Transition-Metal-Free and Redox-Neutral Strategy for Sulfilimines Synthesis *via* S-Arylation of Sulfenamides

Guoling Huang, Xunbo Lu*, Fangpeng Liang

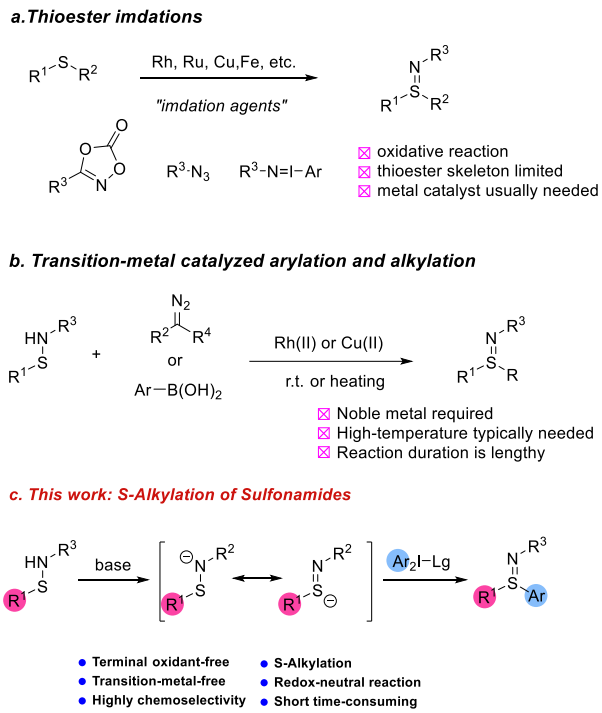
School of Chemistry and Chemical Engineering, Laboratory of Marine Green Fine Chemicals, Lingnan Normal University (LNU), 29 Cunjin road, Zhanjiang, 524048, P. R. China.

KEYWORDS: Redox-Neutral Synthesis, Sulfilimines, S-Arylation, Sulfenamides

ABSTRACT: In this investigation, an unprecedented transition-metal-free and redox-neutral synthesis of sulfilimines was realized through the S-arylation of readily obtainable sulfenamides employing diaryliodonium salts. The pivotal step encompassed the tautomerization between bivalent nitrogen-centered anions, engendered post-deprotonation of sulfenamides under alkaline conditions, and sulfinimidoyl anions. The experimental outcomes demonstrate that sulfinimidoyl anionic species function as efficacious nucleophilic reagents, affording sulfilimines with notable to exceptional yields and superlative chemoselectivity, all executed within a transition-metal-free protocol and under exceptionally mild conditions.

Sulfilimines, with their unique electronic and stereochemical properties, have generated significant scientific interest in recent years. [1] Their highly polarized structure, arising from a sulfur-nitrogen double bond, makes them an attractive option for synthesizing complex molecules and serving as directing groups and chiral auxiliaries in the fields of organic synthesis and materials science. [2] Sulfilimines have also attracted considerable interest in the field of biology, with the discovery of their biologically relevant role in collagen IV networks. [3] Additionally, Chang, Toste, and their team have introduced a groundbreaking method for methionine bioconjugation, demonstrating the potential of sulfilimines in biochemistry. [4] Moreover, the sulfoximine skeleton, which can be easily prepared by oxidizing the sulfilimine group, is a valuable group present in many medicinal molecules. [5] Therefore, there is a high demand for the development of efficient and reliable methods for synthesizing sulfilimines.

Oxidative amination of thioethers has long served as a cornerstone in the intricate assembly of thioimine architectures. Consequently, a myriad of structurally diverse amination reagents, encompassing azides, oxaziridines, sulfonamides, amides, carbamates, sulfamates, and others, have emerged in the past decades. [6] These advanced amination reagents are typically employed in tandem with compatible oxidants, such as hypervalent iodines, to facilitate oxidative amination processes.[7] Moreover, such methodologies often necessitate the utilization of noble or transition metal catalysts, including Rh, Ru, Cu, and the like, to achieve the desired reaction outcomes (Scheme 1a). [8] In recent years, the principles of green chemistry have gained significant attention in the scientific community, emphasizing the development of environmentally sustainable and efficient chemical processes. Hence, the quest to develop an efficient, oxidant-free, and metal catalyst-free approach for constructing sulfilimines remains a pressing challenge in the field of organic synthesis. In this context, Zhao and colleagues have developed a metal-free coupling method for synthesizing sulfilimines through an internal oxidant strategy that enables the cascade



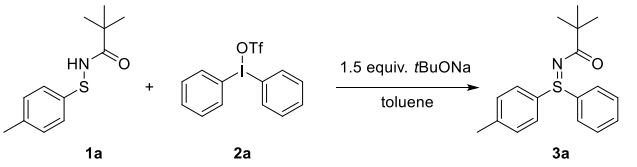
Scheme 1. Prior works and our design

formation of C-S and S=N bonds at room temperature. [9] However, the substrate scope is limited to ortho-hydroxylaryl and Ac-substituted structures. Luisi [10] and Willis [11] independently pioneered sulfilimine synthesis methodologies, which encompass the substitution of Grignard reagents with sulfinimidate esters and the addition of Grignard reagents to sulfinylamines, respectively. While characterized by its oxidant-free nature, is hampered by the limited substrate scope, which requires a high tolerance to the reactive nature of the utilized Grignard reagents. Very recently, Ellman [12] and Jia [13] reported two new methods

for accessing sulfilimines with improved versatility and functional group tolerance (Scheme 1b). Ellman's Rh(II)-catalyzed S-alkylation and Jia's Cu(II)-catalyzed S-arylation of sulfenamides offer new synthetic routes to sulfilimines. However, these transformations require transition-metal catalysts and high temperatures, which could be a drawback in some cases. Further research in this area is needed to develop even more efficient and practical methods for synthesizing sulfilimines.

Sulfenate anions, celebrated for their extraordinary S-nucleophilicity originating from sulfonyl anion species, are universally acknowledged as indispensable reagents in the realm of organic chemistry. [14] In contrast, sulfinimidoyl anions, as analogs of sulfonyl anions, have not garnered significant attention. Inspired by the fascinating properties of sulfenate anions, we hypothesized that tetravalent nucleophilic sulfinimidoyl species could give rise to divalent sulfenamides through deprotonation and tautomerization processes. To our current knowledge, no transition-metal-free S-arylation of sulfenamides under an alkali atmosphere has been reported. With an unyielding dedication to developing sustainable and high-performing reactions, our research group has set out to achieve superior control over chemoselectivity in our transition-metal-free S-arylation process, by carefully selecting sulfenamide substrates and optimizing reaction conditions. This strategic approach harmonizes with our unwavering dedication to the exploration of highly efficient reactions and the advancement of environmentally responsible chemical methodologies. [15]

Table 1 Optimization reaction conditions [a]



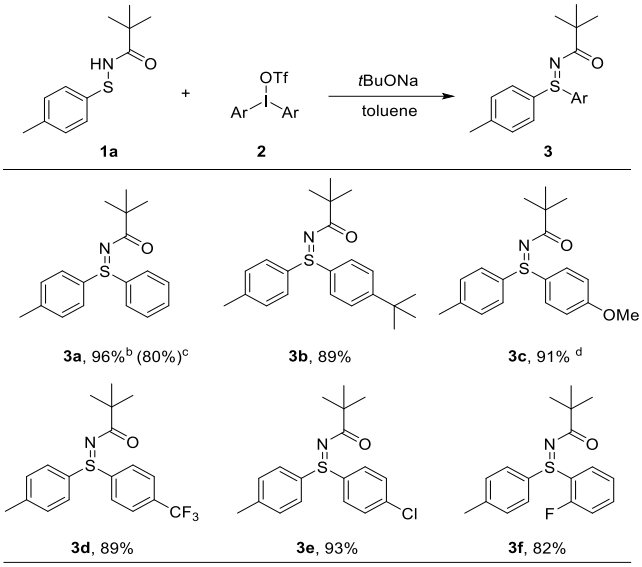
1a **2a** **3a**

Entry	derivation from standard conditions	yield(%)[b]
1	none	94
2	without base	0
3 [c]	*t*BuONa replaced by 2.0 equiv. $NaHCO_3$	N.D.
4 [c]	*t*BuONa replaced by Na_2CO_3	N.D.
5 [c]	*t*BuONa replaced by Cs_2CO_3	43
6 [c]	*t*BuONa replaced by KOH	57
7	1.5mLtoluene and H_2O (1.0 mL) added	90
8	2.0 equiv. *t*BuONa used	92
9	4 hours used	90
10	N_2 atmosphere	93

a Reaction conditions: **1a** (0.1 mmol), **2a** (1.2 equiv), base (1.5 equiv.), and toluene (2.0 mL), and stirred at room temperature for 1 hour under an air atmosphere. b Isolated yield. c 1.5 equiv. base was used. N.D. = not detected.

We started our study by choosing readily accessible N-(p-tolylthio)pivalamide 1a and diaryliodonium salt **2a** as the model substrates to optimize the conditions (Table 1). After extensive screening, the optimal conditions for obtaining a 94% isolated yield of the desired product **3a** were determined to be sulfenamide (**1a**) as the limiting reagent, 1.2 equiv. of diaryliodonium salt (**2a**), and 1.5 equiv. *t*BuONa as the base in toluene at room temperature for 1h. Under the optimal conditions, no N-arylated sulfenamide was observed in TLC. In addition, a series of meticulous control experiments were carried out to investigate the effect of various parameters on the reaction yield. The absence of a desired product in the reaction system devoid of a base elucidates the indispensability of a base for the reaction to proceed. Nevertheless, the utilization of weaker bases such as $NaHCO_3$ or Na_2CO_3 failed to yield the desired product **3a**. Intriguingly, the incorporation of a medium-strong alkali such as Cs_2CO_3 or KOH resulted in a significant reduction of the isolated yield of **3a**, dropping to a mere 43% and 57%, respectively. Moreover, the incorporation of extra water under standard reaction conditions did not influence the acquisition of compound **3a**. It is noteworthy that augmenting the quantity of base or extending the reaction duration had no bearing on the yield of product **3a**. Additionally, the yield of **3a** remained unaltered in a nitrogen atmosphere, signifying that the reaction mechanism does not necessitate the involvement of oxygen.

Scheme 2. Substrate scope of diaryliodonium salts

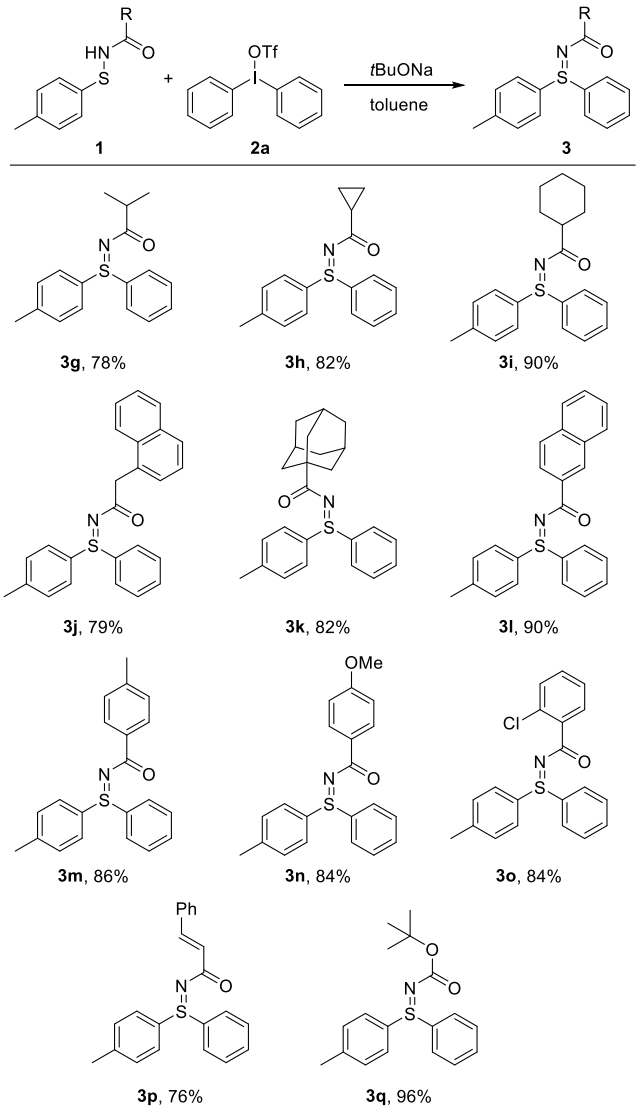


[a] Reaction conditions: **1a** (0.15 mmol, 33.5 mg), **2** (1.2 equiv), *t*BuONa (1.5 equiv., 21.6 mg), and toluene (2.5 mL), and stirred at room temperature for 1 hour under an air atmosphere. Isolated yields. [b] Ph_2IBF_4 was used. [c] The yield provided in parentheses corresponds to a gram-scale reaction. [d] (*p*-OMe-Ph)$_2$IOTs was used.

Following the identification of the optimal reaction conditions, we further explored the substrate scope of diaryliodonium salts **2** in the S-arylation reaction with sulfenamide **1a**, as presented in Scheme 2. It was observed that the nature of the anion in the diaryliodonium salts did not significantly impact the product yield (Scheme 2, **3a**). Concurrently, this condition proved more suitable for gram-level reactions, with a slightly reduced yield. Notably, electron-donating groups such as *tert*-butyl and methoxy groups at the *para*-position of the phenyl group proved to be excellent reaction partners, leading to the isolation of the corresponding products **3b** and **3c** in yields of 89% and 91%, respectively. Moreover, substrates bearing electron-withdrawing groups, such as trifluoromethyl and chloro groups, were also suitable coupling partners, yielding **3d** and **3e** in excellent yields. It is worth mentioning that the reaction exhibited remarkable tolerance to steric hindrance, enabling the

production of the desired diaryl sulfilimines **3f** with high yields of 82%.

Scheme 3. Substrate scope of N-substituent groups of sulfenamides

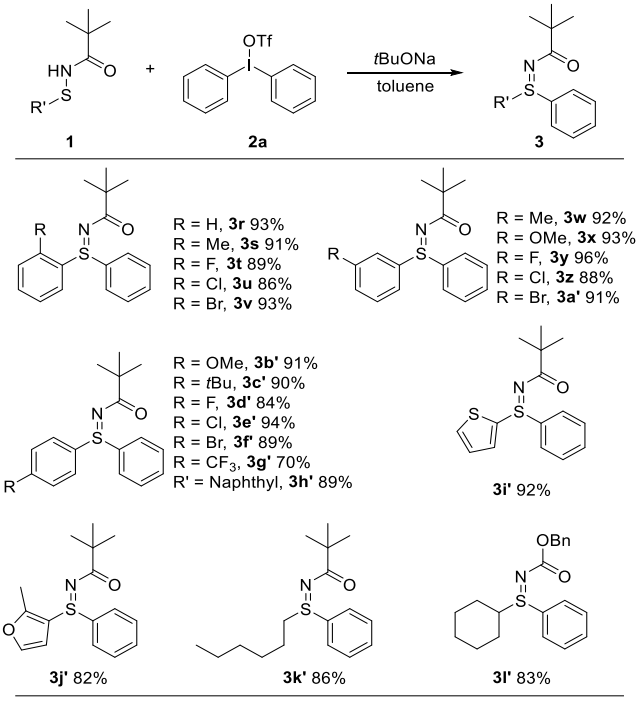


[a] Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), **2a** (1.2 equiv., 77.4 mg), *t*BuONa (1.5 equiv., 21.6 mg), and toluene (2.5 mL), and stirred at room temperature for 1 hour under an air atmosphere. Isolated yields.

Encourage by these promising results, we next examined the substrate scope of sulfenamides **1** with various protecting group on nitrogen (Scheme 3). Generally, the substituted reactions proceeded very well employing N-acyl sulfenamides as nucleophiles and led to the formation of **3g**-**3q** in good to excellent yields. Sulfenamides possessing elaborately branched and cyclic substituents for *N*-alkyl acyl moieties demonstrated remarkable tolerability, deftly furnishing **3g**-**3j** in impressive yields ranging from 78% to 90%. Additionally, the synthesis of sterically hindered *N*-adamantane acyl moieties culminated in a favorable yield, attesting to the remarkable versatility of this synthetic method. Equally remarkable, *N*-aryl acyls, such as 2-naphthyl, *para*-methyl, and methoxyl phenyl, as well as the highly sterically demanding *ortho*-chlorophenyl, displayed exceptional reacting efficacy, yielding the desired products with elevated yields. Furthermore, the tested amides displayed striking robustness in the presence of a C=C double bond, generating **3o** in excellent yields. Notably, sulfenamides derived from tert-butyl carbamate ($BocNH_2$) were compatible with the reaction, producing the desired product **3q** in an impressive 96% yield.

The S-arylation reaction was comprehensively investigated by testing a diverse range of sulfenamides derived from various thiols (Scheme 3). It was observed that the substitution pattern of the arene had no discernible impact on the yield of the corresponding sulfilimines. The majority of the reactions resulted in high to excellent yields, reaching up to 96% (**3r**-**3h'**). However, the products **3d'** and **3g'** were obtained in slightly lower yields of 84% and 70%, respectively. The electron-withdrawing nature of aryl substituents may have influenced the reaction kinetics, necessitating longer reaction times to obtain the desired products. Nevertheless, these results provided robust evidence of the reaction mechanism, confirming the presence of a positive charge at the sulfur atom during the reaction transition state. Furthermore, the synthesis of S-arylated sulfilimines bearing heteroatom-containing aryl groups was successfully accomplished, as exemplified by the formation of **3i'** and **3j'**, which were isolated in 92% and 82% yield, respectively. Notably, sulfenamides derived from aliphatic linear and cyclic thiols also led to sulfilimines in good yields, as evidenced by the synthesis of S-arylated **3k'** and S-phenyl-substituted **3l'**.

Scheme 4 Substrate scope of thiols

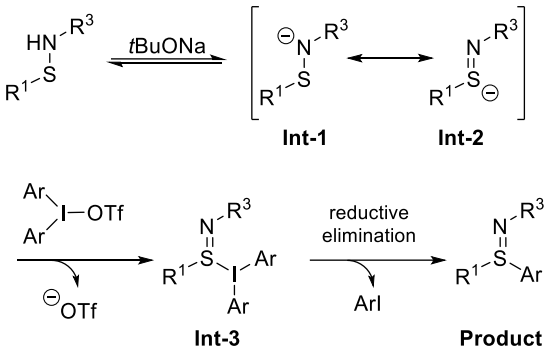


[a] Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), **2a** (1.2 equiv., 77.4 mg), *t*BuONa (1.5 equiv., 21.6 mg), and toluene (2.5 mL), and stirred at room temperature for 1 hour under an air atmosphere. Isolated yields.

We performed a concise mechanistic examination of the S-arylation process involving sulfenamides and diaryliodonium salts under base conditions, incorporating radical scavengers into the study (See Supporting Information for more details). When employing the standard reaction conditions for the combination of sulfenamides **1a** and diaryliodonium salt **2a**, the

subsequent addition of TEMPO facilitated the formation of the target product **3a** with an appreciable yield. Conversely, when BHT was introduced under optimal conditions, only a 22% yield was achieved, likely due to a background reaction between BHT and the diaryliodonium salt. [16] This observation effectively eliminates the likelihood of a free radical pathway contributing to this transformation.

A mechanistic proposal for the transition-metal-free sulfilimine synthesis is presented in Scheme 4. The process unfolds sequentially through several key steps: initially, the base-mediated generation of *N*-anionic sulfenamides occurs *via* a reaction involving the deprotonated compound. Subsequently, tautomerization promotes the transfer of divalent *N*-centered anions **Int-1** to sulfilimine anions, culminating in the formation of a tetravalent S-centered anionic species **Int-2**. This species then undergoes a ligand exchange with the diaryliodonium salt, accompanied by the loss of triflate. Finally, the reductive elimination of intermediate **Int-3** yields the desired sulfilimines.



Scheme 4. Proposed mechanism.

In conclusion, we initially reported the successful utilization of sulfenamides as sulfilimine precursors in nucleophilic substitution reactions, which occurs *via* the tautomerization of divalent nitrogen-centered anions to tetravalent sulfinimidoyl anionic species, functioning as proficient nucleophilic reagents. A comprehensive array of sulfenamides can engage in coupling with diaryliodonium salts, culminating in the generation of sulfilimines with noteworthy to exceptional yields, all while adhering to a redox-neutral and transition-metal-free approach. Given the ready availability of both reagents, we anticipate their applicability in medicinal and material chemistry domains.

ASSOCIATED CONTENT

Supporting Information.

This material is available free of charge via the Internet at http://pubs.acs.org.

General information, experimental section, compound characterization, and NMR spectra (PDF).

AUTHOR INFORMATION

Corresponding Author

*Xunbo Lu - *Department School of Chemistry and Chemical Engineering, Laboratory of Marine Green Fine Chemicals, Lingnan Normal University (LNU), 29 Cunjin road, Zhanjiang, 524048, P. R.* China. E-mail: luxunbo@foxmail.com.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We are grateful to the National Natural Science Foundation of China (22101106) and Lingnan Normal Unervistry Talent Project (ZL2021026).

REFERENCES

(1) (a) Gabriele, B.; Mancuso, R.; Veltri, L. Sulfilimine chemistry: Recent advances. *Synthesis*, **2013**, *45*, 3331. (b) Singh, R.; Singh, P.; Yadav, R. N. Sulfur-Nitrogen compounds: An overview. *Curr. Org. Chem.* **2016**, *20*, 1892.

(2) (a) Raghavan, S.; Kumar, C. N. A stereoselective synthesis of the hexahydroazepine core of (−)-balanol. *Tetrahedron Lett.* **2006**, *47*, 1585. (b) Padwa, A.; Nara, S.; Wang, Q. Additive Pummerer reaction of heteroaromatic sulfilimines with carbon nucleophiles. *Tetrahedron Lett.* **2006**, *47*, 595. (c) Tian, X.; Song, L.; Rudolph, M.; Rominger, F.; Oeser, T.; Hashmi, A. S. K. Sulfilimines as versatile nitrene transfer reagents: facile access to diverse aza-heterocycles. *Angew. Chem., Int. Ed.* **2019**, *58*, 3589.

(3) Vanacore, R.; Ham, A-J. L.; Voehler, M.; Sanders, C. R.; Conrads, T. P.; Veenstra, T. D.; Sharpless, K. B.; Dawson, P. E.; Hudson, B. G. A Sulfilimine bond identified in collagen IV. *Science* **2009**, *325*, 1230.

(4) (a) Lin, S.; Yang, X.; Jia, S.; Weeks, A. M.; Hornsby, M.; Lee, P. S.; Nichiporuk, R. V.; Iavarone, A. T.; Wells, J. A.; Toste, F. D.; Chang, C. J. Redox-based reagents for chemoselective methionine bioconjugation. *Science* **2017**, *355*, 597. (b) Christian, A. H.; Jia, S.; Cao, W.; Zhang, P.; Meza, A. T.; Sigman, M. S.; Chang, C. J.; Toste, F. D. A physical organic approach to tuning reagents for selective and stable methionine bioconjugation. *J. Am. Chem. Soc.* **2019**, *141*, 12657.

(5) For relevant examples see: (a) Lücking, U. Sulfoximines: A Neglected Opportunity in Medicinal Chemistry. *Angew. Chem., Int. Ed.* **2013**, *52*, 9399. (b) Frings, M.; Bolm, C.; Blum, A.; Gnamm, C. Sulfoximines from a medicinal chemist's perspective: Physicochemical and in vitro parameters relevant for drug discovery. *Eur. J. Med. Chem.* **2017**, *126*, 225. (c) Han, Y.; Xing, K.; Zhang, J.; Tong, T.; Shi, Y.; Cao, H.; Yu, H.; Zhang, Y.; Liu, D.; Zhao, L. Application of sulfoximines in medicinal chemistry from 2013 to 2020. *Eur. J. Med. Chem.* **2021**, *209*, 112885.

(6) For selected examples, see: (a) Bach, T.; Körber, C. Iron(II)-mediated Nitrene transfer from *t*-butyloxycarbonyl azide ($BocN_3$) to sulfoxides, sulfides, and ketene acetals. *Tetrahedron Lett.* **1998**, *39*, 5015. (b) Bach, T.; Körber, C. The preparation of *N-tert*-butyloxycarbonyl-(Boc-)protected sulfoximines and sulfimines by an Iron(II)-mediated nitrene transfer from $BocN_3$ to sulfoxides and sulfides. *Eur. J. Org. Chem.* **1999**, 1033. (c) García Mancheño, O.; Bolm, C. Comparative study of metal-catalyzed iminations of sulfoxides and sulfides. *Chem.- Eur. J.* **2007**, *13*, 6674. (d) Lebel, H.; Huard, K.; Lectard, S. *N*-Tosyloxycarbamates as a source of metal nitrenes: Rhodium-catalyzed C−H insertion and aziridination reactions. *J. Am. Chem. Soc.* **2005**, *127*, 14198. (e) Lebel, H.; Piras, H.; Bartholoméüs, J. Rhodium-catalyzed stereoselective amination of thioethers with *N*-mesyloxycarbamates: DMAP and Bis(DMAP)CH_2Cl_2 as key additives. *Angew. Chem., Int. Ed.* **2014**, *53*, 7300. (f) Bizet, V.; Buglioni, L.; Bolm, C. Light-induced Ruthenium-catalyzed nitrene transfer reactions: A photochemical approach towards *N*-acyl sulfimides and sulfoximines. *Angew. Chem., Int. Ed.* **2014**, *53*, 5639. (g) Lebel, H.; Piras, H.; Borduy, M. Iron-catalyzed amination of sulfides and sulfoxides with azides in photochemical continuous flow synthesis. *ACS Catal.* **2016**, *6*, 1109. (h) Lebel, H.; Huard, K. De novo synthesis of Troc-protected amines: Intermolecular Rhodium-catalyzed C−H amination with *N*-tosyloxycarbamates. *Org. Lett.* **2007**, *9*, 639. (i) Lai, C.; Mathieu, G.; Tabarez, L. P. G.; Lebel, H. Batch and continuous-flow iron(II)-catalyzed synthesis of sulfilimines and sulfoximines using *N*-mesyloxycarbamates. *Chem. Eur. J.* **2019**,

25, 9423. (j) Mancheño, O. G.; Dallimore, J.; Plant, A.; Bolm, C. Synthesis of sulfoximines and sulfilimines with aryl and pyrazolylmethyl substituents. *Adv. Synth. Catal.* **2010**, *352*, 309. (k) Bizet, V.; Bolm, C. Sulfur imidations by light-induced Ruthenium-catalyzed nitrene transfer reactions. *Eur. J. Org. Chem.* **2015**, 2854.

(7) For selected examples, see: (a) Wang, J.; Frings, M.; Bolm, C. Enantioselective nitrene transfer to sulfides catalyzed by a chiral iron complex. *Angew. Chem., Int. Ed.* **2013**, *52*, 8661. (b) Wang, J.; Frings, M.; Bolm, C. Iron-catalyzed imidative kinetic resolution of racemic sulfoxides. *Chem. Eur. J.* **2014**, *20*, 966. (c) Zenzola, M.; Doran, R.; Luisi, R.; James A. Synthesis of sulfoximine carbamates by Rhodium-catalyzed nitrene transfer of carbamates to sulfoxides. *Bull J. Org. Chem.* **2015**, *80*, 6391.

(8) (a) Lebel, H.; Piras, H. Stereoselective synthesis of chiral sulfilimines from *N*-mesyloxycarbamates: Metal-nitrenes versus metal-nitrenoids species. *J. Org. Chem.* **2015**, *80*, 3572. (b) Lebel, H.; Laparra, L.M.; Khalifa, M.; Trudel, C.; Audubert, C.; Szponarski, M.; Leduc, C. D.; Azek, E.; Ernzerhof, M. Synthesis of oxazolidinones: rhodium-catalyzed C–H amination of *N*-mesyloxycarbamates. *Org. Biomol. Chem.* **2017**, *15*, 4144. (c) Xiao, X. S.; Huang, S. P.; Tang, S. S.; Jia, G. K.; Ou, G. C.; Li, Y. Y. Ligand-free, quinoline *N*-assisted copper-catalyzed nitrene transfer reaction to synthesize 8-quinolylsulfimides. *J. Org. Chem.* **2019**, *84*, 7618. (d) Leest, N. P.; Vlugt, J. I.; Bruin, B. Catalytic chemoselective sulfimidation with an electrophilic $[Co^{III}(TAML)]^{-}$-nitrene radical complex. *Chem. - Eur. J.* **2021**, *27*, 371.

(9) (a) Xiong, F.; Lu, L.; Sun, T. Y.; Wu, Q.; Yan, D.; Chen, Y.; Zhang, X.; Wei, W.; Lu, Y.; Sun, W. Y.; Li, J. J.; Zhao, J. A bioinspired and biocompatible ortho-sulfiliminyl phenol synthesis. *Nat. Commun.* **2017**, *8*, 15912. (b) Xiong, F.; Zuo, Y.; Song, Y.; Zhang, L.; Zhang, X.; Xu, S.; Ren, Y. Synthesis of *ortho*-phenolic sulfilimines *via* an intermolecular sulfur atom transfer cascade reaction. *Org. Lett.* **2020**, *22*, 3799.

(10) Andresini, M.; Spennacchio, M.; Colella, M.; Losito, G.; Aramini, A.; Degennaro, L.; Luisi, R. Sulfinimidate esters as an electrophilic sulfinimidoyl motif source: Synthesis of *N*-protected sulfilimines from grignard reagents. *Org. Lett.* **2021**, *23*, 6850.

(11) Zhang, Z.-X.; Davies, T. Q.; Willis, M. C. Modular sulfondiimine synthesis Using a stable sulfinylamine reagent. *J. Am. Chem. Soc.* **2019**, *141*, 13022.

(12) Greenwood, N. S.; Champlin, A. T.; Ellman, J. A. Catalytic enantioselective sulfur alkylation of sulfenamides for the asymmetric synthesis of sulfoximines. *J. Am. Chem. Soc.* **2022**, *144*, 17808.

(13) Liang, Q.; Wells, L. A.; Han, K.; Chen, S.; Kozlowski, M. C.; Jia, T. Synthesis of sulfilimines enabled by copper-catalyzed S-arylation of sulfenamides. *J. Am. Chem. Soc.* **2023**, DOI: 10.1021/jacs.2c12947.

(14) (a) Caupène, C.; Boudou, C.; Perrio, S.; Metzner, P. Remarkably mild and simple preparation of sulfenate anions from β-sulfinylesters: A new route to enantioenriched sulfoxides. *Org. Chem.*, **2005**, *70*, 2812. (b) Zhong, L.; Ban, X.; Kee, C. W.; Tan, C.-H. Catalytic enantioselective alkylation of sulfenate anions to chiral heterocyclic sulfoxides using halogenated pentanidium salts. *Angew. Chem., Int. Ed.* **2014**, *53*, 11849. (c) Gelat, F.; Jayashankaran, J.; Lohier, J.-F.; Gaumont, A.-C.; Perrio, S. Organocatalytic asymmetric synthesis of sulfoxides from sulfenic acid anions mediated by a cinchona-derived phase-transfer reagent. *Org. Lett.* **2011**, *13*, 3170 (d) Foucoin, F.; Caupène, C.; Lohier, J.-F.; de Oliveira Santos, J. S.; Perrio, S.; Metznera, P. 2-(Trimethylsilyl)ethyl sulfoxides as a convenient source of sulfenate anions. *Synthesis* **2007**, 1315; (e) Jia, T.; Bellomo, A.; Montel, S.; Zhang, M.; El Baina, K.; Zheng, B.; Walsh, P. J. Diaryl sulfoxides from aryl benzyl sulfoxides: A single Palladium-catalyzed triple relay process. *Angew. Chem., Int. Ed.* **2014**, *53*, 260; (f) Gelat, F.; Lohier, J.-F.; Gaumont, A.-C.; Perrio, S. *tert*-Butyl sulfoxides: Key precursors for Palladium-catalyzed arylation of sulfenate salts. *Adv. Synth. Catal.* **2015**, *357*, 2011. (g) Amos, S. G. E.; Nicolai, S.; Gagnebin, A.; Le Vaillant, F.; Waser, J. Metal-free electrophilic alkynylation of sulfenate anions with ethynylbenziodoxolone reagents. *J. Org. Chem.* **2019**, *84*, 3687. (h) Dai, Q.; Zhang, J. Direct synthesis of sulfinamides by the copper-catalyzed electrophilic amidation of sulfenate anions. *Adv. Synth. Catal.*, **2018**, *360*, 1123. (i) Wang, L.; Chen, M. J.; Zhang, P. C.; Li, W. B.; Zhang, J. L. Palladium/PC-Phos-catalyzed enantioselective arylation of general sulfenate anions: Scope and synthetic applications. *J. Am. Chem. Soc.* **2018**, *140*, 3467.

(15) (a) Lu, X. B.; Shi, Y. F.; Zhong, F. R. Rhodium-catalyzed intermolecular $C(sp^3)$–H amination in a purely aqueous system. *Green Chem.* **2018**, *20*, 113. (b) Shi, Y. F.; Wang, Y. F.; Lu, X. B.; Zhang, Y. L.; Wu, Y. Z.; Zhong, F. R. Rhodium-catalyzed aminohydroxylation of unactivated alkenes in aqueous media for the benign synthesis of 1,2-amino alcohols. *Green Chem.* **2019**, *21*, 780. (c) Lu, X. B.; Bai, Y. L.; Qin, J. Y.; Wang, N.; Wu, Y. Z.; Zhong, F. R. Alleviating catalyst decay enables efficient intermolecular $C(sp^3)$–H amination under mechanochemical conditions. *ACS Sustainable Chem. Eng.* **2021**, *9*, 1684. (d) Lu, X. B.; Yang, K.; Xu, X.; Sun, S.; Feng, S.; Adnan Bashir, M.; Liang, F.; Lin, J.; Huang, G. Rh(II)-catalyzed Doyle–Kirmse reaction: access to unprotected 3-allyl/3-allenyl-3-(thio)oxindoles. *Org. Biomol. Chem.* **2022**, *20*, 9228.

(16) (a) Chan, L.; McNally, A.; Toh, Q. Y.; Mendoza, A.; Gaunt, M. J. A counteranion triggered arylation strategy using diaryliodonium fluorides. *Chem. Sci.*, **2015**, *6*, 1277; (b) Stridfeldt, E.; Lindstedt, E.; Reitti, M.; Blid, J.; Norrby, P.-O.; Olofsson, B. Competing pathways in O-arylations with diaryliodonium salts: Mechanistic insights. *Chem.- Eur. J.* **2017**, *23*, 13249.

Inhere, a transition-metal-free and redox-neutral process to access tetravalent sulfilimines through S-arylation of easily available divalent sulfenamides and diaryliodonium salts under base conditions in a very short-time was first reported. This novel method exhibits a broad substrate scope, high site-selectivity, and are concise, practical, and atom-economic.