Asymmetric aza-[2,3]-Wittig sigmatropic rearrangements: chiral auxiliary control and formal asymmetric synthesis of (2S, 3R, 4R)-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 [1R,2S,5R]-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; νmax(film)/cm⁻¹ 2956, 2870, 1748, 1701; δH (500 MHz; CDCl₃) 0.41 (6H, s, SiMe₂), 0.75-0.77 (3H, m, C₃H₃CH), 0.88-0.92 (6H, m, CMe₂CH), 0.96-2.04 (21H, m, C₃H₂CH(C)OR + CH(CH₃)₂CH₂CH₂CH₂CH₂ + CH₂CH + CHMe₂H + CHCMe₂H + Boc + CH₂CH), 3.67-4.15 (4H, m, C₃H₂NC₃H₂), 4.70-4.77 (1H, m, CO₂C₃H₃), 6.15-6.23 (1H, m, C=C(CH₃)(CH₃)), 7.27 -7.34 (3H, m, C₆H₅), 7.50-7.52 (2H, m, C₆H₅); δC (125 MHz; CDCl₃) -1.6, -1.5, -1.5, 16.3, 18.0, 20.8, 22.0, 23.4, 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 (11, MH₂-Boc), 402 (11, MH₂-Boc), 135 (74, PhMe₂Si⁺), 73 (100, O'Bu⁺), 57 (78, 1Bu⁺).

[N-Boc-[2-(dimethylphenylsilanyl)-but-2-enyl]-amino]-acetic acid [1R,2S]-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 (-)-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; νmax(film)/cm⁻¹ 3028, 2932, 2859, 1736, 1701; δH (500 MHz; CDCl₃) 0.41 (6H, s, SiMe₂), 0.75-0.77 (3H, m, CH₂CH), 0.88-0.92 (6H, m, CMe₂CH), 0.96-2.28 (20H, m, Boc + CH₂CH + CH₂CH₂CH₂CH₂ ), 2.66-2.83 (1H, m, CHPH ), 3.46-4.10 (4H, m, CH₂NCH₂), 5.07-5.22 (1H, m, CO₂CH ), 5.67-5.81 (1H, m, CH₂CH₂), 7.16-7.56 (10H, m, CH₃), δC (125 MHz; CDCl₃) -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⁺ C₃H₄₃NO₄SiNa requires 544.2859), 422 (40, MH⁺-Boc).
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; \( \nu_{\text{max}}(\text{film/cm}^{-1}) \) 2976, 1692 (br); \( \delta_{H} \) (270 MHz; CDCl₃) 0.41-0.43 (6H, s, SiMe₂), 1.06 (d, \( J \) 6.7, \( \text{CH}_3\text{CHNMe}_2 \)), 1.38 (9H, m, \( \text{Boc} \)), 1.48 (9H, m, \( \text{Boc} \)), 1.64-1.67 (3H, m, \( \text{CH}_3\text{C}(\text{H})=\text{C} \)), 2.29 (6H, s, NMe₂), 2.92 (1H, m, CHNMe₂), 3.80-4.21 (4H, m, \( \text{CH}_2\text{NCH}_2 \)), 5.98 (1H, d, \( J \) 5.5, \( \text{CO}_2\text{CH} \)), 6.09-6.19 (1H, m, C=CHCH₃), 7.28-7.32 (8H, m, \( \text{CH}_2\text{Ar} \)), 7.50-7.52 (2H, m, \( \text{CH}_3\text{Ar} \)); \( \delta_{C} \) (67.5 MHz; CDCl₃) -1.6, -1.5, 9.2, 9.3, 17.9, 18.0, 25.0, 25.7, 26.3, 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 (ESI⁺) 525.3141 (45, \( \text{MH}^+ \) \( \text{C}_3\text{H}_5\text{N}_2\text{O}_4\text{Si} \) requires 525.3149), 469 (5, \( \text{MH}^+\text{Bu}^+ \)), 162 (99, \( \text{C}_1\text{H}_6\text{N}^+ \)), 72 (100, \( \text{OBu}^+ \)), 57 (66, \( \text{Bu}^+ \)).

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 \( [1\text{R},2\text{S}]-\)(-)-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; \( \nu_{\text{max}}(\text{film/cm}^{-1}) \) 3360, 2918, 1698, 1666; \( \delta_{H} \) (400 MHz; CDCl₃) 0.40 (6H, s, SiMe₂), 1.06-1.09 (3H, m, \( \text{CH}_3\text{CHNMe} \)), 1.41-1.44 (9H, m, \( \text{Boc} \)), 1.65-1.67 (3H, m, C=CHCH₃), 2.60 (3H, br s, NMe_major rot), 2.76 (3H, br s, NMe_minor rot), 3.15-4.82 (6H, m, \( \text{CHNMe} + \text{CHPh} +\text{CH}_3\text{NCH}_2 \)), 6.00-6.15 (1H, m, C=CHCH₃), 7.24-7.35 (8H, m, \( \text{CH}_2\text{Ar} \)), 7.48-7.50 (2H, m, \( \text{CH}_2\text{Ar} \)); \( \delta_{C} \) (67.5 MHz; CDCl₃) -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, 126.3, 127.4, 127.5, 127.8, 128.1, 128.4, 127.7, 133.6, 139.9, 141.2, 141.8, 155.1, 156.2, 168.4, 169.9, 170.1; m/z (ESI⁺) 533 (13, \( \text{MNa}^+ \)), 511.3018 (100, \( \text{MH}^+\text{C}_2\text{H}_3\text{N}_2\text{O}_4\text{Si} \) requires 511.2992), 455 (25, \( \text{MH}^+\text{Bu}^+ \)), 411 (21, \( \text{MH}^+\text{Boc} \)).

A solution of the acid derived from 14 (490 mg, 1.35 mmol) in \( \text{CH}_2\text{Cl}_2 \) (7 mL) was cooled to -30°C and treated with \( [1\text{R},2\text{S}]-\)(-)-O'-butildimethylsilylephedrine (377 mg, 1.35 mmol), DCC (284 mg, 1.35 mmol, 1.0 eq.) and HOBt (184 mg, 0.507 mmol) and \( [2\text{R},1\text{S}]-\)2-dimethylamino-1-phenyl-propyl ester 23 (262 mg, 98%) as a colourless oil; \( \nu_{\text{max}}(\text{film/cm}^{-1}) \) 3068, 2956, 2930, 2858, 1694, 1657; \( \delta_{H} \) (500 MHz; CDCl₃) -0.25(-0.23) (3H, m, SiMe₂\text{Bu}'); 0.02-0.06 (3H, m, SiMe₂\text{Bu}), 0.40-0.46 (6H, s, SiMe₂Ph), 0.93 (9H, br s, SiMe₂\text{Bu}), 1.13-1.92 (16H, m, NMeCH + C=\( \text{C}(\text{H})\text{CH}_3 + \text{CH}_3\text{CHNMe} + \text{Boc} \)), 2.70-2.87 (3H, m, NMe), 3.45-4.92 (5H, m, \( \text{CHPh} + \text{CH}_2\text{NCH}_2 \)), 5.5, \( \text{CO}_2\text{CH} \)).
6.02-6.28 (1H, m, C=CHCH₃), 7.22-7.30 (4H, m, CH₄, 7.37-7.39 (4H, m, CH₄), 7.53-7.55 (2H, m, CH₂); δC (125 MHz; CDCl₃) -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, 128.0, 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⁺) 674 (4, M⁺Na⁺), 625.3816 (42, M⁺ + Si⁺ requires 625.3857), 525 (100, MH⁺-Boc), 135 (84, PhMe₂Si⁺), 73 (93, O'B⁺), 57 (35, 1'B⁺).

[2-(Dimethylphenylsilyl)-but-2-enyl]-[2S]-[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)-pyrrolidine 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; v_max(film)/cm⁻¹ 3392, 2973, 1694, 1635; δH (500 MHz; CDCl₃) 0.41 (6H, s, SiMe₂), 1.42-1.44 (9H, m, Boc), 1.57-1.59 (1H, m, NCH₂CH₂CH₂), 1.67-1.71 (3H, m, CH₃(CH)(H)=C), 1.82-2.03 (3H, m, NCH₂CH₂CH₂), 3.30-4.29 (9H, m, CH₂NCH₂ + HOCH₂CH₂ + NCH₂CH₂CH₂), 6.16-6.24 (1H, m, C=CHCH₃), 7.34-7.37 (3H, m, CH₃), 7.50-7.52 (2H, m, CH₂); δC (125 MHz; CDCl₃) -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, M⁺Na⁺), 447.2685 (100, M⁺ + C₄H₉N₂O₃Si requires 447.2679), 391 (36, M⁺-Bu⁺), 347 (28, MH⁺-Boc).

[2-(Dimethylphenylsilyl)-but-2-enyl]-[2S]-[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)-(+)methoxypropylpyrrolidene (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; v_max(film)/cm⁻¹ 2976, 1690, 1652; δH (400 MHz; CDCl₃) 0.41 (6H, s, SiMe₂), 1.41-1.45 (9H, s, Boc), 1.65-1.67 (3H, m, C=CHCH₃), 1.86-2.04 (4H, m, CH₂CH₂CH₂N), 3.18-4.24 (12H, m, CH₂NCH₂ + MeOCH₂CH₂NCH₂), 6.15-6.23 (1H, m, C=CHCH₃), 7.34 (3H, m, CH₃), 7.49-7.52 (2H, m, CH₂); δC (100 MHz; CDCl₃) -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, 46.3, 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, 133.6, 138.9, 139.5, 140.8, 155.4, 156.2, 167.4, 167.8; m/z (ES⁺) 483 (22, M⁺Na⁺), 461.2878 (92, M⁺ + C₄H₉N₂O₃Si requires 461.2836), 405 (96, MH⁺-Bu⁺), 361 (100, MH⁺-Boc).

[2-(Dimethylphenylsilyl)-but-2-enyl]-[2S]-[2-(2-hydroxypHENYLmethyl)-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-pyrrolidinemethanol (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; v_max(film)/cm⁻¹ 2978, 1688, 1634; δH (400 MHz; CDCl₃) 0.43 (6H, s, SiMe₂), 1.40-1.55 (11H, m, CH₂CH₂N + Boc), 1.70 (3H, d, J 6.8, C=CHCH₃), 1.83-2.07 (2H, m, CH₂CH₂CH₂N), 2.82-2.86 (1H, m, CH₂CH₂N), 3.1 (1H, q, J 7.6, CH₂CH₂N), 3.25 (1H, q, J 7.6, CH₂CH₂N), 3.39-3.47 (4H, m, CH₂CH₂N), 5.16 (1H, d, J 4.4, 88, PhC(OH)CH), 6.14-6.18 (1H, m, C=CHCH₃), 6.51 (1H, br s, OH rot), 6.67 (1H, br s, OH rot), 7.24-7.37 (13H, m, CH₃), 7.51-7.52 (2H, m, CH₂); δC (100 MHz; CDCl₃) -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, 54.2, 54.6, 66.8.
[2S]-2-[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)-pyrrolidine 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;  

**ESI-MS** 490.2366 (2, MNa^+), 599.3311 (95, MH^+ C_{30}H_{41}N_{2}O_{4}Si requires 599.3305), 581 (100, MH^+cdot H_{2}O), 543 (18, MH^+cdot Bu), 525 (61, MH^+cdot H_{2}O\cdot Bu), 499 (64, MH^+cdot Boc).

**[N-Boc-[2-(dimethylphenylsilanyl)-but-2-enyl]-amino]-acetic acid [1S,5R]-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;  

**ESI-MS** 569.3038 (100, MNa^+ C_{29}H_{46}N_{2}O_{4}Si requires 569.3023), 447 (72, MH^+cdot Boc).

**[tart-Butoxycarbonyl-[2-(dimethyl-phenyl-silanyl)-but-2-enyl]-amino]-acetic acid [1R]-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;  

**ESI-MS** 490.2366 (2, MNa^+), 599.3311 (95, MH^+ C_{30}H_{41}N_{2}O_{4}Si requires 599.3305), 581 (100, MH^+cdot H_{2}O), 543 (18, MH^+cdot Bu), 525 (61, MH^+cdot H_{2}O\cdot Bu), 499 (64, MH^+cdot Boc).
MNa⁺ C_{27}H_{17}NO_4SiNa requires 490.2390, 368 (4, MH⁺-Boc), 230 (39, MH⁺-PhMe₂Si), 73 (100, O′Bu⁺).

[N-Boc-[2-(dimethylphenylsilanyl)-but-2-enyl]-amino]-acetic acid [25]-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; CDCl₃) 0.45 (6H, s, SiMe₂), 1.42-1.48 (9H, m, Boc), 1.68 (3H, d, J 7.7, CH₂CH₂Ot), 1.70 (3H, d, J 7.7, CH₃CH₂ot), 2.72 (1H, t, J 9.1, CH₂CH₂Phot), 2.74 (1H, t, J 9.1, CH₂CH₂Phot), 3.00 (1H, t, J 6.5, CH₂CH₂Phot), 3.03 (1H, t, J 6.5, CH₂CH₂Phot), 3.19-3.26 (1H, m, CHNBn), 3.66-4.19 (9H, m, CH₂NCH₂ + PhCH₂NCH₂Ph + CO₂CH₂), 4.37 (1H, dd, J 11.3, 6.2, CO₂CH₂ot), 4.40 (1H, dd, J 11.2, 6.3, CO₂CH₂ot), 6.17-6.25 (1H, m, C=CHCH₃), 7.06-7.08 (2H, m, CHAr), 7.24-7.29 (13H, m, CHAr), 7.37-7.38 (3H, m, CH₂Ar), 7.53-7.54 (2H, m, CH₂Ar); δ_C (125 MHz; CDCl₃) -1.6, -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, 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⁺) 677.3775 (4, MH⁺ + Boc), 627 (100, MH⁺-1Bu), 575 (100, MH⁺-CH₂Ph), 135 (27, PhMe₂Si⁻), 91 (100, CH₂Ph⁺).

[N-Boc-[2-(dimethylphenylsilanyl)-but-2-enyl]-amino]-acetic acid [1R,2S,4S]-1,7,7-trimethylbicyclo[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, C₆D₆, 67 °C) 0.52 (6H, s, SiMe₂), 0.88 (6H, s, CMe₂), 0.95 (3H, s, OC(H)CCH), 1.15 (1H, dd, J 9.1, 3.5, OC(H)CH₂), 1.33-1.36 (2H, m, CH₂CH₂), 1.52-1.56 (1H, m, OCH₂), 1.56 (9H, s, Boc), 1.64 (3H, d, J 7.1, CH₂C(H)=C), 1.78 (1H, m, CH₂CH₂), 2.14 (1H, m, CH₂CH₂), 2.41 (1H, m, OC(H)CH₂), 3.81 (2H, br s, CH₂NCH₂), 4.33 (2H, br s, CH₂NCH₂), 5.19 (1H, ddd, J 9.9, 3.3, 2.1, CO₂H), 6.30 (1H, q, J 7.0, C=CHCH₃), 7.29-7.33 (3H, m, CH₂Ar), 7.60-7.62 (2H, m, CH₂Ar); δ_C (125 MHz, C₆D₆, 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⁺ + C₂H₄NO₂Si requires 500.3196), 400 (25, MH⁺-Boc), 135 (59, PhMe₂Si⁻), 73 (100, O′Bu⁺), 57 (59, O′Bu⁺).