JOC The Journal of Organic Chemistry

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# Synthesis of Sulfoximine Carbamates by Rhodium-Catalyzed Nitrene Transfer of Carbamates to Sulfoxides

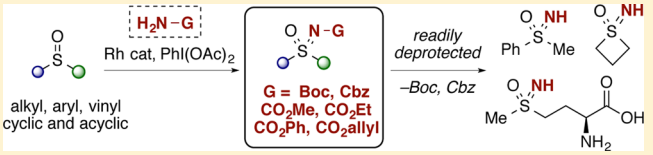
Marina Zenzola,[†,‡] Robert Doran,[†] Renzo Luisi,*[,‡] and James A. Bull*[,†]

[†]Department of Chemistry, Imperial College London, South Kensington, London SW7 2AZ, United Kingdom

[‡]Department of Pharmacy-Drug Sciences, University of Bari "A. Moro", Via E. Orabona 4, Bari 70125, Italy

Supporting Information

**ABSTRACT:** Sulfoximines are of considerable interest for incorporation into medicinal compounds. A convenient synthesis of *N*-protected sulfoximines is achieved, under mild conditions, by rhodium-catalyzed transfer of carbamates to sulfoxides. The first examples of 4-membered thietane-oximines are prepared. Sulfoximines bearing Boc and Cbz groups are stable to further cross coupling reactions, and readily deprotected. This method may facilitate the preparation of *NH*-sulfoximines providing improved (global) deprotection strategies, which is illustrated in the synthesis of methionine sulfoxide (MSO).




## INTRODUCTION

Sulfoximine derivatives have received the attention of synthetic chemists over several decades.[1] Many applications have concerned their use as ligands, and auxiliaries,[2,3] and recently they have been employed as directing groups for catalytic *ortho*-C—H functionalization.[4] Since the identification of methionine sulfoximine (MSO),[5] the first sulfoximine discovered, there has also been significant interest in their effects on biological systems (Figure 1).[6]

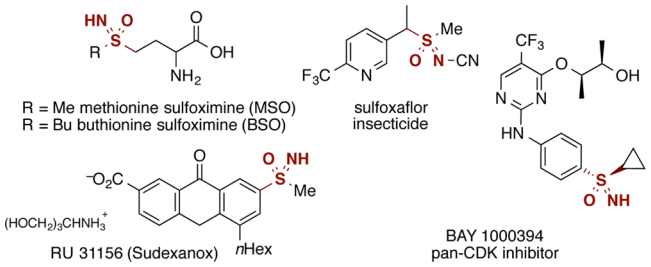



**Figure 1.** Sulfoximines in biologically active compounds.

MSO and buthionine sulfoximine (BSO) are useful tools for the inhibition of the biosynthesis of glutathione (GSH).[7] However, the more general use of the sulfoximine group in medicinal chemistry follows the development of BAY 1000394, a pan-CDK inhibitor that is currently in phase 1 clinical trials for cancer in patients with advanced solid tumors.[8] In this case, the sulfoximine conferred improved solubility versus a sulfonamide predecessor. Sulfoximines are now increasingly intriguing options for inclusion in drug discovery programs.[9] Much of this interest is due to their attractive structural features to improve physicochemical properties. These polar and stable functional groups offer hydrogen bond acceptors and donors, aid solubility, introduce asymmetry at the sulfur atom and provide additional points of substitution through the nitrogen atom.

Advances in their medicinal chemistry usage have necessarily followed the development of improved synthetic routes.[10] Early approaches to sulfoximine synthesis required forcing and hazardous conditions such as sodium azide in concentrated acid.[11] Recently, safer and more tolerant nitrogen transfer methods have been reported, both through imidation of sulfoxides,[12,14−18] and the reverse, imidation of sulfides to form sulfilimines followed by oxidation.[13] In particular, there has been considerable effort aimed at the development of methods for transition metal-catalyzed *N*-transfer to sulfoxides via metal nitrenoid species (Scheme 1).

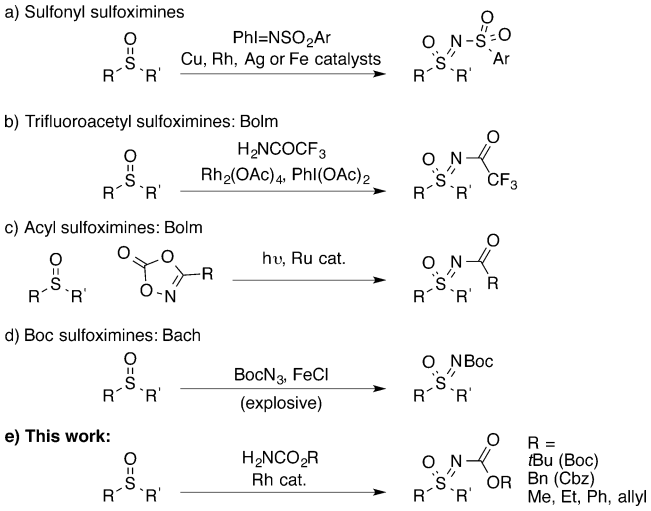
The transfer of sulfonamide groups using activated nitrogen species (e.g., PhI = NNs) has been achieved with Cu,[14] Rh,[15] Ag,[16] and Fe[17] catalysis (Scheme 1a). While Ts groups are challenging to deprotect, the Ns group can be removed by treatment with thiophenol and cesium carbonate.[16] Bolm demonstrated that trifluoroacetamide could be introduced, using $Rh_2(OAc)_4$ and $PhI(OAc)_2$ to generate the active *N*-species in situ (Scheme 1b).[15] Treatment with $K_2CO_3$/MeOH effected deprotection. The transfer of nitrenes derived from simple amides has been unsuccessful under hypervalent iodine mediated conditions. Therefore, Bolm developed the use of 1,4,2-dioxazol-5-ones to transfer a range of amides requiring photochemical activation and a Ru catalyst (Scheme 1c).[18] Richards reported a Rh-catalyzed method for the direct preparation of *NH*-sulfoximines using *O*-(2,4-dinitrophenyl)-hydroxyl-amine with $Rh_2(esp)_2$ as the catalyst.[19] Methods for *N*-functionalization of *NH*-sulfoximines have also undergone significant recent development, including methods for *N*-arylation,[20] acylation,[21] alkynylation,[22] and alkylation.[23]

**Received:** April 16, 2015
**Published:** May 20, 2015

DOI: 10.1021/acs.joc.5b00844
J. Org. Chem. 2015, 80, 6391−6399

**Scheme 1. Catalytic Approaches to Protected Sulfoximines**




We required protected sulfoximines that would be stable to nucleophiles and bases used in further synthetic transformations prior to revealing the *NH*-sulfoximine. We identified sulfoximine carbamates as most suitable. Bolm has previously demonstrated that *N*-Boc sulfoximines were stable to Pd-catalyzed cross-coupling at other positions in the molecule.[24] In that study, the Boc group was introduced by the reaction of preformed *NH*-sulfoximines with $(Boc)_2O$. Similarly, in the reported synthesis of BAY1000394, an *NH*-sulfoximine intermediate was protected as an ethyl carbamate during reduction of a nitro group, before later deprotection.[8] To date, there is no direct and general method for the preparation of carbamate-protected sulfoximines from sulfoxides.[25] The only previous investigation into the preparation of Boc sulfoximines from sulfoxides by Bach used Boc-azide (Scheme 1d).[26] However, the potentially explosive nature of $BocN_3$ has limited the application of this method.

We considered that direct methods for the syntheses of carbamate sulfoximines would be valuable to provide protected sulfoximines that may be revealed selectively or when synthetically most advantageous. In addition, they may provide interesting groups in their own right in medicinal chemistry, or as ligands or auxiliaries. Here we report the direct preparation of sulfoximine carbamates including Boc and Cbz as well as methyl, ethyl, phenyl and allyl derivatives, by the Rh-catalyzed nitrogen transfer of carbamates (Scheme 1e). We demonstrate the stability of the Boc and Cbz groups to further manipulations of sulfoximines, in the form of cross-coupling reactions, as well as their removal. We also report the first preparation of thietane-oximines, and a preparation of MSO via the Boc-sulfoximine.

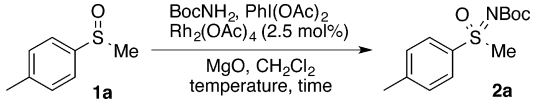
## RESULTS AND DISCUSSION

There are few examples of intermolecular transfer of nitrenoids derived from simple carbamates in any transformation.[27] Inspired by the Bolm method,[15] our study began investigating conditions employing $BocNH_2$ and $PhI(OAc)_2$, intending to generate an activated BocN=IPh species in situ to transfer to a sulfoxide. Using rhodium catalysis and magnesium oxide as base, we were delighted to observe the direct formation of the *N*-Boc sulfoximine **2a** from sulfoxide **1a** in good yield (Table 1, entry 1).[25]

From this starting point, we intended to reduce the reaction times and minimize the excess of reagents required, due to the excess carbamate causing difficulties in purification. Initially reducing the equivalents of carbamate and $PhI(OAc)_2$ led to a reduction of yield (entries 2−3). Warming the reaction gave a slight improvement (entry 4). The crucial variables were the interplay of time and temperature. With the larger excess of reagents, the reaction time could be significantly reduced, and warming to 40 °C gave an 87% yield (entries 5 and 6). At 40 °C with an 8 h reaction time, complete conversion was observed (entry 7). Under these optimized conditions, a 98% yield of the desired *N*-Boc sulfoximine **2a** was obtained (0.6 mmol scale, Scheme 2). No reaction occurred in the absence of the Rh-catalyst (entry 8). At a 4 mmol scale 94% conversion and 80% isolated yield was obtained with 8 h reaction time. The *N*-transfer was stereospecific as performing the reaction on (*S*)-tolyl methyl sulfoxide (*er* 97:3) led to complete retention of the *er* in *N*-Boc-sulfoximine **2a**.[28,29] Importantly, the reaction conditions are not sensitive to air and water; all reactions were performed under air without using anhydrous dichloromethane.

Next, the scope of the reaction was examined using $BocNH_2$ as the nitrogen source (Scheme 2). Variation of the electronics of the aromatic component by using 4-chlorophenylsulfoxide **2b** also gave a good yield. With the isopropyl substituted sulfoximine **2c** the yield was somewhat reduced, as might be expected from the increased steric hindrance. Other substituted alkyl derivatives (**2d** and **2e**) gave excellent yields, as did

**Table 1. Selected Optimization to *N*-Boc-Sulfoximine 2a**



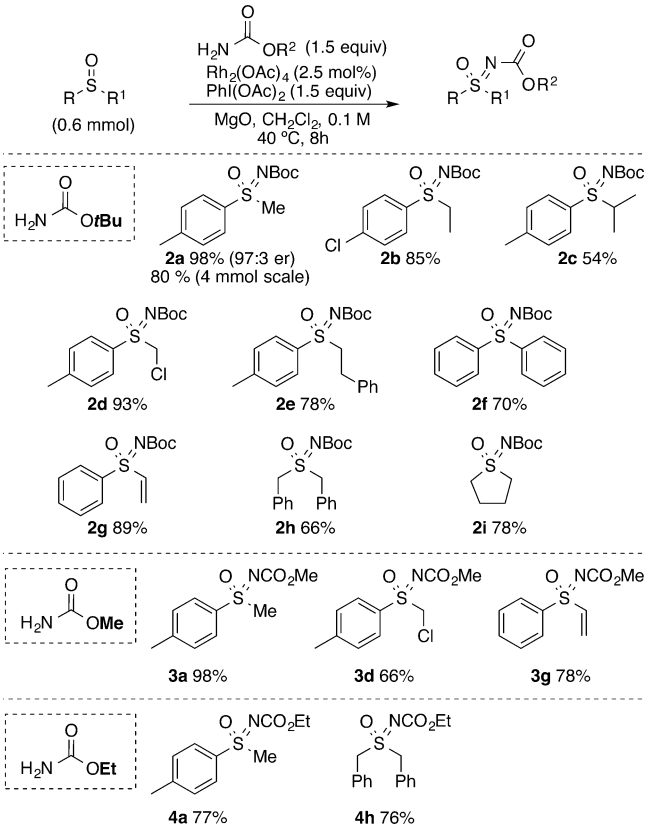

| entry[a] | time (h) | temp (°C) | $BocNH_2$ (equiv) | $PhI(OAc)_2$ (equiv) | convn[b] | yield (%)[c] |
|---|---|---|---|---|---|---|
| 1 | 18 | 20 | 2.0 | 1.5 | 86 | 85 |
| 2 | 18 | 20 | 1.3 | 1.3 | 73 | 72 |
| 3 | 18 | 20 | 1 | 1 | 61 | 59 |
| 4 | 18 | 40 | 1 | 1 | 68 | 63 |
| 5 | 6 | 20 | 2 | 1.5 | 56 | 54 |
| 6 | 6 | 40 | 2 | 1.5 | 88 | 87 |
| **7** | **8** | **40** | **1.5** | **1.5** | **100** | **98** |
| 8[d] | 8 | 40 | 1.5 | 1.5 | 0 | 0 |

[a]Reactions performed on 0.3 mmol scale at 0.1 M **1a**. [b]Conversion measured by $^1H$ NMR of crude reaction mixture through comparison with an internal standard (1,3,5-trimethoxybenzene). [c]Yield of isolated product. [d]Reaction performed in absence of $Rh_2(OAc)_4$.



DOI: 10.1021/acs.joc.5b00844
J. Org. Chem. 2015, 80, 6391−6399

**Scheme 2. Reaction Scope with Alkyl Carbamates**

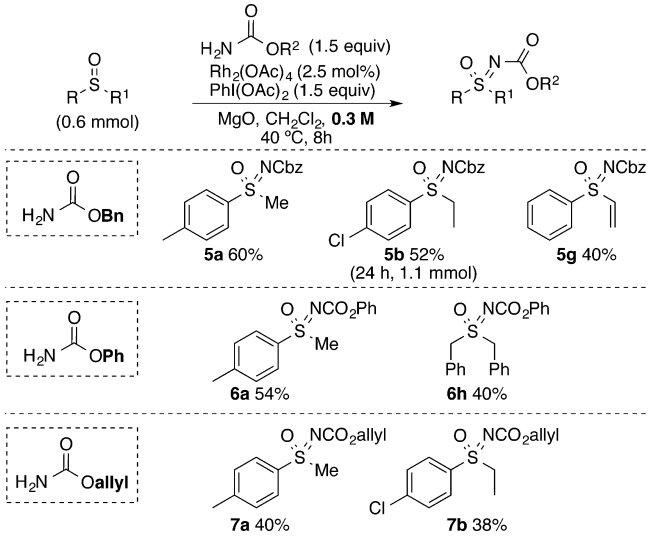



diphenyl sulfoxide and phenyl vinyl sulfoxide to afford respectively sulfoximines **2f** and **2g**. Dibenzyl sulfoxide and tetrahydrothiophene 1-oxide were also successful providing **2h** and **2i**.[30] Methyl carbamate and ethyl carbamate were equally reactive, under the same conditions, generating the corresponding sulfoximines **3** and **4** in high yield (Scheme 2).

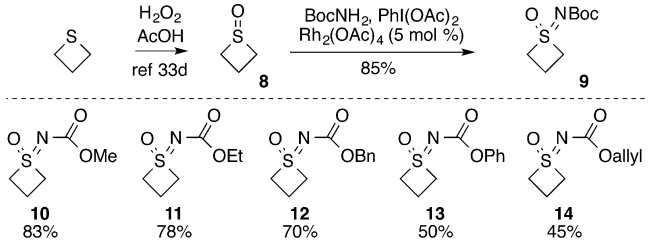
Attempts to directly translate the optimal reaction conditions used above to form Cbz protected sulfoximines gave a significant reduction of the yield (37%). A similar reduction in yield was observed with phenyl carbamate; presumably due to an unfavorable coordination of the $\pi$-system to the catalyst slowing the reaction. The reaction parameters were examined again, and ultimately, increasing the concentration of the reaction from 0.1 to 0.3 M in sulfoxide gave improved yields (60% yield for **5a**, Scheme 3). Under these conditions, for both benzyl and phenyl carbamates, good yields of the corresponding sulfoximines **5b**,**g**, and **6a**,**h**, were achieved, though notably lower than the alkyl carbamates. The use of allyl carbamate was also successful under the more concentrated reaction conditions, forming sulfoximines **7a** and **7b**, but side reactions reduced the yield (Scheme 3). Dimethylurea, methyl 4-aminobenzoate and 2-aminopyridine were also examined as possible reagents but each returned only starting materials.[31]

Next, as part of our interests in the synthesis of novel 4-membered ring heterocycles,[32,33] we examined the preparation of unusual 4-membered cyclic sulfoximines.[34] Thietane oxide **8** was prepared by oxidation of thietane with hydrogen peroxide, as previously reported.[33d] This substrate proved to be reactive and was successful for all carbamates under the conditions reported above (Scheme 4). The alkyl carbamates gave the thietane-oximines **9**-**11** in excellent yields, where as the benzyl, phenyl and allyl gave lower yields (**12**-**14**), indicating the

**Scheme 3. Reaction Scope Performed at Higher Concentration; Benzyl, Phenyl, and Allyl Carbamates**



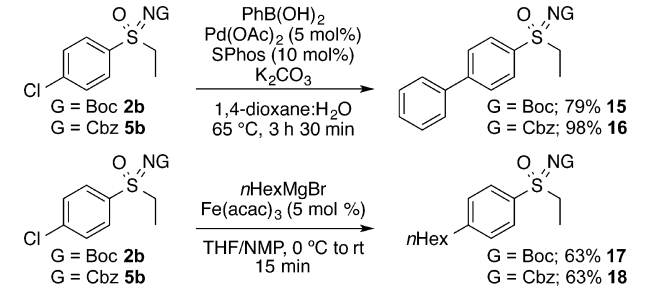

**Scheme 4. Thietane-oximines**




relative reactivity of the nitrogen sources. Further studies with these compounds will be reported in due course.

The stability and utility of the orthogonally protected *N*-Cbz- and *N*-Boc-chlorophenyl sulfoximines (**2b** and **5b**) was demonstrated in Suzuki cross-couplings with aryl boronic acids,[35,36] and Fe-catalyzed cross-couplings of alkyl Grignard reagents (Scheme 5).[29,37] The couplings proceeded in good yields in each case, leading to further elaborated sulfoximine derivatives (**15**−**18**).

**Scheme 5. Cross Coupling of Chloro-Sulfoximine 2b and 5b**



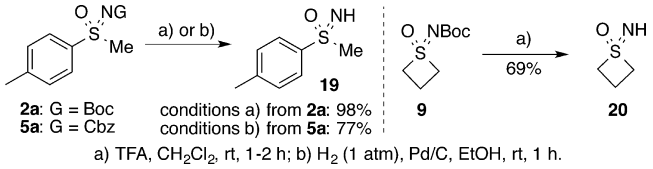

The Boc- and Cbz-sulfoximines **2a** and **5a** were also readily deprotected using standard conditions to generate the free *NH*-sulfoximines in good to excellent yields, highlighting the convenience of these *N*-carbamate sulfoximines (Scheme 6). The parent thietaneoximine **20** was prepared by deprotection of *N*-Boc derivative **9** using TFA.

To illustrate the potential for synthetic advantage of introducing a Boc group, we prepared MSO with a final global



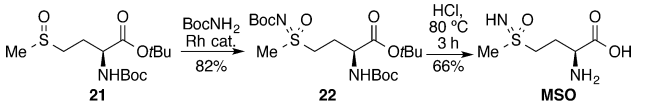
DOI: 10.1021/acs.joc.5b00844
J. Org. Chem. 2015, 80, 6391−6399

**Scheme 6. Boc and Cbz Deprotection of Sulfoximines**




deprotection step, a target recently examined by Bolm to assess alternative protecting group strategies.[38] Our approach involved the direct formation of the *N*-Boc sulfoximine **22**, as a 1:1 mixture of diastereoisomers, from protected methionine sulfoxide **21**. Fully protected **22** could be readily purified. The sulfoximine Boc group was then removed, along with the other Boc group and *tert*-butyl ester, under acidic conditions to afford MSO in 54% yield over the two steps following purification by ion exchange chromatography (Scheme 7).

**Scheme 7. Synthesis of MSO via 1-Pot Deprotection**




## CONCLUSIONS

We have developed a general and convenient procedure for the preparation of sulfoximine carbamates. Under rhodium catalysis, $BocNH_2$ and $CbzNH_2$, as well as methyl, ethyl, phenyl, and allyl carbamates are transferred stereospecifically to a range sulfoxides in high yields. We expect these sulfoximine carbamates to provide interesting variations to chiral auxiliaries or ligands, as well as new motifs for medicinal chemistry. This approach may facilitate synthetic planning by allowing flexible removal of protecting groups to access *NH* sulfoximines.

## EXPERIMENTAL SECTION

**General Considerations.** All reactions were carried out under atmospheric conditions using solvents without specific drying unless otherwise stated. Anhydrous THF was obtained by filtration through alumina drying columns. Commercial reagents were used as supplied, or purified by standard techniques where necessary. Flash column chromatography was performed using 230−400 mesh silica, with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on precoated glass-backed or aluminum-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) and/or stained with aqueous potassium permanganate solution or an acidic vanillin solution. Infrared spectra ($\nu_{max}$, FT-IR ATR) were recorded in reciprocal centimeters ($cm^{-1}$). Nuclear magnetic resonance spectra were recorded on 400 MHz spectrometers. Chemical shifts for $^1$H NMR spectra are recorded in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: $\delta$ = 7.26 ppm, $D_2O$: $\delta$ = 4.79 ppm, DMSO $\delta$ = 2.50 ppm). Data are reported as follows: chemical shift (multiplicity [s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad, app = apparent], coupling constant (in Hz), integration and assignment). $^{13}$C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($^{13}CDCl_3$: 77.16 ppm, $(^{13}CD_3)_2SO$: $\delta$ = 39.5 ppm). Melting points are uncorrected. Observed rotations were recorded at the indicated temperature (T °C) and were converted to the corresponding specific rotations. **Preparation of Sulfoxides 1a-e, 8.** Sulfoxides were obtained from commercial sources (**1f−i**), or by oxidation from the corresponding sulfides (**1a−e**, **8**) with *m*CPBA or $H_2O_2$.[39−44,33d] (*S*)-1-Methanesulfinyl-4-methyl-benzene ((***S*)-1a**) was prepared according to the Jackson method[45] (*er* 97:3).

**Preparation of *N*-Boc, *N*-$CO_2$Me, and *N*-$CO_2$Ethyl Sulfoximines (2,3,4,9,10,11). General Procedure 1** To a suspension of the sulfoxide (0.6 mmol), carbamate (0.9 mmol), MgO (97 mg, 2.4 mmol), and $Rh_2(OAc)_4$ (7.0 mg, 2.5 mol %) in $CH_2Cl_2$ (6 mL) was added $PhI(OAc)_2$ (290 mg, 0.90 mmol) at rt. The resulting mixture was stirred for 8 h at 40 °C. The reaction mixture was filtered through a pad of diatomaceous earth and concentrated in vacuo, and the resulting residue was purified by flash chromatography ($SiO_2$) to the give *N*-substituted sulfoximine.

*tert-Butyl[methyl(4-methylphenyl)oxido-λ⁶-sulfanylidene]carbamate (**2a**).* Prepared according to **General Procedure 1** using sulfoxide **1a** (97 mg, 0.63 mmol) and *tert*-butylcarbamate (111 mg, 0.945 mmol). Purification by flash chromatography (50% EtOAc/hexane) afforded *N*-Boc sulfoximine **2a** (158 mg, 98%) as a white solid. $R_f$ = 0.5 (50% EtOAc/hexane); mp =108−112 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3034, 2980, 2934, 1664, 1267, 1149, 864, 783; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.84 (app d, *J* = 8.3 Hz, 2H), 7.37 (app d, *J* = 8.3 Hz, 2H), 3.21 (s, 3H), 2.44 (s, 3H), 1.38 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.0, 144.9, 135.8 (2C), 130.4 (2C), 127.5, 80.6, 45.0, 28.2 (3C), 21.7; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{13}H_{20}NO_3S^+$ $[M + H]^+$ 270.1164; found 270.1175.

*(S)-tert-Butyl[methyl(4-methylphenyl)oxido-λ⁶-sulfanylidene]carbamate ((S)-**2a**).* $[\alpha]^{25}_D$ = +39 (c 1.0, acetone); Chiral HPLC: OD column, 93:7 (Hexane:*i*-PrOH), 1.0 mL/min, 98:2 *er*, (*S*)-isomer (major): 16.8 min, (*R*)-isomer (minor): 20.0 min.

*tert-Butyl[(4-chlorophenyl)(ethyl)oxido-λ⁶-sulfanylidene]carbamate (**2b**).* Prepared according to **General Procedure 1** using sulfoxide **1b** (117 mg, 0.62 mmol) and *tert*-butylcarbamate (109 mg, 0.930 mmol). Purification by flash chromatography (40% EtOAc/hexane) afforded *N*-Boc-sulfoximine **2b** (160 mg, 85%) as a white solid. $R_f$ = 0.4 (40% EtOAc/hexane); mp =130−136 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3034, 2980, 2934, 1664, 1267, 1149, 864, 783; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.89−7.80 (m, 2H), 7.59−7.49 (m, 2H), 3.44−3.25 (m, 2H), 1.37 (s, 9H), 1.24 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 157.7, 140.6, 135.2, 130.0 (2C), 129.7 (2C), 80.8, 50.8, 28.1 (3C), 7.0; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{13}H_{19}ClNO_3S^+$ $[M + H]^+$ 304.0774, found 304.0777.

*tert-Butyl[(4-methylphenyl)(oxido)propan-2-yl-λ⁶-sulfanylidene]carbamate (**2c**).* Prepared according to **General Procedure 1** using sulfoxide **1c** (118 mg, 0.65 mmol) and *tert*-butylcarbamate (114 mg, 0.970 mmol). Purification by flash chromatography (50% EtOAc/hexane) afforded *N*-Boc-sulfoximine **2c** (104 mg, 54%) as a white solid. $R_f$ = 0.5 (50% EtOAc/hexane); mp =76−80 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 2977, 1667, 1272, 1249, 1155, 1104, 892, 866, 660; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.75 (app d, *J* = 8.2 Hz, 2H), 7.37 (app d, *J* = 8.2 Hz, 2H), 3.46 (sept., *J* = 6.8 Hz 1H), 2.45 (s, 3H), 1.40 (d, *J* = 6.8 Hz, 3H), 1.34 (s, 9H), 1.19 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.3, 144.6, 132.1, 130.1 (2C), 129.1 (2C), 80.2, 56.3, 28.1 (3C), 21.7, 15.9, 15.2; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{15}H_{24}NO_3S^+$ $[M + H]^+$ 298.1477, found 298.1480.

*tert-Butyl[(chloromethyl)(4-methylphenyl)oxido-λ⁶-sulfanylidene]carbamate (**2d**).* Prepared according to **General Procedure 1** using sulfoxide **1d** (121 mg, 0.64 mmol) and *tert*-butylcarbamate (112 mg, 0.960 mmol). Purification by flash chromatography (20% EtOAc/hexane); afforded *N*-Boc-sulfoximine **2d** (180 mg, 93%) as a white solid. $R_f$= 0.35 (20% EtOAc/hexane); mp =87−91 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 2978, 1666, 1274, 1244, 1143, 902, 870, 787, 751; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.90 (app d, *J* = 8.3 Hz, 2H), 7.41 (app d, *J* = 8.3 Hz, 2H), 5.11 (d, *J* = 11.9 Hz, 1H), 4.81 (d, *J* = 11.9 Hz, 1H), 2.48 (s, 3H), 1.45 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 157.4, 146.1, 130.5, 130.3 (2C), 129.5 (2C), 81.4, 58.8, 28.1 (3C), 21.8; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{15}H_{21}N_2O_3SClNa^+$ $[M+ CH_3CN + Na]^+$ 367.0859, found 367.0858.

*tert-Butyl[(4-methylphenyl)(oxido)(2-phenylethyl)-λ⁶-sulfanylidene]carbamate (**2e**).* Prepared according to **General Procedure 1** using sulfoxide **1e** (146 mg, 0.60 mmol) and *tert*-butylcarbamate (105 mg, 0.90 mmol). Purification by flash



DOI: 10.1021/acs.joc.5b00844
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chromatography (30% EtOAc/hexane) afforded *N*-Boc-sulfoximine **2e** (168 mg, 78%) as a white solid. $R_f$ = 0.5 (30% EtOAc/hexane); mp =125−129 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 2979, 1651, 1274, 1143, 893, 855, 762, 726; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.87 (app d, $J$ = 8.3 Hz, 2H), 7.41 (app d, $J$ = 8.3 Hz, 2H), 7.31−7.19 (m, 3H), 7.15−7.06 (m, 2H), 3.67 (ddd, $J$ = 13.8, 12.2, 5.0 Hz, 1H), 3.51 (ddd, $J$ = 13.8, 12.2, 5.0 Hz, 1H), 3.13 (app. td, $J$ = 13, 5.0 Hz, 1H), 2.97 (app. td, $J$ = 13, 5.0 Hz, 1H), 2.49 (s, 3H), 1.42 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.0, 144.9, 137.1, 134.2, 130.4 (2C), 128.9 (2C), 128.5 (2C), 128.1 (2C), 127.1, 80.6, 57.5, 28.4, 28.1 (3C), 21.7; HRMS (ESI-TOF) $m/z$: calcd for $C_{20}H_{26}NO_3S^+$ $[M + H]^+$ 360.1633, found 360.1639.

*tert-Butyl[oxido(diphenyl)-$\lambda^6$-sulfanylidene]carbamate (**2f**).* Prepared according to **General Procedure 1** using sulfoxide **1f** (127 mg, 0.63 mmol) and *tert*-butylcarbamate (110 mg, 0.940 mmol). Purification by flash chromatography (30% EtOAc/hexane) afforded *N*-Boc-sulfoximine **2f** (139 mg, 70%) as a white solid. $R_f$ = 0.3 (30% EtOAc/hexane); mp =97−102 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 2985, 1687, 1446, 1365, 1237, 1092, 913, 780, 763, 726, 684; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.03−8.00 (m, 4H), 7.58−7.49 (m, 6H), 1.33 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 157.3, 140.1 (2C), 133.3 (2C), 129.5 (4C), 127.9 (4C), 80.8, 28.1 (3C); HRMS (ESI-TOF) $m/z$: calcd for $C_{17}H_{20}NO_3S$ $[M + H]^+$ 318.1164, found 318.1164.

*tert-Butyl[ethenyl(oxido)phenyl-$\lambda^6$-sulfanylidene]carbamate (**2g**).* Prepared according to **General Procedure 1** using sulfoxide **1g** (94 mg, 0.62 mmol) and *tert*-butylcarbamate (109 mg, 0.930 mmol). Purification by flash chromatography (50% EtOAC/hexane) afforded *N*-Boc-sulfoximine **2g** (147 mg, 89%) as a white solid. $R_f$ = 0.5 (50% EtOAc/hexane); mp =83−87 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3062, 2973, 1655, 1271, 1232, 1151, 1085, 979, 894, 867, 755, 690; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.95 (app d, $J$ = 7.6 Hz, 2H), 7.64 (t, $J$ = 7.6 Hz, 1H), 7.56 (app t, $J$ = 7.6 Hz, 2H), 6.73 (dd, $J$ = 16.4, 9.6 Hz, 1H), 6.47 (d, $J$ = 16.4 Hz, 1H), 6.12 (d, $J$ = 9.6 Hz, 1H), 1.38 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 157.5, 138.1, 137.3, 133.7, 129.7 (2C), 128.8, 128.0 (2C), 80.9, 28.1 (3C); HRMS (ESI-TOF) $m/z$: calcd for $C_{13}H_{18}NO_3S^+$ $[M + H]^+$ 268.1007, found 268.1010.

*tert-Butyl[dibenzyl(oxido)-$\lambda^6$-sulfanylidene]carbamate (**2h**).* Prepared according to **General Procedure 1** using sulfoxide **1h** (138 mg, 0.60 mmol) and *tert*-butylcarbamate (105 mg, 0.900 mmol). Purification by flash chromatography (40% hexane/EtOAc) and recrystallization ($Et_2O$) afforded *N*-Boc-sulfoximine **2h** (137 mg, 66%) as a white solid. $R_f$ = 0.3 (40% hexane/EtOAc); mp =129−131 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 2984, 1657, 1457, 1365, 1287, 1247, 1146, 912, 771, 697; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.42−7.38 (m, 10H), 4.55 (d, $J$ = 14 Hz, 2H), 4.48 (d, $J$ = 14 Hz, 2H), 1.52 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.6, 131.4 (4C), 129.5 (2C), 129.2 (4C), 126.9 (2C), 80.5, 56.4 (2C), 28.3 (3C); HRMS (ESI-TOF) $m/z$: calcd for $C_{19}H_{24}NO_3S^+$ $[M + H]^+$ 346.1479, found 346.1477.

*tert-Butyl(1-oxidotetrahydro-1H-1$\lambda^4$-thiophen-1-ylidene)-carbamate (**2i**).* Prepared according to **General Procedure 1** using sulfoxide **1i** (70 mg, 0.67 mmol) and *tert*-butylcarbamate (118 mg, 1.00 mmol). Purification by flash chromatography (30% hexane/EtOAc) afforded *N*-Boc-sulfoximine **2i** (115 mg, 78%) as a yellow oil. $R_f$ = 0.3 (30% hexane/ethyl acetate); IR (film) $\nu_{max}$ ($cm^{-1}$): 2975, 1651, 1287, 1155, 727; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 3.55−3.48 (m, 2H), 3.20 (app. dt, $J$ = 12.6, 6.1 Hz, 2H), 2.16−2.28 (m, 4H), 1.41 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 159.1, 80.5, 52.8 (2C), 28.1 (3C), 23.5 (2C); HRMS (ESI-TOF) $m/z$: calcd for $C_{11}H_{20}N_2O_3NaS^+$ $[M + CH_3CN + Na]^+$ 283.1092, found 283.1080.

*tert-Butyl[(Z)-methyl(phenyl)-$\lambda^4$-sulfanylidene]carbamate (**2j**).* To a suspension of the methyl 4-methylphenyl sulfide (98 mg, 0.71 mmol), *tert*-butylcarbamate (125 mg, 1.06 mmol), MgO (97 mg, 2.4 mmol) and $Rh_2(OAc)_4$ (7.0 mg, 2.5 mol %) in $CH_2Cl_2$ (6 mL) was added $PhI(OAc)_4$ (290 mg, 0.900 mmol) at rt. The resulting mixture was stirred for 8 h at 40 °C. The reaction mixture was filtered through a pad of diatomaceous earth and concentrated in vacuo. Purification by flash chromatography (EtOAc) afforded *N*-Boc-sulfilimine **2j** (61 mg, 34%) as a white solid. $R_f$ = 0.3 (EtOAc); mp =152−155 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3013, 2975, 2925, 1626, 1361, 1277, 1246, 1158, 1079, 985, 835, 817, 786, 753, $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.65 (app d, $J$ = 8 Hz, 2H), 7.32 (app d, $J$ = 8 Hz, 2H), 2.77 (s, 3H), 2.41 (s, 3H), 1.46 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 164.6, 143.0, 133.8, 130.6 (2C), 126.3 (2C), 79.0, 36.0, 28.5 (3C), 21.5; HRMS (ESI-TOF) $m/z$: calcd for $C_{13}H_{20}NO_2S$ $[M + H]^+$ 254.1215, found 254.1225.

*Methyl[methyl(4-methylphenyl)oxido-$\lambda^6$-sulfanylidene]-carbamate (**3a**).* Prepared according to **General Procedure 1** using sulfoxide **1a** (98 mg, 0.64 mmol) and methyl carbamate (72 mg, 0.96 mmol). Purification by flash chromatography (30% hexane/EtOAc) afforded sulfoximine **3a** (142 mg, 98%) as a white solid. $R_f$ = 0.5 (30% hexane/EtOAc); mp =92−96 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 2952, 1672, 1251, 1226, 1089, 982, 873, 790; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.84 (app d, $J$ = 8.3 Hz, 2H), 7.37 (app d, $J$ = 8.3 Hz, 2H), 3.63 (s, 3H), 3.27 (s, 3H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 159.5, 145.2, 135.2, 130.4 (2C), 127.4 (2C), 53.2, 44.6, 21.7; HRMS (ESI-TOF) $m/z$: calcd for $C_{10}H_{14}NO_3S^+$ $[M + H]^+$ 228.0694, found 228.0703.

*Methyl[(chloromethyl)(4-methylphenyl)oxido-$\lambda^6$-sulfanylidene]-carbamate (**3d**).* Prepared according to **General Procedure 1** using sulfoxide **1d** (123 mg, 0.65 mmol) and methyl carbamate (73 mg, 0.97 mmol). Purification by flash chromatography (50% EtOAc/hexane) afforded sulfoximine **3d** (113 mg, 66%) as a white solid. $R_f$ = 0.5 (50% ethyl acetate/hexane); mp =80−84 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3017, 2955, 1670, 1439, 1263, 1234, 1192, 1148, 1090, 961, 894, 814, 737; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.90 (app d, $J$ = 8.3 Hz, 2H), 7.41 (app d, $J$ = 8.3 Hz, 2H), 5.18 (d, $J$ = 11.9 Hz, 1H), 4.84 (d, $J$ = 11.9 Hz, 1H), 3.73 (s, 3H), 2.47 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 159.2, 146.5, 130.4 (2C), 130.0, 129.5 (2C), 58.6, 53.7, 21.9; HRMS (ESI-TOF) $m/z$: calcd for $C_{10}H_{13}ClNO_3S^+$ $[M + H]^+$ 262.0305, found 262.0308.

*Methyl[ethenyl(oxido)phenyl-$\lambda^6$-sulfanylidene]carbamate (**3g**).* Prepared according to **General Procedure 1** using sulfoxide **1g** (91 mg, 0.60 mmol) and methyl carbamate (67 mg, 0.90 mmol). Purification by flash chromatography (50% EtOAc/hexane) afforded sulfoximine **3g** (106 mg, 78%) as a white solid. $R_f$ = 0.4 (50% EtOAc/hexane); mp =59−63 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3062, 2957, 1647, 1438, 1252, 1218, 955, 888, 792, 770, 699, 685; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.96 (app d, $J$ = 8.0 Hz, 2H), 7.66 (t, $J$ = 8.0 Hz, 1H), 7.58 (app t, $J$ = 8.0 Hz, 2H), 6.74 (dd, $J$ = 16.3, 9.6 Hz, 1H), 6.51 (d, $J$ = 16.3 Hz, 1H), 6.18 (d, $J$ = 9.6 Hz, 1H), 3.67 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 159.3, 137.5, 136.9, 134.0, 129.8 (2C), 129.3, 128.0 (2C), 53.4; HRMS (ESI-TOF) $m/z$: calcd for $C_{10}H_{12}NO_3S^+$ $[M + H]^+$ 226.0538, found 226.0542.

*Ethyl[methyl(4-methylphenyl)oxido-$\lambda^6$-sulfanylidene]carbamate (**4a**).* Prepared according to **General Procedure 1** using sulfoxide **1a** (101 mg, 0.657 mmol) and ethyl carbamate (87.7 mg, 0.985 mmol). Purification by flash chromatography (30% hexane/EtOAc) afforded sulfoximine **4a** (122 mg, 77%) as a white solid. $R_f$ = 0.4 (30% hexane/EtOAc); mp =57−61 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3018, 2988, 2930, 1664, 1592, 1467, 1412, 1368, 1244, 1219, 1085, 986, 872, 790, 766; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.86 (app d, $J$ = 8.2 Hz, 2H), 7.38 (app d, $J$ = 8.2 Hz, 2H), 4.14−4.02 (m, 2H), 3.28 (s, 3H), 2.45 (s, 3H), 1.22 (t, $J$ = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 159.1, 145.2, 135.4, 130.4 (2C), 127.5 (2C), 62.0, 44.8, 21.7, 14.4; HRMS (ESI-TOF) $m/z$: calcd for $C_{11}H_{16}NO_3S^+$ $[M + H]^+$ 242.0851, found 242.0850. Compound previously reported.[46]

*Ethyl[dibenzyl(oxido)-$\lambda^6$-sulfanylidene]carbamate (**4h**).* Prepared according to **General Procedure 1** using sulfoxide **1h** (139 mg, 0.604 mmol) and ethyl carbamate (80.7 mg, 0.906 mmol). Purification by flash chromatography (30% EtOAc/hexane) afforded sulfoximine **4h** (145 mg, 76%) as a white solid. $R_f$ = 0.3 (30% EtOAc/hexane); mp =98−102 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3065, 2974, 2940, 1646, 1456, 1365, 1273, 1233, 1109, 1003, 905, 785, 695; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.46−7.33 (m, 10H), 4.56 (d, $J$ = 14.0 Hz, 2H), 4.51 (d, $J$ = 14.0 Hz, 2H), 4.17 (q, $J$ = 7.1 Hz, 2H), 1.30 (t, $J$ = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 159.4, 131.4 (4C), 129.6 (2C), 129.2 (4C), 126.6 (2C), 62.3, 56.6 (2C), 14.6; HRMS (ESI-TOF) $m/z$: calcd for $C_{17}H_{20}NO_3S^+$ $[M + H]^+$ 318.1164, found 318.1172.



DOI: 10.1021/acs.joc.5b00844
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*tert-Butyl(1-oxido-1λ⁴-thietan-1-ylidene)carbamate (**9**).* Prepared according to **General Procedure 1** using sulfoxide **8** (70 mg, 0.78 mmol) and *tert*-butylcarbamate (137 mg, 1.17 mmol). Purification by flash chromatography (30% hexane/EtOAc) afforded *N*-Boc-sulfoximine **9** (136 mg, 85%) as a white solid. $R_f$ = 0.3 (30% hexane/EtOAc); mp =76−80 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 1645, 1281, 1152, 843, 715; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 4.39−4.32 (m, 2H), 4.24−4.15 (m, 2H), 2.45−2.36 (m, 2H), 1.49 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.7, 81.2, 62.8 (2C), 28.2 (3C), 9.7; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{10}H_{18}N_2O_3NaS^+$ $[M + CH_3CN + Na]^+$ 269.0936, found 269.0934.

*Methyl(1-oxido-1λ⁴-thietan-1-ylidene)carbamate (**10**).* Prepared according to **General Procedure 1** using sulfoxide **8** (70 mg, 0.77 mmol) and methyl carbamate (86.7 mg, 1.15 mmol). Purification by flash chromatography (EtOAc) afforded sulfoximine **10** (104 mg, 83%) as a colorless gum. $R_f$ = 0.4 (EtOAc); IR (film) $\nu_{max}$ ($cm^{-1}$): 2956, 1655, 1437, 1230, 995, 879, 788; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 4.40−4.33 (m, 2H), 4.27−4.19 (m, 2H), 3.71 (s, 3H), 2.39 (app. tt, *J* = 7.8, 4.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 160.1, 63.0 (2C), 53.4, 9.6; HRMS (ESI-TOF) *m*/*z*: calcd for $C_5H_{10}NO_3S^+$ $[M + H]^+$ 164.0381, found 164.0376.

*Ethyl(1-oxido-1λ⁴-thietan-1-ylidene)carbamate (**11**).* Prepared according to **General Procedure 1** using sulfoxide **8** (59 mg, 0.66 mmol) and ethyl carbamate (87.5 mg, 0.982 mmol). Purification by flash chromatography (30% hexane/EtOAc) afforded sulfoximine **11** (90 mg, 78%) as a colorless gum. $R_f$ = 0.3 (30% hexane/EtOAc); IR (film) $\nu_{max}$ ($cm^{-1}$): 2980, 1651, 1367, 1266, 1227, 1171, 1012, 931, 870, 788; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 4.44−4.32 (m, 2H), 4.27−4.17 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.40 (app. dq, *J* = 9.4, 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 159.6, 63.0, 62.4 (2C), 14.5, 9.6; HRMS (ESI-TOF) *m*/*z*: calcd for $C_6H_{12}NO_3S^+$ $[M+H\ ]^+$ 178.0538, found 178.0534.

**Preparation of *N*-Cbz, *N*-$CO_2$Ph and *N*-Allyl sulfoximines (5, 6, 7, 12, 13, 14). General Procedure 2** To a suspension of the sulfoxide (0.6 mmol), carbamate (0.9 mmol), MgO (97 mg, 2.4 mmol) and $Rh_2(OAc)_4$ (7.0 mg, 2.5 mol %) in $CH_2Cl_2$ (2 mL) was added $PhI(OAc)_2$ (290 mg, 0.90 mmol) at rt. The resulting mixture was stirred for 8 h at 40 °C. The reaction mixture was filtered through a pad of diatomaceous earth and concentrated in vacuo and the resulting residue was purified by flash chromatography to give the *N*-substituted sulfoximine.

*Benzyl[methyl(4-methylphenyl)oxido-λ⁶-sulfanylidene]carbamate (**5a**).* Prepared according to **General Procedure 2** using sulfoxide **1a** (58.4 mg, 0.379 mmol) and benzyl carbamate (86 mg, 0.57 mmol). Purification by flash chromatography (50% EtOAc/hexane) afforded *N*-Cbz-sulfoximine **5a** (69 mg, 60%) as a white solid. $R_f$ = 0.4 (50% EtOAc/hexane); mp =90−94 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3026, 2927, 1657, 1218, 1087, 780, 694; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.84 (app d, *J* = 8.0 Hz, 2H), 7.37 (app d, *J* = 8.0 Hz, 2H), 7.33−7.22 (m, 5H), 5.12 (d, *J* = 12.0 Hz, 1H), 5.03 (d, *J* = 12.0 Hz, 1H), 3.28 (s, 3H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.8, 145.2, 136.3, 135.3, 130.4 (2C), 128.5 (2C), 128.3 (2C), 128.1, 127.5 (2C), 67.9, 44.8, 21.7; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{16}H_{18}NO_3S^+$ $[M + H]^+$ 304.1007, found 304.0999.

*Benzyl[(4-chlorophenyl)(ethyl)oxido-λ⁶-sulfanylidene]carbamate (**5b**).* Prepared according to **General Procedure 2** using sulfoxide **1b** (215 mg, 1.14 mmol) and benzyl carbamate (258 mg, 1.71 mmol), with a reaction time of 24 h. Purification twice by flash chromatography (50% EtOAc/hexane) and (30% hexane/$Et_2O$) afforded *N*-Cbz-sulfoximine **5b** (199 mg, 52%) as a white solid. The second flash chromatography was necessary to remove excess benzyl carbamate. $R_f$ = 0.5 (50% EtOAc/hexane), 0.3 (30% hexane/$Et_2O$); mp =70−73 °C. IR (film) $\nu_{max}$ ($cm^{-1}$): 2942, 1665, 1576, 1455, 1377, 1237, 1086, 901, 783, 727, 697; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.83 (app. dt, *J* = 8.8, 2.3 Hz, 2H), 7.53 (app. dt, *J* = 8.8, 2.3 Hz, 2H), 7.31−7.25 (m, 5H), 5.12 (d, *J* = 12.2 Hz, 1H), 5.00 (d, *J* = 12.2 Hz, 1H), 3.50−3.31 (m, 2H), 1.27 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.5, 140.9, 136.2, 134.8, 130.1 (2C), 129.7 (2C), 128.5 (2C), 128.4 (2C), 128.1, 68.0, 50.9, 7.0; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{16}H_{17}ClNO_3S^+$ $[M + H]^+$ 338.0618, found 338.0613.

*Benzyl[ethenyl(oxido)phenyl-λ⁶-sulfanylidene]carbamate (**5g**).* Prepared according to **General Procedure 2** using sulfoxide **1g** (96 mg, 0.63 mmol) and benzyl carbamate (143 mg, 0.945 mmol). Purification by flash chromatography (30% hexane/$Et_2O$) yielded a white solid, which was washed with $Et_2O$ to remove unreacted sulfoxide affording *N*-Cbz-sulfoximine **5g** (74 mg, 40%) as a white solid. $R_f$ = 0.3 (30% hexane/$Et_2O$); mp =63−66 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3067, 1653, 1449, 1382, 1243, 1220, 1082, 961, 898, 753, 689; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.95 (app d, *J* = 7.4 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.56 (app t, *J* = 7.7 Hz, 2H), 7.32−7.27 (m, 5H), 6.74 (dd, *J* = 16.4, 9.6 Hz, 1H), 6.51 (d, *J* = 16.4 Hz, 1H), 6.16 (d, *J* = 9.6, Hz, 1H), 5.12 (d, *J* = 12.3 Hz, 1H), 5.07 (d, *J* = 12.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.5, 137.5, 136.9, 136.3, 134.0, 129.8 (2C), 129.4, 128.5 (2C), 128.4 (2C), 128.1, 128.0 (2C), 68.1; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{16}H_{16}NO_3S^+$ $[M + H]^+$ 302.0851, found 302.0859.

*Phenyl[methyl(4-methylphenyl)oxido-λ⁶-sulfanylidene]carbamate (**6a**).* Prepared according to **General Procedure 2** using sulfoxide **1a** (103 mg, 0.67 mmol) and phenyl carbamate (138 mg, 1.01 mmol). Purification by flash chromatography (50% hexane/EtOAc) afforded sulfoximine **6a** (96 mg, 54%) as a white solid. $R_f$ = 0.5 (50% hexane/EtOAc); mp =110−116 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3044, 2939, 1671, 1261, 1222, 1177, 1093, 975, 808, 780, 715; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$: 7.92 (app d, *J* = 8.3 Hz, 2H), 7.42 (app d, *J* = 8.3 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.17−7.11 (m, 3H), 3.38 (s, 3H), 2.47 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 157.5, 151.6, 145.5, 134.8, 130.6 (2C), 129.3 (2C), 127.5 (2C), 125.4, 121.8 (2C), 44.7, 21.8; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{15}H_{16}NO_3S^+$ $[M + H]^+$ 290.0851, found 290.0863.

*Phenyl[dibenzyl(oxido)-λ⁶-sulfanylidene]carbamate (**6h**).* Prepared according to **General Procedure 2** using sulfoxide **1h** (138 mg, 0.600 mmol) and phenyl carbamate (123 mg, 0.900 mmol). Purification by flash chromatography (40% EtOAc/hexane) afforded sulfoximine **6h** (86 mg, 40%) as a yellow oil. $R_f$ = 0.5 (40% EtOAc/hexane); IR (film) $\nu_{max}$ ($cm^{-1}$): 3063, 2981, 1775, 1668, 1483, 1275, 1180, 1071, 920, 881, 761, 695; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.49−7.34 (m, 12H), 7.25−7.19 (m, 1H), 7.14 (dd, *J* = 8.5, 1.0 Hz, 2H), 4.65 (d, *J* = 13.8 Hz, 2H), 4.56 (d, *J* = 13.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.0, 151.8, 131.5 (4C), 131.0, 129.8 (2C), 129.4 (2C), 129.3 (4C), 126.2 (2C), 125.6, 121.9 (2C), 56.6 (2C); HRMS (ESI-TOF) *m*/*z*: calcd for $C_{21}H_{20}NO_3S^+$ $[M + H]^+$ 366.1164, found 366.1157.

*Prop-2-en-1-yl[methyl(4-methylphenyl)oxido-λ⁶-sulfanylidene]carbamate (**7a**).* Prepared according to **General Procedure 2** using sulfoxide **1a** (107 mg, 0.695 mmol) and allyl carbamate (105 mg, 1.042 mmol). Purification by flash chromatography (40% EtOAc/hexane) afforded sulfoximine **7a** (70 mg, 40%) as a white solid. $R_f$ = 0.3 (40% EtOAc/hexane); mp =55−58 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 2929, 1668, 1226, 1089, 975, 872, 788; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.86 (app d, *J* = 8.3 Hz, 2H), 7.39 (app d, *J* = 8.3 Hz, 2H), 5.94−5.84 (m, 1H), 5.27 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.17 (dd, *J* = 10.4, 1.3 Hz, 1H), 4.57−4.48 (m, 2H), 3.28 (s, 3H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.8, 145.2, 135.3, 132.6, 130.5 (2C), 127.5 (2C), 118.0, 66.8, 44.8, 21.7; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{12}H_{16}NO_3S^+$ $[M + H]^+$ 254.0851, found 254.0854.

*Prop-2-en-1-yl[(4-chlorophenyl)(ethyl)oxido-λ⁶-sulfanylidene]carbamate (**7b**).* Prepared according to **General Procedure 2** using sulfoxide **1b** (115 mg, 0.61 mmol) and allyl carbamate (92.5 mg, 0.915 mmol). Purification by flash chromatography (30% hexane/$Et_2O$) afforded sulfoximine **7b** (65 mg, 38%) as a white solid. $R_f$ = 0.3 (30% hexane/$Et_2O$); mp =49−53 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3089, 2941, 1668, 1578, 1360, 1236, 1086, 965, 876, 785; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.87 (app d, *J* = 8.7 Hz, 2H), 7.58 (app d, *J* = 8.7 Hz, 2H), 5.93−5.83 (m, 1H), 5.27 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.18 (dd, *J* = 10.3, 1.4 Hz, 1H), 4.59−4.47 (m, 2H), 3.51−3.31 (m, 2H), 1.28 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.6, 141.0, 134.7, 132.5, 130.1 (2C), 129.8 (2C), 118.2, 67.0, 50.9, 7.0; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{12}H_{15}ClNO_3S^+$ $[M + H]^+$ 288.0461, found 288.0464.



DOI: 10.1021/acs.joc.5b00844
*J. Org. Chem.* 2015, 80, 6391−6399

*Benzyl(1-oxido-1λ⁴-thietan-1-ylidene)carbamate (12).* Prepared according to **General Procedure 2** using sulfoxide **8** (55.3 mg, 0.614 mmol) and benzyl carbamate (139 mg, 0.921 mmol). Purification by flash chromatography (20% hexane/EtOAc) afforded *N*-Cbz-sulfoximine **12** (101 mg, 70%) as a colorless gum. $R_f$ = 0.3 (20% hexane/EtOAc); IR (film) $\nu_{max}$ ($cm^{-1}$): 3033, 2961, 1702, 1653, 1378, 1228, 990, 889, 734, 698; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.40−7.28 (m, 5H), 5.15 (s, 2H), 4.41−4.33 (m, 2H), 4.26−4.18 (m, 2H), 2.42−2.34 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 159.4, 136.2, 128.6 (2C), 128.3 (2C), 128.2, 68.2, 63.1 (2C), 9.6; HRMS (ESI-TOF) *m/z*: calcd for $C_{11}H_{14}NO_3S^+$ $[M + H]^+$ 240.0694, found 240.0693.

*Phenyl(1-oxido-1λ⁴-thietan-1-ylidene)carbamate (13).* Prepared according to **General Procedure 2** using sulfoxide **8** (61 mg, 0.68 mmol) and phenyl carbamate (140 mg, 1.02 mmol). Purification by flash chromatography (30% hexane/EtOAc) afforded sulfoximine **13** (69 mg, 50%) as a white solid. $R_f$ = 0.3 (30% hexane/EtOAc); mp =121−125 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3044, 2973, 1666, 1495, 1267, 1241, 1180, 884, 773, 705, 687; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.36 (t, *J* = 8 Hz 2H), 7.22−7.18 (m, 3H), 4.52−4.44 (m, 2H), 4.31−4.23 (m, 2H), 2.52−2.36 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.2, 151.5, 129.4 (2C), 125.7, 121.7 (2C), 63.1 (2C), 9.5; HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_{12}NO_3S^+$ $[M + H]^+$ 226.0536, found 226.0532.

*Prop-2-en-1-yl(1-oxido-1λ⁴-thietan-1-ylidene)carbamate (14).* Prepared according to **General Procedure 2** starting from sulfoxide **8** (69 mg, 0.77 mmol) and allyl carbamate (117 mg, 1.16 mmol). Purification by flash chromatography (40% hexane/EtOAc) afforded sulfoximine **14** (60 mg, 45%) as a yellow oil. $R_f$ = 0.3 (40% hexane/EtOAc); IR (film) $\nu_{max}$ ($cm^{-1}$): 2959, 1656, 1228, 990, 875, 787. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.01−5.90 (m, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 4.61 (d, *J* = 5.7 Hz, 2H), 4.45−4.35 (m, 2H), 4.30−4.19 (m, 2H), 2.49−2.36 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 159.3, 132.4, 118,3, 67.2, 63.1 (2C), 9.6; HRMS (ESI-TOF) *m/z*: calcd for $C_7H_{12}NO_3S^+$ $[M + H]^+$ 190.0538, found 190.0539.

**Cross Coupling Reactions.** The Suzuki cross coupling reactions were carried out according to previously reported reaction conditions,[32b] modified from conditions developed by Buchwald.[35] Conditions developed by Fürstner were used for the Fe-catalyzed cross coupling.[37]

*tert-Butyl[biphenyl-4-yl(ethyl)oxido-λ⁶-sulfanylidene]carbamate (15).* Phenylboronic acid (21 mg, 0.17 mmol), aryl chloride **2b** (40 mg, 0.13 mmol), $Pd(OAc)_2$ (1.5 mg, 0.0066 mmol), SPhos (5.4 mg, 0.013 mmol) and $K_2CO_3$ (37 mg, 0.26 mmol) were dissolved in 1,4-dioxane/water (1.5 mL, 4:1) under $N_2$. The reaction mixture was stirred at 65 °C for 3.5 h, the reaction mixture was cooled to rt and filtered through a plug of diatomaceous earth. The solvent was removed in vacuo and the crude residue purified by silica gel flash column chromatography (30% EtOAc in pentane) to yield the product as a white solid (36 mg, 79%). $R_f$ = 0.20 (30% EtOAc in pentane); mp =68−70 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 2977, 1663, 1593, 1480, 1365, 1269, 1248, 1153 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.01−7.95 (m, 2H), 7.81−7.75 (m, 2H), 7.64−7.58 (m, 2H), 7.52−7.45 (m, 2H), 7.45−7.40 (m, 1H), 3.38 (m, 2H), 1.38 (s, 9H), 1.28 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.0, 146.7, 139.1, 135.1, 129.2 (2C), 128.8 (3C), 128.2 (2C), 127.5 (2C), 80.6, 51.0, 28.1 (3C), 7.0; HRMS: (ESI-TOF) *m/z*: calcd for $C_{21}H_{26}N_2O_3SNa$ [M + MeCN + Na]$^+$ 409.1559, found 409.1569.

*Benzyl[biphenyl-4-yl(ethyl)oxido-λ⁶-sulfanylidene]carbamate (16).* Reaction carried out according to the same procedure as with Boc-protected example (**2b**) using aryl chloride **5b** (45 mg, 0.13 mmol), $Pd(OAc)_2$ (1.5 mg, 0.0066 mmol), SPhos (5.4 mg, 0.013 mmol) and $K_2CO_3$ (37 mg, 0.26 mmol) in 1,4-dioxane/water (1.5 mL, 4:1). The crude product was purified by silica gel flash chromatography (5:4:1, pentane/$Et_2O$/acetone) to yield the product as a white solid (27 mg, 54%). $R_f$ = 0.21 (5:4:1, pentane/$Et_2O$/acetone); mp =104−105 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 2940, 1668, 1592, 1480, 1455, 1236, 1090 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.97 (app d, *J* = 8.5 Hz, 2H), 7.76 (app d, *J* = 8.5 Hz, 2H), 7.64−7.58 (m, 2H), 7.55−7.41 (m, 3H), 7.37−7.20 (m, 5H), 5.14 (d, *J* = 12.0 Hz, 1H), 5.03 (d, *J* = 12.3 Hz, 1H), 3.55−3.33 (m, 2H), 1.30 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.8, 147.0, 139.1, 136.4, 134.6, 129.2 (2C), 128.9, 128.8 (2C), 128.4 (2C), 128.3 (4C), 128.0, 127.5 (2C), 67.9, 51.1, 7.1; HRMS: (ESI-TOF) *m/z*: calcd for $C_{22}H_{22}NO_3S$ [M + H]$^+$ 380.1320, found 380.1332.

*tert-Butyl[(4-hexylphenyl)(ethyl)oxido-λ⁶-sulfanylidene]carbamate (17).* *n*-Hexylmagnesium bromide (79 μL, 2.0 M in $Et_2O$, 0.16 mmol) was added to a solution of aryl chloride **2b** (40 mg, 0.13 mmol) and $Fe(acac)_3$ (2.3 mg, 0.0066 mmol) in THF/NMP (1.3 mL, 9:1) at rt. The reaction was stirred for 15 min, diluted with $Et_2O$ (3 mL) and quenched with 1 M HCl (3 mL). The aqueous layer was separated, extracted with $Et_2O$ (2 × 5 mL) and the combined organic fractions were dried over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the resulting residue was purified by silica gel flash column chromatography (1:1, pentane/EtOAc) to yield the product as a colorless oil (36 mg, 63%). $R_f$ = 0.23 (30% EtOAc in pentane); IR (film) $\nu_{max}$ ($cm^{-1}$): 2929, 2858, 1693, 1665, 1456, 1365, 1271, 1249, 1217, 1156, 1107, 1088 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.84−7.75 (m, 2H), 7.40−7.33 (m, 2H), 3.32 (m, 2H), 2.72−2.63 (m, 2H), 1.62 (quintet, *J* = 7.5 Hz, 2H), 1.41−1.16 (m, 18H), 0.86 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 157.9, 149.6, 133.7, 129.6, 128.3, 80.4, 50.9, 36.0, 31.7, 31.1, 29.8, 29.0, 28.1, 22.6, 14.1, 7.0; HRMS: (ESI-TOF) *m/z*: calcd for $C_{19}H_{32}NO_3S$ [M + H]$^+$ 354.2103, found 354.2112.

*Benzyl[(4-hexylphenyl)(ethyl)oxido-λ⁶-sulfanylidene]carbamate (18).* Reaction carried out according to the same procedure as with Boc-protected example (**2b**) using *n*hexylmagnesium bromide (43 μL, 2.0 M in $Et_2O$, 0.086 mmol), aryl chloride **5b** (24 mg, 0.070 mmol) and $Fe(acac)_3$ (2.3 mg, 0.0034 mmol) in THF/NMP (0.7 mL, 9:1). The crude product was purified by silica gel flash chromatography (5:4:1, pentane/$Et_2O$/acetone) to yield the product as a colorless oil (17 mg, 63%). $R_f$ = 0.36 (5:4:1, pentane/$Et_2O$/acetone); IR (film) $\nu_{max}$ ($cm^{-1}$): 2929, 1673, 1456, 1378, 1245, 1089 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.80 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.30−7.26 (m, 4H), 5.11 (d, *J* = 12.3 Hz, 1H), 5.02 (d, *J* = 12.3 Hz, 1H), 3.49−3.30 (m, 2H), 2.73−2.64 (m, 2H), 1.70−1.56 (m, 2H), 1.38−1.28 (m, 6H), 1.25 (t, *J* = 7.4 Hz, 3H), 0.93−0.84 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 158.85, 150.0, 136.5, 133.1, 129.7 (2C), 128.4 (2C), 128.3 (4C), 128.0, 67.8, 51.0, 36.1, 31.7, 31.1, 29.1, 22.7, 14.2, 7.1; HRMS: (ESI-TOF) *m/z*: calcd for $C_{22}H_{30}NO_3S$ [M + H]$^+$ 388.1946, found 388.1934.

**Deprotection of Sulfoximine Carbamates 2a and 5a.** *1-Methyl-4-(S-methylsulfonimidoyl)benzene (19).* From **2a**: Boc-protected sulfoximine **2a** (50 mg, 0.19 mmol) was dissolved in $CH_2Cl_2$ (0.30 mL) in a 10 mL round-bottom flask. Trifluoroacetic acid (0.10 mL, 1.31 mmol) was added dropwise, and the reaction mixture was stirred at rt for 1 h, diluted with $H_2O$ (3 mL) and quenched with $NaHCO_3$ (solid, 250 mg). The organic layer was separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 5 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and the solvent removed in vacuo. The resulting oil was purified by silica gel flash column chromatography (EtOAc) to yield the product as a white solid (31 mg, 98%). From **5a**: Cbz-protected sulfoximine **5a** (50 mg, 0.19 mmol) and Pd/C (17.5 mg, 0.19 mmol) were suspended in EtOH (1.5 mL) and stirred under 1 atm of $H_2$ (balloon) for 1 h. The reaction mixture was filtered through a plug of diatomaceous earth, washed with MeOH (2 × 3 mL) and the solvent was removed *in vacuo*. The resulting oil was purified by silica gel flash column chromatography (EtOAc) to yield the product as a white solid (21 mg, 77%). $R_f$ = 0.18 (EtOAc); mp =69−70 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3273, 2924, 1597, 1408, 1216, 1093 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.91−7.83 (m, 2H), 7.33 (app d, *J* = 8.2 Hz, 2H), 3.07 (s, 3H), 2.65 (s, 1H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 144.0, 140.7, 130.0, 127.8, 46.43, 21.6; HRMS: (ESI-TOF) *m/z*: calcd for $C_8H_{12}NOS$ [M + H]$^+$ 170.0640, found 170.0640. Analytical data in agreement with those reported in the literature.[47]

*1λ⁴-Thietan-1-imine 1-oxide (20).* TFA (0.15 mL, 1.95 mmol) was added dropwise to a solution of Boc-protected sulfoximine **9** (40 mg, 0.20 mmol) in $CH_2Cl_2$ (1.0 mL) and the reaction was stirred at rt for 2 h. The volatiles were removed in vacuo by azeotropic distillation with



DOI: 10.1021/acs.joc.5b00844
J. Org. Chem. 2015, 80, 6391−6399

toluene. The crude residue was dissolved in $H_2O$ (1 mL) and neutralized with saturated aqueous $Na_2CO_3$ (2 mL). The aqueous layer was extracted with $CH_2Cl_2$ several times until no further product was present, as judged by TLC analysis. The combined organic layers were dried over anhydrous $Na_2SO_4$ and the solvent was removed in vacuo (35 °C, 700 mbar). The crude residue was purified by silica gel flash column chromatography (30% acetone in EtOAc) to yield the product as a pale yellow oil (14.2 mg, 69%). The solvent from the combined product fractions was removed by azeotropic distillation with $Et_2O$ (35 °C, 50 mbar) due to the volatility of the product. $R_f$ = 0.26 (30% acetone in EtOAc); IR (film) $\nu_{max}$ ($cm^{-1}$): 3257, 1652, 1401, 1231, 1205, 1167, 1016 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 4.17−3.97 (m, 4H), 2.87 (br s, 1H), 2.29−2.13 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 66.6 (2C), 7.7; HRMS: (ESI-TOF) $m/z$: calcd for $C_3H_7NOS$ $[M + H]^+$ 105.0248, found 105.0254.

**MSO Synthesis.** Compound **21** (Scheme 7) was prepared as previously reported from *N*-Boc-L-methionine via compound **23**:[48,49]

*(S)-tert-Butyl 2-((tert-butoxycarbonyl)amino)-4-(methylthio)-butanoate (**23**).* *N,N′*-Dicyclohexylcarbodiimide (DCC, 2.15 g, 10.4 mmol) was added to a cooled solution (0 °C) of *N*-Boc-L-methionine (2.00 g, 8.02 mmol), DMAP (80 mg, 0.67 mmol) and *tert*-butanol (0.91 mL, 9.6 mmol) in $CH_2Cl_2$ (20 mL) and the reaction was stirred at 0 °C for 2 h. The reaction mixture was allowed to warm to rt and stirred overnight. The dicyclohexylurea precipitate was filtered off and washed with $CH_2Cl_2$ (2 × 10 mL). The filtrate was washed with 1 M HCl (2 × 5 mL) and dried over anhydrous $Na_2SO_4$. The solvent was removed in vacuo and the crude residue was purified by silica gel flash column chromatography (20% $Et_2O$ in pentane) to yield the product as a colorless oil (2.18 g, 89%). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 5.13 (app. d, $J$ = 8.3 Hz, 1H), 4.30 (app. q, $J$ = 7.1 Hz, 1H), 2.63−2.46 (m, 2H), 2.13 (s, 3H), 2.19−2.07 (m, 1H), 1.92 (m, 1H), 1.48 (app. d, $J$ = 10.4 Hz, 18H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 171.4, 155.3, 82.2, 79.8, 53.4, 32.6, 29.9, 28.3, 28.0, 15.5. All other spectral data were in agreement with those previously reported.[48]

*(2S)-tert-Butyl 2-((tert-butoxycarbonyl)amino)-4-(methylsulfinyl)-butanoate (**21**).* *m*CPBA (≤77%,1.85 g, 8.27 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise to a stirred solution of sulfide **23** (2.11 g, 6.89 mmol) in $CH_2Cl_2$ (10 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 1 h. The solvent was removed in vacuo the crude residue was purified by silica gel column chromatography (20% acetone in EtOAc) to yield sulfoxide **21** as a pale yellow oil (1.804 g, 81% as a mixture of diastereomers (denoted A and B). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 5.26 (app. t, $J$ = 9.6 Hz, 1H), 4.38−4.24 (m, 1H), 2.89−2.66 (m, 2H), 2.60 (s, 3H), 2.42−2.28 (m, 1H), 2.15−1.98 (m, 1H), 1.50 (app. d, $J$ = 1.3 Hz, 9H), 1.46 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 170.7, 155.5, 82.9 (A), 82.8 (B), 80.1, 53.28 (A), 52.88 (B), 50.82 (A), 50.54 (B), 38.75 (A), 38.65 (B), 28.30, 27.99, 26.79 (A), 26.28 (B). All other spectral data were in agreement with those previously reported.[49]

*tert-Butyl (2S)-2-[(tert-butoxycarbonyl)amino]-4-[N-(tert-butoxycarbonyl)-S-methylsulfonimidoyl]-butanoate (**22**).* Prepared according to **General Procedure 1**, heating for 24 h, using sulfoxide **21** (500 mg, 1.55 mmol) and *tert*-butylcarbamate (272 mg, 2.32 mmol). Purification by flash chromatography (40% EtOAc/hexane) afforded *N*-Boc sulfoximine **22** (557 mg, 82%) as a white solid and as a mixture of diastereoisomers: $R_f$ = 0.3 (40% EtOAc/hexane); mp =53−57 °C; IR (film) $\nu_{max}$ ($cm^{-1}$): 3359, 2978, 1711, 1664, 1513, 1366,1278, 1248, 1148, 970, 860, 790; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 5.20 (s, br 1H), 4.31−4.18 (m, 1H), 3.54−3.33 (m, 2H), 3.22−3.19 (2 × s, 3H), 2.46−2.38 (m, 1H), 2.22−2.07 (m, 1H), 1.48 (s, 18H), 1.14 (s, 9H); $^1H$ NMR (400 MHz, DMSO, 383 K) $\delta$ 6.72 (s, 1H), 4.00 (td, $J$ = 8.2, 5.5 Hz, 1H), 3.57−3.33 (m, 2H), 3.23−3.20 (2 × s, 3H), 2.24−2.13 (m, 1H), 2.13−2.01 (m, 1H), 1.44 (app. d, $J$ = 0.8 Hz, 9H), 1.41 (s, 9H), 1.40 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 170.1, 158.5, 155.5, 83.4, 80.7, 80.5, 52.6, 50.7, 50.6, 39.6, 28.4 (3C), 28.2 (3C), 28.1 (3C), 26.4, 26.3; $^{13}C\{^1H\}$ NMR (101 MHz, DMSO, 383 K) $\delta$ 169.7, 156.7, 154.6, 80.6, 78.0, 52.7, 52.7, 50.2, 50.2, 39.0, 39.0, 27.6 (3C), 27.4 (3C), 27.2 (3C), 23.8, 23.7. HRMS (ESI-TOF) $m/z$: calcd for $C_{19}H_{37}N_2O_7S^+$ $[M + H]^+$ 437.2321; found 437.2326.

**Methionine Sulfoximine (MSO).** Protected MSO **22** (200 mg, 0.458 mmol) was dissolved in concentrated HCl (37%, 4.6 mL, 56 mmol) and stirred at 80 °C for 3 h. The conc. HCl was removed in vacuo with azeotropic distillation in toluene and then MeOH. The resulting viscous yellow oil was purified using a Varian Bond Elut SCX ion-exchange column. The crude product was dissolved in MeOH, loaded onto the column and flushed with MeOH (3 × column volumes). The column was then eluted with 3% $NH_4OH$ in MeOH (2 × column volumes) to run off the product. The solvent was removed to yield **MSO** as a white solid (85 mg, 66%). $^1H$ NMR (400 MHz, $D_2O$): $\delta$ 3.93−3.82 (m, 1H), 3.58−3.31 (m, 2H), 3.15 (s, 3H), 2.46−2.27 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $D_2O$): $\delta$ 172.9, 52.99 (A) 52.95 (B), 52.0, 41.1, 24.2 (A), 24.1 (B). (diastereoisomers denoted A and B). All other spectral data were in agreement with those previously reported.[38]

## ■ ASSOCIATED CONTENT

### Supporting Information

$^1H$ and $^{13}C\{^1H\}$ NMR spectra for new compounds (PDF) and HPLC data for racemic and enantioenriched (**1a**, **2a**, **19**). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00844.

## ■ AUTHOR INFORMATION


### Corresponding Authors

*E-mail: renzo.luisi@uniba.it.

*E-mail: j.bull@imperial.ac.uk.


### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

For financial support we gratefully acknowledge the EPSRC (Career Acceleration Fellowship to J.A.B., EP/J001538/1, and Impact Acceleration Account, EP/K503733/1), the Royal Society for a Research Grant (R12014, RG130648) and Imperial College London. We also thank Regione Puglia: "Reti di Laboratori pubblici di ricerca" Project code 20, Project Laboratorio Sistema code PONa300369 financed by MIUR, the University of Bari for financial support.

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