Synthesis and configurational assignment of vinyl sulfoximines and sulfonimidamides

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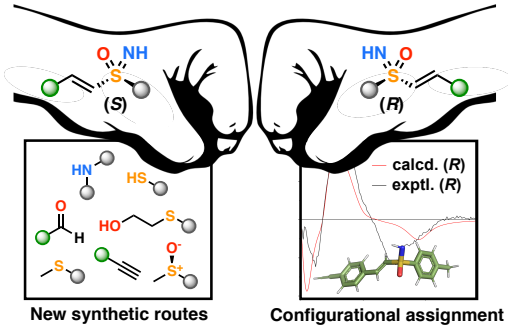


ABSTRACT: Vinyl sulfones and sulfonamides are valued for their use as electrophilic warheads in covalent protein inhibitors. Conversely, the S(VI) aza-isosteres thereof, vinyl sulfoximines and sulfonimidamides, are far less studied and have yet to be applied to the field of protein bioconjugation. Herein, we report a range of different synthetic methodologies for constructing vinyl sulfoximine and vinyl sulfonimidamide architectures that allows access to new areas of electrophilic chemical space. We demonstrate how late stage functionalization can be applied to these motifs to incorporate alkyne tags, generating fully functionalized probes for future chemical biology applications. Finally, we establish a workflow for determining the absolute configuration of enantioenriched vinyl sulfoximines and sulfonimidamides by comparing experimentally and computationally determined electronic circular dichroism spectra, enabling access to configurationally assigned enantiomeric pairs by separation.

INTRODUCTION

Sulfoximines and sulfonimidamides, the mono aza-analogues of sulfones and sulfonamides respectively, are gaining traction as valuable pharmacophores in medicinal chemistry (Figure 1a).[1,2] Architecturally, these motifs carry asymmetry at the tetrahedral sulfur center, offer hydrogen-bond acceptor and donor functionalities for NH derivatives, and afford new vectors along which to generate structural complexity. Bioactive sulfoximines date back to the discovery of methionine sulfoximine, which was later discovered to be a prodrug inhibitor of glutamine synthetase.[3] More recently, new synthetic methodologies have facilitated the incorporation of sulfoximine and sulfonimidamide motifs into drug discovery programs, through which their high chemical and stereochemical stability as well as favourable physicochemical properties have been uncovered.[4] Indeed, three sulfoximine compounds have entered clinical trials in recent years, with their desirable drug metabolism and pharmacokinetics (DMPK) profiles being cited as key triggers for candidate selection.[5]

Vinyl sulfones and sulfonamides are well characterized electrophiles and have been extensively utilized as reactive warheads in protein-targeted covalent probes.[6] For example, substituted vinyl sulfones are found in cysteine-targeting covalent cathepsin inhibitors,[7] terminal vinyl sulfones have been used in lysine-targeting cyclin-dependent kinase 2 (Cdk2) inhibitors[8] and terminal vinyl sulfonamides have been employed to target cysteine residues on a variety of

proteins including mitogen-activated protein kinase 1 (ERK2),[9] mutant KRas(G12C),[10] Bruton's tyrosine kinase (BTK) [11] and ubiquitin specific protease 7 (USP7)[12] (Figure 1b). Synthetic routes to these scaffolds are well established and probe specificity is engineered by installation of pharmacophores that bind the target protein and orientate the electrophile to react with a nearby nucleophilic amino acid.[13]

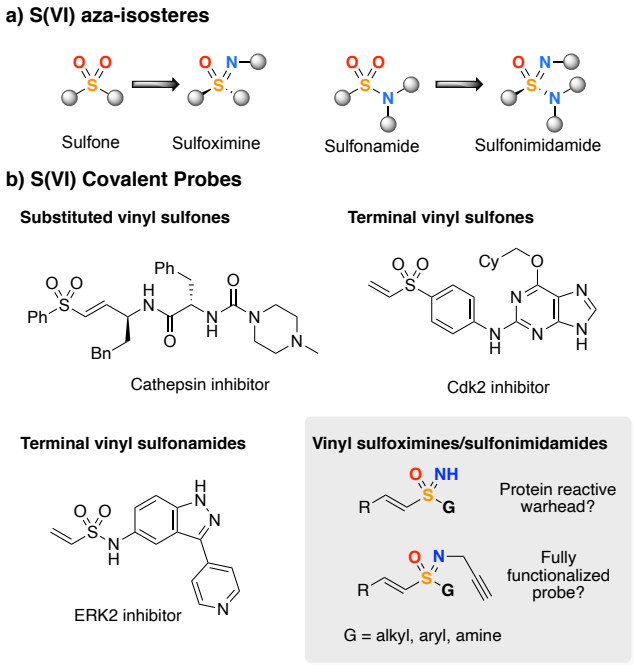
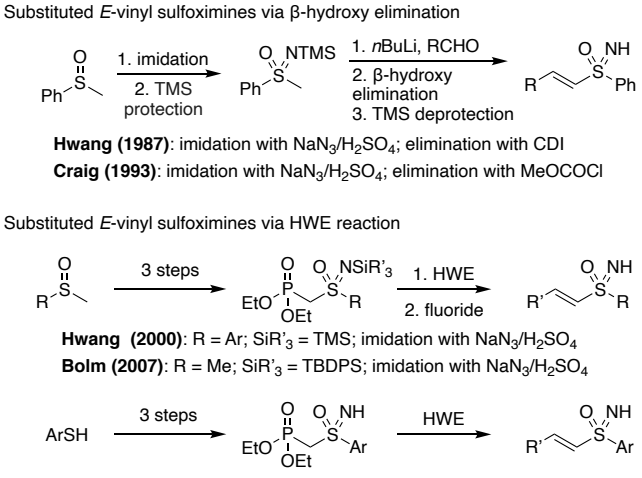


Figure 1. a) S(VI) aza-isosteres. b) Examples of established vinyl sulfone- and sulfonamide-based covalent inhibitors and proposed scaffolds for future aza-analogues.

We speculated that vinyl sulfoximines and sulfonimidamides could similarly act as protein reactive warheads in covalent probes.[14] The value of these aza-analogues compared to the established vinyl S(VI) electrophiles would arise from their ability to offer alternative hydrogen bonding architectures, additional vectors for pharmacophore incorporation and likely different reactivity profiles. Moreover, the new nitrogen center offers a convenient handle for the attachment of chemical biology functionalities, such as alkynes and fluorophores, to generate fully functionalized probes.[15] As these derivatives are chiral at sulfur, they present increased complexity and potential complementarity as probes. Recent work from Cravatt has demonstrated the value of using stereochemically-paired fully functionalised probes in the context of proteomic screening, offering an internal control for non-specific protein binding.[16] More broadly, electrophilic fragments are now routinely screened to identify starting points for covalent probes and novel electrophilic functionalities are desirable to expand the diversity of covalent fragment libraries.[17,18]

Over the last 30 years, *β*-substituted *E*-vinyl sulfoximines have been prepared by a variety of approaches utilizing carbonyl addition then β-hydroxy activation/elimination,[19] Peterson olefination[20] and Horner-Wadsworth-Emmons (HWE) olefination[21] (Scheme 1). More recently, Arvidsson reported an improved HWE sequence that is both high yielding and protecting group free.[22] These methodologies demonstrate the chemical stability and tractability of the vinyl sulfoximine motif and one such recent study has given rise to the first examples of bioactive vinyl sulfoximines that are thought to activate the transcription factor Nuclear factor erythroid 2–related factor 2 (Nrf2), although a covalent mechanism of action was not proposed.[23] However, these synthetic routes have clear limitations; they generally utilize multiple-step sequences that are reliant on the use of hydrazoic acid or *O*-(mesitylenesulfonyl)hydroxylamine MSH for sulfoxide imidation, which are both known for their thermal instability.[24,25] There are very few examples of terminal vinyl sulfoximines or enantioenriched vinyl sulfoximines. Moreover, the first two examples of vinyl sulfonimidamides were only reported very recently,[26] despite the prevalence of the analogous vinyl sulfonamides, which we attribute to the historically limited synthetic methodology regarding sulfonimidamides.

Scheme 1. Previous routes to vinyl sulfoximines.

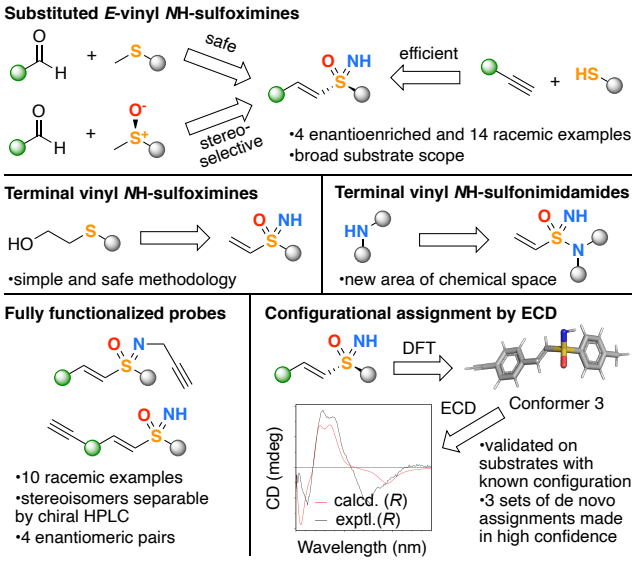


It is notable that in recent years the methods for sulfoximine and sulfonimidamide synthesis have developed considerably.[27–29] In our groups we have developed a safe and effective method for the NH transfer to sulfoxides to form sulfoximines using ammonium carbamate and (diacetoxy)iodobenzene.[30] Similarly, we and others have developed a one-pot oxidation and imidation protocol for the direct conversion of sulfides to sulfoximines.[31,32] Stockman and Lücking established a related process for the preparation of sulfonimidamides from sulfinamides.[33] We have developed the synthesis of sulfonimidamides from sulfenamides by NH and O transfer.[34] It is notable that by using this NH transfer methodology, the reaction of phenylvinylsulfoxide was effective in generating phenyl vinyl sulfoximine, though in moderate yield (54%).[30] However, the corresponding method from the sulfide was ineffective (14% yield for phenylvinyl sulfide),[31a] presumably due to the instability of terminal vinyl sulfides to acid. Improved methods that expand the diversity of accessible products, minimise the use of dangerous reagents and enable the synthesis of fully functionalised probes for future chemical biology investigations would be of considerable interest.

Here we report the development of new and improved synthetic routes for the preparation of vinyl sulfoximines, exploiting recent developments in the synthesis of aza-S(VI) derivatives. Three orthogonal routes to access terminal and substituted vinyl *N*H-sulfoximines are investigated,

including highly enantioenriched examples (Scheme 2). Furthermore, we report some of the first examples of vinyl *N*H-sulfonimidamides. These studies considerably extend the scope of the hypervalent iodine mediated NH-transfer methods and provide a comparison of available routes, highlighting strategies for different substitution patterns. A simple propargylation reaction to convert these products into fully functionalised probes is demonstrated. Finally, we generate stereochemically-paired vinyl sulfoximine and sulfonimidamide derivatives, by late-stage chiral separation, and establish a method for their configurational assignment by combining density functional theory (DFT) calculations and circular dichroism. These approaches allow access to a range of stereochemically defined structures of interest as probes.

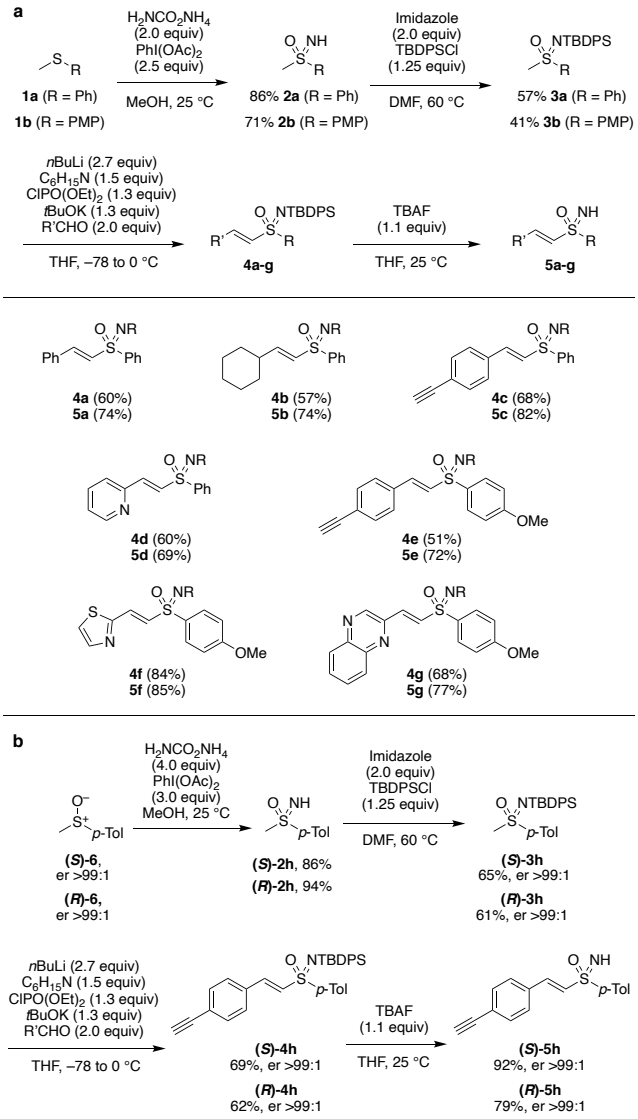
Scheme 2. Synthetic methods described in this work to access vinyl sulfoximines and sulfonimidamides.



RESULTS AND DISCUSSION

Substituted vinyl *E*-sulfoximines from methyl sulfides and sulfoxides. Our initial investigations focussed on the established HWE approach to vinyl sulfoximine synthesis but commencing from simple sulfides and applying recent methods for NH transfer, using (diacetoxy)iodobenzene and ammonium carbamate, to improve the efficiency and safety.[31a] Accordingly, methyl sulfides **1a** and **1b** were converted into the corresponding *N*H-sulfoximines **2a** and **2b** in very good yields (Scheme 3a). After TBDPS-protection of the sulfoximine nitrogen to give intermediates **3a** and **3b**, a one-pot HWE procedure was implemented using a range of aldehyde coupling partners to furnish *N*TBDPS-protected vinyl sulfoximines **4a**–**4g**. Finally, TBDPS-deprotection with TBAF afforded vinyl *N*H-sulfoximines **5a**–**5g**. Both aromatic and aliphatic aldehydes gave similarly high yields for the two steps (**5a** and **5b**). Incorporation of an alkyne functionality was well tolerated (**5c** and **5e**), which is encouraging for the potential to generate future fully functionalised probes. The method also performed well using the more electron rich anisole-derived sulfoximine (**5e**–**5g**) and using heteroaromatic aldehydes (**5d**, **5f**, **5g**).

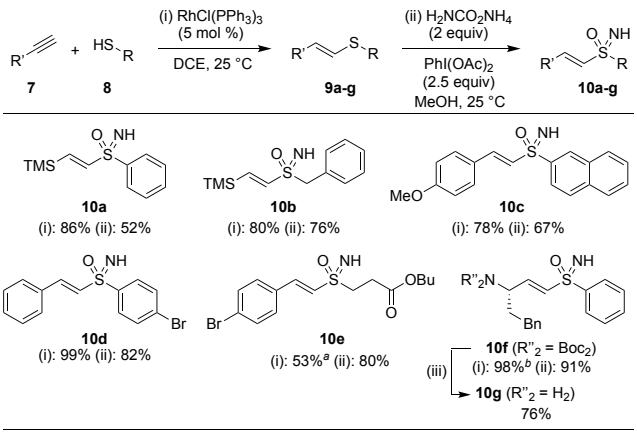
Scheme 3. Synthesis of substituted *E*-vinyl sulfoximines from (a) methyl sulfides and (b) enantioenriched methyl sulfoxides.



Stereochemically enriched sulfoximines are finding increasing utility in drug discovery and asymmetric synthesis but represent synthetically challenging targets.[4,5,35] Application of an analogous synthetic sequence to enantioenriched sulfoxides **(*S*)-6** and **(*R*)-6** using 4-ethynylbenzaldehyde furnished products **(*S*)-5h** and **(*R*)-5h** respectively, with retention of the configuration at sulfur and without loss of enantiomeric excess (Scheme 3b).[30] The stereospecificity of this route and configurational stability of the intermediates and products is encouraging for the design of future stereochemically-defined vinyl sulfoximines. Indeed, powerful methods are well established for the enantioselective oxidation of unsymmetrical methyl sulfides,[36] which could be combined with this HWE route to provide access to a broad range of enantioenriched vinyl sulfoximines. By incorporating alkyne functionalities into **(*S*)-5h** and **(*R*)-5h**, these structures represent the first example of stereochemically-paired fully functionalised vinyl sulfoximine probes.

Substituted *E*-vinyl sulfoximines via alkyne hydrothiolation. Next, we sought to develop a more efficient route to vinyl sulfoximines to expand the product scope, and notably avoid the use of protecting groups and possible regiochemical ambiguity in the deprotonation step of dialkyl sulfoximines. We anticipated that direct oxidation/imidation of vinyl thioethers would be the most direct path. A range of metal-catalysed alkyne hydrothiolation reactions have been developed that facilitate the synthesis of either branched,[37,38] linear *E*-vinyl thioethers[39] or linear *Z*-vinyl thioethers[40] in high selectivity. For this study we were interested in linear *E*-vinyl sulfoximines and applied a Wilkinson's catalyst mediated alkyne thiolalkyation methodology reported by Love which gives high levels of stereocontrol using 1,2-dichloroethane (DCE) as solvent.[41] The *E*-vinyl thioether products **9** were then converted to the corresponding *E*-vinyl sulfoximines **10** using our NH/O transfer method (Scheme 4).[31a] This two-step sequence provided efficient access to a diverse range of vinyl sulfoximines in good to excellent yields, tolerating silyl (**10a**-**10b**), aryl (**10c**-**10e**) and alkyl (**10f**) alkynes in combination with aryl (**10a**, **10c**, **10d** and **10f**) and alkyl (**10b** and **10e**) thiols. The success of this methodology for alkyl thiols is particularly exciting, since access to such products by HWE chemistry is challenging. Indeed, the incorporation of an aryl bromide containing alkyne (**10e**) and thiol (**10d**) will enable elaboration of these scaffolds in multiple vectors using transition metal catalyzed coupling chemistry. Pleasingly, we were also able to remove the Boc protection group from **10f** to afford amine **10g**, offering a useful handle for functionalization at the amine.

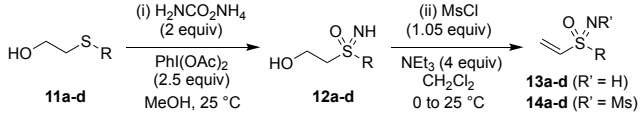
Scheme 4. Synthesis of substituted *E*-vinyl sulfoximines via alkyne hydrothiolation.

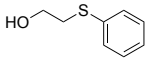
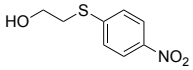
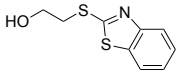
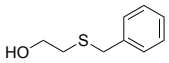


[a] Used 10 mol% $RhCl(PPh_3)_3$, 65°C. [b] **9f** is exemplified in ref 13e using similar conditions

Terminal vinyl sulfoximines via alcohol elimination. An alternative synthetic approach was needed to access terminal vinyl sulfoximines. We implemented a two-step sequence based on the controlled activation and elimination of β-hydroxy ethyl sulfoximines (Table 1). β-Hydroxy thioethers **11a-d** were converted to the corresponding sulfoximines **12a-d** in fair-to-excellent yields. Treating alcohols **12a-d** with a slight excess of methanesulfonyl chloride and base led to activation and elimination of the alcohol to give the desired NH vinyl sulfoximines **13a-d**. The methodology is suitable for producing aromatic (**13a** and **13b**), heteroaromatic (**13c**) and alkyl (**13d**) vinyl sulfoximines. The mesylation step generally proceeded with good *O*/*N* chemoselectivity; however, we were additionally able to isolate the *N*-mesyl vinyl sulfoximines in some cases (**14a** and **14d**) as side products. We anticipate that the *N*-mesyl vinyl sulfoximines would be more electrophilic and reactive than the NH analogues and may represent an interesting new class of electrophile in their own right.

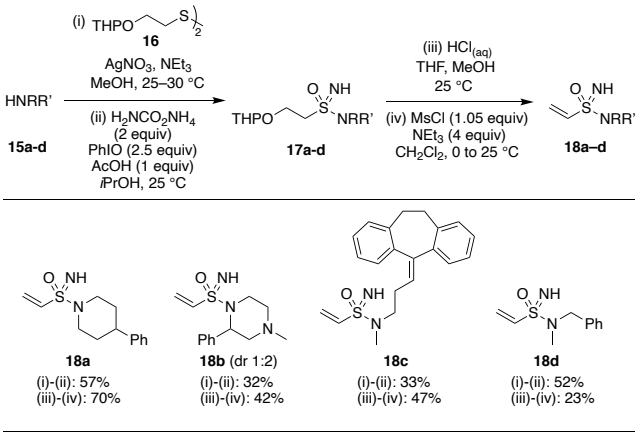
Table 1. Synthesis of terminal vinyl sulfoximines via alcohol elimination.



Sulfide **11**		Yield: Sulfoximine **12** (i)	Yield: NH vinyl sulfoximine **13** (ii)	Yield: NMs vinyl sulfoximine **14** (ii)
	**a**	73%	50%	6%
	**b**	87%	52%	-
	**c**	54%	39%	-
	**d**	91%	35%	29%

Terminal vinyl sulfonimidamides via alcohol elimination. We envisioned that an analogous β-hydroxy ethyl activation/elimination strategy could be implemented to generate vinyl sulfonimidamides by combining it with our sulfenamide oxidation/imidation method.[34] Accordingly, phenyl piperidine (**15a**) was treated with THP-protected β-hydroxy ethyl disulfide (**16**) and silver nitrate to generate the corresponding sulfenamide (Scheme 5). The inclusion of Et_3N, in modified conditions, gave improved results by reducing the acidity of the reaction. The sulfenamide was then simultaneously imidated and oxidized using ammonium carbamate and iodosylbenzene to give the THP-protected β-hydroxy sulfonimidamide **17a** in 57% yield over two steps. After THP-deprotection, mesylation and *in situ* elimination afforded the desired vinyl sulfonimidamide **18a** in 46% over two steps. Notably, the mesylation reaction proceeded with excellent *O*/*N* chemoselectivity for the alcohol over the sulfonimidamide. This novel class of electrophile was stable towards silica gel chromatography and has shown no noticeable degradation when stored at –20 °C in DMSO over six months. To further exemplify the methodology, we synthesised three additional vinyl sulfonimidamides **18b**–**18d**. Starting with racemic 1-methyl-3-phenylpiperazine **16b** gave vinyl sulfonimidamide **18b** (d.r. 1:2). Encouragingly the reaction sequence was successful with nortriptyline **15c**, demonstrating that bioactive motifs can also be converted into vinyl sulfonimidamides. This route has delivered some of the first examples of a chemical motif that has significant potential for future probe design.

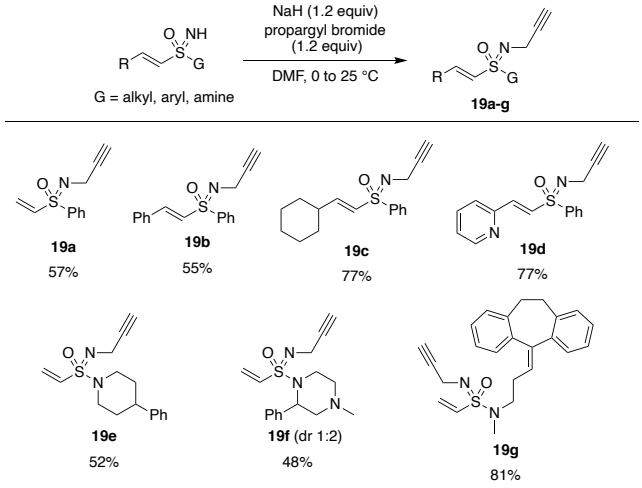
Scheme 5. Synthesis of terminal vinyl sulfonimidamides *via* alcohol elimination.



***N*-Propargylation of vinyl sulfoximines and sulfonimidamides.** The incorporation of alkyne tags onto small molecules is a highly valuable transformation that enables chemical biology experiments such as activity-based protein profiling and fluorescence microscopy.[42] In the context of covalent protein targeting probes, the addition of an alkyne tag generates a fully functionalized probe that facilitates visualization and quantification of target engagement.[15] The majority of the previously established covalent warheads do not possess convenient chemical handles for attachment of alkyne tags.[14b] As such the design of fully functionalised probes often requires preinstallation of the alkyne handle into the pharmacophore which can be synthetically challenging.[43] Therefore, a general method for late-stage propargylation of small molecules would present significant benefits and opportunities to chemical biologists.

Functionalization, including propargylation, of sulfoximine-*N*H groups has been widely reported, though for sulfonimidamides much less so.[44–46] Vinyl sulfoximines and sulfonimidamides are electrophilic in nature which raises potential reaction compatibility concerns. Pleasingly, however, a diverse range of vinyl sulfoximines and sulfonimidamides could be efficiently propargylated using sodium hydride and propargyl bromide (Scheme 6). Terminal (**19a**), substituted (**19b** and **19c**) and heteroaromatic (**19d**) vinyl sulfoximines as well as tertiary amine containing vinyl sulfonimidamides (**19e,f**) and bioactive-pharmacophore containing vinyl sulfonimidamide (**19g**) were all well tolerated.

Scheme 6. *N*-Propargylation of vinyl sulfoximines and sulfonimidamides.



Configurational assignment of enantioenriched vinyl sulfoximines and sulfonimidamides. The binding between proteins and chemical probes often exhibits discriminatory affinity for different stereoisomers. Indeed, the clinical candidate sulfoximine inhibitors roniciclib, atuveciclib and ceralasertib are all enantiopure.[5] Therefore, the development of future probes relies on both access to enantioenriched vinyl sulfoximines and sulfonimidamides and the ability to assign their absolute configuration. Through the HWE reaction sequence, highly enantioenriched vinyl sulfoximines **(*S*)-5h** and **(*R*)-5h** (Scheme 3b) were prepared with synthetically defined configuration. However, the other synthetic routes to vinyl sulfoximines and sulfonimidamides described herein generate racemic products with respect to the chiral sulfur centre. Chiral separation, typically conducted by high-performance liquid chromatography (HPLC) or supercritical fluid chromatography (SFC), offers an alternative method for accessing enantioenriched products and has been highly successful with regards to the production of enantiopure sulfoxide drugs.[47,48] The value of such separation is dependent on reliable assignment of absolute configuration which is typically accomplished by X-ray crystallography,[49] NMR[50] or computational and experimental circular dichroism.[51] Electronic circular dichroism (ECD) is among the most versatile of these techniques and has previously been successfully applied to the stereochemical assignment of sulfoxide drugs and sulfonimidamides.[52–54] To establish whether ECD could be reliably applied to the configurational assignment of vinyl sulfoximines and sulfonimidamides we first investigated whether quantum mechanical calculations could predict the experimentally observed ECD spectrum for **(*R*)-5h** with high confidence.

A conformational search (see Supporting Information) was performed on the vinyl sulfoximine unit using the B3LYP functional and the 6-31G* basis set. The low energy conformers (within 3 kcal/mol of the lowest) were further optimised using cam-B3LYP/6-311++g(d,p) in a conductor-like polarizable continuum (CPCM) model of acetonitrile. We identified four minimum energy conformers of **(*R*)-5h** that are significantly populated at ambient temperature (Figure 2a). In the two lowest energy conformers (3 and 1), the vinyl group eclipses the S=O bond, with the two structures varying in the orientation of the NH group. Conformers 15 and 13, which are slightly higher in energy,

have the vinyl group eclipsing the S=N bond. The electronic transitions of each conformer of **(*R*)-5h** were then calculated and the UV-vis and ECD spectra simulated and summed according to their Boltzmann weighting (Figure 2b). It should be noted that the calculated ECD spectra of conformers 3 and 1 were similar to each other in the experimental range (190-340 nm) whilst the calculated spectra of conformers 13 and 15 were also similar to each other, but with the significant peaks being opposite in sign to those of 3/1. The weighted ECD spectrum is therefore sensitive to the relative conformer energies at the vinyl-S=O dihedral. We then measured the ECD and UV-vis spectra of **(*R*)-5h** in acetonitrile experimentally and compared them to the calculated spectra using SpecDis, a dedicated software package for comparing ECD/UV spectral similarity.[55] Aligning the UV-vis spectra required a 11 nm positive shift correction factor of the calculated spectrum, giving good spectral matches that are characterized by a sharp peak at 197 nm and a broad peak between 270–320 nm. Applying the same 11 nm correction factor to the calculated ECD spectrum gave excellent correlation with the experimental ECD, defined by a trough between 200–217 nm, a double peak between 217–256 nm and a second trough between 256–316 nm. To quantify the ECD spectral match, we applied similarity factor analysis which gave an 80.7% match for the experimental **(*R*)-5h** ECD spectrum with the calculated **(*R*)-5h** spectrum but only a 0.7% match with the calculated **(*S*)-5h** spectrum. The resulting delta score of 80.0% represents a high confidence assignment and validates that this workflow is reliable and should be suitable for assigning the configuration of vinyl sulfoximines and sulfonimidamides with unknown stereochemistry.

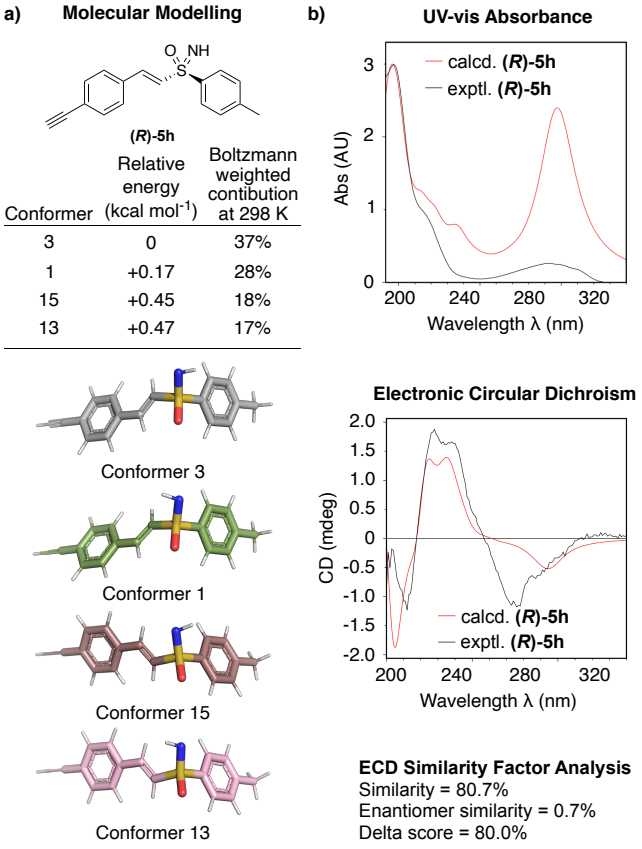


Figure 2. a) Molecular modelling of the low energy conformations of (*R*)-5h. b) Comparison of calculated and experimental UV-vis and ECD spectra for (*R*)-5h.

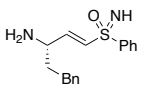
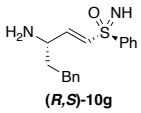
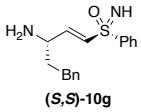
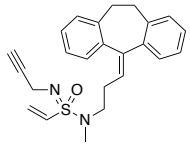
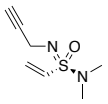
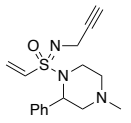
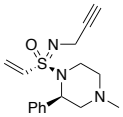
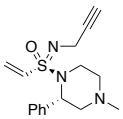
Next, we selected three compounds **10g, 19g** and **19f** for chiral separation, which was performed using the automated HPLC/SFC condition screening system at Reach Separations,[56] and de novo configurational assignment by ECD using the same modelling workflow and parameters as described for **(*R*)-5h** (Table 2)**.** Chiral separation of **10g**, where the carbon stereocenter is synthetically defined as (*S*), gave two diastereoisomers **10g-A** and **10g-B** as neutral amines. ECD calculation for **10g** is challenging because of the presence of the second stereocenter and the conformational flexibility of the acyclic allylic amine. We examined two approaches to simplify this problem. In the first, we used a single fixed, low energy conformation of the vinyl amine portion appended to the four conformers of the allylic sulfoximine unit found for **5h**. We modelled both **(*R*,*S*)-10g** and **(*S*,*S*)-10g** in this way (Figure S1). The **(*R*,*S*)-10g** and **(*S*,*S*)-10g** models gave distinct calculated ECD spectra and comparison with the experimental spectra gave the best match for **10g-A** = **(*R*,*S*)-10g** and **10g-B** = **(*S*,*S*)-10g**, with a mean similarity score of 78.6% (Figure S2). This assignment is made with high confidence given that the mean similarity score for the opposite assignment is only 37.1%. To simplify the modelling further for future applications, we also modelled a phenyl vinyl sulfoximine substructure of **10g** that lacks the chiral amine functionality. We found that comparing the predicted ECD spectrum of **substructure-10g** with the experimental racemic-subtracted ECD spectrum of **10g** gave the same assignment as modelling the full structure with a similar confidence level (delta score = 80.6%) (Figure S3).

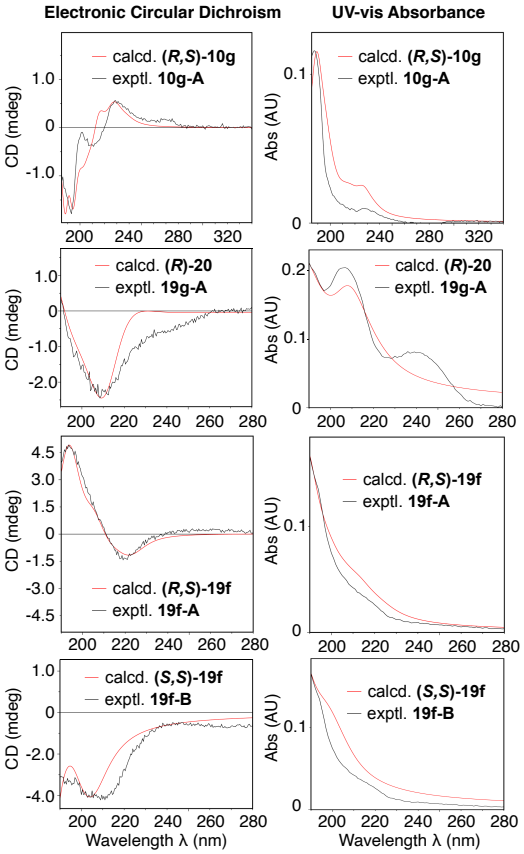
Vinyl sulfonimidamide **19g** was separated into its two enantiomers **19g-A** and **19g-B** which were isolated in very high enantiomeric purity. The biaryl system is achiral and was anticipated not to make a significant contribution to the ECD spectrum, while the flexible nature of the alkyl linker would make the conformational modelling challenging. Accordingly, we modelled **(*R*)-20** as the key substructure which yielded three low energy conformers. In analogy with vinyl sulfoximine **5h** and **10g**, the two lower energy conformers (differing by 0.17 kcal mol^{-1}) have the vinyl group eclipsing the S=O bond, with the two structures varying in the orientation of the N–propargyl group, while for the higher energy conformer (+0.75 kcal mol^{-1}) the vinyl group eclipses the S=N bond (Figure S4). Comparing the calculated and experimental UV-vis and ECD spectra led to an unambiguous assignment of **19g-A** = (*R*) and **19g-B** = (*S*) configuration with high confidence (delta score = 91.5%) (Figure S5).

Chiral separation of **19f** gave four stereoisomers **19f-A–D** that were each isolated in high levels of stereo purity. By comparing the NMR spectra of each isomer, **19f-A** and **19f-D** were assigned as one enantiomeric pair and **19f-B** and **19f-C** the other, although no information about their relative configuration could be obtained. We then modelled both **(*R*,*S*)-19f** and **(*S*,*S*)-19f** which gave four and five low energy (≤1.5 kcal mol^{-1}) conformers respectively, with the piperazine ring adopting a chair-like conformation and the phenyl ring pointing axially in each case (Figure S6). Conformers in which the phenyl ring points equatorially were

substantially higher in energy (≥2.2 kcal mol^{-1}) for both **(*R*,*S*)-19f** and **(*S*,*S*)-19f** and made little-to-no contribution to the calculated ECD. Of note, while for **(*R*,*S*)-19f** the two lowest energy conformers have the vinyl group eclipsing S=O, for **(*S*,*S*)-19f** the lowest four conformers are of very similar energy, two them having the vinyl group eclipsing S=N, and two having it eclipse S=O. Determining the configuration of diastereoisomers by ECD is typically challenging because they often have closely related ECD spectral profiles. However, in this case the calculated Boltzmann-weighted ECD spectra of all four stereoisomers gave strikingly different shapes. Comparing the UV and ECD spectra of each isomer with the modelled spectra, we found that **19f-A** has a nearly exact match (98.9%) with **(*R*,*S*)-19f** and **19f-B** gave an excellent match (97.4%) with **(*S*,*S*)-19f**, allowing us to make a high confidence assignment of all four isomers (Figure S7).

Table 2. Chiral separation and configurational assignment of vinyl sulfoximine and sulfonimidamides stereoisomers by molecular modelling and ECD.

Compound	HPLC purification	Modeled structure/ substructure	ECD similarity score	Assignment
 **10g**	Chiralpak IG (MeOH + 0.2% NH_3) Isomer **10g-A** 99% de (rt = 3.7 min) Isomer **10g-B** 97% de (rt = 4.5 min)	 **(*R*,*S*)-10g**	**10g-A** = 87.1% **10g-B** = 58.8%	**10g-A** = **(*R*,*S*)-10g** **10g-B** = **(*S*,*S*)-10g** Mean similarity score 78.6%
		 **(*S*,*S*)-10g**	**10g-A** = 15.3% **10g-B** = 70.0%	
 **19g**	Chiralpak IG (50:50 heptane:IPA) Isomer **19g-A** 99% ee (rt = 3.8 min) Isomer **19g-B** 98% ee (rt = 4.9 min)	 **(*R*)-20**	**19g-A** = 91.7% **19g-B** = 0.3%	**19g-A** = **(*R*)-19g** **19g-B** = **(*S*)-19g** Delta score 91.5%
 **19f** Enantiomeric pairs determined by NMR: Pair 1 = **19f-A** & **19f-D** Pair 2 = **19f-B** & **19f-C**	Amylose-C (90:10 heptane:EtOH) Isomer **19f-A** 100% ee, 100% de (rt = 4.3 min) Isomer **19f-B** 100% ee, 100% de (rt = 5.8 min) Isomer **19f-C** 96% ee, 100% de (rt = 7.2 min) Isomer **19f-D** 100% ee, 97% de (rt = 8.4 min)	 **(*R*,*S*)-19f**	**19f-A** = 98.9% **19f-B** = 28.1% **19f-C** = 62.8% **19f-D** = 0.1%	**19f-A** = **(*R*,*S*)-19f** **19f-B** = **(*S*,*S*)-19f** **19f-C** = **(*R*,*R*)-19f** **19f-D** = **(*S*,*R*)-19f** Mean similarity score 98.2%
		 **(*S*,*S*)-19f**	**19f-A** = 11.7% **19f-B** = 97.4% **19f-C** = 1.9% **19f-D** = 86.7%	



CONCLUSION

Vinyl sulfoximines and sulfonimidamides offer significant potential as functionalizable electrophilic warheads but have seen little exploration to date. We have developed several new synthetic approaches to these motifs that expand the potential of these motifs and access a much wider range of derivatives. Firstly, we showcased a modified HWE sequence, from methyl sulfides, providing NH vinyl sulfoximines exclusively as the *E*-isomers. Application of this HWE sequence to enantioenriched methyl sulfoxides gave an efficient route to enantioenriched vinyl sulfoximines. Next, we developed a two-step route to vinyl sulfoximines that exploits alkyne hydrothiolation and a highly chemoselective one-pot transfer of NH and O to vinyl sulfides. This route is substantially shorter than previous approaches and works well for both alkyl and aryl vinyl sulfoximines.

Terminal vinyl sulfoximine and sulfonimidamides represent particularly challenging synthetic targets that could have widespread application as warheads in covalent probes. We developed a simple two-step route to terminal vinyl sulfoximines from β-hydroxyethyl thioethers involving sulfoximine formation and alcohol activation/elimination. This approach is also extended to terminal vinyl sulfonimidamides, about which very little is known. Both vinyl sulfoximines and sulfonimidamides can be readily *N*-functionalized with an alkyne tag. These products have the potential to be utilized as fully functionalized probes in a range of chemical biology applications.

Finally, we developed a computational workflow for assigning the configuration of vinyl sulfoximines and sulfonimidamides using ECD. After validating the approach against a vinyl sulfoxide with synthetically defined and known configuration, we apply the approach to the de novo assignment of enantiomeric and diastereoisomeric vinyl sulfoximines and vinyl sulfonimidamides. This

methodology enables the implementation of chiral separation techniques to be applied to separate racemic vinyl sulfoximines and sulfonimidamides and assign their configuration, giving access to a range of new enantioenriched products.

Taken together, the methods we have exemplified in this work provide the tools to access new areas of electrophilic chemical space. Our investigations into the application of vinyl sulfoximines and sulfonimidamides to chemical biology are currently underway.

EXPERIMENTAL SECTION

General experimental considerations. All non-aqueous reactions were carried out under an inert atmosphere (argon) with flame-dried glassware, using standard techniques. Anhydrous solvents were obtained by filtration through drying columns (THF, CH_2Cl_2, toluene). Forward phase flash column chromatography was performed on an Isolera™ Spektra flash purification system using Biotage® SNAP KP-Sil flash purification cartridges or SNAP Ultra flash purification cartridges, with the indicated solvent gradient. Reversed-phase flash column chromatography was performed using Biotage® SNAP Ultra C18 cartridges. Analytical thin-layer chromatography (TLC) was performed on precoated aluminium-backed silica gel plates. Visualisation of the developed chromatogram was performed by UV absorbance (254 nm) and/or stained with aqueous potassium permanganate solution, aqueous ceric ammonium molybdate, or a ninhydrin solution in ethanol. Nuclear magnetic resonance spectra were recorded on a 400 MHz spectrometer. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane with the residual protic solvent resonance as the internal standard (chloroform: δ 7.27 ppm, methanol: δ 3.31 ppm). Data are reported as follows: chemical shift (multiplicity [s = singlet, d = doublet, t = triplet, m = multiplet and br = broad], coupling constant (in Hz), integration). ^{13}C NMR spectra are recorded with complete proton decoupling. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard ($^{13}CDCl_3$: δ 77.0 ppm, $^{13}CD_3OD$: δ 49.0 ppm). ^{19}F NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in parts per million, referenced to fluorobenzene as a standard at δ -113.5 ppm. Commercial reagents were used as supplied or purified by standard techniques where necessary. Optical rotations (α') were recorded at the indicated temperature (T °C) and were converted to the corresponding specific rotations $[\alpha]_D^T$.

General Procedure A: Preparation of NH Sulfoximines from sulfides by one-pot N- and O-transfer. Procedure adapted from Tota *et al*.[31a] The sulfide (4.8 mmol, 1.0 equiv), (diacetoxyiodo)benzene (12.0 mmol, 2.5 equiv) and ammonium carbamate (9.6 mmol, 2.0 equiv) were added to a flask containing a stirrer bar. MeOH (0.5 M) was added and the reaction was stirred at 25 °C for 3 h. The solvent was removed under reduced pressure. Purification by flash chromatography afforded the sulfoximine product.

General Procedure B: TBDPS protection of sulfoximine. A solution of imidazole (5.2 mmol, 2.0 equiv) in anhydrous DMF was added to sulfoximine (2.6 mmol, 1.0 equiv). The reaction mixture was cooled to 0 °C and *tert*-butyldiphenylsilyl chloride (3.3 mmol, 1.25 equiv) was added drop-wise to the mixture. The solution was heated to 60 °C using a heating block and stirred for 64 h under nitrogen after which the reaction was quenched with water (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL) and the organic extracts were washed with water (10 mL) and brine (10 mL). The combined organic extracts were then dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash chromatography afforded the TBDPS protected sulfoximine product.

General Procedure C: Preparation of vinyl sulfoximines by a Horner-Wadsworth-Emmons reaction. *n*BuLi (1.35 mmol, 1.3M in hexane, 2.7 equiv) was added to a solution of diisopropylamine (0.75 mmol, 1.5 equiv) in anhydrous THF at −78 °C under nitrogen. The resulting solution was warmed to room temperature over 30 min, before being cooled to −78 °C again. The TBDPS protected sulfoximine (0.50 mmol, 1.0 equiv) in anhydrous THF was added dropwise to the reaction mixture and stirred at −78 °C for a further 1 h. Diethylchlorophosphate (0.65 mmol, 1.3 equiv) was added dropwise. After 5 min, ^{t}BuOK (0.65 mmol, 1.0M in THF, 1.3 equiv) was added and the mixture was stirred for 10 min after which a solution of aldehyde (1.00 mmol, 2.0 equiv) in anhydrous THF was added. The solution was then allowed to warm to 0 °C and stirred for 2 h. The reaction was quenched with 5% w/w aq. H_3PO_4 (10 mL). The aqueous layer was extracted with Et_2O (3 × 20 mL) and the organic extracts were washed with 5% w/w aq. H_3PO_4 (2 × 20 mL). The combined organic extracts were then dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash chromatography afforded the TBDPS protected vinyl sulfoximine product.

General Procedure D: TBDPS deprotection of vinyl sulfoximines. TBAF (0.29 mmol, 1.0 M in THF, 1.1 equiv) was added dropwise to a solution of TBDPS protected vinyl sulfoximine (0.26 mmol, 1.0 equiv) dissolved in anhydrous THF under nitrogen at room temperature . The reaction mixture was monitored by TLC every hour until the reaction was complete. The reaction mixture was flushed through a silica plug with Et_2O and concentrated *in vacuo*. Purification by flash chromatography afforded the *N*H vinyl sulfoximine product.

General Procedure E: Preparation of NH Sulfoximines from sulfoxides by one-pot N-transfer. Procedure adapted from Zenzola *et al*.[30] The sulfide (1.62 mmol, 1.0 equiv), (diacetoxyiodo)benzene (4.86 mmol, 3.0 equiv) and ammonium carbamate (6.48 mmol, 4.0 equiv) were added to a flask containing a stirrer bar. MeOH (0.5 M) was added and the reaction was stirred at 25 °C for 3 h. The solvent was removed under reduced pressure. Purification by flash chromatography afforded the sulfoximine product.

General Procedure F: Alkyne hydrothiolation. Procedure adapted from Shoai *et al*.[41] $RhCl(PPh_3)_3$ (0.05 mmol, 5 mol%) and any other solid reagents (thiol (1.1 mmol, 1.1 equiv)/alkyne (1.0 mmol, 1.0 equiv)) were added to a microwave vial and sealed. The flask was evacuated and filled with N_2 three times before adding any liquid reagents (thiol (1.1 mmol, 1.1 equiv)/alkyne (1.0 mmol, 1.0 equiv)) and 1,2-dichloroethane (0.1 M) at 25 °C. The flask was left to stir for 18 h before the solvent was removed under reduced pressure. Purification by flash column chromatography afforded the corresponding vinyl sulfide product.

General Procedure G: Terminal vinyl sulfoximine synthesis by alcohol mesylation and in situ elimination. Mesyl Chloride (0.80 mmol, 1 M in CH_2Cl_2, 1.05 equiv) was added dropwise to a stirred solution of triethylamine (3.04 mmol, 4.0 equiv) and alcohol (0.76 mmol, 1.0 equiv) in CH_2Cl_2 (0.1 M) at 0 °C and left to warm to room temperature. After 1 h the solvent was removed under reduced pressure. Purification by flash column chromatography afforded the corresponding vinyl *N*H sulfoximine and in some cases *N*-mesylated vinyl sulfoximine products.

General Procedure H: Synthesis of sulfonimidamides from amines via a sulfenamide intermediate.

Procedure adapted from Briggs *et al*.[34] Amine (3.33 mmol, 1.33 equiv), triethylamine (2.0–3.5 equiv) and silver nitrate (5.0 mmol, 2.0 equiv) were added to a stirred solution of disulfide **16** (2.5 mmol, 1.0 equiv) in MeOH (0.1 M) at 25 °C, under air, for 1 h. The reaction mixture was filtered and washed with MeOH (2 × 50 mL). The filtrate solvent was removed under reduced pressure. H_2O (75 mL) was added to the crude mixture and the aqueous mixture extracted with Et_2O (3 × 75 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent removed under reduced pressure. Purification by filtration through a basic alumina (activity IV) plug (2 cm thick) afforded the corresponding crude sulfenamide intermediate. Iodosylbenzene (6.25 mmol, 2.5 equiv) and ammonium carbamate (5.0 mmol, 2.0 equiv) were added to the crude sulfenamide (2.5 mmol, 1.0 equiv) in a flask containing

a stirrer bar under an argon atmosphere. A solution of acetic acid (0.2 M solution, corresponding to 1.0 equiv of AcOH) in *i*PrOH (0.2 M) was added and the reaction was stirred for 1 h. The solvent was then removed under reduced pressure and to the crude, sat. aq. $NaHCO_3$ was added (20 mL). The aqueous mixture was then extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic layers were dried (Na_2SO_4), filtered and the solvent removed under reduced pressure. Purification by flash chromatography afforded the corresponding sulfonimidamide products.

General Procedure I: Vinyl sulfonimidamides synthesis by THP deprotection and alcohol elimination.

HCl (37% in H_2O, 1 mL) was added to a stirred solution of sulfonimidamide (0.65 mmol, 1 equiv) in MeOH:THF (1:1, 12 mL) at 25 °C. After 30 min sat. aq. $NaHCO_3$ was added (25 mL). The aqueous mixture was then extracted with EtOAc (3 × 50 mL) and the combined organic layers were dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to afford the crude alcohol intermediate. A solution of MsCl (0.68 mmol, 1 M in CH_2Cl_2, 1.05 equiv) was added dropwise to a solution of the crude alcohol (0.65 mmol, 1.0 equiv) and triethylamine (4.0 equiv) in CH_2Cl_2 (0.1 M) at 0 °C and left to warm to room temperature for 16 h. The solvent was removed *in vacuo* and purification by flash chromatography afforded the corresponding vinyl sulfonimidamide products.

General Procedure J: N-Propargylation of vinyl sulfoximines and sulfonimidamides. NaH (0.19 mmol, 60% in mineral oil, 1.2 equiv) was added to a solution of the sulfonimidamide (0.16 mmol, 1.0 equiv) in DMF (0.1 M) at 0 °C and the reaction stirred for 30 min. Propargyl bromide (0.22 mmol, 80% in toluene 1.5 equiv) was added and the reaction allowed to warm to room temperature for 3 h. H_2O (10 mL) was added and the aqueous mixture extracted with EtOAc (3 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and the solvent removed *in vacuo*. Purification flash chromatography afforded the corresponding *N*-propargyl sulfoximine or sulfonimidamide products.

Substituted vinyl sulfoximines **5a**–**5g**.

Imino(methyl)(phenyl)-λ⁶-sulfanone (**2a**). The title compound was prepared according to General Procedure A employing diacetoxyiodobenzene (3.90 g, 12.1 mmol), ammonium carbamate (753 mg, 9.66 mmol) and thioanisole (600 mg, 4.83 mmol) in MeOH (9.6 mL). Purification *via* flash chromatography (KP-Sil, 0% grading to 100% EtOAc/Pentane, product eluted at 100%) afforded **2a** as a yellow oil (644 mg, 86%); R_f = 0.42 (100% EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.95 (m, 2H), 7.58–7.55 (m, 1H), 7.51–7.48 (m, 1H), 3.06 (s, 3H), 2.02 (s, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 143.4, 133.1, 129.3 (2 × C), 127.7 (2 × C), 46.0; HRMS (ESI-TOF) m/z calcd $C_7H_{10}NOS^+$ [M + H]$^+$, 156.0478; found, 156.0482. Analytical data in agreement with those reported in the literature.[34]

Imino(4-methoxyphenyl)(methyl)-λ⁶-sulfanone (**2b**). The title compound was prepared according to General Procedure A employing diacetoxyiodobenzene (10.4 g, 32.4 mmol), ammonium carbamate (2.02 g, 25.9 mmol) and (4-methoxyphenyl)(methyl)sulfane (2.0 g, 13.0 mmol) in MeOH (32 mL). Purification *via* flash chromatography (KP-Sil, 0% grading to 100% EtOAc/Pentane, product eluted at 100%) to afford **2b** (1.70 g, 71%) as an orange oil; R_f = 0.21 (100% EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.91 (d, *J* = 8.9 Hz, 2H), 7.00–6.98 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 3.08 (s, 3H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 163.3, 134.9, 129.88 (2 × C), 114.4 (2 × C), 55.7, 46.5; HRMS (ESI-TOF) *m/z* calcd for $C_8H_{12}NO_2S^+$ [M + H]$^+$, 186.0583; found, 186.0581. Analytical data in agreement with those reported in the literature.[57]

tert-Butyl (methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)carbamate (**3a**). The title compound was prepared according to General Procedure B employing sulfoximine **2a** (400 mg, 2.58 mmol). Purification *via* flash chromatography (KP-Sil, 0% grading to 10% EtOAc/Pentane, product eluted at 8%) afforded sulfoximine **3a** (578 mg, 57%) as a clear oil; R_f = 0.20 (15% EtOAc/Pentane); ^{1}H NMR (400MHz, $CDCl_3$) δ 7.87–7.85 (m, 2H), 7.71–7.69 (m, 2H) 7.65–7.63 (m, 2H), 7.46–7.42 (m, 1H) 7.39–7.35 (m, 2H), 7.30–7.21 (m, 6H), 2.78 (s, 3H) 1.02 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 144.5, 136.23, 136.19, 135.64 (2 × C), 135.60 (2 × C), 132.2, 129.1, 128.9, 128.9 (2 × C), 127.44 (2 × C), 127.41 (2 × C), 127.0, (2 × C), 49.0, 27.2, 19.41 (3 × C). HRMS (ESI-TOF) *m/z* calcd for $C_{23}H_{28}NOSiS^+$ [M + H]$^+$, 394.1655; found, 394.1657. Analytical data in agreement with those reported in the literature.[58]

((*tert*-Butyldiphenylsilyl)imino)(4-methoxyphenyl)(methyl)-λ⁶-sulfanone (**3b**). The title compound was prepared according to General Procedure B employing sulfoximine **2b** (1.70 g, 2.58 mmol). Purification *via* flash chromatography (KP-Sil, 0% grading to 20% EtOAc/Pentane, product eluted at 15%) afforded sulfoximine **3b** (447 mg, 41%) as an off-white solid; R_f = 0.20 (10% EtOAc/Pentane); mp (chloroform) = 83–85 °C; IR (film)/cm^{-1} 3071, 2929, 2855, 1595, 1498, 1308, 1259, 1155, 1107, 1029, 958, 835, 772, 700, 674; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.1 Hz, 2H), 7.78–7.76 (m, 2H), 7.73–7.71 (m, 2H), 7.37–7.28 (m, 6H), 3.85 (s, 3H), 2.83 (s, 3H), 1.09 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 162.6, 136.6, 136.5, 136.4, 135.7 (2 × C), 135.6 (2 × C) 129.1 (1 × C), 129.0, 129.1, 127.42 (3 × C), 127.38 (3 × C), 113.9 (2 × C), 55.6, 49.4, 27.2, 19.4 (3 × C); HRMS (ESI-TOF) *m/z* Calcd for $C_{24}H_{30}NO2SSi^+$ [M + H]$^+$, 424.1767; found, 424.1771.

(*E*)-((*tert*-Butyldiphenylsilyl)imino)(phenyl)(styryl)-λ⁶-sulfanone (**4a**). The title compound was prepared according to General Procedure C employing sulfoximine **3a** (200 mg, 0.51 mmol) in anhydrous THF (3.2 mL), *n*BuLi (1.3 M in hexane, 1.05 mL, 1.37 mmol), diisopropylamine (0.11 mL, 0.72 mmol) in THF (3.2 mL), diethylchlorophosphate (0.14 mL, 0.66 mmol), *t*BuOK (1.0 M in THF, 0.66 mL, 0.66 mmol), benzaldehyde (0.10 mL, 1.02 mmol) in THF (8 mL). Purification *via* flash chromatography (KP-Sil, 0% grading to 100% EtOAc/Pentane, eluted at 9% EtOAc) afforded vinyl sulfoximine **4a** (147 mg, 60%) as a clear oil; R_f = 0.49 (10% EtOAc/Pentane); IR (film)/cm^{-1} 3064, 2930, 2855, 1677, 1614, 1293, 1148, 1107, 969, 816, 745, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.85 (m, 2H), 7.71–7.65 (m, 4H), 7.44–7.40 (m, 1H), 7.37–7.33 (m, 3H), 7.31 (d, *J* = 15.2 Hz, 1H), 7.26–7.20 (m, 8H), 7.14–7.12 (m, 2H), 6.53 (d, *J* = 15.2 Hz), 1.05 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 144.3, 138.9, 136.4, 136.3, 135.69 (2 × C), 135.66 (2 × C), 134.8, 133.0, 132.0, 131.9, 130.3 (2 × C), 128.9 (2 × C), 128.8 (3 × C), 128.3 (2 × C), 27.2, 19.5; HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{32}NOSiS^+$ [M + H]$^+$, 482.1968; found, 482.1982.

(*E*)-((*tert*-Butyldiphenylsilyl)imino)(2-cyclohexylvinyl)(phenyl)-λ⁶-sulfanone (**4b**). The title compound was prepared according to General Procedure C employing sulfoximine **3a** (200 mg, 0.51 mmol) in anhydrous THF (3.2 mL), *n*BuLi (1.3 M in hexane, 1.05 mL, 1.37 mmol), diisopropylamine (0.1 mL, 0.77 mmol) in anhydrous THF (3.2 mL), diethylchlorophosphate (0.09 mL, 0.66 mmol), *t*BuOK (1.0 M in THF, 0.66 mL, 0.66 mmol), cyclohexanecarboxaldehyde (0.12 mL, 1.02 mmol) in anhydrous THF (8.0 mL). Purification *via* flash chromatography (KP-Sil, 0% grading to 10% EtOAc/Pentane, eluted at 7% EtOAc), afforded **4b** (142 mg, 57%) as a clear yellow oil; R_f = 0.66 (10% EtOAc/Pentane); IR (film)/cm^{-1} 3067, 2929, 2855, 1319, 1159, 1107, 820, 745, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.68–7.63 (m, 4H), 7.42–7.38 (m, 1H), 7.35–7.32 (m, 2H), 7.29–7.21 (m, 6H), 6.62–6.57 (dd, *J* = 6.2, 8.6 Hz), 5.98–5.94 (dd, *J* = 1.5, 13.4 Hz), 1.89–1.82 (m, 2H), 1.60–1.45 (m, 6H), 1.18–1.05 (m, 2H), 1.02 (s, 9H), 0.89–0.76 (m, 2H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 147.9, 144.6, 136.6, 136.5, 135.7 (2 × C), 135.6 (2 × C), 132.3 (2 × C), 131.7, 128.9 (2 × C), 128.7 (3 × C), 127.3 (2 × C), 127.2 (2 × C), 39.3, 31.3 (2 × C), 27.2 (3 × C), 25.8 (2 × C) , 25.5, 19.5; HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{38}NOSSi^+$ [M + H]$^+$, 488.2443; found, 488.2447.

(*E*)-((*tert*-Butyldiphenylsilyl)imino)(4-ethynylstyryl)(phenyl)-λ⁶-sulfanone (**4c**). The title compound was prepared according to General Procedure C employing sulfoximine **3a** (600 mg, 0.51 mmol) in THF (9.6 mL), *n*BuLi (1.3 M in hexane, 3.10 mL, 4.14 mmol), diisopropylamine (0.30 mL, 2.25 mmol) in THF (9.6 mL), diethylchlorophosphate (0.30 mL, 1.98 mmol), *t*BuOK (1.0 M in THF, 1.98 mL, 1.98 mmol) and 4-ethynylbenzaldehyde (392 mg,

3.04 mmol) in THF (20 mL). Purification *via* flash chromatography (KP-Sil, 0% grading to 10% EtOAc/Pentane, eluted at 8% EtOAc), afforded **4c** (175 mg, 68%) as an orange oil; IR (film)/cm^{-1} 3067, 2925, 2851, 1325, 1160, 1107, 821, 745; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.93 (m, 2H), 7.77–7.72 (m, 4H), 7.54–7.48 (m, 1H), 7.46–7.44 (m, 2H), 7.41–7.38 (m, 2H), 7.34–7.27 (m, 6H), 7.13–7.11 (m, 2H), 6.57 (d, *J* = 15.1 Hz, 1H), 3.16 (s, 1H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 144.1, 137.6, 136.3, 136.2, 135.69 (2 × C), 135.66 (2 × C), 133.4, 132.8, 132.4 (2 × C), 132.2, 129.0 (2 × C), 128.9 (2 × C), 128.1 (2 × C), 127.5 (2 × C), 127.43 (2 × C), 127.39 (2 × C), 123.9, 83.0, 79.2, 27.2, 19.5; HRMS (ESI-TOF) *m/z* Calcd for $C_{32}H_{32}NOSSi^+$ [M + H]$^+$, 506.1968; found, 506.1970.

(*E*)-((*tert*-Butyldiphenylsilyl)imino)(phenyl)(2-(pyridin-2-yl)vinyl)-λ^6-sulfanone (**4d**). The title compound was prepared according to General Procedure C employing sulfoximine **3a** (200 mg, 0.51 mmol) in anhydrous THF (3.2 mL), *n*BuLi (1.3 M in hexane, 1.05 mL, 1.37 mmol), diisopropylamine (0.10 mL, 0.77 mmol) in THF (3.2 mL), diethylchlorophosphate (0.09 mL, 0.66 mmol), *t*BuOK (1.0 M in THF, 0.66 mL, 0.66 mmol), picolinaldehyde (0.12 mL, 1.02 mmol) in THF (8 mL). Purification *via* flash chromatography (KP-Sil, 0% grading to 20% EtOAc/Petroleum ether, eluted at 20% EtOAc), afforded **4d** (148 mg, 60%) as a yellow oil; R_f = 0.19 (10% EtOAc/Petroleum ether); IR (film)/cm^{-1} 3067, 2929, 2855, 1580, 1468, 1427, 1327, 1170, 1107, 820, 704; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54–8.53 (d, *J* = 4.6 Hz, 1H), 7.97–7.94 (m, H), 7.80–7.74 (m, 4H), 7.64–7.60 (m, 1H), 7.50–7.44 (m, 1H), 7.40–7.36 (m, 2H), 7.32 (d, *J* = 15.2 Hz), 7.32–7.27 (m, 5H), 7.25–7.18 (m, 2H), 7.13–7.11 (d, *J* = 7.8 Hz, 1H), 1.14 (s, 9H). ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 151.9, 150.0, 143.8, 137.1, 136.7, 136.3, 135.7 (2 × C), 135.7 (2 × C), 132.2, 128.9 (3 × C), 127.6 (2 × C), 127.4 (2 × C), 127.3 (2 × C), 124.8, 124.2, 27.3 (3 × C), 19.5. HRMS (ESI-TOF) *m/z* Calcd for $C_{29}H_{31}N_2OSSi^+$ [M + H]$^+$, 483.1926; found: 483.1931.

(*E*)-((*tert*-Butyldiphenylsilyl)imino)(4-ethynylstyryl)(4-methoxyphenyl)-λ^6-sulfanone (**4e**). The title compound was prepared according to General Procedure C employing sulfoximine **3b** (200 mg, 0.47 mmol) in THF (3.2 mL), *n*BuLi (1.3 M in hexane, 1.05 mL, 1.37 mmol), diisopropylamine (0.10 mL, 0.77 mmol) in THF (3.2 mL), diethylchlorophosphate (0.09 mL, 0.66 mmol), *t*BuOK (1.0 M in THF, 0.66 mL, 0.66 mmol), ethynylbenzaldehyde (123 mg, 0.94 mmol) in THF (8 mL). Purification *via* flash chromatography (KP-Sil, 0% grading to 20% EtOAc/Petroleum ether, eluted at 12% EtOAc) afforded **4e** (128 mg, 51%) as a clear oil; R_f = 0.35 (20% EtOAc/Pentane); IR (film)/cm^{-1} 3291, 2929, 2855, 1595, 1495, 1312, 1259, 1148, 1107, 1028, 805, 704; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.9 Hz, 2H), 7.77–7.71 (m, 4H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.35–7.24 (m, 7H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 6.56 (d, *J* = 15.2 Hz, 1H), 3.84 (s, 3H), 3.16 (s, 3H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 162.6 (2 × C), 136.7, 136.5, 136.3, 135.8, 135.7 (3 × C), 133.5, 133.4, 132.4 (2 × C), 129.6 (2 × C), 129.0 (2 × C), 128.0 (2 × C), 127.4 (4 × C), 123.7, 114.1 (2 × C), 83.1, 79.1, 55.6, 27.2 (3 × C), 19.5; HRMS (ESI-TOF) *m/z* Calcd for $C_{33}H_{34}NO_2SSi^+$ [M + H]$^+$, 536.2080; found: 536.2074.

(*E*)-((*tert*-Butyldiphenylsilyl)imino)(4-methoxyphenyl)(2-(thiazol-2-yl)vinyl)-λ^6-sulfanone (**4f**). The title compound was prepared according to General Procedure C employing sulfoximine **3b** (300 mg, 0.71 mmol) in THF (4.8 mL), *n*BuLi (1.3 M in hexane, 1.50 mL, 1.91 mmol), diisopropylamine (0.15 mL, 1.07 mmol) in THF (4.8 mL), diethylchlorophosphate (0.13 mL, 0.92 mmol), *t*BuOK (1.0 M in THF, 0.92 mL, 0.92 mmol), 1,3 thiazole -2-carbaldehyde (0.13 mL, 1.42 mmol) in THF (10 mL). Purification *via* flash chromatography (KP-Sil, 0% grading to 50% EtOAc/Hexane, eluted at 30% EtOAc) afforded **4f** (311 mg, 84%) as a yellow oil; R_f = 0.38 (EtOAc/Hexane); IR (film)/cm^{-1} 3071, 2959, 2855, 1595, 1494, 1312, 1259, 1151, 1107, 1028, 820, 704; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H), 7.81 (d, *J* = 3.2 Hz, 1H), 7.78–7.72 (m, 4H), 7.37 (d, *J* = 15.3 Hz), 7.35 (d, *J* = 3.32 Hz, 1H), 7.32–7.28 (m, 6H), 6.96 (d, *J* = 15.3 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 162.9, 162.0, 144.5, 137.1, 136.1 (2 × C), 135.7 (4 × C), 135.0, 129.9 (2 × C), 129.0, 128.7, 127.4 (6 × C), 121.4, 114.2 (2 × C), 55.6, 27.3 (3 × C), 19.5; HRMS (ESI-TOF) *m/z* Calcd for $C_{28}H_{31}N_2O_2S_2Si^+$ [M + H]$^+$, 519.1591; found, 519.1599.

(*E*)-((*tert*-Butyldiphenylsilyl)imino)(4-methoxyphenyl)(2-(quinoxalin-2-yl)vinyl)-λ^6-sulfanone (**4g**). The title compound was prepared according to General Procedure C employing sulfoximine **3b** (300 mg, 0.71 mmol) in anhydrous THF (4.8 mL), *n*BuLi (1.3 M in hexane, 1.50 mL, 1.91 mmol), diisopropylamine (0.15 mL, 1.07 mmol) in THF (4.8 mL), diethylchlorophosphate (0.13 mL, 0.92 mmol), *t*BuOK (1.0 M in THF, 0.92 mL, 0.92 mmol), quinoxaline-2-carbaldehyde (200 mg, 1.42 mmol) in THF (10 mL). Purification by flash chromatography (KP-Sil, 0% grading to 50% EtOAc/Hexane, eluted at 26% EtOAc) afforded **4g** (271 mg, 68%) as an orange oil; R_f = 0.33 (40% EtOAc/Hexane); IR (film)/cm^{-1} 3071, 2963, 2855, 1595, 1494, 1312, 1259, 1148, 1107, 1058, 820, 764, 704; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.07–8.05 (m, 1H), 8.00–7.97 (m, 1H), 7.93 (d, *J* = 8.9 Hz, 2H), 7.80–7.74 (m, 6H), 7.38 (d, *J* = 15.3 Hz, 1H), 7.28 (d, *J* = 15.3 Hz, 1H), 7.28–7.26 (m, 6H), 6.94 (d, *J* = 8.81 Hz, 2H), 3.85 (s, 3H), 1.15 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 163.0, 147.2, 144.9, 142.3 (2 × C), 139.7, 136.1, 135.7 (4 × C), 134.9, 132.9, 130.7 (2 × C), 130.1 (2 × C), 129.6, 129.2, 129.1 (2 × C), 127.4 (6 × C), 114.3 (2 × C), 55.7, 27.3 (3 × C), 19.5; HRMS (ESI-TOF) *m/z* Calcd for $C_{33}H_{34}N_3O_2SSi^+$ [M + H]$^+$, 564.2141; found, 564.2154.

(*E*)-Imino(phenyl)(styryl)-λ^6-sulfanone (**5a**). The title compound was prepared according to General Procedure D employing vinyl sulfoximine **4a** (125 mg, 0.26 mmol) and TBAF (1.0 M in THF, 0.29 mL, 0.29 mmol) in anhydrous THF (4.7 mL). Purification *via* flash chromatography (KP-Sil, 0% grading to 100% EtOAc/Pentane, eluted at 58% EtOAc) vinyl sulfoximine **5a** as a yellow oil (47 mg, 74%); R_f = 0.58 (100% EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–8.02 (m, 2H), 7.62 (d, *J* = 15.2 Hz, 1H), 7.60–7.56 (m, 1H), 7.55–7.51 (m, 2H), 7.49–7.46 (m, 2H), 7.40–7.37 (m, 3H), 6.93 (d, *J* = 15.3 Hz, 1H), 2.68 (bs, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 142.8, 141.6, 132.8, 132.7, 130.9, 129.5, 129.2 (2 × C), 129.0 (2 × C), 128.5 (2 × C), 127.9 (2 × C); HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{14}NOS^+$ [M + H]$^+$, 244.0807; found, 244.0796. Analytical data in agreement with those reported in the literature.[22]

(*E*)-(2-Cyclohexylvinyl)(imino)(phenyl)-λ^6-sulfanone (**5b**). The title compound was prepared according to General Procedure D employing vinyl sulfoximine **4b** (115 mg, 0.24 mmol) and TBAF (1.0 M in THF, 0.26 mL, 0.26 mmol) in THF (4.5 mL). Purification *via* flash chromatography (KP-Sil, 0% grading to 100% EtOAc/Pentane, eluted at 50% EtOAc) afforded **5b** (44 mg, 74%) as a yellow oil; R_f = 0.42 (50% EtOAc/Pentane); IR (film)/cm^{-1} 3270, 2924, 2851, 1625, 1446, 1226, 1125, 969, 7511, 688; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.93 (m, 2H), 7.59–7.55 (m, 1H), 7.52–7.48 (m, 2H), 6.86 (dd, *J* = 8.7 Hz, 6.5 Hz), 6.30 (dd, *J* = 14.1 Hz, 1.4 Hz, 1H), 2.44 (bs, 1H), 2.20–2.13 (m, 1H), 1.75–1.72 (m, 4H), 1.67–1.64 (m, 1H), 1.31–1.06 (m, 5H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 150.7, 143.1, 132.6, 130.0, 129.10 (2 × C), 127.7 (2 × C), 39.8 (1 × C), 31.4, 31.3, 25.8 (2 × C), 25.6 (1 × C); HRMS (ESI) *m/z* Calcd for $C_{14}H_{20}NOS^+$ [M + H]$^+$, 250.1266; found, 250.1263.

(*E*)-(4-Ethynylstyryl)(imino)(phenyl)-λ^6-sulfanone (**5c**). The title compound was prepared according to General Procedure D employing vinyl sulfoximine **4c** (690 mg, 1.37 mmol) and TBAF (1.0 M in THF, 50 mL, 1.51 mmol) in THF (25 mL). Purification *via* flash chromatography (KP-Sil, 0% grading to 100% EtOAc/Pentane, eluted at 50% EtOAc) afforded **5c** (300 mg, 82%) as a white solid; R_f = 0.43 (50% EtOAc/Pentane); mp ($CHCl_3$) 133–135 °C; IR (film)/cm^{-1} 3279, 3061, 2579, 2361, 1614, 1445, 1217, 1125, 974, 799, 753, 687; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–8.02 (m, 2H), 7.62–7.57 (m, 2H), 7.56–7.52 (m, 2H), 7.47 (d, *J* = 8.5 Hz , 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 15.3 Hz, 1H), 3.19 (s, 1H), 2.95 (bs, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 142.5, 140.4, 133.0, 132.7 (2 × C), 130.5, 129.3 (2 × C), 128.3 (2 × C), 128.0 (2 × C), 124.6, 82.9, 79.7; HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{14}NOS^+$ [M + H]$^+$, 268.0796; found, 268.0804.

(*E*)-Imino(phenyl)(2-(pyridin-2-yl)vinyl)-λ⁶-sulfanone (**5d**). The title compound was prepared according to General Procedure D employing vinyl sulfoximine **4d** (70 mg, 0.15 mmol) and TBAF (1.0 M in THF, 0.16 mL, 0.16 mmol) in THF (2.8 mL). Purification *via* flash chromatography (KP-Sil, 0% grading to 100% EtOAc/Petroleum ether, eluted at 100% EtOAc) afforded **5d** (25 mg, 69%) as a white solid; R_f = 0.39 (100% EtOAc); mp ($CHCl_3$) = 94–96 °C; IR (film)/cm^{-1} 3258, 3056, 1580, 1469, 1431, 1215, 1111, 969, 797, 753, 708; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60–8.59 (d, *J* = 4.5 Hz, 1H), 8.06–8.04 (m, 2H), 7.69 (m, 1H), 7.60 (d, *J* = 15.2 Hz, 1H), 7.59–7.54 (m, 1H), 7.54–7.51 (m, 2H), 7.46 (d, *J* = 15.3 Hz, 1H), 7.40–7.38 (d, *J* = 7.8 Hz, 1H) 2.67 (bs, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 151.4, 150.2, 142.0, 139.6, 137.0, 134.2, 133.0 (2 × C), 129.2 (2 × C), 128.2, 125.2, 124.7; HRMS (ESI-TOF) *m/z* Calcd for $C_{13}H_{13}N_2OS^+$ [M + H]$^+$, 245.0749; found, 245.0755. Analytical data in agreement with those reported in the literature.[22]

(*E*)-(4-Ethynylstyryl)(imino)(4-methoxyphenyl)-λ⁶-sulfanone (**5e**). The title compound was prepared according to General Procedure D employing vinyl sulfoximine **4e** (70 mg, 0.15 mmol) and TBAF (1.0 M in THF, 0.16 mL, 0.16 mmol) in THF (2.8 mL). Purification *via* flash chromatography (KP-Sil, 0% grading to 100% EtOAc/Petroleum ether, eluted at 48% EtOAc) afforded **5e** (32 mg, 72%) as an orange oil; R_f = 0.24 (50% EtOAc/Petroleum ether); IR (film)/cm^{-1} 3283, 3049, 2940, 2840, 1595, 1494, 1461, 1312, 1259, 1215, 1177, 1110, 976, 805; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.93 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 15.4 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 15.4 Hz, 1H), 3.85 (s, 3H), 3.18 (s, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 163.3, 139.4, 133.8, 133.1, 132.6 (2 × C), 131.1, 130.2 (2 × C), 128.2 (2 × C), 124.4, 114.5 (2 × C), 82.9, 79.5, 55.7; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{16}NO_2S^+$ [M + H]$^+$, 298.0902; found, 298.0895.

(*E*)-Imino(4-methoxyphenyl)(2-(thiazol-2-yl)vinyl)-λ⁶-sulfanone (**5f**). The title compound was prepared according to General Procedure D employing vinyl sulfoximine **4f** (250 mg, 0.48 mmol) and TBAF (1.0 M in THF, 0.53 mL, 0.53 mmol) in THF (9 mL). Purification by flash chromatography (KP-Sil, 0% grading to 100% EtOAc/Hexane, eluted at 80% EtOAc) afforded **5f** (114 mg, 85%) as a yellow oil; R_f = 0.40 (80% EtOAc/Hexane); IR (film)/cm^{-1} 3259, 2926, 2840, 1593, 1494, 1312, 1258, 1231, 1126, 1108, 1090, 1021, 833; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.94 Hz, 2H), 7.88 (d, *J* = 3.2 Hz, 1H), 7.65 (d, *J* = 15.2 Hz, 1H), 7.44 (d, *J* = 3.2 Hz, 1H), 7.24 (d, *J* = 15.3 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 2H), 3.86 (s, 3H), 2.93 (bs, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 163.6, 161.4, 144.9, 135.0, 132.8, 131.1, 130.5 (2 × C), 127.1, 122.1, 114.6 (2 × C), 55.7; HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_{13}N_2O_2S_2^+$ [M + H]$^+$, 281.0418; found, 281.0410.

(*E*)-Imino(4-methoxyphenyl)(2-(quinoxalin-2-yl)vinyl)-λ⁶-sulfanone (**5g**). The title compound was prepared according to General Procedure D employing vinyl sulfoximine **4g** (270 mg, 0.48 mmol) and TBAF (1.0 M in THF, 0.53 mL, 0.53 mmol) in THF (9.0 mL). Purification by flash chromatography (KP-Sil, 0% grading to 100% EtOAc/Hexane, eluted at 90% EtOAc) afforded **5g** (120 mg, 77%) as a brown oil; R_f = 0.51 (100% EtOAc/Hexane); IR (film)/cm^{-1} 3250, 3060, 2840, 1591, 1491, 1413, 1364, 1256, 1230, 1178, 1126, 1013, 969, 827, 760, 670; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.10–8.07 (m, 1H), 8.04–8.00 (m, 3H), 7.81–7.77 (m, 3H), 7.67 (d, *J* = 15.2 Hz), 7.00–7.03 (m, 2H), 3.87 (s, 3H), 3.04 (bs, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 163.6, 146.7, 145.0, 142.6, 142.3, 137.8, 135.5, 132.8, 131.0, 130.9, 130.6 (2 × C), 129.7, 129.3, 127.1, 114.6 (2 × C), 55.7; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{16}N_3O_2S^+$ [M + H]$^+$, 326.0958; found, 326.0974.

Enantioenriched vinyl sulfoximines **(*S*)-5h** and **(*R*)-5h**.

(*S*)-Imino(methyl)(p-tolyl)-λ⁶-sulfanone (**(*S*)-2h**). The title compound was prepared according to General Procedure E employing (*S*)-1-methyl-4-(methylsulfinyl)benzene **(S)-6** (500 mg, 3.13 mmol, er >99:1). Purification by flash chromatography (KP-Sil, 0% grading to 100% EtOAc/Pentane, product eluted at 100%) afforded **(*S*)-2h** (473 mg, 86%) as a clear oil; R_f = 0.20 (100% EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.88 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.09 (s, 3H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 144.0, 140.5, 129.9 (2 × C), 127.7 (2 × C), 46.3, 21.5; HRMS (ESI-TOF) *m/z* Calcd $C_8H_{11}NOS^+$ [M + H]$^+$, 170.0640; found, 170.0642. Analytical data in agreement with those reported in the literature.[31e]

(*R*)-Imino(methyl)(p-tolyl)-λ⁶-sulfanone (**(*R*)-2h**). The title compound was prepared according to General Procedure E employing (*R*)-1-methyl-4-(methylsulfinyl)benzene (250 mg, 1.62 mmol, er >99:1). Purification by flash column chromatography (KP-Sil, 0% grading to 100% EtOAc/Pentane, product eluted at 100%) afforded **(*R*)-2h** (255 mg, 94%) as a clear oil. R_f = 0.20 (100% EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.88 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.11 (s, 3H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 143.9, 140.5, 129.9 (2 × C), 127.7 (2 × C), 46.4, 21.6; HRMS (ESI-TOF) *m/z* Calcd $C_8H_{11}NOS^+$ [M + H]$^+$, 170.0640; found, 170.0641. Analytical data in agreement with those reported in the literature.[59]

(*S*)-((*tert*-Butyldiphenylsilyl)imino)(methyl)(*p*-tolyl)-λ⁶-sulfanone (**(*S*)-3h**). The title compound was prepared according to General Procedure B employing **(*S*)-2h** (531 mg, 3.14 mmol). Purification by flash chromatography (KP-Sil, 0% grading to 10% EtOAc/Pentane, product eluted at 10%) afforded **(*S*)-3h** (830 mg, 65%, >99:1 er) as a clear oil; R_f = 0.43 (10% EtOAc/Pentane); IR (film)/cm^{-1} 3049, 2955, 2855, 1599, 1427, 1427, 1326, 1293, 1162, 1107, 964, 820, 767, 741, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.78–7.76 (m, 2H), 7.73–7.70 (m, 2H), 7.41–7.28 (m, 6H), 7.23 (d, *J*= 8.1 Hz, 2H), 2.83 (s, 3H), 2.40 (s, 3H), 1.09 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 138.2, 136.5, 135.64 (2 × C), 135.58 (2 × C), 134.8, 129.7, 129.5 (2 × C), 129.0 (3 × C), 127.4, 127.0 (2 × C) 49.1, 27.2 (9 × C), 21.46, 19.40;. HRMS (ESI-TOF) *m/z* Calcd for $C_{24}H_{30}NOSSi^+$ [M + H]$^+$, 408.1817; found, 408.1834.

(*R*)-((*tert*-Butyldiphenylsilyl)imino)(methyl)(*p*-tolyl)-λ⁶-sulfanone (**(*R*)-3h**). The title compound was prepared according to General Procedure B employing **(*R*)-2h** (236 mg, 1.39 mmol). Purification by flash column chromatography (KP-Sil, 0% grading to 10% EtOAc/Pentane, product eluted at 10%) afforded **(*R*)-3h** (346 mg, 61%, er >99:1) as a clear oil; R_f = 0.43 (10% EtOAc/Pentane) IR (film)/cm^{-1} 3067, 2955, 2855, 1590, 1472, 1427, 1323, 1293, 1162, 1107, 954, 820, 768, 741, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.78–7.76 (m, 2H), 7.73–7.70 (m, 2H), 7.37–7.29 (m, 6H), 7.23 (d, *J* = 9.0 Hz, 2H), 2.83 (s, 3H), 2.40 (s, 3H), 1.09 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 138.2, 136.5, 135.6 (4 × C), 134.8, 129.7, 129.5 (2 × C), 129.0 (3 × C), 127.4, 127.0 (2 × C) 49.1, 27.2 (9 × C), 21.5, 19.4; HRMS (ESI-TOF) *m/z* Calcd for $C_{24}H_{30}NOSSi^+$ [M + H]$^+$, 408.1817; found, 408.1828.

(S,*E*)-((*tert*-Butyldiphenylsilyl)imino)(4-ethynylstyryl)(*p*-tolyl)-λ⁶-sulfanone (**(*S*)-4h**). The title compound was prepared according to General Procedure C employing sulfoximine **(*S*)-3h** (100 mg, 0.25 mmol, er >99:1) in THF (1.6 mL), *n*BuLi (1.3 M in hexane, 0.52 mL, 0.68 mmol), diisopropylamine (0.05 mL, 0.37 mmol) in THF (1.6 mL), diethylchlorophosphate (0.05 mL, 0.32 mmol), *t*BuOK (1.0 M in THF, 0.32 mL, 0.32 mmol), 4-ethynylbenzaldehyde (85 mg, 0.47 mmol) in THF (4 mL). Purification by flash chromatography (KP-Sil, 0% grading to 10% EtOAc/Hexane, producr eluted at 8% EtOAc), afforded **(*S*)-4h** (88 mg, 69%, er >99:1) as a yellow oil; R_f = 0.22 (10% EtOAc/Hexane); IR (film)/cm^{-1} 3291, 3049, 2955, 2855, 1595, 1468, 1427, 1312, 1148, 1107, 1017, 969, 797, 741, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.79–7.73 (m, 5H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.37–7.24 (m, 8H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.57 (d, *J* = 15.3 Hz, 1H), 3.17 (s, 1H), 2.40 (s, 3H), 1.14 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.9, 141.2, 137.2, 136.5, 136.3, 135.7 (2 × C), 134.8, 133.5, 133.2, 132.4, 129.6 (2 × C), 129.0, 128.1, 127.7, 127.6, 127.4 (2 × C), 123.8, 83.1, 79.2, 27.2 (9 × C), 21.5, 19.5; HRMS (ESI-TOF) *m/z* Calcd for $C_{33}H_{34}NOSSi^+$ [M + H]$^+$, 520.2131; found: 520.2120.

(*R,E*)-((*tert*-Butyldiphenylsilyl)imino)(4-ethynylstyryl)(*p*-tolyl)-λ⁶-sulfanone (**(*R*)-4h**). The title compound was prepared

according to General Procedure C employing sulfoximine **(*R*)-3h** (100 mg, 0.25 mmol, er >99:1) in THF (1.6 mL), *n*BuLi (1.3 M in hexane, 0.52 mL, 0.68 mmol), diisopropylamine (0.05 mL, 0.37 mmol) in THF (1.6 mL), diethylchlorophosphate (0.05 mL, 0.32 mmol), *t*BuOK (1.0 M in THF, 0.32 mL, 0.32 mmol), 4-ethynylbenzaldehyde (85 mg, 0.47 mmol) in THF (4 mL). Purification by flash column chromatography (KP-Sil, 0% grading to 10% EtOAc/Hexane, product eluted at 8% EtOAc), afforded **(*R*)-4h** (81 mg, 62%, er >99:1) as a yellow oil; R_f = 0.17 (10% EtOAc/Hexane); IR (film)/cm^{-1} 3291, 3049, 2955, 2855, 1681, 1554, 1472, 1427, 1312, 1151, 1107, 1017, 972, 801, 741, 704; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.78–7.72 (m, 5H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.33–7.23 (m, 8H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.57 (d, *J*= 15.3 Hz, 1H), 3.16 (s, 1H), 2.40 (s, 3H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 142.9, 141.2, 137.2, 136.5, 136.3, 135.7 (2 × C), 134.8, 133.5, 133.2, 132.4, 129.6 (2 × C), 129.0, 128.1, 127.7, 127.6, 127.4 (2 × C), 123.7, 83.1, 79.2, 27.2 (9 × C), 21.5, 19.5; HRMS (ESI-TOF) *m/z* Calcd for $C_{33}H_{34}NOSSi^+$ [M + H]$^+$, 520.2131; found, 520.2130.

(S,*E*)-(4-Ethynylstyryl)(imino)(*p*-tolyl)-λ^6-sulfanone (**(*S*)-5h**). The title compound was prepared according to General Procedure D employing sulfoximine **(*S*)-4h** (80 mg, 0.15 mmol, er >99:1). Purification by flash column chromatography (KP-Sil, 0% grading to 100% EtOAc/Hexane, product eluted at 48% EtOAc), afforded **(*S*)-5h** (39 mg, 92%, er >99:1) as an off-white solid; R_f = 0.34 (50% EtOAc/Hexane); mp ($CHCl_3$) = 147–149 °C; IR (film)/cm^{-1} 3280, 3045, 1599, 1408, 1215, 1114, 1080, 976, 861, 797, 756; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 15.3 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7,41 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 15.2 Hz, 1H), 3.19 (s, 1H), 2.43 (s, 3H), 2.38 (bs, 1H, NH); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 143.9, 139.9, 139.5, 133.0, 132.7 (2 × C), 130.7, 130.0 (2 × C), 128.3 (2 × C), 128.0 (2 × C), 124.4, 82.9, 79.6, 21.56; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{16}NOS^+$ [M + H]$^+$, 282.0953; found, 282.0952.

(*R*,*E*)-(4-Ethynylstyryl)(imino)(*p*-tolyl)-λ^6-sulfanone (**(*R*)-5h**). The title compound was prepared according to General Procedure D employing sulfoximine **(*R*)-4h** (40 mg, 0.08 mmol, er >99:1). Purification by flash column chromatography (KP-Sil, 0% grading to 100% EtOAc/Hexane, product eluted at 48% EtOAc), afforded **(*R*)-5h** (17 mg, 79%, er >99:1) as an off-white solid; R_f = 0.34 (50% EtOAc/Hexane); mp ($CHCl_3$) = 147–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 15.3 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 15.2 Hz, 1H), 3.18 (s, 1H), 2.43 (s, 3H), 2.40 (bs, 1H, NH); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 144.0, 140.0, 133.0 (2 × C), 132.7 (2 × C), 130.7, 130.0 (2 × C), 128.3 (2 × C), 128.1 (2 × C), 124.5, 82.9, 79.6, 21.6; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{16}NOS^+$ [M + H]$^+$, 282.0953; found, 282.0952.

(*E*)-Trimethyl(2-(phenylthio)vinyl)silane (**9a**). The title compound was prepared according to General Procedure F employing $RhCl(PPh_3)_3$ (46 mg, 0.05 mmol), ethynyltrimethylsilane (0.14 mL, 1.0 mmol) and thiophenol (102 µL, 1.0 mmol). Purification by flash column chromatography (KP-Sil, hexane) afforded vinyl sulfide **9a** (179 mg, 86%) as a colourless oil; R_f = 0.80 (hexane); IR (film)/cm^{-1} 3061, 2956, 2895, 1546, 1484, 1439, 1234, 1026, 841, 742; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.01 (m, 5H), 6.59 (d, *J* = 18.0 Hz, 1H), 5.82 (d, *J* = 18.0 Hz, 1H), 0.00 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 145.0, 135.2, 129.4 (2 × C), 129.1 (2 × C), 125.6, 122.8, -0.8 (9 × C); HRMS (APCI$^+$) m/z: Calcd for $C_{11}H_{17}SSi^+$ [M+H]$^+$: 209.0815; found: 209.0817. Analytical data in agreement with those reported in the literature.[60]

(*E*)-(2-(Benzylthio)vinyl)trimethylsilane (**9b**). The title compound was prepared according to General Procedure F employing $RhCl(PPh_3)_3$ (92 mg, 0.10 mmol), ethynyltrimethylsilane (0.28 mL, 2.0 mmol) and benzyl mercaptan (0.23 mL, 2.0 mmol). Purification by flash column chromatography (SiO_2, hexane) afforded vinyl sulfide **9b** (356 mg, 80%) as a colourless oil; R_f = 0.60 (hexane); IR (film)/cm^{-1} 3060, 3027, 2960, 2922, 2859, 1603, 1548, 1495, 1454, 1416, 1374, 1334, 1200, 1103, 1070, 917, 850, 768, 701; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.27 (m, 5H), 6.55 (d, *J* = 18.1 Hz, 1H), 5.79 (d, *J* = 18.1 Hz, 1H), 3.95 (s, 2H), 0.06 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 138.3, 137.3, 129.0 (2 × C), 128.7 (2 × C), 127.4, 125.9, 36.1, -1.0 (9 × C); HRMS (APCI$^+$) m/z: Calcd for $C_{12}H_{18}SSi^+$ [M+H]$^+$: 222.0893; found: 222.0900.

(*E*)-(4-Methoxystyryl)(naphthalen-2-yl)sulfane (**9c**). The title compound was prepared according to General Procedure F employing $RhCl(PPh_3)_3$ (46 mg, 0.05 mmol), naphthalene-2-thiol (176 mg, 1.1 mmol) and 1-ethynyl-4-methoxybenzene (129 µL, 1.0 mmol). Purification by flash column chromatography (SiO_2, 5% Et_2O/hexane) afforded vinyl sulfide **9c** (227 mg, 78%) as a white solid; R_f = 0.40 (5% Et_2O/hexane); mp = 103–105 °C; IR (film)/cm^{-1} 3056, 3004, 1602, 1509, 1252, 1032, 950, 846, 801; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.75 (m, 4H), 7.53–7.44 (m, 3H), 7.38–7.32 (m, 2H), 6.92–6.85 (m, 2H), 6.83 (s, 2H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 159.5, 133.8, 133.4, 133.1, 132.1, 129.4, 128.6, 127.8, 127.5 (2 × C), 127.4, 127.2 (2 × C), 126.6, 125.9, 119.8, 114.2 (2 × C), 55.3; HRMS (APCI$^+$) m/z: Calcd for $C_{19}H_{17}OS^+$ [M+H]$^+$: 293.0995; Found: 293.1003. Analytical data in agreement with those reported in the literature.[61]

(*E*)-(4-Bromophenyl)(styryl)sulfane (**9d**). The title compound was prepared according to General Procedure F employing $RhCl(PPh_3)_3$ (92 mg, 0.1 mmol), 4-bromobenzenethiol (378 mg, 2.0 mmol) and ethynylbenzene (0.22 mL, 2.0 mmol. Purification by flash column chromatography (SiO_2, pentane) afforded vinyl sulfide **9b** (576 mg, 99%) as an off-white solid; R_f = 0.45 (pentane); mp = 77–78 °C; IR (film)/cm^{-1} 3079, 3056, 3019, 2933, 1897, 1774, 1737, 1664, 1599, 1472, 1387, 1230, 1088, 1032, 989, 954, 813, 742, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.42 (m, 2H), 7.39–7.19 (m, 7H), 6.87–6.72 (m, 2H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 136.3, 134.7, 133.1, 132.3 (2 × C), 131.1 (2 × C), 128.8 (2 × C), 128.0, 126.2 (2 × C), 122.3, 120.9; HRMS (APCI$^+$) m/z: Calcd for $C_{14}H_{12}SBr^+$ [M+H]$^+$: 290.9838; Found: 290.9830.

Butyl (*E*)-3-((4-bromostyryl)thio)propanoate (**9e**). The title compound was prepared according to an adaptation of General Procedure F, including heating to 65 °C using a using a heating block and increasing the catalyst loading to 10 mol%. Employing $RhCl(PPh_3)_3$ (92 mg, 0.1 mmol), 1-bromo-4-ethynylbenzene (181 mg, 1.0 mmol), butyl 3-mercaptopropanoate (178 µL, 1.1 mmol). Purification by flash column chromatography (SiO_2, 5% Et_2O/hexane) afforded vinyl sulfide **9e** (185 mg, 53%) as a white solid; R_f = 0.14 (5% Et_2O/hexane); mp = 55–57 °C; IR (film)/cm^{-1} 2959, 2870, 1722, 1595, 1487, 1401, 1364, 1241, 1178, 1107, 939, 827; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.37 (m, 2H), 7.19–7.11 (m, 2H), 6.71 (d, *J* = 15.5 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 3.07 (t, *J* = 7.3 Hz, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 1.66–1.58 (m, 2H), 1.46–1.31 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 171.6, 135.7, 131.7 (2 × C), 127.0 (2 × C), 126.6, 125.1, 120.7, 64.8, 34.6, 30.6, 27.6, 19.1, 13.7; HRMS (APCI$^+$) m/z: Calcd for $C_{15}H_{20}O_2SBr^+$ [M+H]$^+$: 343.0362; Found: 343.0371.

tert-Butyl (*S*,*E*)-(*tert*-butoxycarbonyl)(5-phenyl-1-(phenylthio)pent-1-en-3-yl)carbamate (**9f**). The title compound was prepared according to an adaptation of General Procedure F, increasing the reaction time to 72 h and employing $RhCl(PPh_3)_3$ (73 mg, 0.08 mmol), *tert*-butyl (*S*)-(*tert*-butoxycarbonyl)(5-phenylpent-1-yn-3-yl)carbamate[13e] (950 mg, 2.65 mmol), thiophenol (301 µL, 2.94 mmol). Purification by flash column chromatography (SiO_2, 5% EtOAc/hexane) afforded vinyl sulfide **9f** (1.22 g, 98%) as a colouless oil; R_f = 0.75 (10% EtOAc/hexane); IR (film)/cm^{-1} 2978, 1737, 1799, 1342, 1244, 1140, 1114; ^{1}H NMR (400 MHz, $CDCl_3$) δ δ 7.35–7.27 (m, 5H), 7.26–7.13 (m, 5H), 6.36 (dd, *J* = 15.2, 0.9 Hz, 1H), 6.06 (dd, *J* = 15.2, 7.6 Hz, 1H), 4.76 (q, *J* = 7.4 Hz, 1H), 2.62 (t, *J* = 8.1 Hz, 2H), 2.29–2.14 (m, 1H), 2.14–1.95 (m, 1H), 1.49 (s, 18H). Analytical data in agreement with those reported in the literature.**Error! Bookmark not defined.**

(*E*)-Imino(phenyl)(2-(trimethylsilyl)vinyl)-λ^6-sulfanone (**10a**). The title compound was prepared according to General Procedure A employing vinyl sulfide **9a** (179 mg, 0.86 mmol). Purification by flash column chromatography (KP-Sil, 0% grading to 100% EtOAc/hexane, product eluted at 38% EtOAc) afforded sulfoximine **10a** (107 mg, 52%) as a colourless oil; R_f = 0.40 (50%

EtOAc/hexane); IR (film)/cm^{-1} 2957, 2905, 1504, 1450, 1266, 1213, 978, 841, 789; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.89 (m, 2H), 7.64–7.43 (m, 3H), 7.15 (d, *J* = 17.6 Hz, 1H), 6.69 (d, *J* = 17.6 Hz, 1H), 0.11 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 143.9, 143.4, 142.2, 132.9, 129.3 (2 × C), 128.3 (2 × C), -1.8 (9 × C); HRMS (ESI-TOF) m/z: Calcd for $C_{11}H_{18}NOSSi^+$ $[M+H]^+$: 240.0873; Found: 240.0871.

(*E*)-Benzyl(imino)(2-(trimethylsilyl)vinyl)-λ^6-sulfanone (**10b**). The title compound was prepared according to General Procedure A employing vinyl sulfide **9b** (205 mg, 0.92 mmol). Purification by flash column chromatography (SiO_2, 50% EtOAc/hexane) afforded sulfoximine **10b** (178 mg, 76%) as a colourless oil; R_f = 0.34 (50% EtOAc/hexane); IR (film)/cm^{-1} 2955, 1494, 1453, 1248, 1215, 976, 842; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.32 (m, 5H), 7.05 (d, *J* = 17.8 Hz, 1H), 6.62 (d, *J* = 17.8 Hz, 1H), 4.30 (d, *J* = 13.2 Hz, 1H), 4.20 (d, *J* = 13.2 Hz, 1H), 2.63 (s, 1H), 0.14 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 148.0, 140.7, 130.9, 128.6, 128.5 (2 × C), 128.3, 62.7, -2.1 (9 × C); HRMS (ESI-TOF) m/z: Calcd for $C_{12}H_{20}NOSSi^+$ $[M+H]^+$: 254.1035; Found: 254.1027.

(*E*)-Imino(4-methoxystyryl)(naphthalen-2-yl)-λ^6-sulfanone (**10c**). The title compound was prepared according to General Procedure A employing vinyl sulfide **9c** (197 mg, 0.67 mmol). Purification by flash column chromatography (SiO_2, 50% EtOAc/hexane) afforded sulfoximine **10c** (145 mg, 67%) as a colourless oil; R_f = 0.24 (50% EtOAc/hexane); IR (film)/cm^{-1} 3268, 3056, 2840, 1602, 1509, 1256, 1215, 1174, 1066, 976, 864, 813, 757; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64–8.60 (m, 1H), 8.02–7.94 (m, 3H), 7.92–7.89 (m, 1H), 7.67–7.59 (m, 3H), 7.46–7.41 (m, 2H), 6.91–6.83 (m, 3H), 3.83 (s, 3H), 3.01 (s, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 161.8, 141.5, 140.1, 134.8, 132.4, 130.2 (2 × C), 129.4, 129.3, 128.9, 128.8, 127.8, 127.4, 126.5, 125.3, 123.1, 114.4 (2 × C), 55.4; HRMS (APCI$^+$) m/z: Calcd for $C_{19}H_{18}NO_2S^+$ $[M+H]^+$: 324.1053; Found: 324.1046.

(*E*)-(4-Bromophenyl)(imino)(styryl)-λ^6-sulfanone (**10d**). The title compound was prepared according to General Procedure A employing vinyl sulfide **9d** (291 mg, 1.0 mmol). Purification by flash column chromatography (SiO_2, 30% EtOAc/hexane) afforded sulfoximine **10d** (263 mg, 82%) as a yellow oil; R_f = 0.38 (30% EtOAc/hexane); IR (film)/cm^{-1} 3257, 3056, 1729, 1613, 1572, 1464, 1386, 1237, 965, 790; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.85 (m, 2H), 7.70–7.60 (m, 3H), 7.51–7.45 (m, 2H), 7.44–7.34 (m, 3H), 6.91 (dd, *J* = 15.2, 1.0 Hz, 1H), 2.98 (s, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 142.1, 142.0, 132.4 (3 × C), 131.0, 129.5 (2 × C), 129.0 (2 × C), 129.0, 128.5 (2 × C), 128.0; HRMS (APCI$^+$) m/z: Calcd for $C_{14}H_{13}NOSBr^+$ $[M+H]^+$: 321.9901; Found: 321.9895.

Butyl (*E*)-3-(2-(4-bromophenyl)vinylsulfonimidoyl)propanoate (**10e**). The title compound was prepared according to General Procedure A employing vinyl sulfide **9e** (96 mg, 0.28 mmol). Purification by flash column chromatography (SiO_2, 50% EtOAc/hexane) afforded sulfoximine **10e** (84 mg, 80%) as a white solid; R_f = 0.23 (50% EtOAc/hexane); mp = 57–59 °C; IR (film)/cm^{-1} 3280, 2959, 2870, 1729, 1617, 1487, 1244, 1211, 1185, 1069, 1006, 857, 801; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.52 (m, 2H), 7.47 (d, *J* = 15.3 Hz, 1H), 7.41–7.33 (m, 2H), 6.89 (d, *J* = 15.3 Hz, 1H), 4.04 (t, *J* = 6.7 Hz, 2H), 3.46 (td, *J* = 7.4, 1.7 Hz, 2H), 2.84 (td, *J* = 7.2, 2.2 Hz, 2H), 2.73 (s, 1H), 1.61–1.48 (m, 2H), 1.39–1.24 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 170.5, 142.6, 132.4 (2 × C), 131.3, 129.8 (2 × C), 128.1, 125.6, 65.2, 51.6, 30.4, 28.4, 19.0, 13.6; HRMS (APCI$^+$) m/z: Calcd for $C_{15}H_{21}NO_3SBr^+$ $[M+H]^+$: 374.0420; Found: 374.0437.

tert-Butyl (*tert*-butoxycarbonyl)((3*S*,*E*)-5-phenyl-1-(phenylsulfonimidoyl)pent-1-en-3-yl)carbamate (**10f**). The title compound was prepared according to General Procedure A employing vinyl sulfide **9f** (87 mg, 0.18 mmol). Purification by flash column chromatography (KP-Sil, 0% grading to 10% MeOH/$CHCl_3$, eluted at 8% MeOH) afforded sulfoximine **10f** (55 mg, 91%) as a colouless oil in a 1:1 mixture of diastereoisomers; R_f = 0.60 (5% MeOH/$CHCl_3$); IR (film)/cm^{-1} 2978, 1740, 1703, 1368, 1233, 1140; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.93 (m, 2H), 7.63–7.48 (m, 3H), 7.25–7.11 (m, 5H), 7.05 (dd, *J* = 15.1, 5.1 Hz, 1H), 6.45 (dd, *J* = 15.1, 2.9 Hz, 1H), 5.02–4.89 (m, 1H), 2.88 (s, 1H), 2.70–2.55 (m, 2H), 2.37–2.20 (m, 1H), 2.16–2.00 (m, 1H), 1.45 (s, 9H), 1.45 (s, 9H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 152.3 (2 × C), 144.6, 144.6, 142.5, 140.8, 132.9 (2 × C), 129.3 (2 × C), 128.6 (2 × C), 128.4 (2 × C), 128.0 (2 × C), 126.3, 83.2 (2 × C), 55.8, 34.0, 33.8, 32.4, 28.0 (6 × C); HRMS (ESI-TOF) m/z: Calcd for $C_{27}H_{37}N_2O_5S^+$ $[M+H]^+$: 501.2423; Found: 501.2434.

((*S*,*E*)-3-Amino-5-phenylpent-1-en-1-yl)(imino)(phenyl)-λ6-sulfanone (**10g**). Trifluoroacetic acid (1.1 mL) was added dropwise to a solution of sulfoximine **10f** (194 mg, 0.39 mmol) in CH_2Cl_2 (3.8 mL) at 0 °C and the reaction stirred for 3 h. The solvent was then removed under reduced pressure. The crude was dissolved in 20 mL CH_2Cl_2 and washed with sat. aq. $NaHCO_3$ (3 × 20 mL). The solvent was removed under reduced pressure and purification by flash column chromatography (KP-Sil, 0% grading to 10% MeOH/$CHCl_3$, eluted at 5% MeOH) afforded sulfoximine **10g** (89 mg, 76%) as a yellow oil in a 1:1 mixture of diastereoisomers; R_f = 0.50 (10% MeOH/CH_2Cl_2); IR (film)/cm^{-1} 3273, 3027, 2922, 1602, 1446, 1222, 1088, 969, 749, 685; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.60–7.47 (m, 3H), 7.29–7.22 (m, 2H), 7.20–7.08 (m, 3H), 6.90 (dd, *J* = 14.8, 5.8 Hz, 1H), 6.53 (d, *J* = 14.9 Hz, 1H), 3.55–3.44 (m, 1H), 2.70–2.61 (m, 2H), 2.44 (s, 1H), 1.90–1.70 (m, 2H), 1.39 (s, 2H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 148.9, 148.8, 142.9, 141.1, 141.1, 132.9, 131.7, 129.3 (2 × C), 128.6 (2 × C), 128.4 (2 × C), 128.0 (2 × C), 126.2, 51.6, 38.4, 38.3, 32.1; HRMS (APCI$^+$) m/z: Calcd for $C_{17}H_{21}N_2OS^+$ $[M+H]^+$: 301.1369; Found: 301.1377.

(2-Hydroxyethyl)(imino)(phenyl)-λ^6-sulfanone (**12a**). The title compound was prepared according to General Procedure A employing sulfide **11a** (135 µL, 1.0 mmol) in MeOH (2.0 mL) at 25 °C. After 3 h the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2, 50% acetone/pentane) afforded sulfoximine **12a** (136 mg, 73%) as a colourless oil; R_f = 0.29 (50% acetone/pentane); IR (film)/cm^{-1} 3261, 1446, 1215, 1095, 1059, 987, 760, 723, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.98 (m, 2H), 7.71–7.64 (m, 1H), 7.64–7.57 (m, 2H), 4.70 (t, *J* = 6.1 Hz, 1H), 4.08 (ddd, *J* = 12.6, 6.5, 3.8 Hz, 1H), 3.90–3.78 (m, 1H), 3.32 (dt, *J* = 6.1, 2.9 Hz, 2H), 2.88 (s, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 141.8, 133.6, 129.4 (2 × C), 128.3 (2 × C), 58.2, 56.4; Analytical data in agreement with those reported in the literature.[31b]

2-Hydroxyethyl(imino)(4-nitrophenyl)- λ^6-sulfanone (**12b**). The title compound was prepared according to General Procedure A employing sulfide **11b** (199 mg, 1.0 mmol. Purification by flash column chromatography (SiO_2, 1-5% MeOH/CH_2Cl_2) afforded sulfoximine **12b** (201 mg, 87%) as a white solid; R_f = 0.15 (4% MeOH/CH_2Cl_2); mp = 131–133°C; IR (film)/cm^{-1} 3571, 3381, 3153, 3104, 2960, 1633, 1607, 1521, 1469, 1431, 1349, 1308, 1215, 1141, 1088, 1029, 992, 947, 857, 731; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.39 (d, *J* = 8.9 Hz, 2H), 8.15 (d, *J* = 8.9 Hz, 2H), 3.68 (t, *J* = 6.2 Hz, 2H), 3.41 (t, *J* = 6.2 Hz, 2H); ^{13}C{^{1}H} NMR (101 Hz, DMSO-d_6) δ 149.9, 148.6, 129.9 (2 × C), 124.1 (2 × C), 58.8, 55.7; HRMS (APCI$^+$) m/z: Calcd for $C_8H_{11}N_2O_4S^+$ $[M+H]^+$: 231.0434; Found: 231.0433.

Benzo[*d*]thiazol-2-yl(2-hydroxyethyl)(imino)-λ^6-sulfanone (**12c**). The title compound was prepared according to General Procedure A employing sulfide **11c** (211 mg, 1.0 mmol). Purification by flash column chromatography (SiO_2, 40% acetone/pentane) afforded sulfoximine **12c** (131 mg, 54%) as a white solid; R_f = 0.24 (40% acetone/pentane); mp = 125–127 °C; IR (film)/cm^{-1} 3283, 1468, 1315, 1241, 1212, 1051, 980, 764; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27–8.18 (m, 1H), 8.07–7.98 (m, 1H), 7.69–7.56 (m, 2H), 4.23–4.09 (m, 3H), 3.79–3.68 (m, 1H), 3.66–3.60 (m, 2H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 169.2, 152.7, 137.5, 127.9, 127.7, 125.4, 122.3, 57.8, 56.6; HRMS (APCI$^+$) m/z: Calcd for $C_9H_{11}N_2O_2S_2^+$ $[M+H]^+$: 243.0256; Found: 243.0260.

Benzyl(2-hydroxyethyl)(imino)-λ^6-sulfanone (**12d**). The title compound was prepared according to General Procedure A employing sulfide **11d** (0.15 mL, 1.0 mmol). Purification by flash

column chromatography (SiO_2, 1-5% MeOH/CH_2Cl_2) afforded sulfoximine **12d** (180 mg, 91%) as a white solid; R_f = 0.10 (4% MeOH/CH_2Cl_2); mp = 94–96 °C; IR (film)/cm^{-1} 3258, 3202 (broad), 2989, 2904, 2855, 1495. 1387, 1342, 1275, 1234, 1208, 1167, 1118, 1081, 1029, 998, 876, 835, 723, 693; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.97–6.82 (m, 5H), 4.61 (t, *J* = 5.2 Hz, 1H), 3.88 (s, 2H), 3.16 (s, 1H), 2.85 (s, 2H), 2.01 (q, *J* = 1.8 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 131.1 (2 × C), 130.4, 128.3 (2 × C), 128.0, 61.6, 55.6, 54.3; HRMS (APCI$^+$) m/z: Calcd for $C_9H_{14}NO_2S^+$ [M+H]$^+$: 200.0740; Found: 200.0738.

Imino(phenyl)(vinyl)-λ^6-sulfanone (**13a**) and *N*-(oxo(phenyl)(vinyl)-λ^6-sulfaneylidene)methanesulfonamide (**14a**). The title compounds were prepared according to General Procedure G employing sulfoximine **12a** (141 mg, 0.76 mmol). Purification by flash column chromatography (SiO_2, 50% EtOAc/pentane) afforded vinyl sulfoximine **13a** (63 mg, 50%) and mesylated vinyl sulfoximine **14a** (11 mg, 6%) both as colourless oils; Analytical data for vinyl sulfoximine **13a**: R_f = 0.23 (50% EtOAc/pentane); IR (film)/cm^{-1} 3269, 3064, 1446, 1223, 1129, 977, 731, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.94 (m, 2H), 7.67–7.58 (m, 1H), 7.57–7.51 (m, 2H), 6.75 (dd, *J* = 16.4, 9.5 Hz, 1H), 6.43 (dd, *J* = 16.4, 0.6 Hz, 1H), 5.99 (dd, *J* = 9.5, 0.5 Hz, 1H), 2.88 (s, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 141.7, 140.5, 133.0, 129.2 (2 × C), 128.1 (2 × C), 126.6; Analytical data in agreement with those reported in the literature.[30] Analytical data for mesylated vinyl sulfoximine **14a**: R_f = 0.29 (50% EtOAc/pentane); IR (film)/cm^{-1} 3269, 3060, 1308, 1230, 1140, 1099, 1066, 969, 801, 745; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–7.96 (m, 2H), 7.76–7.67 (m, 1H), 7.67–7.57 (m, 2H), 6.83 (dd, *J* = 16.3, 9.6 Hz, 1H), 6.52 (dd, *J* = 16.3, 1.3 Hz, 1H), 6.23 (dd, *J* = 9.6, 1.4 Hz, 1H), 3.18 (s, 3H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 137.5, 137.0, 134.5, 129.7 (2 × C), 129.4, 128.0 (2 × C), 45.4; Analytical data in agreement with those reported in the literature.[62]

Imino(4-nitrophenyl)(vinyl)-λ^6-sulfanone (**13b**). The title compound was prepared according to General Procedure G employing sulfoximine **12b** (57.5 mg, 0.25 mmol). Purification by flash column chromatography (SiO_2, 0-10% Et_2O/CH_2Cl_2) afforded vinyl sulfoximine **13b** (26.5 mg, 52%) as an off-white solid; R_f = 0.35 (10% Et_2O/CH_2Cl_2); mp = 95–97 °C; IR (film)/cm^{-1} 3280, 3105, 3064, 1607, 1528, 1349, 1312, 1230, 1174, 1141, 977, 857, 738, 705; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51–8.21 (m, 2H), 8.25–8.09 (m, 2H), 6.75 (dd, *J* = 16.3, 9.5 Hz, 1H), 6.53 (dd, *J* = 16.3, 0.7 Hz, 1H), 6.12 (dd, *J* = 9.4, 0.7 Hz, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 150.6, 148.1, 139.7, 129.6 (2 × C), 129.0, 124.5 (2 × C); HRMS (ESI-TOF) m/z: Calcd for $C_8H_9N_2O_3S$ [M+H]$^+$: 213.0334; Found: 213.0339.

Benzo[*d*]thiazol-2-yl(imino)(vinyl)-λ^6-sulfanone (**13c**). The title compound was prepared according to General Procedure G employing sulfoximine **12c** (133 mg, 0.55 mmol). Purification by flash column chromatography (SiO_2, 30% acetone/pentane) afforded vinyl sulfoximine **13c** (48 mg, 39%) as a white solid; R_f = 0.39 (30% acetone/pentane); mp = 99–101 °C; IR (film)/cm^{-1} 3261, 1468, 1315, 1259, 1237, 1111, 977, 760, 723; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.17 (m, 1H), 8.02–7.95 (m, 1H), 7.66–7.53 (m, 2H), 7.02 (dd, *J* = 16.4, 9.5 Hz, 1H), 6.71 (dd, *J* = 16.4, 1.0 Hz, 1H), 6.28 (dt, *J* = 9.5, 0.9 Hz, 1H), 3.56 (s, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 169.5, 153.0, 137.7, 137.5, 131.0, 127.7, 127.4, 125.3, 122.2; HRMS (APCI$^+$) m/z: Calcd for $C_9H_9N_2OS_2^+$ [M+H]$^+$: 225.0151; Found: 225.0153.

Benzyl(imino)(vinyl)-λ^6-sulfanone (**13d**) and *N*-(benzyl(*oxo*)(vinyl)-λ^6-sulfaneylidene)methanesulfonamide (**14d**). The title compounds were prepared according to General Procedure G employing sulfoximine **12d** (70 mg, 0.35 mmol). Purification by flash column chromatography (KP-Sil, 0% grading to 50% acetone in pentane) afforded vinyl sulfoximine **13d** (22 mg, 35%) as a colourless oil and mesylated vinyl sulfoximine **14d** (26 mg, 29%) as a white solid. Analytical data for vinyl sulfoximine **13d**: R_f = 0.30 (50% EtOAc/pentane); IR (film)/cm^{-1} 3273,1215, 967, 701; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42–7.25 (m, 5H), 6.76 (dd, *J* = 16.4, 9.6 Hz, 1H), 6.07–5.92 (m, 2H), 4.34 (s, 2H), 3.93 (br s, 1H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 138.9, 131.0 (2 × C), 130.0, 128.1, 128.0, 127.7, 61.4; HRMS (ESI-TOF) m/z: Calcd for $C_9H_{12}NOS^+$ [M+H]$^+$: 182.0640; Found: 182.0640. Analytical data for mesylated vinyl sulfoximine **14d**: R_f = 0.40 (10% Et_2O/CH_2Cl_2); mp = 139–140 °C; IR (film)/cm^{-1} 3109, 3070, 2982, 2933, 1744, 1532, 1495, 1457, 1409, 1383, 1305, 1230, 1137, 1066, 969, 897, 783, 746, 701; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.38 (m, 5H), 6.53 (dd, *J* = 16.3, 9.7 Hz), 6.36–6.24 (m, 2H), 4.73 (s, 2H), 3.14 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 133.4, 133.2, 131.7 (2 × C), 129.9, 129.2 (2 × C), 126.3, 62.3, 45.4; HRMS (APCI$^+$) m/z: Calcd for $C_{10}H_{14}NO_3S_2^+$ [M+H]$^+$: 260.0415; Found: 260.0408.

Terminal vinyl sulfonimidamides **18a**–**18d.**

1,2-Bis(2-((tetrahydro-2H-pyran-2-yl)oxy)ethyl)disulfane (**16**). Pyridinium *p*-toluenesulfonate (2.00 g, 7.90 mmol) was added to a solution of 2-hydroxyethyl disulfide (10.0 mL, 81.7 mmol) and 3,4-dihydropyran (30.0 mL, 328 mmol) in CH_2Cl_2 (100 mL) at 0 °C. The solution was allowed to warm to room temperature and was stirred for 18 h. The solvent was removed *in vacuo* and the crude residue was purified by flash column chromatography (KP-Sil, 0% grading to 50% Et_2O in pentane, eluted at 10%) which afforded disulfide **16** (22.7 g, 86%) as a colourless oil; R_f = 0.44 (25% Et_2O in pentane); IR (film)/cm^{-1} 3008, 2941, 2870, 1438,1349, 1200, 1118, 1077, 1025, 753; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (dd, *J* = 4.2, 2.9 Hz, 2H), 4.04–3.92 (m, 2H), 3.88 (ddd, *J* = 11.2, 8.0, 3.5 Hz, 2H), 3.69 (dt, *J* = 10.4, 6.7 Hz, 2H), 3.58–3.47 (m, 2H), 3.01–2.85 (m, 4H), 1.89–1.66 (m, 4H), 1.65–1.46 (m, 8H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 99.1 (2 × C), 66.1 (2 × C), 62.4 (2 × C), 39.2 (2 × C), 30.7 (2 × C), 25.6 (2 × C), 19.5 (2 × C); HRMS (APCI$^+$) m/z Calcd for $C_{14}H_{26}O_4S_2^+$ [M]$^+$, 322.1267; found, 322.1276.

4-Phenyl-1-(2-((tetrahydro-2*H*-pyran-2-yl)oxy)ethylsulfonimidoyl)piperidine (**17a**). The title compound was prepared according to General Procedure H employing silver nitrate (603 mg, 4.0 mmol), triethylamine (554 µL, 4.0 mmol), disulfide **16** (644 mg, 2.0 mmol) and 4-phenyl piperidine (427 mg, 2.66 mmol) in MeOH (26 mL) followed by ammonium carbamate (223 mg, 2.86 mmol), iodosylbenzene (788 mg, 3.58 mmol) and acetic acid (80 µL, 1.4 mmol) in *i*PrOH (7 mL). Purification by flash column chromatography (KP-Sil, 50% grading to 100% EtOAc in pentane, product eluted at 100%) afforded sulfonimidamide **17a** (400 mg, 57% over 2 steps, dr 1:1) as a colourless oil; R_f = 0.40 (100% EtOAc); IR (film)/cm^{-1} 3280, 2937, 2847, 1244, 1118, 1028, 931; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 2H), 7.25–7.14 (m, 3H), 4.71–4.57 (m, 1H), 4.24–4.09 (m, 1H), 4.09–3.96 (m, 2H), 3.96–3.81 (m, 2H), 3.60–3.48 (m, 1H), 3.40–3.16 (m, 2H), 2.93–2.75 (m, 2H), 2.57 (td, *J* = 12.1, 3.0 Hz, 1H), 2.28 (d, *J* = 7.8 Hz, 1H), 2.03–1.88 (m, 2H), 1.88–1.64 (m, 5H), 1.64–1.43 (m, 4H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 145.3, 128.8, 126.9, 126.7, 99.6, 99.5, 62.8, 62.0, 61.8, 50.1, 50.0, 47.5, 47.5, 47.2, 47.1, 42.5, 33.8, 33.6, 33.5, 30.8, 30.7, 25.4, 19.8; HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{29}N_2O_3S^+$ [M + H]$^+$, 353.1899; found 353.1901.

4-Methyl-2-phenyl-1-(2-((tetrahydro-2*H*-pyran-2-yl)oxy)ethylsulfonimidoyl)piperazine (**17b**). The title compound was prepared according to General Procedure H employing 1-methyl-3-phenylpiperazine (587 mg, 3.3 mmol), triethylamine (693 µL, 5.0 mmol), silver nitrate (849 mg, 5.0 mmol) and disulfide **16** (806 mg, 2.5 mmol) in MeOH (25 mL) followed by ammonium carbamate (390 mg, 5.0 mmol), iodosylbenzene (1.37 g, 6.25 mmol) and acetic acid (143 µL, 2.5 mmol) in *i*PrOH (13 mL). Purification by flash column chromatography (SiO_2, 70% EtOAc in pentane) afforded sulfonimidamide **17b** (292 mg, 32% over 2 steps) as a complex mixture of diastereomers as a brown oil; R_f = 0.11 (70% EtOAc in pentane); IR (film)/cm^{-1} 3272, 2937, 2870, 2791, 1453, 1244, 1148, 1118, 1029, 976, 917; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.64 (m, 4H), 7.38–7.32 (m, 4H), 7.31–7.27 (m, 2H), 5.14 (d, *J* = 3.4 Hz, 1H), 5.10 (d, *J* = 4.3 Hz, 1H), 4.60–4.53 (m, 2H), 4.13–4.01 (m, 2H), 3.89–3.74 (m, 6H), 3.54–3.45 (m, 2H), 3.41–3.05 (m, 6H), 2.98–2.78 (m, 4H), 2.52–2.47 (m, 2H), 2.31–2.28 (m, 6H), 2.30 (s, 2H), 2.22–2.11 (m, 2H), 1.84–1.64 (m, 4H), 1.64–1.45 (m, 8H);

$^{13}C\{^1H\}$ NMR (101 Hz, $CDCl_3$) δ 139.7, 128.5, 128.4, 128.3, 128.13, 128.10, 127.5, 127.4, 99.1, 99.0, 62.3, 62.2, 61.93, 61.89, 59.1, 58.5, 56.2, 55.9, 55.4, 55.2, 53.64, 53.63, 46.30, 46.27, 42.1, 41.9, 30.4, 30.3, 25.2, 19.32, 19.29; HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{30}N_3O_3S$ $[M + H]^+$, 368.2008; found; 368.2006.

N-(3-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ylidene)propyl)-*N*-methyl-2-((tetrahydro-2*H*-pyran-2-yl)oxy)ethane-1-sulfonimidamide (**17c**). The title compound was prepared according to General Procedure H employing nortriptyline hydrochloride (1.00 g, 3.33 mmol), triethylamine (1.20 mL, 8.75 mmol), silver nitrate (849 mg, 5.0 mmol) and disulfide **16** (806 mg, 2.5 mmol) in MeOH (25 mL) followed by ammonium carbamate (390 mg, 5.0 mmol), iodosylbenzene (1.37 g, 6.25 mmol) and acetic acid (143 μL, 2.5 mmol) in *i*PrOH (13 mL). Purification by flash column chromatography (SiO_2, 20% acetone in pentane) afforded sulfonimidamide **17c** (375 mg, 33% over 2 steps, dr 1:1) containing a small amount of an unidentified and inseparable impurity as a brown oil; R_f = 0.18 (20% acetone in pentane); IR (film)/cm^{-1} 3309, 3015, 2937, 1643, 1483, 1442, 1244, 1121, 1077, 1028, 969, 766; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29–7.25 (m, 1H), 7.23–7.13 (m, 6H), 7.06–7.03 (m, 1H), 5.85 (td, *J* = 7.4, 1.4 Hz, 1H), 4.60 (dd, *J* = 4.5, 3.0 Hz, 1H), 4.10 (ddt, *J* = 10.9, 9.3, 6.1 Hz, 1H), 3.90–3.80 (m, 2H), 3.65–3.13 (m, 9H), 2.97 (s, 1H), 2.76 (s, 3H), 2.44–2.34 (m, 2H), 1.83–1.70 (m, 2H), 1.61–1.49 (m, 4H); $^{13}C\{^1H\}$ NMR (101 Hz, $CDCl_3$) δ 145.1, 140.8, 139.7, 139.4, 137.0, 130.1, 128.5, 128.1, 128.0, 127.6, 127.3, 127.2, 126.1, 125.7, 99.2, 62.6, 61.8, 61.6, 50.5, 50.3, 33.7, 32.0, 30.5, 28.6, 25.2, 19.5; HRMS (ESI-TOF) m/z Calcd for $C_{26}H_{35}N_2O_3S$ $[M + H]^+$, 455.2368; found, 455.2354.

N-Benzyl-*N*-methyl-2-((tetrahydro-2*H*-pyran-2-yl)oxy)ethane-1-sulfonimidamide (**17d**). The title compound was prepared according to General Procedure H employing silver nitrate (603 mg, 4.0 mmol), triethylamine (554 μL, 4.0 mmol), *N*-methylbenzylamine (346 μL, 2.66 mmol) and disulfide **16** (645.0 mg, 2.0 mmol) in MeOH (20 mL) followed by ammonium carbamate (390 mg, 5.0 mmol), iodosylbenzene (1.37 g, 6.25 mmol) and acetic acid (143 μL, 2.5 mmol) in *i*PrOH (13 mL). Purification by flash column chromatography (KP-Sil 0% grading to 100% MeOH in CH_2Cl_2, product eluted at 7%) afforded sulfonimidamide **17d** (324 mg, 52% over 2 steps, dr 1:1) as a yellow oil; R_f = 0.28 (100% EtOAc); IR (film)/cm^{-1} 3280, 2937, 2870, 1454, 1349, 1245, 1122, 1077, 1028, 976, 731; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.27 (m, 5H), 4.65 (m, 1H), 4.52–4.32 (m, 2H), 4.24–4.10 (m, 1H), 3.97–3.84 (m, 2H), 3.58–3.50 (m, 1H), 3.47–3.25 (m, 2H), 2.81 (d, *J* = 3.2 Hz, 3H), 2.34 (d, *J* = 8.3 Hz, 1H), 1.92–1.71 (m, 2H) 1.66–1.47 (m, 4H); $^{13}C\{^1H\}$ NMR (101 Hz, $CDCl_3$) δ 137.0, 128.8, 128.1, 127.8, 99.5, 62.8, 62.0, 61.8, 54.9, 50.9, 35.4, 30.8, 25.4, 19.8; HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{25}N_2O_3S^+$ $[M + H]^+$, 313.1580; found 313.1578.

4-Phenyl-1-(vinylsulfonimidoyl)piperidine (**18a**). The title compound was prepared according to General Procedure I employing sulfonimidamide **17a** (32 mg, 0.09 mmol). Purification by flash column chromatography (KP-Sil, 50% grading to 100% EtOAc in pentane, product eluted at 100%) to give sulfonimidamide **18a** (17 mg, 70% over 2 steps) as a colourless oil; R_f = 0.50 (100% EtOAc); IR (film)/cm^{-1} 3287, 2937, 1244, 1051, 924, 734; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 2H), 7.25–7.13 (m, 3H), 6.52 (dd, *J* = 16.6, 9.9 Hz, 1H), 6.26 (d, *J* = 16.6 Hz, 1H), 6.03 (d, *J* = 9.9 Hz, 1H), 4.02 (ddt, *J* = 11.9, 4.4, 2.5 Hz, 1H), 3.92 (ddt, *J* = 11.9, 4.6, 2.4 Hz, 1H), 2.72–2.44 (m, 3H), 2.37 (s, 1H), 2.01–1.87 (m, 2H), 1.87–1.72 (m, 2H); $^{13}C\{^1H\}$ NMR (101 Hz, $CDCl_3$) δ 145.2, 133.4, 128.7 (2 × C), 127.7, 126.9 (2 × C), 126.7, 47.8, 47.4, 42.3, 33.4, 33.1; HRMS (ESI-TOF) *m/z* Calcd for $C_{13}H_{19}N_2OS^+$ $[M + H]^+$, 251.1218; found 251.1207.

4-Methyl-2-phenyl-1-(vinylsulfonimidoyl)piperazine (**18b**). The title compound was prepared according to General Procedure I employing sulfonimidamide **17b** (238 mg, 0.65 mmol). Purification by flash column chromatography (SiO_2, 20% acetone in pentane) afforded sulfonimidamide **18b** (70 mg, 42% over 2 steps, dr 1:2) as a brown oil; R_f = 0.27 (20% acetone in pentane); IR (film)/cm^{-1} 3272, 2937, 2795, 1453, 1267, 1244, 1148, 973, 924; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.3, 1.9 Hz, 2H), 7.63 (dd, *J* = 7.4, 1.8 Hz, 2H), 7.36–7.32 (m, 4H), 7.31–7.25 (m, 2H), 6.27–6.09 (m, 4H), 5.76–5.71 (m, 2H), 5.05–5.02 (m, 2H), 3.72–3.67 (m, 2H), 3.35–3.13 (m, 4H), 2.84–2.77 (m, 2H), 2.51–2.47 (m, 2H), 2.33 (s, 2H), 2.30–2.17 (m, 6H), 2.24–2.13 (m, 2H); $^{13}C\{^1H\}$ NMR (101 Hz, $CDCl_3$) δ 139.6, 137.1, 136.4, 128.6, 128.4, 128.3, 128.2, 127.5, 125.3, 125.0, 58.8, 57.9, 56.3, 56.2, 54.9, 54.8, 46.3, 42.1, 41.9; HRMS (ESI-TOF) m/z Calcd for $C_{13}H_{20}N_3OS$ $[M + H]^+$, 266.1327; found, 266.1334.

N-(3-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ylidene)propyl)-*N*-methylethenesulfonimidamide (**18c**). The title compound was prepared according to General Procedure I employing sulfonimidamide **17c** (516 mg, 1.13 mmol). Purification by flash column chromatography (SiO_2, 50% EtOAc in pentane) afforded sulfonimidamide **18c** (188 mg, 47%) as a brown oil; R_f = 0.33 (50% EtOAc in pentane); IR (film)/cm^{-1} 3309, 3060, 3015, 2914, 1483, 1453, 1267, 1107, 965, 742; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29–7.27 (m, 1H), 7.26–7.09 (m, 6H), 7.08–7.02 (m, 1H), 6.42 (dd, *J* = 16.6, 9.8 Hz, 1H), 6.19 (d, *J* = 16.6 Hz, 1H), 5.90 (d, *J* = 9.9 Hz, 1H), 5.85 (t, *J* = 7.5 Hz, 1H), 3.46–3.23 (m, 3H), 3.17–3.05 (m, 1H), 3.02–2.92 (m, 1H), 2.85–2.75 (m, 1H), 2.71–2.60 (m, 3H), 2.44–2.32 (m, 2H), 2.09 (s, 1H); $^{13}C\{^1H\}$ NMR (101 Hz, $CDCl_3$) δ 145.2, 140.7, 139.7, 139.4, 137.0, 133.4, 130.1, 128.5, 128.1, 128.0, 127.6, 127.23, 127.20, 126.6, 126.1, 125.8, 50.5 (2 × C), 33.7, 31.9, 28.3; HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{25}N_2OS$ $[M + H]^+$, 353.1688; found, 353.1682.

N-Benzyl-*N*-methylethenesulfonimidamide (**18d**). The title compound was prepared according to General Procedure I employing sulfonimidamide **17d** (144 mg, 0.46 mmol). Purification by flash column chromatography (KP-Sil, 30% grading to 100% EtOAc/pentane, eluted at 50%) gave sulfonimidamide **18d** (22 mg, 23% over 2 steps) as a pale yellow oil; R_f = 0.25 (100% EtOAc); IR (film)/cm^{-1} 3280, 3030, 1358, 1243, 1102, 969, 733; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.27 (m, 5H), 6.56 (dd, *J* = 16.6, 9.9 Hz, 1H), 6.31 (d, *J* = 16.6 Hz, 1H), 6.03(d, *J* = 9.9 Hz, 1H), 4.30 (m, 2H), 2.73 (s, 3H), 2.47 (s, 1H); $^{13}C\{^1H\}$ NMR (101 Hz, $CDCl_3$) δ 136.6, 133.5, 128.8 (2 × C), 128.3 (2 × C), 127.9, 127.2, 55.0, 35.3; HRMS (ESI-TOF) m/z Calcd for $C_{10}H_{15}N_2OS$ $[M + H]^+$, 211.0900; found, 211.0896.

N-Propargyl vinyl sulfoximines and sulfonimidamides **19a**–**19g**. Phenyl(prop-2-yn-1-ylimino)(vinyl)-λ⁶-sulfanone (**19a**). The title compound was prepared according to General Procedure J employing sulfoximine **11a** (36 mg, 0.21 mmol). Purification by flash column chromatography (KP-Sil, 0% grading to 50% EtOAc/pentane, product eluted at 25%) afforded sulfoximine **19a** (25 mg, 57%) as a colourless oil; R_f = 0.45 (50% EtOAc in pentane); IR (film)/cm^{-1} 3295, 2321, 1446, 1267, 1216, 1131, 971, 742; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95–7.90 (m, 2H), 7.62–7.51 (m, 3H), 6.68 (dd, *J* = 16.5, 9.6 Hz, 1H), 6.38 (d, *J* = 16.5 Hz, 1H), 6.03 (d, *J* = 9.9 Hz, 1H), 3.87 (dd, *J* = 17.2, 2.5 Hz, 1H), 3.79 (dd, *J* = 17.3, 2.5 Hz, 1H), 2.19 (t, *J* = 2.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 Hz, $CDCl_3$) δ 138.5, 138.4, 133.3, 129.5 (2 × C), 129.0 (2 × C), 128.2, 83.0, 70.6, 32.6; HRMS (ESI-TOF) *m/z* Calcd for $C_{11}H_{12}NOS^+$ $[M + H]^+$, 206.0640; found, 206.0647.

(*E*)-Phenyl(prop-2-yn-1-ylimino)(styryl)-λ⁶-sulfanone (**19b**). The title compound was prepared according to General Procedure J employing sulfoximine **5a** (36 mg, 0.15 mmol). Purification by flash chromatography (KP-Sil, 0% grading to 100% EtOAc/Hexane, eluted at 35% EtOAc) afforded **19b** (23 mg, 55%) as a dark orange oil; R_f = 0.64 (50% EtOAc/Pentane); IR (film)/cm^{-1} 3295, 3060, 1610, 1446, 1267, 1215, 1133, 1081, 745, 686; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01–7.98 (m, 2H), 7.62–7.52 (m, 4H), 7.48–7.46 (m, 2H), 7.41–7.36 (m, 3H), 6.89 (d, *J* = 15.3 Hz, 1H), 3.91 (dd, *J* = 14.8, 2.5 Hz, 1H) 3.81 (dd, *J* = 14.8, 2.6 Hz, 1H), 2.23 (t, *J* = 2.53 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 Hz, $CDCl_3$) δ 142.9, 139.3, 133.0, 132.7, 131.0, 129.4 (2 × C), 129.0 (2 × C), 128.6 (2 × C), 128.5 (2 × C), 127.2, 83.2, 70.5, 32.7; HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{16}NOS^+$ $[M + H]^+$, 282.0953; found, 282.0960.

(*E*)-(2-Cyclohexylvinyl)(phenyl)(prop-2-yn-1-ylimino)-λ⁶-sulfanone (**19c**).The title compound was prepared according to General Procedure J employing sulfoximine **5b** (40 mg, 0.16 mmol). Purification *via* flash column chromatography (KP-Sil, 0% grading to 100% EtOAc/Petroleum ether, eluted at 35% EtOAc) afforded **19c** (35 mg, 77%) as a clear oil; R_f = 0.61 (50% EtOAc/Pentane); IR (film)/cm^{-1} 3295, 2926, 2851, 1446, 1267, 1218, 1133, 969, 752, 689; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.89 (m, 2H), 7.60–7.56 (m, 1H), 7.54–7.50 (m, 2H), 6.83 (dd, *J* = 8.7, 6.3 Hz, 1H), 6.28 (d, *J* = 15.2 Hz, 1H), 3.81 (dd, *J* = 14.7, 2.6 Hz, 1H), 3.71 (dd, *J* = 14.9, 2.5 Hz, 1H), 2.20 (t, *J* = 2.5 Hz, 1H), 2.18–2.12 (m, 1H) 1.74 (m, 4H) 1.67–1.63 (m, 1H), 1.30–1.09 (m, 5H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 152.1, 139.3, 132.8, 129.3 (2 × C), 128.6 (2 × C), 127.8, 83.2, 70.3, 40.0, 32.6, 31.4, 31.2, 25.7, 25.6 (2 × C); HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{22}NOS^+$ [M + H]$^+$, 288.1422; found, 288.1418.

(*E)*-Phenyl(prop-2-yn-1-ylimino)(2-(pyridin-2-yl)vinyl)-λ⁶-sulfanone (**19d**). The title compound was prepared according to General Procedure J employing sulfoximine **5d** (40 mg, 0.16 mmol). Purification by flash column chromatography (KP-Sil, 0% grading to 100% EtOAc/Pentane, eluted at 56% EtOAc) afforded **19d** (31 mg, 77%) as a brown oil; R_f = 0.30 (50% EtOAc/Pentane); IR (film)/cm^{-1} 3298, 3056, 2926, 1580, 1267, 1215, 1129, 1080, 969, 752, 685; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60–8.59 (d, *J* = 5.5 Hz, 1H), 8.02–8.00 (m, 2H), 7.73–7.69 (m, 1H), 7.59 (d, *J* = 15.1 Hz, 1H), 7.61–7.57 (m, 1H), 7.56–7.51 (m, 2H), 7.40 (d, *J* = 15.0 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.28–7.25 (m, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 151.4, 150.2, 141.3, 138.9, 137.0, 133.1, 131.8, 129.4 (2 × C), 128.8 (2 × C), 125.1, 124.8, 83.1, 70.5, 32.7; HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{15}N_2OS^+$ [M + H]$^+$, 283.0905; found, 283.0920.

4-Phenyl-1-(*N*-(prop-2-yn-1-yl)vinylsulfonimidoyl)piperidine (**19e**). The title compound was prepared according to General Procedure J employing sulfonimidamide **18a** (16 mg, 0.07 mmol). Purification by flash column chromatography (KP-Sil, 35% grading to 100% EtOAc in pentane, eluted at 60%) afforded sulfonimidamide **19e** (10 mg, 52%) as a colourless oil; R_f = 0.70 (100% EtOAc); IR (film)/cm^{-1} 3284, 2918, 2844, 1278, 1230, 1140, 924, 756; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.28 (m, 2H), 7.25–7.16 (m, 3H), 6.52 (dd, *J* = 16.7, 9.9 Hz, 1H), 6.24 (d, *J* = 16.8 Hz, 1H), 6.01 (d, *J* = 10.0 Hz, 1H), 4.12–3.75 (m, 4H), 2.72–2.47 (m, 3H), 2.22 (t, *J* = 2.6 Hz, 1H), 2.02–1.69 (m, 4H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 145.2, 132.9, 128.7 (2 × C), 127.4, 126.9 (2 × C), 126.7, 83.0, 70.1, 47.6, 47.5, 42.2, 33.1, 33.0, 30.7; HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{21}N_2OS^+$ [M + H]$^+$, 289.1369; found, 289.1371.

4-Methyl-2-phenyl-1-(*N*-(prop-2-yn-1-yl)vinylsulfonimidoyl)piperazine (**19f**). The title compound was prepared according to General Procedure J employing sulfonimidamide **18b** (53 mg, 0.20 mmol, dr 1:2). Purification by flash column chromatography (SiO_2, 10% acetone in pentane) afforded sulfonimidamide **19f** (29 mg, 48%, dr 1:2) as a brown oil; R_f = 0.26 (10% acetone in pentane); IR (film)/cm^{-1} 3287, 2937, 2844, 2795, 1457, 1278, 1230, 1148, 972, 917, 767; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.72 (m, 2H), 7.70 (dd, *J* = 7.4, 1.8 Hz, 2H), 7.37–7.24 (m, 6H), 6.29 (dd, *J* = 16.5, 9.5 Hz, 1H), 6.16 (d, *J* = 16.5 Hz, 1H), 6.00 (dd, *J* = 16.5, 9.6 Hz, 1H), 5.89 (d, *J* = 16.5 Hz, 1H), 5.77 (d, *J* = 9.6 Hz, 1H), 5.56 (d, *J* = 9.6 Hz, 1H), 4.98 (d, *J* = 4.2 Hz, 1H), 4.94–4.90 (m, 1H), 3.89–3.85 (m, 4H), 3.66–3.57 (m, 2H), 3.29–3.22 (m, 2H), 3.15 (dt, *J* = 11.9, 1.8 Hz, 1H), 3.10 (dt, *J* = 11.6, 1.8 Hz, 1H), 2.91–2.87 (m, 1H), 2.81–2.77 (m, 1H), 2.56 (dd, *J* = 11.6, 4.5 Hz, 1H), 2.53–2.44 (m, 1H), 2.31–2.27 (m, 8H), 2.21 (t, *J* = 2.5 Hz, 1H), 2.19 (t, *J* = 2.5 Hz, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 139.3, 136.8, 134.3, 129.3, 128.5, 128.2, 128.0, 127.7, 126.1, 124.8, 82.9, 82.6, 70.2, 69.9, 59.2, 57.2, 56.2, 55.9, 54.8, 54.7, 46.2, 41.9, 41.5, 30.8, 30.7; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{22}N_3OS^+$ [M + H]$^+$, 304.1484; found, 304.1497.

N-(3-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ylidene)propyl)-*N*-methyl-*N*'-(prop-2-yn-1-yl)ethenesulfonimidamide (**19g**). The title compound was prepared according to General Procedure J employing sulfonimidamide **18c** (70 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, 30% EtOAc in pentane) afforded sulfonimidamide **19g** (63 mg, 81%) as a brown oil; R_f = 0.53 (50% EtOAc in pentane); IR (film)/cm^{-1} 3287, 3060, 3019, 2914, 2855, 1483, 1442, 1282, 1230, 1148, 969, 756; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.25 (m, 1H), 7.26–7.09 (m, 6H), 7.08–7.02 (m, 1H), 6.49–6.38 (m, 1H), 6.15 (d, *J* = 16.7 Hz, 1H), 5.92–5.81 (m, 2H), 3.82 (d, *J* = 2.9 Hz, 2H), 3.51–3.11 (m, 5H), 3.03–2.93 (m, 1H), 2.87–2.74 (m, 1H), 2.69 (s, 3H), 2.41 (qd, *J* = 7.3, 1.4 Hz, 2H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 145.0, 140.8, 139.7, 139.3, 137.0, 133.1, 130.0, 128.5, 128.1, 128.0, 127.6, 127.2 (2 × C), 126.4, 126.1, 125.8, 82.7, 70.0, 50.4 (2 × C), 33.7, 32.0, 30.6, 28.1; HRMS (ESI-TOF) m/z Calcd for $C_{24}H_{27}N_2OS^+$ [M + H]$^+$, 391.1844; found, 391.1854.

Chiral separation of **10g**. Vinyl sulfoximine **10g** (68 mg) was dissolved to 12 mg/mL in MeOH and was then purified by HPLC using a Chiralpak IG (20 mm × 250 mm, 5 μm) column. Combined fractions of each isomer were evaporated to dryness to afford **10g-A** (12.9 mg, >99% de,), **10g-B** (10.2 mg, 97% de,) as yellow oils.

10g-A; IR (film)/cm^{-1} 3295, 3060, 2926, 1495, 1446, 1222, 753; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.96 (m, 2H), 7.61–7.52 (m, 3H), 7.28–7.09 (m, 5H), 6.93 (dd, *J* = 14.9, 5.8 Hz, 1H), 6.56 (dd, *J* = 14.9, 1.4 Hz, 1H), 3.60–3.51 (m, 1H), 2.73–2.63 (m, 2H), 2.58 (s, 1H), 1.88–1.77 (m, 2H), 1.66 (s, 2H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 148.7, 142.9, 141.2, 133.0, 131.8, 129.3 (2 × C), 128.7 (2 × C), 128.5 (2 × C), 128.1 (2 × C), 126.3, 51.7, 38.4, 32.2.

10g-B; IR (film)/cm^{-1} 3306, 3063, 2922, 1495, 1446, 1222, 987, 752,; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.96 (m, 2H), 7.62–7.52 (m, 3H), 7.28–7.10 (m, 5H), 6.93 (dd, *J* = 14.9, 5.8 Hz, 1H), 6.55 (dd, *J* = 14.9, 1.4 Hz, 1H), 3.60–3.47 (m, 1H), 2.74–2.63 (m, 2H), 2.55 (s, 1H), 1.91–1.78 (m, 2H), 1.66 (s, 2H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 148.9, 143.0, 141.1, 133.0, 131.8, 129.4 (2 × C), 128.7 (2 × C), 128.5 (2 × C), 128.1 (2 × C), 126.3, 51.7, 38.5, 32.12.

Chiral separation of **19f**. Vinyl sulfonimidamide **19f** (21.8 mg) was dissolved to 10 mg/mL in Heptane:EtOH 6:4 and was then purified by HPLC using a Amy-C (20 mm × 250 mm, 5 μm) column. Combined fractions of each isomer were evaporated to dryness to afford **19f-A** (2.5 mg, >99% ee, >99% de, $[\alpha]_D^{21}$ = +28 (*c* 0.003, $CHCl_3$)), **19f-B** (4.4 mg, >99% ee, > 99% de, $[\alpha]_D^{21}$ −37 (*c* 0.002, $CHCl_3$)), **19f-C** (1.9 mg, 96% ee, >99% de, $[\alpha]_D^{21}$ +31 (*c* 0.001, $CHCl_3$)) and **19f-D** (3.6 mg, >99% ee, 97% de, $[\alpha]_D^{21}$ −28 (*c* 0.003, $CHCl_3$))) as clear glassy solids.

Enantiomeric pair **19f-A** and **19f-D**; IR (film)/cm^{-1} 3287, 2937, 2795, 1457, 1282, 1140, 972, 917; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.40–7.27 (m, 3H), 6.00 (dd, *J* = 16.5, 9.6 Hz, 1H), 5.89 (d, *J* = 16.5 Hz, 1H), 5.55 (d, *J* = 9.5 Hz, 1H), 4.91 (d, *J* = 4.3 Hz, 1H), 3.86 (d, *J* = 2.5 Hz, 2H), 3.57 (s, 1H), 3.24 (d, *J* = 3.3 Hz, 1H), 3.09 (d, *J* = 11.6 Hz, 1H), 2.94–2.82 (m, 1H), 2.55 (dd, *J* = 11.7, 4.5 Hz, 1H), 2.28 (s, 3H), 2.27 (m, 1H), 2.19 (t, *J* = 2.5 Hz, 1H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 139.6, 134.6, 129.5, 128.2, 127.8, 126.2, 83.1, 70.1, 59.5, 56.5, 55.0, 46.5, 41.7, 30.9.

Enantiomeric pair **19f-B** and **19f-C**; IR (film)/cm^{-1} 3287, 2939, 2795, 1454, 1278, 1230, 1151, 976, 928; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.62 (m, 2H), 7.38–7.27 (m, 3H), 6.28 (dd, *J* = 16.6, 9.5 Hz, 1H), 6.16 (d, *J* = 16.6 Hz, 1H), 5.76 (d, *J* = 9.5 Hz, 1H), 4.98 (d, *J* = 4.3 Hz, 1H), 3.86 (d, *J* = 2.5 Hz, 2H), 3.71–3.52 (m, 1H), 3.31–3.04 (m, 2H), 2.85–2.71 (m, 1H), 2.45 (dd, *J* = 11.9, 4.4 Hz, 1H), 2.28 (s, 3H), 2.22–2.12 (m, 2H); ^{13}C{^{1}H} NMR (101 Hz, $CDCl_3$) δ 140.5, 137.1, 128.7, 128.4, 127.6, 124.9, 82.5, 70.4, 57.4, 56.1, 54.9, 46.5, 42.1, 31.0.

Chiral separation of **19g**. Vinyl sulfonimidamide **19g** (51.6 mg) was dissolved to 16 mg/mL in 2:1 IPA:CH_2Cl_2 and was then purified by HPLC using a Chiralpak IG (20 mm × 250 mm, 5 μm) column. Combined fractions of each enantiomer were evaporated to dryness to afford **19g-A** (10.6 mg, 99% ee, $[\alpha]_D^{21}$ −33 (*c* 0.01, $CHCl_3$)) and **19g-B** (13.3 mg, 98% ee, $[\alpha]_D^{21}$ +33 (*c* 0.01, $CHCl_3$)) as brown glassy solids.

Computational methods

All calculations were performed using Gaussian 16.[63] Stationary points were confirmed using frequency calculations (default divergence criteria). Conformational searches were carried out as described in the Supporting Information. Electronic Circular Dichroism spectra were calculated for individual conformers using TDDFT calculations at cam-B3LYP/6-311++g(d,p) in a continuum solvent (CPCM) acetonitrile for up to 200 states. Copies of Gaussian log files for optimisations and frequency calculations, TDDFT calculations, and tables of ECD data are available from a data depository via the dataset collection DOIs 10.14469/hpc/7859 (sulfoximines) and 10.14469/hpc/7577 (sulfonimidamides) and datasets cited therein.

Electronic circular dichroism

The circular dichroism and UV-vis spectra were recorded on a Chirascan spectrometer (Applied Photophysics). A 0.1 cm pathlength cuvette was loaded with 200 μL each compound (50 μM in acetonitrile) or acetonitrile blank. The elipticity was measured from 340–195 nm in 1.0 nm intervals (bandwidth = 2.0 nm) for 1.0 s per measurement. Measurements were taken in duplicate and normalised against the acetonitrile control.

Configurational assignment by comparison of the calculated and experimental ECD

Comparative analysis was performed using SpecDis.[55] For each structure/sub-structure, the computed ECD and UV-vis spectra were summed according to their Boltzmann weighting at 298 K. The relevant experimental ECD and UV-vis spectra were then input and similarity analysis performed by first aligning the UV spectra (shift range = −30 to +30 nm; bandwidth = 0.1 to 0.3; energy range = 200 to 340 nm) and then performing a local refinement to optimize the alignment of the ECD. Assignments were made on the basis of both manual inspection of the ECD alignments and the quantification of the similarity scores.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. A version of this manuscript was deposited on the preprint repository ChemRxiv.[64]

Supplementary Information (PDF) contains Supplementary Figures and Supplementary Data. Figures S1–S7 detail the relative energies and structures of conformers of **10g**, **19f** and **19g** and the full comparisons of the computational and experimental UV and ECD spectra. Supplementary Data contains ^{1}H and ^{13}C NMR spectra for novel compounds, HPLC traces of enantioenriched compounds and computational data including Tables S1-S7.

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