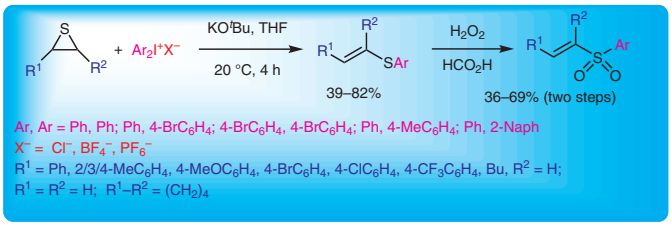
Synthesis J. Dong, J. Xu Paper

Safe and Metal-Free Synthesis of 1-Alkenyl Aryl Sulfides and Their Sulfones from Thiiranes and Diaryliodonium Salts

Jun Dong
Jiaxi Xu*

State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, Faculty of Science, Beijing University of Chemical Technology, Beijing 100029, P. R. of China
jxxu@mail.buct.edu.cn



Received: 22.01.2018
Accepted after revision: 05.03.2018
Published online: 04.04.2018
DOI: 10.1055/s-0036-1591559; Art ID: ss-2018-h0042-op

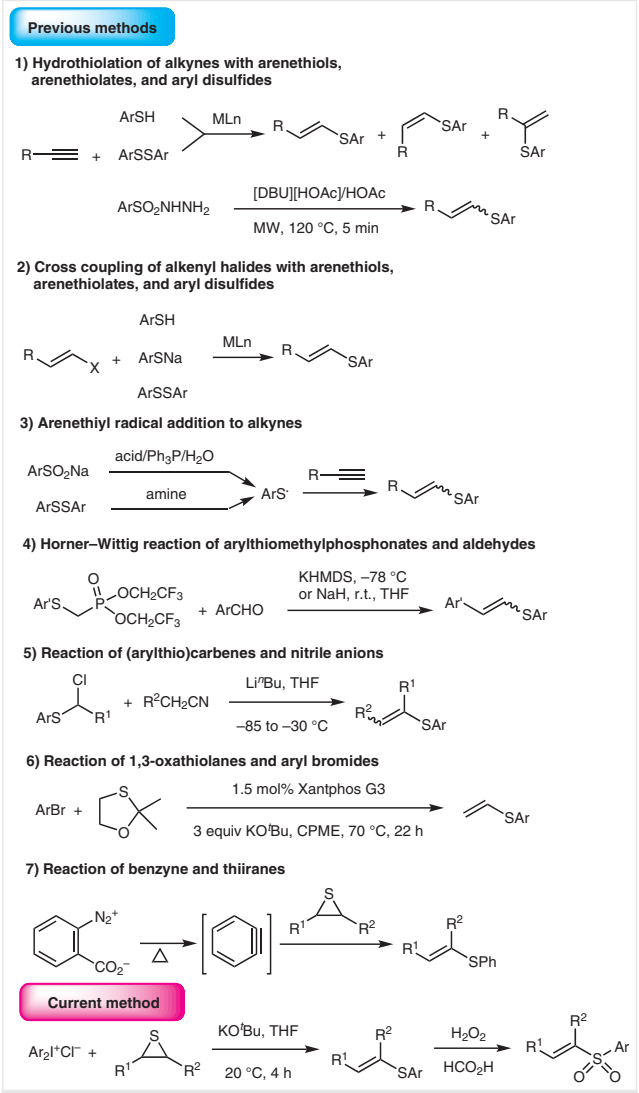
Abstract A series of 1-alkenyl aryl sulfides was synthesized from thiiranes and diaryliodonium salts in tetrahydrofuran in the presence of potassium *tert*-butoxide. The proposed reaction mechanism involves generation of benzynes from the diaryliodonium salts in the presence of the base. Then, nucleophilic attack of the benzynes by thiiranes, followed by hydrogen abstraction and ring opening of the generated thiiranium intermediates, provides the sulfides. These sulfides were further oxidized with performic acid to the corresponding sulfones. The current method provides a metal-free and safe method for the preparation of 1-alkenyl aryl sulfides and their sulfones.

Key words benzynes, diaryliodonium salts, sulfides, sulfones, thiiranes, ring opening

Alkenyl aryl sulfides and sulfones are present in many biologically active compounds.[1] They are also useful synthetic intermediates in organic transformations,[2] including enol substitutions,[3] Diels–Alder cycloadditions,[4] [2+2] cycloadditions,[5] thio-Claisen rearrangements,[6] as Michael acceptors,[7] or in olefin metathesis.[8] Thus, the preparation of 1-alkenyl aryl sulfides has received great attention during recent decades. The main synthetic strategies for 1-alkenyl aryl sulfides include 1) the transition-metal-catalyzed hydrothiolation of terminal alkynes with thiophenols[9] or aryl disulfides[10] with different regioselectivities, and the organic ionic base and Brønsted acid catalyzed hydrothiolation of terminal alkynes with sulfonyl hydrazides,[11] and 2) the transition-metal-catalyzed coupling of 1-alkenyl halides with thiophenols,[12] sodium benzenethiolate,[13] or aryl disulfides[14] (Scheme 1). Alternatively, other synthetic methods have been reported, such as 3) the acid/phosphide-induced arenethiyl radical addition to alkynes,[15] and the amine-induced reductive addition of arenethiyl radical to alkynes,[16] 4) the Horner–Wittig reaction of bis(2,2,2-trifluoroethyl) arylthiomethylphosphonates and aromatic aldehydes,[17] 5) the reaction of (arylthio)carbenes and nitrile anions,[18] 6) the palladium-catalyzed reaction of 1,3-oxathiolanes and aryl bromides,[19] and 7) the reaction of benzyne (generated from 2-aminobenzoate) and thiiranes[20] (Scheme 1).

Thiiranes are important organic synthetic intermediates.[21] During recent years, our research group has been interested in the application of thiiranes in the preparation of sulfur-containing compounds via ring-opening and expansion reactions.[22,23] Diaryliodonium halides are readily available chemicals,[24] and have been verified experimentally to generate arynes.[25] However, they have seldom been applied as safe benzyne precursors in the presence of base.[26]

Hoshino and co-workers already reported the efficient synthesis of alkenyl aryl sulfides using thiiranes and benzyne with 2-carboxybenzenediazonium as a benzyne precursor in 1984.[20] In addition, base-promoted benzyne formation from diaryliodonium salts was reported in 2016 by the Huangs groups.[26] However, the reactions of diaryliodonium salts with thiiranes, or even with other three-membered heterocycles, have not been explored. On the other hand, in the presence of base, thiiranes may undergo nucleophilic ring-opening reactions,[21,22] a competitive reaction with base-promoted benzyne formation from diaryliodonium salts. Thus, it is valuable to explore the reaction of diaryliodonium salts and thiiranes in the presence of base. Furthermore, in Hoshino's work,[20] only benzyne itself was investigated. In our current work, we have attempted the reaction of substituted benzynes, generated from symmetric and unsymmetric bis(substituted phenyl)iodonium salts, with thiiranes and discuss the chemo- and regioselectivities. Notably, diaryliodonium salts are more easily prepared than substituted 2-carboxybenzenediazoniums. More and detailed information on the reaction of thiiranes and diaryliodonium salts are provided. Thus, we herein

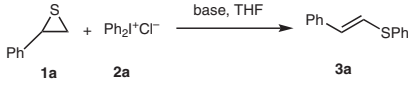


Scheme 1 Synthesis of 1-alkenyl aryl sulfides

present a new and convenient preparation of 1-alkenyl aryl sulfides from readily available thiiranes and diaryliodonium salts in the presence of potassium *tert*-butoxide (KO^{t}Bu) at room temperature (Scheme 1).

The reaction of phenylthiirane (**1a**) and diphenyliodonium chloride (**2a**) on a 0.25-mmol scale was employed as a model reaction to optimize the reaction conditions (Table 1). Initially, a mixture of **1a** and **2a** in tetrahydrofuran was stirred in the presence of KO^{t}Bu (0.375 mmol) for 4 hours at 40, 30, 20, or 0 °C, which afforded the desired product phenyl styryl sulfide (**3a**) in 57%, 57%, 70%, and 56% yields, respectively (Table 1, entries 1–4). When the reaction mixture was stirred in an ice–water bath and then allowed to warm to 30 °C over 4 hours, **3a** was formed in 50% yield (Table 1, entry 5). When the reaction mixture was first stirred at 0 °C for 2 hours and then at 40 °C for another 2 hours, the yield dropped to 27% (Table 1, entry 6). These results reveal that it is more suitable to conduct the reaction at 20 °C. Thus, further optimizations were conducted at 20 °C. Different bases, K_2CO_3 and $Na_2CO_3{\cdot}2\,H_2O$, were evaluated which proved completely inefficient for the transformation (Table 1, entries 7 and 8). NaO^{t}Bu showed a lower efficiency than KO^{t}Bu, producing **3a** in 68% yield (Table 1, entry 9). Prolonging the reaction time to 6 hours resulted in a decreased yield, to 59% (Table 1, entry 10). Increasing the amount of KO^{t}Bu from 0.375 mmol to 0.40 mmol improved the yield slightly (from 70% to 71%) (Table 1, entry 11). Further increase of the base to 0.425 mmol resulted in a weakly decreased yield (from 70% to 68%) (Table 1, entry 12). Two other diphenyliodonium salts, diphenyliodonium tetrafluoroborate ($Ph_2I^+BF_4^-$) (**2b**) and diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) (**2c**), were used instead of chloride **2a**; however, both showed lower efficiencies than **2a** (Table 1, entries 13 and 14).[27] Finally, the optimal conditions were established as KO^{t}Bu (0.40 mmol) at 20 °C for 4 hours (Table 1, entry 11). Only trace amounts (<3%) of phenyl *cis*-styryl sulfide (*cis*-**3a**) were observed on ^{1}H NMR analysis of the reaction mixture in each case. The *cis*-isomer displays a larger coupling constant between its two vicinal olefinic hydrogens than the corresponding *trans*-isomer.

Table 1 Optimization of the Reaction of Phenylthiirane (**1a**) with Diphenyliodonium Chloride (**2a**)[a]



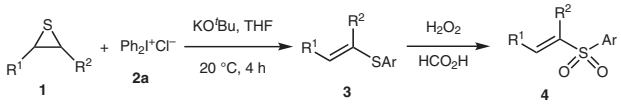
1a **2a** **3a**

Entry	$Ph_2I^+X^-$	Base (mmol)	Temp (°C)	Time (h)	Yield[b] (%)
1	**2a**	KO^{t}Bu (0.375)	40	4	57
2	**2a**	KO^{t}Bu (0.375)	30	4	57
3	**2a**	KO^{t}Bu (0.375)	20	4	70
4	**2a**	KO^{t}Bu (0.375)	0	4	56
5	**2a**	KO^{t}Bu (0.375)	0 to 30	4	50
6	**2a**	KO^{t}Bu (0.375)	0 (2 h) + 40 (2 h)	4	27
7	**2a**	K_2CO_3 (0.40)	20	4	0
8	**2a**	$Na_2CO_3{\cdot}2\,H_2O$ (0.40)	20	4	0
9	**2a**	NaO^{t}Bu (0.375)	20	4	68
10	**2a**	KO^{t}Bu (0.375)	20	6	59
11	**2a**	**KO^{t}Bu (0.40)**	**20**	**4**	**71**
12	**2a**	KO^{t}Bu (0.425)	20	4	68
13	$Ph_2I^+BF_4^-$ (**2b**)	KO^{t}Bu (0.40)	20	4	61
14	$Ph_2I^+PF_6^-$ (**2c**)	KO^{t}Bu (0.40)	20	4	60

[a] Reaction conditions: solution of **1a** (0.25 mmol) and **2a** (0.25 mmol) in THF (3 mL) stirred in the presence of a base at the indicated temperature and time.
[b] Yield on the basis of ^{1}H NMR analysis of the reaction mixture, with 1,3,5-trimethoxybenzene as an internal standard.

With the optimized reaction conditions in hand, the reaction scope was then evaluated (Table 2). Various thiiranes **1** were subjected to the optimal reaction conditions. Phenylthiirane (**1a**) and electron-rich *para*/*meta*/*ortho*-methylphenylthiiranes **1b–d** gave the corresponding sulfide products **3b–d** in satisfactory to good yields (Table 2, entries 1–4). More electron-rich 2-(4-methoxyphenyl)thiirane (**1e**) and electron-deficient 4-chloro/bromo/trifluoromethylphenylthiiranes **1f–h** produced the desired products **3e–h** in satisfactory yields (Table 2, entries 5–8). Cyclohexene sulfide (**1i**) generated 1-cyclohexen-1-yl phenyl sulfide (**3i**) in the highest yield of 82% (Table 2, entry 9). Aliphatic substituted substrate butylthiirane (**1j**) gave the desired product 1-hexen-1-yl phenyl sulfide (**3j**) in 75% yield (Table 2, entry 10). However, thiirane (**1k**) itself produced the corresponding product phenyl vinyl sulfide (**3k**) in a low 57% yield (Table 2, entry 11). Sulfides **3** were difficult to separate from thiiranes and purify, due to the very close polarities. For accuracy, we have reported the NMR yields of sulfides **3** (Table 2). For convenient separation and purification, all obtained sulfides **3** were further oxidized with performic acid (H_2O_2/HCO_2H) as oxidant to the corresponding sulfones **4** in good yields (Table 2 shows isolated overall yields from thiiranes **1**). With the current method, only trace amounts (<3%) of *cis*-1-alkenyl aryl sulfides were observed on ^{1}H NMR analysis of the reaction mixture in each case, indicating high stereoselectivity. The *cis*-isomers display a larger coupling constant between their two vicinal alkenic hydrogens than the corresponding *trans*-isomers. After oxidation, all obtained sulfones **4** were in the *trans*-configuration, assigned by comparison with previously reported data.[28–34]

Table 2 Substrate Scope[a]



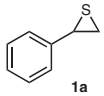
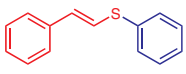
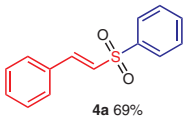
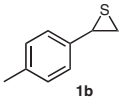
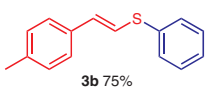
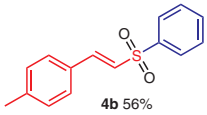
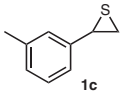
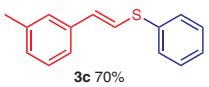
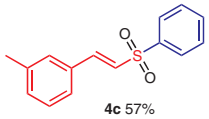
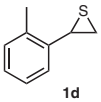
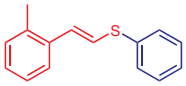
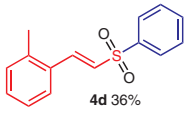
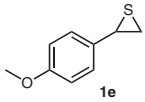
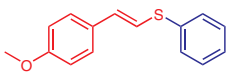
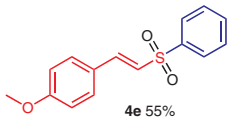
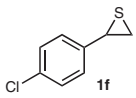
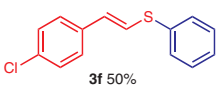
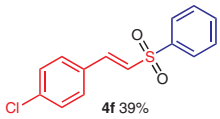
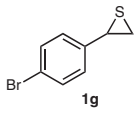
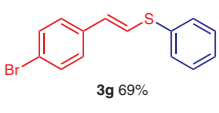
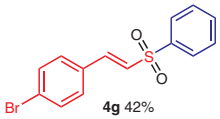
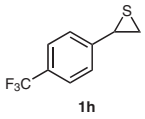
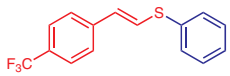
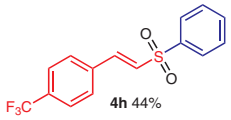
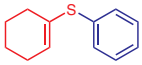
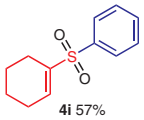
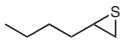
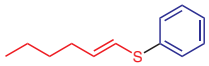
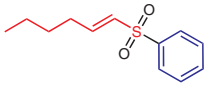
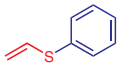
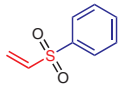
Entry	1	3	4
1	 1a	 **3a** 71%	 **4a** 69%
2	 1b	 **3b** 75%	 **4b** 56%
3	 1c	 **3c** 70%	 **4c** 57%
4	 1d	 **3d** 61%	 **4d** 36%
5	 1e	 **3e** 55%	 **4e** 55%
6	 1f	 **3f** 50%	 **4f** 39%

Table 2 (continued)

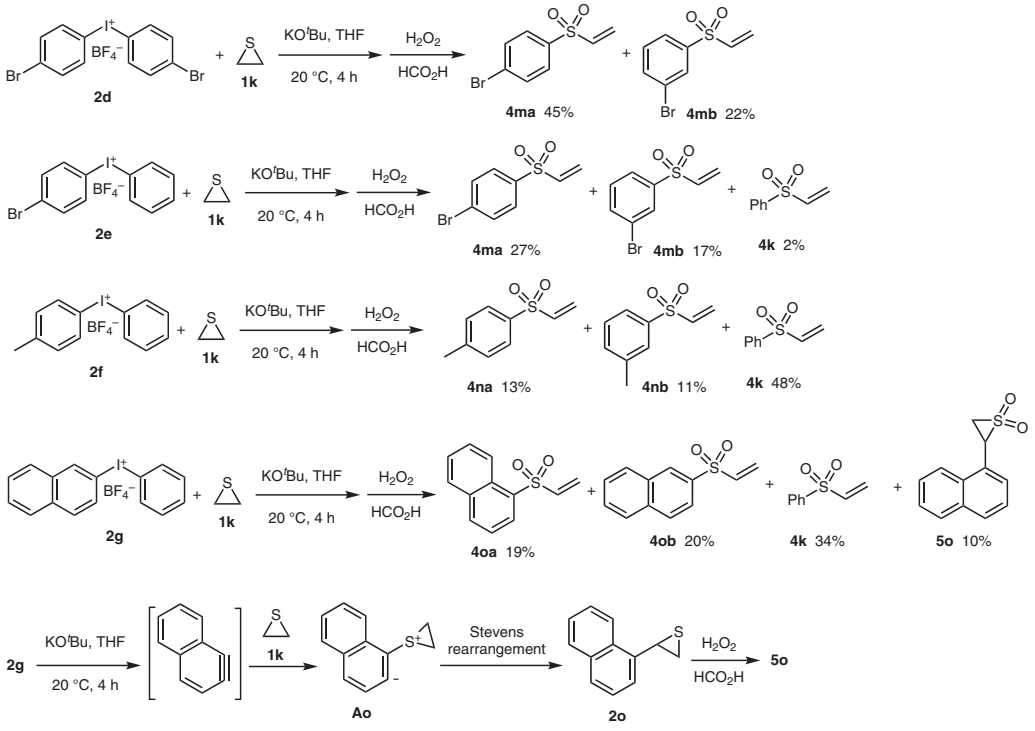
Entry	1	3	4
7	 **1g**	 **3g** 69%	 **4g** 42%
8	 **1h**	 **3h** 50%	 **4h** 44%
9	 **1i**	 **3i** 82%	 **4i** 57%
10	 **1j**	 **3j** 75%	 **4j** 59%
11	 **1k**	 **3k** 57%	 **4k** 55%

[a] Reaction conditions: **1** (0.25 mmol) and **2a** (0.25 mmol) were added in THF (3 mL) into a 10-mL reaction vessel; then, KO^{t}Bu (0.40 mmol) was added and the mixture stirred at 20 °C for 4 h. All obtained sulfides **3** were further oxidized to the corresponding sulfones **4** in good yields with H_2O_2/HCO_2H as oxidant. Yields of sulfones **4** are isolated overall yields from thiiranes **1**. All yields of sulfides **3** were determined on the basis of ^{1}H NMR analysis of the reaction mixture, with 1,3,5-trimethoxybenzene as an internal standard.

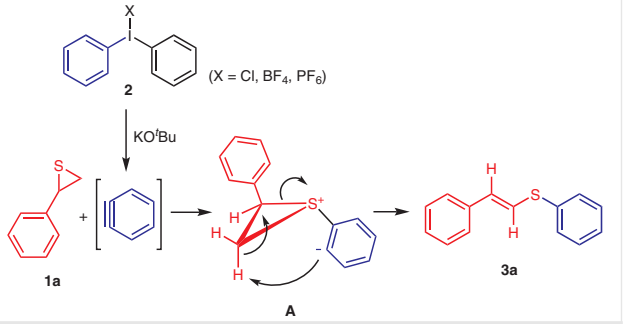
Symmetrically substituted bis(4-bromophenyl)iodonium tetrafluoroborate (**2d**) was treated with thiirane (**1k**), followed by oxidation with performic acid for convenient separation and purification of products, which afforded two regioisomeric products 4-bromophenyl vinyl sulfone (**4ma**) and 3-bromophenyl vinyl sulfone (**4mb**) in 45% and 22% yield, respectively, due to thiirane nucleophilic attack at the different carbon atoms of the 4-bromobenzyne intermediate generated from **2d** (Scheme 2).

Unsymmetrical diaryliodonium salts were also investigated. The reaction of (4-bromophenyl)(phenyl)iodonium tetrafluoroborate (**2e**) and thiirane (**1k**), followed by oxidation, gave not only the regioisomeric products 4-bromophenyl vinyl sulfone (**4ma**) and 3-bromophenyl vinyl sulfone (**4mb**) in 27% and 17% yield, respectively, but also phenyl vinyl sulfone (**4k**) in 2% yield (Scheme 2). However, the reaction of (4-methylphenyl)(phenyl)iodonium tetrafluoroborate (**2f**) and thiirane (**1k**), followed by oxidation, generated the regioisomeric products 4-methylphenyl vinyl sulfone (**4na**) and 3-methylphenyl vinyl sulfone (**4nb**) in 13% and 11% yield, respectively, along with phenyl vinyl sulfone (**4k**) in 48% yield (Scheme 2). These results indicate that the more electron-deficient aryl groups in unsymmetric diaryliodonium salts favor formation of the corresponding benzynes in the presence of base because of their more acidic hydrogen atoms. 2-Naphthyl(phenyl)iodonium tetrafluoroborate (**2g**) reacted with thiirane (**1k**), followed by oxidation, to give rise to the regioisomeric products 1-naphthyl vinyl sulfone (**4oa**) and 2-naphthyl vinyl sulfone (**4ob**), and phenyl vinyl sulfone (**4k**) in 19%, 20%, and 34% yield, respectively, with 10% of 2-(1-naphthyl)thiirane 1,1-dioxide (**5o**). Product **5o** was generated from the corresponding intermediate 1-(thiiran-1-ium-1-yl)naphthalen-2-ide (**Ao**), formed from aryne and thiirane (**1k**), through Stevens rearrangement followed by performic acid oxidation (Scheme 2).

Considering the reaction mechanism, the reaction of phenylthiirane (**1a**) and diphenyliodonium salts **2** is selected as an example to illustrate the proposed mechanism (Scheme 3). First, *tert*-butoxide abstracts a proton from the *ortho*-position of diphenyliodonium salt **2** which is followed by loss of iodobenzene to afford benzyne. Nucleophilic attack of benzyne by triirane **1a** generates ylide intermediate **A**. The phenyl anion intramolecularly abstracts a



Scheme 2 Reactions of thiirane (**1k**) and symmetrically and unsymmetrically substituted diaryliodonium salts in the presence of potassium *tert*-butoxide



Scheme 3 Proposed mechanism for the synthesis of *trans*-1-alkenyl aryl sulfides from thiiranes and diaryliodonium salts in the presence of potassium *tert*-butoxide

cis-proton from the thiiranium ring, which is followed by formation of the C=C bond and ring opening of the thiiranium ring, affording the desired *trans*-product **3a** (Scheme 3).

In summary, we have developed a safe and metal-free method for the synthesis of 1-alkenyl aryl sulfides from thiiranes and diaryliodonium salts with potassium *tert*-butoxide as an efficient base. The proposed reaction mechanism involves generation of benzynes from the diaryliodonium salts in the presence of potassium *tert*-butoxide. Nucleophilic attack of the benzynes by thiiranes is followed by hydrogen abstraction and ring opening of the generated thiiranium intermediates. The sulfides were further oxidized with performic acid to the corresponding sulfones. The current method provides a convenient route for the preparation of 1-alkenyl aryl sulfides and their sulfones under mild conditions.

Unless otherwise noted, all materials were purchased from commercial suppliers. Flash column chromatography was performed using silica gel (normal phase, 200–300 mesh) from Branch of Qingdao Haiyang Chemical Industry. Petroleum ether (PE) used for column chromatography was the 30–60 °C fraction, and the removal of residual solvent was accomplished with a rotary evaporator. Reactions were monitored by TLC on silica gel GF254 coated 0.2 mm plates from Institute of Yantai Chemical Industry. The plates were visualized under UV light, as well as with TLC stains (10% phosphomolybdic acid in EtOH; 1% $KMnO_4$ in H_2O; 10 g of I_2 absorbed on 30 g of silica gel). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker 400 MHz spectrometer, with TMS as an internal standard; chemical shifts (δ) are reported in parts per million (ppm). All coupling constants (*J*) in ^1H NMR spectra are absolute values given in hertz (Hz) with peaks labeled as singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q), and multiplet (m). Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected. Diaryliodonium salts **2** were prepared according to the procedure reported by Olofsson and co-workers.[27] The thiiranes **1** and diaryliodonium salts **2** are known compounds and have analytical data identical to the reported values.[22,27]

Thiiranes 1; General Procedure[22]

A solution of an oxirane (24.0 mmol) and KSCN (9.31 g, 96.0 mmol) in H_2O (30.0 mL) was stirred at 40 °C for 24 h. The resulting mixture was diluted with EtOAc and washed with brine. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE) to give the corresponding thiirane **1**.

2-Phenylthiirane (1a)[22]

Colorless oil; yield: 900 mg (23%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.21 (m, 5 H), 3.88 (dd, *J* = 6.5, 5.6 Hz, 1 H), 2.85 (dd, *J* = 6.6, 1.5 Hz, 1 H), 2.64 (dd, *J* = 5.7, 1.5 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.1, 128.5, 127.6, 126.7, 36.1, 27.3.

2-(4-Methylphenyl)thiirane (1b)[22]

Colorless oil; yield: 400 mg (45%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 7.8 Hz, 2 H), 7.11 (d, *J* = 7.9 Hz, 2 H), 3.88 (dd, *J* = 6.3, 6.3 Hz, 1 H), 2.85 (d, *J* = 6.1 Hz, 1 H), 2.65 (d, *J* = 5.1 Hz, 1 H), 2.33 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.4, 136.0, 129.2, 126.6, 36.2, 27.2, 21.1.

2-(3-Methylphenyl)thiirane (1c)[22]

Colorless oil; yield: 220 mg (25%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (t, *J* = 7.8 Hz, 1 H), 7.12–7.09 (m, 3 H), 3.90 (dd, *J* = 6.2, 6.2 Hz, 1 H), 2.89 (d, *J* = 6.5 Hz, 1 H), 2.69 (d, *J* = 5.6 Hz, 1 H), 2.37 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.0, 138.3, 128.4, 128.4, 127.2, 123.9, 36.2, 27.3, 21.3.

2-(2-Methylphenyl)thiirane (1d)[22]

Colorless oil; yield: 147 mg (10%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19–7.15 (m, 4 H), 4.01 (dd, *J* = 6.4, 6.4 Hz, 1 H), 2.87 (d, *J* = 6.5 Hz, 1 H), 2.74 (d, *J* = 5.9 Hz, 1 H), 2.49 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.8, 136.9, 130.0, 127.5, 126.2, 125.4, 34.4, 25.6, 19.5.

2-(4-Methoxyphenyl)thiirane (1e)[22]

Colorless oil; yield: 107 mg (17%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 8.2 Hz, 2 H), 6.84 (d, *J* = 8.3 Hz, 2 H), 3.89 (dd, *J* = 6.3, 6.3 Hz, 1 H), 3.80 (s, 3 H), 2.84 (d, *J* = 6.5 Hz, 1 H), 2.63 (d, *J* = 5.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.1, 130.9, 127.8, 114.0, 55.3, 36.2, 27.1.

2-(4-Chlorophenyl)thiirane (1f)[22]

Colorless oil; yield: 431 mg (43%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.1 Hz, 2 H), 7.20 (d, *J* = 8.2 Hz, 2 H), 3.84 (dd, *J* = 6.1, 6.1 Hz, 1 H), 2.86 (d, *J* = 6.5 Hz, 1 H), 2.59 (d, *J* = 5.5 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.7, 133.2, 128.7, 128.0, 35.3, 27.4.

2-(4-Bromophenyl)thiirane (1g)[22]

Colorless oil; yield: 407 mg (32%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 3.83 (dd, *J* = 6.1, 6.1 Hz, 1 H), 2.87 (d, *J* = 6.5 Hz, 1 H), 2.59 (d, *J* = 5.5 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.2, 131.6, 128.4, 121.3, 35.4, 27.4.

2-[4-(Trifluoromethyl)phenyl]thiirane (1h)[22]

Colorless oil; yield: 511 mg (42%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.0 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 3.90 (t, *J* = 5.8 Hz, 1 H), 2.92 (d, *J* = 6.2 Hz, 1 H), 2.64 (d, *J* = 5.1 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.4, 129.7 (q, J_{F-C} = 32.4 Hz, 1 C), 127.1, 125.5 (q, J_{F-C} = 3.8 Hz, 1 C), 124.0 (q, J_{F-C} = 271.9 Hz, 1 C), 35.0, 27.6.

7-Thiabicyclo[4.1.0]heptane (1i)[22]

Colorless oil; yield: 450 mg (20%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.29–3.23 (m, 2 H), 2.22–2.10 (m, 4 H), 1.60–1.51 (m, 2 H), 1.32–1.22 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 37.0, 25.8, 19.4.

2-Butylthiirane (1j)[22]

Colorless oil; yield: 450 mg (20%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.88 (dddd, *J* = 7.1, 5.8, 5.8, 5.8 Hz, 1 H), 2.50 (dd, *J* = 6.3, 1.0 Hz, 1 H), 2.15 (dd, *J* = 5.7, 1.0 Hz, 1 H), 1.85–1.78 (m, 1 H), 1.52–1.34 (m, 5 H), 0.92 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 36.3, 36.0, 31.5, 25.9, 22.3, 14.0.

Phenyl Vinyl Sulfones 4; General Procedure

To a stirring solution of a thiirane **1** (0.25 mmol) and a diaryliodonium salt **2** (0.25 mmol) in anhydrous THF (3 mL) open to air at 20 °C was added KO^{t}Bu (45 mg, 0.40 mmol). The resulting mixture was stirred at 20 °C for 4 h. After removal of the solvent, H_2O was added. The solution was extracted with CH_2Cl_2 and the combined organic extracts were concentrated to afford the crude product sulfide **3**, which was used directly in the next step without purification.

For the reactions of thiirane (**1k**) with diaryliodonium salts **2d**–**g**, a solution of **1k** (45 mg, 0.75 mmol) and salt **2** (0.25 mmol) in THF (3 mL) was stirred in the presence of KO^{t}Bu (45 mg, 0.40 mmol) at 20 °C for 4 h.

To a performic acid solution, prepared by mixing and stirring 30% H_2O_2 (0.17 mL, 1.5 mmol) and 88% HCO_2H (1.5 mL) at r.t. for 0.5 h in an ice bath, was added dropwise the crude sulfide **3** obtained from the above step at 0 °C over a period of 10 min. The resulting mixture was stirred and allowed to warm to r.t. for 0.5–1 h. The resulting mixture was washed with H_2O. The organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography to give the sulfone **4** in moderate to good yields.[22] All of the sulfones are known compounds and have analytical data identical to the reported values.[28–34]

[(*E*)-2-(Phenylsulfonyl)vinyl]benzene (4a)[28]

White solid; yield: 42 mg (69%); mp 80–81 °C; R_f = 0.18 (hexanes–EtOAc, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.4 Hz, 2 H), 7.69 (d, *J* = 15.2 Hz, 1 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.55 (t, *J* = 8.1 Hz, 2 H), 7.50–7.47 (m, 2 H), 7.41–7.39 (m, 3 H), 6.87 (d, *J* = 15.4 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.4, 140.7, 133.3, 132.3, 131.2, 129.3, 129.0, 128.5, 127.6, 127.2.

1-Methyl-4-[(*E*)-2-(phenylsulfonyl)vinyl]benzene (4b)[29]

White solid; yield: 36 mg (56%); mp 139–140 °C; R_f = 0.33 (hexanes–EtOAc, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.2 Hz, 2 H), 7.66 (d, *J* = 15.5 Hz, 1 H), 7.61–7.59 (m, 1 H), 7.54 (t, *J* = 7.7 Hz, 2 H), 7.38 (d, *J* = 8.2 Hz, 2 H), 7.19 (d, *J* = 8.2 Hz, 2 H), 6.81 (d, *J* = 15.3 Hz, 1 H), 2.37 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.5, 141.8, 140.9, 133.2, 129.8, 129.6, 129.2, 128.5, 127.5, 126.0, 21.5.

1-Methyl-3-[(*E*)-2-(phenylsulfonyl)vinyl]benzene (4c)[28]

White solid; yield: 37 mg (57%); mp 75–77 °C; R_f = 0.26 (hexanes–EtOAc, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.3 Hz, 2 H), 7.66 (d, *J* = 15.5 Hz, 1 H), 7.62 (t, *J* = 7.0 Hz, 1 H), 7.54 (t, *J* = 7.0 Hz, 2 H), 7.30–7.21 (m, 4 H), 6.85 (d, *J* = 15.4 Hz, 1 H), 2.35 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.7, 140.8, 138.8, 133.3, 132.2, 132.0, 129.3, 129.2, 129.1, 128.9, 127.6, 127.0, 125.8, 21.2.

1-Methyl-2-[(*E*)-2-(phenylsulfonyl)vinyl]benzene (4d)[28]

White solid; yield: 24 mg (36%); mp 74–75 °C; R_f = 0.26 (hexanes–EtOAc, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99–7.95 (m, 3 H), 7.63 (t, *J* = 7.0 Hz, 1 H), 7.56 (t, *J* = 7.5 Hz, 2 H), 7.44 (d, *J* = 7.8 Hz, 1 H), 7.30 (t, *J* = 7.5 Hz, 1 H), 7.23–7.17 (m, 2 H), 6.79 (d, *J* = 15.4 Hz, 1 H), 2.46 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.7, 140.1, 138.2, 133.3, 131.3, 131.0, 130.9, 129.3, 128.2, 127.7, 126.9, 126.5, 19.8.

1-Methoxy-4-[(*E*)-2-(phenylsulfonyl)vinyl]benzene (4e)[29]

White solid; yield: 36 mg (55%); mp 73–74 °C; R_f = 0.18 (hexanes–EtOAc, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 7.84 Hz, 2 H), 7.63 (d, *J* = 15.3 Hz, 1 H), 7.60 (t, *J* = 7.3 Hz, 1 H), 7.53 (t, *J* = 8.0 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 6.71 (d, *J* = 15.3 Hz, 1 H), 3.82 (s, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.0, 142.2, 141.1, 133.1, 130.3, 129.2, 127.4, 124.9, 124.4, 114.5, 55.4.

1-Chloro-4-[(*E*)-2-(phenylsulfonyl)vinyl]benzene (4f)[28]

White solid; yield: 27 mg (39%); mp 139–140 °C; R_f = 0.58 (hexanes–EtOAc, 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.6 Hz, 2 H), 7.65–7.61 (m, 2 H), 7.55 (t, *J* = 7.8 Hz, 2 H), 7.41 (d, *J* = 8.6 Hz, 2 H), 7.36 (d, *J* = 8.6 Hz, 2 H), 6.84 (d, *J* = 15.5 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.9, 140.4, 137.2, 133.5, 130.8, 129.7, 129.4, 127.9, 127.7.

1-Bromo-4-[(*E*)-2-(phenylsulfonyl)vinyl]benzene (4g)[29]

White solid; yield: 34 mg (42%); mp 168–169 °C; R_f = 0.29 (hexanes–EtOAc, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 7.6 Hz, 2 H), 7.65–7.51 (m, 6 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 6.86 (d, *J* = 15.4 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.0, 140.4, 133.5, 132.3, 131.2, 129.9, 129.4, 128.0, 127.7, 125.6.

1-[(*E*)-2-(Phenylsulfonyl)vinyl]-4-(trifluoromethyl)benzene (4h)[30]

White solid; yield: 34 mg (44%); mp 145–146 °C; R_f = 0.20 (hexanes–EtOAc, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.60 Hz, 2 H), 7.71 (d, *J* = 15.7 Hz, 1 H), 7.66–7.64 (m, 3 H), 7.61–7.55 (m, 4 H), 6.96 (d, *J* = 15.3 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.4, 140.1, 135.7, 133.7, 132.6 (q, J_{F-C} = 32.8 Hz, 1 C), 130.0, 129.4, 128.7, 127.8, 126.0 (q, J_{F-C} = 3.8 Hz, 1 C), 123.6 (q, J_{F-C} = 272.3 Hz, 1 C).

(1-Cyclohexen-1-ylsulfonyl)benzene (4i)[31]

Colorless liquid; yield: 31 mg (57%); R_f = 0.21 (hexanes–EtOAc, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.5 Hz, 2 H), 7.59 (t, *J* = 7.5 Hz, 1 H), 7.51 (t, *J* = 7.5 Hz, 2 H), 7.05 (s, 1 H), 2.27–2.23 (m, 2 H), 2.17–2.13 (m, 2 H), 1.65–1.52 (m, 4 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.7, 139.4, 138.4, 133.0, 129.0, 127.9, 25.4, 22.8, 21.7, 20.7.

[(*E*)-1-Hexen-1-ylsulfonyl]benzene (4j)[32]

Colorless liquid; yield: 33 mg (59%); R_f = 0.34 (hexanes–EtOAc, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.9 Hz, 2 H), 7.60 (t, *J* = 7.2 Hz, 1 H), 7.53 (t, *J* = 7.6 Hz, 2 H), 6.99 (dt, *J* = 6.7, 14.6 Hz, 1 H), 6.30 (d, *J* = 14.9 Hz, 1 H), 2.23 (dt, *J* = 7.1, 7.1 Hz, 2 H), 1.44 (quin, *J* = 7.1 Hz, 2 H), 1.33 (tq, *J* = 7.1, 7.1 Hz, 2 H), 0.88 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.3, 140.7, 133.1, 130.3, 129.2, 129.1, 127.5, 31.1, 29.6, 22.1, 13.7.

(Vinylsulfonyl)benzene (4k)[33]

White solid; yield: 23 mg (55%); mp 69–70 °C; R_f = 0.17 (hexanes–EtOAc, 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.8 Hz, 2 H), 7.63 (t, *J* = 7.1 Hz, 1 H), 7.54 (t, *J* = 7.8 Hz, 2 H), 6.66 (dd, *J* = 9.6, 16.5 Hz, 1 H), 6.45 (d, *J* = 16.6 Hz, 1 H), 6.03 (d, *J* = 9.7 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.5, 138.4, 133.6, 129.3, 127.9, 127.7.

Mixture of 1-Bromo-4-(vinylsulfonyl)benzene (4ma) and 1-Bromo-3-(vinylsulfonyl)benzene (4mb)[33]

Colorless liquid; yield: 43 mg (**4ma**: 45%, **4mb**: 22%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (**4ma**) = 7.75 (d, *J* = 8.7 Hz, 2 H), 7.69 (d, *J* = 8.7 Hz, 2 H), 6.68–6.61 (m, 1 H), 6.47 (d, *J* = 11.1 Hz, 1 H), 6.07 (d, *J* = 9.9 Hz, 1 H).

^{1}H NMR (400 MHz, $CDCl_3$): δ (**4mb**) = 8.03 (s, 1 H), 7.83 (d, *J* = 7.0 Hz, 1 H), 7.76–7.74 (m, 1 H), 7.43 (t, *J* = 7.9 Hz, 1 H), 6.68–6.61 (m, 1 H), 6.50 (d, *J* = 16.5 Hz, 1 H), 6.10 (d, *J* = 9.9 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (**4ma** + **4mb**) = 141.5, 139.0, 138.6, 138.1, 137.9, 136.7, 133.4, 132.6, 130.9, 130.8, 129.4, 129.0, 128.8, 128.4, 126.4, 123.2.

Mixture of 1-Bromo-4-(vinylsulfonyl)benzene (4ma), 1-Bromo-3-(vinylsulfonyl)benzene (4mb), and (Vinylsulfonyl)benzene (4k)[33]

White solid; yield: 27 mg (**4ma**: 27%, **4mb**: 17%, **4k**: 2%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (**4ma**) = 7.75 (d, *J* = 8.7 Hz, 2 H), 7.69 (d, *J* = 8.7 Hz, 2 H), 6.68–6.61 (m, 1 H), 6.47 (d, *J* = 11.1 Hz, 1 H), 6.07 (d, *J* = 9.9 Hz, 1 H).

^{1}H NMR (400 MHz, $CDCl_3$): δ (**4mb**) = 8.03 (s, 1 H), 7.83 (d, *J* = 7.0 Hz, 1 H), 7.76–7.74 (m, 1 H), 7.43 (t, *J* = 7.9 Hz, 1 H), 6.68–6.61 (m, 1 H), 6.50 (d, *J* = 16.5 Hz, 1 H), 6.10 (d, *J* = 9.9 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (**4ma** + **4mb** + **4k**) = 141.5, 139.0, 138.6, 138.1, 137.9, 136.7, 133.4, 132.6, 130.9, 130.8, 129.4, 129.0, 128.8, 128.4, 126.4, 123.2.

Mixture of 1-Methyl-4-(vinylsulfonyl)benzene (4na), 1-Methyl-3-(vinylsulfonyl)benzene (4nb), and (Vinylsulfonyl)benzene (4k)[33]

White solid; yield: 31 mg (**4na**: 13%, **4nb**: 11%, **4k**: 48%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (**4na**) = 7.76 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 6.69–6.60 (m, 1 H), 6.47–6.39 (m, 1 H), 6.05–5.98 (m, 1 H), 2.43–2.42 (m, 3H).

^{1}H NMR (400 MHz, $CDCl_3$): δ (**4nb**) = 7.69–7.61 (m, 2 H), 7.43–7.42 (m, 2 H), 6.69–6.60 (m, 1 H), 6.47–6.39 (m, 1 H), 6.05–5.98 (m, 1 H), 2.43–2.42 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (**4na** + **4nb** + **4k**) = 144.7, 139.6, 139.5, 138.7, 138.5, 138.4, 136.5, 134.4, 133.6, 129.9, 129.3, 129.2, 128.1, 127.9, 127.8, 127.7, 127.5, 127.1, 125.0, 21.6, 21.3.

Mixture of 1-(Vinylsulfonyl)naphthalene (4oa) and 2-(Naphthalen-1-yl)thiirane 1,1-Dioxide (5o)[19]

White solid; yield: 15 mg (**4oa**: 19%, **5o**: 10%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (**4oa**) = 8.62 (d, *J* = 8.6 Hz, 1 H), 8.37 (dd, *J* = 7.3, 1.2 Hz, 1 H), 8.13 (d, *J* = 7.4 Hz, 1 H), 7.99–7.94 (m, 1 H), 7.72–7.66 (m, 1 H), 7.64–7.59 (m, 2 H), 6.79 (dd, *J* = 16.5, 9.8 Hz, 1 H), 6.58 (d, *J* = 16.5 Hz, 1 H), 6.08 (d, *J* = 9.8 Hz, 1 H).

^{1}H NMR (400 MHz, $CDCl_3$): δ (**5o**) = 8.13 (d, *J* = 7.4 Hz, 1 H), 8.05 (d, *J* = 8.2 Hz, 1 H), 7.99–7.94 (m, 2 H), 7.72–7.66 (m, 1 H), 7.64–7.59 (m, 2 H), 4.88 (dd, *J* = 9.7, 5.2 Hz, 1 H), 4.24 (dd, *J* = 11.9, 9.7 Hz, 1 H), 3.97 (dd, *J* = 11.9, 5.2 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (**4oa** + **5o**) = 138.6, 135.4, 134.3, 134.1, 133.4, 132.3, 130.3, 129.3, 129.2, 128.7, 128.5, 127.9, 127.8, 127.0, 126.9, 125.8, 125.3, 124.6, 124.2, 120.7, 75.2, 42.8.

Mixture of 2-(Vinylsulfonyl)naphthalene (4ob) and (Vinylsulfonyl)benzene (4k)[34]

White solid; yield: 25 mg (**4ob**: 20%, **4k**: 34%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (**4ob**) = 8.50 (d, *J* = 1.2 Hz, 1 H), 7.99 (d, *J* = 8.4 Hz, 2 H), 7.93–7.89 (m, 1 H), 7.82 (dd, *J* = 8.7, 1.9 Hz, 1 H), 7.69–7.61 (m, 2 H), 6.72 (dd, *J* = 16.5, 9.8 Hz, 1 H), 6.51 (d, *J* = 16.5 Hz, 1 H), 6.06 (d, *J* = 9.6 Hz, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (**4ob** + **4k**) = 139.5, 138.5, 138.4, 136.3, 135.2, 133.6, 132.2, 129.7, 129.7, 129.4, 129.3, 128.0, 127.9, 127.8, 127.7, 127.7, 122.6.

Funding Information

This work was supported by the National Natural Science Foundation of China (Nos. 21572017 and 21772010).

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1591559. Copies of the ^{1}H and ^{13}C NMR spectra of products **4** are included.

References

(1) (a) Meng, D.; Chen, W.; Zhao, W. *J. Nat. Prod.* **2007**, *70*, 824. (b) Szilágyi, Á.; Fenyvesi, F.; Mayercsik, O.; Pelyvás, I. S.; Bácskay, I.; Fehér, P.; Váradi, J.; Vecsernyés, M.; Herczegh, P. *J. Med. Chem.* **2006**, *49*, 5626.
(2) (a) Schaumann, E. *Top. Curr. Chem.* **2007**, *274*, 1. (b) Yang, Z. H.; Yang, S. Y.; Haroone, M. S.; He, W.; Xu, J. X. *Tetrahedron* **2017**, *73*, 3338.
(3) (a) Bratz, M.; Bullock, W. H.; Overman, L. E.; Takemoto, T. *J. Am. Chem. Soc.* **1995**, *117*, 5958. (b) Sasmal, P. K.; Maier, M. E. *Org. Lett.* **2002**, *4*, 1271.
(4) (a) Chou, S.-S. P.; Wey, S.-J. *J. Org. Chem.* **1990**, *55*, 1270. (b) Surasani, S. R.; Peddinti, R. K. *Tetrahedron Lett.* **2011**, *52*, 4615.
(5) (a) Narasaka, K.; Hayashi, Y.; Shimadzu, H.; Niihata, S. *J. Am. Chem. Soc.* **1992**, *114*, 8869. (b) Paquette, L. A.; Sun, L.-Q.; Watson, T. J. N.; Friedrich, D.; Freeman, B. T. *J. Org. Chem.* **1997**, *62*, 8155.
(6) (a) Fernandez de la Pradilla, R.; Tortosa, M.; Viso, A. *Top. Curr. Chem.* **2007**, *275*, 103. (b) Liu, Z.; Mehta, S. J.; Lee, K.-S.; Grossman, B.; Qu, H.; Gu, X.; Nichol, G. S.; Hruby, L. J. *J. Org. Chem.* **2012**, *77*, 1289.
(7) Miller, R. D.; Hassig, R. *Tetrahedron Lett.* **1985**, *26*, 2395.
(8) (a) Liu, Z.; Rainier, J. D. *Org. Lett.* **2005**, *7*, 131. (b) Macnaughtan, M. L.; Gary, J. B.; Gerlach, D. L.; Johnson, M. J. A.; Kampf, J. W. *Organometallics* **2009**, *28*, 2880.
(9) Di Giuseppe, A.; Castrarlenas, R.; Perez-Torrente, J. J.; Crucianelli, M.; Polo, V.; Sancho, R.; Lahoz, F. J.; Oro, L. A. *J. Am. Chem. Soc.* **2012**, *134*, 8171; and references cited therein.
(10) Wang, Z.-L.; Tang, R.-Y.; Luo, P.-S.; Deng, C.-L.; Zhong, P.; Li, J.-H. *Tetrahedron* **2008**, *64*, 10670.
(11) Singh, R.; Raghuvanshi, D. S.; Singh, K. N. *Org. Lett.* **2013**, *15*, 4202.
(12) Kao, H.-L.; Lee, C.-F. *Org. Lett.* **2011**, *13*, 5204; and references cited therein.
(13) Cristau, H. J.; Chabaud, B.; Labaudiniere, R.; Christol, H. *J. Org. Chem.* **1986**, *51*, 875.
(14) Silveira, C. C.; Santos, P. C. S.; Mendes, S. R.; Braga, A. L. *J. Organomet. Chem.* **2008**, *693*, 3787.
(15) Lin, Y.-M.; Lu, G.-P.; Wang, G.-X.; Yi, W.-B. *J. Org. Chem.* **2017**, *82*, 382.
(16) Taniguchi, T.; Fujii, T.; Idota, A.; Ishibashi, H. *Org. Lett.* **2009**, *11*, 3298.
(17) Kokin, K.; Tsuboi, S.; Motoyoshiya, J.; Hayashi, S. *Synthesis* **1996**, 637.
(18) Harada, T.; Karasawa, A.; Oku, A. *J. Org. Chem.* **1986**, *51*, 842.
(19) Schmink, J. R.; Dockrey, S. A. B.; Zhang, T. Y.; Chebet, N.; van Venrooy, A.; Sexton, M.; Lew, S. I.; Chou, S.; Okazaki, A. *Org. Lett.* **2016**, *18*, 6360.
(20) Nakayam, J.; Takeue, S.; Hoshino, M. *Tetrahedron Lett.* **1984**, *25*, 2679.
(21) (a) Xu, J. X. *Top. Heterocycl. Chem.* **2016**, *41*, 311. (b) Zhou, C.; Xu, J. X. *Prog. Chem.* **2012**, *24*, 238.
(22) (a) Yu, H.; Cao, S. L.; Zhang, L. L.; Liu, G.; Xu, J. X. *Synthesis* **2009**, 2205. (b) Li, X. Y.; Xu, J. X. *Tetrahedron* **2011**, *67*, 1681. (c) Huang, J. X.; Wang, F.; Du, D. M.; Xu, J. X. *Synthesis* **2005**, 2122. (d) Huang, J. X.; Du, D. M.; Xu, J. X. *Synthesis* **2006**, 315.
(23) (a) Dong, J.; Xu, J. X. *Org. Biomol. Chem.* **2017**, *15*, 836. (b) Chen, X. P.; Xu, J. X. *Tetrahedron Lett.* **2017**, *58*, 1651. (c) Li, S. Q.; Chen, X. P.; Xu, J. X. *Tetrahedron* **2018**, *74*, 1613.

(24) (a) Stang, P. J. *J. Org. Chem.* **2003**, *68*, 2997. (b) Aradi, K.; Tóth, B. L.; Tolnai, G. L.; Novák, Z. *Synlett* **2016**, *27*, 1456. (c) Bielawski, M.; Malmgren, J.; Pardo, L. M.; Wikmark, Y.; Olofsson, B. *ChemistryOpen* **2014**, *3*, 19. (d) Rousseaux, S.; Vrancken, E.; Campagne, J.-M. *Angew. Chem. Int. Ed.* **2012**, *51*, 2.
(25) (a) Kitamura, T.; Yamane, M.; Inoue, K.; Todaka, M.; Fukatsu, N.; Meng, Z.; Fujiwara, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11674. (b) Cadogan, J. I. G.; Rowley, A. G.; Sharp, J. T.; Sledzinsk, B.; Wilson, N. H. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1072.
(26) Wang, M.; Huang, Z. *Org. Biomol. Chem.* **2016**, *14*, 10185.
(27) Bielawski, M.; Aili, D.; Olofsson, B. *J. Org. Chem.* **2008**, *73*, 4602.
(28) Zhang, N.; Yang, D. S.; Wei, W.; Yuan, L.; Cao, Y. J.; Wang, H. *RSC Adv.* **2015**, *5*, 37013.
(29) Nie, G.; Deng, X. C.; Lei, X.; Hu, Q. Q.; Chen, Y. F. *RSC Adv.* **2016**, *6*, 75277.
(30) Chen, J.; Mao, J. C.; Zheng, Y.; Liu, D. F.; Rong, G. W.; Yan, H.; Zhang, C.; Shi, D. Q. *Tetrahedron* **2015**, *71*, 5059.
(31) Hopkins, P. B.; Fuchs, P. L. *J. Org. Chem.* **1978**, *43*, 1208.
(32) Das, B.; Lingaiah, M.; Damodar, K.; Bhunia, N. *Synthesis* **2011**, 2941.
(33) Dana, D.; Das, T. K.; Kumar, I.; Davalos, A. R.; Mark, K. J.; Ramai, D.; Chang, E. J.; Talele, T. T.; Kumar, S. *Chem. Biol. Drug Des.* **2012**, *80*, 489.
(34) Llamas, T.; Arrayás, R. G.; Carretero, C. J. *Org. Lett.* **2006**, *8*, 1795.