# Cu(acac)$_2$-Catalyzed Synthesis of Functionalized Bis(arylmethyl)zinc Reagents and Their Olefination Reaction with Aromatic Aldehydes

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*Received 17 December 2011; revised 23 January 2012*

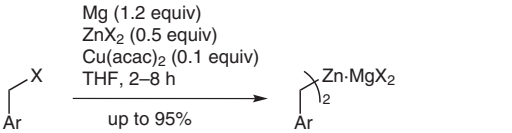
**Abstract:** An efficient and facile copper(II) acetylacetonate catalyzed synthesis of functionalized bis(arylmethyl)zinc reagents from arylmethyl halides and their olefination reaction with aromatic aldehydes is reported. Aluminum trichloride was found to be the key ingredient in these reactions and (*E*)-stilbenes were obtained in high yields.

**Key words:** aldehyde, zinc, nucleophilic addition, olefination, benzylation

Organozinc reagents, due to their great compatibility with a variety of functional groups such as halide, amide, ether, ester, nitrile, or even formyl groups, have become of increasing importance as selective synthetic tools for C–C bond formation.[1] Previously, we reported an interesting olefination reaction whereby arylaldehydes were reacted with arylmethylzinc halides under transition-metal-complex catalysis in the presence of trimethylsilyl chloride to give *trans*-stilbene derivatives only.[2] This protocol provides another facile approach to *trans*-styrenes besides the well-known Wittig reaction. The obvious advantage of this method is its stereospecificity as only *trans*-styrenes were obtained, whereas the Wittig protocol always gives both *cis*- and *trans*-isomers. However, these reactions have some limitations as these organometallic reagents are very sensitive to moisture, which must be excluded from the reaction system. Moreover, the nucleophilicity of some arylmethylzinc halides means that they are too weak to react efficiently with the carbonyl group.

Diorganozincs ($R_2Zn$) are significantly more reactive than organozinc halides (RZnX) towards various electrophilic reagents.[3] However, even though diorganozinc reagents were among the first prepared and practically used organometallic reagent,[4] they are not so widely used in organic synthesis as organolithium reagents, organomagnesium reagents, or even their organozinc sibling, organozinc halides. Diorganozinc reagents, with the exception of a few commercially obtained examples with simple structures, such as dimethylzinc, diethylzinc, or diphenylzinc reagents, are not readily available, they are prepared by iodine–zinc exchange,[5] boron–zinc exchange,[6] or hydrozincation reaction.[7]

Transmetalation of organolithium or organomagnesium reagents with zinc halides is a practical method for the synthesis of organozinc reagent.[8] In order to minimize formation of the coupling byproduct and functionalize the organometallic reagent, an in situ preparation of organozinc halide or diorganozinc reagents by reaction of magnesium metal with organic halides in the presence of lithium chloride and zinc chloride was recently explored by the Knochel group and they found that the reactivity of organozinc reagents can be dramatically enhanced by magnesium chloride in situ in these reaction systems.[9] A similar effect was also observed by Ellman et al. in the reaction of arylmethylzinc reagents with *N*-*tert*-butanesulfinyl aldimines.[10] Encouraged by these findings, we here report a convenient one-pot, in situ preparation of bis(arylmethyl)zinc reagents by reaction of magnesium metal with arylmethyl halides in the presence of zinc halide (0.5 equiv) and copper(II) acetylacetonate (0.1 equiv), and their olefination reaction with aromatic aldehydes (Scheme 1).




**1a** Ar = Ph
**1b** Ar = 4-ClC$_6$H$_4$
**1c** Ar = 4-FC$_6$H$_4$
**1d** Ar = 4-BrC$_6$H$_4$
**1e** Ar = 4-MeOC$_6$H$_4$
**1f** Ar = 3,4,5-(MeO)$_3$C$_6$H$_2$
**1g** Ar = 2-naphthyl
**1h** Ar = 4-PhC$_6$H$_4$

**Scheme 1** Synthesis of functionalized bis(arylmethyl)zinc–magnesium halide complexes

Reaction of magnesium turnings (1.2 equiv) with arylmethyl chloride or arylmethyl bromide in the presence of zinc chloride (0.5 equiv), and copper(II) acetylacetonate (0.1 equiv) in tetrahydrofuran was shown to be a mild and efficient method for the preparation of bis(arylmethyl)zinc reagents **1** in our laboratory (Scheme 1). The addition of copper(II) acetylacetonate to these reaction systems produced a significant enhancement and, in most cases, arylmethyl chlorides can be converted into the corresponding bis(arylmethyl)zinc reagents **1** in 2–8 hours in an ice-water bath. Arylmethyl bromides can be best converted into bis(arylmethyl)zinc reagents **1** by stirring the mixture in a salt-ice bath for 2–6 hours. Quenching the or-

**SYNTHESIS** 2012, 44, 1030–1036
Advanced online publication: 24.02.2012
DOI: 10.1055/s-0031-1289723; Art ID: H115811SS

ganozinc reagents **1** immediately after their preparation with methanol showed that the formation of the homocoupling product bibenzyls can be controlled to less than 7% for benzyl chlorides and no more than 10% for benzyl bromides. Other copper(I) or copper(II) salts or complexes, such as copper sulfate, copper(II) chloride, copper(I) iodide, copper(I) cyanide, and copper(II) acetate, were all effective reagents, but copper(II) acetylacetonate was shown to be the best as it generally gave the lowest yield of coupling byproduct, 1,2-diarylethane.

The role of copper complexes here may be that of an active 'zinc–copper couple' layer formed on the surface of the magnesium turnings via in situ reduction of zinc chloride and copper complex by magnesium metal, which will react readily with the arylmethyl halide to form bis(arylmethyl)zinc reagents **1**, including highly functionalized examples. Although the noncatalytic procedure is a simple and efficient synthetic method,[8c] where bis(arylmethyl)zinc reagents **1** are generated simply by addition of two equivalents of arylmethylmagnesium halides to zinc bromide, the high reactivity of Grignard reagents means that more fragile functional groups cannot be retained in these organometallics. Another advantage of our catalytic procedure is that some of the more reactive arylmethyl halides, especially those with electron-donating substituents on the aryl ring (methoxy, etc.) could be successfully transformed into corresponding bis(arylmethyl)zinc reagents **1** in high yields whereas using the noncatalytic procedures, the synthesis of arylmethyl Grignard reagents itself would be accompanied by the formation of a considerable amount of homocoupling product[11] and the resulting magnesium reagent would decomposes rapidly in the absence of zinc(II) chloride.[9c] Thus they were normally used in excess in the formulated synthetic procedure.

With the desired bis(arylmethyl)zinc reagents **1** in hand, we began to examine their reaction with arylaldehydes **2**. Initially, the reaction of dibenzylzinc reagent **1a** with *p*-anisaldehyde (**2a**) in tetrahydrofuran was investigated as a model system to identify whether stilbene **3a** or an alcohol product **4a** would be formed. As expected no reaction occurred without the addition of a catalytic additive, indicating that organozinc reagents had indeed been effectively formed as the corresponding Grignard reagent would be expected to react with carbonyl compounds easily without the use of a catalyst (Table 1, entry 1). In the presence of two equivalents of trimethylsilyl chloride, only alcohol **4a** was obtained in 84% isolated yield and stilbene **3a** was not detected (entry 2). Addition of transition-metal complexes such as $Ni(PPh_3)_2Cl_2$, $Ni(PPh_3)_4$ $Pd(PPh_3)_2Cl_2$, and $Pd(PPh_3)_4$ together with two equivalents of TMSCl to the reaction of **1a** with **2a** did not induce the formation of the desired (*E*)-stilbene **3a**, and the alcohol **4a** was again obtained (entries 3–6). Reaction of **1a** with aldehyde **2a** in the presence of trimethylsilyl chloride and transition-metal complexes gave only the alcohol product **4a** indicating that the reactivity of dibenzylzinc reagent **1a** is quite different to benzylzinc halides, which under the same reaction conditions give (*E*)-stilbenes stereospecifically in satisfactory yields.[2]

The Lewis acid aluminum trichloride has been reported to be an efficient catalyst for the olefination reaction of benzylzinc halides with aldehyde and ketones.[12] We thus turned our attention to the role of Lewis acids on the reaction of dibenzylzinc reagent **1a** with aldehyde **2a** and, to our delight, aluminum trichloride showed a significant effect on the reaction. Addition of three equivalents of aluminum trichloride did not show any effect on the reaction at room temperature (entry 7). However, an increase in the reaction temperature to 60 °C and stirring the reaction mixture in tetrahydrofuran for eight hours resulted in the formation of the stilbene **3a** and the alcohol **4a** in a 3:1 ratio based on $^1$H NMR spectrum analysis (entry 8). Interestingly, when the reaction was performed in 1,4-dioxane at 80 °C for eight hours in the presence of three equivalents of aluminum trichloride, the alcohol was completely consumed and only *trans*-stilbene **3a** was obtained in 84% isolated yield with no detected *cis*-stilbene (entry 9). The olefination reaction could not be improved by further increasing the amount of aluminum trichloride to five equivalents as the yield of stilbene **3a** was lowered (entry 10). Other Lewis acids such as cerium(III) chloride, lithium chloride, iron(III) chloride, and magnesium chloride gave **4a** only (entries 11–14). In the presence of two equivalents of tin(IV) chloride or titanium(IV) chloride or three equivalents of zinc chloride, the reaction did not occur (entries 15–17). Boron trifluoride–diethyl ether complex can be used to form **3a** in 56% yield after stirring the reaction mixture under the same conditions (entry 18).

To determine whether the both benzyl groups from the dibenzylzinc reagent **1a** could be transferred, two equivalents of aldehyde **2a** were introduced into the reaction system. However, after stirring at 80 °C for 12 hours, only half of the aldehyde had been consumed and stilbene **4a** was obtained in 82% isolated yield based on the recovered aldehyde (entry 19).

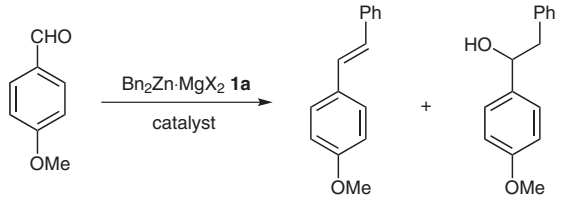
Based on the control experiment given in Table 1, entry 9, the reaction of substituted arylaldehydes **2** and bis(arylmethyl)zinc reagents **1a–h** was performed in the presence of three equivalents of aluminum trichloride (Table 2). Reaction of dibenzylzinc reagent **1a** with various substituted arylaldehydes **2** bearing electron-withdrawing groups and electron-donating groups present in the *para* or *meta* positions all proceeded smoothly and consistently gave the corresponding stilbenes **3b–i** in good to high yield (entries 2–10). However, *ortho*-substituted benzaldehydes did not react cleanly and gave the corresponding stilbene **3k** in low yield (entry 12).

Interestingly, hydroxy-substituted benzaldehydes can be used directly but an extra equivalent of bis(arylmethyl)zinc halide **1a**,**b** was added as the acidic hydroxy group must first be neutralized by the bis(arylmethyl)zinc reagent.[13] The resulting formyl phenolate then reacted with bis(arylmethyl)zinc reagent to give the hydroxylated stilbenes **3e** and **3p** in moderate yields (entries 5 and 17). Ac-

etoxy-substituted benzaldehydes were sensitive to the reaction condition and the product was deacetylated to give the hydroxystilbene **3e** (entry 6). The nitro group in 4-nitrobenzaldehyde was reduced to hydroxylamine with 4-(hydroxylamino)stilbene (**3c**) isolated in 58% yield (entry 3).

Next, we screened the reaction by varying the substituent on the aromatic ring of the bis(arylmethyl)zinc reagents **1**. Bis(arylmethyl)zinc reagents bearing either electron-withdrawing substituents (chloro, bromo, or fluoro, entries 13–19) or electron-donating substituents (methoxy, benzyloxy, or phenyl groups, entries 20–23) on the phenyl ring all reacted efficiently with arylaldehydes **2** to give the corresponding stilbenes **3l–s** in moderate to high yields, which shows that both types of substituents are well tolerated. Some fragile substituents such as cyano and ester groups were not retained in these reactions, although the corresponding functionalized bis(arylmethyl)zinc reagents themselves can be successfully obtained.[9]

**Table 1** Conditions for the Reaction of Dibenzylzinc Reagent **1a** with *p*-Anisaldehyde (**2a**)[a]

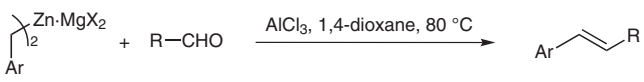



| Entry | Temp (°C) | Time (h) | Additive (equiv) | Solvent | Product[b] | Yield[c] (%) |
|---|---|---|---|---|---|---|
| 1 | 0–20 | 8 | – | THF | – | – |
| 2 | 0–20 | 8 | TMSCl (2) | THF | **4a** | 84 |
| 3 | 0–20 | 8 | TMSCl (2)<br>$Ni(PPh_3)_2Cl_2$ (0.5) | THF | **4a** | 86 |
| 4 | 0–20 | 8 | TMSCl (2)<br>$Ni(PPh_3)_4$ (0.5) | THF | **4a** | 82 |
| 5 | 0–20 | 8 | TMSCl (2)<br>$Pd(PPh_3)_2Cl_2$ (0.3) | THF | **4a** | 83 |
| 6 | 0–20 | 8 | TMSCl (2)<br>$Pd(PPh_3)_4$ (0.3) | THF | **4a** | 82 |
| 7 | 0–20 | 8 | $AlCl_3$ (3) | THF | – | – |
| 8 | 60 | 8 | $AlCl_3$ (3) | THF | **3a/4a** (3:1) | 86 |
| 9 | 80 | 8 | $AlCl_3$ (3) | 1,4-dioxane | **3a** | 84 |
| 10 | 80 | 8 | $AlCl_3$ (5) | 1,4-dioxane | **3a** | 65 |
| 11 | 80 | 8 | $CeCl_3$ (3) | 1,4-dioxane | **4a** | 32 |
| 12 | 80 | 8 | LiCl (3) | 1,4-dioxane | **4a** | 67 |
| 13 | 80 | 8 | $FeCl_3$ (3) | 1,4-dioxane | **4a** | 23 |
| 14 | 80 | 8 | $MgCl_2$ (3) | 1,4-dioxane | **4a** | 54 |
| 15 | 80 | 8 | $ZnCl_2$ (3) | 1,4-dioxane | – | – |
| 16 | 80 | 8 | $SnCl_4$ (2) | 1,4-dioxane | – | – |
| 17 | 80 | 8 | $TiCl_4$ (2) | 1,4-dioxane | – | – |
| 18 | 80 | 8 | $BF_3{\cdot}OEt_2$ (3) | 1,4-dioxane | **3a** | 56 |
| 19 | 80 | 8 | $AlCl_3$ (3) | 1,4-dioxane | **3a** | 82[d] |

[a] Reaction conditions: aldehyde **1a** (1.0 mmol), $Bn_2Zn$ (**2a**, 1.2 mmol), additive [Lewis acid], solvent (10 mL), under $N_2$, 8 h.
[b] Detected by $^1H$ NMR.
[c] Isolated yields.
[d] Aldehyde **2a** (2 equiv) was used.

**Table 2** Reaction of Bis(arylmethyl)zinc Reagents **1a–h** with Aldehydes **2**[a]




**1a–h** **2** **3**

| Entry | Ar | R | Product | Yield[b] (%) |
|---|---|---|---|---|
| 1 | Ph | 4-$MeOC_6H_4$ | **3a** | 84 |
| 2 | Ph | Ph | **3b** | 86 |
| 3 | Ph | 4-$O_2NC_6H_4$ | **3c**[c] | 58 |
| 4 | Ph | 3,4,5-$(MeO)_3C_6H_2$ | **3d** | 83 |
| 5 | Ph | 3-MeO-4-$HOC_6H_3$ | **3e** | 76[d] |
| 6 | Ph | 3-MeO-4-$AcOC_6H_3$ | **3e**[e] | 62[e] |
| 7 | Ph | 3-MeO-4-$BnOC_6H_3$ | **3f** | 82 |
| 8 | Ph | 3,4-$(MeO)_2C_6H_3$ | **3g** | 78 |
| 9 | Ph | 4-$BnOC_6H_4$ | **3h** | 81 |
| 10 | Ph | 4-$PhC_6H_4$ | **3i** | 80 |
| 11 | Ph | CH=CHPh | **3j** | 72 |
| 12 | Ph | 2-$MeOC_6H_4$ | **3k** | 36 |
| 13 | 4-$ClC_6H_4$ | 4-$MeOC_6H_4$ | **3l** | 75 |
| 14 | 4-$ClC_6H_4$ | 4-MeO-3-$BnOC_6H_3$ | **3m** | 86 |
| 15 | 4-$ClC_6H_4$ | 3-MeO-4-$BnOC_6H_3$ | **3n** | 84 |
| 16 | 4-$ClC_6H_4$ | 3,4,5-$(MeO)_3C_6H_2$ | **3o** | 81 |
| 17 | 4-$ClC_6H_4$ | 3-MeO-4-$HOC_6H_3$ | **3p** | 55[d] |
| 18 | 4-$FC_6H_4$ | 4-$ClC_6H_4$ | **3q** | 76 |
| 19 | 4-$BrC_6H_4$ | Ph | **3r** | 85 |
| 20 | 4-$MeOC_6H_4$ | Ph | **3b** | 62 |
| 21 | 3,4,5-$(MeO)_3C_6H_2$ | Ph | **3d** | 76 |
| 22 | 2-naphthyl | 4-$MeOC_6H_4$ | **3s** | 65 |
| 23 | 4-$PhC_6H_4$ | Ph | **3i** | 78 |

[a] Reaction conditions: RCHO **2** (1.0 mmol), $Ar_2Zn$ **1** (1.2 mmol), $AlCl_3$ (3.0 equiv), 1,4-dioxane (10 mL), 80 °C.
[b] Isolated yield.
[c] Nitro was reduced to hydroxylamine.
[d] $Ar_2Zn$ (2.2 mmol) was used.
[e] The acetoxy group was cleaved.

The reaction of cinnamaldehyde with dibenzylzinc reagent **1a** produced (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene (**3j**) in 72% yield (entry 11) indicating that the unsaturated double bond in the aromatic aldehyde could be retained and directly introduced into the product. This protocol could be a good method for the synthesis of conjugated polyenes, which have a plethora of applications in both organic and biological chemistry.

Attempts to expand the substrates to ketones were unsuccessful as the products of these reactions were mainly alcohols. Heterocyclic aldehydes such as furfural and thiophene-2-carbaldehyde gave very low yields of olefin products, probably because these heterocycles are fragile under these reaction conditions.

In summary, we have developed a practical and facile procedure for the synthetic utilization of functionalized bis(arylmethyl)zinc reagents, which, as functionalized organometallic reagents, were efficiently utilized in reactions with arylaldehydes in a C=C bond-forming reaction. Copper(II) acetylacetonate was found to be an efficient catalyst in the synthesis of the functionalized bis(arylmethyl)zinc reagents and aluminum trichloride was shown to be the key Lewis acid in the promotion of these reactions. In most cases, (*E*)-stilbenes were stereoselectively formed in high yields.

All chemicals were obtained from commercial sources. Melting points were measured on an X-4 electrothermal micro melting point apparatus and are uncorrected. IR spectra were measured using an Alpha Centauri FT-IR spectrophotometer. $^1H$ and $^{13}C$ NMR spectra (400 MHz and 100 MHz, respectively) were recorded on Bruker AC-E 400 MHz spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectra were performed on QP-1000A GCMS spectrometer by EI ionization at 70 eV. Purification of products was performed by flash chromatography on 300–400 mesh silica gel (petroleum ether–EtOAc).

### Dibenzylzinc–Magnesium Halide Complex 1a; Typical Procedure

Cut Mg foil (0.36 g, 15 mmol) and $ZnCl_2$ (0.82 g, 6.0 mmol) were added to a dry, three-necked flask equipped with an argon inlet, a thermometer, and an addition funnel. The system was flushed and maintained under argon or $N_2$ atmosphere, 1,2-dibromoethane (0.1 mL) in THF (5 mL) was added, and the mixture was heated to 65 °C for 10 min. The mixture was then cooled to 0–5 °C (ice–water bath), a solution of $Cu(acac)_2$ (0.32 g, 1.2 mmol) in THF (2 mL) was added, and then a soln of BnCl (1.52 g, 12.0 mmol) in THF (15 mL) was added dropwise (for BnBr, the reaction was conducted in an ice-salt bath). The mixture was stirred and the temperature was allowed to rise to r.t. until GLC analysis showed that the starting material was completely consumed (2–8 h).

### 1,2-Diarylethenes 3;General Procedure

Bis(arylmethyl)zinc **1** prepared as above (5.0 mL, about 1.2 mmol) was added to a soln of arylaldehyde **2** (1.0 mmol) and $AlCl_3$ (0.4 g, 3.0 mmol) in 1,4-dioxane (10 mL). The mixture was heated to 80 °C and stirred at this temperature for 8 h. The mixture was allowed to cool to r.t. and the reaction was quenched with aq $NH_4Cl$ (10 mL). EtOAc (10 mL) was added and the organic phase was separated, washed with $H_2O$ (10 mL) and then with brine (10 mL). The aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic phases were dried ($Na_2SO_4$) and concentrated under reduced pressure. (*E*)-Stilbenes **3** were obtained by column chromatography (silica gel, petroleum ether–EtOAc). All products were characterized by IR and $^1H$ and $^{13}C$ NMR.

### (*E*)-4-Methoxystilbene (3a)

White solid; yield: 175 mg (84%); mp 137–139 °C (Lit.[14] 135–137 °C).

IR (KBr): 1600, 1510, 1296, 1248, 1176, 1072 $cm^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, $OCH_3$), 6.90 (dt, *J* = 11.2, 2.8 Hz, 2 H, ArH), 6.97 (d, *J* = 16.4 Hz, 1 H, =CH), 7.07 (d, *J* = 16.4 Hz, 1 H, =CH), 7.23 (t, *J* = 7.2 Hz, 1 H, ArH), 7.34 (t, *J* = 7.6 Hz, 2 H, ArH), 7.45 (dt, *J* = 11.2, 2.8 Hz, 2 H, ArH), 7.49 (br d, *J* = 8.0 Hz, 2 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.3, 114.2, 126.4, 127.3, 127.4, 127.8, 129.8, 135.2, 139.9, 159.9.

**(*E*)-Stilbene (3b)**
White solid; yield: 155 mg (86%); mp 124–126 °C (Lit.[15] 124.5 °C).

IR (KBr): 1635, 1493, 1448, 1138, 1027, 962 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.15 (s, 2 H, =CH), 7.25–7.43 (m, 6 H, ArH), 7.55 (d, *J* = 8 Hz, 4 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 126.4, 127.4, 128.0, 128.7, 135.2.

**(*E*)-*N*-(4-Styrylphenyl)hydroxylamine (3c)**
Pale yellow solid; yield: 120 mg (58%); mp 150–152 °C.

IR (KBr): 3398, 1605, 1514, 1458, 1247, 1179, 1122, 1074, 1026, 963 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 4.15 (br s, 1 H, OH), 4.37 (s, 1 H, NH), 6.63 (d, *J* = 8.6 Hz, 2 H, ArH), 6.90 (d, *J* = 16.3 Hz, 1 H, ArH), 7.02 (d, *J* = 16.3Hz, 1 H, ArH), 7.19 (t, *J* = 7.2 Hz, 1 H, ArH), 7.26–7.34 (m, 4 H, ArH), 7.47 (d, *J* = 7.2 Hz, 2 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 116.5, 124.2, 126.4, 127.4, 128.0, 128.7, 128.9, 135.2, 150.0.

MS (EI, 70 eV): *m*/*z* = 212.3 $[M + H]^+$.

**(*E*)-3,4,5-Trimethoxystilbene (3d)**
White solid; yield: 225 mg (83%); mp 108–110 °C (Lit.[16] 109–110 °C).

IR (KBr): 1633, 1506, 1417, 1188, 1130, 987 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 3 H, $OCH_3$), 3.92 (s, 6 H, $OCH_3$), 6.75 (s, 2 H, ArH), 7.03 (d, *J* = 2.8 Hz, 2 H, =CH), 7.26 (tt, *J* = 7.6, 1.2 Hz, 1 H, ArH), 7.36 (t, *J* = 7.6 Hz, 2 H, ArH), 7.50 (d, *J* = 0.7 Hz, 1 H, ArH), 7.52 (d, *J* = 1.4 Hz, 1 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 56.1, 60.9, 103.4, 126.4, 127.5, 128.1, 128.6, 128.6, 133.0, 137.1, 137.8, 153.3.

**(*E*)-3-Methoxy-4-hydroxystilbene (3e)**
White solid; yield: 170 mg (76%); mp 134–136 °C (Lit.[17] 138 °C).

IR (KBr): 2945, 1593, 1551, 1465, 1073, 963 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 3.94 (s, 3 H, $OCH_3$), 5.67 (br s, 1 H, OH), 6.88–7.09 (m, 5 H, ArH), 7.24 (tt, *J* = 7.2, 1.4 Hz, 1 H, ArH), 7.32 (tt, *J* = 8.0, 2.2 Hz, 2 H, =CH), 7.50 (dt, *J* = 7.0, 1.6 Hz, 2 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 56.0, 109.3, 116.8, 120.4, 125.4, 127.4, 127.9, 128.7, 128.8, 130.8, 135.0, 144.8, 151.3.

**(*E*)-4-(Benzyloxy)-3-methoxystilbene (3f)**
White solid; yield: 258 mg (82%); mp 114–116 °C.

IR (KBr): 1600, 1509, 1460, 1418, 1218, 958 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 3.95 (s, 3 H, $OCH_3$), 5.19 (s, 2 H, $OCH_2$), 6.85 (d, *J* = 8.3 Hz, 1 H, ArH), 6.94–6.99 (m, 2 H, ArH), 7.03 (d, *J* = 1.7 Hz, 1 H, =CH), 7.24 (d, *J* = 1.7 Hz, 1 H, =CH), 7.30 (t, *J* = 8.2 Hz, 1 H, ArH), 7.36 (t, *J* = 8.3 Hz, 4 H, ArH), 7.46 (dd, *J* = 17.0, 7.6 Hz, 5 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.9, 67.3, 109.3, 113.9, 119.7, 126.2, 126.9, 127.3, 127.5, 127.8, 128.2, 128.5, 128.6, 130.8, 136.9, 137.4, 147.9, 149.7.

MS (EI, 70 eV): *m*/*z* = 317.4 $[M + H]^+$.

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37; Found: C, 83.27; H, 6.52.

**(*E*)-3,4-Dimethoxystilbene (3g)**
White solid; yield: 186 mg (78%); mp 128–130 °C (Lit.[16] 129–130 °C).

IR (KBr): 1630, 1515, 1485, 1459, 1073, 963 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 3.95 (s, 3 H, $OCH_3$), 3.90 (s, 3 H, $OCH_3$), 6.88 (t, *J* = 8.6 Hz, 1 H, ArH), 7.03 (q, *J* = 8.8 Hz, 4 H, ArH), 7.25 (t, *J* = 3.6 Hz, 1 H, ArH), 7.35 (tt, *J* = 7.2, 1.6 Hz, 2 H, ArH), 7.50 (dt, *J* = 9.6, 1.6Hz, 2 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.8, 55.9, 108.7, 111.2, 119.8, 126.3, 126.8, 127.3, 128.4, 128.6, 130.4, 137.5, 148.9, 149.1.

**(*E*)-4-(Benzyloxy)stilbene (3h)**
White solid; yield: 230 mg (81%); mp 169–172 °C (Lit.[2c] 168–170 °C).

IR (KBr): 1602, 1508, 1449, 1246, 1074, 964 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 5.09 (s, 2 H), 7.0–6.91 (m, 4 H, ArH), 7.06 (d, *J* = 16.4 Hz, 2 H, =CH), 7.51–7.22 (m, 10 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 70.0, 115.1, 126.7, 127.2, 127.4, 127.0, 128.0, 128.1, 128.5, 128.6, 128.6, 130.4, 136.9, 137.6, 155.4.

**(*E*)-4-Styrylbiphenyl (3i)**
White solid;[18] yield: 205 mg (80%); mp 126–128 °C.

IR (KBr): 3024, 1486, 1446, 165, 1073, 966 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.15 (s, 2 H, =CH), 7.22 (t, *J* = 8.2 Hz, 2 H, ArH), 7.36 (m, *J* = 7.6 Hz, 3 H, ArH), 7.45 (t, *J* = 7.6 Hz, 2 H, ArH), 7.54 (d, *J* = 8.2 Hz, 2 H, ArH), 7.61 (t, *J* = 5.4 Hz, 5 H, ArH).

$^{13}$C NMR (100Hz, $CDCl_3$): δ = 126.5, 127.1, 127.3, 127.6, 128.2, 128.7, 128.8, 136.5, 137.3, 140.3, 140.6.

**(1*E*,3*E*)-1,4-Diphenylbuta-1,3-diene (3j)**
White solid; yield: 148 mg (72%); mp 148–151 °C (Lit.[14] 151 °C).

IR (KBr): 1636, 1537, 1487, 1173, 1071, 991, 911 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 6.68 (ddd, *J* = 18.8, 8.4, 2.8 Hz, 2 H, =CH), 6.98 (ddd, *J* = 18.8, 8.8, 2.9 Hz, 2 H, =CH), 7.48–7.43 (dt, *J* = 8.6, 1.8 Hz, 4 H, ArH), 7.34 (tt, *J* = 7.0, 1.4 Hz, 4 H, ArH), 7.28–7.42 (m, 2 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 126.3, 127.5, 128.6, 129.2, 132.8, 137.3.

**(*E*)-2-Methoxystilbene (3k)**
White solid; yield: 75 mg (36%); mp 56–58 °C (Lit.[16] 56–57 °C).

IR (KBr): 1600, 1591, 1483, 1466, 1030, 965 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 3.96 (s, 3 H, $OCH_3$), 6.93 (d, *J* = 8.0 Hz, 2 H, ArH), 7.08 (d, *J* = 16.6 Hz, 2 H, =CH), 7.29–7.18 (m, 2 H, ArH), 7.21 (tt, *J* = 7.2, 1.6Hz, 2 H, ArH), 7.49–7.61 (m, 3 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): d = 55.5, 110.9, 120.7, 123.5, 126.4, 126.4, 126.5, 127.3, 128.5, 128.6, 129.1, 137.9, 156.9.

**(*E*)-4-Chloro-4′-methoxystilbene (3l)**
White blocks; yield: 185 mg (75%); mp 182–185 °C (Lit.[19] 184 °C).

IR (KBr): 2960, 1604, 1574, 1176, 969 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, $OCH_3$), 6.93 (d, *J* = 8.0 Hz, 2 H, ArH), 6.92 (d, *J* = 16.4 Hz, 1 H, =CH), 7.12 (d, *J* = 16.4 Hz, 1 H, =CH), 7.25–7.32 (m, 3 H, ArH), 7.35–7.48 (m, 3 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.3, 114.2, 125.3, 127.4, 127.7, 128.8, 128.8, 129.8, 132.7, 136.2, 159.5.

**(*E*)-3-(Benzyloxy)-4′-chloro-4-methoxystilbene (3m)**
White solid; yield: 300 mg (86%); mp 128 °C.

IR (KBr): 3028, 2933, 1635, 1599, 1512, 1489, 1383, 1249, 1161, 958 $cm^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 3.90 (s, 3 H, $OCH_3$), 5.20 (s, 2 H, $OCH_2$), 6.81–6.99 (m, 3 H, ArH), 7.07 (dt, *J* = 4.0, 1.9 Hz, 2 H, =CH), 7.26–7.41 (m, 7 H, ArH), 7.45 (d, *J* = 7.6 Hz, 2 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 56.0, 71.1, 111.7, 120.4, 125.4, 127.3, 127.4, 127.9, 128.6, 128.7, 128.8, 128.9, 130.0, 132.7, 135.9, 137.0, 148.3, 149.8.

MS (EI, 70 eV): *m*/*z* = 351.9 $[M + H]^+$.

Anal. Calcd for $C_{22}H_{19}ClO_2$: C, 75.32; H, 5.46; Found: C, 75.21; H, 5.52.

**(*E*)-4-(Benzyloxy)-4′-chloro-3-methoxystilbene (3n)**
White solid; yield: 283 mg (84%); mp 186–190 °C.

IR (KBr): 3013, 1631, 1597, 1512, 1463, 1415, 1383, 1348, 1309, 1269, 1250, 1226, 1138, 957 $cm^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 3.95 (s, 3 H, $OCH_3$), 5.19 (s, 2 H, $OCH_2$), 6.85–7.32 (m, 5 H, ArH), 7.29–7.45 (m, 9 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 56.0, 70.9, 109.3, 113.9, 119.8, 125.6, 127.2, 127.4, 127.9, 128.6, 128.8, 129.0, 130.5, 132.8 136.0, 136.9, 148.1, 149.7.

MS (EI, 70 eV): *m*/*z* = 351.9 $[M + H]^+$.

Anal. Calcd for $C_{22}H_{19}ClO_2$: C, 75.32; H, 5.46; Found: C, 75.18; H, 5.48.

**(*E*)-4′-Chloro-3,4,5-trimethoxystilbene (3o)**
White solid; yield: 246 mg (81%); mp 174–176 °C.

IR (KBr): 1637, 1504, 1419, 1236, 1088, 973 $cm^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 3 H, $OCH_3$), 3.92 (s, 6 H, $OCH_3$), 6.73 (s, 2 H, ArH), 6.98 (dd, *J* = 16.4, 9.2 Hz, 2 H, =CH), 7.32 (d, *J* = 8.8 Hz, 2 H, ArH), 7.43 (d, *J* = 8.8 Hz, 2 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 56.1, 60.9, 103.5, 126.8, 127.5, 128.8, 129.2, 132.7, 133.1, 135.7, 138.0, 153.4.

MS (EI, 70 eV): *m*/*z* = 305.8 $[M + H]^+$.

Anal. Calcd for $C_{17}H_{17}ClO_3$: C, 67.00; H, 5.62; Found: C, 65.88; H, 5.80.

**(*E*)-4′-Chloro-4-hydroxy-3-methoxystilbene (3p)**
Pale yellow solid; yield: 143 mg (55%); mp 165–167 °C.

IR (KBr): 3216, 1593, 1514, 1489, 1451, 1427, 1370, 1277, 1260, 1208, 1156, 1122, 1098, 1026, 959 $cm^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 3.96 (s, 3 H, $OCH_3$), 5.67 (s, 1 H, OH), 6.87–6.92 (m, 2 H, =CH), 6.99–7.03 (m, 3 H, ArH), 7.31 (d, *J* = 8.4 Hz, 2 H, ArH), 7.41 (d, *J* = 8.4 Hz, 2 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.9, 108.2, 114.5, 120.5, 125.1, 127.3, 128.7, 129.6, 129.2, 132.6, 136.0, 145.7.

MS (EI, 70 eV): *m*/*z* = 261.7 $[M + H]^+$.

Anal. Calcd for $C_{15}H_{13}ClO_2$: C, 69.10; H, 5.03; Found: C, 68.86; H, 5.20.

**(*E*)-4-Chloro-4′-fluorostilbene (3q)**
White solid; yield: 176 mg (76%); mp 132–134 °C.

IR (KBr): 3029, 1601, 1576, 1510, 1496, 1448 $cm^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 6.85 (d, *J* = 16.0 Hz, 1 H, =CH), 7.04 (d, *J* = 16.0 Hz, 1 H, =CH), 7.06–7.10 (m, 2 H, ArH), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 7.47 (dd, *J* = 8.4, 5.6 Hz, 2 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 115.7 (*J* = 21.5 Hz), 127.1, 127.6, 128.0, 128.1, 128.9, 130.7, 133.1, 136.6, 162.4 (*J* = 246.2 Hz).

$^{19}$F NMR (376.5 MHz, $CDCl_3$): δ = –114.2.

MS (EI, 70 eV): *m*/*z* = 233.7 $[M + H]^+$.

Anal. Calcd for $C_{14}H_{10}ClF$: C, 72.27; H, 4.33. Found: C, 72.12; H, 4.42.

**(*E*)-4-Bromostilbene (3r)**
White solid; yield: 220 mg (85%); mp 136–138 °C (Lit.[20] 140 °C).

IR (KBr): 1599, 1587, 1575, 1493, 1485, 1447 $cm^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 6.49 (d, *J* = 16.0 Hz, 1 H, =CH), 6.63 (d, *J* = 16.0 Hz, 1 H, =CH), 7.08–7.35 (m, 9 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 120.9, 127.3, 128.3, 128.7, 128.9, 130.5, 130.9, 131.3, 136.0, 136.8.

**(*E*)-2-(4-Methoxystyryl)naphthalene (3s)**
White solid; yield: 202 mg (65%); mp 171–173 °C.

IR (KBr): 3445, 1629, 1595, 1273, 1121, 958 $cm^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 3.18 (s, 3 H, $OCH_3$), 7.36 (dd, *J* = 8.0, 4.0 Hz, 2 H, ArH), 7.40–7.50 (m, 4 H), 7.66 (s, 1 H, ArH), 7.75–7.95 (m, 6 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 38.0, 125.2, 125.9, 126.6, 127.3, 127.5, 127.6, 127.9, 132.0, 133.6, 139.2.

MS (EI, 70 eV): *m*/*z* = 261.3 $[M + H]^+$.

Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.74; H, 6.32.

## Acknowledgment

The authors are grateful for financial support from National Natural Science Foundation of China (No. 20962017), the Natural Science Foundation of Gansu Province, China (No. 1107RJZA263) and Key Laboratory of Eco-Environment-Related Polymer Materials of Ministry of Education, and Key laboratory Polymer Materials of Gansu Province (Northwest Normal University).

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