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Iodine-mediated Reactions

Imino-λ³-iodane and Catalytic Amount of I_2-Mediated Synthesis of *N*-Allylsulfenamides via [2,3]-Sigmatropic Rearrangement

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Abstract: A facile metal-free [2,3]-sigmatropic rearrangement reaction of allyl sulfides via *N*-sulfilimine intermediates has been developed. Treatment of allyl sulfides with imino-λ³-iodanes in the presence of a catalytic amount of elemental iodine allowed the reaction to proceed under mild conditions and gave the corresponding *N*-allylsulfenamide compounds in moderate to good yields. Several *N*-allylsulfenamide structures have been confirmed by single-crystal X-ray crystallography. The reaction initially involves the sulfonylimino group transfer reaction between imino-λ³-iodane and the sulfur atom, resulting in the formation of *N*-sulfilimine species, followed by [2,3]-sigmatropic rearrangement to form the *N*-allylsulfenamide.

Introduction

Sulfur ylide compounds are versatile reagents that are widely useful in organic synthesis, and various types of sulfur ylides have been prepared.[1] Many useful reactions and synthetic procedures have been developed using these ylides. Particularly, [2,3]-sigmatropic rearrangement of sulfur ylides is an important chemical transformation leading to various bond–bond-forming reactions, which have been demonstrated as useful reaction tools for making various sulfur compounds in organic synthesis.[1a,1i–1k] Sulfur–nitrogen ylides, sulfilimines, are known as mono-aza analog of sulfoxides, and these compounds can be used as efficient nitrogen installing reagents in various reactions.[2] Some sulfilimines can also be converted by appropriate oxidants to sulfoximines, which can be used as active materials in medicinal or synthetic chemistry.[3] Sulfilimines with an allyl group are known to be active intermediates, which could be generated from allyl sulfides and nitrogen-based oxidants under appropriate reaction conditions.[4] Several research groups reported that the generation of allylsulfilimines involves [2,3]-sigmatropic rearrangement leading to the formation of *N*-allylsulfenamides under suitable reaction conditions. This transformation reaction is useful for the synthesis of sulfenamide compounds, which have found important applications in bioactivity and material chemistry.[5] The sulfur protective group can be readily removed under mild conditions to produce the unprotected *N*-allylamides.[4f,4g,6]

Organohypervalent iodine compounds are known as powerful oxidizing reagents that can be universally as well as efficiently employed in a variety of important conversion reactions.[7] Some hypervalent iodine(III) reagents allow for a facile oxidative ligand transfer to form the new bond–bond-forming products.[8] Recently, a number of nitrogen transfer reactions such as azidation,[9] amination,[10] and sulfonylimidation[11] using hypervalent iodine(III) reagents with nitrogen ligands have been developed. In particular, imino-λ³-iodanes are an important class of nitrogen ligand transfer reagents, and a variety of nitrogen bond forming reactions with various atoms, including carbon atom or heteroatoms, have been reported using these reagents.[12] Many of reactions using imino-λ³-iodanes require the use of metal salts or metal complexes as a catalyst for generating highly active species. For example, the reaction of allyl sulfides using imino-λ³-iodanes in the presence of a metal catalyst provided the corresponding *N*-allylsulfenamide compounds via [2,3]-sigmatropic rearrangement of the intermediate *N*-sulfilimine species (Scheme 1a).[13] However, some metallic reagents are toxic, expensive, or not easy to prepare. From an environmental issue and handling viewpoint, the development of metal-free reaction conditions is significant for green chemistry. Several groups have reported examples of reactions without the use of metallic reagents.[14] For example, Lamar and Nicholas have developed the metal-free C–H amination reaction using imino-λ³-iodanes in the presence of a catalytic amount of elemental iodine.[14a] Lamar group also reported the reaction of an aldehyde with imino-λ³-iodanes under similar metal-free reaction conditions yielding the imidation products in moderate to good yields.[14b] Minakata and co-workers reported the

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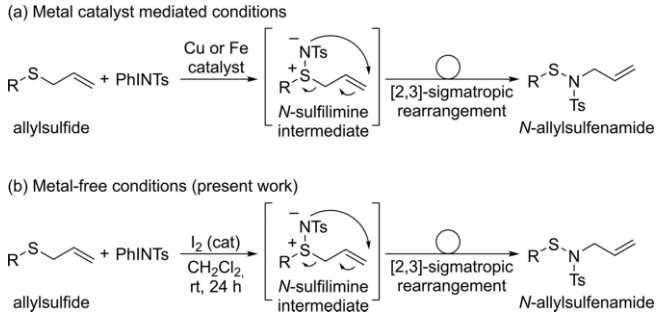
aziridination reactions of styrenes using (*N*-tosylimino)-phenyl-λ^3-iodane under metal-free conditions.[14c] Recently, our group found the metal-free synthetic procedure of (*N*-sulfonyl)-sulfilimine compounds from various sulfides using imino-λ^3-iodanes.[14d]



Scheme 1. Synthesis of *N*-allylsulfenamide from allylsufide using PhINTs.

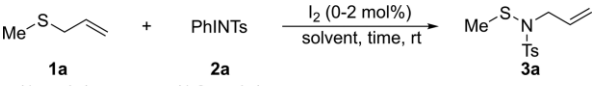
To the best of our knowledge, however, the synthetic approach to *N*-allylsulfenamide from allyl sulfides using imino-λ^3-iodanes under metal-free conditions has not been reported. Herein, we report the straightforward metal-free synthesis of *N*-allylsulfenamide compounds via [2,3]-sigmatropic rearrangement of *N*-sulfilimine intermediates, which can be initially synthesized from allyl sulfides and imino-λ^3-iodanes in the presence of a catalytic amount of elemental iodine (Scheme 1b).

Results and Discussion

Our approach to metal-free synthesis of *N*-allylsulfenamide is based on our group's recently reported synthesis of *N*-sulfilimine from sulfide with imino-λ^3-iodanes in the presence of a catalytic amount of elemental iodine.[14d] In our initial experiments, we investigated the reaction of allyl methyl sulfide **1a** (1 equiv.) with (*N*-tosylimino)-phenyl-λ^3-iodane **2a** (1.2 equiv.) in the presence of a catalytic amount of I_2 (2 mol-%) in various solvents at room temperature (Table 1, entries 1–9). We have found that the reaction in dichloromethane gave the desired product **3a** in 97 % isolated yield. Decreasing the amount of I_2 catalyst from 2 mol-% to 0.5 mol-% afforded the desired product **3a** in slightly lower yields (entries 10 and 11). When the reaction was performed in the absence of I_2, the product **3a** was produced in moderate yield (entry 12). This result indicated that the presence of the I_2 catalyst was effective for the conversion of the desired product. Shortening of the reaction time reduced the desired product **3a** yield (entry 13). Finally, the reaction proceeded efficiently under dark conditions without significant changes (entry 14).[14c,14d]

In the next step, we investigated the preparation of various *N*-allylsulfenamides **3** from the respective substituted allyl sulfides **1** using imino-λ^3-iodanes **2** with 2 mol-% I_2 as catalyst under optimized reaction conditions (Table 2). In general, the reaction of ethyl **1b**, propyl **1c,** or phenyl allyl sulfide **1d** with (*N*-tosylimino)-phenyl-λ^3-iodane **2a** gave the corresponding *N*-allylsulfenamides **3b-d** in good yields (entries 1–4). In the treatment of diallyl sulfide **2e**, the desired product **3e** was obtained in 82 % (entry 5). The reaction of methyl **1a** or phenyl allyl

Table 1. Optimization of preparation of *N*-allylsulfenamide **3a** from allyl methyl sulfide **1a** using (*N*-tosylimino)-phenyl-λ^3-iodane **2a**.[a]



	Solvent	I_2 [mol-%]	Time [h][j]	**3a** Yield[%] [b]
1	MeCN	2	24	93 [c]
2	AcOEt	2	24	92 [c]
3	CH_2Cl_2	2	24	97 (97)
4	$CHCl_3$	2	24	94 [c]
5	MeOH	2	24	40 [c]
6	Heptane	2	24	14[c]
7	$ClCH_2CH_2Cl$	2	24	96[c]
8	PhH	2	24	55
9	Ether	2	24	32[c]
10	CH_2Cl_2	1	24	92 (77)
11	CH_2Cl_2	0.5	24	88 (73)
12	CH_2Cl_2	0	24	(65)
13	CH_2Cl_2	2	12	(78)
14[d]	CH_2Cl_2	2	24	(91)

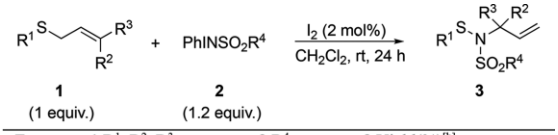
[a] Reaction conditions: allyl methyl sulfide **1a** (0.20 mmol, 1 equiv.) and imino-λ^3-iodane **2a** (0.24 mmol, 1.2 equiv.) with I_2 (0–2 mol-%) stirred in a solvent (2 mL) at room temperature for 12–24 h. [b] Yields of product **3a** determined from ^{1}H NMR spectra of the reaction mixture (using as 1,1,2,2-tetrachloroethane as an internal standard) are shown (numbers in parentheses show an isolated yield of **3a**). [c] Allyl methyl sulfide **1a** was detected from the reaction mixture. [d] Reaction was performed under dark conditions.

sulfide **1d** using imino-λ^3-iodane with different substituents **2b**–**2d** proceeded smoothly producing respective *N*-allylsulfenamides in moderate yields **3f**–**3k** (entries 6–11). It is noteworthy that this reaction method also worked on substituted allyl sulfides to give desired sigmatropic rearrangement products **3l**–**3s** in moderate yields (entries 12–19). Meanwhile, the reaction of 2-vinylthiolane **1i** using imino-λ^3-iodane **2a** afforded the eight-membered ring product **3s** albeit in 20 % yield due to giving complex mixture along with a small amount of **1h** (entry 19). Compared to the previously reported preparation of *N*-allylsulfenamide from allyl sulfide using imino-λ^3-iodane under metal catalyst conditions, our procedure gave the corresponding [2,3]-sigmatropic rearrangement products in comparable or higher yields.[13] In particular, the large scaled reaction of phenyl allyl sulfide **1d** (1 mmol) using optimized conditions gave the desired product **3d** in 70 % (entry 4). The structures of products **3a** and **3q** were established by X-ray crystallography (See Figure1, see the Supporting Information for details).

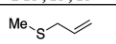
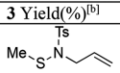
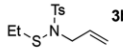
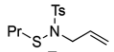
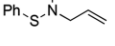
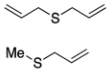
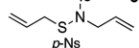
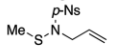
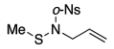
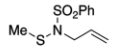
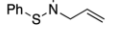
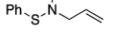
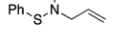
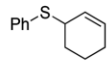
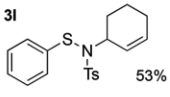
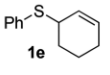
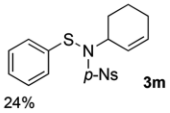
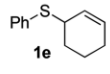
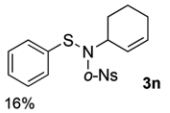
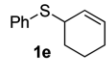
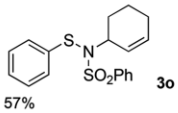
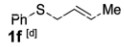
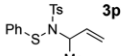
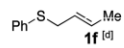
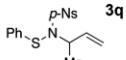
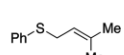
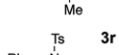
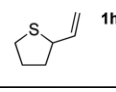
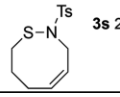
One potential utility of *N*-allylsulfenamides is that they have been known to be easily converted to *N*-allyl sulfonamide.[4g] The reaction of the prepared *N*-allylsulfenamides **3a, 3l** under basic conditions resulted in the S–N bond cleavage to produce the respective *N*-allyl sulfonamides **4a,b** in good yields (Scheme 2).

In order to clarify the reaction mechanism of allyl sulfide with imino-λ^3-idoane in the presence of I_2, we have carried out several control experiments. Based on previously reported reactions, this reaction is probably a two-step reaction.[4b,13–14] Firstly, the reaction of allyl sulfide and imino-λ^3-iodane in the presence of I_2 generated sulfilimine as the initial intermediate, and then [2,3]-sigmatropic rearrangement led to *N*-allyl-sulfen-

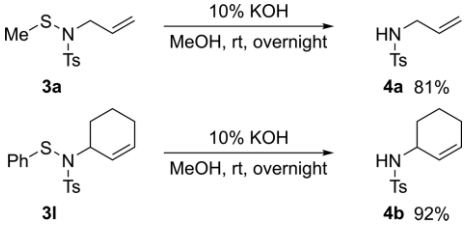
Table 2. Reaction of allyl sulfides **1** using imino-phenyl-λ^3-iodanes **2**.[a]



1 (1 equiv.) + **2** (1.2 equiv.) → **3**

Entry	**1** R^1, R^2, R^3		**2** R^4	**3** Yield(%)[b]
1		**1a**	**2a**, *p*-Tol	 **3a** 97%
2		**1b**	**2a**, *p*-Tol	 **3b** 98%
3		**1c**	**2a**, *p*-Tol	 **3c** 70%
4		**1d**	**2a**, *p*-Tol	 **3d** 80% (70%) [c]
5		**1e**	**2a**, *p*-Tol	 **3e** 82%
6		**1a**	**2b**, *p*-$NO_2C_6H_4$	 **3f** 92%
7		**1a**	**2c**, *o*-$NO_2C_6H_4$	 **3g** 89%
8		**1a**	**2d**, Ph	 **3h** 89%
9		**1d**	**2b**, *p*-$NO_2C_6H_4$	 **3i** 50%
10		**1d**	**2c**, *o*-$NO_2C_6H_4$	 **3j** 18%
11		**1d**	**2d**, Ph	 **3k** 47%
12		**1e**	**2a**, *p*-Tol	**3l**  53%
13	 **1e**		**2b**, *p*-$NO_2C_6H_4$	 **3m** 24%
14	 **1e**		**2c**, *o*-$NO_2C_6H_4$	 **3n** 16%
15	 **1e**		**2d**, Ph	 **3o** 57%
16	 **1f** [d]		**2a**, *p*-Tol	 **3p** 64%
17	 **1f** [d]		**2b**, *p*-$NO_2C_6H_4$	 **3q** 47%
18	 **1g**		**2a**, *p*-Tol	 **3r** 66%
19		**1h**	**2a**, *p*-Tol	 **3s** 20%

[a] Reaction conditions: allyl methyl sulfide **1** (0.20 mmol, 1 equiv.), and imino-λ^3-iodane **2** (0.24 mmol, 1.2 equiv.), with I_2 (2 mol-%) stirred in a dichloromethane at room temperature for 24 h. [b] Isolated yield of **3**. [c] Large scale experiment: phenyl allyl sulfide **1d** (1.0 mmol, 1 equiv.), and imino-λ^3-iodane **2a** (1.2 mmol, 1.2 equiv.) using I_2 (2 mol-%) in dichloromethane (10 mL) were stirred for 24 hours at room temperature. [d] *E*/*Z*-ration = >99:<1.



Scheme 2. Deprotection of *N*-allylsulfenamide **3** under basic conditions.

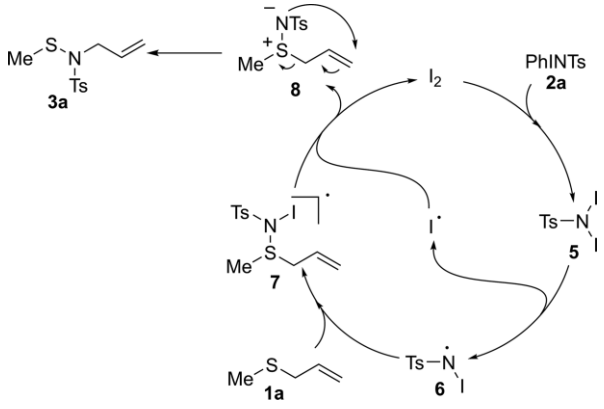
amide. When the reaction of phenyl allyl sulfide **1d** was performed in the presence of TEMPO or BHT as radical scavengers, the desired product **3d** was not obtained, and **1d** was recovered in 76–85 % from the reaction mixture (Scheme 3). The results of the reactions under dark conditions (Table 1, entry 14) imply that the radical pathway is involved in the mechanism. Most likely, the generation of sulfilimine as the first intermediate is induced by the amidyl radical species, which have been reported to be generated from the combination of I_2 and imino-λ^3-iodane.[14d] Through sigmatropic rearrangement, the reactions of allyl sulfides with the methyl group at the terminal position resulted in the shifting of the methyl group from the terminal to the internal position (Table 2, entries 16–18). The X-ray crystallography analysis of **3q** also confirmed the presence of the internal methyl group (Figure 1). Therefore, it is considered that [2,3]-sigmatropic rearrangement might occur during the reaction process.

Scheme 3. Control experiments.

Figure 1. X-ray crystal structures of **3a**. (CCDC 2011021) and **3q**. (CCDC 2011022) Thermal ellipsoids drawn at the 50 % probability level and hydrogen atoms were removed for clarity.

Based on the blank experiment results, and previously reported relative reaction of allyl sulfides with imino-λ^3-iodane, we proposed the reaction mechanism for the formation of *N*-allylsulfenamide compounds (Scheme 4).[4b,13–14] Firstly, *N*,*N*-diiodotosylamide **5**, which can be generated from (*N*-tosylimino)-phenyl-λ^3-iodane **2a** with I_2, is converted into the amidyl radical **6** and iodine radical. The generated amidyl radical **6** reacts with allyl methyl sulfide **1a** to generate sulfilimine spe-

cies **8** and reproduces the I_2 via intermediate **7**. The produced sulfilimine **8** is immediately involved in [2,3]-sigmatropic rearrangement to give the desired *N*-allylsulfenamide product **3a**. Finally, the regenerated I_2 reacts with (*N*-tosylimino)-phenyl-λ^3-iodane **2a** to continue the next reaction cycle.



Scheme 4. Proposed reaction mechanism.

Conclusions

In summary, we have developed the I_2 catalyzed synthesis of *N*-allylsulfenamides from allyl sulfides using imino-λ^3-iodane under metal-free conditions. In comparison with the previously reported procedure using imino-λ^3-iodane in the presence of metal catalyst, our procedure generally affords higher yields. *N*-Allylsulfenamide under basic conditions can be converted into the allylamides in moderate to good yield. The reaction mechanism involves sulfonylimino group transfer reaction to the sulfide atom of allyl sulfides followed by [2,3]-sigmatropic rearrangement to give the corresponding *N*-allylsulfenamides.

Experimental Section

General Experimental Remarks: All reactions were performed under dry argon atmosphere with flame-dried glassware. Dichloromethane was distilled immediately prior to use. All commercial reagents were ACS reagent grade and used without further purification. Melting points were determined in an open capillary tube with a Mel-temp II melting point apparatus. Infrared spectra were recorded on a PerkinElmer 1600 series FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Inova 500, 300 MHz and Bruker 400 MHz NMR spectrometer; ^{13}C NMR spectra were recorded on Varian Inova 500, 300 MHz and Bruker 400 MHz NMR spectrometers at 125, 75 and 100 MHz, respectively. Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C chemical shifts are referenced relative to the tetramethylsilane. X-ray crystal analysis was performed by Rigaku RAPID II XRD Image Plate using graphite-monochromated Cu-K_α radiation (λ = 1.54187 Å) at 173 K. Please see the supporting information or the cif file for more detailed crystallography information. Cyclohex-2-en-1-yl(phenyl)sulfane **1e**,[15] (3-methylbut-2-en-1-yl)(phenyl)sulfane **1g**,[16] and 2-vinyltetrahydrothiophene **1h**[17] were prepared according to the reported procedures. Various imino-λ^3-iodanes **2** (**2a**,[18] **2b, c,**[19] **2d**[14h]) were prepared according to the reported procedures. Other employed reagents were commercially available from chemical companies.

General Procedure for Preparation of *N*-allylsulfenamides 3: Imino-λ^3-iodane **2a** (0.24 mmol) was added at room temperature to a stirred mixture of allyl sulfide **1** (0.20 mmol) and I_2 (2 mol-%) in dichloromethane (2.0 mL). The reaction was stirred at room temperature for 24 hours. After the reaction, 5 % aqueous $Na_2S_2O_3$ (2.5–5.0 mL) was added to the mixture and the solution was extracted with ethyl acetate. The organic layer was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was separated by column chromatography using the hexane/EtOAc (1:1) to afford the pure product **3**.

***N*-Allyl-4-methyl-*N*-(methylthio)benzenesulfonamide (3a):**[13b] Reaction of allyl methyl sulfide **1a** (18 mg, 0.20 mmol) and imino-λ^3-iodane **2a** (90 mg, 0.24 mmol) according to the general procedure afforded 50 mg (97 %) of product **3a**, isolated as a brown solid: m.p. 65.5–66.5 °C (lit.[13b]; m.p. 68.5–69.5 °C); IR (neat) cm^{-1}: $\tilde{\nu}$ = 3067, 2987, 2856, 1651, 1598, 1436, 1347, 1162, 991, 928, 735; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.88–5.77 (m, 1H), 5.25 (dd, *J* = 17.5 Hz, 10.5 Hz, 1H), 5.21 (d, *J* = 10.5 Hz, 1H), 4.06 (d, *J* = 6.0 Hz, 2H), 2.44 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.8, 136.1, 133.2, 129.5, 127.8, 119.2, 56.4, 23.6, 21.6; HRMS (ESI-positive ionization): calcd. for $C_{11}H_{16}NO_2S_2$ ([M + H]$^+$): 258.0622, found 258.0596.

Single crystals of product **3a** suitable for X-ray crystallographic analysis were obtained by slow evaporation of dichloromethane solution. For details on crystal structure of compound **3a** see the CIF file in Supporting Information. CCDC 2011021.

***N*-Allyl-*N*-(ethylthio)-4-methylbenzenesulfonamide (3b):** Reaction of ethyl allyl sulfide **1b** (20 mg, 0.20 mmol) and imino-λ^3-iodane **2a** (90 mg, 0.24 mmol) according to the general procedure afforded 53 mg (99 %) of product **3b**, isolated as a brown oil: IR (neat) cm^{-1}: $\tilde{\nu}$ = 3093, 2978, 2929, 2871, 1647, 1597, 1495, 1329, 1159, 925, 712; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 5.82–5.68 (m, 1H), 5.24–5.12 (m, 2H), 4.04 (d, *J* = 6.5 Hz, 2H), 2.90 (q, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 1.22 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.8, 136.0, 133.1, 129.4, 127.8, 119.2, 57.8, 34.0, 21.5, 12.2; HRMS (APCI-positive ionization): calcd. for $C_{12}H_{18}NO_2S_2$ ([M + H]$^+$): 272.0779, found 272.0789.

***N*-Allyl-4-methyl-*N*-(propylthio)benzenesulfonamide (3c):** Reaction of propyl allyl sulfide **1c** (23 mg, 0.20 mmol) and imino-λ^3-iodane **2a** (90 mg, 0.24 mmol) according to the general procedure afforded 40 mg (70 %) of product **3c**, isolated as a yellow oil: IR (neat) cm^{-1}: $\tilde{\nu}$ = 3087, 2971, 2935, 2877, 1649, 1600, 1496, 1340, 1185, 995, 928, 709; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 5.82–5.70 (m, 1H), 5.24–5.12 (m, 2H), 4.04 (d, *J* = 6.5 Hz, 2H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.43 (s, 3H), 1.68–1.56 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.8, 136.0, 133.1, 129.4, 127.9, 119.2, 57.7, 42.2, 21.6, 20.6, 13.3; HRMS (APCI-positive ionization): calcd. for $C_{13}H_{19}NO_2S_2$ ([M + H]$^+$): 286.0935, found 286.0944.

***N*-Allyl-4-methyl-*N*-(phenylthio)benzenesulfonamide (3d):**[4d] Reaction of phenyl allyl sulfide **1d** (30 mg, 0.20 mmol) and imino-λ^3-iodane **2a** (90 mg, 0.24 mmol) according to the general procedure afforded 51 mg (80 %) of product **3d**, isolated as a light yellow oil; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3062, 2987, 2919, 2865, 1643, 1597, 1582, 1352, 1166, 997, 930, 741; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 2H), 7.35–7.28 (m, 4H), 7.26–7.20 (m, 1H), 5.76–5.65 (m, 1H), 5.17 (dd, *J* = 17.0 Hz, 1.3 Hz, 1H), 5.13 (dd, *J* = 11.5 Hz, 1.3 Hz, 1H), 4.15 (d, *J* = 6.3 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.0, 137.1, 136.2, 132.4, 129.6, 128.9, 127.8, 127.4, 126.3, 119.7, 56.9, 21.6; HRMS (ESI-positive ionization): calcd. for $C_{16}H_{17}NNaO_2S_2$ ([M + Na]$^+$): 342.0598, found 342.0571.

Large scale reaction for preparation of *N*-allyl-4-methyl-*N*-(phenylthio)benzenesulfonamide (3d): Imino-λ^3-iodane **2a** (448 mg, 1.20 mmol) was added at room temperature to a stirred mixture of phenyl allyl sulfide **1d** (150 mg, 1.00 mmol) and I_2 (5 mg, 0.02 mmol) in dichloromethane (10.0 mL) and the reaction was stirred at room temperature for 24 hours. After the reaction, 5 % aqueous $Na_2S_2O_3$ (20 mL) was added, and the mixture was extracted with ethyl acetate. The organic phase was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by column chromatography (hexane/ethyl acetate = 1:1) afforded 223 mg (70 %) of product **3d**.

***N*-Allyl-*N*-(allylthio)-4-methylbenzenesulfonamide (3e):**[13b] Reaction of diallyl sulfide **1e** (23 mg, 0.24 mmol) and imino-λ^3-iodane **2a** (90 mg, 0.24 mmol) according to the general procedure afforded 47 mg (82 %) of product **3e**, isolated as a light brown oil; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3086, 2985, 2924, 2859, 1600, 1496, 1346, 1163, 992, 930, 726; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 5.90–5.67 (m, 2H), 5.26–5.12 (m, 4H), 4.07 (d, *J* = 6.0 Hz, 2H), 3.52 (d, *J* = 7.5 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.8, 136.2, 133.1, 131.4, 129.5, 127.9, 119.9, 119.1, 57.8, 43.7, 21.6; HRMS (APCI-positive ionization): calcd. for $C_{13}H_{17}NO_2S_2$ ($[M + H]^+$): 284.0779, found 284.0787.

***N*-Allyl-*N*-(methylthio)-4-nitrobenzenesulfonamide (3f):** allyl methyl sulfide **1a** (18 mg, 0.20 mmol) and imino-λ^3-iodane **2b** (97 mg, 0.24 mmol) according to the general procedure afforded 53 mg (92 %) of product **3f**, isolated as a white solid: m.p. 111.2–112.7 °C; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3115, 3094, 3072, 2921, 2850, 1644, 1605, 1533, 1353, 1167, 988, 929, 741; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 7.5 Hz, 2H), 8.11 (d, *J* = 7.5 Hz, 2H), 5.86–5.76 (m, 1H), 5.27 (dd, *J* = 18.0 Hz, 1.0 Hz, 1H), 5.25 (d, *J* = 11.0 Hz, 1H), 4.27 (dd, *J* = 6.5 Hz, 1.0 Hz, 2H), 2.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.2, 144.6, 132.4, 129.1, 124.1, 120.0, 57.1, 24.2; HRMS (APCI-positive ionization): calcd. for $C_{10}H_{12}N_2O_4S_2$ ($[M]^+$): 288.0238, found 288.0245.

***N*-Allyl-*N*-(methylthio)-2-nitrobenzenesulfonamide (3g):** allyl methyl sulfide **1a** (18 mg, 0.20 mmol) and imino-λ^3-iodane **2c** (97 mg, 0.24 mmol) according to the general procedure afforded 52 mg (89 %) of product **3g**, isolated as a colorless oil; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3096, 3022, 2986, 2921, 1649, 1591, 1540, 1368, 1167, 999, 933, 746; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.0 Hz, 1H), 7.77–7.66 (m, 3H), 6.0–5.89 (m, 1H), 5.37 (d, *J* = 17.0 Hz, 1H), 5.29 (d, *J* = 10.0 Hz, 1H), 4.22 (d, *J* = 6.5 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.8, 134.0, 133.5, 132.8, 131.9, 131.5, 124.2, 120.0, 57.0, 23.0; HRMS (ESI-positive ionization): calcd. for $C_{10}H_{13}N_2O_4S_2$ ($[M]^+$): 289.0317, found 289.0292.

***N*-Allyl-*N*-(methylthio)benzenesulfonamide (3h):** allyl methyl sulfide **1a** (18 mg, 0.20 mmol) and imino-λ^3-iodane **2d** (86 mg, 0.24 mmol) according to the general procedure afforded 44 mg (89 %) of product **3h**, isolated as a light yellow oil; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3069, 2988, 2919, 2859, 1643, 1587, 1479, 1349, 1166, 999, 931, 757; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.5 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.55–7.49 (m, 2H), 5.88–5.77 (m, 1H), 5.25 (d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 10.5 Hz, 1H), 4.08 (d, *J* = 6.5 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.0, 133.1, 133.0, 128.9, 127.7, 119.3, 56.5, 23.7; HRMS (ESI-positive ionization): calcd. for $C_{10}H_{14}NO_2S_2$ ($[M + H]^+$): 244.0466, found 244.0453.

***N*-Allyl-4-nitro-*N*-(phenylthio)benzenesulfonamide (3i):** Reaction of phenyl allyl sulfide **1d** (30 mg, 0.20 mmol) and imino-λ^3-iodane **2b** (97 mg, 0.24 mmol) according to the general procedure afforded 35 mg (50 %) of product **3i**, isolated as a white solid; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3112, 3070, 2923, 1609, 1480, 1531, 1350, 1312, 1169, 997, 929, 857, 739; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 8.9 Hz, 2H), 8.11 (d, *J* = 8.9 Hz, 2H), 7.46–7.40 (m, 2H), 7.39–7.28 (m, 3H), 5.82–5.65 (m, 1H), 5.28–5.16 (m, 2H), 4.23 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.3, 144.9, 135.8, 131.7, 129.2, 128.3, 127.3, 124.2, 120.4, 57.4; HRMS (APCI-positive ionization): calcd. for $C_{15}H_{15}N_2O_4S_2$ ($[M + H]^+$): 351.0473, found 351.0475.

***N*-Allyl-2-nitro-*N*-(phenylthio)benzenesulfonamide (3j):** Reaction of phenyl allyl sulfide **1d** (30 mg, 0.20 mmol) and imino-λ^3-iodane **2c** (97 mg, 0.24 mmol) according to the general procedure afforded 13 mg (18 %) of product **3j**, isolated as a light yellow oil; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3090, 2929, 2856, 1641, 1540, 1365, 1348, 1169, 995, 926, 854, 742; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 6.9 Hz, 1H), 7.72–7.58 (m, 3H), 7.37–7.29 (m, 3H), 7.28–7.16 (m, 2H), 5.95–5.78 (m, 1H), 5.32–5.18 (m, 2H), 4.34 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.8, 135.7, 134.1, 132.7, 132.6, 131.6, 129.0, 128.0, 127.0, 124.2, 120.0, 57.2; HRMS (APCI-positive ionization): calcd. for $C_{15}H_{15}N_2O_4S_2$ ($[M + H]^+$): 351.0473, found 351.0485.

***N*-Allyl-*N*-(phenylthio)benzenesulfonamide (3k):** Reaction of phenyl allyl sulfide **1d** (30 mg, 0.20 mmol) and imino-λ^3-iodane **2d** (86 mg, 0.24 mmol) according to the general procedure afforded 29 mg (47 %) of product **3k**, isolated as a light brown oil; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3066, 3020, 2987, 2923, 2859, 1643, 1582, 1447, 1349, 1169, 1000, 930, 738; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 6.9 Hz, 2H), 7.64–7.56 (m, 1H), 7.55–7.47 (m, 2H), 7.39 (d, *J* = 6.9 Hz, 2H), 7.35–7.28 (m, 2H), 7.27–7.20 (m, 1H), 5.82–5.64 (m, 1H), 5.18 (dd, *J* = 13.8 Hz, 1.3 Hz, 1H), 5.13 (dd, *J* = 6.5 Hz, 1.3 Hz, 1H), 4.17 (dd, *J* = 6.5 Hz, 1.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.2, 136.9, 133.1, 132.2, 129.0, 129.0, 127.8, 127.6, 126.5, 119.8, 56.9; HRMS (ESI-positive ionization): calcd. for $C_{15}H_{15}NNaO_2S_2$ ($[M + Na]^+$): 328.0442, found 328.0450.

***N*-(Cyclohex-2-en-1-yl)-4-methyl-*N*-(phenylthio)benzenesulfonamide (3l):**[4d] Reaction of cyclohex-2-en-1-yl(phenyl)sulfane **1e** (38 mg, 0.20 mmol) and imino-λ^3-iodane **2a** (90 mg, 0.24 mmol) according to the general procedure afforded 38 mg (53 %) of product **3l**, isolated as a white solid: m.p. 72.0–73.4 °C (lit.[4d]; m.p. 101–102 °C); IR (neat) cm^{-1}: $\tilde{\nu}$ = 3063, 3028, 2932, 2862, 1651, 1600, 1582, 1480, 1361, 1165, 737; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.36–7.27 (m, 4H), 7.19 (t, *J* = 7.1 Hz, 1H), 5.79–5.69 (m, 1H), 4.98–4.76 (m, 2H), 2.43 (s, 3H), 1.98–1.52 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.0, 139.5, 137.1, 132.5, 129.7, 128.7, 127.7, 127.0, 126.6, 124.4, 59.9, 28.6, 24.2, 21.6, 21.2; HRMS (ESI-positive ionization): calcd. for $C_{19}H_{21}NNaO_2S_2$ ($[M + Na]^+$): 382.0911, found 382.0883.

***N*-(Cyclohex-2-en-1-yl)-4-nitro-*N*-(phenylthio)benzenesulfonamide (3m):** Reaction of cyclohex-2-en-1-yl(phenyl)sulfane **1e** (38 mg, 0.20 mmol) and imino-λ^3-iodane **2b** (97 mg, 0.24 mmol) according to the general procedure afforded 19 mg (24 %) of product **3m**, isolated as a colorless solid: m.p. 137.7–138.3 °C; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3065, 3031, 2937, 2864, 1609, 1583, 1531, 1479, 1350, 1170, 738; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.3 Hz, 2H), 8.17 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.37–7.31 (m, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 5.84–5.77 (m, 1H), 5.01–4.95 (m, 2H), 2.01–1.87 (m, 3H), 1.79–1.71 (m, 1H), 1.69–1.52 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.3, 145.5, 138.1, 133.4, 129.0, 128.9, 127.4, 126.3, 124.3, 60.5, 28.7, 24.2, 21.1; HRMS (ESI-positive ionization): calcd. for $C_{18}H_{18}N_2NaO_4S_2$ ($[M + Na]^+$): 413.0606, found 413.0580.

***N*-(Cyclohex-2-en-1-yl)-2-nitro-*N*-(phenylthio)benzenesulfonamide (3n):** Reaction of cyclohex-2-en-1-yl(phenyl)sulfane **1e** (38 mg, 0.20 mmol) and imino-λ^3-iodane **2c** (97 mg, 0.24 mmol) according to the general procedure afforded 12 mg (16 %) of product **3n**, isolated as a light yellow oil; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3063, 3032,

2936, 2865, 1583, 1542, 1481, 1368, 1171, 744; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.19 (d, J = 7.5 Hz, 1H), 7.69–7.55 (m, 3H), 7.36 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 7.5 Hz, 1H), 7.18–7.11 (m, 2H), 5.91–5.84 (m, 1H), 5.44–5.35 (m, 1H), 5.07–5.00 (m, 1H), 2.06–1.89 (m, 3H), 1.81–1.59 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.8, 138.1, 134.0, 132.9, 132.6, 132.3, 131.5, 128.7, 127.5, 127.1, 125.5, 124.0, 60.2, 29.1, 24.3, 21.2; HRMS (ESI-positive ionization): calcd. for $C_{18}H_{18}N_2NaO_4S_2$ ([M + Na]$^+$): 413.0606, found 413.0582.

***N*-(Cyclohex-2-en-1-yl)-*N*-(phenylthio)benzenesulfonamide (3o):** Reaction of cyclohex-2-en-1-yl(phenyl)sulfane **1e** (38 mg, 0.20 mmol) and imino-λ^3-iodane **2d** (86 mg, 0.24 mmol) according to the general procedure afforded 39 mg (57 %) of product **3o**, isolated as a colorless oil; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3063, 3027, 2934, 2863, 1582, 1479, 1359, 1167, 1044, 943; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.55–7.49 (m, 2H), 7.45 (d, J = 7.5 Hz, 2H), 7.35–7.29 (m, 2H), 7.20 (t, J = 7.3 Hz, 1H), 5.78–5.71 (m, 1H), 4.99–4.90 (m, 2H), 2.00–1.84 (m, 3H), 1.75–1.68 (m, 1H), 1.66–1.50 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.0, 139.3, 133.1, 132.6, 129.1, 128.8, 127.7, 126.9, 126.7, 124.6, 60.0, 28.6, 24.2, 21.2; HRMS (ESI-positive ionization): calcd. for $C_{18}H_{19}NNaO_2S_2$ ([M + Na]$^+$): 368.0755, found 368.0727.

***N*-(But-3-en-2-yl)-4-methyl-*N*-(phenylthio)benzenesulfonamide (3p):**[13b] Reaction of (*E*)-but-2-en-1-yl(phenyl)sulfane **1f** (15 mg, 0.10 mmol) and imino-λ^3-iodane **2a** (45 mg, 0.12 mmol) according to the general procedure afforded 21 mg (64 %) of product **3p**, isolated as a colorless oil; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3068, 2981, 2938, 2876, 1598, 1582, 1479, 1354, 1165, 991, 938, 741; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 7.5 Hz, 2H), 7.33–7.27 (m, 4H), 7.20 (t, J = 7.3 Hz, 1H), 5.86–5.43 (m, 1H), 5.15–4.85 (m, 3H), 2.42 (s, 3H), 1.35–1.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.9, 139.0, 137.2, 136.8, 129.5, 128.7, 127.9, 126.9, 125.3, 117.0, 60.1, 21.6, 18.9; HRMS (ESI-positive ionization): calcd. for $C_{17}H_{20}NO_2S_2$ ([M + Na]$^+$): 334.0935, found 334.0906.

***N*-(But-3-en-2-yl)-4-nitro-*N*-(phenylthio)benzenesulfonamide (3q):** Reaction of (*E*)-but-2-en-1-yl(phenyl)sulfane **1f** (15 mg, 0.10 mmol) and imino-λ^3-iodane **2b** (49 mg, 0.12 mmol) according to the general procedure afforded 17 mg (47 %) of product **3q**, isolated as a colorless solid: m.p. 106.2–107.5 °C; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3105, 3067, 2985, 2934, 2868, 1607, 1582, 1531, 1350, 1169, 991, 961, 938, 738; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 7.5 Hz, 2H), 7.39 (d, J = 7.5 Hz, 2H), 7.28–7.23 (m, 1H), 5.70–5.50 (m, 1H), 5.40–4.95 (m, 3H), 1.24 (d, J = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.2, 145.1, 137.7, 136.6, 129.3, 129.0, 127.6, 126.0, 124.0, 117.7, 61.0, 19.2; HRMS (ESI-positive ionization): calcd. for $C_{16}H_{16}N_2NaO_4S_2$ ([M + Na]$^+$): 387.0449, found 387.0421.

Single crystals of product **3q** suitable for X-ray crystallographic analysis were obtained by slow evaporation of ethyl acetate solution. For details on crystal structure of compound **3q** see the CIF file in Supporting Information. CCDC 2011022.

4-Methyl-*N*-(2-methylbut-3-en-2-yl)-*N*-(phenylthiol)benzenesulfonamide (3r):[4d] Reaction of (3-methylbut-2-en-1-yl)(phenyl)-sulfane **1g** (18 mg, 0.10 mmol) and imino-λ^3-iodane **2a** (45 mg, 0.12 mmol) according to the general procedure afforded 23 mg (66 %) of product **3r**, isolated as a colorless oil; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3066, 2983, 2926, 2872, 1600, 1582, 1479, 1347, 1165, 990, 919, 740; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.30–7.25 (m, 2H), 7.23 (d, J = 8.8 Hz, 2H), 7.16 (t, J = 7.3 Hz, 1H), 6.11 (dd, J = 17.3 Hz, 10.8 Hz, 1H), 5.08 (d, J = 17.3 Hz, 1H), 5.04 (d, J = 10.8 Hz, 1H), 2.39 (s, 3H), 1.62–1.45 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.6, 143.6, 139.9, 138.1, 129.1, 128.7, 128.3, 126.5, 124.3, 112.7, 69.3, 28.5, 27.6, 21.5; HRMS (ESI-positive ionization): calcd. for $C_{18}H_{22}NO_2S_2$ ([M + H]$^+$): 348.1092, found 348.1063.

(*Z*)-2-Tosyl-3,6,7,8-tetrahydro-2*H*-1,2-thiazocine (3s):[20] Reaction of 2-vinyltetrahydrothiophene **1h** (23 mg, 0.20 mmol) and imino-λ^3-iodane **2a** (90 mg, 0.24 mmol) according to the general procedure afforded 11 mg (20 %) of product **3s**, isolated as a white solid: m.p. 62.9–64.4 °C (lit.[20]; m.p. 68–69 °C); IR (neat) cm^{-1}: $\tilde{\nu}$ = 3026, 2932, 2853, 1652, 1599, 1351, 1162, 937, 747; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 6.02–5.83 (m, 2H), 4.36–4.02 (m, 2H), 2.92–2.82 (m, 2H), 2.62–2.36 (m, 5H), 1.88 (quint, J = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.7, 136.5, 135.5, 129.5, 128.0, 128.0, 51.0, 38.4, 30.3, 24.4, 21.6.

Deprotection of *N*-allylsulfenamides: *N*-Allylsulfenamide **3a** or **3l** was added at room temperature to a stirred mixture of 10 % KOH in methanol (1.0 mL) and the reaction was stirred at room temperature for overnight. After the reaction, 10 % HCl solution (5 mL) was added, and the mixture was extracted with ethyl acetate. The organic phase was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by column chromatography (hexane/ethyl acetate = 4:1 to 1:1) afforded to afford the pure product **4a, b**.

***N*-Allyl-4-methylbenzenesulfonamide (4a):**[21] Reaction of *N*-allyl-4-methyl-N-(methylthio)benzenesulfonamide **3a** (50 mg, 0.194 mmol) was added at room temperature to a stirred mixture of 10 % KOH in methanol (1.0 mL) and according to the general procedure afforded 33 mg (81 %) of product **4a**, isolated as a colorless solid: m.p. 59.7–60.8 °C (lit.[21]; m.p. 60–62 °C); IR (neat) cm^{-1}: $\tilde{\nu}$ = 3366, 3127, 3091, 3006, 2923, 2852, 1685, 1560, 1445, 1387; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 5.77–5.67 (m, 1H), 5.17 (dd, J = 15.5 Hz, 1.3 Hz, 1H), 5.09 (dd, J = 10.5 Hz, 1.3 Hz, 1H), 4.71 (s, 1H), 3.61–3.55 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.5, 136.9, 133.0, 129.7, 127.1, 117.7, 45.8, 21.5; HRMS (ESI-positive ionization): calcd. for $C_{10}H_{14}NO_2S$ ([M + H]$^+$): 212.0745, found 212.0739.

***N*-(Cyclohex-2-en-1-yl)-4-methylbenzenesulfonamide (4b):**[22] Reaction of *N*-(cyclohex-2-en-1-yl)-4-methyl-*N*-(phenylthio)benzenesulfonamide **3l** (18 mg, 0.05 mmol) was added at room temperature to a stirred mixture of 10 % KOH in methanol (1.0 mL) and according to the general procedure afforded 12 mg (92 %) of product **4b**, isolated as a colorless oil; IR (neat) cm^{-1}: $\tilde{\nu}$ = 3279, 3033, 2933, 1600, 1430, 1318, 1156, 998; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.83–5.71 (m, 1H), 5.42–5.28 (m, 1H), 4.53 (d, J = 8.0 Hz, 1H), 3.89–3.74 (m, 1H), 2.43 (s, 3H), 2.16–1.86 (m, 2H), 1.83–1.68 (m, 1H), 1.65–1.48 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3, 138.4, 131.6, 129.7, 127.1, 127.0, 49.0, 30.3, 24.5, 21.5, 19.3; HRMS (ESI-positive ionization): calcd. for $C_{13}H_{18}NO_2S$ ([M + H]$^+$): 252.1058, found 252.1058.

Deposition Numbers 2011021 and 2011022 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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