

# 1,3-Dipolar Cycloaddition of Dipolar Reagents to bis(Styryl) Sulfones

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**ABSTRACT:** Sulfonyl bis pyrazolines and isoxazolines were prepared by 1,3-dipolar cycloaddition of nitrile imines and nitrile oxides to *E,E*-bis(styryl) sulfones. © 2002 Wiley Periodicals, Inc. *Heteroatom Chem* 13:677–682, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10087

## INTRODUCTION

In recent times, we have been actively involved in 1,3-cycloaddition reactions of dipolar reagents with dipolarophiles for the development of manifold five-membered heterocycles [1]. Prompted by the successful results on this front, we present in this article the utilization of *E,E*-bis(styryl) sulfones as dipolarophiles in the synthesis of sulfonyl bis pyrazolines and isoxazolines by the cycloaddition of dipoles nitrile imines and nitrile oxides, generated from araldehyde phenylhydrazones and araldoximes in the presence of chloramine-T (CAT). In fact, amongst 1,3-dipoles, the nitrile imines and nitrile oxides have been extensively used in the cycloaddition reactions [1a–c,2]. Earlier, these dipolar reagents were generated by the dehydrogenation of araldehyde hydrazones and araldoximes with lead tetraacetate, mercuric acetate, and 1-chlorobenzotriazole [3].

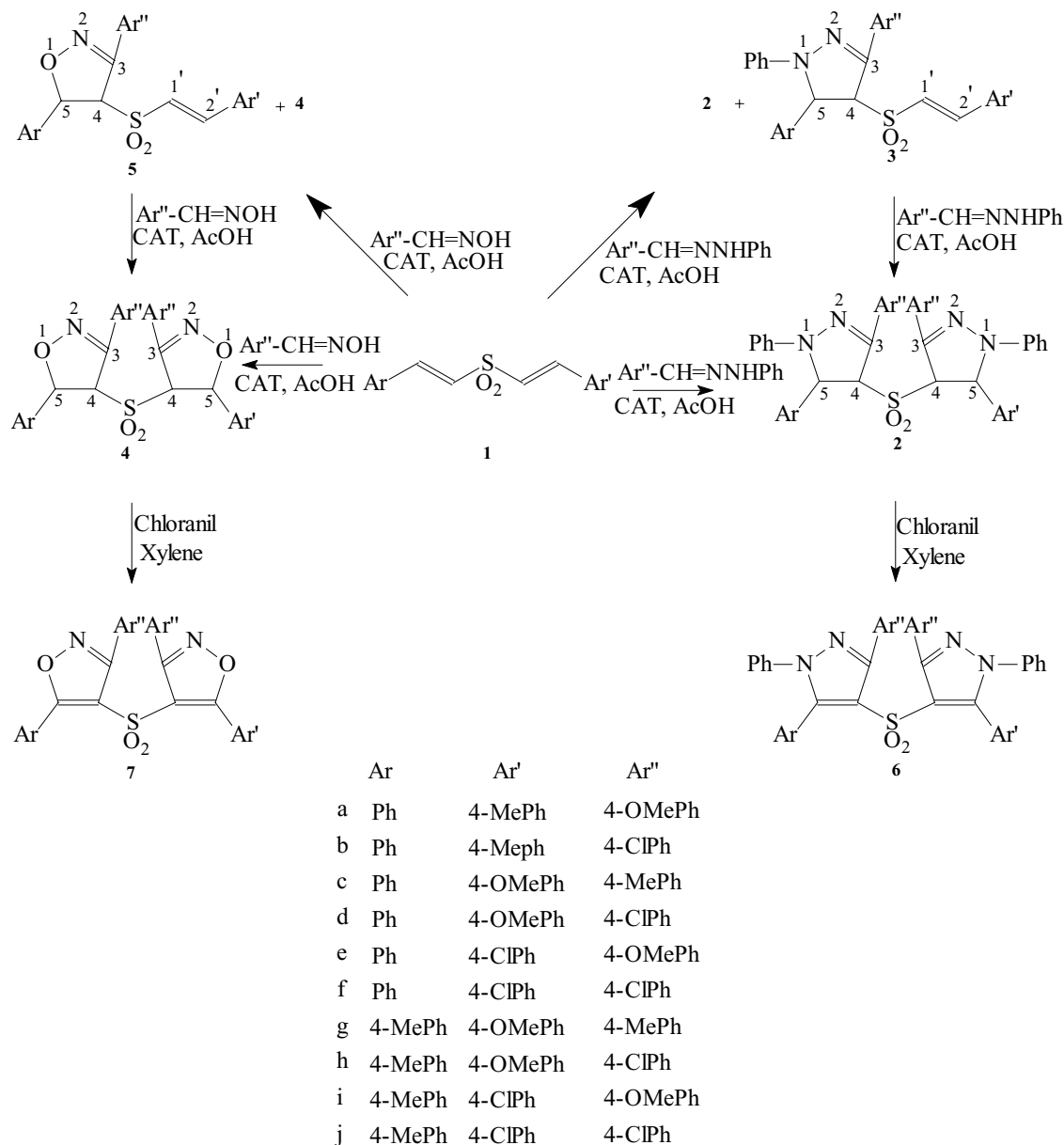
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However, recently CAT was found to be an effective, elegant, and a facile dehydrogenation agent under simpler experimental conditions [1a,4]. By adoption of these conditions, mono styryl sulfones such as phenyl vinyl sulfone and aryl styryl sulfones were indeed converted to sulfonyl pyrazolines and isoxazolines [5a–c].

## RESULTS AND DISCUSSION

*E,E*-bis(styryl) sulfone (**1**) was treated with araldehyde phenylhydrazone/araldoxime in the presence of CAT in AcOH (see Scheme 1). When the reaction of **1** (1 mol) and araldehyde phenylhydrazone (2 mol) was carried out in the presence of CAT (2 mol), a mixture of products was obtained in 3:1 ratio, which were separated by column chromatography. They were identified as bis(1-phenyl-3,5-diaryl-2-pyrazolin-4-yl) sulfone **2a–h** (major) and 1-phenyl-3,5-diaryl-4-styrylsulfonyl-2-pyrazoline **3a–h** (minor) by <sup>1</sup>H NMR spectra. Compound **2** exhibited two doublets at  $\delta$  5.22–5.27 ( $J = 5.9$ –6.1 Hz) and 5.69–5.74 ( $J = 5.9$ –6.1 Hz) for C<sub>4</sub>–H and C<sub>5</sub>–H, respectively. However, compound **3** showed a doublet at  $\delta$  6.58–6.61 ( $J = 16.0$  Hz) for C<sub>1'</sub>–H, while C<sub>2'</sub>–H merged with aromatic protons and appeared in the region 6.94–7.52 as a multiplet. Apart from these, two doublets at  $\delta$  5.24–5.28 (C<sub>4</sub>–H,  $J = 6.0$ –6.3 Hz) and 5.67–5.69 (C<sub>5</sub>–H,  $J = 6.0$ –6.3 Hz) were also observed in the spectrum. A similar reaction of **1** with araldoxime also produced a mixture of products (3:1) which were separated by column chromatography. They



SCHEME 1

were found to be bis(3,5-diaryl-2-isoxazolin-4-yl) sulfone (**4a–h**, major) and 3,5-diaryl-4-styrylsulfonyl-2-isoxazolin-4-yl sulfone (**5a–h**, minor) by  $^1\text{H}$  NMR spectra. Compound **4** exhibited two doublets at  $\delta$  5.27–5.30 ( $J = 6.0$ –6.2 Hz) and 5.86–5.91 ( $J = 6.0$ –6.2 Hz), which were accounted for by  $\text{C}_4$ –H and  $\text{C}_5$ –H. The latter shows only moderate differences in their  $\delta_{\text{H}}$  values, and, in fact, such results were given in a number of instances [1a,b,6]. Thus, in **2–5**, the  $J$  values (5.9–6.3 Hz) indicated that these two protons ( $\text{C}_4$ –H and  $\text{C}_5$ –H) are in the trans geometry [6]. On the other hand, compound **5** showed a doublet at  $\delta$  6.56–6.58 ( $J = 16.0$  Hz) for  $\text{C}_1$ –H while  $\text{C}_2$ –H merged with

aromatic protons and appeared in the region 6.98–7.81 as a multiplet apart from signals because of isoxazolin-4-yl ring protons (see Table 1). The olefinic protons in **3** and **5** could exist as cis and trans isomers, but their  $J$  values at  $\sim 16.0$  Hz indicate that they possess only the trans geometry [7]. The vinyl sulfone group can add the nitrile imines and nitrile oxides in two directions; but the sulfone is an electron-withdrawing group, hence the polarization of the double bond would be only in one direction. Thus, the nitrile imines and nitrile oxides should add usually as indicated in Scheme 1 [8a,b]. In the case of sulfone **1** with different Ar and Ar', the double bond

TABLE 1  $^1\text{H}$  NMR Spectral Data for 2–7

Product	$\delta^1\text{H}$ (ppm) $J$ (Hz)
<b>2a</b>	7.12–8.01 (m, 27H, Ar-H), 5.68 (d, $J = 5.9$ , 2H, H-5), 5.23 (d, $J = 5.9$ , 2H, H-4), 3.89 (s, 6H, H-OCH <sub>3</sub> ), 2.40 (s, 3H, H-CH <sub>3</sub> ).
<b>2b</b>	7.18–8.14 (m, 27H, Ar-H), 5.69 (d, $J = 6.1$ , 2H, H-5), 5.27 (d, $J = 6.1$ , 2H, H-4), 2.41 (s, 3H, H-CH <sub>3</sub> ).
<b>2e</b>	7.09–7.94 (m, 27H, Ar-H), 5.74 (d, $J = 5.9$ , 2H, H-5), 5.22 (d, $J = 5.9$ , 2H, H-4), 3.86 (s, 6H, H-OCH <sub>3</sub> ).
<b>2g</b>	7.04–7.98 (m, 26H, Ar-H), 5.62 (d, $J = 6.1$ , 2H, H-5), 5.14 (d, $J = 6.1$ , 2H, H-4), 3.89 (s, 3H, H-OCH <sub>3</sub> ), 2.51 (s, 9H, H-CH <sub>3</sub> ).
<b>3a</b>	6.94–7.75 (m, 19H, Ar-H & H-2'), 6.58 (d, $J = 16.2$ , 1H, H-1'), 5.69 (d, $J = 6.0$ , 1H, H-5), 5.24 (d, $J = 6.0$ , 1H, H-4), 3.92 (s, 3H, H-OCH <sub>3</sub> ), 2.39 (s, 3H, H-CH <sub>3</sub> ).
<b>3b</b>	7.01–7.78 (m, 19H, Ar-H & H-2'), 6.60 (d, $J = 16.2$ , 1H, H-1'), 5.67 (d, $J = 6.0$ , 1H, H-5), 5.24 (d, $J = 6.0$ , 1H, H-4), 2.37 (s, 3H, H-CH <sub>3</sub> ).
<b>3d</b>	7.01–7.84 (m, 19H, Ar-H & H-2'), 6.49 (d, $J = 16.0$ , 1H, H-1'), 5.67 (d, $J = 6.1$ , 1H, H-5), 5.24 (d, $J = 6.1$ , 1H, H-4), 3.94 (s, 3H, H-OCH <sub>3</sub> ).
<b>3h</b>	7.04–7.86 (m, 18H, Ar-H & H-2'), 6.61 (d, $J = 15.9$ , 1H, H-1'), 5.69 (d, $J = 6.1$ , 1H, H-5), 5.28 (d, $J = 6.1$ , 1H, H-4), 3.73 (s, 3H, H-OCH <sub>3</sub> ), 2.41 (s, 3H, H-CH <sub>3</sub> ).
<b>4a</b>	7.16–8.08 (m, 17H, Ar-H), 5.81 (d, $J = 6.1$ , 2H, H-5), 5.24 (d, $J = 6.1$ , 2H, H-4), 3.81 (s, 6H, H-OCH <sub>3</sub> ), 2.38 (s, 3H, CH <sub>3</sub> ).
<b>4b</b>	7.14–8.06 (m, 17H, Ar-H), 5.86 (d, $J = 5.9$ , 2H, H-5), 5.29 (d, $J = 5.9$ , 2H, H-4), 2.41 (s, 3H, H-CH <sub>3</sub> ).
<b>4e</b>	7.12–8.02 (m, 17H, Ar-H), 5.83 (d, $J = 6.0$ , 2H, H-5), 5.25 (d, $J = 6.0$ , 2H, H-4), 3.80 (s, 6H, H-OCH <sub>3</sub> ).
<b>4g</b>	7.04–7.98 (m, 16H, Ar-H), 5.72 (d, $J = 6.1$ , 2H, H-5), 5.14 (d, $J = 6.1$ , 2H, H-4), 3.89 (s, 3H, H-OCH <sub>3</sub> ), 2.51 (s, 9H, H-CH <sub>3</sub> ).
<b>5a</b>	6.98–7.81 (m, 14H, Ar-H & H-2'), 6.56 (d, $J = 16.0$ , 1H, H-1'), 5.74 (d, $J = 5.8$ , 1H, H-5), 5.30 (d, $J = 5.8$ , 1H, H-4), 3.81 (s, 3H, H-OCH <sub>3</sub> ), 2.40 (s, 3H, H-CH <sub>3</sub> ).
<b>5b</b>	7.01–7.81 (m, 14H, Ar-H & H-2'), 6.52 (d, $J = 16.0$ , 1H, H-1'), 5.74 (d, $J = 5.8$ , 1H, H-5), 5.32 (d, $J = 5.8$ , 1H, H-4), 2.42 (s, 3H, H-CH <sub>3</sub> ).
<b>5d</b>	6.89–7.78 (m, 14H, Ar-H & H-2'), 6.52 (d, $J = 16.0$ , 1H, H-1'), 5.75 (d, $J = 5.8$ , 1H, H-5), 5.28 (d, $J = 5.8$ , 1H, H-4), 3.92 (s, 3H, H-OCH <sub>3</sub> ).
<b>5h</b>	7.01–7.85 (m, 13H, Ar-H & H-2'), 6.57 (d, $J = 16.1$ , 1H, H-1'), 5.78 (d, $J = 6.0$ , 1H, H-5), 5.32 (d, $J = 6.0$ , 1H, H-4), 3.91 (s, 3H, H-OCH <sub>3</sub> ), 2.36 (s, 3H, H-CH <sub>3</sub> ).
<b>6a</b>	6.95–7.98 (m, 27H, Ar-H), 3.74 (s, 6H, H-OCH <sub>3</sub> ), 2.37 (s, 3H, H-CH <sub>3</sub> ).
<b>6c</b>	6.96–7.80 (m, 27H, Ar-H), 3.76 (s, 6H, H-OCH <sub>3</sub> ), 2.40 (s, 3H, H-CH <sub>3</sub> ).
<b>6e</b>	7.12–8.10 (m, 27H, Ar-H), 3.72 (s, 6H, H-OCH <sub>3</sub> ).
<b>6g</b>	6.92–8.06 (m, 26H, Ar-H), 3.74 (s, 3H, H-OCH <sub>3</sub> ), 2.35 (s, 9H, H-CH <sub>3</sub> ).
<b>7a</b>	7.31–8.15 (m, 17H, Ar-H), 3.76 (s, 6H, H-OCH <sub>3</sub> ), 2.37 (s, 3H, H-CH <sub>3</sub> ).
<b>7c</b>	7.02–8.10 (m, 17H, Ar-H), 3.74 (s, 6H, H-OCH <sub>3</sub> ), 2.35 (s, 3H, H-CH <sub>3</sub> ).
<b>7e</b>	6.95–8.02 (m, 17H, Ar-H), 3.74 (s, 6H, H-OCH <sub>3</sub> ).
<b>7g</b>	7.01–7.98 (m, 16H, Ar-H), 3.71 (s, 3H, H-OCH <sub>3</sub> ), 2.32 (s, 9H, H-CH <sub>3</sub> ).

adjacent to Ar<sup>1</sup> accepts the 1,3-dipole in the mono adduct **3/5 a–d, g** and **h**, while the bond adjacent to Ar similarly accepts the dipole in **e** and **f** because of the electron-withdrawing nature of the substituents present in them, respectively. In compounds **2** and **4** there are stereocenters, and, as a result, a mixture of diastereomeric bis adducts was formed. However, we could isolate only one pure compound when the reaction mixture was purified through column chromatography. A small amount of the other isomers, if any, formed could not be isolated by this process. The IR spectra of **2–5** displayed bands in the regions 1120–1144 and 1325–1351 (SO<sub>2</sub>) 1442–1446 (C=N). Apart from these, **3** and **5** showed another band around 1594–1612 (C=C). However, repetition of these reactions with **1** (1 mol), araldehyde phenylhydrazone/araldoxime (2 mol) and a two-fold excess of CAT resulted only **2** and **4**. Compound **3** and **5**

were once again treated with equimolar proportions of araldehyde phenylhydrazone/araldoxime and CAT to provide **2** and **4**. The authenticity of **2** and **4**, obtained by different routes, was confirmed by their mp and  $^1\text{H}$  NMR spectra, and their yields in each method are given in Table 2 (See Table 3 for elemental analyses). In the formation of **3** and **5** one would expect the presence of regioisomers. However, as close observation of their TLC indicated, almost the same  $R_f$  value was observed. Efforts to isolate these products by familiar chromatographic techniques were not met with success. Furthermore, **3** and **5**, which were obtained in lesser amounts, were used to obtain **2** and **4**. In our earlier reports, the equimolar reaction of 1-aroyle-2-arylsulfonylenes, araldehyde phenylhydrazones/araldoximes, and CAT gave a mixture of pyrazoles/isoxazoles and pyrazolines/isoxazolines in minor and major amounts, respectively [1a].

TABLE 2 Physical Data of Compounds 2–7

Product	mp (°C)	Method <sup>a</sup>			Product	mp (°C)	Method <sup>a</sup> A
		A	B	C			
2a	180–181	68	75	63	5a	117–118	21
2b	176–177	65	76	60	5b	121–122	25
2c	174–175	60	71	62	5c	124–125	23
2d	184–185	62	69	65	5d	127–128	25
2e	172–173	64	70	61	5e	130–131	23
2f	169–170	73	67	68	5f	117–118	18
2g	172–173	60	68	64	5g	121–122	24
2h	164–165	63	67	66	5h	124–125	26
3a	124–125	20	–	–	6a	216–217	37
3b	133–134	22	–	–	6b	221–223	35
3c	131–132	25	–	–	6c	204–205	38
3d	118–119	27	–	–	6d	218–219	39
3e	121–122	24	–	–	6e	207–208	38
3f	126–127	18	–	–	6f	214–215	34
3g	122–123	28	–	–	6g	211–212	33
3h	129–130	25	–	–	6h	213–214	34
4a	140–141	70	80	74	7a	180–182	70
4b	136–137	63	76	68	7b	187–189	73
4c	138–139	64	77	65	7c	183–184	72
4d	132–133	61	78	62	7d	191–192	69
4e	129–130	66	69	63	7e	184–185	71
4f	141–142	72	71	70	7f	189–190	64
4g	144–145	65	76	64	7g	179–180	66
4h	135–136	62	68	61	7h	177–179	74

Satisfactory elemental analyses were obtained for representative examples of each series C ± 0.24, H ± 0.12, N ± 0.19.

<sup>a</sup>Values indicate Yield (%).

However, in the presence of excess CAT, only pyrazoles and isoxazoles were obtained. Contrary to this, the 1,2-diarylsulfonylethenes were reported to give only pyrazolines and isoxazolines under similar experimental conditions [1b]. In the present study also, the dehydrogenation reaction, when carried out with equimolar/excess CAT, leading to the formation of pyrazoles/isoxazoles could not take place. However, **2** and **4**, on oxidation with chloranil in xylene, furnished bis(1-phenyl-3,5-diaryl-2-pyrazolyl) sulfones (**6**) and bis(3,5-diaryl-2-isoxazolyl) sulfones (**7**). The absence of two doublets corresponding to pyrazoline/isoxazoline ring protons in their <sup>1</sup>H NMR spectra confirm the formation of **6** and **7**.

## EXPERIMENTAL

Melting points were determined on a Mel-Temp apparatus and are uncorrected. The purity of the compounds was checked by TLC (silica gel H, BDH, ethyl acetate/hexane, 1:3). The IR spectra were recorded on a Perkin-Elmer grating infrared spectrophotometer, model 337 in KBr pellets. The <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub>/DMSO-*d*<sub>6</sub> on a Varian EM-

360 spectrometer (300 MHz) with TMS as an internal standard. The elemental analyses were performed at Dr. Reddy's Research Foundation, Hyderabad, India. The *E,E*-bis(styryl) sulfones were prepared as per the literature procedure [9].

### *Bis(1-phenyl-3,5-diaryl-2-pyrazolin-4-yl) sulfone (2)/1-phenyl-3,5-diaryl-4-styryl sulfonyl-2-pyrazoline (3)*

*Method A.* To a solution of *E,E*-bis(styryl) sulfone (**1**) (10 mmol), araldehyde phenylhydrazone (20 mmol) and CAT (20 mmol) in AcOH (20 ml) were added and refluxed for 4–5 h. Salts formed were filtered off. The filtrate was poured onto crushed ice and the mixture was extracted with methylene chloride (30 ml). The methylene chloride solution was washed with sat. NaHCO<sub>3</sub> solution followed by water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent under reduced pressure gave a mixture of products, which were separated through a column of silica gel (BDH, 60–120 mesh) using hexane/ethyl acetate (10:1) as the eluent. The products were identified as **2** (major) and **3** (minor).

TABLE 3 Elemental Analyses of Compound 2–7

Product	Mol. Formula (mol.wt.)	Found (Calcd) (%)		
		C	H	N
2a	C <sub>45</sub> H <sub>40</sub> N <sub>4</sub> O <sub>4</sub> S (732.90)	73.90 (73.74)	5.56 (5.50)	7.76 (7.64)
2b	C <sub>43</sub> H <sub>34</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>2</sub> S (741.74)	69.76 (69.63)	4.58 (4.62)	7.65 (7.55)
2e	C <sub>44</sub> H <sub>37</sub> ClN <sub>4</sub> O <sub>4</sub> S (753.34)	70.00 (70.15)	4.85 (4.95)	7.52 (7.44)
2g	C <sub>46</sub> H <sub>42</sub> N <sub>4</sub> O <sub>3</sub> S (730.93)	75.73 (75.59)	5.82 (5.79)	7.74 (7.66)
3a	C <sub>31</sub> H <sub>28</sub> N <sub>2</sub> O <sub>3</sub> S (508.64)	73.28 (73.20)	5.46 (5.55)	5.44 (5.51)
3b	C <sub>30</sub> H <sub>25</sub> ClN <sub>2</sub> O <sub>2</sub> S (513.06)	70.14 (70.23)	5.00 (4.91)	5.38 (5.46)
3d	C <sub>30</sub> H <sub>25</sub> ClN <sub>2</sub> O <sub>3</sub> S (529.06)	68.00 (68.11)	4.87 (4.76)	5.22 (5.29)
3h	C <sub>31</sub> H <sub>27</sub> ClN <sub>2</sub> O <sub>3</sub> S (543.09)	68.44 (68.56)	5.10 (5.01)	5.00 (5.16)
4a	C <sub>33</sub> H <sub>30</sub> N <sub>2</sub> O <sub>6</sub> S (582.68)	68.14 (68.02)	5.26 (5.19)	4.72 (4.81)
4b	C <sub>31</sub> H <sub>24</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S (591.51)	63.08 (62.95)	4.01 (4.09)	4.62 (4.73)
4e	C <sub>32</sub> H <sub>27</sub> ClN <sub>2</sub> O <sub>6</sub> S (603.09)	63.60 (63.73)	4.41 (4.51)	4.76 (4.64)
4g	C <sub>34</sub> H <sub>32</sub> N <sub>2</sub> O <sub>5</sub> S (580.70)	70.17 (70.32)	5.60 (5.55)	4.74 (4.82)
5a	C <sub>25</sub> H <sub>23</sub> NO <sub>4</sub> S (433.53)	69.44 (69.26)	5.42 (5.35)	3.20 (3.23)
5b	C <sub>24</sub> H <sub>20</sub> ClNO <sub>3</sub> S (437.95)	65.66 (65.82)	4.54 (4.60)	3.13 (3.20)
5d	C <sub>24</sub> H <sub>20</sub> ClNO <sub>4</sub> S (453.95)	63.66 (63.50)	4.40 (4.44)	3.00 (3.08)
5h	C <sub>25</sub> H <sub>22</sub> ClNO <sub>4</sub> S (467.97)	63.98 (64.16)	4.68 (4.74)	3.15 (2.99)
6a	C <sub>45</sub> H <sub>36</sub> N <sub>4</sub> O <sub>4</sub> S (728.87)	73.94 (74.15)	5.04 (4.98)	7.82 (7.69)
6e	C <sub>44</sub> H <sub>33</sub> ClN <sub>4</sub> O <sub>4</sub> S (749.29)	70.30 (70.53)	4.40 (4.44)	7.38 (7.48)
6g	C <sub>46</sub> H <sub>38</sub> N <sub>4</sub> O <sub>3</sub> S (742.90)	74.26 (74.37)	5.21 (5.15)	7.65 (7.54)
7a	C <sub>33</sub> H <sub>26</sub> N <sub>2</sub> O <sub>6</sub> S (578.64)	68.62 (68.50)	4.61 (4.53)	4.90 (4.84)
7e	C <sub>32</sub> H <sub>23</sub> ClN <sub>2</sub> O <sub>6</sub> S (599.06)	64.32 (64.16)	3.82 (3.87)	4.56 (4.67)
7g	C <sub>34</sub> H <sub>28</sub> N <sub>2</sub> O <sub>5</sub> S (576.67)	70.76 (70.82)	4.80 (4.89)	4.90 (4.86)

*Bis(3,5-diaryl-2-isoxazolin-4-yl) sulfone (4)/  
3,5-diaryl-4-styryl sulfonyl Isoxazoline (5)*

**Method A.** To a solution of **1** (10 mmol) in AcOH (20 ml), araldoxime (20 mmol) and CAT (20 mmol) were added and refluxed for 4–5 h, and the salts formed, if any were removed by filtration. The contents were poured onto crushed ice and extracted with methylene chloride, washed with sat. NaHCO<sub>3</sub> solution followed by water, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuo.

The mixture of products obtained was separated by column chromatography using silica gel (BDH, 60–120 mesh) with hexane/ethyl acetate (10:1) as eluent. The products were identified as **4** (major) and **5** (minor).

*Bis(1-phenyl-3,5-diaryl-2-pyrazolin-4-yl) sulfone (2)/bis(3,5-diaryl-2-isoxazolin-4-yl) sulfone (4)*

**Method B.** Compound **1** (10 mmol), araldehyde phenylhydrazone (20 mmol)/araldoxime (20 mmol), and a two-fold excess of CAT in AcOH (25 ml) were refluxed for 6–7 h. The salts formed were filtered off. The filtrate was poured onto crushed ice and extracted with methylene chloride, washed with sat. NaHCO<sub>3</sub> solution followed by water, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent under reduced pressure gave crude product, which was purified by column chromatography to provide pure **2/4**.

**Method C.** An equimolar (10 mmol) mixture of **3/5**, araldehyde phenylhydrazone/araldoxime and CAT in AcOH (20 ml) was refluxed for 5–6 h. The reaction mixture was processed as mentioned previously to provide **2/4**.

**Dehydrogenation of 2/4.** A mixture of **2/4** (10 mmol) and chloranil (11 mmol) in xylene (20 ml) was refluxed for 30–32 h and the organic layer was washed with 1 N NaOH, followed by water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure. The solid obtained was purified by recrystallization from AcOH to provide **6** and **7**, respectively.

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