Synthesis of tetrasubstituted olefins by stereoselective allylzincation–Negishi tandem reaction of acetylenic sulfones

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Tetrasubstituted olefins containing a 1,3,6-triene structural unit can be regio- and stereoselectively synthesised in good yields under mild conditions in one pot, by allylzincation–Negishi tandem reaction of acetylenic sulfones with allylzinc bromide and alkenyl halides.

Keywords: acetylenic sulfone, allylzincation, Negishi coupling, tandem reaction, tetrasubstituted olefin, stereoselective synthesis

The stereoselective synthesis of polysubstituted alkenes remains a challenging problem in organic synthesis and is still being actively explored because many biologically active compounds have the structural unit of polysubstituted alkenes.[1-6] Vinyl sulfones are important synthetic intermediates since the sulfone group both activates the adjacent multiple carbon-carbon bonds and provides a useful functional group for further transformation by various desulfonylation methods.[7,8] A variety of methods have been developed for their preparation including those involving Horner–Emmons reactions of carbonyl compounds and sulfonyl phosphoranes,[9] Peterson reactions,[10] β-elimination of selenosulfones[11] and selenosulfonation of acetylene.[12] Considering the importance of vinyl sulfones, it is still of interest to develop new routes of synthesis. Carbometallation of alkynes by organometallic reagents has been studied extensively in the synthesis of substituted alkenes.[13] Huang[14] and Xie[15] reported that polysubstituted vinyl sulfones could be synthesised by carbomagnesiation of acetylenic sulfones. Organozinc reagents are very important reagents in organic synthesis due to their high functional group compatibility and their high reactivity in the presence of a palladium or nickel catalyst.[16-19] However, the synthesis of vinyl sulfones by the carbozincation reaction of acetylenic sulfones has received less attention.[20] Here we report that tetrasubstituted olefins containing a 1,3,6-triene structural unit can be regio- and stereoselectively synthesised in good yields under mild conditions, in one pot, by allylzincation of acetylenic sulfones, followed by palladium-catalysed Negishi coupling with alkenyl halides.

Although reports on the carbozincation of alkynes are well-known, trapping of the vinyl zinc intermediates formed by carbozincation of alkynes with an electrophile other than a proton is rare.[16,20] Acetylenic sulfones **1** were prepared according to a literature procedure.[21] It is well known that the allylzincation of acetylenic sulfones **1** with allylzinc bromide in THF proceeds highly regio- and stereoselectively to generate α-arylsulfonyl vinyl zinc reagents **2**; the addition of allylzinc bromide to acetylenic sulfones is in the pure *syn*-fashion.[20] To extend the application of the allylzincation reaction of acetylenic sulfones, considering the fact that alkenyl halides are efficient electrophiles and can undergo cross-coupling reaction with organometallic reagents in the presence of transition metal catalysts, we investigated the palladium-catalysed Negishi coupling reaction of alkenyl halides with α-arylsulfonyl vinyl zinc reagents **2** obtained by allylzincation of acetylenic sulfones.

1-Phenylsulfonyl-1-hexyne and (*E*)-1-iodo-1-hexene were chosen to optimise the reaction conditions and the results are shown in Table 1. Among the palladium catalysts examined, $Pd(PPh_3)_4$ was the most effective (entries 4–6). Both $Pd(OAc)_2$ and $PdCl_2$ were ineffective for this coupling reaction (entries 1 and 2). Ni(II) catalysts such as $Ni(PPh_3)_2Cl_2$ showed no catalytic activity (entry 7). (*E*)-1-Phenylsulfonyl-2-butylpenta-1,4-diene was obtained in 87% yield due to the protonolysis of the corresponding vinyl zinc reagent (entries 1, 2 and 7). Increasing the amount of $Pd(PPh_3)_4$ in the reaction (2-10 mol%) led to an increased yield of the desired (1*E*,3*E*)-1,4-dibutyl-3-phenylsulfonylhepta-1,3,6-triene (**4a**). So, 5 mol% of $Pd(PPh_3)_4$ was used to catalyse the Negishi coupling reaction to avoid a large amount of catalyst loading.

Table 1 The screening of catalysts for the Negishi coupling of α-arylsulfonyl vinyl zinc reagent **2** (R = *n*–C_4H_9) with (*E*)-1-iodo-1-hexene[a]

Entry	Catalyst	Yield[b](%) of **4a**
1	$Pd(OAc)_2$ (5 mol%)	0
2	$PdCl_2$ (5 mol%)	0
3	$Pd(PPh_3)_2Cl_2$ (5 mol%)	38
4	$Pd(PPh_3)_4$ (2 mol%)	65
5	$Pd(PPh_3)_4$ (5 mol%)	83
6	$Pd(PPh_3)_4$ (10 mol%)	85
7	$Ni(PPh_3)_2Cl_2$ (5 mol%)	0

[a]The Negishi reaction was performed with 1.0 mmol of **2** and 1.0 mmol of (*E*)-1-iodohex-1-ene at 25 °C for 12 h.
[b]Isolated yield based on **1** used.

A series of alkenyl halides were subjected to the above optimal reaction conditions (Scheme 1). The results are summarised in Table 2. From Table 2, we can see that the Negishi coupling reactions of the intermediates **2** with a variety of alkenyl iodides proceeded smoothly in the presence of 5 mol% $Pd(PPh_3)_4$ at 25 °C to afford the corresponding tetrasubstituted olefins **4a–k** in good yields after 12 h. Although the reactivity of alkenyl bromides was slightly lower than that of alkenyl iodides, the Negishi coupling reactions of the intermediates **2** with a variety of alkenyl bromides could also proceed smoothly in the presence of 5 mol% $Pd(PPh_3)_4$ at 40 °C to afford the corresponding tetrasubstituted olefins in good yields after 24 h (entries 12–14). The scope of both the acetylenic sulfones **1** and the alkenyl halides **3** is broad

It is well documented that the Negishi coupling reaction of vinyl zinc reagents with alkenyl halides, in the presence of a palladium catalyst, occurs with retention of configuration.[22,23] The (1*E*)-configuration of compounds **4** has been shown by their ^{1}H NMR spectra, which show a doublet at δ = 5.85–6.95 ppm with a coupling constant of 15.6–16.4 Hz; this is also evidence of the retention of the *E*-configuration of the starting alkenyl halides. In addition, the (3*E*)-configuration of compound **4i** was confirmed by NOESY experiments. There was a correlation between the aromatic protons (δ = 7.70 ppm) and the allylic protons (δ = 2.65 ppm) of the butyl group. A correlation between the vinylic proton (δ = 6.16 ppm) and the allylic protons (δ = 2.97 ppm) of the allyl group was also observed. The NOE results indicate that **4i** has the expected

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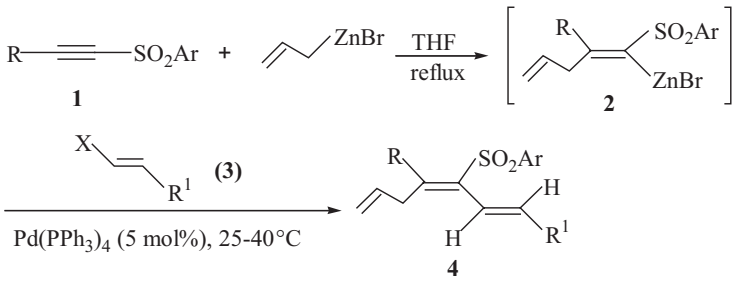

Scheme 1

Table 2 Synthesis of tetrasubstituted olefins containing a 1,3,6-triene structural unit

Entry	R	Ar	R^1	X	Product	Yield[b]/%
1	n-C_4H_9	Ph	n-C_4H_9	I[a]	**4a**	83
2	n-C_4H_9	Ph	Ph	I[a]	**4b**	86
3	n-C_4H_9	Ph	CH_3OCH_2	I[a]	**4c**	75
4	Ph	Ph	n-C_4H_9	I[a]	**4d**	87
5	Ph	Ph	Ph	I[a]	**4e**	85
6	Ph	Ph	CH_3OCH_2	I[a]	**4f**	78
7	n-C_4H_9	4-$CH_3C_6H_4$	n-C_4H_9	I[a]	**4g**	84
8	n-C_4H_9	4-$CH_3C_6H_4$	Ph	I[a]	**4h**	86
9	n-C_4H_9	4-$CH_3C_6H_4$	CH_3OCH_2	I[a]	**4i**	79
10	Ph	4-$CH_3C_6H_4$	Ph	I[a]	**4j**	87
11	Ph	4-$CH_3C_6H_4$	CH_3OCH_2	I[a]	**4k**	77
12	n-C_4H_9	Ph	n-C_4H_9	Br[c]	**4a**	81
13	Ph	Ph	CH_3OCH_2	Br[c]	**4f**	75
14	n-C_4H_9	4-$CH_3C_6H_4$	Ph	Br[c]	**4h**	83

[a]The Negishi reaction was performed with 1.0 mmol of **2**, 1.0 mmol of **3**, and 0.05 mmol of $Pd(PPh_3)_4$ at 25 °C for 12 h.
[b]Isolated yield based on **1** used.
[c]The Negishi reaction was performed with 1.0 mmol of **2**, 1.0 mmol of **3**, and 0.05 mmol of $Pd(PPh_3)_4$ at 40 °C for 24 h.

(1*E*,3*E*)-configuration and the cross-coupling reaction of the intermediates **2** with alkenyl halides occurs with retention of configuration of both the starting intermediates **2** and the alkenyl halides **3**.

In summary, an efficient and stereoselective one-pot synthetic method for tetrasubstituted olefins has been developed by the allylzincation of acetylenic sulfones, followed by the Negishi coupling reaction with alkenyl halides in the presence of a palladium catalyst. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and good yields. These tetrasubstituted olefins may be potential materials in the synthesis of natural products and in other synthetic transformations.

Experimental

THF was distilled from sodium immediately prior to use. IR spectra were obtained with a Perkin-Elmer 683 instrument as neat films. ^{1}H NMR spectra were recorded with a Bruker AC-400 (400 MHz) spectrometer using $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded with a Bruker AC-400 (100 MHz) spectrometer using $CDCl_3$ as solvent. Mass spectra (EI) were determined with a Finnigan 8230 mass spectrometer. Microanalyses were measured with a Yanaco MT-3 CHN microelemental analyser. $Pd(PPh_3)_4$ was prepared according to a literature procedure.[24] (For AA'XX' systems in ^{1}H NMR, $J^* = J_{23} + J_{25}$.)

General procedure for the synthesis of tetrasubstituted olefins **4a–k**
A Schlenk flask with a condenser was charged with dry THF (4.0 ml), activated zinc dust (92 mg, 1.4 mmol), and allyl bromide (0.12 ml, 1.4 mmol) under an argon atmosphere. The mixture was stirred at 0 °C until the zinc dust disappeared (about 1.5 h). Acetylenic sulfone (1.0 mmol) was added and the reaction mixture was stirred for 2–2.5 h at reflux temperature. The reaction mixture was then cooled to 25 °C, and alkenyl iodide (1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 5 mol%), and 4.0 ml of THF were added successively. The mixture was stirred at 25 °C for 12 h, quenched with a saturated NH_4Cl solution and extracted with diethyl ether (3 × 20 ml). The organic layer was combined and dried over $MgSO_4$. After filtration and removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent : light petroleum ether/EtOAc, 9:1).

(1E,3E)-1,4-Dibutyl-3-phenylsulfonylhepta-1,3,6-triene **(4a):** Oil. IR (neat), ν cm^{-1}: 3079, 2957, 2925, 1637, 1605, 1446, 1148, 1089, 725, 689; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.81 (m, 2H), 7.56–7.46 (m, 3H), 5.85 (d, J = 16.0 Hz, 1H), 5.72–5.61 (m, 1H), 5.56 (dt, J = 16.0, 7.2 Hz, 1H), 5.06–4.94 (m, 2H), 2.97 (d, J = 6.4 Hz, 2H), 2.68 (t, J = 7.2 Hz, 2H), 2.05–1.99 (m, 2H), 1.47–1.19 (m, 8H), 0.94–0.83 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 142.0, 140.8, 136.2, 134.4, 132.7, 128.7, 127.6, 122.3, 117.2, 39.8, 32.6, 31.8, 31.2, 30.9, 23.2, 22.2, 13.9, 13.8; MS (EI): *m/z* (%) 346 (M^+, 5.7), 161 (24), 119 (33), 105 (58), 91 (100), 77 (83), 55 (51); Anal. Calcd. for $C_{21}H_{30}SO_2$: C, 72.79; H, 8.73. Found: C, 72.6; H, 8.6.

(1E,3E)-1-Phenyl-3-phenylsulfonyl-4-butylhepta-1,3,6-triene **(4b):** Oil. IR (neat), ν cm^{-1}: 3060, 2957, 2929, 1599, 1446, 1304, 1147, 1087, 726, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85–7.83 (m, 2H), 7.57–7.43 (m, 3H), 7.31–7.22 (m, 5H), 6.62 (d, J = 16.4 Hz, 1H), 6.49 (d, J = 16.4 Hz, 1H), 5.78–5.67 (m, 1H), 5.09–4.96 (m, 2H), 3.04 (d, J = 6.4 Hz, 2H), 2.73 (t, J = 7.6 Hz, 2H), 1.52–1.37 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 142.0, 137.6, 136.3, 134.3, 132.9, 132.2, 128.9, 128.7, 128.4, 127.6, 126.7, 121.4, 117.5, 40.0, 32.3, 31.2, 23.2, 13.9; MS (EI): *m/z* (%) 366 (M^+, 6.5), 235 (34), 143 (42), 125 (52), 123 (64), 91 (57), 81 (86), 77 (100); Anal. Calcd. for $C_{23}H_{26}SO_2$: C, 75.37; H, 7.15. Found: C, 75.6; H, 7.2.

(1E,3E)-1-Methoxymethyl-3-phenylsulfonyl-4-butylhepta-1,3,6-triene **(4c):** Oil. IR (neat), ν cm^{-1}: 3057, 2920, 2852, 1732, 1583, 1447, 1307, 1148, 1088, 725, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.82 (m, 2H), 7.55–7.43 (m, 3H), 6.18 (d, J = 16.0 Hz, 1H), 5.72–5.63 (m, 2H), 5.07–4.95 (m, 2H), 3.92 (d, J = 5.6 Hz, 2H), 3.26 (s, 3H), 2.98 (d, J = 6.0 Hz, 2H), 2.66 (t, J = 7.2 Hz, 2H), 1.44–1.32 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 135.6, 134.1, 132.9, 129.1, 128.9, 128.5, 127.4, 124.5, 117.5, 72.4, 58.1, 39.8, 32.1, 31.1, 23.2, 13.9; MS (EI): *m/z* (%) 334 (M^+, 1.7), 277 (33), 161 (35), 117 (45), 105 (63), 91 (100), 77 (98); Anal. Calcd. for $C_{19}H_{26}SO_3$: C, 68.23; H, 7.84. Found: C, 68.5; H, 8.0.

(1E,3Z)-1-Butyl-3-phenylsulfonyl-4-phenyl-hepta-1,3,6-triene **(4d):** Oil. IR (neat), ν cm^{-1}: 3062, 2921, 2852, 1722, 1638, 1594, 1446, 1305, 1149, 1084, 754, 689; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.43 (m, 3H), 7.34–7.22 (m, 5H), 7.00–6.96 (m, 2H), 6.16 (d, J = 15.6 Hz,

1H), 5.91 (dt, *J* = 15.6, 7.2 Hz, 1H), 5.60–5.49 (m, 1H), 4.99–4.87 (m, 2H), 3.22 (d, *J* = 6.4 Hz, 2H), 2.22–2.16 (m, 2H), 1.43–1.21 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 141.9, 141.5, 139.5, 138.6, 133.4, 132.4, 128.3, 128.2, 127.9, 127.6, 121.6, 117.6, 43.5, 32.9, 31.0, 22.3, 13.9; MS (EI): *m/z* (%) 366 (M^+, 6.8), 225 (61), 181 (55), 167 (84), 141 (80), 115 (67), 91 (100), 77 (54); Anal. Calcd. for $C_{23}H_{26}SO_2$: C, 75.37; H, 7.15. Found: C, 75.1; H, 7.05.

(1E,3Z)-1,4-Diphenyl-3-phenylsulfonylhepta-1,3,6-triene **(4e):** Oil. IR (neat), ν cm^{-1}: 3059, 2922, 1594, 1490, 1447, 1305, 1148, 1084, 748, 689; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.22 (m, 13H), 7.03–7.00 (m, 2H), 6.95 (d, *J* = 16.0 Hz, 1H), 6.83 (d, *J* = 16.0 Hz, 1H), 5.64–5.53 (m, 1H), 5.03–4.93 (m, 2H), 3.30 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 141.5, 139.8, 138.6, 136.1, 133.5, 132.7, 132.2, 129.6, 128.8, 128.5, 128.3, 127.9, 127.7, 127.0, 120.6, 117.8, 43.9; MS (EI): *m/z* (%) 386 (M^+, 17), 294 (100), 277 (63), 245 (74), 202 (58), 183 (78), 141 (74), 115 (57), 91 (53), 77 (50); Anal. Calcd. for $C_{25}H_{22}SO_2$: C, 77.69; H, 5.74. Found: C, 77.5; H, 5.5.

(1E,3Z)-1-Methoxymethyl-3-phenylsulfonyl-4-phenylhepta-1,3,6-triene **(4f):** Oil. IR (neat), ν cm^{-1}: 3079, 2924, 2852, 1593, 1446, 1305, 1148, 1085, 753, 689; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.43 (m, 3H), 7.32–7.19 (m, 5H), 6.97–6.94 (m, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.07 (dt, *J* = 16.0, 5.2 Hz, 1H), 5.61–5.50 (m, 1H), 5.01–4.90 (m, 2H), 4.07 (d, *J* = 5.2 Hz, 2H), 3.38 (s, 3H), 3.23 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 141.4, 138.9, 138.3, 136.6, 133.1, 132.6, 128.4, 128.2, 127.7, 127.6, 123.5, 117.9, 72.4, 58.3, 43.5; MS (EI): *m/z* (%) 354 (M^+, 1.5), 182 (53), 181 (100), 165 (92), 153 (53), 141 (47), 115 (61), 77 (42); Anal. Calcd. for $C_{21}H_{22}SO_3$: C, 71.16; H, 6.23. Found: C, 71.4; H, 6.4.

(1E,3E)-1,4-Dibutyl-3-[(4-methylphenyl)sulfonyl]hepta-1,3,6-triene **(4g):** Oil. IR (neat), ν cm^{-1}: 3061, 2957, 2927, 1719, 1637, 1598, 1457, 1301, 1147, 1090, 813; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (m, *J** = 8.0 Hz, 2H), 7.27 (m, *J** = 8.0 Hz, 2H), 5.86 (d, *J* = 15.6 Hz, 1H), 5.71–5.60 (m, 1H), 5.55 (dt, *J* = 15.6, 7.2 Hz, 1H), 5.05–4.94 (m, 2H), 2.96 (d, *J* = 6.4 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 2.05-1.98 (m, 2H), 1.48–1.21 (m, 8H), 0.94–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 143.5, 140.6, 139.1, 136.5, 134.5, 129.3, 127.7, 122.4, 117.2, 39.8, 32.7, 31.8, 31.2, 30.9, 23.2, 22.2, 21.6, 13.9, 13.8; MS (EI): *m/z* (%) 360 (M^+, 5.5), 205 (21), 161 (28), 119 (36), 105 (64), 91 (100), 79 (62), 55 (52); Anal. Calcd. for $C_{22}H_{32}SO_2$: C, 73.29; H, 8.95. Found: C, 73.5; H, 9.1.

(1E,3E)-1-Phenyl-3-[(4-methylphenyl)sulfonyl]-4-butylhepta-1,3,6-triene **(4h):** Oil. IR (neat), ν cm^{-1}: 3059, 3026, 1636, 1597, 1448, 1315, 1146, 1088, 813, 749, 693; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (m, *J** = 8.0 Hz, 2H), 7.51–7.25 (m, 7H), 6.63 (d, *J* = 16.4 Hz, 1H), 6.50 (d, *J* = 16.4 Hz, 1H), 5.74–5.66 (m, 1H), 5.09–4.95 (m, 2H), 3.03 (d, *J* = 6.0 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.39 (s, 3H), 1.52–1.36 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 143.7, 137.4, 136.6, 134.4, 132.3, 132.2, 129.5, 128.7, 128.3, 127.7, 126.7, 121.6, 117.4, 40.0, 32.3, 31.2, 23.2, 21.6, 14.0; MS (EI): *m/z* (%) 380 (M^+, 14), 294 (51), 225 (43), 183 (41), 167 (45), 123 (48), 91 (100); Anal. Calcd. for $C_{24}H_{28}SO_2$: C, 75.75; H, 7.42. Found: C, 75.5; H, 7.5.

*(1E,3E)-1-Methoxymethyl-3-[(4-methylphenyl)sulfonyl]-4-butylhepta-1,3,6-triene (*4i**):** Oil. IR (neat), ν cm^{-1}: 3056, 2922, 2856, 1730, 1589, 1446, 1308, 1146, 1089, 815; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (m, *J** = 8.0 Hz, 2H), 7.28 (m, *J** = 8.0 Hz, 2H), 6.16 (d, *J* = 16.0 Hz, 1H), 5.73–5.67 (m, 2H), 5.06–4.93 (m, 2H), 3.92 (d, *J* = 5.6 Hz, 2H), 3.27 (s, 3H), 2.97 (d, *J* = 6.0 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.44–1.33 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 143.7, 139.2, 135.8, 135.5, 134.2, 129.4, 127.5, 124.6, 117.4, 72.4, 58.1, 39.7, 32.1, 31.1, 23.1, 21.6, 13.9; MS (EI): *m/z* (%) 348 (M^+, 4.8), 161 (81), 139 (47), 131 (77), 105 (63), 91 (100); Anal. Calcd. for $C_{20}H_{28}SO_3$: C, 68.93; H, 8.10. Found: C, 68.6; H, 8.0.

(1E,3Z)-1,4-Diphenyl-3-[(4-methylphenyl)sulfonyl] hepta-1,3,6-triene **(4j):** Oil. IR (neat), ν cm^{-1}: 3059, 2923, 1596, 1491, 1443, 1315, 1302, 1147, 1085, 813, 699; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.21 (m, 12H), 7.04–7.01 (m, 2H), 6.94 (d, *J* = 16.0 Hz, 1H), 6.82 (d, *J* = 16.0 Hz, 1H), 5.63–5.54 (m, 1H), 5.06–4.92 (m, 2H), 3.29 (d, *J* = 6.8 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 143.8, 139.8, 138.5, 136.2, 133.5, 132.3, 129.8, 128.8, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.0, 120.7, 117.7, 43.9, 21.6; MS (EI): *m/z* (%) 400 (M^+, 22), 245 (91), 229 (55), 202 (93), 165 (55), 115 (47), 91 (100); Anal. Calcd. for $C_{26}H_{24}SO_2$: C, 77.97; H, 6.04. Found: C, 77.7; H, 5.8.

(1E,3Z)-1-Methoxymethyl-3-[(4-methylphenyl)sulfonyl]-4-phenylhepta-1,3,6-triene **(4k):** Oil. IR (neat), ν cm^{-1}: 3079, 2923, 1728, 1637, 1596, 1443, 1318, 1150, 1086, 813, 700; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, *J** = 8.4 Hz, 2H), 7.27–7.22 (m, 3H), 7.10 (m, *J** = 8.4 Hz, 2H), 6.98–6.96 (m, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.03 (dt, *J* = 16.0, 5.6 Hz, 1H), 5.60–5.50 (m, 1H), 5.01–4.89 (m, 2H), 4.07 (d, *J* = 5.6 Hz, 2H), 3.38 (s, 3H), 3.22 (d, *J* = 6.4 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 143.4, 139.0, 138.5, 136.5, 133.2, 129.1, 128.2, 127.9, 127.7, 127.5, 123.7, 117.8, 72.4, 58.3, 43.5, 21.6; MS (EI): *m/z* (%) 368 (M^+, 1.2), 181 (100), 165 (37), 115 (28), 91 (31); Anal. Calcd. for $C_{22}H_{24}SO_3$: C, 71.71; H, 6.57. Found: C, 71.4; H, 6.35.

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