Highly efficient [2,3]-sigmatropic rearrangement of sulfur ylide derived from Rh(II) carbene and sulfides in water

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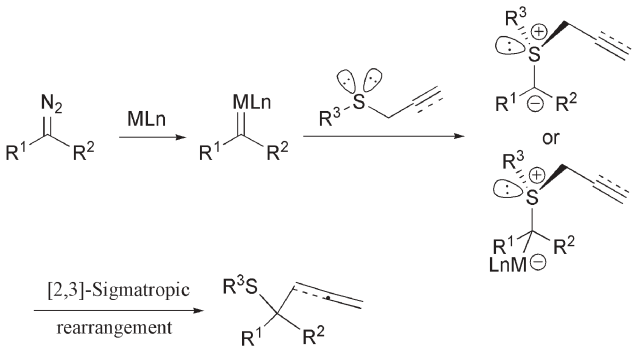
The Doyle–Kirmse reaction, namely the [2,3]-sigmatropic rearrangement of sulfonium ylides generated from transition metal carbenoids and sulfides has been, for the first time, carried out in water.

Introduction

Since their discovery in the late 1960s,[1] the [2,3]-sigmatropic rearrangements of sulfonium ylides have received considerable attention because of their applications in organic synthesis and their probable involvement in biochemical processes.[2] The most common method for sulfonium ylide generation involves the removal of a proton from a sulfonium salt with a strong base.[2a] However, a more direct method makes use of the reaction between a carbene (or carbenoid) and a sulfide. Although suitable for ylide formation, carbenes generated photochemically and thermally from diazo compounds are relatively indiscriminate.[3] The potentially more general catalytic approach to carbenoid generation began to evolve with the use of transition metal-catalyzed reactions of diazo compounds. The [2,3]-sigmatropic rearrangement of sulfonium ylides generated from transition metal carbenoids and sulfides, known as the Doyle–Kirmse reaction, is a powerful method for C–C bond formation (Scheme 1).[4] Therefore, many metal catalysts, such as $Rh_2(OAc)_4$, $Cu(acac)_2$, $[Ru^{II}(TTP)(CO)]$ and $dppeFeCl_2$, were developed to catalyze this reaction.[2,5]

However, the Doyle–Kirmse reaction is always performed in dry organic solvent under inert atmosphere due to the high reactivity of the metal carbenoid intermediates. To the best of our knowledge a metal-catalyzed Doyle–Kirmse reaction in water has not been reported. Water, as the most inexpensive and environmentally benign solvent, has been widely used for organic reactions in the past decade.[6] More recently, a few examples demonstrated that the reactions involving metal carbenoid intermediates, such as cyclopropanation, intramolecular C–H insertion and intermolecular N–H insertion of diazo carbonyl compounds, can be carried out in aqueous conditions.[7] Here we report a highly efficient [2,3]-sigmatropic rearrangement of sulfur ylides derived from Rh(II) carbene and sulfides in water.



Scheme 1

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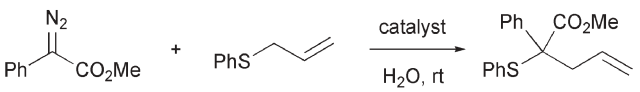
Results and discussion

First, diazo compound **1a** and sulfide **2a** were used as the substrates to optimize the reaction conditions (Table 1). When we treated **1a** and **2a** in 5 mL tap water in the presence of 10 mol% $CuSO_4{\cdot}5H_2O$ at ambient temperature, the reaction proceeded very slowly and **1a** disappeared after 72 h. [2,3]-sigmatropic rearrangement product **3a** was isolated in 31% yield (entry 1). Then a variety of metal salts were explored as catalysts. $Fe(NO_3)_3$, $MnCl_2$, $CoCl_2$ and $NiBr_2$ did not catalyze this reaction under the same conditions (entries 2–5). Use of

Table 1 Effect of the catalysts on the reaction of **1a** and **2a** in water[a]



1a **2a** **3a**

Entry	Catalyst	Reaction time/h	Yield (%)[b]
1	$CuSO_4{\cdot}5H_2O$	72	31
2	$Fe(NO_3)_3$	30	—
3	$MnCl_2$	30	—
4	$CoCl_2$	24	—
5	$NiBr_2$	24	—
6	CuOTf	38	trace
7	$Cu(acac)_2$	72	trace
8	$CuSO_4{\cdot}5H_2O$[c]	72	trace
9	$Rh_2(OAc)_4$[d]	3	91
10[e]	$Rh_2(OAc)_4$[d]	5	93

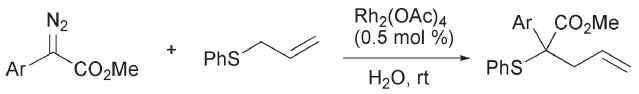
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), 10 mol% catalyst, 5 mL tap water. [b] Isolated yields after column chromatography. [c] 10 mol% sodium dodecylbenzenesulfate was added. [d] 0.5 mol% catalyst was used. [e] The reaction was carried out in deionized distilled water.

10 mol% CuOTf or $Cu(acac)_2$ as catalyst led to very low conversions of the starting materials (entries 6 and 7). Considering the low solubility of the substrates **1a** and **2a** in water, a surfactant was introduced. However, when the reaction was carried out in the presence of a catalytic amount of $CuSO_4 \cdot 5H_2O$ and sodium dodecylbenzenesulfate (SDBS) in water, the result was even worse (entry 8). Considering the "on-water effect" proposed by Sharpless and co-workers,[8] we conceived another possibility to solve this problem by using a less water-soluble catalyst. Thus, Rh(II) carboxylates were applied. To our delight, **3a** was obtained in 91% yield within 3 h when the reaction was catalyzed by a catalytic amount of $Rh_2(OAc)_4$ (entry 9). Although $Rh_2(OAc)_4$ is actually quite soluble in water, the sulfide could coordinate to the rhodium atom, and thus the catalyst might be pulled into organic phase. As a result, the reaction could proceed effectively. For comparison, the reaction was also tested in deionized distilled water and a similar result was obtained (entry 10).

Using the optimized reaction conditions, we carried out the rhodium-catalyzed Doyle–Kirmse reaction of a variety of aryldiazoacetates (**1a–j**) and phenyl allyl sulfide (**2a**). The results were summarized in Table 2. As can be seen, in all cases [2,3]-sigmatropic rearrangement products (**3a–j**) were obtained in good to excellent yields, regardless of the position and electronic effect of the substituent in the phenyl ring. When there was a substituent in the ortho position, the yield decreased to some extent (entries 2 and 8). **1j** (Ar = 1-naphthyl) was also suitable for this reaction (entry 10). Notably, most aryldiazoacetates are solid except **1a**, **1f** and **1j**. **1b** can dissolve in phenyl allyl sulfide, **2a** and other solid substrates were dissolved in a tiny amount of organic solvent (most cases in toluene) before they were subjected to the reaction.

As an extension of the approach, the reaction of aryldiazoacetates and phenyl propargyl sulfide **4a** was then examined. Surprisingly, when we treated **1a** and **4a** in the presence of a catalytic amount of $Rh_2(OAc)_4$ in water, the reaction proceeded very slowly and was completed in about 4 days to afford [2,3]-sigmatropic rearrangement product **5a** in only 74% yield. A hydrophobic Rh(II) catalyst was then considered. We were delighted to find that the reaction proceeded smoothly and finished within 14 h when catalyzed by dirhodium(II) octanoate, $Rh_2(Oct)_4$. Allene derivative **5a** was formed in 93% yield. Subsequently, the reaction condition was applied to **1b–h, j** (Table 3). The reaction worked well and the corresponding rearrangement products **5b–h, j** were all obtained in high yields.

Table 2 Reaction of **1a–j** and **2a** catalyzed by $Rh_2(OAc)_4$ in water[a]

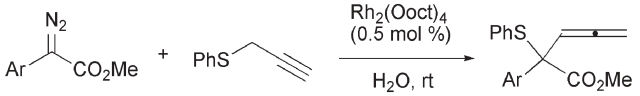


1a-j 2a 3a-j

Entry	Substrate **1** (Ar=)	Reaction time/h	Yield (%)[b]
1	**a**, C_6H_5	3	91
2	**b**, *o*-ClC_6H_4	3	82
3	**c**, *m*-ClC_6H_4[c]	4	92
4	**d**, *p*-ClC_6H_4[c]	16	92
5	**e**, *p*-BrC_6H_4[c]	1	92
6	**f**, *m*-$MeOC_6H_4$	1.5	97
7	**g**, *p*-$MeOC_6H_4$[c]	0.75	96
8	**h**, 2,4-$Cl_2C_6H_3$[c]	6	82
9	**i**, 3,4-$Cl_2C_6H_3$[d]	3	93
10	**j**, 1-naphthyl	5	89

[a] Reaction conditions: **1a–j** (0.2 mmol), **2a** (0.3 mmol), 0.5 mol% $Rh_2(OAc)_4$, 5 mL tap water. [b] Isolated yields after column chromatography. [c] The substrate was dissolved in 0.1 mL toluene. [d] The substrate was dissolved in 0.3 mL CH_2Cl_2.

Table 3 Reaction of **1a–h, j** and **4a** catalyzed by $Rh_2(Oct)_4$ in water[a]



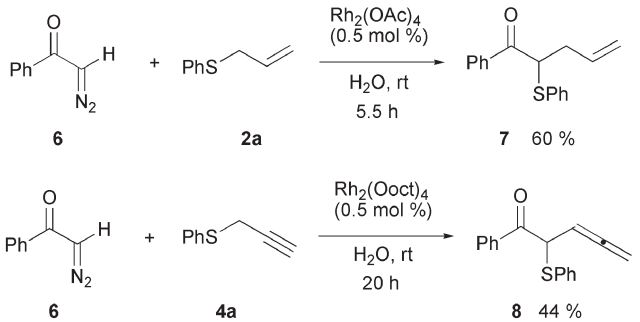
1a-h, j 4a 5a-h, j

Entry	Substrate **1** (Ar=)	Reaction time/h	Yield (%)[b]
1	**a**, C_6H_5	14	93
2	**b**, *o*-ClC_6H_4	8	88
3	**c**, *m*-ClC_6H_4[c]	4	95
4	**d**, *p*-ClC_6H_4	1.5	94
5	**e**, *p*-BrC_6H_4	4	95
6	**f**, *m*-$MeOC_6H_4$	6	96
7	**g**, *p*-$MeOC_6H_4$[c]	3	92
8	**h**, 2,4-$Cl_2C_6H_3$[c]	2	89
9	**j**, 1-naphthyl	7	87

[a] Reaction conditions: **1a–h, j** (0.2 mmol), **2a** (0.3 mmol), 0.5 mol% $Rh_2(Oct)_4$, 5 mL tap water. [b] Isolated yields after column chromatography. [c] The substrate was dissolved in 0.1 mL toluene.

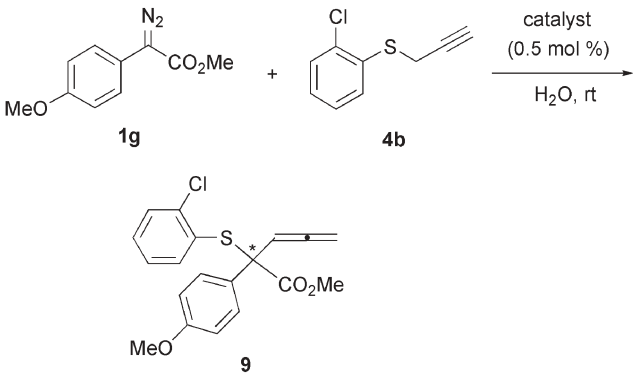
In addition, α-diazoacetophenone, **6**, as substrate was also tested for the Doyle–Kirmse reaction. **6** reacted with **2a** or **4a** and afforded the corresponding rearrangement product in moderate yield under identical reaction conditions (Scheme 2). The low yield obtained may be due to the easy dimerization of **6** as well as the instability of the rearrangement product. Moreover, it should be noted that the reaction of **6** and **4a** in water was much faster than in CH_2Cl_2.

Since the pioneering work of Uemura *et al.* in 1995,[9] asymmetric catalysis in [2,3]-sigmatropic rearrangement of sulfur ylides has attracted considerable attention.[10] Considering the difference between organic solvents and water, we conceived that the enantioselectivity of the asymmetric catalytic [2,3]-sigmatropic rearrangement of sulfur ylides might be improved when carrying out the reaction in water. Thus, diazo compound **1g** and allyl 2-chlorophenyl



Scheme 2

Table 4 Asymmetric [2,3]-sigmatropic rearrangement of sulfur ylide in water[a]



Entry	Catalyst	Reaction time/h	Yield (%)[b]	ee (%)[c]
1	Rh_2(*S*-DOSP)$_4$	0.3	93	48
2	Rh_2(*S*-TBSP)$_4$	1	91	44
3	Rh_2(*S*-BNP)$_4$	1	94	27
4	Rh_2(4*S*-MEAZ)$_4$	38	67	2
5	Rh_2(4*S*-MEOX)$_4$	160	56	2
6	Rh_2(5*S*-MEPY)$_4$	120	41	8
7	Rh_2(4*S*-MPPIM)$_4$	87 (14)[d]	42 (28)[d]	68 (47)[d]
8[e]	Rh_2(*S*-DOSP)$_4$	22	91	48

[a] Reaction conditions: **1g** (0.2 mmol) dissolved in 0.1 mL toluene, **4b** (0.3 mmol), 0.5 mol% catalyst, 5 mL tap water. [b] Isolated yields after column chromatography. [c] Enantiomeric excess values determined by chiral HPLC. [d] The data in parentheses refers to the reaction in toluene. [e] The reaction was carried out at 0 °C.

sulfide **4b** were chose as the substrates to screen the chiral rhodium(II) catalysts (Table 4). When catalyzed by Rh_2(*S*-DOSP)$_4$,[11] Rh_2(*S*-TBSP)$_4$[11] or Rh_2(*S*-BNP)$_4$[12] in water, the reaction proceeded efficiently to give the allenic product in excellent yield. Unfortunately, the enantioselectivity was lower than that performed in toluene (entries 1–3).[10e] A lower temperature significantly slowed down the reaction rate, while the enantioselectivity remained the same (entry 8). Using Rh_2(4*S*-MEAZ)$_4$,[13] Rh_2(4*S*-MEOX)$_4$,[14] Rh_2(5*S*-MEPY)$_4$[15] or Rh_2(4*S*-MPPIM)$_4$[16] as catalyst, the reaction proceeded much more slowly. Rh_2(4*S*-MEAZ)$_4$, Rh_2(4*S*-MEOX)$_4$ and Rh_2(5*S*-MEPY)$_4$ showed low enantioselectivities, whereas Rh_2(4*S*-MPPIM)$_4$ gave the best result (entries 4–7). Since an improvement in enantioselectivities was often observed in toluene media, the reaction catalyzed by Rh_2(4*S*-MPPIM)$_4$ in toluene was also tested. Although the reaction proceeded much faster, both yield and enantioselectivity decreased (entry 7 in parentheses). Other chiral catalysts may be employed to improve the enantioselectivity. This work is still under investigation in our laboratory. The results obtained so far demonstrate that aqueous media does not significantly improve the enantioselectivity in this type of reaction.

Conclusions

In conclusion, we have demonstrated that [2,3]-sigmatropic rearrangement of sulfur ylide generated through Rh(II) carbene and allyl and propargyl sulfides can be efficiently carried out in an aqueous suspension. We consider that this is an example of an "on-water" reaction.

Experimental

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

^{1}H NMR and ^{13}C NMR were measured at 300 MHz and 75 MHz on Varian Mercury 300 spectrometers or at 200 MHz and 50 MHz on Varian Mercury 200 spectrometers. IR spectra were recorded with a Nicolet AVATAR 330 FT-IR infrared spectrometer. Mass spectra were obtained on a VG ZAB-HS mass spectrometer. Elemental analysis was carried out at Elementar Vario EL Instrument. Column chromatography was performed on 200–300 mesh silica gel (Yantai, China) employing a petroleum ethyl acetate mixture (distilled prior to use) as eluent. All solvents were distilled prior to use.

General procedure for the reaction of diazo compound and allyl sulfide catalyzed by $Rh_2(OAc)_4$ in water. Diazo compounds **1a–j**, **6** (0.2 mmol) and sulfide **2a** were charged in a 25 mL round bottomed flask, 5 mL tap water was added followed by $Rh_2(OAc)_4$ (0.001 mmol), the mixture was stirred at room temperature until complete disappearance of the diazo substrate. The reaction mixture was then extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified on a silica gel column (petroleum ether–EtOAc, 15 : 1–50 : 1) to afford the products **3a–j**, **7**.

Methyl 2-(2-chlorophenyl)-2-(phenylthio)pent-4-enoate (3b). 82%; IR (neat) 3074, 2948, 1732, 1438, 1228 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.82–2.90 (m, 1 H), 3.02–3.10 (m, 1 H), 3.61 (s, 3 H), 5.03–5.11 (m, 2 H), 5.81–5.94 (m, 1 H), 7.14–7.42 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.9, 52.5, 63.4, 118.8, 126.1, 128.5, 128.8, 129.4, 129.5, 130.2, 130.8, 132.5, 133.6, 136.9, 137.3, 171.2; EI-MS (*m*/*z*, relative intensity): 332 (M^+, 12), 291 (20), 223 (44), 163 (36), 155 (40), 128 (72), 109 (28), 71 (100). Anal. calcd for $C_{18}H_{17}ClO_2S$: C, 64.95; H, 5.15. Found: C, 64.93; H, 5.07.

Methyl 2-(3-chlorophenyl)-2-(phenylthio)pent-4-enoate (3c). 92%; IR (neat) 3076, 2950, 1732, 1438, 1215 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.77–2.91 (m, 2 H), 3.70 (s, 3 H), 5.04–5.15 (m, 2 H), 5.82–5.95 (m, 1 H), 7.14–7.36 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.6, 52.8, 64.0, 119.2, 125.7, 127.6, 127.7, 128.6, 129.2, 129.5, 130.1, 132.6, 134.0, 136.8, 141.8, 171.7; EI-MS (*m*/*z*, relative intensity): 332 (M^+, 33), 291 (31), 223 (73), 191 (36), 163 (83), 155 (74), 128 (82), 109 (35), 71 (100), 59 (49). Anal. calcd for $C_{18}H_{17}ClO_2S$: C, 64.95; H, 5.15. Found: C, 65.00; H, 5.23.

Methyl 2-(4-chlorophenyl)-2-(phenylthio)pent-4-enoate (3d). 92%; IR (neat) 2950, 1729, 1494, 1474, 1219 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.77–2.90 (m, 2 H), 3.69 (s, 3 H), 5.03–5.14 (m, 2 H), 5.81–5.95 (m, 1 H), 7.16–7.35 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.6, 52.7, 63.8, 119.1, 128.1, 128.6, 128.9, 129.4, 130.3, 132.7, 133.3, 136.8, 138.3, 171.8; EI-MS (*m*/*z*, relative intensity): 332 (M^+, 16), 291 (8), 223 (96), 191

(33), 163 (84), 155 (94), 128 (100), 109 (46), 71 (95), 59 (66). Anal. calcd for $C_{18}H_{17}ClO_2S$: C, 64.95; H, 5.15. Found: C, 64.84; H, 5.12.

Methyl 2-(4-bromophenyl)-2-(phenylthio)pent-4-enoate (3e). 92%; IR (neat) 3076, 2949, 1731, 1489, 1217 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.77–2.90 (m, 2 H), 3.69 (s, 3 H), 5.04–5.14 (m, 2 H), 5.81–5.94 (m, 1 H), 7.15–7.43 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.6, 52.7, 63.9, 119.2, 121.5, 128.6, 129.3, 129.4, 130.2, 131.1, 132.7, 136.8, 138.8, 171.8; EI-MS (*m*/*z*, relative intensity): 376 (M^+, 13), 267 (82), 235 (25), 199 (54), 129 (70), 128 (100), 109 (27), 71 (67). Anal. calcd for $C_{18}H_{17}BrO_2S$: C, 57.30; H, 4.54. Found: C, 57.25; H, 4.55.

Methyl 2-(3-methoxyphenyl)-2-(phenylthio)pent-4-enoate (3f). 97%; IR (neat) 2950, 2836, 1731, 1257, 1215 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.77–2.93 (m, 2 H), 3.69 (s, 3 H), 3.74 (s, 3 H), 5.04–5.14 (m, 2 H), 5.85–5.98 (m, 1 H), 6.78–6.88 (m, 3 H), 7.16–7.33 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.5, 52.6, 55.2, 64.3, 112.8, 113.4, 118.7, 119.7, 128.4, 128.9, 129.2, 130.5, 133.0, 136.7, 141.2, 159.2, 172.1; EI-MS (*m*/*z*, relative intensity): 328 (M^+, 11), 287 (5), 219 (90), 187 (24), 159 (100), 151 (50), 109 (21), 71 (31). Anal. calcd for $C_{19}H_{20}O_3S$: C, 69.48; H, 6.14. Found: C, 69.42; H, 6.24.

Methyl 2-(4-methoxyphenyl)-2-(phenylthio)pent-4-enoate (3g). 96%; IR (neat) 2951, 2837, 1731, 1512, 1252 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.76–2.92 (m, 2 H), 3.69 (s, 3 H), 3.80 (s, 3 H), 5.03–5.13 (m, 2 H), 5.84–5.98 (m, 1 H), 6.79–6.88 (m, 2 H), 7.17–7.33 (m, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.6, 52.6, 55.2, 63.9, 113.3, 118.6, 128.4, 128.6, 129.1, 130.8, 131.7, 133.3, 136.8, 158.7, 172.4; EI-MS (*m*/*z*, relative intensity): 328 (M^+, 0.4), 219 (28), 180 (30), 159 (20), 121 (100), 91 (10), 77 (14), 51 (8). Anal. calcd for $C_{19}H_{20}O_3S$: C, 69.48; H, 6.14. Found: C, 69.35; H, 6.28.

Methyl 2-(2,4-dichlorophenyl)-2-(phenylthio)pent-4-enoate (3h). 82%; IR (neat) 3074, 2944, 1736, 1471, 1216 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.84 (dd, J = 14.4, 7.8 Hz, 1 H), 3.02 (ddt, J = 14.4, 6.6, 1.5 Hz, 1 H), 3.58 (s, 3 H), 5.02–5.12 (m, 2 H), 5.78–5.92 (m, 1 H), 7.14–7.43 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.9, 52.5, 63.0, 119.1, 126.2, 128.6, 129.7, 130.0, 130.4, 130.6, 132.1, 133.9, 134.4, 135.8, 137.3, 170.8; EI-MS (*m*/*z*, relative intensity): 366 (M^+, 13), 325 (10), 257 (39), 189 (33), 162 (30), 128 (40), 109 (54), 71 (100). Anal. calcd for $C_{18}H_{16}Cl_2O_2S$: C, 58.86; H, 4.39. Found: C, 58.82; H, 4.48.

Methyl 2-(3,4-dichlorophenyl)-2-(phenylthio)pent-4-enoate (3i). 93%; IR (neat) 3077, 2951, 1732, 1474, 1217 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.81–2.89 (m, 2 H), 3.70 (s, 3 H), 5.04–5.16 (m, 2 H), 5.79–5.92 (m, 1 H), 7.14–7.38 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.6, 52.8, 63.4, 119.5, 127.1, 128.7, 129.7, 129.8, 129.9, 131.5, 132.1, 132.3, 136.8, 140.0, 171.3; EI-MS (*m*/*z*, relative intensity): 366 (M^+, 23), 325 (14), 257 (86), 225 (33), 189 (78), 162 (52), 109 (34), 71 (100). Anal. calcd for $C_{18}H_{16}Cl_2O_2S$: C, 58.86; H, 4.39. Found: C, 58.87; H, 4.34.

Methyl 2-(1-naphthyl)-2-(phenylthio)pent-4-enoate (3j). 89%; IR (neat) 3053, 2949, 1731, 1438, 1214 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.95–3.11 (m, 2 H), 3.56 (s, 3 H), 5.07–5.17 (m, 2 H), 6.05–6.17 (m, 1 H), 6.89–6.92 (m, 2 H), 7.04–7.10 (m, 2 H), 7.20–7.28 (m, 3 H), 7.46–7.56 (m, 2 H), 7.75–7.78 (m, 1 H), 7.86–7.89 (m, 1 H), 8.19–8.22 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.2, 52.6, 63.9, 118.6, 124.2, 124.5, 125.3, 125.4, 126.1, 128.2, 129.1, 129.2, 129.3,130.5, 131.0, 133.1, 134.2, 134.9, 137.2, 173.3; EI-MS (*m*/*z*, relative intensity): 348 (M^+, 4), 239 (25), 207 (12), 179 (100), 165 (17), 109 (4), 71 (8), 43 (13). HRMS calcd for $C_{22}H_{20}O_2S$: 348.1184; Found: 348.1185.

1-Phenyl-2-(phenylthio)pent-4-en-1-one (7). 60%; IR (neat) 3075, 1678, 1439, 1240 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.54–2.64 (m, 1 H), 2.71–2.81 (m, 1 H), 4.50 (dd, J = 8.1, 6.6 Hz, 1 H), 5.06–5.16 (m, 2 H), 5.82–5.96 (m, 1 H), 7.24–7.38 (m, 5 H), 7.42–7.48 (m, 2 H), 7.54–7.59 (m, 1 H), 7.91–7.95 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.0, 50.7, 117.7, 128.5, 128.6, 128.8, 128.9, 131.4, 133.1, 134.7, 134.8, 136.0, 195.1; EI-MS (*m*/*z*, relative intensity): 268 (M^+, 21), 163 (100), 159 (26), 135 (56), 109 (31), 105 (82), 77 (71), 51 (22). Anal. calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01. Found: C, 76.20; H, 6.07.

General procedure for the reaction of diazo compound and propargyl sulfide catalyzed by $Rh_2(Ooct)_4$ in water. Diazo compounds **1a–h, j**, **6** (0.2 mmol) and sulfide **4a** (0.3 mmol) were charged in a 25 mL round bottomed flask, 5 mL tap water was added followed by $Rh_2(Ooct)_4$ (0.001 mmol), the mixture was stirred at room temperature until complete disappearance of the diazo substrate. The reaction mixture was then extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified on a silica gel column (petroleum ether–EtOAc, 15 : 1–50 : 1) to afford the products **5a–h, j**, **8**.

Methyl 2-(2-chlorophenyl)-2-(phenylthio)penta-3,4-dienoate (5b). 88%; IR (neat) 3061, 2948, 1954, 1734, 1232 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.51 (s, 3 H), 4.70 (d, J = 6.6 Hz, 2 H), 5.96 (t, J = 6.6 Hz, 1 H), 7.22–7.43 (m, 8 H), 7.95–7.98 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.6, 63.7, 78.9, 93.8, 126.1, 128.5, 129.0, 129.6, 130.3, 130.4, 130.9, 134.1, 136.8, 137.0, 169.9, 207.8; EI-MS (*m*/*z*, relative intensity): 330 (M^+, 3), 295 (25), 263 (20), 221 (100), 189 (43), 127 (53), 109 (61), 65 (34). Anal. calcd for $C_{18}H_{15}ClO_2S$: C, 65.35; H, 4.57. Found: C, 65.34; H, 4.72.

Methyl 2-(3-chlorophenyl)-2-(phenylthio)penta-3,4-dienoate (5c). 95%; IR (neat) 3060, 2950, 1955, 1733, 1232 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.69 (s, 3 H), 4.76 (d, J = 6.6 Hz, 2 H), 5.73 (t, J = 6.6 Hz, 1 H), 7.21–7.48 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.0, 63.9, 79.1, 93.5, 126.4, 127.9, 128.4, 128.5, 129.2, 129.4, 130.9, 133.9, 136.7, 140.8, 170.6, 208.3; EI-MS (*m*/*z*, relative intensity): 330 (M^+, 5), 263 (9), 221 (100), 189 (88), 162 (31), 142 (29), 127 (34), 109 (37), 59 (28). Anal. calcd for $C_{18}H_{15}ClO_2S$: C, 65.35; H, 4.57. Found: C, 65.52; H, 4.63.

Methyl 2-(4-bromophenyl)-2-(phenylthio)penta-3,4-dienoate (5e). 95%; IR (neat) 2950, 1955, 1732, 1486, 1232 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 3 H), 4.74 (d, J = 6.6 Hz, 2 H), 5.73 (t, J = 6.6 Hz, 1 H), 7.21–7.46 (m, 9 H); ^{13}C NMR

(75 MHz, $CDCl_3$) δ 52.9, 63.8, 79.1, 93.6, 121.9, 128.5, 129.3, 129.9, 131.0, 136.6, 137.9, 170.7, 208.2; EI-MS (*m*/*z*, relative intensity): 374 (M^+, 5), 315 (6), 265 (100), 235 (72), 186 (94), 155 (88), 142 (60), 127 (74), 109 (69), 59 (34). Anal. calcd for $C_{18}H_{15}BrO_2S$: C, 57.61; H, 4.03. Found: C, 57.66; H, 4.07.

Methyl 2-(3-methoxyphenyl)-2-(phenylthio)penta-3,4-dienoate (5f). 96%; IR (neat) 2950, 1955, 1732, 1599, 1229 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.69 (s, 3 H), 4.69–4.80 (m, 2 H), 5.75 (t, J = 6.6 Hz, 1 H), 6.80–6.84 (m, 1 H), 7.02–7.07 (m, 2 H), 7.20–7.38 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.9, 55.2, 64.3, 78.8, 93.7, 113.2, 113.9, 120.3, 128.4, 129.0, 129.1, 131.5, 136.6, 140.3, 159.2, 171.1, 208.3; EI-MS (*m*/*z*, relative intensity): 326 (M^+, 8), 294 (7), 217 (58), 185 (100), 164 (26), 115 (29), 110 (36), 29 (31). Anal. calcd for $C_{19}H_{18}O_3S$: C, 69.91; H, 5.56. Found: C, 69.86; H, 5.63.

General procedure for the reaction of 1g and 4b catalyzed by chiral Rh(II) complex in water. Diazo compound **1g** (0.2 mmol) and sulfide **4b** (0.3 mmol) were charged in a 25 mL round bottomed flask, 5 mL tap water was added, followed by the chiral Rh(II) complex (0.001 mmol), the mixture was stirred at room temperature until complete disappearance of the diazo substrate. The reaction mixture was then extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified on a silica gel column (petroleum ether–EtOAc, 15 : 1) to afford the product **9**. The enantiomeric excess value determined by chiral HPLC: Chiracel OJ-H; hexane–iso-propanol = 70 : 30.

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