A One-Pot, Stereoselective Synthesis of 1,3- and 1,4-Dienyl Sulfones by Hydrostannylation–Stille Tandem Reaction of Tributyltin Hydride with Acetylenic Sulfones and Alkenyl or Allylic Halides

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Abstract: 1,3-Dienyl and 1,4-dienyl sulfones can be stereoselectively synthesized in one pot under mild conditions, in good yields, by the palladium-catalyzed hydrostannylation of acetylenic sulfones, followed by Stille coupling with alkenyl or allylic halides, respectively.

Key words: acetylenic sulfone, hydrostannylation, Stille coupling, 1,3-dienyl sulfone, 1,4-dienyl sulfone

The stereocontrolled synthesis of conjugated dienes has attracted considerable interest in organic chemistry because of their appearance in a wide variety of biologically active molecules and as key synthetic intermediates.[1] Conjugated dienes are usually prepared by utilizing either a Wittig-type approach[2] or through transition-metal-catalyzed coupling reactions of stereodefined vinyl halides with vinyl organometallic compounds.[3] Recently, Whitby and co-workers reported the insertion of 1-lithio-1-halobutadiene into organozirconocenes, providing a stereocontrolled synthesis of (*E*,*Z*)-1,3-dienes.[4] The 1,4-diene framework also constitutes an important structural assembly in many molecules of biological importance[5] in addition to its application in organic synthesis[6] so, for these reasons, the synthesis of 1,4-dienes has also attracted much interest.[7] Many methods can be used for the stereocontrolled synthesis of 1,4-dienes.[8] Very recently, Kabalka et al. reported a new route to 1,4-pentadienes via microwave-enhanced palladium-catalyzed cross-coupling reactions of potassium vinyltrifluoroborates and allyl acetates.[9]

The stereocontrolled synthesis of 1,3- and 1,4-dienes containing metal or heteroatom functional groups is also of considerable interest in organic synthesis because many useful functional group transformations can be achieved through the introduction and removal of such groups. Heteroatom-substituted 1,3-dienes are also useful precursors for the construction of highly functionalized ring systems in Diels–Alder reactions.[10] The stereoselective synthesis of 1,3-dienyl silanes,[11] 1,4-dienyl silanes,[12] 1,3-dienyl sulfides,[13] 1,3-dienyl selenides,[14] 1,4-dienyl selenides[15] and 1,3-dienyl stannanes[16] have already been described in the literature. 1,3-Dienyl sulfones are extensively used as intermediates in organic synthesis[17] due to the chemical versatility of the sulfone moiety, which can be prepared by oxidation of the corresponding 1,3-dienyl sulfides.[18] However, reports on the stereocontrolled synthesis of 1,3-dienyl sulfones are limited[19] and the synthesis of 1,4-dienyl sulfones has received even less attention.[20] The tandem reaction has recently been of interest for organic synthesis because it offers a convenient and economical method with which to prepare target organic molecules.[21] The palladium-catalyzed hydrostannylation of alkynes and the Stille reaction are acknowledged as useful tools for constructing complex organic molecules, however, there have been no reports on the palladium-catalyzed tandem hydrostannylation–Stille reaction of tributyltin hydride (Bu_3SnH) with alkynes and organic halides to date. Herein we wish to report that 1,3- and 1,4-dienyl sulfones can be stereoselectively synthesized in one pot, under mild conditions, in good yields by the palladium-catalyzed hydrostannylation of acetylenic sulfones, followed by Stille coupling with alkenyl or allylic halides, respectively.

Palladium-catalyzed hydrostannylation of alkynes provides a simple, general route for the synthesis of vinylstannanes.[22] In 1991, Magriotis reported that the palladium-catalyzed hydrostannylation of phenylthioalkynes with tributyltin hydride was highly regio- and stereoselective, giving (*E*)-α-stannylvinyl sulfides in high yields.[23] Paley et al. reported that the palladium-catalyzed hydrostannylation of chiral alkynyl sulfoxides at –78 °C was also highly regio- and stereoselective, affording chiral (*E*)-α-stannylvinyl sulfoxides in good yields.[24] Huang and Ma demonstrated that alkynyl selenides can also undergo palladium-catalyzed hydrostannylation to stereoselectively afford (*E*)-α-stannylvinyl selenides.[25] Xiang et al. reported that palladium-catalyzed hydrostannylation of acetylenic triflones with tributyltin hydride provided α-stannylated vinyl triflones regiospecifically, however the reaction was not stereospecific and afforded a 1:1.7 ratio of *E* and *Z* stereoisomers.[26] Recently, we have found that the palladium-catalyzed hydrostannylation of acetylenic sulfones can proceed highly regio- and stereoselectively, affording (*E*)-α-stannylvinyl sulfones in high yields.[27] (*E*)-α-Stannylvinyl sulfones are new difunctional group reagents in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinylstannanes and as vinyl sulfones.

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Vinylstannanes can undergo the Stille coupling reaction with organic halides.[28] Considering the fact that both the hydrostannylation and Stille reactions were catalyzed by tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$], we tried to combine the two reactions, in one pot, to stereoselectively prepare 1,3-dienyl sulfones (Scheme 1).

We found that, hydrostannylation of acetylenic sulfones **1** with tributyltin hydride using 5 mol% $Pd(PPh_3)_4$ in benzene, followed by solvent exchange (to DMF) and subsequent reaction with alkenyl iodides and 75 mol% copper iodide, gave the (*Z*,*E*)-2-arylsulfonyl-substituted 1,3-dienes **3** in good yields. As can be seen from the experimental results summarized in Table 1, the tandem hydrostannylation–Stille reaction of tributyltin hydride with a variety of acetylenic sulfones and alkenyl iodides proceeded smoothly, under very mild conditions, to afford the corresponding (*Z*,*E*)-2-arylsulfonyl-substituted 1,3-dienes **3** stereoselectively. The Stille coupling reaction of the intermediates **2** with alkenyl bromides was very slow under the same reaction conditions, with only traces of coupling products obtained after 24 hours of reaction time. The Stille coupling reaction of the intermediates **2** with alkenyl chlorides did not occur at all.

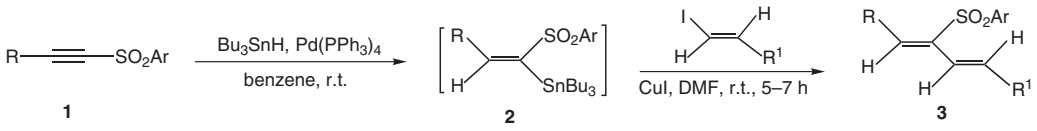
We have also investigated a one-pot, stereoselective synthesis of 1,4-dienyl sulfones by the tandem hydrostannylation–Stille reaction of tributyltin hydride with acetylenic sulfones and allylic bromides (Scheme 2). We observed that, after the hydrostannylation reaction of acetylenic sulfones **1** and subsequent reaction of the intermediate **2** with allylic bromides and copper iodide, in the manner described above, the desired (*Z*)-2-arylsulfonyl-substituted 1,4-dienes **4** were obtained in good yields. The experimental results (summarized in Table 2) show that the tandem hydrostannylation–Stille reaction of tributyltin hydride with a variety of acetylenic sulfones and allylic bromides also proceeded smoothly, under very mild conditions, to give the corresponding (*Z*)-2-arylsulfonyl-substituted 1,4-dienes **4** stereoselectively. When allylic bromides were replaced by allylic chlorides, no Stille reaction was observed.

It is well documented that the Stille coupling reaction of vinylstannanes with organic halides, in the presence of a palladium catalyst, occurs with retention of configuration.[29] The (1*E*)-configuration of compounds **3a–i** and **3l–n** has been shown by their ^{1}H NMR spectra, which show a doublet at δ = 6.02–7.17 ppm with a coupling constant of 15.2–16.2 Hz; this is also evidence of the retention of the *E*-configuration of the starting alkenyl iodides. In addition, the (3*Z*)-configuration of compound **3d** was confirmed by NOESY experiments. An enhancement of the allylic protons was observed as the vinylic proton (δ = 6.28 ppm) of **3d** was irradiated. There was no correlation between the vinylic proton (δ = 6.28 ppm) and the aromatic protons. A correlation between the vinylic proton (δ = 6.28 ppm) and one other vinylic proton (δ = 6.40 ppm) was also observed. The NOE results indicate that **3d** has the expected (1*E*,3*Z*)-configuration and that the cross-

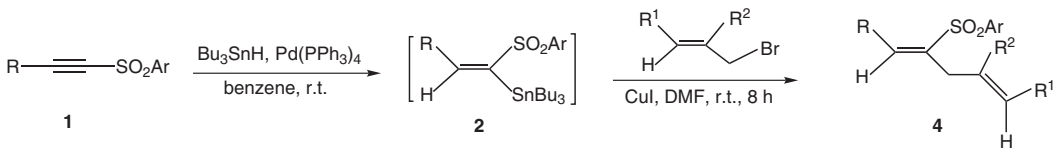
Table 1 Synthesis of (*Z*,*E*)-2-Arylsulfonyl-Substituted 1,3-Dienes **3**

R	Ar	R^1	Product	Yield[a] (%)
n-Bu	4-MeC_6H_4	*n*-Bu	**3a**	72
n-Bu	Ph	Ph	**3b**	81
n-Bu	4-MeC_6H_4	Ph	**3c**	75
n-Bu	4-MeC_6H_4	$MeOCH_2$	**3d**	69
n-Bu	Ph	$MeOCH_2$	**3e**	67
Ph	Ph	$MeOCH_2$	**3f**	65
Ph	Ph	Ph	**3g**	77
Ph	Ph	*n*-Bu	**3h**	83
$MeOCH_2$	Ph	$MeOCH_2$	**3i**	66
$MeOCH_2$	Ph	Ph	**3j**	70
$MeOCH_2$	4-MeC_6H_4	Ph	**3k**	75
$MeOCH_2$	4-MeC_6H_4	*n*-Bu	**3l**	73
$MeOCH_2$	Ph	*n*-Bu	**3m**	71
n-Bu	Ph	*n*-Bu	**3n**	69

[a] Isolated yield based on the alkenyl iodide used.



Scheme 1



Scheme 2

Table 2 Synthesis of (*Z*)-2-Arylsulfonyl-Substituted 1,4-Dienes **4**

R	Ar	R^1	R^2	Product	Yield[a] (%)
n-Bu	Ph	H	H	**4a**	78
n-Bu	4-MeC_6H_4	H	H	**4b**	74
$MeOCH_2$	Ph	H	H	**4c**	70
Ph	Ph	H	H	**4d**	76
n-Bu	Ph	Ph	H	**4e**	75
Ph	Ph	Ph	H	**4f**	72
$MeOCH_2$	4-MeC_6H_4	Ph	H	**4g**	69
n-Bu	Ph	H	Me	**4h**	77
Ph	Ph	H	Me	**4i**	81

[a] Isolated yield based on the allylic bromide used.

coupling reaction of (*E*)-α-stannylvinyl sulfones with alkenyl iodides occurs with retention of configuration of both the starting compounds **2** and the alkenyl iodides. The (4*E*)-configuration of the compounds **4e–g** was demonstrated by their ^{1}H NMR spectra, which show a doublet at δ = 6.53–6.32 ppm with a coupling constant of 15.6–16.0 Hz. In addition, the (1*Z*)-configuration of compound **4h** was confirmed by NOESY experiments. An enhancement of the allylic protons was observed as the vinylic proton (δ = 6.03 ppm) of **4h** was irradiated. There was no correlation between the vinylic proton (δ = 6.03 ppm) and the aromatic protons. A correlation between the vinylic proton (δ = 6.03 ppm) and the allylic protons (δ = 3.03 ppm) was also observed. The NOE results indicate that **4h** has the expected (1*Z*)-configuration and that the cross-coupling reaction of (*E*)-α-stannylvinyl sulfones with allylic bromides occurs with retention of configuration.

In conclusion, we have developed an efficient and stereoselective one-pot method for the synthesis of 1,3- and 1,4-dienyl sulfones. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and good yields. The procedure should find wide application in the synthesis of a large array of naturally occurring substances having a 1,3- or 1,4-diene system.

^{1}H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer using $CDCl_3$ as the solvent. IR spectra were determined on an FTS-185 instrument as neat films. Mass spectra were obtained on a Finigan 8239 mass spectrometer (EI, 70 eV). Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer. All reactions were carried out in pre-dried glassware (150 °C, 4 h) and cooled under a stream of dry Ar. Benzene was distilled from sodium prior to use. DMF was dried by distillation over calcium hydride. Light petroleum ether (PE) used for column chromatograph had a boiling range of 30–60 °C.

(*Z*,*E*)-2-Arylsulfonyl-Substituted 1,3-Dienes 3a–n; General Procedure

A 25 mL, two-necked, round-bottom flask equipped with a magnetic stirring bar under an argon atmosphere, was charged sequentially with acetylenic sulfone **1** (1 mmol), benzene (4 mL), $Pd(PPh_3)_4$ (0.05 mmol) and Bu_3SnH (1.05 mmol). The mixture was stirred at r.t. for 4 h then the solvent was removed under reduced pressure and the residue was dissolved in DMF (10 mL). Alkenyl iodide (0.9 mmol) and CuI (0.7 mmol) were added and the mixture was stirred at r.t. for 5–7 h. The reaction mixture was diluted with Et_2O (30 mL), filtered and then treated with 20% aqueous KF (10 mL) for 30 min before the organic layer was taken, dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica gel (PE–Et_2O, 5:1).

(5*Z*,7*E*)-6-(4-Methylphenyl)sulfonyl-5,7-dodecadiene (3a)

Colorless liquid.

IR (film): 3030, 2957, 2928, 1715, 1620, 1598, 1457, 1321, 1155, 1086, 966, 813, 678 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.73 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 6.16 (t, *J* = 7.6 Hz, 1 H), 6.14 (d, *J* = 15.2 Hz, 1 H), 5.77 (dt, *J* = 15.2, 7.6 Hz, 1 H), 2.69–2.61 (m, 2 H), 2.42 (s, 3 H), 2.09–2.02 (m, 2 H), 1.39–1.22 (m, 8 H), 0.92–0.85 (m, 6 H).

^{13}C NMR ($CDCl_3$): δ = 143.9, 141.8, 140.2, 138.7, 136.3, 129.5, 127.4, 124.5, 32.5, 31.4, 31.0, 28.3, 22.4, 22.1, 21.6, 13.9.

MS: *m*/*z* (%) = 320 (2.4) [M$^+$], 91 (34), 79 (43), 67 (97), 55 (82), 41 (100).

Anal. Calcd for $C_{19}H_{28}SO_2$: C, 71.25; H, 8.74. Found: C, 71.03; H, 8.62.

(1*E*,3*Z*)-1-Phenyl-3-phenylsulfonyl-1,3-octadiene (3b)

Colorless liquid.

IR (film): 3060, 2958, 2929, 1716, 1623, 1585, 1494, 1447, 1305, 1153, 1085, 963, 731, 689 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.89 (d, *J* = 8.0 Hz, 2 H), 7.59–7.26 (m, 8 H), 6.93 (d, *J* = 16.0 Hz, 1 H), 6.69 (d, *J* = 16.0 Hz, 1 H), 6.43 (t, *J* = 8.0 Hz, 1 H), 2.76–2.70 (m, 2 H), 1.46–1.32 (m, 4 H), 0.91 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 143.1, 141.6, 140.1, 136.3, 133.2, 132.9, 129.1, 128.7, 128.4, 127.2, 126.9, 123.0, 31.4, 28.7, 22.4, 13.9.

MS: *m*/*z* (%) = 326 (2.7) [M$^+$], 185 (9), 155 (13), 143 (17), 129 (34), 77 (28), 57 (35), 41 (100).

Anal. Calcd for $C_{20}H_{22}SO_2$: C, 73.62; H, 6.74. Found: C, 73.35; H, 6.53.

(1*E*,3*Z*)-1-Phenyl-3-(4-methylphenyl)sulfonyl-1,3-octadiene (3c)

Colorless liquid.

IR (film): 3059, 2957, 2928, 1714, 1622, 1597, 1495, 1449, 1291, 1151, 1086, 963, 813, 693 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.77 (d, *J* = 8.0 Hz, 2 H), 7.41–7.26 (m, 7 H), 6.93 (d, *J* = 15.6 Hz, 1 H), 6.68 (d, *J* = 15.6 Hz, 1 H), 6.40 (t, *J* = 7.6 Hz, 1 H), 2.76–2.70 (m, 2 H), 2.41 (s, 3 H), 1.46–1.33 (m, 4 H), 0.92 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 144.2, 142.7, 140.3, 138.7, 136.4, 132.8, 129.7, 128.7, 128.4, 127.3, 126.9, 123.1, 31.4, 28.7, 22.5, 21.6, 13.9.

MS: *m*/*z* (%) = 340 (3.8) [M$^+$], 185 (14), 155 (21), 143 (27), 129 (63), 91 (100).

Anal. Calcd for $C_{21}H_{24}SO_2$: C, 74.12; H, 7.05. Found: C, 73.87; H, 7.08.

(2*E*,4*Z*)-1-Methoxy-4-(4-methylphenyl)sulfonyl-2,4-nonadiene (3d)
Colorless liquid.

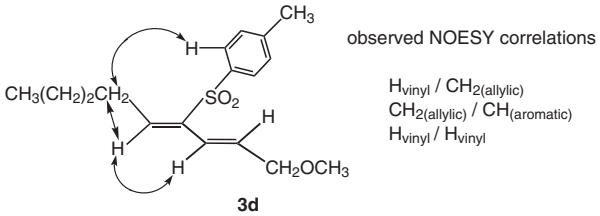
IR (film): 2927, 2872, 1720, 1620, 1597, 1494, 1455, 1302, 1153, 1086, 966, 814, 679 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 6.40 (d, *J* = 15.8 Hz, 1 H), 6.28 (t, *J* = 7.6 Hz, 1 H), 5.92 (dt, *J* = 15.8, 5.8 Hz, 1 H), 3.94 (d, *J* = 5.6 Hz, 2 H), 3.29 (s, 3 H), 2.71–2.65 (m, 2 H), 2.42 (s, 3 H), 1.41–1.26 (m, 4 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 144.1, 143.6, 139.5, 138.6, 130.7, 129.6, 127.3, 126.9, 72.4, 58.1, 31.3, 28.4, 22.4, 21.6, 13.8. For NOESY correlations, see Figure 1.

MS: *m*/*z* (%) = 308 (1.1) [M^+], 139 (16), 110 (100), 91 (37), 45 (23), 41 (14).

Anal. Calcd for $C_{17}H_{24}SO_3$: C, 66.24; H, 7.79. Found: C, 66.13; H, 7.53.



3d

Figure 1

(2*E*,4*Z*)-1-Methoxy-4-phenylsulfonyl-2,4-nonadiene (3e)
Colorless liquid.

IR (film): 3065, 2957, 2929, 1717, 1618, 1584, 1447, 1306, 1155, 1086, 965, 728, 689 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.87–7.85 (m, 2 H), 7.60–7.50 (m, 3 H), 6.42 (d, *J* = 15.6 Hz, 1 H), 6.32 (t, *J* = 7.6 Hz, 1 H), 5.93 (dt, *J* = 15.6, 5.8 Hz, 1 H), 3.94 (d, *J* = 5.6 Hz, 2 H), 3.29 (s, 3 H), 2.72–2.63 (m, 2 H), 1.41–1.30 (m, 4 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 144.1, 141.5, 139.2, 133.2, 130.8, 129.1, 127.2, 126.7, 72.4, 58.1, 31.2, 28.5, 22.4, 13.9.

MS: *m*/*z* (%) = 294 (1.2) [M^+], 121 (24), 110 (100), 105 (29), 79 (53), 45 (27), 41 (30).

Anal. Calcd for $C_{16}H_{22}SO_3$: C, 65.31; H, 7.48. Found: C, 65.14; H, 7.25.

(1*Z*,3*E*)-1-Phenyl-2-phenylsulfonyl-5-methoxy-1,3-pentadiene (3f)
Colorless liquid.

IR (film): 3059, 2924, 2855, 1590, 1447, 1306, 1146, 1095, 970, 784, 744 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.88 (d, *J* = 8.0 Hz, 2 H), 7.58–7.38 (m, 9 H), 6.40 (dt, *J* = 16.2, 4.8 Hz, 1 H), 6.29 (d, *J* = 16.2 Hz, 1 H), 3.93 (d, *J* = 4.4 Hz, 2 H), 3.21 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 140.0, 138.3, 137.5, 136.0, 133.4, 133.1, 130.4, 129.9, 129.0, 128.7, 128.0, 120.2, 72.4, 58.1.

MS: *m*/*z* (%) = 314 (1.5) [M^+], 204 (24), 185 (29), 155 (29), 143 (47), 129 (100), 115 (54), 91 (84), 77 (26).

Anal. Calcd for $C_{18}H_{18}SO_3$: C, 68.80; H, 5.73. Found: C, 68.64; H, 5.50.

(1*Z*,3*E*)-1,4-Diphenyl-2-phenylsulfonyl-1,3-butadiene (3g)
Colorless liquid.

IR (film): 3060, 3027, 1718, 1621, 1585, 1491, 1292, 1159, 1091, 964, 748, 687 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.65 (d, *J* = 7.6 Hz, 2 H), 7.47–7.24 (m, 14 H), 7.17 (d, *J* = 15.6 Hz, 1 H), 6.94 (d, *J* = 15.6 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 142.1, 140.9, 136.8, 136.2, 134.4, 133.9, 133.0, 129.8, 128.9, 128.8, 128.7, 128.6, 127.8, 127.7, 127.1, 123.0.

MS: *m*/*z* (%) = 346 (16) [M^+], 205 (100), 77 (43).

Anal. Calcd for $C_{22}H_{18}SO_2$: C, 76.30; H, 5.20. Found: C, 76.11; H, 5.03.

(1*Z*,3*E*)-1-Phenyl-2-phenylsulfonyl-1,3-octadiene (3h)
Colorless liquid.

IR (film): 3059, 2956, 2928, 1714, 1634, 1586, 1446, 1305, 1150, 1082, 966, 750, 688 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.62 (d, *J* = 7.6 Hz, 2 H), 7.49–7.26 (m, 8 H), 7.18 (s, 1 H), 6.38 (d, *J* = 15.4 Hz, 1 H), 6.08 (dt, *J* = 15.4, 7.2 Hz, 1 H), 2.19–2.14 (m, 2 H), 1.42–1.25 (m, 4 H), 0.92 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 142.1, 140.8, 138.2, 136.3, 134.0, 132.9, 129.6, 128.5, 128.4, 127.7, 124.4, 32.7, 31.0, 22.2, 13.9.

MS: *m*/*z* (%) = 326 (4.8) [M^+], 184 (26), 155 (57), 128 (67), 115 (88), 91 (100), 77 (63), 41 (78).

Anal. Calcd for $C_{20}H_{22}SO_2$: C, 73.62; H, 6.74. Found: C, 73.48; H, 6.49.

(2*Z*,4*E*)-1,6-Dimethoxy-3-phenylsulfonyl-2,4-hexadiene (3i)
Colorless liquid.

IR (film): 3064, 2929, 2824, 1721, 1628, 1584, 1447, 1306, 1153, 962, 734, 689 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.86–7.84 (m, 2 H), 7.63–7.52 (m, 3 H), 6.40 (t, *J* = 5.2 Hz, 1 H), 6.27 (d, *J* = 15.6 Hz, 1 H), 6.02 (dt, *J* = 15.6, 5.6 Hz, 1 H), 4.65 (d, *J* = 5.2 Hz, 2 H), 3.92 (d, *J* = 5.2 Hz, 2 H), 3.39 (s, 3 H), 3.25 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 141.0, 140.3, 138.5, 133.7, 132.3, 129.2, 127.4, 124.8, 72.1, 69.5, 58.7, 58.1.

MS: *m*/*z* (%) = 282 (2.8) [M^+], 141 (29), 125 (61), 109 (79), 77 (67), 45 (100).

Anal. Calcd for $C_{14}H_{18}SO_4$: C, 59.58; H, 6.38. Found: C, 59.31; H, 6.20.

(1*E*,3*Z*)-1-Phenyl-3-phenylsulfonyl-5-methoxy-1,3-pentadiene (3j)
Colorless liquid.

IR (film): 3062, 2941, 1613, 1582, 1447, 1369, 1302, 1151, 950, 740, 684 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.88 (d, *J* = 7.6 Hz, 2 H), 7.63–7.50 (m, 3 H), 7.38–7.26 (m, 5 H), 6.79 (s, 2 H), 6.52 (t, *J* = 5.2 Hz, 1 H), 4.68 (d, *J* = 5.2 Hz, 2 H), 3.42 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 140.5, 139.9, 139.5, 136.0, 134.3, 133.6, 129.2, 128.8, 128.7, 127.4, 126.9, 121.5, 69.6, 58.7.

MS: *m*/*z* (%) = 314 (1.5) [M^+], 157 (21), 141 (35), 129 (47), 115 (33), 77 (56), 45 (100).

Anal. Calcd for $C_{18}H_{18}SO_3$: C, 68.80; H, 5.73. Found: C, 68.53; H, 5.64.

(1*E*,3*Z*)-1-Phenyl-3-(4-methylphenyl)sulfonyl-5-methoxy-1,3-pentadiene (3k)
Colorless liquid.

IR (film): 3061, 2927, 1611, 1596, 1448, 1369, 1303, 1151, 947, 813, 740, 694 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.76 (d, *J* = 8.0 Hz, 2 H), 7.38–7.26 (m, 7 H), 6.79 (s, 2 H), 6.49 (t, *J* = 5.2 Hz, 1 H), 4.68 (d, *J* = 4.8 Hz, 2 H), 3.42 (s, 3 H), 2.42 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 144.7, 139.7, 139.4, 137.5, 136.0, 134.1, 129.9, 128.8, 128.7, 127.4, 126.9, 121.6, 69.7, 58.7, 21.7.

MS: *m*/*z* (%) = 328 (3.3) [M$^+$], 185 (15), 157 (25), 141 (73), 129 (100), 115 (56), 91 (87), 45 (66), 41 (25).

Anal. Calcd for $C_{19}H_{20}SO_3$: C, 69.52; H, 6.09. Found: C, 69.31; H, 5.85.

(2*Z*,4*E*)-1-Methoxy-3-(4-methylphenyl)sulfonyl-2,4-nonadiene (3l)
Colorless liquid.

IR (film): 3030, 2927, 2873, 1718, 1640, 1598, 1494, 1454, 1302, 1152, 967, 814, 679 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.72 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 6.26 (t, *J* = 5.2 Hz, 1 H), 6.02 (d, *J* = 15.4 Hz, 1 H), 5.89 (dt, *J* = 15.4, 6.8 Hz, 1 H), 4.62 (d, *J* = 4.8 Hz, 2 H), 3.39 (s, 3 H), 2.44 (s, 3 H), 2.07–2.01 (m, 2 H), 1.31–1.16 (m, 4 H), 0.84 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 144.5, 139.6, 138.5, 137.8, 137.5, 129.7, 127.5, 123.1, 69.5, 58.6, 32.5, 30.8, 22.0, 21.7, 13.9.

MS: *m*/*z* (%) = 308 (1.2) [M$^+$], 153 (46), 123 (37), 109 (38), 91 (68), 79 (54), 45 (100), 41 (69).

Anal. Calcd for $C_{17}H_{24}SO_3$: C, 66.24; H, 7.79. Found: C, 66.02; H, 7.66.

(2*Z*,4*E*)-1-Methoxy-3-phenylsulfonyl-2,4-nonadiene (3m)
Colorless liquid.

IR (film): 3066, 2930, 2873, 1713, 1640, 1585, 1447, 1306, 1152, 967, 734, 689 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.85–7.83 (m, 2 H), 7.62–7.51 (m, 3 H), 6.29 (t, *J* = 5.2 Hz, 1 H), 6.02 (d, *J* = 15.2 Hz, 1 H), 5.90 (dt, *J* = 15.2, 6.8 Hz, 1 H), 4.63 (d, *J* = 4.8 Hz, 2 H), 3.39 (s, 3 H), 2.05–2.01 (m, 2 H), 1.31–1.25 (m, 2 H), 1.21–1.15 (m, 2 H), 0.84 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 140.4, 139.4, 139.0, 138.0, 133.5, 129.1, 127.5, 123.0, 69.5, 58.6, 32.5, 30.8, 22.0, 13.8.

MS: *m*/*z* (%) = 294 (1.7) [M$^+$], 269 (100), 267 (71), 213 (64), 153 (63), 109 (65), 79 (81), 57 (68), 41 (98).

Anal. Calcd for $C_{16}H_{22}SO_3$: C, 65.31; H, 7.48. Found: C, 65.09; H, 7.32.

(5*Z*,7*E*)-6-Phenylsulfonyl-5,7-dodecadiene (3n)
Colorless liquid.

IR (film): 3065, 2957, 2928, 1714, 1620, 1585, 1446, 1305, 1156, 1086, 966, 728, 688 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.85 (d, *J* = 7.6 Hz, 2 H), 7.59–7.48 (m, 3 H), 6.19 (t, *J* = 7.6 Hz, 1 H), 6.15 (d, *J* = 15.4 Hz, 1 H), 5.79 (dt, *J* = 15.4, 7.2 Hz, 1 H), 2.70–2.64 (m, 2 H), 2.09–2.03 (m, 2 H), 1.41–1.22 (m, 8 H), 0.94–0.86 (m, 6 H).

^{13}C NMR ($CDCl_3$): δ = 142.2, 141.6, 140.0, 136.5, 133.0, 128.9, 127.3, 124.4, 32.4, 31.4, 31.0, 28.4, 22.4, 22.1, 13.9.

MS: *m*/*z* (%) = 306 (3.4) [M$^+$], 294 (27), 183 (44), 122 (65), 95 (72), 77 (100).

Anal. Calcd for $C_{18}H_{26}SO_2$: C, 70.59; H, 8.49. Found: C, 70.31; H, 8.37.

(*Z*)-2-Arylsulfonyl-Substituted 1,4-Dienes 4a–i; General Procedure
A 25 mL, two-necked, round-bottom flask equipped with a magnetic stirring bar under an argon atmosphere, was charged sequentially with acetylenic sulfone **1** (1 mmol), benzene (4 mL), $Pd(PPh_3)_4$ (0.05 mmol) and Bu_3SnH (1.05 mmol). The mixture was stirred at r.t. for 4 h then the solvent was removed under reduced pressure and the residue was dissolved in DMF (10 mL). Allylic bromide (0.9 mmol) and CuI (0.7 mmol) were added and the mixture was stirred at r.t. for 8 h. The reaction mixture was diluted with Et_2O (30 mL), filtered and then treated with 20% aqueous KF (10 mL) for 30 min before the organic layer was taken, dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica gel (PE–Et_2O, 5:1).

(*Z*)-1-Butyl-2-phenylsulfonyl-1,4-pentadiene (4a)
Colorless liquid.

IR (film): 3067, 2958, 1716, 1640, 1584, 1447, 1305, 1154, 921, 744, 689 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.90–7.87 (m, 2 H), 7.61–7.51 (m, 3 H), 6.03 (t, *J* = 7.6 Hz, 1 H), 5.73–5.63 (m, 1 H), 5.11–5.04 (m, 2 H), 3.08–3.06 (m, 2 H), 2.68–2.60 (m, 2 H), 1.37–1.25 (m, 4 H), 0.88 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 144.5, 141.5, 138.9, 134.3, 133.2, 129.1, 127.4, 118.0, 36.8, 31.3, 28.4, 22.3, 13.9.

MS: *m*/*z* (%) = 264 (6.7) [M$^+$], 263 (17) [M$^+$ – 1], 235 (28), 143 (49), 125 (68), 93 (47), 81 (88), 79 (100), 77 (94).

Anal. Calcd for $C_{15}H_{20}SO_2$: C, 68.14; H, 7.63. Found: C, 67.86; H, 7.49.

(*Z*)-1-Butyl-2-(4-methylphenyl)sulfonyl-1,4-pentadiene (4b)
Colorless liquid.

IR (film): 2927, 1713, 1640, 1598, 1458, 1302, 1139, 920, 814, 677 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.76 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 5.99 (t, *J* = 7.6 Hz, 1 H), 5.75–5.63 (m, 1 H), 5.10–5.03 (m, 2 H), 3.06–3.04 (m, 2 H), 2.68–2.61 (m, 2 H), 2.44 (s, 3 H), 1.37–1.24 (m, 4 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 144.1, 144.0, 139.1, 138.5, 134.4, 129.7, 127.5, 117.9, 36.8, 31.3, 28.3, 22.4, 21.6, 13.9.

MS: *m*/*z* (%) = 278 (12) [M$^+$], 178 (29), 157 (43), 139 (40), 91 (100), 57 (35).

Anal. Calcd for $C_{16}H_{22}SO_2$: C, 69.02; H, 7.97. Found: C, 68.79; H, 7.78.

(*Z*)-1-Methoxy-3-phenylsulfonyl-2,5-hexadiene (4c)
Colorless liquid.

IR (film): 2927, 1714, 1641, 1584, 1447, 1308, 1151, 922, 814, 746 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.89–7.87 (m, 2 H), 7.65–7.54 (m, 3 H), 6.16 (t, *J* = 4.8 Hz, 1 H), 5.68–5.57 (m, 1 H), 5.11–5.02 (m, 2 H), 4.64–4.62 (m, 2 H), 3.39 (s, 3 H), 2.98–2.96 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 141.5, 139.9, 138.5, 133.7, 133.1, 129.3, 127.7, 118.9, 69.6, 58.6, 35.9.

MS: *m*/*z* (%) = 252 (1.3) [M$^+$], 141 (12), 125 (21), 111 (100), 95 (43), 77 (35).

Anal. Calcd for $C_{13}H_{16}SO_3$: C, 61.88; H, 6.34. Found: C, 61.62; H, 6.25.

(*Z*)-1-Phenyl-2-phenylsulfonyl-1,4-pentadiene (4d)
Colorless liquid.

IR (film): 3063, 2956, 1714, 1640, 1585, 1446, 1305, 1148, 922, 748, 689 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.55–7.43 (m, 3 H), 7.32–7.15 (m, 7 H), 7.04 (s, 1 H), 5.96–5.86 (m, 1 H), 5.26–5.21 (m, 2 H), 3.34–3.32 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 142.5, 140.4, 139.4, 134.0, 133.9, 132.9, 128.9, 128.5, 128.2, 127.8, 127.7, 118.8, 37.1.

MS: *m*/*z* (%) = 284 (32) [M^+], 269 (63), 142 (100), 141 (86), 97 (58).

Anal. Calcd for $C_{17}H_{16}SO_2$: C, 71.80; H, 5.67. Found: C, 71.57; H, 5.49.

(1*Z*,4*E*)-1-Butyl-2-phenylsulfonyl-5-phenyl-1,4-pentadiene (4e)
Colorless liquid.

IR (film): 3067, 2957, 1635, 1599, 1447, 1305, 1151, 967, 729, 690 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.92–7.89 (m, 2 H), 7.60–7.49 (m, 3 H), 7.30–7.19 (m, 5 H), 6.38 (d, *J* = 15.6 Hz, 1 H), 6.12–5.98 (m, 2 H), 3.24 (d, *J* = 6.8 Hz, 2 H), 2.69–2.62 (m, 2 H), 1.38–1.27 (m, 4 H), 0.88 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 144.7, 141.5, 139.2, 136.9, 133.2, 133.1, 129.1, 128.6, 127.6, 127.5, 126.2, 125.8, 36.3, 31.3, 28.5, 22.4, 13.9.

MS: *m*/*z* (%) = 340 (1.2) [M^+], 169 (22), 156 (100), 141 (81), 128 (53), 115 (62), 91 (44).

Anal. Calcd for $C_{21}H_{24}SO_2$: C, 74.08; H, 7.11. Found: C, 73.82; H, 7.17.

(1*Z*,4*E*)-1,5-Diphenyl-2-phenylsulfonyl-1,4-pentadiene (4f)
Colorless liquid.

IR (film): 3058, 2957, 1714, 1598, 1446, 1305, 1147, 968, 747, 690 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.56–7.20 (m, 15 H), 7.10 (s, 1 H), 6.53 (d, *J* = 16.0 Hz, 1 H), 6.26 (dt, *J* = 16.0, 6.8 Hz, 1 H), 3.48 (d, *J* = 6.8 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 142.8, 140.5, 139.5, 136.8, 134.0, 133.8, 132.9, 129.0, 128.6, 128.5, 128.2, 127.8, 127.7, 126.3, 125.3, 36.5.

MS: *m*/*z* (%) = 360 (1.5) [M^+], 219 (25), 217 (100), 202 (44).

Anal. Calcd for $C_{23}H_{20}SO_2$: C, 76.63; H, 5.59. Found: C, 76.40; H, 5.62.

(1*E*,4*Z*)-1-Phenyl-4-(4-methylphenyl)sulfonyl-6-methoxy-1,4-hexadiene (4g)
Colorless liquid.

IR (film): 2922, 1650, 1595, 1450, 1300, 1151, 962, 827, 692 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.77 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.29–7.21 (m, 5 H), 6.32 (d, *J* = 16.0 Hz, 1 H), 6.18 (t, *J* = 4.8 Hz, 1 H), 5.94 (dt, *J* = 16.0, 7.2 Hz, 1 H), 4.64 (d, *J* = 4.8 Hz, 2 H), 3.38 (s, 3 H), 3.13 (d, *J* = 7.2 Hz, 2 H), 2.41 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 144.8, 141.1, 139.2, 137.1, 136.6, 133.7, 129.9, 128.5, 127.8, 127.6, 126.2, 124.6, 69.6, 58.6, 35.4, 21.6.

MS: *m*/*z* (%) = 342 (3.8) [M^+], 310 (60), 269 (100), 267 (69), 171 (48), 155 (93), 91 (26).

Anal. Calcd for $C_{20}H_{22}SO_3$: C, 70.15; H, 6.48. Found: C, 70.19; H, 6.32.

(*Z*)-1-Butyl-2-phenylsulfonyl-4-methyl-1,4-pentadiene (4h)
Colorless liquid.

IR (film): 3077, 2929, 1715, 1652, 1585, 1446, 1305, 1152, 896, 724, 689 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.90–7.87 (m, 2 H), 7.62–7.50 (m, 3 H), 6.03 (t, *J* = 7.6 Hz, 1 H), 4.86 (s, 1 H), 4.76 (s, 1 H), 3.03 (s, 2 H), 2.69–2.62 (m, 2 H), 1.56 (s, 3 H), 1.37–1.25 (m, 4 H), 0.88 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR ($CDCl_3$): δ = 144.9, 141.5, 141.4, 138.0, 133.1, 129.0, 127.5, 114.5, 40.9, 31.3, 28.4, 22.4, 21.4, 13.9. For NOESY correlations, see Figure 2.

MS: *m*/*z* (%) = 279 (15) [M + H^+], 278 (4.2) [M^+], 137 (100), 121 (37), 95 (68), 81 (67), 79 (44), 77 (38).

Anal. Calcd for $C_{16}H_{22}SO_2$: C, 69.02; H, 7.97. Found: C, 68.87; H, 7.84.

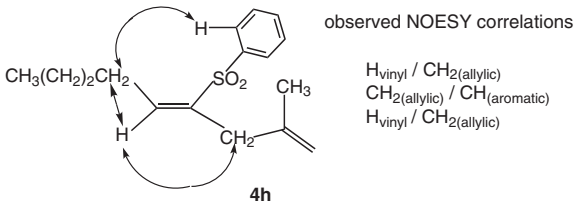


Figure 2

(*Z*)-1-Phenyl-2-phenylsulfonyl-4-methyl-1,4-pentadiene (4i)
Colorless liquid.

IR (film): 3064, 2922, 1651, 1491, 1446, 1305, 1147, 896, 748, 689 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.53–7.41 (m, 3 H), 7.30–7.18 (m, 7 H), 7.05 (s, 1 H), 5.00 (s, 1 H), 4.95 (s, 1 H), 3.27 (s, 2 H), 1.76 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 141.7, 141.5, 140.5, 139.9, 134.1, 132.8, 129.0, 128.4, 128.2, 127.8, 127.7, 114.9, 41.1, 21.8.

MS: *m*/*z* (%) = 298 (4.7) [M^+], 157 (100), 141 (84), 128 (50), 115 (63), 91 (35), 77 (18).

Anal. Calcd for $C_{18}H_{18}SO_2$: C, 72.45; H, 6.08. Found: C, 72.19; H, 5.87.

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