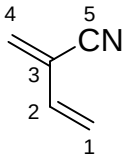
Electronic Supplementary Information (ESI)

Determination of Stereochemistry

The di-substituted double bond was found to be *E* for all but the dialdehyde cases **i** and **j**, on the basis of the large $^{3}J_{HH}$ (~16 Hz) between the alkene protons. The stereochemistry of the tri-substituted alkene was determined as *Z* by nOe experiments in the cases of **4a**, **5a** and **5e**, allowing assignment by analogy to all of the ethyl acrylate derived products **5** and the aliphatic aldehyde based acrylonitrile products **4a-c**. However, no useful nOe data could be obtained for the aromatic aldehyde derived acrylonitrile products **4e**-**j**. In these latter cases, the analysis of ^{1}H-coupled ^{13}C NMR spectra allowed the measurement of the magnitude of ^{1}H-^{13}C coupling constants for C2 and C5 in **4e**. These experimental $^{n}J_{CH}$ values are presented in Table 1 along with the corresponding coupling constants calculated *ab initio* for the corresponding *Z*- and *E*- isomers. Computation of $^{n}J_{CH}$ values for **4e** and **5e** was achieved using the NMR=spinspin option within Gaussian03W and Gaussview interface on a WindowsXP PC (3.6GHz, 2Gb RAM) on geometry optimised CN/CO_2Et substituted butadienes, using DFT with B3LYP functional and 6-311g** basis set.[1] Geometries for the cisoid and transoid conformations were optimised using Density Functional Theory (DFT) with the B3LYP functional and 6-311g* basis set. In both the cases, the transoid was found to be more stable by >10 kJ/mol, and hence only the coupling constants for the transoid form were used to match with the experimental values. There is a clear match between the observed $^{3}J_{CH}$ constants and the calculated values for the *Z*-geometry of the tri-substituted double bond.

Table 1 Experimental and calculated coupling constants.

	J_{CH} (experimental)	J_{CH} (calc.) *Z* geometry	J_{CH} (calc.) *E* geometry
C2	156 Hz	151 Hz (H2)	151 Hz (H2)
	8.3 Hz	8.0 Hz (H4)	11.0 Hz (H4)
C5	14.2 Hz	13.8 Hz (H4)	7.9 Hz (H4)
	8.7 Hz	8.3 Hz (H2)	8.3 Hz (H2)



Similar calculations for the ester **5e** (assigned as *Z* on the basis of nOe studies) showed a similar match for the C2 $^{n}J_{CH}$ values to the *Z*-isomer, although in this case the experimental coupling constants for the ester carbon could not be obtained.

Experimental

General Methods. All reactions were carried out at ambient temperature under a positive nitrogen pressure, unless otherwise stated. Reaction mixtures were stirred magnetically.

Flash column chromatography was performed on silica gel (Merck 60 F_{254}, 230-400 mesh). Analytical TLC was performed on aluminium-coated silica plates (0.2 mm, 60 F_{254}) which were developed using UV fluorescence (254 and 366 nm) and potassium permanganate.

Melting points were determined on a Khöfler hot stage apparatus and are uncorrected.

Infrared spectra were recorded on a Perkin-Elmer (Spectrum One) 157G FT-IR. Only selected absorbance's (ν_{max}/cm^{-1}) are reported.

^1H NMR was recorded at either 400 MHz on a Jeol Delta Eclipse+ 400H or a Jeol Delta GX/400 instrument. Chemical Shifts (δ_H) are quoted in parts per million (ppm), referenced to the NMR solvents residual protons.[2] Coupling constants are quoted in Hertz (Hz). ^{13}C NMR was recorded at 100 MHz on a Jeol Delta Eclipse+ 400H or a Jeol Delta GX/400 instrument at room temperature. Chemical shifts (δ_C) are quoted in parts per million (ppm), referenced to the NMR solvent.[2]

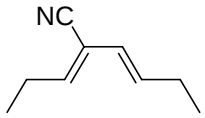
GC-MS (*m/z*) were recorded on an Agilent 6890 GC apparatus equipped with a capillary column, J&W Scientific (DB-5MS, Phenyl Arylene polymer, 15 m x 250 μm x 0.25 μm nominal) under the following conditions: helium 1 ml/min (constant flow mode), detector EI (Agilent MSD 5973), oven: injector 250 ºC (splitless mode), oven 70 ºC (1 min), 25 ºC/min (3.2 min), 45 ºC/min (2.22 min), 250 ºC (3 min), 45 ºC/min (1.11 min), 300 ºC (3 min). Only the molecular ions (M^+), and major peaks are reported with intensities quoted as percentages of the base peak. High resolution mass spectra (HRMS) were obtained using a VG Analytical Autospec instrument with either CI or EI ionization.

All reagents and solvents were used from commercial sources without further purification unless otherwise stated. Dichloromethane and THF for reactions were dried by passing them through a column of activated alumina (A-2) from the dry solvent dispenser at the University of Bristol built by Anhydrous Engineering, based on the Grubbs design.[3] Pure glutaraldehyde was obtained by stirring a 25% aqueous solution of glutaraldehyde (20 mL) with sodium chloride (14 g) for 10 minutes. The mixture was extracted with ether (3*30 mL), dried (Na_2SO_4), evaporated *in vacuo* and the residue distilled under reduced pressure to give pure glutaraldehyde which was used immediately.

General procedure for compound **4a**-**4h**:

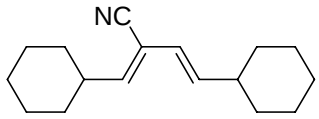
To a solution of acrylonitrile (0.8 mmol), aldehyde (1.0 mmol) and $Ti(O^iPr)_4$ (1.0 mmol) in DCM (2 mL) under nitrogen was added PBu_3 (1.0 mmol) dropwise. The mixture was stirred over night (15 hours) and the solvent removed *in vacuo*. Purification by column chromatography gave **4a**-**4h**.

(2*Z*,3*E*)-2-Propylidenehex-3-enenitrile (4a)



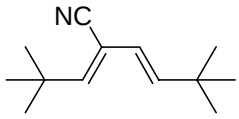
Colourless oil; R_f 0.45 (1% ether in pet. ether); ν_{max}(film) 2961, 2225, 1458, 961; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.18 (t, J = 7.5 Hz, 1H), 6.11 (dt, J = 15.5, 7.5 Hz, 1H), 5.93 (dt, J = 15.5, 0.9 Hz, 1H), 2.43 (app. p, J = 7.5 Hz, 2H), 2.16 (app. pd, J = 7.5, 0.9 Hz, 2H), 1.08 (t, J = 7.5 Hz, 3H), 1.04 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 136.7, 124.6, 122.4, 114.8, 25.4, 24.9, 13.2, 13.1. Analytical data are in accordance with literature.[4]

(2*Z*,3*E*)-4-Cyclohexyl-2-(cyclohexylmethylene)but-3-enenitrile (4b)



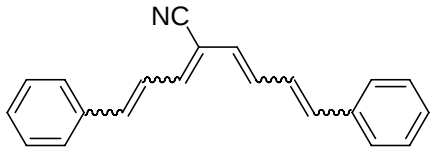
White solid; R_f 0.43 (1% ether in pet. ether); mp. 70-71 ºC (Pet. ether); ν_{max}(film) 2923, 2850, 2225, 1448, 962; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.03 (d, J = 10.5 Hz, 1H), 6.01 (dd, J = 15.6, 6.7 Hz, 1H), 5.86 (d, J = 15.6 Hz, 1H), 2.61-2.52 (m, 1H), 2.09-2.00 (m, 1H), 1.77-1.62 (m, 10H), 1.40-1.05 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 140.7, 125.3, 115.7, 113.3, 40.7, 40.6, 32.5, 32.2, 26.0, 25.9, 25.6, 25.2; m/z (EI) 244 (100%, M^++1), 160 (19%); CI-HRMS m/z calcd 244.2065 $[M+1]^+$, found 244.2057.

(2*Z*,3*E*)-5,5-Dimethyl-2-(2,2-dimethylpropylidene)hex-3-enenitrile (4c)



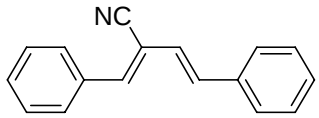
White solid; R_f 0.48 (1% ether in pet. ether); mp. 62-64 ºC (pet. ether); ν_{max}(film) 2954, 2227, 1475, 1364, 976; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.21 (s, 1H), 6.10 (d, J = 16.0 Hz, 1H), 5.83 (d, J = 16.0 Hz, 1H), 1.25 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 144.8, 122.6, 116.6, 111.5, 34.0, 33.3, 29.7, 29.3; m/z (EI) 192 (100%, M^++1), 176 (8%), 136 (11%), 79 (26%); CI-HRMS m/z calcd 192.1752 $[M+1]^+$, found 192.1759.

6-Phenyl-2-(3-phenylallylidene)hexa-3,5-dienenitrile (4d)



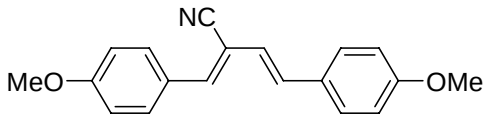
Yellow solid; R_f 0.43 (5% ether in pet. ether); mp. 148-150 ºC (pet. ether/ether); ν_{max}(film) 3025, 2223, 1617, 1447, 970; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.2 Hz, 2H), 7.44 (d, J = 7.4 Hz, 2H), 7.40-7.32 (m, 5H), 7.29-7.25 (m, 2H), 6.91-6.83 (m, 4H), 6.78-6.73 (m, 1H), 6.39-6.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 140.1, 136.8, 135.9, 135.8, 134.2, 129.4, 128.9, 128.7, 128.4, 128.2, 127.6, 127.4, 126.7, 125.1, 115.5, 113.3; m/z (EI) 284 (100%, M^++1), 206 (5%), 194 (6%), 180 (5%), 117 (18%), 91 (32%); CI-HRMS m/z calcd 284.1439 $[M+1]^+$, found 284.1434. Analytical data are in accordance with literature.[4]

(2*Z*,3*E*)-2-Benzylidene-4-phenylbut-3-enenitrile (4e)



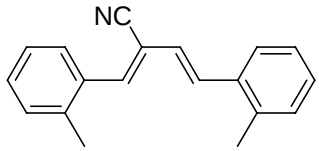
Yellow solid; R_f 0.57 (5% ether in pet. ether); mp. 110-112 ºC (pet. ether); ν_{max}(film) 3034, 2220, 1446, 958; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.83 (m, 2H), 7.50-7.42 (m, 5H), 7.40-7.29 (m, 3H), 7.14 (s, 1H), 7.11 (d, J = 16.0 Hz, 1H), 6.87 (dd, J = 16.0, 0.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 135.7, 133.6, 133.4, 130.3, 129.1, 128.9, 128.8, 128.6, 126.8, 125.8, 116.4, 111.0; m/z (EI) 232 (100%, M^++1), 205 (7%), 154 (14%), 91 (11%); CI-HRMS m/z calcd 232.1126 $[M+1]^+$, found 232.1123. Analytical data are in accordance with literature.[4,5]

(2*Z*,3*E*)-2-(4-Methoxybenzylidene)-4-(4-methoxyphenyl)but-3-enenitrile (4f)



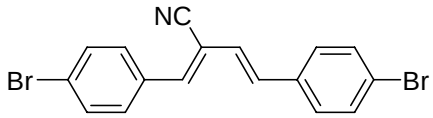
Yellow solid; R_f 0.12 (5% ether in pet. ether); mp. 150-152 ºC (pet. ether/ether); ν_{max}(film) 3010, 2839, 2218, 1601, 1507, 1250, 1175, 1027, 956; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.7 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H), 7.01-6.94 (m, 4H), 6.90 (d, J = 8.7 Hz, 2H), 6.70 (d, J = 15.7 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 159.9, 141.8, 131.8, 130.9, 128.9, 128.1, 126.8, 124.1, 117.0, 114.4, 114.3, 108.6, 55.4, 55.3; m/z (EI) 292 (100%, M^++1), 277 (6%), 184 (16%), 121 (14%); CI-HRMS m/z calcd 292.1338 $[M+1]^+$, found 292.1336.

(2*Z*,3*E*)-2-(2-Methylbenzylidene)-4-*o*-tolylbut-3-enenitrile (4g)



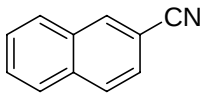
White solid; R_f 0.40 (5% ether in pet. ether); mp. 74-75 ºC (pet. ether/ether); ν_{max}(film) 3019, 2967, 2221, 1481; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 16.0 Hz, 1H), 7.39-7.14 (m, 9H), 6.91 (dd, J = 16.0, 1.0 Hz, 1H), 2.45 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 141.5, 137.2, 136.7, 134.7, 133.8, 133.1, 130.7, 129.6, 128.7, 126.2, 125.9, 125.6, 121.5, 118.1, 115.0, 99.9, 20.0, 19.8; m/z (EI) 259 (M^+, 70%), 244 (100%), 167 (53%), 115 (29%); EI-HRMS m/z calcd 259.1361 $[M]^+$, found 259.1356.

(2*Z*,3*E*)-2-(4-Bromobenzylidene)-4-(4-bromophenyl)but-3-enenitrile (4h)



Yellow solid; R_f 0.13 (5% ether in pet. ether); mp. 165-167 ºC (pet. ether/ether); ν_{max}(film) 3017, 2222, 1485, 1007; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.71 (m, 2H), 7.61-7.58 (m, 2H), 7.54-7.51 (m, 2H), 7.37-7.35 (m, 2H), 7.09 (s, 1H), 7.06 (d, J = 16.0 Hz, 1H), 6.85 (dd, J = 16.0, 0.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 134.6, 132.8, 132.4, 132.3, 132.1, 130.5, 128.4, 126.2, 124.9, 122.8, 116.0, 111.5; m/z (EI) 391/389/387 ($^{81,81}M^+/^{81,79}M^+/^{79,79}M^+$, 9%/18%/9%), 229 (100%), 202 (11%); EI-HRMS m/z calcd 386.9258 [M (two ^{79}Br)]$^+$, found 386.9256.

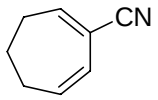
2-Naphthonitrile (4i)



To a solution of acrylonitrile (52 μL, 0.8 mmol), phthaldialdehyde (67 mg, 0.5 mmol) and $Ti(O^iPr)_4$ (296 μL, 1.00 mmol) in DCM (2 mL) under nitrogen was added PBu_3 (250 μL, 1.00 mmol) dropwise. The mixture was stirred over night (15 hours) and the solvent removed *in vacuo*. Purification by column chromatography gave **4i** (58 mg, 76%).

White solid; R_f 0.44 (20% ether in pet. ether); mp. 63-64 ºC (pet. ether); ν_{max}(film) 3063, 2227, 1626, 1595, 1501, 824, 754; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.93-7.89 (m, 3H), 7.67-7.59 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7, 134.1, 132.3, 129.2, 129.0, 128.4, 128.0, 127.6, 126.3, 119.2, 109.4. Analytical data were in accordance with literature data.[6]

(1*E*,6*Z*)-Cyclohepta-1,6-dienecarbonitrile (4j)



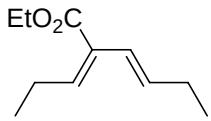
To a solution of acrylonitrile (65 μL, 1.0 mmol), glutaraldehyde (472 μL, 5.00 mmol) and $Ti(O^iPr)_4$ (586 μL, 2.00 mmol) in DCM (30 mL) under nitrogen was added PBu_3 (500 μL, 2.00 mmol) dropwise. The mixture was stirred over night (15 hours) and the solvent removed *in vacuo*. Purification by column chromatography gave **4j** (63 mg, 41%).

Colourless oil; R_f 0.40 (10% ether in pet. ether); ν_{max}(film) 2930, 2222, 1431; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69 (t, J = 5.7 Hz, 1H), 6.03 (dt, J = 11.8, 5.6 Hz, 1H), 5.79 (d, J = 11.8 Hz, 1H), 2.48 (app. q, J = 5.7 Hz, 2H), 2.40 (app. q, J = 5.4 Hz, 2H), 1.88 (app. p, J = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 137.7, 122.3, 120.7, 112.8, 31.9, 31.5, 24.5; m/z (EI) 119 (M^+, 41%), 104 (100%), 91 (60%); EI-HRMS m/z calcd 119.0735 $[M]^+$, found 119.0730.

General procedure for compound **5a**-**5h**:

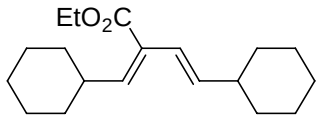
To a solution of ethyl acrylate (0.8 mmol), aldehyde (1.0 mmol) and $Ti(O^iPr)_4$ (1.0 mmol) in DCM (2 mL) under nitrogen was added PBu_3 (1.0 mmol) dropwise. The mixture was stirred over night (15 hours) and the solvent removed *in vacuo*. Purification by column chromatography gave **5a**-**5h**.

(2*Z*,3*E*)-Ethyl 2-propylidenehex-3-enoate (5a)



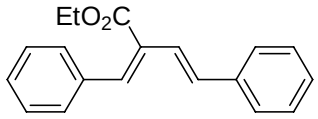
Colourless oil; R_f 0.39 (5% ether in pet. ether); ν_{max}(film) 2966, 1713, 1460, 1229, 1144; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.55 (t, J = 7.5 Hz, 1H), 6.11 (d, J = 16.0 Hz, 1H), 6.03 (dt, J = 16.0, 5.9 Hz, 1H), 4.20 (app. q, J = 7.1 Hz, 2H), 2.29 (app. p, J = 7.5 Hz, 2H), 2.16 (app. bp, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.5 Hz, 3H), 1.03 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 142.9, 137.7, 129.9, 121.0, 60.4, 26.6, 22.0, 14.2, 13.5, 13.4; m/z (EI) 182 (100%, M^+), 167 (18%), 153 (30%), 137 (39%), 125 (50%), 107 (87%), 93 (75%), 80 (95%), 67 (100%); CI-HRMS m/z calcd 183.1385 $[M+1]^+$, found 183.1386.

(2*Z*,3*E*)-Ethyl 4-cyclohexyl-2-(cyclohexylmethylene)but-3-enoate (5b)



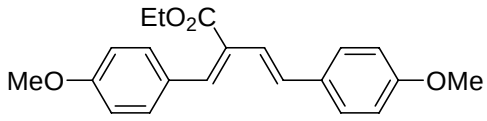
Colourless oil; R_f 0.34 (5% ether in pet. ether); ν_{max}(film) 2976, 1735, 1484, 935; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.37 (d, J = 9.9 Hz, 1H), 6.07 (d, J = 16.0 Hz, 1H), 5.95 (dd, J = 16.0, 6.9 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.52-2.42 (m, 1H), 2.10-2.01 (m, 1H), 1.79-1.62 (m, 10H), 1.32-1.10 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 146.4, 141.4, 128.9, 119.6, 60.4, 41.7, 37.4, 32.8, 32.3, 26.1, 25.9, 25.9, 25.5, 14.2; m/z (EI) 290 (M^+, 51%), 262 (7%), 244 (28%), 207 (35%), 179 (25%), 161 (69%), 133 (63%), 91 (100%),; CI-HRMS m/z calcd 291.2324 $[M+1]^+$, found 291.2323.

(2*Z*,3*E*)-Ethyl 2-benzylidene-4-phenylbut-3-enoate (5e)



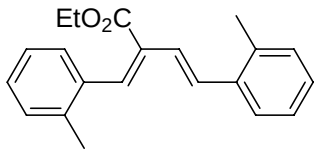
Yellow oil; R_f 0.59 (10% ether in pet. ether); ν_{max}(film) 3024, 2980, 1710, 1233, 1111; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (bs, 1H), 7.46-7.43 (m, 2H), 7.41-7.37 (m, 4H), 7.36-7.31 (m, 3H), 7.30-7.27 (m, 1H) 7.26-7.21 (m, 1H), 7.06 (dd, J = 16.4, 1.0 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 138.7, 137.4, 135.6, 134.7, 130.1, 130.1, 128.6, 128.6, 128.4, 127.8, 126.7, 121.6, 61.0, 14.3; m/z (EI) 278 (M^+, 23%), 231 (14%), 205 (100%), 190 (19%), 128 (18%); EI-HRMS m/z calcd 278.1307 $[M]^+$, found 278.1297.

(2*Z*,3*E*)-Ethyl 2-(4-methoxybenzylidene)-4-(4-methoxyphenyl)but-3-enoate (5f)



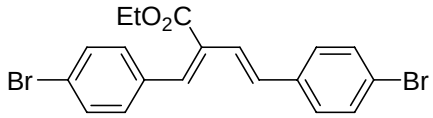
Yellow solid; R_f 0.10 (10% ether in pet. ether); mp. 103-105 ºC (pet.ether/ether); ν_{max}(film) 2935, 1706, 1603, 1508, 1249, 1173; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 1H), 7.45-7.42 (m, 2H), 7.38-7.36 (m, 2H), 7.22 (d, J = 16.4, 1H), 6.95-6.85 (m, 5H), 4.34 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 159.9, 159.4, 137.9, 133.7, 131.8, 130.5, 128.4, 128.4, 127.8, 120.0, 114.1, 113.9, 60.9, 55.3, 55.3, 14.3; m/z (EI) 338 (M^+, 56%), 265 (100%), 250 (18%), 84 (53%); EI-HRMS m/z calcd 338.1518 $[M]^+$, found 338.1513.

(2*Z*,3*E*)-Ethyl 2-(2-methylbenzylidene)-4-*o*-tolylbut-3-enoate (5g)



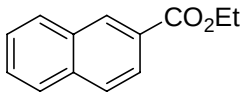
Yellow oil; R_f 0.20 (5% ether in pet. ether); ν_{max}(neat) 2980, 1710, 1483, 1469, 1236; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.48 (d, J =16.4 Hz, 1H), 7.40-7.32 (m, 2H), 7.29-7.19 (m, 3H), 7.17-7.11 (m, 3H), 6.82 (dd, J = 16.4, 1.0 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2H), 2.36 (s, 3H), 2.34 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 138.3, 137.1, 136.5, 136.1, 134.8, 132.1, 130.9, 130.3, 130.2, 129.9, 128.5, 127.7, 126.1, 125.6, 125.0, 122.7, 61.0, 20.1, 19.8, 14.3; m/z (EI) 306 (M^+, 19%), 259 (9%), 245, (11%), 233 (100%), 218 (52%), 202 (36%); EI-HRMS m/z calcd 306.1620 $[M]^+$, found 306.1611.

(2*Z*,3*E*)-Ethyl 2-(4-bromobenzylidene)-4-(4-bromophenyl)but-3-enoate (5h)



White fluffy crystals; R_f 0.40 (5% ether in pet. ether); mp. 126-129 ºC (pet. ether/ether); ν_{max}(film) 3051, 2981, 1723, 1485, 1264, 1210; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.44 (m, 4H), 7.32-7.28 (m, 2H), 7.22-7.18 (m, 2H), 6.84 (dd, J = 16.1, 0.7 Hz, 1H), 6.68 (s, 1H), 6.59 (d, J = 16.1 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 135.5, 134.6, 134.3, 131.9, 131.8, 131.7, 130.3, 129.7, 128.1, 127.7, 122.5, 122.0, 61.6, 14.0; m/z (EI) 438/436/434 ($^{81,81}M^+/^{81,79}M^+/^{79,79}M^+$, 7%/14%/7%), 326/328 (11%/11%), 282/284 (83%/81%), 202 (100%); EI-HRMS m/z calcd 433.9517 M^+, found 433.9522.

Naphthalene-2-carboxylic acid ethyl ester (5i)

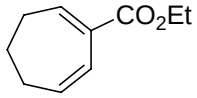


To a solution of ethyl acrylate (65 μL, 0.8 mmol), phthaldialdehyde (67 mg, 0.5 mmol) and $Ti(O^iPr)_4$ (296 μL, 1.00 mmol) in DCM (2 mL) under nitrogen was added PBu_3 (250 μL, 1.00 mmol) dropwise. The mixture was stirred over night (15 hours) and the solvent removed *in vacuo*. Purification by column chromatography gave **5i** (20 mg, 20%).

Colourless oil; R_f 0.58 (10% ether in pet. ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.07 (dd, J = 8.6, 1.7 Hz, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 8.5 Hz, 2H), 7.52-7.26 (m, 2H), 4.45 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

166.8, 135.6, 132.6, 130.9, 129.3, 128.1, 128.1, 127.9, 127.8, 126.6, 125.3, 61.0, 14.4. Analytical data were in accordance with literature data.[5]

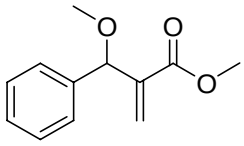
(1*E*,6*Z*)-Ethyl cyclohepta-1,6-dienecarboxylate (5j)



To a solution of ethyl acrylate (110 μL, 1.00 mmol), glutaraldehyde (472 μL, 5.00 mmol) and $Ti(O^iPr)_4$ (586 μL, 2.00 mmol) in DCM (30 mL) under nitrogen was added PBu_3 (500 μL, 2.00 mmol) dropwise. The mixture was stirred over night (15 hours) and the solvent removed *in vacuo*. Purification by column chromatography gave **5j** (85 mg, 43%).

Colourless oil; R_f 0.60 (10% ether in pet. ether); ν_{max}(film) 2930, 1708, 1252, 1211, 1046; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (bt, J = 6.0 Hz, 1H), 6.36 (dq, J = 12.1, 1.4 Hz, 1H), 5.97 (bdt, J = 12.1, 5.3 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.44 (app. q, J = 5.9 Hz, 2H), 2.34 (app. q, J = 5.3 Hz, 2H), 1.87 (app. p, J = 5.9 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 143.6, 134.7, 129.8, 123.0, 60.7, 36.2, 31.5, 30.8, 14.3; m/z (EI) 166 (M^+, 30%), 138 (12%), 121 (14%), 91 (100%); EI-HRMS m/z calcd 166.0994 $[M]^+$, found 166.0990.

Methyl 2-(methoxy(phenyl)methyl)acrylate (6)



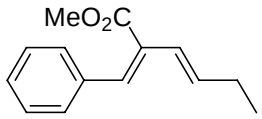
To a solution of methyl acrylate (180 μL, 2.00 mmol) and dimethyl sulphide (300 μL, 4.00 mmol) in DCM under nitrogen at -50 ºC was added TMSOTf (450 μL, 2.40 mmol) and the mixture allowed to reach RT and stirred 30 minutes. The reaction mixture was the cooled to -50 ºC again and a solution of benzaldehyde dimethyl acetal (152 mg, 1.00 mmol) in DCM (2 mL) was added followed by $BF_3{\cdot}OEt_2$ (250 μL, 2.00 mmol). The reaction was allowed to reach RT and stirred over night (15 hours) and then DBU (450 μL, 3.00 mmol) was added. The reaction mixture was diluted with DCM (10 mL) and quenched with 1M HCl. The organic layer was washed successively with 1M HCl, sat. $NaHCO_3$ and brine. Purification by column chromatography afforded **6** (176 mg, 85%).

Colourless oil; R_f 0.32 (5% ether in pet. ether); ν_{max}(film) 2951, 1720, 1438, 1142, 1092; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.27 (m, 5H), 6.34 (dd, J = 1.5, 1.0 Hz, 1H), 5.94 (app. t, J = 1.5 Hz, 1H), 5.14 (bs, 1H), 3.71 (s, 3H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 141.1, 139.5, 128.3, 127.5, 124.9, 80.9, 57.0, 51.8; m/z (EI) 206 (M^+, 23%), 191 (91%), 159 (44%), 146 (25%), 121 (100%), 105 (80%); EI-HRMS m/z calcd 206.0943 $[M]^+$, found 206.0938.

General procedure for compound **7a**-**7e**:

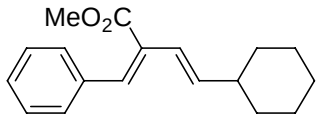
To a solution of methyl 2-(methoxy(phenyl)methyl)acrylate (**6**) (103 mg, 0.50 mmol) and aldehyde (0.50 mmol) in THF (2 mL) under nitrogen was added PBu_3 (150 μL, 0.60 mmol) dropwise. The solution was stirred over night (15 hours), and the solvent removed *in vacuo*. Purification by column chromatography gave **7a**-**7e**.

(2*Z*,3*E*)-Methyl 2-benzylidenehex-3-enoate (7a)



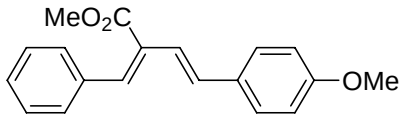
Colourless oil; R_f 0.32 (5% ether in pet. ether); ν_{max}(film) 2964, 1713, 1434, 1233; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.30 (m, 6H), 6.34-6.31 (m, 2H), 3.84 (s, 3H), 2.22-2.15 (m, 2H), 1.04 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 139.4, 136.9, 135.6, 130.3, 129.9, 128.3, 128.2, 121.7, 51.9, 26.6, 13.1; m/z (EI) 216 (M^+, 38%), 187 (37%), 157 (65%), 141 (69%), 129 (100%), 115 (93%), 91 (41%); EI-HRMS m/z calcd 216.1150 $[M]^+$, found 216.1141.

(2*Z*,3*E*)-Methyl 2-benzylidene-4-cyclohexylbut-3-enoate (7b)



Colourless oil; R_f 0.42 (5% ether in pet. ether); ν_{max}(neat) 2922, 1716, 1447, 1241; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.44-7.41 (m, 2H), 7.11-7.07 (m, 2H), 7.03-6.98 (m, 1H), 6.57 (dd, J = 16.1 Hz, J = 6.7 Hz, 1H), 6.48 (d, J = 16.1 Hz, 1H), 3.55 (s, 3H), 2.05-1.96 (m, 1H), 1.79-1.55 (m, 5H), 1.25-1.07 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 143.6, 137.0, 135.8, 130.6, 130.1, 128.5, 128.4, 120.3, 52.1, 41.8, 32.6, 26.3, 26.1; m/z (EI) 270 (M^+, 25%), 238 (11%), 211 (19%), 179 (60%), 129 (100%), 91 (69%); EI-HRMS m/z calcd 270.1620 $[M]^+$, found 270.1613.

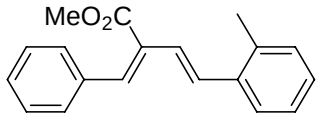
(2*Z*,3*E*)-Methyl 2-benzylidene-4-(4-methoxyphenyl)but-3-enoate (7c)



Yellow oil; R_f 0.14 (10% ether in pet. ether); ν_{max}(neat) 2950, 1716, 1603, 1510, 1240; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 2H), 7.49-7.35 (m, 6H), 7.25 (d, J = 16.4 Hz, 1H), 6.96 (dd, J = 16.4, 1.0 Hz, 1H), 6.90-6.86 (m, 2H), 3.91 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz,

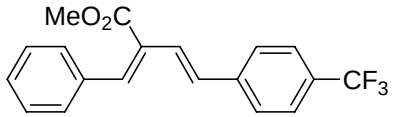
$CDCl_3$): δ 168.1, 159.5, 138.0, 135.7, 134.3, 130.2, 130.1, 130.0, 128.5, 128.4, 128.0, 119.5, 114.1, 55.3, 52.1; m/z (EI) 294 (M^+, 25%), 261 (7%), 235 (100%), 220 (42%), 203 (29%); EI-HRMS m/z calcd 294.1256 $[M]^+$, found 294.1249.

(2*Z*,3*E*)-Methyl 2-benzylidene-4-*o*-tolylbut-3-enoate (7d)



Yellow oil; R_f 0.44 (10% ether in pet. ether); ν_{max}(film) 2949, 1715, 1433, 1236; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.52 (d, J = 16.4 Hz, 1H), 7.50-7.34 (m, 6H), 7.19-7.16 (m, 3H), 6.96 (dd, J = 16.4, 1.0 Hz, 1H), 3.92 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 139.1, 136.5, 136.2, 135.6, 132.8, 130.4, 130.1, 130.0, 128.7, 128.5, 127.8, 126.1, 125.1, 122.6, 52.1, 19.8; m/z (EI) 278 (M^+, 16%), 245 (6%), 219 (100%), 204 (53%), 115 (31%); EI-HRMS m/z calcd 278.1307 $[M]^+$, found 278.1298.

(2*Z*,3*E*)-Methyl 2-benzylidene-4-(4-(trifluoromethyl)phenyl)but-3-enoate (7e)



Slightly yellow oil; R_f 0.29 (10% ether in pet. ether); ν_{max}(film) 2953, 1716, 1321, 1241, 1117, 1105, 1065; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.60-7.56 (m, 2H), 7.52-7.48 (m, 2H), 7.46-7.38 (m, 6H), 7.13 (d, J = 16.2 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 140.9, 140.6, 135.2, 133.2, 130.1, 129.5 (q, J = 32 Hz), 129.1, 129.1, 128.6, 126.8, 125.5 (q, J = 4 Hz), 124.1 (q, J = 272 Hz), 124.0, 52.2; m/z (EI) 332 (M^+, 30%), 273 (100%), 233 (70%), 202 (49%); EI-HRMS m/z calcd 332.1024 $[M]^+$, found 332.1017.

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