Supporting information:

Procedure for allylic alkylation of *cis*-1,4-diacetoxy-2-butene (8) using $[(C_3H_5)PdCl]_2$ and a monodentate phosphine ligand as catalyst.

To an evacuated round bottomed flask containing stirring bead, $[(C_3H_5)PdCl]_2$**,** (12.0 mg, 3.28 x 10^{-5} mol, 2.5 mol%) and Cy_3P (36.8 mg, 1.31 x 10^{-4} mol, 10 mol %) was added dry THF (1.5 ml). The flask was then flushed with nitrogen. This was stirred for a few minutes, before the addition of *cis*-1,4-diacetoxy-2-butene (0.210 ml, 216 mg, 13.12 x 10^{-4} mol) and the sodium dimethylmalonate solution (13.52 x 10^{-4} mol, 4.2 ml of 0.328M soln in THF, 1.02 equiv.). The reaction was then stirred at the desired temperature until conversion was complete as judged by T.L.C.. Solvent was then removed. The ratio of branched to linear products and E /Z isomers was determined by G.C. (Supelco (60 m)β-cyclodextrin column), and by crude NMR of the reaction mixture. When Cy_3P was used as ligand, it was just possible to separate the branched (major) product from the linear one by careful chromatography using 20% Et_2O / hexane as eluant. The linear product is a mixture of *cis* and *trans* isomers which are inseparable by simple methods.

(*E*) and (*Z*) Methyl-6-acetoxy-2-(methoxycarbonyl)-hex-4-enoate (10)

$\upsilon_{max.}$/ cm^{-1} (neat) 3634, 3466, 2956, 1729, 1437, 1366, 2344, 1240, 1158, 1028. ^1H NMR (270 MHz, $CDCl_3$, 20 °C): 2.03 (3H, s, C(=O)C**H**$_3$-*trans*), 2.04 (3H, s, C(=O)C**H**$_3$-*cis*), 2.63 (2H, t, app., ^3J = 6.5 Hz, =CHC**H$_2$**-*trans*), 2.69 (2H, t,app., ^3J = 7.2 Hz-*cis*), 3.44 (1H, m, CH_2C**H**-*cis* and *trans*), 3.72 (6H, s, CH(CO_2**Me**)$_2$-*trans*),

3.73 (6H, s, CH(CO_2**Me**)$_2$-*cis*), 4.47 (2H, d, ^{3}J = 5.0Hz, AcOC**H$_2$**-*trans*), 4.62 (2H,d, ^{3}J = 6.4 Hz, AcOC**H$_2$**-*cis*), 5.55-5.75 (2H, m, C**H=CH**-*cis* and *trans*). ^{13}C NMR (67.9 MHz, $CDCl_3$): 21.36 (CH_3-*cis* and *trans*), 27.32 (CH_2-*cis*), 31.82 (CH_2-*trans*), 51.64 (CH-*cis* and *trans*), 52.94 (CH_3-*trans*), 53.00 (CH_3-*cis*), 60.35 (CH_2-*cis*), 64.81 (CH_2-*trans*), 126.97 (=CH-*cis*), 127.47 (=CH-*trans*), 129.77 (=CH-*cis*), 130.85 (=CH-*trans*), 169.16 (CO_2Me)$_2$-*trans*), 169.20 (CO_2Me)$_2$-*cis*), 170.79 (CH_3CO_2R-*cis*), 170.93 (CH_3CO_2R-*trans*). MS. (C.I.+; m/z) 245(10) [MH+], 185 (100), 171 (10).

Methyl-3-(acetoxymethyl)-2-(methoxycarbonyl)pent-4-enoate (9)

$\upsilon_{max.}$/ cm^{-1} (neat) 3640, 3469, 3083, 2956, 1739, 1643, 1436, 1224, 1040, 931. ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): 2.00 (3H, s, C(=O)C**H$_3$**), 3.13 (1H, m, =CHC**H**CH), 3.54 (1H, d, ^{3}J = 8.2 Hz, =CHCHC**H**), 3.68 (3H, s, CO_2C**H$_3$**), 3.71 (3H, s, CO_2C**H$_3$**), 4.07 (1H, dd, ^{3}J = 11.3, 6.0 Hz, HC**H**OAc), 4.20 (1H, dd, ^{3}J = 11.1, 5.9 Hz, **H**CHOAc), 5.14 (2H, tm [app.], **H$_2$**C=), 5.75 (1H, ddd, ^{3}J = 8.8, 10.2, 17.3 Hz, H_2C=C**H**). ^{13}C NMR (67.9 MHz, $CDCl_3$): 21.18 (CH_3), 43.130 (CH), 52.83 (CH_3), 52.97 (CH_3), 53.40 (CH), 65.00 (CH_2), 119.16 (=CH_2), 134.46 (=CH), 168.15 (**C**O_2Me), 168.31 (**C**O_2Me), 170.69 (O**C**(=O)Me). MS. (F.A.B.+; m/z) 267 (15), 245(50) [MH+], 185 (100), 171 (10). $C_{10}H_{17}O_6$, (MH $^+$) requires 245.1025, Found: 245.1015.

The following compounds were prepared by using a similar procedure to that described above but using 1.5 equivalents of sodium dimethyl malonate nucleophile.

The ratio between products **(2)** and **(3)** was determined using G. C. (Supelco (60 m)β-cyclodextrin column, 70 °C (10 mins)- 150 °C (@ 10 °C min^{-1}) Under these conditions the branched product, the starting material, and both E and Z isomers of the linear product showed up as separate signals. This ratio could also be checked by the crude NMR of the products (see below).

Methyl-2-(methoxycarbonyl)-3-methyl-4-pentenoate (2)

$\upsilon_{max.}$/ cm^{-1} (thin film) 2956, 1737, 1644, 1566, 1436, 1268, 1199, 1154; ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): 1.03 (3H, d, ^{3}J = 6.8 Hz, CHC**H**$_3$), 2.89 (1H, hex (app) C**H**Me), 3.24 (1H, d, ^{3}J = 9.0 Hz, C**H**CH), 3.66 (3H, s, CO_2**Me**), 3.67 (3H, s, CO_2**Me**), 4.99 (2H, ddm, =C**H**$_2$), 5.70 (1H, ddd, =C**H**). ^{13}C NMR (67.9 MHz, $CDCl_3$): 18.38 (CH_3), 38.51 (CH), 52.69 (CH_3), 52.78 (CH_3), 57.89 (CH), 115.76 (CH_2), 139.80 (CH), 168.75 (CO_2Me), 168.81 (CO_2Me).

Methyl-(E)-2-(methoxycarbonyl)-4-hexenoate (3)

^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): 1.56 (3H, dd, C**H**$_3$CH), 2.50 (2H,dd, ^{3}J = 6.7, 7.5 Hz, CHC**H**$_2$), 3.34 (1H, t, ^{3}J = 7.7Hz, CH_2C**H**), 3.64 (6H, s, CO_2Me), 5.30 (1H, m, =C**H**), 5.49 (1H, m, =C**H**). ^{13}C NMR (67.9 MHz, $CDCl_3$): 30.11 (CH_3), 32.31 (CH), 38.51 (CH), 52.32 (CH_3), 126.47 (=CH), 128.76 (=CH), 169.57 (CO_2Me).

Compound **(12)** was determined to be pure by NMR alone. In our previous work[11], we had observed both isomers in ratios of 10:1 and 15:1 using palladium and platinum dppe based catalysts. NMR data for both isomers is given in reference 19.

Methyl-2-(carbomethoxy)-3-methyl-5-phenyl pent-4-enoate (12)

$\upsilon_{max.}$ cm^{-1} (thin film) 3026, 2953, 1738, 1598, 1578, 1494, 1435, 1246, 1194, 1158, 1023, 969; ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): 1.10 (3H, d, ^{3}J = 6.8Hz, CHC**H$_3$**), 3.0-3.1 (1H, m, C**H** CH_3), 3.23 (1H, d, ^{3}J = 7.9 Hz, CHC**H**), 3.58 (1H, s, CO_2**Me**), 3.61 (1H, s, CO_2**Me**), 6.04, (1H, dd, ^{3}J = 8.4, 15.8, =C**H**), 6.36 (1H, d, ^{3}J = 15.9 Hz, =C**H**), 7.1 (5H, m, Ar**H**). ^{13}C NMR (67.9 MHz, $CDCl_3$): 18.37 (CH_3), 37.62 (CH), 52.22 (CH_3), 52.30 (CH_3), 57.70 (CH), 126.16, 127.28, 127.65, 128.39, 130.71, 131.09 (ArCH & =CH), 137.0 (ArC-), 168.50 (C=O). MS. (E. I. m/z) 262 (10) [M+], 202 (20), 143 (55), 131 (100). $C_{15}H_{18}O_4$ requires: 262.1205, Found: 262.1201.