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Zinc Metal-Promoted Stereoselective Olefination of Aldehydes and Ketones with *gem*-Dichloro Compounds in the Presence of Chlorotrimethylsilane

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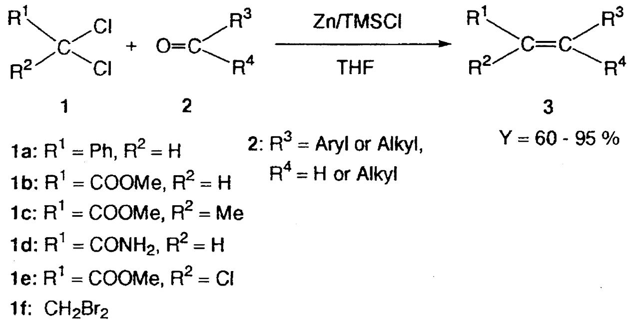
A combination of zinc metal and a catalytic amount of chlorotrimethylsilane has been found to promote the transformation of various aldehydes and ketones with *gem*-dichloro compounds, such as benzylidene dichloride (**1a**) and methyl dichloroacetate (**1b**), to the corresponding cross-coupling products, such as substituted styrene **3** and methyl acrylates **4** derivatives, under mild reaction conditions in THF. The *E*-isomer of the corresponding alkenes was obtained stereoselectively in good-to-excellent yields. The reaction serves as a very convenient one-pot procedure.

The selective transformation of carbonyl groups to carbon–carbon double bonds is very important in organic synthesis. Although the Witting reaction and its modified versions represent a highly effective and general method for olefination from carbonyl compounds,[1] their low selectively for some kinds of ylides, multi-step procedure (commonly three steps), the use of iodo or bromo compounds as a coupling regents, and so on have all encouraged the development of alternative protocols.

Metallic zinc is widely used for the preparation of organozinc reagents from iodo and bromo compounds.[2] Recently, zinc carbenes in the presence of a stoichiometric amount of Lewis acids, such as titanium(IV) chloride, have been found to be a useful reagent for the preparation of alkenes from carbonyl compounds with *gem*-diiodo and dibromo compounds.[3] However, chloro compounds have not been used for these transformations because of the smaller reactivity compared to that of the bromides and the iodides. Various activation methods of metallic zinc have been reported to overcome this difficulty.[4] To our knowledge, *gem*-dichloro compounds have not been used for the transformation of carbonyl compounds to alkenes, although these compounds are easily available.[5]

We now wish to report here on a simple, general, and stereoselective olefination of carbonyl compounds **2** with *gem*-dichloro compounds **1** in the presence of zinc powder and a catalytic amount of chlorotrimethylsilane (TMSCl) in THF (Eq. 1). As compared with the conventional olefinations, this reaction involves only one step using *gem*-dichloro compounds in the absence of Lewis acids.



(1)

Results and Discussion

The reactions were usually carried out at 50 °C for 3 h in anhydrous THF containing powdered metallic zinc, a catalytic amount of TMSCl, and carbonyl compounds. Detailed studies on the reaction of benzylidene dichloride (**1a**) with *p*-tolualdehyde (**2b**) to 4-methylstilbene (**3b**) showed that this catalytic cross-condensation is considerably influenced by the solvents used, kinds of metals, and the molar ratio of Zn to TMSCl, as shown in Table 1.

Noteworthy is the fact that the reaction in the absence of TMSCl gave only a small amount of **3b**, while the presence of a catalytic amount of TMSCl caused a smooth reaction to give product **3b** in good yields. As shown in Table 1, the optimum reaction condition for the formation of **3b** is attained when the molar ratio of **2b** : **1a** : Zn : TMSCl is 1 : 1.5 : 4.5 : 0.1.[6] A reaction with highly pure Zn (99%) resulted in a 68% yield, and the use of Mg powder instead of Zn gave no alkene products. THF is the best choice of solvents.

The cross-coupling reactions between carbonyl compounds and dichloro compounds led to stereoisomeric mixtures of *E* and *Z* olefins. A molar ratio of *E* to *Z* isomer (*E*/*Z*) was determined by means of ^{1}H NMR and GLC analyses. Representative examples are given in Tables 2 and

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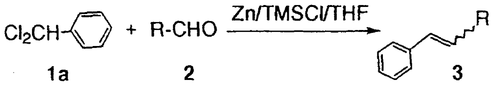
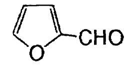
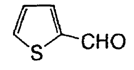
Table 1. Reactions of Benzylidene Dichloride (**1a**) and *p*-Tolualdehyde (**2b**) in the Presence of Zinc Metal

Entry	Metals[a)]	Additives	Solvents	**3b**
	mol equiv	mol equiv		yield/%[b)]
1	Zn (4.5)	None	THF	7
2	Zn (4.5)	TMSCl (0.05)	THF	15
3	Zn (4.5)	TMSCl (0.1)	THF	82
4	Zn (4.5)[c)]	TMSCl (0.1)	THF	68
5	Zn (2.0)	TMSCl (0.1)	THF	35
6	Mg (4.5)	TMSCl (1.8)	THF	—
7	Zn (4.5)	TMSCl (0.1)	DMF	58
8	Zn (4.5)	TMSCl (0.1)	$ClCH_2CH_2Cl$	1

a) Commercially available zinc metal powder with 89% purity was used without any pre-treatment. b) Isolated yield by means of column chromatography (silica gel). c) Commercially available highly pure zinc powder (99%) was used.

Table 2. Reactions of Benzylidene Dichloride (**1a**) with various Aldehydes (**2**) in the Presence of Zinc and TMSCl[a)]

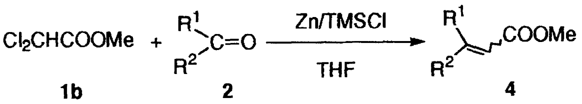


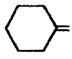
Entry	**2**		**3** (yield/%)[b)]		*E*/*Z*
1	C_6H_5CHO	(**2a**)	**3a**	(107)[c)]	96/4
2	*p*-MeC_6H_4CHO	(**2b**)	**3b**	(82)	89/11
3	*p*-*i*-$C_3H_7C_6H_4CHO$	(**2c**)	**3c**	(97)	83/17
4	*o*-$MeOC_6H_4CHO$	(**2d**)	**3d**	(76)	88/12
5	*o*-ClC_6H_4CHO	(**2e**)	**3e**	(93)	94/6
6	*m*-ClC_6H_4CHO	(**2f**)	**3f**	(96)	90/10
7	*p*-ClC_6H_4CHO	(**2g**)	**3g**	(99)	88/12
8	*p*-NC–C_6H_4CHO	(**2h**)	**3h**	(80)	95/5
9	*p*-$MeOCOC_6H_4CHO$	(**2i**)	**3i**	(78)	95/5
10	*p*-$CF_3C_6H_4CHO$	(**2j**)	**3j**	(85)	92/8
11	*p*-FC_6H_4CHO	(**2k**)	**3k**	(93)	93/7
12		(**2l**)	**3l**	(70)	86/14
13		(**2m**)	**3m**	(53)	90/10
14	C_4H_9CHO	(**2n**)	**3n**	(44)	67/33
15	*s*-C_4H_9CHO	(**2o**)	**3o**	(36)	75/25
16	*t*-C_4H_9CHO	(**2p**)	**3p**	(11)	89/11

a) **2**/**1a**/Zn/TMSCl = 1.0/1.5/4.5/0.1. b) Isolated yield based on **2**. c) Stilbene (**3a**) was additionally obtained from Zn-promoted homo-coupling reaction of **1a**.

3. A combination of zinc metal and a catalytic amount of chlorotrimethylsilane has been found to promote the transformation of various aldehydes and ketones with *gem*-dichloro compounds, such as benzylidene dichloride (**1a**) and methyl dichloroacetate (**1b**), to the corresponding cross-coupling products, such as substituted styrene **3** and methyl acrylate **4** derivatives, under mild reaction conditions. Several comments are worth noting: (1) Aromatic aldehydes reacted more smoothly with **1** than the aliphatic aldehydes; (2) ketones did not react with **1a**; (3) the reaction of **1a** in the absence of **2** gave *trans* stilbene as a homo-coupling product (*E*-**3a**) in a 64% yield; (4) the *E* isomer was obtained as a major isomer; and (5) methyl dichloroacetate (**1b**) reacted smoothly to give the corresponding alkenes in good-to-excellent yields. A high *E* stereoselectivity was also observed in the case of the reaction with aldehydes.

Table 3. Reactions of Methyl Dichloroacetate (**1b**) with Aldehydes and Ketones (**2**) in the Presence of Zinc/TMSCl



Entry	**2**		**4** (yield/%)[a)]		*E*/*Z*
1	C_6H_5CHO	(**2a**)	**4a**	(70)	100/0
2	*p*-MeC_6H_4CHO	(**2b**)	**4b**	(74)	100/0
3	*p*-ClC_6H_4CHO	(**2g**)	**4g**	(80)	100/0
4	*n*-C_4H_9CHO	(**2n**)	**4n**	(83)	94/6
5	*n*-$C_6H_{13}CHO$	(**2q**)	**4q**	(68)	90/10
6	$C_6H_5COCH_3$	(**2r**)	**4r**	(86)	50/50
7	$C_6H_5COC_6H_5$	(**2s**)	**4s**	(92)	—
8	*n*-$C_6H_{13}COCH_3$	(**2t**)	**4t**	(81)	47/53
9		(**2u**)	**4u**	(68)	—
10	$C_6H_5CH{=}CHCOCH_3$	(**2v**)	**4v**	(92)	—[b)]

a) Isolated yield based on **1b**. b) Some of stereoisomers were obtained.

Further applications of the reaction were studied as follows (Table 4). A one-pot synthesis of terminal olefins has been examined using dihalomethanes instead of benzylidene dichloride. Although the reaction of dichloromethane with benzaldehyde under the same reaction conditions did not provide the desired product **5**, the treatment of dibromomethane with benzaldehyde and octanal provided **5** and **6**, respectively, in 80 and 54% yields. Dichloro and trichloro compounds, such as methyl 2,2-dichloropropionate, 2,2-dichloroacetamide, and methyl trichloroacetate, also reacted smoothly with benzaldehyde in the Zn/TMSCl system to provide the corresponding olefins in 40—80% yields.

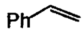
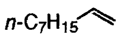
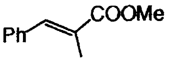
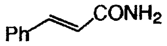
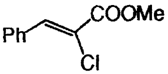
Although the details concerning the mechanism still remain ambiguous, the reaction may proceed through organozinc intermediates, such as zinc-carbenoids or *geminal* dizinc compounds.[4)] These organozinc compounds gave the products alkenes **3** or **4** through a subsequent cross-condensation of the carbonyl compounds.[7)]

In conclusion, the present method using easily available *gem*-dichloro compounds and Zn powder is characterized by high operational simplicity and mild reaction conditions. These reactions provide a route to prepare *E* alkenes with high stereoselectivity in good-to-moderate yields. We believe that this olefination offers one of the most simple and very convenient methods.

Experimental

General. The ^1H and ^{13}C NMR spectra were obtained with JEOL-JNM-EX300 and JEOL-JNM-EX270 spectrometers in $CDCl_3$ solutions. The chemical shifts are expressed in ppm down field from TMS in δ units. The GCMS spectra were recorded

Table 4. Reactions of Dihalo Compounds Using Zn/TMSCl/THF/System

Entry	R in RCHO	Halo compounds		Alkenes (yield/%)[a]		E/Z
1	Ph	Br_2CH_2	(**1f**)		80 (**5**)	—
2	n-C_7H_{15}	Br_2CH_2	(**1f**)		54 (**6**)	—
3	Ph	$MeCCl_2COOMe$	(**1c**)		65 (**7**)	50/50
4	Ph	$Cl_2CHCONH_2$	(**1d**)		40 (**8**)	100/0
5	Ph	$Cl_3CCOOMe$	(**1e**)		71 (**9**)	100/0

a) Isolated yield.

on a JEOL-JMS-DX303-HF spectrometer. The IR spectra were measured with a Shimadzu IR-435 spectrometer in liquid film. Fluorescense X-ray analyses were recorded on a Rigaku System 3083 E2. Silica gel $60F_{254}$ (Merck) was used for TLC and Silica gel 60 (Merck) was used for column chromatography.

Materials. THF was freshly distilled from a Na/benzophenone mixture prior to use. TMSCl was freshly distilled prior to use. Commercially available zinc metal (powder, purchased from Katayama Chemical Ltd., min 85%) and high purity (99%) zinc metal (powder, purchased from Kojundo Kagaku Institute Ltd.) were used without any pretreatment. The amount of lead in the zinc metals was measured by fluorescence X-ray analysis. The contents of lead were 0.09 and 0.36%, respectively. Commercially available carbonyl compounds and dichloro compounds were used without further purification.

General Procedure for the Zn-Promoted Cross-Condensation of Carbonyl Compounds with *gem*-Dichloro Compounds in the Presence of TMSCl. A THF suspension (10 mL) of Zn metal (45 mmol) and TMSCl (1 mmol) was stirred under a nitrogen atmosphere for about 15 min at 50 °C. A mixture of *gem*-dichloro compounds (15 mmol) and carbonyl compounds (10 mmol) in 10 mL of THF was slowly added to the suspended solution, and the reaction mixture was then stirred for about 3 h at the same temperature. The reaction mixture was then poured into 200 mL of saturated aqueous a ammonium chloride solution and the crude reaction products were extracted using three 100 mL portions of ether. The combined ethereal solution was washed with a 100 mL portion of water, and then dried over anhydrous magnesium sulfate. After removing the drying agent by filtration, the solvent was evaporated by distillation. Then, the products were isolated by the silica-gel column chromatography of the resulting residue. The ratio *E*/*Z* was determined by comparing of ^{1}H NMR spectrum with that reported in the literature.[8]

All new compounds, **3** and **4** prepared in this study, were identified by ^{1}H and ^{13}C NMR, IR, and MASS spectroscopies.[8]

(*E*)-4-Isopropylstilbene (3c): Oil; IR (neat) 2950 (C–H), 1593 cm^{-1}; ^{1}H NMR $\delta = 1.25$ (6H, d, $J = 7.6$ Hz, Me), 2.93 (1H, m, CH), 7.07 (2H, d, $J = 1.7$ Hz, CH=CH), 7.22 (3H, m, Ar), 7.33 (2H, m, Ar), 7.40 (4H, m, Ar); ^{13}C NMR $\delta = 23.9$, 33.8, 126.4, 126.5, 126.7, 127.3, 127.7, 128.5, 128.6, 134.9, 137.5, 148.3. HRMS (EI) Found: *m*/*z* 222.1403. Calcd for $C_{17}H_{18}$: M$^+$, 222.1409.

(*E*)-3-Chlorostilbene (3f): Oil; IR (neat) 3010 (C–H), 1589 cm^{-1}; ^{1}H NMR $\delta = 6.94$ (1H, d, $J = 16.5$ Hz, CH=CH), 7.04 (1H, d, $J = 16.5$ Hz, CH=CH), 7.26 (6H, m, Ar), 7.45 (3H, m, Ar); ^{13}C NMR $\delta = 124.7$, 126.3, 126.6, 127.1, 127.4, 128.0, 128.7, 130.0, 134.6, 136.7, 139.2; HRMS (EI) Found: *m*/*z* 214.0545. Calcd for $C_{14}H_{11}Cl$: M$^+$, 214.0549.

(*E*)-4-Cyanostilbene (3h): Oil; IR (neat) 3020 (C–H), 2220 (CN), 1603 cm^{-1}; ^{1}H NMR $\delta = 7.07$ (1H, d, $J = 16.2$ Hz, CH=CH), 7.22 (1H, d, $J = 16.2$ Hz, CH=CH), 7.38 (4H, m), 7.60 (5H, m); HRMS (EI) Found: *m*/*z* 205.2581. Calcd for $C_{15}H_{11}N$: M$^+$, 205.2586.

Methyl (*E*)-4-Stilbenecarboxylate (3i): Oil; IR (neat) 3010 (C–H), 1704 (C=O), 1603, 1274, 1108 cm^{-1}; ^{1}H NMR $\delta = 3.90$ (3H, s, OMe), 7.09 (1H, d, $J = 16.2$ Hz, CH=CH), 7.20 (1H, d, $J = 16.2$ Hz, CH=CH), 7.28 (1H, m, Ar), 7.36 (2H, m, Ar), 7.52 (m, 2H, Ar), 7.55 (2H, d, $J = 8.3$ Hz, Ar), 8.00 (2H, d, $J = 8.3$ Hz, Ar); ^{13}C NMR $\delta = 52.0$, 126.3, 126.7, 127.5, 128.2, 128.7, 128.9, 130.0, 131.2, 136.7, 141.8, 166.8; HRMS (EI) Found: *m*/*z* 238.0998. Calcd for $C_{16}H_{14}O_2$: M$^+$, 238.0994.

(*E*)-4-Trifluoromethylstilbene (3j): Oil; IR (neat) 3020 (CH), 1612, 1324 cm^{-1}; ^{1}H NMR $\delta = 7.13$ (1H, d, $J = 16.2$ Hz, CH=CH), 7.23 (1H, d, $J = 16.2$ Hz, CH=CH), 7.38 (3H, m, Ar), 7.62 (6H, m, Ar); ^{13}C NMR $\delta = 125.6$ (q, $J = 3.7$ Hz), 126.6, 126.8, 127.1, 128.3, 128.8, 131.2, 136.6, 140.8; HRMS (EI) Found: *m*/*z* 248.0809. Calcd for $C_{15}H_{11}F_3$: M$^+$, 248.0813.

2-Styrylfuran (3l): Oil; IR (neat) 3020 (CH), 1595, 730 cm^{-1}; ^{1}H NMR $\delta = 6.33$ (2H, m, Furan), 6.85 (1H, d, $J = 16.2$ Hz, CH=CH), 7.02 (1H, d, $J = 16.2$ Hz, CH=CH), 7.30 (4H, m, Ar), 7.43 (2H, m, Ar+Furan); ^{13}C NMR $\delta = 108.5$, 111.6, 116.5, 126.3, 126.5, 127.1, 127.5, 128.0, 128.6, 142.0; HRMS (EI) Found: *m*/*z* 170.0725. Calcd for $C_{12}H_{10}O$: M$^+$, 170.0731.

2-Styrylthiophene (3m): Oil; IR (neat) 3020 (C–H), 1598, 961, 695 cm^{-1}; ^{1}H NMR $\delta = 6.92$ (3H, m, CH=CH+Thiophene), 7.19, (5H, m, Ar+Thiophene), 7.40 (2H, m, Ar); ^{13}C NMR $\delta =$ 121.7, 124.26, 126.0, 126.3, 126.5, 127.5, 128.3, 128.6, 136.9, 142.8; HRMS (EI) Found: *m*/*z* 186.0500. Calcd for $C_{12}H_{10}S$: M$^+$, 186.0503.

1-Phenyl-1-hexene (3n): Oil; IR (neat) 3010 (C–H), 1596 cm^{-1}; *E*-isomer: ^{1}H NMR $\delta = 0.90$ (3H, m, Me), 1.40 (4H, m, CH_2), 2.20 (2H, m, CH_2), 6.20 (2H, m, CH=CH), 7.23 (5H, m, Ar); *Z*-isomer: ^{1}H NMR $\delta = 0.89$ (3H, m), 1.40 (4H, m), 2.33 (2H, m), 5.65 (2H, m), 7.23 (5H, m); HRMS (EI) Found: *m*/*z* 160.1247. Calcd for $C_{12}H_{16}$: M$^+$, 160.1252.

3-Methyl-1-phenyl-1-pentene (3o): Oil; IR (neat) 3010 (C–H), 2950, 1598 cm^{-1}; *E*-isomer: ^{1}H NMR $\delta = 0.92$ (3H, t, $J = 7.4$ Hz, Me), 1.04, (3H, d, $J = 6.9$ Hz, Me), 1.39 (2H, m, CH_2), 2.18 (1H, m, CH), 6.07 (1H, d/d, $J = 15.8/7.9$ Hz, CH=CH), 6.32 (1H, d, $J = 15.8$ Hz, CH=CH), 7.30 (5H, m, Ar); ^{13}C NMR $\delta = 11.8$, 20.2, 29.8, 38.9, 126.0, 126.7, 128.2, 128.4, 128.6, 136.6, 138.0; *Z*-isomer: ^{1}H NMR $\delta = 0.87$ (3H, t, $J = 7.3$ Hz, Me), 1.02 (3H, d, $J = 6.6$ Hz, Me), 1.39 (2H, m, CH_2), 2.65 (1H, m, CH), 5.41 (1H, m, CH=CH), 6.35 (1H, m, CH=CH), 7.30 (5H, m, Ar); ^{13}C NMR $\delta = 11.8$, 20.7, 30.4, 33.8, 126.3, 127.6, 128.1, 128.4, 128.6, 136.6, 139.3; HRMS (EI) Found: *m/z* 160.1258. Calcd for $C_{12}H_{16}$: M$^+$, 160.1252.

3,3-Dimethyl-1-phenyl-1-butene (3p): Oil; IR (neat) 3020 (C–H), 2950, 1599 cm^{-1}; *E*-isomer: ^{1}H NMR $\delta = 1.12$ (9H, s, Me), 6.27 (1H, d, $J = 16.2$ Hz, CH=CH), 6.29 (1H, d, $J = 16.2$ Hz, CH=CH), 7.28 (5H, m, Ar); ^{13}C NMR $\delta = 29.6$, 33.3, 124.6, 126.0, 126.7, 128.43, 138.0, 141.8. *Z*-isomer: ^{1}H NMR $\delta = 0.98$ (9H, s, Me), 5.57 (1H, s, CH=CH), 5.63 (1H, s, CH=CH), 7.28 (5H, m, Ar); ^{13}C NMR $\delta = 31.2$, 33.3, 124.6, 126.0, 127.5, 128.9, 138.0, 142.6; HRMS (EI) Found: *m/z* 160.1260. Calcd for $C_{12}H_{16}$: M$^+$, 160.1252.

Methyl 2-Nonenoate (4q): Oil; IR (neat) 2920 (C–H), 1728 (C=O), 1600, 1275, 1170 cm^{-1}; ^{1}H NMR $\delta = 0.86$ (3H, t, $J = 6.6$ Hz, Me), 1.28 (8H, m, CH$_2$), 2.20 (2H, m, CH$_2$), 3.72 (3H, s, OMe), 5.81 (1H, m, CH=CH), 6.97 (1H, m, CH=CH); ^{13}C NMR $\delta = 14.0$, 22.5, 27.9, 28.9, 29.0, 31.7, 51.2, 120.7, 149.7, 167.0; HRMS (EI) Found: *m/z* 170.1301. Calcd for $C_{10}H_{18}O_2$: M$^+$, 170.1307.

Methyl β-Methylcinnamate (4r): Oil; IR (neat) 2960 (C–H), 1725 (C=O), 1640, 1278, 1160 cm^{-1}; *E*-isomer ^{1}H NMR $\delta = 2.17$ (3H, d, $J = 1.3$ Hz, Me), 3.55 (3H, s, OMe), 5.91 (1H, d, $J = 1.3$ Hz, CH=C), 7.28 (5H, m, Ar); ^{13}C NMR $\delta = 27.2$, 50.9, 117.1, 126.8, 127.8, 127.9, 140.6, 155.9, 166.2; *Z*-isomer: ^{1}H NMR $\delta = 2.17$ (3H, d, $J = 1.3$ Hz, Me), 3.55 (3H, s, OMe), 5.91 (1H, d, $J = 1.3$ Hz, CH=C), 7.28 (5H, m, Ar); ^{13}C NMR $\delta = 18.0$, 51.1, 116.7, 126.3, 128.5, 129.0, 142.2, 155.9, 167.2; HRMS (EI) Found: *m/z* 176.0831. Calcd for $C_{11}H_{12}O_2$: M$^+$, 176.0837.

Methyl 3,3-Diphenyl-2-propionate (4s): Oil; IR (neat) 3080 (C–H), 3050 (C–H), 2960 (C–H), 1726 (C=O), 1620, 1270, 1164 cm^{-1}; ^{1}H NMR $\delta = 3.60$ (3H, s, OMe), 6.36 (1H, m, CH=C), 7.34 (10H, m, Ar); ^{13}C NMR $\delta = 51.2$, 116.8, 127.8, 128.1, 128.2, 128.3, 129.1, 129.4, 138.8, 140.8, 157.0, 166.3; HRMS (EI) Found: *m/z* 238.0990. Calcd for $C_{16}H_{14}O$: M$^+$, 238.0994.

Methyl 3-Methyl-2-nonenoate (4t): Oil; IR (neat) 2920 (C–H), 1720 (C=O), 1650, 1220, 1145; *E*-isomer: ^{1}H NMR $\delta = 0.89$ (3H, t, $J = 6.6$ Hz, Me), 1.28 (6H, m, CH$_2$), 1.46 (2H, m, CH$_2$), 1.87 (3H, s, Me), 2.12 (2H, m, CH$_2$), 3.67 (3H, s, OMe), 5.66 (1H, m, CH=C); ^{13}C NMR $\delta = 14.0$, 22.5, 27.3, 28.8, 31.6, 40.9, 50.7, 115.0, 147.0, 160.7, 166.8; Z-isomer: ^{1}H NMR $\delta = 0.89$ (3H, t, $J = 6.6$ Hz, Me), 1.28 (6H, m, CH$_2$), 1.46 (2H, m, CH$_2$), 2.15 (3H, s, Me), 2.61 (2H, m, CH$_2$), 3.68 (3H, s, OMe), 5.66 (1H, m, CH=); ^{13}C NMR $\delta = 18.7$, 25.1, 28.1, 29.4, 33.4, 40.9, 50.7, 115.5, 150.8, 161.2, 167.3; HRMS (EI) Found: *m/z* 184.1458. Calcd for $C_{11}H_{20}O_2$: M$^+$, 184.1463.

Methyl Cyclohexylideneacetate (4u): Oil; IR (neat) 3000 (C–H), 2920 (C–H), 1715 (C=O), 1642, 1272, 1155 cm^{-1}; ^{1}H NMR $\delta = 1.67$, (6H, m, CH$_2$), 2.21 (2H, t, $J = 6.27$ Hz, CH$_2$), 2.84 (2H, t, $J = 6.27$ Hz, CH$_2$), 3.68 (3H, s, OMe), 5.61 (1H, s, CH=); ^{13}C NMR $\delta = 26.0$, 27.6, 28.4, 29.6, 37.7, 50.4, 112.4, 163.5, 166.9; HRMS (EI) Found: *m/z* 154.0997. Calcd for $C_9H_{14}O_2$: M$^+$, 154.0994.

Methyl 3-Methyl-5-phenyl-2,4-pentadienoate (4v): Oil; IR (neat) 3020 (C–H), 2950 (C–H), 1710 (C=O), 1600, 1280, 1150 cm^{-1}; ^{1}H NMR $\delta = 2.08$ (3H, s, Me), 3.70 (3H, s, OMe), 5.73 (1H, s, CH=), 6.89 (1H, d, $J = 16.2$ Hz, CH=CH), 7.37 (5H, m, Ar), 8.42 (1H, d, $J = 16.2$ Hz, CH=CH); ^{13}C NMR $\delta = 20.7$, 50.8, 117.1, 125.8, 127.3, 128.5, 128.6, 135.3, 136.6, 150.9, 166.6; HRMS (EI) Found: *m/z* 202.0989. Calcd for $C_{13}H_{14}O_2$: M$^+$, 202.0994.

Methyl α-Chlorocinnamate (9): Oil; IR (neat) 3020 (C–H), 2935 (C–H), 1720 (C=O), 1600, 1278, 1192, 1040 cm^{-1}; ^{1}H NMR $\delta = 3.65$ (3H, s, OMe), 7.40 (3H, m, Ar), 7.80 (2H, m, Ar), 7.97 (1H, s, CH=); ^{13}C NMR $\delta = 52.7$, 121.2, 127.9, 129.7, 130.1, 132.3, 136.6, 163.3; HRMS (EI) Found: *m/z* 196.0287. Calcd for $C_{10}H_9ClO_2$: M$^+$, 196.0291.

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6) Use of high purity (99%) of zinc metal and a couple of high purity Zn/PbCl$_2$ instead of 85% Zn brought about the formation of **3a** in the yield of 68 and 46%, respectively.

7) In this reaction, roles of TMSCl may be postulated mainly two ways, that is, one is activation of zinc metal surface and another one is activation of **2** by coordination to carbonyl group.

8) Assignment of the *E* and *Z*-stereoisomers of the products, and determination of the *E*/*Z* ratio were accomplished by means of ^{1}H NMR and/or gas chromatography according to the reported assignment. For example: O. H. Wheeler and H. N. Barle de Pabon, *J. Org. Chem.*, **30**, 1473 (1965); Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Am. Chem. Soc.*, **91**, 7166 (1969); F. Akiyama, H. Miyazaki, K. Kaneda, S. Teranishi, Y. Fujiwara, M. Abe, and H. Taniguchi, *J. Org. Chem.*, **45**, 2359 (1980).