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Synthesis of Mono-*N*-Methyl Aromatic Amines from Nitroso Compounds and Methylboronic Acid

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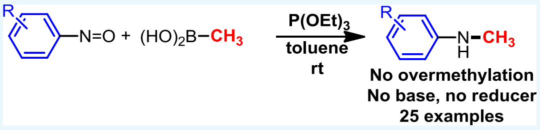
Supporting Information

ABSTRACT: The selective synthesis of mono-*N*-methyl aromatic amines was achieved by the reaction of aromatic nitroso compounds with methylboronic acid promoted by triethylphosphite under transition metal-free conditions. The target compounds are constructed efficiently without overmethylation, under environmentally benign reaction conditions that do not require bases or reductants and therefore are of interest in pharmaceutical, agricultural, and chemical industries.



No overmethylation
No base, no reducer
25 examples

INTRODUCTION

Mono-*N*-methyl aromatic amines are common scaffolds among pharmaceutical, dye, and agrochemical compounds.[1] Despite the apparent simplicity of the NHMe functionality, the synthesis of this motif is far from easy.

Most general methods to prepare these compounds rely on the use of free amines as starting materials (Scheme 1, strategies A and B). Strategy A is centered on the construction of the C(sp^2)−N bond. The most frequent approaches make use of methylamine and functionalized aryl electrophiles under transition-metal catalysis.[2] Specific Pd-based[3] (Buchwald−Hartwig amination) and Cu-based[4] (Ullmann−Goldberg reaction) systems have been developed for the coupling reactions of methylamine with aryl (pseudo)halides, while only some scattered examples under Ni catalysis have been reported.[5]

The Cham−Evans−Lam reaction using arylboronic acids has also been used for the construction a few examples of mono-*N*-methylaniline derivatives.[6] Methylamine is a particularly challenging amine to monoarylate by these procedures due to its tendency to diarylate because of its small size. Apart from the use of toxic and expensive metals, most of these transformations require complicated ancillary ligands and/or the presence of strong bases. In limited cases, transition-metal-free reactions between methylamine and activated substrates are possible by S$_N$Ar or via benzyne intermediates.[7] The Umpolung strategy, ie. the use of aryl organometallics together with nitrogen electrophiles, has scarcely been used for the direct introduction of an NHMe group.[8]

Strategy B (Scheme 1) is based on the construction of the N−Me bond by making use of primary arylamines as starting materials. The reactions of primary arylamines with S$_N$2-methylating agents[9] are usually hampered by overmethylation, as a consequence of the increased nucleophilicity of the monomethylated secondary aromatic amine in comparison to the nonmethylated starting material, and the small steric hindrance of the methyl group. Reductive amination approaches for methylation require the use of formaldehyde as a carbon source together with a reducing agent.[10] Also, the reduction of carbamates[11] or formamides[12] is feasible. However, some of these reduction procedures may be incompatible with the presence of other labile functional groups. To control over-reaction, the use of acyl[13] or sulfonyl[14] derivatives of the starting amines as precursors is frequent, even though this requires the inclusion of protection/deprotection steps in the reaction sequence, which may be cumbersome. More recent approaches have been developed to circumvent some of these issues, such as the use of carbon dioxide[15] or MeOH[16] as C1-building blocks. Even so, these methods require high temperatures and the use of expensive transition metals and complex ligands. In addition to these procedures, the alkylation of (hetero)arylamines can also be accomplished by the Cu-catalyzed Chan−Evans−Lam reaction using alkylboronic acids.[17] However, when applied to methylation, the method requires overstoichiometric quantities of copper salts and methylboronic acid and a basic medium.[18] Dimethylation is frequent under these reaction conditions.

In many occasions, the primary arylamines used as starting materials in strategy B are prepared in advance by the reduction of other nitrogen-containing functional groups. Therefore the direct engagement of these functionalities in amine formation has emerged as a relevant strategy (Scheme 1, strategy C) for the synthesis of secondary arylamines because it eliminates the previous reduction step, and avoids protection of functional groups that may be labile to the reduction conditions. In this realm, nitro compounds[19] have been used most frequently. Nitroso compounds,[20] although less popular, can be used similarly.[21,22] Although successful for the synthesis of various alkylarylamines and diarylamines, this sort of strategy has been elusive for the particular case of the

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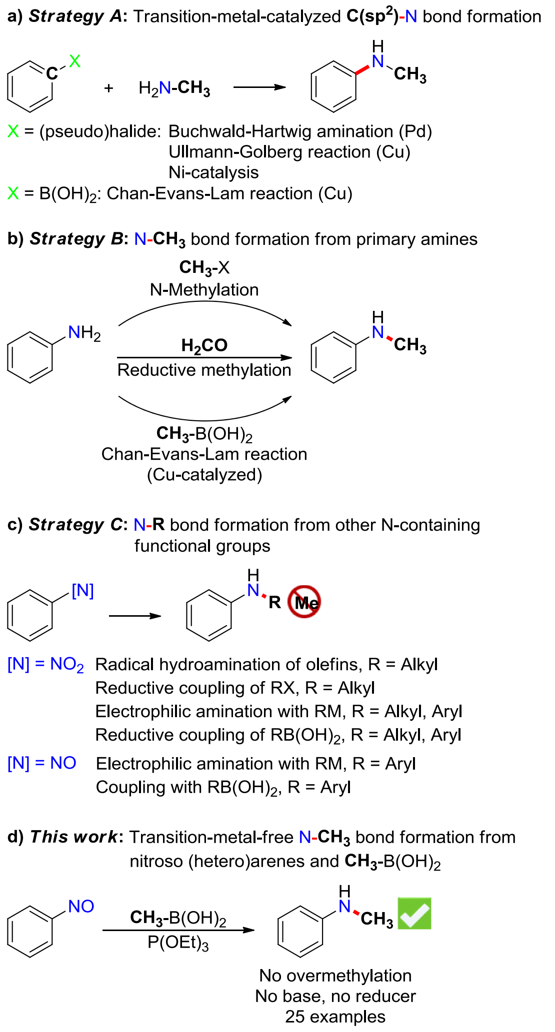
Scheme 1. Previous Strategies and This Work



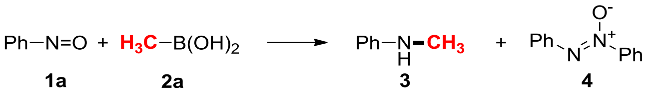
NHMe group.[19] In the present paper, we have addressed this issue and developed conditions that permit the transformation of nitrosoarenes into mono-*N*-methyl arylamines easily.

■ RESULTS AND DISCUSSION

We started our research by adjusting the reaction conditions for the reaction of nitrosobenzene **1a** with methylboronic acid **2a** towards the direct synthesis of *N*-methylaniline **3** (Table 1). Based on our previous experience in the synthesis of diarylamines,[21] we tested different P(III) species as oxygen scavengers.

When using PPh_3 or dppe in toluene, we observed extensive formation of the azoxybenzene **4** (entries 1, 2).[23] On the other hand, the use of $P(OEt)_3$ (1.1 equiv) in toluene significantly increased the ratio of **3** (entry 3). Taking into account the balance between the amount of methylboronic acid **2**, the **3**/**4** ratio, and the isolated yield in **3** (entries 3 and 4), the best conditions were found when using 1.1 equiv of $P(OEt)_3$ in toluene (entry 4). The reactions in tetrahydrofuran (THF) or dichloromethane (DCM) afforded more azoxybenzene **4** and lower yield in **3**.

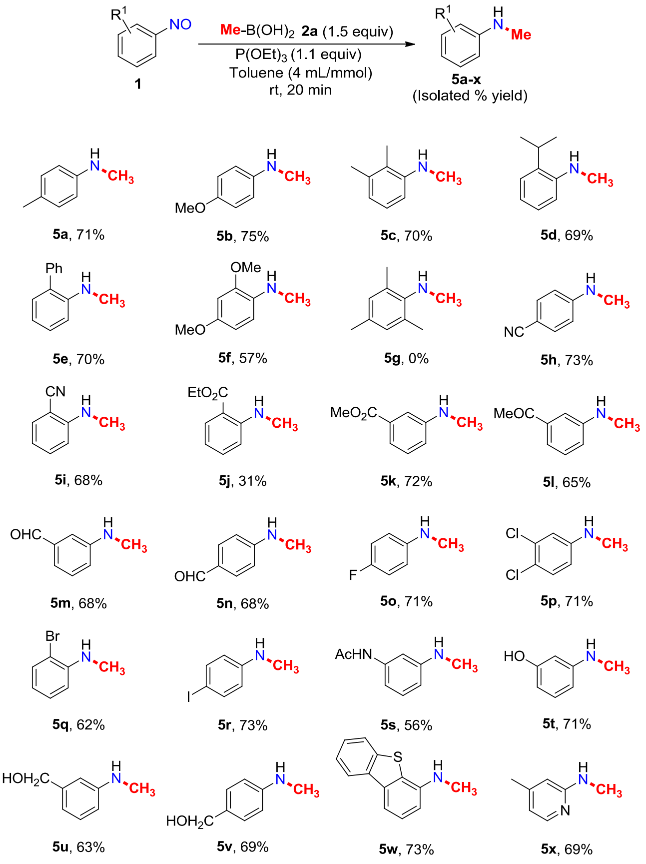
Table 1. Optimization of Reaction Conditions[a]



entry	**2** (equiv)	PR_3 (equiv)	solvent (mL)	**3**/**4** ratio	**3** (%)[b]
1	1.0	PPh_3 (1.1)	toluene (1.0)	51/49	32
2	1.0	dppe (1.1)	toluene (1.0)	60/40	49
2	1.0	$P(OEt)_3$ (1.0)	toluene (1.0)	95/05	71
3	***1.5***	***$P(OEt)_3$*** (1.1)	***toluene*** (1.1)	***98/02***	***82***
4	2.0	$P(OEt)_3$ (1.1)	toluene (1.1)	99/01	83
5	1.5	$P(OEt)_3$ (1.1)	THF (1.1)	65/35	62
6	1.5	$P(OEt)_3$ (1.1)	DCM (1.1)	95/05	72

[a] **1a** (0.28 mmol). Reactions carried out at rt for 20 min. [b] Isolated yields.

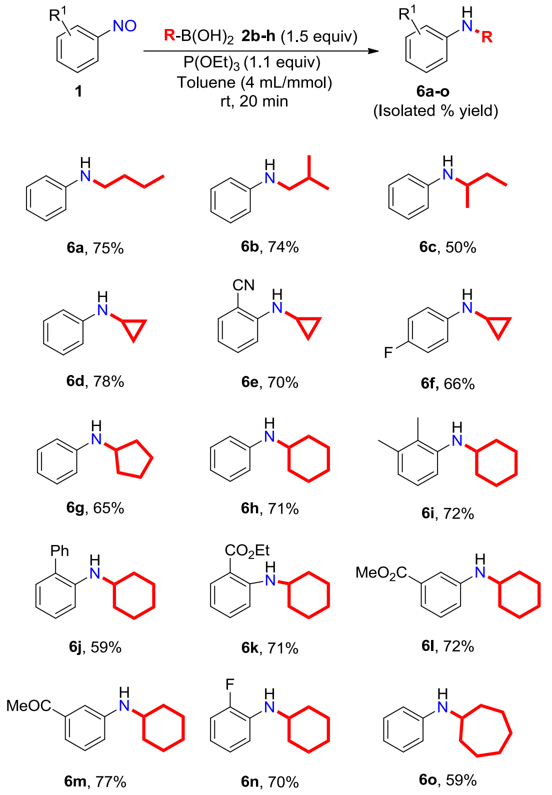
Scheme 2. Synthesis of Mono-*N*-Methyl Aromatic Amines 5a−x



Under optimum reaction conditions for the synthesis of **3** (Table 1, entry 3), we carried out the transformation of a variety of nitrosoarenes into the corresponding *N*-methyl derivatives (Scheme 2), testing for compatibility with labile functional groups such as carbonyls or unprotected OH and NH groups. We observed that nitrosoarenes carrying electron-donating or electron-withdrawing groups were selectively monomethylated to form the corresponding *N*-methylarylamines **5** in good yields. In general, electron-donating substituents, such as methyl, methoxy, isopropyl, or phenyl (**5a**−**5f**) performed well. Sterically demanding ortho-substituted nitrosoarenes (**5c**−**5f**) were also efficiently monomethylated. This constitutes an important feature, because sterically demanding substrates are in general less active in *N*-methylation processes compared to para- or meta-substituted ones.[24] However, double ortho substitution by methyl was not permitted (**5g**). Notably, the reaction could also be applied to substrates bearing reactive functional groups such as cyano, ester, ketone, as well as aldehyde in ortho-, meta or para-positions (**5h**−**5n**). Mono or disubstituted aryl halides were also well tolerated (**5o**−**5r**), thus opening the possibility of further functionalization of the resulting methylamines by conventional cross coupling reactions of the aryl halide. Furthermore, *N*-methylarylamines containing NHAc (**5s**), unprotected phenolic OH (**5t**), and compounds with alcoholic OH groups (**5u**, **5v**) were synthesized in good yields, thus avoiding protection/deprotection reactions that are frequent among other syntheses of *N*-methylanilines. Finally, the reaction could be extended to the monomethylation of heterocyclic nitroso compounds as well (**5w**, **5x**).

In addition to methylation, we were also pleased to find that this procedure was also useful for the transformation of the nitroso group into other mono-*N*-alkylamines **6** different from *N*-methyl (Scheme 3). We tested the reaction of different alkylboronic acids **2**, using nitrosobenzene (**1a**) as a reagent. Under optimum reaction conditions for the synthesis of **3**, mono-*N*-alkylaryl amines were obtained in good yields with primary linear and branched alkyl boronic acids (**6a**−**6c**). However, the reaction with a secondary alkyl boronic acids gave a lower yield (**6c**). On the other hand, the use of cyclic boronic acids such as cyclopropyl (**6d**), cyclopentyl (**6g**), cyclohexyl (**6h**), and cycloheptyl (**6o**), permitted the synthesis of mono-*N*-alkylaryl amines with a good yield. This is an important issue especially for the sometimes challenging synthesis of *N*-arylcyclopropylamines (**6d**).[25] For completeness, some additional new cases were included in the study with differently functionalized nitrosoarenes **1** using cyclopropyl (**6e**, **6f**) and cyclohexylboronic acids as reagents (**6i**−**6n**), including examples with cyano, ester, ketone, and halogens, among others. All reactions took place in good yields, including those carrying ortho-substituents.

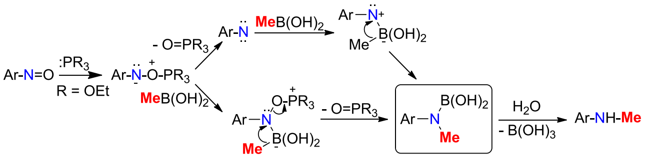
Scheme 3. Synthesis of Mono-*N*-Alkylanilines 6a−o



In order to test the scaling possibilities, we have carried out the 1 g-scale synthesis of the benzothiazole-aniline derivative Pittsburgh compound B (PiB) **8** (Scheme 4). 11C-PiB is currently the most studied radio ligand for positron emission tomography (PET) imaging of cerebral amyloid beta (Aβ) deposits by PET for investigational studies of Alzheimer's disease. The functionalization of its hydroxyl group has permitted the synthesis of a variety of other derivatives with improved pharmacokinetics useful as probes for Aβ by different imaging techniques.[26] Compound **8** was prepared directly from 1 g of hydroxylamine **7** in a 47% overall yield without purification of intermediates. Thus, hydroxylamine **7** was converted with $K_3Fe(CN)_6$ into the corresponding nitroso compound. Without purification, methyl boronic acid **2a** and $P(OEt)_3$ were added to obtain the corresponding *N*-methylarylamine, and the phenolic methyl group was removed in situ using BBr_3.

Based on previous considerations,[21] the reaction can be understood (Scheme 5) by the formation of a key arylmethylaminoboronate from the nucleophilic attack of $P(OEt)_3$ to the starting nitrosobenzene followed by borylation of the resulting intermediate (either the initial tetravalent phosphorous species or a nitrene, the latter generated by unimolecular extrusion of triethyl phosphate).

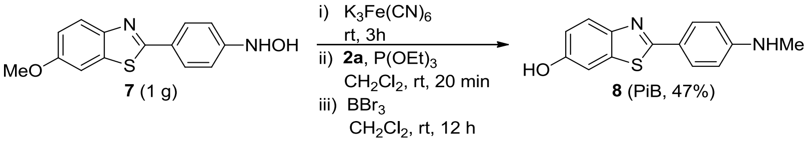
Scheme 5. Proposed Reaction Course



CONCLUSIONS

In summary, the results presented in this paper permit the synthesis of mono-*N*-methyl aromatic amines (25 examples, 31−82% yield) and other mono-*N*-alkyl aromatic amines (15 examples, 50−78% yield) directly from nitroso compounds and boronic acids without overfunctionalization to secondary amines or ammonium salts. The reactions promoted by $P(OEt)_3$ are transition-metal-free and take place in only 20 min at rt, without the need of specially dried solvents, anhydrous conditions, reducing agents, bases, or other additives. The subproducts of the reaction, triethyl phosphate

Scheme 4. Synthesis of 2-(4-(Methylamino)phenyl)benzo[*d*]thiazol-6-ol 8



and boric acid, are of low toxicity, thus minimizing the generation of hazardous substances, as required in contemporary industrial applications.

■ EXPERIMENTAL SECTION

General Information. Unless otherwise stated, all starting materials acids were commercially available research-grade chemicals and used without further purification. Silica gel 60 F254 was used for TLC, and the spots were detected with UV light (254 and/or 366 nm) and/or vanillin solution. Flash column chromatography was carried out on silica gel 60. ^{1}H NMR spectra were recorded at 300 MHz, ^{13}C NMR spectra were recorded at 75 MHz, and ^{19}F NMR spectra were recorded at 282 MHz, all of them in $CDCl_3$, acetone-d_6, or DMSO-d_6 solution. Nitrosobenzene **1a** and boronic acids **2b**−**2g** are commercially available. The syntheses of the rest of nitrosorarenes **1**, boronic acid **2h**, and hydroxylamine **7** were previously reported. These compounds were prepared by reproduction of the corresponding procedures.

Synthesis of 1a−x, 2h and 7. 1-Methyl-4-nitrosobenzene (**1b**), 1-methoxy-4-nitrosobenzene (**1c**), 1,2-dimethyl-3-nitrosobenzene (**1d**), 2-nitroso-1,1′-biphenyl (**1f**), 2,4-dimethoxy-1-nitrosobenzene (**1g**), 1,3,5-trimethyl-2-nitrosobenzene (**1h**), 4-nitrosobenzonitrile (**1i**), methyl 3-nitrosobenzoate (**1l**), 1-(3-nitrosophenyl)ethanone (**1m**), 3-nitrosobenzaldehyde (**1n**), 4-nitrosobenzaldehyde (**1o**), 1-fluoro-4-nitrosobenzene (**1p**), 1,2-dichloro-4-nitrosobenzene (**1q**), 1-iodo-4-nitrosobenzene (**1s**), *N*-(3-nitrosophenyl)acetamide (**1t**), and 4-nitrosodibenzo[*b*,*d*]thiophene (**1x**) were prepared following a previously reported procedure starting from the corresponding potassium aryltrifluoroborates.[27] 1-Isopropyl-2-nitrosobenzene (**1e**),[28] 2-nitrosobenzonitrile (**1j**),[29] ethyl 2-nitrosobenzoate (**1k**),[29] 1-bromo-2-nitrosobenzene (**1r**),[30] (3-nitrosophenyl)methanol (**1v**),[31] 4-methyl-2-nitrosopyridine (**1y**),[32] and 1-fluoro-2-nitrosobenzene (**1z**),[33] were prepared following previously reported procedures starting from anilines. 3-Nitrosophenol (**1u**)[34] and (4-nitrosophenyl)methanol (**1w**)[35] were prepared following previously reported procedures starting from nitro compounds. Cycloheptylboronic acid **2h** was prepared following a previously reported procedure starting from cycloheptene.[36] Hydroxylamine **7** was prepared following a previously reported procedure starting from 6-methoxy-2-(4-nitrophenyl)benzo[*d*]thiazole.[37]

General Procedure for the Reaction of Nitrosoarenes 1 with Boronic Acids. $P(OEt)_3$ (0.31 mmol, 1.1 equiv) was added to a solution of nitrosoarene **1** (0.28 mmol, 1.0 equiv) and boronic acid (0.42 mmol, 1.5 equiv) in toluene (1.1 mL), and the mixture was stirred at rt for 20 min. The reaction mixture was purified by flash column chromatography eluting with hexane/AcOEt or CH_2Cl_2/AcOEt, as indicated.

***N*-Methylaniline (3).** It is a known compound[38] obtained in 82% yield (24.6 mg) from nitrosobenzene (30.2 mg), methylboronic acid (25.1 mg), and $P(OEt)_3$ (53 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.4 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.62 (t, *J* = 7.6 Hz, 2H), 2.84 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.3, 129.2, 117.3, 112.5, 30.8 ppm. Anal. Calcd for C_7H_9N: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.57; H, 8.46; N, 13.04.

***N*,4-Dimethylaniline (5a).** It is a known compound[39] obtained in 71% yield (21.3 mg) from 1-methyl-4-nitrosobenzene (30.5 mg), methylboronic acid (22.2 mg), and $P(OEt)_3$ (47 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.45 (s, 3H), 2.40 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.7, 137.1, 129.8, 119.1, 31.5, 20.8 ppm. Anal. Calcd for $C_8H_{11}NO$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.40; H, 9.11; N, 11.55.

4-Methoxy-*N*-methylaniline (5b). It is a known compound[40] obtained in 75% yield (22.6 mg) from 1-methoxy-4-nitrosobenzene (30.2 mg), methylboronic acid (19.6 mg), and $P(OEt)_3$ (41 μL). Flash column chromatography eluting with hexane/AcOEt 8:2 yielded the compound as yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.80 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 2.80 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.0, 143.6, 114.8, 113.5, 55.7, 31.5 ppm. Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.09; H, 8.03; N, 10.19.

***N*,2,3-Trimethylaniline (5c).** It is a known compound[41] obtained in 70% Yield (21.0 mg) from 1,2-dimethyl-3-nitrosobenzene (30.6 mg), methylboronic acid (19.9 mg), and $P(OEt)_3$ (42 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22 (t, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 3.69 (br s, 1H), 3.02 (s, 3H), 2.44 (s, 3H), 2.18 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.3, 136.3, 126.3, 120.2, 119.3, 107.4, 31.1, 20.7, 12.4 ppm. Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.82; H, 9.60; N, 10.38.

2-Isopropyl-*N*-methylaniline (5d). It is obtained in 69% yield (20.7 mg) from 1-isopropyl-2-nitrosobenzene (30.2 mg), methylboronic acid (18.0 mg), and $P(OEt)_3$ (38 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10−7.20 (m, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 3.80 (br s, 1H), 2.90 (s, 3H), 2.87 (h, *J* = 6.7 Hz, 1H), 1.26 (d, *J* = 6.7 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.0, 132.3, 16.9, 124.9, 117.4, 110.0, 31.2, 27.2, 22.5 ppm. Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.39; H, 10.17; N, 9.35.

***N*-Methyl-[1,1′-biphenyl]-2-amine (5e).** It is a known compound[3f] obtained in 70% yield (21.0 mg) from 2-nitroso-1,1′-biphenyl (30.5 mg), methylboronic acid (14.7 mg), and $P(OEt)_3$ (31 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (dt, *J* = 7.7 Hz, 2H), 6.66 (td, *J* = 7.6 Hz, 2H), 4.67 (br s, 1H), 2.91 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.0, 134.2, 132.5, 117.9, 116.2, 109.9, 95.4, 29.9 ppm. Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.35; H, 7.16; N, 7.60.

2,4-Dimethoxy-*N*-methylaniline (5f). It is a known compound[42] obtained in 57%yield (17.1 mg) from 2,4-dimethoxy-1-nitrosobenzene (30.1 mg), methylboronic acid (16.1 mg), and $P(OEt)_3$ (34 μL). Flash column chromatography eluting with hexane/AcOEt 8:2 yielded the compound as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.50 (m, 3H), 3.80 (s, 3H), 3.76 (s, 3H), 2.83 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.4, 147.6, 133.5, 109.0, 103.3, 98.3, 55.2, 54.9, 30.6 ppm. Anal. Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.69; H, 7.80; N, 8.36.

4-(Methylamino)benzonitrile (5h). It is a known compound[18] obtained in 73% yield (21.9 mg) from 4-nitrosobenzonitrile (30.1 mg), methylboronic acid (20.4

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mg), and P(OEt)$_3$ (43 μL). Flash column chromatography eluting with hexane/AcOEt 8:2 yielded the compound as colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.38 (d, J = 8.8 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H), 4.54 (br s, 1H), 2.83 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 152.2, 133.5, 120.5, 111.7, 98.1, 29.8 ppm. Anal. Calcd for $C_8H_8N_2$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.58; H, 6.17; N, 21.18.

2-(Methylamino)benzonitrile (5i). It is a known compound[18] obtained in 68% yield (20.4 mg) from 2-nitrosobenzonitrile (20.4 mg), methylboronic acid (14.5 mg), and P(OEt)$_3$ (43 μL). Flash column chromatography eluting with hexane/AcOEt 8:2 yielded the compound as a white solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.38−7.44 (m, 1H), 7.17−7.23 (m, 1H), 6.54−6.66 (m, 2H), 4.42 (br s, 1H), 2.89 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 145.9, 132.2, 128.5, 117.6, 110.6, 109.6, 30.6 ppm. Anal. Calcd for $C_8H_8N_2$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.59; H, 6.08; N, 21.27.

Ethyl 2-(Methylamino)benzoate (5j). It is a known compound[43] obtained in 31% yield (9.3 mg) from ethyl 2-nitrosobenzoate (30.0 mg), methylboronic acid (15.0 mg), and P(OEt)$_3$ (32 μL). Flash column chromatography eluting with hexane/AcOEt 8:2 yielded the compound as colorless liquid. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.92 (d, J = 8.0 Hz, 1H), 7.66 (br s, 1H), 7.37 (t, J = 7.2 Hz, 1H), 6.66 (d, J = 8.4 Hz, 1H), 6.58 (t, J = 7.2 Hz, 1H), 4.28−4.33 (m, 2H), 2.90 (d, J = 3.2 Hz, 3H), 1.37 (t, J = 7.2 H, 3H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.7, 152.0, 134.5, 131.5, 114.2, 110.6, 110.1, 60.1, 29.5, 14.3 ppm. Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.92; H, 7.21; N, 7.80.

Methyl 3-(Methylamino)benzoate (5k). It is a known compound[44] obtained in 72% yield (21.6 mg) from methyl 3-nitrosobenzoate (30.2 mg), methylboronic acid (16.3 mg), and P(OEt)$_3$ (34 μL). Flash column chromatography eluting with hexane/AcOEt 8:2 yielded the compound as brown oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.37 (d, J = 7.5 Hz, 1H), 7.26 (s, 1H), 7.22 (t, J = 7.8 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H) 3.88 (s, 3H), 3.80 (br s, 1H), 2.84 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.7, 149.3, 131.0, 129.1, 118.4, 117.0, 112.9, 52.1, 30.7 ppm. Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.53; H, 6.72; N, 8.45.

1-(3-(Methylamino)phenyl)ethanone (5l). It is obtained in 65% yield (19.5 mg) from 1-(3-nitrosophenyl)ethanone (29.6 mg), methylboronic acid (18.1 mg), and P(OEt)$_3$ (38 μL). Flash column chromatography eluting with hexane/AcOEt 8:2 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.25−7.32 (m, 2H), 7.17−7.21 (m, 1H), 6.80 (dt, J = 6.4, 2.5 Hz, 1H), 3.93 (br s, 1H), 2.88 (s, 3H), 2.58 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 198.9, 149.6, 138.2, 129.3, 117.7, 117.3, 111.0, 30.7, 26.8 ppm. Anal. Calcd for $C_9H_{11}NO$: C, 72.46; H, 7.43; N, 9.39. Found: C, 72.40; H, 7.46; N, 9.41.

3-(Methylamino)benzaldehyde (5m). It is obtained in 68% yield (20.4 mg) from 3-nitrosobenzaldehyde (30.5 mg), methylboronic acid (20.3 mg), and P(OEt)$_3$ (42 μL). Flash column chromatography eluting with hexane/AcOEt 8:2 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.91 (s, 1H), 7.32 (t, J = 7.9 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 7.06 (s, 1H), 6.85 (dm, J = 7.9 Hz, 1H), 3.99 (br s, 1H), 2.87 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 193.1, 149.8, 137.5, 129.7, 120.1, 119.1, 110.8, 30.6 ppm. Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.19; H, 6.68; N, 10.42.

4-(Methylamino)benzaldehyde (5n). It is a known compound[45] obtained in 68% yield (20.3 mg) from 4-nitrosobenzaldehyde (30.7 mg), methylboronic acid (20.3 mg), and P(OEt)$_3$ (42 μL). Flash column chromatography eluting with hexane/AcOEt 8:2 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.72 (s, 1H), 7.70 (d, J = 9.0 Hz, 2H), 6.62 (d, J = 9.0 Hz, 2H), 4.53 (br s, 1H), 2.92 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 190.4, 154.3, 132.3, 126.3, 111.5, 30.0 ppm. Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.15; H, 6.76; N, 10.37.

4-Fluoro-*N*-methylaniline (5o). It is a known compound[46] obtained in 71% yield (21.3 mg) from 1-fluoro-4-nitrosobenzene (30.5 mg), methylboronic acid (21.5 mg), and P(OEt)$_3$ (45 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.89 (t, J = 8.9 Hz, 2H), 6.52−6.55 (m, 2H) 2.80 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 156.7, 154.8, 145.7, 115.6, 115.4, 113.1, 113.0, 31.3. ppm. ^{19}F NMR (282 MHz, CDCl$_3$): δ −128.5 ppm. Anal. Calcd for C_7H_8FN: C, 67.18; H, 6.44; N, 11.19. Found: C, 67.35; H, 6.47; N, 11.22.

3,4-Dichloro-*N*-methylaniline (5p). It is obtained in 71% yield (21.3 mg) from 1,2-dichloro-4-nitrosobenzene (30.2 mg), methylboronic acid (15.3 mg), and P(OEt)$_3$ (32 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.18 (d, J = 8.7 Hz, 1H), 6.64 (d, J = 2.9 Hz, 1H), 6.42 (dd, J = 8.7 Hz, J = 2.9 Hz, 1H), 3.78 (br s, 1H), 2.80 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 148.8, 132.9, 130.6, 120.7, 113.3, 112.4, 30.7 ppm. Anal. Calcd for $C_7H_7Cl_2N$: C, 47.76; H, 4.01; N, 7.96. Found: C, 47.66; H, 3.98; N, 7.99.

2-Bromo-*N*-methylaniline (5q). It is a known compound[47] obtained in 62% yield (18.6 mg) from 1-bromo-2-nitrosobenzene (30.4 mg), methylboronic acid (14.5 mg), and P(OEt)$_3$ (30 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as pale yellow oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.38−7.44 (m, 1H), 7.17−7.23 (m, 1H), 6.54−6.66 (m, 2H), 4.42 (br s, 1H), 2.89 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 145.9, 132.2, 128.5, 117.6, 110.6, 109.6, 30.6 ppm. Anal. Calcd for C_7H_8BrN: C, 45.19; H, 4.33; N, 7.53. Found: C, 44.97; H, 4.43; N, 7.39.

4-Iodo-*N*-methylaniline (5r). It is a known compound[9b] obtained in 73% yield (21.9 mg) from 1-iodo-4-nitrosobenzene (30.3 mg), methylboronic acid (11.6 mg), and P(OEt)$_3$ (24 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.40−7.50 (m, 2H), 6.44−6.47 (m, 2H), 3.37 (br s, 1H), 2.81 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 148.8, 137.8, 115.2, 31.0. ppm. Anal. Calcd for C_7H_8IN: C, 36.08; H, 3.46; N, 6.01. Found: C, 35.98; H, 3.48; N, 6.06.

***N*-(3-(Methylamino)phenyl)acetamide (5s).** It is obtained in 56% yield (16.8 mg) from *N*-(3-nitrosophenyl)-acetamide (29.5 mg), methylboronic acid (16.4 mg), and P(OEt)$_3$ (34 μL). Flash column chromatography eluting with CH_2Cl_2/AcOEt 1:1 yielded the compound as brown oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.13 (br s, 1H), 7.10 (t, J = 8.0 Hz, 1H), 7.03 (s, 1H), 6.62 (d, J = 8.2 Hz, 1H), 6.36 (d, J = 8.0 Hz, 1H), 3.78 (br s, 1H), 2.82 (s, 3H), 2.15 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.3, 150.2, 139.0, 129.7, 108.6, 108.5, 104.1, 29.8, 24.9 ppm. Anal. Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.95; H, 7.29; N, 17.09.

3-(Methylamino)phenol (5t). It is a known compound[48] obtained in 71% yield (21.3 mg) from 3-nitrosophenol (30.5 mg), methylboronic acid (21.9 mg), and $P(OEt)_3$ (46 μL). Flash column chromatography eluting with hexane/AcOEt 7:3 yielded the compound as brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01 (t, J = 8.0 Hz, 1H), 6.22−6.16 (m, 2H), 6.08 (t, J = 2.3 Hz, 1H), 2.75 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.7, 150.7, 130.1, 105.8, 104.8, 99.8, 30.8 ppm. Anal. Calcd for C_7H_9NO: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.15; H, 7.31; N, 11.35.

(3-(Methylamino)phenyl)methanol (5u). It is a known compound[49] obtained in 63% yield (18.9 mg) from (3-nitrosophenyl)methanol (28.9 mg), methylboronic acid (19.6 mg), and $P(OEt)_3$ (41 μL). Flash column chromatography eluting with hexane/AcOEt 1:1 yielded the compound as pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16 (t, J = 7.8 Hz, 1H), 6.68 (d, J = 7.4 Hz, 1H), 6.61 (s, 1H), 6.53 (dd, J = 8.0, 2.2 Hz, 1H), 4.60 (s, 2H), 2.82 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.69, 142.18, 129.48, 115.88, 111.88, 110.88, 65.88, 30.73 ppm. Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.09; H, 8.15; N, 10.18.

(4-(Methylamino)phenyl)methanol (5v). It is a known compound[50] obtained in 69% yield (20.7 mg) from (4-nitrosophenyl)methanol (30.2 mg), methylboronic acid (19.6 mg), and $P(OEt)_3$ (41 μL). Flash column chromatography eluting with hexane/AcOEt 1:1 yielded the compound as a light brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 8.5 Hz, 2H), 4.74 (br s, 1H), 4.52 (s, 2H), 2.82 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.7, 129.3, 127.7, 111.1, 63.0, 29.7 ppm. Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.19; H, 8.10; N, 10.13.

***N*-Methyldibenzo[*b*,*d*]thiophen-4-amine (5w).** It is obtained in 73% yield (21.9 mg) from 4-nitrosodibenzo[*b*,*d*]-thiophene (30.3 mg), methylboronic acid (12.6 mg), and $P(OEt)_3$ (26 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10−8.17 (m, 1H), 7.85−7.92 (m, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.36−7.50 (m, 3H), 6.74 (d, J = 7.7 Hz, 1H), 3.73 (br s, 1H), 3.06 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.0, 138.6, 136.8, 136.3, 126.5, 126.2, 125.4, 124.6, 123.1, 122.1, 111.4, 106.9, 31.0 ppm. Anal. Calcd for $C_{13}H_{11}NS$: C, 73.20; H, 5.20; N, 6.57. Found: C, 73.11; H, 5.17; N, 6.59.

***N*,4-Dimethylpyridin-2-amine (5x).** It is a known compound[51] obtained in 69% yield (20.7 mg) from 4-methyl-2-nitrosopyridine (30.4 mg), methylboronic acid (22.0 mg), and $P(OEt)_3$ (46 μL). Flash column chromatography eluting with hexane/AcOEt 3:7 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, J = 5.2 Hz, 1H), 6.41 (d, J = 5.0 Hz, 1H), 6.19 (s, 1H), 4.81 (br s, 1H), 2.95 (s, 3H), 2.22 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.9, 148.4, 147.7, 114.3, 106.4, 29.2, 21.3 ppm. Anal. Calcd for $C_7H_{10}N_2$: C, 68.82; H, 8.25; N, 22.93. Found: C, 68.80; H, 8.21; N, 22.98.

***N*-Butylaniline (6a).** It is a known compound[52] obtained in 75% (yield 31.4 mg) from nitrosobenzene (30.1 mg), butylboronic acid (42.8 mg), and $P(OEt)_3$ (53 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09 (m, 2H), 6.61 (t, J = 7.3 Hz, 1H), 6.52 (d, J = 7.7 Hz, 2H), 3.51 (br s, 1H), 3.03 (t, J = 7.1 Hz, 2H), 1.52 (m, 2H), 1.35 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.67, 129.33, 117.18, 112.79, 43.79, 31.81, 20.44, 14.05 ppm. Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.39; H, 10.15; N, 9.39.

***N*-Isobutylaniline (6b).** It is a known compound[53] obtained in 74% yield (30.9 mg) from nitrosobenzene (30.3 mg), isobutylboronic acid (42.8 mg), and $P(OEt)_3$ (53 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16 (t, J = 7.3 Hz, 2H), 6.61 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 8.0 Hz, 2H), 3.67 (br s, 1H), 2.93 (d, J = 6.8 H, 2H), 1.89 (dp, J = 13.3 Hz, J = 6.7 Hz, 1H), 0.98 (d, J = 6.7 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 1148.5, 129.2, 116.9, 112.6, 51.8, 27.9, 20.5 ppm. Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.59; H, 10.11; N, 9.37.

***N*-(Sec-butyl)aniline (6c).** It is a known compound[19g] obtained in 50% yield (20.9 mg) from nitrosobenzene (30.0 mg), sec-butylboronic acid (42.8 mg), and $P(OEt)_3$ (53 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13−7.19 (m, 2H), 6.64−6.68 (m, 1H), 6.56−6.60 (m, 2H), 1.56−1.65 (m, 1H), 1.42−1.52 (m, 2H), 1.17 (d, J = 6.3 Hz, 3H), 0.96 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.6, 129.2, 116.7, 113.0, 49.7, 29.6, 20.2, 10.3 ppm. Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.53; H, 10.13; N, 9.37.

***N*-Cyclopropylaniline (6d).** It is a known compound[54] obtained in 78% yield (29.1 mg) from nitrosobenzene (30.1 mg), cyclopropylboronic acid (36.1 mg), and $P(OEt)_3$ (53 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19−7.23 (t, J = 7.6 Hz, 2H), 6.74−6.82 (m, 3H), 4.17 b (s, 1H), 2.42−2.45 (m, 1H), 0.70−0.76 (m, 2H), 0.53 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.6, 129.0, 117.6, 113.1, 25.2, 7.03 ppm. Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.32; N, 10 .52. Found: C, 81.27; H, 8.30; N, 10.51.

2-(Cyclopropylamino)benzonitrile (6e). It is obtained in 70% yield (25.1 mg) from 2-nitrosobenzonitrile (30.0 mg), cyclopropylboronic acid (29.2 mg), and $P(OEt)_3$ (43 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34−7.49 (m, 2H), 7.09 (d, J = 8.5 Hz, 1H), 6.72 (t, J = 7.6 Hz, 1H), 4.98 (br s, 1H), 2.50 (h, J = 3.4 Hz, 1H), 0.78−0.88 (m, 2H), 0.55−0.65 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.0, 134.1, 132.6, 117.9, 112.1, 95.6, 24.7, 7.7 ppm. Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.98; H, 6.31; N, 17.68.

***N*-Cyclopropyl-4-fluoroaniline (6f).** It is obtained in 66% yield (23.9 mg) from 1-fluoro-4-nitrosobenzene (30.5 mg), cyclopropylboronic acid (30.9 mg), and $P(OEt)_3$ (45 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.86−6.98 (m, 2H), 6.70−6.79 (m, 2H), 4.06 (br s, 1H), 2.36−2.46 (m, 1H), 0.69−0.78 (m, 2H), 0.48−0.56 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.8, 154.7, 145.1, 145.0, 115.8, 115.4, 114.0, 113.9, 25.8, 7.5 ppm. Anal. Calcd for $C_9H_{10}FN$: C, 71.50; H, 6.67; N, 9.26. Found: C, 71.50; H, 6.67; N, 9.26.

***N*-Cyclopentylaniline (6g).** It is a known compound[55] obtained in 65% yield (29.4 mg) from nitrosobenzene (30.4 mg), cyclopentylboronic acid (31.9 mg), and $P(OEt)_3$ (53 μL). Flash column chromatography eluting with hexane/

AcOEt 9:1 yielded the compound as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16 (t, J = 7.7 Hz, 2H), 6.67 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 7.7 Hz, 2H), 3.78 (q, J = 6.1 Hz, 1H), 3.63 (br s, 1H), 2.02 (dd, J = 12.4 Hz, J = 6.2 Hz, 2H), 1.39–1.83 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.1, 129.2, 116.9, 113.2, 54.7, 33.6, 24.1 ppm. Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38; N, 8.69. Found: C, 81.92; H, 9.38; N, 8.69.

***N*-Cyclohexylaniline (6h).** It is a known compound[56] obtained in 71% yield (34.9 mg) from nitrosobenzene (30.0 mg), cyclohexylboronic acid (53.8 mg), and $P(OEt)_3$ (53 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.14 (t, J = 6.9 Hz, 2H), 6.65 (t, J = 7.3 Hz, 1H), 6.59 (d, J = 7.6 Hz, 2H), 3.48 (br s, 1H), 3.21–3.28 (m, 2H), 2.05 (m, 2H), 1.76–1.78 (m, 2H), 1.63–1.67 (m, 1H), 1.32–1.41 (m, 2H), 1.11–1.26 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.3, 129.2, 116.8, 113.1, 51.7, 33.4, 25.9, 25.0 ppm. Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.20; H, 9.79; N, 8.02.

***N*-Cyclohexyl-2,3-dimethylaniline (6i).** It is obtained in 72% yield (32.5 mg) from 1,2-dimethyl-3-nitrosobenzene (30.2 mg), cyclohexylboronic acid (42.6 mg), and $P(OEt)_3$ (42 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01 (7, J = 7.7 Hz, 1H), 6.56 (d, J = 7.7 Hz, 2H), 3.24–3.37 (m, 1H), 3.15 (br s, 1H), 2.29 (s, 3H), 2.00–2.16 (m, 2H), 2.04 (s, 3H), 1.62–1.85 (m, 3H), 1.14–1.50 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.3, 136.8, 126.2, 120.1, 118.8, 108.7, 51.8, 33.8, 26.2, 25.2, 21.0, 12.7 ppm. Anal. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.58; H, 10.47; N, 6.87.

***N*-Cyclohexyl-[1,1′-biphenyl]-2-amine (6j).** It is obtained in 59% yield (24.2 mg) from 2-nitroso-1,1′-biphenyl (30.6 mg), cyclohexylboronic acid (31.4 mg), and $P(OEt)_3$ (31 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30–7.54 (m, 7H), 6.68–6.75 (m, 2H), 3.55 (br s, 1H), 3.23–3.34 (m, 1H), 1.93–2.07 (m, 2H), 1.52–1.73 (m, 3H), 1.02–1.41 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.4, 139.9, 132.4, 132.1, 130.5, 129.5, 129.0, 128.9, 128.8, 128.0, 127.2, 124.2, 116.4, 111.2, 51.7, 33.4, 26.0, 25.0 ppm. Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found: C, 86.16; H, 8.48; N, 5.53.

Ethyl 2-(Cyclohexylamino)benzoate (6k). It is obtained in 71% yield (29.4 mg) from ethyl 2-nitrosobenzoate (30.5 mg), cyclohexylboronic acid (32.1 mg), and $P(OEt)_3$ (32 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (dd, J = 8.1 Hz, J = 1.7 Hz, 1H), 7.75 (br s, 1H), 7.31 (td, J = 8.0 Hz, J = 1.7 Hz, 1H), 6.70 (d, J = 8.5 Hz, 1H), 6.53 (td, J = 7.6, 1.1 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 3.31–3.50 (m, 1H), 1.96–2.11 (m, 2H), 1.71–1.86 (m, 2H), 1.56–1.69 (m, 1H), 1.22–1.49 (m, 8H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.9, 150.5, 134.5, 131.9, 13.9, 111.7, 109.8, 60.2, 50.6, 33.0, 26.0, 24.8, 14.5 ppm. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.76; H, 8.50; N, 5.64.

Methyl 3-(Cyclohexylamino)benzoate (6l). It is obtained in 72% yield (30.5 mg) from methyl 3-nitrosobenzoate (30.3 mg), cyclohexylboronic acid (34.9 mg), and $P(OEt)_3$ (34 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (d, J = 7.6 Hz, 1H), 7.15–7.27 (m, 2H), 6.75 (d, J = 8.1 Hz, 1H), 3.88 (s, 3H), 3.68 (br s, 1H), 3.24–3.36 (m, 1H), 1.98–2.12 (m, 2H), 1.59–1.84 (m, 3H), 1.06–1.49 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.8, 147.5, 131.2, 129.3, 118.1, 117.7, 113.8, 52.1, 51.7, 33.5, 26.0, 25.1 ppm. Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.00; H, 8.26; N, 6.03.

1-(3-(Cyclohexylamino)phenyl)ethanone (6m). It is obtained in 77% yield (33.6 mg) from 1-(3-nitrosophenyl)-ethanone (30.1 mg), cyclohexylboronic acid (38.6 mg), and $P(OEt)_3$ (38 μL). Flash column chromatography eluting with hexane/AcOEt 8:2 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11–7.19 (m, 2H), 7.08 (s, 1H), 6.64–6.73 (m, 1H), 3.65 (br s, 1H), 3.17–3.32 (m, 1H), 2.45 (s, 3H), 1.90–2.02 (m, 2H), 1.52–1.76 (m, 3H), 1.00–1.40 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.8, 147.7, 138.3, 129.4, 117.9, 117.3, 112.0, 51.6, 33.4, 26.8, 26.0, 25.0 ppm. Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.26; H, 8.77; N, 6.47.

***N*-Cyclohexyl-2-fluoroaniline (6n).** It is obtained in 70% yield (32.4 mg) from 1-fluoro-2-nitrosobenzene (30.2 mg), cyclohexylboronic acid (46.0 mg), and $P(OEt)_3$ (45 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.91–7.03 (m, 2H), 6.71 (t, J = 8.2 Hz, 1H), 6.53–6.62 (m, 1H), 3.79 (br s, 1H), 3.27 (t, J = 10.0 Hz, 1H), 2.03–2.13 (m, 2H), 1.61–1.86 (m, 3H), 1.11–1.47 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.3, 150.1, 136.1, 135.9, 124.6, 124.5, 116.1, 116.0, 114.7, 114.5, 112.7, 112.6, 51.6, 33.6, 23.0, 25.0 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −136.8 ppm. Anal. Calcd for $C_{12}H_{16}FN$: C, 74.58; H, 8.34; N, 7.25. Found: C, 74.43; H, 8.39; N, 7.29.

***N*-Phenylcycloheptanamine (6o).** It is a known compound[55] obtained in 59% yield (31.3 mg) from nitrosobenzene (30.0 mg), cycloheptylboronic acid (59.6 mg), and $P(OEt)_3$ (53 μL). Flash column chromatography eluting with hexane/AcOEt 9:1 yielded the compound as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (t, J = 7.9 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.64 (d, J = 7.8 Hz, 2H), 3.65 (br s, 1H), 3.55 (m, 1H), 2.03–2.21 (m, 2H), 1.48–1.88 (m, 10H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.4, 129.3, 116.8, 113.3, 53.7, 34.9, 28.5, 24.51 ppm. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.59; H, 10.10; N, 7.38.

2-(4-(Methylamino)phenyl)benzo[*d*]thiazol-6-ol (8). *N*-(4-(6-methoxybenzo[*d*]thiazol-2-yl)phenyl)hydroxylamine (**7**) (1 g, 3.49 mmol) was dissolved in ethanol (35 mL) and cooled to 0 °C. A solution of $K_3Fe(CN)_6$ (11.5 g, 34.9 mmol) in H_2O (175 mL) was added. The mixture was stirred at rt for 3 h. Then, ethanol was evaporated in vacuo and $CHCl_3$ was added and the layers were separated. The aqueous one was extracted several times with $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The resulting solid was dissolved in CH_2Cl_2 (35 mL), and $P(OEt)_3$ (0.7 mL, 4.07 mmol) and methylboronic acid **2** (332.2 mg, 5.55 mmol) were successively added. The mixture was stirred at rt for 20 min. Then, BBr_3 (1 M in CH_2Cl_2, 12.5 mL, 12.5 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. After quenching with water, the reaction mixture was extracted with ethyl acetate. The organic layers were combined, washed with water, and dried over $MgSO_4$. The crude product was purified by flash chromatography (hexanes: ethyl acetate = 1:8). It is a known compound[26a] obtained in 47% yield (4 mg). The compound was yielded as a yellow solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.69 (br s, 1H, OH), 7.76−7.68 (m, 3H), 7.32 (d, J = 2.4 Hz, 1H), 6.91 (dd, J = 8.7 Hz, J = 2.4 Hz, 1H), 6.63 (d, J = 8.8 Hz, 2H), 6.37 (br s, 1H, NH), 2.74 (d, J = 4.9 Hz, 3H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.9, 155.3, 152.5, 147.8, 135.5, 128.6, 122.8, 120.9, 115.9, 111.9, 107.2, 29.8 ppm. Anal. Calcd for $C_{14}H_{12}N_2OS$: C, 65.60; H, 4.72; N, 10.93. Found: C, 65.26; H, 5.15; N, 10.11.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01608.

Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds **3**, **5a−x**, **6a−o**, and **8** (PDF)

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Notes

The authors declare no competing financial interest.

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