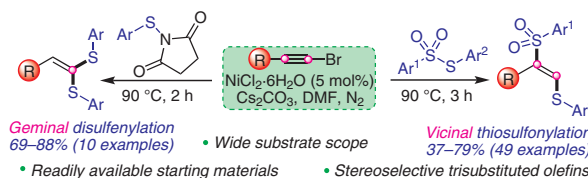


# Nickel-Catalyzed Difunctionalization of Alkynyl Bromides with Thiosulfonates and *N*-Arylthio Succinimides: A Convenient Synthesis of 1,2-Thiosulfonylethenes and 1,1-Dithioethenes

Arram Haritha Kumari<sup>a</sup>  
 Jangam Jagadesh Kumar<sup>a</sup>  
 Gamidi Rama Krishna<sup>b</sup>  
 Raju Jannapu Reddy<sup>a\*</sup>



<sup>a</sup> Department of Chemistry, University College of Science, Osmania University, Hyderabad 500 007, India  
 rajuchem77@osmania.ac.in  
 rajuchem08@yahoo.co.in  
 https://www.rjreddyresearchgroup.com/

<sup>b</sup> X-ray Crystallography, CSIR-National Chemical Laboratory, Pune 411 008, India

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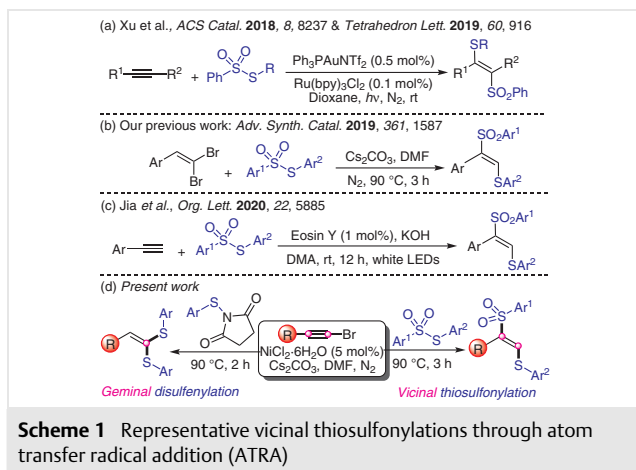
**Abstract** An efficient nickel-catalyzed vicinal thiosulfonylation of 1-bromoalkynes with thiosulfonates in the presence of cesium carbonate is described. An operationally simple and highly regioselective atom transfer radical addition (ATRA) of alkynyl bromides provides a wide range of (*E*)-1,2-thiosulfonylethenes ( $\alpha$ -aryl- $\beta$ -thioarylvinyl sulfones) in moderate to high yields. The extensive substrate scope of both alkynyl bromides and thiosulfonates is explored with a broad range of functional groups. Indole-derived 1,1-bromoalkenes were also successfully explored in this 1,2-thiosulfonylation process. Moreover, the nickel-catalyzed *geminal*-dithiolation of alkynyl bromides with *N*-arylthio succinimides provides 1,1-dithioalkenes in high yields. The present protocol is reliable on gram scale, and a sequential one-pot bromination and thiosulfonylation of phenylacetylene is achieved in a scale-up synthesis. Following control experiments, a plausible mechanism is proposed to rationalize the experimental outcome and the vicinal thiosulfonylation.

**Key words** alkynyl bromides, atom transfer radical addition (ATRA), thiosulfonylation, thiosulfonates, vinyl thiosulfones

Stereoselective vicinal difunctionalization of carbon-carbon multiple bonds represents an attractive strategy for the rapid construction of molecular complexity from simple starting materials.<sup>1</sup> Of the many catalytic difunctionalizations, Ni-catalyzed difunctionalization has emerged to introduce two functional groups across an unsaturated carbon-carbon bond in a one-step operation.<sup>2</sup> Atom transfer radical addition (ATRA)<sup>3</sup> has been recognized as a powerful approach for installing two functional groups on the vicinal carbons of a  $\pi$ -system, a process generally known as Kharasch addition.<sup>4</sup> Despite these achievements, installing diverse functional groups on alkynes in a rapid, flexible and efficient manner in order to generate highly substituted alkenes remains a challenging task.

Organosulfur compounds<sup>5</sup> containing sulfone and thioether moieties are attractive compounds in organic synthesis<sup>6</sup> and the pharmaceutical industry.<sup>7</sup> Recently, thiosulfonates ( $RS-SO_2R^1$ )<sup>8–10</sup> have been utilized to install two distinct C–S bonds (sulfenyl and sulfonyl) in alkenes and alkynes through atom transfer thiosulfonylation.<sup>9,10</sup> Compared to the thiosulfonylation of alkenes,<sup>9</sup> investigations of alkynes and their equivalents are considerably limited, probably due to stereo- and regioselective concerns.<sup>10</sup> In this context, Xu and co-workers developed the first example of the atom transfer thiosulfonylation of alkynes using  $PhSO_2SR$  and a combination of an Au/Ru-catalytic system under visible-light irradiation (Scheme 1, a).<sup>10a</sup> Subsequently, our group employed the  $Cs_2CO_3$ -mediated vicinal thiosulfonylation of 1,1-dibromo-1-alkenes with thiosulfonates, leading to a reversal of regioselectivity in the thiosulfonylated products (Scheme 1, b).<sup>10c</sup> Very recently, the Jia group successfully disclosed the visible-light-driven atom transfer radical addition of aryl alkynes with thiosulfonates under the catalytic influence of Eosin Y to furnish the desired vinyl thiosulfones with the same regioselectivity (Scheme 1, c).<sup>10d</sup> Regardless of these innovative approaches, the use of expensive reagents and prolonged reaction times were disadvantages in their scale-up synthesis. Therefore, a general, mild and robust vicinal thiosulfonylation using a cheap and readily available catalyst is still desirable. Accordingly, we envisioned that alkynyl bromides would be alternative starting materials for the regioselective construction of two different C–S bonds on the vicinal carbons in a single operation (Scheme 1, d).

Generally, alkynyl bromides are versatile building blocks, and their chemistry has been widely explored in organic synthesis.<sup>11</sup> As a result, we were interested in investigating the atom transfer thiosulfonylation of alkynyl bromides with thiosulfonates in order to furnish vinyl thiosulfone products whilst delivering the anticipated



regioselectivity. In continuation of our interest in organosulfur chemistry<sup>12</sup> and thiosulfonates,<sup>10c,12c,12e-i</sup> we report herein an efficient Ni-catalyzed intermolecular vicinal thiosulfonylation of alkynyl bromides with thiosulfonates under mild conditions. A variety of substrates was explored allowing the synthesis of a wide range of (*E*)-1,2-thiosulfonylethenes. In addition, the methodology was further applied to the synthesis of 1,1-dithioalkenes in high yields. From a synthetic point of view, the present protocol has also been achieved on gram scale.

Our investigations began with 4-(bromoethynyl)-1,2-dimethoxybenzene (**1a**) and *S*-phenyl benzenesulfonylthioate (**2a**) as model substrates (Table 1). An extensive survey of the reaction conditions was undertaken by investigating different parameters, including the catalyst, solvent, temperature, concentration, etc. (see Table S1 in the Supporting Information). An initial experiment was performed at 90 °C for the thiosulfonylation of **1a** with **2a** in the presence of Cs<sub>2</sub>CO<sub>3</sub>, which gave the desired product **3aa** in 39% yield (entry 1). Next, the copper-catalyzed thiosulfonylation afforded a slightly improved yield of product **3aa** (entries 2 and 3). To our surprise, the NiCl<sub>2</sub>·6H<sub>2</sub>O-catalyzed vicinal thiosulfonylation proceeded smoothly with 3 equivalents of Cs<sub>2</sub>CO<sub>3</sub> in DMF at 90 °C (entries 4–6). The use of 5 mol% of NiCl<sub>2</sub>·6H<sub>2</sub>O afforded the thiosulfonylated product **3aa** in 81% yield with excellent stereoselectivity (entry 6). Inspired by these results, we screened different Ni catalysts, however, none of these proved beneficial in improving the yield of **3aa** (entries 7–10). Lowering the amount of Cs<sub>2</sub>CO<sub>3</sub>, elevating the temperature or performing the reaction under aerobic conditions were unsuccessful in giving better outcomes (entries 11–13). Next, our attention turned to developing a visible-light-induced thiosulfonylation under the influence of an organic dye as the photocatalyst. Gratifyingly, the standard reaction performed with Rose Bengal (RB) (2 mol%) under irradiation with blue LEDs for 16 hours led to the desired product **3aa**, albeit in only 61% yield (entry 14). Disappointingly, our subsequent efforts using Rose Bengal,

Eosin Y and Eosin B gave **3aa** in lower yields compared with the conventional procedure (see Table S2 in the Supporting Information). No reaction was observed in the absence of Cs<sub>2</sub>CO<sub>3</sub>, thus indicating that the role of Cs<sub>2</sub>CO<sub>3</sub> was crucial for this transformation (entry 15).

**Table 1** Optimization of the Vicinal Thiosulfonylation Using 1-Bromoalkyne **1a** with *S*-Phenyl Thiosulfonate **2a**<sup>a</sup>

Entry	Catalyst (mol%)	Cs <sub>2</sub> CO <sub>3</sub>	Time	Yield of <b>3aa</b> <sup>b</sup>	<i>E/Z</i> <sup>c</sup>
1	none	4 equiv	6 h	39%	19:1
2	CuClO <sub>4</sub> ·6H <sub>2</sub> O (20 mol%)	3 equiv	6 h	59%	25:1
3	CuSO <sub>4</sub> ·5H <sub>2</sub> O (20 mol%)	3 equiv	6 h	53%	25:1
4	NiCl <sub>2</sub> ·6H <sub>2</sub> O (20 mol%)	3 equiv	4 h	72%	25:1
5	NiCl <sub>2</sub> ·6H <sub>2</sub> O (10 mol%)	3 equiv	4 h	75%	30:1
6	<b>NiCl<sub>2</sub>·6H<sub>2</sub>O (5 mol%)</b>	<b>3 equiv</b>	<b>3 h</b>	<b>81%</b>	<b>30:1</b>
7	NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (5 mol%)	3 equiv	3 h	71%	30:1
8	Ni(dppp)Cl <sub>2</sub> (5 mol%)	3 equiv	3 h	58%	25:1
9	NiBr <sub>2</sub> ·6H <sub>2</sub> O (5 mol%)	3 equiv	3 h	69%	25:1
10	NiClO <sub>4</sub> ·6H <sub>2</sub> O (5 mol%)	3 equiv	3 h	72%	30:1
11	NiCl <sub>2</sub> ·6H <sub>2</sub> O (5 mol%)	2 equiv	5 h	59%	25:1
12 <sup>d</sup>	NiCl <sub>2</sub> ·6H <sub>2</sub> O (5 mol%)	3 equiv	5 h	67%	25:1
13 <sup>e</sup>	NiCl <sub>2</sub> ·6H <sub>2</sub> O (5 mol%)	3 equiv	5 h	55%	20:1
14 <sup>f</sup>	NiCl <sub>2</sub> ·6H <sub>2</sub> O (5 mol%)	3 equiv	16 h	61%	Nd
15	NiCl <sub>2</sub> ·6H <sub>2</sub> O (5 mol%)	none	24 h	trace	–

<sup>a</sup> Unless otherwise specified, all reactions were performed on a 0.2 mmol scale of **1a** (1.0 equiv), **2a** (1.5 equiv), catalyst (5–20 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (2 to 4 equiv) in anhydrous DMF (1 mL) under N<sub>2</sub> at 90 °C.

<sup>b</sup> Isolated yield.

<sup>c</sup> *E/Z* mixture based on <sup>1</sup>H NMR analysis; nd = not determined.

<sup>d</sup> Reaction at 110 °C.

<sup>e</sup> Reaction under an O<sub>2</sub> atmosphere.

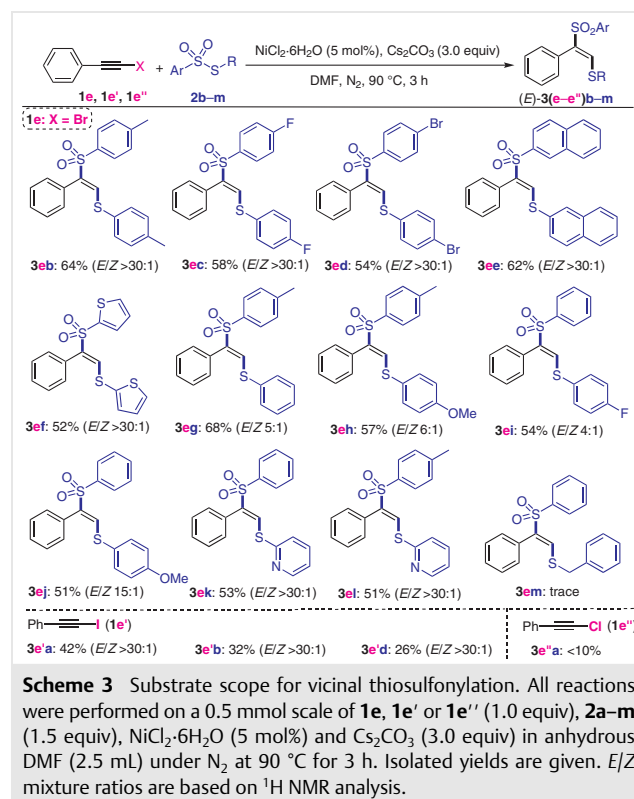
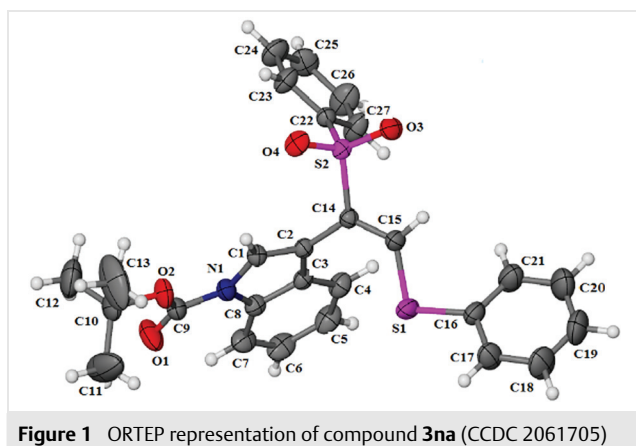
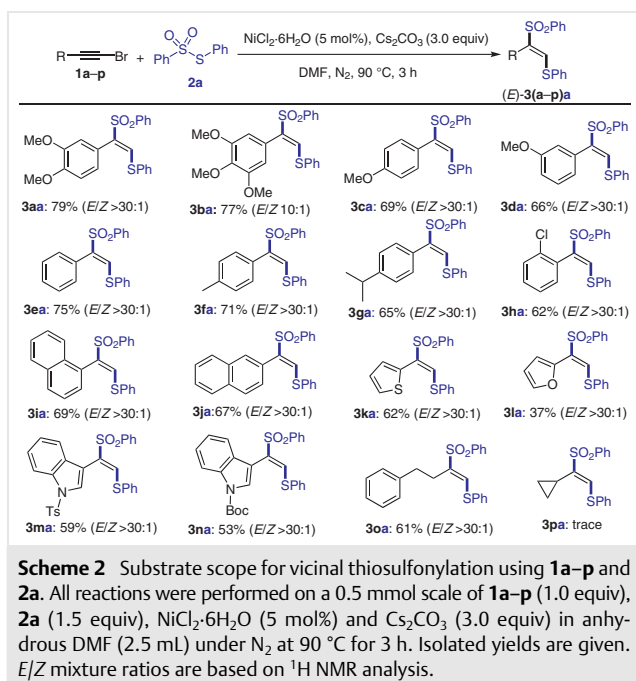
<sup>f</sup> Irradiation with blue LEDs in the presence of Rose Bengal (2 mol%) at room temperature.

With optimized reaction conditions in hand (see Table 1, entry 6), we next explored the generality of the vicinal thiosulfonylation (Scheme 2). A series of 1-bromoalkynes (**1a–p**) employed for 1,2-thiosulfonylation with *S*-phenyl benzenesulfonylthioate (**2a**) to deliver the corresponding (*E*)-1,2-thiosulfonylethenes **3(a–o)a** in 37–79% yields with excellent stereoselectivities. Notably, the nature and position of the substituent(s) on the benzene ring had little influence on the outcome of the transformation (compare **3ba**, **3da** and **3ha**). The reason behind the observed low selectivity (*E/Z* = 10:1) of product **3ba** was not clear; however, it can be assumed that the strong electron-donating groups (OMe) on the benzene ring might lead to a mixture of isomers. Both 1- and 2-naphthyl-derived 1-bromoalkynes **1i** and **1j** smoothly afforded the desired products **3ia** and **3ja**

in 69% and 67% yields, respectively. Interestingly, various heteroaryl bearing alkynyl bromides **1k–n** were well tolerated, leading to the expected products **3ka–na** in good yields and stereoselectivities. The structure and stereochemistry of **3na** were further established by single-crystal X-ray analysis (see Figure 1 and the Supporting Information).<sup>13</sup> Moreover, the alkyl-substituted 1-bromoalkynes **1o** and **1p** were also reacted under the same conditions. Remarkably, the corresponding vinyl thiosulfone **3oa** was smoothly obtained in 61% yield, whereas the product **3pa** was only formed in a trace amount.

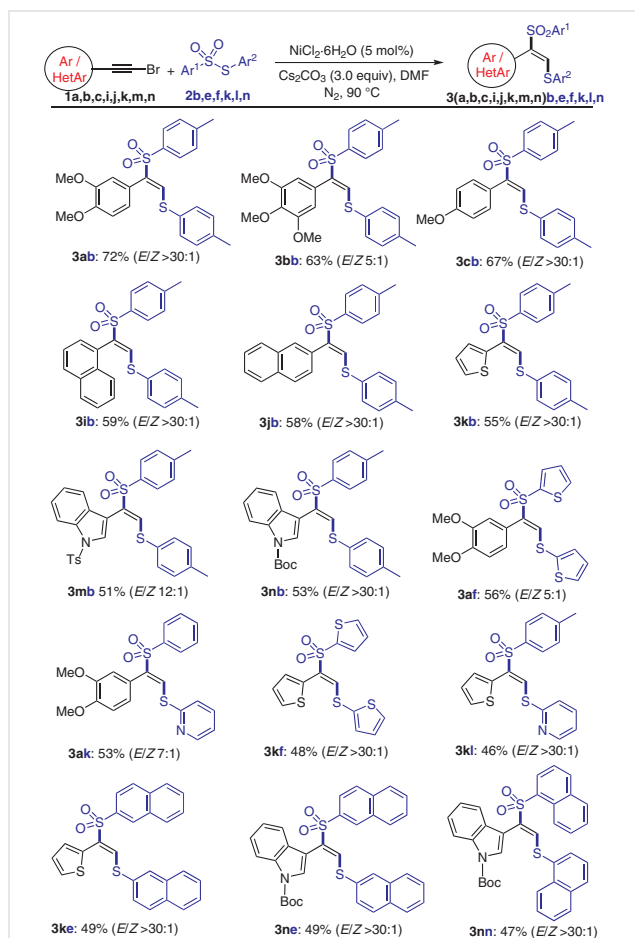
Encouraged by these results, we sought to evaluate the scope of various thiosulfonates (**2b–m**) with (bromoethynyl)benzene (**1e**) (Scheme 3). Different symmetrical and unsymmetrical thiosulfonates smoothly participated in

the vicinal thiosulfonylation to deliver the anticipated (*E*)-1,2-thiosulfonylethenes in satisfactory yields. Symmetrical aryl and heteroaryl thiosulfonates **2b–f** reacted with **1e** with no adverse effect on the outcome. Disappointingly, the unsymmetrical thiosulfonates **2g–j** significantly influenced the stereoselectivity, albeit thiosulfonylated products **3eg**, **3eh**, **3ei** and **3ej** were obtained in satisfactory yields. To our surprise, the 2-pyridyl-derived thiosulfonates **2k** and **2l** afforded the corresponding products **3ek** and **3el** in satisfactory yields, predominantly as the *E*-isomers. Unfortunately, *S*-benzyl thiosulfonate **2m** was found to be unsuitable as a substrate for this transformation. Next, (iodoethynyl)benzene (**1e'**) was reacted with different thiosulfonates (**2a, b, d**) to generate the corresponding products **3e'(a, b, d)** in modest yields. The less reactive (chloroethynyl)benzene (**1e''**) reacted sluggishly with **2a** to form the desired product.

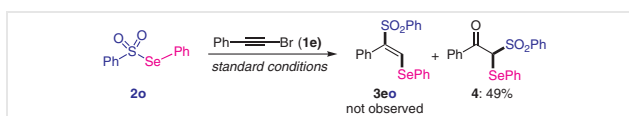


Moreover, the scope of the vicinal thiosulfonylation reaction could be extended to construct representative classes of thiosulfonylated products (Scheme 4). Several aryl- and heteroaryl-derived alkynyl bromide substrates were readily reacted with **2b** to form the corresponding products **3(a–c, i, j, k, m, n)b** in reasonably good yields. Similarly, the heteroaryl-derived thiosulfonates **2f** and **2k** furnished thiosulfonylated products **3af**, **3ak**, **3kf** and **3kl** in acceptable yields. Additionally, the naphthyl-containing thiosulfonates **2e** and **2n** gave the corresponding  $\alpha$ -heteroaryl-substituted

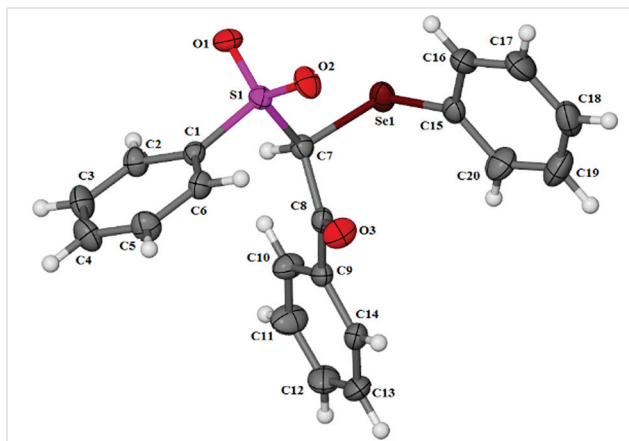
vinyl sulfones **3ke**, **3ne** and **3nn** in moderate yields. It is worth noting that these multifunctional vinyl (thio)sulfones are potentially valuable compounds in organic and medical chemistry.<sup>14</sup> Interestingly, the thiophene-based vinyl sulfones **3af** and **3kf** are promising structural scaffolds in advanced functional materials.<sup>15</sup>



Moreover, the protocol was also extended to Se-phenyl benzeneselenosulfonate (**2o**) under the optimized conditions. As presented in Scheme 5, the reaction of **1e** with **2o** did not afford the anticipated product **3eo**. Instead, the unexpected  $\beta$ -keto selenosulfone **4** was obtained in 49% yield. Further, the structure of **4** was ambiguously confirmed by single-crystal X-ray analysis (Figure 2 and the Supporting Information).<sup>13</sup>



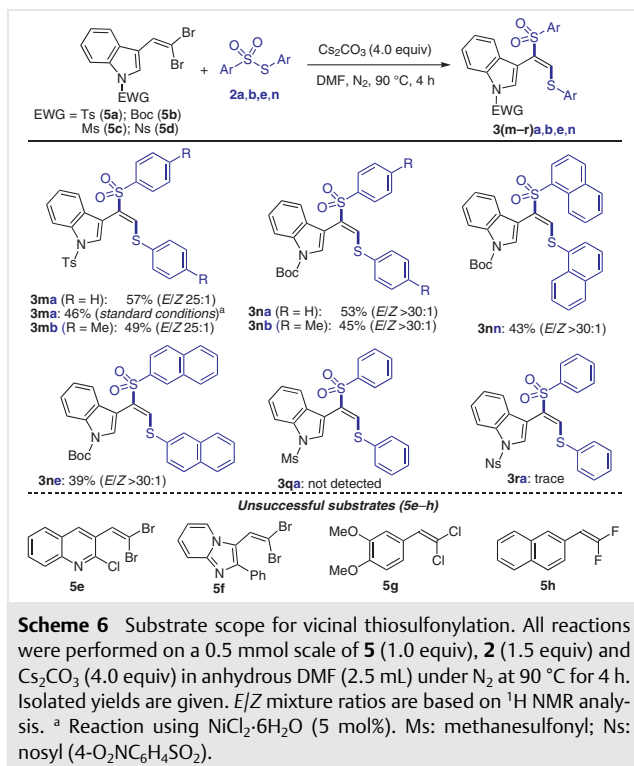
**Scheme 5** Synthesis of  $\beta$ -keto selenosulfone **4** using **1e** and **2o**



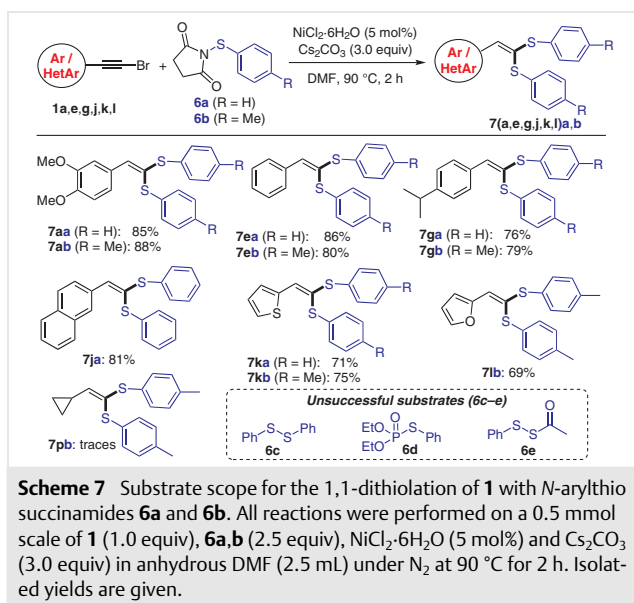
**Figure 2** ORTEP representation of compound **4** (CCDC 2061706)

Next, the robustness of vicinal thiosulfonylation was further examined by using dihaloalkene substrates **5a–h**, which were previously unexplored.<sup>10c</sup> Indeed, the Cs<sub>2</sub>CO<sub>3</sub>-mediated 1,2-thiosulfonylation afforded fruitful results compared to the present Ni-catalyzed standard conditions (Scheme 6). Thus, *N*-Ts/*N*-Boc-indole-derived dibromoalkenes **5a** and **5b** were studied and were found to smoothly react with different thiosulfonates (**2a,b,e,n**) in the presence of Cs<sub>2</sub>CO<sub>3</sub> (4 equiv) to deliver the expected thiosulfonates **3(m,n)a,b,e,n** in good yields. Disappointingly, *N*-Ms/*N*-Ns-indole-, 3-chloroquinoline- and imidazopyridine-derived dibromoolefins **5c–f** were either degraded or reacted sluggishly under the same conditions (see the Supporting Information). Similarly, dichloroalkene **5g** and difluoroalkene **5h** were also challenging substrates for this protocol.

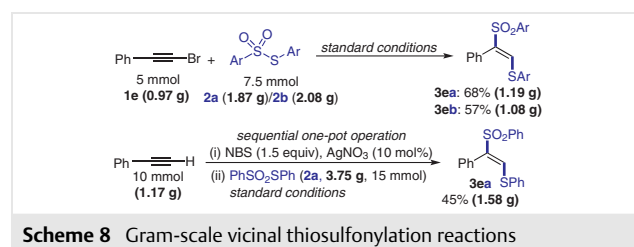
To understand the generality of the vicinal difunctionalization, we turned our attention to more valuable substrates **6a–e** in order to install diverse substituents on the products (Scheme 7). In this direction, we performed the vicinal amidosulfonylation of **1a** with *N*-phenylthio succinamide (**6a**) under the optimized conditions. Unfortunately, we did not obtain the expected amido-sulfonylated product; instead a 1,1-dithiolated-alkene was observed. Yang and co-workers<sup>16</sup> had previously developed the synthesis of 1,1-dithio-1-alkenes using 1,1-dibromoalkenes with thiols in the presence of DBU. It is worth mentioning that our protocol has the advantage of using bench-stable and odorless sulfenylating reagents **6a** and **6b** instead of thiols. Using 2.5 equivalents of **6a**, the yield of **7aa** (85%) significantly improved under similar conditions (Scheme 7). With fine-



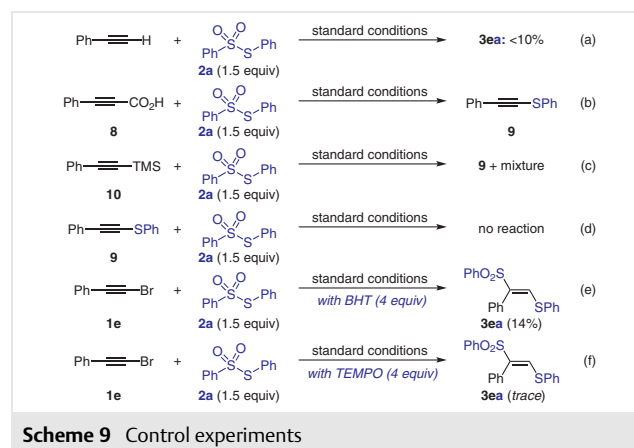
tuned reaction conditions in hand, we probed the scope of 1-bromoalkynes **1a,e,g,j,k,l** and *N*-arylthio succinimides **6a** and **6b** to provide the corresponding 1,1-dithioalkenes **7(a,e,g,k)a,b**, **7ja** and **7lb** in 69–88% yields. However, the cyclopropyl-derived 1,1-dithio-1-alkene **7pb** was detected in only a trace amount. This protocol was also applied to other sulfenylating agents (**6c–e**) under the same conditions but failed to give the desired products.



Reactions were next carried out on gram scale under the optimized conditions to highlight the efficacy of the 1,2-thiosulfonylation process. As shown in Scheme 8, reactions of (bromoethynyl)benzene (**1e**) with *S*-aryl arylsulfonothioates **2a,b** were performed on 5 mmol scale to produce **3ea** in 68% (1.19 g) and **3eb** in 57% (1.08 g) yields; thus the protocol proved to be scalable with only a minor deviation in the outcome. Developing a sequential one-pot operation offers attractive insights into a step-economic perspective, thereby avoiding the separation of intermediates.<sup>17</sup> Accordingly, a successive bromination with NBS followed by vicinal thiosulfonylation of phenylacetylene with **2a** was performed on 10 mmol scale to give **3ea** in 45% (1.58 g) yield.

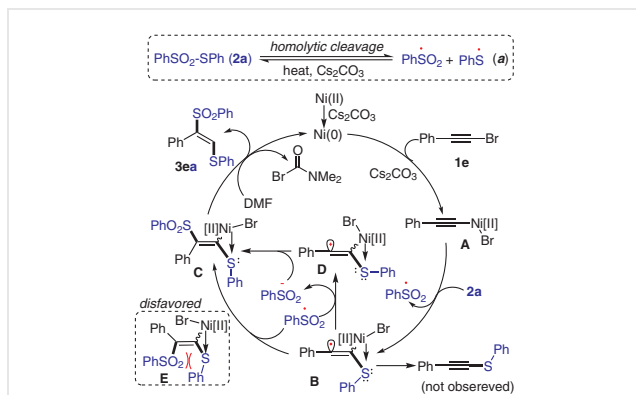


Control experiments were performed on the 1,2-thiosulfonylation under the standard conditions to gain insights into the reaction mechanism (Scheme 9). The reaction of **2a** with phenylacetylene gave the desired product **3ea** in <10% yield (Scheme 9, a). In contrast, the reaction of **2a** with 3-phenylpropionic acid (**8**) formed alkynyl thioether **9**,<sup>18</sup> whilst the use of TMS-derived phenylacetylene **10** afforded a mixture of products along with **9** (Schemes 9, b and c). Additionally, thioalkyne **9** failed to react with **2a** under the same conditions (Scheme 9, d). Moreover, the standard reaction was performed in the presence of radical scavengers. Using BHT (4 equiv), the desired product **3ea** was formed in only 14% yield (Scheme 9, e). Furthermore, the reaction was almost totally inhibited in the presence of TEMPO (4 equiv),



with only a trace amount of **3ea** being detected (Scheme 9, f). Overall, these results indicate that the thiosulfonylation process possibly involves a radical pathway.

Based on the above results and literature precedent,<sup>10,19–21</sup> a plausible mechanism has been proposed for this transformation (Scheme 10). The thermal homolytic cleavage of thiosulfonate **2a** can generate a thiyl radical<sup>19</sup> and a sulfonyl radical species (Scheme 10, a).<sup>20</sup> Firstly, Ni(II) is reduced to Ni(0), which can react with **1e** to form the alkynyl-Ni species **A**.<sup>2a</sup> The sulfonyl radical would react with **A** to form transient alkenyl radical **B**,<sup>10d</sup> which can then react with the sulfonyl radical to give intermediate **C**. Alternately, the radical **B** can undergo oxidation with the sulfonyl radical to generate alkenyl cation **D** and a sulfonyl anion. Reaction with the sulfonyl anion subsequently produces intermediate **C**. Finally, hydrogen may be abstracted from DMF<sup>21</sup> to produce the desired product **3ea** and the Ni catalyst is regenerated to continue the catalytic process. Additionally, the transition-state model **E** can explain the steric repulsion between the sulfone and the thioether, which may form the *Z*-isomer as a minor product. The mechanism for the formation of 1,1-dithioalkenes **7** is still not clear.<sup>16</sup> However, a tentative mechanism has been proposed in the Supporting Information based on experimental results.



**Scheme 10** A plausible mechanism for the vicinal thiosulfonylation

In summary, we have successfully demonstrated the Ni-catalyzed vicinal thiosulfonylation of alkynyl bromides with thiosulfonates in the presence of  $\text{Cs}_2\text{CO}_3$  under mild reaction conditions. The atom transfer radical addition (ATRA) protocol has been utilized to efficiently generate a series of (*E*)-1,2-thiosulfonylethenes in good to high yields and with high levels of stereoselectivity. Substantial variation of both the alkynyl bromides and thiosulfonates demonstrates the broad functional group tolerance and compatibility of the process. Indole-derived 1,1-bromoalkenes have also been employed as valuable substrates for the stereoselective synthesis of vinyl thiosulfones. In addition, the methodology has been further extended to the 1,1-dithiolation of alkynyl bromides with *N*-arylthio suc-

cinimides to furnish 1,1-dithio-1-alkenes in high yields. The protocol is also amenable to large-scale synthesis, which is quite challenging when using other thiosulfonylation methods. A step-economic, sequential one-pot bromination and thiosulfonylation approach has been achieved on gram scale, which offers an additional benefit to the described process. Finally, a plausible mechanism has been presented to rationalize the experimental outcome.

All reagents were purchased from Sigma-Aldrich, TCI, Alfa Aesar, SD-Fine, SRL, Spectrochem and AVRA chemicals, and were used without further purification unless otherwise stated. Solvents were dried over activated 4 Å molecular sieves for all reactions carried out under an inert atmosphere. The progress of reactions was monitored by thin-layer chromatography (TLC) using Silica gel 60 F254 plates. Visualization of samples was achieved by a combination of ultraviolet light (254 nm) and staining with potassium permanganate solution, iodine or *p*-anisaldehyde. Flash column chromatography was performed using SRL silica gel (100–200 mesh) as the stationary phase. Melting points were measured in open capillaries using a DBK digital melting point apparatus and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker AVIII 400 spectrometer ( $^1\text{H}$ : 400 MHz;  $^{13}\text{C}$ : 101 MHz) at 300 K. Chemical shifts ( $\delta$ ) are given in ppm relative to TMS and the coupling constants (*J*) are quoted in Hz. For spectra recorded in  $\text{CDCl}_3$ , the signals at  $\delta$  7.26 (due to residual  $\text{CHCl}_3$ ) and at  $\delta$  77.16 (the resonance of  $\text{CDCl}_3$ ) were used as internal references.  $^1\text{H}$  NMR spectral data are reported as follows: chemical shift (multiplicity, coupling constant, integration). The following abbreviations are used for multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), td (triplet of doublets), quin (quintet), sept (septet), m (multiplet). All NMR spectra were processed using MestReNova version 6.0.2(v). High-resolution mass spectrometry (HRMS) was performed using a Thermo scientific ExactiveTM Orbitrap mass spectrometer or Q STAR XL Hybrid MS/MS spectrometer by employing ESI-TOF techniques. Spectra were obtained using a lock-mass to adjust the calibrated mass scale.

XRD experiments were performed by measuring the X-ray intensity data on a Bruker SMART APEX III single-crystal X-ray CCD diffractometer using graphite-monochromated radiation ( $\text{Mo-K}\alpha = 0.71073$ ) at low temperature (100 K). The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from a total of 36 frames. The optimized strategy used for data collection consisted of different sets of  $\phi$  and  $\omega$  scans with  $0.5^\circ$  steps  $\phi/\omega$ . Data were collected with a timeframe of 10 seconds for all the components by keeping the sample-to-detector distance fixed at 40 cm. All the data are corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS (Bruker, 2016). SHELX-97 was used for structure solution and full-matrix least-squares refinement on F2 with anisotropic displacement parameters for non-H atoms. Hydrogen atoms associated with carbon atoms were fixed in geometrically constrained positions. The hydrogen atoms associated with oxygen and nitrogen atoms were included in the located positions. ORTEP diagrams were generated by using the X-Seed software package (version 2.0).

#### (*E*)-1,2-Thiosulfonylethenes; General Procedure 1 (GP1)

A heat-gun-dried Schlenk tube was charged with alkynyl bromide **1a–p** (0.5 mmol, 1.0 equiv), thiosulfonate **2a–o** (0.75 mmol, 1.5 equiv),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5.9 mg, 0.025 mmol, 0.05 equiv) and  $\text{Cs}_2\text{CO}_3$  (1.5

mmol, 3.0 equiv) in DMF (2.5 mL). The reaction mixture was stirred at 90 °C for 3 h under N<sub>2</sub>. The progress was monitored by TLC (until the reaction appeared to be complete or was not proceeding any further). The mixture was quenched by the addition of H<sub>2</sub>O (10 mL) followed by extraction with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (2 × 10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, 100–200 mesh, eluting with 8% to 10% EtOAc/PE) to afford the corresponding (*E*)-1,2-thiosulfonylethene.

#### (*E*)-[2-(3,4-Dimethoxyphenyl)-2-(phenylsulfonyl)vinyl]-(phenyl)sulfane (**3aa**)

Following GP1 using 4-(bromoethynyl)-1,2-dimethoxybenzene (**1a**) (120.5 mg, 0.5 mmol), *S*-phenyl benzenesulfonylthioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3aa** as a colorless solid (162.9 mg, 79%, >30:1 mixture of *E/Z* isomers).

Mp 94–96 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.11 (s, 1 H), 7.64 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.53 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.50–7.47 (m, 2 H), 7.43–7.37 (m, 5 H), 6.81 (d, *J* = 8.2 Hz, 1 H), 6.77–6.73 (m, 2 H), 3.88 (s, 3 H), 3.78 (s, 3 H).

These data are consistent with literature values.<sup>10c</sup>

#### (*E*)-Phenyl[2-(phenylsulfonyl)-2-(3,4,5-trimethoxyphenyl)vinyl]sulfane (**3ba**)

Following GP1 using 5-(bromoethynyl)-1,2,3-trimethoxybenzene (**1b**) (135.5 mg, 0.5 mmol), *S*-phenyl benzenesulfonylthioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ba** as a colorless solid (170.4 mg, 77%, >10:1 mixture of *E/Z* isomers).

Mp 142–144 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.11 (s, 1 H), 7.68 (d, *J* = 7.6 Hz, 2 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 7.48 (d, *J* = 6.0 Hz, 2 H), 7.45–7.37 (m, 5 H), 6.38 (s, 2 H), 3.85 (s, 3 H), 3.72 (s, 6 H).

These data are consistent with literature values.<sup>10c</sup>

#### (*E*)-[2-(4-Methoxyphenyl)-2-(phenylsulfonyl)vinyl](phenyl)sulfane (**3ca**)

Following GP1 using 1-(bromoethynyl)-4-methoxybenzene (**1c**) (105.0 mg, 0.5 mmol), *S*-phenyl benzenesulfonylthioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ca** as a colorless solid (132.0 mg, 69%, >30:1 mixture of *E/Z* isomers).

Mp 96–97 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.14 (s, 1 H), 7.65 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.53 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.49–7.46 (m, 2 H), 7.43–7.37 (m, 5 H), 7.24 (t, *J* = 7.9 Hz, 1 H), 6.92–6.88 (m, 1 H), 6.78–6.75 (m, 2 H), 3.74 (s, 3 H).

These data are consistent with literature values.<sup>10c</sup>

#### (*E*)-[2-(3-Methoxyphenyl)-2-(phenylsulfonyl)vinyl](phenyl)sulfane (**3da**)

Following GP1 using 1-(bromoethynyl)-3-methoxybenzene (**1d**) (105.5 mg, 0.5 mmol), *S*-phenyl benzenesulfonylthioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3

mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3da** as a yellow viscous liquid (126.2 mg, 66%, >30:1 mixture of *E/Z* isomers).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.14 (s, 1 H), 7.66 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.53 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.49–7.46 (m, 2 H), 7.43–7.37 (m, 5 H), 7.22 (d, *J* = 8.0 Hz, 1 H), 6.92–6.89 (m, 1 H), 6.78–6.74 (m, 2 H), 3.73 (s, 3 H).

These data are consistent with literature values.<sup>10c</sup>

#### (*E*)-Phenyl[2-phenyl-2-(phenylsulfonyl)vinyl]sulfane (**3ea**)

Following GP1 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), *S*-phenyl benzenesulfonylthioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 8% EtOAc/PE) yielded the title compound **3ea** as a colorless solid (132.0 mg, 75%, >30:1 mixture of *E/Z* isomers).

Mp 91–93 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.15 (s, 1 H), 7.63 (dd, *J* = 8.3, 1.1 Hz, 2 H), 7.53 (t, *J* = 7.4 Hz, 1 H), 7.49–7.46 (m, 2 H), 7.42–7.33 (m, 8 H), 7.21 (dd, *J* = 7.9, 1.6 Hz, 2 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 144.2, 139.4, 136.1, 133.2, 132.9, 131.3 (2 C), 130.7, 130.3 (2 C), 129.7 (2 C), 129.6, 128.9, 128.8 (3 C), 128.3.

These data are consistent with literature values.<sup>10c</sup>

#### (*E*)-Phenyl[2-(phenylsulfonyl)-2-(*p*-tolyl)vinyl]sulfane (**3fa**)

Following GP1 using 1-(bromoethynyl)-4-methylbenzene (**1f**) (97.5 mg, 0.5 mmol), *S*-phenyl benzenesulfonylthioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3fa** as a colorless solid (130.1 mg, 71%, >30:1 mixture of *E/Z* isomers).

Mp 135–137 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.11 (s, 1 H), 7.63 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.53 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.49–7.46 (m, 2 H), 7.43–7.36 (m, 5 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 8.2 Hz, 2 H), 2.35 (s, 3 H).

These data are consistent with literature values.<sup>10c</sup>

#### (*E*)-[2-(4-Isopropylphenyl)-2-(phenylsulfonyl)vinyl](phenyl)sulfane (**3ga**)

Following GP1 using 1-(bromoethynyl)-4-isopropylbenzene (**1g**) (111.5 mg, 0.5 mmol), *S*-phenyl benzenesulfonylthioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ga** as a colorless solid (128.2 mg, 65%, >30:1 mixture of *E/Z* isomers).

Mp 140–142 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.12 (s, 1 H), 7.63 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.54 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.49–7.46 (m, 2 H), 7.42–7.36 (m, 5 H), 7.19 (d, *J* = 8.2 Hz, 2 H), 7.12 (d, *J* = 8.3 Hz, 2 H), 2.89 (sept, *J* = 6.9 Hz, 1 H), 1.24 (d, *J* = 6.9 Hz, 6 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 150.3, 143.9, 139.6, 136.2, 133.1, 133.0, 131.3 (2 C), 130.1 (2 C), 129.7 (2 C), 128.9 (2 C), 128.7, 128.3 (2 C), 127.9, 126.9 (2 C), 34.0, 23.9 (2 C).

HRMS (ESI-TOF): *m/z* [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>23</sub>O<sub>2</sub>S<sub>2</sub>: 395.1139; found: 395.1140.

**(E)-[2-(2-Chlorophenyl)-2-(phenylsulfonyl)vinyl](phenyl)sulfane (3ha)**

Following GP1 using 1-(bromoethynyl)-2-chlorobenzene (**1h**) (107.7 mg, 0.5 mmol), *S*-phenyl benzenesulfonothioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ha** as a colorless solid (119.9 mg, 62%, >30:1 mixture of *E/Z* isomers).

Mp 100–102 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.19 (s, 1 H), 7.60 (d, *J* = 8.5 Hz, 2 H), 7.56 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.49–7.46 (m, 2 H), 7.42 (d, *J* = 7.7 Hz, 2 H), 7.39–7.36 (m, 5 H), 7.33–7.31 (m, 2 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 146.0, 138.9, 134.9, 133.4, 133.2, 132.9, 132.5, 131.4 (2 C), 131.1, 129.8, 129.7 (2 C), 129.1, 129.0 (2 C), 128.9, 128.7 (2 C), 127.1.

HRMS (ESI-TOF): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>15</sub>ClNaO<sub>2</sub>S<sub>2</sub>: 409.0100; found: 409.0095.

**(E)-[2-(Naphthalen-1-yl)-2-(phenylsulfonyl)vinyl](phenyl)sulfane (3ia)**

Following GP1 using 1-(bromoethynyl)naphthalene (**1i**) (115.5 mg, 0.5 mmol), *S*-phenyl benzenesulfonothioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ia** as a colorless solid (138.9 mg, 69%, >30:1 mixture of *E/Z* isomers).

Mp 69–71 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.31 (s, 1 H), 7.79 (d, *J* = 8.2 Hz, 1 H), 7.73 (d, *J* = 8.1 Hz, 1 H), 7.47 (d, *J* = 7.5 Hz, 2 H), 7.42 (d, *J* = 8.4 Hz, 1 H), 7.35–7.31 (m, 5 H), 7.27–7.19 (m, 6 H), 7.12 (d, *J* = 6.9 Hz, 1 H).

These data are consistent with literature values.<sup>10c</sup>

**(E)-[2-(Naphthalen-2-yl)-2-(phenylsulfonyl)vinyl](phenyl)sulfane (3ja)**

Following GP1 using 2-(bromoethynyl)naphthalene (**1j**) (173.3 mg, 0.5 mmol), *S*-phenyl benzenesulfonothioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ja** as a yellow liquid (134.8 mg, 67%, >30:1 mixture of *E/Z* isomers).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.22 (s, 1 H), 7.84–7.77 (m, 3 H), 7.73 (s, 1 H), 7.64 (d, *J* = 7.4 Hz, 2 H), 7.53–7.48 (m, 5 H), 7.41–7.34 (m, 5 H), 7.30 (dd, *J* = 8.5, 1.5 Hz, 1 H).

These data are consistent with literature values.<sup>10c</sup>

**(E)-2-[1-(Phenylsulfonyl)-2-(phenylthio)vinyl]thiophene (3ka)**

Following GP1 using 2-(bromoethynyl)thiophene (**1k**) (93.5 mg, 0.5 mmol), *S*-phenyl benzenesulfonothioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ka** as a light yellow solid (111.1 mg, 62%, >30:1 mixture of *E/Z* isomers).

Mp 99–100 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.20 (s, 1 H), 7.74 (d, *J* = 7.2 Hz, 2 H), 7.55–7.50 (m, 3 H), 7.45–7.40 (m, 6 H), 7.20 (dd, *J* = 3.7, 1.2 Hz, 1 H), 7.04–7.02 (m, 1 H).

These data are consistent with literature values.<sup>10c</sup>

**(E)-2-(1-(Phenylsulfonyl)-2-(phenylthio)vinyl)furan (3la)**

Following GP1 using 2-(bromoethynyl)furan (**1l**) (85.4 mg, 0.5 mmol), *S*-phenyl benzenesulfonothioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3la** as a colorless solid (63.3 mg, 37%, >30:1 mixture of *E/Z* isomers).

Mp 101–103 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.07 (s, 1 H), 7.87 (d, *J* = 7.3 Hz, 2 H), 7.60–7.52 (m, 3 H), 7.50–7.38 (m, 6 H), 6.83 (d, *J* = 3.5 Hz, 1 H), 6.43 (dd, *J* = 3.5, 1.8 Hz, 1 H).

These data are consistent with literature values.<sup>10c</sup>

**(E)-2-[1-(Phenylsulfonyl)-2-(phenylthio)vinyl]-1-tosyl-1H-indole (3ma)**

Following GP1 using 2-(bromoethynyl)-1-tosyl-1H-indole (**1m**) (187.1 mg, 0.5 mmol), *S*-phenyl benzenesulfonothioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ma** as a colorless solid (161.0 mg, 59%, >30:1 mixture of *E/Z* isomers).

Mp 140–142 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.30 (s, 1 H), 7.95 (d, *J* = 8.4 Hz, 1 H), 7.74 (d, *J* = 8.4 Hz, 2 H), 7.54 (s, 1 H), 7.52 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.47–7.42 (m, 3 H), 7.39 (dd, *J* = 5.1, 2.0 Hz, 2 H), 7.31–7.26 (m, 3 H), 7.24 (m, 3 H), 7.25–7.21 (d, *J* = 7.4 Hz, 1 H), 7.14 (t, *J* = 7.9 Hz, 1 H), 2.38 (s, 3 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 146.6, 145.4, 139.1, 135.1, 134.7, 133.3, 132.5, 131.4 (2 C), 130.1 (2 C), 129.8 (2 C), 129.0, 128.9 (2 C), 128.5, 128.2 (2 C), 128.1, 127.8, 127.1 (2 C), 125.3, 123.6, 120.7, 113.8, 112.0, 21.8.

HRMS (ESI-TOF): *m/z* [M + H]<sup>+</sup> calcd for C<sub>29</sub>H<sub>24</sub>NO<sub>4</sub>S<sub>3</sub>: 546.0867; found: 546.0863.

**(E)-tert-Butyl 2-[1-(Phenylsulfonyl)-2-(phenylthio)vinyl]-1H-indole-1-carboxylate (3na)**

Following GP1 using *tert*-butyl 2-(bromoethynyl)-1H-indole-1-carboxylate (**1n**) (160.1 mg, 0.5 mmol), *S*-phenyl benzenesulfonothioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3na** as a brown solid (130.3 mg, 53%, >30:1 mixture of *E/Z* isomers).

Mp 115–117 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.32 (s, 1 H), 7.70 (d, *J* = 8.5 Hz, 2 H), 7.58 (s, 1 H), 7.49–7.45 (m, 3 H), 7.41–7.33 (m, 6 H), 7.31–7.26 (m, 1 H), 7.13–7.05 (m, 2 H), 1.67 (s, 9 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 149.3, 146.2, 139.5, 135.1, 133.2, 132.7, 131.3 (2 C), 129.7 (2 C), 129.0 (2 C), 128.8, 128.2 (2 C), 127.9, 127.7, 127.3, 124.9, 122.9, 120.0, 115.4, 110.0, 84.6, 28.3 (3 C).

HRMS (ESI-TOF): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>27</sub>H<sub>25</sub>NNaO<sub>4</sub>S<sub>2</sub>: 514.1123; found: 514.1117.

**(E)-Phenyl[4-phenyl-2-(phenylsulfonyl)but-1-en-1-yl]sulfane (3oa)**

Following GP1 using 4-bromobut-3-yn-1-ylbenzene (**1o**) (104.9 mg, 0.5 mmol), *S*-phenyl benzenesulfonothioate (**2a**) (187.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5



mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **30a** as a colorless liquid (116.0 mg, 61%, >30:1 mixture of *E/Z* isomers).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.10–8.04 (m, 2 H), 7.67 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.58 (t, *J* = 7.6 Hz, 2 H), 7.32–7.28 (m, 3 H), 7.26–7.20 (m, 3 H), 7.19–7.16 (m, 2 H), 7.01 (d, *J* = 6.6 Hz, 2 H), 6.66 (s, 1 H), 2.77 (t, *J* = 7.3 Hz, 2 H), 2.63 (t, *J* = 7.4 Hz, 2 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 143.0, 140.9, 140.1, 135.9, 133.8, 132.2, 131.0 (2 C), 129.4 (2 C), 129.3 (2 C), 128.9 (2 C), 128.6 (2 C), 128.3, 127.6 (2 C), 126.3, 35.2, 34.4.

HRMS (ESI-TOF): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>20</sub>NaO<sub>2</sub>S<sub>2</sub>: 403.0802; found: 403.0797.

#### (*E*)-(2-Phenyl-2-tosylvinyl)(*p*-tolyl)sulfane (**3eb**)

Following GP1 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), *S-p*-tolyl 4-methylbenzenesulfonothioate (**2b**) (208.8 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3eb** as a colorless solid (121.8 mg, 64%, >30:1 mixture of *E/Z* isomers).

Mp 178–180 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.07 (s, 1 H), 7.49 (d, *J* = 8.2 Hz, 2 H), 7.37–7.33 (m, 5 H), 7.22–7.17 (m, 6 H), 2.38 (s, 3 H), 2.37 (s, 3 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 144.5, 144.0, 139.1, 136.5, 135.8, 131.6 (2 C), 130.9, 130.42 (2 C), 130.35 (2 C), 129.6 (2 C), 129.43, 129.38, 128.7 (2 C), 128.3 (2 C), 21.7, 21.3.

HRMS (ESI-TOF): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>20</sub>NaO<sub>2</sub>S<sub>2</sub>: 403.0802; found: 403.0797.

These data are consistent with literature values.<sup>10d</sup>

#### (*E*)-(4-Fluorophenyl){2-[(4-fluorophenyl)sulfonyl]-2-phenylvinyl}sulfane (**3ec**)

Following GP1 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), *S*-(4-fluorophenyl) 4-fluorobenzenesulfonothioate (**2c**) (143.1 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ec** as a colorless solid (112.6 mg, 58%, >30:1 mixture of *E/Z* isomers).

Mp 98–100 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.01 (s, 1 H), 7.63–7.58 (m, 2 H), 7.48–7.44 (m, 2 H), 7.39–7.33 (m, 3 H), 7.20 (dd, *J* = 7.9, 1.6 Hz, 2 H), 7.12–7.04 (m, 4 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 165.5 (d, *J* = 255.9 Hz), 163.4 (d, *J* = 264.1 Hz), 144.5, 136.0, 135.3 (d, *J* = 3.2 Hz), 134.0 (d, *J* = 8.5 Hz, 2 C), 131.1 (d, *J* = 9.5 Hz, 2 C), 130.3 (d, *J* = 6.3 Hz, 3 C), 129.8 (2 C), 128.9 (3 C), 127.8 (d, *J* = 3.5 Hz), 116.99 (d, *J* = 22.2 Hz), 116.26 (d, *J* = 22.6 Hz).

HRMS (ESI-TOF): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>14</sub>F<sub>2</sub>NaO<sub>2</sub>S<sub>2</sub>: 411.0301; found: 411.0295.

#### (*E*)-(4-Bromophenyl){2-[(4-bromophenyl)sulfonyl]-2-phenylvinyl}sulfane (**3ed**)

Following GP1 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), *S*-(4-bromophenyl) 4-bromobenzenesulfonothioate (**2d**) (306.1 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ed** as a colorless solid (137.7 mg, 54%, >30:1 mixture of *E/Z* isomers).

Mp 188–190 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.04 (s, 1 H), 7.54–7.50 (m, 4 H), 7.44 (d, *J* = 8.7 Hz, 2 H), 7.39–7.31 (m, 5 H), 7.20 (dd, *J* = 7.9, 1.5 Hz, 2 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 143.7, 138.3, 136.3, 132.9 (2 C), 132.8 (2 C), 132.3 (2 C), 131.8, 130.3 (2 C), 130.2, 129.9, 129.8 (2 C), 129.0 (2 C), 128.6, 123.3.

HRMS (ESI-TOF): *m/z* [M + K]<sup>+</sup> calcd for C<sub>20</sub>H<sub>14</sub>Br<sub>2</sub>KO<sub>2</sub>S<sub>2</sub>: 546.8439; found: 546.8433.

#### (*E*)-Naphthalen-2-yl[2-(naphthalen-2-ylsulfonyl)-2-phenylvinyl]sulfane (**3ee**)

Following GP1 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), *S*-naphthalen-1-yl naphthalene-1-sulfonothioate (**2e**) (175.2 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ee** as a yellow solid (140.3 mg, 62%, >30:1 mixture of *E/Z* isomers).

Mp 150–152 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.31 (s, 1 H), 8.20 (s, 1 H), 7.98 (s, 1 H), 7.89–7.82 (m, 6 H), 7.65–7.59 (m, 2 H), 7.58–7.54 (m, 4 H), 7.37–7.30 (m, 3 H), 7.24 (dd, *J* = 8.1, 1.6 Hz, 2 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 144.3, 136.33, 136.31, 135.1, 133.7, 132.9, 132.1, 130.7, 130.5, 130.4 (2 C), 130.03, 130.00, 129.65, 129.62, 129.5, 129.22, 129.16, 128.9 (2 C), 128.1, 128.02, 127.99, 127.8, 127.6, 127.3, 127.2, 123.2.

HRMS (ESI-TOF): *m/z* [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>28</sub>H<sub>24</sub>NO<sub>2</sub>S<sub>2</sub>: 470.1248; found: 470.1248.

#### (*E*)-2-[[2-Phenyl-2-(thiophen-2-ylsulfonyl)vinyl]thio]thiophene (**3ef**)

Following GP1 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), *S*-thiophen-2-yl thiophene-2-sulfonothioate (**2f**) (131.2 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ef** as a yellow solid (94.7 mg, 52%, >30:1 mixture of *E/Z* isomers).

Mp 116–118 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.92 (s, 1 H), 7.59 (dd, *J* = 5.0, 1.3 Hz, 1 H), 7.47 (dd, *J* = 5.4, 1.2 Hz, 1 H), 7.41–7.36 (m, 3 H), 7.32 (dd, *J* = 3.8, 1.3 Hz, 1 H), 7.29–7.26 (m, 2 H), 7.25 (dd, *J* = 3.6, 1.2 Hz, 1 H), 7.06–7.03 (m, 1 H), 6.99 (dd, *J* = 4.9, 3.8 Hz, 1 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 145.5, 140.3, 136.1, 135.4, 134.4, 134.1, 131.4, 130.3 (2 C), 130.1, 129.9, 129.2, 128.9 (2 C), 128.2, 127.6.

HRMS (ESI-TOF): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>16</sub>H<sub>12</sub>NaO<sub>2</sub>S<sub>4</sub>: 386.9618; found: 386.9613.

#### (*E*)-Phenyl(2-phenyl-2-tosylvinyl)sulfane (**3eg**)

Following GP1 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), *S*-phenyl 4-methylbenzenesulfonothioate (**2g**) (198.3 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3eg** as a colorless solid (124.6 mg, 68%, >5:1 mixture of *E/Z* isomers).

Mp 118–120 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.11 (s, 1 H), 7.52–7.45 (m, 4 H), 7.39–7.34 (m, 6 H), 7.23–7.18 (m, 4 H), 2.38 (s, 3 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 144.1, 143.6, 136.4, 132.9, 131.6, 131.2 (2 C), 130.8, 130.3 (2 C), 129.7 (2 C), 129.6 (2 C), 129.5, 128.9, 128.7 (2 C), 128.3 (2 C), 21.7.

HRMS (ESI-TOF):  $m/z$  [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>21</sub>H<sub>22</sub>NO<sub>2</sub>S<sub>2</sub>: 384.1092; found: 384.1087.

These data are consistent with literature values.<sup>10d</sup>

#### (E)-(4-Methoxyphenyl)(2-phenyl-2-tosylvinyl)sulfane (3eh)

Following GP1 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), *S*-(4-methoxyphenyl)-4-methylbenzenesulfonothioate (**2h**) (220.8 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3eh** as a colorless solid (113.0 mg, 57%, >6:1 mixture of *E/Z* isomers).

Mp 175–172 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.00 (s, 1 H), 7.48 (d, *J* = 8.3 Hz, 2 H), 7.41 (d, *J* = 8.9 Hz, 2 H), 7.36–7.31 (m, 3 H), 7.22–7.17 (m, 4 H), 6.91 (d, *J* = 8.9 Hz, 2 H), 3.83 (s, 3 H), 2.38 (s, 3 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 160.5, 145.5, 144.0, 136.6, 135.3, 134.0 (2 C), 132.8, 130.9, 130.4 (2 C), 129.6, 129.4, 128.7, 128.3 (2 C), 123.3, 115.3 (2 C), 114.7, 55.7, 21.7.

HRMS (ESI-TOF):  $m/z$  [M + NH<sub>4</sub>]<sup>+</sup> calcd for C<sub>22</sub>H<sub>24</sub>NO<sub>2</sub>S<sub>2</sub>: 414.1198; found: 414.1195.

These data are consistent with literature values.<sup>10d</sup>

#### (E)-(4-Fluorophenyl)[2-phenyl-2-(phenylsulfonyl)vinyl]sulfane (3ei)

Following GP1 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), *S*-(4-fluorophenyl) benzenesulfonothioate (**2i**) (201.2 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ei** as a yellow solid (100.0 mg, 54%, >30:1 mixture of *E/Z* isomers).

Mp 115–117 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.02 (s, 1 H), 7.61 (d, *J* = 9.3 Hz, 2 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.48–7.44 (m, 2 H), 7.42–7.31 (m, 5 H), 7.21–7.17 (m, 2 H), 7.11–7.06 (m, 2 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 163.2 (d, *J* = 250.0 Hz), 144.4 (d, *J* = 20.8 Hz), 139.2, 136.2, 134.05 (d, *J* = 4.5 Hz), 133.96 (d, *J* = 4.4 Hz), 131.1 (d, *J* = 9.5 Hz), 130.5, 130.3 (2 C), 129.8, 129.6, 128.9 (2 C), 128.8 (2 C), 128.3 (2 C), 116.9 (d, *J* = 22.2 Hz), 116.3 (d, *J* = 22.6 Hz).

HRMS (ESI-TOF):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>15</sub>FN<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: 393.0395; found: 393.0395.

#### (E)-(4-Methoxyphenyl)[2-phenyl-2-(phenylsulfonyl)vinyl]sulfane (3ej)

Following GP1 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), *S*-(4-methoxyphenyl) benzenesulfonothioate (**2j**) (210.3 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ej** as a yellow liquid (97.5 mg, 51%, >15:1 mixture of *E/Z* isomers).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.03 (s, 1 H), 7.61 (d, *J* = 7.2 Hz, 2 H), 7.52 (t, *J* = 7.4 Hz, 1 H), 7.43–7.39 (m, 4 H), 7.37–7.31 (m, 3 H), 7.20 (dd, *J* = 7.9, 1.6 Hz, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 3.83 (s, 3 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 160.5, 146.1, 139.5, 135.0, 134.0 (2 C), 133.2, 130.7, 130.4 (2 C), 129.5, 128.9 (2 C), 128.8 (2 C), 128.3 (2 C), 123.2, 115.3 (2 C), 55.6.

HRMS (ESI-TOF):  $m/z$  [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>19</sub>O<sub>2</sub>S<sub>2</sub>: 383.0776; found: 383.0769.

#### (E)-2-[[2-Phenyl-2-(phenylsulfonyl)vinyl]thio]pyridine (3ek)

Following GP1 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), *S*-pyridin-2-yl benzenesulfonothioate (**2k**) (188.5 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ek** as a yellow liquid (93.6 mg, 53%, >30:1 mixture of *E/Z* isomers).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 9.14 (s, 1 H), 8.61–8.58 (m, 1 H), 7.67 (dd, *J* = 8.4, 1.2 Hz, 2 H), 7.58 (td, *J* = 7.9, 1.8 Hz, 1 H), 7.52 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.42–7.32 (m, 5 H), 7.19–7.14 (m, 4 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 153.4, 150.3, 139.4, 138.9, 137.1, 136.7, 133.2, 131.4, 130.2 (2 C), 129.5, 128.9 (2 C), 128.8 (2 C), 128.4 (2 C), 123.1, 121.8.

HRMS (ESI-TOF):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>19</sub>H<sub>15</sub>NNaO<sub>2</sub>S<sub>2</sub>: 376.0442; found: 376.0437.

#### (E)-2-[[2-Phenyl-1-tosylvinyl]thio]pyridine (3el)

Following GP1 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), *S*-pyridin-2-yl 4-methylbenzenesulfonothioate (**2l**) (199.0 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3el** as a colorless liquid (93.7 mg, 51%, >30:1 mixture of *E/Z* isomers).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 9.10 (s, 1 H), 8.60–6.58 (m, 1 H), 7.59 (dd, *J* = 7.5, 1.9 Hz, 1 H), 7.56–7.52 (m, 2 H), 7.37–7.31 (m, 3 H), 7.20–7.15 (m, 6 H), 2.38 (s, 3 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 153.6, 150.3, 144.1, 138.3, 137.1, 137.0, 136.5, 131.6, 130.3 (2 C), 129.6 (2 C), 129.5, 128.8 (2 C), 128.5 (2 C), 123.1, 121.8, 21.8.

HRMS (ESI-TOF):  $m/z$  [M + H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>18</sub>NO<sub>2</sub>S<sub>2</sub>: 368.0773; found: 368.0767.

These data are consistent with literature values.<sup>10d</sup>

#### (E)-[2-(3,4-Dimethoxyphenyl)-2-tosylvinyl](*p*-tolyl)sulfane (3ab)

Following GP1 using 4-(bromoethynyl)-1,2-dimethoxybenzene (**1a**) (120.5 mg, 0.5 mmol), *S*-*p*-tolyl 4-methylbenzenesulfonothioate (**2b**) (208.8 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ab** as a white solid (158.6 mg, 72%, >30:1 mixture of *E/Z* isomers).

Mp 126–127 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.03 (s, 1 H), 7.51 (d, *J* = 8.3 Hz, 2 H), 7.36 (d, *J* = 8.1 Hz, 2 H), 7.20–7.16 (m, 4 H), 6.82–6.76 (m, 2 H), 6.75 (s, 1 H), 3.87 (s, 3 H), 3.78 (s, 3 H), 2.37 (s, 3 H), 2.36 (s, 3 H).

These data are consistent with literature values.<sup>10d</sup>

#### (E)-*p*-Tolyl[2-tosyl-2-(3,4,5-trimethoxyphenyl)vinyl]sulfane (3bb)

Following GP1 using 5-(bromoethynyl)-1,2,3-trimethoxybenzene (**1b**) (135.5 mg, 0.5 mmol), *S*-*p*-tolyl 4-methylbenzenesulfonothioate (**2b**) (208.8 mg, 0.75 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3bb** as a colorless solid (148.2 mg, 63%, >5:1 mixture of *E/Z* isomers).

Mp 167–169 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.04 (s, 1 H), 7.54 (d, *J* = 8.3 Hz, 2 H), 7.36 (d, *J* = 8.1 Hz, 2 H), 7.22–7.17 (m, 4 H), 7.11 (s, 1 H), 6.40 (s, 1 H), 3.85 (s, 3 H), 3.73 (s, 6 H), 2.38 (s, 3 H), 2.37 (s, 3 H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 153.2, 144.3, 144.1, 139.1, 138.8, 136.6, 135.6, 131.5 (2 C), 130.4 (2 C), 130.3, 129.5 (2 C), 129.4, 128.4 (2 C), 125.9, 107.3, 106.9, 61.0, 56.2 (2 C), 21.6, 21.3.

These data are consistent with literature values.<sup>10c</sup>

#### (E)-[2-(4-Methoxyphenyl)-2-tosylvinyl](p-tolyl)sulfane (3cb)

Following GP1 using 1-(bromoethynyl)-4-ethoxybenzene (**1c**) (105.0 mg, 0.5 mmol), *S-p*-tolyl 4-methylbenzenesulfonothioate (**2b**) (208.8 mg, 0.75 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5.9 mg, 0.025 mmol) and  $\text{Cs}_2\text{CO}_3$  (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3cb** as a colorless solid (137.5 mg, 67%, >30:1 mixture of *E/Z* isomers).

Mp 92–94 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.06 (s, 1 H), 7.52 (d,  $J$  = 8.3 Hz, 2 H), 7.36 (d,  $J$  = 8.1 Hz, 2 H), 7.25–7.21 (m, 1 H), 7.21–7.18 (m, 4 H), 6.91–6.88 (m, 1 H), 6.78–6.75 (m, 2 H), 3.75 (s, 3 H), 2.38 (s, 3 H), 2.37 (s, 3 H).

These data are consistent with literature values.<sup>13,14</sup>

#### (E)-[2-(Naphthalen-1-yl)-2-tosylvinyl](p-tolyl)sulfane (3ib)

Following GP1 using 1-(bromoethynyl)-1-naphthaene (**1i**) (115.5 mg, 0.5 mmol), *S-p*-tolyl 4-methylbenzenesulfonothioate (**2b**) (208.8 mg, 0.75 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5.9 mg, 0.025 mmol) and  $\text{Cs}_2\text{CO}_3$  (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ib** as a colorless solid (127.0 mg, 59%, >30:1 mixture of *E/Z* isomers).

Mp 104–106 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.32 (s, 1 H), 7.88 (d,  $J$  = 8.3 Hz, 1 H), 7.83 (d,  $J$  = 8.1 Hz, 1 H), 7.56 (d,  $J$  = 8.4 Hz, 1 H), 7.45–7.40 (m, 4 H), 7.35–7.30 (m, 3 H), 7.18–7.16 (m, 3 H), 7.10 (d,  $J$  = 8.0 Hz, 2 H), 2.36 (s, 3 H), 2.33 (s, 3 H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.3, 144.1, 139.0, 136.0, 134.3, 133.7, 131.5 (2 C), 131.1, 130.4 (2 C), 130.2, 129.52, 129.49 (2 C), 129.2, 128.6 (2 C), 128.5, 128.0, 126.7, 126.2, 125.3, 125.1, 21.7, 21.3.

HRMS (ESI-TOF):  $m/z$  [ $\text{M} + \text{NH}_4$ ] $^+$  calcd for  $\text{C}_{26}\text{H}_{26}\text{NO}_2\text{S}_2$ : 448.1405; found: 448.1399.

These data are consistent with literature values.<sup>10d</sup>

#### (E)-[2-(Naphthalen-2-yl)-2-tosylvinyl](p-tolyl)sulfane (3jb)

Following GP1 using 1-(bromoethynyl)-2-naphthaene (**1j**) (156.0 mg, 0.5 mmol), *S*-(4-tolyl) 4-methylbenzenesulfonothioate (**2b**) (208.79 mg, 0.75 mmol) and  $\text{Cs}_2\text{CO}_3$  (651.6 mg, 2 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3jb** as a yellow solid (124.8 mg, 58%, >30:1 mixture of *E/Z* isomers).

Mp 180–182 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.15 (s, 1 H), 7.84–7.76 (m, 3 H), 7.74 (s, 1 H), 7.53–7.46 (m, 4 H), 7.37 (d,  $J$  = 8.1 Hz, 2 H), 7.31 (dd,  $J$  = 8.5, 1.7 Hz, 1 H), 7.17 (dd,  $J$  = 15.6, 8.0 Hz, 4 H), 2.37 (s, 3 H), 2.36 (s, 3 H).

These data are consistent with literature values.<sup>10d</sup>

#### (E)-2-[2-(p-Tolylthio)-1-tosylvinyl]thiophene (3kb)

Following GP1 using 2-(bromoethynyl)thiophene (**1k**) (93.5 mg, 0.5 mmol), *S-p*-tolyl 4-methylbenzenesulfonothioate (**2b**) (208.8 mg, 0.75 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5.9 mg, 0.025 mmol) and  $\text{Cs}_2\text{CO}_3$  (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3kb** as a colorless solid (106.3 mg, 55%, >30:1 mixture of *E/Z* isomers).

Mp 128–130 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.13 (s, 1 H), 7.60 (d,  $J$  = 8.3 Hz, 2 H), 7.41–7.38 (m, 3 H), 7.22–7.18 (m, 5 H), 7.03 (dd,  $J$  = 5.1, 3.7 Hz, 1 H), 2.38 (s, 3 H), 2.38 (s, 3 H).

These data are consistent with literature values.<sup>10c,d</sup>

#### (E)-2-[2-(p-Tolylthio)-1-tosylvinyl]-1-tosyl-1H-indole (3mb)

Following GP1 using 2-(bromoethynyl)-1-tosyl-1H-indole (**1m**) (187.1 mg, 0.5 mmol), *S-p*-tolyl 4-methylbenzenesulfonothioate (**2b**) (208.8 mg, 0.75 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5.9 mg, 0.025 mmol) and  $\text{Cs}_2\text{CO}_3$  (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3mb** as a colorless solid (146.3 mg, 51%, >12:1 mixture of *E/Z* isomers).

Mp 135–138 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.23 (s, 1 H), 7.94 (d,  $J$  = 8.3 Hz, 1 H), 7.87–7.80 (m, 1 H), 7.74 (d,  $J$  = 8.3 Hz, 2 H), 7.52 (s, 1 H), 7.40 (d,  $J$  = 8.2 Hz, 2 H), 7.34–7.29 (m, 4 H), 7.24 (s, 1 H), 7.19–7.16 (m, 3 H), 7.04 (d,  $J$  = 7.9 Hz, 2 H), 2.37 (s, 6 H), 2.33 (s, 3 H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 147.0, 145.4, 144.1, 139.3, 136.2, 135.1, 134.7, 134.0, 131.7 (2 C), 130.5 (2 C), 130.1 (2 C), 129.5 (2 C), 129.0, 128.6, 128.2 (2 C), 127.7, 127.1 (2 C), 125.2, 123.6, 121.0, 113.7, 112.3, 21.8, 21.7, 21.3.

HRMS (ESI-TOF):  $m/z$  [ $\text{M} + \text{Na}$ ] $^+$  calcd for  $\text{C}_{31}\text{H}_{27}\text{NNaO}_4\text{S}_3$ : 596.0995; found: 596.1000.

#### (E)-tert-Butyl 2-[2-(p-Tolylthio)-1-tosylvinyl]-1H-indole-1-carboxylate (3nb)

Following GP1 using *tert*-butyl 2-(bromoethynyl)-1H-indole-1-carboxylate (**1n**) (160.1 mg, 0.5 mmol), *S-p*-tolyl 4-methylbenzenesulfonothioate (**2b**) (208.8 mg, 0.75 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5.9 mg, 0.025 mmol) and  $\text{Cs}_2\text{CO}_3$  (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3nb** as a yellow solid (137.7 mg, 53%, >30:1 mixture of *E/Z* isomers).

Mp 130–132 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.25 (s, 1 H), 7.59–7.55 (m, 3 H), 7.35 (d,  $J$  = 8.1 Hz, 2 H), 7.32–7.28 (m, 1 H), 7.21–7.14 (m, 4 H), 7.14–7.09 (m, 3 H), 2.37 (s, 3 H), 2.33 (s, 3 H), 1.67 (s, 9 H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 149.3, 146.4, 144.1, 139.1, 136.7, 131.6 (2 C), 130.4 (2 C), 129.7, 129.6 (2 C), 129.3, 128.5, 128.3 (2 C), 127.7, 125.6, 124.8, 122.8, 120.2, 115.4, 110.2, 84.5, 28.3 (3 C), 21.7, 21.3.

HRMS (ESI-TOF):  $m/z$  [ $\text{M} + \text{Na}$ ] $^+$  calcd for  $\text{C}_{29}\text{H}_{29}\text{NNaO}_4\text{S}_2$ : 542.1436; found: 542.1432.

#### (E)-2-[[2-(3,4-Dimethoxyphenyl)-2-(thiophen-2-ylsulfonyl)-vinyl]thio]thiophene (3af)

Following GP1 using 4-(bromoethynyl)-1,2-dimethoxybenzene (**1a**) (120.5 mg, 0.5 mmol), *S*-thiophen-2-yl thiophene-2-sulfonothioate (**2f**) (131.2 mg, 0.75 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5.9 mg, 0.025 mmol) and  $\text{Cs}_2\text{CO}_3$  (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3af** as a brown liquid (118.9 mg, 56%, >5:1 mixture of *E/Z* isomers).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.89 (s, 1 H), 7.59 (dd,  $J$  = 5.0, 1.3 Hz, 1 H), 7.47 (dd,  $J$  = 5.4, 1.3 Hz, 1 H), 7.35 (dd,  $J$  = 3.8, 1.3 Hz, 1 H), 7.24 (dd,  $J$  = 3.6, 1.3 Hz, 1 H), 7.04 (dd,  $J$  = 5.4, 3.6 Hz, 1 H), 6.99 (dd,  $J$  = 4.9, 3.8 Hz, 1 H), 6.84 (d,  $J$  = 1.1 Hz, 2 H), 6.81 (s, 1 H), 3.89 (s, 3 H), 3.82 (s, 3 H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.2, 149.0, 145.2, 140.4, 135.9, 135.3, 134.3, 134.0, 131.4, 129.4, 128.2, 127.6, 123.3, 122.1, 112.8, 111.1, 56.1, 55.9.

HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{NH}_4]^+$  calcd for  $\text{C}_{18}\text{H}_{20}\text{NO}_4\text{S}_4$ : 442.0275; found: 442.0269.

**(E)-2-[[2-(3,4-Dimethoxyphenyl)-2-(phenylsulfonyl)vinyl]thio]pyridine (3ak)**

Following GP1 using 4-(bromoethynyl)-1,2-dimethoxybenzene (**1a**) (120.5 mg, 0.5 mmol), *S*-pyridin-2-yl benzenesulfonylthioate (**2k**) (188.5 mg, 0.75 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5.9 mg, 0.025 mmol) and  $\text{Cs}_2\text{CO}_3$  (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ak** as a yellow liquid (109.6 mg, 53%, >30:1 mixture of *E/Z* isomers).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.09 (s, 1 H), 8.60–8.57 (m, 1 H), 7.69 (d,  $J$  = 7.2 Hz, 2 H), 7.58 (td,  $J$  = 7.9, 1.8 Hz, 1 H), 7.52 (tt,  $J$  = 7.4, 1.2 Hz, 1 H), 7.40 (t,  $J$  = 7.7 Hz, 2 H), 7.19 (d,  $J$  = 8.0 Hz, 1 H), 7.17–7.13 (m, 1 H), 6.80 (d,  $J$  = 8.3 Hz, 1 H), 6.73 (dd,  $J$  = 8.2, 2.0 Hz, 1 H), 6.68 (d,  $J$  = 1.9 Hz, 1 H), 3.87 (s, 3 H), 3.74 (s, 3 H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 153.6, 150.3, 149.9, 148.9, 139.5, 138.7, 137.1, 136.5, 133.1, 128.9 (2 C), 128.5 (2 C), 123.5, 123.2, 123.1, 121.8, 112.8, 111.0, 56.0, 55.9.

HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{21}\text{H}_{19}\text{NNaO}_4\text{S}_2$ : 436.0653; found: 436.0648.

**(E)-2-[[2-(Thiophen-2-yl)-2-(thiophen-2-ylsulfonyl)vinyl]thio]thiophene (3kf)**

Following GP1 using 2-(bromoethynyl)thiophene (**1k**) (93.5 mg, 0.5 mmol), *S*-thiophen-2-yl thiophene-2-sulfonylthioate (**2f**) (131.2 mg, 0.75 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5.9 mg, 0.025 mmol) and  $\text{Cs}_2\text{CO}_3$  (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 8% EtOAc/PE) yielded the title compound **3kf** as a brown solid (88.9 mg, 48%, >30:1 mixture of *E/Z* isomers).

Mp 120–122 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.99 (s, 1 H), 7.60 (dd,  $J$  = 5.0, 1.3 Hz, 1 H), 7.49 (dd,  $J$  = 5.4, 1.3 Hz, 1 H), 7.47 (d,  $J$  = 1.1 Hz, 1 H), 7.45 (td,  $J$  = 1.6 Hz, 1 H), 7.30–7.26 (m, 2 H), 7.07 (td,  $J$  = 5.4, 3.6 Hz, 2 H), 7.02 (dd,  $J$  = 5.0, 3.8 Hz, 1 H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.8, 140.2, 135.5, 134.4, 134.2, 133.4, 131.6, 131.1, 129.9, 129.5, 129.1, 128.3, 127.6, 127.4.

HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{NH}_4]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{NO}_2\text{S}_5$ : 387.9628; found: 387.9623.

**(E)-2-[[2-(Thiophen-2-yl)-2-tosylvinyl]thio]pyridine (3kl)**

Following GP1 using 2-(bromoethynyl)thiophene (**1k**) (93.5 mg, 0.5 mmol), *S*-pyridin-2-yl benzenesulfonylthioate (**2l**) (199.0 mg, 0.75 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5.9 mg, 0.025 mmol) and  $\text{Cs}_2\text{CO}_3$  (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 8% EtOAc/PE) yielded the title compound **3kl** as a yellow liquid (85.9 mg, 46%, >30:1 mixture of *E/Z* isomers).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.21 (s, 1 H), 8.61–8.58 (m, 1 H), 7.65 (d,  $J$  = 8.3 Hz, 2 H), 7.63–7.59 (m, 2 H), 7.40 (dd,  $J$  = 5.1, 1.2 Hz, 1 H), 7.24 (d,  $J$  = 8.0 Hz, 1 H), 7.21 (d,  $J$  = 8.6 Hz, 2 H), 7.17 (dd,  $J$  = 3.6, 1.2 Hz, 1 H), 7.02 (dd,  $J$  = 5.1, 3.7 Hz, 1 H), 2.37 (s, 3 H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 153.2, 150.3, 149.6, 144.2, 139.5, 137.5, 137.2, 136.4, 130.5, 129.6, 128.6, 128.3, 127.2, 123.2, 122.0, 121.2, 119.8, 21.7.

HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{NO}_2\text{S}_3$ : 374.0343; found: 374.0331.

**(E)-2-[1-(Naphthalen-2-ylsulfonyl)-2-(naphthalen-2-ylthio)vinyl]thiophene (3ke)**

Following GP1 using 2-(bromoethynyl)thiophene (**1k**) (93.5 mg, 0.5 mmol), *S*-naphthalen-1-yl naphthalene-1-sulfonylthioate (**2e**) (175.2 mg, 0.75 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5.9 mg, 0.025 mmol) and  $\text{Cs}_2\text{CO}_3$  (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ke** as a light yellow solid (112.3 mg, 49%, >30:1 mixture of *E/Z* isomers).

Mp 150–152 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.38 (s, 1 H), 8.35 (s, 1 H), 8.03 (s, 1 H), 7.92–7.85 (m, 6 H), 7.69 (dd,  $J$  = 8.7, 1.8 Hz, 1 H), 7.65–7.61 (m, 1 H), 7.59–7.55 (m, 4 H), 7.41 (dd,  $J$  = 5.1, 1.1 Hz, 1 H), 7.24 (dd,  $J$  = 3.7, 1.1 Hz, 1 H), 7.02 (dd,  $J$  = 5.1, 3.7 Hz, 1 H).

These data are consistent with literature values.<sup>10c</sup>

**tert-Butyl (E)-2-[1-(Naphthalen-2-ylsulfonyl)-2-(naphthalen-2-ylthio)vinyl]-1H-indole-1-carboxylate (3ne)**

Following GP1 using *tert*-butyl 2-(bromoethynyl)-1H-indole-1-carboxylate (**1n**) (160.1 mg, 0.5 mmol), *S*-naphthalen-2-yl naphthalene-2-sulfonylthioate (**2e**) (175.2 mg, 0.75 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5.9 mg, 0.025 mmol) and  $\text{Cs}_2\text{CO}_3$  (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3ne** as a yellow solid (145.0 mg, 49%, >30:1 mixture of *E/Z* isomers).

Mp 99–101 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.49 (s, 1 H), 8.30 (d,  $J$  = 1.5 Hz, 1 H), 7.97 (d,  $J$  = 1.6 Hz, 1 H), 7.89–7.81 (m, 7 H), 7.69 (dd,  $J$  = 8.7, 1.8 Hz, 1 H), 7.63–7.58 (m, 1 H), 7.56–7.52 (m, 6 H), 7.17 (d,  $J$  = 7.8 Hz, 1 H), 7.07 (t,  $J$  = 7.5 Hz, 1 H), 1.59 (s, 9 H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 149.2, 146.2, 136.4, 135.1, 133.6, 133.0, 132.1, 130.6, 130.5, 130.0, 129.8, 129.6, 129.5, 129.3, 129.1, 129.0, 128.1, 128.03, 127.99 (2 C), 127.8, 127.5, 127.33, 127.28, 127.2, 125.0, 123.1, 122.9, 120.1, 115.5, 110.1, 84.5, 28.2 (3 C).

HRMS (ESI-TOF):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{35}\text{H}_{29}\text{NNaO}_4\text{S}_2$ : 614.1436; found: 614.1436.

**tert-Butyl (E)-2-[1-(naphthalen-1-ylsulfonyl)-2-(naphthalen-1-ylthio)vinyl]-1H-indole-1-carboxylate (3nn)**

Following GP1 using *tert*-butyl 2-(bromoethynyl)-1H-indole-1-carboxylate (**1n**) (160.1 mg, 0.5 mmol), *S*-naphthalen-1-yl naphthalene-1-sulfonylthioate (**2n**) (175.2 mg, 0.75 mmol),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (5.9 mg, 0.025 mmol) and  $\text{Cs}_2\text{CO}_3$  (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 10% EtOAc/PE) yielded the title compound **3nn** as a colorless solid (139.0 mg, 47%, >30:1 mixture of *E/Z* isomers).

Mp 106–108 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.49 (s, 1 H), 8.30 (s, 1 H), 8.13 (d,  $J$  = 8.3 Hz, 1 H), 7.97 (s, 1 H), 7.89–7.81 (m, 6 H), 7.70 (dd,  $J$  = 8.7, 1.8 Hz, 1 H), 7.64–7.57 (m, 2 H), 7.57–7.50 (m, 5 H), 7.17 (d,  $J$  = 7.8 Hz, 1 H), 7.07 (t,  $J$  = 7.5 Hz, 1 H), 1.59 (s, 9 H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 149.2, 146.2, 136.3, 135.1, 133.6, 133.0, 132.1, 130.5, 130.0, 129.8, 129.6, 129.5, 129.3, 129.1, 129.0, 128.2, 128.1, 128.0 (2 C), 127.9, 127.8, 127.5, 127.33, 127.29, 127.2, 125.0, 123.1, 123.0, 120.1, 115.5, 110.1, 84.5, 28.2 (3 C).

HRMS (ESI-TOF):  $m/z$   $[M + Na]^+$  calcd for  $C_{35}H_{29}NNaO_4S_2$ : 614.1436; found: 614.1432.

#### (S)-1-Phenyl-2-(phenylselanyl)-2-(phenylsulfonyl)ethanone (4)

Following GP1 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), *Se*-phenyl benzenesulfonoselenoate (**2o**) (222.9 mg, 0.75 mmol),  $NiCl_2 \cdot 6H_2O$  (5.9 mg, 0.025 mmol) and  $Cs_2CO_3$  (487.3 mg, 1.5 mmol) for 3 h. Purification by flash column chromatography (silica gel, 8% EtOAc/PE) yielded the title compound **4** as a yellow solid (101.6 mg, 49%).

Mp 100–102 °C.

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 8.02 (dd,  $J$  = 8.4, 1.1 Hz, 2 H), 7.76 (dd,  $J$  = 8.4, 1.1 Hz, 2 H), 7.63 (t,  $J$  = 7.5 Hz, 1 H), 7.59–7.50 (m, 5 H), 7.42–7.38 (m, 2 H), 7.35 (d,  $J$  = 7.4 Hz, 1 H), 7.28–7.24 (m, 2 H), 5.79 (s, 1 H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  = 189.5, 137.1, 135.9 (2 C), 135.1, 134.4, 134.3, 130.7 (2 C), 129.8, 129.6 (2 C), 129.0 (2 C), 128.9 (2 C), 128.8 (2 C), 127.7, 68.2.

HRMS (ESI-TOF):  $m/z$   $[M + NH_4]^+$  calcd for  $C_{20}H_{20}NO_3S_2$ : 434.0329; found: 434.0315.

#### 1,1-Disulfenylethenes; General Procedure 2 (GP2)

A heat-gun-dried Schlenk tube was charged 1-bromoalkene **1(a,e,f,g,j,k,l)** (0.5 mmol, 1.0 equiv), *N*-arylthiosuccinamide **6a,b** (1.25 mmol, 2.5 equiv),  $NiCl_2 \cdot 6H_2O$  (0.025 mmol, 0.05 equiv) and  $Cs_2CO_3$  (1.5 mmol, 3.0 equiv) in DMF (2.5 mL). The reaction mixture was stirred at 90 °C for 3 h. The progress was monitored by TLC (until the reaction appeared to be complete or was not proceeding any further). The mixture was quenched by the addition of  $H_2O$  (10 mL) followed by extraction with EtOAc (3  $\times$  20 mL). The combined organic layers was washed with brine (2  $\times$  20 mL), dried over anhydrous  $Na_2SO_4$ , and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, 100–200 mesh, eluting with 5% EtOAc/PE) to afford the corresponding 1,1-disulfenylethene.

#### [2-(3,4-Dimethoxyphenyl)ethene-1,1-diyl]bis(phenylsulfane) (7aa)

Following GP2 using 4-(bromoethynyl)-1,2-dimethoxybenzene (**1a**) (120.5 mg, 0.5 mmol), 1-(phenylthio)pyrrolidine-2,5-dione (**6a**) (259.1 mg, 1.25 mmol),  $NiCl_2 \cdot 6H_2O$  (5.9 mg, 0.025 mmol) and  $Cs_2CO_3$  (487.3 mg, 1.5 mmol) for 2 h. Purification by flash column chromatography (silica gel, 5% EtOAc/PE) yielded the title compound **7aa** as a colorless solid (161.7 mg, 85%).

Mp 92–94 °C.

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.52–7.49 (m, 2 H), 7.36 (t,  $J$  = 7.3 Hz, 2 H), 7.32–7.28 (m, 1 H), 7.27–7.24 (m, 2 H), 7.18 (t,  $J$  = 7.6 Hz, 2 H), 7.14–7.09 (m, 3 H), 7.07 (d,  $J$  = 2.2 Hz, 1 H), 6.74 (d,  $J$  = 8.4 Hz, 1 H), 3.83 (s, 3 H), 3.80 (s, 3 H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  = 147.7, 147.6, 134.4, 133.7, 132.7, 130.7, 129.4 (2 C), 128.7, 128.2 (2 C), 128.0, 127.8 (2 C), 127.5, 126.4, 125.0, 118.4, 109.8, 109.1, 54.8 (2).

HRMS (ESI-TOF):  $m/z$   $[M + H]^+$  calcd for  $C_{22}H_{21}O_2S_2$ : 381.0983; found: 381.0982.

#### [2-(3,4-Dimethoxyphenyl)ethene-1,1-diyl]bis(*p*-tolylsulfane) (7ab)

Following GP2 using 4-(bromoethynyl)-1,2-dimethoxybenzene (**1a**) (120.5 mg, 0.5 mmol), 1-(*p*-tolylthio)pyrrolidine-2,5-dione (**6b**) (276.6 mg, 1.25 mmol),  $NiCl_2 \cdot 6H_2O$  (5.9 mg, 0.025 mmol) and  $Cs_2CO_3$

(487.3 mg, 1.5 mmol) for 2 h. Purification by flash column chromatography (silica gel, 5% EtOAc/PE) yielded the title compound **7ab** as a colorless solid (179.7 mg, 88%).

Mp 78–80 °C.

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.40 (d,  $J$  = 8.1 Hz, 2 H), 7.19–7.14 (m, 4 H), 7.10 (dd,  $J$  = 8.3, 2.2 Hz, 1 H), 7.06 (d,  $J$  = 2.1 Hz, 1 H), 7.02 (s, 1 H), 6.99 (d,  $J$  = 8.0 Hz, 2 H), 6.73 (d,  $J$  = 8.4 Hz, 1 H), 3.83 (s, 3 H), 3.80 (s, 3 H), 2.36 (s, 3 H), 2.25 (s, 3 H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  = 148.70, 148.68, 137.7, 136.0, 134.1, 132.02, 131.98, 131.2, 130.9 (2 C), 130.1 (2 C), 129.8, 129.7 (2 C), 129.0 (2 C), 119.5, 110.9, 110.3, 55.9 (2 C), 21.2, 21.1.

HRMS (ESI-TOF):  $m/z$   $[M + H]^+$  calcd for  $C_{24}H_{25}O_2S_2$ : 409.1296; found: 409.1281.

#### (2-Phenylethene-1,1-diyl)bis(phenylsulfane) (7ea)

Following GP2 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), 1-(phenylthio)pyrrolidine-2,5-dione (**6a**) (259.1 mg, 1.25 mmol),  $NiCl_2 \cdot 6H_2O$  (5.9 mg, 0.025 mmol) and  $Cs_2CO_3$  (487.3 mg, 1.5 mmol) for 2 h. Purification by flash column chromatography (silica gel, 5% EtOAc/PE) yielded the title compound **7ea** as a yellow liquid (137.8 mg, 86%).

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.59–7.54 (m, 2 H), 7.52–7.47 (m, 2 H), 7.39–7.34 (m, 2 H), 7.30 (tt,  $J$  = 7.2, 1.3 Hz, 1 H), 7.27–7.22 (m, 5 H), 7.21–7.16 (m, 3 H), 7.08 (tt,  $J$  = 7.2, 1.2 Hz, 1 H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  = 138.9, 136.7, 135.3, 134.8, 130.7 (2 C), 129.4 (3 C), 129.0 (2 C), 128.5 (2 C), 128.3 (2 C), 127.75, 127.70, 126.9 (2 C), 126.0.

HRMS (ESI-TOF):  $m/z$   $[M + H]^+$  calcd for  $C_{20}H_{17}S_2$ : 321.0772; found: 321.0784.

#### (2-Phenylethene-1,1-diyl)bis(*p*-tolylsulfane) (7eb)

Following GP2 using (bromoethynyl)benzene (**1e**) (90.5 mg, 0.5 mmol), 1-(*p*-tolylthio)pyrrolidine-2,5-dione (**6b**) (276.6 mg, 1.25 mmol),  $NiCl_2 \cdot 6H_2O$  (5.9 mg, 0.025 mmol) and  $Cs_2CO_3$  (487.3 mg, 1.5 mmol) for 2 h. Purification by flash column chromatography (silica gel, 5% EtOAc/PE) yielded the title compound **7eb** as a colorless solid (139.4 mg, 80%).

Mp 76–78 °C.

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.57–7.54 (m, 2 H), 7.41 (d,  $J$  = 8.1 Hz, 2 H), 7.27–7.23 (m, 2 H), 7.20–7.15 (m, 6 H), 7.01 (d,  $J$  = 8.0 Hz, 2 H), 2.37 (s, 3 H), 2.24 (s, 3 H).

These data are consistent with literature values.<sup>16</sup>

#### [2-(4-Isopropylphenyl)ethene-1,1-diyl]bis(phenylsulfane) (7ga)

Following GP2 using 1-(bromoethynyl)-4-isopropylbenzene (**1g**) (111.5 mg, 0.5 mmol), 1-(phenylthio)pyrrolidine-2,5-dione (**6a**) (259.1 mg, 1.25 mmol),  $NiCl_2 \cdot 6H_2O$  (5.9 mg, 0.025 mmol) and  $Cs_2CO_3$  (487.3 mg, 1.5 mmol) for 2 h. Purification by flash column chromatography (silica gel, 5% EtOAc/PE) yielded the title compound **7ga** as a colorless liquid (137.7 mg, 76%).

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.52–7.47 (m, 4 H), 7.35 (t,  $J$  = 7.3 Hz, 2 H), 7.31–7.25 (m, 4 H), 7.19 (t,  $J$  = 7.7 Hz, 2 H), 7.13–7.07 (m, 3 H), 2.85 (sept,  $J$  = 6.9 Hz, 1 H), 1.20 (d,  $J$  = 6.9 Hz, 6 H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  = 148.6, 136.5, 136.2, 135.5, 135.1, 130.6 (2 C), 129.4 (2 C), 129.2, 129.0 (2 C), 128.0 (2 C), 127.6, 126.7 (2 C), 126.6 (2 C), 125.8, 33.8, 24.0 (2 C).

HRMS (ESI-TOF):  $m/z$   $[M + H]^+$  calcd for  $C_{23}H_{23}S_2$ : 363.1241; found: 363.1228.

**[2-(4-Isopropylphenyl)ethene-1,1-diyl]bis(*p*-tolylsulfane) (7gb)**

Following GP2 using 1-(bromoethynyl)-4-isopropylbenzene (**1g**) (111.5 mg, 0.5 mmol), 1-(*p*-tolylthio)pyrrolidine-2,5-dione (**6b**) (276.6 mg, 1.25 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 2 h. Purification by flash column chromatography (silica gel, 5% EtOAc/PE) yielded the title compound **7gb** as a colorless liquid (154.2 mg, 79%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.48 (d, *J* = 8.4 Hz, 2 H), 7.39 (d, *J* = 8.1 Hz, 2 H), 7.19–7.15 (m, 5 H), 7.10 (d, *J* = 8.2 Hz, 2 H), 7.01 (d, *J* = 8.0 Hz, 2 H), 2.85 (sept, *J* = 6.9 Hz, 1 H), 2.36 (s, 3 H), 2.25 (s, 3 H), 1.20 (d, *J* = 6.9 Hz, 6 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 148.4, 137.7, 136.72, 136.70, 135.7, 132.0, 131.5, 131.0 (2 C), 130.1 (2 C), 129.8 (2 C), 128.9, 128.3 (2 C), 126.7 (2 C), 126.6 (2 C), 33.8, 24.0 (2 C), 21.2, 21.1.

These data are consistent with literature values.<sup>15</sup>

**[2-(Naphthalen-2-yl)ethene-1,1-diyl]bis(phenylsulfane) (7ja)**

Following GP2 using 2-(bromoethynyl)naphthalene (**1j**) (173.3 mg, 0.5 mmol), 1-(phenylthio)pyrrolidine-2,5-dione (**6a**) (259.1 mg, 1.25 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 2 h. Purification by flash column chromatography (silica gel, 5% EtOAc/PE) yielded the title compound **7ja** as a colorless solid (150.0 mg, 81%).

Mp 88–90 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.06 (s, 1 H), 7.80–7.75 (m, 2 H), 7.72 (d, *J* = 1.6 Hz, 2 H), 7.58–7.54 (m, 2 H), 7.45–7.37 (m, 5 H), 7.36–7.30 (m, 3 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 7.07 (tt, *J* = 7.2, 1.2 Hz, 1 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 137.5, 136.2, 135.3, 134.8, 133.4, 132.9, 130.8 (2 C), 129.5 (2 C), 129.2, 129.0 (2 C), 128.33, 128.27 (2 C), 128.2, 127.8, 127.6, 126.4, 126.17, 126.04, 125.96, 124.7.

HRMS (ESI-TOF): *m/z* [M + H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>19</sub>S<sub>2</sub>: 371.0928; found: 371.0913.

**2-[2,2-Bis(phenylthio)vinyl]thiophene (7ka)**

Following GP2 using 2-(bromoethynyl)thiophene (**1k**) (93.5 mg, 0.5 mmol), 1-(phenylthio)pyrrolidine-2,5-dione (**6a**) (259.1 mg, 1.25 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 2 h. Purification by flash column chromatography (silica gel, 5% EtOAc/PE) yielded the title compound **7ka** as a yellow liquid (115.9 mg, 71%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.44–7.41 (m, 2 H), 7.33–7.28 (m, 3 H), 7.27–7.25 (m, 3 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 7.11–7.07 (m, 2 H), 7.05 (dd, *J* = 5.1, 1.1 Hz, 1 H), 6.82 (dd, *J* = 5.1, 3.7 Hz, 1 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 144.2, 135.9, 134.9, 134.8, 130.7 (2 C), 129.5 (2 C), 129.1 (2 C), 128.1 (2 C), 127.8, 127.7, 126.2, 125.0, 124.8, 122.9.

HRMS (ESI-TOF): *m/z* [M + H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>15</sub>S<sub>3</sub>: 327.0336; found: 327.0322.

**2-[2,2-Bis(*p*-tolylthio)vinyl]thiophene (7kb)**

Following GP2 using 2-(bromoethynyl)thiophene (**1k**) (93.5 mg, 0.5 mmol), 1-(*p*-tolylthio)pyrrolidine-2,5-dione (**6b**) (276.6 mg, 1.25 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 2 h. Purification by flash column chromatography (silica gel, 5% EtOAc/PE) yielded the title compound **7kb** as a yellow solid (132.9 mg, 75%).

Mp 78–80 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.40 (d, *J* = 8.1 Hz, 2 H), 7.27–7.25 (m, 3 H), 7.19 (d, *J* = 7.9 Hz, 2 H), 7.14 (dd, *J* = 3.7, 1.2 Hz, 1 H), 7.11 (dd, *J* = 5.1, 1.2 Hz, 1 H), 7.07 (d, *J* = 7.9 Hz, 2 H), 6.89 (dd, *J* = 5.1, 3.7 Hz, 1 H), 2.38 (s, 3 H), 2.30 (s, 3 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 144.4, 138.0, 136.3, 136.2, 131.4, 131.2, 131.1 (2 C), 130.2 (2 C), 129.9 (2 C), 128.5 (2 C), 127.6, 124.8, 124.6, 122.7, 21.2, 21.1.

HRMS (ESI-TOF): *m/z* [M + H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>19</sub>S<sub>3</sub>: 355.0649; found: 355.0636.

**2-[2,2-Bis(*p*-tolylthio)vinyl]furan (7lb)**

Following GP2 using 2-(bromoethynyl)furan (**1l**) (85.5 mg, 0.5 mmol), 1-(*p*-tolylthio)pyrrolidine-2,5-dione (**6b**) (276.6 mg, 1.25 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (5.9 mg, 0.025 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (487.3 mg, 1.5 mmol) for 2 h. Purification by flash column chromatography (silica gel, 5% EtOAc/PE) yielded the title compound **7lb** as a brown liquid (116.7 mg, 69%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.47 (s, 1 H), 7.39 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 1.7 Hz, 1 H), 7.24 (d, *J* = 8.2 Hz, 2 H), 7.17 (d, *J* = 7.9 Hz, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 6.36 (d, *J* = 3.3 Hz, 1 H), 6.30 (dd, *J* = 3.4, 1.8 Hz, 1 H), 2.36 (s, 3 H), 2.29 (s, 3 H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 153.3, 142.4, 137.9, 136.5, 136.1, 131.41, 131.39, 131.1 (2 C), 130.1 (2 C), 129.9 (2 C), 128.2 (2 C), 118.0, 111.7, 107.6, 21.3, 21.2.

HRMS (ESI-TOF): *m/z* [M + H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>19</sub>OS<sub>2</sub>: 339.0877; found: 339.0867.

**Conflict of Interest**

The authors declare no conflict of interest.

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**Supporting Information**

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