Palladium-Catalyzed Reactions of Allenes with 2-Iodobenzenesulfonamides: Simple Synthesis of Benzosultams under Green Conditions

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Abstract: A palladium-catalyzed reaction for the synthesis of benzosultams from allenes and 2-iodobenzenesulfonamides in poly(ethylene glycol) medium is described. This route is compared with a second method involving an internal Heck reaction of alkene-functionalized 2-iodobenzenesulfonamides. Key products were characterized by single-crystal X-ray crystallography.

Key words: palladium, catalysis, allenes, sulfonamides, green chemistry

Among sulfur-containing compounds, sulfonamides and their derivatives have had a profound influence on the development of chemistry, particularly biological chemistry.[1] In particular, benzosultams (cyclic sulfonamides) are important structural motifs that are widely encountered in the drug-development process.[2] Examples of biologically important sultams include the HIV integrase inhibitor **I** (Figure 1),[3a] the carbonic anhydrase inhibitor **II**,[3b] the calpain I inhibitor **III**,[3c] the antiviral, antibacterial, and antimicrobial agent **IV**,[3d] and the nonsteroidal antiinflammatory agent **V**.[3e] In addition to their medicinal value, sultams are indispensable as chiral auxiliaries,[4a,b] artificial sweeteners (saccharin),[4c] and agrochemicals.[4d] Consequently, a wide range of methods have been devised for synthesizing benzosultams and related structures.[5]

In recent decades, significant progress has been made on palladium-catalyzed annulation reactions.[6] Allenes can participate in such reactions to give carbocycles or heterocycles.[7] For the synthesis of benzosultams, diverse methods have been developed,[5a,8] but there have been only two reports on the use of allenes in syntheses of these compounds.[9] These involve nickel-catalyzed annulation reactions of 2-methyl-2*H*-1,2,3,4-benzothiatriazine 1,1-dioxide with allenes,[9a] and the palladium-catalyzed reaction of 2-iodobenzenesulfonamide with allene (one example), respectively.[9b] The development of a new and efficient method for synthesizing benzosultams by using allenes is therefore an important challenge. In this context, and in continuation of our interest in metal-catalyzed annulation reactions of allenes,[10,11] we report mild and environmentally benign conditions for the synthesis of benzosultams from allenes **1a**–**h** and 2-iodobenzenesulfonamides **2a**–**f**; we also report the synthesis of sultams by intramolecular Heck reactions of the *N*-alkenyl sulfonamides **3a** and **3b** (Figure 2).

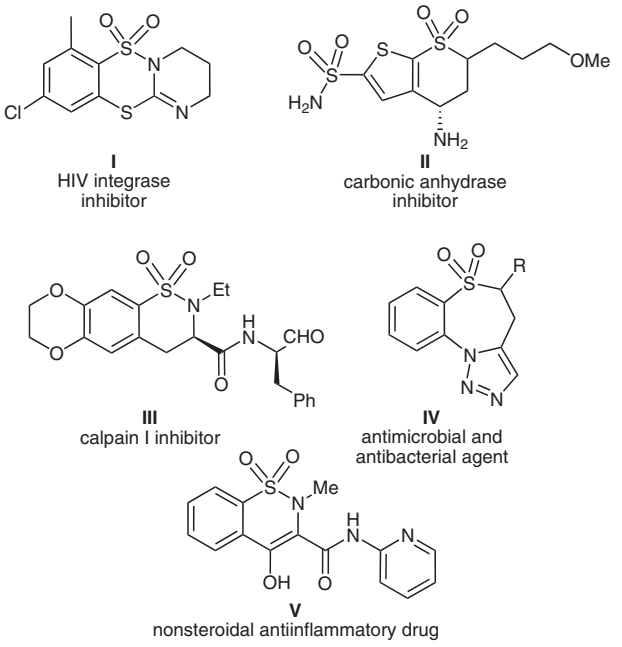

Figure 1 Examples of pharmaceutically important benzosultams

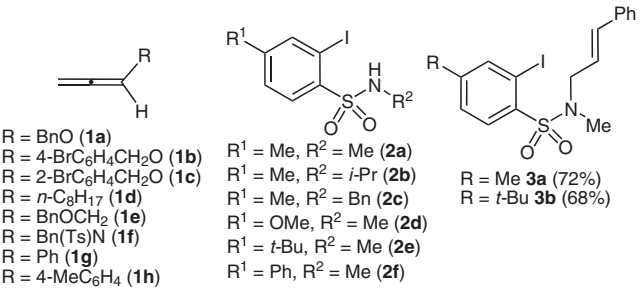

Figure 2 Precursors used in the present study

Initially, we examined the reaction of (benzyloxy)allene (**1a**) with 2-iodo-*N*,4-dimethylbenzenesulfonamide (**2a**) in the presence of a palladium catalyst in acetonitrile. To our delight, this strategy gave the (β,α)-cyclized product **5**, along with the noncyclized α-addition product **4** (Scheme 1). In the ^{13}C NMR spectrum of compound **5**, the peak associated with *C*-I was absent, as expected. The absence of the N*H* peak and the disappearance of the allenic C*H* peak in the ^{1}H NMR spectrum in **5**, with concomitant appearance of an OC*H* peak, are clearly indicative of ring

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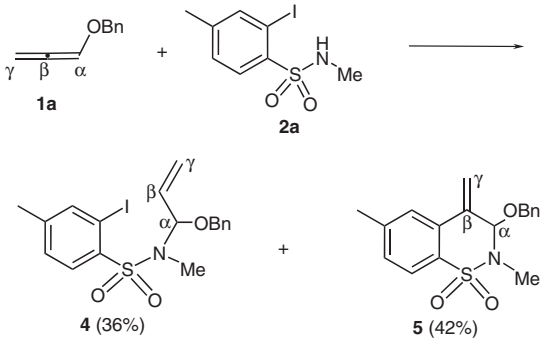
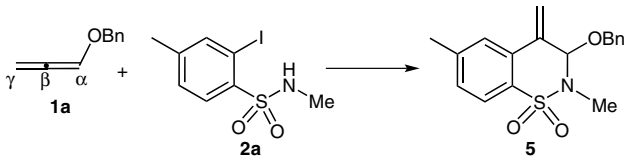
formation. Compound **4** is a monosubstituted alkene; its formation is possible only when the sulfonamide attacks at the α-position of the allene.[12b]



Scheme 1 Palladium-catalyzed reaction of (benzyloxy)allene (**1a**) with 2-iodo-*N*,4-dimethylbenzenesulfonamide (**2a**). *Reagents and conditions*: $Pd(OAc)_2$ (5 mol%), Ph_3P (10 mol%), K_2CO_3 (2.0 equiv), MeCN, 80 °C, 12 h.

Inspired by these results, we screened various palladium catalysts, bases, and solvents to optimize the reaction conditions (Table 1). Of the solvents tested, poly(ethylene glycol) (molecular weight 400; PEG-400) was the best. In the absence of a phosphine ligand, the yield decreased (entry 10). The best combination involved palladium(II) acetate and triphenylphosphine as the catalyst system, potassium carbonate as the base, and PEG-400 as the solvent (entry 4); this gave benzosultam **5** regiospecifically with

Table 1 Effects of Various Catalysts, Bases, and Solvents on the Yield of Sultam **5**



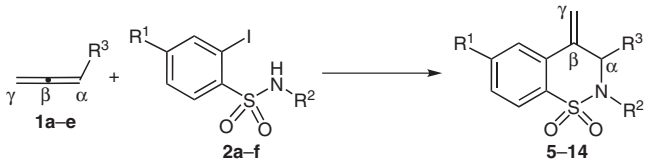
Entry[a]	Catalyst	Base	Solvent	Yield[b] (%)
1	$Pd(OAc)_2$	K_2CO_3	DMF	45
2	$Pd(OAc)_2$	K_2CO_3	toluene	56
3	$Pd(OAc)_2$	K_2CO_3	Et_2CO_3	–
4	**$Pd(OAc)_2$**	**K_2CO_3**	**PEG-400**	**77**
5	$PdCl_2$	K_2CO_3	PEG-400	62
6	$PdCl_2(MeCN)_2$	K_2CO_3	PEG-400	55
7	$Pd_2(dba)_3$	K_2CO_3	PEG-400	49
8	$Pd(OAc)_2$	Na_2CO_3	PEG-400	56
9	$Pd(OAc)_2$	K_3PO_4	PEG-400	49
10	$Pd(OAc)_2$	CsF	PEG-400	45[c]

[a] Reaction conditions: Pd catalyst (5 mol%), Ph_3P (10 mol%), base (2.0 equiv), solvent (1 mL), 80 °C (oil bath), 12 h.
[b] Isolated yield.
[c] In the absence of Ph_3P.

none of the (β,γ)-cyclized product. We were pleased that PEG-400 worked well as a solvent, because it is known to be an environmentally friendly medium.[13] PEG is also known to generate and stabilize nanoparticles of palladium in the course of the reaction.[14]

Under our optimized conditions, the annulation reaction of allenes **1a**–**e** with 2-iodobenzenesulfonamides **2a**–**f** gave the corresponding benzosultams **5**–**14** (Table 2). All these compounds are the (β,α)-cyclized products. The initial attack of the arylpalladium species occurs at the β-position of the allene,[15] and cyclization then takes place regiospecifically at the α-position utilizing the sulfonamide-N*H*. The (β,α)-cyclization route was confirmed by X-ray crystallographic analysis of sultam **12** (Figure 3).

Table 2 : Scope of the Palladium-Catalyzed Annulations Reaction of Allenes **1a**–**e** with 2-Iodobenzenesulfonamides **2a**–**f**



Entry	Reactants	Product	R^1	R^2	R^3	Yield[a] (%)
1	**1a** + **2a**	**5**	Me	Me	OBn	77
2	**1a** + **2b**	**6**	Me	*i*-Pr	OBn	77
3	**1a** + **2c**	**7**	Me	Bn	OBn	69
4	**1a** + **2d**	**8**	OMe	Me	OBn	81
5	**1a** + **2e**	**9**	*t*-Bu	Me	OBn	75
6	**1a** + **2f**	**10**	Ph	Me	OBn	67
7	**1b** + **2a**	**11**	Me	Me	$OCH_2C_6H_4$-4-Br	65
8	**1c** + **2a**	**12**[b]	Me	Me	$OCH_2C_6H_4$-2-Br	63
9	**1d** + **2a**	**13**	Me	Me	*n*-C_8H_{17}	85
10	**1e** + **2a**	**14**	Me	Me	CH_2OBn	62

[a] Yields of the isolated products.
[b] Structure confirmed by x-ray crystallography.

In contrast to the above, the annulation reaction of the aminoallene **1f** with 2-iodobenzenesulfonamides **2a**, **2b**, **2d**, and **2e** in the presence of the palladium catalyst gave the (β,γ)-cyclized products **15**–**18** in good yields (Scheme 2). In this case, a proton shift from the γ-carbon to the α-carbon was observed. The structure of compound **16** was confirmed by X-ray crystallography (Figure 4). The C(7)–C(8) bond length [1.334(4) Å] indicated that it is a double bond, whereas that of C(7)–C(9) [1.489(4) Å] indicated that this is a single bond, confirming that isomerization had occurred. Generally O- and N-substituted allenes give (β,α)-cyclized products.[12] The difference in reactivity observed in the case of **1f** might therefore be due to the bulk

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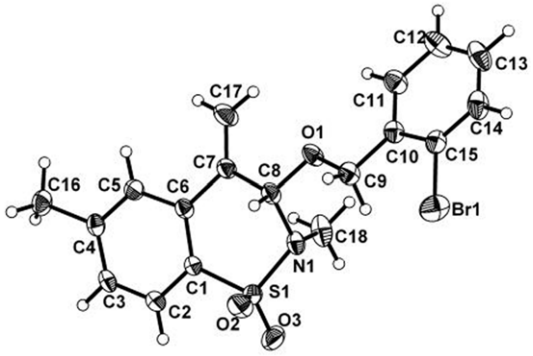
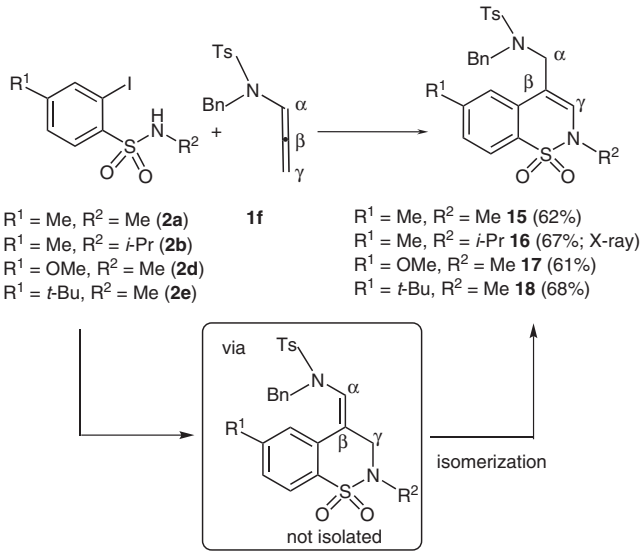


Figure 3 ORTEP drawing of benzosultam **12**. Selected bond lengths (with estimated standard deviations in parentheses): C(6)–C(7) 1.480(4), C(7)–C(8) 1.496(4), C(7)–C(17) 1.311(5), C(8)–N(1) 1.483(4), S(1)–O(2) 1.427(3), S(1)–N(1) 1.619(3) Å.

of the substituents around the nitrogen atom, which favors the (β,γ)-cyclized product. A highlight of the current work is that one product is formed regioselectively by using an environmentally benign (green) solvent, PEG-400.



Scheme 2 Palladium-catalyzed reactions of allene **1f** with 2-iodobenzenesulfonamides. *Reagents and conditions*: $Pd(OAc)_2$ (5 mol%), Ph_3P (10 mol%), K_2CO_3 (2.0 equiv), PEG-400 (1 mL), 80 °C, 12 h.

Having successfully used heteroatom- and alkyl-substituted allenes in our cyclization, we turned our attention to the use of aryl-substituted allenes. Palladium-catalyzed annulation reactions of aryl allenes **1g** and **1h** with **2a** gave the (β,γ)-cyclized product **19** and **21** predominantly, along with minor quantities of the corresponding (β,α)-cyclized products **20** and **22** after isomerization (Scheme 3). The structure of compound **19** was confirmed by X-ray crystallography (Figure 5).

In contrast to the above, treatment of 5,5-dimethyl-2-(1-phenylpropa-1,2-dien-1-yl)-1,3,2-dioxaphosphinane 2-oxide with 2-iodo-*N*-methyl-4-methylbenzenesulfonamide (**2a**) in the presence of a palladium catalyst gave the

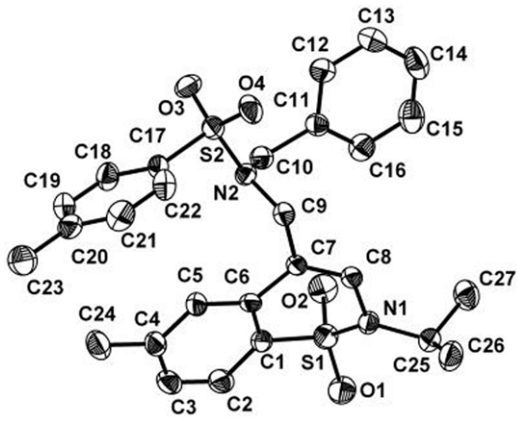
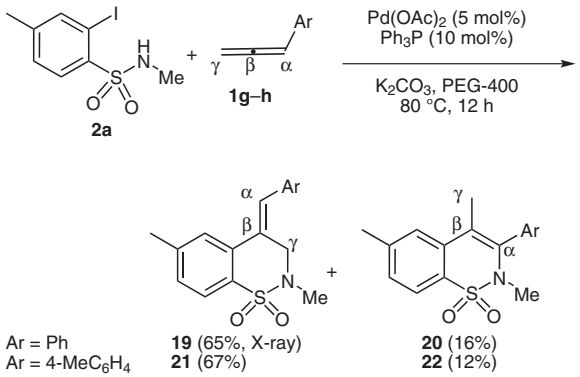


Figure 4 ORTEP drawing of benzosultam **16** (hydrogen atoms are omitted for clarity). Selected bond lengths with estimated standard deviations in parentheses: C(6)–C(7) 1.453(4), C(7)–C(8) 1.334(4), C(7)–C(9) 1.489(4), C(9)–N(2) 1.459(4), S(1)–N(1) 1.627(3), C(8)–N(1) 1.383(4), S(2)–N(2) 1.629(3) Å.



Scheme 3 Palladium-catalyzed reactions of aryl allenes **1g** and **1h**

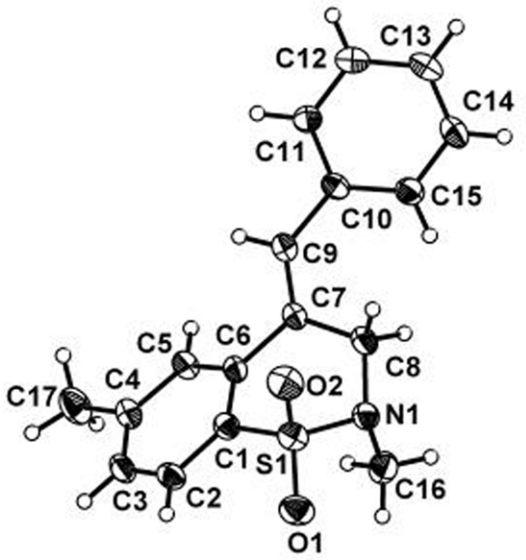


Figure 5 ORTEP drawing of benzosultam **19**. Selected bond lengths with estimate standard deviations in parentheses: C(6)–C(7) 1.473(3), C(7)–C(9) 1.329(4), S(1)–O(1) 1.414(2), S(1)–N(1) 1.630(2) Å.

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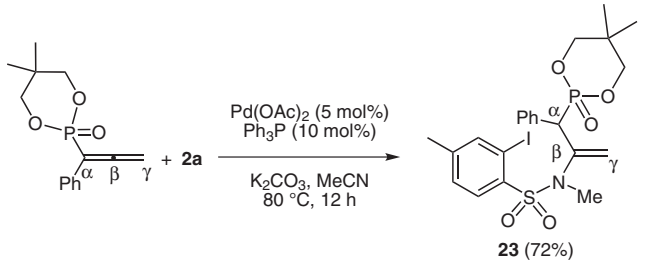
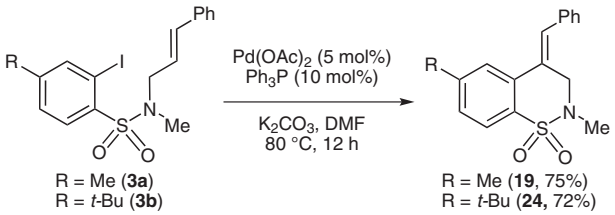
nucleophilic addition product **23** (Scheme 4). We have previously reported similar reactions.[16]



Scheme 4 Palladium-catalyzed reaction of an allenylphosphonate with 2-iodobenzenesulfonamide **2a** to give addition product **23**

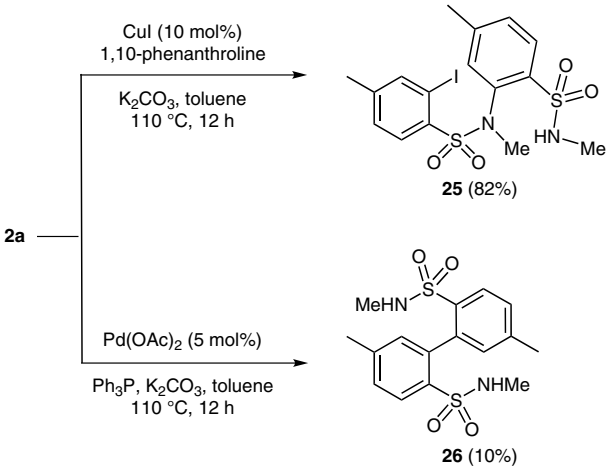
We then examined an alternative method for synthesizing similar products from a single sulfonamide substrate in the presence of a palladium catalyst. We prepared the *N*-alkenyl sulfonamides **3a** and **3b** by the Mitsunobu reaction,[17] and subjected them to a Heck reaction in the presence of a palladium catalyst. In PEG-400 medium the substrate **3a** remained even after 12 hours (based on the ^{1}H NMR spectrum of the crude mixture), whereas when *N*,*N*-dimethylformamide was used as the solvent, the reaction was complete in 12 hours. This reaction gave the cyclized products **19** and **24** in reasonable yields (Scheme 5). However, many steps are required to synthesize substrates with substituents on the NCH_2 carbon, and therefore this route is not convenient for synthesizing substituted benzosultams of the type obtained from allenes.



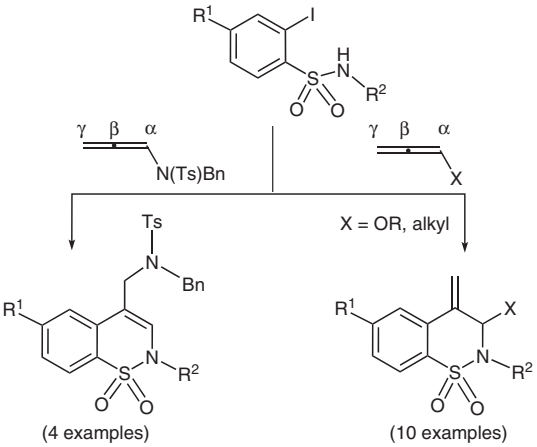
Scheme 5 Heck reaction on substrates **3a** and **3b**

Finally, we checked the reactivity and stability of substrate **2a** in the presence of palladium catalysts and copper catalysts (Scheme 6). In the presence of a copper catalyst, sulfonamide **2a** gave the self-coupled product **25**, with formation of a new C–N bond. In the presence of palladium catalyst, however, the coupled product **26** was isolated in 10% yield along with unreacted **2a**.

In conclusion, we have developed a simple method for the palladium-catalyzed regiospecific annulation reactions of allenes with 2-iodobenzenesulfonamides in PEG-400 to give benzosultams in good yields (Scheme 7). The (β,α)-cyclization product is preferred in the case of O-substituted or alkyl allenes **1a**–**e**, whereas (β,γ)-cyclized products are formed and undergo a subsequent proton shift the case of the N-substituted allene **1f**. The aryl allenes **1g** and **1h** showed an intermediate behavior in which the (β,γ)-cyclization products were predominant. Similar benzosultams were also synthesized by means of a Heck protocol, but this route may be restricted to the synthesis of less-substituted products.



Scheme 6 Formation of self-coupled products **25** and **26** from **2a** in the presence of copper and palladium catalysts



Scheme 7 Overall summary of the synthesis of benzosultams from allenes. *Reaction conditions:* $Pd(OAc)_2$ (5 mol%), Ph_3P (10 mol%), K_2CO_3 (2.0 equiv), PEG-400 (1 mL), 80 °C, 12 h.

Solvents were dried by known methods as appropriate.[18] ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, by using a Bruker AV-400 spectrometer in $CDCl_3$ (unless otherwise stated); shifts are referenced to Me_4Si (δ = 0 ppm). IR spectra were recorded on a Jasco model 5300 FTIR spectrophotometer. Melting points were determined by using a local hot-stage melting-point apparatus and are uncorrected. High-resolution mass spectra were recorded by using Bruker maXis mass spectrometer operated in the ESI–QTOF-II mode. Single-crystal X-ray diffraction data were collected with an Oxford diffractometer using Mo Kα (λ = 0.71073 Å) radiation. The structure was solved and refined by standard methods.[19–20] The syntheses of precursors **1a**–**h**,[7c,21] **2a**–**f**,[5b,22] **3a**, and **3b**[17] are described in the Supporting Information.

***N*-[1-(Benzyloxy)prop-2-en-1-yl]-2-iodo-*N*,4-dimethylbenzenesulfonamide (4)**

A Schlenk tube was charged with allene **1a** (110 mg, 0.75 mmol), sulfonamide **2a** (156 mg, 0.5 mmol), $Pd(OAc)_2$ (0.025 mmol), Ph_3P

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(0.05 mmol), and K_2CO_3 (139 mg, 1.0 mmol). MeCN (1 mL) was added, and the mixture was heated at 80 °C (oil-bath temperature) for 12 h then cooled to r.t. The mixture was diluted with EtOAc (5 mL) and passed through a pad of Celite (~1 g), which was washed with additional EtOAc (20 mL). The organic phases were combined and concentrated to give a residue that was purified by column chromatography [silica gel, hexane–EtOAc (4:1)] to give **4**. Product **5** (42%) was also isolated along with compound **4** (see below).

Gummy liquid; yield: 0.082 g (36%).

IR (neat): 2926, 2844, 1732, 1584, 1490, 1452, 1342, 1162, 910, 811 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.95 (s, 1 H, Ar-*H*), 7.28–7.35 (m, 6 H, Ar-*H*), 5.82–5.90 (m, 1 H, *H*C=CH_2), 5.72–5.73 (m, 1 H, OC*H*), 5.52 (dd, *J* = 18.8 and 1.6 Hz, 1 H, HC=C$H_a$$H_b$), 5.33 (dd, *J* = 10.8 and 1.6 Hz, 1 H, HC=C$H_a$$H_b$), 4.77 (d, *J* = 12.0 Hz, 1 H, OC$H_a$$H_b$), 4.54 (d, *J* ≈ 12.0 Hz, 1 H, OC$H_a$$H_b$), 2.77 (s, 3 H, C$H_3$), 2.37 (s, 3 H, C$H_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 143.6, 138.8, 137.7, 133.7, 131.7, 129.0, 128.4, 127.8, 127.7, 119.3, 92.3, 85.3, 69.7, 28.6, 20.8.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{20}INNaO_3S$: 480.0107; found: 480.0110.

3-(Benzyloxy)-2,6-dimethyl-4-methylene-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (5); Typical Procedure

A Schlenk tube containing sulfonamide **2a** (156 mg, 0.5 mmol), $Pd(OAc)_2$ (0.025 mmol), Ph_3P (0.05 mmol), K_2CO_3 (0.139 g, 1.0 mmol), and PEG-400 (1 mL) was evacuated for 15 min, and then allene **1a** (110 mg, 0.75 mmol) was added. The contents were then heated at 80 °C for 12 h. The resulting mixture was diluted with H_2O (10 mL) and extracted with Et_2O (4 × 10 mL). The organic extracts were dried (Na_2SO_4), filtered, and concentrated under vacuum to give a residue that was purified by column chromatography [silica gel, hexane–EtOAc (4:1)] to give a gummy liquid; yield: 0.126 g (77%).

IR (neat): 2926, 2882, 1605, 1457, 1336, 1161, 1090, 914, 816, 701 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.55 (s, 1 H, Ar-*H*), 7.28–7.45 (m, 6 H, Ar-*H*), 6.04 (s, 1 H, alkene-*H*), 5.88 (s, 1 H, alkene-*H*), 5.81 (s, 1 H, OC*H*), 4.97 (d, *J* = 9.6 Hz, 1 H, OC$H_a$$H_b$), 4.76 (d, *J* = 9.6 Hz, 1 H, OC$H_a$$H_b$), 2.65 (s, 3 H, C$H_3$), 2.44 (s, 3 H, C$H_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1, 136.7, 134.8, 131.1, 130.8, 130.5, 128.6, 128.2, 128.1, 125.5, 116.2, 86.0, 69.8, 29.0, 21.7.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{19}NNaO_3S$: 352.0984; found: 352.0986.

3-(Benzyloxy)-2-isopropyl-6-methyl-4-methylene-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (6)

Gummy liquid; yield: 0.137 g (77%).

IR (neat): 3030, 2926, 2860, 1715, 1627, 1458, 1321, 1167, 816, 740, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 7.6 Hz, 1 H, Ar-*H*), 7.27–7.44 (m, 7 H, Ar-*H*), 5.86 (s, 1 H, alkene-*H*), 5.72 (s, 1 H, alkene-*H*), 5.58 (s, 1 H, OC*H*), 4.86 (d, *J* ≈ 12.0 Hz, 1 H, OC$H_a$$H_b$), 4.72 (d, *J* = 12.0 Hz, 1 H, OC$H_a$$H_b$), 4.17–4.21 [m, 1 H, C*H*(CH_3)$_2$], 2.42 (s, 3 H, CH_3), 1.37 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.02 (d, *J* = 6.8 Hz, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ =142.8, 137.5, 137.4, 135.1, 132.8, 129.9, 128.6, 128.1, 127.9, 126.4, 123.4, 115.6, 85.8, 68.0, 49.5, 23.0, 21.7, 19.9.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{20}H_{24}NO_3S$: 358.1478; found: 358.1480.

2-Benzyl-3-(benzyloxy)-6-methyl-4-methylene-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (7)

Gummy liquid; yield: 0.140 g (69%).

IR (neat): 2932, 1600, 1562, 1463, 1332, 1238, 1167, 1058, 882, 762, 701 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.55 (s, 1 H, Ar-*H*), 7.42–7.44 (m, 2 H, Ar-*H*), 7.25–7.35 (m, 7 H, Ar-*H*), 7.13–7.15 (m, 2 H, Ar-*H*), 6.06 (s, 1 H, alkene-*H*), 5.86 (s, 1 H, alkene-*H*), 5.80 (s, 1 H, OC*H*), 4.57 (d, *J* = 11.6 Hz, 1 H, OC$H_a$$H_b$), 4.48 (d, *J* = 11.6 Hz, 1 H, OC$H_a$$H_b$), 4.28 (d, *J* = 15.2 Hz, 1 H, NC$H_a$$H_b$), 4.15 (d, *J* = 15.2 Hz, 1 H, NC$H_a$$H_b$), 2.44 (s, 3 H, C$H_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2, 137.7, 136.6, 135.6, 132.4, 131.4, 130.4, 128.7, 128.5, 128.4, 128.3, 128.1, 127.4, 125.8, 125.3, 116.5, 87.4, 70.1, 47.7, 21.8.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{24}H_{24}NO_3S$: 406.1478; found: 406.1473.

3-(Benzyloxy)-6-methoxy-2-methyl-4-methylene-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (8)

Gummy liquid; yield: 0.139 g (81%).

IR (neat): 2975, 2860, 1726, 1627, 1458, 1315, 1222, 1162, 811, 762 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.4 Hz, 1 H, Ar-*H*), 7.33–7.44 (m, 5 H, Ar-*H*), 7.19 (s, 1 H, Ar-*H*), 7.00 (dd, *J* ≈ 8.4 and 2.4 Hz, 1 H, Ar-*H*), 6.00 (s, 1 H, alkene-*H*), 5.88 (s, 1 H, alkene-*H*), 5.80 (s, 1 H, OC*H*), 4.95 (d, *J* = 12.0 Hz, 1 H, OC$H_a$$H_b$), 4.74 (d, *J* = 12.0 Hz, 1 H, OC$H_a$$H_b$), 3.88 (s, 3 H, C$H_3$), 2.63 (s, 3 H, C$H_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6, 136.7, 135.0, 133.3, 128.7, 128.3, 128.2, 127.5, 126.0, 116.6, 115.5, 110.0, 86.1, 69.8, 55.7, 29.1.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{20}NO_4S$: 346.1114; found: 346.1111.

3-(Benzyloxy)-6-*tert*-butyl-2-methyl-4-methylene-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (9)

White solid; yield: 0.139 g (75%); mp 108–110 °C.

IR (KBr): 2964, 2877, 1600, 1556, 1479, 1342, 1167, 1090, 899, 756, 701 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.73–7.77 (m, 2 H, Ar-*H*), 7.51–7.53 (m, 1 H, Ar-*H*), 7.33–7.45 (m, 5 H, Ar-*H*), 6.03 (s, 1 H, alkene-*H*), 5.87 (s, 1 H, alkene-*H*), 5.79 (s, 1 H, OC*H*), 4.96 (d, *J* = 12.0 Hz, 1 H, OC$H_a$$H_b$), 4.75 (d, *J* = 12.0 Hz, 1 H, OC$H_a$$H_b$), 2.65 (s, 3 H, C$H_3$), 1.35 [s, 9 H, C(C$H_3$)$_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 136.7, 135.2, 130.9, 128.7, 128.3, 128.2, 127.3, 125.3, 121.8, 116.0, 86.0, 69.7, 35.4, 31.1, 29.0.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{21}H_{26}NO_3S$: 372.1634; found: 372.1636.

3-(Benzyloxy)-2-methyl-4-methylene-6-phenyl-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (10)

Gummy liquid; yield: 0.131 g (67%).

IR (neat): 3036, 2926, 1600, 1551, 1458, 1332, 1162, 1096, 888, 767, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.92 (m, 2 H, Ar-*H*), 7.69 (d, *J* = 8.4 Hz, 1 H, Ar-*H*), 7.59 (d, *J* = 8.0 Hz, 2 H, Ar-*H*), 7.30–7.52 (m, 8 H, Ar-*H*), 6.12 (s, 1 H, alkene-*H*), 5.93 (s, 1 H, alkene-*H*), 5.86 (s, 1 H, OC*H*), 4.98 (d, *J* = 12.0 Hz, 1 H, OC$H_a$$H_b$), 4.78 (d, *J* ≈ 12.0 Hz, 1 H, OC$H_a$$H_b$), 2.69 (s, 3 H, C$H_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.7, 139.5, 136.7, 134.9, 132.2, 131.7, 129.2, 128.7, 128.6, 128.3, 127.7, 127.4, 126.1, 123.9, 116.7, 86.1, 69.9, 29.1.

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HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{23}H_{22}NO_3S$: 392.1321; found: 392.1292.

3-[(4-Bromobenzyl)oxy]-2,6-dimethyl-4-methylene-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (11)
White solid; yield: 0.132 g (65%); mp 81–83 °C.

IR (KBr): 2926, 1595, 1485, 1326, 1151, 1090, 882, 816 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.50–7.54 (m, 3 H, Ar-*H*), 7.29–7.32 (m, 3 H, Ar-*H*), 6.02 (s, 1 H, =C*H*), 5.82 (s, 1 H, =C*H*), 5.75 (s, 1 H, OC*H*), 4.89 (d, *J* = 12.0 Hz, 1 H, CH_aH_b), 4.70 (d, *J* = 12.0 Hz, 1 H, CH_aH_b), 2.62 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2, 135.7, 134.7, 131.8, 131.0, 130.8, 130.6, 129.9, 125.5, 122.2, 116.1, 86.0, 69.0, 29.1, 21.8.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{18}H_{18}BrNNaO_3S$: 430.0089 and 432.0247; found: 430.0090 and 432.0073.

3-[(2-Bromobenzyl)oxy]-2,6-dimethyl-4-methylene-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (12)
White solid; yield: 0.128 g (63%); mp 90–92 °C. Crystallization [EtOAc–hexane (1:1)] at 4 °C gave crystals suitable for X-ray structure determination.

IR (KBr): 2926, 1599, 1451, 1331, 1166, 1084, 1024, 881, 750 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.52–7.61 (m, 3 H, Ar-*H*), 7.35 (t, *J* ≈ 7.6 Hz, 1 H, Ar-*H*), 7.29 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.21 (t, *J* = 7.6 Hz, 1 H, Ar-*H*), 6.05 (s, 1 H, =C*H*), 5.91 (s, 1 H, =C*H*), 5.84 (s, 1 H, OC*H*), 5.02 (d, *J* = 12.4 Hz, 1 H, CH_aH_b), 4.81 (d, *J* = 12.4 Hz, 1 H, CH_aH_b), 2.65 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2, 136.1, 134.6, 133.0, 131.1, 130.8, 130.6, 130.2, 129.8, 127.6, 125.6, 125.5, 123.7, 116.4, 86.5, 69.6, 29.2, 21.8.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{18}H_{18}BrNO_3SNa$: 430.0089 and 432.0247; found: 430.0089 and 432.0070.

X-ray crystal data: colorless block, $C_{18}H_{18}BrNO_3S$, *M* = 408.30, triclinic, space group $P\bar{1}$, *a* = 7.6487(9), *b* = 10.6266(14), *c* = 11.6799(16) Å, *α* = 67.77(13), *β* = 86.971(10), *γ* = 78.624(10)°, *V* = 861.26(19) Å^3, *Z* = 2, *μ* = 2.524 mm^{-1}; data/restraints/parameters: 3519/0/219, *R* indices [*I* > 2σ(*I*)]: *R*1 = 0.0502, *wR*2 (all data) = 0.099.

2,6-Dimethyl-4-methylene-3-octyl-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (13)
Gummy liquid; yield: 0.142 g (85%).

IR (neat): 2926, 2849, 1611, 1468, 1332, 1167, 910, 811, 745, 707 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.6 Hz, 1 H, Ar-*H*), 7.47 (s, 1 H, Ar-*H*), 7.26–7.28 (m, 1 H, Ar-*H*), 5.92 (s, 1 H, alkene-*H*), 5.33 (s, 1 H, alkene-*H*), 4.65 (t, *J* ≈ 7.6 Hz, 1 H, C*H*), 2.62 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 1.84 (q, *J* ≈ 7.6 Hz, 2 H, CH_2), 1.28–1.57 (m, 12 H, 6 CH_2), 0.88 (t, *J* = 6.0 Hz, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 137.4, 133.4, 131.5, 130.4, 125.5, 115.0, 61.0, 31.9, 30.6, 29.7, 29.5, 29.3, 25.5, 22.7, 21.7, 14.2.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{19}H_{30}NO_2S$: 336.1998; found: 336.1996.

3-[(Benzyloxy)methyl]-2,6-dimethyl-4-methylene-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (14)
Gummy liquid; yield: 0.106 g (62%).

IR (neat): 2926, 2860, 1605, 1441, 1332, 1173, 1058, 910, 740 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.48 (s, 1 H, Ar-*H*), 7.29–7.38 (m, 6 H, Ar-*H*), 5.93 (s, 1 H, =C*H*), 5.43 (s, 1 H, =C*H*), 5.84 (s, 1 H, C*H*), 4.81 (dd, *J* = 10.0 and 6.8 Hz, 1 H, CH_aH_b), 4.62 (s, 2 H, CH_2), 3.98 (dd, *J* = 10.0 and 5.6 Hz, 1 H, CH_aH_b), 2.77 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.0, 137.8, 135.2, 133.2, 131.2, 130.2, 128.6, 127.9, 127.1, 125.8, 125.2, 116.3, 73.4, 71.0, 62.9, 34.8, 21.8.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{19}H_{21}NNaO_3S$: 366.1140; found: 366.1149.

***N*-Benzyl-*N*-[(2,6-dimethyl-1,1-dioxido-2*H*-1,2-benzothiazin-4-yl)methyl]-4-methylbenzenesulfonamide (15)**
White solid; yield: 0.149 g (62%); mp 152–154 °C.

IR (KBr): 3057, 2937, 1627, 1600, 1463, 1326, 1156, 1090, 926, 877, 679 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.78 (m, 3 H, Ar-*H*), 7.32 (d, *J* = 8.0 Hz, 2 H, Ar-*H*), 7.21–7.27 (m, 5 H, Ar-*H*), 7.12–7.14 (m, 2 H, Ar-*H*), 5.90 (s, 1 H, =C*H*), 4.37 (s, 2 H, CH_2), 4.31 (s, 2 H, CH_2), 3.17 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 142.9, 137.3, 135.9, 134.3, 132.0, 129.9, 128.7, 128.5, 128.2, 127.7, 127.4, 124.3, 122.1, 110.4, 50.4, 46.7, 33.9, 21.9, 21.6.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{25}H_{27}N_2O_4S_2$: 483.1413; found: 483.1413.

***N*-Benzyl-*N*-[(2-isopropyl-6-methyl-1,1-dioxido-2*H*-1,2-benzothiazin-4-yl)methyl]-4-methylbenzenesulfonamide (16)**
White solid; yield: 0.170 g (67%); mp 123–125 °C. Crystallized [CH_2Cl_2–hexane (1:1)] at 4 °C to give crystals suitable for X-ray structure determination.

IR (KBr): 2975, 1616, 1594, 1446, 1314, 1216, 1150, 1035, 881 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.79 (m, 3 H, Ar-*H*), 7.23–7.32 (m, 7 H, Ar-*H*), 7.15–7.17 (m, 2 H, Ar-*H*), 6.12 (s, 1 H, =C*H*), 4.55–4.59 [m, 1 H, C*H*(CH_3)$_2$], 4.38 (s, 4 H, 2 CH_2), 2.44 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 1.20 [d, *J* = 6.8 Hz, 6 H, HC(CH_3)$_2$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.6, 142.6, 137.5, 135.8, 131.6, 129.9, 128.9, 128.6, 128.5, 128.4, 128.3, 127.6, 127.3, 124.3, 121.8, 111.7, 49.9, 47.9, 46.5, 22.5, 21.8, 21.6.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{27}H_{30}N_2NaO_4S_2$: 533.1545; found: 533.1545.

X-ray crystal data: colorless block, $C_{27}H_{30}N_2O_4S_2$, *M* = 510.65, triclinic, space group $P\bar{1}$, *a* = 9.5321(13), *b* = 11.7426(16), *c* = 12.4656(16) Å, *α* = 71.077(12), *β* = 73.117(12), *γ* = 85.644(11)°, *V* = 1262.7(3) Å^3, *Z* = 2, *μ* = 0.247 mm^{-1}; data/restraints/parameters: 5134/0/320, *R* indices [*I* > 2σ(*I*)]: *R*1 = 0.0622, *wR*2 (all data) = 0.1119.

***N*-Benzyl-*N*-[(6-methoxy-2-methyl-1,1-dioxido-2*H*-1,2-benzothiazin-4-yl)methyl]-4-methylbenzenesulfonamide (17)**
White solid; yield: 0.152 g (61%); mp 125–127 °C.

IR (KBr): 2967, 1621, 1584, 1439, 1320, 1209, 1121, 1015, 872 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.81 (m, 3 H, Ar-*H*), 7.33–7.35 (m, 3 H, Ar-*H*), 7.15–7.16 (m, 3 H, Ar-*H*), 6.97–7.01 (m, 3 H, Ar-*H*), 5.87 (s, 1 H, =C*H*), 4.32 and 4.34 (2 s, 4 H, 2 CH_2), 3.91 (s, 3 H, OCH_3), 3.17 (s, 3 H, CH_3), 2.47 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7, 143.8, 136.9, 135.8, 134.8, 134.2, 130.0, 128.4, 128.1, 127.6, 127.2, 124.0, 123.1, 115.6, 110.0, 107.7, 56.2, 50.6, 47.9, 33.8, 21.6.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{25}H_{26}N_2NaO_5S_2$: 521.1181; found: 521.1181.

***N*-Benzyl-*N*-[(6-*tert*-butyl-2-methyl-1,1-dioxido-2*H*-1,2-benzothiazin-4-yl)methyl]-4-methylbenzenesulfonamide (18)**
White solid; yield: 0.179 g (68%); mp 111–113 °C.

IR (KBr): 2962, 1618, 1591, 1443, 1318, 1226, 1130, 1025, 885 cm^{-1}.

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^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (s, 1 H, Ar-*H*), 7.81 (d, *J* = 8.4 Hz, 1 H, Ar-*H*), 7.74 (d, *J* = 8.4 Hz, 2 H, Ar-*H*), 7.52 (dd, *J* = 8.4 and 1.6 Hz, 1 H, Ar-*H*), 7.32 (d, *J* = 8.0 Hz, 2 H, Ar-*H*), 7.09–7.14 (m, 3 H, Ar-*H*), 6.95–6.97 (m, 2 H, Ar-*H*), 5.91 (s, 1 H, =C*H*), 4.38 and 4.31 (2 s, 4 H, 2 CH_2), 3.18 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 1.38 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 143.7, 136.9, 135.8, 134.0, 131.8, 130.0, 128.7, 128.3, 128.1, 127.5, 127.3, 125.4, 121.8, 121.7, 110.9, 50.6, 50.0, 35.7, 33.8, 31.2, 21.6.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{28}H_{32}N_2NaO_4S_2$: 547.1701; found: 547.1700.

(4*Z*)-4-Benzylidene-2,6-dimethyl-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (19) and 2,4,6-Trimethyl-3-phenyl-2*H*-1,2-benzothiazine 1,1-Dioxide (20)

These compounds were prepared from sulfonamide **2a** (156 mg, 0.5 mmol) and phenylallene (**1g**; 87 mg, 0.75 mmol) by following a route similar to that used to prepare sultam **5**. The products were separated by chromatography using a hexane–EtOAc mixture (90:10 for **19**; 95:5 for **20**).

(4*Z*)-4-Benzylidene-2,6-dimethyl-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (19)

White solid; yield: 0.097 g (65%); mp 108–110 °C. Crystallization from EtOAc–hexane (1:1) at 4 °C gave crystals suitable for X-ray structure determination.

IR (KBr): 2926, 1595, 1496, 1332, 1162, 1140, 926, 822, 690 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.64 (s, 1 H, Ar-*H*), 7.36–7.47 (m, 4 H, Ar-*H*), 7.27–7.31 (m, 3 H, vinyl-*H* + Ar-*H*), 4.66 (s, 2 H, NCH_2), 2.69 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.0, 135.6, 134.1, 131.5, 130.5, 129.9, 129.3, 128.8, 128.3, 126.3, 125.6, 125.1, 52.0, 36.4, 21.9.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{17}H_{18}NO_2S$: 300.1059; found: 300.1059.

X-ray crystal data: colorless block, $C_{17}H_{17}NO_2S$, *M* = 299.38, monoclinic, space group $P2_1/c$, *a* = 12.054(2), *b* = 15.383(3), *c* = 8.0462(13) Å, *β* = 104.651(17)°, *V* = 1443.4(4) Å^3, *Z* = 4, μ = 0.228 mm^{-1}; data/restraints/parameters: 2453/0/192, *R* indices [$I > 2\sigma(I)$]: *R*1 = 0.0478, *wR*2 (all data) = 0.106.

2,4,6-Trimethyl-3-phenyl-2*H*-1,2-benzothiazine 1,1-Dioxide (20)

White solid; yield: 0.024 g (16%, minor product); mp 108–110 °C.

IR (KBr): 2926, 1600, 1436, 1326, 1173, 1145, 1019, 827, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.43–7.57 (m, 6 H, Ar-*H*), 7.35 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 2.82 (s, 3 H, CH_3), 2.51 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 135.4, 134.7, 130.2, 129.8, 129.2, 128.8, 128.5, 126.0, 122.3, 117.4, 35.0, 22.0, 16.5.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{17}H_{18}NO_2S$: 300.1059; found: 300.1058.

(4*Z*)-2,6-Dimethyl-4-(4-methylbenzylidene)-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (21) and 2,4,6-Trimethyl-3-(4-methylphenyl)-2*H*-1,2-benzothiazine 1,1-Dioxide (22)

These compounds were prepared from sulfonamide **2a** (156 mg, 0.5 mmol) and 4-tolylallene (**1h**; 98 mg, 0.75 mmol) by following a route similar to that used to prepare **5**. The products were separated by chromatography using a hexane–EtOAc mixture (90:10 for **21**; 95:5 for **22**).

(4*Z*)-2,6-Dimethyl-4-(4-methylbenzylidene)-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (21)

White solid; yield: 0.105 g (67%); mp 159–161 °C.

IR (KBr): 2926, 1600, 1509, 1447, 1326, 1162, 1068, 910, 816, 701, 559 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.62 (s, 1 H, Ar-*H*), 7.43 (s, 1 H, alkene-*H*), 7.27–7.28 (m, 1 H, Ar-*H*), 7.23 (d, *J* ≈ 8.0 Hz, 2 H, Ar-*H*), 7.17 (d, *J* = 8.0 Hz, 2 H, Ar-*H*), 4.66 (s, 2 H, NCH_2), 2.68 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.0, 138.4, 134.3, 132.7, 131.6, 130.3, 129.7, 129.5, 129.3, 125.5, 125.0, 52.1, 36.4, 21.9, 21.4.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{18}H_{20}NO_2S$: 314.1215; found: 314.1213.

2,4,6-Trimethyl-3-(4-tolyl)-2*H*-1,2-benzothiazine 1,1-Dioxide (22)

White solid; yield: 0.019 g (12%); mp 160–162 °C.

IR (KBr): 2921, 1923, 1595, 1452, 1337, 1173, 1145, 1014, 844, 816, 553 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.39–7.42 (m, 3 H, Ar-*H*), 7.34 (d, *J* = 7.6 Hz, 1 H, Ar-*H*), 7.27–7.28 (m, 2 H, Ar-*H*), 2.82 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 139.8, 139.2, 135.5, 131.8, 130.1, 129.7, 129.2, 128.7, 125.9, 122.2, 117.0, 35.0, 22.1, 21.5, 16.5.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{18}H_{20}NO_2S$: 314.1215; found: 314.1214.

***N*-{1-[(5,5-Dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)(phenyl)methyl]vinyl}-2-iodo-*N*,4-dimethylbenzenesulfonamide (23)**

This compound was prepared from 5,5-dimethyl-2-(1-phenylpropa-1,2-dien-1-yl)-1,3,2-dioxaphosphinane 2-oxide[23] (132 mg, 0.5 mmol) and sulfonamide **2a** (187 mg, 0.6 mmol) by following a route similar to that used to prepare compound **4**. The compound was isolated by chromatography with hexane–EtOAc (3:2) as the eluent.

White solid; yield: 0.207 g (72%); mp 106–108 °C.

IR (KBr): 3036, 2964, 1715, 1638, 1595, 1458, 1353, 1260, 1156, 1058, 1008, 833, 785 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (s, 1 H, Ar-*H*), 7.82 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.50–7.52 (m, 2 H, Ar-*H*), 7.29–7.35 (m, 3 H, Ar-*H*), 7.20 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 5.74 (s, 1 H, alkene-*H*), 5.02 (s, 1 H, alkene-*H*), 4.67 (d, *J* = 22.4 Hz, 1 H, PC*H*), 4.27 (dd, *J* = 11.2 and ~7.0 Hz, 1 H, OCH$_a$H$_b$), 4.08 (dd, *J* = 15.6 and ~7.0 Hz, 1 H, OCH$_a$H$_b$), 3.88–3.90 (m, 2 H, OCH_2), 3.05 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 1.19 and 0.91 (2 s, 6 H, 2 CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 144.1, 143.8, 136.9, 133.6 (d, *J* = 7.0 Hz), 132.4, 129.9 (d, *J* = 7.0 Hz), 128.9, 128.8, 127.9, 119.4, 92.2, 48.2 [d, ^1J(PC) = 28.0 Hz], 40.3, 32.5 (d, *J* = 7.0 Hz), 21.9, 20.9, 20.7.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 16.7.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{22}H_{28}INO_5PS$: 576.0471; found: 576.0473.

(4*Z*)-4-Benzylidene-2,6-dimethyl-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide (19; Alternative Procedure); Typical Procedure

A Schlenk tube was charged with sulfonamide **3a** (214 mg, 0.5 mmol), $Pd(OAc)_2$ (0.025 mmol), Ph_3P (0.05 mmol), K_2CO_3 (139 mg, 1.0 mmol), and DMF (1 mL), and the mixture was heated at 80 °C for 12 h. The resulting mixture was diluted with H_2O (10 mL) and extracted with Et_2O (4 × 10 mL). The extracts were combined, dried (Na_2SO_4), filtered, and concentrated in a vacuum. The residue was purified by column chromatography [silica gel, hexane–EtOAc (2:1)] to give a white solid; yield: 0.112 g (75%).

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HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{17}H_{18}NO_2S$: 300.1059; found: 300.1057.

Other data were as reported above.

(4*Z*)-4-Benzylidene-6-*tert*-butyl-2-methyl-3,4-dihydro-2*H*-1,2-benzothiazine 1,1-Dioxide(24)

Prepared in a similar manner to **19** (above) from sulfonamide **3b** (234 mg, 0.5 mmol) as a white solid; yield: 0.123 g (72%); mp 148–150 °C.

IR (KBr): 2959, 2871, 1589, 1496, 1479, 1332, 1178, 1151, 1118, 921, 701, 674 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.81 (m, 2 H, Ar-*H*), 7.53 (dd, *J* = 8.4 and 1.6 Hz, 1 H, Ar-*H*), 7.42–7.47 (m, 3 H, Ar-*H*), 7.36 (t, *J* ≈ 7.6 Hz, 1 H, Ar-*H*), 7.27–7.30 (m, 2 H, alkene-*H*+Ar-*H*), 4.66 (s, 2 H, NCH_2), 2.71 (s, 3 H, CH_3), 1.39 [s, 9 H, C(CH_3)$_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 135.5, 133.8, 131.5, 130.5, 129.3, 128.8, 128.3, 126.7, 126.6, 125.2, 121.4, 52.0, 36.3, 35.4, 31.2.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{20}H_{24}NO_2S$: 342.1528; found: 342.1528.

2-Iodo-*N*,4-dimethyl-*N*-{5-methyl-2-[(methylamino)sulfonyl]phenyl}benzenesulfonamide (25)

A Schlenk tube was charged with sulfonamide **2a** (156 mg, 0.5 mmol), CuI (0.1 mmol), 1,10-phenathroline monohydrate (0.2 mmol), and K_2CO_3 (139 mg, 1.0 mmol). Toluene (1 mL) was added, and the mixture heated at 110 °C (oil-bath temperature) for 12 h then cooled to r.t. The mixture was then diluted with EtOAc (5 mL) and passed through a pad of Celite (~1 g), which was washed with additional EtOAc (20 mL).The organic phases were combined and concentrated, and the residue was purified by column chromatography [silica gel, hexane–EtOAc (4:1)] to give a white solid; yield: 0.10 g (82%); mp 132–134 °C.

IR (KBr): 3436, 2926, 1605, 1567, 1353, 1293, 1173, 1063, 805, 707, 674 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.4 Hz, 1 H, Ar-*H*), 7.94 (s, 1 H, Ar-*H*), 7.58 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.32 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 6.50 (d, *J* = 8.4 Hz, 1 H, Ar-*H*), 6.47 (s, 1 H, Ar-*H*), 6.05 (br s, 1 H, N*H*), 3.36 (s, 3 H, CH_3), 2.82 (d, *J* = 4.8 Hz, 3 H, NHCH_3), 2.39 and 2.34 (2 s, 6 H, 2 CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.1, 147.7, 145.4, 143.1, 140.2, 132.9, 131.9, 129.1, 116.5, 113.4, 112.0, 92.3, 35.3, 30.0, 22.2, 21.0.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{16}H_{20}IN_2O_4S_2$: 494.9910; found: 494.9907.

***N*,*N*',5,6′-Tetramethylbiphenyl-2,3′-disulfonamide (26)**

A mixture of sulfonamide **2a** (156 mg, 0.5 mmol), $Pd(OAc)_2$ (0.05 mmol), Ph_3P (0.1 mmol), and K_2CO_3 (139 mg, 1.0 mmol) in toluene (1 mL) was heated at 110 °C (oil-bath temperature) for 12 h. Work-up by a procedure similar to that used for compound **25**, but with chromatography using hexane–EtOAc (3:2) as the eluent, gave a white solid; yield: 0.010 g (10%); mp 150–152 °C.

IR (KBr): 3359, 3277, 2975, 2910, 1600, 1567, 1468, 1320, 1167, 1151, 822, 712, 663 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (dd, *J* = 8.0 and 2.4 Hz, 2 H, Ar-*H*), 7.34 (d, *J* ≈ 8.0 Hz, 2 H, Ar-*H*), 7.10 (s, 2 H, Ar-*H*), 4.43 (br s, 2 H, N*H*), 2.62 (d, *J* = 2.4 Hz, 3 H, NHCH_3), 2.61 (d, *J* ≈ 2.4 Hz, 3 H, NHCH_3), 2.43 (s, 6 H, 2 CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 138.0, 133.7, 132.9, 129.8, 129.1, 29.6, 21.4.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{16}H_{21}N_2O_4S_2$: 369.0943; found: 369.0946.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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