Stereoselective Synthesis of Tetrasubstituted (*Z*)-Alkenes from Aryl Alkyl Ketones Utilizing the Horner–Wadsworth–Emmons Reaction

Shigeki SANO,* Tomoka TAKEHISA, Shiho OGAWA, Kenji YOKOYAMA, and Yoshimitsu NAGAO

Faculty of Pharmaceutical Sciences, The University of Tokushima; Sho-machi, Tokushima 770–8505, Japan.
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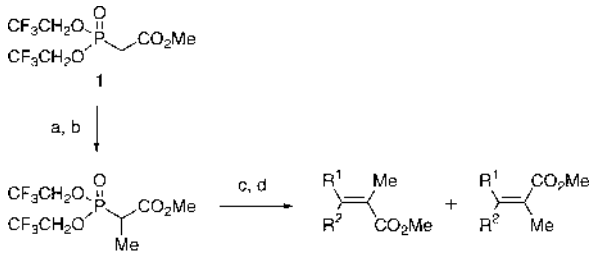
Tetrasubstituted (*Z*)-alkenes were readily prepared through the Horner–Wadsworth–Emmons reactions of methyl 2-[bis(2,2,2-trifluoroethyl)phosphono]propionate with aryl alkyl ketones by employing $Sn(OSO_2CF_3)_2$ and *N*-ethylpiperidine.

Key words Horner–Wadsworth–Emmons reaction; tetrasubstituted alkene; aryl alkyl ketone; α,β-unsaturated ester; methyl 2-[bis(2,2,2-trifluoroethyl)phosphono]propionate; Wittig reaction

The Horner–Wadsworth–Emmons (HWE) reaction is the most popular method of synthesizing α,β-unsaturated esters.[1] We have recently reported a new approach to the stereoselective HWE reaction of methyl bis(2,2,2-trifluoroethyl)-phosphonoacetate (**1**)[2] or ethyl 2-fluoro-2-diethylphosphonoacetate[3] with aryl alkyl ketones by using $Sn(OSO_2CF_3)_2$ and *N*-ethylpiperidine.[4—8] While a number of methods have been developed for the stereoselective synthesis of alkenes, few accounts have appeared in the literature describing the convenient preparation of tetrasubstituted (*Z*)-alkenes with excellent selectivity.[9—13] We have already presented a facile method for obtaining tetrasubstituted (*E*)-fluoroalkenes.[5] Herein we describe a stereoselective synthesis of tetrasubstituted (*Z*)-alkenes based on the HWE reactions of methyl 2-[bis(2,2,2-trifluoroethyl)phosphono]propionate (**2**) with aryl alkyl ketones **3a**—**h**, as shown in Chart 1.

Phosphonate **2**[2,14] was prepared by the methylation of phosphonate **1** with *tert*-BuOK and MeI in 53% yield. The reactions of phosphonate **2** with aryl alkyl ketones **3a**—**h** using $Sn(OSO_2CF_3)_2$ and *N*-ethylpiperidine were examined. All results are summarized in Table 1. Treatment of **2** with phenyl ethyl ketone (**3b**) at 0 °C produced tetrasubstituted (*Z*)-alkene **4b** with an *E*:*Z* ratio of 6:94, and in 38% yield (Table 1, entry 3). A significant improvement in the yield (86%) and a similar *Z*-selectivity (*E*:*Z*=7:93) were found in the reaction of **2** with **3b** under reflux (Table 1, entry 2). In the HWE reactions of aryl alkyl ketones **3a**—**c**, **e**, **f**, the stereoselectivities were in a range of *E*:*Z* ratios of 8:92—3:97, as shown in Table 1. No reaction occurred in the case of ketone **3d** bearing a bulky *tert*-butyl group (Table 1, entry 5). Each reaction of aryl alkyl ketones **3g**, **h** having an electron-withdrawing nitro group on the aromatic moiety, proceeded even at 0 °C, but resulted in a lower stereoselectivity (*E*:*Z*=25:75 or 27:73) (Table 1, entries 8 and 9). In the HWE reactions employing NaH, the *E*:*Z* stereoselectivities of the products were moderate, with ratios of 41:59—11:89, as listed in Table 2. It is worth noting that the reaction of ketone **3c** bearing a relatively bulky isopropyl group did not occur under the NaH conditions (Table 2, entry 4), while it readily proceeded under the $Sn(OSO_2CF_3)_2$ conditions (Table 1, entry 4). The $Sn(OSO_2CF_3)_2$-mediated HWE reactions therefore seem to proceed in a chelation-controlled manner as we have proposed in a previous report, whereas the NaH-mediated HWE reactions proceed in a non-chelation-controlled manner.[4] The geometry of **4a**—**c**, **e**—**h** was confirmed by ^1H–^1H nuclear Overhauser effect (NOE) (400 MHz, $CDCl_3$) experiments. The *E*:*Z* ratios of **4a**—**c**, **e**—**h** were determined by utilizing ^1H-NMR analysis (400 MHz, $CDCl_3$).

As mentioned above, the HWE reactions of phosphonate **2** with various aryl alkyl ketones **3a**, **b**, **e**—**h** under the NaH conditions gave tetrasubstituted (*Z*)-alkenes **4a**, **b**, **e**—**h** with moderate selectivity. However, the *Z*-selectivities of tetrasubstituted alkenes under the NaH conditions were better than the prediction from the viewpoint of the previous results re-



a: R^1 = Ph, R^2 = Me; **b**: R^1 = Ph, R^2 = Et; **c**: R^1 = Ph, R^2 = *i*-Pr; **d**: R^1 = Ph, R^2 = *t*-Bu; **e**: R^1 = *p*-MeO-Ph, R^2 = Me; **f**: R^1 = *p*-MeO-Ph, R^2 = Et; **g**: R^1 = *p*-NO_2-Ph, R^2 = Me; **h**: R^1 = *m*-NO_2-Ph, R^2 = Et

a) *t*-BuOK, b) MeI, c) $Sn(OSO_2CF_3)_2$ - *N*-ethylpiperidine or NaH, d) R^1COR^2 (**3a**-**h**)

Chart 1

Table 1. $Sn(OSO_2CF_3)_2$-Mediated Horner–Wadsworth–Emmons Reactions of **2** with Ketones **3a**—**h**[a]

Entry	Ketone	Temp.	Yield (%)[b]	Alkene (*E*/*Z*)[c]
1	**3a**	Reflux	42[d]	**4a** (8:92)
2	**3b**	Reflux	86	**4b** (7:93)
3	**3b**	0 °C	38	**4b** (6:94)
4	**3c**	Reflux	66	**4c** (4:96)
5	**3d**	Reflux	—[e]	—
6	**3e**	Reflux	14[d]	**4e** (4:96)
7	**3f**	Reflux	49	**4f** (3:97)
8	**3g**	0 °C	65	**4g** (25:75)
9	**3h**	0 °C	56	**4h** (27:73)

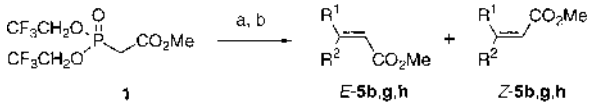
a) Conditions: CH_2Cl_2, 20 h, **2**/$Sn(OSO_2CF_3)_2$/*N*-ethylpiperidine/**3** (1.4:1.68:1.54:1). *b*) Isolated yields. *c*) ^1H-NMR (400 MHz, $CDCl_3$) analysis. *d*) Aldol product was obtained (entry 1: 20%, entry 6: 34%). *e*) No reaction.

* To whom correspondence should be addressed. e-mail: ssano@ph2.tokushima-u.ac.jp

Table 2. NaH-Mediated Horner–Wadsworth–Emmons Reactions of **2** with Ketones **3a**—**h**[a]

Entry	Ketone	Temp.	Yield (%)[b]	Alkene (*E*/*Z*)[c]
1	**3a**	Reflux	95	**4a** (14 : 86)
2	**3b**	Reflux	70	**4b** (12 : 88)
3	**3b**	0 °C	Trace	—[d]
4	**3c**	Reflux	—[e]	—
5	**3d**	Reflux	—[e]	—
6	**3e**	Reflux	90	**4e** (41 : 59)
7	**3f**	Reflux	79	**4f** (11 : 89)
8	**3g**	0 °C	100	**4g** (15 : 85)
9	**3h**	0 °C	73	**4h** (25 : 75)

a) Conditions: THF, 20 h, **2**/NaH/**3** (1.7 : 1.5 : 1). *b*) Isolated yields. *c*) ^{1}H-NMR (400 MHz, $CDCl_3$) analysis. *d*) Not determined. *e*) No reaction.



1 *E*-**5b**,**g**,**h** *Z*-**5b**,**g**,**h**

b: R^1 = Ph, R^2 = Et; **g**: R^1 = *p*-NO_2-Ph, R^2 = Me; **h**: R^1 = *m*-NO_2-Ph, R^2 = Et

a) NaH , b) R^1COR^2 (**3b**,**g**,**h**)

Chart 2

Table 3. NaH-Mediated Horner–Wadsworth–Emmons Reactions of **1** with Ketones **3b**, **g**, **h**[a]

Entry	Ketone	Temp.	Yield (%)[b]	Alkene (*E*/*Z*)[c]
1	**3b**	Reflux	86	**5b** (41 : 59)
2[d]	**3g**	0 °C	99	**5g** (35 : 65)
3	**3h**	0 °C	99	**5h** (34 : 66)

a) Conditions: THF, 20 h, **1**/NaH/**3** (1.7 : 1.5 : 1). *b*) Isolated yields. *c*) ^{1}H-NMR (400 MHz, $CDCl_3$) analysis. *d*) 19 h, ref. 8.

garding the stereoselective synthesis of trisubstituted (*Z*)-alkenes.[4] In order to compare the stereoselectivity of phosphonate **2** with that of phosphonate **1** toward aryl alkyl ketones, the HWE reactions of ketones **3b**, **g**, **h** with phosphonate **1** using NaH were examined. The results showed that the *Z*-selectivity of tetrasubstituted alkenes **4b**, **g**, **h** (*E* : *Z*= 12 : 88, 15 : 85, or 25 : 75) were superior to that of trisubstituted alkenes **5b**, **g**, **h** (*E* : *Z*=41 : 59, 35 : 65, or 34 : 66), respectively, as shown in Tables 2 and 3. A CH/π attraction between the α-methyl group of phosphonate **2** and the phenyl group of ketones **3b**, **g**, **h** may participate in the transition state for the formation of pro-(*Z*)-oxyanion intermediates.[15—17] However, the mechanism governing the stereoselective outcome giving tetrasubstituted alkenes **4b**, **g**, **h** under NaH conditions is not yet clear. The geometry and the diastereomer ratios of **5b**, **g**, **h** were confirmed on the basis of ^{1}H–^{1}H NOE experiments (400 MHz, $CDCl_3$) and ^{1}H-NMR (400 MHz, $CDCl_3$) analysis, respectively

In summary, we have demonstrated that the $Sn(OSO_2CF_3)_2$-mediated HWE reactions are applicable to the stereoselective synthesis of tetrasubstituted (*Z*)-alkenes. Clarification of the details of the reaction mechanisms of the stereoselective HWE reactions is currently underway in our laboratory.

Experimental

All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. IR spectra were obtained using a Perkin–Elmer 1720 or JASCO FT/IR-420 IR Fourier transform spectrometer. ^{1}H-NMR (200 and 300 MHz) spectra were recorded on a JEOL JNM-FX 200 or JEOL JNM-AL300 spectrometer. Chemical shifts are given in δ values (ppm) using tetramethylsilane (TMS) as an internal standard. Electron impact (EI)-MS spectra were recorded on a JEOL JMS SX-102A spectrometer. Elementary combustion analyses were performed using a Yanaco CHN CORDER MT-5. All reactions were monitored by TLC employing 0.25-mm silica gel plates (Merck 5715; 60 F_{254}). Preparative TLC (PTLC) was performed on 0.5-mm silica gel plates (Merck 5744; 60 F_{254}). Column chromatography was carried out on silica gel [Katayama Chemical K070; 70—300 mesh, Kanto Chemical N60 (spherical, neutral); 63—210 mm, Merck 9385; 230—400 mesh]. The usual workup refers to washing an organic portion with brine, drying it over anhydrous $MgSO_4$, filtration, and concentration *in vacuo*. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under N_2. *N*-Ethylpiperidine and CH_2Cl_2 were distilled from CaH_2. All other solvents were distilled prior to use. All reagents were used as purchased.

Methyl 2-[Bis(2,2,2-trifluoroethyl)phosphono]propionate (2) To a solution of *tert*-BuOK (1.9 g, 17.0 mmol) in THF (20 ml) was slowly added methyl bis(2,2,2-trifluoroethyl)phosphonoacetate (**1**) (3.0 ml, 14.2 mmol) at 0 °C under nitrogen. The mixture was stirred at 0 °C for 30 min under nitrogen, and methyl iodide (4.42 ml, 70.9 mmol) was slowly added at 0 °C. After being stirred at room temperature for 14 h under nitrogen, the reaction mixture was treated with an aqueous solution saturated with NH_4Cl and then extracted with AcOEt (50 ml×3). The extract was submitted to the usual workup to give an oily residue, which was purified by column chromatography on silica gel [*n*-hexane/AcOEt (2 : 1)] to afford **2** (2.22 g, 53%) as a colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.52 (3H, dd, $^4J_{H,P}$=19.3 Hz, J=7.3 Hz), 3.21 (1H, dq, $^2J_{H,P}$=22.9 Hz, J=7.3 Hz), 3.78 (3H, s), 4.36—4.51 (4H, m); IR (neat) 1748, 1421, 1386, 1264, 1173, 1077, 964, 871 cm^{-1}; EI-MS calcd for $C_8H_{11}O_5F_6P$ MW 332.0249, found *m*/*z* 332.0230 (M^+); *Anal.* Calcd for $C_8H_{11}O_5F_6P$: C, 28.93; H, 3.34. Found: C, 28.82; H, 3.31.

Typical Procedure for the HWE Reaction with $Sn(OSO_2CF_3)_2$ To a suspension of $Sn(OSO_2CF_3)_2$ (309 mg, 0.74 mmol) in anhydrous CH_2Cl_2 (5 ml) was added a solution of phosphonate **2** (206 mg, 0.62 mmol) in anhydrous CH_2Cl_2 (3 ml) and stirred at room temperature for 5 min under argon. After adding of *N*-ethylpiperidine (110 ml, 0.68 mmol), the mixture was stirred at 0 °C for 1 h under argon, and phenyl ethyl ketone (**3b**) (59 μl, 0.44 mmol) was slowly added to the refluxing solution. After being refluxed for 20 h under argon, the reaction mixture was poured into H_2O (5 ml) and then extracted with $CHCl_3$ (20 ml×3). To the $CHCl_3$ extract was added *n*-hexane (120 ml), and the mixture was submitted to filtration through a silica gel short column [*n*-hexane/$CHCl_3$ (2 : 1)]. The filtrate was evaporated *in vacuo* to afford a crude product **4b** (*E* : *Z*=7 : 93), which was purified by column chromatography on silica gel [*n*-hexane/Et_2O (25 : 1)] to afford *E*-**4b** (6.3 mg, 7%) and *Z*-**4b** (81.1 mg, 79%) as a pale yellow oil and a colorless oil, respectively.

Typical Procedure for the HWE Reaction with NaH To a suspension of NaH (abs. 60% in oil, 22 mg, 0.55 mmol) in anhydrous THF (5 ml) was added a solution of phosphonate **2** (207 mg, 0.62 mmol) in anhydrous THF (3 ml) at 0 °C. The mixture was stirred at 0 °C for 1 h under argon, and phenyl ethyl ketone (**3b**) (49 ml, 0.37 mmol) was added to the refluxing solution. After being refluxed for 20 h under argon, 5% HCl (15 ml) was added and then extracted with Et_2O (20 ml×3). The extract was submitted to the usual workup to give a crude product **4b** (*E* : *Z*=12 : 88), which was purified by column chromatography on silica gel [*n*-hexane/Et_2O (25 : 1)] to afford *E*-**4b** (6.6 mg, 9%) and *Z*-**4b** (45.6 mg, 61%) as a pale yellow oil and a colorless oil, respectively.

Methyl (*E*)-2-Methyl-3-phenyl-2-butenoate [(*E*)-**4a**]: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.75 (3H, q, J=1.4 Hz), 2.26 (3H, q, J=1.4 Hz), 3.80 (3H, s), 7.12—7.15 (2H, m), 7.27—7.38 (3H, m); IR (neat) 2949, 1716, 1433, 1253, 1133, 1099 cm^{-1}; EI-MS calcd for $C_{12}H_{14}O_2$ MW 190.0994, found *m*/*z* 190.1000 (M^+).

Methyl (*Z*)-2-Methyl-3-phenyl-2-butenoate [(*Z*)-**4a**]: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.05 (3H, q, J=0.6 Hz), 2.09 (3H, q, J=0.6 Hz), 3.39 (3H, s), 7.12—7.14 (2H, m), 7.23—7.32 (3H, m); IR (neat) 2947, 1714, 1433, 1316, 1243, 1139 cm^{-1}; EI-MS calcd for $C_{12}H_{14}O_2$ MW 190.0994, found *m*/*z* 190.0996 (M^+); *Anal.* Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.49; H, 7.53.

Methyl (*E*)-2-Methyl-3-phenyl-2-pentenoate [(*E*)-**4b**]: Pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.94 (3H, t, J=7.3 Hz), 1.71 (3H, s), 2.61

(2H, q, J=7.3 Hz), 3.80 (3 H, s), 7.09—7.12 (2H, m), 7.28—7.38 (3H, m); IR (neat) 2922, 2851, 1718, 1684, 1598, 1260, 1098, 1026 cm^{-1}; EI-MS calcd for $C_{13}H_{16}O_2$ MW 204.1150, found m/z 204.1141 (M^+).

Methyl (*Z*)-2-Methyl-3-phenyl-2-pentenoate [(*Z*)-**4b**]: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.94 (3H, t, J=7.5 Hz), 2.03 (3H, s), 2.47 (2H, q, J=7.5 Hz), 3.36 (3 H, s), 7.09—7.12 (2H, m), 7.23—7.31 (3H, m); IR (neat) 2931, 1716, 1600, 1434, 1305, 1238, 1138 cm^{-1}; EI-MS calcd for $C_{13}H_{16}O_2$ MW 204.1150, found m/z 204.1161 (M^+); *Anal.* Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.18; H, 7.95.

Methyl (*E*)-2,4-Dimethyl-3-phenyl-2-pentenoate [(*E*)-**4c**]: Pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.94 (6H, d, J=6.8 Hz), 1.57 (3H, s), 3.29 (1H, sept, J=6.8 Hz), 3.80 (3 H, s), 7.00—7.02 (2H, m), 7.22—7.37 (3H, m); IR (neat) 2922, 1732, 1646, 1457, 1260, 1024 cm^{-1}; EI-MS calcd for $C_{14}H_{18}O_2$ MW 218.1307, found m/z 218.1340 (M^+).

Methyl (*Z*)-2,4-Dimethyl-3-phenyl-2-pentenoate [(*Z*)-**4c**]: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.95 (6H, t, J=6.8 Hz), 2.03 (3H, s), 3.06 (1H, sept, J=6.8 Hz), 3.30 (3 H, s), 7.01—7.04 (2H, m), 7.20—7.30 (3H, m); IR (neat) 2965, 1716, 1433, 1314, 1241, 1135 cm^{-1}; EI-MS calcd for $C_{14}H_{18}O_2$ MW 218.1307, found m/z 218.1292 (M^+); *Anal.* Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.84; H, 8.36.

Methyl (*E*)-2-Methyl-3-(*p*-methoxyphenyl)-2-butenoate [(*E*)-**4e**]: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.78 (3H, d, J=1.4 Hz), 2.25 (3H, d, J=1.4 Hz), 3.79 (3H, s), 3.82 (3H, s), 6.87—6.91 (2H, m), 7.06—7.10 (2H, m); IR (neat) 2950, 1714, 1608, 1510, 1248, 1132, 1032 cm^{-1}; EI-MS calcd for $C_{13}H_{16}O_3$ MW 220.1100, found m/z 220.1082 (M^+).

Methyl (*Z*)-2-Methyl-3-(*p*-methoxyphenyl)-2-butenoate [(*Z*)-**4e**]: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.01 (3H, d, J=0.9 Hz), 2.07 (3H, d, J=0.9 Hz), 3.44 (3H, s), 3.80 (3H, s), 6.81—6.85 (2H, m), 7.05—7.10 (2H, m); IR (neat) 2948, 1711, 1608, 1509, 1288, 1247, 1179, 1138, 1032 cm^{-1}; EI-MS calcd for $C_{13}H_{16}O_3$ MW 220.1100, found m/z 220.1087 (M^+); *Anal.* Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.93; H, 7.48.

Methyl (*E*)-2-Methyl-3-(*p*-methoxyphenyl)-2-pentenoate [(*E*)-**4f**]: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.93 (3H, t, J=7.5 Hz), 1.73 (3H, s), 2.59 (2H, q, J=7.5 Hz), 3.79 (3H, s), 3.82 (3H, s), 6.87—6.92 (2H, m), 7.02—7.07 (2H, m); IR (neat) 2925, 1716, 1608, 1509, 1246, 1133 cm^{-1}; EI-MS calcd for $C_{14}H_{18}O_3$ MW 234.1256, found m/z 234.1245 (M^+).

Methyl (*Z*)-2-Methyl-3-(*p*-methoxyphenyl)-2-pentenoate [(*Z*)-**4f**]: Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.93 (3H, t, J=7.5 Hz), 2.02 (3H, s), 2.45 (2H, q, J=7.5 Hz), 3.41 (3H, s), 3.80 (3H, s), 6.81—6.86 (2H, m), 7.02—7.07 (2H, m); IR (neat) 2968, 1713, 1608, 1510, 1248, 1138 cm^{-1}; EI-MS calcd for $C_{14}H_{18}O_3$ MW 234.1256, found m/z 234.1249 (M^+); *Anal.* Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.84; H, 7.92.

Methyl (*E*)-2-Methyl-3-(*p*-nitrophenyl)-2-butenoate [(*E*)-**4g**]: Colorless needles (*n*-hexane–Et_2O): mp 70.5—71 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.74 (3H, q, J=1.4 Hz), 2.26 (3H, q, J=1.4 Hz), 3.82 (3H, s), 7.31—7.34 (2H, m), 8.23—8.26 (2H, m); IR (KBr) 2960, 1722, 1594, 1509, 1349, 1301, 1252, 1132, 858 cm^{-1}; EI-MS calcd for $C_{12}H_{13}NO_4$ MW 235.0844, found m/z 235.0857 (M^+); *Anal.* Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95. Found: C, 61.57; H, 5.67; N, 5.95.

Methyl (*Z*)-2-Methyl-3-(*p*-nitrophenyl)-2-butenoate [(*Z*)-**4g**]: Pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.06 (3H, s), 2.11 (3H, s), 3.44 (3H, s), 7.26—7.29 (2H, m), 8.16—8.19 (2H, m); IR (neat) 2949, 1719, 1596, 1518, 1345, 1245, 1140, 857 cm^{-1}; EI-MS calcd for $C_{12}H_{13}NO_4$ MW 235.0844, found m/z 235.0842 (M^+); *Anal.* Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95. Found: C, 61.42; H, 5.64; N, 5.93.

Methyl (*E*)-2-Methyl-3-(*m*-nitrophenyl)-2-pentenoate [(*E*)-**4h**]: Pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.95 (3H, t, J=7.5 Hz), 1.71 (3H, s), 2.63 (2H, q, J=7.5 Hz), 3.82 (3H, s), 7.44—7.47 (1H, m), 7.54—7.59 (1H, m), 8.00—8.01 (1H, m), 8.15—8.18 (1H, m); IR (neat) 2969, 1716, 1530, 1349, 1266, 1141, 1100 cm^{-1}; EI-MS calcd for $C_{13}H_{15}NO_4$ MW 249.1001, found m/z 249.0988 (M^+).

Methyl (*Z*)-2-Methyl-3-(*m*-nitrophenyl)-2-pentenoate [(*Z*)-**4h**]: Pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.96 (3H, t, J=7.5 Hz), 2.07 (3H, s), 2.50 (2H, q, J=7.5 Hz), 3.43 (3H, s), 7.41—7.51 (2H, m), 7.97—8.01 (1H, m), 8.11—8.14 (1H, m); IR (neat) 2972, 1719, 1529, 1433, 1351, 1303, 1238, 1143, 1102 cm^{-1}; EI-MS calcd for $C_{13}H_{15}NO_4$ MW 249.1001, found m/z 249.0991 (M^+); *Anal.* Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 63.00; H, 6.17; N, 5.60.

Methyl (*E*)-3-Phenyl-2-pentenoate [(*E*)-**5b**]: Colorless oil; ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.08 (3H, t, J=7.4 Hz), 3.12 (2H, q, J=7.4 Hz), 3.75 (3H, s), 6.02 (1H, s), 7.34—7.47 (5H, m); IR (neat) 1718, 1626, 1576, 1495, 1434, 1240, 1040, 1002, 874, 733, 697 cm^{-1}; EI-MS calcd for $C_{12}H_{14}O_2$ MW 190.0994, found m/z 190.0987 (M^+); *Anal.* Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.47; H, 7.45.

Methyl (*Z*)-3-Phenyl-2-pentenoate [(*Z*)-**5b**]: Colorless oil; ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.05 (3H, t, J=7.3 Hz), 2.47 (2H, q, J=7.3 Hz), 3.54 (3H, s), 5.88 (1H, s), 7.13—7.36 (5H, m); IR (neat) 1730, 1641, 1601, 1493, 1371, 1227, 1165, 1031, 1004, 966, 871 cm^{-1}; EI-MS calcd for $C_{12}H_{14}O_2$ MW 190.0994, found m/z 190.1004 (M^+).

Methyl (*E*)-3-(*p*-Nitrophenyl)-2-butenoate [(*E*)-**5g**][8]: Colorless needles (EtOH): mp 206—208.5 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 2.60 (3H, d, J=1.0 Hz), 3.79 (3H, s), 6.19 (1H, q, J=1.0 Hz), 7.60—7.64 (2H, m), 8.22—8.26 (2H, m); IR (KBr) 3079, 2958, 1743, 1729, 1515, 1345, 1292, 1147, 1010, 853 cm^{-1}; EI-MS calcd for $C_{11}H_{11}NO_4$ MW 221.0688, found m/z 221.0701 (M^+); *Anal.* Calcd for $C_{11}H_{11}NO_4$: C, 59.73; H, 5.01; N, 6.33. Found: C, 59.65; H, 5.10; N, 6.23.

Methyl (*Z*)-3-(*p*-Nitrophenyl)-2-butenoate [(*Z*)-**5g**][8]: Colorless needles (EtOH): mp 117.5—120 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 2.20 (3H, d, J=1.2 Hz), 3.57 (3H, s), 6.01 (1H, q, J=1.2 Hz), 7.33—7.37 (2H, m), 8.21—8.25 (2H, m); IR (KBr) 2953, 1743, 1728, 1632, 1515, 1345, 1010, 852 cm^{-1}; EI-MS calcd for $C_{11}H_{11}NO_4$ MW 221.0688, found m/z 221.0707 (M^+); *Anal.* Calcd for $C_{11}H_{11}NO_4$: C, 59.73; H, 5.01; N, 6.33. Found: C, 59.77; H, 5.09; N, 6.26.

Methyl (*E*)-3-(*m*-Nitrophenyl)-2-pentenoate [(*E*)-**5h**]: Colorless plates (*n*-hexane–Et_2O): mp 56—57 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.09 (3H, t, J=7.5 Hz), 3.14 (2H, q, J=7.5 Hz), 3.78 (3H, s), 6.08 (1H, s), 7.55—7.60 (1H, m), 7.74—7.77 (1H, m), 8.21—8.29 (2H, m); IR (KBr) 1710, 1622, 1529, 1349, 1191, 879 cm^{-1}; EI-MS calcd for $C_{12}H_{13}NO_4$ MW 235.0845, found m/z 235.0835 (M^+); *Anal.* Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.59. Found: C, 61.25; H, 5.59; N, 5.98.

Methyl (*Z*)-3-(*m*-Nitorophenyl)-2-pentenoate [(*Z*)-**5h**]: Pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.09 (3H, t, J=7.5 Hz), 2.49 (2H, q, J=7.5 Hz), 3.56 (3H, s), 5.98 (1H, s), 7.47—7.56 (2H, m), 8.01—8.05 (1H, m), 8.17—8.20 (1H, m); IR (neat) 2971, 1725, 1646, 1530, 1434, 1349, 1233, 1175, 874 cm^{-1}; EI-MS calcd for $C_{12}H_{13}NO_4$ MW 235.0845, found m/z 235.0833 (M^+); *Anal.* Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.59. Found: C, 61.25; H, 5.60; N, 5.61.

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