Chem. Commun. Supporting Information

$Au(PPh_3)Cl/AgSbF_6$-Catalyzed Rearrangement of Propargylic 1,3-Dithianes: Formation of 8-Membered 1,3-Bisthio-Substituted Cyclic Allenes

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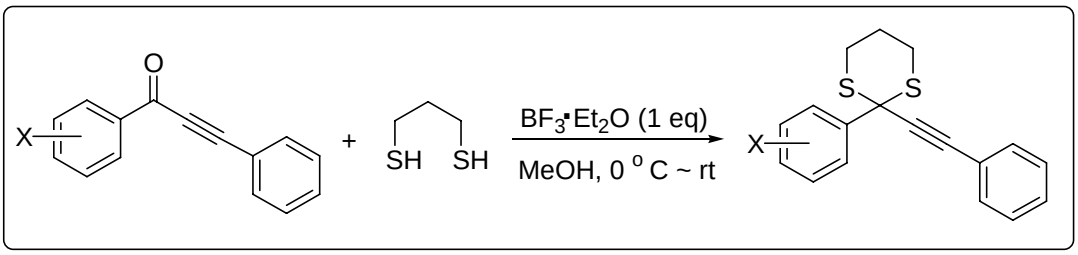
Contents

General All solvents were distilled prior to use. The solvents for reaction were distilled to remove water over Na, CaH_2 or K_2CO_3. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 300 MHz (or 200 MHz) and 75 MHz (or 50 MHz) with Varian Mercury 300 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. Mass spectra were obtained on a VG ZAB-HS mass spectrometer or on a GCT-MS Micromass UK mass spectrometer.



Typical Procedure for preparation of propargylic dithioacetals[1]

Methanolic solution (5 mL) of propargylic ketone (1.0 mmol), 1,3-propanedithiol (1.2 mmol) and $BF_3{\cdot}Et_2O$ (1.2 mmol) was stirred at room temperature for 4 h. The mixture was treated with NaOH (10%) and extracted with Et_2O. The combined organic layers were dried by Na_2SO_4 and evaporated, and the residue was purified by a silica gel column eluted with petroleum ether/EtOAc (300:1) to afford the corresponding propargylic ketones.

There are two ways to prepare the propargylic ketones: Method A and Method B.

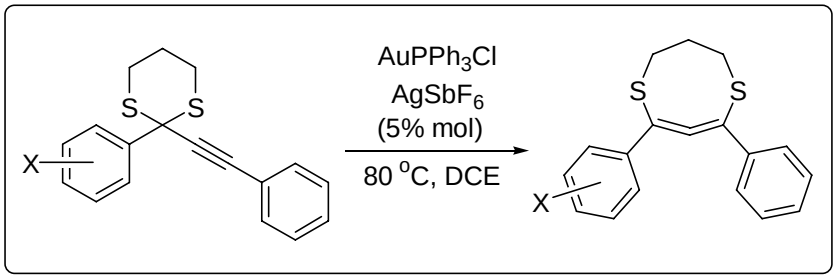
Method A Under a nitrogen atmosphere, benzoyl chloride (15.0 mmol) and phenylacetylene (10.0 mmol) were mixed in THF (25 mL). $PdCl_2(PPh_3)_2$ (0.1 mmol)/CuI (0.3 mmol) were then added. The solution was allowed to stir for 10 min; then, triethylamine (12.5 mmol) in 5 mL of THF was added slowly at 0 ^oC. The mixture was warmed to room temperature and then was stirred for an additional 3 h. The reaction was quenched with saturated NH_4Cl, and most of the organic solvent was removed in vacuum. The mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by a silica gel column eluted

with petroleum ether/EtOAc (100:1) to afford the corresponding propargylic ketones.

Method B. A flame-dried, two-necked flask was charged with dry THF (20 mL) and phenylacetylene (10.0 mmol). The solution was cooled to -78 °C, and *n*-BuLi (10.0 mmol, 2.5 M in hexane) was added slowly. The solution was allowed to stir for 0.5 h at -78 °C; then, aldehyde (10.0 mmol) in 20 mL of THF was added slowly over 20 min. The mixture was stirred for an additional 1 h at -78 °C; then, the dry ice/acetone bath was removed, and the mixture was allowed to warm to room temperature. After about 30 min, it was quenched the system with saturated NH_4Cl, and most of the organic solvent was removed in vacuum. The mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by a silica gel column eluted with petroleum ether/EtOAc (20:1) to afford the corresponding propargylic alcohol.

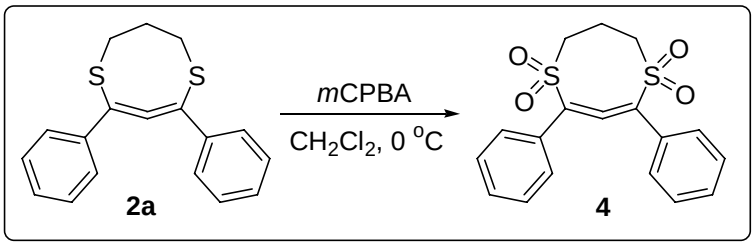
A solution of propargylic alcohol (10.0 mmol) in CH_2Cl_2 (50 mL) was cooled to 0 °C, and Dess-Martin reagent (12.0 mmol) was added by portion. This mixture was stirred at room temperature for 2 h. Then, the solid was removed by filtration. The filtrate was evaporated, and the crude residue was purified by a silica gel column eluted with petroleum ether/EtOAc (100:1) to afford the propargylic ketone (for the synthesis of **1b-d**,**1f-g**).

A solution of propargylic alcohol (10.0 mmol) in CH_2Cl_2 (50 mL) was cooled to 0 °C, and MnO_2 (50.0 mmol) was added by portion. This was kept in the ice bath for another 2 h. Then, the solid was removed by filtration. The filtrate was evaporated, and the crude residue was purified by a silica gel column eluted with petroleum ether/EtOAc (100:1) to afford the propargylic ketone (for the synthesis of **1e**).

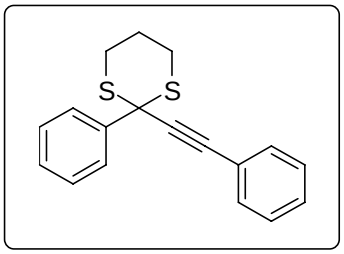


Typical Procedure for the rearrangement reaction. Under a nitrogen atmosphere, $Au(PPh_3)Cl$

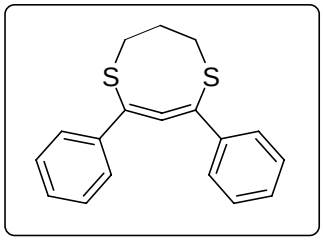
(0.01 mmol) and $AgSbF_6$ (0.01 mmol) were mixed in dry CH_2ClCH_2Cl and stirred at room temperature for 0.5 h; then propargylic dithioacetal (0.2 mmol) in CH_2ClCH_2Cl was added. The mixture was heated to 80 °C in oil bath. The temperature was kept at 80 °C until the reaction was completed as judged by TLC analysis. Removal of the solvent in vacuo gave a crude residue, which was purified by a silica gel column eluted with petroleum ether to afford **2a-g**.



Oxidation of sulfide **2a** with *m*CPBA. Under a nitrogen atmosphere, the cyclic allene (0.2 mmol) and *m*CPBA (0.8 mmol) were mixed in CH_2Cl_2 and stirred at 0 °C for 2 h. Two hours later, saturated $NaHCO_3$ was added, and the mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by a silica gel column eluted with petroleum ether/EtOAc (2:1) to afford **4**.

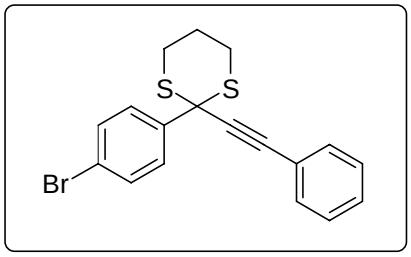


2-Phenyl-2-(phenylethynyl)-1,3-dithiane 1a. Yield 32 %; solid; m.p. 90-92 °C; IR (film) 3059, 2905, 1597, 1490, 1263, 756.1, 726.7, 691.1 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.00-7.98 (m, 2H), 7.60-7.57 (m, 2H), 7.44-7.32 (m, 6H) 3.67-3.57 (m, 2H), 2.97-2.90 (m, 2H), 2.52-1.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.3, 131.8, 128.9, 128.6, 128.4, 127.3, 127.2, 122.5, 90.2, 86.2, 49.9, 30.6, 24.8; EI-MS (*m/z*, relativeintensity): 296 (M+, 31), 222 (100); HRMS Calcd for $C_{18}H_{16}S_2$ [M] 296.0693. Found 296.0695.

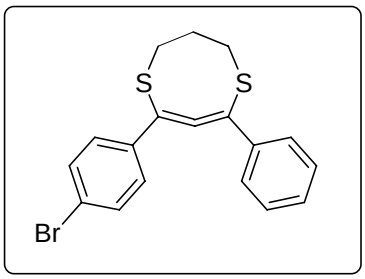


1,3-Diphenyl Dithiocyclic Allene 2a. Yield 82 %; solid; m.p. 167-168 °C; IR (film) 3063, 2969, 2099, 1613, 1439, 1369, 1300, 797.0, 778.3 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.71 (d, J = 6 Hz, 4H), 7.43-7.32 (m, 6H), 3.15-3.05 (m, 2H), 2.81-2.73 (m, 2H),

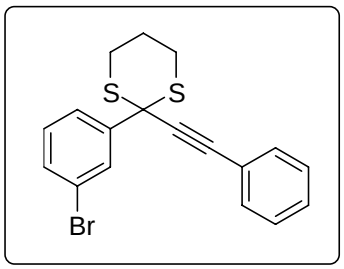
2.29-2.21 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.6, 134.9, 128.7, 128.5, 127.4, 119.5, 37.9, 29.2; EI-MS (*m/z*, relative intensity): 296 (M+, 31), 222 (100); HRMS Calcd for $C_{18}H_{16}S_2$ [M] 296.0693. Found 296.0695.



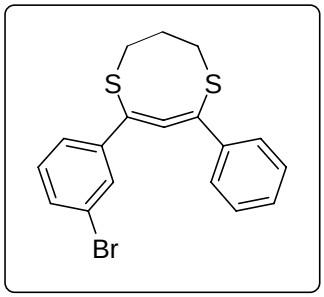
2-(4-Bromophenyl)-2-(phenylethynyl)-1,3-dithiane 1b. Yield 18 %; solid; IR (film) 2923, 2849, 1597, 1484, 1010, 755, 694; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.59-7.24 (m, 7H), 3.64-3.55 (m, 2H), 2.98-2.91 (m, 2H), 2.26-1.91 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.4, 131.8, 131.7, 129.0, 128.8, 128.4, 123.0, 122.2, 90.4, 86.3, 49.4, 30.6, 24.7; EI-MS (*m/z*, relative intensity): 374 (M+, 33), 300 (100); HRMS Calcd for $C_{18}H_{15}S_2{}^{79}Br$ [M] 373.9799. Found 373.9803.



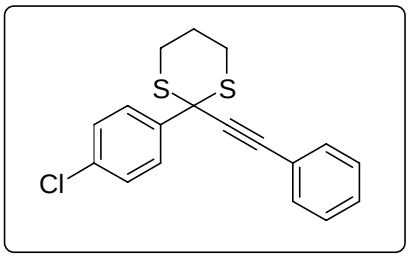
1-(Bromophenyl)-3-phenyl dithiocyclic allene 2b. Yield 60 %; solid; m.p. 138-140 ^{o}C; IR (film) 3053, 2926, 2850, 1870, 1485, 1008, 881, 831, 759, 737, 686; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69-7.65 (m, 2H), 7.57-7.47 (m, 4H), 7.43-7.31 (m, 3H), 3.13-3.00 (m, 2H), 2.80-2.73 (m, 2H), 2.28-2.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.6, 134.6, 133.9, 131.6, 128.9, 128. 8, 128.6, 127.3, 122.6, 120.2, 118.5, 37.8, 29.3, 29.2; EI-MS (*m/z*, relative intensity): 374 (M+, 33), 300 (100); HRMS Calcd for $C_{18}H_{15}S_2{}^{79}Br$ [M] 373.9799. Found 373.9801.



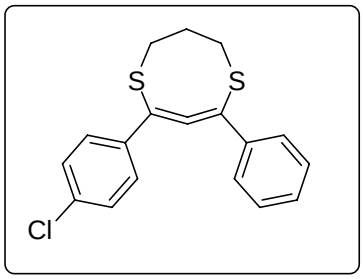
2-(3-Bromophenyl)-2-(phenylethynyl)-1,3-dithiane 1c. Yield 31 %; solid; m.p. 78-80 ^{o}C; IR (film) 3054, 2904, 1589, 1565, 1470, 753; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.13 (t, *J* = 1.8 Hz, 1H), 7.94-7.91 (m, 1H), 7.61-7.56 (m, 2H), 7.51-7.47 (m, 1H), 7.41-7.36 (m, 3H), 7.31-7.27 (m, 1H), 3.65-3.55 (m, 2H), 3.00-2.92 (m, 2H), 2.28-1.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.5, 132.1, 131.8, 130.5, 130.1, 128.8, 128.4, 126.0, 122.6, 122.3, 90.7, 86.1, 49.3, 30.6, 24.7; EI-MS (*m/z*, relative intensity): 374 (M+, 50), 300 (100); HRMS Calcd for $C_{18}H_{15}S_2{}^{79}Br$ [M] 373.9799. Found 373.9797.



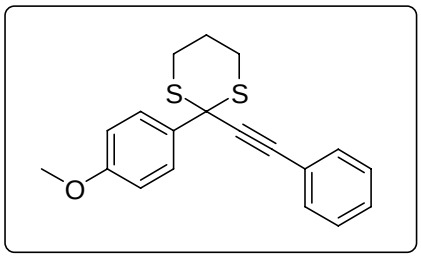
1-(3-Bromophenyl)-3-phenyl dithiocyclic allene 2c. Yield 76 %; solid; m.p. 124-126 ^{o}C; IR (film) 3054, 2917, 2849, 1874, 1413, 1071, 885, 722, 682; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.82 (t, J = 1.8 Hz, 1H), 7.69-7.59 (m, 3H), 7.47-7.22 (m, 5H), 3.13-3.00 (m, 2H), 2.82-2.73 (m, 2H), 2.28-2.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.8, 137.2, 134.5, 131.6, 130.1, 130.0, 129.0, 128.6, 127.4, 125.9, 122.7, 120.4, 118.1, 37.8, 29.2; EI-MS (*m/z*, relative intensity): 374 (M+, 53), 300 (100); HRMS Calcd for $C_{18}H_{15}S_2{}^{79}Br$ [M] 373.9799. Found 373.9801.



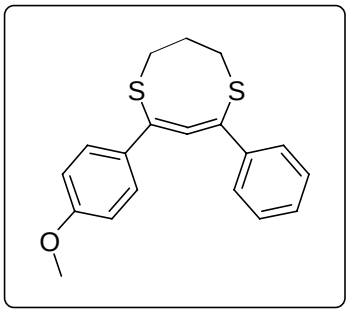
2-(4-Chlorophenyl)-2-(phenylethynyl)-1,3-dithiane 1d. Yield 27 %; solid; IR (film) 2904, 1595, 1487, 1092, 755, 691; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.95-7.90 (m, 2H), 7.59-7,56 (m, 2H), 7.40-7.35 (m, 5H), 3.65-3.55 (m, 2H), 2.99-2.91 (m, 2H), 2.27-1.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.93, 134.7, 131.8, 128.8, 128.5, 128.4, 128.2, 122.3, 90.4, 86.4, 30.6, 24.7; EI-MS (*m/z*, relative intensity): 330 (M+, 32), 256 (100); HRMS Calcd for $C_{18}H_{15}S_2Cl$ [M] 330.0304. Found 330.0300.



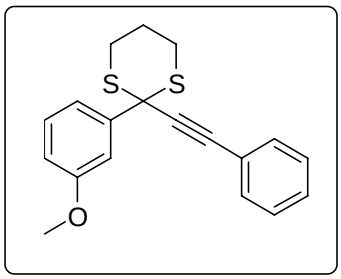
1-(4-Chlorophenyl)-3-phenyl Dithiocyclic Allene 2d. Yield 60 %; solid; m.p. 140-142 ^{o}C; IR (film) 3058, 2916, 1874, 1486, 1084, 1012, 828, 731, 690; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69-7.43 (m, 4H), 7.42-7.31 (m, 5H), 3.13-3.00 (m, 2H), 2.81-2.74 (m, 2H), 2.28-2.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.6, 134.6, 134.4, 133.4, 128.9, 128.7, 128.6, 128.5, 127.3, 120.2, 118.5, 37. 8, 29.3, 29.2; EI-MS (*m/z*, relative intensity): 330 (M+, 34), 256 (100); HRMS Calcd for $C_{18}H_{15}S_2Cl$ [M] 330.0304. Found 330.0302.



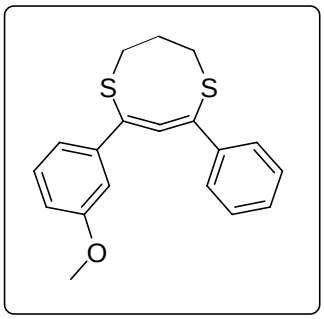
2-(4-Methoxyphenyl)-2-(phenylethynyl)-1,3-dithiane 1e: Yield 21 %; solid; m.p. 98-100 ^{o}C; IR (film) 2908, 1606, 1509, 1255, 1033, 758; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.91 (q, *J* = 1.8 Hz, 2H), 7.60-7.56 (m, 2H), 7.37-7.35 (m, 3H), 6.94-6.91 (m, 2H), 3.78 (s, 3H), 3.65-3.55 (m, 2H), 2.96-2.89 (m, 2H), 2.25-1.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.8, 131.8, 131.4, 128.6, 128.5, 128.3, 122.5, 113.8, 89.8, 87.0, 55.3, 49.2, 30.8, 24.8; EI-MS (*m/z*, relative intensity): 326 (M+, 44), 220 (100); HRMS Calcd for $C_{19}H_{18}OS_2$ [M] 326.0799. Found 326.0794.



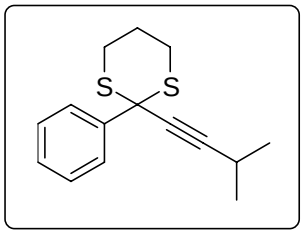
1-(4-Methoxyphenyl)-3-phenyl Dithiocyclic Allene 2e. Yield 90 %; solid; m.p. 106-108 ^{o}C; IR (film) 2958, 2913, 2835, 1873, 1604, 1507, 1251, 1174, 832; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71-7.61 (m, 4H), 7.41-7.32 (m, 4H), 6.94-6.91 (dd, *J* = 2.1, 4.5 Hz, 2H), 3.83 (s, 3H), 3.08-3.03 (m, 2H), 2.78-2.72 (m, 2H), 2.25-2.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 195.9, 160.0, 135.1, 128.6, 128.5, 127.3, 127.2, 119.4, 119.081, 113.9, 55.4, 37.9, 29.2, 29.1; EI-MS (*m/z*, relative intensity): 326 (M+, 71), 220 (100); HRMS Calcd for $C_{19}H_{18}OS_2$ [M] 326.0799. Found 326.0791.



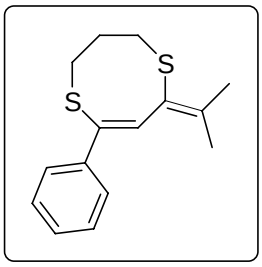
2-(3-Methoxyphenyl)-2-(phenylethynyl)-1,3-dithiane 1f. Yield 26 %; solid; IR (film) 2904, 2826, 1597, 1289, 754; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60-7.56 (m, 4H), 7.38-7.30 (m, 4H), 6.92-6.88 (m, 4H), 3.84 (S, 3H), 3.67-3.57 (m, 2H), 2.97-2.90 (m, 2H), 2.21-2.20 (m, 1H), 2.02-1.96 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.6, 140.7, 131.8, 129.6, 128.6, 128.4, 122.5, 119.5, 114.6, 112.8, 90.2, 86.8, 55.3, 49.9, 30.6, 24.8; EI-MS (*m/z*, relative intensity): 326 (M+, 78), 252 (100); HRMS Calcd for $C_{19}H_{18}OS_2$ [M] 326.0799. Found 326.0791.



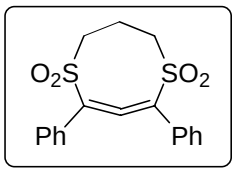
1-(3-Methoxyphenyl)-3-phenyl Dithiocyclic Allene 2f. Yield 64 %; solid; IR (film) 2961, 2901, 2827, 1872, 1595, 1481, 1259, 1047, 780, 764, 703; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71-7.67 (m, 2H), 7.43-7.24 (m, 6H), 6.91-6.87 (m, 1H), 3.83 (s, 3H), 3.15-3.04 (m, 2H), 2.81-2.72 (m, 2H), 2.28-2.21 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 196.6, 159.7, 136.4, 134.8, 129.5, 128.8, 128.6, 127.3, 119.9, 119.4, 114.4, 112.7, 55.3, 37.8, 29.2; EI-MS (*m/z*, relative intensity): 326 (M+, 80), 252 (100); HRMS Calcd for $C_{19}H_{18}OS_2$ [M] 326.0799. Found 326.0796.



2-(3-Methylbut-1-ynyl)-2-phenyl-1,3-dithiane 1g. Yield 46 %; solid; m.p. 32-34 ^{o}C; IR (film) 2966, 2904, 1597, 1490, 906, 755, 690; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.49-7.24 (m, 5H), 3.47-3.36 (m, 2H), 2.88-2.81 (m, 2H), 2.25 (q, *J* = 6.9 Hz, 1H), 2.22-2.10 (m, 1H), 1.91-1.77 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 131.6, 128.2, 122.7, 87.8, 87.5, 52.9, 38.3, 28.7, 25.7, 18.3; EI-MS (*m/z*, relative intensity): 262 (M+, 40), 219 (100); HRMS Calcd for $C_{15}H_{18}S_2$ [M] 262.0850. Found 262.0852.



(***Z***)**-8-Phenyl-6-(propan-2-ylidene)-2,3,4,6-tetrahydro-1,5-dithiocine 2g.** Yield 69%; solid; m.p. 40-42 ^{o}C; IR (film) 2978, 2901, 1589, 1443, 1417, 1260, 1073, 1044, 766, 753, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61-7.58 (m, 2H), 7.38-7.31 (m, 3H), 6.18 (t, *J* = 1.8 Hz, 1H), 3.31 (t, *J* = 5.9 Hz, 2H), 3.08 (t, *J* = 5.9 Hz, 2H), 2.35-2.27 (m, 2H), 1.98 (d, *J* = 1.8 Hz, 3H), 1.88 (d, *J* = 0.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.2, 140.9, 132.0, 128.3, 128.2, 127.5, 124.3, 122.9, 38.0, 28.7, 28.6, 22.6, 21.1; EI-MS (*m/z*, relative intensity): 262 (M+, 100); HRMS Calcd for $C_{15}H_{18}S_2$ [M] 262.0850. Found 262.0848.



1,3-Diphenyl disulfonylcyclic allene 4. Yield 71 %; solid; m.p. 182-184 ^{o}C; IR (film) 3058, 2925, 1935, 1725, 1698, 1316, 1126, 762, 707, 687; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75-7.70 (m, 4H), 7.51-7.46 (m, 6H), 3.76-3.67 (m, 2H), 3.34-3.25 (m, 2H), 2.66-2.62 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 204.6, 131.0, 129.5, 128.8, 125.0, 120.8, 52.8, 52.7, 19.6; EI-MS (*m/z*, relative intensity): 360 (M+, 1.7), 204 (100); HRMS Calcd for $C_{18}H_{16}O_4S_2$ [M] 360.0490. Found 360.0488.

(1) Peng, L.; Zhang, X.; Zhang, S.; Wang, J. *J. Org. Chem.* **2007**, *72*, 1192.

^{1}H and ^{13}C NMR Spectra