# Sequential Reduction and Dehydration of Phenacyl-(*E*)-Styryl Sulfones to Unsymmetrical (*E*,*E*)-Bis(styryl) Sulfones

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**Abstract:** β-Keto vinylic sulfones, the key building blocks for the synthesis of the title compounds, were prepared by two different routes. $NaBH_4$ reduction of these compounds afforded β-hydroxy vinylic sulfones which were dehydrated with acetic anhydride and $BF_3{\cdot}Et_2O$ to obtain bis(styryl) sulfones. Alternatively, one-pot synthesis of these bis(styryl) sulfones was also achieved directly from β-keto vinylic sulfones by treating with $NaBH_4$ in EtOH followed by refluxing with concentrated HCl.

**Key words:** β-keto vinylic sulfones, β-hydroxy-(*E*)-vinylic sulfones, (*E*,*E*)-bis(styryl) sulfones, styrylsulfinate, Knoevenagel condensation

Sulfone, a functional group that resembles the carbonyl group, is associated with a high degree of thermodynamic stability and survives a large number of transformations. The important properties of sulfones thus culminated in the synthesis and structural studies of a vast number of compounds incorporating such a moiety.[1–4] It is only within the last two or three decades that a more diverse range of sulfur chemistry has been explored. Sulfones have also acquired importance chemotherapeutically as this moiety is found to be a potential pharmacophore in many carbocyclic and heterocyclic systems.[5–8] β-Keto vinyl sulfones have also served as a class of compounds of proven value in organic synthesis as excellent acceptors for the Michael additions [9] and 2π partners in cycloaddition reactions[6] due to the activation of the double bond by the sulfone group.

β-Hydroxy sulfones are useful chiral synthons in organic synthesis.[10] Their preparation in enantiomerically pure form has attracted considerable interest.[11–13] They have been successfully used in the synthesis of biologically active molecules such as γ-butenolides,[14] γ-butyrolactones,[14,15] δ-valerolactones[16] and other β-hydroxy substituted sulfones.[17] They are also useful synthetic intermediates for the preparation of enantiomerically pure 2,5-disubstituted tetrahydrofuran[18] units found in many natural products. While looking for pharmaceutically promising analogs of sulfones, and as part of our ongoing interest on styryl sulfones, we paid attention to the synthesis of unsymmetrical (*E*,*E*)-bis(styryl) sulfones. These compounds have been used as valuable precursors in the synthesis of various carbocyclic and heterocyclic systems such as cyclopropanes,[19] thiomorpholines,[20] dithiane-1,1-dioxides,[21] pyrazolines,[22] isoxazoles,[23] 1,4-substituted butadienes[24] and spiro heterocyclic systems.[25] Recently, bis(styrylsulfonyl) methanes and bis(styryl) sulfones have also been reported as potential HIV-1 integrase inhibitors[26] and anticancer agents, respectively.[27]

Although some symmetrical bis(styryl) sulfones (both aromatic rings having the same substituents) with (*E*,*E*)-configuration have been known for some time, the synthesis of unsymmetrical (*E*,*E*)-bis(styryl) sulfones (with different substitutions on each aromatic rings) are less familiar. Kamigata et al.[28] synthesized *E*,*E*-unsymmetrical bis(styryl) sulfones by ruthenium(II) complex catalyzed addition of arylethenesulfonyl chlorides to styrenes.

Earlier, we have reported[19] the synthesis of *E*,*E*- and *Z*,*E*-unsymmetrical bis(styryl) sulfones by Knoevenagel condensation of styryl sulfonyl acetic acids with araldehydes in the presence of a catalytic amount of benzylamine. Encouraged by their increasing interest in organic synthesis and their significant biological activity, we herein report a novel and convenient method for the synthesis of unsymmetrical (*E*,*E*)-bis(styryl) sulfones. The β-keto vinylic sulfones **5**, which are the key intermediates in the preparation of bis(styryl) sulfones, were synthesized by two different methods (Schemes 1 and 2).

The first step of the sequence is a reaction between phenacyl bromide (**1**) and mercaptoacetic acid (**2**) to generate phenacylthioacetic acid (**3**), which on oxidation, yielded phenacylsulfonylacetic acid (**4**).[29] Condensation of **4** with substituted benzaldehydes in glacial AcOH in the presence of a catalytic amount of benzylamine produced phenacyl (*E*)-styryl sulfones **5** (Scheme 1, Table 1). Alternatively, **5** were also prepared by the condensation of sodium (*E*)-styrylsulfinates **8** with phenacyl bromides, essentially following the procedure as described by Reddy et al.[29] Sodium (*E*)-styrylsulfinates **8** were made from (*E*)-styrylsulfonyl chlorides **7** which are prepared by treating sulfuryl chloride with styrene **6** in DMF at 0 °C (Scheme 2, Table 1). $NaBH_4$ reduction of phenacyl (*E*)-styryl sulfones **5** that were prepared following Method A (Scheme 1) produced β-hydroxy vinylic sulfones **9** in excellent yields (Table 1).

A number of reagents have been employed for dehydration of alcohols, such as phosphorus pentoxide,[30] cerium(III) chlorides,[31] chromium dichloride[32] and phthalic anhydride.[30] Some of these dehydrations were carried out by first acetylating the hydroxyl group followed by elim-

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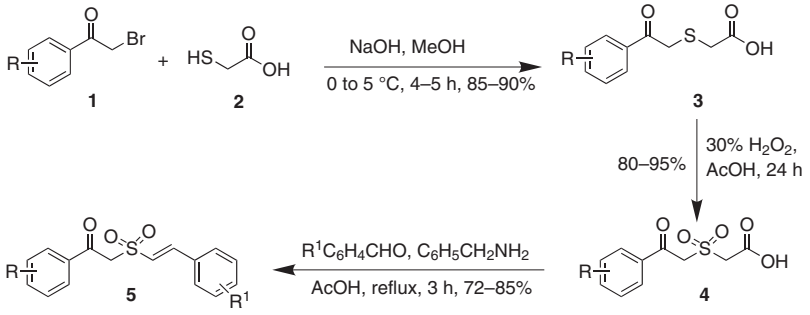
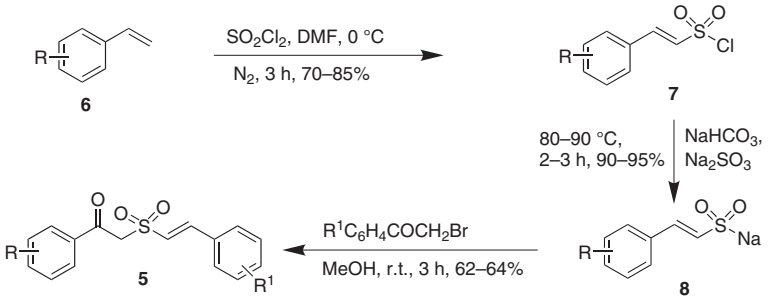



**Scheme 1**




**Scheme 2**

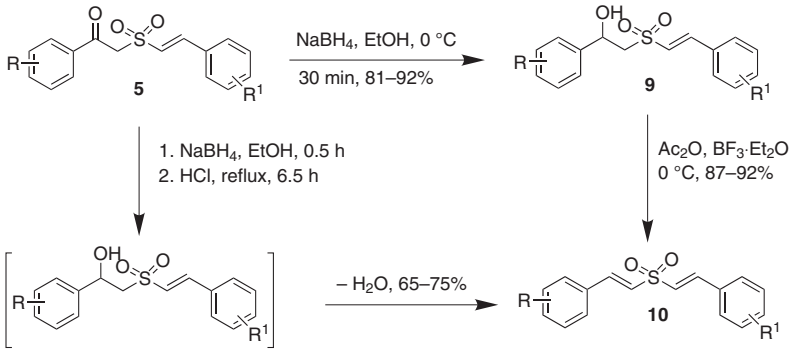
**Table 1** Synthesis and Overall Yields of Prepared Compounds **5**, **9** and **10**

| Compound | R | $R^1$ | Mp (°C) | Yield (%) | |
|---|---|---|---|---|---|
| | | | | Method A | Method B |
| **5a** | H | 4-Cl | 135–136 | 80 | – |
| **5b** | 4-Cl | 4-Cl | 190–192 | 85 | – |
| **5c** | 4-$CH_3$ | 4-$OCH_3$ | 126–127 | 72 | 62 |
| **5d** | 4-$CH_3$ | 4-H | 142–143 | 73 | 64 |
| **5e** | 4-$CH_3$ | 4-Cl | 165–166 | 76 | – |
| **9a** | H | 4-Cl | 122–124 | 86 | – |
| **9b** | 4-Cl | 4-Cl | 177–179 | 92 | – |
| **9c** | 4-$CH_3$ | 4-$OCH_3$ | 110–111 | 81 | – |
| **9d** | 4-$CH_3$ | 4-H | 122–123 | 84 | – |
| **9e** | 4-$CH_3$ | 4-Cl | 147–148 | 82 | – |
| **10a** | 4-H | 4-Cl | 146–147 | 91 | 73 |
| **10b** | 4-Cl | 4-Cl | 218–219 | 87 | 75 |
| **10c** | 4-$CH_3$ | 4-$OCH_3$ | 166–168 | 89 | 68 |
| **10d** | 4-$CH_3$ | 4-H | 119–121 | 92 | 65 |
| **10e** | 4-$CH_3$ | 4-Cl | 151–153 | 87 | 66 |

ination with NaOAc. Dehydration of alcohols was also achieved by mesylation of the hydroxyl group, followed by the basic elimination of methanesulfonic acid with $Et_3N$.[33] However, in our experience the yields obtained using these methods were low and variable. Conversely, when **9** were dehydrated with $Ac_2O/BF_3{\cdot}Et_2O$ at 0 °C, the dehydration process proceeded rapidly with complete diastereoselectivity, resulting in (*E*,*E*)-bis(styryl) sulfones **10** (Scheme 3, Table 1). All the yields reported in the Table 1 for **10** (Scheme 3) are based on the molar equivalents of β-hydroxy (*E*)-vinyl sulfones **9** (Scheme 3) taken in the reaction. Alternatively **10** were also obtained directly from **5** (Scheme 1) by one-pot $NaBH_4$ reduction in EtOH followed by dehydration with concentrated HCl. (Scheme 3, Method B, Table 1) and the yields of formation of **10** are based on **5**.

In conclusion, we report two new, mild and convenient approaches for the synthesis of β-keto vinylic sulfones which are the common precursors for both β-hydroxy vinylic sulfones and *E*,*E*-asymmetrical bis(styryl) sulfones. Also, we have developed a novel one-pot synthesis of bis(styryl) sulfones from β-keto vinylic sulfones. The new methods herein reported are straightforward, tolerate a variety of functional groups and gave good yields with complete diastereoselectivity.

All chemicals and solvents were purchased from commercial sources and were used without further treatment unless otherwise indicated. Solvents were dried using standard procedures and reactions requiring anhydrous conditions were performed under $N_2$. Reactions were monitored by TLC on silica gel plates (60 Å; Aldrich) and visualized under 254 nm UV light. Yields were of purified product and were not optimized. Melting points were determined in




**Scheme 3**

open capillary tubes using a Mel-Temp® electro thermal apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240-C spectrophotometer using KBr optics. $^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer using TMS as an internal standard. Chemical shifts are expressed in ppm and the values are given in δ scale, multiplicity (s = singlet, d = doublet, m = multiplet, br s = broad singlet), integration, coupling constant (*J*, Hz). Elemental analyses were performed by Quantitative Technologies Inc. White House, New Jersey. Phenacylsulfonylacetic acids were prepared according to the procedure reported in the literature.[29]

**Phenacyl (*E*)-Styryl Sulfones 5, General Procedure**
**Method A**

A mixture of phenacylsulfonylacetic acid (**4**; 10 mmol), araldehyde (10 mmol), AcOH (10 mL), and a catalytic amount of benzyl amine (2–3) drops was refluxed for about 3 h. After cooling, the precipitated product was filtered and washed with *i*-PrOH. If solid was not formed, the reaction mixture was diluted with $Et_2O$. The organic layer was washed with sat. $NaHCO_3$, dilute HCl and dried over $Na_2SO_4$. The solvent was removed under vacuum to obtain the desired product **5**.

**Method B**
**Sodium (*E*)-Styrylsulfinate (8)**

Sulfuryl chloride (0.5 mol) was added dropwise to stirred anhyd DMF (37 mL) cooled to 0 °C under $N_2$. After the addition was completed, the mixture was warmed to r.t. and stirred further for 0.5 h. Styrene **6** (0.25 mol) was then added in three portions and the reaction mixture was gradually heated on a water bath at 90 °C for 3 h. The reaction mixture was cooled and then poured onto the crushed ice and the separated oily layer was extracted with $Et_2O$ and dried. Evaporation of the solvent gave **7** (70–85%) as colorless crystals. Recrystallization from $CHCl_3$–light petroleum ether mixture yielded pure product of sodium (*E*)-styrylsulfinate.

A solution of sodium sulfite (0.3 mol) and $NaHCO_3$ (0.31 mol) in water (200 mL) was stirred on water bath maintained at 80–90 °C. The appropriate (*E*)-styrylsulfonyl chloride **7** (0.16 mol) was added to this solution in portions over a period of 0.5 h with stirring. After completion of the addition, the mixture was stirred at 80–90 °C for a further period of 2–3 h and then allowed to cool to r.t. The sodium (*E*)-styrylsulfinate **8** thus separated as long colorless crystals was collected on a Buchner filter and dried.

A mixture of phenacyl bromide (10 mmol), sodium (*E*)-styrylsulfinate (12 mmol) and aq MeOH (3:1, 100 mL) was stirred at r.t. for 3 h and then poured onto crushed ice. The solid that separated out was filtered, washed with excess water and dried. The product, phenacyl (*E*)-styryl sulfone **5** was recrystallized from *i*-PrOH.

**5a**

Solid; mp 135–136 °C.

IR (KBr): 1680, 1620, 1315, 1140, 1010 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 4.74 (s, 2 H, $CH_2$), 7.03 (d, *J* = 15.6 Hz, 1 H), 7.17–8.00 (m, 10 H).

$^{13}$C NMR ($CDCl_3$): δ = 187.9 (C=O), 144.6 (4-$ClC_6H_4CH$=), 141.8, 138.2, 134.4 (=$CHSO_2$), 131.0, 130.8, 130.4, 129.9, 129.8, 125.6, 63.0 ($CH_2$).

Anal. Calcd for $C_{16}H_{13}ClO_3S$: C, 59.91; H, 4.08. Found: C, 60.32; H, 4.04.

**5b**

Solid; mp 190–192 °C.

IR (KBr): 1670, 1625, 1340, 1130, 1015 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 4.78 (s, 2 H, $CH_2$), 7.12 (d, *J* = 15.4 Hz, 1 H), 7.21–8.05 (m, 9 H).

$^{13}$C NMR ($CDCl_3$): δ = 188.0 (C=O), 144.6 (4-$ClC_6H_4CH$=), 141.8, 138.2, 134.4 (=$CHSO_2$), 131.0, 130.8, 130.4, 129.9, 129.8, 125.6, 63.1 ($CH_2$).

Anal. Calcd for $C_{16}H_{12}Cl_2O_3S$: C, 54.10; H, 3.40. Found: C, 54.14; H, 3.37.

**5c**

Solid; mp 126–127 °C.

IR (KBr): 1690, 1625, 1335, 1145, 1015 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 2.26 (s, 3 H, $ArCH_3$), 3.82 (s, 3 H, $ArOCH_3$), 4.72 (s, 2 H, $CH_2$), 7.01 (d, *J* = 15.5 Hz, 1 H), 7.19–8.02 (m, 9 H).

$^{13}$C NMR ($CDCl_3$): δ = 189.4 (C=O), 145.1 (4-$CH_3OC_6H_4CH$=), 141.9, 138.1, 134.0 (=$CHSO_2$), 131.5, 130.8, 130.3, 129.8, 129.4, 126.0, 62.2 ($CH_2$), 53.2 (4-$CH_3OC_6H_4$), 21.4 (4-$CH_3C_6H_4$).

Anal. Calcd for $C_{18}H_{18}O_4S$: C, 65.43; H, 5.49. Found: C, 65.39; H, 5.52.

**5d**

Solid; mp 142–143 °C.

IR (KBr): 1670, 1610, 1320, 1140, 1000 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 2.28 (s, 3 H, $ArCH_3$), 4.71 (s, 2 H, $CH_2$), 7.04 (d, *J* = 15.6 Hz, 1 H), 7.21–8.03 (m, 10 H).

$^{13}$C NMR ($CDCl_3$): δ = 188.8 (C=O), 145.6 ($C_6H_4CH$=), 142.1, 138.1, 134.5 (=$CHSO_2$), 131.9, 131.0, 130.5, 129.9, 129.6, 125.8, 62.8 ($CH_2$), 21.6 (4-$CH_3C_6H_4$).

Anal. Calcd for $C_{17}H_{16}O_3S$: C, 67.97; H, 5.37. Found: C, 68.02; H, 5.35.

**5e**
Solid; mp 165–166 °C.

IR (KBr): 1690, 1625, 1340, 1130, 1020 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 2.30 (s, 3 H, $ArCH_3$), 4.75 (s, 2 H, $CH_2$), 7.05 (d, *J* = 15.4 Hz, 1 H), 7.19–8.00 (m, 9 H).

$^{13}C$ NMR ($CDCl_3$): δ = 188.8 (C=O), 145.6 (4-$ClC_6H_4CH$=), 142.0, 138.5, 134.4 (=$CHSO_2$), 131.6, 130.9, 130.6, 129.9, 129.5, 125.5, 62.8 ($CH_2$), 21.5 (4-$CH_3C_6H_4$).

Anal. Calcd for $C_{17}H_{15}ClO_3S$: C, 60.98; H, 4.52. Found: C, 60.95; H, 4.56.

**β-Hydroxy-(*E*)-vinylic Sulfone (9); General Procedure**
To an ethanolic solution (20 mL) of phenacyl (*E*)-styryl sulfones **5** (from Method A) (10 mmol) maintained at 0 °C, was slowly added $NaBH_4$ (10 mmol) under $N_2$ atmosphere. The reaction mixture was maintained at 0 °C for 0.5 h. After completion of the reaction (monitored by TLC), the contents were poured on to the crushed ice. The solid separated out was filtered, washed with water and dried under vacuum to get the desired product **9**.

**9a**
Solid; mp 122–124 °C.

IR (KBr): 3450, 1615, 1310, 1145, 1010 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 1.91 (br s, 1 H, OH), 3.10–3.31 (m, 2 H, $CH_2$), 5.16 (d, 1 H, CH), 6.83 (d, *J* = 15.5 Hz, 1 H), 7.07–7.77 (m, 10 H).

$^{13}C$ NMR ($CDCl_3$): δ = 143.9 (CH=), 139.6, 138.1, 134.8 (=$CHSO_2$), 130.9, 130.2, 129.9, 129.5, 127.5, 126.3, 68.8 (CHOH), 63.2 ($CH_2$).

Anal. Calcd for $C_{16}H_{15}ClO_3S$: C, 59.53; H, 4.68. Found: C, 59.67; H, 4.63.

**9b**
Solid; mp 177–179 °C.

IR (KBr): 3465, 1620, 1320, 1140, 1015 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 1.94 (br s, 1 H, OH), 3.11–3.36 (m, 2 H, $CH_2$), 5.17 (d, 1 H, CH), 6.87 (d, *J* = 15.6 Hz, 1 H), 7.05–7.81 (m, 9 H).

$^{13}C$ NMR ($CDCl_3$): δ = 143.9 (CH=), 139.6, 138.1, 134.8 (=$CHSO_2$), 130.9, 130.2, 129.9, 129.5, 127.5, 126.3, 68.7 (CHOH), 63.2 ($CH_2$).

Anal. Calcd for $C_{16}H_{14}Cl_2O_3S$: C, 53.79; H, 3.95. Found: C, 53.81; H, 3.96.

**9c**
Solid; mp 110–111 °C.

IR (KBr): 3445, 1625, 1335, 1145, 1015 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 1.92 (br s, 1 H, OH), 2.26 (s, 3 H, $ArCH_3$), 3.09–3.29 (m, 2 H, $CH_2$), 3.80 (s, 3 H, $ArOCH_3$), 5.16 (d, 1 H, CH), 6.83 (d, *J* = 15.5 Hz, 1 H), 7.06–7.78 (m, 9 H).

$^{13}C$ NMR ($CDCl_3$): δ = 145.1 (CH=), 139.0, 137.8, 134.1 (=$CHSO_2$), 130.8, 130.4, 129.9, 129.7, 127.3, 126.7, 69.3 (CHOH), 63.4 ($CH_2$), 53.7 (4-$CH_3OC_6H_4$), 21.5 (4-$CH_3C_6H_4$).

Anal. Calcd for $C_{18}H_{20}O_4S$: C, 65.04; H, 6.06. Found: C, 65.02; H, 6.04.

**9d**
Solid; mp 122–123 °C.

IR (KBr): 3480, 1610, 1320, 1140, 1010 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 1.92 (br s, 1 H, OH), 2.29 (s, 3 H, $ArCH_3$), 3.11–3.30 (m, 2 H, $CH_2$), 5.15 (d, 1 H, CH), 6.82 (d, *J* = 15.4 Hz, 1 H), 7.09–7.72 (m, 10 H).

$^{13}C$ NMR ($CDCl_3$): δ = 145.1 (CH=), 143.9, 138.2, 134.1 (=$CHSO_2$), 130.8, 130.7, 129.9, 129.6, 127.3, 126.9, 69.3 (CHOH), 63.8 ($CH_2$), 21.5 (4-$CH_3C_6H_4$).

Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.09. Found: C, 67.56; H, 5.99.

**9e**
Solid; mp 147–148 °C.

IR (KBr): 3450, 1620, 1340, 1130, 1020 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 1.95 (br s, 1 H, OH), 2.27 (s, 3 H, $ArCH_3$), 3.16–3.33 (m, 2 H, $CH_2$), 5.16 (d, 1 H, CH), 6.81 (d, *J* = 15.6 Hz, 1 H), 7.10–7.81 (m, 9 H).

$^{13}C$ NMR ($CDCl_3$): δ = 145.1 (CH=), 143.5, 138.4, 134.0 (=$CHSO_2$), 131.1, 131.0, 129.9, 129.2, 128.9, 126.9, 69.3 (CHOH), 61.6 ($CH_2$), 21.4 (4-$CH_3C_6H_4$).

Anal. Calcd for $C_{17}H_{17}ClO_3S$: C, 60.62; H, 5.09. Found: C, 60.65; H, 5.08.

**(*E*,*E*)-Bis(styryl) Sulfones (10); General Procedure**
**Method A**
$BF_3{\cdot}Et_2O$ (5 mmol) was added to a solution of **9** (5 mmol) in $Ac_2O$ (10 mL) at 0 °C. The mixture was stirred for 0.5 h and poured into $CHCl_3$ (25 mL). The organic layer was washed with sat. $NaHCO_3$ (2 × 25 mL), water (2 × 25 mL) and dried over $Na_2SO_4$. The solvent was removed under vacuum and the residue was recrystallized from *i*-PrOH to get the desired product **10** in excellent yields. The yields of **10** were calculated from **9**.

**10a**
Solid; mp 146–147 °C.

IR (KBr): 1615, 1330, 1125, 1020 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 6.57 (d, *J* = 15.4 Hz, 1 H), 7.29 (d, *J* = 15.5 Hz, 1 H), 7.16–7.58 (m, 11 H).

$^{13}C$ NMR ($CDCl_3$): δ = 151.4 ($C_6H_5CH$=), 142.6 (4-$ClC_6H_4CH$=), 141.6, 134.9, 130.8, 128.8, 128.4, 127.7, 126.4 ($SO_2CH$=), 126.2, 123.7, 118.2 (=$CHSO_2$).

Anal. Calcd for $C_{16}H_{13}ClO_2S$: C, 63.04; H, 4.30. Found; C, 63.22; H, 4.26.

**10b**
Solid; mp 218–219 °C.

IR (KBr): 1620, 1325, 1130, 1010 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 6.75 (d, *J* = 15.4 Hz, 1 H), 7.34 (d, *J* = 15.3 Hz, 1 H), 7.16–7.58 (m, 10 H).

$^{13}C$ NMR ($CDCl_3$): δ = 152.3 (4-$ClC_6H_4CH$=), 143.9, 139.6, 134.8, 128.8, 127.6, 125.3 (=$CHSO_2CH$=), 119.4.

Anal. Calcd for $C_{16}H_{12}Cl_2O_2S$: C, 56.65; H, 3.56. Found; C, 56.82; H, 3.57.

**10c**
Solid; mp 166–168 °C.

IR (KBr): 1610, 1320, 1110, 1020 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 2.26 (s, 3 H, $ArCH_3$), 3.75 (s, 3 H, $ArOCH_3$), 6.50 (d, *J* = 15.4 Hz, 1 H), 7.33 (d, *J* = 15.4 Hz, 1 H), 6.77–7.47 (m, 10 H).

$^{13}C$ NMR ($CDCl_3$): δ = 162.4, 144.6 (4-$CH_3C_6H_4CH$=), 141.6 (4-$CH_3OC_6H_4CH$=), 140.7, 139.8, 133.1, 130.5, 130.2, 129.3, 125.5

($SO_2CH$=), 123.7, 114.8 (=$CHSO_2$), 55.8 (4-$CH_3OC_6H_4$), 21.8 (4-$CH_3C_6H_4$).

Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.76; H, 5.77. Found; C, 69.00; H, 5.69.

**10d**

Solid; mp 119–121 °C.

IR (KBr): 1615, 1330, 1115, 1020 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 2.25 (s, 3 H, $ArCH_3$), 6.64 (d, *J* = 15.4 Hz, 1 H), 7.38 (d, *J* = 15.4 Hz, 1 H), 7.01–7.50 (m, 11 H).

$^{13}C$ NMR ($CDCl_3$): δ = 145.6 (4-$CH_3C_6H_4CH$=), 143.6 ($C_6H_5CH$=), 141.9, 136.9, 135.5, 131.9, 129.1, 128.4, 127.8 ($SO_2CH$=), 125.8, 119.6 (=$CHSO_2$), 21.7 (4-$CH_3C_6H_4$).

Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found; C, 72.02; H, 5.74.

**10e**

Solid; mp 151–153 °C.

IR (KBr): 1620, 1335, 1130, 1015 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 2.25 (s, 3 H, $ArCH_3$), 6.84 (d, *J* = 15.5 Hz, 1 H), 7.66 (d, *J* = 15.5 Hz, 1 H), 6.92–7.72 (m, 10 H).

$^{13}C$ NMR ($CDCl_3$): δ = 149.9 (4-$CH_3C_6H_4CH$=), 145.4 (4-$ClC_6H_4CH$=), 143.4, 141.0, 134.5, 133.0, 128.4, 127.6 ($SO_2CH$=), 126.0, 125.5, 119.2 (=$CHSO_2$), 21.7 (4-$CH_3C_6H_4$).

Anal. Calcd for $C_{17}H_{15}ClO_2S$: C, 64.04; H, 4.74. Found; C, 64.29; H, 4.84.

**Method B**

To a cooled solution of phenacyl (*E*)-styryl sulfone **5a** (from Method A) (5 mmol) in EtOH (50 mL), $NaBH_4$ (5 mmol) was added and stirred for 30 min. A few crystals of bromocresol blue were added as pH indicator and the mixture was refluxed for 1 h. A few drops of concd HCl was added to the solution until the color changed to yellow. After refluxing for 5 h, the solution was diluted with water (50 mL), cooled to 0 °C and stirred for 0.5 h. The solid formed was filtered, washed with water (2 × 25 mL) and dried to give a colorless solid which is identical to the compound **10a** reported in the Method A. The yields of **10** were calculated based on the starting material **5**.

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