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Transition-Metal-Catalyzed Hydrosulfoximination and Oxidation Reaction for the Synthesis of Sulfoximine Derivatives

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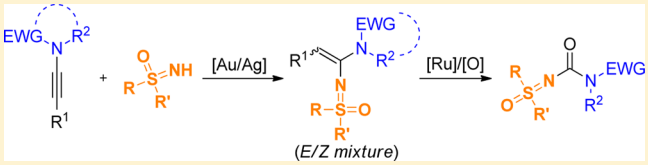
Supporting Information

ABSTRACT: We report herein a Au/Ag-cocatalyzed chemoselective hydrosulfoximination reaction of simple ynamides with free *N*H-sulfoximines, which produces the *N*-alkenylated sulfoximidoyl derivatives with quantitative atom efficiency and good to excellent yields. Further elaborations of the enamine isomers under Ru-catalyzed oxidative conditions to cleave the C═C double bonds can selectively afford urea-type sulfoximines. The aforementioned catalytic reactions provide new opportunities for the convergent and straightforward access to sulfoximine derivatives.



INTRODUCTION

The sulfoximidoyl moiety is ubiquitous in a wide range of biologically active molecules. Compounds that hold a sulfoximidoyl group have recently emerged as fascinating subjects in medicinal chemistry (Figure 1).[1] For instance, the diphenyl sulfoximine was developed as a pharmacophore in the 1970s.[2] Later, targeted lead optimization with this class of medicine culminated in the discovery of suloxifen and HE-HK 52, which are both effective by oral and parenteral dosage.[3] The heterocyclic sulfoximine Go4962 is known as a partial benzodiazepine receptor agonist.[3a,4] The functionalized sulfoximines provide the additional potential of chirality to increase molecular diversity.[5] Additionally, sulfoximines have been recently found applications as directing groups in C−H activation reactions[6] or as chiral auxiliaries in catalytic asymmetric synthesis.[7]

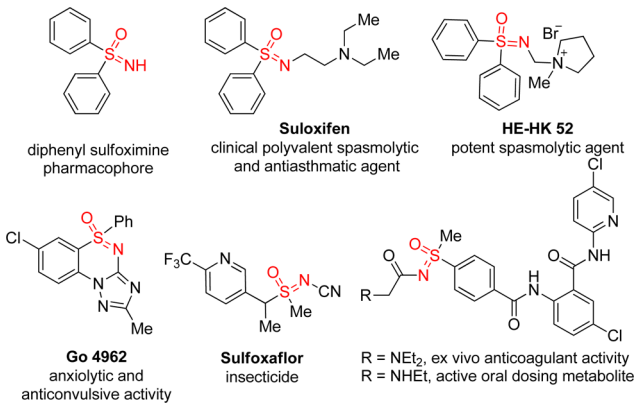


Figure 1. Biologically active sulfoximidoyl-based molecules.

For preparation of the sulfoximidoyl-containing molecules, classic methods utilizing *N*-protected sulfoximines as versatile building blocks have been studied.[8] Recently, a more direct strategy employing free *N*H-sulfoximines[9] for further elaborations has been recognized to synthesize sulfoximidoyl-based molecules, such as *N*-alkynyl,[10] *N*-alkenyl,[11] *N*-alkyl,[12] and *N*-aryl[13] sulfoximidoyl derivatives, thanks to the seminal contributions by Bolm and co-workers. The *N*-alkynylated sulfoximines are highly reactive species, which can be transformed into hydroacyloxylated and hydroaminated sulfoximines under very gentle conditions (Scheme 1a).[11]

Inspired by the recent development of ynamides[14,15] and our interest in the synthesis and biological evaluation program of natural-product-like molecules utilizing ynamides as the building blocks,[16] we envisioned that a more convenient transition-metal-catalyzed chemoselective hydrosulfoximination reaction of ynamides with free *N*H-sulfoximines would be workable (Scheme 1b). The current research is a full implementation of an atom-economical synthesis of biologically active amine derivatives and could serve as an alternative strategy for the divergent transformation of valuable *N*H-sulfoximines.

RESULTS AND DISCUSSION

To verify the possibility of the reaction, ynamide **1a** and *N*H-sulfoximine **2a** were employed in a model reaction. Initially, no reaction was observed under metal-free nucleophilic conditions (Table 1, entry 1). Given the mildly basic nature of the nitrogen atom (free NH; pK_a = 24 in DMSO and pK_a NH_2^+ = 2.7 in water) in *N*H-sulfoximine **2a**,[1] we reasoned that activation of the alkyne group in ynamide **1a** is indispensable in the reaction. The coinage-metal cations (Au, Ag) are known as π-electrophilic Lewis acids, because they usually exhibit strong coordination properties toward the unactivated alkynes,[16c,d,17]

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Scheme 1. One-Pot Synthesis of Sulfoximidoyl Enamines 3 and Further Transformations of 3 To Produce Urea-Type Sulfoximines 4

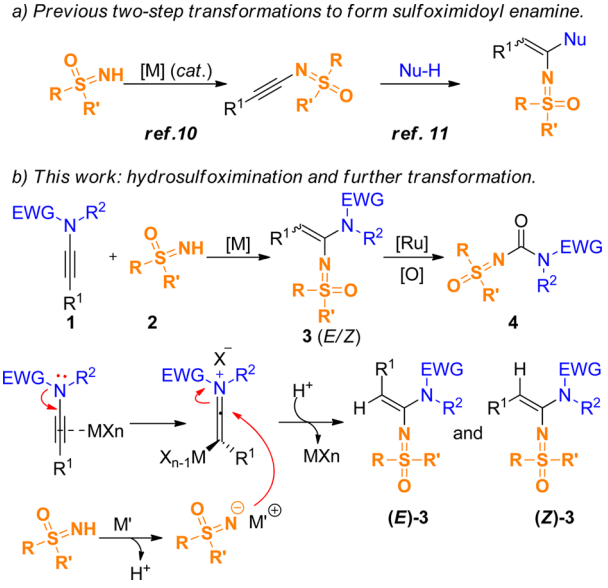
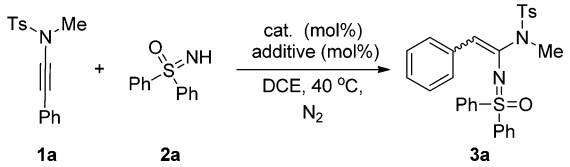


Table 1. Reaction Optimization for the Formation of 3a



entry	cat. (amt/mol %)	time/h	yield/%[a]	*E*:*Z*[a]
1		12	n.r.	
2	$AgBF_4$ (5)	12	18	2:1
3	$AgSbF_6$ (5)	12	22	2.7:1
4	AgOTf (5)	12	37	2.1:1
5	$Zn(OTf)_2$ (5)	12	31	n.d.
6	AuCl	12	trace	
7	Ph_3PAuCl (5)	12	n.r.	
8	IPrAuCl (5)	12	n.r.	
9	AuI (5)	12	41	n.d.
10	$AuBr_3$ (5)	12	57	n.d.
11	AuCl (5)/AgOTf (5)	12	61	1.4:1
12	$Ph_3PAuNTf_2$ (5)	12	71	1.6:1
13	Ph_3PAuCl (5)/AgOTf (5)	12	70	1.8:1
14	$Ph_3PAuNTf_2$(5)/AgOTf (5)	10	33	1.8:1
15	IPrAuCl (5)/AgOTf (5)	12	42	1.9:1
16	Ph_3PAuCl (10)/AgOTf (5)	12	44	2:1
17	Ph_3PAuCl (5)/AgOTf (10)	12	82	2:1
18	Ph_3PAuCl (5)/AgOTf (5)	18	71[b]	1.8:1
19	Ph_3PAuCl (5)/AgOTf (5)	18	63[c]	2.6:1
20	Ph_3PAuCl (5)/AgOTf (5)	18	56[d]	1.25:1
21	Ph_3PAuCl (5)/AgOTf (5)	18	62[e]	1.8:1
22	Ph_3PAuCl (5)/AgOTf (5)	6	80[f]	1.5:1

[a]Reaction conditions unless specified otherwise: ynamide **1a** (0.22 mmol) and *NH*-sulfoximine **2a** (0.20 mmol) in 2.0 mL of solvent at 40 °C under N_2 for 12 h. The *E*:*Z* ratio was determined by crude ^1H NMR spectroscopy. n.r. = no reaction. n.d. = not determined. [b]DCM as the solvent. [c]CH_3CN as the solvent. [d]Toluene as the solvent. [e]At 25 °C. [f]At 60 °C.

which are frequently utilized in the activation mode of alkyne or alkene groups.[18] Therefore, we decided to explore the reaction further by adding a catalytic amount of π-acidic coinage-metal catalysts. To our delight, the desired product **3a** was indeed produced upon the catalysis of $AgBF_4$, AgOTf, or $AgSbF_6$, albeit in relatively low yields (Table 1, entries 2−4). The structure of compound (*E*)-**3a** was identified unambiguously by X-ray diffraction analysis.[19,20]

The other Au^I catalysts, such as AuCl, Ph_3PAuCl, and IPrAuCl, were proved to be inert for the transformation, whereas a modest yield of **3a** was obtained on catalysis by AuI (Table 1, entries 6−9). A 57% yield of product **3a** was observed when Au^{III} catalyst was added (Table 1, entry 10). The gold catalyst AuOTf, formed in situ by treating AuCl with AgOTf, was shown to be optimal. The result could be further improved to 71% when a more acidic Lewis acid, $Ph_3PAuNTf_2$, was used (Table 1, entries 11 and 12). A catalytic system slightly modified by increasing the amount of Ph_3PAuCl to 10 mol % only led to a lower yield. Interestingly, when the AgOTf loading was increased to 10 mol % while the Ph_3PAuCl was kept at 5 mol % scale, a good yield of 82% was observed after 12 h (Table 1, entries 16 and 17). The reaction worked smoothly in the less polar solvent dichloromethane, giving the desired product **3a** in 71% yield (Table 1, entry 18). Inferior yields were observed when the reactions were carried out in MeCN and THF, and no reaction was occurred in DMF and DMSO. Remarkably, the reaction is highly atom economical, and easily handled, because only the nonsensitive catalysts are required to facilitate the expected reaction under gentle conditions.

Under the optimal reaction conditions (5 mol % of Ph_3PAuCl and 10 mol % of AgOTf in 2 mL of DCE at 40 °C), the scope of this hydrosulfoximination reaction was next investigated (Table 2). The Au/Ag catalysis reaction of ynamide **1** with free *NH*-sulfoximine **2** could be expanded to gram-scale synthesis without difficulty, since **3a** could be isolated in 74% yield on a 5.06 mmol scale of the starting materials **1a**. Substrates bearing either an electron-donating group (4-Me, 4-MeO; **1b,c**) or an electron-withdrawing group (4-NO_2, 4-CN, 4-Br; **1d−f**) on the phenyl ring of the ynamides were well tolerated, led to the corresponding products **3b−f** in good yields (63−90%). The 1-naphthalenyl substituted ynamide **1g** reacted with **2a** to give the desired product **3g** in 67% yield. The 2-thienyl heterocycle furnished the desired product **3h** in 82% yield with an *E*:*Z* isomer ratio of 1.5:1.

The efficiency of this hydrosulfoximination reaction was not compromised in terms of the alkyl-substituted ynamides—this was demonstrated by the long-chain alkyl (*n*Bu), bulky alkyl (*t*Bu), and strained alicyclic cyclopropyl-substituted products (**3k−m**) being isolated in serviceable yields, ranging from 47 to 74%. A good yield was observed when a benzyl group was attached at the N atom of substrate **1o**. Pleasingly, the cyclic oxazolidin-2-one ynamide **1p** was also tolerated, although a higher temperature was necessary to promote the transformation, thus leading to the desired product **3p** in acceptable yield, with the *E*:*Z* isomer ratio 4.5:1. A complex result was observed for the reaction of allyl-substituted ynamide **1q** with **2a** under the standard conditions; however, when $Ph_3PAuNTf_2$ served as the catalyst instead of Ph_3PAuCl/AgOTf, the desired product **3q** was nicely formed in 51% yield.

It was found that the hydrosulfoximination reaction could be successfully extended to the alkyl-substituted *NH*-sulfoximine **2**. For instance, the *S*-methyl-*S*-phenyl sulfoximine compound **2b** reacted with *N*-methyl-*N*-sunfonyl ynamides **1a,g,i** smoothly to afford products **3r,s,v** in good yields, respectively. A distinct substituent effect was observed when the ynamide substrate was

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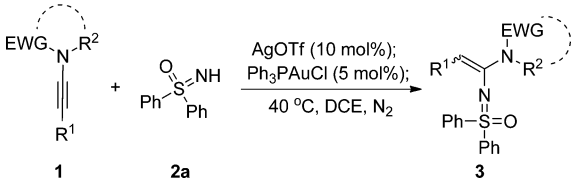
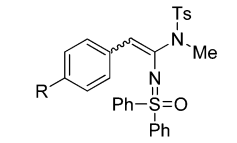
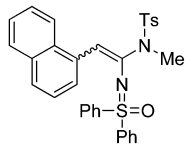
Table 2. Coinage-Metal-Cocatalyzed Hydrosulfoximination Reaction of Ynamides 1 with *NH*-Sulfoximine 2a[a]



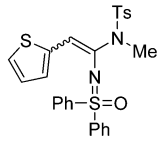
1 2a 3



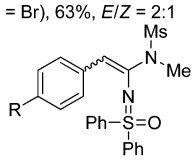
3a (R = H), 74%, *E*/*Z* = 2:1[b]
3b (R = Me), 83%, *E*/*Z* = 2:1
3c (R = OMe), 89%, *E*/*Z* = 1.5:1
3d (R = NO_2), 81%, *E*/*Z* = 1.5:1
3e (R = CN), 64%, *E*/*Z* = 2:1
3f(R = Br), 63%, *E*/*Z* = 2:1



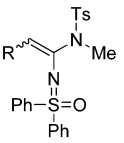
3g
66%,
E/*Z* = 1.5:1



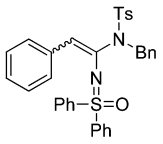
3h
82%
E/*Z* = 1.5:1



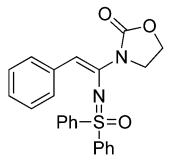
3i (R = H),64%, *E*/*Z* = 2:1
3j (R = Cl), 80%, *E*/*Z* = 2.5:1



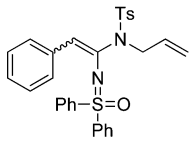
3k (R = *n*Bu), 74%, *E*/*Z* = 1.5:1
3l (R = *t*Bu), 47%, *E*/*Z* = 5:1
3m (R = cyclopropyl), 65%, *E*/*Z* = 1:2
3n (R = TMS), n.r.



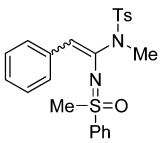
3o, 87%, *E*/*Z* = 1.3:1



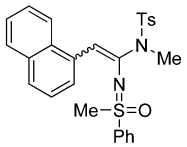
3p, 48%, *E*/*Z* = 4.5:1[c]



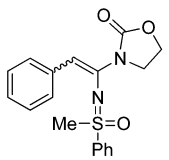
3q, 51%, *E*/*Z* = 1.5:1[d]



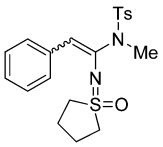
3r, 83%, *E*/*Z* = 2:1



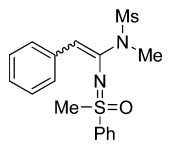
3s, 70%, *E*/*Z* = 1:1



3t, trace



3u, 91%, *E*/*Z* = 1.5:1



3v, 61%, *E*/*Z* = 1.1:1

[a]Reaction conditions unless specified otherwise: ynamide **1** (0.22 mmol), *NH*-sulfoximine **2a** (0.20 mmol), Ph_3PAuCl (5 mol %), and AgOTf (10 mol %) in 2.0 mL of DCE for 12−18 h. Isolated yield based on **2a**. [b]Gram-scale synthesis: 5.06 mmol of **1a** as a starting material. [c]At 80 °C, 12 h. [d]$Ph_3PAuNTf_2$ (5 mol %) instead of Ph_3PAuCl/AgOTf.

changed to the cyclic oxazolidin-2-one ynamide **1p** with *S*-methyl-*S*-phenyl sulfoximine **2b**; thus, only a trace amount of conversion was observed when the reaction was conducted under the standard conditions. In contrast, good conversion was obtained for the reaction of ynamide **1a** with alicyclic sulfoximine **2c**; the corresponding product **3u** was formed in excellent yield and with an *E*:*Z* ratio of 1.5:1.

To further expand the synthetic potential of the current reaction, attempts to selectively cleave the C═C bond of the product **3** were commenced. As shown in Table 3, treatment of the *E*/*Z* isomer mixture of product **3a** under Ru-catalyzed oxidative conditions afforded the urea-type sulfoximine **4a**. The structure of this compound was established via X-ray analysis.[19,21]

Interestingly, unlike the previous report using $NaIO_4$ as an oxidant to prepare sulfoximine diketones,[11,22] we have found that a gentle oxidant such as H_2O_2 (30% aqueous) could be workable in the synthesis of urea **4** (entries 1−5, Table 3). Upon catalyst screening, Rh and Pd catalysts were found to be totally inert for this urea formation reaction (entries 6 and 7, Table 3). In addition, other oxidants, such as $NaIO_4$, *t*BuOOH, and HIO_4, were less efficient than H_2O_2 (entries 4, 6, 8, and 9, Table 3). The product **4a** could be isolated in 71% yield when $[RuCl_2(p\text{-cymene})_2]_2$ (5 mol %) was employed in the presence of 5.0 equiv of H_2O_2, in a DCM/CH_3CN solvent mixture (1/1) at room temperature for open air 6 h (entry 10, Table 3). A blank experiment clearly indicated that the metal catalyst was crucial (entry 11, Table 3). No reaction was found when a radical scavenger such as BHT or TEMPO was added to the reaction mixture, thus suggesting a radical process is likely to be involved in this oxidative process (entries 12−13, Table 3).[23]

Following the optimized reaction conditions, the synthesis of different urea-type sulfoximines **4** were next studied in Table 4. The MeO- and NO_2-substituted compounds **3c,d** were found to be tolerated in the reaction, affording the targeted product **4a** in modest yields, respectively (entries 2 and 3, Table 4). The methanesulfonyl-protected (Ms) urea **4b** and benzyl-protected (Bn) urea **4c** could also be isolated in serviceable yields (entries 4−6, Table 4). It should be noted that removal of the Ts, Ms, Bn, and even Me protecting groups in compound **4** should yield a sulfoximidoyl-containing free urea, which is found to be versatile in the relevant biological assay or serve as a building block in the divergent synthesis of sulfoximine derivatives.

We proposed the following mechanism for this unique Ru-catalyzed oxidative reaction to produce urea-type sulfoximines **4** as depicted in Scheme 2. A homolytic reaction of H_2O_2 first generated the hydroxide radical,[24] which subsequently reacted with compound **3** to produce 1,2-diol intermediate **A**. The next electrophilic metalation reaction of **A** with $[RuCl_2(p\text{-cymene})_2]_2$ gave the pentannulation complex **B**. Intramolecular transformation of **B** delivered the observed product **4** and byproduct R^1CHO, along with a low-valent Ru^0 complex catalyst. Finally, oxidation of $Ru^0(p\text{-cymene})_2$ with the assistance of H_2O_2 and HCl regenerated the active catalyst $[RuCl_2(p\text{-cymene})_2]_2$ to complete the catalytic cycle. In comparison with this radical process, another more preferential mechanism involved the oxidation of $[RuCl_2(p\text{-cymene})_2]_2$ to give the mono Ru^{IV}-oxo intermediate **C**, which then underwent an epoxidation reaction with alkene **3** to deliver the intermediate **D**.[25] The subsequent nucleophilic ring-opening reaction of **D** with H_2O under the catalysis of Ru^{2+} would give the 1,2-diol **A**.

In conclusion, we have developed a fully atom economical synthesis of sulfoximidoyl enamine derivatives, via Au/Ag cocatalyzed chemoselective and scalable hydrosulfoximination reactions of simple ynamides with free *NH*-sulfoximines. The further Ru-catalyzed oxidative cleavage of the alkene group in the obtained sulfoximidoyl enamines afforded a series of urea-type sulfoximines in modest to good yields. These transformations are highlighted as practical, because they can be conducted under very mild conditions, using easily accessible compounds as the starting materials, and tolerated a broad range of functional groups. Thus, these methods could serve as

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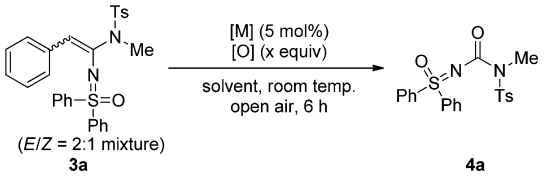
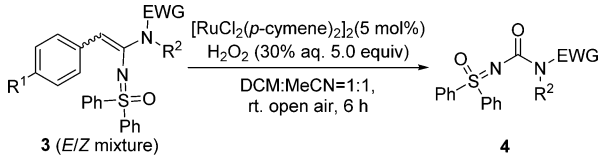
Table 3. Reaction Screen for the Synthesis of Urea 4a



entry	[M] (5 mol %)	[O] (x/equiv)	solvent	yield/%[a]
1	$[Ru(p\text{-cymene})Cl_2]_2$	H_2O_2 (5.0)	MeCN	17[b]
2	$[Ru(p\text{-cymene})Cl_2]_2$	H_2O_2 (5.0)	DCM	67
3	$RuCl_2(COD)$	H_2O_2 (5.0)	DCM/MeCN 1/1	26
4	$RuCl_2(COD)$	$NaIO_4$ (2.0)	DCM/MeCN/H_2O 1/1/2	21
5	$RuCl_2(PPh_3)_3$	H_2O_2 (5.0)	DCM/MeCN 1/1	27
6	$(Ph_3P)_3RhCl$	$NaIO_4$ (2.0)	DCM/MeCN/H_2O 1/1/2	n.r.
7	$Pd(OAc)_2$	H_2O_2 (5.0)	DCM/MeCN 1/1	n.r.
8	$[RuCl_2(p\text{-cymene})_2]_2$	tBuOOH	DCM/MeCN 1/1	35
9	$[RuCl_2(p\text{-cymene})_2]_2$	HIO_4 (2.0)	DCM/MeCN 1/1	31
10	$[RuCl_2(p\text{-cymene})_2]_2$	H_2O_2 (5.0)	DCM/MeCN 1/1	(71)[c]
11		H_2O_2 (5.0)	DCM/MeCN 1/1	0
12	$[RuCl_2(p\text{-cymene})_2]_2$	H_2O_2 (5.0)	DCM/MeCN 1/1	n.r.[d]
13	$[RuCl_2(p\text{-cymene})_2]_2$	H_2O_2 (5.0)	DCM/MeCN 1/1	n.r.[e]

[a]Reaction conditions unless specified otherwise: enamine **1** (0.20 mmol), [Ru] (5 mol %), [O] (x equiv) in 2.0 mL of solvent for 6 h. Estimated GC yield with naphthalene as an internal standard. n.r. = no reaction. [b]H_2O_2 (30% aqueous). [c]Isolated yield in parentheses. [d]BHT (2.0 equiv) as an additive. BHT = 2,6-di-*tert*-butyl-4-methylphenol. [e]TEMPO (2.0 equiv) as an additive.

Table 4. Ru-Catalyzed Synthesis of the Urea-Type Sulfoximines 4



entry	enamine **3**	R^2, EWG (**4**)	yield/%[a]
1	**3a**	Me, Ts (**4a**)	71
2	**3c**	(**4a**)	48
3	**3d**	(**4a**)	63
4	**3i**	Me, Ms (**4b**)	60
5	**3j**	(**4b**)	68
6	**3o**	Bn, Ts (**4c**)	65

[a]Reaction conditions: enamine **1** (Z/E isomer, 0.20 mmol), $[RuCl_2(p\text{-cymene})_2]_2$ (5 mol %), H_2O_2 (30% aqueous, 5.0 equiv) in 2.0 mL of solvent for about 6 h in an air atmosphere. Isolated yield.

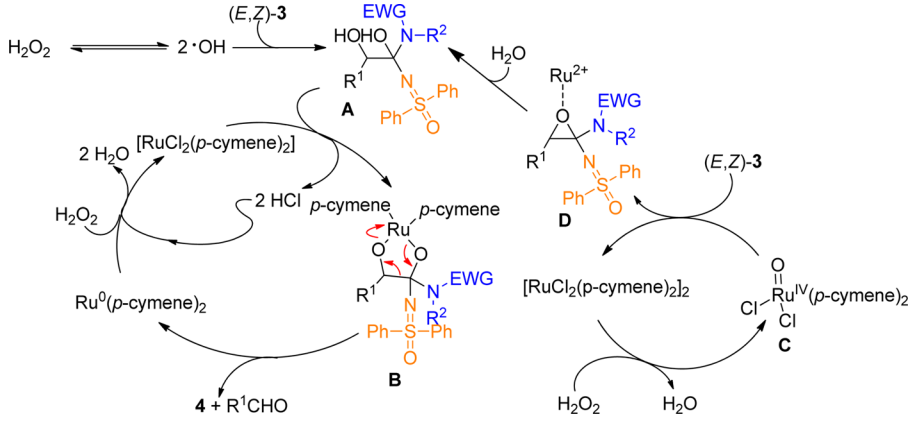
useful tools in the expedient synthesis of valuable sulfoximine derivatives.

EXPERIMENTAL SECTION

General Experimental Methods. Unless otherwise noted, commercial reagents were purchased from commercial suppliers and were used as received. All solvents were dried and distilled according to standard procedures before use. Reactions were conducted with standard Schlenk techniques on a vacuum line. Analytical thin-layer chromatography (TLC) was performed using glass plates precoated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Flash column chromatography was performed using silica gel (60 Å pore size, 32–63 μm, standard grade). Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Nuclear magnetic resonance (NMR) spectra were recorded in parts per million (ppm) from the internal standard tetramethylsilane (TMS) on the δ scale. High-resolution mass spectrometry (HRMS) analysis was performed by electrospray ionization (ESI-micrOTOF).

General Procedure for the Coinage-Metal Cocatalyzed Hydroamination Reaction of Ynamides with *NH*-Sulfoximines. To a mixture of Ph_3AuCl (0.01 mmol, 5 mol %) and AgOTf (0.02 mmol, 10 mol %) in 2 mL of DCE were added compound **1** (0.2 mmol, 1.0 equiv) and **2** (0.22 mmol, 1.1 equiv) at room temperature. The solution was gently warmed to 40 °C and stirred for 6 h under a

Scheme 2. Proposed Mechanism



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nitrogen atmophere. After the solution was cooled to room temperature, the volatiles were removed under reduced pressure, and the pure product was obtained via flash chromatography (silica; *n*-pentane/EtOAc/DCM 30 6 1).

*N,4-Dimethyl-N-(1-((oxodiphenyl-l6-sulfanylidene)amino)-2-phenylvinyl)benzenesulfonamide (**3a**).* Yield: 82.3 mg, 82%. White solid, mp 145−147 °C. *E*:*Z* isomer ratio 2:1.

The following NMR data are of the (*E*)-**3a** isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 7.6 Hz, 4H), 7.49 (t, J = 7.4 Hz, 2H), 7.40 (t, J = 7.6 Hz, 6H), 7.20 (t, J = 8.7 Hz, 4H), 7.07 (t, J = 7.4 Hz, 1H), 5.79 (s, 1H), 2.98 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 139.5, 138.6, 137.0, 135.6, 133.0, 129.7, 129.2, 128.7, 128.5, 128.4, 128.4, 128.2, 128.1, 128.1, 127.3, 126.1, 113.4, 36.5, 21.6. HRMS: calcd for $C_{28}H_{26}N_2O_3S_2$ $(M + H)^+$ 503.1463, found 503.1458.

*N,4-Dimethyl-N-(1-((oxodiphenyl-l6-sulfanylidene)amino)-2-(p-tolyl)vinyl)benzenesulfonamide (**3b**).* Yield, 85.6 mg, 83%. White solid, mp 77−79 °C. *E*:*Z* isomer ratio 2:1.

The following NMR data are of the *E*/*Z* isomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07−8.02 (m, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 7.5 Hz, 4H), 7.66 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 8.1 Hz, 1H), 7.55−7.46 (m, 5H), 7.41 (t, J = 7.7 Hz, 4H), 7.30 (d, J = 8.1 Hz, 2H), 7.27−7.20 (m, 3H), 7.13 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 5.77 (s, 1H), 2.97 (s, 3H), 2.41 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 141.5, 139.5, 137.9, 137.4, 137.1, 135.8, 133.0, 132.7, 129.2, 128.9, 128.8, 128.6, 128.5, 128.4, 128.4, 128.0, 113.6, 38.5, 36.5, 21.6. HRMS: calcd for $C_{29}H_{28}N_2O_3S_2$ $(M + H)^+$ 517.1620, found 517.1619.

*N-(2-(4-Methoxyphenyl)-1-((oxodiphenyl-l6-sulfanylidene)-amino)vinyl)-N,4-dimethylbenzenesulfonamide (**3c**).* Yield: 95 mg, 89%. Yellow solid, mp 81−83 °C. *E*:*Z* isomer ratio 1.5:1.

The following NMR data are of the E/*Z* isomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00−8.10 (m, 2H), 7.93 (d, J = 8.3 Hz, 2H), 7.86−7.80 (m, 4H), 7.68−7.61 (m, 3H), 7.53−7.51 (m, 6H), 7.42 (t, J = 7.7 Hz, 4H), 7.35 (d, J = 8.7 Hz, 3H), 7.29−7.20 (m, 4H), 6.86 (d, J = 8.8 Hz, 1H), 6.77 (d, J = 8.8 Hz, 2H), 5.74 (s, 1H), 3.76 (s, 3H), 2.97 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 142.9, 141.5, 139.6, 136.9, 136.4, 132.9, 132.7, 129.9, 129.3, 129.2, 128.6, 128.5, 128.4, 128.4, 127.3, 113.6, 55.2, 36.4, 21.6. HRMS: calcd for $C_{29}H_{28}N_2O_4S_2$ $(M + H)^+$ 533.1569, found 533.1554.

*N,4-Dimethyl-N-(2-(4-nitrophenyl)-1-((oxodiphenyl-l6-sulfanylidene)amino)vinyl)benzenesulfonamide (**3d**).* Yield: 88.6 mg, 81%. Yellow solid, mp 72−74 °C. *E*:*Z* isomer ratio 1.5:1.

The following NMR data are of the (*E*)-**3d** isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 9.0 Hz, 2H), 7.90 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 7.5 Hz, 4H), 7.57 (m, 3H), 7.53−7.40 (m, 6H), 7.26 (d, J = 8.3 Hz, 1H), 5.78 (s, 1H), 3.03 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 143.5, 142.8, 142.4, 139.0, 136.2, 133.4, 133.2, 129.4, 129.3, 128.7, 128.6, 128.5, 128.2, 128.1, 123.7, 123.5, 111.0, 36.6, 21.6. HRMS: calcd for $C_{28}H_{25}N_3O_5S_2$ $(M + H)^+$ 548.1314, found 548.1308.

*N-(2-(4-Cyanophenyl)-1-((oxodiphenyl-l6-sulfanylidene)amino)-vinyl)-N,4-dimethylbenzenesulfonamide (**3e**).* Yield: 67 mg, 64%. White solid, mp 81−83 °C. *E*:*Z* isomer ratio 2:1.

The following NMR data are of the (*E*)-**3e** isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 7.4 Hz, 4H), 7.77 (d, J = 8.4 Hz, 2H), 7.64−7.51 (m, 10H), 7.31−7.24 (m, 2H), 5.13 (s, 1H), 2.71 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 141.6, 141.1, 141.0, 134.0, 133.1, 131.8, 129.4, 129.3, 128.8, 128.6, 128.2, 119.5, 111.8, 108.8, 38.6, 21.6. HRMS: calcd for $C_{29}H_{25}N_3O_3S_2$ $(M + H)^+$ 528.1416, found 528.1410.

*N-(2-(4-Bromophenyl)-1-((oxodiphenyl-l6-sulfanylidene)amino)-vinyl)-N,4-dimethylbenzenesulfonamide (**3f**).* Yield: 73 mg, 63%. White solid, mp 71−73 °C. *E*:*Z* isomer ratio 2:1.

The following NMR data are of the (*E*)-**3f** isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.3 Hz, 2H), 7.86−7.79 (m, 4H), 7.54−7.53 (m, 2H), 7.42 (t, J = 7.7 Hz, 4H), 7.33−7.20 (m, 6H), 5.70 (s, 1H), 2.98 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 139.3, 139.2, 136.7, 134.6, 133.1, 131.2, 131.1, 130.2, 129.7, 129.3, 128.5, 128.3, 128.2, 127.3, 124.8, 119.6, 112.3, 36.4, 21.6. HRMS: calcd for $C_{28}H_{25}BrN_2O_3S_2$ $(M + H)^+$ 581.0568, found 581.0543.

*N,4-Dimethyl-N-(2-(naphthalen-1-yl)-1-((oxodiphenyl-l6-sulfanylidene)amino)vinyl)benzenesulfonamide (**3g**).* Yield: 72.8 mg, 66%. White solid, mp 181−183 °C. *E*:*Z* isomer ratio 1.5:1.

The following NMR data are of the (*E*)-**3g** isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.5 Hz, 4H), 7.73 (d, J = 8.1 Hz, 1H), 7.64 (t, J = 7.9 Hz, 3H), 7.57 (t, J = 7.2 Hz, 3H), 7.50 (t, J = 7.5 Hz, 4H), 7.38−7.31 (m, 3H), 7.25−7.23 (m, 1H), 7.03 (d, J = 8.1 Hz, 1H), 6.08 (s, 1H), 2.87 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 140.6, 139.5, 137.1, 133.3, 133.0, 132.9, 131.8, 129.4, 129.0, 128.8, 128.1, 128.0, 126.7, 126.5, 125.7, 125.4, 124.6, 110.3, 37.1, 21.5. HRMS: calcd for $C_{32}H_{28}N_2O_3S_2$ $(M + H)^+$ 553.1620, found 553.1614.

*N,4-Dimethyl-N-(1-((oxodiphenyl-l6-sulfanylidene)amino)-2-(thiophen-2-yl)vinyl)benzenesulfonamide (**3h**).* Yield: 83 mg, 82%. Yellow solid, mp 59−61 °C. *E*:*Z* isomer ratio 1.5:1.

The following NMR data are of the (*E*)-**3h** isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (m, 4H), 7.64 (d, J = 8.2 Hz, 2H), 7.59−7.48 (m, 7H), 7.33−7.18 (m, 4H), 5.24 (s, 1H), 2.66 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 141.4, 137.4, 137.0, 134.3, 132.7, 129.2, 129.2, 128.7, 128.6, 128.3, 124.3, 122.3, 109.4, 38.6, 21.6. HRMS: calcd for $C_{26}H_{24}N_2O_3S_3$ $(M + H)^+$ 509.1027, found 509.1022.

*N-Methyl-N-(1-((oxodiphenyl-l6-sulfanylidene)amino)-2-phenylvinyl)methanesulfonamide (**3i**).* Yield: 54.5 mg, 64%. Colorless oil. *E*:*Z* isomer ratio 2:1.

The following NMR data are of the *E*/*Z* isomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14−8.12 (m, 4H), 7.51 (d, J = 7.3 Hz, 6H), 7.40−7.24 (m, 4H), 7.20 (t, J = 7.7 Hz, 2H), 7.07 (t, J = 7.3 Hz, 1H), 5.59 (s, 1H), 3.17 (s, 3H), 3.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 139.3, 135.5, 133.2, 132.8, 129.6, 129.3, 128.9, 128.4, 128.3, 128.0, 127.5, 126.1, 110.9, 43.1, 38.8. HRMS: calcd for $C_{22}H_{22}N_2O_3S_2$ $(M + H)^+$ 427.1150, found 427.1145.

*N-(2-(4-Chlorophenyl)-1-((oxodiphenyl-l6-sulfanylidene)amino)-vinyl)-N-methylmethanesulfonamide (**3j**).* Yield: 73.6 mg, 80%. White solid, mp 158−160 °C. *E*:*Z* isomer ratio 2.5:1.

The following NMR data are of the (*E*)-**3j** isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13−8.10 (m, 4H), 7.58−7.47 (m, 6H), 7.26 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 5.53 (s, 1H), 3.19 (s, 3H), 3.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 139.2, 134.0, 133.3, 131.5, 129.6, 129.2, 128.4, 128.3, 109.6, 38.7, 36.8. HRMS: calcd for $C_{22}H_{21}ClN_2O_3S_2$ $(M + H)^+$ 461.0760, found 461.0755.

*N,4-Dimethyl-N-(1-((oxodiphenyl-l6-sulfanylidene)amino)hex-1-en-1-yl)benzenesulfonamide (**3k**).* Yield: 71 mg, 74%. Colorless oil. *E*:*Z* isomer ratio 1.5:1.

The following NMR data are of the *E*/*Z* isomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03−7.98 (m, 3H), 7.90 (d, J = 8.2 Hz, 2H), 7.72−7.69 (m, 5H), 7.56−7.44 (m, 7H), 7.40 (t, J = 7.7 Hz, 4H), 7.25 (t, J = 8.2 Hz, 4H), 4.83 (t, J = 7.2 Hz, 1H), 2.93 (s, 3H), 2.57 (s, 2H), 2.41 (s, 3H), 2.10 (q, J = 7.2 Hz, 2H),1.14−1.03 (m, 2H), 1.01−0.96 (m, 2H), 0.72 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 141.6, 139.7, 136.4, 132.7, 129.1, 129.1, 129.0, 129.0, 128.5, 128.4, 128.4, 128.3, 116.9, 36.4, 31.6, 27.3, 21.9, 21.6, 13.9. HRMS: calcd for $C_{26}H_{30}N_2O_3S_2$ $(M + H)^+$ 483.1776, found 483.1771.

*N-(3,3-Dimethyl-1-((oxodiphenyl-l6-sulfanylidene)amino)but-1-en-1-yl)-N,4-dimethylbenzenesulfonamide (**3l**).* Yield: 45 mg, 47%. White solid, mp 54−56 °C. *E*:*Z* isomer ratio 5:1.

The following NMR data are of the *E*/*Z* isomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00−7.96 (m, 1H), 7.93 (d, J = 8.3 Hz, 2H), 7.61 (t, J = 8.7 Hz, 4H), 7.54−7.49 (m, 4H), 7.38 (d, J = 7.2 Hz, 4H), 7.24 (d, J = 8.0 Hz, 2H), 4.86 (s, 1H), 2.87 (s, 3H), 2.42 (s, 3H), 0.99 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 139.9, 136.5, 134.5, 133.1, 132.6, 129.4, 129.1, 129.0, 128.8, 128.6, 128.5, 127.6, 127.2, 53.0, 37.2, 30.7, 21.6. HRMS: calcd for $C_{26}H_{30}N_2O_3S_2$ $(M + H)^+$ 483.1776, found 483.1771.

*N-(2-Cyclopropyl-1-((oxodiphenyl-l6-sulfanylidene)amino)vinyl)-N,4-dimethylbenzenesulfonamide (**3m**).* Yield: 60.6 mg, 65%. Colorless oil. *E*:*Z* isomer ratio 1:2.

The following NMR data are of the *E*/*Z* isomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07−7.99 (m, 4H), 7.91 (d, J = 8.2 Hz, 1H), 7.76−7.66

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(m, 4H), 7.56−7.44 (m, 8H), 7.41 (t, J = 7.7 Hz, 2H), 7.29−7.20 (m, 3H), 3.92 (d, J = 9.7 Hz, 1H), 3.00 (s, 3H), 2.57 (s, 3H), 2.39 (s, 3H), 1.99−1.90 (m, 1H), 0.75−0.68 (m, 2H), 0.22−0.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 141.4, 139.8, 135.2, 132.7, 132.6, 129.2, 129.0, 129.0, 128.5, 128.4, 128.4, 122.5, 120.8, 37.8, 21.6, 10.0, 7.1. HRMS: calcd for $C_{25}H_{26}N_2O_3S_2$ $(M + H)^+$ 467.1463, found 467.1458.

*N-Benzyl-4-methyl-N-(1-((oxodiphenyl-l6-sulfanylidene)amino)-2-phenylvinyl)benzenesulfonamide (**3o**).* Yield: 100.6 mg, 87%. White solid, mp 57−59 °C. *E*:*Z* isomer ratio 1.3:1.

The following NMR data are of the (*E*)-**3o** isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 7.7 Hz, 4H), 7.49 (t, J = 7.4 Hz, 2H), 7.39 (t, J = 7.7 Hz, 4H), 7.17 (d, J = 8.2 Hz, 4H), 7.12−7.02 (m, 8H), 5.67 (s, 1H), 4.52 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 139.8, 137.4, 135.7, 135.6, 135.4, 132.9, 129.4, 129.2, 129.1, 129.1, 129.0, 128.7, 128.4, 128.3, 128.0, 128.0, 127.9, 127.7, 127.5, 125.9, 115.8, 52.8, 21.6. HRMS: calcd for $C_{34}H_{30}N_2O_3S_2$ $(M + H)^+$ 579.1776, found 579.1771.

*3-(1-((Oxodiphenyl-l6-sulfanylidene)amino)-2-phenylvinyl)-oxazolidin-2-one (**3p**).* Yield: 39 mg, 48%. Yellow oil. *E*:*Z* isomer ratio 4.5:1.

The following NMR data are of the *E*/*Z* isomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31−8.28 (m, 4H), 8.06−8.03 (m, 3H), 7.55−7.43 (m, 11H), 7.32 (d, J = 4.2 Hz, 1H), 7.19 (t, J = 7.5 Hz, 2H), 7.15−7.05 (m, 3H), 5.80(s, 1H), 4.28 (t, J = 8.0 Hz, 2H), 3.62−3.55 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 143.4, 139.3, 136.8, 136.0, 133.1, 132.6, 129.4, 129.2, 129.2, 128.4, 127.9, 127.7, 126.1, 110.1, 62.7, 45.4. HRMS: calcd for $C_{23}H_{20}N_2O_3S$ $(M + H)^+$ 405.1273, found 405.1267.

*N-Allyl-4-methyl-N-(1-((oxodiphenyl-l6-sulfanylidene)amino)-2-phenylvinyl)benzenesulfonamide (**3q**).* Yield: 48.5 mg, 46%. White solid, mp 126−128 °C. *E*:*Z* isomer ratio 1.5:1.

The following NMR data are of the (*E*)-**3q** isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.3 Hz, 2H), 7.85 (d, J = 7.7 Hz, 4H), 7.51 (t, J = 7.4 Hz, 2H), 7.42 (t, J = 7.8 Hz, 6H), 7.20 (m, 4H), 7.08 (t, J = 7.3 Hz, 1H), 5.81 (s, 1H), 5.71−5.57 (m, 1H), 5.07−4.89 (m, 2H), 3.99 (d, J = 6.6 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 139.7, 137.6, 136.0, 135.7, 132.9, 132.6, 129.2, 129.2, 128.6, 128.4, 128.2, 128.1, 126.1, 118.4, 115.1, 51.8, 21.6. HRMS: calcd for $C_{30}H_{28}N_2O_3S_2$ $(M + H)^+$ 529.1620, found 529.1614.

*N,4-Dimethyl-N-(1-((methyl(oxo)(phenyl)-l6-sulfanylidene)-amino)-2-phenylvinyl)benzenesulfonamide (**3r**).* Yield: 73 mg, 83%. White solid, mp 123−125 °C. *E*:*Z* isomer ratio 2:1.

The following NMR data are of the (*E*)-**3r** isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 8.1 Hz, 2H), 7.62 (t, J = 7.0 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.46 (d, J = 7.7 Hz, 2H), 7.26 (t, J = 8.3 Hz, 4H), 7.13 (t, J = 7.1 Hz, 1H), 5.82 (s, 1H), 3.22 (s, 3H), 2.94 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 140.0, 138.3, 137.1, 135.4, 133.6, 129.5, 129.2, 128.4, 128.2, 128.0, 126.2, 111.3, 42.4, 36.6, 21.6. HRMS: calcd for $C_{23}H_{24}N_2O_3S_2$ $(M + H)^+$ 441.1307, found 441.1302.

*N,4-Dimethyl-N-(1-((methyl(oxo)(phenyl)-l6-sulfanylidene)-amino)-2-(naphthalen-1-yl)vinyl)benzenesulfonamide (**3s**).* Yield: 68.6 mg, 70%. Colorless oil. *E*:*Z* isomer ratio 1.5:1.

The following NMR data are of the (*E*)-**3s** isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 7.5 Hz, 2H), 7.82−7.71 (m, 4H), 7.69−7.64 (m, 3H), 7.59−7.54 (m, 2H), 7.46−7.31 (m, 4H), 7.15 (d, J = 8.2 Hz, 2H), 6.25 (s, 1H), 3.32 (s, 3H), 2.75 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 141.8, 138.3, 137.5, 133.6, 133.5, 132.7, 131.8, 129.5, 129.1, 128.7, 128.3, 127.8, 126.8, 126.5, 125.8, 125.7, 125.5, 124.6, 108.1, 42.8, 37.1, 21.5. HRMS: calcd for $C_{27}H_{26}N_2O_3S_2$ $(M + H)^+$: 491.1463, found 491.1458.

*N,4-Dimethyl-N-(1-((1-oxidotetrahydro-1l6-thiophen-1-ylidene)-amino)-2-phenylvinyl)benzenesulfonamide (**3u**).* Yield: 73.5 mg, 91%. Colorless oil. *E*:*Z* isomer ratio 1.5:1.

The following NMR data are of the (*E*)-**3u** isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 7.4 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.26−7.22 (m, 2H), 7.12 (t, J = 7.3 Hz, 1H), 4.77 (s, 1H), 3.83−3.75 (m, 2H), 3.40−3.33 (m, 2H), 3.12 (s, 3H), 2.48 (s, 3H), 2.30 (br, J = 7.3 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 139.0, 135.9, 133.5, 129.4, 128.8, 128.3, 128.0, 126.2, 112.4, 54.6, 39.5, 29.7, 23.5, 21.6. HRMS: calcd for $C_{20}H_{24}N_2O_3S_2$ $(M + H)^+$ 405.1307, found 405.1301.

*N-Methyl-N-(1-((methyl(oxo)(phenyl)-l6-sulfanylidene)amino)-2-phenylvinyl)methanesulfonamide (**3v**).* Yield: 44 mg, 61%. Colorless oil. *E*:*Z* isomer ratio 1.1:1.

The following NMR data are of the (*E*)-**3v** isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 7.5 Hz, 2H), 7.70−7.55 (m, 3H), 7.40 (d, J = 7.7 Hz, 2H), 7.25 (t, J = 7.5 Hz, 2H), 7.11 (t, J = 7.3 Hz, 1H), 5.70 (s, 1H), 3.34 (s, 3H), 3.14 (s, 3H), 2.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.6, 138.1, 135.4, 133.8, 129.6, 128.4, 128.2, 128.0, 126.1, 109.7, 42.4, 39.0, 36.7. HRMS: calcd for $C_{17}H_{20}N_2O_3S_2$ $(M + H)^+$ 365.0994, found 365.0988.

General Procedure and Characterization Data of Compound 4. A solution of H_2O_2 (30% aqueous solution, 3 equiv) was added to the *N*-alkenylated sulfoximines **3** (0.2 mmol, *E*/*Z* mixture) and $[Ru(p\text{-cymene})Cl_2]_2$ (6.1 mg, 5 mol %) in a mixture of acetonitrile (0.5 mL) and DCM (0.5 mL). After that, the reaction was stirred at room temperature for 1 h and monitored by TLC. Upon completion, the reaction mixture was diluted with DCM (10 mL) and washed with brine (10 mL), and the aqueous phase was extracted with DCM (2 × 5 mL). The combined organic phase was dried over $MgSO_4$, filtered, and concentrated. The product **4** was then purified by silica gel column chromatography.

*N-Methyl-N-tosyl-N′-sulfoximinyl Urea (**4a**).* Yield: 60.7 mg, 71% from **3a**; 41 mg, 48% from **3c**; 53.9 mg, 63% yield from **3d**. White solid, mp 57−59 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03−7.97 (m, 4H), 7.78 (d, J = 8.3 Hz, 2H), 7.59 (t, J = 7.3 Hz, 2H), 7.52 (t, J = 7.5 Hz, 4H), 7.15 (d, J = 8.1 Hz, 2H), 3.41 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 143.8, 139.2, 137.5, 133.6, 129.6, 129.2, 127.7, 127.5, 33.6, 21.5. HRMS: calcd for $C_{21}H_{20}N_2O_4S_2$ $(M + H)^+$ 429.0943, found 429.0945.

*N-Methyl-N-mesyl-N′-sulfoximinyl Urea (**4b**).* Yield: 42 mg, 60% yield from **3i**; 47.8 mg, 68% yield from **3j**. White solid, mp 73−75 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16−8.04 (m, 4H), 7.64−7.49 (m, 6H), 3.40 (s, 3H), 3.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 139.2, 133.7, 129.8, 127.7, 41.6, 32.5. HRMS: calcd for $C_{15}H_{16}N_2O_4S_2$ $(M + H)^+$ 353.0630, found 353.0635.

*N-Benzyl-N-tosyl-N′-sulfoximinyl Urea (**4c**).* Yield: 65 mg, 65% from **3o**. White solid, mp 53−55 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88−7.77 (m, 4H), 7.56−7.52 (m, 4H), 7.46 (t, J = 7.7 Hz, 6H), 7.38−7.22 (m, 3H), 7.03 (d, J = 8.2 Hz, 2H), 5.19 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 143.6, 139.1, 138.2, 137.6, 133.5, 129.6, 129.0, 128.4, 128.2, 127.9, 127.7, 127.4, 49.8, 21.5. HRMS: calcd for $C_{27}H_{24}N_2O_4S_2$ $(M + H)^+$ 505.1256, found 505.1261.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01891.

Experimental details, characterization data, and ^{1}H and ^{13}C NMR spectra for new compounds (PDF)

X-ray crystallography data for compound (*E*)-**3a** (CIF)

X-ray crystallography data for compound **4a** (CIF)

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Notes

The authors declare no competing financial interest.

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