A quantitative structure–reactivity relationship in decarboxylative Claisen rearrangement reactions of allylic tosylmalonate esters

Donald Craig* and Nikolay K. Slavov

Experimental

General Laboratory Procedures

All reactions were performed under nitrogen unless otherwise stated. Melting points were determined using Stuart Scientific SMP1 melting point apparatus and are uncorrected. Infrared spectra were recorded on Mattson 5000 FTIR and Perkin-Elmer Spectrum RX FT-IR System spectrometers. Proton nuclear magnetic resonance (^{1}H NMR), carbon nuclear magnetic resonance (^{13}C NMR) and fluorine magnetic resonance (^{19}F NMR) spectra were recorded in $CDCl_3$ unless otherwise stated on Bruker AV-400 or Bruker DRX-400 spectrometer. Chemical shifts are in parts per million (ppm) and are referenced relative to the residual proton-containing solvent (^{1}H-NMR: 7.26 ppm for $CDCl_3$; ^{13}C-NMR: 77.0 ppm for $CDCl_3$). For ^{19}F-NMR spectra hexafluorobenzene (–162.9 PPM) was used as an internal standard. Mass spectra (CI) were recorded using Micromass AutoSpec-Q or Micromass Platform II instruments. Elemental analyses were performed at the microanalytical laboratories of the London Metropolitan University. Analytical thin layer chromatography (TLC) was performed on precoated aluminium-backed Merck Kieselgel 60 F_{254} plates. Visualisation was effected with ultraviolet light, potassium permanganate or vanillin as appropriate. Flash column chromatography was performed using BDH (40–63 μm) silica gel unless otherwise stated. Standard solvents were distilled under nitrogen prior to use: Et_2O from sodium–benzophenone ketyl, CH_2Cl_2 from CaH_2, DMSO under reduced pressure from CaH_2, MeOH from magnesium and toluene from sodium. All other solvents were reagent grade. Petrol refers to petroleum ether of the fraction bp 40–60 °C. BSA was purchased from Alfa Aesar Lancaster and distilled prior to use. Potassium acetate was oven-dried at 120 °C for several days prior to use. Microwave-assisted reactions were performed in a Biotage initiator instrument.

General procedure (I) for the preparation of (E)-ethyl 3-(aryl)propenoates

A solution of 4-substituted benzaldehyde (1 equiv.) and carbethoxymethylenetriphenylphosphorane (1 equiv.) in dry DMSO (1 M) was irradiated in the microwave at 120 °C. After completion of the reaction the mixture was poured into water and extracted with ether. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was filtered through silica gel with 25 % EtOAc–petrol and evaporated to give the desired product which was used in the next step without further purification.

(*E*)-Ethyl 3-*p*-tolylpropenoate

General procedure (I) was applied, using 4-methylbenzaldehyde (2.000 g, 16.6 mmol), carbethoxymethylenetriphenylphosphorane (5.783 g, 16.6 mmol) and DMSO (15 mL). The mixture was irradiated for 20 min to give (*E*)-ethyl 3-*p*-tolylpropenoate (2.727 g, 86 %) as a colourless oil, mixed with the *Z*-isomer (*E*:*Z*=93.5:6.5); R_f 0.68 (17 % EtOAc–petrol); ν_{max} (film) 2981, 1712, 1637, 1610, 1571, 1514, 1446, 1413, 1366, 1311, 1269, 1205, 1174, 1117, 1038, 984, 813, 666 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.66 (1H, d, *J* 16.0 Hz, -O(CO)-CH=C*H*-Ar), 7.42 (2H, d, *J* 8.1 Hz, *o*-Ar), 7.19 (2H, d, *J* 8.0 Hz, *m*-Ar), 6.39 (1H, d, *J* 16.0 Hz, -O(CO)-C*H*=CH-Ar), 4.26 (2H, q, *J* 7.1 Hz, -CH_2-CH_3), 2.37 (3H, s,-CH_3), 1.34 (t, 3H, *J* 7.1 Hz, -CH_2-CH_3); δ_C (101 MHz, $CDCl_3$) 167.2 (C=O), 144.6 (-C=C-), 140.6 (4°, Ar), 131.7 (4°, Ar), 129.6 (3°, Ar), 128.0 (3°, Ar), 117.1 (-C=C-), 60.4 (O-CH_2-), 21.4 (-CH_3), 14.3 (H_3C-CH_2-); *m/z* (CI) (%) 49 (11), 83 (28), 145 (11), 191 (25) $[M+H]^+$, 208 (100) $[M+NH_4]^+$, 381 (4) $[2M+NH_4]^+$, 398 (8) $[2M+H]^+$; (*Z*)-ethyl 3-*p*-tolylpropenoate: δ_H (400 MHz, $CDCl_3$) 7.52 (2H, d, *J* 8.1 Hz, *o*-Ar), 7.16 (2H, d, *J* 8.4 Hz, *m*-Ar), 6.90 (1H, d, *J* 12.6 Hz, -O(CO)-CH=C*H*-Ar), 5.89 (1H, d, *J* 12.7 Hz, -O(CO)-C*H*=CH-Ar), 4.18 (2H, q, *J* 7.1 Hz, -CH_2-CH_3), 2.36 (3H, s,-CH_3), 1.26 (3H, t, *J* 7.1 Hz, -CH_2-CH_3); data were in agreement with those previously reported.[1]

(*E*)-Ethyl 3-(4-fluorophenyl)propenoate

General procedure (I) was applied, using 4-fluorobenzaldehyde (2.000 g, 16.1 mmol), carbethoxymethylenetriphenylphosphorane (5.612 g, 16.1 mmol) and DMSO (15 mL). The mixture was irradiated for 10 min to give (*E*)-ethyl 3-(4-fluorophenyl)propenoate (2.742 g, 88 %) as a colourless oil, mixed with the *Z*-isomers (*E*:*Z*=93.0:7.0); R_f 0.70 (17 % EtOAc–petrol); ν_{max} (film) 3073, 3048, 2983, 2939, 2910, 2875, 1712, 1643, 1600, 1511, 1465, 1448, 1415, 1391, 1367, 1315, 1278, 1233, 1197, 1177, 1097, 1037, 1026, 940, 883, 832, 790, 768

cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.65 (1H, d, *J* 16.0 Hz, -O(CO)-CH=C*H*-Ar), 7.51 (2H, dd, *J* 5.4 Hz, *J* 8.7 Hz, *m*-Ar), 7.08 (2H, d, *J* 8.6 Hz, *o*-Ar), 6.39 (1H, d, *J* 16.0 Hz, -O(CO)-C*H*=CH-Ar), 4.26 (2H, q, *J* 7.1 Hz, -CH_2-CH_3), 1.34 (t, 3H, *J* 7.1 Hz, -CH_2-CH_3); δ_C (101 MHz, $CDCl_3$) 166.8 (C=O), 163.8 (d, $^1J_{C\text{-}F}$ 250.9 Hz, 4°, Ar), 143.2 (-C=C-), 130.7 (d, $^4J_{C\text{-}F}$ 2.8 Hz, 4°, Ar) 129.9 (d, $^3J_{C\text{-}F}$ 8.9 Hz, 3°, Ar), 118.0 (-C=C-), 115.9 (d, $^2J_{C\text{-}F}$ 22.2 Hz, 3°, Ar), 60.5 (O-CH_2-), 14.3 (H_3C-CH_2-); *m/z* (CI) (%) 149 (13), 195 (23) $[M+H]^+$, 212 (100) $[M+NH_4]^+$, 229 (10); (*Z*)-ethyl 3-(4-fluorophenyl)propenoate: δ_H (400 MHz, $CDCl_3$) (aromatic hydrogen signals could not be detected because of the strong signals of the *E*-isomer in this range), 6.89 (1H, d, *J* 12.7 Hz, -O(CO)-CH=C*H*-Ar), 5.93 (1H, d, *J* 12.7 Hz, -O(CO)-C*H*=CH-Ar), 4.18 (2H, q, *J* 7.2 Hz, -CH_2-CH_3), 1.26 (3H, t, *J* 7.1 Hz, -CH_2-CH_3); data were in agreement with those previously reported.[2]

(*E*)-Ethyl 3-(4-chlorophenyl)propenoate

General procedure (I) was applied, using 4-chlorobenzaldehyde (2.000 g, 14.2 mmol), carbethoxymethylenetriphenylphosphorane (4.957 g, 14.2 mmol) and DMSO (15 mL). The mixture was irradiated for 10 min to give (*E*)-ethyl 3-(4-chlorophenyl)propenoate (2.780 g, 93 %) as a colourless oil, mixed with the *Z*-isomer (*E*:*Z*=93.5:6.5); R_f 0.73 (17 % EtOAc–petrol); ν_{max} (film) 3067, 3035, 2983, 2941, 2904, 2873, 2360, 2341, 1904, 1712, 1642, 1593, 1568, 1540, 1492, 1465, 1446, 1407, 1392, 1367, 1312, 1270, 1313, 1202, 1178, 1091, 1037, 1015, 982, 945, 882, 823, 748, 726, 687 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.63 (1H, d, *J* 16.0 Hz, -O(CO)-CH=C*H*-Ar), 7.45 (2H, d, *J* 8.5 Hz, *o*-Ar), 7.36 (2H, d, *J* 8.6 Hz, *m*-Ar), 6.41 (1H, d, *J* 16.1 Hz, -O(CO)-C*H*=CH-Ar), 4.27 (2H, q, *J* 7.2 Hz, -CH_2-CH_3), 1.34 (t, 3H, *J* 7.1 Hz, -CH_2-CH_3); δ_C (101 MHz, $CDCl_3$) 166.7 (C=O), 143.1 (-C=C-), 136.1 (4°, Ar), 132.9 (4°, Ar), 129.2 (3°, Ar), 129.1 (3°, Ar), 118.8 (-C=C-), 60.6 (O-CH_2-), 14.3 (H_3C-CH_2-); *m/z* (CI) (%) 165 (17), 199 (10), 210 (14) $[M]^+$, 211 (7) $[M+H]^+$, 228 (100) $[M+NH_4]^+$, 438 (10) $[2M+NH_4]^+$; (*Z*)-ethyl 3-(4-chlorophenyl)propenoate: δ_H (400 MHz, $CDCl_3$) 7.55 (2H, d, *J* 8.6 Hz, *o*-Ar), 7.32 (2H, d, *J* 8.5 Hz, *m*-Ar), 6.88 (1H, d, *J* 12.6 Hz, -O(CO)-CH=C*H*-Ar), 5.96 (1H, d, *J* 12.6 Hz, -O(CO)-C*H*=CH-Ar), 4.18 (2H, q, *J* 7.1 Hz, -CH_2-CH_3), 1.26 (3H, t, *J* 7.1 Hz, -CH_2-CH_3); data were in agreement with those previously reported.[3]

(*E*)-Ethyl 3-(4-bromophenyl)propenoate

General procedure (I) was applied, using 4-bromobenzaldehyde (2.000 g, 10.8 mmol), carbethoxymethylenetriphenylphosphorane (3.766 g, 10.8 mmol) and DMSO (15 mL). The mixture was irradiated for 25 min to give (*E*)-ethyl 3-(4-bromophenyl)propenoate (2.590 g, 94

%) as a colourless oil, mixed with the *Z*-isomers (*E*:*Z*=94.5:5.5), R_f 0.73 (17 % EtOAc–petrol); ν_{max} (film) 3064, 3029, 2981, 2937, 2905, 2865, 1712, 1638, 1587, 1565, 1488, 1466, 1448, 1402, 1366, 1311, 1271, 1252, 1201, 1177, 1108, 1095, 1072, 1037, 1010, 981, 946, 881, 819, 743, 725, 685 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.61 (1H, d, *J* 16.0 Hz, -O(CO)-CH=C*H*-Ar), 7.52 (2H, d, *J* 8.5 Hz, *o*-Ar), 7.38 (2H, d, *J* 8.5 Hz, *m*-Ar), 6.42 (1H, d, *J* 15.9 Hz, -O(CO)-C*H*=CH-Ar), 4.26 (2H, q, *J* 7.2 Hz, -CH_2-CH_3), 1.34 (3H, t, *J* 7.1 Hz, -CH_2-CH_3); δ_C (101 MHz, $CDCl_3$) 166.7 (C=O), 143.2 (-C=C-), 133.3 (4°, Ar), 132.1 (3°, Ar), 129.4 (3°, Ar), 124.4 (4°, Ar), 119.0 (-C=C-), 60.6 (O-CH_2-), 14.3 (H_3C-CH_2-); *m/z* (CI) (%) 102 (11), 147 (12), 194 (100) $[M-Br+NH_4]^+$, 209/211 (20) $[M-OEt]^+$, 254/256 (11) $[M]^+$, 211 (7) $[M+H]^+$, 272/274 (93) $[M+NH_4]^+$, 289/291 (11); (*Z*)-ethyl 3-(4-chlorophenyl)propenoate: δ_H (400 MHz, $CDCl_3$) 7.78 (2H, d, *J* 8.4 Hz, *o*-Ar), 7.71 (2H, d, *J* 8.4 Hz, *m*-Ar), 6.88 (1H, d, *J* 12.7 Hz, -O(CO)-CH=C*H*-Ar), 5.99 (1H, d, *J* 12.5 Hz, -O(CO)-C*H*=CH-Ar), 4.20 (2H, q, *J* 7.1 Hz, -CH_2-CH_3), 1.28 (3H, t, *J* 7.2 Hz, -CH_2-CH_3); data were in agreement with those previously reported.[4]

_E_-4-Cyanocinnamaldehyde

A solution of 4-cyanobenzaldehyde (2.0 g, 15.25 mmol) and (formylmethylene)triphenylphosphorane in 15 mL dry DMSO was irradiated in the microwave at 120 °C for 30 min. After completion of the reaction the mixture was poured in water and extracted with ether. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was filtered through silica gel (25 % EtOAc–petrol), after evaporation of the volatiles it was purified by crystallisation in EtOAc–hexane solution to give *E*-4-cyanocinnamaldehyde (1.17 g, 48 %) as yellow crystalline solid, mixed with the *Z*-isomers (*E*:*Z* = 98:2); mp. 122–124 °C (lit. mp. 132 °C); R_f 0.45 (25 % EtOAc–petrol); ν_{max} (film) 3093, 3071, 3058, 2822, 2721, 2717, 2360, 2342, 2223, 1683, 1625, 1606, 1558, 1544, 1504, 1417, 1392, 1305, 1290, 1253, 1125, 1010, 979, 958, 865, 814, 736, 716 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 9.76 (1H, d, *J* 7.4 Hz, H(CO)-), 7.73 (2H, d, *J* 8.5 Hz, *o*-Ar), 7.67 (2H, d, *J* 8.4 Hz, *m*-Ar), 7.48 (1H, d, *J* 16.1 Hz, -(CO)-CH=C*H*-Ar), 6.78 (1H, dd, *J* 16.0, 7.5 Hz, -(CO)-C*H*=CH-Ar); δ_C (101 MHz, $CDCl_3$) 192.9 (CO), 149.5 (C=C), 138.1 (4°, Ar), 132.8 (3°, Ar), 131.1 (C=C), 128.7 (3°, Ar), 118.1 (CN), 114.2 (4°, Ar); *m/z* (CI) (%) 52 (98), 157 (20) $[M]^+$, 175 (100) $[M+NH_4]^+$, 192 (27), 206 (12); *Z*-4-Cyanocinnamaldehyde: δ_H (400 MHz, $CDCl_3$) 9.66 (1H, d, *J* 7.4 Hz, H(CO)-), (aromatic hydrogen signals could not be detected because of the strong signals of the *E*-isomer in this range), 7.59 (2H, d, *J* 8.4 Hz, *m*-

Ar), 7.04 (1H, d, *J* 15.4 Hz, -(CO)-CH=C*H*-Ar), 6.34 (1H, dd, *J* 15.1, 7.5 Hz, -(CO)-C*H*=CH-Ar); data were in agreement with those previously reported.[5]

General procedure (II) for the preparation of (E)-3-arylprop-2-en-1-ols

To a solution of (*E*)-ethyl 3-(aryl)propenoate (1 equiv.) in dry CH_2Cl_2 (0.3 M) at –55 °C was added slowly DIBAL-H in CH_2Cl_2 (1.0 M, 2.3 equiv.) and the mixture allowed to warm to –40 °C. After stirring for 1 h the reaction mixture was diluted with ether and quenched with Rochelle's salt (1.5 M solution in water). The solution was heated at 40 °C for 15 min and extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in hot hexane and after slow cooling at 0 °C the desired product crystallised.

(*E*)-3-*p*-Tolylprop-2-en-1-ol

General procedure (II) was applied, using (*E*)-ethyl 3-*p*-tolylpropenoate (2.645 g, 13.9 mmol), DIBAL-H (21.31 mL, 31.9 mmol) and CH_2Cl_2 (60 mL). Crystallisation gave (*E*)-3-*p*-tolylprop-2-en-1-ol (1.689 g, 82 %) as colourless crystalline solid; mp. 49–50 °C (lit. mp. 52 °C); ν_{max} (film) 3290, 3276, 3246, 3080, 3047, 3020, 2971, 2946, 2919, 2855, 1512, 1463, 1435, 1415, 1378, 1337, 1316, 1304, 1294, 1269, 1219, 1201, 1182, 1090, 1010, 973, 848, 834, 794, 757, 738, 705, 684, 675, 657, 640 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.29 (2H, d, *J* 8.1 Hz, *m*-Ar), 7.13 (2H, d, *J* 8.0 Hz, *o*-Ar), 6.59 (1H, d, *J* 15.9 Hz, -HC=C*H*-Ar), 6.32 (1H, dt, *J* 15.9, 5.8 Hz, -*H*C=CH-Ar), 4.31 (2H, dd, *J* 5.9, 1.3 Hz, O-CH_2-), 2.34 (3H, s, Ar-CH_3); δ_C (101 MHz, $CDCl_3$) 137.5 (4°, Ar), 133.8 (4°, Ar), 131.1 (3°, Ar), 129.3 (C=C), 127.4 (3°, Ar), 126.3 (C=C), 63.8 (HO-CH_2-), 21.2 (Ar-CH_3); *m/z* (CI) (%) 131 (100) $[M\text{-}OH]^+$, 148 (42) $[M]^+$; data were in agreement with those previously reported.[6]

(*E*)-3-(4-Fluorophenyl)prop-2-en-1-ol

General procedure (II) was applied, using (*E*)-ethyl 3-(4-fluorophenyl)propenoate (2.642 g, 13.6 mmol), DIBAL-H (31.28 mL, 31.28 mmol) and CH_2Cl_2 (50 mL). Crystallisation gave (*E*)-3-(4-fluorophenyl)prop-2-en-1-ol (1.531 g, 74 %) as colourless crystalline solid; mp. 57–58 °C; ν_{max} (film) 3320, 3308, 3070, 3051, 3018, 2934, 2875, 2846, 1600, 1510, 1458, 1412, 1386, 1350, 1311, 1300, 1232, 1197, 1158, 1101, 1088, 1007, 971, 923, 848, 825, 803, 810, 780, 738 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.35 (2H, dd, *J* 8.7, 5.4 Hz, *m*-Ar), 7.01 (2H, t, *J* 8.7 Hz, *o*-Ar), 6.59 (1H, d, *J* 15.9 Hz, -HC=C*H*-Ar), 6.29 (1H, dt, *J* 15.9, 5.7 Hz, -*H*C=C*H*-Ar), 4.32 (2H, dd, *J* 5.7, 1.2 Hz, O-CH_2-); δ_C (101 MHz, $CDCl_3$) 162.3 (d, $^1J_{C\text{-}F}$ 246.6 Hz, 4° Ar), 132.8 (4°, Ar), 129.9 (C=C), 128.2 (C=C), 127.9 (d, $^3J_{C\text{-}F}$ 8.4 Hz, 3° Ar), 115.5 (d, $^2J_{C\text{-}F}$ 21.1 Hz, 3°

Ar), 63.5 (HO-CH_2-); *m/z* (CI) (%) 135 (100) $[M\text{-}OH]^+$, 152 (90) $[M]^+$, 169 (50) $[M\text{-}H+NH_4]^+$; data were in agreement with those previously reported.[6]

(*E*)-3-(4-Chlorophenyl)prop-2-en-1-ol

General procedure (II) was applied, using (*E*)-ethyl 3-(4-chlorophenyl)propenoate (2.694 g, 12.8 mmol), DIBAL-H (29.42 mL, 29.4 mmol) and CH_2Cl_2 (47 mL). Crystallisation gave (*E*)-3-(4-chlorophenyl)prop-2-en-1-ol (1.654 g, 77 %) as colourless crystalline solid; mp. 52–54 °C (lit. mp. 55–56 °C); ν_{max} (film) 3667, 3648, 3626, 3586, 3565, 3335, 3324, 3082, 3052, 3035, 3018, 2929, 2873, 2819, 1491, 1455, 1406, 1350, 1311, 1297, 1266, 1089, 1010, 974, 937, 923, 844, 800, 781, 738, 710, 680, 667, 638, 627 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.30 (4H, d, *J* 4.4 Hz, Ar), 6.58 (1H, d, *J* 15.9 Hz, -HC=C*H*-Ar), 6.34 (1H, dt, *J* 16.0, 5.7 Hz, -*H*C=CH-Ar), 4.33 (2H, dd, *J* 5.5, 1.5 Hz, O-CH_2-); δ_C (101 MHz, $CDCl_3$) 135.1 (4°, Ar), 133.3 (4°, Ar), 129.7 (C=C), 129.1 (C=C), 128.7 (3°, Ar), 127.6 (3°, Ar), 63.5 (HO-CH_2-); *m/z* (CI) (%) 151 (100) $[M\text{-}OH]^+$, 168 (60) $[M]^+$, 185 (5) $[M+NH_4]^+$; data were in agreement with those previously reported.[7]

(*E*)-3-(4-Bromophenyl)prop-2-en-1-ol

General procedure (II) was applied, using (*E*)-ethyl 3-(4-bromophenyl)propenoate (2.523 g, 9.9 mmol), DIBAL-H (22.75 mL, 22.8 mmol) and CH_2Cl_2 (37 mL). Crystallisation gave (*E*)-3-(4-bromophenyl)prop-2-en-1-ol (1.772 g, 84 %) as colourless crystalline solid; mp. 67–68 °C (lit. mp. 68–69 °C); ν_{max} (film) 3347, 3073, 3052, 3034, 3016, 2927, 2871, 2834, 1487, 1454, 1401, 1350, 1265, 1091, 1073, 1014, 973, 922, 840, 798, 779, 741, 703, 692, 644, 626 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.44 (2H, d, *J* 8.5 Hz, *m*-Ar), 7.25 (2H, d, *J* 8.0 Hz, *o*-Ar), 6.56 (1H, d, *J* 15.9 Hz, -HC=C*H*-Ar), 6.36 (1H, dt, *J* 15.8, 5.5 Hz, -*H*C=CH-Ar), 4.32 (2H, dt, *J* 5.7, 1.3 Hz O-CH_2-), 1.47 (1H, t, *J* 5.8 Hz, -OH); δ_C (101 MHz, $CDCl_3$) 135.6 (4º, Ar), 131.7 (3º, Ar), 129.7 (C=C), 129.3 (C=C), 127.9 (3º, Ar), 121.4 (4º, Ar), 63.5 (HO-CH_2-); m/z (CI) (%) 195/197 (20) $[M\text{-}OH]^+$, 212/214 (70) $[M+H]^+$, 229/231 (100) $[M+NH_4]^+$; data were in agreement with those previously reported.[8]

(*E*)-4-(3-Hydroxyprop-1-enyl)benzonitrile

To a solution of 4-cyanocinnamaldehyde (2.420 g, 15.40 mmol) in 200 mL dry MeOH was added $CeCl_3 \cdot 7H_2O$ (5.738 g, 22.79 mmol). The mixture was stirred at rt. until dissolution of the cerium salt and cooled to 0 °C. $NaBH_4$ (1.165 g, 30.8 mmol) was slowly added in small portions. After 35 min the reaction was quenched with 10% NaOH (aq.). The mixture was

filtrated to remove the $Ce(OH)_3$ and extracted with CH_2Cl_2 and ether. The combined organic phases were washed with brine and dried over $MgSO_4$. The solution was concentrated under reduced pressure. The residue was dissolved in hot ether and cooled slowly at 0 °C to crystallise (*E*)-4-(3-hydroxyprop-1-enyl)benzonitrile (1.481 g, 60 %) as yellow crystalline solid; mp. 81–83 °C (lit.[45] mp. 85 °C); ν_{max} (film) 3390, 3300, 3069, 3042, 3004, 2938, 2945, 2871, 2835, 2219, 1652, 1604, 1411, 1340, 1089, 1014, 975, 856, 838, 799, 785, 728, 705, 663, 648 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.60 (2H, d, *J* 8.4 Hz, *o*-Ar), 7.46 (2H, d, *J* 8.3 Hz, *m*-Ar), 6.66 (1H, d, *J* 16.0 Hz, -HC=C*H*-Ar), 6.49 (1H, dt, *J* 16.0, 5.1 Hz, -*H*C=CH-Ar), 4.38 (2H, dd, *J* 5.1, 1.6 Hz, O-CH_2-); δ_C (101 MHz, $CDCl_3$) 141.2 (4°, Ar), 132.6 (-C=*C*-Ar), 132.4 (3°, Ar), 128.7 (-*C*=C-Ar), 126.9 (3°, Ar), 118.9 (CN), 110.7 (4°, Ar), 63.1 (HO-CH_2-); *m/z* (CI) (%) 177 (100) $[M+NH_4]^+$, 194 (20) $[M-H+2NH_4]^+$, 336 (10) $[2M+NH_4]^+$ (Found: $[M+NH_4]^+$, 177.1033. $C_{10}H_9NO$ requires $[M+NH_4]^+$, 177.1028) (Found: C, 75.66; H, 5.71; N, 8.82. $C_{10}H_9NO$ requires C, 75.45; H, 5.70; N, 8.80%).

Preparation of methyl malonate

A mixture of Meldrum's acid (1 equiv.) and methanol (1 equiv.) was heated at 85 °C for 20 h. After evaporation of volatile material the residue was dissolved in water and Na_2CO_3 was added to pH 8.5. The solution was extracted diethyl ether (4 × 70 mL). The aqueous phase was treated with HCl to pH 1.0. The resulting mixture was extracted with diethyl ether (4 × 70 mL), and the organic layers combined and dried ($MgSO_4$). Evaporation of solvent gave methyl malonate (6.615 g, 67 %) as colourless liquid which was used directly in the next step without further purification; ν_{max} (film) 2960, 1747, 1441, 1335, 1209, 1159, 1020, 929, 666 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.79 (3H, s, O-CH_3), 3.45 (2H, s, -(CO)-CH_2-(CO)-); δ_C (101 MHz, $CDCl_3$) 170.9 (-COOH), 167.4 (MeO(CO)-), 52.8 (O-CH_3), 40.4 (-(CO)*C*H_2COOH); *m/z* (CI) (%) 136 (100) $[M+NH_4]^+$, 174 (17), 254 (23) $[2M+NH_4]^+$; data were in agreement with those previously reported.[9]

General procedure (III) for preparation of allylic malonate esters

To a solution of methyl malonate (1 equiv.), allylic (cinnamyl) alcohol (1 equiv.) and 4-dimethylaminopyridine (0.1 equiv.) in CH_2Cl_2 were added at 15 °C 1,3-dicyclohexylcarbodiimide (1 equiv.). After 60 min irradiation at 70 °C in the microwave the mixture was filtered through Celite and the residue washed with brine. The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography on silica gel of the residue gave allylic malonate esters.

Cinnamyl methyl malonate

General procedure (III) was applied, using (*E*)-3-phenylprop-2-en-1-ol (1.700 g, 12.7 mmol), methyl malonate (1.663 g, 12.7 mmol), DCC (2.614 g, 12.7 mmol), DMAP (155 mg, 1.3 mmol) and CH_2Cl_2 (14.9 mL). Chromatography (22 % EtOAc–petrol) gave cinnamyl methyl malonate (2.335 g, 79 %) as yellow liquid; R_f 0.50 (22 % EtOAc–petrol); ν_{max} (film) 3081, 3056, 3027, 3005, 2955, 2891, 2855, 1753, 1715, 1659, 1601, 1578, 1494, 1439, 1411, 1379, 1335, 1272, 1204, 1151, 1063, 1019, 970, 914, 848, 837, 797, 786, 747, 694 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.32 (5H, ddd, *J* 18.0, 15.9, 7.1 Hz, -Ph), 6.67 (1H, d, *J* 15.9 Hz, -CH=C*H*-Ph), 6.28 (1H, dt, *J* 15.9, 6.5 Hz, -C*H*=CH-Ph), 4.81 (2H, dd, 6.5, 1.1 Hz, -OCH_2-), 3.76 (3H, s, -OCH_3), 3.44 (2H, s, -(CO)-CH_2-(CO)-); δ_C (101 MHz, $CDCl_3$) 166.9 (MeO(*C*O)-), 166.3 (-*C*$OOCH_2$-), 136.0 (4°, -Ph), 134.8 (-C=*C*-Ph), 128.6 (3°, *m*-Ph), 128.2 (3°, *p*-Ph), 126.7 (3°, *o*-Ph), 122.4 (-*C*=C-Ph), 66.1 (-O-CH_2-), 52.6 (O-CH_3), 41.3 (-(CO)*C*H_2COOCH_2-); *m/z* (CI) (%) 117 (43), 134 (40), 252 (100) $[M+NH_4]^+$, 368 (60), 486 (3) $[2M+NH_4]^+$; data were in agreement with those previously reported.[10]

(*E*)-3-(4-Methoxyphenyl)-2-propenyl methyl malonate

General procedure (III) was applied, using (*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol (1.725 g, 10.5 mmol), methyl malonate (1.241 g, 10.5 mmol), DCC (2.169 g, 10.5 mmol), DMAP (128 mg, 1.1 mmol) and CH_2Cl_2 (12.4 mL). Chromatography (25 % EtOAc–petrol) gave (*E*)-3-(4-methoxyphenyl)-2-propenyl methyl malonate (2.254 g, 81 %) as colourless liquid; R_f 0.63 (25 % EtOAc–petrol); ν_{max} (film) 3649, 3636, 3582, 3553, 3529, 3507, 3463, 3144, 3122, 3033, 3003, 2954, 2915, 2838, 2553, 2051, 2000, 1887, 1739, 1662, 1612, 1577, 1513, 1453, 1431, 1419, 1407, 1379, 1334, 1305, 1203, 1205, 1176, 1151, 1062, 1029, 987, 908, 846, 815, 757, 686 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.33 (2H, d, *J* 8.7 Hz, *o*-Ar), 6.86 (2H, d, *J* 8.8 Hz, *m*-Ar), 6.62 (1H, d, *J* 15.8 Hz, -CH=C*H*-Ph), 6.14 (1H, dt, *J* 15.8, 6.7 Hz, -C*H*=CH-Ph), 4.78 (2H, dd, *J* 6.7, 0.9 Hz, -OCH_2-), 3.81 (3H, s, Ar-OMe), 3.76 (3H, s, -(CO)-OCH_3), 3.43 (2H, s, -(CO)-CH_2-(CO)-); δ_C (101 MHz, $CDCl_3$) 166.9 (MeO(*C*O)-), 166.3 (-*C*$OOCH_2$-), 159.7 (4°, Ar-O-), 134.6 (-C=*C*-Ar), 128.8 (4°, -A*r*), 127.9 (3°, *m*-Ar), 120.0 (3°, *o*-Ar), 114.0 (-*C*=C-Ar), 66.4 (-O-CH_2-), 55.3 (-Ar-OCH_3), 52.5 (O-CH_3), 41.4 (-(CO)*C*H_2COOCH_2-); *m/z* (CI) (%) 147 (100), 264 (7) $[M]^+$, 282 (5) $[M+NH_4]^+$ (Found: $[M+NH_4]^+$, 264.1007. $C_{14}H_{16}O_5$ requires $[M+NH_4]^+$, 270.0998) (Found: C, 63.77; H, 6.28. $C_{14}H_{16}O_5$ requires C, 63.63; H, 6.10%).

(*E*)-Methyl 3-*p*-tolyl-2-propenyl malonate

General procedure (III) was applied, using (*E*)-3-*p*-tolylprop-2-en-1-ol (1.465 g, 9.9 mmol), methyl malonate (1.168 g, 9.9 mmol), DCC (2.041 g, 9.9 mmol), DMAP (121 mg, 1.0 mmol) and CH_2Cl_2 (11.6 mL). Chromatography (22 % EtOAc–petrol) gave (*E*)-methyl 3-*p*-tolyl-2-propenyl malonate (2.005 g, 81 %) as colourless liquid; R_f 0.45 (22 % EtOAc–petrol); ν_{max} (film) 3649, 3640, 3637, 3555, 3539, 3506, 3470, 3126, 3085, 3024, 3004, 2953, 2977, 2885, 1905, 1754, 1737, 1656, 1612, 1571, 1513, 1438, 1412, 1378, 1334, 1272, 1318, 1151, 1064, 1019, 971, 907, 846, 794, 686 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.29 (2H, d, *J* 8.1 Hz, *m*-Ar), 7.14 (2H, d, *J* 8.0 Hz, -*o*-Ar), 6.64 (1H, d, *J* 15.9 Hz, -CH=C*H*-Ph), 6.23 (1H, dt, *J* 15.8, 6.6 Hz, -C*H*=CH-Ph), 4.79 (2H, dd, *J* 6.7, 0.9 Hz, -OCH_2-), 3.76 (3H, s, -OCH_3), 3.43 (2H, s, -(CO)-CH_2-(CO)-), 2.34 (1H, s, Ar-CH_3); δ_C (101 MHz, $CDCl_3$) 166.9 (MeO(*C*O)-), 166.3 (-*C*OOCH_2-), 138.1 (4°, *p*-Ar), 134.9 (-C=*C*-Ar), 133.2 (4°, -A*r*), 129.3 (3°, *m*-Ar), 126.6 (3°, *o*-Ar), 121.2 (-*C*=C-Ar), 66.3 (-O-CH_2-), 52.6 (O-CH_3), 41.3 (-(CO)*C*H_2COOCH_2-), 21.2 (-Ar-CH_3); *m/z* (CI) (%) 131 (100), 148 (29), 248 (11) $[M]^+$, 261 (32), 266 (30) $[M+NH_4]^+$, 396 (27), 514 (5) $[2M+NH_4]^+$ (Found: $[M+NH_4]^+$, 266.1400. $C_{14}H_{16}O_4$ requires $[M+NH_4]^+$, 266.1392) (Found: C, 67.81; H, 6.59. $C_{14}H_{16}O_4$ requires C, 67.73; H, 6.50%).

(*E*)-3-(4-Fluorophenyl)-2-propenyl methyl malonate

General procedure (III) was applied, using (*E*)-3-(4-fluorophenyl)prop-2-en-1-ol (1.470 g, 9.6 mmol), methyl malonate (1.141 g, 9.6 mmol), DCC (1.993 g, 9.6 mmol), DMAP (118 mg, 1.0 mmol) and CH_2Cl_2 (11.4 mL). Chromatography (22 % EtOAc–petrol) gave (*E*)-3-(4-fluorophenyl)-2-propenyl methyl malonate (2.015 g, 82 %) as colourless liquid; R_f 0.41 (22 % EtOAc–petrol); ν_{max} (film) 3646, 3617, 3564, 3548, 3539, 3528, 3505, 3471, 3110, 3072, 3040, 3004, 2954, 2888, 2852, 1754, 1742, 1658, 1601, 1557, 1509, 1439, 1413, 1379, 1336, 1299, 1272, 1228, 1205, 1155, 1096, 1065, 1018, 971, 908, 850, 811, 771, 722 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.36 (2H, d, *J* 8.7, 5.4 Hz, *m*-Ar), 7.02 (2H, d, *J* 8.7 Hz, *o*-Ar), 6.64 (1H, d, *J* 15.9 Hz, -CH=C*H*-Ph), 6.19 (1H, dt, *J* 15.9, 6.5 Hz, -C*H*=CH-Ph), 4.79 (2H, dd, *J* 6.5, 1.1 Hz, -OCH_2-), 3.76 (3H, s, -OCH_3), 3.44 (2H, s, -(CO)-CH_2-(CO)-); δ_F (376 MHz, $CDCl_3$) 114.63 (1F, bs); δ_C (101 MHz, $CDCl_3$) 166.9 (MeO(*C*O)-), 166.3 (-*C*OOCH_2-), 162.3 (d, $^1J_{C\text{-}F}$ 247.3 Hz, 4º Ar), 133.7 (-C=*C*-Ar), 132.2 (d, $^4J_{C\text{-}F}$ 3.7 Hz, 4º Ar), 128.2 (d, $^3J_{C\text{-}F}$ 8.2 Hz, 3º Ar), 122.1 (-*C*=C-Ar), 115.6 (d, $^2J_{C\text{-}F}$ 22.1 Hz, 3º Ar), 66.0 (-O-CH_2-), 52.6 (O-CH_3), 41.3 (-(CO)*C*H_2COOCH_2-); *m/z* (CI) (%) 135 (100), 152 (62), 169 (14), 270 (82) $[M+NH_4]^+$, 404 (65) $[2M]^+$ (Found: $[M+NH_4]^+$, 270.1149, $C_{13}H_{13}FO_4$ requires $[M+NH_4]^+$, 270.1142) (Found: C, 61.92; H, 5.07. $C_{13}H_{13}FO_4$ requires C, 61.90; H, 5.19%).

(*E*)-3-(4-Chlorophenyl)-2-propenyl methyl malonate

General procedure (III) was applied, using (*E*)-3-(4-chlorophenyl)prop-2-en-1-ol (1.627 g, 9.7 mmol), methyl malonate (1.139 g, 9.7 mmol), DCC (1.991 g, 9.7 mmol), DMAP (118 mg, 1.0 mmol) and CH_2Cl_2 (11.4 mL). Chromatography (22 % EtOAc–petrol) gave (*E*)-3-(4-chlorophenyl)-2-propenyl methyl malonate (2.305 g, 89 %) as colourless liquid; R_f 0.42 (22 % EtOAc–petrol); ν_{max} (film) 3655, 3645, 3554, 3528, 3471, 3452, 3028, 3004, 2954, 2705, 2842, 1754, 1739, 1660, 1594, 1492, 1438, 1408, 1378, 1336, 1274, 1203, 1151, 1092, 1066, 1008, 964, 907, 848, 800, 675 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.30 (4H, m, *J* 2.6 Hz, Ar), 6.62 (1H, d, *J* 15.9 Hz, -CH=C*H*-Ph), 6.25 (1H, dt, *J* 15.9, 6.4 Hz, -C*H*=CH-Ph), 4.80 (2H, dd, *J* 6.4, 1.2 Hz, -OCH_2-), 3.76 (3H, s, -(CO)-OCH_3), 3.44 (2H, s, -(CO)-CH_2-(CO)-); δ_C (101 MHz, $CDCl_3$) 166.9 (MeO(*C*O)-), 166.2 (-*C*$OOCH_2$-), 134.5 (4°, Ar-Cl), 133.9 (4°, -A*r*), 133.4 (-C=*C*-Ar), 128.8 (3°, *m*-Ar), 127.8 (3°, *o*-Ar), 123.1 (-*C*=C-Ar), 65.8 (-O-CH_2-), 52.6 (O-CH_3), 41.3 (-(CO)*C*H_2COOCH_2-); *m/z* (CI) (%) 151 (50), 168 (40), 185 (20), 286 (100) $[M+NH_4]^+$, 436 (60), 554 (37) $[2M+NH_4]^+$ (Found: $[M+NH_4]^+$, 286.0843. $C_{13}H_{13}ClO_4$ requires $[M+NH_4]^+$, 286.0846) (Found: C, 58.02; H, 4.83. $C_{13}H_{13}ClO_4$ requires C, 58.11; H, 4.88%).

(*E*)-3-(4-Bromophenyl)-2-propenyl methyl malonate

General procedure (III) was applied, using (*E*)-3-(4-bromophenyl)prop-2-en-1-ol (1.713 g, 8.0 mmol), methyl malonate (0.949 g, 8.0 mmol), DCC (1.659 g, 8.0 mmol), DMAP (98 mg, 0.8 mmol) and CH_2Cl_2 (9.5 mL). Chromatography (22 % EtOAc–petrol) gave (*E*)-3-(4-bromophenyl)-2-propenyl methyl malonate (2.080 g, 83 %) as colourless liquid; R_f 0.43 (22 % EtOAc–petrol); ν_{max} (film) 3648, 3633, 3565, 3554, 3527, 3506, 3471, 3462, 3026, 3003, 2953, 2885, 2846, 1754, 1741, 1660, 1588, 1487, 1406, 1405, 1377, 1335, 1274, 1203, 1150, 1071, 1003, 942, 907, 846, 762, 688, 653 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.45 (2H, d, *J* 8.5 Hz, *m*-Ar), 7.25 (2H, d, *J* 8.0 Hz, *o*-Ar), 6.61 (1H, d, *J* 16.0 Hz, -CH=C*H*-Ph), 6.26 (1H, dt, *J* 15.8, 6.4 Hz, -C*H*=CH-Ph), 4.79 (2H, dd, *J* 6.4, 1.2 Hz, -OCH_2-), 3.76 (3H, s, -(CO)-OCH_3), 3.44 (2H, s, -(CO)-CH_2-(CO)-); δ_C (101 MHz, $CDCl_3$) 166.9 (MeO(*C*O)-), 166.2 (-*C*$OOCH_2$-), 134.9 (4°, Ar), 133.4 (-C=*C*-Ar), 131.8 (3°, *o*-Ar), 128.1 (3°, *m*-Ar), 123.2 (-*C*=C-Ar), 122.0 (4°, -A*r*), 65.8 (-O-CH_2-), 52.6 (O-CH_3), 41.3 (-(CO)*C*H_2COOCH_2-); *m/z* (CI) (%)195 (23), 212 (25), 229 (24), 332 (100) $[M+NH_4]^+$, 526 (60), 644 (57) $[2M+NH_4]^+$ (Found: $[M+NH_4]^+$, 330.0338, 332.0319. $C_{13}H_{13}{}^{79}BrO_4$, $C_{13}H_{13}{}^{81}BrO_4$, requires $[M+NH_4]^+$, 330.0341, 332.0320) (Found: C, 49.93; H, 4.20. $C_{13}H_{13}BrO_4$ requires C, 49.86; H, 4.18%).

(*E*)-3-(4-Cyanophenyl)-2-propenyl methyl malonate

General procedure (III) was applied, using (*E*)-4-(3-hydroxyprop-1-enyl) benzonitrile (1.395 g, 8.8 mmol), methyl malonate (1.035 g, 8.8 mmol), DCC (1.807 g, 8.8 mmol), DMAP (107 mg, 0.9 mmol) and CH_2Cl_2 (10.3 mL). Chromatography (36 % EtOAc–petrol) gave (*E*)-3-(4-cyanophenyl)-2-propenyl methyl malonate (1.888 g, 83 %) as colourless liquid; R_f 0.51 (36 % EtOAc–petrol); ν_{max} (film) 3677, 3649, 3628, 3621, 3552, 3091, 3037, 3002, 2954, 2229, 1754, 1711, 1658, 1629, 1605, 1504, 1438, 1413, 1380, 1336, 1305, 1275, 1203, 1176, 1150, 1066, 1018, 976, 908, 856, 807, 684 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.61 (2H, d, *J* 8.4 Hz, *m*-Ar), 7.47 (2H, d, *J* 8.3 Hz, *o*-Ar), 6.68 (1H, d, *J* 16.0 Hz, -CH=C*H*-Ar), 6.39 (1H, dt, *J* 15.9, 6.0 Hz, -C*H*=CH-Ar), 4.84 (2H, dd *J* 6.1, 1.3 Hz, -OCH_2-), 3.76 (3H, s, -(CO)-OCH_3), 3.45 (2H, s, -(CO)-CH_2-(CO)-); δ_C (101 MHz, $CDCl_3$) 166.8 (MeO(*C*O)-), 166.1 (-*C*$OOCH_2$-), 140.5 (4°, Ar), 132.5 (3°, *m*-Ar), 132.3 (-C=*C*-Ar), 127.1 (3°, *o*-Ar), 126.5 (-*C*=C-Ar), 118.7 (4°, Ar-CN), 111.5 (4°, -A*r*), 65.3 (-O-CH_2-), 52.6 (O-CH_3), 41.2 (-(CO)*C*H_2-$COOCH_2$-); *m/z* (CI) (%) 277 (100) $[M+NH_4]^+$ (Found: $[M+NH_4]^+$, 277.1190. $C_{14}H_{13}NO_4$ requires $[M+NH_4]^+$, 277.1188) (Found: C, 64.82; H, 4.85; N, 5.28. $C_{14}H_{13}NO_4$ requires C, 64.86; H, 5.05; N, 5.40%).

*General procedure (IV) for preparation of allylic methyl 2-(toluene-4-sulfonyl) malonates **1***

To a solution of the allylic methyl malonate (2 equiv.) in dry DMSO (2 M) was added slowly at room temperature and under nitrogen solid potassium *tert*-butoxide (2 equiv.). The mixture was stirred for 20 min until the *t*BuOK dissolved and toluene-4-sulfonyl fluoride (1 equiv.) was added. After 23 h of stirring at rt, the mixture was poured into aqueous HCl (10 %) and extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography on silica gel gave recovered excess allylic methyl malonates, followed by the desired allylic methyl (toluene-4-sulfonyl)malonates **1**. Yields cited for the products are based on tosyl fluoride; yields cited for recovered starting material are calculated from the total recoverable amount based on the yield of product and of consumed starting material. For example, a 66 % yield of the product means that the maximum recoverable amount of the starting material is (2 – 0.66) = 1.34 equiv.; 70 % recovery means that (0.70 x 1.34 = 0.94 equiv.) of the allylic malonate ester was recovered.

Cinnamyl methyl 2-tosylmalonate (1a)

General procedure (IV) was applied, using cinnamyl methyl malonate (2.266 g, 9.7 mmol), toluene-4-sulfonyl fluoride (843 mg, 4.8 mmol), potassium *tert*-butoxide (1.085 g, 9.7 mmol) and DMSO (4.84 mL). Chromatography (25 % EtOAc–petrol) gave cinnamyl 3-methyl 2-tosylmalonate **1a** (1.239 g, 66 %) as a colourless gum; Also isolated was unreacted starting material (1.058 g, 70 % recovery); **1a:** R_f 0.47 (25 % EtOAc–petrol); ν_{max} (film) 4069, 3647, 3469, 3058, 3028, 2954, 1745, 1659, 1597, 1494, 1449, 1436, 1403, 1379, 1337, 1269, 1181, 1150, 1083, 1019, 969, 926, 849, 816, 739, 706, 673, 641, 566, 515 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.85 (2H, d, *J* 8.3 Hz, *o*-Ts), 7.34 (7H, m, -Ph, *m*-Ts), 6.64 (1H, d, 15.9 Hz, -CH=C*H*-Ph), 6.17(1H, dt, *J* 15.9, 6.5 Hz, -C*H*=CH-Ph), 5.01 (1H, s, -(CO)-CH(Ts)-(CO)-), 4.82 (2H, ddd, *J* 6.5, 3.9, 1.1 Hz, -OCH_2-), 3.80 (3H, s, -(CO)-OCH_3), 2.39 (3H, s, -CH_3 (Ts)); δ_C (101 MHz, $CDCl_3$) 161.4 (MeO(*C*O)-), 160.8 (-*C*$OOCH_2$-), 146.1 (4°, Ar-Me (Ts)), 135.8 (4°, Ar-SO_2-), 135.7 (-C=*C*-Ph), 134.1 (4°, Ph), 130.2 (*m*-Ar (Ts)), 129.5 (*m*-Ph), 128.7 (*o*-Ar (Ts)), 128.4 (3°, *p*-Ph), 126.7 (3°, *o*-Ph) 121.2 (-*C*=C-Ph), 74.5 (-(CO)*C*H(Ts)$COOCH_2$-), 67.5 (-O-CH_2-), 53.7 (O-CH_3), 21.7 (-CH_3 (Ts)); *m/z* (CI) (%) 117 (37), 134 (34), 246 (30), 289 (12), 304 (87), 406 (100) $[M+NH_4]^+$, 522 (28), 590 (7), 692 (15), 794 (23) $[2M+NH_4]^+$; data were in agreement with those previously reported.[10]

(*E*)-(3-(4-Methoxyphenyl)-2-propenyl) methyl 2-tosylmalonate

General procedure (IV) was applied, using (*E*)-3-(4-methoxyphenyl)-2-propenyl methyl malonate (2.086 g, 7.9 mmol), toluene-4-sulfonyl fluoride (688 mg, 4.0 mmol), potassium *tert*-butoxide (878 mg, 7.9 mmol) and DMSO (3.95 mL). Chromatography (25 % EtOAc–petrol) gave (*E*)-1-(3-(4-methoxyphenyl)-2-propenyl) 3-methyl 2-tosylmalonate (1.020 g, 62 %) as a colourless gum; also isolated was unreacted starting material (0.747 g, 52 % recovery); (*E*)-(3-(4-methoxyphenyl)-2-propenyl) methyl 2-tosylmalonate: R_f 0.25 (25 % EtOAc–petrol); ν_{max} (film) 2956, 2839, 2360, 1744, 1654, 1607, 1577, 1513, 1438, 1377, 1336, 1251, 1176, 1150, 1083, 1031, 970, 844, 815, 736, 706, 671, 640 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.84 (2H, d, *J* 8.4 Hz, *o*-Ts), 7.29 (4H, m, *m*-Ar, *m*-Ts), 6.87 (2H, d, *J* 8.7 Hz, *o*-Ar), 6.58 (1H, d, *J* 15.9 Hz, -CH=C*H*-Ar), 6.03 (1H, dt, *J* 15.9, 6.8 Hz, -C*H*=CH-Ar), 5.01 (1H, s, -(CO)-CH(Ts)-(CO)-), 4.78 (2H, ddd, *J* 6.8, 4.0, 0.9 Hz, -OCH_2-), 3.81 (3H, s, -(CO)-OCH_3), 3.79 (3H, s, -OMe (Ar)), 2.39 (3H, s, -CH_3 (Ts)); δ_C (101 MHz, $CDCl_3$) 161.4 (MeO(*C*O)-), 160.8 (-*C*$OOCH_2$-), 159.8 (4°, Ar), 146.0 (4°, Ar-Me (Ts)), 135.6 (-C=*C*-Ar), 134.0 (4°, Ar-SO_2-), 130.1 (3°, *m*-Ar (Ts)), 129.5 (3°, *o*-Ar (Ts)), 128.5 (4°, Ar), 128.0 (3°, *o*-Ar), 118.9 (-*C*=C-Ar), 114.0 (3°, *m*-Ar), 74.4 (-(CO)*C*H(Ts)$COOCH_2$-), 67.8 (-O-CH_2-), 55.3 (Ar-

OCH_3), 53.7 (O-CH_3), 21.7 (-CH_3 (Ts)); *m/z* (CI) (%) 147 (97), 246 (100), 289 (50), 304 (75), 392 (48), 436 (17) $[M+NH_4]^+$ (Found: $[M+NH_4]^+$, 436.1435. $C_{21}H_{22}O_7S$ requires $[M+NH_4]^+$, 436.1430).

(*E*)-Methyl (3-*p*-tolyl-2-propenyl) 2-tosylmalonate (1b)

General procedure (IV) was applied, using (*E*)-methyl 3-*p*-tolyl-2-propenyl malonate (1.864 g, 7.5 mmol), toluene-4-sulfonyl fluoride (655 mg, 3.8 mmol), potassium *tert*-butoxide (843 mg, 7.5 mmol) and DMSO (3.70 mL). Chromatography (25 % EtOAc–petrol) gave (*E*)-methyl (3-*p*-tolyl-2-propenyl) 2-tosylmalonate **1b** (1.046 g, 69 %) as a colourless gum; also isolated was unreacted starting material (0.867 g, 71 % recovery); **1b**: R_f 0.52 (25 % EtOAc–petrol); ν_{max} (film) 2954, 2360, 1744, 1596, 1514, 1436, 1378, 1336, 1269, 1151, 1083, 1019, 971, 815, 706, 670 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.85 (2H, d, *J* 8.4 Hz, *o*-Ts), 7.29 (4H, m, *m*-Ar, *m*-Ts), 7.15 (2H, d, *J* 9.1 Hz, *o*-Ar), 6.61 (1H, d, *J* 15.9 Hz, -CH=C*H*-Ar), 6.12 (1H, dt, *J* 15.9, 6.7 Hz, -C*H*=CH-Ar), 5.01 (1H, s, -(CO)-CH(Ts)-(CO)-), 4.80 (2H, ddd, *J* 6.7, 3.9, 0.9 Hz, -OCH_2-), 3.80 (3H, s, -(CO)-OCH_3), 2.40 (3H, s, -CH_3 (Ts)), 2.35 (3H, s, -CH_3 (Ar)); δ_C (101 MHz, $CDCl_3$) 161.4 (MeO(*C*O)-), 160.8 (-*C*OOCH_2-), 146.0 (4°, Ar-Me (Ts)), 138.4 (4°, Ar-SO_2-), 135.8 (-C=*C*-Ar), 134.0 (4°, Ar), 133.0 (4°, Ar), 130.2 (3°, *m*-Ar (Ts)), 129.5 (3°, *m*-Ar), 129.4 (3°, *o*-Ar (Ts)), 126.6 (3°, *o*-Ar) 120.1 (-*C*=C-Ar), 74.4 (-(CO)*C*H(Ts)$COOCH_2$-), 67.7 (-O-CH_2-), 53.7 (O-CH_3), 21.7 (-CH_3 (Ts)), 21.2 (-CH_3 (Ar)); m*/z* (CI) (%) 131 (18), 246 (80), 288 (28), 304 (100), 420 (60) $[M+NH_4]^+$) (Found: $[M+NH_4]^+$, 420.1480. $C_{21}H_{22}O_6S$ requires $[M+NH_4]^+$, 420.1481) (Found: C, 62.81; H, 5.42. $C_{21}H_{22}O_6S$ requires C, 62.67; H, 5.51%).

(*E*)-(3-(4-Fluorophenyl)-2-propenyl) methyl 2-tosylmalonate (1c)

General procedure (IV) was applied, using (*E*)-3-(4-fluorophenyl)-2-propenyl methyl malonate (1.904 g, 7.6 mmol), toluene-4-sulfonyl fluoride (658 mg, 3.8 mmol), potassium *tert*-butoxide (840 mg, 7.6 mmol) and DMSO (3.77 mL). Chromatography (25 % EtOAc–petrol) gave (*E*)-(3-(4-fluorophenyl)-2-propenyl) methyl 2-tosylmalonate **1c** (1.006 g, 66 %) as a colourless gum; also isolated was unreacted starting material (0.820 g, 64 % recovery); **1c:** R_f 0.43 (25 % EtOAc–petrol); ν_{max} (film) 2956, 1745, 1599, 1510, 1437, 1336, 1306, 1229, 1152, 1083, 1018, 971, 848, 815, 738, 706, 673 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.85 (2H, d, *J* 8.3 Hz, *o*-Ts), 7.35 (2H, dd, *J* 8.7, 5.4 Hz, *m*-Ar), 7.30 (2H, d, *J* 8.3 Hz, *m*-Ar (Ts)), 7.03 (2H, t, *J* 8.7 Hz, *o*-Ar), 6.62 (1H, d, *J* 15.9 Hz, -CH=C*H*-Ar), 6.11 (1H, dt, *J* 15.9, 6.6 Hz, -C*H*=CH-Ar), 5.01 (1H, s, -(CO)-CH(Ts)-(CO)-), 4.81 (2H, ddd, *J* 6.6, 4.0, 0.8 Hz, -OCH_2-),

3.80 (3H, s, -(CO)-OCH_3), 2.41 (3H, s, -CH_3 (Ts)); δ_F (376 MHz, $CDCl_3$) -114.23 (1F, tt, 1H, *J* 8.8, 5.5 Hz,); δ_C (101 MHz, $CDCl_3$) 162.8 (d, $^1J_{C\text{-}F}$ 247.3 Hz, 4º Ar), 161.4 (MeO(*C*O)-), 160.8 (-*C*OOCH_2-), 146.1 (4°, Ar-Me (Ts)), 134.4 (-C=*C*-Ar), 134.1 (4°, Ar-SO_2-), 132.0 (d, $^4J_{C\text{-}F}$ 2.9 Hz, 4°, Ar), 130.1 (3°, *m*-Ar (Ts)), 129.5 (3°, *o*-Ar (Ts)), 128.3 (d, $^3J_{C\text{-}F}$ 8.5 Hz, 3°, *o*-Ar), 121.0 (-*C*=C-Ar), 115.6 (d, $^2J_{C\text{-}F}$ 21.2 Hz, 3°, *m*-Ar), 74.4 (-(CO)*C*H(Ts)$COOCH_2$-), 67.3 (-O-CH_2-), 53.7 (O-CH_3), 21.7 (-CH_3 (Ts)); *m/z* (CI) (%) 135 (43), 246 (50), 304 (100), 424 (57) $[M+NH_4]^+$ (Found: $[M+NH_4]^+$, 424.1233. $C_{20}H_{19}FO_6S$ requires $[M+NH_4]^+$, 424.1230) (Found: C, 59.31; H, 4.61. $C_{20}H_{19}FO_6S$ requires C, 59.10; H, 4.71%).

(*E*)-(3-(4-Chlorophenyl)-2-propenyl) methyl 2-tosylmalonate (1d)

General procedure (IV) was applied, using (*E*)-3-(4-chlorophenyl)-2-propenyl methyl malonate (2.031 g, 7.6 mmol), toluene-4-sulfonyl fluoride (658 mg, 3.8 mmol), potassium *tert*-butoxide (841 mg, 7.6 mmol) and DMSO (3.78 mL). Chromatography (25 % EtOAc–petrol) gave (*E*)-(3-(4-chlorophenyl)-2-propenyl) methyl 2-tosylmalonate **1d** (1.102 g, 69 %) as a colourless gum; also isolated was unreacted starting material (0.871 g, 66 % recovery); **1d**: R_f 0.47 (25 % EtOAc–petrol); ν_{max} (film) 2955, 1745, 1596, 1493, 1436, 1407, 1379, 1336, 1274, 1181 1151, 1084, 1014, 971, 846, 816, 737, 706, 671 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.85 (2H, d, *J* 8.3 Hz, *o*-Ts), 7.31 (6H, m, *m*-Ar, *m*-Ts, *o*-Ar), 6.61 (1H, dt, *J* 15.8, 1.3 Hz, -CH=C*H*-Ar), 6.16 (1H, dt, *J* 15.8, 6.4 Hz, -C*H*=CH-Ar), 5.01 (1H, s, -(CO)-CH(Ts)-(CO)-), 4.81 (2H, ddd, *J* 6.4, 3.5, 1.3 Hz, -OCH_2-), 3.80 (3H, s, -(CO)-OCH_3), 2.41 (3H, s, -CH_3 (Ts)); δ_C (101 MHz, $CDCl_3$) 161.4 (MeO(*C*O)-), 160.7 (-*C*OOCH_2-), 146.1 (4°, Ar-Me (Ts)), 134.3 (4°, Ar-SO_2-), 134.2 (3°, -C=*C*-Ar), 134.1 (2 × C, 4°, Ar, Ar-Cl), 130.1 (3°, *m*-Ar), 129.5 (3°, *m*-Ar (Ts)), 128.8 (3°, *o*-Ar), 127.9 (3°, *o*-Ar (Ts)), 121.9 (-*C*=C-Ar), 74.4 (-(CO)*C*H(Ts)$COOCH_2$-), 67.2 (-O-CH_2-), 53.7 (O-CH_3), 21.7 (-CH_3 (Ts)); *m/z* (CI) (%) 61 (40), 124 (13), 246 (55), 304 (100), 440 (2) $[M+NH_4]^+$ (Found: $[M+NH_4]^+$, 440.0941. $C_{20}H_{19}ClO_6S$, requires $[M+NH_4]^+$, 440.0935) (Found: C, 56.94; H, 4.45. $C_{20}H_{19}ClO_6S$ requires C, 56.80; H, 4.53%).

***E*)-(3-(4-Bromophenyl)-2-propenyl) methyl 2-tosylmalonate (1e)**

General procedure (IV) was applied, using (*E*)-3-(4-bromophenyl)-2-propenyl methyl malonate (1.977 g, 6.3 mmol), toluene-4-sulfonyl fluoride (550 mg, 3.2 mmol), potassium *tert*-butoxide (702 mg, 6.3 mmol) and DMSO (3.15 mL). Chromatography (25 % EtOAc–petrol) gave (*E*)-1-(3-(4-bromophenyl)-2-propenyl) 3-methyl 2-tosylmalonate **1e** (1.007 g, 68

%) as a colourless gum; also isolated was unreacted starting material (0.839 g, 64 % recovery); **1e**: R_f 0.48 (25 % EtOAc–petrol); ν_{max} (film) 3029, 2954, 1745, 1596, 1488, 1436, 1403, 1378, 1336, 1273, 1181, 1151, 1083, 1009, 970, 848, 815, 736, 706, 674 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.84 (2H, d, *J* 8.3 Hz, *o*-Ts), 7.46 (2H, d, *J* 8.5 Hz, *m*-Ar), 7.31 (2H, d, *J* 8.3 Hz, *m*-Ts), 7.23 (2H, d, *J* 8.5 Hz, *o*-Ar), 6.59 (1H, d, *J* 15.9 Hz, -CH=C*H*-Ar), 6.17 (1H, dt, *J* 15.9, 6.4 Hz, -C*H*=CH-Ar), 5.01 (1H, s, -(CO)-CH(Ts)-(CO)-), 4.81 (2H, ddd, *J* 6.4, 3.5, 1.0 Hz, -OCH_2-), 3.79 (3H, s, -(CO)-OCH_3), 2.41 (3H, s, -CH_3 (Ts)); δ_C (101 MHz, $CDCl_3$) 161.4 (MeO(*C*O)-), 160.8 (-*C*$OOCH_2$-), 146.1 (4°, Ar-Me (Ts)), 134.7 (4°, Ar-SO_2-) 134.2 (-C=*C*-Ar), 134.1 (4°, Ar), 131.8 (3°, *m*-Ar), 130.1 (3°, *m*-Ar (Ts)), 129.5 (3°, *o*-Ar), 128.2 (3°, *o*-Ar (Ts)), 122.3 (-*C*=C-Ar), 122.1 (4°, Ar-Br), 74.4 (-(CO)*C*H(Ts)$COOCH_2$-), 67.1 (-O-CH_2-), 53.7 (O-CH_3), 21.7 (-CH_3 (Ts)); *m/z* (CI) (%) 61 (100), 124 (35), 150 (20), 246 (10), 484/486 (2) $[M+NH_4]^+$ (Found: $[M+NH_4]^+$, 484.0446, 486.0428. $C_{20}H_{19}{}^{79}BrO_6S$, $C_{20}H_{19}{}^{81}BrO_6S$ requires $[M+NH_4]^+$, 484.0429, 486.0409) (Found: C, 51.41; H, 3.99. $C_{20}H_{19}BrO_6S$ requires C, 51.40; H, 4.10%).

(*E*)-(3-(4-Cyanophenyl)-2-propenyl) methyl 2-tosylmalonate (1f) and (3*R, 4*S**)-methyl 4-(4-cyanobenzyl)-2-oxotetrahydrofuran-3-carboxylate (4)**

General procedure (IV) was applied, using (*E*)-3-(4-cyanophenyl)-2-propenyl methyl malonate (1.792 g, 6.9 mmol), toluene-4-sulfonyl fluoride (602 mg, 3.5 mmol), potassium *tert*-butoxide (769 mg, 6.9 mmol) and DMSO (3.50 mL). Chromatography (25 % EtOAc–petrol, 14 % Et_2O–petrol) gave (*E*)-(3-(4-cyanophenyl)-2-propenyl) methyl 2-tosylmalonate **1f** (140 mg, 10 %) as a yellow gum, and (3*R**, 4*S**)-methyl 4-(4-cyanobenzyl)-2-oxotetrahydrofuran-3-carboxylate **4** (155 mg, 17 %) as colourless crystalline solid; Also isolated was unreacted starting material (0.207 g, 12 % recovery); **25g**: R_f 0.27 (36 % EtOAc–petrol); ν_{max} (film) 2955, 2352, 2226, 1746, 1605, 1504, 1454, 1435, 1336, 1306, 1269, 1150, 1083, 1018, 972, 860, 816, 736, 706, 674 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.85 (2H, d, *J* 8.4 Hz, *o*-Ts), 7.63 (2H, d, *J* 8.3 Hz, *o*-Ar), 7.46 (2H, d, *J* 8.4 Hz, *m*-Ts), 7.33 (2H, d, *J* 8.3 Hz, *m*-Ar), 6.69 (1H, d, *J* 16.0 Hz, -CH=C*H*-Ar), 6.32 (1H, dt, *J* 16.0, 6.0 Hz, -C*H*=CH-Ar), 5.02 (1H, s, -(CO)-CH(Ts)-(CO)-), 4.87 (2H, ddd, *J* 6.0, 3.5, 1.3 Hz, -OCH_2-), 3.79 (3H, s, -(CO)-OCH_3), 2.42 (3H, s, -CH_3 (Ts)); δ_C (101 MHz, $CDCl_3$) 161.3 (MeO(*C*O)-), 160.7 (-*C*$OOCH_2$-), 146.2 (4°, Ar-Me (Ts)), 140.3 (4°, Ar), 134.1 (4°, Ar-SO_2-), 132.9 (-C=*C*-Ar), 132.5 (3°, *m*-Ar), 130.1 (3°, *m*-Ar (Ts)), 129.6 (3°, *o*-Ar), 127.2 (3°, *o*-Ar (Ts)), 125.3 (-*C*=C-Ar), 118.7 (4°, CN), 111.6 (4°, Ar-CN), 74.4 (-(CO)*C*H(Ts)$COOCH_2$-), 66.5 (-O-CH_2-), 53.7 (O-CH_3), 21.7 (-CH_3 (Ts)); *m/z* (CI) (%) 135 (17), 177 (23), 246 (43), 304 (100), 431 (22) $[M+NH_4]^+$

(Found: $[M+NH_4]^+$, 431.1282. $C_{21}H_{19}NO_6S$ requires $[M+NH_4]^+$, 431.1277); **4**: R_f 0.23 (36 % EtOAc–petrol); ν_{max} (film) 2955, 2352, 2226, 1746, 1605, 1504, 1454, 1435, 1336 1306, 1269, 1150, 1083, 1018, 972, 860, 816, 736, 706, 674 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.62 (2H, d, *J* 8.2 Hz, *m*-Ar), 7.29 (2H, d, *J* 8.2 Hz, *o*-Ar), 4.44 (1H, dd, *J* 9.1, 7.0 Hz, -(CO)OC*H*H-CH-), 3.98 (1H, dd, *J* 9.1, 7.0 Hz, -(CO)OCH*H*-CH-) 3.68 (3H, s, OMe), 3.31 (2H, m, -$(CO)_2$C*H*C*H*-), 2.90 (2H, m, CH_2-Ar); δ_C (101 MHz, $CDCl_3$) 171.0 (-(CO)O-), 167.3 (-(CO)OMe), 142.5 (4°, Ar), 132.6 (3°, *m*-Ar), 129.6 (3°, *o*-Ar), 118.4 (-CN), 111.2 (4°, Ar-CN), 71.0 (-O-*C*H_2CH-), 53.1 ((CO)*C*H(CO)), 51.6 (OMe), 41.0 (-CH_2-Ar), 37.8 (-O-CH_2*C*H-); *m/z* (CI) (%) 52 (10), 277 (100) $[M+NH_4]^+$, 536 (10) $[2M+NH_4]^+$ (Found: $[M+NH_4]^+$, 277.1194. $C_{14}H_{13}NO_4$ requires $[M+NH_4]^+$, 277.1188).

*General procedure (V) for preparation of reference samples of **3***

To a solution of tosylmalonate **1** in CH_2Cl_2 (0.3 M) was added at rt. under nitrogen TBDMSOTf (2.1 equiv.) and DBU (2.1 equiv.). After 40 min of stirring, the reaction mixture was concentrated under reduced pressure. Chromatography on silica gel afforded the decarboxylated rearranged product **3**.

Methyl 3-phenyl-2-tosylpent-4-enoate (3a)

General procedure (V) was applied, using cinnamyl methyl 2-tosylmalonate **1a** (120 mg), TBDMSOTf (0.149 mL), DBU (0.097 mL) and CH_2Cl_2 (1 mL). Chromatography (20 % EtOAc–petrol) gave methyl 3-phenyl-2-tosylpent-4-enoate **3a** (81 mg, 76 %) as a colourless solid, mixture of two diastereomers (40:60); R_f 0.50 (20 % EtOAc–petrol); ν_{max} (film) 3062, 3030, 2953, 2353, 2328, 1745, 1597, 1494, 1455, 1434, 1326, 1288, 1268, 1214, 1146, 1084, 1019, 989, 925, 814, 762, 742, 702, 666, 648 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.81 (2H, d, *J* 8.3 Hz, *o*-Ts, minor isomer), 7.35 (2H, d, *J* 8.3 Hz, *o*-Ts, major isomer), 7.14 (7H, m, -Ph, *m*-Ts, 2 × diastereomers), 6.14 (1H, ddd, *J* 16.9, 10.1, 8.6 Hz, -C*H*=CH_2, minor isomer), 5.87 (1H, ddd, *J* 16.9, 10.1, 8.7 Hz, -C*H*=CH_2, major isomer), 5.17 (1H, d, *J* 10.1, -CH=C*H*H, minor isomer), 5.15 (1H, d, *J* 16.8, -CH=CH*H*, minor isomer), 5.11 (1H, d, *J* 17.0 Hz, -CH=CH*H*, major isomer), 5.05 (1H, d, *J* 10.1 Hz, -CH=C*H*H, major isomer), 4.51 (1H, d, *J* 10.7 Hz, CH-Ts, major isomer), 4.47 (1H, d, *J* 11.5 Hz, CH-Ts, minor isomer), 4.18 (1H, dd, *J* 11.4, 8.9 Hz, CH-Ph, major isomer), 4.06 (1H, dd, *J* 11.4, 8.7 Hz, CH-Ph, minor isomer), 3.74 (3H, s, -OMe, major isomer), 3.26 (3H, s, -OMe, minor isomer), 2.46 (3H, s, Me (Ts), major isomer), 2.37 (3H, s, Me (Ts), minor isomer); δ_C (101 MHz, $CDCl_3$) [165.6, 165.5] (C=O), [145.4, 144.6] (4°, Ar-Me (Ts)), 139.3, 137.8, 136.7, 136.6, 136.0, 134.9, 129.7, 129.5, 129.3,

128.8, 128.6 (2 ×), 128.3, 127.8, 127.5, 127.3, 118.1, 177.6, [75.4, 75.0] (CH-Ts), [53.0, 52.5] (O-CH_3), [49.4, 49.1] (CH-Ph), [21.7, 21.6] (-CH_3 (Ts)); *m/z* (CI) (%) 208 (100), 362 (60) $[M+NH_4]^+$; data were in agreement with those previously reported.[10]

Methyl 3-*p*-tolyl-2-tosylpent-4-enoate (3b)

General procedure (V) was applied, using (*E*)-methyl (3-*p*-tolyl-2-propenyl) 2-tosylmalonate **1b** (125 mg), TBDMSOTf (0.149 mL), DBU (0.097 mL) and CH_2Cl_2 (1 mL). Chromatography (20 % EtOAc–petrol) gave methyl 3-*p*-tolyl-2-tosylpent-4-enoate **3b** (84 mg, 76 %) as a colourless solid, mixture of two diastereomers (42:58); R_f 0.55 (20 % EtOAc–petrol); ν_{max} (film) 3027, 2953, 2360, 1744, 1637, 1597, 1514, 1435, 1325, 1269, 1218, 1146, 1084, 1020, 990, 921, 814, 739, 707, 650 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.80 (2H, d, *J* 8.3 Hz, *o*-Ts, minor isomer), 7.36 (2H, d, *J* 8.3 Hz, *o*-Ts, major isomer), 7.35 (2H, d, *J* 7.4 Hz, m-Ts, minor isomer), 7.04 (10H, m, -Ar, *m*-Ts), 6.12 (1H, ddd, *J* 16.7, 10.3, 8.7 Hz, -C*H*=CH_2, minor isomer), 5.85 (1H, ddd, *J* 16.9, 10.0, 8.6 Hz, -C*H*=CH_2, major isomer), 5.14 (1H, d, *J* 9.5 Hz, -CH=C*H*H, minor isomer), 5.13 (1H, d, *J* 17.1 Hz, -CH=CH*H*, minor isomer), 5.10 (1H, d, *J* 17.0 Hz, -CH=CH*H*, major isomer), 5.02 (1H, d, *J* 10.2 Hz, -CH=C*H*H, major isomer), 4.48 (1H, d, *J* 10.8 Hz, CH-Ts, major isomer), 4.45 (1H, d, *J* 11.8 Hz, CH-Ts, minor isomer), 4.13 (1H, dd, *J* 10.6, 8.8 Hz, CH-Ar, major isomer), 4.06 (1H, dd, *J* 11.4, 8.7 Hz, CH-Ar, minor isomer), 3.74 (3H, s, -OMe, major isomer), 3.29 (3H, s, -OMe, minor isomer), 2.46 (3H, s, Me (Ts), minor isomer), 2.38 (3H, s, Me (Ts), major isomer), 2.28 (3H, s, Ar-Me, major isomer), 2.27 (3H, s, Ar-Me, minor isomer); δ_C (101 MHz, $CDCl_3$) [165.6, 165.5] (C=O), [145.4, 144.5] (4°, Ar-Me (Ts)), 137.1, 137.0, 136.9, 136.8, 136.2, 136.0, 135.0, 134.7, 129.7, 129.5 (2 ×), 129.2 (2 ×), 128.6, 128.1, 127.5, 117.8, 117.4, [75.5, 75.1] (CH-Ts), [53.0, 52.5] (O-CH_3), [49.0, 48.8] (CH-Ar), [21.7, 21.6] (-CH_3 (Ts)), 21.0 (2 ×, Ar-Me); *m/z* (CI) (%) 376 (100) $[M+NH_4]^+$, 734 (80) $[2M+NH_4]^+$ (Found: $[M+NH_4]^+$, 376.1593. $C_{20}H_{22}O_4S$ requires $[M+NH_4]^+$, 376.1583).

Methyl 3-(4-fluorophenyl)-2-tosylpent-4-enoate (3c)

General procedure (V) was applied, using (*E*)-(3-(4-fluorophenyl)-2-propenyl) methyl 2-tosylmalonate **1c** (126 mg), TBDMSOTf (0.149 mL), DBU (0.097 mL) and CH_2Cl_2 (1 mL). Chromatography (20 % EtOAc–petrol) gave methyl 3-(4-fluorophenyl)-2-tosylpent-4-enoate **3c** (90 mg, 80 %) as a colourless solid; mixture of two diastereomers (50:50); R_f 0.45 (20 % EtOAc–petrol); ν_{max} (film) 3070, 2954, 2360, 1744, 1637, 1600, 1509, 1436, 1324, 1270, 1226, 1146, 1084, 1018, 990, 929, 840, 815, 792, 741, 707, 649 cm^{-1}; δ_H (400 MHz, $CDCl_3$)

7.80 (2H, d, *J* 8.3 Hz, *o*-Ts, 1st diastereomer), 7.36 (4H, d, *J* 8.3 Hz, *o*-Ts, *m*-Ts), 6.99 (10H, m, -Ar, *m*-Ts), 6.13 (1H, ddd, *J* 16.9, 10.1, 8.4 Hz, -C*H*=CH_2, 1st diastereomer), 5.83 (1H, ddd, *J* 17.0, 10.1, 8.5 Hz, -C*H*=CH_2, 2nd diastereomer), 5.18 (1H, d, *J* 10.2 Hz, -CH=C*H*H, 1st diastereomer), 5.13 (1H, d, *J* 17.0 Hz, -CH=CH*H*, 1st diastereomer), 5.10 (1H, d, *J* 16.8 Hz, -CH=CH*H*, 2nd diastereomer), 5.06 (1H, d, *J* 10.2 Hz, -CH=C*H*H, 2nd diastereomer), 4.45 (1H, d, *J* 10.9 Hz, CH-Ts, 2nd diastereomer), 4.41 (1H, d, *J* 11.3 Hz, CH-Ts, 1st diastereomer), 4.19 (1H, dd, *J* 10.7, 8.6 Hz, CH-Ar, 2nd diastereomer), 4.07 (1H, dd, *J* 11.3, 8.5 Hz, CH-Ar, 1st diastereomer), 3.73 (3H, s, -OMe, 2nd diastereomer), 3.28 (3H, s, -OMe, 1st diastereomer), 2.46 (3H, s, Me (Ts), 1st diastereomer), 2.39 (3H, s, Me (Ts), 2nd diastereomer); δ_F (376 MHz, $CDCl_3$) -115.75 (1F, m, 1st diastereomer), -116.14(1F, m, 2nd diastereomer); δ_C (101 MHz, $CDCl_3$) [165.5, 165.4] (C=O),[162.0, 161.9] (d, $^1J_{C\text{-}F}$ 246.2 Hz, 4º Ar), [145.5, 144.8] (4°, Ar-Me (Ts)), 136.5, 135.9, 135.0 (d, $^4J_{C\text{-}F}$ 2.9 Hz, 4° Ar), 134.8, 133.5, 130.0 (d, $^3J_{C\text{-}F}$ 8.5 Hz, 3° Ar), 129.6, 129.5 (2 ×), 129.4 (2 ×), 128.5, 118.2, 117.8, 115.7 (d, $^2J_{C\text{-}F}$ 21.3 Hz, 3° Ar, 1st diastereomer), 115.4 (d, $^2J_{C\text{-}F}$ 22.0 Hz, 3° Ar, 2nd diastereomer), [75.4, 75.1] (CH-Ts), [53.0, 52.6] (O-CH_3), [48.5, 48.3] (CH-Ar), [21.7, 21.6] (-CH_3 (Ts)); *m/z* (CI) (%) 380 (100) $[M+NH_4]^+$ (Found: $[M+NH_4]^+$, 380.1317. $C_{19}H_{19}FO_4S$ requires $[M+NH_4]^+$, 380.1332).

Methyl 3-(4-chlorophenyl)-2-tosylpent-4-enoate (3d)

General procedure (V) was applied, using (*E*)-(3-(4-chlorophenyl)-2-propenyl) methyl 2-tosylmalonate **1d** (131 mg), TBDMSOTf (0.149 mL), DBU (0.097 mL) and CH_2Cl_2 (1 mL). Chromatography (20 % EtOAc–petrol) gave methyl 3-(4-chlorophenyl)-2-tosylpent-4-enoate **3d** (78 mg, 66 %) as a colourless solid, mixture of two diastereomers (38:62); R_f 0.44 (20 % EtOAc–petrol); ν_{max} (film) 2954, 2838, 2361, 1745, 1636, 1610, 1597, 1514, 1456, 1435, 1324, 1305, 1288, 1250, 1214, 1181, 1146, 1084, 1033, 991, 928, 813, 744, 724, 648 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.79 (2H, d, *J* 8.3 Hz, *o*-Ts, minor isomer), 7.35 (4H, d, *J* 8.3 Hz, *o*-Ts, *m*-Ts), 7.23 (2H, d, *J* 8.4 Hz, *o*-Ar, minor isomer), 7.14 (2H, d, *J* 8.1 Hz, *m*-Ts, major isomer), 7.10 (2H, d, *J* 8.4 Hz, *o*-Ar, major isomer), 7.07 (2H, d, *J* 8.5 Hz, *m*-Ar, minor isomer), 6.99 (2H, d, *J* 8.5 Hz, *m*-Ar, major isomer), 6.11 (1H, ddd, *J* 17.0, 10.2, 8.5 Hz, -C*H*=CH_2, minor isomer), 5.81 (1H, ddd, *J* 17.0, 10.1, 8.6 Hz, -C*H*=CH_2, major isomer), 5.18 (1H, d, *J* 10.2 Hz, -CH=C*H*H, minor isomer), 5.13 (1H, d, *J* 17.0 Hz, -CH=CH*H*, minor isomer), 5.11 (1H, d, *J* 16.8 Hz, -CH=CH*H*, major isomer), 5.06 (1H, d, *J* 10.2 Hz, -CH=C*H*H, major isomer), 4.45 (1H, d, *J* 10.9 Hz, CH-Ts, major isomer), 4.42 (1H, d, *J* 11.4 Hz, CH-Ts, minor isomer), 4.17 (1H, dd, *J* 10.8, 8.7 Hz, CH-Ar, major isomer), 4.06 (1H, dd, *J* 11.3, 8.5 Hz, CH-Ar, minor isomer), 3.75 (3H, s, -OMe, major isomer), 3.29 (3H, s, -$COOCH_3$, minor isomer), 2.46 (3H,

s, Me (Ts), minor isomer), 2.40 (3H, s, Me (Ts), major isomer); δ_C (101 MHz, $CDCl_3$) [165.4, 165.3] (C=O), [145.6, 144.9] (4°, Ar-Me (Ts)), 137.8, 136.2 (2 ×), 135.9, 134.7, 133.3, 129.7, 129.6, 129.5, 129.4, 129.2, 129.0, 128.7, 128.4,118.4, 118.0, [75.1, 74.9] (CH-Ts), [53.1, 52.6] (-COO*C*H_3), [48.7, 48.4] (CH-Ar), [21.7, 21.6] (-CH_3 (Ts)); *m/z* (CI) (%) 168 (20), 174 (30), 396 (100) $[M+NH_4]^+$ (Found: $[M+NH_4]^+$, 396.1050. $C_{19}H_{19}ClO_4S$ requires $[M+NH_4]^+$, 396.1036).

Methyl 3-(4-bromophenyl)-2-tosylpent-4-enoate (3e)

General procedure (V) was applied, using (*E*)-(3-(4-bromophenyl)-2-propenyl) methyl 2-tosylmalonate **1e** (148 mg), TBDMSOTf (0.149 mL), DBU (0.097 mL) and CH_2Cl_2 (1 mL). Chromatography (20 % EtOAc–petrol) gave methyl 3-(4-bromophenyl)-2-tosylpent-4-enoate **3e** (106 mg, 81 %) as a colourless solid, mixture of two diastereomers (40:60); R_f 0.46 (20 % EtOAc–petrol); ν_{max} (film) 2953, 2360, 1744, 1596, 1489, 1435, 1406, 1324, 1291, 1214, 1146, 1084, 1010, 930, 815, 737, 708 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.79 (2H, d, *J* 8.4 Hz, *o*-Ts, minor isomer), 7.38 (2H, d, *J* 8.4 Hz, *m*-Ts, minor isomer), 7.35 (2H, d, *J* 8.4 Hz, *o*-Ar, minor isomer), 7.34 (2H, d, *J* 8.3 Hz, *o*-Ts, major isomer), 7.24 (2H, d, *J* 8.4 Hz, *m*-Ts, major isomer), 7.13 (2H, d, *J* 8.0 Hz, *o*-Ar, major isomer), 7.01 (2H, d, *J* 8.5 Hz, *m*-Ar, minor isomer), 6.92 (2H, d, *J* 8.4 Hz, *m*-Ar, major isomer), 6.11 (1H, ddd, *J* 16.8, 10.1, 8.4 Hz, -C*H*=CH_2, minor isomer), 5.80 (1H, ddd, *J* 16.9, 10.1, 8.5 Hz, -C*H*=CH_2, major isomer), 5.18 (1H, d, *J* 10.1 Hz, -CH=C*H*H, minor isomer), 5.13 (1H, d, *J* 17.0 Hz, -CH=CH*H*, minor isomer), 5.11 (1H, d, *J* 17.0 Hz, -CH=CH*H*, major isomer), 5.06 (1H, d, *J* 10.0 Hz, -CH=C*H*H, major isomer), 4.45 (1H, d, *J* 10.9 Hz, CH-Ts, major isomer), 4.42 (1H, d, *J* 11.5 Hz, CH-Ts, minor isomer), 4.15 (1H, dd, *J* 10.9, 8.6 Hz, CH-Ar, major isomer), 4.05 (1H, dd, *J* 11.4, 8.5 Hz, CH-Ar, minor isomer), 3.75 (3H, s, -OMe, major isomer), 3.29 (3H, s, -$COOCH_3$, minor isomer), 2.46 (3H, s, Me (Ts), minor isomer), 2.41 (3H, s, Me (Ts), major isomer); δ_C (101 MHz, $CDCl_3$) [165.4, 165.2] (C=O), [145.6, 144.9] (4°, Ar-Me (Ts)), 138.3, 136.7, 136.1 (2 ×), 135.9, 134.8, 132.0, 131.6, 130.1, 129.6, 129.5 (2 ×), 129.4, 128.4, 121.4, 118.5, 118.1, [75.1, 74.9] (CH-Ts), [53.1, 52.7] (-COO*C*H_3), [48.8, 48.4] (CH-Ar), [21.7, 21.6] (-CH_3 (Ts)); *m/z* (CI) (%) 442 (100) $[M+NH_4]^+$ (Found: $[M+NH_4]^+$, 440.0534, 442.0521. $C_{19}H_{19}{}^{79}BrO_4S$, $C_{19}H_{19}{}^{81}BrO_4S$ requires $[M+NH_4]^+$, 440.0531, 442.0511).

Methyl 3-(4-cyanophenyl)-2-tosylpent-4-enoate (3f)

General procedure (V) was applied, using (*E*)-(3-(4-cyanophenyl)-2-propenyl) methyl 2-tosylmalonate **1f** (68 mg), TBDMSOTf (0.108 mL), DBU (0.05 mL) and CH_2Cl_2 (0.57 mL). Chromatography (25 % EtOAc–petrol) gave methyl 3-(4-cyanophenyl)-2-tosylpent-4-enoate **3f** (49 mg, 80 %) as a colourless solid, mixture of two diastereomers (45:55); R_f 0.70 (25 % EtOAc–petrol); ν_{max} (film) 2954, 2361, 2229, 1743, 1636, 1597, 1506, 1436, 1326, 1292, 1198, 1146, 1084, 1018, 989, 932, 816, 737, 707 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.78 (2H, d, *J* 8.3 Hz, *o*-Ts, minor isomer), 7.57 (2H, d, *J* 8.3 Hz, *o*-Ar, minor isomer), 7.49 (2H, d, *J* 8.3 Hz, *o*-Ts, major isomer), 7.40 (2H, d, *J* 8.3 Hz, *m*-Ts, major isomer), 7.36 (2H, d, *J* 8.1 Hz, *m*-Ts, minor isomer), 7.26 (2H, d, *J* 8.3 Hz, *m*-Ar, minor isomer), 7.24 (2H, d, *J* 8.3 Hz, *o*-Ar, major isomer), 7.18 (2H, d, *J* 8.1 Hz, *m*-Ar, major isomer), 6.11 (1H, ddd, *J* 17.0, 10.2, 8.5 Hz, -C*H*=CH_2, minor isomer), 5.81 (1H, ddd, *J* 16.9, 10.1, 8.5 Hz, -C*H*=CH_2, major isomer), 5.23 (1H, d, *J* 10.2 Hz, -CH=C*H*H, minor isomer), 5.16 (1H, d, *J* 16.8 Hz, -CH=CH*H*, minor isomer), 5.15 (1H, d, *J* 16.8 Hz, -CH=CH*H*, major isomer), 5.12 (1H, d, *J* 9.5 Hz, -CH=C*H*H, major isomer), 4.48 (1H, d, *J* 11.0 Hz, CH-Ts, major isomer), 4.44 (1H, d, *J* 11.4 Hz, CH-Ts, minor isomer), 4.27 (1H, dd, *J* 10.8, 8.6 Hz, CH-Ar, major isomer), 4.17 (1H, dd, *J* 11.2, 8.4 Hz, CH-Ar, minor isomer), 3.70 (3H, s, -OMe, major isomer), 3.27 (3H, s, -$COOCH_3$, minor isomer), 2.47 (3H, s, Me (Ts), minor isomer), 2.42 (3H, s, Me (Ts), major isomer); δ_C (101 MHz, $CDCl_3$) [165.4, 165.3] (C=O), [145.6, 144.9] (4°, Ar-Me (Ts)), 136.2, 135.9, 133.3, 129.7, 129.6 (2 ×), 129.4, 129.2, 129.0, 128.7, 128.4, 118.5, 118.0, [75.2, 74.9] (CH-Ts), [53.1, 52.7] (-COO*C*H_3), [48.7, 48.4] (CH-Ar), [21.7, 21.6] (-CH_3 (Ts)); *m/z* (CI) (%) 121 (45), 138 (20), 174 (20), 233 (22), 246 (25), 387 (100) $[M+NH_4]^+$ (Found: $[M+NH_4]^+$, 387.1379. $C_{20}H_{19}NO_4S$ requires $[M+NH_4]^+$, 387.1379).

General procedure (VI) for the kinetic study of the DCR reaction

To a solution of allylic methyl 2-tosylmalonates **1** (0.065 mmol, 1 equiv.), potassium acetate (0.6 mg, 0.007 mmol, 0.1 equiv.) in d-CCl_2H_2 (0.086 M) was added BSA (36 µl, 0.150 mmol, 2.3 equiv.) with a syringe under nitrogen in the NMR tube at T= (293.7 ± 0.2) K . The NMR tube was agitated and immediately set in the NMR spectrometer to shim. After shimming (3–5 min) the probe was acquired at defined intervals:

Methyl 3-phenyl-2-tosylpent-4-enoate (3a)

General procedure VI was applied, using cinnamyl methyl 2-tosylmalonate **1a** (25.1 mg).

Intervals:

From spectrum Nr. 11 to Nr. 60 every 30 s

From spectrum Nr. 60 to Nr. 61	80 s
From spectrum Nr. 61 to Nr. 72	every 1200 s

Methyl 3-*p*-tolyl-2-tosylpent-4-enoate (3b)

General procedure VI was applied, using (*E*)-methyl (3-*p*-tolyl-2-propenyl) 2-tosylmalonate **1b** (26.0 mg).

Intervals:

From spectrum Nr. 1 to Nr. 101	every 20 s

Methyl 3-(4-fluorophenyl)-2-tosylpent-4-enoate (3c)

General procedure VI was applied, using (*E*)-(3-(4-fluorophenyl)-2-propenyl) methyl 2-tosylmalonate **1c** (26.2 mg).

Intervals:

From spectrum Nr. 20 to Nr. 80	every 20 s
From spectrum Nr. 80 to Nr. 81	120 s
From spectrum Nr. 81 to Nr. 99	every 1200 s

Methyl 3-(4-chlorophenyl)-2-tosylpent-4-enoate (3d)

General procedure VI was applied, using (*E*)-1-(3-(4-chorophenyl)-2-propenyl) 3-methyl 2-tosylmalonate **1d** (27.3 mg).

Intervals:

From spectrum Nr. 100 to Nr. 149	every 30 s
From spectrum Nr. 149 to Nr. 150	540 s
From spectrum Nr. 150 to Nr. 168	every 1200 s

Methyl 3-(4-bromophenyl)-2-tosylpent-4-enoate (3e)

General procedure VI was applied, using (*E*)-(3-(4-bromophenyl)-2-propenyl) methyl 2-tosylmalonate **1e** (30.1 mg).

Intervals:

From spectrum Nr. 1 to Nr. 50	every 30 s
From spectrum Nr. 50 to Nr. 51	780 s
From spectrum Nr. 51 to Nr. 65	every 1200 s

Methyl 3-(4-cyanophenyl)-2-tosylpent-4-enoate (3f)

General procedure VI was applied, using (*E*)-(3-(4-cyanophenyl)-2-propenyl) methyl 2-tosylmalonate **1f** (26.6 mg).

Intervals:

From spectrum Nr. 20 to Nr. 45	every 180 s
From spectrum Nr. 45 to Nr. 46	540 s
From spectrum Nr. 51 to Nr. 65	every 3600 s

Determination of reaction rate constants

Calculation for the determination of the reaction rate constant for substrate **1a** (S = H)

Range of integrated signals (δ in ppm)

5a: [δ 4.877–4.763] (br d): $MeO_2CCTs=C(OTMS)OC\boldsymbol{H}_2CH=CH(p\text{-}C_6H_4S)$: integral = $I_{\mathbf{5a}}$

6a: [δ 4.763–4.652] (2 × br d): $MeO_2CC(Ts)(CO_2TMS)C\boldsymbol{H}(p\text{-}C_6H_4S)CH=CH_2$: integral = $I_{\mathbf{6a}}$

3a: [δ 4.545–4.452] (2 × d): $MeO_2CC\boldsymbol{H}(Ts)CH(p\text{-}C_6H_4S)CH=CH_2$: integral = $I_{\mathbf{3a}}$

$[A]/[A]_0 = I_{\mathbf{5a}}/[I_{\mathbf{5a}} + 2I_{\mathbf{6a}} + 2I_{\mathbf{3a}}]$; integral values given in Table 1 are based on $I_{\mathbf{5a}}$ set to 1.

Table 1: Measured ^{1}H nmr integrals vs time for substrate 1a

t (s)	measured integral values		$[A]/[A]_0$
	[δ 4.763–4.652]	[δ 4.545–4.452]	
0	0.61	-0.04	0.4673
30	0.63	-0.04	0.4587
60	0.65	-0.04	0.4505
90	0.66	-0.04	0.4464
120	0.68	-0.04	0.4386
150	0.69	-0.04	0.4348
180	0.71	-0.04	0.4274
210	0.72	-0.04	0.4237
240	0.74	-0.04	0.4167
270	0.75	-0.04	0.4132
300	0.77	-0.04	0.4065
330	0.79	-0.04	0.4000
360	0.79	-0.04	0.4000
390	0.80	-0.04	0.3968
420	0.82	-0.04	0.3906
450	0.83	-0.04	0.3876
480	0.85	-0.04	0.3817
510	0.86	-0.04	0.3788
540	0.88	-0.04	0.3731
570	0.90	-0.04	0.3676
600	0.90	-0.04	0.3676
630	0.92	-0.04	0.3623
660	0.93	-0.04	0.3597
690	0.95	-0.04	0.3546
720	0.96	-0.04	0.3521
750	0.98	-0.04	0.3472
780	0.99	-0.04	0.3448
810	1.01	-0.03	0.3378
840	1.02	-0.04	0.3378
870	1.04	-0.03	0.3311
900	1.06	-0.04	0.3289
930	1.06	-0.04	0.3289
960	1.09	-0.03	0.3205
990	1.09	-0.03	0.3205
1020	1.12	-0.03	0.3145
1050	1.14	-0.03	0.3106

1080	1.14	-0.03	0.3106
1110	1.15	-0.03	0.3086
1140	1.17	-0.03	0.3049
1170	1.19	-0.03	0.3012
1200	1.20	-0.03	0.2994
1230	1.22	-0.02	0.2941
1260	1.25	-0.02	0.2890
1290	1.26	-0.02	0.2874
1320	1.27	-0.02	0.2857
1350	1.28	-0.02	0.2841
1380	1.30	-0.02	0.2809
1410	1.31	-0.02	0.2793
1440	1.33	-0.01	0.2747
1470	1.35	-0.02	0.2732
1550	1.43	-0.01	0.2604
2750	2.12	0.09	0.1845
3950	2.92	0.28	0.1351
5150	3.62	0.54	0.1073
6350	4.32	0.88	0.0877
7550	4.93	1.27	0.0746
8750	5.21	1.63	0.0681
9950	5.59	2.12	0.0609
11150	5.59	2.48	0.0583
12350	5.72	2.97	0.0544
13550	5.69	3.40	0.0521
14750	5.60	3.94	0.0498

Calculation for the determination of the reaction rate constant for substrate **1b** (S = Me)

Range of integrated signals (δ in ppm)

5b: [δ 4.834–4.734] (br d): $MeO_2CCTs=C(OTMS)OC\boldsymbol{H}_2CH=CH(p\text{-}C_6H_4S)$: integral = $I_{\mathbf{5b}}$

6b: [δ 4.734–4.638] (2 × br d): $MeO_2CC(Ts)(CO_2TMS)C\boldsymbol{H}(p\text{-}C_6H_4S)CH=CH_2$: integral = $I_{\mathbf{6b}}$

3b: [δ 4.507–4.426] (2 × d): $MeO_2CC\boldsymbol{H}(Ts)CH(p\text{-}C_6H_4S)CH=CH_2$: integral = $I_{\mathbf{3b}}$

$[A]/[A]_0 = I_{\mathbf{5b}}/[I_{\mathbf{5b}} + 2I_{\mathbf{6b}} + 2I_{\mathbf{3b}}]$; integral values given in Table 2 are based on $I_{\mathbf{5b}}$ set to 1.

Table 2: Measured ^{1}H nmr integrals vs time for substrate 1b

t (s)	measured integral values		$[A]/[A]_0$
	[δ 4.734–4.638]	[δ 4.507–4.426]	
0	0.85	-0.02	0.3759
20	0.93	-0.03	0.3571
40	1.01	-0.03	0.3378
60	1.07	-0.03	0.3247
80	1.15	-0.03	0.3086
100	1.24	-0.03	0.2924
120	1.32	-0.03	0.2793
140	1.39	-0.03	0.2688
160	1.48	-0.03	0.2564
180	1.56	-0.03	0.2463
200	1.65	-0.03	0.2358
220	1.72	-0.03	0.2283
240	1.83	-0.03	0.2174
260	1.87	-0.03	0.2137
280	2.00	-0.03	0.2024
300	2.05	-0.03	0.1984
320	2.17	-0.03	0.1894
340	2.24	-0.02	0.1838
360	2.31	-0.02	0.1792
380	2.38	-0.02	0.1748
400	2.52	-0.02	0.1667
420	2.57	-0.02	0.1639
440	2.62	-0.01	0.1608
460	2.71	-0.02	0.1567
480	2.87	-0.02	0.1493
500	2.93	-0.02	0.1466
520	3.03	-0.01	0.1420
540	3.14	-0.01	0.1377
560	3.26	-0.01	0.1333
580	3.35	-0.01	0.1302
600	3.40	-0.01	0.1285
620	3.48	-0.01	0.1259
640	3.67	0.00	0.1199
660	3.69	0.00	0.1193
680	3.79	0.01	0.1163
700	3.92	0.01	0.1129
720	3.99	0.02	0.1109
740	4.12	0.02	0.1078
760	4.22	0.03	0.1053
780	4.39	0.04	0.1014

800	4.28	0.04	0.1037
820	4.52	0.04	0.0988
840	4.46	0.05	0.0998
860	4.61	0.07	0.0965
880	4.67	0.07	0.0954
900	4.68	0.07	0.0952
920	4.87	0.08	0.0917
940	4.98	0.10	0.0896
960	5.15	0.11	0.0868
980	5.28	0.11	0.0849
1000	5.28	0.13	0.0846
1020	5.47	0.12	0.0821
1040	5.44	0.14	0.0822
1060	5.54	0.15	0.0808
1080	5.58	0.15	0.0803
1100	5.93	0.15	0.0760
1120	5.64	0.18	0.0791
1140	5.68	0.20	0.0784
1160	6.21	0.20	0.0724
1180	6.02	0.20	0.0744
1200	6.19	0.23	0.0723
1220	6.33	0.23	0.0708
1240	6.21	0.23	0.0720
1260	6.36	0.24	0.0704
1280	6.58	0.26	0.0681
1300	6.68	0.27	0.0671
1320	6.65	0.26	0.0675
1340	6.98	0.30	0.0643
1360	6.96	0.30	0.0644
1380	6.94	0.33	0.0644
1400	7.08	0.32	0.0633
1420	7.28	0.35	0.0615
1440	7.03	0.35	0.0635
1460	7.14	0.37	0.0624
1480	7.23	0.39	0.0616
1500	7.40	0.39	0.0603
1520	7.51	0.42	0.0593
1540	7.32	0.41	0.0608
1560	7.58	0.42	0.0588
1580	7.52	0.42	0.0592
1600	7.58	0.44	0.0587
1620	7.70	0.49	0.0575
1640	7.82	0.47	0.0569
1660	7.95	0.49	0.0559
1680	7.89	0.52	0.0561

Calculation for the determination of the reaction rate constant for substrate **1c** (S = F)

Range of integrated signals (δ in ppm)

5c: [δ 3.783–3.740] (br s): ***Me***$O_2CCTs=C(OTMS)OCH_2CH=CH(p\text{-}C_6H_4S)$: integral = I_{5c}

6c: [δ 3.740–3.726, 3.505–3.478] (2 × s): ***Me***$O_2CC(Ts)(CO_2TMS)CH(p\text{-}C_6H_4S)CH=CH_2$: integral = I_{6c}

3c: [δ 3.695–3.675, 3.258–3.221] (2 × s): ***Me***$O_2CCH(Ts)CH(p\text{-}C_6H_4S)CH=CH_2$: integral = I_{3c}

$[A]/[A]_0 = I_{5c}/[I_{5c} + I_{6c} + I_{3c}]$; integral values given in Table 1 are based on I_{5c} set to 1.

Table 3: Measured ^{1}H nmr integrals vs time for substrate 1c

t (s)	measured integral values				$[A]/[A]_0$
	[δ 3.740–3.726]	[δ 3.505–3.478]	[δ 3.695–3.675]	[δ 3.258–3.221]	
0	0.14	0.17	0.02	0.00	0.75188
20	0.14	0.18	0.02	0.00	0.746269
40	0.15	0.20	0.02	0.00	0.729927
60	0.16	0.22	0.02	0.00	0.714286
80	0.17	0.23	0.02	0.00	0.704225
100	0.17	0.25	0.02	0.00	0.694444
120	0.18	0.26	0.02	0.00	0.684932
140	0.18	0.28	0.02	0.00	0.675676
160	0.19	0.29	0.02	0.00	0.666667
180	0.20	0.31	0.02	0.00	0.653595
200	0.20	0.32	0.02	0.00	0.649351
220	0.21	0.34	0.02	0.00	0.636943
240	0.22	0.36	0.02	0.00	0.625
260	0.22	0.37	0.02	0.00	0.621118
280	0.23	0.39	0.02	0.00	0.609756
300	0.23	0.40	0.02	0.00	0.606061
320	0.24	0.42	0.02	0.00	0.595238
340	0.25	0.44	0.02	0.00	0.584795
360	0.25	0.45	0.02	0.00	0.581395
380	0.26	0.47	0.02	0.00	0.571429
400	0.26	0.48	0.03	0.00	0.564972
420	0.27	0.50	0.03	0.00	0.555556
440	0.28	0.51	0.03	0.00	0.549451
460	0.28	0.53	0.03	0.00	0.543478
480	0.29	0.55	0.03	0.00	0.534759
500	0.29	0.56	0.03	0.00	0.531915
520	0.30	0.58	0.03	0.00	0.52356
540	0.30	0.59	0.03	0.00	0.520833
560	0.31	0.61	0.03	0.00	0.512821
580	0.32	0.63	0.03	0.00	0.505051
600	0.33	0.65	0.03	0.00	0.497512
620	0.33	0.66	0.03	0.00	0.49505
640	0.34	0.68	0.03	0.00	0.487805
660	0.35	0.70	0.03	0.00	0.480769
680	0.35	0.71	0.03	0.00	0.478469
700	0.36	0.72	0.03	0.00	0.473934
720	0.37	0.74	0.03	0.00	0.46729

740	0.37	0.76	0.03	0.00	0.462963
760	0.38	0.78	0.03	0.00	0.456621
780	0.38	0.79	0.03	0.00	0.454545
800	0.39	0.81	0.04	0.00	0.446429
820	0.40	0.83	0.04	0.00	0.440529
840	0.41	0.84	0.04	0.00	0.436681
860	0.41	0.86	0.04	0.01	0.431034
880	0.42	0.87	0.04	0.01	0.42735
900	0.43	0.89	0.04	0.01	0.421941
920	0.43	0.91	0.04	0.01	0.41841
940	0.43	0.92	0.04	0.01	0.416667
960	0.44	0.93	0.04	0.01	0.413223
980	0.45	0.96	0.04	0.01	0.406504
1000	0.46	0.98	0.04	0.01	0.401606
1020	0.46	0.99	0.04	0.01	0.4
1040	0.47	1.00	0.04	0.01	0.396825
1060	0.48	1.02	0.04	0.01	0.392157
1080	0.48	1.04	0.05	0.01	0.387597
1100	0.49	1.05	0.04	0.01	0.3861
1120	0.50	1.07	0.05	0.01	0.380228
1140	0.50	1.09	0.05	0.01	0.377358
1160	0.51	1.10	0.05	0.01	0.374532
1180	0.52	1.12	0.05	0.01	0.37037

Calculation for the determination of the reaction rate constant for substrate **1d** (S = Cl)

Range of integrated signals (δ in ppm)

5d: [δ 4.871–4.759] (br d): $MeO_2CCTs=C(OTMS)OC\boldsymbol{H}_2CH=CH(p\text{-}C_6H_4S)$: integral = $I_{\mathbf{5d}}$

6d: [δ 4.759–4.673] (2 × br d): $MeO_2CC(Ts)(CO_2TMS)C\boldsymbol{H}(p\text{-}C_6H_4S)CH=CH_2$: integral = $I_{\mathbf{6d}}$

3d: [δ 4.507–4.410] (2 × d): $MeO_2CC\boldsymbol{H}(Ts)CH(p\text{-}C_6H_4S)CH=CH_2$: integral = $I_{\mathbf{3d}}$

$[A]/[A]_0 = I_{\mathbf{5d}}/[I_{\mathbf{5d}} + 2I_{\mathbf{6d}} + 2I_{\mathbf{3d}}]$; integral values given in Table 4 are based on $I_{\mathbf{5d}}$ set to 1.

Table 4: Measured ^{1}H nmr integrals vs time for substrate 1d

t (s)	measured integral values		$[A]/[A]_0$
	[δ 4.759–4.673]	[δ 4.507–4.410]	
0	0.51	0.06	0.46729
30	0.50	0.05	0.47619
60	0.50	0.06	0.471698
90	0.50	0.05	0.47619
120	0.50	0.06	0.471698
150	0.50	0.06	0.471698
180	0.50	0.06	0.471698
210	0.53	0.06	0.458716
240	0.53	0.06	0.458716
270	0.54	0.06	0.454545
300	0.54	0.06	0.454545
330	0.54	0.06	0.454545
360	0.57	0.06	0.442478
390	0.57	0.07	0.438596
420	0.57	0.07	0.438596
450	0.58	0.07	0.434783
480	0.58	0.07	0.434783
510	0.59	0.07	0.431034
540	0.60	0.07	0.42735
570	0.60	0.07	0.42735
600	0.61	0.08	0.420168
630	0.60	0.07	0.42735
660	0.61	0.07	0.423729
690	0.62	0.07	0.420168
720	0.62	0.08	0.416667
750	0.62	0.08	0.416667
780	0.62	0.07	0.420168
810	0.63	0.07	0.416667
840	0.63	0.08	0.413223
870	0.64	0.08	0.409836
900	0.64	0.08	0.409836
930	0.64	0.08	0.409836
960	0.64	0.08	0.409836
990	0.64	0.08	0.409836
1020	0.65	0.08	0.406504
1050	0.66	0.08	0.403226
1080	0.65	0.08	0.406504
1110	0.66	0.08	0.403226
1140	0.67	0.08	0.4
1170	0.67	0.08	0.4

1200	0.67	0.08	0.4
1230	0.67	0.09	0.396825
1260	0.68	0.09	0.393701
1290	0.68	0.09	0.393701
1320	0.68	0.09	0.393701
1350	0.69	0.08	0.393701
1380	0.68	0.09	0.393701
1410	0.70	0.09	0.387597
1440	0.69	0.09	0.390625
1470	0.71	0.09	0.384615
2010	0.75	0.10	0.37037
3210	0.87	0.14	0.331126
4410	0.99	0.18	0.299401
5610	1.09	0.24	0.273224
6810	1.19	0.32	0.248756
8010	1.28	0.39	0.230415
9210	1.41	0.49	0.208333
10410	1.49	0.59	0.193798
11610	1.60	0.72	0.177305
12810	1.72	0.86	0.162338
14010	1.79	1.00	0.151976
15210	1.91	1.16	0.140056
16410	1.99	1.35	0.130208

Calculation for the determination of the reaction rate constant for substrate **1e** (S = Br)

Range of integrated signals (δ in ppm)

5e: [δ 4.862–4.747] (br d): $MeO_2CCTs=C(OTMS)OC\boldsymbol{H}_2CH=CH(p\text{-}C_6H_4S)$: integral = $I_{\mathbf{5e}}$

6e: [δ 4.747–4.665] (2 × br d): $MeO_2CC(Ts)(CO_2TMS)C\boldsymbol{H}(p\text{-}C_6H_4S)CH=CH_2$: integral = $I_{\mathbf{6e}}$

3e: [δ 4.497–4.408] (2 × d): $MeO_2CC\boldsymbol{H}(Ts)CH(p\text{-}C_6H_4S)CH=CH_2$: integral = $I_{\mathbf{3e}}$

$[A]/[A]_0 = I_{\mathbf{5e}}/[I_{\mathbf{5e}} + 2I_{\mathbf{6e}} + 2I_{\mathbf{3e}}]$; integral values given in Table 5 are based on $I_{\mathbf{5e}}$ set to 1.

Table 5: Measured ^{1}H nmr integrals vs time for substrate 1e

t (s)	measured integral values		$[A]/[A]_0$
	[δ 4.747–4.665]	[δ 4.497–4.408]	
0	0.33	0.01	0.595238
30	0.34	0.01	0.588235
60	0.34	0.00	0.595238
90	0.34	0.01	0.588235
120	0.34	0.00	0.595238
150	0.35	0.01	0.581395
180	0.34	0.00	0.595238
210	0.35	0.01	0.581395
240	0.35	0.00	0.588235
270	0.35	0.01	0.581395
300	0.35	0.00	0.588235
330	0.35	0.01	0.581395
360	0.36	0.01	0.574713
390	0.35	0.00	0.588235
420	0.36	0.00	0.581395
450	0.36	0.00	0.581395
480	0.36	0.01	0.574713
510	0.37	0.01	0.568182
540	0.36	0.01	0.574713
570	0.36	0.01	0.574713
600	0.37	0.01	0.568182
630	0.37	0.01	0.568182
660	0.38	0.01	0.561798
690	0.38	0.01	0.561798
720	0.38	0.01	0.561798
750	0.38	0.00	0.568182
780	0.39	0.01	0.555556
810	0.38	0.01	0.561798
840	0.39	0.00	0.561798
870	0.39	0.00	0.561798
900	0.39	0.01	0.555556
930	0.39	0.01	0.555556
960	0.39	0.00	0.561798
990	0.40	0.01	0.549451
1020	0.40	0.01	0.549451
1050	0.40	0.00	0.555556
1080	0.40	0.01	0.549451
1110	0.40	0.01	0.549451
1140	0.41	0.01	0.543478
1170	0.41	0.01	0.543478

1200	0.41	0.01	0.543478
1230	0.41	0.01	0.543478
1260	0.41	0.01	0.543478
1290	0.41	0.01	0.543478
1320	0.42	0.01	0.537634
1350	0.42	0.01	0.537634
1380	0.43	0.01	0.531915
1410	0.42	0.01	0.537634
1440	0.43	0.01	0.531915
1470	0.43	0.01	0.531915
2250	0.48	0.01	0.505051
3450	0.57	0.03	0.454545
5850	0.74	0.09	0.37594
7050	0.83	0.13	0.342466
8250	0.92	0.18	0.3125
9450	0.98	0.24	0.290698
10650	1.02	0.30	0.274725
11850	1.09	0.39	0.252525

Calculation for the determination of the reaction rate constant for substrate **1f** (S = CN)

Range of integrated signals (δ in ppm)

5f: [δ 3.801–3.732] (br s): ***Me***O_2CCTs=C(OTMS)OCH_2CH=CH(*p*-C_6H_4S): integral = I_{5f}

6f: [δ 3.732–3.704, 3.545–3.511] (2 × s): ***Me***O_2CC(Ts)(CO_2TMS)CH(*p*-C_6H_4S)$CH=CH_2$: integral = I_{6f}

3f: [δ 3.695–3.640, 3.282–3.202] (2 × s): ***Me***O_2CCH(Ts)CH(*p*-C_6H_4S)$CH=CH_2$: integral = I_{3f}

$[A]/[A]_0 = I_{5f}/[I_{5f} + I_{6f} + I_{3f}]$; integral values given in Table 6 are based on I_{5f} set to 1.

Table 6: Measured ^{1}H nmr integrals vs time for substrate 1f

t (s)	measured integral values				$[A]/[A]_0$
	[δ 3.732–3.478]	[δ 3.545–3.511]	[δ 3.695–3.640]	[δ 3.282–3.202]	
0	0.01	0.00	0.01	0.00	0.980392
300	0.01	0.00	0.01	0.00	0.980392
600	0.01	0.00	0.01	0.00	0.980392
900	0.02	0.00	0.01	0.00	0.970874
1200	0.02	0.01	0.01	0.00	0.961538
1500	0.02	0.01	0.01	0.00	0.961538
1800	0.02	0.01	0.01	0.00	0.961538
2100	0.02	0.01	0.02	0.00	0.952381
2400	0.03	0.01	0.02	0.00	0.943396
2700	0.03	0.01	0.02	0.00	0.943396
3000	0.03	0.01	0.02	0.00	0.943396
3300	0.03	0.01	0.02	0.00	0.943396
3600	0.03	0.02	0.02	0.00	0.934579
3900	0.03	0.02	0.02	0.00	0.934579
4200	0.03	0.02	0.02	0.00	0.934579
4500	0.04	0.02	0.02	0.00	0.925926
4800	0.04	0.02	0.02	0.00	0.925926
5100	0.04	0.02	0.02	0.00	0.925926
5400	0.04	0.02	0.02	0.00	0.925926
5700	0.04	0.03	0.02	0.00	0.917431
6000	0.04	0.03	0.02	0.00	0.917431
6300	0.04	0.03	0.02	0.00	0.917431
6600	0.04	0.03	0.02	0.00	0.917431
6900	0.04	0.03	0.02	0.00	0.917431
7200	0.04	0.03	0.02	0.00	0.917431
7500	0.04	0.03	0.02	0.00	0.917431
8040	0.04	0.04	0.03	0.00	0.900901
11640	0.05	0.06	0.04	0.02	0.854701
15240	0.06	0.09	0.05	0.03	0.813008
18840	0.08	0.11	0.07	0.05	0.763359
22440	0.10	0.13	0.09	0.08	0.714286
26040	0.12	0.16	0.12	0.11	0.662252
29640	0.14	0.18	0.16	0.14	0.617284
33240	0.16	0.20	0.20	0.18	0.574713
36840	0.18	0.21	0.25	0.23	0.534759
40440	0.20	0.24	0.30	0.28	0.49505
44040	0.23	0.25	0.36	0.34	0.458716
47640	0.25	0.27	0.43	0.41	0.423729

51240	0.28	0.29	0.50	0.47	0.393701
54840	0.30	0.31	0.59	0.56	0.362319
58440	0.33	0.33	0.69	0.64	0.334448
62040	0.37	0.36	0.81	0.74	0.304878
65640	0.41	0.38	0.94	0.85	0.27933
69240	0.44	0.39	1.09	0.98	0.25641
72840	0.47	0.41	1.25	1.11	0.235849
76440	0.51	0.42	1.41	1.27	0.21692
80040	0.51	0.43	1.58	1.36	0.204918
83640	0.54	0.44	1.75	1.50	0.191205
87240	0.62	0.46	2.07	1.78	0.168634
90840	0.60	0.45	2.20	1.84	0.164204
94440	0.63	0.46	2.36	1.97	0.155763
98040	0.68	0.48	2.71	2.28	0.13986
101640	0.68	0.47	2.81	2.33	0.137174
105240	0.69	0.47	2.91	2.37	0.134409
108840	0.73	0.46	3.34	2.66	0.1221
112440	0.77	0.50	3.81	3.02	0.10989
116040	0.78	0.48	3.84	3.01	0.109769
119640	0.81	0.46	4.28	3.30	0.101523
123240	0.87	0.52	4.91	3.75	0.090498
126840	0.86	0.47	4.87	3.67	0.091996
130440	0.91	0.47	5.52	4.10	0.083333
134040	0.95	0.47	6.10	4.48	0.076923
137640	0.99	0.49	7.03	5.13	0.068306
141240	1.01	0.49	7.42	5.35	0.065488
144840	1.03	0.46	7.37	5.26	0.066138
148440	1.04	0.47	8.25	5.85	0.060205
152040	1.19	0.61	10.16	7.11	0.049826
155640	1.26	0.53	11.46	7.93	0.045086
159240	1.25	0.57	11.08	7.63	0.046447
162840	1.22	0.51	12.40	8.50	0.042319
166440	1.29	0.56	13.79	9.37	0.038447
170040	1.36	0.62	14.94	10.07	0.035727
173640	1.43	0.67	16.38	10.95	0.032862
177240	1.45	0.53	18.37	12.28	0.029735
180840	1.40	0.47	19.39	12.86	0.028474
191640	1.59	0.56	22.18	14.44	0.0251
195240	1.74	0.78	27.57	17.84	0.0204
198840	1.51	0.53	23.22	14.99	0.0242
202440	1.42	0.39	24.85	16.06	0.0229
206040	1.50	0.46	29.24	18.87	0.0196
209640	1.38	0.38	26.55	17.09	0.0216
213240	1.70	0.69	38.72	24.66	0.0150
216840	1.39	0.38	28.25	17.93	0.0204
220440	1.50	0.40	30.44	19.30	0.0190
224040	1.39	0.30	30.00	19.06	0.0193
227640	1.50	0.44	35.20	22.18	0.0166
231240	1.49	0.46	39.40	24.99	0.0149
234840	1.27	0.20	37.21	23.56	0.0158
238440	1.36	0.18	40.00	25.20	0.0148
242040	2.14	0.88	75.30	47.19	0.0079
245640	2.01	0.78	75.35	47.03	0.0079

References

1. L.Wang, and Z.Huang, *J. Chem. Res.*, 2005, 446.
2. Zeitler, K. *Org. Lett.*, 2006, **8**, 637.
3. V. K.Aggarwal, J. R. Fulton, C. G. Sheldon, and J. Vicente, *J. Am. Chem. Soc.***,** 2003, **125**, 6034.

4. A. Costa, C. Najera and J. M.Sansano, *J. Org. Chem.*, 2002, **67**, 5216.
5. H.-J.Knölker, G.Baumb, N.Foitzika, H.Goesmannb, P.Gonsera, P. G. Jones and H. Röttele, *Eur. J. Inorg. Chem.*, 1998, 993.
6. R. Takeuchi, N. Ue, K. Tanabe, K. Yamashita and N. Shiga, *J. Am. Chem. Soc.***,** 2001, **123**, 9525.
7. J. Lehmann and G. C. Lloyd-Jones, *Tetrahedron*, 1995, **51**, 8863.
8. E. A. Couladouros, I. C. Soufli, V. I. Moutsos, and R. K. Chadha, *Chem. Eur. J.***,** 1998, **4**, 33.
9. P. C. B. Page, J. P. G. Moore; I. Mansfield, M. J. McKenzie, W. B. Bowler and J. A. Gallagher, *Tetrahedron*, 2001, **57**, 1837.
10. D. Craig and F. Grellepois, *Org. Lett.*, 2005, **7**, 463.