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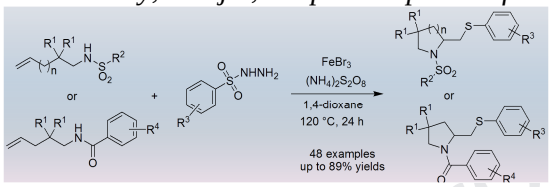

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$FeBr_3$-Catalyzed Regioselective Intramolecular Sulfenoamination of Unactivated Terminal Olefins

Lin-Chuang Zheng [a], Lin Li [a], Lili Duan, [a] Yue-Ming Li [a, b,*]

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ABSTRACT: A method for regioselective intramolecular sulfenoamination of unactivated terminal olefins was reported. Using sulfonyl hydrazides as the sulfur sources, $FeBr_3$ as the catalyst and $(NH_4)_2S_2O_8$ as the oxidant, different sulfenylmethylpyrrolidines and sulfenylmethylpiperidines were obtained in moderate to high yields via intramolecular sulfenoamination of (sulfon)amidopentenes or (sulfon)amidohexenes.

Keywords:

$FeBr_3$

Sulfenoamination

Sulfenylmethylpyrrolidine

Sulfenylmethylpiperidine

Alkenyl sulfonamide

1. Introduction

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Heterocyclic compounds such as pyrrolidines or piperidines can be widely found in natural products, agrochemicals and pharmaceuticals, and have played important roles in organic synthesis and drug synthesis [1]. In particular, interesting bioactivities could be obtained when additional heteroatoms such as sulfur atom was introduced to piperidines or pyrrolidines [2]. For example, compounds **A** and **B** showed interesting anti-inflammatory activity [3], compounds **C** were designed as monoamine transporter inhibitors [4], compound **D** can be used as anti-mycobacterial agent [5] and compound **E** can be used as TNF-α converting enzyme (TACE) inhibitor (Fig. 1) [3c].

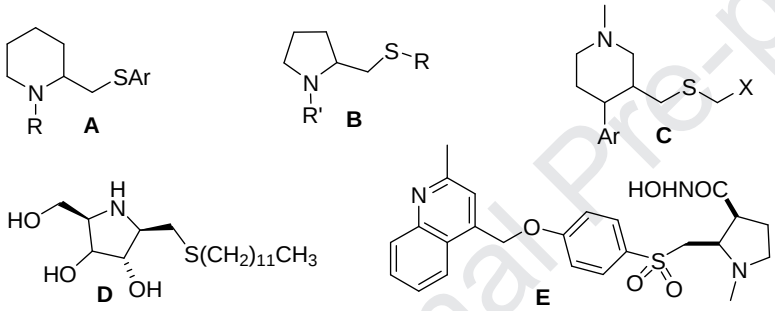

Fig. 1. Examples of Vicinal Thioamine Skeletons in Medicinal Chemistry.

So far, a number of important pharmaceutical agents bearing sulfur-based fragments in the adjacent position of the nitrogen heterocycles have been developed, and it is of high interest to find straightforward methods for the construction of sulfenylated N-heterocycles. While conventional functional group transformations have been extensively developed as general methods for the construction of heterocyclic structures, it is still highly desirable to develop new methods for the straightforward formation of functionalized piperidines and pyrrolidines. As a consequence, direct functionalization of unactivated olefins such as hydroxysulfenylation [6], alkoxysulfenylation [7], and disulfidation [8] of olefins were developed as efficient routes to various

sulfur-containing heterocycles.

Vicinal addition of amino and sulfur fragments across a C=C double bond, namely inter- or intramolecular sulfenoamination (or thioamination) allows the direct introduction of sulfur atom and nitrogen atom to C=C double bond in one step, and can be regarded as a straightforward method for the preparation of vicinal sulfenoamines. For example, progresses have been achieved on sulfenoamination [9] which allow the assembly of sulfenylated structures in a single step. Denmark et al. reported an efficient sulfenoamination protocol in which thiiranium ions were generated from arylthiophthalimides, and subsequent capture of the thiiranium ion intermediate with certain nucleophiles (Scheme 1a) furnished a variety of sulfur-containing heterocycles [10]. Zhu et al. reported a regioselective free radical 1,2- thioamidation of terminal alkenes in the presence of NFSI and thiols (Scheme 1b) [9d].

Generally, these methods will use disulfides or thiols as the sulfenylating agents. Such reagents are normally air and/or moisture sensitive, and are not always acceptable by users due to the unpleasant odor of these compounds. Therefore, it is highly desirable to develop sulfenoamination reactions using easily available sulfenylating agents as thiol surrogates. We are interested in the preparation of different functionalized heterocyclic compounds [11]. Herein, we report the sulfenoamination of unactivated terminal olefins as a continuation of our program on the synthesis of substituted piperidines and pyrrolidines (Scheme 1c).

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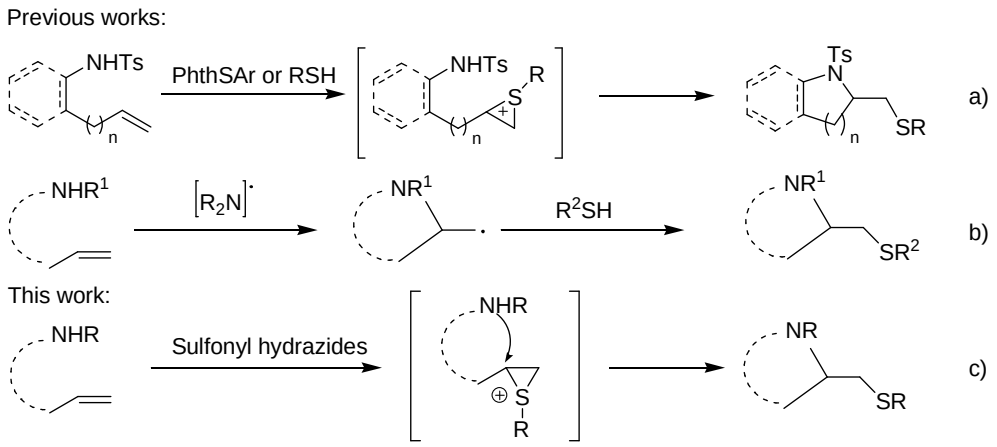


Scheme 1. Strategies for Intramolecular Sulfenoamination of Alkenes.

2. Results and Discussion

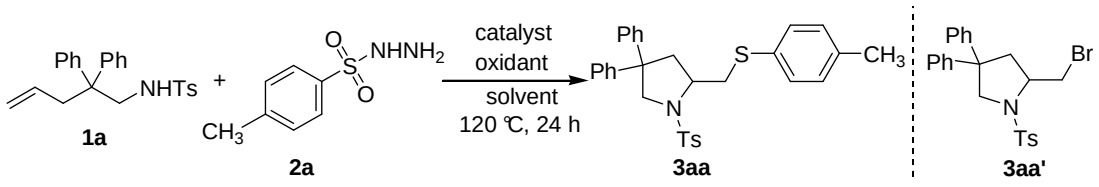
Sulfonyl hydrazides can be easily prepared via reactions of sulfonyl chlorides with hydrazine hydrate [12]. They are generally shelf-stable solids and have been found widespread application in organic synthesis [13]. Recently, these compounds are also utilized as sulfonyl sources [14] and sulfenyl sources [15] via the cleavage of N-S bond and as aryl sources through the cleavage of C-S bond under certain conditions [16]. Enlightened by these results, intramolecular sulfenoamination of unactivated terminal olefins were proposed using sulfonyl hydrazides as the electrophilic sulfenylating agents in an attempt to generate various sulfenylated N-heterocycles. Thus, N-(2,2-diphenylpent-4-en-1-yl)-4-methylbenzenesulfonamide (**1a**) and *p*-toluenesulfonyl hydrazide (**2a**) were subjected to the sulfenoamination reaction using $FeBr_3$ as the catalyst and $Na_2S_2O_8$ as the oxidant. The preliminary results are summarized in Table 1. As these results showed, in the presence of 20 mol% of $FeBr_3$ and 4 equiv of $Na_2S_2O_8$ [6e], the reaction of **1a** (0.25 mmol) and **2a** (0.5 mmol) in 1,4-dioxane at 120 °C provided the desired product in 46% yield (Table 1, entry 1).

Encouraged by this preliminary result, promoters containing different halogens were

further screened to find the most suitable reaction systems, and $FeBr_3$ still showed the best performance among the reactions (Table 1, entry 1 vs entries 2-10). A mixture of **3aa** and **3aa'** was obtained in a radio of 3 to 1 when $CuBr_2$ was used as the reaction promoter (Table 1, entry 4). The latter compound was formed possibly via the intramolecular bromoamination reaction [11a]. Various reaction media were also screened (Table 1, entry 11-14), and 1,4-dioxane was found to be the most suitable solvent for the reaction. Screening on the oxidants showed that $(NH_4)_2S_2O_8$ was the most suitable oxidant for the reaction, and the desired product **3aa** was obtained in 76% yield (Table 1, entry 16). The good performance of $(NH_4)_2S_2O_8$ may be due to its good solubility in 1,4-dioxane. Further screening on the amount of oxidant showed that no significant decrease in the yield of **3aa** was observed when the amount of $(NH_4)_2S_2O_8$ was reduced to 2 equiv (Table 1, entry 17). Lowering the reaction temperature caused the reduce of reaction rate, and prolonged reaction time was needed to get meaningful yield of the product. Reaction under argon atmosphere produced the product with similar yield, and no significant difference was observed when further increasing the amount of $FeBr_3$ (Table 1, entries 18-20) [17]. The reaction proceeded rather sluggishly in the absence of $FeBr_3$ (Table 1, entry 21).

Table 1

Optimization of the Reaction Conditions.[a]



entry	catalyst	solvent	oxidant	yield (%)[b]
1	$FeBr_3$	1,4-dioxane	$Na_2S_2O_8$	46
2	$ZnBr_2$	1,4-dioxane	$Na_2S_2O_8$	28
3	$MgBr_2$	1,4-dioxane	$Na_2S_2O_8$	16
4	$CuBr_2$	1,4-dioxane	$Na_2S_2O_8$	51 (3:1)[c]
5	MnI_2	1,4-dioxane	$Na_2S_2O_8$	trace
6	FeI_2	1,4-dioxane	$Na_2S_2O_8$	trace
7	ZnI_2	1,4-dioxane	$Na_2S_2O_8$	not detected
8	$FeCl_3$	1,4-dioxane	$Na_2S_2O_8$	34
9	$MgCl_2$	1,4-dioxane	$Na_2S_2O_8$	12
10	I_2	1,4-dioxane	$Na_2S_2O_8$	38
11	$FeBr_3$	DCE	$Na_2S_2O_8$	28
12	$FeBr_3$	DMF	$Na_2S_2O_8$	40
13	$FeBr_3$	MeCN	$Na_2S_2O_8$	42
14	$FeBr_3$	toluene	$Na_2S_2O_8$	21
15	$FeBr_3$	1,4-dioxane	$K_2S_2O_8$	45
16	$FeBr_3$	1,4-dioxane	$(NH_4)_2S_2O_8$	76
17[d]	$FeBr_3$	1,4-dioxane	$(NH_4)_2S_2O_8$	75
18[d,e]	$FeBr_3$	1,4-dioxane	$(NH_4)_2S_2O_8$	72
19[d,f]	$FeBr_3$	1,4-dioxane	$(NH_4)_2S_2O_8$	52
20[d,g]	$FeBr_3$	1,4-dioxane	$(NH_4)_2S_2O_8$	70
21	-	1,4-dioxane	$(NH_4)_2S_2O_8$	< 10

Reaction conditions:

[a] The reactions were carried out with **1a** (0.25 mmol), **2a** (0.5 mmol, 2.0 equiv), catalyst (0.2 equiv), oxidant (1.0 mmol, 4.0 equiv) in 2 mL of solvent at 120 °C under air atmosphere for 24 h.

[b] Isolated yield based on **1a**.

[c] Ratio of the desired product and the bromide in parentheses, determined by ^{1}H NMR.

[d] $(NH_4)_2S_2O_8$ (0.5 mmol, 2.0 equiv).

[e] Under argon atmosphere.

[f] Reaction was carried out at 100 °C for 48 h.

[g] $FeBr_3$ (0.3 equiv).

To further confirm the structure of the product, **3aa** was carefully crystalized and the single crystal was subjected to X-ray diffraction experiment. The ORTEP drawing of the compound clearly showed the sulfenylmethylpyrrolidine structure (Fig. 2).

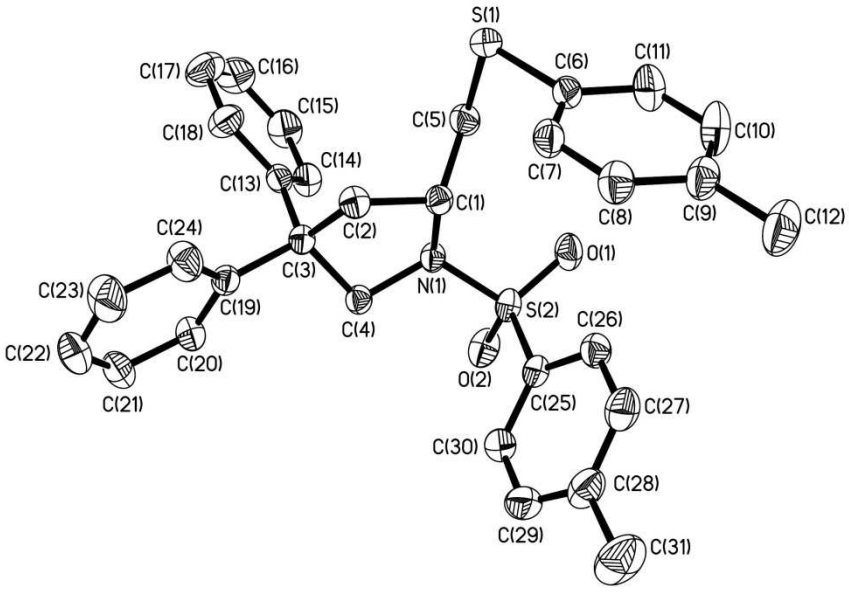
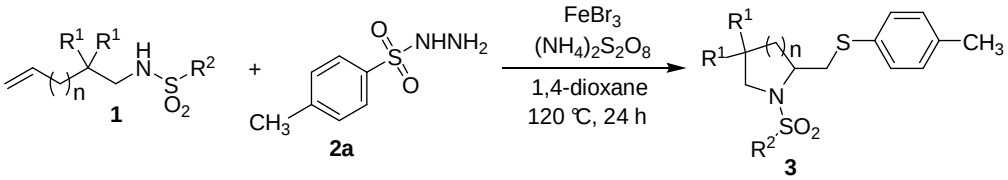


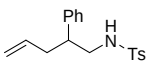
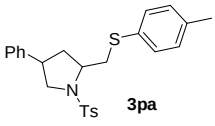
Fig. 2. ORTEP drawing of compound **3aa** at 30% probability displacement ellipsoid (the hydrogen atoms are omitted for clarity).

After the establishment of the optimal reaction conditions, the scope of the reaction was explored with a variety of N-sulfonamide protected alkenes **1** as the substrates and *p*-toluenesulfonyl hydrazide **2a** as the sulfur source. The results are summarized in Table 2. As shown in Table 2, the sulfenoamination reactions tolerated a wide range of N-sulfonyl groups. The substituted phenylsulfonyl groups with different steric and electronic substitution patterns showed no significant effect on the course of the reactions. For example, substrates bearing whether electron-donating (**3fa**), or electron-withdrawing groups (**3ba**, **3ca**, **3da**, **3ga**) could all be employed in the reactions and the desired products were obtained in satisfactory yields. Aliphatic sulfonamides were tolerated as well, and pyrrolidines **3ha** and **3ia** bearing methyl or n-butyl groups were obtained in good yields (74% and 79% yields, respectively). Other substrates bearing *gem*-disubstituents such as cyclopentyl, cyclohexyl or dimethyl groups also provided the desired products **3la**-**3oa** in satisfactory isolated yields. Monosubstituted substrate was also compatible with the reaction conditions, delivering the desired product **3pa** in good yield. Reactions of substrates without *gem*-disubstituents were less successful, giving the corresponding products **3qa**-**3ta** in slightly lower yields of 57-73% possibly due to the lack of Thorpe-Ingold groups. Generally, the reactions were less efficient for the formation of six-membered rings, the desired sulfenomethylated piperidine derivatives **3ua**-**3va** were obtained in only 49-68% yields.

Table 2

Scope of the Substrates.[a,b]



entry	substrate	R^1	R^2	n	product	yield (%)
1	**1a**	Ph	4-MeC_6H_4	1	**3aa**	75
2	**1b**	Ph	4-FC_6H_4	1	**3ba**	71
3	**1c**	Ph	4-BrC_6H_4	1	**3ca**	70
4	**1d**	Ph	4-$O_2NC_6H_4$	1	**3da**	78
5	**1e**	Ph	Ph	1	**3ea**	73
6	**1f**	Ph	3-MeC_6H_4	1	**3fa**	78
7	**1g**	Ph	2-$O_2NC_6H_4$	1	**3ga**	78
8	**1h**	Ph	Me	1	**3ha**	74
9	**1i**	Ph	*n*-butyl	1	**3ia**	79
10	**1j**	Ph	2-naphthyl	1	**3ja**	80
11	**1k**	Ph	1-naphthyl	1	**3ka**	79
12	**1l**	-$(CH_2)_4$-	4-$O_2NC_6H_4$	1	**3la**	57
13	**1m**	-$(CH_2)_4$-	4-MeC_6H_4	1	**3ma**	73
14	**1n**	-$(CH_2)_5$-	4-MeC_6H_4	1	**3na**	74
15	**1o**	Me	4-$O_2NC_6H_4$	1	**3oa**	40
16	**1p**				 **3pa**	71 (d.r.=1.5:1)

						[c]
17	**1q**	H	4-MeC_6H_4	1	**3qa**	73
18	**1r**	H	4-$MeOC_6H_4$	1	**3ra**	57
19	**1s**	H	2-MeC_6H_4	1	**3sa**	69
20	**1t**	H	4-ClC_6H_4	1	**3ta**	62
21	**1u**	Ph	4-MeC_6H_4	2	**3ua**	49
22	**1v**	-$(CH_2)_4$-	4-MeC_6H_4	2	**3va**	68

Reaction conditions:

[a] The reactions were carried out with **1** (0.25 mmol), **2a** (0.5 mmol, 2.0 equiv), $FeBr_3$ (0.2 equiv), $(NH_4)_2S_2O_8$ (0.5 mmol, 2.0 equiv) in 2 mL of 1,4-dioxane at 120 °C under air atmosphere for 24 h.

[b] Isolated yield based on **1**.

[c] Determined by ^1H NMR.

When sulfonyl group was used as the nitrogen protecting groups, intramolecular sulfenoamination reactions provided the N-sulfonylated piperidines or pyrrolidines as the final products. To the best of our knowledge, removal of sulfonyl group from sulfonamides generally required harsh conditions [18]. This limitation also called for protective groups which could be readily removed under relatively mild conditions. Given that removal of benzoyl group from benzamides is easier than that of sulfonyl group from sulfonamides, preparation of N-benzoyl sulfenyl heterocycles would exhibit more application potential.

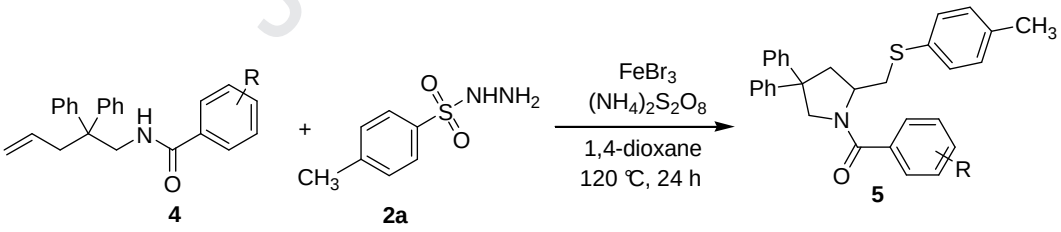
In this regard, the sulfonamide substrates were replaced with carboxamide substrates to

further expand the scope of the reaction [9a]. The results are summarized in Table 3. To our delight, a wide range of benzamides with different electronic substitution patterns could be employed, and good to high yields (62-87%) were recorded for the respective adducts (**5aa**-**5fa**, shown in Table 3).

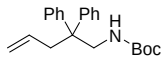
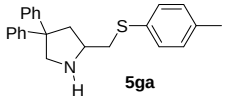
It is worth mentioning that the corresponding free amine product **5ga** was obtained in 51% yield when N-*tert*-butyloxycarbonylamino (N-Boc) alkene **4g** was used as the substrate (Table 3, entry 7). No desired product **5ga** was obtained when free amine was subjected to the reaction under the same condition, suggesting that **5ga** was produced via deprotection of the cyclization product. Replacing the N-Boc group with Fmoc or Cbz was also possible, but the products were obtained as mixtures of both the piperidines and pyrrolidines (Table 3, entries 8 and 9). Separation of these isomers was generally difficult, and studies on these substrates were not further pursued at this stage.

Table 3

Reaction Scope of Alkenes **2**.[a]



entry	substrate	R	product	yield (%)[b]
1	**4a**	4-FC_6H_4	**5aa**	80
2	**4b**	4-ClC_6H_4	**5ba**	87
3	**4c**	4-BrC_6H_4	**5ca**	64
4	**4d**	Ph	**5da**	62

5	**4e**	4-MeC_6H_4	**5ea**	65
6	**4f**	4-$MeOC_6H_4$	**5fa**	74
7	**4g**		 **5ga**	51

Reaction conditions:

[a] The reactions were carried out with **4** (0.25 mmol), **2a** (0.5 mmol, 2.0 equiv), $FeBr_3$ (0.2 equiv), $(NH_4)_2S_2O_8$ (0.5 mmol, 2.0 equiv) in 2 mL of 1,4-dioxane at 120 °C under air atmosphere for 24 h.

[b] Isolated yield based on **4**.

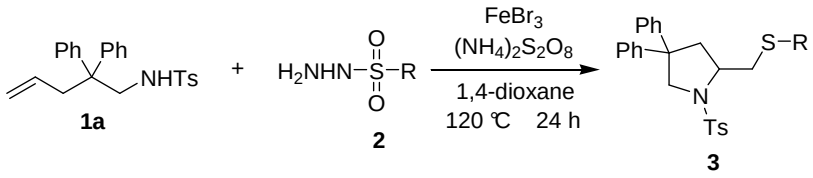
[c] Determined by ^1H NMR.

Next, different sulfonyl hydrazides were used as sulfur sources to test the feasibility of the reaction. The results are summarized in Table 4. Studies showed that sulfonyl hydrazides with different types of substituents at the *para*-positions of the benzene rings, either electron-donating or electron-withdrawing, could be tolerated, giving the desired products in good to high yields, except for 4-Br (**3ae**) and 4-*t*-Bu (**3ah**) which gave products in slightly lower yields. Further, the position of the substituent on *m*- or *p*- of benzene rings has a negligible effect on this reaction under standard conditions (**3aa** and **3aj**). However, when the *o*-substituted substrates were employed, dramatically different results were observed. *o*-Fluoro substituted substrate **2k** gave product **3ak** in high yield (89%), and *o*-nitro substituted substrate **2l** gave product **3al** in poor yield (36%), possibly due to the larger steric hindrance of the nitro group than fluorine atom. Alkyl sulfonyl hydrazide **2n** could be employed as sulfur source, but the desired product **2an** was obtained in low yield, possibly due to the low stability of the aliphatic sulfenyl

intermediate under the reaction conditions.

Table 4

Reaction Scope of Sulfonyl Hydrazides.[a]



entry	**2**	R	product	yield (%)[b]
1	**2b**	Ph	**3ab**	84
2	**2c**	4-FC_6H_4	**3ac**	84
3	**2d**	4-ClC_6H_4	**3ad**	76
4	**2e**	4-BrC_6H_4	**3ae**	62
5	**2f**	4-$NO_2C_6H_4$	**3af**	72
6	**2g**	4-$CF_3C_6H_4$	**3ag**	72
7	**2h**	4-*t*-BuC_6H_4	**3ah**	53
8	**2i**	4-$MeOC_6H_4$	**3ai**	80
9	**2j**	3-MeC_6H_4	**3aj**	75
10	**2k**	2-FC_6H_4	**3ak**	89
11	**2l**	2-$O_2NC_6H_4$	**3al**	36
12	**2m**	2-naphthyl	**3am**	82
13	**2n**	*n*-butyl	**3an**	36

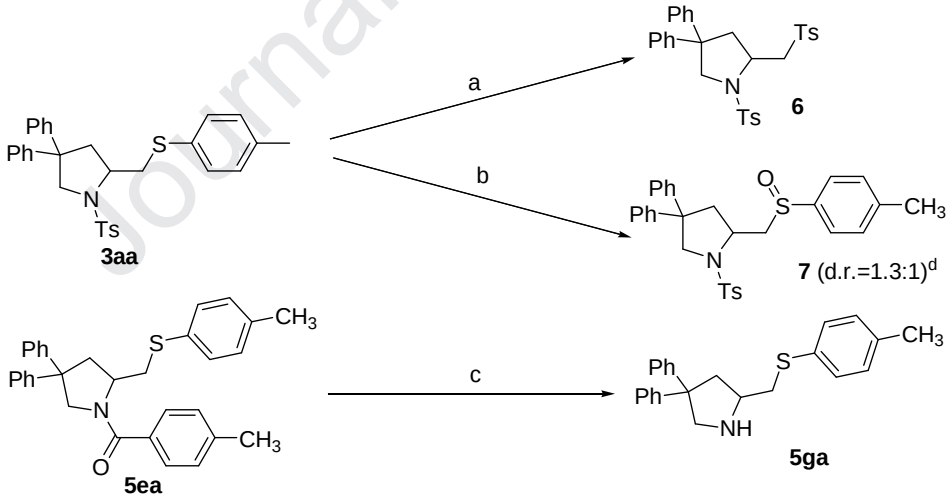
Reaction conditions:

[a] The reactions were carried out with **1a** (0.25 mmol), **2** (0.5 mmol, 2.0 equiv), $FeBr_3$ (0.2 equiv), $(NH_4)_2S_2O_8$ (0.5 mmol, 2.0 equiv) in 2 mL of 1,4-dioxane at 120 °C under air

atmosphere for 24 h.

[b] Isolated yield based on **1a**.

To demonstrate the application potential of this reaction, several derivatization reactions were carried out using N-tosylpyrrolidine **3aa** and N-(p-methylbenzoyl)pyrrolidine **5ea** as the model compounds. As shown in Scheme 2, treatment of **3aa** with 2.0 equiv of *m*-chloroperbenzoic acid (*m*-CPBA) furnished sulfone **6** in 93% yield [6e]; treatment of **3aa** with 1.0 equiv amount of PIDA furnished sulfoxide **7** in 88% yield [10f]. The removal of *p*-methylbenzoyl group was readily accomplished by treating **5ea** with 6 N HCl, and the corresponding deprotection product **5ga** was obtained in 72% yield [19]. The current methods thus provided entries to different important sulfur-containing heterocycles.

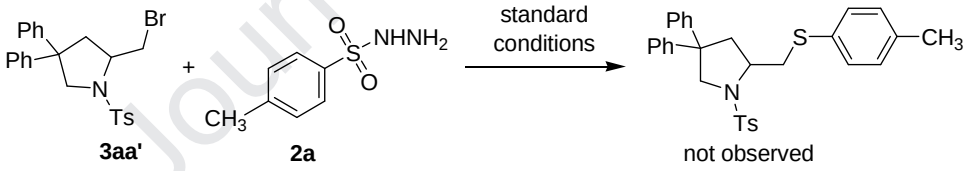


Reaction conditions: [a] **3aa**, *m*-CPBA, DCM, r. t., overnight. [b] **3aa**, $AlCl_3$, PIDA, MeOH/DCM, r. t., overnight. [c] **5ea**, 6 N HCl, reflux, 24 h. [d] Isolated yield.

Scheme 2. Functional Group Transformation Using **3aa** and **5ea** as Precursors.

Wirth et al. reported an alkene thioamination protocol in which hypervalent iodine reagents were used. In this method, the substrate first underwent intramolecular

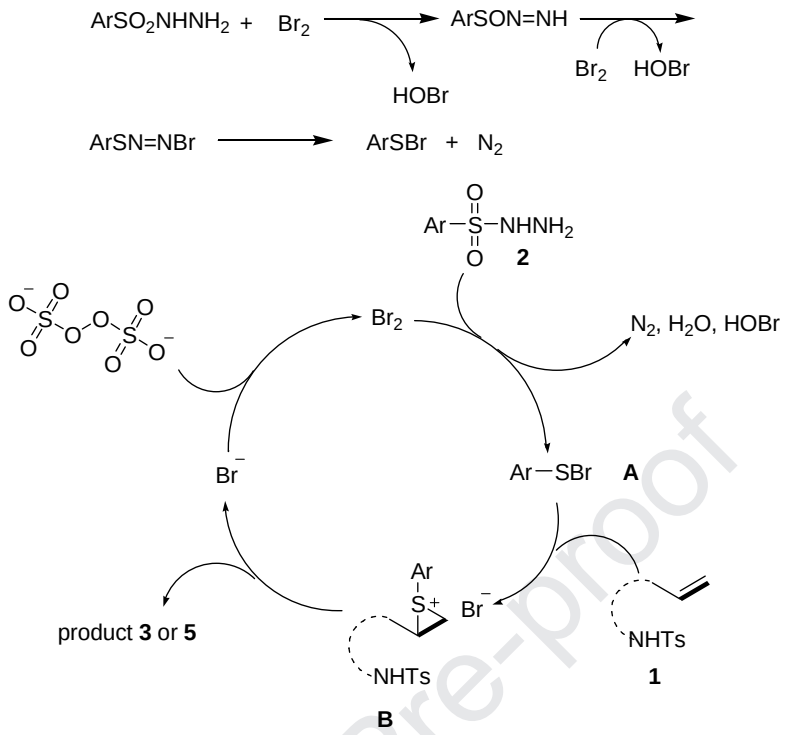
iodoamination, and subsequent nucleophilic substitution with the thiolate provided the sulfenoamination product [10d]. As mentioned in the reaction condition optimization step, bromoamination product was observed when $CuBr_2$ was used as the bromide source (Table 1, Entry 4). Control reactions were then carried out to see if the products could be obtained from the bromoamination product under current reaction conditions (Scheme 3). Study showed that no desired product **3aa** was obtained when **1a** was replaced by **3aa'** under otherwise identical conditions, suggesting that sulfenoamination pathway was more likely under current reaction conditions. In previous reports, molecular oxygen was involved in an iodine-triggered aerobic sulfonylation of styrenes [14f]. In the current study, reactions carried out under air atmosphere or under argon atmosphere gave product in similar isolated yields, suggesting that molecular oxygen made no contribution to the formation of the products.



Scheme 3. Control Reaction.

Combining the above observations with previous reports and our previous study [6e,15a,20], a plausible reaction pathway is proposed in Scheme 4. Bromine is generated in situ when bromide anion and suitable oxidant are present in the reaction mixture. Sulfenyl bromide intermediate **A** is produced in situ from sulfonyl hydrazide **2** by the action of bromine as reported previously.[13b] Electrophilic addition of intermediate **A** to alkene **1** produces thiiranium ion intermediate **B**, and subsequent nucleophilic ring opening gives the desired products **3** or **5**. At the same time, the released bromide anion

is oxidized to bromine to complete the catalytic cycle.



Scheme 4. Possible Pathway of the Reactions.

3. Conclusion

In summary, we reported a highly regioselective intramolecular sulfenoamination of unactivated terminal olefins with sulfonyl hydrazides. A range of sulfonyl hydrazides were compatible with the current reaction system, and the desired products bearing the sulfur units adjacent to the nitrogen-containing heterocycles were obtained in moderate to high yields. Application of this transformation in organic synthesis is underway.

4. Experimental Section

4.1. General Experimental Information

Reactions were carried out with commercially available reagents in oven-dried apparatus. ^{1}H and ^{13}C NMR spectra were recorded at 298 K using deuterated chloroform as solvent and TMS as internal reference. Column chromatography was performed

employing 200-300 mesh silica gel unless otherwise noted. Thin layer chromatography (TLC) was performed on silica gel GF_{254}. Melting points were measured on a digital melting-point apparatus without correction of the thermometer. HRMS analyses were carried out with Varian FTICR-MS 7.0T. IR spectra were recorded on a BRUKER TENSOR 37. Unless otherwise indicated, starting materials and reagents used in the study were purchased and were used as received without further purification.

4.2. Typical procedure for the intramolecular sulfenoamination of alkenes with 4-methyl benzene sulfonyl hydrazide

A 35 mL Schlenk-type tube (with a Teflon high pressure valve) equipped with a magnetic stir bar was charged with N-(2,2-diphenylpent-4-en-1-yl)-4-methylbenzenesulfonamide (**1a**, 0.25 mmol, 97.9 mg) and *p*-toluenesulfonyl hydrazide (**2a**, 0.5 mmol, 93.2 mg). $FeBr_3$ (0.05 mmol, 14.8 mg), $(NH_4)_2S_2O_8$ (0.5 mmol, 0.114 g) and 1,4-dioxane (2 mL) were added to this system. The tube was sealed and placed in an oil bath at 120 °C. The reaction mixture was allowed to cool to ambient temperature after 24 hours of reaction at this temperature. The tube was opened with care (Caution!). The reaction mixture was filtered and concentrated to give the crude product. The residue was purified by column chromatography (petroleum ether: ethyl acetate = 50: 1, v/v) to afford the desired product **3aa**.

*4.2.1. 4,4-Diphenyl-2-((4-tolylthio)methyl)-1-tosylpyrrolidine (**3aa**)*

Compound **3aa** was prepared according to the general procedure and was isolated as white solid (96.3 mg, 75% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 118-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.0 Hz,

2H), 7.29 (q, J = 9.7, 8.5 Hz, 6H), 7.18 – 7.07 (m, 8H), 7.04 (d, J = 7.4 Hz, 2H), 4.50 (d, J = 10.0 Hz, 1H), 3.61 (d, J = 13.8 Hz, 2H), 3.43 (d, J = 10.1 Hz, 1H), 2.73 – 2.56 (m, 2H), 2.37 (s, 3H), 2.35 (s, 3H), 2.19 (t, J = 12.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 144.9, 143.4, 136.5, 131.2, 130.4, 129.8, 129.6, 128.7, 128.6, 127.6, 126.8, 126.6, 126.4, 126.4, 58.6, 52.1, 41.7, 38.5, 21.5, 21.1. The NMR data were in agreement with reported results [11a].

Crystal data for **3aa** (CCDC 1920628): $C_{31}H_{31}NO_2S_2$, M = 513.69, a = 14.1662(8) Å, b = 16.2771(7) Å, c = 13.1633(7) Å, α = 90°, β = 112.579(6)°, γ = 90°, V = 2802.6(3) Å^3, T = 294.15 K, space group $P121/c1$, Z = 4, μ(MoKα) = 0.218 mm^{-1}, 37951 reflections measured, 6940 independent reflections (R_{int} = 0.0458). The final R_1 values were 0.0422 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1007 ($I > 2\sigma(I)$). The final R_1 values were 0.0767 (all data). The final $wR(F^2)$ values were 0.1136 (all data). The goodness of fit on F^2 was 1.017.

*4.2.2. 1-((4-Fluorophenyl)sulfonyl)-4,4-diphenyl-2-((4-tolylthio)methyl)pyrrolidine (**3ba**)*

Compound **3ba** was prepared according to the general procedure and was isolated as white solid (91.9 mg, 71% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 146-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.28 – 7.24 (m, 2H), 7.19 (d, J = 2.2 Hz, 2H), 7.13 – 7.02 (m, 7H), 6.99 – 6.93 (m, 3H), 6.84 (t, J = 8.6 Hz, 2H), 4.41 (dd, J = 10.3, 1.2 Hz, 1H), 3.71 – 3.26 (m, 3H), 2.69 (dd, J = 13.1, 8.4 Hz, 1H), 2.64 – 2.47 (m, 1H), 2.30 (s, 3H), 2.28 – 2.17 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 144.6, 136.7, 130.9, 130.1, 130.0, 129.9, 128.7, 128.7, 127.7, 126.71, 126.7, 126.7, 126.6, 126.4, 116.2, 116.0, 59.1, 58.8, 52.2, 42.0, 39.0, 21.1. ^{19}F NMR (376

MHz, $CDCl_3$) δ -105.3. IR (KBr): 2929, 1591, 1492, 1338, 1232, 1166, 1083, 833, 810, 705, 545 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{30}H_{29}FNO_2S_2^+$: 518.1618; found: 518.1622.

*4.2.3. 1-((4-Bromophenyl)sulfonyl)-4,4-diphenyl-2-((4-tolylthio)methyl)pyrrolidine (**3ca**)*

Compound **3ca** was prepared according to the general procedure and was isolated as white solid (101.3 mg, 70% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 134-136 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.2 Hz, 4H), 7.17 (tq, J = 6.8, 4.1, 2.9 Hz, 6H), 7.12 – 7.08 (m, 4H), 7.04 (dt, J = 5.1, 2.8 Hz, 2H), 6.95 – 6.91 (m, 2H), 4.38 (d, J = 10.4 Hz, 1H), 3.63 – 3.50 (m, 3H), 2.76 (dd, J = 13.2, 7.9 Hz, 1H), 2.51 (dd, J = 13.1, 5.1 Hz, 1H), 2.31 (s, 3H), 2.29 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 144.3, 136.8, 135.3, 132.1, 131.1, 130.9, 129.9, 128.8, 128.7, 128.7, 127.7, 126.7, 126.6, 126.6, 126.3, 59.3, 58.9, 52.3, 42.1, 39.2, 21.1. IR (KBr): 2922, 1571, 1490, 1344, 1164, 1072, 1043, 813, 700, 607 cm-1. HRMS (m/z): $[M + H]^+$ calcd for $C_{30}H_{29}BrNO_2S_2^+$: 579.0851; found: 579.0854.

*4.2.4. 1-((4-Nitrophenyl)sulfonyl)-4,4-diphenyl-2-((4-tolylthio)methyl)pyrrolidine (**3da**)*

Compound **3da** was prepared according to the general procedure and was isolated as yellow solid (106.2 mg, 78% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 159-162 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.20 – 7.16 (m, 2H), 7.15 – 7.07 (m, 5H), 6.97 – 6.93 (m, 3H), 6.92 – 6.88 (m, 2H), 4.37 (d, J = 10.8 Hz, 1H), 3.79 (d, J = 10.7 Hz, 1H), 3.66 (dd, J = 13.4, 2.9 Hz, 1H), 3.62 – 3.57 (m, 1H), 2.94 (dd, J = 13.4, 7.4 Hz, 1H), 2.53 – 2.39 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 144.8, 143.9, 142.3,

137.2, 131.3, 131.0, 123.0, 128.8, 128.6, 128.2, 126.8, 126.6, 126.4, 126.4, 123.9, 60.1, 59.1, 52.4, 42.4, 39.7, 21.1. IR (KBr): 2925, 1529, 1350, 1166, 1031, 705, 611, 561 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{30}H_{29}N_2O_4S_2^+$:545.1563; found; 545.1566.

*4.2.5. 4,4-Diphenyl-1-(phenylsulfonyl)-2-((4-tolylthio)methyl)pyrrolidine (**3ea**)*

Compound **3ea** was prepared according to the general procedure and was isolated as white solid (91.2 mg, 73% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 157-159 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 3H), 7.34 – 7.28 (m, 8H), 7.18 – 7.09 (m, 6H), 7.07 – 7.04 (m, 2H), 4.50 (dd, J = 10.1, 1.4 Hz, 1H), 3.69 – 3.57 (m, 2H), 3.46 (d, J = 10.1 Hz, 1H), 2.74 – 2.58 (m, 2H), 2.37 (s, 3H), 2.25 – 2.15 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 144.8, 136.5, 136.1, 132.7, 131.1, 130.6, 129.8, 129.0, 128.7, 128.6, 127.5, 126.8, 126.7, 126.6, 126.3, 58.6, 58.6, 52.1, 41.8, 38.6, 21.1. IR (KBr): 2974, 2923, 1490, 1446, 1340, 1164, 1089, 1031, 813, 748, 694, 597, 570, 507 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{30}H_{30}NO_2S_2^+$: 500.1712; found: 500.1708.

*4.2.6. 4,4-Diphenyl-1-(3-tolylsulfonyl)-2-((4-tolylthio)methyl)pyrrolidine (**3fa**)*

Compound **3fa** was prepared according to the general procedure and was isolated as pale yellow viscous oil (100.2 mg, 78% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, J = 8.6, 2.2 Hz, 5H), 7.22 – 7.12 (m, 6H), 7.09 – 7.02 (m, 5H), 6.99 – 6.94 (m, 3H), 4.42 (dd, J = 10.1, 1.4 Hz, 1H), 3.62 – 3.55 (m, 2H), 3.37 (d, J = 10.1 Hz, 1H), 2.67 – 2.51 (m, 2H), 2.26 (s, 3H), 2.17 (s, 3H), 2.11 (dd, J = 14.2, 11.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 144.9, 139.2, 133.6, 130.3, 129.9, 128.9, 128.7, 128.6, 128.4, 127.9, 127.8, 126.8, 126.7, 126.6,

126.4, 124.8, 58.6, 52.2, 41.8, 38.4, 21.4, 21.1. IR (KBr): 2922, 2360, 1494, 1340, 1157, 1016, 750, 698, 611, 578, 491 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{32}NO_2S_2^+$: 514.1869; found: 514.1871.

*4.2.7. 1-((2-Nitrophenyl)sulfonyl)-4,4-diphenyl-2-((4-tolylthio)methyl)pyrrolidine (**3ga**)*

Compound **3ga** was prepared according to the general procedure and was isolated as pale yellow solid (106.2 mg, 78% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 75-77 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.27 (t, J = 7.7 Hz, 1H), 7.18 – 7.13 (m, 4H), 7.13 – 7.06 (m, 5H), 7.04 – 6.96 (m, 4H), 6.93 (d, J = 7.2 Hz, 1H), 4.24 (d, J = 10.9 Hz, 1H), 4.19 – 4.06 (m, 2H), 3.42 (dd, J = 13.3, 3.2 Hz, 1H), 2.96 (dd, J = 13.1, 7.3 Hz, 1H), 2.62 – 2.48 (m, 2H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 142.6, 135.4, 132.4, 130.5, 130.4, 129.2, 129.1, 128.8, 127.6, 127.5, 125.7, 125.6, 125.5, 125.4, 122.8, 58.6, 57.8, 51.7, 41.6, 38.1, 20.0. IR (KBr): 2920, 2360, 1541, 1492, 1352, 1166, 1029, 775, 702, 603, 574 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{30}H_{29}N_2O_4S_2^+$: 545.1563; found: 545.1565.

*4.2.8. 1-(Methylsulfonyl)-4,4-diphenyl-2-((4-tolylthio)methyl)pyrrolidine (**3ha**)*

Compound **3ha** was prepared according to the general procedure and was isolated as pale yellow solid (90 mg, 74% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 60-62 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 8H), 7.15 – 7.08 (m, 4H), 7.02 (d, J = 8.0 Hz, 2H), 4.16 (d, J = 11.0 Hz, 1H), 4.06 (d, J = 1.6 Hz, 1H), 3.90 – 3.79 (m, 1H), 3.53 (dd, J = 13.3, 3.2 Hz, 1H), 3.14 (ddd, J = 13.4, 7.2, 1.6 Hz, 1H), 2.66 (dd, J = 13.3, 9.9 Hz, 1H), 2.45 (dd, J = 13.4, 7.5 Hz, 1H), 2.23 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 144.4, 136.3, 131.6, 129.9, 129.6, 128.9, 128.8, 127.1,

126.8, 126.5, 59.7, 59.0, 53.2, 42.7, 39.3, 35.7, 21.0. IR (KBr): 2925, 2360, 1596, 1494, 1448, 1336, 1153, 1029, 968, 806, 752, 700, 516 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{25}H_{28}NO_2S_2^+$: 438.1556; found: 438.1560.

*4.2.9. 1-(Butylsulfonyl)-4,4-diphenyl-2-((4-tolylthio)methyl)pyrrolidine (**3ia**)*

Compound **3ia** was prepared according to the general procedure and was isolated as pale yellow viscous oil (94.8 mg, 79% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 1.2 Hz, 2H), 7.24 – 7.17 (m, 6H), 7.16 – 7.09 (m, 4H), 7.03 (d, J = 8.0 Hz, 2H), 4.15 (dd, J = 10.8, 1.6 Hz, 1H), 4.05 (d, J = 10.8 Hz, 1H), 3.98 – 3.91 (m, 1H), 3.49 (dd, J = 13.2, 3.1 Hz, 1H), 3.07 (ddd, J = 13.2, 7.1, 1.6 Hz, 1H), 2.71 (dd, J = 13.3, 9.5 Hz, 1H), 2.50 (dd, J = 13.2, 7.8 Hz, 1H), 2.46 – 2.39 (m, 1H), 2.32 – 2.26 (m, 1H), 2.24 (s, 3H), 1.62 – 1.43 (m, 2H), 1.21 – 1.09 (m, 2H), 0.75 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 144.4, 136.3, 131.7, 129.8, 129.6, 128.8, 128.7, 126.9, 126.8, 126.7, 126.6, 59.3, 58.7, 53.2, 50.2, 42.7, 39.2, 25.0, 21.6, 21.0, 13.5. IR (KBr): 2958, 2929, 2871, 1596, 1494, 1330, 1147, 1029, 806, 700, 611, 530 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{28}H_{34}NO_2S_2^+$: 480.2025; found: 480.2029.

*4.2.10. 1-(Naphthalen-2-ylsulfonyl)-4,4-diphenyl-2-((4-tolylthio)methyl)pyrrolidine (**3ja**)*

Compound **3ja** was prepared according to the general procedure and was isolated as white solid (110 mg, 80% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 67-69 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 1.7 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.6 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.37 (dd, J = 8.7, 1.8 Hz, 1H), 7.27 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 6.5 Hz, 4H), 7.08 (dd,

J = 11.7, 7.3 Hz, 3H), 6.86 (d, J = 6.7 Hz, 4H), 6.81 – 6.76 (m, 1H), 4.45 (d, J = 10.2 Hz, 1H), 3.70 – 3.65 (m, 2H), 3.51 (d, J = 10.2 Hz, 1H), 2.58 (t, J = 7.3 Hz, 2H), 2.31 (s, 3H), 2.21 (dd, J = 14.0, 11.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 144.5, 136.5, 134.8, 133.3, 132.1, 131.2, 130.5, 130.0, 129.3, 129.2, 128.9, 128.8, 128.7, 128.4, 127.8, 127.3, 126.8, 126.7, 126.4, 126.3, 122.8, 58.9, 58.8, 52.2, 41.9, 38.7, 21.2. IR (KBr): 3055, 2922, 2868, 1492, 1340, 1163, 1076, 1029, 810, 748, 700, 661, 545 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{34}H_{32}NO_2S_2^+$: 550.1869; found: 550.1872.

*4.2.11. 1-(Naphthalen-1-ylsulfonyl)-4,4-diphenyl-2-((4-tolylthio)methyl)pyrrolidine (**3ka**)*

Compound **3ka** was prepared according to the general procedure and was isolated as white solid (108.6 mg, 79% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 66-68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, J = 8.6, 1.1 Hz, 1H), 7.98 (dd, J = 7.4, 1.3 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.77 (dd, J = 8.1, 1.4 Hz, 1H), 7.45 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.38 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.31 (dd, J = 8.1, 7.4 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.13 – 7.02 (m, 7H), 6.94 – 6.86 (m, 5H), 4.18 (dd, J = 10.2, 1.0 Hz, 1H), 4.06 – 4.01 (m, 1H), 3.79 (d, J = 10.1 Hz, 1H), 3.49 (dd, J = 13.5, 3.2 Hz, 1H), 2.75 (dd, J = 13.0, 8.0 Hz, 1H), 2.64 – 2.53 (m, 1H), 2.28 (s, 3H), 2.26 (d, J = 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 143.1, 135.4, 133.4, 133.3, 132.9, 129.1, 128.9, 128.8, 127.9, 127.8, 127.5, 127.2, 127.0, 125.7, 125.6, 125.6, 125.4, 125.1, 124.0, 123.0, 57.8, 57.1, 51.5, 41.3, 37.6, 20.0. IR (KBr): 3057, 2922, 2360, 1492, 1330, 1161, 1130, 1029, 804, 771, 700, 601, 518 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{34}H_{32}NO_2S_2^+$: 550.1869; found: 550.1873.

*4.2.12. 2-((4-Nitrophenyl)sulfonyl)-3-((4-tolylthio)methyl)-2-azaspiro[4.4]nonane (**3la**)*

Compound **3la** was prepared according to the general procedure and was isolated as yellow solid (63.4 mg, 57% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 90-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.34 – 7.23 (m, 2H), 7.11 (d, J = 7.9 Hz, 2H), 3.72 (dd, J = 13.4, 3.0 Hz, 1H), 3.54 – 3.46 (m, 1H), 3.28 (d, J = 10.2 Hz, 1H), 2.97 (d, J = 10.2 Hz, 1H), 2.81 (dd, J = 13.4, 10.4 Hz, 1H), 2.33 (s, 3H), 1.88 (dd, J = 12.9, 7.7 Hz, 1H), 1.73 (dd, J = 13.0, 6.7 Hz, 1H), 1.61 – 1.33 (m, 6H), 1.01 – 0.90 (m, 1H), 0.87 – 0.80 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 142.9, 136.9, 131.2, 130.7, 129.9, 128.6, 124.1, 60.5, 59.6, 48.6, 43.5, 39.9, 36.7, 36.4, 24.6, 24.3, 21.1. IR (KBr): 2962, 2923, 2869, 2368, 1533, 1346, 1161, 1085, 813, 611, 572 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{22}H_{27}N_2O_4S_2^+$: 447.1407; found: 447.1403.

*4.2.13. 3-((4-Tolylthio)methyl)-2-tosyl-2-azaspiro[4.4]nonane (**3ma**)*

Compound **3ma** was prepared according to the general procedure and was isolated as pale yellow viscous oil (75.9 mg, 73% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.8 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.14 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 3.80 (d, J = 13.5 Hz, 1H), 3.47 (d, J = 8.5 Hz, 1H), 3.23 (dd, J = 10.5, 3.2 Hz, 1H), 2.94 – 2.87 (m, 1H), 2.83 – 2.72 (m, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 1.80 (d, J = 9.7 Hz, 1H), 1.68 (q, J = 7.0, 5.7 Hz, 1H), 1.57 – 1.33 (m, 6H), 0.94 – 0.85 (m, 1H), 0.81 – 0.75 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 136.3, 133.8, 131.6, 130.1, 129.8, 129.5, 127.6, 60.3, 59.2, 48.4, 43.5, 39.8, 36.7, 36.5, 24.6, 24.2, 21.6, 21.1. IR (KBr): 2954, 2866, 1596, 1492, 1344, 1159, 804, 663,

590, 551, 491 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{23}H_{30}NO_2S_2^+$: 416.1712; found: 416.1716.

*4.2.14. 3-((4-Tolylthio)methyl)-2-tosyl-2-azaspiro[4.5]decane (**3na**)*

Compound **3na** was prepared according to the general procedure and was isolated as pale yellow viscous oil (79.5 mg, 74% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 3.82 (dd, J = 13.3, 3.0 Hz, 1H), 3.51 – 3.44 (m, 1H), 3.12 (s, 2H), 2.77 (dd, J = 13.3, 10.4 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 1.84 (dd, J = 13.1, 7.5 Hz, 1H), 1.54 – 1.45 (m, 1H), 1.38 – 1.26 (m, 4H), 1.19 – 1.00 (m, 4H), 0.70 – 0.62 (m, 1H), 0.54 – 0.45 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 136.3, 134.1, 131.8, 130.2, 129.8, 129.5, 127.5, 59.1, 58.4, 44.3, 41.2, 40.6, 36.3, 34.3, 25.8, 23.6, 22.9, 21.5, 21.1. The NMR data were in agreement with reported results [9d].

*4.2.15. 4,4-Dimethyl-1-((4-nitrophenyl)sulfonyl)-2-((4-tolylthio)methyl)pyrrolidine (**3oa**)*

Compound **3oa** was prepared according to the general procedure and was isolated as yellow solid (42.1 mg, 40% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 109-111 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.13 (m, 2H), 7.76 – 7.68 (m, 2H), 7.26 (d, J = 7.7 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 3.72 (dd, J = 13.4, 2.9 Hz, 1H), 3.59 (d, J = 7.3 Hz, 1H), 3.17 (d, J = 10.4 Hz, 1H), 3.02 (d, J = 10.4 Hz, 1H), 2.83 (dd, J = 13.3, 9.9 Hz, 1H), 2.32 (s, 3H), 1.83 (dd, J = 13.1, 7.5 Hz, 1H), 1.61 (dd, J = 13.0, 7.9 Hz, 1H), 1.00 (s, 3H), 0.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 143.3, 136.9,

131.3, 130.7, 129.9, 128.5, 124.1, 62.1, 59.6, 45.8, 40.3, 37.6, 26.1, 25.9, 21.1. IR (KBr): 2962, 2923, 2368, 1533, 1346, 1163, 1085, 813, 730, 611, 572 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{20}H_{25}N_2O_4S_2^+$: 421.1250; found: 421.1250.

*4.2.16. 4-Phenyl-2-((4-tolylthio)methyl)-1-tosylpyrrolidine (**3pa**)*

Compound **3pa** was prepared according to the general procedure and was isolated as pale yellow oil (77.7 mg, 71% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 30.8, 8.2 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.22 – 7.06 (m, 7H), 6.99 – 6.93 (m, 2H), 3.86 – 3.58 (m, 3H), 3.45 – 3.28 (m, 1H), 2.91 – 2.72 (m, 1H), 2.50 – 2.36 (m, 1H), 2.33 (d, J = 6.7 Hz, 3H), 2.32 – 2.26 (m, 3H), 2.25 (d, J = 5.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 142.6, 138.1, 135.3, 133.4, 132.1, 130.5, 130.2, 129.0, 128.9, 128.9, 128.8, 128.8, 128.8, 128.7, 128.6, 127.6, 127.5, 126.6, 126.5, 126.4, 126.0, 125.9, 125.9, 58.9, 57.8, 54.5, 54.4, 41.8, 40.2, 39.2, 38.4, 37.9, 35.0, 20.5, 20.5, 20.0. The NMR data were in agreement with reported results [9d].

*4.2.17. 2-((4-Tolylthio)methyl)-1-tosylpyrrolidine (**3qa**)*

Compound **3qa** was prepared according to the general procedure and was isolated as pale yellow oil (66 mg, 73% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2H), 7.31-7.26 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 3.62-3.48 (m, 2H), 3.46-3.36 (m, 1H), 3.05-2.99 (m, 1H), 2.72-2.61 (m, 1H), 2.33 (s, 3H), 2.29 (s, 3H), 1.84-1.76 (m, 1H), 1.76-1.68 (m, 1H), 1.60-1.50 (m, 1H), 1.48-1.40 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 136.2, 133.9, 131.6, 129.8, 129.7, 129.6, 127.5, 59.0, 49.7, 39.0, 30.3, 23.8, 21.5,

21.1. The NMR data were in agreement with reported results [9d].

*4.2.18. 1-((4-Methoxyphenyl)sulfonyl)-2-((4-tolylthio)methyl)pyrrolidine (**3ra**)*

Compound **3ra** was prepared according to the general procedure and was isolated as pale yellow solid (53.8 mg, 57% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 77-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.48 (m, 2H), 7.29 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 6.87-6.78 (m, 2H), 3.78 (s, 3H), 3.60-3.47 (m, 2H), 3.43-3.37 (m, 1H), 3.05-2.96 (m, 1H), 2.67 (dd, J = 13.2, 10.4 Hz, 1H), 2.29 (s, 3H), 1.85-1.75 (m, 1H), 1.73 (dd, J = 12.2, 6.8 Hz, 1H), 1.62-1.51 (m, 1H), 1.46 (td, J = 6.9, 3.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 136.1, 131.6, 129.8, 129.7, 129.6, 128.6, 114.1, 59.0, 55.6, 49.8, 39.1, 30.3, 23.8, 21.1. IR (KBr): 2873, 2360, 1593, 1496, 1332, 1155, 1024, 811, 667, 557 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{19}H_{24}NO_3S_2^+$: 378.1192; found: 378.1197.

*4.2.19. 1-(2-Tolylsulfonyl)-2-((4-tolylthio)methyl)pyrrolidine (**3sa**)*

Compound **3sa** was prepared according to the general procedure and was isolated as pale yellow oil (62.4 mg, 69% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.35 (d, J = 6.7 Hz, 1H), 7.24-7.11 (m, 4H), 7.02 (d, J = 5.6 Hz, 2H), 3.87 (d, J = 3.5 Hz, 1H), 3.25 (q, J = 6.1, 5.6 Hz, 3H), 2.68-2.56 (m, 1H), 2.53 (s, 3H), 2.24 (s, 3H), 1.97-1.66 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 137.1, 136.3, 132.8, 131.5, 129.8, 129.8, 129.4, 126.1, 58.8, 48.9, 38.5, 30.4, 24.1, 21.0, 20.7. IR (KBr): 2972, 2873, 1683, 1492, 1315, 1068, 806, 709, 611, 491 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{19}H_{24}NO_2S_2^+$: 362.1243; found: 362.1246.

*4.2.20. 1-((4-Chlorophenyl)sulfonyl)-2-((4-tolylthio)methyl)pyrrolidine (**3ta**)*

Compound **3ta** was prepared according to the general procedure and was isolated as pale yellow oil (53.7 mg, 62% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 7.4, 3.8 Hz, 2H), 7.36-7.25 (m, 4H), 7.13-7.06 (m, 2H), 3.59-3.37 (m, 3H), 3.00 (d, J = 9.0 Hz, 1H), 2.75-2.59 (m, 1H), 2.30 (s, 3H), 1.89-1.69 (m, 2H), 1.64-1.43 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 136.4, 135.4, 131.3, 130.1, 129.8, 129.3, 128.9, 59.2, 49.8, 39.1, 30.3, 23.8, 21.1. IR (KBr): 2923, 2871, 1585, 1475, 1350, 1163, 1091, 827, 756, 628, 580, 482 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{18}H_{21}ClNO_2S_2^+$: 382.0697; found: 382.0695.

*4.2.21. 5,5-Diphenyl-2-((4-tolylthio)methyl)-1-tosylpiperidine (**3ua**)*

Compound **3ua** was prepared according to the general procedure and was isolated as white solid (64.7 mg, 49% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 129-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.26 (m, 4H), 7.16 (d, J = 7.9 Hz, 6H), 7.10 (dd, J = 7.7, 2.6 Hz, 4H), 7.03 (dd, J = 7.8, 2.7 Hz, 4H), 4.63 (d, J = 13.2 Hz, 1H), 3.75 (dd, J = 10.7, 4.7 Hz, 1H), 3.13 (dd, J = 13.2, 3.1 Hz, 1H), 2.95 (t, J = 12.5 Hz, 1H), 2.86 (d, J = 13.0 Hz, 1H), 2.41-2.32 (m, 1H), 2.29 (s, 3H), 2.26 (s, 3H), 2.18-2.06 (m, 1H), 2.04 (d, J = 14.3 Hz, 1H), 1.49 (q, J = 10.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 143.5, 143.3, 137.0, 136.9, 131.1, 130.9, 129.8, 129.6, 128.5, 128.4, 128.0, 127.5, 126.6, 126.4, 126.1, 51.6, 48.5, 45.7, 31.7, 28.8, 21.8, 21.5, 21.1. IR (KBr): 2954, 2864, 2360, 1494, 1340, 1159, 947, 811, 700, 663, 549 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{32}H_{34}NO_2S_2^+$: 528.2025; found: 528.2030.

*4.2.22. 8-((4-Tolylthio)methyl)-7-tosyl-7-azaspiro[4.5]decane (**3va**)*

Compound **3va** was prepared according to the general procedure and was isolated as

white solid (73.1 mg, 68% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 87-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 9.3 Hz, 2H), 7.14 (d, J = 8.0 Hz, 4H), 7.04 (d, J = 8.0 Hz, 2H), 3.96 (dd, J = 11.9, 4.5 Hz, 1H), 3.34 (d, J = 12.9 Hz, 1H), 2.92 (t, J = 14.0 Hz, 1H), 2.71-2.56 (m, 2H), 2.33 (s, 3H), 2.27 (s, 3H), 1.96 (d, J = 13.8 Hz, 1H), 1.61-1.41 (m, 6H), 1.37 (d, J = 14.0 Hz, 1H), 1.23 (t, J = 7.5 Hz, 3H), 1.11 (d, J = 10.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 138.1, 136.8, 131.2, 130.8, 129.8, 129.5, 127.0, 51.3, 49.4, 42.4, 38.5, 33.9, 32.3, 30.8, 24.6, 24.1, 23.0, 21.5, 21.1. IR (KBr): 2943, 2862, 2360, 1490, 1340, 1159, 950, 806, 661, 547, 501 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{24}H_{32}NO_2S_2^+$: 430.1869; found: 430.1874.

*4.2.23. (4,4-Diphenyl-2-((4-tolylthio)methyl)pyrrolidin-1-yl)(4-fluorophenyl)methanon (**5aa**)*

Compound **5aa** was prepared according to the general procedure and was isolated as pale yellow solid (93.4 mg, 80% yield) after flash chromatography (petroleum ether: ethyl acetate = 40: 1, v/v). m.p. 107-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.2 Hz, 2H), 7.21-7.09 (m, 8H), 7.07-7.02 (m, 3H), 6.97 (dd, J = 8.5, 1.9 Hz, 3H), 6.94-6.89 (m, 2H), 4.36-4.25 (m, 1H), 4.15 (dd, J = 11.1, 1.8 Hz, 1H), 3.75 (d, J = 11.1 Hz, 1H), 3.57 (dd, J = 14.0, 6.4 Hz, 1H), 3.26 (dd, J = 14.0, 2.7 Hz, 1H), 2.82 (dd, J = 8.4, 5.7 Hz, 2H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 143.8, 142.8, 134.9, 131.5, 128.8, 128.7, 128.6, 128.1, 127.6, 127.6, 125.7, 125.7, 125.6, 125.2, 114.4, 114.2, 59.3, 55.2, 52.7, 40.5, 35.2, 19.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.2. IR (KBr): 2868, 2358, 1618, 1496, 1419, 1218, 852, 754, 700 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{29}FNOS^+$: 482.1948; found: 482.1950.

*4.2.24. (4-Chlorophenyl)(4,4-diphenyl-2-((4-tolylthio)methyl)pyrrolidin-1-yl)methanone (**5ba**)*

Compound **5ba** was prepared according to the general procedure and was isolated as pale yellow solid (108.4 mg, 87% yield) after flash chromatography (petroleum ether: ethyl acetate = 40: 1, v/v). m.p. 134-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 7.8 Hz, 4H), 7.18 (d, J = 7.7 Hz, 2H), 7.12 (dd, J = 8.5, 6.4 Hz, 3H), 7.10-7.00 (m, 5H), 6.98 (d, J = 7.9 Hz, 2H), 6.91 (dd, J = 7.1, 1.8 Hz, 2H), 4.36-4.27 (m, 1H), 4.12 (dd, J = 11.1, 1.9 Hz, 1H), 3.74 (d, J = 11.2 Hz, 1H), 3.58 (dd, J = 13.9, 6.3 Hz, 1H), 3.26 (dd, J = 14.0, 2.7 Hz, 1H), 2.91-2.72 (m, 2H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 144.8, 143.8, 136.5, 136.0, 134.7, 132.5, 129.9, 129.1, 128.9, 128.7, 128.6, 128.5, 126.8, 126.7, 126.7, 126.2, 60.3, 56.3, 53.8, 41.5, 36.3, 21.0. IR (KBr): 2866, 2360, 1622, 1494, 1423, 1089, 750, 700 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{29}ClNOS^+$: 498.1653; found: 498.1650.

*4.2.25. (4-Bromophenyl)(4,4-diphenyl-2-((4-tolylthio)methyl)pyrrolidin-1-yl)methanone (**5ca**)*

Compound **5ca** was prepared according to the general procedure and was isolated as pale yellow solid (86.4 mg, 64% yield) after flash chromatography (petroleum ether: ethyl acetate = 40: 1, v/v). m.p. 72-74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 7.22-7.16 (m, 3H), 7.12 (t, J = 7.4 Hz, 3H), 7.08-7.02 (m, 3H), 7.00-6.96 (m, 4H), 6.92 (d, J = 7.5 Hz, 2H), 4.36-4.25 (m, 1H), 4.12 (d, J = 11.1 Hz, 1H), 3.75 (d, J = 11.2 Hz, 1H), 3.57 (dd, J = 14.1, 6.4 Hz, 1H), 3.26 (d, J = 13.8 Hz, 1H), 2.89-2.72 (m, 2H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 144.8, 143.8, 136.0, 135.2, 132.5, 131.5, 129.9, 129.2, 129.1, 128.7, 128.6, 126.8, 126.7, 126.2, 124.8, 60.3,

56.3, 53.8, 41.5, 36.3, 21.0. IR (KBr): 2920, 2875, 2358, 1635, 1490, 1417, 1066, 806, 752, 698 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{29}BrNOS^+$: 542.1148; found: 542.1149.

*4.2.26. (4,4-Diphenyl-2-((4-tolylthio)methyl)pyrrolidin-1-yl)(phenyl)methanone (**5da**)*

Compound **5da** was prepared according to the general procedure and was isolated as pale yellow solid (71.9 mg, 62% yield) after flash chromatography (petroleum ether: ethyl acetate = 40: 1, v/v). m.p. 71-73 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, J = 7.1 Hz, 1H), 7.34-7.22 (m, 4H), 7.22-7.16 (m, 5H), 7.12 (dd, J = 7.6, 5.2 Hz, 3H), 7.05 (t, J = 7.5 Hz, 3H), 6.99 (d, J = 7.9 Hz, 2H), 6.95-6.91 (m, 2H), 4.36-4.26 (m, 1H), 4.18 (dd, J = 11.1, 1.9 Hz, 1H), 3.77 (d, J = 11.1 Hz, 1H), 3.53 (dd, J = 13.9, 6.6 Hz, 1H), 3.34 (dd, J = 13.9, 2.7 Hz, 1H), 2.90-2.74 (m, 2H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 145.0, 143.9, 136.4, 135.9, 132.6, 130.4, 129.9, 129.1, 128.7, 128.6, 128.3, 127.4, 126.8, 126.7, 126.6, 126.3, 60.2, 56.2, 53.7, 41.8, 36.4, 21.0. IR (KBr): 2918, 2873, 2360, 1633, 1492, 1406, 1028, 806, 698 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{30}NOS^+$: 464.2043; found: 464.2047.

*4.2.27. (4,4-Diphenyl-2-((4-tolylthio)methyl)pyrrolidin-1-yl)(4-tolyl)methanone (**5ea**)*

Compound **5ea** was prepared according to the general procedure and was isolated as pale yellow solid (77.7 mg, 65% yield) after flash chromatography (petroleum ether: ethyl acetate = 40: 1, v/v). m.p. 62-64 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.1 Hz, 3H), 7.11 (d, J = 5.0 Hz, 6H), 7.04 (d, J = 7.5 Hz, 3H), 6.98 (d, J = 7.9 Hz, 2H), 6.93 (d, J = 7.7 Hz, 2H), 4.29 (d, J = 8.2 Hz, 1H), 4.22 (d, J = 11.4 Hz, 1H), 3.76 (d, J = 11.2 Hz, 1H), 3.48 (dd, J = 13.9, 6.7 Hz, 1H), 3.35 (d, J = 13.8 Hz, 1H), 2.88-2.71 (m,

2H), 2.32 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 145.1, 144.0, 140.6, 135.9, 133.5, 129.8, 129.1, 128.9, 128.7, 128.6, 128.5, 127.5, 126.8, 126.7, 126.6, 126.3, 60.2, 56.1, 53.7, 41.9, 36.5, 21.5, 21.0. IR (KBr): 2920, 2873, 2360, 1635, 1492, 1411, 750, 698 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{32}H_{32}NOS^+$: 478.2199; found: 478.2203.

*4.2.28. (4,4-Diphenyl-2-((4-tolylthio)methyl)pyrrolidin-1-yl)(4-methoxyphenyl)methanone (**5fa**)*

Compound **5fa** was prepared according to the general procedure and was isolated as dark yellow oil (91.4 mg, 74% yield) after flash chromatography (petroleum ether: ethyl acetate = 40: 1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 7.9 Hz, 2H), 7.24-7.14 (m, 5H), 7.11 (dd, J = 9.7, 7.0 Hz, 3H), 7.05 (d, J = 7.8 Hz, 3H), 6.97 (d, J = 7.9 Hz, 2H), 6.91 (d, J = 7.7 Hz, 2H), 6.79 (d, J = 8.3 Hz, 2H), 4.26 (d, J = 10.8 Hz, 2H), 3.76 (d, J = 8.5 Hz, 4H), 3.49 (dd, J = 13.9, 6.7 Hz, 1H), 3.32 (dd, J = 13.9, 2.7 Hz, 1H), 2.80 (dd, J = 8.7, 5.9 Hz, 2H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 144.0, 143.0, 134.8, 128.8, 128.6, 128.4, 128.0, 127.6, 127.5, 127.5, 125.7, 125.6, 125.5, 125.4, 125.3, 112.4, 59.3, 55.1, 54.3, 52.7, 40.7, 35.4, 19.9. IR (KBr): 2922, 2871, 2358, 1624, 1492, 1419, 1253, 840, 806, 698 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{32}H_{32}NO_2S^+$: 494.2148, found: 494.2153.

*4.2.29. 4,4-Diphenyl-2-((4-tolylthio)methyl)pyrrolidine (**5ga**)*

Compound **5ga** was prepared according to the general procedure. The pH value of the reaction mixture was adjusted to 9 with saturated aqueous $NaHCO_3$ solution, and the mixture was extracted with CH_2Cl_2 (20 mL). The organic layer was washed with saturated brine, dried over Na_2SO_4, and was concentrated in vacuo. Product **5ga** was isolated as yellow oil (45.8 mg, 51% yield) after flash chromatography. ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.29-7.24 (m, 8H), 7.23-7.20 (m, 2H), 7.21-7.12 (m, 2H), 7.08 (d, J = 7.9 Hz, 2H), 3.78-3.72 (m, 1H), 3.69 (dd, J = 6.7, 2.8 Hz, 1H), 3.53-3.44 (m, 2H), 3.07 (dd, J = 12.6, 6.6 Hz, 1H), 2.96 (dd, J = 12.6, 6.8 Hz, 1H), 2.89 (dd, J = 13.0, 6.9 Hz, 1H), 2.31 (s, 3H), 2.20 (dd, J = 13.0, 8.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 146.3, 136.2, 132.6, 130.15, 129.7, 128.5, 128.4, 127.0, 126.8, 126.2, 126.2, 57.5, 56.9, 56.86, 44.4, 41.6, 21.0. IR (KBr): 3338, 3022, 2920, 1596, 1492, 1446, 1091, 804, 752, 700. HRMS (m/z): $[M + H]^+$ calcd for $C_{24}H_{26}NS^+$: 360.1780; found: 360.1783.

*4.2.30. (9H-Fluoren-9-yl)methyl 4,4-diphenyl-2-((4-tolylthio)methyl)pyrrolidine-1-carboxylate and (9H-fluoren-9-yl)methyl 3,3-diphenyl-5-(4-tolylthio)piperidine-1-carboxylate (**5ha** and **5ha'**)*

Compound **5ha** and **5ha'** was prepared according to the general procedure and was isolated as white solid (106.2 mg, 73% yield) after flash chromatography (petroleum ether: ethyl acetate = 40: 1, v/v). m.p. 61-63 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 7.6, 2.5 Hz, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.53-7.45 (m, 1H), 7.38-7.28 (m, 2H), 7.30-7.17 (m, 5H), 7.13 (q, J = 7.2 Hz, 7H), 7.09-7.03 (m, 4H), 6.92 (d, J = 7.9 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 4.63-4.38 (m, 1H), 4.33-4.22 (m, 1H), 4.17-3.87 (m, 2H), 3.75-3.32 (m, 2H), 3.15-2.97 (m, 1H), 2.87-2.76 (m, 1H), 2.73-2.57 (m, 1H), 2.57-2.26 (m, 1H), 2.12 (d, J = 8.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 154.4, 145.5, 145.3, 145.0, 144.8, 144.1, 144.0, 143.9, 143.9, 141.4, 141.4, 141.3, 141.2, 136.3, 136.0, 132.3, 132.2, 130.2, 130.0, 129.7, 129.7, 129.3, 129.1, 128.7, 128.6, 128.6, 127.8, 127.7, 127.7, 127.6, 127.1, 127.1, 126.8, 126.7, 126.6, 126.5, 126.4, 126.4, 125.1, 125.0, 124.9, 124.8, 120.0, 120.0, 120.0, 67.3, 67.2, 56.6, 56.5, 56.5, 56.1, 52.8, 52.7, 47.3, 47.2, 43.7, 42.4, 38.8, 37.1, 21.0, 20.9.

HRMS (m/z): $[M + Na]^+$ calcd for $C_{39}H_{35}NNaO_2S^+$: 604.2281; found: 604.2285.

*4.2.31. Benzyl 4,4-diphenyl-2-((4-tolylthio)methyl)pyrrolidine-1-carboxylate and benzyl 3,3-diphenyl-5-(4-tolylthio)piperidine-1-carboxylate (**5ia** and **5ia'**)*

Compound **5ia** was prepared according to the general procedure and was isolated as yellow oil (83.9 mg, 68% yield) after flash chromatography (petroleum ether: ethyl acetate = 40: 1, v/v). 1H NMR (400 MHz, CDCl3) δ 7.30-7.24 (m, 2H), 7.22 (d, J = 7.3 Hz, 3H), 7.18-7.15 (m, 2H), 7.16-7.10 (m, 5H), 7.08 (s, 2H), 7.06-7.02 (m, 3H), 6.97 (d, J = 7.8 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 5.08 (dd, J = 37.8, 12.4 Hz, 1H), 4.92 (dd, J = 27.4, 12.4 Hz, 1H), 4.50 (dd, J = 66.6, 11.5 Hz, 1H), 3.95-3.75 (m, 1H), 3.67 (dd, J = 15.5, 11.5 Hz, 1H), 3.46-3.29 (m, 1H), 3.06-2.78 (m, 1H), 2.81-2.67 (m, 1H), 2.62-2.47 (m, 1H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 154.5, 145.4, 145.0, 144.9, 136.9, 136.5, 136.2, 136.0, 132.4, 132.1, 129.8, 129.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 126.8, 126.8, 126.6, 126.6, 126.4, 126.4, 67.2, 66.9, 56.7, 56.5, 56.4, 56.1, 53.0, 52.7, 43.8, 42.5, 38.6, 37.3, 21.0. HRMS (m/z): $[M + H]^+$ calcd for $C_{32}H_{32}NO_2S^+$: 494.2148; found: 494.2150.

*4.2.32. 4,4-Diphenyl-2-((phenylthio)methyl)-1-tosylpyrrolidine (**3ab**)*

Compound **3ab** was prepared according to the general procedure and was isolated as white solid (105 mg, 84% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 128-130 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.2, 3.7 Hz, 4H), 7.30-7.13 (m, 7H), 7.12-7.00 (m, 6H), 6.97 (d, J = 7.2 Hz, 2H), 4.44 (d, J = 9.1 Hz, 1H), 3.59 (d, J = 14.4 Hz, 2H), 3.35 (d, J = 10.4 Hz, 1H), 2.66-2.47 (m, 2H), 2.27 (s, 3H), 2.14 (t, J = 12.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 144.9, 143.5, 135.0, 133.0,

129.6, 129.1, 128.7, 128.6, 127.7, 127.6, 126.8, 126.7, 126.5, 126.3, 126.3, 58.6, 58.5, 52.2, 41.7, 37.9, 21.5. The NMR data were in agreement with reported results [10d].

*4.2.33. 2-(((4-Fluorophenyl)thio)methyl)-4,4-diphenyl-1-tosylpyrrolidine (**3ac**)*

Compound **3ac** was prepared according to the general procedure and was isolated as white solid (108.7 mg, 84% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 7.5 Hz, 4H), 7.20 (q, J = 7.6 Hz, 4H), 7.13-7.02 (m, 6H), 6.97 (d, J = 4.4 Hz, 4H), 4.44 (d, J = 10.1 Hz, 1H), 3.51 (d, J = 12.7 Hz, 2H), 3.34 (d, J = 10.1 Hz, 1H), 2.65-2.45 (m, 2H), 2.28 (s, 3H), 2.12 (t, J = 12.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 144.8, 143.6, 132.9, 132.5, 132.4, 129.7, 128.7, 128.6, 127.5, 126.8, 126.7, 126.5, 126.3, 116.3, 116.0, 58.5, 58.5, 52.2, 41.7, 39.0, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.2. IR (KBr): 2923, 2358, 1587, 1488, 1336, 1164, 1039, 835, 703, 663, 547 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{30}H_{29}FNO_2S_2^+$: 518.1618; found: 518.1617.

*4.2.34. 2-(((4-Chlorophenyl)thio)methyl)-4,4-diphenyl-1-tosylpyrrolidine (**3ad**)*

Compound **3ad** was prepared according to the general procedure and was isolated as white solid (101.5 mg, 76% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 149-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.9 Hz, 2H), 7.28-7.15 (m, 8H), 7.12-7.02 (m, 6H), 6.98-6.93 (m, 2H), 4.43 (d, J = 10.1 Hz, 1H), 3.62-3.50 (m, 2H), 3.35 (d, J = 10.1 Hz, 1H), 2.64-2.46 (m, 2H), 2.28 (s, 3H), 2.14 (dd, J = 14.2, 11.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 143.8, 142.6, 132.6, 132.0, 131.3, 129.9, 128.7, 128.1, 127.7, 127.6, 126.5, 125.7, 125.7, 125.5, 125.3, 57.5, 57.4, 51.2, 40.7, 37.1, 20.5. IR (KBr): 2923, 2860, 2360, 1475, 1340, 1164, 813, 698, 663, 549 cm^{-1}. HRMS

(m/z): $[M + H]^+$ calcd for $C_{30}H_{29}ClNO_2S_2^+$: 534.1323; found: 534.1328.

*4.2.35. 2-(((4-Bromophenyl)thio)methyl)-4,4-diphenyl-1-tosylpyrrolidine (**3ae**)*

Compound **3ae** was prepared according to the general procedure and was isolated as white solid (89.7 mg, 62% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, J = 7.0 Hz, 4H), 7.24-7.14 (m, 6H), 7.05 (d, J = 8.1 Hz, 6H), 6.95 (d, J = 7.4 Hz, 2H), 4.42 (d, J = 10.1 Hz, 1H), 3.54 (d, J = 12.6 Hz, 2H), 3.36 (d, J = 10.1 Hz, 1H), 2.56 (t, J = 7.2 Hz, 2H), 2.27 (s, 3H), 2.15 (t, J = 12.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 143.7, 134.4, 133.1, 132.1, 131.2, 129.8, 128.7, 128.6, 127.5, 127.4, 126.8, 126.7, 126.5, 126.3, 120.2, 58.5, 58.5, 52.2, 41.8, 38.1, 21.6. IR (KBr): 2916, 2860, 2358, 1475, 1344, 1164, 815, 698, 665, 549 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{30}H_{29}BrNO_2S_2^+$: 580.0797; found: 580.0799.

*4.2.36. 2-(((4-Nitrophenyl)thio)methyl)-4,4-diphenyl-1-tosylpyrrolidine (**3af**)*

Compound **3af** was prepared according to the general procedure and was isolated as yellow solid (98.1 mg, 72% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 155-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 7.2 Hz, 4H), 7.11 (dd, J = 15.9, 7.7 Hz, 6H), 6.99 (d, J = 7.4 Hz, 2H), 4.46 (d, J = 10.1 Hz, 1H), 3.74 (s, 1H), 3.67 (d, J = 14.4 Hz, 1H), 3.36 (d, J = 10.0 Hz, 1H), 2.59 (d, J = 8.1 Hz, 2H), 2.31 (s, 3H), 2.30-2.15 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 145.3, 144.6, 144.6, 144.0, 133.1, 129.9, 128.8, 128.7, 127.5, 126.9, 126.7, 126.7, 126.5, 126.3, 124.1, 58.2, 52.4, 41.8, 36.2, 21.5. IR (KBr): 2958, 2873, 2358, 1575, 1504, 1334, 1164, 1089, 698, 665, 553 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{30}H_{29}N_2O_4S_2^+$: 545.1563; found: 545.1563.

*4.2.37. 4,4-Diphenyl-1-tosyl-2-(((4-(trifluoromethyl)phenyl)thio)methyl)pyrrolidine (**3ag**)*

Compound **3ag** was prepared according to the general procedure and was isolated as white solid (102.2 mg, 72% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 146-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.3 Hz, 2H), 7.43-7.34 (m, 4H), 7.25-7.16 (m, 4H), 7.11-7.01 (m, 6H), 6.98-6.95 (m, 2H), 4.45 (dd, J = 10.1, 1.4 Hz, 1H), 3.71-3.49 (m, 2H), 3.34 (d, J = 10.1 Hz, 1H), 2.66-2.49 (m, 2H), 2.26 (s, 3H), 2.18 (dd, J = 14.5, 11.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 143.8, 140.8, 133.0, 129.8, 128.8, 128.7, 128.0, 127.5, 126.8, 126.8, 126.6, 126.3, 125.8, 125.8, 125.8, 58.4, 58.3, 52.3, 41.8, 36.8, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3. IR (KBr): 2868, 2358, 1602, 1496, 1323, 1166, 1093, 1014, 700, 665, 603 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{29}F_3NO_2S_2^+$: 568.1586; found: 568.1590.

*4.2.38. 2-(((4-(tert-Butyl)phenyl)thio)methyl)-4,4-diphenyl-1-tosylpyrrolidine (**3ah**)*

Compound **3ah** was prepared according to the general procedure and was isolated as white solid (73.7 mg, 53% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 67-69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 1.3 Hz, 3H), 7.24-7.16 (m, 4H), 7.10-6.95 (m, 9H), 4.44 (dd, J = 10.1, 1.4 Hz, 1H), 3.66-3.51 (m, 2H), 3.33 (d, J = 10.1 Hz, 1H), 2.65-2.44 (m, 2H), 2.26 (s, 3H), 2.10 (dd, J = 14.2, 11.8 Hz, 1H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 145.0, 144.9, 143.4, 133.0, 131.3, 129.7, 129.6, 128.7, 128.6, 127.6, 126.8, 126.7, 126.5, 126.4, 126.1, 58.6, 58.5, 52.1, 41.7, 38.1, 34.6, 31.4, 21.6. IR (KBr): 2958, 2866, 2360, 1490, 1346, 1164, 1029, 815, 700, 663, 547 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{34}H_{38}NO_2S_2^+$:

556.2338; found: 556.2341.

*4.2.39. 2-(((4-Methoxyphenyl)thio)methyl)-4,4-diphenyl-1-tosylpyrrolidine (**3ai**)*

Compound **3ai** was prepared according to the general procedure and was isolated as white solid (106 mg, 80% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.26-7.15 (m, 7H), 7.10-6.96 (m, 8H), 6.83 (d, J = 8.8 Hz, 2H), 4.43 (dd, J = 10.2, 1.4 Hz, 1H), 3.76 (s, 3H), 3.54-3.40 (m, 2H), 3.34 (d, J = 10.1 Hz, 1H), 2.65-2.48 (m, 2H), 2.28 (s, 3H), 2.15-1.97 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 144.9, 143.4, 133.4, 129.6, 128.6, 128.6, 128.4, 127.8, 127.6, 126.8, 126.8, 126.6, 126.4, 126.4, 114.7, 58.7, 58.6, 55.5, 52.1, 41.7, 39.7, 21.5. IR (KBr): 2925, 2360, 1591, 1490, 1336, 1163, 833, 700, 661, 547 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{32}NO_3S_2^+$: 530.1818; found: 530.1821.

*4.2.40. 4,4-Diphenyl-2-((3-tolylthio)methyl)-1-tosylpyrrolidine (**3aj**)*

Compound **3aj** was prepared according to the general procedure and was isolated as white solid (96.4 mg, 75% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 100-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.7 Hz, 2H), 7.25-7.12 (m, 7H), 7.10-7.01 (m, 6H), 6.98 (d, J = 7.0 Hz, 3H), 4.45 (d, J = 10.1 Hz, 1H), 3.60 (d, J = 12.6 Hz, 2H), 3.34 (d, J = 10.1 Hz, 1H), 2.64 (d, J = 13.7 Hz, 1H), 2.54 (dd, J = 13.3, 8.2 Hz, 1H), 2.29 (d, J = 4.1 Hz, 6H), 2.12 (t, J = 13.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 144.9, 143.4, 138.9, 134.7, 133.0, 130.0, 129.6, 128.9, 128.7, 128.6, 127.6, 127.1, 126.8, 126.7, 126.5, 126.5, 126.3, 58.5, 58.5, 52.1, 41.7, 37.7, 21.5, 21.4. IR (KBr): 2923, 2860, 2360, 1488, 1338, 1168, 1010, 779, 696, 665, 603, 549 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{32}NO_2S_2^+$: 514.1869; found: 514.1871.

*4.2.41. 2-(((2-Fluorophenyl)thio)methyl)-4,4-diphenyl-1-tosylpyrrolidine (**3ak**)*

Compound **3ak** was prepared according to the general procedure and was isolated as white solid (115.2 mg, 89% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, J = 7.7 Hz, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.19 (dq, J = 14.5, 7.4 Hz, 5H), 7.13-7.00 (m, 8H), 6.97 (d, J = 7.7 Hz, 2H), 4.43 (d, J = 10.1 Hz, 1H), 3.63-3.47 (m, 2H), 3.37 (d, J = 10.1 Hz, 1H), 2.69-2.51 (m, 2H), 2.28 (s, 3H), 2.17 (dd, J = 13.5, 11.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 144.8, 143.5, 132.1, 129.7, 128.7, 128.6, 128.5, 128.4, 127.8, 127.5, 126.8, 126.7, 126.5, 126.3, 124.8, 115.9, 115.6, 58.7, 58.5, 52.2, 41.8, 37.5, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.0. IR (KBr): 2925, 2862, 2360, 1488, 1338, 1166, 1012, 750, 698, 665, 551 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{30}H_{29}FNO_2S_2^+$: 518.1618; found: 518.1619.

*4.2.42. 2-(((2-Nitrophenyl)thio)methyl)-4,4-diphenyl-1-tosylpyrrolidine (**3al**)*

Compound **3al** was prepared according to the general procedure and was isolated as yellow solid (49.1 mg, 36% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 93-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 8.3, 1.5 Hz, 1H), 7.65 (dd, J = 8.3, 1.3 Hz, 1H), 7.57 (ddd, J = 8.3, 7.1, 1.5 Hz, 1H), 7.53-7.50 (m, 2H), 7.32-7.18 (m, 6H), 7.17-7.07 (m, 5H), 7.04-6.98 (m, 2H), 4.47 (dd, J = 10.0, 1.4 Hz, 1H), 3.86-3.68 (m, 1H), 3.64 (dd, J = 13.8, 2.9 Hz, 1H), 3.33 (d, J = 10.0 Hz, 1H), 2.72-2.62 (m, 1H), 2.55 (dd, J = 13.1, 8.5 Hz, 1H), 2.31 (s, 3H), 2.19 (dd, J = 13.8, 11.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 144.7, 144.5, 143.9, 136.0, 133.7, 133.0, 129.9, 128.8, 128.7, 127.5, 127.2, 126.9, 126.7, 126.6, 126.3, 125.0, 58.0, 57.7, 52.4, 42.0, 36.6, 21.5. IR (KBr): 2923, 2868, 2360, 1517, 1338, 1163, 702, 665, 547 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for

$C_{30}H_{29}N_2O_4S_2^+$: 545.1563; found: 545.1559.

*4.2.43. 2-((Naphthalen-2-ylthio)methyl)-4,4-diphenyl-1-tosylpyrrolidine (**3am**)*

Compound **3am** was prepared according to the general procedure and was isolated as pale yellow solid (112.7 mg, 82% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). m.p. 121-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.73 (dd, J = 10.5, 7.4 Hz, 2H), 7.44-7.35 (m, 2H), 7.24 (dd, J = 8.1, 2.1 Hz, 3H), 7.20-7.12 (m, 4H), 7.09 (d, J = 6.6 Hz, 2H), 7.01 (t, J = 5.4 Hz, 2H), 6.96 (q, J = 6.8 Hz, 3H), 6.76 (d, J = 7.9 Hz, 2H), 4.46 (d, J = 10.1 Hz, 1H), 3.72 (dd, J = 13.9, 2.8 Hz, 1H), 3.68-3.57 (m, 1H), 3.32 (d, J = 10.1 Hz, 1H), 2.66 (dd, J = 13.0, 3.5 Hz, 1H), 2.55 (dd, J = 13.1, 8.5 Hz, 1H), 2.24-2.17 (m, 1H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 143.4, 133.9, 132.4, 131.9, 129.7, 129.6, 128.7, 128.7, 128.6, 128.4, 127.8, 127.7, 127.5, 127.4, 127.2, 126.8, 126.7, 126.5, 126.4, 125.9, 58.6, 58.3, 52.2, 41.9, 37.7, 21.4. IR (KBr): 2958, 2929, 2360, 1338, 1166, 748, 700, 661, 547 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{34}H_{32}NO_2S_2^+$: 550.1869; found: 550.1870.

*4.2.44. 2-((Butylthio)methyl)-4,4-diphenyl-1-tosylpyrrolidine (**3an**)*

Compound **3an** was prepared according to the general procedure and was isolated as pale yellow oil (43.2 mg, 36% yield) after flash chromatography (petroleum ether: ethyl acetate = 50: 1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.3 Hz, 2H), 7.22-7.17 (m, 4H), 7.12 (d, J = 8.0 Hz, 2H), 7.10-7.04 (m, 4H), 7.04-6.99 (m, 2H), 4.34 (dd, J = 10.2, 1.1 Hz, 1H), 3.77-3.66 (m, 1H), 3.55 (d, J = 10.2 Hz, 1H), 3.01 (dd, J = 13.1, 3.3 Hz, 1H), 2.67 (dd, J = 13.0, 8.1 Hz, 1H), 2.60-2.49 (m, 1H), 2.41 (q, J = 7.1 Hz, 2H), 2.32 (s, 3H), 2.06 (dd, J = 13.1, 10.8 Hz, 1H), 1.48-1.37 (m, 2H), 1.30 (q, J = 7.3 Hz, 2H), 0.83 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 144.9, 143.5, 134.0, 129.7, 128.6, 127.4, 126.7, 126.6, 126.5, 126.4, 59.6, 58.5, 52.3, 42.2, 37.4, 32.4, 31.9, 21.9, 21.5, 13.7. IR (KBr): 2954, 2925, 2869, 1596, 1444, 1344, 1164, 702, 665, 547 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{28}H_{34}NO_2S_2^+$: 480.2025; found: 480.2024.

*4.3. 4,4-Diphenyl-1-tosyl-2-(tosylmethyl)pyrrolidine (**6**)*

To a 25 mL flask were added **3aa** (130.9 mg, 0.25 mmol), *m*-CPBA (87 mg, 0.5 mmol) and dry CH_2Cl_2 (10 mL). The resulting mixture was stirred overnight at room temperature. Then CH_2Cl_2 (10 mL) was added and the mixture was washed with aqueous $Na_2S_2O_3$ and aqueous $NaHCO_3$. The CH_2Cl_2 layer was dried with Na_2SO_4, and concentrated to give crude residue, which was purified by flash column chromatography (petroleum ether: ethyl acetate = 10: 1) to give **6** (126.9 mg, 93% yield). White solid. m.p. 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.34 (dd, J = 8.4, 1.4 Hz, 2H), 7.31-7.27 (m, 4H), 7.21-7.11 (m, 6H), 7.08-7.04 (m, 2H), 4.52 (dd, J = 10.0, 1.7 Hz, 1H), 3.88-3.76 (m, 2H), 3.23 (d, J = 10.0 Hz, 1H), 3.02-2.92 (m, 1H), 2.70 (dd, J = 13.2, 8.9 Hz, 1H), 2.60 (dd, J = 14.1, 11.1 Hz, 1H), 2.49 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 144.4, 144.0, 144.0, 136.3, 131.9, 129.9, 129.8, 128.8, 128.7, 128.2, 127.6, 126.9, 126.8, 126.7, 126.3, 59.9, 57.4, 53.8, 52.4, 42.2, 21.7, 21.6. IR (KBr): 3085, 2936, 1598, 1494, 1474, 1165, 703, 664 cm^{-1}. HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{32}NO_4S_2^+$: 546.1767; found: 546.1770.

*4.4. 4,4-Diphenyl-2-((4-tolylsulfinyl)methyl)-1-tosylpyrrolidine (**7**)*

To a 25 mL flask were added **3aa** (130.9 mg, 0.25 mmol), MeOH (1 mL), DCM (9 mL) and $AlCl_3$ (17.4 mg, 0.13 mmol) and the mixture was stirred at room temperature for 1 min.

Then $PhI(OAc)_2$ (81 mg, 0.25 mmol) was added and the reaction mixture was stirred at room temperature for 8 hours. The solvent was removed under reduced pressure to give crude residue, which was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1) to give **7** (66.2 mg, 50% yield) and ***epi*-7** (50.3 mg, 38% yield).

7: white solid, m.p. 166-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 6H), 7.23 (t, J = 7.7 Hz, 2H), 7.19-7.12 (m, 3H), 7.09-7.01 (m, 4H), 7.00-6.96 (m, 3H), 4.43 (dd, J = 10.2, 1.4 Hz, 1H), 3.80-3.71 (m, 1H), 3.31-3.22 (m, 2H), 2.93-2.84 (m, 1H), 2.70 (dd, J = 13.2, 8.4 Hz, 1H), 2.49 (dd, J = 13.8, 10.6 Hz, 1H), 2.39 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 144.4, 143.6, 141.1, 139.2, 132.4, 129.9, 129.6, 128.8, 128.6, 127.5, 126.9, 126.7, 126.5, 126.4, 124.2, 59.3, 57.7, 54.5, 52.6, 42.5, 21.5, 21.4. IR (KBr): 2918, 1598, 1492, 1344, 1161, 1045, 811, 702, 665, 559, 547. HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{32}NO_3S_2^+$: 530.1818; found: 530.1817.

***epi*-7**: white solid, m.p. 70-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.24-7.17 (m, 6H), 7.14 (d, J = 8.0 Hz, 2H), 7.10-7.03 (m, 4H), 6.96 (dd, J = 8.0, 1.7 Hz, 2H), 4.36 (d, J = 10.1 Hz, 1H), 4.07-3.95 (m, 1H), 3.32 (d, J = 10.1 Hz, 1H), 3.27 (dd, J = 13.3, 2.8 Hz, 1H), 2.67-2.63 (m, 2H), 2.42-2.37 (m, 1H), 2.34 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 144.3, 143.9, 141.7, 140.7, 130.0, 129.9, 129.8, 128.7, 128.6, 127.7, 126.9, 126.7, 126.5, 126.3, 124.2, 62.4, 57.5, 55.8, 52.7, 43.2, 21.6, 21.5. IR (KBr): 2922, 1596, 1494, 1342, 1164, 1087, 1047, 813, 702, 665, 549. HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{32}NO_3S_2^+$: 530.1818; found: 530.1817.

*4.5. 4,4-Diphenyl-2-((4-tolylthio)methyl)pyrrolidine (**5ga**):*

5ea (50 mg, 0.1 mmol) was refluxed with 1 mL of 6 N HCl for 24 h, and the mixture was

cooled to room temperature. The solution was treated with aqueous $NaHCO_3$. The mixture was extracted with CH_2Cl_2, the organic phase was dried with Na_2SO_4 and was concentrated to give a crude residue, which was purified by flash column chromatography (dichloromethane : methanol = 20:1) to give **5ga** (26 mg, 72% yield).

5. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2019.XX.XXX.

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