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Asymmetric aza-[2,3]-Wittig sigmatropic rearrangements: chiral auxiliary control and formal asymmetric synthesis of (2*S*, 3*R*, 4*R*)-4-hydroxy-3-methylproline and (-)-kainic acid.

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Synthesis of chiral auxiliary aza-[2,3]-Wittig precursors **21-33.**

[*N*-Boc-[2-(dimethylphenylsilanyl)-but-2-enyl]-amino]-acetic acid [1*R*,2*S*,5*R*]-menthol ester 21
In an identical procedure to the preparation of **12** the acid derived from **14** (1.4 g, 3.9 mmol) and (-)-menthol (610 mg, 3.9 mmol) gave a crude product which was purified by flash column chromatography (10 % EtOAc/pet. ether) to give **21** (1.58 g, 81 %) as a colourless oil; ν_{max}(film)/cm^{-1} 2956, 2870, 1748, 1701; δ_H (500 MHz; $CDCl_3$) 0.41 (6H, s, Si*Me*$_2$), 0.75-0.77 (3H, m, C*H*$_3$CH), 0.88-0.92 (6H, m, C*Me*$_2$CH), 0.96-2.04 (21H, m, C*H*$_2$CH(C)OR + CH(CH$_3$)C*H*$_2$CH$_2$ + CH(CH$_3$)CH$_2$C*H*$_2$ + CH$_3$C*H* + C*H*CMe$_2$H + CHCMe$_2$*H* + *Boc* + C*H*$_3$CH), 3.67-4.15 (4H, m, C*H*$_2$NC*H*$_2$), 4.70-4.77 (1H, m, CO$_2$C*H*), 6.15-6.23 (1H, m, C=C*H*(CH$_3$)), 7.27-7.34 (3H, m, C*H*$_{Ar}$), 7.50-7.52 (2H, m, C*H*$_{Ar}$); δ_C (125 MHz; $CDCl_3$) -1.6, -1.5, -1.5, 16.3, 18.0, 20.8, 22.0, 23.4, 26.2, 26.2, 28.3, 31.4, 34.2, 34.3, 40.9, 41.0, 46.6, 46.7, 47.0, 47.1, 54.0, 54.5, 74.9, 80.0, 80.1, 127.9, 128.9, 129.0, 133.4, 133.6, 133.7, 138.8, 139.0, 141.2, 141.7, 155.2, 155.8, 169.7; m/z (ES$^+$) 524 (11, MNa$^+$), 502.3325 (MH$^+$ $C_{29}H_{48}NO_4Si$ requires 502.3353), 402 (11, MH$^+$-Boc), 135 (74, PhMe$_2$Si$^+$), 73 (100, O^{t}Bu$^+$), 57 (78, ^{t}Bu$^+$).

[*N*-Boc-[2-(dimethylphenylsilanyl)-but-2-enyl]-amino]-acetic acid [1*R*,2*S*]-2-phenyl-cyclohexyl ester 22
In an identical procedure to the preparation of **12** the acid derived from **14** (1.01 g, 2.79 mmol) and (1*R*,2*S*)-2-phenyl-cyclohexanol (541 mg, 3.07 mmol, 1.1 eq.) gave a crude product which was purified by flash column chromatography (10 % EtOAc/pet. ether) to give **22** (1.20 g, 82 %) as a colourless oil; ν_{max}(film)/cm^{-1} 3028, 2932, 2859, 1736, 1701; δ_H (270 MHz; $CDCl_3$) 0.42 (6H, s, Si*Me*$_2$), 1.37-2.28 (20H, m, *Boc* + C*H*$_3$CH + C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$), 2.66-2.83 (1H, m, C*H*Ph), 3.46-4.10 (4H, m, C*H*$_2$NC*H*$_2$), 5.07-5.22 (1H, m, CO$_2$C*H*), 5.67-5.81 (1H, m, C*H*CH$_3$), 7.16-7.56 (10H, m, C*H*$_{Ar}$); δ_C (67.5 MHz; $CDCl_3$) -1.5, -1.4, 17.9, 24.8, 25.9, 28.4, 32.5, 34.4, 46.1, 46.2, 19.9, 50.1, 54.0, 54.4, 76.3, 76.4, 79.8, 80.0, 126.5, 127.6, 127.9, 128.5, 128.9, 129.0, 133.1, 133.6, 138.9, 139.1, 141.8, 142.6, 146.1, 155.1, 155.7, 169.2, 169.5; m/z (ES$^+$) 544.2854 (100, MNa$^+$ $C_{31}H_{43}NO_4SiNa$ requires 544.2859), 422 (40, MH$^+$-Boc).

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[*N*-Boc-[2-(dimethylphenylsilanyl)-but-2-enyl]-amino]-acetic acid [2*R*,1*S*]-2-dimethylamino-1-phenyl-propyl ester 23

In an identical procedure to the preparation of **12** the acid derived from **14** (184 mg, 0.507 mmol) and *N*-methyl ephedrine (457 mg, 2.54 mmol, 5 eq.) gave a crude product which was purified by flash column chromatography (1% AcOH, 19 % EtOAc/ pet. ether) to give **23** (262 mg, 98 %) as a colourless oil; ν_{max}(film)/cm^{-1} 2976, 1692 (br); δ_H (270 MHz; $CDCl_3$) 0.41-0.43 (6H, s, Si*Me*$_2$), 1.06 (d, *J* 6.7, C*H*$_3$CHNMe$_2$), 1.38 (9H, m, *Boc*$_{rot}$), 1.48 (9H, m, *Boc*$_{rot}$), 1.64-1.67 (3H, m, C*H*$_3$C(H)=C), 2.29 (6H, s, N*Me*$_2$), 2.92 (1H, m, C*H*NMe$_2$), 3.80-4.21 (4H, m, C*H*$_2$NC*H*$_2$), 5.98 (1H, d, *J* 5.5, CO_2CH), 6.09-6.19 (1H, m, C=C*H*CH$_3$), 7.28-7.32 (8H, m, C*H*$_{Ar}$), 7.50-7.52 (2H, m, C*H*$_{Ar}$); δ_C (67.5 MHz; $CDCl_3$) -1.6, -1.5, 9.2, 9.3, 17.9, 18.0, 25.0, 25.7, 26.3, 28.3, 28.3, 28.4, 34.0, 40.8, 41.1, 46.9, 54.0, 54.6, 63.5, 63.8, 75.8, 80.3, 80.4, 126.2, 126.4, 126.8, 127.8, 127.9, 128.0, 128.4, 128.4, 128.9, 129.1, 133.2, 133.5, 133.6, 138.7, 139.0, 139.4, 141.1, 141.6, 155.1, 155.8, 169.2; m/z (ES$^+$) 525.3141 (45, MH$^+$ $C_{30}H_{45}N_2O_4Si$ requires 525.3149), 469 (5, MH$^+$-^{t}Bu), 162 (99, $C_{11}H_{16}N^+$), 72 (100, O^{t}Bu$^+$), 57 (66, ^{t}Bu$^+$).

[2-(Dimethylphenylsilanyl)-but-2-enyl]-[1*R*,2*S*]-[[(2-hydroxy-1-methyl-2-phenylethyl)-methyl-arbamoyl]-methyl]-carbamic acid *tert*-butyl ester 24

A solution of the acid derived from **14** (429 mg, 1.18 mmol) in THF (23 mL) was cooled to -30 °C and treated with (1*R*, 2*S*)-(-)-ephedrine (195 mg, 1.18 mmol), DCC (248 mg, 1.18 mmol, 1.0 eq.) and HOBt (159 mg, 1.18 mmol, 1.0 eq.), warmed to rt and stirred for 26 h. The reaction was then heated to reflux and stirred for a further 14 h. The reaction was cooled to rt and the solvent removed *in vacuo* and replaced with EtOAc (25 mL). The resultant suspension was filtered *via* Celite® and solvent removed *in vacuo* to furnish the crude product which was purified by flash column chromatography (45 % EtOAc/pet. ether) to give **24** (390 mg, 65 %). as a colourless oil; ν_{max}(film)/cm^{-1} 3360, 2918, 1698, 1666; δ_H (400 MHz; $CDCl_3$) 0.40 (6H, s, Si*Me*$_2$), 1.06-1.09 (3H, m, CH$_3$CHNMe), 1.41-1.44 (9H, m, *Boc*), 1.65-1.67 (3H, m, C=CHC*H*$_3$), 2.60 (3H, br s, N*Me*$_{major\ rot}$), 2.76 (3H, br s, N*Me*$_{minor\ rot}$), 3.15-4.82 (6H, m, C*H*NMe + C*H*Ph +C*H*$_2$NC*H*$_2$), 6.00-6.15 (1H, m, C=C*H*CH$_3$), 7.24-7.35 (8H, m, C*H*$_{Ar}$), 7.48-7.50 (2H, m, C*H*$_{Ar}$); δ_C (67.5 MHz; $CDCl_3$) -1.5, -1.4, 11.9, 17.8, 25.0, 25.6, 28.3, 31.5, 31.9, 46.6, 46.8, 54.3, 54.4, 57.5, 76.8, 77.0, 79.6, 80.0, 126.0, 126.3, 127.4, 127.5, 127.8, 128.1, 128.4, 127.7, 128.9, 133.6, 139.9, 141.2, 141.8, 155.1, 156.2, 168.4, 169.9, 170.1. m/z (ES$^+$) 533 (13, MNa$^+$), 511.3018 (100, MH$^+$ $C_{29}H_{43}N_2O_4Si$ requires 511.2992), 455 (25, MH$^+$-^{t}Bu), 411 (21, MH$^+$-Boc).

[1*R*,2*S*]-([[2-(*tert*-Butyldimethylsilanyloxy)-1-methyl-2-phenylethyl]-methylcarbamoyl]-methyl)-[2-(dimethylphenylsilanyl)-but-2-enyl]-carbamic acid *tert*-butyl ester 25

A solution of the acid derived from **14** (490 mg, 1.35 mmol) in CH_2Cl_2 (7 mL) was cooled to -30 °C and treated with (1*R*, 2*S*)-(-)-*O*-^{t}butyldimethylsilylephedrine (377 mg, 1.35 mmol), DCC (284 mg, 1.35 mmol, 1.0 eq.) and HOBt (182 mg, 1.35 mmol, 1.0 eq.), warmed to rt over 1 h and then refluxed for a further 12 h or until tlc analysis showed no starting material. The reaction was cooled to rt and the solvent removed *in vacuo* and replaced with EtOAc (15 mL). The resultant suspension was filtered *via* Celite® and solvent removed *in vacuo* to furnish the crude product which was purified by flash column chromatography (20 % EtOAc/pet. ether) to give **25** (481 mg, 57 %) as a colourless oil; ν_{max}(film)/cm^{-1} 3068, 2956, 2930, 2858, 1694, 1657; δ_H (500 MHz; $CDCl_3$) -0.25-(-0.23) (3H, m, Si*Me*$_2$^{t}Bu), 0.02-0.06 (3H, m, Si*Me*$_2$^{t}Bu), 0.40-0.46 (6H, s, Si*Me*$_2$Ph), 0.93 (9H, br s, SiMe$_2$^{t}*Bu*), 1.13-1.92 (16H, m, NMeC*H* + C=C(H)C*H*$_3$ + C*H*$_3$CHNMe + *Boc*), 2.70-2.87 (3H, m, N*Me*), 3.45-4.92 (5H, m, C*H*Ph + C*H*$_2$NC*H*$_2$),

6.02-6.28 (1H, m, C=C*H*CH$_3$), 7.22-7.30 (4H, m, C*H*$_{Ar}$), 7.37-7.39 (4H, m, C*H*$_{Ar}$), 7.53-7.55 (2H, m, C*H*$_{Ar}$); δ_C (125 MHz; $CDCl_3$) -5.2, -4.7, -4.6, -1.7, -1.6, -1.5, -1.4, -1.3, 11.3, 14.5, 17.8, 18.0, 18.0, 25.5, 25.8, 26.2, 28.3, 30.6, 32.4, 46.6, 46.7, 46.9, 54.2, 54.3, 54.4, 58.4, 76.6, 79.4, 79.6, 79.7, 126.2, 126.4, 127.1, 127.2, 127.8, 128.2, 128.7, 128.8, 133.5, 133.6, 134.2, 138.1, 139.0, 139.4, 140.9, 141.8, 142.5, 155.6, 156.1, 168.3, 168.5; m/z (ES^+) 647 (4, MNa^+), 625.3816 (42, MH^+ $C_{35}H_{57}N_2O_4Si_2$ requires 625.3857), 525 (100, MH^+-Boc), 135 (84, $PhMe_2Si^+$), 73 (93, O^tBu^+), 57 (35, $^tBu^+$).

[2-(Dimethylphenylsilanyl)-but-2-enyl]-[2*S*]-[2-(2-hydroxymethylpyrrolidin-1-yl)-2-oxo-ethyl]-carbamic acid *tert*-butyl ester 26

In an identical procedure to the preparation of **25** the acid derived from **14** (236 mg, 0.650 mmol) and (*S*)-pyrollidine methanol (65 µL, 0.65 mmol, 1.0 eq.) gave a crude product which was purified by flash column chromatography (20 % EtOAc/ pet. ether) to give **26** (284 mg, 98 %) as a colourless oil; ν_{max}(film)/cm^{-1} 3392, 2973, 1694, 1635; δ_H (500 MHz; $CDCl_3$) 0.41 (6H, s, Si*Me*$_2$), 1.42-1.44 (9H, m, *Boc*), 1.57-1.59 (1H, m, NCH$_2$C*H*$_2$C*H*$_2$), 1.67-1.71 (3H, m, C*H*$_3$C(H)C=C), 1.82-2.03 (3H, m, NCH$_2$C*H*$_2$C*H*$_2$), 3.30-4.29 (9H, m, C*H*$_2$NC*H*$_2$ + HOC*H*$_2$C*H* + NC*H*$_2$CH$_2$CH$_2$), 6.16-6.24 (1H, m, C=C*H*CH$_3$), 7.34-7.37 (3H, m, C*H*$_{Ar}$), 7.50-7.52 (2H, m, C*H*$_{Ar}$); δ_C (125 MHz; $CDCl_3$) -1.7, -1.5, 17.9, 24.5, 28.0, 28.3, 47.0, 47.3, 47.5, 54.6, 61.6, 61.7, 66.7, 67.3, 79.9, 80.3, 126.7, 127.8, 127.9, 128.8, 129.0, 133.5, 133.7, 134.3, 138.8, 139.3, 134.3, 138.8, 139.3, 141.4, 155.3, 156.3, 170.0, 170.6; MS (ES^+): m/z 469 (12, MNa^+), 447.2685 (100, MH^+ $C_{24}H_{39}N_2O_4Si$ requires 447.2679), 391 (36, MH^+-^{t}Bu), 347 (28, MH^+-Boc).

[2-(Dimethylphenylsilanyl)-but-2-enyl]-[2*S*]-[2-(2-methoxymethylpyrrolidin-1-yl)-2-oxo-ethyl]-carbamic acid *tert*-butyl ester 27

In an identical procedure to the preparation of **25** the acid derived from **14** (444 mg, 1.22 mmol) and (*S*)-(+)-methoxymethylpyrrolidene (151 µL, 1.22 mmol) gave a crude product which was purified by flash column chromatography (40 % EtOAc/ pet. ether) to give **27** (514 mg, 91 %) as a colourless oil; ν_{max}(film)/cm^{-1} 2976, 1690, 1652; δ_H (400 MHz; $CDCl_3$) 0.41 (6H, s, Si*Me*$_2$), 1.41-1.45 (9H, s, *Boc*), 1.65-1.67 (3H, m, C=CHC*H*$_3$), 1.86-2.04 (4H, m, C*H*$_2$C*H*$_2$CH$_2$N), 3.19-4.24 (12H, m, C*H*$_2$NC*H*$_2$ + *Me*OC*H*$_2$C*H*NC*H*$_2$), 6.16-6.23 (1H, m, C=C*H*CH$_3$), 7.34 (3H, m, C*H*$_{Ar}$), 7.49-7.52 (2H, m, C*H*$_{Ar}$); δ_C (100 MHz; $CDCl_3$) -1.6, -1.5, 14.2, 17.8, 21.0, 21.5, 21.6, 24.2, 24.3, 27.1, 27.2, 28.4, 28.8, 45.6, 46.2, 46.2, 46.3, 46.8, 47.1, 47.2, 54.3, 54.3, 56.2, 56.7, 58.9, 59.0, 72.2, 72.3, 74.1, 79.5, 79.8, 127.7, 127.8, 128.7, 128.8, 133.6, 138.9, 139.5, 140.8, 155.4, 156.2, 167.4, 167.8; m/z (ES^+) 483 (22, MNa^+), 461.2878 (92, MH^+ $C_{25}H_{41}N_2O_4Si$ requires 461.2836), 405 (96, MH^+-^{t}Bu), 361 (100, MH^+-Boc).

[2-(Dimethylphenylsilanyl)-but-2-enyl]-[2*S*]-[2-[2-(hydroxydiphenylmethyl)-pyrrolidin-1-yl]-2-oxo-ethyl]-carbamic acid *tert*-butyl ester 28

In an identical procedure to the preparation of **25** the acid derived from **14** (561 mg, 1.54 mmol) and (*S*)-(-)-α,α-diphenyl-2-pyrrolidenemethanol (390 mg, 1.54 mmol) gave a crude product which was purified by flash column chromatography (20 % EtOAc/ pet. ether) to give **28** (596 mg, 65 %) as a colourless oil; ν_{max}(film)/cm^{-1} 2978, 1688, 1634; δ_H (400 MHz; $CDCl_3$) 0.43 (6H, s, Si*Me*$_2$), 1.40-1.55 (11H, m, C*H*$_2$CH$_2$N + *Boc*), 1.70 (3H, d, *J* 6.8, C=CHC*H*$_3$), 1.83-2.07 (2H, m, C*H*$_2$CH$_2$CH$_2$N), 2.82-2.86 (1H, m, CH$_2$C*H*$_2$N), 3.1 (1H, q, *J* 7.6, CH$_2$C*H*$_2$N$_{rot}$), 3.25 (1H, q, *J* 7.6, CH$_2$C*H*$_2$N$_{rot}$), 3.39-4.37 (4H, m, C*H*$_2$NC*H*$_2$), 5.16 (1H, dd, *J* 4.4, 8.8, Ph$_2$C(OH)C*H*), 6.14-6.18 (1H, m, C=C*H*CH$_3$), 6.51 (1H, br s, O*H*$_{rot}$), 6.67 (1H, br s, O*H*$_{rot}$), 7.24-7.37 (13H, m, C*H*$_{Ar}$), 7.51-7.52 (2H, m, C*H*$_{Ar}$); δ_C (100 MHz; $CDCl_3$) -1.6, -1.5, -1.3, 18.0, 18.0, 23.3, 28.3, 28.4, 29.1, 29.2, 47.0, 47.1, 47.2, 47.2, 54.2, 54.6, 66.8,

67.1, 80.0, 80.2, 81.6, 81.7, 127.2, 127.4, 127.7, 127.8, 127.9, 128.1, 128.8, 128.9, 133.6, 133.6, 133.7, 134.2, 138.9, 139.3, 141.1, 141.5, 143.5, 146.2, 146.3, 155.5, 156.2, 171.2, 171.5; m/z (ES^+) 621 (11, MNa^+), 599.3311 (95, MH^+ $C_{36}H_{47}N_2O_4Si$ requires 599.3305), 581 (100, MH^+-H_2O), 543 (18, MH^+-^{t}Bu), 525 (61, MH^+-H_2O-^{t}Bu), 499 (64, MH^+-Boc).

[2*S*]-2-(2-[*N*-Boc-[2-(dimethylphenylsilanyl)-but-2-enyl]-amino]-acetoxymethyl)-pyrrolidine-1-carboxylic acid *tert*-butyl ester 29

In an identical procedure to the preparation of **12** the acid derived from **14** (375 mg, 1.03 mmol) and *N*-Boc-(*S*)-pyrollidine methanol (207 mg, 1.03 mmol, 1.00 eq.) gave a crude product which was purified by flash column chromatography (30% EtOAc/ pet. ether) to give **29** (471 mg, 84 %) as a colourless oil; ν_{max}(film)/cm^{-1} 3068, 2975, 1754, 1693; δ_H (400 MHz; $CDCl_3$) 0.37 (6H, s, Si*Me*$_2$), 1.38-1.42 (19H, m, 2 x *Boc* + $NCH_2CH_2CH_2$), 1.62-1.64 (3H, m, CH_3CH), 1.71-2.01 (3H, m, $NCH_2CH_2CH_2$), 3.22-4.21 (11H, m, CH_2NCH_2 + CO_2CH_2CH + $NCH_2CH_2CH_2$), 6.13-6.18 (1H, m, C=C*H*CH$_3$), 7.29-7.30 (3H, m, CH_{Ar}), 7.43-7.45 (2H, m, CH_{Ar}); δ_C (100 MHz; $CDCl_3$) -2.0, -1.9, -1.8, -1.6, -1.5, -1.4, 17.8, 17.8, 22.9, 23.7, 27.7, 28.0, 28.2, 28.3, 28.3, 28.4, 28.4, 28.5, 28.5, 28.6, 28.6, 28.7, 46.4, 46.5, 46.6, 54.1, 54.5, 55.4, 64.7, 65.0, 77.4, 79.2, 79.6, 80.0, 80.1, 127.7, 127.8, 128.7, 128.8, 133.2, 133.4, 133.5, 133.5, 133.6, 133.6, 138.5, 138.8, 140.9, 141.8, 154.2, 154.4, 154.9, 155.6, 169.8 169.9; m/z (ES^+) 569.3038 (100, MNa^+ $C_{29}H_{46}N_2O_6Si$ requires 569.3023), 447 (72, MH^+- Boc).

[*N*-Boc-[2-(dimethylphenylsilanyl)-but-2-enyl]-amino]-acetic acid [1*S*,5*R*]-2-(6,6-dimethylbicyclo[3.1.1]hept-2-en-3-yl)-ethyl ester 30

In an identical procedure to the preparation of **12** the acid derived from **14** (300 mg, 0.83 mmol) and (-)-nopol (138 mg, 0.830 mmol) gave a crude product which was purified by flash column chromatography (10% EtOAc/ pet. ether) to give **30** (309 mg, 73 %) as a colourless oil; ν_{max}(film)/cm^{-1} 2976, 2917, 1752, 1701; δ_H (400 MHz; $CDCl_3$) 0.41 (6H, s, Si*Me*$_2$), 0.82 (3H, s, C*Me*$_2$), 1.14 (1H, d, *J* 8.5, CH_2CHC=C), 1.26 (3H, s, C*Me*$_2$), 1.43-1.46 (9H, m, *Boc*), 1.64-1.67 (3H, m, CH_3C(H)=C), 2.02-2.37 (7H, m, CH_2CHCH_2C=C + CH_2CHCH_2C=C + CH_2CHCH_2C=C + $CO_2CH_2CH_2$), 3.63-4.14 (6H, m, CO_2CH_2 + CH_2NCH_2), 5.33 (1H, br s, C=CH), 6.15-6.22 (1H, m, C=C*H*CH$_3$), 7.27-7.35 (3H, m, CH_{Ar}), 7.48-7.53 (2H, m, CH_{Ar}); δ_C (100 MHz; $CDCl_3$) -1.6, -1.5, 17.9, 21.0, 21.1, 26.3, 28.3, 31.3, 31.6, 35.9, 38.0, 40.7, 45.6, 46.5, 46.6, 54.2, 54.6, 63.0, 80.0, 80.1, 118.8, 118.9, 127.8, 127.9, 128.8, 128.9, 133.4, 133.5, 133.8, 138.7, 139.0, 140.8, 141.8, 143.8, 143.9, 155.1, 155.8, 170.0, 170.1; m/z (FAB^+) 534 (3, MNa^+), 512.3202 (11, MH^+ $C_{30}H_{46}NO_4Si$ requires 512.3196), 412 (17, MH^+-Boc), 149 (89, $C_{11}H_{17}^+$), 135 (100, $PhMe_2Si^+$), 57 (94, ^{t}Bu$^+$).

[*tert*-Butoxycarbonyl-[2-(dimethyl-phenyl-silanyl)-but-2-enyl]-amino]-acetic acid [1*R*]-1-phenyl-ethyl ester 31

In an identical procedure to the preparation of **12** the acid derived from **14** (300 mg, 0.830 mmol) and (*R*)-1-phenyl ethanol (100 µL, 0.830 mmol, 1.0 eq.) gave a crude product which was purified by flash column chromatography (10% EtOAc/ pet. ether) to give **31** (367 mg, 95 %) as a colourless oil; ν_{max}(film)/cm^{-1} 3067, 2978, 2933, 1750, 1697; δ_H (400 MHz; $CDCl_3$) 0.47 (6H, s, Si*Me*$_2$), 1.42-1.51 (9H, m, *Boc*), 1.59 (3H, d, *J* 6.4, CH_3C(H)C=C), 1.69 (3H, d, *J* 6.4, CH_3C(H)Ph), 3.86-4.14 (4H, m, CH_2NCH_2), 6.01 (1H, q, *J* 6.3, C=C*H*CH$_3$), 6.14-6.30 (1H, m, OC*H*(CH_3)Ph), 7.31-7.38 (8H, m, CH_{Ar}), 7.55-7.59 (2H, m, CH_{Ar}); δ_C (100 MHz; $CDCl_3$) -1.9, -1.6, 17.7, 22.1, 28.2, 47.0, 54.2, 72.8, 80.0, 126.0, 127.0, 127.8, 128.4, 128.8, 133.5, 138.9, 140.9, 141.4, 141.7, 155.0, 169.2; m/z (ES^+) 490.2366 (2,

MNa^+ $C_{27}H_{37}NO_4SiNa$ requires 490.2390), 368 (4, MH^+-Boc), 230 (39, MH^+-$PhMe_2Si$), 73 (100, O^tBu^+).

[*N*-Boc-[2-(dimethylphenylsilanyl)-but-2-enyl]-amino]-acetic acid [2*S*]-2-dibenzylamino-3-phenylpropyl ester 32

In an identical procedure to the preparation of **12** the acid derived from **14** (300 mg, 0.830 mmol) and *N*,*N*-dibenzyl-(*S*)-phenylalaninol (275 mg, 0.830 mmol, 1.0 equiv.) gave a crude product which was purified by flash column chromatography (10% EtOAc/ pet. ether) to give **32** (504 mg, 90 %) as a colourless oil; ν_{max}(film)/cm^{-1} 3063, 3026, 2975, 2802, 1751, 1697; δ_H (500 MHz; $CDCl_3$) 0.45 (6H, s, Si*Me*$_2$), 1.42-1.48 (9H, m, *Boc*), 1.68 (3H, d, *J* 7.7, C*H*$_3$CH$_{rot}$), 1.70 (3H, d, *J* 7.7, C*H*$_3$CH$_{rot}$), 2.72 (1H, t, *J* 9.1, CHC*H*$_2$Ph$_{rot}$), 2.74 (1H, t, *J* 9.1, CHC*H*$_2$Ph$_{rot}$), 3.00 (1H, t, *J* 6.5, CHC*H*$_2$Ph$_{rot}$), 3.03 (1H, t, *J* 6.5, CHC*H*$_2$Ph$_{rot}$), 3.19-3.26 (1H, m, C*H*NBn$_2$), 3.66-4.19 (9H, m, C*H*$_2$NC*H*$_2$ + PhC*H*$_2$NC*H*$_2$Ph + CO_2CH_2), 4.37 (1H, dd, *J* 11.3, 6.2, CO_2CH_{2rot}), 4.40 (1H, dd, *J* 11.2, 6.3, CO_2CH_{2rot}), 6.17-6.25 (1H, m, C=C*H*CH$_3$), 7.06-7.08 (2H, m, C*H*$_{Ar}$), 7.24-7.29 (13H, m, C*H*$_{Ar}$), 7.37-7.38 (3H, m, C*H*$_{Ar}$), 7.53-7.54 (2H, m, C*H*$_{Ar}$); δ_C (125 MHz; $CDCl_3$) -1.6, -1.4, 17.9, 28.4, 34.5, 34.6, 46.7, 54.1, 54.4, 54.7, 58.1, 64.1, 80.2, 80.4, 126.2, 126.2, 126.9, 127.0, 127.9, 128.3, 128.4, 128.6, 128.9, 129.1, 129.4, 133.6, 133.9, 139.4, 139.7, 139.8, 140.8, 141.9, 155.1, 155.9, 170.2; m/z (ES^+) 677.3749 (4, MH^+ $C_{42}H_{53}N_2O_4Si$ requires 677.3775), 625 (100, MH^+-^{t}Bu), 585 (100, MH^+-CH_2Ph), 135 (27, $PhMe_2Si^+$), 91 (100, CH_2Ph^+).

[*N*-Boc-[2-(dimethylphenylsilanyl)-but-2-enyl]-amino]-acetic acid [1*R*,2*S*,4*S*]-1,7,7-trimethyl-bicyclo[2.2.1]hept-2-yl ester 33

In an identical procedure to the preparation of **12** the acid derived from **14** (302 mg, 0.830 mmol) and (-)-endo-borneol (128 mg, 0.830 mmol) gave a crude product which was purified by flash column chromatography (10% EtOAc/ pet. ether) to give **33** (363 mg, 88 %) as a colourless oil; ν_{max}(film)/cm^{-1} 3068, 3049, 2955, 1750, 1701; δ_H (500 MHz, C_6D_6, 67 °C) 0.52 (6H, s, Si*Me*$_2$), 0.88 (6H, s, C*Me*$_2$), 0.95 (3H, s, OC(H)CC*H*$_3$), 1.15 (1H, dd, *J* 9.1, 3.5, OC(H)C*H*$_2$), 1.33-1.36 (2H, m, C*H*$_2$CH$_2$), 1.52-1.56 (1H, m, C*H*CMe$_2$), 1.56 (9H, s, *Boc*), 1.64 (3H, d, *J* 7.1, C*H*$_3$C(H)=C), 1.78 (1H, m, C*H*$_2$CH$_2$), 2.14 (1H, m, C*H*$_2$CH$_2$), 2.41 (1H, m, OC(H)C*H*$_2$), 3.81 (2H, br s, C*H*$_2$NCH$_2$), 4.33 (2H, br s, C*H*$_2$NCH$_2$), 5.19 (1H, ddd, *J* 9.9, 3.3, 2.1, CO_2CH), 6.30 (1H, q, *J* 7.0, C=C*H*CH$_3$), 7.29-7.33 (3H, m, C*H*$_{Ar}$), 7.60-7.62 (2H, m, C*H*$_{Ar}$); δ_C (125 MHz, C_6D_6, 67 °C) -2.5, -2.3, 12.4, 13.7, 17.7, 18.3, 18.6, 26.5, 27.2, 27.4, 36.0, 44.3, 46.4, 46.9, 48.0, 55.8, 78.6, 79.3, 126.7, 126.9, 127.0, 132.8, 133.1, 133.5, 138.2, 139.9, 140.5, 154.3, 168.9; m/z (ES^+) 522 (5, MNa^+), 500.3167 (3, MH^+ $C_{29}H_{46}NO_4Si$ requires 500.3196), 400 (25, MH^+-Boc), 135 (59, $PhMe_2Si^+$), 73 (100, O^tBu^+), 57 (59, $^tBu^+$).