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Perspective

Strategic Synthesis of Sulfinamides as Versatile S(IV) Intermediates

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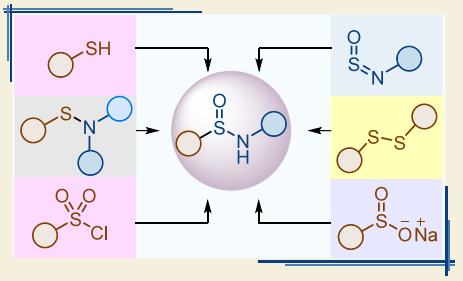
ABSTRACT: Sulfinamides constitute adaptable S(IV) intermediates with a sulfur stereocenter, having emerging interest in divergent synthesis of high-valent S(VI) functional bioisosteres. Recent years have witnessed the strategic development of mild and selective synthetic routes for highly functionalized sulfinamides, employing stable organometallic reagents, carbon-centered radical precursors, and other abundant coupling partners merged with various sulfur reagents in the arena of metal, photoredox, and organocatalysis. Furthermore, asymmetric metal and organocatalysis have enabled the stereoselective synthesis of enantioenriched sulfinamides. In this Perspective, we present the recent (2021 to present) advancement of various synthetic methods toward sulfinamides.



KEYWORDS: *Sulfur chemistry, Sulfinamides, Asymmetric synthesis, Photocatalysis, Metal catalysis*

1. INTRODUCTION

Sulfur-derived functional groups are prolifically introduced in pharmaceutical drugs, agrochemicals, foodstuffs, polymers, among others, relying on the variable oxidation states of sulfur.[1] In a survey in 2021, 28% of the top-selling 200 small-molecule pharmaceutical drugs contain sulfur as an element, thus highlighting its critical role in modern drug development.[2] In this regard, as a versatile S(VI) functionality, the sulfonamide moiety prevalent in drugs (e.g., Celecoxib, Sulfamethazine, Sulfadiazine, Chlorthalidone) that are used to treat numerous diseases and syndromes.[1,3,4] Sulfonamides are further valued for their flexibility and usefulness in various chemical transformations.[1] In parallel, sulfoxide as a S(IV) functional group is omnipresent in several marketed drugs (e.g., Pantoprazole, Sulfinpyrazone, Modafinil), flavors, fragrances, and commodity chemicals (Figure 1).[5] Furthermore, enantioenriched sulfoxides serve as chiral ligands, auxiliary ligands, as well as important synthetic building blocks in asymmetric organic synthesis (Figure 1).[5] Bioisosterism is an elegant strategy employed by medicinal chemists to modify lead compounds in a rational way, transforming them into safer and more clinically effective drugs.[6] Notably, sulfinamide has emerged as an amide bond bioisostere and transition state analog in the medicinal chemistry forum, especially in the form of peptidosulfinamides, having enhanced chemical stability, altered metabolic pathways, or improved pharmacokinetic profiles, among others.[7]

In a simplified retrosynthetic analysis, sulfinamide scaffolds are majorly accessed via effective construction of C−S, N−S, or S−O bond(s), using well-defined sulfur synthons, as depicted in Figure 2. The reaction of organometallic reagents including organo-lithium, magnesium, or zinc reagents as carbon nucleophiles or stable carbon-centered radical precursors with sulfur-based reagents (e.g., *N*-sulfinylamines) has been disclosed for versatile syntheses of sulfinamides via C−S bond formation.[8] Alternatively, selective S−N bond formation of sulfur building blocks, such as thiols, disulfides, sulfinyl chlorides, or sulfinate derivatives, among others, has emerged as an enabling technique to deliver distinctly substituted sulfinamides.[9] Moreover, catalytic oxidation of sulfenamides in a controlled manner is an alternative route to sulfinamides.[10]

Intriguingly, sulfinamides having an intermediate oxidation state S(IV) have expediently been transformed to a multitude of important S(VI) functional groups in divergent synthesis (Figure 3). Specifically, the mild oxidation of sulfinamides delivers corresponding sulfonamides and chiral sulfonimidamides as a monoaza variant of sulfonamides.[11] Notably, sulfonamides serve as well-known H-bond acceptors whereas sulfoximines and sulfonimidamides exhibit H-bond donor as well as acceptor abilities alongside the existence of chirality.[12] Additionally, sulfonimidoyl fluorides as aza-analogs of sulfonyl-fluorides have received ample attention as a SuFEx reagent in

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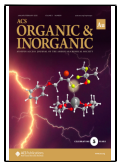

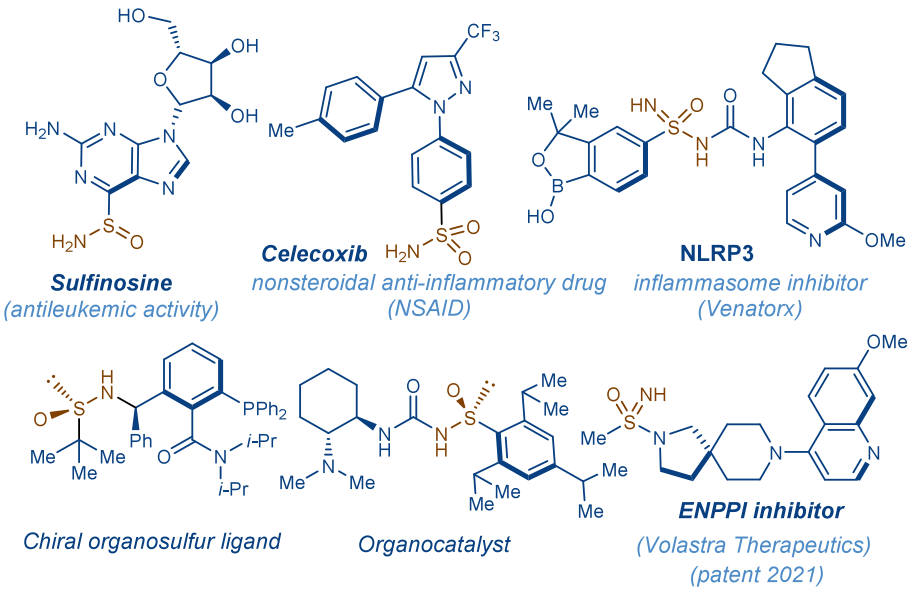

Figure 1. Prevalence of the S(IV) and S(VI) functionalities.

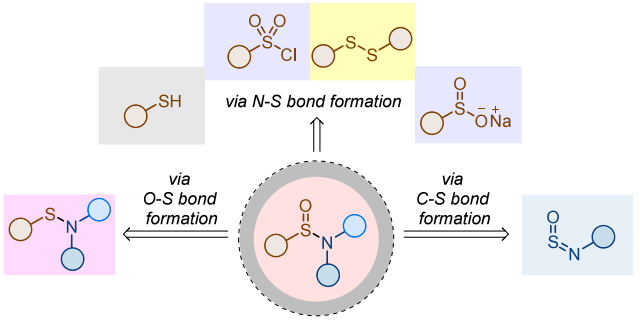

Figure 2. Different approaches toward sulfinamide synthesis.

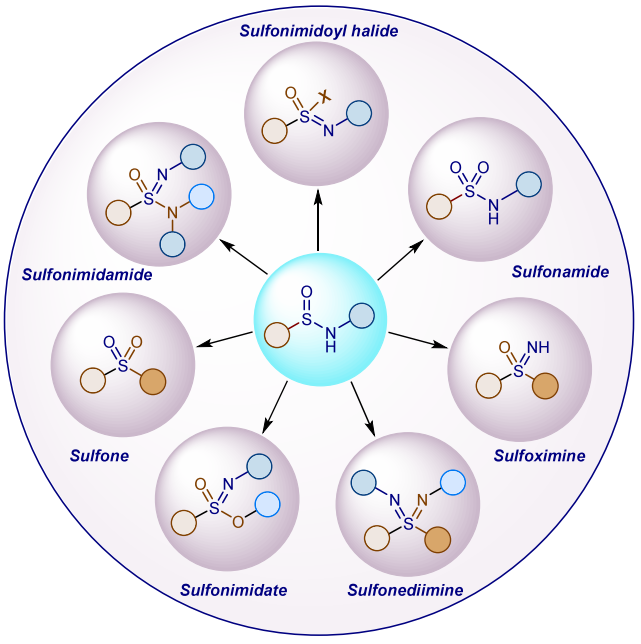

Figure 3. Diversification of S(IV) sulfinamides to other S(VI) functionalities.

accessing unstable and toxic sulfonimidoyl chlorides via halogen exchange.[13] Nevertheless, other S(VI) functional groups, including sulfones, sulfonediimines, and sulfonimidates, have also appeared in the limelight, rendering widespread applications.[14]

While the traditional methods allowed access to S(IV) and S(VI) compounds,[9] however, they often demand for harsh reaction conditions, such as cryogenic temperatures, and utilization of sensitive and/or pyrophoric reagents. This limits their adaptability to complex molecular architectures with functional group compatibility and confines their utility to relatively simple substrates. Hence, the development of mild and more versatile synthetic strategies is essential for advancing bioisosteres of sulfur functionality, enhancing their flexibility, expanding their application, and fostering innovation in the design of novel compounds. In this Perspective, we present the recent development of synthetic strategies for versatile sulfinamides in particular, collating the reports published since 2021. The scope of other sulfur functionalities is beyond the scope of this Perspective and have been reviewed elsewhere.[15]

2. SYNTHETIC STRATEGY FOR SULFINAMIDES

2.1. Sulfinamide Synthesis from Sulfinylamines

Earlier, in 1920s, Gilman and Morris disclosed the synthesis of sulfinamides by direct reaction of organomagnesium reagents with *N*-sulfinylamines.[16] The strategy remained dormant for several decades. Over the last 10 years, various groups have contributed to the synthesis of sulfinamides, employing organometallic reagents coupled with *N*-sulfinylamines. Despite the challenges of utilizing unstable *N*-sulfinylamines,[17] the Willis group has enormously contributed to developing stable, yet reactive, *N*-sulfinylamines reagents tuned by sterics and electronics.[18] The utilization of these stable reagents offers synthetic flexibility and convenience for preparation and easy-handling. In this regard, recently, Saito has also reported a bench stable "SO" donor reagent to treat with Grignard reagents, releasing sulfinates that subsequently converted to primary, secondary, and tertiary sulfinamides upon reacting with amines under oxidative conditions.[19]

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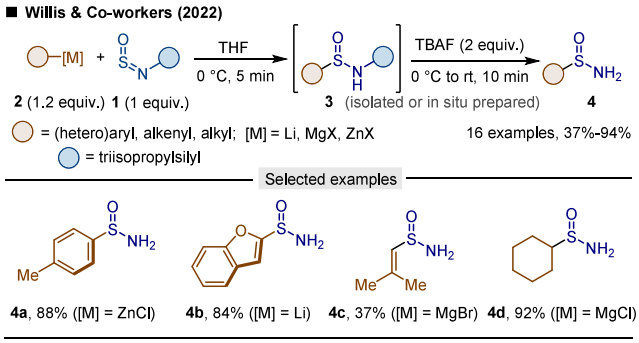
In 2022, the Willis group introduced *N*-triisopropylsilyl sulfinylamine (TIPS-NSO, **1**) with optimal reactivity and stability toward the synthesis of primary sulfinamides upon silyl deprotection under acid- or base-free conditions.[20] Various organometallic reagents, including organolithium, organomagnesium, and organozinc reagents, promptly reacted with TIPS-NSO at 0 °C in THF to deliver *N*-silylsulfinamide (**3**) that was directly converted to primary sulfinamides (**4**) upon desilylation with tetrabutylammonium fluoride (TBAF) (Scheme 1). This reagent enables the rapid synthesis of

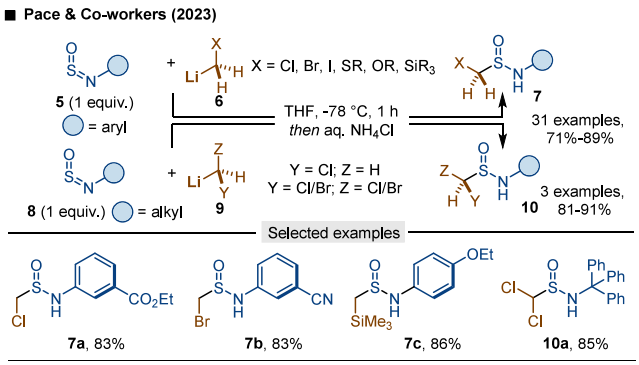
Scheme 1. Synthesis of Sulfinamides from Silyl Sulfinylamine and Organometallic Reagents



distinctly substituted (hetero)aryl, alkenyl, and alkyl primary sulfinamides that are amenable to the synthesis of sulfonimidamides.

Recently, Pace and co-workers described the preparation of α-substituted sulfinamides by the homologation of nucleophilic LCH_2X (**6**) or LCHYZ (**9**) reagents with electrophilic *N*-sulfinylamines (**5**, **8**) in THF at −78 °C for 1 h (Scheme 2).[21]

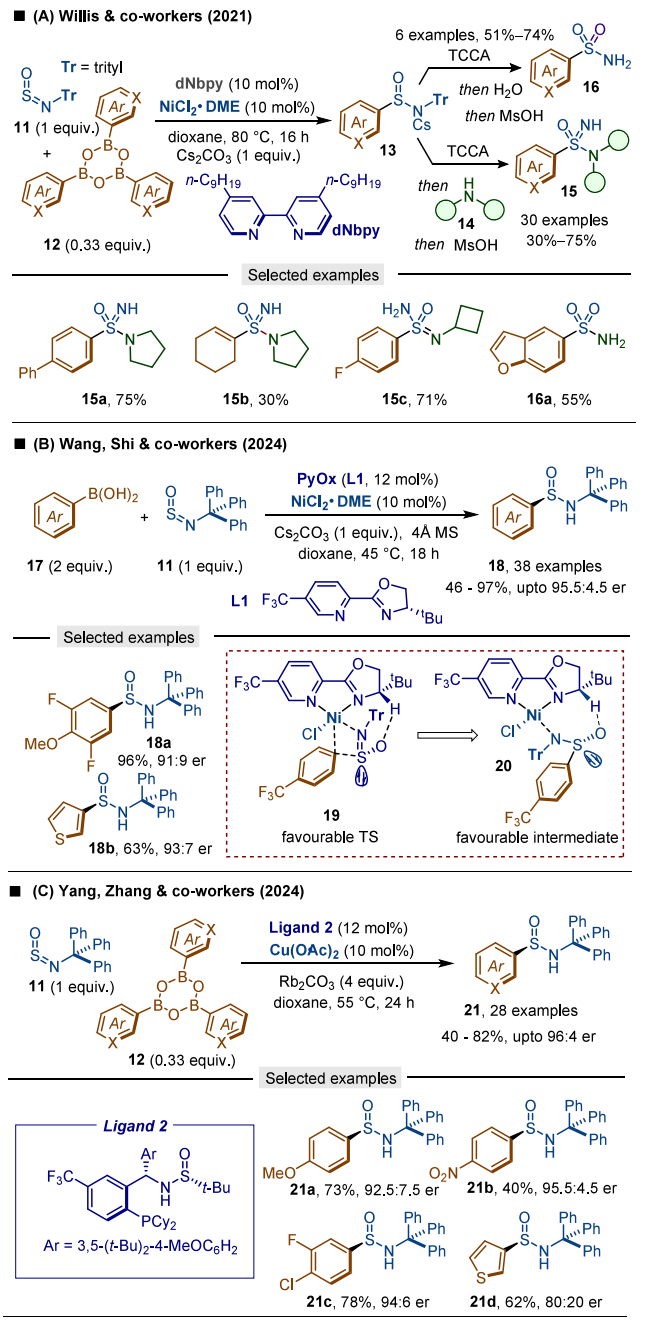
Scheme 2. Synthesis of α-Substituted Sulfinamides by Homologation of Organolithium with *N*-Sulfinylamines



The method is well-accommodating of numerous sensitive functional groups with high chemoselectivity. As described by the authors, the steric or/and electronic influences of substituents on the nitrogen center are insignificant due to the high electrophilicity of the sulfur center. The optimal amount of lithium carbenoid reagent was required for achieving high efficiency when its lower amount encouraged the formation of methyl sulfinamide as a side product. The cryogenic temperature (−78 °C) was somewhat essential because the reaction efficiency deteriorated upon raising the reaction temperature (to −50 °C). As mentioned by the authors, Barbier-type conditions are necessary for lithium carbenoid, likely due to its inherent instability. Nucleophilic magnesium carbenoid reagents remain ineffective in this transformation.

In contrast to the direct addition of reactive organolithium, magnesium, or zinc reagents, in 2021, Willis and co-workers reported redox-neutral Ni(II)/bipyridine-catalyzed (hetero)-aryl and alkenyl boroxines (**12**) addition to *N*-sulfinyltritylamine (TrNSO) (**11**) at 80 °C in the presence of Cs_2CO_3 base, en route to sulfinamides (**13**) that are in situ converted to sulfonamides (**16**) and sulfonimidamides (**15**) upon oxidative treatment (Scheme 3A).[11] A plethora of diversely substituted sulfonimidamides and sulfonamides were obtained in good yields with broad functional group tolerance. Notably, the

Scheme 3. Synthesis of Sulfinamides, Sulfonimidamides, and Primary Sulfonamides from Organoboron Reagents and *N*-Sulfinylamines Enabled by Ni and Cu Catalysis



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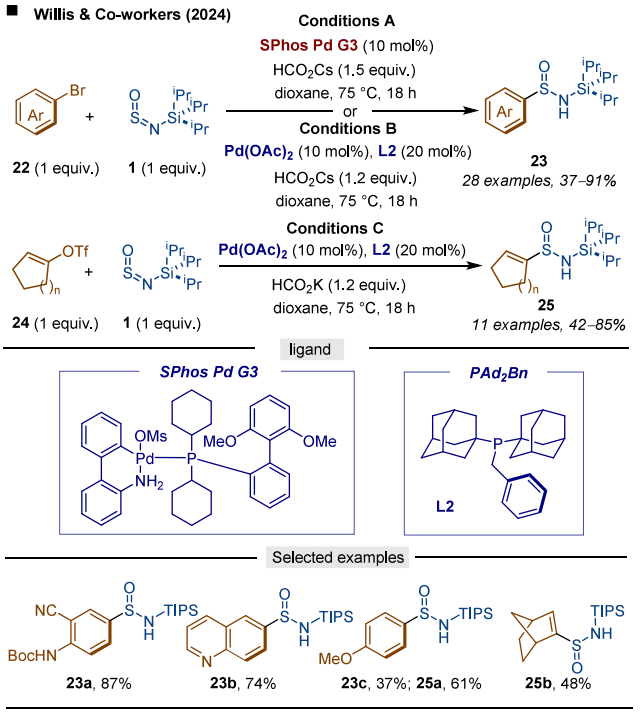
utilization of (hetero)aryl boroxines, instead of boronic acids, was critical for higher reaction efficiency, because *N*-sulfinylamine is hydrolyzed by water, generated upon trimerization of aryl boronic acids. Also, aryl trifluoroborates or boron pinacol esters remained inefficient in this transformation. Indeed, this is a landmark report on the usage of readily available, stable, and operationally simple organometallic reagent, such as organoboron reagent.

In 2024, Wang, Shi, and co-workers established a modular and efficient method for synthesizing a broad array of S-chirogenic sulfinamides *via* asymmetric addition of arylboronic acid (**17**) to *N*-sulfinyltritylamine (**11**) (Scheme 3B).[22] A nickel catalyst supported with enantiopure PyOx ligand (**L1**), in the presence of Cs_2CO_3 base and 4 Å molecular sieves at 45 °C achieved remarkable enantioselectivity in this transformation. A large variety of (hetero)aryl boronic acids could be employed with excellent functional group compatibility, resulting in various aryl sulfinamides in good yields and high enantioselectivity. The bulky substituent on the nitrogen atom was essential for high conversion and enantioselectivity, and it allows for the incorporation of diverse arylboronic acids at the sulfur center. As the authors demonstrated, aryl boronic acid is more effective than the corresponding boroxine. Additionally, aryl boronic acid with a *para*-electron-withdrawing group reacts faster than that containing a *para*-electron-donating group, underscoring the enhanced Lewis acidity of boron or negative charge stabilization during transmetalation. From DFT calculations, the migratory insertion of N=S bond to PyOx ligand-bound Aryl-Ni species is crucial step for determining enantioselectivity. As described by the authors, the hydrogen-bonding interaction between the oxygen atom of the sulfoxide group and C−H bond of the oxazolidine backbone of the chiral ligand (**L1**) plays a crucial role for stabilizing the transition state (**19**) and corresponding intermediate (**20**) for the *R*-enantiomer in the reaction mechanism. Concurrently, in 2024, Yang, Zhang, and co-workers reported the successful development of a well-developed Sadphos ligand-enabled copper-catalyzed asymmetric addition of boroxines to sulfinylamines, leading to the synthesis of a diverse range of chiral sulfinamides (Scheme 3C).[23]

In 2024, the group of Willis disclosed Pd-catalyzed reductive C−S coupling of different (hetero)aryl bromides (**22**) and alkenyl triflates (**24**) with *N*-triisopropylsilyl sulfinylamine (**1**) in the presence of HCO_2Cs as the reductant to deliver (hetero)aryl and alkenyl sulfinamides (**23**, **25**) in good yields and with excellent functional group compatibility (Scheme 4).[24] Electron-deficient (hetero)aryl bromides were conveniently transformed to (hetero)aryl sulfinamides reacting with *N*-triisopropylsilyl sulfinylamine in the presence of the preformed SPhos Pd G3 catalyst in 1,4-dioxane at 75 °C for 18 h. It was noted by the authors that the SPhos Pd G3 catalyst was less efficient for electron-rich and even electron-neutral aryl bromides. Notably, the combination of $Pd(OAc)_2$ and di(1-adamantyl)benzyl phosphine (**L2**) with a reduced amount of reductant enabled the authors to efficiently prepare aryl sulfinamides from electron-rich and neutral aryl bromides. Moving further, the group extended the substrate scope to cyclic alkenyl triflates reacting with *N*-triisopropylsilyl sulfinylamine (**1**) where $Pd(OAc)_2$ and di(1-adamantyl)benzyl phosphine (**L2**) remained effective catalyst in the presence of HCO_2K as a reductant, instead of HCO_2Cs. As demonstrated by the authors, sulfinamides could be converted

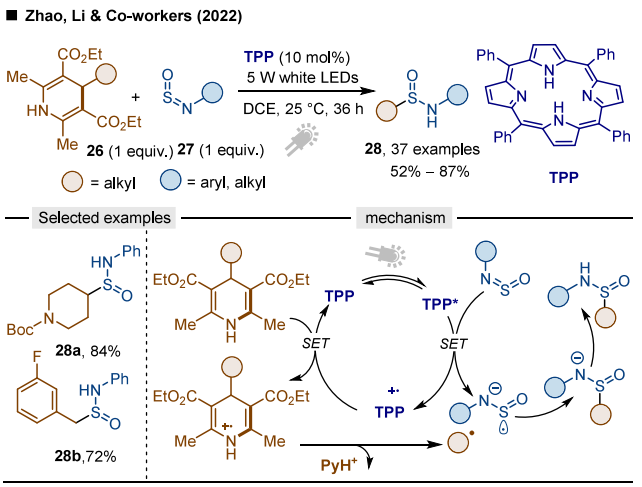
Scheme 4. Pd-Catalyzed Synthesis of Sulfinamide from Aryl Bromides



to various high valent sulfur functional groups via oxidative postmodifications.

Recently, in 2022, Zhao, Li and co-workers revealed an organo-photocatalyzed sulfinamide (**28**) synthesis utilizing 4-alkyl-1,4-dihydropyridines (**26**) as Csp^3 radical precursor, instead of nucleophilic organometallic reagents, and *N*-sulfinylamines (**27**) in the presence of commercially available *meso*-tetraphenyl chlorin (TPP) in 1,2-dichloroethane and light irradiation from white LEDs (Scheme 5).[25] Benzylic, secondary, and tertiary alkyl fragments were effectively incorporated into sulfinamides *via* C−S bond formation, and subsequently, sulfinamides were transformed to sulfonimidamides and sulfonimidate esters. In a mechanistic portrayal, *N*-sulfinylamine is reduced by photoexcited TPP* via single

Scheme 5. Photocatalytic Synthesis of Sulfinamides from 4-Alkyl-1,4-Dihydropyridines and *N*-Sulfinylamines



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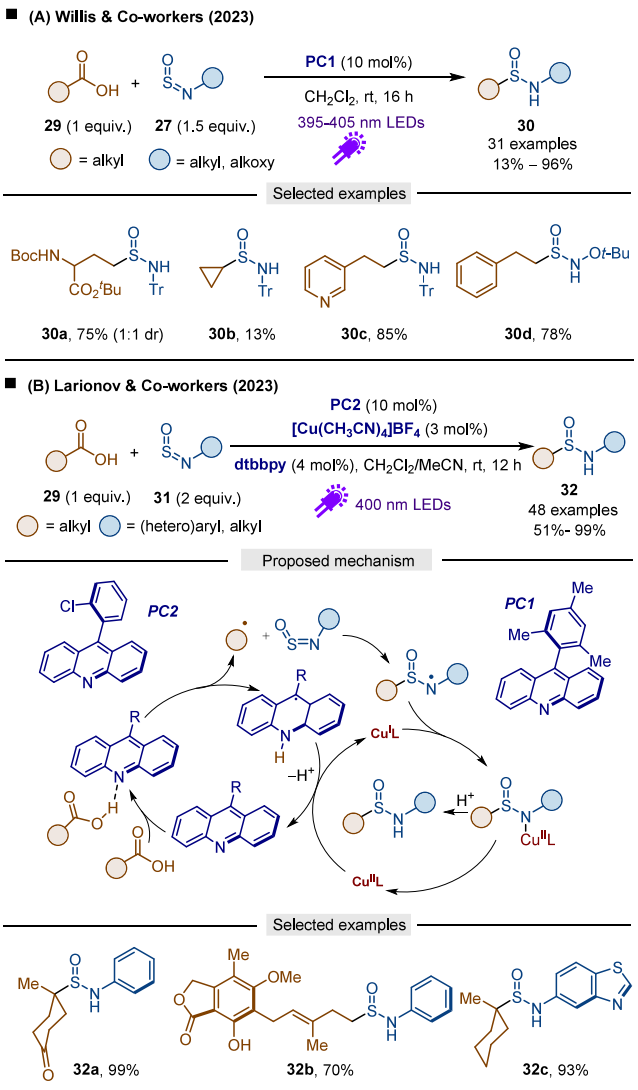
electron transfer. The so-formed $TPP^{+\bullet}$ enables single electron oxidation of DHP precursor to release alkyl radical alongside the regeneration of ground-state TPP. Lastly, the radical and radical anion combination delivers final sulfinamide following a protonation step (Scheme 5).

Later, in 2023, the Willis group and the Larionov group independently demonstrated a direct decarboxylative sulfinamidation of readily available aliphatic carboxylic acids with *N*-sulfinylamines via photoinduced proton-coupled electron transfer (PCET) in the presence of acridine as organophotocatalyst.[26,27] Willis et al. reported that the combination of aliphatic carboxylic (**29**) acid and acridine (**PC1**, 10 mol %) in dichloromethane under irradiation of 395−405 nm light led to the formation of sulfinamides (**30**) (Scheme 6A).[26] In this

Scheme 6. Synthesis of Sulfinamides by PCET Decarboxylation of Carboxylic Acids



protocol, numerous aliphatic carboxylic acids, containing a multitude of sensitive functional groups, promptly reacted with *N*-sulfinyltritylamine (**27**) to afford a variety of alkylsulfinamides (**30**) with a trityl substituent. Nevertheless, the utilization of *N*-*O*-*t*-Bu-sulfinylamine in this reaction enables the smooth conversion of so-formed *N*-alkoxy sulfinamides to sulfonamides and various sulfonimidamides. Likewise, Larionov and co-workers developed a similar decarboxylative sulfinamidation of carboxylic acids via PCET in the presence of acridine (**PC2**, 10 mol %) and $[Cu(MeCN)_4]BF_4$/dtbbpy cocatalyst, illuminated with 400 nm light (Scheme 6B).[27] This method accommodated a variety of (hetero)aryl- and alkyl-substituted *N*-sulfinylamines (**31**) alongside highly functionalized carboxylic acids (**29**). A plethora of drug candidates was explored to exchange carboxylic acid functionality with sulfinamide in both the protocols. From a mechanistic standpoint, shown in Scheme 6B, photoinduced PCET of hydrogen-bonded acridine and carboxylic acid adduct furnishes alkyl radical upon CO_2 extrusion. Later, the radical addition to *N*-sulfinylamine forms an aminosulfinyl radical that is reduced by Cu(I) complex and further stabilized as a Cu(II) complex. Finally, SET between Cu(II) complex and acridinyl radical liberates sulfinamide product, regenerating Cu(I) catalyst.

While in the previous reports, (hetero)aryl organoboron reagents were elegantly investigated for the synthesis of (hetero)aryl sulfinamides and corresponding S(VI) congeners, organoboron reagents remained unexplored. In 2024, the group of Li and Zhang and the Sahoo group independently studied on aliphatic organotrifluoroborate salts for photocatalytic C−S coupling with *N*-sulfinylamines toward the synthesis of alkylsulfinamides.[28,29] In this regard, Sahoo et al. demonstrated a metal-free, mild, and efficient photocatalytic technique for the synthesis of diverse alkyl sulfinamides (**28**) from organotrifluoroborate salts (**33**) and *N*-sulfinylamines (**27**) using Fukuyama's acridinium dye as organophotoredox catalyst in dichloromethane under visible light irradiation from blue LEDs (Scheme 7A). In this protocol, *N*-sulfinylamines derived from electron-rich, electron-poor, and sterically encumbered aromatic amines and also aliphatic amines consistently delivered sulfinamides in excellent yields and exceptional functional group tolerance.

Additionally, structurally and functionally diverse primary, secondary, and tertiary alkyltrifluoroborates were successfully transformed to corresponding sulfinamides. The authors illustrated a regiodivergent as well as site-selective synthesis of sulfinamides by converting alkenes into alkyltrifluoroborate salts and subsequent sulfinamidation with *N*-sulfinylamines (Scheme 7A). Mechanistically, the reaction proceeds through a redox-neutral radical-polar pathway, involving C-centered radical formation upon single electron oxidation of organoboron reagent, radical addition, and last reduction event to release product (Scheme 7A). Zhang, Li and co-workers reported a similar synthetic method, engaging organotrifluoroborates (**37**) with *N*-sulfinylamines (**38**) in the presence of acridinium dye in 1,2-dichloroethane under visible light irradiation from white LEDs (Scheme 7B). The protocol effectively employed both alkyl and aryl trifluoroborates with various *N*-sulfinylamines to deliver various sulfinamides (**39**), showcasing a good functional group tolerance.

In 2024, Wei, Hu, and co-workers described a direct sulfinamidation of inert $C(sp^3)$−H bond of alkanes (**40**) via light-promoted ligand-to-metal charge transfer (LMCT) and hydrogen atom transfer (HAT) in the presence of $FeCl_3$ catalyst and 390 nm LEDs (Scheme 8).[30] A variety of aromatic and aliphatic amine-derived *N*-sulfinylamines (**35**) were successfully converted to sulfinamides (**41**). When cycloalkanes of different ring sizes were transformed to sulfinamides in a single isomer; however, bicyclic and acyclic alkanes delivered the products with moderate regioselectivity. Mechanistically, described in Scheme 8, photoexcited

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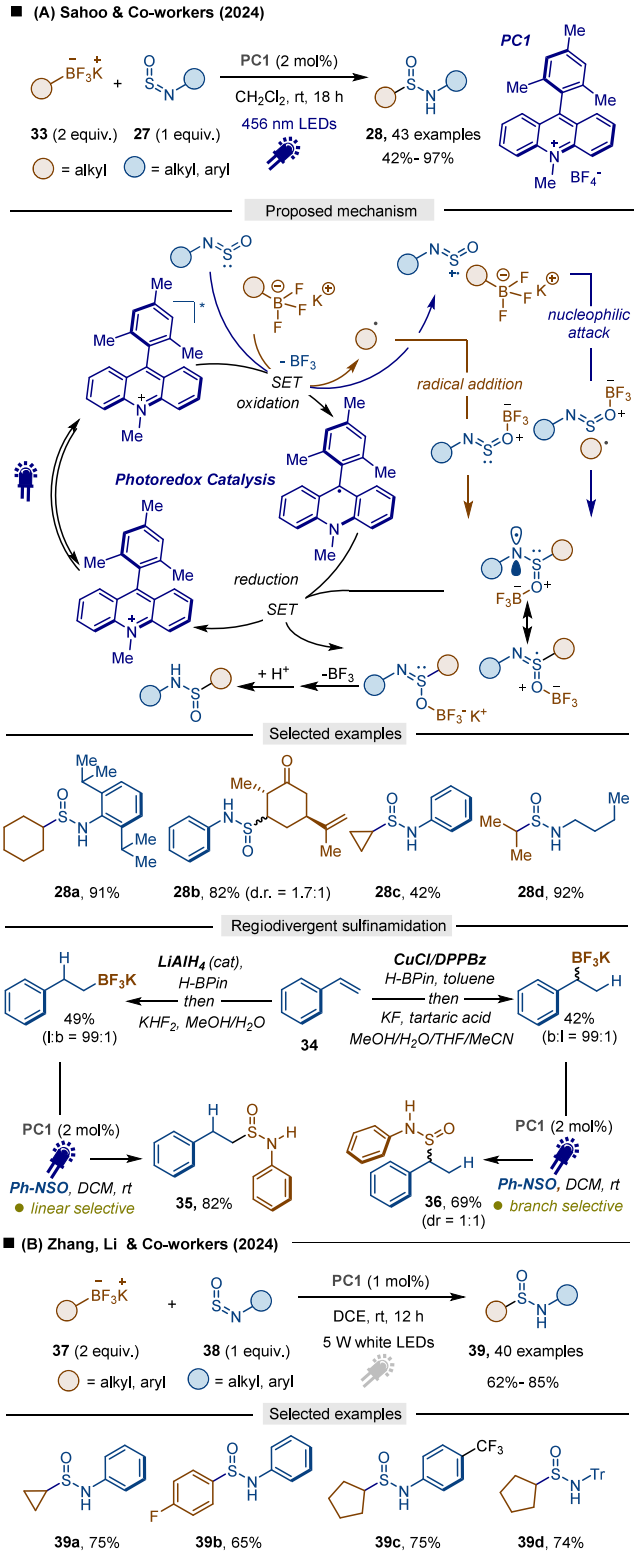
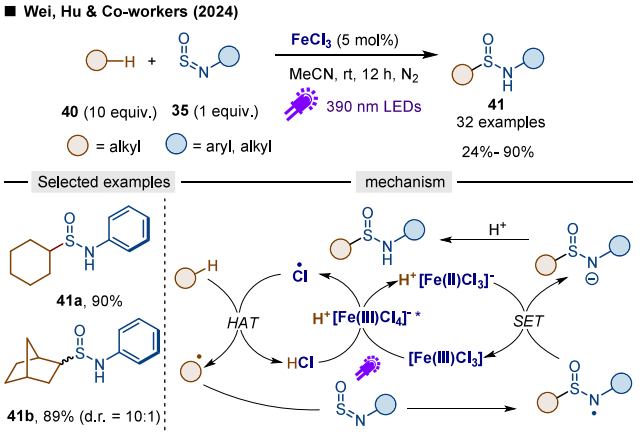
Scheme 7. Photocatalytic Synthesis of Sulfinamides from Potassium Alkyltrifluoroborates and *N*-Sulfinylamines

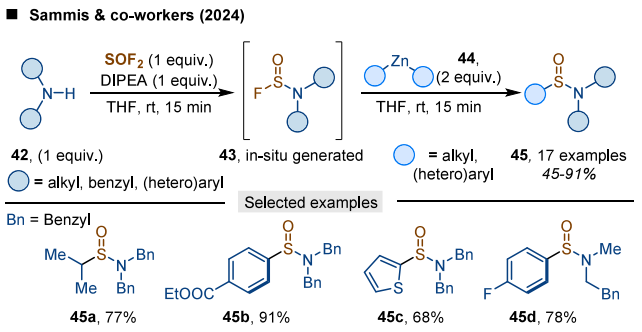


Scheme 8. C−H Sulfinamidation of Alkanes by Light-Mediated Iron Catalysis



In 2024, Sammis and co-workers introduced a rapid and efficient method for synthesizing sulfinamides (**45**) via SuFEx. This reaction employs secondary amine (**42**), thionyl fluoride (SOF_2), and organozinc reagent (**44**) under ambient conditions, achieving high efficiency (Scheme 9).[31] In this

Scheme 9. Synthesis of Sulfinamides from Secondary Amine, SOF_2, and Organometallic Reagents



method, the reaction of thionyl fluoride and a secondary amine generates an amino sulfinyl fluoride intermediate (**43**), which is subsequently intercepted by an organozinc reagent to furnish the sulfinamide (**45**). As mentioned by the authors, strong nucleophiles such as Grignard reagents and organolithium compounds were inferior in this protocol, predominantly leading to the inevitable formation of sulfoxides as the major product.

In 2024, the Gao group reported palladium-catalyzed [3 + 2] annulation reaction involving *N*-sulfinylanilines (**48**) with vinyl epoxides (**46**) and vinylethylenecarbonates (**47**) toward 1,2,3-oxathiazolidine-2-oxides. This transformation utilizes $Pd_2(dba)_3$ as the catalyst and DPEphos as the ligand, with potassium methoxide as the base, operating under mild conditions (Scheme 10).[32] Mechanistically, the vinyl motif was crucial for the reaction, as it enabled the formation of the key allylic palladium intermediate with pendant alkoxide, which is essential for subsequent nucleophilic addition (Scheme 10). Hence, a nucleophilic attack on *N*-sulfinylaniline by an internal alkoxide generates a nitrogen-centered anion that subsequently undergoes a conjugate addition at the allylic position. Lastly, the formation of the final product regenerates the palladium catalyst for catalytic turnover.

$[Fe^{III}Cl_3]$* upon 390 nm light irradiation generates a chlorine radical and $Fe^{II}Cl_2$ via LMCT. Subsequently, an alkyl radical is formed via HAT between a chlorine radical and Csp^3−H bond. Later, the alkyl radical undergoes addition to *N*-sulfinylamine and reduction with $Fe^{II}Cl_2$ followed by protonation provide sulfinamide, regenerating the Fe(III) species.

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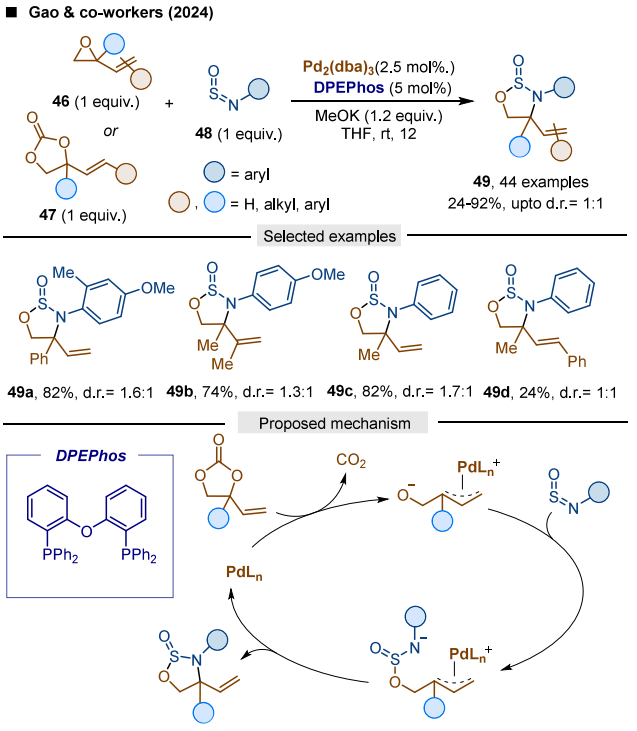
Scheme 10. Palladium-Catalyzed [3 + 2] Annulation Reaction Involving *N*-Sulfinylanilines with Vinylethylenecarbonates and Vinyl Epoxides



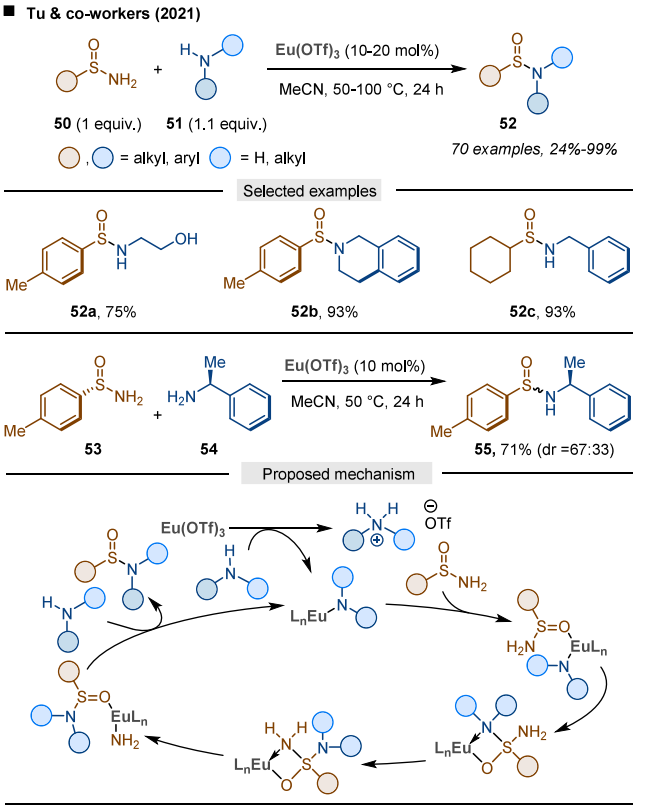
2.2. Sulfinamide Synthesis via Transsulfinamidation

Similar to transamidation of amides, the transsulfinamidation of sulfinamides with various amines represents an elegant, straightforward strategy, yet much less exploited, to furnish a diverse set of *N*-functionalized sulfinamides. In 2018, Bolm and co-workers developed a practical and efficient method for synthesizing secondary and tertiary sulfinamides via transsulfinamidation of primary sulfinamides.[33]

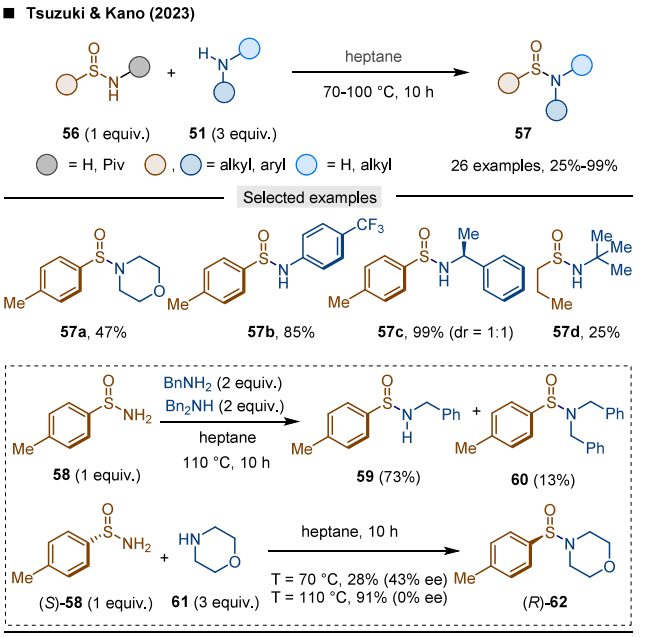
In 2021, the Tu group described a Lewis acid-catalyzed transsulfinamidation of primary sulfinamides (**50**) with alkyl and aryl amines (**51**) for streamlined synthesis of distinctly functionalized secondary and tertiary sulfinamides (**52**) in high yields (Scheme 11).[34] In this method, primary aryl sulfinamides were smoothly converted to secondary and tertiary aryl sulfinamides in the presence of $Eu(OTf)_3$ (10 mol %) in MeCN at 50 °C; however, less nucleophilic arylamines as well as primary aliphatic sulfinamides required higher catalyst loading of $Eu(OTf)_3$ (20 mol %), yet achieving moderate efficiency. As demonstrated by the authors, the employment of (*S*)-1-phenylethylamine (**54**) as nucleophile with the (*S*)-4-tolylsulfinamide (**53**) electrophile resulted in a mixture of diastereomers. The authors further elaborated that amine binds relatively stronger than primary sulfinamide to Eu(III)-Lewis acid, as analyzed by ^{1}H NMR spectroscopy. As proposed, mechanistically, the reaction proceeds *via* a four-membered amine and sulfinamide-chelated Eu(III) complex as a key intermediate (Scheme 11).

Recently, in 2023, Tsuzuki and Kano demonstrated a metal- and additive-free synthesis of secondary and tertiary sulfinamides (**57**) in decent-to-high yields from *N*-substituted or unsubstituted sulfinamides (**56**) *via* transsulfinamidation in nonpolar heptane solvent at variable temperature (70−110 °C) (Scheme 12).[35] A large number of primary and secondary

Scheme 11. Europium-Catalyzed Transsulfinamidation of Primary Sulfinamides with Amines



Scheme 12. Metal- and Additive-Free Transsulfinamidation of Sulfinamides with Amines



amines (**51**) were successfully employed in this transsulfinamidation, despite the limitation on the sulfinamide substrate. As described by the authors, a competition experiment using a 1:1 mixture of benzylamine and dibenzylamine resulted in the formation of secondary sulfinamide **59** as the major product and tertiary sulfinamide **60** as the minor

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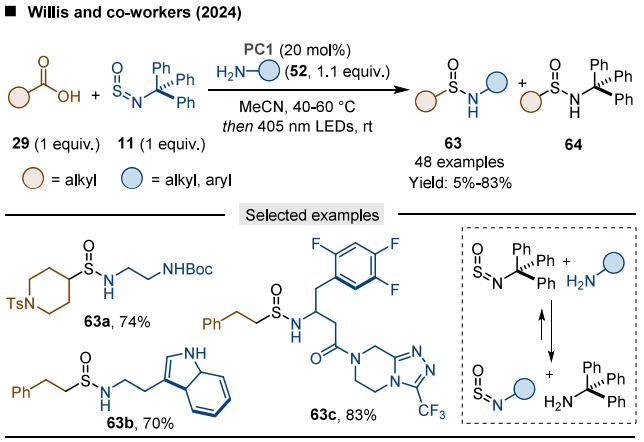
product, thus indicating rapid reaction with a sterically less hindered primary amine compared to secondary amine. The reaction of an enantiopure (*S*)-sulfinamide (*S*-**58**) with achiral secondary amine (**61**) delivered a transsulfinamidation product in partial or complete racemization, thereby suggesting a nucleophilic attack to the stereogenic "S(IV)" center of sulfinamide.

Very recently, in 2024, Willis and co-workers adopted a unique trans-sulfinylation strategy to address the challenge associated the preparation and isolation of aliphatic *N*-sulfinylamines due to hydrolytic instability, where numerous highly functionalized *N*-alkyl sulfinamides (**63**) were synthesized utilizing diverse primary amines (**52**) and aliphatic carboxylic acids (**29**) (Scheme 13).[36] In this protocol, a bench-

Scheme 13. Decarboxylative Sulfinamidation of *N*-Sulfinylamines via *trans*-Sulfinylation

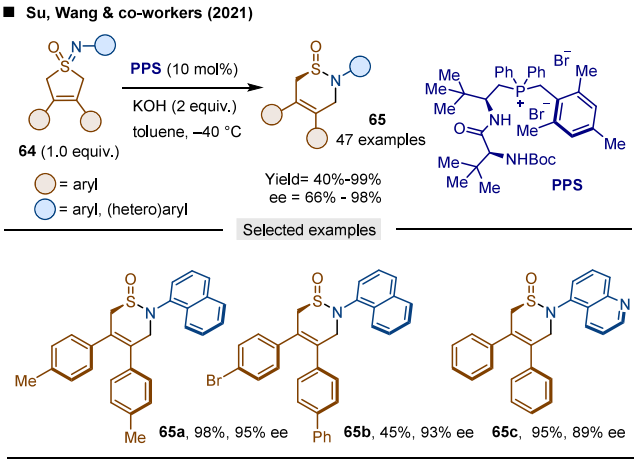


stable *N*-sulfinyltritylamine along with a primary amine was used to in situ prepare alkyl or aryl *N*-sulfinylamine in equilibrium that later engages in decarboxylative alkylation via photoinduced PCET to furnish *N*-alkyl or arylsulfinamide. A plethora of primary amines as well as carboxylic acids were transformed to distinctly functionalized sulfinamides, tolerating various functional groups. As described by the authors, a pre-equilibrium between *N*-sulfinyl tritylamine and alkyl or arylamine in acetonitrile at 60 °C is established prior to the decarboxylative alkylation event.

2.3. Conversion of Sulfoximines to Sulfinamides

The reduction of S(VI) sulfoximines to S(IV) sulfinamides via skeletal reorganization is exemplified as a direct and target-specific synthetic approach. Recently, in 2021, Su, Wang, and co-workers described an organocatalytic desymmetrization of prochiral cyclic sulfoximines or kinetic resolution of racemic cyclic sulfoximines (**64**) to cyclic sulfinamides (**65**) in high yields and enantioselectivity, using a highly tunable peptide mimic phosphonium salt (PPS) as a chiral catalyst (Scheme 14).[37] As demonstrated by the authors, enantioselective reorganization of sulfoximines to sulfinamides involves two distinct steps, such as ring-opening of cyclic sulfoximines via high energy demanding C−S bond cleavage leading to the formation of an anionic intermediate that is captured inside the chiral pocket of PPS catalyst via H-bonding and ion-pair interaction and subsequent asymmetric ring-closing of the so-formed anionic intermediate forming a C−N bond to deliver enantioenriched cyclic sulfinamides. The *N*-aryl substituent was critical for the stability and reactivity of sulfoximines.

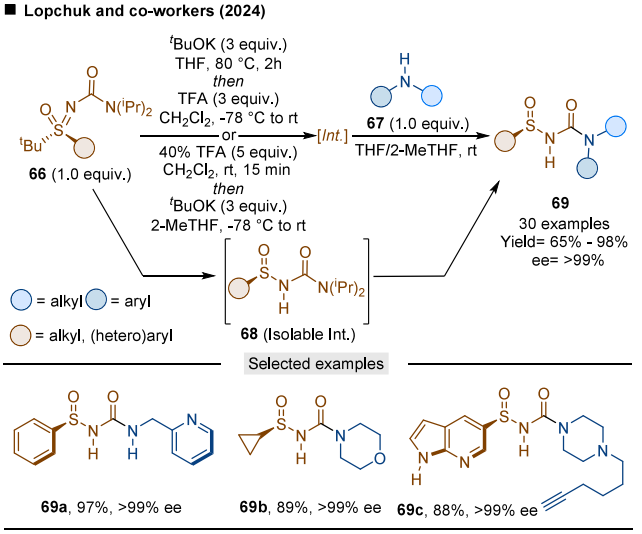
Scheme 14. Skeletal Reorganization of Sulfoximine to Sulfinamides by Peptide-Mimic Phosphonium Catalysis



Symmetric sulfoximines with various aryl moieties, including both electron-donating and -withdrawing groups at different positions, were well-tolerated, affording sulfinamides in good to excellent yields and enantioselectivity.

Very recently, in 2024, Lopchuk and co-workers developed a chiral pool method for converting enantioenriched *tert*-butyl sulfoximines to enantioenriched sulfinyl ureas in two consecutive steps via an activated sulfinyl urea intermediate. In this process, a chiral sulfoximine (**66**) is thermally activated by potassium *tert*-butoxide followed by trifluoroacetic-acid-mediated neutralization to generate activated sulfinyl urea intermediate (**68**) which is convertible to various sulfinyl ureas (**69**) by amine exchange (Scheme 15).[38] The bulky *N*,*N*-

Scheme 15. Synthesis of Stereogenic S(IV) Center via Amine Exchange of Sulfinyl Urea



diisopropyl group attached to the carbamoyl group in **68** promotes efficient amine exchange due to strain in the amide bond. As reported by the authors, room temperature or 60 °C favored the stereogenic control whereas a prolonged heating at 80 °C caused a decrease in sulfur stereogenicity mostly for *secondary* and *tertiary* sulfinyl urea derivatives. Various primary and secondary amines, including pharmaceutical intermediates

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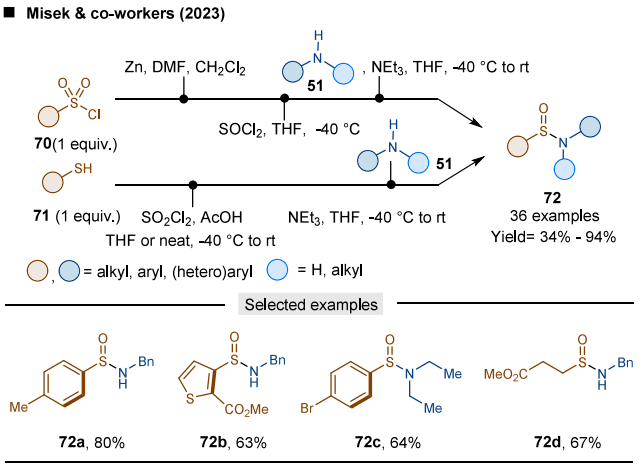
successfully furnished the final products conserving enantiopurity.

2.4. Sulfinamide Synthesis from Thiols and Its Derivatives

In 2007, Harmata and co-workers reported the synthesis of various sulfinamides from arylsulfonyl chlorides and primary and secondary amines using triphenylphosphine as the reductant and triethylamine base.[39] The method was limited to the utilization of aromatic sulfonyl chlorides. Recently, in 2023, Misek and co-workers developed a one-pot protocol for the efficient synthesis of diversely functionalized sulfinamides (**72**) from alkyl- and (hetero)arylsulfonyl chlorides (**70**) and amines using a Zn reductant and DMF additive in dichloromethane (Scheme 16).[40] In this process, sulfinate salts are

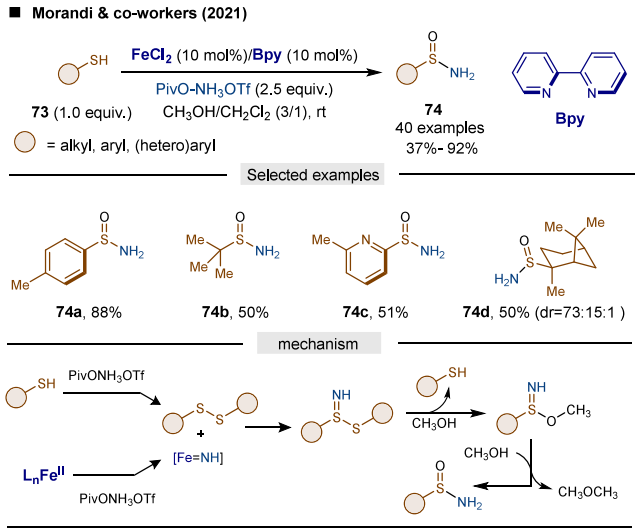
Scheme 16. Sulfinamide Synthesis from Sulfonyl Chlorides or thiols



formed by the reduction of sulfonyl chlorides with Zn, where DMF is used to improve the yield of sulfinates. Subsequently, sulfonates are converted to sulfinamides by thionyl chloride and triethylamine base and primary and secondary amines as nucleophile. In same report, the authors further described an oxidative protocol for sulfinamide synthesis, using thiols (**71**), in lieu of sulfonyl chlorides, and amines in the presence of sulfuryl chloride (Scheme 16).[40] Notably, an electron-rich heteroaryl substrate (e.g., thiophene) was employed in reductive conditions whereas electron-deficient heteroaryl substrates remained successful in oxidative conditions.

Recently, in 2021, Morandi and co-workers reported the direct synthesis of primary sulfinamides from free thiols (**73**) using a stable *O*-pivaloyl-protected hydroxylamine triflic acid salt as both the nitrogen source and oxidant, enabled by iron catalysis (Scheme 17).[41] As described by the authors, the combination of $FeCl_2$ and 2,2′-bipyridine in a methanol/dichloromethane mixture was suitable for the effective conversion of thiols to sulfinamides, where various electron-rich and electron-poor thiols participated well. Mechanistically, a disulfide intermediate is formed from thiol by oxidation with a hydroxylamine reagent. Later, the reaction of disulfide with the in situ formed iron-nitrene (Fe═NH) intermediate precedes the replacement of thiol with methanol to deliver sulfiximine ether. Finally, this highly reactive intermediate is rearranged to primary sulfinamide in the presence of a methanol solvent. Notably, the authors revealed the formation of both S═O and S−N bonds from the S−H bond. The electron-rich thiols afforded sulfinamides in slightly higher

Scheme 17. Iron-Catalyzed Synthesis of Sulfinamides from Thiols



yield due to facile reaction of disulfide with the electrophilic Fe═NH intermediate. In this context, it is worth-noting that Roschenthaler, Han, and co-workers reported a selectfluor-mediated oxidative synthesis of sulfinamides from aryl disulfides and secondary amines.[42]

In 2022, Shen, Cao, and co-workers described a visible light photoredox-catalyzed synthesis of sulfinamides from nitroarenes (**77**) and thiols (**76**) or disulfides (**75**) in the presence of $Ru(dmbpy)_3(PF_6)_2$ (2 mmol %) and Hünig base in DMSO (Scheme 18).[43] Mechanistically, a reductive quenching of photoexcited $Ru(dmbpy)_3(PF_6)_2$ with thiol generates disulfide and subsequently nitrosobenzene upon reduction with reduced photocatalyst. The nucleophilic addition of thiol to nitrobenzene, followed by hydroxyl elimination, results in a nitrenium intermediate that is captured by water to deliver sulfinamide. A variety of aromatic thiols and nitroarenes remain well-tolerated in this transformation with the survival of different functional groups. Notably, the electron-rich nitroarenes reacted better than the electron-deficient nitroarenes, furnishing sulfinamides in slightly higher yields.

As illustrated by the authors, electron-deficient nitroarenes undergo ready reduction to anilines without prolong survival of nitrosobenzenes that need to be reacted by thiol. In recent years, the group of Qin, Lan, and Yan and the group of Zhang and Tan independently reported organocatalytic enantioselective synthesis of sulfinate esters whereas asymmetric synthesis of sulfinamides in enantiopure form remained unsuccessful.[44,45] Very recently, in 2024, Tian, Xie, Guo and co-workers demonstrated an organocatalytic asymmetric sulfinylation of sulfinate salts (**79**) using a chiral 4-arylpyridine *N*-oxide (ArPNO) bifunctional catalyst which enabled access to enantioenriched sulfinamides (**81**) via an acyl transfer reaction (Scheme 19).[46] A bulkier chloroformate activator was utilized in the acryl transfer reaction of chiral pyridine *N*-oxide for the activation of sulfinate, forming a mixed anhydride, and its bulky substituent influences the nucleophilic attack of amine selectively to the stereogenic S(IV) center, instead of to the carbonyl carbon center. The presence of an amide N−H bond in chiral ArPNO (**C1**) plays a critical role in determining enantioinduction in the sulfinamide product. As described by the authors, the presence of a trace amount of water (10 mol

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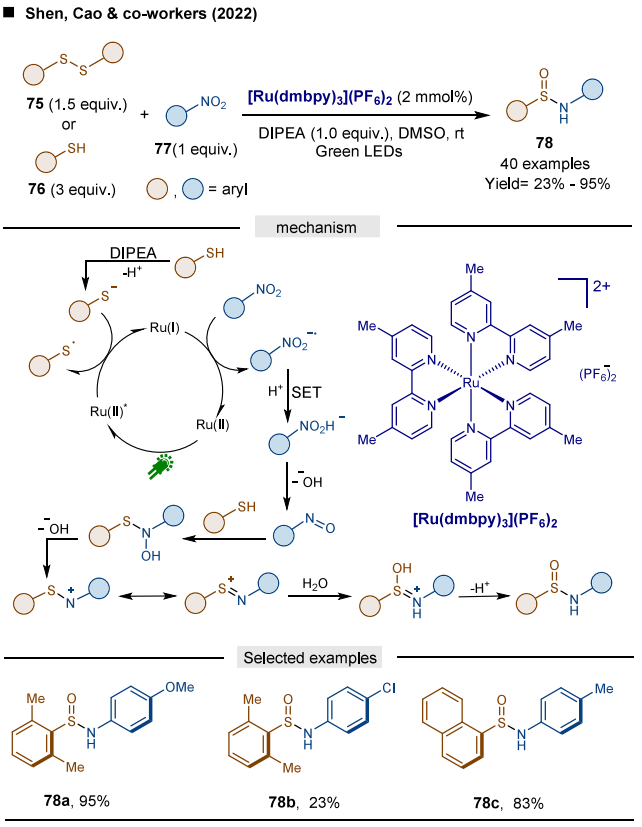
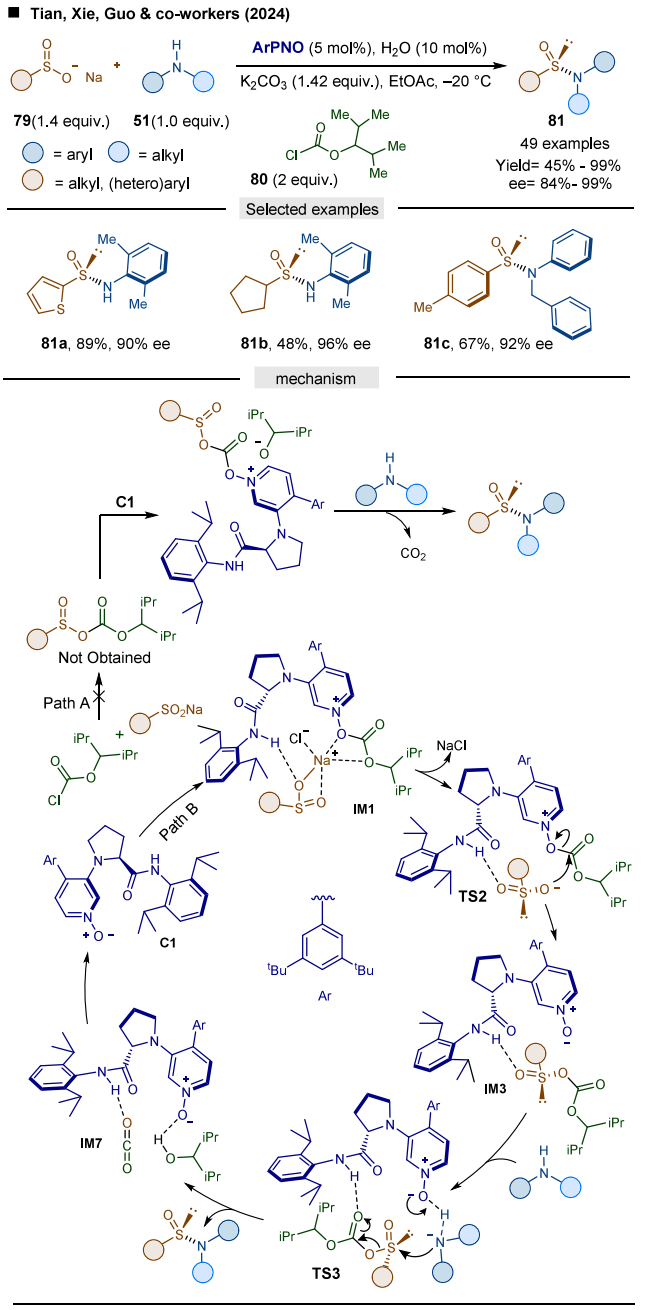
Scheme 18. Photocatalytic Synthesis of Sulfinamide Using Thiols/Disulfides and Nitroarenes



Scheme 19. Enantioselective Synthesis of Sulfinamides from Sulfonates Using ArPNO as a Bifunctional Catalyst



%) was vital for harnessing high enantioselectivity. A broad range of sodium salts of alkyl and (hetero)aryl sulfinates was employed, yielding chiral sulfinamides in good-to-excellent yields and high enantioselectivities. Substituted anilines provided the products in moderate to good yields and high enantioselectivity, while secondary amines consistently delivered sulfinamides with exceptional enantioselectivity.

3. SUMMARY AND OUTLOOK

Sulfinamide constitutes a key S(IV) intermediate with an S-center stereogenicity. Because of the chirality at the S(IV)-center, this motif presents paramount significance as a chiral auxiliary, organocatalyst, and supporting ligand in asymmetric synthesis. Furthermore, due to a lower S(IV) oxidation state, sulfinamides spontaneously respond to oxidative treatment, furnishing high-valent S(VI) functional bioisosteres. Achieving functional group compatibility and structural diversity remained restricted until the recent development of various catalytic synthetic methods that selectively function under milder conditions. In this Perspective, we have concisely summarized the recent development of various mild and selective synthetic methods using stable and less reactive organometallic reagents, radical precursors, and abundant coupling partners in the arena of metal, photoredox, and organocatalysis. The utilization of abundant and robust reagents in the synthesis of highly substituted sulfinamides under mild and ambient conditions still remains less explored and sets up an emerging trend in the arena of aza-sulfur chemistry. Despite a few recent reports, the full potential of stereoselective synthesis of sulfinamides has yet to be explored.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study is available in the published article.

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Author Contributions

The manuscript was written through contributions of all authors./All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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