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Trifluoroacetic acid-mediated selective oxidation of arylamines to nitroarenes *via in situ* formed peroxytrifluoroacetic acid

Shiyun Li,^{†*} Lulu Wang,^{†^a} Jianyin Hu,^a Yan An,^a Jun Huang,^b Bin Wen,^b Yuanqing Dong,^{*^a} Tiesen Li^{†^a} and Xingquan Chen^b

The importance of selectively oxidizing an amine into a value-added nitro compound is well-recognized in organic synthesis. However, the lack of control over selectivity and the complex synthesis of costly catalysts significantly hinder the industrial application of these reactions. In this work, an environmentally friendly approach was developed for the selective oxidization of arylamines to nitroarenes. This method used 30% peroxide as the oxidant and trifluoroacetic acid (TFA) as both the solvent and reactant and *in situ* formed peroxytrifluoroacetic acid without the addition of any metals or additives. This reaction exhibited excellent oxidative selectivity and a broad substrate scope. Various electron-rich and/or electron-deficient arylamines, diamino aromatics and drug molecules were selectively and effectively oxidized to the corresponding nitro compounds in high yields (up to 100%). Mechanism studies show that the reaction proceeds *via* a nitrosobenzene intermediate pathway.

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Introduction

Nitroarenes are valuable organic compounds with various practical applications, including in pharmaceuticals, agrochemicals, explosives, and other functional materials.¹ The nitro group is considered as one of the most versatile functional groups for transformation, making nitroarenes vital precursors to a wide variety of chemicals, including amides, anilines, azoxyaromatics and heterocycles.² Nitro derivatives also hold particular importance in developing mechanistic concepts.³ The “classical” route to access nitroarenes usually involves direct electrophilic nitration of aromatic derivatives under harsh reaction conditions. However, this method faces significant challenges due to limited functional group tolerance and inadequate regioselectivity, marking its major limitations.⁴ Consequently, a broad range of alternative nitration reagents and methodologies—including transition-metal-catalyzed ipso-nitration methodologies—have emerged as powerful tools for the synthesis of nitroarenes.⁵ Moreover, the direct oxidation of readily available and cheap anilines solves the issues related to regioselectivity and provides an attractive, alternative, and fascinating route for the synthesis of nitro derivatives.⁶ The oxidation process involves the sequential oxidation of aniline, phenylhydroxylamine and nitrosobenzene. Meanwhile, phenylhydroxylamine and nitrosobenzene can condense rapidly

to form azoxybenzene, aniline and nitrosobenzene *via* the Mills reaction to form azobenzene (Scheme 1a).

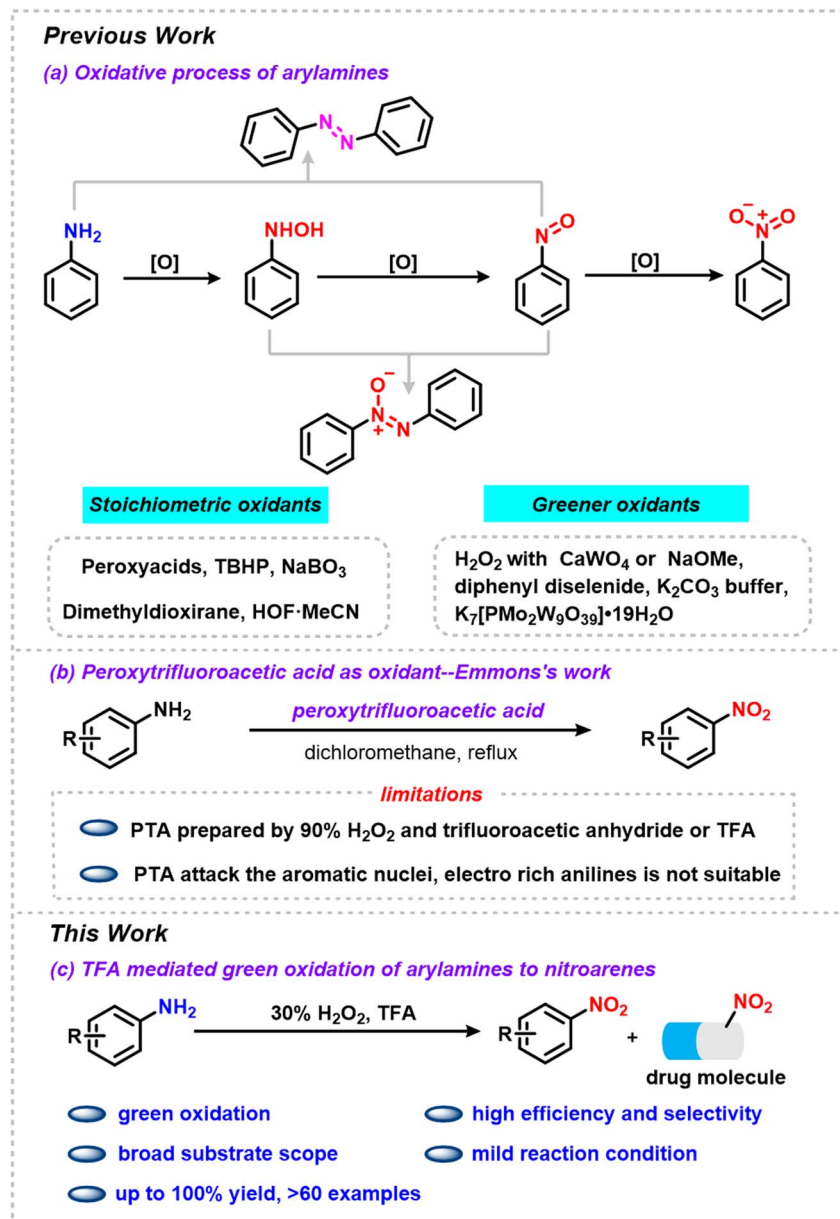
Various oxidizing agents have been utilized for this transformation, including performic acid, peracetic acid, peroxytrifluoroacetic acid (PTA), *m*-CPBA, TBHP with KI, HOF-CAN, nonanebis, sodium perborate, and dimethyldioxirane.⁷ However, the majority of the documented approaches exhibit limitations, including unregulated oxidation, reliance on harsh reaction conditions, low yields, extended reaction durations, and poor selectivity. Employing H₂O₂ as an oxidative agent has been acknowledged for its cost-effectiveness and eco-friendly nature, generating only water as the byproduct.⁸ However, due to the relatively weak oxidizing attributes of H₂O₂, it necessitates combining with a catalyst or reagent to induce oxidation by activating reactive intermediates. Numerous reagent combinations with H₂O₂ can be employed to achieve the transformation (Scheme 1b), such as with CaWO₄, heteropolyanions, diphenyl diselenide, and K₂CO₃ buffer.⁹ However, these systems offer unpredictable selectivity, leading to azoxybenzene being the primary by-product. Therefore, the development of a mild, effective and selective oxidation protocol in this field is highly desirable.

Our group is dedicated to developing a sustainable and green oxidation method for amines by utilizing dioxygen or hydrogen peroxide as a green oxidant.¹⁰ Interestingly, in our previous work on the oxidation of anilines, we found that the alkalinity strength of the base could modify the selectivity; a mild base (NaF) facilitated azoxybenzene formation, while a stronger base (NaOMe) enabled the synthesis of nitroarenes.¹¹ Moreover, we developed a safe and highly efficient method for

^aCollege of Chemical Engineering, Fuzhou University, Fuzhou 350108, China. E-mail: 1372814708@qq.com; 1347889486@qq.com; litiesen@fzu.edu.cn

^bQingyuan Innovation Laboratory, Quanzhou, 362801, China

[†] These authors contributed equally to this work.

Scheme 1 Synthetic approaches of aniline oxidation to nitro compounds.

the dinitration of various aromatics, using KNO₃ as the nitrating agent and polyphosphoric acid as the solvent and catalyst.¹² During the continuous research on the oxidation of aniline, we turned our attention to acid-catalyzed oxidation and found that in the presence of trifluoroacetic acid, aniline can be selectively oxidized to nitrobenzene. In 1954, Emmons reported the oxidation of anilines to nitrobenzenes by using PTA as the oxidant.⁷ PTA was prepared by 90% H₂O₂ and trifluoroacetic anhydride or trifluoroacetic acid. It is worth mentioning that 30% hydrogen peroxide is not a suitable reagent for this oxidation reaction under their conditions. However, a more serious limitation to the use of PTA in the synthesis of nitroarenes is that it has a very high order of reactivity toward aromatic nuclei. Therefore, some electro-rich anilines are not suitable for this transformation. Interestingly, in this work, to

adjust the amounts of trifluoroacetic acid, the anilines bearing an electron-withdrawing group and/or electron-donating group all could be selectively oxidized to nitroarenes by using 30% H₂O₂ as an oxidant. This research provides a practical and alternative approach for selectively oxidizing arylamines to nitroarenes Scheme 1.

Results and discussion

Initially, 2-chloroaniline (**1a**) was utilized as a model substrate along with various acids at 40 °C, using MeCN as the solvent and 30% H₂O₂ as the green oxidant. Encouragingly, in a preliminary experiment using TFA as the acid, it was found that the nitro product (**2a**) and azoxyarene (**3a**) were obtained with the yields of 32% and 33%, respectively (Table 1, entry 1).

Table 1 Optimization of the reaction conditions^a

Reaction scheme: 2-chloroaniline (**1a**) reacts with Acid, H₂O₂ in Solvent at 40 °C, 4 h to produce 2-chloro-1-nitrobenzene (**2a**), 2-chloro-1-azoxybenzene (**3a**), and 2-chloro-1-azobenzene (**4a**).

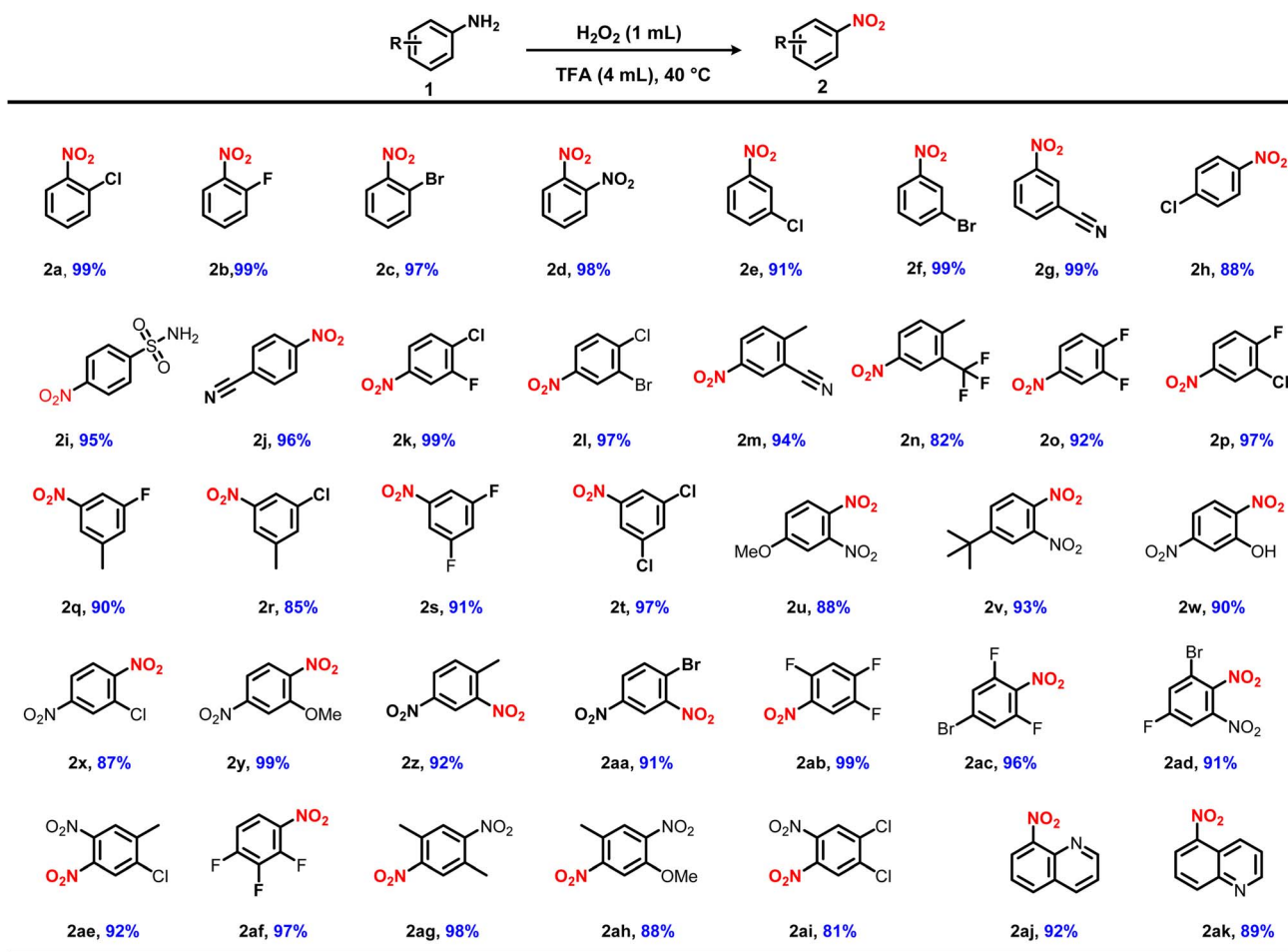
Entry	Acid	MeCN (mL)	H ₂ O ₂ (eq.)	Conv. (%) ^b	Yield 2a ^b (%)	Yield 3a ^b (%)	Yield 4a ^b (%)
1	TFA	4	10	65	32	33	0
2	HOAc	4	10	30	0	18	12
3	TfOH	4	10	10	5	0	5
4	FA	4	10	60	9	11	40
5	PFA	4	10	12	2	0	10
6	TFA ^c	4	10	90	62	28	0
7	TFA ^d	4	10	99	83	13	3
8	TFA ^e	4	10	100	91	5	4
9	TFA ^e	—	10	100	100	0	0
10	—	4	10	2	0	2	0
11	TFA ^e	—	2	26	26	0	0
12	TFA ^e	—	4	67	67	0	0
13	TFA ^e	—	6	84	84	0	0
14	TFA ^e	—	8	91	91	0	0
15	TFA ^e	—	20	100	100	0	0
16	TFA ^{e,f}	—	10	100	100	0	0
17	TFA ^{e,g}	—	10	86	70	0	16

^a Reaction conditions: **1a** (1 mmol) in solvent (4 mL), acid (1 mL), and 30% H₂O₂ (10 equiv.) were added consecutively. The reaction mixture was left for stirring at 40 °C for 4 h. ^b Conversion rate and yield was determined by GC. ^c TFA (2 mL). ^d TFA (3 mL). ^e TFA (4 mL). ^f 60 °C. ^g Room temperature.

Other acids such as acetic acid (HOAc), trifluoromethanesulfonic acid (TfOH), formic acid (FA) and perfluoropropionic acid (PFA) had little nitro product (Table 1, entries 2–5), but the azoxy (**3a**) and azo (**4a**) compounds were the main products. To enhance the selectivity and yield of the nitro product, an investigation was conducted into the amount of TFA. Interestingly, an increase in both the reaction's conversion and the yield of nitro compound (**2a**) was observed as the amount of TFA was increased (Table 1, entries 6–8). Fortunately, when TFA (4 mL) was used as the solvent, **1a** smoothly reacted with H₂O₂, yielding the nitro product (**2a**) in high yields, reaching up to 100% with exceptional selectivity (Table 1, entry 9). However, when trifluoroacetic acid was absent in the reaction system, the azoxy compound (**3a**) was the main product (Table 1, entry 10). Subsequent reactions investigated the impact of the H₂O₂ quantity, where a gradual increase in both yield and selectivity of the nitro compound (**2a**) was observed upon increasing H₂O₂ from 2 to 10 equivalents, producing yields from 26% to 100% (Table 1, entries 11–15). Increasing the amount of H₂O₂ to 20 equivalents can reduce the reaction time to 0.5 h without affecting the yield. Furthermore, the influence of temperature was investigated at 60 °C and room temperature instead of 40 °C. As a result, the reaction provided **2a** with 100% yields at 60 °C. Meanwhile, at room temperature, there was a decreased yield (70%) and selectivity. This suggested that 40 °C is the optimal temperature for this reaction (Table 1, entries 16–17).

Having established the optimal reaction conditions for facilitating the aniline selective oxidation to nitroarene, the versatility and scope of this methodology were assessed. Like the model reaction (**2a**), substrates bearing an electron-withdrawing group (fluoro-, chloro-, bromo-, cyano-, sulfonamide-) at the *ortho*-, *meta*- or *para*-position exhibited excellent functional group tolerance, resulting in the formation of the corresponding nitroarenes **2b–2i** in excellent yields (>90%). Interestingly, the steric hindrance effect has almost no influence on the reaction, regardless of whether the substituents are in the *ortho*-, *meta* or *para* position. For example, *o*-chloroaniline (**1a**), *m*-chloroaniline (**1e**) and *p*-chloroaniline (**1h**) underwent smooth reactions to give the corresponding nitro products in 88–99% yields. Anilines with two functional groups (including at least one electron-withdrawing group) also reacted well, yielding the nitroarenes in 82–99% yields (**2k–2aa**). For example, the 3,4-disubstituted nitroarenes, such as 1-chloro-2-fluoro-4-nitrobenzene (**2k**), 2-bromo-1-chloro-4-nitrobenzene (**2l**), and 2-methyl-5-nitrobenzonitrile (**2m**); the 3,5-disubstituted nitroarenes like 1-fluoro-3-methyl-5-nitrobenzene (**2q**), 1,3-difluoro-5-nitrobenzene (**2s**), and 1,3-dichloro-5-nitrobenzene (**2t**); the 2,4-disubstituted nitroarenes, including 4-methoxy-1,2-dinitrobenzene (**2u**) and 2,5-dinitrophenol (**2w**); and the 2,5-disubstituted nitroarenes such as 1-methyl-2,4-dinitrobenzene (**2z**) and 1-bromo-2,4-dinitrobenzene (**2aa**), were obtained in high yield. Furthermore, substrates with multiple substituents (at least one electron-withdrawing group) were amenable to oxidation, yielding the desired nitroarenes in





Scheme 2 Substrate scope of arylamines containing at least one electron-withdrawing group^a. Reaction condition A: 1 (1 mmol), TFA (4 mL), 30% H_2O_2 (10 mmol, 1 mL), 40°C , 4–10 h, isolated yield.

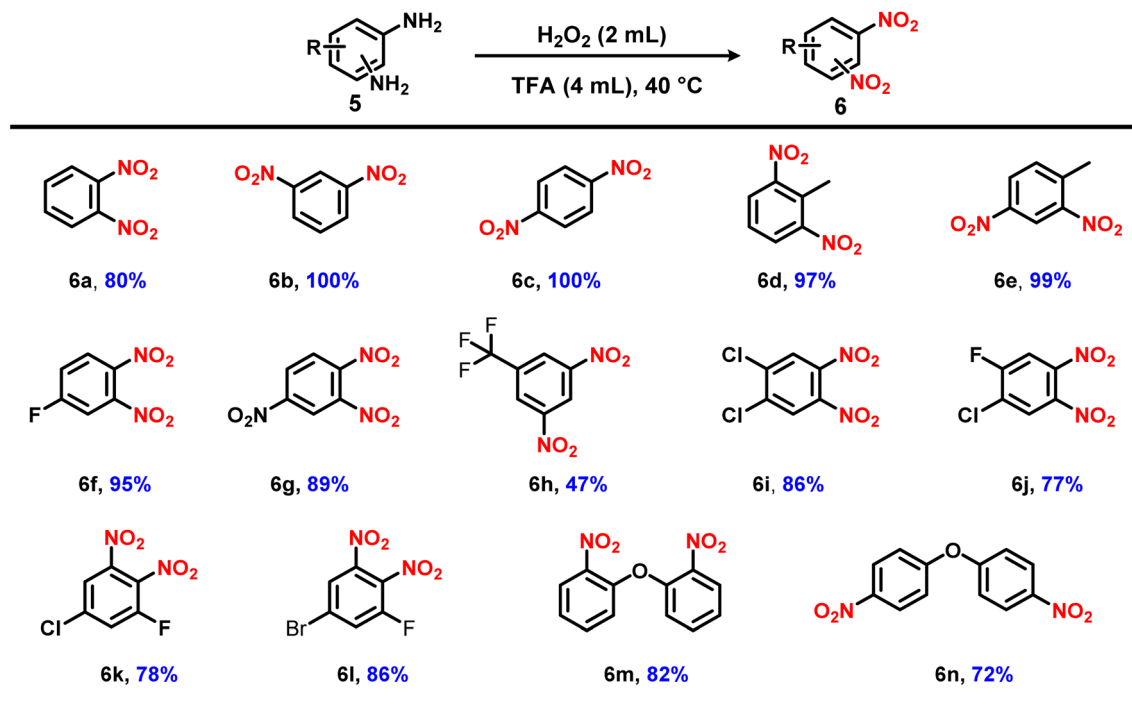
excellent yields (2ab–2ai, 81–99%). It is worth mentioning that the polyfluorinated nitroarenes (2o, 2s, 2ab, 2af) and dinitroarenes (2u–2aa, 2ad, 2ag–2ai) were also suitable for the transformation. A heterocycle nitroarene such as 8-nitroquinoline (2aj) and 5-nitroquinoline (2ak) was also obtained *via* this method in 89–92% yields. However, the reaction condition A was not appropriate for amines substituted by all electron-donating groups Scheme 2.

Next, we tried to oxidize diamino arenes to dinitroarenes. The diamino arenes at the *ortho*-, *meta*- or *para*-position exhibited excellent functional group tolerance, resulting in the formation of the corresponding dinitrobenzenes 6a–6c in moderate to excellent yields (>80%). Diamino arenes containing electron-donating groups and electron-withdrawing groups were well accommodated, yielding the respective dinitroarenes in good yields (6d–6h). The explosive 1,2,4-trinitrobenzene (6g) could also be obtained in 89% yield. The oxidation of multi-substituted diamino arenes had also been investigated. Various substituent positioned at diverse sites on the aromatic ring were employed, resulting in the formation of the respective multi-substituted dinitroarenes with moderate to high yields (6i–6l) Scheme 3. The diamino group on different benzene rings

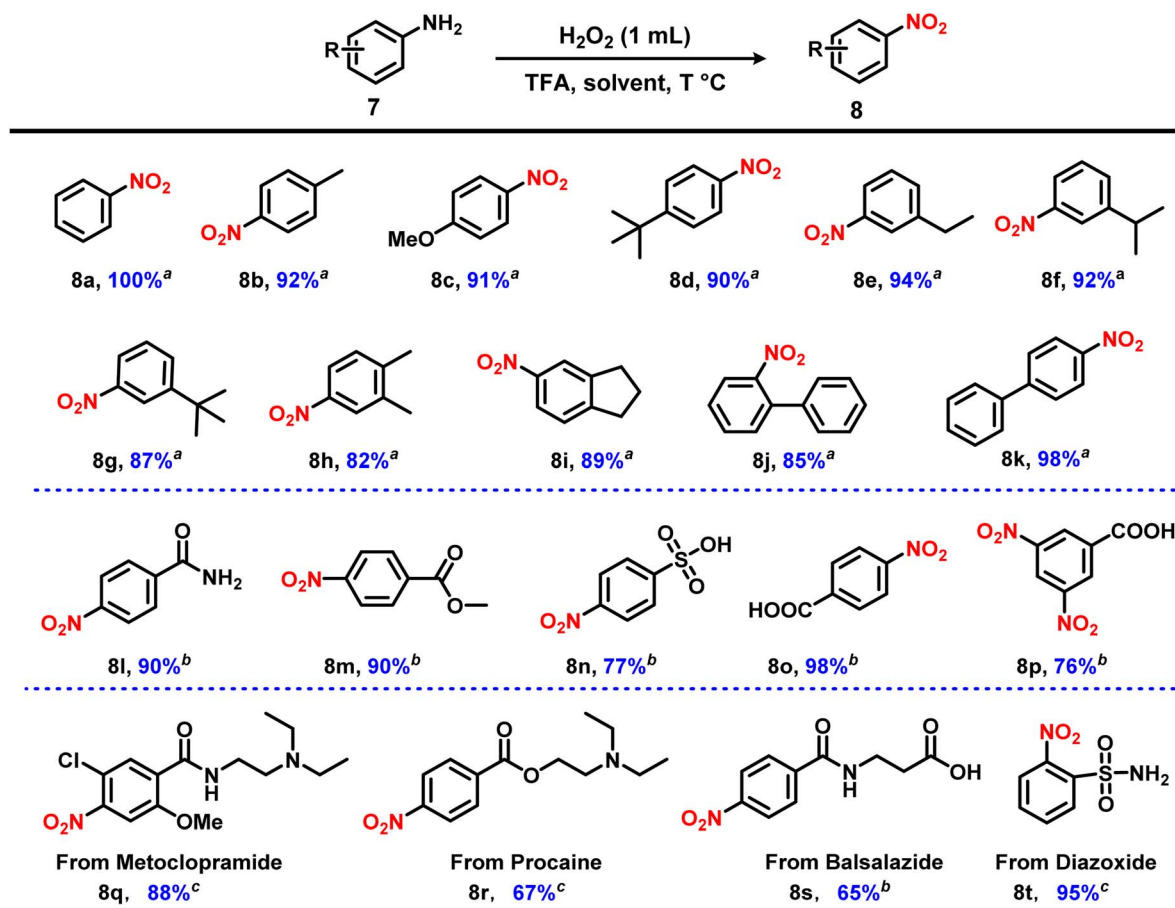
also reacted well to afford the corresponding dinitroarenes in 72–82% yields (6m–6n).

To further enhance the functional group compatibility of the aniline oxidative reaction, we turned our attention to the electron-donating group substituted aniline. After a simple condition screening (Table S1, details see in the SI), the reaction condition B was used. A 100% isolated yield of nitrobenzene 8a was achieved using aniline (7a) as the model substrate. Anilines containing electron-donating groups such as methyl-, methoxy-, ethyl-, isopropyl-, and *tert*-butyl were well accommodated, producing the corresponding nitroaromatics in high yields (8b–8g). Anilines bearing two electron-donating groups were also suitable for these conditions (8h). Additionally, 5-nitro-2,3-dihydro-1*H*-indene (8i), 2-nitro-1,1'-biphenyl (8j), and 4-nitro-1,1'-biphenyl (8k) were obtained in this protocol.

Unfortunately, the anilines containing amide, carboxyl, or sulfonic acid groups were not suitable for conditions A and B. When the amount of TFA was reduced to 2 equivalents, these functional groups exhibited good compatibility and were successfully converted into the corresponding nitroarenes in 76–98% yield (8l–8p).



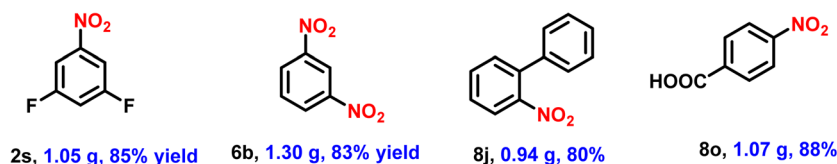
Scheme 3 Substrate scope of diamino arenes^a. Reaction condition A: 5 (1 mmol), TFA (4 mL), 30% H₂O₂ (20 mmol, 2 mL), 40 °C, 4–10 h, isolated yield.



Scheme 4 Substrate scope of electron-enriching anilines, acyl-substituted anilines and drug molecules.^a Reaction condition B: aniline (1 mmol), TFA (1 mL), H₂O₂ (10 mmol, 1 mL), DCE (4 mL), 80 °C, 4–10 h, isolated yield. ^b Reaction condition C: aniline (1 mmol), TFA (2 eq.), H₂O₂ (10 mmol, 1 mL), DCE (4 mL), 80 °C, 10 h, isolated yield. ^c Reaction condition A: aniline (1 mmol), TFA (4 mL), H₂O₂ (10 mmol, 1 mL), 40 °C, 4–10 h, isolated yield.

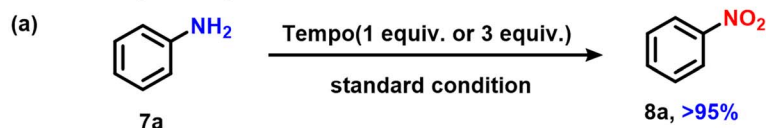


Gram-scale synthesis

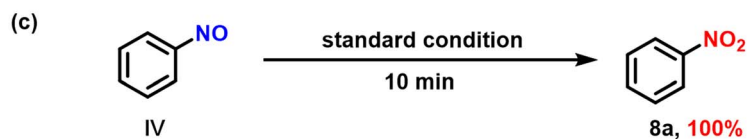


Scheme 5 Gram-scale experiment.

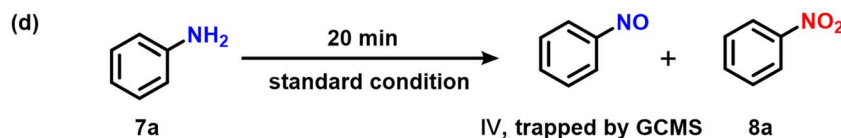
1. Radical capture experiment



2. Control experiment



3. Intermediate trapping experiment



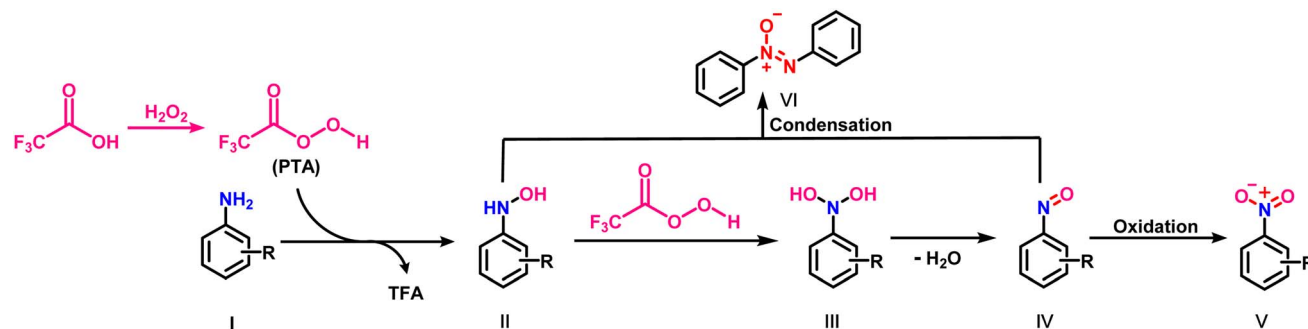
Scheme 6 Mechanistic studies.

Inspired by the interesting biological profile of the nitrated compounds,¹³ we next explored the potential of this methodology for late-stage modifications of the drug molecules or intermediates. Metoclopramide (7q) is an effective and orally active 5-HT₃ and dopamine D₂ receptor antagonist, which can be easily oxidized into a nitro compound (8q). Similarly, the DNA-demethylating agent procaine was oxidized into the nitro compound (8r) in 67% yield. Additionally, the key drug intermediate *N*-(4-aminobenzoyl)- β -alanine from balsalazide and 2-aminobenzenesulfonamide from diazoxide were well tolerated. The nitro products (8s, 8t) were obtained in 67% and 95% yields, respectively Scheme 4.

Next, we tried to explore the synthetic utility of the trifluoroacetic acid-mediated oxidation of amines to nitro compounds. Gram-scale reactions of 1s (1 g, 7.75 mmol) and 5b (1 g, 9.25 mmol) were separately carried out under condition A, successfully yielding the corresponding nitroarenes (2s and 6b) in 85% and 83% yield, respectively. Similarly, 2-nitro-1,1'-biphenyl (8j) and 4-nitrobenzoic acid (8o) were obtained on

a gram scale under condition B and condition C, respectively Scheme 5.

Two established mechanisms are believed to govern the oxidation of anilines: the nitrosobenzene intermediate mechanism and the aniline radical mechanism.¹⁴ To investigate the mechanism of this conversion, radical trapping experiments were initially conducted. When the radical trapping agent 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was added to the reaction system, the yields of nitrobenzene (8a) exhibited no noticeable change (Scheme 6a). This result confirmed that the reaction is unlikely to proceed through a radical process. Under the optimal reaction conditions, the reactions of 7a with H₂O₂ did not produce nitrobenzene in the absence of TFA. Instead, the azoxybenzene was obtained as the major product (Scheme 6b). In addition, an oxidation experiment of nitrosobenzene was conducted, revealing that nitrosobenzene can be rapidly oxidized into nitrobenzene under TFA conditions (Scheme 6c). An intermediate trapping experiment was conducted and the nitrosobenzene (IV) intermediate was detected by GCMS



Scheme 7 Proposed mechanism.

(Scheme 6d). This result indicated that the reaction proceeded *via* the nitrosobenzene intermediate mechanism.

Therefore, on the basis of the above studies and previous reports, a plausible mechanism for the TFA-mediated selective oxidation of aniline to nitrobenzene is illustrated in Scheme 7 [7a]. The addition of H_2O_2 to trifluoroacetic acid leads to the *in situ* formation of peroxytrifluoroacetic acid (PTA). PTA oxidizes the nitrogen atom of aniline (I) in a sequential manner to form phenylhydroxylamine (II) and *N*-hydroxy-*N*-phenylhydroxylamine (III). Subsequently, III rapidly eliminates one water molecule to generate the nitrosobenzene intermediate (IV).¹⁵ The nitrosobenzene intermediate (IV) is rapidly oxidized by PTA to yield nitrobenzene (V). Notably, phenylhydroxylamine (II) and nitrosobenzene intermediate (IV) can condense to form azoxybenzene (VI).

Conclusions

In conclusion, a mild, highly efficient, and selective protocol has been developed for oxidizing arylamines into nitroarenes. This process involves utilizing the eco-friendly 30% H_2O_2 as the oxidant and trifluoroacetic acid as both the solvent and reactant, leading to the *in situ* formation of peroxytrifluoroacetic acid without the addition of any metals or additives. The optimized protocol was also applied for the selective oxidation of various substituted aromatic amines, where the electron-rich and/or electron-deficient aromatic amines, diamino aromatics and drug molecules were selectively and effectively oxidized to the corresponding nitro compounds in high yields (up to 100%). This modified protocol would be beneficial for many organic oxidative transformations.

Author contributions

S. L.-Methodology; S. L., Y. D., T. L. and X. C conceived the project; S. L. and L. W performed the experiments; Y. A., J. Y. and J. H. analysed the data; S. L. wrote the manuscript; S. L., T. L. and B. W revised the manuscript. S. L. and L. W. contributed equally to this work.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supporting information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5ra06600j>.

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