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Rare-Earth-Catalyzed Transsulfinamidation of Sulfinamides with Amines

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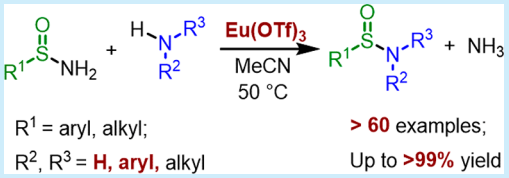
ABSTRACT: A rare-earth-catalyzed transsulfinamidation of primary sulfinamides with alkyl, aryl, and heterocyclic amines for the synthesis of diverse secondary and tertiary sulfinamides has been realized. Unlike transition metal-catalyzed cross-coupling approaches restricted to non-commercially available disubstituted *O*-benzoyl hydroxylamines, this newly developed protocol is suitable for diverse readily available primary and secondary amines without any modifications. Excellent catalytic activity and selectivity are achieved with $Eu(OTf)_3$ under mild reaction conditions, which extends the applicability of rare-earth catalysis.

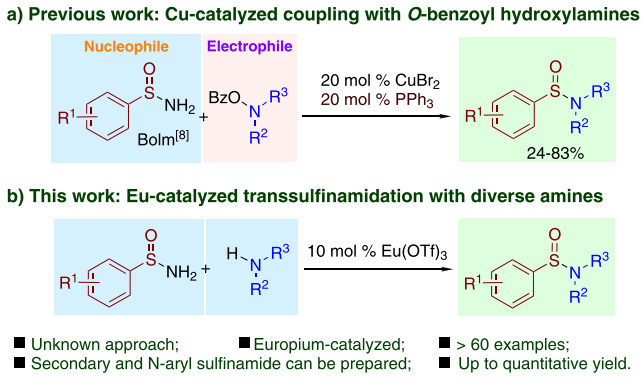


Transamidation represents one of the most highly valuable reactions for synthesis of diverse amides.[1] Unlike the significant advances achieved in the transamidation of amides, to the best of our knowledge, the direct transformation of sulfonamides or sulfinamides has not been reported (Scheme 1a). Sulfonamides and sulfinamides are widely found in bioactive, pharmaceutical, and polymeric molecules.[2] For example, sulfinamides are considered as one of the most widespread and privileged ligands,[3] easily deprotectable *N*-sulfinyl protecting groups, as well as precursors of sulfonamides.[4] Conventional approaches[5] for syntheses of sulfinamides often include multistep homolytic substitution of sulfinic acids, sulfonates, sulfinyl chlorides, and disulfides. Various efforts have thus been devoted to developing practical, straightforward, and one-step approaches for syntheses of sulfinamides and their derivatives.[6]

We have recently reported the first convenient copper-catalyzed electrophilic amination of sodium sulfinates to produce diverse functional sulfonamides by using *O*-benzoyl hydroxylamines (OBzs) as amino sources.[7] Subsequently, Bolm and co-workers realized the first example of copper-catalyzed transsulfinamidation of nucleophilic primary sulfinamides with air-sensitive triphenylphosphine as a ligand at 20 mol % catalyst loading (Scheme 1a).[8] In both reactions, the commercially unavailable and atom un-economic amino reagents OBzs have to be used, which hampered the practicability and applicability of the protocols. Furthermore, the OBzs have to be disubstituted to increase their stability, restricted to the formation of mainly tertiary sulfinamides. Therefore, efficient transsulfinamidation of sulfinamides with readily available amines to yield not only tertiary but also secondary sulfinamides is highly desirable.

However, the direct transamidation of sulfinamides with amines is still unknown because both substrates are nucleophilic.[9] In light of the good performance of metal Lewis acids, especially lanthanides salts, in the catalytic transformation of amines with alkenes, alkynes, and cyanides,[10] we conceived that the possible four-member-ring intermediate mediated by Lewis acid may also aid the direct transamidation of sulfinamides (Scheme 1b). The four-member-ring species may not only activate both substrates simultaneously but also accelerate the nucleophilic transformation.[11] With this hypothesis in mind, herein we realize a rare-earth-catalyzed transamidation of primary sulfinamides to secondary and tertiary sulfinamides by direct reaction with diverse alkyl, aryl, and heterocyclic amines under mild reaction conditions

Scheme 1. Represented Synthetic Approaches for Sulfinamides and Sulfonamides



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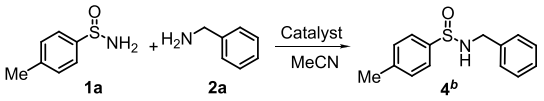
(Scheme 1b). Unlike unsatisfactory outcomes in the Lewis acid-accelerated equilibrium transamidation of amides with amines,[12] up to quantitative yields were achieved in our newly developed europium-catalyzed transsulfinamidation.

Initially, 4-tolylsulfinamide (**1a**) and benzylamine (**2a**) were selected to test our hypothesis with several Lewis acids (Table 1). The desired secondary sulfinamide **4** was obtained in 39%

Table 1. Optimization of the Reaction Conditions[a]



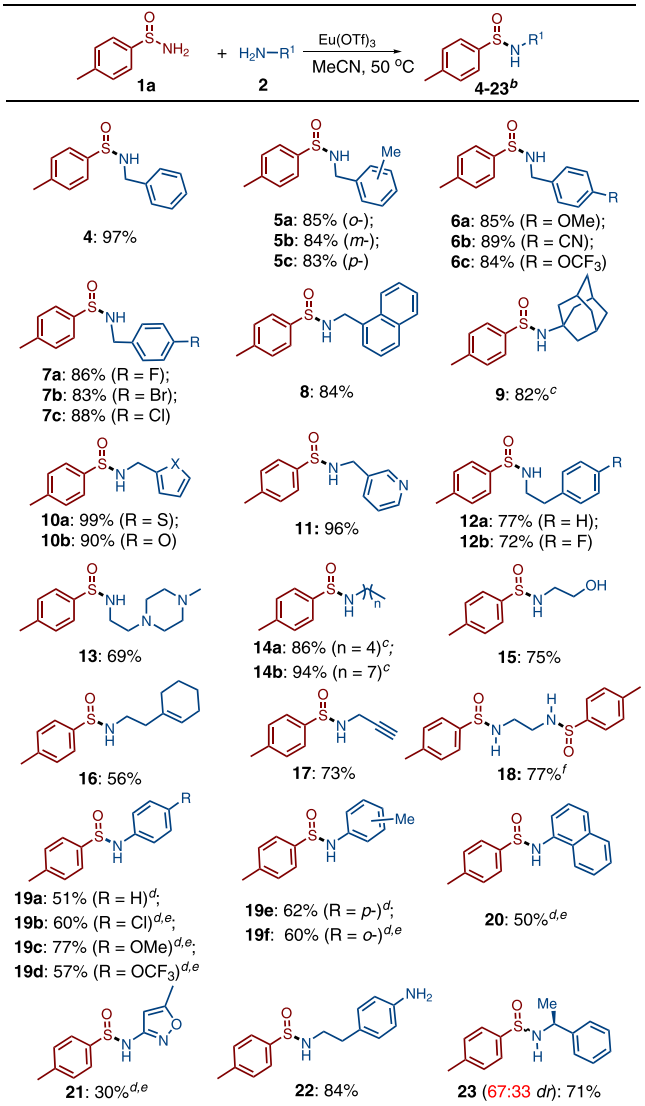
entry	catalyst	yield[b] (%)
1	$CoCl_2·6H_2O$	39
2	$Ni(OAc)_2·4H_2O$	trace
3	$CuCl_2$	36
4	$Zn(OAc)_2$	9
5	$HAuCl_4·6H_2O$	47
6	$Sc(OTf)_3$	88
7	$La(OTf)_3$	91
8	$Ce(OTf)_3$	87
9	$Nd(OTf)_3$	91
10	$Eu(OTf)_3$	97
11	$Tb(OTf)_3$	88
12	$Yb(OTf)_3$	89
13	–	8

[a]Under a N_2 atmosphere, a catalyst (10 mol %), 4-tolylsulfinamide **1a** (0.5 mmol), and benzylamine **2a** (0.55 mmol) were stirred in 2 mL of MeCN at 50 °C for 24 h. [b]Isolated yield.

yield with 10 mol % $CoCl_2·6H_2O$ in acetonitrile at 50 °C for 24 h (Table 1, entry 1). When other Lewis acids were involved, chloroauric acid showed the best catalytic activity (entries 2–5). Considering the strong acidity of lanthanide salts and their excellent performance in many reactions,[13] a number of lanthanide triflates were also applied (entries 6–12). To our delight, excellent yields (87–97%) were obtained. Among these, europium triflate displayed the best activity (97%, entry 10). As a comparison, in the case without any catalyst, <10% of yields were obtained (entry 13). The solvent effect was also investigated (Table S1), and acetonitrile was found to be the best choice. Further optimization with a decrease in temperature or the catalyst loading all led to inferior yields.

With the optimal reaction conditions in hand, the feasibility of the newly developed protocol was then investigated (Scheme 2). The position of the methyl group on benzylamine has almost no influence on the transformation (83–85%, **5a–5c**). Electron-rich or electron-deficient benzylamines all led to the formation of corresponding sulfinamides **6a–7c** in very good yields (83–89%), including benzylamines with methoxy, cyano, trifluoromethoxy, or halogen substituents. The amines with bulky naphthalene or adamantane rings could also be converted into corresponding sulfinamides in good yields (82–84%, **8** and **9**). All selected heterocyclic benzylamines also resulted in excellent yields (≤99%, **10–11**), even on a gram scale (Scheme S1). In addition to phenethylamines, the primary amines with longer alkyl chains were all compatible with the protocol (69–94%, **12a–14b**). Remarkably, primary amines containing sensitive functional groups gave good yields, as well (56–75%, **15–17**). For instance, the selected aminoalcohol, ethanolamine, with a global annual demand of

Scheme 2. Substrate Scope of Various Primary Amines[a]



[a]The reaction was carried out with 4-tolylsulfinamide **1a** (0.5 mmol), primary amines **2** (0.55 mmol), and $Eu(OTf)_3$ (10 mol %) in 2.0 mL of MeCN under a N_2 atmosphere at 50 °C for 24 h. [b]Isolated yields. [c]At 100 °C. [d]With 20 mol % $Eu(OTf)_3$. [e]With 4 equiv of **2**. [f]With 4-tolylsulfinamide **1a** (1.1 mmol) and ethylenediamine (0.5 mmol).

2 million tons,[14] resulted in product **15** in a yield of 75%. The alkyl diamine was also successfully converted to disulfinamide **18** under the standard reaction conditions.

Aromatic amines, which are less nucleophilic, were also involved in this transsulfinamidation, though the yields were slightly lower (**19a–21**). The selectivity of the substrates with different types of amino groups was then investigated. The aliphatic amino was much more reactive than the aromatic amine, and product **22** with an unchanged aromatic amino group was produced in a very good yield (84%). The reaction with chiral substrates was also investigated, and a mixture of diastereomers (dr 67:33) **23** was formed when using (*S*)-4-tolylsulfinamide and (*S*)-1-phenylethylamine as reactants. Such results may be helpful for the further understanding of the plausible mechanism.

We further paid our attention to the feasibility of secondary amines (Scheme 3). The acyclic secondary amines were all

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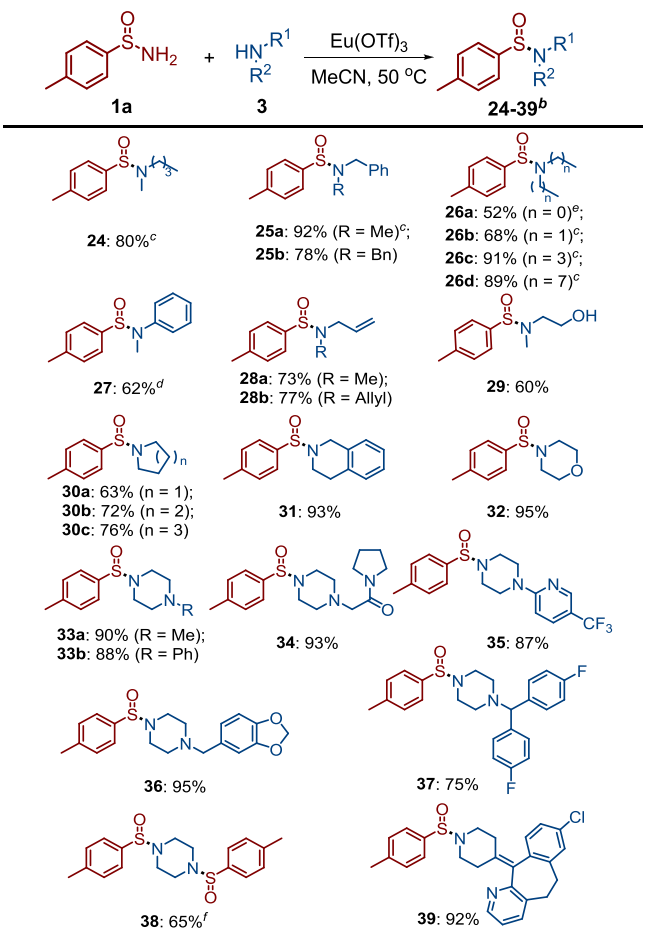
Scheme 3. Substrate Scope of Various Secondary Amines[a]



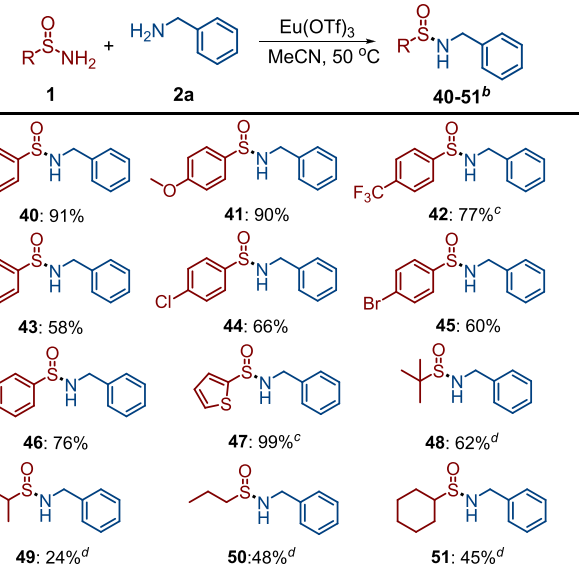
[a]With 4-tolylsulfinamide **1a** (0.5 mmol), secondary amines **3** (0.55 mmol), and $Eu(OTf)_3$ (10 mol %) in 2.0 mL of MeCN under a N_2 atmosphere at 50 °C for 24 h. [b]Isolated yields. [c]At 100 °C. [d]With 20 mol % $Eu(OTf)_3$ and 4 equiv of **3**. [e]With 0.275 mmol of $Me_2NH_2^+Me_2NCOO^-$ salt as an amino source. [f]With 4-tolylsulfinamide **1a** (1.1 mmol) and piperazine (0.5 mmol).

compatible and readily converted into the corresponding sulfinamides **24**−**27** in moderate to excellent yields (52−92%). Due to the low boiling point of dimethylamine, dimethylammonium dimethylcarbamate ($Me_2NH_2^+Me_2NCOO^-$)[15] was used instead, leading to a 52% yield for product **26a**. Secondary aryl amines were also suitable for this transformation (62%, **27**). Sensitive functional groups were well tolerated. When *N*-allylmethylamine and diallylamine were involved, the corresponding products **28a** and **28b** were produced in good yields (73% and 77%, respectively), in which the allylic moieties were untouched. When a substituted amino alcohol was applied, moderate yield was attained (60%, **29**) without the generation of sulfonimidamides or esterification products.

In addition to the acyclic amines, cyclic secondary amines were also compatible. The ring size of amines slightly affected the catalytic efficiency (63−76%, **30a**−**30c**). Amines derived from tetrahydroisoquinoline, morphiline, and piperazine delivered the corresponding sulfinamides in good to excellent yields (88−95%, **31**−**33**). Piperazines with an amide groups and trifluoromethyl, pyridine, piperonyl, and bis(4-fluorophenyl)methyl substituents resulted in moderate to excellent yields (75−93%, **34**−**37**). Secondary diamine was also tolerated (65%, **38**). A derivative of desloratadine, which was a new antihistamine showing anti-inflammatory properties *in vitro*,[16] could also be obtained via our strategy (92%, **39**). These results clearly demonstrated the versatility and applicability of our newly developed protocol.

After investigation of the scope of amines, a series of sulfinamides were subsequently selected as reaction partners (Scheme 4). The electron-rich substrates were quite

Scheme 4. Substrate Scope of Diverse Sulfinamides[a]



[a]With sulfinamide **1** (0.5 mmol), primary amines **2a** (0.55 mmol), and $Eu(OTf)_3$ (10 mol %) in 2.0 mL of MeCN under a N_2 atmosphere at 50 °C for 24 h. [b]Isolated yields. [c]At 100 °C. [d]With 20 mol % $Eu(OTf)_3$ at 140 °C.

compatible, and good to excellent yields were found (90%−91%, **40** and **41**), whereas the electron-deficient sulfinamides were slightly less active (58−77%, **42**−**45**). Our protocol was also compatible with sulfinamides even with bulky, heterocyclic, and alkyl groups (≤99% yield, **46**−**51**). Among them, *tert*-butyl sulfinamide derivatives, which are widely used in organic synthesis and chiral catalysis,[17] could be prepared by this strategy (62%, **48**).

To explore the plausible mechanism, several control experiments were performed. With the addition of a drop of mercury or 1.5 equiv of 2,2,6,6-tetramethylpiperidinooxy (TEMPO) to the reaction mixture, no obvious impact on the transformation was observed (Scheme 5a), excluding nanoparticles catalyzed and free radical reaction pathways.[18] To understand the role of europium, ^{1}H NMR studies were performed (Scheme 5b). After the addition of europium triflate to the $CDCl_3$ solution mixture containing 4-tolylsulfinamide (**1a**) or morpholine (**3a**), obvious changes of chemical shifts were found in both cases, indicating both partners could coordinate with europium. However, in a $CDCl_3$ solution containing both **1a** and **3a**, after the addition of $Eu(OTf)_3$, the signals for **3a** were shifted downfield much more obviously than those for **1a**, suggesting the ability of **3a** to coordinate to the Eu center was stronger than that of **1a**.

The irritating gas ammonia was released, and a small amount of white precipitate was also observed during the reaction. ^{19}F

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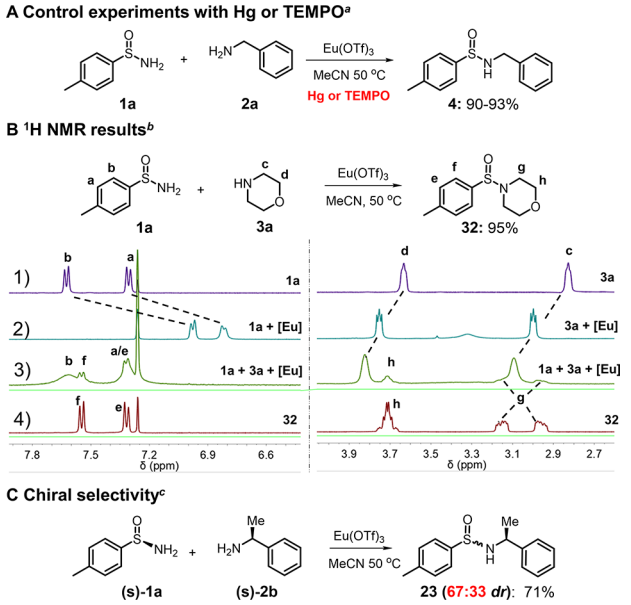
Scheme 5. Control Experiments



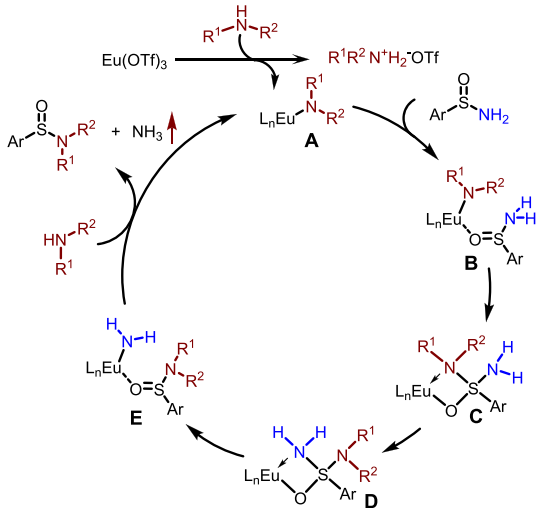
[a]Control experiment with a drop of mercury or 1.5 equiv of TEMPO under standard conditions. [b]^{1}H NMR spectra for (1) **1a** and **3a**, (2) **1a** or **3a** with Eu(OTf)$_3$ (10 mol %) in 2.0 mL of MeCN under a N_2 atmosphere at 50 °C for 1 h, (3) **1a**, **3a**, and Eu(OTf)$_3$ (10 mol %) in 2.0 mL of MeCN under a N_2 atmosphere at 50 °C for 1 h, or (4) product **32**. [c]With (*S*)-**1a** (0.5 mmol) and (*S*)-**2b** (0.55 mmol) as reactants under standard conditions.

NMR spectra (Figures S1 and S2) revealed the white solid might be generated ammonium triflate. To verify the possible four-member-ring species generated during the transsulfinamidation, a control experiment involving chiral substrates was also carried out (Scheme 5c). If the four-member ring was involved, the products of two different configurations could be obtained because the attack from both sides of S═O was possible; otherwise, chiral products with retained configuration would be generated. The control experiment using sulfinamide (*S*)-**1a** and amines (*S*)-**2b** as reactants resulted in a mixture of diastereomers in a yield of 71%, confirming the formation of possible four-member-ring species.

On the basis of our results, and combined with previously reported mechanistic studies on lanthanide catalysis and transamidation of amides,[19] a plausible mechanism is proposed (Scheme 6). Initially, Lewis acid Eu(OTf)$_3$ coordinates with amine to generate species **A** along with the formaiton of ammonium salts. Then sulfinamide and species **A** form the key four-member-ring intermediate **C**. Further isomerization yields another crucial four-membered-ring intermediate **D**. Subsequent ring opening (**E**) and ligand exchange with amine led to the formation of the desired product and ammonia along with the regeneration of active catalytic species **A**.

In summary, a direct transsulfinamidation of sulfinamides with various readily available amines was realized for the first time by using europium triflate as a catalyst under mild reaction conditions. Unlike previous studies on the transition metal-catalyzed cross-coupling approaches with disubstituted *O*-benzoyl hydroxylamines, this newly developed protocol is quite compatible with a broad range of alkyl, aryl, and heterocylic primary and secondary amines directly, generating diverse secondary and tertiary sulfinamides in good to excellent yields. A plausible mechanism involving a key europium-chelated four-member-ring intermediate has been proposed, which extends the applicability of rare-earth catalysis.

Scheme 6. Proposed Mechanism



■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01106.

Instrumentation and chemicals, optimization of reaction condition, detailed mechanistic studies, and characterization data for products (PDF)

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Notes

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