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A convenient synthesis of olefins via deacylation reaction

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Abstract—A convenient and environmentally-friendly synthetic method of olefins via deacylation reaction is described. The reaction gives olefins by condensation of aldehydes with a variety of 1,3-dicarbonyl compounds in the presence of anhydrous potassium carbonate at room temperature in high yields (70–90%) in one step. The synthetic potential of this strategy can be used as an alternative procedure to the Wittig, Wittig–Horner reactions. The stereochemistry of the resulted olefins was determined by NOE experiment with correct radio frequency and X-ray analysis. The *E*/*Z* selectivity of the deacylation reaction depends on the α-substituents of the 1,3-dicarbonyl compounds.

1. Introduction

Many natural products possess various di- and tri-substituted alkene components. In the synthesis of these natural products, α,β-unsaturated esters and ketones are important building blocks. In the olefin synthesis, highly selective stereo-control is one of the most important objectives of organic synthetic chemists.

More than 40 different synthetic methods for olefins synthesis are known.[1] The most famous olefin syntheses are the Wittig reaction[1a] and the Wittig–Horner reaction.[1b] Dehydration olefin synthesis[1c] is also a representative method. Other synthetic methods of olefins are Peterson olefination,[1d] Johnson methylenation,[1e] Julia olefination,[1f] Knovenagel reaction,[1g] olefin metathesis,[1h] Tebbe reaction,[1i] McMurry reaction[1j] and Takai olefination reaction,[1k] etc. Furthermore, some eliminations[1l] and addition–elimination reactions,[1m] reductions of alkynes,[1n] catalytic coupling reactions,[1o] reactions of alkynes[1p] with organometallic reagents are well-known methods.

In 1978, Tsuboi et al. found a new, simple, convenient method for the synthesis of 5,5,5-trichloro-3-penten-2-one (**1a**) by the reaction of chloral with 2,4-pentanedione (**A-1**) in the presence of anhydrous potassium carbonate at room temperature. Furthermore, this method was extended to the synthesis of other α,β-unsaturated carbonyl compounds, and some results were communicated in our previous paper.[2] The olefin geometry was tentatively determined, and 4-membered ring transition states of the deacylation reaction were also postulated.[2]

Recently, the scope and limitations of this method were finely reinvestigated and the olefin geometry was absolutely determined by NMR experiments. This paper provides a full description of our previous communication (Scheme 1).[2]

This paper reports a convenient, operationally simple and environmentally-friendly synthetic method of α,β-unsaturated ketones, esters, and lactones using deacylation reaction, and the olefin geometry was determined with NOE experiments and X-ray analysis of the olefines obtained. Reactivity and stereoselectivity among the Wittig, Wittig–Horner and deacylation reactions were also compared. Furthermore, we examined the competitive reaction between deacetylation and debenzoylation reactions.

In order to establish the generality of the deacylation reaction in the presence of potassium carbonate at room temperature, we investigated reactions of various of aldehydes with some 1,3-dicarbonyl compounds such as 2,4-pentanedione (**A-1**), 3-chloro-2,4-pentanedione (**A-2**), ethyl 3-oxobutanoate (**B-1**), ethyl 2-chloro-3-oxobutanoate (**B-2**), ethyl 2-methyl-3-oxobutanoate (**B-3**), ethyl 3-oxo-3-phenylpropionate (**C-1**), ethyl 2-chloro-3-oxo-3-phenylpropionate (**C-2**), and α-acetyl-γ-butyrolactones (**D**).

Keywords: Wittig reaction; Wittig–Horner reactions; Aldehydes; Unsaturated esters.
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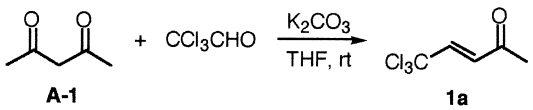
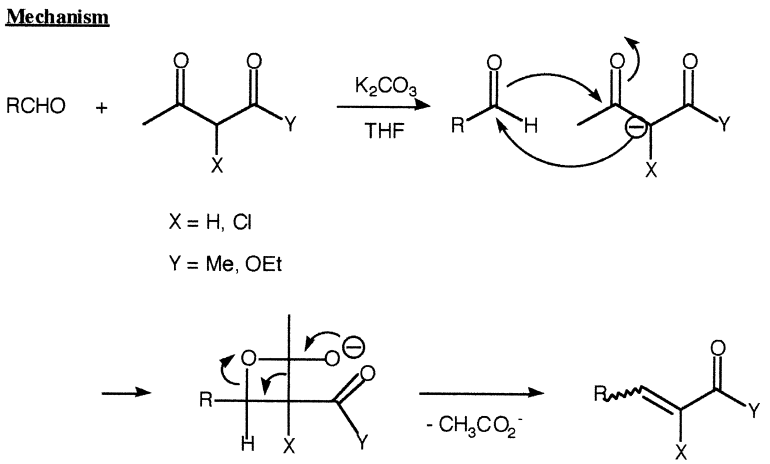
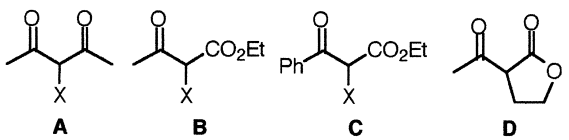




Scheme 1.



A1 ; X = H **B1** ; X = H **C1** ; X = H

A2 ; X = Cl **B2** ; X = Cl **C2** ; X = Cl

B3 ; X =Me

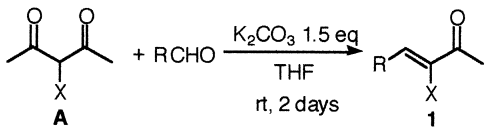
A summary of this paper is shown in Scheme 2. In this paper the reactions of acyl compounds of R′=Me and Ph in $R'COCHW_1W_2$ are called 'deacetylation' and 'debenzoylation', respectively. In Scheme 2, electron-withdrawing group W_1 is acetyl, ester, and chlorine groups, and W_2 is H or Me. As shown in Scheme 2, deacylation reaction between 1,3-dicarbonyl compounds and aldehydes was carried out in THF in the presence of potassium carbonate (1.5 equiv.) at room temperature to give olefins, and the geometry was absolutely determined by NMR experiments.

2. Results and discussion

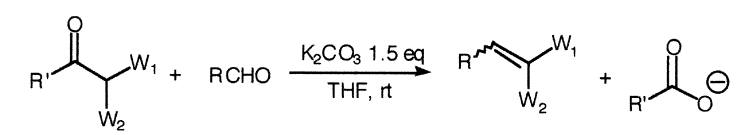
Tables 1–3 summarize the results obtained by the reaction of 1,3-dicarbonyl compounds (**A**, **B** and **C**) with several aldehydes.

Table 1 shows a synthesis of α,β-unsaturated methyl ketones by the reaction of **A** with aldehydes via deacetylation reaction. All reactions proceeded in 2 days. In the case of X=H, only the *E*-isomer is produced and in the case of X=Cl, only the *Z*-isomer is produced, respectively. Reactive aldehydes such as dichloroacetaldehyde ($R=CHCl_2$) and chloral ($R=CCl_3$) gave the desired products in moderate to good yields. Inactive normal alkyl

Table 1. Synthesis of α,β-unsaturated ketones via deacetylation reaction



Entry	X	R	Yield (%)	*E*/*Z*	Compounds No.
1	H	CCl_3-	74	100:0	**1a**
2	H	C_2H_5-	28	100:0	**1b**
3	Cl	$CHCl_2-$	56	0:100	**1d**
4	Cl	CCl_3-	51	0:100	**1e**
5	Cl	C_2H_5-	37	0:100	**1f**
6	Cl	$n\text{-}C_6H_{13}-$	49	0:100	**1g**



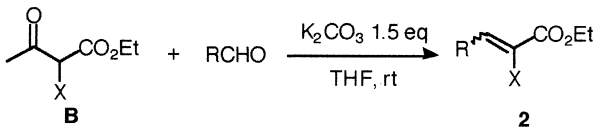
R' = Me, Ph

W_1 = electron withdrawing groups (CH_3CO, CO_2Et, Cl)

W_2 = H, Me

Scheme 2. Deacylation reaction (deacetylation, debenzoylation).

Table 2. Synthesis of α,β-unsaturated esters via deacetylation reaction



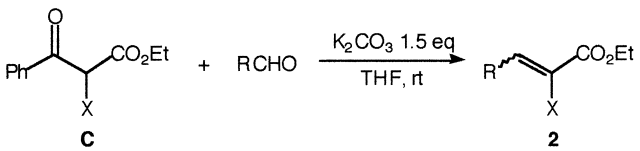
Entry	X	R	Reaction time (day)	Yield (%)	*E*/*Z*	Compounds No.
1	H	CCl_3–	2	38	100:0	**2a**
2	Cl	$CHCl_2$–	5	67	100:0	**2b**
3	Cl	CCl_3–	5	83	100:0	**2c**
4	Cl	C_2H_5–	6	50	86:14	**2d**
5	Cl	$(MeO)_2CHCH_2$–	1	20	75:25	**2e**
6	Cl	*n*-C_6H_{13}–	5	53	83:17	**2f**
7	CH_3	$CHCl_2$–	1	7	92:8	**2h**
8	CH_3	CCl_3–	2	90	100:0	**2l**

aldehydes (R=Et, *n*-Hex) gave the product in moderate to poor yields.

A synthesis of α,β-unsaturated esters by the reaction of ethyl acetoacetates **B** with aldehydes via deacetylation reaction is shown in Table 2. Most of the reactions proceeded in 2 days. In the case of X=H, only the *E*-isomer was produced as the same as in Table 1. However, in the case of X=Me and Cl, the *E*-isomer was obtained predominantly. Reactive aldehydes, chloral (R=CCl_3) gave the desired products in good yields, except entry 1. Electron-donating aldehyde (R=*p*-$MeOC_6H_4$) did not give any products. In the case of X=Me, reactions with inactive alkyl aldehydes (R=C_2H_5, CH_3CH=CH–) and aromatic aldehydes (R=Ph) did not give any products. The result of synthesis of α,β-unsaturated esters by the reaction of benzoylacetate **C** with aldehydes via debenzoylation reaction[3] is shown in Table 3. All reactions except entry 5 proceeded in good yields, but the stereoselectivity decreased somewhat.

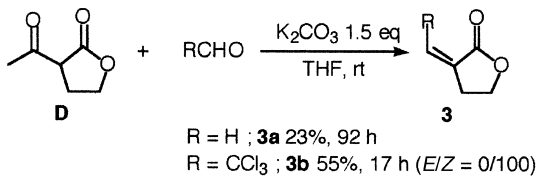
Generally, reactive aldehydes such as chloral (R=CCl_3) and dichloroacetaldehyde (R=$CHCl_2$) gave the desired products in good yields. Normal alkyl aldehydes (R=Et, *n*-Hex) and aromatic aldehydes (R=Ph) gave the product in moderate to poor yields. The deacylation reaction proceeded smoothly with 100% *E*-selectivity when the 1,3-diketo compounds have no substituents at the α-position (X=H).

Table 3. Synthesis of α,β-unsaturated esters via debenzoylation reaction



Entry	X	R	Reaction time (day)	α,β-Unsaturated esters **2**		
				No.	Yield (%)	*E*/*Z*
1	H	CCl_3–	3	**2a**	82	100:0
2	Cl	C_2H_5–	2.5	**2d**	74	73:27
3	Cl	$(MeO)_2CHCH_2$–	0.5	**2e**	78	75:25
4	Cl	*p*-$NO_2C_6H_4$–	4.5	**2g**	72	33:67
5	Cl	*p*-$MeOC_6H_4$–	2	—	0	N.R.

In addition, the deacetylation reaction for cyclic compounds was investigated and the result is summarized in Scheme 3. The reaction with α-acetyl-γ-butyrolactone **D** gave α-alkylidene lactones.



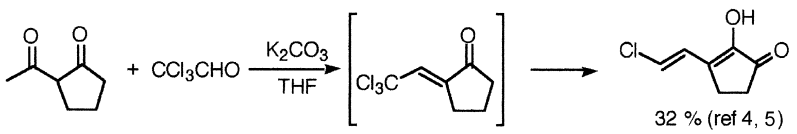
Scheme 3. Synthesis of α,-alkylidene lactones via deacetylation reaction.

On the other hand, the reaction with α-acetylcyclopentanone gave 3-(2′-chlorovinyl)-2-hydroxy-2-cyclopentenone, which is thought to be derived from α-trichloroethylidenecyclopentanone, in 32% yield (Scheme 4).[4,5]

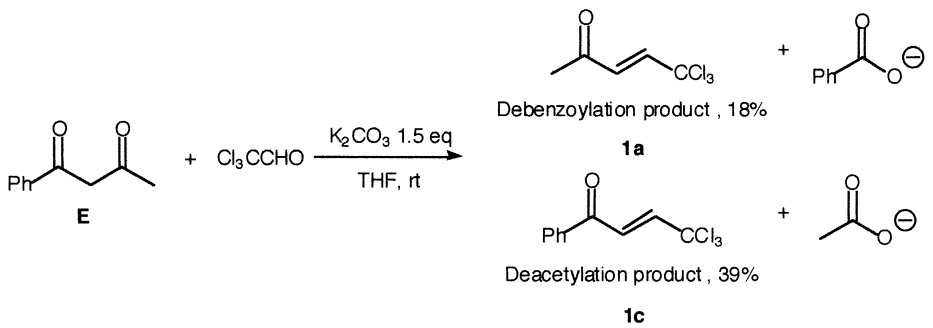
It is worthwhile to point out that in cases of unsymmetrical 1,3-diketones such as **E**, the less sterically hindered carboxylate is expelled (Scheme 5). When there is no significant difference in steric hindrance between the Me and Ph groups, mixtures of the two possible α,β-unsaturated ketones were isolated. This phenomenon was observed by using 1-phenyl-1,3-butandione **E** where the formation of the compound with the bigger Ph group was favored [39% **1c** (deacetylation product)]. 18% **1a** (debenzoylation product), respectively]. The small acetyl group was expelled predominantly. In the competitive reactions of deacetylation and debenzoylation, the deacetylation reaction proceeded 2 times faster than the debenzoylation reaction.

We investigated the solvent effect of our deacetylation reaction and the result is summarized in Table 4. From the table it is envisioned that aprotic ether type solvents such as THF, DME (entry 1–3, 7) give the product in good yield.

Acetone was also a good solvent (entry 8) and it is better than polar aprotic solvent DMF (entry 9). The reaction in nonpolar solvent, hexane gave the product in low yield. So, reaction media should be a little polar (entry 1–3, 7–9). When a carbonate ion is produced, some polar stability is necessary. Several kinds of THF were used as a solvent (entry 1–5). Almost the same results were obtained as shown in intries 1–3. The reaction in wet THF containing



Scheme 4.

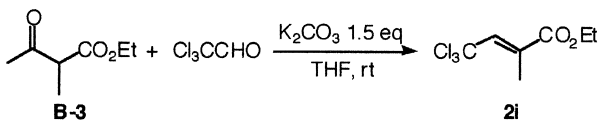


Scheme 5. Competition reaction between deacetylation reaction and debenzoylation reaction.

0.5 equiv. of water to the substrate (entry 4) afforded the product in a reduced yield (52%). Furthermore, the reaction in THF/H_2O (1:1) (entry 5) did not proceed. Results as shown in entries 1, 2, and 3 show that the drying method for THF is not so important.

The base effect of the present reaction was examined for the reaction of 1,3-dicarbonyl compound **B-3** with chloral, and the result is summarized in Table 5. The reaction using 1.5 equiv. of anhydrous K_2CO_3 as a base (entry 1) gave the olefin **2i** in the best yield (90%). The use of hydrate K_2CO_3 (0.5 equiv. H_2O, entry 2) gave the olefin in a moderate yield. However, the use of other alkali metal bases such as Li_2CO_3, $MgCO_3$, and $KHCO_3$ did not give significant results (entry 4–6). In most of the cases we recovered a part of the starting material. Use of KOAc found to be effective as shown in entry 7, in which the reaction gave **2i** in 80% yield with the same stereochemistry (*E*-form) as others.

Table 4. Solvent effect in the synthesis of α,β-unsaturated ester **2i**



Entry	Solvent	Time (day)	Yield (%)	*E*/*Z*
1	THF[a]	2	90	100:0
2	THF[b]	5.5	92	100:0
3	THF[c]	5.5	89	100:0
4	THF[d]	0.5	52	100:0
5	THF/H_2O=1/1	4	0	N.R.
6	H_2O	3.5	0	N.R.
7	DME	2	95	100:0
8	Acetone	2	81	100:0
9	DMF[c]	2	60	100:0
10	Hexane	7	39	100:0

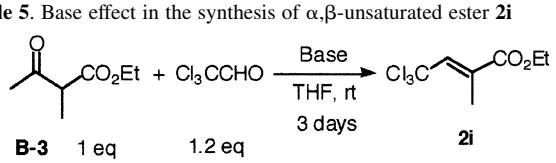
[a] Dried over Na wires and benzophenone.
[b] Commercial one was used without drying.
[c] Dried over $CaCl_2$.
[d] H_2O (0.5 equiv.) was added.

We examined the olefin synthesis among the Wittig reaction, the Wittig–Horner reaction, and the present deacetylation reaction. We tried three reactions to synthesize ethyl 4,4,4-trichloro-2-methyl-2-butenoate.

As shown in Table 6, yield and *E*-stereoselectivity of the deacetylation reaction with chloral were better than those of the Wittig reaction. In the case of dichloroacetaldehyde, yield of the deacetylation reaction became low, but *E*-selectivity was better than that of the Wittig–Horner reaction. As acidity of the α-proton of dichloroacetaldehyde is stronger than that of ethyl 2-methylacetoacetate, aldol reaction of the aldehyde itself may take place.

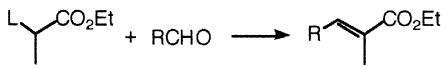
Our synthetic strategy has been applied to the synthesis of some natural products. We have utilized this halogen-substituted α,β-unsaturated olefin moiety towards the synthesis of a series of halogeno α-amino acids which possess interesting biological activities.[6–8] Electrochemical reduction of the α,β-unsaturated ketones towards the synthesis of *exo*-5-acetyl-*endo*-6-dichloromethylbicyclo [2.2.1]hept-2-ene, and *exo*-5-acetyl-*endo*-6-chloromethyl-bicyclo[2.2.1]hept-2-ene[9] was also reported. 3-Hexen-2-one (**1b**) can be transformed to substituted porphyrin.[10] Other olefinic compounds, for example, (**3a**), can be used for the synthesis of compounds possessing antifungal, antitumor,

Table 5. Base effect in the synthesis of α,β-unsaturated ester **2i**



Entry	Base	Equiv. to **B-3**	Yield (%)	Recovery (%)	*E*/*Z*
1	K_2CO_3	1.5	90	0	100:0
2	K_2CO_3	1.5+H_2O (0.5)	52	23	100:0
3	K_2CO_3	0.5	37	63	100:0
4	$KHCO_3$	1.5	67	21	100:0
5	Li_2CO_3	1.5	3	71	100:0
6	$MgCO_3$	1.5	0	78	N.R.
7	KOAc	1.5	80	6	100:0

Table 6. Comparison of olefin synthesis



Entry	Reaction	L	R	Yield	*E*/*Z*
1	Wittig	$=PPh_3$	CCl_3	73	96:4
			$CHCl_2$	76	96:4
2	Wittig–Horner	O P(OEt)2	CCl_3	38	57:43
			$CHCl_2$	58	35:65
3	Deacetylation	O	CCl^3	90	100:0
			$CHCl_2$	7	92:8

and plant growth inhibitory activities, for example, tulipalin A which can be further transformed to pentaacetyl tuliposide A, 3-methyl-2(3*H*)-dihydrofuranone.[11,12] If (*E*)-ethyl 4,4,4-trichloro-2-methyl-2-butenoate can be transformed to (*E*)-ethyl 2-methyl-2-butenoate, it will be applicable to a part of an insect pheromone and it can be used for the synthesis of other compounds.[13,14]

Furthermore, the other unsaturated esters and ketones moiety can be used for different types of reactions, for example, Diels–Alder reaction,[9,15] Favorskii reaction,[16,17] and halogen allyl rearrangement[18,19] and so on.

Olefin geometries were determined by NMR spectra assisted by NOESY experiments as depicted in Figure 1. For α,β-unsaturated ester, we examined NOE effect among methylene protons of the ethoxy groups (4.2–4.3 ppm), olefin protons (6.4–7.9 ppm), and allylic protons of the alkyl side chain (2.3–2.9 ppm). Stereochemistry between olefin protons and the carbonyl groups was examined by using allylic alcohols after reduction with DIBAL. In the case of ester **2f**, methylene protons of ethoxy and the olefin proton showed cross peaks in NOESY. After reduction of ester **2f** to alcohol **2′f**, methylene protons of alcohol (4.1 ppm) showed a more clear NOE effect with olefin protons (5.8 ppm) than with allylic protons of the alkyl side chain (2.2 ppm). Polychlorinated ester **2b** showed cross peaks between the terminal methyne proton (6.56 ppm) and methylene protons (4.34 ppm) of the ethoxy group. For α,β-unsaturated ketone, we examined NOE effect among methyl protons of the acetyl group (2.4–2.5 ppm), olefin proton (6.9–7.6 ppm) and allylic protons of the alkyl side chain (2.4 ppm). Unfortunately, in the case of ketone **1f**, methyl protons of the acetyl group (2.4 ppm) and allylic proton of the alkyl side chain (2.4 ppm) overlapped in ^1H NMR. After reduction of ketone **1f** to alcohol **1′f**, methyne proton of alcohol (4.3 ppm) showed more clear cross peaks with olefin proton (5.8 ppm) than with allylic protons of the alkyl side chain (2.2 ppm). Compound **1e** showed NOE effect between olefin proton and methyl protons of the acetyl group. The geometry of trichloroethylidenedihydrofuranone **3b** was also determined as *Z*-form by the NOESY experiment.

NOE and HMQC spectra of **2h** (*E*/*Z*=2:7), which was prepared by Wittig–Horner reaction, are shown in Figures 2 and 3, respectively. Upon irradiation of CH_3 signal at 1.98 ppm a NOE enhancement of the signals $CHCl_2$

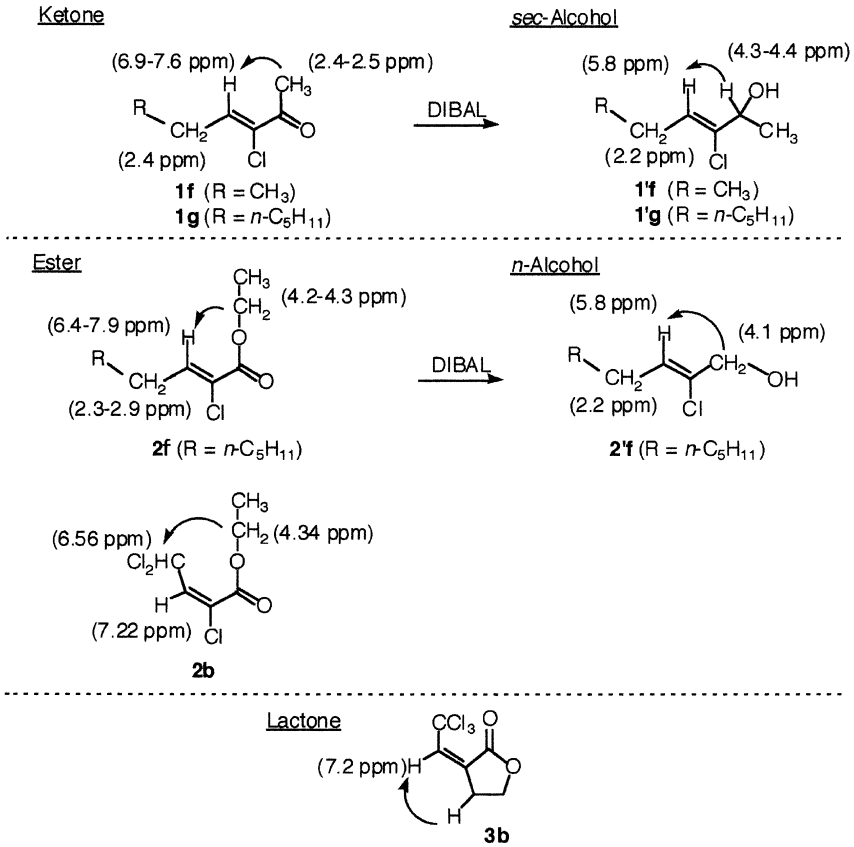


Figure 1. Determination of olefin geometry by NOESY.

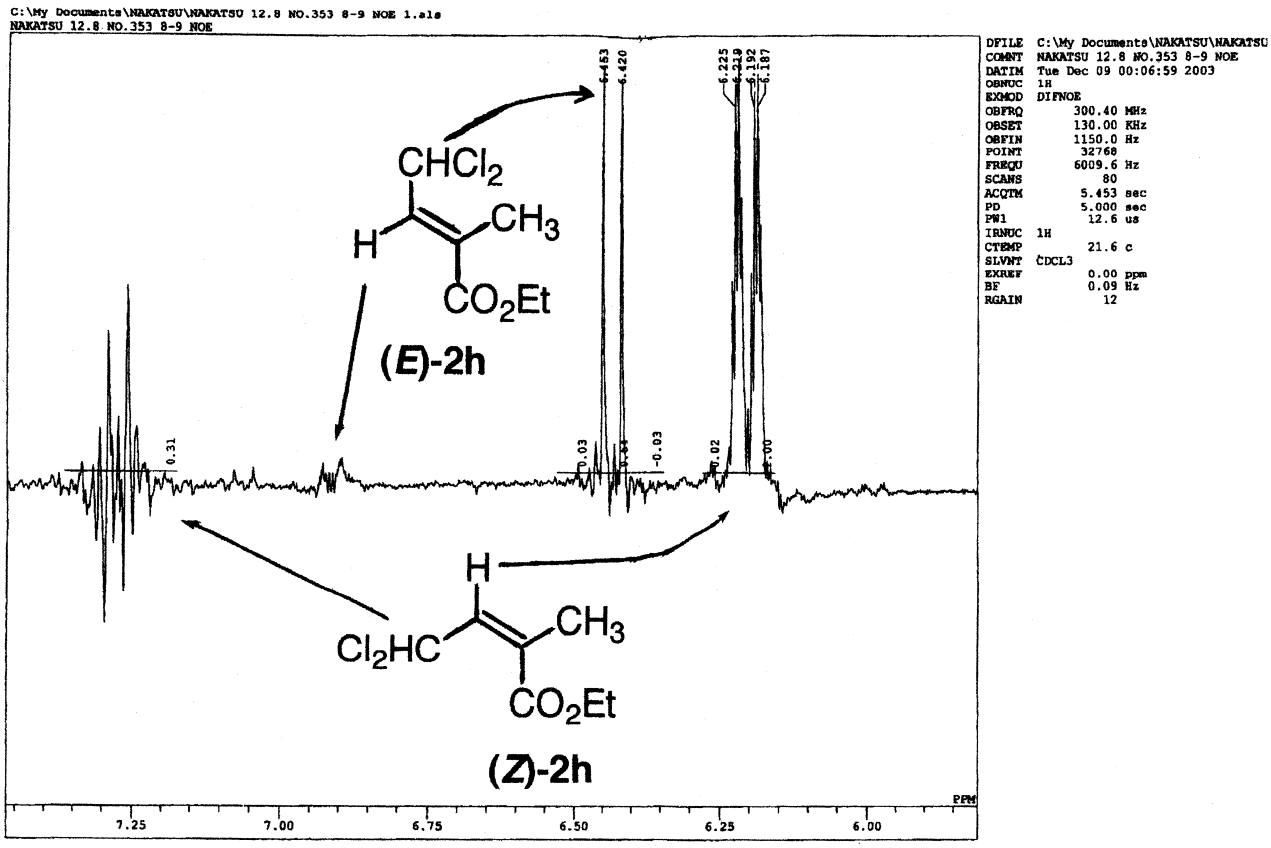


Figure 2. NOE of **2h** (*E*/*Z*=2:7).

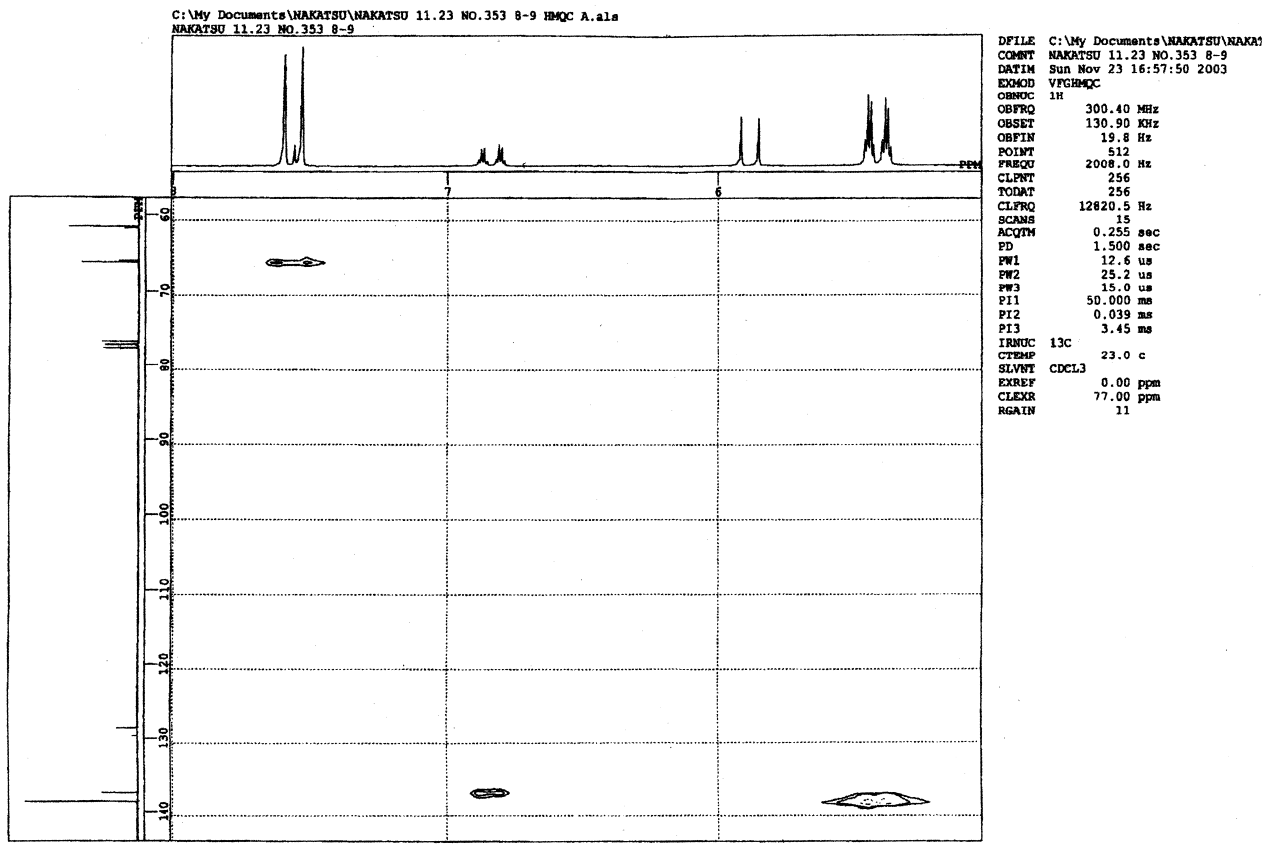
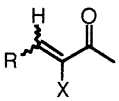
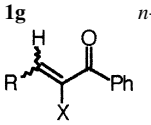
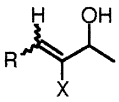
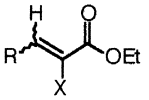
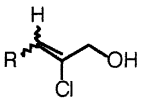
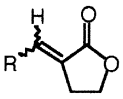


Figure 3. HMQC of 2h (*E*/*Z*=2:7).

Table 7. Olefin geometry and chemical shifts of olefin protons

Compounds	R	X	*E*/*Z*	*H* (ppm)	*J* (Hz)
					
1a	CCl_3	H	*E*	7.03	d 15.0
1b	C_2H_5	H	*E*	6.86	dt 15.8, 6.4
1d	$CHCl_2$	Cl	*Z*	7.06	d 9.0
1e	CCl_3	Cl	*Z*	7.56	s
1f	C_2H_5	Cl	*Z*	6.93	t 7.2
1g	*n*-C_6H_{13}	Cl	*Z*	6.95	t 7.2
					
1c	CCl_3	H	*E*	7.42	d 14.2
					
1′f	C_2H_5	Cl	*Z*	5.75	t 7.0
1′g	*n*-C_6H_{13}	Cl	*Z*	5.77	t 7.0
					
2a	CCl_3	H	*E*	7.22	d 15.0
2b	$CHCl_2$	Cl	*E*	7.22	d 9.4
2c	CCl_3	Cl	*E*	7.72	s
2d	C_2H_5	Cl	*Z*	6.43	t 7.8
			E	7.05	t 7.2
2e	$CH_2CH(OCH_3)_2$	Cl	*Z*	6.48	t 7.4
			E	7.07	t 7.0
2f	*n*-C_6H_{13}	Cl	*Z*	6.44	t 7.8
			E	7.07	t 7.4
2g	*p*-$NO_2C_6H_4$	Cl	*E*	7.26	s
			Z	7.94	s
2h	$CHCl_2$	Me	*Z*	6.20	dq 9.5, 1.5
			E	6.91	dq 9.8, 1.5
2i	CCl_3	Me	*Z*	6.21	q 1.5
			E	7.40	q 1.6
					
2′f	*n*-C_6H_{13}		*Z*	5.79	t 7.0, 1.0
					
3b	CCl_3		*Z*	7.19	t 3.1

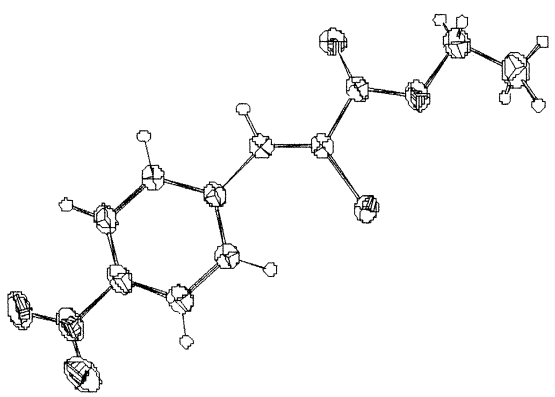


Figure 4. ORTEP drawing of (*Z*)-**2g**.

(1.92%) of (*E*)-**2h** and olefin H (6.0%) of (*Z*)-**2h** was detected. As shown in Figure 3, signals of $CHCl_2$ (6.43 ppm: *E*-form, 7.27 ppm: *Z*-form) and olefin proton (6.20 ppm: *Z*-form, 6.92 ppm: *E*-form) in ^1H NMR showed cross peaks to those of carbons of CH= (137.18 ppm: *E*-form, 138.33 ppm: *Z*-form) and $CHCl_2$ (65.96 ppm: *E*-form, 66.16 ppm: *Z*-form) in ^{13}C NMR clearly, and signals of ^1H and ^{13}C NMR spectra of **2h** were assigned as shown in the Section 3, and the *E*/*Z* ratio was determined clearly with the aid of these spectra.

Geometry and NMR data of olefins obtained by deacylation reaction are summarized in Table 7.

In the case of the α-chlorinated ester, an olefin proton of the (*Z*)-isomers appears further upfield than that of (*E*)-isomers. However, the olefin proton of ester **2g** showed the opposite chemical shift. This may be due to the effect of the electron-withdrawing nitro group and the benzene ring. The stereochemistry of (*Z*)-**2g** was definitely confirmed by X-ray analysis of the single crystal. The ORTEP drawing of (*Z*)-**2g** is shown in Figure 4.

The present reaction has the following five advantages: (1) it is highly stereoselective, (2) it proceeds under room temperature, (3) it uses a weak and cheap base, K_2CO_3, (4) it does not produce any phosphorus compounds harmful to the environment, (5) experimental operation is simple. This reaction contains a clean and environmentally-friendly process because points (2)–(4) contribute to a hazard-free environment.[20]

The present method for the synthesis of α-chloro-α,β-unsaturated esters and ketones seems to be superior to the known methods such as the Wittig reaction and the dehydroxylation reaction using sulfuric acid. Further exploitation of this strategy towards the syntheses of nucleoside analog, zidovudine (AZT)[21a] and insect pheromones of pines,[21b] and study on the mechanistic aspects are currently under way in our group and the results will be published elsewhere.

3. Experimental

NMR spectra were recorded on Varian Gemini 200 or JEOL AL300 instruments and calibrated using residual undeuterated solvent as an internal reference. All IR spectra were recorded on a JASCO FT/IR-5000 infrared spectrophotometer as films. Elemental analyses were performed on Perkin–Elmer 2400 series II CHNS/O analyser. For thin layer chromatography aluminum sheets Merck silica gel coated 60 F254 plates were used and the plates were visualized with UV light and phosphomolybdic acid (5% in EtOH). Merck silica gel 60 N (spherical, neutral) (40–50 μm) was used for the flash chromatography. The progress of the reaction was monitored by GC-MS Shimazu QP 5000 at 70 eV. Some stereoisomers of synthesized olefin were separated by preparative GC (Yanagimoto G-2800): column (6/5 mmϕ×2 m) packed with 10% liq. phase Apieson Grease L supported on chromosorb W.

All reactions were carried out in oven-dried, septum-capped flasks under N_2. All liquid reagents were transferred via oven-dried syringes. Solvents and reagents were dried and distilled before use. THF was distilled from Na-benzophenone ketyl before use.

3.1. General procedure for the deacetylation reaction (typical synthesis of (*E*)-1a)

In a typical experimental procedure, 1.30 g (9.38 mmol) of anhydrous potassium carbonate and 0.64 mL (6.25 mmol) of 2,4-pentanedione in 5 mL of anhydrous THF were placed in a 10 mL round bottomed flask. To this mixture, 0.73 mL (7.5 mmol) of chloral was added at room temperature via syringe under N_2 atmosphere. After 2 days, the reaction mixture was diluted with 10–15 mL of water and extracted with ether (20 mL×3). After removal of the solvent, the residue was subjected for column chromatography over silica gel using hexane and then hexane–ethyl acetate (10–12%) as an eluent to furnish the title compound as an yellow oil: the ketone **1a** (0.867 g) (74%) (*E*/*Z*, 100:0).

3.1.1. (*E*)-5,5,5-Trichloro-3-penten-2-one (*E*)-1a.[18,22,23] Yellow oil; R_f 0.45 (hexane/EtOAc, 4:1); IR (neat) ν 3044, 3012, 1709, 1682, 1630, 1427, 1363, 1305, 1267, 1255, 1174, 1096, 1046, 1023, 1002, 965, 911, 853, 768, 729 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.37 (s, 3H), 6.59 (d, J=15 Hz, 1H), 7.03 (d, J=15 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 28.79, 92.58, 127.96, 144.32, 196.49.

3.1.2. (*E*)-3-Hexen-2-one (*E*)-1b.[10,24] Pale yellow oil; R_f 0.48 (hexane/EtOAc, 4:1); IR (neat) ν 3586, 3536, 3316, 2974, 2940, 2882, 1698, 1680, 1630, 1547, 1512, 1462, 1427, 1363, 1336, 1286, 1257, 1183, 1131, 1093, 1071, 1023, 980, 907, 876, 835, 768 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.08 (t, 3H, J=7.4 Hz, CH_3), 2.25 (s, 3H, O=C–CH_3), 2.25 (bdqd, 2H, CH_2–CH_3), 6.07 (dt, 1H, J=15.8, 1.6 Hz, CH_2CH=CH), 6.86 (dt, 1H, J=15.8, 6.4 Hz, CH_2 CH=CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.22, 25.53, 26.82, 130.41, 149.82, 198.86.

3.1.3. (*Z*)-3,5,5-Trichloro-3-penten-2-one (*Z*)-1d.[18] Pale orange oil: R_f 0.54 (hexane/EtOAc, 4:1); IR (neat) ν 3064, 3020, 2930, 2860, 1709, 1620, 1423, 1363, 1288, 1245, 1209, 1112, 1021, 994, 934, 917, 857, 756, 716, 659, 586 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.49 (s, 3H), 6.58 (d, J=9.2 Hz, 1H) 7.06 (d, J=9.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$), δ 26.59, 65.22, 132.09, 135.20, 191.21.

3.1.4. (*Z*)-3,5,5,5-Tetrachloro-3-penten-2-one (*Z*)-1e.[25] Light yellow oil; R_f 0.49 (hexane/EtOAc, 4:1); IR (neat) ν 3058, 2980, 2930, 2872, 2348, 1796, 1711, 1605, 1421, 1363, 1303, 1278, 1214, 1094, 1019, 992, 942, 924, 855, 791, 731, 669, 615 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.52 (s, 3H) 7.56 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.70, 89.48, 135.43, 139.47, 191.97.

3.1.5. (*Z*)-3-Chloro-3-hexen-2-one (*Z*)-1f.[2,7] Yellow oil; R_f 0.41 (hexane/EtOAc, 4:1); IR (neat) ν 3366, 2976, 2942, 2882, 1692, 1620, 1547, 1512, 1462, 1427, 1361, 1330, 1265, 1234, 1133, 1071, 1023, 1002, 975, 944, 899, 859, 795 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.11 (t, 3H, J=7.4 Hz, CH_3), 2.41 (s, 3H, O=C–CH_3), 2.41 (dq, 2H, J=7.4, 7.4 Hz, CH_2), 6.93 (t, 1H, J=7.2 Hz, CH_2CH=C); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.11, 23.07, 26.40, 133.26, 143.11, 192.15.

3.1.6. (*Z*)-3-Chloro-3-decen-2-one (*Z*)-1g. Yellow oil; R_f 0.45 (hexane/EtOAc, 4:1); IR (neat) ν 2960, 2932, 2862, 1692, 1620, 1361, 1228 cm^{-1}; ^1H NMR (500 MHz, $CDCI_3$) δ 0.89 (t, J=7.0 Hz, 3H), 1.23–1.40 (m, 6H), 1.50 (tt, J=7.5, 7.5 Hz, 2H), 2.39 (dt, J=7.5, 7.5 Hz, 2H), 2.41 (s, 3H), 6.95 (t, J=7.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.03, 22.52, 26.49, 27.70, 29.02, 29.69, 31.51, 133.67, 142.02, 192.19. Anal. calcd for $C_{10}H_{17}CIO$: C, 63.65; H, 9.08. Found C, 63.76; H, 9.31.

3.2. General procedure for the deacetylation reaction: typical synthesis of 2a. (Procedure for solvent effect and base effect are also same as this procedure)

In a typical experimental procedure, 1.30 g (9.38 mmol) of anhydrous potassium carbonate and 0.80 mL (6.25 mmol) of ethyl acetoacetate in 5 mL of anhydrous THF were placed in a 10 mL round bottomed flask. To this mixture, 0.73 mL (7.5 mmol) of chloral was added at room temperature by a syringe under N_2 atmosphere. After being stirring for 2 days, the reaction mixture was diluted with 10–15 mL of water and the organic layer was extracted with ether (20 mL×3). After removal of the solvent, the residue was subjected for column chromatography over silica gel using hexane and then hexane–ethyl acetate (10–12%) as an eluent to furnish the title compound as a colorless oil: the ester **(*E*)-2a** (0.517 g) (38%) (*E*/*Z*, 100:0).

3.2.1. (*E*)-Ethyl 4,4,4-trichloro-2-butenoate (*E*)-2a.[26] Colorless oil; R_f 0.60 (hexane/EtOAc, 4:1); IR (neat) ν 2986 (C–C), 1729 (ester C=O), 1657 (C=C), 1468 (C=C). 1448 (C=C), 1396 (C=C), 1371 (C=C), 1309, 1276, 1183, 1096, 1033, 965, 866, 816, 774 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.33 (3H, t, J=7.0 Hz, OCH_2CH_3), 4.27 (2H, q, J=7.0 Hz, OCH_2CH_3), 6.39 (1H, d, J=15.0 Hz, Cl_3 CCH=CH). 7.22 (1H, d, J=15.0 Hz, Cl_3CCH=CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.13, 61.54, 92.16, 121.70, 146.01, 164.70.

3.2.2. (*E*)-Ethyl 2,4,4-trichloro-2-butenoate (*E*)-2b. Colorless oil; R_f 0.53 (hexane/EtOAc, 4:1); IR (neat) ν 3066, 2988, 2942, 2912, 2876, 1725, 1632, 1526, 1466, 1448, 1394, 1371, 1336, 1270, 1218, 1104, 1042, 1000, 948, 880, 808, 762, 716, 640, 611 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.37 (t, J=7.2 Hz, 3H), 4.34 (q, J=7.0 Hz, 1H), 6.56 (d, J=9.4 Hz, 1H), 7.22 (d, J=9.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.06, 63.28, 65.00, 125.53, 136.64, 161.04. Anal. calcd for $C_6H_7Cl_3O_2$: C, 33.14; H, 3.24. Found C. 33.22; H, 3.01.

3.2.3. (*E*)-Ethyl 2,4,4,4-tetrachloro-2-butenoate (*E*)-2c.[27] Colorless oil: R_f 0.63 (hexane/EtOAc, 4:1); IR (neat) ν 3066, 2988, 2944, 2912, 1734, 1622, 1466, 1448, 1394, 1371, 1292, 1255, 1174, 1089, 1044, 1004, 862, 828, 797, 772, 710, 650, 634, 603, 584 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.37 (t, J=7.2 Hz, 3H) 4.35 (q, 2H, J=7.2 Hz) 7.72 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.01, 63.50, 89.25, 129.79 141.51, 161.12.

3.2.4. Ethyl 2-chloro-2-pentenoate (2d) (*E/Z*, 4:1). Colorless oil; R_f 0.55 (hexane/EtOAc, 4:1); IR (neat) ν 2980, 2942, 2882, 1734, 1632, 1543, 1510, 1462, 1396, 1369, 1348, 1272, 1247, 1174, 1135, 1096, 1048, 986, 917, 864, 837, 774, 752 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.09 (t, J=7.6 Hz, 3H), 1.33 (t, J=7.2 Hz, 3H). 2.37 (dq, J=7.6, 7.6 Hz, 1.6H), 2.55 (dq, J=7.6, 7.6 Hz, 0.4H), 4.27 (q, J=7.2 Hz, 2H), 6.43 (t, J=7.8 Hz, 0.2H), 7.05 (t, J=7.2 Hz, 0.8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.03, 14.13, 22.75, 62.07, 124.25, 143.49, 162.54. Anal. calcd for $C_7H_{11}ClO_2$: C, 51.70; H, 6.82. Found C, 51.48; H, 7.05.

3.2.5. (*Z*)-Ethyl 2-chloro-2-pentenoate ((*Z*)-2d). Colorless oil; R_f 0.55 (hexane/EtOAc, 4:1); ^1H NMR (200 MHz, $CDCl_3$) δ 1.07 (t, J=7.6 Hz, 3H), 1.35 (t, J=7.2 Hz, 3H), 2.56 (dq, J=7.6, 7.6 Hz, 2H), 4.28 (q, J=7.2 Hz, 2H), 6.44 (t, J=7.8 Hz, 1H).

3.2.6. (*E*)-Ethyl 2-chloro-2-pentenoate ((*E*)-2d). Colorless oil: R_f 0.55 (hexane/EtOAc, 4:1); IR (neat) ν 2980, 2942, 2882, 1734, 1632, 1462, 1369, 1272, 1247, 1133, 1096, 1048, 986, 919, 864, 752 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.09 (t, J=7.6 Hz, 3H), 1.33 (t, J=7.2 Hz, 3H), 2.36 (dq, J=7.6, 7.6 Hz, 2H), 4.27 (q, J=7.0 Hz, 2H), 7.05 (t, J=7.2 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.09, 14.16, 22.80, 62.13, 124.25, 143.59, 162.61.

3.2.7. Ethyl 5,5-dimethoxy-2-chloro-2-pentenoate (2e) (*E/Z*, 3:1). Pale yellow oil; R_f 0.45 (hexane/EtOAc, 4:1); IR (neat) ν 3400, 2330, 1638, 1620, 1369, 1176, 994, 735, 709 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.33 (t, J=7.2 Hz. 2.25H), 1.34 (t, J=7.2 Hz, 0.75H), 2.69 (dd, J=7.0, 5.6 Hz, 1.5H), 2.90 (dd, J=7.4, 5.6 Hz, 0.5H), 3.35 (s, 4.5H), 3.36 (s, 1.5H), 4.28 (q, J=7.2 Hz, 2H), 4.45 (t, J=5.6 Hz, 0.25H), 4.53 (t, J=5.6 Hz, 0.75H), 6.48 (t, J=7.4 Hz, 0.25H), 7.07 (t, J=7.0 Hz, 0.75H). Anal. calcd for $C_9H_{15}ClO_4$: C, 48.55; H, 6.79. Found C, 48.46; H, 6.65.

3.2.8. Ethyl 2-chloro-2-nonenoate (2f) (*E/Z*, 82:18).[28] Colorless oil; R_f 0.61 (hexane/EtOAc, 4:1); IR (neat) ν 2938, 2836, 1721, 1638, 1450, 1371, 1338, 1270, 1125, 1052, 967, 866, 750 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (bs, 3H), 1.16–1.54 (m, 8H), 2.34 (dt, J=7.2, 7.2 Hz, 1.64H), 2.53 (dt, J=7.4, 7.4 Hz, 0.36H), 4.27 (q, J=7.2 Hz, 2H), 6.44 (t, J=7.8 Hz, 0.18H), 7.06 (t, J=7.4 Hz, 0.82 Hz); ^{13}C NMR (50 MHz, $CDCl_3$)[29] δ 14.01, (14.51), 22.51, (22.63), 27.64, (28.87), 28.96, 29.39, 29.93, 31.52, (61.82) 62.10, (122.45), 124.63, 142.47, (145.08), 162.60.

3.2.9. (*Z*)-Ethyl 2-methyl-4,4-dichloro-2-butenoate ((*Z*)-2h). Pale yellow oil; R_f 0.61 (hexane/EtOAc, 4:1); IR (neat) ν 2986, 2934, 1717, 1651, 1452, 1373, 1350, 1286, 1261, 1222, 1143, 1098, 1023, 1006, 884, 748, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.33 (t, J=7.0 Hz, 3H), 1.98 (d, J=1.5 Hz, 3H), 4.25 (q, J=7.0 Hz, 2H), 6.20 (dq, J=10.0, 1.5 Hz, 1H), 7.27 (d, J=9.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.07, 19.86, 61.34, 66.16, 128.46, 138.33, 165.87. Anal. calcd for $C_7H_{10}Cl_2O_2$: C, 42.66; H, 5.11. Found C, 42.71; H, 4.97.

3.2.10. (*E*)-Ethyl 2-methyl-4,4-dichloro-2-butenoate ((*E*)-2h). Pale yellow oil; R_f 0.61 (hexane/EtOAc, 4:1); IR (neat) ν 2986, 1721, 1651, 1462, 1446, 1371, 1280, 1228, 1131, 1096, 1031, 977, 899, 760 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.33 (t, J=7.0 Hz, 3H), 1.95 (d, J=1.5 Hz, 3H), 4.25 (q, J=7.0 Hz, 2H), 6.43 (dq, J=9.5 Hz, 1H), 6.92 (dq, J=9.5, 1.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.64, 14.15, 61.50, 65.96, 129.43, 137.18, 166.61. Anal. calcd for $C_7H_{10}Cl_2O_2$: C, 42.66; H, 5.11. Found C, 42.71; H, 4.97.

3.2.11. (*E*)-Ethyl 2-methyl-4,4,4-trichloro-2-butenoate (*E*)-2i.[30] Pale yellow oil; R_f 0.60 (hexane/EtOAc, 4:1); IR (neat) ν 2986, 2942, 2912, 1775, 1721, 1642, 1460, 1446, 1388, 1371, 1348, 1261, 1129, 1027, 971, 878, 816, 774, 665 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.34 (t, J=7.1 Hz, 3H), 2.22 (d, J=1.4 Hz, 3H), 4.25 (q, J=7.1 Hz, 2H), 7.40 (q, J=1.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.91, 14.11, 61.79, 91.49, 135.42, 142.97, 166.58.

3.2.12. (*Z*)-Ethyl 2-methyl-4,4,4-trichloro-2-butenoate ((*Z*)-2i). Pale yellow oil; R_f 0.60 (hexane/EtOAc, 4:1); ^1H NMR δ 1.34 (dt, J=7.1, 1.5 Hz, 3H), 2.04 (d, J=1.4 Hz, 3H), 4.26 (q, J=7.1, 1.4 Hz, 2H), 6.21 (q, J=1.5 Hz, 1H).

3.3. General procedure for the synthesis of 2-chloro-1,3-dicarbonyl compounds. Synthesis of ethyl α-chloro-benzoylacetate as a typical example

To ethyl benzoylacetate, thionyl chloride (1.1 equiv.) was slowly added at 0 °C. The reaction mixture was stirred for 17 h at rt, and then poured into H_2O (50 mL). The organic compound was extracted with EtOAc (3×50 mL) and the combined organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure, and the crude residue was distilled to give target molecule.

3.4. General procedure for the debenzoylation reaction (*E*)-2a

In a typical experimental procedure, 1.30 g (9.38 mmol) of anhydrous potassium carbonate and 1.08 mL (6.25 mmol) of ethyl benzoylacetate in 5 mL of anhydrous THF were placed in a 10 mL round bottomed flask. To this mixture, 0.73 mL (7.5 mmol) of chloral was added at room temperature by a syringe under N_2 atmosphere. After being stirred for 3 days, the reaction mixture was diluted with 10–15 mL of water and extracted with ether (20 mL×3). After removal of the solvent, the residue was subjected to column chromatography over silica gel using hexane and then hexane–ethyl acetate (10–12%) as an eluent to furnish the title compound as a colorless oil: ester **2a** 1.115 g (5.13 mmol) (82%) (*E/Z*, 100:0).

3.4.1. Ethyl 2-chloro-3-(4-nitrophenyl)-2-propenoate (2g) (*E/Z*, 33:67).[30–32] Green crystal; mp 88–92 °C (from hexane); R_f 0.35 (hexane/EtOAc, 4:1); IR (KBr) ν 3100, 2992, 2902, 2850, 1717, 1618, 1597, 1520, 1475, 1462, 1446, 1412, 1348, 1323, 1292, 1267, 1203, 1112, 1073, 1035, 996, 926, 890, 855, 814, 760, 745, 692, 685 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.20 (t, J=7.2 Hz, 0.99H), 1.40 (t, J=7.2 Hz, 2.01H), 4.22 (q, J=7.2 Hz, 0.68H), 4.38 (q, J=7.2 Hz, 1.32H), 7.26 (s, 0.33H), 7.46 (d, J=8.4 Hz, 0.35H), 7.94 (s, 0.67H), 7.96 (d, J=9.2 Hz, 0.65H), 8.21 (d, J=8.8 Hz, 0.35H), 8.28 (d, J=8.8 Hz, 0.65H); ^{13}C NMR (50 MHz, $CDCl_3$)[29] δ (13.72), 14.15, (62.64), 63.06,

(123.49), 123.65, 126.07, (129.25), 131.07, 134.22, (134.86), 139.07, 147.95, 162.54.

3.5. X-ray structure determination of (*Z*)-2g

Crystallographic data for **(*Z*)-2g**. $C_{11}H_{10}O_4N_1Cl_1$, colorless crystal of dimension 0.1×0.2×0.3 mm^3, mol.weight 255.66, monoclinic, $P2_1/n$, a=15.347(3), b=4.011(4), c=19.21(2) Å, b=105.64(6)°, V=1139(1) $Å^3$, Z=4, r=1.49 g cm^{-3}. The X-rays diffraction data were collected on a CAD4 Enraf-Nonius automatic four-circle diffractometer (graphite monochromator, Cu Kα radiation (1.54184≈), $\omega-2\theta$ scan method, $\theta \leq 57.3°$).

A total of 2477 reflections were measured, of which 1975 were unique with $I>3\sigma$. The stability of crystals and of experimental conditions was checked every 2 h using three control reflections, while the orientation was monitored every 200 reflections by centering two standards. Corrections for Lorentz and polarization effects and absorption correction were applied (μ=30.56 cm^{-1}). The structure was solved by direct methods and difference Fourier syntheses using SIR program[33] and MolEN package.[34] All non-hydrogen atoms were refined anisotropically, H-atoms were located in ΔF maps and were refined isotropically. The final R values were R=0.051, Rw=0.064 for 1857 unique reflections with $F^2 \geq 3\sigma$. All calculations were carried out on a DEC Alpha Station 200 computer, all figures were made using the program PLATON.[35]

Crystallographic data for the structure **1** will be deposited with the Cambridge Crystallographic Data Centre.

3.6. General procedure for the deacetylation reaction (typical synthesis of (*Z*)-3b)

In a typical experimental procedure, 1.30 g (9.38 mmol) of anhydrous potassium carbonate, 0.67 mL (6.25 mmol) of 2-acetylbutyrolactone in 5 mL of anhydrous THF was placed in a 10 mL round bottomed flask. To this mixture, 0.73 mL (7.5 mmol) of chloral was added at room temperature via syringe under N_2 atmosphere. After being stirring for 17 h, the reaction mixture was diluted with 10–15 mL of water and extracted with ether (20 mL×3). After removal of the solvent, the residue was subjected for column chromatography over silica gel using hexane and then hexane–ethyl acetate (10–12%) as an eluent to furnish the title compound as a yellow oil. It was gave the lactone **3b** 0.739 g (3.43 mmol) (55%) (*E*/*Z*, 0:100).

3.6.1. 3-Methylene-2(3*H*)-dihydrofuranone (3a).[11,12] Colorless oil; R_f 0.13 (hexane/EtOAc, 4:1); IR (neat) ν 3586, 3514, 3104, 2994, 2924, 2730, 2526, 2382, 2232, 2032, 1883, 1760, 1667, 1638, 1528, 1489, 1439, 1402, 1373, 1267, 1118, 1027, 965, 948, 812, 766, 696, 617 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.96 (tdd, 2H, J=7.4, 2.8, 2.8 Hz, $-CH_2-$), 4.35 (t, 2H, J=7.4 Hz, $-CH_2-O-$), 5.65 (t, 1H, J=2.6 Hz, C═CH), 6.21 (t, 1H, J=2.8 Hz, C═CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.20, 65.18, 122.09, 133.46, 170.63.

3.6.2. (*Z*)-3-(2,2,2-Trichloroethylidene)-2(3*H*)-dihydrofuranone (*Z*)-3b.[36] Yellow oil; R_f 0.35 (hexane/EtOAc, 4:1); IR (neat) ν 3058, 2990, 2928, 1773, 1671, 1562, 1522, 1481, 1460, 1423, 1386, 1342, 1278, 1207, 1120, 1042, 969, 926, 886, 837, 760, 623, 588, 551, 443 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.35 (dt, 2H, J=7.2, 3.2 Hz, $-CH_2-$). 4.48 (t, 2H, J=7.2 Hz, $-CH_2-O-$), 7.26 (t, 1H, J=3.2 Hz, C═CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.01, 66.02, 91.40, 129.07, 139.78, 170.19. Anal. calcd for $C_6H_5Cl_3O_2$: C, 33.45; H, 2.34. Found C, 33.25; H, 2.44.

3.7. Competition reaction

Anhydrous potassium carbonate (1.34 g, 9.68 mmol) and 1.08 g (6.67 mmol) of 1-phenyl-1,3-butanedione in 5 mL of anhydrous THF was placed in a 10 mL round bottomed flask. To this mixture, 0.75 mL (7.74 mmol) of chloral was added at room temperature via syringe under N_2 atmosphere. After being stirred for 16 h, the reaction mixture was diluted with 10–15 mL of water and the organic layer was extracted with ether (20 mL×3). After removal of the solvent, the residue was subjected for column chromatography over silica gel using hexane and then hexane–ethyl acetate (10–12%) as an eluent to furnish the title compound as an yellow oil: the ketone **1a** (0.219 g, 18%) (*E*/*Z*, 100:0), and the ketone **1c** (0.646 g, 39% (*E*/*Z*, 100:0) as a pale yellow crystal.

3.7.1. (*E*)-1-Phenyl-4,4,4-trichloro-2-penten-1-one (*E*)-1c.[15,19] Pale yellow crystal; mp 95–97 °C (from hexane);R_f 0.50 (hexane/EtOAc,4:1); IR (KBr) ν 3050, 2366, 2330, 1995, 1972, 1903, 1818, 1773, 1678, 1626, 1597, 1578, 1495, 1452, 1398, 1346, 1334, 1311, 1296, 1278, 1214, 1187, 1164, 1100, 1033, 1013, 955, 870, 793, 768, 733, 714, 685, 675, 615, 565, 524, 497 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$), δ 7.27 (d, 1H, J=14.2 Hz, C*H*═CHCCl_3, 7.42 (d, 1H, J=14.2 Hz, CH═C*H*CCl_3), 7.47–7.70 (m, 3H, Ph), 7.99 (d, 2H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) δ 92.91, 124.03, 128.71, 128.88, 133.86, 136.72, 145.40, 188.77.

3.8. General procedure for the Wittig reaction (typical synthesis of 2i)

To a suspension of (carbethoxyethylidene) triphenyl phosphorane (0.391 g, 1.08 mmol) in 5 mL of THF was added dropwise the chloral (0.1 mL, 1.04 mmol). The reaction mixture was stirred at room temperature for 16 h. The reaction mixture was poured into ice cold brine (20 mL) and extracted by diethyl ether (20 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and the solvent removed under reduced pressure. The crude material was subjected for column chromatography over silica gel using hexane and then hexane–ethyl acetate (10–12%) as an eluent to furnish the title compound as a pale yellow oil: the ester **2i** (73%) (*E*/*Z*-96.4).

3.9. General procedure for the Wittig–Horner reaction (typical synthesis of 2i)

To a suspension of sodium hydride (60% in oil, 0.087 g, 2.18 mmol) in 5 mL of THF was added dropwise triethyl 2-phosphonopropionate (0.223 mL, 1.04 mmol). After the evolution of hydrogen ceased, chloral (0.1 mL, 0.153 g, 1.04 mmol) was added. The reaction mixture was stirred at room temperature for 16 h. Then reaction mixture was

poured into ice-cold water (20 mL) and the organic compound was extracted by ether. After drying over organic layer by $MgSO_4$, the solvent was evaporated. Silica gel column chromatography afforded the ester **2i** (31%) *(E/Z*, 57:43).

3.10. Reduction of α,β-unsaturated carbonyl compounds

3.10.1. (*Z*)-3-Chloro-3-hexen-2-ol (*Z*)-1′f. A solution of compound **1f** (0.138 g, 1.04 mmol) in dry THF (5 mL) was purged with N_2 and cooled to −78 °C, and then a 0.9 M solution of diisobutylaluminum hydride (DIBAL) (1.12 mL, 1.01 mmol) in hexane was slowly added. The mixture was stirred at −60 °C for 2 h. The reaction mixture was quenched with 10% aq. HCl. and the organic compounds were extracted with ether (20 mL×3). The combined organic phase was dried over ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by column chromatography using hexane/EtOAc, (10:1); as an eluent to yield 76 mg (54%) of a **1′f** as **(*Z*)** colorless oil R_f 0.24 (hexane/EtOAc, 4:1); IR (neat) ν 3330, 2974, 2938, 2880, 1659, 1462, 1412, 1373, 1323, 1288, 1168, 1125, 1081, 1023, 965, 913, 874, 787, 760, 688 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.99 (td, J=7.5, 2.0 Hz, 3H), 1.36 (dd, J=6.5, 2.0 Hz, 3H), 2.10 (bs, 1H), 2.19 (dq, J=7.5, 7.5 Hz, 2H), 4.34 (q, J=6.5 Hz, 1H), 5.75 (t, J=7.0 Hz, 1H) ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.88, 21.42, 21.47, 71.30, 127.27, 136.92. Anal. calcd for $C_6H_{11}ClO$: C, 53.54; H, 8.24. Found C, 53.41; H. 8.21.

3.10.2. (*Z*)-3-Chloro-3-decen-2-ol (1′g). Yellow oil; R_f 0.27 (hexane/EtOAc, 4:1); IR (neat) ν 3330, 2960, 2930, 2862, 1659, 1462, 1373, 1290, 1151, 1125, 1071, 963, 874 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (bt, J=6.4 Hz, 3H), 1.15–1.45 (m, 8H), 1.37 (d, J=6.4 Hz, 3H), 1.90 (d, J=5.6 Hz, 1H), 2.18 (dt, J=7.0, 7.0 Hz, 2H), 4.36 (dt, J=6.2, 6.2 Hz, 1H), 5.77 (t, J=7.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.06, 21.61, 22.57, 28.05, 28.39, 28.88, 31.61, 71.46, 125.99, 137.41. Anal. calcd for $C_{10}H_{19}ClO$: C, 62.98; H, 10.04. Found C, 63.24; H, 10.03.

3.10.3. (*Z*)-2-Chloro-2-nonenol (*Z*)-2′f. To a solution of compound **2f** (0.104 g, 0.475 mmol) in dry THF (5 mL) was purged with N_2 and cooled to 0 °C, and then a 0.9 M solution of diisobutylauminum hydride (DIBAL) (0.51 mL, 0.459 mmol) in hexane was slowly added. The mixture was stirred at 0 °C for 3 h and then at room temperature for 2 h. Then the mixture was cooled to 0 °C and a 0.9 M solution of diisobutylaluminum hydride (DIBAL) (0.51 mL, 0.459 mmol) in hexane was slowly added. The mixture was stirred at 0 °C for 1 h and then the temperature was raised to room temperature and mixture was stirred for 17 h. The reaction mixture was quenched with 10% aq. HCl and extracted with ether. The combined organic phases was dried over ($MgSO_4$) and the solvents was removed under reduced pressure, and the residue was purified by column chromatography over silica gel using hexane/EtOAc (10:1) as an eluent to yield **(*Z*)-2′f** (71 mg, 85%) as a colorless oil: R_f 0.28 (hexane/EtOAc, 4:1); IR (neat) ν 3386, 2960, 2928, 2862, 1659, 1640, 1462, 1454, 1412, 1379, 1098, 1015 cm^{-1}; ^1H NMR (500 MHz, $(CD_3)_2C{=}O$) δ 0.87 (t, J=7.0 Hz, 3H), 1.22–1.44 (m, 8H), 2.18 (q, J=7.5 Hz, 2H), 4.09 (dd, J=6.0, 1.5 Hz, 2H) 4.38 (t, J=6.5 Hz, 1H), 5.70 (t, J=8.0 Hz, 0.004H) 5.87 (tt, J=7.0, 1.0 Hz, 0.996H) (500 MHz, $CDCl_3$) δ 0.88 (t, J=7.0 Hz, 3H), 1.20–1.44 (m, 8H), 1.94 (bs, 1H), 2.20 (q, J=7.5 Hz, 2H), 4.18 (s, 2H), 5.79 (td, J=7.0, 1.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.05, 22.57, 28.13, 28.35, 28.88, 31.61, 66.94, 127.63, 132.95. Anal. calcd for $C_9H_{17}ClO$: C, 61.18; H, 9.70. Found: C, 60.98; H, 9.79.

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