Novel Stereospecific Synthesis of 3-Chloroacrylate Esters via Palladium-Catalyzed Carbonylation of Terminal Acetylenes

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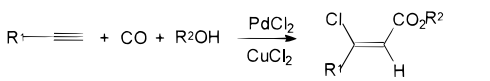
A simple and effective method for the highly regio- and stereospecific synthesis of (*Z*)-3-chloroacrylate esters is described. Using terminal acetylenes and primary, secondary, and tertiary aliphatic alcohols as substrates, the carbonylation reactions were carried out under carbon monoxide (1 atm) at room temperature in the presence of a catalytic amount of $PdCl_2$ and 3 equiv of cupric chloride. Isolated yields of (*Z*)-3-chloroacrylate esters ranging from 30% to 72% were obtained. Our results show that the polarity of the alcohol−benzene solvent plays an important role in the stereochemistry of the products.

Introduction

3-Chloroacrylate esters are valuable intermediates in organic synthesis[1] and are known to exhibit some biological properties.[2] There are many ways to synthesize 3-chloroacrylate esters,[3] as a mixture of Z- and E-isomers, with the E-isomers predominating. The stereospecific synthesis of (*Z*)-3-chloroacrylate esters can be effected by the esterification of the corresponding acids.[3b,4] It has also been reported that (*Z*)-3-chloroacrylate esters can be synthesized stereospecifically by the reaction of lithium chloride in acetic acid with actylenecarboxylates.[5] Currently, the transition-metal-catalyzed carbonylation of terminal acetylenes may be one of the most useful strategies for the synthesis of (*Z*)-3-chloroacrylate esters. Heck has reported that 3-chloroacrylate esters (the E-isomers predominating) were observed as byproducts in the dicarbonylation of terminal acetylenes using $PdCl_2$ and mercuric dichloride.[6] A related synthesis of unsaturated β-chlorolactones (E-isomers) occurred when propargylic alcohols were mercurated and then carbonylated with a palladium catalyst.[7] Unfortunately, the mercuration was successful only with relatively low molecular weight or symmetrically substituted propargylic alcohols. Thus, new and effective stereospecific synthesis routes to (*Z*)-3-chloroacrylate esters are still of considerable interest to synthetic organic chemists. In this paper, we report that (*Z*)-3-chloroacrylate esters can be efficiently produced with high regio- and stereospecificity using terminal acetylenes, aliphatic alcohols, and carbon monoxide in the presence of a catalytic amount of $PdCl_2$ and an excess of cupric chloride (eq 1).



(1)

1 2 3(only Z-isomers)

1a R^1 = Ph
1b R^1 = C_5H_{11}

2a R^2 = Me
2b R^2 = Bu
2c R^2 = *i*-Pr
2d R^2 = *s*-Bu
2e R^2 = *t*-Bu
2f R^2 = *t*-Pentyl

3a R^1 = Ph, R^2 = Me; **3g** R^1 = C_5H_{11}, R^2 = Me
3b R^1 = Ph, R^2 = Bu; **3h** R^1 = C_5H_{11}, R^2 = Bu
3c R^1 = Ph, R^2 = *i*-Pr; **3i** R^1 = C_5H_{11}, R^2 = *i*-Pr
3d R^1 = Ph, R^2 = *s*-Bu; **3j** R^1 = C_5H_{11}, R^2 = *s*-Bu
3e R^1 = Ph, R^2 = *t*-Bu; **3k** R^1 = C_5H_{11}, R^2 = *s*-Bu
3f R^1 = Ph, R^2 = *t*-Pentyl **3l** R^1 = C_5H_{11}, R^2 = *t*-Pentyl

Result and Discussion

Preliminary results showed that the polarity of the solvent (alcohol−benzene) could affect the yield and Z/E ratio of **3a**. Thus, we tried adding different amounts of methanol to vary the polarity of the solvent. A mixture of phenylacetylene (**1a**, 102 mg, 1 mmol) and methanol (**2a**, 0.04 mL, 1 mmol) reacted under CO (1 atm) in benzene (10 mL) at room temperature for 2 h in the presence of $PdCl_2$ (10 mg, 0.056 mmol) and $CuCl_2$ (269 mg, 2 mmol) (entry 1 in Table 1). The conversion of **1a** was only 50%, and methyl 3-chloro-3-phenylacrylate (**3a**) was obtained in 20% GC yield (Z/E = 84:16). The assignment of the stereochemistry of the product **3a** is based upon the chemical shift of the olefinic proton (δ = 6.53 in the ^{1}H NMR spectra).[3b,8] All of the results from

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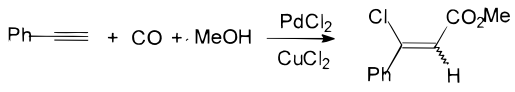
Table 1. Reaction of Phenylacetylene (1a) with MeOH (2a) under Carbon Dioxide in the Presence of $PdCl_2$ and $CuCl_2$[a]

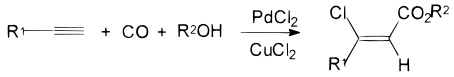


1a 2a 3a

entry	MeOH (mL)	$CuCl_2$ (mmol)	yield of **3a**, % (Z/E)[b]
1	0.04	2	20 (84/16)
2	0.5	2	47 (98/2)
3[c]	0.6	2	48 (98/2)
4	0.7	2	25 (only Z)
5	0.6	3	58 (only Z) (31%)[d]
6	0.6	4	57 (only Z)
7[e]	0.3	3	53 (only Z) (30%)[d]
8[f]	10	3	trace

[a] Reaction conditions: **1a** (1 mmol) and $PdCl_2$ (0.056 mmol) in C_6H_6 (10 mL) under CO (1 atm) at room temperature for 2 h. [b] Determined by GC analysis using an internal standard. [c] The conversion of **1a** was 58%. [d] Isolated yields. [e] Reacted in 5 mL of C_6H_6. [f] Only methanol as solvent.

Table 2. Palladium-Catalyzed Carbonylation of Terminal Acetylenes[a]



1 2 3(only Z-isomers)

entry	R^1	R^2	products	isolated yield (%)[b]
1	Ph	Bu	**3b**	63 (77)
2	Ph	*i*-Pr	**3c**	66 (82)
3	Ph	*s*-Bu	**3d**	72 (90)
4	Ph	*t*-Bu	**3e**	70 (86)
5	Ph	*t*-pentyl	**3f**	50 (58)
6	C_5H_{11}	Me	**3g**	43 (60)
7	C_5H_{11}	Bu	**3h**	67 (81)
8	C_5H_{11}	*i*-Pr	**3i**	65 (81)
9	C_5H_{11}	*s*-Bu	**3j**	49 (60)
10	C_5H_{11}	*t*-Bu	**3k**	43 (49)
11	C_5H_{11}	*t*-pentyl	**3l**	45 (55)

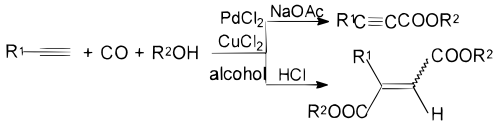
[a] Reaction conditions: **1** (1 mmol), **2** (0.6 mL), $PdCl_2$ (0.056 mmol), and $CuCl_2$ (3 mmol) in C_6H_6 (10 mL) under CO (1 atm) at room temperature for 2 h. [b] Isolated yields; GC yields are given in parentheses.

Table 1 indicate that the addition of 0.6 mL of methanol appears to be most effective (48% GC, Z/E = 98/2) (entry 3). To examine this result more closely, we decreased the amount of methanol and benzene at the same ratio, which still resulted in a high yield (Table 1, entry 7). Therefore, the optimal ratio of methanol/benzene (v/v) is 0.6/10.

Increasing the cupric chloride concentration has been reported by Heck[6] to cause an increasing formation of 3-chloroacrylic esters, so the amount of cupric chloride was the next variable examined. Indeed, the amount of cupric chloride affected the yield of **3a** in our experiments. By increasing the amount of cupric chloride from 2 to 3 mmol, the yields of **3a** were increased from 48% to 58% (GC yields, only Z-isomer) (entries 3 and 5). When the amount of $CuCl_2$ was increased to 4 mmol, the yield remained at 57% (entry 6). The above results encouraged us to use the palladium-catalyzed carbonylation for a general synthesis of (*Z*)-3-chloroacrylate esters.

The results in Table 2 indicate that terminal acetylenes could be employed successfully in the carbonylation reaction, together with aliphatic alcohols, to give fair to good yields of (*Z*)-3-chloroacrylate esters.[9] To our surprise, some sterically hindered aliphatic alcohols, such as *s*-BuOH (**2d**), *t*-BuOH (**2e**), and *t*-pentanol (**2f**), showed high activity in the reaction, indicating that this may be a simple and efficient method for the preparation of some sterically hindered esters. When terminal acetylenes reacted with the same alcohol, the activity of **1a** is higher than that of **1b**. It is of interest to note that an internal acetylene (4-octyne) did not afford 3-chloroacrylate esters under the same condition.[10]

Scheme 1



When the experiments were carried out in a sealed system, the reaction was not clean and a mixture was formed. An open system may allow the majority of HCl gas generated in the reaction to be released into the air, thus delaying the acidification of the reaction mixture.

In comparing the carbonylation products with the reaction conditions, we can come to some valuable conclusions. In polar solvents such as methanol, adding base (NaOAc)[11] or acid (HCl)[12] to the palladium-catalyzed carbonylation of acetylenes in the presence of cupric chloride afforded acetylenecarboxylates or unsaturated diesters, respectively. No 3-chloroacrylate esters were detected (Scheme 1). We found that the carbonylation reaction of **1a** in MeOH without added acid or base afforded a mixtrue of unsaturated diesters and trace methyl (*Z*)-3-chloro-3-phenylacrylate (entry 8 in Table 1). Tsuji gave results similar to ours.[11]

When alcohol−benzene, a less polar solvent, was used in the reaction, 3-chloroacrylate esters were predominate in the products. In the presence of base (NaOAc), however, the reaction in the same solvent afforded (Z)-unsaturated diesters with high stereoselectivity.[13] All the results suggest that selectivity of the products may strongly depend on the polarity of solvent and the effect of added acid or base.

It is interesting to hypothesize how the reaction proceeds mechanistically. The question regarding the first step of the reaction is whether chloropalladation of acetylenes or acylpalladation of acetylenes occurred first. Heck[6] observed that the chloro esters were formed as byproducts in the 1-phenyl-1-propyne and 3,3-dimethyl-1-butyne dicaroxylation reactions. He hypothesized that

(9) Z- and E-isomers of such compounds may be separated by TLC on silica gel using light petroleum−ethyl ether (10:1) as eluant, but we did not detect any E-isomer. The chemical shifts of the olefinic proton in the ^1H NMR ($CDCl_3$) spectra for the alkyl (*Z*)-3-chlorophenylacrylates are all about $\delta = 6.50$ and for alkyl (*Z*)-3-chloro-2-octenoates they are $\delta = 5.90-6.00$. GC analysis also showed that the products contained <1% of E-isomers.

(10) The reaction condition: 4-octyne (1 mmol), $PdCl_2$ (0.056 mmol), $CuCl_2$ (3 mmol), and *s*-BuOH (0.6 mL) in C_6H_6 (10 mL) under CO (1 atm) or in the absence of CO at room temperature for 10 h. After filtration, the benzene was removed by rotary evaporation to give crude hexapropylbenzene. Hexapropylbenzene was then purified by preparative TLC using light petroleum−ethyl ether (10:1) as eluent on silica gel and recrystallized. The isolated yield was 98%. See: (a) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93. (b) Yokota, T.; Sakurai, Y.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **1997**, *38*, 3923.

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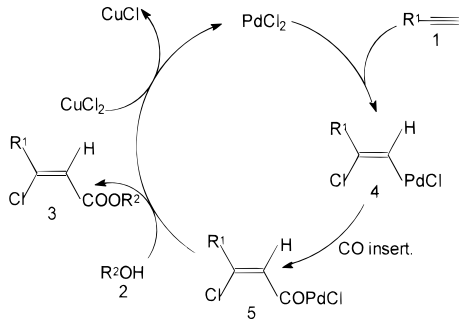
(12) Alper, H.; Despeyroux, B.; Woell, J. B. *Tetrahedron Lett.* **1983**, *24*, 5691.

(13) This paper has been accepted by *Synth. Commun.*

Scheme 2



the chloro esters may be formed either by a reductive elimination of Pd(0) from the monocarboalkoxylated intermediate or by $PdCl_2$ addition of acetylenes, followed by carbonylation and alcoholysis. In fact, no carbonylation products of 4-octyne were detected in our experiments,[10] indicating that chloropalladation of acetylenes might be faster than acylpalladation of acetylenes in the less polar solvent. Therefore, our hypothesis is that the *cis*-addition of acetylenes and $PdCl_2$ may form the *cis*-chloropalladation intermediate **4**,[14] followed by migratory insertion of carbon monoxide and alcoholysis[15] to afford (*Z*)-3-chloroacrylate esters **3**. $CuCl_2$ then oxidizes the palladium from intermediate **5** to regenerate the active palladium species (Scheme 2).

In summary, we have developed a novel method for the highly regio- and stereospecific synthesis of (*Z*)-3-chloroacrylate esters under mild conditions. The method may also provide a new, efficient route for the synthesis of some sterically hindered alkyl esters.

Experimental Section

General Information. All ^1H and ^{13}C NMR spectra were recorded at 400 MHz with $CDCl_3$ as solvent. MS data were obtained using HP 5973 GC−MS. TLC was performed using commercially prepared 100−400 mesh silica gel plates (HF_{254}), and visualization was effected at 254 nm. $CuCl_2$ was dried at 130 °C under HCl gas. All other reagents were used directly as obtained commercially.

General Procedure for the Carbonylation of Terminal Acetylenes. To a mixture of $PdCl_2$ (0.056 mmol) and $CuCl_2$ (3 mmol) in C_6H_6 (10 mL) were added alcohol **2** (0.6 mL) and substrate **1** (1 mmol) under CO (1 atm). The reaction was stirred at room temperature for 2 h. After filtration, the benzene was removed by rotary evaporation to give crude **3**. Then the products **3** were purified by preparative TLC using light petroleum−ethyl ether (10:1) as eluent on silica gel. All products were obtained as colorless liquids.

Methyl (*Z*)-3-Chloro-3-phenylacrylate (3a).[6] IR (film) 768, 1439, 1620, 1730, 3062 cm^{-1}; ^1H NMR δ 3.79 (s, 3H, CH_3), 6.53 (Z-isomer) (s, 1H, HC═), 7.38−7.42, 7.65−7.68 (m, 5H, C_6H_5); ^{13}C NMR δ 51.6, 52.5 (CH_3), 116.0, 119.3 (═CH), 126.8, 127.0, 127.2, 127.5, 127.9, 128.1, 128.4, 128.6, 129.1, 129.5, 130.0, 130.3, 130.4, 130.7, 137.2 (C_6H_5), 146.5, 150.2 (ClC═), 164.6(C═O); MS *m*/*z* 198 ($M^+(^{37}Cl)$), 196 ($M^+(^{35}Cl)$, 167 ($M^+(^{37}Cl) - OCH_3$), 165 ($M^+(^{35}Cl) - OCH_3$), 139 ($M^+(^{37}Cl) - CO_2CH_3$), 137 ($M^+(^{35}Cl) - CO_2CH_3$), 102 ($M^+ - Cl - CO_2CH_3$).

Butyl (*Z*)-3-Chloro-3-phenylacrylate (3b). IR (film) 766, 1385, 1450, 1491, 1618, 1724, 3062 cm^{-1}; ^1H NMR δ 0.94 (t, 3H, J = 7.2 Hz, CH_3), 1.41 (m, 2H, CH_2), 1.66 (m, 2H, CH_2), 4.20 (t, 2H, J = 6.8 Hz, CH_2), 6.53 (s, 1H, HC═), 7.37−7.41, 7.66−7.68 (m, 5H, C_6H_5); ^{13}C NMR δ 13.6 (CH_3), 19.1 (CH_2), 30.3, 30.6, 30.9 (CH_2), 64.2, 64.4, 64.7 (OCH_2), 116.1, 116.4 (═CH), 126.6, 126.7, 126.9, 127.1, 127.6, 127.7, 127.8, 128.0, 128.1, 128.5, 128.8, 128.9, 129.8, 130.3, 130.5, 130.8, 137.2 (C_6H_5), 146.0 (ClC═), 164.2 (C═O); MS *m*/*z* 240 ($M^+(^{37}Cl)$), 238 ($M^+(^{35}Cl)$), 183 ($M^+(^{37}Cl) - C_4H_9$), 181 ($M^+(^{35}Cl) - C_4H_9$), 167 ($M^+(^{37}Cl) - OC_4H_9$), 165 ($M^+(^{35}Cl) - OC_4H_9$), 139 ($M^+(^{37}Cl) - CO_2C_4H_9$), 137 ($M^+(^{35}Cl) - CO_2C_4H_9$), 102 ($M^+ - Cl - CO_2C_4H_9$). Anal. Calcd for $C_{13}H_{15}ClO_2$: C, 65.41; H, 6.33. Found: C, 65.25; H, 6.38.

Isopropyl (*Z*)-3-Chloro-3-phenylacrylate (3c).[6] IR (film) 766, 853, 1373, 1448, 1492, 1618, 1722, 3062 cm^{-1}; ^1H NMR δ 1.25 (d, 6H, J = 6 Hz, $2CH_3$), 5.14 (m, 1H, CH), 6.50 (s, 1H, HC═), 7.36−7.43, 7.65−7.68 (m, 5H, C_6H_5); ^{13}C NMR δ 21.9 ($2CH_3$), 68.1 (O−C), 116.9 (═CH), 127.2, 128.6, 130.5, 137.5 (C_6H_5), 144.5 (ClC═), 163.5 (C═O); MS *m*/*z* 226 ($M^+(^{37}Cl)$), 224 ($M^+(^{35}Cl)$), 183 ($M^+(^{37}Cl) - C_3H_7$), 181 ($M^+(^{35}Cl) - C_3H_7$), 167 ($M^+(^{37}Cl) - OC_3H_7$), 165 ($M^+(^{35}Cl) - OC_3H_7$), 139 ($M^+(^{37}Cl) - CO_2C_3H_7$), 137 ($M^+(^{35}Cl) - CO_2C_3H_7$), 102 ($M^+ - Cl - CO_2C_3H_7$).

***sec*-Butyl (*Z*)-3-Chloro-3-phenylacrylate (3d).** IR (film) 1001, 1380, 1448, 1493, 1618, 1716, 2975 cm^{-1}; ^1H NMR δ 0.93 (t, 3H, J = 7.4 Hz, CH_3), 1.27 (d, 3H, J = 6.4 Hz, CH_3), 1.62 (m, 2H, CH_2), 4.98 (m, 1H, CH), 6.52 (s, 1H, HC═), 7.37−7.41, 7.66−7.68 (m, 5H, C_6H_5); ^{13}C NMR δ 9.7 (CH_3), 19.0, 19.5 (CH_2), 28.8 (CH_2), 72.7 (OCH), 117.0 (═CH), 127.2, 127.9, 128.6, 129.6, 129.7, 130.5, 137.4 (C_6H_5), 145.7 (ClC═), 163.9 (C═O); MS *m*/*z* 240 ($M^+(^{37}Cl)$), 238 ($M^+(^{35}Cl)$), 183 ($M^+(^{37}Cl) - C_4H_9$), 181 ($M^+(^{35}Cl) - C_4H_9$), 167 ($M^+(^{37}Cl) - OC_4H_9$), 165 ($M^+(^{35}Cl) - OC_4H_9$), 140 ($M^+(^{37}Cl) + 1 - CO_2C_4H_9$), 138 ($M^+(^{35}Cl) + 1 - CO_2C_4H_9$), 102 ($M^+ - Cl - CO_2C_4H_9$). Anal. Calcd for $C_{13}H_{15}ClO_2$: C, 65.41; H, 6.33. Found: C, 65.50; H, 6.30.

***tert*-Butyl (*Z*)-3-Chloro-3-phenylacrylate (3e).** IR (film) 764, 1035, 1390, 1450, 1616, 1722, 3060 cm^{-1}; ^1H NMR δ 1.52 (s, 9H, $3CH_3$), 6.45 (s, 1H, HC═), 7.37−7.40, 7.63−7.66 (m, 5H, C_6H_5); ^{13}C NMR δ 27.7, 27.9, 28.2, 28.5, 28.6 ($3CH_3$), 81.3 (O−C), 118.2 (═CH), 126.6, 126.7, 127.1, 127.6, 127.9, 128.1, 128.5, 129.3, 130.4, 137.5 (C_6H_5), 144.6 (ClC═), 163.5 (C═O); MS *m*/*z* 238 ($M^+(^{35}Cl)$), 183 ($M^+(^{37}Cl) - C_4H_9$), 181 ($M^+(^{35}Cl) - C_4H_9$), 167 ($M^+(^{37}Cl) - OC_4H_9$), 165 ($M^+(^{35}Cl) - OC_4H_9$), 139 ($M^+(^{37}Cl) - CO_2C_4H_9$), 137 ($M^+(^{35}Cl) - CO_2C_4H_9$), 102 ($M^+ - Cl - CO_2C_4H_9$). Anal. Calcd for $C_{13}H_{15}ClO_2$: C, 65.41; H, 6.33. Found: C, 65.77; H, 6.47.

***tert*-Pentyl (*Z*)-3-Chloro-3-phenylacrylate (3f).** IR (film) 766, 1068, 1452, 1490, 1616, 1722, 3062 cm^{-1}; ^1H NMR δ 0.91 (t, 3H, J = 7.6 Hz, CH_3), 1.49 (s, 3H, CH_3), 1.82 (q, 2H, J = 7.6 Hz, CH_2), 6.45 (s, 1H, HC═), 7.37−7.40, 7.63−7.66 (m, 5H, C_6H_5); ^{13}C NMR δ 8.2 (CH_3), 25.1, 25.6, 26.0 ($2CH_3$), 33.5 (CH_2), 83.9 (O−C), 118.2 (═CH), 126.7, 126.9, 127.2, 127.9, 128.1, 128.5, 129.6, 129.9, 130.3, 137.5 (C_6H_5), 144.5 (ClC═), 163.5 (C═O); MS *m*/*z* 252 ($M^+(^{35}Cl)$), 183 ($M^+(^{37}Cl) - C_5H_{11}$), 181 ($M^+(^{35}Cl) - C5H_{11}$), 167 ($M^+(^{37}Cl) - OC_5H_{11}$), 165 ($M^+(^{35}Cl) - OC_5H_{11}$), 139 ($M^+(^{37}Cl) - CO_2C_5H_{11}$), 137 ($M^+(^{35}Cl) - CO_2C_5H_{11}$), 102 ($M^+ - Cl - CO_2C_5H_{11}$). Anal. Calcd for $C_{14}H_{17}ClO_2$: C, 66.53; H, 6.78. Found: C, 66.56; H, 6.76.

Methyl (*Z*)-3-Chloro-2-octenoate (3g).[6] IR (film) 650, 849, 1007, 1375, 1462, 1635, 1720, 2933 cm^{-1}; ^1H NMR δ 0.88 (t, 3H, J = 7.2 Hz, CH_3), 1.25 (m, 4H, $2CH_2$), 1.60 (m, 2H, CH_2), 2.42 (t, 2H, J = 7.2 Hz, CH_2), 3.70 (s, 3H, CH_3), 6.00 (s, 1H, HC═); ^{13}C NMR δ 13.8 (CH_3), 22.3 (CH_2), 26.8 (CH_2), 30.6 (CH_2), 41.2 (CH_2), 51.3 (OCH_3), 115.7 (═CH), 151.0 (ClC═), 164.4 (C═O); MS *m*/*z* 190 ($M^+(^{35}Cl)$), 161 ($M^+(^{37}Cl) - OCH_3$), 159 ($M^+(^{35}Cl) - OCH_3$), 155 ($M^+ - Cl$), 95 ($M^+ - 1 - Cl - CO_2CH_3$).

Butyl (*Z*)-3-Chloro-2-octenoate (3h). IR (film) 660, 852, 1022, 1383, 1462, 1639, 1730, 2960 cm^{-1}; ^1H NMR δ 0.86−0.94 (m, 6H, $2CH_3$), 1.26−1.39 (m, 8H, $4CH_2$), 1.61 (m, 2H, CH_2), 2.41 (t, 2H, J = 7.6 Hz, CH_2), 4.13 (t, 2H, J = 6.8 Hz, CH_2), 5.98 (s, 1H, HC═); ^{13}C NMR δ 13.6 (CH_3), 13.7 (CH_3), 19.1 (CH_2), 22.2 (CH_2), 26.8 (CH_2), 30.6 ($2CH_2$), 41.1 (CH_2), 64.1 (OCH_2), 116.1 (═CH), 150.4 (ClC═), 164.0 (C═O); MS *m*/*z* 233 ($M^+(^{35}Cl) + 1$), 197 ($M^+ - Cl$), 179 ($M^+(^{37}Cl) + 2 - C_4H_9$), 177 ($M^+(^{35}Cl) + 2 - C_4H_9$), 161 ($M^+(^{37}Cl) - OC_4H_9$), 159

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($M^+(^{35}Cl) - OC_4H_9$), 95 ($M^+ - 1 - Cl - CO_2C_4H_9$). Anal. Calcd for $C_{12}H_{21}ClO_2$: C, 61.93; H, 9.09. Found: C, 62.49; H, 9.40.

Isopropyl (*Z*)-3-Chloro-2-octenoate (3i). IR (film) 654, 850, 1001, 1377, 1462, 1639, 1726, 2933 cm^{-1}; ^1H NMR δ 0.88 (t, 3H, J = 6.8 Hz, CH_3), 1.25 (d, 6H, J = 6 Hz, $2CH_3$), 1.26−1.32 (m, 4H, $2CH_2$), 1.60 (m, 2H, CH_2), 2.40 (t, 2H, J = 7.6 Hz, CH_2), 5.10 (m, 1H, CH), 5.96 (s, 1H, HC═); ^{13}C NMR δ 13.9 (CH_3), 21.8 ($2CH_3$), 22.3 (CH_2), 26.9 (CH_2), 30.7 (CH_2), 41.2 (CH_2), 67.7 (OCH), 116.6 (═CH), 150.2 (ClC═), 163.6 (C═O); MS *m*/*z* 218 ($M^+(^{35}Cl)$), 183 ($M^+ - Cl$), 179 ($M^+(^{37}Cl) + 2 - C_3H_7$), 177 ($M^+(^{35}Cl) + 2 - C_3H_7$), 161 ($M^+(^{37}Cl) - OC_3H_7$), 159 ($M^+(^{35}Cl) - OC_3H_7$), 141 ($M^+ + 1 - Cl - C_3H_7$), 95 ($M^+ - 1 - Cl - CO_2C_3H_7$). Anal. Calcd for $C_{11}H_{19}ClO_2$: C, 60.41; H, 8.76. Found: C, 62.03; H, 9.09

***sec*-Butyl (*Z*)-3-Chloro-2-octenoate (3j).** IR (film) 652, 854, 1001, 1358, 1460, 1637, 1720, 2933 cm^{-1}; ^1H NMR δ 0.88 (t, 6H, J = 7.2 Hz, $2CH_3$), 1.22 (d, 3H, J = 6 Hz, CH_3), 1.28−1.30 (m, 4H, $2CH_2$), 1.55−1.62 (m, 4H, $2CH_2$), 2.40 (t, 2H, J = 7.6 Hz, CH_2), 4.90 (m, 1H, CH), 5.97 (s, 1H, HC═); ^{13}C NMR δ 9.6 (CH_3), 13.8 (CH_3), 19.4 (CH_3), 22.3 (CH_2), 26.8 (CH_2), 28.8 (CH_2), 30.7 (CH_2), 41.1 (CH_2), 72.3 (OCH), 116.5 (═CH), 150.1 (ClC═), 163.7 (C═O); MS *m*/*z* 233 ($M^+(^{35}Cl) + 1$), 197 ($M^+ - Cl$), 179 ($M^+(^{37}Cl) + 2 - C_4H_9$), 177 ($M^+(^{35}Cl) + 2 - C_4H_9$), 161 ($M^+(^{37}Cl) - OC_4H_9$), 159 ($M^+(^{35}Cl) - OC_4H_9$), 95 ($M^+ - 1 - Cl - CO_2C_4H_9$). Anal. Calcd for $C_{12}H_{21}ClO_2$: C, 61.93; H, 9.09. Found: C, 61.88; H, 9.22.

***tert*-Butyl (*Z*)-3-Chloro-2-octenoate (3k).** IR (film) 650, 854, 999, 1369, 1390, 1460, 1637, 1720, 2933, 2960 cm^{-1}; ^1H NMR δ 0.88 (t, 3H, J = 7.2 Hz, CH_3), 1.29 (m, 4H, $2CH_2$), 1.47 (s, 9H, $3CH_3$), 1.60 (m, 2H, CH_2), 2.38 (t, 2H, J = 6.4 Hz, CH_2), 5.91 (s, 1H, HC═); ^{13}C NMR δ 13.8 (CH_3), 22.3 (CH_2), 26.9 (CH_2), 27.5, 27.6, 27.7, 27.9, 28.1, 28.4, 28.5 ($3CH_3$), 30.7 (CH_2), 41.1 (CH_2), 80.9 (O−C), 117.6 (═CH), 149.0 (ClC═), 163.4 (C═O); MS *m*/*z* 197 ($M^+ - Cl$), 179 ($M^+(^{37}Cl) + 2 - C_4H_9$), 177 ($M^+(^{35}Cl) + 2 - C_4H_9$), 161 ($M^+(^{37}Cl) - OC_4H_9$), 159 ($M^+(^{35}Cl) - OC_4H_9$), 95 ($M^+ - 1 - Cl - CO_2C_4H_9$). Anal. Calcd for $C_{12}H_{21}ClO_2$: C, 61.93; H, 9.09. Found: C, 62.20; H, 9.29.

***tert*-Pentyl (*Z*)-3-Chloro-2-octenoate (3l).** IR (film) 659, 852, 1018, 1120, 1435, 1639, 1734, 2954 cm^{-1}; ^1H NMR δ 0.88 (t, 6H, J = 6.4 Hz, $2CH_3$), 1.28 (m, 4H, $2CH_2$), 1.44 (s, 6H, $2CH_3$), 1.59 (m, 2H, CH_2), 1.79 (q, 2H, J = 7.6 Hz, CH_2), 2.38 (t, 2H, J = 7.6 Hz, CH_2), 5.91 (s, 1H, HC═); ^{13}C NMR δ 8.2 (CH_3),13.9 (CH_3), 22.3 (CH_2), 25.3, 25.6, 25.9 ($2CH_3$), 26.9 (CH_2), 30.7 (CH_2), 33.4 (CH_2), 41.1 (CH_2), 83.4 (O−C), 117.6 (═CH), 148.9 (ClC═), 163.4 (C═O); MS *m*/*z* 231 ($M^+(^{35}Cl) - CH_3$), 211 ($M^+ - Cl$), 179 ($M^+(^{37}Cl) + 2 - C_5H_{11}$), 177 ($M^+(^{35}Cl) + 2 - C_5H_{11}$), 161 ($M^+(^{37}Cl) - OC_5H_{11}$), 159 ($M^+(^{35}Cl) - OC_5H_{11}$), 95 ($M^+ - 1 - Cl - CO_2C_5H_{11}$). Anal. Calcd for $C_{13}H_{23}ClO_2$: C, 63.27; H, 9.39. Found: C, 63.44; H, 9.79.

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Supporting Information Available: Spectral data (^1H and ^{13}C NMR, IR, and MS) of all the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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