Electronic Supplementary Information for

Exopericyclic stereocontrol in Claisen rearrangements of allylic sulfides

Donald Craig, John W. Harvey, Alexander G. O'Brien and Andrew J. P. White

General experimental

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 FT-IR or Perkin-Elmer Spectrum RX FT-IR System spectrometers. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded in $CDCl_3$ unless otherwise stated on a Brüker AV-400 or Brüker AV-500 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 $CDCl_3$). Coupling constants are given in hertz (Hz). The following abbreviations are used to indicate the multiplicities: s, singlet, br, broad signal; d, doublet; t, triplet; m multiplet. Mass spectra (CI, EI and ESI) were recorded using Micromass AutoSpec-Q, Micromass Platform II or Micromass AutoSpec Premier instruments. Elemental analyses were performed at the microanalytical laboratories of the London Metropolitan University. Analytical thin layer chromatography (TLC) was performed on pre-coated glass-backed Merck Kieselgel 60 F254 plates. Visualisation was effected with ultraviolet light, potassium permanganate or vanillin as appropriate. Flash column chromatography was performed using a Biotage Flash+ reservoir system with Biotage SNAP HP-Sil (30 μm) silica gel cartridges or using a Teledyne Isco Companion system fitted with RediSep (35–70 μm) silica gel cartridges. Standard solvents were distilled under nitrogen prior to use; ether and THF from sodium-benzophenone ketyl, CH_2Cl_2 and acetonitrile from CaH_2. All other solvents were distilled prior to use. Petrol refers to petroleum ether of the fraction bp 40–60 °C. Ether refers to diethyl ether. TBME refers to *tert*-butylmethyl ether All liquid reagents with the exception of HCl were distilled prior to use.

General procedure A: preparation of (*E*)-γ-sulfenyl-α,β-unsaturated esters

To a solution of triethylamine (3.90 mL, 28.0 mmol, 1.4 equiv.) in THF (40 mL) was added thiophenol (2.05 mL, 20.0 mmol, 1.0 equiv.) dropwise *via* syringe. The colourless solution was stirred at rt for 10 min and a solution of chloroaldehyde (20.0 mmol, 1.0 equiv.) in THF (20 mL) was added dropwise via syringe. The rapid formation of a colourless precipitate was observed upon addition, and the resulting suspension was stirred at rt for 1 h. In a separate flask, a solution of triethyl phosphonoacetate (4.80 mL, 24.0 mmol, 1.2 equiv.) in THF (80 mL) was added to a suspension of sodium hydride (60% w/w in mineral oil, 1.20 g, 30.0 mmol, 1.5 equiv.) in THF (40 mL) at 0 ºC *via* cannula. The mixture was allowed to warm to rt with stirring until all sodium hydride had dissolved. The previously prepared sulfenyl-aldehyde solution was filtered under nitrogen and added *via* cannula to the phosphonate anion solution at 0 ºC. After stirring for 1 h at 0 °C saturated aqueous NH_4Cl (100 mL) was added and the mixture extracted with EtOAc (3 x 100 mL). The combined organic extracts were washed with brine (150 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Purification over silica gel afforded the *E*-ester.

General procedure B: preparation of (*Z*)-γ-sulfenyl-α,β-unsaturated esters

To a solution of triethylamine (3.90 mL, 28.0 mmol, 1.4 equiv.) in THF (40 mL) was added thiophenol (2.05 mL, 20.0 mmol, 1.0 equiv.) dropwise *via* syringe. The colourless solution was stirred at rt for 10 min and a solution of chloroaldehyde (20.0 mmol, 1.0 equiv.) in THF (20 mL) was added dropwise *via* syringe. The rapid formation of a white precipitate was observed upon addition and the resulting suspension was stirred at rt for 1 h. In a separate flask, a solution of ethyl 2-(diphenylphosphonyl)acetate (6.41 g, 20.0 mmol, 1.0 equiv.) in THF (80 mL) was added to a suspension of sodium hydride (60% w/w in mineral oil, 1.20 g, 30.0 mmol, 1.5 equiv.) in THF (40 mL) at 0 ºC *via* cannula. The mixture was allowed to warm to rt with stirring until all sodium hydride had dissolved. The previously prepared sulfenyl-aldehyde solution was filtered under nitrogen and added *via* cannula to the phosphonate anion solution at –78 ºC. After stirring for 1 h at –78 ºC saturated aqueous NH_4Cl (150 mL) was added and the mixture extracted with EtOAc (3 x 100 mL). The combined organic extracts were washed with brine (150 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Purification over silica gel afforded the *Z*-ester.

General procedure C: preparation of allylic alcohols 6a–f

To a solution of the ester prepared as described above (4.91 mmol, 1.0 equiv.) in THF (50 mL) at 0 ºC was added diisobutylaluminium hydride (14.7 mL of a 1.0 M solution in toluene, 14.7 mmol, 3.0 equiv.) dropwise *via* syringe. The resulting colourless solution was warmed to rt and stirred for 1.5 h. The reaction mixture was diluted with dichloromethane (60 mL) and quenched with MeOH (5 mL). Water (10 mL) was added, followed by saturated aqueous sodium hydrogencarbonate (20 mL) and the mixture was filtered. The filtrate was extracted with dichloromethane (3 x 65 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Purification over silica gel (5–75 % TBME/heptane) afforded the allylic alcohol **6**.

General procedure D: preparation of esters 7

To a solution of the allylic alcohol **6** (1.57 mmol, 1.0 equiv.) in rigorously degassed (three freeze-vacuum pump-thaw cycles) triethyl orthoacetate (20.4 mmol, 13.0 equiv.) was added propionic acid (0.314 mmol, 0.2 equiv.) dropwise *via* syringe. After heating under reflux until the starting material had been consumed (TLC), the reaction mixture was cooled to rt and concentrated under reduced pressure to give the ester **7**.

2-Chloropropanal

To a solution of propanal (54.6 mL, 750 mmol, 1.0 equiv.) in dichloromethane (30 mL) at –10 ºC was added sulfuryl chloride (60.3 mL, 750 mmol, 1.0 equiv.) dropwise *via* an addition funnel over 30 minutes and the reaction mixture was allowed to warm to rt overnight. The reaction mixture was heated to reflux for 2 h, cooled and distilled through a 15 cm Vigreux column, collecting the fraction containing 2-chloropropanal (33.1 g, 66%) as a colourless oil: bp_{760} 82–84 ºC; δ_H (400 MHz, $CDCl_3$) 9.54 (1H, s (br), H-1), 4.30 (1H, dq, *J* 7.0, 2.0 H-2), 1.63 (3H, d, *J* 7.0, H-3); δ_C (101 MHz, $CDCl_3$) 195.1 (C-1), 58.8 (C-2), 18.3 (C-1), *m/z* (CI) 388, 294 $[(3M)NH_4]^+$, 260, 92 $[M]^+$; in agreement with published data.[1]

2-Chloroheptanal

To a solution of heptanal (3.94 mL, 26.8 mmol, 1.0 equiv.) in dichloromethane (1 mL) at 0 ºC was added D,L–proline (313 mg, 2.68 mmol, 0.1 equiv.), followed by *N*-

[1] C.-H. Wong, F. P. Mazenod and G. M. Whitesides, *J. Org. Chem.*, 1983, **48**, 3493.

chlorosuccinimide (4.85 g, 34.8 mmol, 1.3 equiv.). The suspension was warmed to rt, stirred for 16 h and pentane (100 mL) was added. The mixture was filtered and concentrated under reduced pressure. The residue was added to pentane (50 mL), filtered, concentrated under reduced pressure and distilled under reduced pressure to afford 2-chloroheptanal (3.37 g, 85%) as a colourless oil: bp_{90} 80–82 ºC; ν_{max} (film) 1735, 1466, 1379, 1102 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 9.47 (1H, d, *J* 2.5, H-1), 4.14 (1H, dt, *J* 5.5, 2.5, H-2), 2.00–1.78 (2H, m, H-3), 1.36–1.29 (6H, m, H-4,5,6), 0.89 (3H, t, *J* 7.0, H-7); δ_C (101 MHz, $CDCl_3$) 185.2 (C-1), 64.1 (C-2), 32.3, 31.1, 25.4, 22.5, 14.1; *m/z* (CI), 148 $[M]^+$, 166 $[MNH_4]^+$, 462, 428 $[(3M)NH_4]^+$; in agreement with published data.[2]

2-Chloro-3-methylbutanal

To a solution of 3-methylbutanal (5.36 mL, 50.0 mmol, 1.0 equiv.) in dichloromethane (2 mL) at 0 ºC was added D,L–prolinamide (571 mg, 5.00 mmol, 0.1 equiv.), followed by N-chlorosuccinimide (5.46 g, 65.0 mmol, 1.3 equiv.). The reaction mixture was warmed to rt during 16 h and pentane (100 mL) was added. The mixture was filtered and concentrated under reduced pressure. The residue was added to pentane (50 mL), filtered, concentrated under reduced pressure and distilled to afford 2-chloro-3-methylbutanal (3.88 g, 64%) as a colourless oil: bp_{760} 130–132 ºC; ν_{max} (film) 1737, 1465, 1369, 1058, 830 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 9.42 (1H, d, *J* 3.0, H-1), 3.95 (1H, dd, *J* 5.5, 3.0, H-2), 2.28 (1H, dsept, *J* 7.0, 5.5, H-3), [1.00 (3H, d, *J* 7.0) and 0.98 (3H, d, *J* 7.0), H-4]; δ_C (101 MHz, $CDCl_3$) 196.1 (C-1), 70.6 (C-2), 31.1 (C-3), 17.8 (C-4); *m/z* (CI) 120 $[M]^+$, 138 $[MNH_4]^+$, 344, 378 $[(3M)NH_4]^+$; in agreement with published data.[3]

Ethyl (*E*)-4-(phenylthio)pent-2-enoate

According to general procedure **A**, reaction of 2-chloropropanal (2.29 mL, 20.0 mmol, 1.0 equiv.) gave ethyl (*E*)-4-(phenylthio)pent-2-enoate (2.38 g, 47%) as a colourless oil after purification over silica gel (5–20% ether/heptane): ν_{max} (film) 1716, 1650, 747, 692 cm^{-1}; δ_H (400 MHz, $CDCl_3$) [7.42–7.40 (2H, m) and 7.34–7.28 (3H, m), SPh], 6.89 (1H, dd, *J* 15.5, 8.0, H-3), 5.60 (1H, d, *J* 15.5, H-2), 4.18 (2H, q,

[2] B. Kang, J. Mowat, T. Pinter and R. Britton, *Org. Lett.*, 2009, **11**, 1717.
[3] N. Halland, A. Braunton, S. Bachmann, M. Marigo and K. A. Jørgensen, *J. Am. Chem. Soc.*, 2004, **126**, 4790.

J 7.0, OCH_2), 3.81 (1H, dq, *J* 8.0, 7.0, H-4), 1.45 (3H, d, *J* 7.0, H-5), 1.28 (3H, t, *J* 7.0 OCH_2CH_3); δ_C (101 MHz, $CDCl_3$) 166.3 (C-1), 148.4 (C-3), 133.5 (*o*-SPh), 133.3, (*i*-SPh), 128.9 (*m*-SPh), 127.9 (*p*-SPh), 120.5 (C-2), 60.4 (OCH_2), 44.9 (C-4), 19.5 (C-5), 14.2 (OCH_2CH_3); *m/z* (CI) 254 $[MNH_4]^+$, 237 $[MH]^+$, 146 $[M\text{-}(SPh)NH_4]^+$ (Found: $[MNH_4]^+$, 254.1219. $C_{13}H_{16}O_2S$ requires 254.1215); in agreement with published data.[4]

Ethyl (*Z*)-4-(phenylthio)pent-2-enoate

According to general procedure **B**, reaction of 2-chloropropanal (2.29 mL, 20.0 mmol, 1.0 equiv.) gave *ethyl (Z)-4-(phenylthio)pent-2-enoate* (1.37 g, 29%) as a colourless oil after purification over silica gel (5–20% ether/heptane): ν_{max} (film) 2979, 1715, 1639, 1186, 1029, 826, 744, 692 cm^{-1}; δ_H (400 MHz, $CDCl_3$) [7.40–7.30 (2H, m) and 7.27–7.21 (3H, m), SPh], 6.02 (1H, dd, *J* 11.5, 10.5, H-3), 5.61 (1H, d, *J* 11.5, H-2), 5.25 (1H, dq, *J* 10.5, 7.0, H-4), 4.05 (2H, q, *J* 7.0, OCH_2), 1.39 (3H, d, *J* 7.0, H-5), 1.21 (3H, t, *J* 7.0, OCH_2CH_3); δ_C (101 MHz, $CDCl_3$) 166.3 (C-1), 150.3 (C-3), 134.1, 133.2, 128.9, 127.5, 118.9 (C-2), 60.2 (OCH_2), 40.4 (C-4), 32.1, 20.0, 14.4; *m/z* (CI) 254 $[MNH_4]^+$, 237 $[MH]^+$ (Found: C, 65.84; H, 6.80. $C_{13}H_{16}O_2S$ requires C, 66.07; H, 6.82).

Ethyl (*E*)-4-(phenylthio)non-2-enoate

According to general procedure **A**, reaction of 2-chloroheptanal (743 mg, 5.0 mmol, 1.0 equiv.) gave *ethyl (*E*)-4-(phenylthio)non-2-enoate* (785 mg, 57%) as a colourless oil after purification over silica gel (5–40% ether/heptane): ν_{max} (film) 2931, 1720, 1648, 1438, 1160, 746, 692 cm^{-1}; δ_H (400 MHz, $CDCl_3$) [7.38–7.35 (2H, m) and 7.31–7.23 (3H, m), SPh], 6.77 (1H, dd, *J* 15.5, 9.0, H-3), 5.50 (1H, dd, *J* 15.5, 1.0, H-2), 4.15 (2H, q, *J* 7.0, OCH_2), 3.60 (1H, dt, *J* 9.0, 6.5, H-4), 1.79–1.61 (2H, m, H-5), 1.47–1.29 (6H, m, H-6,7,8), 1.26 (3H, t, *J* 7.0, OCH_2CH_3), 0.89 (3H, t, *J* 7.0, H-9); δ_C (101 MHz, $CDCl_3$) 166.4 (C-1), 147.9 (C-3), 133.7, 129.1, 128.0, 124.0, 121.3 (C-2), 60.5 (OCH_2), 51.1 (C-4), 33.8, 31.7, 27.2, 22.7, 14.4, 14.2; *m/z* (CI) 310 $[MNH_4]^+$, 293 $[MH]^+$, 282, 268 (Found: $[MH]^+$, 293.1581. $C_{17}H_{24}O_2S$ requires $[MH]^+$ 293.1575) (Found C, 69.63; H, 8.29. $C_{17}H_{24}O_2S$ requires C, 69.82; H, 8.27).

[4] T. Bach and C. Körber, *J. Org. Chem.*, 2000, **65**, 2358.

Ethyl (*Z*)-4-(phenylthio)non-2-enoate

According to general procedure **B**, reaction of 2-chloroheptanal (2.91 ml, 20.0 mmol, 1.0 equiv.) gave *ethyl (Z)-4-(phenylthio)non-2-enoate* (4.35 g, 73%) as a colourless oil after purification over silica gel (5–40% ether/heptane): ν_{max} (film) 2931, 2859, 1717, 1640, 1583, 1178, 1026, 744, 692 cm^{-1}; δ_H (400 MHz, $CDCl_3$) [7.43–7.41 (2H, m) and 7.29–7.45 (3H, m), SPh], 5.99 (1H, dd, *J* 11.0, 11.5, H-3), 5.65 (1H, d, *J* 11.5, H-2), 5.20–5.14 (1H, m, H-4), 4.05 (2H, q, *J* 7.5, OCH_2), 1.64–1.28 (8H, m, H-5,6,7,8), 1.23 (3H, t, *J*, 7.5, $OCH_2C\mathit{H}_3$), 0.93–0.89 (3H, m, H-9); δ_C (101 MHz, $CDCl_3$) 166.1 (C-1), 149.1 (C-3), 133.9, 133.0, 128.6, 127.2, 119.4 (C-2), 60.0 (OCH_2), 45.2, 34.0, 31.5, 26.8, 22.5, 14.2, 14.0; *m/z* (CI) 310 $[MNH_4]^+$, 293 $[MH]^+$, 268 (Found: $[MH]^+$, 293.1579. $C_{17}H_{24}O_2S$ requires $[MH]^+$, 293.1575).

Ethyl (*E*)-5-methyl-4-(phenylthio)hex-2-enoate

According to general procedure **A**, reaction of 2-chloro-3-methylbutanal (551 mg, 5.0 mmol, 1.0 equiv.) gave *ethyl (*E*)-5-methyl-4-(phenylthio)hex-2-enoate* (795 mg, 60%) as a colourless oil after purification over silica gel (5–40% ether/heptane): ν_{max} (film) 1717, 1682, 1583, 1182, 1026, 744, 690 cm^{-1}; δ_H (400 MHz, $CDCl_3$) [7.30–7.27 (2H, m) and 7.22–7.16 (3H, m), SPh], 6.75 (1H, dd, *J* 15.5, 10.0, H-3), 5.40 (1H, d, *J* 15.5, H-2), 4.07 (2H, q, *J* 7.0, OCH_2), 3.36 (1H, dd, *J* 10.0, 6.5, H-5), 1.18 (3H, t, *J* 7.0, $OCH_2C\mathit{H}_3$), [1.03 (3H, d, *J* 6.5) and 0.98 (3H, d, *J* 6.5), H-6]; δ_C (101 MHz, $CDCl_3$) 166.3 (C-1), 146.2 (C-3), 136.5, 133.5, 129.1, 127.8, 121.8 (C-2), 60.5 (OCH_2), 59.0 (C-4), 32.4 (C-5), [20.8 and 20.1, (C-6)], 14.4 ($OCH_2\mathit{C}H_3$); *m/z* (CI) 282 $[MNH_4]^+$, 265 $[MH]^+$, 233 (Found: $[MNH_4]^+$, 282.1357. $C_{15}H_{20}O_2S$ requires $[MNH_4]^+$, 282.1528) (Found: C, 67.49; H, 7.68. $C_{15}H_{20}O_2S$ requires C, 68.14; H, 7.62).

Ethyl (*Z*)-5-methyl-4-(phenylthio)hex-2-enoate

According to general procedure **B**, reaction of 2-chloro-3-methylbutanal (2.41 g, 20.0 mmol, 1.0 equiv.) gave *ethyl (Z)-5-methyl-4-(phenylthio)hex-2-enoate* (1.41 g, 27%) as a colourless oil after purification over silica gel (5–20% ether/heptane): ν_{max} (film) 1716, 1683, 1583, 1182, 1026, 744, 691 cm^{-1}; δ_H (400 MHz, $CDCl_3$) [7.40 (2H, d, *J* 7.0) and 7.28–7.19 (3H, m), SPh], 6.10 (1H, dd, *J* 11.5, 11.0, H-3), 5.68 (1H, d, *J* 11.5, H-2), 5.02 (1H, dd, *J* 11.0, 7.0, H-4), 4.03 (2H, q, *J* 7.0, OCH_2), 1.96 (1H, sext, *J* 7.0, H-5), 1.22 (3H, t, *J* 7.0, $OCH_2C\mathit{H}_3$), [1.15 (3H, d, *J* 7.0) and 1.06 (3H, d, *J* 7.0), H-6]; δ_C (101 MHz, $CDCl_3$) 166.2 (C-1), 147.5 (C-3), 134.3 (*i*-SPh) 132.9 (*o*-SPh),

128.6 (*m*-SPh), 127.1 (*p*-SPh), 119.6 (C-2), 59.9 (OCH_2), 32.2 (C-5), [20.5 and 19.8, (C-6)], 14.2 (OCH_2CH_3); *m/z* (CI) 282 $[MNH_4]^+$, 265 $[MH]^+$ (Found: $[MH]^+$, 265.1265. $C_{15}H_{20}O_2S$ requires $[MH]^+$, 265.1262) (Found: C, 68.19; H, 7.62. $C_{15}H_{20}O_2S$ requires C, 68.14; H, 7.62).

Base-catalysed conversion of ethyl (*Z*)-4-(phenylthio)pent-2-enoate into *E*- and *Z*-5 (R = CH_3)

To a solution of ethyl (*Z*)-4-(phenylthio)pent-2-enoate (20 mg, 0.09 mmol, 1.0 equiv) in d_6-DMSO (0.7 mL) in an NMR tube was added potassium *tert*-butoxide (5 mg, 0.045 mmol, 0.5 equiv) in one portion. The tube was shaken and a red colour developed. The ^1H NMR spectrum of the mixture was recorded at intervals of 10 min, 1 h and 16 h, after which time complete conversion to a 70:30 mixture of e*thyl (*E*)-4-(phenylthio)pent-3-enoate* (*E*)-**5** and *ethyl (Z)-4-(phenylthio)pent-3-enoate* (*Z*)-**5** was observed: δ_H (400 MHz, $CDCl_3$) *inter alia* 7.35–7.02 (5H, m, SPh both isomers), [6.64 (t, *J* 7.5, $CH_3C(SPh)=CH$ for (*E*)-**5**) and 6.39 (t, *J* 7.0) $CH_3C(SPh)=CH$ for (*Z*)-**5**; combined integral 1H], 4.07–3.95 (2H, m, OCH_2), 2.50 (2H, m, H-2).

(*E*)-4-(Phenylthio)pent-2-en-1-ol (6a)

According to general procedure **C**, reaction of ethyl (*E*)-4-(phenylthio)pent-2-enoate (1.16 g, 4.91 mmol, 1.0 equiv.) gave (*E*)-4-(phenylthio)pent-2-en-1-ol **6a** (676 mg, 71%) as a colourless oil after purification over silica gel (5–75 % TBME/heptane): ν_{max} (film) 3378, 1639, 1372, 1196, 750, 693 cm^{-1}; δ_H (400 MHz, $CDCl_3$) [7.35–7.69 (3H, m,) and 7.43–7.41 (2H, m), SPh], 5.69 (1H, ddt, *J* 15.5, 9.0, 1.5, H-3), 5.52 (1H, dt, 15.5, 6.0, H-2), 4.05 (2H, m, H-1), 3.80 (1H, dq, *J* 9.0, 7.5, H-4), 1.42 (3H, d, *J* 7.5, H-5), 1.15 (1H, s (br), OH); δ_C (101 MHz, $CDCl_3$) 134.6 (C-3), 133.7, 133.15, 129.5, 128.7, 127.4 (C-2), 63.1 (C-1), 45.3 (C-4), 20.3 (C-5); *m/z* (EI) 194 $[M]^+$, 163 $[M\text{-}CH_2OH]^+$, 110 $[SPh]^+$, 84 $[M\text{-}SPh]^+$ (Found: $[M]^+$, 194.0765. $C_{11}H_{14}OS$ requires $[M]^+$, 194.0762); in agreement with published data.[4]

(*Z*)-4-(Phenylthio)pent-2-en-1-ol (6b)

According to general procedure **C**, reaction of ethyl (*Z*)-4-(phenylthio)pent-2-enoate (1.16 g, 4.91 mmol, 1.0 equiv.) gave *(Z)-4-(phenylthio)pent-2-en-1-ol* **6b** (670 mg, 70%) as a colourless oil after purification over silica gel (5–75% TBME/heptane): ν_{max} (film) 3366, 1651, 1583, 1474, 1438, 1195, 1041, 1013, 750, 692 cm^{-1}; δ_H (400 MHz, $CDCl_3$), [7.52–7.50 (2H, m) and 7.36–7.29 (3H, m), SPh], 5.56–5.50 (1H, m,

H-2), 5.44 (1H, dd, *J* 11.0, 10.5, H-3), 4.10 (1H, dq, *J* 10.5, 7.0, H-4), [3.83 (1H, dd, *J* 13.0, 6.0) and 3.73 (1H, dd, *J* 13.0, 7.0), H-1], 1.60 (1H, s, OH), 1.40 (3H, d, *J* 7.0, H-5); δ_C (101 MHz, $CDCl_3$) 134.8 (SPh), 134.4 (C-3), 132.1 (*i*-SPh), 128.9 (SPh), 128.2, 126.8 (C-2), 58.3 (C-1), 42.0 (C-4), 20.7 (C-5); *m/z* (CI) 212 $[MNH_4]^+$, 194, $[M]^+$, 177 $[M\text{-}OH]^+$, 163 (Found: $[MNH_4]^+$, 212.1113. $C_{11}H_{14}OS$ requires $[MNH_4]^+$, 212.1109).

(*E*)-4-(Phenylthio)non-2-en-1-ol (6c)

According to general procedure **C**, reaction of ethyl (*E*)-4-(phenylthio)non-2-enoate (746 mg, 2.55 mmol, 1.0 equiv.) gave *(*E*)-4-(phenylthio)non-2-en-1-ol* **6c** (531 mg, 83%) as a colourless oil after purification over silica gel (5–60% TBME/heptane): ν_{max} (film) 3350, 1663, 1583, 1438, 747, 691 cm^{-1}; δ_H (400 MHz, $CDCl_3$) [7.38–7.36 (2H, m) and 7.29–7.23 (3H, m), SPh], 5.55 (1H, dd, *J* 15.5, 9.0, H-3), 5.42 (1H, dt, *J* 15.5, 5.5, H-2), 3.99 (2H, t, *J* 6.0, H-1), 3.59 (1H, m, H-4), 1.80–1.20 (8H, m, H-5,6,7,8), 0.85 (3H, t, *J*, 7.0, H-9); δ_C (400 MHz, $CDCl_3$) 135.0 (*i*-SPh), 133.5 (C-3), 133.1 (*o*-SPh), 130.6 (*m*-SPh), 128.8 (C-2), 127.4 (*p*-SPh), 62.3 (C-1), 51.5 (C-4), 34.5 (C-5), 31.8 (C-6), 27.2 (C-7), 22.7 (C-8), 14.2 (C-9); *m/z* (CI) 268 $[MNH_4]^+$, 251 $[MH]^+$, 233 $[M\text{-}OH]^+$ (Found: $[MNH_4]^+$, 268.1738. $C_{15}H_{22}OS$ requires $[MNH_4]^+$, 268.1735) (Found: C, 71.42; H, 8.81. $C_{15}H_{22}OS$ requires C, 71.95; H, 8.86).

(*Z*)-4-(Phenylthio)non-2-en-1-ol (6d)

According to general procedure **C**, reaction of ethyl (*Z*)-4-(phenylthio)non-2-enoate (3.00 g, 10.3 mmol, 1.0 equiv.) gave*(Z)-4-(phenylthio)non-2-en-1-ol* **6d** (1.54 g, 60%) as a colourless oil after purification over silica gel (5–75% TBME/heptane): ν_{max} (film) 3388, 1651, 1583, 1467, 1438, 1378, 1176, 1025, 747, 692 cm^{-1}; δ_H (400 MHz, $CDCl_3$) [7.52–7.50 (2H, m) and 7.36–7.33 (3H, m), SPh], 5.57 (1H, dt, *J* 11.0, 7.0, H-2), 5.39 (1H, dd, *J* 11.0, 9.0, H-3), 3.91 (1H, dt, *J* 9.0, 5.5, H-4), 3.80–3.71 (2H, m, H-1), 1.60 (1H, s (br), OH), 1.44–1.40 (2H, m, H-5), 1.37–1.31 (6H, m, H-6,7,8), 0.91 (3H, t, *J* 7.0, H-9); δ_C (101 MHz, $CDCl_3$) 134.9, 134.3, 133.5, 129.4, 128.9, 128.2, 58.4 (C-1), 47.4 (C-4), 34.5, 31.5, 31.3, 27.2, 22.5, 14.0; *m/z* (CI) 268 $[MNH_4]^+$, 251 $[MH]^+$, 233, 158 (Found: C, 72.03; H, 8.72. $C_{15}H_{22}OS$ requires C, 71.95; H, 8.86).

(*E*)-5-Methyl-4-(phenylthio)hex-2-en-1-ol (6e)

According to general procedure **C**, reaction of ethyl (*E*)-5-methyl-4-(phenylthio)hex-2-enoate (279 mg, 1.06 mmol) gave *(*E*)-5-methyl-4-(phenylthio)hex-2-en-1-ol* **6e** (195 mg, 83%) as a colourless oil after purification over silica gel (5–75% TBME/heptane): ν_{max} (film) 3367, 1663, 1583, 1438, 969, 748, 692 cm^{-1}; δ_H (400 MHz, $CDCl_3$) [7.38–7.36 (2H, m) and 7.27–7.20 (3H, m), SPh], 5.58 (1H, dd, *J* 15.0, 9.5, H-3), 5.38 (1H, dt, *J* 15.0, 6.0, H-2), 3.98 (1H, t, *J* 6.0, H-1), 3.45 (1H, dd, *J* 9.50, 6.5, H-4), 1.96 (1H, sext, *J* 6.5, H-5), [1.06 (3H, d, *J* 6.5) and 1.03 (3H, d, *J* 6.64), H-6], 0.93 (1H, t, *J* 6.0, OH); δ_C (400 MHz, $CDCl_3$) 135.4, 133.4, 131.3, 131.0, 128.8, 127.3, 63.3 (C-1), 59.3 (C-4), 32.3 (C-5), 20.9, 19.8 (C-6); *m/z* (CI) 240 $[MNH_4]^+$, 223 $[MH]^+$, 205 $[M\text{-}OH]^+$ (Found: $[MH]^+$, 223.1166. $C_{13}H_{18}OS$ requires $[MH]^+$, 223.1157) (Found: C, 70.28; H, 8.13. $C_{13}H_{18}OS$ requires C, 70.22; H, 8.16).

(*Z*)-5-Methyl-4-(phenylthio)hex-2-en-1-ol (6f)

According to general procedure **C**, reaction of ethyl (*Z*)-5-methyl-4-(phenylthio)hex-2-enoate (81 mg, 0.31 mmol, 1.0 equiv.) gave *(Z)-5-methyl-4-(phenylthio)hex-2-en-1-ol* **6f** (36 mg, 54%) as a colourless oil after purification over silica gel (5–20% TBME/heptane): ν_{max} (film) 3350, 1650, 1583, 750, 690 cm^{-1}; δ_H (400 MHz, $CDCl_3$) [7.51–7.49 (2H, dd, *J* 8.0, 2.0) and 7.37–7.29 (3H, m), SPh], 5.62–5.48 (2H, m, H-2,3), 3.77–3.70 (3H, m, H-1,4), 1.92 (1H, sext, *J* 6.5, H-5), [1.10 (3H, d, *J* 6.5) and 1.03 (3H, d, *J* 6.5), H-6]; δ_C (101 MHz, $CDCl_3$) 134.9 (C-3), 134.7, 131.3, 129.5, 128.9, 128.0, 58.2 (C-1), 54.8 (C-4), 32.0 (C-5), 20.8 (C-6), 19.6 (C-6); *m/z* (CI) 240 $[MNH_4]^+$, 223 $[MH]^+$ (Found: C, 70.34; H, 8.17. $C_{13}H_{18}OS$ requires C, 70.22; H, 8.16).

Ethyl 3-(1-(phenylthio)ethyl)pent-4-enoate (7: R = CH_3)

From **6a**:

According to general procedure **D**, reaction of allylic alcohol **6a** (100 mg, 0.515 mmol, 1.0 equiv.) gave *ethyl 3-(1-(phenylthio)ethyl)pent-4-enoate* **7** (R = CH_3) (133 mg, 98%, 1:1 *syn*:*anti* mixture of diastereomers) as a colourless oil.

From **6b**:

According to general procedure **D**, reaction of allylic alcohol **6b** (100 mg, 0.515 mmol, 1.0 equiv.) gave *ethyl 3-(1-(phenylthio)ethyl)pent-4-enoate* **7** (R = CH_3) (131 mg, 97%, 3:1 *syn*:*anti* mixture of diastereoisomers) as a colourless oil.

Data for the mixture: ν_{max} (film) 1734, 1639, 1584, 1479, 1176, 1090 cm-1; *m/z* (ESI) 454, 391, 265 $[MH]^+$, 219, 177 $[M\text{-}SPhNa]^+$ (Found: $[MH]^+$, 265.1269. $C_{15}H_{20}O_2S$ requires $[MH]^+$, 265.1262).

NMR data for *syn*-**7** (R = CH_3): δ_H (400 MHz, d_6-acetone) [7.46 (2H, d, *J* 7.0), 7.35 (2H, dd, *J* 7.5, 7.0) and 7.27 (1H, dd, *J* 7.5, 7.0), SPh], 5.81 (1H, ddd, *J* 16.5, 11.0, 8.0, C*H*CH_2), 5.11 (1H, d, *J* 11.0, *trans*-CHCH_2), 5.10 (1H, d, *J* 16.5, *cis*-CHCH_2), 4.06 (2H, q, *J* 7.0, OCH_2), 3.51 (1H, dq, *J* 7.0, 3.5, H-4), 2.85–2.80 (1H, m, H-3), [2.75 (1H, dd, *J* 15.0, 5.5) and 2.43 (1H, dd, *J* 15.0, 9.0), H-2], 1.27 (3H, d, *J* 7.0, H-5), 1.18 (3H, t, *J* 7.0, OCH_2C*H*$_3$); δ_C (101 MHz, d_6-acetone) 172.1 (C-1), 138.3 (*C*HCH_2), 136.1 (*i*-SPh), 132.2, 129.6, 127.4, 117.1 (CH*C*H_2), 60.3 (OCH_2), 47.9 (C-4), 45.3 (C-3), 36.1 (C-2), 18.5 (C-5), 14.2 (OCH_2*C*H_3)

NMR data for *anti*-**7** (R = CH_3): δ_H (400 MHz, d_6-acetone) [7.46 (2H, d, *J* 7.0), 7.35 (2H, dd, *J* 7.5, 7.0) and 7.27 (1H, dd, *J* 7.5, 7.0), SPh], 5.83 (1H, ddd, *J* 17.0, 11.0, 8.0, C*H*CH_2), 5.10 (1H, d, *J* 11.0, *trans*-CHCH_2), 5.07 (1H, d, *J* 17.0, *cis*-CHCH_2), 4.06 (2H, q, *J* 7.0, OCH_2), 3.41 (1H, dq, *J* 13.5, 6.5, H-4), 2.82–2.77 (1H, m, H-3), [2.73 (1H, dd, *J* 15.0, 5.5) and 2.45 (1H, dd, *J* 15.0, 8.5), H-2], 1.25 (3H, d, *J* 7.0, H-5), 1.18 (3H, t, *J* 7.0, OCH_2C*H*$_3$); δ_C (101 MHz, d_6-acetone) 172.8 (C-1), 137.9 (*C*HCH_2), 135.7 (*i*-SPh), 132.2, 129.5, 127.4, 117.1 (CH*C*H_2), 60.3 (OCH_2), 46.6 (C-4), 45.3 (C-3), 37.7 (C-2), 17.8 (C-5), 14.2 (OCH_2*C*H_3).

Ethyl 3-ethenyl-4-(phenylthio)nonanoate (7: R = *n*C_5H_{11})

From **6c**:

According to general procedure **D**, reaction of allylic alcohol **6c** (65 mg, 0.26 mmol, 1.0 equiv.) gave *ethyl 3-ethenyl-4-(phenylthio)nonanoate* **7** (R = *n*C_5H_{11}) (82 mg, 98%, 1:1 *syn*:*anti* mixture of diastereomers) as a colourless oil.

From **6d**:

According to general procedure **D**, reaction of allylic alcohol **6d** (65 mg, 0.26 mmol, 1.0 equiv.) gave *ethyl 3-ethenyl-4-(phenylthio)nonanoate* **7** (R = *n*C_5H_{11}) (78 mg, 94%, 5:1 *syn*:*anti* mixture of diastereomers) as a colourless oil.

Data for the mixture: ν_{max} (film) 1733, 1639, 1584, 1479, 1351, 1173, 745, 692 cm^{-1}; *m/z* (CI) 328 $[MNH_4]^+$, 321 $[MH]^+$, 264, 233 (Found: $[MH]^+$, 321.1909. $C_{19}H_{28}O_2S$ requires $[MH]^+$, 321.1888).

NMR data for *syn*-**7** (R = *n*C_5H_{11}): δ_H (400 MHz, d_6-acetone) [7.47 (2H, d, *J* 8.0), 7.35 (2H, dd, *J* 8.0, 6.5) and 7.26 (1H, dd, *J* 8.0, 6.5), SPh], 5.83 (1H, ddd, *J* 17.0,

10.0, 8.0, C*H*CH_2), 5.13 (1H, d, *J* 10.0, *trans*-CHC*H*$_2$), 5.11 (1H, d, *J* 17.0, *cis*-CHC*H*$_2$), 4.07 (2H, q, *J* 7.0, OCH_2), 3.83–3.33 (1H, m, H-4), 2.92 (1H, m, H-3), [2.79 (1H, dd, *J* 15.0, 6.0) and 2.46 (1H, dd, *J* 15.0, 8.0), H-2], 1.75–1.27 (8H, m, H-5,6,7,8), 1.18 (3H, t, *J* 7.0, OCH_2CH_3); δ_C (101 MHz, d_6-acetone) 171.6 (C-1), 137.6 (*C*HCH_2), 131.3 (*o*-SPh), 136.5, 129.0 (*m*-SPh), 126.6 (*p*-SPh), 116.6 ($CHCH_2$), 59.8 (OCH_2), 53.5 (C-4), 43.7 (C-3), 33.0, 31.3, 26.9, 22.3, 13.7, 13.4.

NMR data for *anti*-**7** (R = nC_5H_{11}): δ_H (400 MHz, d_6-acetone) [7.47 (2H, d, *J* 8.0), 7.35 (2H, dd, *J* 8.0, 6.5) and 7.26 (1H, dd, *J* 8.0, 6.5), SPh], 5.86 (1H, ddd, *J* 17.0, 10.0, 8.0, C*H*CH_2), 5.13 (1H, d, *J* 10.0, *trans*-CHC*H*$_2$), 5.11 (1H, d, *J* 17.0, *cis*-CHC*H*$_2$), 4.08 (2H, q, *J* 7.0, OCH_2), 3.29–3.24 (1H, m, H-4), 2.90–2.83 (1H, m, H-3), [2.78 (1H, dd, *J* 15.0, 5.5) and 2.45 (1H, dd, *J* 15.0, 9.0), H-2], 1.75–1.27 (8H, m, H-5,6,7,8), 1.18 (3H, t, *J* 7.0, OCH_2CH_3); δ_C (101 MHz, d_6-acetone) 171.4 (C-1), 138.2 (*C*HCH_2), 136.5, 131.4 (*o*-SPh), 128.9 (*m*-SPh), 127.4 (*p*-SPh), 116.4 ($CHCH_2$), 59.8 (OCH_2), 52.7 (C-4), 44.5 (C-3), 36.9 (C-2), 36.2 (C-2), 33.0, 31.4, 26.5, 22.3, 13.7, 13.4.

Ethyl 3-ethenyl-5-methyl-4-(phenylthio)hexanoate (7: R = *i*C_3H_7)

From **6e**:

According to general procedure **D**, reaction of allylic alcohol **6e** (58 mg, 0.26 mmol, 1.0 equiv.) gave *ethyl 3-ethenyl-5-methyl-4-(phenylthio)hexanoate* **7** (R = *i*C_3H_7) (71 mg, 93%, 3:2 *syn*:*anti* mixture of diastereoisomers) as a colourless oil.

From **6f**:

According to general procedure **D**, reaction of allylic alcohol **6f** (36 mg, 0.16 mmol, 1.0 equiv.) gave *ethyl 3-ethenyl-5-methyl-4-(phenylthio)hexanoate* **7** (R = *i*C_3H_7) (41 mg, 87%, 3:1 *syn*:*anti* mixture of diastereoisomers) as a colourless oil.

Data for the mixture: ν_{max} (film) 1734, 1640, 1582, 1440, 1351, 745, 692 cm^{-1}; *m/z* (CI) 310 $[MNH_4]^+$, 293 $[MH]^+$, 205, 117 (Found: $[MH]^+$, 293.1587. $C_{17}H_{24}O_2S$ requires $[MH]^+$, 293.1575).

NMR data for *syn*-**7** (R = *i*C_3H_7): δ_H (400 MHz, $CDCl_3$) [7.83–7.80 (2H, m) and 7.67–7.56 (3H, m), SPh], 6.21 (1H, ddd, *J* 17.0, 10.0, 8.0, C*H*CH_2), 5.54 (1H, d, *J* 17.0, *cis*-CHC*H*$_2$), 5.48 (1H, d, *J* 10.0, *trans*-CHC*H*$_2$), 3.95–3.87 (2H, m, OCH_2), 3.95–3.87 (1H, m, OCH_2), 3.21–3.13 (1H, m, H-3), [2.74 (1H, dd, *J* 15.5, 6.0) and 2.51 (1H, dd, *J* 15.5, 7.0), H-2], 2.00–1.91 (1H, m, H-4), 1.19–1.15 (3H, m, OCH_2CH_3), [1.16 (3H, d, *J* 7.0) and 1.10 (3H, d, *J* 7.0), H-6], 1.08–1.02 (2H, m, H-5);

δ_C (101 MHz, $CDCl_3$) 171.9 (C-1), 138.3 (*C*HCH$_2$), 134.4, 130.9, 129.5, 126.6, 117.1 (CH*C*H$_2$), 60.3 (OCH$_2$), 43.4 (C-3), 38.7 (C-2), 33.1 (C-4), [21.1 and 21.0 (C-6)], 16.1, 14.7.

NMR data for *anti*-**7** (R = *i*C_3H_7): δ_H (400 MHz, $CDCl_3$) [7.83–7.80 (2H, m) and 7.67–7.56 (3H, m), SPh], 6.36 (1H, ddd, *J* 16.5, 10.0, 7.0, C*H*CH$_2$), 5.50 (1H, d, *J* 16.5, *cis*-CHC*H*$_2$), 5.42 (1H, d, *J* 10.0, *trans*-CHC*H*$_2$), 3.95–3.87 (2H, m, OCH$_2$), 3.95–3.87 (1H, m, OCH$_2$), 3.21–3.13 (1H, m, H-3), [2.97 (1H, dd, *J* 14.5, 4.0) and 2.36 (1H, dd, *J* 14.5, 9.5), H-2], 2.00–1.91 (1H, m, H-4), 1.19–1.15 (3H, m, OCH$_2$C*H*$_3$), 1.08–1.02 (2H, m, H-5), [0.95 (3H, d, *J* 7.0) and 0.89 (3H, d, *J* 7.9), H-6]; δ_C (101 MHz, $CDCl_3$) 172.0 (C-1), 138.7 (*C*HCH$_2$), 133.3, 130.6, 129.4, 126.5, 116.5 (CH*C*H$_2$), 60.2 (OCH$_2$), 43.4 (C-3), 38.6 (C-2), 33.1 (C-4), [22.2 and 21.9 (C-6)], 16.1, 14.2.

3-(1-(Phenylthio)ethyl)pent-4-enoic acid

To a solution of esters **7** (R = CH_3) (1.20 g, 4.24 mmol, 1.0 equiv., 3:1 mixture of diastereomers) in THF (15 mL) and water (15 mL) was added lithium hydroxide (1.01 g, 42.4 mmol, 10.0 equiv.) in one portion at rt. The stirred mixture was heated under reflux for 4 h, cooled to rt, quenched with aqueous HCl (2 M, 30 mL) and extracted with ether (3 x 25 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated under reduced pressure to afford an inseparable mixture of *3-(1-(phenylthio)ethyl)pent-4-enoic acid* (0.93 g, 93%, 3:1 mixture of diastereomers) as a colourless oil which was used without further purification.

Data for *syn*-isomer: ν_{max} (film) 3075, 1709, 1639, 1584, 1480, 1438, 1284, 923, 741, 692; δ_H (400 MHz, $CDCl_3$) 7.44 (2H, d, *J* 7.0, *o*-SPh), 7.33–7.24 (3H, m, *m,p*-SPh), 5.79 (1H, ddd, *J* 17.0, 10.0, 8.0, C*H*CH$_2$), 5.18 (1H, d, *J* 10.0, *trans*-CHC*H*$_2$), 5.14 (1H, d, *J* 17.0, *cis*-CHC*H*$_2$), 3.40 (1H, dq, *J* 7.0, 4.0, H-4), 2.91–2.78 (2H, m, H-2,3), 2.51 (1H, dd, *J* 14.0, 8.0, H-2'), 1.29 (3H, d, *J* 7.0, H-5); δ_C (101 MHz, $CDCl_3$), 178.0 (C-1), 137.0 (*C*HCH$_2$), 135.0 (*i*-SPh), 132.2 (*o*-SPh), 129.0 (*m*-SPh), 127.1 (*p*-SPh), 117.6 (CH*C*H$_2$), 47.9 (C-4), 44.3 (C-3), 35.4 (C-2), 18.2 (C-5).

Selected data for *anti*-isomer: δ_H (400 MHz, $CDCl_3$) *inter alia* 4.12–4.04 (1H, m, H-4), 1.39 (3H, d, *J* 6.5, H-5); δ_C (101 MHz, $CDCl_3$) 46.7 (C-4), 44.7 (C-3), 37.2 (C-2), 18.1 (C-5).

_N_-(3,5-Dinitrophenyl)-3-(1-(phenylthio)ethyl)pent-4-enamide (8)

To a solution of 3-(1-(phenylthio)ethyl)pent-4-enoic acid (919 mg, 3.89 mmol, 1.0 equiv., 3:1 mixture of diastereoisomers) in dichloromethane (20 mL) was added DCC (803 mg, 3.89 mmol, 1.0 equiv.) and DMAP (47.5 mg, 0.389 mmol, 0.1 equiv.) at rt. The mixture was stirred for 5 min and a solution of 2,4-dinitroaniline (783 mg, 4.28 mmol, 1.1 equiv.) in dichloromethane (20 mL) was added dropwise *via* syringe. The resulting yellow mixture was stirred overnight at rt and filtered over Celite. The filtrate was washed with sodium hydrogencarbonate (30 mL) and aqueous HCl (2 M, 30 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the residue over silica gel (15% ether/hexane) afforded N-*(3,5-dinitrophenyl)-3-(1-(phenylthio)ethyl)pent-4-enamide* **8** (967 mg, 62%, 3:1 mixture of diastereoisomers) as a yellow solid. Further purification of the mixture over silica gel (5–15% ether/hexane) and recrystallisation (EtOAc) afforded an analytical sample of *syn*-**8** (435 mg, 28%) as a yellow crystalline solid.

Data for *syn*-**8**: mp 82–83 °C; ν_{max} (film) 1712, 1615, 1599, 1499, 1335, 1307, 1141, 748, 696; δ_H (400 MHz, $CDCl_3$) 10.54 (1H, s (br), NH), 9.13 (1H, d, *J* 2.5, 3-Ar), 9.06 (1H, d, *J* 9.5, 4-Ar), 8.46 (1H, dd, *J* 9.5, 2.5, 5-Ar), [7.42 (2H, d, *J* 8.5), 7.28–7.24 (2H, m) and 7.21–7.16 (1H, m), SPh], 5.87 (1H, ddd, *J* 17.0, 10.0, 8.5, C*H*CH_2), 5.22 (1H, d, *J* 10.0, *trans*-CHCH_2), 5.18 (1H, d, *J* 17.0 *cis*-CHCH_2), 3.50 (1H, dq, *J* 9.5, 7.0, H-4), 3.05–2.96 (2H, m, H-2,3), 2.66 (1H, dd, *J* 14.0, 7.5, H-2), 1.36 (3H, d, *J* 7.0, H-5); δ_C (101 MHz, $CDCl_3$) 171.1 (C-1), 141.7, 139.6, 136.5 (*C*HCH_2), 135.1, 134.8, 131.7 (SPh), 130.1 (5-Ar), 129.1 (SPh), 127.0 (SPh), 122.3 (4-Ar), 122.0 (3-Ar), 118.5 (CH*C*H_2), 47.7 (C-4), 45.2 (C-3), 40.6 (C-2), 18.8 (C-5); *m/z* (CI) 419 $[MNH_4]^+$, 402 $[MH]^+$, 369, 326, 201 (Found: $[MNH_4]^+$ 419.1388; $C_{19}H_{19}N_3O_5S$ requires $[MNH_4]^+$ 419.1389) (Found: C, 56.88; H, 4.74; N, 10.41. $C_{19}H_{19}N_3O_5S$ requires C, 56.85; H, 4.77; N, 10.47).

NMR Data for *anti*-**8**: δ_H (400 MHz, $CDCl_3$) 10.68 (1H, s (br), NH), 9.13 (1H, d, *J* 2.5, 3-Ar), 9.11 (1H, d, *J* 9.5, 4-Ar), 8.47 (1H, dd, *J* 9.5, 2.5, 5-Ar), 7.42–7.19 (5H, m, SPh), 5.80 (1H, ddd, *J* 17.0, 10.5, 8.5, C*H*CH_2), 5.16 (1H, d, *J* 10.5, *trans*-CHCH_2), 5.12 (1H, d, *J* 17.0, *cis*-CHCH_2), 3.49 (1H, dq, *J* 10.0, 7.0, H-4), 3.01–2.95 (1H, m, H-3), [2.83 (1H, dd, *J* 15.0, 6.5) and 2.85 (1H, dd, *J* 15.0, 7.5), H-2], 1.30 (3H, d, *J* 7.0, H-5); δ_C (101 MHz, $CDCl_3$) 171.7 (C-1), 153.8, 137.6, 137.2 (*C*HCH_2), 135.5,

131.9, 131.1, 129.0, 126.9, 126.7, 122.3, 122.0, 117.6 (CH*C*H_2), 47.4 (C-4), 45.4 (C-3), 37.3 (C-2), 18.4 (C-5).

The X-ray crystal structure of *syn*-8

The N(13) nitro group was found to be disordered. Two orientations of *ca*. 85 and 15% partial occupancy were identified, their geometries optimised and only the atoms of the major occupancy orientation were refined anisotropically. The N(1)–H hydrogen atom was located from a Δ*F* map and refined freely subject to an N–H distance constraint of 0.90 Å.

Fig. S1 The molecular structure of *syn*-**8** (30% probability ellipsoids).

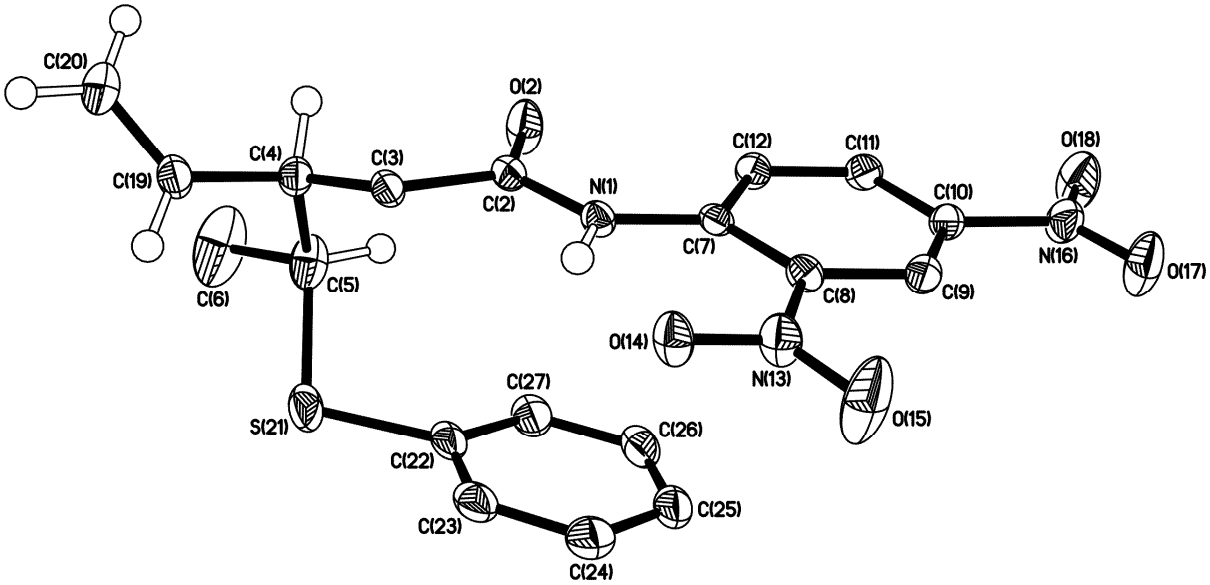

Fig. S1