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Stereoselective synthesis of vinyl sulfones by carbomagnesiation of acetylenic sulfone in the presence of CuCN

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Abstract

Carbomagnesiation of acetylenic sulfone in the presence of catalytic amount of CuCN gave α-sulfonyl vinyl magnesium reagent, which further reacted with aldehydes to afford polysubstituted vinyl sulfones in moderate to good yields.

Keywords: Carbomagnesiation; Acetylenic sulfone; Vinyl sulfone; Stereoselectivity

1. Introduction

Many biologically active compounds have the structural unit of polysubstituted alkenes and the stereoselective synthesis of polysubstituted alkenes remains a challenging problem in organic synthesis [1]. Vinyl sulfones are useful precursors of alkenes due to the further transformation of sulfonyl [2]. The available methodology for vinyl sulfones synthesis mainly consists of Horner–Emmons reactions of carbonyl compounds and sulfonyl phosphoranes [3], Peterson reactions [4], β-elimination of selenosulphones [5] and selenosulfonation of acetylene [6]. Considering the importance of vinyl sulfones, it is still of interest to find new method to prepare vinyl sulfones. Carbometallation of alkynes by organometallic reagents is widely studied in the synthesis of substituted alkenes [7]. Organomagnesium reagents are important reagents in organic chemistry [8]. However, little attention has been paid to the synthesis of vinyl sulfones by carbomagnesiation of acetylenic sulfones. It has been reported that the reaction of Grignard reagents with acetylenic sulfone to afford the products of overall substitution of the sulfone moiety [9]. In the course of our study, we find that carbomagnesiation of acetylenic sulfones with Grignard reagents happened smoothly in the presence of catalytic amount of CuCN. Herein, we wish to report the carbomagnesiation of acetylenic sulfones and its application in the stereoselective synthesis of polysubstituted vinyl sulfones.

2. Results and discussion

Firstly, the carbomagnesiation reaction of arylmagnesium bromides with acetylenic sulfone and its further reaction with aldehydes were studied. Carbomagnesiation of 1-phenyl-2-(*p*-tolylsulfonyl)ethyne with arylmagnesium bromide in the presence of 10 mol% of CuCN in THF/CH_2Cl_2 gave α-sulfonyl vinyl Grignard reagents **2**, which further reacted with aldehydes **3** to afford tetrasubstituted alkenes **4** containing allylic alcohol structural unit stereoselectively (Scheme 1). The results are summarized in Table 1. Table 1 shows that different substituted aromatic aldehydes and *n*-butyraldehyde

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Table 1
Synthesis of compounds **4a**–**4h**

Entry	Ar	R	Product	Yield[a] (%)
1	C_6H_5–	*p*-ClC_6H_4–	**4a**	72
2	C_6H_5–	*p*-$NO_2C_6H_4$–	**4b**	80
3	C_6H_5–	C_6H_5–	**4c**	48
4	C_6H_5–	*p*-$CH_3OC_6H_4$–	**4d**	47
5	C_6H_5–	*n*-C_3H_7–	**4e**	22
6	*p*-$CH_3C_6H_4$–	*p*-$NO_2C_6H_4$–	**4f**	67
7	*p*-$CH_3C_6H_4$–	C_6H_5–	**4g**	59
8	*p*-$CH_3C_6H_4$–	*p*-$(CH_3)_2NC_6H_4$–	**4h**	58

[a] Isolated yield based on the acetylenic sulfone used.

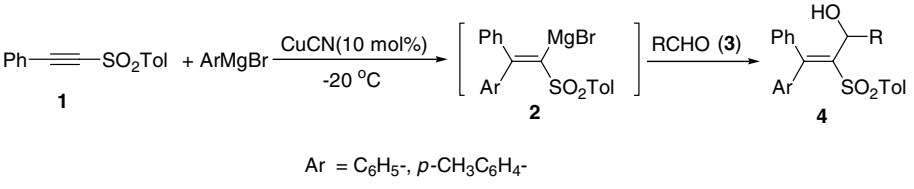
can be used as electrophiles. The products were obtained in moderate to good yields when the aromatic aldehydes were used as electrophiles. While low yield was obtained when the *n*-butyraldehyde is used.

The stereoselectivity of the addition of arylmagnesium bromides to acetylenic sulfone and its further reaction with aldehydes was confirmed by the X-ray structure of 1, 3-diphenyl-3-tolyl-2-(*p*-tolylsulfonyl)-allylic alcohol **4g** [10] (Fig. 1). Although high quality crystals cannot be obtained, Fig. 1 shows that *p*-tolyl is *cis* to sulfonyl, which suggests that the addition of arylmagnesium bromides to acetylenic sulfone is in the *anti*-fashion.

1,4-Dienes are typical structure of many natural compounds and their synthesis has attracted much interest [11]. So, we further investigated the addition of allylmagnesium bromide to acetylenic sulfone for the hope to synthesis tetrasubstituted alkenes containing 1,4-diene structural unit. In the case of the reaction of allylmagnesium bromide with 1-phenyl-2-(*p*-tolylsulfonyl)ethyne, Et_2O/CH_2Cl_2 was used as solvent instead of THF/CH_2Cl_2 for the reason that higher yield of the products could be obtained when the reactions were carried out in Et_2O/CH_2Cl_2. In the presence of 10 mol% of CuCN, addition of allylmagnesium bromide to 1-phenyl-2-(*p*-tolylsulfonyl)ethyne in Et_2O/CH_2Cl_2 gave α-sulfonyl vinyl Grignard reagents **5**, which reacted with aldehydes **3** to afford tetrasubstituted alkenes **6**,which contain 1,4-diene and allylic alcohol structural units (Scheme 2). The expected products were obtained in moderate yield with stereoselectivity of $Z{:}E = 85{:}15 \sim >95{:}5$.

This stereochemistry was verified by the NOESY spectra of the major product (*Z*)-1,3-diphenyl-2-(*p*-tolylsulfonyl)-2, 5-hexadiene-1-ol((*Z*)-**6b**). It shows that there are strong correlations between the allylic protons of the allyl group and the protons adjacent to hydroxyl, which suggests that the major addition of allylmagnesium bromide to acetylenic sulfone was in the *syn*-fashion. The results are summarized in Table 2.

In conclusion, we have developed a new one-pot method to prepare polysubstituted vinyl sulfones with moderate to good yields. This method has the advantages of readily available starting materials, simple procedures, mild reaction conditions and good



Scheme 1.

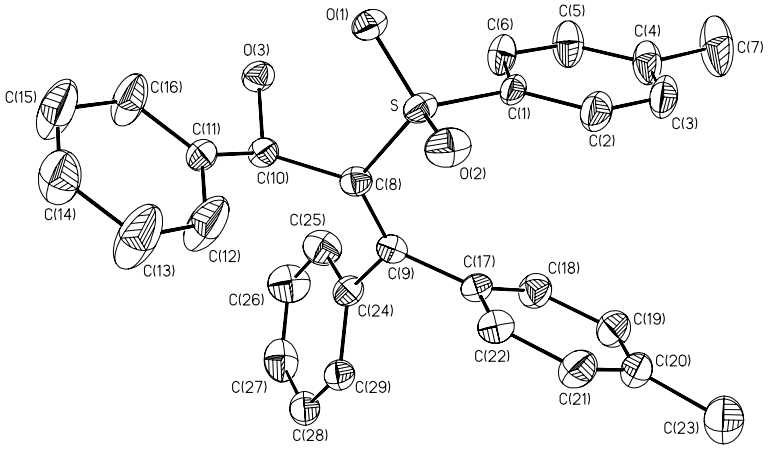
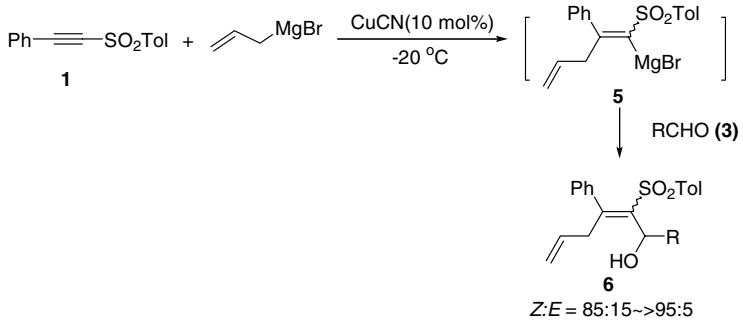


Fig. 1. The molecular structure of **4g**.



Scheme 2.

Table 2
Synthesis of compounds **6a–6e**

Entry	R	Product	Yield[a] (%) (*Z*/*E*)
1	*p*-$NO_2C_6H_4$–	**6a**	58 (85:15)
2	C_6H_5–	**6b**	64 (>95:5)
3	*p*-$(CH_3)_2NC_6H_4$–	**6c**	55 (>95:5)
4	*n*-C_3H_7–	**6d**	43 (>95:5)
5	C_6H_5CH = CH–	**6e**	66 (67:10)

[a] Isolated yield based on the acetylenic sulfone used.

stereoselectivity. Further studies on the application of the reaction are now in progress.

3. Experimental

All the solid products were recrystallized from ethyl acetate and hexane and the melting points are uncorrected. All reactions were carried out under an argon atmosphere. THF and Et_2O were distilled from sodium/benzophenone. CH_2Cl_2 was distilled from calcium hydride. NMR spectra were recorded at 300 MHz (^1H) and 75.47 MHz (^{13}C) on a Bruker AV-300 NMR spectrometer in $CDCl_3$. Acetylenic sulfone **1** were prepared according to the literature procedure [12].

*3.1. General procedure for the synthesis of **4a–4h** by the reaction of arylmagnesium bromides, acetylenic sulfone and aldehydes*

To the solution of ArMgBr (0.6 mmol) in THF/CH_2Cl_2 (v/v = 1/4, 5 ml) was added CuCN (10 mol%) and 1-phenyl-2-(*p*-tolylsulfonyl)ethyne (0.4 mmol) at −20 °C with stirring. After carbomagnesiation was complete (monitored by TLC), aldehyde 0.5 mmol was added and stirred at −20 °C for 3–4 h. The reaction was quenched with saturated NH_4Cl and extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4. After filtration and removal of solvent in vacuo, the crude product was purified with flash chromatography (silanes/hexanes–ethyl acetate 10:1 v/v). The desired products **4a–4h** were obtained.

*3.1.1. **4a**: 1-(p-Chlorophenyl)-3,3-diphenyl-2-(p-tolylsulfonyl)-2-propen-1-ol: m.p. 196 °C*

IR (KBr):*v* (cm^{-1}) 3514, 1490, 1295, 1135. ^1H NMR (300 MHz, $CDCl_3$): δ 7.51 (d, J = 8.41 Hz, 2H), 7.39–6.91 (m, 16H), 5.88 (s, 1H), 4.67 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ (ppm): 156.11, 143.36, 143.22, 140.06, 139.95, 138.39, 138.23, 133.20, 129.77, 129.26, 128.86, 128.74, 128.51, 127.71, 127.40, 127.04, 73.09, 21.51. MS(EI): *m*/*z*(%) 456 (0.90, $M^+ - H_2O$, ^{35}Cl), 458 (0.34, $M^+ - H_2O$, ^{37}Cl), 319 (20.28, ^{35}Cl), 321 (5.74, ^{37}Cl), 178 (100.00). Anal. Calc. for $C_{28}H_{23}ClO_3S$: C, 70.87; H, 4.88. Found: C, 70.85; H, 4.90%.

*3.1.2. **4b**: 3,3-Diphenyl-1-(p-nitrophenyl)-2-(p-tolylsulfonyl)-2-propen-1-ol: m.p. 145 °C*

IR (KBr): *v* (cm^{-1}) 3450, 1511, 1340, 1287, 1133. ^1H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, J = 8.75 Hz, 2H), 7.74 (d, J = 8.45 Hz, 2H), 7.34–6.91 (m, 14H), 5.98 (d, J = 11.57 Hz, 1H), 4.94 (d,J = 11.69 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 149.01, 143.61, 142.69, 139.70, 137.98, 129.85, 129.57, 128.95, 128.84, 127.78, 127.37, 126.59, 123.60, 73.04, 21.52. MS(EI): *m*/*z*(%) 329 (100, $M^+ - SO_2Tol$), 311 (20.34), 252 (15.67), 178 (60.91), 178 (100.00). Anal. Calc. for $C_{28}H_{23}NO_5S$: C, 69.26; H, 4.77; N, 2.88. Found: C, 69.20; H, 4.87; N, 2.66%.

*3.1.3. **4c**: 2-(p-Tolylsulfonyl)-1,3,3-triphenyl-2-propen-1-ol: m.p. 187 °C*

IR (KBr): *v* (cm^{-1}) 3508, 1590, 1491, 1286, 1134. ^1H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, J = 7.42 Hz, 2H), 7.45–7.21 (m, 9H), 7.12–7.07 (t, 4H), 6.97 (d, J = 8.09 Hz, 4H), 5.95 (d, J = 12.05 Hz, 1H), 4.87 (d, J = 11.95 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 155.79, 143.69, 143.22, 141.45, 140.14, 138.67, 138.38, 129.78, 129.10, 128.80, 128.75, 128.70, 128.42, 128.39, 127.68, 127.48, 127.36, 125.55, 73.56, 21.51. MS(EI): *m*/*z*(%) 422 (1.12), 285 (47.73, $M^+ - SO_2Tol - H_2O$), 284 (100.00), 178 (84.26). Anal. Calc. for $C_{28}H_{24}SO_3$: C, 76.34; H, 5.49. Found: C, 76.06; H, 5.76%.

*3.1.4. **4d**: 3,3-Diphenyl-1-(p-methoxyphenyl)-2-(p-tolylsulfonyl)-2-propen-1-ol: m.p. 170 °C*

IR (KBr): ν (cm^{-1}) 3501, 1510, 1442, 1289, 1173, 1131. ^1H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, J = 8.40 Hz, 2H), 7.29 (d, J = 11.46 Hz, 4H), 7.19–7.04 (m, 6H), 6.96–6.89 (m, 6H), 5.87 (d, J = 11.97 Hz, 1H), 4.83 (d, J = 12.00 Hz, 1H), 3.82 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 158.89, 155.33, 143.72, 143.14, 140.14, 138.77, 138.41, 133.54, 129.77, 129.04, 128.77, 128.73, 128.65, 128.34, 127.64, 127.43, 126.76, 113.82, 73.35, 55.31, 21.49. MS(EI): *m/z*(%) 315 (19.74, $M^+ - SO_2Tol$), 296 (100.00, $M^+ - SO_2Tol - H_2O$), 265 (25.59), 178 (72.71). Anal. Calc. for $C_{29}H_{26}SO_4$: C, 74.02; H, 5.57. Found: C, 73.71; H, 5.53%.

*3.1.5. **4e**: 1,1-Diphenyl-2-(p-tolylsulfonyl)-1-hexen-3-ol: m.p. 120 °C*

IR (KBr): ν (cm^{-1}) 3533, 1445, 1291, 1273, 1235, 1128. ^1H NMR (300 MHz, $CDCl_3$): δ 7.30–7.27 (m, 3H), 7.23–7.12 (m, 5H), 7.03–6.93 (m, 4H), 6.77 (s, 2H), 4.66–4.57 (m, 1H), 4.18 (d, J = 11.86 Hz, 1H), 2.30 (s, 3H), 2.27–2.11 (m, 2H), 1.52–1.40 (m, 2H), 0.90 (t, J = 14.69 Hz, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 154.07, 144.14, 143.00, 140.49, 138.72, 138.62, 129.91, 128.77, 128.73, 128.52, 128.21, 127.53, 127.18, 73.52, 39.18, 21.48, 19.82, 13.85. MS(ESI): *m/z* 429.2 ($M + Na^+$). Anal. Calc. for $C_{25}H_{26}O_3S$: C, 73.86; H, 6.45. Found: C, 73.15; H, 6.67%.

*3.1.6. **4f**: (Z)-3-(p-Methylphenyl)-1-(p-nitrophenyl)-3-phenyl-2-(p-tolylsulfonyl)-2-propen-1-ol: m.p. 140 °C*

IR (KBr): ν (cm^{-1}) 3484, 1518, 1345, 1289, 1135. ^1H NMR (300 MHz, $CDCl_3$): δ 8.26 (d, J = 7.29 Hz, 2H), 7.73 (d, J = 8.69 Hz, 2H), 7.32 (s, 2H), 7.21–7.05 (m, 6H), 6.96–6.89 (dd, J = 7.60 Hz, 7.61 Hz, 4H), 6.78 (d, J = 7.80 Hz, 1H), 6.00–5.92 (d, J = 24.73 Hz, 1H), 5.00 (d, J = 11.72 Hz, 1H), 2.31 (s, 6H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 129.93, 129.49, 128.93, 128.93, 128.77, 128.72, 128.38, 127.72, 127.44, 127.35, 126.60, 123.56, 73.12 (d, J = 18.9 Hz), 21.50, 21.29. MS(EI): *m/z*(%) 326 (100.00, $M^+ - SO_2Tol\text{-}H_2O$), 344 (34.93, $M^+ - SO_2Tol$), 280 (16.56), 297 (13.96). Anal. Calc. for $C_{29}H_{25}NO_5S$: C, 69.72; H, 5.04; N, 2.80. Found: C, 69.76; H, 5.00; N, 2.71%.

*3.1.7. **4g**: (Z)-1,3-Diphenyl-3-(p-methylphenyl)-2-(p-tolylsulfonyl)-2-propen-1-ol: m.p. 173 °C*

IR (KBr): ν (cm^{-1}) 3501, 1598, 1491, 1447, 1292, 1133. ^1H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, J = 7.59 Hz, 2H), 7.42 (t, J = 15.01 Hz, 2H), 7.30 (s, 3H), 7.22–7.17 (t, J = 14.58 Hz, 2H), 7.13–7.04 (q, 4H), 6.95–6.87 (q, 4H), 6.80(m, 1H), 5.96 (t, J = 22.72 Hz, 1H), 54.89–4.84 (dd, J = 1.31 Hz, 1.41 Hz, 1H), 2.30 (s, 6H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 129.84, 129.77, 129.33, 129.02, 128.79, 128.74, 128.63, 128.58, 128.33, 128.28, 127.61, 127.54, 127.47, 127.28, 125.58, 73.61 (d, J = 12.9 Hz), 21.50 (d, J = 8.1 Hz), 21.24. MS(ESI): *m/z* 477.2 ($M + Na^+$). Anal. Calc. for $C_{29}H_{26}SO_3$: C, 76.62; H, 5.76. Found: C, 76.07; H, 5.71%.

*3.1.8. **4h**: (Z)-1-(p-Dimethylaminophenyl)-3-(p-methylphenyl)-3-phenyl-2-(p-tolylsulfonyl)-2-propen-1-ol: m.p. 97 °C*

IR (KBr): ν (cm^{-1}) 3504, 1613, 1521, 1293, 1133. ^1H NMR (300 MHz, $CDCl_3$): δ 7.42 (d, J = 8.24 Hz, 2H), 7.28 (d, J = 6.67 Hz, 3H), 7.17–7.09 (m, 6H), 6.95–6.77 (m, 6H), 5.90–5.81 (t, J = 25.96 Hz, 1H), 4.81–4.77 (dd, J = 2.62 Hz, 2.60 Hz, 1H), 2.96 (s, 6H), 2.30 (s, 3H), 2.29 (s, 3H). MS(ESI): *m/z* 520.2 ($M + Na^+$). Anal. Calc. for $C_{28}H_{23}NO_5S$: C, 74.82; H, 6.28; N, 2.82. Found: C, 74.89; H, 6.30; N, 2.96%.

*3.2. General procedure for the synthesis of **6a–6e** by the reaction of allylmagnesium bromide, acetylenic sulfone and aldehydes*

To the solution of allylmagnesium bromide (0.6 mmol) in Et_2O/CH_2Cl_2 (v/v = 1/4, 5 ml) was added CuCN (10 mol%) and 1-phenyl-2-(*p*-tolylsulfonyl)ethyne (0.4 mmol) at −20 °C with stirring. After carbomagnesiation was complete (monitored by TLC), aldehyde 0.5 mmol was added and stirred at −20 °C for 3–4 h. The reaction was quenched with saturated NH_4Cl and extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4. After filtration and removal of solvent in vacuo, the crude product was purified with flash chromatography (silanes/hexanes–ethylacetate 10:1 v/v).The desired products **6a–6e** were obtained.

*3.2.1. (Z)-**6a**: 1-(p-Nitrophenyl)-3-phenyl-2-(p-tolylsulfonyl)-2,5-hexadien-1-ol: m.p. 46 °C*

IR (KBr): ν (cm^{-1}) 3485, 1597, 1520, 1346, 1287, 1139. ^1H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, J = 8.77 Hz, 2H), 7.83 (d, J = 8.45 Hz, 2H), 7.27–76.92 (m, 9H), 6.22 (d, J = 10.87 Hz, 1H), 5.59–5.48 (m, 1H), 5.06–4.93 (m, 2H), 4.63 (d, J = 10.91 Hz, 1H), 3.43–3.36 (m, 1H), 3.43–3.17 (m, 1H), 2.35 (s, 3H). MS(EI): *m/z*(%) 449 (0.21, M^+), 431 (1.22, $M^+ - H_2O$), 276 (81.77, $M^+ - SO_2Tol - H_2O$), 230 (34.71), 142 (44.56), 91 (100). Anal. Calc. for $C_{28}H_{23}NO_5S$: C, 66.80; H, 5.16; N, 3.11. Found: C, 66.04; H, 5.43; N, 2.81%.

*3.2.2. (E)-**6a**: (E)-1-(p-Nitrophenyl)-3-phenyl-2-(p-tolylsulfonyl)-2, 5-hexadien-1-ol: yellow oil*

IR (KBr): ν (cm^{-1}) 3514, 1598, 1523, 1348, 1265, 1137. ^1H NMR (300 MHz, $CDCl_3$): δ 8.11 (d, J = 8.79 Hz, 2H), 7.69 (d, J = 8.28 Hz, 2H), 7.52–7.26 (m, 7H), 7.17–7.15 (m, 2H), 5.63 (d, J = 11.49 Hz, 1H), 5.33–5.22 (m, 1H), 4.90–4.70 (m, 2H), 4.43 (d,

J = 11.64 Hz, 1H), 3.75–3.68 (m, 1H), 3.50–3.43 (m, 1H), 2.44 (s, 3H). HRMS calcd. for $C_{25}H_{23}NaNO_5S$ ($M + Na^+$), 472.1191; found: 472.1189.

*3.2.3. (Z)-**6b**: (Z)-1,3-Diphenyl-2-(p-tolylsulfonyl)-2,5-hexadien-1-ol: m.p. 106 °C*

IR (KBr): ν (cm^{-1}) 3472, 1595, 1491, 1447, 1276, 1134. ^1H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, J = 7.88 Hz, 2H), 7.53–7.43 (m, 2H), 7.38–7.33 (m, 2H), 7.23 (d, J = 7.36 Hz, 1H), 7.17–7.14 (m, 2H), 7.04–6.89 (m, 5H), 6.22 (d, J = 10.73 Hz, 1H), 5.58–5.49 (m, 1H), 5.03–4.91 (m, 1H), 4.49 (d, J = 10.84 Hz, 1H), 3.30–3.27 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): 153.59, 143.30, 143.10, 141.51, 138.79, 138.07, 131.85, 128.86, 128.54, 127.78, 127.50, 125.61, 118.49, 71.59, 42.44, 21.50. MS(ESI): m/z 427.1($M + Na^+$). Anal. Calc. for $C_{25}H_{24}O_3S$: C, 74.23; H, 5.98. Found: C, 74.32; H, 5.96%.

*3.2.4. (Z)-**6c**: (Z)-1-(p-Dimethylaminophenyl)-3-phenyl-2-(p-tolylsulfonyl)-2,5-hexadien-1-ol: m.p. 119 °C*

IR (KBr): ν (cm^{-1}) 3449, 1614, 1523, 1443, 1281, 1135, 1081. ^1H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, J = 8.28 Hz, 2H), 7.33–7.14 (m, 9H), 6.69 (d, J = 8.79 Hz, 2H), 5.53 (d, J = 11.93 Hz, 1H), 5.41–5.30 (m, 1H), 4.89 (d, J = 10.00 Hz, 1H), 4.78–4.72 (dd, J = 1.30 Hz, 1.31 Hz, 1H), 3.65–3.58 (m, 1H), 3.49–3.42 (m, 1H), 2.95 (s, 6H), 2.44 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 132.22, 129.55, 128.46, 128.24, 127.37, 127.33, 126.65, 118.51, 112.51, 73.11, 40.73, 40.32, 21.60. MS(ESI): m/z 448.2 ($M + H^+$). Anal. Calc. for $C_{27}H_{29}NO_3S$: C, 72.45; H, 6.53; N, 3.13. Found: C, 72.42; H, 6.43; N, 3.33%.

*3.2.5. (Z)-**6d**: (Z)-3-Phenyl-1-(n-propyl)-2-(p-tolylsulfonyl)-2,5-hexadien-1-ol: oil*

IR (KBr): ν (cm^{-1}) 3517, 2959, 2872, 1596, 1491, 1443, 1285, 1134. ^1H NMR (300 MHz, $CDCl_3$): δ 7.14–6.92 (m, 9H), 5.56–5.50 (m, 1H), 5.03–4.85 (m, 3H), 4.01 (d, J = 11.28 Hz, 1H), 3.31–3.26 (m, 1H), 3.08–3.03 (m, 1H), 2.30 (s, 3H), 2.15–2.00 (m, 2H), 1.65–1.50 (m, 2H), 1.06 (t, J = 14.68 Hz, 3H). HRMS calcd. for $C_{22}H_{26}NaO_3S$ ($M + Na^+$), 393.1494; found: 393.1495.

*3.2.6. (Z)-**6e**: (Z)-6-Phenyl-5-(p-tolylsulfonyl)-5,8-azelaic dialken-4-ol: oil*

IR (KBr): ν (cm^{-1}) 3450, 1722, 1596, 1493, 1448, 1291, 1145. ^1H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, J = 7.13 Hz, 2H), 7.33–7.20 (m, 3H), 7.12 (d, J = 8.12 Hz, 2H), 7.01 (s, 2H), 6.92 (d, J = 8.07 Hz, 2H), 6.79–6.67 (m, 4H), 5.61–5.52 (m, 2H), 5.02–4.94 (m, 2H), 4.35 (d, J = 10.18 Hz, 1H), 3.37–3.30 (m, 1H), 3.17–3.10 (m, 1H), 2.26 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 152.31, 143.32, 142.87, 138.82, 138.18, 136.55, 132.05, 129.57, 128.98, 128.68, 128.62, 128.03, 127.74, 127.48, 127.39, 126.90, 126.52, 118.32, 71.67, 42.16, 21.54. HRMS calcd. for $C_{27}H_{25}O_3S$ ($M - H^+$), 429.1520; found: 429.1519.

*3.2.7. (E)-**6e**: (4Z)-1,5-Diphenyl-4-(p-tolylsulfonyl)-1,4,7-octatrien-3-ol: oil*

IR (KBr): ν (cm^{-1}) 3373, 1717, 1597, 1449, 1303, 1148. ^1H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 8.15 Hz, 2H), 7.31–7.20 (m, 10H), 7.04 (d, J = 5.27 Hz, 2H), 6.44–6.29 (m, 2H), 5.24–5.10 (m, 1H), 4.97–4.91 (m, 1H), 4.77 (d, J = 9.98 Hz, 1H), 4.62 (d, J = 17.02 Hz, 1H), 3.99 (d, J = 11.36 Hz, 1H), 3.46–3.33 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 144.22, 131.89, 131.65, 129.83, 128.53, 128.43, 127.91, 127.36, 127.29, 126.75, 118.56, 73.07, 40.23, 21.63. HRMS calcd. for $C_{27}H_{25}O_3S$ ($M - H^+$), 429.1520; found: 429.1519.

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