Synthesis of Divinylsulfides

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Abstract: Arylacetylenes react with sodium sulfide in the presence of water to yield divinylsulfides. The reaction proceeds in good to excellent yield for both electron-neutral and electron-deficient aromatic systems; for electron-rich aryls, longer reaction times are necessary. The sulfides represent useful substrates for further transformations, for example, oxidation to the corresponding divinylsulfoxides and divinylsulfones. Three selected divinylsulfide derivatives were oxidized selectively to the corresponding sulfoxides or sulfones.

Key words: alkynes, divinylsulfoxide, sulfoxide, sulfone, sodium sulfide

Organosulfur compounds contain highly diverse functional groups that allow further transformations and, more importantly, asymmetric synthesis.[1] In particular, the sulfoxides and sulfones have attracted significant interest from organic chemists. The sulfoxides allow a wide array of auxiliary controlled asymmetric synthesis to be applied, and a number of procedures have been developed for the stereoselective oxidation of sulfides.[2] The sulfone group has been recognized for its ability to stabilize anions,[3] radicals[4] and for its ability to function as a leaving group.[4]

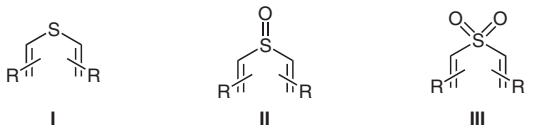


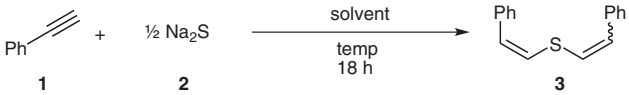
Figure 1 Divinysulfide (**I**), divinylsulfoxide (**II**) and divinylsulfone (**III**)

Especially, divinylsulfoxides and divinylsulfones (**II** and **III**, Figure 1) display a highly diverse reactivity, because the activation of the double bonds can be modulated by the three oxidation states of the sulfur atom. The double bonds are active in nucleophilic conjugate additions,[5] which lead to the formation of chalcogen- and nitrogen-containing heterocycles,[6] sulfoxide-bridged bisphosphines[7] and addition products.[8] Furthermore, cyclopropanations[9] and cycloadditions[10] have also been reported. Thus, synthesis of the corresponding divinylsulfides is of central interest because the sulfoxides and sulfones can generally be obtained using a suitable oxidation method.[1,2] Generally, divinylsulfides are obtained either by Wittig reaction of α,α′-diphosphonium sulfides with aldehydes[11] or by decomposition of cysteine with sodium ethoxide in the presence of phenyl acetylene (**1**).[12] These procedures furnish the divinylsulfides either as *cis*,*trans* isomers or as *cis*,*cis* isomers in low yield.

It is well known that terminal alkynes can be attacked by nucleophiles such as amines, phosphines and thiols.[13] Accordingly, we found that the addition of sodium sulfide (**2**) to phenyl acetylene (**1**) furnishes bis(2-phenylvinyl)sulfide. Examples of this reaction have been reported by Trofimov.[14] Here, we present a simple and practical procedure for the synthesis of bis(arylvinyl)sulfides that does not require the use of α,α′-dichlorosulfides or elemental alkali metals.

We started to investigate this reaction by optimizing the reaction conditions with phenyl acetylene (**1**) as the arylacetylene component (Table 1).

Table 1 Optimization of the Reaction of Phenyl Acetylene (**1**) with Sodium Sulfide (**2**)[a]



Entry	Solvent	Additive	Temp (°C)	Conversion (%)[b,d]
1	DMF	–	24	–
2	DMF	–	40	14
3	DMF	–	70	31
4	DMF	H_2O[c]	24	9
5	DMF	H_2O[c]	40	45
6	DMF	H_2O[c]	70	77 (80)
7	EtOH	–	24	–
8	EtOH	–	40	2
9	EtOH	–	70	20 (25; other isomers)
10	DMA	H_2O[c]	70	98 (80)

[a] Using Na_2S (1 M) in the corresponding solvent.
[b] Conversion to **3** determined by calibrated GC.
[c] Amount of additive: 2 equiv.
[d] Value in parentheses corresponds to the yield of **3** after purification by column chromatography.

We initially chose to use anhydrous dimethylformamide (DMF) as solvent because of its ability to dissolve a wide

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array of alkali salts. The reaction proceeded at elevated temperatures (entries 2 and 3) and the bis(2-phenylvinyl)sulfide (**3**) was formed in 31% yield at 70 °C. The addition of two equivalents of water led to a significant increase in yield; the product was furnished in 45% yield compared to 14% under anhydrous conditions (entries 2 and 5). Raising the reaction temperature from 40 °C to 70 °C resulted in an increase in the yield to give **3** in 77% (entry 6). On a millimole scale (1 mmol), **3** was furnished in 80% yield (compared to 67% yield using conditions reported in the literature)[14c] as a mixture of diastereomers (*cis*,*cis* to *cis*,*trans* ratio 5.5:1). This increase in the efficiency of the process can be attributed to the partial hydrolysis of **2** to more active reagent sodium hydrosulfide (NaSH; **4**).[15] Hence, the application of a protic solvent, e.g. ethanol, should also provide **4** to a certain extent, and would offer a less toxic alternative for this process. Indeed, choosing ethanol as solvent at a temperature of 70 °C resulted in the formation of significant amounts of **3**, together with some other isomers (entry 9). However, dimethyl acetamide (DMA) was the solvent of choice, because both **2** and **4** are capable of cleaving DMF[16] to form thioformic acid and dimethylamine. The reaction still proceeded in good yield (entry 10) and the product was furnished with the same isolated yield as that obtained in DMF.

The scope of the reaction was explored using the optimized reaction conditions. We first investigated aryl-substituted terminal alkynes as suitable substrates (Table 2).

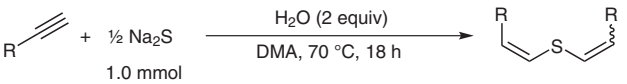
Generally, the reaction proceeds in good yield for both electron-rich and electron-deficient aromatic alkynes. Electron-withdrawing and electron-donating groups are both tolerated in the *ortho* position (Table 2, entries 2, 3, and 4). An electron-donating functionality in the *para* position retards the reaction and results in longer reaction times (Table 2, entry 3). The chlorobenzene derivative proved to be reactive under the reaction conditions and provided the product in excellent yield (85%). Heterocyclic substrates, such as pyridyl-substituted alkynes, were activated enough to allow the reaction to be performed even at lower temperature (Table 2, entry 5).[17] The reaction proceeded sluggishly with unactivated alkynes such as 1-octyne (Table 2, entry 7) and failed completely with *tert*-butylacetylene. More activated alkynes, such as *p*-cyanophenylacetylene or propynic ester, furnished oligomeric and polymeric material. The divinylsulfides were obtained after column chromatography as a mixture of isomers. For the (2-arylvinyl)sulfides **3**–**9**, the *cis*,*cis*-configuration of the double bond was observed by ^{1}H NMR spectroscopy to constitute the major isomer (Table 2).

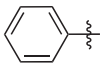
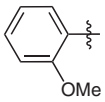
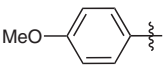
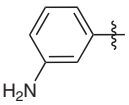
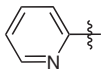
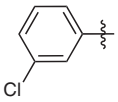
The products are valuable substrates for further derivatization, for example, oxidation to the sulfoxides and sulfones. The oxidation of the 5.5:1 mixture of double bond isomers of **3** with two equivalents of Oxone® yielded the symmetric sulfoxide **11** (Scheme 1).[5,18]

After column chromatography, the *cis*,*cis* divinylsulfoxide **11** was furnished in excellent yield of 89%. Lower yields were obtained when electron-rich (**5**) or electron-poor (**9**) divinylsulfides were employed (as mixtures of isomers). The configuration of the double bond was retained, which was easily observed by ^{1}H NMR spectroscopy (the vicinal coupling constant was 10 Hz, which is in the typical range for *Z*-olefins).

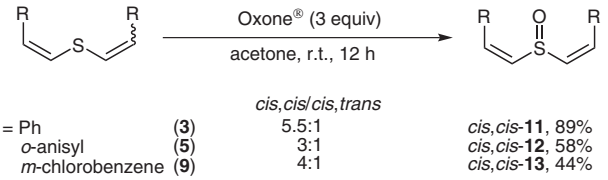
The direct oxidation of **3** to the corresponding sulfone **14** could be achieved by the reaction of the sulfide, as a mixture of isomers, with *m*-chloroperbenzoic acid (MCPBA)[19] in 59% yield after column chromatography (Scheme 2). The predominant *Z*-configuration of the double bond was conserved as the major diastereomer (J = 12.1 Hz for the vinylic protons).

Table 2 Substrate Scope of the Reaction of **2** with Terminal Alkynes[a]

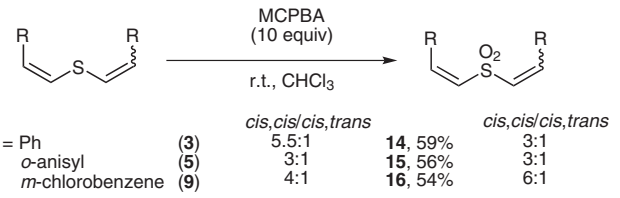


Entry	R	Product	Yield (%)[b]	Ratio of isomers *cis*,*cis*/*cis*,*trans*[c]
1		**3**	80	5.5:1
2		**5**	70	3:1
3		**6**	56[d]	8:1
4		**7**	59	5.5:1
5		**8**	57, 72[e]	1.5:1
6		**9**	85	4:1
7		**10**	11[f]	n.d.

[a] Reaction conditions: **2** (1 M), DMA, 70 °C, 18 h.
[b] Average yield of two experiments after purification by column chromatography.
[c] Determined by ^{1}H NMR.
[d] The reaction was not carried to completion.
[e] The reaction was performed at r.t. for 48 h.
[f] Compound was characterized by GC-MS.



Scheme 1 Oxidation of divinylsulfides to the divinylsulfoxides



		cis,cis/cis,trans		cis,cis/cis,trans
R = Ph	(**3**)	5.5:1	**14**, 59%	3:1
o-anisyl	(**5**)	3:1	**15**, 56%	3:1
m-chlorobenzene	(**9**)	4:1	**16**, 54%	6:1

Scheme 2 Oxidation of divinylsulfides to divinylsulfones

The yields for electron-rich and electron-poor divinylsulfones **15** and **16** were 56% and 54%, respectively, indicating that the electronic substitution pattern does not influence the oxidation process substantially.

The pyridyl-substituted sulfide **8** contains three heteroatoms that are arranged appropriately for metal coordination,[20,21] however, only the saturated derivative has been reported in the literature so far.[20] The unsaturated compound **8** has a more rigid structure, which results in a smaller bite-angle of the N-S-donor atoms. This new framework should lead to new developments in the coordination chemistry of N,S,N-tridentate ligands.

In conclusion, we have established a protocol for the generation of bis(arylvinyl)sulfides, which is complementary to known procedures with respect to starting materials and the scope of the reaction. The addition of sodium sulfide to arylacetylenes furnishes the corresponding bis(arylvinyl)sulfides in good to excellent yield. The sulfides can be converted chemoselectively into the sulfoxides and sulfones. These substances can serve as valuable substrates for further derivatizations such as cycloadditions, hydrogenations and cross-coupling reactions. The pyridyl-substituted divinylsulfide could act as tridentate ligand for transition metals and should form a more rigid scaffold than the corresponding saturated sulfides.

Synthesis of Bis(2-phenylvinyl)sulfide (3); Typical Procedure A
A vial was charged with Na_2S (382 mg, 4.89 mmol) and DMA (5 mL) was added to form a 1 M solution. The vial was sealed and treated with ultrasound (Bandelin, SONOREX, TK 524) at r.t. for 30 sec. H_2O (2 equiv, 176 μL, 176 mg, 9.79 mmol), followed by phenyl acetylene (1.00 g, 9.79 mmol), were added by syringe. The mixture was stirred at 70 °C for 18 h. After cooling to r.t., the mixture was diluted with EtOAc (100 mL) and washed with H_2O (3 × 100 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed in vacuo. The residue was purified by column chromatography (hexane–EtOAc, 20:1) to give the divinylsulfide (**3**).

Yield: 80% (949 mg, 80% first run; 932 mg, 80% second run); yellow oil; mixture of diastereomers: *cis*,*cis* to *cis*,*trans*, 5.5:1.

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 7.61 (m, 4 H, Ar-$H_{cis,cis}$), 7.50 (m, 4 H, Ar-H), 7.43 (m, 4 H, Ar-$H_{cis,trans}$), 7.37 (m, 2 H, Ar-$H_{cis,cis}$), 6.93 (d, *J* = 15.6 Hz, 1 H, C=$CH_{cis,trans}$), 6.79 (d, *J* = 15.6 Hz, 1 H, C=$CH_{cis,trans}$), 6.71 (d, *J* = 10.7 Hz, 1 H, C=$CH_{cis,trans}$), 6.65 (d, *J* = 10.8 Hz, 2 H, C=$CH_{cis,cis}$), 6.37 (d, *J* = 10.7 Hz, 1 H, C=$CH_{cis,trans}$), 6.46 (d, *J* = 10.8 Hz, 2 H, C=$CH_{cis,cis}$).

***cis*,*cis*-Diastereomer**
^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 136.4, 128.9, 128.6, 127.3, 127.0, 126.2.

***cis*,*trans*-Diastereomer**
^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 136.6, 136.5, 129.9, 128.9, 128.5, 127.7, 127.5, 126.0, 124.1, 124.0 (two carbon atoms were not detected).

IR (DRIFT): 3057 (s), 3022 (s), 2926 (m), 2594 (w), 2317 (w), 1947 (m), 1869 (m), 1680 (m), 1593 (s), 1490 (s), 1444 (s), 1345 (s), 1075 (m), 944 (m), 834 (s), 772 (s), 681 (s), 521 (s) cm^{-1}.

HRMS: *m*/*z* calcd for $C_{16}H_{14}S$: 238.0816; found: 238.015.

Anal. Calcd for $C_{16}H_{14}S$: C, 80.63; H, 5.92; S, 13.45. Found: C, 80.34; H, 5.74; S, 13.90.

Bis[2-(2-anisyl)vinyl]sulfide (5)
According to typical procedure A, compound **5** was isolated from the reaction of 2-methoxyphenylacetylene (264 mg, 2.0 mmol), Na_2S (78 mg, 1.0 mmol) and H_2O (36 mg, 2.0 mmol) in DMA (1 mL).

Yield: 70% (195 mg, 65% first run; 223 mg, 75% second run); yellow oil; mixture of diastereomers: *cis*,*cis* to *cis*,*trans*, 3:1.

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 7.62 (dd, *J* = 1.6, 7.6 Hz, 2 H, Ar-$H_{cis,cis}$), 7.36 (dd, *J* = 1.6, 7.6 Hz, 1 H, Ar-$H_{cis,trans}$), 7.32–7.23 (m, 4 H, Ar-H), 7.08–6.88 (m, 4 H, Ar-H), 6.84 (d, *J* = 10.8 Hz, 2 H, C=$CH_{cis,cis}$), 6.56 (d, *J* = 10.4 Hz, 1 H, C=$CH_{cis,trans}$), 6.44 (d, *J* = 10.8 Hz, 2 H, C=$CH_{cis,cis}$), 3.89 (s, 3 H, $CH_3O_{cis,trans}$), 3.88 (s, 3 H, $CH_3O_{cis,trans}$), 3.87 (s, 6 H, $CH_3O_{cis,cis}$).

cis,*cis*-Diastereomer

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 156.2, 129.2, 128.6, 126.3, 125.3, 121.6, 120.3, 110.4, 55.5.

cis,*trans*-Diastereomer

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 156.6, 156.4, 134.2, 130.3, 129.3, 128.4, 126.9, 124.9, 124.8, 128.6, 124.4, 122.2, 120.7, 120.2, 110.9, 110.6, 55.7, 55.5.

IR (DRIFT): 3284 (w), 3033 (w), 2939 (m), 2045 (w), 1897 (w), 1596 (s), 1568 (m), 1484 (s), 1461 (s), 1435 (m), 1290 (m), 1246 (vs), 1179 (m), 1163 (m), 1109 (s), 934 (w), 750 (vs), 583 (w), 496 (w) cm^{-1}.

HRMS: *m*/*z* calcd for $C_{18}H_{18}O_2S$: 298.1028; found: 298.1029.

Anal. Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08; S, 10.75. Found: C, 72.93; H, 6.00; S, 10.39.

Bis[2-(4-anisyl)vinyl]sulfide (6)
According to typical procedure A, compound **6** was isolated from the reaction of 4-methoxyphenylacetylene (264 mg, 2.0 mmol), Na_2S (78 mg, 1.0 mmol) and H_2O (36 mg, 2.0 mmol).

Yield: 56% (157 mg, 53% first run; 177 mg, 59% second run); yellow oil; mixture of diastereomers: *cis*,*cis* to *cis*,*trans*, 8:1.

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 7.38 (d, *J* = 8.8 Hz, 4 H, Ar-H), 6.86 (d, *J* = 8.8 Hz, 4 H, Ar-H), 6.41 (d, *J* = 10.7 Hz, 2 H, C=CH), 6.25 (d, *J* = 10.7 Hz, 2 H, C=CH), 3.75 (s, 6 H, CH_3O).

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 158.6, 130.2, 129.2, 126.3, 123.7, 113.9, 55.3.

IR (DRIFT): 3284 (w), 3033 (w), 2939 (m), 2834 (m), 1596 (s), 1568 (s), 1484 (vs), 1461 (vs), 1435 (s), 1246 (vs), 1163 (w,) 1109 (m), 1027 (s), 750 (vs), 496 (w) cm^{-1}.

HRMS: *m*/*z* calcd for $C_{18}H_{18}O_2S$: 298.1028; found: 298.1029.

Anal. Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08; S, 10.75. Found: C, 72.28; H, 5.91; S, 10.76.

Bis[2-(3-aminophenyl)vinyl]sulfide (7)
According to Typical Procedure A, compound **7** was isolated from the reaction of 3-aminophenylacetylene (234 mg, 2.0 mmol), Na_2S (78 mg, 1.0 mmol) and H_2O (36 mg, 2.0 mmol).

Yield: 56% (141 mg, 53% first run; 158 mg, 59% second run); brown oil; mixture of diastereomers: *cis*,*cis* to *cis*,*trans*, 5.5:1.

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 7.10 (t, *J* = 7.6 Hz, 2 H, Ar-H), 6.83 (d, *J* = 7.6 Hz, 2 H, Ar-H), 6.75 (m, 2 H, Ar-H), 6.54–6.50 (m, 2 H, Ar-H), 6.38 (d, *J* = 10.8 Hz, 2 H, C=CH), 6.25 (d, *J* = 10.8 Hz, 2 H, C=CH), 3.46 (br, 4 H, NH_2).

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 146.4, 137.3, 129.3, 127.0, 126.1, 119.4, 115.2, 114.3.

IR (DRIFT): 3430 (s), 3352 (s), 3214 (s), 3032 (m), 1600 (vs), 1494 (s), 1442 (m), 1319 (m), 1167 (m), 993 (w), 865 (m), 782 (s), 680 (m), 465 (w) cm^{-1}.

HRMS: *m*/*z* calcd for $C_{16}H_{16}N_2S$: 268.1034; found: 268.1037.

Bis[2-(2-pyridyl)vinyl]sulfide (8)
According to Typical Procedure A, compound **8** was isolated from the reaction of 2-pyridylacetylene (234 mg, 2.0 mmol), Na_2S (78 mg, 1.0 mmol) and H_2O (36 mg, 2.0 mmol).

Yield: 57% (136 mg, 57% first run; 136 mg, 57% second run); off-white solid; mixture of diastereomers: *cis*,*cis* to *cis*,*trans*, 1.5:1.

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 8.70–8.62 (m, 3 H, Ar-H), 8.50–8.44 (m, 1 H, Ar-$H_{cis,trans}$), 7.62–7.50 (m, 4 H, Ar-H), 7.25 (m, 2 H, Ar-$H_{cis,cis}$), 7.16 (m, 1 H, Ar-$H_{cis,trans}$), 7.07 (m, 1 H, Ar-$H_{cis,trans}$), 7.05–7.7.00 (m, 3 H, Ar-H), 6.81 (d, *J* = 10.4 Hz, 1 H, C=$CH_{cis,trans}$), 6.68 (d, *J* = 15.8 Hz, 1 H, C=$CH_{cis,trans}$), 6.67 (d, *J* = 10.7 Hz, 2 H, C=$CH_{cis,cis}$), 6.52 (d, *J* = 10.7 Hz, 2 H, C=$CH_{cis,cis}$).

***cis*,*cis*-Diastereomer**
^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 155.4, 149.1, 136.0, 134.7, 124.6, 123.6, 120.8.

***cis*,*trans*-Diastereomer**
Mp 129 °C.

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 154.5, 149.6, 148.7, 136.7, 136.1, 133.5, 130.5, 127.2, 123.8, 123.7, 121.8, 121.7.

IR (DRIFT): 3007 (m), 2327 (w), 1772 (w), 1735 (w), 1589 (vs), 1545 (vs), 1470 (vs), 1425 (s), 1353 (s), 1215 (m), 1151 (m), 1095 (m), 991 (m), 944 (m), 800 (vs), 746 (s), 540 (m) cm^{-1}.

HRMS: *m*/*z* calcd for $C_{14}H_{12}N_2S$: 240.0721; found: 240.0718.

Anal. Calcd for $C_{14}H_{12}N_2S$: C, 69.97; H, 5.03; N, 11.66; S, 13.34. Found: C, 69.82; H, 4.97; N, 11.67; S, 13.26.

Bis[2-(3-chlorophenyl)vinyl]sulfide (9)
According to Typical Procedure A, compound **9** was isolated from the reaction of 3-chlorophenylacetylene (234 mg, 2.0 mmol), Na_2S (78 mg, 1.0 mmol) and H_2O (36 mg, 2.0 mmol).

Yield: 85% (253 mg, 82% first run; 272 mg, 89% second run); yellow oil; mixture of diastereomers: *cis*,*cis* to *cis*,*trans*, 4:1.

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 7.45–7.10 (m, 16 H, Ar-H), 6.76 (d, *J* = 15.5 Hz, 2 H, C=$CH_{cis,trans}$), 6.52 (d, *J* = 15.5 Hz, 2 H, C=$CH_{cis,trans}$), 6.41 (d, *J* = 10.8 Hz, 2 H, C=$CH_{cis,cis}$), 6.34 (d, *J* = 10.8 Hz, 2 H, C=$CH_{cis,cis}$).

***cis*,*cis*-Diastereomer**
^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 137.8, 134.4, 129.7, 128.7, 127.4, 127.2, 126.7, 125.9.

***cis*,*trans*-Diastereomer**
^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 138.1, 137.9, 134.7, 134.3, 130.0, 129.6, 128.7, 128.3, 127.5, 127.3, 126.9, 126.3, 125.8, 125.3, 125.2, 124.1.

IR (DRIFT): 3035 (m), 2924 (w), 1936 (w), 1859 (w), 1590 (s), 1560 (s), 1476 (s), 1408 (s), 1346 (s), 1178 (m), 995 (m), 934 (m), 880 (s), 785 (vs), 753 (s), 671 (s), 559 (m), 451 (m) cm^{-1}.

HRMS: *m*/*z* calcd for $C_{16}H_{12}Cl_2S$: 306.0037; found: 306.0040.

Anal. Calcd for $C_{16}H_{12}Cl_2S$: C, 62.55; H, 3.94; S, 10.44. Found: C, 63.06; H, 3.95; S, 9.44.

Synthesis of *cis*,*cis*-Bis(2-phenylvinyl)sulfoxide (11); Typical Procedure B
To a solution of a diastereomeric mixture (5.5:1) of **3** (756 mg, 3.17 mmol) in acetone (76 mL), Oxone (3 equiv, 5.86 g, 9.52 mmol) dissolved in H_2O (29 mL) was added dropwise. The mixture was stirred at r.t. for 24 h then the mixture was diluted with EtOAc (50 mL) and H_2O (100 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The *cis*,*cis*-divinylsulfoxides were separated from small amounts of the *cis*,*trans* isomer by column chromatography (SiO_2; EtOAc–hexane, 1:3→1:1→3:1).

Yield: 89% (718 mg, 2.82 mmol); white solid; mp 95 °C.

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 7.50–7.10 (m, 10 H, Ar-H), 7.03 (d, *J* = 9.6 Hz, 2 H, C=$CH_{cis,cis}$), 6.71 (d, *J* = 15.6 Hz, 1 H, C=$CH_{cis,trans}$), 6.52 (d, *J* = 9.6 Hz, 2 H, C=$CH_{cis,cis}$).

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 138.5, 135.1, 133.8, 129.6, 129.4, 128.5.

IR (DRIFT): 3054 (m), 3016 (m), 2923 (w), 2029 (w), 1955 (w), 1888 (w), 1761 (m), 1600 (m), 1570 (m), 1443 (s), 1022 (s), 787 (s), 693 (m), 540 (m) cm^{-1}.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}OS$: 255.0843; found: 255.0842.

Anal. Calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.55; S, 12.61. Found: C, 75.79; H, 5.54; S, 12.47.

***cis*,*cis*-Bis[2-(2-anisyl)vinyl]sulfoxide (12)**
According to Typical Procedure B, compound **12** was obtained from the reaction of **5** (195 mg, 0.65 mmol; mixture of *cis*,*cis* and *cis*,*trans* diastereomers, 3:1) and Oxone (1.19 g, 1.95 mmol).

Yield: 58% (119 mg, 0.38 mmol); isomerically pure white solid (only *cis*,*cis* diastereomer); mp 106 °C.

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 7.30–7.17 (m, 4 H, Ar-H, C=$CH_{cis,cis}$), 7.02 (dd, *J* = 7.7, 1.5 Hz, 2 H, Ar-H), 7.79 (d, 2 H, *J* = 7.8 Hz, Ar-H), 6.57 (m, 2 H, Ar-H), 6.51 (d, *J* = 10.5 Hz, 2 H, C=$CH_{cis,cis}$), 3.73 (s, 6 H, CH_3O).

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 157.3, 135.0, 134.2, 131.2, 130.8, 123.1, 120.2, 110.4, 55.5.

IR (DRIFT): 3054 (w), 3014 (m), 2952 (m), 2835 (m), 2535 (w), 2042 (w), 1911 (w), 1594 (s), 1483 (s), 1468 (s), 1435 (s), 1306 (s), 1034 (s), 1017 (s), 976 (s), 758 (s), 725 (m) cm^{-1}.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{19}O_3S$: 315.1055; found: 315.1052.

Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.76; H, 5.77; S, 10.20. Found: C, 68.67; H, 5.79; S, 10.35.

***cis*,*cis*-Bis[2-(3-chlorophenyl)vinyl]sulfoxide (13)**
According to Typical Procedure B, compound **13** was obtained from the reaction of **9** (272 mg, 0.88 mmol; mixture of *cis*,*cis* and *cis*,*trans* diastereomers, 4:1) and Oxone (1.62 g, 2.64 mmol).

Yield: 44% (125 mg, 0.39 mmol); isomerically pure (only *cis*,*cis* diastereomer); white solid; mp 59 °C.

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 7.28–7.16 (m, 8 H, Ar-H), 6.99 (d, *J* = 10.7 Hz, 2 H, C=$CH_{cis,cis}$), 6.57 (d, *J* = 10.7 Hz, 2 H, C=$CH_{cis,cis}$).

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 137.4, 136.2, 135.4, 134.7, 129.9, 129.6, 129.3, 127.6.

IR (DRIFT): 3073 (w), 3013 (m), 2926 (w), 2016 (w), 1591 (m), 1561 (m), 1474 (m), 1410 (m), 1410 (m), 1222 (w), 1178 (w), 1014 (s), 875 (m), 790 (s), 683 (s), 628 (m) cm^{-1}.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{13}Cl_2OS$: 323.0064; found: 323.0066.

Anal. Calcd for $C_{16}H_{12}Cl_2OS$: C, 59.45; H, 3.74; S, 9.92. Found: C, 59.48; H, 3.88; S, 9.61.

Synthesis of Bis(2-phenylvinyl)sulfone (14); Typical Procedure C

To a solution of **3** (80 mg, 0.34 mmol; mixture of diastereomers, 5.5:1) in $CHCl_3$ (5 mL), were added MCPBA (10 equiv, 586 mg, 3.4 mmol; 99% pure) in one portion. After 3 h the benzoic acid started to precipitate and the mixture was stirred for an additional 12 h. The mixture was diluted with EtOAc (10 mL) and sat. Na_2CO_3 (10 mL). The organic phase was separated and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic phase was dried over $MgSO_4$, filtered and the solvent was removed in vacuo. The residue was purified by column chromatography (SiO_2; hexane–EtOAc, 50:1) to give sulfone **14**.

Yield: 59% (54 mg); light-yellow oil; mixture of diastereomers: *cis*,*cis* to *cis*,*trans*, 3:1.

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 7.55–7.51 (m, 1 H, Ar-$H_{cis,trans}$), 7.52–7.44 (m, 4 H, Ar-$H_{cis,cis}$), 7.37 (d, *J* = 14.7 Hz, 1 H, C=$CH_{cis,trans}$), 7.35 (m, 6 H, Ar-$H_{cis,cis}$), 7.08 (d, *J* = 12.1 Hz, 1 H, C=$CH_{cis,trans}$), 6.83 (d, *J* = 12.2 Hz, 2 H, C=$CH_{cis,cis}$), 6.62 (d, *J* = 15.4 Hz, 1 H, C=$CH_{cis,trans}$), 6.46 (d, *J* = 12.1 Hz, 1 H, C=$CH_{cis,trans}$), 6.24 (d, *J* = 12.2 Hz, 2 H, C=$CH_{cis,cis}$).

cis,*cis*-Diastereomer

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 141.6, 132.6, 130.5, 130.3, 130.2, 128.3.

cis,*trans*-Diastereomer

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 143.8, 141.7, 132.6, 132.4, 131.2, 130.9, 130.1, 130.0, 129.0, 128.4, 126.0 (one carbon atom resonance was not detected).

IR (DRIFT): 3053 (s), 2932 (w), 1709 (w), 1605 (s), 1574 (m), 1493 (s), 1447 (s), 1295 (s), 1122 (s), 857 (m), 778 (s), 690 (s), 543 (m) cm^{-1}.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}O_2S$: 271.0797; found: 271.794.

Bis[2-(2-anisyl)vinyl)]sulfone (15)

According to Typical Procedure C, compound **15** was obtained from the reaction of **5** (165 mg, 0.55 mmol; mixture of *cis*,*cis* and *cis*,*trans* diastereomers, 3:1) and MCPBA (954 mg, 5.53 mmol; 99%).

Yield: 56% (102 mg); light-yellow oil; mixture of diastereomers: *cis*,*cis* to *cis*,*trans*, 3:1.

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 7.74–7.69 (m, 1 H, Ar-$H_{cis,trans}$), 7.70–7.65 (m, 2 H, Ar-$H_{cis,cis}$), 7.53 (d, *J* = 15.5 Hz, 1 H, C=$CH_{cis,trans}$), 7.32–7.12 (m, Ar-$H_{cis,trans\ and\ cis,cis}$), 7.14 (d, *J* = 11.9 Hz, 2 H, C=$CH_{cis,cis}$), 6.95–6.56 (m, Ar-$H_{cis,trans\ and\ cis,cis}$), 6.44 (d, *J* = 11.6 Hz, 1 H, C=$CH_{cis,trans}$), 6.25 (d, *J* = 11.9 Hz, 2 H, C=$CH_{cis,cis}$), 3.75 (s, 3 H, $CH_3O_{cis,trans}$), 3.73 (s, 6 H, $CH_3O_{cis,cis}$), 3.70 (s, 3 H, $CH_3O_{cis,trans}$).

cis,*cis*-Diastereomer

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 157.4, 137.1, 132.2, 131.5, 129.9, 121.7, 120.2, 110.1, 55.5.

cis,*trans*-Diastereomer

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 158.7, 157.2, 139.4, 137.4, 132.3, 132.0, 131.3, 130.9, 130.8, 127.0, 121.9, 121.4, 120.7, 120.1, 111.1, 55.4 (two carbon atom resonances were not detected).

IR (DRIFT): 3046 (s), 2940 (s), 2838 (s), 2046 (w), 1702 (w), 1599 (s), 1485 (s), 1464 (s), 1437 (s), 1368 (m), 1293 (s), 1252 (s), 1109 (s), 1049 (m), 1024 (s), 876 (w), 756 (s), 676 (m), 581 (m), 552 (m), 518 (m), 473 (m) cm^{-1}.

HRMS: *m*/*z* calcd for $C_{18}H_{18}O_4S$: 330.0926; found: 330.0923.

Anal. Calcd for $C_{18}H_{18}O_4S$: C, 65.43; H, 5.49; S, 9.70. Found: C, 65.56; H, 5.53; S, 9.70.

Bis[2-(3-chlorophenyl)vinyl]sulfone (16)

According to Typical procedure C, compound **16** was obtained from the reaction of **9** (193 mg, 0.63 mmol; mixture of *cis*,*cis* and *cis*,*trans* diastereomers, 4:1) and MCPBA (1.08 g, 6.30 mmol; 99%).

Yield: 54% (115 mg); light-yellow oil; mixture of diastereomers: *cis*,*cis* to *cis*,*trans*, 6:1.

^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 7.51–7.41 (m, 1 H, Ar-$H_{cis,trans}$), 7.42–7.36 (m, 4 H, Ar-$H_{cis,cis}$), 7.35–7.08 (m, Ar-$H_{cis,trans\ and\ cis,cis}$), 7.05 (d, *J* = 12.1 Hz, 1 H, C=$CH_{cis,trans}$), 6.82 (d, *J* = 12.1 Hz, 2 H, C=$CH_{cis,cis}$), 6.60 (d, *J* = 15.0 Hz, 1 H, C=$CH_{cis,trans}$), 6.50 (d, *J* = 12.1 Hz, 1 H, C=$CH_{cis,trans}$), 6.29 (d, *J* = 12.1 Hz, 2 H, C=$CH_{cis,cis}$).

cis,*cis*-Diastereomer

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 140.2, 134.3, 134.0, 131.5, 130.1, 130.0, 129.6, 128.5.

cis,*trans*-Diastereomer

^{13}C NMR ($CDCl_3$, 100.1 MHz): δ = 142.7, 140.3, 135.1, 134.1, 134.0, 132.0, 131.2, 130.4, 129.8, 129.6, 128.2, 128.1, 127.1, 126.7 (two carbon atom resonances were not detected).

IR (DRIFT): 3053 (s), 2929 (w), 1611 (s), 1592 (s), 1564 (s), 1474 (s), 1425 (m), 1299 (s), 1222 (m), 1164 (m), 1127 (s), 1079 (m), 973 (w), 867 (m), 793 (s), 731 (m), 679 (s), 566 (w), 518 (w), 456 (w) cm^{-1}.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{13}Cl_2O_2S$: 339.0013; found: 339.0011.

Anal. Calcd for $C_{16}H_{12}Cl_2O_2S$: C, 56.65; H, 3.57; S, 9.45. Found: C, 57.16; H, 3.67; S, 8.95.

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