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Stereoselective Synthesis of Trisubstituted Alkenes Containing (*Z*)-Allylthio Units from the Acetates of Baylis–Hillman Adducts

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ABSTRACT: *A series of trisubstituted alkenes containing (Z)-allylthio moieties as key structural units, that is, sodium (Z)-allyl thiosulfates, symmetrical di(Z-allyl) sulfides, and di(Z-allyl) disulfides, unsymmetrical diallyl sulfides were prepared in moderate to good yields via chemical transformations from the acetates of Baylis–Hillman adducts.* Heteroatom Chem 19:188–198, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20394

INTRODUCTION

Trisubstituted alkenes have received much attention as a class of important compounds in organic synthesis because such moieties manifested a significant role in many biologically active compounds, such as terpenoids, insect pheromones, and antibiotics and so on [1]. The biological properties of these alkenes are highly dependent on the configuration of the C=C bonds [2]. Therefore, a number of methods have been developed for the stereoselective synthesis of trisubstituted alkenes [2,3]. In view of their significance in organic synthesis and potential bioactivity, it is still desirable to extend the scope of trisubstituted alkene family and develop new and convenient synthetic routes.

The Baylis–Hillman reaction is well known as a powerful carbon–carbon bond-forming reaction providing synthetically useful multifunctional adducts [4]. These adducts have been widely utilized as useful precursors for stereoselective synthesis of various trisubstituted alkenes [4,5].

Organosulfur compounds possessing allylthio moieties serve as important building blocks in organic synthesis [6–9] and have potential bioactivity [10]. As our interest in conversion of Baylis–Hillman adducts into trisubstituted alkenes [11], we herein report the results on the stereoselective synthesis of a series of trisubstituted alkenes containing allylthio moieties, that is, sodium (*Z*)-allyl thiosulfates, symmetrical di(*Z*-allyl) sulfides, and di(*Z*-allyl) disulfides, unsymmetrical diallyl sulfides, via chemical transformations from the acetates of Baylis–Hillman adducts (derived from acrylate esters). A part of preliminary results have been published [12]. Some allyl sulfide analogs prepared from Baylis–Hillman alcohols or Baylis-Hillman bromides by other approaches have been previously reported in the literature [13].

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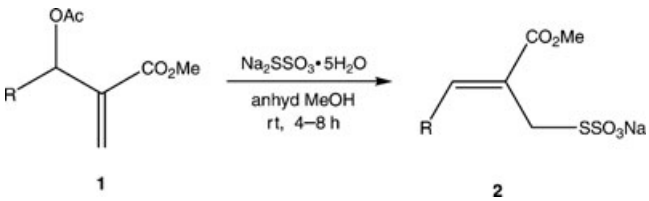
RESULTS AND DISCUSSION

Synthesis of Sodium(Z)-allyl Thiosulfates and Symmetrical DI(Z-allyl) Sulfides

At the beginning of this study, synthesis of sodium (*Z*)-allyl thiosulfates (Baylis–Hillman adduct-derived Bunte salts) was tried. Treatment of Baylis–Hillman acetates **1** with sodium thiosulfate pentahydrate in anhydrous methanol at room temperature afforded the corresponding Bunte salts **2** in almost quantitative yields (Scheme 1 and Table 1).

A series of solvents were tested to optimize the reaction conditions (Table 1, entry 1 and 2). When Et_2O, CH_2Cl_2, THF, and CH_3CN were used as solvent, the reaction proceeded slowly and gave poor yields of products; fairly good yield was obtained in DMF, whereas the best result was found in anhydrous MeOH. A variety of substrates were used in this reaction to establish the generality and efficiency, and all reactions proceeded smoothly under similar conditions. The experimental results showed that the present method was effective for substrates possessing either aryl groups (Table 1, entries 2–10) or alkyl ones (Table 1, entries 11 and 12). Among substrates bearing aryl groups, those containing electron-withdrawing functionalities reacted more slowly and gave slightly reduced yields of products (Table 1, entry 9).

The reactions exhibited high stereoselectivity. In all cases, the allylthio moieties in **2** took a *Z* configuration. The *Z* configuration of the products was assigned by comparing the chemical shifts in ^{1}H NMR with reported relevant values of trisubstituted alkenes. According to the reports published in the literature, in the ^{1}H NMR spectrum of a trisubstituted alkene the β-vinylic proton, cis- and trans- to the ester group are known to resonate at δ 7.5 and δ 6.5, respectively, when alkene is substituted by an aryl group; whereas the same proton cis- and trans- to an ester group appears at δ 6.8 and δ 5.7, respectively, when substituted by an alkyl one [14]. It was finally confirmed by NOESY experiments. According to these experiments, there is no NOE correlation between the signal of the internal olefin proton and the allylic methylene protons.

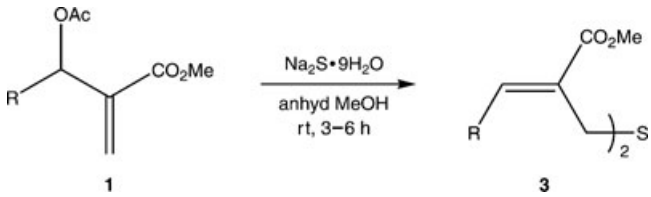


SCHEME 1

TABLE 1 Preparation of Sodium (*Z*)-Allyl Thiosulfates **2** from the Baylis–Hillman Acetates **1**[a]

Entry	R	Product (**2**)[b]	Solvent	Time (h)	Yield[c] (%)
1	C_6H_5 (**1a**)	**2a**	Et_2O	4.0	30
			CH_2Cl_2	4.0	45
			THF	4.0	38
			CH_3CN	4.0	52
			DMF	4.0	84
2	C_6H_5 (**1a**)	**2a**	MeOH	4.0	97
3	4-$CH_3C_6H_4$ (**1b**)	**2b**	MeOH	4.0	98
4	4-ClC_6H_4 (**1c**)	**2c**	MeOH	4.0	95
5	2-ClC_6H_4 (**1d**)	**2d**	MeOH	4.0	94
6	4-$CH_3OC_6H_4$ (**1e**)	**2e**	MeOH	4.0	97
7	2-$CH_3OC_6H_4$ (**1f**)	**2f**	MeOH	4.0	96
8	3,4-$OCH_2OC_6H_3$ (**1g**)	**2g**	MeOH	4.0	95
9	2-$NO_2C_6H_4$ (**1h**)	**2h**	MeOH	8.0	93
10	2-Furyl (**1i**)	**2i**	MeOH	4.0	95
11	$C_6H_5CH_2CH_2$ (**1j**)	**2j**	MeOH	5.0	94
12	*n*-C_7H_{15} (**1k**)	**2k**	MeOH	5.0	92

[a]Reagents and conditions: **1** (1 mmol), $Na_2SSO_3{\cdot}5H_2O$ (1 mmol), MeOH (15 mL), room temperature, 4.0–8.0 h.
[b]All new products were characterized by ^{1}H NMR, MS, IR, and elemental analysis.
[c]Isolated yields.



SCHEME 2

Encouraged by the successful synthesis of **2** from **1** and $Na_2SSO_3{\cdot}5H_2O$, we expected that symmetrical diallyl sulfides would be obtained if **1** would be allowed to react with Na_2S. Indeed, when 1 equivalent of **1** was treated with 0.55 equivalent of $Na_2S{\cdot}9H_2O$ in anhydrous methanol under similar reaction conditions, symmetrical di(*Z*-allyl) sulfides **3** were produced in high yields (Scheme 2 and Table 2). It was found that the required reaction time, effect of substituted groups, and stereoselectivity of the reaction were similar to the cases in the reaction of **1** with $Na_2SSO_3{\cdot}5H_2O$.

Synthesis of Unsymmetrical Diallyl Sulfides

With sodium (*Z*)-allyl thiosulfates were in hand, we next investigated whether the in situ prepared Bunte salts **2** could be used as intermediates for further transformations without purification, since the process showed very clean conversion, thus giving opportunities to synthesize other advanced molecules in convenient one-pot manner. For the initial try,

TABLE 2 Preparation of Symmetrical Di(*Z*-allyl) Sulfides **3** from the Baylis–Hillman Acetates **1**[a]

Entry	*R*	*Product* (**3**)[b]	*Time (h)*	*Yield*[c] *(%)*
1	C_6H_5 (**1a**)	**3a**	3.0	94
2	4-$CH_3C_6H_4$ (**1b**)	**3b**	3.0	95
3	4-ClC_6H_4 (**1c**)	**3c**	3.0	91
4	2-ClC_6H_4 (**1d**)	**3d**	3.0	92
5	2-$CH_3OC_6H_4$ (**1f**)	**3f**	3.0	90
6	3,4-$OCH_2OC_6H_3$ (**1g**)	**3g**	3.0	90
7	2-$NO_2C_6H_4$ (**1h**)	**3h**	6.0	89
8	2-Furyl (**1i**)	**3i**	3.0	91
9	$C_6H_5CH_2CH_2$ (**1j**)	**3j**	5.0	90
10	*n*-C_7H_{15} (**1k**)	**3k**	5.0	88
11	Et (**1l**)	**3l**	5.0	87

[a]Reagents and conditions: **1** (1 mmol), $Na_2S{\cdot}9H_2O$ (0.55 mmol), MeOH (15 mL), room temperature, 3.0–6.0 h.
[b]All new products were characterized by ^{1}H NMR, MS, IR, and elemental analysis.
[c]Isolated yields.

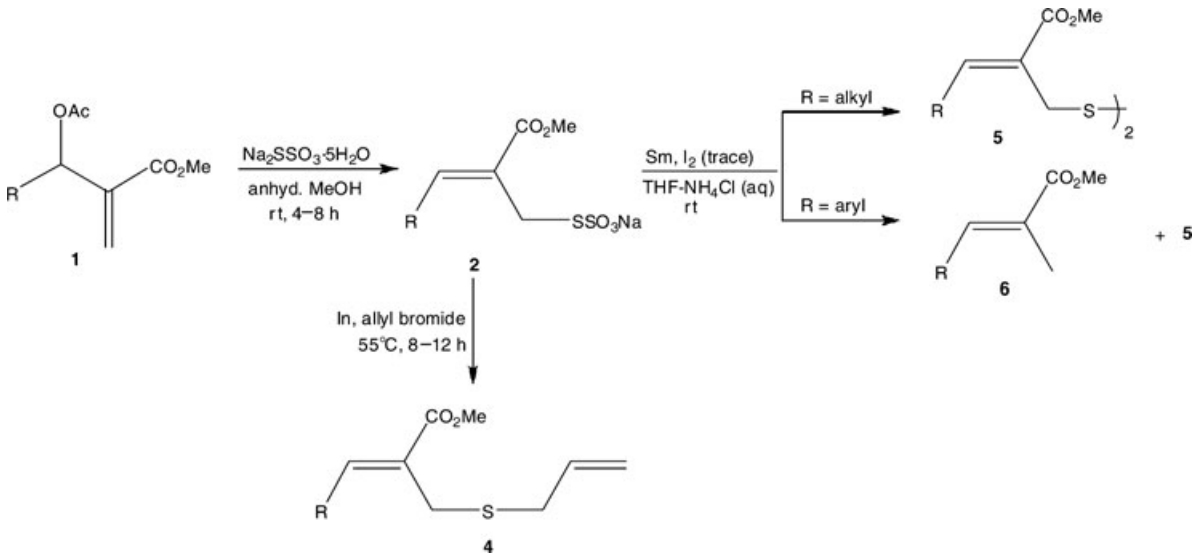
TABLE 3 Preparation of Unsymmetrical Diallyl Sulfides **4** from the Allylic Acetates **1**, $Na_2SSO_3{\cdot}5H_2O$, and Allyl Bromide Promoted by Indium[a]

Entry	*R*	*Product* (**4**)[b]	*Time (h)*[c]	*Yield*[d] *(%)*
1	C_6H_5 (**1a**)	**4a**	8.0	75
				0[e]
				38[f]
2	4-$CH_3C_6H_4$ (**1b**)	**4b**	8.0	76
3	4-ClC_6H_4 (**1c**)	**4c**	8.0	74
4	2-ClC_6H_4 (**1d**)	**4d**	8.0	58
5	4-$CH_3OC_6H_4$ (**1e**)	**4e**	8.0	67
6	2-$CH_3OC_6H_4$ (**1f**)	**4f**	8.0	65
7	3,4-$OCH_2OC_6H_3$ (**1g**)	**4g**	8.0	63
8	2-$NO_2C_6H_4$ (**1h**)	**4h**	8.0	64
9	2-Furyl (**1i**)	**4i**	8.0	68
10	$C_6H_5CH_2CH_2$ (**1j**)	**4j**	12.0	63
11	*n*-C_7H_{15} (**1k**)	**4k**	12.0	61

[a]Reagents and conditions: **1** (1 mmol), $Na_2SSO_3{\cdot}5H_2O$ (1 mmol), MeOH (15 mL), room temperature., 4.0–8.0 h, then allyl bromide (3 mmol), In (1.5 mmol), 55°C, 8.0–12.0 h.
[b]All products were characterized by ^{1}H NMR, MS, IR, and elemental analysis.
[c]Time needed for indium-mediated allylation.
[d]Isolated yields.
[e]Indium-mediated allylation was carried out at room temperature.
[f] 1 mmol allyl bromide and 1 mmol indium were used.

indium-mediated reaction [15] of allyl bromide with **2** was tested. Successfully, the reaction afforded unsymmetrical diallylsulfides **4** in moderate to good yields (Scheme 3 and Table 3).

The indium-mediated allylation of **2** proceeded smoothly at 55°C, whereas no reaction occurred at room temperature (Table 3, entry 1). To obtain desirable yield of products, using excessive amount of allyl bromide (3 equivalents) and indium (1.5 equivalents) was necessary for the reaction (Table 3, entry 1). The generality of the reaction was established by examining various substrates. The acetates of Baylis–Hillman alcohols having either aryl (with electron-donating as well as electron-withdrawing functionalities) or alkyl groups could be converted to the corresponding unsymmetrical diallylsulfides in moderate to good yields. Upon formation of **4**, the *Z* configuration of the allylthio moiety in **2** was entirely conserved. Besides, the reaction exhibited excellent regioselectivity. Only *S*-allylated products **4** were obtained, whereas no 1,4- or 1,2-allylated derivatives were detected if taking **2** as α,β-unsaturated carbonyl compounds.



SCHEME 3

TABLE 4 Preparation of Symmetrical Di(*Z*-allyl) Disulfides **5** or Methyl Cinnamic Esters **6**[a]

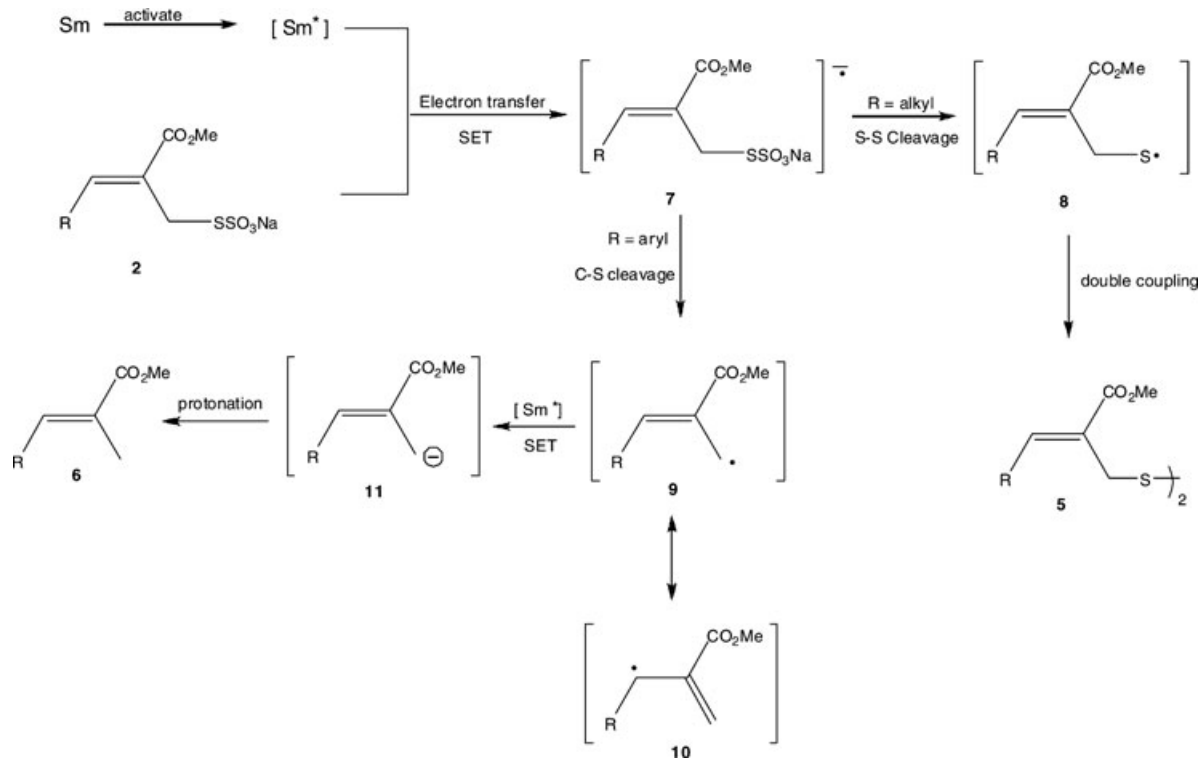
			Yield[c] *(%)*	
Entry	*R*	*Time (h)*[b]	**5**[d]	**6**[d]
1	$C_6H_5CH_2CH_2$ (**1j**)	3.0	84 (**5j**)	–[e]
2	*n*-C_7H_{15} (**1k**)	3.0	82 (**5k**)	–[e]
3	Et (**1l**)	3.0	74 (**5l**)	–[e]
4	C_6H_5 (**1a**)	4.0	<5	83 (**6a**)
5	4-$CH_3C_6H_4$ (**1b**)	4.0	<5	85 (**6b**)
6	4-ClC_6H_4 (**1c**)	4.0	Trace	84 (**6c**)
7	2-ClC_6H_4 (**1d**)	4.0	Trace	80 (**6d**)
8	2-$CH_3OC_6H_4$ (**1f**)	4.0	<7	78 (**6f**)
9	3,4-$OCH_2OC_6H_3$ (**1g**)	4.0	<5	77 (**6g**)

[a]Reagents and conditions: **1** (1 mmol), $Na_2SSO_3{\cdot}5H_2O$ (1 mmol), MeOH (15 mL), room temperature, 4.0–8.0 h, then samarium (1 mmol), I_2 (trace), THF (20 mL), NH_4Cl saturated solution (4 mL), room temperature, 3.0–4.0 h.
[b]Time needed for Sm/I_2(trace) system-mediated reduction.
[c]Isolated yields.
[d]All new products were characterized by ^{1}H NMR, MS, IR, and elemental analysis.
[e]Not detected.

Synthesis of Symmetrical Diallyl Disulfides or Methyl Cinnamic Esters via Selective Cleavage of S–S or C–S bonds in **2** *Promoted by a Sm/I_2 (trace) System*

Diallyl disulfides are a class of useful and important building blocks in organic synthesis as well as potential bioactive compounds [6,10]. Encouraged by the successful synthesis of **4** from the in situ prepared **2**, we further wanted to obtain symmetrical diallyl disulfides in one-pot strategy by treatment of **2** with a Sm/I_2(trace) system under aqueous media [16]. Interestingly, selective cleavage of the S–S or C–S bonds in Bunte salts **2** was achieved to form corresponding di(*Z*-allyl) disulfides or methyl cinnamic esters in moderate to good yields (Scheme 3 and Table 4). Thus, when **2** derived from those alkyl-substituted **1** was used as substrates, the reaction proceeded smoothly and gave di(*Z*-allyl) disulfides **5** in moderate to good yields (Table 3, entries 1–3). However, when **2** derived from those aryl-substituted **1** was allowed to react in the same conditions, selective cleavage of the C–S bonds predominated to give methyl cinnamic esters **6** (methyl cinnamic eaters prepared from Baylis–Hillman adducts or derivatives by other approaches, see [17]) in moderate to good yields whereas di(*Z*-allyl) disulfides **5** from the cleavage of the S–S bonds were only obtained in very less amount (Table 3, entries 4–9).

A possible mechanism for the selective cleavage of the S–S or C–S bonds in **2** is depicted in Scheme 4. Perhaps the samarium powder was activated by I_2 and aqueous NH_4Cl [16b,18], thus an electron was transferred to the substrate **2** to form the radical



SCHEME 4

anion **7** [19]; when R was an alkyl group, selective cleavage of the S—S bond occurred to form S-radical intermediate **8**, which then dimerized to afford the di(*Z*-allyl) disulfide **5**; but when R was an aryl group, cleavage of the C—S bond may be predominated to give allyl radical species **9** or **10**. Then, **9** received another electron from Sm to produce allyl anion intermediate **11**. Here, the attached aryl group in the allyl moiety may be capable of stabilizing the allyl anion, so that the methyl cinnamic ester **6** could be formed by protonation of the intermediate **11**.

CONCLUSION

In summary, a series of trisubstituted alkenes containing *Z*-allylthio moieties as the key structural units were prepared in moderate to good yields via chemical transformations from the acetates of Baylis–Hillman adducts. These compounds included sodium (*Z*)-allyl thiosulfates, symmetrical di(*Z*-allyl) sulfides and di(*Z*-allyl) disulfides, and unsymmetrical diallyl sulfides. Besides, it was found that the Sm and a trace amount of I_2 system could be used for the selective cleavage of the S—S or C—S bonds in sodium (*Z*)-allyl thiosulfates depending on the substituents (alkyl or aryl group) to give the corresponding di(*Z*-allyl) disulfides or methyl cinnamic esters, respectively. The notable advantages of these reactions were easy availability of the starting materials, high stereoselectivity and/or regioselectivity, simple one-pot operation, and mild reaction conditions.

EXPERIMENTAL

General

Melting points are uncorrected. IR spectra were recorded on a Bruker Victor 22 spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AC-400 spectrometer for solutions in $CDCl_3$ or DMSO-d^6 with TMS as internal standard. Chemical shifts (δ) are expressed in ppm, and coupling constants J are given in hertz. Mass spectra were obtained on a HP 5989B mass spectrometer. Elemental analyses were performed on a EA-1110 instrument. All Baylis–Hillman acetates were prepared according to the reported methods in the literature [20].

General Procedure for Preparation of Sodium (Z)-Allyl Thiosulfates **2** from the Baylis–Hillman Acetates **1** and Sodium Thiosulfate Pentahydrate

In a 25-mL flask, $Na_2SSO_3{\cdot}5H_2O$ (0.25 g, 1 mmol), Baylis–Hillman acetate **1** (1 mmol), and anhydrous MeOH (15 mL) were added. The mixture was stirred at room temperature for 4–8 h. Then to the resultant mixture, silica gel powder (2.0 g) was added. After evaporation of solvent, we got silica gel-absorbed powder of crude product, which was loaded to chromatography column for further purification using MeOH-EtOAc (1:1) as eluent.

Compound **2a**. White solid. mp 106–108°C; IR (KBr): 3082, 3026, 1714 (C=O), 1625 (C=C), 1250, 1147 (SO_3^-) cm^{-1}; ^{1}H NMR (DMSO-d^6, 400 MHz) δ: 3.71 (s, 3H, OCH_3), 4.05 (s, 2H, methylene-*H*), 7.38–7.46 (m, 3H, Ar*H*), 7.63 (s, 1H, ArC*H*=), 7.67–7.72 (m, 2H, Ar*H*); ^{13}C NMR (d^6-DMSO, 100 MHz) δ 31.49, 52.35, 127.33, 128.86, 129.56, 130.42, 134.24, 140.77, 167.28; EI-MS (70 eV) *m/z*: 207 ($M^+ - SO_3Na$); Anal. Calcd for $C_{11}H_{11}NaO_5S_2$: C 42.57; H 3.57. Found: C 42.89; H 3.65.

Compound **2b**. White solid. mp 200–202°C; IR (KBr): 3078, 3022, 1720 (C=O), 1624 (C=C), 1210, 1164 (SO_3^-) cm^{-1};^{1}H NMR (DMSO-d^6, 400 MHz) δ: 2.35 (s, 3H, CH_3), 3.76 (s, 3H, OCH_3), 4.05 (s, 2H, methylene-*H*), 7.26 (d, 2H, $J = 8.0$ Hz, Ar*H*), 7.62–7.65 (m, 3H, Ar*H* overlapped with ArC*H*=); ^{13}C NMR (d^6-DMSO, 100 MHz) δ: 21.0, 31.43, 52.18, 126.24, 129.40, 130.48, 131.41, 139.35, 140.74, 167.26; EI-MS (70 eV) *m/z*: 221 ($M^+ - SO_3Na$); Anal. Calcd for $C_{12}H_{13}NaO_5S_2$: C 44.44; H 4.04. Found: C 44.76; H 3.96.

Compound **2c**. White solid. mp 168–170°C; IR (KBr): 3083, 3020, 1713 (C=O), 1627 (C=C), 1214, 1164 (SO_3^-) cm^{-1}; ^{1}H NMR (DMSO-d^6, 400 MHz) δ: 3.78 (s, 3H, OCH_3), 4.04 (s, 2H, methylene-*H*), 7.50 (d, 2H, $J = 8.8$ Hz, Ar*H*), 7.65 (s, 1H, ArC*H*=), 7.77 (d, 2H, $J = 8.8$ Hz, Ar*H*); ^{13}C NMR (d^6-DMSO, 100 MHz) δ: 30.84, 52.33, 128.23, 128.73, 132.13, 133.12, 134.11, 139.21, 167.01; EI-MS (70 eV) *m/z*: 241 (^{35}Cl—$M^+ - SO_3Na$), 243 (^{37}Cl $M^+ - SO_3Na$); Anal. Calcd for $C_{11}H_{10}ClNaO_5S_2$: C 38.32; H 2.92. Found: C 38.60; H 2.98.

Compound **2d**. White solid. mp 213–215°C; IR (KBr): 3080, 3020, 1713 (C=O), 1629 (C=C), 1212, 1166 (SO_3^-) cm^{-1}; ^{1}H NMR (DMSO-d^6, 400 MHz) δ: 3.63 (s, 3H, OCH_3), 3.78 (s, 2H, methylene-*H*), 7.23–7.32 (m, 2H, Ar*H*), 7.37–7.41 (m, 1H, Ar*H*), 7.55 (s, 1H, ArC*H*=), 7.72–7.75 (m, 1H, Ar*H*); ^{13}C NMR (d^6-DMSO, 100 MHz) δ: 31.85, 53.36, 128.23, 129.95, 130.24, 131.38, 131.76, 132.85, 134.10, 138.17, 167.57; EI-MS (70 eV) *m/z*: 241 (^{35}Cl—$M^+ - SO_3Na$), 243 (^{37}Cl—$M^+ - SO_3Na$); Anal. Calcd for $C_{11}H_{10}ClNaO_5S_2$: C 38.32; H 2.92. Found: C 38.03; H 2.96.

Compound **2e**. White solid. mp 180–182°C; IR (KBr): 3071, 3018, 1708 (C=O), 1626 (C=C), 1242, 1128 (SO_3^-) cm^{-1}; ^1H NMR (DMSO-d^6, 400 MHz) δ: 3.76 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 4.08 (s, 2H, methylene-*H*), 7.01 (d, 2H, $J = 8.8$ Hz, Ar*H*), 7.63 (s, 1H, ArC*H*=), 7.75 (d, 2H, $J = 8.8$ Hz, Ar*H*); ^{13}C NMR (d^6-DMSO, 100 MHz) δ: 32.33, 53.10, 56.05, 115.06, 124.20, 127.12, 133.28, 142.12, 161.10, 168.38; EI-MS (70 eV) *m/z*: 237 ($M^+ - SO_3Na$); Anal. Calcd for $C_{12}H_{13}NaO_6S_2$: C 42.35; H 3.85. Found: C 42.70; H 3.76.

Compound **2f**. White solid. mp 62–64°C; IR (KBr): 3074, 3022, 1709 (C=O), 1627 (C=C), 1246, 1164 (SO_3^-) cm^{-1}; ^1H NMR (DMSO-d^6, 400 MHz) δ: 3.77 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.03 (s, 2H, methylene-*H*), 6.98–7.12 (m, 2H, Ar*H*), 7.41–7.46 (m, 1H, Ar*H*), 7.83–7.86 (m, 2H, Ar*H* overlapped with ArC*H*=); ^{13}C NMR (d^6-DMSO, 100 MHz) δ: 32.25, 53.05, 56.28, 111.79, 121.29, 123.18, 127.01, 130.62, 132.18, 137.32, 158.21, 168.09; EI-MS (70 eV) *m/z*: 237 ($M^+ - SO_3Na$); Anal. Calcd for $C_{12}H_{13}NaO_6S_2$: C 42.35; H 3.85. Found: C 42.78; H 3.77.

Compound **2g**. White solid. mp 192–194°C; IR (KBr): 3078, 3021, 1730 (C=O), 1635 (C=C), 1217, 1165 (SO_3^-) cm^{-1}; ^1H NMR (DMSO-d^6, 400 MHz) δ: 3.76 (s, 3H, OCH_3), 4.08 (s, 2H, methylene-*H*), 6.11 (s, 2H), 6.99 (d, 1H, $J = 8.4$ Hz, Ar*H*), 7.25 (m, 1H, $J = 8.4$ Hz, Ar*H*), 7.43 (s, 1H), 7.60 (s, 1H); ^{13}C NMR (d^6-DMSO, 100 MHz) δ: 32.23, 53.12, 102.41, 109.33, 110.22, 124.54, 127.26, 128.59, 142.17, 148.52, 149.23, 168.26; EI-MS (70 eV) *m/z*: 251 ($M^+ - SO_3Na$); Anal. Calcd for $C_{12}H_{11}NaO_7S_2$: C 40.68; H 3.13. Found: C 40.43; H 3.20.

Compound **2h**. Light yellow solid. mp 103–104°C; IR (KBr): 3083, 3018, 1712 (C=O), 1626 (C=C), 1219, 1159 (SO_3^-) cm^{-1}; ^1H NMR (DMSO-d^6, 400 MHz) δ: 3.79 (s, 3H, OCH_3), 3.81 (s, 2H, methylene-*H*), 7.66–7.73 (m, 1H, Ar*H*), 7.78–7.84 (m, 2H), 7.89 (s, 1H), 8.19 (d, 1H, $J = 8.0$ Hz, Ar*H*); ^{13}C NMR (d^6-DMSO, 100 MHz) δ: 31.50, 53.32, 125.58, 129.66, 130.69, 130.98, 131.79, 135.18, 139.14, 147.67, 167.44; EI-MS (70 eV) *m/z*: 252 ($M^+ - SO_3Na$); Anal. Calcd for $C_{11}H_{10}NNaO_7S_2$: C 37.18; H 2.84. Found: C 36.90; H 2.91.

Compound **2i**. Brown solid. mp 109–110°C; IR (KBr): 1708 (C=O), 1622 (C=C), 1284, 1217 (SO_3^-) cm^{-1}; ^1H NMR (DMSO-d^6, 400 MHz) δ: 3.76 (s, 3H, OCH_3), 4.17 (s, 2H, methylene-*H*), 6.73 (dd, 1H, $J_1 = 4.0$ Hz, $J_2 = 1.6$ Hz), 7.30 (d, 1H, $J = 4.0$ Hz), 7.45 (s, 1H, ArC*H*=), 7.93 (d, 1H, $J = 1.6$ Hz); ^{13}C NMR (DMSO-d^6, 100 MHz) δ: 32.03, 53.20, 113.97, 118.41, 123.28, 128.50, 146.89, 150.40, 168.0; EI-MS (70 eV) *m/z*: 197 ($M^+ - SO_3Na$); Anal. Calcd for $C_9H_9NaO_6S_2$: C 36.00; H 3.02. Found: C 36.26; H 2.95.

Compound **2j**. White solid. mp 73–75°C; IR (KBr): 1709 (C=O), 1619 (C=C), 1297, 1201 (SO_3^-) cm^{-1}; ^1H NMR (DMSO-d^6, 400 MHz) δ: 2.48 (q, 2H, $J = 7.0$ Hz), 2.63 (t, 2H, $J = 7.0$ Hz), 3.66 (s, 3H, OCH_3), 4.05 (s, 2H), 6.79 (t, 1H, $J = 7.0$ Hz, alkyl-C*H*=), 7.10–7.15 (m, 3H, Ar*H*), 7.20–7.24 (m, 2H, Ar*H*); ^{13}C NMR (d^6-DMSO, 100 MHz) δ: 29.95, 30.25, 34.03, 51.90, 126.08, 128.43, 128.50, 128.88, 141.25, 144.36, 166.64; EI-MS (70 eV) *m/z*: 235 ($M^+ - SO_3Na$); Anal. Calcd for $C_{13}H_{15}NaO_5S_2$: C 46.14; H 4.47. Found: C 46.38; H 4.39.

Compound **2k**. White solid. mp 104–106°C; IR (KBr): 1708 (C=O), 1618 (C=C), 1276, 1219 (SO_3^-) cm^{-1}; ^1H NMR (DMSO-d^6, 400 MHz) δ: 0.86 (t, 3H, $J = 6.8$ Hz), 1.26–1.42 (m, 10H), 2.30 (q, 2H, $J = 7.5$ Hz), 3.66 (s, 3H, OCH_3), 3.78 (s, 2H), 6.73 (t, 1H, $J = 7.5$ Hz, alkyl-C*H*=); ^{13}C NMR (d^6-DMSO, 100 MHz) δ: 14.60, 22.83, 28.82, 28.98, 29.27, 29.46, 30.48, 31.96, 52.70, 128.29, 147.10, 167.53; EI-MS (70 eV) *m/z*: 229 ($M^+ - SO_3Na$); Anal. Calcd for $C_{12}H_{21}NaO_5S_2$: C 43.36; H 6.37. Found: C 43.70; H 6.29.

General Procedure for Preparation of Symmetrical Di(Z-allyl) Sulfides **3**

In a 25-mL flask $Na_2S{\cdot}9H_2O$ (0.13 g, 0.55 mmol), **1** (1 mmol), and anhydrous MeOH (15 mL) were added. The mixture was stirred at room temperature for 3–6 h. Upon completion, the reaction mixture was extracted with Et_2O (2×30 mL), washed with brine (15 mL), and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by chromatography using cyclohexane: EtOAc (6:1) as eluent.

Compound **3a**. Thick yellow oil. IR (film): 1715 (C=O), 1627 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.75 (s, 4H, CH_2), 3.84 (s, 6H, OCH_3), 7.32–7.40 (m, 6H, Ar*H*), 7.49–7.51 (m, 4H, Ar*H*), 7.76 (s, 2H, ArC*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 30.06, 52.22, 128.57, 128.73, 128.95, 129.62, 134.75, 140.71, 167.73; EI-MS (70 eV) *m/z*: 382 (M^+); Anal. Calcd for $C_{22}H_{22}O_4S$: C 69.09; H 5.80. Found: C 69.38; H 5.86.

Compound **3b**. Thick yellow oil. IR (film): 1713 (C=O), 1629 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.36 (s, 6H, CH_3), 3.77 (s, 4H, CH_2), 3.83 (s, 6H, OCH_3), 7.19 (d, 4H, $J = 8.0$ Hz, Ar*H*), 7.42 (d, 4H,

$J = 8.0$ Hz, Ar*H*), 7.74 (s, 2H, ArC*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.25, 30.03, 52.06, 127.65, 129.26, 129.73, 131.83, 139.15, 141.09, 167.82; EI-MS (70 eV) *m/z*: 410 (M^+); Anal. Calcd for $C_{24}H_{26}O_2S$: C 70.22; H 6.38. Found: C 70.56; H 6.35.

Compound **3c**. Thick yellow oil. IR (film): 1715 (C=O), 1629 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.71 (s, 4H, CH_2), 3.85 (s, 6H, OCH_3), 7.37 (d, 4H, $J = 8.0$ Hz, Ar*H*), 7.44 (d, 4H, $J = 8.0$ Hz, Ar*H*), 7.69 (s, 2H, ArC*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 29.99, 52.30, 128.86, 129.09, 130.92, 133.08, 135.05, 139.77, 167.41; EI-MS (70 eV) *m/z*: 450 (M^+); Anal. Calcd for $C_{22}H_{20}Cl_2O_4S$: C 58.54; H 4.47. Found: C 58.19, H 4.54.

Compound **3d**. Thick yellow oil. IR (film): 1719 (C=O), 1632 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.56 (s, 4H, CH_2), 3.84 (s, 6H, OCH_3), 7.29–7.31 (m, 4H, Ar*H*), 7.38–7.41 (m, 2H, Ar*H*), 7.52–7.55 (m, 2H, Ar*H*), 7.81 (s, 2H, ArC*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 30.11, 52.33, 126.83, 129.61, 130.04, 130.44, 130.59, 133.35, 134.17, 137.82, 167.20; EI-MS (70 eV) *m/z*: 450 (M^+); Anal. Calcd for $C_{22}H_{20}Cl_2O_4S$: C 58.54; H 4.47. Found: C 58.21; H 4.41.

Compound **3f**. Thick yellow oil. IR (film): 1713 (C=O), 1625 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.66 (s, 4H, CH_2), 3.79 (s, 6H, OCH_3), 3.84 (s, 6H, OCH_3), 6.87 (d, 2H, $J = 8.0$ Hz, Ar*H*), 6.99 (t, 2H, $J = 8.0$ Hz, Ar*H*), 7.33 (t, 2H, $J = 8.0$ Hz, Ar*H*), 7.56 (d, 2H, $J = 8.0$ Hz, Ar*H*), 7.91 (s, 2H, ArC*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 30.47, 52.07, 55.34, 110.34, 120.49, 123.89, 128.68, 130.20, 130.45, 136.82, 157.57, 167.79; EI-MS (70 eV) *m/z*: 442 (M^+); Anal. Calcd for $C_{24}H_{26}O_6S$: C 65.14; H 5.92. Found: C 65.51; H 5.99.

Compound **3g**. Thick yellow oil. IR (film); 1711 (C=O), 1622 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.74 (s, 4H, CH_2), 3.84 (s, 6H, OCH_3), 6.01 (s, 4H, OCH_2O), 6.74 (s, 2H, Ar*H*), 6.85 (d, 2H, $J = 8.0$ Hz, Ar*H*), 7.06 (d, 2H, $J = 8.0$ Hz, Ar*H*), 7.67 (s, 2H, ArC*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 30.15, 52.25, 101.41, 108.55, 109.68, 123.38, 125.11, 128.85, 135.50, 141.05, 148.02, 167.95; EI-MS (70 eV) *m/z*: 470 (M^+); Anal. Calcd for $C_{24}H_{22}O_8S$: C 61.27; H 4.71. Found: C 60.91; H 4.64.

Compound **3h**. Thick yellow oil. IR (film): 1718 (C=O), 1636 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.41 (s, 4H, CH_2), 3.82 (s, 6H, OCH_3), 7.51 (d, 2H, $J = 8.0$ Hz, Ar*H*), 7.56 (t, 2H, $J = 8.0$ Hz, Ar*H*), 7.71 (t, 2H, $J = 8.0$ Hz, Ar*H*), 7.92 (s, 2H, ArC*H*=), 8.16 (d, 2H, $J = 8.0$ Hz, Ar*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 30.01, 55.80, 124.94, 129.51, 130.39, 130.74, 131.06, 133.73, 137.73, 147.46, 166.68; EI-MS (70 eV) *m/z*: 472 (M^+); Anal. Calcd for $C_{22}H_{20}N_2O_8S$: C 55.93; H 4.27. Found: C 55.58; H 4.32.

Compound **3i**. Thick yellow oil. IR (film) 1709 (C=O), 1630 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.82 (s, 6H, OCH_3), 4.0 (s, 4H, CH_2), 6.48 (dd, 2H, $J_1 = 4.0$ Hz, $J_2 = 1.6$ Hz, Ar*H*), 6.72 (d, 2H, $J = 4.0$ Hz, Ar*H*), 7.46 (s, 2H, ArC*H*=), 7.54 (d, 2H, $J = 1.6$ Hz, Ar*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 29.50, 52.20, 112.20, 116.71, 125.02, 126.72, 144.86, 150.83, 167.88; EI-MS (70 eV) *m/z*: 362 (M^+); Anal. Calcd for $C_{18}H_{18}O_6S$: C 59.66; H 5.01. Found: C 59.96; H 5.06.

Compound **3j**. Thick yellow oil. IR (film): 1718 (C=O), 1643 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.53 (q, 4H, $J = 8.0$ Hz, CH_2), 2.75 (t, 4H, $J = 8.0$ Hz, CH_2), 3.36 (s, 4H, CH_2), 3.72 (s, 6H, OCH_3), 6.88 (t, 2H, $J = 8.0$ Hz, C*H*=), 7.16–7.29 (m, 10H, Ar*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 28.07, 29.64, 35.31, 51.90, 126.14, 128.32, 128.41, 129.32, 140.76, 143.91, 167.15; EI-MS (70 eV) *m/z*: 438 (M^+); Anal. Calcd for $C_{26}H_{30}O_4S$: C 71.20; H 6.89. Found: C 71.58, H 6.81.

Compound **3k**. Thick yellow oil. IR (film): 1723 (C=O), 1644 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.88 (t, 6H, $J = 6.8$ Hz), 1.27–1.45 (m, 20H), 2.23 (q, 4H, $J = 7.5$ Hz), 3.49 (s, 4H), 3.76 (s, 6H), 6.85 (t, 2H, $J = 7.5$ Hz, alkyl-C*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.01, 22.56, 28.71, 28.79, 29.04, 29.15, 29.29, 31.68, 51.82, 128.69, 145.43, 167.33; EI-MS (70 eV) *m/z* : 426 (M^+); Anal. Calcd for $C_{24}H_{42}O_4S$: C 67.56; H 9.92. Found: C 67.90; H 9.82.

Compound **3l**. Thick yellow oil. IR (film): 1721 (C=O), 1643 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.07 (t, 6H, $J = 7.6$ Hz), 2.27 (q, 4H, $J = 8.0$ Hz), 3.49 (s, 4H), 3.76 (s, 6H), 6.84 (t, 2H, $J = 8.0$ Hz, alkyl-C*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 13.24, 22.17, 28.13, 51.89, 128.36, 146.47, 167.41; EI-MS (70 eV) *m/z*: 286 (M^+); Anal. Calcd for $C_{14}H_{22}O_4S$: C 58.71; H 7.74. Found: C 58.36; H 7.79.

General Procedure for Preparation of Unsymmetrical Diallysulfides **4**

After the sodium (*Z*)-allyl thiosulfate was readily prepared under an inert atmosphere according to the procedure mentioned above, allyl bromide (3 mmol) and In (1.5 mmol) were added to the Bunte salts solution, the resulting mixture was stirred at room temperature for 30 min. Then, the mixture was stirred at 55°C for 8–12 h. Upon completion, the reaction

mixture was cooled down to room temperature and extracted by Et_2O (2×30 mL), washed with brine (15 mL), and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by chromatography using cyclohexane:ethyl acetate (6:1) as eluent.

Compound **4a**. Thick yellow oil. IR (film): 3081, 3060, 3026, 1716 (C=O), 1633 (C=C), 1597 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.16 (d, 2H, $J = 6.8$ Hz), 3.59 (s, 2H), 3.86 (s, 3H), 4.84–5.04 (m, 2H), 5.77 (ddt, 1H, $J_1 = 17.2$ Hz, $J_2 = 10.0$ Hz, $J_3 = 6.8$ Hz), 7.26–7.50 (m, 5H, Ar*H*), 7.76 (s, 1H, ArC*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 28.11, 36.14, 52.44, 117.33, 125.72, 127.88, 128.82, 129.11, 129.84, 134.34, 140.81, 168.24; EI-MS (70 eV) *m/z*: 248 (M^+); Anal. Calcd for $C_{14}H_{16}O_2S$: C 67.71; H 6.49. Found: C 67.50; H 6.62.

Compound **4b**. Thick yellow oil. IR (film): 3078, 3057, 3023, 1718 (C=O), 1631 (C=C), 1593 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.37 (s, 3H, CH_3), 3.17 (d, 2H, $J = 7.2$ Hz), 3.61 (s, 2H), 3.83 (s, 3H), 4.92–5.02 (m, 2H), 5.80 (ddt, 1H, $J_1 = 16.8$ Hz, $J_2 = 10.0$ Hz, $J_3 = 7.2$ Hz), 7.18 (d, 2H, $J = 8.0$ Hz, Ar*H*), 7.40 (d, 2H, $J = 8.0$ Hz, Ar*H*), 7.72 (s, 1H, ArC*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.37, 28.01, 35.98, 52.20, 117.14, 125.51, 129.34, 129.76, 132.04, 134.13, 139.21, 140.85, 168.06; EI-MS (70 eV) *m/z*: 262 (M^+); Anal. Calcd for $C_{15}H_{18}O_2S$: C 68.67; H 6.92. Found: C 68.40; H 6.84.

Compound **4c**. Thick yellow oil. IR (film): 3076, 3054, 3023, 1718 (C=O), 1632 (C=C), 1593 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.19 (d, 2H, $J = 6.8$ Hz), 3.55 (s, 2H), 3.86 (s, 3H), 4.96–5.06 (m, 2H), 5.80 (ddt, 1H,$J_1 = 17.2$ Hz, $J_2 = 10.0$ Hz, $J_3 = 6.8$ Hz), 7.39 (d, 2H, $J = 8.0$ Hz, Ar*H*), 7.46 (d, 2H, $J = 8.0$ Hz, Ar*H*), 7.69 (s, 1H, ArC*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 27.82, 36.06, 52.35, 117.33, 125.51, 128.86, 129.70, 130.94, 133.29, 133.93, 139.39, 167.66; EI-MS (70 eV) *m/z*: 282 (^{35}Cl—M^+), 284 (^{37}Cl—M^+); Anal. Calcd for $C_{14}H_{15}ClO_2S$: C 59.46; H 5.35. Found: C 59.21; H 5.43.

Compound **4d**. Thick yellow oil. IR (film): 3083, 3061, 3025, 1715 (C=O), 1634 (C=C), 1590 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.05 (d, 2H, $J = 7.2$ Hz), 3.42 (s, 2H), 3.83 (s, 3H), 4.71–4.89 (m, 2H), 5.65 (ddt, 1H, $J_1 = 16.8$ Hz, $J_2 = 10.0$ Hz, $J_3 = 7.2$ Hz), 7.24–7.31 (m, 2H, Ar*H*), 7.38–7.47 (m, 2H, Ar*H*), 7.77 (s, 1H, ArC*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 27.45, 35.88, 52.35, 117.02, 126.72, 129.62, 129.95, 130.58, 131.30, 133.59, 133.96, 134.20, 137.17, 167.35; EI-MS (70 eV) *m/z*: 282 (^{35}Cl—M^+), 284 (^{37}Cl—M^+); Anal. Calcd for $C_{14}H_{15}ClO_2S$: C 59.46; H 5.35. Found: C 59.18; H 5.40.

Compound **4e**. Thick yellow oil. IR (film): 3075, 3058, 3023, 1714 (C=O), 1632 (C=C), 1605 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.21 (d, 2H, $J = 6.8$ Hz), 3.62 (s, 2H), 3.84 (s, 3H), 3.85 (s, 3H), 4.99–5.07 (m, 2H), 5.84 (ddt, 1H, $J_1 = 16.8$ Hz, $J_2 = 10.0$ Hz, $J_3 = 6.8$ Hz), 6.94 (d, 2H, $J = 9.2$ Hz, Ar*H*), 7.50 (d, 2H, $J = 9.2$ Hz, Ar*H*), 7.71 (s, 1H, ArC*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 28.17, 35.22, 52.16, 55.31, 113.70, 114.07, 117.15, 127.41, 128.80, 131.63, 134.12, 140.71, 160.26, 168.17; EI-MS (70 eV): *m/z* (%) 278 (M^+); Anal. Calcd for $C_{15}H_{18}O_3S$: C 64.72; H 6.52. Found: C 64.96; H 6.62.

Compound **4f**. Thick yellow oil. IR (film) 3078, 3060, 3025, 1715 (C=O), 1634 (C=C), 1598 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.12 (d, 2H, $J = 6.8$ Hz), 3.52 (s, 2H), 3.85 (s, 3H), 3.86 (s, 3H), 4.82–4.96 (m, 2H), 5.73 (ddt, 1H, $J_1 = 17.2$ Hz, $J_2 = 10.0$ Hz, $J_3 = 6.8$ Hz), 6.90 (d, 1H, $J = 7.6$ Hz, Ar*H*), 6.99 (t, 1H, $J = 7.6$ Hz, Ar*H*), 7.35 (t, 1H, $J = 7.6$ Hz, Ar*H*), 7.49 (d, 1H, $J = 7.6$ Hz, Ar*H*), 7.89 (s, 1H, ArC*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 28.06, 35.70, 52.10, 55.46, 110.50, 116.88, 120.40, 130.05, 130.23, 130.41, 130.64, 134.22, 136.53, 157.64, 167.88; EI-MS (70 eV) *m/z*: 278 (M^+); Anal. Calcd for $C_{15}H_{18}O_3S$: C 64.72; H 6.52. Found: C 64.40; H 6.38.

Compound **4g**. Thick yellow oil. IR (film): 3079, 3060, 3023, 1714 (C=O), 1624 (C=C), 1596 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.21 (d, 2H, $J = 7.2$ Hz), 3.60 (s, 2H), 3.85 (s, 3H), 5.00–5.08 (m, 2H), 5.84 (ddt, 1H, $J_1 = 16.8$ Hz, $J_2 = 10.0$ Hz, $J_3 = 7.2$ Hz), 6.01 (s, 2H), 6.85 (d, 1H, $J = 8.4$ Hz, Ar*H*), 7.02 (d, 1H, $J = 8.4$ Hz, Ar*H*), 7.11 (s, 1H, Ar*H*), 7.65 (s, 1H, ArC*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 28.13, 36.08, 52.22, 101.50, 109.65, 117.21, 125.00, 127.36, 128.92, 134.09, 140.68, 148.02, 148.37, 168.02; EI-MS (70 eV) *m/z*: 292 (M^+); Anal. Calcd for $C_{15}H_{16}O_4S$: C 61.62; H 5.52. Found: C 61.30; H 5.41.

Compound **4h**. Thick yellow oil. IR (film): 3080, 3061, 3020, 1720 (C=O), 1636 (C=C), 1607 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.09 (d, 2H, $J = 7.6$ Hz), 3.35 (s, 2H), 3.88 (s, 3H), 4.80–4.93 (m, 2H), 5.65 (ddt, 1H, $J_1 = 16.6$ Hz, $J_2 = 10.4$ Hz, $J_3 = 7.6$ Hz), 7.54–7.58 (m, 2H, Ar*H*), 7.70 (t, 1H, $J = 7.2$ Hz, Ar*H*), 7.96 (s, 1H, ArC*H*=), 8.18 (d, 1H,$J = 7.2$ Hz, Ar*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 27.71, 35.99, 52.68, 117.34, 125.23, 129.73, 131.33, 131.55, 133.84, 134.19, 137.39, 147.88, 167.22; EI-MS (70 eV) *m/z*: 293 (M^+); Anal. Calcd for $C_{14}H_{15}NO_4S$: C 57.32; H 5.15. Found: C 57.01; H 5.27.

Compound **4i**. Thick yellow oil. IR (film): 3123, 3081, 1711 (C=O), 1632 (C=C), 1598 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.21 (d, 2H, $J = 6.8$ Hz), 3.83 (s, 3H), 3.86 (s, 2H), 5.06–5.11 (m, 2H), 5.85 (ddt, 1H, $J_1 = 16.8$ Hz, $J_2 = 10.0$ Hz, $J_3 = 6.8$ Hz), 6.50 (dd, 1H, $J_1 = 3.2$ Hz, $J_2 = 1.2$ Hz), 6.71 (d, 1H, $J = 3.2$ Hz), 7.44 (s, 1H, ArC*H*=), 7.55 (d, 1H, $J = 1.2$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 28.07, 35.41, 52.23, 112.52, 116.90, 117.21, 126.00, 126.60, 134.80, 144.99, 151.13, 167.98; EI-MS (70 eV) *m/z*: 238 (M^+); Anal. Calcd for $C_{12}H_{14}O_3S$: C 60.48; H 5.92. Found: C 60.16; H 5.81.

Compound **4j**. Thick yellow oil. IR (film): 3083, 3062, 1719 (C=O), 1638 (C=C), 1600 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.56 (q, 2H, $J = 7.6$ Hz), 2.77 (t, 2H, $J = 7.6$ Hz), 3.12 (d, 2H, $J = 7.2$ Hz), 3.33 (s, 2H), 3.76 (s, 3H), 5.08–5.13 (m, 2H), 5.81 (ddt, 1H,$J_1 = 17.0$ Hz, $J_2 = 10.0$ Hz, $J_3 = 7.6$ Hz), 6.88 (t, 1H, $J = 7.6$ Hz, alkyl-C*H*=), 7.20–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 26.56, 30.74, 34.85, 35.39, 51.96, 117.11, 126.21, 128.35, 128.50, 129.64, 134.39, 140.81, 143.74, 167.32; EI-MS (70 eV) *m/z*: 276 (M^+); Anal. Calcd for $C_{16}H_{20}O_2S$: C 69.53; H 7.29. Found: C 69.18; H 7.40.

Compound **4k**. Thick yellow oil. IR (film): 3082, 1719 (C=O), 1639 (C=C), 1601 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.89 (t, 3H, $J = 6.8$ Hz), 1.26–1.50 (m, 10H), 2.23 (q, 2H, $J = 7.6$ Hz), 3.15 (d, 2H, $J = 6.8$ Hz), 3.40 (s, 2H), 3.77 (s, 3H), 5.10–5.20 (m, 2H), 5.85 (ddt, 1H, $J_1 = 17.2$ Hz, $J_2 = 10.0$ Hz, $J_3 = 6.8$ Hz), 6.86 (t, 1H, $J = 7.6$ Hz, alkyl-C*H*=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.06, 22.61, 26.64, 28.76, 28.90, 29.07, 29.33, 31.73, 35.42, 51.88, 116.99, 127.46, 134.53, 145.29, 167.48; EI-MS (70 eV) *m/z*: 270 (M^+); Anal. Calcd for $C_{15}H_{26}O_2S$: C 66.62; H 9.69. Found: C 66.38; H 9.57.

General Procedure for the One-Pot Synthesis of Symmetrical Di(Z-allyl) Disulfides **5** *or Methyl Cinnamic Esters* **6**

In a 25-mL flask, $Na_2SSO_3 \cdot 5H_2O$ (0.25 g, 1.0 mmol), **1** (1.0 mmol), and anhydrous MeOH (15 mL) were added. The mixture was stirred at room temperature for 4–8 h until the sodium (*Z*)-allyl thiosulfates were readily prepared. Methanol was removed and changed solvent into THF (20 mL) under an inert atmosphere. Then Sm (0.15 g, 1 mmol) and a trace amount of I_2 were added to the resulting mixture followed by dropwise addition of saturated NH_4Cl aqueous solution (4 mL). The mixture was stirred at room temperature for the time given in Table 1. Upon completion, the reaction mixture was quenched with diluted HCl (5%, 15 mL) and extracted with Et_2O (2×30 mL), washed with brine (15 mL), and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by chromatography using cyclohexane:EtOAc (9:1) (R = alkyl groups) or cyclohexane:EtOAc (6:1) (R = aryl groups) as eluent.

Compound **5j**. Thick yellow oil. IR (film): 1716 (C=O), 1643 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.62 (q, 4H, $J = 8.0$ Hz), 2.78 (t, 4H, $J = 8.0$ Hz), 3.62 (s, 4H), 3.72 (s, 6H), 6.98 (t, 2H, $J = 8.0$ Hz), 7.19–7.32 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 31.32, 35.23, 35.38, 52.29, 126.49, 128.66, 128.77, 128.86, 141.01, 145.43, 167.13; EI-MS (70 eV) *m/z*: 470 (M^+); Anal. Calcd for $C_{26}H_{30}O_4S_2$: C 66.35; H 6.42. Found: C 66.72; H 6.48.

Compound **5k**. Thick yellow oil. IR (film): 1721 (C=O), 1642 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.88 (t, 6H, $J = 7.2$ Hz), 1.25–1.47 (m, 20H), 2.32 (q, 4H, $J = 7.2$ Hz), 3.70 (s, 4H), 3.77 (s, 6H), 6.95 (t, 2H, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 22.59, 28.84, 29.09, 29.19, 29.24, 29.32, 31.71, 35.29, 51.89, 127.92, 146.78, 166.99; EI-MS (70 eV) *m/z*: 458 (M^+); Anal. Calcd for $C_{24}H_{42}O_4S_2$: C 62.84; H 9.23. Found: C 62.51; H 9.28.

Compound **5l**. Thick yellow oil. IR (film): 1719 (C=O), 1642 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.10 (t, 6H, $J = 7.2$ Hz), 2.30–2.37 (m, 4H), 3.69 (s, 4H), 3.77 (s, 6H), 6.93 (t, 2H, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 13.34, 22.47, 35.00, 51.85, 127.44, 147.90, 166.97; EI-MS (70 eV) *m/z*: 318 (M^+); Anal. Calcd for $C_{14}H_{22}O_4S_2$: C 52.80; H 6.96. Found: C 53.23; H 6.90.

Compound **6a** *[17d]*. Thick yellow oil. IR (film): 1709 (C=O), 1606 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.19 (s, 3H), 3.89 (s, 3H), 7.37–7.46 (m, 5H), 7.78 (s, 1H); EI-MS (70 eV) *m/z*: 176 (M^+).

Compound **6b** *[17d]*. Thick yellow oil. IR (film): 1711 (C=O), 1632 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.11 (s, 3H), 2.36 (s, 3H), 3.80 (s, 3H), 7.19 (d, 2H, $J = 8.0$ Hz), 7.31 (d, 2H, $J = 8.0$ Hz), 7.67 (s, 1H); EI-MS (70 eV) *m/z*: 190 (M^+).

Compound **6c** *[17d]*. Thick yellow oil. IR (film): 1714 (C=O), 1630 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.10 (s, 3H), 3.82 (s, 3H), 7.31 (d, 2H, $J = 8.0$ Hz), 7.36 (d, 2H, $J = 8.0$ Hz), 7.62 (s, 1H); EI-MS (70 eV) *m/z*: 210 (^{35}Cl—M^+), 212 (^{37}Cl—M^+).

Compound **6d** *[17d]*. Thick yellow oil. IR (film): 1717 (C=O), 1635 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400

MHz) δ: 2.02 (s, 3H), 3.86 (s, 3H), 7.28–7.47 (m, 4H), 7.78 (s, 1H); EI-MS (70 eV) *m/z*: (%) 210 ($^{35}Cl-M^+$), 212 ($^{37}Cl-M^+$).

Compound **6f** *[17d].* Thick yellow oil. IR (film) 1717 (C=O), 1598 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.06 (s, 3H), 3.81 (s, 3H), 3.86 (s, 3H), 6.91–7.34 (m, 4H), 7.84 (s, 1H); EI-MS (70 eV) *m/z*: 206 (M^+).

Compound **6g** *[17d].* White solid. mp 75–76°C; IR (KBr): 1691 (C=O), 1600 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.11 (s, 3H), 3.81 (s, 3H), 5.99 (s, 2H), 6.82–6.93 (m, 3H), 7.59 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.2, 52.1, 101.3, 108.4, 109.6, 124.7, 126.6, 129.9, 138.7, 147.6, 147.7, 169.3; EI-MS (70 eV) *m/z*: 220 (M^+).

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