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Catalytic asymmetric [2,3] sigmatropic rearrangement of sulfur ylides generated from carbenoids and propargyl sulfides

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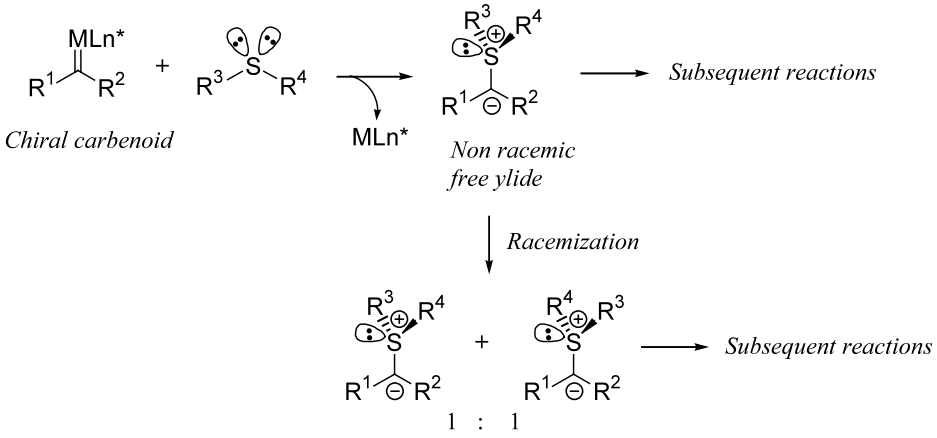
Abstract—Catalytic asymmetric [2,3] sigmatropic rearrangement of sulfur ylides generated from aryldiazoacetates and propargyl sulfides with a number of chiral Rh(II) and Cu(I) catalysts have been investigated and moderately high enantioselectivities (up to 81% ee) have been achieved.

1. Introduction

It is generally believed that the rearrangement reactions of the ylides generated by transition metal complex-catalyzed reaction of diazo compounds in the presence of sulfide occur from the free ylide rather than the metal-associated ylide.[1] However, asymmetric induction is still possible since the sulfonium ylide has considerable stability, therefore the subsequent rearrangement of the sulfonium ylide may be faster than its racemization (Scheme 1).[2] In 1995 Uemura reported the first catalytic asymmetric [2,3] sigmatropic rearrangement with chiral Cu(OTf)/bisoxazoline-catalyzed reaction of *trans*-cinnamyl phenyl sulfide with diazoacetate, although the enantioselectivity was low (up to 22% ee).[3] Since Uemura's pioneering work, catalytic asymmetric induction in the [2,3] sigmatropic rearrangement of sulfur ylides has attracted considerable attention, and the enantioselectivity of the rearrangement reaction has been improved.[4]

All of the previous investigations in this area have used allyl sulfides to generate the sulfur ylide by reaction with a metal carbene. Because the corresponding sulfur ylides generated from propargyl sulfides can also undergo similar [2,3] sigmatropic rearrangement to give



Scheme 1.

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allenic derivatives,[5] it would be a natural extension to investigate the catalytic asymmetric induction in this reaction. Here we present the investigation in this area.

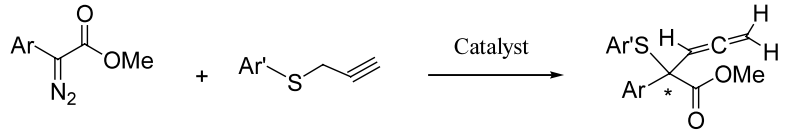
2. Results and discussion

p-Methoxyphenyldiazoacetate **1** (Ar = *p*-$MeOC_6H_4$) was used as the diazo substrate to optimize the reaction (Scheme 2).[6] A series of chiral Rh(II) and Cu(I) catalysts, which have been widely used for analogous asymmetric carbenoid reactions such as C–H insertions and cyclopropanations,[7] are examined in the current reaction and they are listed in Scheme 3. The optimization results are collected in Table 1.

Chiral Rh(II) catalysts Rh_2(5*S*-MEPY)$_4$ **4** and Rh_2(*S*-BNP)$_4$ **5** are found to give only low enantioselectivities (Table 1, entries 1 and 2). The C_2-symmetric diamine–$Cu(MeCN)_4PF_6$ complex **8** gives moderately high enantioselectivity (entry 3). Changing the aryl group of the sulfides from Ph to 2-MePh and to 2-ClPh can slightly improve the selectivity. The $Cu(MeCN)_4PF_6$/bisoxazoline **9** gives similar result (entry 6). As our previous study on analogous [2,3] sigmatropic rearrangement with allyl aryl sulfide, the $Cu(MeCN)_4PF_6$/bisoxazoline **10a** and **10b** again give the better enantioselectivity in the current reaction. We then focused on the catalyst **10b** and proceeded to further evaluate the effect of other reaction parameters. The structure of the sulfide can have a slight affect on the selectivity, and propargyl 2-chlorophenyl sulfide is found to be the best sulfide. Solvent can markedly affect the reaction. Benzene and toluene are better solvents than dichloromethane and carbon tetrachloride (compare entries 11, 14, 15 and 16). Although low temperature can improve the ee values slightly, the reaction takes much longer at low temperatures (compare entries 11 and 12).

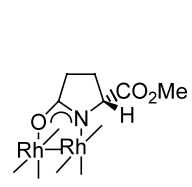
Davies et al. have applied chiral Rh(II) catalysts Rh_2(*S*-TBSP)$_4$ **6** and Rh_2(*S*-DOSP)$_4$ **7** in the catalytic asymmetric C–H insertions and cyclopropanations with aryldiazoacetates as carbenoid source, and exceptionally high enantioselectivities in those catalytic systems have been achieved.[8] Therefore, it would be worthwhile to examine those catalysts in the current reaction. The experiments demonstrated that both **6** and **7** were effective in promoting the rearrangements and to give the enantioselectivities that are comparable to the Cu(I) catalyst **10b** (compare entries 12, 17 and 20). Moreover, **6** and **7** have higher catalytic activity than **10b**. In contrast to 10 mol% of Cu(I) catalyst used in the reaction, only 1 mol% Rh(II) catalyst was sufficient to achieve the comparable reaction rate. In Rh(II) catalyzed reaction, it is possible to run the reaction at lower temperature with acceptable reaction time. However, it appears that the enantioselectivity is not improved significantly at low temperature (entries 18, 19, 21, 22).

The optimization experiments indicated that higher enantioselectivity could be obtained with $Cu(MeCN)_4PF_6$/ bisoxazoline **10b** in toluene with

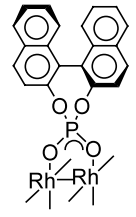


1 **2** **3**

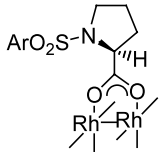
Scheme 2.



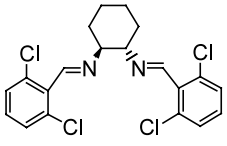
4 Rh_2(5*S*-MEPY)$_4$



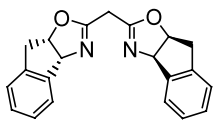
5 Rh_2(*S*-BNP)$_4$



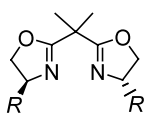
6 Rh_2(*S*-TBSP)$_4$ (Ar = 4-^{t}BuC_6H_4)
7 Rh_2(*S*-DOSP)$_4$ (Ar = 4-$CH_3(CH_2)_{10\text{-}12}C_6H_4$)



$Cu(MeCN)_4PF_6$
8



$Cu(MeCN)_4PF_6$
9



$Cu(MeCN)_4PF_6$
10a, R = Ph
10b, R = *t*Bu

Scheme 3.

Table 1. Enantioselectivity of the reaction of *p*-methoxyphenyldiazoacetate and propargyl aryl sulfide with chiral Cu(I) or Rh(II) catalyst

Entry	Catalyst[a]	Sulfide (Ar′=)	Solvent	Temp. (°C)	Time (h)	Ee (%)[b]	$[\alpha]_D$ (*c*, $CHCl_3$)	Yield[c] (%)
1	**4**	C_6H_5	Toluene	25	20	5	+3.2 (0.64)	47
2	**5**	C_6H_5	Toluene	25	2	37	−23.9 (0.83)	52
3	**8**	C_6H_5	Benzene	25	3	50	+31.8 (0.72)	45
4	**8**	2-$CH_3C_6H_4$	Benzene	25	3	52	+43.6 (0.88)	91
5	**8**	2-ClC_6H_4	Benzene	25	3	54	+33.5 (0.91)	81
6	**9**	C_6H_5	Benzene	25	3	50	+31.9 (0.81)	93
7	**10a**	C_6H_5	Benzene	25	2	51	−32.5 (0.64)	74
8	**10a**	C_6H_5	Toluene	0	20	66	−42.1 (0.80)	78
9	**10b**	C_6H_5	Benzene	25	3	57	−36.3 (0.71)	70
10	**10b**	2,6-$(CH_3)_2C_6H_3$	Benzene	0	17	61	−49.92 (0.59)	59
11	**10b**	2-ClC_6H_4	Toluene	25	3	70	−44.1 (0.74)	83
12	**10b**	2-ClC_6H_4	Toluene	0–25	18	80	−49.6 (0.89)	79
13	**10b**	2-ClC_6H_4	Toluene	−40	16	73	−45.6 (0.63)	52
14	**10b**	2-ClC_6H_4	CH_2Cl_2	25	3	59	−36.6 (0.84)	83
15	**10b**	2-ClC_6H_4	CCl_4	25	30	2	–	51
16	**10b**	2-ClC_6H_4	Benzene	25	4	69	−43.9 (0.73)	81
17	**6**	2-ClC_6H_4	Toluene	0	1	70	−44.6 (0.85)	84
18	**6**	2-ClC_6H_4	Toluene	−23	3	73	−46.8 (0.89)	96
19	**6**	2-ClC_6H_4	Toluene	−53	12	71	−43.9 (0.72)	69
20	**7**	2-ClC_6H_4	Toluene	0	1	67	−42.7 (0.84)	87
21	**7**	2-ClC_6H_4	Toluene	−23	3	70	−43.9 (0.85)	91
22	**7**	2-ClC_6H_4	Toluene	−53	12	73	−47.0 (0.86)	92

[a] For Cu(I) catalyst: chiral ligand (11 mol%) was mixed with $Cu(MeCN)_4PF_6$ (10 mol%); for Rh(II) catalyst: 1% mol catalyst is used.
[b] Ee's determined by chiral HPLC; Chiracel OJ; hexane/*iso*-propanol.
[c] Isolated yields.

propargyl 2-chlorophenyl sulfide. Thus, this reaction condition was applied to a series of aryldiazoacetates. Moreover, the effectiveness of Rh(II) catalysts **6** and **7** were also tested with other aryldiazoacetates. The results are summarized in Table 2.

The results summarized in Table 2 demonstrates that with Cu(I) catalyst **10b**, moderately high enantioselectivity can be achieved with a series of aryl diazoacetates. As in the analogous [2,3] sigmatropic reaction with allyl sulfides, there is no obvious dependence of the enantioselectivity on the substituents in the phenyl ring of the aryl diazoacetate substrates. When chiral Rh(II) catalysts **6** and **7** were used, the reaction became faster and approximately the same level of enantioselectivity could be achieved in some cases (entries 2, 3, 12, 13, 15). However, for the diazosubstrates bearing a *meta* substituent, the Rh(II) catalysts gave lower ee values (entries 5, 6, 9, 10).

Table 2. Enantioselectivity of the reaction of aryldiazoacetate **1** and propargyl 2-chlorophenyl sulfide **2** (Ar′ = 2-ClC_6H_4) with chiral Cu(I) and Rh(II) catalyst)

Entry	Diazo compound **1** (Ar=)	Catalyst[a]	Reaction time (h)[b]	Ee (%)[c]	$[\alpha]_D$ (*c*, $CHCl_3$)	Yield (%)[d]
1	*p*-$MeOC_6H_4$	**10b**	18	80	−49.6 (0.89)	79
2	*p*-$MeOC_6H_4$	**6**	1	70	−44.6 (0.85)	84
3	*p*-$MeOC_6H_4$	**7**	1	67	−42.7 (0.84)	87
4	*m*-$MeOC_6H_4$	**10b**	20	75	−43.8 (1.0)	89
5	*m*-$MeOC_6H_4$	**6**	5	36	−21.0 (0.49)	44
6	*m*-$MeOC_6H_4$	**7**	5	27	−15.8 (0.41)	48
7	*m*-MeC_6H_4	**10b**	20	81	−38.5 (0.88)	82
8	*m*-ClC_6H_4	**10b**	36	75	−40.9 (0.66)	33
9	*m*-ClC_6H_4	**6**	12	35	−19.1 (0.41)	46
10	*m*-ClC_6H_4	**7**	12	30	−16.4 (0.52)	47
11	*p*-PhC_6H_4	**10b**	20	74	−48.7 (1.1)	87
12	*p*-PhC_6H_4	**6**	12	68	−44.7 (0.69)	65
13	*p*-PhC_6H_4	**7**	12	63	−40.3 (0.70)	64
14	1-Naphthyl	**10b**	3	55	−56 (1.0)	76
15	1-Naphthyl	**7**	12	68	−69 (0.63)	42

[a] For Cu(I) catalyst: chiral ligand (11 mol%) was mixed with $Cu(MeCN)_4PF_6$ (10 mol%); for Rh(II) catalyst: 1% mol catalyst is used.
[b] For **10b** catalyzed reaction, the temperature is 0–25°C; for Rh(II) catalyzed reaction, the temperature is 0°C.
[c] Ee's determined by chiral HPLC using the condition given in Table 1.
[d] Isolated yields.

3. Conclusion

In summary, we have conducted the first investigation of the catalytic asymmetric [2,3] sigmatropic rearrangement of sulfur ylides generated from aryldiazoacetates and propargyl sulfides. Moderate to good enantioselectivities have been obtained.

4. Experimental

4.1. General

All reactions were performed under a nitrogen atmosphere in a flame-dried reaction flask, and the components were added via syringe. All solvents were distilled prior to use. For chromatography, 100–200 mesh silica gel (Qindao, China) was employed. ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz with a Varian Mercury 200 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as the internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. Mass spectra were obtained on a VG ZAB-HS mass spectrometer. Aryl diazoacetates[9] and $Cu(MeCN)_4PF_6$[10] were prepared according to literature procedures. Chiral bisoxazoline ligands, and chiral Rh(II) catalysts Rh_2(*S*-TBSP)$_4$ **6** and Rh_2(*S*-DOSP)$_4$ **7** were purchased from Aldrich. HPLC analysis was performed using an HP 1100 apparatus equipped with a Chiracel OJ column.

4.2. Typical procedure for the reaction of aryl diazoacetate with sulfide catalyzed by Cu(I) complex

Under a nitrogen atmosphere, $Cu(MeCN)_4PF_6$ (2.33 mg, 6.25×10^{-3} mmol) and ligand **10b** (2.21 mg, 7.5×10^{-3} mmol) were added to a 25 mL round-bottomed flask. Dry toluene (2 mL) was introduced and the solution was stirred for 1 h at 0°C. To the slightly blue solution was then added aryl sulfide **2** (Ar′ = 2-ClC_6H_4, 17.1 mg, 9.38×10^{-2} mmol) in toluene (1 mL). Then methyl *p*-methoxyphenyldiazoacetate (**1**, Ar = *p*-$MeOC_6H_4$) (12.88 mg, 6.25×10^{-2} mmol,) in dry toluene (2 mL) was added via a syringe over 30 min. The solution was stirred for an additional 17 h, during which the reaction temperature rise to room temperature. Solvent was removed by evaporation and the green oily residue was purified by column chromatography (petroleum ether/ethyl acetate = 20:1) to give **3** (Ar = *p*-$MeOC_6H_4$, Ar′ = 2-ClC_6H_4) as an oil (17.8 mg, 79%).

4.3. Typical procedure for the reaction of aryl diazoacetate with sulfide catalyzed by Rh(II) complex

Under a nitrogen atmospere, Rh(II) catalyst **6** (1.81 mg, 1.25×10^{-3} mmol) were added to a round-bottomed flask (25 mL) and then toluene (4 mL) was introduced. After cooling the flask in an ice bath, aryl sulfide **2** (Ar′ = 2-ClC_6H_4, 34.2 mg, 1.88×10^{-1} mmol,) in toluene (2 mL). Methyl *p*-methoxyphenyl diazoacetate (**1**, Ar = *p*-$MeOC_6H_4$) (1.25×10^{-1} mmol, 25.8 mg) in toluene (4 mL) was added via syringe over 30 min. The solution was stirred for an additional 1 h at 0°C. Solvent was removed by evaporation and the green oily residue was purified by column chromatography (petroleum/ethyl acetate = 20: 1) to give **3** (Ar = *p*-$MeOC_6H_4$, Ar′ = 2-ClC_6H_4) as an oil (37.8 mg, 84%).

4.4. Methyl 2-(*p*-methoxyl)phenyl-2-thiophenyl-3,4-pentadienoate (3, Ar = *p*-$MeOC_6H_4$, Ar′ = C_6H_5)

IR ($CDCl_3$): 1955 (m), 1733 (s); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.66 (s, 3H), 3.81 (s, 3H), 4.72 (d, J = 6.6 Hz, 2H), 5.73 (dd, J = 6.6 Hz, J = 6.8 Hz, 1H), 6.81–6.87 (m, 2H), 7.21–7.42 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 52.70, 55.12, 63.87, 78.62, 94.03, 113.31, 128.27, 128.89, 129.21, 130.75, 131.75, 136.38, 158.98, 171.24, 208.26; MS (m/z, relative intensity): 326 (M^+, 17), 265 (13), 217 (100), 202 (36), 185 (54), 158 (73), 115 (34), 110 (52), 43 (68); HPLC (254 nm): t_R = 41.09 min, t_R = 80.05 min; HRMS calcd M^+ for $C_{19}H_{18}O_3S$: 326.0986; found: 326.0976.

4.4.1. Methyl 2-(*m*-chloro)phenyl-2-thio(2-chlorophenyl)-3,4-pentadienoate (3, Ar = *m*-ClC_6H_4, Ar′ = 2-ClC_6H_4).

IR ($CDCl_3$): 1955 (m), 1735 (s); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.70 (s, 3H), 4.70 (d, J = 6.6 Hz, 2H), 5.80 (dd, J = 6.6 Hz, J = 6.8 Hz, 1H), 7.10–7.57 (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 53.01, 63.59, 78.94, 93.013, 126.36, 126.48, 127.99, 128.33, 129.14, 129.73, 129.95, 130.94, 133.81, 137.02, 139.14, 140.08, 170.14, 208.45; MS (m/z, relative intensity): 364 (M^+, 11), 326 (12), 267 (21), 220 (100), 189 (95), 162 (50), 144 (59); HPLC (254 nm): t_R = 16.427 min, t_R = 18.638 min; HRMS calcd M^+ for $C_{18}H_{14}Cl_2O_2S$: 364.0095; found: 364.0091.

4.4.2. Methyl 2-(*p*-phenyl)phenyl-2-thio(2-chlorophenyl)-3,4-pentadienoate (3, Ar = *p*-PhC_6H_4, Ar′ = 2-ClC_6H_4).

IR ($CDCl_3$): 1955 (m), 1733 (s); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.58 (s, 3H), 4.57 (d, J = 6.4 Hz, 2H), 5.76 (dd, J = 6.4 Hz, J = 6.8 Hz, 1H), 6.94–7.00 (m, 2H), 7.01–7.54 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 52.93, 63.97, 78.73, 93.30, 126.42, 126.65, 126.87, 127.36, 128.45, 128.64, 129.49, 129.67, 131.76, 136.50, 137.11, 138.66, 140.11, 140.64, 170.71, 208.54; MS (m/z, relative intensity): 406 (M^+, 25), 263 (96), 231 (100), 204 (77), 181 (38), 144 (36); HPLC (254 nm): t_R = 29.83 min, t_R = 35.22 min; HRMS calcd M^+ for $C_{24}H_{19}ClO_2S$: 406.0777; found: 406.0794.

4.4.3. Methyl 2-(*m*-methoxyl)phenyl-2-thio(2-chlorophenyl)-3,4-pentadienoate (3, Ar = *m*-$MeOC_6H_4$, Ar′ = 2-ClC_6H_4).

IR ($CDCl_3$): 1955 (m), 1734 (s); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.69 (s, 3H), 3.76 (s, 3H), 4.69 (d, J = 6.4 Hz, 2H), 5.83 (dd, J = 6.6 Hz, J = 6.8 Hz, 1H), 6.81–6.88 (m, 1H), 7.09–7.41 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 53.01, 55.17, 64.18, 78.66, 93.19, 113.35, 114.10, 120.34, 126.44, 129.06, 1259.50, 129.69, 131.77, 136.52, 138.67, 139.64, 159.27, 170.74, 208.55; MS (m/z, relative intensity): 360 (M^+, 7), 322 (20), 263 (19), 217 (70), 202 (26), 185 (100), 151 (49), 135 (84); HPLC (254 nm): t_R = 28.88 min, t_R = 32.68 min; HRMS calcd M^+ for $C_{19}H_{17}ClO_3S$: 360.0572; found: 360.0586.

4.4.4. Methyl 2-(*p*-methoxyl)phenyl-2-thio(2,6-dimethylphenyl)-3,4-pentadienoate (3, Ar = *p*-MeOC$_6$H$_4$, Ar′ = 2,6-(CH$_3$)$_2$C$_6$H$_3$). IR ($CDCl_3$): 1954 (w), 1729 (s); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.47 (s, 6H), 3.67 (s, 3H), 3.82 (s, 3H), 4.55 (d, J = 6.6 Hz, 2H), 5.89 (dd, J = 6.8 Hz, J = 6.2 Hz, 1H), 6.87–6.93 (m, 2H), 7.09–7.20 (m, 3H), 7.56–7.61 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 22.66, 52.50, 55.00, 62.17, 77.94, 94.28, 112.89, 127.89, 129.44, 129.56, 130.47, 131.05, 146.03, 158.78, 172.00, 207.94; MS (m/z, relative intensity): 354 (M^+, 50), 339 (10), 217 (100), 202 (37), 189 (19), 185 (38), 158 (52), 137 (29); HPLC (254 nm): t_R = 21.87 min, t_R = 38.12 min; HRMS calcd M^+ for $C_{21}H_{22}O_3S$: 354.1282; found: 354.1289.

4.4.5. Methyl 2-(*m*-methyl)phenyl-2-thio(2-chlorophenyl)-3,4-pentadienoate (3, Ar = *m*-MeC$_6$H$_4$, Ar′ = 2-ClC$_6$H$_4$). IR ($CDCl_3$): 1955 (w), 1734 (s); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.32 (s, 3H), 3.69 (s, 3H), 4.67 (d, J = 6.4 Hz, 2H), 5.83 (dd, J = 6.4 Hz, J = 6.6 Hz, 1H), 7.04–7.41 (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.39, 52.91, 64.220, 78.54, 93.30, 124.96, 126.36, 127.97, 128.46, 128.73, 129.37, 129.63, 131.92, 136.43, 137.72, 138.03, 138.56, 170.87, 208.54; MS (m/z, relative intensity): 344 (M^+, 10), 201 (84), 169 (100), 144 (27), 142 (68), 115 (50), 108 (27); HPLC (254 nm): t_R = 20.50 min, t_R = 24.73 min; HRMS calcd M^+ for $C_{19}H_{17}ClO_2S$: 344.0622; found: 344.0637.

4.4.6. Methyl 2-(*p*-methoxyl)phenyl-2-thio(2-chlorophenyl)-3,4-pentadienoate (3, Ar = *p*-MeOC$_6$H$_4$, Ar′ = 2-ClC$_6$H$_4$). IR ($CDCl_3$): 1956 (w), 1731 (s); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.69 (s, 3H), 3.76 (s, 3H), 4.67 (d, J = 6.4 Hz, 2H), 5.85 (dd, J = 6.4 Hz, J = 6.8 Hz, 1H), 6.85 (d, J = 9 Hz, 2H), 7.07–7.39 (m, 4H), 7.50 (d, J = 9.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 52.80, 54.99, 63.59, 78.52, 93.38, 113.32, 126.32, 129.19, 129.53, 129.88, 131.98, 136.03, 138.19, 159.06, 170.79, 208.41; MS (m/z, relative intensity): 360 (M^+, 16), 301 (10), 217.1 (100), 202 (52), 185 (57), 158 (87), 144 (37); HPLC (254 nm): t_R = 42.433 min, t_R = 52.569 min; HRMS calcd M^+ for $C_{19}H_{17}ClO_3S$: 360.0576; found: 360.0586.

4.4.7. Methyl 2-naphthyl-2-thio(2-chlorophenyl)-3,4-pentadienoate (3, Ar = naphthyl, Ar′ = 2-ClC$_6$H$_4$). IR ($CDCl_3$): 1732 (m); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.56 (s, 3H), 4.34 (dd, J = 6.6 Hz, J = 6.6 Hz, 1H), 4.60 (dd, J = 6.4 Hz, J = 6.4 Hz, 1H), 6.01 (dd, J = 6.6 Hz, J = 6.4 Hz, 1H), 7.12–7.16 (m, 1H), 7.23–7.31 (m, 1H), 7.42–7.50 (m, 5H), 7.80–7.91 (m, 3H), 8.09–8.12 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 52.68, 60.084, 63.87, 78.22, 93.95, 124.47, 1124.59, 125.13, 125.79, 126.29, 126.39, 128.82, 129.11, 129.75, 130.36, 130.48, 131.01, 133.94, 134.02, 139.07, 140.46, 171.40, 208.28; MS (m/z, relative intensity): 380 (M^+, 6), 237 (23), 200 (45), 199 (64), 171 (31), 155 (97), 141 (100), 127 (72); HPLC (254 nm): t_R = 28.68 min, t_R = 39.68 min; HRMS calcd M^+ for $C_{22}H_{17}ClO_2S$: 380.0620; found: 380.06378.

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