JOC Article

Studies on Hydrozirconation of 1-Alkynyl Sulfoxides or Sulfones and the Application for the Synthesis of Stereodefined Vinyl Sulfoxides or Sulfones

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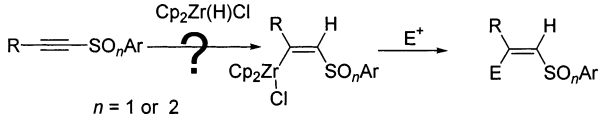
The hydrozirconation reaction of 1-alkynyl sulfoxides or sulfones with $Cp_2Zr(H)Cl$ in THF at room temperature predominantly gave *Z*-*β*-zirconated vinyl sulfoxides or sulfones with excellent regioselectivity. Compared with 1-alkynyl sulfoxides, the hydrozirconation reaction of 1-alkynyl sulfones exhibits great synthetic potential, leading to the efficient preparation of *Z*-*β*-halovinyl sulfones, *Z*-*β*-sulfonyl α,*β*-unsaturated ketones, and *Z*-*β*-alkynyl vinyl sulfones. Although the reaction mechanisms are still not clear, the neighboring group participation of the sulfinyl or sulfonyl group may be playing an important role in this unique hydrozirconation reaction.

Introduction

1-Alkenylzirconium (IV) complexes can be readily prepared by the cis-insertion of C,C-triple bonds into the Zr−H bond of Schwartz's reagent [$Cp_2Zr(H)Cl$].[1] It is well-documented that these alkenylzirconocenes can undergo many transformations with the retention of the configurations of the C,C-double bonds.[2] The hydrozirconation of a heteroatom-substituted alkyne provides a convenient approach to an alkenylic intermediate with two functionalities, which may be utilized for the stereoselective synthesis of polysubstituted alkenes. In these reactions, the zirconium group occupies the position α to these heteroatoms highly regioselectively and the stereoselectivity exhibits cis-addition exclusively.[3]

Efficient and highly stereoselective methodologies for the synthesis of vinyl sulfoxides and sulfones are of current interest[4,5] due to their importance in organic synthesis.[6] In our preliminary communication,[7] the hydrozirconation reaction of aryl-substituted acetylenic sulfones exhibited nice regioselectivity and yielded the trans-addition product *Z*-2-zirconated-1-alkenyl sulfones. Thus, we envisioned that the hydrozirconation reaction of 1-alkynyl sulfoxides or sulfones could provide a highly efficient synthetic approach to stereodefined vinyl sulfoxides or sulfones (eq 1).[7] In this paper, we



report the hydrozirconation of 1-alkynyl sulfoxides and sulfones and demonstrate its potential application to the synthesis of vinyl sulfoxides or sulfones in detail.

Results and Discussions

Hydrozirconation Reaction of 1-Alkynyl Sulfoxides. When phenylacetylenic sufoxide **1a** was treated with $Cp_2Zr(H)Cl$ in THF at room temperature followed by protonolysis, *E*-vinyl sulfoxides **3a** was obtained exclusively. The *E*-olefin geometry was verified by the coupling constant of the two olefinic protons ($^3J_{HH} = 15.2$ Hz).[8] When the in-situ formed alkenylzirconium intermediate **2a** was treated with NBS at room temperature, *Z*-*β*-bromovinyl sufoxide **4a** was formed exclusively. Its configuration was determined by the comparison with the authentic sample prepared from the trans-hydrobromination reaction of **1a**[9] (Scheme 1).

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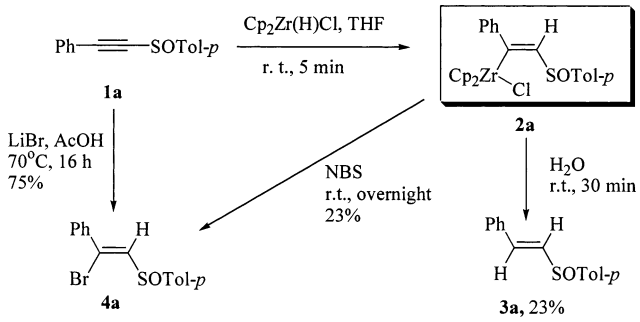
SCHEME 1



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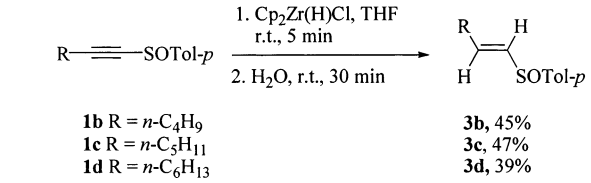

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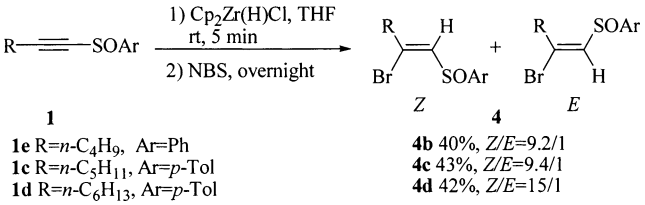


On the basis of the structures of these products, it can be concluded that the hydrozirconation reaction exhibits a trans-addition stereoselectivity, affording *Z*-alkenylzirconocene intermediate **2a**, in which the zirconium group occupies the 2-position highly regioselectively.

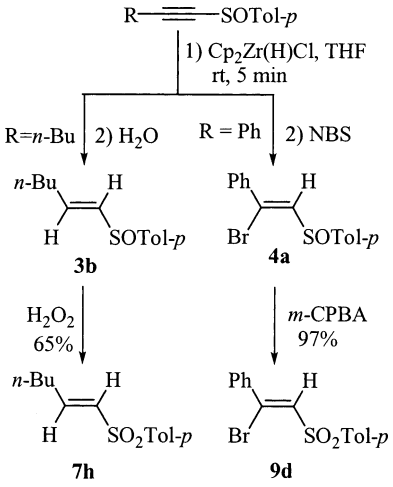
In addition, the hydrozirconation of alkyl-substituted acetylenic sulfoxides **1b**−**1d** followed by subsequent protonolysis also produced *E*-vinyl sulfoxides **3b**−**3d** predominantly, with a trace amount of the opposite stereoisomers. The *E*-configurations were established by the comparison with the literature data[5b] (Scheme 2).

The subsequent treatment of alkyl-substituted acetylenic sulfoxides **1c**−**e** with $Cp_2Zr(H)Cl$ and NBS gave inseparable mixtures of two *Z* (major) and *E* (minor) stereoisomers **4b**−**d** (Scheme 3) with good selectivity. The *Z*-configuration of product **4c** was verified by its $^1H-^1H$ 2D NOESY spectrum.

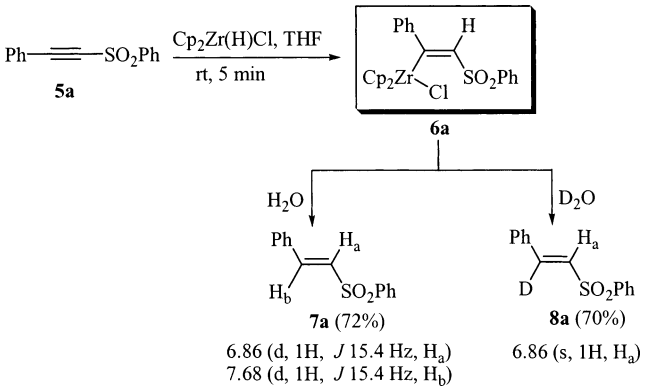
Several points should be noted: (1) No α-bromovinyl sufoxides were formed, indicating a high regioselectivity. (2) By increasing the bulkiness of the substituents attached to acetylenic bond, more trans-addition product was obtained [compare **4d** (15/1) with **4b** (9.2/1)] (Scheme 3). (3) Low yields are ascribed to the instability of both the substrates and products.[10]

Transformation of Vinyl Sulfoxides to Vinyl Sulfones.[11] The synthesis of stereodefined vinyl sulfones can be realized by the hydrozirconation/oxidization sequence of 1-alkynyl sulfoxides. *E*-1-(4′-Tolylsulfinyl)hex-1-ene **3b** was stereoselectively oxidized to *E*-1-(4′-tolylsulfonyl)hex-1-ene **7h** with H_2O_2, while *Z*-β-bromovinyl sulfoxide **4a** was converted to *Z*-2-bromo-2-phenyl-1-(4′-tolylsulfonyl)-ethene **9d** with *m*-CPBA (Scheme 4).

SCHEME 4



SCHEME 5



Hydrozirconation Reaction of 1-Alkynyl Sulfones. When phenylacetylenic sulfone **5a** was treated with 1.2 equiv of $Cp_2Zr(H)Cl$ in THF at room temperature, the reaction gave a clear yellow solution within about 5 min, which shows the end of hydrozirconation. After the mixture was divided into two equal parts via a graduated syring, H_2O and D_2O were added to quench the reaction, respectively. After the usual workup, pure products were obtained and their structures were determined by ^1H NMR spectra (Scheme 5).

Again, we observed that deuterium atom occupies the 2-position in **8a** [verified by its H_a chemical shift (6.86 ppm)] and locates at the same side of the carbon−carbon double bond with the sulfonyl group [as determined by the coupling constant of olefinic protons (15.4 Hz) in **7a**],[12] indicating a trans-addition type reaction of **5a** with Schwartz's reagent.

This reaction can be extended to other arylacetylenic sulfones (Table 1). The substituents attached to sulfonyl groups have little effect on the results (entries 2 and 3, Table 1), while the aryl substituents attached to the acetylenic bond affect the stereochemical outcome slightly. In entries 2 and 4−7 of Table 1, small amounts of *Z*-products were also formed.

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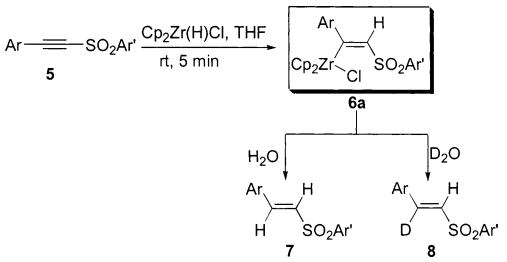
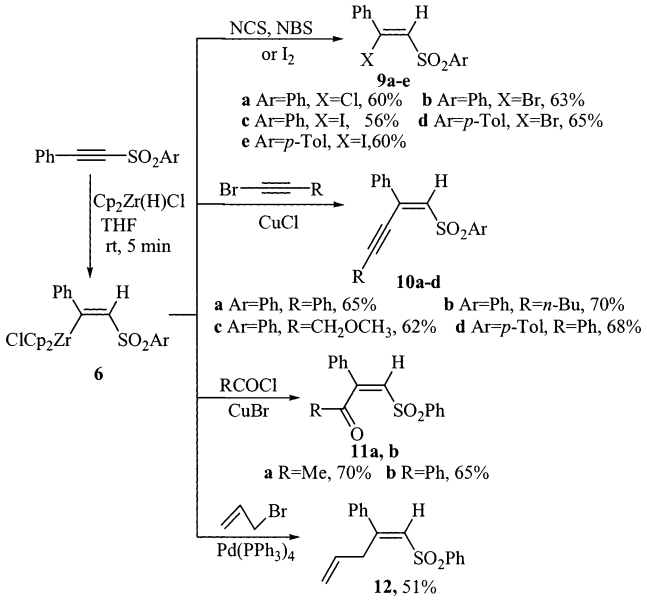
TABLE 1. Hydrozirconation of 1-Alkynyl Sulfones 5a and Subsequently Protonolysis with H_2O or D_2O[a]



entry	Ar	Ar′	alkyne	product[a]	yield (%)[b]	*E*/*Z*[c]
1	Ph	Ph	**5a**	**7a**	72	>99
2	Ph	*p*-Tol	**5b**	**7b**	69	>98/2
3	Ph	*p*-ClC_6H_4	**5c**	**7c**	68	>99
4	*p*-ClC_6H_4	Ph	**5d**	**7d**	64	96/4
5	*p*-BrC_6H_4	Ph	**5e**	**7e**	68	95/5
6	*p*-MeC_6H_4	Ph	**5f**	**7f**	65	94/6
7	*p*-$MeOC_6H_4$	Ph	**5g**	**7g**	72	94.5/5.5
8	Ph	Ph	**5a**	**8a**	70	95/5
9	*p*-ClC_6H_4	Ph	**5d**	**8b**	65	95.5/4.5

[a] Reaction conditions: (1) $Cp_2ZrH(Cl)$ (1.2 equiv), THF, rt, 5 min; (2) 10 equiv of H_2O or D_2O, THF, rt, 30 min. [b] Isolated yields from 1-alkynyl sulfones. [c] Determined by ^1H NMR spectra.

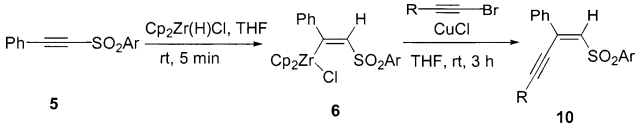
SCHEME 6



Synthetic Applications of the Hydrozirconation Reaction of 1-Alkynyl Sulfones (Scheme 6). The alkenylzirconium intermediates can react with different electrophiles with the retention of configuration.[2] When *Z*-*β*-sulfonyl alkenylzirconocenes **6** were treated with halogenation reagents such as NCS, NBS, or iodide at room temperature, *Z*-*β*-halovinyl sulfones **9** were formed exclusively in 56−65% yields. The configuration of **9b** was determined by the comparison with the product from the trans-hydrobromination reaction of **5a**.[9]

Alk-3-yn-1-enyl sulfones are one of most versatile organic synthetic intermediates,[13] which are usually not easily available by the known methods.[14,15] Utilizing the coupling reaction of ethenyl bifunctional group reagents **6** with 1-alkynyl bromides in the presence of CuCl at room temperature,[16] *Z*-polysubstituted-3-yn-1-enyl sulfones **10** can be prepared in 62−70% yields (Table 2). The *Z*-configuration of product **10c** was determined by its $^1H-^1H$ 2D NOESY spectrum.

TABLE 2. Hydrozirconation of 1-Alkynyl Sulfones and Subsequently Coupling Reactions of Alkenylzirconium Complexes with 1-Alkynyl Bromides in the Presence of CuCl[a]



entry	Ar	R	products[a]	yield (%)[b]	*Z*/*E*[c]
1	Ph	Ph	**10a**	65	88/12
2	Ph	*n*-Bu	**10b**	70	100/0
3	Ph	CH_3OCH_2	**10c**	62	100/0
4	*p*-Tol	Ph	**10d**	68	95/5

[a] The reaction was carried out at room temperature using 1.2 equiv of CuCl and 1.2 equiv of 1-alkynyl bromides for 3 h under a nitrogen atmosphere. [b] Isolated yields from 1-alkynyl sulfones. [c] Measured by ^1H NMR spectra.

Following the reported protocols, either a mixture of two stereoisomers of *β*-sulfonyl α,*β*-unsaturated ketones[17] or only *E*-isomer can be obtained.[18] In our study, acylation of the alkenyl zirconocenes **6** in the presence of copper(I) bromide at room temperature[19] could produce *Z*-*β*-sulfonyl α,*β*-unsaturated ketones **11a** and **11b** smoothly in 70% and 65% yields, respectively. Their configurations were verified by $^1H-^1H$ 2D NOESY spectra and the X-ray diffraction study of compound **11b**.[20]

Under the catalysis of $Pd(PPh_3)_4$, the cross-coupling reaction of alkenylzirconocene 6a with allyl bromide provided a facile synthesis of *Z*-2-phenyl-1-phenylsulfonyl-1,4-pentadiene **12**, whose configuration was verified by its $^1H-^1H$ 2D NOESY spectrum and X-ray diffraction study.[21]

There are some regio- and stereochemical issues associated with the addition of $Cp_2Zr(H)Cl$ to the unsymmetrical acetylenic sulfoxides or sulfones. A slight temperature effect on the stereoselectivity of this reaction (*Z*/*E*: −27 °C, >99: 1; 20 °C, 98: 2; 45 °C, 96: 4) was observed. In addition, when different amounts of methyl phenyl sulfone were added to the reaction mixture, a change of the stereoselectivity (from >99/1 for 0.2 equiv to 96/4 for 10 equiv) was observed, indicating that the sulfonyl group may play an important role in this hydrozirconation reaction, which could be related to the ability of their neighboring group participation (Scheme 7).

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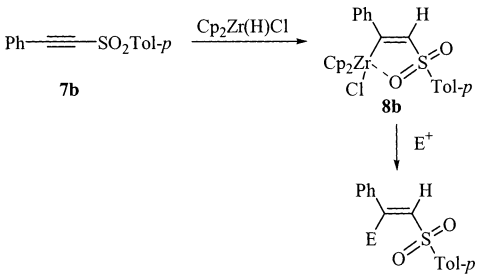
SCHEME 7



Conclusion

The treatments of 1-alkynyl sulfoxides or sulfones with $Cp_2Zr(H)Cl$ afforded *Z*-*β*-zirconated vinyl sulfoxides or sulfones predominantly. Compared with 1-alkynyl sulfoxides, the hydrozirconation reaction of 1-alkynyl sulfones has more synthetic potential. So it was explored for further synthetic transformation to *Z*-*β*-halovinyl sulfones, *Z*-*β*-sulfonyl-α,*β*-unsaturated ketones, and *Z*-*β*-alkynyl-substituted vinyl sulfones, providing a complementary synthetic approach to stereodefined *Z*-polysubstituted vinyl sufones.

Experimental Section

Melting points were uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ with TMS as internal standard. MS and HRMS spectra were performed with electron impact ionization (EI). THF was distilled from sodium−benzophenone ketyl immediately before use. Sodium sulfinate,[23] iodophenylacetylene,[24] 1-bromoalkynes,[25] $Cp_2Zr(H)Cl$,[26] 1-alkynyl sulfoxides **1a**−**1e**,[5b] phenylacetylenic sulfones **5a**−**5c**,[27] and acetylenic sulfones **5d**−**5g**[15] were prepared by the literature methods.

General Procedure for the Preparation of *E*-*β*-Monosubstituted Vinyl Sulfoxides 3 by the Hydrolysis of Alkenylzirconocenes 2. To a suspension of $Cp_2Zr(H)Cl$ (309 mg, 1.2 mmol) in THF (5 mL) in a Schlech reaction tube was added 1-alkynyl sulfoxide **1** (1.0 mmol) under nitrogen. The mixture was stirred for 5 min at room temperature to obtain a clear yellowish green solution of *Z*-alkenylzirconocene **2**, to which was added H_2O (0.2 mL), and the mixture was stirred for 30 min to obtain a nearly white turbid solution. After being diluted with 5 mL of light petroleum ether and stirred for further 5 min, the supernatant layer was filtered through a short plug of silica gel. After evaporation, the residue was purified by preparative TLC on silica gel (light petroleum ether/ethyl acetate 10/1) to yield *E*-vinyl sulfoxide **3**.

***E*-2-Phenyl-1-(4′-tolylsulfinyl)ethene (3a)**. Yield: 23%, colorless crystal. Mp: 81−82 °C (petroleum ether) (lit.[8] mp: 82 °C). IR (KBr): 2998, 1492, 1044 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 2.34 (s, 3H), 6.75 (d, *J* = 15.0 Hz, 1H), 7.19−7.39 (m, 8H), 7.51 (d, *J* = 8.1 Hz, 2H). MS (*m*/*z*): 243 (M^+ + 1, 1), 194 (100).

***E*-1-(4′-Tolylsulfinyl)hex-1-ene (3b).**[5b] Yield: 45%, pale yellow oil. IR (neat): 2929, 1558, 1457, 1041, 755 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.89 (t, *J* = 7.2 Hz, 3H), 1.32−1.36 (m, 2H), 1.42−1.46 (m, 2H), 2.19−2.25 (m, 2H), 2.41 (s, 3H), 6.21 (d t, *J* = 15.2 Hz, 1.4 Hz, 1H), 6.59 (d t, *J* = 15.2 Hz, 6.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H). MS (*m*/*z*): 223 (M^+ + 1, 100).

***E*-1-(4′-Tolylsulfinyl)hept-1-ene (3c).**[5b] Yield: 47%, pale yellow oil. IR (neat): 2956, 1492, 1457, 1044 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.88 (t, *J* = 7.4 Hz, 3H), 1.27−1.30 (m, 4H), 1.41−1.47 (m, 2H), 2.18−2.24 (m, 2H), 2.40 (s, 3H), 6.21 (d t, *J* = 15.2 Hz, 1.4 Hz, 1H), 6.59 (d t, *J* = 15.2 Hz, 6.8 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H). MS (*m*/*z*): 237 (M^+ + 1, 100).

***E*-1-(4′-Tolylsulfinyl)oct-1-ene (3d).**[5b] Yield: 39%, pale yellow oil. IR (neat): 1733, 1595, 1457 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.87 (t, *J* = 7.0 Hz, 3H), 1.23−1.33 (m, 6H), 1.41−1.47 (m, 2H), 2.19−2.24 (m, 2H), 2.40 (s, 3H), 6.21 (d t, *J* = 15.2 Hz, 1.4 Hz, 1H), 6.59 (d t, *J* = 15.2 Hz, 6.8 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H). MS (*m*/*z*): 251 (M^+ + 1, 11), 131 (100).

General Procedure for the Preparation of *Z*-*β*-Bromovinyl Sulfoxides 4. To the yellowish green solution **2** (prepared as described above) was added 2.5 equiv of NBS and the mixture was stirred overnight. After usual workup, the residue was purified by preparative TLC on silica gel (light petroleum ether/ethyl acetate 4/1 or 10/1) to yield **4**.

***Z*-2-Bromo-2-phenyl-1-(4′-tolylsulfinyl)ethene (4a).** Yield: 23%. IR (KBr): 2997, 1490, 1045 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 2.32 (s, 3H), 6.98 (s, 1H,), 7.24−7.29 (m, 5H), 7.46−7.49 (m, 2H), 7.61 (d, *J* = 8.1 Hz). MS (*m*/*z*): 323 [M^+ + 1 (^{81}Br), 2], 321 [M^+ + 1 (^{79}Br), 2], 193 (100). HRMS (EI): calcd for $C_{15}H_{13}BrOS$ (M^+ − O) 304.0121, found 303.9919.

***Z*-2-Bromo-1-phenylsulfinylhex-1-ene (4b).** Yield: 40%, pale yellow oil. IR (neat): 2924, 1594, 1085, 813 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.87 (t, *J* = 7.4 Hz, 3H), 1.25−1.31 (m, 2H), 1.51−1.57 (m, 2H), 2.53 (t, *J* = 7.1 Hz, 2H), 6.58 (s, 1H), 7.49−7.53 (m, 3H), 7.70−7.72 (m, 2H). MS (*m*/*z*): 289 [M^+ + 1 (^{81}Br), 36], 287 [M^+ + 1 (^{79}Br), 36], 209 (100). HRMS (EI): calcd for $C_{12}H_{15}BrOS$ (M^+ − O) 270.0278, found 270.0075.

***Z*-2-Bromo-1-(4′-tolylsulfinyl)hept-1-ene (4c).** Yield: 43%, pale yellow oil. IR (neat): 2929, 1732, 1045, 805 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.86 (t, *J* = 7.2 Hz, 3H), 1.23−1.29 (m, 4H), 1.55−4.59 (m, 2H), 2.41 (s, 3H), 2.52 (t, *J* = 7.0 Hz, 2H), 6.58 (s, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H). MS (*m*/*z*): 317 [M^+ + 1 (^{81}Br), 100], 315 [M^+ + 1 (^{79}Br), 100]. HRMS (EI): calcd for $C_{14}H_{19}BrOS$ (M^+ − O) 298.0591, found 298.0393.

***Z*-2-Bromo-1-(4′-tolylsulfinyl)oct-1-ene (4d).** Yield: 42%, pale yellow oil. IR (neat): 2927, 2856, 1595, 1047 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.85 (t, *J* = 7.0 Hz, 3H), 1.24 (m, 6H), 1.54−1.58 (m, 2H), 2.41 (s, 3H), 2.51 (t, *J* = 7.5 Hz, 2H), 6.57 (s, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H). MS (*m*/*z*): 331 [M^+ + 1 (^{81}Br), 43], 329 [M^+ + 1 (^{79}Br), 43]. HRMS (EI): calcd for $C_{15}H_{21}BrOS$ (M^+ − O) 312.0747, found 312.0538.

General Procedure for the Preparation of *E*-*β*-Monosubstituted Vinyl Sulfones 7 by the Protonolysis of Alkenylzirconocenes 6. To a suspension of $Cp_2Zr(H)Cl$ (155 mg, 0.6 mmol) in THF (4 mL) under nitrogen was added an acetylenic sulfone **5**. The mixture was stirred for 5 min at room temperature to obtain a clear yellow solution of alkenylzirconocene **6**. To this yellow solution was added H_2O (0.2 mL) and the mixture was stirred for 30 min to obtain a nearly white turbid solution. After usual workup, the residue was purified by preparative TLC on silica gel (light petroleum/ethyl acetate 15/1) to yield **7**.

***E*-2-Phenyl-1-(phenylsulfonyl)ethene (7a).** Yield: 72%, colorless solid. Mp: 74.5−75.5 °C (cyclohexane) [lit.[12a] mp: 76°C (C_6H_6)]. IR (KBr): 1620, 1450, 1320, 1140 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 6.86 (d, *J* = 15.4 Hz, 1H), 7.39−7.58 (m, 8H), 7.69 (d, *J* = 15.4 Hz, 1H), 7.94−7.97 (m, 2H). MS (*m*/*z*): 244 (M^+, 18), 91 (100).

***E*-2-Phenyl-1-(4′-tolylsulfonyl)ethene (7b).** Yield: 69%, colorless solid. Mp: 120−121 °C (cyclohexane) (lit.[6a] mp: 120−121 °C). IR (KBr): 1640, 1310, 1140 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 2.36 (s, 3H), 6.80 (d, *J* = 15.4 Hz, 1H), 7.26−7.42

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(m, 7H), 7.69 (d, J = 15.4 Hz, 1H), 7.77 (d, J = 8.2 Hz, 2H). MS (m/z): 258 (M^+, 36), 91 (100).

***E*-1-(4′-Chlorophenylsulfonyl)-2-phenylethene (7c).** Yield: 68%, colorless solid. Mp: 82−84 °C (cyclohexane) (lit.[6d] mp:78−78.5 °C). IR (KBr): 1630, 1600, 1320, 1150 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.83 (d, J = 15.4 Hz, 1H), 7.40−7.54 (m, 7H), 7.70 (d, J = 15.4 Hz, 1H), 7.89 (d, J = 7.8 Hz, 2H). MS (m/z): 280 [M^+ (^{37}Cl), 5], 278 [M^+ (^{35}Cl), 15], 91 (100).

***E*-2-(4′-Chlorophenyl)-1-(phenylsulfonyl)ethene (7d).** Yield: 64%, colorless solid. Mp: 129−130 °C (cyclohexane) (lit.[28] mp:130 °C). IR (KBr): 1617, 1486, 1321, 1309, 1149 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.85 (d, J = 15.4 Hz, 1H), 7.40 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 7.55−7.66 (m, 4H), 7.96 (m, 2H). MS (m/z): 280 [M^+ (^{37}Cl), 10], 278 [M^+ (^{35}Cl), 24], 136(100).

***E*-2-(4′-Bromophenyl)-1-(phenylsulfonyl)ethene (7e).** Yield: 68%, colorless solid. Mp: 150−152 °C (cyclohexane) (lit.[29] mp: none reported). IR (KBr): 1620, 1583, 1485, 1447, 1308, 1154 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.86 (d, J = 15.4 Hz, 1H), 7.35 (d, J = 8.3 Hz, 2H), 7.42−7.66 (m, 6H), 7.95 (m, 2H). MS (m/z): 324 [M^+ (^{81}Br), 37], 322 [M^+ (^{79}Br), 36], 182 (100).

***E*-2-(4′-Tolyl)-1-(phenylsulfonyl)ethene (7f).** Yield: 65%, colorless solid. Mp: 139−140 °C (cyclohexane) (lit.[30] mp: 138−139 °C). IR (KBr): 1606, 1308, 1147 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.37 (s, 3H), 6.81 (d, J = 15.4 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.53−7.62 (m, 3H), 7.66 (d, J = 15.4 Hz, 1H), 7.95 (d, J = 7.3 Hz, 2H). MS (m/z): 258 (M^+, 25), 116 (100).

***E*-2-(4′-Methoxylphenyl)-1-(phenylsulfonyl)ethene (7g).** Yield: 72%, colorless solid. Mp: 120−121 °C (cyclohexane) [lit.[31] mp: 123−124 °C (MeOH)]. IR (KBr): 1604, 1512, 1310, 1264, 1143 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.83 (s, 3H), 6.71(d, J = 15.3 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 7.52−7.61 (m, 3H), 7.64 J = 15.3 Hz, 1H), 7.95 (d, J = 7.5 Hz, 2H). MS (m/z): 274 (M^+, 23), 132 (100).

General Procedure for the Preparation of *E*-2-Deuteriovinyl Sulfones 8 by the Deuteriolysis of Alkenylzirconocenes 6. To this yellow solution of **6** (prepared as described above) was added 0.2 mL of D_2O, and the mixture was stirred for 30 min to obtain a nearly white turbid solution. After usual workup, the residue was purified by preparative TLC on silica gel (light petroleum ether/ethyl acetate = 15/ 1) to yield a pure product **8**.

***E*-2-Deutero-2-phenyl-1-(phenylsulfonyl)ethene (8a).** Yield: 70%, colorless solid. Mp: 73.5−75 °C (cyclohexane) (lit.[12b] mp: none reported). IR (KBr): 1620, 1450, 1320, 1140 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.86 (s, 1H), 7.38−7.63 (m, 8H), 7.95−7.97 (m, 2H). MS (m/z): 245 (M^+, 7), 92 (100). Anal. Calcd for $C_{14}H_{11}DO_2S$: C 68.55, H 5.34. Found: C 68.50, H 5.35.

***E*-2-Deutero-2-(4′-chlorophenyl)-1-(phenylsulfonyl)-ethene (8b).** Yield: 65%, colorless solid. Mp: 128−129 °C (cyclohexane). IR (KBr): 1618, 1321, 1149 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.84 (s, 1H), 7.37 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.55−7.64 (m, 3H), 7.94−7.96 (m, 2H). MS (m/z): 281 [M^+ (^{37}Cl), 10], 279 [M^+ (^{35}Cl), 24], 136 (100). Anal. Calcd for $C_{14}H_{10}DClO_2S$: C 60.01, H 4.32. Found: C 60.07, H 4.30.

General Procedure for the Preparation of *Z*β-Halovinyl Sulfones 9. To the yellow solution of **6** (prepared as described above) was added 1.25 mmol of NCS or NBS or 0.75 mmol of I_2 and the mixture was then stirred for 2 h at room temperature. After workup as described above, the residue was purified by preparative TLC on silica gel (petroleum ether/ethyl acetate 10/1 as eluent) to yield **9**.

***Z*-2-Chloro-2-phenyl-1-(phenylsulfonyl)ethene (9a).** Yield: 60%, colorless solid. Mp: 83−84 °C (methanol) (lit.[32b] mp: 84 °C). IR (KBr): 1595, 1320, 1305, 1235, 1175, 1145 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.15 (s, 1H), 7.41−7.67 (m, 8H), 8.05−8.09 (m, 2H). MS (m/z): 280 [M^+ (^{37}Cl), 8], 278 [M^+ (^{35}Cl), 22], 77 (100).

***Z*-2-Bromo-2-phenyl-1-(phenylsulfonyl)ethene (9b).** Yield: 63%, pale yellow solid. Mp: 89.5−90.5 °C (methanol) (lit.[32a] mp: 88 °C). IR (KBr): 1605, 1460, 1325, 1150 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.33 (s, 1H), 7.38−7.43 (m, 3H), 7.55−7.66 (m, 5H), 8.06−8.08 (m, 2H). MS (m/z): 324 [M^+ (^{81}Br), 8], 322 [M^+, (^{79}Br), 8], 77 (100).

***Z*-2-Iodo-2-phenyl-1-(phenylsulfonyl)ethene (9c).** Yield: 56%, pale yellow solid. Mp: 113−115 °C (methanol). IR (KBr): 1460, 1320, 1150, 1090 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.27 (s, 1H), 7.31−7.71 (m, 8H), 8.06−8.09 (m, 2H). MS (m/z): 371(M^+ + 1, 13), 77 (100). Anal. Calcd for $C_{14}H_{11}IO_2S$: C 45.42, H 2.99. Found: C 45.18, H 2.87.

***Z*-2-Bromo-2-phenyl-1-(4′-tolylsulfonyl)ethene (9d).** Yield: 65%, colorless solid. Mp: 109−110 °C (methanol) (lit.[32a] mp: 108 °C). IR (KBr): 1610, 1580, 1450, 1330, 1160 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.46 (s, 3H), 7.31 (s, 1H), 7.36−7.44 (m, 5H), 7.55 (m, 2H), 7.95 (d, J = 8.3 Hz, 2H). MS (m/z): 338 [M^+ (^{81}Br), 8], 336 [M^+ (^{79}Br), 8], 91 (100).

***Z*-2-Iodo-2-phenyl-1-(4′-tolylsulfonyl)ethene (9e).** Yield: 60%, slight brown solid. Mp: 98−100 °C (methanol). IR (KBr): 1610, 1330, 1150, 750, 660 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.39 (s, 3H), 7.17−7.41 (m, 8H), 7.88 (d, J = 8.3 Hz, 2H). MS (m/z): 385 (M^+ + 1, 17), 91 (100). Anal. Calcd for $C_{15}H_{13}IO_2S$: C 46.89, H 3.41. Found: C 46.88, H 3.39.

General Procedure for the Preparation of *Z*-Alk-3-yn-1-enyl Sulfones 10. To the yellow solution of **6** (prepared as described above) were added CuCl (59 mg, 0.6 mmol) and phenylacetylenic bromide (109 mg, 0.6 mmol). The mixture was stirred for 3 h at room temperature. After workup as described above, the residue was purified by preparative TLC on silica gel (petroleum ether/ethyl acetate 12/1 as eluent) to yield **10**.

***Z*-2, 4-Diphenyl-1-(phenylsulfonyl)but-1-en-3-yne (10a).** Yield: 65%, colorless solid. Mp: 136−137°C (cyclohexane). IR (KBr): 2215, 1655, 1570, 1465, 1325, 1160, 1095 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.13 (s, 1H), 7.40−7.72 (m, 13H), 8.08 (d, J = 7.3 Hz, 2H). MS (m/z): 344 (M^+, 11), 178 (100). Anal. Calcd for $C_{22}H_{16}O_2S$: C 76.72, H 4.68. Found: C 76.88, H 4.63.

***Z*-2-Phenyl-1-(phenylsulfonyl)oct-1-en-3-yne (10b).** Yield: 70%, colorless solid. Mp: 66−68 °C (cyclohexane). IR (KBr): 3130, 2218, 1650, 1570, 1330, 1320, 1160 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.95 (t, J = 7.0 Hz, 3H), 1.43−1.67 (m, 4H), 2.52 (t, J = 7.2 Hz, 2H), 7.07 (s, 1H), 7.37−7.64 (m, 8H), 8.03−8.06 (m, 2H). MS (m/z): 325 (M^+ + 1, 33), 115 (100). Anal. Calcd for $C_{20}H_{20}O_2S$: C 74.04, H 6.21. Found: C 74.16, H 6.20.

***Z*-5-Methoxy-2-phenyl-1-(phenylsulfonyl)pent-1-en-3-yne (10c).** Yield: 62%, colorless solid. Mp: 67−69 °C (cyclohexane). IR (KBr): 3030, 2215, 1650, 1590, 1465, 1330, 1165, 1090 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.49 (s, 3H), 4.42 (s, 2H). 7.09 (s, 1H), 7.38−7.64 (m, 8H), 8.04−8.06 (m, 2H). MS (m/z): 313 (M^+ + 1, 17), 85 (100). Anal. Calcd for $C_{18}H_{16}O_3S$: C 69.21, H 5.16. Found: C 69.44, H 5.36.

***Z*-2,4-Diphenyl-1-(4′-tosyl)but-1-en-3-yne (10d).** Yield: 68%, colorless solid. Mp: 117−118 °C (cyclohexane). IR (KBr): 2230, 1615, 1570, 1460, 1360, 1330, 1315, 1160, 1095 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.41 (s, 3H), 7.11 (s, 1H), 7.28−7.44 (m, 8H), 7.62−7.71 (m, 4H), 7.96 (d, J = 8.3 Hz, 2H). MS (m/z): 358 (M^+, 9), 192 (100). Anal. Calcd for $C_{23}H_{18}O_2S$: C 77.07, H 5.06. Found: C 77.30, H 5.16.

General Procedure for the Preparation of *Z*-β-Sulfonyl-α,β-unsaturated Ketones 11. To the yellow solution

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of **6** (prepared as described above) were added CuBr (86 mg, 0.6 mmol) and acyl chloride (64 mg, 0.6 mmol). The mixture was stirred for 3 h at room temperature. After workup as described above, the residue was purified by preparative TLC on silica gel (petroleum ether/ethyl acetate 8/1 as eluent) to yield **11**.

***Z*-3-Phenyl-4-phenylsulfonylbut-3-en-2-one (11a).** Yield: 70%, colorless solid. Mp: 115−116 °C (cyclohexane/ethyl acetate 10/1). IR (KBr): 1738, 1615, 1588, 1455, 1340, 1315, 1170, 1150 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.54 (s, 3H), 6.44 (s, 1H), 7.34−7.62 (m, 8H), 7.95−7.98 (m, 2H). MS (*m*/*z*): 287 ($M^+ + 1$, 44), 102 (100). Anal. Calcd for $C_{16}H_{14}O_3S$: C 67.11, H 4.93. Found: C 67.44, H 4.96.

***Z*-1,2-Diphenyl-3-phenylsulfonylprop-2-en-1-one (11b).** Yield: 65%, colorless solid. Mp: 141−143 °C (cyclohexane/ethyl acetate 10/1). IR (KBr): 3085, 3062, 1690, 1610, 1460, 1340, 1320, 1240, 1222, 1160 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.80 (s, 1H), 7.35−7.58 (m, 11H), 7.93−7.98 (m, 4H). MS (*m*/*z*): 349 ($M^+ + 1$, 20), 105 (100). Anal. Calcd for $C_{21}H_{16}O_3S$: C 72.39, H 4.63. Found: C 72.44, H 4.66.

The Procedure for Preparation of *E*-2-Phenyl-1-phenylsulfonyl-1,4-pentadiene 12. To a yellow solution of **6** (prepared as described above) were added $Pd(PPh_3)_4$ (0.025 mmol, 29 mg) and allyl bromide (73 mg, 0.6 mmol). The mixture was stirred for 12 h at 40 °C. After workup as described above, pure product **12** (73 mg, 51%) was obtained by preparative TLC on silica gel with petroleum ether/ethyl acetate 10/1 as eluent to yield a colorless solid. Mp: 69−70 °C (cyclohexane). IR (KBr): 3045, 1610, 1485, 1310, 1155 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.79−3.82 (m, 2H), 4.91−4.99 (m, 2H), 5.56−5.72 (m, 1H), 6.50 (s, 1H), 7.29−7.56 (m, 8H), 7.89−7.94 (m, 2H). MS (*m*/*z*): 285 ($M^+ + 1$, 4), 284 (M^+, 8), 142 (100). Anal. Calcd for $C_{17}H_{16}O_2S$: C 71.80, H 5.67. Found: C 71.75, H 5.67.

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Supporting Information Available: Experimental details for the preparation of the starting materials, the procedure of trans-hydrohalogenation of compound **1a** and **5a**, and the oxidation of vinyl sulfoxides; ^1H NMR spectra copies of compounds **3a**−**3d**, **4a**−**4d**, **7a**−**7h**, **8a**−**8b**, **9a**−**9e**,**10a**−**10d**, **11a**−**11b**, **12**; ORTEP drawing of compounds **11b** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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