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Enantioselective Oxidative Coupling of β-Ketocarbonyls and Anilines by Joint Chiral Primary Amine and Selenium Catalysis

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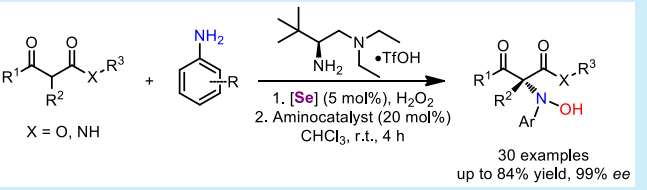
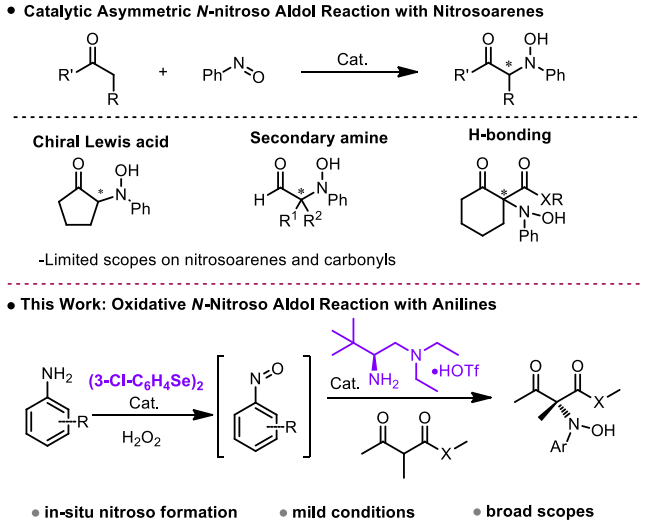
Supporting Information

ABSTRACT: An enantioselective primary amine-catalyzed total *N*-selective nitroso aldol reaction (*N*-NA) was achieved through the oxidation of primary aromatic amines to the corresponding nitrosoarenes catalyzed by selenium reagents and 30% H_2O_2. This protocol provides a facile and highly efficient access to α-hydroxyamino carbonyls bearing chiral quaternary centers under exceedingly mild and green reaction conditions with high chemo- and enantiocontrol.



Chiral aniline groups are key structural units in many biologically active natural products and therapeutic reagents.[1] The *N*-nitroso aldol reaction with nitrosoarenes represents one of the most straightforward approaches to access chiral anilines. In 2004, Yamamoto reported the first example of a catalytic enantioselective *N*-nitroso aldol reaction using BINAP-silver complexes.[2] Later on, chiral amino-catalysis[3] and H-bonding bifunctional catalysis[4,5] were also reported for similar reactions with aldehydes and β-ketocarbonyls, respectively. Despite this progress, catalytic asymmetric *N*-selective nitroso aldol reactions are still limited regarding their applicability and scope (Scheme 1). In particular, nitrosoarenes[6] are notoriously unstable and easily undergo polymerization and decomposition. Hence the preparations and handling of nitrosoarenes pose serious issues, limiting their synthetic applications. An easily conceivable solution is to in-situ-generate nitroso compounds under oxidative conditions.[7] In this regard, anilines are the most promising candidates because they are readily available precursors for nitrosoarenes. However, such a catalytic asymmetric oxidative *N*-nitroso aldol reaction of anilines remains a considerable challenge and has not been reported.[8]

Scheme 1. Asymmetric *N*-Selective Nitroso Aldol Reaction of β-Ketocarbonyls



Recently, we have examined the enantioselective coupling of acyclic β-keto esters and nitrosobenzene, for which high stereocontrol has not been achieved so far. In the presence of our chiral primary amine catalysts, the reactions of the benchmark nitrosobenzene afforded the regioselective *N*-nitroso aldol adduct with high enantioselectivity (Scheme 2, **3a**, 64% yield, 98% *ee* and **3b**, 71% yield, 97% *ee*). However, the extension to other nitrosoarenes such as those electron-withdrawing-group-substituted ones led to a serious reduction in both yield and enantioselectivity, likely as a result of background reactions and the decomposition of the nitrosobenzenes (observed). An in situ oxidative strategy was hence pursued to address this issue.

As known, nitrosoarenes could be prepared by the oxidation of primary amines and hydroxylamines or the reduction of nitroarenes.[9] The selenium-catalyzed oxidation of aryl amines with H_2O_2 developed by Bäckvall appeared to be one of the most attractive routes to synthesize nitroso compounds.[10] However, the oxidation of anilines is highly dependent on the substitution pattern, and successful examples of unactivated anilines with electron-withdrawing substitutes are still rare. In addition, the compatibility of the oxidative conditions with delicate asymmetric catalysis remains an open question, and no example has been reported. Intrigued by the intrinsic green credentials of the Se/H_2O_2 system, we investigated the chiral

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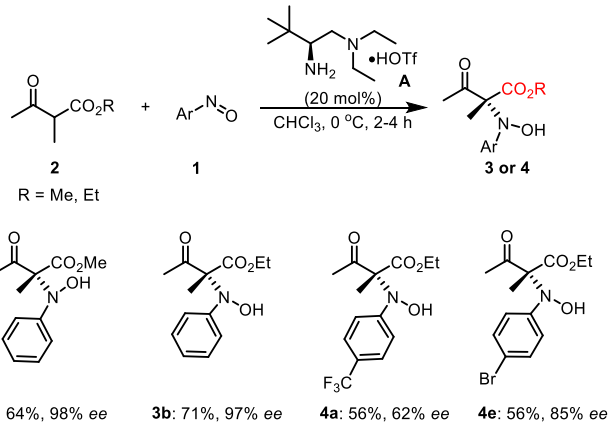
Scheme 2. *N*-Nitroso Aldol Reaction with Nitrosoarenes[a]



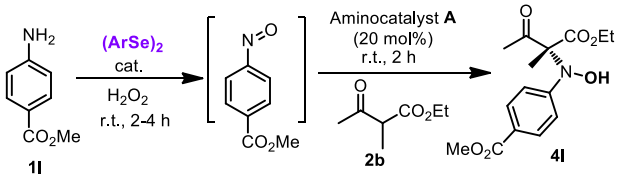
[a]All reactions were performed at 0 °C in 0.5 mL of $CHCl_3$ with **2** (0.10 mmol), **1** (0.15 mmol), **A** (20 mol %), 2−4 h. Isolated yields. *Ee* was determined by HPLC analysis.

primary amine and selenium combined catalysis for the oxidative *N*-nitroso aldol reactions with anilines.[11] A diaryl diselenide catalyst was identified to effectively facilitate the oxidation of anilines to nitrosoarenes, and its successful coupling with *β*-ketocarbonyls was achieved in the presence of a primary amine catalyst.

In this study, a primary challenge is the oxidative compatibility of aminocatalysis under the oxidative selenium conditions because the aminocatalyst may be readily oxidized. Inspired by Bäckvall's work,[10] a two-stage operation was utilized to obviate this problem. As such, the oxidation of aniline was first conducted, and the organic phase after complete conversion was then treated with aminocatalyst and carbonyl compounds to initialize enantioselective C−N coupling. In the first stage, it was found that the simple removal of an aqueous uplayer was critical for productivity, and the reasons might be two-fold: to remove excess H_2O_2 that is potentially detrimental to the aminocatalyst and to eliminate the inhibiting effect of water on the enamine catalysis. The whole process did not require any isolation or purification of the unstable nitroso intermediates (Table 1).

An electron-deficient 4-aminobenzoate **1l** was chosen as a model substrate for screening and optimization. Initially, the readily available diphenyl diselenide was found to give the desired product **4l** in 32% yield with 99% *ee* (Table 1, entry 1), showing a better outcome compared with $PhSeO_2H$ or selenium dioxide (Table 1, entry 1 vs 2). Chloroform was identified as the optimal solvent in terms of both productivity and enantioselectivity (Table 1, entries 1 vs 3 and 4). Decreasing the loading of the selenium catalyst led to a reduced yield (entry 5), but increasing the loading showed no obvious effect (entry 6). Using excess aniline gave improved yields (based on the limiting **2b**) with maintained enantioselectivity (entries 7 and 8) along with a large amount of azoxyarene side products. The results obtained were encouraging but still far from satisfaction with respect to the conversion of aniline as well as the formation of side products. Therefore, we next explored substituted selenium catalysts, and a series of diaryl diselenides were prepared according to known methods.[12] A general trend was observed, with the electron-deficient selenium catalyst showing superior productivity to their electron-rich counterpart (Table 1, entries 11−14 vs 9 and 10). The diselenide-bearing 3-chloro substitute turned out to be the optimal catalyst to give 70% yield with 99% *ee* (Table 1, entry 14). A more electron-deficient one with a ditrifluoromethyl group provided a slightly lower yield (Table 1, entry 15). In control experiments without a selenium catalyst, no desired product was detected (Table 1, entry 16), pinpointing the critical role of selenium catalysis in the in situ generation of nitrosoarene.

Table 1. Screening and Optimization of the Oxidative Coupling to Aniline[a]



entry	Se cat. (X mol %) Ar =	1l/2b	$CHCl_3$	yield (%)[b]	*Ee* (%)[c]
1	Ph (5 mol %)	1:2	$CHCl_3$	32	99
2	$PhSeO_2H$ (10 mol %)	1:2	$CHCl_3$	21	96
	SeO_2 (20 mol %)	1:2	$CHCl_3$	10	97
3	Ph (5 mol %)	1:2	MeCN	36	76
4	Ph (5 mol %)	1:2	MeOH	10	70
5	Ph (2.5 mol %)	1:2	$CHCl_3$	14	97
6	Ph (10 mol %)	1:2	$CHCl_3$	32	97
7	Ph (5 mol %)	2:1	$CHCl_3$	62	97
8	Ph (5 mol %)	3:1	$CHCl_3$	70	97
9	3-MeO-C_6H_4	1:2	$CHCl_3$	27	94
10	4-MeO-C_6H_4	1:2	$CHCl_3$	39	96
11	2-F-C_6H_4	1:2	$CHCl_3$	45	97
12	3-F-C_6H_4	1:2	$CHCl_3$	55	96
13	4-Cl-C_6H_4	1:2	$CHCl_3$	53	98
14	3-Cl-C_6H_4	1:2	$CHCl_3$	70	99
15	3,5-$(CF_3)_2$-C_6H_3	1:2	$CHCl_3$	60	97
16	none	1:2	$CHCl_3$	N.D.	

[a]Reactions were performed with **1l** (0.10 mmol), **2** (0.20 mmol), catalyst **A** (20 mol %), and Se catalyst (5 mol %, entries 9−15), H_2O_2 (30%) (2.2 equiv) at room temperature in 0.5 mL of solvent, 4−6 h total reaction time. [b]Yields were determined by ^1H NMR analysis. [c]*Ee* was determined by the HPLC analysis on a chiral stationary phase. N.D. = no desired product.

With the optimized conditions in hand, we first examined the scope of *β*-ketocarbonyl substrates, of which the results are summarized in Scheme 3. First, using *β*-keto esters with different ester moieties (Me, Et, *n*/*i*Pr, *t*Bu, allyl, Bn) all gave the desired products in moderate to good yield and with high enantioselectivities (Scheme 3, **3a**−**g**, 44−55% yield, 96−98% *ee*). The substrate scope could be further extended to *β*-ketoamides. Both *N*-aryl (**2h**−**j**) and *N*-aliphatic amides (**2k**) worked well under such reaction conditions to afford the desired *α*-oxyamination adducts in good yield and with high enantioselectivities as well (Scheme 3, **3h**−**k**, 53−65% yield, 97−98%*ee*). Furthermore, six-membered-ring cyclic ketoester and ketoamides could be transformed into the corresponding products with high enantioselectivities (Scheme 3, 57% yield, >99% *ee* for **3l**; 55% yield, 95% *ee* for **3m**). Unfortunately, *β*-ketoesters bearing a larger *α*-alkyl group and 1,3-diketones did not work well, leading to rather poor yields (not shown).

Then, we turned our attention toward the scope of substituted anilines in this tandem oxidation−*N*-nitroso aldol reaction. To achieve excellent transformation of nitroso derivatives, it is necessary to avoid peroxidation to the

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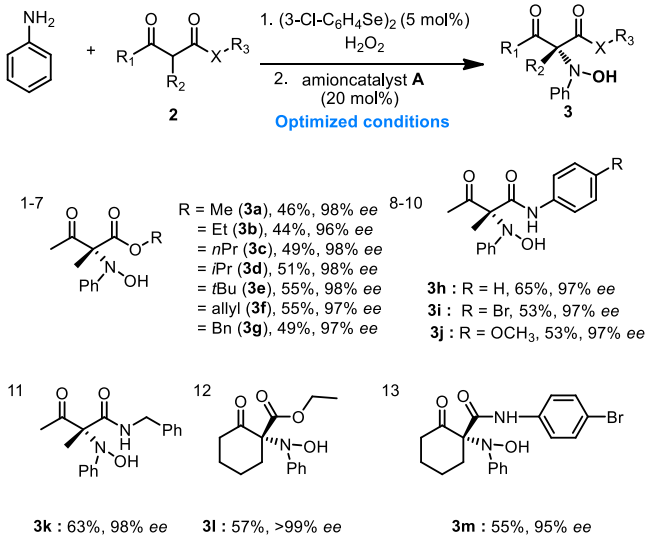
Scheme 3. Substrate Scope of β-Ketocarbonyls[a]



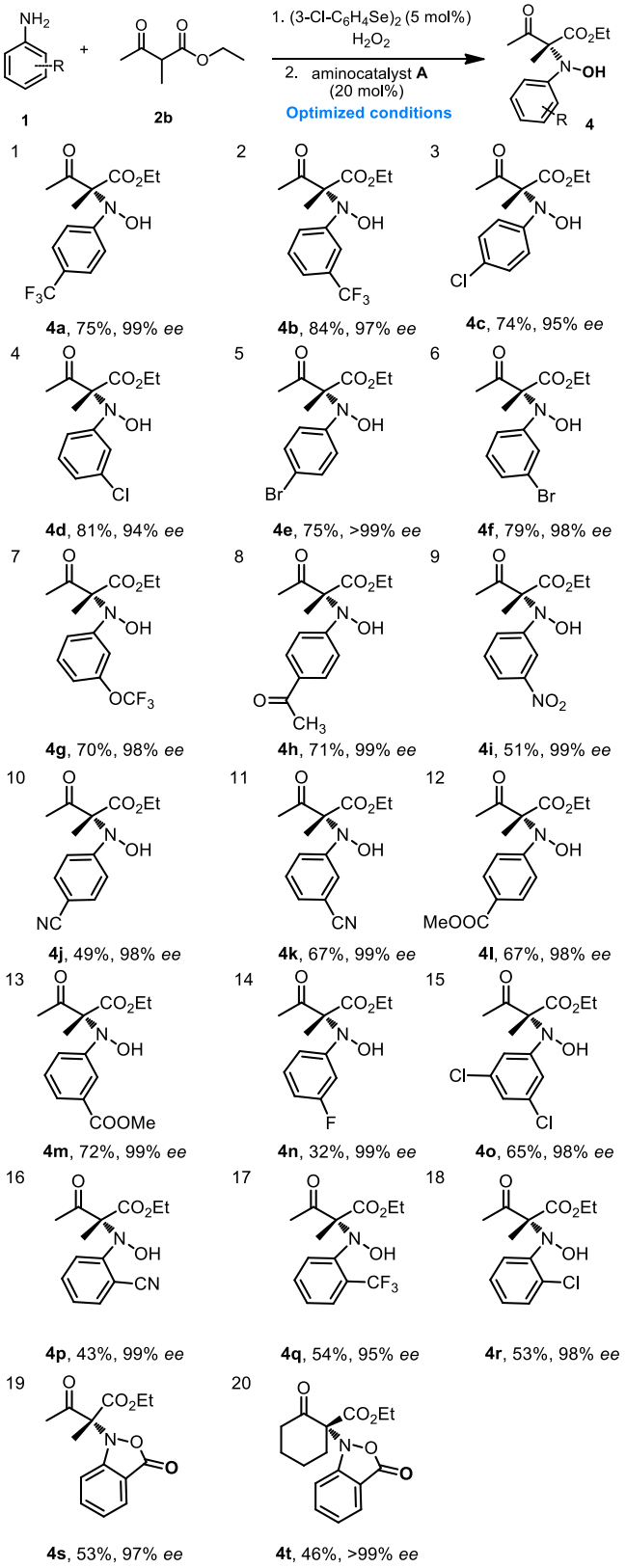
[a]All reactions were performed with aniline **1a** (0.10 mmol), **2** (0.20 mmol), **A** (20 mol %), (3-Cl-$C_6H_4Se)_2$ (5 mol %), and H_2O_2 (30%) (2.2 equiv) at room temperature in 0.5 mL of chloroform for 2−4 h. Isolated yields. *Ee* was determined by HPLC analysis.

corresponding nitro derivatives or dimerization to the respective azo derivatives. It was found that a reaction time of 2 h was sufficient to ensure the maximization of nitroso conversion while minimizing overoxidation, and in cases with electron-deficient anilines, slightly prolonging the reaction time to 4 h was necessary to ensure conversion. Reactions with anilines containing electron-deficient substituents formed the final products via the respective nitroso compounds in moderate to good isolated yield and with high enantioselectivities (Scheme 4, **4a−g**, 70−84% yield, 94−99%*ee*). It is noteworthy that anilines with strong electron-withdrawing groups on the aromatic ring including 4-keto-, 3-nitro, 4- or 3-cyano, and 4- or 3-carboxylate substitutes could be well tolerated to the desired products in moderate to good yield and with high enantioselectivities (Scheme 4, **4h−m**, 49−72% yield, 98−99%*ee*). 3-Fluoroaniline could be oxidized rather quickly to complicate byproducts, leading to inferior results in low yield but with high enantioselectivity (Scheme 4, **4n**, 32% yield, 99% *ee*). Disubstituted aniline also worked well (Scheme 4, **4o**, 65% yield, 98% *ee*). Ortho-substituted anilines gave slightly lower yields probably due to steric effect (Scheme 4, **4p−4r**, 43−54% yields, 95−99%*ee*). For *o*-methyl formate aniline, the targeted product was not obtained, but an intramolecular cyclization product was isolated (Scheme 4, **4s**, 53% yield, 97% *ee* and **4t**, 46% yield, >99% *ee*). These results clearly reveal that the present method was well applicable for the oxidation of a series of aromatic primary amines.

To further demonstrate the synthetic utility of this methodology, a gram-scale reaction was carried out in the presence of 10 mol % of chiral primary amine catalyst (Scheme 5). This transformation worked well with a comparable yield and enantioselectivity.

As known, anilines can be directly oxidized to the corresponding nitroso derivatives using benzene seleninoperoxoic acid PhSe(O)OOH as the real active oxidant, which was generated in situ by the oxidation of diphenyl diselenide by H_2O_2 in this system after further hydrolysis.[13] The observed

Scheme 4. Substrate Scope of Anilines[a]



[a]All reactions were performed at room temperature in 0.5 mL of $CHCl_3$ with **1** (0.10 mmol), **2b** (0.20 mmol), **A** (20 mol %), (3-Cl-$C_6H_4Se)_2$ (5 mol %), and H_2O_2 (30%) (2.2 equiv) for 2−4 h. Isolated yields. *Ee* was determined by HPLC analysis.

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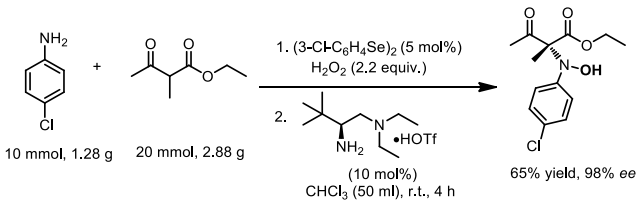
Scheme 5. Gram-Scale Synthesis



chemo- and enantioselectivities could be explained by a protonated N−H H-bonding network to the nitroso moiety, as we previously reported[14](Figure 1).

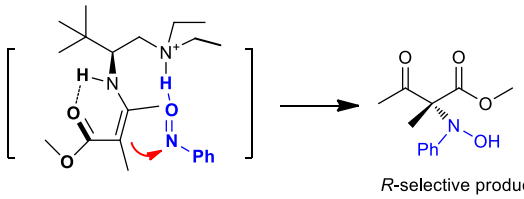
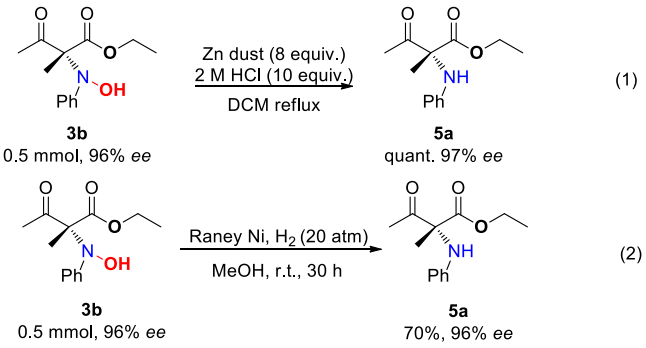


Figure 1. Proposed transition state.

To confirm the N/O selectivity of this methodology, the reduction of product **3b** to the corresponding aniline **5a** was carried out in quantitative yield by using hydrochloric acid and zinc dust as the reducing agent (Scheme 6, eq 1). Moreover,

Scheme 6. Cleavage of N−O Bond



the reductive N−O cleavage could also be achieved in the presence of Raney Ni under H_2 (Scheme 6, eq 2). This transformation further validated the formation of the *N*-selective product.

In summary, we have developed an oxidative approach of α-oxyamination of β-ketocarbonyls by means of an electrophilic *N*-nitroso aldol reaction with joint chiral primary amine/selenium catalysis. Aromatic amines were oxidized by Se/H_2O_2 catalytic systems, furnishing aromatic nitroso species in situ in good yield. This oxidative catalytic strategy enables a facile and highly efficient access to functionalized *N*-selective nitroso aldol compounds with an enantioenriched chiral quaternary carbon center. We believe that the simple reaction setting and the mild reaction conditions of this new approach will stimulate further research of the synthetic utility.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02636.

Experimental procedures, screening data, steric parameters and model development, computational details, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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