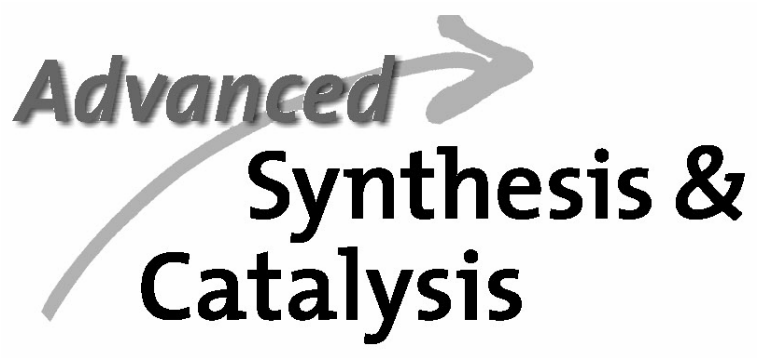

Supporting Information

Alkenes from Alcohols by Tandem Hydrogen Transfer and Condensation

Supporting Information.

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General Methods:
Reactions that required the use of anhydrous, inert atmosphere techniques were carried out under an atmosphere of argon or nitrogen. All reactions were carried out in oven dried, nitrogen (or argon) purged glassware, unless stated otherwise. In all cases, solvents were obtained by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. All reagents were purchased from commercial suppliers: Acros Organics, Alfa Aesar, Avocado, Fluka, Lancaster, Sigma Aldrich or Strem, unless preparative details are provided.

TLC using aluminium backed plates precoated with Machery-Nagel Sil G/UV$_{254nm}$ neutral silica were used to follow reactions and flash chromatography. Visualisation of TLC plates was by 254 nm UV light and. Flash chromatography was carried out using Davisil LC 60Å silica gel (35-70 micron) purchased from Fluorochem.

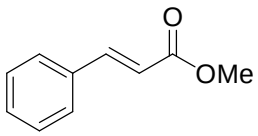
NMR spectra were routinely run in $CDCl_3$ on either a Bruker Avance 250 (250 MHz) or a Bruker Avance 300 (300 MHz) instrument and recorded at the following frequencies: proton (^{1}H – 250/300 MHz) and carbon (^{13}C – 62.9/75.4 MHz). Chemical shifts are reported relative to the residual solvent peak where possible or alternatively to $SiMe_4$ (0.00 ppm) as the internal standard. Coupling constants (*J*) are given in Hz and multiplicities are denoted as: singlet (s), doublet (d), triplet (t), quartet (q), unresolved multiplet (m) or broad (br.). Signals are assigned as general assignments classified as aromatic (Ar), phenyl (Ph), quaternary carbon (C), methyne carbon (CH), methylene carbon (CH_2) and methyl carbon (CH_3). Structural assignments of both proton and carbons were achieved with comparisons from analogous literature compounds; references are given in all cases.

Experimental Methods:

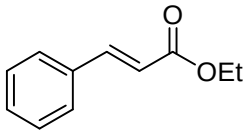
Preparation of $Ru(PPh_3)_3(CO)H_2$:[1] To a nitrogen purged, 3-necked round bottomed flask charged with triphenylphosphine (6.28 g, 23.9 mmol) was added degassed anhydrous methanol (200 mL). The mixture was heated at reflux for 10 minutes, forming a solution. In quick succession, ruthenium trichloride hydrate (1.04 g, 4.0 mmol) in methanol (40 mL), aqueous formaldehyde (37% w/w) (40 mL) and potassium hydroxide (1.20 g, 21.4 mmol) in methanol (40 mL) were added. The resulting solution was heated for 30 minutes at reflux and then cooled in an ice bath with stirring for a further 30 minutes. The grey precipitate was collected by vacuum filtration and washed with absolute ethanol (50 mL), water (50 mL), absolute ethanol (50 mL) and finally hexane (50 mL). The crude product was dissolved in toluene and filtered through a column of neutral alumina and washed through thoroughly with toluene. The toluene solution was concentrated *in vacuo* to approximately 20 mL and layered with anhydrous methanol producing a precipitate which was collected by

vacuum filtration as a white solid ($Ru(PPh_3)_3(CO)H_2$) (2.50 g, 68%).

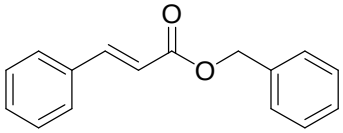
Representative procedure for the addition of malonates to alcohols. Procedure A: To oven dried, argon purged Radley's carousel tubes containing $Ru(PPh_3)_3(CO)H_2$ (22.9 mg, 0.025 mmol, 0.025 equiv.), Xantphos (14.5 mg, 0.025 mmol, 0.025 equiv.) and pyrrolidine (25 µL, 0.30 mmol, 0.30 equiv.) was added toluene (1 ml), benzyl alcohol (109 µL , 1 mmol, 1 equiv.), crotononitrile (122 µL, 1.5 mmol, 1.5 equiv.) and monoethyl malonate (145.25 µL, 1.1 mmol, 1.1 equiv.). The reactions were heated to reflux for 2 hours, cooled to room temperature and the solvent was removed *in vacuo*. The resultant oil was purified by column chromatography. **Procedure B:** As for procedure A except methyl potassium malonate (160mg, 1.1 mmol, 1.1 equiv) or ethyl potassium malonate (187 mg, 1.1 mmol, 1.1 equiv) were used. Acetic acid (59 µL, 1.1 mmol 1.1 equiv) was also added. The crude mixture was dissolved in ether, washed with saturated ammonium chloride, saturated sodium carbonate, water and dried over magnesium sulfate. The product was concentrated *in vacuo* and purified by column chromatography.



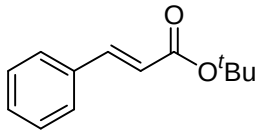
(*E*)-Methyl cinnamate (Table 1, entry 1):[2] According to representative **procedure B** using benzyl alcohol (436 µL, 4 mmol, 1 equiv), methyl potassium malonate (640 mg, 4.4 mmol, 1.1 equiv) and acetic acid (236 µL, 4.4 mmol, 1.1 equiv), the title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/diethyl ether, R_f = 0.44) affording the product as a white solid (485 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) d_{ppm} = 7.65 (d, 1H, *J* = 15.9 Hz), 7.54-7.36 (m, 5H), 6.46 (d, 1H, *J* = 15.9 Hz), 3.8 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) d_{ppm} = 167.3, 144.8, 134.2, 130.2, 128.8, 128.0, 117.7, 51.6.



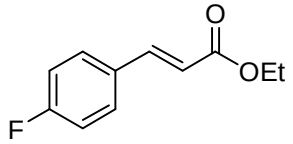
(*E*)-Ethyl cinnamate (Table 1, entry 2 and 3):[2] According to representative **procedure B** using benzyl alcohol (436 µL, 4 mmol, 1 equiv), ethyl potassium malonate (749mg, 4.4 mmol, 1.1 equiv) and acetic acid (236 µL, 4.4 mmol, 1.1 equiv), the title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/diethyl ether, R_f = 0.31) affording the product as a pale yellow oil (502 mg, 71%). Using **procedure A** with mono-ethyl malonate (581 µL 4.4 mmol, 1.1 equiv). The title compound was obtained as above. (679.5 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) d_{ppm} = 7.70 (d, 1H, *J* = 15.9 Hz), 7.55-7.36 (m, 5H), 6.45 (d, 1H, *J* = 15.9 Hz), 4.27 (q, 2H, *J* = 7.2 Hz), 1.35 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) d_{ppm} = 166.9, 144.5, 130.1, 128.8, 127.9, 118.2, 60.4, 14.2.



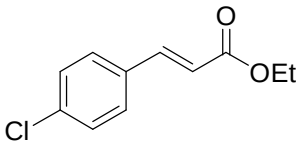
(*E*)-Benzyl cinnamate (Table 1, entry 4):[2] According to representative **procedure A** using benzyl alcohol (436 µL, 4 mmol, 1 equiv), and mono-benzyl malonate (854.mg, 4.4 mmol, 1.1 equiv), the title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/diethyl ether, R_f = 0.41) affording the product as a clear oil (80 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) d_{ppm} = 7.45 (d, 1H, *J* = 15.9 Hz), 7.28-7.0 (m, 10H), 6.23 (d, 1H, *J* = 15.9 Hz), 4.99 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) d_{ppm} = 166.7, 145.1, 136.0, 134.3, 130.3, 128.8, 128.5, 128.2, 128.0, 117.8, 66.3.



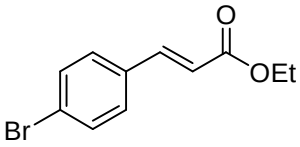
(*E*)-*tert*-Butyl cinnamate (Table 1, entry 5):[3] According to representative **procedure A** using benzyl alcohol (436 µL, 4 mmol, 1 equiv), and mono-*tert*-butyl malonate (650 µL, 4.4 mmol, 1.1 equiv), the title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/diethyl ether, R_f = 0.46) affording the product as a clear oil (575 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) d_{ppm} = 7.60 (d, 1H, *J* = 16.2 Hz), 7.53-7.35 (m, 5H), 6.37 (d, 1H, *J* = 16.2 Hz), 1.55 (s, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) d_{ppm} = 166.3, 143.5, 134.7, 129.9, 128.8, 127.9, 120.2, 80.5, 28.2.



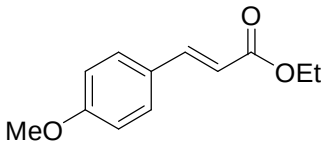
Ethyl (*E*)-3-(4-fluorophenyl)-2-propanoate (Table 1, entry 6):[2] According to representative **procedure A** using 4-fluoro benzyl alcohol (431 µL, 4 mmol, 1 equiv), and mono-ethyl malonate (581 µL, 4.4 mmol, 1.1 equiv), the title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/diethyl ether, R_f = 0.35) affording the product as a pale yellow oil (675 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) d_{ppm} = 7.65 (d, 1H, *J* = 15.9 Hz), 7.53 (d, 1H *J* = 5.7 Hz), 7.5 (d, 1H *J* = 5.7 Hz) 7.07 (ps-t, 2H, *J* = 8.7Hz), 6.5 (d, 1H, *J* = 15.9 Hz), 4.26 (q, 2H, *J* = 7.2 Hz), 1.34 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) d_{ppm} = 166.8, 163.8 (d, $^1J_{CF}$ = 250 Hz), 143.2, 130.6 (d, $^4J_{CF}$ = 3.4 Hz), 129.8 (d, $^3J_{CF}$ = 8.4 Hz), 118.0 (d, $^5J_{CF}$ = 2.3 Hz), 116.0 (d, $^2J_{CF}$ = 21.7 Hz), 60.5, 14.3.



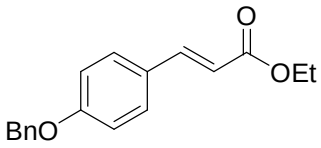
Ethyl (*E*)-3-(4-chlorophenyl)-2-propanoate (Table 1, entry 7):[4] According to representative **procedure A** using 4-chloro benzyl alcohol (431 µL, 4 mmol, 1 equiv), and mono-ethyl malonate (581 µL, 4.4 mmol, 1.1 equiv) The title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/diethyl ether, R_f = 0.35) affording the product as a pale yellow oil (770 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) d_{ppm} = 7.63 (d, 1H, *J* = 15.9 Hz), 7.44 (d, 2H *J* = 8.4 Hz), 7.35 (d, 2H, *J* = 8.4 Hz), 6.40 (d, 2H, *J* = 15.9 Hz), 4.27 (q, 2H, *J* = 7.2 Hz), 1.34 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) d_{ppm} = 166.6, 143.0, 136.0, 132.9, 129.1, 128.5, 118.8, 60.6, 14.2.



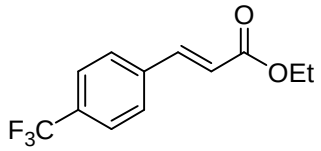
Ethyl (*E*)-3-(4-bromophenyl)-2-propanoate (Table 1, entry 8):[5] According to representative **procedure A** using 4-bromo benzyl alcohol (748 mg, 4 mmol, 1 equiv), and mono-ethyl malonate (581 µL, 4.4 mmol, 1.1 equiv) The title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/diethyl ether, R_f = 0.35) affording the product as a pale yellow oil (747 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) d_{ppm} = 7.62 (d, 1H, *J* = 15.9 Hz), 7.52 (d, 2H, *J* = 9.0 Hz), 7.44 (d, 2H, *J* = 9.0 Hz), 6.42 (d, 1H, *J* = 15.9 Hz), 4.27 (q, 2H, *J* = 7.2 Hz), 1.34 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) d_{ppm} = 166.7, 143.1, 133.4, 132.5, 132.1, 130.9, 129.4, 124.4, 119.0, 60.6, 14.3.



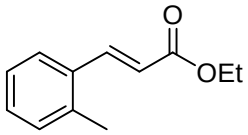
Ethyl (*E*)-3-(4-methoxyphenyl)-2-propanoate (Table 1, entry 9):[4] According to representative **procedure A** using 4-methoxy-benzyl alcohol (498 µL, 4 mmol, 1 equiv), and mono-ethyl malonate (581 µL, 4.4 mmol, 1.1 equiv), the title compound was synthesised and purified by column chromatography (3:1 Hexane/EtOAc R_f = 0.43) affording the product as a yellow oil (589 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) d_{ppm} = 7.64 (d, 1H, *J* = 15.9 Hz), 7.46 (d, 2H *J* = 8.7 Hz), 6.90 (d, 2H, *J* = 8.7 Hz), 6.31 (d, 2H, *J* = 15.9 Hz), 4.25 (q, 2H, *J* = 7.2 Hz), 3.83 (s, 3H), 1.33 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) d_{ppm} = 167.2, 161.2, 144.1, 129.6, 127.13, 115.7, 114.2, 60.2, 55.2, 14.3.



Ethyl (*E*)-3-(4-(benzyloxy)phenyl)-2-propanoate (Table 1, entry 10):[6] According to representative **procedure A** using 4-benzyloxy benzyl alcohol (857 mg, 4 mmol, 1 equiv), and mono-ethyl malonate (581 µL, 4.4 mmol, 1.1 equiv), the title compound was synthesised and purified by column chromatography (3:1 Hexane/EtOAc, R_f = 0.47) affording the product as a white solid (931.5 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$) d_{ppm} = 7.64 (d, 1H, *J* = 15.9 Hz), 7.50-7.35 (m, 7H), 6.99 (d, 1H, *J* = 9.6 Hz), 6.32 (d, 1H, *J* = 15.9 Hz), 5.10 (s, 2H), 4.26 (q, 2H, *J* = 7.2 Hz), 1.34 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) d_{ppm} = 167.3, 160.5, 144.1, 136.5, 129.7, 128.6, 128.1, 127.4, 115.9, 115.2, 70.0, 60.3, 14.3.



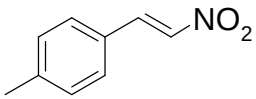
Ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)-2-propanoate (Table 1, entry 11):[4] According to the representative **procedure A** using 4-trifluoromethyl-benzyl alcohol (547 µL, 4 mmol, 1 equiv), and mono-ethyl malonate (581 µL, 4.4 mmol, 1.1 equiv), the title compound was synthesised and purified by column chromatography (9:1 Hexane/EtOAc R_f = 0.34) affording the product as a white solid (725 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) d_{ppm} = 7.73-7.61 (m, 5H) 6.51 (d, 1H *J* = 16.2 Hz), 4.29 (q, 2H, *J* = 7.2 Hz), 1.35 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) d_{ppm} = 166.4, 142.7, 137.8, 128.1, 125.7 (q, *J* = 3.8Hz), 120.8, 60.8, 14.2.



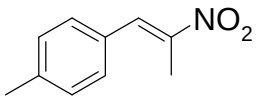
Ethyl (*E*)-3-(o-tolyl)-2-propanoate (Table 1, entry 12):[3] According to the representative **procedure A** using 2-methyl benzyl alcohol (488 mg, 4 mmol, 1 equiv), and mono-ethyl malonate (581 µL, 4.4 mmol, 1.1 equiv) The title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/diethyl ether, R_f = 0.38) affording the product as a pale yellow oil (552 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) d_{ppm} = 7.89 (d, 1H, *J* = 15.9 Hz), 7.47 (d, 1H *J* = 7.2 Hz), 7.16 (m 3H), 6.25 (d, 1H, *J* = 15.9 Hz), 4.19 (q, 2H, *J* = 7.2 Hz), 2.36 (s, 3H), 1.26 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) d_{ppm} = 167.0, 142.2, 137.5, 133.4, 130.7, 129.9, 126.3, 119.3, 60.4, 19.7, 14.3.

Representative procedure for the addition of nitroalkanes to alcohols: To oven dried, argon purged Radley's carousel tubes containing $Ru(PPh_3)_3(CO)H_2$ (22.9 mg, 0.025 mmol, 0.025 equiv.), Xantphos (14.5 mg, 0.025 mmol, 0.025 equiv.) and piperidinium acetate (29 mg, 0.25 mmol, 0.25 equiv.) was added toluene (1 ml), para-methyl benzyl alcohol (122 mg, 1 mmol, 1 equiv.), crotononitrile (122 µL, 1.5 mmol, 1.5 equiv.) and nitroethane (93 µL, 1.3 mmol, 1.3 equiv.) The reactions were heated

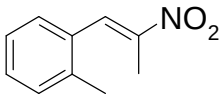
to reflux for 8 hours, cooled to room temperature and the solvent was removed *in vacuo*. Products were isolated by column chromatography.



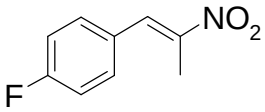
(*E*)-1-Methyl-4-(2-nitrovinyl)benzene[7] **(Table 2, entry 1):** According to the representative procedure, using 4-methylbenzyl alcohol (122 mg, 1 mmol, 1 equiv.) and nitromethane (71 μL, 1.3 mmol, 1.3 equiv.), the title compound was synthesised in 100% conversion after 8 hours. The product was not isolated; conversion was determined to be complete from the absence of 4-methylbenzyl alcohol and 4-methylbenzaldehyde in the crude ^{1}H NMR spectrum. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): d_{ppm} = 8.00 (d, 1H, *J* = 13.7 Hz), 7.58 (d, 1H, *J* = 13.6 Hz), 7.46 (d, 2H, *J* = 8.2 Hz), (d, 2H, *J* = 7.8 Hz), 2.43 (s, 3H)



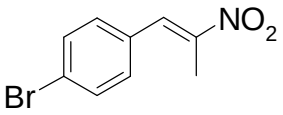
(*E*)-1-Methyl-4-(2-nitroprop-1-enyl)benzene[8,9] **(Table 2, entry 2):** According to the representative procedure, using 4-methylbenzyl alcohol (611 mg, 5 mmol, 1 equiv.), the title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/diethyl ether, R_f = 0.40), affording the product as a pale yellow solid (744 mg, 84%) ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): d_{ppm} = 8.09 (s, 1H, -C<u>H</u>), 7.36 (d, 2H, *J* = 8.1 Hz), 7.28 (d, 2H, *J* = 8.1 Hz), 2.47 (d, 3H, *J* = 0.9 Hz), 2.42 (s, 3H) ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): d_{ppm} = 146.9, 140.5, 133.7, 130.1, 129.6, 129.4, 21.4, 14.1. The NOESY spectrum contained a cross-peak between the signal at 2.47 (allylic H_3C) and the aryl ortho CH protons at 7.36, but not to the alkenyl proton at 8.09.



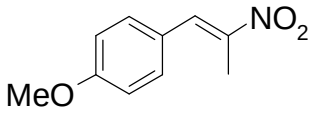
(*E*)-1-Methyl-2-(2-nitroprop-1-enyl)benzene[8,9] **(Table 2, entry 3):** According to the representative procedure, using 2-methylbenzyl alcohol (611 mg, 5 mmol, 1 equiv.), the title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/diethyl ether, R_f = 0.45), affording the product as a pale yellow solid (735 mg, 84%) ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): d_{ppm} = 8.11 (s, 1H), 7.26-7.18 (m, 4H), 2.29 (s, 3H), 2.27 (d, 3H, *J* = 1.2 Hz) ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): d_{ppm} = 148.3, 137.8, 132.6, 131.7, 130.5, 129.6, 128.7, 126.0, 19.9, 13.8.



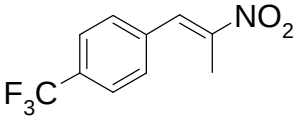
(*E*)-1-Fluoro-4-(2-nitroprop-1-enyl)benzene[12] **(Table 2, entry 4):** According to the representative procedure, using 4-fluorobenzyl alcohol (631 mg, 5 mmol, 1 equiv.), the title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/diethyl ether, R_f = 0.36), affording the product as a pale yellow solid (661 mg, 73%) ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): d_{ppm} = 8.07 (s, 1H), 7.48-7.42 (m, 2H), 7.2-7.13 (m, 2H), 2.46 (s, 3H) ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): d_{ppm} = 163.4 (d, *J* = 250.4 Hz), 147.4, 132.5, 132 (d, *J* = 8.5 Hz), 128.5 (d, *J* = 3.5 Hz), 116.2 (d, *J* = 21.9 Hz), 14.38



(*E*)-1-Bromo-4-(2-nitroprop-1-enyl)benzene[13] **(Table 2, entry 5):** According to the representative procedure, using 4-bromobenzyl alcohol (1156 mg, 5 mmol, 1 equiv.), the title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/ethyl acetate, R_f = 0.38), affording the product as a pale yellow solid (750 mg, 62%) ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): d_{ppm} = 8.02 (s, 1H), 7.80 (d, 2H, *J* = 8.5 Hz), 7.30 (d, 2H, *J* = 8.5 Hz), 2.44 (d, 3H, *J* = 1 Hz) ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): d_{ppm} = 148.1, 132.2, 132.2, 131.3, 131.3, 124.4, 14.0

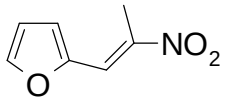


(*E*)-1-Methoxy-4-(2-nitroprop-1-enyl)benzene[8,12] **(Table 2, entry 6):** According to the representative procedure, using 4-methoxybenzyl alcohol (691 mg, 5 mmol, 1 equiv.), the title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/diethyl ether, R_f = 0.20), affording the product as a pale yellow solid (705 mg, 73%). ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): d_{ppm} = 8.1 (s, 1H), 7.43 (d, 2H, *J* = 8.8 Hz), 6.98 (d, 2H, *J* = 8.9 Hz), 3.87 (s, 3H), 2.48 (3H, d, *J* = 1 Hz) ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): d_{ppm} = 161.1, 145.67, 133.57, 132.0, 124.7, 114.44, 55.39, 14.08

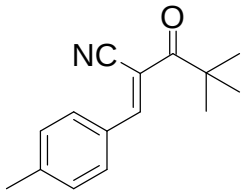


(*E*)-1-(2-Nitroprop-1-enyl)-4-(trifluoromethyl)benzene[13] **(Table 2, entry 7):** According to the representative procedure, using 4-trifluoromethyl benzyl alcohol (881 mg, 5 mmol, 1 equiv.), the title compound was synthesised and purified by column chromatography (9:1 petroleum ether (b.p. 40-60 °C)/diethyl ether, R_f = 0.38), affording the product as a pale yellow solid (769 mg, 67%) ^{1}H NMR (250 MHz,

$CDCl_3$, 25 °C): d_{ppm} = 8.1 (s, 1H), 7.73 (d, 2H, *J* = 8.3 Hz), 7.54 (d, 2H, *J* = 8.3 Hz), 2.45 (d, 3H, *J* = 1 Hz) ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): d_{ppm} = 149.4, 136.0 (d, *J* = 1.4 Hz), 131.6, 131.4 (q, *J* = 32.8 Hz), 130.0, 125.8 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.3 Hz), 13.9



(*E*)-2-(2-Nitroprop-1-enyl)furan[14] **(Table 2, entry 8):** According to the representative procedure, using furfuryl alcohol (98.10 mg, 5 mmol, 1 equiv.), the title compound was synthesised in 100% conversion after 8 hours. The product was not isolated; conversion was calculated from peak integrals characteristic of furfuryl alcohol, furfuryaldehyde and the title compound.in the crude ^1H NMR spectrum. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): d_{ppm} = 7.87 (s, 1H), 7.65 (d, 1H, *J* = 1.6 Hz), 6.83 (d, 1H, *J* = 3.5 Hz), 6.59 (m, 1H), 2.59 (d, 3H, *J* = 5.7 Hz)



(*E*)-4,4-Dimethyl-2-(4-methylbenzylidene)-3-oxopentanenitrile (Scheme 4): According to the representative procedure, using 4-methylbenzyl alcohol alcohol (122.1 mg, 1 mmol, 1 equiv.) and 4,4-dimethyl-3-oxopentanenitrile (125 mg, 1 mmol, 1 equiv.) the title compound was synthesised in 100% conversion after 16 hours. The product was isolated as a colourless oil. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): d_{ppm} = 8.14 (s, 1H), 7.89 (d, 2H, *J* = 8.2 Hz), 7.30 (d, 2H, *J* = 8.2 Hz), 2.44 (s, 3H), 1.59 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): d_{ppm} = 198.0, 156.0, 144.1, 131.2, 129.7, 129.3, 118.4, 105.8, 44.4, 26.3, 21.6. IR: (nujol, cm^{-1}): 2210 ($?_{CN}$), 1690 ($?_{CO}$). HRMS (ESI): m/z = 250.1201 (calcd 250.1207 for $[M+H]^+$). Evidence for the expected (*E*)-geometry of the alkene was provided by nOe spectroscopy – irradiation of the 9H singlet at 1.59 due to $C(CH_3)_3$ gave rise to an nOe enhancement of the alkenyl proton at 8.14.

References:

1. Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45.
2. Zeitler, K. *Org. Lett.* **2006**, *4*, 637.
3. Duguet, N.; Harrison-Marchand, A.; Maddaluno, J.; Tomioka, K. *Org. Lett.* **2006**, *25*, 5745.
4. Chen, Y.; Huang, L.; Ranade, M.A.; Zhang, X.P. *J. Org. Chem.* **2003**, *68*, 3714.
5. Couladouros, E.A.; Soufli, I.C.; Moustos, V.I.; Chanda R.K. *Chem. Eur. J.* **1998**, *4*, 33.
6. Reddy, S. H. K.; Lee, S.; Datta, A.; Georg, G. I. *J. Org. Chem.* **2003**, *66*, 8211.
7. Deng, X.; Mani, N. S. *Org. Lett*, **2006**, *8*, 3505.

8. Kawai, Y.; Inaba, Y.; Tokitoh, N. *Tetrahedron: Asymmetry,* **2001**, *19*, 309.
9. Dawson, B. A.; By, A. W.; Avdovich, H. W. *Magn. Reson. Chem.* **1993**, *31*, 104.
10. Plenevaux, A.; Dewey, S. L.; Fowler, J. S.; Guillaume, M.; Wolf, A. P. *J. Med. Chem,* **1990**, *33*, 2015.
11. Mourad, M. S.; Varma, R. S.; Kabalka, G. W. *J. Org. Chem,* **1985**, *50,* 133.
12. Dawson, B. A.; By, A. W.; Avdovich, H. W. *Magn. Reson. Chem.* **1991**, *29*, 188.
13. Denmark, S. E.; Kesler, B. S.; Moon, Y. C. *J. Org. Chem*, **1992**, *57*, 4912.
14. Vallejos, G.; Fierro, A.; Caroli Rezende, M.; Sepúlveda-Boza, S.; Reyes-Parada, M. *Bioorg. Med. Chem.* **2005**, *13*, 4450.