Asymmetric [2,3]-Rearrangement of Glycine-Derived Allyl Ammonium Ylids

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Supporting Information

General Experimental Procedures

'Light petroleum' refers to the fraction with boiling range 40-60 °C. Diethyl ether, 1,2-dimethoxyethane, tetrahydrofuran and toluene were dried by distillation from sodium-benzophenoneketyl radical. Dichloromethane was dried by distillation from calcium hydride. Acetonitrile, benzene, methanol, 1,2-dichloroethane, dimethylformamide and *p*-xylene were used as purchased from Sigma-Aldrich (Sure/SealTM). Sodium hydride was purchased as a 60% dispersion in mineral oil and carefully washed prior to use with sodium-dried light petroleum. Spherical molecular sieves (3 Å) were activated prior to use by strong heating, either under vacuum or in a microwave oven.

Melting points were recorded on an Electrothermal digital melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 881 spectrophotometer either neat or as a thin film in CHCl₃ between KBr plates. Optical rotations were measured, using a Perkin Elmer 241MC polarimeter, at 589 nm and are quoted in 10⁻¹ deg cm² g⁻¹. Mass spectra were recorded on a Fisons VG Autospec spectrometer using chemical ionisation with ammonia gas. ¹H and ¹³C-NMR spectra were recorded on a Bruker DPX-250 or AMX-400 spectrometer. Unless otherwise stated, deuteriochloroform was used as solvent and tetramethylsilane was used as the internal standard. Chemical shifts in ¹H-NMR spectra are expressed as ppm downfield from tetramethylsilane, and in ¹³C-NMR, relative to the internal solvent standard. Coupling constants are quoted in Hertz. Absolute stereochemistry was determined by X-ray crystallography wherever possible, using an ENRAF Nonius FR590 X-ray generator linked to a MARresearch imaging plate detector.

Reactions involving chemicals or intermediates sensitive to air and/or moisture were performed under a nitrogen atmosphere in flame- or oven-dried apparatus. Flash column chromatography was performed (unless otherwise stated) using Merck kieselgel 60 silica (particle size 0.040-0.063nm,

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230-400 mesh ASTM) with head pressure provided by hand bellows, in a similar, but slightly modified, procedure to that reported by Still.¹ Analytical thin layer chromatography (tlc) was performed on pre-coated Merck Kieselgel 60 F₂₅₄ glass backed plates.

1. Preparation of ammonium salts

***N*-(2-[allyldimethylammonium]acetyl)-(1*S*, 2*R*)-bornane-10,2-sultam bromide (4a)**

N-bromoacetyl-(1*S*, 2*R*)-bornane-10,2-sultam (1.68 g, 5.0 mmol) dissolved in THF (10 mL) was added to a stirred solution of *N*-allyl-*N,N*-dimethyl amine (0.60 mL, 5.0 mmol) in THF (10 mL) under a nitrogen atmosphere. The reaction mixture was refluxed for 6 hours during which the solid product began to precipitate. After this time, the mixture was cooled, triturated with light petroleum and the precipitate collected over a glass sinter. The precipitate was then dissolved in methanol and the sample lyophilised to give **4a** (2.06 g, 98%) as a colourless deliquescent solid; $[\alpha]_{\text{D}}^{20}$ -87.5 (*c* 1, CHCl₃); m.p. 114.3-115.9 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl₃) 1692 (C=O), 1642 (C=C), 1339, 1170 (SO₂); δ_{H} (250 MHz, CD₃OD) 1.04 (3H, s, (CH₃)₂CR₂), 1.17 (3H, s, (CH₃)₂CR₂), 1.24-1.52 and 1.89-2.89 (7H, br m, CH₂CH₂CH(R)CH₂ camphor), 3.37 (3H, s, NCH₃), 3.38 (3H, s, NCH₃), 3.70 (1H, d, *J* 14.2, CH₂SO₂), 3.83 (1H, d, *J* 14.2, CH₂SO₂), 4.02 (1H, m, C(O)NCH₂R₂), 4.29 (2H, d, *J* 7.4, NCH₂CH), 4.56 (2H, m, NCH₂CONR₂), 5.72 (2H, br m, CH=CH₂), 6.08 (1H, br m, NCH₂CH); δ_{C} (62.5 MHz, CD₃OD) 20.5 ((CH₃)₂CR₂), 21.8 ((CH₃)₂CR₂), 27.6 (CR₂HCH₂CH₂CR₃), 34.0 (CR₂HCH₂CH₂CR₃), 39.5 (CR₂HCH₂C(R)HN), 43.1 (CR₂HCH₂C(R)HN), 46.6 ((CH₃)₂CR₂CH₂), 51.0 ((CH₃)₂CR₂CH₂), 53.1 (2 x NCH₃), 53.7 (CH₂SO₂), 62.1 (NCH₂CH), 66.8 (CR₂HNSO₂), 69.2 (NCH₂CONR₂), 126.2 (NCH₂CH), 130.8 (CH=CH₂), 163.1 (C=O); *m/z* (CI) 341.1886 (M⁺-Br, C₁₇H₂₉N₂O₃S requires 341.1899) 341 (83%), 98 (100), 58 (74).

***N*-(2-[diallylmethylammonium]acetyl)-(1*R*, 2*S*)-bornane-10,2-sultam iodide (4b)**

1. To a stirred mixture of *N,N*-diallylamine (0.39 g, 0.50 mL, 4.0 mmol) and anhydrous potassium carbonate (2.60 g, 21 mmol) in distilled acetone (25 mL), was added *N*-bromoacetyl-(1*R*, 2*S*)-bornane-10,2-sultam (1.14 g, 3.4 mmol) in one portion at 0 °C initially, allowing to rise to room temperature overnight. The reaction mixture was then filtered over a glass sinter and the residue washed with acetone (20 mL). Solvent was removed *in vacuo* to leave a viscous liquid which was washed several times with chloroform (2 x 5 mL) and evaporated to dryness to give (1*R*, 2*S*)-*N*-(2'-[diallylamino]acetyl)bornane-10,2-sultam (1.23 g, 100%) as a colourless waxy solid; $[\alpha]_{\text{D}}^{20}$ +84.5 (*c* 1, CHCl₃); $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl₃) 1704 (C=O), 1642 (C=C), 1331, 1165 (SO₂); δ_{H} (250 MHz, CDCl₃) 0.90

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(3H, s, (CH₃)₂CR₂), 1.06 (3H, s, (CH₃)₂CR₂), 1.23-1.37 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.79-2.10 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 3.12-3.28 (4H, m, 2 x NCH₂CH), 3.33 (1H, d, *J* 13.8, CH₂SO₂), 3.41 (1H, d, *J* 13.8, CH₂SO₂), 3.65 (2H, s, NCH₂CONR₂), 3.81 (1H, t, *J* 6.5, NCH(R)₂ camphor), 4.95-5.15 (4H, m, 2 x CH=CH₂), 5.72-5.88 (2H, m, 2 x CH=CH₂); δ_C (62.5 MHz, CDCl₃) 20.3 ((CH₃)₂CR₂), 21.2 ((CH₃)₂CR₂), 26.8 (CR₂HCH₂CH₂CR₃), 33.3 (CR₂HCH₂CH₂CR₃), 38.9 (CR₂HCH₂C(R)HN), 45.1 (CR₂HCH₂C(R)HN), 48.2 ((CH₃)₂CR₂CH), 49.2 (CR₂HCH₂CH₂CR₃), 53.3 (CH₂SO₂), 55.2 (NCH₂CONR₂), 57.6 (2 x NCH₂CH), 65.6 (CH₂C(R)HN), 118.6 (2 x CH=CH₂), 135.7 (2 x CH=CH₂), 170.7 (CO); m/z (CI) 353.1888 (MH⁺, C₁₈H₂₉N₂O₃S requires 353.1899), 353 (2%), 352 (11), 264 (7), 219 (50), 145 (15), 98 (15).

2. Methyl iodide (1.28 g, 0.56 mL, 9.0 mmol) was added dropwise over 5 minutes to a stirred solution of *N*-[2'-(diallylamino)acetyl]-(1*R*, 2*S*)-bornane-10,2-sultam (0.53 g, 1.5 mmol) in distilled THF (15 mL). The reaction mixture was further stirred at room temperature for 96 hours, during which the product began to precipitate. The mixture was then triturated with light petroleum and the precipitate collected over a glass sinter. The precipitate was then washed through with a small amount of methanol, the bulk of the solvents removed *in vacuo* and the concentrated product solution was lyophilised to give **4b** (0.60 g, 81%) as a colourless deliquescent solid; [α]_D²⁰ +86.7 (*c* 1, CHCl₃); m.p. 124.4-126.2 °C; ν_{max}/cm⁻¹ (CHCl₃) 1693 (C=O), 1642 (C=C), 1341, 1170 (SO₂); δ_H (250 MHz, CDCl₃) 0.98 (3H, s, (CH₃)₂CR₂), 1.11 (3H, s, (CH₃)₂CR₂), 1.36-1.57 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.82-2.24 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 3.53 (3H, s, NCH₃), 3.58 (1H, d, *J* 16.4, CH₂SO₂), 3.66 (1H, d, *J* 16.4, CH₂SO₂), 4.15 (1H, br m, C(O)NCH₂R₂), 4.37-4.74 (6H, m, 2 x NCH₂CH and NCH₂CONR₂), 5.77-5.93 (4H, m, 2 x CH=CH₂), 6.00-6.17 (2H, m, 2 x CH=CH₂); δ_C (62.5 MHz, CDCl₃) 20.2 ((CH₃)₂CR₂), 21.4 ((CH₃)₂CR₂), 26.4 (CR₂HCH₂CH₂CR₃), 33.2 (CR₂HCH₂CH₂CR₃), 38.5 (CR₂HCH₂C(R)HN), 45.3 (CR₂HCH₂C(R)HN), 48.7 ((CH₃)₂CR₂CH), 49.9 (NCH₃), 50.0 (CR₂HCH₂CH₂CR₃), 53.2 (CH₂SO₂), 58.4 (NCH₂CONR₂), 65.1 (CH₂C(R)HN), 65.5 (2 x NCH₂CH), 124.3 (2 x CH=CH₂), 131.4 (CH=CH₂), 131.5 (CH=CH₂), 162.9 (CO); m/z (CI) 367.2055 (M⁺ - I, C₁₉H₃₁N₂O₃S requires 367.2055), 367 (5%), 327 (13), 124 (6), 84 (100).

***N*-(2-[triallylammonium]acetyl)-(1*R*, 2*S*)-bornane-10,2-sultam iodide (4c)**

1. *N*-(2-[diallylamino]acetyl)-(1*R*, 2*S*)-bornane-10,2-sultam

To a stirred mixture of *N,N*-diallylamine (0.39 g, 0.50 mL, 4.0 mmol) and anhydrous potassium carbonate (2.60 g, 21 mmol) in distilled acetone (25 mL), was added *N*-bromoacetyl-(1*R*, 2*S*)-bornane-10,2-sultam (1.14 g, 3.4 mmol) in one portion at 0 °C; the reaction was then allowed to warm to room temperature overnight. The mixture was then filtered over a glass sinter and the residue

washed with acetone (20 mL). Solvent was removed *in vacuo* to leave a viscous liquid which was washed several times with chloroform (2 x 5 mL) and evaporated to dryness to give (1*R*, 2*S*)-*N*-[2'-(diallylamino)acetyl]bornane-10,2-sultam (1.23 g, 100%) as a waxy white solid; $[\alpha]_{\text{D}}^{20} +84.5$ (*c* 1, CHCl₃); $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl₃) 1704 (C=O), 1642 (C=C), 1331, 1165 (SO₂); δ_{H} (250 MHz, CDCl₃) 0.90 (3H, s, (CH₃)₂CR₂), 1.06 (3H, s, (CH₃)₂CR₂), 1.23-1.37 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.79-2.10 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 3.12-3.28 (4H, m, 2 x NCH₂CH), 3.33 (1H, d, *J* 13.8, CH₂SO₂), 3.41 (1H, d, *J* 13.8, CH₂SO₂), 3.65 (2H, s, NCH₂CONR₂), 3.81 (1H, t, *J* 6.5, NCH(R)₂ camphor), 4.95-5.15 (4H, m, 2 x CH=CH₂), 5.72-5.88 (2H, m, 2 x CH=CH₂); δ_{C} (62.5 MHz, CDCl₃) 20.3 ((CH₃)₂CR₂), 21.2 ((CH₃)₂CR₂), 26.8 (CR₂HCH₂CH₂CR₃), 33.3 (CR₂HCH₂CH₂CR₃), 38.9 (CR₂HCH₂C(R)HN), 45.1 (CR₂HCH₂C(R)HN), 48.2 ((CH₃)₂CR₂CH), 49.2 (CR₂HCH₂CH₂CR₃), 53.3 (CH₂SO₂), 55.2 (NCH₂CONR₂), 57.6 (2 x NCH₂CH), 65.6 (CH₂C(R)HN), 118.6 (2 x CH=CH₂), 135.7 (2 x CH=CH₂), 170.7 (C=O); *m/z* (CI) 353.1888 (MH⁺, C₁₈H₂₉N₂O₃S requires 353.1899), 353 (2%), 352 (11), 264 (7), 219 (50), 145 (15), 98 (15).

2. *N*-(2-[triallylammonium]acetyl)-(1*R*, 2*S*)-bornane-10,2-sultam iodide (**4c**)

Following the method described above for preparation of **4b**, allyl iodide (3.43 g, 1.86 mL, 20.4 mmol) was added to a stirred solution of (1*R*, 2*S*)-*N*-[2'-(diallylamino)acetyl]bornane-10,2-sultam (1.20 g, 3.4 mmol) in distilled THF (35 mL), to give **4c** (1.27 g, 72%) as a brown gum;² $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl₃) 1696 (C=O), 1640 (C=C), 1338, 1169 (SO₂); δ_{H} (250 MHz, CDCl₃) 1.02 (3H, s, (CH₃)₂CR₂), 1.13 (3H, s, (CH₃)₂CR₂), 1.41-1.67 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.89-2.27 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 3.59 (2H, s, CH₂SO₂), 4.06 (1H, m, C(O)NCH₂R₂), 4.24-4.36 (8H, m, 3 x NCH₂CH and NCH₂CONR₂), 5.82-5.97 (6H, m, 3 x CH=CH₂), 6.03-6.20 (3H, m, 3 x CH=CH₂); δ_{C} (62.5 MHz, CDCl₃) 20.3 ((CH₃)₂CR₂), 21.4 ((CH₃)₂CR₂), 26.6 (CR₂HCH₂CH₂CR₃), 33.2 (CR₂HCH₂CH₂CR₃), 38.6 (CR₂HCH₂C(R)HN), 45.2 (CR₂HCH₂C(R)HN), 48.6 ((CH₃)₂CR₂CH), 50.1 (CR₂HCH₂CH₂CR₃), 53.2 (CH₂SO₂), 56.3 (NCH₂CONR₂), 63.9 (CH₂C(R)HN), 65.5 (3 x NCH₂CH), 123.7 (3 x CH=CH₂), 132.3 (3 x CH=CH₂), 162.1 (C=O); *m/z* (CI) 393.2209 (M⁺-I, C₂₁H₃₃N₂O₃S requires 393.2212), 393 (4%), 353 (18), 311 (20), 110 (100), 68 (5).

N-(2-[diallylbenzylammonium]acetyl)-(1*R*, 2*S*)-bornane-10,2-sultam bromide (**4d**)

Following the method described above for preparation of **4b**, benzyl bromide (0.73 g, 0.51 mL, 4.26 mmol) was added to a stirred solution of (1*R*, 2*S*)-*N*-[2'-(diallylamino)acetyl]bornane-10,2-sultam (0.25 g, 0.71 mmol) in distilled THF (10 mL), to give **4d** (0.33 g, 88%) as an extremely hygroscopic yellow gum, which was used in subsequent reactions without further purification.

3. Optical rotation was difficult to measure due to the opacity of the samples.

***N*-(2-[crotyldimethylammonium]acetyl)-(1*R*, 2*S*)-bornane-10,2-sultam bromide (4e)**

1. *N*-(2-[dimethylamino]acetyl)-(1*R*, 2*S*)-bornane-10,2-sultam bromide

N-bromoacetyl-(1*R*, 2*S*)-bornane-10,2-sultam (0.84 g, 2.5 mmol) in diethyl ether (5 mL) was added to a stirred solution of dimethylamine (5.0 mL, 2.0 M in THF, 10 mmol) in diethyl ether (5 mL) at 0 °C, under a nitrogen atmosphere. After 12 hours the solution was filtered and solvent removed *in vacuo* to give the crude product as a white solid, which was purified by column chromatography, eluting with (4:1) diethyl ether/light petroleum to give (1*R*, 2*S*)-*N*-[2'-(dimethylamino)acetyl]bornane-10,2-sultam (0.75 g, 100%) as a colourless solid; *R*_f 0.17 (diethyl ether/light petroleum, 4:1); [α]_D²⁰ +100.5 (*c* 0.2, CHCl₃); m.p. 123.7-124.5 °C; ν_{max} /cm⁻¹ (CHCl₃) 1705 (C=O), 1330, 1164 (SO₂); δ_{H} (250 MHz, CDCl₃) 0.98 (3H, s, (CH₃)₂CR₂), 1.16 (3H, s, (CH₃)₂CR₂), 1.32-1.46 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.88-2.17 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 2.39 (6H, s, N(CH₃)₂), 3.43 (1H, d, *J* 13.8, CH₂SO₂), 3.51 (1H, d, *J* 13.8, CH₂SO₂), 3.58 (2H, s, NCH₂C(O)N), 3.92 (1H, dd, *J* 5.8, 7.0, NCH(R)₂ camphor); δ_{C} (62.5 MHz, CDCl₃) 20.3 ((CH₃)₂CR₂), 21.2 ((CH₃)₂CR₂), 26.8, 33.3 (CHR₂CH₂CH₂CR₃), 38.9 (NCHCH₂), 45.1 (CHC(CH₃)₂), 45.9 (2 x NCH₃), 48.2 (C(CH₃)₂), 49.2 (CCH₂SO₂), 53.4 (CH₂SO₂), 61.6 (COCH₂N), 65.6 (CHN), 169.7 (CO); *m/z* (CI) 301.1577 (MH⁺, C₁₄H₂₄N₂O₃S requires 301.1586), 301 (76%), 58 (100).

2. Following the method described above for preparation of **4b**, crotyl bromide (0.27 g, 0.21 mL, 2.0 mmol) was added dropwise over 5 minutes to a stirred solution of (1*R*, 2*S*)-*N*-(2'-[dimethylamino]acetyl]bornane-10,2-sultam (0.45 g, 1.5 mmol) in distilled THF (15 mL), under a nitrogen atmosphere. The reaction mixture was refluxed for 6 hours during which the product began to precipitate. Once cooled, the mixture was triturated with light petroleum and the precipitate collected over a glass sinter. The precipitate was then washed through with a small amount of methanol, solvents removed *in vacuo* and lyophilised to give **4e** (0.59 g, 90%) as a colourless gum; [α]_D²⁰ +93.1 (*c* 2, CHCl₃); ν_{max} /cm⁻¹ (CHCl₃) 1691 (C=O), 1639 (C=C), 1339, 1171 (SO₂); δ_{H} (250 MHz, (CD₃)₂SO) 0.94 (3H, s, (CH₃)₂CR₂), 1.06 (3H, s, (CH₃)₂CR₂), 1.25-1.49 and 1.73-2.09 (7H, br m, CH₂CH₂CH(R)CH₂ camphor), 1.74 (3H, d, *J* 5.06, CH=CHCH₃), 3.23 (3H, s, NCH₃), 3.25 (3H, s, NCH₃), 3.73 (1H, d, *J* 14.4, CH₂SO₂), 3.96 (1H, d, *J* 14.4, CH₂SO₂), 3.99 (1H, m, C(O)NCH(R)₂), 4.14 (2H, d, *J* 7.4, NCH₂CH), 4.45 (1H, d, *J* 17.0, NCH₂CONR₂), 4.54 (1H, d, *J* 17.0, NCH₂CONR₂), 5.66-5.73 (1H, br m, NCH₂CH), 5.96-6.05 (1H, br m, CH=CHCH₃); δ_{C} (100 MHz, (CD₃)₂SO) 18.4 (CH=CHCH₃), 19.8 ((CH₃)₂CR₂), 21.1 ((CH₃)₂CR₂), 26.1 (CR₂HCH₂CH₂CR₃), 32.4 (CR₂HCH₂CH₂CR₃), 37.8 (CR₂HCH₂C(R)HN), 44.7 (CR₂HCH₂C(R)HN), 47.5 ((CH₃)₂CR₂CH), 49.1 ((CH₃)₂CR₂CH), 51.5 (2 x NCH₃), 52.1 (CH₂SO₂), 60.2 (NCH₂CH), 64.3 (CR₂HNSO₂), 66.4

(NCH₂CONR₂), 118.5 (NCH₂CH), 140.7 (CH=CH), 163.4 (CO); m/z (CI) 355.2055 (M⁺ - Br, C₁₈H₃₁N₂O₃S requires 355.2055), 355 (48%), 341 (52), 301 (100), 237 (13), 216 (11), 112 (11), 98 (79), 58 (94), 44 (19).

***N*-(2-[(3',3'-dimethyl)allyldimethylammonium]acetyl)-(1*R*, 2*S*)-bornane-10,2-sultam bromide (4f)**

4-Bromo-2-methyl-2-butene (1.17 g, 0.91 mL, 7.9 mmol) was added dropwise over 5 minutes to a stirred solution of (1*S*, 2*R*)-*N*-[2'-(dimethylamino)acetyl]bornane-10,2-sultam (0.40 g, 1.3 mmol) in distilled THF (20 mL), under a nitrogen atmosphere. The reaction mixture was further stirred at room temperature for 72-96 hours, during which the product began to precipitate. The mixture was then triturated with light petroleum and the precipitate collected over a glass sinter. The precipitate was then washed through with a small amount of methanol, solvents removed *in vacuo* and lyophilised to give **4f** (0.54 g, 93%) as a colourless deliquescent solid; $[\alpha]_D^{20}$ -117.2 (c 1, CHCl₃); m.p. 147.4-149.4 °C; $\nu_{\max}/\text{cm}^{-1}$ (CHCl₃) 1694 (C=O), 1649 (C=C), 1341, 1170 (SO₂); δ_{H} (400 MHz, CD₃OD) 1.07 (3H, s, (CH₃)₂CR₂), 1.20 (3H, s, (CH₃)₂CR₂), 1.39-1.45 and 1.52-1.57 (2H, m, C(R)₂HCH₂CH₂ camphor), 1.88 (3H, d, *J* 1.3, CH=C(CH₃)₂), 1.91-2.26 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 1.95 (3H, d, *J* 1.3, CH=C(CH₃)₂), 3.36 (6H, s, N(CH₃)₂), 3.74 (1H, d, *J* 14.2, CH₂SO₂), 3.87 (1H, d, *J* 14.2, CH₂SO₂), 4.05 (1H, dd, *J* 4.9, 7.8, C(O)NCH₂R₂), 4.26 (2H, m, NCH₂CH), 4.54 (1H, d, *J* 16.8, NCH₂CONR₂), 4.61 (1H, d, *J* 16.8, NCH₂CONR₂), 5.48 (1H, m, NCH₂CH); δ_{C} (62.5 MHz, CDCl₃) 19.8 (CH=C(CH₃)₂), 20.2 ((CH₃)₂CR₂), 21.4 ((CH₃)₂CR₂), 26.5 (CR₂HCH₂CH₂CR₃), 26.9 (2 x CH=CCH₃), 33.2 (CR₂HCH₂CH₂CR₃), 38.5 (CR₂HCH₂C(R)HN), 45.3 (CR₂HCH₂C(R)HN), 48.4 ((CH₃)₂CR₂), 49.7 ((CH₃)₂CR₂), 51.1 (N(CH₃)₂), 51.6 (N(CH₃)₂), 53.1 (CH₂SO₂), 61.0 (NCH₂CONR₂), 63.6 (NCH₂CH), 65.1 (CR₂HNSO₂), 110.7 (NCH₂CH), 150.7 (CH=C(CH₃)₂), 163.7 (CO); m/z (CI) 369.2202 (M⁺ - Br, C₁₉H₃₃N₂O₃S requires 369.2212), 369 (100%).

***N*-(2-[(3-methoxycarbonyl)allyldimethylammonium]acetyl)-(1*R*, 2*S*)-bornane-10,2-sultam bromide (4g)**

Following the method described above for preparation of **4a**, *N*-bromoacetyl-(1*R*, 2*S*)-bornane-10,2-sultam (0.51 g, 1.5 mmol) dissolved in THF (10 mL) was added to a stirred solution of methyl (*E*)-4-(dimethylamino)but-2-enoate (0.29 g, 2.0 mmol) in THF (5 mL) to give **4g** (0.56 g, 78%) as white deliquescent solid; $[\alpha]_D^{20}$ +12.7 (c 1, CH₃OH); m.p. 132.3-133.7 °C; $\nu_{\max}/\text{cm}^{-1}$ (CHCl₃) 1723 (CO₂), 1672 (C=O), 1649 (C=C), 1324, 1166 (SO₂); δ_{H} (250 MHz, (CD₃)₂SO) 0.94 (3H, s, (CH₃)₂CR₂), 1.04 (3H, s, (CH₃)₂CR₂), 1.27-1.47 and 1.83-2.08 (7H, br m, CH₂CH₂CH(R)CH₂ camphor), 3.34 (3H, s, NCH₃), 3.35 (3H, s, NCH₃), 3.71 (3H, s, OCH₃), 3.72-3.93 (2H, m, CH₂SO₂), 3.97 (1H, m,

C(O)NCH₂R₂), 4.24-5.08 (4H, m, NCH₂CH and NCH₂CONR₂), 6.27-6.43 (1H, m, NCH₂CH), 6.82-7.06 (1H, m, CH=CHCO₂); δ_C (100 MHz, (CD₃)₂SO) 19.4 ((CH₃)₂CR₂), 20.7 ((CH₃)₂CR₂), 25.7 (CR₂HCH₂CH₂CR₃), 32.0 (CR₂HCH₂CH₂CR₃), 37.4 (CR₂HCH₂C(R)HN), 42.0 (CR₂HCH₂C(R)HN), 47.5 ((CH₃)₂CR₂CH), 49.2 ((CH₃)₂CR₂CH), 50.1 (OCH₃), 51.8 (2 x NCH₃), 51.9 (CH₂SO₂), 60.9 (NCH₂CH), 63.9 (CR₂HNSO₂), 64.4 (NCH₂CONR₂), 130.7 (NCH₂CH), 133.7 (CH=CH), 164.7 (CO), 165.0 (CO); m/z (CI) 399.1940 (M⁺ - Br, C₁₉H₃₁N₂O₅S requires 399.1954), 399 (64%), 359 (13), 301 (100), 144 (93), 99 (32), 58 (87).

***N'*-(*[E]*)-[4-{methoxycarbonylmethyl}dimethylammonium]-but-2-enoyl)-(1*R*, 2*S*)-bornane-10,2-sultam] bromide (6)**

Following the method described above for preparation of **4a**, methyl *N,N*-dimethyl glycinate (0.32 g, 0.34 mL, 2.7 mmol) in THF (5 mL) was added to a stirred solution of (1*R*, 2*S*)-*N*-[(2*E*)-4-bromobut-2-enoyl]bornane-10,2-sultam (0.72 g, 2.0 mmol) dissolved in THF (15 mL) to give **6** (608 mg, 64%) as a white solid; $[\alpha]_D^{20}$ +103.0 (c 1, CH₃OH); m.p. 184.6-186.3 °C; ν_{max}/cm^{-1} (CHCl₃) 1749 (CO₂), 1680 (C=O), 1645 (C=C), 1329, 1168 (SO₂); δ_H (250 MHz, (CD₃)₂SO) 0.95 (3H, s, (CH₃)₂CR₂), 1.08 (3H, s, (CH₃)₂CR₂), 1.24-1.52 and 1.80-2.00 (7H, br m, CH₂CH₂CH(R)CH₂ camphor), 3.34 (6H, s, N(CH₃)₂), 3.71 (1H, d, *J* 14.2, CH₂SO₂), 3.76 (3H, s, OCH₃), 3.93 (1H, m, C(O)NCH₂R₂), 3.94 (1H, d, *J* 14.2, CH₂SO₂), 4.41-4.47 (4H, m, NCH₂CH and NCH₂CONR₂), 6.82 (1H, d, *J* 14.9, CH₂CH=CH), 6.94-7.06 (1H, m, CH₂CH=CH); δ_C (62.5 MHz, (CD₃)₂SO) 19.8 ((CH₃)₂CR₂), 21.1 ((CH₃)₂CR₂), 26.2 (CR₂HCH₂CH₂CR₃), 32.3 (CR₂HCH₂CH₂CR₃), 38.3 (CR₂HCH₂C(R)HN), 44.7 (CR₂HCH₂C(R)HN), 47.7 ((CH₃)₂CR₂CH), 49.0 ((CH₃)₂CR₂CH), 51.7 (2 x NCH₃), 52.5 (CH₂SO₂), 53.3 (OCH₃), 61.1 (NCH₂CH), 64.5 (CR₂HNSO₂), 64.6 (NCH₂CO₂), 130.9, 133.8 ((NCH₂CH=CH), 162.1 (CO), 165.5 (CO); m/z (CI) 399.1938 (M⁺ - Br, C₁₉H₃₁N₂O₅S requires 399.1954), 399 (15%), 327 (17), 284 (49), 216 (100), 134 (27), 104 (28), 58 (29).

2. [2,3]-Sigmatropic Rearrangements

***N*-(*[N,N]*-dimethyl]allylglycinoyl)-(1*S*, 2*R*)-bornane-10,2-sultam (5a)**

Sodium hydride (7.2 mg, 0.30 mmol) was added to a cooled (0 °C) vigorously stirred suspension of **4a** (0.127 g, 0.30 mmol) in DME (6 mL) containing molecular sieves, under a nitrogen atmosphere. The reaction mixture was further stirred at 0 °C for 3 hours, after which diethyl ether (25 mL) was added. This mixture was then filtered through a small pad of Celite[®], supported on a glass sinter, washing well with further diethyl ether (2 x 15 mL). Solvents were removed *in vacuo* to give a solid,

which was purified by column chromatography, eluting with diethyl ether/light petroleum (2:1) to give (2'*R*)-**5a** (2 mg, 2%) and (2'*S*)-**5a** (99 mg, 97%) as colourless crystalline solids.

(2'*R*)-**5a**

R_f 0.44 (diethyl ether/light petroleum, 2:1); $[\alpha]_D^{20}$ -42.7 (c 0.3, CHCl_3); m.p. 138.0-139.9 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl_3) 1687 (C=O), 1642 (C=C), 1330, 1165 (SO_2); δ_{H} (250 MHz, CDCl_3) 0.91 (3H, s, $(\text{CH}_3)_2\text{CR}_2$), 1.11 (3H, s, $(\text{CH}_3)_2\text{CR}_2$), 1.13-1.38 (2H, m, $\text{C(R)}_2\text{HCH}_2\text{CH}_2$ camphor) and 1.81-2.05 (5H, m, $\text{CH}_2\text{C(R)HCH}_2\text{CH}_2$ camphor), 2.31 (6H, s, $\text{N}(\text{CH}_3)_2$), 2.36 (2H, m, NC(R)HCH_2), 3.35 (1H, d, J 13.8, CH_2SO_2), 3.44 (1H, d, J 13.8, CH_2SO_2), 3.87 (2H, m, NCH(R)CH_2 and NCH(R)_2 camphor), 5.00 (2H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.75 (1H, m, $\text{CH}_2\text{CH}=\text{CH}_2$); δ_{C} (62.5 MHz, CDCl_3) 20.3 ($(\text{CH}_3)_2\text{CR}_2$), 21.4 ($(\text{CH}_3)_2\text{CR}_2$), 26.8 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 32.9 ($\text{CH}_2\text{CH}=\text{CH}_2$), 33.4 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 39.5 ($\text{CR}_2\text{HCH}_2\text{C(R)HN}$), 41.7 (2 x NCH_3), 45.2 ($\text{CR}_2\text{HCH}_2\text{C(R)HN}$), 48.1 ($(\text{CH}_3)_2\text{CRCH}_2\text{R}$), 48.6 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 53.7 (CH_2SO_2), 65.9 ($\text{CH}_2\text{C(R)HN}$), 66.0 ($(\text{CH}_3)_2\text{NC(R)HCO}$), 117.7 ($\text{CH}_2\text{CH}=\text{CH}_2$), 135.0 ($\text{CH}_2\text{CH}=\text{CH}_2$), 171.7 (CO); m/z (CI) 341.1893 (MH^+ , $\text{C}_{17}\text{H}_{29}\text{N}_2\text{O}_3\text{S}$ requires 341.1899), 341 (100%), 98 (36).

(2'*S*)-**5a**

R_f 0.23 (diethyl ether/light petroleum, 2:1); $[\alpha]_D^{20}$ -93.6 (c 1, CHCl_3); m.p. 131.6-133.4 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl_3) 1694 (C=O), 1641 (C=C), 1334, 1165 (SO_2); δ_{H} (250 MHz, CDCl_3) 0.89 (3H, s, $(\text{CH}_3)_2\text{CR}_2$), 1.07 (3H, s, $(\text{CH}_3)_2\text{CR}_2$), 1.11-1.38 (2H, m, $\text{C(R)}_2\text{HCH}_2\text{CH}_2$ camphor) and 1.78-2.00 (5H, m, $\text{CH}_2\text{C(R)HCH}_2\text{CH}_2$ camphor), 2.36 (6H, s, $\text{N}(\text{CH}_3)_2$), 2.47 (2H, m, NC(R)HCH_2), 3.36 (1H, d, J 13.8, CH_2SO_2), 3.44 (1H, d, J 13.8, CH_2SO_2), 3.79-3.89 (2H, m, NCH(R)CH_2 and NCH(R)_2 camphor), 5.02 (2H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.79 (1H, m, $\text{CH}_2\text{CH}=\text{CH}_2$); δ_{C} (62.5 MHz, CDCl_3) 20.3 ($(\text{CH}_3)_2\text{CR}_2$), 21.2 ($(\text{CH}_3)_2\text{CR}_2$), 26.8 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 33.3 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 34.9 ($\text{CH}_2\text{CH}=\text{CH}_2$), 38.7 ($\text{CR}_2\text{HCH}_2\text{C(R)HN}$), 42.3 (2 x NCH_3), 44.9 ($\text{CR}_2\text{HCH}_2\text{C(R)HN}$), 48.1 ($(\text{CH}_3)_2\text{CRCH}_2\text{R}$), 48.6 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 53.6 (CH_2SO_2), 65.6 ($\text{CH}_2\text{C(R)HN}$), 66.5 ($(\text{CH}_3)_2\text{NC(R)HCO}$), 118.1 ($\text{CH}_2\text{CH}=\text{CH}_2$), 134.4 ($\text{CH}_2\text{CH}=\text{CH}_2$), 173.3 (CO); m/z (CI) 341.1906 (MH^+ , $\text{C}_{17}\text{H}_{29}\text{N}_2\text{O}_3\text{S}$ requires 341.1899), 341 (100%), 216 (16), 152 (16), 98 (80).

N-([*N*-allyl-*N*-methyl]allylglycinoyl)-(1*R*, 2*S*)-bornane-10,2-sultam (**5b**)

Following the method described above for **5a**, sodium hydride (10 mg, 0.42 mmol) was added to a vigorously stirred suspension of **4b** (210 mg, 0.42 mmol) in DME (8 mL) containing molecular sieves to give a crude mixture, which was purified by column chromatography, eluting with light

petroleum/ethyl acetate (5:1), to furnish (2'*S*)-**5b** (5 mg, 3%) and (2'*R*)-**5b** (147 mg, 97%) as colourless crystalline solids.

(2'*S*)-**5b**

R_f 0.29 (light petroleum/ethyl acetate, 5:1); [α]_D²⁰ +65.0 (c 0.1, CHCl₃); m.p. 91.4-92.7 °C; ν_{max} /cm⁻¹ (CHCl₃) 1677 (C=O), 1642 (C=C), 1327, 1166 (SO₂); δ_{H} (250 MHz, CDCl₃) 0.81 (3H, s, (CH₃)₂CR₂), 1.13 (3H, s, (CH₃)₂CR₂), 1.15-1.38 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.80-2.03 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 2.23 (3H, s, NCH₃), 2.40 (2H, m, NC(R)HCH₂), 3.11 (2H, ddd, *J* 6.5, 13.9, 25.3, NCH₂CH), 3.33 (1H, d, *J* 13.8, CH₂SO₂), 3.43 (1H, d, *J* 13.8, CH₂SO₂), 3.86 (1H, dd, *J* 6.1, 6.5, NCH(R)₂ camphor), 3.94 (1H, dd, *J* 7.4, 7.4, NCH(R)CH₂), 4.96-5.11 (4H, m, 2 x (CH₂CH=CH₂)), 5.68-5.76 (2H, m, 2 x (CH₂CH=CH₂)); δ_{C} (62.5 MHz, CDCl₃) 20.3 ((CH₃)₂CR₂), 21.4 ((CH₃)₂CR₂), 26.8 (CR₂HCH₂CH₂CR₃), 32.1 (CH₂CH=CH₂), 33.4 (CR₂HCH₂CH₂CR₃), 38.0 (NCH₃), 39.4 (CR₂HCH₂C(R)HN), 45.2 (CR₂HCH₂C(R)HN), 48.1 ((CH₃)₂CR₂CH), 48.6 (CR₂HCH₂CH₂CR₃), 53.7 (CH₂SO₂), 56.9 (2 x NCH₂CH), 65.8 (CH₂C(R)HN), 65.9 ((CH₃)₂NC(R)HCO), 117.0 (NCH₂CH=CH₂), 117.6 (CH₂CH=CH₂), 135.0 (CH₂CH=CH₂), 136.9 (NCH₂CH=CH₂), 172.0 (C=O); *m/z* (CI) 367.2043 (MH⁺, C₁₉H₃₁N₂O₃S requires 367.2055), 367 (16%), 325 (15), 124 (100), 82 (8).

(2'*R*)-**5b**

R_f 0.24 (light petroleum/ethyl acetate, 5:1); [α]_D²⁰ +71.5 (c 1, CHCl₃); m.p. 106.8-107.9 °C; ν_{max} /cm⁻¹ (CHCl₃) 1681 (C=O), 1640 (C=C), 1327, 1166 (SO₂); δ_{H} (250 MHz, CDCl₃) 0.89 (3H, s, (CH₃)₂CR₂), 1.06 (3H, s, (CH₃)₂CR₂), 1.13-1.38 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.78-2.00 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 2.30 (3H, s, NCH₃), 2.48 (2H, m, NC(R)HCH₂), 3.22 (2H, ddd, *J* 6.6, 14.1, 21.5, NCH₂CH), 3.35 (1H, d, *J* 13.8, CH₂SO₂), 3.42 (1H, d, *J* 13.8, CH₂SO₂), 3.85 (1H, dd, *J* 6.3, 6.5, NCH(R)₂ camphor), 3.99 (1H, dd, *J* 7.2, 7.2, NCH(R)CH₂), 4.95-5.13 (4H, m, 2 x (CH₂CH=CH₂)), 5.71-5.81 (2H, m, 2 x (CH₂CH=CH₂)); δ_{C} (62.5 MHz, CDCl₃) 20.3 ((CH₃)₂CR₂), 21.1 ((CH₃)₂CR₂), 26.8 (CR₂HCH₂CH₂CR₃), 33.2 (CR₂HCH₂CH₂CR₃), 34.9 (CH₂CH=CH₂), 38.3 (NCH₃), 38.7 (CR₂HCH₂C(R)HN), 44.9 (CR₂HCH₂C(R)HN), 48.1 ((CH₃)₂CR₂CH), 48.7 (CR₂HCH₂CH₂CR₃), 53.6 (CH₂SO₂), 57.3 (2 x NCH₂CH), 65.6 (CH₂C(R)HN), 65.8 ((CH₃)₂NC(R)HCO), 117.1 (NCH₂CH=CH₂), 117.9 (CH₂CH=CH₂), 134.7 (CH₂CH=CH₂), 136.9 (NCH₂CH=CH₂), 173.8 (C=O); *m/z* (CI) 367.2023 (MH⁺, C₁₉H₃₁N₂O₃S requires 367.2055), 367 (100%), 327 (11), 233 (12), 152 (28), 124 (38), 84 (9).

N-([*N,N*-diallyl]allylglycinoyl)-(1*R*, 2*S*)-bornane-10,2-sultam (**5c**)

Following the method described above for **5a**, sodium hydride (9 mg, 0.35 mmol) was added to a vigorously stirred suspension of **5c** (180 mg, 0.35 mmol) in DME (7 mL) containing molecular sieves to give a crude mixture, which was purified by column chromatography, eluting with light

petroleum/ethyl acetate (7:1), to furnish (2'*R*)-**5c** (114 mg, 83%) and (2'*S*)-**5c** (4 mg, 3%) as colourless gums.

(2'*R*)-5c :

R_f 0.33 (light petroleum/ethyl acetate, 7:1); $[\alpha]_D^{20} +39.7$ (c 1, CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl_3) 1696 (C=O), 1641 (C=C), 1335, 1164 (SO_2); δ_H (250 MHz, CDCl_3) 0.89 (3H, s, $(\text{CH}_3)_2\text{CR}_2$), 1.05 (3H, s, $(\text{CH}_3)_2\text{CR}_2$), 1.13-1.39 (2H, m, $\text{C(R)}_2\text{HCH}_2\text{CH}_2$ camphor) and 1.78-1.98 (5H, m, $\text{CH}_2\text{C(R)HCH}_2\text{CH}_2$ camphor), 2.45 (2H, m, NC(R)HCH_2), 3.21-3.36 (4H, m, 2 x (NCH_2CH)), 3.33 (1H, d, J 13.8, CH_2SO_2), 3.41 (1H, d, J 13.8, CH_2SO_2), 3.83 (1H, dd, J 6.3, 6.4, NCH(R)_2 camphor), 4.11 (1H, dd, J 6.2, 8.5, NCH(R)CH_2), 4.94-5.13 (6H, m, 3 x ($\text{CH}_2\text{CH}=\text{CH}_2$)), 5.66-5.80 (3H, m, 3 x ($\text{CH}_2\text{CH}=\text{CH}_2$)); δ_C (62.5 MHz, CDCl_3) 20.3 ($(\text{CH}_3)_2\text{CR}_2$), 21.1 ($(\text{CH}_3)_2\text{CR}_2$), 26.9 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 33.2 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 35.5 ($\text{CH}_2\text{CH}=\text{CH}_2$), 38.7 ($\text{CR}_2\text{HCH}_2\text{C(R)HN}$), 44.8 ($\text{CR}_2\text{HCH}_2\text{C(R)HN}$), 48.2 ($(\text{CH}_3)_2\text{CRCH}_2\text{H}$), 48.7 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 53.5 (CH_2SO_2), 53.6 (2 x NCH_2CH), 63.6 ($(\text{RCH}_2)_2\text{NC(R)HCO}$), 65.5 ($\text{CH}_2\text{C(R)HN}$), 116.9 ($\text{NCH}_2\text{CH}=\text{CH}_2$), 117.0 ($\text{NCH}_2\text{CH}=\text{CH}_2$), 117.6 ($\text{CH}_2\text{CH}=\text{CH}_2$), 135.0 ($\text{CH}_2\text{CH}=\text{CH}_2$), 137.1 (2 x $\text{NCH}_2\text{CH}=\text{CH}_2$), 174.9 (CO); m/z (CI) 393.2211 (MH^+ , $\text{C}_{21}\text{H}_{33}\text{N}_2\text{O}_3\text{S}$ requires 393.2212), 393 (38%), 351 (31), 216 (6), 150 (100), 108 (6), 66 (29).

(2'*S*)-5c :

R_f 0.25 (light petroleum/ethyl acetate, 7:1); $[\alpha]_D^{20} +121.7$ (c 0.3, CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl_3) 1701 (C=O), 1642 (C=C), 1330, 1165 (SO_2); δ_H (250 MHz, CDCl_3) 0.91 (3H, s, $(\text{CH}_3)_2\text{CR}_2$), 1.10 (3H, s, $(\text{CH}_3)_2\text{CR}_2$), 1.19-1.36 (2H, m, $\text{C(R)}_2\text{HCH}_2\text{CH}_2$ camphor) and 1.83-2.10 (5H, m, $\text{CH}_2\text{C(R)HCH}_2\text{CH}_2$ camphor), 2.33 (2H, m, NC(R)HCH_2), 3.06 (2H, dd, J 7.8, 14.5, 2 x (NCH_2CH)), 3.32 (2H, m, 2 x (NCH_2CH)), 3.36 (1H, d, J 14.0, CH_2SO_2), 3.44 (1H, d, J 14.0, CH_2SO_2), 3.58 (1H, ddd, J 6.9, 8.4, 13.7, NCH(R)CH_2), 3.82 (1H, dd, J 5.1, 7.7, NCH(R)_2 camphor), 4.89-5.18 (6H, m, 3 x ($\text{CH}_2\text{CH}=\text{CH}_2$)), 5.63-5.78 (3H, m, 3 x ($\text{CH}_2\text{CH}=\text{CH}_2$)); δ_C (62.5 MHz, CDCl_3) 19.9 ($(\text{CH}_3)_2\text{CR}_2$), 20.8 ($(\text{CH}_3)_2\text{CR}_2$), 26.5 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 32.8 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 34.3 ($\text{CH}_2\text{CH}=\text{CH}_2$), 38.0 ($\text{CR}_2\text{HCH}_2\text{C(R)HN}$), 44.6 ($\text{CR}_2\text{HCH}_2\text{C(R)HN}$), 47.9 ($(\text{CH}_3)_2\text{CRCH}_2\text{H}$), 49.5 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 52.6 (CH_2SO_2), 53.3 (2 x NCH_2CH), 61.6 ($(\text{RCH}_2)_2\text{NC(R)HCO}$), 65.0 ($\text{CH}_2\text{C(R)HN}$), 116.9 ($\text{CH}_2\text{CH}=\text{CH}_2$), 117.2 (2 x $\text{NCH}_2\text{CH}=\text{CH}_2$), 134.9 ($\text{CH}_2\text{CH}=\text{CH}_2$), 136.5 (2 x $\text{NCH}_2\text{CH}=\text{CH}_2$), 171.9 (CO); m/z (CI) 393.2216 (MH^+ , $\text{C}_{21}\text{H}_{33}\text{N}_2\text{O}_3\text{S}$ requires 393.2212), 393 (100%), 351 (37%), 150 (45), 108 (6).

***N*-([*N*-allyl-*N*-benzyl]allylglycinoyl)-(1*R*, 2*S*)-bornane-10,2-sultam (**5d**)**

Following the method described above for **5a**, sodium hydride (13 mg, 0.54 mmol) was added to a vigorously stirred suspension of *N',N'*-diallyl-*N'*-benzyl-*N'*-(*N*-carbonyl-(1*R*, 2*S*)-bornane-10,2-sultam)methylammonium bromide (283 mg, 0.54 mmol) in DME (11 mL) containing molecular sieves to give a crude mixture, which was purified by column chromatography, eluting with light petroleum/ethyl acetate (10:1), to furnish (2'*R*)-**5d** (190 mg, 80 %) as a colourless gum; *R*_f 0.28 (light petroleum/ethyl acetate, 10:1); $[\alpha]_{\text{D}}^{20} +30.9$ (c 0.45, CHCl₃); $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl₃) 1696 (C=O), 1641, 1494, 1454 (C=C), 1334, 1164 (SO₂); δ_{H} (250 MHz, CDCl₃) 0.88 (3H, s, (CH₃)₂CR₂), 1.05 (3H, s, (CH₃)₂CR₂), 1.15-1.36 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.79-1.99 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 2.52 (2H, m, NC(R)HCH₂), 3.16-3.35 (2H, m, NCH₂CH), 3.33 (1H, d, *J* 13.8, CH₂SO₂), 3.40 (1H, d, *J* 13.8, CH₂SO₂), 3.84 (1H, dd, *J* 6.0, 6.6, NCH(R)₂ camphor), 3.87 (1H, d, *J* 14.9, ArCCH₂), 3.98 (1H, d, *J* 14.9, ArCCH₂), 4.19 (1H, dd, *J* 5.9, 9.0, NCH(R)CH₂), 4.95-5.09 (4H, m, 2 x (CH₂CH=CH₂), 5.71-5.84 (2H, m, 2 x (CH₂CH=CH₂)), 7.12-7.30 (5H, m, 5 x (ArCH)); δ_{C} (62.5 MHz, CDCl₃) 20.3 ((CH₃)₂CR₂), 21.1 ((CH₃)₂CR₂), 26.9 (CR₂HCH₂CH₂CR₃), 33.2 (CR₂HCH₂CH₂CR₃), 35.6 (NC(R)HCH₂), 38.7 (CR₂HCH₂C(R)HN), 44.9 (CR₂HCH₂C(R)HN), 48.2 ((CH₃)₂CR₂CH), 48.8 (CR₂HCH₂CH₂CR₃), 53.5 (CH₂SO₂), 54.1 (ArCCH₂), 54.4 (NCH₂CH), 63.5 (CH₂C(R)HN), 65.5 (NCH(R)₂ camphor), 117.3 (CH=CH₂), 117.7 (CH=CH₂), 127.0, 128.4, 128.8 (ArCH), 135.1 (CH=CH₂), 136.7 (CH=CH₂), 141.0 (ArC), 175.1 (CO); *m/z* (CI) 443.2360 (MH⁺, C₂₅H₃₅N₂O₃S requires 443.2368), 443 (36%), 403 (11), 341 (7), 216 (78), 152 (100), 91 (61).

***N*-([*N,N*-dimethyl]crotylglycinoyl)-(1*R*, 2*S*)-bornane-10,2-sultam (**5e**)**

Sodium hydride (14 mg, 0.58 mmol) was added to a cooled (0 °C) vigorously stirred suspension of *N'*-(but-2-enyl)-*N',N'*-dimethyl-*N'*-(*N*-carbonyl-(1*R*, 2*S*)-bornane-10,2-sultam) methylammonium bromide (0.25 g, 0.58 mmol) in DME (11 mL) containing molecular sieves, under a nitrogen atmosphere. The reaction mixture was further stirred at 0 °C for 3 hours, after which diethyl ether (10 mL) was added. This mixture was then filtered through a small pad of Celite[®], supported on a glass sinter, washing well with further diethyl ether (2 x 5 mL). Solvents were removed *in vacuo* to give a solid, which was purified by column chromatography, eluting with light petroleum/ethyl acetate (5:1) to give (2'*S*, 3'*S*)-**5e** (7 mg, 3%) and (2'*R*, 3'*R*)-**5e** (169 mg, 83%) as colourless crystalline solids.

(2'*S*, 3'*S*)-5e:

R_f 0.28 (light petroleum/ethyl acetate, 5:1); $[\alpha]_D^{20} +34.4$ (c 0.25, CHCl_3); m.p. 100.2-102.1 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl_3) 1694 (C=O), 1641 (C=C), 1333, 1164 (SO_2); δ_{H} (250 MHz, CDCl_3) 0.88 (3H, s, $(\text{CH}_3)_2\text{CR}_2$), 1.06 (3H, d, J 6.8, $\text{CH}(\text{R})\text{CH}_3$), 1.07 (3H, s, $(\text{CH}_3)_2\text{CR}_2$), 1.18-1.36 (2H, m, $\text{C}(\text{R})_2\text{HCH}_2\text{CH}_2$ camphor) and 1.74-1.98 (5H, m, $\text{CH}_2\text{C}(\text{R})\text{HCH}_2\text{CH}_2$ camphor), 2.41 (6H, s, $\text{N}(\text{CH}_3)_2$), 2.62 (1H, m, $\text{NC}(\text{R})\text{HCH}(\text{R})_2$), 3.35 (1H, d, J 13.8, CH_2SO_2), 3.43 (1H, d, J 13.8, CH_2SO_2), 3.52 (1H, d, J 10.0, $\text{NCH}(\text{R})\text{CH}$), 3.86 (1H, dd, J 6.4, 6.5, $\text{NCH}(\text{R})_2$ camphor), 4.82 (1H, dd, J 2.0, 9.9, *cis*- $\text{CH}=\text{CH}_2$), 4.98 (1H, ddd, J 0.6, 2.0, 16.9, *trans*- $\text{CH}=\text{CH}_2$), 5.76 (1H, ddd, J 9.9, 9.9, 16.9, $\text{CH}=\text{CH}_2$); δ_{C} (62.5 MHz, CDCl_3) 18.9 ($\text{CH}(\text{R})\text{CH}_3$), 20.4 ($(\text{CH}_3)_2\text{CR}_2$), 21.2 ($(\text{CH}_3)_2\text{CR}_2$), 26.8 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 33.5 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 38.4 ($\text{CR}_2\text{HCH}_2\text{C}(\text{R})\text{HN}$), 41.5 ($\text{CH}(\text{R})\text{CH}=\text{CH}_2$), 42.0 (2 x NCH_3), 44.9 ($\text{CR}_2\text{HCH}_2\text{C}(\text{R})\text{HN}$), 48.0 ($(\text{CH}_3)_2\text{CRCR}_2\text{H}$), 48.2 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 53.8 (CH_2SO_2), 66.0 ($\text{CH}_2\text{C}(\text{R})\text{HN}$), 69.5 ($(\text{CH}_3)_2\text{NC}(\text{R})\text{HCO}$), 116.5 ($\text{CH}=\text{CH}_2$), 141.0 ($\text{CH}=\text{CH}_2$), 173.7 (CO); m/z (CI) 355.2044 (MH^+ , $\text{C}_{18}\text{H}_{31}\text{N}_2\text{O}_3\text{S}$ requires 355.2055), 355 (100%), 299 (47), 216 (20), 112 (51).

(2'R, 3'R)-5e:

R_f 0.25 (light petroleum/ethyl acetate, 5:1); $[\alpha]_D^{20} +65.4$ (c 1, CHCl_3); m.p. 138.1-139.3 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ (CHCl_3) 1684 (C=O), 1642 (C=C), 1326, 1168 (SO_2); δ_{H} (250 MHz, CDCl_3) 0.90 (3H, s, $(\text{CH}_3)_2\text{CR}_2$), 0.98 (3H, d, J 6.8, $\text{CH}(\text{R})\text{CH}_3$), 1.07 (3H, s, $(\text{CH}_3)_2\text{CR}_2$), 1.18-1.39 (2H, m, $\text{C}(\text{R})_2\text{HCH}_2\text{CH}_2$ camphor) and 1.80-2.07 (5H, m, $\text{CH}_2\text{C}(\text{R})\text{HCH}_2\text{CH}_2$ camphor), 2.40 (6H, s, $\text{N}(\text{CH}_3)_2$), 2.73 (1H, m, $\text{NC}(\text{R})\text{HCH}(\text{R})_2$), 3.38 (1H, d, J 13.8, CH_2SO_2), 3.46 (1H, d, J 13.8, CH_2SO_2), 3.66 (1H, d, J 9.6, $\text{NCH}(\text{R})\text{CH}$), 3.89 (1H, dd, J 6.5, 6.5, $\text{NCH}(\text{R})_2$ camphor), 4.96-5.08 (2H, m, $\text{CHCH}=\text{CH}_2$), 5.84 (1H, ddd, J 8.0, 10.3, 17.2, $\text{CHCH}=\text{CH}_2$); δ_{C} (62.5 MHz, CDCl_3) 17.6 ($\text{CH}(\text{R})\text{CH}_3$), 20.4 ($(\text{CH}_3)_2\text{CR}_2$), 21.1 ($(\text{CH}_3)_2\text{CR}_2$), 26.8 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 33.5 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 38.9 ($\text{CR}_2\text{HCH}_2\text{C}(\text{R})\text{HN}$), 39.8 ($\text{CH}(\text{R})\text{CH}=\text{CH}_2$), 42.2 (2 x NCH_3), 44.9 ($\text{CR}_2\text{HCH}_2\text{C}(\text{R})\text{HN}$), 48.1 ($(\text{CH}_3)_2\text{CRCR}_2\text{H}$), 48.3 ($\text{CR}_2\text{HCH}_2\text{CH}_2\text{CR}_3$), 53.7 (CH_2SO_2), 65.9 ($\text{CH}_2\text{C}(\text{R})\text{HN}$), 70.2 ($(\text{CH}_3)_2\text{NC}(\text{R})\text{HCO}$), 115.0 ($\text{CH}=\text{CH}_2$), 141.9 ($\text{CH}=\text{CH}_2$), 173.1 (CO); m/z (CI) 355.2070 (MH^+ , $\text{C}_{18}\text{H}_{31}\text{N}_2\text{O}_3\text{S}$ requires 355.2055), 355 (100%), 299 (17), 233 (20), 152 (15), 112 (19).

***N*-([*N,N*-dimethyl]-3,3-dimethylallylglycinoyl)-(1*R*, 2*S*)-bornane-10,2-sultam (5f)**

Following the method described above for **5a**, sodium hydride (21 mg, 0.70 mmol) was added to a vigorously stirred suspension of *N'*-(3-methyl-2-butene)-*N'*,*N'*-dimethyl-*N'*-(*N*-carbonyl-(1*S*)-bornane-10,2-sultam)methylammonium bromide (313 mg, 0.70 mmol) in DME (18 mL) containing molecular sieves to give a crude mixture, which was purified by column chromatography, eluting with light

petroleum/ethyl acetate (5:1) to give (2'*R*)-**5f** (6 mg, 2%) and (2'*S*)-**5f** (175 mg, 68%) as colourless crystalline solids.

(2'*R*)-5f:

R_f 0.41 (light petroleum/ethyl acetate, 5:1); [α]_D²⁰ -4.0 (c 0.1, CHCl₃); m.p. 129.9-130.8 °C; $\nu_{\max}/\text{cm}^{-1}$ (CHCl₃) 1692 (C=O), 1639 (C=C), 1329, 1162 (SO₂); δ_{H} (250 MHz, CDCl₃) 0.90 (3H, s, (CH₃)₂CR₂ camphor), 1.02 (3H, s, (CH₃)₂CR₂), 1.08 (3H, s, (CH₃)₂CR₂), 1.16 (3H, s, (CH₃)₂CR₂ camphor), 1.29-1.40 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.80-2.13 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 2.38 (6H, s, N(CH₃)₂), 3.36 (1H, d, *J* 13.7, CH₂SO₂), 3.44 (1H, d, *J* 13.7, CH₂SO₂), 3.54 (1H, s, NCH(R)C(R)₃), 3.89 (1H, dd, *J* 5.1, 7.6, NCH(R)₂ camphor), 4.88-4.97 (2H, m, CH=CH₂), 5.76 (1H, dd, *J* 10.9, 17.5, CH=CH₂); δ_{C} (62.5 MHz, CDCl₃) 20.3 ((CH₃)₂CR₂ camphor), 21.6 ((CH₃)₂CR₂ camphor), 24.6 ((CH₃)₂CR₂), 25.4 ((CH₃)₂CR₂), 26.9 (CR₂HCH₂CH₂CR₃), 33.4 (CR₂HCH₂CH₂CR₃), 39.9 (CR₂HCH₂C(R)HN), 42.0 ((CH₃)₂CR₂), 45.0 (CR₂HCH₂C(R)HN), 45.5 (2 x NCH₃), 47.8 ((CH₃)₂CR₂), 48.1 (CR₂HCH₂CH₂CR₃), 53.8 (CH₂SO₂), 66.2 (CH₂C(R)HN), 74.2 ((CH₃)₂NC(R)HCO), 112.2 (CH=CH₂), 146.2 (CH=CH₂), 171.1 (CO); m/z (CI) 369.2202 (MH⁺, C₁₉H₃₃N₂O₃S requires 369.2212), 369 (4%), 299 (17), 216 (18), 126 (5), 66 (100).

(2'*S*)-5f:

R_f 0.35 (light petroleum/ethyl acetate, 5:1); [α]_D²⁰ -53.3 (c 1, CHCl₃); m.p. 136.9-138.1 °C; $\nu_{\max}/\text{cm}^{-1}$ (CHCl₃) 1690 (C=O), 1639 (C=C), 1312, 1164 (SO₂); δ_{H} (250 MHz, CDCl₃) 0.98 (3H, s, (CH₃)₂CR₂ camphor), 1.14 (3H, s, (CH₃)₂CR₂), 1.16 (3H, s, (CH₃)₂CR₂ camphor), 1.19 (3H, s, (CH₃)₂CR₂), 1.36-1.47 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.87-2.11 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 2.51 (6H, s, N(CH₃)₂), 3.45 (1H, d, *J* 13.8, CH₂SO₂), 3.53 (1H, d, *J* 13.8, CH₂SO₂), 3.73 (1H, s, NCH(R)C(R)₃), 3.97 (1H, dd, *J* 6.3, 6.6, NCH(R)₂ camphor), 4.95-5.06 (2H, m, CH=CH₂), 6.09 (1H, dd, *J* 10.8, 17.5, CH=CH₂); δ_{C} (62.5 MHz, CDCl₃) 20.4 ((CH₃)₂CR₂ camphor), 21.0 ((CH₃)₂CR₂ camphor), 24.4 ((CH₃)₂CR₂), 26.3 ((CH₃)₂CR₂), 26.9 (CR₂HCH₂CH₂CR₃), 33.8 (CR₂HCH₂CH₂CR₃), 38.9 (CR₂HCH₂C(R)HN), 43.6 ((CH₃)₂CR₂), 44.9 (CR₂HCH₂C(R)HN), 45.3 (2 x NCH₃), 47.9 ((CH₃)₂CR₂), 48.1 (CR₂HCH₂CH₂CR₃), 53.9 (CH₂SO₂), 66.1 (CH₂C(R)HN), 73.3 ((CH₃)₂NC(R)HCO), 112.3 (CH=CH₂), 146.2 (CH=CH₂), 171.0 (CO); m/z (CI) 369.2219 (MH⁺, C₁₉H₃₃N₂O₃S requires 369.2212), 369 (100%), 299 (56), 233 (5), 126 (16), 58 (17).

***N*-([*N,N*-dimethyl]-3-(methoxycarbonyl)allylglycinoyl)-(1*R*, 2*S*)-bornane-10,2-sultam (**5g**)**

Following the method described above for **5a**, sodium hydride (10 mg, 0.41 mmol) was added to a vigorously stirred suspension of *N'*-(but-2-enoic acid methyl ester)-*N',N'*-dimethyl-*N'*-(*N*-carbonyl-(1*R*, 2*S*)-bornane-10,2-sultam)methylammonium bromide (199 mg, 0.41 mmol) in DME (8 mL) containing molecular sieves to give a crude mixture, which was purified by column chromatography, eluting with light petroleum/ethyl acetate (5:1), to furnish (2'*R*, 3'*R*)-**5g** (104 mg, 64 %), as a white crystalline solid. From analysis of the ¹H nmr spectra of the crude product, (2'*S*, 3'*S*)-**5g** (<1 %, estimated from ¹H-NMR) was also adjudged to be present, but this compound could not be isolated from the crude product. The ¹H nmr spectrum also indicated the presence of trace amounts (<1%) of the other possible diastereoisomers, along with products yielding from the [1,2]-migration of the allyl-functionality.

(2'*R*, 3'*R*)-5g:

*R*_f 0.26 (light petroleum/ethyl acetate, 5:1); [α]_D²⁰ +128.1 (c 0.7, CHCl₃); m.p. 127.4-129.6 °C; ν_{max} /cm⁻¹ (CHCl₃) 1731 (CO₂), 1686 (C=O), 1638 (C=C), 1336, 1166 (SO₂); δ_{H} (250 MHz, CDCl₃) 0.88 (3H, s, (CH₃)₂CR₂), 1.10 (3H, s, (CH₃)₂CR₂), 1.11-1.35 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.78-2.10 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 2.40 (6H, s, N(CH₃)₂), 3.34 (1H, d, *J* 13.8, CH₂SO₂), 3.42 (1H, d, *J* 13.8, CH₂SO₂), 3.57 (3H, s, OCH₃), 3.73-3.86 (2H, m, NCH(R)CH and NCH(R)₂ camphor), 4.22 (1H, d, *J* 10.1, NCH(R)CH), 5.17 (1H, dd, *J* 1.2, 9.9, *cis*-CHCH=CH₂), 5.25 (1H, d, *J* 17.0, *trans*-CHCH=CH₂), 5.86 (1H, ddd, *J* 9.9, 9.9, 17.0 Hz, CHCH=CH₂); δ_{C} (62.5 MHz, CDCl₃) 20.4 ((CH₃)₂CR₂), 20.8 ((CH₃)₂CR₂), 26.9 (CR₂HCH₂CH₂CR₃), 33.2 (CR₂HCH₂CH₂CR₃), 38.4 (CR₂HCH₂C(R)HN), 41.8 (2 x NCH₃), 44.7 (CR₂HCH₂C(R)HN), 48.2 ((CH₃)₂CR₂), 48.8 (CR₂HCH₂CH₂CR₃), 50.7 (CH(R)CH=CH₂), 52.5 (OCH₃), 53.5 (CH₂SO₂), 65.7 (CH₂C(R)HN), 66.8 ((CH₃)₂NC(R)HCO), 120.2 (CH=CH₂), 134.0 (CH=CH₂), 170.0 (CO), 172.3 (CO); *m/z* (CI) 399.1947 (MH⁺, C₁₉H₃₁N₂O₅S requires 399.1954), 399 (100%), 233 (33), 216 (27), 156 (38), 131 (23), 48 (14).

(2'*S*, 3'*S*)-5g:³

*R*_f 0.15 (diethyl ether/light petroleum, 2:1); δ_{H} (250 MHz, CDCl₃) 0.90 (3H, s, (CH₃)₂CR₂), 1.05 (3H, s, (CH₃)₂CR₂), 1.10-1.42 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.80-2.05 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 2.33 (6H, s, N(CH₃)₂), 3.36 (2H, m, CH₂SO₂), 3.64 (3H, s, OCH₃), 3.82 (2H, m, NCH(R)CH and NCH(R)₂ camphor), 4.30 (1H, d, *J* 10.9, NCH(R)CH), 5.01 (1H, dd, *J* 1.5, 9.9, *cis*-CHCH=CH₂), 5.16 (1H, m, CH=CH₂), 5.86 (1H, m, CH=CH₂).

³ Due to the small amount of compound available, full characterization was not feasible.

***N*-([*E*]-[3'-methoxycarbonyl-2'-dimethylamino]-pent-4-enoyl)-(1*R*, 2*S*)-bornane-10,2-sultam]
bromide (7)**

Following the method described above for **5a**, sodium hydride (11 mg, 0.44 mmol) was added to a vigorously stirred suspension of **6** (0.21 g, 0.44 mmol) in DME (10 mL) containing molecular sieves to give a crude mixture, which was purified by column chromatography, eluting with light petroleum/ethyl acetate (gradient of 5:1-3:1), to furnish (2'*R*, 3'*S*)-**7** (6 mg, 3%), (2'*S*, 3'*R*)-**7** (159 mg, 91%) as white crystalline solids, and an inseparable mixture of (2'*S*, 3'*S*)-(**7**) and (2'*R*, 3'*R*)-(**7**) (6 mg, 3%, diastereomer ratio tentatively estimated as (2'*S*, 3'*S*): (2'*R*, 3'*R*) = 15:1) as a colourless gum.

(2'*R*, 3'*S*)-7**:**

*R*_f 0.22 (light petroleum/ethyl acetate, 5:1); [α]_D²⁰ +76.0 (*c* 0.1, CHCl₃); m.p. 122.6-124.1 °C; ν_{max} /cm⁻¹ (CHCl₃) 1735 (CO₂), 1692 (C=O), 1640 (C=C), 1329, 1165 (SO₂); δ_{H} (250 MHz, CDCl₃) 0.90 (3H, s, (CH₃)₂CR₂), 1.12 (3H, s, (CH₃)₂CR₂), 1.18-1.36 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.78-2.11 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 2.23 (6H, s, N(CH₃)₂), 3.35 (1H, d, 13.8, CH₂SO₂), 3.45 (1H, d, *J* 13.8, CH₂SO₂), 3.61 (3H, s, OCH₃), 3.64 (1H, d, *J* 11.1, NCH(R)CH), 3.82 (1H, dd, *J* 5.0, 7.5, NCH(R)₂ camphor), 4.19 (1H, dd, *J* 8.4, 11.1, NCH(R)CH), 5.15 (1H, dd, *J* 1.4, 10.2, *cis*-CHCH=CH₂), 5.29 (1H, d, *J* 16.9, *trans*-CHCH=CH₂), 5.67 (1H, ddd, *J* 8.4, 10.2, 16.9, CHCH=CH₂); δ_{C} (62.5 MHz, CDCl₃) 20.3 ((CH₃)₂CR₂), 20.8 ((CH₃)₂CR₂), 26.9 (CR₂HCH₂CH₂CR₃), 33.2 (CR₂HCH₂CH₂CR₃), 38.5 (CR₂HCH₂C(R)HN), 42.8 (2 x NCH₃), 45.1 (CR₂HCH₂C(R)HN), 48.2 ((CH₃)₂CR₂), 48.8 (CR₂HCH₂CH₂CR₃), 50.1 (CH(R)CH=CH₂), 51.2 (OCH₃), 53.7 (CH₂SO₂), 65.8 (CH₂C(R)HN), 71.6 ((CH₃)₂NCH(R)HCO), 121.2 (CH=CH₂), 131.9 (CH=CH₂), 169.2 (CO), 171.3 (CO); *m/z* (CI) 399.1966 (MH⁺, C₁₉H₃₁N₂O₅S requires 399.1954), 399 (31%), 116 (100).

(2'*S*, 3'*R*)-7**:**

*R*_f 0.14 (light petroleum/ethyl acetate, 5:1); [α]_D²⁰ +178.5 (*c* 1, CHCl₃); m.p. 145.1-146.6 °C; ν_{max} /cm⁻¹ (CHCl₃) 1724 (CO₂), 1674 (C=O), 1639 (C=C), 1330, 1166 (SO₂); δ_{H} (250 MHz, CDCl₃) 0.90 (3H, s, (CH₃)₂CR₂), 1.16 (3H, s, (CH₃)₂CR₂), 1.27-1.37 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.79-2.01 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 2.29 (6H, s, N(CH₃)₂), 3.35 (1H, d, *J* 13.8, CH₂SO₂), 3.43 (1H, d, *J* 13.8, CH₂SO₂), 3.62 (3H, s, OCH₃), 3.68 (1H, d, *J* 10.3, NCH(R)CH), 3.82 (1H, dd, *J* 5.3, 7.5, NCH(R)₂ camphor), 3.99 (1H, dd, *J* 8.8, 10.3, NCH(R)CH), 5.23 (1H, ddd, *J* 0.9, 0.9, 10.2, *cis*-CHCH=CH₂), 5.28 (1H, ddd, *J* 0.9, 0.9, 17.5, *trans*-CHCH=CH₂), 5.79 (1H, ddd, *J* 8.3, 10.2, 17.5 Hz, CHCH=CH₂); δ_{C} (62.5 MHz, CDCl₃) 20.4 ((CH₃)₂CR₂), 20.9 ((CH₃)₂CR₂), 26.9 (CR₂HCH₂CH₂CR₃), 33.3 (CR₂HCH₂CH₂CR₃), 38.7 (CR₂HCH₂C(R)HN), 42.3 (2 x NCH₃), 45.0 (CR₂HCH₂C(R)HN), 48.2

((CH₃)₂CRCR₂H), 48.9 (CR₂HCH₂CH₂CR₃), 49.5 (CH(R)CH=CH₂), 51.6 (OCH₃), 53.4 (CH₂SO₂), 65.7 (CH₂C(R)HN), 70.2 ((CH₃)₂NC(R)HCO), 119.9 (CH=CH₂), 133.3 (CH=CH₂), 171.2 (CO), 171.4 (CO); m/z (CI) 399.1961 (MH⁺, C₁₉H₃₁N₂O₅S requires 399.1954), 399 (46%), 116 (100).

3. Preparation of (*R*)-allylglycine

(a.) A solution of *N*-([*N,N*-diallyl]allylglycinoyl)-(1*R*, 2*S*)-bornane-10,2-sultam (**5c**) (275 mg, 0.70 mmol) in distilled degassed CH₂Cl₂ (3 mL) was added to a single-neck round bottom flask containing *tetrakis*(triphenylphosphine)palladium (16 mg, 0.014 mmol) and 1,3-dimethyl barbituric acid (0.66 g, 4.20 mmol), under a nitrogen atmosphere. An oven dried reflux condenser was added to the flask and the mixture was then stirred at 35 °C for 3 hours. After cooling, the CH₂Cl₂ was removed *in vacuo* and replaced by ether. The ethereal mixture was extracted twice with small volumes of saturated aqueous sodium carbonate, and the organic layer then acidified with HCl (1M) until the pH of the solution was <2. The aqueous layer was removed, washed several times with ethyl acetate (3x1mL), diluted with an equal volume of ethanol and concentrated *in vacuo*, to give the hydrochloride salt of *N*-(allylglycinoyl)-(1*R*, 2*S*)-bornane-10,2-sultam as a colourless solid (244 mg, ~100%), which was utilized without further purification; [α]_D²⁰ +107.8 (c 1, CH₃OH); m.p. 180.4-182.5 °C; ν_{max}/cm⁻¹ (CHCl₃) 2961, 1503 (NH₃⁺), 1698 (C=O), 1642 (C=C), 1333, 1168 (SO₂); δ_H (250 MHz, CD₃OD) 1.04 (3H, s, (CH₃)₂CR₂), 1.16 (3H, s, (CH₃)₂CR₂), 1.35-1.56 (2H, m, C(R)₂HCH₂CH₂ camphor) and 1.89-2.08 (5H, m, CH₂C(R)HCH₂CH₂ camphor), 2.68-2.89 (2H, m, NCH(R)CH₂), 3.72 (1H, d, *J* 14.2, CH₂SO₂), 3.78 (1H, d, *J* 14.2, CH₂SO₂), 4.01 (1H, dd, *J* 5.5, 7.0, NCH(R)₂ camphor), 4.54 (1H, m, NCH(R)CH₂), 5.28 (1H, s, CH₂CH=CH₂), 5.33 (1H, d, *J* 7.5, CH₂CH=CH₂) 5.77 (1H, m); δ_C (62.5 MHz, CD₃OD) 20.6 ((CH₃)₂CR₂), 21.8 ((CH₃)₂CR₂), 27.7 (CR₂HCH₂CH₂CR₃), 33.9 (CR₂HCH₂CH₂CR₃), 37.3 (CH₂CH=CH₂), 39.5 (CR₂HCH₂C(R)HN), 46.5 (CR₂HCH₂C(R)HN), 48.2 ((CH₃)₂CRCR₂H), 49.4 (CR₂HCH₂CH₂CR₃), 53.9 (CH₂SO₂), 54.4 (NC(R)HCO), 66.8 (CH₂C(R)HN), 122.6 (CH₂CH=CH₂), 131.4 (CH₂CH=CH₂), 169.4 (CO); m/z (CI) 313.1590 (M⁺-Cl, C₁₅H₂₅N₂O₃S requires 313.1586), 313 (23%), 216 (12), 152 (9), 132 (6), 85 (8), 66 (100).

(b.) Lithium hydroxide monohydrate (118 mg, 2.80 mmol) was added to a stirred solution of *N*-(allylglycinoyl)-(1*R*, 2*S*)-bornane-10,2-sultam hydrochloride (244 mg, 0.70 mmol) in a THF/H₂O mixture (10 mL, (4:1) v/v). This mixture was stirred at room temperature for 6 hours after which the solvent was removed *in vacuo* to give a crude mixture, to which water (10 mL) and CH₂Cl₂ (10 mL) were added. The layers were separated and the aqueous layer further extracted with CH₂Cl₂ (3 x 10 mL). The organic extracts were combined, dried (MgSO₄), and solvent removed *in vacuo* to furnish (1*R*, 2*S*)-bornane-10,2-sultam (150 mg, 99%) as a colourless crystalline solid. The aqueous layer was then acidified (pH 4) by addition of aqueous 1M HCl and then stirred overnight with Amberlite®

IR-120(plus) ion exchange resin (5 g). The resin was carefully by filtration through a plug of cotton wool and washed thoroughly with water, until the washings no longer turned cloudy upon addition of silver nitrate. The amino acid was released from the resin *via* addition of aqueous NH_4OH solution (4M, ~30 mL) with vigorous stirring for 4 hours. Removal of the resin by filtration and concentration of the resulting liquor *in vacuo* gave (2*R*)-2-aminopent-4-enoic acid (79 mg, 98%) as a colourless deliquescent solid; $[\alpha]_{\text{D}}^{20} +32.0$ (*c* 1, H_2O); m.p. 239.3-241.2 °C;^{4, 5} $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 2965, 1513 (NH_3^+), 1584, 1400 (CO_2); δ_{H} (250 MHz, D_2O) 2.42 (2H, br m, NCH(R)CH_2), 3.55 (1H, br m, NCH(R)CH_2), 5.06-5.13 (2H, m, $\text{CH}_2\text{CH=CH}_2$), 5.63 (1H, ddt, *J* 7.3, 10.0, 17.1, $\text{CH}_2\text{CH=CH}_2$); δ_{C} (62.5 MHz, D_2O) 36.2 (NCH(R)CH_2), 54.5 (NCH(R)CH_2), 120.2 ($\text{CH}_2\text{CH=CH}_2$), 132.3 ($\text{CH}_2\text{CH=CH}_2$), 176.8 (CO); *m/z* (CI) 116.0710 (MH^+ , $\text{C}_5\text{H}_{10}\text{NO}_2$ requires 116.0712), 116 (100%), 66 (71).

This product was converted by standard means to the *N*-Cbz-OMe derivative and assessed by chiral HPLC. The absolute stereochemistry of the derivative was confirmed to be $\geq 95\%$ (*R*) by comparison with authentic material and the racemate (HPLC 4000-4; Chiralcel OD column; injection volume 50 μL ; solvent system hexane/isopropyl alcohol (9:1); 215nm absorbance; (*S*)-isomer peak area 15064124; retention time 7.200; (*R*)-isomer peak area 285855136; retention time 10.075). A typical trace is shown below.

4. Kardassis, G.; Brungs, P.; Nothelfer, C.; Steckhan, E. *Tetrahedron*, **1998**, 54, 3479.

5. Broxterman, Q. B.; Kaptein, B.; Kamphuis, J.; Schoemaker, H. E. *J. Org. Chem.*, **1992**, 57, 6286.

X-Ray Structures

($R_C = (2S)$ -Camphorsultam)

($R_C = (2R)$ -Camphorsultam)

($R_C=(2R)$ -Camphorsultam)

($R_C=(2R)$ -Camphorsultam)

NMR data

HPLC data

Retention time 7.621
Peak area 18666968

7.200
15064124

Ratio = 5:95 in both cases.

Retention time 7.483
Peak area 218716480

Ratio = 1:1.