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Reductive Molybdenum-Catalyzed Direct Amination of Boronic Acids with Nitro Compounds

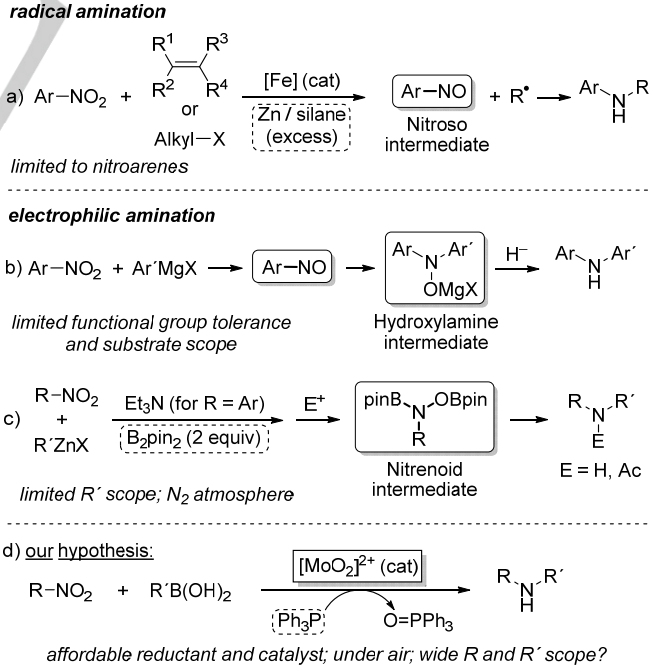
Samuel Suárez-Pantiga,* Raquel Hernández-Ruiz, Cintia Virumbrales, María R. Pedrosa, and Roberto Sanz*

Dedicated to Prof. Dr. Francisco J. Fañanás on the occasion of his retirement.

Abstract: The synthesis of aromatic amines is of utmost importance in a wide range of chemical contexts. We report a direct amination of boronic acids with nitro compounds to yield (hetero)aryl amines. The novel combination of a dioxomolybdenum(VI) catalyst and triphenylphosphine as inexpensive reductant has revealed to be decisive to achieve this new C–N coupling. Our methodology has proven to be scalable, air and moisture tolerant, highly chemoselective and engages both aliphatic and aromatic nitro compounds. Moreover, this general and step-economical synthesis of aromatic secondary amines showcases orthogonality to other aromatic amine syntheses as it tolerates aryl halides and carbonyl compounds.

The prevalence of aromatic amines in the chemical, materials, agrochemical and pharmaceutical industries is a constant driver for the innovation of synthetic methods.[1] The most general transformations to prepare (hetero)aryl amines include direct alkylation of amines with alkyl halides,[2] Buchwald-Hartwig,[3] Chan-Lam-Evans[4] or Ullman-type[4a,5] C–N cross-coupling reactions and reductive amination.[6] These amination methodologies employ amines as the nitrogen source, particularly anilines, which are usually obtained by reduction of nitroarene derivatives. As an alternative, other nitrogen-containing compounds have also been used as starting materials in C–N bond forming aminations like nitrosoarenes,[7] nitrenoids,[8] or hydroxylamines,[9] which are not commercially available and, again, must be obtained in a previous synthetic step by partial reduction of the nitro function. Therefore, the development of a general and efficient methodology for the synthesis of aromatic amines directly from abundant and readily available nitro(hetero)arenes is very attractive and remains an active research field. The use of nitro compounds as starting materials not only improves step-economy, saving time and cost, but may also allow tolerance of functional groups such as unprotected amine.[10]

Although nitroaromatics are efficiently engaged as starting materials in C–N bond forming reductive cyclizations to synthesize indoles or carbazoles,[11] the intermolecular amination to afford anilines in one single operational step has proved to be more challenging. The scarcely reported methodologies have in common that the nitro group evolves to a partially reduced intermediate, which reacts with a proper alkylating or arylating reagent. Therefore, the key success factor lies in reducing the nitro group to the corresponding intermediate avoiding its strongly favored over-reduction or its evolution through side-reactions. In this field, Baran's and Hu's groups have described the Fe-catalyzed synthesis of *N*-alkylanilines through an *in situ* generated nitroso intermediate, which is subsequently trapped by highly reactive alkyl radicals derived from alkenes[12] and alkyl halides,[13] respectively (Scheme 1a). Conceptually different electrophilic aminations have also been reported.[14] Within this framework, Knochel developed the construction of diarylamines by initial addition of arylmagnesium compounds to nitroarenes, involving the intermediacy of arylnitroso and diarylhydroxylamine derivatives (Scheme 1b).[15] More recently, Niggemann has described an elegant reductive coupling of zinc organyls with both aromatic and aliphatic nitro compounds. This is based in the partial reduction of the nitro group with B_2Pin_2 that yields a nitrenoid as the electrophilic amination reagent (Scheme 1c).[16] Despite the potential of this transformation, it is currently underexploited since a fine tuning of the nitrenoid could allow the amination of less nucleophilic reagents such as boronic acids.



Scheme 1. Direct amination with nitroarenes: state-of-the-art.

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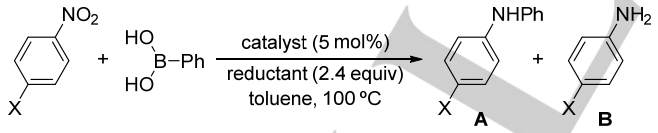
Boronic acids are a relevant class of intermediates as they exhibit wide functional group compatibility and synthetic versatility and are readily available from commercial sources or easily synthesized.[17] Based on these features, achieving a direct amination of boronic acids with nitro compounds is a major milestone, which repurposes these two accessible and simple building blocks as coupling partners delivering an excellent platform to easily construct diverse libraries of valuable aromatic amines. Only very recently, during the preparation of this manuscript, a protocol for this reaction by using $PhSiH_3$ as reductant and phosphetane P(III)/O=P(V) catalysis was reported by Radosevich and co-workers.[18] Ideally, the design of a moisture and air tolerant procedure and the utilization of an affordable reducing agent would be crucial to provide a general, simple and scalable methodology. Based on our experience in molybdenum catalyzed reactions,[19] we hypothesized that the Mo-catalyzed formation of a partially-reduced intermediate from a nitro compound may allow the direct electrophilic amination of boronic acids (Scheme 1d).

Initially, model reaction between phenylboronic acid and 1-chloro-4-nitrobenzene was chosen (Table 1) and a screen of several reducing agents was performed.[20] Pinacol proved to be unsuitable for this transformation as only direct reduction to the corresponding aniline **B** was observed (entry 1).[19a] However, PPh_3 and $P(OEt)_3$ were identified as viable reductants leading to high yields of diarylamine **A** and only minor amounts of the aniline side-product **B** (entries 2 and 3). However, when nitrobenzene was tested as substrate the conversion decayed considerably (entries 4 and 5). This decrease was even clearer with 4-nitrotoluene as starting material (entry 6). After some reoptimization,[20] best results were achieved by simple addition of 2,2'-bipyridine (bpy) as ligand and using PPh_3 as reductant (entries 7–9). When pre-formed $MoO_2Cl_2(bpy)_2$ was used instead, similar results were obtained although conversion was slightly lower (entry 10).

Table 1. Optimization of the Mo-catalyzed reductive coupling.[a]



Entry	X	Catalyst	Reductant	Conversion [%][b]	Yield[b] **A**:**B** [%]
1	Cl	$MoO_2Cl_2(dmf)_2$	Pinacol	70	–:54
2	Cl	$MoO_2Cl_2(dmf)_2$	PPh_3	94	78:12
3	Cl	$MoO_2Cl_2(dmf)_2$	$P(OEt)_3$	95	72:16
4	H	$MoO_2Cl_2(dmf)_2$	PPh_3	70	55:8
5	H	$MoO_2Cl_2(dmf)_2$	$P(OEt)_3$	62	40:15
6	Me	$MoO_2Cl_2(dmf)_2$	PPh_3	66	35:15
7	Cl	$MoO_2Cl_2(dmf)_2$/bpy	PPh_3	>95	>95:<5
8	H	$MoO_2Cl_2(dmf)_2$/bpy	PPh_3	>95	88:6
9	Me	$MoO_2Cl_2(dmf)_2$/bpy	PPh_3	>95	84:7
10	Me	$MoO_2Cl_2(bpy)_2$	PPh_3	88	82:<5

[a] Reaction conditions: nitroarene (0.2 mmol), $PhB(OH)_2$ (0.3 mmol), reductant (0.48 mmol), catalyst (5 mol%) in toluene (0.6 mL) at 100 ºC for 20 h, under air. [b] Determined by ^1H NMR analysis with CH_2Br_2 as internal standard.

With an optimized set of conditions in hand, the scope of both the nitro compound and the boronic acid partners was extensively studied. The ability of the reaction to tolerate sensitive functional groups in the nitroaromatic component is exceptional (Scheme 2). Halides are well tolerated in different positions with excellent yields (**2**–**4**, **13**, **14**, **17**–**19**), allowing for downstream C–C, C–O, and C–N cross-coupling chemistry. Alkyl (**5**, **20**) and methoxy (**6**) electron-donating groups (EDG) were also tested and remain unscathed. However, starting from 4-nitroanisole MW irradiation was required to achieve full conversion. Particularly remarkable is that amination takes place selectively over the nitro group when free amine is also present without the need for protecting group chemistry (**25**). This example clearly shows that the reaction does not proceed through the amino group, which would allow unconventional disconnections in retrosynthetic analysis. Notable performance is accomplished with nitroarenes bearing strong electron-withdrawing groups (EWG) such as cyano (**7**, **21**), ester (**10**, **22**) or amide (**11**). Despite being a reductive process, ketones (**8**, **9**, **23**) and even aldehydes (**15**) are not reduced, as opposed to the classic reductive amination that would again require protection of these functional groups. Moreover, α,β-unsaturated carbonyls and alkenes emerged unaltered affording the corresponding diarylamines in good yields (**12**, **16**). The process has also revealed to be compatible with nitroarenes bearing several functional groups in the same ring (**24**–**27**) and with highly sterically demanding *ortho*-disubstituted nitroarenes (**30**), although with more moderate yields. At the same time, polycyclic nitroarenes are well tolerated (**28**, **29**). Remarkably, nitroheteroarenes can also be used to deliver medicinally relevant building blocks containing indole (**31**), pyridine (**32**) and quinoline (**33**) scaffolds. Interestingly, selective mono-amination could be achieved in molecules bearing more than one nitro group (**34**).

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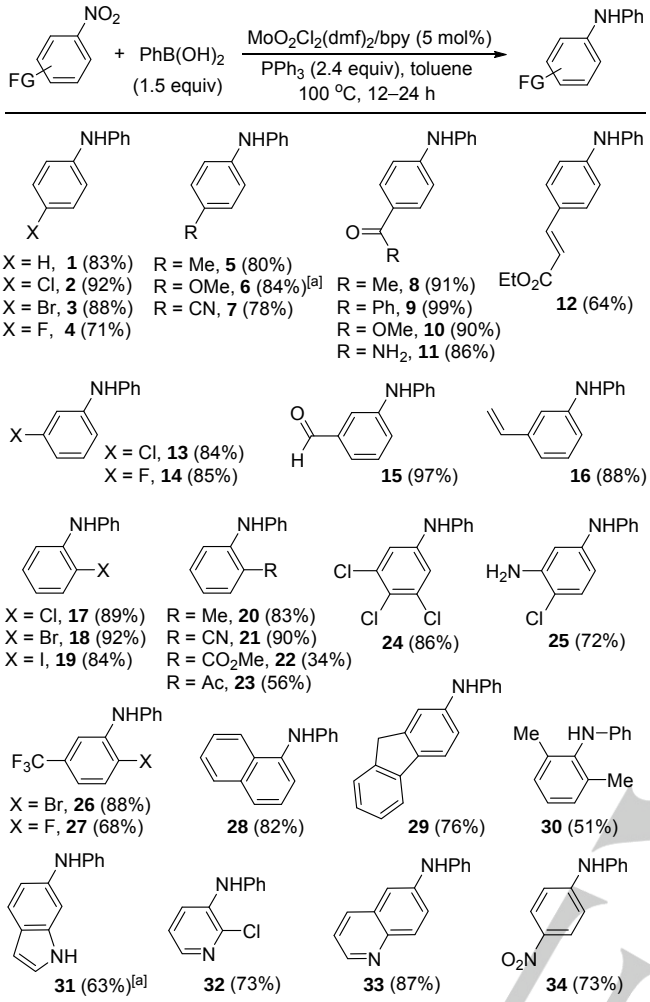
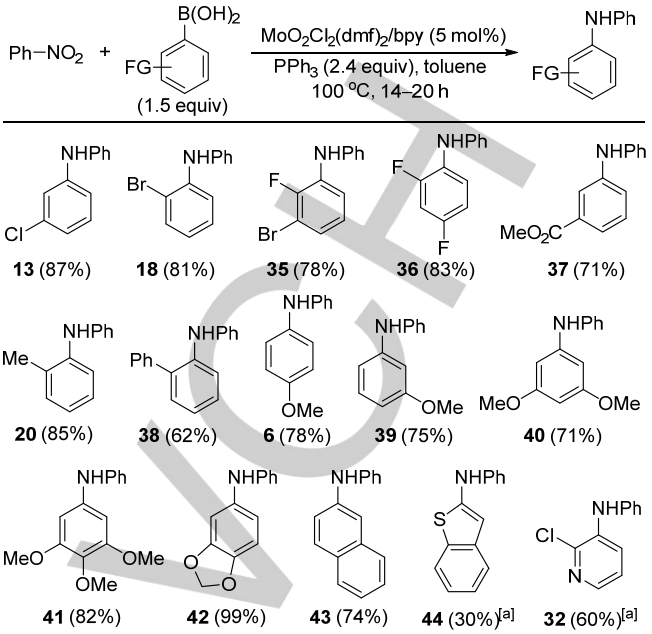


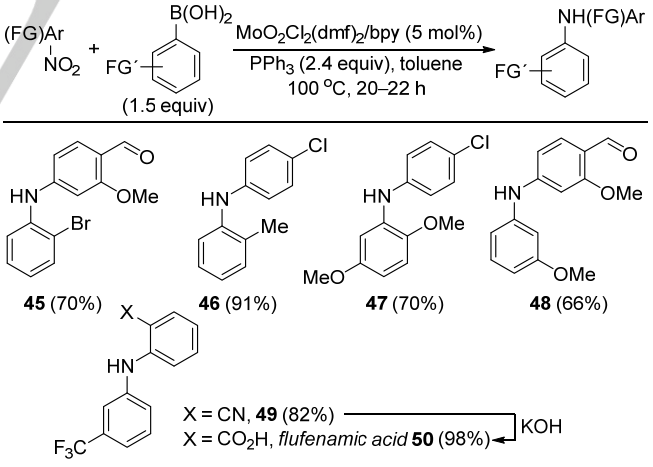
Scheme 2. Nitroarene scope (isolated yields). Conditions: nitroarene (0.5 mmol), in toluene (1.5 mL), under air. [a] Performed under MW irradiation (135 ºC, 25–40 min).

Next, a screen of diverse boronic acids was evaluated (Scheme 3). The transformation took efficiently place with excellent yields in presence of EWG in the aromatic ring such as halides (**13**, **18**, **35**, **36**) and ester (**37**). Moreover, *o*-substituted boronic acids also proved to effectively promote the transformation (**20**, **38**). At the same time, electron-donating alkoxy substituents were evaluated in different positions (**6**, **39**–**42**) providing satisfactory results without the need of MW irradiation, thus ideally complementing the nitroarene scope.[21] In addition, naphthyl (**43**), benzothienyl (**44**) and pyridinyl (**32**) boronic acids revealed also suitable.



Scheme 3. (Hetero)aryl boronic acid scope (isolated yields). Conditions: nitrobenzene (0.5 mmol), in toluene (1.5 mL), under air. [a] Performed under MW irradiation (135 ºC, 25 min).

Afterwards, diarylamines, such as **45**–**49**, possessing both functionalized coupling partners were also synthesized in high yields (Scheme 4). The usefulness of this protocol in the synthesis of bioactive compounds is shown with the efficient preparation of flufenamic acid (**50**), an anthranylic acid derivative.[22]



Scheme 4. Synthesis of highly functionalized diarylamines (isolated yields). Conditions: nitroarene (0.5 mmol), in toluene (1.5 mL), under air.

Remarkably, alkyl boronic acids were also compatible with this methodology as it was demonstrated with the synthesis of alkyl aryl amines **51**–**54**. Both primary and secondary alkyl boronic acids could undergo amination with selected

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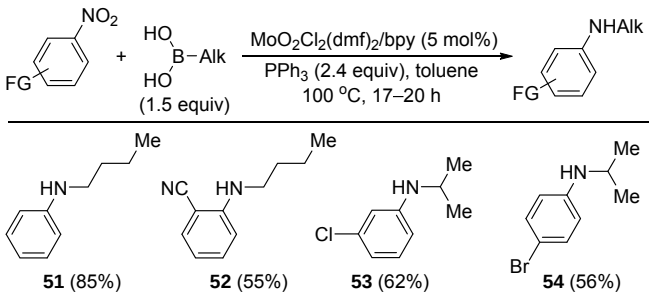
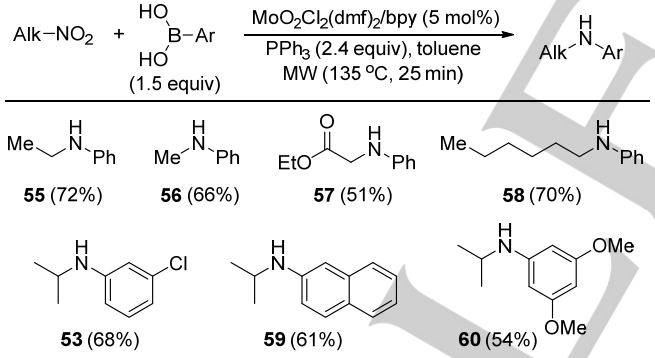
functionalized nitroarenes, although lower yields were obtained compared with the formation of C_{sp2}–N bonds (Scheme 5).



Scheme 5. Amination of alkyl boronic acids (isolated yields). Conditions: nitroarene (0.5–1 mmol), in toluene (1.5–3 mL), under air.

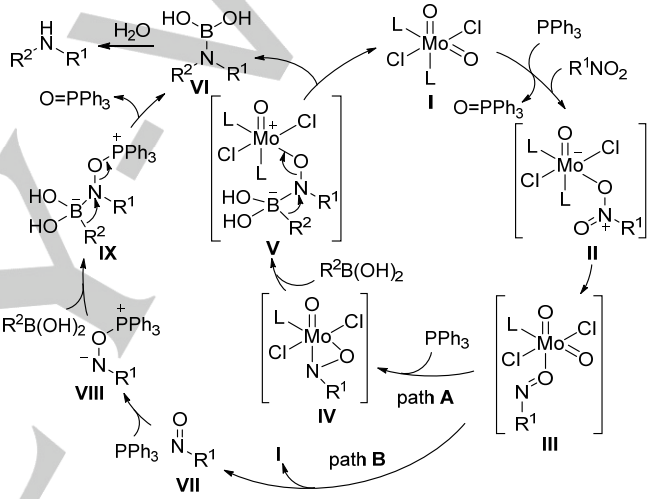
Finally, amination with the more challenging nitroalkanes was evaluated,[23] in which only Niggemann's very recent approach was able to succeed.[16b] Preliminary results under conventional heating at 100 ºC showcased low conversion and so, MW irradiation was tested. To our delight, high conversion to the desired alkylated anilines was achieved. Several primary and more sterically demanding secondary nitroalkanes were converted in presence of different aromatic boronic acids leading to alkyl aryl amines **53** and **55**–**60** in moderate to good yields (Scheme 6). Interestingly, when nitromethane is employed as substrate this procedure offers a facile access to selectively monomethylated *N*-methylanilines alternatively to the problematic mono *N*-methylation of anilines.



Scheme 6. Nitroalkane scope (isolated yields). Conditions: nitroalkane (1 mmol), in toluene (1.5 mL), under air.

The described procedure is amenable to scale up due to the ready availability of both nitro compounds and boronic acids, as well as, the use of inexpensive PPh_3 as reductant in combination with a dioxomolybdenum(VI) catalyst easily prepared from affordable Na_2MoO_4.[24] Accordingly, several nitroarenes were submitted to the reaction conditions at 7 mmol scale to provide gram amounts of aromatic amines **10** (1.42 g, 92%), **15** (1.19 g, 86%), **46** (1.33 g, 88%), and **51** (10 mmol scale, 1.10 g, 74%).

A plausible mechanism is depicted in Scheme 7. It is well known that dioxomolybdenum(VI) catalyst **I** is easily reduced by PPh_3 to a Mo(IV) species,[25] which upon coordination to the nitro compound would afford **II**. Next, reoxidation of the Mo center by the coordinated nitro compound would deliver intermediate **III** bearing a nitroso ligand. At this point two different pathways could be considered. Path **A** would involve a second deoxygenation of **III** with PPh_3 giving rise, after reduction of the nitroso ligand and reoxidation of the metal center, to a new molybdooxaziridine (or η^2-nitroso) species **IV**.[26] The attack of the N atom to the boronic acid would afford nitrenoid intermediate **V**, whose subsequent rearrangement would generate aminoboronic acid **VI**. Alternatively, path **B** would involve the release of free nitroso compound **VII**,[7c] which after reaction with a second equiv of PPh_3 would generate reduced adduct **VIII**. Its interaction with the boronic acid would deliver nitrenoid borate intermediate **IX**, which would eventually release $O{=}PPh_3$ and the same aminoboronic acid **VI** through 1,2-migration of a nucleophilic R^2 group.[27] Final hydrolysis would provide the isolated secondary aromatic amine.



Scheme 7. Mechanistic proposal.

In summary, we have described a practical, efficient, scalable, air and moisture tolerant procedure for the general synthesis of secondary aromatic amines from nitro compounds in a single synthetic operation. As these results demonstrate, the covered chemical space of our methodology is much wider and diverse than that achieved with classical reactions and includes the synthesis of many highly substituted and functionalized amines. Not only nitroarenes but also nitroalkanes proved to be suitable substrates for this transformation. The wide availability of nitro compounds and boronic acids, in conjunction with the use of affordable PPh_3 as reductant and an easily available Mo(VI) catalyst, make this simple strategy advantageous to construct libraries of (hetero)aryl amines.

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Keywords: amination • boronic acids • molybdenum • nitro compounds • reduction

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[27] The results with nitroalkanes would suggest that no free nitroso is generated, because a primary or secondary nitroso alkane would rapidly suffer tautomerization to oxime making inaccessible the subsequent C–N amination. However, nitrosoarene compounds efficiently afforded the corresponding diarylamines when subjected to the standard reaction. So, regarding the reaction with nitroaromatics, the participation of free nitrosoarenes is feasible. See Supporting Information for further details.

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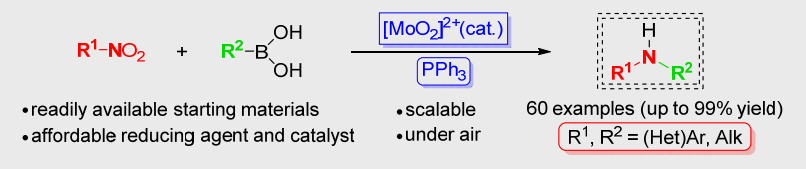

C–N Coupling: In the present work a new electrophilic amination of boronic acids with simple and inexpensive nitro compounds has been developed allowing the preparation of a variety of highly substituted and functionalized aromatic secondary amines. The reported process employs affordable PPh_3 as reducing agent, in the presence of an easily available and highly stable dioxomolybdenum(VI) complex as catalyst.

Samuel Suárez-Pantiga, Raquel Hernández-Ruiz, Cintia Virumbrales, María R. Pedrosa and Roberto Sanz**

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Reductive Molybdenum-Catalyzed Direct Amination of Boronic Acids with Nitro Compounds