

Conversion of Aryl Azides to Aminopyridines

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ABSTRACT: A longstanding challenge in fundamental functional group interconversion has been the direct transformation of benzene into pyridine via nitrogen insertion and carbon deletion. Herein, we report a protocol for the transformation of aryl azides, easily accessible from their corresponding anilines, to 2-aminopyridines using blue light and oxygen. Mechanistic studies corroborate that the arene to pyridine conversion is achieved by nitrogen insertion into the benzene ring followed by oxidative carbon extrusion.

Functional group interconversions are fundamental to synthetic organic chemistry. Despite this, direct interconversion of numerous common motifs remains elusive. A prime example of this is the direct conversion of benzene into pyridine via carbon to nitrogen atom exchange (Figure 1A). Pyridine is the most common aromatic heterocycle and the second most common heterocycle found in FDA-approved drugs in the United States.¹ It is known as an important benzene isostere and used to modulate lipophilicity and improve aqueous solubility, metabolic stability, and hydrogen-bond capability, while still maintaining benzene-like characteristics such as planarity and π -stacking, attributes which saturated carbocyclic isosteres dramatically disrupt.^{2–5} Indeed, drug discovery programs routinely undergo systematic nitrogen atom scans (N-scans), wherein a CH unit in a lead compound is replaced with a nitrogen atom in an effort to improve molecular and physicochemical properties.^{2,3} This so-called “necessary nitrogen atom” effect has been shown to improve a variety of key pharmacological parameters including potency anywhere from 10- to 1000-fold (Figure 1B). However, current strategies for conducting N-scans rely upon the bottom-up resynthesis of lead compounds and their derivatives. In an ideal scenario, chemists would be able to directly exchange a CH group for a nitrogen atom in a single reaction without the need to develop completely new routes to a desired molecular target.

Reactions which modify the core of common molecular entities have garnered intense interest from chemists for over a century. The earliest examples of this class of reactions include well-known processes such as the Ciamician–Dennstedt rearrangement, the Beckmann rearrangement, and the Baeyer–Villiger oxidation. In recent years, exciting advances include Levin’s nitrogen⁶ and carbon deletion,⁷ and Sarpong’s photochemical ring contraction of saturated heterocycles.⁸ While ring expansions and contractions have been explored extensively, single atom exchange is considerably underdeveloped.^{9–14} Some have even deemed the ability to replace one atom in a ring system with another without changing the ring size “the ultimate goal of skeletal editing”.¹⁵ Notably, the conversion of benzene to pyridine has remained elusive despite being a notable problem in the collective consciousness of

synthetic chemists. Herein, we report a protocol for the conversion of aryl azides, easily accessible from their corresponding anilines without column chromatography, to aminopyridines (Figure 1C), common motifs in numerous pharmaceuticals (Figure 1D).^{16,17}

At the outset of this work, we were inspired by a 1972 report by Sundberg and co-workers, which carefully parsed out the product mixture that arose from the photolysis of alkyl- and aryl-substituted phenyl azides in diethylamine with a medium-pressure mercury lamp.¹⁸ These authors observed the formation of two 2-aminopyridine products in 2–20% and 1–8% yield in addition to two other major byproducts (Figure 2A). While these results are impressive, several problems exist with the Sundberg protocol. The nucleophile, diethylamine, is used in solvent quantities, and a medium-pressure mercury lamp is employed as the light source, limiting functional group tolerance. Moreover, the reaction is low-yielding and produces a mixture of several products, including two differentially substituted pyridines, which necessitated separation using preparative gas chromatography.

We sought to develop a protocol which addressed these issues and began by examining the photochemical reaction of aryl azide **1a** (Figure 2B). Under a variety of irradiation conditions in the presence of oxygen, small amounts ($\leq 9\%$) of 2-aminopyridine **3a** were observed, along with 3H-azepine **2a** as the major identifiable product. Hypothesizing that **2a** may be a key intermediate in this process, we initially explored this nitrogen insertion. While lower yields and product decomposition resulted from high-energy light sources (medium-pressure Hg lamp), we questioned whether a lower energy light source could be used.¹⁹ We found that irradiation of azide **1a** in the presence of acridine orange yielded azepine **2a** in high (80%) yield (Scheme 1A, entry 1). Unexpectedly, in the absence of the photosensitizer the ring expansion proceeded in

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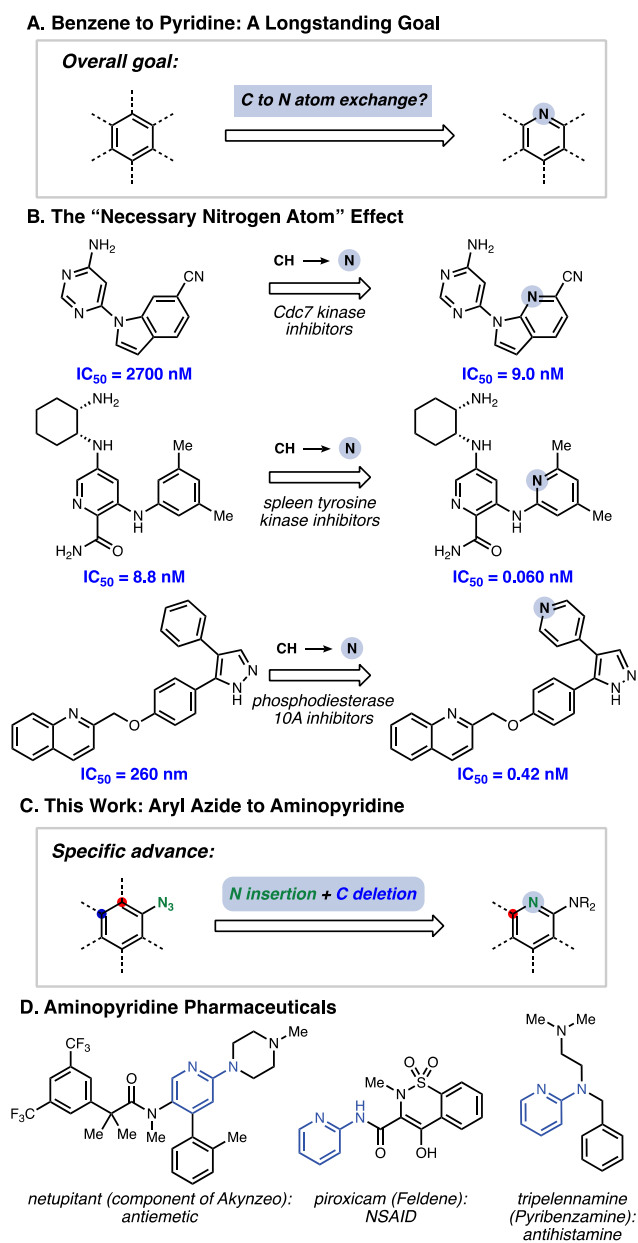
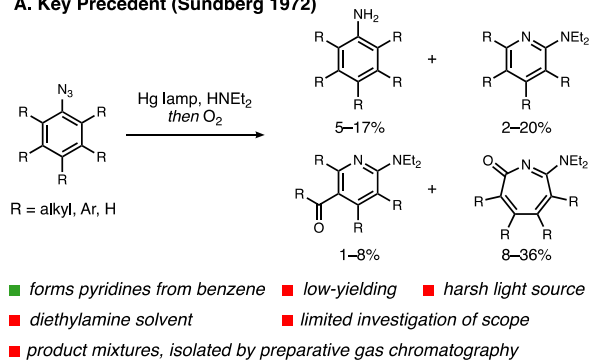


Figure 1. (A) A longstanding goal in molecular editing. (B) Examples of the “necessary nitrogen atom” effect. (C) This work. (D) Examples of aminopyridine pharmaceuticals.

an improved 92% yield (Scheme 1A, entry 2). In addition, we found that the amount of diethylamine could be reduced to near-stoichiometric amounts rather than solvent quantities, affording azepine **2a** in near quantitative yield (Scheme 1A, entry 3). Finally, performing the ring expansion under air in place of a nitrogen atmosphere improved the operational simplicity of the reaction without a significant impact on the yield (Scheme 1A, entry 4).

Next, we attempted to perform a ring contraction to convert 3H-azepine **2a** to a pyridine.²⁰ Sundberg proposed a mechanism whereby triplet oxygen promotes conversion of a 1H-azepine into an aminopyridine.^{18a} However, when we subjected azepine **2a** to triplet oxygen or a combination of triplet oxygen and a secondary oxidant, we observed no pyridine formation (Scheme 1B, entries 1 and 2). This led us

A. Key Precedent (Sundberg 1972)



B. Initial Observations

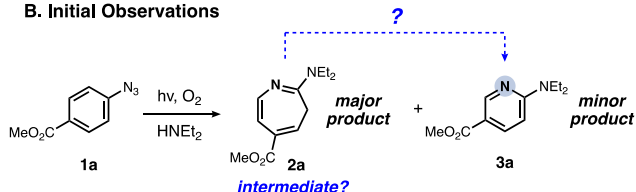


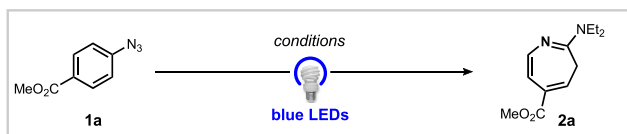
Figure 2. (A) Sundberg's precedent. (B) Our initial observations.

to examine the reaction of **2a** with singlet oxygen rather than its triplet counterpart. Gratifyingly, irradiation with red LEDs²¹ in the presence of oxygen and methylene blue as a photosensitizer provided 2-aminopyridine **3a** in 21% yield (Scheme 1B, entry 3). A control experiment irradiating azepine **2a** with blue light under an oxygen atmosphere in the absence of a photosensitizer afforded pyridine **3a** in an identical 21% yield (Scheme 1B, entry 4), possibly due to **2a** itself acting as a photosensitizer. A diminished yield was observed when air was used in place of an oxygen atmosphere (Scheme 1B, entry 5), and no product was formed when a nitrogen atmosphere was employed (Scheme 1B, entry 6). Many aromatic molecules are known to be singlet oxygen photosensitizers.²² After surveying a wide range of photosensitizers (selected examples: Scheme 1B, entries 7 and 8; see Figure S3 for full optimization), we found that acenaphthylene provided pyridine **3a** in 54% yield (Table 2, entry 9). While acenaphthylene is an unusual sensitizer for the generation of singlet oxygen,²³ this was confirmed in a control reaction with α -terpinene to form its endoperoxide adduct (see Figure S5). We determined that 1 atm of O₂ is optimal, as constant sparging led to overoxidation and formation of a pyridine N-oxide. We also examined several singlet oxygen chemical equivalents, none of which was superior to singlet oxygen itself (see Figure S6).

With the nitrogen insertion and carbon deletion steps optimized, we sought to combine them into a convenient one-pot protocol. First, the ring expansion was carried out in THF, then acenaphthylene was added, and the reaction mixture was sparged with oxygen and irradiated with blue light. To our dismay, this protocol yielded the desired pyridine in only 2% yield (Scheme 1C, entry 1). Repeating this protocol but using MeOH as the only solvent improved the yield to 22% (Scheme 1C, entry 2). However, conducting the ring expansion in THF, then performing a solvent swap to MeOH for the ring contraction afforded pyridine **3a** in 39% yield (Scheme 1C, entry 3). We observed a significant amount of intermediate azepine **2a** in the crude reaction mixture, so a second treatment of oxygen and acenaphthylene was performed, providing **3a** in 57% yield (Scheme 1C, entry 4). Finally, lowering the acenaphthylene loading from 50% to 10% had no

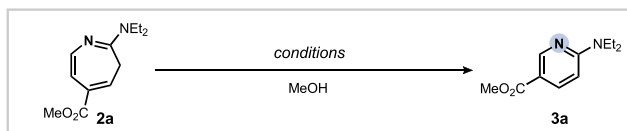
Scheme 1. Optimization

A. Nitrogen Insertion

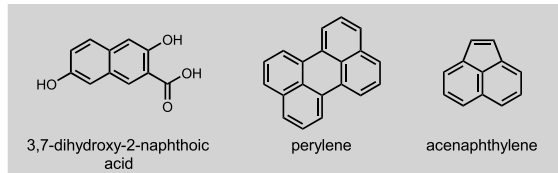


Entry	Conditions	Solvent	Atmosphere	Yield
1	acridine orange (20%)	MeOH/Et ₂ NH (9:1)	N ₂	80% ^a
2	—	MeOH/Et ₂ NH (9:1)	N ₂	92% ^a
3	Et ₂ NH (1.1 equiv)	THF	N ₂	>99% ^a
4	Et ₂ NH (1.1 equiv)	THF	air	90% ^b

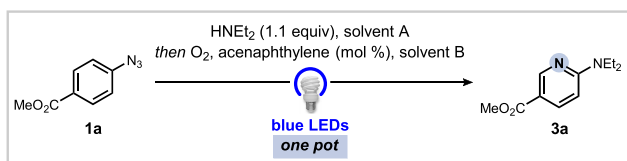
B. Carbon Deletion



Entry	Conditions	Yield ^a
1	O ₂ , 21–40 °C	NR
2	O ₂ , FeCl ₃ (1 equiv)	NR
3	O ₂ , methylene blue (0.1%)	21% ^c
4	O ₂	21%
5	air	7% ^c
6	N ₂	0%
7	O ₂ , 3,7-dihydroxy-2-naphthoic acid (10%)	44%
8	O ₂ , perylene (10%)	44%
9	O ₂ , acenaphthylene (10%)	54%



C. One-Pot Protocol



Nitrogen Insertion		Carbon Deletion		Yield ^a
Entry	Solvent A	Solvent B	Acenaphthylene (mol %)	
1	THF	THF	50%	2%
2	MeOH	MeOH	50%	22%
3	THF	MeOH	50%	39%
4	THF	MeOH	50% x2	57%
5	THF	MeOH	10% x2	57%
6	MeOH	MeOH	10% x2	39%

^aYield determined by ¹H NMR using 1,4-dinitrobenzene as an internal standard. ^bIsolated yield. ^cYield based on recovered starting material.

observable effect on the overall yield, (Scheme 1C, entry 5). In lieu of a solvent swap, the entire reaction sequence can be run in MeOH, but the yield is slightly diminished, producing 3a in 39% yield (Scheme 1C, entry 6). Attempts to treat 1a with

diethylamine, oxygen, acenaphthylene, and blue light simultaneously were unsuccessful, furnishing 2a as the major product.

Next, we examined the scope of *para*-substituted azides (Scheme 2A). Various electron-withdrawing groups perform well, including esters (3a), amides (3c,d), nitrile (3e), and pyridine (3f). In examining the scope of the nucleophile, we found that volatile secondary (3g–k) and primary (3l) amines still afforded aminopyridines in good yields. While nonvolatile amines did afford aminopyridines in a one-pot protocol, the yields were significantly diminished, and we opted for a two-step protocol involving isolation of the intermediate azepine in such cases (3m–q). Finally, we derivatized benzocaine, a local anesthetic, to yield pyridine 3b. Alcohols were competent nucleophiles in the nitrogen insertion step, but the resulting azepines were unreactive to our carbon deletion conditions.

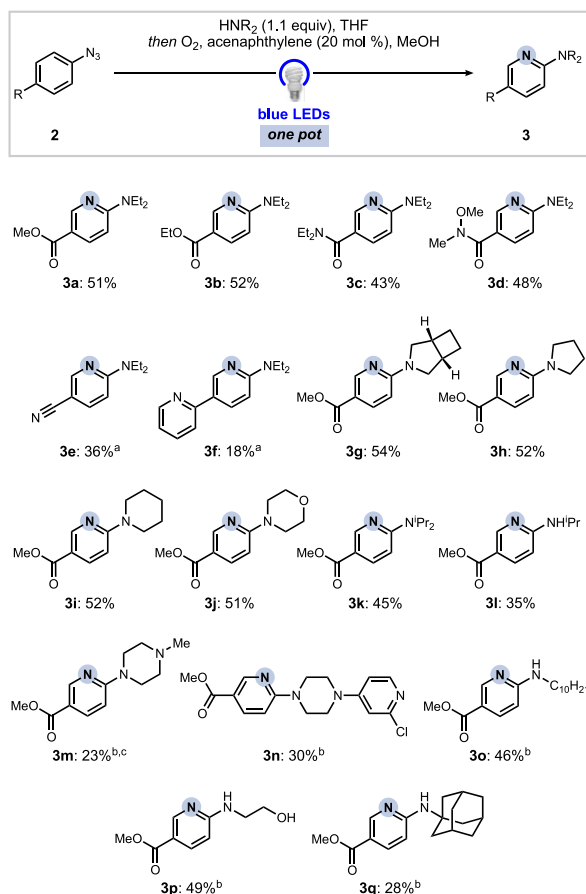
Several differentially substituted azides gave rise to interesting pyridine products, some of which were highly informative for the mechanism discussed below (Scheme 2B). Azides 4a–c all formed formyl-substituted pyridine 5a, with the methyl amide 4c affording the highest yield (Scheme 2B, entry 1). *Meta,para*-disubstituted azide 4d produced a mixture of 3a and 5b, with the former being the major product (Scheme 2B, entry 2). In contrast, *meta*-disubstituted azide 4e selectively formed 5b in 59% yield (Scheme 2B, entry 3). *Ortho,para*-disubstituted azide 4f was converted to pyridine 5c in 19% yield (Scheme 2B, entry 4), and *ortho*-substituted azides 4g and 4h yielded trisubstituted pyridines 5d and 5e, respectively (Scheme 2B, entries 5 and 6). Neutral, electron-rich, and other substitution patterns have thus far been unsuccessful (see Figure S1).

While a likely mechanism for converting aryl azides into 3H-azepines has been established,²⁴ the oxidative carbon deletion remained less clear. Toward this goal, we first aimed to determine which carbon is lost from the aryl azide and intermediate azepine. Based on the pyridine product regiochemistry, we inferred that a carbon *meta* or *ortho* to the azide-substituted carbon is extruded from the arene. To interrogate the *ortho* carbons, we synthesized 77% 2,6-*d*₂-labeled aryl azide 6 (Scheme 3A). Upon exposing this substrate to our standard conditions, we found that C6 (pyridine numbering) on the resulting pyridine 8 was 74% deuterated, while C3 was 52% deuterated. As 3H-azepine 7 is a known intermediate that has undergone protonation at C3 (azepine numbering), it follows that the resulting pyridine 8 would not retain full deuteration at this carbon. Since both positions remained deuterated, we ruled out the *ortho* carbons being deleted from 6.

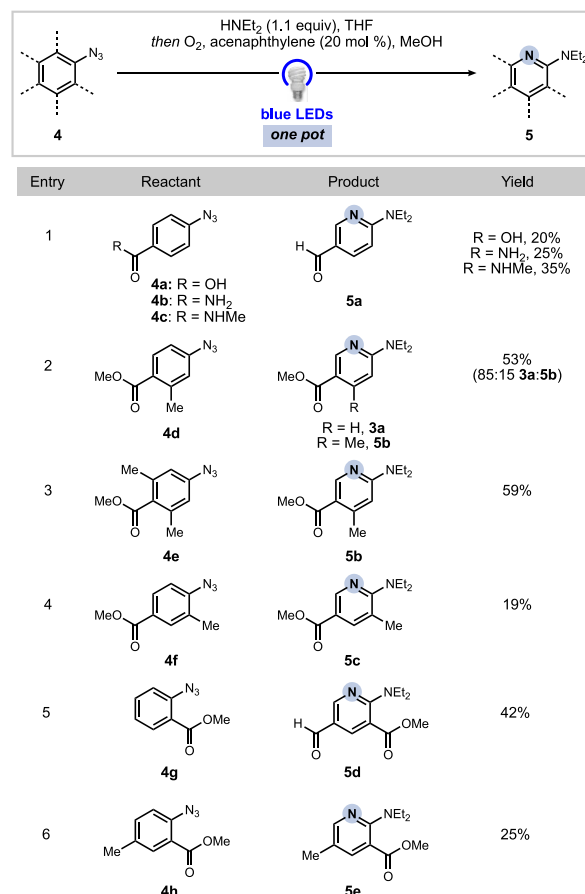
The fidelity of carbons *meta* to the azide was questioned with 4d, which gave rise to a product mixture consisting of both desmethylpyridine 3a and methylpyridine 5b (Scheme 3A). From these results, along with the conversion of 4e to 5b (Scheme 2B, entry 4), we concluded that a *meta* carbon is lost in the second stage.

Regarding the identity of the carbon-containing byproduct, when the carbon deletion protocol was performed on 3H-azepine 2a in methanol-*d*₄, methyl formate-*d*₃ (10-*d*₃) was observed in the crude reaction mixture (Scheme 3B). From this result, we surmised that the deleted carbon is oxidized and then excised as a formyl unit and envisioned that an aldehyde intermediate is likely present along the reaction pathway. One possibility is the presence of a dearomatized Wheland intermediate of general structure 9 that could release methyl formate through an aromatizing addition–elimination reaction.

Scheme 2. Substrate Scope

A. Reaction Scope for *para*-Substituted Azides

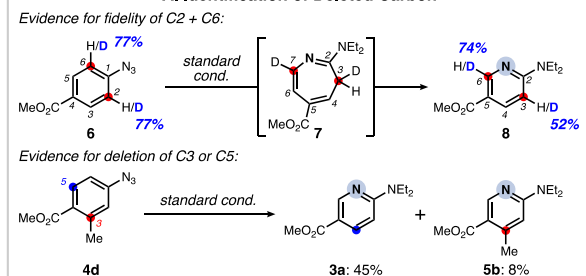
B. Reaction Scope for Variably Functionalized Azides



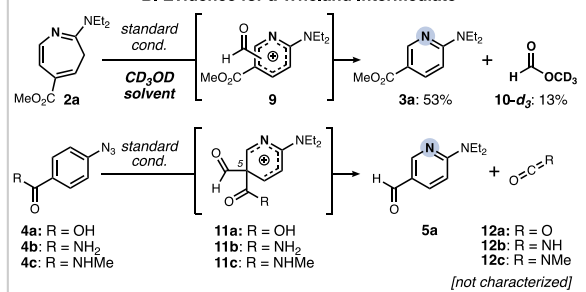
^a30% acenaphthylene added in three portions. ^bReactions utilizing nonvolatile amines were conducted in two steps with isolation of the intermediate azepine. ^cYield based on recovered starting material.

Scheme 3. Mechanistic Investigations

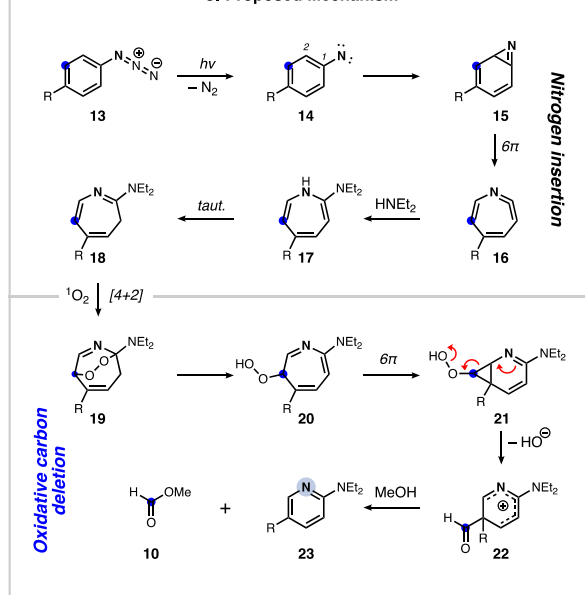
A. Identification of Deleted Carbon



B. Evidence for a Wheland Intermediate



C. Proposed Mechanism



Additionally, benzoic acid **4a**, benzamide **4b**, and methyl benzamide **4c** all yielded the same formyl-substituted pyridine **5a** (Scheme 3B). In these cases, we imagine the loss of carbon dioxide, isocyanic acid, and isocyanatomethane (**12a–c**) acting as carbon deletion sinks, via specific Wheland intermediates **11a–c**. *Para*-unsubstituted substrate **4g** does not undergo loss of a formyl unit, likely due to its Wheland intermediate aromatizing via simple deprotonation (Scheme 2B, entry 5).

With these indications in hand, we propose the following mechanism (Scheme 3C). Upon irradiation with blue light, azide **13** generates nitrene **14** which inserts into the C1–C2 arene π -bond to yield a strained 2*H*-azirine **15**.²⁴ This species can then undergo a thermal 6π electrocyclic opening to electrophilic ketenimine **16**, which reacts with the amine nucleophile to give 1*H*-azepine **17** and then observable 3*H*-azepine **18** after subsequent tautomerization.

For the carbon deletion stage, initial oxidation with singlet oxygen could occur through a variety of mechanisms, one possibility being a [4+2] cycloaddition to endoperoxide **19** followed by ring opening to peroxide-substituted azepine **20**. Another 6π electrocyclization would give cyclopropyl-fused dihydropyridine **21**. Concomitant cyclopropane opening and loss of hydroxide would lead to Wheland intermediate **22**, which upon methanol-mediated deformylation would yield the final 2-aminopyridine **23** and methyl formate **10**.

In summary, based on precedent from Sundberg, we have developed a mild and simple one-pot protocol to convert aryl azides to aminopyridines. This disruptive transformation should prove useful in the synthesis and derivatization of medicinally relevant compounds. While the aforementioned protocol has its limitations, we foresee the disclosure of this strategy prompting exciting progress in molecular editing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c08464>.

Supplementary Figures S1–S9, experimental procedures, characterization data, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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