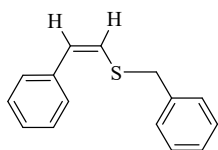


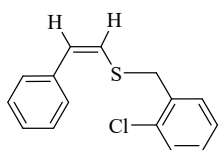
**CuI-catalyzed regioselective hydrothiolation of alkynes: A thiol-free  
route to (*Z*)- $\beta$ -alkenyl sulfides**

### (Z)-Benzyl(styryl)sulfane (4a)



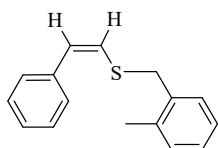
Isolated as light-yellow oil in 95% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.37-7.17 (m, 10H), 6.34 (d,  $J=10.8$  Hz, 1H), 6.18 (d,  $J=10.8$  Hz, 1H), 3.92 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  138.1, 137.4, 136.9, 129.0, 128.5, 128.2, 127.4, 127.0, 126.7, 126.0, 39.5. Anal. Calcd for  $\text{C}_{15}\text{H}_{14}\text{S}$ : C, 79.60; H, 6.23; S, 14.16. Found: C, 79.54; H, 6.25; S, 14.21.

### (Z)-(2-Chlorobenzyl)(styryl)sulfane (4b)



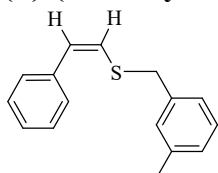
Isolated as light-yellow oil in 88% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.51-7.38 (m, 6H), 7.30-7.24 (m, 3H), 6.50 (d,  $J=10.8$  Hz, 1H), 6.36 (d,  $J=10.8$  Hz, 1H), 4.17 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  136.8, 135.4, 134.2, 130.9, 129.9, 128.9, 128.7, 128.3, 127.1, 126.8, 126.1, 125.9, 37.3. Anal. Calcd for  $\text{C}_{15}\text{H}_{13}\text{ClS}$ : C, 69.09; H, 5.02; Cl, 13.59; S, 12.29. Found: C, 69.19; H, 5.09; S, 12.17.

### (Z)-(2-Methylbenzyl)(styryl)sulfane (4c)



Isolated as light-yellow oil in 92% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.54 (d,  $J=7.6$  Hz, 2H), 7.46-7.38 (m, 3H), 7.32-7.30 (m, 4H), 6.54 (d,  $J=10.8$  Hz, 1H), 6.40 (d,  $J=10.8$  Hz, 1H), 4.10 (s, 2H), 2.53 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  136.9, 135.0, 130.8, 130.0, 128.7, 128.3, 127.9, 127.3, 126.8, 126.2, 126.1, 125.7, 37.9, 19.4. Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{S}$ : C, 79.95; H, 6.71; S, 13.34. Found: C, 79.83; H, 6.88; S, 13.29.

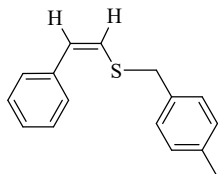
### (Z)-(3-Methylbenzyl)(styryl)sulfane (4d)



Isolated as light-yellow oil in 90% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.53 (d,  $J=8.0$  Hz, 2H), 7.41 (t,  $J=8.0$  Hz, 2H), 7.29-7.25 (m, 4H), 7.15 (d,  $J=8.0$  Hz, 1H), 6.49 (d,  $J=10.8$  Hz, 1H), 6.33 (d,  $J=10.8$  Hz, 1H), 4.02 (s, 2H), 2.42 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  138.5,

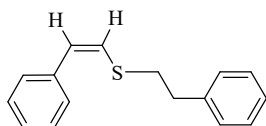
137.3, 136.9, 129.8, 128.7, 128.6, 128.3, 126.7, 126.2, 126.1, 125.9, 125.7, 37.5, 21.5. Anal. Calcd for C<sub>16</sub>H<sub>16</sub>S: C, 79.95; H, 6.71; S, 13.34. Found: C, 80.07; H, 6.64; S, 13.29.

**(Z)-(4-Methylbenzyl)(styryl)sulfane (4e)**



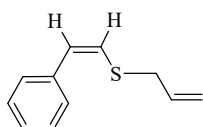
Isolated as light-yellow oil in 95% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.33-7.20 (m, 5H), 6.47 (d, *J* = 10.8 Hz, 1H), 6.32 (d, *J* = 10.8 Hz, 1H), 4.02 (s, 2H), 2.40 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 137.1, 136.9, 134.3, 129.4, 128.9, 128.6, 128.2, 126.7, 126.1, 125.7, 39.4, 21.1. Anal. Calcd for C<sub>16</sub>H<sub>16</sub>S: C, 79.95; H, 6.71; S, 13.34. Found: C, 79.94; H, 6.57; S, 13.49.

**(Z)-Phenethyl(styryl)sulfane (4g)**



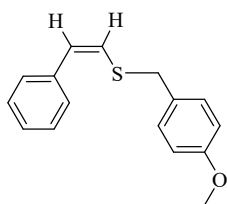
Isolated as a light-yellow oil in 95% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.61-7.58 (m, 2H), 7.48-7.38 (m, 5H), 7.34-7.30 (m, 3H), 6.57 (d, *J* = 10.8 Hz, 1H), 6.35 (d, *J* = 10.8 Hz, 1H), 3.14-3.07 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz) δ 140.1, 137.2, 128.99, 128.95, 128.91, 128.58, 127.3, 127.0, 126.8, 126.2, 37.4, 37.1. Anal. Calcd for C<sub>16</sub>H<sub>16</sub>S: C, 79.95; H, 6.71; S, 13.34. Found: C, 79.80; H, 6.69; S, 13.51.

**(Z)-Allyl(styryl)sulfane (4i)**



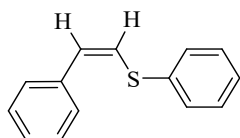
Isolated as a light-yellow oil in 85% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.30-7.24 (m, 1H), 6.53 (d, *J* = 10.8 Hz, 1H), 6.26 (d, *J* = 10.8 Hz, 1H), 5.97-5.87 (m, 1H), 5.28 (d, *J* = 16.8 Hz, 1H), 5.23 (d, *J* = 10.0 Hz, 1H), 3.44 (d, *J* = 6.8 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 136.9, 133.9, 128.6, 128.3, 126.7, 125.9, 125.7, 118.1, 38.0. Anal. Calcd for C<sub>11</sub>H<sub>12</sub>S: C, 74.95; H, 6.86; S, 18.19. Found: C, 74.85; H, 6.80; S, 18.35.

### (Z)-(4-Methoxybenzyl)(styryl)sulfane (4k)



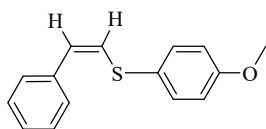
Isolated as yellow solid in 88% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.38-7.36 (m, 2H), 7.28 (t,  $J = 8.0$  Hz, 2H), 7.20-7.16 (m, 1H), 7.11-7.09 (m, 2H), 6.82 (d,  $J = 8.0$  Hz, 2H), 6.57 (d,  $J = 10.8$  Hz, 1H), 6.44 (d,  $J = 10.8$  Hz, 1H), 3.97 (s, 2H), 3.75 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  162.7, 137.3, 131.0, 130.6, 130.0, 128.6, 128.3, 127.4, 125.9, 116.8, 56.5, 37.7. Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{OS}$ : C, 74.96; H, 6.29; S, 12.51. Found: C, 74.83; H, 6.34; S, 12.69.

### Z-Phenyl(styryl)sulfane (6a)



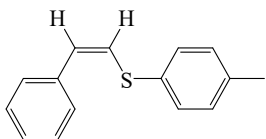
Isolated as a light-yellow oil in 95% yield,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.62-7.60 (m, 2H), 7.55-7.53 (m, 2H), 7.49-7.40 (m, 5H), 7.36-7.35 (m, 1H), 6.67 (d,  $J = 10.8$  Hz, 1H), 6.57 (d,  $J = 10.8$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  136.5, 135.4, 132.3, 130.1, 129.9, 129.2, 128.8, 128.4, 127.2, 126.1. Anal. Calcd for  $\text{C}_{14}\text{H}_{12}\text{S}$ : C, 79.20; H, 5.70; S, 15.10. Found: C, 79.25; H, 5.83; S, 14.92.

### (Z)-(4-Methoxyphenyl)(styryl)sulfane (6b)



Isolated as a white solid in 96% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.56 (d,  $J = 7.2$  Hz, 2H), 7.47-7.41 (m, 4H), 7.31-7.28 (m, 1H), 6.93 (d,  $J = 9.2$  Hz, 2H), 6.52 (d,  $J = 10.8$  Hz, 1H), 6.44 (d,  $J = 10.8$  Hz, 1H), 3.85 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  159.5, 136.6, 133.0, 128.7, 128.4, 128.3, 127.0, 125.7, 114.9, 114.8, 55.4. Anal. Calcd for  $\text{C}_{15}\text{H}_{14}\text{OS}$ : C, 74.35; H, 5.82; S, 13.23. Found: C, 74.51; H, 5.92; S, 13.11.

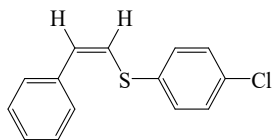
### (Z)-Styryl(*p*-tolyl)sulfane (6c)



Isolated as light-yellow oil in 95% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.46-7.43 (m, 2H), 7.35-7.28 (m, 5H), 7.27-7.25 (m, 2H), 6.47 (d,  $J = 10.8$  Hz, 1H), 6.39 (d,  $J = 10.8$  Hz, 1H),

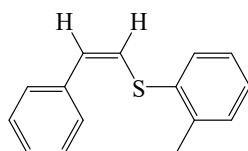
2.25 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  137.3, 136.6, 131.0, 130.0, 128.6, 128.3, 127.4, 126.4, 125.9, 124.4, 21.1. Anal. Calcd for  $\text{C}_{15}\text{H}_{14}\text{S}$ : C, 79.60; H, 6.23; S, 14.16. Found: C, 79.58; H, 6.13; S, 14.29.

**(Z)-(4-Chlorophenyl)(styryl)sulfane (6d)**



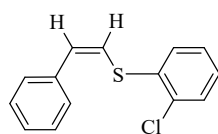
Isolated as light-yellow oil in 93% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.56-7.54 (m, 2H), 7.52-7.48 (m, 2H), 7.45-7.41 (m, 2H), 7.38-7.33 (m, 2H), 7.32-7.29 (m, 1H), 6.68 (d,  $J = 10.8$  Hz, 1H), 6.46 (d,  $J = 10.8$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  136.4, 135.7, 132.5, 131.7, 129.0, 128.6, 128.4, 127.6, 125.1, 121.4. Anal. Calcd for  $\text{C}_{14}\text{H}_{11}\text{ClS}$ : C, 68.15; H, 4.49; S, 12.99. Found: C, 68.21; H, 4.47; Cl, S, 13.13.

**(Z)-Styryl(o-tolyl)sulfane (6e)**



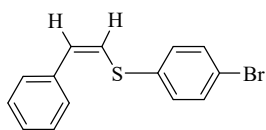
Isolated as light-yellow oil in 90% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.50 (d,  $J = 7.2$  Hz, 2H), 7.39-7.37 (m, 1H), 7.34-7.30 (m, 2H), 7.24-7.11 (m, 4H), 6.51 (d,  $J = 10.8$  Hz, 1H), 6.30 (d,  $J = 10.8$  Hz, 1H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  138.8, 136.6, 135.3, 131.1, 130.4, 128.8, 128.3, 127.6, 127.1, 126.3, 126.0, 123.3, 20.8. Anal. Calcd for  $\text{C}_{15}\text{H}_{14}\text{S}$ : C, 79.60; H, 6.23; S, 14.16. Found: C, 79.74; H, 6.25; S, 14.01.

**(Z)-(2-Chlorophenyl)(styryl)sulfane (6f)**



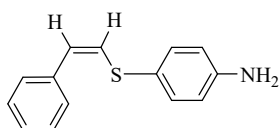
Isolated as light-yellow oil in 92% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.58 (d,  $J = 8.0$  Hz, 2H), 7.47-7.39 (m, 4H), 7.31-7.25 (m, 2H), 7.22-7.18 (m, 1H), 6.75 (d,  $J = 10.8$  Hz, 1H), 6.43 (d,  $J = 10.8$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  136.0, 135.4, 134.0, 132.4, 130.4, 129.88, 129.81, 128.9, 128.4, 127.9, 127.5, 123.4. Anal. Calcd for  $\text{C}_{14}\text{H}_{11}\text{ClS}$ : C, 68.15; H, 4.49; S, 12.99. Found: C, 68.30; H, 4.53; S, 12.85.

**(Z)-(4-Bromophenyl)(styryl)sulfane (6g)**



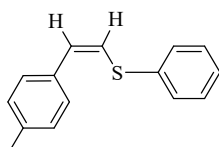
Isolated as light-yellow oil in 94% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.56-7.49 (m, 4H), 7.45-7.40 (m, 2H), 7.39-7.29 (m, 3H), 6.67 (d,  $J = 10.8$  Hz, 1H), 6.46 (d,  $J = 10.8$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  136.2, 135.4, 132.3, 131.5, 131.1, 128.8, 128.4, 127.4, 126.2, 124.9. Anal. Calcd for  $\text{C}_{14}\text{H}_{11}\text{BrS}$ : C, 57.74; H, 3.81; S, 11.01. Found: C, 57.88; H, 3.70; S, 11.16.

**(Z)-4-(Styrylthio)aniline (6h)**



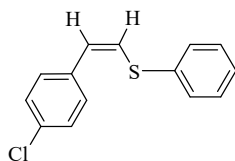
Isolated as a brown solid in 93% yield,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.62 (d,  $J = 8.0$  Hz, 2H), 7.48 (t,  $J = 8.0$  Hz, 2H), 7.39-7.33 (m, 3H), 6.69 (d,  $J = 8.0$  Hz, 2H), 6.51 (q,  $J = 12.0$  Hz, 2H), 3.80 (broad s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  146.8, 136.9, 133.4, 129.7, 128.8, 128.5, 127.0, 125.1, 123.6, 115.8. Anal. Calcd for  $\text{C}_{14}\text{H}_{13}\text{NS}$ : C, 73.97; H, 5.76; N, 6.16; S, 14.10. Found: C, 73.90; H, 5.60; N, 6.26; S, 14.24.

**(Z)-(4-methylstyryl)(phenyl)sulfane (6i)**



Isolated as light-yellow oil in 90% yield,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.66-7.63 (m, 2H), 7.54-7.43 (m, 3H), 7.39-7.24 (m, 4H), 6.65 (d,  $J = 10.8$  Hz, 1H), 6.43 (d,  $J = 10.8$  Hz, 1H), 2.52 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  137.6, 135.6, 133.8, 132.4, 129.5, 129.4, 129.1, 126.8, 126.0, 121.8, 21.2. Anal. Calcd for  $\text{C}_{15}\text{H}_{14}\text{S}$ : C, 79.60; H, 6.23; S, 14.16. Found: C, 79.55; H, 6.15; S, 14.30.

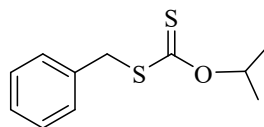
**(Z)-(4-chlorostyryl)(phenyl)sulfane (6j)**



Isolated as a cream solid in 88% yield,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.59-7.52 (m, 1H), 7.50-7.46 (m, 2H), 7.42-7.38 (m, 3H), 7.35-7.30 (m, 3H), 6.69 (d,  $J = 10.8$  Hz, 1H), 6.91 (d,  $J = 10.8$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  135.1, 134.7, 133.1, 130.2, 129.8, 129.3, 128.8,

127.2, 127.1, 124.7. Anal. Calcd for C<sub>14</sub>H<sub>11</sub>ClS: C, 68.15; H, 4.49; S, 12.99. Found: C, 68.31; H, 4.55; S, 12.90.

**S-Benzyl O-isopropyl carbonodithioate (7)**



Isolated as a light-yellow oil in 96% yield, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.28-7.20 (m, 5H), 5.71-5.66 (m, 1H), 4.26 (s, 2H), 1.30 (d, *J* = 6.4 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 213.3, 135.8, 129.1, 128.6, 127.5, 78.1, 40.2, 21.3, 21.1. Anal. Calcd for C<sub>11</sub>H<sub>14</sub>OS<sub>2</sub>: C, 58.37; H, 6.23; S, 28.33. Found: C, 58.25; H, 6.30; S, 28.21.

