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Regio- and stereospecific synthesis of vinyl halides via carbozincation of acetylenic sulfones followed by halogenation

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ABSTRACT

Polysubstituted vinyl halides can be constructed regio- and stereospecifically by treatment of acetylenic sulfones with organozinc reagents in tetrahydrofuran followed by halogenation.

1. Introduction

The role and importance of halogenated building blocks in organic synthesis is long established and undisputed, owing to the wealth of reactions they can easily undergo [1–3]. Vinyl halides, in particular, are versatile substrates in many useful organic transformations including the well-known Stille, Suzuki, and Sonogashira coupling reactions [4–10]. The importance of vinyl halides in organic synthesis has stimulated a great deal of interest and much attention has been devoted to the synthesis of vinyl halides and their derivatives [11–16].

Polysubstituted alkenes are key structural elements of many natural products and pharmaceuticals such as Nileprost and Tamoxifen [17–21]. Polysubstituted alkenes can also be used as intermediates in asymmetric transformations that generate quaternary centers such as osmylations, epoxidations, and conjugate additions [22–24]. The efficient synthesis of polysubstituted alkenes in a regio- and stereoselective fashion is an important goal in organic chemistry [25–28]. Carbometallation of alkynes is a time-tested technique for the synthesis of substituted alkenes since the resulting alkenylmetals can be transformed to various substituted alkenes in a stereoselectivity [29–34]. Polysubstituted vinyl halides are potential precursors of various substituted alkenes due to the versatile reactivity of halogen. In a preliminary communication, we have reported an efficient synthesis of tetrasubstituted alkenes regio- and stereospecifically by three-component tandem reaction of allylzinc bromide, acetylenic sulfones and halohydrocarbons [35]. As an extension of this research, we investigated the carbozincation of acetylenic sulfones with various organozinc reagents (i.e. allylzinc bromide, benzylzinc bromide, *n*-butylzinc chloride and phenylzinc chloride) and further halogenation of the *in situ* formed vinylzinc reagents, hoping to prepare differently substituted vinyl halides. Herein we wish to describe the regio- and stereospecific synthesis of polysubstituted vinyl halides by carbozincation of acetylenic sulfones followed by halogenation.

2. Results and discussion

In the preliminary communication, we have reported that the allylzincation reaction of acetylenic sulfones proceeded smoothly when acetylenic sulfone was treated with 1.5 equiv. of allylzinc bromide in refluxing THF [35]. With this experience, the carbozincation reactions of various organozinc reagents with acetylenic sulfones were conducted in the similar reaction conditions. It was found that differently substituted α-sulfonyl vinyl halides could be prepared in high yields by the carbozincation of acetylenic sulfones followed by halogenation (Scheme 1). The results are summarized in Table 1. From Table 1 we can see that different organozinc reagents can react with acetylenic sulfones. R^1ZnX can be allylzinc bromide (**2a**), benzylzinc bromide (**2b**), *n*-butylzinc chloride (**2c**) or phenylzinc chloride (**2d**). The vinyl halides can

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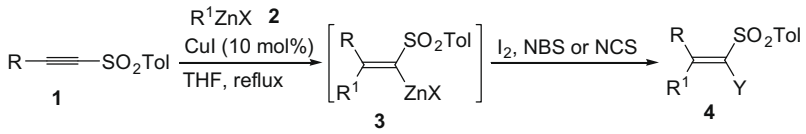


Scheme 1. Carbozincation of acetylenic sulfones followed by halogenation.

Table 1
Preparation of vinyl halides by carbozincation–halogenation tandem reaction.

Entry	R	R^1ZnX[a]	Y	Yield (%)[b]
1	C_6H_5	$CH_2{=}CHCH_2ZnBr$ (**2a**)	I	**4a** 93
2	n-C_5H_{11}–	**2a**	I	**4b** 92
3	C_6H_5–	**2a**	Br	**4c** 90
4	n-C_5H_{11}–	**2a**	Br	**4d** 89
5	C_6H_5–	**2a**	Cl	**4e** 80
6	$C_6H_5^-$	$C_6H_5CH_2ZnBr$ (**2b**)	I	**4f** 85
7	n-C_5H_{11}–	**2b**	I	**4g** 89
8	C_6H_5–	**2b**	Br	**4h** 84
9	n-C_5H_{11}–	**2b**	Br	**4i** 81
10	C_6H_5–	n-C_4H_9ZnCl(**2c**)	I	**4j** 87
11	C_6H_5–	**2c**	Cl	**4k** 78
12	C_6H_5–	C_6H_5ZnCl(**2d**)	I	**4l** 84
13	n-C_5H_{11}–	**2d**	I	**4m** 83
14	C_6H_5–	**2d**	Br	**4n** 85
15	n-C_5H_{11}–	**2d**	Br	**4o** 85
16	C_6H_5–	**2d**	Cl	**4p** 80

[a] In the case of **2a**, no CuI was added.
[b] Isolated yield based on **1**.

be vinyl iodides, vinyl bromides or vinyl chloride. It should be noted that 10 mol% of CuI was needed in cases of benzylzinc bromide, *n*-butylzinc chloride or phenylzinc chloride. This may be due to the fact that these organozinc reagents are less reactive than allylzinc bromide [36].

The molecular structure of compound **4f** was unambiguously determined by X-ray diffraction analysis (Fig. 1) [37]. From Fig. 1 we can see that the benzyl group is *cis* to iodo and *trans* to *p*-tolylsulfonyl group, which indicates that the tandem carbozincation-halogenation proceeded in a *syn*-fashion. No *anti* carbozincation-halogenation products were obtained.

Vinyl halides can obviously be applied as useful intermediates in organic synthesis. Here we examined a Negishi coupling reaction of vinyl iodide **4a** with vinylzinc bromide **3a**, which was prepared *in situ* from acetylenic sulfone **1a** and allylzinc bromide. Polysubstituted conjugated diene **5** was obtained in 56% yield (Scheme 2).

The molecular structure of compound **5** was confirmed by X-ray diffraction analysis (Fig. 2) [38], which shows that the coupling reaction proceeded with complete retention of the configuration of the two carbon–carbon double bonds in **4a** and **3a**.

In summary, we have developed a simple and efficient method to synthesize polysubstituted vinyl halides regio- and stereospecifically by the carbozincation of acetylenic sulfone followed by halogenation. The method has the advantages of readily available starting materials, mild reaction conditions and excellent regio- and stereoselectivity.

3. Experimental

All reactions were carried out in pre-dried glassware under an argon atmosphere. All solid products were recrystallized from ethyl acetate and hexane, and the melting points are uncorrected. THF was distilled from sodium/benzophenone immediately before use. ^1H NMR spectra were measured at 300 MHz and ^{13}C NMR spectra were measured at 75 MHz in $CDCl_3$ or in C_6D_6 with TMS as the internal standard. Acetylenic sulfones [39] and organozinc reagents [40,41] were prepared according to the literature procedures.

*3.1. General procedure for the preparation of **4** by carbozincation of acetylenic sulfone followed by halogenation*

To a solution of R^1ZnX (0.6 mmol) in THF (1.4 mL) was added acetylenic sulfone (0.5 mmol) and CuI (0.06 mmol, 10 mol%) at 0 °C. The reaction mixture was then stirred at refluxing temperature. Once the carbozincation of acetylenic sulfone was complete (monitored by TLC), iodine, NBS or NCS (0.75 mmol, 1.5 equiv.) was added to the reaction flask at room temperature. The reaction mixture was stirred at room temperature for 0.5 h and then was quenched with saturated NH_4Cl solution. After usual workup, the crude product was purified by flash chromatography on silica gel (hexane/ethyl acetate = 20:1 v/v) to give the desired pure product **4**.

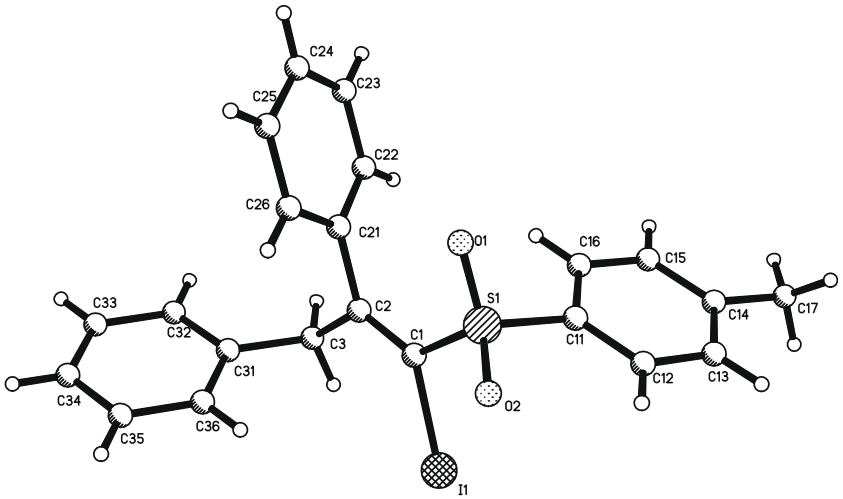
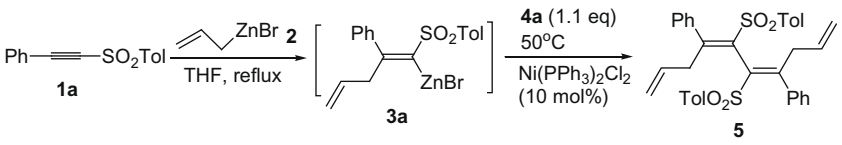


Fig. 1. The molecular structure of compound **4f**.



Scheme 2. Negishi coupling reaction of vinyl iodide **4a** and vinylzinc bromide **3a.**

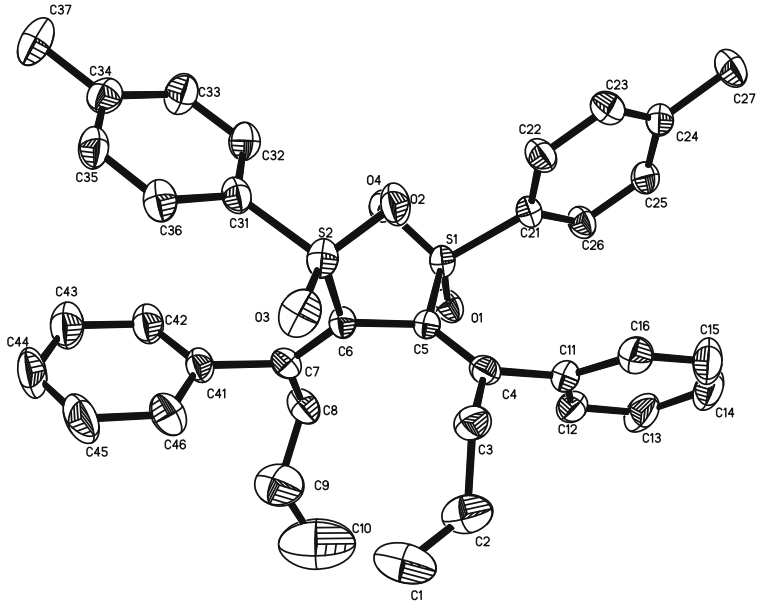


Fig. 2. The molecular structure of compound **5**.

*3.1.1. (E)-1-Iodo-2-phenyl-1-(p-tolylsulfonyl)-1,4-pentadiene (**4a**)*

White solid; m.p. 78–79 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J = 6.6 Hz, 2H), 7.22–7.19 (m, 3H), 7.10 (d, J = 8.0 Hz, 2H), 6.91–6.88 (m, 2H), 5.64–5.51 (m, 1H), 5.08–5.00 (m, 2H), 3.40–3.37 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 144.1, 137.9, 136.2, 130.5, 129.2, 128.5, 128.0, 127.7, 118.9, 105.1, 52.6, 21.6; HRMS (ESI), calcd for $C_{18}H_{18}IO_2S$ (MH^+), 425.0072, found, 425.0066; IR (KBr) 2922, 1596, 1442, 1322, 1151 cm^{-1}.

*3.1.2. (Z)-1-Iodo-2-pentyl-1-(p-tolylsulfonyl)-1,4-pentadiene (**4b**)*

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 7.1 Hz, 2H), 7.33 (d, J = 7.4 Hz, 2H), 5.74–5.61 (m, 1H), 5.18–5.07 (m, 2H), 3.19 (d, J = 6.0 Hz, 2H), 2.82 (t, J = 7.2 Hz, 2H), 2.43 (s, 3H), 1.50–1.25 (m, 6H), 0.86–0.81 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5, 144.5, 137.2, 131.7, 129.9, 129.7, 128.2, 118.3, 49.8, 34.0, 31.9, 28.6, 22.4, 21.7, 14.1; HRMS (ESI), calcd for $C_{17}H_{23}INaO_2S$ (MNa^+), 441.0361, found, 441.0359; IR (KBr) 2954, 2928, 1636, 1595, 1320, 1149, 1085 cm^{-1}.

*3.1.3. (E)-1-Bromo-2-phenyl-1-(p-tolylsulfonyl)-1,4-pentadiene (**4c**)*

Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 8.1 Hz, 2H), 7.32–7.26 (m, 3H), 7.21 (d, J = 8.1 Hz, 2H), 7.06–7.04 (m, 2H), 5.68–5.55 (m, 1H), 5.10–5.01 (m, 2H), 3.36 (d, J = 6.7 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 144.6, 138.1, 136.4, 130.4, 129.4, 128.7, 128.2, 127.8, 127.5, 123.6, 118.9, 47.2, 21.7; HRMS (ESI), calcd for $C_{18}H_{18}BrO_2S$ (MH^+), 377.0211, found, 377.0205; IR (KBr) 2922, 1596, 1443, 1331, 1156 cm^{-1}.

*3.1.4. (Z)-1-Bromo-2-pentyl-1-(p-tolylsulfonyl)-1,4-pentadiene (**4d**)*

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 5.77–5.64 (m, 1H), 5.12–5.06 (m, 2H), 3.14 (d, J = 6.5 Hz, 2H), 2.82 (t, J = 7.8 Hz, 2H), 2.45 (s, 3H), 1.60–1.49 (m, 2H), 1.48–1.26 (m, 4H), 0.92 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.0, 144.8, 136.9, 131.6, 129.7, 128.3, 120.1, 118.2, 44.3, 33.8, 32.0, 28.6, 22.4, 21.7, 14.1; HRMS (ESI), calcd for $C_{17}H_{23}BrNaO_2S$ (MNa^+), 393.0500, found, 393.0494; IR (KBr) 2955, 1637, 1596, 1455, 1326, 1152, 1086 cm^{-1}.

*3.1.5. (E)-1-Chloro-2-phenyl-1-(p-tolylsulfonyl)-1, 4-pentadiene (**4e**)*

White solid; m.p. 72–73 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.32–7.29 (m, 3H), 7.23–7.20 (m, 2H), 7.09–7.06 (m, 2H), 5.69–5.50 (m, 1H), 5.06–4.97 (m, 2H), 3.33–3.30 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6, 144.6, 137.4, 136.2, 130.9, 130.5, 129.4, 128.6, 128.2, 127.9, 127.5, 118.9, 44.1, 21.7; HRMS (ESI) calcd for $C_{18}H_{18}ClO_2S$, (MH^+) 333.0716, found, 333.0710; IR (KBr) 2919, 1595, 1443, 1332, 1157 cm^{-1}.

*3.1.6. (E)-2,3-Diphenyl-1-iodo-1- (p-tolylsulfonyl)-1-propylene (**4f**)*

White solid; m.p. 119–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 2H), 7.21–7.19 (m, 4H), 7.14–7.08 (m, 4H), 7.04–7.02 (m, 2H), 6.72 (d, J = 7.3 Hz, 2H), 4.07 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 144.2, 137.3, 136.3, 135.3, 129.3, 129.0, 128.6, 128.5, 128.1, 128.0, 127.5, 127.2, 105.9, 54.2, 21.7; HRMS (ESI), calcd for $C_{22}H_{19}INaO_2S$ (MNa^+), 497.0048, found, 497.0043; IR (KBr) 3024, 1646, 1598, 1318, 1150, 1071 cm^{-1}.

*3.1.7. (Z)-2-Benzyl-1-iodo-1-(p-tolylsulfonyl)-1-heptylene (**4g**)*

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.26–7.22 (m, 3H), 7.11–7.08 (m, 2H), 3.87 (s, 2H), 2.76 (t, J = 7.8 Hz, 2H), 2.45 (s, 3H), 1.45–1.35 (m, 2H), 1.30–1.20 (m, 4H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 144.6, 137.3, 136.4, 129.7, 128.8, 128.4, 128.3, 127.1,

101.9, 50.9, 33.5, 31.9, 29.1, 22.3, 21.7, 14.0; HRMS (ESI), calcd for $C_{21}H_{25}INaO_2S$ (MNa^+), 491.0518, found, 491.0514; IR (KBr) 2954, 1596, 1494, 1317, 1148, 1083 cm^{-1}.

*3.1.8. (E)-1-Bromo-2,3-diphenyl-1-(p-tolylsulfonyl)-1-propylene (**4h**)*

White solid; m.p. 96–97 °C; ^1H NMR (300 MHz, C_6D_6) δ 7.75 (d, J = 8.2 Hz, 2H), 7.02–6.99 (m, 6H), 6.97–6.96 (m, 2H), 6.90–6.87 (m, 2H), 6.73 (d, J = 7.9 Hz, 2H), 3.81 (s, 2H), 1.89 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 153.6, 144.0, 138.0, 137.5, 135.5, 129.2, 129.1, 128.9, 128.5, 128.0, 127.9, 127.5, 127.0, 124.7, 48.5, 21.0; HRMS (ESI), calcd for $C_{22}H_{19}BrNaO_2S$ (MNa^+), 449.0187, found, 449.0187; IR (KBr) 3058, 1594, 1491, 1332, 1152, 1085 cm^{-1}.

*3.1.9. (Z)-2-Benzyl-1-bromo-1-(p-tolylsulfonyl)-1-heptylene (**4i**)*

White solid; m.p. 94–95 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.28–7.22 (m, 3H), 7.10 (d, J = 7.4 Hz, 2H), 3.78 (s, 2H), 2.74 (t, J = 7.8 Hz, 2H), 2.45 (s, 3H), 1.55–1.45 (m, 2H), 1.35–1.22 (m, 4H), 0.87 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.8, 144.8, 136.9, 136.4, 129.7, 128.5, 128.3, 127.9, 127.0, 120.6, 45.2, 33.3, 31.9, 29.1, 22.3, 21.7, 14.0; HRMS (ESI), calcd for $C_{21}H_{25}BrNaO_2S$ (MNa^+), 443.0656, found, 443.0650; IR (KBr) 3058, 2957, 1595, 1491, 1333, 1152, 1086 cm^{-1}.

*3.1.10. (E)-1-Iodo-2-phenyl-1-(p-tolylsulfonyl)-1-hexylene (**4j**)*

White solid; m.p. 77–79 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 8.3 Hz, 2H), 7.28–7.23 (m, 3H), 7.13–7.10 (m, 2H), 6.94–6.91 (m, 2H), 2.63 (t, J = 7.4 Hz, 2H), 2.38 (s, 3H), 1.35–1.25 (m, 4H), 0.85 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4, 143.9, 138.1, 136.3, 129.1, 128.5, 127.9, 127.7, 127.6, 103.6, 48.5, 28.4, 22.4, 21.6, 13.8; HRMS (ESI), calcd for $C_{19}H_{21}INaO_2S$ (MNa^+), 463.0205, found, 463.0201; IR (KBr) 2951, 2924, 1594, 1491, 1314, 1147, 1083 cm^{-1}.

*3.1.11. (E)-1-Chloro-2-phenyl-1-(p-tolylsulfonyl)-1-hexylene (**4k**)*

White solid; m.p. 55–57 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 8.3 Hz, 2H), 7.33–7.31 (m, 3H), 7.23–7.20 (m, 2H), 7.09–7.06 (m, 2H), 2.56 (t, J = 7.6 Hz, 2H), 2.38 (s, 3H), 1.34–1.25 (m, 4H), 0.82 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7, 144.6, 137.7, 136.4, 129.5, 128.9, 128.2, 127.9, 127.6, 127.1, 39.6, 28.9, 22.5, 21.7, 13.8; HRMS (ESI), calcd for $C_{19}H_{21}ClNaO_2S$ (MNa^+), 371.0848, found, 371.0843; IR (KBr) 3058, 2952, 1595, 1490, 1442, 1322, 1157, 1083, 811 cm^{-1}.

*3.1.12. 1, 1-Diphenyl-2-iodo-2-(p-tolylsulfonyl)ethylene (**4l**)*

White solid; m.p. 183–185 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 8.3 Hz, 2H), 7.30–7.09 (m, 12H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7, 145.7, 144.2, 138.6, 136.1, 129.2, 128.7, 128.6, 128.5, 127.8, 127.6, 103.9, 21.6; HRMS (ESI), calcd for $C_{21}H_{17}INaO_2S$ (MNa^+), 482.9892, found, 482.9899; IR (KBr) 3062, 1593, 1490, 1310, 1302, 1145, 1082 cm^{-1}.

*3.1.13. (Z)-1-Iodo-2-phenyl-1-(p-tolylsulfonyl)-1-heptylene (**4m**)*

White solid; m.p. 81–82 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.94–7.92 (m, 2H), 7.38–7.32 (m, 5H), 7.04–7.01 (m, 2H), 3.09 (t, J = 8.1 Hz, 2H), 2.46 (s, 3H), 1.35–1.21 (m, 6H), 0.82 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 146.1, 144.6, 136.8, 129.6, 128.4, 128.3, 128.1, 126.4, 100.9, 36.5, 31.5, 27.6, 22.2, 21.6, 13.8; HRMS (ESI), calcd for $C_{20}H_{23}INaO_2S$ (MNa^+), 477.0361, found, 477.0355; IR (KBr) 3047, 2952, 1634, 1592, 1489, 1346, 1145, 1049 cm^{-1}.

*3.1.14. 1-Bromo-2,2-diphenyl-1-(p-tolylsulfonyl)ethylene (**4n**)*

White solid; m.p. 170–171 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.32–7.25 (m, 8H), 7.19–7.17 (m, 4H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 144.6, 141.9, 138.6, 136.3, 129.4, 129.0, 128.8, 128.7, 128.3, 128.1, 127.9, 122.8, 21.6; HRMS (ESI), calcd for $C_{21}H_{17}BrNaO_2S$ (MNa^+), 435.0026, found, 435.0024; IR (KBr) 3061, 1595, 1489, 1328, 1155, 1087, 813 cm^{-1}.

*3.1.15. (Z)-1-Bromo-2-phenyl-1-(p-tolylsulfonyl)-1-heptylene (**4o**)*

Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.94–7.91 (m, 2H), 7.39–7.29 (m, 5H), 7.11–7.08 (m, 2H), 3.12 (t, J = 7.9 Hz, 2H), 2.45 (s, 3H), 1.39–1.25 (m, 6H), 0.84 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 144.8, 139.9, 136.6, 129.7, 129.2, 128.3, 128.1, 126.6, 120.3, 36.2, 31.5, 27.7, 22.2, 21.6, 13.8; HRMS (ESI), calcd for $C_{20}H_{23}BrNaO_2S$ (MNa^+), 429.0501, found, 429.0498; IR (KBr) 3047, 2953, 1592, 1489, 1315, 1149, 1083 cm^{-1}.

*3.1.16. 1-Chloro-2, 2-diphenyl-1-(p-tolylsulfonyl)ethylene (**4p**)*

White solid; m.p. 169–170 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.35–7.25 (m, 8H), 7.21–7.19 (m, 4H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 144.8, 139.7, 138.0, 136.2, 130.5, 129.5, 129.1, 128.9, 128.8, 128.6, 128.3, 128.1, 127.9, 21.7; HRMS (ESI), calcd for $C_{21}H_{17}ClNaO_2S$ (MNa^+), 391.0535, found, 391.0530; IR (KBr) 3049, 1648, 1595, 1492, 1329, 1158, 1088, 816 cm^{-1}.

*3.2. Procedure for the preparation of **5** by Negishi coupling reaction of vinyl iodide **4a** and vinylzinc bromide **3a***

Vinyl iodide **4a** (0.5 mmol), $Ni(PPh_3)_2Cl_2$ (10 mol%) and 3.0 mL of THF were added successively to the THF solution of vinylzinc bromide **3a**, which was prepared *in situ* from 1-phenyl-2-(*p*-tolylsulfonyl)ethyne **1a** (0.6 mmol) and allylzinc bromide (0.6 mmol). The reaction mixture was stirred at 50 °C overnight. The reaction was quenched with saturated NH_4Cl solution. After usual workup, the crude product was purified by flash chromatography on silica gel (hexane/ethyl acetate = 15:1 v/v) to give the desired pure product **5**.

*3.2.1. (4Z,6Z)-4,7-Diphenyl-5,6-bis(p-tolylsulfonyl)-1,4,6,9-decatetraene (**5**)*

White solid; m.p. 124–126 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, J = 8.1 Hz, 4H), 7.21–7.11 (m, 4H), 7.06–6.92 (m, 10H), 5.60–5.47 (m, 2H), 5.03–4.96 (m, 4H), 3.91–3.83 (m, 2H), 3.43–3.37 (m, 2H), 2.32 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 143.0, 142.9, 138.3, 136.6, 132.2, 128.7, 128.4, 127.8, 127.6, 127.4, 118.8, 44.4, 21.5; MS (ESI), 617.1 (MNa^+); Anal. Calcd. for $C_{36}H_{34}O_4S_2$, C, 72.70; H, 5.76. Found: C, 72.65; H, 5.74%. IR (KBr) 3048, 2834, 1568, 1441, 1308, 1152 cm^{-1}.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.006.

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[37] The CCDC deposition number for compound **4f** is 699217; crystal data: $C_{22}H_{19}IO_2S$, MW = 474.33, monoclinic, space group *P2(1)/c*, $a = 5.7758(6)$, $b = 18.474(2)$, $c = 19.807(2)$ Å; $\alpha = 90°$, $\beta = 106.835(2)°$, $\gamma = 90°$. $V = 2022.9(4)$ Å^3, $T = 293$ K, $Z = 4$, $D_c = 1.557$ g cm^{-1}, $\mu = 1.699$ mm^{-1}, $\lambda = 0.71073$ Å; $F(000)$ 944, 5042 independent reflections ($R_{int} = 0.0362$), 14085 reflections collected; refinement method, full-matrix least-squares on F^2; goodness-of-fit on $F^2 = 1.018$; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0420$, $wR_2 = 0.0945$.
[38] The CCDC deposition number for compound **5** is 699219; crystal data: $C_{36}H_{34}O_4S_2$, MW = 594.75, monoclinic, space group *P2(1)/c*, $a = 16.849(3)$, $b = 11.533(2)$, $c = 18.945(4)$ Å; $\alpha = 90°$, $\beta = 119.63(3)°$, $\gamma = 90°$. $V = 3200.1(11)$ Å^3, $T = 293$ K, $Z = 4$, $D_c = 1.234$ g cm^{-1}, $\mu = 0.204$ mm^{-1}, $\lambda = 0.71073$ Å; $F(000)$ 1256, 5636 independent reflections ($R_{int} = 0.0899$), 5839 reflections collected; refinement method, full-matrix least-squares on F^2; goodness-of-fit on $F^2 = 0.948$; final R indices [$I > 2\sigma(I)$], $R_1 = 0.0722$, $wR_2 = 0.1658$.
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