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Straightforward and highly efficient catalyst-free regioselective reaction of thiol to β-nitrostyrene: a concise synthesis of vinyl sulfide and nitro sulfide

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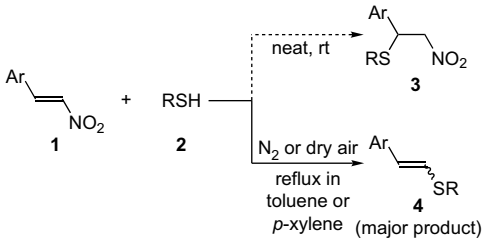
ABSTRACT

Under catalyst-free reaction conditions, solvent-mediated addition of thiol **2** to β-nitrostyrene **1** proceeded with regioselective control to afford either adduct **3** or vinyl sulfide **4** in good to excellent yield. Thermodynamic and autocatalytic reaction mechanisms were proposed to rationalize the products thus formed.

1. Introduction

β-Nitrostyrenes are versatile building blocks in organic synthesis reactions.[1] Conjugated nitroalkenes are excellent Michael acceptors due to the strong electron-withdrawing nature of the nitro group. Many classes of compounds have been prepared via classical Michael addition using conjugated nitroalkanes. Recently, it was discovered that substitution of β-nitrostyrenes to generate corresponding alkenes is facilitated by an electrophilic carbon-centered radical process.[2,3] Based on these preliminary results, we try to expand the scope of protocols to further applications. After intensive investigation, we determined that, under catalyst-free reaction conditions, nucleophilic addition of thiol radicals to β-nitrostyrenes proceeds in a regiospecific manner, resulting in an efficient production of vinyl sulfides.

Vinyl sulfides are versatile synthons in organic syntheses.[4–6] Because there are only a few systems available for the synthesis of vinyl sulfides, including addition of thiols to alkynyl analogues,[7] transition metal-mediated cross coupling of vinyl halides with various thiols,[8] and other unusual methods,[9] development of new methods for the synthesis of vinyl sulfides is urgently needed. Herein, we report a novel procedure to synthesize vinyl sulfides in high yield. As shown in Scheme 1, execution of this novel procedure is quite simple.



1a: Ar = Ph
1b: Ar = 1-naphthalenyl
1c: Ar = 4-ClC_6H_4
1d: Ar = 4-FC_6H_4
1e: Ar = 4-$MeOC_6H_4$
1f: Ar = 2-$NO_2C_6H_4$
1g: Ar = 2-furyl
1h: Ar = 2-thienyl

2a: R = Ph
2b: R = $C_6H_5CH_2$
2c: R = *c*-C_6H_{11}
2d: R = *t*-C_4H_9
2e: R = C_6H_{13}
2f: R = C_3H_7
2g: R = HOC_2H_4
2h: R = 2-naphthalenyl
2i: R = 4-$MeOC_6H_4$
2j: R = 4-$NO_2C_6H_4$

Scheme 1.

2. Results and discussion

Table 1 lists representative examples of reaction yield under various reaction conditions. Our initial efforts focused primarily on the efficiency of various solvents. Reactions were performed using 1 equiv of β-nitrostyrene **1a** and 3 equiv of thiophenol **2a** under catalyst-free conditions. The results of these experiments demonstrate that regioselective differences were highly attributed to differences between protic and aprotic solvents. For example, ethanol (entry 5) and toluene (entry 15) afforded **3aa** and **4aa**, respectively, in quantitative yield. The temperature-dependent substitution reaction proceeded with obvious regioselectivity in nearly every aprotic solvent except for DMSO (entry 11), which produced a large amount of diphenyl disulfide at high-temperature. A further

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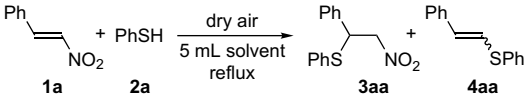
Table 1
Reaction of β-nitrostyrene **1a** with thiophenol **2a** in various solvents in absence of catalyst[a]



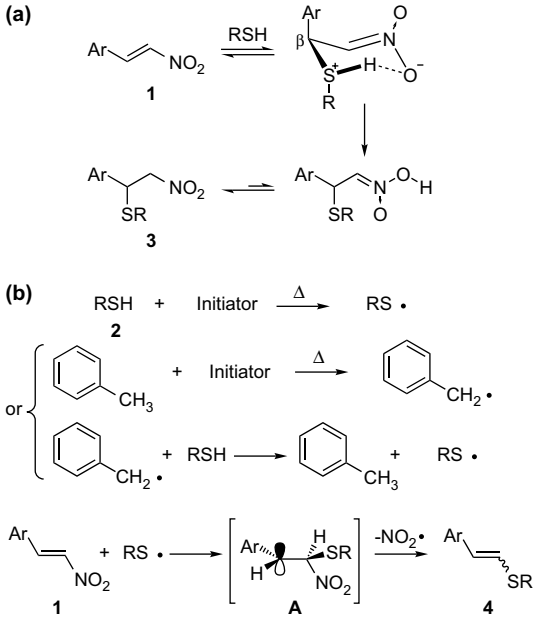
1a **2a** **3aa** **4aa**

Entry	Solvent	Time	**3aa** (%)[b]	**4aa** (%)/[sel.][b]
1	Neat/rt/O_2	1 h	82	—
2	Neat/rt/air[c]	30 min	98	—
3	Neat/rt/air/TEMPO	1 h	89	—
4	Neat/rt/argon	1 h	85	—
5	EtOH	3 h	98	2/[5.3:1]
6	HOAc	3 h	95	5/[4.0:1]
7	MeCN	3 h	75	15/[6.5:1]
8	CH_2Cl_2	3 h	10	2/[5.4:1]
9	THF	3 h	8	9/[5.8:1]
10	EtOAc	3 h	15	39/[6.3:1]
11	DMSO	3 h	12	46/[4.8:1]
12	C_6H_6	3 h	15	61/[5.1:1]
13	1,4-Dioxane	3 h	25	75/[6.5:1]
14	Toluene/argon	3 h	—	97/[6.5:1]
15	Toluene	3 h	—	98/[6.1:1]
16	Toluene/TEMPO	3 h	tr	12/[8.0:1]

[a] Conditions: a solution of 2.0 mmol of β-nitrostyrene **1a** and 6 mmol of thiophenol **2** in 5 mL of indicated solvent was refluxed under dry atmosphere.
[b] Yields and the ratio of trans/cis isomers were determined by ^{1}H NMR and GC.
[c] In the presence of normal atmosphere.

examination was also done by mixing toluene with the radical scavenger, TEMPO, which markedly inhibited formation of the substituted product **4aa** (entry 16). In addition, when the reaction was carried out in the absence of solvent, it did not proceed efficiently (entry 3). Thus, the mechanism for this reaction pathway appears to involve an autocatalytic/nucleophilic reaction of the thiol. In fact, these results helped us to determine that 1,4-addition of thiols to β-nitrostyrenes proceeds efficiently in the absence of acid/base catalysts, which contrasts with other methods that are unsatisfactory due to multiple limitations.[10]

While the exact reaction mechanism remains unidentified, plausible mechanisms for autocatalytic addition and radical substitution are depicted in Scheme 2. During the nucleophilic reaction, hydrogen bond formation between the sulfhydryl hydrogen of the thiol and the nitro oxygen atom of the β-nitrostyrene increases electrophilicity of the β-carbon. In other words, hydrogen bond formation simultaneously activates both the β-nitrostyrene and the thiol. In this way, an intramolecular nucleophilic attack at the β-site of the nitrostyrene by the sulfur atom followed by a series of proton rearrangement, results in conjugate addition. During the radical substitution reaction, a suitable initiator such as triplet oxygen, or perhaps the process of thermolysis, initiates the liberation of a thiyl radical. Another proposed route is the formation of a carrier-benzylic radical when the initiator first reacts with toluene first. The resulting benzylic radical can abstract the hydrogen from thiol **2** to generate a thiyl radical.[11] Thus, a thiyl moiety will attack at the α-position of β-nitrostyrene to form the stable benzylic radical followed by the loss of a NO_2 radical. A reddish-brown corrosion was always observed on the septa during the course of the reaction. However, the outcome of the geometric isomers was quite different from previously established examples with carbon-centered radicals.[2] The *E*-isomers are exclusively obtained when β-nitrostyrene is conducted with carbon-centered radicals using a similar process. Once the intermediate A forms, the relatively sulfur group, which is relatively larger compared with the general carbon group, will retard the rapid rotation of the single bond, resulting in the formation of *E*/*Z* isomers after the release of NO_2. Moreover, the sulfur atom helps with reduction of the steric hindrance between the aryl and alkyl groups.

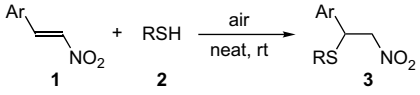


Scheme 2. Plausible reaction mechanisms and roles of (a) nucleophilic thiol in autocatalytic addition and (b) electrophilic thiyl radical in the pathway with β-nitrostyrenes.

Autocatalytic addition is generally applicable to thiols, as shown in Table 2. In fact, the rate of thiol reaction with a common β-nitrostyrene was influenced by the ability of the various thiols to form hydrogen bonds. For example, the reaction with thiophenol was faster than reactions with α-toluenethiol and alkyl thiol (entries 1–5). As the sulfhydryl hydrogen atom of aliphatic thiols is less acidic than that of aromatic thiols,[12] hydrogen bond formation between the sulfhydryl hydrogen atom and the nitro oxygen atom of β-nitrostyrene was reduced in aliphatic thiols.

The application of the new method to the radical substitution of β-nitrostyrene with thiols in the absence of a catalyst to generate vinyl sulfide was also examined. The method was compatible with

Table 2
Autocatalytic addition of thiols **2** to β-nitrostyrenes **1** in the absence of solvent[a]

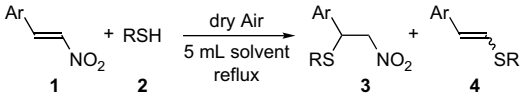


1 **2** **3**

Entry	**1**	**2**	Time	Product **3**	Yields[b] (%)
1	**1a**	**2a**	30 min	**3aa**	96
2	**1a**	**2b**	2 h	**3ab**	92
3	**1a**	**2c**	32 h	**3ac**	92
4	**1a**	**2e**	36 h	**3ae**	91
5	**1a**	**2f**	10 h	**3af**	93
6	**1b**	**2a**	1 h	**3ba**	94
7	**1c**	**2a**	30 min	**3ca**	93
8	**1d**	**2a**	30 min	**3da**	95
9	**1e**	**2a**	7 h	**3ea**	93
10	**1e**	**2b**	3 h	**3eb**	96
11	**1e**	**2c**	18 h	**3ec**	94
12[c]	**1e**	**2e**	24 h	**3ee**	96
13[c]	**1g**	**2a**	72 h	**3ga**	90
14	**1h**	**2a**	1 h	**3ha**	93

[a] Conditions: the mixture of 2.0 mmol of β-nitrostyrene **1** and 4 mmol of thiol **2** stirred under normal atmosphere.
[b] Yields are for isolated, chromatographically pure products.
[c] Ethanol (0.5 mL) was added.

Table 3
Radical substitution of various thiols **2** with β-nitrostyrenes **1** in the absence of catalyst[a]



1 2 3 4

Entry	1	2	Solvent/time	Yields (%)[b]	
				3	4aa/[sel.]
1	**1a**	**2a**	Toluene/3 h	**3aa**/—	**4aa**/93[5.6:1]
2	**1a**	**2b**	*p*-Xylene/7 h	**3ab**/8	**4ab**/69[3.5:1]
3	**1a**	**2c**	*p*-Xylene/10 h	**3ac**/6	**4ac**/80[4.2:1]
4	**1a**	**2d**	*p*-Xylene/6 h	**3ad**/—	**4ad**/70[3.4:1]
5	**1a**	**2e**	*p*-Xylene/24 h	**3ae**/20	**4ae**/52[12:1]
6	**1a**	**2f**[c]	*p*-Xylene/12 h	**3af**/3	**4af**/30[5.2:1]
7	**1a**	**2i**	Toluene/2.5 h	**3ai**/—	**4ai**/92[5.9:1]
8	**1a**	**2j**	*p*-xylene/3 h	**3aj**/29	**4aj**/65[4.2:1]
9	**1b**	**2a**	Toluene/3 h	**3ba**/—	**4ba**/95[5.4:1]
10	**1c**	**2a**	Toluene/4 h	**3ca**/tr	**4ca**/85[5.7:1]
11	**1d**	**2a**	Toluene/4 h	**3da**/tr	**4da**/96[4.8:1]
12	**1e**	**2a**	Toluene/3 h	**3ea**/—	**4ea**/94[12.9:1]
13	**1e**	**2b**	*p*-Xylene/10 h	**3eb**/19	**4eb**/62[3.4:1]
14	**1e**	**2c**	*p*-Xylene/10 h	**3ec**/tr	**4ec**/93[3.4:1]
15	**1e**	**2d**	*p*-Xylene/12 h	**3ed**/—	**4ed**/60[3.6:1]
16	**1e**	**2e**	*p*-Xylene/14 h	**3ee**/7	**4ee**/55[5.1:1]
17	**1g**	**2a**	Toluene/1 h	**3ga**/—	**4ga**/92[2.3:1]
18	**1h**	**2a**	Toluene/1 h	**3ha**/—	**4ha**/94[1.9:1]

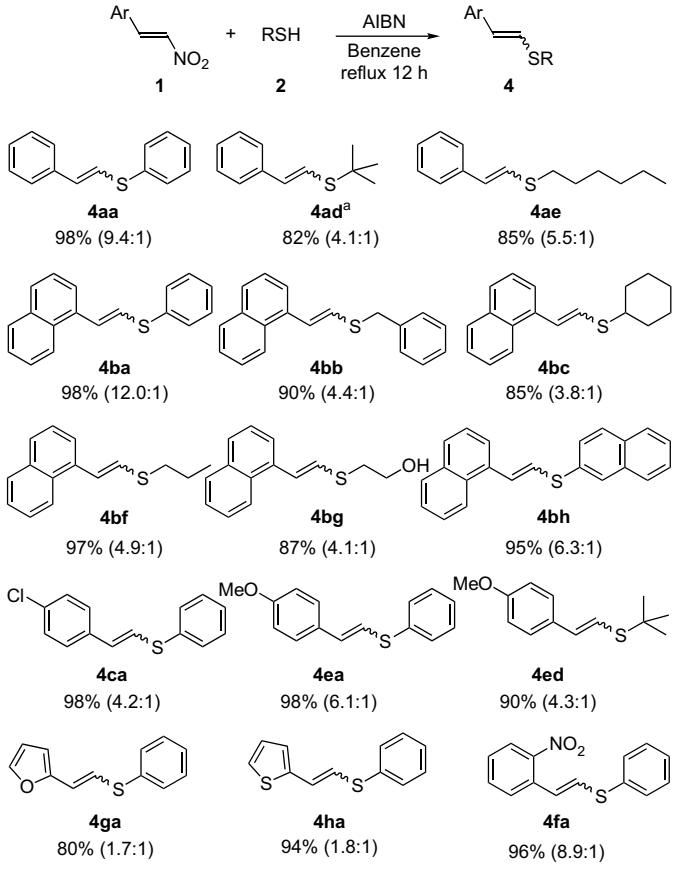
[a] Conditions: a solution of 2.0 mmol of β-nitrostyrene **1** and 6 mmol of thiol **2** in 5 mL of purified solvent was refluxed as indicated period.
[b] Isolation yields and the ratio of trans/cis isomers were determined by ^{1}H NMR and GC.
[c] Thiol (10 mmol, 5 equiv) was used.

various functional substituents on the phenyl group of β-nitrostyrene, including alkyl, halo, and even heteroaryl groups (Table 3). The *para*-site of halo-substituted β-nitrostyrene reacted efficiently with thiophenol, and the vinyl sulfide products were obtained in 85–96% yields (entries 10–11). For substituted thiophenol **2a** and 4-methoxybenzenethiol **2i**, bearing electron-donating groups, provided the corresponding vinyl sulfide **4aa** in 93% and **4ai** in 92% isolated yields. However, an absence of the activating substituent lowered the radical product yields. Thus, 4-nitrobenzenethiol **2j** yielded corresponding vinyl sulfide **4aj** and nitro sulfide **3aj** in 65% and 29% yields, respectively (entries 1 and 7–8).

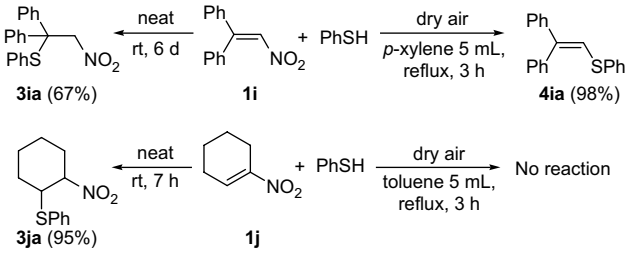
In general, the lower reactivity and boiling point of aliphatic thiols increased the formation of dialkyl disulfide during the reaction, resulting in poor product yield and regioselectivity. For example, 5 equiv of 1-propanethiol **2f** (bp=67–68 °C) were converted to vinyl sulfide **4af** in 30% isolated yield under refluxing *p*-xylene (entry 6). Similarly, **4ae** and **4ee** were isolated in moderate yields from the reaction of 1-hexanethiol **2e** with the nitrostyrenes **1a** and **1e**, respectively (entries 5 and 16).

Addition of the initiator, AIBN, dramatically improved the efficiency and regioselectivity of the reaction. All the reactions can be completed under refluxing for 12 h in benzene. Thus, addition of AIBN significantly improved the efficiency and reactivity of the low-boiling-point thiols, as exemplified in Scheme 3.

The thiyl radical derived from **2a** also reacted with α-diphenyl nitrostyrene **1i** to efficiently produce **4ia**. However, the sterically hindered nitrostyrene was not a good substrate for the nucleophilic thiol derived from **2a** (Scheme 4), giving the expected sulfide **3ia** in moderate yield. So far, attempts to extend the substitution reaction to the general nitroalkene, 1-nitro-1-cyclohexene **1j**, with the thiyl radical **2a** have failed. This result may be explained by the formation of a stable benzylic radical, i.e., intermediate **A**, as shown in Scheme 2.



Scheme 3. Substitution of β-nitrostyrenes **1** with various thiols **2** in the presence of AIBN. Conditions: a solution of 2.0 mmol of β-nitrostyrene **1**, 6 mmol of thiol **2**, and 6 mmol of AIBN in 13 mL of benzene was refluxed for 12 h. (a) thiol (10 mmol, 5 equiv) was used. (b) Isolation yields and the trans/cis isomers were determined by ^{1}H NMR and GC.



Scheme 4.

3. Conclusion

In summary, we have demonstrated either substitution of the nitro group by appropriate electrophilic thiyl radicals, or a novel protocol for the autocatalytic addition of thiols to β-nitrostyrene under mild and neutral conditions. Of note, the high regioselectivity of this method did not require a catalyst. It is also noteworthy that the present reaction opens the possibility of a synthetic vinyl sulfide crossover to the transition-metal-catalyzed addition of alkyne or a vinyl halide coupling reaction with thiols. Although peroxide-initiated reactions of mercaptans with various substrates have been reported, addition of excess AIBN is the more facile method and results in absolute regioselective formation of vinyl sulfide derivatives.

4. Experimental section

4.1. General methods

All reactions were performed in oven-dried glassware and some reactions were carried out under a positive pressure of argon when the reactions were sensitive to moisture or oxygen. Analytical thin layer chromatography was performed with E. Merck silica gel 60F glass plates and flash chromatography by use of E. Merck silica gel 60 (230–400 mesh). GC was measured by SHIMADZU GC-14B. MS or HRMS were measured by JEOL JMS-D300 or JEOL JMS-HX110 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance EX 400 FT NMR.

Compounds **1a**, **1c–1e**, **1g–1h**, **1j**, thiols **2a–2h**, and solvents were obtained from commercial sources and were purified before used if necessary. Compound **1b**,[13a] **1f**,[13b] and **1i**,[13c] were prepared according to the literature procedures and all spectral data were consistent with the literature reports.

4.2. Method A: general procedure for the autocatalytic addition of thiophenol 2a to β-nitrostyrene 1a under solvent-free condition to generate (2-nitro-1-phenylethyl) phenyl sulfide (3aa)

In a typical experiment β-nitrostyrene **1a** (0.298 g, 2.0 mmol) and thiophenol **2a** (0.41 mL, 4 mmol) were mixed together in a 10 mL round bottle flask, and the solution vigorously stirred at room temperature under an air atmosphere for 30 min. After completion of the reaction (monitored by TLC and GC), the crude products were purified by a flash column chromatography on silica gel with ethyl acetate–hexane (4:100, v/v) to afford 96% yield of **3aa** as a white solid whose spectral data are consistent with the literature report:[14] mp 73–74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.27 (m, 10H), 7.34–7.21 (m, 3H), 4.93–4.83 (m, 2H), 4.75 (dd, J=11.9, 5.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.48, 133.97, 132.09, 129.57, 129.20, 129.01, 128.85, 127.85, 78.74, 50.07. m/z (relative intensity) 259 (M^+, 11), 212 (10), 149 (11), 135 (28), 125 (26), 110 (71), 104 (100),103 (27), 77 (50), 66 (27), 65 (26), 51 (33). HRMS calcd for $C_{14}H_{13}NO_2S$ 259.0662, found 259.0676.

4.2.1. Benzyl(2-nitro-1-phenylethyl)sulfide (**3ab**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.22 (m, 10H), 4.71–4.60 (m, 2H), 4.42 (dd, J=8.8, 6.9 Hz, 1H), 3.69 (d, J=13.6 Hz, 1H), 3.60 (d, J=13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.23, 137.08, 129.22, 129.11, 128.89, 128.69, 127.97, 127.71, 79.25, 46.10, 36.19. m/z (relative intensity) 273 (M^+, 2), 104 (25), 91 (100), 77 (18), 65 (17), 51 (11). HRMS calcd for $C_{15}H_{15}NO_2S$ 273.0818, found 273.0822.

4.2.2. Cyclohexyl(2-nitro-1-phenylethyl)sulfide (**3ac**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.25 (m, 5H), 4.73–4.70 (m, 2H), 4.63 (dd, J=8.8, 6.9 Hz, 1H), 2.62–2.54 (m, 1H), 1.97–1.81 (m, 2H), 1.77–1.65 (m, 2H), 1.62–1.50 (m, 1H), 1.40–1.15 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.28, 129.17, 128.48, 127.74, 80.00, 45.30, 44.12, 33.61, 33.59, 25.99, 25.89, 25.79. m/z (relative intensity) 256 (M^+, 3), 235 (11), 219 (4), 137 (50), 136 (30), 104 (100), 81 (58), 77 (24), 67 (24), 55 (58). HRMS calcd for $C_{14}H_{19}NO_2S$ 265.1131, found 265.1141.

4.2.3. Hexyl(2-nitro-1-phenylethyl)sulfide (**3ae**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.26 (m, 5H), 4.74 (d like, J=7.9 Hz, 2H), 4.56 (dd, J=7.6, 8.1 Hz, 1H), 2.43 (t, J=7.3 Hz, 2H), 1.51 (quint, J=7.3 Hz, 2H), 1.35–1.13 (m, 6H), 0.86 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.65, 129.13, 128.53, 127.77, 79.48, 46.70, 31.81, 31.40, 29.23, 28.51, 22.60, 14.13. m/z (relative intensity) 267 (M^+, 2), 237 (4), 221 (3), 220 (3), 205 (4), 149 (10), 136 (18), 134 (14), 117 (14), 105 (25), 104 (100), 103 (16), 91 (16), 77 (22), 55 (17). HRMS calcd for $C_{14}H_{21}NO_2S$ 267.1288, found 267.1292.

4.2.4. (2-Nitro-1-phenylethyl)propyl sulfide (**3af**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.25 (m, 5H), 4.754 (d like, J=7.79 Hz, 2H), 4.56 (dd, J=7.8, 8.0 Hz, 1H), 2.42 (t, J=7.2 Hz, 2H), 1.57 (sext, J=7.2 Hz, 2H), 0.93 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.72, 129.20, 128.60, 127.82, 79.59, 46.73, 33.88, 22.74, 13.52. m/z (relative intensity) 225 (M^+, 2), 179 (3), 137 (11), 136 (30), 134 (21), 105 (23), 104 (100), 103 (25), 91 (15), 86 (50), 84 (76), 78 (17), 77 (24), 51 (46). HRMS calcd for $C_{11}H_{15}NO_2S$ 225.0818, found 225.0828.

4.2.5. (2-Nitro-1-phenylethyl)(4-nitrophenyl)sulfide (**3aj**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dt, J=8.9, 1.5 Hz, 2H), 7.45 (dt, J=8.9, 2.0 Hz, 2H), 7.40–7.32 (m, 5H), 5.12 (dd, J=8.3, 7.1 Hz, 1H), 4.86 (dd, J=13.2, 8.4 Hz, 1H), 4.77 (dd, J=13.2, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.11, 142.29, 135.58, 130.90, 129.57, 129.41, 127.83, 124.42, 78.65, 49.11. m/z (relative intensity) 304 (M^+, 18), 257 (16), 155 (100), 149 (78), 125 (49), 104 (52), 91 (38), 66 (15).

4.2.6. (1-(Naphthalen-1-yl)-2-nitroethyl)phenyl sulfide (**3ba**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J=8.5 Hz, 1H), 7.91 (d, J=8.0 Hz, 1H), 7.82 (d, J=8.2 Hz, 1H), 7.64 (tt, J=6.9, 1.2 Hz, 1H), 7.55 (tt, J=7.1, 0.8 Hz, 1H), 7.37–7.24 (m, 6H), 7.22 (d, J=7.1 Hz, 1H), 5.71 (t, J=7.4 Hz, 1H), 5.08 (dd, J=13.3, 8.4 Hz, 1H), 4.93 (dd, J=13.3, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.40, 134.36, 131.93, 131.81, 130.83, 129.55, 129.48, 129.44, 129.15, 127.17, 126.41, 125.18, 124.62, 122.87, 78.15, 45.21. m/z (relative intensity) 309 (M^+, 12), 200 (14), 154 (100), 153 (65), 152 (55), 138 (41), 134 (24), 110 (64), 109 (31), 86 (53), 84 (90), 77 (24), 66 (24), 65 (21), 51 (51). HRMS calcd for $C_{18}H_{15}NO_2S$ 309.0818, found 309.0827.

4.2.7. (1-(4-Chlorophenyl)-2-nitroethyl)phenyl sulfide (**3ca**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.28 (m, 7H), 7.20 (d, J=8.5 Hz, 2H), 4.86 (dd, J=9.2, 6.0 Hz, 1H), 4.82–4.75 (m, 1H), 4.73 (dd, J=12.5, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.13, 134.74, 134.18, 131.58, 129.66, 129.40, 129.27, 129.20, 78.52, 49.47. m/z (relative intensity) 293 (M^+, 7), 246 (11), 218 (66), 185 (12), 183 (16), 140 (30), 138 (100), 136 (21), 125 (27), 110 (37), 109 (61), 102 (23), 101 (21), 75 (15). HRMS calcd for $C_{14}H_{12}ClNO_2S$ 293.0272, found 293.0278.

4.2.8. (1-(4-Fluorophenyl)-2-nitroethyl)phenyl sulfide (**3da**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.20 (m, 7H), 7.00 (tt, J=8.6, 2.0 Hz, 2H), 4.89 (dd, J=9.4, 6.2 Hz, 1H), 4.82–4.75 (m, 1H), 4.72 (dd, J=12.8, 6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.05 (d, J_{C-F}=247 Hz), 134.10, 132.34 (d, J_{C-F}=3 Hz), 131.71, 129.65 (d, J_{C-F}=8 Hz), 129.63, 129.18, 116.29 (d, J_{C-F}=21 Hz), 78.72, 49.34. m/z (relative intensity) 277 (M^+, 11), 230 (8), 168 (7), 135 (11), 125 (14), 122 (100), 121 (12), 110 (25), 109 (29), 101 (13), 96 (10), 75 (7), 65 (11). HRMS calcd for $C_{14}H_{12}FNO_2S$ 277.0567, found 277.0578.

4.2.9. (1-(4-Methoxyphenyl)-2-nitroethyl)phenyl sulfide (**3ea**)[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.30 (m, 5H), 7.21 (d, J=8.7 Hz, 2H), 6.86 (d, J=8.6 Hz, 2H), 4.88 (dd, J=9.6, 5.8 Hz, 1H), 4.83–4.76 (m, 1H), 4.70 (dd, J=12.4, 5.7 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.94, 133.83, 132.35, 129.57, 129.05, 128.91, 128.28, 114.60, 78.97, 55.51, 49.54. m/z (relative intensity) 289 (M^+, 3), 180 (20), 154 (8), 138 (9), 135 (10), 134 (100), 119 (14), 110 (23), 91 (15), 77 (13), 65 (13), 57 (8), 51 (7). HRMS calcd for $C_{15}H_{15}NO_3S$ 289.0767, found 289.0772.

4.2.10. Benzyl(1-(4-methoxyphenyl)-2-nitroethyl)sulfide (**3eb**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.22 (m, 5H), 7.20 (d, J=8.6 Hz, 2H), 6.88 (d, J=8.6 Hz, 2H), 4.69–4.57 (m, 2H), 4.39 (dd, J=8.8, 7.0 Hz, 1H), 3.80 (s, 3H), 3.68 (d, J=13.6 Hz, 1H), 3.59 (d, J=13.6 Hz,

1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.80, 137.22, 129.18, 129.11, 129.00, 128.90, 127.69, 114.60, 79.48, 55.51, 45.64, 36.15. *m*/*z* (relative intensity) 303 (M^+, 5), 256 (4), 202 (6), 193 (34), 180 (14), 178 (10), 135 (9), 134 (100), 115 (22), 91 (69), 71 (17), 65 (14), 57 (25), 55 (11). HRMS calcd for $C_{16}H_{17}NO_3S$ 303.0924, found 303.0930.

*4.2.11. Cyclohexyl(1-(4-methoxyphenyl)-2-nitroethyl)sulfide (**3ec**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J*=8.7 Hz, 2H), 6.88 (d, *J*=8.7 Hz, 2H), 4.68 (d like, *J*=7.5 Hz, 2H), 4.59 (t like, *J*=7.8 Hz, 1H), 3.77 (s, 3H), 2.60–2.52 (m, 1H), 1.97–1.80 (m, 2H), 1.76–1.63 (m, 2H), 1.62–1.50 (m, 1H), 1.39–1.14 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.54, 129.99, 128.83, 114.45, 80.07, 55.37, 44.68, 43.89, 33.56, 33.51, 25.94, 25.84, 25.76. *m*/*z* (relative intensity) 295 (M^+, 4), 240 (4), 180 (10), 166 (4), 135 (9), 134 (100), 119 (7), 91 (7), 77 (5), 65 (4), 55 (8). HRMS calcd for $C_{15}H_{21}NO_3S$ 295.1237, found 295.1237.

*4.2.12. Hexyl(1-(4-methoxyphenyl)-2-nitroethyl)sulfide (**3ee**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J*=8.6 Hz, 2H), 6.89 (d, *J*=8.6 Hz, 2H), 4.73 (d like, *J*=7.9 Hz, 2H), 4.52 (t like, *J*=7.9 Hz, 1H), 3.81 (s, 3H), 2.44 (t, *J*=7.4 Hz, 2H), 1.53 (quint, *J*=7.3 Hz, 2H), 1.37–1.18 (m, 6H), 0.87 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.77, 129.50, 129.00, 114.59, 79.78, 55.51, 46.27, 31.85, 31.49, 29.34, 28.61, 22.67, 14.18. *m*/*z* (relative intensity) 297 (M^+, 4), 180 (10), 179 (8), 135 (12), 134 (100), 132 (12), 119 (8), 117 (6), 91 (7), 77 (6), 65 (5), 55 (4). HRMS calcd for $C_{15}H_{23}NO_3S$ 297.1393, found 297.1388.

*4.2.13. 2-(2-Nitro-1-(phenylthio)ethyl)furan (**3ga**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.15 (m, 6H), 6.29 (dd, *J*=3.2, 1.9 Hz, 1H), 6.13 (d, *J*=3.2 Hz, 1H), 4.98 (dd, *J*=8.8, 6.8 Hz, 1H), 4.86 (dd, *J*=8.8, 13.2 Hz, 1H), 4.71 (dd, *J*=13.2, 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.11, 143.14, 134.82, 130.93, 129.45, 129.35, 110.82, 108.84, 76.44, 43.54. *m*/*z* (relative intensity) 249 (M^+, 4), 218 (7), 203 (30), 140 (10), 110 (24), 109 (66), 94 (100), 77 (12), 69 (13), 66 (27), 65 (47), 63 (11), 51 (14). HRMS calcd for $C_{12}H_{11}NO_3S$ 249.0460, found 249.0464.

*4.2.14. 2-(2-Nitro-1-(phenylthio)ethyl)thiophene (**3ha**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.26 (m, 6H), 6.91 (dd, *J*=5.0, 3.7 Hz, 1H), 6.85 (d, *J*=3.4 Hz, 1H), 5.20 (dd, *J*=8.8, 6.6 Hz, 1H), 4.83 (dd, *J*=8.9, 13.1 Hz, 1H), 4.71 (dd, *J*=13.1, 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.56, 134.28, 131.59, 129.58, 129.30, 127.14, 126.51, 126.23, 79.25, 45.53. *m*/*z* (relative intensity) 265 (M^+, 5), 220 (4), 219 (13), 218 (31), 185 (8), 156 (19), 154 (9), 135 (6), 110 (100), 109 (40), 84 (8), 77 (6), 69 (7), 66 (11), 65 (19), 51 (5). HRMS calcd for $C_{12}H_{11}NO_2S_2$ 265.0226, found 265.0239.

*4.2.15. (2-Nitro-1,1-diphenylethyl)phenyl sulfide (**3ia**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.25 (m, 11H), 7.13 (t, *J*=7.8 Hz, 2H), 7.00 (d, *J*=7.2 Hz 2H), 5.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.82, 137.74, 130.04, 129.77, 129.06, 128.85, 128.23, 128.01, 82.70, 61.62. *m*/*z* (relative intensity) 335 (M^+, 2), 288 (3), 226 (85), 181 (35), 180 (100), 179 (73), 178 (74), 165 (77), 152 (18), 110 (37), 109 (21), 89 (16), 77 (16), 76 (14). HRMS calcd for $C_{20}H_{17}NO_2S$ 335.0975, found 335.0977.

*4.2.16. (2-Nitrocyclohexyl)phenyl sulfide (**3ja**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.41 (m, 2H), 7.33–7.25 (m, 3H), 4.59 (dt, *J*=9.7, 4.2 Hz, 1H), 3.86–3.81 (m, 1H), 2.23–2.01 (m, 3H), 1.94–1.73 (m, 3H), 1.58–1.48 (m, 1H), 1.44–1.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.35, 133.30, 129.32, 128.16, 85.79, 51.07, 30.98, 26.61, 22.88, 21.50. *m*/*z* (relative intensity) 237 (M^+, 11), 218 (10), 125 (68), 123 (12), 110 (22), 109 (23), 81 (100), 79 (19), 77 (12), 65 (13). HRMS calcd for $C_{12}H_{15}NO_2S$ 237.0818, found 237.0827.

4.3. Method B: general procedure for the radical substitution of thiophenol 2a with β-nitrostyrene 1a to generate phenyl(styryl)sulfane (4aa)

β-Nitrostyrene **1a** (0.298 g, 2.0 mmol) and anhydrous toluene (5 mL) were charged into a 25 mL round bottom flask. A stir bar and heating mantle were added; then a 15 cm Liebig condenser with 10 °C chilling water and drying tube were attached to the flask. The solution was preheated to reflux (150 °C) for 3 min, and thiophenol **2a** (0.62 mL, 6 mmol) was charged into flask. After 3 h, the orange reaction mixture was allowed to cool to room temperature, and the solvent was removed in vacuo. Flash column chromatography (SiO_2; ethyl acetate/hexane, 0.5:100) of the residue offered 93% yield of **4aa** as an (*E*)/(*Z*) (6:1 by NMR) mixture of colorless oil whose spectral data are consistent with the literature report.[8f,16] *(E)-isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J*=7.9 Hz, 2H), 7.36–7.22 (m, 8H), 6.91 (d, *J*=15.5 Hz, 1H), 6.75 (d, *J*=15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.56, 135.25, 131.84, 129.87, 129.19, 128.72, 127.62, 126.98, 126.05, 123.43. *m*/*z* (relative intensity) 212 (M^+, 100), 212 (10), 211 (65), 178 (40), 167 (35), 135 (22), 134 (22), 126 (36), 110 (10), 103 (12), 91 (20), 77 (25), 65 (8), 51 (18).

*4.3.1. Benzyl(styryl)sulfane (**4ab**)[17]*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.16 (m, 10H, (*E*) isomer and (*Z*) isomer), 6.73 (d, *J*=15.5 Hz, 1H, (*E*) isomer), 6.55 (d, *J*=15.5 Hz, 1H, (*E*) isomer), 6.43 (d, *J*=10.9 Hz, 1H, (*Z*) isomer), 6.26 (d, *J*=10.9 Hz, 1H, (*Z*) isomer), 4.01 (d, *J*=6.0 Hz, 2H, (*E*) isomer and (*Z*) isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.62 ((*Z*) isomer), 137.47, 137.18, 137.10 ((*Z*) isomer), 129.21 ((*Z*) isomer), 129.05, 128.91 ((*Z*) isomer), 128.90, 128.84, 128.44 ((*Z*) isomer), 128.25, 127.63 ((*Z*) isomer), 127.56, 127.22, 126.95 ((*Z*) isomer), 126.22 ((*Z*) isomer), 126.14 ((*Z*) isomer), 125.83, 124.59, 39.77 ((*Z*) isomer), 37.63. *m*/*z* (relative intensity) 226 (M^+, 22), 178 (4), 135 (14), 134 (15), 92 (9), 91 (100), 89 (3), 77 (3), 65 (16), 63 (2), 51 (3). HRMS calcd for $C_{15}H_{14}S$ 226.0811, found 226.0817.

*4.3.2. Cyclohexyl(styryl)sulfane (**4ac**)[8f]*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J*=7.4 Hz, 2H, (*Z*) isomer), 7.32 (t, *J*=7.5 Hz, 2H, (*Z*) isomer), 7.32–7.27 (m, 4H, (*E*) isomer), 7.23–7.14 (m, 1H, (*E*) isomer and (*Z*) isomer), 6.78 (d, *J*=15.6 Hz, 1H, (*E*) isomer), 6.59 (d, *J*=15.6 Hz, 1H, (*E*) isomer), 6.44 (d, *J*=11.0 Hz, 1H, (*Z*) isomer), 6.35 (d, *J*=11.0 Hz, 1H, (*Z*) isomer), 3.03–2.94 (m, 1H, (*E*) isomer), 2.94–2.84 (m, 1H, (*Z*) isomer), 2.12–2.01 (m, 2H, (*E*) isomer and (*Z*) isomer), 1.84–1.74 (m, 2H, (*E*) isomer and (*Z*) isomer), 1.68–1.57 (m, 1H, (*E*) isomer and (*Z*) isomer), 1.50–1.21 (m, 5H, (*E*) isomer and (*Z*) isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.41, 137.37 ((*Z*) isomer), 128.88, 128.85 ((*Z*) isomer), 128.81, 128.40 ((*Z*) isomer), 127.10, 126.70 ((*Z*) isomer), 126.12 ((*Z*) isomer), 125.80, 125.26 ((*Z*) isomer), 124.27, 47.99 ((*Z*) isomer), 45.56, 33.89 ((*Z*) isomer), 33.83, 26.24, 25.90, 25.83 ((*Z*) isomer). *m*/*z* (relative intensity) 218 (M^+, 41), 207 (8), 163 (11), 137 (12), 136 (100), 135 (52), 94 (30), 91 (29), 83 (11), 77 (14), 65 (11), 55 (30), 51 (10). HRMS calcd for $C_{14}H_{18}S$ 218.1129, found 218.1130.

*4.3.3. tert-Butyl(styryl)sulfane (**4ad**)[8f]*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J*=7.2 Hz, 2H, (*Z*) isomer), 7.43–7.31 (m, 4H, (*E*) isomer, and 2H, (*Z*) isomer), 7.27–7.20 (m, 1H, (*E*) isomer and (*Z*) isomer), 6.94 (d, *J*=15.4 Hz, 1H, (*E*) isomer), 6.78 (d, *J*=15.4 Hz, 1H, (*E*) isomer), 6.54 (d, *J*=11.2 Hz, 1H, (*Z*) isomer), 6.50 (d, *J*=11.2 Hz, 1H, (*Z*) isomer), 1.47 (s, 9H, (*Z*) isomer), 1.45 (s, 9H, (*E*) isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.36 ((*Z*) isomer), 137.24, 132.19, 128.89 ((*Z*) isomer), 128.79, 128.33 ((*Z*) isomer), 127.43, 126.71 ((*Z*) isomer), 126.07, 125.55 ((*Z*) isomer), 123.62 ((*Z*) isomer), 122.24, 44.66 ((*Z*) isomer), 44.51, 31.21, 30.95 ((*Z*) isomer). *m*/*z* (relative intensity) 192 (M^+, 35), 136 (100), 135 (70), 91 (37), 77 (6), 65 (5), 57 (26), 51 (5).

*4.3.4. Hexyl(styryl)sulfane (**4ae**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J=7.3 Hz, 2H, (*Z*) isomer), 7.35 (t, J=7.6 Hz, 2H, (*Z*) isomer), 7.32–7.27 (m, 4H, (*E*) isomer), 7.23–7.14 (m, 1H, (*E*) isomer and (*Z*) isomer), 6.75 (d, J=15.6 Hz, 1H, (*E*) isomer), 6.48 (d, J=15.6 Hz, 1H, (*E*) isomer), 6.44 (d, J=10.9 Hz, 1H, (*Z*) isomer), 6.26 (d, J=10.9 Hz, 1H, (*Z*) isomer), 2.80 (t, J=7.4 Hz, 2H), 1.69 (quint, J=7.4 Hz, 2H), 1.44 (quint, J=7.4 Hz, 2H), 1.37–1.24 (m, 4H), 0.90 (t, J=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.40, 128.83, 128.41 ((*Z*) isomer), 126.96, 126.88, 125.66, 125.58, 32.85, 31.59, 29.63, 28.71, 22.75, 14.23. *m*/*z* (relative intensity) 220 (M^+, 100), 136 (67), 135 (54), 134 (10), 91 (26), 77 (5), 65 (3), 51 (3). HRMS calcd for $C_{14}H_{20}S$ 220.1286, found 220.1285.

*4.3.5. (4-Methoxyphenyl)(styryl)sulfane (**4ai**)*[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J=7.7 Hz, 2H, (*Z*) isomer), 7.46 (d, J=8.6 Hz, 2H, (*E*) isomer), 7.33–7.29 (d, J=4.3 Hz, 4H, (*E*) isomer), 7.28–7.21 (m, 1H, (*E*) isomer), 6.95 (d, J=8.6 Hz, (*E*) isomer), 6.88 (d, J=15.4 Hz, (*E*) isomer), 6.56 (d, J=15.4 Hz, (*E*) isomer), 6.45 (d, J=10.8 Hz, (*Z*) isomer), 3.85 (s, 3H, (*E*) isomer), 3.84 (s, 3H, (*Z*) isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.71, 136.88, 133.61, 129.09, 128.78, 127.33, 125.96, 125.88, 115.05, 55.50. *m*/*z* (relative intensity) 243 (M^+,100), 241 (43), 227 (36), 221 (62), 197 (95), 178 (10), 165 (20), 151 (19), 134 (6), 121 (52), 103 (2).

*4.3.6. (4-Nitrophenyl)(styryl)sulfane (**4aj**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.14 (d, J=8.9 Hz, 2H, (*E*) isomer, and m, 2H, (*Z*) isomer), 7.54–7.49 (m, 4H, (*Z*) isomer), 7.45–7.31 (m, 7H, (*E*) isomer, and 3H, (*Z*) isomer), 7.03 (d, J=15.36 Hz, 1H, (*E*) isomer), 6.87 (d, J=15.36 Hz, 1H, (*E*) isomer, and 1H, (Z) isomer), 6.52 (d, J=10.52 Hz, 1H, (*Z*) isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.71, 145.97, 138.16, 135.80, 129.09, 128.95, 127.23, 126.74, 124.32, 118.36. *m*/*z* (relative intensity) 257 (M^+, 100), 213 (7), 210 (48), 184 (6), 179 (12), 178 (43), 166 (36), 135 (20), 103 (8).

*4.3.7. (2-(Naphthalen-1-yl)vinyl)(phenyl)sulfane (**4ba**)*[19a]

(E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dt, J=7.2, 1.9 Hz, 1H), 7.82 (dt, J=7.1, 2.3 Hz, 1H), 7.75 (d, J=8.2 Hz, 1H), 7.56 (d, J=7.2 Hz, 1H), 7.51–7.36 (m, 6H), 7.32 (tt, J=7.6, 1.8 Hz, 2H), 7.24 (tt, J=7.4, 2.0 Hz, 1H), 6.94 (d, J=15.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.34, 134.26, 133.77, 130.92, 129.93, 129.30, 128.94, 128.64, 128.20, 127.11, 126.31, 126.26, 126.01, 125.69, 123.78, 123.71. *m*/*z* (relative intensity) 262 (M^+, 100), 229 (23), 228 (21), 218 (40), 185 (25), 184 (22), 155 (29), 153 (63), 152 (100), 151 (26), 128 (21), 127 (36), 110 (24), 109 (39), 77 (20), 65 (20), 57 (26). HRMS calcd for $C_{18}H_{14}S$ 262.0811, found 262.0814.

4.4. Method C: general procedure for the radical substitution of α-toluenethiol 2b with (*E*)-1-(2-nitrovinyl)naphthalene 1b in the peroxide of AIBN to generate benzyl(2-(naphthalen-1-yl)vinyl)sulfane (4bb)

α-Toluenethiol **2b** (0.7 mL, 6.0 mmol), 2,2′-azobis(2-methylpropionitrile) (AIBN, 0.99 g, 6 mmol), and anhydrous benzene (8 mL) were charged into a 25 mL round bottom flask. A stir bar and heating mantle were added; then a 15 cm Liebig condenser with 10 °C chilling water and additional funnel were attached to the flask. The solution was preheated to reflux (100 °C) for 1 min, and a solution (*E*)-1-(2-nitrovinyl)naphthalene **1b** (0.40 g, 2 mmol) in 5 mL of dry benzene was added dropwise (one drop every 5–10 s). After 12 h, the reaction mixture was allowed to cool to room temperature, and the solvent was removed in vacuo. Flash column chromatography (SiO_2; ethyl acetate/hexane, 1:100) of the residue offered 90% yield of **4bb** as an (*E*)/(*Z*) (4.4:1 by NMR) mixture of colorless oil. *(E)-isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.91 (m, 1H), 7.83–7.79 (m, 1H), 7.73 (d, J=8.0 Hz, 1H), 7.49–7.21 (m, 10H), 6.76 (d, J=15.2 Hz, 1H), 4.10 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.33, 134.72, 133.68, 130.76, 128.87, 128.75, 128.48, 127.58, 127.38, 126.98, 126.02, 125.85, 125.64, 125.47, 123.82, 123.29, 37.53. *m*/*z* (relative intensity) 276 (M^+, 68), 186 (42), 185 (100), 184 (94), 152 (60), 141 (21), 92 (17), 91 (87). HRMS calcd for $C_{19}H_{16}S$ 276.0967, found 276.0965.

*4.4.1. Cyclohexyl(2-(naphthalen-1-yl)vinyl)sulfane (**4bc**)*

(E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J=7.9 Hz, 1H), 7.85–7.75 (m, 1H), 7.74 (d, J=8.1 Hz, 1H), 7.54–7.36 (m, 4H), 7.34 (d, J=15.3 Hz, 1H), 6.82 (d, J=15.3 Hz, 1H), 3.07–2.96 (m, 1H), 2.14–2.02 (m, 2H), 1.86–1.73 (m, 2H), 1.67–1.57 (m, 1H), 1.55–1.19 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.11, 133.88, 130.95, 128.66, 127.66, 127.09, 126.19, 125.98, 125.95, 125.81, 124.02, 123.36, 45.68, 33.85, 26.24, 25.88. *(Z)-isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–8.01 (m, 1H), 7.86–7.80 (m, 1H), 7.76 (d, J=8.2 Hz, 1H), 7.67 (d, J=7.1 Hz, 1H), 7.53–7.43 (m, 3H), 7.08 (d, J=10.7 Hz, 1H), 6.60 (d, J=10.7 Hz, 1H), 2.94–2.82 (m, 1H), 2.09–2.02 (m, 2H), 1.83–1.75 (m, 2H), 1.66–1.59 (m, 1H), 1.49–1.17 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.67, 133.56, 131.39, 128.57, 128.02, 127.47, 126.24, 125.83, 125.66, 125.23, 124.11, 122.58, 47.10, 33.73, 26.05, 25.64. *m*/*z* (relative intensity) 268 (M^+, 22), 186 (24), 1858 (57), 184 (100), 153 (33), 152 (62), 1395 (19), 115 (13), 83 (47), 55 (48). HRMS calcd for $C_{18}H_{20}S$ 268.1286, found 268.1278.

*4.4.2. (2-(Naphthalen-1-yl)vinyl)(phenyl)sulfane (**4bf**)*

(E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J=8.0 Hz, 1H), 7.85–7.80 (m, 1H), 7.74 (d, J=8.1 Hz, 1H), 7.53–7.38 (m, 4H), 7.24 (d, J=15.4 Hz, 1H), 6.78 (d, J=15.4 Hz, 1H), 2.85 (t, J=7.3 Hz, 2H), 1.79 (sext, J=7.3 Hz, 2H), 1.07 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.11, 133.91, 130.93, 128.69, 128.40, 127.57, 126.18, 125.98, 125.85, 124.20, 123.98, 123.33, 35.10, 23.15, 13.64. *m*/*z* (relative intensity) 228 (M^+, 61), 185 (100), 184 (75), 153 (43), 152 (66), 141 (22), 139 (18), 115 (16), 57 (24), 55 (13). HRMS calcd for $C_{15}H_{16}S$ 228.0973, found 228.0976.

*4.4.3. 2-(2-(Naphthalen-1-yl)vinylthio)ethanol (**4bg**)*

(E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J=7.9 Hz, 1H), 7.86–7.81 (m, 1H), 7.77 (d, J=8.1 Hz, 1H), 7.54–7.41 (m, 4H), 7.37 (d, J=15.3 Hz, 1H), 6.74 (d, J=15.3 Hz, 1H), 3.90 (t, J=6.0 Hz, 2H), 3.06 (t, J=6.0 Hz, 2H), 1.96 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.50, 133.77, 130.77, 128.64, 127.84, 126.93, 126.25, 125.99, 125.88, 125.75, 123.79, 123.42, 61.27, 36.06. *(Z)-isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.97 (m, 1H), 7.87–7.81 (m, 1H), 7.78 (d, J=8.2 Hz, 1H), 7.65 (d, J=7.12 Hz, 1H), 7.53–7.45 (m, 3H), 7.13 (d, J=10.5 Hz, 1H), 6.47 (d, J=10.5 Hz, 1H), 3.77 (t, J=5.9 Hz, 2H), 2.90 (t, J=5.9 Hz, 2H), 2.03 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.70, 133.22, 131.35, 128.68, 128.61, 127.93, 126.35, 126.12, 125.92, 125.25, 124.54, 124.11, 61.52, 38.02. *m*/*z* (relative intensity) 230 (M^+, 59), 185 (88), 184 (64), 165 (30), 153 (68), 152 (100), 141 (20), 115 (19), 71 (26), 69 (24), 57 (43), 55 (30). HRMS calcd for $C_{14}H_{14}OS$ 230.0760, found 230.0765.

*4.4.4. (2-(Naphthalen-1-yl)vinyl)(naphthalen-2-yl)sulfane (**4bh**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J=7.8 Hz, 1H), 7.92–7.73 (m, 6H), 7.65–7.41 (m, 8H), 7.31 (d, J=10.6 Hz, 0.1H, (*Z*) isomer), 7.06 (d, J=15.2 Hz, 1H, (*E*) isomer), 6.88 (d, J=10.6 Hz, 0.1H, (*Z*) isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.41, 134.07, 133.92, 132.84, 132.48, 131.08, 129.51, 129.03, 128.78, 128.41, 128.34, 128.01, 127.75, 127.53, 126.95, 126.49, 126.34, 126.17, 126.14, 125.84, 123.93, 123.92. *m*/*z* (relative intensity) 312 (M^+, 100), 279 (56), 278 (24), 185 (41), 184 (43), 153 (34), 152 (89), 57 (31). HRMS calcd for $C_{22}H_{16}S$ 312.0967, found 312.0966.

*4.4.5. (4-Chlorostyryl)(phenyl)sulfane (**4ca**)*[19a]

(E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.39 (m, 2H), 7.36–7.31 (m, 2H), 7.29–7.21 (m, 5H), 6.88 (d, J=15.4 Hz, 1H), 6.65 (d, J=15.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.10, 134.73, 133.15,

130.25, 129.79, 129.27, 128.87, 127.27, 127.15, 124.71. *m*/*z* (relative intensity) 246 (M^+, 100), 218 (28), 211 (41), 210 (24), 201 (23), 178 (50), 166 (18), 165 (23), 134 (28), 121 (24), 109 (27), 71 (19), 57 (33). HRMS calcd for $C_{14}H_{11}ClS$ 246.0265, found 246.0264.

*4.4.6. (4-Fluorostyryl)(phenyl)sulfane (**4da**)*[7i]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.44 (m, 6H, (*Z*) isomer), 7.42 (d, *J*=8.2 Hz, 2H, (*E*) isomer), 7.37–7.23 (m, 5H, (*E*) isomer), 7.07 (t, *J*=8.6 Hz, 2H, (*Z*) isomer), 6.99 (t, *J*=8.6 Hz, 2H, (*E*) isomer), 6.88 (d, *J*=15.4 Hz, 1H, (*E*) isomer), 6.70 (d, *J*=15.4 Hz, 1H, (*E*) isomer), 6.56 (d, *J*=10.7 Hz, 1H, (*Z*) isomer), 6.48 (d, *J*=10.7 Hz, 1H, (*Z*) isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.71 (d, J_{C-F}=246 Hz), 163.10 (d, J_{C-F}=247 Hz, (*Z*) isomer), 136.13 ((*Z*) isomer), 135.29, 132.99 (d, J_{C-F}=3 Hz), 132.86 (d, J_{C-F}=3 Hz, (*Z*) isomer), 130.79, 130.67 (d, J_{C-F}=8 Hz, (*Z*) isomer), 130.27 ((*Z*) isomer), 130.09, 129.39, 129.26 ((*Z*) isomer), 127.78 (d, J_{C-F}=8 Hz), 127.48 ((*Z*) isomer), 127.23, 126.40 ((*Z*) isomer), 125.82 (d, J_{C-F}=2 Hz, (*Z*) isomer), 123.35 (d, J_{C-F}=2 Hz), 115.94 (d, J_{C-F}=22 Hz), 115.56 (d, J_{C-F}=22 Hz, (*Z*) isomer). *m*/*z* (relative intensity) 230 (M^+, 100), 229 (28), 196 (19), 185 (21), 165 (13), 139 (11), 121 (17), 109 (20). HRMS calcd for $C_{14}H_{11}FS$ 230.0560, found 230.0571.

*4.4.7. (4-Methoxystyryl)(phenyl)sulfane (**4ea**)*[19]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J*=8.7 Hz, 2H, (*Z*) isomer), 7.45 (d, *J*=7.3 Hz, 2H, (*Z*) isomer), 7.39 (d, *J*=7.4 Hz, 2H, (*E*) isomer), 7.35–7.25 (m, 4H, (*E*) isomer, and 1H, (*Z*) isomer), 7.25–7.18 (m, 1H, (*E*) isomer, and 2H, (*Z*) isomer), 6.93 (d, *J*=8.7 Hz, 2H, (*Z*) isomer), 6.86 (d, *J*=8.7 Hz, 2H, (*E*) isomer), 6.77 (d, *J*=15.4 Hz, 1H, (*E*) isomer), 6.72 (d, *J*=15.4 Hz, 1H, (*E*) isomer), 6.56 (d, *J*=10.6 Hz, 1H, (*Z*) isomer), 6.38 (d, *J*=10.6 Hz, 1H, (*Z*) isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.55, 136.13, 132.92, 130.35 ((*Z*) isomer), 130.04 ((*Z*) isomer), 129.56, 129.42, 129.31 ((*Z*) isomer), 129.26, 127.56, 127.40 ((*Z*) isomer), 127.19 ((*Z*) isomer), 126.77, 123.40 ((*Z*) isomer), 120.24, 114.32, 113.93 ((*Z*) isomer), 55.50. *m*/*z* (relative intensity) 242 (M^+, 23), 218 (39), 152 (21), 135 (100), 121 (14), 110 (20), 109 (39), 107 (18), 92 (20), 77 (38), 65 (23). HRMS calcd for $C_{15}H_{14}OS$ 242.0760, found 242.0767.

*4.4.8. Benzyl(4-methoxystyryl)sulfane (**4eb**)*[20]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J*=8.7 Hz, 2H, (*Z*) isomer), 7.37–7.22 (m, 5H, (*E*) isomer and (*Z*) isomer), 7.19 (d, *J*=8.6 Hz, 2H, (*E*) isomer), 6.88 (d, *J*=8.7 Hz, 2H, (*Z*) isomer), 6.82 (d, *J*=8.6 Hz, 2H, (*E*) isomer), 6.56 (d, *J*=15.5 Hz, 1H, (*E*) isomer), 6.51 (d, *J*=15.5 Hz, 1H, (*E*) isomer), 6.38 (d, *J*=10.8 Hz, 1H, (*Z*) isomer), 6.12 (d, *J*=10.8 Hz, 1H, (*Z*) isomer), 3.97 (s, 2H, (*E*) isomer and (*Z*) isomer), 3.79 (s, 3H, (*Z*) isomer), 3.78 (s, 3H, (*E*) isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.08, 158.51 ((*Z*) isomer), 137.65, 130.22 ((*Z*) isomer), 130.05, 129.98 ((*Z*) isomer), 129.18 ((*Z*) isomer), 129.03, 128.86 ((*Z*) isomer), 128.82, 128.69, 127.55 ((*Z*) isomer), 127.45, 127.05, 125.76 ((*Z*) isomer), 123.62 ((*Z*) isomer), 121.73, 114.25, 113.85 ((*Z*) isomer), 55.50, 39.67 ((*Z*) isomer), 37.85. *m*/*z* (relative intensity) 256 (M^+, 79), 165 (71), 150 (65), 134 (15), 122 (14), 121 (19), 91 (100), 65 (18). HRMS calcd for $C_{16}H_{16}OS$ 256.0922, found 256.0919.

*4.4.9. Cyclohexyl(4-methoxystyryl)sulfane (**4ec**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J*=8.6 Hz, 2H, (*Z*) isomer), 7.22 (d, *J*=8.6 Hz, 2H, (*E*) isomer), 6.88 (d, *J*=8.6 Hz, 2H, (*Z*) isomer), 6.82 (d, *J*=8.6 Hz, 2H, (*E*) isomer), 6.61 (d, *J*=15.5 Hz, 1H, (*E*) isomer), 6.55 (d, *J*=15.5 Hz, 1H, (*E*) isomer), 6.37 (d, *J*=10.9 Hz, 1H, (*Z*) isomer), 6.18 (d, *J*=10.9 Hz, 1H, (*Z*) isomer), 2.95–2.87 (m, 1H, (*E*) isomer), 2.88–2.80 (m, 1H, (*Z*) isomer), 2.05–1.98 (m, 2H, (*E*) isomer and (*Z*) isomer), 1.81–1.73 (m, 2H, (*E*) isomer and (*Z*) isomer), 1.64–1.56 (m, 1H, (*E*) isomer and (*Z*) isomer), 1.48–1.20 (m, 5H, (*E*) isomer and (*Z*) isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.89, 158.22 ((*Z*) isomer), 130.14 ((*Z*) isomer), 130.02, 129.27, 126.90, 124.76 ((*Z*) isomer), 123.37 ((*Z*) isomer), 121.22, 114.10, 113.67 ((*Z*) isomer), 55.32, 55.28 ((*Z*) isomer), 47.67 ((*Z*) isomer), 45.45, 33.75 ((*Z*) isomer), 33.69, 26.11, 25.80, 25.72 ((*Z*) isomer). *m*/*z* (relative intensity) 248 (M^+, 55), 219 (17), 166 (100), 151 (63), 135 (29), 121 (26), 107 (8), 91 (11), 77 (12), 55 (23). HRMS calcd for $C_{15}H_{20}OS$ 248.1235, found 248.1242.

*4.4.10. tert-Butyl(4-methoxystyryl)sulfane (**4ed**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J*=8.6 Hz, 2H, (*Z*) isomer), 7.30 (d, *J*=8.6 Hz, 2H, (*E*) isomer), 6.90 (d, *J*=8.6 Hz, 2H, (*Z*) isomer), 6.86 (d, *J*=8.6 Hz, 2H, (*E*) isomer), 6.70 (s, 2H, (*E*) isomer), 6.45 (d, *J*=11.1 Hz, 1H, (*Z*) isomer), 6.32 (d, *J*=11.1 Hz, 1H, (*Z*) isomer), 3.81 (s, 3H, (*E*) isomer and (*Z*) isomer), 1.42 (s, 9H, (*Z*) isomer), 1.39 (s, 9H, (*E*) isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.33, 158.41 ((*Z*) isomer), 133.13, 130.33 ((*Z*) isomer), 130.26, 130.17 ((*Z*) isomer), 127.41, 125.36 ((*Z*) isomer), 121.09 ((*Z*) isomer), 119.28, 114.27, 113.79 ((*Z*) isomer), 5.53, 55.48 ((*Z*) isomer), 44.59 ((*Z*) isomer), 44.51, 31.18, 30.98 ((*Z*) isomer). *m*/*z* (relative intensity) 222 (M^+, 29), 166 (100), 165 (26), 151 (12), 150 (11), 135 (24), 121 (21), 77 (6), 57 (15), 51 (3). HRMS calcd for $C_{13}H_{18}OS$ 222.1078, found 222.1078.

*4.4.11. Hexyl(4-methoxystyryl)sulfane (**4ee**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J*=8.6 Hz, 2H, (*Z*) isomer), 7.24 (d, *J*=8.6 Hz, 2H, (*E*) isomer), 6.90 (d, *J*=8.6 Hz, 2H, (*Z*) isomer), 6.85 (d, *J*=8.6 Hz, 2H, (*E*) isomer), 6.57 (d, *J*=15.6 Hz, 1H, (*E*) isomer), 6.46 (d, *J*=11.1 Hz, 1H, (*E*) isomer), 6.39 (d, *J*=10.8 Hz, 1H, (*Z*) isomer), 6.12 (d, *J*=10.8 Hz, 1H, (*Z*) isomer), 3.81 (s, 3H, (*Z*) isomer), 3.80 (s, 3H, (*E*) isomer), 2.77 (t, *J*=7.4 Hz, 2H, (*E*) isomer and (*Z*) isomer), 1.68 (quint, *J*=7.4 Hz, 2H, (*E*) isomer and (*Z*) isomer), 1.43 (quint, *J*=7.4 Hz, 2H, (*E*) isomer and (*Z*) isomer), 1.35–1.25 (m, 4H, (*E*) isomer and (*Z*) isomer), 0.89 (t, *J*=6.9 Hz, 3H, (*E*) isomer and (*Z*) isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.73, 158.22 ((*Z*) isomer), 130.17 ((*Z*) isomer), 130.02 ((*Z*) isomer), 129.95, 127.09, 126.68, 125.11 ((*Z*) isomer), 124.94 ((*Z*) isomer), 122.63, 114.09, 113.66 ((*Z*) isomer), 55.33, 55.29 ((*Z*) isomer), 35.85 ((*Z*) isomer), 32.89, 31.41, 30.22 ((*Z*) isomer), 29.51, 28.51, 28.32 ((*Z*) isomer), 22.56, 14.04. *m*/*z* (relative intensity) 251 (M+1, 26), 250 (M^+, 100), 248 (22), 166 (88), 165 (53), 151 (47), 150 (46), 135 (45), 134 (65), 121 (52), 91 (14), 89 (13), 77 (16), 55 (15). HRMS calcd for $C_{15}H_{22}OS$ 250.1391, found 250.1370.

*4.4.12. (2-Nitrostyryl)(phenyl)sulfane (**4fa**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J*=8.2 Hz, 1H, (*Z*) isomer), 7.93 (d, *J*=8.2 Hz, 1H, (*E*) isomer), 7.77 (d, *J*=7.7 Hz, 1H, (*Z*) isomer), 7.69 (d, *J*=7.9 Hz, 1H, (*Z*) isomer), 7.64 (t like, *J*=7.7 Hz, 1H, (*Z*) isomer), 7.58–7.25 (m, 8H, (*E*) isomer, and 5H, (*Z*) isomer), 7.09 (d, *J*=15.3 Hz, 1H, (*E*) isomer), 7.01 (d, *J*=10.6 Hz, 1H, (*Z*) isomer), 6.98 (d, *J*=15.4 Hz, 1H, (*E*) isomer), 6.71 (d, *J*=10.6 Hz, 1H, (*Z*) isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.20, 137.02, 133.49, 133.23, 133.02 ((*Z*) isomer), 132.35, 131.59, 131.32, 131.23 ((*Z*) isomer), 130.37 ((*Z*) isomer), 130.28 ((*Z*) isomer), 129.62, 129.48 ((*Z*) isomer), 128.20, 127.86, 127.69 ((*Z*) isomer), 125.03, 124.96 ((*Z*) isomer), 123.92, 123.65 ((*Z*) isomer).

*4.4.13. 2-(2-(Phenylthio)vinyl)furan (**4ga**)*[21]

(E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dt like, *J*=7.1, 1.4 Hz, 2H), 7.34–7.26 (m, 3H), 7.22 (tt like, *J*=7.4, 1.2 Hz, 1H), 6.84 (d, *J*=15.3 Hz, 1H), 6.48 (d, *J*=15.3 Hz, 1H), 6.33 (dd, *J*=3.3, 1.8 Hz, 1H), 6.14 (d, *J*=3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.22, 142.16, 134.94, 130.11, 129.29, 127.16, 122.29, 119.70, 111.55, 107.51. *(Z)-isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.42 (m, 3H), 7.33 (t, *J*=7.1 Hz, 2H), 7.26 (tt like, *J*=7.3, 1.2 Hz, 1H), 6.55 (d, *J*=3.4 Hz, 1H), 6.46 (dd, *J*=3.4, 1.9 Hz, 1H), 6.46 (d, *J*=10.8 Hz, 1H), 6.39 (d, *J*=10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.15, 141.78, 135.91, 130.28, 129.26, 127.38, 124.30, 115.16, 111.72, 109.94. *m*/*z* (relative intensity) 202 (M^+, 100), 173 (23), 157 (18), 141 (15), 121 (14), 91

(24), 77 (15), 69 (45), 64 (27), 57 (21). HRMS calcd for $C_{12}H_{10}OS$ 202.0447, found 202.0452.

4.4.14. 2-(2-(Phenylthio)vinyl)thiophene (**4ha**)[22]

(E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dt, J=7.4, 1.3 Hz, 2H), 7.32 (tt, J=7.3, 1.0 Hz, 2H), 7.24 (tt, J=7.0, 1.2 Hz, 1H), 7.14 (d, J=5.0 Hz, 1H), 6.96 (dd, J=5.0, 3.6 Hz, 1H), 6.91 (d, J=3.1 Hz, 1H), 6.86 (d, J=15.2 Hz, 1H), 6.71 (d, J=15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.45, 135.10, 129.86, 129.25, 127.57, 127.07, 125.54, 125.31, 124.43, 122.51. *(Z)-isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J=7.7 Hz, 2H), 7.38–7.30 (m, 3H), 7.26 (t, J=7.4 Hz, 1H), 6.17 (d, J=3.4 Hz, 1H), 7.06 (dd, J=4.9, 3.8 Hz, 1H), 6.84 (d, J=10.3 Hz, 1H), 6.40 (d, J=10.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.02, 135.81, 129.92, 129.26, 128.03, 127.20, 126.95, 126.22, 123.00, 121.55. m/z (relative intensity) 218 (M^+, 100), 185 (33), 184 (30), 173 (34), 121 (23), 109 (10), 97 (15), 77 (7), 69 (7), 65 (13), 51 (8). HRMS calcd for $C_{12}H_{10}S_2$ 218.0218, found 218.0220.

4.4.15. (2,2-Diphenylvinyl)(phenyl)sulfane (**4ia**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.21 (m, 15H), 6.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.66, 141.28, 139.38, 136.69, 129.96, 129.72, 129.32, 128.59, 128.51, 128.02, 127.50, 127.40, 126.98, 124.30. m/z (relative intensity) 288 (M^+, 85), 287 (36), 178 (55), 165 (24), 109 (17), 105 (100), 77 (31), 57 (27). HRMS calcd for $C_{20}H_{16}S$ 288.0967, found 288.0967.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.02.074.

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