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# Silver(I)-Promoted *ipso*-Nitration of Carboxylic Acids by Nitronium Tetrafluoroborate

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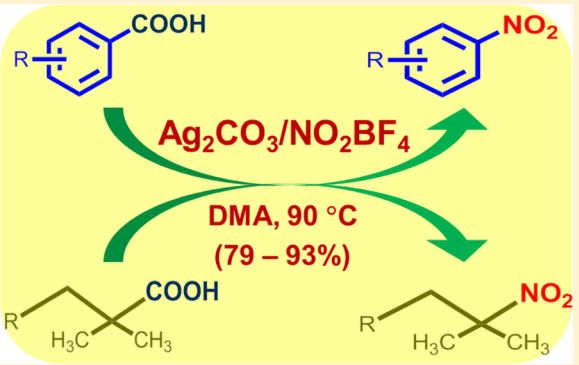
Supporting Information

**ABSTRACT:** A novel and efficient method for the regioselective nitration of a series of aliphatic and aromatic carboxylic acids to their corresponding nitro compounds using nitronium tetrafluoroborate and silver carbonate in dimethylacetamide has been described. This transformation is believed to proceed via the alkyl-silver or aryl-silver intermediate, which subsequently reacts with the nitronium ion to form nitro substances. Mild reaction conditions, tolerant of a broad range of functional groups, and formation of only the *ipso*-nitrated products are the key features of this methodology when compared to known methods for syntheses of nitroalkyls and nitroarenes.




## INTRODUCTION

The *ipso*-nitration reaction,[1] employed for the synthesis of a wide variety of nitro compounds, is a practical alternative to the classical electrophilic nitration reaction that encounters several problems including polynitration and competitive oxidation of substrates. Although several leaving groups such as alkyls,[2] acyls,[3] boronic acids,[4] esters,[3] halogens,[3c,5] sulfonic acids,[6] and carboxylic acids[7] were found to be displaced by a nitro group, only *ipso*-nitration of arylboronic acids has been studied intricately and consistently.[4] Undoubtedly, reported methods of deborylative nitration of arylboronic acids are useful; however, the principal drawbacks associated with these protocols are use of highly toxic and explosive reagents such as bismuth nitrate,[4a] cadmium nitrate,[4b] mixture of sodium nitrate and palladium,[4c] etc.[1] Moreover, many boronic acids[8] are unstable (readily lose water/boron at ambient conditions) and expensive.[9] As a consequence, the elaborate and systematic study of replacement of other substituent/s (i.e., alkyls/acyls/carboxylic esters/halogens/sulfonic acids/carboxylic acids) by a nitro group is very desirable and remains a challenging area for exploration.

Carboxylic acids[10] have long served as precursors for a wide array of organic transformations, because they are inexpensive,[9] easy to handle, chemically nontoxic, straightforward to synthesize, air and moisture insensitive, and readily available in great structural forms.[10c] In addition, huge numbers of homo- and cross-coupling reactions making use of carboxyl substituents as leaving groups for regioselective couplings have been reported.[11] Circumstantially only a single report on the *ipso*-nitration of aromatic carboxylic acids, using cellulose supported copper nanoparticles and bismuth(III) nitrate, has been described so far.[12] Further investigations would thus be crucial to make the decarboxylative nitration reaction more efficient and practical for the synthesis of potentially useful nitro compounds.

It is well-known that carboxylic acids undergo decarboxylation most efficiently in the presence of silver salts (relative to copper salts) to generate a carbon nucleophile *in situ*.[13] This proficiency is likely due to their (silver salts) lower electronegativity and greater expansion of d-orbitals, which promote the decarboxylation of substrates.[13a] Of course, various silver salts have been employed as catalysts for the decarboxylative carbon−carbon, carbon−silicon, carbon−oxygen, carbon−boron, carbon−sulfur, carbon−phosphorus, and carbon−halogen bond-forming reactions.[11,13,14] Inspired by these reports and our previous works on the decarboxylative oxidation of polycyclic aromatic compounds,[15] herein we describe a novel and efficient approach for the *ipso*-nitration of a broad range of carboxylic acids with nitronium tetrafluoroborate ($NO_2BF_4$) as a nitrating agent and silver carbonate ($Ag_2CO_3$) as a decarboxylation reagent in dimethylacetamide (DMA), cf., Scheme 1. To the best of our knowledge, no attempt to perform the *ipso*-nitration of carboxylic acids using a mixture of $NO_2BF_4$ and $Ag_2CO_3$ has been reported in the literature.

## RESULTS AND DISCUSSION

In order to optimize the reaction condition, benzoic acid (**1C**) was chosen as a model substrate, and $NO_2BF_4$ and $Ag_2CO_3$, respectively, were used as nitrating as well as decarboxylation agents. The results of optimization reactions performed under a variety of conditions are summarized in Table 1. Investigations of the model reaction in various anhydrous solvents including

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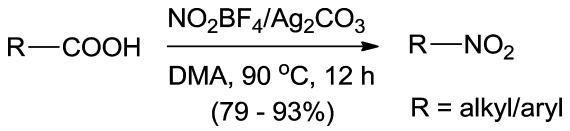
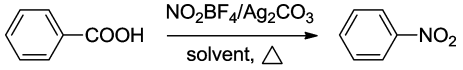
**Scheme 1. $NO_2BF_4$ and $Ag_2CO_3$ Mediated Decarboxylative Nitration of Carboxylic Acids to Their Corresponding Nitro Compounds Reported in This Work**




acetonitrile, chloroform, dichloromethane, dichloroethane, DMA, tetrahydrofuran, and tetrachloroethane suggested that anhydrous DMA was the best medium for the *ipso*-nitration of **1C** (Table 1 and entry 5). This likely reason is that a relatively polar solvent is necessary to dissolve $Ag_2CO_3$ and $NO_2BF_4$, since they have limited solubility in medium polar solvents.

There was next an attempt to arrive at an optimum stoichiometry of $Ag_2CO_3$ and $NO_2BF_4$ to **1C** (1.0 mmol) for **1N** synthesis in DMA. As shown in Table 1 (entries 5, 9, 10, and 11), higher amounts of $Ag_2CO_3$ neither increased the product yield nor lowered the reaction time drastically. The best result (Table 1 and entry 8) was obtained by carrying out the reaction with 0.5 mmol of $Ag_2CO_3$ to 1.0 mmol of **1C**. Under this stoichiometric condition, alternative bases such as $K_2CO_3$ (Table 1 and entry 12) and $Na_2CO_3$ (Table 1 and entry 13) provided no product indicating the importance of a silver ion that helps stabilize the resulting anion upon loss of carbon dioxide. Similar behaviors have been reported for several silver(I) catalyzed decarboxylative cross-coupling reactions.[13,14] Further optimization of the amount of $NO_2BF_4$ showed that a slight excess (0.5 mmol) is necessary to achieve high yields (Table 1 and entry 14) of **1N** in short duration. It is noteworthy that $NO_2BF_4$ was effective only in the presence of $Ag_2CO_3$ (Table 1 and entry 18). Likewise, in the absence of $NO_2BF_4$ but with 1.0/2.0 mmol of $Ag_2CO_3$ (Table 1 and entries 19 and 20) no nitration was detected. Clearly, both $NO_2BF_4$ and $Ag_2CO_3$ are essential for the reaction. Finally, raising the temperature from 80 to 120 °C with 10 °C increments/experiment led to **1N** in more than 90% yield in significantly short duration, cf., Table 1 and entries 21−23. No product formation was noticed when the reaction was carried out at room temperature (Table 1 and entry 24). Thus, the optimized conditions for the *ipso*-nitration of carboxylic acids can be defined as follows: 1.0 mmol of substrate, 1.5 mmol of $NO_2BF_4$, 0.5 mmol of $Ag_2CO_3$, anhydrous DMA, and 90 ± 5 °C. Under this optimized condition, formation of **1N** from **1C** was confirmed by the $^1$H NMR titration experiments as well, cf., Figure 1. The easily recognizable *ortho* protons (of **1C**) at $\delta$

**Table 1. Optimization of Reaction Conditions for Silver Carbonate-Promoted *ipso*-Nitration of Carboxylic Acids[a]**




**1C** **1N**

| entry | $Ag_2CO_3$[b] (mmol) | $NO_2BF_4$[b] (mmol) | $T$ (°C) | solvent[c] | time (h) | yield[d] (%) |
|---|---|---|---|---|---|---|
| 1 | 1.0 | 1.0 | 80 | acetonitrile | 36 | < 5 |
| 2 | 1.0 | 1.0 | 80 | chloroform | 36 | < 5 |
| 3 | 1.0 | 1.0 | 80 | dichloromethane | 36 | NR |
| 4 | 1.0 | 1.0 | 80 | dichloroethane | 36 | NR |
| 5 | 1.0 | 1.0 | 80 | DMA | 18 | 88 |
| 6 | 1.0 | 1.0 | 80 | tetrahydrofuran | 36 | <5 |
| 7 | 1.0 | 1.0 | 80 | tetrachloroethane | 36 | NR |
| 8 | 0.5 | 1.0 | 80 | DMA | 18 | 87 |
| 9 | 1.5 | 1.0 | 80 | DMA | 18 | 89 |
| 10 | 2.0 | 1.0 | 80 | DMA | 16 | 87 |
| 11 | 3.0 | 1.0 | 80 | DMA | 16 | 88 |
| 12 | 0.5[e] | 1.0 | 80 | DMA | 36 | NR |
| 13 | 0.5[f] | 1.0 | 80 | DMA | 36 | NR |
| 14 | 0.5 | 1.5 | 80 | DMA | 15 | 93 |
| 15 | 0.5 | 2.0 | 80 | DMA | 14 | 92 |
| 16 | 0.5 | 2.5 | 80 | DMA | 12 | 93 |
| 17 | 0.5 | 3.0 | 80 | DMA | 12 | 94 |
| 18 | 0 | 2.0 | 80 | DMA | 36 | NR[g] |
| 19 | 1.0 | 0 | 80 | DMA | 36 | NR[h] |
| 20 | 2.0 | 0 | 80 | DMA | 36 | NR[h] |
| 21 | 0.5 | 1.5 | 90 | DMA | 13 | 92 |
| 22 | 0.5 | 1.5 | 100 | DMA | 12 | 91 |
| 23 | 0.5 | 1.5 | 110 | DMA | 12 | 89 |
| 24 | 0.5 | 1.5 | 20 | DMA | 48 | NR |
| 25 | 0.5 | 1.0 | 80 | DMA | 18 | 79[i] |
| 26 | 0.5 | 1.5 | 90 | DMA | 13 | 84[i] |
| 27 | 0.5 | 1.5 | 110 | DMA | 12 | 81[i] |

[a]Unless otherwise stated, all reactions were carried out with 1.0 mmol of **1C** and the indicated amounts of $Ag_2CO_3$ and $NO_2BF_4$ under nitrogen gas atmosphere. [b]$Ag_2CO_3$ and $NO_2BF_4$ were dried under vacuum before use. [c]Double distilled solvents were employed. [d]Yield of **1N** was determined by GC analysis using an internal standard. [e]$K_2CO_3$ used instead of $Ag_2CO_3$. [f]$Na_2CO_3$ used instead of $Ag_2CO_3$. [g]Obtained 3-nitrobenzoic acid (<10%). [h]Detected decarboxylated compound. [i]Reaction performed under open air atmosphere. DMA: dimethylacetamide. NR: no reaction.



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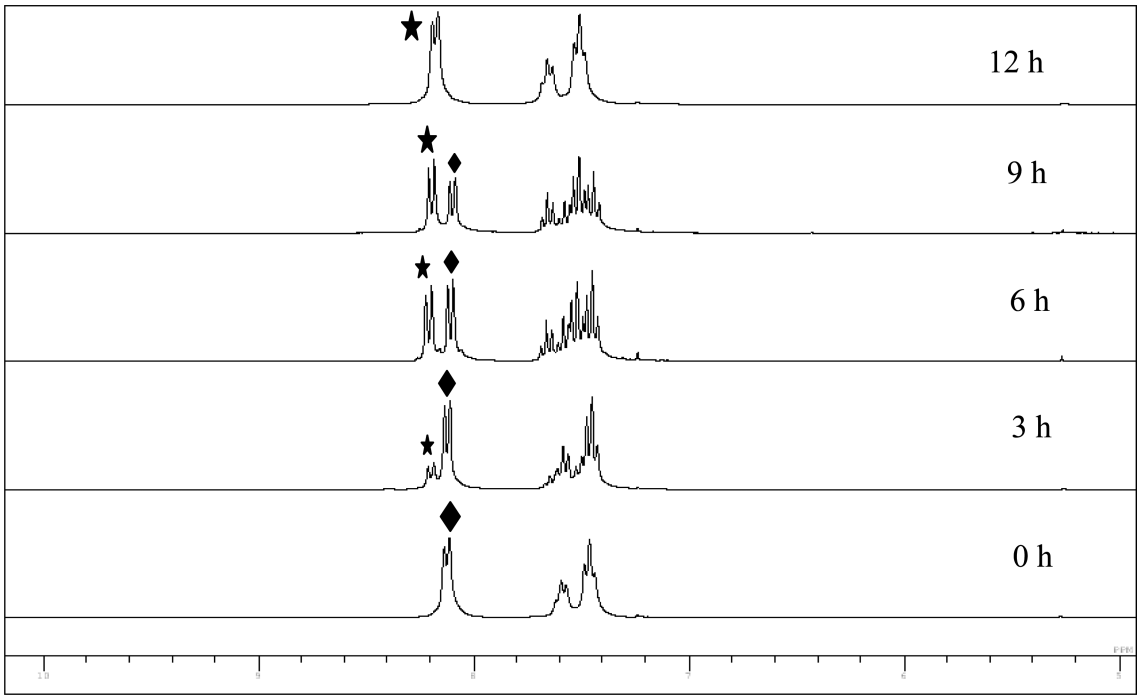


**Figure 1.** $^1$H NMR spectroscopic monitoring (0−12 h) of conversion of **1C** into **1N** in DMA-$d_3$ solution. Notice that a new peak (*) at 8.19 ppm gradually appeared, while a signal (♦) at 8.12 ppm has disappeared indicating the product (**1N**) formation.

= 8.12 ppm completely disappeared within 12 h, while a new peak at $\delta$ = 8.19 ppm corresponding to **1N** originated.

Encouraged by the remarkable results obtained with the above reaction conditions (Table 1), and to show the generality of this new protocol, it was applied to a series of electronically diversified aliphatic and aromatic carboxylic acids (Table 2). We were delighted to find that our protocol tolerates a wide range of functionalities. Indeed, aryl-/heteroaryl-/polyaryl carboxylic acids with electron donating ($CH_3$, $OCH_3$, $C_6H_5$) and withdrawing (F, Cl, Br, CN, $CF_3$, CHO, $COOCH_3$) groups afforded moderate to good yields of corresponding nitroarenes (Table 2). Similarly, no significant effect was observed for sterically demanding substrates that gave good yields of expected nitro compounds (Table 2 and entries 3, 10, 12, 16, 20−28). This method, moreover, is applicable to the nitrodecarboxylation of aliphatic carboxylic acids (Table 2 and entries 22−28) too. Therefore, the present methodology proved of general applicability for the *ipso*-nitration of carboxylic acids to nitro derivatives.

To demonstrate the applicability of this method, we aimed to prepare two nitro drugs, namely, fexinidazole (**30N**)[43] and nitazoxanide (**31N**)[44] (Scheme 2), from their carboxylic acid precursors under standard conditions described in Table 1. In both cases, the reactions were complete within 12 h affording the desired products in 71−82% yield. Thus, the *ipso*-nitration reaction described here offers a domain for synthesis of highly functionalized nitro compounds (Table 2) including nitro drugs (Scheme 2) that cannot be achieved by traditional electrophilic nitration reaction[1] known to overoxidize the substrate.

The plausible reaction mechanism for the *ipso*-nitration of carboxylic acids is outlined in Figure 2 on the basis of blank experiments (Table 1 and entries 18−20 and 25−27) and earlier reports.[45] To understand the roles of $NO_2BF_4$ and $Ag_2CO_3$, we carried out blank experiments with **1C** and $NO_2BF_4$ (in the absence of $Ag_2CO_3$, Table 1 and entry 18) as well as with **1C** and $Ag_2CO_3$ (in the absence of $NO_2BF_4$, Table 1 and entries 19−20), and the reactions did not succeed, indicating both $NO_2BF_4$ and $Ag_2CO_3$ played an important role in the product formation. Ag(I) salts have been shown to mediate the decarboxylation of carboxylic acids in solutions.[13,14] Accordingly, the proposed mechanism (Figure 2) starts with an anion exchange at the silver center to give the metal carboxylate, which in turn provides an arylmetal species by extrusion of carbon dioxide. A subsequent reaction with nitronium ion results in the desired nitro compound forming, leaving the silver tetrafluoroborate as a byproduct. It is noteworthy to mention that, in the absence of $NO_2BF_4$, only the decarboxylated compound was detected indicating the formation of aryl-silver species as an intermediate.

## CONCLUSIONS

In summary, we have introduced the mixture of nitronium tetrafluoroborate and silver carbonate as an efficient and novel reagent system for the synthesis of a variety of nitro compounds including fexinidazole (**30N**) and nitazoxanide (**31N**) from their carboxylic acid precursors. The principal advantages of this method include regioselectivity, use of relatively inexpensive carboxylic acids as precursors, broad tolerance of functional groups, moderate to good yields of targeted products, as well as avoidance of the use of strong acids. We believe that the *ipso*-nitration reaction reported here may be a valuable methodology for the synthesis of a wide range of functional materials[46] including drugs, dyes, explosives, pharmaceuticals, and plastics derived from nitro feedstocks.

## EXPERIMENTAL SECTION

**General Aspects.** Solvents were double distilled prior to use. All commercial chemicals were used as received. All reactions were carried out under nitrogen gas atmosphere using standard Schlenk techniques. Reactions were monitored by analytical thin layer chromatography on silica gel with visualization under UV light. Column chromatography was carried out on silica gel using 60−120 mesh powder. NMR spectra



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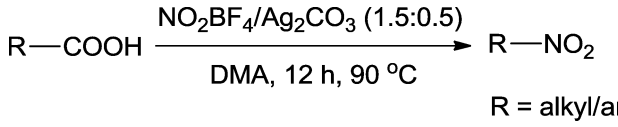
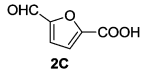
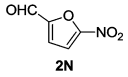
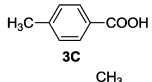
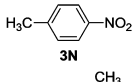
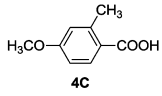
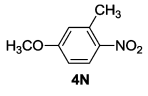
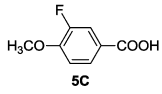
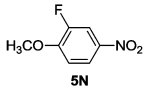
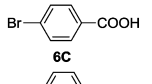
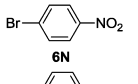
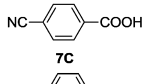
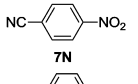
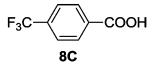
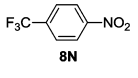
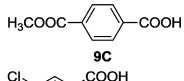
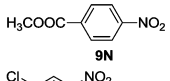
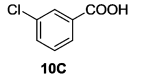
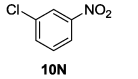
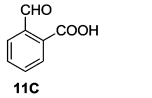
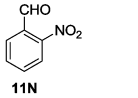
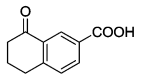
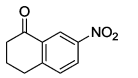
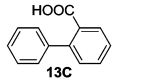
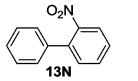
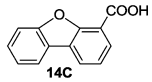
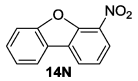
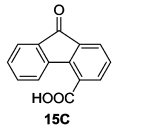
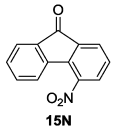
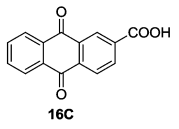
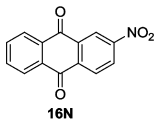
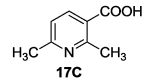
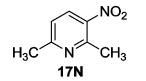
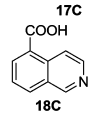
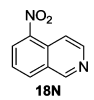
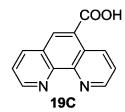
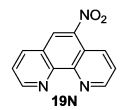
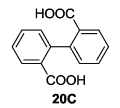
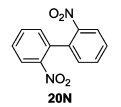
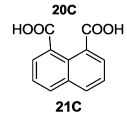
**Table 2. Substrate Scope for the Decarboxylative Nitration of Alkyl and Aryl Carboxylic Acids to Nitro Compounds**[a]




| Entry | Substrate | Product | [b]Yield (%) | mp (lit. mp,°C) |
|---|---|---|---|---|
| 1 |  2C |  2N | 87 | 35 (35-36)[16] |
| 2 |  3C |  3N | 85 | 52-53 (52)[17] |
| 3 |  4C |  4N | 79 | 54-55 (54-55)[18] |
| 4 |  5C |  5N | 78 | 96-97 (95-96)[19] |
| 5 |  6C |  6N | 84 | 124-125 (123-124)[20] |
| 6 |  7C |  7N | 81 | 141-142 (140-142)[21] |
| 7 |  8C |  8N | 86 | 40 (39-41)[22] |
| 8 |  9C |  9N | 87 | 90-91 (91-92)[23] |
| 9 |  10C |  10N | 80 | 45-46 (46-47)[24] |
| 10 |  11C |  11N | 78 | 43 (42-44)[25] |
| 11 |  12C |  12N | 87 | 104-105 (103-104)[26] |
| 12 |  13C |  13N | 88 | 35-36 (36-37)[27] |
| 13 |  14C |  14N | 84 | 137-138 (137-138)[28] |
| 14 |  15C |  15N | 83 | 174-175 (174-176)[29] |
| 15 |  16C |  16N | 86 | 186 (185-186)[30] |
| 16 |  17C |  17N | 74 | 37 (38)[31] |
| 17 |  18C |  18N | 79 | 108-109 (108-110)[32] |
| 18 |  19C |  19N | 81 | 199-201 (200)[33] |
| 19 |  20C |  20N | 83 | 121-122 (120-122)[34] |
| 20 |  21C |  21N | 81 | 169-171 (171-172)[35] |
| 21 |  22C |  22N | 86 | 295 (296)[36] |
| 22 |  23C |  23N | 79 | oil (oil)[37] |
| 23 |  24C |  24N | 82 | oil (oil)[38] |
| 24 |  25C |  25N | 79 | 158-159 (159)[39] |
| 25 |  26C |  26N | 77 | oil (oil)[40] |
| 26 |  27C |  27N | 80 | oil (oil)[40] |
| 27 |  28C |  28N | 78 | oil (oil)[41] |
| 28 |  29C |  29N | 69 | 215 (214)[42] |

[a]Unless stated otherwise, all reactions were performed with carboxylic acid (1.0 mmol), $NO_2BF_4$ (1.5 mmol), and $Ag_2CO_3$ (0.5 mmol) in DMA at 90 ± 5 °C under nitrogen gas atmosphere. [b]Isolated yield. The products were characterized by their comparison with known compounds.

were recorded using a 300 MHz spectrometer in deuterated solvents. Melting points were obtained at a heating rate of 2°/min and are uncorrected.

**General Procedure for the *ipso*-Nitration of Carboxylic Acids.** To a suspension of carboxylic acid (1.0 mmol) and $Ag_2CO_3$ (0.5 mmol) in 10 mL of DMA was added $NO_2BF_4$ (1.5 mmol). The resultant mixture was stirred at 90 ± 5 °C for 12 h. Subsequently, the reaction mixture was cooled down to room temperature, diluted with 20 mL of water, and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine (2 × 15 mL), dried over anhydrous $Na_2SO_4$, and evaporated in a rotary evaporator under reduced pressure. The crude product was purified by either column chromatography on silica gel using 5−20% ethyl acetate in hexane or recrystallization employing ethyl acetate−hexane mixture to afford the desired product. The purity of the compound was confirmed by melting point and $^1H$ and $^{13}C$ NMR measurements, vide infra.



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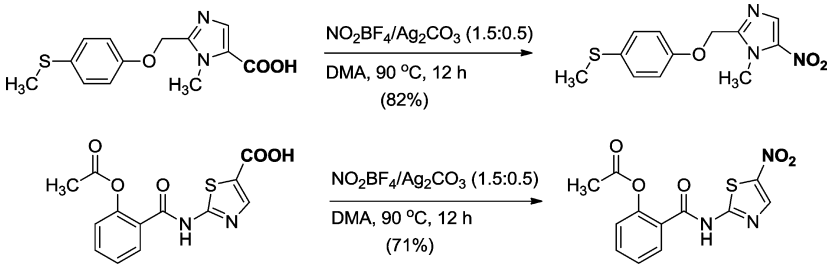
**Scheme 2. Synthesis of Fexinidazole (30N, Top) and Nitazoxanide (31N, Bottom) from their Carboxylic Acid Precursors**



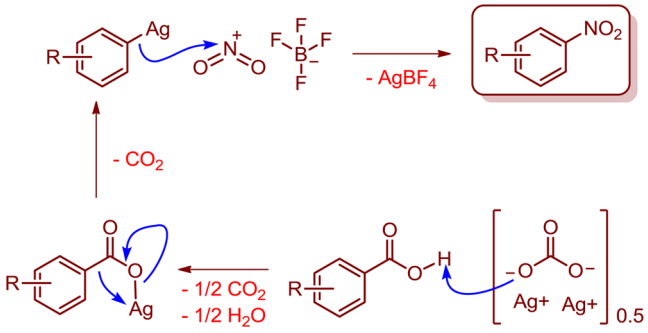




**Figure 2.** Proposed reaction mechanism for the decarboxylative nitration reaction.

*Nitrobenzene* (**1N**). Pale yellow oil (115 mg, 93%). $R_f$ 0.81 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.52 (m, 2H), 7.64 (m, 1H), 8.19 (d, $J$ = 8.4 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 123.4, 129.4, 134.7, 148.1.

*5-Nitro-2-furaldehyde* (**2N**).[16] Yellow solid (123 mg, 87%), mp 35 °C (lit. 35−36 °C).[16] $R_f$ 0.67 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.82 (d, $J$ = 8.2 Hz, 1H), 7.85 (d, $J$ = 8.2 Hz, 1H), 9.97 (s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 111.8, 119.3, 151.2, 178.9.

*4-Nitrotoluene* (**3N**).[17] Light-yellow solid (117 mg, 85%), mp 52−53 °C (lit. 52 °C).[17] $R_f$ 0.80 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 2.46 (s, 3H), 7.33 (d, $J$ = 8.4 Hz, 2H), 8.01 (d, $J$ = 8.4 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 21.5, 123.5, 129.8, 146.1, 146.5.

*3-Methyl-4-nitroanisole* (**4N**).[18] Light-yellow solid (130 mg, 79%), mp 54−55 °C (lit. 54−55 °C).[18] $R_f$ 0.72 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 2.62 (s, 3H), 3.86 (s, 3H), 6.79 (s, 1H), 6.83 (d, $J$ = 8.4 Hz, 1H), 8.09 (d, $J$ = 8.4 Hz, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 21.6, 55.8, 111.9, 117.5, 127.5, 137.0, 142.2, 163.2.

*2-Fluoro-4-nitroanisole* (**5N**).[19] Tan solid (134 mg, 78%), mp 96−97 °C (lit. 95−96 °C).[19] $R_f$ 0.71 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 4.01 (s, 3H), 7.05 (d, $J$ = 8.8 Hz, 1H), 7.98 (s, 1H), 8.06 (d, $J$ = 8.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 56.9, 112.4 (d, $J$ = 24 Hz), 120.9, 140.8 (d, $J$ = 6.7 Hz), 149.4, 152.3 (d, $J$ = 215 Hz), 153.6.

*4-Bromonitrobenzene* (**6N**).[20] Yellow solid (170 mg, 84%), mp 124−125 °C (lit. 123−124 °C).[20] $R_f$ 0.82 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.69 (d, $J$ = 8.4 Hz, 2H), 8.11 (d, $J$ = 8.4 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 125.0, 129.9, 132.7, 147.1.

*4-Nitrobenzonitrile* (**7N**).[21] Light-yellow solid (120 mg, 81%), mp 141−142 °C (lit. 140−142 °C).[21] $R_f$ 0.56 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.88 (d, $J$ = 8.4 Hz, 2H), 8.33 (d, $J$ = 8.4 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 116.8, 118.2, 124.3, 133.5, 149.9.

*4-(Trifluoromethyl)nitrobenzene* (**8N**).[22] Yellow solid (164 mg, 86%), mp 40 °C (lit. 39−41 °C).[22] $R_f$ 0.72 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.86 (d, $J$ = 8.8 Hz, 2H), 8.48 (d, $J$ = 8.8 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 121.7, 124.4 (q, $J$ = 32 Hz), 127.5, 137.2 (q, $J$ = 3 Hz), 150.3 (q, $J$ = 260 Hz).

*Methyl-4-nitrobenzoate* (**9N**).[23] Light-yellow solid (158 mg, 87%), mp 90−91 °C (lit. 91−92 °C).[23] $R_f$ 0.54 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 3.99 (s, 3H), 8.24 (d, $J$ = 9.6 Hz, 2H), 8.28 (d, $J$ = 9.6 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 52.8, 123.4, 130.7, 135.5, 150.6, 165.0.

*3-Chloronitrobenzene* (**10N**).[24] Light-yellow solid (126 mg, 80%), mp 45−46 °C (lit. 46−47 °C).[24] $R_f$ 0.79 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.49−7.53 (m, 1H), 7.68 (d, $J$ = 8.4 Hz, 1H), 8.15 (d, $J$ = 8.4 Hz, 1H), 8.22 (s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 121.7, 123.8, 130.5, 134.7, 135.5, 148.9.

*2-Nitrobenzaldehyde* (**11N**).[25] Light-yellow solid (118 mg, 78%), mp 43 °C (lit. 42−44 °C).[25] $R_f$ 0.57 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.76−7.84 (m, 3H), 8.05−8.13 (m, 1H), 10.43 (s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 124.5, 129.7, 131.4, 133.8, 134.3, 149.6, 188.2.

*7-Nitro-1-tetralone* (**12N**).[26] Yellow solid (166 mg, 87%), mp 104−105 °C (lit. 103−104 °C).[26] $R_f$ 0.55 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 2.04−2.09 (m, 2H), 2.72−2.80 (m, 4H), 7.63 (d, $J$ = 8.8 Hz, 1H), 8.42 (d, $J$ = 8.8 Hz, 1H), 8.49 (s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 22.2, 29.7, 38.6, 122.5, 127.0, 130.2, 133.3, 147.2, 150.9, 195.9.

*2-Nitrobiphenyl* (**13N**).[27] Light-yellow solid (175 mg, 88%), mp 35−36 °C (lit. 36−37 °C).[27] $R_f$ 0.72 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.34−7.39 (m, 2H), 7.42−7.48 (m, 3H), 7.54 (dd, $J$ = 7.6, 1.2 Hz, 1H), 7.59−7.78 (m, 2H), 7.91 (dd, $J$ = 7.6, 1.2 Hz, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 125.8, 129.7, 130.1, 130.6, 133.7, 134.5, 137.6, 139.5, 151.4.

*4-Nitrodibenzo[b,d]furan* (**14N**).[28] Yellow solid (179 g, 84%), mp 137−138 °C (lit. 137−138 °C).[28] $R_f$ 0.67 in ethyl acetate−hexane (1:9). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.46−7.51 (m, 2H), 7.57 (t, $J$ = 7.4 Hz, 1H), 7.68−7.79 (m, 2H), 7.99 (d, $J$ = 7.2 Hz, 1H), 8.26 (d, $J$ = 7.2 Hz, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 112.4, 120.8, 122.2, 122.7, 122.9, 124.0, 126.9, 128.3, 128.9, 134.0, 148.5, 156.8.

*4-Nitro-9-fluorenone* (**15N**).[29] Lemon-yellow solid (187 mg, 83%), mp 174−175 °C (lit. 174−176 °C).[29] $R_f$ 0.57 in ethyl acetate−hexane (1:9). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.44−7.48 (m, 2H), 7.63 (d, $J$ = 7.6 Hz, 1H), 7.78 (d, $J$ = 8.4 Hz, 1H), 7.98 (d, $J$ = 7.4 Hz, 1H), 8.03 (m, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 124.9, 125.9, 128.6, 129.9, 130.3, 134.4, 135.7, 136.5, 137.2, 140.5, 145.0, 191.2.

*2-Nitroanthraquinone* (**16N**).[30] Yellow solid (218 mg, 86%), mp 186 °C (lit. 185−186 °C).[30] $R_f$ 0.47 in ethyl acetate−hexane (2:8). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.86−7.92 (m, 2H), 8.35−8.47 (m, 2H), 8.52 (d, $J$ = 8.4 Hz, 1H), 8.61 (m, 1H), 9.14 (d, $J$ = 8.4 Hz, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 121.2, 126.27, 126.31, 126.6, 127.8, 131.7, 131.8, 133.2, 133.6, 135.5, 149.8, 179.6, 180.1.

*3-Nitro-2,6-lutidine* (**17N**).[31] Brownish yellow solid (113 mg, 74%), mp 37 °C (lit. 38 °C).[31] $R_f$ 0.32 in ethyl acetate−hexane (2:8). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 2.61 (s, 3H), 2.86 (s, 3H), 7.16 (d, $J$ = 8.4 Hz, 1H), 8.20 (d, $J$ = 8.4 Hz, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 24.5, 24.9, 121.8, 133.5, 143.9, 154.1, 163.8.

*5-Nitroisoquinoline* (**18N**).[32] Yellow solid (138 mg, 79%), mp 108−109 °C (lit. 108−110 °C).[32] $R_f$ 0.30 in ethyl acetate−hexane (2:8). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.72−7.75 (m, 1H), 8.33 (d, $J$ = 8.0 Hz, 1H), 8.51 (d, $J$ = 8.0 Hz, 1H), 8.57 (d, $J$ = 8.0 Hz, 1H), 8.81 (d, $J$ = 8.4 Hz, 1H), 9.38 (s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 115.8, 126.0, 128.1, 128.6, 129.9, 135.0, 144.5, 146.5, 153.1.



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*5-Nitro-1,10-phenanthroline (**19N**).*[33] Light-yellow solid (183 mg, 81%), mp 199−201 °C (lit. 200 °C).[33] $R_f$ 0.16 in ethyl acetate−hexane (2:8). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.77−7.83 (m, 2H), 8.42 (d, $J$ = 8.4 Hz, 1H), 8.66 (s, 1H), 8.98 (d, $J$ = 8.4 Hz, 1H), 9.29 (d, $J$ = 4.8 Hz, 1H), 9.36 (d, $J$ = 4.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 120.7, 124.2, 124.3, 125.3, 125.4, 132.1, 137.8, 143.9, 145.9, 147.3, 151.4, 153.4.

*2,2′-Dinitrobiphenyl (**20N**).*[34] Brown solid (203 mg, 83%), mp 121−122 °C (lit. 120−122 °C).[34] $R_f$ 0.32 in ethyl acetate−hexane (1:9). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.29−7.34 (m, 2H), 7.58−7.68 (m, 4H), 8.18−8.23 (m, 2 H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 124.7, 129.1, 131.0, 133.4, 134.2, 147.2.

*1,8-Dinitronaphthalene (**21N**).*[35] Brown solid (177 mg, 81%), mp 169−171 °C (lit. 171−172 °C).[35] $R_f$ 0.33 in ethyl acetate−hexane (1:9). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.92−7.97 (m, 2H), 8.51 (d, $J$ = 8.4 Hz, 2H), 8.60 (d, $J$ = 8.4 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 115.1, 127.0, 127.4, 134.6, 134.8, 144.6.

*2,7-Dinitro-9-fluorenone (**22N**).*[36] Brown solid (232 mg, 86%), mp 295 °C (lit. 296 °C).[36] $R_f$ 0.48 in ethyl acetate−hexane (2:8). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 7.89 (d, $J$ = 8.0 Hz, 2H), 8.55−8.67 (m, 4H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 119.5, 124.7, 131.5, 136.0, 147.8, 150.1, 190.8.

*2-Methyl-2-nitropropane (**23N**).*[37] Light-yellow oil (82 mg, 79%). $R_f$ 0.94 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 1.62 (s, 9H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 27.9, 85.2.

*Nitrocyclohexane (**24N**).*[38] Light-yellow oil (106 mg, 82%). $R_f$ 0.91 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 1.09−2.46 (m, 10H), 4.37−4.42 (m, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 24.2, 24.8, 31.0, 84.7.

*1-Nitroadamantane (**25N**).*[39] Pale-yellow solid (143 mg, 79%), mp 158−159 °C (lit. 159 °C).[39] $R_f$ 0.89 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 1.64−1.67 (m, 6H), 2.15 (s, 6H), 2.18 (s, 3H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 29.7, 35.5, 40.8, 84.7.

*2-Methyl-2-nitrohexane (**26N**).*[40] Colorless oil (112 mg, 77%). $R_f$ 0.92 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 0.83 (t, 3H), 1.18−1.52 (m, 10H), 1.99−2.01 (m, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 13.8, 19.8, 23.2, 25.5, 41.9, 88.2.

*3-Nitropentane (**27N**).*[40] Pale-yellow oil (94 mg, 80%). $R_f$ 0.92 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 0.95 (t, $J$ = 7.2 Hz, 6H), 1.77−2.0 (m, 4H), 4.27−4.35 (m, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 10.3, 26.9, 91.9.

*Nitrocyclopentane (**28N**).*[41] Colorless oil (90 mg, 78%). $R_f$ 0.92 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 1.65−2.46 (m, 8H), 4.76−4.96 (m, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 24.7, 32.6, 87.0.

*2,3-Dimethyl-2,3-dinitrobutane (**29N**).*[42] Light-yellow solid (122 mg, 69%), mp 215 °C (lit. 214 °C).[42] $R_f$ 0.67 in ethyl acetate−hexane (0.5:9.5). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 2.76 (s, 12H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 23.6, 92.8.

*Fexinidazole (**30N**).*[43] Colorless solid (230 mg, 82%), mp 51−54 °C (lit. 50−54 °C).[43] $R_f$ 0.28 in ethyl acetate−hexane (2:8). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 2.42 (s, 3H), 3.91 (s, 3H), 5.28 (s, 2H), 7.01−7.09 (m, 2H), 7.21−7.30 (m, 2H), 8.07 (s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 27.7, 30.6, 56.9, 117.9, 129.8, 131.0, 131.3, 142.9, 157.8, 161.8.

*Nitazoxanide (**31N**).*[44] Light-yellow solid (218 mg, 71%), mp 200−202 °C (lit. 202 °C).[44] $R_f$ 0.19 in ethyl acetate−hexane (2:8). $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 2.29 (s, 3H), 7.24−7.31 (m, 1H), 7.37−7.46 (m, 1H), 7.60−7.68 (m, 1H), 7.81−7.86 (m, 1H), 8.56 (s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$ (ppm): 20.6, 123.2, 125.2, 125.6, 129.6, 133.2, 141.7, 142.2, 148.7, 161.9, 165.0, 168.6.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02133.

$^1$H and $^{13}$C spectra for all compounds prepared by the method described (PDF)

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### Notes

The authors declare no competing financial interest.

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