# Electronic Supplementary Information

## Ethyl (Benzothiazol-2-ylsulfonyl)acetate: A New Reagent for the Stereoselective Synthesis of $\alpha,\beta$-Unsaturated Esters from Aldehydes

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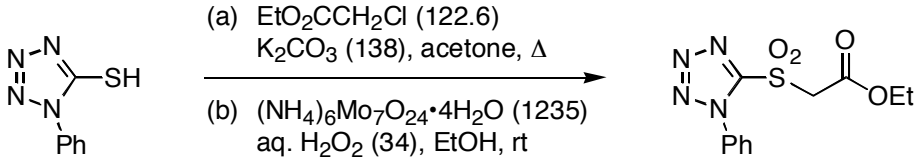
*General techniques:* All reactions requiring anhydrous conditions were conducted in flame-dried glass apparatus under an atmosphere of $N_2$. THF was freshly distilled from sodium benzophenone ketyl prior to use. Preparative chromatographic separations were performed on silica gel 60 (35-75 $\mu$m) and reactions followed by TLC analysis using silica gel 60 plates (2-25 $\mu$m) with fluorescent indicator (254 nm) and visualized with UV or phosphomolybdic acid. All commercially available reagents were used as received unless otherwise noted.

Melting points were recorded on a melting point stage and are uncorrected. Infra-red spectra were recorded in Fourier transform mode using a thin film supported between NaCl plates for liquid samples and an ATR probe for solids. $^1$H and $^{13}$C NMR spectra were recorded in Fourier transform mode at the field strength specified and from the indicated deuterated solvents in standard 5 mm diameter tubes. Chemical shift in ppm is quoted relative to residual solvent signals calibrated as follows: $CDCl_3$ $\delta_H$ ($CHCl_3$) = 7.26 ppm, $\delta_C$ = 77.2 ppm. Multiplicities in the $^1$H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Numbers in parentheses following carbon atom chemical shifts refer to the number of attached hydrogen atoms as revealed by the DEPT spectral editing technique. Low (MS) and high resolution (HRMS) mass spectra were obtained using either electron impact (EI) or electrospray (ES) ionization techniques. Ion mass/charge ($m/z$) ratios are reported as values in atomic mass units.

### Preparation of Sulfonylacetates 7 and 8

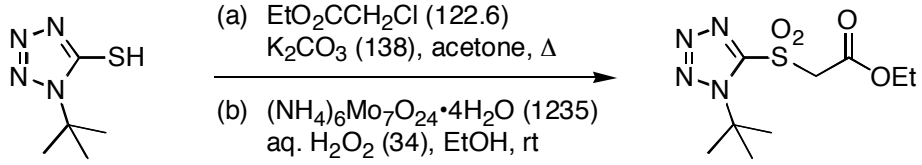



$C_7H_6N_4S$ (**4**) (178.21)

$C_{11}H_{12}N_4O_4S$ (**7**) (296.30)

**Ethyl (1-phenyl-1*H*-tetrazol-5-ylsulfonyl)acetate (7)**. A stirred suspension of 1-phenyl-1*H*-tetazole-5-thiol (**4**, 5.00 g, 28.1 mmol) and $K_2CO_3$ (4.6 g, 33 mmol) in acetone (100 mL) was treated with neat ethyl chloroacetate (3.5 mL, d = 1.16, 4.1 g, 33 mmol). The mixture was heated at reflux for 20 h, allowed to cool and filtered. Concentration of the filtrate *in vacuo* yielded 7.4 g of crude ethyl (1-phenyl-1*H*-tetrazol-5-ylsulfanyl)acetate as an orange oil which solidified on standing. A stirred solution of this material in EtOH (150 mL) was treated with $(NH_4)_6Mo_7O_{24}$•$4H_2O$ (3.5 g, 2.8 mmol) followed by aq. $H_2O_2$ (10.8 mL, d = 1.18, 12.7 g, 30 wt.%, 112 mmol) and stirred for 75 h at rt. After this time, the bulk of the EtOH solvent was removed *in vacuo* and the residue partitioned between EtOAc (50 mL) and $H_2O$ (50 mL). The layers were separated and the aqueous phase extracted with EtOAc (3x25 mL). The combined organic extracts were washed with brine (20 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. The crude residue

(6.8 g) was purified by column chromatography (eluting with 50% EtOAc in hexanes) to yield ethyl (1-phenyl-1*H*-tetrazol-5-ylsulfonyl)acetate (**7**, 4.70 g, 15.9 mmol, 57%) as a colourless solid: mp 63-64 °C (EtOH), IR (neat) 3000, 1736, 1341, 1251, 1160, 1015, 765, 655 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.68-7.60 (5H, m), 4.67 (2H, s), 4.22 (2H, q, *J* = 7.1 Hz), 1.24 (3H, t, *J* = 7.2 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 161.3 (0), 153.3 (0), 132.9 (0), 131.7 (1), 129.9 (2C, 1), 125.6 (2C, 1), 63.3 (2), 59.5 (2), 13.9 (3) ppm; MS (ES+) *m/z* 297 $(M+H)^+$; Anal. Calcd. for $C_{11}H_{12}N_4O_4S$: C, 44.59; H, 4.08; N, 18.91. Found: C, 44.50; H, 4.10; N, 18.75.




$C_5H_{10}N_4S$ (**5**) (158.22)

$C_9H_{16}N_4O_4S$ (**8**) (276.31)

**Ethyl (1-*tert*-butyl-1*H*-tetrazol-5-ylsulfonyl)acetate (8)**. A stirred suspension of 1-*tert*-butyl-1*H*-tetazole-5-thiol[1] (**5**, 6.00 g, 37.9 mmol) and $K_2CO_3$ (6.3 g, 45 mmol) in acetone (100 mL) was treated with neat ethyl chloroacetate (4.8 mL, d = 1.16, 5.6 g, 45 mmol). The mixture was heated at reflux for 20 h, allowed to cool and filtered. Concentration of the filtrate *in vacuo* yielded 9.8 g of crude ethyl (1-*tert*-butyl-1*H*-tetrazol-5-ylsulfanyl)acetate as an orange solid. A stirred solution of this material in EtOH (40 mL) at 0 °C was treated with $(NH_4)_6Mo_7O_{24}•4H_2O$ (5.0 g, 4.0 mmol) followed by aq. $H_2O_2$ (15.4 mL, d = 1.18, 18.2 g, 30 wt.%, 160 mmol) and stirred for 42 h at rt. After this time, the bulk of the EtOH solvent was removed *in vacuo* and the residue partitioned between EtOAc (50 mL) and $H_2O$ (50 mL). The layers were separated and the aqueous phase extracted with EtOAc (3x25 mL). The combined organic extracts were washed with brine (20 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. The crude residue (8.2 g) was purified by column chromatography (eluting with 20% EtOAc in hexanes) to yield ethyl (1-*tert*-butyl-1*H*-tetrazol-5-ylsulfonyl)acetate (**8**, 3.66 g, 13.2 mmol, 35%) as a colourless solid: mp 46-48 °C (TBME); IR (neat) 2983, 2923, 1742, 1478, 1363, 1314, 1207, 1124, 1017, 894, 784 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 4.82 (2H, s), 4.24 (2H, q, *J* = 7.2 Hz), 1.87 (9H, s), 1.25 (3H, t, *J* = 7.1 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 161.5 (0), 154.1 (0), 65.7 (0), 63.1 (2), 59.8 (2), 29.7 (3C, 3), 14.0 (3) ppm; MS (ES+) *m/z* 299 $(M+Na)^+$; Anal. Calcd. for $C_9H_{16}N_4O_4S$: C, 39.12; H, 5.84; N, 20.28. Found: C, 39.45; H, 5.75; N, 21.15.

## Alkene Stereoisomer Assignment and Characterization Data

Isomeric ratios were determined by integration of appropriate signals in 300 MHz $^1H$ NMR spectra: (*E*)-isomers were identified by their characteristic alkenyl vicinal coupling constants of *ca* 16 Hz, while (*Z*)-isomers were revealed by smaller alkenyl vicinal coupling constants of *ca* 12 Hz.[2] Where the minor *cis* isomer could not be detected by $^1H$ NMR spectroscopy, stereoselectivity was recorded as *E:Z* > 98:2. No attempt was made to separate (*E*)- and (*Z*)-isomers and data which follow were determined from isomeric product mixtures. Where signals in NMR spectra could be clearly attributed to a particular isomer this is indicated; unattributed signals for isomeric mixtures are due to a combination of both major and minor isomers.

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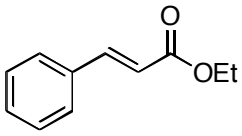
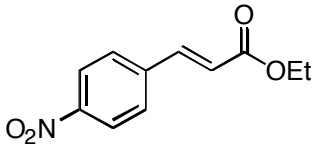
[1] H. Quast and L. Bieber, *Chem. Ber.*, 1981, **114**, 3253.

[2] E. Pretsch, T. Clerc, J. Seibl and W. Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd Ed., Springer-Verlag, Berlin, 1989 (Bieman, K. translator).



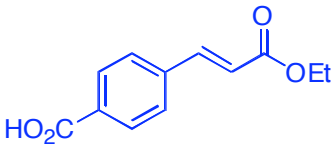

$C_{11}H_{12}O_2$

**Ethyl (*E*)-3-phenylprop-2-enoate (Table 1, Entry 1, 63%, *E:Z* > 98:2):** colourless oil; IR (neat) 2981, 1707, 1638, 1311, 1176, 1039, 768 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.69 (1H, d, *J* = 16.0 Hz), 7.55-7.50 (2H, m), 7.40-7.36 (3H, m), 6.44 (1H, d, *J* = 16.0 Hz), 4.27 (2H, q, *J* = 7.1 Hz), 1.34 (3H, q, *J* = 7.1 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 167.2 (0), 144.8 (1), 134.6 (0), 130.4 (1), 129.0 (2C, 1), 128.2 (2C, 1), 118.4 (1), 60.7 (2), 14.5 (3) ppm. Data are in agreement with those previously reported.[3]

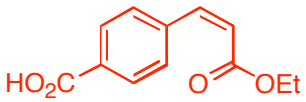



$C_{11}H_{11}NO_4$

**Ethyl (*E*)-3-(4-nitrophenyl)prop-2-enoate (Table 2, Entry 1, 89%, *E:Z* > 98:2):** IR (neat) 2977, 1712, 1517, 1337, 1191, 978, 844 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.23 (2H, d, *J* = 8.9 Hz), 7.69 (1H, d, *J* = 15.8 Hz), 7.66 (2H, d, *J* = 8.7 Hz), 6.55 (1H, d, *J* = 16.1 Hz), 4.28 (2H, q, *J* = 7.1 Hz), 1.34 (3H, t, *J* = 7.1 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 166.2 (0), 148.6 (0), 141.8 (1), 140.7 (0), 128.8 (2C, 1), 124.3 (2C, 1), 122.7 (1), 61.2 (2), 14.4 (3) ppm. Data are in agreement with those previously reported.[4]

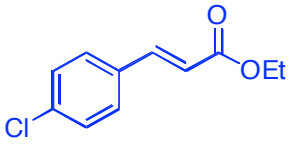



$C_{12}H_{12}O_4$

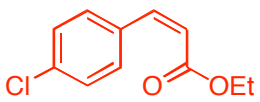



$C_{12}H_{12}O_4$

**Ethyl (*E*)- and (*Z*)-3-[4-(hydroxycarbonyl)phenyl]prop-2-enoate (Table 2, Entry 2, 57%, *E:Z* = 96:4):** IR (neat) 2982, 1696, 1289, 1173, 987, 845, 774 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.13 (2H, d, *J* = 8.2 Hz), 7.72 ($1H^E$, d, *J* = 16.1 Hz), 7.62 (2H, d, *J* = 8.3 Hz), 7.01 ($1H^Z$, d, *J* = 12.5 Hz), 6.54 ($1H^E$, d, *J* = 16.1 Hz), 6.07 ($1H^Z$, d, *J* = 12.5 Hz), 4.29 (2H, q, *J* = 7.1 Hz), 1.35 (3H, t, *J* = 7.1 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) (*E*)-isomer δ 171.5 (0), 166.7 (0), 143.2 (1), 139.6 (0), 130.9 (2C, 1), 128.2 (2C, 1), 121.2 (1), 61.0 (2), 14.5 (3) ppm. Data are in agreement with those previously reported.[5]




$C_{11}H_{11}ClO_2$

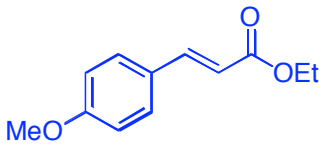



$C_{11}H_{11}ClO_2$

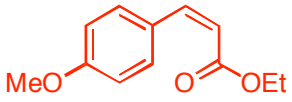
**Ethyl (*E*)- and (*Z*)-3-(4-chlorophenyl)prop-2-enoate (Table 2, Entry 3, 77%, *E:Z* = 95:5):** colourless oil; IR (neat) 2981, 2928, 1715, 1640, 1593, 1492, 1311, 1174, 1090, 982, 822; $^1H$ NMR (300 MHz,

[3] V. K. Aggarwal, J. R. Fulton, C. G. Sheldon and J. de Vincente, *J. Am. Chem. Soc.*, 2003, **125**, 6034.
[4] C. Qian and L. Wang, *Tetrahedron*, 2000, **56**, 7193.
[5] A. J. Spencer, *Organomet. Chem.*, 1984, **265**, 323.

$CDCl_3$) δ 7.63 ($1H^E$, d, *J* = 16.0 Hz), 7.46 (2H, d, *J* = 8.6 Hz), 7.36 (2H, d, *J* = 8.6 Hz), 6.88 ($1H^Z$, d, *J* = 12.7 Hz), 6.41 ($1H^E$, d, *J* = 16.0 Hz), 5.96 ($1H^Z$, d, *J* = 12.6 Hz), 4.26 (2H, q, *J* = 7.1 Hz), 1.33 (3H, t, *J* = 7.1 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) (*E*)-isomer δ 166.9 (0), 143.3 (1), 136.3 (0), 133.1 (0), 129.4 (4C, 1), 119.0 (1), 60.8 (2), 14.5 (3) ppm. Data are in agreement with those previously reported.[3]

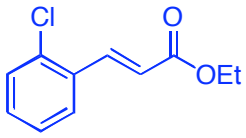



$C_{12}H_{14}O_3$

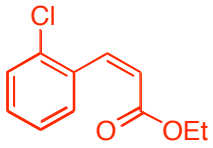



$C_{12}H_{14}O_3$

**Ethyl *(E)*- and *(Z)*-3-(4-methoxyphenyl)prop-2-enoate (Table 2, Entry 4, 93%, *E:Z* = 92:8):** colourless oil; IR (neat) 2931, 1710, 1634, 1605, 1513, 1252, 1165, 1032, 828 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.64 ($1H^E$, d, *J* = 16.0 Hz), 7.48 (2H, d, *J* = 8.9 Hz), 6.90 (2H, d, *J* = 8.8 Hz), 6.31 ($1H^E$, d, *J* = 16.0 Hz), 5.82 ($1H^Z$, d, *J* = 12.8 Hz), 4.25 (2H, q, *J* = 7.1 Hz), 3.83 (3H, s), 1.33 (3H, t, *J* = 7.1 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) (*E*)-isomer δ 167.5 (0), 161.5 (0), 144.4 (1), 127.3 (0), 129.8 (2C, 1), 115.9 (1), 114.4 (2C, 1), 60.5 (2), 55.5 (3), 14.5 (3) ppm. Data are in agreement with those previously reported.[3]

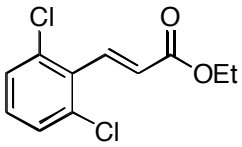



$C_{11}H_{11}ClO_2$




$C_{11}H_{11}ClO_2$

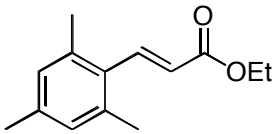
**Ethyl *(E)*- and *(Z)*-3-(2-chlorophenyl)prop-2-enoate (Table 2, Entry 5, 72%, *E:Z* = 95:5):** colourless oil; IR (neat) 2928, 1710, 1636, 1471, 1315, 1268, 1179, 1039, 760 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.09 ($1H^E$, d, *J* = 16.0 Hz), 7.63-7.59 (1H, m), 7.42-7.38 (1H, m), 7.32-7.25 (2H, m), 7.13 ($1H^Z$, *J* = 12.3 Hz), 6.43 ($1H^E$, d, *J* = 16.0 Hz), 6.08 ($1H^Z$, d, *J* = 12.2 Hz), 4.28 ($2H^E$, q, *J* = 7.2 Hz),4.12 ($2H^Z$, q, *J* = 7.2 Hz), 1.35 (3H, t, *J* = 7.2 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) (*E*)-isomer δ 166.6 (0), 140.5 (1), 135.0 (0), 132.8 (0), 131.1 (1), 130.3 (1), 127.7 (1), 127.3 (1), 121.0 (1), 60.8 (2), 14.4 (3) ppm. Data are in agreement with those previously reported.[6]




$C_{11}H_{10}Cl_2O_2$

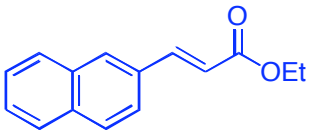
**Ethyl *(E)*-3-(2,6-dichlorophenyl)prop-2-enoate (Table 2, Entry 6, 83%, *E:Z* > 98:2):** colourless oil; IR (neat) 2927, 1717, 1644, 1428, 1304, 1188, 1035, 979, 778 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.78 (1H, d, *J* = 16.4 Hz), 7.37-7.32 (2H, m), 7.18 (1H, dd, *J* = 8.7, 7.4 Hz), 6.59 (1H, d, *J* = 16.4 Hz), 4.29 (2H, q, *J* = 7.1 Hz), 1.35 (3H, t, *J* = 7.1 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 166.4 (0), 138.2 (1), 135.1 (0), 132.1 (0), 129.9 (1), 129.0 (2C, 1), 127.0 (1), 61.0 (2), 14.4 (3) ppm. Data are in agreement with those previously reported.[7]

[6] Z.-Z. Huang and Y. Tang, *J. Org. Chem.*, 2002, **67**, 5320.
[7] R. Arad-Yellin, B. S. Green and K. A. Muszkat, *J. Org. Chem.*, 1983, **48**, 2578.

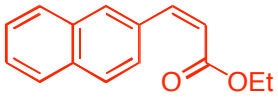


$C_{14}H_{18}O_2$

**Ethyl *(E)*-3-(2,4,6-trimethylphenyl)prop-2-enoate (Table 2, Entry 7, 70%, *E:Z* > 98:2):** light yellow solid; mp 34-36 °C (lit.[8] 33-35 °C); IR (neat) 2924, 1717, 1459, 1304, 1174, 1036, 852, 755 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.86 (1H, *J* = 16.4 Hz), 6.91 (2H, s), 6.07 (1H, d, *J* = 16.4 Hz), 4.29 (2H, q, *J* = 7.1 Hz), 2.34 (9H, s), 1.36 (3H, t, *J* = 7.1 Hz) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) δ 167.2 (0), 143.3 (1), 138.4 (0), 137.0 (2C, 0), 131.1 (0), 129.3 (2C, 1), 123.3 (1), 60.6 (2), 21.2 (2C, 3), 21.2 (3), 14.5 (3) ppm. Data are in agreement with those previously reported.[8]

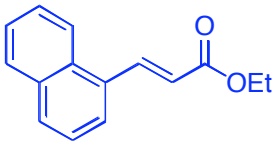


$C_{15}H_{14}O_2$

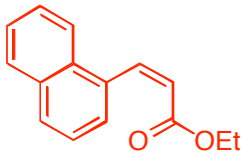


$C_{15}H_{14}O_2$

**Ethyl *(E)*- and *(Z)*-3-(2-naphthyl)prop-2-enoate (Table 2, Entry 8, 65%, *E:Z* = 93:7):** light yellow solid; mp 70-72 °C (lit.[9] 73 °C); IR (neat) 2981, 1717, 1634, 1175, 992, 823, 753 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.93-7.80 ($4H^Z$+$5H^E$, m), 7.66 (1H, dd, *J* = 8.6, 1.4 Hz), 7.53-7.48 (2H, m), 7.09 ($1H^Z$, d, *J* = 12.6 Hz), 6.56 ($1H^E$, d, *J* = 16.0 Hz), 6.04 ($1H^Z$, d, *J* = 12.7 Hz), 4.31 ($2H^E$, q, *J* = 7.1 Hz), 4.21 ($2H^Z$, q, *J* = 7.1 Hz), 1.37 (3H, t, *J* = 7.1 Hz) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) *(E)*-isomer δ 167.2 (0), 144.8 (1), 134.3 (0), 133.4 (0), 132.1 (0), 130.1 (1), 128.8 (1), 128.7 (1), 127.5 (1), 126.8 (1), 126.3 (1), 123.6 (1), 118.5 (1), 60.7 (2), 14.5 (3) ppm. Data are in agreement with those previously reported.[9]



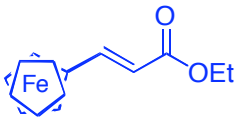
$C_{15}H_{14}O_2$



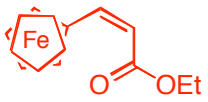
$C_{15}H_{14}O_2$

**Ethyl *(E)*- and *(Z)*-3-(1-naphthyl)prop-2-enoate (Table 2, Entry 9, 86%, *E:Z* = 96:4):** light yellow oil; IR (neat) 2928, 1713, 1633, 1305, 1178, 1041, 977, 776 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) δ 8.56 ($1H^E$, d, *J* = 15.8 Hz), 8.22 (1H, dm, *J* = 8.2 Hz), 7.92-7.85 (2H, m), 7.76 (1H, d, *J* = 7.2 Hz), 7.62-7.45 (3H, m), 6.55 ($1H^E$, d, *J* = 15.8 Hz), 6.26 ($1H^Z$, d, *J* = 12.1 Hz), 4.34 (2H, q, *J* = 7.1 Hz), 1.40 (3H, t, *J* = 7.1 Hz) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) *(E)*-isomer δ 167.0 (0), 141.7 (1), 133.8 (0), 131.9 (0), 131.5 (0), 130.6 (1), 128.8 (1), 127.0 (1), 126.3 (1), 125.6 (1), 125.1 (1), 123.5 (1), 121.0 (1), 60.7 (2), 14.5 (3) ppm. Data are in agreement with those previously reported.[10]

[8] E. Medina, A. Moyano, M. A. Pericàs and A. Riera, *Helv. Chim. Acta.*, 2000, **83**, 972.
[9] R. A. Rao and R. R. Rao, *Ind. J. Chem.*, 1968, **6**, 130.
[10] D.-J. Baek, S. B. Daniels, P. E. Reed and J. A. Katzenellenbogen, *J. Org. Chem.*, 1989, **54**, 3963.

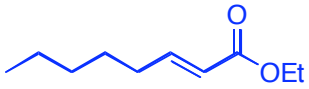



$C_{15}H_{16}FeO_2$

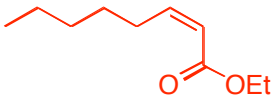



$C_{15}H_{16}FeO_2$

**Ethyl *(E)*- and *(Z)*-3-(ferrocenyl)prop-2-enoate (Table 2, Entry 10, 82%, *E:Z* = 96:4):** viscous red oil; IR (neat) 2975, 1700, 1634, 1470, 1396, 1317, 1210, 1174, 1043, 980, 824 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.57 ($1H^E$, d, *J* = 15.7 Hz), 6.67 ($1H^Z$, d, *J* = 12.6 Hz), 6.03 ($1H^E$, d, *J* = 15.7 Hz), 5.71 ($1H^Z$, d, *J* = 12.6 Hz), 4.48 (2H, t, *J* = 1.9 Hz), 4.39 (2H, t, *J* = 1.9 Hz), 4.22 (2H, q, *J* = 7.2 Hz), 4.15 (5H, s), 1.32 (3H, t, *J* = 7.1 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) (*E*)-isomer δ 167.4 (0), 145.7 (1), 115.0 (1), 78.8 (0), 70.9 (2C, 1), 69.8 (5C, 1), 68,7 (2C, 1), 60.3 (2), 14.5 (3) ppm; LRMS (ES+) *m/z* 285 $(M+H)^+$.

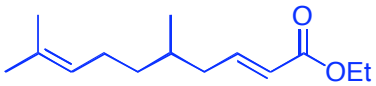



$C_{10}H_{18}O_2$

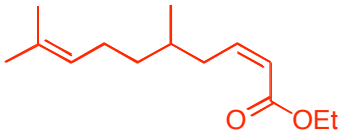



$C_{10}H_{18}O_2$

**Ethyl *(E)*- and *(Z)*-oct-2-enoate (Table 2, Entry 11, 41%, *E:Z* = 19:81):** colourless oil; IR (neat) 2929, 1720, 1644, 1415, 1177, 1037, 818 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 6.96 ($1H^E$, dt, *J* = 15.6, 7.0 Hz), 6.20 ($1H^Z$, dt, *J* = 11.5, 7.5 Hz), 5.81 ($1H^E$, dt, *J* = 15.6, 1.5 Hz), 5.74 ($1H^Z$, dt, *J* = 11.5, 1.6 Hz), 4.15 (2H, q, *J* = 7.1 Hz), 2.63 ($2H^Z$, qd, *J* = 7.4, 1.6 Hz), 2.19 ($2H^E$, qd, *J* = 7.1, 1.5 Hz), 1.51-1.27 (6H, m), 1.29 (3H, t, *J* = 7.1 Hz), 0.89 (3H, t, *J* = 6.8 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) (*E*)-isomer δ 167.0 (0), 149.7 (1), 121.4 (1), 60.3 (2), 32.3 (2), 31.5 (2), 27.9 (2), 22.6 (2), 14.5 (3), 14.1 (3) ppm; (*Z*)-isomer δ 166.7 (0), 150.8 (1), 119.7 (1), 59.9 (2), 31.6 (2), 29.1 (2), 28.9 (2), 22.6 (2), 14.4 (3), 14.1 (3) ppm. Data are in agreement with those previously reported.[11]



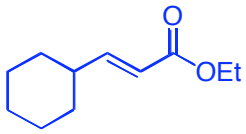

$C_{14}H_{24}O_2$



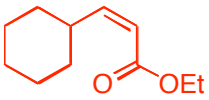

$C_{14}H_{24}O_2$

**Ethyl *(E)*- and *(Z)*-5,9-dimethyldeca-2,8-dienoate (Table 2, Entry 12, 64%, *E:Z* = 30:70):** colourless oil; IR (neat) 2925, 1720, 1654, 1450, 1377, 1270, 1182, 1044, 983, 745 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 6.93 ($1H^E$, dt, *J* = 15.6, 7.5 Hz), 6.22 ($1H^Z$, dt, *J* = 11.6, 7.6 Hz), 5.80 ($1H^E$, dt, *J* = 15.6, 1.5 Hz), 5.79 ($1H^Z$, dt, *J*, 11.5, 1.6 Hz), 5.12-5.04 (1H, m), 4.15 (2H, q, *J* = 7.1 Hz), 2.70-1.85 (4H, m), 1.67 (3H, bs), 1.59 (3H, bs), 1.42-1.10 (3H, m), 1.28 ($3H^E$, t, *J* = 7.1 Hz), 1.27 ($3H^Z$, t, *J* = 7.1 Hz), 0.91 ($3H^Z$, d, *J* = 6.7 Hz), 0.89 ($3H^E$, d, *J* = 6.7 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) (*E*)-isomer δ 166.8 (0), 148.6 (1), 131.6 (0), 124.6 (1), 122.5 (1), 60.3 (2), 39.8 (2), 36.8 (2), 32.2 (1), 25.9 (3), 25.6 (2), 19.6 (3), 17.8 (3), 14.4 (3) ppm; (*Z*)-isomer δ 166.7 (0), 149.7 (1), 131.4 (0), 124.8 (1), 120.5 (1), 59.9 (2), 36.9 (2), 36.1 (2), 33.0 (1), 25.9 (3), 25.7 (2), 19.6 (3), 17.8 (3), 14.4 (3) ppm. Data are in agreement with those previously reported.[12]

[11] I. Fleming, J. M. Mwaniki, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1237.
[12] M.-L. Wong, N.-W. Chung, L. He, X.-C. Wang, Z. Yan, Y.-C. Tang and D. Tang, *J. Org. Chem.*, 2003, **68**, 6321.

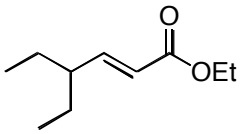



$C_{11}H_{18}O_2$



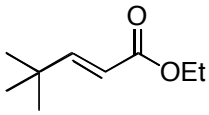

$C_{11}H_{18}O_2$

**Ethyl (*E*)- and (*Z*)-3-cyclohexylprop-2-enoate (Table 2, Entry 13, 80%, *E*:*Z* = 80:20):** Colourless oil; IR (neat) 2928, 1722, 1651, 1449, 1275, 1173, 1046, 983, 852 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 6.90 ($1H^E$, dd, *J* = 15.8, 6.8 Hz), 6.00 ($1H^Z$, dd, *J* = 11.5, 9.8 Hz), 5.74 ($1H^E$, dd, *J* = 15.8, 1.2 Hz), 5.63 ($1H^Z$, dd, 11.5, 0.6 Hz), 4.16 (2H, q, *J* = 7.1 Hz), 3.35-3.18 ($1H^Z$, m), 2.17-2.03 ($1H^E$, m), 1.79-1.60 (4H, m), 1.32-1.02 (6H, m), 1.27 (3H, t, *J* = 7.1 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) (*E*)-isomer δ 167.3 (0), 154.5 (1), 119.0 (1), 60.3 (2), 40.5 (1), 31.8 (2C, 2), 26.1 (2), 25.9 (2C, 2), 14.4 (3) ppm; (*Z*)-isomer δ 167.3 (0), 155.8 (1), 117.8 (1), 59.9 (2), 37.5 (1), 32.5 (2C, 2), 25.9 (2), 25.6 (2C, 2), 14.4 (3) ppm. Data are in agreement with those previously reported.[3]



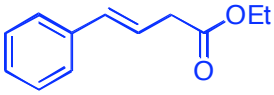

$C_{10}H_{18}O_2$

**Ethyl (*E*)-4-ethylhex-2-enoate (Table 2, Entry 14, 88%, *E*:*Z* > 98:2):** IR (neat) 2930, 1731, 1461 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 6.74 (1H, dd, *J* = 15.7, 9.2 Hz), 5.79 (1H, dm, *J* = 15.7 Hz), 4.19 (2H, q, *J* = 7.1 Hz), 1.98 (1H, dtt, *J* = 9.2, 8.3, 6.0 Hz), 1.57-1.41 (2H, m), 1.39-1.24 (2H, m), 1.30 (3H, t, *J* = 7.1 Hz), 0.85 (6H, t, *J* = 7.1 Hz) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 167.0 (0), 153.5 (1), 121.5 (1), 60.3 (2), 46.2 (1), 27.0 (2C, 2), 14.5 (3), 11.8 (2C, 3) ppm. Data are in agreement with those previously reported.[13]

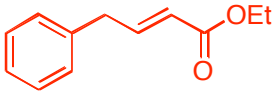



$C_9H_{16}O_2$

**Ethyl (*E*)-4,4-dimethylpent-2-enoate (Table 2, Entry 15, 21%, *E*:*Z* > 98:2):** $^1H$ NMR (300 MHz, $CDCl_3$) δ 6.97 (1H, d, *J* = 15.9 Hz), 5.73 (1H, d, *J* = 15.9 Hz), 4.19 (2H, q, *J* = 7.1 Hz), 1.29 (3H, t, *J* = 7.1 Hz), 1.08 (9H, s) ppm; $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 167.6 (0), 159.3 (1), 116.9 (1), 60.4 (2), 33.9 (0), 28.8 (3C, 3), 14.5 (3) ppm. Data are in agreement with those previously reported.[14]




$C_{12}H_{14}O_2$




$C_{12}H_{14}O_2$

**Ethyl (*E*)-4-phenylbut-3-enoate (*β,γ*) and ethyl (*E*)-4-phenylbut-2-enoate (*α,β*) (Table 2, Entry 16, 80%, *β,γ*:*α,β* = 87:13, both *E*:*Z* > 98:2):** IR (neat) 2928, 1737, 1268, 1159, 1029, 966, 693 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.40-7.20 (5H, m), 7.10 ($1H^{\alpha\beta}$, dt, *J* = 15.5, 6.8 Hz), 6.47 ($1H^{\beta\gamma}$, dt, *J* = 15.9,

[13] B. W. Gung and M. M. Yanik, *J. Org. Chem.*, 1996, **61**, 947.
[14] C. Jimeno, M. Pastó, A. Riera and M. A. Pericàs, *J. Org. Chem.*, 2003, **68**, 3130.

1.2 Hz), 6.30 (1H$^{\beta\gamma}$, dt, *J* = 15.9, 7.0 Hz), 5.80 (1H$^{\alpha\beta}$, dt, *J* = 15.6, 1.6 Hz), 4.17 (2H, q, *J* = 7.1 Hz), 3.51 (2H$^{\alpha\beta}$, dd, *J* = 6.8, 1.5 Hz) 3.23 (2H$^{\beta\gamma}$, dd, *J* = 7.0, 1.3 Hz), 1.27 (3H, t, *J* = 7.1 Hz) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) (*β*,*γ*)–isomer δ 171.7 (0), 137.0 (0), 133.5 (1), 128.8 (2C, 1), 127.6 (1), 126.4 (2C, 1), 122.0 (1), 60.9 (2), 38.6 (2), 14.4 (3) ppm. Data are in agreement with those previously reported.[15]

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[15] R. M. Gerkin and B. Rickborn, *J. Am. Chem. Soc.*, 1967, **89**, 5850.