Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

for

Function-Oriented Investigations of a Peptide-Based Catalyst that Mediates Enantioselective Allylic Alcohol Epoxidation.

Nadia C. Abascal, Phillip A. Lichtor, Michael W. Giuliano, Scott J. Miller*

Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107, United States.

1. General Information

Nuclear magnetic resonance was carried out on either 400, 500, or 600 MHz Bruker and Varian spectrometers at ambient temperatures. All samples were prepared in $CDCl_3$ and referenced to tetramethyl silane (TMS) or residual solvent.[1] NMR data is reported as chemical shift with multiplicity, coupling constant, and integration accompanying. Multiplicity is reported in the following manner: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), triplet (t), quartet (q), pentet (p), multiplet (m).

Gas chromatography (GC) was performed on an instrument equipped with HP-5 columns (30 m, 0.320 mm diameter, 0.25 μm film thickness). The instrument employed flame ionization detectors using He as a carrier gas.

Analytical thin layer chromatography (TLC) was performed on silica gel 60 Å F_{254} pre-coated plates (0.25 thickness). The developed plates were visualized by a UV lamp and/or cerium ammonium molybdate (CAM) or $KMnO_4$ stains. Preparative thin layer chromatography (prep-TLC) was generally performed using 1000 μm thick plates coated with silica gel GF (Uniplate) with UV 254 indicator.

Flash column chromatography was performed with silica gel 60 Å (32-63 microns).

Optical rotations were collected on a polarimeter using the sodium D line (1.0 dm path length) at 20 °C. Solutions for optical rotation were prepared in $CHCl_3$ at a concentration of 1 g/100 mL.

High-resolution liquid chromatography-mass spectrometry (HRLC/MS) was carried out on an instrument equipped with an ESI, a QToF mass spectrometer, and a photodiode array detector.

High resolution mass spectrometry (HRMS) data were acquired by the FT-ICR Mass Spectrometry Resource of the Keck Biotechnology Resource Laboratory. The mass spectral data were obtained from a Bruker (Billerica, MA) 9.4 Tesla Apex-Qe Hybrid Qe-Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer consisting of an Apollo II electrospray ionization source. The sample was directly infused into the FT-ICR MS via a TriVersa NanoMate (Advion BioScience) utilizing a D-chip configuration which consisted of a 384-nozzle nanoESI chip (for flow rate between 2-15nL/min) with each nozzle having a 4.5 μm id at the electrospray tip. The entrance to the Apollo II source is grounded and ~1400V potential was applied on the nanoESI chip, with back pressure on the syringe at 0.6 psi. The mass spectrometer (running Compass Software with APEX control acquisition component (v.1.2) is setup to acquire single fid (512K) data and with a mass range (m/z) from 100 to 2000. Exact mass were obtained for the entire broadband spectrum. Subsequently, various instrument parameters were adjusted to maximize the signal(s) around the peak of interest. Bruker Daltonics

[1] Gottlieb, H. E., Kotlyar, V. Nudelman, A. J. Org. Chem. 1997, *62*, 7512-7515.

DataAnalysis software (v. 3.4) was utilized for the analysis of the data and assignments were made based on exact mass measurements and fit of isotopic peaks to that of theoretical isotopic patterns (IsotopePattern algorithm, Bruker). Collected time transient data were zero filled, Fourier transformed, magnitude calculations to generated m/z mass spectrum.

Enantiomeric excess (ee) values were acquired using a chiral analytical HPLC with chiral columns at 20 ºC. The HPLC was equipped with a diode array detector collecting at 210, 230, and 254 nm.

Some reactions were carried out with solvents purified from a Seca Solvent Purification System by GlassContour. However, all other chemicals were purchased and used as received unless otherwise noted.

Dr. Danielle Gray University of Illinois School of Chemical Sciences determined the reported crystal structure. See SI-29 and attached file for relevant details.

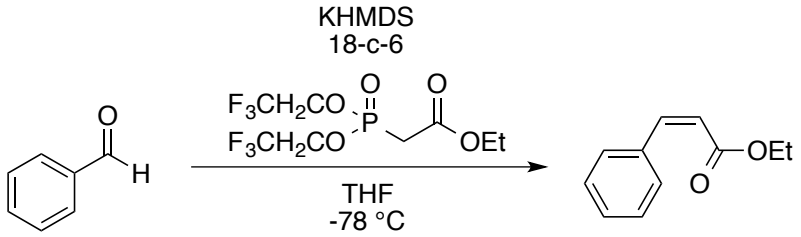
2. Experimental Procedures

2.1 General Procedure for Racemic Epoxide. An allylic alcohol (1.0 equiv) was loaded into a round bottom flask. The material was dissolved in dichloromethane (0.2 M in substrate) and de-ionized water (2.0 M in substrate). *meta*-Chloroperoxybenzoic acid (77% w/w, 1.0 equiv) and dibasic sodium phosphate (2 equiv) were added in a single portion. The solution was allowed to stir at room temperature until TLC no longer showed the presence of starting material. Following this, the reaction mixture was diluted with dichloromethane and poured into a separatory funnel containing sat. aq. Na_2SO_3. The organic layer was separated and washed with sat. aq. $NaHCO_3$. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude residue was purified by flash column chromatography using the appropriate solvent system (noted in the characterization of each compound). Where necessary, an aliquot of the mixture was taken forward to be derivatized with a chromophore for HPLC analysis.

2.2 General Procedure for Peptide-Catalyzed Epoxidation. Peptide (0.1 equiv) was loaded into a flask, followed by an allylic alcohol (1.0 equiv). A solution of HOBt•H_2O (0.1 equiv), DMAP (0.1 equiv), and, for the so-called conditions b, triethyl amine (0.1 equiv) in chloroform (filtered through basic alumina, 0.2 M in substrate) was added to the mixture. Aqueous hydrogen peroxide (30% w/w, 2.0 equiv) was pipetted into the reaction vessel and it was placed in an ice bath. Diisopropylcarbodiimide (1.0 equiv) was delivered and the reaction mixture was transported to a cold room to stir for 7 hours at 4 °C. The solution was washed with sat. aq. Na_2SO_3 and sat. aq. $NaHCO_3$. This biphasic mixture was extracted with EtOAc and vortexed. The newly buoyant organic layer was concentrated under a stream of nitrogen and extracted again with EtOAc (x 3). The combined organic layers were concentrated under a stream of N_2 and either taken forward to be derivatized with a chromophore for HPLC analysis or chromatographed by the specifications noted in the characterization of each compound.

2.3 General Procedure for DIBAL-H Reduction of Esters (*Procedure A*)**.** [2] Dichloromethane (0.3 M in substrate) was loaded into a flamed-dried flask and placed under N_2. The ester (1.0 equiv) was added to the solvent and the solution was brought to -78 °C. A 1.0 M solution of DiBAl-H in hexanes (2.2 equiv) was added dropwise. The reaction mixture was allowed to stir for 100 min. Following this, the mixture was brought to 0 °C and an aqueous solution of Rochelle salt was added dropwise until a gel-like substance formed and took up the volume of the flask. Diethyl ether was added, followed by $MgSO_4$, which was added until the particulates were free flowing. The contents of the flask were filtered through a fritted funnel packed first with Celite and topped with $MgSO_4$. The pad of Celite and $MgSO_4$ was washed with Et_2O. The filtrate was concentrated *in vacuo*. The crude residue was chromatographed according to the details specified in the characterization of each compound.

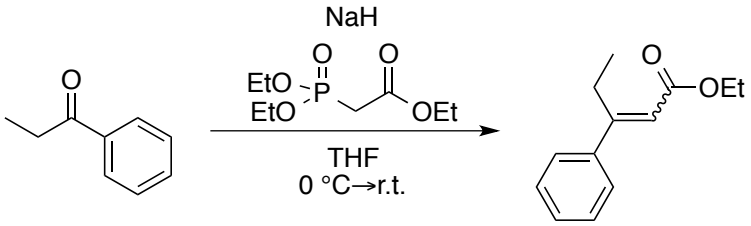
2.4 General Procedure for Derivatization of Epoxide with Benzoyl Chloride (*Procedure B)***.** An aliquot of the crude epoxide (1.0 equiv, assumed to be only epoxide) was delivered to a 2 mL vial and concentrated under a stream of N_2. DMAP (2.5 equiv) was added, and the vial's contents were dissolved in dichloromethane (0.2 M in substrate). Benzoyl chloride was added, and the mixture was allowed to sit for 40-45 minutes. The solution was quenched with sat. aq. $NaHCO_3$ and extracted with hexanes. The top layer of the biphasic mixture (the organic layer) was concentrated under and stream of nitrogen. The mixture was then extracted with EtOAc (x 3) and the combined organic layers were concentrated under a stream of N_2. The crude reside was purified by prep-TLC with a 100% dichloromethane eluent.



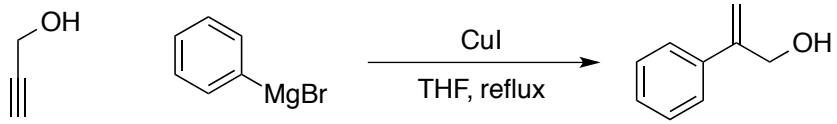
2.5 Preparation of Ethyl (*Z*)-3-phenylacrylate (SI 1):[3] A flame-dried, round bottom flask was charged with ethyl 2-(bis(2,2,2-trifluoroethoxy)phosphoryl)acetate (0.782 g, 2.36 mmol), 18-crown-6 (3.11 g, 11.8 mmol), and anhydrous THF (47.1 mL, 0.05 M in aldehyde). The mixture was then brought to -78 °C and the flask was flushed with N_2. Potassium bis(trimethylsilyl)amide (20% in toluene, 2.72 mL, 2.36 mmol) was added and the mixture was allowed to stir for 30 min. The aldehyde (0.239 mL, 2.36 mmol) was added slowly, and the mixture was stirred until TLC indicated that all of the starting material had been consumed. The reaction mixture was then allowed to come to room temperature, and sat. aq. NH_4Cl was added to the flask. The mixture was diluted with Et_2O and transferred to a separatory funnel. The aqueous layer was extracted twice with

[2] Peris, G.; Jakobsche, C.E.; Miller, S.J. *J. Am. Chem. Soc.* **2007**, *129*, 8710-8711.
[3] Still, W.C.; Gennari, C. *Tet. Lett.* **1983**, *24*. 4405-4408.

Et_2O. The combined organic layers were dried over $NaSO_4$, filtered, and concentrated *in vacuo*. The crude residue was chromatographed on silica (200 mL SiO_2, gradient 10% to 20% EtOAc in hexanes) to yield 0.1815 g (45% yield) of a clear and colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.63–7.51 (m, 2H), 7.39–7.27 (m, 3H), 6.93 (d, J = 12.6 Hz, 1H), 5.94 (d, J = 12.6 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H). **MS:** Exact mass calculated for mass $[C_{11}H_{12}O_2 + H]^+$ requires m/z = 177.09; found 177.09.

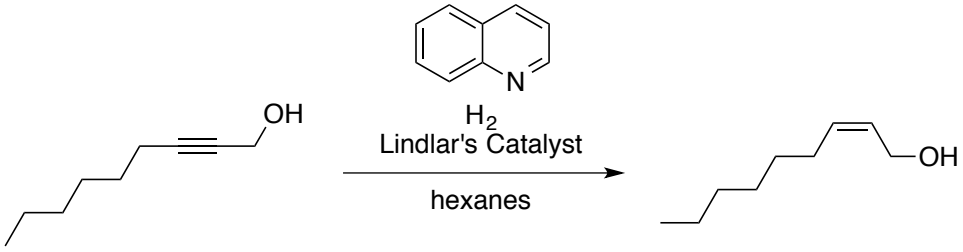


2.6 Preparation of (*E*)- and (*Z*)-Ethyl 3-Phenylpent-2-enoate (SI 2): Dry NaH (0.130 g, 5.40 mmol) was added to a flame-dried 100 mL round-bottom flask equipped with a stir bar. The material was dissolbed in anhydrous THF (18.0 mL) and the vessel was placed in an ice bath. Triethyl phosphonoacetate (1.29 mL, 6.48 mmol) was added slowly *via* syringe and the mixture was allowed to stir at 0 °C for 20 minutes. Following this period, a solution of propiophenone (0.479 mL, 3.60 mmol) in anhydrous THF (5.4 mL) was added to the mixture while it still stirred in the ice bath. The reaction mixture was then allowed to stir at room temperature overnight. The reaction was quenched with sat. aq. NH_4Cl (20 mL). The biphasic mixture was transferred to a separatory funnel containing sat. aq. NH_4Cl (10 mL). The aqueous layer was extracted with Et_2O (10 mL, 3x) and dried over $MgSO_4$. The material was filtered and concentrated *in vacuo*. The crude residue was chromatographed (50 mL SiO_2, 5% to 10% to 15% EtOAc in hexanes gradient) and the (*E*) and (*Z*) isomers were isolated in 0.362 g (49% yield) and 0.198 g (40% yield), respectively. Each isomer was then reduced by DiBAl-H according to the procedure above. (*E*)-ethyl 3-phenylpent-2-enoate: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48–7.26 (m, 5H), 6.01 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.11 (q, J = 7.5 Hz, 2H), 1.36 –1.14 (m, 3H), 1.08 (t, J = 7.5 Hz, 3H). (*Z*)-ethyl 3-phenylpent-2-enoate: **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.32–7.10 (m, 3H), 7.12–6.99 (m, 2H), 5.78 (t, J = 1.4 Hz, 1H), 3.89 (q, J = 7.1 Hz, 2H), 2.36 (qd, J = 7.3, 1.5 Hz, 2H), 0.96 (td, J = 7.2, 2.4 Hz, 6H). **MS:** Exact mass calculated for mass $[C_{13}H_{16}O_2 + H]^+$ requires m/z = 205.12; found 205.12.

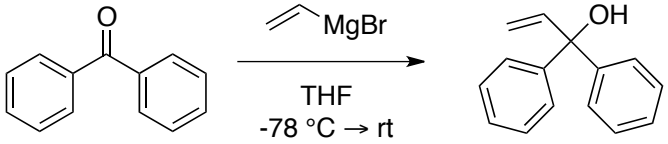


2.7 Preparation of 2-Phenylprop-2-en-1-ol (SI 3): A flame-dried three neck 100 mL round bottom flask was equipped with a cold water condenser and charged with CuI (0.143 g, 0.750 mmol) and a solution of phenyl Grignard (0.5 M in THF, 30 mL). Propargyl alcohol (0.289 mL, 5.00 mmol) in anhydrous THF (5.0 mL) was added slowly to the flask. The solution was allowed to reflux overnight. After cooling, the reaction mixture was quenched with sat. aq. NH_4Cl (30 mL) and transferred to a separatory funnel containing sat. aq. NH_4Cl (10 mL). The aqueous layer was extracted with Et_2O

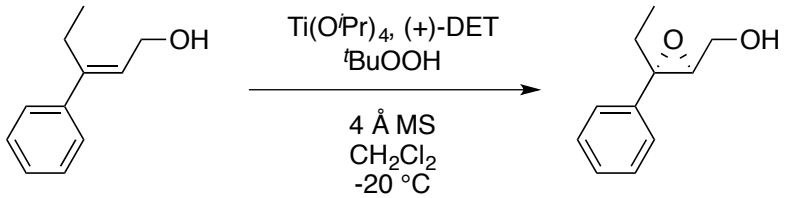
(10 mL, 3x) and dried over $MgSO_4$. The material was filtered and concentrated *in vacuo*. The crude residue was chromatographed (50 mL SiO_2, 30% Et_2O in pentane) to afford 0.242 g (36% yield) of a clear oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49–7.27 (m, 5H), 5.48 (q, J = 1.0 Hz, 1H), 5.36 (q, J = 1.4 Hz, 1H), 4.59–4.50 (m, 2H), 1.68 (s, 1H). **MS:** Exact mass calculated for mass $[C_9H_{10}O + H]^+$ requires m/z = 135.07; found 135.07.



2.8 Preparation of (*Z*)-Non-2-en-1-ol (SI 4): Non-2-yn-1-ol (0.161 mL, 1.00 mmol), quinoline (0.177 mL, 1.50 mmol), Lindlar's Catalyst (0.0168 g), and hexanes (15.7 mL) were loaded into a flame-dried 25 mL round bottom flask. A balloon filled with hydrogen gas was placed on the flask and the flask was sparged with H_2. The mixture was allowed to stir for 1 hour before it was filtered through celite and concentrated *in vacuo*. The desired (*Z*)-non-2-en-1-ol was isolated and chromatographed (50 mL SiO_2, 40% EtOAc in hexanes) to afford 0.128 g (90% yield) of a clear oil. **^{1}H NMR (**500 MHz, $CDCl_3$) δ 5.69–5.52 (m, 2H), 4.22 (d, J = 6.3 Hz, 2H), 2.14–2.02 (m, 2H), 1.45–1.20 (m, 9H), 0.97–0.87 (m, 3H). **MS:** Exact mass calculated for mass $[C_9H_{18}O + H]^+$ requires m/z = 143.14; found 143.02.

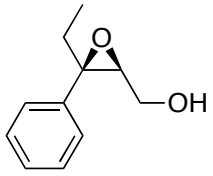


2.9 Preparation of 1,1-Diphenylprop-2-en-1-ol (SI 5): Benzophenone (0.9111 g, 5.00 mmol) was loaded into an oven-dried 100 mL round-bottom flask and dissolved in anhydrous THF (5 mL). The solution was then allowed to come to -78 °C. A solution of 0.6 M vinyl Grignard in THF (26 mL, 15.00 mmol) was cannulated into the benzophenone solution. The reaction mixture was then allowed to stir at -78 °C for two hours. Following these 2 hours, the mixture was allowed to stir for 2 hours at room temperature. The reaction was quenched with ice, poured into a separatory funnel containing sat. aq. NH_4Cl, and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was chromatographed (50 mL SiO_2, eluting with 10% EtOAc in hexanes) to afford a clear and colorless liquid (0.3877 g, 37% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.29 (10H, m), 6.56 (1H, dd, J = 10.4, 17.5 Hz), 5.39 (1H, d, J = 1.3 Hz), 5.35 (1H, s), 2.35 (1H, s). **MS:** Exact mass calculated for mass $[C_{15}H_{14}O - OH]^+$ requires m/z = 193.10; found 193.13.



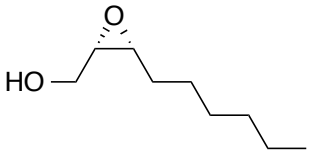
2.10 Sharpless Asymmetric Epoxidation to Determine Absolute Stereochemistry of 16:[4] An oven-dried round bottom flask was equipped with a teflon-coated stir bar, charged with 4 Å molecular sieves (0.025 g), and sparged with N_2. anhydrous DCM (1.59 mL, 0.3 M) was loaded into the flask and mixture was brought to -20 °C. L-(+)-Diethyl tartrate (0.1106 mL, 0.53 mmol) and $Ti(O^iPr)_4$ (0.142 mL, 0.48 mmol) were delievered to the stirring heterogeneous mixture followed by *tert*-butyl hydrogen peroxide (0.1739 mL, 0.96 mmol, 5.5 M in decane). This mixture was allowed to age for 3 h at -20 °C. (*E*)-3-Phenylpent-2-en-1-ol (0.078 g and 0.48 mmol) was added as a solution (2 M) in anhydrous DCM (0.24 mL) and the resulting mixture was allowed to stir -20 °C for 30 min. Following this period, the reaction mixture was brought to 0 °C and 1.00 mL of water were added to the flask. The biphasic mixture was allowed to stir for 30 min as it warmed to room temperature. Then, 2.00 mL of a 30% aqueous solution of NaOH saturated with NaCl was added and the mixture stirred for 10 min. Finally, DCM was added to the mixture and the organic layer was separated. The separated organic layer was then concentrated *in vacuo*. The crude residue was chromatographed with an eluent of 40% Et_2O in pentane to yield a clear and colorless oil. Spectral data, as well as the HPLC order of elution of major and minor enantiomers (See Table SI1), matched that of the (3-ethyl-3-phenyloxiran-2-yl)methanol produced by our method. This confirmed the stereochemical assignment of the epoxide of (*Z*)-3-phenylpent-2-en-1-ol formed *via* our method.

3. Analytical Data

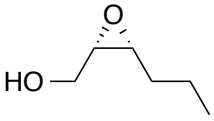


((2*S*,3*R*)-3-Ethyl-3-phenyloxiran-2-yl)methanol (13): R_f = 0.4 (40% EtOAc in hexanes, UV, CAM stain). Material was chromatographed with 40% Et_2O in pentane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45–7.18 (m, 5H), 3.51–3.38 (m, 1H), 3.31 (dd, J = 6.7, 4.2 Hz, 1H), 3.27–3.13 (m, 1H), 2.25–2.06 (m, 1H), 1.78–1.67 (m, 2H), 0.89 (t, J = 7.5 Hz, 3H). $[\alpha]_D^{20} = -58.4°$. **MS:** Exact mass calculated for mass $[C_{11}H_{14}O_2 + H]^+$ requires m/z = 179.11; found 179.11. Absolute stereochemistry determined by X-ray crystallography of bromobenzolyated compound. See attached files on SI-29.

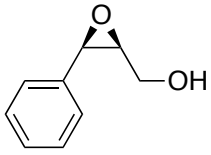
[4] Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765-5780.



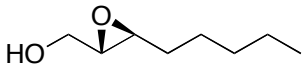
((2*S*,3*R*)-3-Hexyloxiran-2-yl)methanol (14): R_f = 0.5 (50% EtOAc in hexanes, CAM stain). Material was chromatographed with 50% Et_2O in pentane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.85 (m, 1H), 3.66 (m, 1H), 3.15 (dt, J = 7.0, 4.2 Hz, 1H), 3.02 (ddd, J = 6.7, 5.5, 4.3 Hz, 1H), 1.92 (dd, J = 7.1, 4.3 Hz, 1H), 1.65–1.19 (m, 10H), 0.95–0.81 (m, 3H). $[\alpha]_D^{20} = -6.7°$.[5] **MS:** Exact mass calculated for mass $[C_9H_{18}O_2 + H]^+$ requires m/z = 159.14; found 159.13.



((2*S*,3*R*)-3-Propyloxiran-2-yl)methanol (15): R_f = 0.3 (40% EtOAc in hexanes, UV, CAM stain). Material was chromatographed with a gradient of 50% to 60% Et_2O in pentane **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.86 (dd, J = 12.1, 4.1 Hz, 1H), 3.68 (dd, J = 12.1, 6.9 Hz, 1H), 3.16 (dt, J = 6.9, 4.2 Hz, 1H), 3.04 (dtd, J = 6.5, 4.4, 2.0 Hz, 1H), 1.71–1.39 (m, 5H), 1.02–0.92 (m, 3H). $[\alpha]_D^{20} = -3.6°$.[6] **MS:** Exact mass calculated for mass $[C_6H_{12}O_2 + H]^+$ requires m/z = 117.09; found 117.10.



((2*S*,3*R*)-3-Phenyloxiran-2-yl)methanol (16): R_f = 0.6 (70% EtOAc in hexanes, UV, CAM stain). Material was chromatographed with 60% Et_2O in pentane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58–6.90 (m, 5H), 6.54 (dt, J = 11.8, 1.8 Hz, 1H), 5.85 (dt, J = 11.7, 6.4 Hz, 1H), 4.41 (dd, J = 6.4, 1.7 Hz, 2H), 2.10 (s, 1H). $[\alpha]_D^{20} = -33.5°$.[7] **MS:** Exact mass calculated for mass $[C_9H_{10}O_2 + H]^+$ requires m/z = 151.08; found 151.08.



((2*S*, 3*S*)-3-Pentyloxiran-2-yl)methanol (17): R_f = 0.4 (20% EtOAc in hexanes, CAM stain). Material was chromatographed with 20% Et_2O in pentane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.91 (ddd, J = 12.6, 5.1, 2.6 Hz, 1H), 3.62 (ddd, J = 12.6, 6.8, 4.2 Hz, 1H), 2.99-2.88 (m, 1H), 1.80 (t, J = 6.4 Hz, 1H), 1.67 (s, 1 H), 1.63-1.52 (m, 2H), 1.51- 1.38 (m, 2H), 1.37-1.26 (m, 4H), 0.89 (ddt, J = 7.3, 4.9, 1.8 Hz, 3H). $[\alpha]_D^{20} = -19.9°$.[4] **MS:** Exact mass calculated for mass $[C_8H_{16}O_2 + H]^+$ requires m/z = 145.12; found 145.13.

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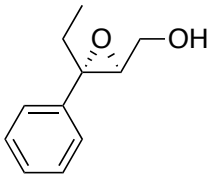
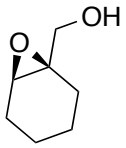
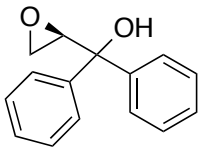
[5] Sarabia, F.; Vivar-Garcia, C.; Carcia-Castro, M.; Martin-Ortiz, J. *J. Org. Chem.* **2011**, *76*, 3129-3150.
[6] Katsuki, T.; Oguma, T.; Egami, H. *J. Am. Chem. Soc.* **2010**, *132*, 5886-5895.
[7] Wang, B.; Wu, X.-Y.; Wong, O.A.; Nettles, B.; Zhao, M.-X.; Chen, D.; Shi, Y. *J. Org. Chem.* **2009**, *74*, 3986-3989.



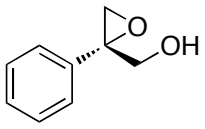
((2*S*,3*S*)-3-Ethyl-3-phenyloxiran-2-yl)methanol (18): R_f = 0.4 (40% EtOAc in hexanes, UV, CAM stain). Material was chromatographed with 40% Et_2O in pentane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.18 (m, 5H), 3.99 (m, 1H), 3.85 (m, 1H), 3.12 (dd, *J* = 6.6, 4.3 Hz, 1H), 2.13 (dq, *J* = 14.2, 7.6 Hz, 1H), 1.98 (m, 1H), 1.79 (dq, *J* = 14.6, 7.4 Hz, 1H), 0.94 (t, *J* = 7.5 Hz, 3H). $[\alpha]_D^{20} = -2.5°$.[8] **MS:** Exact mass calculated for mass $[C_{11}H_{14}O_2 + H]^+$ requires m/z = 179.11; found 179.11. Absolute stereochemistry determined by analogy to product epoxidized using Sharpless Asymmetric Epoxidation conditions. See SI-7 for details.



((1*R*,6*R*)-7-Oxabicyclo[4.1.0]heptan-1-yl)methanol (19): R_f = 0.3 (60% EtOAc in hexanes, UV, CAM stain). Material was chromatographed with 60% Et_2O in pentane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.61 (dd, *J* = 12.2, 4.0 Hz, 1H), 3.52 (dd, *J* = 12.1, 8.8 Hz, 1H), 3.20 (dt, *J* = 3.7, 1.1 Hz, 1H), 2.01-1.84 (m, 1H), 1.84-1.69 (m, 3H), 1.69-1.55 (m, 1H), 1.49-1.30 (m, 2H), 1.22 (dddd, *J* = 14.1, 9.0, 4.1, 2.6 Hz, 2H). $[\alpha]_D^{20} = 3.5$.[9] **MS:** Exact mass calculated for mass $[C_7H_{12}O_2 + H]^+$ requires m/z = 129.09; found 129.10.



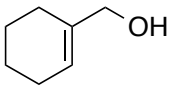
(*R*)-Oxiran-2-yldiphenylmethanol (20): R_f = 0.6 (20% EtOAc in hexanes, UV, CAM stain). Material was chromatographed with via preparatory TLC with an eluent of 20% EtOAc in hexanes. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.46 (m, 2H), 7.42–7.27 (m, 8H), 3.81 (dd, *J* = 4.0, 2.7 Hz, 1H), 3.00 (dd, *J* = 5.1, 2.7 Hz, 1H), 2.80 (dd, *J* = 5.1, 4.0 Hz, 1H), 2.54 (s, 1H). **MS:** Exact mass calculated for mass $[C_{15}H_{14}O_2 + H]^+$ requires m/z = 227.11; found 227.11. The absolute stereochemistry was determined by comparison to reported HPLC elution times of enantiomers.[10]



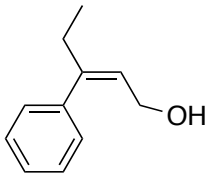
(*S*)-(2-Phenyloxiran-2-yl)methanol (21): R_f = 0.4 (20% EtOAc in hexanes, UV, CAM stain). Material was chromatographed with 40% Et_2O in pentane. **^{1}H**

[8] Wang, B.; Wong, O.A.; Zhao, M.-X.; Shi, Y. *J. Org. Chem.* **2008**, *73*, 9539-9543.
[9] Lifchits, O.; Mahlau, M.; Reisinger, C.M.; Lee, A.; Fares, C.; Polyak, I.; Gopakumar, G.; Theil, W.; List, B. *J. Am. Chem. Soc.* **2013**, *135*, 6677-6693.
[10] Olivares-Romero, J.L.; Li, Z.; Yamamoto, H. *J. Am. Chem. Soc.* **2013**, *135*, 3411-3413.

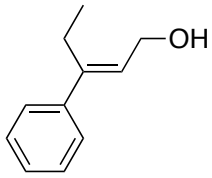
NMR (400 MHz, $CDCl_3$) δ 7.48–7.43 (m, 2H), 7.39–7.28 (m, 3H), 5.48 (q, J = 1.0 Hz, 1H), 5.36 (q, J = 1.4 Hz, 1H), 4.56 (ddd, J = 6.2, 1.4, 0.8 Hz, 2H), 1.55 (d, J = 4.5 Hz, 1H). $[\alpha]_D^{20} = -6.8°$.[8] **MS:** Exact mass calculated for mass $[C_9H_{10}O_2 + H]^+$ requires m/z = 151.08; found 151.08.



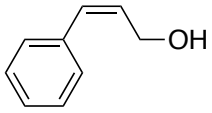
Cyclohex-1-en-1-ylmethanol (SI 6): Prepared from the corresponding ester using SI-2.3. R_f=0.5 (40% EtOAc in hexanes, CAM stain). Material was chromatographed with 40% Et_2O in pentane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.68 (broad s, 1H), 3.98 (d, J = 1.6 Hz, 2H), 2.02 (m, 4H), 1.71–1.50 (m, 4H), 0.92 (d, J = 6.7 Hz, 1H). **MS:** Exact mass calculated for mass $[C_7H_{12}O + H]^+$ requires m/z = 113.10; found 113.04.



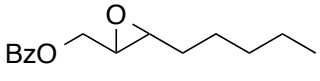
(*Z*)-3-Phenylpent-2-en-1-ol (SI 7): Prepared from the corresponding ester using SI-2.3. **R_f** = 0.4 (40% EtOAc in hexanes, UV, CAM stain). Material was chromatographed with 40% Et_2O in pentane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.22 (m, 3H), 7.16–7.07 (m, 2H), 5.66 (tt, J = 7.0, 1.4 Hz, 1H), 4.03 (dt, J = 6.9, 1.0 Hz, 2H), 2.39 (qq, J = 7.1, 1.1 Hz, 2H), 1.60–1.47 (m, 1H), 0.99 (t, J = 7.4 Hz, 3H). **MS:** Exact mass calculated for mass $[C_{11}H_{14}O + H]^+$ requires m/z = 163.11; found 163.09.



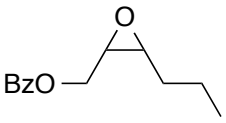
(*E*)-3-Phenylpent-2-en-1-ol (SI 8): Prepared from the corresponding ester using SI-2.3. **R_f** = 0.3 (20% EtOAc in hexanes, UV, CAM stain). Material was chromatographed with 40% Et_2O in pentane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56–7.07 (m, 5H), 5.83 (t, J = 6.8 Hz, 1H), 4.34 (d, J = 6.8 Hz, 2H), 2.53 (q, J = 7.5 Hz, 2H), 1.87–1.66 (m, 1H), 0.98 (t, J = 7.6 Hz, 3H). **MS:** Exact mass calculated for mass $[C_{11}H_{14}O + H]^+$ requires m/z = 163.11; found 163.08.



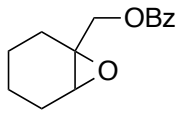
(*Z*)-3-Phenylprop-2-en-1-ol (SI 9): Prepared from the corresponding ester using SI-2.3. **R_f** = 0.3 (30% EtOAc in hexanes, UV, CAM stain). Material was chromatographed with a gradient of 10% to 20% to 30% Et_2O in pentane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58–6.90 (m, 5H), 6.54 (dt, J = 11.8, 1.8 Hz, 1H), 5.85 (dt, J = 11.7, 6.4 Hz, 1H), 4.41 (dd, J = 6.4, 1.7 Hz, 2H), 2.10 (s, 1H). **MS:** Exact mass calculated for mass $[C_9H_{10}O - OH]^+$ requires m/z = 117.07; found 117.04.



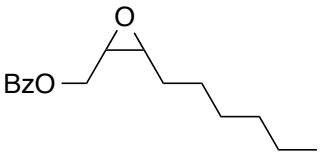
(3-Pentyloxiran-2-yl)methyl benzoate (SI 10): Prepared from corresponding alcohol using SI-2.4. $\mathbf{R_f}$ = 0.5 (40% EtOAc in hexanes, UV, CAM stain). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10–8.04 (m, 2H), 7.61–7.54 (m, 1H), 7.49–7.41 (m, 2H), 4.60 (dd, J = 12.2, 3.4 Hz, 1H), 4.20 (dd, J = 12.2, 6.2 Hz, 1H), 3.14–3.07 (m, 1H), 2.94 (td, J = 5.6, 2.2 Hz, 1H), 1.63–1.57 (m, 1H), 1.48 (dq, J = 11.5, 7.8, 7.3 Hz, 2H), 1.38–1.28 (m, 5H), 0.94–0.84 (m, 3H). **MS:** Exact mass calculated for mass $[C_{15}H_{20}O_3 + H]^+$ requires m/z = 249.15; found 249.15.



(3-Propyloxiran-2-yl)methyl benzoate (SI 11): Prepared from corresponding alcohol using SI-2.4. $\mathbf{R_f}$ = 0.5 (100% DCM, UV, CAM stain). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12–8.05 (m, 2H), 7.64–7.52 (m, 1H), 7.50–7.40 (m, 2H), 4.58 (dd, J = 12.1, 4.3 Hz, 1H), 4.30 (dd, J = 12.1, 7.0 Hz, 1H), 3.33 (dt, J = 7.1, 4.3 Hz, 1H), 3.08 (td, J = 6.1, 4.3 Hz, 1H), 1.72–1.41 (m, 4H), 1.06–0.88 (m, 3H). **MS:** Exact mass calculated for mass $[C_{13}H_{16}O_3 + H]^+$ requires m/z = 221.12; found 221.12.

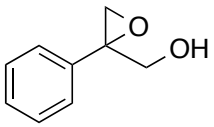
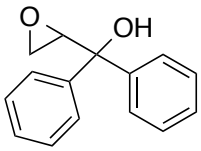
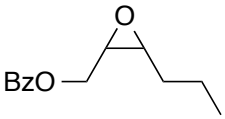
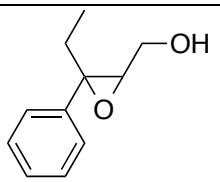
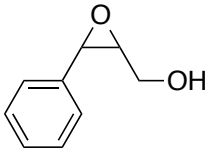
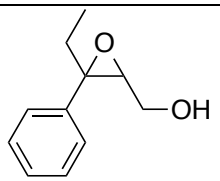
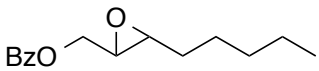
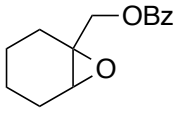
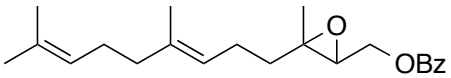


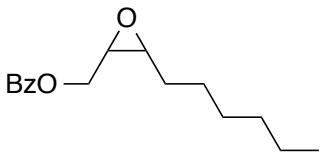
(7-Oxabicyclo[4.1.0]heptan-1-yl)methyl benzoate (SI 12): Prepared from corresponding alcohol using SI-2.4. $\mathbf{R_f}$ = 0.2 (100% DCM, UV, CAM stain). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12–7.94 (m, 2H), 7.62–7.54 (m, 1H), 7.50–7.38 (m, 2H), 4.47 (d, J = 11.9 Hz, 1H), 4.19 (d, J = 11.9 Hz, 1H), 3.21 (dt, J = 3.6, 1.1 Hz, 1H), 2.11–1.81 (m, 4H), 1.48 (tdt, J = 9.6, 7.6, 5.3 Hz, 2H), 1.36–1.19 (m, 2H). **MS:** Exact mass calculated for mass $[C_{14}H_{16}O_3 + H]^+$ requires m/z = 233.12; found 233.11.



(3-Hexyloxiran-2-yl)methyl benzoate (SI 13): Prepared from corresponding alcohol using SI-2.4. $\mathbf{R_f}$ = 0.5 (100% DCM, UV, CAM stain). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05–7.96 (m, 2H), 7.51 (ddt, J = 7.9, 6.9, 1.4 Hz, 1H), 7.43–7.32 (m, 2H), 4.57–4.44 (m, 1H), 4.24 (dd, J = 12.1, 7.0 Hz, 1H), 3.26 (dt, J = 7.0, 4.3 Hz, 1H), 3.00 (ddd, J = 6.7, 5.8, 4.3 Hz, 1H), 1.63–1.15 (m, 10H), 0.82 (td, J = 5.7, 4.8, 2.2 Hz, 3H). **MS:** Exact mass calculated for mass $[C_{16}H_{22}O_3 + H]^+$ requires m/z = 263.16; found 263.16.

Table SI1: HPLC Conditions

Substrate	Column[a]	Conditions
	Chiralcel AS-H	5% ^{i}PrOH in hexanes, 1.0 mL/min, 40 min Major: 15.1 min, Minor: 23.0 min Observed at 210 nm
	Chiralcel AD-H	7% EtOH in hexanes, 1.0 mL/min, 20 min Minor: 8.2 min, Major: 9.7 min Observed at 210 nm
	Chiralcel OJ-H	1% ^{i}PrOH in hexanes, 1.0 mL/min, 20 min Minor: 11.1 min, Major: 12.9 min Observed at 230 nm
	Chiralcel OJ	10% ^{i}PrOH in hexanes, 1.0 mL/min, 20 min Major: 9.4 min, Minor: 13.6 min Observed at 210 nm
	Chiralcel OD-H	7% ^{i}PrOH in hexanes, 1.0 mL/min, 20 min Minor: 10.7 min, Major: 13.9 min Observed at 230 nm
	Chiralcel OJ-H	7% ^{i}PrOH in hexanes, 1.0 mL/min, 20 min Minor: 11.0 min, Major: 12.9 min Observed at 210 nm
	Chiralcel OJ-H	1% ^{i}PrOH in hexanes, 1.0 mL/min, 20 min Major: 8.4 min, Minor: 9.9 min Observed at 230 nm
	Chiralcel AD-H	1% ^{i}PrOH in hexanes, 1.0 mL/min, 20 min Minor: 8.6 min, Major: 10.2 min Observed at 230 nm
	Chiralcel OJ-H	1% ^{i}PrOH in hexanes, 1.0 mL/min, 20 min Major: 8.5 min, Minor: 14.8 min Observed at 230 nm

	Chiralcel OJ-H	1% ^{i}PrOH in hexanes, 1.0 mL/min, 20 min Minor: 8.4 min, Major: 10.0 min Observed at 230 nm

[a]All columns used have the dimensions 4.6 mm Φ × 250 mm

4. General Protocols for Truncated Peptide Synthesis

4.1 Solution peptide synthesis. To peptide acid (1 equiv) was added amine coupling partner (1.0-1.1 equiv), EDC•HCl (1.1 equiv), HOBt•H_2O (1.1 equiv), and DCM (to 0.1 M in peptide acid). $^{i}Pr_2EtN$ or Et_3N (1.2 equiv) was also added if the amine coupling partner was the hydrochloride salt. The resulting solution was allowed to stir until the reaction was deemed complete as determined by LCMS, usually 3-48 h. The reaction solution was diluted with additional DCM and then washed with aqueous 0.5 M citric acid, half-saturated brine, and sat. aq. $NaHCO_3$. The combined organics were dried over Na_2SO_4, filtered, and concentrated.

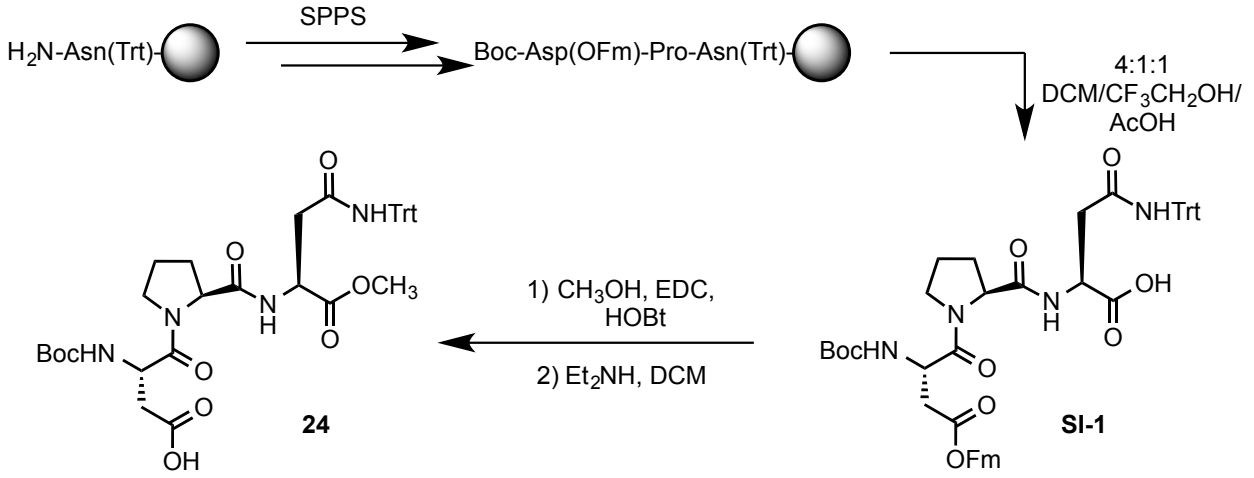
4.2 Solid phase peptide coupling protocol. To pre-swollen resin was added Fmoc-protected amino acid (3 equiv), HBTU (3 equiv), HOBt•H_2O (3 equiv) with DMF, followed by $^{i}Pr_2EtN$ (6 equiv). The resin mixture was sealed and mixed for 3-6 h on a rotary mixer and then drained, washing with a combination of DMF, DCM, and/or CH_3OH. If required for the next coupling, the Fmoc-protecting group was removed with two treatments of 20% piperidine in DMF (v/v) for 20 min each.

4.3 Standard Fm-ester deprotection. To protected peptide was added 1:1 (v/v) solution of Et_2NH and DCM. The resulting solution was swirled occasionally over the course of 30-60 min before concentrating via rotary evaporator. The resulting material was dissolved in DCM and then concentrated further. Typically, the crude material was loaded on a silica gel column as a solution in DCM, where it was eluted with a gradient of 1% CH_3OH to 4% CH_3OH in 1% AcOH/DCM.

5. Synthesis and Characterization of Truncated Peptides

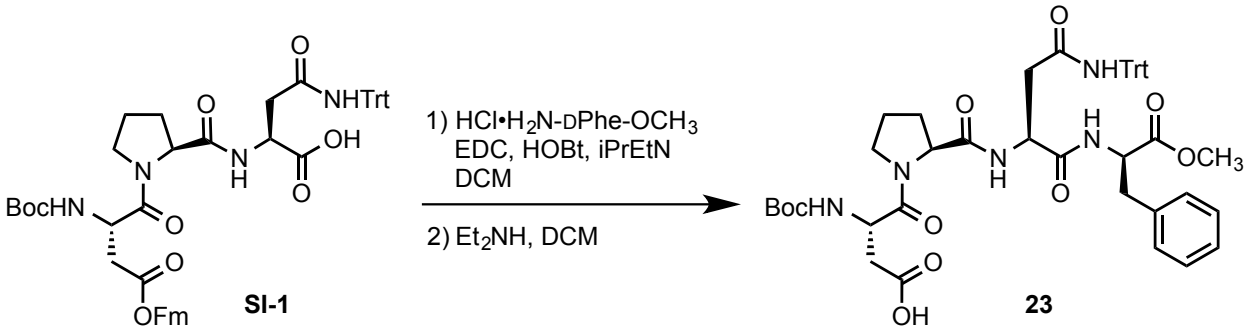
Synthesis of peptides **23** and **24** began from common intermediate **SI-1** (SI Figure 1), which was synthesized starting with 2-chlorotrityl resin, preloaded with Asn(Trt), and then coupling the appropriate amino acid monomers (Fmoc-Pro-OH and then Boc-Asp(OFm)-OH) using the Solid Phase Peptide Coupling protocol. Resin was cleaved with a 4:1:1 mixture of DCM: 2,2,2-trifluoroethanol: acetic acid, treating for 30-60 min before draining. The resulting solution, along with washes, was concentrated a couple of times with additional toluene. The concentrated material was purified by eluting through a silica gel column with a gradient of 1% CH_3OH/1% AcOH to 4% CH_3OH/1% AcOH in DCM. Collection and concentration resulted in a flaky solid with a light brownish color.

SI Figure 1.



Intermediate **SI-1** was coupled to CH_3OH, which was used as co-solvent with DCM using the Solution Peptide Synthesis protocol. After work-up, the crude material was deprotected using the Standard Fm-ester Deprotection protocol, and upon concentration, was purified with a silica gel column eluted with a gradient of 1% to 4% CH_3OH in 1% AcOH/DCM (as described in the standard protocol). A portion of this material was further purified by reverse phase chromatography using a Biotage C18 column eluting with a gradient of 40% CH_3OH to 100% CH_3OH in water with 0.1% formic acid.

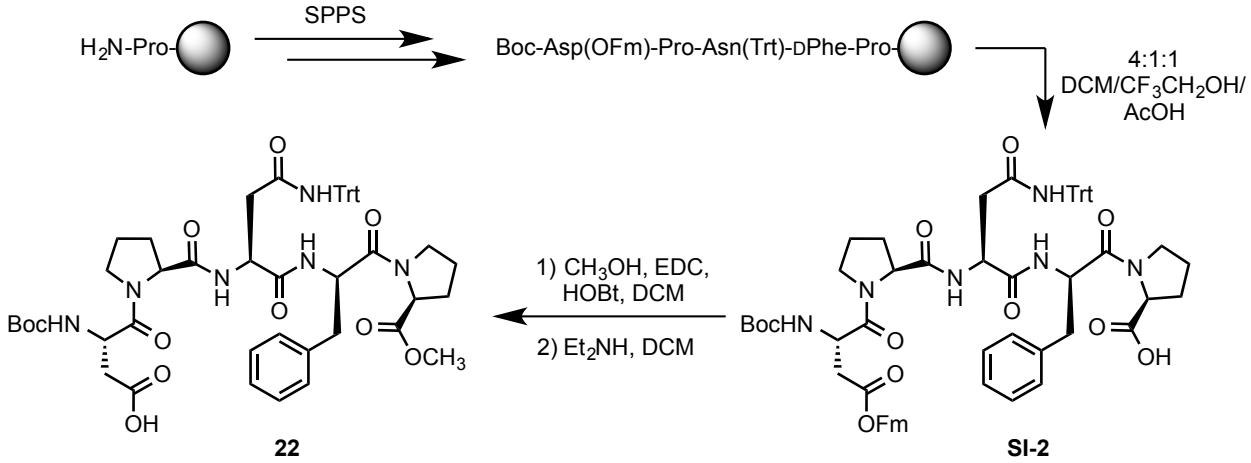
Peptide **24**: White solid. **TLC**: 5% CH_3OH, 1% AcOH in DCM (R_f =0.38), visualized by UV, I_2/silica, and CAM stain. **^{1}H NMR** (500 MHz, $CDCl_3$, 20 mM): δ 7.33 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.21 (m, 9H), 7.20 – 7.13 (m, 6H), 7.10 (s, 1H), 5.20 (d, *J* = 8.7 Hz, 1H), 4.78 (dt, *J* = 12.7, 6.2 Hz, 1H), 4.62 (dt, *J* = 8.0, 5.0 Hz, 1H), 4.48 (dd, *J* = 8.4, 3.3 Hz, 1H), 3.77 (t, *J* = 6.7 Hz, 2H), 3.64 (s, 3H), 2.98 – 2.89 (m, *J* = 4.6 Hz, 2H), 2.85 (dd, *J* = 16.5, 9.6 Hz, 1H), 2.61 (dd, *J* = 16.3, 4.5 Hz, 1H), 2.17 – 2.10 (m, 1H), 2.10 – 1.99 (m, 1H), 1.99 – 1.86 (m, 2H), 1.43 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 172.6, 171.7, 171.3, 171.1, 169.9, 155.1, 144.3, 128.8, 128.1, 127.3, 80.5, 71.1, 60.7, 52.8, 49.6, 48.3, 47.6, 38.7, 37.8, 29.3, 28.5, 24.5. **IR** (film in/from DCM, cm^{-1}): 3318, 2977, 1711, 1648, 1510, 1492, 1446, 1367, 1162. **HRMS**: calculated mass for $[C_{38}H_{44}N_4O_9+H]^+$ requires m/z = 701.3181, ESI+ found 701.3165.



Intermediate **SI-1** was coupled to HCl•H-DPhe-OCH_3 using the Solution Peptide Synthesis protocol. After work-up, the crude material was deprotected using the Standard Fm-ester Deprotection protocol, and upon concentration, was purified with a

silica gel column eluted with a gradient of 1% to 3% CH_3OH in 1% AcOH/DCM (as described in the standard protocol). A portion of this material was further purified by reverse phase chromatography using a Biotage C18 column eluting with a gradient of 40% CH_3CN to 100% CH_3CN in water with 0.1% formic acid. This material was used for characterization and for one of the two reactions with farnesol.

Peptide **23**: white solid. **TLC**: 5% CH_3OH, 1% AcOH in DCM (R_f =0.42) visualized by UV, I_2/silica, and CAM stain. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.43 – 7.32 (m, 2H, estimated), 7.30 – 7.16 (m, 16H, estimated based on zTOCSY and expected integration), 7.16 – 7.10 (m, 6H), 5.29 (d, *J* = 9.1 Hz, 1H), 4.74 (td, *J* = 8.7, 4.4 Hz, 1H), 4.69 (td, *J* = 7.8, 4.9 Hz, 1H), 4.54 (dt, *J* = 8.2, 6.9 Hz, 1H), 4.44 (dd, *J* = 8.6, 4.7 Hz, 1H), 3.72 – 3.65 (m, 1H), 3.61 (s, 3H), 3.58 – 3.49 (m, 1H), 3.12 – 3.02 (m, part of an unresolved ABX pattern 2H), 2.88 (dd, *J* = 15.8, 8.5 Hz, 1H), 2.84 – 2.73 (m, part of an unresolved ABX pattern, 2H), 2.66 (dd, *J* = 15.8, 4.6 Hz, 1H), 2.19 – 2.10 (m, 1H), 2.01 – 1.92 (m, 1H), 1.88 – 1.79 (m, 1H), 1.79 – 1.69 (m, 1H), 1.43 (s, 9H). **^{13}C NMR** (151 MHz, 20 mM in $CDCl_3$): δ 173.6, 172.5, 171.5, 171.2, 170.9, 169.9, 155.0, 144.4, 136.3, 129.4, 128.8, 128.6, 128.0, 127.1, 127.1, 80.5, 70.9, 61.6, 55.0, 52.7, 50.2, 48.8, 47.8, 38.6, 37.5, 37.2, 29.4, 28.4, 24.8. Other less intense peaks possibly from another conformer or an impurity were also identified: δ 133.1, 129.8, 128.5, 69.4, 64.1. **IR** (film in/from DCM, cm^{-1}): 3312, 1712, 1666, 1635, 1511, 1493, 1446, 1367, 1266, 1249, 1213, 1162. **HRMS**: calculated mass for $[C_{47}H_{53}N_5O_{10}+H]^+$ requires m/z = 848.3865, ESI+ found 848.3868.



Peptide **22** was synthesized starting with 2-chlorotrityl resin preloaded with proline, and then coupling the appropriate amino acid monomers (Fmoc-DPhe-OH, Fmoc-Asn(Trt)-OH, Fmoc-Pro-OH, and then Boc-Asp(OFm)-OH) using the Solid Phase Peptide Coupling protocol. Resin was cleaved with a 4:1:1 mixture of DCM: 2,2,2-trifluoroethanol: acetic acid, treating for about 1 h before draining. The resulting solution, along with washes, was concentrated a couple of times with additional toluene. The concentrated material was purified by eluting through a silica gel column with a gradient of 1% CH_3OH/1% AcOH to 4% CH_3OH/1% AcOH in DCM. The fractions were then collected and concentrated to afford **SI-2**.

Intermediate **SI-2** was coupled to CH_3OH, which was used as solvent along with DCM (1:1 CH_3OH:DCM to *ca.* 0.05 M) using the Solution Peptide Synthesis protocol. After work-up, the crude material was deprotected using the Standard Fm-ester Deprotection protocol, and upon concentration, was purified with a silica gel column eluting with a gradient of 1% to 4% CH_3OH in 1% AcOH/DCM (as described in the standard protocol). A portion of this material was further purified by reverse phase chromatography using a Biotage C18 column eluting with a gradient of 10% CH_3CN to 100% CH_3CN in water with 0.1% formic acid. This material was used for characterization and for one of the two reactions with farnesol.

Peptide **22**: white solid. **TLC**: 5% CH_3OH, 1% AcOH in DCM (R_f =0.42), visualized by UV, I_2/silica, and CAM stain. NMR indicates a mixture of species that are present in a mixture of approximately 7:3, which we suspect to be rotamers. Although, we cannot exclude the possibility of epimers, the material appears as a single peak by UPLC. Furthermore, the proton chemical shift data are consistent with what might be observed for amide rotamers about the *i*+4 DPhe and *i*+5 Pro. Variable temperature 1D NMR studies from ambient temperature to 60 ºC in $CDCl_3$ were inconclusive, although two sets of peaks assigned to N*H*-Asp and *α*-Asn(Trt) did seem to coalesce, which suggests that there may be additional rotamers present. Data for the major isomer is as follows, where the assignment of integration values was assisted by zTOCSY and the peak assignments were made by referencing gCOSY, zTOCSY, and HMBC: **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.46 (s, 1H, Asn(N*H*), 7.34 – 7.16 (m, 19H), 7.16 – 7.11 (m, 2H), 7.04 (d, *J* = 8.3 Hz, 1H), 5.47 (d, *J* = 9.2 Hz, 1H), 4.85 – 4.79 (m, 1H, *α*-Asp), 4.76 (td, *J* = 8.6, 4.9 Hz, 1H, *α*-Asn(Trt)), 4.63 (dt, *J* = 10.1, 6.2 Hz, 1H, *α*-DPhe), 4.44 (dd, *J* = 8.7, 5.1 Hz, 1H, *α*-Pro(2)), 4.24 – 4.18 (m, 1H, *α*-Pro(5), overlaps with peak from minor isomer *α*-DPhe), 3.87 – 3.80 (m, 1H, *δ*-Pro(5)), 3.70 – 3.65 (m, 1H, *δ*-Pro(2)), 3.65 – 3.58 (m, 1H, *δ*-Pro(2)) overlaps with peak from minor isomer 2 *δ*-Pro(5)), 3.57 (s, 3H), 3.16 – 3.03 (m, 2H, *β*-DPhe), 2.98 – 2.85 (m, 2H, *β*-Asn/Asp), 2.77 – 2.69 (m, 1H, *β*-Asp), 2.67 – 2.59 (m, 2H, *β*-Asn and *δ*-Pro(5)), 2.23 – 2.11 (m, 1H, *β*-Pro(2), overlaps with peak from minor isomer 2*β*-Pro(5)), 2.00 – 1.71 (m, 6H), 1.55 – 1.47 (m, 1H), 1.40 (s, 9H). Peaks with different chemical shifts assigned to the minor isomer are as follows: 6.99 (d, *J* = 8.8 Hz, 1H, N*H*-Asn), 5.52 (d, *J* = 9.2 Hz, 1H, N*H*-Asp), 5.20 (dd, *J* = 7.9, 3.1 Hz, 1H, *α*-Pro(5)), 4.71 (dt, *J* = 8.5, 4.2 Hz, 1H, *α*-Asn(Trt)), 4.48 (dd, *J* = 8.7, 4.8 Hz, 1H, *α*-Pro(2)), 3.72 (s, 3H), 1.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 173.8, 173.6, 172.7, 172.5, 172.1, 171.6, 171.3, 171.3, 170.6, 170.3, 169.0, 168.9, 155.2, 155.1, 144.7, 144.7, 137.1, 136.2, 129.5, 129.4, 128.9, 128.8, 128.7, 128.6, 128.0, 128.0, 127.3, 127.1, 127.0, 80.5, 70.7, 61.9, 61.8, 60.0, 59.5, 54.7, 53.8, 52.8, 52.3, 50.7, 50.0, 49.2, 47.7, 47.5, 47.4, 47.3, 39.5, 37.7, 37.6, 37.5, 36.6, 31.3, 29.6, 29.5, 29.0, 28.4, 28.4, 24.9, 24.8, 24.4, 22.6. **IR** (film in/from DCM, cm^{-1}): 3326, 3058, 3030, 2977, 2879, 1750, 1713, 1676, 1656, 1626, 1518, 1482, 1447, 1366, 1276, 1249, 1197, 1172. **HRMS**: calculated mass for $[C_{52}H_{60}N_6O_{11}+H]^+$ requires m/z = 945.4393, ESI+ found 945.4398.

6. Kinetics

6.1 Procedure for Determining Response Factor (f_r) of Dodecane Internal Standard: Three standard solutions of *cis*-hex-2-en-1-ol and dodecane in $CHCl_3$ (filtered through basic Al_2O_3 prior to mixing with substrates) were prepared in a 10.00 mL volumetric flask. The 1:1 solution was prepared with 0.0545 mL of dodecane (0.250 mmol) and 0.030 mL of *cis*-hex-2-en-1-ol. (0.250 mmol) The 2:1 solution was prepared with 0.055 mL of dodecane (0.250 mmol) and 0.015 mL of *cis*-hex-2-en-1-ol (0.125 mmol). Finally, the 4:1 solution was prepared with 0.055 mL of dodecane (0.250 mmol) and 0.0074 mL of *cis*-hex-2-en-1-ol (0.063 mmol). An aliquot of each standard solution was dissolved in hexanes and analyzed by GC. The formula

$$f_r = \left(\frac{[\text{standard}]}{[\text{analyte}]}\right)\left(\frac{\text{area}_{\text{analyte}}}{\text{area}_{\text{standard}}}\right)$$

was evaluated and the value was used to calculate the concentration of *cis*-hex-2-en-1-ol in the reaction mixture during various time points (procedure detailed below). The average f_r was found to be 0.38 ± 0.04.

6.2 Procedure for Gathering Kinetics Data

Gas Chomatographic Method: 250 °C inlet, 280 °C detector, flow 1.5 mL/min, oven temperature program: 60 °C for 2 min; 2 °C/min ramp to 112 °C; 10 °C/min ramp to 170 °C; hold at 170 °C for 2 min. *cis*-Hex-2-en-1-ol appears at 6.10 min and dodecane appears at 22.1 min.

With peptide catalyst: A standard solution of 4-dimethylamino pyridine (0.024 g, 0.20 mmol), hydroxybenzotriazole (0.031 g, 0.20 mmol), dodecane (0.436 mL, 2.00 mmol), and *cis*-hex-2-en-1-ol (0.236 mL, 2.00 mmol) in $CDCl_3$ (10.00 mL, filtered through basic Al_2O_3) was prepared in a volumetric flask. Eight 2 dram vials were fitted with Teflon-coated stir bars and caps. Each vial was charged with peptide catalyst (0.020 g, 0.016 mmol). Aliquots of the standard solution (0.780 mL) were delivered to each of the eight vials. An aqueous 30% w/w solution of H_2O_2 (0.035 mL, 0.34 mmol) was delivered via micropipette and each vial was placed in an ice bath. *N,N*'-Diisopropylcarbodiimide (DIC) (0.025 mL, 0.16 mmol) was added to each vial and the time was noted. A single aliquot from each vial was taken at the 8 time points throughout the course of the reaction from 5 minutes after the addition of DIC until 7 h after its addition. The aliquots were passed through a plug of solid sodium sulfite with dichloromethane and analyzed via GC. The concentration of *cis*-hex-2-en-1-ol at each time point was determined from the formula

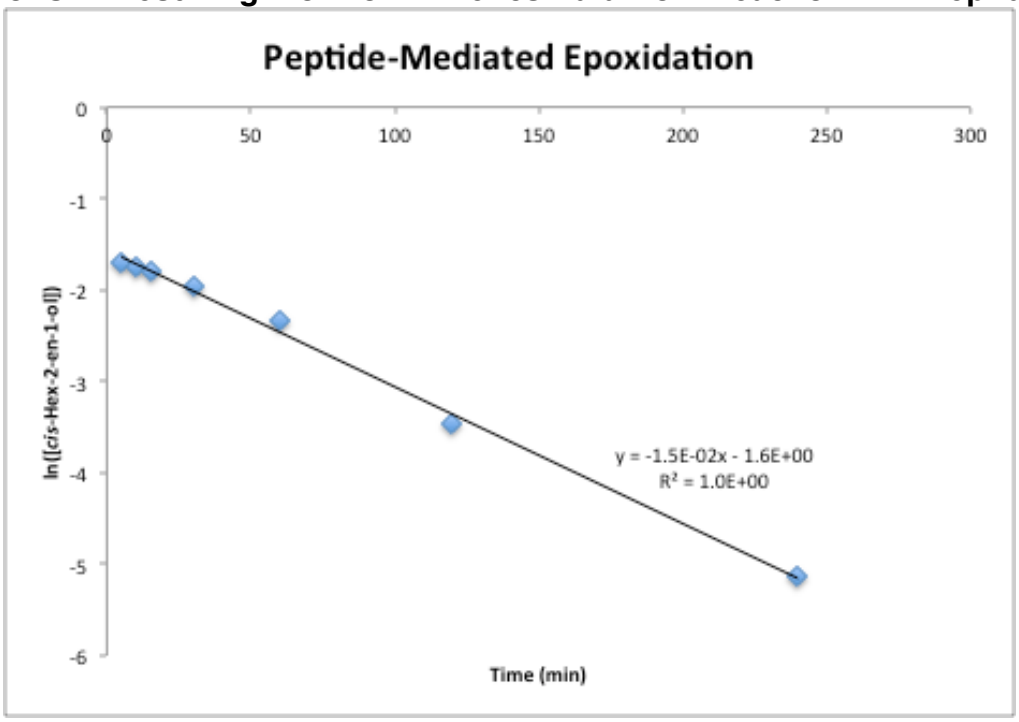
$$[\text{analyte}] = \left(\frac{[\text{standard}]}{f_r}\right)\left(\frac{\text{area}_{\text{analyte}}}{\text{area}_{\text{standard}}}\right)$$

where f_r=0.38.

Table SI2: Raw Kinetics Data from Reaction with Peptide

Time (min)	Hex-2-en-1-ol (area)	[hex-2-en-1-ol] (M)	Dodecane (area)	ln[hexenol]
5	831.93	0.18	2371.55	-1.69
10	919.26	0.17	2796.77	-1.76
15	865.99	0.17	2739.44	-1.80
30	787.30	0.14	2902.61	-1.95
60	584.72	0.10	3145.62	-2.33
120	183.56	0.03	3076.86	-3.46
240	32.31	0.01	2892.94	-5.14
420	31.89	0.01	2902.69	-5.16

Plot SI1: Resulting Plot from Kinetics Data from Reaction with Peptide



With propionic acid: A standard solution of 4-dimethylamino pyridine (0.200 mmol, 0.0244 g), hydroxybenzotriazole (0.200 mmol, 0.0306 g), propionic acid (0.200 mmol, 0.0149 mL), dodecane (2.00 mmol, 0.436 mL), and *cis*-hex-2-en-1-ol (2.00 mmol, 0.236 mL) in $CDCl_3$ (10.00 mL, filtered through basic Al_2O_3) was prepared in a volumetric flask. Eight, 2 dram vials were fitted with Teflon-coated stir bars and caps. Each vial was charged with peptide catalyst (0.0156 mmol, 0.0203 g). Aliquots of the standard solution (0.780 mL) were delivered to each of the eight vials. An aqueous 30% w/w solution of H_2O_2 (0.343 mmol, 0.0354 mL) was delivered via micropipette and each vial was placed in an ice bath. *N,N'*-Diisopropylcarbodiimide (DIC) (0.156 mmol, 0.0245 mL) was added to each vial and the time was noted. A single aliquot from each vial was taken at the 8 time points throughout the course of the reaction from 5 minutes after the addition of DIC until 7 h after its addition. The aliquots were passed through a plug of solid sodium

sulfite with dichloromethane and analyzed via GC. The concentration of *cis*-hex-2-en-1-ol at each time point was determined from the formula

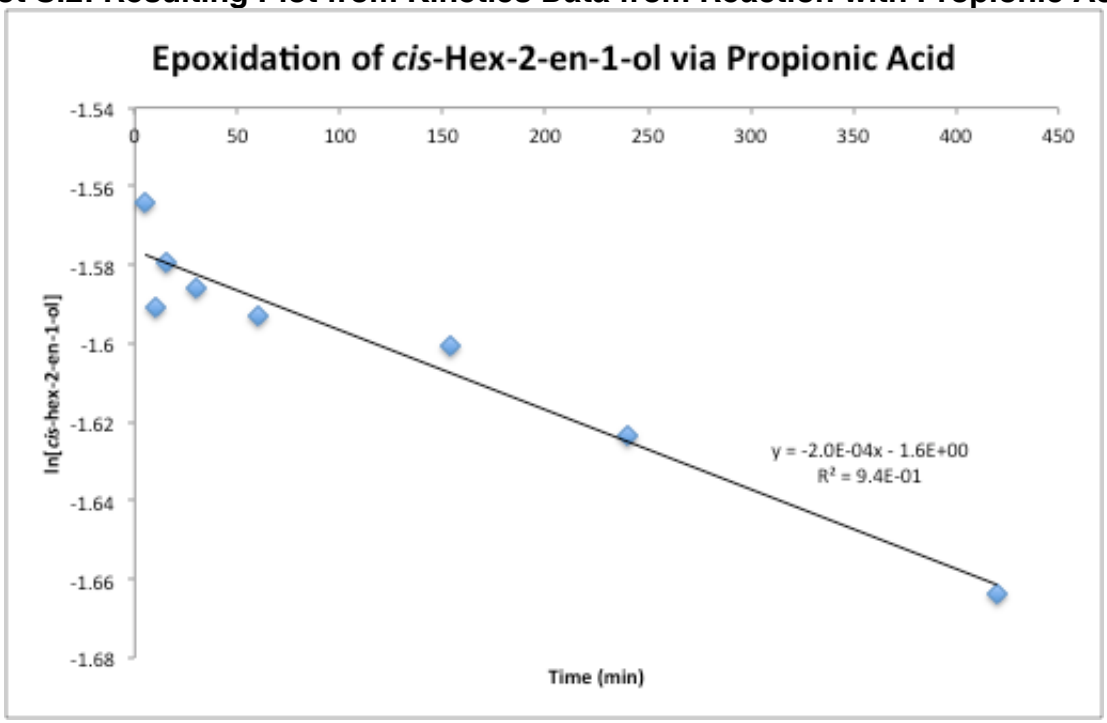
$$[\text{analyte}] = \left(\frac{[\text{standard}]}{f_r}\right)\left(\frac{\text{area}_{\text{analyte}}}{\text{area}_{\text{standard}}}\right)$$

where f_r=0.38.

Table SI3: Raw Kinetics Data from Reaction with Propionic Acid

Time (min)	Hex-2-en-1-ol (area)	[hex-2-en-1-ol] (M)	Dodecane (area)	ln[hexenol]
5	964.81	0.21	2419.12	-1.56
10	803.93	0.20	2070.28	-1.59
15	714.33	0.21	1818.58	-1.58
30	1253.36	0.20	3211.47	-1.59
60	773.12	0.20	1995.17	-1.59
154	996.03	0.20	2590.50	-1.60
240	768.95	0.20	2046.45	-1.62
420	778.29	0.19	2156.35	-1.66

Plot SI2: Resulting Plot from Kinetics Data from Reaction with Propionic Acid



7. NMR Experiments

Data acquired for the Peptide 6: Proton, gCOSY, zTOCSY, and ROESY experiments that were used to supply data for the NMR structure elucidation of **6** were collected on a Varian Inova 500 MHz spectrometer equipped with VnmrJ 2.2D. The pulse sequences for all experiments were provided by Varian. The sample was prepared in $CDCl_3$ (with TMS as reference) to afford peptide in a 0.02 M solution, the concentration of the peptide during the epoxidation reaction.

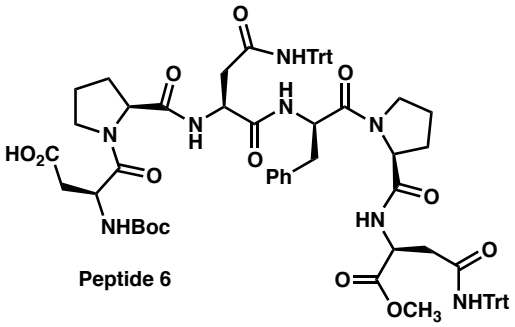
ROESY data was acquired at 25 °C with a 275 ms mixing time, spectral width of 5102.4 Hz, 128 transients, and d1 of 2.9 s. In the f2 dimension, 765 points were collected and 487 points were collected in the f1 dimension. The data was processed with Mestrenova v8.1.1-11591. Zero filling sized the spectrum to 1024, 1024. Automatic phasing was used along with manual adjustments and apodization was carried out with a sine bell function. The spectrum was treated with an automatic baseline correction with a polynomial fit.

The conditions of the other NMR experiments are tabulated below.

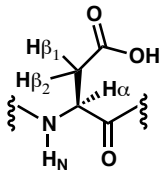
Table SI3: NMR Experiment Conditions

Sample	Experiment	Sample Conentration (M)	Solvent	Points in f1	Points in f2
Peptide **6**	zTOCSY	0.02	$CDCl_3$ (w/ TMS)	487	765
	gCOSY			239	765

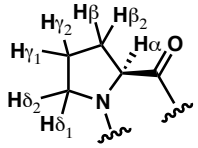
^{1}H types in peptide 6:



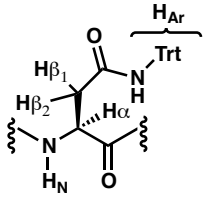
Peptide 6



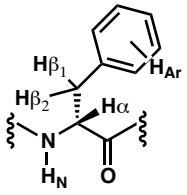
Aspartic Acid (Asp)



Proline (Pro)

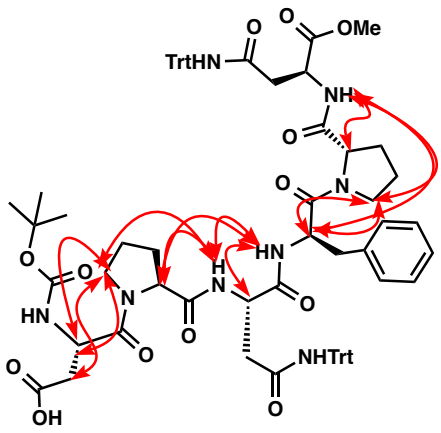


N-trityl-Asparagine (AsnTrt)



D-Phenylalanine (D-Phe)

Diastereotopic protons (e.g. $H\gamma_1$ and $H\gamma_2$ of proline) were designated 1 and 2 such that proton 2 had the further downfield chemical shift. In the case of overlap, the resonances are referred to as a single peak (e.g. $H\gamma_{12}$).



6

Peptide **6** **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.52 (s, 1H, DPhe(4)NH), 7.43 (d, *J* = 7.5 Hz, 1H, Asn(6)NH), 7.36-7.05 (m, 40H, aryl protons from two Asn(Trt) residues, DPhe(4) RNH from two Asn(Trt) residues), 6.96 (d, *J* = 8.0 Hz, 1H, Asn(3)NH), 5.35 (s, 1H, Asp (1)NH), 4.84 (s, 2H, Asn(3)Hα and Asp(1)Hα), 4.52 (q, *J* = 6.8 Hz, 1H, Asn(6)Hα), 4.41 (dd, *J* = 8.6, 5.5 Hz, 1H, Pro(2)Hα), 4.37 (d, *J* = 5.4 Hz, 1H, Pro(5)Hα), 4.22 (s, 1H, DPhe(4)Hα), 3.78 (s, 1H, Pro(2)Hδ_2), 3.63 (s, 1H, Pro(2)Hδ_1), 3.53 (s, 3H, Asn(6)-OCH_3), 3.30 (s, 1H, Pro(5)Hδ_2), 3.17-3.07 (m, 2H, DPhe(4)Hβ_1 and DPhe(4)Hβ_2) 2.94-2.84 (m, 3H, Asp(1)Hβ_2, Asn(3)Hβ_2, and Asn(6)Hβ_2), 2.68 (m, 2H, Asp(1)Hβ_1 and Asn(6)Hβ_1), 2.56 (m, 1H, Asn(3)Hβ_1), 2.36-2.11 (m, 2H, Pro(2)Hβ_2 and Pro(2)Hδ_1), 2.00-1.76 (m, 4H, Pro(5)Hβ_2, Pro(2)Hβ_1, Pro(2)Hγ_1, and Pro(2)Hγ_2), 1.72-1.56 (m, 2H, Pro(5)Hγ_2 and Pro(5)Hβ_1), 1.39-1.36 (s, 10H, Asp(1)-Boc and Pro(5)Hγ_1).

8. NMR Structure Elucidation

8.1 Modeling of peptide 6: A distance, $r_{ij,}$ between protons whose through-space interactions manifested in a ROESY crosspeak were calculated using the equation[11]:

$$r_{ij} = \mathrm{r}_{ref} \sqrt[6]{\left(\frac{v_{ref} c_{ref}}{v_{ij} c_{ij}}\right)}$$

The value of c_{ij} is defined as:

$$c_{ij} = \frac{1}{\sin^2 q_i \times \sin^2 q_j}$$

The constant c_{ref} is the average of all c_{ij} values across all peaks. This correction was applied to offset the inherent decrease in peak intensity relative to a peak's distance from the spectral center.

The value of q is defined as:

[11] a) Ammalahti, E.; Bardet, M.; Molko, D.; Cadet, J. *J. Magn. Res. A.* **1996**, *122*, 230-232. b)NMR Experiments on the Bruker 400 and 500 http://www.columbia.edu/cu/chemistry/groups/nmr/noe-99.html (accessed 15 June 2014).

$$q_i = \tan^{-1}\left(\frac{gB_1}{\varpi_i - \varpi_o}\right)$$

The value of gB_1 spin lock power of the instrument and the $(\omega_I - \omega_0)$ is the differenece between the peak in question and the transmitter center.

The reference volume, v_{ref}, was set to the volume of the crosspeaks showing a correlation between the two δ protons on proline 5. These crosspeaks were chosen as reference because they were completely free of obstruction from other protons and a reference distance, r_{ref}, of 1.8 Å—a known distance between proline δ protons, extracted from crystal structures—could be assigned to v_{ref}.

Distances were calculated from the integrations of crosspeaks between protons, v_{ij}. These distances were averaged from crosspeaks on both sides of the diagonal to give distance estimations that were then assigned to appropriate bins for use in the *Crystallography & NMR Systems* (CNS) modeling.[12] These estimated distances are tabulated in the table below.

Table SI4: Peptide 6 Proton Distances

Proton i	Proton j	Average Distance (Å)
Asp(1)-HB1	Pro(2)-HD2	2.7
Asp(1)-HA	Pro(2)-HD1	2.3
Asp(1)-HA	Pro(2)-HD2	2.2
Pro(2)-HA	Asn(3)-HN	3.1
Pro(2)-HD1	Asn(3)-HN	3.1
Asn(3)-HN	Dphe(4)-HN	2.5
Dphe(4)-HA	Pro(5)-HD1	2.2
Dphe(4)-HA	Pro(5)-HD2	2.2
Pro(5)-HD2	Asn(6)-HN	3.2
Pro(5)-HA	Asn(6)-HN	2.8
Dphe(4)-HA	Asn(6)-NH	3.5
Asn(3)-HA	Dphe(4)-NH	3.0
Pro(2)-HA	Dphe(4)-HN	3.5

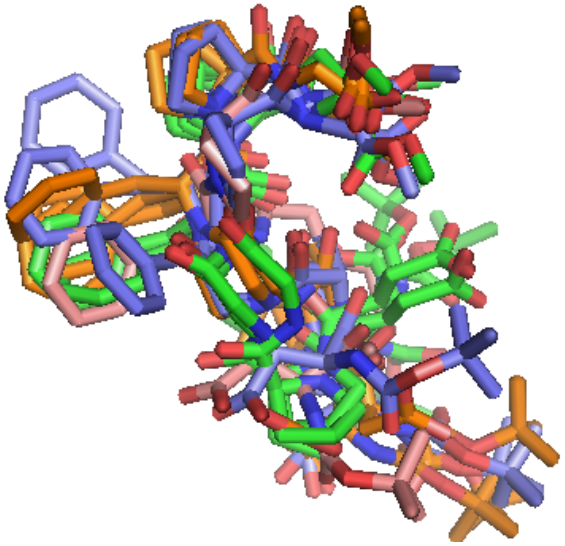
These distances were grouped according to predetermined distance ranges. The peptide's methyl ester; trityl and Boc groups; and DPhe were constructed manually using the distances and angles from known crystal structures in combination with the amino acid topology/parameter files provided by CNS. Various bins were used to derive 1000 structures through simulated annealing of extended peptide **6**. The ten lowest energy conformations were chosen and analyzed further.

[12] (a) Brunger, A.T.; Adams, P.D.; Clore, G.M.; Gros, P.; Kunstleve-Grosse, R.W.; Kuszewski, J.; Nilges, N.; Pannu, N.S.; Read, R.J.; Rice, L.M.; Simonson, T.; Warren, G.L. *Acta Cryst.* **1998**, *54*, 905-921. (b) Brunger, A.T. *Nature Protocols* **2007**, *2*, 2728-2733.

Different binning systems were examined that grouped strong to weak peaks differently. The final binning system chosen (1, as listed below) was done so because, by visual inspection, it produced an ensemble of ten low energy conformations that seemed to have the most internal consistency. Additionally, the bins analyzed in the text of the manuscript (bins 1) are based upon bins with precedented utility in calculations involving proteins and peptides.

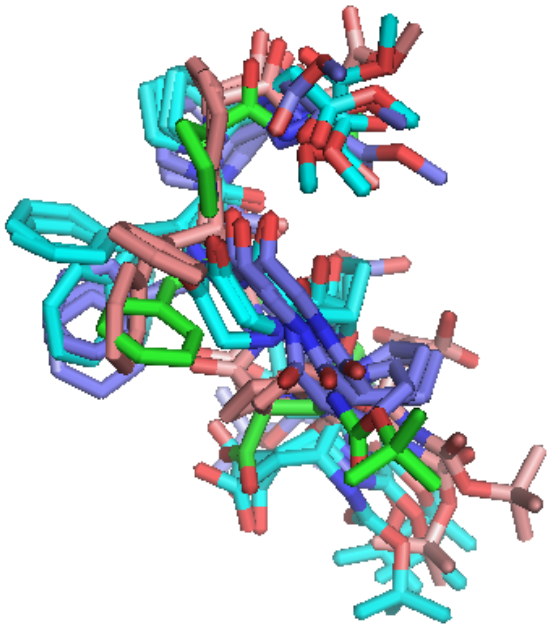
8.2 Calculated NMR structures of Peptide 6 and the respective binning procedures

1. Bins are as follows: very strong = 1.8-2.5 Å; strong = 1.8-3.0 Å; medium = 1.8-3.5 Å; weak = 1.8-4.5 Å.[13]

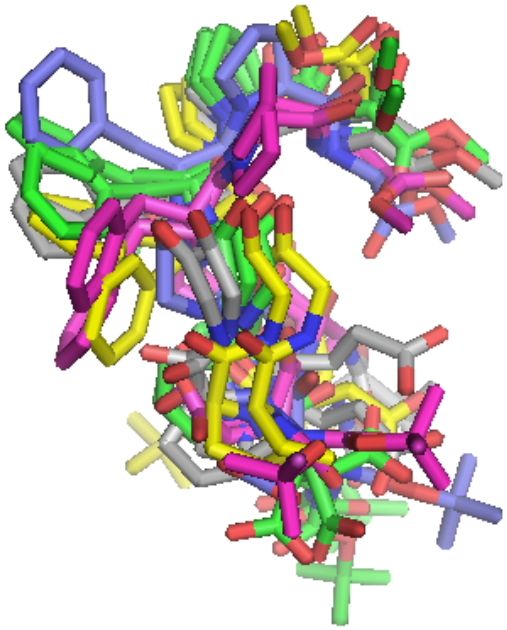


[13] Slightly modified bins from Ref 14.

2. Bins are as follows: strong = 1.8-2.7 Å; medium = 1.8-3.3 Å; weak = 1.8-5.0 Å.[14]



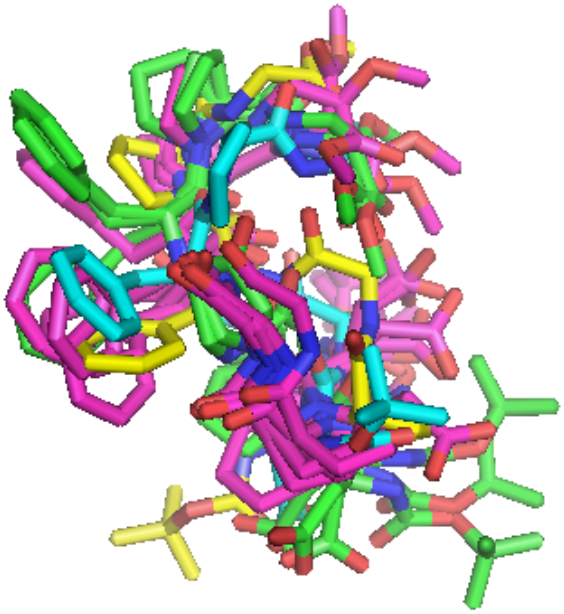
3. Bins are as follows: strong = 1.8-2.5 Å; medium = 1.8-3.0 Å; weak = 1.8-4.0 Å; non-sequential involving α-H and NH: 1.8-4.0 Å; non-sequential involving side chains: 1.8-5.0 Å.[15]



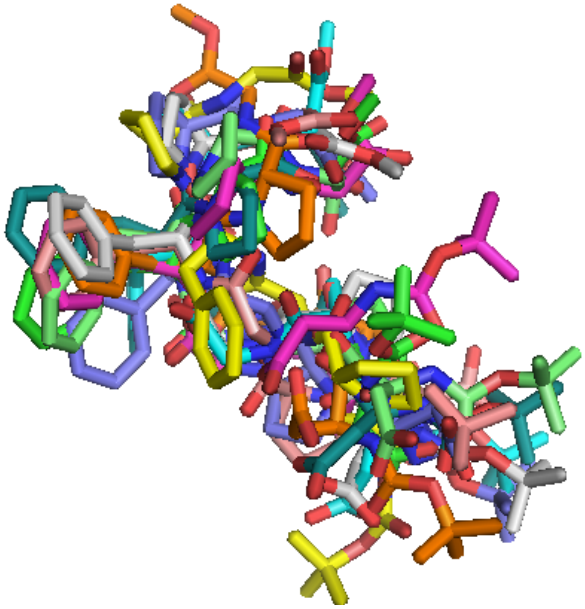
[14] Cavanagh, J.; Fairbrother, W.J.; Palmer, A.G.; Rance, M; Skelton, N.G. Protein NMR Spectroscopy: Principles and Practice, 3rd Ed. Elsevier Academic Press: Boston, 2007.

[15] Wuthrich, K. NMR of Proteins and Nucleic Acids. Wiley-Interscience Publication: New York, 1986.

4. Bins are as follows: (Calculated distance between protons × 1.2) Å



5. Bins are as follows: 1.8-5.0 Å.[16]



[16] Guntert, P. *Methods Mol. Biol.* **2004**, *278*, 352-378.

Table SI5: NMR Statistics for Peptide 6 using Bin 1

NMR constraints	13
Distance constraints	
Total ROE	13
Intra-residue	0
Inter-residue	13
Sequential ($\|i-j\| = 1$)	11
Medium-range ($\|i-j\| < 4$)	2
Long-range ($\|i-j\| > 5$)	0
Intermolecular	0
Hydrogen bonds	0
Total dihedral angle restraints	
ϕ	0
ψ	0
Structure statistics	
Violations (mean and s.d.)	7 ± 2*
Distance constraints (Å)	0.005 ± 0.004
Max. distance constraint violation (Å)	0
Deviations from idealized geometry	
Bond lengths (Å)	± 0.0021
Bond angles (º)	± 0.535
Impropers (º)	± 0.308
Average pairwise r.m.s. deviation (Å) (10 Structures)	
Side Chain	1.4 ± 0.5
Backbone	7 ± 2

*This comes from a conflict between non-idealized geometry within our manually built monomers and CNS. This does not reflect a conflict within our data.

9. Tabulated RMSD (Å) values for pairwise fitting of different backbone regions of peptide 6.

Because the C-terminal region of peptide **6** seemed to adopt a γ-turn conformation across all structures, we wondered if there were other regions of uniformity in the peptide sequence. The following RMSD values for the described regions were obtained using the pair-fitting algorithm in Pymol.[17] Each atom was selected from an ensemble structure and then all selections were collectively fit to their corresponding atoms (peptides are treated as rigid bodies) in a reference structure. Because no one structure was more or less likely than any other, we selected the average structure of the NMR ensemble as this reference, so that our measurements would then be reflective of uniformity or hetereogeneity of conformation within the ensemble as a whole.

Region 1: Atoms N, C, CA, and O of residues Asp(1) and Pro(2). These residues are referred to in the text as *i* and *i+1*, respectively. The atom names come from the PDB

[17] The Pymol Molecular Graphics System, Version 1.5.0.4, Schrodinger, LLC.

file nomenclature. Below is the structure with atoms highlighted in red and image of the overlay of the ensemble structures.

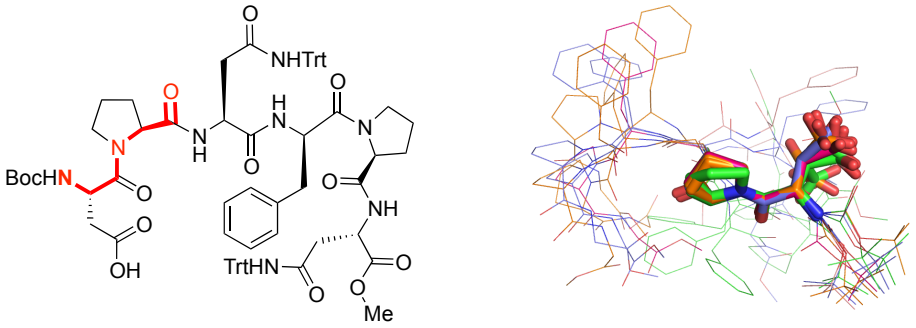
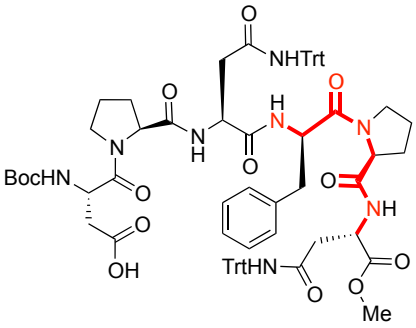


Table S6. RMSD values (Å) for pairwise fitting of Region 1 of peptide **6**.

Structure	RMSD (Å)
1	0.195
2	0.046
3	0.084
4	0.151
5	0.134
6	0.040
7	0.070
8	0.038
9	0.136
10	0.070
Avg.	0.10 ± 0.05

Note: We do not deem measurements to the one-thousandth of an angstrom significant. The extra significant digit was carried for rounding purposes and is not reflected in the average value.

Region 2: Atoms N, C, CA, and O of residues D-Phe (4), Pro(5), and AsnTrt(6), excluding the atoms from the C-terminal ester of residue 6. These residues are referred to in the text as *i+3*, *i+4*, and *i+*5, respectively. The atom names come from the PDB file nomenclature. Below is the structure with atoms highlighted in red an image of the overlay of the ensemble structures.



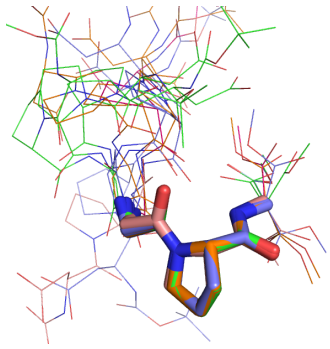


Table S7. RMSD values (Å) for pairwise fitting of Region 2 of peptide **6**.

Structure	RMSD (Å)
1	0.157
2	0.104
3	0.153
4	0.103
5	0.165
6	0.012
7	0.073
8	0.127
9	0.022
10	0.170
Avg.	0.11 ± 0.06

Region 3: Atoms N, C, CA, and O of residue AsnTrt(3) (*i+2* in the manuscript), including the C and O atoms from the preceding residue and the N atom the trailing residue. The inclusion of these atoms is necessary to evaluate the conformation of this residue, as they (other than the carbonyl oxygen) are required for the calculation of any residue's ϕ/ψ backbone dihedral angles. The atom names come from the PDB file nomenclature. Below is the structure with atoms highlighted in red an image of the overlay of the ensemble structures.

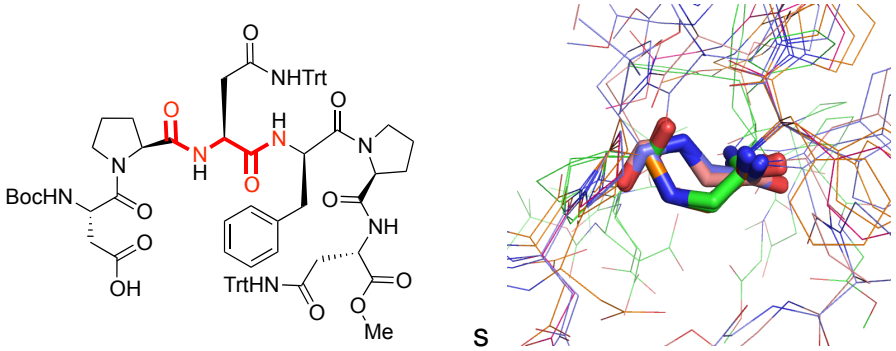


Table S8. RMSD values (Å) for pairwise fitting of Region 3 of peptide **6**.

Structure	RMSD (Å)
1	1.235
2	1.232
3	0.053
4	1.201
5	1.208
6	0.025
7	1.250
8	0.010
9	0.090
10	0.034
Avg.	0.6 ± 0.6

9. Crystallographic Data

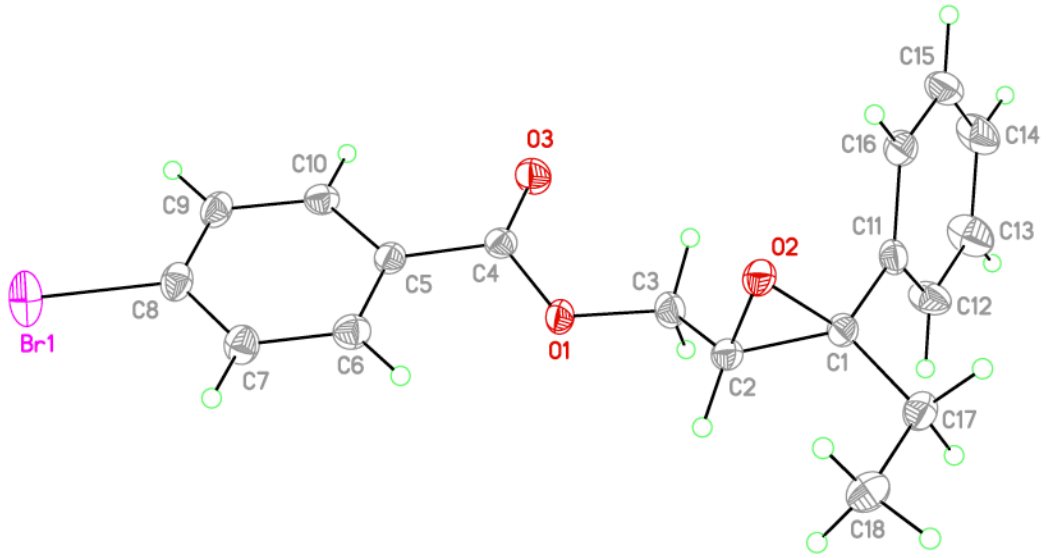


Table SI6. Crystal data and structure refinement for ((2*S*,3*R*)-3-Ethyl-3-phenyloxiran-2-yl)methyl 4-bromobenzoate.

Identification code	cm18cas	
Empirical formula	C18 H17 Br O3	
Formula weight	361.23	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.4484(19) Å	a= 90°.
	b = 6.0156(13) Å	b= 104.755(3)°.
	c = 16.494(4) Å	g = 90°.
Volume	810.6(3) $Å^3$	
Z	2	
Density (calculated)	1.480 Mg/m^3	
Absorption coefficient	2.545 mm^{-1}	
F(000)	368	
Crystal size	0.334 x 0.237 x 0.098 mm^3	
Theta range for data collection	2.49 to 25.37°.	
Index ranges	-10<=h<=10, -7<=k<=7, -19<=l<=19	
Reflections collected	11991	

Independent reflections	2923 [R(int) = 0.0386]
Completeness to theta = 25.37°	99.9 %
Absorption correction	Integration
Max. and min. transmission	0.8350 and 0.5003
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2923 / 1 / 200
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0250, wR2 = 0.0583
R indices (all data)	R1 = 0.0281, wR2 = 0.0599
Absolute structure parameter	-0.008(7)
Largest diff. peak and hole	0.318 and -0.395 e.$Å^{-3}$

Table SI7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)for cm18cas.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-3430(1)	9652(1)	5393(1)	47(1)
O(1)	3278(2)	3278(3)	6995(1)	31(1)
O(2)	4882(2)	1423(3)	8830(1)	28(1)
O(3)	4608(2)	6375(3)	6775(1)	36(1)
C(1)	5912(2)	-337(5)	8636(1)	24(1)
C(2)	4539(3)	572(4)	7980(1)	25(1)
C(3)	4816(3)	2127(4)	7328(2)	31(1)
C(4)	3351(3)	5395(4)	6748(1)	26(1)
C(5)	1689(3)	6369(4)	6439(1)	26(1)
C(6)	281(3)	5301(4)	6532(2)	32(1)
C(7)	-1251(3)	6276(5)	6227(2)	32(1)
C(8)	-1347(3)	8307(4)	5832(1)	31(1)
C(9)	29(3)	9422(5)	5731(1)	31(1)
C(10)	1551(3)	8426(4)	6038(1)	28(1)
C(11)	7616(3)	386(4)	8644(1)	26(1)
C(12)	8467(3)	-729(5)	8148(2)	38(1)
C(13)	10033(3)	-48(7)	8141(2)	49(1)
C(14)	10759(3)	1727(6)	8624(2)	46(1)
C(15)	9923(3)	2842(5)	9114(2)	39(1)
C(16)	8355(3)	2185(4)	9128(2)	30(1)
C(17)	5770(3)	-2564(4)	9036(2)	30(1)
C(18)	4059(3)	-3273(5)	9052(2)	36(1)

Table SI8. Bond lengths [Å] and angles [°] for cm18cas.

Br(1)-C(8)	1.904(2)
O(1)-C(4)	1.343(3)
O(1)-C(3)	1.451(3)
O(2)-C(2)	1.451(3)
O(2)-C(1)	1.456(3)
O(3)-C(4)	1.206(3)
C(1)-C(2)	1.476(3)
C(1)-C(11)	1.501(3)
C(1)-C(17)	1.511(4)
C(2)-C(3)	1.487(3)
C(2)-H(2)	1.0000
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.486(3)
C(5)-C(10)	1.394(4)
C(5)-C(6)	1.394(3)
C(6)-C(7)	1.393(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.378(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.388(4)
C(9)-C(10)	1.392(3)
C(9)-H(9)	0.9500
C(10)-H(10)	0.9500
C(11)-C(12)	1.390(3)
C(11)-C(16)	1.395(3)
C(12)-C(13)	1.388(4)
C(12)-H(12)	0.9500
C(13)-C(14)	1.379(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.376(4)
C(14)-H(14)	0.9500
C(15)-C(16)	1.388(4)
C(15)-H(15)	0.9500

C(16)-H(16)	0.9500
C(17)-C(18)	1.514(4)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800

C(4)-O(1)-C(3)	117.5(2)
C(2)-O(2)-C(1)	61.01(13)
O(2)-C(1)-C(2)	59.33(14)
O(2)-C(1)-C(11)	114.4(2)
C(2)-C(1)-C(11)	118.1(2)
O(2)-C(1)-C(17)	115.53(18)
C(2)-C(1)-C(17)	120.9(2)
C(11)-C(1)-C(17)	115.83(19)
O(2)-C(2)-C(1)	59.67(14)
O(2)-C(2)-C(3)	116.5(2)
C(1)-C(2)-C(3)	121.6(2)
O(2)-C(2)-H(2)	115.7
C(1)-C(2)-H(2)	115.7
C(3)-C(2)-H(2)	115.7
O(1)-C(3)-C(2)	106.45(18)
O(1)-C(3)-H(3A)	110.4
C(2)-C(3)-H(3A)	110.4
O(1)-C(3)-H(3B)	110.4
C(2)-C(3)-H(3B)	110.4
H(3A)-C(3)-H(3B)	108.6
O(3)-C(4)-O(1)	124.1(2)
O(3)-C(4)-C(5)	124.5(2)
O(1)-C(4)-C(5)	111.5(2)
C(10)-C(5)-C(6)	119.4(2)
C(10)-C(5)-C(4)	118.1(2)
C(6)-C(5)-C(4)	122.6(2)
C(7)-C(6)-C(5)	120.4(2)
C(7)-C(6)-H(6)	119.8

C(5)-C(6)-H(6)	119.8
C(8)-C(7)-C(6)	118.8(2)
C(8)-C(7)-H(7)	120.6
C(6)-C(7)-H(7)	120.6
C(7)-C(8)-C(9)	122.3(2)
C(7)-C(8)-Br(1)	119.61(19)
C(9)-C(8)-Br(1)	118.1(2)
C(8)-C(9)-C(10)	118.2(3)
C(8)-C(9)-H(9)	120.9
C(10)-C(9)-H(9)	120.9
C(9)-C(10)-C(5)	120.9(2)
C(9)-C(10)-H(10)	119.6
C(5)-C(10)-H(10)	119.6
C(12)-C(11)-C(16)	119.2(2)
C(12)-C(11)-C(1)	119.6(2)
C(16)-C(11)-C(1)	121.2(2)
C(13)-C(12)-C(11)	120.0(3)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(14)-C(13)-C(12)	120.6(3)
C(14)-C(13)-H(13)	119.7
C(12)-C(13)-H(13)	119.7
C(15)-C(14)-C(13)	119.8(2)
C(15)-C(14)-H(14)	120.1
C(13)-C(14)-H(14)	120.1
C(14)-C(15)-C(16)	120.4(3)
C(14)-C(15)-H(15)	119.8
C(16)-C(15)-H(15)	119.8
C(15)-C(16)-C(11)	120.1(2)
C(15)-C(16)-H(16)	120.0
C(11)-C(16)-H(16)	120.0
C(1)-C(17)-C(18)	116.1(2)
C(1)-C(17)-H(17A)	108.3
C(18)-C(17)-H(17A)	108.3
C(1)-C(17)-H(17B)	108.3
C(18)-C(17)-H(17B)	108.3

H(17A)-C(17)-H(17B)	107.4
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table SI9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cm18cas.

The anisotropicdisplacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	34(1)	60(1)	48(1)	17(1)	13(1)	17(1)
O(1)	24(1)	24(1)	42(1)	9(1)	2(1)	1(1)
O(2)	24(1)	26(1)	36(1)	-2(1)	9(1)	5(1)
O(3)	29(1)	34(1)	45(1)	6(1)	7(1)	-6(1)
C(1)	23(1)	24(1)	26(1)	-3(1)	6(1)	4(1)
C(2)	22(1)	23(1)	31(1)	-1(1)	6(1)	1(1)
C(3)	22(1)	32(2)	37(1)	4(1)	6(1)	2(1)
C(4)	30(1)	25(2)	21(1)	-2(1)	4(1)	-1(1)
C(5)	29(1)	24(1)	23(1)	-1(1)	5(1)	2(1)
C(6)	34(1)	28(2)	32(1)	2(1)	9(1)	-3(1)
C(7)	29(1)	34(2)	35(1)	2(1)	12(1)	2(1)
C(8)	34(1)	32(2)	26(1)	-1(1)	7(1)	9(1)
C(9)	38(1)	25(1)	28(1)	5(1)	6(1)	6(1)
C(10)	32(1)	26(1)	27(1)	0(1)	6(1)	-4(1)
C(11)	22(1)	29(2)	26(1)	1(1)	3(1)	5(1)
C(12)	28(1)	43(2)	44(1)	-20(1)	10(1)	-2(1)
C(13)	28(1)	65(2)	56(2)	-21(2)	16(1)	1(2)
C(14)	20(1)	61(2)	56(2)	-11(2)	9(1)	-5(1)
C(15)	28(1)	39(2)	44(2)	-10(1)	1(1)	-4(1)
C(16)	28(1)	30(1)	33(1)	-4(1)	7(1)	5(1)
C(17)	33(1)	27(1)	31(1)	1(1)	8(1)	5(1)
C(18)	43(2)	29(2)	39(1)	4(1)	14(1)	-2(1)

Table SI10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cm18cas.

	x	y	z	U(eq)
H(2)	3555	-407	7804	30
H(3A)	5693	3200	7577	37
H(3B)	5141	1296	6878	37
H(6)	367	3899	6805	38
H(7)	-2212	5553	6291	38
H(9)	-65	10827	5460	37
H(10)	2508	9158	5974	34
H(12)	7977	-1956	7815	46
H(13)	10609	-810	7800	59
H(14)	11834	2178	8618	55
H(15)	10421	4069	9445	46
H(16)	7785	2961	9468	36
H(17A)	6456	-2529	9620	36
H(17B)	6232	-3713	8732	36
H(18A)	4119	-4620	9393	55
H(18B)	3415	-3576	8479	55
H(18C)	3536	-2081	9296	55

Table SI11. Torsion angles [°] for cm18cas.

C(2)-O(2)-C(1)-C(11)	109.4(2)
C(2)-O(2)-C(1)-C(17)	-112.3(2)
C(1)-O(2)-C(2)-C(3)	-112.8(2)
C(11)-C(1)-C(2)-O(2)	-103.1(3)
C(17)-C(1)-C(2)-O(2)	103.2(2)
O(2)-C(1)-C(2)-C(3)	104.3(2)
C(11)-C(1)-C(2)-C(3)	1.2(4)
C(17)-C(1)-C(2)-C(3)	-152.4(2)
C(4)-O(1)-C(3)-C(2)	146.8(2)
O(2)-C(2)-C(3)-O(1)	-90.7(2)
C(1)-C(2)-C(3)-O(1)	-159.9(2)
C(3)-O(1)-C(4)-O(3)	1.2(3)
C(3)-O(1)-C(4)-C(5)	-178.8(2)
O(3)-C(4)-C(5)-C(10)	10.0(3)
O(1)-C(4)-C(5)-C(10)	-170.0(2)
O(3)-C(4)-C(5)-C(6)	-170.4(2)
O(1)-C(4)-C(5)-C(6)	9.7(3)
C(10)-C(5)-C(6)-C(7)	0.0(4)
C(4)-C(5)-C(6)-C(7)	-179.6(2)
C(5)-C(6)-C(7)-C(8)	0.2(4)
C(6)-C(7)-C(8)-C(9)	-0.4(4)
C(6)-C(7)-C(8)-Br(1)	178.95(18)
C(7)-C(8)-C(9)-C(10)	0.5(4)
Br(1)-C(8)-C(9)-C(10)	-178.90(17)
C(8)-C(9)-C(10)-C(5)	-0.3(4)
C(6)-C(5)-C(10)-C(9)	0.0(4)
C(4)-C(5)-C(10)-C(9)	179.7(2)
O(2)-C(1)-C(11)-C(12)	-152.5(2)
C(2)-C(1)-C(11)-C(12)	-85.7(3)
C(17)-C(1)-C(11)-C(12)	69.3(3)
O(2)-C(1)-C(11)-C(16)	26.4(3)
C(2)-C(1)-C(11)-C(16)	93.2(3)
C(17)-C(1)-C(11)-C(16)	-111.8(3)
C(16)-C(11)-C(12)-C(13)	0.0(4)

C(1)-C(11)-C(12)-C(13)	178.9(3)
C(11)-C(12)-C(13)-C(14)	0.2(5)
C(12)-C(13)-C(14)-C(15)	-0.4(5)
C(13)-C(14)-C(15)-C(16)	0.3(5)
C(14)-C(15)-C(16)-C(11)	-0.1(4)
C(12)-C(11)-C(16)-C(15)	-0.1(4)
C(1)-C(11)-C(16)-C(15)	-179.0(2)
O(2)-C(1)-C(17)-C(18)	40.6(3)
C(2)-C(1)-C(17)-C(18)	-27.5(3)
C(11)-C(1)-C(17)-C(18)	178.3(2)

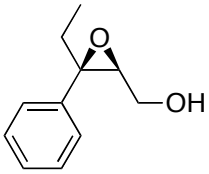
Symmetry transformations used to generate equivalent atoms.

Spectral Data
for
Function-Oriented Investigations of a Peptide-Based Catalyst that Mediates Enantioselective Allylic Alcohol Epoxidation.

Nadia C. Abascal, Phillip A. Lichtor, Michael W. Giuliano, Scott J. Miller*

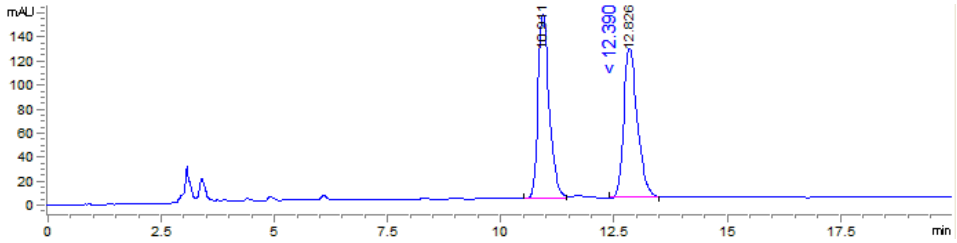
Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107, United States.

HPLC Traces

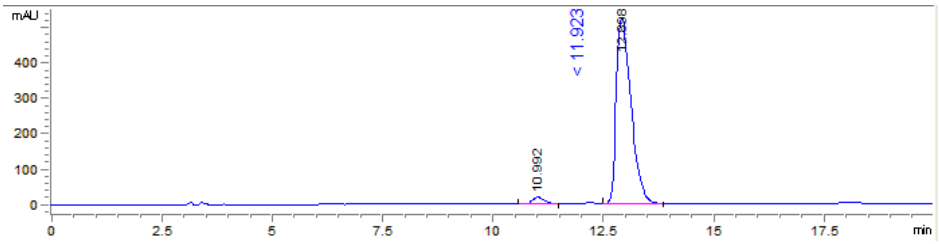


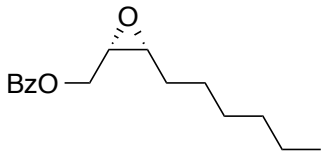
((2*S*,3*R*)-3-Ethyl-3-phenyloxiran-2-yl)methanol (13)

Racemic



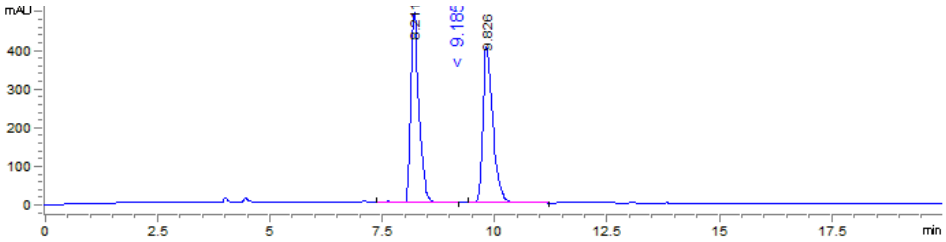
Enantioenriched





((2*S*,3*R*)-(3-Hexyloxiran-2-yl)methyl benzoate (SI 13)

Racemic



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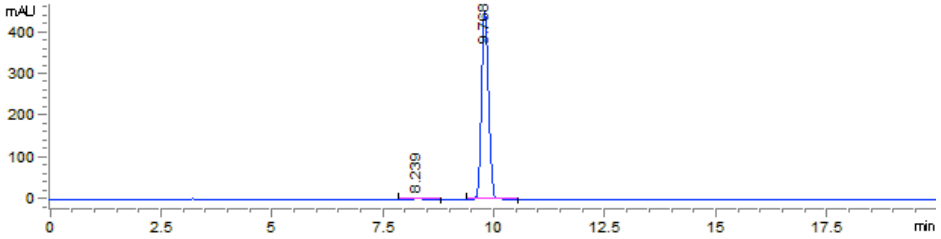
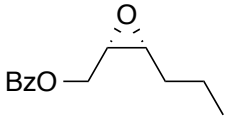
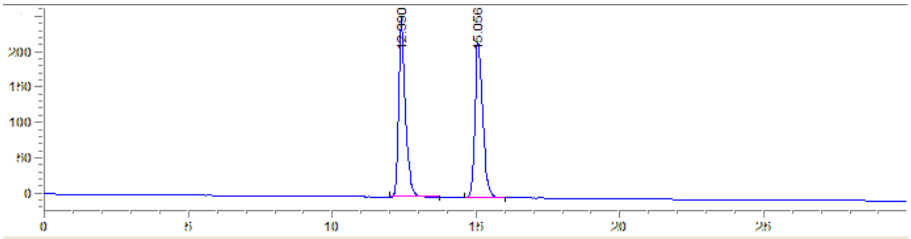




((2*S*,3*R*)- (3-Propyloxiran-2-yl)methyl benzoate (SI 11)

Racemic



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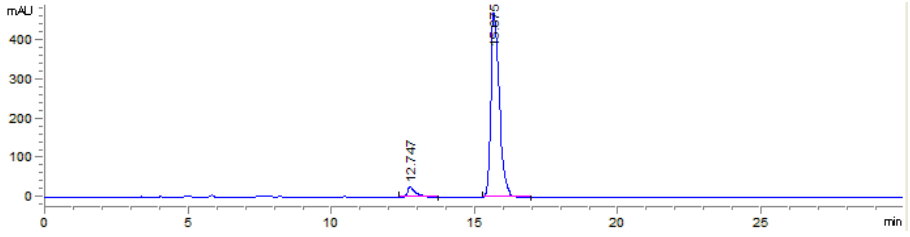
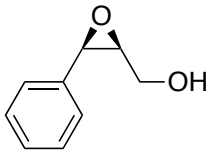
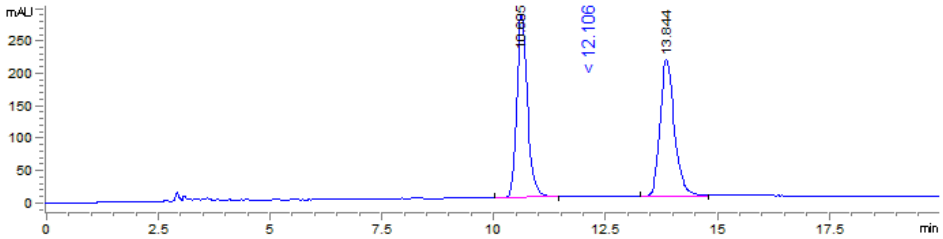




((2*S*,3*R*)-3-Phenyloxiran-2-yl)methanol (16)

Racemic



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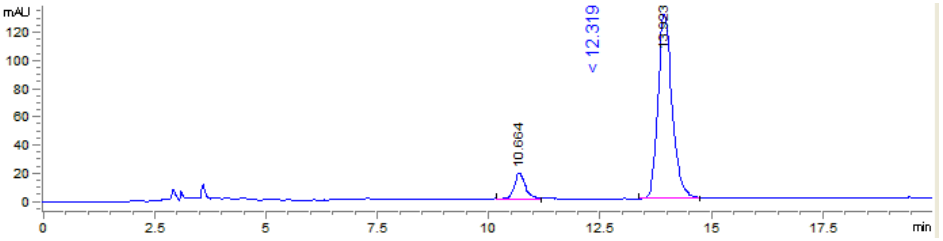
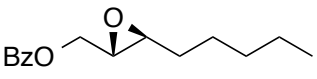
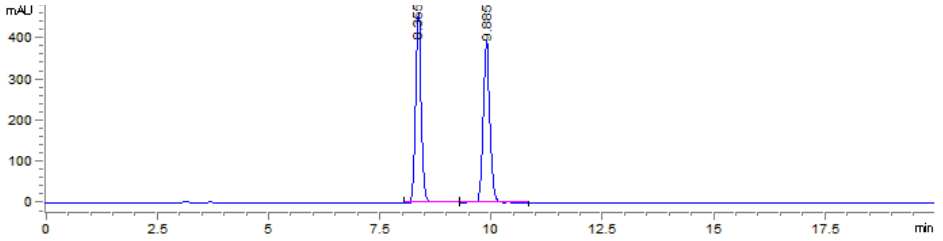




((2*S*, 3*S*)- (3-Pentyloxiran-2-yl)methyl benzoate (SI 10)

Racemic



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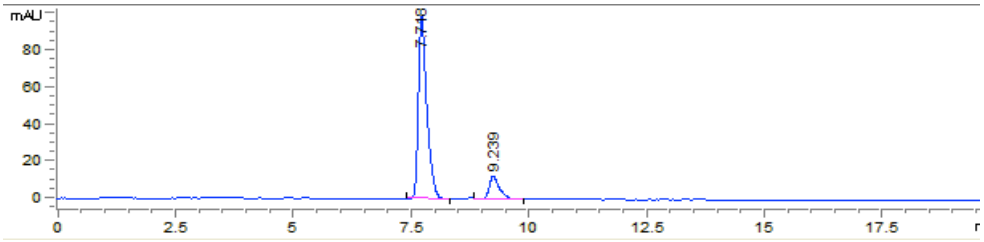
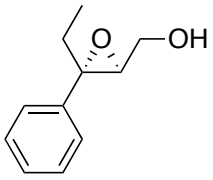
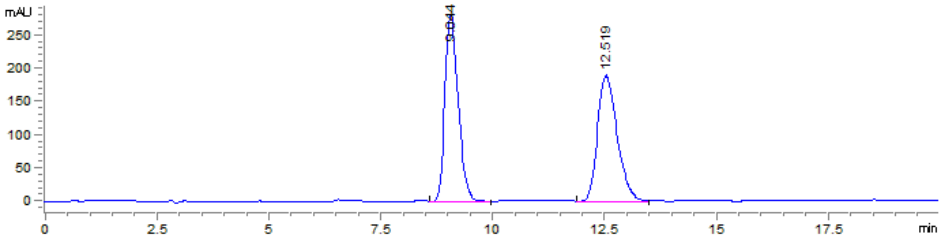




((2*S*,3*S*)-3-Ethyl-3-phenyloxiran-2-yl)methanol (18)

Racemic



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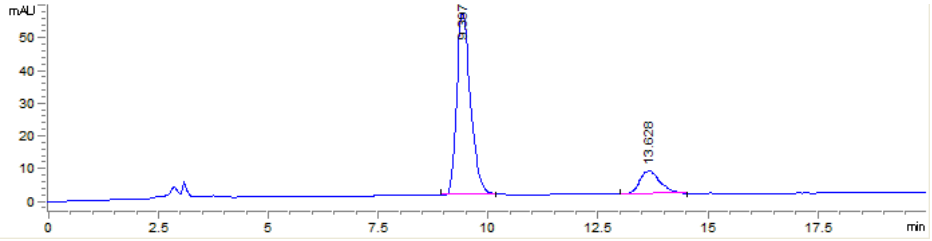
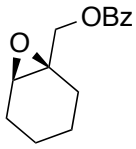
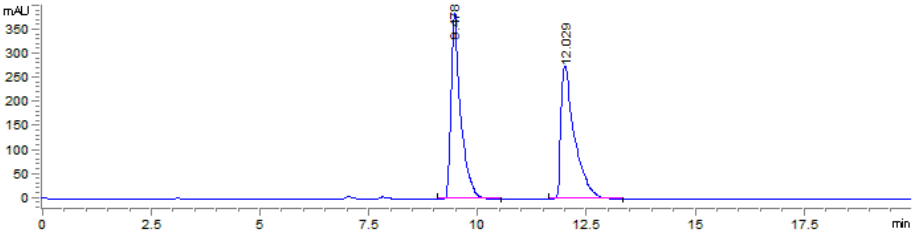




((1*R*,6*R*)- (7-Oxabicyclo[4.1.0]heptan-1-yl)methyl benzoate (SI 12)

Racemic



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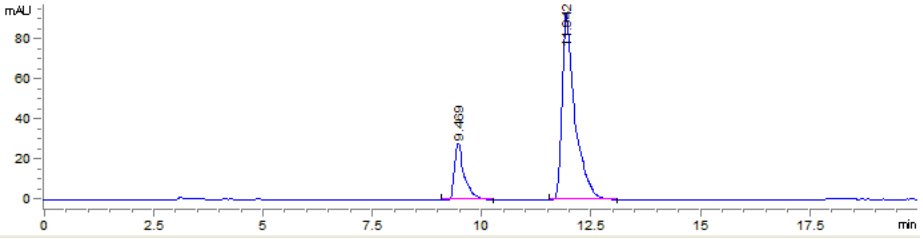
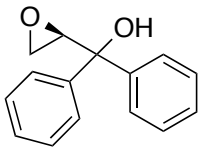
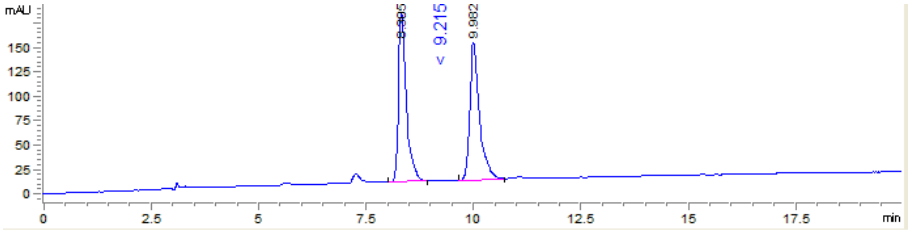




(*R*)-Oxiran-2-yldiphenylmethanol (20)

Racemic



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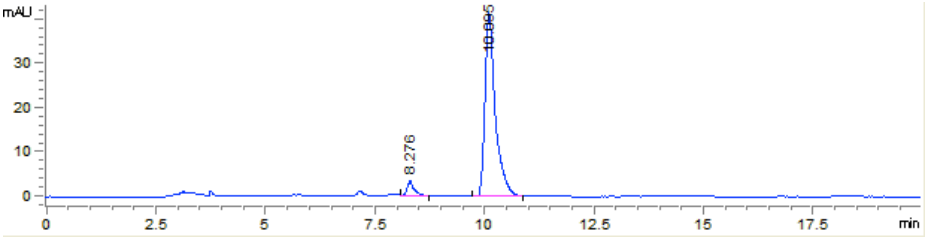
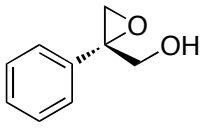
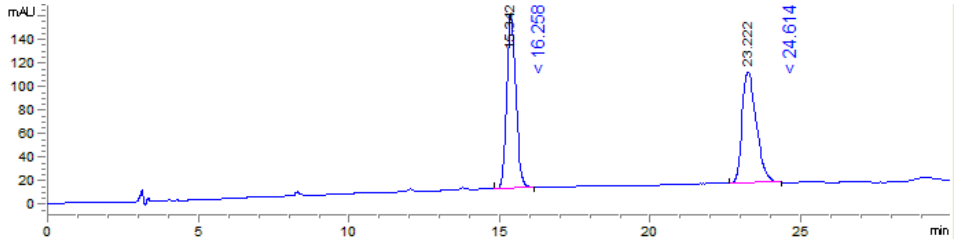




(*S*)-(2-Phenyloxiran-2-yl)methanol (21)

Racemic



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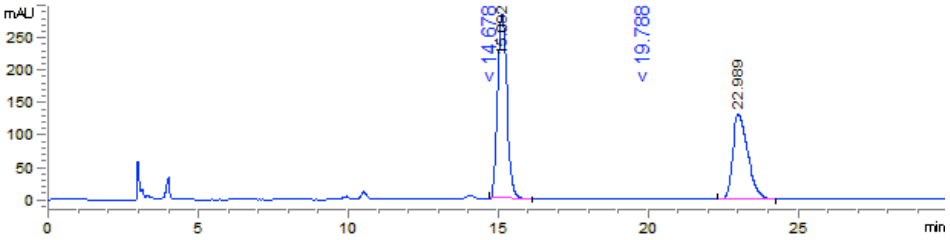
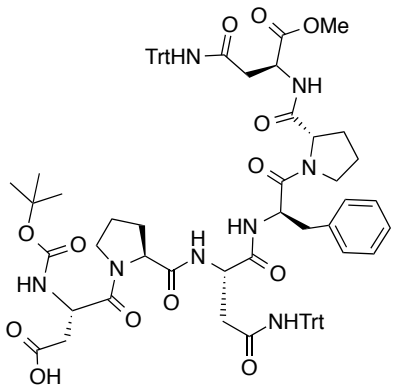
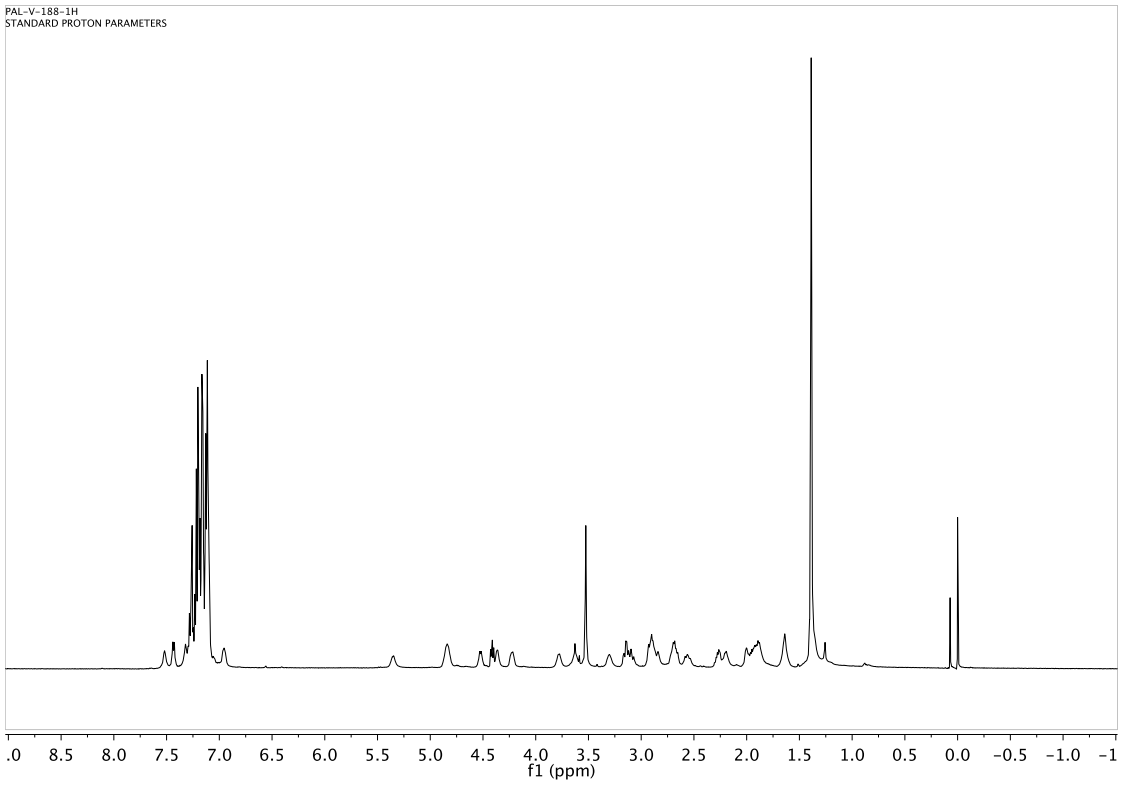


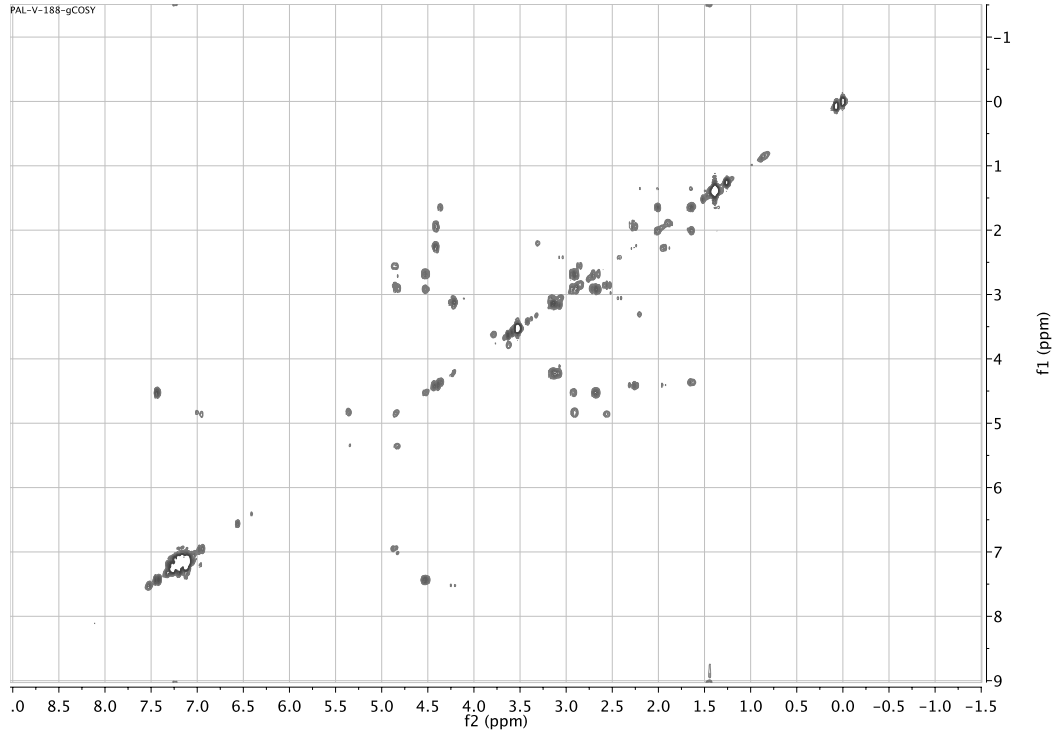
*Catalyst **6** NMR Data*



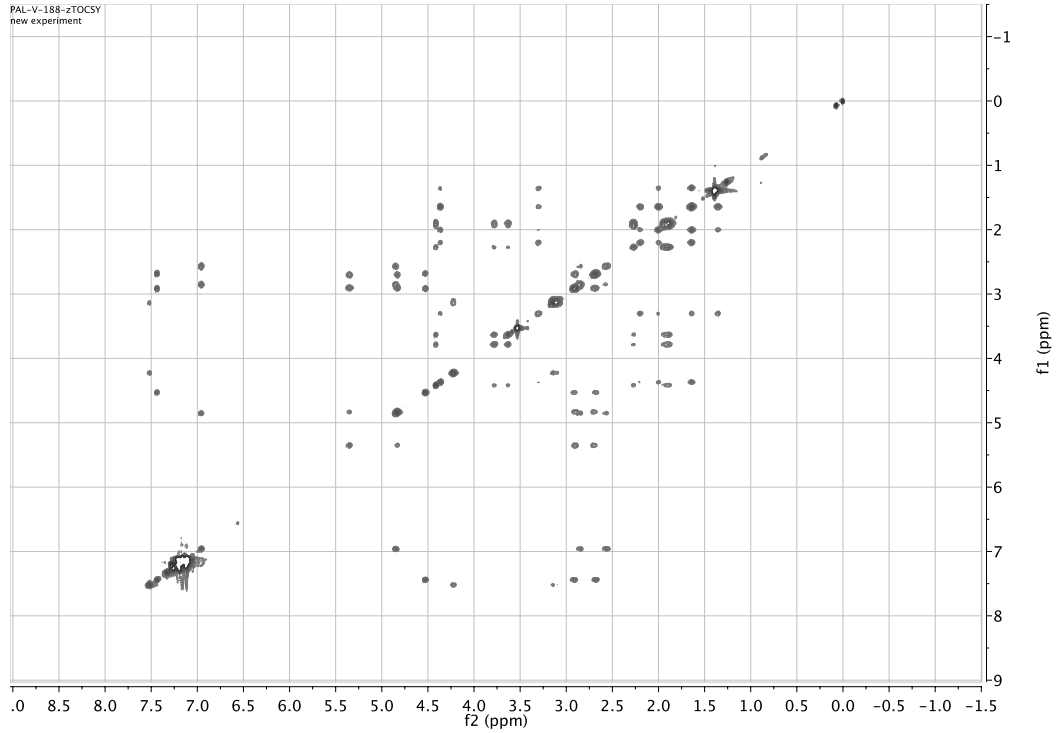
1D ^{1}H NMR



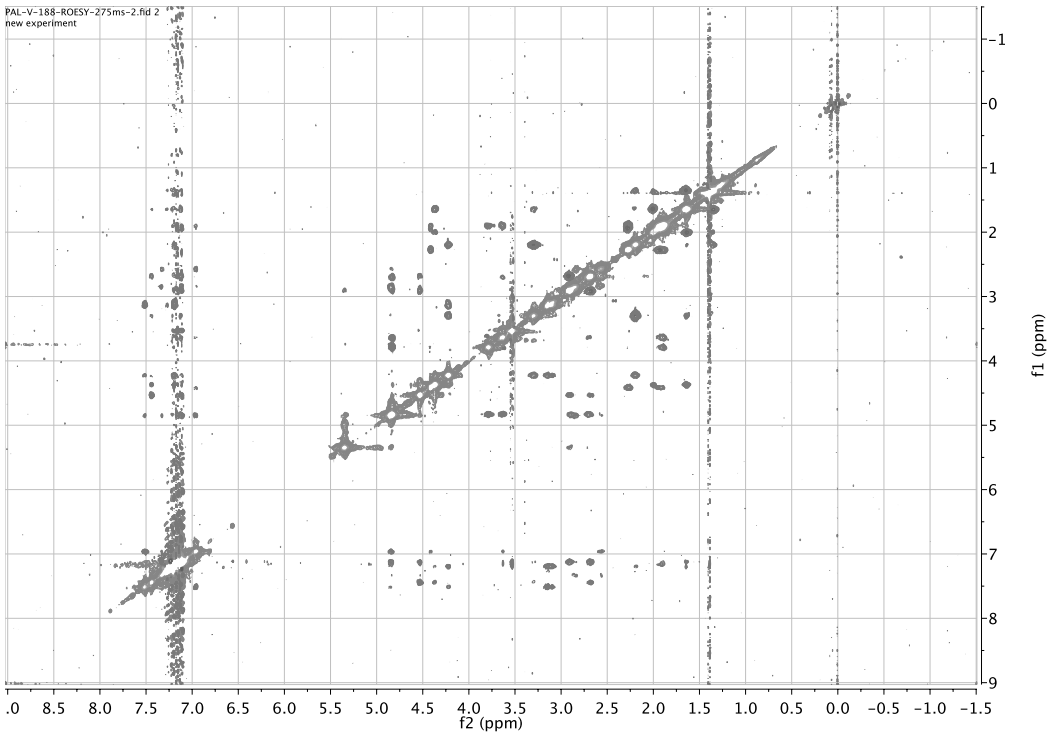
2D gCOSY NMR



2D zTOCSY NMR

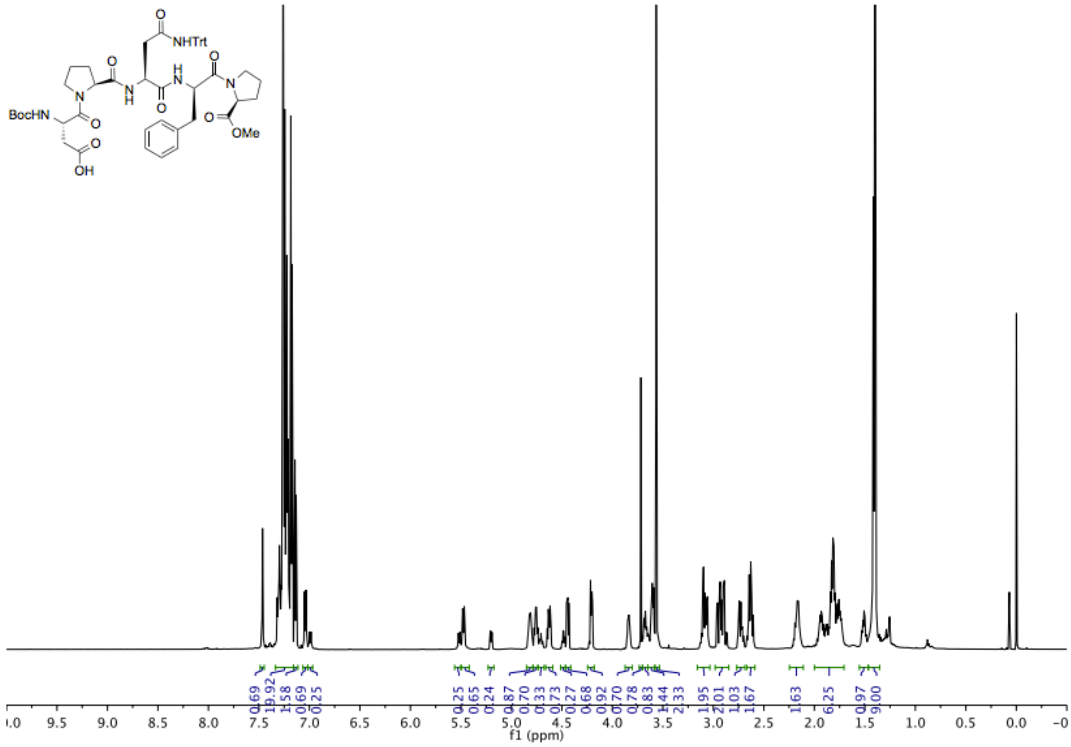


2D ROESY NMR

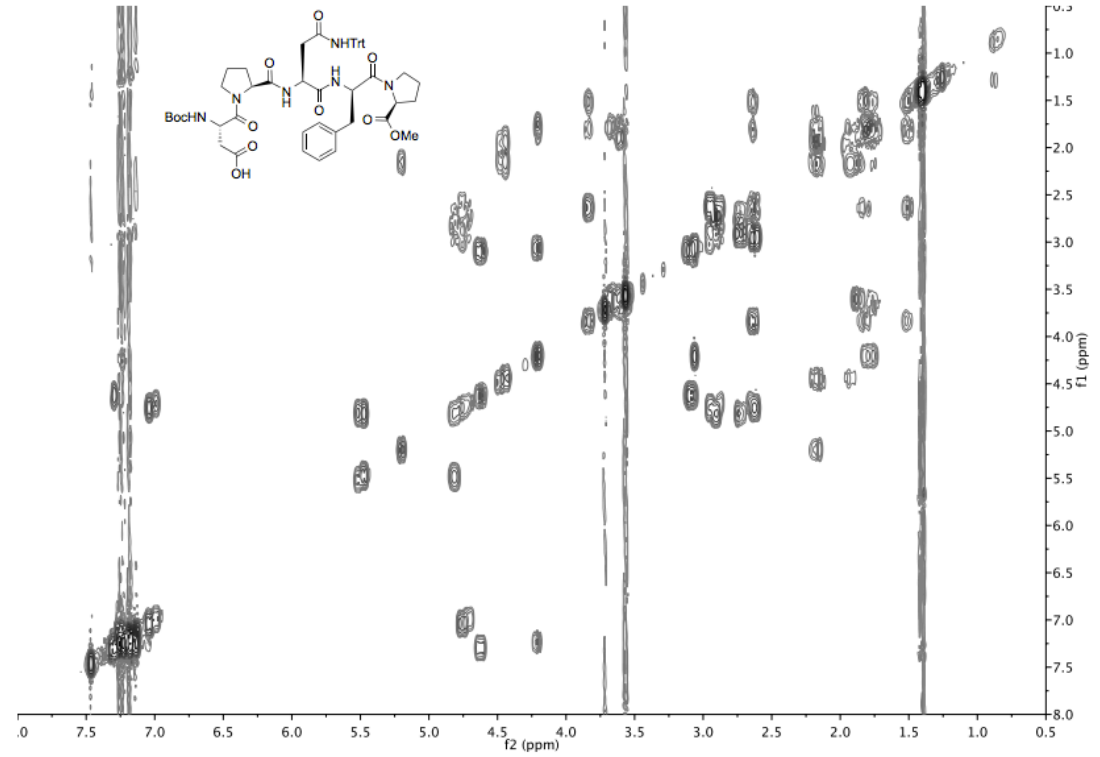


Truncation Peptides NMR Data

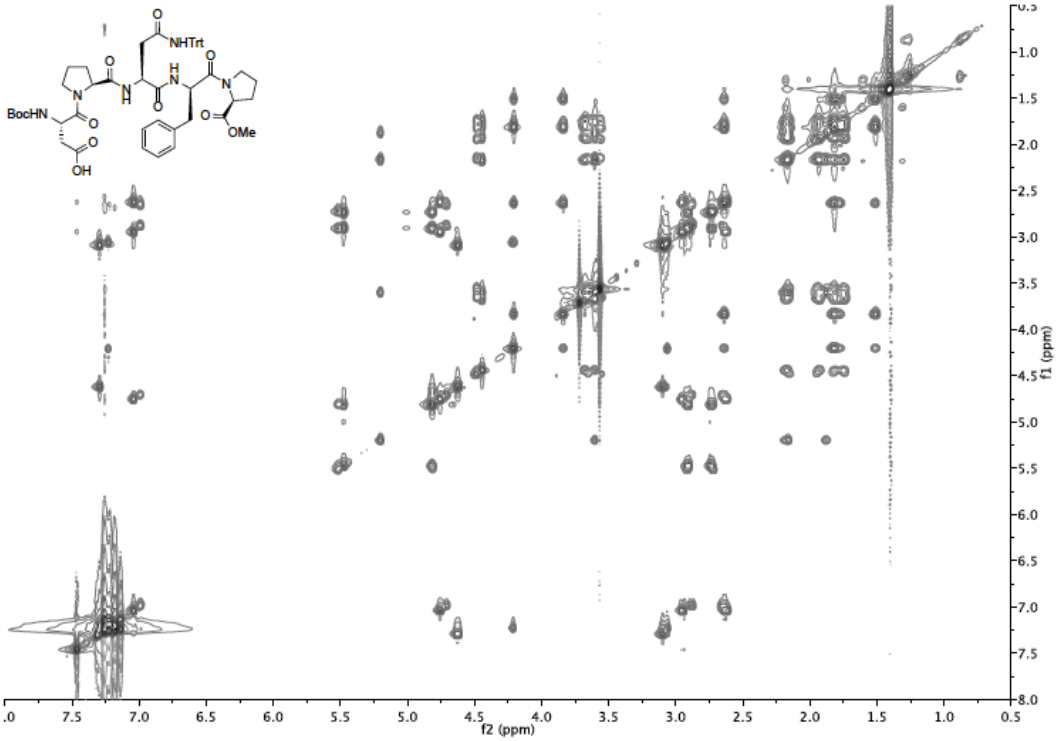
Catalyst **22** 1D ^{1}H NMR



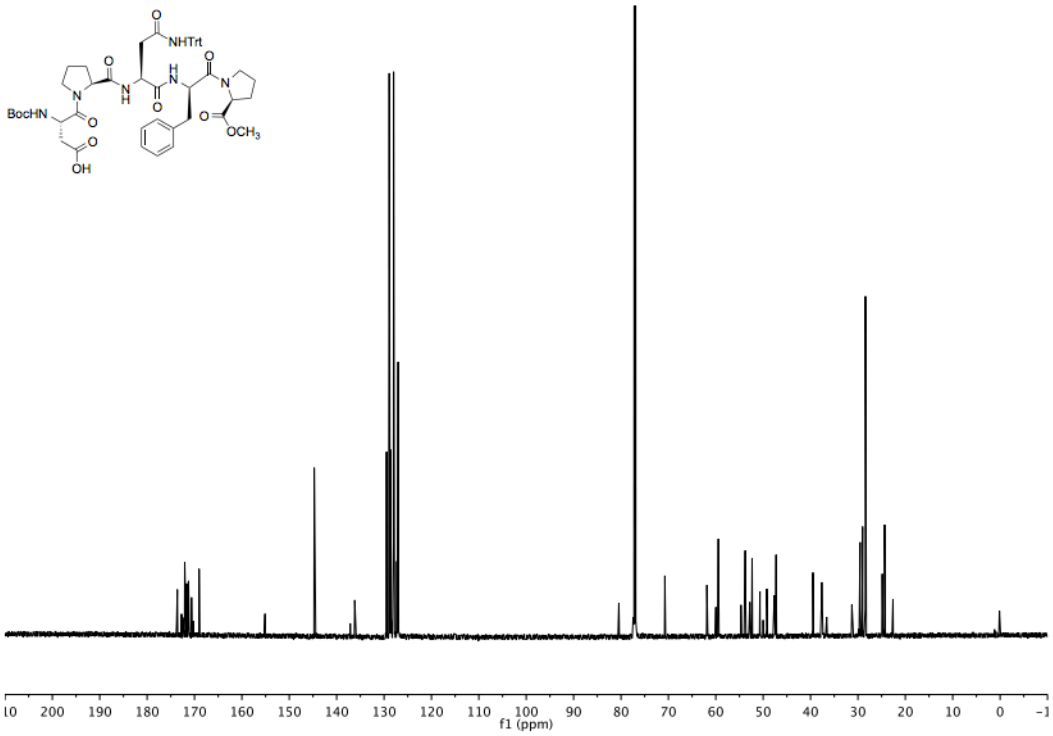
Catalyst **22** 2D gCOSY NMR



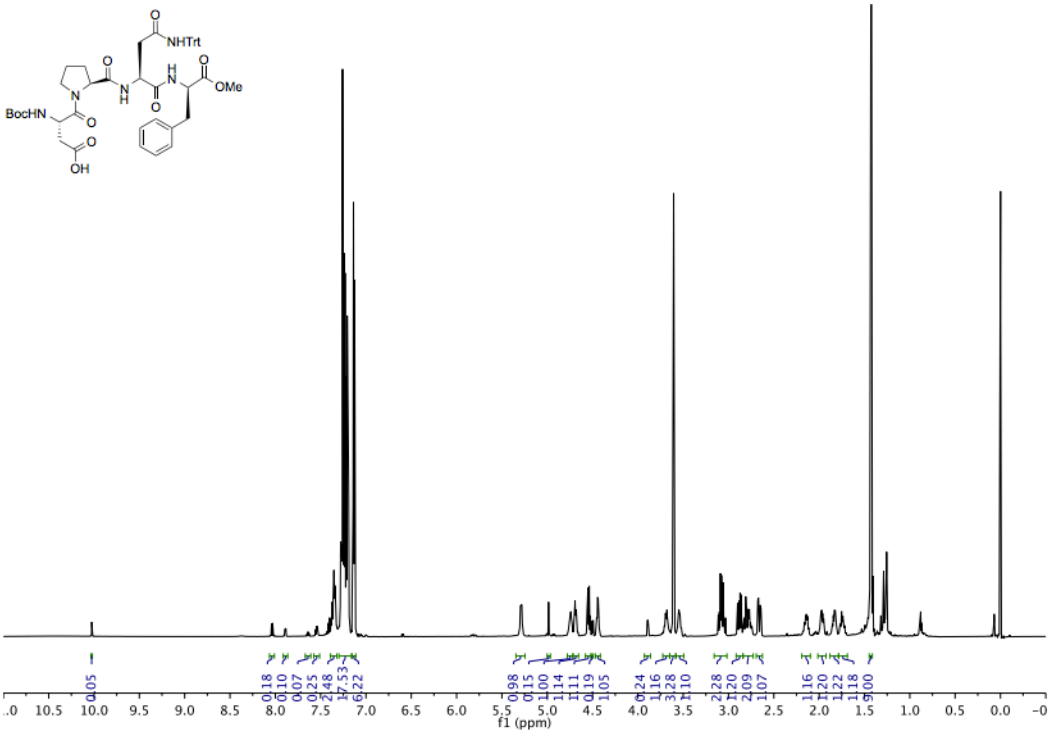
Catalyst **22** 2D zTOCSY NMR



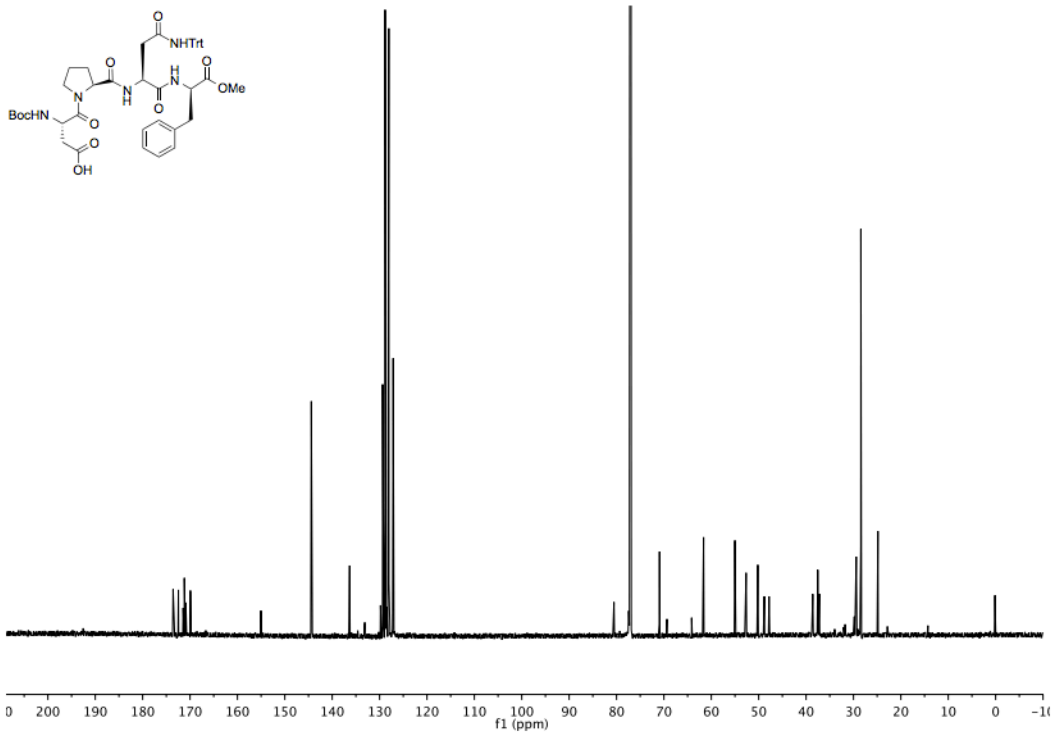
Catalyst **22** 1D ^{13}C NMR



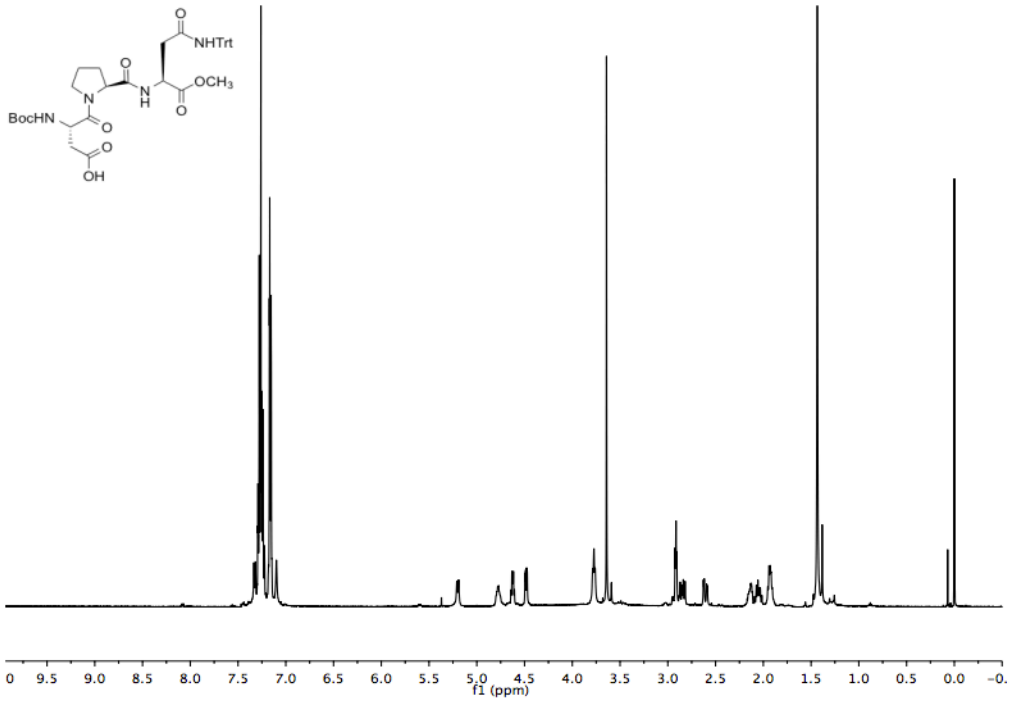
Catalyst **23** 1D ^{1}H NMR



Catalyst **23** 1D ^{13}C NMR



Catalyst **24** 1D ^{1}H NMR



Catalyst **24** 1D ^{13}C NMR