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# A Novel Stereoselective Synthesis of (*Z*)-α-Arylsulfanyl-α,β-Unsaturated Ketones via Stille Coupling of (*E*)-α-Arylsulfanylvinylstannanes with Acyl Halides

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ABSTRACT: *(E)-α-Arylsulfanylvinylstannanes react with acyl halides in the presence of a catalytic amount of $Pd(PPh_3)_4$ and CuI cocatalyst to give stereoselectively the corresponding (Z)-α-arylsulfanyl-α,β-unsaturated ketones in good yields.* © 2009 Wiley Periodicals, Inc. Heteroatom Chem 20:218–223, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20536

## *INTRODUCTION*

α,β-Unsaturated ketones are one of the most widely used synthetic building blocks, and a variety of synthetic methods for the synthesis of α,β-unsaturated ketones have been reported. Of these methods, the aldol condensation is one of the most powerful synthetic tools for them [1,2]. The Friedel–Crafts reaction of acyl chlorides, acids, or anhydrides with olefins is also an important route to the α,β-unsaturated ketones [3]. The hydrozirconation of alkynes, followed by aluminum chloride promoted acylation of the resulting vinylzirconium compounds, has provided a convenient method for stereoselective synthesis of α,β-unsaturated ketones [4].

The synthesis of heteroatom-containing α,β-unsaturated ketones has also attracted considerable interest in organic synthesis because many useful functional group transformations can be achieved by introduction and removal of heteroatom functions. Sung et al. reported that hydrozirconation of acetylenic tellurides, followed by the reaction with acyl halides in the presence of CuI, gave α-organotelluro-α,β-unsaturated ketones [5]. Zhao and Huang described the synthesis of (*Z*)-β-selenyl-α,β-unsaturated ketones by CuX-catalyzed selenocarbonylation addition reaction of selenoesters to nonactivated terminal alkynes [6]. (*Z*)-α-Selenyl-α,β-unsaturated ketones could be prepared by utilizing either a Wittig-type reaction of α-phenylselanyl arsonium ylides with carbonyl compounds [7] or through palladium-catalyzed acylation of (*E*)-α-selanylvinylstannanes with acyl halides [8]. α-Arylthio- or alkylthio-α,β-unsaturated ketones are very useful synthetic intermediates [9–12]. For example, they have been used in preparation of 2,3-dihydrofurans [13], 1,4- and 1,5-dicarbonyl

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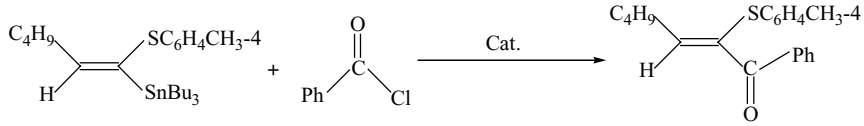
compounds [14], in the regioselective alkylation of cyclohexanones [11]. Some methods for the synthesis of α-arylthio- or alkylthio-α,β-unsaturated ketones have been developed including the Pummerer rearrangement of 2-arylsulfinyl ketones [15–17], the NaOH-catalyzed thiolysis of α,β-epoxyketones [18], and the Rh-catalyzed diazo decomposition of the β-thio group α-diazo ketones [19]. Despite considerable methodological differentiation, the reported procedures usually require starting materials which are not readily available, there still exists a need for new selective and convenient methods. Our group has reported the Stille coupling reactions of (*E*)-α-arylsulfanyl- or selenenyl-substituted vinylstannanes with organic halides in the presence of a catalytic amount of $Pd(PPh_3)_4$ and CuI cocatalyst, providing new methods for stereoselective synthesis of 1,2-disubstituted vinyl sulfides [20] and 2-selenenyl-substituted 1,3- and 1,4-dienes [21,22]. Very recently, we have found that (*E*)-α-arylsulfonyl-substituted vinylstannanes can also be coupled with aryl iodides or alkynyl bromides in the presence of $Pd(PPh_3)_4$ and CuI cocatalyst, to afford 1,2-disubstituted vinyl sulfones [23] and 2-sulfonyl-substituted 1,3-enynes [24], respectively. However, to the best of our knowledge, there has been no general study of the Stille coupling reaction of (*E*)-α-arylsulfanylvinylstannanes with acyl halides described to date. Herein we wish to report that (*Z*)-α-arylsulfanyl-α,β-unsaturated ketones can be conveniently synthesized by the Stille coupling reaction of (*E*)-α-arylsulfanylvinylstannanes with acyl halides in the presence of a catalytic amount of $Pd(PPh_3)_4$ and CuI cocatalyst in good yields.

## *RESULTS AND DISCUSSION*

Palladium-catalyzed hydrostannylation of alkynes provides a simple, general route for the synthesis of vinylstannanes [25]. Palladium-catalyzed hydrostannylation of arylsulfanylalkynes has been reported to be high regio- and stereoselective, giving (*E*)-α-arylsulfanylvinylstannanes in high yields [26]. (*E*)-α-Arylsulfanylvinylstannanes are the difunctional group reagents in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinylstannanes and as vinyl sulfides. Vinylstannanes can undergo the Stille coupling with organic halides [27,28]. The coupling reaction of (*E*)-α-arylsulfanylvinylstannanes with vinylic halides was conducted in the presence of a palladium-copper cocatalyst and gave 2-arylsulfanyl-substituted 1,3-dienes stereoselectively [29]. With the extended application of the (*E*)-α-arylsulfanylvinylstannanes in organic synthesis, we attempted to carry out the coupling reaction of (*E*)-α-arylsulfanylvinylstannanes with acyl halides in the presence of a palladium-copper cocatalyst.

Initially, to determine the optimum conditions, the cross-coupling reaction of benzoyl chloride (1.1 equiv) with (*E*)-1-(4-methylphenyl)sulfanyl-1-tributylstannyl-1-hexene was examined under various reaction conditions (Scheme 1). The results are summarized in Table 1. Among the palladium-phosphine complexes screened, $Pd(PPh_3)_4$ showed the best catalytic activity (yield 82%); whereas the yields were low in the presence of other palladium-phosphine complexes such as $PdCl_2(PPh_3)_2$ (21%), $PdBnCl(PPh_3)_2$ (29%), and $PdCl_2$(dppe) (trace) even under sealed-tube conditions. Phosphine-free palladium catalysts such as $PdCl_2$, $Pd(OAc)_2$, and $Pd_2(dba)_3$ exhibited no catalytic activity for the reaction. It was found that benzene was the best solvent among those tested, such as DMF, THF, $CH_2Cl_2$, and toluene. The same reaction performed in toluene afforded the coupled product in moderate yield. The cross-coupling reaction proceeded smoothly in benzene at reflux temperature in the presence of 5 mol% $Pd(PPh_3)_4$ and 75 mol% CuI, affording the corresponding coupled product in 82% yield after 7 h; while the same reaction under sealed-tube conditions gave the coupled product in only 83% yield. The reaction did not occur in the presence of $Pd(PPh_3)_4$ without the cocatalyst (CuI) after 72 h even under sealed-tube conditions. It may be a possible mechanistic explanation for the role of CuI that a preliminary transmetallation from the organostannane to a more reactive organocopper intermediate has taken place during the Stille coupling reaction [30]. Tin to copper transmetallation has also been suggested in other studies, utilizing organostannanes in conjunction with copper [31–34]. On the other hand, the reaction also did not occur in the presence of CuI without any palladium catalyst.



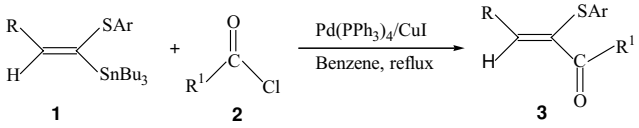

**SCHEME 1**

**TABLE 1** Cross-Coupling of (*E*)-1-(4-Methylphenyl)sulfanyl-1-tributylstannyl-1-hexene with Benzoyl Chloride[a]

| *Catalyst*[b] | *Additive*[c] | *Solvent* | *Temp. (°C)* | *Time (h)* | *Yield (%)*[d] |
|---|---|---|---|---|---|
| $PdCl_2(PPh_3)_2$ | CuI | DMF | r.t.[e] (or 65°C) | 72 | 0 |
| $PdCl_2(PPh_3)_2$ | CuI | $C_6H_6$ | r.t. (or reflux) | 72 | 0 |
| $PdCl_2(PPh_3)_2$ | CuI | $C_6H_6$ | 120 (sealed tube) | 72 | 21 |
| $PdCl_2(PPh_3)_2$ | CuI | THF | r.t. (or reflux) | 72 | 0 |
| $PdCl_2(PPh_3)_2$ | CuI | THF | 120 (sealed tube) | 72 | 0 |
| $PdBnCl(PPh_3)_2$ | CuI | DMF | r.t. (or 65 °C) | 72 | 0 |
| $PdBnCl(PPh_3)_2$ | CuI | $C_6H_6$ | 120 (sealed tube) | 72 | 29 |
| $PdBnCl(PPh_3)_2$ | CuI | THF | 120 (sealed tube) | 72 | Trace |
| $PdCl_2$(dppe) | CuI | DMF | r.t. (or 65 °C) | 72 | 0 |
| $PdCl_2$(dppe) | CuI | $C_6H_6$ | Reflux or 120 | 72 | Trace |
| $Pd(PPh_3)_4$ | CuI | DMF | r.t. (or 65 °C) | 72 | 0 |
| $Pd(PPh_3)_4$ | CuI | THF | 120 (sealed tube) | 72 | 0 |
| $Pd(PPh_3)_4$ | CuI | $CH_2Cl_2$ | 120 (sealed tube) | 72 | 0 |
| $Pd(PPh_3)_4$ | CuI | $C_6H_6$ | r.t. | 72 | 0 |
| $Pd(PPh_3)_4$ | CuI | $C_6H_6$ | Reflux | 4 | 77 |
| $Pd(PPh_3)_4$ | CuI | $C_6H_6$ | Reflux | 7 | 82 |
| $Pd(PPh_3)_4$ | CuI | $C_6H_6$ | 120 (sealed tube) | 7 | 83 |
| $Pd(PPh_3)_4$ | CuI | Toluene | Reflux | 24 | 48 |
| $Pd(PPh_3)_4$ | | $C_6H_6$ | Reflux or 120 | 72 | 0 |
| | CuI | $C_6H_6$ | Reflux or 120 | 72 | 0 |

[a]Reaction was carried out with 1.0 mmol of (*E*)-1-(4-methylphenyl)sulfanyl-1-tributylstannyl-1-hexene and 1.1 mmol of benzoyl chloride under argon.
[b]5 mol% of Pd catalyst was used.
[c]0.75 (equiv) CuI was used.
[d]Isolated yield.
[e]r.t. = Room temperature.

The Stille coupling reactions of a variety of (*E*)-α-arylsulfanylvinylstannanes with acyl halides were examined in the presence of a catalytic amount (5 mol%) of $Pd(PPh_3)_4$ and CuI (0.75 equiv) in benzene at reflux temperature (Scheme 2), and the results are summarized in Table 2. In all cases, the reaction proceeded smoothly to afford the corresponding coupled products in good yields. Electron-donating and electron-withdrawing groups such as $CH_3$, Cl, and $NO_2$ on aromatic acyl halides were well tolerated. Unfortunately, the




**SCHEME 2**

Stille coupling of (*E*)-α-arylsulfanylvinylstannanes with aliphatic acyl halides did not occur under the same conditions. To get insight into the stereoselectivity of this coupling reaction, we prepared

**TABLE 2** Synthesis of (*Z*)-α-Arylsulfanyl-α,β-unsaturated Ketones

| *Entry* | *R* | *Ar* | *R*[1] | *Product* | *Yield (%)*[a] |
|---|---|---|---|---|---|
| 1 | *n*-$C_4H_9$ | Ph | Ph | **3a** | 81 |
| 2 | *n*-$C_4H_9$ | Ph | 4-$O_2NC_6H_4$ | **3b** | 80 |
| 3 | *n*-$C_4H_9$ | 4-$CH_3C_6H_4$ | Ph | **3c** | 82 |
| 4 | *n*-$C_4H_9$ | 4-$CH_3C_6H_4$ | 4-$ClC_6H_4$ | **3d** | 79 |
| 5 | $CH_3OCH_2$ | Ph | Ph | **3e** | 76 |
| 6 | $CH_3OCH_2$ | Ph | 4-$CH_3C_6H_4$ | **3f** | 81 |
| 7 | $CH_3OCH_2$ | Ph | 4-$ClC_6H_4$ | **3g** | 73 |
| 8 | $CH_3OCH_2$ | Ph | 4-$O_2NC_6H_4$ | **3h** | 75 |
| 9 | $CH_3OCH_2$ | 4-$CH_3C_6H_4$ | Ph | **3i** | 77 |
| 10 | Ph | Ph | Ph | **3j** | 86 |
| 11 | Ph | 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | **3k** | 79 |

[a]Isolated yield based on the (*E*)-α-arylsulfanylvinylstannane **1** used.

(*Z*)-α-arylsulfanylvinylstannanes by hydrozirconation of alkynylstannanes, followed by the reaction with arylsulfenyl chlorides. We investigated the cross-coupling reaction of (*Z*)-α-arylsulfanylvinylstannanes with acyl chlorides under the same conditions, and it was found that the cross-coupling reaction did not occur even under sealed-tube conditions due to the presence of steric hindrance. It is well documented that the Stille coupling reaction of vinylstannanes with organic halides, in the presence of a palladium catalyst, occurs with retention of configuration [27, 35]. In addition, the *Z*-configuration of compound **3c** was confirmed by NOESY experiments. An enhancement of the allylic protons was observed as the vinylic proton of **3c** was irradiated. A correlation between the allylic protons and the aromatic protons ($\delta$ = 7.14) of the (4-methylphenyl)sulfanyl group was observed. The NOE results indicate that compound **3c** has the expected *Z*-configuration and that the cross-coupling reaction of (*E*)-α-arylsulfanylvinylstannanes with acyl halides occurs with retention of configuration.

In conclusion, a new method for the stereoselective synthesis of (*Z*)-α-arylsulfanyl-α,β-unsaturated ketones has been developed based on the Stille coupling reaction of (*E*)-α-arylsulfanylvinylstannanes with acyl halides. This shows the usefulness of (*E*)-α-arylsulfanylvinylstannanes for the synthesis of highly functionalized organosulfur compounds. The investigations of the synthetic applications of (*Z*)-α-arylsulfanyl-α,β-unsaturated ketones are in progress.

## *EXPERIMENTAL*

$^1$H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. $^{13}$C NMR (100 MHz) spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer using $CDCl_3$ as the solvent. IR spectra were determined on an FTS-185 instrument as neat films. Mass spectra were obtained on a Finnigan 8239 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer. All reactions were carried out in predried glassware (150°C, 4 h) and cooled under a stream of dry argon. Benzene and THF were distilled from sodium prior to use. DMF was dried by distillation over calcium hydride.

### *General Procedure for the Synthesis of (Z)-α-Arylsulfanyl-α,β-Unsaturated Ketones (***3a–k***)*

To a solution of (*E*)-α-arylsulfanylvinylstannane (1.0 mmol) and acyl halide (1.1 mmol) in benzene (2.0 mL) under argon, $Pd(PPh_3)_4$ (0.05 mmol) and CuI (0.75 mmol) were added, the resulting mixture was stirred at reflux for 7 h, cooled to room temperature, and diluted with light petroleum. The supernatant was filtered through a short plug of silica gel and the filtrate evaporated. The residue was purified by preparative TLC on silica gel to afford the corresponding compounds.

*(Z)-1-Benzoyl-1-phenylthio-1-hexene* **3a**. Oil. IR (film): $\nu$ (cm$^{-1}$) 3060, 2928, 1665, 1597, 1447, 1258, 741, 690; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.69 (d, $J$ = 8.4 Hz, 2H), 7.49–7.47 (m, 1H), 7.37 (t, $J$ = 7.6 Hz, 2H), 7.24–7.10 (m, 5H), 6.73 (t, $J$ = 7.2 Hz, 1H), 2.61–2.55 (m, 2H), 1.52–1.48 (m, 2H), 1.43–1.38 (m, 2H), 0.94 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 194.11, 149.69, 137.45, 135.72, 134.40, 132.34, 129.88, 129.39, 128.93, 128.12, 126.63, 30.69, 30.33, 22.54, 13.89; MS (EI, 70 eV): *m/z* 296 (M$^+$, 100), 105 (93), 77 (45); Anal. calcd for $C_{19}H_{20}OS$: C, 77.00; H, 6.80. Found: C, 76.74; H, 6.61.

*(Z)-1-(4-Nitrobenzoyl)-1-phenylthio-1-hexene* **3b**. Oil. IR (film): $\nu$ (cm$^{-1}$) 2928, 1670, 1592, 1519, 1345, 848, 690; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.07 (d, $J$ = 8.8 Hz, 2H), 7.68 (d, $J$ = 8.8 Hz, 2H), 7.18–7.06 (m, 5H), 6.55 (t, $J$ = 7.2 Hz, 1H), 2.63–2.57 (m, 2H), 1.55–1.50 (m, 2H), 1.45–1.37 (m, 2H), 0.95 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 194.52, 147.01, 143.50, 134.72, 132.38, 129.32, 128.93, 128.58, 128.13, 126.07, 123.53, 31.31, 30.99, 22.50, 13.97; MS (EI, 70 eV): *m/z* 341 (M$^+$, 9.3), 109 (100), 57 (35); Anal. calcd for $C_{19}H_{19}NO_3S$: C, 66.85; H, 5.61. Found: C, 66.56; H, 5.69.

*(Z)-1-Benzoyl-1-(4-methylphenyl)thio-1-hexene* **3c**. Oil. IR (film): $\nu$ (cm$^{-1}$) 2927, 1666, 1596, 1448, 1258, 1089, 806, 717; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.69 (d, $J$ = 8.4 Hz, 2H), 7.51–7.49 (m, 1H), 7.38 (t, $J$ = 7.6 Hz, 2H), 7.14 (d, $J$ = 8.0 Hz, 2H), 6.98 (d, $J$ = 8.0 Hz, 2H), 6.64 (t, $J$ = 7.6 Hz, 1H), 2.59–2.54 (m, 2H), 2.24 (s, 3H), 1.51–1.44 (m, 2H), 1.42–1.35 (m, 2H), 0.94 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 194.15, 148.43, 137.53, 136.80, 136.36, 132.28, 130.53, 129.70, 129.42, 128.00, 127.48, 30.73, 30.21, 22.53, 21.00, 13.89; MS (EI, 70 eV): *m/z* 310 (M$^+$, 37), 186 (25), 105 (100), 91 (43); Anal. calcd for $C_{20}H_{22}OS$: C, 77.39; H, 7.14. Found: C, 77.15; H, 6.95.

*(Z)-1-(4-Chlorobenzoyl)-1-(4-methylphenyl)thio-1-hexene* **3d**. Oil. IR (film): $\nu$ (cm$^{-1}$) 2926, 1667, 1588, 1492, 1253, 1091, 806, 756; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.63 (d, $J$ = 8.4 Hz, 2H), 7.34 (d, $J$ = 8.4 Hz, 2H), 7.10 (d, $J$ = 8.0 Hz, 2H), 6.98 (d, $J$ = 8.0 Hz,

2H), 6.61 (t, $J = 7.2$ Hz, 1H), 2.60–2.54 (m, 2H), 2.24 (s, 3H), 1.53–1.49 (m, 2H), 1.44–1.38 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 193.00, 147.82, 138.66, 137.04, 136.11, 135.74, 135.02, 130.76, 130.67, 129.76, 128.39, 30.74, 30.13, 22.53, 21.02, 13.90; MS (EI, 70 eV): *m/z* 346 ($M^+$, $^{37}$Cl, 16), 344 ($M^+$, $^{35}$Cl, 45), 139 (100), 91 (29); Anal. calcd for $C_{20}H_{21}OSCl$: C, 69.65; H, 6.14. Found: C, 69.38; H, 5.86.

*(Z)-1-Benzoyl-1-phenylthio-3-methoxypropene* **3e**. Oil. IR (film): $\nu$ ($cm^{-1}$) 3060, 2929, 1667, 1597, 1580, 1448, 1248, 1100, 745, 690; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.73 (d, $J = 8.0$ Hz, 2H), 7.53–7.34 (m, 3H), 7.27–7.14 (m, 5H), 6.69 (t, $J = 5.6$ Hz, 1H), 4.40 (d, $J = 5.6$ Hz, 2H), 3.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 192.97, 143.20, 136.87, 136.73, 133.08, 132.72, 130.70, 129.46, 129.06, 128.26, 127.29, 70.08, 58.79; MS (EI, 70 eV): *m/z* 284 ($M^+$, 41), 253 (100), 144 (36), 109 (41), 105 (87); Anal. calcd for $C_{17}H_{16}O_2S$: C, 71.82; H, 5.67. Found: C, 71.55; H, 5.79.

*(Z)-1-(4-Methylbenzoyl)-1-phenylthio-3-methoxypropene* **3f**. Oil. IR (film): $\nu$ ($cm^{-1}$) 3061, 2928, 1666, 1596, 1583, 1447, 1249, 1101, 690; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.67 (d, $J = 8.0$ Hz, 2H), 7.28–7.24 (m, 3H), 7.21–7.15 (m, 4H), 6.64 (t, $J = 5.6$ Hz, 1H), 4.39 (d, $J = 5.6$ Hz, 2H), 3.42 (s, 3H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 192.63, 143.67, 142.47, 136.87, 134.01, 133.16, 130.66, 129.72, 129.24, 128.99, 127.23, 70.03, 58.73, 21.66; MS (EI, 70 eV): *m/z* 298 ($M^+$, 6.8), 296 (100), 282 (85), 253 (34), 239 (40), 105 (58), 91 (62); Anal. calcd for $C_{18}H_{18}O_2S$: C, 72.47; H, 6.08. Found: C, 72.19; H, 5.87.

*(Z)-1-(4-Chlorobenzoyl)-1-phenylthio-3-methoxypropene* **3g**. Oil. IR (film): $\nu$ ($cm^{-1}$) 2929, 1669, 1593, 1580, 1402, 1093, 691; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.49 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 7.15–7.13 (m, 5H), 6.43 (t, $J = 5.6$ Hz, 1H), 4.39 (d, $J = 5.6$ Hz, 2H), 3.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 193.27, 134.93, 134.33, 130.65, 129.44, 129.01, 128.94, 128.87, 128.69, 128.42, 126.18, 70.71, 58.48; MS (EI, 70 eV): *m/z* 318 ($M^+$, $^{35}$Cl, 1.4), 259 (26), 123 (55), 111 (64), 109 (100); Anal. calcd for $C_{17}H_{15}O_2SCl$: C, 64.05; H, 4.74. Found: C, 63.77; H, 4.49.

*(Z)-1-(4-Nitrobenzoyl)-1-phenylthio-3-methoxypropene* **3h**. Oil. IR (film): $\nu$ ($cm^{-1}$) 2928, 1672, 1595, 1521, 1404, 1346, 1093, 690; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.08 (d, $J = 8.8$ Hz, 2H), 7.70 (d, $J = 8.8$ Hz, 2H), 7.16–7.07 (m, 5H), 6.56 (t, $J = 5.6$ Hz, 1H), 4.43 (d, $J = 5.6$ Hz, 2H), 3.46 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 193.41, 145.63, 137.74, 134.97, 133.47, 130.19, 129.37, 129.06, 128.46, 126.70, 123.58, 70.68, 58.68; MS (EI, 70 eV): *m/z* 329 ($M^+$, 53), 298 (25), 115 (91), 109 (100); Anal. calcd for $C_{17}H_{15}NO_4S$: C, 62.00; H, 4.59. Found: C, 61.73; H, 4.73.

*(Z)-1-Benzoyl-1-(4-methylphenyl)thio-3-methoxypropene* **3i**. Oil. IR (film): $\nu$ ($cm^{-1}$) 2927, 1667, 1597, 1592, 1448, 1403, 1094, 808, 716; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.72 (d, $J = 8.4$ Hz, 2H), 7.51–7.35 (m, 3H), 7.16 (d, $J = 8.0$ Hz, 2H), 6.99 (d, $J = 8.0$ Hz, 2H), 6.59 (t, $J = 5.6$ Hz, 1H), 4.40 (d, $J = 5.6$ Hz, 2H), 3.43 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 193.08, 141.84, 137.57, 136.79, 133.46, 132.71, 131.33, 129.83, 129.54, 129.15, 128.23, 70.01, 58.75, 21.05; MS (EI, 70 eV): *m/z* 298 ($M^+$, 54), 267 (66), 105 (100); Anal. calcd for $C_{18}H_{18}O_2S$: C, 72.47; H, 6.08. Found: C, 72.64; H, 6.25.

*(Z)-1-Benzoyl-1-phenylthio-2-phenylethene* **3j**. White solid. Mp. 75–76°C (lit. [36] Mp. 74–75°C). IR (KBr): $\nu$ ($cm^{-1}$) 3060, 1667, 1581, 1447, 1241, 745, 690; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.80 (d, $J = 7.6$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.50–7.34 (m, 6H), 7.27–7.11 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 194.47, 139.87, 137.38, 135.58, 134.63, 133.08, 132.50, 131.29, 130.42, 129.45, 128.96, 128.56, 128.48, 128.12, 127.38; MS (EI, 70 eV): *m/z* 316 ($M^+$, 8.3), 211 (17), 109 (34), 105 (100); Anal. calcd for $C_{21}H_{16}OS$: C, 79.73; H, 5.10. Found: C, 79.54; H, 5.23%.

*(Z)-1-(4-Chlorobenzoyl)-1-(4-chlorophenyl)thio-2-phenylethene* **3k**. White solid. Mp. 81–83°C. IR (KBr): $\nu$ ($cm^{-1}$) 2925, 1665, 1587, 1475, 1092, 819, 762; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.80–7.76 (m, 2H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.47–7.31 (m, 5H), 7.24–7.13 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 192.98, 140.42, 139.09, 137.18, 135.47, 134.51, 134.23, 133.43, 132.55, 130.92, 130.74, 130.45, 129.22, 129.03, 128.57; MS (EI, 70 eV): *m/z* 384 ($M^+$, $^{35}$Cl, 39), 139 (45), 111 (66), 109 (100); Anal. calcd for $C_{21}H_{14}OSCl_2$: C, 65.63; H, 3.67. Found: C, 65.41; H, 3.85.

## *REFERENCES*

[1] Nielsen, A. T.; Houlihan, W. Org React 1968, 16, 15.
[2] Chong, B. D.; Ji, Y. I.; Oh, S. S.; Yang, J. D.; Baik, W.; Koo, S. J Org Chem 1997, 62, 9323.
[3] Nenitzescu, C. D.; Balaban, A. T. Friedel–Crafts Relat React 1964, 3, 1035.

[4] Carr, D. B.; Schwartz, J. J Am Chem Soc 1977, 99, 639.
[5] Sung, J. W.; Jang, W. B.; Oh, D. Y. Tetrahedron Lett 1996, 37, 7537.
[6] Zhao, C. Q.; Huang, X. Tetrahedron Lett 1998, 39, 1933.
[7] Huang, Z. Z.; Huang, X.; Huang, Y. Z. J Chem Soc, Perkin Trans 1 1995, 95.
[8] Ma, Y.; Li, B.; Huang, X. J Organomet Chem 1999, 590, 234.
[9] Oki, M.; Kobayashi, K. Bull Chem Soc Japan 1970, 43, 1223.
[10] Mukayama, T.; Hosoi, K.; Inokuma, S.; Kumamoto, T. Bull Chem Soc Japan 1971, 44, 2453.
[11] Schultz, A. G.; Kashdan, D. S. J Org Chem 1973, 38, 3814.
[12] Markeley, L. D. J Org Chem 1973, 38, 3417.
[13] Mukayama, T.; Adachi, T.; Kumamota, T. Bull Chem Soc Japan 1971, 44, 3155.
[14] Cregge, R. J.; Herrmann, J. L.; Schlessinger, R. H. Tetrahedron Lett 1973, 2603.
[15] Monteiro, H. J.; Gemal, A. L. Synthesis 1975, 437.
[16] Durman, J.; Grayson, J. I.; Hunt, P. G.; Warren, S. J Chem Soc, Perkin Trans 1 1986, 1939.
[17] Yechezkel, T.; Ghera, E.; Ostercamp, D.; Hassner, A. J Org Chem 1995, 60, 5135.
[18] Fringuell, F.; Pizzo, F.; Vaccaro, L. J Org Chem 2004, 69, 2315.
[19] Xu, F.; Shi, W.; Wang, J. J Org Chem 2005, 70, 4191.
[20] Hao, W.; Wang, D.; Cai, M. J Chem Res 2007, 418.
[21] Hao, W.; Yu, L.; Cai, M. J Chem Res 2007, 177.
[22] Yu, L.; Hao, W.; Cai, M. Chin Chem Lett 2008, 19, 1047.
[23] Hu, R.; Yu, Y.; Cai, M. J Chem Res 2008, 592.
[24] Zhao, H.; Zhang, H.; Cai, M. Chin J Chem 2008, 26, 799.
[25] Trost, B. M.; Li, C. J. Synthesis 1994, 1267.
[26] Magriotis, P. A.; Brown, J. T.; Scott, M. E. Tetrahedron Lett 1991, 32, 5047.
[27] Stille, J. K. Angew Chem, Int Ed Engl 1986, 25, 508.
[28] Mitchell, T. N. J Organomet Chem 1986, 304, 1.
[29] Cai, M.-Z.; Wang, D.; Wang, P.-P. J Organomet Chem 2006, 691, 737.
[30] Liebeskind, L. S.; Fengl, R. W. J Org Chem 1990, 55, 5359.
[31] Linderman, R. J.; Siedleck, J. M. J Org Chem 1996, 61, 6492.
[32] Piers, E.; Wong, T. J Org Chem 1993, 58, 3609.
[33] Falck, J. R.; Bhatt, R. K.; Ye, J. J Am. Chem Soc 1995, 117, 5973.
[34] Beletskaya, I. P.; Cheprakov, A. V. Coord Chem Rev 2004, 248, 2337.
[35] Stille, J. K. Pure Appl Chem 1985, 57, 1771.
[36] Kroehnke, F.; Ahrenholz, G. W.; Gross, K. F. J Prakt Chem 1960, 11, 256.