, 128.1, 130.4, 131.6, 137.2, 138.8, 140.6, 142.4, 143.6; MS(EI): *m/z* (%) 390 (36), 388 (M^+, 100), 216 (47); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{13}H_{10}N_2O_2^{35}ClI$: 387.9476; found: 387.9471.

*4.8.16. N-(4-Methylphenyl)-5-methoxy-2-nitroaniline (**4w**)*

Yellow crystals; mp 87–88 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 3.72 (s, 3 H), 6.31 (dd, *J* = 9.5, 2.8 Hz, 1 H), 6.48 (d, *J* = 2.8 Hz, 1 H), 7.16–7.24 (m, 4 H), 8.17 (d, 9.5 Hz, 1 H), 9.71 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.0, 55.6, 97.1, 106.3, 125.0, 127.2, 129.0, 130.3, 135.8, 135.9, 146.2, 165.6; MS(EI): *m/z* (%) 258 (M^+, 100), 224 (42), 168 (25).

HRMS(EI): *m/z* $[M]^+$ calcd for $C_{14}H_{14}N_2O_3$: 258.1004; found: 258.1002.

*4.8.17. N-(4-Chlorophenyl)-5-fluoro-2-nitroaniline (**4x**)*

Fine orange crystals; mp 143–146 °C [lit.[39] 149–150 °C (MeOH)]; IR (KBr): 3321, 3102, 1631, 1572, 1500, 1340, 1253, 1205,

1076, 996, 820, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.51 (ddd, J = 9.6, 2.6, J_{HF} = 7.0 Hz, 1 H), 6.75 (dd, J = 2.6 J_{HF} = 11.1 Hz, 1 H), 7.21–7.24 (m, 2 H), 7.40–7.43 (m, 2 H), 8.27 (dd, J = 9.6, J_{HF} = 6.1 Hz, 1 H), 9.56 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 101.3 (d, J_{CF} = 28.3 Hz), 106.3 (d, J_{CF} = 24.9), 126.2, 129.9 (d, J_{CF} = 12.4 Hz), 130.0, 130.1, 131.9, 136.6, 145.2 (d, 12.7 Hz), 167.2 (d, J_{CF} = 256 Hz); MS(EI): *m/z* (%) 268 (42), 266 (M^+, 100), 232 (42), 219 (41), 185 (46); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{12}H_8^{35}ClFN_2O_2$: 266.0258; found: 266.0264.

4.9. Oxidation of N-aryl-2-nitrosoanilines 5 with IBX. Synthesis of 2-nitrodiarylamines 6

N-Aryl-2-nitrosoaniline **5** (1 mmol) and IBX (308 mg, 1.1 mmol) were stirred in DMSO (8 mL) at room temperature for ca. 20 h. The mixture was then poured into diluted brine and extracted with EtOAc. The extract was washed with water, brine and dried with Na_2SO_4. The solvent was evaporated and the crude product was purified by column chromatography (SiO_2, hexane/EtOAc).

4.10. Characterization of 2-nitrodiarylamines 6

4.10.1. N-(4-Methylphenyl)-2-nitro-5-(pyrrolidin-1-yl)aniline (**6a**)

Orange crystals; mp 146–148 °C; IR (KBr): 3273, 2973, 2855, 1620, 1561, 1495, 1414, 1312, 1168, 805 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.95–2.00 (m, 4H), 2.37 (s, 3 H), 3.25–3.32 (m, 4 H), 5.99 (d, J = 2.5 Hz, 1 H), 6.04 (dd, J = 9.5, 2.5 Hz, 1 H), 7.17–7.22 (m, 4 H), 8.1 (d, 9.7 Hz, 1 H), 9.91 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.0, 25.3, 47.7, 92.7, 104.8, 123.8, 124.6, 129.1, 130.1, 135.0, 136.5, 146.1, 152.6; MS(EI): *m/z* (%) 297 (M^+, 100), 263 (48), 251 (55), 180 (35); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{17}H_{19}N_3O_2$: 2971477; found: 297.1473.

4.10.2. N-(4-Chlorophenyl)-5-(morpholin-1-yl)-2-nitroaniline (**6b**)

Yellow crystals; mp 190–192 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.22–3.26 (m, 4 H), 3.77–3.81 (m, 4 H), 6.32–6.36 (m, 2 H), 3.22–3.25 (m, 2 H), 7.37–7.40 (m, 2 H), 8.12–8.15 (m, 1 H), 9.75 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 46.9, 66.3, 95.9, 105.6, 125.8, 128.9, 129.8, 130.7, 137.6, 145.0, 155.7, one signal missing; MS(EI): *m/z* (%) 335 (34), 333 (M^+, 100), 275 (39); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{16}H_{16}N_3O_3^{35}Cl$: 333.0880; found: 333.0865.

4.10.3. N-(4-Chlorophenyl)-2-nitro-5-(pyrrolidin-1-yl)aniline (**6c**)

Yellow crystals; mp 172–176 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.98–2.02 (m, 4 H), 3.28–3.32 (m, 4 H), 5.99 (d, J = 2.5 Hz, 1 H), 6.08 (dd, J = 2.5, 9.5 Hz, 1 H), 7.24–7.27 (m, 2 H), 7.34–7.37 (m, 2 H), 8.12 (d, J = 9.5 Hz, 1 H), 9.90 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.3, 47.8, 92.9, 105.1, 124.1, 125.6, 129.2, 129.6, 130.2, 138.0, 145.2, 152.6; MS(EI): *m/z* (%) 319 (41), 317 (M^+, 100), 287 (52), 236 (66); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{16}H_{16}N_3O_2^{35}Cl$: 317.0931; found: 317.0919.

4.10.4. 5-n-Butylamino-N-(4-methylphenyl)-2-nitroaniline (**6d**)

Yellow crystals; mp 78–80 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.2 Hz, 3 H), 1.31–1.39 (m, 2 H), 1.50–1.57 (m, 3 H), 2.37 (s, 3 H), 3.04 (t, J = 7.2 Hz, 2 H), 4.38 (br s, 1 H), 5.98 (dd, J = 2.4, 9.4 Hz, 1 H), 6.01 (d, J = 2.4 Hz, 2 H), 7.16–7.22 (m, 4 H), 8.06 (d, J = 9.4 Hz, 1 H), 9.91 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7, 20.0, 21.0, 31.1, 42.8, 92.4, 105.6, 124.4, 125.0, 129.2, 130.1, 135.3, 136.2, 146.7, 154.1; MS(EI): *m/z* (%) 299 (M^+, 100), 256 (89); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{17}H_{21}N_3O_2$: 299.1634; found: 299.1619.

4.10.5. 5-tert-Butylamino-N-(4-chlorophenyl)-2-nitroaniline (**6e**)

Yellow crystals; mp 181–184 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.31 (s, 9 H), 4.42 (br s, 1 H), 6.02 (dd, J = 9.5, 2.4 Hz, 1 H), 6.14 (d, J = 2.4 Hz, 1 H), 7.21–7.24 (m, 2 H), 7.36–7.39 (m, 2 H), 8.03 (d, J = 9.5 Hz, 1 H), 9.87 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.5, 51.6, 94.5, 107.9, 124.3, 126.0, 128.9, 129.7, 130.6, 137.7, 145.4, 152.9; MS(EI): *m/z* (%) 321 (18), 319 (M^+, 55), 304 (100); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{16}H_{18}N_3O_2^{35}Cl$: 319.1088; found: 319.1072.

4.10.6. 5-n-Butylamino-N-(4-chlorophenyl)-2-nitroaniline (**6f**)

Yellow crystals; mp 110–112 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.3 Hz, 3 H), 1.33–1.42 (m, 2 H), 1.53–1.59 (m, 2 H), 3.06 (t, J = 7.0 Hz, 2 H), 4.41 (br s, 1 H), 6.0–6.04 (m, 2 H), 7.22–7.25 (m, 2 H), 7.35–7.38 (m, 2 H), 8.05–8.08 (m, 1 H), 9.90 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7, 20.0, 31.1, 42.8, 92.5, 105.9, 124.7, 125.9, 129.3, 129.6, 130.5, 137.7, 145.8, 154.2; MS(EI): *m/z* (%) 321 (25), 319 (M^+, 77), 276 (100); HRMS(EI): *m/z* $[M]^+$ calcd for $C_{16}H_{18}N_3O_2^{35}Cl$: 319.1088; found: 319.1088.

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