Enantioselective Synthesis of a Mitosane Core Assisted by Diversity-Based Catalyst Discovery

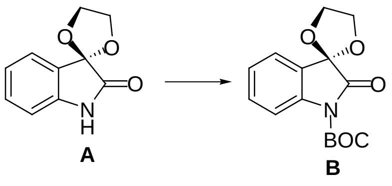
Nikolaos Papaioannou, Catherine A. Evans, Jarred T. Blank and Scott J. Miller*

Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467-3860

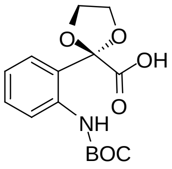
Supporting Information

General Procedures. Proton NMR spectra were recorded on Varian 500, 400, or 300 spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.0) or with the solvent reference relative to TMS employed as the internal standard ($CDCl_3$, δ 7.26 ppm; d_6-DMSO, δ 2.50 ppm; C_6D_6, δ 7.16 ppm). Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m)], coupling constants [Hz], integration). Carbon NMR spectra were recorded on Varian 500 (125 MHz), 400 (100 MHz) or 300 (75 MHz) spectrometers with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.0). NMR data were collected at 25 °C, unless otherwise indicated. Infrared spectra were obtained on a Perkin-Elmer Spectrum 1000 spectrometer. Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F254 precoated plates (0.25 mm thickness). TLC R_f values are reported. Visualization was accomplished by irradiation with a UV lamp and/or staining with ceric ammonium molybdenate (CAM) solution. Flash column chromatography was performed using Silica Gel 60Å (32-63 μm) from Scientific Adsorbants Inc. Optical rotations were recorded on a Rudolf Research Analytical Autopol IV Automatic polarimeter at the sodium D line (path length 50 mm). Elemental analyses were performed by Robertson Microlit (Madison, NJ). High resolution mass spectra were obtained at the Mass Spectrometry Facilities either of the University of Illinois (Urbana-Champaign, IL), Harvard University (Cambridge, MA) or Boston College (Chestnut Hill, MA). The method of ionization is given in parentheses.

Analytical normal phase HPLC was performed on a Hewlett-Packard 1100 Series chromatograph equipped with a diode array detector (214 nm and 254 nm). All reactions were carried out under an argon or nitrogen atmosphere employing oven- and flame-dried glassware. All solvents were distilled from appropriate drying agents prior to use. Acetic anhydride was distilled prior to use and stored in a Schlenk tube for no more than 1 week.

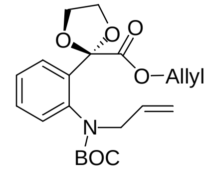


(B) To a solution of isatin ketal **A** (0.990g, 5.18 mmol) in 10.0 mL of dry methylene chloride was added triethylamine (0.720 mL, 5.18 mmol) followed by di-*tert*-butyl dicarbonate (2.26 g, 10.4 mmol) and 4-(dimethylamino)pyridine (0.630 g, 5.18 mmol). The solution was stirred for 6 h at ambient temperature under an argon atmosphere. The solution was diluted to 50 mL with methylene chloride, washed with citric acid (3 x 20 mL) and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (30% ethyl acetate:hexanes) to afford 1.30 g (86%) of the desired product. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.90 (d, J = 8.8 Hz, 1H), 7.43 (app. t, 2H), 7.21 (t, J = 7.3 Hz, 1H), 4.57 (m, 2H), 4.35 (m, 2H), 1.63 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 171.6, 148.9, 141.0, 132.1, 125.1, 124.9, 123.0, 115.7, 101.5, 84.8, 66.2, 28.4; **TLC** **R_f** 0.30 (15% EtOAc/Hex); **IR** (film, cm^{-1}) 2980, 2904, 1784, 1734, 1614, 1469; **Anal.** Calcd. for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81. Found: C, 61.83; H, 5.81; N, 4.69; **Exact mass** calcd for [$C_{15}H_{17}NO_5$ + Na] requires *m/z* 314.1004. Found: 314.0992 (ESI+).



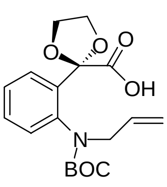
C

(C): To a solution of BOC isatin **B** (25.4 g, 87.3 mmol) in 300 mL (5:2) THF/H_2O was added NaOH (6.98 g, 175 mmol). The solution was heated to reflux for 1 h then cooled to ambient temp. The volitiles were removed under reduced pressure and the resulting slurry was partitioned between 10% citric acid (700 mL) and methylene chloride (1 L). The acidic aqueous layer was extracted with methylene chloride (2 x 1 L) and the organic layers were combined and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure to afford 27.0 g (99%) of pure product. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 10.40 (br s, 1H), 7.90 (br d, J=7.3 Hz, 1H), 7.84 (s, 1H), 7.60 (d, J=7.9 Hz, 1H), 7.33 (t, J=7.7 Hz, 1H), 7.08 (t, J=7.7, 1H), 4.21-4.16 (m, 2H), 4.13-4.07 (m, 2H), 1.48 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.4, 153.7, 136.2, 130.1, 126.4, 123.3, 122.4, 105.1, 80.8, 65.9, 28.5; **TLC** **R_f** 0.34 (30% EtOAc/Hex); **IR** (film, cm^{-1}) 3402, 2980, 2936, 2904, 2615, 1734, 1595, 1513, 1444 ; **Anal.** Calcd**.** for $C_{15}H_{19}NO_6$: C, 58.25; H, 6.19; N, 4.53. Found: C, 58.14; H, 6.21; N, 4.35.



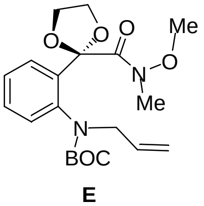
4

(4): To a solution of carboxylic acid **C** (23.6, g 76.3 mmol) in 400 mL dry DMF was added allyl bromide (65.9 mL, 763 mmol). The resulting solution was cooled to 0 °C and sodium hydride (5.49 g, 229 mmol) was added in small portions. After 10 min at 0 °C the reaction was allowed to reach ambient temp. The reaction was stirred for 3h at ambient temp under a nitrogen atmosphere. The reaction was cooled to 0 °C and a dilute aqueous solution of ammonium chloride was added dropwise to the reaction. When gas evolution ceased, dilute ammonium chloride (1 L) was added to the mixture. The solution was separated into two portions and the following work-up was repeated twice. The mixture was poured into a separatory funnel and the aqueous solution was washed with diethyl ether (5 x 500 mL). The combined ether layer was then washed with 500 mL of brine. The organics were combined and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (20% ethyl acetate:hexanes) to afford 25.9 g (87%) of the desired product. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.77 (br s, 1H), 7.33 (br m, 2H), 7.10 (br s, 1H), 6.00-5.80 (m, 2H), 5.30-5.00 (m, 4H), 4.73-4.68 (br dd, J=13.4, 5.7 Hz, 1H), 4.50 (br s, 2H), 4.26 (br s, 1H), 4.17-4.08 (m, 3H), 3.67-3.58 (dd, J=15.6, 7.1 Hz, 1H), 1.46 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 167.8, 154.8, 140.2, 134.2, 131.7, 131.0, 129.7, 127.3, 127.2, 118.3, 117.2, 105.0, 80.2, 66.5, 66.1, 65.7, 54.3, 28.6; **TLC** ***R$_f$*** 0.27 (20% EtOAc/Hex); **IR** (film, cm^{-1}) 3081, 2974, 2898, 1765, 1696, 1646; **Anal.** Calcd. for $C_{21}H_{27}NO_6$: C, 64.77; H, 6.99; N, 3.60. Found: C, 64.92; H, 6.99; N, 3.42; **Exact mass** calcd for $[C_{21}H_{27}NO_6]$+H requires *m/z* 390.1917. Found 390.1899 (ESI+).



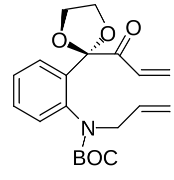
D

(D): To a solution of allyl ester **4** (24.9 g, 63.7 mmol) in 400 mL of 1:1 THF/H_2O was added NaOH (5.12 g, 128 mmol). The solution was heated to reflux for 5 h then cooled to ambient temp. The solvent was partially removed under reduced pressure and the resulting slurry was partitioned between 10% citric acid (500 mL) and methylene chloride (1 L). The acidic aqueous layer was rinsed several times with methylene chloride (2 x 500 mL) and the organic layers were combined and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure to afford 22.2 g (99%) of pure product. **^{1}H NMR** (C_6D_6, 300 MHz, 70 ^{o}C) δ 9.37 (br s, 1H), 7.82 (m, 1H), 7.04-6.99 (m, 3H), 6.02-5.89 (m, 1H), 5.03-4.96 (m, 2H), 4.57-4.50 (br m, 1H), 3.92-3.58 (m, 5H), 1.40 (s, 9H); **^{13}C NMR** (C_6D_6, 75 MHz, 70 ^{o}C) δ 169.9, 156.0, 140.2, 135.6, 134.7, 130.8, 129.7, 128.9(br), 117.2, 106.2, 80.8, 66.0, 65.5, 54.3, 28.5; **TLC** ***R$_f$*** 0.31 (80% EtOAc/Hex); **IR** (film, cm^{-1}) 3081, 2986, 1759, 1709, 1658, 1488, 1457; **Anal.** Calcd. for $C_{18}H_{23}NO_6$: C, 61.88; H, 6.64; N, 4.01. Found: C, 61.90; H, 6.48; N, 4.29; **Exact mass** calcd for $[C_{18}H_{23}NO_6]$+H requires *m/z* 350.1604. Found 350.1599 (ESI+).



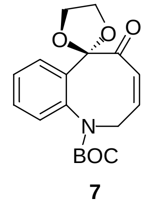
E

(E): To a solution of carboxylic acid **D** (3.93 g, 11.3 mmol) in 500 mL dry methylene chloride was added triethylamine (7.84 mL, 56.3 mmol), 4-(dimethylamino)pyridine (1.37 g, 11.3 mmol), *N,O*-dimethylhydroxylamine hydrochloride (3.29 g, 33.8 mmol), and 1-(3-dimethylamino-propyl)-3-ethyl-carbodiimide hydrochloride (EDC, 2.37 g, 12.4 mmol) sequentially. The solution was stirred at ambient temperature under a nitrogen atmosphere overnight. The reaction mixture was diluted to 150 mL with methylene chloride, the organic layer was washed with 5% citric acid (3 x 50 mL) and saturated aqueous $NaHCO_3$ (1x 50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography (50% ethyl acetate:hexanes) to afford 2.85g (64%) of the desired product. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.78 (br s, 1H), 7.31 (br m, 2H), 7.18 (br s, 1H), 5.98-5.87 (br m, 1H), 5.08-5.00 (br m, 2H), 4.45 (br dd, J=15.8, 4.8 Hz, 1H), 4.23-4.03 (m, 4H), 3.76 (br dd, J=16.1, 7.0 Hz, 1H), 3.07 (br s, 6H), 1.45 (br s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 167.1, 154.9, 140.0, 137.5, 134.4, 131.6, 129.2, 127.4, 126.1, 117.9, 105.6, 80.1, 66.6, 65.4, 59.8, 54.6, 32.4, 28.6; **TLC R*f*** 0.34 (50% EtOAc/Hex); **IR** (film, cm^{-1}) 3081, 2967, 2936, 2898, 2250, 1702, 1683; **Anal.** Calcd. for $C_{20}H_{29}N_2O_6$: C, 61.21; H, 7.19; N, 7.14. Found: C, 61.16; H, 7.19; N, 7.00; **Exact mass** calcd for $[C_{20}H_{29}N_2O_6]$+H requires *m/z* 393.2026. Found: 393.2009 (ESI+).



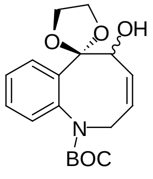
5

(5): To a solution of Weinreb amide **E** (2.00 g, 5.10 mmol) in 80 mL dry THF at 0 °C was added freshly prepared vinylmagnesium bromide (9.00 mL, 10.4 mmol) dropwise as a 1.15 M solution in THF. The reaction was stirred for 15 min or until TLC analysis indicated completion. To the reaction was added acetic anhydride (3.00 mL) followed by methanol (3.00 mL). The solution was reduced to one quarter the volume under reduced pressure then diluted to 1 L with diethyl ether. The solution was washed with dilute aqueous ammonium chloride solution (2 x 200 mL) and dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure at ambient temperature to avoid decomposition. The crude product was purified by flash chromatography (20% ethyl acetate:hexanes) to afford 1.83 g (99%) of the desired product. **^{1}H NMR** (C_6D_6, 500 MHz, 70 °C) δ 7.81 (br m, 1H), 7.08 (br m, 3H), 6.63-6.57 (dd, J=17.1, 10.3 Hz, 1H), 6.33-6.29 (d, J=17.6 Hz, 1H), 6.07-5.98 (m, 1H), 5.32-5.29 (d, J=11.7 Hz, 1H), 5.04-5.00 (d, J=17.1 Hz, 1H), 4.99-4.97 (d, J=9.3 Hz, 1H), 4.69-4.66 (br d, J=13.2 Hz, 1H), 3.87-3.83 (dd, J=15.1, 7.3 Hz, 1 H), 3.82-3.74 (br m, 1H), 3.62-3.54 (br m, 3H), 1.38 (s, 9H); **^{13}C NMR** (C_6D_6, 125 MHz, 70 °C) δ 191.4, 155.0, 142.0, 136.6, 135.3, 132.6, 132.5, 130.0, 128.5, 127.7, 117.5, 108.3, 80.1, 66.6, 65.5, 54.5, 28.2; **TLC R*f*** 0.28 (20% EtOAc/Hex); **IR** (film, cm^{-1}) 3087, 2993, 2942, 2898, 1709, 1620, 1501, 1451; **Anal.** Calcd. for $C_{20}H_{25}NO_5$: C, 66.83; H, 7.01; N, 3.90. Found: C, 66.65; H, 6.82; N, 3.68; **Exact mass** calcd for $[C_{20}H_{25}NO_5]$+ H requires *m/z* 360.1811. Found: 360.1827 (ESI+).



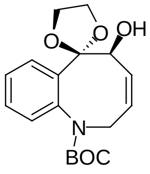
7

(7): To a solution of diene **5** (0.500 g, 1.39 mmol) in 280 mL dry methylene chloride was added ruthenium alkylidene **6** (0.118 g, 0.139 mmol). The solution was heated to reflux under an argon atmosphere for 4 h. The solvent was then removed under reduced pressure and the crude product was purified by flash chromatography (30% ethyl acetate:hexanes) to afford 0.382 g (83%) of the desired product. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.64 (m, 1H), 7.43 (m, 2H), 7.13 (br s, 1H), 6.12-6.08 (m, 1H), 5.68-5.64 (m, 1H), 5.04 (br d, J=17.2 Hz, 1H), 4.34-4.20 (m, 3H), 4.05-3.99 (m, 1H), 3.58 (br d, J=18.3 Hz, 1H), 1.36 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.3, 153.9,139.0, 138.4, 130.7, 130.6, 128.2, 127.6, 127.3, 126.9, 106.7, 81.4, 66.7, 65.2, 50.1, 28.0; **TLC R*f*** 0.52 (50% EtOAc/Hex); **IR** (film, cm^{-1}) 2980, 2936, 2898, 1715, 1608, 1495, 1463; **Anal.** Calcd. For $C_{18}H_{21}NO_5$: C, 65.24; H, 6.39; N, 4.23. Found: C, 65.05; H, 6.30; N, 3.93; **Exact mass** calcd for $[C_{18}H_{21}NO_5]$+Na requires *m/z* 354.1317. Found: 354.1317 (ESI+).



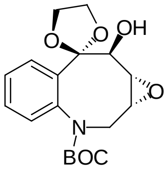
(±)-3

[(±)-3]: To a solution of enone **7** (0.150 g, 0.450 mmol) in 25.0 mL dry diethyl ether at 0 °C was added lithium aluminum hydride (52.0 mg, 1.40 mmol). After 10 min, 0.500 mL water was added dropwise, followed by 0.500 mL 15 % NaOH and finally 0.500 mL water. The slurry was the filtered through a plug of celite and the celite cake was washed with copious amounts of diethyl ether. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (30% ethyl acetate:hexanes) to afford 0.149 g (99%) of the desired product. Allylic alcohol **3** can also be purified by recrystallization using ethyl acetate and hexanes. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.49-7.47 (d, J=7.7 Hz, 1H), 7.37-7.29 (m, 2H), 7.05-7.03 (br d, J=7.0 Hz, 1H), 5.48-5.44 (br m, 1H), 5.40-5.25 (br m, 2 H), 5.10 (br d, J=17.2 Hz, 1H), 4.40 (br m, 1H), 4.20 (br m, 2H), 3.80 (br m, 1H), 3.56-3.51 (br dd, J=16.5, 4.8 Hz, 1H), 2.50 (br s, 1H), 1.55-1.33 (br s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 154.5, 139.2, 138.1, 133.1, 129.9, 129.2, 127.4, 127.3, 125.8, 112.4, 80.5, 73.1, 68.4, 64.2, 48.2, 28.58; **TLC R_f** 0.36 (50% EtOAc/Hex); **IR** (film, cm^{-1}) 3452, 2993, 2917, 1696, 1495, 1457; **Anal.** Calcd. for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.73; H, 6.89; N, 4.28; **Exact mass** calcd for $[C_{18}H_{23}NO_5]$+Na requires *m/z* 356.1474. Found: 356.1470 (ESI+).



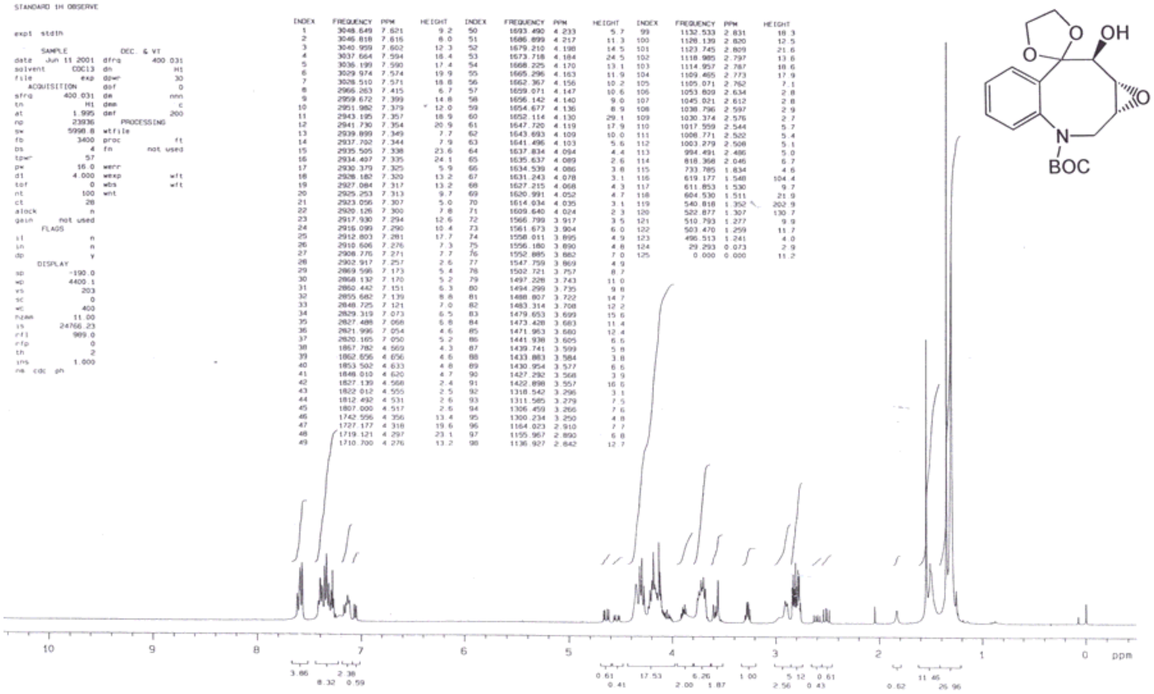
(-)-**3**

[(-)-3]: To a solution of racemic allylic alcohol (±)- **3** (0.25g, 0.75 mmol) in 150 mL of toluene was added peptide catalyst **9** (0.013g, 0.015 mmol) followed by triethylamine (0.63 mL, 4.5 mmol). The solution was cooled to 0 °C and acetic anhydride (0.36 mL, 3.75 mmol) was added dropwise. The reaction was stirred for 3 d at 0 °C and was quenched with 20 mL MeOH. The solvent was removed under reduced pressure and the crude material was purified by flash chromatography (25% ethyl acetate:hexanes) to afford 0.12g (47%) of recovered allylic alcohol. **Assay of enantiomeric purity.** Enantiomers of starting material and product **3-Ac** were separated by chiral HPLC employing a Chiracel AD column (Alltech), eluting with 5% 2-propanol/hexanes at a flow rate of 1.5 mL/min. Retention Times: **3**: $R_{t(S)}$ = 16.4 min; $R_{t(R)}$ = 24.1 min. Retention Times: **3-Ac**: $R_{t(S)}$ = 9.1 min; $R_{t(R)}$ = 13.2 min. Recovered **3** was produced with 90% ee (53% conversion, k_{rel}=27). The recovered allylic alcohol was recrystallized to optical purity. **$[\alpha]_D$** -18 [(at >99% ee) *c* = 0.097 g/100mL, CH_2Cl_2)].



11

(11): To a solution of optically pure allylic alcohol (-)-**3** (0.105 g, 0.315 mmol) in 10 mL of 3:1 acetone/H_2O was added $NaHCO_3$ (0.151 g, 1.80 mmol) followed by oxone (0.369 g, 0.600 mmol). The solution was stirred at ambient temp. overnight. The solvent was partially removed under reduced pressure then the resulting slurry was partitioned between saturated aqueous $NaHCO_3$ (1 x 10 mL) and ethyl acetate (75 mL). The aqueous layer was washed with ethyl acetate (2 x 75 mL) and the organic layers were combined and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The crude product was eluted through a plug of silica gel with ethyl acetate. The resulting solution was concentrated under reduced pressure to afford 0.110 g (99%) of analytically pure product. Epoxyalcohol **11** exhibits a complex ^{1}H NMR spectrum (shown below) at room temperature. However, upon quantitative TFA deprotection, the free amine exhibits sharp ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra (scanned in below).



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STANDARD 1H OBSERVE

expt  stdih

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tn               H1  dmm                 c
at            1.995  dmf               200
np            23936       PROCESSING
sw           5998.8  wtfile
fb             3400  proc               ft
bs                4  fn           not used
tpwr             57
pw             16.0  werr
d1            4.000  wexp              wft
tof               0  wbs               wft
nt              100  wnt
ct               28
alock             n
gain       not used
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in                n
dp                y
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sc                0
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nm  cdc  ph
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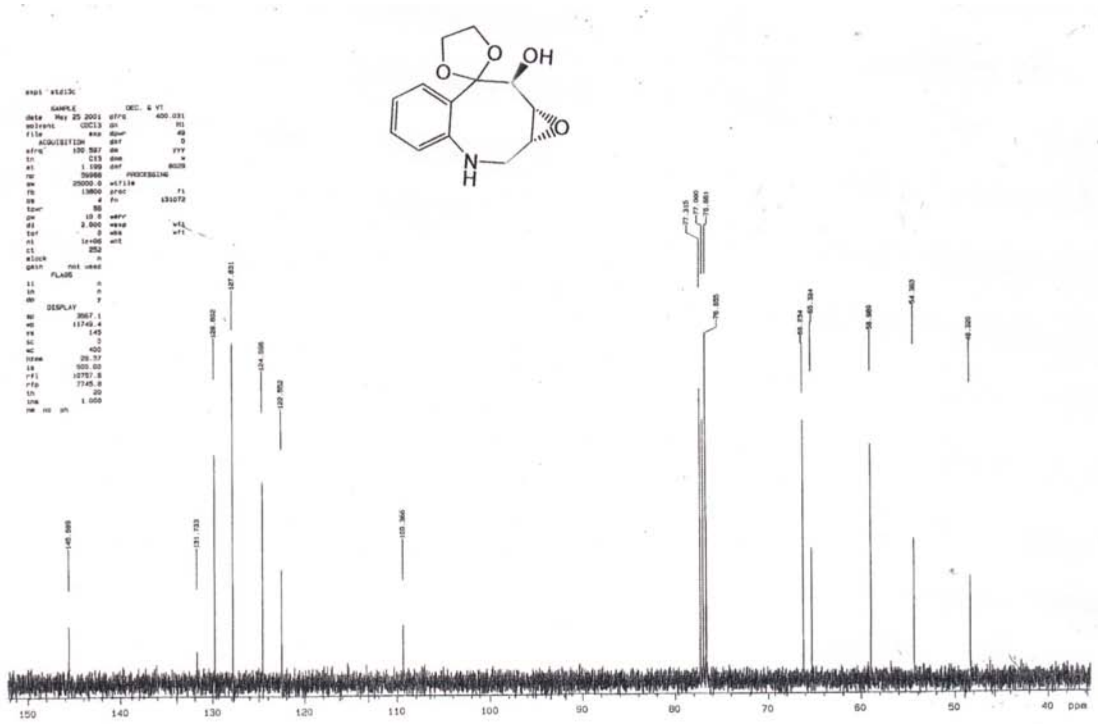
2	3046.818	7.616	6.0	51	1686.899	4.217	11.3	100	1128.139	2.820	12.5
3	3040.959	7.602	12.3	52	1679.210	4.198	14.5	101	1123.745	2.809	21.6
4	3037.664	7.594	16.4	53	1673.718	4.184	24.5	102	1118.985	2.797	13.6
5	3036.199	7.590	17.4	54	1668.225	4.170	13.1	103	1114.957	2.787	18.6
6	3029.974	7.574	19.9	55	1665.296	4.163	11.9	104	1109.465	2.773	17.9
7	3028.510	7.571	18.8	56	1662.367	4.156	10.2	105	1105.071	2.762	7.1
8	2966.263	7.415	6.7	57	1659.071	4.147	10.6	106	1053.809	2.634	2.8
9	2959.672	7.399	14.8	58	1656.142	4.140	9.0	107	1045.021	2.612	2.8
10	2951.982	7.379	12.0	59	1654.677	4.136	8.9	108	1038.796	2.597	2.9
11	2943.195	7.357	18.9	60	1652.114	4.130	29.1	109	1030.374	2.576	2.7
12	2941.730	7.354	20.9	61	1647.720	4.119	17.9	110	1017.559	2.544	5.7
13	2939.899	7.349	7.7	62	1643.693	4.109	10.0	111	1008.771	2.522	5.4
14	2937.702	7.344	7.9	63	1641.496	4.103	5.6	112	1003.279	2.508	5.1
15	2935.505	7.338	23.6	64	1637.834	4.094	4.4	113	994.491	2.486	5.0
16	2934.407	7.335	24.1	65	1635.637	4.089	2.6	114	818.368	2.046	6.7
17	2930.379	7.325	5.9	66	1634.539	4.086	3.8	115	733.785	1.834	4.6
18	2928.182	7.320	13.2	67	1631.243	4.078	3.1	116	619.177	1.548	104.4
19	2927.084	7.317	13.2	68	1627.215	4.068	4.3	117	611.853	1.530	9.7
20	2925.253	7.313	9.7	69	1620.991	4.052	4.7	118	604.530	1.511	21.9
21	2923.056	7.307	5.0	70	1614.034	4.035	3.1	119	540.818	1.352	202.9
22	2920.126	7.300	7.8	71	1609.640	4.024	2.3	120	522.877	1.307	130.7
23	2917.930	7.294	12.6	72	1566.799	3.917	3.5	121	510.793	1.277	9.9
24	2916.099	7.290	10.4	73	1561.673	3.904	6.0	122	503.470	1.259	11.7
25	2912.803	7.281	17.7	74	1558.011	3.895	4.9	123	496.513	1.241	4.0
26	2910.606	7.276	7.3	75	1556.180	3.890	4.8	124	29.293	0.073	2.9
27	2908.776	7.271	7.7	76	1552.885	3.882	7.0	125	0.000	0.000	11.2
28	2902.917	7.257	2.6	77	1547.759	3.869	4.9				
29	2869.596	7.173	5.4	78	1502.721	3.757	8.7				
30	2868.132	7.170	5.2	79	1497.228	3.743	11.0				
31	2860.442	7.151	6.3	80	1494.299	3.735	9.8				
32	2855.682	7.139	8.8	81	1488.807	3.722	14.7				
33	2848.725	7.121	7.0	82	1483.314	3.708	12.2				
34	2829.319	7.073	6.5	83	1479.653	3.699	15.6				
35	2827.488	7.068	6.8	84	1473.428	3.683	11.4				
36	2821.996	7.054	4.6	85	1471.963	3.680	12.4				
37	2820.165	7.050	5.2	86	1441.938	3.605	6.6				
38	1867.782	4.669	4.3	87	1439.741	3.599	5.8				
39	1862.656	4.656	4.6	88	1433.883	3.584	3.8				
40	1853.502	4.633	4.8	89	1430.954	3.577	6.6				
41	1848.010	4.620	4.7	90	1427.292	3.568	3.9				
42	1827.139	4.568	2.4	91	1422.898	3.557	16.6				
43	1822.012	4.555	2.5	92	1318.542	3.296	3.1				
44	1812.492	4.531	2.6	93	1311.585	3.279	7.5				
45	1807.000	4.517	2.6	94	1306.459	3.266	7.6				
46	1742.556	4.356	13.4	95	1300.234	3.250	4.8				
47	1727.177	4.318	19.6	96	1164.023	2.910	7.7				
48	1719.121	4.297	23.1	97	1155.967	2.890	6.8				
49	1710.700	4.276	13.2	98	1136.927	2.842	12.7				

Data for **11**: **^{13}C NMR** ($CDCl_3$, 100 MHz) major peaks δ 154.5, 153.8, 140.6, 138.5, 138.2, 130.9, 130.2, 129.8, 129.3, 128.6, 128.2, 127.9, 126.6, 126.1, 108.8, 80.3, 76.2, 75.6, 74.6, 67.7, 66.2, 65.5, 63.8, 62.4, 58.7, 57.0, 53.4, 52.5, 51.6, 51.2, 49.6, 48.2, 46.8, 29.1, 27.7, 26.5; **TLC** **R_f** 0.32 (50% EtOAc/Hex); **IR** (film, cm^{-1}) 3471, 2974, 2942, 2898, 1702, 1608, 1482, 1400; **$[\alpha]_D$** -35.9 (c=0. 548 g/100mL, CH_2Cl_2); **Anal**. Calcd. for $C_{18}H_{23}NO_6$: C,61.88; H, 6.64; N, 4.01. Found: C, 61.50; H, 6.71; N ,3.90; **Exact mass** calcd for $[C_{18}H_{23}NO_6]$+Na requires *m/z* 3372.1423. Found 372.1406 (ESI+).

The**^{1}H NMR** ($CDCl_3$, 400 MHz) and **^{13}C NMR** ($CDCl_3$, 100 MHz) spectra for the deprotected amino alcohol derived from **11** are scanned in on the next page.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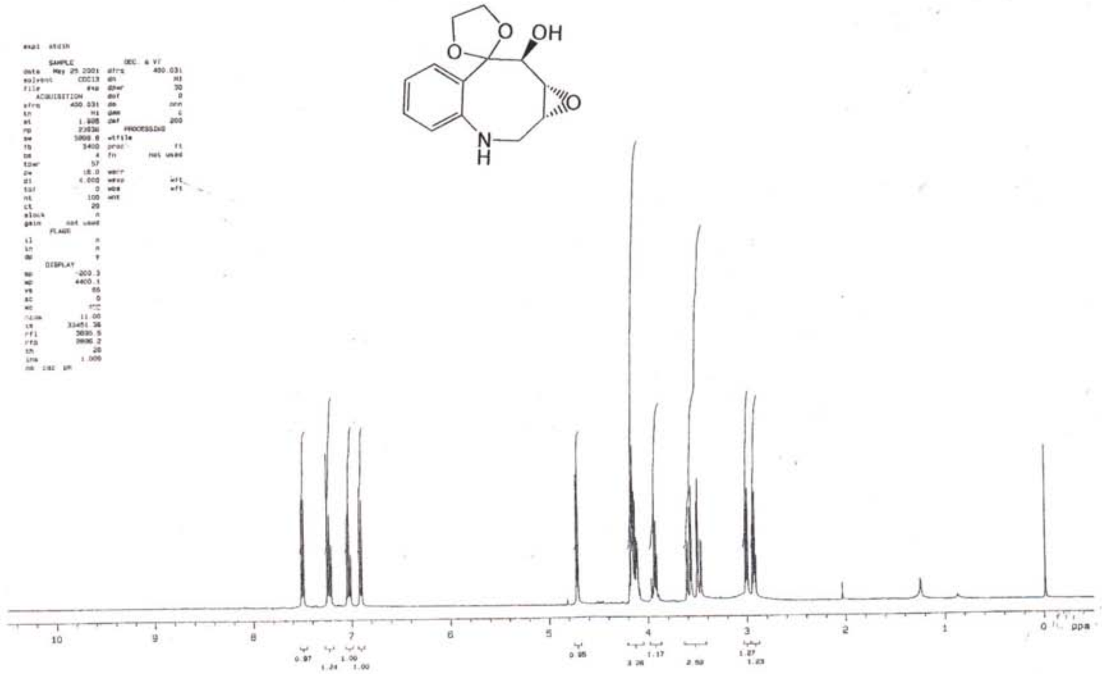
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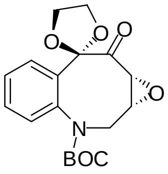
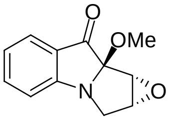


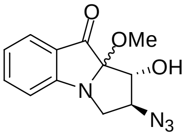
12

(12): To a solution of oxalyl chloride (81.0 µL, 0.940 mmol) in 10 mL dry methylene chloride at - 78 °C was added dimethylsulfoxide (0.110 mL, 1.60 mmol) dropwise. After 15 min, epoxyalcohol **11** (0.109 g, 0.312 mmol) was added in 10.0 mL of dry methylene chloride via cannula. The solution was stirred at - 78 °C for an additional 15 min after which triethylamine (0.700 mL, 4.99 mmol) was added and the reaction was allowed to reach ambient temp. After 1 h the mixture was diluted to 100 mL with methylene chloride and washed with 5% citric acid (2 x 20 mL) and saturated aqueous $NaHCO_3$ (1 x 10 mL). The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (30% ethyl acetate:hexanes) to afford 0.102 g (94%) of the desired product. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.56 (m, 1H), 7.37 (m, 2H), 7.03 (br s, 1H), 4.70 (br d, J=15.0 Hz, 1H), 4.34-4.20 (m, 3H), 4.10-4.05 (m, 1H), 3.65 (d, J=4.0 Hz, 1H), 3.58 (br d, J=15.8 Hz, 1H), 3.50 (dd, J=4.0, 1.8 Hz, 1H), 1.33 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 195.2, 153.9, 140.4, 139.0, 130.2, 128.2, 127.0, 125.8, 105.8, 81.9, 66.9, 65.8, 61.8, 56.1, 45.6, 28.1; **TLC R*f*** 0.41 (50% EtOAc/Hex); **IR** (film, cm^{-1}) 2993, 2930, 2262, 1727, 1702, 1614; **[α]$_D$** -33.0 (c=0.404 g/100 mL, CH_2Cl_2); **Anal.** Calcd. for $C_{18}H_{21}NO_6$: C, 62.24; H, 6.09; N, 4.03. Found: C, 62.17; H, 6.02; N, 3.83; **Exact mass** calcd for $[C_{18}H_{21}NO_6]$+Na requires m/z 370.1267 Found 370.1272 (ESI+).



13

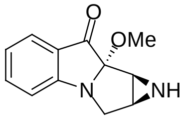
(13): To a solution of epoxyketone **12** (57.0 mg, 0.164 mmol) in 5 mL methanol, in a sealed tube, was added water (9.00 µL, 0.492 mmol) and a solution of nitric acid (0.200 mL, 0.042 M in MeOH). The tube was sealed under an atmosphere of nitrogen and placed into an oil bath at 135 °C. After 30 min. the tube was cooled to 0 °C and the contents of the tube were partitioned between methylene chloride (100 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was washed with methylene chloride (2 x 50 mL) and the organic layers were combined and dried over Na_2SO_4. The solution was filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (30% ethyl acetate:hexanes) to afford 29.0 mg (81%) of the desired product. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.60-7.50 (m, 2H), 6.90 (t, J=7.0 Hz, 1H), 6.80 (d, J=8.1 Hz, 1H), 3.80-3.75 (dd, J=6.6, 2.6 Hz, 2H), 3.70-3.55 (dd, J=30.8, 12.8 Hz, 2H), 3.29 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.9, 164.5, 138.3, 124.4, 122.4, 121.0, 112.9, 99.4, 57.7, 56.2, 52.1, 51.3; **TLC R*f*** 0.33 (30% EtOAc/Hex); **IR** (film, cm^{-1}) 2942, 1721, 1627, 1482, 1318; ; **[α]$_D$** 342 (c=0.266 g/100mL, CH_2Cl_2); **Anal.** Calcd. for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.09; H, 4.91; N, 6.29.



14

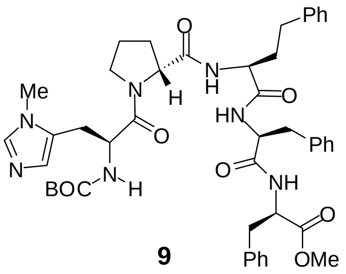
(14): To a solution of epoxide **13** (73.0 mg, 0.336 mmol) in 2 mL dry methylene chloride was added Sm(O-*i*-Pr)$_3$ (52.0 mg, 0.160 mmol) followed by trimethylsilyl azide (0.178 mL, 1.34 mmol). The solution was stirred at ambient temp under an argon atmosphere for 24 h. The solution was concentrated under reduced pressure and the crude product was purified by flash chromatography (30% diethyl ether:hexanes) to afford 46.0 mg

(52%) of the desired product along with 38.0 mg (34%) of the TMS ether. The two were combined and dissolved in 10 mL of a 0.04 M HCl/MeOH solution. After 1 h, the solution was quenched with saturated aqueous $NaHCO_3$ and concentrated under reduced pressure to one quarter the volume. The resulting suspension was partitioned between methylene chloride (100 mL) and H_2O (20 mL). The organic layer was concentrated under reduced pressure to afford **14** as a mixture of diastereomers in quantitative yield. The material was used in the subsequent step without further purification. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.63-7.52 (m, 4H), 7.03-6.88 (m, 4H), 4.55-4.44 (d, J=2.9 Hz, 1H), 4.44-4.38 (dd, J=15.7, 8.1 Hz, 1H), 4.05-4.01 (m, 1H), 3.95-3.91 (dd, J=10.6, 7.3 Hz, 1H), 3.84-3.80 (dd, J=12.1, 7.0 Hz, 1H), 3.76-3.74 (br d, 1H, J=7.7 Hz), 3.66-3.61 (dd, J=11.7, 4.8 Hz, 1H), 3.30 (s, 3H), 3.23 (s, 3H), 3.05 (s, 1H), 3.01-2.96 (dd, J=10.6, 7.7 Hz, 1H); **Exact mass** calcd for $[C_{12}H_{12}N_4O_3]$+H requires *m/z* 261.0988. Found 261.0982 (ESI+).



1

(1): To a 0 °C solution of azido-alcohol **14** (34.0 mg, 0.133 mmol) in 5.00 mL methylene chloride was added triethylamine (56.0 μL, 0.399 mmol) followed by methanesulfonyl chloride (21.0 μL, 0.266 mmol). The reaction was stirred under an atmosphere of nitrogen for 1 h. The reaction mixture was diluted to 50 mL with diethyl ether and washed with 5% citric acid (1 x 10 mL) and 5% sodium bicarbonate (1 x 10 mL). The organics were dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure to afford crude product. The crude material was dissolved in 10.0 mL THF:H_2O (10:1) and transferred into a round bottom flask. To the solution was added Hunig's base (46.0 μL, 0.266 mmol) and triphenylphosphine polystyrene resin (0.200 g, ~0.20 mmol) followed by heating to 65 °C for 1 h. The reaction mixture was filtered through a plug of cotton and concentrated under reduced pressure. The product was purified by flash chromatography (75% ethyl acetate:hexanes) to afford 12.2 mg (42%) of the ***trans*-mitosane 1** (*cis*-mitocene 1 was not isolated). Data for ***trans*-1** follow. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.56-7.50 (m,2H), 6.90 (t, J=7.3 Hz, 1H), 6.78 (d, J=8.1 Hz, 1H), 3.55 (br s, 2H), 3.29 (s, 3H), 3.02 (br s, 1H), 2.93 (br s, 1H), **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 198.7, 164.8, 138.3, 124.4, 122.6, 120.5, 112.4, 100.4, 51.8, 51.5, 37.2, 36.7; **TLC** $\mathbf{R_f}$ 0.40 (ethyl acetate); **IR** (film, cm^{-1}) 3314, 2943, 1715, 1620, 1482, 1318; $\mathbf{[\alpha]_D}$ -130 (c=.08 g/100mL, CH_2Cl_2); **Exact mass** calcd for $[C_{12}H_{12}N_2O_2]$+H requires m/z 217.0977. Found 217.0968 (ESI+).



9

Peptide 9. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.84, (d, J = 9.2 Hz, 1H), 7.32 (s, 1H), 7.26-7.12 (m, 11H), 7.05-6.99 (m, 6H), 6.81 (s, 1H), 6.51 (d, J = 9.2 Hz, 1H), 4.70 (m, 3H), 4.25 (m, 1H), 4.02 (t, J = 7.3 Hz, 1H), 3.65 (overlapping s and m, 4H), 3.54 (s, 3H), 3.39 (m, 2H), 3.19 (dd, J=15.0, 7.7 Hz, 1H), 3.07-2.94 (overlapping m and dd, J = 15.2, 6.4 Hz, 4H), 2.45 (t, J = 7.7 Hz, 2H), 2.17-1.99 (overlapping m and m, 4H), 1.92-1.77 (m, 2H), 1.41 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 172.4 (2C), 170.8, 170.7, 170.0, 155.5, 140.5, 137.6, 137.5, 136.0, 129.0, 128.9, 128.4, 128.3, 128.2 (2C), 127.6 (2C), 126.7, 126.5, 126.1, 79.8. 61.4, 54.4, 54.3, 54.0, 52.3, 51.8, 47.6, 38.0, 36.8, 32.1, 31.8, 31.5, 29.0, 28.4, 27.2, 25.6; **IR** (film, cm-1) 3315, 3195, 3062, 3026, 2979, 2953, 2931, 1736, 1708, 1671, 1630; **TLC R_f** 0.36 (8% MeOH/CH_2Cl_2); **Exact mass** calcd for [$C_{46}H_{57}N_7O_8$+H]+ requires *m/z* 836.4347. Found 836.4346 (ESI+). Analytical HPLC. Purity of peptide **9** was assayed using a reverse phase RP-18 X Terra (Waters) column at a flow rate of 0.2 mL/min with the following gradient : 50% methanol/water to 70% methanol/water over 20 min, hold until 25 min. Retention time = 18.7 min.

Data for Peptide Library.[i]

Library A

Peptide	Sequence	Calcd M+H	Obs. M+H	k_{rel} @ 25 °C
9	BOC-Pmh-D-Pro-Hfe-Phe-D-Phe-OMe	837.00	836.22	9.7
A1	BOC-Pmh-D-Pro-Aib-Cha-Phe-OMe	766.95	767.07	3.4
A2	Boc-Pmh-D-Pro-Dbg-Val-Phe-OMe	797.02	797.14	2.6
A3	Boc-Pmh-D-Pro-Cha-1-amino-1-cyclohexane carboxylic acid-Phe-OMe	807.02	806.87	2.7
A4	BOC-Pmh-D-Pro-Phe-1-amino-1-cyclopentane carboxylic acid-Phe-OMe	786.94	787.03	2.0
A5	BOC-Pmh-D-Pro-1-amino-1-cyclohexane carboxylic acid-Chg-Phe-OMe	792.99	792.34	4.3
A6	BOC-Pmh-D-Pro-Aib-Phe-OMe	613.73	613.79	3.4
A7	BOC-Pmh-D-Pro-Hfe-Phe-OMe	689.82	689.91	2.7
A8	BOC-Pmh-D-Pro-Cha-Phe-OMe	681.84	681.93	2.8
A9	BOC-Pmh-D-Pro-Chg-Phe-OMe	667.82	667.88	1.8
A10	BOC-Pmh-D-Pro-1-amino-1-cyclopentane carboxylic acid-Phe-OMe	639.76	639.86	3.1
A11	BOC-Pmh-D-Pro-1-amino-1-cyclohexane carboxylic acid-Phe-OMe	653.79	653.88	3.1
A12	BOC-Pmh-D-Pro-Gly-Phe-OMe	585.67	585.79	2.0
A13	BOC-Pmh-D-Pro-L-Pro-Phe-OMe	625.74	625.87	1.1
A14	BOC-Pmh-D-Pip-Aib-Phe-OMe	627.75	627.87	1.5
A15	BOC-Pmh-D-Pip-Gly-Phe-OMe	599.66	599.79	1.2
A16	BOC-Pmh-D-Pip-1-amino-1-cyclopentane carboxylic acid-Phe-OMe	653.80	653.88	2.1
A17	BOC-Pmh-D-Pip-1-amino-1-cyclohexane carboxylic acid-Phe-OMe	667.82	667.92	1.8
A18	BOC-Pmh-D-Pip-Dbg-Phe-OMe	711.91	712.07	1.1
A19	BOC-Pmh-Aib-D-Pro-Phe-OMe	613.73	613.83	1.0
A20	BOC-Pmh-Aib-L-Pro-Phe-OMe	613.73	613.88	3.4
A21	BOC-Pmh-Phe-L-Pro-Phe-OMe	675.80	675.90	1.1
A22	BOC-Pmh-L-Pro-L-Pro-Phe-OMe	625.74	625.87	1.2
A23	BOC-Pmh-L-Pro-D-Pro-Phe-OMe	625.74	625.86	1.1
A24	BOC-Pmh-L-Pro-Dbg-Phe-OMe	697.89	698.02	1.1
A25	BOC-Pmh-D-Pro-Aib-Gly-Phe-OMe	670.78	670.91	2.9
A26	BOC-Pmh-D-Pro-Aib-Hfe-Phe-OMe	774.93	775.05	3.4
A27	BOC-Pmh-D-Pro-Phe-1-amino-1-cyclohexane carboxylic	800.97	801.08	1.7

	acid-Phe-OMe			
A28	BOC-Pmh-D-Pro-Hfe-Phe-Phe-OMe	837.00	837.05	5.8
A29	BOC-Pmh-D-Pro-1-amino-1-cyclohexane carboxylic acid-Val-Phe-OMe	752.92	753.05	3.8
A30	BOC-Pmh-D-Pro-Hfe-D-Phe-OMe	689.82	689.95	1.9
A31	BOC-Pmh-D-Pro-1-amino-1-cyclohexane carboxylic acid-Val-D-Phe-OMe	752.92	753.09	4.2
A32	BOC-Pmh-D-Pro-Hfe-Gly-D-Phe-OMe	746.87	747.04	4.1
A33	BOC-Pmh-D-Pro-Aib-Hfe-D-Phe-OMe	774.93	775.05	2.6
A34	BOC-Pmh-D-Pro-Aib-Phe-D-Phe-OMe	760.90	761.05	6.5
A35	BOC-Pmh-D-Pro-2-amino-2-indan carboxylic acid-Phe-OMe	687.81	687.29	2.3
A36	BOC-Pmh-D-Pro-2-amino-2-indan carboxylic acid-D-Phe-OMe	687.81	687.23	2.0
A37	BOC-Pmh-D-Pro-1-amino-1-cylcooctane carboxylic acid-Phe-Ome	681.84	681.27	1.7
A38	BOC-Pmh-D-Pip-Hfe-D-Phe-OMe	703.85	703.24	1.7
A39	BOC-Pmh-D-Pip-1-amino-1-cylcooctane carboxylic acid-Phe-OMe	695.87	695.32	2.1
A40	BOC-Pmh-D-Pro-2-amino-2-indan carboxylic acid-Phe-Phe-OMe	834.98	834.26	3.8
A41	BOC-Pmh-D-Pro-2-amino-2-indan carboxylic acid-Hfe-Phe-OMe	849.01	848.25	2.7
A42	BOC-Pmh-D-Pro-1-amino-1-cyclooctane carboxylic acid-Cha-Phe-OMe	834.06	834.36	3.0
A43	BOC-Pmh-D-Pro-1-amino-1-cyclooctane carboxylic acid-Chg-Phe-OMe	821.04	820.38	2.7
A44	BOC-Pmh-D-Pro-1-amino-1-cyclohexane carboxylic acid-Cha-Phe-OMe	807.01	806.37	4.7
A45	BOC-Pmh-D-Pro-1-amino-1-cyclohexane carboxylic acid-Leu-Phe-OMe	766.95	766.38	4.8
A46	BOC-Pmh-D-Pro-1-amino-1-cyclohexane carboxylic acid-Ile-Phe-OMe	766.95	766.38	3.8
A47	BOC-Pmh-D-Pro-Hfe-D-Phe-Phe-OMe	837.00	836.27	1.9
A48	BOC-Pmh-D-Pro-Gly-1-amino-1-cylcohexane carboxylic acid-Phe-OMe	710.84	710.25	2.0
A49	BOC-Pmh-D-Pip-1-amino-1-cyclopentane carboxylic acid-Hfe-Phe-OMe	814.99	814.25	5.5
A50	BOC-Pmh-D-Pip-1-amino-1-cyclohexane carboxylic acid-Hfe-Phe-OMe	829.02	828.28	3.8
A51	BOC-Pmh-D-Pip-Hfe-Phe-Phe-OMe	851.02	850.23	4.1
A52	BOC-Pmh-D-Pip-Aib-Cha-Phe-OMe	780.98	780.32	5.2
A53	BOC-Pmh-D-Pro-Phe-Hfe-D-Phe-OMe	835.99	836.43	2.2
A54	BOC-Pmh-D-Pro-Hfe-Cha-D-Phe-OMe	842.03	842.48	4.9
A55	BOC-Pmh-D-Pro-Cha-Phe-D-Phe-OMe	828.01	828.37	2.9
A56	BOC-Pmh-D-Pro-Hfe-Phe-D-Phe-Phe-OMe	983.16	983.51	2.3
A57	BOC-Pmh-D-Pip-Asn(Trt)-Trp(Boc)-Phe-OMe	1184.38	1185.28	1.8
A58	BOC-Pmh-D-Pip-Hfe-Asn(Trt)-Phe-OMe	1059.26	1060.25	1.2
A59	BOC-Pmh-D-Pip-D-Val-Trp(Boc)-D-Phe-OMe	927.10	928.26	1.1
A60	BOC-Pmh-Asn(Trt)-1-amino-1-cyclopentane carboxylic acid-Trp(Boc)-D-Phe-OMe	1184.38	1185.28	1.8

A61	BOC-Pmh-D-Val-Aib-D-Ala-Ala-OMe	610.73	611.08	1.4
A62	BOC-Pmh-D-Glu(OBut)-Aib-Cha-Ala-OMe	778.96	779.12	1.3
A63	BOC-Pmh-Asn(Trt)-His(πBn)-Asp-OBut-Ala-OMe	1110.28	1110.11	1.1
A64	BOC-Pmh-Thr(But)-D-Glu(OBut)-Hfe-Ala-OMe	859.04	859.14	1.4
A65	BOC-Pmh-D-Val-Ile-Chg-Ala-OMe	706.90	707.16	1.5
A66	BOC-Pmh-Aib-Chg-Phe-Ala-OMe	726.88	727.14	4.7
A67	BOC-Pmh-His(πBn)-D-Glu(OBut)-Aib-Ala-OMe	853.00	853.17	1.2
A68	BOC-Pmh-Phe-Phe-Leu-Ala-OMe	762.92	763.12	1.4
A69	BOC-Pmh-Trp(Boc)-D-Ala-Glu(OBut)-Ala-OMe	898.04	898.12	1.5
A70	BOC-Pmh-Glu(OcHx)-D-Ala-Ile-Ala-OMe	750.90	751.16	1.9
A71	BOC-Pmh-Leu-Asn(Trt)-Chg-Ala-OMe	964.19	964.16	1.1
A72	BOC-Pmh-Cha-D-Glu(OBut)-Phe-Ala-OMe	841.03	841.16	2.4
A73	BOC-Pmh-Leu-Ile-Phe-Ala-OMe	728.90	729.16	1.5
A74	BOC-Pmh-D-Val-D-Glu(OBut)-Asp-OBut-Ala-OMe	810.96	811.12	1.3
A75	BOC-Pmh-Ile-Leu-Asp-OBut-Ala-OMe	752.92	753.16	1.7
A76	BOC-Pmh-Cha-D-Ala-Hfe-Ala-OMe	740.91	741.13	1.8
A77	BOC-Pmh-Phe-D-Glu(OBut)-Asn(Trt)-Ala-OMe	1044.22	1044.15	4.2
A78	BOC-Pmh-Asn(Trt)-D-Ala-D-Glu(OBut)-Ala-OMe	968.13	968.12	1.6
A79	BOC-Pmh-Asp-OBut-Leu-D-Glu(OBut)-Ala-OMe	824.98	825.17	1.4
A80	BOC-Pmh-Cha-Hfe-Asn(Trt)-Ala-OMe	1026.25	1026.17	1.4
A81	BOC-Pmh-Ile-Cha-Aib-Ala-OMe	706.90	707.16	1.8
A82	BOC-Pmh-Ile-D-Val-D-Glu(OBut)-Ala-OMe	752.92	753.16	2.0
A83	BOC-Pmh-D-Ala-D-Glu(OBut)-Hfe-Ala-OMe	772.91	773.11	1.8
A84	BOC-Pmh-D-Ala-Asn(Trt)-Hfe-Ala-OMe	944.11	944.11	2.7
A85	BOC-Pmh-Aib-Cha-Trp(Boc)-Ala-OMe	866.04	865.98	4.6
A86	BOC-Pmh-Thr(But)-Thr(But)-Phe-Ala-OMe	817.01	816.99	1.1
A87	BOC-Pmh-Asn(Trt)-Trp(Boc)-Aib-Ala-OMe	1083.26	1082.94	1.1
A88	BOC-Pmh-Aib-Hfe-Glu(OcHx)-Ala-OMe	812.97	813.01	1.8
A89	BOC-Pmh-D-Val-Aib-Glu(OcHx)-Ala-OMe	750.90	751.02	1.5
A90	BOC-Pmh-D-Val-Ile-D-Ala-Ala-OMe	638.78	639.03	1.4
A91	BOC-Pmh-D-Glu(OBut)-Trp(Boc)-Asn(Trt)-Ala-OMe	1183.37	1182.94	1.4
A92	BOC-Pmh-D-Val-Cha-Cha-Ala-OMe	760.99	761.11	1.9
A93	BOC-Pmh-Phe-Glu(OcHx)-Glu(OcHx)-Ala-OMe	925.10	925.05	1.5
A94	BOC-Pmh-Glu(OcHx)-Cha-His(πBn)-Ala-OMe	947.15	947.09	2.0
A95	BOC-Pmh-D-Ala-D-Ala-Cha-Ala-OMe	650.79	651.07	2.8
A96	BOC-Pmh-Asp-OBut-Asn(Trt)-Thr(But)-Ala-OMe	1040.23	1040.09	1.3
A97	BOC-Pmh-Ile-His(πBn)-Glu(OcHx)-Ala-OMe	907.09	907.05	1.8
A98	BOC-Pmh-Hfe-Trp(Boc)-D-Val-Ala-OMe	902.07	902.09	1.1
A99	BOC-Pmh-Asp-OBut-Asn(Trt)-Phe-Phe-OMe	1106.29	1106.16	1.8
A100	BOC-Pmh-D-Val-His(πBn)-His(πBn)-Phe-OMe	985.16	985.17	1.8
A101	BOC-Pmh-His(πBn)-D-Glu(OBut)-D-Glu(OBut)-Phe-OMe	1029.21	1029.16	1.4
A102	BOC-Pmh-His(πBn)-D-Glu(OBut)-D-Ala-Phe-OMe	915.07	915.15	1.7
A103	BOC-Pmh-Aib-D-Glu(OBut)-Hfe-Phe-OMe	863.03	863.13	3.3
A104	BOC-Pmh-Glu(OcHx)-Phe-Asn(Trt)-Phe-OMe	1146.36	1146.18	1.6
A105	BOC-Pmh-Phe-Thr(But)-D-Val-Phe-OMe	835.02	835.15	1.3
A106	BOC-Pmh-Cha-D-Ala-Hfe-Phe-OMe	817.01	817.13	2.4
A107	BOC-Pmh-Aib-Chg-Phe-Phe-OMe	802.98	803.16	4.5
A108	BOC-Pmh-Thr(But)-Trp(Boc)-His(πBn)-Phe-OMe	1102.31	1102.26	1.2
A109	BOC-Pmh-Thr(But)-Thr(But)-D-Val-Phe-OMe	845.06	845.20	1.1

A110	BOC-Pmh-D-Ala-Thr(But)-Ile-Phe-OMe	772.95	773.15	3.2
A111	BOC-Pmh-Phe-Aib-Asp-OBut-Phe-OMe	834.98	834.70	2.5
A112	BOC-Pmh-Asn(Trt)-Chg-Aib-Phe-OMe	1012.22	1012.17	1.3
A113	BOC-Pmh-Asp-OBut-His(πBn)-Hfe-Phe-OMe	991.16	991.26	1.6
A114	BOC-Pmh-Ile-Phe-D-Val-Phe-OMe	790.97	791.16	1.4
A115	BOC-Pmh-Phe-D-Ala-Leu-Phe-OMe	762.92	763.17	3.4
A116	BOC-Pmh-Thr(But)-His(πBn)-Asn(Trt)-Phe-OMe	1172.40	1172.27	1.2
A117	BOC-Pmh-Ile-Glu(OcHx)-D-Glu(OBut)-Phe-OMe	941.14	941.24	1.7
A118	BOC-Pmh-Aib-D-Val-Trp(Boc)-Phe-OMe	902.07	902.20	2.2
A119	BOC-Pmh-D-Ala-D-Ala-Leu-Phe-OMe	686.82	687.15	2.3
A120	BOC-Pmh-D-Val-Trp(Boc)-D-Glu(OBut)-Phe-OMe	1002.18	1002.25	1.3
A121	BOC-Pmh-D-Glu(OBut)-D-Val-Chg-Phe-OMe	855.05	855.26	1.5
A122	BOC-Pmh-D-Glu(OBut)-Cha-D-Ala-Phe-OMe	841.03	841.25	1.1
A123	BOC-Pmh-Leu-Ile-Glu(OcHx)-Phe-OMe	869.08	869.28	1.5
A124	BOC-Pmh-Asp-OBut-D-Ala-Glu(OcHx)-Phe-OMe	884.03	N.A.	1.4
A125	BOC-Pmh-Phe-Aib-Asn(Trt)-Phe-OMe	1020.20	1020.24	3.7
A126	BOC-Pmh-Asn(Trt)-D-Glu(OBut)-D-Val-OMe	1072.28	1072.29	1.3
A127	BOC-Pmh-Trp(Boc)-D-Val-D-Val-Phe-OMe	916.10	916.23	2.0
A128	BOC-Pmh-Leu-Chg-Hfe-Phe-OMe	845.06	845.25	2.8
A129	BOC-Pmh-Cha-Leu-Trp(Boc)-Phe-OMe	984.21	984.31	3.0
A130	BOC-Pmh-Asn(Trt)-Ile-Hfe-Phe-OMe	1062.28	1062.29	1.7
A131	BOC-Pmh-Asn(Trt)-Aib-His(πBn)-Phe-OMe	1100.29	1100.28	1.4
A132	BOC-Pmh-His(πBn)-Cha-D-Ala-Phe-OMe	883.07	883.26	1.2
A133	BOC-Pmh-Glu(OcHx)-Glu(OcHx)-D-Glu(OBut)-Phe-OMe	1039.24	1039.33	1.8
A134	BOC-Pmh-Cha-Asn(Trt)-Aib-Phe-OMe	1026.25	1026.28	1.1
A135	BOC-Pmh-Hyp(But)-Aib-Cha-Ala-OMe	761.95	763.36	1.1
A136	BOC-Pmh-Hyp(But)-1-amino-1-cyclohexane carboxylic acid-Asn(Trt)-Phe-OMe	1081.30	1082.38	1.2
A137	BOC-Pmh-Hyp(But)-Aib-Hfe-Phe-OMe	846.02	847.32	1.1
A138	BOC-Pmh-Hyp(But)-D-Val-Cha-Ala-OMe	776.00	777.37	1.1
A139	BOC-Pmh-Hyp(But)-Chg-Cha-Phe-OMe	892.13	893.44	1.3
A140	BOC-Pmh-D-Tic-Hfe-Val-Phe-OMe	850.01	851.34	3.2
A141	BOC-Pmh-D-Tic-Trp(Boc)-Leu-Phe-OMe	989.17	990.35	3.0
A142	BOC-Pmh-D-Tic-1-amino-1-cyclohexane carboxylic acid-Asn(Trt)-Ala-OMe	995.17	996.40	1.5
A143	BOC-Pmh-D-Tic-1-amino-1-cyclopentane carboxylic acid-Hfe-Phe-OMe	862.02	863.33	2.8
A144	BOC-Pmh-Val-Thr-($\Psi^{Me,Me}$)pro-Aib-Leu-Ala-OMe	792.96	794.37	1.1
A145	BOC-Pmh-Val-Thr-($\Psi^{Me,Me}$)pro-Aib-Hfe-Phe-OMe	917.10	918.24	1.1
A146	BOC-Pmh-Phe-2-Abz-Leu-Ala-OMe	733.85	735.31	1.9
A147	BOC-Pmh-Hfe-2-Abz-Hfe-Phe-OMe	872.02	873.54	2.0
A148	BOC-Pmh-Val-2-Abz-Hfe-Phe-OMe	809.95	811.25	1.3
A149	BOC-Pmh-Asp-OBut-Asp-OBut-Phe-Phe-OMe	920.06	921.38	1.6
A150	BOC-Pmh-Val-Val-D-Pro-Gly-Leu-Val-Val-OMe	947.17	947.56	1.4
A151	BOC-Pmh-Thr(But)-D-Val-His(Trt)-D-Phe-D-Val-Thr(But)-Ile-OMe	1436	1436	2.7

[1] Unnatural amino acid abbreviations: 2-Abz = 2-aminobenzoic acid, Aib = α-aminomethylalanine, Cha = 3-cyclohexylalanine, Chg = α-cyclohexylglycine, Dbg = di-n-butylglycine, Hfe = homophenylalanine, Hyp(But) = O-t-butyl-L-trans-4-hydroxyproline, D-Pip = D-pipecolic acid, Pmh = π-methyl histidine, D-Tic = (3R)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid. Protecting group abbreviations: Trt = trityl, But = t-butyl, cHx = cyclohexyl, Bn = benzyl.
