Electronic Supplementary Information for

**Claisen Rearrangements of Equilibrating Allylic Azides**

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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\(_2\)Cl\(_2\) 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. 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 (MgSO₄) 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 NH₄Cl (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 (MgSO₄) 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 ºC. The resulting white suspension was stirred at 0 ºC for 1 h and quenched with saturated aqueous NH₄Cl (30 mL). The phases were separated and the aqueous layer was extracted with ether (30 mL). The combined organic extracts were dried
(Na₂SO₄) 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 NH₄Cl (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 (Na₂SO₄), 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 (MgSO₄) 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 (MgSO₄) 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: bp4 100–102 °C; ν_{max} (film) 1677, 1628, 1466, 1360, 1253, 1176, 982 cm^{-1}; δ_H (400 MHz, CDCl₃) 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, CDCl₃) 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 [MNH₄]^+, 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 95–100 °C, ν_{max} (film) 1698, 1676, 1624, 1449, 1357, 1253, 980 cm^{-1}; δ_H (400 MHz, CDCl₃) 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, CDCl₃) 199.2 (C-2), 153.4 (C-3), 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 [MNH₄]^+, 153 [MH]^+ (Found: [MH]^+, 153.1281. C₁₀H₁₆O 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: bp₄ 120–125 °C; ν_{max} (film) 1667, 1621, 1583, 1469, 1432, 1359, 1312, 1200, 1152, 980, 766 cm^{-1}; δ_H (400 MHz, CDCl₃) 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, CDCl₃) 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. C₉H₉NO 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 NH₄Cl (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 (MgSO₄) 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 120–125 °C; νmax (film) 1668, 1624, 1577, 1449, 1296, 1220, 966 cm⁻¹; δH (400 MHz, CDCl₃) 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); δC (101 MHz, CDCl₃) 190.1 (C-1), 145.1, 143.5, 137.9, 132.6, 128.5, 128.2, 18.6 (Me); m/z (CI) 164 [MNH₄]+, 147 [MH]+, 131; in agreement with published data.3

(E)-1-Chloronon-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-chloronon-3-en-2-ol S2a (1.42 g, 81%) as a colourless oil after purification over silica gel (20% ether/petrol): νmax (film) 3354, 1671, 972, 760, 730 cm⁻¹; δH (400 MHz, CDCl₃) 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); δC (101 MHz, CDCl3) 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 [MNH4]+, 176 [M]+ (Found: [MNH4]+, 194.1313. C9H17ClO requires [MNH4]+, 194.1312) (Found: C, 61.08; H, 9.72. C9H17ClO 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): νmax (film) 3411, 1669, 1457, 1376, 745 cm⁻¹; δH (400 MHz, CDCl3) 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); δC (101 MHz, CDCl3) 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 [MNH4–H2O]+, 177, 172 [M–OH]+, 137 (Found: [MNH4–H2O]+, 190.1363. C10H19ClO requires [MNH4–H2O]+, 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): νmax (film) 3419, 1671, 1450, 968, 801, 743 cm⁻¹; δH (400 MHz, CDCl3) 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); δC (101 MHz, CDCl3) 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 [MNH4–H2O]+, 100 (Found: [MNH4–H2O]+, 134.0739. C6H11ClO requires [MNH4–H2O]+, 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): \( \nu_{\text{max}} \) (film) 3430, 1668, 1449, 1373, 1263, 970, 745 cm\(^{-1}\); \( \delta_H \) (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); \( \delta_C \) (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): \( \nu_{\text{max}} \) (film) 3390, 3026, 1659, 1598, 1578, 1494, 1449, 1296, 1071, 967, 754, 693 cm\(^{-1}\); \( \delta_H \) (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]; \( \delta_C \) (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%


(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): \( \nu_{\text{max}} \) (film) 3466, 1667, 1623, 1494, 1448, 1336, 1161, 1050, 967, 724, 699 cm\(^{-1}\); \( \delta_{\text{H}} \) (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); \( \delta_{\text{C}} \) (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 \([\text{MNH}_4]^+\), 198, 196 \([\text{MH}]^+\), 181, 179 (Found: \([\text{MNH}_4]^+\), 214.1003. C\(_{11}\)H\(_{13}\)ClO requires \([\text{MNH}_4]^+\), 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: \( \nu_{\text{max}} \) (film) 1669, 1466, 1369, 1245, 964, 835, 771, 727 cm\(^{-1}\); \( \delta_{\text{H}} \) (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).
7.0, H-9); δ C (101 MHz, CDCl₃) 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 [MNH₄]⁺, 141 [MH⁺], 123 [M−OH]⁺ (Found: [MNH₄]⁺, 158.1545. C₉H₁₆O requires [MNH₄]⁺, 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, CDCl₃) 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, CDCl₃) 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. C₁₀H₁₈O 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 ¹H-NMR analysis, 46%): δ H (400 MHz, CDCl₃) 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, CDCl₃) 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: \( \nu_{\text{max}} \) (film) 1677, 1449, 1387, 1064, 968 cm\(^{-1}\); \( \delta_{\text{H}} \) (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); \( \delta_{\text{C}} \) (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 S\(_{2e}\) (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: \( \nu_{\text{max}} \) (film) 3027, 1601, 1578, 1492, 1393, 1244, 1134, 1072, 965 747, 693 cm\(^{-1}\); \( \delta_{\text{H}} \) (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 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]; \( \delta_{\text{C}} \) (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\(_2\)O]\(^+\) (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 S\(_{2f}\) (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: \( \nu_{\text{max}} \) (film) 1654, 1555, 1387, 1305, 1150, 1065, 973, 907, 793, 766, 742, 611 cm\(^{-1}\); \( \delta_{\text{H}} \) (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); \( \delta_{\text{C}} \) (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 S$_{2g}$ (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$_{\text{max}}$ (film) 1681, 1598, 1484, 760, 700 cm$^{-1}$; δ$_{\text{H}}$ (400 MHz, CDCl$_3$) 7.44–7.32 (5H, m, Ph), 5.73–5.70 (2H, m, CHCHMe), [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$_{\text{C}}$ (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$_{\text{max}}$ (film) 3352, 2101, 1667, 1462, 1240, 1072 cm$^{-1}$; $m/z$ (CI) 201 [MNH$_4$]+, 191, 158, 126 (Found: [MNH$_4$]+, 201.1715. C$_{9}$H$_{17}$N$_3$O requires [MNH$_4$]+, 201.1715.

NMR data for 5a: δ$_{\text{H}}$ (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$_{\text{C}}$ (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$_{\text{H}}$ (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); δC (101 MHz, CDCl₃) 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).


NMR data for 5b: δH (400 MHz, CDCl₃) 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); δC (101 MHz, CDCl₃) 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: δH (400 MHz, CDCl₃) 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); δC (101 MHz, CDCl₃) 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: $\nu_{\text{max}}$ (film) 3374, 2105, 1652, 1379, 1250, 1052, 970 cm$^{-1}$; m/z (CI) 159 [$\text{MNH}_4]^+$, 116, 114, 96 (Found: [$\text{MNH}_4]^+$, 159.1248. C$_6$H$_{11}$N$_3$O requires [$\text{MNH}_4]^+$, 159.1246).

NMR data for 5c: $\delta$ (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); $\delta$ (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: $\delta$ (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); $\delta$ (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: $\nu_{\text{max}}$ (film) 3359, 2103, 1665, 1448, 1250, 1052, 970 cm$^{-1}$; m/z (CI) 227 [$\text{MNH}_4]^+$, 210 [MH$^+$], 184, 149 (Found: [$\text{MNH}_4]^+$, 227.1870. C$_{11}$H$_{19}$N$_3$O requires [$\text{MNH}_4]^+$, 227.1872).

NMR data for 5d: $\delta$ (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); $\delta$ (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: $\delta$ (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); $\delta$ (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): \(\nu_{\text{max}}\) (film) 2109, 1650, 1449, 1246, 750, 693 cm\(^{-1}\); \(\delta\)\(_{\text{H}}\) (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); \(\delta\)\(_{\text{C}}\) (101 MHz, CDCl\(_3\)) 135.7 (i-Ph), 135.9 (C-4), 128.5 (o-Ph), 128.5 (p-Ph), 122.9 (C-3), 66.3 (C-2), 65.1 (C-1); m/z (Cl) 207 \([\text{MNH}_4]^+\), 189 \([\text{M}]^+\), 164, 147 (Found: \([\text{MNH}_4]^+\), 207.1247. C\(_{10}\)H\(_{11}\)N\(_3\)O requires \([\text{MNH}_4]^+\), 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): \(\nu_{\text{max}}\) (film) 3339, 2105, 1656, 1590, 1473, 1260, 1153, 975, 766 cm\(^{-1}\); \(\delta\)\(_{\text{H}}\) (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); \(\delta\)\(_{\text{C}}\) (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 \([\text{MH}]^+\), 164, 145, 102 (Found: \([\text{MH}]^+\), 205.1081. C\(_{10}\)H\(_{12}\)N\(_4\)O requires \([\text{MH}]^+\), 205.1076) (Found: C, 58.88; H, 5.87; N, 27.59. C\(_{10}\)H\(_{12}\)N\(_4\)O 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 (Na₂SO₄) 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.


NMR data for E-6g: δH (500 MHz, CDCl₃) [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); δC (126 MHz, CDCl₃), 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: δH (500 MHz, CDCl₃) [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); δC (126 MHz, CDCl₃), 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 NH₄Cl (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 (MgSO₄) 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<sub>max</sub> (film) 3435, 2252, 1671, 1467, 1042, 973 cm<sup>-1</sup>; δ<sub>H</sub> (400 MHz, CDCl₃) 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, CH₂), 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<sub>C</sub> (101 MHz, CDCl₃) 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 [MNH₄]+, 52 (Found: [MNH₄]+, 185.1660. C₁₀H₁₇NO requires [MNH₄]+, 185.1654) (Found: C, 71.89; H, 10.26; N, 8.43. C₁₀H₁₇NO 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<sub>max</sub> (film) 3433, 1671, 1456, 1074, 1027, 971 cm<sup>-1</sup>; δ<sub>H</sub> (400 MHz, CDCl₃) 5.77 (1H, dt, J 15.5, 6.5, H-4), 5.19–5.13 (4H, m, J 17.0, 7.0, CHC₂), 4.14 (2H, q, J 7.5) and 4.15 (2H, q, J 7.5), syn:anti OCH₂, [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 OCH₂CH₃], 0.91 (6H, t, J 6.0

**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<sub>max</sub> (film) 2102, 1736, 1641, 1465, 1257, 923 cm<sup>-1</sup>; δ<sub>H</sub> (400 MHz, CDCl₃) 5.74 (1H, dddd, J 17.0, 10.0, 4.0), 5.65 (1H, dddd, J 17.0, 10.0, 4.0), syn:anti CHCH₂₂, 5.19–5.13 (4H, m, syn:anti CHCH₂₂), [4.14 (2H, q, J 7.5) and 4.15 (2H, q, J 7.5), syn:anti OCH₂], [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 OCH₂CH₃], 0.91 (6H, t, J 6.0
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: \( \nu_{\text{max}} \) (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\(_3\)O\(_2\) requires [MH\(^+\)], 268.2025).

NMR data for \textit{syn}-9b: \( \delta \)\( H \) (400 MHz, CDCl\(_3\)) 4.94 (1H, t, \( J \) 1.5, \textit{trans}-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\(_2\)CH\(_3\)), 0.93 (6H, t, \( J \) 6.5, H-9); \( \delta \)\( C \) (101 MHz, CDCl\(_3\)) 172.1 (C-1), 143.4 (CMeCH\(_2\)), 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 \textit{anti}-9b: \( \delta \)\( H \) (400 MHz, CDCl\(_3\)) 4.93 (1H, t, \( J \) 1.5, \textit{trans}-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\(_2\)CH\(_3\)), 0.93 (6H, t, \( J \) 6.5, H-9); \( \delta \)\( C \) (101 MHz, CDCl\(_3\)) 172.2 (C-1), 143.8 (CMeCH\(_2\)), 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: \( \nu_{\text{max}} \) (film) 2101, 1736, 1650, 1446, 1378, 1258, 1034 cm\(^{-1}\); \( m/z \) (CI) 229 \([\text{MNH}_4]^+\), 212 \([\text{MH}]^+\), 184, 117 (Found: \([\text{MNH}_4]^+\), 229.1666. C\(_{10}\)H\(_{17}\)N\(_3\)O\(_2\) requires \([\text{MNH}_4]^+\), 229.1665).

NMR data for *syn*-9c: \( \delta \)H (400 MHz, CDCl\(_3\)) 4.93 (1H, t, J 1.5, *trans*-CMeC\(_2\)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, CMeCH\(_2\)), 1.27 (3H, t, J 7.0, OCH\(_2\)CH\(_3\)), 1.25 (3H, d, J 6.0, H-5); \( \delta \)C (101 MHz, CDCl\(_3\)) 162.6 (C-1), 139.3 (CMeCH\(_2\)), 111.7 (CMeCH\(_2\)), 60.1 (OCH\(_2\)), 46.6 (C-4), 43.9 (C-3), 34.8 (C-2), 20.3 (CMeCH\(_2\)), 14.3 (C-5), 14.0 (OCH\(_2\)CH\(_3\)).

NMR data for *anti*-9c: \( \delta \)H (400 MHz, CDCl\(_3\)) 4.89 (1H, t, J 1.5, *trans*-CMeCH\(_2\)), 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, CMeCH\(_2\)), 1.26 (3H, t, J 7.0, OCH\(_2\)CH\(_3\)), 1.24 (3H, d, J 6.5, H-5); \( \delta \)C (101 MHz, CDCl\(_3\)) 162.7 (C-1), 139.3 (CMeCH\(_2\)), 111.0 (CMeCH\(_2\)), 60.0 (OCH\(_2\)), 47.0 (C-4), 44.0 (C-3), 33.4 (C-2), 20.3 (CMeCH\(_2\)), 14.3 (C-5), 13.9 (OCH\(_2\)CH\(_3\)).

**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: \( \nu_{\text{max}} \) (film) 2099, 1738, 1647, 1449, 1256, 1156, 1038, 899 cm\(^{-1}\); \( m/z \) (CI) 297 \([\text{MNH}_4]^+\), 280 \([\text{MH}]^+\), 252 (Found: \([\text{MH}]^+\), 280.2018 C\(_{15}\)H\(_{25}\)N\(_3\)O\(_2\) requires \([\text{MH}]^+\), 280.2025).
NMR data for syn-9d: δH (400 MHz, CDCl3) [4.92 (1H, s) and 4.88 (1H, s), CMeCH2], 4.13 (2H, q, J 7.0, OCH2), 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, CMeCH2), 1.70–1.10 (11H, m, cyclohexyl), 1.28–1.23 (3H, m, OCH2C6H5); δC (101 MHz, CDCl3) 172.2 (C-1), 143.7 (CMeCH2), 114.3 (CMeCH2), 71.4 (C-4), 60.4 (OCH2), 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: δH (400 MHz, CDCl3) [4.93 (1H, s) and 4.90 (1H, s), CMeCH2], 4.14 (2H, q, J 7.0, OCH2), 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, CMeCH2), 1.70–1.10 (11H, m, cyclohexyl), 1.28–1.23 (3H, m, OCH2C6H5); δC (101 MHz, CDCl3) 171.9 (C-1), 143.6 (CMeCH2), 115.1 (CMeCH2), 70.8 (C-4), 60.5 (OCH2), 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 ethyl 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):
νmax (film) 2105, 1734, 1631, 1256, 1176, 1037 cm⁻¹;
δH (400 MHz, CDCl3) 7.46–7.33 (10H, m, syn+anti Ph), [5.41 (2H, d, J 3.0) and 5.19 (2H, s (br)), syn+anti CPhCH2], [4.17 (2H, q, J 7.0) and 4.03 (2H, q, J 7.0), syn+anti OCH2], [3.65 (1H, dq, J 6.5, 4.5) and 3.54 (1H, dq, J 7.0, 6.5), syn+anti CHN3], [3.46 (1H, dt, J 6.5, 5.5) and 3.21 (1H, dt, J 6.5, 5.5), syn+anti CHCPhH2)], 2.84–2.63 (4H, m, syn+anti CH2CO2Et), [1.27 (3H, t, J 7.0) and 1.24 (3H, t, J 7.0), syn+anti OCH2CH3], [1.27 (3H, d, J 6.5) and 1.16 (3H, d, J 6.5), syn+anti Me]; δC (101 MHz, CDCl3) [172.3 and 172.1 (syn+anti C=O)], [149.2 and 148.1 (syn+anti CPhCH2)], [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 CPhCH2)], [60.7 and 60.6 (syn+anti OCH2)], [60.6 and 58.9 (syn+anti CHN3)], [46.0 and 44.7 (syn+anti CHCPhH2)], [36.1 and 34.4 (syn+anti CH2CO2Et)], [18.0 and 15.1 (syn+anti Me)], 14.2 (syn+anti OCH2CH3); m/z (CI) 291
[\text{[MNH}_4]^+], 274 [\text{[MH]}^+], 246, 205 \text{ (Found: [MH]}^+\text{, 274.1563. C}_{13}\text{H}_{19}\text{N}_{3}\text{O}_2 \text{ 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: $\delta$H (400 MHz, CDCl3) 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, CMeCH$_2$), 1.31–1.23 (3H, m, OCH$_2$C$_3$); $\delta$C (101 MHz, CDCl3) 149.7 (6-pyridyl), 136.8 (4-pyridyl), 114.5 (CMeCH$_2$), 68.9 (C-4), 60.4 (OCH$_2$), 47.4 (C-3), 35.5 (C-2), 20.3 (CMeCH$_2$), 14.0 (OCH$_2$C$_3$).

NMR data for anti-9f inter alia: $\delta$H (400 MHz, CDCl3) 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, CMeCH$_2$), 1.31–1.23 (3H, m, OCH$_2$CH$_3$); $\delta$C (101 MHz, CDCl3) 149.5 (6-pyridyl), 136.7 (4-pyridyl), 69.1 (C-4), 60.4 (OCH$_2$), 47.4 (C-3), 20.9 (CMeCH$_2$), 14.0 (OCH$_2$CH$_3$).

**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: $\nu_{\text{max}}$ (film) 3321, 1693, 1652 cm$^{-1}$; m/z (CI) 157 $[\text{MNH}_4]^+$, 140 $[\text{MH}]^+$ (Found: $[\text{MH}]^+$, 140.1081. C$_8$H$_{13}$NO requires $[\text{MH}]^+$, 140.1075).

NMR data for syn-10: $\delta$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, CMeCH$_2$), 0.97 (3H, d, $J$ 6.0, 5-Me); $\delta$C (126 MHz, CDCl$_3$) 177.5 (C-2), 143.2 (CMeCH$_2$), 112.5 (CMeCH$_2$), 51.7 (C-5), 45.6 (C-4), 32.6 (C-3), 21.9 (CMeCH$_2$), 16.5 (5-Me).

NMR data for anti-10: $\delta$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, CMeCH$_2$), 1.21 (3H, d, $J$ 6.0, 5-Me); $\delta$C (126 MHz, CDCl$_3$) 176.9 (C-2), 141.9 (CMeCH$_2$), 112.4 (CMeCH$_2$), 53.6 (C-5), 50.7 (C-4), 36.0 (C-3), 20.7 (CMeCH$_2$), 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: \( \nu_{\text{max}} \) (film) 2932, 2099, 1747, 1598, 1455, 1330, 1152, 1085, 975, 814, 728, 646, cm\(^{-1}\); \( \delta_C \) (126 MHz, CDCl\(_3\)) 162.2, 162.1, 138.7, 133.2, 129.9, 128.5, 125.9, 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\(_3\)O\(_4\)S requires [MNH\(_4\)]\(^+\), 397.1910).

\(^1\)H-NMR data for 11a: \( \delta_H \) (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\(_2\)Ts), 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: \( \delta_H \) (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\(_2\)Ts), 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: νmax (film) 2099, 1745, 1673, 1597, 1454, 1331, 1157, 1085, 831, 727 cm⁻¹; δ C (101 MHz, CDCl₃) 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 [MNH₄]⁺, 366, 207, 137 (Found: [MNH₄]⁺, 411.2074. C₁₉H₂₇N₃O₄S requires [MNH₄]⁺, 411.2066).

1H-NMR data for 12b: δH (400 MHz, CDCl₃), 7.84 (2H, d, J 7.5, o-Ts), 7.39 (2H, d, J 7.5, m-Ts), 4.16 (2H, s, CH₂Ts), 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).

1H-NMR data for 11b: δH (400 MHz, CDCl₃), 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, CH₂Ts), 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: $\nu_{\text{max}}$ (film) 2102, 1744, 1664, 1597, 1328, 1152, 1085, 813, 727 cm$^{-1}$; $\delta_{\text{C}}$ (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 [$\text{MNH}_4^+$], 310, 295, 201 (Found: [$\text{MNH}_4^+$], 355.1446. C$_{15}$H$_{19}$N$_3$O$_4$S requires [$\text{MNH}_4^+$], 355.1440).

$^1$H-NMR data for 12c: $\delta_{\text{H}}$ (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$_2$Ts), 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: $\delta_{\text{H}}$ (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$_2$Ts), 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: $\nu_{\text{max}}$ (film) 2096, 1742, 1650, 1598, 1450, 1329, 1152, 1085, 813, 727, 697, 603 cm$^{-1}$; $\delta_{\text{C}}$ (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 [$\text{MNa}^+$], 378, 309, 149 (Found: [$\text{MNa}^+$], 428.1635. C$_{20}$H$_{27}$N$_3$O$_4$S requires [$\text{MNa}^+$], 428.1620).

$^1$H-NMR data for 12d: $\delta_{\text{H}}$ (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$_2$Ts), 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: $\delta_H$ (400 MHz, CDCl₃) 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, J 7.0, H-4), 5.36 (1H, d, J 16.0, H-3), 4.58 (2H, s, CH₂Ts), 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): $\nu_{\text{max}}$ (film) 2109, 1747, 1598, 1328, 1151, 1085, 971, 814, 754, 695, 646 cm$^{-1}$; $\delta_H$ (400 MHz, CDCl₃) 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, CH₂Ts), 4.13–4.07 (2H, m, H-1), 2.42 (3H, s, TsMe); $\delta_C$ (101 MHz, CDCl₃) 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 (CH₂Ts), 60.9 (C-1), 21.7 (TsMe); m/z (CI) 403 [MNH₄]$^+$, 355, 244, 212 (Found: [MNH₄]$^+$, 403.1445. C$_{19}$H$_{19}$N$_3$O$_4$S requires [MNH₄]$^+$, 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): $\nu_{\text{max}}$ (film) 2106, 1748, 1586, 1329, 1151, 1085, 970, 768 cm$^{-1}$; $\delta_H$ (400 MHz, CDCl₃) 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, CH₂Ts), 4.17 (2H, d, J 2.0, H-1), 2.47 (3H, s, TsMe), 1.53 (3H, s, 2-Me); $\delta_C$ (101 MHz, CDCl₃) 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 (CH₂Ts), 21.7
(TsMe), 21.0 (2-Me); m/z (CI) 401 [MH]+, 360, 188 (Found: [MH]+, 401.1276.

(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: νmax (film) 2101, 1742, 1598, 1329, 1151, 1055, 814 cm⁻¹; δC
(101 MHz, CDCl₃) 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 CH₂Ts), 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. C₂₀H₂₁N₃O₄S requires [MNa]+, 422.1150).

¹H-NMR data for E-12g: δH (400 MHz, CDCl₃) 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, CH₂Ts), 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).

¹H-NMR data for Z-12g: δH (400 MHz, CDCl₃) 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, CH₂Ts), 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, CDCl₃) 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, CHCH₂), 5.17 (1H, d, J 10.0, trans-CHCH₂), 5.12 (1H, d, J 17.0, cis-CHCH₂), 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, CDCl₃) 144.9 (Ts), 136.9 (Ts), 133.7 (CHCH₂), 130.0 (m-Ts), 128.0 (o-Ts), 119.5 (CHCH₂), 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 (Cl) 353 [MNH₄⁺], 310, 226, 174, 152; m/z (Cl) 353 [MNH₄⁺], 310, 226, 152 (Found: [MNH₄⁺], 353.2020. C₁₇H₂₅N₃O₂S requires [MNH₄⁺], 353.2011) (Found: C, 60.95; H, 7.47; N, 12.48. C₁₇H₂₅N₃O₂S requires C, 60.87; H, 7.51; N, 12.53).
NMR data for **anti-14a**: δH (400 MHz, CDCl3) 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, CHCH2), 5.17 (1H, d, J 10.0, trans-CHCH2), 5.16 (1H, d, J 17.5, cis-CHCH2), 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); δC (101 MHz, CDCl3) 144.4 (Ts), 135.9 (Ts), 135.5 (CCH2), 129.9 (m-Ts), 128.1 (o-Ts), 118.9 (CHC=H), 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**: νmax (film) 2103, 1647, 1597, 1455, 1303, 1142, 1088, 899, 815 cm⁻¹; δH (400 MHz, CDCl3) 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=H2), 4.78 (1H, s, cis-CMeC=H2), 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, CMeC=H2), 1.49–1.23 (8H, m, H-4,5,6,7), 0.87 (3H, t, J 6.5, H-8); δC (101 MHz, CDCl3) 144.8, 141.4, 136.9, 129.9 (o-Ts), 128.0 (m-Ts), 116.4 (CMeC=H2), 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 [MNH₄]⁺, 350 [MH]⁺, 324, 240 (Found: [MNH₄]⁺, 367.2172. C₁₈H₂₇N₅O₂S requires [MNH₄]⁺, 367.2168).

NMR data for **anti-14b**: δH (400 MHz, CDCl3) 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=H2), 4.83 (1H, s, cis-CMeC=H2), [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-4,5,6,7), 0.87 (3H, t, J 6.5, H-8); δC (101 MHz, CDCl3) 144.7, 141.8,
136.8, 129.8 (o-Ts), 128.1 (m-Ts), 116.2 (CMeCH₂), 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: νmax (film) 2110, 1648, 1598, 1452, 1304, 1146, 1087, 871, 693 cm⁻¹; δH (400 MHz, CDCl₃) 7.81 (2H, d, J 8.0, o-Ts), 7.38 (2H, d, J 8.0, m-Ts), 4.95 (1H, s, trans-CMeCH₂), 4.83 (1H, s, cis-CMeCH₂), 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, CMeCH₂), 1.26 (3H, d, J 6.5, H-4); δC (101 MHz, CDCl₃) 144.8, 141.2, 136.8, 129.8 (m-Ts), 116.5 (CMeCH₂), 58.7 (C-3), 56.8 (C-1), 45.7 (C-2), 21.7 (TsMe), 21.1 (CMeCH₂), 16.9 (C-4); m/z (CI), 311 [MNH₄]⁺, 294 [MH]⁺, 268 (Found: [MNH₄]⁺, 311.1542. C₁₄H₁₉N₃O₂S requires [MNH₄]⁺, 311.1542).

NMR data for anti-14c inter alia: δH (400 MHz, CDCl₃) 7.79 (2H, d, J 7.5, o-Ts), 7.37 (2H, d, J 7.5, m-Ts), 4.87 (1H, s, trans-CMeCH₂), 4.54 (1H, s, cis-CMeCH₂), 2.06–1.93 (1H, m, H-3), 1.05 (3H, d, J 7.0, H-4), δC (101 MHz, CDCl₃) 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: $\nu_{\text{max}}$ (film) 2100, 1646, 1597, 1449, 1302, 1143, 1087, 815, 761 cm$^{-1}$; $m/z$ (Cl) 379 $[\text{MNH}_4]^+$, 336, 240, 184, 112 (Found: $[\text{MNH}_4]^+$, 379.2170. C$_{19}$H$_{27}$N$_3$O$_2$S requires $[\text{MNH}_4]^+$, 379.2168).

NMR data for syn-14d: $\delta$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-CMeC$_2$H), 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, CMeCH$_2$); $\delta$C (101 MHz, CDCl$_3$) 144.8 (i-Ts), 141.9 (p-Ts), 129.9 (m-Ts), 116.6 (CMeCH$_2$), 77.2 (CMeCH$_2$), 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: $\delta$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, CMeCH$_2$); $\delta$C (101 MHz, CDCl$_3$) 144.6 (i-Ts), 136.9 (p-Ts), 128.2 (m-Ts), 115.8 (CMeCH$_2$), 77.2 (CMeCH$_2$), 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: $\nu_{\text{max}}$ (film) 2104, 1640, 1598, 1300, 1146, 1087, 755, 662 cm$^{-1}$; $m/z$ (Cl) 359 $[\text{MNH}_4]^+$, 342 $[\text{M}]^+$, 316, 311, 266 (Found: $[\text{MNH}_4]^+$, 359.1546. C$_{18}$H$_{19}$N$_3$O$_2$S requires $[\text{MNH}_4]^+$, 359.1542).

NMR data for syn-14e: $\delta$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, CHCH$_2$), 5.38
(1H, d, J 17.5, cis-CHCH₂), 5.19 (1H, d, J 10.0, trans-CHCH₂), 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); δC (101 MHz, CDCl₃) 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: δH (400 MHz, CDCl₃) 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, CHCH₂), 5.10 (1H, d, J 10.0, trans-CHCH₂), 4.91 (1H, d, J 8.5, H-3), 4.85 (1H, d, J 17.0, cis-CHCH₂), [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); δC (101 MHz, CDCl₃) 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).


NMR data for syn-14g: δH (400 MHz, CDCl₃) 7.82 (2H, d, J 8.0, o-Ts), 7.38–7.32 (7H, m-Ts, CPhCH₂), [5.43 (1H, s) and 5.19 (1H, s, CPhCH₂), 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); δC (101 MHz, CDCl₃) 145.9 (CPhCH₂), 144.9, 142.0, 136.9, 130.0, 129.8, 128.6, 128.1, 128.0, 117.0 (CPhCH₂), 58.8 (C-3), 57.1 (C-1), 42.8 (C-2), 21.7 (TsMe), 16.2 (C-4).

NMR data for anti-14g: δH (400 MHz, CDCl₃) 7.75 (2H, d, J 8.0, o-Ts), 7.38–7.32 (7H, m-Ts, CPhCH₂), [5.12 (1H, s) and 5.39 (1H, s, CPhCH₂), 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); δC (101 MHz, CDCl₃) inter alia 147.1 (CPhCH₂), 141.1, 128.5, 127.9, 127.0, 126.5, 116.4 (CPhCH₂), 60.3 (C-3), 57.0 (C-1), 44.7 (C-2), 21.7 (TsMe), 17.7 (C-4).