A New Reactivity Pattern for Vinyl Bromides; *Cine*-Substitution *via* Palladium Catalysed C-N Coupling/Michael Addition Reactions

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Electronic Supplementary Information

General Experimental

^{1}H NMR spectra were recorded on JEOL 400 EX or Bruker AM-300 spectrometers at 400 MHz and 300 MHz respectively. Residual protic solvent $CHCl_3$ (δ_H = 7.26 ppm) or TMS (δ_H = 0 ppm) were used as internal references. Coupling constants were measured in Hz. ^{13}C spectra were recorded in $CDCl_3$, unless otherwise stated, at 100 MHz or 75 MHz on JEOL 400 EX and Bruker AM-300 spectrometers respectively, using the resonance of $CDCl_3$ (δ_C = t, 77 ppm) as the internal reference. Infra red spectra were recorded in the range of 4000-600 cm^{-1} on a Perkin Elmer FT 1000 spectrometer with internal calibration. Mass spectra were carried out at the University of Wales Swansea (Finnigan MAT 900 XLT instrument).

Analytical thin layer chromatography was carried out using glass backed plates coated with Merck Kieselgel 60 GF_{254} or aluminium backed plates coated with Merck G/UV_{254}. Plates were visualised under UV light (at 254 nm) or by staining with potassium permanganate, vanillin or cerium ammonium molybdate followed by heating. Flash chromatography was carried out using either Merck 60 H silica or Merck Florisil®. Samples were pre-absorbed on silica or used as saturated solutions in an appropriate solvent.

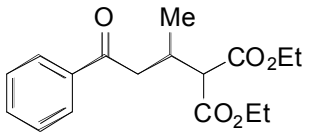
All the reactions were performed under a positive pressure of nitrogen or argon in oven or flame dried apparatus.

General procedure for the addition of α-bromostyrene to alkylidene malonates

A flask was charged with $Pd(OAc)_2$ (3 mg, 0.01 mmol, 1 mol. %), (*rac*)-BINAP (19 mg , 0.03 mmol, 3 mol. %), toluene (4 ml) under a nitrogen atmosphere and heated to 80°C until the solution became homogeneous (5 mins). The reaction was cooled to room temperature, α-bromostyrene (130 μL, 1.0 mmol), pyrrolidine (85 μL, 1.02 mmol), sodium *tert*-butoxide (106 mg, 1.1 mmol) were added, and the reaction heated to 80°C for 3 hours. The reaction was cooled to room temperature, alkylidine malonate (1.2-2.0 mmol) in toluene (1 ml) was added and the reaction allowed to stir for 20 hours at room temperature. The reaction was quenched with sat. NH_4Cl (1 ml) and partitioned between EtOAc (20 ml) and H_2O (10 ml). The aqueous phase was extracted

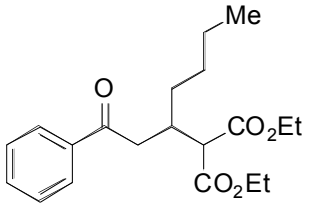
with EtOAc (3 × 10 ml) and the organic portions combined, washed with H_2O (10 ml), sat. NaCl (10 ml), dried over $MgSO_4$ and reduced *in vacuo*. The residue was purified by column chromatography (SiO_2) to produce the desired compound.

2-(1-Methyl-3-oxo-3-phenyl-propyl)-malonic acid diethyl ester (Table 1, entry 2)



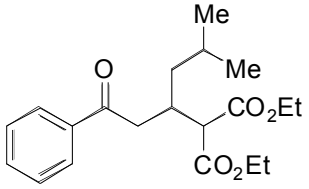
General procedure using 1.2 equivalents of alkylidene malonate gave the product as a yellow oil (283 mg, 92 %). Data in accordance with that in the literature.[1]

2-[1-(2-Oxo-2-phenyl-ethyl)-pentyl]-malonic acid diethyl ester (Table 1, entry 3)



General procedure using 1.2 equivalents of alkylidene malonate gave the product as a light yellow oil (303 mg, 87 %). ν_{max} (NaCl)/cm^{-1} 1688, 1724, 1744; δ_H ($CDCl_3$, 300 MHz) 7.98 (2 H, d, *J* 7.3, Ar), 7.55 (1 H, t, *J* 7.3, Ar), 7.45 (2 H, t, *J* 7.3, Ar), 4.19 (2 H, q, *J* 7.2, OC*H*$_2$CH$_3$), 4.17 (2 H, q, *J* 7.2, OC*H*$_2$CH$_3$), 3.65 (1 H, d, *J* 5.5, C*H*CO$_2$), 3.31 (1 H, dd, *J* 5.2, 17.4, C(O)C*H*$_a$H$_b$), 3.05 (1 H, dd, *J* 7.2, 17.4, C(O)CH$_a$*H*$_b$), 2.94-2.83 (1 H, m, C*H*CHCO$_2$), 1.50-1.43 (2 H, m, C*H*$_2$), 1.32-1.25 (4 H, m, C*H*$_2$), 1.26 (3 H, t, *J* 7.1, OCH$_2$*CH*$_3$), 1.23 (3 H, t, *J* 7.1, OCH$_2$*CH*$_3$), 0.86 (3 H, t, *J* 7.1, CH$_2$CH$_2$C*H*$_3$); δ_C ($CDCl_3$, 100 MHz) 199.0, 169.0, 168.9, 137.1, 133.0, 128.6 (2 × C), 128.1(2 × C), 61.3, 61.2, 54.2, 40.3, 33.0, 31.8, 29.2, 22.6, 14.1, 14.0, 13.9; *m/z* (CI) 349 (100 %, MH$^+$), 246 (15 %, MH$^+$-HCO$_2$Et$_2$), 189 (86 %, MH$^+$-H$_2$C(CO$_2$Et)$_2$); HRMS: *m/z* [M+H]$^+$ calc for $C_{20}H_{29}O_5$: 349.2010, found: 349.2007.

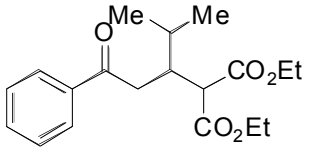
2-[3-Methyl-1-(2-oxo-2-phenyl-ethyl)-butyl]-malonic acid diethyl ester (Table 1, entry 4)



General procedure using 1.2 equivalents of alkylidene malonate gave the product as a yellow oil (285 mg, 83 %). ν_{max}(NaCl)/cm^{-1} 1687, 1734, 1745; δ_H ($CDCl_3$, 300 MHz) 7.98 (2 H, d, *J* 7.3, Ar), 7.56 (1 H, t, *J* 7.3, Ar), 7.46 (2 H, t, *J* 7.3, Ar), 4.20 (2 H, q, *J* 7.2, OC*H*$_2$CH$_3$), 4.16 (2 H, q, *J* 7.2, OC*H*$_2$CH$_3$), 3.66 (1 H, d, *J* 4.7, C*H*CO$_2$), 3.34 (1 H, dd, *J* 5.2, 17.3, C(O)C*H*$_a$H$_b$), 3.09-2.92 (2 H, m, C(O)CH$_a$*H*$_b$), 1.66-1.53 (1 H, m, C*H*(CH$_3$)$_2$), 1.34 (2 H, ddd, *J* 2.7, 2.8, 3.3, C*H*$_2$CH(CH$_3$)$_2$), 1.27 (3 H, t, *J* 5.5, OCH$_2$*CH*$_3$), 1.22 (3 H, t, *J* 5.5, OCH$_2$*CH*$_3$), 0.91 (3 H, d, *J* 3.8, CH*CH*$_3$), 0.89 (3 H, d, *J* 3.7, CH*CH*$_3$); δ_C ($CDCl_3$, 100 MHz) 199.0, 169.1, 168.9, 137.1, 133.0, 128.6 (2 × C), 128.0 (2 × C), 61.3, 61.2, 54.1, 41.4, 40.4, 31.8, 25.5, 22.7, 22.4, 14.1, 14.0; *m/z* (CI) 349 (100 %, MH$^+$), 246

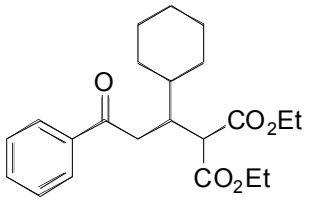
(14 %, MH^+-HCO_2Et_2), 189 (89 %, MH^+-$H_2C(CO_2Et)_2$); HRMS: *m/z* $[M+H]^+$ calc for $C_{20}H_{29}O_5$: 349.2010, found: 349.2010.

2-[2-Methyl-1-(2-oxo-2-phenyl-ethyl)-propyl]-malonic acid diethyl ester (Table 1, entry 5)



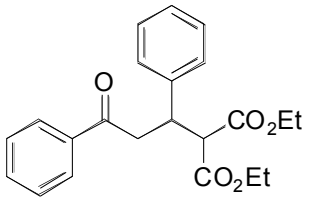
General procedure using 1.5 equivalents of alkylidene malonate gave the product as a yellow oil (261 mg, 78 %). ν_{max}(NaCl)/cm^{-1} 1688, 1728, 1750; δ_H ($CDCl_3$, 300 MHz) 7.98 (2 H, d, *J* 7.3, Ar), 7.54 (1 H, t, *J* 7.3, Ar), 7.45 (2H, t, *J* 7.3, Ar), 4.18-4.08 (4 H, m, 2 × OCH_2CH_3), 3.62 (1 H, d, *J* 6.4, $CHCO_2$), 3.30 (1 H, dd, *J* 5.0, 18.0, C(O)CH_aH_b), 3.08 (1 H, dd, *J* 6.0, 18.0, C(O)CH_aH_b), 3.00-2.92 (1 H, m, $CHCHCO_2$), 1.89-1.73 (1 H, m, $CH(CH_3)_2$), 1.23 (3 H, t, *J* 7.1, OCH_2CH_3), 1.22 (3 H, t, *J* 7.1, OCH_2CH_3), 0.95 (3 H, d, *J* 6.8, $CHCH_3$), 0.88 (3 H, d, *J* 6.8, $CHCH_3$); δ_C ($CDCl_3$, 100 MHz) 198.8, 169.2, 169.0, 137.1, 132.9, 128.5 (2 × C), 128.1 (2 × C), 61.4, 61.2, 53.7, 39.1, 37.9, 30.5, 20.6, 19.3, 14.0 (2 × C); *m/z* (CI) 335 (100 %, MH^+), 175 (58 %, MH^+-$H_2C(CO_2Et)_2$); HRMS: *m/z* $[M+H]^+$ calc for $C_{19}H_{27}O_5$: 335.1853, found: 335.1850.

2-(1-Cyclohexyl-3-oxo-3-phenyl-propyl)-malonic acid diethyl ester (Table 1, entry 6)



General procedure using 2.0 equivalents of alkylidene malonate gave the product as a yellow oil (273 mg, 73 %). ν_{max}(NaCl)/cm^{-1} 1683, 1729, 1749; δ_H ($CDCl_3$, 300 MHz) 7.98 (2 H, d, *J* 7.3, Ar), 7.54 (1 H, t, *J* 7.3, Ar), 7.45 (2 H, t, *J* 7.3, Ar), 4.19-4.09 (4 H, m, 2 × OCH_2CH_3), 3.69 (1 H, d, *J* 5.9, $CHCO_2$), 3.29 (1 H, dd, *J* 4.9, 18.3, C(O)CH_aH_b), 3.15 (1 H, dd, *J* 6.2, 18.3, C(O)CH_aH_b), 2.99-2.91 (1 H, m, $CHCHCO_2$), 1.80-1.54 (4 H, m, Cy), 1.47-1.35 (1 H, m, Cy) 1.26-0.93 (10 H, m, 2 × OCH_2CH_3, Cy); δ_C ($CDCl_3$, 100 MHz) 198.7, 169.5, 169.1, 137.1, 132.9, 128.5 (2 × C), 128.1 (2 × C), 61.4, 61.2, 53.2, 40.7, 38.5, 38.4, 31.0, 30.0, 26.5 (2 × C), 26.3, 14.0 (2 × C); *m/z* (CI) 375 (61 %, MH^+), 215 (61 %, MH^+-$H_2C(CO_2Et)_2$); HRMS: *m/z* $[M+H]^+$ calc for $C_{22}H_{31}O_5$: 375.2166, found: 375.2165.

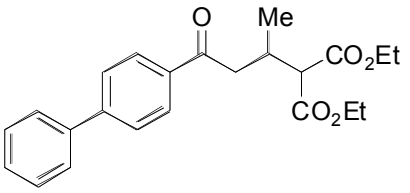
2-(3-Oxo-1,3-diphenyl-propyl)-malonic acid diethyl ester (Table 1, entry 8)



The general procedure using 1.2 equivalentss of alkylidene malonate gave the product as a white solid (328 mg, 89 %). Recrystallisation from EtOAc/Petrol produced data in accordance with that in the literature.[2]

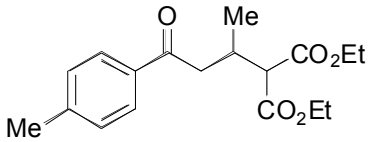
General procedure for the addition of vinyl bromides to diethyl ethylidene malonate
A flask was charged with $Pd(OAc)_2$ (3 mg, 0.01 mmol, 1 mol %), (*rac*)-BINAP (19 mg, 0.03 mmol, 3 mol %), toluene (2 ml) under a nitrogen atmosphere and heated to 80 °C until the solution became homogeneous (5 mins). The reaction was cooled to room temperature and the vinyl bromide (1.0 mmol) was weighed into a vial and added in toluene (1 ml + 1 ml vial wash). Pyrrolidine (85 μL, 1.02 mmol), sodium *tert*-butoxide (106 mg, 1.1 mmol) were added and the reaction heated to 80 °C until vinyl bromide was consumed by TLC. The reaction was cooled to room temperature and diethyl ethylidene malonate (1.2-3.0 mmol) in toluene (1 ml) was added and the reaction allowed to stir for 20 hours. The reaction was quenched with sat. NH_4Cl (1 ml) and partitioned between EtOAc (20 ml) and H_2O (10 ml). The aqueous phase was extracted with EtOAc (3 × 10 ml) and the organic portions combined, washed with H_2O (10 ml), sat. NaCl (10 ml), dried ($MgSO_4$) and reduced *in vacuo*. The residue was purified by column chromatography (SiO_2) to produce the desired compound.

2-(3-Biphenyl-4-yl-1-methyl-3-oxo-propyl)-malonic acid diethyl ester (Table 2, entry 1)



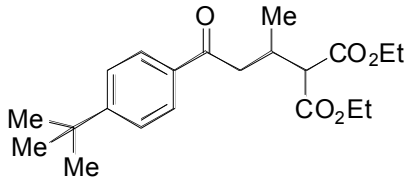
General procedure using 1.7 equivalents of alkylidene malonate gave the product as a white solid (290 mg, 76 %). Recrystallisation from EtOAc/Petrol. ν_{max}(KBr)/cm^{-1} 1679, 1726, 1747; δ_H ($CDCl_3$, 300 MHz) 8.07 (2 H, d, *J* 8.4, Ar), 7.69 (2 H, d, *J* 8.4, Ar), 7.63 (2 H, d, *J* 7.0, Ar), 7.49-7.37 (3 H, m, Ar), 4.27-4.17 (4 H, m, 2 × OC*H*$_2$CH$_3$), 3.49 (1 H, d, *J* 6.4, C*H*CO$_2$), 3.33 (1 H, dd, *J* 3.3, 15.4, C(O)C*H*$_a$H$_b$), 3.07-2.90 (3 H, m, C(O)CH$_a$*H*$_b$C*H*), 1.31-1.24 (6 H, m, 2 × OCH$_2$C*H*$_3$), 1.17 (3 H, d, *J* 6.5, CHC*H*$_3$); δ_C($CDCl_3$, 100 MHz) 198.4, 168.7, 168.6, 145.8, 139.9, 135.7, 128.9 (2 × C), 128.8, 128.2 (2 × C), 127.3 (4 × C), 61.3 (2 × C), 56.6, 42.8, 29.6, 17.8, 14.1 (2 × C); *m*/*z* (EI) 382 (33 %, M$^+$), 337 (43 %, M$^+$-OEt); 308 (28 %, M$^+$-HCO$_2$Et); HRMS: *m*/*z* [M+H]$^+$ calc for $C_{23}H_{27}O_5$: 383.1853, found: 383.1853.

2-(1-Methyl-3-oxo-3-*p*-tolyl-propyl)-malonic acid diethyl ester (Table 2, entry 2)



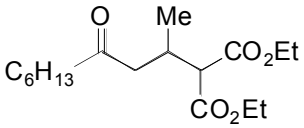
General procedure using 1.5 equivalents of alkylidene malonate gave the product as a yellow oil (260 mg, 81 %). ν_{max}(NaCl)/cm^{-1} 1681, 1730, 1749; δ_H ($CDCl_3$, 300 MHz) 7.89 (2 H, d, *J* 8.2, Ar), 7.26 (2 H, d, *J* 8.2, Ar), 4.21 (2 H, q, *J* 7.1, OC*H*$_2$CH$_3$), 4.20 (2 H, q, *J* 7.1, OC*H*$_2$CH$_3$), 3.47 (1 H, d, *J* 6.5, C*H*CO$_2$), 3.25 (1 H, dd, *J* 3.8, 15.7, C(O)C*H*$_a$H$_b$), 3.03-2.92 (1 H, m, C*H*CHCO$_2$), 2.88 (1 H, dd, *J* 8.6, 15.7, C(O)CH$_a$*H*$_b$), 2.41 (3 H, s, C*H*$_3$Ar), 1.27 (3 H, t, *J* 7.1, OCH$_2$C*H*$_3$), 1.26 (3 H, t, *J* 7.1, OCH$_2$C*H*$_3$), 1.09 (3 H, d, *J* 6.6, CHC*H*$_3$); δ_C($CDCl_3$, 100 MHz) 198.4, 168.7, 168.6, 143.9, 134.5, 129.3 (2 × C), 128.3 (2 × C), 61.3 (2 × C), 56.6, 42.6, 29.6, 21.6, 17.7, 14.1 (2 × C); *m*/*z* (CI) 338 (86 %, [M+NH$_4$]$^+$), 321 (100 %, MH$^+$); HRMS: *m*/*z* [M+H]$^+$ calc for $C_{18}H_{25}O_5$: 321.1697, found: 321.1698.

2-[3-(4-*tert*-Butyl-phenyl)-1-methyl-3-oxo-propyl]-malonic acid diethyl ester (Table 2, entry 3)



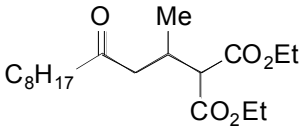
General procedure using 1.2 equivalents of alkylidene malonate gave the product as a yellow oil (322 mg, 89 %). ν_{max}(NaCl)/cm^{-1} 1684, 1731, 1750; δ_H ($CDCl_3$, 300 MHz) 7.93 (2 H, d, *J* 8.6, Ar), 7.48 (2 H, d, *J* 8.6, Ar), 4.21 (2 H, q, *J* 7.1, OCH_2CH_3), 4.20 (2 H, q, *J* 7.1, OCH_2CH_3), 3.47 (1 H, d, *J* 6.6, $CHCO_2$), 3.26 (1 H, dd, *J* 3.9, 15.7, $C(O)CH_aH_b$), 3.02-2.93 (1 H, m, $CHCHCO_2$), 2.87 (1 H, dd, *J* 8.6, 15.7, $C(O)CH_aH_b$), 1.34 (9 H, s, $(CH_3)_3CAr$), 1.28 (3 H, t, *J* 7.1, OCH_2CH_3), 1.26 (3 H, t, *J* 7.1, OCH_2CH_3), 1.08 (3 H, d, *J* 6.6, $CHCH_3$); δ_C($CDCl_3$, 100 MHz) 198.5, 168.7, 168.6, 156.8, 134.4, 128.1 (2 × C), 125.5 (2 × C), 61.3 (2 × C), 56.6, 42.7, 35.1, 31.1, 29.6, 17.7, 14.1 (2 × C); *m/z* (EI) 362 (100 %, M^+), 347 (54 %, M^+-Me) 333 (7 %, M^+-Et), 317 (7 %, M^+-OEt); HRMS: *m/z* $[M+H]^+$ calc for $C_{21}H_{31}O_5$: 363.2166, found: 363.2165.

2-(1-Methyl-3-oxo-nonyl)-malonic acid diethyl ester (Table 2, entry 4)



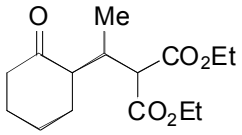
General procedure using 3 mol % $Pd(OAc)_2$, 6 mol % (*rac*)-BINAP, 1.2 equivalents of alkylidene malonate gave the product as a yellow oil (236 mg, 76 %). ν_{max}(NaCl)/cm^{-1} 1731, 1749; δ_H ($CDCl_3$, 300 MHz) 4.19 (4 H, q, *J* 7.1, 2 × OCH_2CH_3), 3.37 (1 H, d, *J* 6.7, $CHCO_2$), 2.85-2.72 (1 H, m, $CHCHCO_2$), 2.65 (1 H, dd, *J* 4.7, 17.0, $C(O)CH_aH_bCH$), 2.44-2.35 (3 H, m, $CH_2C(O)CH_aH_b$), 1.60-1.51 (2 H, m, CH_2), 1.36-1.24 (12 H, m, 3 × CH_2, 2 × OCH_2CH_3), 1.02 (3 H, d, *J* 6.8, $CHCH_3$), 0.88 (3H, t, *J* 6.3, CH_3); δ_C($CDCl_3$, 100 MHz) 209.7, 168.6 (2 × C), 61.2 (2 × C), 56.2, 46.7, 43.2, 31.6, 28.9 (2 × C), 23.8, 22.5, 17.7, 14.1 (2 × C), 14.0; *m/z* (CI) 332 (100 %, $[M+NH_4]^+$), 315 (32 %, MH^+), 286 (3 %, MH^+-Et); HRMS: *m/z* $[M+NH_4]^+$ calc for $C_{17}H_{34}NO_5$: 332.2431, found: 332.2434.

2-(1-Methyl-3-oxo-undecyl)-malonic acid diethyl ester (Table 2, entry 5)



General procedure using 3 mol % $Pd(OAc)_2$, 6 mol % (*rac*)-BINAP, 1.4 equivalents of alkylidene malonate gave the product as a yellow oil (273 mg, 80 %). ν_{max}(NaCl)/cm^{-1} 1714, 1732, 1750; δ_H ($CDCl_3$, 300 MHz) 4.19 (4 H, q, *J* 7.1, 2 × OCH_2CH_3), 3.37 (1 H, d, *J* 6.7, $CHCO_2$), 2.85-2.72 (1 H, m, $CHCHCO_2$), 2.65 (1 H, dd, *J* 4.7, $CH_2C(O)CH_aH_b$), 2.44-2.35 (3 H, m, $CH_2C(O)CH_aH_b$), 1.60-1.48 (2 H, m, CH_2), 1.34-1.20 (16 H, m, 5 × CH_2, 2 × OCH_2CH_3), 1.02 (3 H, d, *J* 6.8, $CHCH_3$), 0.88 (3 H, t, *J* 6.8, CH_3); δ_C($CDCl_3$, 100 MHz) 209.7, 168.6 (2 × C), 61.2 (2 × C), 56.2, 46.7, 43.2, 31.8, 29.4, 29.2, 29.1, 28.9, 23.8, 22.7, 17.7, 14.1 (3 × C); *m/z* (CI) 360 (100 %, $[M+NH_4]^+$), 343 (32 %, MH^+) 332 (7 %, $[MH^++NH_4]^+$-Et); HRMS: *m/z* $[M+NH_4]^+$ calc for $C_{19}H_{38}NO_5$: 360.2744, found: 360.2743.

2-[1-(2-Oxo-cyclohexyl)-ethyl]-malonic acid diethyl ester (Table 2, entry 6)



General procedure using 3.0 equivalents of alkylidene malonate gave the product as a yellow oil (207 mg, 73 %) as an inseparable 4:1 mixture of diastereoisomers. ν_{max}(NaCl)/cm^{-1} 1714, 1732, 1750; δ_H ($CDCl_3$, 300 MHz) 4.23 (4 H, m, 2 × OC*H*$_2$CH$_3$), 3.77 (0.2 H, d, *J* 8.1, C*H*CO$_2$), 3.43 (0.8 H, d, *J* 8.1, C*H*CO$_2$), 2.96-2.85 (0.8 H, m), 2.52-2.35 (2 H, m), 2.40-2.19 (1.2 H, m), 2.13-1.97 (2H, m), 1.95-1.83 (1 H, m), 1.74-1.59 (2.2 H, m), 1.49-1.35 (0.8 H, m), 1.30-1.23 (6 H, m, 2 × OCH$_2$C*H*$_3$), 1.06 (0.6 H, d, *J* 6.9, CHC*H*$_3$), 0.95 (2.4 H, d, *J* 6.9, CHC*H*$_3$); δ_C($CDCl_3$, 100 MHz) 211.7 (minor), 211.4 (major), 169.3 (minor), 169.0 (minor), 168.9 (major), 168.7 (major), 61.2, 55.2, 54.7, 52.6, 52.4, 42.7, 42.4, 34.0, 31.9, 31.0, 28.8, 27.7, 25.2, 14.2, 14.1, 13.7; *m*/*z* (CI) 302 (100 %, [M+NH_4]$^+$), 285 (74 %, MH$^+$), 256 (9 %, [MH-Et]$^+$), 239 (7 %, [M-EtOH]$^+$); HRMS: *m*/*z* [M+H]$^+$ calcd for $C_{15}H_{25}O_5$: 285.1697, found: 285.1696.

Reaction employing α-chlorostyrene (Table 2, entry 8)

A flask was charged with $Pd_2(dba)_3$ (5 mg, 0.005 mmol, 1 mol %), ligand **1** (12 mg, 0.02 mmol, 2 mol %), toluene (2 mL) under a nitrogen atmosphere and heated to 80 °C until the solution became homogeneous (~5 mins). The reaction was cooled to room temperature and the vinyl chloride (139 mg, 1.0 mmol) was weighed into a vial and added in toluene (1 mL + 1 mL vial wash). Pyrrolidine (85 μL, 1.02 mmol) and sodium *tert*-butoxide (106 mg, 1.1 mmol) were added and the reaction heated to 80 °C until vinyl chloride was consumed by TLC. The reaction was cooled to room temperature and diethyl ethylidene malonate (223 mg, 1.2 mmol) in toluene (1 mL) was added and the reaction allowed to stir for 20 hours. The reaction was quenched with sat. NH_4Cl (1 mL) and worked up as described in the general procedure above. Purification by column chromatography (SiO_2) gave the product as a yellow oil (266mg, 87 %).

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[2] P. H. Lee, D. Seamoon, K. Lee, K. Heo, *J. Org. Chem.*, 2003, **68**, 2510-2513.