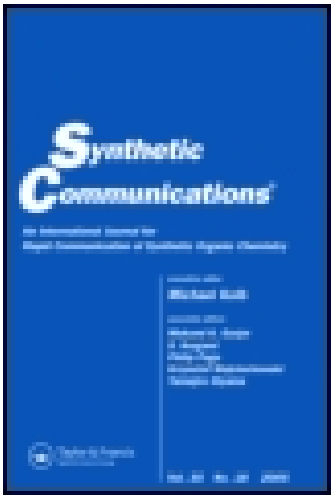

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Highly Regio- and Stereoselective Synthesis of β-Phenyl-chalcogenyl Allyl Sulfones by Hydrochalcogenation Reaction of 1,2-Allenyl Sulfones

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Abstract: The hydrochalcogenation of allenyl sulfones with sodium organyl chalcogenolates can proceed smoothly to give β-phenylchalcogenyl allyl sulfones in high yields with exclusive regioselectivity. For the asymmetric allenyl sulfone, the reaction has both high regio- and stereoselectivity with the predominace of *E*-isomer. Some applications of β-phenyltelluro and β-phenylselanyl allyl sulfone in organic synthesis are also investigated.

Keywords: Allenyl sulfones, allyl sulfones, hydrochalcogenation, regioselectivity, stereoselectivity

Allyl sulfones are important and versatile intermediates in organic synthesis, especially in the synthesis of various functionlized compounds[1] and natural products.[2] β-Functionalized allyl sulfones[3] are another class of compounds

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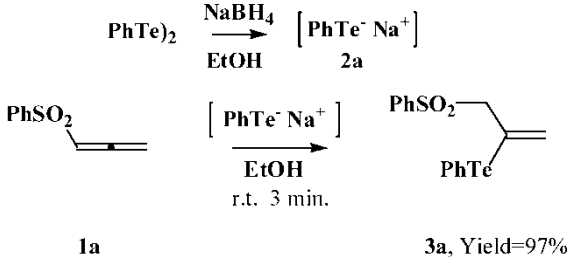
that has received great attention. Consequently, a general and convenient procedure preparing for such compounds would be useful.

β-Organolchalcogenyl substituted allyl sulfones are interesting structures because they are a composite of an allyl sulfone and vinylic chalcogenide subunit. Vinylic chacogenides and their synthetic application have attracted remarkable interest during the past decades.[4] These compounds have a pronounced ambident characters and are intermediates of great synthetic potential. Our group[5] and others [6–8] have found that electron-deficient carbon–carbon triple bond can undergo hydrochalcogenation reaction regio- and stereoselectively, affording an efficient method for the synthesis of functionalized vinylic chalcogenides. Another class of compounds attracting our interest is electron-deficient 1,2-dienes, which have unique reactivities due to the presence of cumulated carbon–carbon double bond.[9,10] Usually, one of them can be selectively reacted to give vinylic products via delicate the tuning of the steric and electronic factors. Accordingly, hydrochalcogenation of electron-deficient allenes would be one of the most efficient and convenient ways to prepare β-organolchalcogenyl substituted allyl compounds. As an extension of the studies on this area,[11] herein we describe the regio-and stereoselectively hydrochalogenation reaction of allenyl sulfones.

Initially, the reaction of 1,2-allenyl sulfones **1a** with sodium phenyltellurolates **2a**, prepared by reduction of diphenylditelluride with sodium borohydride at room temperature, was examined as shown in Scheme 1. Thus, to an ethanol solution of sodium phenyltellurolates **2a** was added the 1,2-allenyl sulfones **1a**. Fortunately, the β-phenyltelluro allyl sulfone **3a** was formed in high yields with perfect regioselectivity.

Encouraged by the good results, we synthesized a series of allenyl sulfones[12] to investigate the hydrochalcogenation reaction. As shown in Table 1, the substrates can be mono- (entry 1), di- (entry 2), and trisubstituted (entries 3,4) allenyl sulfones (Scheme 2). Having established reaction conditions, various substituted allenyl sulfones were subjected to synthesize β-phenylselanyl allyl sulfones (entries 5–8).



Scheme 1.

Table 1. Preparation of β-phenylchalcogenyl allyl sulfones

Entry	R^1	R^2	R^3	PhY	Yields (%)[a]	Products
1	H	H	H	C_6H_5Te	97	**3a**
2	H	H	Ph	C_6H_5Te	91	**3b**
3	-$(CH_2)_5$-		H	C_6H_5Te	89	**3c**
4	CH_3	CH_3	H	C_6H_5Te	94	**3d**
5	H	H	H	C_6H_5Se	91	**3e**
6	H	H	Ph	C_6H_5Se	87	**3f**
7	-$(CH_2)_5$-		H	C_6H_5Se	90	**3g**
8	CH_3	CH_3	H	C_6H_5Se	92	**3h**

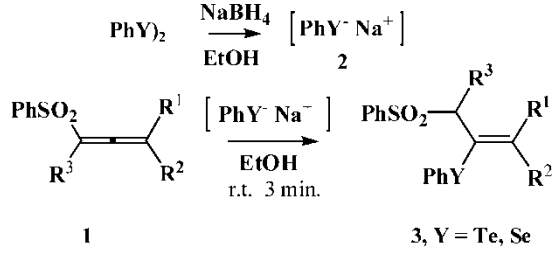
[a]Isolated yields based on the allenyl sulfones.

From the results in Table 1, we were pleased to find that these reactions have exclusively regioselectivity, and only one regioisomer (**3a**–**h**) was obtained. For the mono-, di-, or trisubstrituted allenyl sulfones, yields to give the β-phenylselanyl (products **3a**–**h**) allyl sulfones were very high.

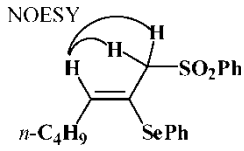
The mechanism for the current regioselective hydrochalogenation reaction is a nucleophilic conjugate addition of RY^- to allenyl sulfones at the β-position to afford an allyl carbanion stabilized by the sulfone group.

Interestingly, when $R^1 \neq R^2$, the stereoselectivity of this reaction is due to the steric facts. The two isomers can be separated carefully by chromatography on silica gel; the (*E*) isomers are predominant. The configuration of the carbon–carbon double bond was determined by 2D H^1-H^1 NOESY experiment of **3l** which is *Z*-isomer (Scheme 3).

As shown in Table 2, when $R^1 \neq R^2$, the mixture of *E*- or *Z*-β-phenylselanyl allyl sulfones was obtained. For the steric reason, the *E*-isomers are major products. The PhSe group is opposite to the bulky group on the double bond. The nucleophilic conjugate addition of RY^- to allenyl sulfones to give the thermodynamically more stable product (higher *E*-selectivity). As the size of the subtituent increases relatively, so does steric hindrance to attack, and the more *E*-isomer was correspondingly obtained.



Scheme 2.



Scheme 3.

β-Phenylchalcogenyl allyl sulfones **3** are useful intermediates and have many transformations in organic chemistry. We found that under the catalysis of $PdCl_2$/CuI, compound **3a** could react with alkyne to give the β-allynyl sulfones **4a** and **4b** in good yields (Scheme 4). Moreover compound **3e** reacted with RMgBr to produce the β-alkyl allyl sulfone **5** in moderate yields under the catalysis of $NiCl_2(PPh_3)_2$ (Scheme 5). Compounds **3** can also undergo many important transformations in organic synthesis, such as 1,3-rearrangement,[13] 1,3-dipolar cycloaddition,[14] and radical allylation.[15]

In conclusion, we have developed a highly efficient regioselective and the nicer stereoselective hydrohalcogenation of allenyl sulfones to afford synthetically important β-phenylchalcogenyl allyl sulfones. The generality of this methodology was illustrated using different allenyl sulfones. Preliminary application studies have demonstrated the utility of β-phenyltelluro allyl sulfone **3a** and β-phenylselanyl allyl sulfone **3e** as precursors for certain potentially useful compounds.

EXPERIMENTAL

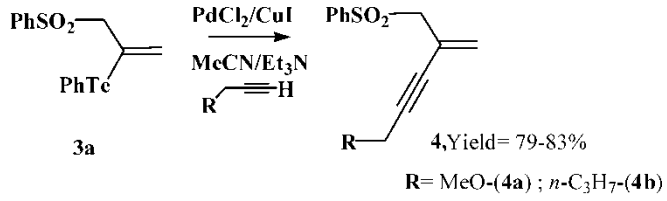
General

^{1}H NMR spectra were recorded on Bruker Avance-400 (400 MHz) spectrometer in $CDCl_3$ using TMS as the internal standard (chemical shifts in parts per million, ppm, and *J* values in Hertz, Hz). IR spectra were run on a Bruker vector 22 spectrometer. EIMS were determined with a HP5989B

Table 2. Preparation of *E* (or*Z*)-β-phenylselanyl allyl sulfones

Entry	R^1	R^2	R^3	PhY	Yields (%)[a]	Products
9	*p*-ClC_6H_4	H	H	C_6H_5Se	89	**3i**(E); **3j**(Z) ($E/Z = 86/14$)
10	*n*-C_4H_9	H	H	C_6H_5Se	85	**3k**(E); **3l**(Z) ($E/Z = 80/20$)
11	*p*-ClC_6H_4	CH_3	H	C_6H_5Se	86	**3m**(E); **3n**(Z) ($E/Z = 61/39$)

[a]Isolated yields based on the allenyl sulfones.



Scheme 4.

mass spectrometer. Elemental analyses were performed on an EA-1110 instrument.

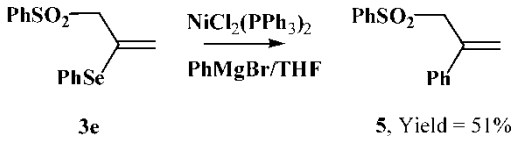
General Procedure for the Synthesis of 3a–h

To a solution of RYNa, prepared in situ by reduction of $(RY)_2$ (0.3 mmol) with sodium borohydride (0.7 mmol) in 2 mL of ethanol at room temperature under nitrogen, allenyl sulfones (0.5 mmol) in 2 mL of EtOH were added dropwise. After the reaction completed (3 min), the reaction was diluted with saturated brine (10 mL) and extracted with ethyl acetate (3 × 20 mL). The organic layer was dried over anhydrous $MgSO_4$. After filtration and removal of the solvent in vacuo, the residue was purified via chromatography on silica gel with n-hexane/ethyl acetate (6:1) as the eluent to give the product **3**.

Data

3a: Oil, ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.89$ (d, $J = 9.44$ Hz, 2H), 7.74 (m, 2H), 7.65 (t, 1H), 7.55 (t, 2H), 7.35 (t, 1H), 7.24 (t, 2H), 6.04 (s, 1H), 5.60 (s, 1H), 4.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 139.7$, 137.9, 133.8, 133.2, 129.5, 128.9, 128.7, 128.5, 113.9, 112.6, 67.1; IR ν_{max} (neat): 3062, 1317, 1137, 743 cm^{-1}; MS (EI, 70 eV): m/z (%) = 57 (100), 386 (1) [M$^+$]. Anal. calcd. for $C_{15}H_{14}O_2STe$: C, 46.68; H, 3.66; found: C, 46.61; H, 3.72.

3b: Solid, mp 134–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.63$ (d, $J = 7.80$ Hz, 2H), 7.59 (m, 3H), 7.37 (m, 4H), 7.14 (m, 6H), 7.03



Scheme 5.

(s, 1H), 6.04 (s, 1H), 4.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 139.6$, 138.2, 133.4, 131.1, 130.6, 130.3, 129.5, 128.9, 128.8, 128.6, 128.5, 128.3, 118.3, 113.7, 78.1; IR ν_{max} (neat): 3061, 1314, 1146, 787 cm^{-1}; MS (EI, 70 eV): m/z (%) = 115 (100), 462 (5) [M$^+$]. Anal. calcd. for $C_{21}H_{18}O_2STe$: C, 54.59; H, 3.93; found: C, 54.64; H, 3.98.

3c: Oil, ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.84$ (m, 3H), 7.60 (m, 2H), 7.52 (m, 5H), 4.50 (s, 2H), 2.45 (m, 2H), 2.23 (m, 2H), 1.44 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 159.4$, 138.7, 136.7, 133.4, 128.9, 128.8, 128.7, 127.1, 126.9, 115.4, 95.3, 63.9, 41.7, 26.1, 25.6, 23.7; IR ν_{max} (neat): 2930, 1306, 1142, 731 cm^{-1}; MS (EI, 70 eV): m/z (%) = 101 (100), 454 (17) [M$^+$]. Anal. calcd. for $C_{20}H_{22}O_2STe$: C, 52.90; H, 4.88; found: C, 52.84; H, 4.97.

3d: Solid, mp 70–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.81$ (m, 2H), 7.57 (m, 5H), 7.24 (m, 1H), 7.19 (m, 2H), 4.40 (s, 2H), 2.01 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 152.4$, 139.1, 137.4, 133.7, 129.4, 129.0, 128.7, 127.6, 115.2, 98.1, 64.7, 31.3, 20.6; IR ν_{max} (neat): 3060, 1306, 1138, 740 cm^{-1}; MS (EI, 70 eV): m/z (%) = 77 (100), 414 (13) [M$^+$]. Anal. calcd. for $C_{17}H_{18}O_2STe$: C, 49.32; H, 4.38; found: C, 49.44; H, 4.37.

3e: Oil, ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.88$ (m, 2H), 7.60 (m, 3H), 7.40 (m, 2H), 7.30 (m, 3H), 5.71 (s, 1H), 5.40 (s, 1H), 3.99 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.1$, 134.9, 133.9, 129.5, 129.1, 129.0, 128.8, 128.7, 128.6, 125.5, 63.5; IR ν_{max} (neat): 3059, 1318, 1146, 688 cm^{-1}; MS (EI, 70 eV): m/z (%) = 77 (100), 338 (15) [M$^+$]. Anal. calcd. for $C_{15}H_{14}O_2SSe$: C, 53.41; H, 4.18; found: C, 53.48; H, 4.12.

3f: Solid, mp 151–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.56$ (m, 3H), 7.38 (m, 2H), 7.32 (m, 4H), 7.23 (m, 6H), 6.70 (s, 1H), 5.82 (s, 1H), 4.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.0$, 134.5, 133.4, 132.7, 130.5, 130.1, 129.4, 128.9, 128.9, 128.6, 128.3, 128.2, 128.1, 124.0, 75.2; IR ν_{max} (neat): 3060, 1318, 1147, 754 cm^{-1}; MS (EI, 70 eV): m/z (%) = 84 (100), 414 (3) [M$^+$]. Anal. calcd. for $C_{21}H_{18}O_2SSe$: C, 61.01; H, 4.39; found: C, 61.09; H, 4.33.

3g: Oil, ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.83$ (m, 3H), 7.60 (m, 1H), 7.49 (m, 3H), 7.17 (m, 3H), 4.23 (s, 2H), 3.53 (m, 2H), 2.26 (m, 2H), 1.50 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 157.9$, 139.1, 133.6, 130.9, 129.1, 128.9, 128.6, 127.2, 126.5, 108.4, 61.5, 36.3, 32.1, 27.8, 27.6, 25.9; IR ν_{max} (neat): 2930, 1131, 1142, 737 cm^{-1}; MS (EI, 70 eV): m/z (%) = 107 (100), 406 (10) [M$^+$]. Anal. calcd. for $C_{20}H_{22}O_2SSe$: C, 59.25; H, 5.47; found: C, 59.33; H, 5.50.

3h: Solid, mp 88–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.80$ (d, $J = 7.84$ Hz, 2H), 7.61 (m, 1H), 7.50 (m, 2H), 7.18 (m, 5H), 4.18

(s, 2H), 2.02 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 150.3$, 139.2, 133.7, 131.3, 130.8, 129.2, 129.0, 128.6, 126.8, 111.4, 62.0, 26.4, 21.8; IR ν_{max} (neat): 2914, 1307, 1139, 743 cm^{-1}; MS (EI, 70 eV): m/z (%) = 183 (100), 366 (18) [M$^+$]. Anal. calcd. for $C_{17}H_{18}O_2SSe$: C, 55.89; H, 4.97; found: C, 55.94; H, 5.01.

3i: Solid, mp 76–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.83$ (d, $J = 9.32$ Hz, 2H), 7.63 (t, 1H), 7.49 (t, 2H), 7.44 (m, 2H), 7.26 (m, 5H), 7.08 (d, $J = 8.36$ Hz, 2H), 6.99 (s, 1H), 4.26 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 139.8$, 139.1, 134.4, 133.9, 133.8, 133.7, 129.4, 129.3, 129.2, 129.0, 128.6, 128.4, 128.3, 122.8, 59.7; IR ν_{max} (neat): 3061, 1316, 1140, 742 cm^{-1}; MS (EI, 70 eV): m/z (%) = 115 (100), 448 (14) [M$^+$]. Anal. calcd. for $C_{21}H_{17}ClO_2SSe$: C, 56.32; H, 3.83; found: C, 56.24; H, 3.91.

3j: Solid, mp 107–109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.83$ (d, $J = 8.40$ Hz, 2H), 7.67 (t, 1H), 7.55 (t, 2H), 7.30 (m, 9H), 6.97 (s, 1H), 3.97 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 140.3$, 138.7, 134.5, 133.7, 133.6, 133.4, 130.1, 129.4, 129.3, 129.0, 128.7, 128.5, 128.4, 121.9, 55.7; IR ν_{max} (neat): 3060, 1314, 1138, 744 cm^{-1}; MS (EI, 70 eV): m/z (%) = 115 (100), 448 (19) [M$^+$]. Anal. calcd. for $C_{21}H_{17}ClO_2SSe$: C, 56.32; H, 3.83; found: C, 56.27; H, 3.93.

3k: Solid, mp 67–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.87$ (d, $J = 7.40$ Hz, 2H), 7.66 (t, 1H), 7.54 (t, 2H), 7.31 (m, 2H), 7.25 (m, 3H), 6.28 (t, 1H), 4.08 (s, 2H), 1.99 (m, 2H), 1.27 (m, 4H), 0.91 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 147.7$, 138.9, 133.8, 132.8, 129.7, 129.2, 129.0, 128.7, 127.5, 116.5, 59.6, 30.7, 30.1, 22.2, 13.8; IR ν_{max} (neat): 2955, 1309, 1148, 746 cm^{-1}; MS (EI, 70 eV): m/z (%) = 252 (100), 394 (11) [M$^+$]. Anal. calcd. for $C_{19}H_{22}O_2SSe$: C, 58.01; H, 5.64; found: C, 58.11; H, 5.56.

3l: Solid, mp 73–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.87$ (d, $J = 7.41$ Hz, 2H), 7.65 (t, 1H), 7.53 (t, 2H), 7.27 (m, 5H), 6.07 (t, 1H), 3.93 (s, 2H), 2.27 (m, 2H), 1.30 (m, 4H), 0.89 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 146.1$, 138.5, 133.7, 132.8, 129.3, 129.1, 128.9, 128.8, 127.5, 118.4, 64.0, 32.2, 30.8, 22.2, 13.8; IR ν_{max} (neat): 2961, 1307, 1141, 741 cm^{-1}; MS (EI, 70 eV): m/z (%) = 95 (100), 394 (11) [M$^+$]. Anal. calcd. for $C_{19}H_{22}O_2SSe$: C, 58.01; H, 5.64; found: C, 58.07; H, 5.49.

3m: Solid, mp 96–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.68$ (d, $J = 7.32$ Hz, 2H), 7.63 (t, 1H), 7.47 (t, 2H), 7.35 (m, 2H), 7.26 (m, 5H), 6.94 (d, $J = 8.40$ Hz, 2H), 4.10 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.5$, 139.8, 139.6, 133.5, 133.4, 132.0, 130.3, 129.4, 129.0, 128.9, 128.7, 128.5, 127.3, 116.6, 62.0, 27.1; IR ν_{max} (neat): 3060, 2920, 1312, 1141, 739 cm^{-1}; MS (EI, 70 eV): m/z (%) = 129 (100), 462 (29) [M$^+$]. Anal. calcd. for $C_{22}H_{19}ClO_2SSe$: C, 57.21; H, 4.15; found: C, 57.29; H, 4.08.

3n: Solid, mp 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.91$ (d, $J = 6.80$ Hz, 2H), 7.67 (t, 1H), 7.60 (t, 2H), 7.24 (m, 7H), 7.02 (d, $J = 8.41$ Hz, 2H), 4.18 (s, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 149.2$, 142.6, 139.6, 134.2, 134.0, 133.8, 130.0, 129.6, 129.4, 129.1, 129.0, 128.8, 128.1, 116.6, 60.6, 23.5; IR ν_{max} (neat): 3061, 2923, 1315, 1141, 738 cm^{-1}; MS (EI, 70 eV): m/z (1%) = 321 (100), 462 (33) [M^+]. Anal. calcd. for $C_{22}H_{19}ClO_2SSe$: C, 57.21; H, 4.15; found: C, 57.17; H, 4.12.

Preparation of β-Alkynyl Allyl Sulfone 4

The mixture of **3a** (0.386 g, 1 mmol), terminal acetylene (2.0 mmol), $PdCl_2$ (10 mol%), CuI (10 mol%), and Et_3N (1.0 mmol) in 2 mL of MeCN was stirred at room temperature for about 24 h under N_2. After the reaction completed, the reaction was diluted with saturated brine (10 mL) and extracted with ethyl acetate (3 × 15 mL). The organic layer was dried over anhydrous $MgSO_4$. After filtration and removal of the solvent in vacuo, the residue was purified via chromatography on silica gel with n-hexane/ethyl acetate (3:1) as the eluent to give the products.

Data

4a: Oil, ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.93$ (m, 2H), 7.57 (m, 3H), 5.66 (s, 1H), 5.44 (s, 1H), 4.00 (s, 2H), 3.89 (s, 2H), 3.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 138.1$, 133.7, 130.3, 128.8, 128.7, 118.7, 86.5, 84.4, 62.7, 59.7, 57.4; IR ν_{max} (neat): 2929, 2361, 1733, 1313, 1150 cm^{-1}; MS (EI, 70 eV): m/z (%) = 77 (100), 125 (83), 250 (3) [M^+]. Anal. calcd. for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. found: C, 62.45, H, 5.57.

4b: Oil, ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.92$ (t, 2H), 7.64 (m, 1H), 7.54 (t, 2H), 5.52 (s, 1H), 5.35 (s, 1H), 3.87 (s, 2H), 2.07 (t, 2H), 1.32 (m, 4H), 0.89 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 138.3$, 133.6, 128.7, 128.6, 128.2, 119.7, 92.2, 78.9, 63.2, 30.2, 21.7, 18.6, 13.4; IR ν_{max} (neat): 3004, 2343, 1729, 1161 cm^{-1}; MS (EI, 70 eV): m/z (%) = 77 (100), 109 (47), 262 (2) [M^+]. Anal. calcd. for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92. found: C, 68.73, H, 6.85.

Preparation of β-Aryl Allyl Sulfone 5

Grignard reagent (5 mmol) in 10 ml of THF was added dropwise to a mixture of **3e** (0.338 g, 1 mmol) and $NiCl_2(PPh_3)_2$ (0.020 mg, 3 mol%) in 5 mL of dry THF, and the mixture was stirred at room temperature for about 27 h under N_2. After the reaction completed, it was followed by protolysis with saturated

aqueous NH_4Cl (5 mL) and then extracted with diethyl ether (3 × 15 mL). The organic layer was dried over anhydrous $MgSO_4$. After filtration and removal of the solvent in vacuo, the residue was purified via chromatography on silica gel with n-hexane/ethyl acetate (7:1) as the eluent to give the products.

Data

5: Oil, ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.92$ (m, 2H), 7.68 (t, 1H), 7.58 (t, 2H), 7.32 (m, 3H), 7.26 (m, 2H), 5.42 (s, 1H), 5.19 (s, 1H), 3.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.2$, 133.9, 133.4, 133.2, 131.3, 129.4, 129.1, 128.9, 128.6, 121.3, 61.9; MS (EI, 70 eV): m/z (%) = 77 (100), 258 (22) [M^+]. Anal. calcd. for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46. found: C, 69.68, H, 5.55

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