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J Org Chem. Author manuscript; available in PMC 2013 May 04.

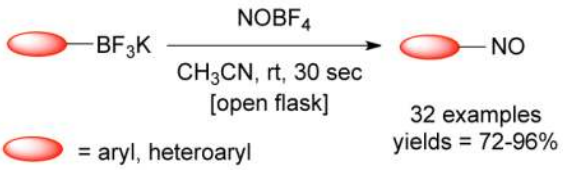
Published in final edited form as:
J Org Chem. 2012 May 4; 77(9): 4402–4413. doi:10.1021/jo300551m.

NITROSATION OF ARYL AND HETEROARYLTRIFLUOROBORATES WITH NITROSONIUM TETRAFLUOROBORATE

Gary A. Molander and **Livia N. Cavalcanti**
Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323

Gary A. Molander: gmolandr@sas.upenn.edu

Abstract



Organotrifluoroborates have emerged as an alternative to toxic and air- and moisture sensitive organometallic species for the synthesis of functionalized aryl and heteroaryl compounds. It has been shown that the trifluoroborate moiety can be easily converted into a variety of different substituents in a late synthetic stage. In this paper we disclose a mild, selective, and convenient method for the *ipso*-nitrosation of organotrifluoroborates using nitrosonium tetrafluoroborate ($NOBF_4$). Aryl- and heteroaryltrifluoroborates were converted into the corresponding nitroso products in good to excellent yields. This method proved to be tolerant of a broad range of functional groups.

Keywords

Nitrosation; organotrifluoroborates; *ipso*-substitution

Introduction

Nitroso compounds are versatile synthetic intermediates and have been utilized in a variety of transformations[1] such as nitroso aldol reactions,[2] [4+2],[3] [3+3],[4] and [2+2][5] cycloadditions, ene reactions,[6] addition of Grignard reagents,[7] reactions with alkynes to yield indoles,[8] coupling with amines to afford azo compounds,[9] oxidation to nitro compounds[10] and reduction to amines[11] (Scheme 1). Additionally, aromatic nitroso species have shown some activity against HIV-1 infectivity.[12] Despite their potentially wide applications, many of these reported methods utilize a single or limited subset of nitroso aromatics, presumably because of the lack of synthetic methods available to synthesize a diverse set of functionalized nitrosoarenes.

Correspondence to: Gary A. Molander, gmolandr@sas.upenn.edu.

Supporting Information Available: Copies of ^{1}H, ^{13}C, and ^{19}F spectra for all compounds prepared by the method described. This material is available free of charge *via* the Internet at http://pubs.acs.org

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The first synthesis of nitrosobenzene was published by Baeyer over a century ago.[13] Since then, various methods have been published to afford nitrosoarenes.[14] Among them, the oxidation of anilines to the corresponding nitrosoarene is the most widely utilized.[15] Although many protocols for this conversion are reported in the literature, their reliance on the availability of anilines makes them somewhat limited in scope. Furthermore, the use of oxidants restricts the range of functional groups allowed in this transformation. As an example, aldehyde-containing nitrosoarenes cannot be made by this method. Another problem generally associated with this method is the formation of undesired side products such as azo and azoxy compounds.[14] Moreover, few heteroarylnitroso compounds have been obtained by this method, and those that have been accessed have been confined to nitrogen-containing heterocycles.[16] Nitrosation of simple arenes[17] and arylmetallics (e.g., organotin,[18] thallium[19] and silicon[20] compounds) have also been reported in the literature using electrophilic nitrosonium reagents. For both of these types of transformations the reaction only works for aryl species containing electron-donating groups, which limits the breadth of nitroso products that can be accessed. Because of the limited examples using organometallic species and the drawbacks associated with oxidation reactions of aryl and heteroarylnitroso synthesis (e.g., functional group tolerance and side product formation), we were interested in finding a novel, rapid, and mild method to synthesize nitrosoarene derivatives.

The *ipso*-substitution of arylboron species, as previously demonstrated for halogenation[21] and nitration[22] of arylboronic acids, provides a potential means to accomplish this goal. Recently, our group published the chlorodeboronation of aryl and heteroaryltrifluoroborates, which most likely occurs by an *ipso*-substitution (Scheme 2).[23]

Trifluoroborates have emerged as an alternative to toxic organometallic species, such as organostannanes, and to boronic acids, which, although non-toxic, are compounds susceptible to undesired side reactions with common reagents, such as acids and bases.[24] The tetracoordinate nature of the trifluoroborates makes them resistant to a variety of reaction conditions and, therefore, allows one to build complexity into a molecule while leaving the carbon-boron bond intact. This valuable bond can then be further converted in a later synthetic step into a variety of groups such as boronic acids,[25] alcohols[26] and halogens.[21a–c,23] Moreover, trifluoroborates can be synthesized by a variety of complementary methods, including transmetalation (via metal-halogen exchange or directed metalation), Miyaura borylation, and C-H activation, all of which combine to afford an enormous diversity of available substructures (Scheme 3). Furthermore, in contrast to the corresponding aryl and heteroarylboronic acids, trifluoroborates are air and moisture stable and can be stored on the bench for months without appreciable decomposition.[27]

In this paper we disclose the *ipso*-nitrosation of a broad range of aryl and heteroaryltrifluoroborates containing both electron-donating and electron-withdrawing groups. To the best of our knowledge, this is the first nitrosation of an organoboron species, and the transformation presented is arguably the most broadly applicable approach to this underrepresented class of molecules.

RESULTS AND DISCUSSION

Based on the *ipso*-nitration of boronic acids with nitrate salts developed by Olah and co-workers,[23] we began the screening for nitrosation of organotrifluoroborates with sodium nitrite in different solvents (Table 1). The choice of this nitrite salt was made by the ready availability and low cost of this reagent. After optimization, we determined that the reaction of potassium trifluoro(4-methoxyphenyl)borate with $NaNO_2$ (1.5 equiv) in heptane: H_2O at 50 °C afforded the desired nitrosated product in 89% isolated yield.

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With these conditions in hand, we began to examine the nitrosation of a variety of aryltrifluoroborates (Scheme 4). Phenyltrifluoroborates bearing electron-donating groups were successfully converted into the corresponding nitrosobenzene in good yields. Unfortunately, electron-neutral aryltrifluoroborates (e.g., biphenyl) and electron-withdrawing (ester) groups inhibited this transformation, and only the protodeboronated products were obtained.

The results obtained further demonstrated that the reaction does not occur in the absence of water and that only electron-rich aryltrifluoroborates afforded the desired product. Thus, we hypothesized that aqueous conditions are necessary to form the tricoordinate boron species *in situ*,[28] and this species, now possessing a Lewis acidic boron moiety with an empty p-orbital, could then undergo attack of sodium nitrite to form an ate-complex and a more electrophilic NO^+, with subsequent *ipso*-substitution affording the nitroso product (Scheme 5).

To improve the scope of this reaction, the nitrosation of potassium [1,1′-biphenyl]-4-yltrifluoroborate was further optimized. A variety of solvents, additives, nitrosating agents and temperatures were investigated. As illustrated in Table 2, the use of other nitrite salts, such as KNO_2 and $AgNO_2$ (entries 1–3), were inefficient for this transformation. The use of acid additives for *in situ* formation of NO^+ [18c,29] also did not afford the desired nitroso product, and only protodeboronation was observed (entries 4–7). Fortunately, the use of nitrosonium tetrafluoroborate (1.03 equiv) in CH_3CN (0.2 M) at room temperature in an open flask proved to be efficient for this transformation, affording the nitroso product in 90% isolated yield. Importantly, the reaction can be followed visually. The slurry formed by the trifluoroborate in CH_3CN becomes a bright green, homogeneous solution almost immediately. The crude reaction is then worked up by addition of water followed by dichloromethane extraction, with subsequent filtration through a plug of silica providing the product in high purity. A prolonged reaction time leads to oxidation of the formed nitroso product and affords a mixture of this compound along with the corresponding nitroaromatic. The use of more than 1.03 equivalents of nitrosonium tetrafluoroborate does not fully convert the nitroso into the nitro group. Instead, a mixture of nitroso, nitro and protodeboronation products is observed.

With the optimal conditions in hand, the scope of the reaction for electron-donating and electron neutral aryltrifluoroborates was investigated (Table 3). In all cases, the reaction was complete in only 30 seconds and afforded the desired product in good to excellent yields. The method proved to be selective, and aryltrifluoroborates containing ortho, meta and para substituents were readily converted to the corresponding nitrosobenzene (Table 3, entries 1–3). This regioselectivity cannot be attained by the direct nitrosation of arenes. The reaction was scaled up to 1 g, and the product was obtained in excellent yield (Table 3, entry 1). Sterically hindered substrates also afforded the desired product in good yield. Importantly, potassium (3,5-diisopropylphenyl)trifluoroborate, made by direct C-H activation of arenes[30] was converted into 1,3-diisopropyl-5-nitrosobenzene in 88% yield (Table 3, entry 9). This illustrates a unique substitution pattern, because the corresponding aryl chloride (necessary for preparation of the amine utilized for the oxidation method previously mentioned) has very limited availability. Surprisingly, the reaction of potassium trifluoro(4-hydroxyphenyl)borate yielded the corresponding nitrophenol as a mixture of regioisomers (eq 1).

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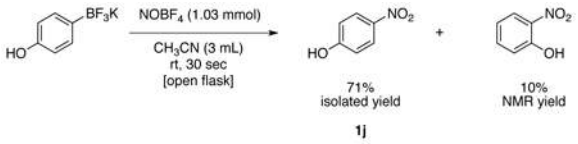
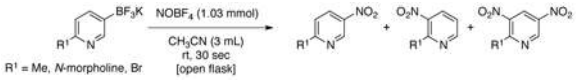


(1)

Subsequently, the reaction of aryltrifluoroborates bearing electron-withdrawing groups was investigated (Table 4). Methods such as direct nitrosation of arenes and other organometallic species have proven inefficient in the production of nitrosobenzenes with electron-poor groups.[18–21] In our hands, aryltrifluoroborates containing ester, ketone, aldehyde, nitrile, amide, nitro and carboxylic acid groups (Table 4, entries 1–9) were converted into the corresponding nitroso compounds in good yields without affecting the aforementioned, embedded functional groups. The reaction was regiospecific, and ortho, meta, and para substituted nitrosobenzenes were obtained. Importantly, aldehyde-containing aryltrifluoroborates afforded the corresponding nitrosobenzaldehyde in good yields and high regioselectivity without oxidation of the aldehyde group (Table 4, entries 4–6). These aldehyde-containing nitroso products were previously obtained only by a four step procedure from the corresponding nitroarene.[31] As illustrated previously with potassium (3,5-diisopropylphenyl)trifluoroborate (Table 3, entry 9), we were able to synthesize methyl 3-methyl-5-nitrosobenzoate and 1-methoxy-3-nitroso-5-(trifluoromethyl)benzene (Table 4, entries 10 and 11) from trifluoroborates made by C-H activation. Furthermore, the conversion of aryltrifluoroborates containing halogens into the corresponding nitroso product was accomplished in good yields (Table 4, entries 12–15).

To expand the scope of this reaction further we turned our attention to the reaction of heteroaryltrifluoroborates. Once more, this transformation was accomplished for a variety of substrates, including dibenzofuranyl, dibenzothienyl, benzothienyl, indolyl, pyrimidinyl and pyridinyl derivatives, affording the nitrosoheteroaryl products in good yields (Table 5). Furthermore, products **3e**, **3f** and **3g** (Table 5 entries 5– 6) were obtained with no observed nitrosation of the heterocyclic nitrogen.[32] To the best of our knowledge, all compounds illustrated in Table 5 were never before synthesized by any other method. However, for 5-membered heteroaryltrifluoroborates (e.g., thienyl, furanyl, pyrrolyl, isoxazolyl and pyrazolyl) and fused system with the trifluoroborate substituent within the 5-membered heterocycle (e.g., 2- or 3-substituted dibenzofuranyl, dibenzothienyl and indolyl), the reaction was inefficient, and only protodeboronated product was recovered. Moreover, the reaction with 3-trifluoroboratopyridines containing a substituent at the 6 position afforded a mixture of nitro and dinitro products, and no nitroso derivatives were observed (eq 2). The use of more than 1 equivalent of $NOBF_4$ did not give the dinitro product; instead a mixture of products along with protodeboronation was observed. The same pattern was observed for quinolines bearing trifluoroborates at the 2, 3 and 4 positions, where a mixture of nitro and dinitro derivatives was obtained.



(2)

Interestingly, 5-nitrosoisoquinoline **3h** (Table 5, entry 8) was obtained as a yellow solid that upon exposure to air would turn black and could not be further purified. The crude material

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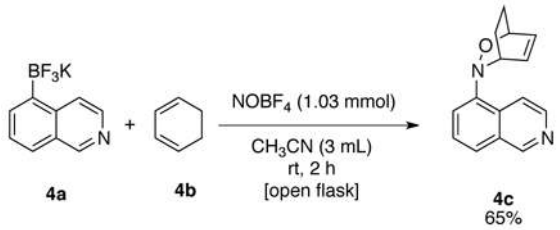
appeared to be very pure by ^{1}H NMR (see spectra in Supporting Information), which led to the conclusion that the nitroso product obtained is not stable. To circumvent this problem, a one-pot nitrosation of potassium trifluoro(isoquinolin-5-yl)borate, **4a**, followed by Diels-Alder reaction with cyclohexa-1,3-diene **4b**, was investigated (eq 3).[13a] The reaction afforded the Diels-Alder adduct in 65% yield over two steps.



(3)

With the success of the nitroso one-pot Diels-Alder reaction, we were interested in illustrating other reactions that potentially unstable arylnitroso compounds can undergo (Scheme 6). Nitrogen-containing compounds are found in a variety of pharmaceuticals and are also the building blocks for important synthetic transformations.[33] Therefore, potassium methyl 3-trifluoroboratobenzoate was subjected to the nitrosation protocol followed by different transformations, and diverse nitrogen-containing products were obtained. The one-pot reaction of the aforementioned trifluoroborate with $NOBF_4$ followed by addition of $NaBH_4$ afforded the corresponding azoxy product, **5a**, in 87% overall yield. Methyl 3-nitrobenzoate **5b** was also obtained by a two-step procedure from the corresponding trifluoroborate. In this case, a minimal work-up of the nitrosation reaction was necessary before addition of the oxidant. Nevertheless, the desired product was obtained in 86% yield over the two steps. The one-pot nitrosation-reduction of the *in situ* formed methyl 3-nitrosobenzoate was performed, and the methyl 3-aminobenzoate, **5c**, was obtained in 72% overall yield. The one-pot nitrosation/Diels-Alder reaction was also accomplished, with the oxazabicyclo benzoate **5d** being isolated in 82% yield.

Finally, as illustrated in Scheme 7, different boron derivatives were tested under the same reaction conditions. 4-Methoxyphenylboronic acid afforded the product in nearly the same yield as the trifluoroborates, while the boronate esters were not successful in this transformation, instead providing the nitroso product in moderate yields after 1 h with starting material being recovered.

In summary, it has been demonstrated that the nitrosation of a broad range of aryl and heteroaryltrifluoroborates can be carried out under extraordinarily mild reaction conditions. Aryltrifluoroborates containing different functional groups, such as esters, ketones, aldehydes, nitriles and amides were successfully converted into the nitroso product, while leaving the aforementioned groups intact. Furthermore, nitrogen-containing heteroaryltrifluoroborates underwent nitrosation selectively, and no nitrosation of the nitrogen atom was observed. Despite their simplicity, most of the nitroso compounds prepared were previously unknown, highlighting the lack of synthetic methods available for this important class of molecules. The versatility of the nitroso products obtained has been illustrated by converting these intermediates in a variety of one-pot transformations, demonstrating that even those nitrosoarenes that may have limited stability can be employed as useful substrates for further synthetic applications.

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Experimental Section

General Procedure for the Preparation of Potassium Aryl and Heteroaryltrifluoroborates from Boronic Acids

Following a published literature procedure,[34] to a solution of the corresponding boronic acid in MeOH (3.5 M or enough MeOH to give a free flowing suspension) under N_2 was added KHF_2 (3 equiv of a 4.5 M solution in H_2O) dropwise at 0° C. The ice-water bath was removed, and the reaction was stirred at rt until ^{11}B NMR indicated completion of the reaction (~2 min). The crude mixture was concentrated and dried overnight in vacuo. The crude solid was purified using continuous Soxhlet extraction (4 h) with acetone (60 mL). The collected solvent was concentrated and then redissolved in a minimal amount of acetone (5 mL). The addition of Et_2O (30 mL) led to the precipitation of the product. The product was filtered, concentrated, and dried in vacuo to afford the pure organotrifluoroborates.

General Procedure for Aryl C-H borylation

Following the procedure published by Hartwig and co-workers,[35] in a glove box, to an oven-dried glass vessel capable of being sealed with a Teflon cap (for microwave vials) was added B_2pin_2, (1 equiv), $[Ir(COD)(OMe)]_2$ (0.1 mol %) and dtbpy (0.2 mol %). The vessel was sealed and removed from the glovebox. THF (1 M degassed) was added via syringe followed by the addition of the 1,3-substituted arene (1.5 equiv). The reaction mixture was heated in a sealed vessel at 80 °C for 16 h. The reaction was allowed to cool to rt, and then KHF_2 (3 equiv of a 4.5 M solution in H_2O) was added dropwise at 0° C. The ice-water bath was removed, and the reaction was stirred at rt until ^{11}B NMR indicated completion of the reaction (~2 min). The crude mixture was concentrated and dried overnight in vacuo. The crude solid was purified using continuous Soxhlet extraction (4 h) with acetone (60 mL). The collected solvent was concentrated and then redissolved in a minimal amount of acetone (5 mL). The addition of Et_2O (30 mL) led to the precipitation of the product. The product was filtered, concentrated, and dried in vacuo to afford the pure organotrifluoroborates.

General Procedure A: Nitrosation of Aryltrifluoroborates with $NaNO_2$

To a 20 mL glass microwave vial containing a solution of potassium organotrifluoroborate (1 mmol) in heptane: H_2O (1:1, 5 mL, 0.2 M) was added $NaNO_2$ (104 mg, 1.5 mmol, 1.5 equiv) in one portion. The reaction was stirred open to air at 50 °C until the trifluoroborate was consumed (as indicated by ^{11}B NMR). To the crude mixture was added H_2O (20 mL) and CH_2Cl_2 (10 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The products were obtained in high purity after filtration through a small plug of silica topped with Celite, eluting with CH_2Cl_2.

General Procedure B: Nitrosation of Aryl and Heteroaryltrifluoroborates with $NOBF_4$

To a 20 mL glass microwave vial containing a solution of potassium organotrifluoroborate (1 mmol) in CH_3CN (3 mL, 0.33 M) was added $NOBF_4$ (120 mg, 1.03 mmol, 1.03 equiv) in one portion. The reaction was stirred open to air at rt until the reaction became homogeneous. The reaction changed from a white slurry to a green or black solution. To the crude mixture was added H_2O (20 mL) and CH_2Cl_2 (10 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. In general the product was obtained in high purity after filtration through a small plug of silica topped with Celite, eluting with CH_2Cl_2/hexanes. In specific cases trace impurities were removed by column chromatography using CH_2Cl_2/hexanes or EtOAc/hexanes to afford the desired pure product.

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1-Methoxy-4-nitrosobenzene (1a).[8a]—General procedure B was employed using potassium 4-methoxyphenyltrifluoroborate (214 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 95% yield (130 mg, 0.95 mmol) as a green oil after filtration through a short plug of silica topped with Celite using hexanes/CH_2Cl_2 (3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 6.5 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.6, 163.9, 124.3, 113.8, 55.9. IR (neat) 1598, 1504, 1411, 1263, 1020, 837 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_8NO_2$ $(M+H)^+$ 138.0555, found 138.0558.

1-Methoxy-3-nitrosobenzene (1b)—General procedure B was employed using potassium 3-methoxyphenyltrifluoroborate (214 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 89% yield (122 mg, 0.89 mmol) as a green oil after column chromatography with hexanes/CH_2Cl_2 (3:1) as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (m, 1H), 7.60 (t, *J* = 8 Hz, 1H), 7.28 (m, 1H), 6.89 (t, *J* = 2 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.9, 160.5, 130.5, 122.9, 119.8, 99.8, 55.8. IR (neat) 1604, 1483, 1384, 1041, 789 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_8NO_2$ $(M+H)^+$ 138.0555, found 138.0558.

2,4-Dimethoxy-1-nitrosobenzene (1c)—General procedure B was employed using potassium (2,4-dimethoxyphenyl)trifluoroborate (244 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 91% yield (152 mg, 0.91 mmol) as a green solid, mp 93–95 °C, after filtration through a short plug of silica topped with Celite using hexanes/CH_2Cl_2 (3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.65 (d, *J* = 2.5 Hz, 1H), 6.50 (d, *J* = 9 Hz, 1H) 6.34 (m, 1H), 4.22 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.5, 164.4, 157.1, 112.1, 105.8, 98.5, 56.9, 56.2. IR (neat) 1600, 1397, 1246, 1014, 837 cm−1. HRMS (ESI) *m/z* calcd. for C8H10NO3 (M+H)+ 168.0661, found 168.0664.

1-(Benzyloxy)-4-nitrosobenzene (1d)—General procedure B was employed using potassium (4-(benzyloxy)phenyl)trifluoroborate (290 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 92% yield (196 mg, 0.92 mmol) as a blue solid, mp 81–83 °C, after filtration through a short plug of silica topped with Celite using hexanes/CH_2Cl_2 (3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (brs, 2H), 7.45 – 7.37 (m, 5H), 7.10 (t, *J* = 8 Hz, 2H), 5.21 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.9, 164.1, 135.6, 129.0, 128.7, 127.7, 114.9, 70.8. IR (neat) 1598, 1502, 1262, 1117, 844, 730 cm−1. HRMS (ESI) *m/z* calcd. for C13H11NO2 (M)+ 213.0790, found 213.0797.

6-Nitroso-2,3-dihydrobenzo[b][1,4]dioxine (1e)—General procedure B was employed using potassium (2,3-dihydrobenzo[b][1,4]dioxin-6-yl)trifluoroborate (242 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 91% yield (150 mg, 0.91 mmol) as a green solid, mp 88–90 °C, after column chromatography with hexanes/CH_2Cl_2 (3:1) as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 1H), 7.13 (s, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 4.38 – 4.36 (m, 2H), 4.33 – 4.31 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 163.6, 150.9, 143.9, 120.8, 117.6, 107.7, 65.1, 64.2. IR (neat) 1591, 1495, 1280, 1054, 913 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_8NO_3$ $(M+H)^+$ 166.0504, found 166.0504.

4-Nitrosobiphenyl (1f).[36]—General procedure B was employed using potassium biphenyl-4-yltrifluoroborate (260 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 90% yield (165 mg, 0.90 mmol) as an orange solid, mp 72–74 °C (lit.[34] 73–74 °C), after filtration

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through a short plug of silica topped with Celite using hexanes/CH_2Cl_2 (3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8 Hz, 2H), 7.68 – 7.66 (m, 2H), 7.52 – 7.49 (m, 2H), 7.45 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.12, 148.2, 139.3, 129.3, 129.1, 128.0, 127.6, 121.8. IR (neat) 1483, 1249, 760, 695 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_{10}NO$ (M+H)$^+$ 184.0762, found 184.0758.

1-*tert*-Butyl-4-nitrosobenzene (1g)—General procedure B was employed using potassium (4-*tert*-butylphenyl)trifluoroborate (240 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 93% yield (152 mg, 0.93 mmol) as a green oil after filtration through a short plug of silica topped with Celite using hexanes/CH_2Cl_2 (3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 9 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.3, 159.9, 126.2, 121.1, 35.7, 31.1. IR (neat) 1601, 1509, 1453, 1124, 1099, 840, 710 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{10}H_{14}NO$ (M+H)$^+$ 164.1075, found 164.1082.

1,3,5-Trimethyl-2-nitrosobenzene (1h).[17a]—General procedure B was employed using potassium trifluoro(mesityl)borate (260 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 92% yield (137 mg, 0.90 mmol) as a white solid, mp 120–122 °C (lit.[17a] 121–122 °C), after filtration column chromatography with hexanes/CH_2Cl_2 (3:1) as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (s, 2H), 2.62 (s, 2H), 2.41 (s, 4H), 2.34 (s, 1H), 2.33 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 140.7, 139.3, 132.7, 129.9, 21.2, 18.7. IR (neat) 1603, 1475, 1245, 807 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_9H_{12}NO$ (M+H)$^+$ 150.0919, found 150.0919.

1,3-Diisopropyl-5-nitrosobenzene (1i)—General procedure B was employed using potassium (3,5-diisopropylphenyl)trifluoroborate (268 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. The desired pure product was obtained in 88% yield (168 mg, 0.88 mmol) as a green oil after filtration through a short plug of silica topped with Celite using hexanes/CH_2Cl_2 (3:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 2H), 7.46 (s, 1H), 3.07 – 3.01 (m, 2H), 1.32 (d, *J* = 7 Hz, 12 H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.4, 150.5, 132.7, 117.0, 34.1, 24.0. IR (neat) 1608, 1493, 1096, 886, 694 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_{18}NO$ (M+H)$^+$ 192.1388, found 192.1384.

4-Nitrophenol (1j).[37]—General procedure B was employed using potassium trifluoro(4-hydroxyphenyl)borate (200 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 seconds. In this case no nitroso product was observed and a mixture of 4-nitrophenol and 2-nitrophenol (10% NMR yield) was obtained. The pure 4-nitrophenol product was obtained in 71% yield (99 mg, 0.71 mmol) as a yellow solid, mp 108–110 °C (lit.[38] 109–110 °C), after column chromatography with hexanes/CH_2Cl_2 (2:1) as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 9.5 Hz, 2H), 6.92 (d, *J* = 9 Hz, 2H), 5.72 (s, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 161.6, 141.7, 126.5, 115.9. IR (neat) 3359, 1592, 1488, 1331, 1113, 844 cm^{-1}.

Methyl 4-Nitrosobenzoate (2a).[39]—General procedure B was employed using potassium trifluoro(4-(methoxycarbonyl)phenyl)borate (242 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 95% yield (157 mg, 0.95 mmol) as a light yellow solid, mp 123–125 °C (lit.[40] 129.5 °C), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8 Hz, 2H), 7.92 (d, *J* = 8 Hz, 2H), 3.97 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.9, 164.5, 135.3, 131.2, 120.5, 52.9. IR (neat) 1727, 1441, 1266, 766, 694 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_8NO_3$ (M+H)$^+$ 166.0504, found 166.0510.

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Methyl 3-Nitrosobenzoate (2b).[15b]—General procedure B was employed using potassium trifluoro(3-(methoxycarbonyl)phenyl)borate (242 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 96% yield (158 mg, 0.96 mmol) as a light yellow solid, mp 91–93 °C (lit.[41] 93 °C), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (t, *J* = 1.5 Hz, 1H), 8.39 (m, 1H), 8.01 (m, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 4.01 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.8, 164.9, 135.8, 131.9, 129.7, 123.9, 122.6, 52.8. IR (neat) 1727, 1433, 1259, 754, 685 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_8NO_3$ $(M+H)^+$ 166.0504, found 166.0510.

1-(3-Nitrosophenyl)ethanone (2c)—General procedure B was employed using potassium (3-acetylphenyl)trifluoroborate (226 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 94% yield (140 mg, 0.94 mmol) as a light yellow solid, mp 78–80 °C (lit.[38] 81.5 °C), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (t, *J* = 1.5 Hz, 1H), 8.33 (m, 1H), 8.05 (m, 1H), 7.75 (t, *J* = 8 Hz, 1H), 2.73 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 196.8, 165.0, 138.2, 134.3, 130.0, 124.3, 121.0, 26.9. IR (neat) 1691, 1248, 800, 676 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_8H_8NO_2$ $(M+H)^+$ 150.0555, found 150.0557.

3-Nitrosobenzaldehyde (2d)—General procedure B was employed using potassium trifluoro(3-formylphenyl)borate (212 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 88% yield (119 mg, 0.88 mmol) as a light yellow solid, mp 106–108 °C (lit.[42] 106.5–107 °C), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.38 (s, 1H), 8.26 (m, 1H), 8.15 (m, 1H), 7.83 (t, *J* = 8 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 190.9, 164.7, 137.4, 135.0, 130.5, 125.7, 121.7. IR (neat) 1689, 1257, 1121, 678 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_6NO_2$ $(M+H)^+$ 136.0399, found 136.0402.

4-Nitrosobenzaldehyde (2e).[31a]—General procedure B was employed using potassium trifluoro(4-formylphenyl)borate (212 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 94% yield (127 mg, 0.94 mmol) as a light yellow solid, mp 135–137 °C (lit.[41] 135–136 °C), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 8 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 191.4, 163.9, 139.6, 131.2, 121.2. IR (neat) 1691, 1259, 789 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_7H_5NO_2$ $(M)^+$ 135.0320, found 135.0322.

2-Nitrosobenzaldehyde (2f).[43]—General procedure B was employed using potassium trifluoro(2-formylphenyl)borate (212 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 78% yield (105 mg, 0.78 mmol) as a light yellow solid, mp 110–112 °C (lit.[12] 110 °C), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.1 (s, 1H), 8.22 (m, 1H), 7.91 (t, *J* = 7.5 Hz, 1H), 7.69 (m, 1H), 6.44 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 193.5, 162.2, 136.6, 134.2, 132.8, 127.8, 106.7. IR (neat) 1702, 1248, 1196, 768 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_6NO_2$ $(M+H)^+$ 136.0399, found 136.0404.

4-Nitrosobenzonitrile (2g).[44]—General procedure B was employed using potassium (4-cyanophenyl)trifluoroborate (209 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 89% yield (117

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mg, 0.94 mmol) as a light yellow solid, mp 128–130 °C (lit.[42] 128–129 °C), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 4 H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 162.3, 134.1, 120.9, 118.5, 117.6. IR (neat) 2239, 1499, 1252, 868 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_4N_2O$ (M)$^+$ 132.0324, found 132.032.

***N*-(3-Nitrosophenyl)acetamide (2h)—**General procedure B was employed using potassium (3-acetamidophenyl)trifluoroborate (241 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 91% yield (149 mg, 0.91 mmol) as a light yellow solid, mp 118–120 °C, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8 Hz, 1H), 7.84 (d, *J* = 8 Hz, 1H), 7.79 (s, 1H), 7.61 (t, *J* = 8 Hz, 1H), 7.55 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.9, 165.9, 139.2, 130.2, 126.5, 118.8, 110.3, 24.8. IR (neat) 1672, 1598, 1492, 1076, 800 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_9N_2O_2$ (M+H)$^+$ 165.0664, found 165.0659.

3-Nitro-5-nitrosobenzoic acid (2i)—General procedure B was employed using potassium (3-carboxy-5-nitrophenyl)trifluoroborate (273 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 92% yield (180 mg, 0.92 mmol) as a green solid, mp 148–150 °C, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (t, *J* = 2 Hz, 1H), 9.10 (s, 1H), 8.78 (t, *J* = 1.5 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.6, 162.5, 149.5, 132.8, 129.6, 128.0, 118.2. IR (neat) 3095, 1700, 1545, 1294, 1177, 918, 736 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_3N_2O_5$ (M–H)$^-$ 195.0042, found 195.0045.

Methyl 3-Methyl-5-nitrosobenzoate (2j)—General procedure B was employed using potassium trifluoro(3-(methoxycarbonyl)-5-methylphenyl)borate (256 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 91% yield (163 mg, 0.91 mmol) as a yellow solid, mp 68–70 °C, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.20 (s, 1H), 7.73 (s, 1H), 3.99 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.9, 165.3, 140.1, 136.3, 131.6, 123.9, 120.6, 52.7, 21.2. IR (neat) 1726, 1445, 1253, 1134, 760 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_9H_{10}NO_3$ (M+H)$^+$ 180.0661, found 180.0667.

1-Methoxy-3-nitroso-5-(trifluoromethyl)benzene (2k)—General procedure B was employed using potassium trifluoro(3-methoxy-5-(trifluoromethyl)phenyl)borate (282 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 10 min. The desired pure product was obtained in 81% yield (166 mg, 0.81 mmol) as a green oil after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.50 (s, 1H), 7.21 (m, 1H), 3.93 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 165.2, 161.0, 133.4 (d, *J* = 34 Hz), 123.3 (m), 118.4 (d, *J* = 3.5 Hz), 114.0 (d, *J* = 3.5 Hz), 104.8, 56.3. ^{19}F NMR (470.8 MHz, $CDCl_3$) δ −62.9. IR (neat) 1507, 1325, 1131, 1046, 873, 688 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_7NO_2F_3$ (M+H)$^+$ 206.0429, found 206.0431.

1-Iodo-4-nitrosobenzene (2l).[45]—General procedure B was employed using potassium trifluoro(4-iodophenyl)borate (310 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 92% yield (214 mg, 0.92 mmol) as a green solid, mp 100–102 °C (lit.[46] 104 –106 °C), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.3, 138.9, 122.0, 105.6. IR (neat) 1579, 1481, 1113, 822 cm^{-1}.

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1-Bromo-4-nitrosobenzene (2m).[8a]—General procedure B was employed using potassium (4-bromophenyl)trifluoroborate (263 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 94% yield (175 mg, 0.94 mmol) as a light yellow solid, mp 92–94 °C (lit.[8a] 99–101 °C), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.0, 132.9, 131.8, 122.3. IR (neat) 1478, 1257, 1011, 856 cm^{-1}. HRMS (ESI) *m/z* calcd. for C_6H_5NOBr $(M+H)^+$ 185.9554, found 185.9555.

1-Chloro-4-nitrosobenzene (2n).[15d]—General procedure B was employed using potassium (4-chlorophenyl)trifluoroborate (219 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 1 min. The desired pure product was obtained in 92% yield (130 mg, 0.92 mmol) as a light yellow solid, mp 87–89 °C (lit.[47] 88–89 °C), after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 9 Hz, 2H), 7.60 (d, J = 9 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.0, 142.6, 129.8, 122.3. IR (neat) 1481, 1256, 1089, 857 cm^{-1}. HRMS (CI) *m/z* calcd. for C_6H_5NOCl $(M+H)^+$ 142.0060, found 142.0056.

1,4-Difluoro-2-nitrosobenzene (2o)—General procedure B was employed using potassium (2,5-difluorophenyl)trifluoroborate (220 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 10 min. The desired pure product was obtained in 81% yield (116 mg, 0.81 mmol) as a white solid, mp 35–37 °C, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (m, 1H), 6.87 (m, 1H), 6.61 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.9 (d, J = 12 Hz), 166.9 (m), 164.8 (d, J = 13 Hz), 153.3 (d, J = 4 Hz), 112.0 (m), 106.4 (m). ^{19}F NMR (470.8 MHz, $CDCl_3$) δ –94.4, –123.7. IR (neat) 1613, 1501, 1241, 845 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_6H_4NOF_2$ $(M+H)^+$ 144.0261, found 144.0260.

4-Nitrosodibenzo[*b*,*d*]furan (3a)—General procedure B was employed using potassium dibenzo[*b*,*d*]furan-4-yltrifluoroborate (274 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 85% yield (168 mg, 0.85 mmol) as a green solid, mp 84–86 °C, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (m, 1H), 8.01 (m, 1H), 7.78 (d, J = 8 Hz, 1H), 7.59 – 7.56 (m, 2H), 7.49 – 7.44 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 157.4, 153.3, 148.8, 128.7, 128.5, 128.4, 124.1, 122.6, 122.5, 121.0, 116.3, 112.7. IR (neat) 1456, 1417, 1174, 1107, 830, 744 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_{12}H_8NO_2$ $(M+H)^+$ 198.0555, found 198.0553.

4-Nitrosodibenzo[*b*,*d*]thiophene (3b)—General procedure B was employed using potassium dibenzo[*b*,*d*]thiophen-4-yltrifluoroborate (290 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 80% yield (171 mg, 0.80 mmol) as a green solid, mp 115–117 °C, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (m, 1H), 8.46 (m, 1H), 8.15 (m, 1H), 7.93 – 7.89 (m, 2H), 7.53 – 7.50 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 162.9, 142.1, 138.1, 137.9, 132.4, 128.2, 127.8, 125.9, 125.5, 123.7, 121.7, 120.1. IR (neat) 1421, 1190, 1086, 920, 750 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_8NOS$ $(M+H)^+$ 214.0327, found 214.0336.

4-Nitrosobenzo[*b*]thiophene (3c)—General procedure B was employed using potassium benzo[*b*]thiophen-4-yltrifluoroborate (240 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 81% yield (132 mg, 0.81 mmol) as a yellow solid, mp 76–78 °C, after filtration through a

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short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8 Hz, 1H), 8.31 (m, 1H), 8.22 (d, *J* = 8 Hz, 1H), 7.86 (d, *J* = 5.5 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 160.6, 142.8, 134.1, 130.2, 127.0, 126.8, 124.2, 121.7. IR (neat) 1450, 1265, 861, 746 cm^{-1}. HRMS (ESI) *m/z* calcd. for C_8H_6NOS $(M+H)^+$ 164.0170, found 164.0168.

***tert*-Butyl 5-Nitroso-1*H*-indole-1-carboxylate (3d)—**General procedure B was employed using potassium (1-(*tert*-butoxycarbonyl)-1*H*-indol-5-yl)trifluoroborate (323 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 73% yield (180 mg, 0.73 mmol) as a green solid, mp 101–103 °C, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 4 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 3.5 Hz, 1H), 1.70 (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.8, 149.2, 139.0, 130.6, 128.8, 119.7, 115.3, 115.1, 109.3, 85.2, 28.2. IR (neat) 1743, 1467, 1325, 1155, 1071, 721 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{13}H_{13}N_2O_3$ $(M-H)^-$ 245.0926, found 245.0932.

2,4-Dimethoxy-5-nitrosopyrimidine (3e)—General procedure B was employed using potassium (2,4-dimethoxypyrimidin-5-yl)trifluoroborate (246 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 82% yield (139 mg, 0.82 mmol) as a green solid, mp 78–80 °C, after filtration through a short plug of silica topped with Celite using CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 4.33 (s, 3H), 4.16 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.6, 166.3, 149.6, 149.2, 56.5, 55.4. IR (neat) 1594, 1547, 1474, 1314, 1054, 796 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_6H_8N_3O_3$ $(M+H)^+$ 170.0566, found 170.0570.

4-(5-Nitrosopyrimidin-2-yl)morpholine (3f)—General procedure B was employed using potassium trifluoro(2-morpholinopyrimidin-5-yl)borate (271 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 76% yield (148 mg, 0.76 mmol) as a green solid, mp 151–153 °C, after column chromatography with CH_2Cl_2 as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 2H), 4.00 (t, *J* = 5 Hz, 4H), 3.79 (t, *J* = 5 Hz, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 161.5, 154.8, 133.6, 66.6, 44.8. IR (neat) 2359, 1601, 1548, 1329, 1109, 790 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_{11}N_4O_2$ $(M+H)^+$ 195.0882, found 195.0884.

2,6-Dimethoxy-3-nitrosopyridine (3g)—General procedure B was employed using potassium (2,6-dimethoxypyridin-3-yl)trifluoroborate (245 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 72% yield (121 mg, 0.72 mmol) as a green solid, mp 95–97 °C, after column chromatography with CH_2Cl_2 as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (d, *J* = 8.5 Hz, 1H), 6.23 (d, *J* = 8.5 Hz, 1H), 4.37 (s, 3H), 4.11 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 168.3, 165.6, 151.2, 122.1, 103.3, 54.8. IR (neat) 1588, 1384, 1286, 1001, 825 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_9N_2O_3$ $(M+H)^+$ 169.0613, found 169.0618.

5-Nitrosoisoquinoline (3h)—General procedure B was employed using potassium trifluoro(isoquinolin-5-yl)borate (235 mg, 1 mmol) and $NOBF_4$ (120 mg, 1.03 mmol). The reaction was complete in 30 sec. The desired pure product was obtained in 62% yield (NMR yield) as a yellow solid that upon exposure to air becomes black after column chromatography with EtOAc/CH_2Cl_2 (1:1) as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.49 (s, 1H), 9.41 (d, *J* = 6 Hz, 1H), 8.97 (d, *J* = 6 Hz, 1H), 8.40 (d, *J* = 8 Hz, 1H), 7.73 (t, *J* = 8 Hz, 1H), 7.14 (q, *J* = 1 and 8 Hz, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 157.7, 152.6, 147.2, 136.4, 131.5, 129.6, 126.2, 116.2, 114.0.

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General Procedure C: One-pot Nitrosation/Diels-Alder

Adapted from a previously reported method.[15a] To a 20 mL glass microwave vial containing a solution of potassium organotrifluoroborate (1 mmol) in CH_3CN (3 mL, 0.33 M) was added 1,3-cyclohexadiene (114 μL, 1.2 mmol, 1.2 equiv). To the mixture was added $NOBF_4$ (120 mg, 1.03 mmol, 1.03 equiv) in one portion. The flask was then capped (exothermic reaction) and stirred for 2 h. To the crude mixture was added H_2O (20 mL) and EtOAc (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The product was purified by column chromatography using EtOAc/hexanes.

3-(Isoquinolin-5-yl)-2-Oxa-3-azabicyclo[2.2.2]oct-5-ene (4c)—General procedure C was employed using potassium trifluoro(isoquinolin-5-yl)borate (235 mg, 1 mmol), 1,3-cyclohexadiene (114 μL, 1.2 mmol, 1.2 equiv), and $NOBF_4$ (120 mg, 1.03 mmol). The desired pure product was obtained in 65% yield (155 mg, 0.65 mmol) as a yellow solid, mp 68–70 °C, after column chromatography with EtOAc/hexanes (1:1) as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.51 (d, *J* = 6 Hz, 1H), 7.91 (d, *J* = 6 Hz, 1H), 7.64 (d, *J* = 8 Hz, 1H), 7.45 (t, *J* = 8 Hz, 1H), 7.37 (m, 1H), 6.75 (d, *J* = 2 and 6.5 Hz, 1H), 5.96 (t, *J* = 6.5 Hz, 1H), 4.82 (m, 1H), 4.34 (m, 1H), 2.51 (m, 1H), 2.36 (m, 1H), 1.60 (m, 1H), 1.50 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 152.6, 146.1, 142.5, 132.1, 129.1, 129.1, 128.9, 126.8, 123.1, 120.5, 116.0, 69.5, 56.9, 23.7, 22.0. IR (neat) 1579, 1371, 1271, 932, 838, 768 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{15}H_{15}N_2O$ $(M+H)^+$ 239.1184, found 239.1183.

Methyl 3-(-2-Oxa-3-azabicyclo[2.2.2]oct-5-en-3-yl)benzoate (5d)—General procedure C was employed using potassium trifluoro(3-(methoxycarbonyl)phenyl)borate (242 mg, 1 mmol), 1,3-cyclohexadiene (114 μL, 1.2 mmol, 1.2 equiv), and $NOBF_4$ (120 mg, 1.03 mmol). The desired pure product was obtained in 82% yield (201 mg, 0.82 mmol) as a yellow solid, mp 87–89 °C, after column chromatography with EtOAc/hexanes (5:1) as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.58 (m, 1H), 7.26 (t, *J* = 8 Hz, 1H), 7.19 (m, 1H), 6.57 (m, 1H), 6.12 (m, 1H), 4.73 (m, 1H), 4.48 (m, 1H), 3.88 (s, 3H), 2.29 – 2.22 (m, 2H), 1.57 (m, 1H), 1.38 (m, 1H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.3, 152.7, 131.9, 130.5, 129.9, 128.6, 123.3, 122.1, 118.4, 69.5, 56.6, 52.2, 24.0, 21.4. IR (neat) 1719, 1439, 1270, 944, 759 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{14}H_{16}NO_3$ $(M+H)^+$ 246.1130, found 246.1130.

One-pot Procedure for Formation of Azoxy Compound: Synthesis of 1,2-Bis(3-(methoxycarbonyl)phenyl)diazene Oxide (5a):[48]—Adapted from a previously reported method.[49] To a 20 mL glass microwave vial containing potassium trifluoro(3-(methoxycarbonyl)phenyl)borate (242 mg, 1 mmol) in CH_3CN (3 mL, 0.33 M) was added $NOBF_4$ (120 mg, 1.03 mmol, 1.03 equiv) in one portion. After 30 sec the solvent was removed and EtOH was added (3.5 mL, 0.3M), followed by $(NH_4)_2SO_4$ (1 g, 5 mmol, 5 equiv) and $NaBH_4$ (661 mg, 3 mmol, 3 equiv). The flask was then capped (exothermic reaction) and stirred at rt for 30 min. The reaction mixture changed from green to yellow. To the crude mixture was added H_2O (20 mL) and EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by filtration through a short plug of silica topped with Celite using EtOAc afforded the pure product in 87% yield (137 mg, 0.44 mmol) as a yellow solid, mp 135–137 °C (lit.[46] 135 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (d, *J* = 2 Hz, 1H), 8.77 (t, *J* = 2 Hz, 1H), 8.51 (m, 1H), 8.42 (m, 1H), 8.25 (d, *J* = 7.5 Hz, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 3.99 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.5, 165.8, 148.4, 143.9, 132.9, 131.4, 131.1, 130.8, 129.6, 129.3, 129.0, 127.2, 126.7,

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123.7, 52.7, 52.5. IR (neat) 1726, 1466, 1301, 1267, 1083, 753 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}N_2O_5$ $(M+H)^+$ 315.0981, found 315.0981.

Procedure for Formation of Nitro Compounds: Synthesis of Methyl 3-Nitrobenzoate (5b):[50]—Adapted from a previously reported method.[15b] To a 20 mL glass microwave vial containing potassium trifluoro(3-(methoxycarbonyl)phenyl)borate (242 mg, 1 mmol), in CH_3CN (3 mL, 0.33 M) was added $NOBF_4$ (120 mg, 1.03 mmol, 1.03 equiv) in one portion. After 30 sec the crude mixture was filtered through a plug of silica topped with Celite using CH_2Cl_2, the solvent was removed, and acetone: H_2O (1:1, 5 mL) was added. To the solution was then added Oxone (461 mg, 1.5 mmol, 1.5 equiv). The flask was then capped and stirred at 60 °C for 2 h. The reaction solution changed from green to yellow. To the crude mixture was added H_2O (20 mL) and EtOAc (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by filtration through a short plug of silica topped with Celite using EtOAc afforded the pure product in 86% yield (156 mg, 0.86 mmol) as a yellow solid, mp 75–77 °C (lit.[48] 77–79 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (t, *J* = 1.5 Hz, 1H), 8.42 (m, 1H), 8.37 (m, 1H), 7.67 (t, *J* = 8.5 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.9, 148.3, 135.2, 131.9, 129.6, 127.4, 124.6, 52.8. IR (neat) 3098, 1718, 1527, 1350, 1290, 1269, 1134, 720 cm^{-1}.

One-pot Procedure for Formation of Aniline Compounds: Synthesis of Methyl 3-Aminobenzoate (5c):[51]—Adapted from a previously reported method.[52] To a 20 mL glass microwave vial containing potassium trifluoro(3-(methoxycarbonyl)phenyl)borate (242 mg, 1 mmol) in CH_3CN (3 mL, 0.33 M) was added nitrosonium tetrafluoroborate (120 mg, 1.03 mmol, 1.03 equiv) in one portion. EtOH (2 mL) and $SnCl_2$•$2H_2O$ (1.13 g, 5 mmol, 5 equiv) were added after 30 sec. The flask was then capped, and the reaction was stirred at 80 °C for 2 h. To the crude mixture was added 5% $NaHCO_3$ (3 mL, or enough to make the pH slightly basic, 7–9). The resulting emulsion was filtered, and the solid was washed with H_2O (10 mL) and EtOAc (10 mL). The layers of the filtrate were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by filtration through a short plug of silica topped with Celite using EtOAc afforded the pure product as a yellow oil in 72% yield (109 mg, 0.72 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (m, 1H), 7.35 (t, *J* = 2 Hz, 1H), 7.21 (t, *J* = 8 Hz, 1H), 6.85 (m, 1H), 3.89 (s, 3H), 3.79 (brs, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.4, 146.6, 131.3, 129.4, 119.8, 119.5, 115.9, 52.2. IR (neat) 3372, 2951, 1710, 1603, 1239, 753 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_{10}NO_2$ $(M+H)^+$ 152.0712, found 152.0713.

Supplementary Material

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Acknowledgments

This work was generously supported by the NIGMS (R01 GM086209, GM035249). We acknowledge Conselho Nacional de Desenvolvimento Cientifico e Tecnologico (CNPq) for Graduate Research Fellowship to L.N.C. We also acknowledge Aldrich, BoroChem, and Frontier Scientific for their donation of the boronic acids used to prepare the organotrifluoroborates. Dr. Rakesh Kohli (University of Pennsylvania) is acknowledged for obtaining the HRMS data.

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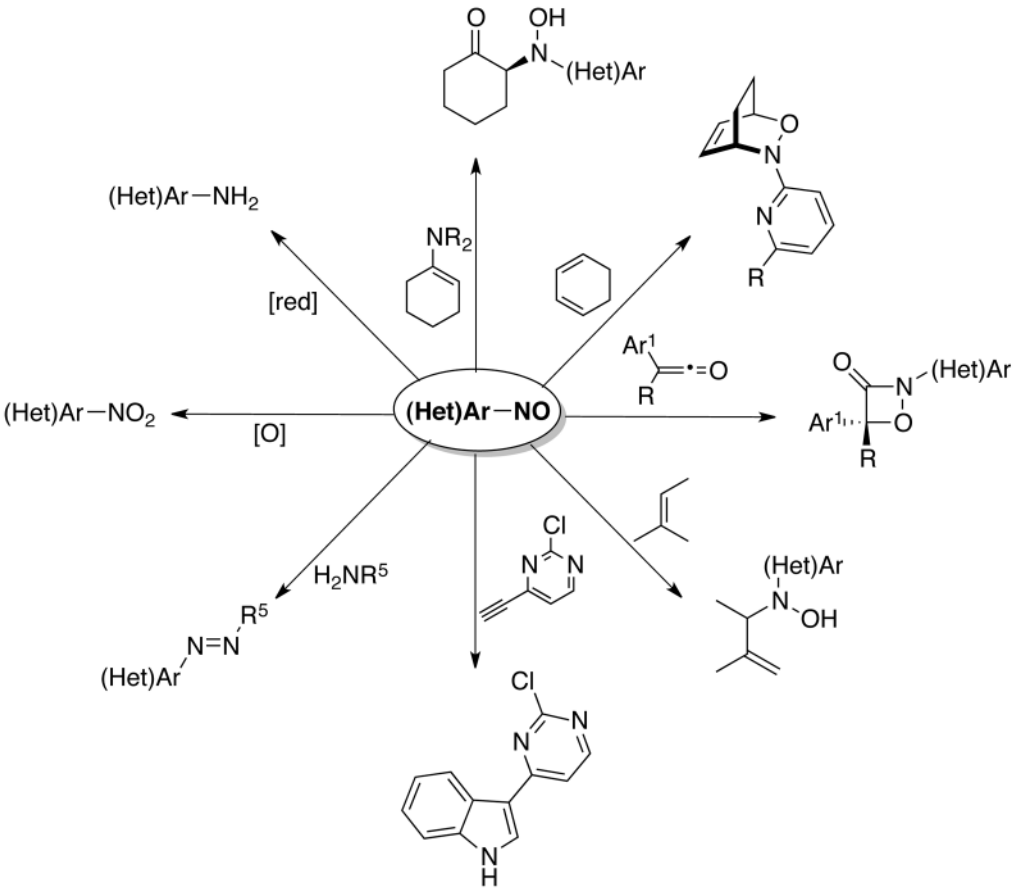

Scheme 1.

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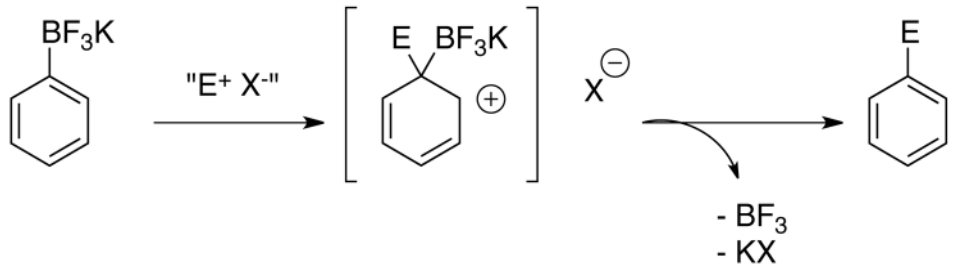

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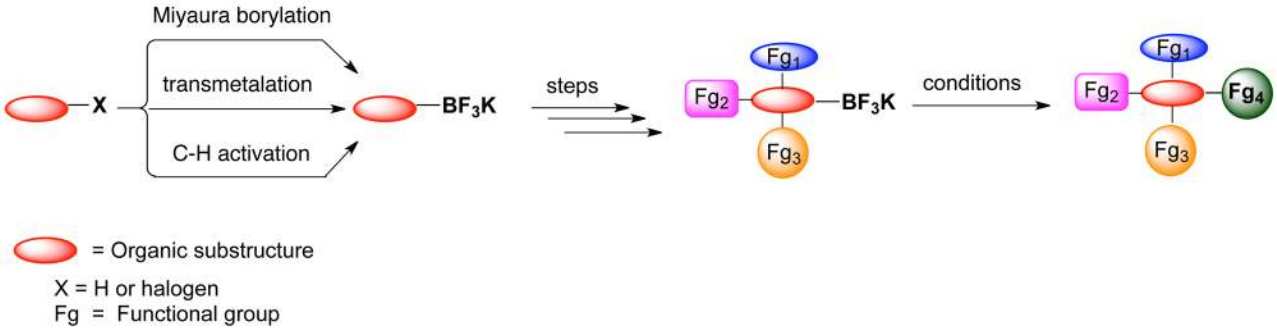

Scheme 3.

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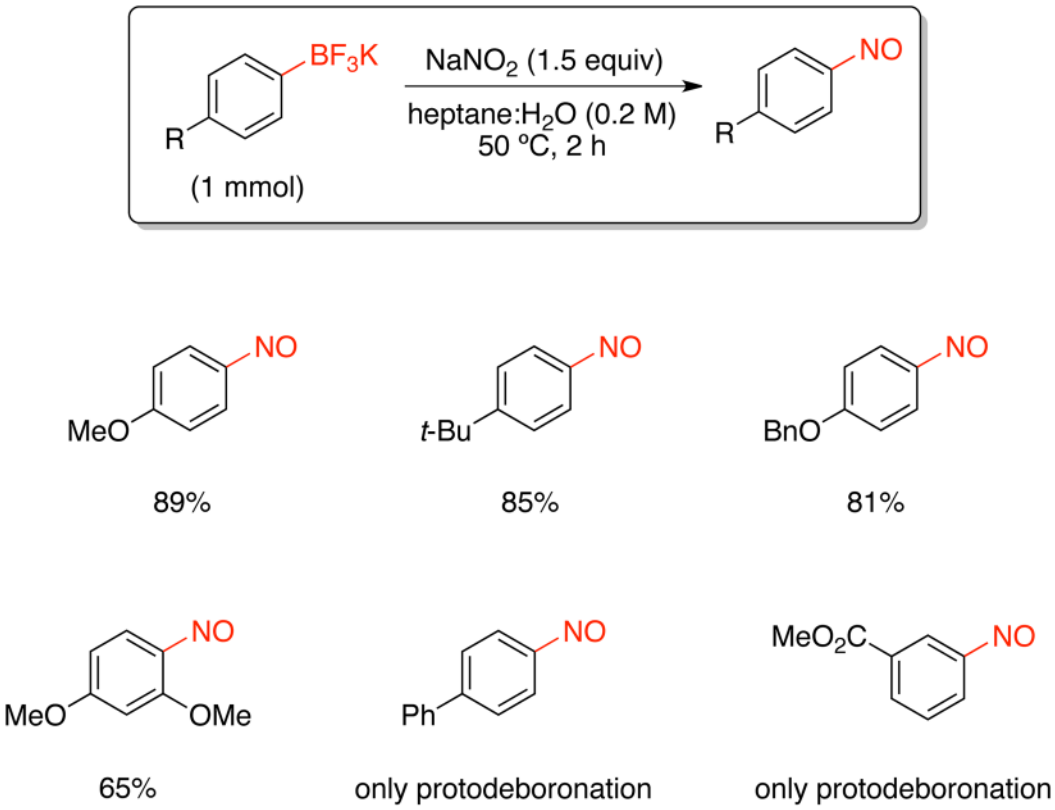
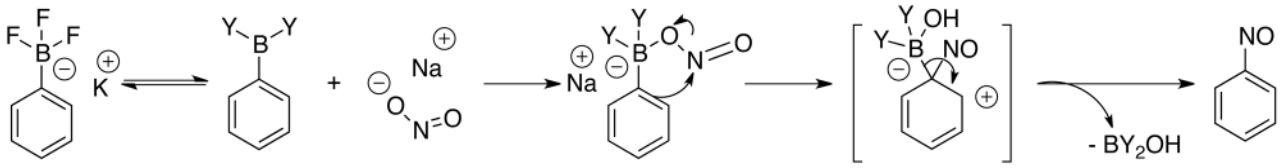
NIH-PA Author Manuscript



Scheme 4.



Scheme 5.

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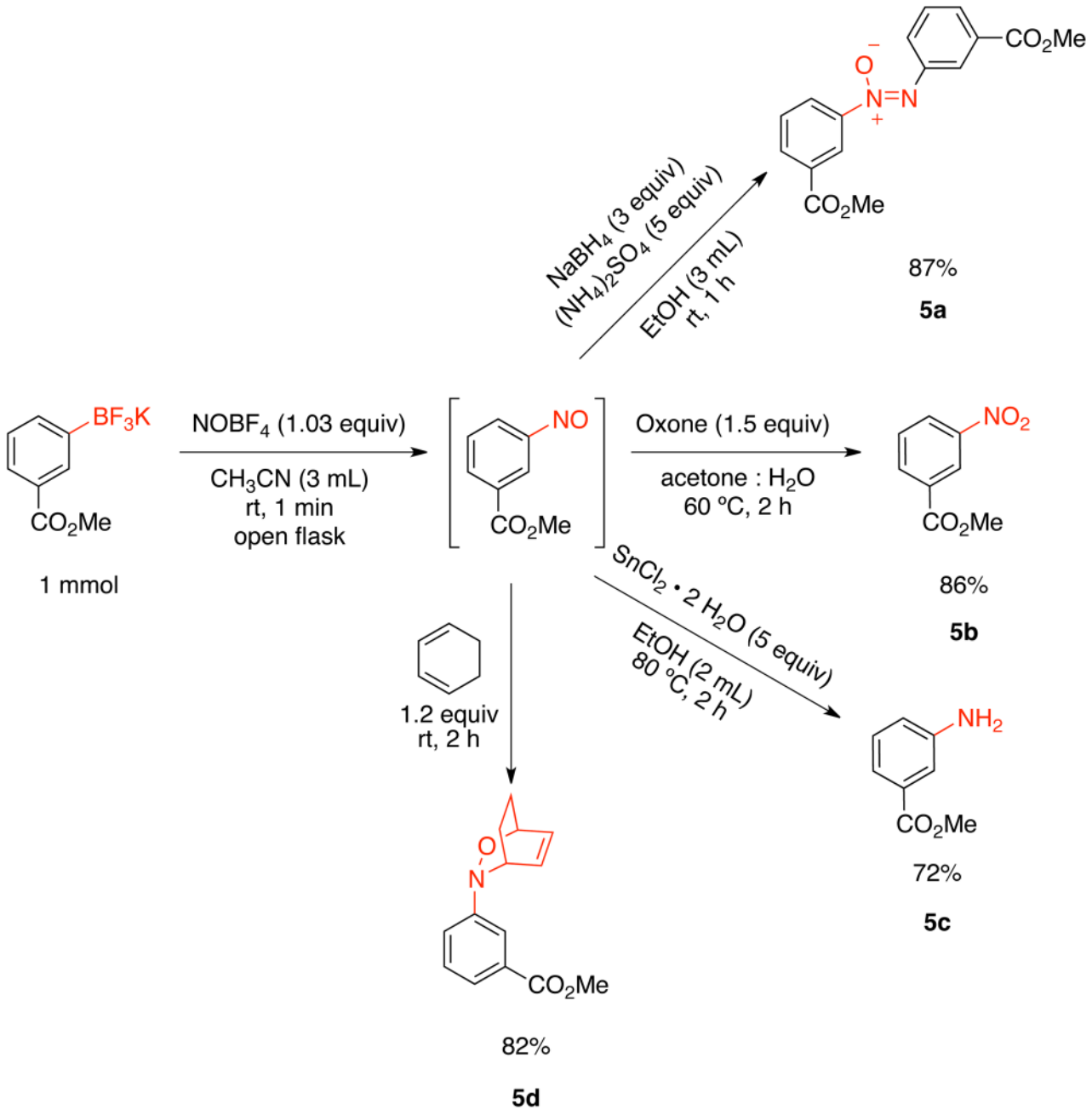
NIH-PA Author Manuscript



Scheme 6.

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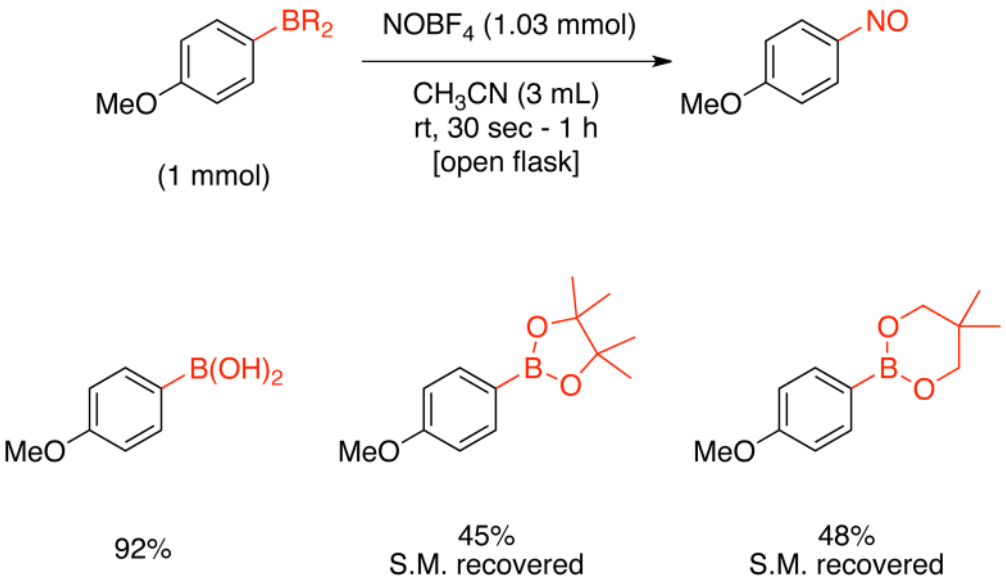

Scheme 7.

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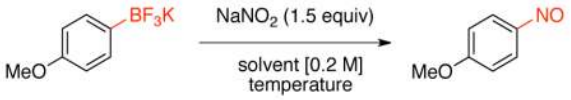
Table 1

Optimization with Sodium Nitrite



1a

entry	solvent	temperature	reaction time (h)	^{11}B NMR/GC/MS
1	EtOAc	rt	48	S.M.
2	CH_3CN	rt	48	S.M.
3	heptane	rt	48	S.M.
4	H_2O	rt	4	**1a**: protodeboronation (1:1)
5	EtOAc:H_2O	rt	4	**1a**: protodeboronation (3:1)
6	CH_3CN:H_2O	rt	4	**1a**: protodeboronation (2:1)
7	heptane:H_2O	rt	4	**1a**
8	heptane:H_2O	50 °C	2	**1a** (89% isolated yield)

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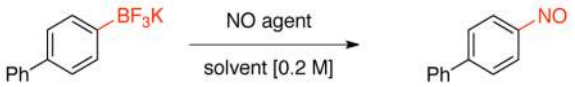
Table 2

Optimization of the Nitrosation of Potassium [1,1′-Biphenyl]-4-yltrifluoroborate



entry	NO agent	solvent	reaction time	GC/MS
1	$NaNO_2$	heptane:H_2O (1:1)	4 h	protodeboronation
2	KNO_2	heptane:H_2O (1:1)	4 h	protodeboronation
3	$AgNO_2$	heptane:H_2O (1:1)	2 h	protodeboronation
4	$NaNO_2$:HCl	heptane:H_2O (1:1)	1 h	protodeboronation
5	KNO_2:HCl	heptane:H_2O (1:1)	1 h	protodeboronation
6	$AgNO_2$:HCl	heptane:H_2O (1:1)	1 h	protodeboronation
7	$NaNO_2$:TMSCl	CH_2Cl_2:H_2O (1:1)	1 h	protodeboronation
8	$NOBF_4$	CH_3CN	30 sec	product (90% isolated yield)

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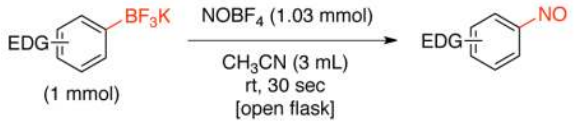
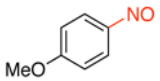
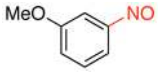
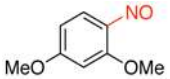
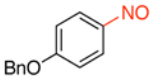
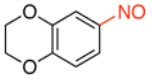
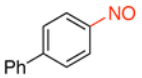
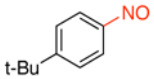
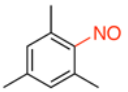
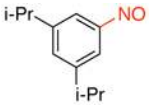
Table 3

Nitrosation of Electron-rich and Electron-neutral Potassium Aryltrifluoroborates



entry	product	yield (%)
1	 **1a**	95[a]
2	 **1b**	89
3	 **1c**	91
4	 **1d**	92
5	 **1e**	91
6	 **1f**	90
7	 **1g**	93
8	 **1h**	92
9	 **1i**	88

Reaction conditions: 1 mmol of aryltrifluoroborate and $NOBF_4$ (1.03 equiv) in 3 mL of CH_3CN for 30 sec at room temperature in an open flask.

[a]5 mmol scale.

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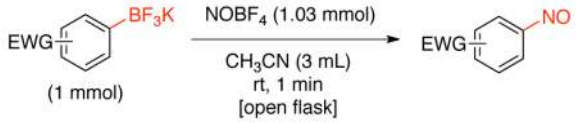
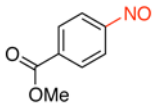
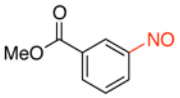
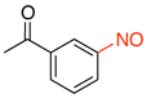
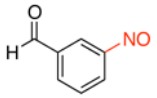
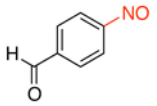
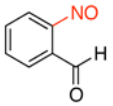
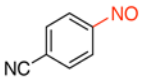
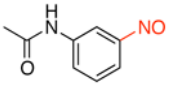
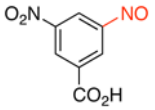
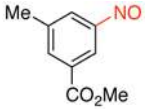
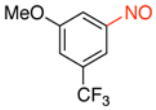
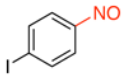
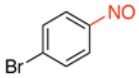
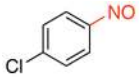
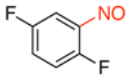
Table 4

Nitrosation of Electron-poor Potassium Aryltrifluoroborates



entry	product	yield (%)
1	 **2a**	96
2	 **2b**	95
3	 **2c**	94
4	 **2d**	91
5	 **2e**	94
6	 **2f**	78
7	 **2g**	89
8	 **2h**	91
9	 **2i**	90

entry	product	yield (%)
10	 **2j**	91
11	 **2k**	81
12	 **2l**	92
13	 **2m**	94
14	 **2n**	92
15	 **2o**	79

Reaction conditions: 1 mmol of aryltrifluoroborate and $NOBF_4$ (1.03 equiv) in 3 mL of CH_3CN for 30 sec at room temperature in an open flask.

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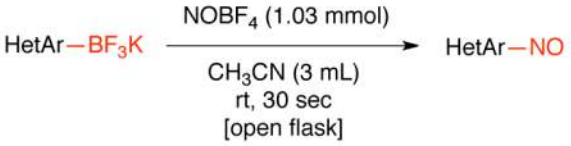
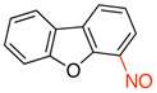
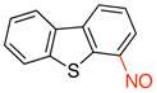
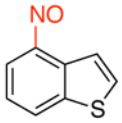
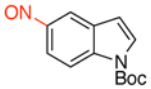
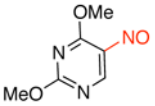
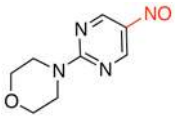
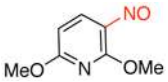
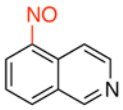
Table 5

Nitrosation of Potassium Heteroaryltrifluoroborates



entry	product	yield (%)
1	 **3a**	85
2	 **3b**	80
3	 **3c**	81
4	 **3d**	73
5	 **3e**	82
6	 **3f**	76
7	 **3g**	72
8	 **3h**	62[a]

Reaction conditions: 1 mmol of aryltrifluoroborate and $NOBF_4$ (1.03 equiv) in 3 mL of CH_3CN for 30 sec at room temperature in an open flask.

[a]NMR yield using EtOAc as internal standard