

Use of β -Chloropropionaldehyde as an Acrolein Equivalent in the Wadsworth-Emmons Modification of the Wittig Reaction

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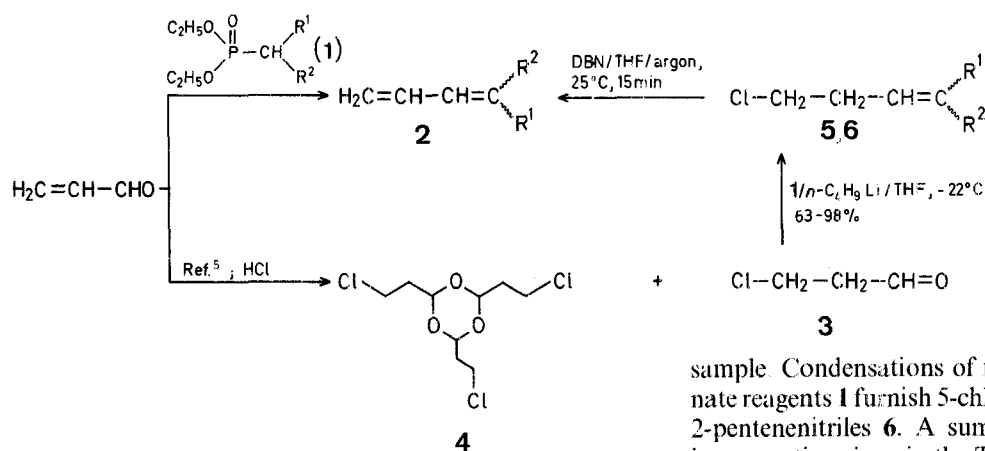
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β -Chloropropionaldehyde (**3**) has been used as an acrolein equivalent to prepare 5-chloro-2-pentenoates **5** and 5-chloro-2-pentenitriles **6** by condensing with phosphonates **1**.

In connection with an interest in the preparation of 2-substituted 2,4-pentadienenitriles and 2,4-pentadienoates, we examined the Wadsworth-Emmons condensation of phosphonates **1** with acrolein to give the olefins **2**. Although analogous condensations of substituted triphenylphosphorane reagents with acrolein proceed successfully¹⁻⁴, we invariably encountered low yields of **2** using the corresponding phosphonate reagents **1** as a consequence of acrolein poly-

merization. We found, however, that β -chloropropionaldehyde⁵ (**3**) serves as a suitable acrolein equivalent in such phosphonate Wittig reactions.

β -Chloropropionaldehyde (**3**) is readily prepared from acrolein in ~40% yield and is usually contaminated with 10–30% of the trioxane **4** depending on the age of the



sample. Condensations of freshly distilled **3** with phosphonate reagents **1** furnish 5-chloro-2-pentenoates **5** or 5-chloro-2-pentenitriles **6**. A summary of the yields and (*E/Z*)-isomer ratios given in the Table indicates that the phosphonates **1** bearing an ester substituent give predominantly the (*E*)-stereoisomer whereas the phosphonate reagents **1** bearing the less bulky nitrile substituent give predominantly the (*Z*)-stereoisomer. This generalization must be qualified, however, by the statement that the alkyl group *R*¹ also exerts a definite influence on the (*E/Z*)-ratio as the data in the Table clearly shows. Dehydrochlorination using 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) furnishes the desired dienes in high yield as illustrated by the conversion of **5f** to **2** in 83% yield.

5	<i>R</i> ¹	<i>R</i> ²	6	<i>R</i> ¹	<i>R</i> ²
a	H	COOC ₂ H ₅	a	H	CN
b	CH ₃	COOC ₂ H ₅	b	CH ₃	CN
c	C ₂ H ₅	COOC ₂ H ₅	c	C ₂ H ₅	CN
d	H	COOC ₃ H ₇ - <i>i</i>	d	<i>i</i> -C ₃ H ₇	CN
e	H	COOC ₄ H ₉ - <i>t</i>	e	<i>n</i> -C ₆ H ₁₃	CN
f	CH ₂ -C ₆ H ₅	COOCH ₃	f	CH ₂ -C ₆ H ₅	CN
			g	OC ₄ H ₉ - <i>t</i>	CN

Table. Compounds **5** and **6** prepared

Prod- uct	Yield [%]	<i>E/Z</i> - ratio	Molecular Formula ^a	Exact mass spectrum (<i>M</i> ⁺)		M.S. (70 eV), <i>m/e</i> (relative intensity, %)	¹ H-N.M.R. (CDCl ₃ /TMS) δ [ppm]
				calc.	found		
5a	81	6.5 : 1	C ₇ H ₁₁ ClO ₂ (162.6)	(<i>E</i>)-isomer:	162.0450	162 (<i>M</i> ⁺ , 0.05); 127 (<i>M</i> ⁺ - Cl, 35); 117 (<i>M</i> ⁺ - OC ₂ H ₅ , 100); 99 (76)	1.30 (t, 3H, <i>J</i> = 7.3 Hz, CH ₂ -CH ₃); 2.68 (q, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 3.62 (t, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 4.20 (q, 2H, <i>J</i> = 7.3 Hz, CH ₂ -CH ₃); 5.29 (d, 1H, <i>J</i> = 16.8 Hz, 2-H _{vinyl}); 6.92 (dt, 1H, <i>J</i> = 16.8 and 6.6 Hz, 3-H _{vinyl})
				(<i>Z</i>)-isomer ^b	147.0236 147.0213	147 (<i>M</i> ⁺ - CH ₃ , 2); 127 (<i>M</i> ⁺ - Cl, 18); 117 (9); 99 (9); 67 (71); 57 (100)	1.30 (t, 3H, <i>J</i> = 7.3 Hz, CH ₂ -CH ₃); 3.14 (m, 2H, CH ₂ -CH ₂ -Cl); 3.64 (t, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 4.18 (q, 2H, <i>J</i> = 7.3 Hz, CH ₂ -CH ₃); 5.91 (d, 1H, <i>J</i> = 11.2 Hz, 2-H _{vinyl}); 6.31 (dt, 1H, <i>J</i> = 11.2 and 7.3 Hz, 3-H _{vinyl})
5b	81	1.5 : 1	C ₈ H ₁₃ ClO ₂ (176.6)	(<i>E</i>)-isomer	176.0613 176.0605	176 (<i>M</i> ⁺ , 6); 141 (<i>M</i> ⁺ - Cl, 88); 131 (<i>M</i> ⁺ - OC ₂ H ₅ , 88); 113 (100); 103 (28)	1.31 (t, 3H, <i>J</i> = 7.3 Hz, CH ₂ -CH ₃); 1.87 (s, 3H, =C-CH ₃); 2.66 (m, 2H, CH ₂ -CH ₂ -Cl); 3.61 (t, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 4.21 (q, 2H, <i>J</i> = 7.3 Hz, CH ₂ -CH ₃); 6.74 (t, 1H, =CH)
				(<i>Z</i>)-isomer	176.0637 176.0605	176 (<i>M</i> ⁺ , 3); 141 (<i>M</i> ⁺ - Cl, 81); 131 (<i>M</i> ⁺ - OC ₂ H ₅ , 40); 113 (63); 103 (12); 93 (100)	1.31 (t, 3H, <i>J</i> = 7.3 Hz, CH ₂ -CH ₃); 1.94 (s, 3H, =C-CH ₃); 2.94 (m, 2H, CH ₂ -CH ₂ -Cl); 3.60 (t, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 4.21 (q, 2H, <i>J</i> = 7.3 Hz, CH ₂ -CH ₃); 6.01 (t, 1H, 3-H _{vinyl})

Table. (continued)

Prod- uct	Yield [%]	<i>(E/Z)</i> - ratio	Molecular Formula ^a	Exact mass spectrum (M^+)		M.S. (70 eV), m/e (relative intensity, %)	¹ H-N.M.R. (CDCl ₃ /TMS) δ [ppm]
				calc.	found		
5c	91	1.3 : 1	C ₉ H ₁₅ ClO ₂ (190.7)	(<i>E</i>)-isomer 190.0761	190.0760	190 (M^+ , 8); 155 (M^+ - Cl, 39); 145 (M^+ - OC ₂ H ₅ , 36); 127 (42); 69 (100)	1.03 (t, 3H, J = 7.3 Hz, CH ₂ -CH ₃); 1.31 (t, 3H, J = 6.6 Hz, OCH ₂ -CH ₃); 2.34 (q, 2H, J = 6.6 Hz, CH ₂ -CH ₃); 2.67 (q, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 3.60 (t, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 4.21 (q, 2H, J = 6.6 Hz, OCH ₂ -CH ₃); 6.68 (t, 1H, J = 7.3 Hz, 3-H _{vinyl})
				(<i>Z</i>)-isomer 190.0761	190.0784	190 (M^+ , 5); 155 (M^+ - Cl, 100); 145 (M^+ - OC ₂ H ₅ , 54); 127 (89); 69 (78)	1.05 (t, 3H, J = 7.3 Hz, CH ₂ -CH ₃); 1.31 (t, 3H, J = 6.5 Hz, OCH ₂ -CH ₃); 2.32 (q, 2H, J = 7.3 Hz, CH ₂ -CH ₃); 2.90 (q, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 3.60 (t, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 4.22 (q, 2H, J = 6.5 Hz, OCH ₂ -CH ₃); 5.92 (t, 1H, J = 6.5 Hz, 3-H _{vinyl})
5d	78	3.4 : 1	C ₈ H ₁₃ ClO ₂ (176.7)	(<i>E</i>)-isomer 176.0605	176.0615	176 (M^+ , 0.2); 135 (50); 117 (M^+ - O-C ₃ H ₇ -i, 100); 84 (32); 69 (77)	1.7 [d, 6H, J = 6.0 Hz, CH(CH ₃) ₂]; 2.67 (m, 2H, CH ₂ -CH ₂ -Cl); 3.62 (t, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 5.07 [m, 1H, CH(CH ₃) ₂]; 5.90 (d, 1H, J = 15.8 Hz, 2-H _{vinyl}); 6.90 (dt, 1H, J = 15.8 and 6.6 Hz, 3-H _{vinyl})
				(<i>Z</i>)-isomer —	—	—	1.27 [d, 6H, J = 6.6 Hz, CH(CH ₃) ₂]; 3.13 (m, 2H, CH ₂ -CH ₂ -Cl); 3.64 (t, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 5.07 [m, 1H, CH(CH ₃) ₂]; 5.88 (d, 1H, J = 11.2 Hz, 2-H _{vinyl}); 6.29 (dt, 1H, J = 11.2 and 7.3 Hz, 3-H _{vinyl})
5e	63	(<i>E</i>)-isomer only	C ₉ H ₁₅ ClO ₂ (190.7)	(<i>E</i>)-isomer 117.0107 ^c	117.0132	175 (M^+ - CH ₃ , 1.2); 117 (M^+ - O-C ₄ H ₉ -t, 65); 127 (3); 99 (31); 93 (54); 69 (60); 57 (100)	1.49 [s, 9H, C(CH ₃) ₃]; 2.66 (m, 2H, CH ₂ -CH ₂ -Cl); 3.63 (t, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 5.85 (d, 1H, J = 15.2 Hz, 2-H _{vinyl}); 6.81 (dt, 1H, J = 15.2 and 6.59 Hz, 3-H _{vinyl})
5f	97	1.9 : 1	C ₁₃ H ₁₅ ClO ₂ (238.7)	(<i>E</i>)-isomer 238.0761	238.0768	207 (M^+ - OCH ₃ , 9); 203 (M^+ - Cl, 6); 178 (22); 143 (49); 91 (28); 69 (100); 58 (59)	2.74 (q, 2H, J = 7.3 Hz, CH ₂ -CH ₂ -Cl); 3.59 (t, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 3.71 (s, 5H, CH ₂ -C ₆ H ₅ + OCH ₃); 6.93 (t, 1H, 3-H _{vinyl}); 7.15-7.29 (m, 5H _{arom})
				(<i>Z</i>)-isomer 238.0761	238.0775	207 (M^+ - OCH ₃ , 4); 203 (M^+ - Cl, 3); 178 (11); 143 (31); 91 (18); 69 (100); 58 (40)	2.96 (q, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 3.60 (t, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 3.68 (s, 5H, CH ₂ -C ₆ H ₅ + OCH ₃); 6.00 (t, 1H, 3-H _{vinyl}); 7.19-7.28 (m, 5H _{arom})
6a	74	2.3 : 1	C ₅ H ₆ ClN (115.6)	(<i>E</i>)-isomer —	—	—	2.70 (q, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 3.62 (t, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 5.49 (d, 1H, J = 16.5, 2-H _{vinyl}); 6.72 (dt, 1H, J = 16.5 and 6.6 Hz, 3-H _{vinyl})
				(<i>Z</i>)-isomer 115.0189	115.0208	115 (M^+ , 12); 88 (M^+ - HCN, 4); 80 (M^+ - Cl, 100); 79 (M^+ - HCl, 15); 69 (56); 62 (97)	2.90 (m, 2H, CH ₂ -CH ₂ -Cl); 3.66 (t, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 5.46 (d, 1H, J = 11.2 Hz, 2-H _{vinyl}); 6.59 (dt, 1H, J = 11.2 and 7.3 Hz, 3-H _{vinyl})
6b	76	1.1 : 1	C ₆ H ₈ ClN (129.6)	(<i>E</i>)-isomer 129.0346	129.0370	129 (M^+ , 34); 94 (M^+ - Cl, 79); 80 (100); 69 (44)	1.92 (s, 3H, CH ₃); 2.66 (q, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 3.60 (t, 2H, J = 6.6 Hz, CH ₂ -CH ₂ -Cl); 6.37 (t, 1H, J = 6.6 Hz, 3-H _{vinyl})

Table. (continued)

Product	Yield [%]	(E/Z)-ratio	Molecular Formula ^a	Exact mass spectrum (M ⁺)		M.S. (70 eV), <i>m/e</i> (relative intensity, %)	¹ H-N.M.R. (CDCl ₃ /TMS) δ [ppm]
				calc.	found		
6c	93	1:1.3	C ₇ H ₁₀ ClN (143.6)	(Z)-isomer 129.0346	129.0367	129 (M ⁺ , 34); 94 (M ⁺ - Cl, 100); 80 (87); 69 (46)	1.99 (s, 3H, CH ₃); 2.81 (m, 2H, CH ₂ -CH ₂ -Cl); 3.61 (t, 2H, <i>J</i> = 6.0 Hz, CH ₂ -CH ₂ -Cl); 6.24 (m, 1H, 3-H _{vinyl})
				(E)-isomer 143.0502	143.0517	143 (M ⁺ , 44); 108 (M ⁺ - Cl, 100); 94 (63); 80 (81); 69 (65)	1.17 (t, 3H, <i>J</i> = 7.9 Hz, CH ₂ -CH ₃); 2.27 (q, 2H, <i>J</i> = 7.9 Hz, CH ₂ -CH ₃); 2.67 (m, 2H, CH ₂ -CH ₂ -Cl); 3.59 (t, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 6.32 (t, 1H, <i>J</i> = 7.3 Hz, 3-H _{vinyl})
				(Z)-isomer 143.0502	143.0513	143 (M ⁺ , 35); 108 (M ⁺ - Cl, 82); 94 (53); 80 (55); 69 (100)	1.16 (t, 3H, <i>J</i> = 7.3 Hz, CH ₂ -CH ₃); 2.29 (q, 2H, <i>J</i> = 7.3 Hz, CH ₂ -CH ₃); 2.83 (m, 2H, CH ₂ -CH ₂ -Cl); 3.62 (t, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 6.23 (t, 1H, <i>J</i> = 7.3 Hz, 3-H _{vinyl})
6d	98	1:3.7	C ₈ H ₁₂ ClN (157.6)	(E)-isomer 157.0659	157.0673	157 (M ⁺ , 15); 131 (M ⁺ - CN, 25); 122 (M ⁺ - Cl, 9); 108 (31); 94 (47); 80 (69); 69 (100)	1.15 [d, 6H, <i>J</i> = 6.6 Hz, CH(CH ₃) ₂]; 2.12 [m, 1H, CH(CH ₃) ₂]; 2.69 (q, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 3.58 (t, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 6.23 (t, 1H, <i>J</i> = 7.3 Hz, 3-H _{vinyl})
				(Z)-isomer 157.0659	157.0673	157 (M ⁺ , 23); 137 (M ⁺ - CN, 34); 122 (M ⁺ - Cl, 15); 108 (49); 94 (65); 80 (100); 69 (61)	1.16 [d, 6H, <i>J</i> = 7.3 Hz, CH(CH ₃) ₂]; 2.14 [m, 1H, CH(CH ₃) ₂]; 2.82 (m, 2H, CH ₂ -CH ₂ -Cl); 3.61 (t, 2H, CH ₂ -CH ₂ -Cl); 6.22 (t, 1H, <i>J</i> = 7.3 Hz, 3-H _{vinyl})
6e	93	1:1.8	C ₁₁ H ₁₈ ClN (199.7)	(E)-isomer 199.1129	199.1121	199 (M ⁺ , 0.5); 164 (M ⁺ - Cl, 17); 131 (23); 94 (31); 80 (20); 69 (100)	0.89 (t, 3H, <i>J</i> = 7.3 Hz, CH ₃); 1.3-1.6 [m, 8H, (CH ₂) ₄ -CH ₃]; 2.22 [m, 2H, CH ₂ -(CH ₂) ₄ -CH ₃]; 2.66 (q, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 3.5-3.55 (m, 2H, CH ₂ -CH ₂ -Cl); 6.34 (t, 1H, <i>J</i> = 7.3 Hz, 3-H _{vinyl})
				(Z)-isomer 199.1129	199.1119	199 (M ⁺ , 0.5); 164 (M ⁺ - Cl, 43); 131 (30); 94 (50); 80 (33); 69 (100)	0.89 (t, 3H, <i>J</i> = 7.3 Hz, CH ₃); 1.3-1.6 [m, 8H, (CH ₂) ₄ -CH ₃]; 2.24 [t, 2H, <i>J</i> = 7.3 Hz, CH ₂ -(CH ₂) ₄ -CH ₃]; 2.82 (m, 2H, CH ₂ -CH ₂ -Cl); 3.61 (t, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 6.21 (t, 1H, <i>J</i> = 7.3 Hz, 3-H _{vinyl})
6f	96	1.3:1	C ₁₂ H ₁₂ ClN (205.7)	(E)-isomer 205.0659	205.0665	205 (M ⁺ , 23); 170 (M ⁺ - Cl, 33); 156 (8); 142 (34); 91 (56); 78 (81); 69 (100)	2.78 (m, 2H, CH ₂ -CH ₂ -Cl); 3.58 (s, 2H, CH ₂ -C ₆ H ₅); 3.61 (t, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 6.47 (m, 1H, 3-H _{vinyl}); 7.20-7.37 (m, 5H _{arom})
				(Z)-isomer 205.0659	205.0665	205 (M ⁺ , 37); 170 (M ⁺ - Cl, 23); 156 (16); 142 (90); 91 (76); 78 (17); 69 (100)	2.84 (m, 2H, CH ₂ -CH ₂ -Cl); 3.55 (s, 2H, CH ₂ -C ₆ H ₅); 3.61 (t, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 6.26 (m, 1H, 3-H _{vinyl}); 7.20-7.37 (m, 5H _{arom})
6g	73	1:5.9	C ₉ H ₁₄ ClNO (187.7)	(E)-isomer —	—	—	1.38 [s, 9H, OC(CH ₃) ₃]; 2.76 (q, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 3.61 (t, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 5.96 (t, 1H, <i>J</i> = 7.9 Hz, 3-H _{vinyl})
				(Z)-isomer ^c 114.0111	114.0089	174 (3); 172 (M ⁺ - CH ₃ , 10); 114 (M ⁺ - O-C ₄ H ₉ -t, 3); 93 (3); 57 (100)	1.42 [s, 9H, OC(CH ₃) ₂]; 2.69 (q, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 3.66 (t, 2H, <i>J</i> = 6.6 Hz, CH ₂ -CH ₂ -Cl); 5.83 (t, 1H, <i>J</i> = 7.9 Hz, 3-H _{vinyl})

^a Satisfactory microanalyses obtained: C ± 0.15, H ± 0.04.^b No M⁺ was found, the value calculated is for M⁺ - CH₃.^c No M⁺ was found, the value calculated is for M⁺ - OC₄H₉-t.

Methyl 5-Chloro-2-benzyl-2-pentenoate (5f); Typical Procedure:

To a solution of methyl 3-phenyl-2-(diethylphosphinyl)propanoate (**1f**; 1.94 g, 6.49 mmol) in anhydrous tetrahydrofuran (50 ml) at -23°C is added a 1.55 molar solution of *n*-butyllithium in hexane (3.5 ml, 5.43 mmol). The mixture is stirred for 1 h and freshly distilled β -chloropropionaldehyde (**3**; 1 ml, ~ 10 mmol) is added. The solution is stirred at -23°C for 1 h and 25°C for 0.5 h, quenched with water (15 ml) and extracted with ether (2×20 ml). The combined organic phase is dried with anhydrous magnesium sulfate, concentrated and chromatographed on a low-pressure liquid chromatograph (LC) using ethyl acetate/hexane (1 : 5) to afford (*Z*)-**5f**; yield: 823 mg (64%), and (*E*)-**5f**; yield: 426 mg (33%) (Table).

Methyl (2Z)-2-Benzyl-2,4-pentadienoate (Z-2;

$\text{R}^1 = \text{CH}_2-\text{C}_6\text{H}_5, \text{R}^2 = \text{COOCH}_3$);

To a solution of (*Z*)-**5f** (131 mg; 0.55 mmol) in anhydrous tetrahydrofuran (2 ml) at 25°C is added 1,5-diazabicyclo[4.3.0]non-5-ene (112 mg, 0.90 mmol) under an argon atmosphere. After 15 min, the mixture is diluted with dichloromethane (40 ml), washed with water (2×20 ml) and dried with anhydrous magnesium sulfate. The crude product is purified by preparative T.L.C. on silica gel (Machery-Nagel) using ethyl acetate/hexane (1 : 5) as eluent; yield: 93 mg (84%).

$\text{C}_{13}\text{H}_{14}\text{O}_2$ Molecular weight from exact M.S.: calc. 202.0994; (202.3) found 202.0997

M.S. (70 eV): m/e (relative intensity, %) = 202 (M^+ , 52); 143 (100); 142 (60); 141 (55); 128 (75); 115 (38); 91 (45).

$^1\text{H-N.M.R.}$ (CDCl_3/TMS): δ = 3.66 (s, 2 H, $\text{CH}_2-\text{C}_6\text{H}_5$); 3.72 (s, 3 H, OCH_3); 5.36 (d, 1 H, $J = 9.9$ Hz, 5- H_{vinyl}); 5.38 (d, 1 H, $J = 17.1$ Hz, 5- H_{vinyl}); 6.39 (d, 1 H, $J = 11.9$ Hz, 3- H_{vinyl}); 7.15–7.35 ppm (m, 6 H, 4- H_{vinyl} + H_{arom}).

Methyl (2E)-2-Benzyl-2,4-pentadienoate (E-2; $\text{R}^1 = \text{CH}_2-\text{C}_6\text{H}_5$, $\text{R}^2 = \text{COOCH}_3$);

This is prepared by repeating the above experiment using (*E*)-**5f** (130 mg, 0.55 mmol); yield: 94 mg (85%).

$\text{C}_{13}\text{H}_{14}\text{O}_2$ Molecular weight from exact M.S.: calc. 202.0994; (202.3) found 202.1011

M.S. (70 eV): m/e (relative intensity, %) = 202 (M^+ , 53); 171 (20); 143 (100); 142 (68); 141 (61); 128 (72); 115 (39); 91 (41).

$^1\text{H-N.M.R.}$ (CDCl_3/TMS): δ = 3.72 (s, 3 H, OCH_3); 3.79 (s, 2 H, $\text{CH}_2-\text{C}_6\text{H}_5$); 5.53 (d, 1 H, $J = 9.9$ Hz, 5- H_{vinyl}); 5.67 (d, 1 H, $J = 17.1$ Hz, 5- H_{vinyl}); 6.79 (m, 1 H, 4- H_{vinyl}); 7.15–7.30 (m, 5 H_{arom}); 7.35 ppm (d, 1 H, $J = 11.9$ Hz, 3- H_{vinyl}).

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