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电化学氧化芳基端炔的硫氰化磺化反应

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摘要 硫氰基和磺酰基作为重要的官能团, 广泛存在于天然产物、农药和药物中, 同时它们作为合成中间体可以转化为其它多种官能团. 到目前为止, 合成兼具硫氰基和磺酰基这两类官能团的化合物的研究较少. 报道了一种简单的芳基端炔、亚磺酸钠和硫氰酸铵电化学氧化三组反应, 合成了一类硫氰代烯基砜类化合物. 该反应利用廉价易得的原料, 并具有无需外源氧化剂、反应条件温和及立体选择性高等特点. 此外, 该方法实现了一步反应中两个 C—S 键的同时构建.

关键词 炔烃; 双官能团化; 电化学; 自由基; 硫氰化; 磺化; 绿色化学

Electrochemical Oxidative Thiocyanosulfonylation of Aryl Acetylenes

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Abstract Thiocyano and sulfonyl groups as important functional groups are widely existing in natural products, agrochemicals and medicines. They are also versatile synthetic intermediates that could be converted into various functionalities. There are limited reports on the synthesis of compounds that contain these two functional groups. A simple three-component thiocyanatosulfonylation of aryl acetylenes with sodium sulfinates and NH_4SCN through electrochemical oxidation to construct thiocyanated vinylsulfones has been established. The reaction employs easily accessible starting materials and features the characterization of external oxidant-free, mild reaction conditions, and high stereoselectivity. Moreover, this method enables two C—S bonds to be simultaneously formed in a one-step reaction.

Keywords alkyne; difunctionalization; electrochemistry; radical; thiocyanation; sulfonylation; green chemistry

1 Introduction

Alkynes are easily available and fundamental building blocks that can participate in many transformations leading to various compounds.[1] Among them, the difunctionalization of alkynes has been regarded as a direct and efficient strategy for the synthesis of multisubstituted alkenes. Relying on this straightforward approach, different combinations of two new bonds including C—C, C—N, C—O, C—S and C—X (halide) were constructed in a one-step reaction, resulting in divergent alkenes with molecular complexity.[2-6] On the other hand, thiocyano and sulfonyl groups are both not only important motifs widely existing in natural products, agrochemicals and medicines, but also versatile synthetic intermediates that could be converted into various functionalities.[7-8] Therefore, the construction of a compound that possesses thiocyano and/or sulfonyl groups is potentially useful in organic and medicinal chemistry. Actually, many examples of practical methods have been developed for installing thiocyano and/or sulfonyl groups into alkynes via difunctionalization. For example, the group of He[9] and Majee[10] independently reported the dithiocyanation of alkynes using oxone and $Na_2S_2O_8$ as oxidants, respectively (Scheme 1, a). These two

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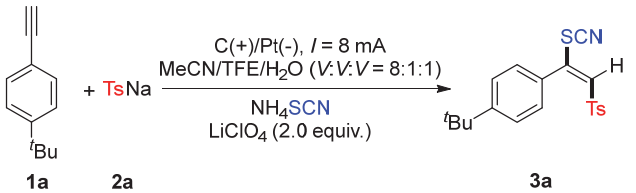
methods enable the construction of various alkenyl dithiocyanates under metal-free and mild conditions, however, rely on stoichiometric oxidants. In 2020, Tang and co-workers[11] described copper(I) and bromodifluoroacetate co-catalyzed disulfonylation of alkynes with sodium arylsulfinates in dimethyl sulfoxide (DMSO) resulting in (*E*)-1,2-disulfonylethenes, but the reaction needs to be performed at 100 ℃. Soon afterward, Ning and co-workers[12] presented the disulfonation of alkynes promoted by a hypervalent iodine(III) reagent to access the same 1,2-disulfonylation products under a relatively lower temperature of 60 ℃ (Scheme 1, b). However, excess chemical oxidant was indispensable. Very recently, Zeng group[13] disclosed a novel three-component thiocyanosulfonylation of terminal alkynes with NH_4SCN and sulfonyl hydrazides to prepare thiocyanated vinylsulfones using $Na_2S_2O_8$ as an oxidant in aqueous solution (Scheme 1, c). The above-mentioned methods suffered from some disadvantages such as the use of stochiometric chemical oxidants, transition metals and harsh conditions.

In recent years, electrosynthesis has become one of the most attractive and alternative methods for organic synthesis.[14] One advantage of this approach is using electrons as traceless and green reactants, thereby liberating the dependence on stoichiometric chemical oxidants. As far as we are aware, there is no report on the construction of thiocyanated vinylsulfones via an electrochemically oxidative strategy. Herein, we present a simple electrochemical method to synthesize thiocyanated vinylsulfones (Scheme 1, d). This method employs $LiClO_4$ as an electrolyte under electrochemical oxidation condition, thereby avoiding the use of a stoichiometric chemical oxidant.

2 Results and discussion

Our investigation with the three-component coupling reaction of 4-*tert*-butylphenylacetylene (**1a**), sodium *p*-toluenesulfinate **2a** (TsNa) and NH_4SCN was first commenced (Table 1). In an undivided cell with graphite as the anode, Pt as the cathode, and $LiClO_4$ as an electrolyte in MeCN/2,2,2-trifluoroethanol (TFE)/H_2O (V∶V∶V=9∶1∶1) under 8 mA constant current, the desired thiocyanatosulfonylation product **3a** was isolated in 58% yield. The replacement of TFE with 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP) led to a trace of the product (Entry 2). The absence of TFE gave a decreased yield of 39%, meanwhile, H_2O was essential for the occurrence of the reaction (Entry 3). Using KSCN as an SCN source instead of NH_4SCN, or $TsNHNH_2$ instead of TsNa extremely suppressed the reaction (Entries 4, 5). Attempts to cut down the amount of TsNa and NH_4SCN were unsuccessful, affording 27% and 41% yield of product, respectively (Entry 6). Without the addition of auxiliary electrolyte resulted in decreased yield

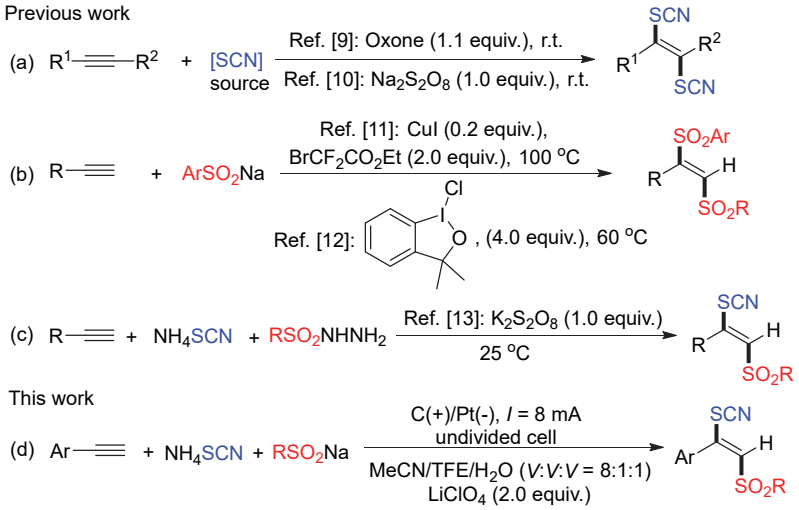
Table 1 Optimization of reaction conditions



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

Entry	Variation from standard conditions	Yield[b]/%
1	None	58
2	HFIP instead of TFE	Trace
3	No TFE or no H_2O	39, 0
4	KSCN instead of NH_4SCN	Trace
5	$TsNHNH_2$ instead of TsNa	Trace
6	TsNa (4.0 equiv.) or NH_4SCN (3.0 equiv.)	27, 41
7	No $LiClO_4$	38
8	5 mA instead of 8 mA	42
9	LiCl (2.0 equiv.) or $^nBu_4NClO_4$ (2.0 equiv.)	44, 22
10	MeCN/TFE/H_2O (V∶V∶V=9∶1∶1)	66
11	MeCN/TFE/H_2O (V∶V∶V=8∶1∶2)	47
12	C(+)/Ni(−)	55
13	No electric current	0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.2 mmol), NH_4SCN (0.8 mmol) in MeCN/TFE/H_2O (11 mL, V∶V∶V=9∶1∶1), $LiClO_4$ (0.4 mmol), graphite plate as the anode and platinum plate as the cathode, undivided cell, 8 mA, r.t., 16 h. [b] Isolated yield.



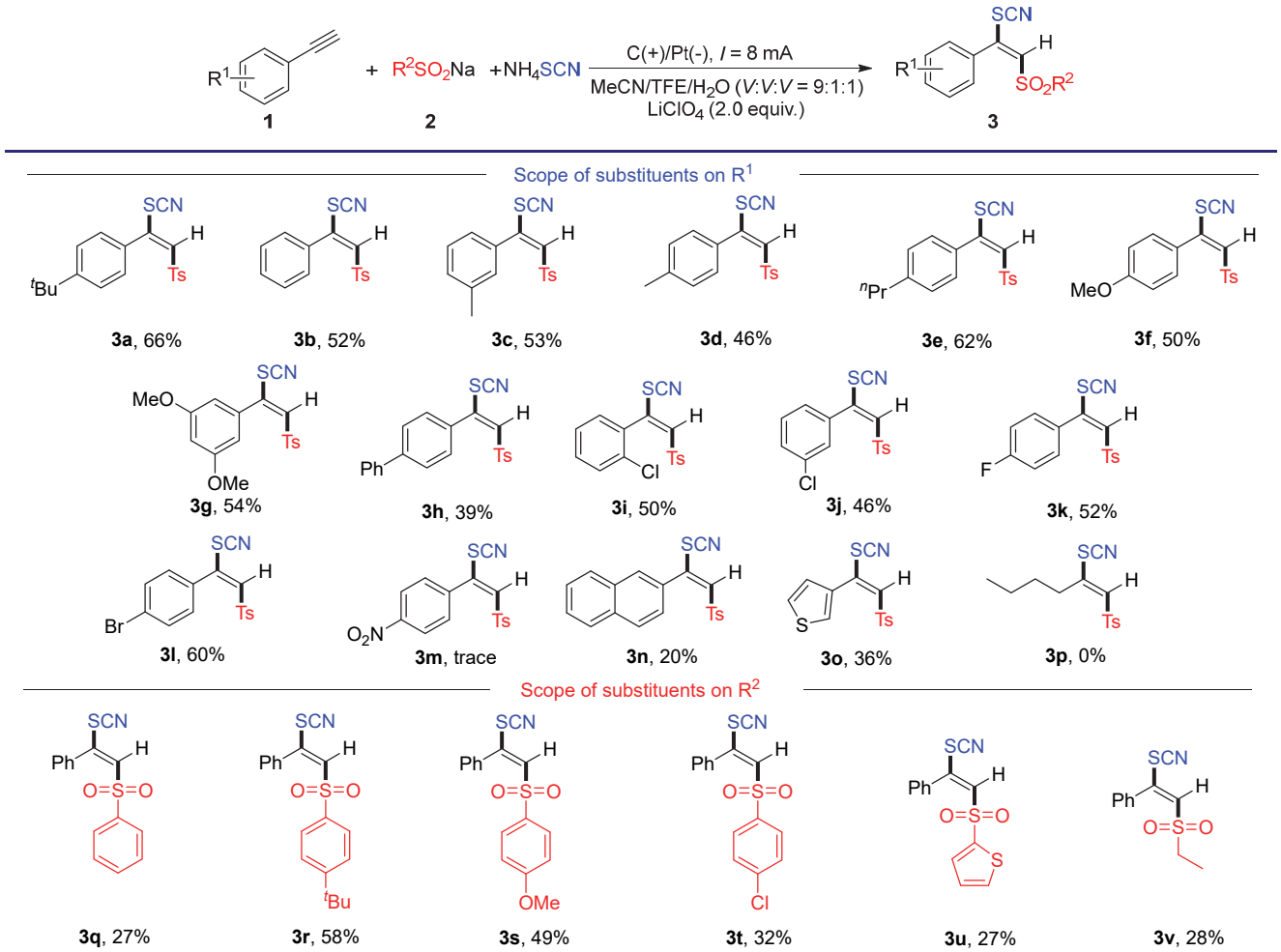
Scheme 1 Difunctionalization of alkynes installs thiocyanated and/or sulfonated compounds

(Entry 7). Lowering the constant current to 5 mA had a negative impact on the yield (Entry 8). Other auxiliary electrolytes such as LiCl (2.0 equiv.) or $^{n}Bu_4NClO_4$ (2.0 equiv.) did not give better results (Entry 9). Interestingly, the yield of **3a** could be further improved to 66% by increasing the amount of MeCN (Entry 10). However, more H_2O provided better solubility of reactants did not benefit the reaction (Entry 11). Using nickel plate as the cathode gave a relatively lower yield (Entry 12). In addition, the control experiment confirmed that electricity was crucial to the reaction (Entry 13).

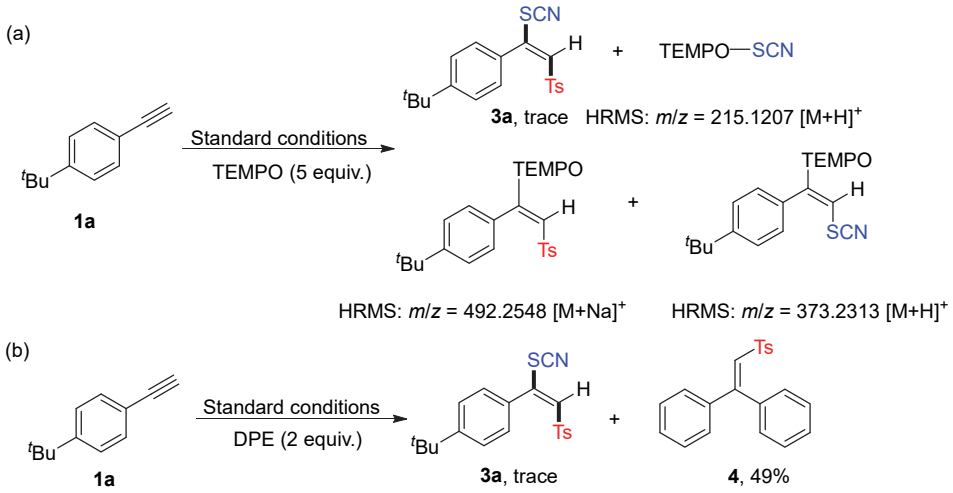
Under the optimal conditions, the generality and limitations of the transformation were then evaluated. In general, different substitutes on the phenyl ring of alkynes including electron-donating groups and electron-withdrawing groups were tolerated and yielded the corresponding thiocyanatosulfonylation products in moderate to good yields (Table 2). The *meta*-methyl and *para*-methyl groups on the phenyl ring did not influence the reaction efficiency (**3c** and **3d**). Other electron-donating groups including 4-^{n}Pr, 4-OMe, 3,5-OMe_2 and 4-Ph were all compatible with the current conditions, affording the desired products in moderate yields (**3e**～**3h**). Weak electron-withdrawing groups including *ortho*-Cl, *meta*-Cl, *para*-F and *para*-Br were also smoothly converted to the expected products **3i**～**3l** in 46%～60% yields. Unfortunately, the strong electron-withdrawing group NO_2 was inert in this transformation, which is consistent with the previous study,[13] reflecting that the electronic effect influences the reaction. 2-Ethynylnaphthalene and 3-ethynylthiophene were amenable substrates, whereas aliphatic alkyne 1-hexyne failed to afford the target product. Subsequently, the substrate scope of sodium sulfonates with phenylacetylene as a partner was tested. The electron-donating groups on the phenyl ring of aryl sulfinates (^{t}Bu, OMe) were more reactive than the electron-donating group (Cl), providing the desired products in moderate yields. Thiophene-2-sulfinate and alkyl sulfonate were also tolerated and delivered the target products in lower yields (**3u** and **3v**).

To gain some understanding of the possible mechanism, several control experiments were performed (Scheme 2). Firstly, radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to the reaction mixture under standard conditions, the formation of **3a** was inhibited and

Table 2 Substrate scope



[a] Conditions: **1** (0.2 mmol), **2a** (6.0 equiv.), NH_4SCN (4.0 equiv.), $LiClO_4$ (2.0 equiv.), MeCN/TFE/H_2O (V∶V∶V=9∶1∶1), carbon felt anode, Pt plate cathode, I=8 mA, undivided cell, room temperature, 8 h. [b] Isolated yields.



Scheme 2 Mechanistic investigations

three types of radicals including SCN radical were trapped by TEMPO (Scheme 2, a). These TEMPO adducts were confirmed by HRMS. In addition, when radical scavenger 1,1-diphenylethylene (DPE) was applied, the reaction was suppressed with only trace of **3a** observed, and the DPE adduct product **4** was isolated in 49% yield, which was confirmed by the ^{1}H NMR spectrum (Scheme 2, b). These results implied that the reaction involved a radical pathway. Then, cyclic voltammetry (CV) studies were performed. The oxidation potentials of TsNa (**2a**) (red curve) and NH_4SCN (blue curve) were observed at 0.96 and 1.56 V, respectively, which are in accordance with those measured in previous studies,[15] suggesting that **2a** was easier to be oxidized at the anode (Figure 1). The oxidation peak was observed at about 2.01 V for **1a** (gray curve). Interestingly, the mixture of **2a** and NH_4SCN displayed two apparent oxidation peaks at 0.85 and 1.48 V (green curve), implying that they were chemically interacting with each other. The addition of **1a** or TFE to the reaction mixture has no obvious influence on the oxidation potentials of **2a** and NH_4SCN (orange and purple curves).

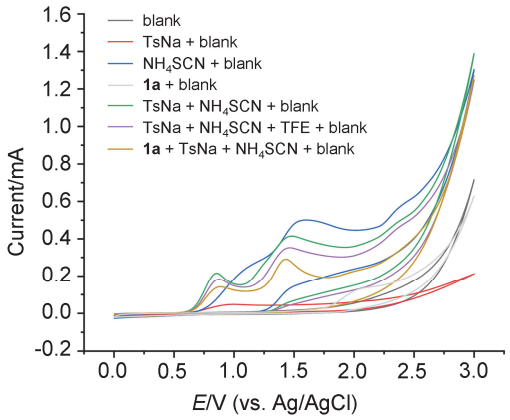
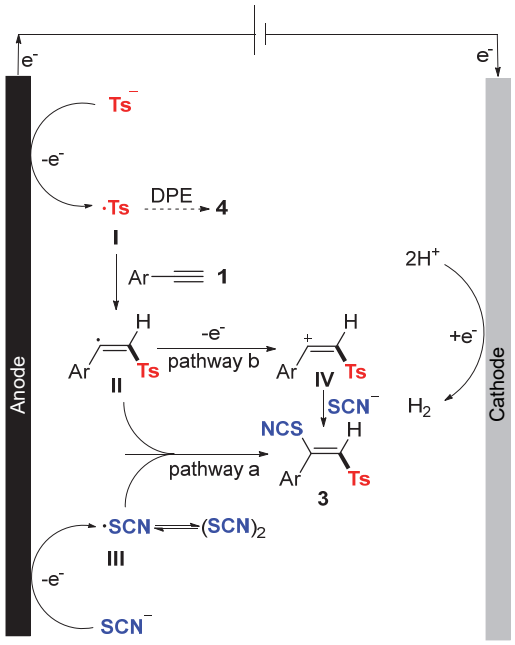


Figure 1 CV studies

On the basis of the above investigations and previous works of literature,[9,10,13,16] a plausible mechanism was proposed as outlined in Scheme 3. Firstly, *p*-toluenesulfinate anion was oxidized preferentially to afford the sulfone radical **I** at the anode, which was confirmed by the isolation of DPE adduct **4**. Vinyl sulfone radical **II** was then generated upon radical addition of **I** to alkyne **1**. In the meantime, SCN radical **III** was formed at the anode. Finally, radical-radical coupling between radicals **II** and **III** delivered the final product **3** (pathway a). Besides, vinyl radical **II** was further oxidized to vinyl cation **IV**, followed by the nucleophilic addition with SCN^-, affording product **3** can not be ruled out (pathway b).



Scheme 3 Plausible mechanism

CVs obtained in MeCN/H_2O (10 mL, V : V = 9 : 1) containing 0.1 mol/L $LiClO_4$ with TsNa (0.01 mol/L), NH_4SCN (0.01 mol/L), **1a** (0.02 mol/L), TFE (1 mL) as indicated, the scan rate was 0.1 V/s, ranging from 0 V to 3.0 V. The working electrode was a glassy carbon electrode, and the counter electrode was a platinum wire. The refer-

ence was an Ag/AgCl electrode submerged in KCl (3 mol/L) solution.

3 Conclusions

In summary, an electrochemical oxidative three-component thiocyanatosulfonylation of aryl acetylenes with sodium sulfinates and NH_4SCN to access various thiocyanated vinylsulfones has been developed in an undivided cell at room temperature. This protocol has the advantages of exogenous oxidant-free, mild reaction conditions, and high stereoselectivity and realizes the formation of two C—S bonds simultaneously.

4 Experimental section

4.1 Instruments and reagents

The instrument for electrolysis is a domestic dual display DC stabilized power supply (UTP1303/UTP3305). Cyclic voltammograms were obtained on a CHI600E potentiostat. The anode electrode is graphite plates (1.0 cm×1.0 cm×0.3 cm) and the cathode electrode is platinum plates (1.0 cm×1.0 cm×0.2 mm). Reactions were monitored using thin layer chromatography (TLC) carried out on Merck silica gel plates (60F-254) using UV light as the visualizing agent. HRMS data were recorded on ThermoFisher LTQ Orbitrap XL or Agilent 6500QTOFMS-ESI. All ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on Bruker DRX600 instruments. All reagents were used as received from commercial suppliers unless otherwise indicated.

4.2 General procedure for the synthesis of **3**

In an oven-dried undivided three-necked bottle (10.0 mL) equipped with a stir bar, alkyne **1a** (0.2 mmol), sodium sulfite **2a** (1.2 mmol), ammonium thiocyanate (0.8 mmol), $LiClO_4$ (0.4 mmol), H_2O (1 mL), TFE (1 mL) and MeCN (9 mL) were added. The bottle was equipped with a graphite plate electrode (1.0 cm×1.0 cm×0.2 cm) as the anode and a platinum plate electrode (1.0 cm×1.0 cm×0.2 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA for 16 h under an air atmosphere. After completion of the reaction, the solvent was removed with a rotary evaporator. The pure product was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate, V∶V 10∶1～8∶2).

(*E*)-1-(*tert*-Butyl)-4-(1-thiocyanato-2-tosylvinyl)benzene (**3a**): Pale yellow oil, 66% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.45 (d, J=8.1 Hz, 2H), 7.37 (d, J=8.3 Hz, 2H), 7.21 (d, J=8.3 Hz, 2H), 7.17 (d, J=7.9 Hz, 2H), 7.02 (s, 1H), 2.39 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 155.1, 144.8, 144.2, 137.3, 129.7, 129.5, 129.2, 128.0, 127.3, 125.7, 107.3, 35.1, 31.3, 21.7; HRMS (ESI) calcd for $C_{20}H_{21}NNaO_2S_2$ [M＋Na]$^+$ 394.0906, found 394.0888.

(*E*)-1-Methyl-4-((2-phenyl-2-thiocyanatovinyl)sulfonyl)-benzene (**3b**):[13] Colorless oil, 52% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.51～7.47 (m, 3H), 7.43～7.39 (m, 2H), 7.31～7.29 (m, 2H), 7.23 (d, J=8.0 Hz, 1H), 7.01 (s, 1H), 2.41 (s, 3H).

(*E*)-1-Methyl-3-(1-thiocyanato-2-tosylvinyl)benzene (**3c**):[13] Pale yellow oil, 53% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.48 (d, J=8.3 Hz, 2H), 7.30～7.27 (m, 2H), 7.22 (d, J=8.0 Hz, 2H), 7.12～7.09 (m, 1H), 7.02～7.00 (m, 2H), 2.41 (s, 3H), 2.34 (s, 3H).

(*E*)-1-Methyl-4-((2-thiocyanato-2-(*p*-tolyl)vinyl)sulfonyl)benzene (**3d**):[13] Colorless oil, 46% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.52 (t, J=8.2 Hz, 2H), 7.25～7.21 (m, 6H), 6.96 (s, 1H), 2.42 (s, 3H), 2.41 (s, 3H).

(*E*)-1-Methyl-4-((2-(4-propylphenyl)-2-thiocyanato-vinyl)sulfonyl)benzene (**3e**): Colorless oil, 62% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.49 (d, J=8.1 Hz, 2H), 7.23～7.17 (m, 6H), 6.99 (s, 1H), 2.66～2.60 (m, 2H), 2.41 (s, 3H), 1.75～1.62 (m, 2H), 0.97 (t, J=7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 146.8, 145.0, 144.3, 137.4, 129.8, 129.3, 129.2, 128.8, 128.0, 127.6, 107.3, 38.0, 24.4, 21.8, 13.9; HRMS (ESI) calcd for $C_{19}H_{19}NNaO_2S_2$ [M＋Na]$^+$ 380.0749, found 380.0728.

(*E*)-1-Methoxy-4-(1-thiocyanato-2-tosylvinyl)benzene (**3f**):[13] Pale yellow oil, 50% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.53 (d, J=8.3 Hz, 2H), 7.31～7.28 (m, 2H), 7.24 (d, J=8.0 Hz, 2H), 6.94 (s, 1H), 6.92～6.89 (m, 2H), 3.85 (s, 3H), 2.41 (s, 3H).

(*E*)-1,3-Dimethoxy-5-(1-thiocyanato-2-tosylvinyl)-benzene (**3g**):[13] Colorless oil, 54% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.52 (d, J=8.1 Hz, 2H), 7.22 (d, J=8.1 Hz, 2H), 7.00 (s, 1H), 6.51 (s, 1H), 6.38～6.33 (m, 2H), 3.77 (s, 6H), 2.41 (s, 3H).

(*E*)-4-(1-Thiocyanato-2-tosylvinyl)-1,1'-biphenyl (**3h**): Yellow oil, 39% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.64～7.58 (m, 4H), 7.54 (d, J=8.3 Hz, 2H), 7.49 (t, J=7.6 Hz, 2H), 7.42 (d, J=7.4 Hz, 1H), 7.41～7.38 (m, 2H), 7.23 (d, J=8.0 Hz, 2H), 7.04 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 145.6, 144.8, 144.1, 140.1, 137.7, 130.3, 130.2, 130.0, 129.5, 128.7, 128.4, 127.7, 127.6, 107.4, 21.5; HRMS (ESI) calcd for $C_{22}H_{17}NNaO_2S_2$ [M＋Na]$^+$ 414.0593, found 414.0571.

(*E*)-1-Chloro-2-(1-thiocyanato-2-tosylvinyl)benzene (**3i**):[13] Colorless oil, 50% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.55 (d, J=8.3 Hz, 2H), 7.46～7.43 (m, 1H), 7.42～7.36 (m, 2H), 7.33 (dd, J=7.6, 1.5 Hz, 1H), 7.27 (d, J=8.2 Hz, 2H), 7.02 (s, 1H), 2.43 (s, 3H).

(*E*)-1-Chloro-3-(1-thiocyanato-2-tosylvinyl)benzene (**3j**): Colorless oil, 46% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.50 (d, J=8.3 Hz, 2H), 7.45 (ddd, J=8.1, 2.0, 1.0 Hz, 1H), 7.37 (t, J=7.9 Hz, 1H), 7.28～7.23 (m, 3H), 7.12 (t, J=1.8 Hz, 1H), 7.04 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 145.5, 142.0, 137.1, 134.9, 132.0, 131.5, 131.0, 130.2, 130.1, 128.9, 128.1, 127.8, 106.6, 21.8; HRMS (ESI) calcd for $C_{16}H_{12}ClNNaO_2S_2$ [M＋Na]$^+$ 371.9890, found 371.9867.

(*E*)-1-Fluoro-4-(1-thiocyanato-2-tosylvinyl)benzene (**3k**):[13] Colorless oil, 52% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.52 (d, J=8.3 Hz, 2H), 7.35～7.31 (m, 2H), 7.26 (d, J=8.1 Hz, 2H), 7.14～7.08 (m, 2H), 7.00 (s,

1H), 2.42 (s, 3H).

(*E*)-1-Bromo-4-(1-thiocyanato-2-tosylvinyl)benzene (**3l**):[13] Yellow oil, 60% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.60～7.51 (m, 4H), 7.27 (d, J=8.1 Hz, 2H), 7.19 (d, J=8.4 Hz, 2H), 7.00 (s, 1H), 2.44 (s, 3H).

(*E*)-2-(1-Thiocyanato-2-tosylvinyl)naphthalene (**3n**): Colorless oil, 20% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.89～7.80 (m, 3H), 7.75 (s, 1H), 7.59 (dt, J=14.2, 6.9 Hz, 2H), 7.45 (d, J=8.2 Hz, 2H), 7.35 (dd, J=8.4, 1.4 Hz, 1H), 7.13～7.09 (m, 3H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 145.1, 144.0, 137.3, 134.3, 132.4, 130.1, 129.9, 129.8, 128.8, 128.7, 128.3, 128.06, 128.05, 127.7, 127.3, 125.5, 107.1, 21.7; HRMS (ESI) calcd for $C_{20}H_{15}NNaO_2S_2$ $[M+Na]^+$ 388.0486, found 388.0413.

(*E*)-3-(1-Thiocyanato-2-tosylvinyl)thiophene (**3o**):[13] Colorless oil, 36% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.64 (dd, J=3.0, 1.3 Hz, 1H), 7.53 (d, J=8.3 Hz, 2H), 7.36 (dd, J=5.0, 3.0 Hz, 1H), 7.24 (d, J=8.1 Hz, 2H), 7.11 (dd, J=5.1, 1.2 Hz, 1H), 7.00 (s, 1H), 2.41 (s, 3H).

(*E*)-((2-Phenyl-2-thiocyanatovinyl)sulfonyl)benzene (**3q**):[13] Colorless oil, 27% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.62～7.56 (m, 3H), 7.51～7.47 (m, 1H), 7.45～7.38 (m, 4H), 7.31～7.27 (m, 2H), 7.04 (s, 1H).

(*E*)-1-(*tert*-Butyl)-4-((2-phenyl-2-thiocyanatovinyl)sulfonyl)benzene (**3r**):[13] Colorless oil, 58% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.55～7.52 (m, 2H), 7.47 (t, J=7.5 Hz, 1H), 7.45～7.41 (m, 2H), 7.41～7.36 (m, 2H), 7.30～7.28 (m, 2H), 7.03 (s, 1H), 1.32 (s, 9H).

(*E*)-1-Methoxy-4-((2-phenyl-2-thiocyanatovinyl)sulfonyl)benzene (**3s**): Colorless oil, 49% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.53～7.50 (m, 2H), 7.50～7.46 (m, 1H), 7.42～7.38 (m, 2H), 7.31～7.28 (m, 2H), 7.02 (s, 1H), 6.89～6.85 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 164.0, 143.4, 131.7, 131.4, 130.5, 130.2, 130.1, 129.3, 128.8, 114.5, 107.1, 55.9; HRMS (ESI) calcd for $C_{16}H_{13}NNaO_3S_2$ $[M+Na]^+$ 354.0229, found 354.0201.

(*E*)-1-Chloro-4-((2-phenyl-2-thiocyanatovinyl)sulfonyl)-benzene (**3t**):[13] Colorless oil, 32% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.53～7.49 (m, 1H), 7.43～7.37 (m, 1H), 7.28 (d, J=7.4 Hz, 1H), 7.03 (s, 1H).

(*E*)-2-((2-Phenyl-2-thiocyanatovinyl)sulfonyl)thiophene (**3u**): Yellow oil, 27% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.67 (dd, J=4.9, 1.3 Hz, 1H), 7.51 (t, J=7.5 Hz, 1H), 7.46～7.42 (m, 2H), 7.39～7.33 (m, 3H), 7.09 (s, 1H), 7.03 (dd, J=4.9, 3.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 144.7, 141.4, 135.0, 134.7, 131.6, 130.2, 129.3, 129.3, 128.9, 128.0, 107.0; HRMS (ESI) calcd for $C_{13}H_9NNaO_2S_3$ $[M+Na]^+$ 329.9688, found 329.9658.

(*E*)-(2-(Ethylsulfonyl)-1-thiocyanatovinyl)benzene (**3v**):[13] Colorless oil, 28% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.55～7.51 (m, 1H), 7.50～7.45 (m, 4H), 6.88 (s, 1H), 2.90 (q, J=7.4 Hz, 2H), 1.32 (t, J=7.5 Hz, 3H).

(2-Tosylethene-1,1-diyl)dibenzene (**4**):[13] Colorless oil, 49% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.48 (d, J=8.3 Hz, 2H), 7.37 (q, J=7.5 Hz, 2H), 7.30 (td, J=7.7, 2.3 Hz, 4H), 7.22～7.19 (m, 2H), 7.15 (d, J=8.2 Hz, 2H), 7.12～7.09 (m, 2H), 7.00 (s, 1H), 2.38 (s, 3H).

Supporting Information ^{1}H NMR and ^{13}C NMR spectra of compounds **3a**～**3l**, **3n**, **3o**, **3q**～**3v**, **4**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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