有机化学 DOI: 10.6023/cjoc202302008 研究论文
Chinese Journal of Organic Chemistry ARTICLE

水相中抗坏血酸钠促进铁催化合成含硫芳香伯胺化合物

陈乡萍[a] 孟晨湘[b] 李梦娜[b] 楚尚敏[b] 朱欣欣[b] 许 凯*,[b]
刘澜涛*,[b,c] 王 涛[b] 张凤华[a] 李 飞*,[a]
([a]辽宁石油化工大学石油化工学院 辽宁抚顺 113001)
([b]商丘师范学院化学化工学院 药物绿色合成河南省工程实验室 河南商丘 476000)
([c]郑州大学化学学院 郑州 450001)

摘要 水相中在抗坏血酸钠的促进下, 铁催化硝基取代的芳基氟代物与硫酚合成含硫芳香伯胺化合物. 该方法可构建C—S键并原位还原硝基. 这种水相中“一锅”两步反应的显著特点包括直接使用毒性较低的铁催化剂和天然存在的抗坏血酸钠添加剂, 得到中等至优秀的收率, 表现出良好的官能团耐受性以及可扩量能力.

关键词 水相反应; 还原反应; 铁; 催化; 芳香伯胺

Fe-Catalyzed Synthesis of Sulfide-Based Aromatic Primary Amines in Water Promoted by Sodium-Ascorbate

Chen, Xiangping[a] Meng, Chenxiang[b] Li, Mengna[b] Chu, Shangmin[b] Zhu, Xinxin[b]
Xu, Kai*,[b] Liu, Lantao*,[b,c] Wang, Tao[b] Zhang, Fenghua[a] Li, Fei*,[a]
([a] *College of Petrochemical Engineering, Liaoning Petrochemical University, Fushun, Liaoning 113001*)
([b] *Henan Engineering Laboratory of Green Synthesis for Pharmaceuticals, College of Chemistry and Chemical Engineering, Shangqiu Normal University, Shangqiu, Henan 476000*)
([c] *College of Chemistry, Zhengzhou University, Zhengzhou 450001*)

Abstract A practical method for Fe-catalyzed and sodium-ascorbate-promoted synthesis of sulfide-based aromatic primary amines in water from nitroaryl fluorides and thiols has been established. This protocol enables the construction of C—S bonds and the reduction of nitro groups *in situ*. The remarkable features of this one-pot two-step reaction in water include the direct usage of both a less toxic iron catalyst and naturally occurring sodium-ascorbate as the additive, mostly decent to excellent yields, good functional group tolerance as well as the ability to be scaled up.

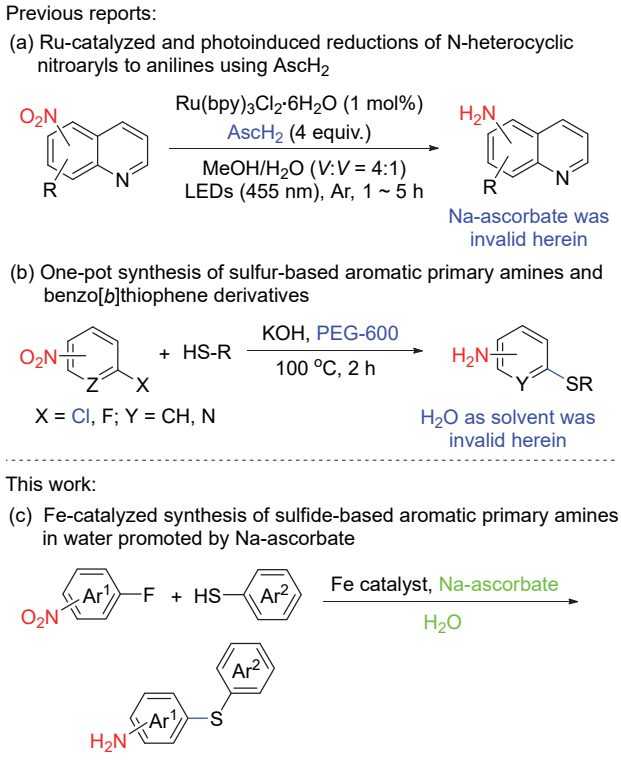
Keywords aqueous phase reaction; reduction reaction; iron; catalysis; aromatic primary amine

1 Introduction

One-pot syntheses involving the utilization of natural feedstocks and/or water as an environmentally innocuous solvent, are devoted to greener and more sustainable organic transformations, thus holding the paramount importance in green synthetic chemistry.[1] Given the characteristic of high abundance, low toxicity and cost, iron-catalyzed organic conversions have drawn more and more attention.[2] Sulfide-based aromatic primary amines as valuable motifs have greatly potential applications in the field of pharmaceutical drugs, material science and organic syntheses.[3] Over the past decades, besides the conventional stepwise procedure,[4] several efficient and ingenious works toward the direct generation of sulfide-based aromatic primary amines have been presented, either through

* Corresponding authors. E-mail: liult05@iccas.ac.cn; xuk1008@163.com; lnpulf@126.com
Received February 9, 2023; revised April 9, 2023; published online April 26, 2023.
Project supported by the National Natural Science Foundation of China (Nos. 21572126, 21202095), the Technicians Troop Construction Projects of Henan Province (No. C20150030), the Program of Science and Technology Innovation Talents of Henan Province (No. 184100510011), the Natural Science Foundation of Henan Province (No. 212300410379), the Key Scientific, Technological Project of Henan Province (No. 192102110222), the Young Core Instructor Project from the Higher Education Institutions of Henan Province (No. 2021GGJS136) and the Leading Talent Funding Project of Shangqiu Talent Support Plan in Henan Province (No. SQRC202212004).
国家自然科学基金(Nos. 21572126, 21202095)、河南省科技创新团队建设计划(No. C20150030)、河南省高校科技创新人才支持计划(No. 184100510011)、河南省自然科学基金(No. 212300410379)、河南省科技攻关项目(No. 192102110222)、河南省高等学校青年骨干教师培养计划(No. 2021GGJS136)和河南省商丘市人才支持计划领军人才(No. SQRC202212004)资助项目.

the construction of C—S bond[5] or through reduction of nitro compounds[6], while the pre-functionalization of substrates was indispensable in these processes. In this context, the former could be realized mainly depending on the cross-coupling originated from halogenated or pseudohalogenated aromatic amine[5a-5i], as well as the C—H arylthiolation of anilines[5j-5o]. Based on the concept of green syntheses, various reaction systems on microwave-assited,[5b] solvent-free[5f] or transition-metal-free[5l,5o] C—S bonds construction have been continuously explored. In particular, the challenging synthesis of sulfur-based aromatic primary amines in water was presented by Velmathi[5d] and Yi'[5k] groups separately. Until now, the latter involving the direct reduction of nitro compounds or the one with concomitant post-functionalization was still widely concerned. Despite the catalytic hydrogenation delivered the corresponding amines fairly efficiently, it should be admitted that the transfer hydrogenation was an attractive alternative to avoid the utilization of the high-pressure instruments and potential toxic metals.[7] And a series of elegant researches on transfer hydrogenation relied on the use of various reductants, such as no-noble metals,[8] silanes,[9] thiols,[10] phosphines,[11] borates,[12] 1,4-dihydropyridines,[13] vasicine[14] and *D*-glucose[15]. Herein, Helaja and coworkers[16] demonstrated the Ru-catalyzed and photoinduced reductions of N-heterocyclic nitroaryls to anilines assisted by the naturally abundant ascorbic acid. Intriguingly, Na-ascorbate exhibited no reduction capabilities (Scheme 1a). Furthermore, apart from the two strategies referring to C—S bond coupling or reduction of nitro compounds mentioned above, Liu's groups[10a] disclosed one-pot synthesis of sulfur-based aromatic primary amines from nitroaryl halides with a combination of KOH and PEG-600, which highlights the advantages of no transition metal, low cost and easy operation. Unfortunately, it is not competent to use water as reaction solvent at all (Scheme 1b). Therefore, one-pot synthesis of aromatic amines in aqueous phase with naturally abundant feedstocks as reductants is still of great significance.



Scheme 1 One-pot synthesis of sulfide-based aromatic primary amines in a green manner

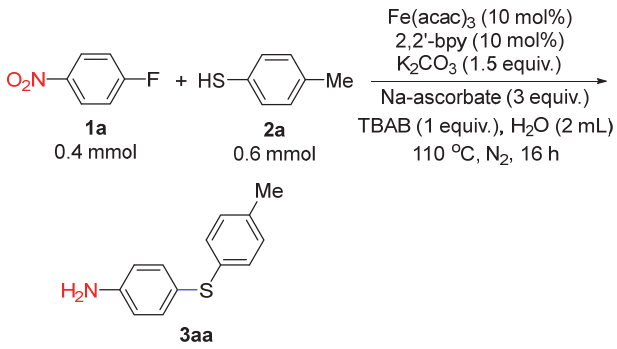
With our ongoing interests in aqueous-phase reaction system[17] and organosulfur chemistry[18], from a green perspective, we envisioned that the Fe-catalyzed and sodium-ascorbate-promoted one-pot two-step synthesis of sulfide-based aromatic primary amines in water could be achieved (Scheme 1c).

2 Results and discussion

Firstly, the reaction with 4-nitrofluorobenzene (**1a**) and 4-methylbenzenethiol (**2a**) in deionized water towards 4-(*p*-tolylthio)aniline (**3aa**) was conducted as a model reaction. After a detailed survey of reaction parameters, an isolated yield of 88% could be obtained in the presence of $Fe(acac)_3$ (10 mol%), 2,2'-bipyridine (10 mol%), K_2CO_3 (1.5 equiv.), Na-ascorbate (3 equiv.) and tetrabutylammonium bromide (TBAB) (1 equiv.) in H_2O (2 mL) at 110 ℃ under N_2 for 16 h (Table 1, Entry 1). Halving the quantity of both $Fe(acac)_3$ and 2,2'-bpy led to relatively poorer performance, and the yield dropped sharply when the two was cut thoroughly (Table 1, Entries 2～3). Other metal salts such as $FeCl_2$, $FeCl_3$ or $Fe(OAc)_2$ had a negative effect on this one-pot synthesis again (Table 1, Entries 4～6). Upon the replacement of 2,2'-bpy by 1,10-phenanthroline, an acceptable yield of 76% was afforded (Table 1, Entry 7). Then various bases were screened deliberately, the yields for **3aa** had not been improved (Table 1, Entries 8～10).[19] Differ from the work by Helaja,[16] the usage of Na-ascorbate as external reductant was really responsible for the high yield of this reaction. As expected, Na-erythorbate was also effective, albeit with a lower yield. In the case of $AscH_2$, only a moderate yield was afforded, which could be attributed to its instability in water (Table 1, Entries 11～13). Subsequently, analogous phase transfer catalysts were also examined, TBAI could deliver the target product **3aa** with a comparable yield (Table 1, Entries 14～15). Investigation of the solvents showed that other organic solvents were not superior to H_2O (Table 1, Entries 16). Meanwhile, once the nitrogen atmosphere switched to air, the yield decreased, presumably due to the influence of oxygen on nitro reduction (Table 1, Entry 17). Moreover, the reaction was dramatically suppressed at room temperature (Table 1, Entry 18).

The scope of both nitroaryl fluorides and thiols in this one-pot two-step synthesis of sulfur-based aromatic primary amines was then investigated, as shown in Table 2. Generally, electron-donating (**3aa**～**3ag**), electron-neutral (**3ah**～**3aj**) or electron-withdrawing (**3ak**～**3an**) groups on

Table 1 Optimization of reaction condition[a]



Entry	Deviation from the model conditions	Yield[b]/%
1	None	88
2	$Fe(acac)_3$ (5 mol%), 2,2'-bpy (5 mol%)	83
3	No $Fe(acac)_3$, no 2,2'-bpy	17
4	$FeCl_2$ instead of $Fe(acac)_3$	75
5	$FeCl_3$ instead of $Fe(acac)_3$	45
6	$Fe(OAc)_2$ instead of $Fe(acac)_3$	72
7	1,10-Phenanthroline instead of 2,2'-bpy	76
8	Cs_2CO_3 instead of K_2CO_3	70
9	K_3PO_4 instead of K_2CO_3	53
10	KOAc instead of K_2CO_3	44
11	No Na-ascorbate	20
12	Na-erythorbate instead of Na-ascorbate	74
13	$AscH_2$ instead of Na-ascorbate	48
14	TBAI instead of TBAB	86
15	TBAC instead of TBAB	71
16	DMF, DMSO, toluene, 1,4-dioxane, CH_3CN, DCE, CH_3CH_2OH instead of H_2O	62/61/27/28/11/＜5/8
17	Air atmosphere	69
18	Room temperature	＜5

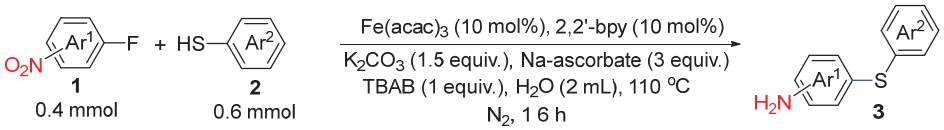
[a] Reagents and conditions: 4-nitrofluorobenzene (0.4 mmol), 4-methylbenzenethiol (0.6 mmol), $Fe(acac)_3$ (10 mol%), 2,2'-bipyridine (10 mol%), K_2CO_3 (0.6 mmol), Na-ascorbate (1.2 mmol) and TBAB (0.4 mmol) in H_2O (2 mL) at 110 ℃ under N_2 for 16 h. [b] Isolated yield based on the amount of 4-nitrofluorobenzene.

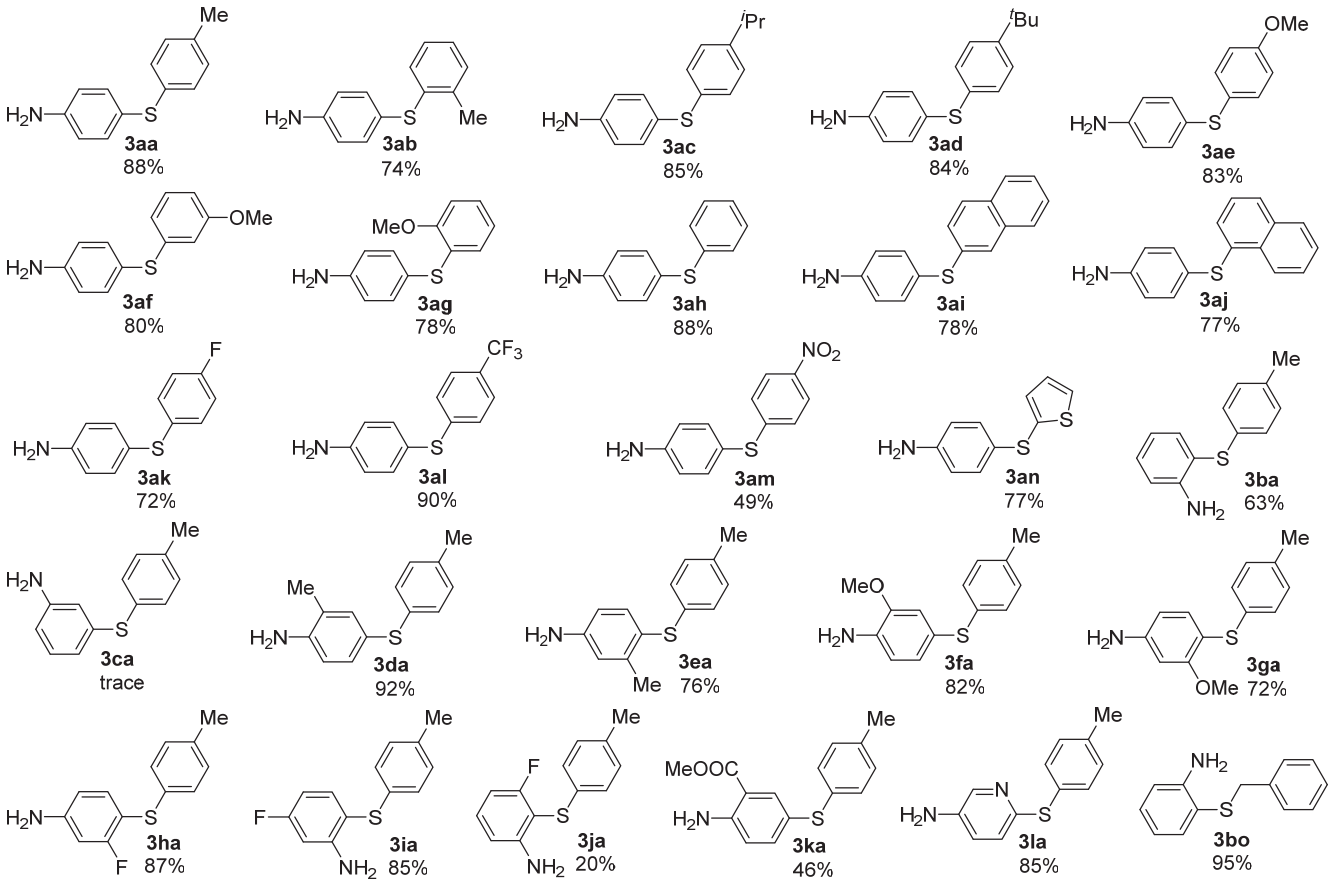
the aromatic rings of thiols were well tolerated to deliver the corresponding products with yields ranging from 49% to 90%. Especially, several substituents such as condensed ring, fluorine, trifluoromethyl, nitryl and heteroaromatic groups could also survive in this transformation (**3ai**～**3an**). The increased steric bulk with respect to thiols resulted in a slight loss of efficiency (**3aa** vs **3ab**, **3ae** vs **3af** and **3ag**, **3ai** vs **3aj**). Next, when 4-methylbenzenethiol (**2a**) was set as the model partner, nitroaryl fluorides bearing various groups including methyl, methoxy, fluorine, methoxy formyl, together with heteroaryl, could be mostly accommodated with the established conditions (**3ba**～**3la**). And nitroaryl fluorides containing electron donor groups showed relatively higher reactivity than substrates containing electron acceptors (**3da**, **3fa** vs **3ka**, **3la**). Notably, the fluorine atom located on the *meta*-position of nitro group would keep intact, while it seemed more inclined to be substituted by thiols when located on the *ortho* or *para*-position resulting in the formation of sulfur-based aromatic primary amines. This rule, in agreement with Liu's report,[10a] had been repeatedly confirmed in the given examples (**3ca**, **3ha**～**3ja**). In addition, the steric hindrance effect of the substituent at the *ortho* position of the fluorine atom to be reacted was more obvious than that at the *ortho* position of the nitro group (**3da** vs **3ea**, **3fa** vs **3ga**, **3ai** vs **3aj**). Different from the previous report on cyclization synthesis of 2-arylbenzothiazole,[10a] a rather high yield of 95% for 2-(benzylthio)aniline (**3bo**) could be afforded with 2-nitrofluorobenzene and benzyl mercaptan as effective candidates.

Subsequently, a set of reasonable controlling experiments were conducted to make clear the reaction mechanism referring to this one-pot two-step synthesis of sulfur-based aromatic primary amines. The reaction from **1a** and **2a** on a scale of 2.0 mmol was also performed to produce desired product **3aa** with a comparable yield of 85% (Scheme 2a). Based on the observation that (4-nitrophenyl)(*p*-tolyl)sulfane (**4aa**), rather than 4-fluoroaniline (**1a'**), was the key intermediate (Schemes 2b and 2c), we speculated logically that the step involving the construction of C—S bond was prior to the reduction of nitro groups *in situ*. To determine the role of iron catalytic cycle in the two steps, **1a** and **4aa** were used separately as reaction substrate in the absence of $Fe(acac)_3$ and 2,2'-bpy. **1a** was completely consumed and mostly converted into **4aa** accompanied by the formation of few reduction products (Scheme 2d). The yield for **3aa** was still not improved significantly even from the intermediate **4aa** (Scheme 2e). Therefore, the iron catalytic cycle was critical to the step of nitro group reduction, but had no obvious effect on C—S bond coupling. Meanwhile, since the replacement of **2a** by **2aa** free of sulfhydryl hydrogen led to a sharply decreased yield of 39% for **3aa**, it reflected that the resulted hydrogen atom on primary amine partly originated from thiols (Scheme 2f). To be clearer, **2a-d1** and D_2O were further used as deuterium source, and **3aa-d2** could be afforded with 7% and 83% of deuterium incorporation, respectively, based on ^1H NMR analysis. These results confirmed that both thiophenol and water might serve as the H-source for nitro reduction (Schemes 2g and 2h). Then commercially available diphenyl diselenide (**2pp**) was incidentally attempted, and the corresponding selenide-based aromatic primary amines (**3ap**) could be afforded in a yield of 18% (Scheme 2i).

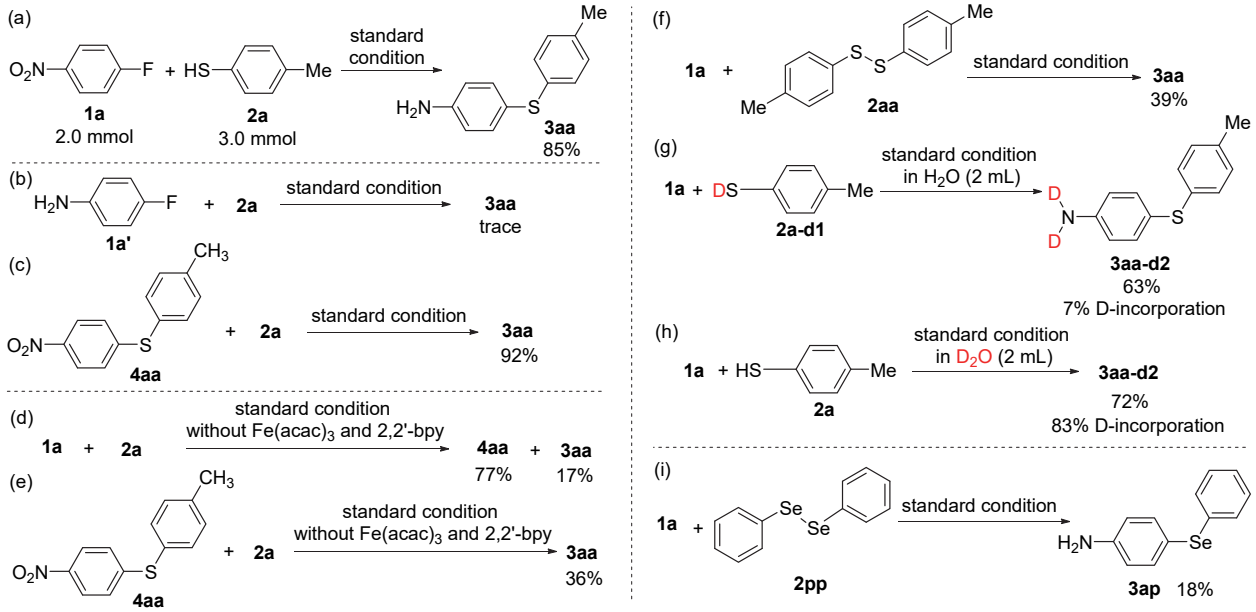
Based on the aforementioned results and the related reports,[2a-2e,10a] a plausible mechanism for the aqueous Fe-catalyzed synthesis of sulfide-based aromatic primary amines was proposed briefly in Scheme 3. Initially, the nucleophilic substitution of **2** towards **1** took place, generating the key intermediate **4**. In parallel, Fe(III)-catalyst was reduced by Na-ascorbate and Ar^2SH to provide lower valent iron species **A**, which would convert to activated Fe hydride species **B** assisted by H_2O and Ar^2SH. Fe hydride **B** was responsible for the reduction of nitroarene **4** to nitrosoarene **5** along with the regeneration of **A** and libera-

Table 2 Substrate scope[a]

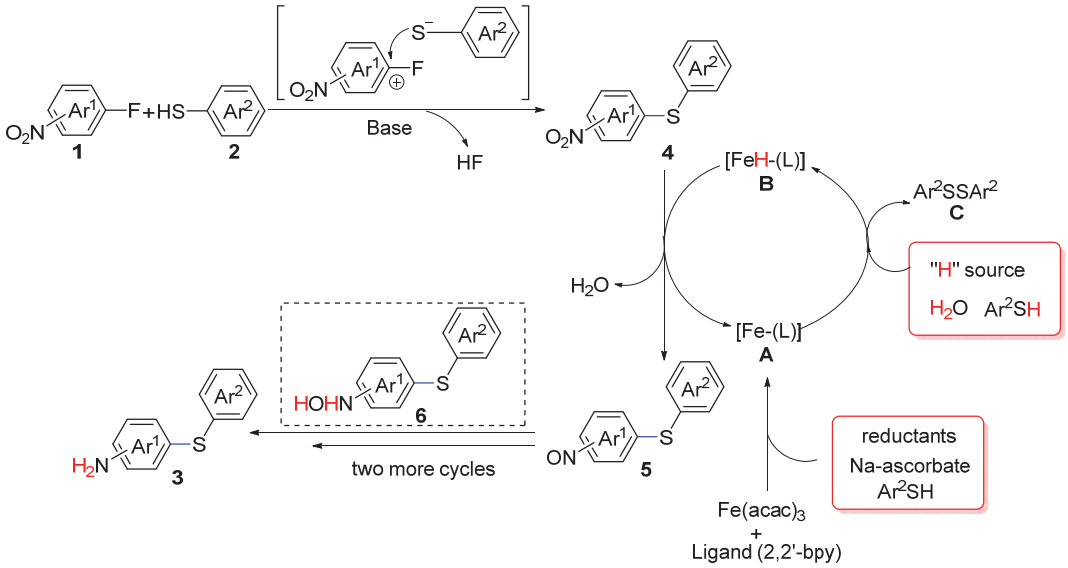




[a] Reagents and conditions: nitroaryl fluorides (0.4 mmol), thiols (0.6 mmol), $Fe(acac)_3$ (10 mol%), 2,2'-bipyridine (10 mol%), K_2CO_3 (0.6 mmol), Na-ascorbate (1.2 mmol) and TBAB (0.4 mmol) in H_2O (2 mL) at 110 ℃ under N_2 for 16 h. Isolated yield based on the amount of nitroaryl fluorides.



Scheme 2 Controlling experiments



Scheme 3 Proposed mechanism

tion of H_2O. Then through two more consecutive hydrogenation cycle, nitrosoarene **5** proceeded to generate hydroxylamine **6** and finally gave rise to an amine **3**.

3 Conclusions

In conclusion, a practical and green method for the one-pot two-step synthesis of sulfide-based aromatic primary amines in water *via* Fe-catalyzed C—S cross-coupling and sequential *in situ* nitro group reduction had been well-established. In this aqueous reaction, either a less toxic iron catalyst or naturally occurring sodium-ascorbate were essential, which especially conformed to the perspective of green synthesis. Also, it could be scaled up and the sequence of reaction steps was clarified by the controlling experiments. Further exploration of the substrate scope and synthetic applications of these methodologies are currently under way in our laboratory.

4 Experimental section

4.1 General information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker DPX-400 spectrometer at room temperature with $CDCl_3$ as the solvent and TMS as an internal standard. GC-MS analysis was performed on an Agilent 7000D GC/TQ system. High-resolution mass spectra were collected on a MALDI-FTMS. Melting points were measured using a XT4A microscopic apparatus. (4-nitrophenyl)(*p*-tolyl)sulfane (**4aa**) and deuterated 4-methylbenzenethiol (**2a-d1**) were synthesized according to the reported literature.[20,25] Solvents and chemicals were bought from commercial sources and used directly unless otherwise stated.

4.2 General procedure for the synthesis of sulfide-based aromatic primary amine

A solution of nitroaryl fluorides (0.4 mmol), thiols (0.6 mmol), $Fe(acac)_3$ (10 mol%), 2,2'-bipyridine (10 mol%), K_2CO_3 (0.6 mmol), Na-ascorbate (1.2 mmol) and TBAB (0.4 mmol) in deionized H_2O (2 mL) was stirred in a 10 mL well-sealed thick-walled glass tube at 110 ℃ under N_2 for 16 h. The reaction mixture was cooled down and extracted with dichloromethane (10 mL) for three times. Then the combined organic layer was dried over anhydrous Na_2SO_4 and filtered. The resulting filtrate was concentrated and purified by flash chromatography over silica gel (ethyl acetate/hexane) to give the pure product.

4-(*p*-Tolylthio)aniline (**3aa**): Brown solid, yield 88%. m.p. 67～68 ℃ (lit.[5l] 70～71 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (d, J=8.4 Hz, 2H), 7.05 (q, J=8.0 Hz, 4H), 6.64 (d, J=8.8 Hz, 2H), 3.76 (s, 2H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.7, 135.6, 135.5, 135.4, 129.7, 128.2, 121.7, 115.8, 21.0.

4-(*o*-Tolylthio)aniline (**3ab**): Brown solid, yield 74%. m.p. 40～41 ℃ (lit.[5o] light-pink liquid); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23～7.19 (m, 2H), 7.13～7.09 (m, 1H), 7.04～6.97 (m, 2H), 6.90～6.87 (m, 1H), 6.62～6.58 (m, 2H), 3.71 (s, 2H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.0, 138.5, 136.0, 135.8, 130.1, 127.7, 126.5, 125.5, 120.3, 116.1, 20.3.

4-((4-*iso*-Propylphenyl)thio)aniline (**3ac**):[4b] Brown oil, yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30～7.26 (m, 2H), 7.08 (s, 4H), 6.67～6.62 (m, 2H), 3.76 (s, 2H), 2.89～2.77 (m, 1H), 1.21 (s, 3H), 1.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.8, 146.4, 136.1, 135.7, 127.9, 127.1, 121.3, 115.9, 33.7, 24.0.

4-((4-(*tert*-Butyl)phenyl)thio)aniline (**3ad**):[4b] Brown oil, yield 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31～7.27 (m, 2H), 7.26～7.22 (m, 2H), 7.10～7.06 (m, 2H), 6.66～6.62 (m, 2H), 3.76 (s, 2H), 1.27 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.6, 146.9, 135.9, 135.8, 127.5, 125.9, 121.1, 115.9, 34.4, 31.3.

4-((4-Methoxyphenyl)thio)aniline (**3ae**):[21] Pale brown solid, yield 83%. m.p. 64～65 ℃ (lit.[26] yellow oil); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23～7.19 (m, 4H), 6.83～6.78 (m, 2H), 6.64～6.59 (m, 2H), 3.77～3.72 (m, 5H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 158.5, 146.2, 134.0, 131.5, 128.8, 123.5, 115.8, 114.6, 55.4.

4-((3-Methoxyphenyl)thio)aniline (**3af**):[21] Brown oil, yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.29 (m, 2H), 7.12 (t, J=8.0 Hz, 1H), 6.71～6.62 (m, 5H), 3.81～3.72 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 159.9, 147.2, 141.3, 136.3, 129.6, 120.0, 119.4, 115.9, 112.6, 110.9, 55.2.

4-((2-Methoxyphenyl)thio)aniline (**3ag**):[5n] Pale brown solid, yield 78%. m.p. 59～60 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35～7.30 (m, 2H), 7.11～7.06 (m, 1H), 6.84～6.76 (m, 2H), 6.73～6.67 (m, 3H), 3.90～3.82 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 155.2, 147.2, 136.9, 128.6, 127.0, 125.9, 121.1, 118.8, 116.0, 110.2, 55.8.

4-(Phenylthio)aniline (**3ah**):[5l] Pale brown solid, yield 88%. m.p. 81～82 ℃ (lit.[5l] 92～93 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (d, J=8.4 Hz, 2H), 7.20～7.16 (m, 2H), 7.13～7.04 (m, 3H), 6.63～6.59 (m, 2H), 3.75 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.2, 139.8, 136.2, 128.9, 127.3, 125.4, 120.3, 115.9.

4-(Naphthalen-2-ylthio)aniline (**3ai**):[21] Brown solid, yield 78%. m.p. 126～127 ℃ (lit.[5n] 132～138 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, J=7.6 Hz, 1H), 7.68 (d, J=8.8 Hz, 1H), 7.64 (d, J=8.0 Hz, 1H), 7.52 (s, 1H), 7.44～7.33 (m, 4H), 7.28～7.25 (m, 1H), 6.71～6.66 (m, 2H), 3.81 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.1, 137.1, 136.0, 133.8, 131.5, 128.4, 127.7, 127.1, 126.4, 126.1, 125.4, 125.3, 120.6, 116.0.

4-(Naphthalen-1-ylthio)aniline (**3aj**):[21] Pale brown solid, yield 77%. m.p. 40～41 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (d, J=8.0 Hz, 1H), 7.82～7.79 (m, 1H), 7.64 (d, J=8.0 Hz, 1H), 7.54～7.45 (m, 2H), 7.30～7.24 (m, 3H), 7.19～7.16 (m, 1H), 6.63～6.59 (m, 2H), 3.71 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.8, 136.3, 135.3, 133.9, 131.6, 128.5, 126.6, 126.5, 126.34, 126.30, 125.8, 124.6, 120.8, 116.0.

4-((4-Fluorophenyl)thio)aniline (**3ak**): Brown solid, yield 72%. m.p. 84～85 ℃ (lit.[5o] purple-black liquid); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28～7.23 (m, 2H), 7.16～7.10 (m, 2H), 6.95～6.88 (m, 2H), 6.66～6.61 (m, 2H), 3.78 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 161.3 (d, J=243.6 Hz), 147.0, 135.5, 134.3 (d, J=3.2 Hz), 129.9 (d, J=7.9 Hz), 121.3, 116.0 (d, J=13.8 Hz), 115.8 (d, J=8.0 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −117.1.

4-((4-(Trifluoromethyl)phenyl)thio)aniline (**3al**): Brown solid, yield 90%. m.p. 40～41 ℃ (lit.[5n] 117～118 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, J=8.4 Hz, 2H), 7.32 (d, J=8.4 Hz, 2H), 7.10 (d, J=8.4 Hz, 2H), 6.71～6.67 (m, 2H), 3.88 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.9, 145.8, 137.1, 126.8 (q, J=32.5 Hz), 125.8, 125.5 (q, J=3.9 Hz), 123.0 (t, J=271.8 Hz), 117.8, 116.1; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −62.2.

4-((4-Nitrophenyl)thio)aniline (**3am**):[5l] Yellow solid, yield 49%. m.p. 122～123 ℃ (lit.[5l] 137～138 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05～8.00 (m, 2H), 7.35～7.31 (m, 2H), 7.11～7.06 (m, 2H), 6.76～6.72 (m, 2H), 3.97 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 151.0, 148.4, 144.8, 137.2, 125.2, 123.9, 116.4, 116.1.

4-(Thiophen-2-ylthio)aniline (**3an**):[21] Brown oil, yield 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (dd, J=5.2, 1.2 Hz, 1H), 7.23～7.18 (m, 2H), 7.14 (dd, J=3.6, 1.2 Hz, 1H), 6.95 (dd, J=5.2, 3.6 Hz, 1H), 6.60～6.56 (m, 2H), 3.68 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.2, 135.9, 132.7, 132.3, 129.3, 127.5, 124.9, 115.7.

2-(*p*-Tolylthio)aniline (**3ba**):[22] Brown solid, yield 63%. m.p. 43～44 ℃ (lit.[27] 47～49 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (dd, J=8.0, 1.6 Hz, 1H), 7.19～7.14 (m, 1H), 7.00 (s, 4H), 6.73～6.68 (m, 2H), 4.21 (s, 2H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.7, 137.2, 135.5, 133.1, 130.9, 129.9, 127.2, 118.8, 115.4, 115.3, 21.0.

2-Methyl-4-(*p*-tolylthio)aniline (**3da**):[21] Brown oil, yield 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17 (s, 1H), 7.16～7.12 (m, 1H), 7.07～7.04 (m, 2H), 7.01～6.98 (m, 2H), 6.58 (d, J=8.0 Hz, 1H), 3.66 (s, 2H), 2.25 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 145.2, 136.4, 135.9, 135.4, 133.3, 129.7, 128.2, 123.3, 121.2, 115.7, 21.0, 17.3.

3-Methyl-4-(*p*-tolylthio)aniline (**3ea**):[5n] Brown oil, yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (d, J=8.4 Hz, 1H), 7.01～6.92 (m, 4H), 6.57 (d, J=2.4 Hz, 1H), 6.47 (dd, J=8.0, 2.4 Hz, 1H), 3.70 (s, 2H), 2.27 (s, 3H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.5, 143.5, 137.5, 135.6, 134.8, 129.7, 126.9, 120.0, 117.2, 113.5, 21.0, 20.9.

2-Methoxy-4-(*p*-tolylthio)aniline (**3fa**):[5n] Brown oil, yield 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08～7.00 (m, 4H), 6.95～6.90 (m, 2H), 6.63 (d, J=8.0 Hz, 1H), 3.89 (s, 2H), 3.76 (s, 3H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.5, 136.9, 135.8, 135.4, 129.7, 128.0, 127.7, 121.1, 116.2, 115.1, 55.6, 21.0.

3-Methoxy-4-(*p*-tolylthio)aniline (**3ga**): Brown solid, yield 72%. m.p. 82～83 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (d, J=8.4 Hz, 1H), 7.05～6.99 (m, 4H), 6.26～6.23 (m, 2H), 3.81～3.76 (m, 5H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 160.6, 149.0, 137.2, 135.0, 134.9, 129.5, 127.7, 109.2, 107.8, 98.8, 55.8, 20.9; HRMS (ESI) calcd for $C_{14}H_{16}NOS$ $[M+H]^+$ 246.0947, found 246.0943.

3-Fluoro-4-(*p*-tolylthio)aniline (**3ha**): Brown solid, yield 87%. m.p. 77～78 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24～7.19 (m, 1H), 7.08～6.99 (m, 4H), 6.38～6.33 (m, 2H), 3.86 (s, 2H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 163.7 (d, J=243.9 Hz), 149.7 (d, J=10.8 Hz), 137.6 (d, J=2.2 Hz), 135.8, 134.2, 129.8, 128.0, 111.5 (d, J=2.3 Hz), 107.6 (d, J=19.2 Hz), 102.5 (d, J=26.3 Hz), 21.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −106.7; HRMS (ESI) calcd for $C_{13}H_{13}FNS$ $[M+H]^+$ 234.0747, found 234.0747.

5-Fluoro-2-(*p*-tolylthio)aniline (**3ia**): Brown oil, yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41～7.35 (m, 1H), 7.03～6.95 (m, 4H), 6.45～6.40 (m, 2H), 4.36 (s, 2H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 164.9 (d, J=245.5 Hz), 150.4 (d, J=12.0 Hz), 139.1 (d, J=10.2 Hz),

135.6, 133.1 (d, J=1.2 Hz), 129.9, 126.7, 110.4 (d, J=2.6 Hz), 105.8 (d, J=22.0 Hz), 101.8 (d, J=25.1 Hz), 21.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −110.1; HRMS (ESI) calcd for $C_{13}H_{13}FNS$ $[M+H]^+$ 234.0747, found 234.0744.

3-Fluoro-2-(*p*-tolylthio)aniline (**3ja**): Pale brown oil, yield 20%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.13～7.07 (m, 1H), 7.04～6.98 (m, 4H), 6.50～6.45 (m, 2H), 4.44 (s, 2H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 164.4 (d, J=243.5 Hz), 150.9 (d, J=3.0 Hz), 135.8, 132.1, 131.6 (d, J=10.8 Hz), 129.9, 127.1, 110.5 (d, J=2.9 Hz), 104.7 (d, J=24.0 Hz), 103.2 (d, J=21.7 Hz), 21.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: −105.5; HRMS (ESI) calcd for $C_{13}H_{13}FNS$ $[M+H]^+$ 234.0747, found 234.0746.

Methyl 2-amino-5-(*p*-tolylthio)benzoate (**3ka**): Brown solid, yield 46%. m.p. 65～66 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (d, J=2.0 Hz, 1H), 7.34 (dd, J=8.8, 2.4 Hz, 1H), 7.08～7.02 (m, 4H), 6.63 (d, J=8.4 Hz, 1H), 5.88 (s, 2H), 3.84 (s, 3H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.0, 150.6, 140.1, 137.6, 135.6, 135.3, 129.7, 128.1, 119.3, 117.9, 111.3, 51.7, 20.9; HRMS (ESI) calcd for $C_{15}H_{16}NO_2S$ $[M+H]^+$ 274.0896, found 274.0905.

6-(*p*-Tolylthio)pyridin-3-amine (**3la**): Brown solid, yield 85%. m.p. 61～62 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, J=2.4 Hz, 1H), 7.32 (d, J=8.0 Hz, 2H), 7.11 (d, J=8.0 Hz, 2H), 6.92～6.88 (m, 1H), 6.82～6.78 (m, 1H), 3.81 (s, 2H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.2, 141.1, 137.8, 137.3, 132.6, 130.7, 130.1, 125.0, 123.2, 21.2; HRMS (ESI) calcd for $C_{12}H_{13}N_2S$ $[M+H]^+$ 217.0794, found 217.0792.

2-(Benzylthio)aniline (**3bo**):[23] Pale brown solid, yield 95%. m.p. 63～64 ℃ (lit.[28] 37～38 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27～7.19 (m, 4H), 7.15～7.08 (m, 3H), 6.69 (dd, J=8.0, 0.8 Hz, 1H), 6.62 (dt, J=7.8, 1.2 Hz, 1H), 4.24 (s, 2H), 3.89 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.6, 138.3, 136.5, 130.1, 128.9, 128.4, 127.0, 118.5, 117.4, 114.9, 39.6.

4-(*p*-Tolylselanyl)aniline (**3ap**):[24] Yellow solid, yield 18%. m.p. 75～76 ℃ (lit.[29] 87～91 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, J=8.8 Hz, 2H), 7.30～7.27 (m, 2H), 7.21～7.11 (m, 3H), 6.62 (d, J=8.8 Hz, 2H), 3.76 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.9, 137.2, 134.2, 130.1, 129.1, 126.1, 116.4, 116.1.

Supporting Information ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of compounds **3aa**～**3an**, **3ap**, **3ba**, **3da**～**3la** and **3bo**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

References

[1] For reviews, see: (a) Kim, Y.; Li, C. J. *Green Synth. Catal.* **2020**, *1*, 1.
(b) Gawande, M. B.; Bonifácio, V. D.; Luque, R.; Branco, P. S.; Varma, R. S. *Chem. Soc. Rev.* **2013**, *42*, 5522.
(c) Bauer, I.; Knölke, H. J. *Chem. Rev.* **2015**, *115*, 3170.
(d) Kar, S.; Sanderson, H.; Roy, K.; Benfenati, E.; Leszczynski, J. *Chem. Rev.* **2022**, *122*, 3637.

[2] (a) Wienhofer, G.; Baseda-Kruger, M.; Ziebart, C.; Westerhaus, F. A.; Baumann, W.; Jackstell, R.; Junge, K.; Beller, M. *Chem. Commun.* **2013**, *49*, 9089.
(b) Feng, H. D.; Li, Y.; Lin, S. J.; Eycken, E.; Song, G. H. *Sustain. Chem. Process* **2014**, *2*, 14.
(c) Formenti, D.; Ferretti, F.; Scharnagl, F. K.; Beller, M. *Chem. Rev.* **2019**, *119*, 2611.
(d) Rahman, T.; Borah, G.; Gogoi, P. K. *J. Chem. Sci.* **2021**, *133*, 1.
(e) Vengatesh, G.; Nanjan, P. *Curr. Org. Chem.* **2022**, *26*, 1.
(f) Zhang, Z. G.; Li, J. L.; Zhang, G. S.; Ma, N. N.; Liu, Q. F.; Liu, T. X. *J. Org. Chem.* **2015**, *80*, 6875.
(g) Wei, D.; Darcel, C. *Chem. Rev.* **2019**, *119*, 2550.
(h) Guo, N.; Zhu, S. F. *Chin. J. Org. Chem.* **2015**, *35*, 1383 (in Chinese).
(郭娜, 朱守非, 有机化学, **2015**, *35*, 1383.)
(i) Li, J. H.; Liu, K. M.; Duan, X. F.; Liu, J. B. *Chin. J. Org. Chem.* **2017**, *37*, 314 (in Chinese).
(李娟华, 刘昆明, 段新方, 刘晋彪, 有机化学, **2017**, *37*, 314.)

[3] (a) Feng, M.; Tang, B.; Liang, S. H.; Jiang, X. *Curr. Top. Med. Chem.* **2016**, *16*, 1200.
(b) Boyd, D. A. *Angew. Chem., Int. Ed.* **2016**, *55*, 15486.
(c) Dunbar, K. L.; Scharf, D. H.; Litomska, A.; Hertweck, C. *Chem. Rev.* **2017**, *117*, 5521.
(d) Du, X.; Kleitz, F.; Li, X.; Huang, H.; Zhang, X.; Qiao, S. Z. *Adv. Funct. Mater.* **2018**, *28*, 1707325.

[4] (a) Wrobel, Z. *Tetrahedron* **2003**, *59*, 101.
(b) Clark, R. D.; Jahangir, A.; Severance, D.; Salazar, R.; Chang, T.; Chang, D.; Jett, M. F.; Smith, S.; Bley, K. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 1053.
(c) Jarkas, N.; McConathy, J.; Voll, R. J.; Goodman, M. M. *J. Med. Chem.* **2005**, *48*, 4254.

[5] For the construction of C—S bonds, see: (a) Ravi, V.; Mujahid, A. M.; Srinivas, R. A. *Chem. Lett.* **2004**, *33*, 1614.
(b) Ranu, B. C.; Ranjan Jana, A. S. *Adv. Synth. Catal.* **2007**, *349*, 2690.
(c) Fernández-Rodríguez, M. A.; Hartwig, J. F. *J. Org. Chem.* **2009**, *74*, 1663.
(d) Velmathi, S.; Vijayaraghavan, R.; Amarendar, C.; Pal, R. P.; Vinu, A. *Synlett* **2010**, *18*, 2733.
(e) Su, K.; Qiu, Y. T.; Yao, Y. W.; Zhang, D. Y.; Jiang, S. *Synlett* **2012**, *23*, 2853.
(f) Mohammadinezhad, A.; Akhlaghinia, B. *New J. Chem.* **2019**, *43*, 15525.
(g) Wang, H. F.; Jiang, L. L.; Chen, T.; Li, Y. M. *Eur. J. Org. Chem.* **2019**, *2019*, 2138.
(h) Martín, M. T.; Marín, M.; Maya, C.; Prieto, A.; Nicasio, M. C. *Chem. - Eur. J.* **2021**, *27*, 12320.
(i) Zhang, W. G.; Huang, M. J.; Zou, Z. L.; Wu, Z. G.; Ni, S. Y.; Kong, L. Y.; Zheng, Y. X.; Wang, Y.; Pan, Y. *Chem. Sci.* **2021**, *12*, 2509.
(j) Fang, X. L.; Tang, R. Y.; Zhang, X. G.; Li, J. H. *Synthesis* **2011**, *7*, 1099.
(k) Lin, Y. M.; Lu, G. P.; Wang, G. X.; Yi, W. B. *Adv. Synth. Catal.* **2016**, *358*, 4100.
(l) Raghuvanshi, D. S.; Verma, N. *RSC Adv.* **2017**, *7*, 22860.
(m) Wei, Y. T.; Liu, Y. L.; He, J.; Li, X. Z.; Liu, P.; Zhang, J. *Tetrahedron* **2020**, *76*, 131646.
(n) Jiang, X. P.; Shen, Z. F.; Zheng, C.; Fang, L. Y.; Chen, K. D.; Yu, C. M. *Tetrahedron Lett.* **2020**, *61*, 152141.
(o) Zhao, W. Q.; Zhang, F.; Deng, G. J. *J. Org. Chem.* **2021**, *86*, 291.

[6] For the reduction of nitro compounds, see: (a) Braunerová, G.; Buchta, V.; Silva, L.; Kuneš, J.; Palát, K., Jr. *Farmaco* **2004**, *59*, 443.
(b) Guo, Z. B.; Wang, R. F.; Guo, Y. Y.; Jiang, J. W.; Wang, Z. Q.; Li, W.; Zhang, M. H. *ACS Catal.* **2022**, *12*, 15193.

[7] For reviews, see: (a) Orlandi, M.; Brenna, D.; Harms, R.; Jost, S.; Benaglia, S. *Org. Process Res. Dev.* **2018**, *22*, 430.
(b) Formenti, D.; Ferretti, F.; Scharnagl, F. K.; Beller, M. *Chem.*

Rev. **2019**, *119*, 2611.
(c) Ferretti, F.; Ramadan, D. R.; Ragaini, F. *ChemCatChem* **2019**, *11*, 4450.
[8] (a) Hudson, R.; Hamasaka, G.; Osako, T.; Yamada, Y. M. A.; Li, C. J.; Uozumi, Y.; Moores, A. *Green Chem.* **2013**, *15*, 2141.
(b) Zhao, Z. K.; Yang, H. L.; Li, Y.; Guo, X. W. *Green Chem.* **2014**, *16*, 1274.
(c) Cheung, C. W.; Ploeger, M. L.; Hu, X. L. *ACS Catal.* **2017**, *7*, 7092.
(d) Cheung, C. W.; Ploeger, M. L.; Hu, X. L. *Chem. Sci.* **2018**, *9*, 655.
(e) Cheung, C. W.; Ma, J. A.; Hu, X. L. *J. Am. Chem. Soc.* **2018**, *140*, 6789.
(f) Cheung, C. W.; Shen, N.; Wang, S. P.; Ullah, A.; Hu, X. L.; Ma, J. A. *Org. Chem. Front.* **2019**, *6*, 756.
(g) He, H. D.; Zhang, Z. K.; Tang, H. B.; Xu, Y. Q.; Xu, X. B.; Cao, Z. Y.; Xu, H.; Li, Y. *Org. Chem. Front.* **2022**, *9*, 4875.
(h) Liu, Y. Z.; Bao, Z. P.; Qi, X. X.; Wu, X. F. *Org. Chem. Front.* **2022**, *9*, 2079.
[9] (a) Pesti, J.; Larson, G. L. *Org. Process Res. Dev.* **2016**, *20*, 1164.
(b) Zhao, S. L.; Mankad, N. P. *Org. Lett.* **2019**, *21*, 10106.
(c) Song, H.; Yang, Z. Y.; Tung, C. H.; Wang, W. G. *ACS Catal.* **2020**, *10*, 276.
(d) Cao, Y.; Yang, S. M.; Huo, Y. P.; Hu, X. Q. *Adv. Synth. Catal.* **2020**, *362*, 3971.
(e) Qu, Z. H.; Chen, X.; Zhong, S.; Deng, G. J.; Huang, H. W. *Org. Lett.* **2021**, *23*, 5349.
(f) Behera, R. R.; Panda, S.; Ghosh, R.; Kumar, A. A.; Bagh, B. *Org. Lett.* **2022**, *24*, 9179.
(g) Li, Q. Y.; Dai, P.; Tang, H. D.; Zhang, M. L.; Wu, J. *Chem. Sci.* **2022**, *13*, 9361.
[10] (a) Duan, Z.; Ranjit, S.; Liu, X. *Org. Lett.* **2010**, *12*, 2430.
(b) Li, Q. Y.; Dai, P.; Tang, H. D.; Zhang, M. L.; Wu, J. *Chem. Sci.* **2022**, *13*, 9361.
[11] (a) Freeman, A. W.; Urvoy, M.; Criswell, M. E. *J. Org. Chem.* **2005**, *70*, 5014.
(b) Bao, Z. W.; Lü, J.; Jin, Z. C. *Chin. J. Org. Chem.* **2021**, *41*, 4773 (in Chinese).
(鲍兆伟, 吕洁, 金智超, 有机化学, **2021**, *41*, 4773.)
[12] (a) Wang, B.; Ma, J. W.; Ren, H. Y.; Lu, S.; Xu, J. K.; Liang, Y.; Lu, C. S. *Chin. Chem. Lett.* **2022**, *33*, 2420.
(b) Lu, H. T.; Geng, Z. Y.; Li, J. Y.; Zou, D. P.; Wu, Y. S.; Wu, Y. J. *Org. Lett.* **2016**, *18*, 2774.
(c) Hosoya, H.; Castro, L. C. M.; Sultan, I.; Nakajima, Y.; Ohmura, T.; Sato, K.; Tsurugi, H.; Suginome, M.; Mashima, K. *Org. Lett.* **2019**, *21*, 9812.
(d) Jang, M.; Lim, T.; Park, B. Y.; Han, M. S. *J. Org. Chem.* **2022**, *87*, 910.
[13] Jiang, H. M.; Qin, J. H.; Sun, Q.; Zhang, D.; Jiang, J. P.; Ouyang, X. H.; Song, R. J.; Li, J. H. *Org. Chem. Front.* **2022**, *9*, 4070.
[14] Sharma, S.; Kumar, M.; Kumar, V.; Kumar, N. *J. Org. Chem.* **2014**, *79*, 9433.
[15] Kumar, M.; Sharma, U.; Sharma, S.; Kumar, V.; Singh, B.; Kumar, N. *RSC Adv.* **2013**, *3*, 4894.
[16] Todorov, A. R.; Aikonen, S.; Muuronen, M.; Helaja, J. *Org. Lett.* **2019**, *21*, 3764.
[17] Xu, K.; Yang, F.; Zhang, G. D.; Wu, Y. J. *Green Chem.* **2013**, *15*, 1055.
[18] (a) Xu, K.; Li, Z. Y.; Cheng, F. Y.; Zuo, Z. Z.; Wang, T.; Wang, M. C.; Liu, L. T. *Org. Lett.* **2018**, *20*, 2228.
(b) Liu, L. T.; Guo, Z. H.; Xu, K.; Hui, S. S.; Zhao, X. F.; Wu, Y. J. *Org. Chem. Front.* **2018**, *5*, 3315.
(c) Xu, K.; Xu, Z. L.; Zhang, M. Z.; Yan, X. X.; Mao, G. L.; Wang, T.; Wu, Y. J.; Liu, L. T. *Org. Chem. Front.* **2021**, *8*, 5831.
[19] Ouyang, K. B.; Xi, Z. F. *Acta Chim. Sinica* **2013**, *71*, 13 (in Chinese).
(欧阳昆冰, 席振峰, 化学学报, **2013**, *71*, 13.)
[20] Xuan, M. J.; Lu, C. L.; Lin, B. L. *Chin. Chem. Lett.* **2020**, *31*, 84.
[21] Yang, D. S.; Yan, K. L.; Wei, W.; Zhao, J.; Zhang, M. Q.; Sheng, X. G.; Li, G. Q.; Lu, S. L.; Wang, H. *J. Org. Chem.* **2015**, *80*, 6083.
[22] Panova, Y. S.; Kashin, A. S.; Vorobev, M. G.; Degtyareva, E. S.; Ananikov, V. P. *ACS Catal.* **2016**, *6*, 3637.
[23] Xu, Z. B.; Lu, G. P.; Cai, C. *Catal. Commun.* **2017**, *99*, 57.
[24] Bai, R.; Dabaria, K. K.; Badsara, S. S. *Synthesis* **2022**, *54*, 2487.
[25] Nie, S. Z.; Lu, A.; Kuker, E. L.; Dong, V. M. *J. Am. Chem. Soc.* **2021**, *143*, 6176.
[26] Pan, L.; Cooke, M. V.; Spencer, A.; Laulhé, S. *Adv. Synth. Catal.* **2022**, *364*, 420.
[27] Davis, F. A.; Horner, C. J.; Fretz, E. R.; Stackhouse, J. F. *J. Org. Chem.* **1973**, *38*, 695.
[28] Ham, J.; Cho, S. J.; Ko, J.; Chin, J.; Kang, H. *J. Org. Chem.* **2006**, *71*, 5781.
[29] Ricordi, V. G.; Thurow, S.; Penteado, F.; Schumacher, R. F.; Perin, G.; Lenardão, E. J.; Alves, D. *Adv. Synth. Catal.* **2015**, *357*, 933.

(Cheng, F.)

