# Catalytic Asymmetric [2,3]-Sigmatropic Rearrangement of Sulfur Ylides Generated from Carbenoids and Allenic 2-Methylphenyl Sulfide†

**ZHANG, Xiao-Mei**[a](张晓梅) **MA, Ming**[a](马明) **WANG, Jian-Bo***[,a,b](王剑波)

[a] *Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, Department of Chemical Biology, College of Chemistry, Peking University, Beijing 100871, China*

[b] *State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China*

**The first investigation on catalytic asymmetric [2,3]-sigmatropic rearrangement of sulfur ylides generated from carbenoids and allenic phenyl sulfide was carried out. Up to 55% *ee* value was obtained.**

**Keywords** carbenoid, sulfur ylide, [2,3]-sigmatropic rearrangement, catalytic asymmetric synthesis

## Introduction

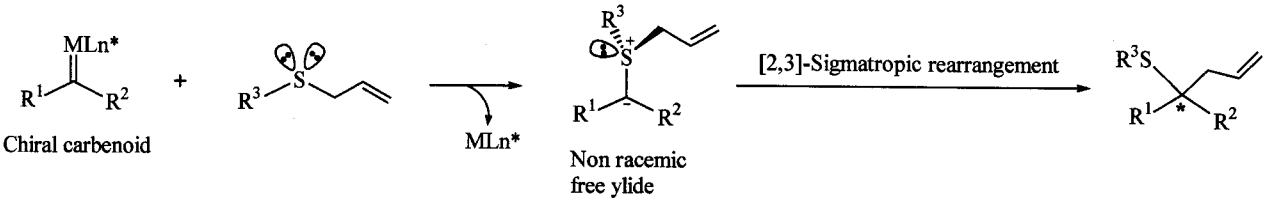
The catalytic asymmetric reactions of oxygen or sulfur ylides generated from carbenoids have attracted considerable attention in recent years.[1] High enantioselectivities have been achieved in the 1,3-dipolar cycloaddition reaction and [2,3]-sigmatropic rearrangement of oxygen ylides.[1,2] In contrast to the oxygen ylide, the corresponding catalytic asymmetric reaction of sulfur ylide is less developed. Compared to oxygen ylides, the sulfur ylides are more stable and experimental evidence supports a free ylide rather than a metal-bound ylide as reaction intermediate.[3] It means that the enantio-control must be in the step of the ylide formation. If the subsequent reaction such as [2,3]-sigmatropic rearrangement or 1,3-dipolar cycloaddition is a concerted process and is faster than the racemization of the chiral ylide intermediate, the catalytic asymmetric sulfur ylide reaction will be possible. Several groups have pioneered in this area, and moderate enantioselectivities have been achieved[4] (Scheme 1).

We have recently studied the catalytic asymmetric [2,3]-sigmatropic rearrangements of sulfur ylides generated from carbenoids and allyl sulfides or propargyl sulfides (Scheme 2). Up to 78% *ee* and 81% *ee* have been achieved, and these are the highest enantioselectivities ever reported in these types of reactions.[5] Since the sulfur ylides generated from carbenoids and allenic sulfides can rearrange to give sulfide containing propargyl group,[6] it would be a natural extension to further study the enantioselectivity of this transformation with chiral catalysts (Scheme 3).

The methyl *p*-methoxyphenyldiazoacetate (**1**) (Ar = *p*-$MeOC_6H_4$) was used as the substrate. The Rh(II) and Cu(I) chiral catalysts commonly used in catalytic asymmetric carbenoid reaction have been evaluated in the current reaction. Two allenic sulfides, **6a** and **6b**, were studied. The results are summarized in Table 1.

The data in Table 1 clearly indicates that the Rh(II) catalysts **8** and **9**, and Cu(I) catalysts **12** and **13** are less efficient compared to the catalysts **10**, **11**, **14a** and **14b** (Scheme 4). Rh(II) catalysts are found to be more reactive than Cu(I) catalysts. Consequently, less Rh(II) catalysts are required and the reaction time is much shorter.

**Scheme 1**




* E-mail: wangjb@pku.edu.cn

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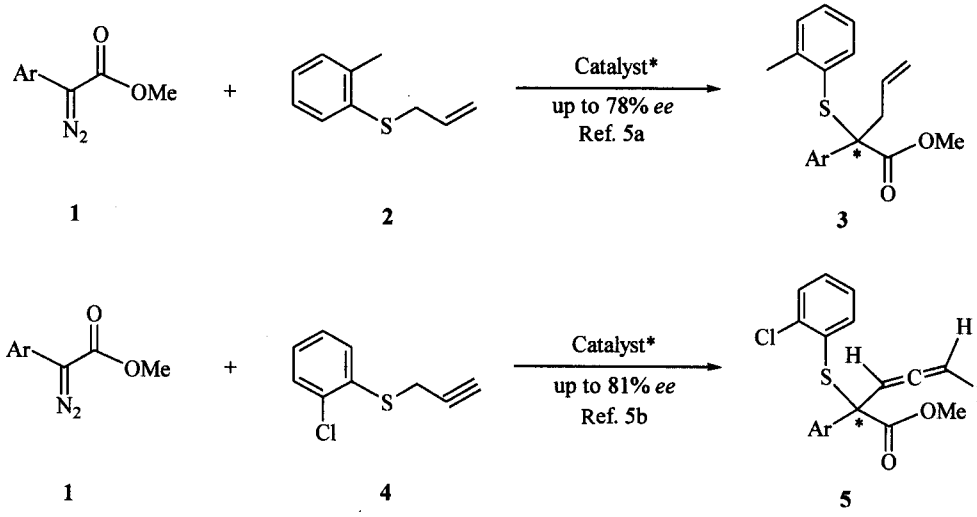
†Dedicated to Professor ZHOU Wei-Shan on the occasion of his 80th birthday.

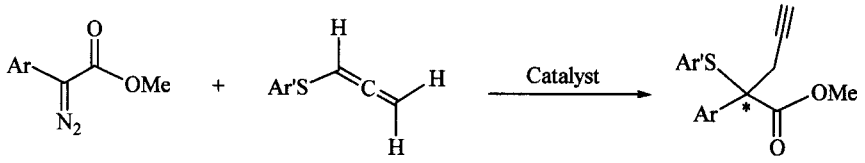
**Scheme 2**




1 2 3

1 4 5

**Scheme 3**




1 **6a** Ar = $C_6H_5$ **6b** Ar' = *o*-$ClC_6H_4$ 7

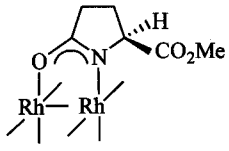
**a** Ar = $C_6H_5$, Ar' = $C_6H_5$
**b** Ar = *p*-$MeOC_6H_4$, Ar' = $C_6H_4$
**c** Ar = *m*-$MeOC_6H_4$, Ar' = $C_6H_4$
**d** Ar = *m*-$ClC_6H_4$, Ar' = $C_6H_4$
**e** Ar = *p*-$BrC_6H_4$, Ar' = $C_6H_4$
**f** Ar = *p*-$ClC_6H_4$, Ar' = $C_6H_4$
**g** Ar =  , Ar' = $C_6H_4$
**h** Ar = *p*-$PhC_6H_4$, Ar' = $C_6H_4$
**i** Ar = *p*-$MeOC_6H_4$, Ar' = *o*-$ClC_6H_4$

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

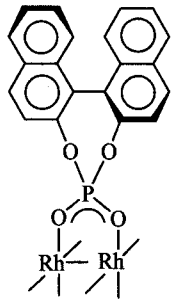
| Entry | Catalyst[a] | Sulfide (Ar' = ) | Solvent | Temp. (℃) | Time (h) | *ee*[b] (%) | Yield[c] (%) |
|---|---|---|---|---|---|---|---|
| 1 | **8** | $C_6H_5$ | Toluene | r.t. | 8 | 0 | 40 |
| 2 | **9** | $C_6H_5$ | Toluene | r.t. | 1 | 0 | 38 |
| 3 | **10** | $C_6H_5$ | Toluene | r.t. | 0.1 | 34 | 45 |
| 4 | **11** | $C_6H_5$ | Toluene | r.t. | 0.1 | 30 | 47 |
| 5 | **12** | $C_6H_5$ | Toluene | r.t. | 16 | 6 | 49 |
| 6 | **13** | $C_6H_5$ | Toluene | r.t. | 12 | 12 | 69 |
| 7 | **14a** | $C_6H_5$ | Toluene | r.t. | 12 | 41 | 92 |
| 8 | **14b** | $C_6H_5$ | Toluene | r.t. | 16 | 40 | 79 |
| 9 | **14b** | *o*-$ClC_6H_4$ | Toluene | r.t. | 12 | 28 | 72 |
| 10 | **10** | $C_6H_5$ | Toluene | 0.5 | 37 | 51 | — |
| 11 | **14b** | $C_6H_5$ | Toluene | 0 | 30 | 46 | 63 |
| 12 | **11** | $C_6H_5$ | Toluene | −23 | 4.5 | 47 | 48 |
| 13 | **10** | $C_6H_5$ | Toluene | −23 | 4.5 | 44 | 50 |
| 14 | **11** | $C_6H_5$ | Toluene | −40 | 14 | 44 | < 10 |
| 15 | **11** | $C_6H_5$ | Toluene | −40 | 14 | 36 | < 10 |
| 16 | **11** | $C_6H_5$ | *n*-Hexane | −50—0 | 10 | 55 | 79 |
| 17 | **14b** | $C_6H_5$ | *n*-Hexane | r.t. | 12 | 20 | 31 |
| 18 | **11** | $C_6H_5$ | $CH_2Cl_2$ | 0 | 1 | 23 | 49 |
| 19 | **10** | $C_6H_5$ | *n*-Hexane | −50—0 | 10 | 36 | 65 |

[a] For Cu(I) catalyst: chiral ligand (11 mol%) was mixed with $Cu(MeCN)_4PF_6$ (10 mol%); for Rh(II) catalyst: 0.5 mol% catalyst is used; [b] *ee* values were determined by chiral HPLC; Chiracel OJ; hexane/*iso*-propanol; [c] isolated yields.

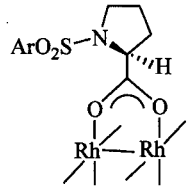
**Scheme 4**



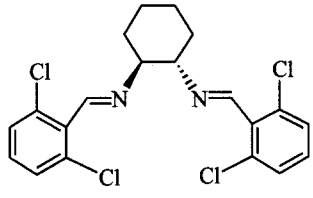
**8** $Rh_2(5S\text{-MEPY})_4$



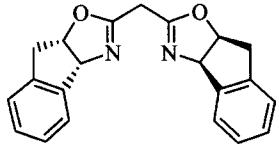
**9** $Rh_2(R\text{-BNP})_4$



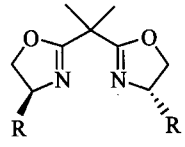
**10** $Rh_2(S\text{-TBSP})_4$ (Ar = 4-*t*-$BuC_6H_4$)
**11** $Rh_2(S\text{-DOSP})_4$ (Ar = 4-$CH_3(CH_2)_{10-12}C_6H_4$)



$Cu(MeCN)_4PF_6$
**12**



$Cu(MeCN)_4PF_6$
**13**



$Cu(MeCN)_4PF_6$
**14a** R = Ph
**14b** R = *t*-Bu

These results are similar to what was observed in our previous studies with allyl and propargyl sulfides. We then focused on the catalysts **10**, **11**, **14a** and **14b**, and proceeded to evaluate the effect of temperature, solvent and the structure of sulfide. Since the aryl sulfide with *ortho* substituent in the phenyl ring gave superior results, we expected the sulfide **6b** might give better enantioselectivity. However, we observed an opposite result, the *ee* value dropped from 40% to 28% when the sulfide was changed from **2a** to **2b** (compare Entries 8 and! 9). The temperature can generally enhance the enantioselectivity, but the reaction becomes slower at lower temperature. For the Cu(I) catalysts, even the reactions at room temperature take long time (12—16 h). Finally, the solvent is found to have an effect on the enantioselectivity. Nonpolar solvent such as *n*-hexane can enhance the *ee* values (compare Entries 15 and 16). Thus, it can be concluded that the reaction with the catalysts **10**, **11**, **14a** or **14b**, in *n*-hexane at 0 ℃ can give the optimized results in terms of enantioselectivity and the reaction time. Then this condition was applied to other methyl aryldiazoacetates, and the results are summarized in Table 2.

The data collected in Table 2 show that moderately high enantioselectivity could be achieved under the optimized condition for diazo substrates. There is apparent effect of the substituent in the phenyl ring on the enantioselectivity. The diazo substrate with *meta* substituent gave diminished *ee* % (Entries 4, 6 and 7).

In conclusion, we have carried out the first investigation on catalytic asymmetric [2,3]-sigmatropic rearrangement

**Table 2** Enantioselectivity of the reaction of aryldiazoacetate **1** and allenic phenyl sulfide **6a** with chiral Cu(I) and Rh(II) catalyst

| Entry | Diazo compound **1** (Ar = ) | Catalyst[a] | Reaction time (h) | *ee*[b] (%) | $[\alpha]_D^{20}$ (*c*, $CHCl_3$) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | *p*-$MeOC_6H_4$ | **14b**/$Cu(MeCN)_4PF_6$ | 16 | 40 | −34.6 (0.46) | 67 |
| 2 | *p*-$MeOC_6H_4$ | **10**[c] | 24 | 36 | −31.2 (0.57) | 65 |
| 3 | *p*-$MeOC_6H_4$ | **11**[c] | 10 | 55 | −42.9 (0.62) | 79 |
| 4 | *m*-$MeOC_6H_4$ | **11**[c] | 24 | 10 | −10.8 (0.33) | 32 |
| 5 | $C_6H_4$ | **11**[c] | 7 | 33 | +25.6 (0.45) | 58 |
| 6 | *m*-$ClC_6H_4$ | **14b**/$Cu(MeCN)_4PF_6$ | 24 | 27 | −19.5 (0.6) | 50 |
| 7 | *m*-$ClC_6H_4$ | **11**[c] | 7 | 22 | +14.1 (0.46) | 50 |
| 8 | *p*-$BrC_6H_4$ | **14b**/$Cu(MeCN)_4PF_6$ | 24 | 32 | −27.8 (0.77) | 65 |
| 9 | *p*-$BrC_6H_4$ | **11**[c] | 7 | 32 | +25.4 (0.54) | 56 |
| 10 | *p*-$PhC_6H_4$ | **11**[c] | 7 | 35 | +40.3 (0.33) | 49 |
| 11 | *p*-$ClC_6H_4$ | **11**[c] | 7 | 38 | +23.2 (0.7) | 56 |
| 12 | 1-Thienyl | **11**[c] | 18 | 51 | −30.9 (0.53) | 64 |

[a] Bisoxazoline ligand (11 mol%) was mixed with $Cu(MeCN)_4PF_6$ (10 mol%); [b] *ee* values determined by chiral HPLC using the condition given in Table 1; [c] 0.5 mol% catalyst is used.

of sulfur ylides generated from carbenoids and allenic 2-methylphenyl sulfide, and obtained up to 55% *ee* value. Further investigation is needed in order to improve the enantioselectivity for this type of reaction.

## Experimental

*General consideration*

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 NMR and $^{13}$C NMR spectra were recorded respectively at 300 and 75 MHz with Varian Mercury 300 spectrometer. Chemical shifts were reported 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. Aryl diazoacetates and $Cu(MeCN)_4PF_6$ were prepared according to the reported procedure.[7] Chiral bisoxazoline ligands, and chiral Rh(II) catalysts $Rh_2$(S-TBSP)$_4$ (**10**) and $Rh_2$(S-DOSP)$_4$ (**11**) were purchased from Aldrich. HPLC analysis was performed at HP 1100 apparatus with Chiracel OJ column.

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

In nitrogen atmosphere, $Cu(MeCN)_4PF_6$ ($6.25\times10^{-3}$ mmol, 2.3 mg) and ligand **14b** ($7.5\times10^{-3}$ mmol, 2.2 mg) were added to a 25 mL round-bottom flask. Dry *n*-hexane (4 mL) was introduced and the solution was stirred for 1 h. To this slightly blue solution was then added aryl sulfide **6a** (Ar′ = $C_6H_4$, $9.4\times10^{-2}$ mmol, 13.9 mg) in *n*-hexane (1 mL). The flask was put into an ice bath, then methyl *p*-methoxyphenyldiazoacetate (**1**, Ar = *p*-$MeOC_6H_4$) ($6.25\times10^{-2}$ mmol, 12.9 mg) in dry *n*-hexane (10 mL) was added via a syringe over 30 min. The solution was stirred for additional 10 h. Solvent was removed by evaporation and the green oily residue was purified by column chromatography (petroleum ether/ethyl acetate = 20∶1) to give **7b** (*ee* = 44%, Ar = *p*-$MeOC_6H_4$, Ar′ = $C_6H_4$) as oil (13.8 mg, 67%).

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

In nitrogen atmosphere, catalyst **11** ($3.13\times10^{-4}$ mmol, 0.6 mg) was added to a 25 mL round-bottom flask. Dry *n*-hexane (4 mL) was introduced and the solution was stirred for 1 h. To the slightly blue solution was then added aryl sulfide **6a** (Ar′ = $C_6H_4$, $9.4\times10^{-2}$ mmol, 13.9 mg) in *n*-hexane (1 mL). The flask was put into an ice bath, then methyl *p*-methoxyphenyldiazoacetate (**1**, Ar = *p*-$MeOC_6H_4$) ($6.25\times10^{-2}$ mmol, 12.9 mg) in dry *n*-hexane (10 mL) was added via a syringe over 30 min. The solution was stirred for additional 10 h. Solvent was removed by evaporation and the green oily residue was purified by column chromatography (petroleum ether∶ethyl acetate = 20∶1) to give **7b** (*ee* = 55%, Ar = *p*-$MeOC_6H_4$, Ar′ = $C_6H_4$) as oil (16.1 mg, 79%).

*Methyl 2-phenyl-2-thiophenyl-4-pentynoate* (**7a**, Ar = $C_6H_5$, Ar′ = $C_6H_5$)

$^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 2.10 (dd, $J$ = 2.7, 2.4 Hz, 1H), 2.97 (dq, $J$ = 16.8, 2.7, 2.4 Hz, 2H), 3.72 (s, 3H), 7.22—7.39 (m, 10 H); $^{13}$CNMR (75 MHz, $CDCl_3$) $\delta$: 27.92, 52.90, 62.98, 72.02, 79.74, 127.17, 127.89, 128.12, 128.72, 129.74, 129.89, 137.04, 138.24, 171.56; IR (KBr) $\nu$: 2122 (w), 1732 (s) cm$^{-1}$; MS (70 eV) *m/z* (%): 296 ($M^+$, 12), 237 (8), 187 (58), 155 (42), 128 (67), 105 (70), 86 (100); HPLC (254 nm) $t_R$ = 42.393 min, $t_R$ = 57.418 min. HRMS calcd for $C_{18}H_{16}O_2S$ 296.0871, found 296.0870.

*Methyl 2-(p-methoxyl) phenyl-2-thiophenyl-4-pentynoate* (**7b**, Ar = *p*-$MeOC_6H_4$, Ar′ = $C_6H_5$)

$^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 2.10 (dd, $J$ = 2.7, 2.4 Hz, 1H), 2.95 (dq, $J$ = 16.8, 2.7, 2.4 Hz, 2H), 3.72 (s, 3H), 3.77 (s, 3H), 6.82—6.88 (m, 1H), 7.21—7.49 (m, 8H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 27.82, 52.74, 55.04, 62.38, 71.92, 79.86, 128.42, 128.62, 128.85, 128.95, 129.59, 130.03, 136.89, 171.60; IR (KBr) $\nu$: 2121 (w), 1731 (s) cm$^{-1}$; MS (70 eV) *m/z* (%): 326 ($M^+$, 5), 287 (17), 217 (100), 185 (46), 157 (80), 135 (47); HPLC (254 nm) $t_R$ = 39.343 min, $t_R$ = 64.070 min. HRMS calcd for $C_{19}H_{18}O_3S$ 326.0976, found 326.0983.

*Methyl 2-(m-methoxyl) phenyl-2-thiophenyl-4-pentynoate* (**7c**, Ar = *m*-$MeOC_6H_4$, Ar′ = $C_6H_5$)

$^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 2.11 (dd, $J$ = 2.7, 1.8 Hz, 1H), 2.95 (dq, $J$ = 16.9, 2.7, 2.4 Hz, 2H), 3.73 (s, 3H), 3.747 (s, 3H), 6.81—6.85 (m, 1H), 6.92—6.95 (m, 2H), 7.20—7.28 (m, 3H), 7.33—7.40 (m, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 27.89, 52.91, 55.16, 62.92, 72.03, 79.73, 113.21, 119.41, 128.70, 129.06, 129.73, 129.87, 137.00, 139.71, 171.44; IR (KBr) $\nu$: 2121 (w), 1732 (s) cm$^{-1}$; MS (70 eV) *m/z* (%): 326 ($M^+$, 26), 287 (19), 267 (13), 227 (10), 217 (100), 185 (97), 158 (85), 128 (44); HPLC (254 nm) $t_R$ = 38.426 min, $t_R$ = 42.242 min. HRMS calcd for $C_{19}H_{18}O_3S$ 326.0976; found 326.0979.

*Methyl 2-(m-chloro) phenyl-2-thiophenyl-4-pentynoate* (**7d**, Ar = *m*-$ClC_6H_4$, Ar′ = $C_6H_5$)

$^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 2.12 (dd, $J$ = 2.7,

2.4 Hz, 1H), 2.95 (dq, $J$ = 16.8, 2.7, 2.4 Hz, 2H), 3.74 (s, 3H), 7.27—7.39 (m, 9H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 27.95, 53.04, 62.46, 72.30, 79.28, 125.56, 127.66, 128.09, 128.85, 129.30, 129.47, 130.00, 134.06, 137.06, 140.22, 170.99; IR (KBr) $\nu$: 2127 (w), 1704 (s) cm$^{-1}$; MS (70 eV) $m/z$ (%): 330 ($M^+$, 22.5), 291 (13.8), 273 (6), 231 (11), 221 (58), 189 (53), 162 (34), 155 (39), 142 (44), 127 (58), 110 (100); HPLC (254 nm) $t_R$ = 37.376 min, $t_R$ = 43.787 min. HRMS calcd for $C_{18}H_{15}O_2SCl$ 330.0481; found 330.0478.

*Methyl 2-(p-bromo)phenyl-2-thiophenyl-4-pentynoate* (**7e**, Ar = $p$-$BrC_6H_4$, Ar′ = $C_6H_5$)

$^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 2.10 (dd, $J$ = 2.7, 2.4 Hz, 1H), 2.94 (dq, $J$ = 16.8, 2.7, 2.4 Hz, 2H), 3.74 (s, 3H), 7.24—7.47 (m, 9H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 27.93, 52.99, 62.38, 72.28, 79.40, 122.07, 128.88, 129.17, 129.58, 129.97, 131.21, 137.21, 137.03, 137.28, 171.09; IR (KBr) $\nu$: 2123 (w), 1732 (s) cm$^{-1}$; MS (70 eV) $m/z$ (%): 374 ($M^+$, 20), 315 (10), 267 (100), 235 (45), 201 (270, 185 (69), 155 (36); HPLC (254 nm) $t_R$ = 19.817 min, $t_R$ = 24.004 min. HRMS calcd for $C_{18}H_{15}O_2SBr$ 373.9976; found 373.9984.

*Methyl 2-(p-chloro)phenyl-2-thiophenyl-4-pentynoate* (**7f**, Ar = $p$-$ClC_6H_4$, Ar′ = $C_6H_5$)

$^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 2.10 (dd, $J$ = 2.7, 2.4 Hz, 1H), 2.94 (dq, $J$ = 15.6, 2.7, 2.4 Hz, 2H), 3.72 (s, 3H), 7.13—7.40 (m, 9H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 27.99, 53.00, 62.34, 72.25, 79.44, 128.26, 128.87, 129.62, 129.97, 133.84, 136.31, 136.74, 137.03, 171.16; IR (KBr) $\nu$: 2121 (w), 1733 (s) cm$^{-1}$; MS (70 eV) $m/z$ (%): 330 ($M^+$, 17), 298 (6), 271 (12), 231 (6), 221 (97), 189 (69), 162 (50), 139 (100), 110 (46); HPLC (254 nm) $t_R$ = 41.098 min, $t_R$ = 80.051 min. HRMS calcd for $C_{18}H_{15}O_2SCl$ 330.0481, found 330.0466.

*Methyl 2-(3-thiophen)-2-thiophenyl-4-pentynoate* (**7g**, Ar = $m$-$C_4H_3S$, Ar′ = $C_6H_5$)

$^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 2.07 (dd, $J$ = 2.7, 2.4 Hz, 1H), 2.98 (dq, $J$ = 17.3, 2.7, 2.4 Hz, 2H), 7.19—7.39 (m, 8H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 27.86, 52.94, 59.73, 71.97, 79.85, 123.43, 125.44, 127.52, 128.74, 129.83, 130.02, 136.96, 138.48, 170.85; IR (KBr) $\nu$: 2098 (w), 1732 (s) cm$^{-1}$; MS (70 eV) $m/z$ (%): 302 ($M^+$, 9), 243 (9), 193 (58), 161 (52), 134 (46), 111 (100); HPLC (254 nm) $t_R$ = 32.201 min, $t_R$ = 40.668 min. HRMS calcd for $C_{16}H_{14}O_2S_2$ 302.0435, found 302.0436.

*Methyl 2-(p-phenyl)phenyl-2-thiophenyl-4-pentynoate* (**7h**, Ar = $p$-$PhC_6H_4$, Ar′ = $C_6H_5$)

$^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 2.11 (dd, $J$ = 2.7, 2.4 Hz, 1H), 3.01 (dq, $J$ = 16.9, 2.7, 2.4Hz, 2H), 3.72 (s, 3H), 7.18—7.70 (m, 14H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 27.86, 52.89, 62.74, 72.14, 79.74, 126.69, 126.92, 127.41, 127.66, 128.73, 129.75, 129.88, 137.03, 137.14, 140.09, 140.55, 171.47; IR (KBr) $\nu$: 2123 (w), 1732 (s) cm$^{-1}$; MS (70 eV) $m/z$ (%): 372 ($M^+$, 5), 263 (83), 231 (24), 203 (45), 181 (23), 152 (15), 86 (99), 84 (98), 47 (100); HPLC (254 nm) $t_R$ = 20.788 min, $t_R$ = 24.984 min. HRMS calcd for $C_{24}H_{20}O_2S$ 372.1184, found 372.1179.

*Methyl 2-(p-methoxyl)phenyl-2-thio(2-chlorophenyl)-4-pentynoate* (**7i**, Ar = $p$-$MeOC_6H_4$, Ar′ = 2-$ClC_6H_5$)

$^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 2.05 (t, $J$ = 2.4 Hz, 1H), 3.06 (d, $J$ = 2.4 Hz, 2H), 3.75 (s, 3H), 3.78 (s, 3H), 6.84—7.46 (m, 7H), 8.00—8.03 (m, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 28.81, 52.97, 55.21, 62.59, 71.97, 79.91, 113.41, 114.21, 126.84, 128.98, 129.52, 130.09, 130.87, 132.62, 138.93, 140.73, 171.31; IR (KBr) $\nu$: 1735 (s) cm$^{-1}$; MS (70 eV) $m/z$ (%): 360 ($M^+$, 1.4), 301 (3), 217 (100), 189 (8), 185 (27), 157 (34), 151 (11), 115 (21); HPLC (254 nm) $t_R$ = 43.972 min, $t_R$ = 71.765 min. HRMS calcd for $C_{19}H_{17}O_3SCl$ 360.0594, found 360.0587.

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