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Supporting Information

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Transition Metal Catalyzed Rearrangement of Allenyl Sulfides: A New Approach to Furan Derivatives

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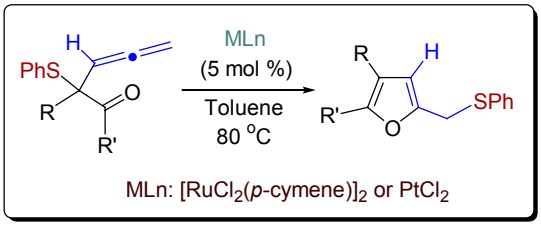
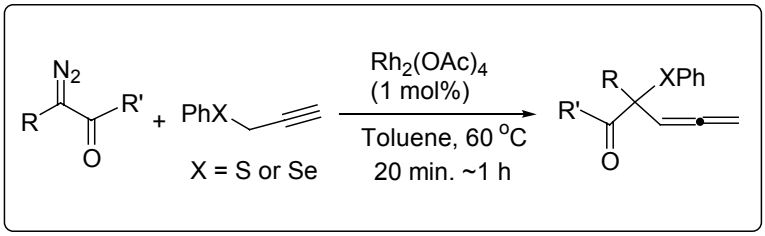


Experimental Section

Caution. All diazo compounds are highly toxic or presumed to be toxic. Diazo compounds are potentially explosive. They should be handled with care in a well-ventilated fumehood.

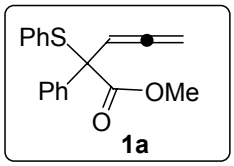
General. All reactions were performed under a nitrogen atmosphere in a flame-dried reaction flask. All solvents were distilled prior to use. Toluene was distilled over sodium. For chromatography, 200-300 mesh silica gel (Yantai, China) or 200-300 mesh neutral Al_2O_3 (Shanghai, China) was employed. ^1H 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. Elemental analysis was measured with Elementar Vario apparatus.

Preparation of 1a~i, 9, 11a, b, 13 with [2,3]-Sigmatropic Rearrangement.



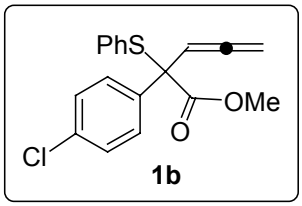
Under a nitrogen atmosphere, $Rh_2(OAc)_4$ (0.005 mmol) was added to a 25 mL round-bottomed flask with 2 mL dry toluene. To the solution was then added phenyl propargyl sulfide (0.50 mmol), followed by dropwisely adding diazoacetate (0.55 mmol) in anhydrous toluene (5 mL) at 60 °C in about 20 minutes. The reaction was kept at the same temperature until the yellow solution turned light yellow or colorless and the diazo compound disappeared as judged by TLC. Removal of the

solvent in vacuo gave a crude residue, which was purified by silica gel column. Elution with petroleum ether/ethyl acetate (100 : 1) afforded pure product of allenyl sulfides or selenyl sulfide.



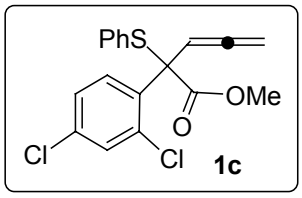
1a

Methyl 2-Phenyl-2-(phenylthio)penta-3,4-dienoate (1a)
Yield 96 %; Oil; IR (film) 1955, 1735, 1234, 694 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.68 (s, 3H), 4.73 (dd, *J* = 3.9, 6.6 Hz, 2H), 5.77 (t, *J* = 6.6 Hz, 1H), 7.19-7.37 (m, 8H), 7.44-7.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.84, 64.33, 78.78, 93.85, 127.74, 127.92, 128.00, 128.34, 129.06, 131.37, 136.56, 138.73, 171.16, 208.19; EI-MS (*m/z*, relative intensity): 296 (M^+, 3), 281 (3), 237 (9), 187 (97), 155 (100), 128 (90), 109 (23). Anal. calcd for $C_{18}H_{16}O_2S$: C, 72.94; H, 5.44. Found: C, 72.81; H, 5.65.



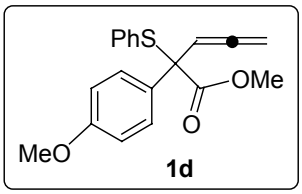
1b

Methyl 2-(4-Chlorophenyl)-2-(phenylthio)penta-3,4-dienoate (1b)
Yield 92 %; Oil; IR (film) 1955, 1732, 1233, 751 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.68 (s, 3H), 4.74 (d, *J* = 6.6 Hz, 2H), 5.74 (t, *J* = 6.6 Hz, 1H), 7.22-7.36 (m, 7H), 7.41-7.44 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.96, 63.78, 79.09, 93.69, 128.10, 128.49, 129.33, 129.61, 131.03, 133.63, 136.63, 137.30, 170.78, 208.21; EI-MS (*m/z*, relative intensity): 330 (M^+, 4), 299 (5), 271 (8), 221 (94), 189 (100), 142 (52), 109 (59). Anal. calcd for $C_{18}H_{15}ClO_2S$: C, 65.35; H, 4.57. Found: C, 65.33; H, 4.71.



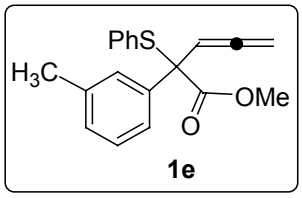
1c

Methyl 2-(2,4-Dichlorophenyl)-2-(phenylthio)penta-3,4-dienoate (1c)
Yield 88 %; white solid; IR (film) 1955, 1736, 1231, 750, 685 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.48 (s, 3H), 4.71 (d, *J* = 6.6 Hz, 2H), 5.95 (t, *J* = 6.6 Hz, 1H), 7.24-7.42 (m, 7H), 7.98 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.64, 63.34, 79.11, 93.58, 126.30, 128.60, 129.77, 130.17, 130.68, 131.32, 134.07, 134.82, 135.62, 136.88, 169.42, 207.80; EI-MS (*m/z*, relative intensity): 364 (M^+, 4), 329 (19), 297 (16), 255 (83), 109 (100). HRMS calcd for $C_{18}H_{14}Cl_2O_2S$ [M] 364.00876. Found 364.00916.



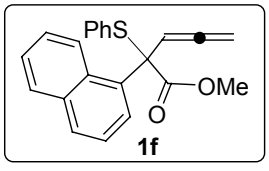
1d

Methyl 2-(4-Methoxyphenyl)-2-(phenylthio)penta-3,4-dienoate (1d)[1]
Yield 94 %; Oil; IR (film) 1955, 1731, 1510, 1252, 1233, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.68 (s, 3H), 3.80 (s, 3H), 4.73 (dd, *J* = 1.8, 6.6 Hz, 2H), 5.74 (t, *J* = 6.6 Hz, 1H), 6.83-6.86 (m, 2H), 7.21-7.42 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.84, 55.19, 63.90, 78.73, 94.00, 113.32, 128.34, 128.99, 129.23, 130.72, 131.65, 136.48, 158.96, 171.34, 208.21; EI-MS (*m/z*, relative intensity): 326 (M^+, 2), 311 (1), 217 (100), 185 (50), 158 (59), 109 (13).



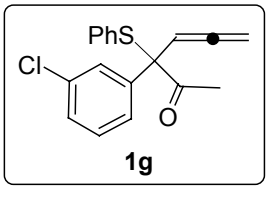
1e

Methyl 2-(3-Methylphenyl)-2-(phenythio)penta-3,4-dienoate (1e)
Yield 90 %; Oil; IR (film) 1956, 1733, 1226, 750, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 3H), 3.68 (s, 3H), 4.67-4.80 (m, 2H), 5.76 (t, *J* = 6.6 Hz, 1H), 7.07-7.09 (m, 1H), 7.17-7.31 (m, 6H), 7.34-7.37 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.41, 52.80, 64.30, 78.67, 93.79, 124.86, 127.90, 128.26, 128.38, 128.51, 128.98, 131.45, 136.54, 137.62, 138.59, 171.21, 208.16; EI-MS (*m/z*, relative intensity): 310 (M^+, 3), 278 (7), 201 (67), 169 (100), 141 (53), 115 (45). Anal. calcd for $C_{19}H_{18}O_2S$: C, 73.52; H, 5.84. Found: C, 73.66; H, 6.13.



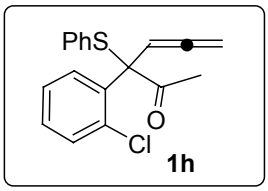
1f

Methyl 2-(1-Naphthyl)-2-(phenylthio)penta-3,4-dienoate (1f)
Yield, 85%; white solid; IR (film) 1955, 1727, 1233, 781, 733, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.44 (s, 3H), 4.43-4.49 (m, 1H), 4.60-4.66 (m, 1H), 6.03 (t, *J* = 6.6 Hz, 1H), 7.14-7.19 (m, 2H), 7.24-7.32 (m, 3H), 7.35-7.46 (m, 3H), 7.76-7.84 (m, 2H), 7.92-7.99 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 52.59, 64.02, 78.62, 94.61, 124.52, 124.83, 125.30, 125.91, 126.61, 128.36, 128.96, 129.16, 129.40, 131.11, 134.08, 134.47, 137.06, 171.86, 208.13; EI-MS (*m/z*, relative intensity): 346 (M^+, 3), 237 (36), 205 (73), 155 (100), 127 (80). HRMS calcd for $C_{22}H_{18}O_2S$ [M] 346.1021. Found 346.1027.

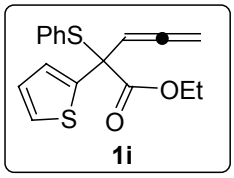


1g

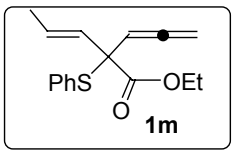
3-(3-Chlorophenyl)-3-(phenylthio)hexa-4,5-dien-2-one (1g)
Yield 86 %; Oil; IR (film) 1953, 1705, 1173, 852, 750, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.18 (s, 3H), 4.64-4.76 (m, 2H), 5.63 (t, *J* = 6.6 Hz, 1H), 7.24-7.38 (m, 8H), 7.44-7.45 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.66, 69.20, 78.55, 92.65, 126.38, 128.15, 128.27, 128.69, 129.46, 129.61, 130.14, 134.40, 136.78, 140.20, 200.91, 208.34; EI-MS (*m/z*, relative intensity): 314 (M^+, 2), 271 (14), 236 (6), 205 (36), 139 (100), 111 (46), 43 (97). HRMS calcd for $C_{18}H_{15}{}^{35}ClOS$ [M] 314.0533. Found 314.0532.



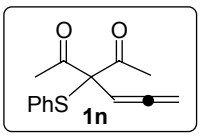
3-(2-Chlorophenyl)-3-(phenylthio)hexa-4,5-dien-2-one (1h)
Yield, 72 %; Oil; IR (film) 1954, 1705, 1182, 849, 749, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.20 (s, 3H), 4.58-4.70 (m, 2H), 5.74 (t, *J* = 6.6 Hz, 1H), 7.26-7.43 (m, 8H), 7.90-7.93 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.68, 68.10, 77.95, 92.29, 126.69, 128.69, 129.27, 129.48, 129.90, 130.01, 130.62, 133.86, 136.66, 137.64, 197.48, 207.86; EI-MS (*m/z*, relative intensity): 314 (M^+, 6), 279 (11), 271 (47), 236 (23), 205 (73), 109 (15), 43 (100). HRMS Calcd. for $C_{18}H_{15}{}^{35}ClOS$ [M] 314.0533. Found 314.0532.



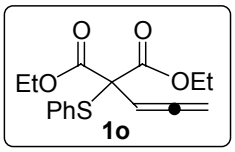
Ethyl 2-(Phenylthio)-2-(2-thienyl)penta-3,4-dienoate (1i)
Yield 86 %; Oil; IR (film) 1955, 1729, 1223, 852, 703, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.19 (t, *J* = 7.2 Hz, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.74-4.86 (m, 2H), 5.84 (t, *J* = 6.6 Hz, 1H), 6.91-6.94 (m, 1H), 7.10-7.12 (m, 1H), 7.22-7.35 (m, 4H), 7.38-7.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.78, 60.17, 62.26, 79.47, 94.31, 126.15, 126.37, 127.78, 128.39, 129.28, 131.74, 136.40, 142.85, 169.66, 208.49; EI-MS (*m/z*, relative intensity): 316 (M^+, 28), 271 (7), 243 (35), 207 (100), 179 (100), 161 (59), 134 (67), 109 (64). Anal. calcd for $C_{17}H_{16}O_2S_2$: C, 64.53; H, 5.10. Found: C, 64.81; H, 5.35.



(E)-ethyl 2-(phenylthio)-2-(prop-1-enyl)penta-3,4-dienoate (1m)
Yield 42 %; Oil; IR (film) 1956, 1728, 1473, 1439, 1227, 1096, 1026, 965, 855, 750, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.20 (t, *J* = 7.2 Hz, 3H), 1.74 (d, *J* = 4.8Hz, 3H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.79-4.90 (m, 2H), 5.53 (t, *J* = 6.6 Hz, 1H), 5.71-5.86 (m, 2H), 7.27-7.39 (m, 3H), 7.47-7.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.95, 17.95, 59.53, 61.81, 78.75, 92.62, 128.30, 128.51, 129.02, 129.23, 131.71, 136.56, 170.45, 208.30; EI-MS (*m/z*, relative intensity): 274 (M^+, 17), 245 (22), 201 (19), 165 (67), 137 (100), 119 (39), 109 (38). HRMS Calcd. for $C_{16}H_{18}O_2S$ [M] 274.1028. Found 274.1025

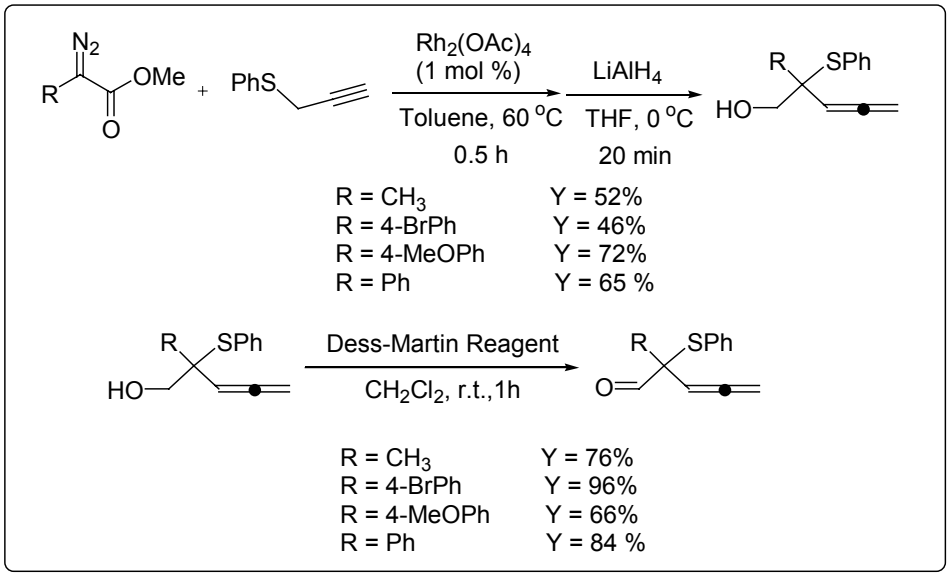


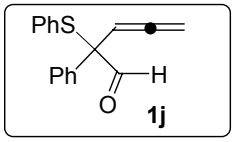
3-(Phenylthio)-3-(propa-1,2-dienyl)penta-2,4-dione (1n)
Yield 67 %; Solid; IR (film) 1952, 1701, 1356, 1195, 858, 750, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ2.32 (s, 6H), 4.95 (d, *J* = 6.9 Hz, 2H), 5.66 (t, *J* = 6.9 Hz, 1H), 7.27-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.97, 78.85, 88.17, 128.88, 129.35, 129.45, 135.60, 198.69, 208.63; EI-MS (*m/z*, relative intensity): 246 (M^+, 2), 204 (29), 161 (41), 137 (83), 128 (23), 109 (18), 43 (100). Anal. calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73. Found: C, 68.27; H, 5.75.



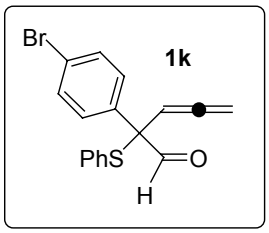
Diethyl 2-(phenylthio)-2-(propa-1,2-dienyl)malonate (1o)
Yield 79 %; Oil; IR (film) 1957, 1732, 1249, 1036, 855, 754, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22 (t, *J* = 7.2 Hz, 6H), 4.14-4.25 (m, 4H), 4.89 (d, *J* = 6.6 Hz, 2H), 5.68 (t, *J* = 6.6 Hz, 1H), 7.29-7.42 (m, 3H), 7.42-7.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.83, 62.30, 63.94, 79.21, 89.90, 128.52, 129.66, 129.93, 137.00, 167.01, 207.86; EI-MS (*m/z*, relative intensity): 306 (M^+, 5), 197 (39), 169 (45), 141 (47), 123 (100), 109 (23). Anal. calcd for $C_{16}H_{18}O_4S$: C, 62.72; H, 5.92. Found: C, 62.75; H, 5.94.

1j, k, **l**, and **p** are prepared by the following reactions.

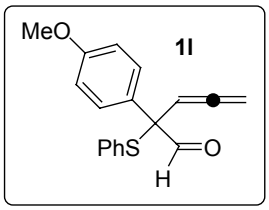




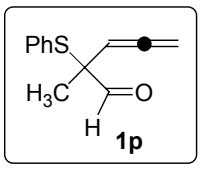
2-phenyl-2-(phenylthio)penta-3,4-dienal (1j)
White solid; IR (film) 1951, 1719, 854, 749, 693 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.61 (dd, *J* = 6.6, 11.7 Hz, 1H), 4.79 (dd, *J* = 6.6, 11.7 Hz, 1H), 5.54 (t, *J* = 6.6 Hz, 1H), 7.25-7.49 (m,10H), 9.52 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 65.76, 78.36, 90.57, 128.42, 128.60, 128.81, 129.56, 129.67, 135.62, 137.29, 190.26, 209.19; EI-MS (*m/z*, relative intensity): 266 (M^+, 8), 237 (12), 223 (5), 157 (75), 128 (100), 109 (26). Anal. calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30. Found: C, 76.75; H, 5.30.



2-(4-Bromophenyl)-2-(phenylthio)penta-3,4-dienal (1k)
Solid; IR (film) 1951, 1718, 1486, 1076, 1009, 855, 750, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.67 (dd, *J* = 6.6, 11.7 Hz, 1H), 4.82 (dd, *J* = 6.6, 11.7 Hz, 1H), 5.49 (t, *J* = 6.6 Hz, 1H), 7.27-7.42 (m, 7H), 7.49-7.53 (m, 2H), 9.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 65.04, 78.85, 90.29, 122.63, 128.91, 129.10, 129.85, 130.21, 131.63, 134.75, 137.23, 189.75, 209.05; EI-MS (m/z, relative intensity): 344 (M^+, 9), 315 (6), 235 (68), 156 (39), 128 (100), 109 (43). HRMS calcd for $C_{17}H_{13}OS^{79}Br$ [M] 343.9871. Found: 343.9874.

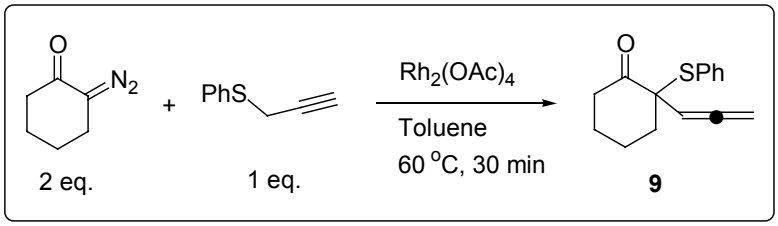


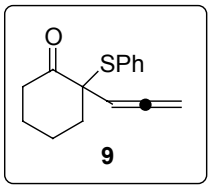
2-(4-Methoxyphenyl)-2-(phenylthio)penta-3,4-dienal (1l)
Solid; IR (film) 2837, 1952, 1716, 1509, 1253, 1182, 1034, 831, 750, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.81 (s, 3H), 4.62 (dd, *J*= 6.6, 11.7Hz, 1H), 4.79 (dd, *J* = 6.6, 11.7Hz, 1H), 5.51(t, *J* = 6.6 Hz, 1H), 6.89-76.94 (m, 2H), 7.27-7.45 (m, 7H), 9.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.21, 65.29, 78.32, 90.68, 113.94, 127.32, 128.78, 129.61, 129.71, 137.25, 159.47, 190.44, 209.11; EI-MS (m/z, relative intensity): 296 (M^+, 5), 267 (4), 234 (3), 187 (100), 159 (40), 144 (28), 128 (28), 115 (66), 109 (12). Anal. calcd for $C_{18}H_{16}O_2S$: C, 72.94; H, 5.44. Found: C, 72.88; H, 5.40.



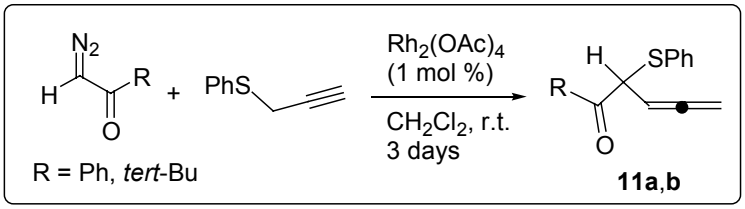
2-Methyl-2-(phenylthio)penta-3,4-dienal (1p)
Oil; IR (film) 3062, 2815, 1952, 1717, 1474, 1439, 1069, 857, 751, 693 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.40 (s, 3H), 4.89-5.01 (m, 2H), 5.32 (t, *J* = 6.6 Hz, 1H), 7.27-7.45 (m, 5H), 9.38 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.97, 57.09, 79.00, 90.09, 128.92, 129.32, 129.76, 137.21, 192.54, 208.16; EI-MS (m/z, relative intensity): 204 (M^+, 6), 175 (41), 160 (12), 147 (13), 110 (41), 95 (100). HRMS calcd for $C_{12}H_{12}OS$ [M] 204.0609. Found: 204.0616.

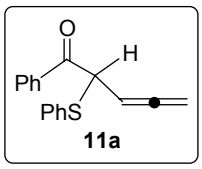
For the synthesis of **9**, 2 equivalents of diazo compound was added.





2-Allenyl-2-(phenylthio)cyclohexanone (9)
Yield 82 %; white solid; IR (film) 2940, 1953, 1702, 853, 750, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.72-1.79 (m, 2H), 1.96-2.20 (m, 4H), 2.38-2.46 (m, 1H), 3.09-3.20 (m, 1H), 4.68-4.84 (m, 2H), 5.56 (t, *J* = 6.6 Hz, 1H), 7.27-7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.36, 26.93, 36.84, 37.93, 60.30, 78.16, 92.90, 128.60, 129.34, 130.22, 136.95, 205.65, 207.32; EI-MS (*m/z*, relative intensity): 244 (M^+, 0.1), 135(100), 109 (8). Anal. calcd For $C_{15}H_{16}OS$: C, 73.73; H, 6.60. Found: C, 73.77; H, 6.70.

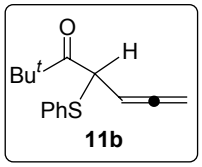




11a

1-Phenyl-2-(phenylthio)penta-3,4-dien-1-one (11a)

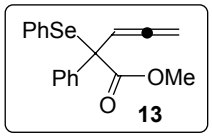
Yield 62 %; Oil; IR (film) 3056, 1952, 1666, 1278, 864, 754, 686 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.68-4.83 (m, 2H), 5.17-5.21 (m, 1H), 5.52-5.59 (m, 1H), 7.26-7.35 (m, 3H), 7.43-7.50 (m, 4H), 7.56-7.62 (m, 1H), 7.99-8.02 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 53.22, 76.96, 88.06, 128.52, 128.61, 128.81, 128.88, 132.33, 133.41, 134.40, 135.12, 193.76, 209.05; EI-MS (*m/z*, relative intensity): 266 (M^+, 15), 161 (45), 157 (100), 128 (54), 109 (11), 105 (84). HRMS calcd for $C_{17}H_{14}OS$ [M] 266.0763. Found 266.0765.



11b

2,2-Dimethyl-4-(phenylthio)hepta-5,6-dien-3-one (11b)

Yield 59 %; Oil; IR (film) 2969, 1953, 1705, 1476, 1060, 852, 746, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.19 (s, 9H), 4.58-4.77 (m, 3H), 5.32-5.39 (m, 1H), 7.31-7.33 (m, 3H), 7.47-7.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.18, 44.46, 52.61, 76.57, 88.95, 128.27, 128.72, 133.05, 134.19, 208.69, 209.29; EI-MS (*m/z*, relative intensity): 246 (M^+, 0.8), 189 (8), 161 (100), 137 (70), 128 (38), 57 (36). HRMS Calcd. for $C_{15}H_{18}OS$ [M] 246.1083. Found 246.1078.

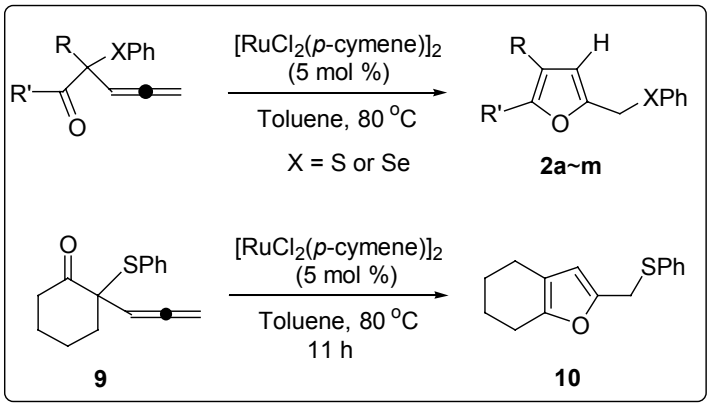


13

Methyl 2-Phenyl-2-(phenylselenyl)penta-3,4-dienoate（13）

Yield 84%; Oil; IR (film) 1953, 1726, 1437, 1232, 854, 741, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.66 (s, 3H), 4.71 (dd, *J* = 0.9, 6.6 Hz, 2H), 5.83 (t, *J* = 6.6 Hz, 1H), 7.18-7.35 (m, 6H), 7.41-7.46 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.76, 59.28, 78.64, 94.45, 127.52, 127.93, 128.34, 128.42, 129.10, 137.79, 138.90, 171.66, 208.03; EI-MS (*m/z*, relative intensity): 344 (M^+, 8), 187 (100), 172 (15), 155 (100), 128 (100). HRMS Calcd. for $C_{18}H_{16}O_2Se$ [M]344.0316. Found 344.0318.

Typical Procedure for Ru(II)-Catalyzed Rearrangement Reactions of 1a~p, 9, 13:

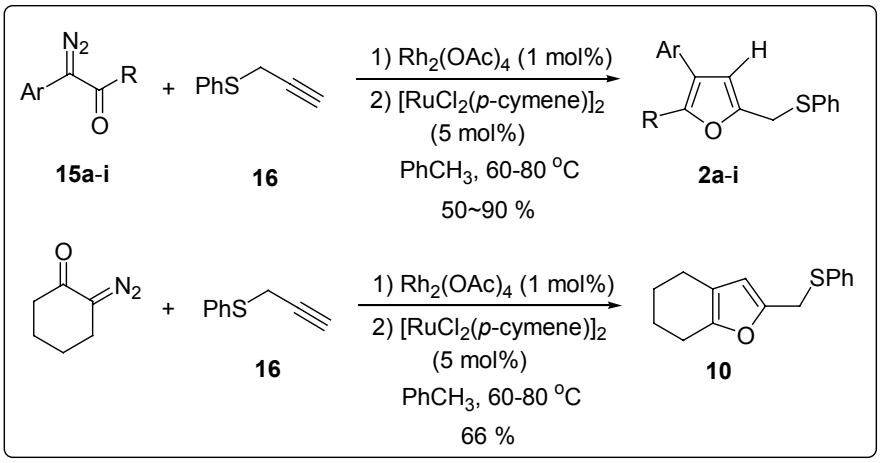


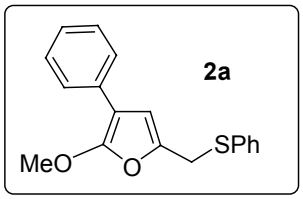
Under a nitrogen atmosphere, $[RuCl_2(p\text{-cymene})]_2$ (0.025 mmol) and allenylic sulfide (0.50 mmol) were mixed in dry toluene, the solution was heated at 80 °C by a boil bath. The reaction was kept at the same the temperature until the reaction was completed as judged by TLC. Removal of the solvent in *vacuo* gave a crude residue, which was purified by neutral Al_2O_3. Elution with petroleum ether/ethyl acetate (200 : 1) afforded pure product of furan derivatives.

For the catalytic reactions of **11a** and **11b**, similar procedure was followed except that for these two substrates 5 mol % $PtCl_2$ was employed.

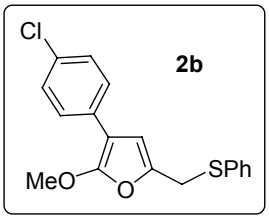
Typical Procedure for One-pot Reaction

Under a nitrogen atmosphere, $Rh_2(OAc)_4$ (0.005 mmol) was added to a 25 mL round-bottomed flask with 2 mL anhydrous toluene. To the solution was added phenyl propargyl sulfide (0.50 mmol), followed by dropwisely adding diazoacetate (0.55 mmol) in anhydrous toluene (5 mL) at 60 °C in about 20 minutes. The reaction was kept at the temperature until the yellow solution turned light yellow or colorless, and the diazo compound disappeared as judged by TLC. The temperature was raised to 80 °C and $[RuCl_2(p\text{-cymene})]_2$ (0.025 mmol) was added to the solution. Heating at the temperature was continued until the reaction was completed as judged by TLC. Removal of the solvent in vacuo afforded a crude residue, which was purified by neutral Al_2O_3. Elution with petroleum ether/ethyl acetate (200 : 1) afforded pure product of furan derivatives.

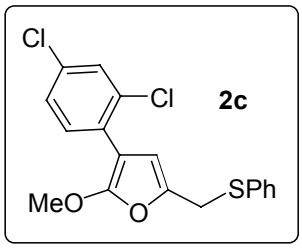




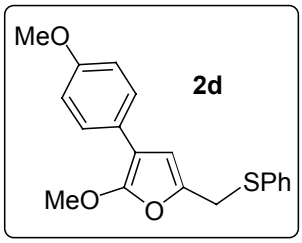
2-Methoxy-3-phenyl-5-[(phenylthio)methyl]furan (2a)
Oil; IR (film) 1633, 1586, 1389, 1013, 762, 739, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.96 (s, 3H), 4.04 (d, J = 0.6 Hz, 2H), 6.32 (s, 1H), 7.13-7.42 (m, 8H), 7.49-7.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.16, 58.58, 108.48, 125.38, 125.49, 126.88, 128.45, 128.86, 130.97, 132.32, 135.52, 138.33, 141.03, 155.27; EI-MS (*m/z*, relative intensity): 296 (M^+, 2), 281 (0.4), 187 (100), 155 (39), 109 (23). Anal. calcd for $C_{18}H_{16}O_2S$: C, 72.94; H, 5.44. Found: C, 73.33; H, 5.76.



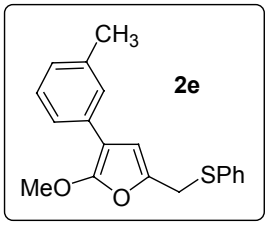
3-(4-Chlorophenyl)-2-methoxy-5-[(phenylthio)methyl]furan (2b)
Oil; IR (film) 1632, 1586, 1498, 1382, 1092, 1010, 831, 738, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.94 (s, 3H), 4.01 (s, 2H), 6.26 (s, 1H), 7.21-7.30 (m, 5H), 7.37-7.42 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.94, 58.33, 98.41, 108.09, 126.54, 126.84, 128.47, 128.84, 130.63, 130.79, 135.37, 141.11, 155.22; EI-MS (*m/z*, relative intensity): 330 (M^+, 2), 221 (100), 189 (32), 109 (22). Anal. calcd for $C_{18}H_{15}ClO_2S$: C, 65.35; H, 4.57. Found: C, 65.57; H, 4.71.



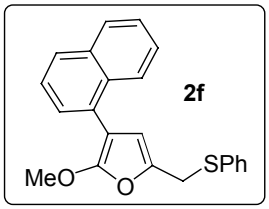
3-(2,4-Dichlorophenyl)-2-methoxy-5-[(phenylthio)methyl]furan (2c)
Oil; IR (film) 1635, 1583, 1483, 1011, 811, 741, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.90 (s, 3H), 4.03 (d, J = 0.6 Hz, 2H), 6.30 (s, 1H), 7.18-7.34 (m, 5H), 7.38-7.42 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.14, 58.55, 96.57, 111.19, 126.84, 126.94, 128.84, 129.61, 129.72, 131.18, 131.72, 132.40, 133.16, 135.26, 140.26, 155.73; EI-MS (*m/z*, relative intensity): 364 (M^+, 0.7), 255 (100), 223 (8), 109 (23). Anal. calcd for $C_{18}H_{14}Cl_2O_2S$: C, 59.19; H, 3.86. Found: C, 59.15; H, 3.89.



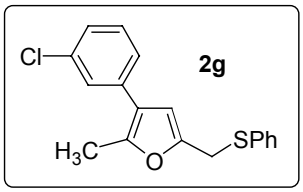
2-Methoxy-3-(4-methoxyphenyl)-5-[(phenylthio)methyl]furan (2d)
Oil; IR (film) 1637, 1585, 1516, 1248, 1016, 1007, 833, 740, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.77 (s, 3H), 3.92 (s, 3H), 4.01 (s, 2H), 6.26 (s, 1H), 6.86-6.88 (m, 2H), 7.18-7.30 (m, 3H), 7.37-7.44 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.98, 55.15, 58.66, 99.61, 108.44, 113.86, 124.84, 126.62, 126.73, 128.79, 130.72, 135.50, 140.80, 154.54, 157.40; EI-MS (*m/z*, relative intensity): 326 (M^+, 4), 217 (100), 202 (13), 185 (31), 158 (32), 109 (10). Anal. calcd for $C_{19}H_{18}O_3S$: C, 69.91; H, 5.56. Found: C, 69.84; H, 5.79.



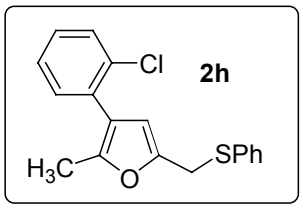
2-Methoxy-3-(3-methylphenyl)-5-[(phenylthio)methyl]furan (2e)
Oil; IR (film) 1632, 1585, 1258, 1036, 786, 738, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.34 (s, 3H), 3.94 (s, 3H), 4.02 (s, 2H), 6.31 (s, 1H), 6.96-6.98 (m, 1H), 7.18-7.32 (m, 6H), 7.37-7.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.51, 32.05, 58.52, 99.72, 108.56, 122.59, 126.16, 126.79, 128.33, 128.82, 130.83, 132.14, 135.46, 137.90, 140.83, 155.17; EI-MS (*m/z*, relative intensity): 310 (M^+, 1), 201 (64), 186 (2), 169 (36), 142 (16), 105 (100). Anal. calcd for $C_{19}H_{18}O_2S$: C, 73.52; H, 5.84. Found: C, 73.68; H, 5.98.



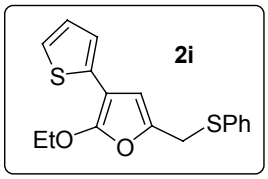
2-Methoxy-3-(1-naphthyl)-5-[(phenylthio)methyl]furan (2f)
Oil; IR (film) 1635, 1583, 997, 800, 777, 739, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.80 (s, 3H), 4.07 (s, 2H), 6.19 (s, 1H), 7.19-7.33 (m, 3.5H), 7.40-7.49 (m, 5.5H), 7.74-7.77 (m, 1H), 7.82-7.89 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.26, 59.12, 98.65, 112.56, 125.32, 125.61, 125.73, 125.84, 126.95, 127.22, 127.31, 128.25, 128.83, 129.98, 131.39, 131.78, 133.72, 135.24, 140.38, 155.69; EI-MS (*m/z*, relative intensity): 346 (M^+, 2), 237 (100), 222 (5), 205 (64), 177 (23). Anal. calcd for $C_{22}H_{18}O_2S$: C, 76.27; H, 5.24. Found: C, 76.27; H, 5.53.



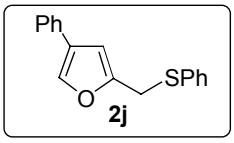
3-(3-Chlorophenyl)-2-methyl-5-[(phenylthio)methyl]furan (2g)
Oil; IR (film) 1598, 1565, 1480, 1222, 1091, 784, 738, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.40 (s, 3H), 4.07 (s, 2H), 6.20 (s, 1H), 7.16-7.31 (m, 3H), 7.35-7.39 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.07, 31.60, 108.98, 120.54, 125.39, 126.25, 126.74, 127.28, 128.84, 129.70, 130.47, 134.32, 135.54, 135.80, 147.86, 148.88; EI-MS (*m/z*, relative intensity): 314 (M^+, 5), 205 (100), 147 (24), 109 (14), 43 (77). Anal. calcd. for $C_{18}H_{15}ClOS$: C, 68.67; H, 4.80. Found: C, 68.66; H, 4.85.



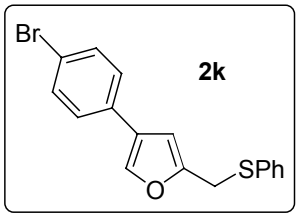
3-(2-Chlorophenyl)-2-methyl-5-[(phenylthio)methyl]furan (2h)
Oil; IR (film) 1572, 1479, 1438, 1225, 1067, 755, 739, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.24 (s, 3H), 4.08 (s, 2H), 6.18 (s, 1H), 7.18-7.31 (m, 6H), 7.38-7.43 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.65, 31.87, 110.98, 119.39, 126.51, 126.76, 128.26, 128.78, 129.76, 130.84, 131.40, 132.79, 133.47, 135.48, 148.00, 148.76; EI-MS (*m/z*, relative intensity): 314 (M^+, 3), 205 (100), 147 (8), 109 (10), 43 (64). Anal. calcd for $C_{18}H_{15}ClOS$: C, 68.67; H, 4.80. Found: C, 68.66; H, 4.87.



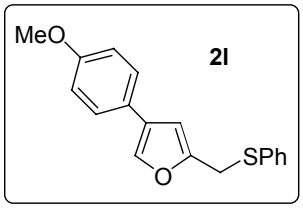
2-Ethoxy-3-(2-thienyl)-5-[(phenylthio)methyl]furan (2i)
Oil; IR (film) 1640, 1587, 1017, 738, 689 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.38 (t, J = 7.2 Hz, 3H), 3.98 (s, 2H), 4.24 (q, J = 7.2 Hz, 2H), 6.21 (s, 1H), 6.94-7.39 (m, 8H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.03, 31.88, 68.46, 97.05, 108.21, 121.78, 122.30, 126.87, 127.04, 128.87, 130.88, 134.75, 135.41, 141.54, 153.91; EI-MS (*m/z*, relative intensity): 316 (M^+, 6), 287 (2), 207 (100), 179 (97) 109 (16). Anal. calcd for $C_{17}H_{16}O_2S_2$: C, 64.53; H, 5.10. Found: C, 64.67; H, 5.16.



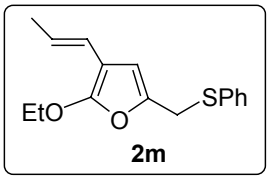
4-Phenyl-2-(phenylthiomethyl)furan (2j)
White solid; IR (film) 1481, 1139, 948, 754, 731, 689 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.10 (s, 2H), 6.41 (s, 1H), 7.20-7.42 (m,10H), 7.63 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.77, 107.04, 125.67, 126.84, 126.95, 127.22, 128.72, 128.89, 130.61, 132.27, 135.36, 137.87, 152.17; EI-MS (*m/z*, relative intensity): 266 (M^+, 13), 157 (100), 129 (42), 109 (13). Anal. calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30. Found: C, 76.61; H, 5.29.



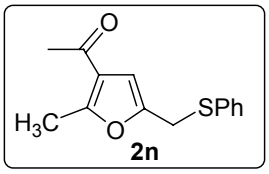
4-Bromophenyl-2-(phenylthiomethyl)furan (2k)
solid; IR (film) 1548, 1480, 1141, 1074, 927, 833, 768, 735 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) 4.09 (s, 2H), 6.36 (s, 1H), 6.36-7.46 (m, 9H), 7.62 (d, J = 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) 31.64, 106.72, 120.59, 126.18, 126.88, 127.18, 128.90, 130.53, 131.18, 131.78, 135.21, 137.98, 152.47; EI-MS (*m/z*, relative intensity): 344 (M^+, 13), 266 (3), 235 (100), 156 (29), 128 (79), 109 (17). HRMS calcd for $C_{17}H_{13}OS^{79}Br$ [M] 343.9870. Found 343.9870.



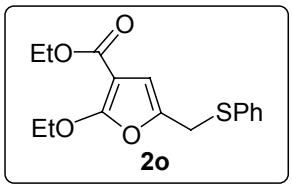
4-Methoxyphenyl-2-(phenylthiomethyl)furan (2l)
Solid; IR (film) 3014, 2837, 1552, 1504, 1466, 1318, 1252, 1180, 1147, 1025, 949, 829, 812, 769, 730, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.78 (s, 3H), 4.09 (s, 2H), 6.35 (s, 1H), 6.86-6.89 (m, 2H), 7.20-7.38 (m, 7H), 7.55 (d, J = 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.66, 55.19, 107.04, 114.09, 124.81, 126.74, 126.77, 128.84, 130.44, 137.01, 151.89, 158.62; EI-MS (*m/z*, relative intensity): 296 (M^+, 29), 187 (100), 159 (35), 144 (19), 127 (13), 115 (18), 109 (7). HRMS calcd for $C_{18}H_{16}O_2S$ [M] 296.0871. Found 296.0862.



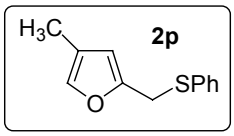
(*E*)-2-ethoxy-5-(phenylthiomethyl)-3-(prop-1-enyl)furan (2m)
Oil; IR (film) 1733, 1669, 1618, 1582, 1439, 1227, 1024, 963, 739, 691cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.32 (t, *J* = 7.2 Hz, 3H), 1.77 (dd, *J* = 1.5, 6.6Hz, 3H), 3.96 (d, *J* = 0.6Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 5.62-5.74 (m, 1H), 6.04-6.13 (m, 2H), 7.17-7.30 (m, 3H), 7.32-7.37 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.99, 18.33, 31.94, 68.59, 100.98, 106.92, 119.52, 122.20, 126.61, 128.75, 130.52, 135.59, 141.44, 154.27; EI-MS (*m/z*, relative intensity): 274 (M^+, 3), 165 (95), 137 (100), 123 (11), 109 (22), 91 (24). HRMS Calcd. for $C_{16}H_{18}O_2S$ [M] 274.1028. Found 274.1021.



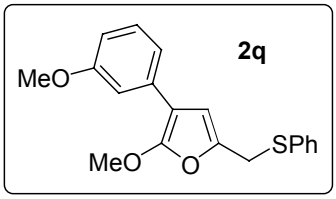
1-(2-Methyl-5-(phenylthiomethyl)furan-3-yl)ethanone (2n)
Oil; IR (film) 1675, 1626, 1123, 973, 748, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 3H), 2.55 (s, 3H), 4.02 (s, 2H), 6.30 (s, 1H), 7.23-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.31, 29.00, 31.37, 108.25, 122.02, 126.96, 128.87, 130.67, 134.98, 148.84, 158.00, 193.88; EI-MS (*m/z*, relative intensity): 246 (M^+, 6), 137 (100), 109 (9), 91 (10), 43 (41). HRMS Calcd. for $C_{14}H_{14}O_2S$ [M] 246.0714. Found 246.0713.



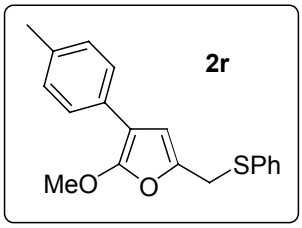
Ethyl 2-ethoxy-5-(phenylthiomethyl)furan-3-carboxylate (2o)
Oil; IR (film) 1712, 1596, 1077, 777, 741, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.29 (t, *J* = 7.2 Hz, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 3.96 (s, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 2H),4H), 6.30 (s, 1H), 7.20-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.30, 14.85, 31.67, 59.73, 67.83, 92.69, 109.13, 126.95, 128.86, 130.87, 135.00, 140.47, 161.22, 162.87; EI-MS (*m/z*, relative intensity): 306 (M^+, 2), 261 (4), 218 (5), 197 (59), 169 (42), 141 (54), 123 (100), 109 (27). HRMS Calcd. for $C_{16}H_{18}O_4S$ [M] 306.0926. Found 306.0928.



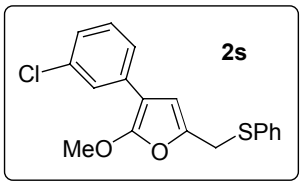
4-Methyl-2-(phenylthiomethyl)furan (2p)
Oil; IR (film) 2926, 1481, 1439, 947, 812, 738, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.95 (d, *J* = 0.9 Hz, 3H), 5.98 (s, 1H), 7.11 (d, *J* = 0.9 Hz, 3H), 7.20-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.68, 31.53, 110.48, 120.71, 126.53, 128.78, 130.14, 135.69, 138.70, 150.84; EI-MS (*m/z*, relative intensity): 204 (M^+, 14), 109 (10), 95 (100). HRMS calcd for $C_{12}H_{12}OS$ [M] 204.0609. Found 204.0616.



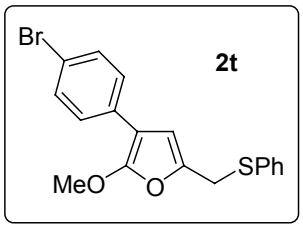
3-(3-Methoxyphenyl)-2-methoxy-5-[(phenylthio)methyl]furan (2q)
Oil; IR (film) 2944, 1632, 1609, 1585, 1246, 1227, 1022, 783, 742, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.79 (s, 3H), 3.94 (s, 3H), 4.02 (s, 2H), 6.30 (s, 1H), 6.69-6.72 (m,1H), 7.08-7.10 (m, 2H), 7.18-7.30 (m, 4H), 7.37-7.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.99, 55.06, 58.43, 99.42, 108.46, 110.56, 111.25, 117.97, 126.80, 128.80, 129.36, 130.83 , 133.62, 135.39, 140.86, 155.29, 159.64; EI-MS (*m/z*, relative intensity): 326 (M^+, 5), 229 (20), 217 (100), 185 (89), 155 (30), 115 (18), 109 (20). HRMS calcd for $C_{19}H_{18}O_3S$ [M] 326.0977. Found 326.0972.



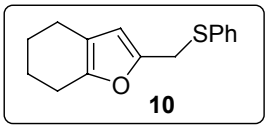
3-(4-Methylphenyl)-2-methoxy-5-[(phenylthio)methyl]furan (2r)
Oil; IR (film) 2943, 1634, 1587, 1518, 1383, 1257, 1149, 1107, 1024, 1012, 816, 740, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 3H), 3.94 (s, 3H), 4.02 (s, 2H), 6.29 (s, 1H), 7.12-7.30 (m, 5H), 7.37-7.41 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.07, 32.10, 58.63, 99.84, 108.52, 125.40, 126.80, 128.83, 129.12, 129.33, 130.86, 134.96, 135.51, 140.84, 154.98; EI-MS (*m/z*, relative intensity): 310 (M^+, 6), 201 (100), 186 (11), 169 (75), 142 (46), 115 (45), 105 (46). HRMS calcd for $C_{19}H_{18}O_2S$ [M] 310.1027. Found 310.1025.



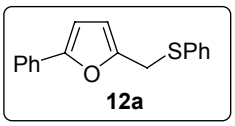
3-(3-Chlorophenyl)-2-methoxy-5-[(phenylthio)methyl]furan (2s)
Oil; IR (film) 2948, 1631, 1598, 1588, 1482, 1389, 1372, 1272, 1151, 1025, 979, 783, 739, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.96 (s, 3H), 4.02 (s, 2H), 6.28 (s, 1H), 7.08-7.12 (m,1H), 7.19-7.40 (m, 7H), 7.49-7.50 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.97, 58.28, 98.11, 108.07, 123.30, 125.14, 125.23, 126.89, 128.86, 129.60, 130.87, 134.18, 134.29, 135.32, 141.15, 155.50; EI-MS (*m/z*, relative intensity): 330 (M^+, 2), 221 (100), 189 (23), 109 (17). HRMS calcd for $C_{18}H_{15}O_2S^{35}Cl$ [M] 330.0481. Found 330.0482.



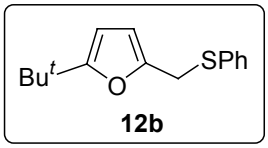
3-(4-Bromophenyl)-2-methoxy-5-[(phenylthio)methyl]furan (2t)
Oil; IR (film) 2947, 1631, 1584, 1494, 1380, 1007, 828, 740, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.95 (s, 3H), 4.02 (s, 2H), 6.27 (s, 1H), 7.22-7.44 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.99, 58.35, 98.45, 108.06, 118.67, 126.88, 126.92, 128.86, 130.86, 131.28, 131.43, 135.36, 141.16, 155.30; EI-MS (*m/z*, relative intensity): 374 (M^+, 3), 265 (100), 233 (21), 183 (44), 171 (40), 155 (33), 142 (27), 123 (17), 109 (51). HRMS calcd for $C_{18}H_{15}O_2S^{79}Br$ [M] 373.9976. Found 373.9959.



2-[(Phenylthio)methyl]-4,5,6,7-tetrahydrobenzofuran (10)
Oil; IR (film) 2931, 1480, 1439, 968, 738, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.59-1.67 (m, 2H), 1.71-1.78 (m, 2H), 2.27-2.31 (m, 2H), 2.48-2.50 (m, 2H), 4.03 (s, 2H), 5.89 (s, 1H), 7.12-7.34 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.98, 22.98, 23.02, 23.12, 31.76, 108.82, 117.60, 126.37, 128.78, 129.91, 136.10, 148.15, 150.51; EI-MS (*m/z*, relative intensity): 244 (M^+, 4), 135 (100), 109 (3). Anal. calcd For $C_{15}H_{16}OS$: C, 73.73; H, 6.60. Found: C, 73.97; H, 6.82.

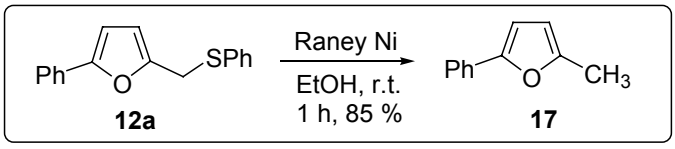


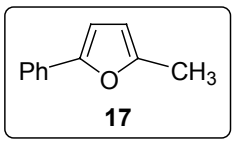
2-Phenyl-5-[(Phenylthio)methyl]furan (12a)
Oil; IR (film) 1481, 1021, 759, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.12 (s, 2H), 6.14 (d, J = 3.3 Hz, 1H), 6.49 (d, J = 3.3 Hz, 1H), 7.17-7.40 (m, 8H), 7.57-7.60 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.84, 105.76, 109.84, 123.53, 126.76, 127.15, 128.53, 128.81, 130.62, 130.73, 135.46, 150.75, 153.38; EI-MS (*m/z*, relative intensity): 266 (M^+, 10), 157 (100), 128 (25), 109 (11). Anal. calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30. Found: C, 76.61; H, 5.27.



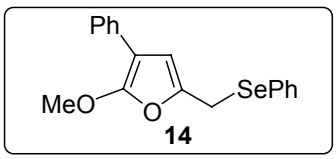
2-*tert*-Butyl-5-[(phenylthio)methyl]furan (12b)
Oil; IR (film) 2966, 1480, 1014, 785, 738, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.23 (s, 9H), 4.06 (s, 2H), 5.82 (d, J = 3.3 Hz, 1H), 5.97 (d, J = 3.3 Hz, 1H), 7.17-7.29 (m, 3H), 7.35-7.38 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.96, 31.75, 32.54, 102.58, 107.93, 126.54, 128.72, 130.57, 135.78, 148.92, 163.81; EI-MS (*m/z*, relative intensity): 246 (M^+, 6), 137 (100), 122 (15), 107 (11). Anal. calcd for $C_{15}H_{18}OS$: C, 73.13; H, 7.36. Found: C, 73.39; H, 7.35.

The structure of furan derivative **12a** was further confirmed by converting it to a known compound **17**.[2]





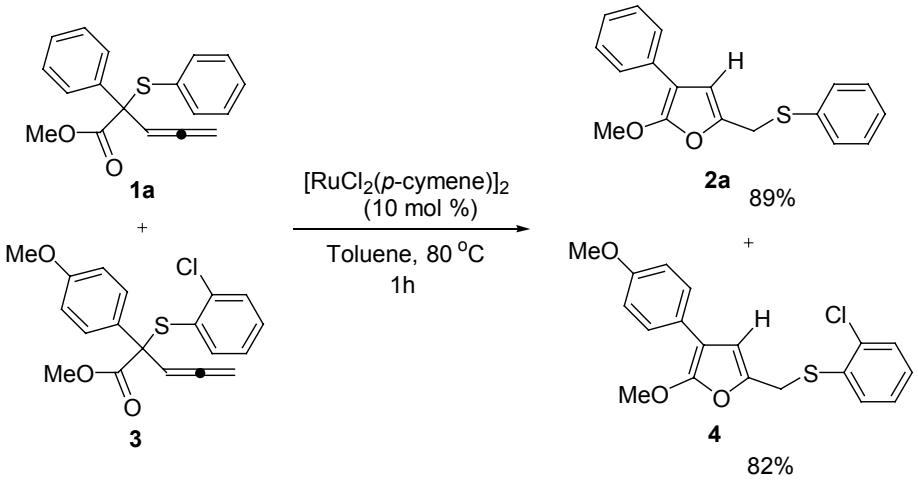
IR (film) 1549, 1022, 784, 757, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.34 (d, J = 0.3 Hz, 3H), 6.02-6.04 (m, 1H), 6.52 (d, J = 3 Hz, 1H), 7.16-7.22 (m, 1H), 7.30-7.37 (m, 2H), 7.60-7.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.58, 105.85, 107.69, 123.30, 126.75, 128.61, 131.21, 151.97, 152.34; EI-MS (*m/z*, relative intensity): 158 (100), 129 (13), 115 (36), 105 (10).



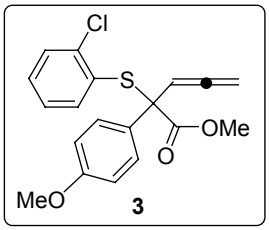
2-Methoxy-3-phenyl-5-(phenylselanylmethyl)furan (14)
Oil; IR (film) 1631, 1581, 1503, 1387, 1145, 1013, 762, 738, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.93 (s, 3H), 4.00 (s, 2H), 6.23 (s, 1H), 7.12-7.17 (m, 1H), 7.25-7.34 (m, 5H), 7.47-7.55 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.78, 58.45, 99.73, 108.04, 125.30, 125.41, 126.92, 127.52, 128.41, 128.93, 132.29, 134.16, 141.86, 155.11; EI-MS (*m/z*, relative intensity): 344 (M^+, 1), 312 (2), 187 (100), 172 (6), 155 (32), 137 (11), 128 (29). HRMS Calcd. for $C_{18}H_{16}O_2Se$ [M]344.0316. Found 344.0292.

Mechanistic Studies

1) The following crossover experiments indicate the 1,4-sulfanyl migration group is intramolecular.

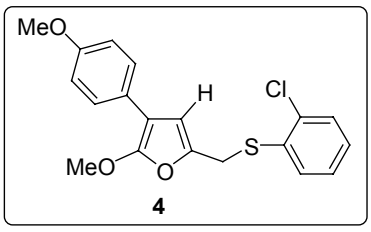


Under a nitrogen atmosphere, $[RuCl_2(p\text{-cymene})]_2$ (0.05 mmol) and allenylic sulfide **1a** (0.50 mmol) and **3** (0.50 mmol) were mixed in dry toluene, the solution was heated at 80 °C by an oil bath. The reaction was kept at the same temperature until the reaction was completed as judged by TLC. Removal of the solvent in *vacuo* gave a crude residue, which was purified by neutral Al_2O_3. Elution with petroleum ether/ethyl acetate (200 : 1) then petroleum ether /ethyl acetate (60 : 1) afforded the furan product of **2a** and **4** separately in 89% and 82% yields, based on the respective starting materials. No crossover products could be identified.



Methyl 2-(2-Chlorophenylthio)-2-(4-methoxyphenyl)penta-3,4-dienoate (3)[1]

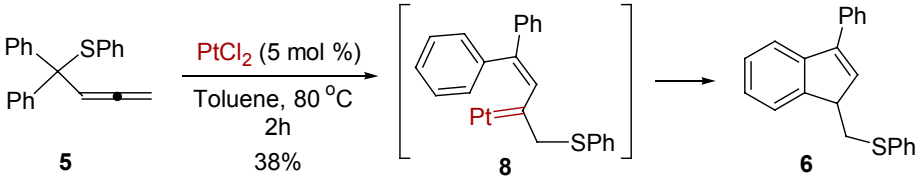
White solid; IR (film) 1954, 1731, 1509, 1252, 1233, 1182, 1035, 830, 754 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.72 (s, 3H), 3.81 (s, 3H), 4.69 (d, J = 6.6 Hz, 2H), 5.83 (t, J = 6.6 Hz, 1H), 6.84-6.89 (m, 2H), 7.08-7.14 (m, 1H), 7.18-7.24 (m, 1H), 7.35-7.41 (m, 2H), 7.47-7.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 53.07, 55.21, 63.71, 78.71, 93.46, 113.45, 126.48, 129.36, 129.72, 129.99, 132.05, 136.24, 138.42, 159.17, 171.04, 208.56; EI-MS (*m/z*, relative intensity): 360 (M^+, 5), 301 (4), 217 (100), 202 (22), 185 (53), 158 (66), 143 (29), 108 (19).

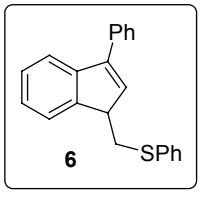


2-Methoxy-3-(4-Methoxyphenyl)-5-[(2-chlorophenylthio)methyl]furan (4)

White solid; IR (film) 1586, 1518, 1250, 1150, 1009, 836, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.79 (s, 3H), 3.94 (s, 3H), 4.08 (d, J = 0.6 Hz, 2H), 6.31 (s, 1H), 6.85-6.90 (m, 2H), 7.11-7.25 (m, 2H), 7.36-7.43 (m, 4H),; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.54, 55.21, 58.72, 99.78, 108.88, 113.90, 124.79, 126.66, 127.05, 127.54, 129.67, 130.79, 134.65, 134.78, 139.94, 154.66, 157.47; EI-MS (*m/z*, relative intensity): 360 (M^+, 3), 217 (100), 202 (22), 185 (31), 158 (35), 143 (15). HRMS calcd for $C_{19}H_{17}{}^{35}Cl\ O_3S$ [M] 360.0585. Found 360.0587.

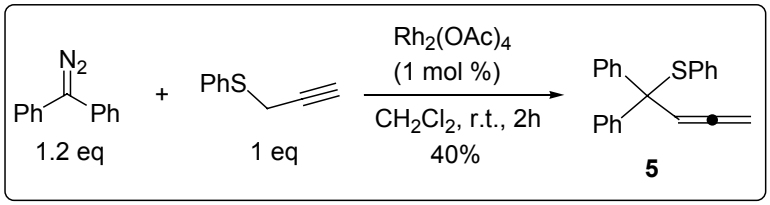
2) The following experiment supports metal carbene as intermediate.



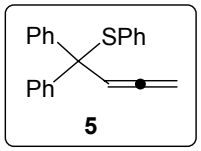


Oil; IR (film) 3059, 1583, 1480, 1025, 774, 738, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.02 (dd, J = 9.0, 12.9 Hz, 1H), 3.48 (dd, J = 6.0, 12.9 Hz, 1H), 3.75-3.80 (m, 1H), 6.63 (d, J = 2.1 Hz, 1H), 7.17-7.45 (m, 11H), 7.54-7.61 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 36.51, 48.53, 120.64, 123.56, 125.30, 126.26, 127.04, 127.64, 127.76, 128.53, 128.99, 129.70, 134.63, 135.51, 136.49, 143.38, 144.75, 147.00; EI-MS (*m/z*, relative intensity): 314 (M^+, 7), 237 (4), 204 (100), 167 (18), 123 (13), 110 (41). HRMS calcd for $C_{22}H_{18}S$ [M] 314.1126. Found 314.1129.

Allenyl sulfide **5** was prepared by the following reaction.



1, 1-Diphenylbuta-2, 3-dienyl(phenyl)sulfide (5)



Oil; IR (film) 1953, 848, 746, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.59 (d, *J* = 6.6 Hz, 2H), 5.79 (t, *J* = 6.6Hz, 1H), 7.09-7.40 (m, 11H), 7.45-7.49 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 64.00, 78.35, 97.58, 127.01, 127.65, 128.19, 128.34, 129.30, 132.86, 135.87, 143.50; EI-MS (*m/z*, relative intensity): 314 (M^+, 3), 205 (100), 190 (11), 178 (7), 165 (6), 127 (5). HRMS calcd for $C_{22}H_{18}S$ [M] 314.1130. Found 314.1129.

References

[1] X. Zhang, M. Ma, J. Wang *Tetrahedron: Asymmetry*, **2003**, *14*, 891.
[2] H. Imagawa, T. Kurisaki, M. Nishizawa, *Org. Lett.* **2004,** *6,* 3679.