Applications of aryl-sulfinamides in the synthesis of N-heterocycles

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Enantiopure aryl-sulfinamides are important chiral auxiliaries in the asymmetric synthesis of amines and their derivatives. Here, we provide an overview of arylsulfinamide mediated asymmetric methods towards N-heterocycle synthesis. This methodology through sulfinylimines offers general access to structurally diverse piperidines, pyrrolidines, aziridines and their derivatives which represent the structural motif of many natural products and therapeutically important compounds. The review covers articles from 2006–2020 and we have categorized the review based on the ring size as 3-, 5-, and 6-membered heterocycles and their derivatives.

1. Introduction

The advent of chiral sulfoxide N-protecting groups as chiral inductors opened up efficient methodologies towards the preparation of chiral amines, which forms part of various bioactive compounds. A series of enantiopure sulfinyl motifs were designed over time by different research groups to regulate the reactivity of the sulfinimines towards the desired direction. The first report on the synthesis of sulfinimines came from the research group of Davis through the synthesis of p-toluene-sulfinimines over 45 years ago, followed by the generation of its enantiopure form by Cinquini et al. in 1982. Later, the introduction of enantiopure tert-butanesulfinamide by Ellman and co-workers offered facile access to tert-butyl-sulfinimines.

The highly stereodirecting nature of the sulfinyl group is applied in numerous methodologies and its easy deprotection enabled further modification of substrates. Among the different chiral sulfoxides, p-toluene- and tert butyl-sulfinimines stay well explored in asymmetric synthesis. One of the notable advantages of p-toluensulfinimines is that being UV active, the reactions can be easily monitored. Nucleophilic addition onto enantiopure sulfinimines remains the finest method for the asymmetric construction of chiral building blocks that can be transformed to a series of nitrogen heterocycles including aziridines, pyrrolidines and piperidines. In view of the obvious presence of N-heterocycles in nucleic acids, hormones, vitamins, drugs and agrochemicals, novel methodologies

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towards their synthesis are always in great demand. The reports utilizing enantiopure sulfamimines are increasing day by day proving their importance in constructing bioactive molecules, natural products and pharmaceuticals. The pioneers of the field, Davis et al. carefully summarized their major contributions till 2006. In the same year, Stockman et al. compiled a review that presented the significance of chiral non-racemic sulfamimines in asymmetric synthesis. Recently, our group contributed a review outlining the synthetic methods towards N-heterocycles mediated by tert-butanesulfamimide. The current review aims to discuss the application of aryl sulfamimines, majorly p-toluene sulfamimine in the synthesis of N-heterocycles. The review covers the relevant articles from 2006 to 2020 and is organized based on the ring size as 3-, 5-, and 6-membered heterocycles and their derivatives.

2. Three-membered ring

Davis’ group devised a method for the synthesis of 2-substituted 2H-azirine 3-carboxylates 6 in an optically pure form via the dehydrochlorination of methyl 2-chloroaziridine 2-carboxylates 5. Initially, lithium enolate of methyl dichloroacetate 2 was added to sulfamimines 1 to yield single enantiomers of β-amino esters 3 followed by cyclization with the use of KH to obtain 2-chloroaziridines 4 in good yields (Scheme 1). Then the aza Diels–Alder reaction between azirine 6 obtained after photo-desulfonylation, and diene 7 underwent smoothly and provided with the tricyclic aziridine carboxylates 8 in enantiopure form.

In 2009, a simple protocol towards the synthesis of chiral aziridines from cyclic alkenes was developed. Herein, the lithium salt of p-toluenesulfamid, was added to cyclic α-haloenones 9 to afford the anticipated aziridines 11a and 11b in 30–65% of diastereomeric excess (Scheme 2). Analysis with different cyclic olefins concluded that yield and selectivity were

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higher with 6-membered \( \alpha \)-bromoenones. The remarkably low diastereoselectivity observed with alkenes that are not part of the ring suggested the importance of the conformational restriction offered by cyclic alkenes in chiral induction.

Stockman and coworkers conducted an aza-Darzens reaction of optically active sulfinimines with substituted 2-bromoesters forming trisubstituted aziridines (Scheme 3). Both mesityl- and \( \text{t} \)-butanesulfinimines smoothly underwent aziridination where better \( \text{cis} / \text{trans} \) ratios were obtained when mesityl sulfinimines possessing a C3-aliphatic chain were employed rather than an aromatic imine. On the other hand, Ellman’s auxiliary was found suitable for aromatic imines. They also demonstrated the successive removal of the auxiliaries and predicted the applicability of the present three step protocol in preparing optically active N-H aziridines.

Further to their previous studies, they examined the synthetic utility of the aforementioned vinyl aziridine 2-carboxylates in the generation of cyclic sulfoximines. They devised a one-pot strategy that employed sulfinimines as the starting material that gave cyclic sulfoximines in high yields and excellent stereoselectivity (Scheme 4). They made a mechanistic hypothesis that the ester species activated the alkene to conduct the thermal sigmatropic rearrangement. To exemplify the reactivity of the products, the formal synthesis of biologically active trachelanthamidine was carried out via the conversion of the cyclic sulfoximine into a pyrrole.

### 3. Five-membered ring

A novel method for the synthesis of chiral \( N \)-tosyl \( \alpha \)-amino aldehydes from \( N \)-sulfinyl \( \alpha \)-amino 1,3-dithioacetals was developed by the research group of Davis in 2006. They made use of DBDMH (1,3-dibromo-5,5-dimethylhydantoin) as the hydrolyzing agent for this transformation. Besides, they presented the formal synthesis of \( -\text{2,3-trans,3,4-cis} \)-dihydroxyproline to demonstrate the application of the obtained \( \alpha \)-amino aldehydes (Scheme 5). Here, the aldehyde obtained after hydrolysis underwent a sequence of reactions to construct the pyrrolidine after ring-closing metathesis. Further functionalization could access the dihydroxyproline derivative.

Synthesis of \( \text{trans}-2,5\)-disubstituted pyrrolidines in enantiopure form was accomplished by the same research group through an iodocyclization strategy. To illustrate the utility of the method, the stereoselective synthesis of \( -\text{pyrrolidine} \) 197B was conducted (Scheme 6). The strategy began with the addition reaction on sulfinimine leaving the ester as a single diastereomer. The precursor for iodocyclization, the homoallylic sulfonamide was prepared from the sulfinimine derived ester in 4 steps. The iodocyclization step using \( \text{I}_2 / \text{K}_2\text{CO}_3 / \text{H}_2\text{O} / \text{MeCN} \) afforded the corresponding 3-iodo \( \text{trans}-2,5\)-disubstituted pyrrolidine which was then transformed to the final cyclized product. Hence, the present method to access
the significant N-containing ring is applicable in constructing similar motifs of bioactive compounds.

In 2008, Lautens’ group introduced an iodide-mediated Mannich/cyclization sequence to afford trans-2,3-disubstituted pyrrolidines 36 and 38 in a single step from methylenecyclopropyl amides 35.\textsuperscript{19} They utilized magnesium iodide to conduct the reaction between diverse methylenecyclopropyl amides with aromatic, heteroaromatic imines 34 and α,β-unsaturated imines 37 which gave good to excellent yields and selectivities (Scheme 7). Later, cleavage of the auxiliary was conducted under mild reaction conditions to furnish pyrrolidines in highly enantioenriched form (dr up to >20 : 1).

Viso and Pradilla with coworkers designed a method for the stereoselective synthesis of 3-sulfonyl and 3-sulfonyl 2,5-cis-dihydropyrroles via chiral sulfinimines.\textsuperscript{20} They performed a highly diastereoselective addition of chiral α-metalated vinyl and dienyl sulfoxides onto enantiopure N-sulfinimines 39 that offered respective allylic amines 41 in good yields (93–98% yield) and selectivity (dr up to 99 : 1) (Scheme 8). Herein, the highly diastereoselective construction of the new C-C bond was attributed to the stereoinduction by chiral sulfinyl groups present in both the starting compounds. Starting from 41a, cis-2,5-disubstituted dihydropyrroles 42 were prepared via an electrophilic cyclization reaction.

The research group of Kamimura established an elegant methodology towards the synthesis of chiral 2-alkyl-substituted 2,5-dihydropyrroles 45.\textsuperscript{21} This method made use of their earlier protocol of Michael/iminoaldol domino reaction with an acrylate and a p-tolylsulfinimine to produce aza-Baylis–Hillman adduct 44 in high optical purity (Scheme 9).\textsuperscript{22} With 44 in hand, a short and simple three step conversion gave optically active 2,5-dihydropyrroles 45 through N-allyl-β-amino-R-methylene ester intermediate. Moreover, they demonstrated the synthetic utility of the method in preparing (−)-trachelanthamidine 52, a pyrrolizidine alkaloid with anticipated biological activity. From the chiral sulfinimine 46, a highly stereoselective formal synthesis of (−)-trachelanthamidine was accomplished in 11
steps. Since chiral 2,5-dihydropyrroles are considered a potent starting point in the synthesis of heterocyclic compounds, they predicted the synthetic applicability of the method in future.

Davis’ group devised an efficient protocol for the preparation of indolizidine alkaloids (+)-monomorine 58 and (-)-indolizidine 1958 57 from sulfonimine-derived common intermediates. In the initial steps, the stable 5-diazophosphonate 55 prepared from β-amino ester 53 was heated with Rh2(OAc)4 that conducted a diastereoselective intramolecular reaction which provided the 3-oxo pyrrolidine phosphonate 56 (Scheme 10). Then, 56 acted as the common intermediate for the stereo-selective synthesis of the functionalized pyrrolidines 57 and 58.

4. Six-membered ring

Substituted piperidines have shown applications in pharmaceutical chemistry forming important building units of bioactive compounds. Davis et al. established a synthetic route to Nuphar alkaloids having 2,3,6-trisubstituted piperidines via an intramolecular Mannich reaction of sulfonimine-derived amino ketone (Scheme 11).24 The amino ketone 60 was afforded majorly as a single diastereomer from (R)-(-)-N-(3-furyl-methylene)-p-toluensulfonamide 59 via the addition of potassium enolate of methyl ethyl ketone. Starting from the common precursor 64 obtained after Mannich cyclization, they discussed the synthesis of Nuphar alkaloids (-)-nupharamine 65 and (-)-(S,S,R,R)-5-(3-furyl)-8-methyltricyclicdolizidine 66.

In 2006, Kawecki presented theaza Diels–Alder reaction of chiral sulfonimines with the highly active Rawal diene 68 to furnish enantioenriched dihydropyridone.25 The reaction was performed in presence of TMSOTf and with 1-isobornylsulfonimines, 8-methylsulfonimines, t-butyl and p-tolylsulfonimines as optically active sulfonimine partners. With p-tolylsulfonimine 67, open chain enamino 69 was obtained in 89% ee which then underwent a cyclization step with acid and gave 2-phenyl substituted dihydropyridone 70 (Scheme 12). The method provided access to 2-aryl substituted dihydropyridones in modest stereoselectivity.

The research group of Davis established protected 2,3-diamino esters as valuable synthetic units towards the preparation of piperidine derivative (+)-CP-99,994 76, an effective neurokinin substance P receptor antagonist via a 12 step protocol.26 In the initial step sulfonimine 72 underwent the addition of a prochiral enolate moiety, constructing the compound 73 bearing different N-protecting groups and two newly generated stereo-directing groups. From 73 various synthetic transformations followed, wherein a Kocienski-modified Julia olefination and Grubbs-Hoveyda catalyst enabled ring-closing metathesis formed the key conversions. The final stage functionalization of tetrahydropyridine 75 offered the expected amino piperidine in 4 steps.

Considering the significance of 2,6-disubstituted piperidine derivatives as bioactive agents, the research group of Davis achieved a newer and general procedure for the generation of 1,2,5,6-tetrahydropyridines, important building units for the stereo-selective preparation of trans-2,6-disubstituted piperidines.27 They utilized N-sulfinyl δ-amino β-ketophosphonates 77 as the precursor to initiate the reaction through a one-pot strategy involving treatment with dimethylformamide dimethyl acetal and successive addition of 4N HCl to access the dihydropyridine 79 (Scheme 14). Subjecting the dihydropyridone to a sequence of conversions comprising a stereoselective organocuprate addition provided with trans-2,6-disubstituted piperidines.83 In addition, they presented the utility of the protocol in synthesizing the quinolizidine alkaloid (-)-myrtine 86.

An elegant synthesis of the hydroxyl piperidines, (+)-epipinidinol 96 and (-)-pinidinol 94 was established by the same
group in 2008. The synthesis commenced with the stereo-selective addition of Weinreb amide enolate on the masked oxo sulfinimine to provide, the N-sulfinyl-b-amino amide in a diastereomeric ratio of 22 : 1 (Scheme 15). The key step in the synthetic strategy involved a selective reduction of the common N-sulfinyl-b-amino ketone with Li[t-BuO]3AlH and LiEt3BH to give the syn- and anti- 1,3-amino alcohols in high diastereoselectivity. In the final stage, they devised a newer acido-catalyzed reaction of an N-sulfinylamino silyl protected alcohol ketal which rendered and starting from 91 and 95 respectively.

In the following year, they reported an unprecedented total synthesis of (+/)-5,9-Z-indolizidine 221T. The synthetic route started from sulfinimine derived from (+)-2,4,6-triisopropylphenylsulfinamide which formed 1 : 5.1 ratio of 99 a and 99 b, anti and syn-b-amino Weinreb amides (Scheme 16). Importantly, 2,4,6-triisopropylphenyl (TIPP) sulfinamide was particularly chosen as the chiral auxiliary based on the previous studies that suggested best syn:anti selectivities with the same. Thereafter, the sulfinimine derived aminoketone was reacted with crotonaldehyde and Ti(OEt)4 to afford the imine which in turn was subjected to an intramolecular
Mannich cyclization in presence of pTSA in toluene to construct the piperidone 101. Finally, the targeted compound 102 was achieved after a few functional group conversions.

In 2009, Davis employed anti-2,3-diamino esters derived from sulfimines in the synthesis of (2S,3R)-(-)-epi-CP-99,994 109. Here, the syn-analog of 109 is a known neurokinin substance P receptor antagonist. The synthesis commenced with their previously disclosed protocol for the addition of Z-lithium enolate of N117b and a mixture upon NaHMDS upon N-tetrahydroisoquinolines 117a from 115. Undertook sequential reduction, deprotection and a treatment with aqueous HCl yielded the cyclic imine in greater than 80% diastereomeric excess (Scheme 18).

Cyanopyridine stereoselective addition of base treated 4-methyl-3-anilinoester provided the sulfonylimine which underwent dia-nylation followed by the Pictet-Spengler cyclization conditions to yield the tetrahydroisoquinolines 117a and 117b as a 2 : 1 mixture. 117a and 117b differed merely in their configuration at sulfur and the mixture upon N-desulfinylation provided with the diastereomeric sulfoxides (Scheme 19). Then, these sulfoxides were subjected to Pictet–Spengler cyclization conditions to afford (S)-(-)-xylopinine 118. Importantly, this key step represented the first-time ipso electrophilic substitution of a sulfinyl group and the authors foresee more synthetic implications in this direction. The method stands superior among the known synthetic routes towards 118 due to the high stereocontrol and short sequence of transformations.

Mastranzo and coworkers established an efficient asymmetric synthetic route to (S)-(-)-tetrahydropalmatine and (S)-(-)-canadine via a three step methodology. In the initial step, the carbanionic nucleophile generated from 119 was added to p-tolylsulfynylimines 120 to yield the tetrahydroisoquinolines 121 in excellent diastereoselectivity (>96% de) after an intramolecular cyclization (Scheme 20). The p-tolyl group ensured better control of selectivity during this key step. Then, N-desulfinylation followed by the Pictet–Spengler cyclization with the use of TFA and paraformaldehyde under microwave radiation at 140 °C performed cyclization and successive C-desulfinylation to achieve enantiopure (S)-(-)-tetrahydropalmatine 123 and (S)-(-)-canadine 124.

An elegant protocol to access homotropinones like (-)-euphococinine and (-)-adaline was proposed by Davis et al. in 2009. In the initial step, N-sulfinyln-b-amino ketals 127

5. Miscellaneous

An effective method for the synthesis of (-)-normalindine in enantioenriched form has been introduced in 2006. The initial reactions provided the sulfimine 110 which underwent diastereoselective addition of base treated 4-methyl-3-cyanopyridine 111 in the key step to furnish the sulfimamide 112 in greater than 80% diastereomeric excess (Scheme 18). Exposure of the sulfimamide 112 with MeLi and successive treatment with aqueous HCl yielded the cyclic imine 113 which undertook sequential reduction, deprotection and a final cyclization to accomplish the desired alkaloid 114. The usefulness of the method is expected in the synthesis of analogous tetrahydronaphthyridines and tetrahydroisoquinolines.

Yuste and Ruano with coworkers successfully established a novel strategy towards the asymmetric synthesis of (S)-(-)-xylopinine. Initially, N-sulfinyl benzyl carbanion obtained from 115 was condensed with (S)-(E)-sulfinylimine 116 to yield tetrahydroisoquinolines 117a and 117b as a 2 : 1 mixture. 117a and 117b differed merely in their configuration at sulfur and the mixture upon N-desulfinylation provided with the

Scheme 18 Synthesis of enantiomerically enriched (–)-normalindine.

Scheme 19 Asymmetric synthesis of (S)-(−)-xylopinine.

Scheme 20 Asymmetric synthetic route to (S)-(−)-tetrahydro-palmatine and (S)-(−)-canadine.
were synthesized as inseparable diastereomers through the addition of metal enolates of N-methoxy-N-methyl acetamide 126 onto masked oxo-sulfinimine 125 (Scheme 21). Then, a subsequent Grignard addition offered respective N-sulfinyl β-amino ketone ketal 128 in high yields and diastereoselectivity. These methyl ketones 128a and 128b upon heating with buffer solution NH₄OAc : HOAc carried out a four-step intramolecular Mannich cyclization to furnish the anticipated homotropinones 129, 130 and substituted homotropinone 131.

Davis’ group devised protocols for the synthesis of tropane alkaloids owing to their important biological properties. In the first step, masked oxo sulfinimines 132 after twofold treatment with an excess of the enolate of methyl acetate offered N-sulfinyl δ-amino-ketoester ketal 133 as the major diastereoisomer (Scheme 22). When 133 was subjected to hydrolysis, dehydropropyridoline species 134 was produced. Then, 134 underwent cyclization via intramolecular Mannich reaction upon treatment with (Boc)₂O/DMAP which furnished the tropinone 135 in good yields. Similarly, substituted tropanes 137 and 139 were accessed from dehydropropyridoline ketones 136 and 138 respectively.

In 2010, Davis’ group described the first synthetic route to C-1 analogs of cocaine, 146 and (S)-(+-)cocaine 148 in high optical purity. The synthesis comprised of nine steps commencing from masked oxo sulfinimine 140. The sulfinimines 140 on reaction with sodium enolate of methyl acetate 141 yielded single diastereoisomers of the respective N-sulfinyl β-amino ester ketal 142 at −78 °C in Et₂O (Scheme 23). In the key step, α,β-unsaturated pyrrolidine nitrones 144 derived from sulfinimines underwent a highly stereoselective intramolecular [3 + 2] cycloaddition upon heating with Al(O-t-Bu)₃ to furnish tricyclic isoxazolidines 145 in good yields. These tricyclic compounds after a three step conversion provided the desired C-1 analogs 146 in enantiopure form. In a similar manner, (S)-(+-)cocaine 148 was synthesized from the sulfinimine 147 in nine steps.

Expanding their efforts in preparing derivatives of cocaine, they synthesized different cocaine analogues having methyl, ethyl, n-propyl, n-pentyl, and phenyl substituents at the C-1 or bridgehead position of its tropane skeleton. Both chiral t-buty1 and p-tolyl sulfinimines were explored to access differently substituted cocaine derivatives. As described before, synthesis commenced from masked oxo-sulfinimines 140, wherein the aforementioned key conversions afforded the sulfinimine-derived α,β-unsaturated pyrrolidine nitrones 144 (Scheme 24). Lewis acid assisted intramolecular [3 + 2] cycloaddition of the nitrone 144 afforded tricyclic isoxazolidines 145 which were easily converted to the anticipated cocaine analogues 146.
Differently, in the absence of any Lewis acid, the nitrones \( \text{144} \) underwent rearrangement to the lactam \( \text{145} \) via an oxaziridine intermediate. In addition, they disclosed a rare Pd- and base-promoted rearrangement of \( \text{146} \), to form bridged bicyclic [4.2.1] isoxazolidines \( \text{147} \).

6. Conclusion

Methodologies employing enantiopure sulfinamides have emerged as effective synthetic routes to access \( N \)-heterocyclic compounds owing to their high stereocontrol and easy cleavage after the reaction. In this review, we have summarized the recent reports on the application of aryl sulfinamides in the synthesis of optically pure \( N \)-heterocycles through sulfinimine intermediates. Even though most of the reports are with \( p \)-toluene sulfinamide, mesityl sulfinamide has also proven useful in \( N \)-heterocycle synthesis notably in aziridine synthesis. Other aryl derivatives of sulfinamides are utilized in other asymmetric reactions to meet specific requirements.

When some articles presented novel protocols towards \( N \)-heterocycles with substrate scope studies, others described the total synthesis of natural products containing \( N \)-heterocycles. Importantly, some examples achieved simple and short asymmetric total syntheses of targeted natural products including alkaloids like C-1 analogues of cocaine and other tropane alkaloids. A close look at the literature suggests that a major contribution in the field comes from Davis’ group and their insightful research to unveil the chemistry of sulfinamides inspired scientists around the globe. Although being the first introduced sulfinamide, \( p \)-toluene sulfinamide is less explored in recent decades. Exploring the applicability of available aryl sulfinamides and designing differently substituted analogues to access currently unexplored heterocyclic motifs will be appreciated in future. We expect that the varied strategies discussed may benefit people across the fields of medicinal chemistry, synthetic chemistry, and agrochemistry.

Conflicts of interest

There are no conflicts to declare.

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