Novel stereoselective synthesis of 1,3-dien-2-yl esters by a palladium-catalysed cross-coupling reaction of (*E*)-α-iodo-α,β-unsaturated esters

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(*E*)-α-Stannyl-α,β-unsaturated esters underwent an iododestannylation reaction to afford (*E*)-α-iodo-α,β-unsaturated esters, which reacted with (*E*)-alkenylzirconium(IV) complexes produced *in situ* by hydrozirconation of terminal alkynes in the presence of $Pd(PPh_3)_4$ to afford stereoselectively a variety of 1,3-dien-2-yl esters in good yields.

Keywords: hydrozirconation, functionalised 1,3-diene, palladium, cross-coupling, iododestannylation, 1,3-dien-2-yl esters

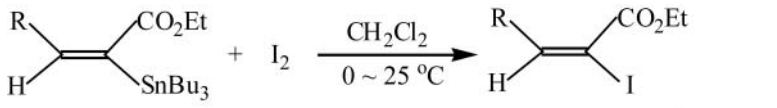
The stereoselective synthesis of conjugated dienes has attracted considerable interest in organic chemistry because of their appearance in a wide variety of biologically active molecules and because they are key synthetic intermediates.[1,2] The synthesis of 1,3-dienes for use in the Diels–Alder reaction is still an important challenge in organic synthesis[3] although other elegant uses of these compounds have been developed.[4] The transition metal-catalysed cross-coupling reactions of stereodefined vinyl halides with vinyl organometallic compounds have provided a straightforward and convenient route for the stereocontrolled synthesis of conjugated dienes.[5,6] Kasatkin and Whitby reported the insertion of 1-lithio-1-halobutadiene into organozirconocenes providing a stereocontrolled synthesis of (*E,Z*)-1,3-dienes.[7] Recently, Molander and Yokoyama reported one-pot stereoselective synthesis of trisubstituted 1,3-dienes via sequential Suzuki–Miyaura cross-coupling with alkenyl- and alkyl-trifluoroborates.[8]

The stereocontrolled synthesis of functionalised 1,3-dienes is also of high interest in organic synthesis.[9] Heteroatom-substituted 1,3-dienes are useful precursors to construct highly functionalised ring systems in Diels–Alder reactions.[10,11] The stereoselective synthesis of 1,3-dienylsilanes,[12–14] 1,3-dienyl sulfides,[15–17] 1,3-dienyl selenides,[18–20] 1,3-dienyl sulfones,[21,22] and 1,3-dienylstannanes[23–25] has already been described in the literature. 2-Alkoxycarbonyl-substituted 1,3-dienes have been extensively studied in recent years as potential starting materials for organic synthesis, in particular for various [4 + 2] cycloadditions. A number of these compounds have proved to be valuable precursors for functionalised alkyl 1-cyclohexene-1-carboxylates,[26] naturally occurring cyclopentanoid terpenic acids,[27] and biologically important litsenolides.[28] Many methods for the synthesis of 2-alkoxycarbonyl-substituted 1,3-dienes have been developed including aldol-type condensation of metallated alkene carboxylates,[27,28] Wittig olefination of aldehydes,[29] titanium(IV) chloride catalysed reaction of 1-ethoxy-3-trimethylsilylprop-1-yne with 1-haloketones,[30] Pd(0)-catalysed coupling of lithium (α-alkoxycarbonyl)alkenyl cuprates with vinyl halides,[31] and the Horner-Emmons reaction of the allylphosphonates with aldehydes.[32] Recently, Aggarwal *et al*. have reported the synthesis of 2-ethoxycarbonyl-substituted 1,3-dienes from aldehydes and ethyl acrylate in the presence of a phosphine and a Lewis acid through a modification of the Morita reaction.[33] Despite considerable methodological differentiation, the reported procedures mostly suffer from some drawbacks such as limited scope,[27,28] scarce availability of substrates,[30–32] moderate yields,[28,29] and low stereoselectivity.[33] We now report that 1,3-dien-2-yl esters can be conveniently synthesised stereoselectively by the palladium-catalysed cross-coupling reaction of (*E*)-α-iodo-α,β-unsaturated esters with (*E*)-alkenylzirconium(IV) complexes produced *in situ* by hydrozirconation of terminal alkynes.

Palladium-catalysed hydrostannylation of alkynyl esters can proceed highly regio- and stereoselectively, affording (*E*)-α-stannyl-α,β-unsaturated esters in high yields.[34] (*E*)-α-Stannyl-α,β-unsaturated esters were subjected to an iododestannylation reaction under mild conditions to afford (*E*)-α-iodo-α,β-unsaturated esters **1** in high yields (Scheme 1).

(*E*)-α-Iodo-α,β-unsaturated esters **1** are difunctional group reagents in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinyl iodides and α,β-unsaturated esters. It is well known that vinyl iodides can undergo a palladium-catalysed cross-coupling reaction with alkenylzirconium(IV) complexes to give 1,3-dienes with retention of configuration.[35] With a convenient route to the (*E*)-α-iodo-α,β-unsaturated esters **1** we decided to investigate the feasibility of using **1** in palladium-catalysed cross-coupling reaction with (*E*)-alkenylzirconium(IV) complexes **2**. We observed that, when the cross-coupling reactions of **1** with a variety of (*E*)-alkenylzirconium(IV) complexes **2** produced *in situ* by hydrozirconation of terminal alkynes were performed in THF at room temperature using $Pd(PPh_3)_4$ as a catalyst (Scheme 2), fairly rapid reactions occurred affording stereoselectively the desired coupled products **3** in good yields. The experimental results are summarised in Table 1.

The 3*E*-configuration of the compounds **3a–k** was established by their ^{1}H NMR spectra which show a doublet at δ = 6.00–6.88 with a coupling constant of 15.6–16.4 Hz, indicating the retention of the *E*-configuration of the starting compounds **2**. In addition, the 1*Z*-configuration of the compound **3c** was confirmed by the NOESY in the ^{1}H NMR spectrum. An enhancement of the allylic protons was observed as the vinylic



1a: R = *n*-C_4H_9, Yield 89%
1b: R = Ph, Yield 87%
1c: R = *n*-C_6H_{13}, Yield 90%

Scheme 1

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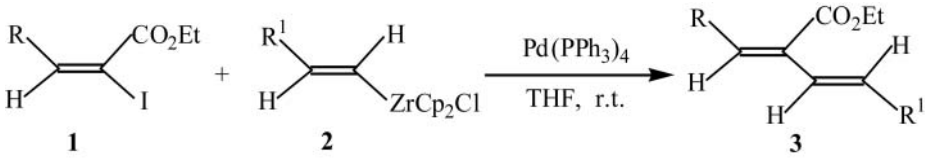

Scheme 2

Table 1 Synthesis of 1,3-dien-2-yl esters (**3a–k**)

Entry	R	R^1	Product	Yield[a]/%
1	*n*-C_4H_9	*n*-C_4H_9	**3a**	78
2	*n*-C_4H_9	Ph	**3b**	83
3	*n*-C_4H_9	CH_3OCH_2	**3c**	72
4	*n*-C_4H_9	*n*-C_6H_{13}	**3d**	80
5	*n*-C_4H_9	$CH_3OCH_2CH_2$	**3e**	84
6	Ph	CH_3OCH_2	**3f**	73
7	Ph	Ph	**3g**	79
8	Ph	*n*-C_4H_9	**3h**	82
9	Ph	*n*-C_6H_{13}	**3i**	78
10	Ph	$CH_3OCH_2CH_2$	**3j**	81
11	*n*-C_6H_{13}	$CH_3OCH_2CH_2$	**3k**	76

[a]Isolated yield based on (*E*)-α-iodo-α,β-unsaturated ester **1** used.

proton (δ = 5.92) of **3c** was irradiated. There was no correlation between the allylic protons (δ = 2.26–2.32) and the vinylic proton (δ = 6.24). The correlation between the vinylic proton (δ = 5.92) and another vinylic proton (δ = 6.24) was observed. The NOE results indicate that **3c** has the expected 1*Z*-configuration and the palladium-catalysed cross-coupling reaction of (*E*)-α-iodo-α,β-unsaturated esters **1** with (*E*)-alkenylzirconium(IV) complexes **2** occurs with the configuration retention of both the starting compounds **1** and the compounds **2**.

In conclusion, a convenient synthetic method for 1,3-dien-2-yl esters has been developed by the palladium-catalysed cross-coupling reactions of (*E*)-α-iodo-α,β-unsaturated esters with (*E*)-alkenylzirconium(IV) complexes. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions, high stereoselectivity, and good yields.

Experimental

IR spectra were obtained using a Perkin-Elmer 683 instrument. ^{1}H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded on a Bruker AC-P400 (100 MHz) spectrometer using $CDCl_3$ as the solvent. Mass spectra were obtained on a Finnigan 8239 mass spectrometer. Microanalyses were obtained using a Perkin-Elmer 240 elemental analyzer. All reactions were carried out in pre-dried glassware (150 °C, 4 h) and cooled under a stream of dry Ar. All solvents were dried, deoxygenated and freshly distilled before use.

Synthesis of (E)-α-iodo-α,β-unsaturated esters **1a–c;** *general procedure*

A solution of iodine (1.7 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise to a solution of (*E*)-α-stannyl-α,β-unsaturated ester (1.5 mmol) in dry CH_2Cl_2 (10 mL) over 30 min at 0 °C under argon. After being stirred for 30 min at 0 °C, the mixture was stirred for 1 h at room temperature and quenched with sat. aq. $Na_2S_2O_3$ (5 mL). The organic layer was washed with sat. aq. $Na_2S_2O_3$ (5 mL) and water (3 × 5 mL) and dried ($MgSO_4$). Removal of the solvent under a reduced pressure gave an oil, which was purified by column chromatography on silica gel (eluent: light petroleum ether/EtOAc, 19:1).

(E)-1-(Ethoxycarbonyl)-1-iodohex-1-ene (**1a**): Oil. IR (film): ν (cm^{-1}) 2959, 1714, 1607, 1465, 1367, 1216; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (t, *J* = 7.6 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 2.49–2.43 (m, 2H), 1.45–1.25 (m, 7H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 156.5, 84.5, 62.2, 33.1, 30.8, 22.2, 14.1, 13.8; MS (EI, 70 eV): *m/z* 282 (M^+, 57), 203 (84), 91 (100). Anal. Calcd for $C_9H_{15}O_2I$: C, 38.30; H, 5.36. Found: C, 38.03; H, 5.17%.

(E)-1-(Ethoxycarbonyl)-1-iodo-2-phenylethene (**1b**)*:* Oil. IR (film): ν (cm^{-1}) 3059, 2981, 1721, 1604, 1575, 1494, 1446, 1369, 1211, 1024, 752, 693; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 1H), 7.35–7.23 (m, 5H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 146.2, 136.5, 128.9, 128.4, 127.9, 84.5, 62.4, 13.7; MS (EI, 70 eV): *m/z* 302 (M^+, 17), 223 (100), 193 (77), 176 (71). Anal. Calcd for $C_{11}H_{11}O_2I$: C, 43.72; H, 3.67. Found: C, 43.89; H, 3.53%.

(E)-1-(Ethoxycarbonyl)-1-iodooct-1-ene (**1c**): Oil. IR (film): ν (cm^{-1}) 2928, 2857, 1715, 1608, 1465, 1368, 1215; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (t, *J* = 7.2 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 2.50–2.42 (m, 2H), 1.46–1.24 (m, 11H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 156.2, 84.5, 62.2, 33.4, 31.5, 28.8, 28.7, 22.6, 14.1, 13.9; MS (EI, 70 eV): *m/z* 310 (M^+, 91), 109 (100). Anal. Calcd for $C_{11}H_{19}O_2I$: C, 42.58; H, 6.17. Found: C, 42.29; H, 6.31%.

Synthesis of 1,3-dien-2-yl esters **3a–k**; *general procedure*

A dry 25 mL round-bottomed flask was charged with $Cp_2Zr(H)Cl$ (1.1 mmol) under argon. THF (4 mL) was injected, followed by addition of the terminal alkyne (1.1 mmol). The mixture was stirred at room temperature for 40 min to yield a clear solution of (*E*)-alkenylzirconium(IV) complex **2.** (*E*)-α-iodo-α,β-unsaturated ester **1** (1 mmol) and $Pd(PPh_3)_4$ (0.05 mmol) were the added and the mixture stirred at room temperature for 12 h. The mixture was diluted with diethyl ether (25 mL) and the diluted mixture was filtered through a short plug of silica gel and concentrated to give a residue, which was purified by column chromatography on silica gel (eluent: light petroleum ether/EtOAc, 19:1).

(5Z,7E)-6-(Ethoxycarbonyl)dodeca-5,7-diene (**3a**): Oil. IR (film): ν (cm^{-1}) 2959, 2931, 2873, 1717, 1650, 1465, 1226, 1120, 696; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.00 (d, *J* = 15.6 Hz, 1H), 5.75 (t, *J* = 7.6 Hz, 1H), 5.68 (dt, *J* = 15.6, 7.2 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.25–2.20 (m, 2H), 2.10–2.06 (m, 2H), 1.43–1.25 (m, 11H), 0.92–0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 136.2, 133.4, 131.8, 127.8, 60.5, 32.6, 31.4, 31.3, 29.3, 22.3, 22.2, 14.3, 13.9; MS (EI, 70 eV): *m/z* 238 (M^+, 6.4), 209 (22), 149 (100), 85 (61), 57 (82). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.31; H, 10.76%.

(1E,3Z)-1-Phenyl-3-(ethoxycarbonyl)octa-1,3-diene (**3b**): Oil. IR (film): ν (cm^{-1}) 3131, 2958, 2929, 2871, 1718, 1619, 1452, 1227, 1096, 698; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.20 (m, 5H), 6.74 (d, *J* = 16.4 Hz, 1H), 6.58 (d, *J* = 16.4 Hz, 1H), 6.02 (t, *J* = 7.6 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 2.35–2.29 (m, 2H), 1.49–1.22 (m, 7H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 139.3, 137.2, 133.5, 129.3, 128.6, 127.5, 126.9, 126.4, 60.7, 31.4, 29.7, 22.4, 14.4, 13.9; MS (EI, 70 eV): *m/z* 258 (M^+, 33), 229 (15), 201 (28), 105 (100), 77 (61). Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.85; H, 8.31%.

(2E,4Z)-1-Methoxy-4-(ethoxycarbonyl)nona-2,4-diene (**3c**): Oil. IR (film): ν (cm^{-1}) 3064, 2929, 1713, 1450, 1402, 1198, 1095, 698; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.24 (d, *J* = 16.0 Hz, 1H), 5.92 (t, *J* = 7.6 Hz, 1H), 5.80 (dt, *J* = 16.0, 5.2 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.97 (d, *J* = 5.2 Hz, 2H), 3.34 (s, 3H), 2.32–2.26 (m, 2H), 1.43–1.25 (m, 7H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 139.7, 132.4, 130.3, 126.6, 72.8, 60.6, 58.0, 31.3, 29.4, 22.3, 14.3, 13.8; MS (EI, 70 eV): *m/z* 226 (M^+, 17), 197 (65), 73 (100), 57 (95). Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.71; H, 9.68%.

(5Z,7E)-6-(Ethoxycarbonyl)tetradeca-5,7-diene (**3d**): Oil. IR (film): ν (cm^{-1}) 2928, 1727, 1606, 1464, 1378, 1156, 962, 862; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.02 (d, *J* = 16.0 Hz, 1H), 5.77 (t, *J* = 7.6 Hz, 1H), 5.69 (dt, *J* = 16.0, 7.6 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 2.27–2.20 (m, 2H), 2.13–2.06 (m, 2H), 1.45–1.21 (m, 15H), 0.91–0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 136.1, 133.6, 131.9,

127.7, 60.5, 32.9, 31.7, 31.4, 29.3, 29.1, 28.9, 22.6, 22.3, 14.3, 14.1, 13.9; MS (EI, 70 eV): *m/z* 266 (M^+, 100), 221 (45), 177 (20). Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.37; H, 11.09%.

(3E,5Z)-1-Methoxy-5-(ethoxycarbonyl)deca-3,5-diene (**3e**): Oil. IR (film): *v* (cm^{-1}) 2929, 1725, 1464, 1380, 1155, 1121, 964; ^1H NMR (400 MHz, $CDCl_3$): δ 6.08 (d, *J* = 15.6 Hz, 1H), 5.81 (t, *J* = 7.6 Hz, 1H), 5.69 (dt, *J* = 15.6, 7.6 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.43 (t, *J* = 6.8 Hz, 2H), 3.34 (s, 3H), 2.40–2.34 (m, 2H), 2.27–2.22 (m, 2H), 1.43–1.27 (m, 7H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 137.5, 133.1, 129.7, 127.5, 72.1, 60.5, 58.6, 33.3, 31.4, 29.3, 22.3, 14.3, 13.9; MS (EI, 70 eV): *m/z* 240 (M^+, 55), 221 (45), 209 (26), 194 (100). Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.72; H, 10.19%.

(1Z,3E)-1-Phenyl-2-(ethoxycarbonyl)-5-methoxypenta-1,3-diene (**3f**): Oil. IR (film): *v* (cm^{-1}) 3065, 2959, 2873, 1717, 1619, 1466, 1380, 1153, 1096, 965, 893, 792; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35–7.26 (m, 5H), 6.63 (s, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 5.86 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.04 (d, *J* = 5.6 Hz, 2H), 3.37 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 135.3, 133.4, 132.7, 130.5, 128.7, 128.5, 128.3, 128.2, 72.6, 61.3, 58.2, 13.9; MS (EI, 70 eV): *m/z* 246 (M^+, 12), 202 (48), 115 (64), 105 (100), 77 (63). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.87; H, 7.22%.

(1Z,3E)-1,4-Diphenyl-2-(ethoxycarbonyl)buta-1,3-diene (**3g**): Oil. IR (film): *v* (cm^{-1}) 3073, 2934, 2863, 1721, 1565, 1201, 1095, 967, 804; ^1H NMR (400 MHz, $CDCl_3$): δ 7.45–7.24 (m, 10H), 6.88 (d, *J* = 16.4 Hz, 1H), 6.75 (s, 1H), 6.64 (d, *J* = 16.4 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 137.5, 136.7, 135.6, 134.3, 132.7, 131.1, 130.2, 128.7, 128.5, 128.3, 128.0, 126.7, 61.5, 14.4; MS (EI, 70 eV): *m/z* 278 (M^+, 24), 205 (100), 202 (37), 105 (82), 77 (25). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.72; H, 6.38%.

(1Z,3E)-1-Phenyl-2-(ethoxycarbonyl)octa-1,3-diene (**3h**): Oil. IR (filmt): *v* (cm^{-1}) 3067, 2927, 2854, 1716, 1494, 1451, 1094, 1027, 963, 756, 697; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37–7.22 (m, 5H), 6.51 (s, 1H), 6.16 (d, *J* = 16.0 Hz, 1H), 5.80 (dt, *J* = 16.0, 7.2 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.20–2.13 (m, 2H), 1.45–1.25 (m, 4H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 135.7, 134.5, 134.2, 130.1, 128.7, 128.4, 128.1, 127.9, 61.2, 32.7, 31.2, 22.3, 14.0, 13.9; MS (EI, 70 eV): *m/z* 258 (M^+, 2.4), 229 (15), 205 (35), 105 (100), 77 (44). Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.26; H, 8.35%.

*(1Z,3E)-1-Phenyl-2-(ethoxycarbonyl)deca-1,3-diene (**3i**):* Oil. IR (film): *v* (cm^{-1}) 3059, 2924, 1728, 1637, 1598, 1574, 1447, 1149, 1022, 960, 696; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.23 (m, 5H), 6.51 (s, 1H), 6.16 (d, *J* = 15.6 Hz, 1H), 5.80 (dt, *J* = 15.6, 7.2 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.18–2.12 (m, 2H), 1.44–1.38 (m, 2H), 1.33–1.25 (m, 6H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 135.7, 134.5, 134.3, 130.1, 128.7, 128.4, 128.1, 127.9, 61.1, 33.0, 31.7, 29.0, 28.9, 22.6, 14.1, 13.9; MS (EI, 70 eV): *m/z* 286 (M^+, 100), 241 (43), 159 (46), 143 (82), 129 (97). Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.40; H, 9.29%.

*(1Z,3E)-1-Phenyl-2-(ethoxycarbonyl)-6-methoxyhexa-1,3-diene (**3j**):* Oil. IR (film): *v* (cm^{-1}) 2928, 1725, 1448, 1381, 1225, 1147, 1118, 961, 753, 696; ^1H NMR (400 MHz, $CDCl_3$): 7.32–7.21 (m, 5H), 6.55 (s, 1H), 6.23 (d, *J* = 16.0 Hz, 1H), 5.80 (dt, *J* = 16.0, 7.2 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.46 (t, *J* = 6.8 Hz, 2H), 3.35 (s, 3H), 2.47–2.41 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 135.6, 134.1, 131.1, 131.0, 130.5, 129.9, 128.4, 128.1, 71.8, 61.2, 58.7, 33.4, 13.9; MS (EI, 70 eV): *m/z* 260 (M^+, 42), 215 (25), 201 (44), 169 (58), 155 (89), 159 (46), 141 (100), 128 (64). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.56; H, 7.49%.

*(3E,5Z)-1-Methoxy-5-(ethoxycarbonyl)dodeca-3,5-diene (**3k**):* Oil. IR (film): *v* (cm^{-1}) 2928, 2857, 1726, 1462, 1380, 1189, 1153, 1121, 963; ^1H NMR (400 MHz, $CDCl_3$): δ 6.08 (d, *J* = 15.6 Hz, 1H), 5.81 (t, *J* = 7.6 Hz, 1H), 5.69 (dt, *J* = 15.6, 7.6 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.43 (t, *J* = 6.8 Hz, 2H), 3.34 (s, 3H), 2.40–2.33 (m, 2H), 2.26–2.21 (m, 2H), 1.44–1.26 (m, 11H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 137.6, 133.1, 129.7, 127.5, 72.1, 60.6, 58.6, 33.3, 31.7, 29.7, 29.2, 29.0, 22.6, 14.3, 13.9; MS (EI, 70 eV): *m/z* 268 (M^+, 51), 237 (35), 222 (100). Anal. Calcd for $C_{16}H_{28}O_3$: C, 71.60; H, 10.52. Found: C, 71.37; H, 10.29%.

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