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ARTICLE

Intermolecular sulfenoamination of alkenes with sulfonamides and *N*-sulfanylsuccinimides to access β-sulfonylamino sulfides and dihydrobenzothiazines

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An acid-catalyzed intermolecular sulfenoamination reaction of alkenes is developed with sulfonamides as nitrogen source and *N*-sulfanylsuccinimides as sulfur source. This methodology provides a straightforward and general way to synthesize various β-sulfonylamino sulfides with high regio- and diastereoselectivity. The developed method was coupled with intramolecular C-N coupling in a one-pot procedure to afford a series of dihydrobenzothiazine derivatives, one kind of important heterocycles as biologically active compounds in medicinal chemistry.

Introduction

β-Amino sulfides are important building blocks in organic synthesis, and have been widely used in synthetic chemistry as well as modern pharmaceutical industry (Figure 1). For example, these scaffolds exist in commercially approved drugs including Amoxicillin (a β-lactam-based antibiotic) and Viracept (an antiretroviral drug),[1a] in bioactive non-natural compounds like K_{ATP} channel openers (embedding a dihydrobenzothiazine core) [1b] and in some N-S bidentate ligands for transition metal catalysis.[1c]

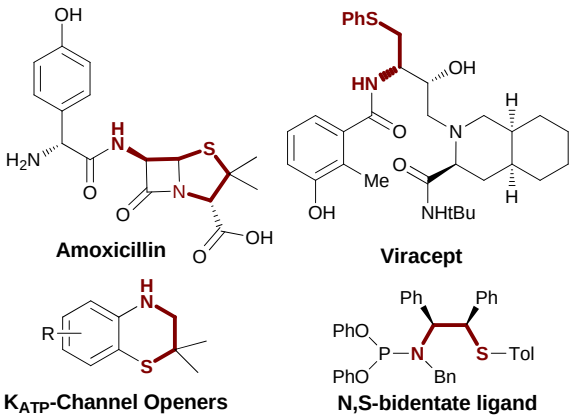
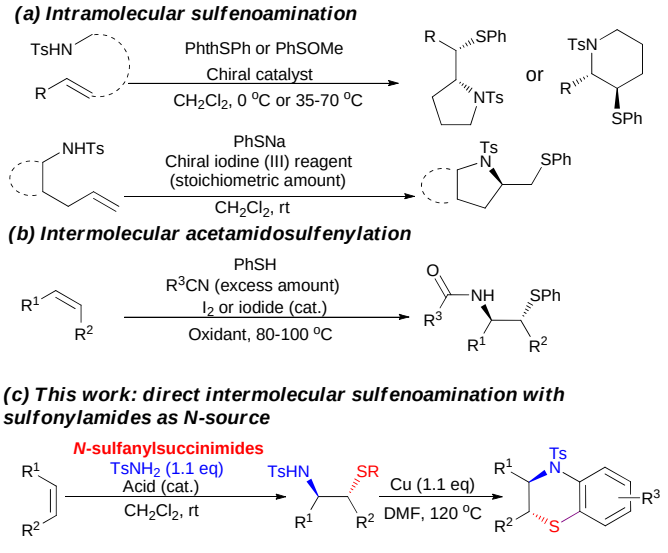


Figure 1. Useful structures containing β-amino sulfides

Sulfenoamination reaction of alkenes directly couples two common groups, sulfenyl group and amino group to C-C double bond, which is abundant and readily available in nature, and is one of the most useful tools to construct β-amino sulfides. Specifically, several methods for the intramolecular sulfenoamination using *N*-alkenyl sulfonamides as substrates have been well investigated to prepare *N*-heterocyclic sulfides. Denmark and Shi groups separately reported the enantioselective intramolecular reaction of *N*-alkenyl sulfonamides with electrophilic sulfenyl reagent methyl benzenesulfenate (MeOSPh) or phenylthiophthalimide (PhthSPh).[2] Most recently, Wirth and coworkers also described an efficient and enantioselective intramolecular sulfenoamination of *N*-alkenyl sulfonamides mediated by iodine(III) reagents with sulfur nucleophiles (Scheme 1a).[3] However, compared with intramolecular process,



Scheme 1. Different methods for sulfenoamination of alkenes

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† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [Conditions optimization for the synthesis of **11a**, Mass Spectrometry for mechanism study, Copies of NMR and IR spectra for all new compounds; X-ray crystal data for **4m** and **9** (CIF)]. See DOI: 10.1039/x0xx00000x

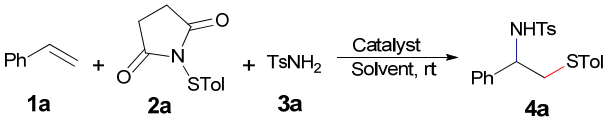
which are kinetically and thermodynamically favoured, the development of catalytic intermolecular sulfenoamination is more challenging and highly desirable.[4] To realize an intermolecular sulfenoamination of alkenes, an alternative option was assisted with nitriles as solvent and *N*-nucleophiles,[5] and successful examples on the synthesis of β-acetamino sulfides have been disclosed using nitrile as nitrogen source and thiol as sulfur source through a Ritter-type reaction (Scheme 1b).[6] In addition, the electrophilic fluorinating agents *N*-fluorobenzenesulfonimide (NFSI),[7a,b] could also serve as nitrogen source for intermolecular sulfenoamination under copper catalysis. However, direct intermolecular sulfenoamination of alkenes using simple sulfonamides as nitrogen source, to the best of our knowledge, has been scarcely explored.

N-Sulfanylsuccinimides, bench stable and readily accessible reagents, have been widely used to introduce sulfenyl groups to various molecules.[8] For example, our group have recently developed an efficient method for the synthesis of 3-sulfenylated coumarins through the electrophilic cyclization of alkynoates with *N*-sulfanylsuccinimides as sulfur sources.[9a] Fu and coworkers reported the isothiocyanatophenylthiation and azidoarylthiation of alkenes using the combination of *N*-sulfanylsuccinimides and superstoichiometric amount of trimethylsilyl derivatives (TMSNCS or $TMSN_3$).[10] Although β-sulfonamino sulfides could be accessed through ring-opening of *N*-tosylaziridines with sulfur nucleophiles,[11] the preparation of *N*-tosylaziridines and the lower stereoselectivity of nucleophilc substitution often made these methods not practicable.[11a-c] Considering the availability, the safety and enviromental issues of nitrogen source, the direct, stereoselective sulfenoamination of alkene to access β-amino sulfides using stoichiometric amount of sulfonamides and *N*-sulfanylsuccinimides is more attractive and highly warranted. In continuation of our research work on C-heteroatom bond formation,[9] we herein report an acid-catalyzed regio- and stereoselective intermolecular sulfenoamination for the synthesis of β-sulfonylamino sulfides using simple alkenes, stoichiometric amount of sulfonamides and *N*-sulfanylsuccinimides as starting materials, and a new strategy for the synthesis of dihydrobenzothiazine derivatives has also be developed through this intermolecular sulfenoamination reaction coupled with copper-mediated intramolecular C-N coupling in a one-pot procedure (Scheme 1c).

Results and discussion

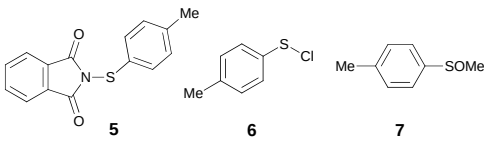
Initially, styrene (**1a**), *N*-(*p*-tolylthio)succinimide (**2a**), and *p*-toluenesulfonamide (**3a**) were used as model substrates to investigate the intermolecular sulfenoamination reaction (Table 1). To our delight, *p*-toluenesulfonamide could serve as nitrogen source in 1.1 equivalent amount for the sulfenoamination of styrene in the presence of catalytic amount of Brønsted or Lewis acid (entries 1-8), and the desired product **4a** was regioselectively produced in 84% yield when $BF_3{\cdot}Et_2O$ was used as the catalyst (entry 8). Further evaluation on reaction solvents showed that CH_2Cl_2 was more suitable for this transformation than other solvents (entries 9-14), and no desired product was detected when the reaction was performed in MeCN, THF and EtOAc (entries 11, 12 and 14). Moreover, we also tested three sulfenylating reagents such as *p*-tolylthiophthalimide (**5**), *p*-tolylthio chloride (**6**), and methyl *p*-tolylsulfenate (**7**), that were previously used for intramolecular sulfenoamination of olefins,[2] while none of them could give better results than **2a** (entries 15-17). For example, **5** had weak reactivity for the intermolecular sulfenoamination, and **4a** was only obtained in 41% yield even the reaction was stirred for 24 h (entry 15); as for sulfenylating reagents **6** and **7**, β-sulfonylamino sulfide **4a** was produced in low yield, while the corresponding β-chloro sulfide or β-methoxyl sulfide was isolated as a major product (entries 16 and 17).

Table 1. Evaluation of reaction conditions[a]



1a 2a 3a 4a

Entry	R-S-Tol	Cat. (10 mol %)	Solvent	Yield (%)[b]
1	**2a**	0	CH_2Cl_2	0
2	**2a**	TfOH (10)	CH_2Cl_2	70
3	**2a**	TfOH (20)	CH_2Cl_2	74
4	**2a**	MsOH (20)	CH_2Cl_2	80
5	**2a**	H_3PO_4 (20)	CH_2Cl_2	trace
6	**2a**	TFA (20)	CH_2Cl_2	trace
7	**2a**	$FeCl_3$ (20)	CH_2Cl_2	20
8	**2a**	$BF_3{\bullet}Et_2O$ (20)	CH_2Cl_2	84
9	**2a**	$BF_3{\bullet}Et_2O$ (20)	DCE	73
10	**2a**	$BF_3{\bullet}Et_2O$ (20)	$CHCl_3$	76
11	**2a**	$BF_3{\bullet}Et_2O$ (20)	MeCN	0
12	**2a**	$BF_3{\bullet}Et_2O$ (20)	THF	0
13	**2a**	$BF_3{\bullet}Et_2O$ (20)	Toluene	70
14	**2a**	$BF_3{\bullet}Et_2O$ (20)	EtOAc	0
15[c]	**5**	$BF_3{\bullet}Et_2O$ (20)	CH_2Cl_2	41
16[d]	**6**	$BF_3{\bullet}Et_2O$ (20)	CH_2Cl_2	21
17[e]	**7**	$BF_3{\bullet}Et_2O$ (20)	CH_2Cl_2	0



5 6 7

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), **3a** (0.33 mmol), catalyst(10 mol %), in CH_2Cl_2 (1 mL), at room temperature for 4-8 h. [b] Isolated yields. [c] Reaction time: 24 h. [d] (2-Chloro-2-phenylethyl)(*p*-tolyl)sulfane was isolated in 41% yield. [e] (2-Methoxy-2-phenylethyl)(p-tolyl)sulfane was isolated in 67% yield.

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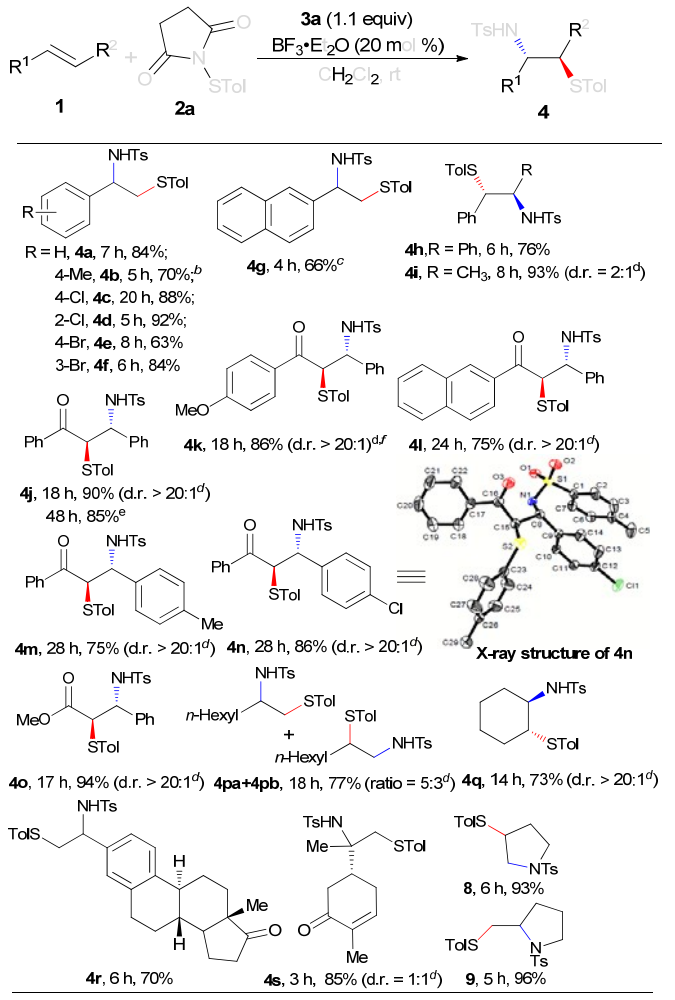
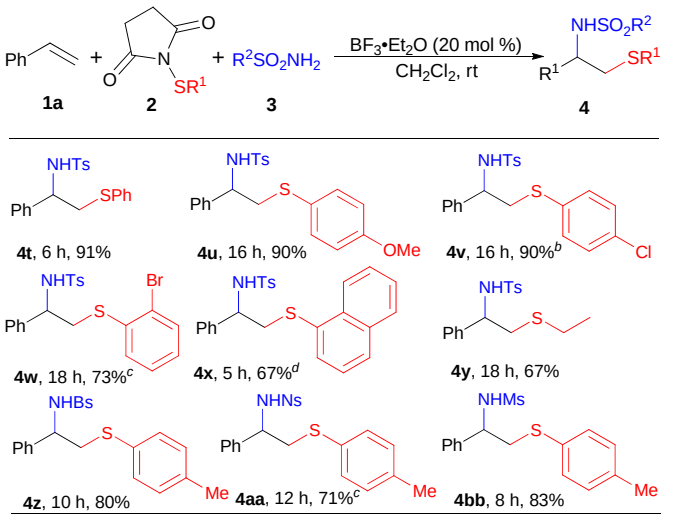
Next, our efforts focused on exploring the scope and limitation of the regioselective intermolecular sulfenoamination reaction. As shown in Table 2, a variety of styrene derivatives with different functional groups were firstly subjected to the optimal reaction conditions (Table 1, entry 6). In general, various functional groups on the aryl ring of alkenes are well-tolerated, including *p*-methyl, *p*- or *o*-chloro, and *p*- or *m*-bromo groups (**4b**-**f**). 2-Vinylnaphthalene was also compatible with this transformation, and **4g** was afforded in 66% yield. In addition to terminal alkenes, several substrates bearing internal C-C double bond were also examined for the present transformation, affording the corresponding β-sulfonylamido sulfides in good to excellent yields. For example, *trans*-stillbene gave the corresponding stereospecific product **4h** in 76% yield; as for *trans*-β-methyl styrene, the desired product **4i** was obtained in 94% yield with lower diasteroslectivity. Due to their electron-deficient nature, α,β-unsaturated carbonyl compounds are particularly challenging substrates for difunctionalization reactions. Nevertheless, the sulfenoamination reactions using chalcones bearing either electron-rich or -poor groups on different aryl moieties also proceeded well, and delivered the corresponding α-sulfenyl-β-sulfonamido ketones **4j**-**n** with high reactivity and diastereoselectivity. The exact structure and stereoselectivity of **4n** was unambiguously confirmed by its X-ray crystallography. The α,β-unsaturated ester **1o** was also tested for this reaction, and gave the product **4o** with high yield and diastereoselectivity. The practicality of such process was also tested for a gram-scale synthesis of **4j** with a lower catalyst loading (5 mol % of $BF_3{\cdot}Et_2O$). To our delight, the reaction could produce 2.13 g of **4j** in 85% yield with no significant loss of efficiency. As for the aliphatic alkenes, both the regio- and stereoselectivity of sulfenoamination reaction were tested using different substrates: the sulfenoamination reaction of linear 1-octene (**1p**) displayed poor regioselectivity, and gave a mixed β-sulfonamido sulfides **4pa** and **4pb** in 77% yield; cyclohexene was a good substrate for this transformation, and the desired product **4q** was diastereoselectively obtained in 73% yield. Furthermore, for the complex olefin substrates, excellent regioselectivities were also observed. For example, the regioselective product **4r** with a steroid skeleton could be obtained in 70% yield, and even for the molecule with two C-C double bonds such as (*S*)-(+)-Carvone, the sulfenoamination only regioselectively occurred at the terminal position, delivering the desired product **4s** in 85% yield, but with lower diastereoselectivity. Additionally, the present transformation was also suitable for intramolecular sulfenoamination reaction, and both β-tosylamido and γ-tosylamido alkenes gave the kinetically favoured sulfenyl pyrrolidines **8** and **9** in excellent yields (for the X-ray structure of **9**, see Supporting Information).

Table 2. Screening of alkenes for sulfenoamination reaction[a]



[a] Typical conditions: **1** (0.3 mmol), **2a** (0.45 mmol), **3a** (0.33 mmol), $BF_3{\cdot}Et_2O$ (0.06 mmol), in CH_2Cl_2 (1.0 mL), at room temperature. [b] TfOH (0.03 mmol) was instead of $BF_3{\cdot}Et_2O$. [c] TfOH (0.06 mmol) was instead of $BF_3{\cdot}Et_2O$. [d] The ratio of two isomers was determined by ^1H NMR. [e] The reaction was performed with **1** (5 mmol), **2a** (7.5 mmol), **3a** (0.25 mmol) in CH_2Cl_2 (20 mL), at room temperature. [f] $BF_3{\cdot}Et_2O$ (0.12 mmol) was used.

Table 3. Screening of *N*-sulfanylsuccinimides and amides for the intermolecular sulfenoamination reaction[a]

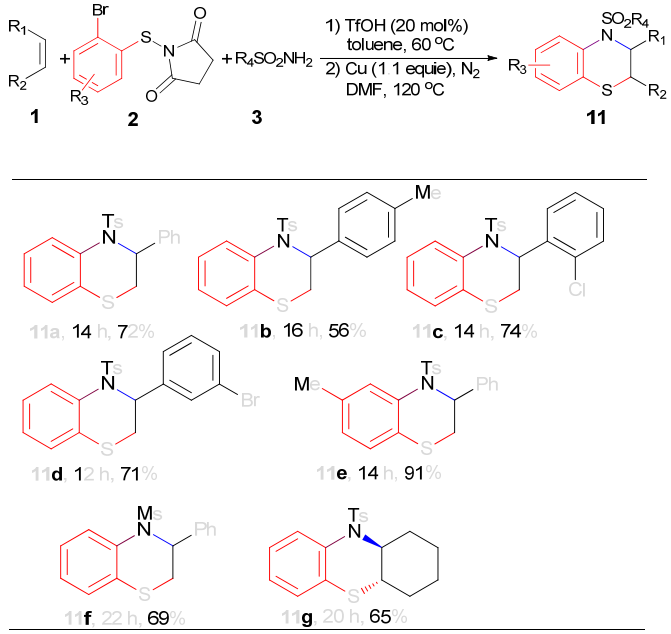


[a] Typical conditions: **1a** (0.3 mmol), **2** (0.45 mmol), **3** (0.33 mmol), $BF_3{\cdot}Et_2O$ (0.06 mmol), in CH_2Cl_2 (1.0 mL), at room temperature. [b] $BF_3{\cdot}Et_2O$ (0.12 mmol) was used. [c] TfOH (0.06 mmol) was instead of $BF_3{\cdot}Et_2O$. [d] TfOH (0.03 mmol) was instead of $BF_3{\cdot}Et_2O$.

Furthermore, a series of *N*-sulfanylsuccinimides and amides were also examined in the present reaction system (Table 3). Likewise, substitutions on the thiophenol moiety, including electron-rich and -poor groups did not affect the reaction efficiency, and the desired products **4t**-**x** were produced in moderate to excellent yields. Even if *N*-sulfanylsuccinimide was derived from aliphatic ethanethiol, the sulfenoamination reaction of styrene could also afford **4y** in 67% yield. Apart from *p*-toluenesulfonamide, other sulfonamides, including benzenesulfonamide, *p*-nitrobenzenesulfonamide and methanesulfonamide, were all suitable substrates, which could transform to the corresponding products **4z**, **4aa** and **4bb** in good yields. However, this protocol also suffered the limitation of amino sources, and the attempts with acetoamide, succinimide or benzylamine as amino source failed to give any desired product.

As one of the most important heterocycles, dihydro-2*H*-benzo[*b*][1,4]thiazine and their derivatives exhibit a broad spectrum of bio- and pharmacological activities.[12] After the efficient and regioselective synthesis of various β-sulfonylamino sulfides containing β-aryl group, we envisaged that dihydrobenzothiazines could be accessed using β-sulfonylamino sulfides through intramolecular C-N coupling. To our delight, after condition optimization (for details, see Supporting Information), the preparation of 3-aryl dihydro-2*H*-benzo[*b*][1,4]thiazines could be realized with the use of simple alkenes, sulfonamides and *N*-(*o*-bromothiophenol)succinimides in a one-pot procedure. As is shown in Table 4, various aromatic alkenes, regardless of electron-poor or -rich properties of

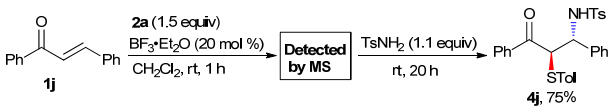
Table 4. Substrate scope for the one-pot synthesis of dihydrobenzothiazines[a]



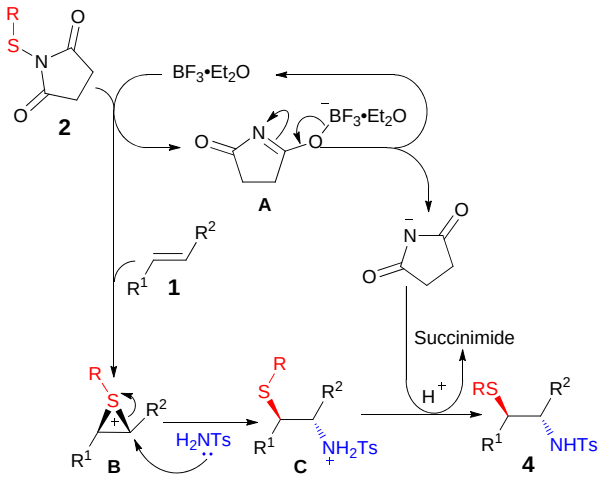
[a] Reaction conditions: (1) **1** (0.2 mmol), **2** (0.3 mmol), **3** (0.22 mmol), TfOH (0.04 mmol), in toluene (0.5 mL), at 60 °C for 2 h; (2) Cu powder (0.22 mmol), in DMF (1 mL) at 120 °C for 12 h under N_2.

substitution on the aryl ring, could be transformed to the corresponding dihydrobenzothiazines **11a**-**e** in moderate to excellent yields. Methanesulfonamide was also suitable for this one-pot two-step reaction, and gave the desired product **11f** in 69% yield. Moreover, with cyclohexene as a substrate, the dihydrobenzothiazine **11g** could be stereoselectively synthesized in 65% yield.

To gain insight into the mechanism of presented intermolecular sulfenoamination reaction, several control experiments were performed as shown in Scheme 2. First, when chalcone **1j** was treated with *N*-(*p*-tolylthio)succinimide **2a** under standard conditions for 1 h in the absence of $TsNH_2$, a sulfur-containing intermediate (331.24) was detected in mass spectroscopy (for details, see Supplementary Information); the addition of $TsNH_2$ (1.1 equiv) to this mixture could also stereoselectively gave the desired product in 75% yield. These experiments indicated that the thiiranium ion, which contained a three-membered episulfonium structure,[13] was possibly involved in the sulfenoamination reaction, and stereoselectively converted to products by the nucleophilic attack of sulfonamides.



Scheme 2. Control experiments for intermolecular sulfenoamination reaction

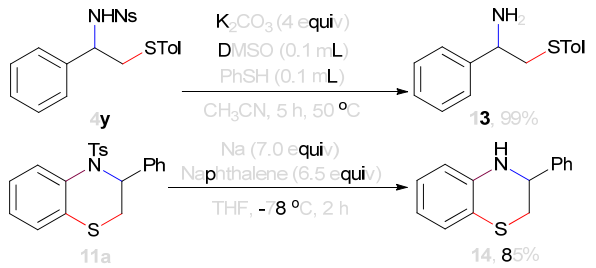


Scheme 3. A Tentative mechanism for intermolecular sulfenoamintion

Based on these results and previous reports,[2-8, 13] a tentative mechanism was proposed in Scheme 3. Initially, sulfenylating agent **2** was activated by $BF_3{\cdot}Et_2O$ and then transferred the sulfenyl moiety to alkenes (**1**) forming thiiranium ion **B**. Next, selective capture of intermediate **B** with $TsNH_2$[14] on the opposite side and subsequent deprotonation resulted in the desired product **4** in high diastereoselectivity.

Although the *N*-sulfonyl groups are robust protecting groups of amines, the present β-sulfonylamino sulfides can be readily desulfonated into the corresponding amines in high efficiency (Scheme 4). For example, the removal of *N*-nosyl group of **4y** can be achieved in almost quantitative yield upon treatment with K_2CO_3 in the mixed solvent of DMSO/PhSH/CH_3CN; *N*-

tosylated dihydrobenzothiazine **11a** can be detosylated to **14** in 85% yield with the use of sodium naphthalide.



Scheme 4. Desulfonation of **4w** and **11a**

Conclusions

In conclusion, an acid-catalyzed intermolecular sulfenoamination reaction of alkenes with sulfonamides as sources has been developed for the synthesis of various β-sulfonylamino sulfides with high regio- and diastereoselectivity. Synthetically, the preparation of **4i** can be scaled up in a reduced catalyst loading (5 mol %) with no obvious loss of efficiency. Furthermore, by coupling with Cu-mediated intramolecular C-N bond formation, dihydrobenzothiazine derivatives were also accessed through intermolecular sulfenoamination of alkenes and intramolecular C-N coupling in a one-pot procedure. Both the *N*-nosyl and -tosyl groups of products can be readily removed to release the corresponding amines. Mild reaction conditions, ready availability of starting materials, high reaction efficiency and selectivity, broad substrate scope, as well as feasible desulfonation of products make the present method valuable and practical for the synthesis of various β-amino sulfides and dihydrobenzothiazine derivatives.

Experimental

General information.

^{1}H NMR spectra were recorded at 600 MHz or 400 MHz and ^{13}C NMR spectra were measured at 150 MHz or 100 MHz using NMR spectrometers with $CDCl_3$ as the solvent. Chemical shifts (δ) were measured in ppm and referenced to the deuterated chloroform (^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.00 ppm). High-resolution mass spectrometry (HRMS) was performed on a TOF-Q spectrometer instrument with an ESI source. IR spectra were recorded on a FT-IR spectrometer in KBr pellets. Melting points were measured with a RD-II type melting point apparatus. X-ray structural analysis was obtained with an X-ray single-crystal diffractometer. *N*-Sulfanylsuccinimides are prepared following previous reports and the known compounds are identified by the comparison of their NMR spectra with reported data in literatures.[9a] Unless otherwise noted, reagents obtained from commercial sources were directly used without further purification; all solvents were obtained from commercial sources and were purified according to standard procedures. Petroleum ether (PE), where used, has the boiling point range 60-90 °C. Column chromatography was performed on silica gel (200-300 mesh) by using ester acetate and petroleum ether as eluent.

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General procedure for the synthesis of β-sulfonamino sulfide 4. To a solution of alkene (0.3 mmol, 1.0 equiv), *N*-sulfanylsuccinimides (0.45 mmol, 1.5 equiv) and *p*-toluenesulfonamide (0.33 mmol, 1.1 equiv) in CH_2Cl_2 (1.0 mL) was added $BF_3{\cdot}Et_2O$ (0.06 mmol, 0.2 equiv) dropwise at room temperature. The reaction mixture was continuously stirred until the starting material was consumed. The resulting mixture was then quenched with H_2O, extracted with ethyl acetate (3 × 10 mL), and dried over anhydrous Na_2SO_4. After the organic solvent was removed under reduced pressure, the crude product was purified by flash chromatography (Eluent: PE/EtOAc = 90:10).

4-Methyl-N-(1-phenyl-2-(p-tolylthio)ethyl)benzenesulfonamide (4a).[15] Yield: 120 mg (84%); time: 7 h; yellow solid; m.p. 100-102 °C; TLC, R_f = 0.35 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, 2H, J = 8.0 Hz), 7.22-7.17 (m, 3H), 7.15-7.10 (m, 4H), 7.09-7.03 (m, 4H), 5.48-5.30 (m, 1H), 4.26 (q, 1H, J = 5.2 Hz), 3.14 (d, 2H, J = 7.2 Hz), 2.37 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.2, 139.2, 137.1, 136.8, 131.1, 130.2, 129.9, 129.3, 128.5, 127.9, 127.2, 126.8, 56.5, 41.9, 21.5, 21.1; HRMS (ESI) m/z calcd. for $C_{22}H_{27}N_2O_2S_2$ $[M+NH_4]^+$: 415.1508, found: 415.1516.

4-Methyl-N-(1-(p-tolyl)-2-(p-tolylthio)ethyl)benzenesulfonamide (4b). Yield: 86.3 mg (70%); time: 5 h; white solid; m.p. 89-91 °C; TLC, R_f = 0.33 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, 2H, J = 8.0 Hz), 7.18-7.09 (m, 4H), 7.06 (d, 2H, J = 8.0 Hz), 7.01 (d, 2H, J = 7.6 Hz), 6.96 (d, 2H, J = 8.0 Hz), 5.45-5.30 (m, 1H), 4.30-4.12 (m, 1H), 3.24-3.06 (m, 2H), 2.38 (s, 3H), 2.34 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.1, 137.7, 137.0, 136.8, 136.2, 130.9, 130.4, 129.8, 129.3, 129.2, 127.2, 126.7, 56.3, 41.7, 21.4, 21.0; HRMS (ESI) m/z calcd. for $C_{23}H_{29}N_2O_2S_2$ $[M+NH_4]^+$: 429.1665, found: 429.1661.

N-(1-(4-Chlorophenyl)-2-(p-tolylthio)ethyl)-4-methylbenzenesulfonamide (4c). Yield: 114 mg (88%); time: 20 h; white solid; m.p. 138-140 °C; TLC, R_f = 0.34 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, 2H, J = 8.0 Hz), 7. 18-7.08 (m, 6H), 7.05 (d, 2H, J = 8.0 Hz), 7.00 (d, 2H, J = 8.4 Hz), 5.40 (s, 1H), 4.26 -4.16 (m, 1H), 3.14-3.00 (m, 2H), 2.39 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.4, 137.7, 137.5, 136.6, 133.7, 131.3, 129.9, 129.8, 129.4, 128.6, 128.3, 127.2, 55.8, 41.9, 21.5, 21.1; HRMS (ESI) m/z calcd. for $C_{22}H_{26}ClN_2O_2S_2$ $[M+NH_4]^+$: 449.1119, found: 449.1121.

N-(1-(2-Chlorophenyl)-2-(p-tolylthio)ethyl)-4-methylbenzenesulfonamide (4d). Yield: 119.6 mg (92%); time: 5 h; white solid; m.p. 88-90 °C; TLC, R_f = 0.35 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, 2H, J = 8.4 Hz), 7. 39-7.33 (m, 1H), 7.23-7.18 (m, 1H), 7.16-7.09 (m, 4H), 7.08-7.03 (m, 2H), 7.00 (d, 2H, J = 8.0 Hz), 5.65 (d, 1H, J = 4.8 Hz), 4.76-4.68 (m, 1H), 3.28-3.19 (m, 1H), 3.02-2.93 (m, 1H), 2.36 (s, 3H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.2, 136.9, 136.8, 136.1, 132.0, 130.8, 129.7, 129.6, 129.5, 129.3, 128.8, 127.2, 126.9, 53.4, 40.1, 21.4, 21.0; HRMS (ESI) m/z calcd. for $C_{22}H_{26}ClN_2O_2S_2$ $[M+NH_4]^+$: 449.1119, found: 449.1113.

N-(1-(4-Bromophenyl)-2-(p-tolylthio)ethyl)-4-methylbenzenesulfonamide (4e). Yield: 88 mg (63%); time: 8 h; white solid; m.p. 138-140 °C; TLC, R_f = 0.30 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, 2H, J = 8.0 Hz), 7. 32-7.26 (m, 2H), 7.16-7.08 (m, 4H), 7.05 (d, 2H, J = 8.4 Hz), 6.97-6.91 (m, 2H), 5.34 (d, 1H, J = 4.4 Hz), 4.23-4.16 (m, 1H), 3.13-2.99 (m, 2H), 2.40 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.5, 138.2, 137.5, 136.6, 131.6, 131.4, 130.0, 129.7, 129.4, 128.6, 127.2, 121.9, 55.9, 41.9, 21.5, 21.1; HRMS (ESI) m/z calcd. for $C_{22}H_{26}BrN_2O_2S_2$ $[M+NH_4]^+$: 495.0593, found: 495.0591.

N-(1-(3-Bromophenyl)-2-(p-tolylthio)ethyl)-4-methylbenzenesulfonamide (4f). Yield: 117.6 mg (84%); time: 6 h; white solid; m.p. 95-97 °C; TLC, R_f = 0.34 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, 2H, J = 8.4 Hz), 7.29-7.25 (m, 1H), 7.12 (d, 4H, J = 8.0 Hz), 7.09-7.01 (m, 5H), 5.65 (d, 1H, J = 4.8 Hz), 4.28-4.19 (m, 1H), 3.13-3.00 (m, 2H), 2.38 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.4, 141.4, 137.4, 136.6, 131.3, 130.8, 129.93, 129.89, 129.8, 129.3, 127.1, 125.6, 122.4, 56.0, 41.7, 21.5, 21.0; HRMS (ESI) m/z calcd. for $C_{22}H_{26}BrN_2O_2S_2$ $[M+NH_4]^+$: 493.0614, found: 493.0609.

4-Methyl-N-(1-(naphthalen-2-yl)-2-(p-tolylthio)ethyl)benzenesulfonamide (4g). Yield: 89.3 mg (66%); time: 4 h; white solid; m.p. 118-120 °C; TLC, R_f = 0.31 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.73 (m, 1H), 7.68-7.62 (m, 2H), 7.52-7.41 (m, 5H), 7.23-7.11 (m, 3H), 7.05 (d, 2H, J = 7.6 Hz), 6.98 (d, 2H, J = 8.0 Hz), 5.53 (d, 1H, J = 4.8 Hz), 4.49-4.41(m, 1H), 3.22 (d, 2H, J = 7.2 Hz), 2.33 (s, 3H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.2, 137.2, 136.8, 136.3, 132.95, 132.91, 131.2, 130.2, 129.9, 129.2, 128.4, 127.8, 127.5, 127.2, 126.3, 126.12, 126.07, 124.3, 56.7, 41.8, 21.3, 21.0; HRMS (ESI) m/z calcd. for $C_{26}H_{29}N_2O_2S_2$ $[M+NH_4]^+$: 465.1665, found: 465.1663.

N-(1,2-Diphenyl-2-(p-tolylthio)ethyl)-4-methylbenzenesulfonamide (4h). Yield: 104.0 mg (76%); time: 6 h; white solid; m.p. 146-148 °C; TLC, R_f = 0.30 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, 2H, J = 8.4 Hz), 7.24-7.11 (m, 4H), 7.10-6.92 (m, 10H), 6.79 (d, 2H, J = 7.2 Hz), 5.48 (d, 1H, J = 8.0 Hz), 4.80-4.71 (m, 1H), 4.33 (d, 1H, J = 5.6 Hz), 2.32 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.9, 137.5, 137.4, 137.12, 137.09, 132.4, 130.3, 129.6, 129.1, 128.8, 128.3, 127.8, 127.7, 127.57, 127.54, 127.1, 61.3, 61.0, 21.4, 21.0; HRMS (ESI) m/z calcd. for $C_{28}H_{31}N_2O_2S_2$ $[M+NH_4]^+$: 491.1821, found: 491.1819.

4-Methyl-N-(1-phenyl-2-(p-tolylthio)propyl)benzenesulfonamide (4i). Yield: 108.7 mg (93%); time: 8 h; colourless oil; TLC, R_f = 0.37 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz, two isomers ratio: 2:1): δ 7.50 (d, 1.36H, J = 8.0 Hz), 7.43 (d, 0.64H, J = 8.0 Hz), 7.23 (d, 0.74H, J = 8.4 Hz), 7.19-7.00 (m, 10.3H), 5.86 (s, 0.34H), 5.46 (d, 0.68H, J = 6.0 Hz), 4.44-4.37 (m, 0.69H), 4.13-4.07 (m, 0.34H), 3.42-3.32 (m, 0.68H), 3.24-3.14 m, 0.35H), 2.34 (d, 6H, J = 6.4 Hz), 1.15 (d, 2H, J = 7.2 Hz), 1.02 (d, 1H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.0, 137.7, 137.5, 137.0, 134.3, 132.7, 130.0, 129.9, 129.8, 129.2, 129.1, 128.1, 128.0, 127.7, 127.6, 127.5, 127.4, 127.2, 61.6, 60.2, 51.1, 49.5, 21.4, 21.14, 21.12, 18.4, 16.7; HRMS (ESI) m/z calcd. for $C_{23}H_{29}N_2O_2S_2$ $[M+NH_4]^+$: 429.1665, found: 429.1666.

4-Methyl-N-(3-oxo-1,3-diphenyl-2-(p-tolylthio)propyl)benzenesulfonamide (4j). Yield: 135.0 mg (90%); time: 18 h; white solid; m.p. 117-119 °C; TLC, R_f = 0.30 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, 4H, J = 7.6 Hz), 7.66 (t, 1H, J = 7.2 Hz), 7.48 (t, 2H, J = 7.6 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.30-7.22 (m, 9H), 7.02 (d, 1H, J = 7.6 Hz), 5.29-5.21 (m, 1H), 4.97 (d, 1H，J = 5.2 Hz), 2.54 (s, 3H), 2.52 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.0, 142.6, 139.2, 138.1, 137.8, 136.0, 134.3, 133.5, 129.9, 129.1, 129.0, 128.4, 128.3, 128.2, 127.5, 127.04, 126.95, 59.9, 57.2, 21.3, 21.1; HRMS (ESI) m/z calcd. for $C_{29}H_{31}N_2O_3S_2$ $[M+NH_4]^+$: 519.1771, found: 519.1775.

N-(3-(4-Methoxyphenyl)-3-oxo-1-phenyl-2-(p-tolylthio)propyl)-4-methylbenzenesulfonamide (4k). Yield: 91 mg (88%); time: 18 h; colorless oil; TLC, R_f = 0.28 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59-7.50 (m, 4H), 7.21-7.15 (m, 2H), 7.11-6.97 (m, 9H), 6.89 (d, 1H, J = 7.6 Hz), 6.73 (d, 2H, J = 8.8 Hz), 5.03-4.95 (m, 1H), 4.70 (d, 1H, J = 4.4 Hz), 3.79 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.7, 163.9, 142.6, 139.1, 138.4, 138.0, 134.3, 130.8, 130.0, 129.5, 129.0, 128.9, 128.2, 127.4, 127.1, 126.9, 113.7, 60.1, 56.8, 55.4, 21.4, 21.2; HRMS (ESI) m/z calcd. for $C_{30}H_{33}N_2O_4S_2$ $[M+NH_4]^+$: 549.1876, found: 549.1888.

4-Methyl-N-(3-(naphthalen-2-yl)-3-oxo-1-phenyl-2-(p-tolylthio)propyl)benzenesulfonamide (4l). Yield: 83 mg (75%); time: 24 h; colorless oil; TLC, R_f = 0.35 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (s, 1H), 7.78 (d, 1H, J = 8.0 Hz), 7.73 (s, 2H), 7.63 (d, 1H, J = 8.0 Hz), 7.59-7.51 (m, 3H), 7.49-7.43 (m, 1H), 7.15 (d, 2H, J = 8.0 Hz), 7.12-6.98 (m, 9H), 6.87 (d, 1H, J = 8.8 Hz), 5.17-5.09 (m, 1H), 4.88 (d, 1H, J = 4.8 Hz), 2.29 (s, 3H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 196.8, 142.7, 139.3, 138.2, 137.9, 135.6, 134.6, 133.4, 132.0, 130.5, 130.0, 129.6, 129.5, 129.0, 128.8, 128.3, 127.6, 127.5, 127.09, 127.06, 126.7, 123.8, 60.2, 57.5, 21.3, 21.1; HRMS (ESI) m/z calcd. for $C_{33}H_{33}N_2O_3S_2$ $[M+NH_4]^+$: 569.1927, found: 569.1912.

4-Methyl-N-(3-oxo-3-phenyl-1-(p-tolyl)-2-(p-tolylthio)propyl)benzenesulfonamide (4m). Yield: 76 mg (75%); time: 28 h; white solid; m.p. 136-138 °C; TLC, R_f = 0.36 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.53 (m, 4H), 7.47 (t, 1H, J = 7.2 Hz), 7.33-7.26 (m, 2H), 7.16 (d, 2H, J = 8.0 Hz), 7.11-7.01 (m, 4H), 6.98-6.82 (m, 4H), 6.76-6.64 (m, 1H), 5.00 (s, 1H), 4.82-4.69 (m, 1H), 2.33 (s, 6H), 2.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.0, 142.6, 139.1, 138.0, 137.2, 136.1, 135.1, 134.3, 133.4, 129.9, 129.2, 129.0, 128.9, 128.40, 128.38, 127.1, 126.9, 59.8, 57.2, 21.3, 21.2, 20.9; HRMS (ESI) m/z calcd. for $C_{30}H_{33}N_2O_3S_2$ $[M+NH_4]^+$: 533.1927, found: 533.1933.

N-(1-(4-Chlorophenyl)-3-oxo-3-phenyl-2-(p-tolylthio)propyl)-4-methylbenzenesulfonamide (4n). Yield: 93 mg (86%); time: 28 h; colorless oil; TLC, R_f = 0.34 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (d, 2H, J = 7.6 Hz), 7.55-7.44 (m, 3H), 7.35-7.27 (m, 2H), 7.20-6.90 (m, 10H), 6.82-6.65 (m, 1H), 5.50-4.93 (m, 1H), 4.71 (d, 1H, J = 4.8 Hz), 2.34 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 196.4, 143.0, 139.3, 137.6, 136.6, 135.8, 134.4, 133.6, 133.4, 130.0, 129.1, 128.7, 128.6, 128.5, 128.4, 128.3, 127.0, 59.3, 56.8, 21.3, 21.1; HRMS (ESI) m/z calcd. for $C_{29}H_{30}ClN_2O_3S_2$ $[M+NH_4]^+$: 533.1381, found: 533.1387.

Methyl 3-(4-methylphenylsulfonamido)-3-phenyl-2-(p-tolylthio)propanoate (4o). Yield: 128.4 mg (94%); time: 17 h;

white solid; m.p. 136-138 °C; TLC, R_f = 0.39 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, 2H, J = 8.4 Hz), 7.22 (d, 2H, J = 8.0 Hz), 7.18-7.11 (m, 3H), 7.08 (t, 4H, J = 7.6 Hz), 7.04-7.00 (m, 2H), 6.29-6.20 (m, 1H), 4.89-4.83 (m, 1H), 3.84 (d, 1H, J = 5.6 Hz), 3.51 (s, 3H), 2.33 (d, 6H, J = 4.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.0, 142.9, 138.8, 137.71, 137.68, 137.7, 133.6, 129.9, 129.2, 129.1, 129.2, 128.4, 127.8, 127.1, 126.6, 59.0, 57.4, 52.4, 21.4, 21.1; HRMS (ESI) m/z calcd. for $C_{24}H_{29}N_2O_4S_2$ $[M+NH_4]^+$: 473.1563, found: 473.1563.

4-Methyl-N-(1-(p-tolylthio)octan-2-yl)benzenesulfonamide (4p). Yield: 92.0 mg (77%); time: 18 h; colorless oil; TLC, R_f = 0.48 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, 2H, J = 8.4 Hz), 7.21 (d, 2H, J = 8.0 Hz), 7.16 (d, 2H, J = 8.0 Hz), 7.07 (d, 2H, J = 8.0 Hz), 4.93 (d, 1H, J = 8.0 Hz), 3.37-3.25 (m, 1H), 3.12-3.02 (m, 1H), 2.79-2.69 (m, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 1.68-1.56 (m, 1H), 1.45-1.32 (m, 1H), 1.23-0.96 (m, 8H), 0.83 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.2, 137.5, 136.6, 131.5, 130.5, 129.7, 129.5, 127.0, 52.9, 39.9, 33.5, 31.5, 28.7, 25.1, 22.4, 21.4, 21.0, 14.0; HRMS (ESI) m/z calcd. for $C_{22}H_{32}NO_2S_2$ $[M+H]^+$: 406.1869, found: 406.1877.

4-Methyl-N-(2-(p-tolylthio)cyclohexyl)benzenesulfonamide (4q). Yield: 82.2 mg (73%); time: 14 h; white solid; m.p. 90-92 °C; TLC, R_f = 0.40 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, 2H, J = 8.4 Hz), 7.29 (d, 2H, J = 8.0 Hz), 7.15 (d, 2H, J = 8.0 Hz), 7.05 (d, 2H, J = 8.0 Hz), 5.36 (d, 1H, J = 4.0 Hz), 3.00-2.88 (m, 1H), 2.85-2.74 (m, 1H), 2.44 (s, 3H), 2.33 (s, 3H), 2.32-2.24 (m, 1H), 2.04-1.94 (m, 1H), 1.65-1.52 (m, 2H), 1.34-1.16 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.3, 138.0, 137.2, 133.9, 129.7, 129.6, 128.5, 127.3, 55.3, 51.8, 32.5, 31.8, 24.8, 23.4, 21.5, 21.1; HRMS (ESI) m/z calcd. for $C_{20}H_{26}NO_2S_2$ $[M+H]^+$: 376.1399, found: 376.1398.

3-(2-(*p*-Tolylthio)-1-(*p*-tosylamino)ethyl)-1,3,5(10)-estratrien-17-one (4r). Yield: 120 mg (70%); time:6 h; colorless oil; TLC, R_f = 0.36 (PE:EtOAc = 7:3); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (dd, 2H, J = 8.0, 4.4 Hz), 7.15-7.09 (m, 5H), 7.05 (d, 2H, J = 8.0 Hz), 6.85 (t, 1H, J = 6.0 Hz), 6.74 (s, 1H), 5.32 (dd, 1H, J = 6.8, 4.8 Hz), 4.24-4.16 (m, 1H), 3.14 (dd, 2H, J = 6.8, 3.6 Hz), 2.78-2.66 (m, 2H), 2.51 (dd, 1H, J = 9.4, 8.8 Hz), 2.38 (s, 3H), 2.33 (s, 3H), 2.26-1.95 (m, 6H), 1.68-1.30 (m, 5H), 0.91 (d, 3H, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 220.7, 143.0, 139.5, 137.0, 136.9, 136.5, 136.4, 131.0, 130.9, 130.4, 129.8, 129.2, 127.4, 127.3, 125.4, 124.3, 56.2, 50.4, 47.9, 44.3, 41.6, 38.0, 35.8, 31.5, 29.2, 26.4, 25.6, 21.6, 21.5, 21.0, 13.8. HRMS (ESI) m/z calcd. for $C_{34}H_{39}NO_3S_2Na$ $[M+Na]^+$: 596.2264, found: 596.2261.

(5*R*)-5-(1-(*p*-Tolylthio)-2-(*p*-tosylamino)propan-2-yl)-2-methylcyclohex-2-en-1-one (4s). Yield: 113 mg (85%); time: 3 h; colorless oil; TLC, R_f = 0.40 (PE:EtOAc = 7:3) ; ^{1}H NMR ($CDCl_3$, 400 MHz, two isomers): δ 7.15 (d, 1H, J = 8.4 Hz), 7.78 (d, 1H, J = 8.0 Hz), 7.24-7.14 (m, 4H), 7.11-7.05 (m, 2H), 6.66 (dd, 1H, J = 28.4, 6.0 Hz), 5.52 (d, 1H, J = 30.0 Hz), 3.14 (d, 0.5H, J = 13.2 Hz), 3.08 (s, 1H), 2.93 (d, 0.5H, J = 13.2 Hz), 2.60-2.40 (m, 2H), 2.39 (d, 3H, J = 2.4 Hz), 2.35-2.29 (m, 4H), 2.20-2.05 (m, 2H), 1.74 (s, 3H), 1.19 (d, 3H, J = 4.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.8 (198.4), 144.6, 143.9, 143.3 (143.2), 139.7 (139.6), 137.1 (137.0), 135.4 (135.3), 131.9 (131.8), 131.0, 130.9, 129.9, 129.6, 127.0 (126.9), 61.1 (61.0), 44.9 (44.8), 42.8, 42.5, 38.9 (38.8), 26.9 (26.7), 21.5, 21.0, 19.8, 19.6, 15.5. HRMS (ESI) m/z calcd. for $C_{24}H_{30}NO_3S_2$ $[M+H]^+$: 444.1662, found: 444.1651.

3-(p-Tolylthio)-1-tosylpyrrolidine (8). Yield: 96.8 mg (93%); time: 6 h; colorless oil; TLC, R_f = 0.46 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (d, 2H, J = 8.4 Hz), 7.32 (d, 2H, J = 8.0 Hz), 7.21-7.15 (m, 2H), 7.09 (d, 2H, J = 8.0 Hz), 3.68-3.60 (m, 1H), 3.58-3.49 (m, 1H), 3.36 (t, 2H, J = 7.2 Hz), 3.14-3.07 (m, 1H), 2.44 (s, 3H), 2.33 (s, 3H), 2.20-2.09 (m, 1H), 1.81-1.70 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.6, 137.9, 133.7, 132.6, 130.0, 129.9, 129.7, 127.6, 53.7, 46.9, 45.2, 31.8, 21.6, 21.1; HRMS (ESI) m/z calcd. for $C_{18}H_{22}NO_2S_2$ $[M+H]^+$: 348.1086, found: 348.1098.

2-((p-Tolylthio)methyl)-1-tosylpyrrolidine (9). Yield: 104.0 mg (96%); time: 5 h; white solid; m.p. 78-80 °C; TLC, R_f = 0.46 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, 2H, J = 8.4 Hz), 7.39-7.33 (m, 2H,), 7.23 (d, 2H, J = 8.0 Hz), 7.16 (d, 2H, J = 8.0 Hz), 3.68-3.55 (m, 2H), 3.51-3.44 (m, 1H), 3.14-3.04 (m, 1H), 2.79-2.68 (m, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 1.94-1.73 (m, 2H), 1.68-1.61 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.4, 136.2, 133.9, 131.6, 129.8, 129.7, 129.6, 127.5, 59.0, 49.7, 39.0, 30.2, 27.8, 21.5, 21.1; HRMS (ESI) m/z calcd. for $C_{19}H_{24}NO_2S_2$ $[M+H]^+$: 362.1243, found: 362.1247.

4-Methyl-N-(1-phenyl-2-(phenylthio)ethyl)benzenesulfonamide (4t). Yield: 105.3mg (91%); time: 6 h; white solid; m.p. 104-106 °C; TLC, R_f = 0.36 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (d, 2H, J = 8.4 Hz), 7.26-7.18 (m, 8H), 7.12 (d, 2H, J = 8.0 Hz), 7.10-7.05 (m, 2H), 5.33 (s, 1H), 4.35-4.23 (m, 1H), 3.27-3.13 (m, 2H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.3, 139.1, 136.7, 134.1, 130.3, 129.4, 129.1, 128.6, 128.0, 127.2, 126.83, 126.77, 56.5, 41.1, 21.5; HRMS (ESI) m/z calcd. for $C_{21}H_{25}N_2O_2S_2$ $[M+NH_4]^+$: 401.1352, found: 401.1350.

N-(2-((4-Methoxyphenyl)thio)-1-phenylethyl)-4-methylbenzenesulfonamide (4u). Yield: 112.4 mg (90%); time: 16 h; yellow solid; m.p. 113-115 °C; TLC, R_f = 0.36 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (d, 2H, J = 8.4 Hz), 7.22-7.15 (m, 5H), 7.12 (d, 2H, J = 8.0Hz), 7.08-7.02 (m, 2H), 6.82-6.76 (m, 2H), 5.44 (s, 1H), 4.26-4.17 (m, 1H), 3.81 (s, 3H), 3.07 (d, 2H, J = 6.8 Hz), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.4, 143.1, 139.2, 136.8, 134.0, 129.3, 128.4, 127.8, 127.2, 126.8, 124.1, 114.7, 56.5, 55.3, 43.1, 21.4; HRMS (ESI) m/z calcd. for $C_{22}H_{27}N_2O_3S_2$ $[M+NH_4]^+$: 431.1458, found: 431.1466.

N-(2-((4-Chlorophenyl)thio)-1-phenylethyl)-4-methylbenzenesulfonamide (4v). Yield: 84.0 mg (68%); time: 20 h; white solid; m.p. 128-130 °C; TLC, R_f = 0.33 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (d, 2H, J = 8.4 Hz), 7.24-7.18 (m, 5H), 7.17-7.10 (m, 4H), 7.08-7.02 (m, 2H), 5.25-5.14 (m, 1H), 4.30-4.20 (m, 1H), 3.28-3.13 (m, 2H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.5, 138.9, 136.6, 133.0, 132.6, 131.7, 129.4, 129.2, 128.7, 128.2, 127.2, 126.7, 56.4, 41.3, 21.5; HRMS (ESI) m/z calcd. for $C_{21}H_{24}ClN_2O_2S_2$ $[M+NH_4]^+$: 435.0962, found: 435.0957.

N-(2-((2-Bromophenyl)thio)-1-phenylethyl)-4-methylbenzenesulfonamide (4w). Yield: 100.0 mg (73%); time: 18 h; white solid; m.p. 128-130 °C; TLC, R_f = 0.33 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (t, 3H, J = 5.2 Hz), 7.25-7.18 (m, 5H), 7.16-7.09 (m, 4H), 7.08-7.02 (m, 1H), 5.33-5.24 (m, 1H), 4.42-4.32 (m, 1H), 3.25 (d, 2H, J = 6.8 Hz), 2.35 (s, 3H); ^{13}C

NMR ($CDCl_3$, 100 MHz): δ 143.3, 139.0, 136.6, 135.5, 133.2, 129.7, 129.4, 128.7, 128.1, 127.8, 127.6, 127.1, 126.7, 124.8, 56.2, 40.1, 21.5; HRMS (ESI) m/*z* calcd. for $C_{21}H_{24}BrN_2O_2S_2$ $[M+NH_4]^+$: 479.0457, found: 479.0449.

4-Methyl-N-(2-(naphthalen-2-ylthio)-1-phenylethyl)benzenesulfonamide (4x). Yield: 87.0 mg (67%); time: 5 h; white solid; m.p. 118-120 °C; TLC, R_f = 0.40 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84-7.78 (m, 1H), 7.76-7.69 (m, 2H), 7.68-7.65 (m, 1H), 7.55-7.44 (m, 4H), 7.29 (dd, 1H, *J* = 8.0, 2.0 Hz), 7.25-7.19 (m, 3H), 7.14-7.07 (m, 2H), 6.97 (d, 2H, *J* = 8.0 Hz), 5.41 (d, 1H, *J* = 4.8 Hz), 4.39-4.28 (m, 1H), 3.40-3.24 (m, 2H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.2, 139.1, 136.4, 133.6, 132.0, 131.5, 129.3, 128.64, 128.60, 128.3, 128.1, 127.7, 127.5, 127.2, 127.1, 126.8, 126.7, 126.1, 56.5, 40.7, 21.3; HRMS (ESI) m/*z* calcd. for $C_{25}H_{27}N_2O_2S_2$ $[M+NH_4]^+$: 451.1508, found: 451.1503.

N-(2-(Ethylthio)-1-phenylethyl)-4-methylbenzenesulfonamide (4y). Yield: 67 mg (67%); time: 18 h; colorless oil; TLC, R_f = 0.44 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (d, 2H, *J* = 8.4 Hz), 7.22-7.16 (m, 4H), 7.16-7.10 (m, 3H), 5.57 (d, 1H, *J* = 4.8 Hz), 4.40-4.30 (m, 1H), 2.91-2.71 (m, 2H), 2.37 (s, 3H), 2.32-2.18 (m, 2H), 1.12 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.2, 139.6,136.9, 129.3, 128.4, 127.7, 127.2, 126.7, 56.4, 38.8, 25.7, 21.4, 14.3; HRMS (ESI) m/*z* calcd. for $C_{17}H_{25}N_2O_2S_2$ $[M+NH_4]^+$: 353.1352, found: 353.1368.

N-(1-Phenyl-2-(p-tolylthio)ethyl)benzenesulfonamide (4z). Yield: 91.0 mg (80%); time: 10 h; yellow solid; m.p. 86-88 °C; TLC, R_f = 0.36 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, 2H, *J* = 8.4 Hz), 7.46 (t, 1H, *J* = 7.2Hz), 7.32 (t, 2H, *J* = 7.6 Hz), 7.21-7.11 (m, 5H), 7.10-7.02 (m, 4H), 5.62-5.46 (m, 1H), 4.35-4.26 (m, 1H), 3.15 (d, 2H, *J* = 6.8 Hz), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.8, 139.0, 137.2, 132.3, 131.2, 130.2, 129.9, 128.7, 128.5, 127.9, 127.1, 126.8, 55.6, 41.9, 21.0; HRMS (ESI) m/*z* calcd. for $C_{21}H_{25}N_2O_2S_2$ $[M+NH_4]^+$: 401.1352, found: 401.1362.

4-Nitro-N-(1-Phenyl-2-(p-tolylthio)ethyl)benzenesulfonamide (4aa). Yield: 91.0 mg (71%); time: 12 h; yellow solid; m.p. 148-150 °C; TLC, R_f = 0.31 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (d, 2H, *J* = 8.8 Hz), 7.68 (d, 2H, *J* = 8.8 Hz), 7.22-7.13 (m, 5H), 7.12-7.02 (m, 4H), 5.68-5.59 (m, 1H), 4.39-4.30 (m, 1H), 3.26-3.16 (m, 1H), 3.09-2.98 (m, 1H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.6, 145.6, 138.5, 137.7, 130.9, 130.1, 129.5, 128.7, 128.3, 126.9, 123.7, 55.5, 41.5, 21.0; HRMS (ESI) m/*z* calcd. for $C_{21}H_{24}N_3O_4S_2$ $[M+NH_4]^+$: 446.1203, found: 446.1197.

N-(1-Phenyl-2-(p-tolylthio)ethyl)methanesulfonamide ***(4bb)***. Yield: 79.6 mg (83%); time: 8 h; yellow solid; m.p. 75-77 °C; TLC, R_f = 0.36 (PE:EtOAc = 8:2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.27 (m, 7H), 7.13 (d, 2H, *J* = 8.0 Hz), 5.45 (s, 1H), 4.55-4.46 (m, 1H), 3.30-3.22 (m, 1H), 3.18-3.08 (m, 1H), 2.62 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.8, 137.5, 131.3, 130.0，128.9, 128.4, 126.9, 56.6, 42.1, 41.8, 21.0; HRMS (ESI) m/*z* calcd. for $C_{16}H_{23}N_2O_2S_2$ $[M+NH_4]^+$: 339.1195, found: 339.1196.

Preparation of 3-phenyl-4-tosyl-3,4-dihydro-2*H*-benzo[*b*][1,4]thiazine. To a solution of olefin (0.20 mmol, 1.0 equiv) and 1-((2-bromophenyl)thio)pyrrolidine-2,5-dione (0.30 mmol, 1.5 equiv) in toluene (0.5 mL) was added TfOH (0.04 mmol, 0.2 equiv) dropwise at room temperature. The reaction mixture was stirred at 60 °C for 2 h and a solution of copper powder (0.22 mmol, 1.1 equiv) in DMF (1.0 mL) was then added. After stirring for another 12 h at 120 °C under argon, the resulting mixture was cooled to room temperature, washed with water, and extracted with ethyl acetate (3 × 10 mL), and dried over anhydrous Na_2SO_4. The organic solvent was removed under reduced pressure, and the crude product was purified by flash chromatography (Eluent: PE/EtOAc = 20:1).

3-Phenyl-4-tosyl-3,4-dihydro-2H-benzo[b][1,4]thiazine ***(11a)***. Yield: 54.6 mg (72%); time: 14 h; white solid; m.p. 119-121 °C; TLC, R_f = 0.36 (PE:EtOAc = 20:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, 1H, *J* = 8.0 Hz), 7.46-7.37 (m, 4H), 7.34-7.27 (m, 2H), 7.26-7.15 (m, 4H), 7.12-7.05 (m, 2H), 5.73 (t, 1H, *J* = 6.8 Hz), 3.26-3.18 (m, 1H), 3.03-2.95 (m, 1H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.7, 139.8, 136.1, 134.5, 132.2, 130.0, 129.4, 128.6, 128.2, 127.6, 127.4, 126.4, 126.3, 126.1, 60.8, 34.5, 21.6; HRMS (ESI) m/*z* calcd. for $C_{21}H_{23}N_2O_2S_2$ $[M+NH_4]^+$: 399.1195, found: 399.1198.

3-(p-Tolyl)-4-tosyl-3,4-dihydro-2H-benzo[b][1,4]thiazine (11b). Yield: 44.2 mg (56%); time: 16 h; white solid; m.p. 138-140 °C;TLC, R_f = 0.34 (PE:EtOAc = 20:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, 1H, *J* = 8.0 Hz), 7.43 (d, 2H, *J* = 8.4 Hz), 7.28 (d, 2H, *J* = 8.0 Hz), 7.21-7.15 (m, 3H), 7.12-7.06 (m, 4H), 5.70 (t, 1H, *J* = 6.4 Hz), 3.24-3.16 (m, 1H), 3.04-2.95 (m, 1H), 2.40 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.7, 137.3, 136.7, 136.2, 134.4, 132.0, 129.9, 129.4, 129.3, 128.1, 127.4, 126.4, 126.3, 126.0, 60.2, 34.1, 21.6, 21.0; HRMS (ESI) m/*z* calcd. for $C_{22}H_{22}NO_2S_2$ $[M+H]^+$: 396.1086, found: 396.1084.

3-(2-Chlorophenyl)-4-tosyl-3,4-dihydro-2H-benzo[b][1,4]thiazine (11c). Yield: 59.6 mg (74%); time: 14 h; white solid; m.p. 169-171 °C; TLC, R_f = 0.35 (PE:EtOAc = 20:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (d, 1H, *J* = 8.4 Hz), 7.53 (d, 1H, *J* = 7.6 Hz), 7.44-7.31 (m, 4H), 7.29-7.22 (m, 2H), 7.22-7.14 (m, 4H), 5.97-5.90 (m, 1H), 3.40-3.31 (m, 1H), 2.64-2.54 (m, 1H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.7, 139.5, 136.5, 135.11, 135.08, 131.3, 130.2, 129.6, 129.4, 129.3, 128.9, 127.6, 127.5, 127.2, 126.6, 62.8, 37.1, 21.6; HRMS (ESI) m/*z* calcd. for $C_{21}H_{22}ClN_2O_2S_2$ $[M+NH_4]^+$: 433.0806, found: 433.0799.

3-(3-Bromophenyl)-4-tosyl-3,4-dihydro-2H-benzo[b][1,4]thiazine (11d). Yield: 62.5 mg (71%); time: 12 h; white solid; m.p. 140-142 °C; TLC, R_f = 0.34 (PE:EtOAc = 20:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85-7.81 (m, 1H), 7.54-7.50 (m, 1H), 7.43-7.31 (m, 4H), 7.26-7.15 (m, 4H), 7.14-7.07 (m, 2H), 5.69-5.62 (m, 1H), 3.23-3.13 (m, 1H), 2.96-2.86 (m, 1H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.9, 142.3, 135.7 134.3, 132.3, 130.8, 130.2, 130.0, 129.44, 129.43, 128.4, 127.4, 126.6, 126.4, 125.0, 122.7, 60.7, 34.7, 21.6; HRMS (ESI) m/*z* calcd. for $C_{21}H_{19}BrNO_2S_2$ $[M+H]^+$: 460.0035, found: 460.0031.

6-Methyl-3-phenyl-4-tosyl-3,4-dihydro-2H-benzo[b][1,4]thiazine (11e). Yield: 79 mg (91%); time: 14 h; white solid; m.p. 122-124 °C; TLC, R_f = 0.32 (PE:EtOAc = 20:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (s, 1H), 7.46-7.37 (m, 4H), 7.31 (t, 2H, *J* = 7.6 Hz), 7.26-7.21 (m, 1H), 7.18 (d, 2H, *J* = 8.4 Hz), 7.02-6.97 (m, 1H), 6.95-6.90 (m, 1H), 5.72-5.65 (m, 1H), 3.24-3.14 (m, 1H), 2.98-2.86 (m, 1H), 2.40 (s, 3H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.6, 140.2, 136.3, 136.0, 134.5, 130.5, 129.3,

129.1, 128.6, 128.0, 127.6, 127.42, 127.38, 126.3, 61.6, 35.3, 21.6, 21.2; HRMS (ESI) m/*z* calcd. for $C_{22}H_{22}NO_2S_2$ $[M+H]^+$: 396.1086, found: 396.1087.

4-(Methylsulfonyl)-3-phenyl-3,4-dihydro-2H-benzo[b][1,4]thiazine (11f). Yield: 42.0 mg (69%); time: 22 h; white solid; m.p. 99-101 °C; TLC, R_f = 0.34 (PE:EtOAc = 20:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (dd, 1H, *J* = 8.0, 1.2 Hz), 7.37-7.27 (m, 5H), 7.26-7.21 (m, 2H), 7.20-7.15 (m, 1H), 5.76-5.69 (m, 1H), 3.55-3.46 (m, 1H), 3.13-3.04 (m, 1H), 2.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.3, 135.4, 133.0, 129.8, 129.2, 128.7, 127.8, 127.2, 126.8, 126.1, 63.0, 38.3, 37.4; HRMS (ESI) m/*z* calcd. for $C_{15}H_{16}NO_2S_2$ $[M+H]^+$: 306.0617, found: 306.0607.

10-Tosyl-2,3,4,4a,10,10a-hexahydro-1H-phenothiazine (11g). Yield: 44.7mg (65%); time: 20 h; white solid, mp 116-118 °C; TLC, R_f = 0.34 (PE:EtOAc = 20:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, 1H, *J* = 8.0 Hz), 7.25-7.18 (m, 3H), 7.13-7.05 (m, 4H), 3.92-3.80 (m, 1H), 2.62-2.53 (m, 1H), 2.49-2.40 (m, 1H), 2.35 (s, 3H), 2.10-1.99 (m, 1H), 1.88-1.72 (m, 2H), 1.60-1.35 (m, 3H), 1.30-1.15 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.3, 136.0, 135.5, 134.6, 130.3, 129.4, 128.9, 127.4, 126.6, 126.2, 70.2, 51.8, 36.3, 31.7, 25.6, 24.8, 21.5; HRMS (ESI) m/*z* calcd. for $C_{19}H_{22}NO_2S_2$ $[M+H]^+$: 360.1086, found: 360.1079.

Preparation of 1-phenyl-2-(*p*-tolylthio)ethanamine (13).[1c] To a stirred mixture of **4y** (64.6 mg, 0.15 mmol), K_2CO_3 (84 mg, 0.6 mmol) and DMSO (0.1 mL) in CH_3CN (3.0 mL) was added PhSH (0.1 mL). Upon stirring at 50 °C for 6 h, the resulting mixture was concentrated to remove CH_3CN, washed with saturated aq. NH_4Cl and brine, extracted with CH_2Cl_2 (3 × 10 mL), and dried over anhydrous Na_2SO_4. After the organic solvent was removed under reduced pressure, the crude product was purified by flash chromatography (Eluent: PE/EtOAc = 7:3) to give **13**. Yield: 36.2 mg (99%); time: 6 h; colorless oil; TLC, R_f = 0.28 (PE:EtOAc = 7:3); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32-7.25 (m, 6H), 7.24 (m, 1H), 7.11 (d, 2H, *J* = 8.0 Hz), 4.04 (dd, 1H, *J* = 9.6, 3.6 Hz), 3.28-3.21 (m, 1H,), 3.01-2.90 (m, 1H), 2.31 (s, 3H), 1.88 (brs, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.2, 136.5, 131.8, 130.5, 129.8, 128.5, 127.4, 126.4, 54.5, 44.5, 21.0.

Preparation of 3-phenyl-3,4-dihydro-2H-benzo[*b*][1,4]thiazine (14).[16] To a solution of sodium (32.2 mg, 1.4 mmol) in dry THF (2.0 mL) was added naphthalene (167.0 mg, 1.30 mmol) in dry THF (2.0 mL) and stirred at room temperature for 4 h. **11a** (76.0 mg, 0.20 mmol) in dry THF (2.0 mL) was subjected to the above mentioned solution of sodium naphthalide at -78 °C. After complete disappearance of starting materials (monitored by TLC), the reaction was quenched with saturated aq. NH_4Cl and extracted with ethyl acetate (3 × 10 mL). After thhe combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the crude product was purified by flash chromatography (Eluent: PE/EtOAc = 50:1). Yield: 38.6 mg (85%); time: 2 h; colorless oil; TLC, R_f = 0.40 (PE:EtOAc = 50:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44-7.31 (m, 5H), 7.08 (dd, 1H, *J* = 7.6, 1.2 Hz), 6.98-6.91 (m, 1H), 6.72-6.63 (m, 1H), 6.54 (d, 1H, *J* = 8.0 Hz), 4.68 (dd, 1H, *J* = 8.8, 2.8 Hz), 4.16 (s, 1H), 3.24-3.12 (m, 1H), 3.06-2.98 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.8, 142.2, 128.9, 128.2, 127.4, 126.7, 125.6, 118.3, 115.4, 115.3, 56.1, 33.1.

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