Electronic Supplementary Information for

Claisen Rearrangements of Equilibrating Allylic Azides

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

1 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 FT-IR or Perkin-Elmer Spectrum RX FT-IR System spectrometers. Proton nuclear magnetic resonance (^{1}H NMR), carbon nuclear magnetic resonance (^{13}C NMR) and fluorine nuclear magnetic resonance (^{19}F 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). 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. Kugelrohr distillations were performed using a Büchi D56 Kugelrohr oven and controller system. The quoted boiling point corresponds to the internal oven temperature. Standard solvents were distilled under nitrogen prior to use; ether and THF from sodium-benzophenone ketyl, CH_2Cl_2 and acetonitrile from CaH_2 and toluene from sodium. 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. All liquid

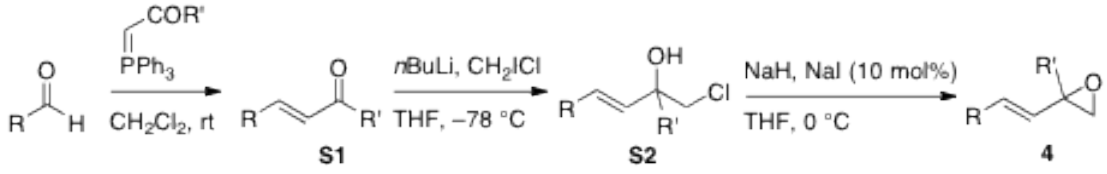
reagents were distilled prior to use. Potassium acetate was oven-dried at 120 °C for several days prior to use. Microwave reactions were performed in a Biotage Initiator upgraded to version 2.5 and cooled using compressed air (4 bar) following the reaction.

2 Safety note

The preparation of numerous potentially explosive low molecular weight organic azides is reported herein. Although we did not experience any explosive behaviour during the course of our studies, all reactions involving azides were carried out behind a blast shield. Particular care was taken during the concentration and purification of organic azides. Sodium azide was handled using non-metallic utensils.

3 Preparation of oxirane starting materials 4a–g

Oxiranes **4a–g** were prepared according to the procedure of Lautens.[1] Non-commercially available α,β-unsaturated ketones **S1b,d,f,h** were prepared from the corresponding aldehyde.



4 General synthetic procedures

General procedure A, for the preparation of α,β-unsaturated ketones S1b,d,f,h

To a solution of 1-(triphenylphosphanylidene)propan-2-one (22.5 mmol, 1.5 equiv) in dichloromethane (15 mL) was added the aldehyde (15.0 mmol, 1.0 equiv) dropwise *via* syringe at rt. The resulting mixture was stirred until TLC (20% EtOAc/petrol) confirmed the consumption of starting material. Aqueous HCl (2 M, 15 mL) was added, the phases were separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was taken up in ether, filtered and purified by Kugelrohr distillation to afford the α,β-unsaturated ketone **S1**.

General procedure B, for the preparation of chlorohydrins S2a–g

To a solution of α,β-unsaturated carbonyl **S1** (10.0 mmol, 1.0 equiv) in THF (20 mL) at –78 ºC was added chloroiodomethane (15.0 mmol, 1.5 equiv), followed by slow addition of *n*-butyllithium (6.0 mL of a 2.50 M solution in hexanes, 15.0 mmol, 1.5 equiv) over 30 min. The resulting yellow solution was stirred at –78 ºC for 1 h and quenched with saturated aqueous NH_4Cl (25 mL). The mixture was warmed to rt and ether (50 mL) was added. The phases were separated and the aqueous layer was extracted with ether (2 x 50 mL), dried ($MgSO_4$) and concentrated. Purification over silica gel afforded the chlorohydrin **S2**.

General procedure C, for the preparation of oxiranes 4a–g

To a suspension of pentane-washed sodium hydride (60% w/w in mineral oil, 10.2 mmol, 1.3 equiv) and sodium iodide (0.78 mmol, 0.1 equiv) in THF (11 mL) was added a solution of the chlorohydrin **S2** (7.8 mmol, 1.0 equiv) in THF (11 mL) at 0 °C. The resulting white suspension was stirred at 0 °C for 1 h and quenched with saturated aqueous NH_4Cl (30 mL). The phases were separated and the aqueous layer was extracted with ether (30 mL). The combined organic extracts were dried

(Na_2SO_4) and concentrated under reduced pressure to give the oxirane **4**, which were used without further purification.

General procedure D, for the preparation of allylic azidoalcohols 5/6a–g

To a solution of oxirane **4** (31.5 mmol, 1.0 equiv) in acetone (45 mL) and water (19 mL) was added sodium azide (94.5 mmol, 3.0 equiv) in one portion. After heating the resulting solution under reflux for 8 h, the reaction mixture was cooled to rt and NH_4Cl (5.0 g) was added. Water (50 mL) was added and the reaction mixture was concentrated under reduced pressure to remove acetone. The remaining aqueous layer was extracted with dichloromethane (3 x 100 mL). The combined organic extracts were dried (Na_2SO_4), concentrated under reduced pressure and purified over silica gel to give a mixture of the allylic azidoalcohols **5**/**6**.

General procedure E, for the preparation of esters 9a–g

To a solution of the allylic alcohol (1.57 mmol, 1.0 equiv) in 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, the reaction mixture was cooled to rt and concentrated under reduced pressure to give the ester **9**.

General procedure F, for the preparation of allylic azidoesters 11/12a–g

To a solution of azidoalcohols **5**/**6** (5.46 mmol, 1.0 equiv) in dichloromethane (10 mL) was added DMAP (0.546 mmol, 0.1 equiv), followed by a solution of DCC (6.01 mmol, 1.1 equiv) in dichloromethane (10 mL) at rt. The mixture was stirred for 5 min before addition of 2-*p*-toluenesulfonylacetic acid (1.29 g, 6.01 mmol, 1.1 equiv). After stirring the colourless suspension for 16 h, the reaction mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. Purification of the residue over silica gel afforded mixtures of the esters **11**/**12**.

General procedure G, for the preparation of homoallylic sulfones 14a,c,f,g

To a solution of the azidoesters **11**/**12** (0.132 mmol 1.0 equiv) in acetonitrile (1.0 M) was added *N*,*O*-bistrimethylsilylacetamide (0.396 mmol, 3.0 equiv) and TEA (0.158 mmol, 1.2 equiv) in a capped microwave vial. The mixture was heated by microwave at 160 °C until TLC showed consumption of the starting material. The reaction mixture was cooled to rt, quenched with aqueous HCl (2 M, 10 mL) and extracted with dichloromethane (3 x 10 mL). The combined organic extracts were passed though an SCX ion exchange column (conditioned with 10% MeOH/dichloromethane) and concentrated under reduced pressure to afford the acid intermediate without further purification. To solution of the crude acid (1.0 equiv) in DMF (1.0 M) was added sodium hydrogencarbonate (1.2 equiv) in a microwave vial. The mixture was heated by microwave at 160 °C for 35 min and cooled to rt. Water (10 mL) was added and the mixture was extracted with dichloromethane (3 x 10 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the residue over silica gel afforded sulfone **14**.

General procedure H, for the preparation of homoallylic sulfones 14b,d,e

To solution of the azidoesters **11**/**12** (0.132 mmol 1.0 equiv) in acetonitrile (1.0 M) was added *N*,*O*-bistrimethylsilylacetamide (0.660 mmol, 5.0 equiv) and TEA (0.264 mmol, 2.0 equiv) in a capped microwave vial. The mixture was heated by microwave at 160 °C until TLC showed consumption of the starting material. The reaction mixture was cooled to rt, quenched with aqueous HCl (2 M, 10 mL) and extracted with dichloromethane (3 x 10 mL). The combined organic extracts were passed though an SCX ion exchange column (conditioned with 10% MeOH/dichloromethane) and concentrated under reduced pressure to afford the acid without further purification. To solution of the crude acid (1.0 equiv) in DMF (1.0 M) was added sodium hydrogencarbonate (1.2 equiv) in a microwave vial. The mixture was heated by microwave at 160 °C for 35 min and cooled to rt. Water (10 mL) was added and the mixture was extracted with dichloromethane (3 x 10 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the residue over silica gel afforded sulfone **14**.

5 Data for individual compounds

(*E*)-Non-3-en-2-one (S1b)

Hexanal (1.85 mL, 15.0 mmol, 1.0 equiv) was reacted according to general procedure **A** to afford (*E*)-non-3-en-2-one **S1b** (1.07 g, 51%) as a colourless oil: bp_4 100–102 °C; ν_{max} (film) 1677, 1628, 1466, 1360, 1253, 1176, 982 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.92 (1H, dt, *J* 16.0, 7.0, H-4), 6.08 (1H, d, *J* 16.0, H-3), 2.25 (3H, s, H-1), 2.25–2.21 (2H, m, H-5), 1.52–1.44 (2H, m, H-6), 1.36–1.27 (4H, m, H-7,8), 0.90 (3H, t, *J* 6.5, H-9); δ_C (101 MHz, $CDCl_3$) 198.8 (C-2), 148.7 (C-4), 131.3 (C-3), 32.4, 31.3, 27.8, 26.8, 22.4, 14.0; *m/z* (CI) 158 $[MNH_4]^+$, 141 $[MH]^+$, 125; in agreement with published data.[2]

(*E*)-4-(Cyclohexyl)-but-3-en-2-one (S1d)

Cyclohexanecarboxaldehyde (1.82 mL, 15.0 mmol, 1.0 equiv) was reacted according to general procedure **A** to afford *(*E*)-4-(cyclohexyl)-but-3-en-2-one* **S1d** (917 mg, 40%) as a colourless oil: bp_4 95–100 °C, ν_{max} (film) 1698, 1676, 1624, 1449, 1357, 1253, 980 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.73 (1H, dd, *J* 16.0, 7.0, H-4), 6.05 (1H, d, *J* 16.0, H-3), 2.45 (3H, s, H-1), 2.20–2.12 (1H, m, H-5), 1.78 (4H, d, *J* 11.0, cyclohexyl), 1.69 (1H, d, *J* 13.5, cyclohexyl), 1.36–1.15 (5H, m, cyclohexyl); δ_C (101 MHz, $CDCl_3$) 199.2 (C-2), 153.4 (C-4), 128.8 (C-3), 40.6 (C-5), 31.8 (cyclohexyl) 26.8 (C-1), 25.9 (cyclohexyl), 25.7 (cyclohexyl); *m/z* (CI) 170 $[MNH_4]^+$, 153 $[MH]^+$ (Found: $[MH]^+$, 153.1281. $C_{10}H_{16}O$ requires $[MH]^+$, 153.1279).

(*E*)-4-(Pyridin-2-yl)-but-3-en-2-one (S1f)

2-Pyridinecarboxaldehyde (1.43 mL, 15.0 mmol, 1.0 equiv) was reacted according to general procedure **A** to afford *(*E*)-4-(pyridin-2-yl)-but-3-en-2-one* **S1f** (1.41 g, 64%) as a colourless oil: bp_4 120–125 °C; ν_{max} (film) 1667, 1621, 1583, 1469, 1432, 1359, 1312, 1200, 1152, 980, 766 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.57 (1H, s (br), 6-pyridyl), 7.75–7.71 (1H, m, pyridyl), 7.52 (1H, d, *J* 16.5, H-4), 7.50–7.48 (1H, m, pyridyl), 7.30–7.27 (1H, m, pyridyl), 7.14 (1H, d, *J* 16.5, H-3), 2.41 (3H, s, H-1); δ_C (101

MHz, $CDCl_3$) 198.6 (C-2), 153.1 (2-pyridyl), 150.1 (6-pyridyl), 141.9 (C-4), 136.9 (pyridyl), 130.2 (C-3), 124.4, 124.3 (pyridyl), 28.1 (C-1); *m/z* (ESI) 148 $[MH]^+$, 130, 120 (Found: $[MH]^+$, 148.0754. C_9H_9NO requires $[MH]^+$, 148.0762).

(*E*)-1-Phenylbut-2-en-1-one (S1g)

A solution of phenylmagnesium chloride (26.3 mL of a 1.90 M solution in THF, 50.0 mmol, 1.0 equiv) was added to a flask containing THF (150 mL) at 0 °C and crotonaldehyde (4.1 mL, 50.0 mmol, 1.0 equiv) was added. After stirring at 0 °C for 30 min, the reaction was quenched with saturated aqueous NH_4Cl (25 mL). The reaction mixture was warmed to rt, partially concentrated under reduced pressure to remove THF and extracted with ether (2 x 120 mL). The combined organic extracts were washed with aqueous HCl (2 M, 40 mL), water (2 x 40 mL) and brine (40 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was taken up in DMF (10 mL) and added to a stirred solution of pyridinium dichromate (20.4 g, 1.08 equiv) in DMF (40 mL). After 1 h, the reaction mixture was diluted with ether (100 mL) and poured onto water (100 mL). The phases were separated and the organic layer was washed with water (2 x 100 mL) and brine (40 mL). Concentration under reduced pressure and Kugelrohr distillation afforded (*E*)-1-phenylbut-2-en-1-one **S1g** (2.02 g, 28%) as a colourless oil: bp_4 120–125 °C; ν_{max} (film) 1668, 1624, 1577, 1449, 1296, 1220, 966 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.58–7.42 (5H, m, Ph), 7.10 (1H, dq, *J* 15.0, 7.0, H-3), 6.93 (1H, d, *J* 15.0, H-2), 2.03 (3H, d, *J* 7.0, H-4); δ_C (101 MHz, $CDCl_3$) 190.1 (C-1), 145.1, 143.5, 137.9, 132.6, 128.5, 128.2, 18.6 (Me); *m/z* (CI) 164 $[MNH_4]^+$, 147 $[MH]^+$, 131; in agreement with published data.[3]

(*E*)-1-Chlorononon-3-en-2-ol (S2a)

Octen-2-al **S1a** (1.49 mL, 10.0 mmol, 1.0 equiv) was reacted according to general procedure **B** to afford *(*E*)-1-chlorononon-3-en-2-ol* **S2a** (1.42 g, 81%) as a colourless oil after purification over silica gel (20% ether/petrol): ν_{max} (film) 3354, 1671, 972, 760, 730 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.84 (1H, dt, *J* 15.5, 7.5, H-4), 5.48 (1H, ddt, *J* 15.5, 7.5, 1.5, H-3), 4.32 (1H, m, H-2), [3.65 (1H, dd, *J* 11.0, 3.5) and 3.52 (1H, dd, *J* 11.0,

7.5), H-1], 2.08 (1H, m, H-5), 1.45–1.29 (6H, m, H-6,7,8), 0.91 (3H, t, *J* 6.5, H-9); δ_C (101 MHz, $CDCl_3$) 135.2 (C-4), 127.9 (C-3), 72.4 (C-2), 50.0 (C-1), 32.2 (C-5), 31.3 (C-6), 28.6 (C-7), 22.5 (C-8), 14.0 (C-9); *m/z* (CI) 194 $[MNH_4]^+$, 176 $[M]^+$ (Found: $[MNH_4]^+$, 194.1313. $C_9H_{17}ClO$ requires $[MNH_4]^+$, 194.1312) (Found: C, 61.08; H, 9.72. $C_9H_{17}ClO$ requires C, 61.18; H, 9.70).

(*E*)-1-Chloro-2-methylnon-3-en-2-ol (S2b)

3-Nonen-2-one **S1b** (936 mg, 6.68 mmol, 1.0 equiv) was reacted according to general procedure **B** to afford *(*E*)-1-chloro-2-methylnon-3-en-2-ol* **S2b** (1.17 g, 92%) as a colourless oil after purification over silica gel (20% TBME/petrol): ν_{max} (film) 3411, 1669, 1457, 1376, 973, 745 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.80 (1H, dt, *J* 15.5, 6.5, H-4), 5.53 (1H, dt, *J* 15.5, 1.0, H-3), 3.55 (2H, AB quartet, *J* 10.0, H-1), 2.10 (2H, dt, *J* 13.0, 6.5, H-5), 1.39 (3H, s, 2-Me), 1.40–1.30 (6H, m, H-6,7,8), 0.92 (3H, t, *J* 7.0, H-9); δ_C (101 MHz, $CDCl_3$) 132.8 (C-3), 131.3 (C-4), 72.0 (C-2), 54.7 (C-1), 32.2 (C-5), 31.3 (C-6), 28.8 (C-7), 25.6 (2-Me), 14.1 (C-9); *m/z* (CI) 190 $[MNH_4–H_2O]^+$, 177, 172 $[M–OH]^+$, 137 (Found: $[MNH_4–H_2O]^+$, 190.1363. $C_{10}H_{19}ClO$ requires $[MNH_4–H_2O]^+$, 190.1357).

(*E*)-1-Chloro-2-methylpent-3-en-2-ol (S2c)

3-Penten-2-one **S1c** (2.44 mL, 25.0 mmol, 1.0 equiv) was reacted according to general procedure **B** to afford *(*E*)-1-chloro-2-methylpent-3-en-2-ol* **S2c** (1.18 g, 35%) as a colourless oil after purification over silica gel (20% ether/petrol): ν_{max} (film) 3419, 1671, 1450, 968, 801, 743 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.82 (1H, dq, *J* 15.5, 6.5, H-4), 5.55 (1H, d, *J* 15.5, H-3), 3.53 (2H, AB quartet, *J* 15.0, H-1), 2.16 (1H, s (br), OH), 1.74 (3H, dd, *J* 6.5, 1.5, H-5), 1.38 (3H, s, 2-Me); δ_C (101 MHz, $CDCl_3$) 134.1 (C-3), 125.9 (C-4), 72.0 (C-2), 54.6 (C-1), 25.5 (C-5), 17.8 (2-Me); *m/z* (CI) 136 $[M–H]^+$, 134 $[MNH_4–H_2O]^+$, 100 (Found: $[MNH_4–H_2O]^+$, 134.0739. $C_6H_{11}ClO$ requires $[MNH_4–H_2O]^+$, 134.0737).

(*E*)-1-Chloro-4-cyclohexyl-2-methylbut-3-en-2-ol (S2d)

(*E*)-4-(Cyclohexyl)-but-3-en-2-one **S2d** (508 mg, 3.94 mmol, 1.0 equiv) was reacted according to general procedure **B** to afford *(*E*)-1-chloro-4-cyclohexyl-2-methylbut-3-en-2-ol* **S2d** (562 mg, 84%) as a colourless oil after purification over silica gel (10% ether/hexane): ν_{max} (film) 3430, 1668, 1449, 1373, 1263, 970, 745 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.75 (1H, dd, *J* 15.5, 7.5, H-4), 5.46 (1H, dd, *J* 15.5, 1.5, H-3), 3.53 (2H, AB quartet, *J* 11.0, H-1), 2.18 (1H, s (br), OH), 2.04–1.95 (1H, m, H-5), 1.78–1.65 (5H, m, cyclohexyl), 1.39 (3H, s, 2-Me), 1.38–1.05 (5H, m, cyclohexyl); δ_C (101 MHz, $CDCl_3$) 136.9 (C-4), 130.3 (C-3), 72.0 (C-2), 54.7 (C-1), 40.3 (C-5), 32.8, 26.1, 26.0 (cyclohexyl), 25.7 (2-Me); *m/z* (CI) 222, 220 $[MNH_4]^+$, 204, 202 $[M]^+$, 187, 185 (Found: $[MNH_4]^+$, 220.1473. $C_{11}H_{19}ClO$ requires $[MNH_4]^+$, 220.1468) (Found: C, 65.13; H, 9.36. $C_{11}H_{19}ClO$ requires C, 65.17; H, 9.45).

(*E*)-1-Chloro-4-phenylbut-3-en-2-ol (S2e)

Cinnamaldehyde **S1e** (1.50 g, 11.35 mmol, 1.0 equiv) was reacted according to general procedure **B** to afford (*E*)-1-chloro-4-phenylbut-3-en-2-ol **S2e** (2.06 g, 99%) as a colourless oil after purification over silica gel (10% ether/petrol): ν_{max} (film) 3390, 3026, 1659, 1598, 1578, 1494, 1449, 1296, 1071, 967, 754, 693 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.43 (2H, d, *J* 7.5, *o*-Ph), 7.37 (2H, dd, *J* 13.5, 7.5, *m*-Ph), 7.31 (1H, dd, *J* 13.5, 6.5, *p*-Ph), 6.76 (1H, d, *J* 15.5, H-4), 6.24 (1H, dd, *J* 15.5, 6.0, H-3), 4.57 (1H, dt, *J* 7.0, 6.0, H-2), [3.57 (1H, dd, *J* 11.0, 3.5) and 3.64 (1H, dd, *J* 11.0, 6.5), H-1]; δ_C (101 MHz, $CDCl_3$) 136.1 (*i*-Ph), 132.8 (C-4), 128.7 (*m*-Ph), 128.2 (*p*-Ph), 127.2 (C-3), 126.7 (*o*-Ph), 72.3 (C-2), 49.7 (C-1); *m/z* (CI) 200 $[MNH_4]^+$, 182 $[M]^+$, 165 (Found: $[MNH_4]^+$, 200.0842. $C_{10}H_{11}ClO$ requires $[MNH_4]^+$, 200.0842); in agreement with published data.[4]

(*E*)-1-Chloro-2-methyl-4-(pyridin-2-yl)but-3-en-2-ol (S2f)

(*E*)-4-(Pyridin-2-yl)-but-3-en-2-one **S1f** (1.00 g, 6.80 mmol, 1.0 equiv) was reacted according to general procedure **B** to afford *(*E*)-1-chloro-2-methyl-4-(pyridin-2-yl)but-3-en-2-ol* **S2f** (1.18 g, 88%) as a yellow oil after purification over silica gel (25%

EtOAc, 5% TEA/hexane): ν_{max} (film) 3348, 1657, 1589, 1566, 1472, 1432, 1371, 977, 801, 768, 747 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.58 (1H, d, *J* 5.5, 6-pyridyl), 7.66 (1H, ddd, *J* 9.5, 8.0, 2.0, 4-pyridyl), 7.29 (1H, d, *J* 8.0, 3-pyridyl), 7.16 (1H, ddd, *J* 7.5, 5.0, 2.0, 5-pyridyl), 6.84 (2H, d, *J* 17.0, H-3, H-4), 3.67 (2H, AB quartet, *J* 11.0, H-1), 2.70 (1H, s (br), OH), 1.29 (3H, s, 2-Me); δ_C (101 MHz, $CDCl_3$) 154.7 (2-pyridyl), 149.6 (6-pyridyl), 137.0 (C-4), 136.7 (4-pyridyl), 129.4 (C-3), 122.5 (5-pyridyl), 122.4 (3-pyridyl), 72.6 (C-2), 54.2 (C-1), 25.7 (2-Me); *m/z* (ESI) 201, 200, 198 $[MH]^+$ (Found: $[MH]^+$, 198.0680. $C_{10}H_{12}ClNO$ requires $[MH]^+$, 198.0686) (Found: C, 60.69; H, 6.03; N, 6.99. $C_{10}H_{12}ClNO$ requires C, 60.76; H, 6.12; N, 7.09).

(*E*)-1-Chloro-2-phenyl-pent-3-en-2-ol (S2g)

(*E*)-1-Phenylbut-2-en-1-one **S1g** (1.89 g, 12.91 mmol, 1.0 equiv) was reacted according to general procedure **B** to afford *(*E*)-1-chloro-2-phenyl-pent-3-en-2-ol* **S2g** (1.31 g, 52%) as a colourless oil after purification over silica gel (10% ether/hexane): ν_{max} (film) 3466, 1667, 1623, 1494, 1448, 1336, 1161, 1050, 967, 724, 699 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.49 (2H, d, *J* 8.5, *o*-Ph), 7.40 (2H, dd, *J* 8.5, 7.0, *m*-Ph), 7.32 (1H, dd, *J* 7.5, 7.0, *p*-Ph), 5.83–5.80 (2H, m, H-3 and H-4), 3.89 (2H, AB quartet, *J* 11.5, H-1), 2.74 (1H, s, OH), 1.78 (3H, dd, *J* 5.0, 1.5, H-5); δ_C (101 MHz, $CDCl_3$) 142.8 (*i*-Ph), 133.5, 128.5 (*m*-Ph), 128.4, 127.6, 125.6 (*o*-Ph), 75.9 (C-2), 54.0 (C-1), 17.8 (C-5); *m/z* (CI) 216, 214 $[MNH_4]^+$, 198, 196 $[MH]^+$, 181, 179 (Found: $[MNH_4]^+$, 214.1003. $C_{11}H_{13}ClO$ requires $[MNH_4]^+$, 214.0999) (Found: C, 67.24; H, 6.59. $C_{11}H_{13}ClO$ requires C, 67.18; H, 6.66).

(*E*)-2-(Hept-1-enyl)oxirane (4a)

Chlorohydrin **S2a** (1.38 g, 7.82 mmol, 1.0 equiv) was reacted according to general procedure **C** to afford *(*E*)-2-(hept-1-enyl)oxirane* **4a** (1.06 g, 97%) as a yellow oil: ν_{max} (film) 1669, 1466, 1369, 1245, 964, 835, 771, 727 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.98 (1H, dt, *J* 15.5, 6.5, H-4), 5.15 (1H, ddt, *J* 15.5, 8.0, 1.5, H-3), 3.34 (1H, ddd, *J* 8.0, 4.0, 3.0), [2.95 (1H, dd, *J* 5.0, 4.0) and 2.67 (1H, dd, *J* 5.0, 3.0), H-1], 2.09 (2H, dt, *J* 7.5, 6.5, H-5), 1.46–1.38 (2H, m, H-6), 1.37–1.28 (4H, m H-7,8), 0.91 (3H, t, *J*

7.0, H-9); δ_C (101 MHz, $CDCl_3$) 137.4 (C-4), 127.4 (C-3), 52.7 (C-2), 48.8 (C-1), 32.3 (C-5), 31.3 (C-7), 28.6 (C-6), 22.5 (C-8), 14.0 (C-9); *m/z* (CI) 158 $[MNH_4]^+$, 141 $[MH]^+$, 123 $[M–OH]^+$ (Found: $[MNH_4]^+$, 158.1545. $C_9H_{16}O$ requires $[MNH_4]^+$, 158.1545).

(*E*)-2-Methyl-2-(hept-1-enyl)oxirane (4b)

Chlorohydrin **S2b** (1.12 g, 5.88 mmol, 1.0 equiv) was reacted according to general procedure **C** to afford *(*E*)-2-methyl-2-(hept-1-enyl)oxirane* **4b** (1.06 g, 40%) as a colourless oil: ν_{max} (film) 1668, 1585, 1457, 1379, 968, 905 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.81 (1H, dt, *J* 16.0, 7.0, H-4), 5.27 (1H, dt, *J* 16.0, 1.5, H-3), [2.82 (1H, d, *J* 5.0) and 2.75 (1H, d, *J* 5.0), H-1], 2.06 (2H, dt, *J* 8.0, 7.0, H-5), 1.46–1.23 (6H, m, H-6,7,8), 0.90 (3H, t, *J* 7.5, H-9); δ_C (101 MHz, $CDCl_3$) 134.0 (C-4), 130.9, (C-3), 55.8 (C-1), 55.6 (C-2), 32.4 (C-5), 31.4 (C-6), 28.8 (C-7), 22.5 (C-8), 19.7 (2-Me), 14.0 (C-9); *m/z* (CI) 155 $[MH]^+$ (Found: $[MH]^+$, 155.1434. $C_{10}H_{18}O$ requires $[MH]^+$, 155.1436).

(*E*)-2-Methyl-2-(prop-1-enyl)oxirane (4c)

Chlorohydrin **S2c** (1.13 g, 8.40 mmol, 1.0 equiv) was reacted according to general procedure **C**. Incomplete concentration under reduced pressure of the combined organic extracts afforded *(*E*)-2-methyl-2-(prop-1-enyl)oxirane* **4c** (1.06 g of a colourless solution, 35% w/w in THF by ^{1}H-NMR analysis, 46%): δ_H (400 MHz, $CDCl_3$) 5.83 (1H, dq, *J* 15.5, 6.5, H-4), 5.30 (1H, d, *J* 15.5, H-3), [2.81 (1H, d, *J* 5.0) and 2.75 (1H, d, *J* 5.0), H-1], 1.75 (3H, dd, *J* 6.5, 1.5, H-5), 1.46 (3H, s, 2-Me); δ_C (101 MHz, $CDCl_3$) 132.2 (C-3), 128.5 (C-4), 60.4 (C-2), 55.7 (C-1), 19.7 (2-Me), 17.8 (C-5).

2-[(*E*)-2-Cyclohexylethenyl]-2-methyloxirane (4d)

Chlorohydrin **S2d** (0.533 g, 2.64 mmol, 1.0 equiv) was reacted according to general procedure **C** to afford *2-[(*E*)-2-Cyclohexylethenyl]-2-methyloxirane* **4d** (431 mg,

98%) as a colourless oil: ν_{max} (film) 1677, 1449, 1387, 1064, 968 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.75 (1H, dd, *J* 16.0, 6.5, H-4), 5.23 (1H, dd, *J* 16.0, 1.5, H-3), [2.82 (1H, d, *J* 5.0) and 2.75 (1H, d, *J* 4.0), H-1], 2.03–1.96 (1H, m, H-5), [1.78–1.61 and 1.35–1.03 (10H, m, cyclohexyl)], 1.46 (3H, s, 2-Me); δ_C (101 MHz, $CDCl_3$) 139.5 (C-4), 128.5 (C-3), 55.9 (C-1), 55.7 (C-2), 40.5 (C-5), 32.7, 26.1, 26.0, 19.7 (2-Me); *m/z* (CI) 184 $[MNH_4]^+$, 165 $[M–H]^+$, 149 (Found: $[MNH_4]^+$, 184.1700. $C_{11}H_{18}O$ requires $[MNH_4]^+$, 184.1701).

(*E*)-2-Styryloxirane (4e)

Chlorohydrin **S2e** (1.20 g, 6.59 mmol, 1.0 equiv) was reacted according to general procedure **C** to afford (*E*)-2-styryloxirane **4e** (963 mg, >99%) as a yellow oil: ν_{max} (film) 3027, 1601, 1578, 1492, 1393, 1244, 1134, 1072, 965 747, 693 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.43–7.27 (5H, m, Ph), 6.85 (1H, d, *J* 16.5, H-4), 5.91 (1H, dd, *J* 16.5, 7.5, H-3), 3.56 (1H, ddd, *J* 7.5, 5.0, 3.0, H-2), [3.10 (1H, dd, *J* 5.5, 4.0) and 2.81 (1H, dd, *J* 5.0, 3.0), H-1]; δ_C (101 MHz, $CDCl_3$) 136.3 (*i*-Ph), 134.6 (C-4), 128.7, 128.1 (Ph), 127.0 (C-3), 126.5 (Ph), 52.7 (C-2), 49.3 (C-1); *m/z* (CI) 164 $[MNH_4]^+$, 147 $[MH]^+$, 129 $[M–H_2O]^+$ (Found: $[MH]^+$, 147.0812. $C_{10}H_{10}O$ requires $[MH]^+$, 147.0810); in agreement with published data.[4]

2-[(*E*)-2-(2-Methyloxiran-2-yl)ethenyl]pyridine (4f)

Chlorohydrin **S2f** (1.16 g, 5.87 mmol, 1.0 equiv) was reacted according to general procedure **C** to afford *2-[(*E*)-2-(2-Methyloxiran-2-yl)ethenyl]pyridine* **4f** (623 mg, 66%) as yellow oil: ν_{max} (film) 1654, 1555, 1387, 1305, 1150, 1065, 973, 907, 793, 766, 742, 611 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.57 (1H, d, *J* 5.0, 6-pyridyl), 7.65 (1H, ddd, *J* 9.5, 8.0, 2.0, 4-pyridyl), 7.29 (1H, d, *J* 8.0, 3-pyridyl), 7.16 (1H, ddd, *J* 8.0, 5.0, 2.0, 5-pyridyl), [6.77 (1H, d, *J* 16.0) and 6.57 (1H, d, *J* 16.0), H-3,4], [2.94 (1H, d, *J* 5.0) and 2.89 (1H, d, *J* 5.0), H-1], 1.61 (3H, s, 2-Me); δ_C (101 MHz, $CDCl_3$) 154.8 (2-pyridyl), 149.6 (6-pyridyl), 136.6 (4-pyridyl), [135.2 and 131.3 (C-3 and C-4)], 122.4 (5-pyridyl), 121.7 (3-pyridyl), 55.3 (C-1), 55.7 (C-2), 19.7 (2-Me); *m/z* (ESI) 181,

180, 162 $[MH]^+$, 130 (Found: $[MH]^+$, 162.0912. $C_{10}H_{11}NO$ requires $[MH]^+$, 162.0919).

(*E*)-2-Methyl-2-styryloxirane (4g)

Chlorohydrin **S2g** (1.26 g, 6.43 mmol, 1.0 equiv) was reacted according to general procedure **C** to afford *(*E*)-2-Methyl-2-styryloxirane* **4g** (1.01 g, 98%): ν_{max} (film) 1681, 1598, 1495, 1448, 965, 760, 700 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.44–7.32 (5H, m, Ph), 5.73–5.70 (2H, m, C*H*C*H*Me), [3.14 (1H, d, *J* 5.5) and 3.00 (1H, d, *J* 5.5), OCH_2], 1.77 (3H, dd, *J* 5.0, 2.0, Me); δ_C (101 MHz, $CDCl_3$) 153.0 (*i*-Ph), 131.2, 130.4, 128.2 (*o*-Ph), 127.7 (*p*-Ph), 127.0 (*m*-Ph), 60.1 (C-2), 56.7 (OCH_2), 17.8 (Me); *m/z* (CI) 178 $[MNH_4]^+$, 161 $[MH]^+$, 143, 105 (Found: $[MNH_4]^+$, 178.1231. $C_{11}H_{12}O$ requires $[MNH_4]^+$, 178.1232).

(*E*)-2-Azidonon-3-en-1-ol (5a) and (*E*)-4-azidonon-2-en-1-ol (6a)

Oxirane **4a** (4.41 g, 31.5 mmol, 1.0 equiv) was reacted according to general procedure **D** to afford a 73:27 mixture of *(*E*)-2-azidonon-3-en-1-ol* **5a** and *(*E*)-4-azidonon-2-en-1-ol* **6a** respectively (4.04 g, 70%) as a colourless oil after purification over silica gel (30% TBME/petrol).

Data for the mixture: ν_{max} (film) 3352, 2101, 1667, 1462, 1240, 1072 cm^{-1}; *m/z* (CI) 201 $[MNH_4]^+$, 191, 158, 126 (Found: $[MNH_4]^+$, 201.1715. $C_9H_{17}N_3O$ requires $[MNH_4]^+$, 201.1715.

NMR data for **5a**: δ_H (500 MHz, $CDCl_3$) 5.85 (1H, dt, *J* 15.5, 6.5, H-4), 5.40 (1H, ddt, *J* 15.5, 8.0, 1.5, H-3), 4.03 (1H, dt, *J* 11.5, 5.0, H-2), [3.60 (1H, dd, *J* 11.5, 5.0) and 3.52 (1H, dd, *J* 11.5, 7.5), H-1], 2.09–2.11 (2H, m, H-5), 1.66 (2H, s (br), OH), 1.43–1.25 (12H, m, H-6,7,8), 0.89 (6H, t, *J* 7.0, H-9); δ_C (101 MHz, $CDCl_3$) 138.2, 123.4, 66.3, 65.0, 32.3, 31.2, 28.7, 22.4, 14.0.

NMR data for **6a**: δ_H (500 MHz, $CDCl_3$) 5.88 (1H, dt, *J* 15.0, 5.5, H-2), 5.66 (1H, ddt, *J* 15.5, 7.5, 1.5, H-3), 4.21 (2H, dd, *J* 5.5, 1.5, H-1), 3.85 (1H, dt, *J* 14.0, 7.5, H-4), 1.66 (2H, s (br), OH), 1.56–1.49 (2H, m, H-5), 1.43–1.25 (12H, m, H-6,7,8), 0.89

(6H, t, *J* 7.0, H-9); δ_C (101 MHz, $CDCl_3$) 132.9, 128.9, 64.0, 62.6, 34.5, 31.4, 35.5, 22.5, 14.0.

(*E*)-2-Azido-2-methylnon-3-en-1-ol (5b) and (*E*)-4-azido-2-methylnon-2-en-1-ol (6b)

Oxirane **4b** (497 mg, 3.22 mmol, 1.0 equiv) was reacted according to general procedure **D** to afford a 61:39 mixture of *(*E*)-2-azido-2-methylnon-3-en-1-ol* **5b** and *(*E*)-4-azido-2-methylnon-2-en-1-ol* **6b** respectively (150 mg, 25%) as a colourless oil after purification over silica gel (20% TBME/hexane).

Data for the mixture: ν_{max} (film) 3370, 2102, 1666, 1456, 1379, 1247, 1056 cm^{-1}; *m/z* (CI) 215 $[MNH_4]^+$, 172, 155 $[M\text{-}N_3]^+$, 137 (Found: $[MNH_4]^+$, 215.1872. $C_{10}H_{19}N_3O$ requires $[MNH_4]^+$, 215.1871).

NMR data for **5b**: δ_H (400 MHz, $CDCl_3$) 5.82 (1H, dt, *J* 16.0, 7.0, H-4), 5.50 (1H, dt, *J* 16.0, 2.0, H-3), 3.46 (2H, AB quartet, *J* 11.5, H-1), 2.11 (2H, dt, *J* 9.0, 7.0, H-5), 1.71–1.55 (1H, s (br), OH), 1.40 (3H, s, 2-Me), 1.38–1.27 (6H, m, H-6,7,8), 0.99 (3H, t, *J* 6.5, H-9); δ_C (101 MHz, $CDCl_3$) 134.1 (C-4), 128.5 (C-3), 69.3 (C-1), 66.1 (C-2), 32.5, 31.3, 28.9, 22.4 (2-Me), 20.2, 14.0 (C-9).

NMR data for **6b**: δ_H (400 MHz, $CDCl_3$) 5.44 (1H, d, *J* 10.0, H-3), 4.22–4.15 (1H, m, H-4), 4.11 (2H, s, H-1), 1.77 (3H, s, 2-Me), 1.71–1.55 (1H, s (br), OH), 1.38–1.27 (8H, m, H-5,6,7,8), 0.99 (3H, t, *J* 6.5, H-9); δ_C (101 MHz, $CDCl_3$) 140.3 (C-2), 122.7 (C-3), 67.7 (C-1), 59.4 (C-4), 35.0, 31.5, 25.5, 22.5 (2-Me), 14.3, 14.0 (C-9).

(*E*)-2-Azido-2-methylpent-3-en-1-ol (5c) and (*E*)-4-azido-2-methylpent-2-en-1-ol (6c)

A solution of oxirane **4c** in THF (6.36 mmol, 1.0 equiv) was reacted according to general procedure **D** to afford a 64:36 mixture of *(*E*)-2-azido-2-methylpent-3-en-1-ol* **5c** and *(*E*)-4-azido-2-methylpent-2-en-1-ol* **6c** respectively (634 mg, 71%) as a colourless oil after purification over silica gel (20% ether/petrol).

Data for the mixture: ν_{max} (film) 3374, 2105, 1652, 1449, 1379, 1250, 1052, 970 cm^{-1}; *m/z* (CI) 159 $[MNH_4]^+$, 116, 114, 96 (Found: $[MNH_4]^+$, 159.1248. $C_6H_{11}N_3O$ requires $[MNH_4]^+$, 159.1246).

NMR data for **5c**: δ_H (400 MHz, $CDCl_3$) 5.85 (1H, dq, *J* 15.5, 6.5, H-4), 5.53 (1H, dd, *J* 15.5, 1.5, H-3), 3.47 (2H, AB quartet, *J* 12.0, H-1), 1.80 (3H, dd, *J* 6.5, 1.5, H-5), 1.41 (3H, s, 2-Me); δ_C (101 MHz, $CDCl_3$) 129.9 (C-3), 128.6 (C-4), 69.2 (C-1), 67.5 (C-2), 20.1 (2-Me), 18.0 (C-5).

NMR data for **6c**: δ_H (400 MHz, $CDCl_3$) 5.46 (1H, dd, *J* 9.5, 1.5, H-3), 4.37 (1H, dq, *J* 9.5, 6.5, H-4), 4.10 (2H, s, H-1), 1.77 (3H, s, 2-Me), 1.28 (3H, d, *J* 6.5, H-5); δ_C (101 MHz, $CDCl_3$) 139.5 (C-2), 123.7 (C-3), 66.0 (C-1), 54.7 (C-4), 20.8 (C-Me), 14.1 (C-5).

(*E*)-2-Azido-4-cyclohexyl-2-methylbut-3-en-1-ol (5d) and (*E*)-4-azido-4-cyclohexyl-2-methylbut-2-en-1-ol (6d)

Oxirane **4d** (265 mg, 1.60 mmol, 1.0 equiv) was reacted according to general procedure **D** to afford a 72:28 mixture of *(*E*)-2-azido-4-cyclohexyl-2-methylbut-3-en-1-ol* **5d** and *(*E*)-4-azido-4-cyclohexyl-2-methylbut-2-en-1-ol* **6d** respectively (196 mg, 59%) as a colourless oil after purification over silica gel (15% ether/hexane).

Data for the mixture: ν_{max} (film) 3359, 2103, 1665, 1448, 1250, 1052, 970 cm^{-1}; *m/z* (CI) 227 $[MNH_4]^+$, 210 $[MH]^+$, 184, 149 (Found: $[MNH_4]^+$, 227.1870. $C_{11}H_{19}N_3O$ requires $[MNH_4]^+$, 227.1872).

NMR data for **5d**: δ_H (400 MHz, $CDCl_3$) 5.76 (1H, dd, *J* 15.5, 6.5, H-4), 5.45 (1H, dd, *J* 15.5, 1.5, H-3), 3.50 (2H, m, H-1), 2.08–0.85 (11H, m, cyclohexyl), 1.40 (3H, s, 2-Me); δ_C (101 MHz, $CDCl_3$) 139.9 (C-4), 125.9 (C-3), 69.3 (C-1), 42.4 (C-2), 40.7, 33.0, 32.9, 25.9, 20.2.

NMR data for **6d**: δ_H (400 MHz, $CDCl_3$) 5.47 (1H, d, *J* 10.0, H-3), 4.12 (2H, d, *J* 4.0, H-1), 3.96 (1H, dd, *J* 10.0, 7.5, H-4), 2.08–0.85 (11H, m, cyclohexyl), 1.75 (3H, s, 2-Me); δ_C (101 MHz, $CDCl_3$) 121.2 (C-3), 67.7 (C-1), 65.9 (C-2), 64.6 (C-4), 29.5, 29.3, 26.3, 26.0, 14.3.

(*E*)-2-Azido-4-phenylbut-3-en-1-ol (5e)

Oxirane **4e** (950 mg, 6.50 mmol, 1.0 equiv) was reacted according to general procedure **D** to afford (*E*)-2-azido-4-phenylbut-3-en-1-ol **5e** (739 mg, 60%) as a yellow oil after purification over silica gel (20% EtOAc/hexane): ν_{max} (film) 2109, 1650, 1449, 1246, 1040, 969, 750, 693 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.45 (1H, d, *J* 8.0, *p*-Ph), 7.38 (2H, dd, *J* 8.0, 7.5, *m*-Ph), 7.35 (2H, d, *J* 7.5, *o*-Ph), 6.76 (1H, d, *J* 17.0, H-4), 6.18 (1H, dd, *J* 17.0, 8.0, H-3), 4.28 (1H, dt, *J* 8.0, 4.5, H-2), [3.76 (1H, dd, *J* 11.0, 4.5) and 3.67 (1H, dd, *J* 11.0, 7.0), H-1], 1.99 (1H, s (br), OH); δ_C (101 MHz, $CDCl_3$) 135.7 (*i*-Ph), 135.4 (C-4), 128.7 (*o*-Ph), 128.5 (*p*-Ph), 126.7 (*m*-Ph), 122.9 (C-3), 66.3 (C-2), 65.0 (C-1); *m/z* (CI) 207 $[MNH_4]^+$, 189 $[M]^+$, 164, 147 (Found: $[MNH_4]^+$, 207.1247. $C_{10}H_{11}N_3O$ requires $[MNH_4]^+$, 207.1246); in agreement with published data.[4]

(*E*)-2-Azido-2-methyl-4-(pyridin-2-yl)but-3-en-1-ol (5f)

Oxirane **4f** (600 mg, 3.73 mmol, 1.0 equiv) was reacted according to general procedure **D** to afford *(*E*)-2-azido-2-methyl-4-(pyridin-2-yl)but-3-en-1-ol* **5f** (600 mg, 79%) as a colourless oil after purification over silica gel (20% EtOAc/5% TEA/hexane): ν_{max} (film) 3339, 2105, 1656, 1590, 1473, 1260, 1153, 1061, 975, 766 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.55 (1H, d, *J* 5.0, 6-pyridyl), 7.68 (1H, dt, *J* 7.5, 1.5, 4-pyridyl), 7.32 (1H, d, *J* 7.5, 3-pyridyl), 7.19 (1H, dd, *J* 8.0, 7.5, 5-pyridyl), 6.81 (1H, d, *J* 16.0, H-4), 6.77 (1H, d, *J* 16.0, H-3), 3.64 (2H, dd, *J* 3.0, 2.5, H-1), 1.55 (3H, s, 2-Me); δ_C (101 MHz, $CDCl_3$) 154.4 (2-pyridyl), 149.6 (6-pyridyl), 136.8 (4-pyridyl), [133.3 and 131.2, (C-3) and (C-4)], 122.8 (5-pyridyl), 122.5 (3-pyridyl), 69.1 (C-1), 66.0 (C-2), 20.4 (2-Me); *m/z* (CI), 205 $[MH]^+$, 164, 145, 102 (Found: $[MH]^+$, 205.1081. $C_{10}H_{12}N_4O$ requires $[MH]^+$, 205.1076) (Found: C, 58.88; H, 5.87; N, 27.59. $C_{10}H_{12}N_4O$ requires C, 58.81; H, 5.92; N, 27.43).

(*E*)-4-Azido-2-methyl-4-phenylbut-2-en-1-ol (*E*-6g) and (*Z*)-4-azido-2-methyl-4-phenylbut-2-en-1-ol (*Z*-6g)

To a solution of oxirane **4g** (490 mg, 3.06 mmol, 1.0 equiv) in acetone (10 mL) and water (3 mL) was added sodium azide (597 mg, 9.18 mmol, 3.0 equiv) in one portion. The reaction mixture was stirred at rt for 4 h, and ammonium chloride (500 mg) was added. The resulting mixture was stirred at rt for 10 min. Water (10 mL) was added and the mixture was concentrated under reduced pressure to remove acetone. The aqueous layer was extracted with dichloromethane (3 x 15 mL) and the combined organic extracts were dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue over silica gel (10% EtOAc/petrol) afforded a 75:25 mixture of *(*E*)-4-azido-2-methyl-4-phenylbut-2-en-1-ol E*-**6g** and (Z)-4-azido-2-methyl-4-phenylbut-2-en-1-ol *Z*-**6g** respectively (461 mg, 74%) as a colourless oil.

Data for the mixture: ν_{max} (film) 3366, 2101, 1492, 1446, 1238, 1074, 702 cm^{-1}; *m/z* (CI) 221 $[MNH_4]^+$, 210, 178 $[MNH_4–N_3]^+$, 161 $[MH–N_3]^+$ (Found: $[MNH_4]^+$, 221.1411. $C_{11}H_{13}N_3O$ requires $[MNH_4]^+$, 221.1402).

NMR data for *E*-**6g**: δ_H (500 MHz, $CDCl_3$) [7.47–7.38 (3H, m) and 7.19–7.17 (2H, m), Ph], 5.71 (1H, dt, *J* 10.0, 1.5, H-3), 4.36 (2H, s (br), H-1), 4.06 (1H, dq, *J* 10.0, 6.5, H-4), 1.62 (1H, s (br), OH), 1.24 (3H, d, *J* 6.5, H-5); δ_C (126 MHz, $CDCl_3$), 144.5, 136.9, 128.6, 128.5, 126.9, 125.6 (C-3), 66.9 (C-1), 55.4 (C-4), 20.6 (C-5).

NMR data for *Z*-**6g**: δ_H (500 MHz, $CDCl_3$) [7.47–7.38 (3H, m) and 7.19–7.17 (2H, m), Ph], 5.47 (1H, d, *J* 9.0, H-3), 4.62 (2H, s (br), H-1), 4.59 (1H, dq, *J* 9.0, 7.0, H-4), 1.57 (1H, s (br), OH), 1.39 (3H, d, *J* 7.0, H-5); δ_C (126 MHz, $CDCl_3$), 142.7, 139.6, 130.0 (C-3), 128.1, 127.9, 126.7, 60.1 (C-1), 54.7 (C-4), 20.8 (C-5).

(*E*)-2-(Hydroxymethyl)non-3-enenitrile (7) and (*E*)-non-3-ene-1,2-diol (8)

To a solution of oxirane **4a** (1.19 g, 8.52 mmol, 1.0 equiv) in acetone (10 mL) and water (5 mL) was added potassium cyanide (0.61 g, 9.37 mmol, 1.1 equiv) in one portion at rt. The resulting solution was stirred at rt for 30 min and heated to reflux for 16 h. The reaction mixture was cooled to rt and NH_4Cl (500 mg) was added. After stirring for 10 min, the reaction mixture was concentrated under reduced pressure to

remove acetone and the residue was extracted with dichloromethane (3 x 10 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the residue over silica gel (25% ether/petrol) afforded less polar *(*E*)-2-(hydroxymethyl)non-3-enenitrile* **7** (271 mg, 19%) as a colourless oil: ν_{max} (film) 3435, 2252, 1671, 1467, 1042, 973 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.84 (1H, dt, *J* 15.5, 6.5, H-4), 5.55 (1H, ddt, *J* 15.5, 6.5, 2.0, H-3), 4.42 (1H, dt, *J* 6.5, 6.0, H-2), 2.60 (2H, doublet of AB quartets, *J* 16.5, 6.0, CH_2), 2.33 (1H, s (br), OH), 2.08 (2H, dt, *J* 7.5, 6.5, H-5), 1.44–1.27 (6H, m, H-6,7,8), 0.91 (3H, t, *J* 7.0, H-9); δ_C (101 MHz, $CDCl_3$) 135.3 (C-4), 129.2 (C-3), 117.4 (CN), 68.7 (C-2), 32.0 (C-5), 31.3 (C-6), 28.5 (C-7), 26.3 (C-1), 22.5 (C-8), 14.0 (C-9); *m/z* (CI) 185 $[MNH_4]^+$, 52 (Found: $[MNH_4]^+$, 185.1660. $C_{10}H_{17}NO$ requires $[MNH_4]^+$, 185.1654) (Found: C, 71.89; H, 10.26; N, 8.43. $C_{10}H_{17}NO$ requires C, 71.81; H, 10.25; N, 8.37); and more polar *(*E*)-non-3-ene-1,2-diol* **8** (82 mg, 6%) as a colourless oil: ν_{max} (film) 3433, 1671, 1456, 1074, 1027, 971 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.77 (1H, dt, *J* 15.5, 6.5, H-4), 5.44 (1H, dd, *J* 15.5, 6.5, H-3), 4.19 (1H, dt, *J* 7.0, 3.5, H-2), [3.62 (1H, dd, *J* 11.0, 3.5) and 3.47 (1H, dd, *J* 11.0, 8.0), H-1], 3.02 (1H, s (br), OH), 2.04 (2H, dt, *J* 7.5, 7.0, H-5), 1.42–1.24 (6H, m, H-6,7,8), 0.90 (3H, t, *J* 7.0, H-9); δ_C (101 MHz, $CDCl_3$) 134.2 (C-4), 128.2 (C-3), 73.2 (C-2), 66.6 (C-1), 32.3 (C-5), 31.4 (C-6), 28.7 (C-7), 22.5 (C-8), 14.0 (C-9); *m/z* (CI) 176 $[MNH_4]^+$, 158 $[MH]^+$, 96 (Found: $[MNH_4]^+$, 176.1653. $C_9H_{18}O_2$ requires $[MNH_4]^+$, 176.1651).

Ethyl 4-azido-3-ethenylnonanoate (9a)

A 73:27 mixture of allylic azides **5a** and **6a** respectively (100 mg, 0.546 mmol, 1.0 equiv) was reacted according to general procedure **E** to afford *ethyl 4-azido-3-ethenylnonanoate* **9a** (137 mg, 99%, 50:50 *syn*:*anti* mixture of diastereomers) as a colourless oil without further purification: ν_{max} (film) 2102, 1736, 1641, 1465, 1257, 923 cm^{-1}; δ_H (400 MHz, $CDCl_3$) [5.74 (1H, ddd, *J* 17.0, 10.0, 4.0), and 5.65 (1H, ddd, *J* 17.0, 10.0, 4.0), *syn*+*anti* C*H*CH_2), 5.19–5.13 (4H, m, *syn*+*anti* CHC*H*$_2$), [4.14 (2H, q, *J* 7.5) and 4.15 (2H, q, *J* 7.5), *syn*+*anti* OCH_2], [3.84–3.43 (1H, m) and 3.26–3.06 (1H, m), *syn*+*anti* H-4], 2.77–2.69 (2H, m, *syn*+*anti* H-3), [2.56 (2H, dd, *J* 15.0, 5.0) and 2.41 (2H, dd, *J* 15.0, 8.0), *syn*+*anti* H-2], 1.62–1.32 (16H, m, *syn*+*anti* H-5,6,7,8), [1.27 (3H, t, *J* 7.5), and 1.26 (3H, t, *J* 7.5), *syn*+*anti* OCH_2CH_3], 0.91 (6H, t, *J* 6.0

syn+anti H-9); δ_C (101 MHz, $CDCl_3$) 172.0 (C-1), [137.2 and 135.6, (*C*HCH_2)], [118.3 and 117.8, ($CHCH_2$)], [65.8 and 65.3, (C-4)], 60.5 (OCH_2), [44.9 and 44.5, (C-3)], [37.0 and 36.3, (C-2)], 32.2, 32.0, 31.5, 26.0, 25.8, 22.5, 14.2, 14.0; *m/z* (CI) 271 $[MNH_4]^+$, 254 $[MH]^+$, 226 (Found: $[MH]^+$, 254.1858. $C_{13}H_{23}N_3O_2$ requires $[MH]^+$, 254.1869).

Ethyl 4-azido-3-(prop-1-enyl)nonanoate (9b)

A 61:39 mixture of allylic azides **5b** and **6b** respectively (88 mg, 0.446 mmol, 1.0 equiv) was reacted according to general procedure **E** to afford *ethyl 4-azido-3-(prop-1-enyl)nonanoate* **9b** (86 mg, 72%, 59:41 *syn*:*anti* mixture of diastereomers) as a colourless oil after purification over silica gel (10% ether/hexane).

Data for the mixture: ν_{max} (film) 2012, 1733, 1648, 1464, 1379, 1273, 1123, 1073, 899 cm^{-1}; *m/z* (CI) 285 $[MNH_4]^+$, 268 $[MH]^+$, 240 (Found: $[MH]^+$, 268.2025 $C_{14}H_{25}N_3O_2$ requires $[MH]^+$, 268.2025).

NMR data for *syn*-**9b**: δ_H (400 MHz, $CDCl_3$) 4.94 (1H, t, *J* 1.5, *trans*-$CMeCH_2$), 4.86 (1H, s (br), *cis*-$CMeCH_2$), 4.15 (2H, q, *J* 7.0, OCH_2), 3.44–3.39 (1H, m, H-4), 2.81 (1H, dt, *J* 8.0, 6.0, H-3), 2.49 (2H, dd, *J* 15.0, 9.0, H-2), 1.80 (3H, s, Me), 1.60–1.25 (8H, m, H-5,6,7,8), 1.27 (3H, t, *J* 7.0, OCH_2CH_3), 0.93 (6H, t, *J* 6.5, H-9); δ_C (101 MHz, $CDCl_3$) 172.1 (C-1), 143.4 (*C*$MeCH_2$), 114.5 ($CMeCH_2$), 65.1 (C-4), 60.5 (OCH_2), 47.0 (C-3), 35.7, 31.7, 31.6, 26.2, 22.5, 21.0, 14.0.

NMR data for *anti*-**9b**: δ_H (400 MHz, $CDCl_3$) 4.93 (1H, t, *J* 1.5, *trans*-$CMeCH_2$), 4.86 (1H, s (br), *cis*-$CMeCH_2$), 4.13 (2H, q, *J* 7.0, OCH_2), 3.24 (1H, dt, *J* 8.0, 3.0, H-4), 2.67 (1H, dt, *J* 8.0, 5.0, H-3), 2.57 (2H, dd, *J* 15.0, 6.0, H-2), 1.74 (3H, s, Me), 1.60–1.25 (8H, m, H-5,6,7,8), 1.26 (3H, t, *J* 7.0, OCH_2CH_3), 0.93 (6H, t, *J* 6.5, H-9); δ_C (101 MHz, $CDCl_3$) 172.2 (C-1), 143.8 (*C*$MeCH_2$), 114.3 ($CMeCH_2$), 64.6 (C-4), 60.4 (OCH_2), 47.9 (C-3), 36.3, 32.5, 31.5, 25.9, 22.5, 20.1, 14.2.

Ethyl 4-azido-3-(prop-1-enyl)pentanoate (9c)

A 64:36 mixture of allylic azides **5c** and **6c** respectively (88 mg, 0.446 mmol, 1.0 equiv) was reacted according to general procedure **E** to afford *ethyl 4-azido-3-(prop-1-enyl)pentanoate* **9c** (86 mg, 86%, 60:40 *syn*:*anti* mixture of diastereomers) as a colourless oil after purification over silica gel (10% ether/hexane).

Data for the mixture: ν_{max} (film) 2101, 1736, 1650, 1446, 1378, 1258, 1034 cm^{-1}; *m/z* (CI) 229 $[MNH_4]^+$, 212 $[MH]^+$, 184, 117 (Found: $[MNH_4]^+$, 229.1666. $C_{10}H_{17}N_3O_2$ requires $[MNH_4]^+$, 229.1665).

NMR data for *syn*-**9c**: δ_H (400 MHz, $CDCl_3$) 4.93 (1H, t, *J* 1.5, *trans*-CMeC*H*$_2$), 4.83 (1H, s (br), *cis*-CMeC*H*$_2$), 4.13 (2H, q, *J* 7.0, OCH_2), 3.64 (1H, dq, *J* 13.0, 6.0, H-4), 2.74–2.69 (1H, m, H-3), 2.56–2.36 (2H, m, H-2), 1.78 (3H, s, C*Me*CH_2), 1.27 (3H, t, *J* 7.0, OCH_2CH_3), 1.25 (3H, d, *J* 6.0, H-5); δ_C (101 MHz, $CDCl_3$) 176.2 (C-1), 139.3 (*C*MeCH$_2$), 116.7 (CMe*C*H$_2$), 60.1 (OCH_2), 46.6 (C-4), 43.9 (C-3), 34.8 (C-2), 20.3 (C*Me*CH_2), 14.3 (C-5), 14.0 (OCH_2CH_3).

NMR data for *anti*-**9c**: δ_H (400 MHz, $CDCl_3$) 4.89 (1H, t, *J* 1.5, *trans*-CMeC*H*$_2$), 4.83 (1H, s (br), *cis*-CMeC*H*$_2$), 4.12 (2H, q, *J* 7.0, OCH_2), 3.40 (1H, dq, *J* 9.0, 6.5, H-4), 2.74–2.69 (1H, m, H-3), 2.56–2.36 (2H, m, H-2), 1.72 (3H, s, C*Me*CH_2), 1.26 (3H, t, *J* 7.0, OCH_2CH_3), 1.24 (3H, d, *J* 6.5, H-5); δ_C (101 MHz, $CDCl_3$) 176.7 (C-1), 139.9 (*C*MeCH$_2$), 116.0 (CMe*C*H$_2$), 60.0 (OCH_2), 47.0 (C-4), 44.0 (C-3), 33.4 (C-2), 20.3 (C*Me*CH_2), 14.3 (C-5), 13.9 (OCH_2CH_3).

Ethyl 4-azido-4-cyclohexyl-3-(prop-1-enyl)pentanoate (9d)

A 63:37 mixture of allylic azides **5d** and **6d** respectively (50 mg, 0.239 mmol, 1.0 equiv) was reacted according to general procedure **E** to afford *ethyl 4-azido-4-cyclohexyl-3-(prop-1-enyl)pentanoate* **9d** (86 mg, 94%, 63:37 *syn*:*anti* mixture of diastereomers) as a colourless oil without further purification.

Data for the mixture: ν_{max} (film) 2099, 1738, 1647, 1449, 1256, 1156, 1038, 899 cm^{-1}; *m/z* (CI) 297 $[MNH_4]^+$, 280 $[MH]^+$, 252 (Found: $[MH]^+$, 280.2018 $C_{15}H_{25}N_3O_2$ requires $[MH]^+$, 280.2025).

NMR data for *syn*-**9d**: δ_H (400 MHz, $CDCl_3$) [4.92 (1H, s) and 4.88 (1H, s), CMeC*H*$_2$], 4.13 (2H, q, *J* 7.0, OCH_2), 3.17–3.13 (1H, m, H-4), 2.82 (1H, dt, *J* 10.0, 4.5, H-3), 2.63–2.42 (2H, m, H-2), 1.75 (3H, s, C*Me*CH_2), 1.70–1.10 (11H, m, cyclohexyl), 1.28–1.23 (3H, m, OCH_2CH_3); δ_C (101 MHz, $CDCl_3$) 172.2 (C-1), 143.7 (*C*MeCH$_2$), 114.3 (CMe*C*H$_2$), 71.4 (C-4), 60.4 (OCH_2), 45.0 (C-3), 40.6 (C-5), 36.0 (C-2), 31.3, 27.1, 26.0, 20.0, 14.2.

NMR data for *anti*-**9d**: δ_H (400 MHz, $CDCl_3$) [4.93 (1H, s) and 4.90 (1H, s), CMeC*H*$_2$], 4.14 (2H, q, *J* 7.0, OCH_2), 3.17–3.13 (1H, m, H-4), 2.93 (1H, dt, *J* 9.0, 6.5, H-3), 2.63–2.42 (2H, m, H-2), 1.79 (3H, s, C*Me*CH_2), 1.70–1.10 (11H, m, cyclohexyl), 1.28–1.23 (3H, m, OCH_2CH_3); δ_C (101 MHz, $CDCl_3$) 171.9 (C-1), 143.6 (*C*MeCH$_2$), 115.1 (CMe*C*H$_2$), 70.8 (C-4), 60.5 (OCH_2), 44.5 (C-3), 40.3 (C-5), 36.8 (C-2), 31.1, 27.8, 26.3, 26.1, 20.5, 14.2.

Ethyl 3-(1-azidoethyl)-4-phenylpent-4-enoate (9g)

A 75:25 mixture of allylic azide *E*-**6g** and *Z*-**6g** respectively (100 mg, 0.492 mmol, 1.0 equiv) was reacted according to general procedure **E** to afford e*thyl 3-(1-azidoethyl)-4-phenylpent-4-enoate* **9g** (100 mg, 75%, 50:50 *syn*:*anti* mixture of diastereomers) as a colourless oil after purification over silica gel (5% ether/hexane): ν_{max} (film) 2105, 1734, 1631, 1256, 1176, 1037 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.46–7.33 (10H, m, *syn*+*anti* Ph), [5.41 (2H, d, *J* 3.0) and 5.19 (2H, s (br)), *syn*+*anti* CPhC*H*$_2$], [4.17 (2H, q, *J* 7.0) and 4.03 (2H, q, *J* 7.0), *syn*+*anti* OCH_2], [3.65 (1H, dq, *J* 6.5, 4.5) and 3.54 (1H, dq, *J* 7.0, 6.5), *syn*+*anti* CHN_3)], [3.46 (1H, dt, *J* 6.5, 5.5) and 3.21 (1H, dt, *J* 6.5, 5.5), *syn*+*anti* C*H*CPhCH$_2$)], 2.84–2.63 (4H, m, *syn*+*anti* C*H*$_2$CO$_2$Et), [1.27 (3H, t, *J* 7.0) and 1.24 (3H, t, *J* 7.0), *syn*+*anti* OCH_2CH_3)], [1.27 (3H, d, *J* 6.5) and 1.16 (3H, d, *J* 6.5), *syn*+*anti* Me)]; δ_C (101 MHz, $CDCl_3$) [172.3 and 172.1 (*syn*+*anti* C=O)], [149.2 and 148.1 (*syn*+*anti C*PhCH$_2$)], [142.3 and 142.2 (*syn*+*anti i*-Ph)], [128.5, 128.4, 127.8, 127.7, 126.9 and 126.7 (*syn*+*anti* Ph)], [115.1 and 114.8 (*syn*+*anti* CPhC*H*$_2$)], [60.7 and 60.6 (*syn*+*anti* OCH_2)], [60.6 and 58.9 (*syn*+*anti* CHN_3)], [46.0 and 44.7 (*syn*+*anti C*HCPhCH$_2$)], [36.1 and 34.4 (*syn*+*anti C*H$_2$CO$_2$Et)], [18.0 and 15.1 (*syn*+*anti* Me)], 14.2 (*syn*+*anti* OCH_2CH_3); *m/z* (CI) 291

$[MNH_4]^+$, 274 $[MH]^+$, 246, 205 (Found: $[MH]^+$, 274.1563. $C_{15}H_{19}N_3O_2$ requires $[MH]^+$, 274.1556).

Ethyl 4-azido-4-(pyridin-2-yl)-3-(prop-1-enyl)pentanoate (9f)

Allylic azide **5f** (80 mg, 0.392 mmol, 1.0 equiv) was reacted according to general procedure **E** to afford an impure sample of *ethyl 4-azido-4-(pyridin-2-yl)-3-(prop-1-enyl)pentanoate* **9f** (4 mg, <4%, 77:23 *syn*:*anti* mixture of diastereomers) as a brown oil after purification over silica gel (10% ether/5% TEA/petrol).

NMR data for *syn*-**9f** *inter alia*: δ_H (400 MHz, $CDCl_3$) 8.60 (1H, d, *J* 5.0, 6-pyridyl), 7.78–7.67 (1H, m, 4-pyridyl), 7.34–7.19 (2H, m, 3,5-pyridyl), 4.80 (1H, s, *trans*-CMeCH_2), 4.77 (1H, s, *cis*-CMeCH_2), 4.58 (1H, d, *J* 8.0, H-4), 4.20–4.05 (2H, m, OCH_2), 3.26, 1H, dd, *J* 8.0, 5.0, H-3), [2.73 (1H, dd, *J* 14.5, 4.0) and 2.59 (1H, dd, *J* 14.5, 9.5), H-2], 1.69 (3H, s, C*Me*CH_2), 1.31–1.23 (3H, m, OCH_2CH_3); δ_C (101 MHz, $CDCl_3$) 149.7 (6-pyridyl), 136.8 (4-pyridyl), 114.5 (CMe*C*H_2), 68.9 (C-4), 60.4 (OCH_2), 47.4 (C-3), 35.5 (C-2), 20.3 (C*Me*CH_2), 14.0 (OCH_2CH_3).

NMR data for *anti*-**9f** *inter alia*: δ_H (400 MHz, $CDCl_3$) 8.63 (1H, d, *J* 5.0, 6-pyridyl), 7.78–7.67 (1H, m, 4-pyridyl), 7.34–7.19 (2H, m, 3,5-pyridyl), 5.00 (1H, s, *trans*-CMeCH_2), 4.96 (1H, s, *cis*-CMeCH_2), 4.51 (1H, d, *J* 9.5, H-4), 4.20–4.05 (2H, m, OCH_2), 3.35–3.28 (1H, m, H-3), [2.34 (1H, dd, *J* 15.0, 10.0) and 2.21 (1H, dd, *J* 15.0, 5.0), H-2], 1.83 (3H, C*Me*CH_2), 1.31–1.23 (3H, m, OCH_2CH_3); δ_C (101 MHz, $CDCl_3$) 149.5 (6-pyridyl), 136.7 (4-pyridyl), 69.1 (C-4), 60.4 (OCH_2), 47.4 (C-3), 20.9 (C*Me*CH_2), 14.0 (OCH_2CH_3).

5-Methyl-4-(prop-1-enyl)pyrrolidin-2-one (10)

Procedure using polystyrene-PPh_3:

To a solution of ester **9c** (51 mg, 0.242 mmol, 1.0 equiv) in THF (242 μL) in a 0.2–0.5 mL microwave vial was added polystyrene supported diphenylphosphine (286 mg of a 1.10 mmol/g resin, 0.314 mmol, 1.3 equiv) and water (5.6 μL, 0.314 mmol, 1.3 equiv). The vial was flushed with nitrogen gas and capped. After heating by

microwave at 120 °C for 30 min, the mixture was cooled and filtered, washing the resin with dichloromethane (15 mL). The filtrate was concentrated under reduced pressure and the residue purified over silica gel (20–30 % EtOAc/dichloromethane) to afford *5-methyl-4-(prop-1-enyl)pyrrolidin-2-one* **10** (33 mg, 87% 60:40 *syn*:*anti* mixture of diastereomers) as a colourless oil after purification over silica gel (20–30 % EtOAc/dichloromethane).

Data for the mixture: ν_{max} (film) 3321, 1693, 1652 cm^{-1}; *m/z* (CI) 157 $[MNH_4]^+$, 140 $[MH]^+$ (Found: $[MH]^+$, 140.1081. $C_8H_{13}NO$ requires $[MH]^+$, 140.1075).

NMR data for *syn*-**10**: δ_H (500 MHz, $CDCl_3$) 6.83 (1H, s, NH), 4.81 (1H, s, *trans*-$CMeCH_2$) 4.76 (1H, s, *cis*-$CMeCH_2$), 3.85 (1H, dq, *J* 7.0, 6.0, H-5), 3.06 (1H, dt, *J* 10.0, 7.0, H-4), [2.43 (1H, dd, *J* 17.0, 4.0) and 2.23 (1H, dd, *J* 17.0, 8.0), H-3], 1.73 (3H, s, C*Me*CH_2), 0.97 (3H, d, *J* 6.0, 5-Me); δ_C (126 MHz, $CDCl_3$) 177.5 (C-2), 143.2 (*C*$MeCH_2$), 112.5 (CMe*C*H_2), 51.7 (C-5), 45.6 (C-4), 32.6 (C-3), 21.9 (C*Me*CH_2), 16.5 (5-Me).

NMR data for *anti*-**10**: δ_H (500 MHz, $CDCl_3$) 6.83 (1H, s, NH), 4.93 (1H, s, *trans*-$CMeCH_2$), 4.81 (1H, s, *cis*-$CMeCH_2$), 3.59 (1H, dq, *J* 7.0, 6.0, H-5), 2.57 (1H, dt, *J* 9.5, 7.0, H-4), [2.45 (1H, dd, *J* 16.5, 4.5) and 2.32 (1H, dd, *J* 16.5, 10.0), H-3], 1.72 (3H, s, C*Me*CH_2), 1.21 (3H, d, *J* 6.0, 5-Me); δ_C (126 MHz, $CDCl_3$) 176.9 (C-2), 141.9 (*C*$MeCH_2$), 112.4 (CMe*C*H_2), 53.6 (C-5), 50.7 (C-4), 36.0 (C-3), 20.7 (C*Me*CH_2), 19.7 (5-Me).

Following an alternative procedure using PMe_3, epimerisation of the mixture occurred:

To a mixture of ester **9c** (85 mg, 0.40 mmol, 1.0 equiv, 60:40 *syn*:*anti* mixture of diastereomers) and water (6.5 μL, 0.60 mmol, 1.5 equiv) was added trimethylphosphine (0.66 mL of a 1 M solution in THF, 0.66 mmol, 1.5 equiv) dropwise *via* syringe at rt. The resulting solution was stirred until TLC (20% ether/petrol) confirmed consumption of the starting material. Water (5 mL) was added and the mixture was extracted with ether (3 x 5 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to afford *5-methyl-4-*

(prop-1-enyl)pyrrolidin-2-one **10** (33 mg, 59% 45:55 *syn*:*anti* mixture of diastereomers) as a colourless oil after purification over silica gel (20–30 % EtOAc/dichloromethane).

(*E*)-2-Azidonon-3-enyl 2-tosylacetate (11a) and (*E*)-4-azidonon-2-enyl 2-tosylacetate (12a)

A 73:27 mixture of allylic azides **5a** and **6a** respectively (1.00 g, 5.46 mmol, 1.0 equiv) was reacted according to general procedure **F** to afford a 58:42 mixture of the esters *(*E*)-2-azidonon-3-enyl 2-tosylacetate* **11a** and *(*E*)-4-azidonon-2-enyl 2-tosylacetate* **12a** (2.05 g, 99%) respectively as a colourless oil after purification over silica gel (25% ether/petrol).

Data for the mixture: ν_{max} (film) 2932, 2099, 1747, 1598, 1455, 1330, 1152, 1085, 975, 814, 728, 646, cm^{-1}; δ_C (126 MHz, $CDCl_3$) 162.2, 162.1, 138.7, 133.2, 129.9, 128.5, 125.9, 128.5, 125.9, 122.3, 67.1, 65.5, 63.5, 62.0, 60.8, 34.2, 32.2, 31.4, 31.2, 28.5, 25.4, 22.5, 22.4, 21.7, 14.0; *m/z* (CI) 397 $[MNH_4]^+$, 352, 243 (Found: $[MNH_4]^+$, 397.1926. $C_{18}H_{25}N_3O_4S$ requires $[MNH_4]^+$, 397.1910).

^{1}H-NMR data for **11a**: δ_H (500 MHz, $CDCl_3$) 7.85–7.81 (2H, m, *o*-Ts), 7.39–7.37 (2H, m, *m*-Ts), 5.82 (1H, dt, *J* 15.0, 7.0, H-4), 5.31 (1H, ddt, *J* 15.0, 7.0, 1.5, H-3), 4.62 (2H, d, *J* 5.0, H-1), 4.13 (2H, d, *J* 5.0, CH_2Ts), 4.10–3.90 (1H, m, H-2), 2.47 (3H, s, TsMe), 2.10–2.15 (2H, m, H-5), 1.57–1.28 (6H, m, H-6,7,8), 0.89 (3H, t, *J* 7.5, H-9).

^{1}H-NMR data for **12b**: δ_H (500 MHz, $CDCl_3$) 7.85–7.81 (2H, m, *o*-Ts), 7.39–7.37 (2H, m, *m*-Ts), 5.74–5.65 (2H, m, H-2,3), 4.62 (2H, d, *J* 5.0, H-1), 4.13 (2H, d, *J* 5.0, CH_2Ts), 3.82 (1H, dt, *J* 14.0, 7.0, H-4), 2.47 (3H, s, TsMe), 1.57–1.28 (8H, m, H-5,6,7,8), 0.89 (3H, t, *J* 7.5, H-9).

(*E*)-2-Azido-2-methylnon-3-enyl 2-tosylacetate (11b) and (*E*)-4-azido-2-methylnon-2-enyl 2-tosylacetate (12b)

A 61:39 mixture of allylic azides **5b** and **6b** respectively (795 mg, 4.03 mmol, 1.0 equiv) was reacted according to general procedure **F** to afford a 65:35 mixture of the esters *(*E*)-4-azido-2-methylnon-3-enyl 2-tosylacetate* **12b** and *(*E*)-2-azido-2-methylnon-2-enyl 2-tosylacetate* **11b** respectively (1.09 g, 69%) as a colourless oil after purification over silica gel (20% ether/petrol).

Data for the mixture: ν_{max} (film) 2099, 1745, 1673, 1597, 1454, 1331, 1157, 1085, 831, 727 cm^{-1}; δ_C (101 MHz, $CDCl_3$) 162.2, 162.1, 145.6, 145.5, 135.8, 134.5, 134.1, 130.2, 129.9, 129.34, 129.1, 128.5, 127.7, 127.3, 70.7, 70.4, 62.9, 61.0, 60.8, 59.1, 34.7, 33.6, 32.4, 31.5, 31.2, 28.8, 27.7, 26.1, 25.4, 22.5, 21.7, 20.9, 14.4; *m/z* (CI) 411 $[MNH_4]^+$, 366, 207, 137 (Found: $[MNH_4]^+$, 411.2074. $C_{19}H_{27}N_3O_4S$ requires $[MNH_4]^+$, 411.2066).

^{1}H-NMR data for **12b**: δ_H (400 MHz, $CDCl_3$), 7.84 (2H, d, *J* 7.5, *o*-Ts), 7.39 (2H, d, *J* 7.5, *m*-Ts), 5.42, (1H, d, *J* 9.5, H-3), 4.16 (2H, s, CH_2Ts), 4.02 (2H, AB quartet, *J* 11.0, H-1), 2.48 (3H, s, TsMe), 1.72 (3H, d, *J* 1.5, 2-Me), 1.63–1.26 (8H, m, H-5,6,7,8), 0.91 (6H, t, *J* 7.0, H-9).

^{1}H-NMR data for **11b**: δ_H (400 MHz, $CDCl_3$), 7.83 (2H, d, *J* 7.5, *o*-Ts), 7.40 (2H, d, *J* 7.5, *m*-Ts), 5.79 (1H, dt, *J* 15.5, 7.0, H-4), 5.40 (1H, d, *J* 15.5, H-3), 4.57 (2H, s, CH_2Ts), 4.14–4.11 (2H, m, H-1), 2.48 (3H, s, TsMe), 2.09 (2H, dt, *J* 7.5, 7.0, H-5), 1.63–1.26 (6H, m, H-6,7,8), 1.35 (3H, s, 2-Me), 0.91 (6H, t, *J* 7.0, H-9).

(*E*)-2-Azido-2-methylpent-3-enyl 2-tosylacetate (11c) and (*E*)-4-azido-2-methylpent-2-enyl 2-tosylacetate (12c)

A 64:36 mixture of allylic azides **5c** and **6c** respectively (300 mg, 2.13 mmol, 1.0 equiv) was reacted according to general procedure **F** to afford a 70:30 mixture of *(*E*)-4-azido-2-methylpent-3-enyl 2-tosylacetate* **12c** and *(*E*)-2-azido-2-methylpent-2-enyl 2-tosylacetate* **11c** respectively (667 mg, 97%) as a colourless oil after purification over silica gel (30% ether/petrol).

Data for the mixture: ν_{max} (film) 2102, 1744, 1664, 1597, 1450, 1328, 1152, 1085, 813, 727 cm^{-1}; δ_C (101 MHz, $CDCl_3$) 162.2, 162.1, 145.6, 145.55, 135.9, 133.9, 130.4, 130.0, 129.1, 128.6, 128.3, 70.7, 70.3, 63.0, 61.1, 60.9, 54.5, 32.4, 30.5, 25.9, 24.8, 21.8, 20.8, 20.3, 18.0, 14.3; *m/z* (CI) 355 $[MNH_4]^+$, 310, 295, 201 (Found: $[MNH_4]^+$, 355.1446. $C_{15}H_{19}N_3O_4S$ requires $[MNH_4]^+$, 355.1440).

^{1}H-NMR data for **12c**: δ_H (400 MHz, $CDCl_3$) 7.85 (2H, d, *J* 7.5, *o*-Ts), 7.00 (2H, d, *J* 7.5 *m*-Ts), 5.44 (1H, d, *J* 9.5, H-3), 4.33 (1H, dq, *J* 9.5, 7.0, H-4), 4.17 (2H, s, CH_2Ts), 3.98 (2H, s, H-1), 2.46 (3H, s, TsMe), 1.68 (3H, d, *J* 1.5, 2-Me), 1.24 (3H, d, *J* 7.0, H-5).

^{1}H-NMR data for **11c**: δ_H (400 MHz, $CDCl_3$) 7.85 (2H, d, *J* 7.5, *o*-Ts), 7.00 (2H, d, *J* 7.5 *m*-Ts), 5.83 (1H, dq, *J* 15.5, 6.5, H-4), 5.45 (1H, d, *J* 15.5, H-3), 4.56 (2H, s, CH_2Ts), 4.16 (2H, s, H-1), 2.46 (3H, s, TsMe), 1.32 (3H, s, 2-Me), 1.21 (3H, d, *J* 6.5, H-5).

(*E*)-2-Azido-4-cyclohexyl-2-methylbut-3-enyl 2-tosylacetate (11d) and (*E*)-4-azido-4-cyclohexyl-2-methylbut-2-enyl 2-tosylacetate (12d).

A 72:28 mixture of allylic azides **5d** and **6d** respectively (618 mg, 2.96 mmol, 1.0 equiv) was reacted according to general procedure **F** to afford a 68:32 mixture of *(*E*)-4-azido-4-cyclohexyl-2-methylbut-3-enyl 2-tosylacetate* **12d** and *(*E*)-2-azido-4-cyclohexyl-2-methylbut-2-enyl 2-tosylacetate* **11d** respectively (1.10 g, 92%) as a colourless oil after purification over silica gel (20% ether/petrol).

Data for the mixture: ν_{max} (film) 2096, 1742, 1650, 1598, 1450, 1329, 1152, 1085, 813, 727, 697, 603 cm^{-1}; δ_C (101 MHz, $CDCl_3$) 162.2, 145.6, 145.5, 140.1, 135.8, 135.7, 134.6, 129.9, 128.5, 128.4, 128.3, 127.9, 125.9, 125.2, 70.7, 70.5, 64.4, 64.3, 62.9, 61.0, 42.3, 40.6, 32.9. 32.8, 29.5, 26.3, 25.9, 25.8, 21.7, 20.9, 14.5; *m/z* (ESI) 428 $[MNa]^+$, 378, 309, 149 (Found: $[MNa]^+$, 428.1635. $C_{20}H_{27}N_3O_4S$ requires $[MNa]^+$, 428.1620).

^{1}H-NMR data for **12d**: δ_H (400 MHz, $CDCl_3$) 7.84 (2H, d, *J* 7.5, *o*-Ts), 7.39 (2H, d, *J* 7.5, *m*-Ts), 5.45 (1H, d, *J* 9.5, H-3), 4.16 (2H, s, CH_2Ts), 4.02 (2H, AB quartet, *J*

11.5, H-1), 3.91 (1H, dd, *J* 9.5, 8.0, H-4), 4.28 (3H, s, TsMe), [1.77–1.58 and 1.45–0.88 (11H, m, cyclohexyl)], 1.71 (3H, s, 2-Me).

^{1}H-NMR data for **11d**: δ_H (400 MHz, $CDCl_3$) 7.84 (2H, d, *J* 7.5, *o*-Ts), 7.39 (2H, d, *J* 7.5, *m*-Ts), 5.73 (1H, dd, *J* 16.0, 7.0, H-4), 5.36 (1H, d, *J* 16.0, H-3), 4.58 (2H, s, CH_2Ts), 4.15–4.12 (2H, m, H-1), 4.28 (3H, s, TsMe), 2.05– 1.96 (1H, m, A-5), [1.77–1.58 and 1.45–0.88 (10H, m, cyclohexyl)], 1.34 (3H, s, 2-Me).

(*E*)-2-Azido-4-phenylbut-3-enyl 2-tosylacetate (11e)

Allylic azide **5e** (500 mg, 2.64 mmol, 1.0 equiv) was reacted according to general procedure **F** to afford *(*E*)-2-azido-4-phenylbut-3-enyl 2-tosylacetate* **11e** (1.03 g, 97%) as a colourless oil after purification over silica gel (15% EtOAc/hexane): ν_{max} (film) 2109, 1747, 1598, 1328, 1151, 1085, 971, 814, 754, 695, 646 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.81 (2H, d, *J* 8.5, *o*-Ts), 7.40–7.28 (5H, m, Ph), 7.34 (2H, d, *J* 8.5, *m*-Ts), 6.69 (1H, d, *J* 16.0, H-4), 6.04 (1H, dd, *J* 16.0, 7.5, H-3), 4.28–4.20 (1H, m, H-2), 4.14 (2H, s, CH_2Ts), 4.13–4.07 (2H, m, H-1), 2.42 (3H, s, TsMe); δ_C (101 MHz, $CDCl_3$) 162.2, 145.6, 135.9 (C-4), 135.7, 135.3, 129.9, 128.8, 128.7, 128.6, 126.8 (*m*-Ts), 121.7 (C-3), 67.0 (C-2), 62.2 (CH_2Ts), 60.9 (C-1), 21.7 (TsMe); *m/z* (CI) 403 $[MNH_4]^+$, 355, 244, 212 (Found: $[MNH_4]^+$, 403.1445. $C_{19}H_{19}N_3O_4S$ requires $[MNH_4]^+$, 403.1440).

(*E*)-2-Azido-2-methyl-4-(pyridin-2-yl)but-3-enyl 2-tosylacetate (11f)

Allylic azide **5f** (532 mg, 1.24 mmol, 1.0 equiv) was reacted according to general procedure **F** to afford *(*E*)-2-azido-2-methyl-4-(pyridin-2-yl)but-3-enyl 2-tosylacetate* **11f** (259 mg, 52%) as a yellow oil after purification over silica gel (30% EtOAc/5% TEA/hexane): ν_{max} (film) 2106, 1748, 1586, 1329, 1151, 1085, 970, 768 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.61 (1H, d, *J* 5.0, 6-pyridyl), 7.85 (2H, d, *J* 8.0, *o*-Ts), 7.70 (1H, dt, *J* 7.5, 2.0, 4-pyridyl), 7.38 (2H, d, *J* 8.0, *m*-Ts), 7.35 (1H, d, *J* 7.5, 3-pyridyl), 7.22 (1H, dd, *J* 7.5, 5.0, 5-pyridyl), 6.79 (1H, d, *J* 16.0, H-4), 6.73 (1H, d, *J* 16.0, H-3), 4.19 (2H, s, CH_2Ts), 4.17 (2H, d, *J* 2.0, H-1), 2.47 (3H, s, TsMe), 1.53 (3H, s, 2-Me); δ_C (101 MHz, $CDCl_3$) 162.1 (C=O), 154.0 (2-pyridyl), 149.7 (6-pyridyl), 145.6, 136.8

(4-pyridyl), 135.7, [131.8 and 131.7 (C-3) and [C-4)], 130.0 (*m*-Ts), 128.5 (*o*-Ts), 123.0 (5-pyridyl) 122.7 (3-pyridyl), 7.05 (C-1), 63.1 (C-2), 60.9 (CH_2Ts), 21.7 (TsMe), 21.0 (2-Me); *m/z* (CI) 401 $[MH]^+$, 360, 188 (Found: $[MH]^+$, 401.1276. $C_{19}H_{20}N_4O_4S$ requires $[MH]^+$, 401.1284).

(*E*)-4-Azido-2-methyl-4-phenylbut-2-enyl 2-tosylacetate (*E*-12g) and (*Z*)-4-azido-2-methyl-4-phenylbut-2-enyl 2-tosylacetate (*Z*-12g)

Allylic azide **6g** (212 mg, 1.04 mmol, 1.0 equiv) was reacted according to general procedure **F** to afford a 75:25 mixture of *(*E*)-4-azido-2-methyl-4-phenylbut-2-enyl 2-tosylacetate E*-**12g** and *(*Z*)-4-azido-2-methyl-4-phenylbut-2-enyl 2-tosylacetate Z*-**12g** respectively (313 mg, 75%) as a colourless oil after purification over silica gel (25% ether/hexane).

Data for the mixture: ν_{max} (film) 2101, 1742, 1598, 1329, 1151, 1055, 814 cm^{-1}; δ_C (101 MHz, $CDCl_3$) 162.3 (*Z* C-1), 162.1 (*E* C-1), 148.5, 138.9, 138.4, 136.4, 136.0, 135.8, 135.7, 133.6, 129.9, 129.6, 128.7, 128.6, 128.5, 128.4, 128.2, 126.4, 69.1 (*E* C-1), 62.4 (*Z* C-1), 60.9 (*E* and *Z* CH_2Ts), 55.2 (*E* C-4), 54.9 (*Z* C-4), 21.7 (*E* and *Z* TsMe), 20.7 (*Z* C-5), 20.4 (*E* C-5); *m/z* (ESI) 423 $[MHNa]^+$, 422 $[MNa]^+$, 417, 394, 196, 143 (Found: $[MNa]^+$, 422.1153. $C_{20}H_{21}N_3O_4S$ requires $[MNa]^+$, 422.1150).

^{1}H-NMR data for *E*-**12g**: δ_H (400 MHz, $CDCl_3$) 7.80 (2H, d, *J* 8.5, *m*-Ts), 7.43–7.35 (5H, m, Ph), 7.17 (2H, d, *J* 8.5, *o*-Ts), 5.72 (1H, dt, *J* 9.5, 1.5, H-3), 4.83 (2H, d, *J* 1.5, H-1), 4.13 (2H, s, CH_2Ts), 4.05 (1H, dq, *J* 9.5, 6.5, H-4), 2.48 (3H, s, TsMe), 1.25 (3H, d, *J* 6.5, H-5).

^{1}H-NMR data for *Z*-**12g**: δ_H (400 MHz, $CDCl_3$) 7.77 (2H, d, *J* 8.5, *m*-Ts), 7.43–7.35 (5H, m, Ph), 7.33 (2H, d, *J* 8.5, *o*-Ts), 5.93 (1H, d, *J* 9.5, H-3), 5.09 (2H, AB quartet, *J* 12.5, H-1), 4.54 (1H, dq, *J* 9.5, 6.5, H-4), 4.10 (2H, s, CH_2Ts), 2.47 (3H, s, *Z* TsMe), 1.36 (3H, d, *J* 6.5, H-5).

1-[(3-Azido-2-ethenyloctane)sulfonyl]-4-methylbenzene (14a)

A 58:42 mixture of allylic azides **11a** and **12a** respectively (50 mg, 0.132 mmol, 1.0 equiv) was reacted according to general procedure **G** to afford *1-[(3-azido-2-ethenyloctane)sulfonyl]-4-methylbenzene* **14a** (38 mg, 86%, 84:16 *syn*:*anti* mixture of diastereomers) as a white solid after purification over silica gel (2–10% ether/petrol).

*An alternative one-step procedure gave **14a** in a lower yield:*

N,*N*-bis(trimethylsilyl)acetamide (0.484 mL, 1.98 mmol, 5.0 equiv), a 58:42 mixture of allylic azides **11a** and **12a** respectively (150 mg, 0.396 mmol, 1.0 equiv) and potassium acetate (4 mg, 0.396 mmol, 0.1 equiv) were combined in a 0.2–0.5 mL microwave vial. The vial was flushed with nitrogen, sealed and heated under microwave irradiation at 170 °C for two cycles of 5 min. The reaction mixture was concentrated under reduced pressure and the residue was purified over silica gel (2–10% ether/petrol) to afford *1-[(3-azido-2-ethenyloctane)sulfonyl]-4-methylbenzene* **14a** (42 mg, 32%, 84:16 *syn*:*anti* mixture of diastereomers) as a white solid. Repeated purification over silica gel (2–10% ether/petrol) followed by recrystallisation (EtOAc/petrol) afforded an analytical sample of *syn*-**14a** and an analytical sample enriched in *anti*-**14a**.

Data for *syn*-**14a**: m.p 72–74 °C; ν_{max} (film) 2902, 2100, 1456, 1142, 880, 771, 706, 670 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.81 (2H, d, *J* 8.5, *o*-Ts), 7.39 (2H, d, *J* 8.5, *m*-Ts), 5.60 (1H, ddd, *J* 17.0, 10.0, 8.5, C*H*CH_2), 5.17 (1H, d, *J* 10.0, *trans*-CHCH_2), 5.12 (1H, d, *J* 17.0, *cis*-CHCH_2), 3.70 (1H, ddd, *J* 8.5, 5.5, 3.0, H-3), [3.40 (1H, dd, *J* 14.0, 7.0) and 3.15 (1H, dd, *J* 14.0, 6.0), H-1], 2.90 (1H, dddd, *J* 12.5, 9.5, 6.0, 3.0, H-2), 2.48 (3H, s, TsMe), 1.62–1.31 (8H, m, H-4,5,6,7), 0.92 (3H, t, *J* 6.0, H-8); δ_C (101 MHz, $CDCl_3$) 144.9 (Ts), 136.9 (Ts), 133.7 (*C*HCH_2), 130.0 (*m*-Ts), 128.0 (*o*-Ts), 119.5 (CH*C*H_2), 64.3 (C-3), 58.1 (C-1), 42.5 (C-2), 32.2 (C-4), 31.5 (C-5), 25.8 (C-6), 22.5 (C-7), 21.7 (TsMe), 14.0 (C-8); *m/z* (CI) 353 $[MNH_4]^+$, 310, 226, 174, 152; *m/z* (CI) 353 $[MNH_4]^+$, 310, 226, 152 (Found: $[MNH_4]^+$, 353.2020. $C_{17}H_{25}N_3O_2S$ requires $[MNH_4]^+$, 353.2011) (Found: C, 60.95; H, 7.47; N, 12.48. $C_{17}H_{25}N_3O_2S$ requires C, 60.87; H, 7.51; N, 12.53).

NMR data for *anti*-**14a**: δ_H (400 MHz, $CDCl_3$) 7.79 (2H, d, *J* 8.0, *o*-Ts), 7.38 (2H, d, *J* 8.0, *m*-Ts), 5.68 (1H, ddd, *J* 17.5, 10.0, 8.5, C*H*CH_2), 5.17 (1H, d, *J* 10.0, *trans*-CHC*H*$_2$), 5.16 (1H, d, *J* 17.5, *cis*-CHC*H*$_2$), 3.41–3.36 (1H, m, H-3), [3.31 (1H, dd, *J* 14.5, 3.5) and 3.20 (1H, dd, *J* 14.5, 9.0), H-1], 2.80–2.74 (1H, m, H-2), 2.48 (3H, s, TsMe), 1.63–1.28 (8H, m, H-4,5,6,7), 0.91 (3H, t, *J* 7.0, H-8); δ_C (101 MHz, $CDCl_3$) 144.4 (Ts), 135.9 (Ts), 135.5 (*C*HCH_2), 129.9 (*m*-Ts), 128.1 (*o*-Ts), 118.9 (CH*C*H$_2$), 65.8 (C-3), 56.9 (C-1), 43.0 (C-2), 31.6 (C-4), 31.4 (C-5), 25.3 (C-6), 22.4 (C-7), 21.7 (TsMe), 13.6 (C-8).

1-{[3-Azido-2-(prop-1-en-2-yl)octane]sulfonyl}-4-methylbenzene (14b)

A 68:32 mixture of allylic azides **12b** and **11b** respectively (161 mg, 0.41 mmol, 1.0 equiv) was reacted according to general procedure **H** to afford *1-{[3-azido-2-(prop-1-en-2-yl)octane]sulfonyl}-4-methylbenzene* **14b** (97 mg, 68%, 68:32 *syn*:*anti* mixture of diastereomers) as a colourless oil after purification over silica gel (15% ether/petrol). Further purification over silica gel (10% ether/petrol) afforded an analytical sample of *syn*-**14b** and an analytical sample enriched in *anti*-**14b**.

Data for *syn*-**14b**: ν_{max} (film) 2103, 1647, 1597, 1455, 1303, 1142, 1088, 899, 815 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.68 (2H, d, *J* 8.0, *o*-Ts), 7.34 (2H, d, *J* 8.0, *m*-Ts), 4.87 (1H, t, *J* 1.5, *trans*-CMeC*H*$_2$), 4.78 (1H, s, *cis*-CMeC*H*$_2$), 3.61 (1H, dt, *J* 7.0, 5.0, H-3), [3.37 (1H, dd, *J* 14.5, 6.5) and 3.19 (1H, dd, *J* 14.5, 6.5), H-1], 2.86 (1H, dt, *J* 6.5, 5.0, H-2), 2.43 (3H, s, TsMe), 1.64 (3H, s, C*Me*CH_2), 1.49–1.23 (8H, m, H-4,5,6,7), 0.87 (3H, t, *J* 6.5, H-8); δ_C (101 MHz, $CDCl_3$) 144.8, 141.4, 136.9, 129.9 (*o*-Ts), 128.0 (*m*-Ts), 116.4 (CMe*C*H$_2$), 64.2 (C-3), 57.1 (C-1), 44.7 (C-2), 32.3, 31.5, 26.2, 22.5, 21.0, 14.0 (C-8); *m/z* (CI) 367 $[MNH_4]^+$, 350 $[MH]^+$, 324, 240 (Found: $[MNH_4]^+$, 367.2172. $C_{18}H_{27}N_3O_2S$ requires $[MNH_4]^+$, 367.2168).

NMR data for *anti*-**14b**: δ_H (400 MHz, $CDCl_3$) 7.74 (2H, d, *J* 8.0, *o*-Ts), 7.32 (2H, d, *J* 8.0, *o*-Ts), 4.89 (1H, t, *J* 1.5, *trans*-CMeC*H*$_2$), 4.83 (1H, s, *cis*-CMeC*H*$_2$), [3.94 (1H, dd, *J* 14.5, 3.0) and 3.27 (1H, dd, *J* 14.5, 8.0), H-1], 3.17–3.12 (1H, m, H-3), 2.60 (1H, ddd, *J* 10.0, 8.0, 3.0, H-2), 2.43 (3H, s, TsMe), 1.63 (3H, s, C*Me*CH_2), 1.49–1.23 (8H, m, H-4,5,6,7), 0.87 (3H, t, *J* 6.5, H-8); δ_C (101 MHz, $CDCl_3$) 144.7, 141.8,

136.8, 129.8 (*o*-Ts), 128.1 (*m*-Ts), 116.2 (CMe*C*H_2), 64.7 (C-3), 56.2 (C-1), 45.8 (C-2), 32.1, 31.4, 25.8, 21.6, 19.8, 14.0 (C-8).

1-[2-(1-Azidoethyl)-3-methylbut-3-ene-1-sulfonyl]-4-methylbenzene (14c)

A 70:30 mixture of allylic azides **12c** and **11c** respectively (50 mg, 0.16 mmol, 1.0 equiv) was reacted according to general procedure **G** to afford *1-[2-(1-azidoethyl)-3-methylbut-3-ene-1-sulfonyl]-4-methylbenzene* **14c** (36 mg, 82%, 91:9 *syn*:*anti* mixture of diastereomers) as a colourless oil after purification over silica gel (10% ether/petrol). Further purification over silica gel (10% ether/petrol) afforded an analytical sample of *syn*-**14c** and an analytical sample enriched in *anti*-**14c**.

Data for *syn*-**14c**: ν_{max} (film) 2110, 1648, 1598, 1452, 1304, 1146, 1087, 871, 693 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.81 (2H, d, *J* 8.0, *o*-Ts), 7.38 (2H, d, *J* 8.0, *m*-Ts), 4.95 (1H, s, *trans*-CMeCH_2), 4.83 (1H, s, *cis*-CMeCH_2), 3.89 (1H, dq, *J* 6.5, 5.0, H-3), [3.40 (1H, dd, *J* 14.0, 6.0) and 3.25 (1H, dd, *J* 14.0, 7.0), H-1], 2.81 (1H, dt, *J* 6.0, 5.0, H-2), 2.48 (3H, s, TsMe), 1.70 (3H, s, C*Me*CH_2), 1.26 (3H, d, *J* 6.5, H-4); δ_C (101 MHz, $CDCl_3$) 144.8, 141.2, 136.8, 129.8 (*m*-Ts), 128.0 (*o*-Ts), 116.5 (CMe*C*H_2), 58.7 (C-3), 56.8 (C-1), 45.7 (C-2), 21.7 (TsMe), 21.1 (C*Me*CH_2), 16.9 (C-4); *m/z* (CI), 311 $[MNH_4]^+$, 294 $[MH]^+$, 268 (Found: $[MNH_4]^+$, 311.1542. $C_{14}H_{19}N_3O_2S$ requires $[MNH_4]^+$, 311.1542).

NMR data for *anti*-**14c** *inter alia*: δ_H (400 MHz, $CDCl_3$) 7.79 (2H, d, *J* 7.5, *o*-Ts), 7.37 (2H, d, *J* 7.5, *m*-Ts), 4.87 (1H, s, *trans*-CMeCH_2), 4.54 (1H, s, *cis*-CMeCH_2), 2.06–1.93 (1H, m, H-3), 1.05 (3H, d, *J* 7.0, H-4), δ_C (101 MHz, $CDCl_3$) 129.7 (*m*-Ts), 128.1 (*o*-Ts).

1-{2-[Azido(cyclohexyl)methyl]-3-methylbut-3-ene-1-sulfonyl}-4-methylbenzene (14d)

A 65:35 mixture of allylic azides **12d** and **11d** respectively (234 mg, 0.58 mmol, 1.0 equiv) was reacted according to general procedure **H** to afford *1-{2-[azido(cyclohexyl)methyl]-3-methylbut-3-ene-1-sulfonyl}-4-methylbenzene* **14d** (92

mg, 44%, 82:18 *syn*:*anti* mixture of diastereomers) as a colourless gum after purification over silica gel (15% ether/petrol).

Data for the mixture: ν_{max} (film) 2100, 1646, 1597, 1449, 1302, 1143, 1087, 815, 761 cm^{-1}; *m/z* (CI) 379 $[MNH_4]^+$, 336, 240, 184, 112 (Found: $[MNH_4]^+$, 379.2170. $C_{19}H_{27}N_3O_2S$ requires $[MNH_4]^+$, 379.2168).

NMR data for *syn*-**14d**: δ_H (400 MHz, $CDCl_3$) 7.82 (2H, d, *J* 8.5, *o*-Ts), 7.39 (2H, d, *J* 8.5, *m*-Ts), 4.90 (1H, t, *J* 1.5, *trans*-CMeCH_2), 4.85 (1H, s, *cis*-CMeCH_2), 3.85–3.42 (2H, m, H-1 and H-3), 3.21 (1H, dd, *J* 14.5, 6.0, H-1), 3.08 (1H, dt, *J* 7.5, 6.0, H-2), 2.49 (3H, s, TsMe), 1.89–1.07 (11H, m, cyclohexyl), 1.67 (3H, s, C*Me*CH_2); δ_C (101 MHz, $CDCl_3$) 144.8 (*i*-Ts), 141.9 (*p*-Ts), 129.9 (*m*-Ts), 128.1 (*o*-Ts), 116.6 (CMe*C*H_2), 77.2 (*C*MeCH_2), 70.1 (C-3), 57.7 (C-1), 42.2 (C-2), 40.6, 30.5, 29.1, 26.1, 25.8, 20.8.

NMR data for *anti*-**14d**: δ_H (400 MHz, $CDCl_3$) 7.79 (2H, d, *J* 8.5, *o*-Ts), 7.37 (2H, d, *J* 8.5, *m*-Ts), 4.95 (1H, t, *J* 1.5, *trans*-CMeCH_2), 4.91 (1H, s, *cis*-CMeCH_2), 3.43–3.29 (2H, m, H-1), 3.08–3.04 (1H, m, H-3), 2.87 (1H, m, H-2), 2.48 (3H, s, TsMe), 1.89–1.07 (11H, m, cyclohexyl), 1.70 (3H, s, C*Me*CH_2); δ_C (101 MHz, $CDCl_3$) 144.6 (*i*-Ts), 136.9 (*p*-Ts), 129.7 (*m*-Ts), 128.2 (*o*-Ts), 115.8 (CMe*C*H_2), 77.2 (*C*MeCH_2), 71.5 (C-3), 56.0 (C-1), 42.6 (C-2), 40.6, 30.8, 27.6, 25.7, 21.7, 20.0.

1-{2-[Azido(phenyl)methyl]but-3-ene-1-sulfonyl}-4-methylbenzene (14e)

Allylic azide **11e** (213 mg, 0.55 mmol, 1.0 equiv) was reacted according to general procedure **H** to afford *1-{2-[azido(phenyl)methyl]but-3-ene-1-sulfonyl}-4-methylbenzene* **14e** (36 mg, 22%, 75:25 *syn*:*anti* mixture of diastereomers) after purification over silica gel (10% ether/petrol).

Data for the mixture: ν_{max} (film) 2104, 1640, 1598, 1300, 1146, 1087, 755, 662 cm^{-1}; *m/z* (CI) 359 $[MNH_4]^+$, 342 $[MH]^+$, 316, 311, 266 (Found: $[MNH_4]^+$, 359.1546. $C_{18}H_{19}N_3O_2S$ requires $[MNH_4]^+$, 359.1542).

NMR data for *syn*-**14e**: δ_H (400 MHz, $CDCl_3$) 7.81 (2H, d, *J* 8.0, *o*-Ts), 7.38 (2H, d, *J* 8.0, *m*-Ts), 7.31–7.17 (5H, m, Ph), 5.68 (1H, ddd, *J* 17.5, 10.0, 7.5, C*H*CH_2), 5.38

(1H, d, *J* 17.5, *cis*-CHC*H*$_2$), 5.19 (1H, d, *J* 10.0, *trans*-CHC*H*$_2$), 4.96 (1H, d, *J* 8.5, H-3), [3.41 (1H, dd, *J* 14.5, 9.5) and 3.38 (1H, dd, *J* 14.5, 5.5), H-1], 3.24–3.18 (1H, m, H-2), 2.48 (3H, s, TsMe); δ_C (101 MHz, $CDCl_3$) 144.5, 135.3, 129.9, 129.6, 129.4, 128.0, 127.9, 127.4, 127.3, 117.3, 67.8 (C-3), 56.7 (C-1), 45.7 (C-2), 21.7 (TsMe).

NMR data for *anti*-**14e**: δ_H (400 MHz, $CDCl_3$) 7.78 (2H, d, *J* 8.0, *o*-Ts), 7.37 (2H, d, *J* 8.0, *m*-Ts), 7.31–7.17 (5H, m, Ph), 5.57 (1H, ddd, *J* 17.0, 10.0, 8.5, C*H*CH$_2$), 5.10 (1H, d, *J* 10.0, *trans*-CHC*H*$_2$), 4.91 (1H, d, *J* 8.5, H-3), 4.85 (1H, d, *J* 17.0, *cis*-CHC*H*$_2$), [3.26 (1H, dd, *J* 14.5, 7.0) and 3.10 (1H, dd, *J* 14.5, 7.0), H-1], 3.03–2.96 (1H, m, H-2), 2.43 (3H, s, TsMe); δ_C (101 MHz, $CDCl_3$) *inter alia* 141.1, 133.9, 130.0, 128.5, 119.7, 65.5 (C-3), 57.3 (C-1), 44.7 (C-2), 21.1 (TsMe).

1-[2-(1-Azidoethyl)-3-phenylbut-3-ene-1-sulfonyl]-4-methylbenzene (14g)

A 75:25 mixture of allylic azides *E*-**12g** and *Z*-**12g** respectively (297 mg, 0.74 mmol, 1.0 equiv) was reacted according to general procedure **G** to afford *1-[2-(1-azidoethyl)-3-phenylbut-3-ene-1-sulfonyl]-4-methylbenzene* **14g** (87 mg, 32%, 73:27 *syn*:*anti* mixture of diastereomers) as a colourless oil after purification over silica gel (10–40% ether/hexane).

Data for the mixture: ν_{max} (film) 2109, 1626, 1597, 1494, 1317, 1143, 1087, 907, 815, 779 cm^{-1}; *m/z* (CI) 373 $[MNH_4]^+$, 355 $[M]^+$, 330, 178 (Found: $[MNH_4]^+$, 373.1698. $C_{19}H_{21}N_3O_2S$ requires $[MNH_4]^+$, 373.1698).

NMR data for *syn*-**14g**: δ_H (400 MHz, $CDCl_3$) 7□82 (2H, d, *J* 8.0, *o*-Ts), 7.38–7.32 (7H, *m*-Ts, C*Ph*CH$_2$), [5.43 (1H, s) and 5.19 (1H, s), CPhC*H*$_2$], 3.94 (1H, dq, 6.5, 4.0, H-3), 3.63–3.42 (3H, m, H-1,2), 2.48 (3H, s, TsMe), 1.15 (3H, d, *J* 6.5, H-4); δ_C (101 MHz, $CDCl_3$) 145.9 (*C*PhCH$_2$), 144.9, 142.0, 136.9, 130.0, 129.8, 128.6, 128.1, 128.0, 117.0 (CPh*C*H$_2$), 58.8 (C-3), 57.1 (C-1), 42.8 (C-2), 21.7 (TsMe), 16.2 (C-4).

NMR data for *anti*-**14g**: δ_H (400 MHz, $CDCl_3$) 7.75 (2H, d, *J* 8.0, *o*-Ts), 7.38–7.32 (7H, *m*-Ts, C*Ph*CH$_2$), [5.12 (1H, s) and 5.39 (1H, s), CPhC*H*$_2$], 3.63–3.42 (3H, m, H-1,3), 3.20 (1H, ddd, *J* 9.0, 6.5, 3.0, H-2), 2.46 (3H, s, TsMe), 1.29 (3H, d, *J* 6.5, H-4); δ_C (101 MHz, $CDCl_3$) *inter alia* 147.1 (*C*PhCH$_2$), 141.1, 128.5, 127.9, 127.0, 126.5, 116.4 (CPh*C*H$_2$), 60.3 (C-3), 57.0 (C-1), 44.7 (C-2), 21.7 (TsMe), 17.7 (C-4).

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