Monatsh Chem
DOI 10.1007/s00706-016-1661-6

ORIGINAL PAPER

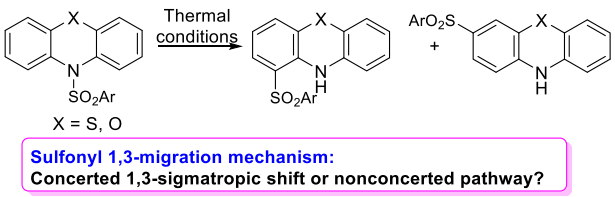
Mechanistic insight into thermal 1,3- and 1,5-sulfonyl migrations of *N*-arenesulfonylphenothiazines and *N*-arenesulfonylphenoxazines

Jiandong Wang[1] · Kwon-Il Son[1] · Jiaxi Xu[1]

Received: 17 November 2015 / Accepted: 7 January 2016

Abstract The substrate scope and mechanistic insight of the thermal-induced 1,3- and 1,5-sulfonyl migration reactions of various sulfonamides have been investigated. The results indicate that both *N*-arenesulfonylphenothiazines and *N*-arenesulfonylphenoxazines can undergo 1,3- and 1,5-sulfonyl migrations to afford the corresponding aryl sulfone derivatives in modest regioselectivities and yields under thermal and neutral conditions. The homolytic cleavage of the sulfonamide bond and intermolecular radical–radical coupling reaction mechanism was proposed for the 1,3- and 1,5-sulfonyl migrations on the basis of intercrossing and competitive capture experiments.

Graphical abstract



Keywords Thermal rearrangement · Sulfonyl shift · Mechanism · Phenothiazine · Phenoxazine

✉ Jiaxi Xu
jxxu@mail.buct.edu.cn

[1] State Key Laboratory of Chemical Resource Engineering, Faculty of Science, Department of Organic Chemistry, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

Introduction

The sulfonyl rearrangement reactions, which occur as C- to C-, N- to O-, or N- to C-migrations, are ones of powerful strategies for the construction of biologically active molecules via facilitating the formation of a new C–S or O–S bond and have drawn intense attention due to their mechanistic interest and synthetic application [1–4].

1,3-Allylic sulfonyl migrations which proceed as C- to C transfers have been found to occur by intimate ion pairs [5, 6], free radical chain addition–elimination [7–9], and even [1,3] -sigmatropic shift mechanism [10]. The 1,3-sulfonyl migrations from N- to O-shift have been observed in *N*-sulfonylpyridinones [11–13] and further probed in quinazolin-4(3*H*)-ones and thienopyrimidin-4(3*H*)-ones [14].

1,3-Sulfonyl shifts involving N- to C migrations have been described and play a critical role in the framework construction of heterocycle derivatives. For instance, 4-(sulfonylmethyl)oxazoles can be prepared by the silver-catalyzed [3,3] rearrangement of *N*-sulfonyl propargylamides accompanying with 1,3-sulfonyl migration which proceed in both intra- and intermolecular manners [15]. The sulfonyl group in *N*-methyl-2-(1-phenyl)-*N*-tosylaniline intramolecularly migrates to the 3-position of the indole skeleton in the presence of 10 mol% $AuBr_3$ [16]. A regioselective 1,3-sulfonyl group migration from *N*-alkane/arene/heteroarenesulfonylindoles to 7-sulfonyl functionalized indoles has been found to be non-concerted processes by a crossover experiment [17]. For the construction of pyrroles, Wan's group reported the first example of intermolecular sulfonyl migration from *N*-(4-methylbenzene)sulfonyl-protected 3-aza-1,5-enyne derivatives to α branch of pyrroles via allene intermediates produced by the aza-Claisen rearrangement [18]. 1-Substituted 3-sulfonyl-1*H*-pyrroles can be prepared via the gold(I)-

Published online: 22 February 2016

catalyzed domino aminocyclization/intramolecular 1,3-sulfonyl migration of *N*-sulfonylaminobut-3-yn-2-ols [19]. For the formation of pyrazoles, an intermolecular 1,3-migration of sulfonyl groups has been observed in the silver(I)-catalyzed construction of pyrazoles from propargyl *N*-sulfonylhydrazones [20]. In the presence of Lewis base, multisubstituted 4-sulfonyl-1*H*-pyrazoles can be prepared from *N*-propargylic *N*-sulfonylhydrazone derivatives via allenic sulfonamides as intermediates followed by an intramolecular 1,3-sulfonyl shift [21]. In addition, an intramolecular 1,3-sulfonyl migration after the 6π-ECR of aminoallene intermediates can afford tetrasubstituted imidazoles [22]. Cyclic nitrones can be provided from *N*-sulfonyl alkylhydroxylamines via the gold catalyzed oxygen-transfer and 1,3-sulfonyl migration [23]. Additionally, the $\pi(C_\alpha{=}C_\beta){-}\sigma^*(N{-}SO_2)$ interaction in 4-vinylidene-2-oxazolidinone weakens the N-SO_2 bond so that the N- to C_α-1,3-sulfonyl shift even can be promoted by allylsilanes and enol ethers via a four-membered sulfurane oxide intermediate [24].

It has been well known that base or noble metal catalyst or Lewis acid is necessary to trigger the N- to C-sulfonyl migration in relatively active substrates bearing particular structures. Therefore, there are only limited reports devote to the thermal induced N- to C-sulfonyl migration. Wuldl and coworkers provided the first thermal uncatalyzed sulfonyl migration from *N*-(4-methylbenzene)sulfonyl ynamide to nitrile via a first-order reaction process [25]. Recently, it was reported that *N*-allyl-*N*-sulfonyl ynamides underwent a sequence of tandem sigmatropic rearrangement, an aza-Claisen reaction followed by a very fast N- to C-1,3-sulfonyl shift, under thermal conditions [26].

Recently, our efforts have been directed to heteroatom 1,3-sigmatropic shifts (O and N [1,3]-sigmatropic shifts) [27, 28]. In our continuous interest on heteroatom 1,3-sigmatropic shift reactions, we have concentrated on N- to C-sulfonyl migration now. We wonder whether it is possible that the unusual thermal-induced sulfonyl migration including the breaking of a relatively stable sulfonamide bond would be observed in more common and robust reaction systems rather than in particular cases involving less stable intermediates such as *N*-sulfonyl ketenimines. In 1989, Chakraborty's group discovered 1,3- and 1,5-sulfonyl shifts triggered by photochemistry in *N*-sulfonylcarbazoles and envisioned an intrasolvent-cage radical–radical trapping mechanism for the formation of photo-rearranged products [Eq. (1), Scheme 1] [29]. Thus, we have a curiosity to know whether it was possible that similar *N*-sulfonyl aromatic heterocyclic compounds would undergo an uncatalyzed thermal N- to C-sulfonyl migration to afford the corresponding heterocycles equipped with sulfonyl functionality. To get a thorough understanding on sulfonyl migration under thermal conditions, various sulfonamides bearing different aromatic heterocyclic nuclei were prepared and employed in our systematical investigation. Finally, we found that *N*-arenesulfonylphenothiazines and *N*-arenesulfonylphenoxazines can undergo 1,3- and 1,5-sulfonyl migrations to afford the corresponding nitrogen-containing heteroaryl sulfone derivatives in moderate yields under mild, thermal, and neutral conditions. Herein, we report our results on the substrate scope and mechanistic insight.

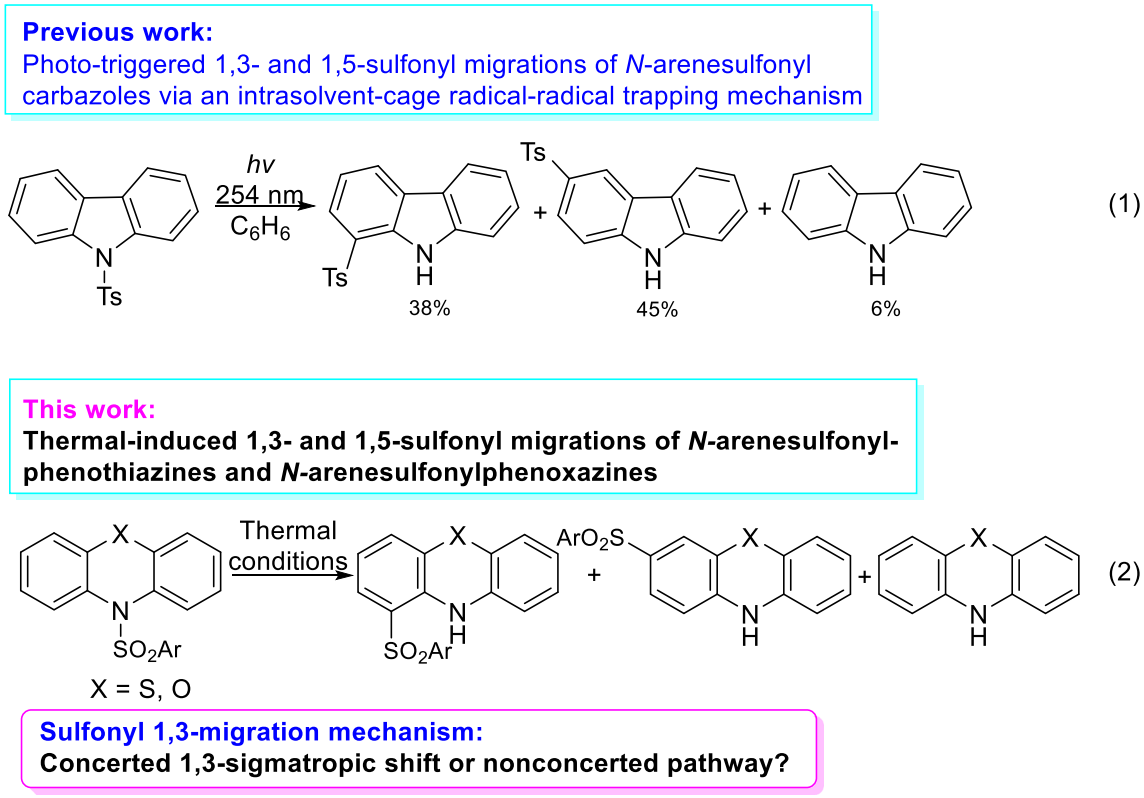
Results and discussion

In the [1, 3]-sigmatropic migration of sulfonyl group from *exo*-methylenecycloalkyl sulfones to *endo*-isomers, the experimental order of migration reactivity was apparently in correlation with the dihedral angle values (C=C–C–S), which indicated that the arenesulfonyl groups favored a near-axial direction in the four-membered *exo*-isomers [5, 6]. If it exists, it is logical to hypothesize that the concerted thermal-induced N- to C-1,3-sulfonyl migration would involve a four-membered cyclic transition state (TS) such as TS in Scheme 2. In other words, a relatively lower bond angle (Φ) value (C_1–C_2–N) in initial sulfonamides would favor the formation of the four-membered ring transition state in the sulfonyl migration step if this transformation proceeds in a concert process. Thus, the study commenced with screening various sulfonamides bearing different bond angle values to demonstrate our assumption.

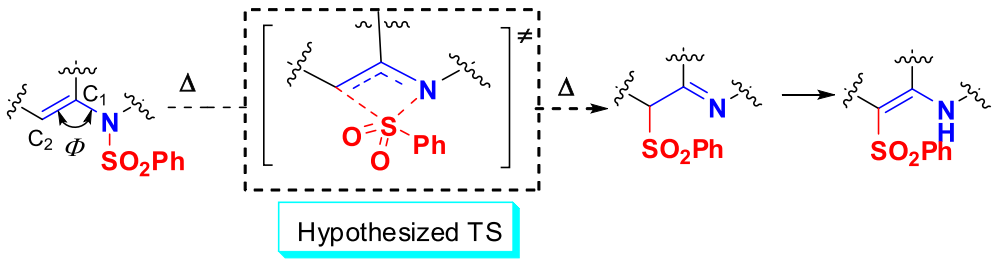
The thermal rearrangement reactions generally require relatively higher temperature and longer reaction time. Thus, mesitylene, *o*-dichlorobenzene (DCB), ethylene glycol, and even biphenyl were chosen as solvents due to their gradually increased boiling points. Then several types of sulfonamides, such as more flexible acyclic sulfonamides **1a**–**1c**, normal cyclic *N*-(phenylsulfonyl)-1,2,3,4-tetrahydroquinoline (**1d**), and cyclic sulfonamides **1e**–**1g** with conformational restriction or highly strained rings, were screened at different temperatures for 20–24 h (Fig. 1). However, the TLC analysis clearly indicated that there was almost no reaction happened for **1a**–**1f**, even they were subjected to very harsh thermal conditions (200 °C in biphenyl for 20 h).

Although the thermal sulfonyl migration was not detected in most cases (**1a**–**1f** in Fig. 1), when **1g** was first refluxed in mesitylene for 24 h, the thermal-rearranged products were separated readily via silica gel column chromatography to afford 1,3-sulfonyl migration product **2g** (22 % yield) and 1,5-sulfonyl migration product **3g** (38 % yield) and the dissociation product phenothiazine (6 % yield). However, 10-(phenylsulfonyl)-10*H*-phenothiazine-5-oxide (**1h**), which was prepared by oxidation of the corresponding phenothiazine (**1g**) with *m*-

Scheme 1



Scheme 2



chloroperoxybenzoic acid (MCPBA), did not achieve the rearrangement reaction under the same reaction conditions due to the modification of the heterocyclic nucleus. Therefore, the thermal-induced sulfonyl migration has been proven to be highly substrate-dependent.

Phenothiazine and their derivatives are one class of extremely useful organic molecules and have various significant applications. Phenothiazines have been extensively used as drugs, such as chlorpromazine, trifluprom azine, promethazine, antibacterial, antiviral, and even anti-AIDS [30–34]. Meanwhile, phenothiazines are recognized as high-performance organic photosensitizers and always serve as powerful donor in common solar dye-design [35–38]. Thus, the thermal 1,3- and 1,5-sulfonyl migrations of *N*-sulfonylphenothiazines direct toward the corresponding functionalized phenothiazines would possess potential applications in medical chemistry and optoelectronic materials.

Subsequently, the optimization of the reaction from **1g** to **2g** and **3g** was conducted and summarized in Table 1. The rearrangement reaction was highly dependent to reaction temperature and had obvious solvent effect. When

Fig. 1 Sulfonamides explored on thermal sulfonyl migration

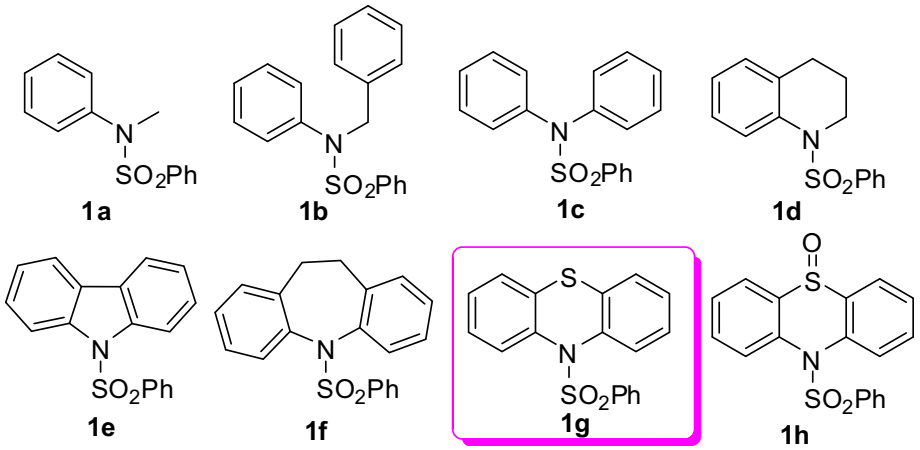
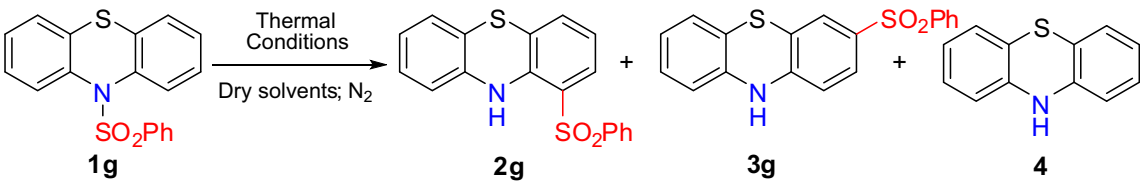


Table 1 Reactions of 10-(phenylsulfonyl)-10*H*-phenothiazine under various thermal conditions



Entry	Solvent[a]	Temp./°C	Time/h	Yield/%[b]		
				2g	**3g**	**4**
1	Toluene	Reflux	24	0	0	0
2	*p*-Xylene	Reflux	24	0	0	0
3	Mesitylene	Reflux	24	22	38	6
4	Mesitylene	165	1	20	34	7
5	DCB	165	0.5	12	38	3
6	Ethylene glycol	165	0.5	ND[c]	81	ND[c]
7	Mesitylene	160	2	18	47	3

All the reactions were conducted on 0.3 mmol scale in 3.0 cm^3 of solvent

[a] All the solvents were dried prior to use

[b] Isolated yield by column chromatography

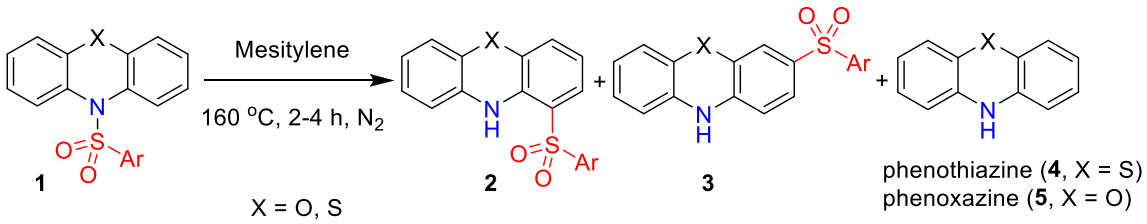
[c] The desired products were not detected on TLC analysis

choosing toluene and *p*-xylene as reaction solvents, respectively (Table 1, entries 1 and 2), no reaction occurred when prolonged the reaction time to 24 h and only starting material **1g** was detected on TLC analysis due to relatively low reaction temperature (110–138 °C). When carefully tracing the reaction progress through gradually increasing reaction temperature, we found that **1g** was totally consumed in mesitylene at 165 °C for just 1 h and it generated the corresponding formal 1,3-sulfonyl shift product **2g** in 20 % yield and 1,5-sulfonyl shift product **3g** in 34 % yield and the dissociation product phenothiazine in 7 % yield (Table 1, entry 3). When the reaction was performed in DCB at 165 °C (Table 1, entry 5), substrate **1g** gave rise to **2g** in relatively lower yield (12 %) and **3g** in similar yield (38 %) in a short reaction time (30 min). Meanwhile, protic solvent with high boiling point such as ethylene glycol was also screened for this conversion in consideration of accelerated effect of protic solvent in facilitating isomerization or proton shift step after sulfonyl migration [19]. However, although **3g** was readily separated by column chromatography in 81 % yield, no **2g** and phenothiazine was detected in ethylene glycol at 165 °C for 30 min. In the view of the Lewis acid catalyzed 3-arenesulfonylation of phenothiazine [39], **1g** probably proceeded a heterolytic pathway promoted by ethylene glycol and subsequently Friedel–Crafts reaction to

specifically afford more stable 1,5-sulfonyl migration product **3g** as a result of directing effect of electron-donating moiety and steric hindrance in **1g**. Finally, slightly lowering the temperature to 160 °C in mesitylene for 2 h would serve as the most appropriate reaction conditions because less dissociation product (3 %), similar yield (18 %) of **2g**, and more yield (47 %) of **3g** were obtained (Table 1, entry 7).

With the optimized conditions in hand, we conducted a series of reactions of sulfonamides **1g–1q** bearing different arenesulfonyl substituents, and the results are summarized in Table 2. When electron-donating groups (Me, MeO, and AcNH) and relatively weak electron-withdrawing group (Cl) occupied on the *para*-position of the benzenesulfonyl moiety in *N*-arenesulfonylphenothiazines, sulfonamides **1g–1l** gave rise to the corresponding desired products with moderate regioselectivities (**2g–2l** in 18–29 % yields vs. **3g–3l** in 38–48 % yields) and relatively low yields (2–7 %) for dissociation product **4** (Table 2, entries 2-6). Thus, the electronic property in the arenesulfonyl moiety played little impact on the yield and regioselectivity. Therefore, both electron-rich and electron-deficient aromatic groups were well tolerated. In contrast, the formal 1,3-sulfonyl shift was sluggish when *N*-(2,4,6-trimethylbenzene)sulfonylphenothiazine (**1m**) was subjected to standard conditions, and the corresponding 1,3-sulfonyl migration product **2 m** was obtained in only 6 % yield and 1,5-sulfonyl migration product **3m** in 46 % yield as similar with other cases (Table 2, entry 7). The result apparently indicated that the steric hindrance in arenesulfonyl substituents exerted a profound impact on the reactivity of 1,3-sulfonyl migration rather than 1,5-sulfonyl migration. Subsequently, *N*-(2-naphthalenesulfonyl)phenothiazine (**1n**) afforded **2n** in 39 % yield and **3n** in 29 % yield, showing reversal regioselectivity (Table 2, entry 8). Comparing with the *N*-arenesulfonylphenothiazines **1g–1m**, *N*-arenesulfonylphenoxazines **1o–1q** afforded the desired products **2o–2q** in 30–38 % yields, **3o–3q** in 27–32 % yields and dissociation product **5** in low yields (1–2 %) under standard reaction conditions. Therefore, the thermal-induced rearrangement reactions of *N*-sulfonyl phenoxazines **1o–**

Table 2 Thermal-induced sulfonyl migration reactions of sulfonamides **1g–1q**



Entry	1	X	Ar	Yield/%[a]		
				2	3	4 or 5
1	**1g**	S	Ph	18	47	3
2	**1i**	S	4-MeC_6H_4	25	47	5
3	**1i**[b]	S	4-MeC_6H_4	22	44	4
4	**1j**	S	4-$MeOC_6H_4$	29	38	7
5	**1k**	S	4-ClC_6H_4	28	48	4
6	**1l**	S	4-$AcNHC_6H_4$	18	43	2
7	**1m**	S	2,4,6-$Me_3C_6H_2$	6	46	11
8	**1n**	S	2-Naphthalenyl	39	29	1
9	**1o**	O	Ph	30	28	2
10	**1p**	O	4-MeC_6H_4	35	27	2
11	**1q**	O	4-ClC_6H_4	38	32	1

All reaction were conducted on 0.3 mmol scale in 3.0 cm^3 of mesitylene and reaction time (2 h for **1g**, **1i–1k**, **1m**, **1n**; 3 h for **1l**; 4 h for **1o**, **1p**) and determined on TLC analysis

[a] Isolated yield by chromatography on silica gel

[b] Daylight was prevented simply by wrapping the flask with aluminum foil

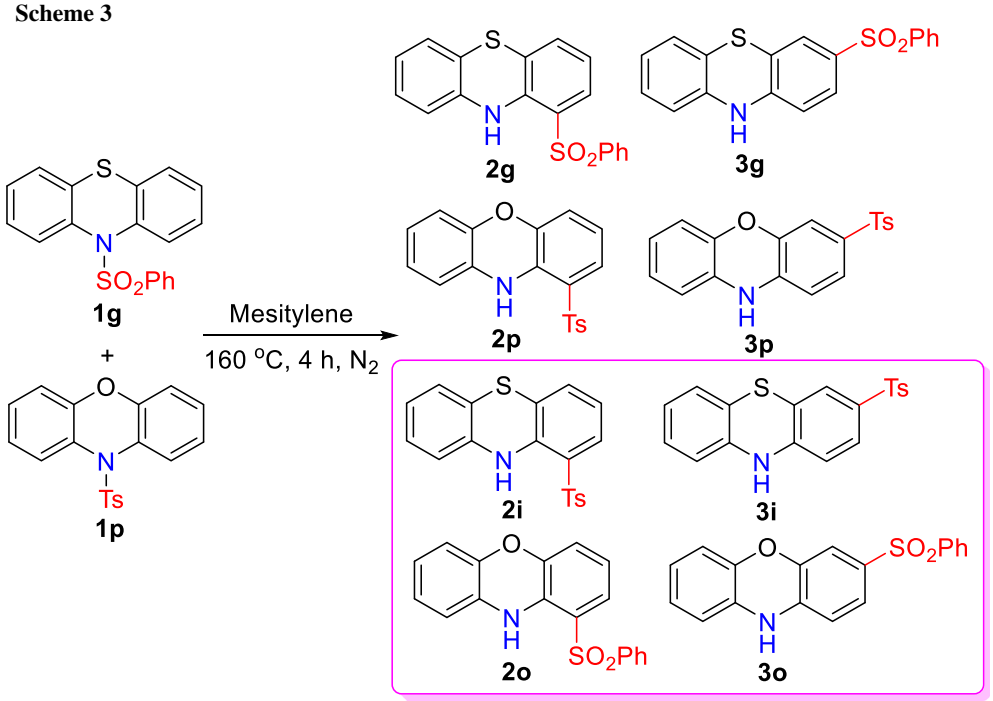
1q showed low regioselectivity with the ratio of 1,3- and 1,5-migration products nearly 1:1.

Although similar sulfonyl migration in *N*-sulfonylcarbazoles under irradiation of UV light was observed via a fast intrasolvent-cage radical–radical trapping mechanism [29], it is still unclear that the thermal-induced 1,3- and 1,5-sulfonyl migrations of *N*-sulfonylphenothiazine or phenoxazine derivatives occurred in an intramolecular or intermolecular version. To clarify the rearrangement process under thermal and neutral conditions, we performed a crossover experiment. A mixture of equimolar amounts (0.3 mmol) of sulfonamides **1g** and **1p** was conducted in mesitylene at 160 °C for 4 h. After removing the solvent via column chromatography, the residue was subjected to HPLC analysis.

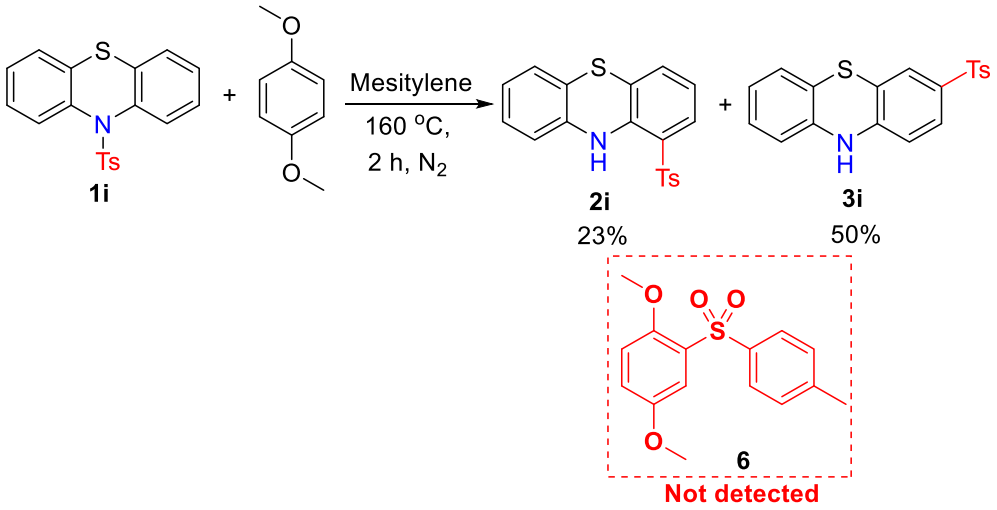
Crossover products **2i**, **2o** and **3i**, **3o** were detected obviously and the results clearly suggested that migration of sulfonyl group proceeded in a non-concerted manner (Scheme 3). Although the intermolecular pathway has been revealing by the crossover experiment, the thermal-induced sulfonyl migration provide a feasible methodology to construction 1-sulfonyl phenothiazine and phenoxazine derivatives which have been considered to be difficulty to be synthesized by conventional strategies. To further establish whether the migration of sulfonyl group occurred in a heterolytic or homolytic manner in the formation of **2g–2q** and **3g–3q**, a competition experiment was also performed employing a 1:1 mixture of electron-rich 1,4-dimethoxybenzene and substrate **1i** under standard reaction conditions (Scheme 4). The results indicated that the trapper (1,4-dimethoxybenzene) have no significant effect on the sulfonyl migration reactions without detecting the crossover product **6**. Almost no loss of yields for sulfonyl migration products **2i** and **3i** (the isolated yields for **2i** and **3i** were 23 and 50 %, respectively) ultimately to rule out an ion pair mechanism.

According to the above results, we are inclined to consider that the most reasonable explanation for the facile thermal rearrangement reaction is as follows (Scheme 5). In aprotic solvent, free radicals (**I**) and arenesulfonyl radicals were generated from *N*-sulfonylphenothiazines or phenoxazines via a thermal-induced homolytic cleavage of N-$(SO)_2$ bond. Meanwhile, intermediates **I** can easily convert to two resonances structures **II** and **III** through electron delocalization. A probable explanation for the homolytic cleavage process occurred only in the structures **1g** and **1i–1q** rather than *N*-sulfonamides **1a–1f** and **1h**, is that the conformation of molecules bearing a phenothiazine or phenoxazine nucleus possess nonplanar 'butterfly' structure in ground state [40]. Subsequently, the formation of intermediates **IV** and **V** could be rationalized by the recombination of sulfonyl radicals and free radicals **II** and **III**, leading to formal 1,3-and 1,5-sulfonyl migrations. Finally, the isomerization of intermediates **IV** and **V** are able to provide the final products **2** and **3**, respectively. Additionally, free radicals **I** can abstract H from a neighbouring molecule, such as solvent, thereby to produce dissociation product phenothiazine **4** or phenoxazine **5**,

Scheme 3



Scheme 4



which also is another evidence for the radical mechanism. Thus, we have proposed a homolysis of N–$(SO)_2$ bond and intermolecular radical–radical coupling mechanism accounting for the thermal-induced sulfonyl migration reactions under neutral and thermal conditions.

However, in protic solvent, such as ethylene glycol, only 1,5-sulfonyl migration products **3** were obtained. The migration proceeded a heterolytic pathway promoted by ethylene glycol served as protic acid and subsequently Friedel–Crafts reaction to specifically afford more stable 1,5-sulfonyl migration products **3** due to directing effect of electron-donating moiety and steric hindrance, similar to the Lewis acid catalyzed 3-arenesulfonylation of phenothiazine [39].

To explain the absence of the homo-coupling products resulted from the interaction of two identical free radicals in our proposed radical mechanism, our recent investigation indicate that electron-rich radicals prefer to react with electron-deficient substrates, while electron-deficient radicals favor to react with electron-rich substrates [41, 42]. We may rationalize that, for radical coupling, electron-rich radicals prefer coupling with electron-deficient radicals. Thus, electron-rich aromatic radicals prefer coupling with electron-deficient sulfonyl radicals rather than themselves. That is the reason why no radical homo-coupling products were observed.

Conclusion

Thermal-induced 1,3- and 1,5-sulfonyl migration reactions of various sulfonamides have been investigated, including the substrate scope and mechanistic insight. The results indicate that both *N*-arenesulfonylphenothiazines and *N*-arenesulfonylphenoxazines can undergo 1,3- and 1,5-sulfonyl migrations to afford the corresponding heteroaryl sulfone derivatives in moderate regioselectivities and yields under mild, thermal, and neutral conditions. The homolytic cleavage of the sulfonamide bond and intermolecular resulting radical–radical coupling reaction mechanism was proposed for the 1,3- and 1,5-sulfonyl migrations on the basis of crossover and competitive trapping experiments.

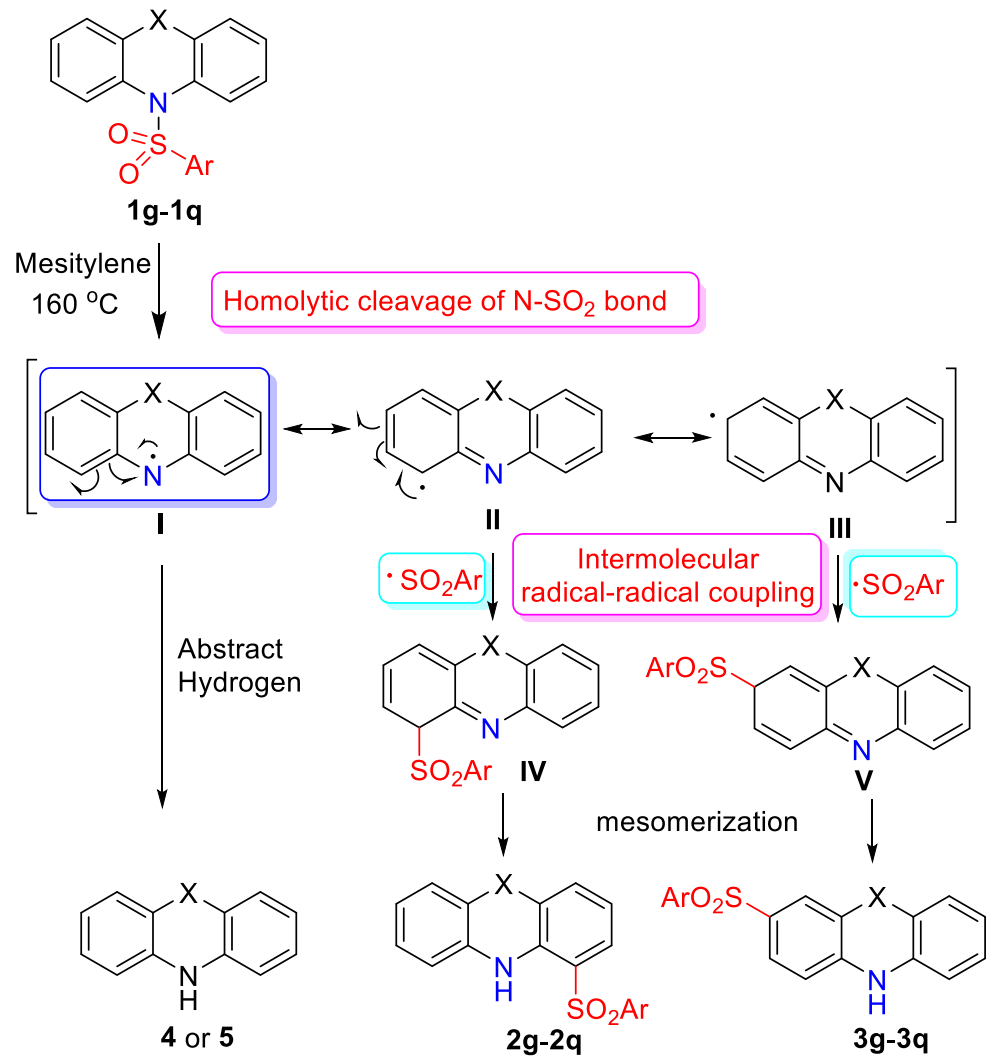
Experimental

Mesitylene, toluene, and *p*-xylene were dried over $CaCl_2$ and refluxed with sodium wire and benzophenone as an indicator under nitrogen, and freshly distilled prior to use. 1,2-Dichlorobenzene was dried over $CaCl_2$ and refluxed over CaH_2 under nitrogen and freshly distilled prior to use. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as an internal standard and the chemical shifts (δ) are reported in parts per million (ppm). IR spectra were taken directly on a FT-IR spectrometer with KBr. HRMS spectra were obtained with an LC/MSD TOF mass spectrometer. Melting points were obtained on a melting point apparatus. TLC analysis was performed on silica gel GF_{254} plates. Spots were visualized with UV light or iodine. Column chromatography was performed on silica gel (200-300 mesh) with a mixture of petroleum ether (PE) (60–90 °C) and ethyl acetate (EA) or a mixture of PE (60–90 °C) and dichloromethane (DCM) as an eluent with gradient elution.

General procedure for the synthesis of acyclic sulfonamides 1a–1c

N-Methylaniline, or diphenylamine, or *N*-benzylaniline (20 mmol) was dissolved in 20 cm^3 $CHCl_3$ in a 50 cm^3 one-

Scheme 5



necked flask. To the flask was slowly added 3.163 g pyridine (40 mmol) at 0 °C. The resultant solution was stirred at the same temperature for 30 min. Subsequently, 4.238 g benzenesulfonyl chloride (24 mmol) was portionwise added and the resulting solution was stirred for 2–4 h at room temperature. The reaction mixture was neutralized with 5 % HCl and extracted with diethyl ether (20 × 3 cm^3), and the combined organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification by recrystallization from methanol gave rise to pure products **1a**–**1c**.

N-Methyl-N-phenylbenzenesulfonamide (**1a**)
Colorless crystals; yield: 3.848 g (70 %); m.p.: 80–81 °C (MeOH) (Ref. [43] 79 °C).

N-Benzyl-N-phenylbenzenesulfonamide (**1b**)
Yellow crystals; yield: 2.531 g (36 %); m.p.: 120–122 °C (PE/EA) (Ref. [44] 117–118 °C).

N,N-Diphenylbenzenesulfonamide (**1c**)
Colorless crystals; yield: 5.489 g (89 %); m.p.: 127–128 °C (MeOH) (Ref. [43] 124–125 °C).

General procedure for the synthesis of cyclic sulfonamides 1d–1q

To a solution of cyclic arylamine (such as 1,2,3,4-tetrahydroquinoline, 10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine, 10*H*-phenothiazine, and 10*H*-phenoxazine) in pyridine (1 mmol/1 cm^3) was portionwise added 1.755 g benzenesulfonyl chloride (10 mmol) at 50 °C in an oil bath under nitrogen atmosphere. The resulting mixture was stirred for 20–24 h monitored by TLC at the same temperature. Then the reaction mixture was neutralized with 5 % HCl and extracted with diethyl ether (20 × 3 cm^3), and the organic layer was washed with brine and dried over Na_2SO_4.

Evaporation of the solvent and purification by recrystallization from methanol or column chromatography (PE/DCM = 20:1) afforded the desired products **1d**–**1q**. Additionally, 10-(phenylsulfonyl)-10*H*-phenothiazine-5-oxide (**1h**) was prepared by oxidation of the corresponding 10-(phenylsulfonyl)-10*H*-phenothiazine (**1g**) via MCPBA. To a solution of 339 mg sulfonamide **1h** (1.0 mmol) in 10 cm^3 dichloromethane (DCM) was slowly added 202 mg MCPBA (85 %, 1.0 mmol) in 10 cm^3 DCM at 0 °C and the resultant mixture continued to be stirred for 30 min. Then the reaction mixture was allowed to warm to room temperature and was stirred for 1–2 h monitored by TLC at the same temperature. Subsequently, the resulting solution was washed with sodium bicarbonate and brine and dried over Na_2SO_4. After concentration in vacuo, the residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH as eluent) to give the desired product **1g** as colorless crystals. Yield: 329 mg (93 %).

*1-(Phenylsulfonyl)-1,2,3,4-tetrahydroquinoline (**1d**)*
Brown crystals; yield: 1.351 g (97 %); m.p.: 63–65 °C (PE/EA) (Ref. [45] 63 °C).

*9-(Phenylsulfonyl)-9H-carbazole (**1e**, $C_{18}H_{13}NO_2S$) [29]*
Colorless crystals; yield: 4.008 g (66 %); m.p.: 143–144 °C (MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 7.7 Hz, 2H), 7.81 (d, J = 7.6 Hz, 2H), 7.51–7.45 (m, 2H), 7.41 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.8 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.3, 137.9, 133.7, 129.0, 127.4, 126.4, 126.4, 124.0, 120.0, 115.1 ppm.

*5-(Phenylsulfonyl)-10,11-dihydro-5H-dibenzo[b,f]azepine (**1f**, $C_{20}H_{17}NO_2S$)*
Colorless crystals; yield: 1.275 g (76 %); m.p.: 155–158 °C (MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.51–7.46 (m, 2H), 7.44 (t, J = 7.7 Hz, 2H), 7.20 (d, J = 6.2 Hz, 4H), 7.12–7.06 (m, 2H), 3.00–2.93 (m, 2H), 2.77–2.35 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.8, 139.2, 137.8, 132.7, 130.3, 129.8, 128.9, 128.3, 127.6, 126.8, 30.4 ppm; IR (KBr): $\bar{\nu}$ = 3064, 2925, 1487, 1446, 1352, 1164 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{20}H_{18}NO_2S^+$ 336.1053 ($[M + H]^+$), found 336.1055.

*10-(Phenylsulfonyl)-10H-phenothiazine (**1g**)*
Colorless crystals; yield: 2.550 g (10 mmol scale) (85 %); m.p.: 193–195 °C (MeOH) (Ref. [46] 171 °C).

*10-(Phenylsulfonyl)-10H-phenothiazine-5-oxide (**1h**, $C_{18}H_{13}NO_3S_2$)*
Colorless crystals; yield: 329 mg (1.0 mmol scale) (93 %); m.p.: 213–215 °C ($CHCl_3$/MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (dd, J = 7.9, 0.8 Hz, 2H), 7.73 (dd, J = 7.7, 1.4 Hz, 2H), 7.61 (td, J = 7.7, 1.6 Hz, 2H), 7.58–7.49 (m, 3H), 7.32 (t, J = 7.9 Hz, 2H), 7.23–7.18 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.7, 136.2, 134.1, 130.9, 130.7, 129.3, 129.1, 128.5, 127.4, 124.3 ppm; IR (KBr): $\bar{\nu}$ = 1632, 1580, 1467, 1447, 1366, 1171, 1090 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}NO_3S_2^+$ 356.0410 ($[M + H]^+$), found 356.0416.

*10-(4-Methylphenylsulfonyl)-10H-phenothiazine (**1i**)*
Colorless crystals; yield: 2.900 g (10 mmol scale) (82 %); m.p.: 164–165 °C (MeOH) (Ref. [47] 155–156 °C).

*10-(4-Methoxyphenylsulfonyl)-10H-phenothiazine (**1j**, $C_{19}H_{15}NO_4S_2$)*
Colorless crystals; yield: 219 mg (1.0 mmol scale) (59 %); m.p.: 168–170 °C (PE/EA); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (dd, J = 8.0, 1.1 Hz, 2H), 7.32 (d, J = 1.2 Hz, 2H), 7.21 (d, J = 1.2 Hz, 2H), 7.17 (d, J = 8.9 Hz, 2H), 7.11 (dd, J = 7.8, 1.3 Hz, 2H), 6.71 (d, J = 8.9 Hz, 2H), 3.81 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.6, 135.9, 132.9, 130.6, 130.1, 129.7, 127.6, 127.1, 126.8, 113.8, 55.5 ppm; IR (KBr): $\bar{\nu}$ = 2954, 2921, 1655, 1496, 1383, 1359, 1260, 1164, 1142 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{19}H_{16}NO_3S_2^+$ 370.0566 ($[M + H]^+$), found 370.0562.

*10-(4-Chlorophenylsulfonyl)-10H-phenothiazine (**1k**)*
Colorless crystals; yield: 209 mg (1.0 mmol scale) (55 %); m.p.: 148–150 °C (PE/EA) (Ref. [48] 153–154 °C).

*N-[4-(10H-Phenothiazine-10-sulfonyl)phenyl]acetamide (**1l**)*
Colorless crystals; yield: 899 mg (5.0 mmol scale) (45 %); m.p.: 205–207 °C (EA/DCM) (Ref. [49] 204–206 °C).

*10-(2,4,6-Trimethylphenylsulfonyl)-10H-phenothiazine (**1m**, $C_{21}H_{19}NO_2S_2$)*
Colorless crystals; yield: 660 mg (5.0 mmol scale) (33 %); m.p.: 157–159 °C (PE/EA); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dd, J = 8.0, 1.0 Hz, 2H), 7.30 (td, J = 7.7, 1.6 Hz, 2H), 7.22 (td, J = 7.6, 1.3 Hz, 2H), 7.16 (dd, J = 7.7, 1.4 Hz, 2H), 6.73 (s, 2H), 2.23 (s, 3H), 1.86 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.6, 140.0, 136.3, 134.9, 134.0, 132.1, 130.0, 127.7, 127.2, 126.9, 23.0, 20.9 ppm; IR (KBr): $\bar{\nu}$ = 1602, 1461, 1377, 1357, 1231, 1196, 1166 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{21}H_{20}NO_2S_2^+$ 382.0930 ($[M + H]^+$), found 382.0933.

*10-(2-Naphthalenylsulfonyl)-10H-phenothiazine (**1n**)*
Colorless crystals; yield: 219 mg (1.0 mmol scale) (56 %); m.p.: 135–136 °C (PE/EA) (Ref. [48] 140–141 °C).

*10-(Phenylsulfonyl)-10H-phenoxazine (**1o**)*
Colorless crystals; yield: 236 mg (1.0 mmol scale) (73 %); m.p.: 160–161 °C (PE/EA) (Ref. [49] 160–161 °C).

*10-(4-Methylphenylsulfonyl)-10H-phenoxazine (**1p**)*
Colorless crystals; yield: 256 mg (1.0 mmol scale) (76 %); m.p.: 176–178 °C (PE/EA) (Ref. [50] 174–176 °C).

*10-(4-Chlorophenylsulfonyl)-10H-phenoxazine (**1q**)*
Colorless crystals; yield: 256 mg (1.0 mmol scale) (76 %); m.p.: 182–184 °C (PE/EA) (Ref. [30] 178–179 °C).

General procedure for thermal-induced 1,3- and 1,5-sulfonyl migration reactions

A solution of *N*-arenesulfonylphenothiazines **1g–1n** or *N*-arenesulfonylphenoxazines **1o–1q** (0.3 mmol) in 3 cm^3 dry mesitylene was heated at 160 °C for 2–4 h under nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature. Then the resulting solution was subjected to flash chromatography with petroleum ether as an eluent to remove the solvent (mesitylene) with high boiling point. After no mesitylene was detected by TLC, DCM was employed as eluent to afford a crude mixture of 1,3- and 1,5-migration products. After concentration in vacuo, the residue was purified by column chromatography on silica gel (a mixture of petroleum ether (PE) (60–90 °C) and dichloromethane (DCM) as an eluent with gradient elution) to give desired products **2** and **3**.

1-(Phenylsulfonyl)-10H-phenothiazine
*(**2g**, $C_{18}H_{13}NO_2S_2$)*
Yellowish solid; yield: 13 mg (13 %); m.p.: 167–169 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (s, 1H), 7.99–7.78 (m, 2H), 7.62–7.55 (m, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.07 (d, J = 7.6 Hz, 1H), 7.03 (td, J = 7.7, 1.7 Hz, 1H), 6.90 (td, J = 7.2, 1.1 Hz, 1H), 6.89–6.84 (m, 1H), 6.82 (t, J = 7.8 Hz, 1H), 6.66 (d, J = 7.8 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.7, 141.4, 139.5, 133.5, 131.9, 129.4, 128.1, 127.8, 126.8, 126.5, 123.8, 122.8, 121.7, 121.6, 117.8, 115.8 ppm; IR (KBr): $\bar{\nu}$ = 3353, 1591, 1482, 1447, 1316, 1139 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}NO_2S_2^+$ 340.0460 ($[M + H]^+$), found 340.0451.

3-(Phenylsulfonyl)-10H-phenothiazine
*(**3g**, $C_{18}H_{13}NO_2S_2$)*
Yellow solid; yield: 47 mg (47 %); m.p.: 205–206 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.21 (s, 1H), 7.91 (d, J = 7.5 Hz, 2H), 7.73–7.62 (m, 1H), 7.60 (t, J = 7.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.41 (s, 1H), 7.00 (dd, J = 7.2, 1.2 Hz, 1H), 6.91 (d, J = 7.3 Hz, 1H), 6.80 (t, J = 7.0 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 6.67 (d, J = 7.8 Hz, 1H) ppm; ^{13}C NMR (101 MHz, DMSO-d_6): δ = 146.5, 141.9, 139.8, 133.2, 132.9, 129.6, 128.0, 127.9, 126.9, 126.3, 125.2, 123.1, 117.5, 115.4, 115.0, 114.2 ppm; IR (KBr): $\bar{\nu}$ = 3330, 1569, 1472, 1316, 1146 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}NO_2S_2^+$ 340.0460 ($[M + H]^+$), found 340.0456.

1-(4-Methylphenylsulfonyl)-10H-phenothiazine
*(**2i**, $C_{19}H_{15}NO_3S_2$)*
Yellow solid; yield: 27 mg (25 %); m.p.: 132–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.56 (dd, J = 8.0, 1.0 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 7.4 Hz, 1H), 7.04–7.00 (m, 1H), 6.90 (t, J = 7.2 Hz, 1H), 6.86 (t, J = 7.3 Hz, 1H), 6.81 (t, J = 7.8 Hz, 1H), 6.66 (d, J = 7.8 Hz, 1H), 2.39 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.6, 141.3, 139.6, 138.7, 131.7, 130.0, 128.0, 127.8, 126.8, 126.5, 123.8, 123.3, 121.6, 121.5, 117.8, 115.8, 21.6 ppm; IR (KBr): $\bar{\nu}$ = 3353, 2955, 2917, 1636, 1585, 1463, 1309, 1143 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{19}H_{16}NO_2S_2^+$ 354.0617 ($[M + H]^+$), found 354.0624.

3-(4-Methylphenylsulfonyl)-10H-phenothiazine
*(**3i**, $C_{19}H_{15}NO_3S_2$)*
Yellow solid; yield: 50 mg (47 %); m.p.: 248–249 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.20 (s, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.49 (dd, J = 8.4, 2.1 Hz, 1H), 7.39 (d, J = 6.3 Hz, 2H), 7.38 (s, 1H), 7.01 (td, J = 7.8, 1.4 Hz, 1H), 6.90 (dd, J = 7.6, 1.0 Hz, 1H), 6.81 (td, J = 7.6, 1.0 Hz, 1H), 6.73 (d, J = 8.5 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C NMR (101 MHz, DMSO-d_6): δ = 146.3, 143.7, 139.8, 139.1, 133.4, 130.0, 127.9, 127.7, 126.9, 126.3, 125.0, 123.1, 117.5, 115.4, 115.0, 114.1, 20.9 ppm; IR (KBr): $\bar{\nu}$ = 3327, 2914, 1594, 1476, 1322, 1155 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{19}H_{16}NO_2S_2^+$ 354.0617 ($[M + H]^+$), found 354.0622.

1-(4-Methoxyphenylsulfonyl)-10H-phenothiazine
*(**2j**, $C_{19}H_{15}NO_4S_2$)*
Yellow solid; yield: 32 mg (29 %); m.p.: 105–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 7.83 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 8.1 Hz, 1H), 7.03 (t, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.90 (t, J = 7.8 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 6.80 (t, J = 7.8 Hz, 1H), 6.67 (d, J = 7.8 Hz, 1H), 3.83 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.6, 141.1, 139.6, 133.1, 131.5, 129.0, 127.8, 127.8, 126.5, 123.7, 121.5, 121.5, 117.8, 115.7, 114.6, 55.7 ppm; IR (KBr): $\bar{\nu}$ = 3356, 2927, 1594, 1447, 1316, 1271, 1143 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{19}H_{16}NO_3S_2^+$ 370.0566 ($[M + H]^+$), found 370.0556.

3-(4-Methoxyphenylsulfonyl)-10H-phenothiazine
*(**3j**, $C_{19}H_{15}NO_4S_2$)*
Yellow solid; yield: 43 mg (38 %); m.p.: 222–224 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 7.83 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 8.1 Hz, 1H), 7.03 (t, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.90 (t, J = 7.8 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 6.80 (t, J = 7.8 Hz, 1H), 6.67 (d, J = 7.8 Hz, 1H), 3.83 (s, 3H) ppm; ^{13}C NMR (101 MHz, DMSO-d_6): δ = 162.8, 146.1,

139.9, 133.9, 133.4, 129.2, 128.0, 127.4, 126.3, 124.8, 123.1, 117.4, 115.4, 115.0, 114.8, 114.1, 55.7 ppm; IR (KBr): $\bar{\nu}$ = 3282, 2959, 1652, 1466, 1312, 1258, 1155 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{19}H_{16}NO_3S_2^+$ 370.0566 ($[M + H]^+$), found 370.0559.

*1-(4-Chlorophenylsulfonyl)-10H-phenothiazine (**2k**, $C_{18}H_{12}ClNO_3S_2$)*

Yellow solid; yield: 32 mg (28 %); m.p.: 133–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (s, 1H), 7.84 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.1 Hz, 1H), 7.48 (d, J = 8.5 Hz, 2H), 7.07 (t, J = 6.2 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.96–6.85 (m, 2H), 6.82 (t, J = 7.8 Hz, 1H), 6.66 (d, J = 7.8 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.5, 140.3, 140.2, 139.3, 132.1, 129.8, 128.3, 128.1, 128.0, 126.7, 124.0, 122.4, 121.9, 121.7, 117.8, 115.8 ppm; IR (KBr): $\bar{\nu}$ = 3343, 1572, 1472, 1447, 1316, 1146, 771 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{13}ClNO_2S_2^+$ 374.0071 ($[M + H]^+$), found 374.0065.

*3-(4-Chlorophenylsulfonyl)-10H-phenothiazine (**3k**, $C_{18}H_{12}ClNO_3S_2$)*

Yellow solid; yield: 54 mg (48 %); m.p.: 231–233 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.24 (s, 1H), 7.93 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 7.52 (dd, J = 8.4, 1.9 Hz, 1H), 7.43 (s, 1H), 7.01 (d, J = 7.4 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 6.83 (d, J = 7.4 Hz, 1H), 6.75 (d, J = 8.5 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H) ppm; ^{13}C NMR (101 MHz, DMSO-d_6): δ = 146.7, 140.8, 139.7, 138.3, 132.3, 129.7, 128.9, 127.99, 127.97, 126.3, 125.3, 123.2, 117.6, 115.4, 115.1, 114.2 ppm; IR (KBr): $\bar{\nu}$ = 3269, 1671, 1559, 1469, 1325, 1155, 755 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{13}ClNO_2S_2^+$ 374.0071 ($[M + H]^+$), found 374.0069.

*N-[4-(10H-Phenothiazine-1-sulfonyl)phenyl]acetamide (**2l**, $C_{20}H_{16}N_2O_3S_2$)*

Yellow solid; yield: 22 mg (18 %); m.p.: 131–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (s, 1H), 7.81 (d, J = 8.6 Hz, 2H), 7.70 (s, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.03 (dd, J = 16.7, 7.7 Hz, 2H), 6.90 (d, J = 6.9 Hz, 1H), 6.88–6.83 (m, 1H), 6.80 (t, J = 7.8 Hz, 1H), 6.64 (d, J = 7.8 Hz, 1H), 2.17 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.7, 142.8, 141.2, 139.4, 135.9, 131.8, 128.1, 127.9, 126.5, 123.8, 123.1, 121.7, 121.6, 119.5, 117.7, 115.8, 24.7 ppm; IR (KBr): $\bar{\nu}$ = 3346, 2923, 2843, 1703, 1665, 1597, 1444, 1322, 1139 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{20}H_{17}N_2O_3S_2^+$ 397.0675 ($[M + H]^+$), found 397.0671.

*N-[4-(10H-Phenothiazine-3-sulfonyl)phenyl]acetamide (**3l**, $C_{20}H_{16}N_2O_3S_2$)*

Yellow solid; yield: 51 mg (43 %); m.p.: 276–278 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.37 (s, 1H), 9.19 (s, 1H), 7.85 (d, J = 8.7 Hz, 2H), 7.79 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.5 Hz, 1H), 7.38 (s, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 7.5 Hz, 1H), 6.80 (t, J = 7.5 Hz, 1H), 6.74 (d, J = 8.5 Hz, 1H), 6.68 (d, J = 7.9 Hz, 1H), 2.09 (s, 3H) ppm; ^{13}C NMR (101 MHz, DMSO-d_6): δ = 169.1, 146.2, 143.5, 139.9, 135.2, 133.7, 128.2, 127.9, 127.5, 126.3, 124.9, 123.1, 118.9, 117.4, 115.4, 115.0, 114.1, 24.1 ppm; IR (KBr): $\bar{\nu}$ = 3279, 3019, 1690, 1585, 1463, 1319, 1139 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{20}H_{17}N_2O_3S_2^+$ 397.0675 ($[M + H]^+$), found 397.0668.

*1-(2,4,6-Trimethylphenylsulfonyl)-10H-phenothiazine (**2m**, $C_{21}H_{19}NO_2S_2$)*

Yellow solid; yield: 7 mg (6 %); m.p.: 144–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (s, 1H), 7.06–7.00 (m, 2H), 6.98–6.93 (m, 4H), 6.87 (t, J = 7.5 Hz, 1H), 6.70 (t, J = 7.8 Hz, 1H), 6.65 (d, J = 7.9 Hz, 1H), 2.61 (s, 6H), 2.31 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.8, 141.4, 139.8, 139.8, 134.5, 132.3, 130.6, 127.8, 126.8, 126.5, 125.0, 123.6, 121.6, 121.1, 117.7, 115.9, 22.5, 21.0 ppm; IR (KBr): $\bar{\nu}$ = 3327, 2971, 2911, 1601, 1450, 1437, 1296, 1133 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{21}H_{20}NO_2S_2^+$ 382.0930 ($[M + H]^+$), found 382.0924.

*3-(2,4,6-Trimethylphenylsulfonyl)-10H-phenothiazine (**3m**, $C_{21}H_{19}NO_2S_2$)*

Yellow solid; yield: 52 mg (46 %); m.p.: 234–236 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.19 (s, 1H), 7.37 (dd, J = 8.5, 1.9 Hz, 1H), 7.20 (d, J = 1.7 Hz, 1H), 7.04 (s, 2H), 7.06–6.98 (m, 1H), 6.89 (d, J = 7.6 Hz, 1H), 6.80 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 8.5 Hz, 1H), 6.69 (d, J = 7.8 Hz, 1H), 2.53 (s, 6H), 2.26 (s, 3H) ppm; ^{13}C NMR (101 MHz, DMSO-d_6): δ = 146.0, 142.9, 140.0, 138.9, 134.9, 134.3, 132.1, 127.9, 126.6, 126.3, 123.8, 123.0, 117.1, 115.4, 115.0, 113.9, 22.3, 20.4 ppm; IR (KBr): $\bar{\nu}$ = 3285, 2959, 2905, 1661, 1593, 1471, 1318, 1159 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{21}H_{20}NO_2S_2^+$ 382.0930 ($[M + H]^+$), found 382.0929.

*1-(2-Naphthalenylsulfonyl)-10H-phenothiazine (**2n**, $C_{22}H_{15}NO_2S_2$)*

Yellow solid; yield: 46 mg (39 %); m.p.: 168–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (s, 1H), 8.52 (s, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.80 (dd, J = 8.7, 1.4 Hz, 1H), 7.66–7.57 (m, 3H), 7.05 (d, J = 7.2 Hz, 1H), 7.03–6.98 (m, 1H), 6.89 (d, J = 6.5 Hz, 1H), 6.86 (d, J = 7.2 Hz, 1H), 6.84–6.78 (m, 1H), 6.71 (d, J = 7.9 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.5, 139.5, 138.4, 135.1, 132.1, 131.9, 129.9, 129.4, 129.3, 128.2, 128.2, 127.9, 127.8, 127.8, 126.6, 123.8, 122.9, 121.8, 121.7, 121.6, 117.8, 115.8 ppm; IR (KBr): $\bar{\nu}$ = 3344, 1562, 1444, 1435, 1309, 1146 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{22}H_{16}NO_2S_2^+$ 390.0617 ($[M + H]^+$), found 390.0623.

*3-(2-Naphthalenylsulfonyl)-10H-phenothiazine (**3n**, $C_{22}H_{15}NO_2S_2$)*

Yellow solid; yield: 35 mg (29 %); m.p.: 226–228 °C; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 9.22$ (s, 1H), 8.65 (s, 1H), 8.20 (d, $J = 7.8$ Hz, 1H), 8.12 (d, $J = 8.7$ Hz, 1H), 8.03 (d, $J = 7.7$ Hz, 1H), 7.89 (dd, $J = 8.7$, 1.4 Hz, 1H), 7.70 (dd, $J = 8.6$, 7.2 Hz, 2H), 7.59 (dd, $J = 8.5$, 1.7 Hz, 1H), 7.49 (d, $J = 1.7$ Hz, 1H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 7.3$ Hz, 1H), 6.80 (t, $J = 7.5$ Hz, 1H), 6.75 (d, $J = 8.5$ Hz, 1H), 6.67 (d, $J = 7.9$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, DMSO-d_6): $\delta = 146.5$, 139.8, 138.8, 134.4, 132.9, 131.8, 129.8, 129.4, 129.2, 128.0, 128.0, 127.8, 127.7, 126.3, 125.2, 123.1, 122.3, 117.5, 115.4, 115.0, 114.2 ppm; IR (KBr): $\bar{\nu} = 3258$, 1668, 1565, 1463, 1309, 1127 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{22}H_{16}NO_2S_2^+$ 390.0617 ($[M + H]^+$), found 390.0613.

*1-(Phenylsulfonyl)-10H-phenoxazine (**2o**, $C_{18}H_{13}NO_3S$)*

Yellow solid; yield: 31 mg (32 %); m.p.: 171–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.91$ (d, $J = 7.5$ Hz, 2H), 7.76 (s, 1H), 7.60 (t, $J = 7.3$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 2H), 7.30–7.18 (m, 1H), 6.83–6.74 (m, 1H), 6.70 (t, $J = 8.0$ Hz, 2H), 6.64 (d, $J = 8.0$ Hz, 1H), 6.60 (d, $J = 7.0$ Hz, 1H), 6.50 (d, $J = 7.6$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 144.6$, 143.1, 141.6, 133.5, 132.6, 129.4, 129.2, 126.7, 124.2, 123.7, 122.7, 121.5, 120.4, 120.1, 115.6, 114.5 ppm; IR (KBr): $\bar{\nu} = 3365$, 1498, 1460, 1312, 1136 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}NO_3S^+$ 324.0689 ($[M + H]^+$), found 324.0686.

*3-(Phenylsulfonyl)-10H-phenoxazine (**3o**, $C_{18}H_{13}NO_3S$)*

Yellow solid; yield: 30 mg (30 %); m.p.: 227–229 °C; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 8.94$ (s, 1H), 7.90 (d, $J = 7.5$ Hz, 2H), 7.67 (t, $J = 7.2$ Hz, 1H), 7.60 (t, $J = 7.5$ Hz, 2H), 7.30 (dd, $J = 8.3$, 1.7 Hz, 1H), 7.00 (d, $J = 1.7$ Hz, 1H), 6.83–6.71 (m, 1H), 6.60–6.65 (m, 2H), 6.52 (d, $J = 8.3$ Hz, 1H), 6.47 (d, $J = 7.6$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, DMSO-d_6): $\delta = 142.8$, 142.4, 142.0, 137.7, 133.2, 131.1, 130.3, 129.6, 126.8, 124.8, 124.4, 121.8, 115.2, 113.9, 113.5, 112.9 ppm; IR (KBr): $\bar{\nu} = 3426$, 1668, 1501, 1325, 1155 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}NO_3S^+$ 324.0689 ($[M + H]^+$), found 324.0683.

*1-(4-Methylphenylsulfonyl)-10H-phenoxazine (**2p**, $C_{19}H_{15}NO_3S$)*

Yellow solid; yield: 35 mg (35 %); m.p.: 195–196 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.79$ (d, $J = 8.3$ Hz, 2H), 7.74 (s, 1H), 7.31 (d, $J = 8.1$ Hz, 2H), 7.22 (dd, $J = 8.1$, 1.4 Hz, 1H), 6.77 (td, $J = 7.6$, 1.3 Hz, 1H), 6.70 (d, $J = 7.8$ Hz, 1H), 6.69–6.66 (m, 1H), 6.63 (d, $J = 8.0$ Hz, 1H), 6.61–6.58 (m, 1H), 6.49 (dd, $J = 7.7$, 1.4 Hz, 1H), 2.41 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 144.5$, 144.5, 143.0, 138.7, 132.4, 129.9, 129.3, 126.8, 124.1, 123.6, 122.6, 121.9, 120.3, 119.9, 115.6, 114.5, 21.6 ppm; IR (KBr): $\bar{\nu} = 3365$, 2955, 2853, 1655, 1469, 1316, 1133 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{19}H_{16}NO_3S^+$ 338.0845 ($[M + H]^+$), found 338.0838.

*3-(4-Methylphenylsulfonyl)-10H-phenoxazine (**3p**, $C_{19}H_{15}NO_3S$)*

Yellow solid; yield: 28 mg (27 %); m.p.: 181–183 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.76$ (d, $J = 8.3$ Hz, 2H), 7.33–7.21 (m, 3H), 7.05 (d, $J = 1.8$ Hz, 1H), 6.77–6.68 (m, 1H), 6.66 (s, 1H), 6.59 (d, $J = 7.8$ Hz, 1H), 6.35 (t, $J = 7.6$ Hz, 2H), 5.79 (s, 1H), 2.38 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 143.8$, 143.6, 142.9, 139.1, 136.8, 133.0, 129.8, 129.6, 127.2, 124.2, 124.1, 122.5, 115.7, 114.6, 113.8, 112.8, 21.5 ppm; IR (KBr): $\bar{\nu} = 3337$, 2959, 2930, 1575, 1501, 1312, 1152 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{19}H_{16}NO_3S^+$ 338.0845 ($[M + H]^+$), found 338.0853.

*1-(4-Chlorophenylsulfonyl)-10H-phenoxazine (**2q**, $C_{18}H_{12}ClNO_3S$)*

Yellow solid; yield: 41 mg (38 %); m.p.: 148–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.84$ (d, $J = 8.4$ Hz, 2H), 7.70 (s, 1H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 8.1$ Hz, 1H), 6.78 (t, $J = 7.5$ Hz, 1H), 6.71 (t, $J = 8.2$ Hz, 2H), 6.64 (d, $J = 8.0$ Hz, 1H), 6.61 (d, $J = 7.3$ Hz, 1H), 6.50 (d, $J = 7.6$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 144.6$, 143.0, 140.2, 140.1, 132.6, 129.7, 128.9, 128.2, 124.2, 123.6, 122.9, 121.1, 120.5, 120.3, 115.6, 114.6 ppm; IR (KBr): $\bar{\nu} = 3371$, 1566, 1494, 1471, 1313, 1146 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{13}ClNO_3S^+$ 358.0299 ($[M + H]^+$), found 358.0293.

*3-(4-Chlorophenylsulfonyl)-10H-phenoxazine (**3q**, $C_{18}H_{12}ClNO_3S$)*

Yellow solid; yield: 34 mg (32 %); m.p.: 195–198 °C; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 8.98$ (s, 1H), 7.92 (d, $J = 8.5$ Hz, 2H), 7.67 (d, $J = 8.5$ Hz, 2H), 7.31 (d, $J = 8.3$ Hz, 1H), 7.02 (s, 1H), 6.76 (t, $J = 7.4$ Hz, 1H), 6.66 (d, $J = 7.9$ Hz, 1H), 6.61 (d, $J = 6.9$ Hz, 1H), 6.53 (d, $J = 8.3$ Hz, 1H), 6.48 (d, $J = 7.6$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, DMSO-d_6): $\delta = 142.8$, 142.4, 140.9, 138.2, 137.9, 130.5, 130.1, 129.7, 128.8, 124.9, 124.4, 121.9, 115.2, 113.9, 113.5, 112.9 ppm; IR (KBr): $\bar{\nu} = 3298$, 1684, 1517, 1304, 1159 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{13}ClNO_3S^+$ 358.0299 ($[M + H]^+$), found 358.0302.

Acknowledgments This work was supported in part by the National Basic Research Program of China (No. 2013CB328905), the National Natural Science Foundation of China (Nos. 21372025 and 21172017), and specialized Research Fund for the Doctoral Program of Higher Education, Ministry of Education of China (No. 20110010110011).

References

1. Bur SK (2007) Top Curr Chem 274:125
2. Braverman S, Cherkinsky M, Raj P (1999) Sulfur Rep 22:49
3. Yang H, Carter RG, Zakharov LN (2008) J Am Chem Soc 130:9238
4. Yang H, Carter RG (2010) J Org Chem 75:4929
5. Bordwell FG, Pagani GA (1975) J Am Chem Soc 97:118
6. Ogura K, Iihama T, Kiuchi S, Kajiki T, Koshikawa O, Takahashi K, Iida H (1986) J Org Chem 51:700
7. Knight DJ, Lin P, Whitham GH (1987) J Chem Soc Perkin Trans 1:2707
8. Padwa A, Bullock WH, Dyszlewski AD (1990) J Org Chem 55:955
9. Fox JM, Morris CM, Smyth GD, Whitham GH (1994) J Chem Soc Perkin Trans 1:731
10. Roy S, Das I, Bhanuprakash K, Gupta BD (1994) Tetrahedron 50:1847
11. Fujita R, Watanabe K, Ikeura W, Ohtake Y, Hongo H, Harigaya Y, Matsuzaki H (2001) Tetrahedron 57:8841
12. Teyssot ML, Lormier AT, Chataigner I, Piettre SR (2007) J Org Chem 72:2364
13. Chou SSP, Wang HC, Chen PW, Yang CH (2008) Tetrahedron 64:5291
14. Mertens MD, Pietsch M, Schnakenburg G, Gütschow M (2013) J Org Chem 78:8966
15. Hu Y, Yi R, Wu F, Wan B (2013) J Org Chem 78:7714
16. Nakamura I, Yamagishi U, Song D, Konta S, Yamamoto Y (2007) Angew Chem Int Ed 46:2284
17. Prasad B, Adepu R, Sandra S, Rambabu D, Krishna GR, Reddy CM, Deora GS, Misra P, Pal M (2012) Chem Commun 48:10434
18. Xin X, Wang D, Li X, Wan B (2012) Angew Chem Int Ed 51:1693
19. Teo WT, Rao W, Koh MJ, Chan PWH (2013) J Org Chem 78:7508
20. Lee YT, Chung YK (2008) J Org Chem 73:4698
21. Zhu Y, Lu WT, Sun HC, Zhan ZP (2013) Org Lett 15:4146
22. Jiang Z, Lu P, Wang Y (2012) Org Lett 14:6266
23. Yeom HS, So E, Shin S (2011) Chem Eur J 17:1764
24. Kimura M, Horino Y, Mori M, Tamaru Y (2007) Chem Eur J 13:9686
25. Bendikov M, Duong HM, Bolanos E, Wudl F (2005) Org Lett 7:783
26. DeKorver KA, Johnson WL, Zhang Y, Hsung RP, Dai H, Deng J, Lohse AG, Zhang YS (2011) J Org Chem 76:5092
27. Hou SL, Li XY, Xu JX (2012) J Org Chem 77:10856
28. Hou SL, Li XY, Xu JX (2014) Org Biomol Chem 12:4952
29. Chakrabarti A, Biswas GK, Chakraborty DP (1989) Tetrahedron 45:5059
30. Yu MJ, McCowan JR, Thrasher KJ, Keith PT, Luttman CA, Ho PPK, Towner RD, Bertsch B, Horng JS (1992) J Med Chem 35:716
31. Chan C, Yin H, Garforth J, McKie JH, Jaouhari R, Speers P, Douglas KT, Rock PJ, Yardley V, Croft SL, Fairlamb AH (1998) J Med Chem 41:148
32. Khan MOF, Austin SE, Chan C, Yin H, Marks D, Vaghjiani SN, Kendrick H, Yardley V, Croft SL, Douglas KT (2000) J Med Chem 43:3148
33. Wesołowska O, Hendrich AB, Motohashi N, Kawase M, Dobryszycki P, Ożyhar A, Michalak K (2004) Biophys Chem 109:399
34. Mayer M, Lang PT, Gerber S, Madrid PB, Pinto IG, Guy RK, James TJ (2006) Chem Biol 13:993
35. Hart AS, Chandra BKC, Subbaiyan NK, Karr PA, D'Souza F (2012) ACS Appl Mater Interfaces 4:5813
36. Golriz AA, Kaule T, Untch MB, Kolman K, Berger R, Gutmann JS (2013) ACS Appl Mater Interfaces 5:2485
37. Hua Y, Chang S, Huang D, Zhou X, Zhu X, Zhao J, Chen T, Wong WY, Wong WK (2013) Chem Master 25:2146
38. Baheti A, Thomas KRJ, Li CT, Lee CP, Ho KC (2015) ACS Appl Mater Interfaces 7:2249
39. Lafferty JJ, Garvey E, Nodiff EA, Thompson WE, Zirkle CL (1962) J Org Chem 27:1346
40. Yao L, Sun S, Xue S, Zhang S, Wu X, Zhang H, Pan Y, Gu C, Li F, Ma Y (2013) J Phys Chem 117:14189
41. Gao SM, Zhang Y, Dong J, Chen N, Xu JX (2016) Org Biomol Chem 14:1002. doi:10.1039/C5OB02297E
42. Kakaei S, Xu JX (2013) Org Biomol Chem 11:5481
43. Shafer SJ, Closson WD (1975) J Org Chem 40:889
44. Hurd CD, Rudner B (1951) J Am Chem Soc 73:5157
45. Tamaddon F, Nasiri A, Farokhi S (2011) Catal Commun 12:1477
46. Hazlet SE, Roderuck CE (1945) J Am Chem Soc 67:495
47. Bernstein HI, Rothstein LR (1944) J Am Chem Soc 66:1886
48. Karpishchenko LS, Burmistrov SI (1976) Khim Geterotsikl Soedin 1365
49. Bostan R, Varvara S, Găină L, Mureşan LM (2012) Corrosion Sci 63:275
50. Hernandez-Olmos V, Abdelrahman A, Freudendahl D, Weinhausen S, Mueller CE (2012) J Med Chem 55:9576