Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information for

A Bottom Up Approach Towards Artificial Oxygenases by Combining Iron Coordination Complexes and Peptides

Olaf Cussó,[1] Michael W. Giuliano, [2] Xavi Ribas,[1] Scott J. Miller[3,*] and Miquel Costas[1,*]

[1] QBIS-CAT Research Group, Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Campus Montilivi, Girona E-17071, Catalonia, Spain.

[2] Department of Chemistry and Biochemistry at the College of Charleston, South Carolina, United States.

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

Contents

1) Experimental Section

1.1) Materials

Reagents and solvents used were of commercially available reagent quality unless stated otherwise. Solvents were purchased from SDS and Scharlab. Solvents were purified and dried by passing through an activated alumina purification system (M-Braun SPS-800) or by conventional distillation techniques. For solid-phase peptide synthesis we used a cylindrical vessel with a fritted disc and a removable lid equipped The iron complexes were previously reported.[1]

1.2) Instrumentation

Oxidation products were identified by comparison of their GC or HPLC retention times with those of independently prepared racemate compounds, and/or by ^{1}H and $^{13}C\{^{1}H\}$-NMR analyses. IR spectra were taken in a Mattson-Galaxy Satellite FT-IR spectrophotometer using a MKII Golden Gate single reflection ATR system. Elemental analyses were performed using a CHNS-O EA-1108 elemental analyzer from Fisons. NMR spectra were taken on BrukerDPX300 and DPX400 spectrometers using standard conditions (Spectra were taken in $CDCl_3$ and referenced to either TMS at 0.00 ppm). Electrospray ionization mass spectrometry (ESI-MS) experiments were performed on a Bruker Daltonics Esquire 3000 Spectrometer using a 1 > mM solution of the analyzed compound. High resolution mass spectra (HRMS) were recorded on a Bruker MicroTOF-Q II^{TM} instrument with a ESI source at Serveis Tècnics of the University of Girona (for substrates and isolated epoxides the mass error were 5>ppm, and in the case of peptides were 3>ppm). Samples were introduced into the mass spectrometer ion source by direct infusion through a syringe pump and were externally calibrated using sodium formate. Chromatographic resolution of enantiomers was performed on an Agilent GC-7820-A chromatograph using a CYCLOSIL-B column, Sigma-Aldrich Supelco Astec CHIRALDEX G-TA column. HPLC data were recorded using an Agilent HP1100 chromatograph with CHIRALPAK IA, IB, IC, AS-H, OJ-H, OD-H, and OB-H columns

2) Synthesis of substrates

The following olefins were prepared according to the reported procedures.

(**S2**) 4-F α-methylstyrene. ^{1}H NMR data agree with values reported[2]

Published yield (not reported), obtained yield (72%)

(**S3**) 3-CF_3 α-methylstyrene. ^{1}H NMR data agree with values reported[3]

Published yield (87%), obtained yield (81%)

(**S4**) 2-Me α-methylstyrene. ^{1}H NMR data agree with values reported[4]

Published yield (83%), obtained yield (78%)

(**S5**) 2-F α-methylstyrene. ^{1}H NMR data agree with values reported[4]

Published yield (88%), obtained yield (72%)

(**S6**) 2-Cl α-methylstyrene. ^{1}H NMR data agree with values reported[5]

Published yield (81%), obtained yield (80%)

(**S7**) 2-Br α-methylstyrene. ^{1}H NMR data agree with values reported[6]

Published yield (96%), obtained yield (77%)

(**S9**) 2-Me α-ethylstyrene. ^{1}H NMR data agree with values reported[7]

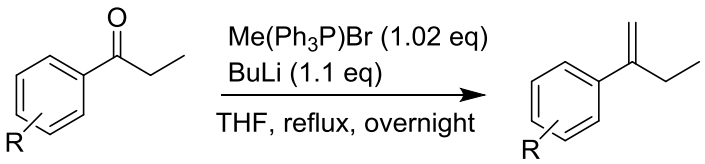
Published yield (93%), obtained yield (65%)

(**S12**) *Cis-β*-ethylstyrene. ^{1}H NMR data agree with values reported[8]

Published yield (98%), obtained yield (94%)

Substrates **S1** and **S11** are commercially available.

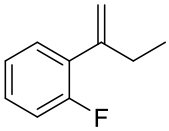
Synthesis of alkenes from ketones (S8 and S10)



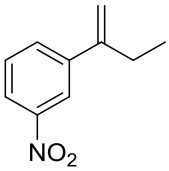
R = o-F, m-NO_2,

Representative procedure.

To a suspension of 2.32 g of methyltriphenylphosphinum bromide (6.34 mmol) in THF (30 mL) was added dropwise a solution of *n*-BuLi (4.4 mL, 1.6 M in hexane, 6.9 mmol) at 0ºC during 30 minutes. The white suspension changed to a red solution and was stirred at 0ºC for 90 min. The commercially available ketone (1.22 g, 6.22 mmol) was then added and the solution was stirred for 20 min at this temperature and then warmed to 70ºC and stirred overnight. Afterward, the reaction was quenched with water (5 mL) and the organic layer separated using a separatory funnel. The aqueous layer was extracted with diethyl ether (3 × 50 mL), dried over $MgSO_4$, and the solvent was removed under reduced pressure. Finally, purification by flash chromatography over silica (hexane/ethyl acetate 98/2) was performed.



S8, Colorless oil; (44% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm 7.30 – 7.26 (m, 1H), 7.26 – 7.23 (m, 1H), 7.12 (td, *J* = 7.5, 1.2 Hz, 1H), 7.09 – 7.03 (m, 1H), 5.26 – 5.24 (m, 1H), 5.17 (dd, *J* = 1.5, 0.8 Hz, 1H), 2.56 – 2.46 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 158.6, 146.7, 130.3, 130.2, 130.0, 130.0, 128.6, 128.5, 123.9, 123.8, 115.8, 115.5, 114.4, 114.4, 29.3, 12.7. HRMS(ESI+) *m/z* calculated for $C_{10}H_{11}FNa$ $[M+Na]^+$ 173.0737, found 173.0736.



S10, Yellow oil; (62% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm 8.27 (dt, *J* = 2.3, 1.1 Hz, 1H), 8.15 – 8.10 (m, 1H), 7.74 (ddd, *J* = 7.8, 1.8, 1.1 Hz, 1H), 7.53 – 7.47 (m, 1H), 5.45 – 5.37 (m, 1H), 5.23 (q, *J* = 1.4 Hz, 1H), 2.62 – 2.50 (m, 2H), 1.14 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 147.9, 143.2, 132.0, 129.2, 122.1, 120.9, 113.5, 27.8, 12.7. HRMS(ESI+) *m/z* calculated for $C_{10}H_{11}NO_2Na$ $[M+Na]^+$ 200.0682, found 200.0677.

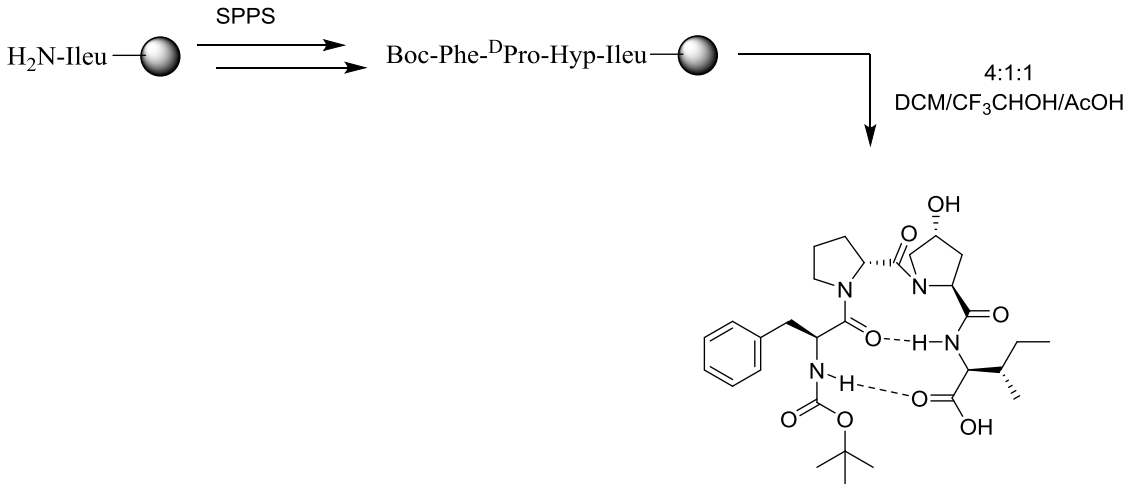
3) Synthesis of peptides by solid phase

3.1 Solid phase peptide coupling and Fmoc deprotection protocol

To pre-swollen resin (Chlorotrityl polystyrene resin that has been pre-loaded with L-isoleucine.) (0.35 mmols, ~30 min. in DCM) was added Fmoc-protected amino acid (1.75 mmols, 5 equiv.), HCTU (1.75 mmols, 5 equiv.), 6-Cl-HOBt•H_2O (1.75 mmols, 5 equiv.) with DMF (25 mL), followed by NMM (3.5 mmols, N-methylmorpholine) (10 equiv.). The resin mixture was sealed and mixed for 2 h on a rotary mixer and then drained, washing with a combination of DMF (2 x 20 mL), DCM (2 x 20 mL), the Fmoc-protecting group was removed with two treatments of 20% piperidine in DMF (v/v)(~25 mL) for 20 min. each, then washing with a combination of DMF (2 x 20 mL) and DCM (2 x 20 mL).

Resin was cleaved with a 4:1:1 mixture of DCM: 2,2,2-trifluoroethanol: acetic acid (25 mL), treating for 30-60 min before draining. The resulting solution, along with washes, was concentrated a couple of times with additional toluene.

We used 0.013 mmols in the case of small-scale peptide synthesis



Boc-Phe-^{D}Pro-Hyp-Ileu-OH

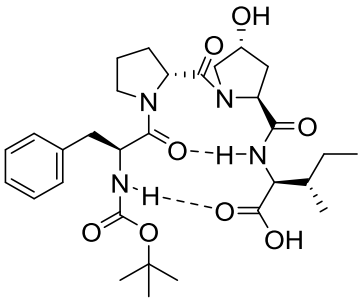
Large-scale peptide purification. Peptide purification was carried out using a Biotage Isolera 1 system on a 30 g C18 column using the following:

Solvent A: 0.1 % formic acid in H_2O

Solvent B: 0.1 % formic acid in acetonitrile

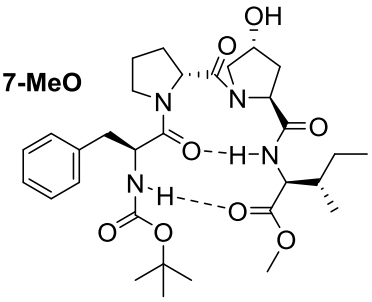
Method: hold at 5 % B for 2 CV, gradient from 5% B to 100 % B over 14 CV, hold at 100 % B for 4 CV, re-equilibrate at 5 % CV for 2 CV.

1 CV ~ 20 mL



Peptide 7. White solid; (180 mg, 88% yield,); ^{1}H-NMR ($CDCl_3$, 600 MHz, 300K) δ, ppm 7.56 (br, 1H), 7.28-7.13 (m, 5H), 6.54 (br, 1H), 5.57 (br, 1H), 4.70-4.42 (m, 3H), 4.38-4.32 (m, 2H), 4.10 (br, 1H), 3.97 (br, 1H), 3.53-3.49 (m, 1H), 3.00-2.91 (m,1H), 2.35-2.25 (m, 2H), 2.11-1.88 (m, 4), 1.61-1.45 (m, 3H), 1.41-1.36 (m, 3H), 1.25-1.17 (m, 3H), 0.99-0.90 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 173.7, 172.1, 171.6, 171.0, 169.2, 156.0, 154.9, 136.8, 129.5, 128.5, 126.8, 80.8, 80.0, 69.4, 59.3, 57.9, 55.3, 53.5, 49.8, 47.3, 40.4, 39.7, 38.7, 37.8, 36.1, 28.1, 25.0, 15.6, 11.6. HRMS(ESI+) *m/z* calculated for $C_{30}H_{44}N_4O_8Na$ $[M+Na]^+$ 611.3051, found 611.3046

peptide 7-MeO



To peptide 7 (5 mg, 0.008mmols, 1 equiv) was added EDC•HCl (1.1 equiv), HOBt•H_2O (1.1 equiv), and MeOH (300 µL). The resulting solution was allowed to stir 48 h. The solvent was removed under reduced pressure and then it was diluted with DCM and washed with aqueous 0.5 M citric acid, half-saturated brine, and saturated aqueous $NaHCO_3$. The combined organics were dried over Na_2SO_4, filtered, and concentrated. Transparent oil was obtained, 86 % yield (4.4 mg, 0.007 mmols).

4) Catalytic studies

4.1. General procedure for epoxidation reaction (Scheme 3 and scheme 4)

An acetonitrile solution (0.6 mL) of a given olefin (0.013 mmol, final reaction concentration 0.02 M) and **^{Me2N}1Fe** (0.2 mg, 0.26 µmol, 2 mol %, final reaction

concentration 0.43 mM) was prepared in a vial (3 mL) equipped with a stir bar at 0ºC. 0.52 µmol (4 mol %) of peptide solution in CH_3CN was added directly to the solution Then, 27 µL of 0.011M solution of hydrogen peroxide solution 30% (2 equiv.) in CH_3CN was added by syringe pump over a period of 30 min at 0ºC. The solution was further stirred at 0 ºC for 10 minutes. At this point, the internal standard trimethoxybenzene was added and the solution was filtered through a silica gel plug and basic alumina plug, and the solvent was removed under reduced pressure to afford the epoxide product. To determine the conversion and enantioselectivity, the residue was dissolved in hexanes with a few drops of isopropanol and then was analyzed by HPLC (IC column)

The procedure for **table 2** was the same but at -30ºC using a cooled acetonitrile bath

4.2. General procedure for epoxide isolation (Table 3)

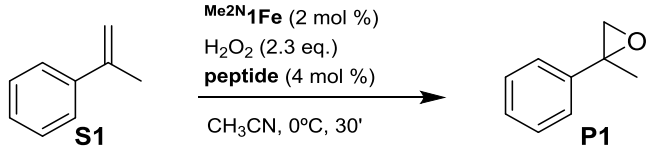
An acetonitrile solution (6 mL) of a given olefin (0.460 mmol, final reaction concentration 0.08 M) and **(*S,S*`)^{Me2N}1Fe** (7 mg, 9.2 µmol, 2 mol %, final reaction concentration 1.5 mM) was prepared in a vial (30 mL) equipped with a stir bar and cooled in an acetonitrile frozen bath. 10.8 mg of peptide **7** (18.5 µmol, 4 mol %) was added directly to the solution Then, 310 µL of 1:9 v:v acetonitrile:hydrogen peroxide solution 70% (2 equiv.) was added by syringe pump over a period of 30 min. The solution was further stirred at -30 ºC for 30 minutes. At this point, 15 mL of an aqueous $NaHCO_3$ saturated solution was added to the mixture. The resultant solution was extracted with DCM (3 x 10 mL). Organic fractions were combined, dried over $MgSO_4$, filtered through a silica gel plug, and the solvent was removed under reduced pressure to afford the epoxide product. This residue was purified by flash column chromatography over silica gel to obtain the pure epoxide (Hexane/AcOEt : 98/2). Finally, the epoxide product was dissolved in hexane and some drops of isopropanol and the was injected to HPLC

In the case of **S7**, catalyst loading was 8 mol % for **(*S,S*`)^{Me2N}1Fe** and 16 mol% for peptide **7**

4.3. Peptide screening

This screening was performed with non purified peptides, just as they were cleaved from resin.

Table SI.1. Screening of peptides in the epoxidation reaction of *α*-methylstyrene and **^{Me2N}1Fe** catalyst and hydrogen peroxide



	(*S,S'*)^{Me2N}1Fe		(*R,R'*)^{Me2N}1Fe	
Peptides	**Conv. (%)**	**ee (%)**	**Conv. (%)**	**ee (%)**
peptide 11 (Boc-***t***-Leu-^{D}Pro-Val-Ileu-OH)	81	36	65	36
peptide 12 (Boc-Val-^{D}Pro-Val-Ileu-OH)	82	30	70	36
peptide 13 (Boc-Ileu-^{D}Pro-Aib-Ileu-OH)	67	44	45	32
peptide 14 (Boc-Val-^{D}Pro-Aib-Ileu-OH)	82	36	68	36
peptide 15 (Ac-Phe-^{D}Pro-Aib-Ileu-OH)	33	22	54	28
peptide 16 (Fmoc-Phe-^{D}Pro-Aib-Ileu-OH)	24	26	32	28
peptide 17 (Z-Phe-^{D}Pro-Aib-Ileu-OH)	65	38	58	38
peptide 18 (Boc-Phe-^{D}Pro-Dibutgly-Ileu-OH)	72	32	95	35
peptide 19 (Boc-Phe-^{D}Pro-Cle-Ileu-OH)	71	38	94	24
peptide 20 (Boc-Phe-^{D}Pro-AC6C-Ileu-OH)	91	36	94	38
peptide 21 (Boc-Phe-^{D}Pro-Gly-Ileu-OH)	83	40	91	27
peptide 22 (Boc-Phe-^{D}Pro-Pro-Ileu-OH)	97	56	95	45
peptide 23 (Boc-Phe-Pro-^{D}Pro-Ileu-OH)	83	37	90	28
peptide 24 (Boc-Phe-^{D}Pro-Pip-Ileu-OH)	95	46	93	45
peptide 25 (Boc-Phe-^{D}Pro-Hyp(Bz)-Ileu-OH)	94	56	89	42
peptide 26 (Boc-Phe-^{D}Pro-Hyp(tBu)-Ileu-OH)	95	54	82	46
peptide 27 (Boc-Thr(tBu)-^{D}Pro-Aib-Ileu-OH)	81	40	96	34
peptide 28 (Boc-Phe(4-I)-^{D}Pro-Aib-Ileu-OH)	85	54	88	37
peptide 29 (Boc-3-(2-pyr)-Ala--^{D}Pro-Aib-Ileu-OH)	64	31	86	36
peptide 30 (Boc-2-Naph-^{D}Pro-Aib-Ileu-OH)	85	49	90	37
peptide 31 (Boc-^{D}Phe-^{D}Pro-Aib-Ileu-OH)	15	30	45	32
peptide 32 (Boc-Bip-^{D}Pro-Aib-Ileu-OH)	45	41	57	36
peptide 33 (Boc-^{5F}Phe-^{D}Pro-Aib-Ileu-OH)	60	50	88	54

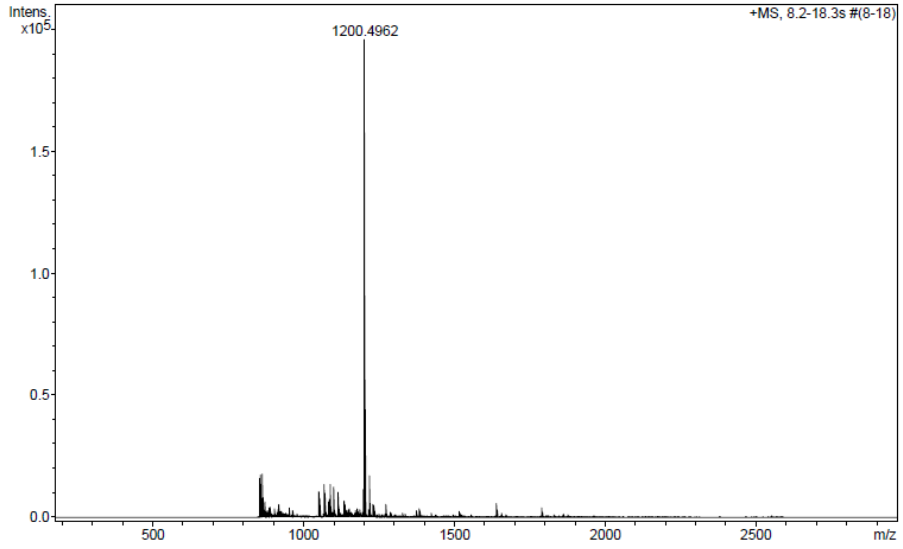
peptide 34 (Boc-Hfe-^{D}Pro-Aib-Ileu-OH)	44	46	60	44
peptide 35 (Boc-Phg-^{D}Pro-Aib-Ileu-OH)	38	32	67	36
peptide 36 (Boc-Ala(1-Naph)-^{D}Pro-Aib-Ileu-OH)	17	40	40	37
peptide 37 (Boc-2CN-Phe-^{D}Pro-Aib-Ileu-OH)	88	52	83	40
peptide 38 (Boc-Tyr(tBu)-^{D}Pro-Aib-Ileu-OH)	72	48	87	44
peptide 39 (Boc-Tyr(Bn)-^{D}Pro-Aib-Ileu-OH)	87	44	88	42
peptide 40 (Boc-2CN-Phe-^{D}Pro-Hyp-Ileu-OH)	95	52	94	46
peptide 41 (Boc-Phe(4-I)-^{D}Pro-HYp-Ileu-OH)	88	52	85	45
peptide 42 (Boc-^{5F}Phe-^{D}Pro-Hyp-Ileu-OH)	88	56	83	52
peptide 43 (NPha-Phe-^{D}Pro-Hyp-Ileu-OH)	81	32	72	36
peptide 44 (Boc-Val-Phe-^{D}Pro-Hyp-Ileu-OH)	87	34	83	29
peptide 45 (Boc-^{D}Val-Phe-^{D}Pro-Hyp-Ileu-OH)	92	41	91	42
peptide 46 (Boc-Phe-Phe-^{D}Pro-Hyp-Ileu-OH)	73	35	81	36
peptide 47 (Boc-^{D}Phe-Phe-^{D}Pro-Hyp-Ileu-OH)	85	38	84	40
peptide 7-MeO (Boc-Phe-^{D}Pro-Hyp-Ileu-OMe)	-	-	-	-

Unless stated, reaction conditions are ^{Me2N}**1Fe (**2 mol%, 0.43 mM), *α*-methylstyrene (0.013 mmol, 0.021 M, 1 equiv.), H_2O_2 (2.3 equiv.) and peptide (4 mol %) in CH_3CN (0.6 mL) at 0ºC during 30 min. Conversions determined by HPLC with trimethoxybenzene as internal standard. Ee's determined by HPLC (IC column)

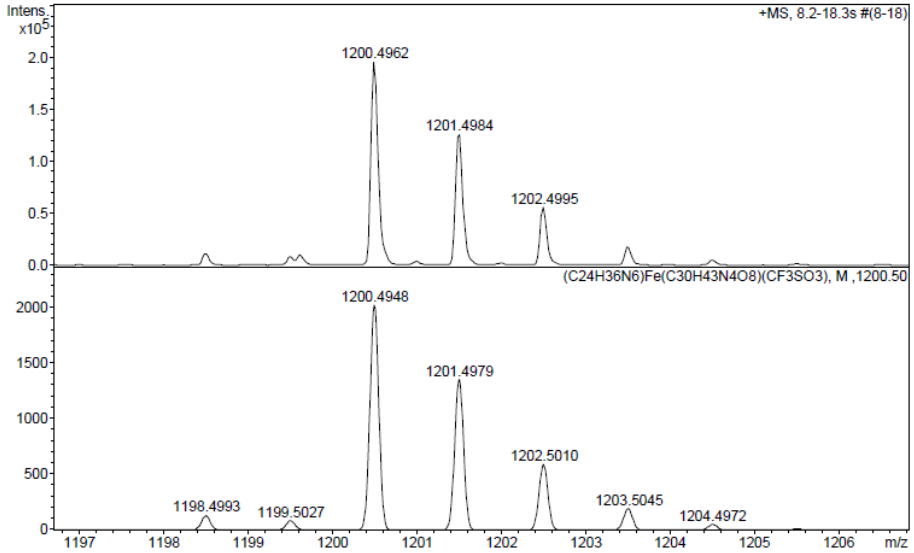
4.4. HRMS spectrum of the catalyst under catalysis conditions

Figure SI.1. a) HRMS spectrum obtained during H_2O_2 addition (1 min since beginning of addition) in the catalytic oxidation of **S1** by **(*S,S'*)^{Me2N}Fe** in presence of peptide **7** (1 equiv. respect to the catalyst). b) Amplified experimental (top) and simulated (bottom) peaks corresponding to **(*S,S'*)-[Fe(CF_3SO_3)(peptide7-H^+)(^{Me2N}pdp)]$^+$**

a)

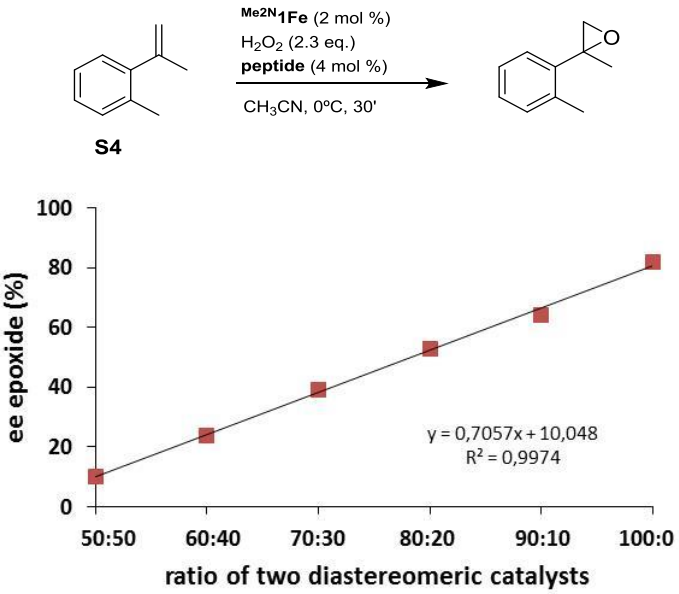


b)



4.5. Study of non-linear effects

Fig. SI. 2. Demonstration of linear correlation between ee's of catalyst and epoxide in the asymmetric epoxidation of *ortho*-methyl-*α*-methylstyrene (**S4**)



Reaction conditions are 2 mol%, ^{Me2N}**1Fe**, peptide (4 mol %), H_2O_2 (2.3 equiv.) and in CH_3CN at 0ºC during 30 min. Ee's determined by chiral GC

50:50 represents: 1 mol % of (S,S') enantiomer: 1 mol % of (R,R') enantiomer.

60:40 represents: 1.2 mol % of (S,S') enantiomer: 0.8 mol % of (R,R') enantiomer

70:30 represents: 1.4 mol % of (S,S') enantiomer: 0.6 mol % of (R,R') enantiomer

80:20 represents: 1.6 mol % of (S,S') enantiomer: 0.4 mol % of (R,R') enantiomer

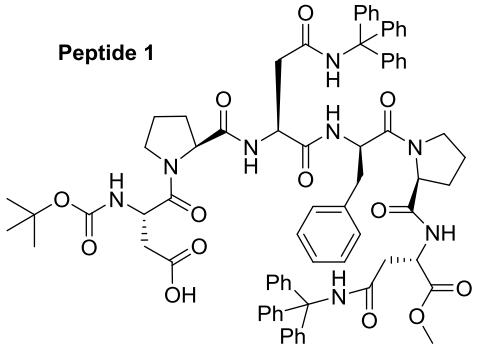
90:10 represents: 1.8 mol % of (S,S') enantiomer: 0.2 mol % of (R,R') enantiomer

100:0 represents: 2 mol % of (S,S') enantiomer: 0 mol % of (R,R') enantiomer

5) Characterization of peptides and epoxides

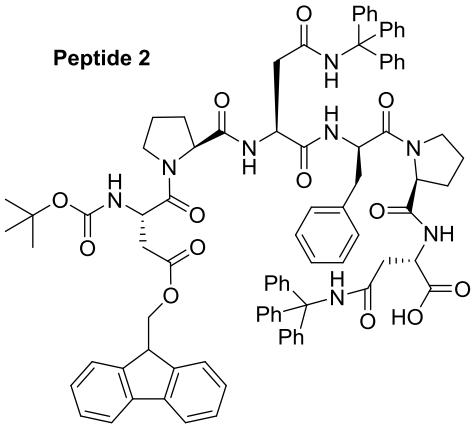
5.1. Mass spectrometry analyses of peptides

Peptide 1



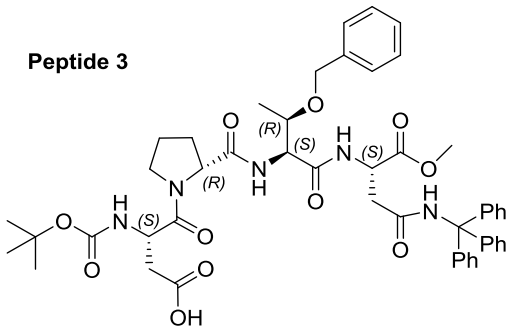
reported by Miller and co-worlers [9]

Peptide 2



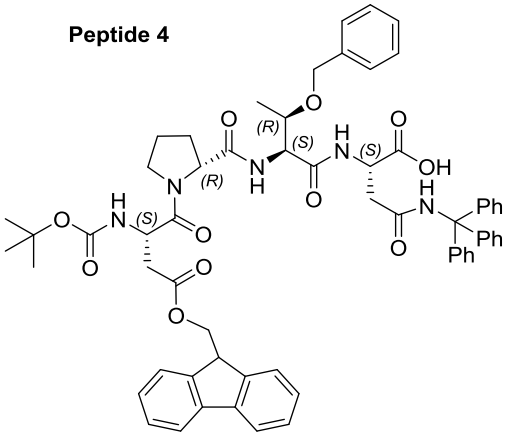
Chemical Formula: $C_{88}H_{88}N_8O_{13}$
Exact Mass: 1464,65
16.3 mg: 73 % yield
HRMS: Calculated/Observed for $C_{88}H_{88}N_8O_{13}Na^{2+}$ 755.3128/ 755.3110

Peptide 3



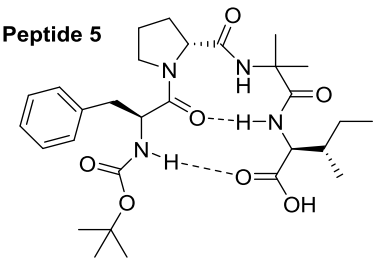
reported by Miller and co-workers [10]

Peptide 4



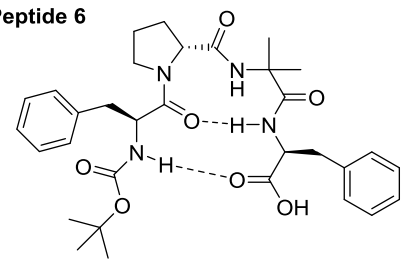
Chemical Formula: $C_{62}H_{65}N_5O_{11}$
Exact Mass: 1055,47
14.5 mg: 90 % yield
HRMS: Calculated/Observed for $C_{62}H_{65}N_5O_{11}Na$ 1078.4573/ 1078.4549

Peptide 5



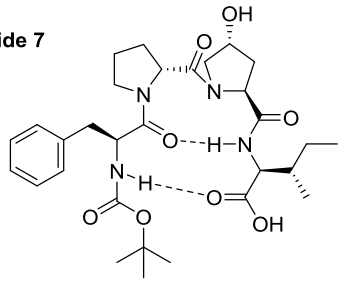
Chemical Formula: $C_{29}H_{44}N_4O_7$
Exact Mass: 560,32
3.9 mg: 53 % yield
HRMS: Calculated/Observed for $C_{29}H_{44}N_4O_7Na$ 583.3102/ 583.3115

Peptide 6



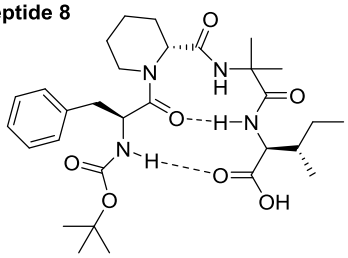
Chemical Formula: $C_{32}H_{42}N_4O_7$
Exact Mass: 594,31
7.3 mg: 94 % yield
HRMS: Calculated/Observed for $C_{32}H_{43}N_4O_7^+$ 617.2946/ 617.2961

Peptide 7



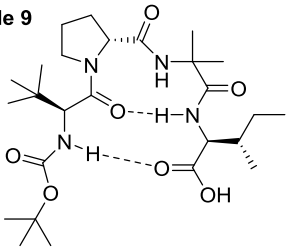
Chemical Formula: $C_{30}H_{44}N_4O_8$
Exact Mass: 588,32
180 mg: 88 % yield
HRMS: Calculated/Observed for $C_{30}H_{44}N_4O_8Na^+$ 611.3051./ 611.3046

Peptide 8



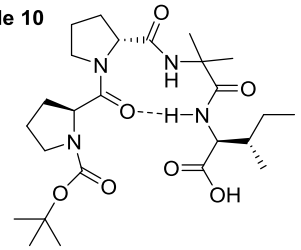
Chemical Formula: $C_{30}H_{46}N_4O_7$
Exact Mass: 574,34
8.1 mg: 82 % yield
HRMS: Calculated/Observed for $C_{30}H_{46}N_4O_7Na$ 597.3259/ 597.3254

Peptide 9



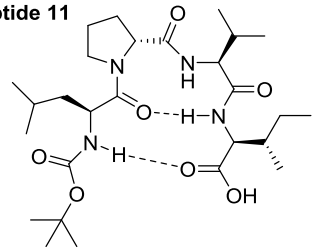
Chemical Formula: $C_{26}H_{46}N_4O_7$
Exact Mass: 526,34
9.1 mg: 92 % yield
HRMS: Calculated/Observed for $C_{26}H_{46}N_4O_7Na$ 549.3259/ 549.3254

Peptide 10



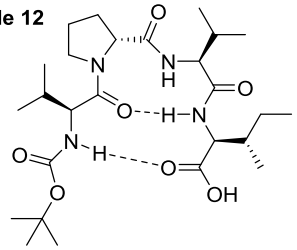
Chemical Formula: $C_{25}H_{42}N_4O_7$
Exact Mass: 510,31
5.8 mg: 70 % yield
HRMS: Calculated/Observed for $C_{25}H_{42}N_4O_7Na$ 533.2946/ 533.2941

Peptide 11



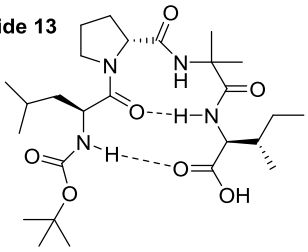
Chemical Formula: $C_{27}H_{48}N_4O_7$
Exact Mass: 540,35
6.2 mg: 86 % yield
HRMS: Calculated/Observed for $C_{27}H_{48}N_4O_7Na$ 563.3415/ 563.3414

Peptide 12



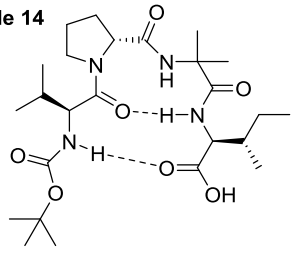
Chemical Formula: $C_{26}H_{46}N_4O_7$
Exact Mass: 526,34
4.5 mg: 66 % yield
HRMS: Calculated/Observed for $C_{26}H_{46}N_4O_7Na$ 549.3259/ 549.3262

Peptide 13



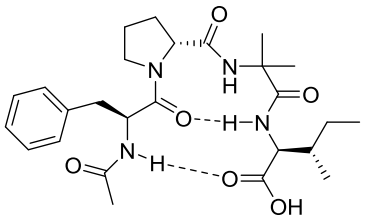
Chemical Formula: $C_{26}H_{46}N_4O_7$
Exact Mass: 526,34
4.3 mg: 61 % yield
HRMS: Calculated/Observed for $C_{26}H_{47}N_4O_7^+$ 549.3259/ 549.3260

Peptide 14



Chemical Formula: $C_{25}H_{44}N_4O_7$
Exact Mass: 512,32
4.4 mg: 66 % yield
HRMS: Calculated/Observed for $C_{25}H_{44}N_4O_7Na$ 535.3102/ 531.3117

Peptide 15

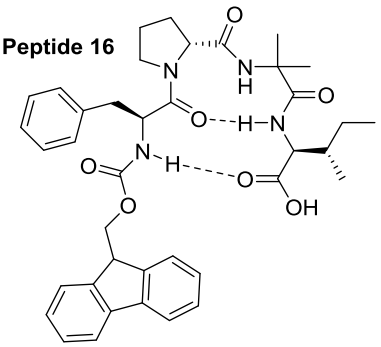


Chemical Formula: $C_{26}H_{38}N_4O_6$
Exact Mass: 502,28

6.2 mg: 95 % yield

HRMS: Calculated/Observed for $C_{26}H_{38}N_4O_6Na$ 525.2684/ 525.2689

Peptide 16

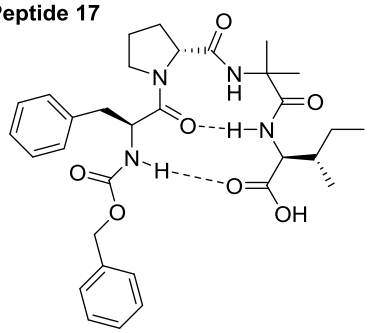


Chemical Formula: $C_{39}H_{46}N_4O_7$
Exact Mass: 682,34

7.1 mg: 90 % yield

HRMS: Calculated/Observed for $C_{39}H_{46}N_4O_7Na$ 705.3259/ 705.3261

Peptide 17

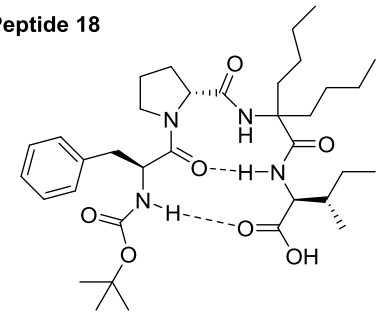


Chemical Formula: $C_{32}H_{42}N_4O_7$
Exact Mass: 594,31

3.5 mg: 42 % yield

HRMS: Calculated/Observed for $C_{32}H_{42}N_4O_7Na$ 617.2946/ 617.2948

Peptide 18

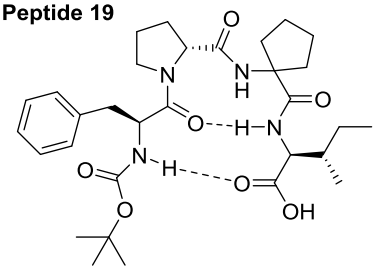


Chemical Formula: $C_{35}H_{56}N_4O_7$
Exact Mass: 644,41

4.5 mg: 59 % yield

HRMS: Calculated/Observed for $C_{35}H_{56}N_4O_7Na$ 667.4068/ 667.4041

Peptide 19

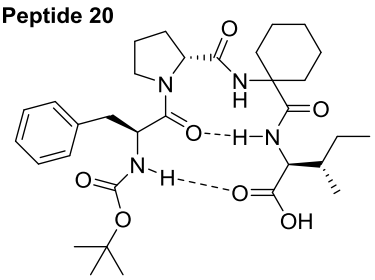


Chemical Formula: $C_{31}H_{46}N_4O_7$
Exact Mass: 586,34

6.7 mg: 90% yield

HRMS: Calculated/Observed for $C_{31}H_{46}N_4O_7Na$ 609.3259/ 609.3260

Peptide 20

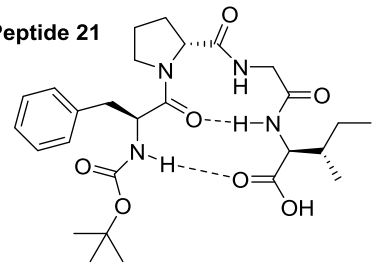


Chemical Formula: $C_{32}H_{48}N_4O_7$
Exact Mass: 600,35

6 mg: 80 % yield

HRMS: Calculated/Observed for $C_{32}H_{48}N_4O_7Na$ 623.3415/ 623.3426

Peptide 21

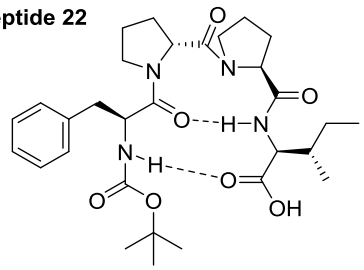


Chemical Formula: $C_{27}H_{40}N_4O_7$
Exact Mass: 532,29

6.2 mg: 83 % yield

HRMS: Calculated/Observed for $C_{27}H_{40}N_4O_7Na$ 555.2789/ 55.2773

Peptide 22

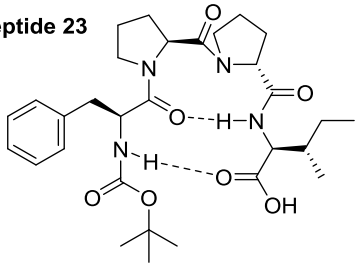


Chemical Formula: $C_{30}H_{44}N_4O_7$
Exact Mass: 572,32

4 mg: 54 % yield

HRMS: Calculated/Observed for $C_{30}H_{44}N_4O_7Na$ 595.3102/ 595.3094

Peptide 23

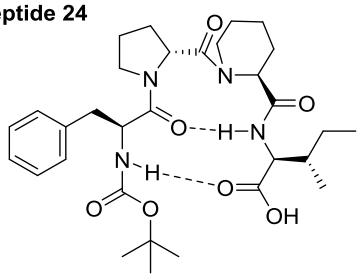


Chemical Formula: $C_{30}H_{44}N_4O_7$
Exact Mass: 572,32

6.1 mg: 62 % yield

HRMS: Calculated/Observed for $C_{30}H_{44}N_4O_7Na$ 595.3102/ 595.3111

Peptide 24

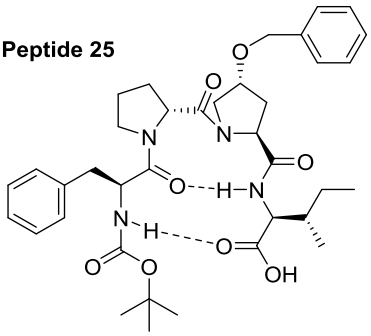


Chemical Formula: $C_{31}H_{46}N_4O_7$
Exact Mass: 586,34

3.9 mg: 52 % yield

HRMS: Calculated/Observed for $C_{31}H_{46}N_4O_7^+$ 609.3259/ 609.3256

Peptide 25

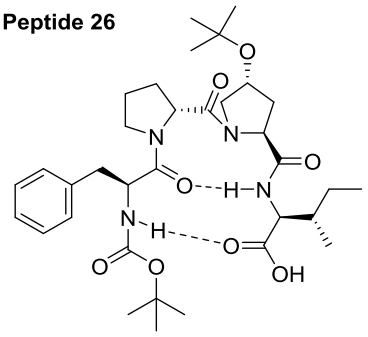


Chemical Formula: $C_{37}H_{50}N_4O_8$
Exact Mass: 678,36

5.4 mg: 73 % yield

HRMS: Calculated/Observed for $C_{37}H_{50}N_4O_8Na$ 701.3521/ 701.3512

Peptide 26

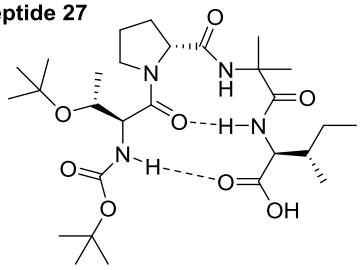


Chemical Formula: $C_{34}H_{52}N_4O_8$
Exact Mass: 644,38

4.4 mg: 58 % yield

HRMS: Calculated/Observed for $C_{34}H_{52}N_4O_8Na$ 667.3677/ 667.3667

Peptide 27

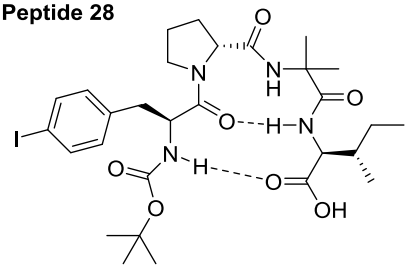


Chemical Formula: $C_{28}H_{50}N_4O_8$
Exact Mass: 570,36

3.3 mg: 41 % yield

HRMS: Calculated/Observed for $C_{28}H_{50}N_4O_8Na$ 593.3521/ 593.3506

Peptide 28

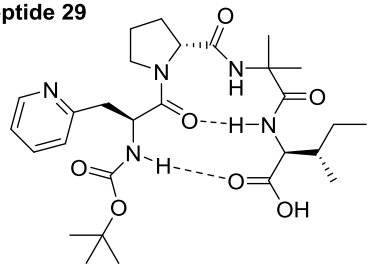


Chemical Formula: $C_{29}H_{43}IN_4O_7$
Exact Mass: 686,22

4.9 mg: 56 % yield

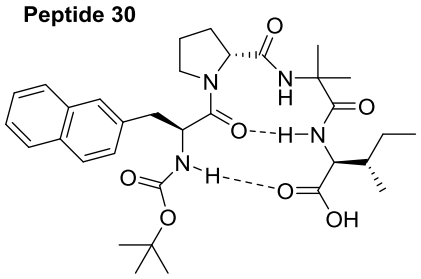
HRMS: Calculated/Observed for $C_{29}H_{43}IN_4O_7Na$ 709.2069/ 709.2058

Peptide 29



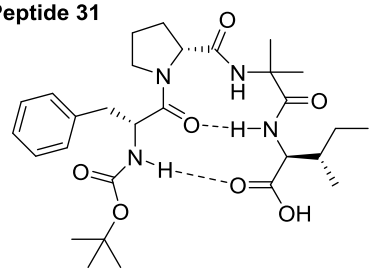
Chemical Formula: $C_{28}H_{43}N_5O_7$
Exact Mass: 561,32
5.3 mg: 66 % yield
HRMS: Calculated/Observed for $C_{28}H_{43}N_5O_7Na$ 584.3055/ 584.3026

Peptide 30



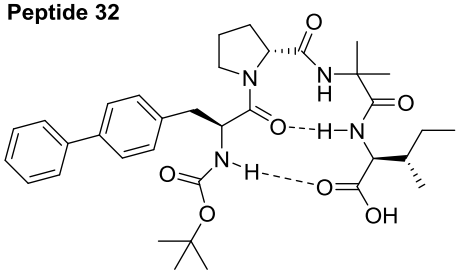
Chemical Formula: $C_{33}H_{46}N_4O_7$
Exact Mass: 610,34
39 mg: 43 % yield
HRMS: Calculated/Observed for $C_{33}H_{46}N_4O_7Na$ 633.3259/ 633.3237

Peptide 31



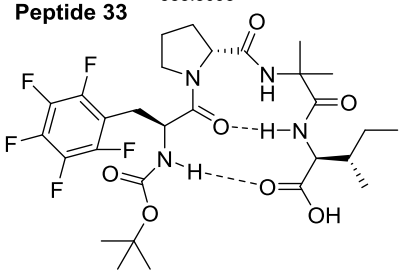
Chemical Formula: $C_{29}H_{44}N_4O_7$
Exact Mass: 560,32
7.1 mg: 76 % yield
HRMS: Calculated/Observed for $C_{29}H_{44}N_4O_7Na$ 583.3102/ 583.3093

Peptide 32



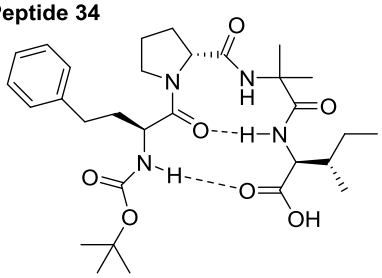
Chemical Formula: $C_{35}H_{48}N_4O_7$
Exact Mass: 636,35
3.4 mg: 46 % yield
HRMS: Calculated/Observed for $C_{35}H_{48}N_4O_7Na$ 659.3415/ 659.3400

Peptide 33



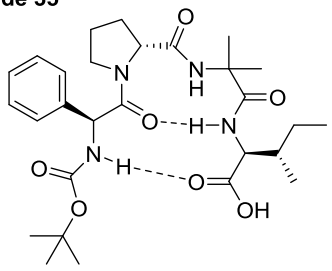
Chemical Formula: $C_{29}H_{39}F_5N_4O_7$
Exact Mass: 650,27
3.6 mg: 51% yield
HRMS: Calculated/Observed for $C_{29}H_{39}F_5N_4O_7Na$ 673.2631/ 673.2620

Peptide 34



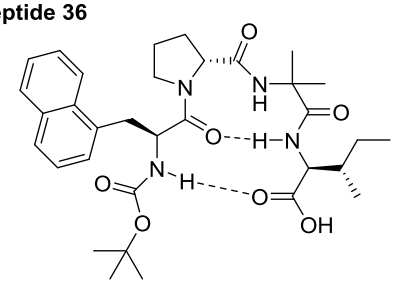
Chemical Formula: $C_{30}H_{46}N_4O_7$
Exact Mass: 574,34
4.4 mg: 56 % yield
HRMS: Calculated/Observed for $C_{30}H_{46}N_4O_7Na$ 597.3259/ 597.3250

Peptide 35



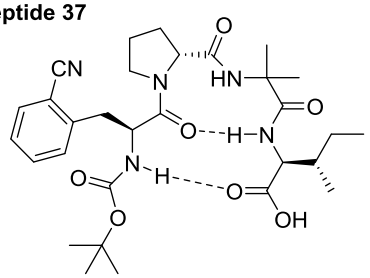
Chemical Formula: $C_{28}H_{42}N_4O_7$
Exact Mass: 546,31
6.6 mg: 87 % yield
HRMS: Calculated/Observed for $C_{28}H_{42}N_4O_7Na$ 569.2946/ 569.2931

Peptide 36



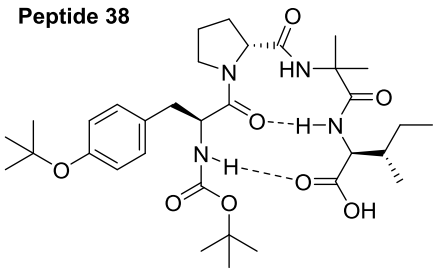
Chemical Formula: $C_{33}H_{46}N_4O_7$
Exact Mass: 610,34
5.6 mg: 68 % yield
HRMS: Calculated/Observed for $C_{33}H_{46}N_4O_7Na$ 633.3259/ 633.3239

Peptide 37



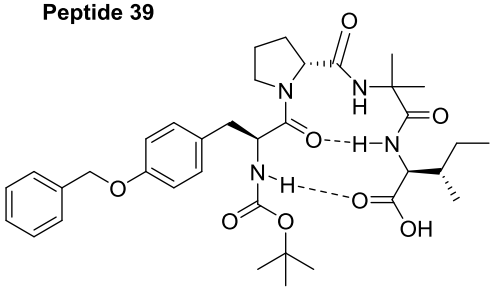
Chemical Formula: $C_{30}H_{43}N_5O_7$
Exact Mass: 585,32
6.6 mg: 77 % yield
HRMS: Calculated/Observed for $C_{30}H_{44}N_5O_7Na_2^+$ 630.2874/ 630.2863

Peptide 38



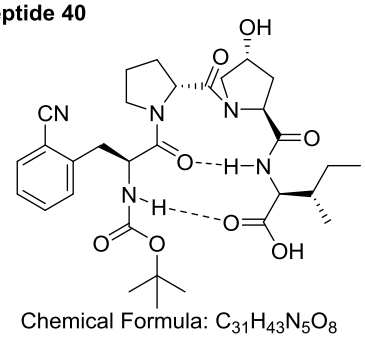
Chemical Formula: $C_{33}H_{52}N_4O_8$
Exact Mass: 632,38
6.5 mg: 79 % yield
HRMS: Calculated/Observed for $C_{33}H_{53}N_4O_8Na$ 655.3677/ 655.3674

Peptide 39



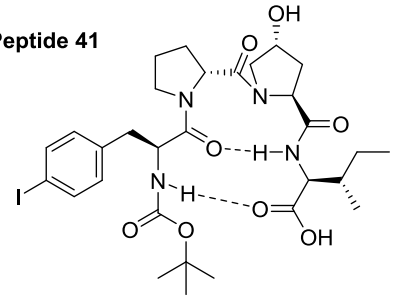
Chemical Formula: $C_{36}H_{50}N_4O_8$
Exact Mass: 666,36
6 mg: 66 % yield
HRMS: Calculated/Observed for $C_{36}H_{50}N_4O_8Na$ 689.3521/ 689.3501

Peptide 40



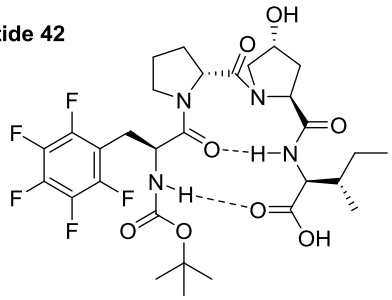
Chemical Formula: $C_{31}H_{43}N_5O_8$
Exact Mass: 613,31
4.9 mg: 62 % yield
HRMS: Calculated/Observed for $C_{31}H_{43}N_5O_8Na$ 636.3004/ 636.3004

Peptide 41



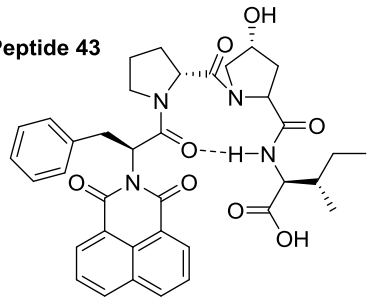
Chemical Formula: $C_{30}H_{43}IN_4O_8$
Exact Mass: 714,21
7.1 mg: 81 % yield
HRMS: Calculated/Observed for $C_{30}H_{43}IN_4O_8Na$ 737.2018/ 737.2006

Peptide 42



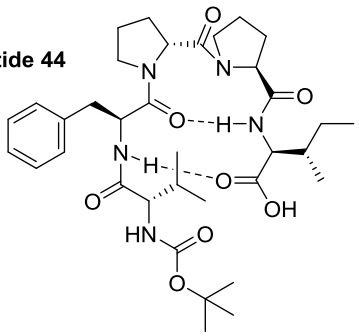
Chemical Formula: $C_{30}H_{39}F_5N_4O_8$
Exact Mass: 678,27
6.7 mg: 76 % yield
HRMS: Calculated/Observed for $C_{30}H_{39}F_5N_4O_7Na$ 701.2580/ 701.2567

Peptide 43



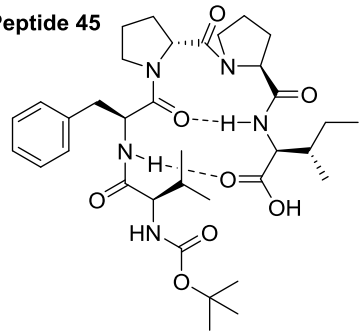
Chemical Formula: $C_{37}H_{40}N_4O_8$
Exact Mass: 668,28
5.9 mg: 68 % yield
HRMS: Calculated/Observed for $C_{37}H_{40}N_4O_8Na$ 691.2738/ 691.2712

Peptide 44



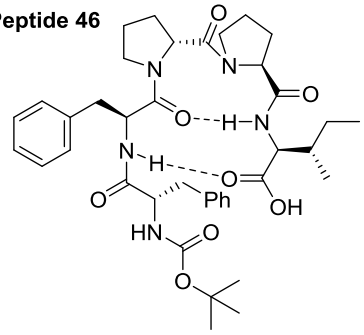
Chemical Formula: $C_{35}H_{53}N_5O_8$
Exact Mass: 671,39
7.2 mg: 83 % yield
HRMS: Calculated/Observed for $C_{35}H_{53}N_5O_8Na$ 694.3786/ 694.3787

Peptide 45



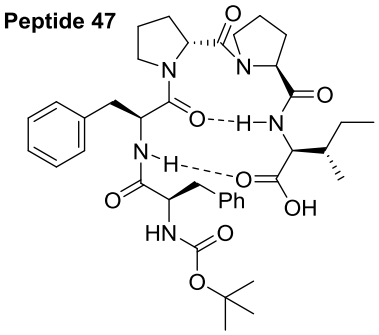
Chemical Formula: $C_{35}H_{53}N_5O_8$
Exact Mass: 671,39
7.3 mg: 84 % yield
HRMS: Calculated/Observed for $C_{35}H_{53}N_5O_8Na$ 694.3786/ 694.3789

Peptide 46



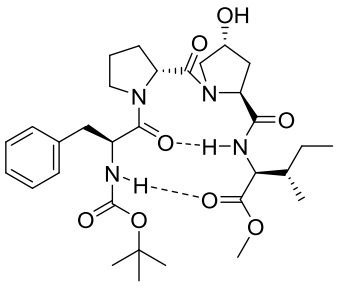
Chemical Formula: $C_{39}H_{53}N_5O_8$
Exact Mass: 719,39
6.4 mg: 69 % yield
HRMS: Calculated/Observed for $C_{39}H_{53}N_5O_8Na$ 742.3786/ 742.3787

Peptide 47



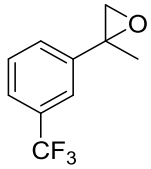
Chemical Formula: $C_{39}H_{53}N_5O_8$
Exact Mass: 719,39
6 mg: 64 % yield
HRMS: Calculated/Observed for $C_{39}H_{53}N_5O_8Na$ 742.3786/ 742.3782

Peptide 7-MeO

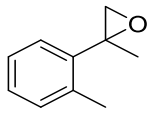


Chemical Formula: $C_{31}H_{46}N_4O_8$
Exact Mass: 602,33
4.4 mg: 86% yield
HRMS: Calculated/Observed for $C_{31}H_{46}N_4O_8Na$ 625.3208./ 625.3199.

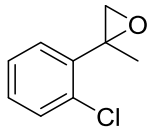
5.2. Characterization of isolated epoxides



S3, colorless oil; (75% yield, 68% ee); ^{1}H-NMR ($CDCl_3$, 600 MHz, 300K) δ, ppm 7.62 (s, 1H), 7.54 (t, *J* = 9.0 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 3.00 (d, *J* = 5.3 Hz, 1H), 2.78 (d, *J* = 5.3 Hz, 1H), 1.74 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 142.3, 131.1, 130.9, 130.7, 130.5, 128.8, 128.7, 126.7, 124.9, 124.3, 124.3, 124.3, 124.2, 123.1, 122.2, 122.2, 122.2, 122.1, 121.3, 57.0, 56.3, 21.5. HRMS(ESI+) *m/z* calculated for $C_{10}H_9F_3ONa$ $[M+Na]^+$ 225.0498, found 225.0493. HPLC-separation conditions: Chiralpack OB-H 25ºC, 220 nm, 99.9/0.1 hexane/*i*-PrOH, 1.0 mL/min; r.t.(major) = 8.7 min, r.t.(minor) = 10.2 min

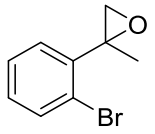


S4, colorless oil; (80% yield, 92% ee); ^{1}H-NMR ($CDCl_3$, 600 MHz, 300K) δ, ppm 7.38 – 7.34 (m, 1H), 7.18 (t, *J* = 6.3 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 1H), 2.96 (d, *J* = 5.3 Hz, 1H), 2.82 (d, *J* = 5.3 Hz, 1H), 2.41 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 139.8, 135.1, 130.0, 127.5, 126.8, 125.8, 58.3, 54.7, 23.49, 19.1. HRMS(ESI+) *m/z* calculated for $C_{10}H_{12}ONa$ $[M+Na]^+$ 171.0780, found 171.0789. Chiral GC analysis with CYCLOSIL-B

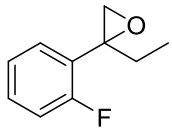


S6, colorless oil; (82% yield, 84% ee); ^{1}H-NMR ($CDCl_3$, 600 MHz, 300K) δ, ppm 7.47 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.32 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.27 – 7.22 (m, 3H), 3.00 (d, *J* = 5.1 Hz, 1H), 2.83 (d, *J* = 5.1 Hz, 1H), 1.65 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 139.6, 132.2, 129.1, 128.6, 128.4, 126.9, 57.8, 55.1. HRMS(ESI+) *m/z* calculated for C_9H_9ClONa $[M+Na]^+$ 191.0234, found

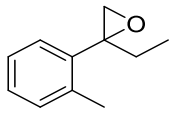
191.0223. HPLC-separation conditions: Chiralpack IB 25ºC, 220nm, 98/2 hexane/*i*-PrOH, 1.0 mL/min; r.t.(minor) = 4.5 min, r.t.(major) = 4.8 min



S7, yellow oil; (67% yield, 90% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm 7.55 – 7.52 (m, 1H), 7.51 – 7.47 (m, 1H), 7.32 (td, *J* = 7.5, 1.2 Hz, 1H), 7.17 (ddd, *J* = 8.0, 7.4, 1.8 Hz, 1H), 3.04 (d, *J* = 5.1 Hz, 1H), 2.86 (d, *J* = 5.8 Hz, 1H), 1.68 (s, 4H).^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 141.3, 132.3, 129.1, 128.8, 127.5, 121.7, 59.2, 55.4, 22.7. HRMS(ESI+) *m/z* calculated for C_9H_9BrONa $[M+Na]^+$ 234.9729, found 234.9731. Chiral GC analysis with astec CHIRALDEX G-TA

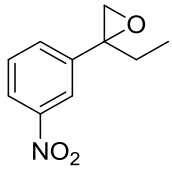


S8, colorless oil; (88% yield, 90% ee); ^{1}H-NMR ($CDCl_3$, 600 MHz, 300K) δ, ppm 7.38 (t, *J* = 7.5 Hz, 1H), 7.26 (m, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.04 – 7.00 (m, 1H), 2.99 (d, *J* = 5.2 Hz, 1H), 2.83 – 2.78 (d, *J* = 5.2 Hz, 1H), 2.08 (m, 1H), 1.79 (m, 1H), 0.94 – 0.86 (m, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 161.1, 159.5, 129.3, 129.2, 128.9, 128.9, 127.4, 127.3, 123.9, 123.9, 115.3, 115.1, 58.9, 53.4, 29.1, 8.9. HRMS(ESI+) *m/z* calculated for $C_{10}H_{11}OFNa$ $[M+Na]^+$ 189.0686, found 189.0681. HPLC-separation conditions: Chiralpack AS-H 25ºC, 254nm, 99.6/0.4 hexane/*i*-PrOH, 1.0 mL/min; r.t.(major) = 5.6 min, r.t.(minor) = 5.9 min

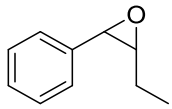


S9, colorless oil; (66% yield, 90% ee); ^{1}H-NMR ($CDCl_3$, 600 MHz, 300K) δ, ppm 7.31 (d, *J* = 7.2 Hz, 1H), 7.21 – 7.11 (m, 3H), 3.00 (d, *J* = 5.2 Hz, 1H), 2.78 (d, *J* = 5.2 Hz, 1H), 2.38 (s, 3H), 1.93 (m, 1H), 1.79 (m, 1H), 0.91 (t, *J* = 7.5 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 138.4, 135.3, 130.0, 128.0, 127.4, 125.4, 61.6, 53.1, 29.1, 19.1, 9.0. HRMS(ESI+) *m/z* calculated for $C_{11}H_{14}ONa$ $[M+Na]^+$ 185.0937, found 185.0933. HPLC-separation conditions: Chiralpack

OJ-H 25ºC, 220nm, 99.8/0.2 hexane/*i*-PrOH, 1.0 mL/min; r.t.(major) = 7.8 min, r.t.(minor) = 8.4 min



S10, colorless oil; (99% yield, 86% ee); ^{1}H-NMR ($CDCl_3$, 600 MHz, 300K) δ, ppm 8.23 (s, 1H), 8.13 (d, *J* = 9.4 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 3.04 (d, *J* = 5.1 Hz, 1H), 2.73 (d, *J* = 5.1 Hz, 1H), 2.27 (m, 1H), 1.83 (m, 1H), 0.94 (t, *J* = 7.5 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ ppm 148.4, 142.4, 132.0, 129.4, 122.5, 121.2, 60.2, 55.5, 27.7, 8.8. HRMS(ESI+) *m/z* calculated for $C_{10}H_{11}NO_3FNa$ $[M+Na]^+$ 216.0631, found 216.0632. HPLC-separation conditions: Chiralpack IC 25ºC, 220nm, 99/1 hexane/*i*-PrOH, 1.0 mL/min; r.t.(minor) = 12.7 min, r.t.(major) = 13.2 min



S12, colorless oil; (70% yield, 91% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm 7.42 – 7.29 (m, 5H), 4.11 (d, *J* = 4.2 Hz, 1H), 3.24 – 3.16 (m, 1H), 1.55 – 1.39 (m, 1H), 1.34 – 1.20 (m, 1H), 0.93 (t, *J* = 7.5 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 135.7, 128.0, 127.4, 126.5, 60.6, 57.5, 20.2, 10.0.HRMS(ESI+) *m/z* calculated for $C_{10}H_{12}ONa$ $[M+Na]^+$ 171.0780, found 171.0784. Chiral GC analysis with CYCLOSIL-B

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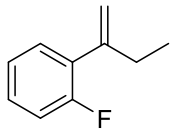
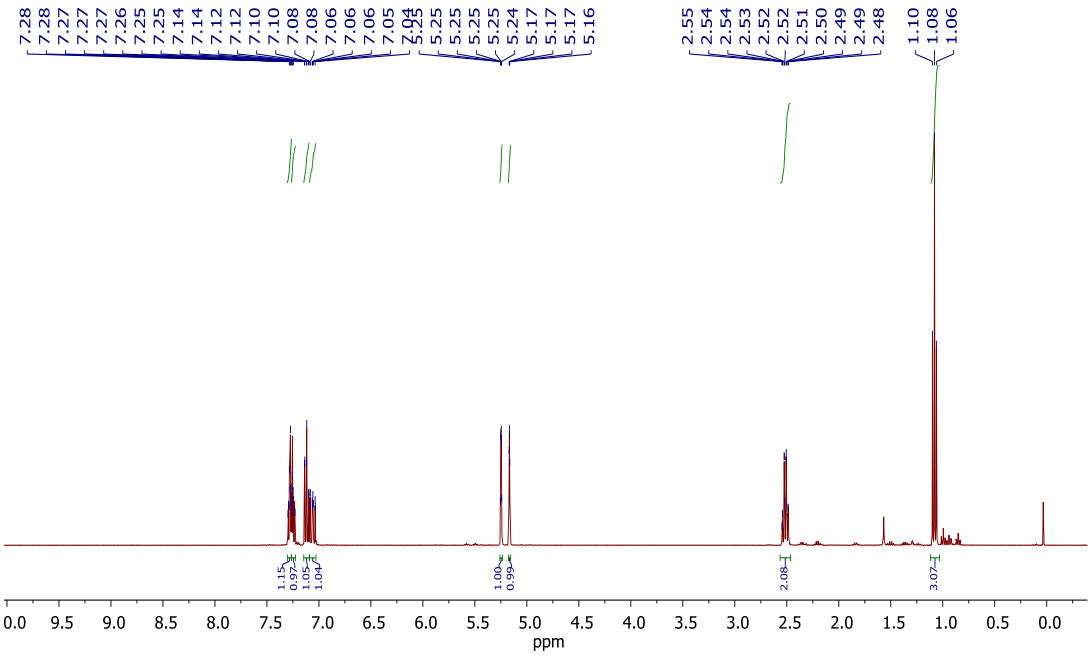
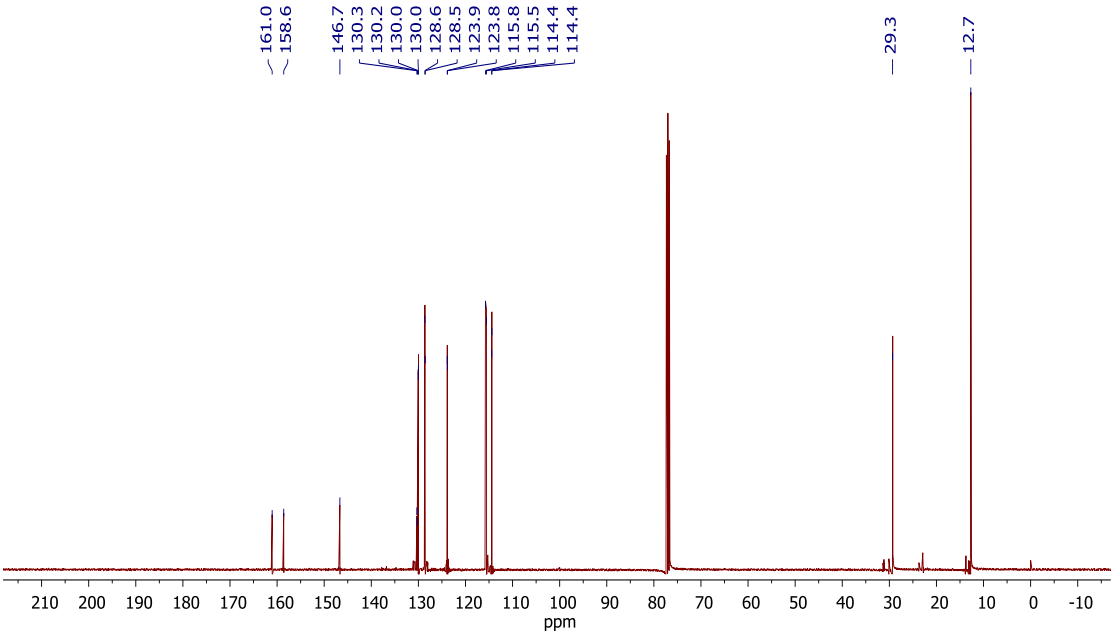
A1) ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of substrates

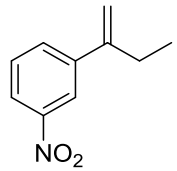


^{1}H-NMR of 2-F-alphaethylstyrene in $CDCl_3$

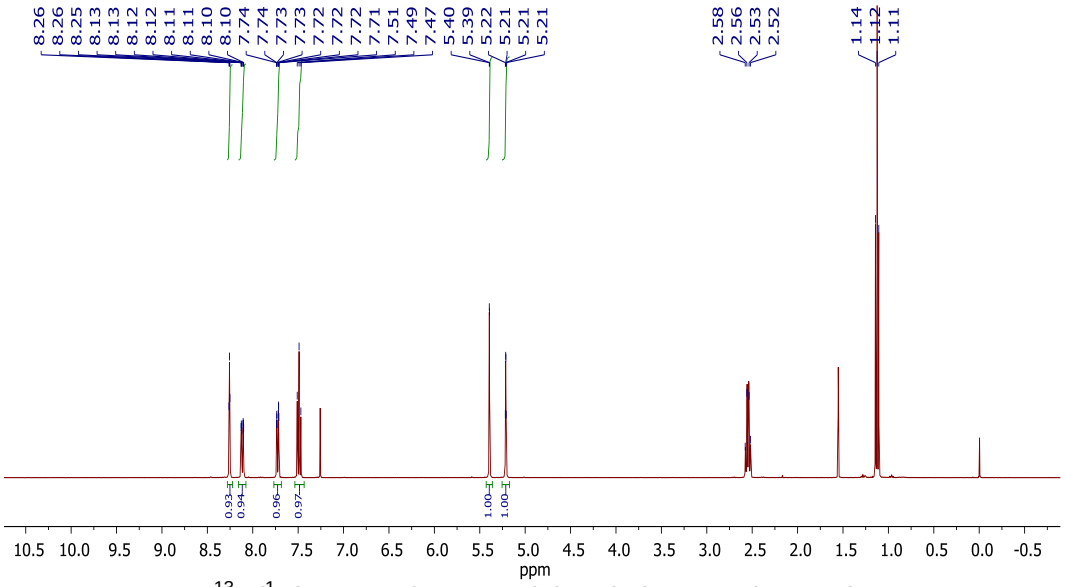


$^{13}C\{^{1}H\}$-NMR of 2-F-alphaethylstyrene in $CDCl_3$

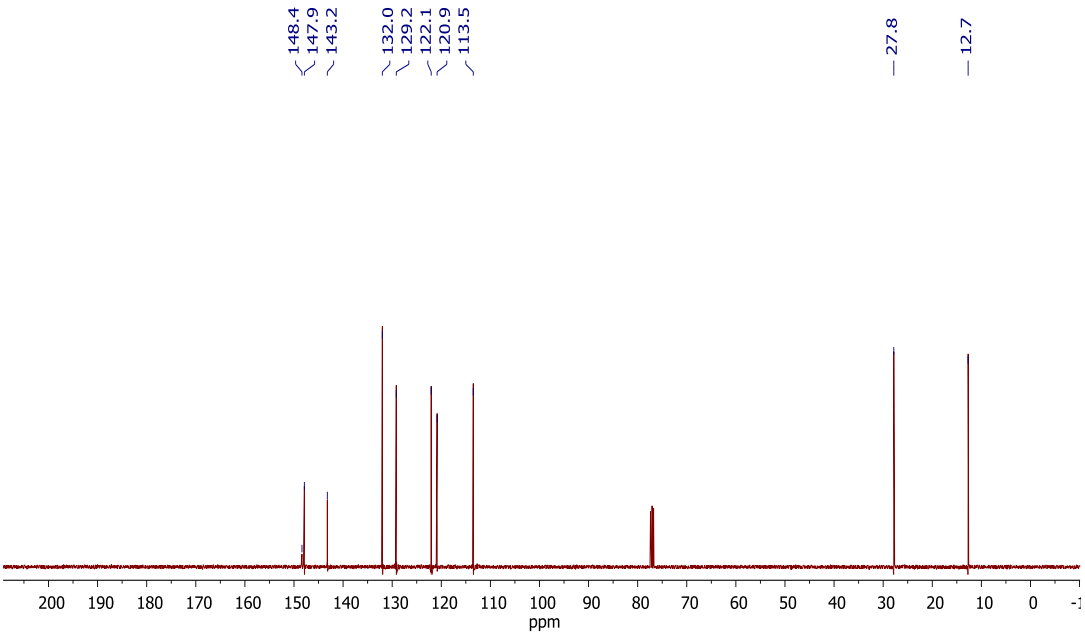




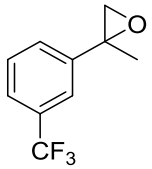
^{1}H-NMR of 3-NO_2-alphaethylstyrene in $CDCl_3$



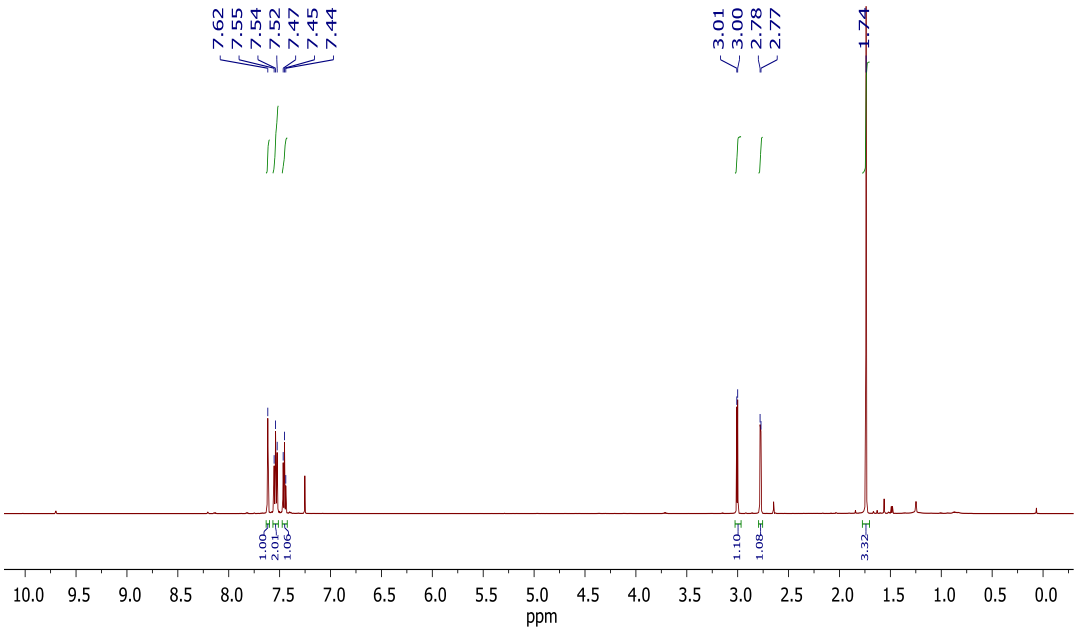
^{13}C{^{1}H}-NMR of 3-NO_2-alphaethylstyrene in $CDCl_3$



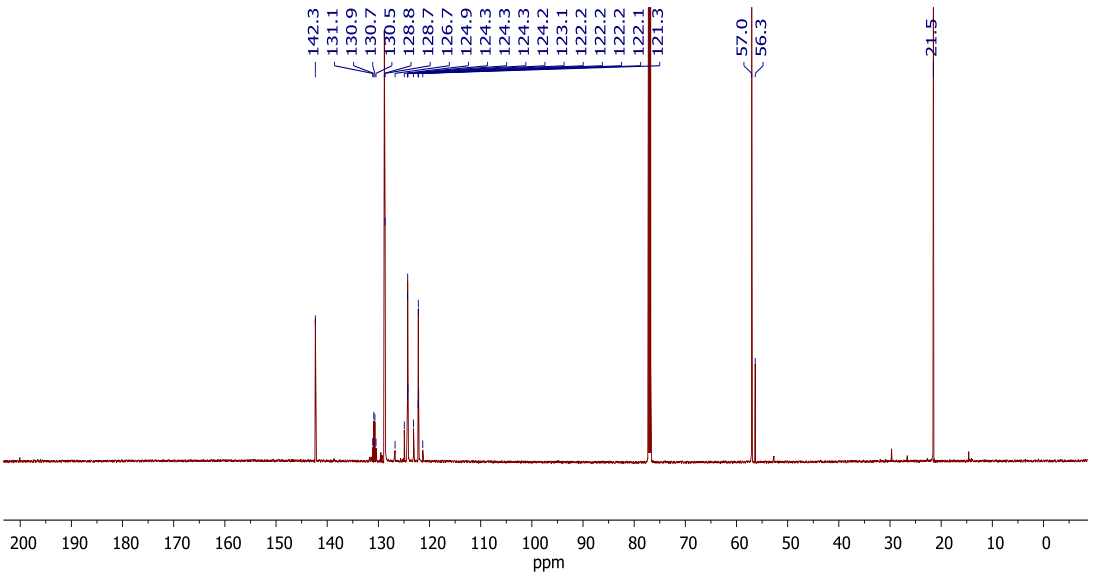
A2) 1H and 13C{1H} NMR spectra of isolated epoxides

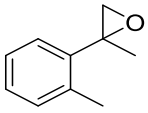


^{1}H-NMR of **S3** in $CDCl_3$

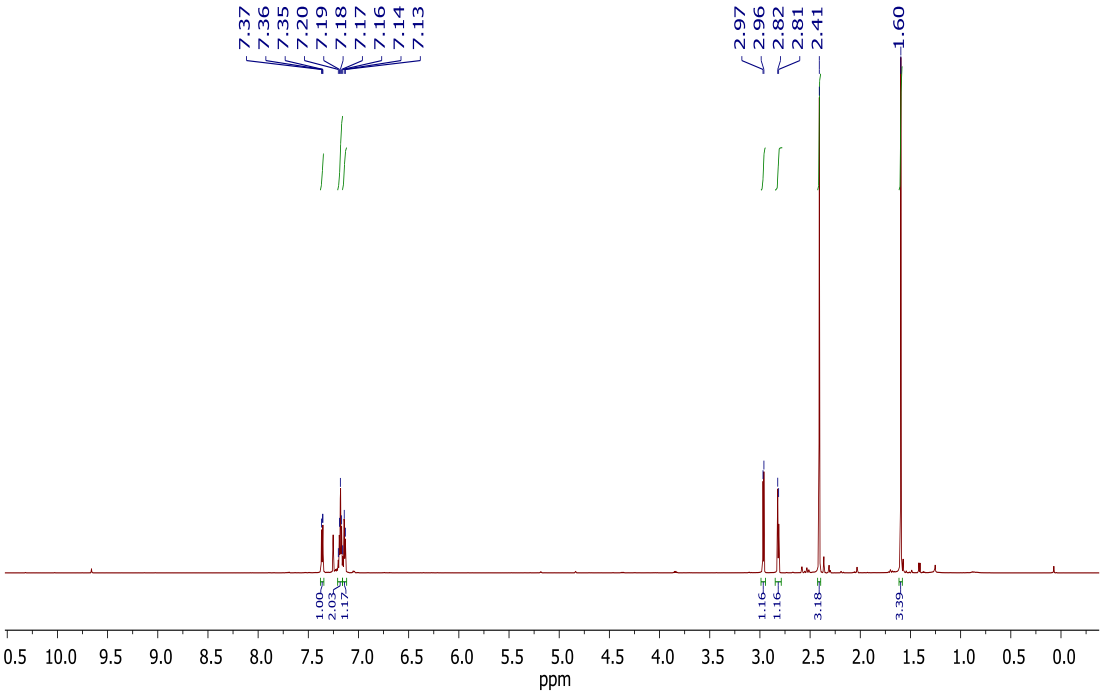


^{13}C{^{1}H}-NMR of **S3** in $CDCl_3$

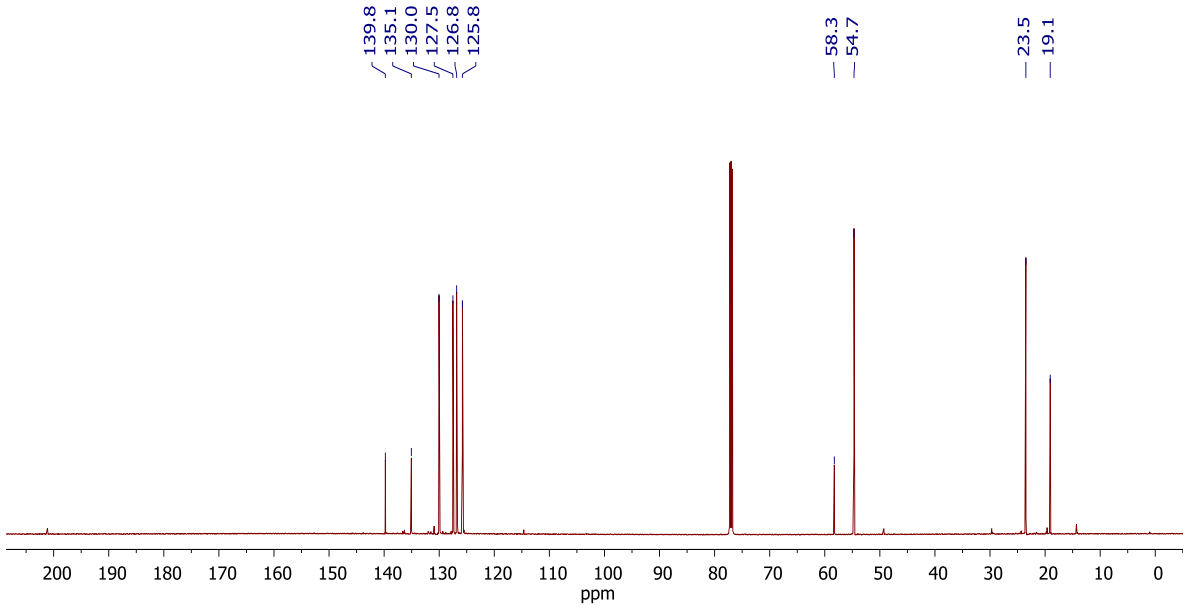


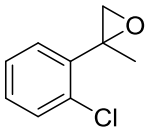


^{1}H-NMR of **S4** in $CDCl_3$

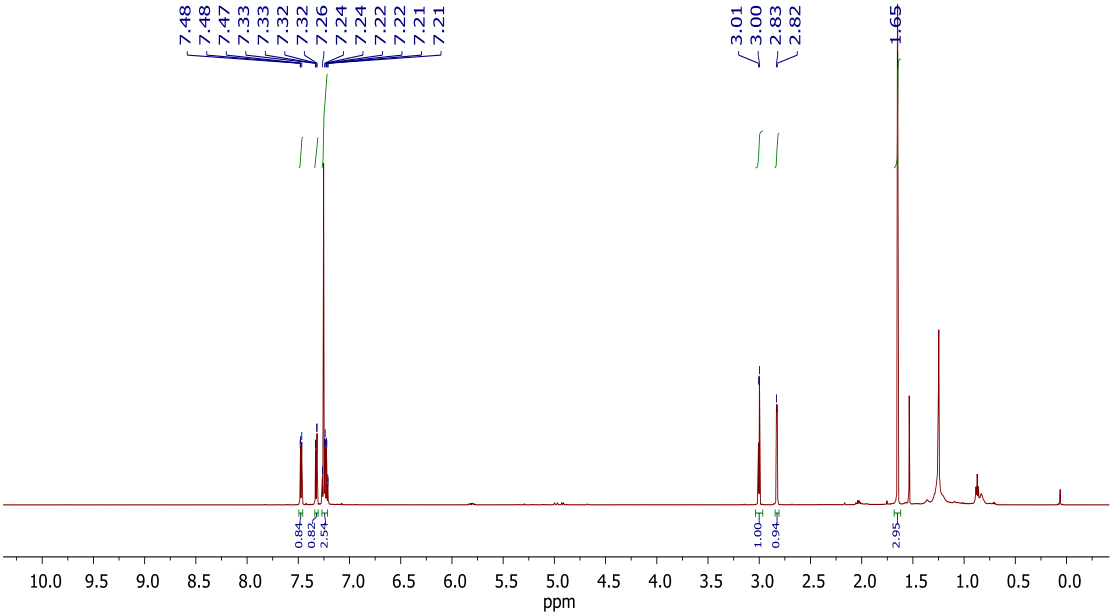


^{13}C{^{1}H}-NMR of **S4** in $CDCl_3$

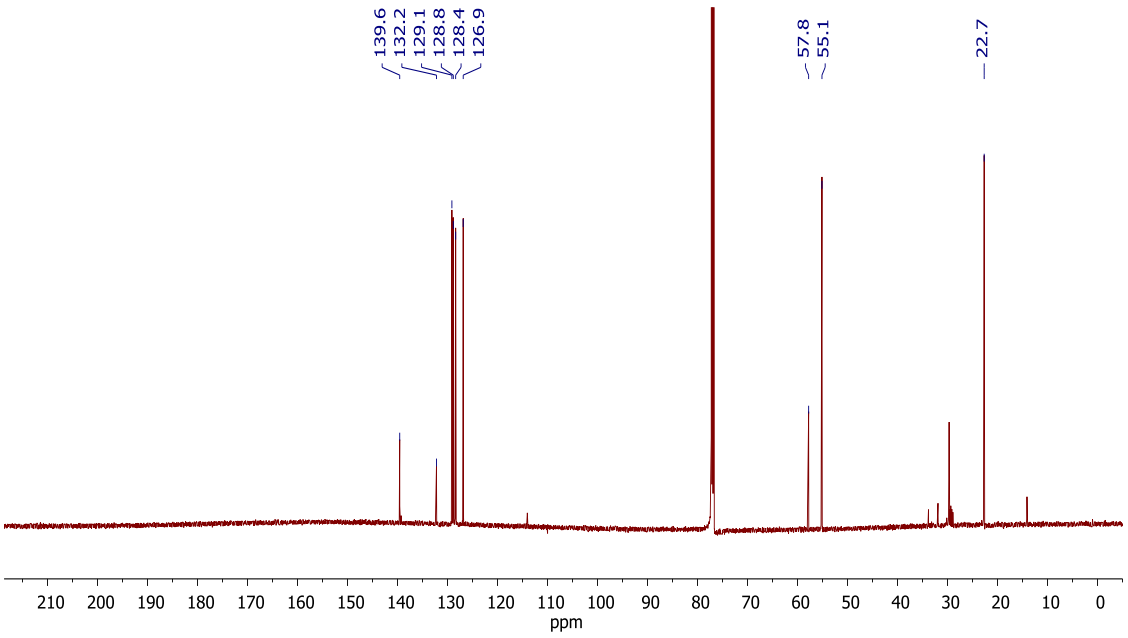


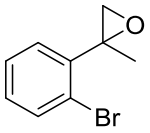


^{1}H-NMR of **S6** in $CDCl_3$

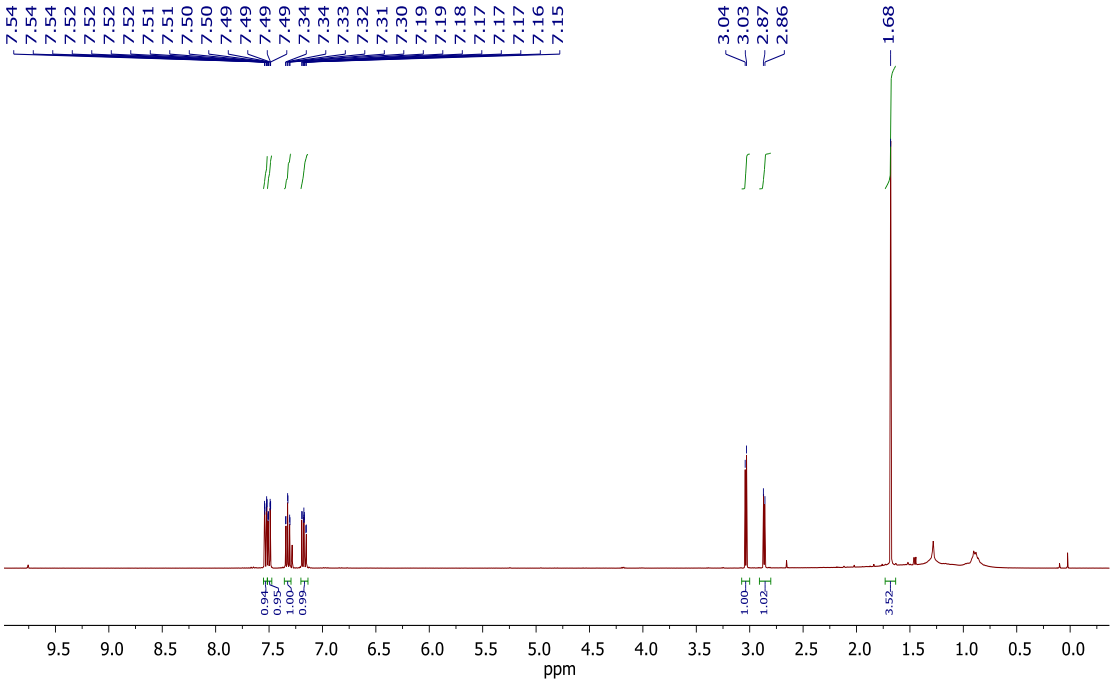


^{13}C{^{1}H}-NMR of **S6** in $CDCl_3$

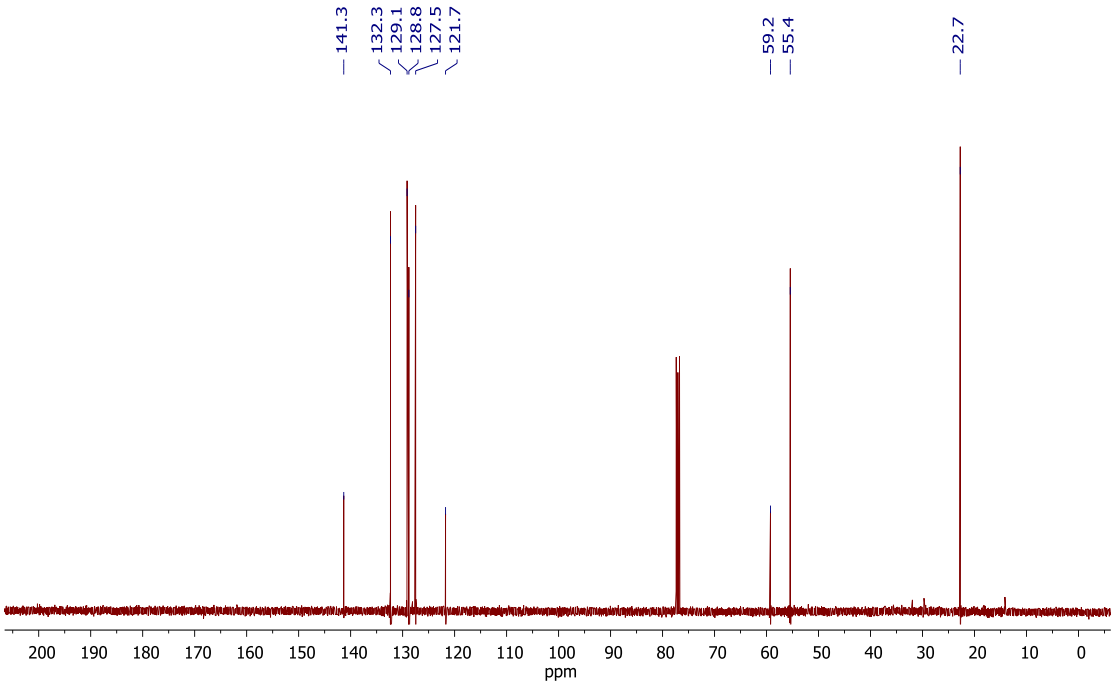


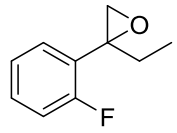


^{1}H-NMR of **S7** in $CDCl_3$

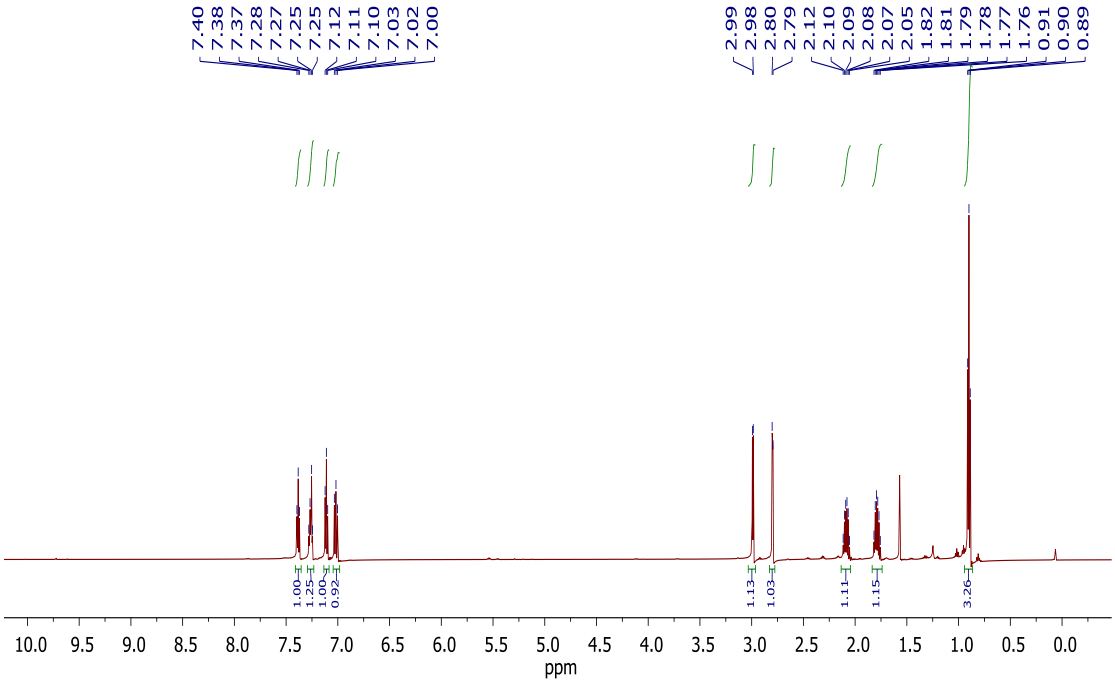


^{13}C{^{1}H}-NMR of **S7** in $CDCl_3$

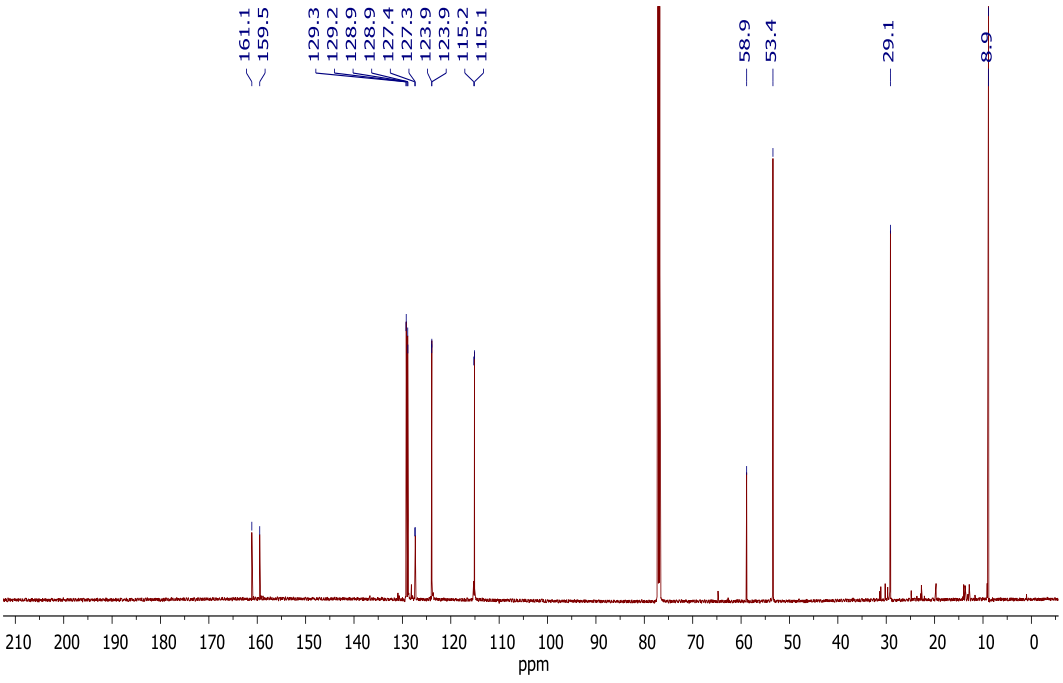


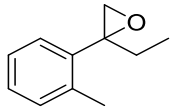


^{1}H-NMR of **S8** in $CDCl_3$

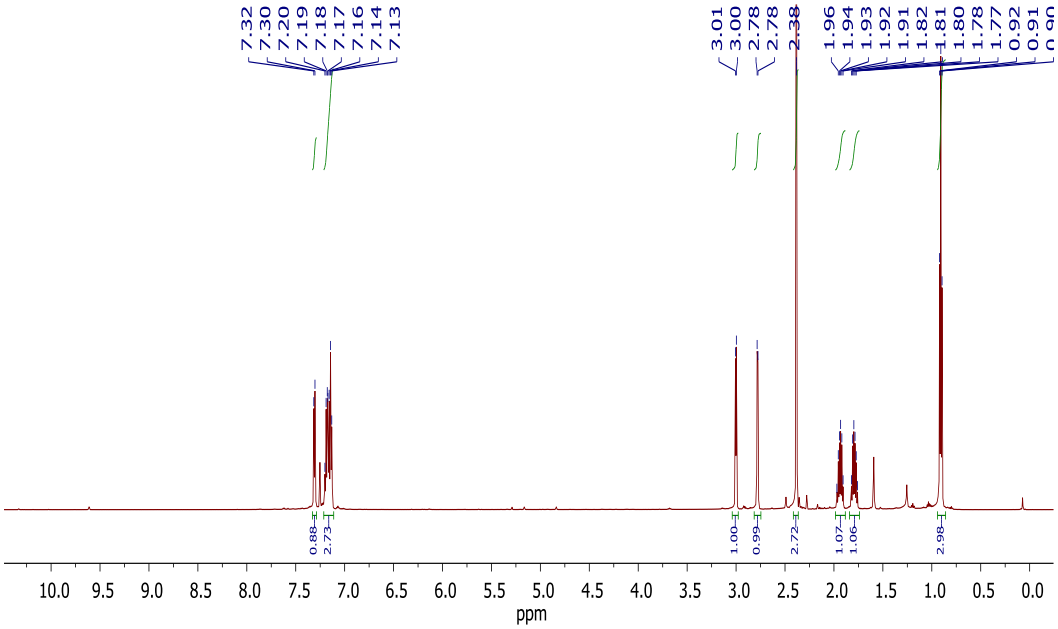


^{3}C{^{1}H}-NMR of **S8** in $CDCl_3$

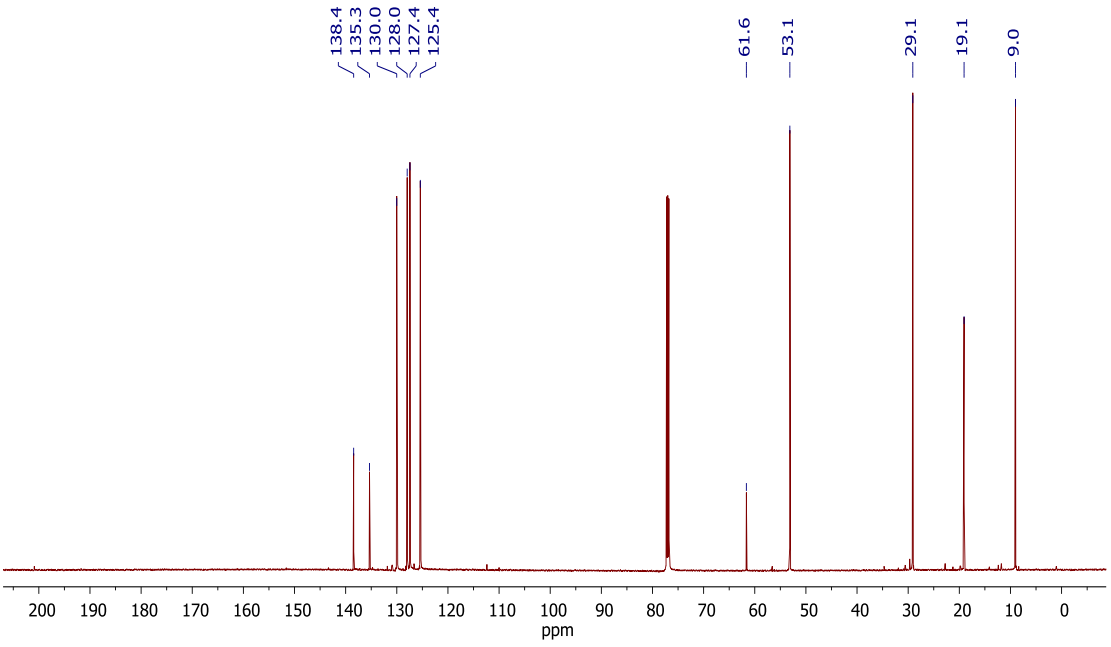


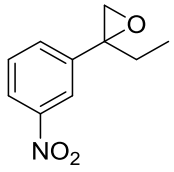


^{1}H-NMR of **S9** in $CDCl_3$

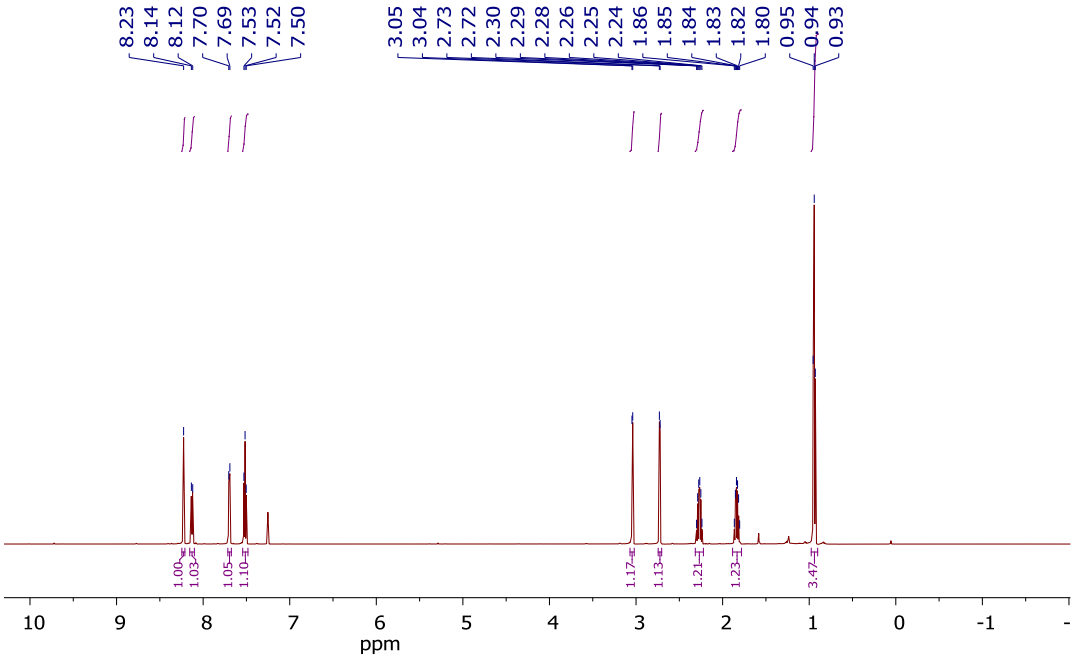


^{13}C{^{1}H}-NMR of **S9** in $CDCl_3$

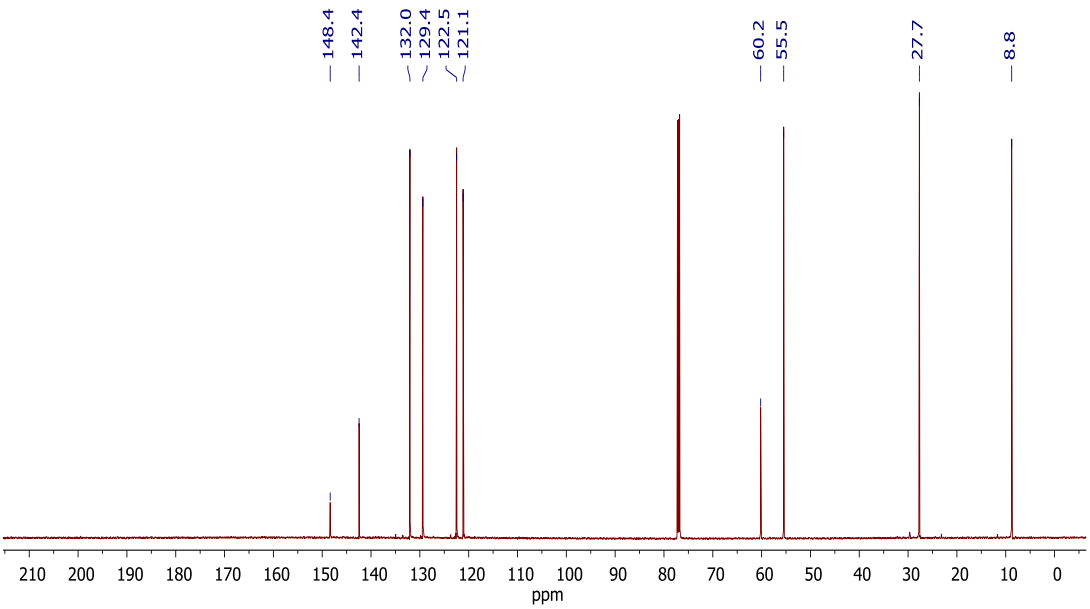


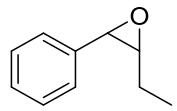


^{1}H-NMR of **S10** in $CDCl_3$

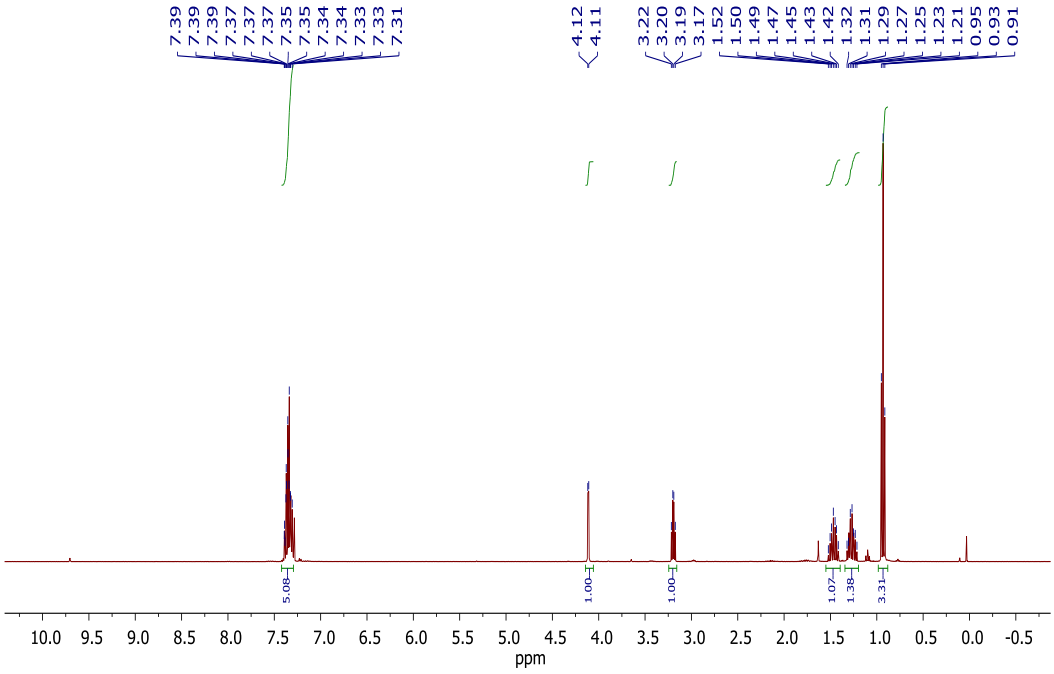


^{13}C{^{1}H}-NMR of **S10** in $CDCl_3$

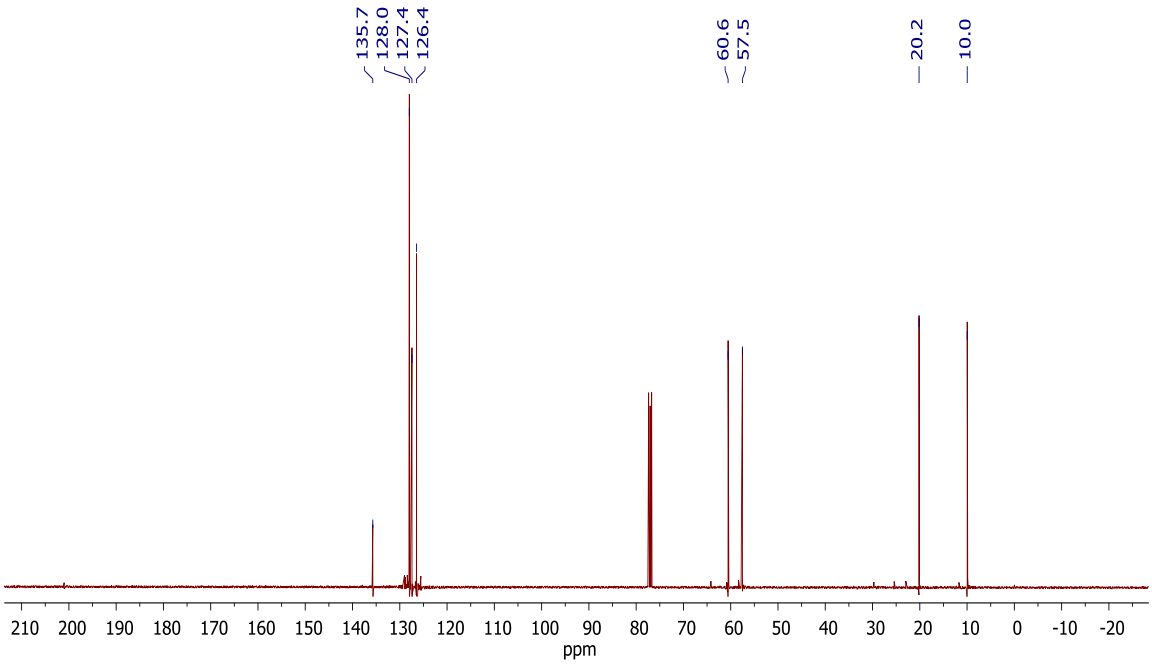




^{1}H-NMR of **S12** in $CDCl_3$

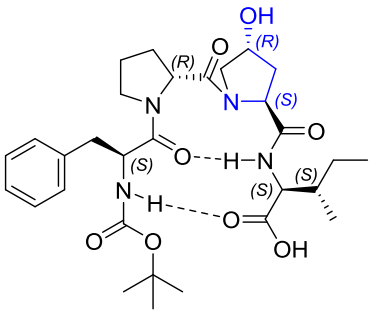


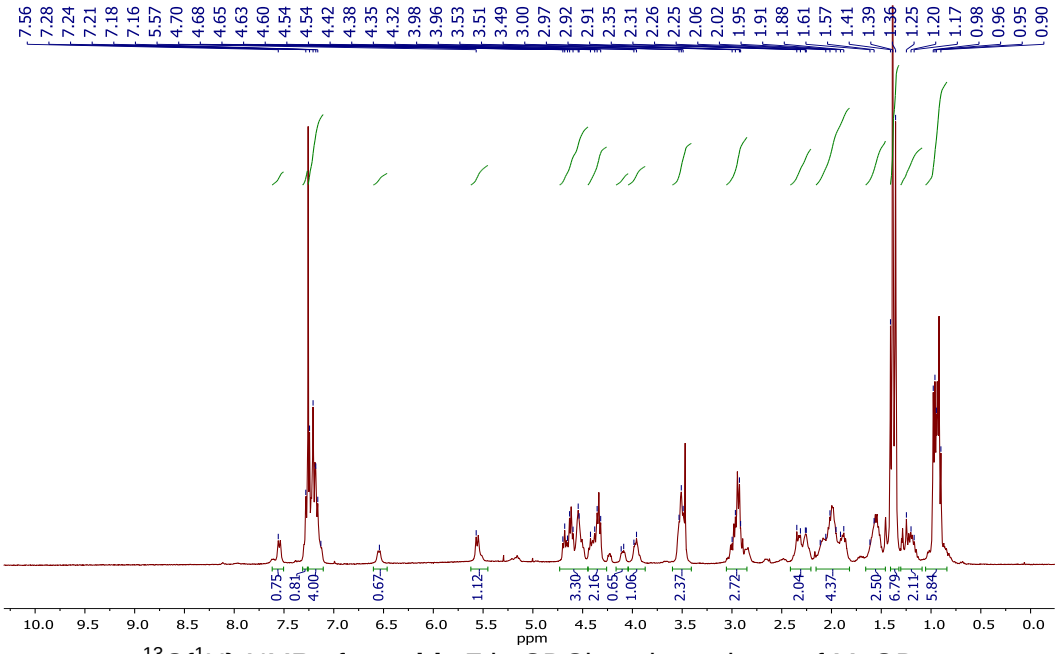
^{13}C{^{1}H}-NMR of **S12** in $CDCl_3$



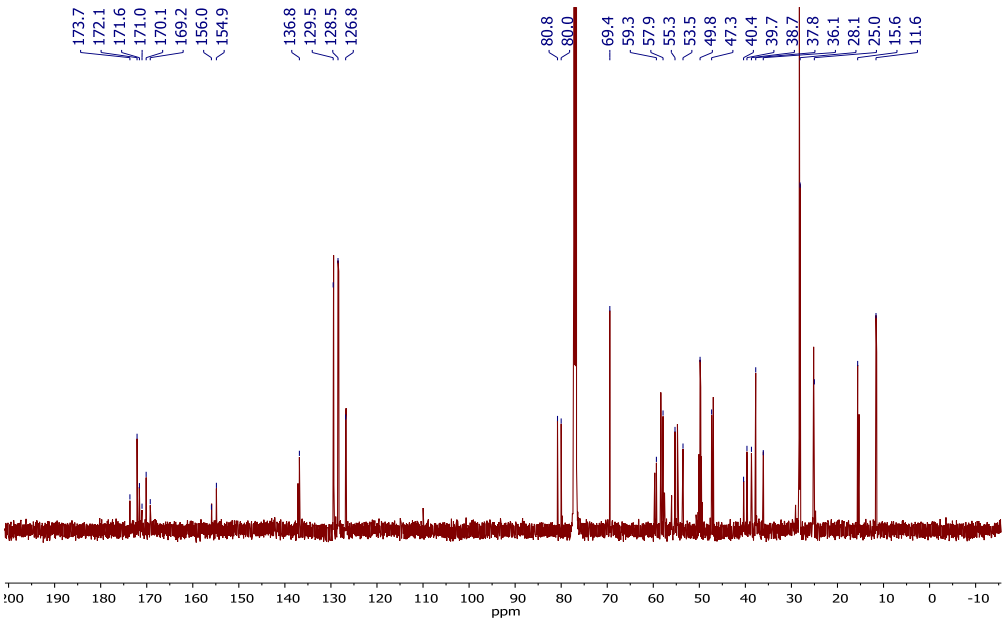
A3) 1H NMR spectra of peptides

^{1}H-NMR of **peptide 7** in $CDCl_3$ and two drops of MeOD

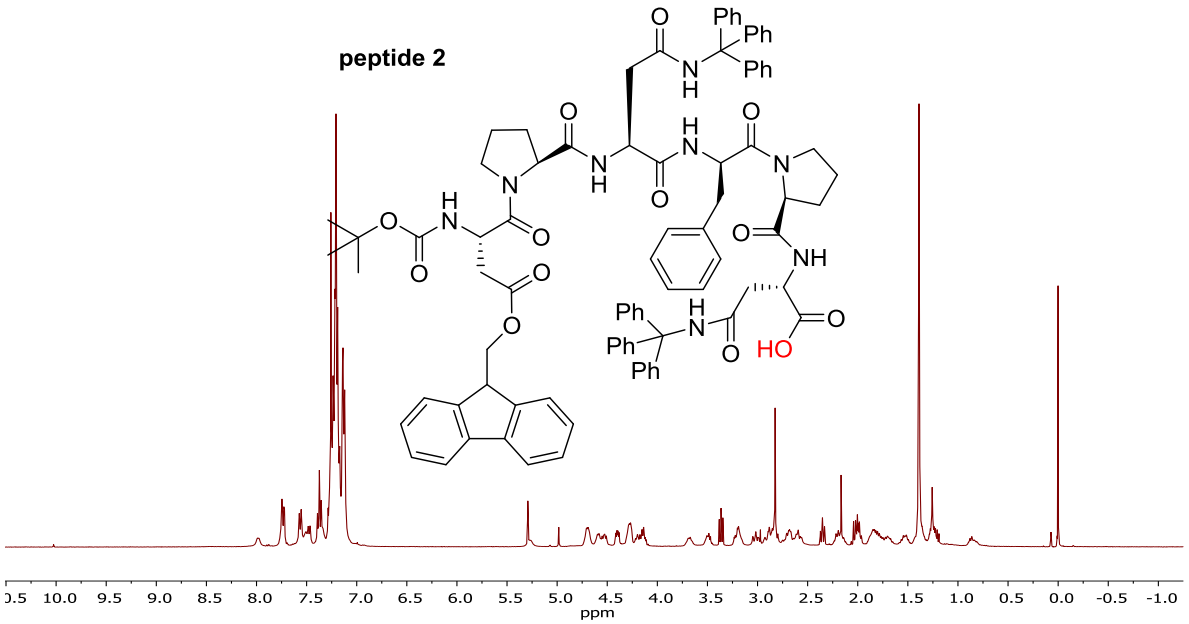


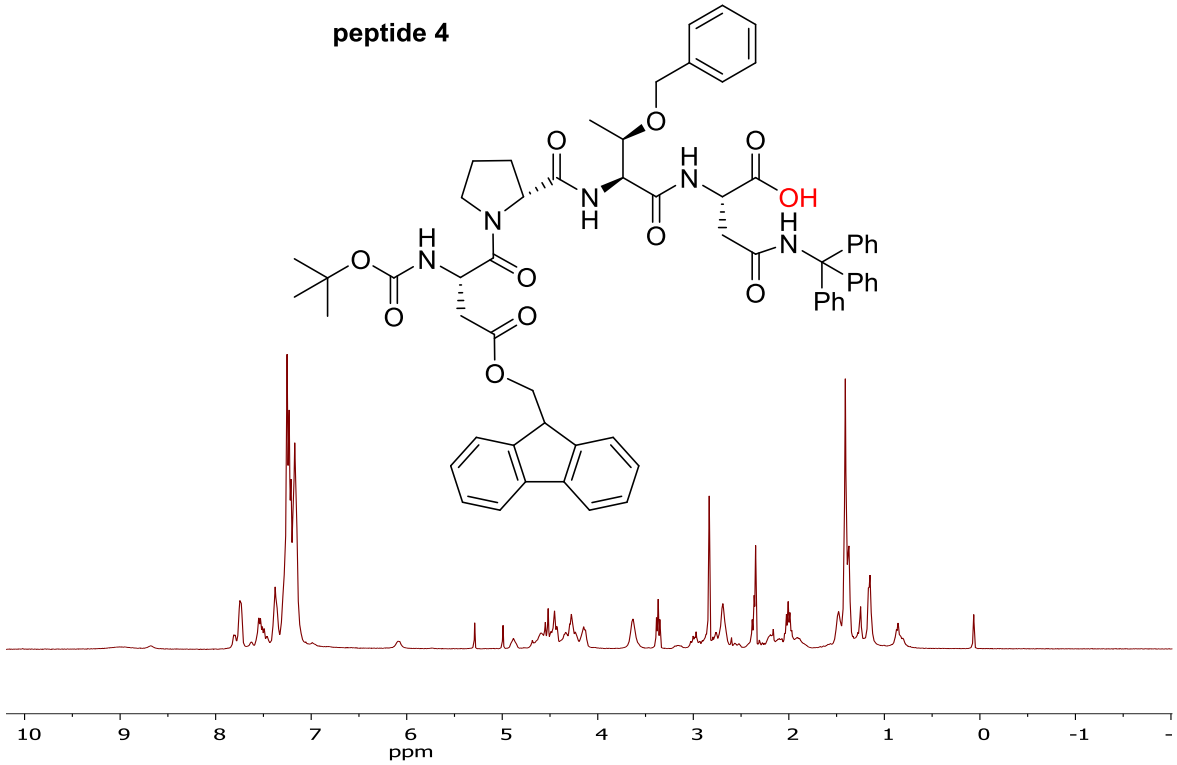


^{13}C{^{1}H}-NMR of **peptide 7** in $CDCl_3$ and two drops of MeOD

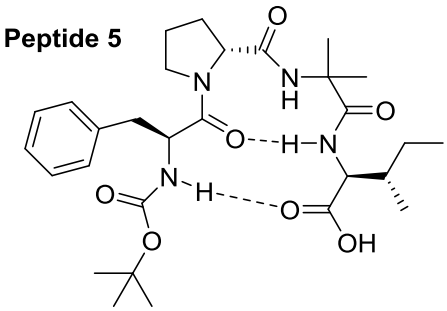


^{1}H-NMR of non purified **peptides** in $CDCl_3$

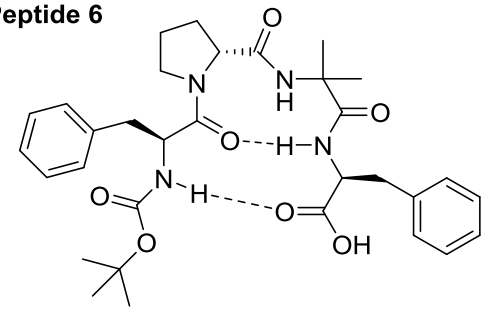


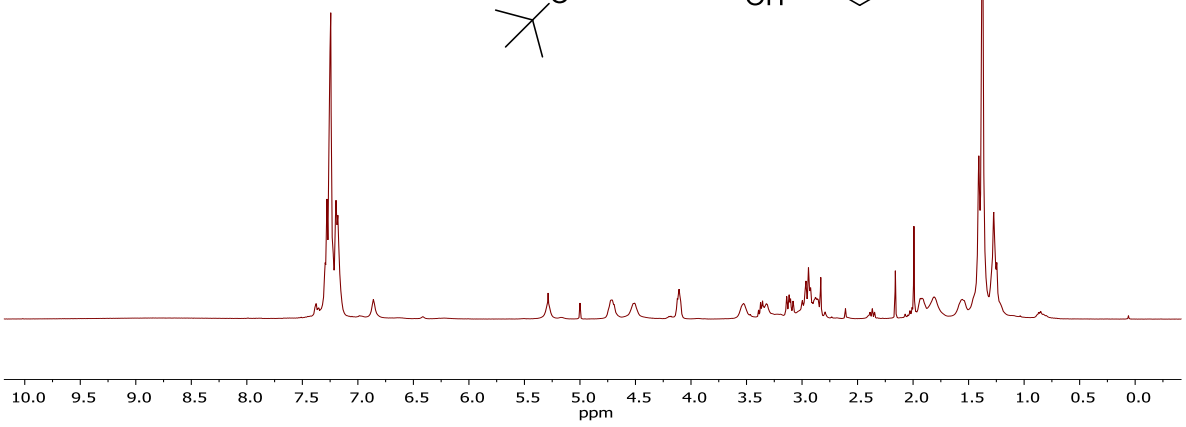


Peptide 5

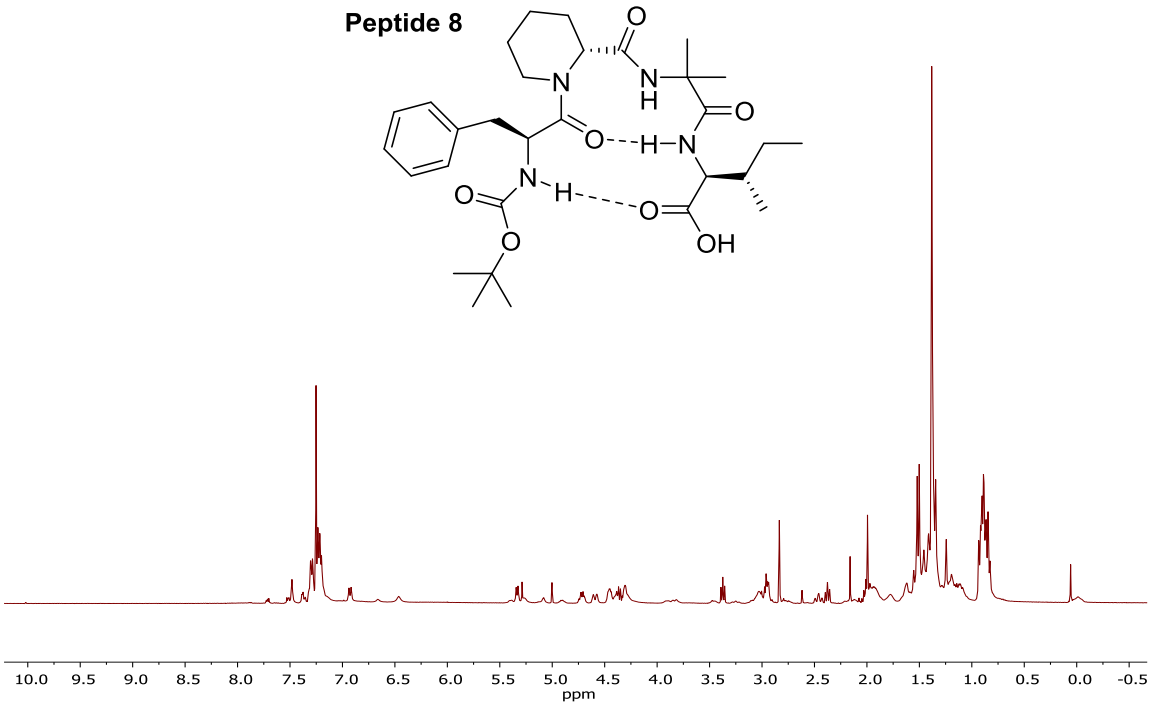


Peptide 6

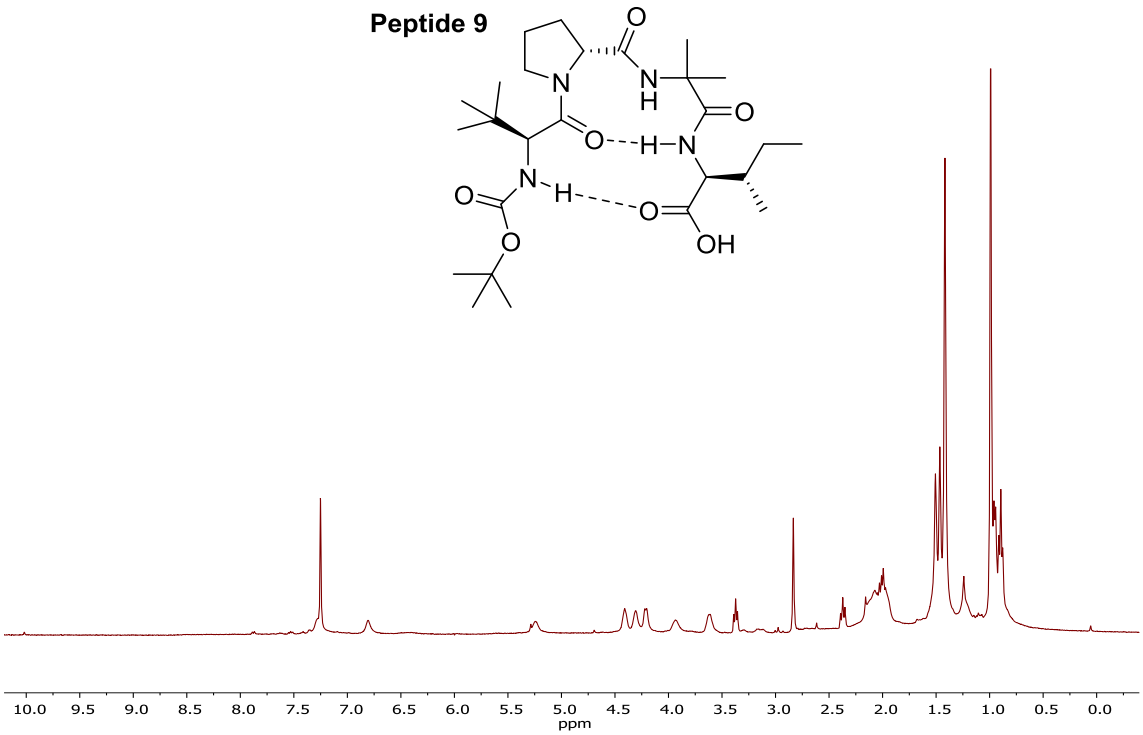




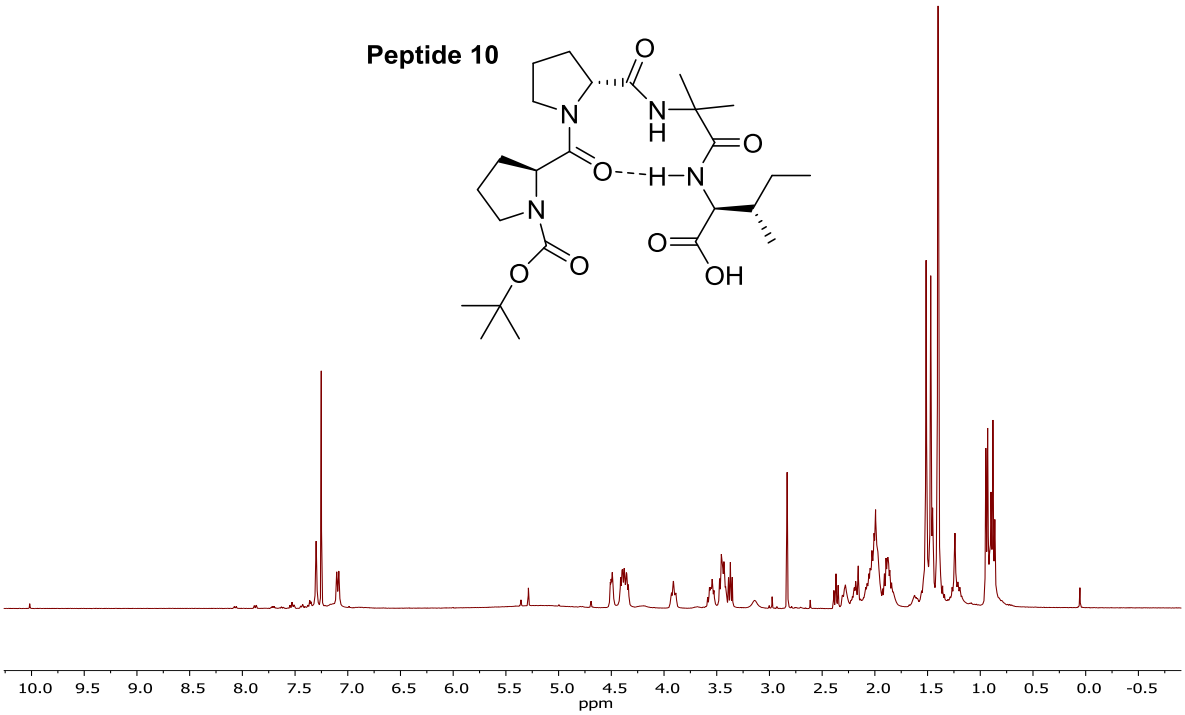
Peptide 8



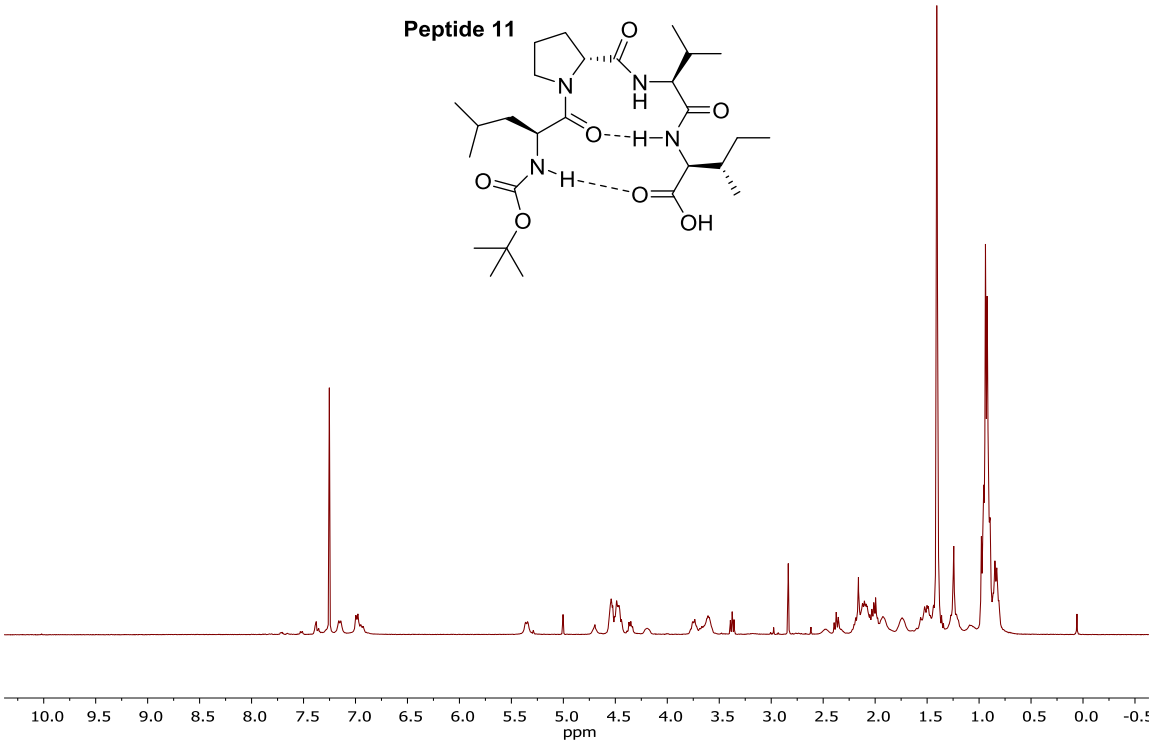
Peptide 9



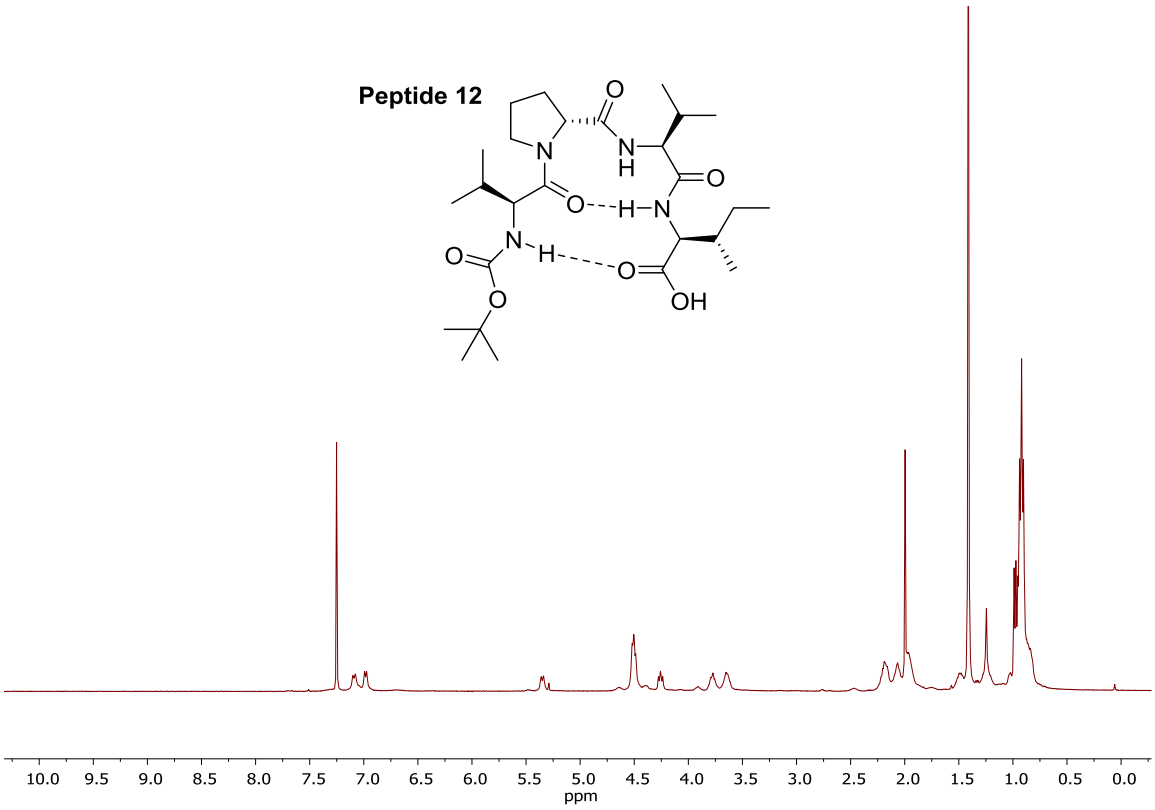
Peptide 10



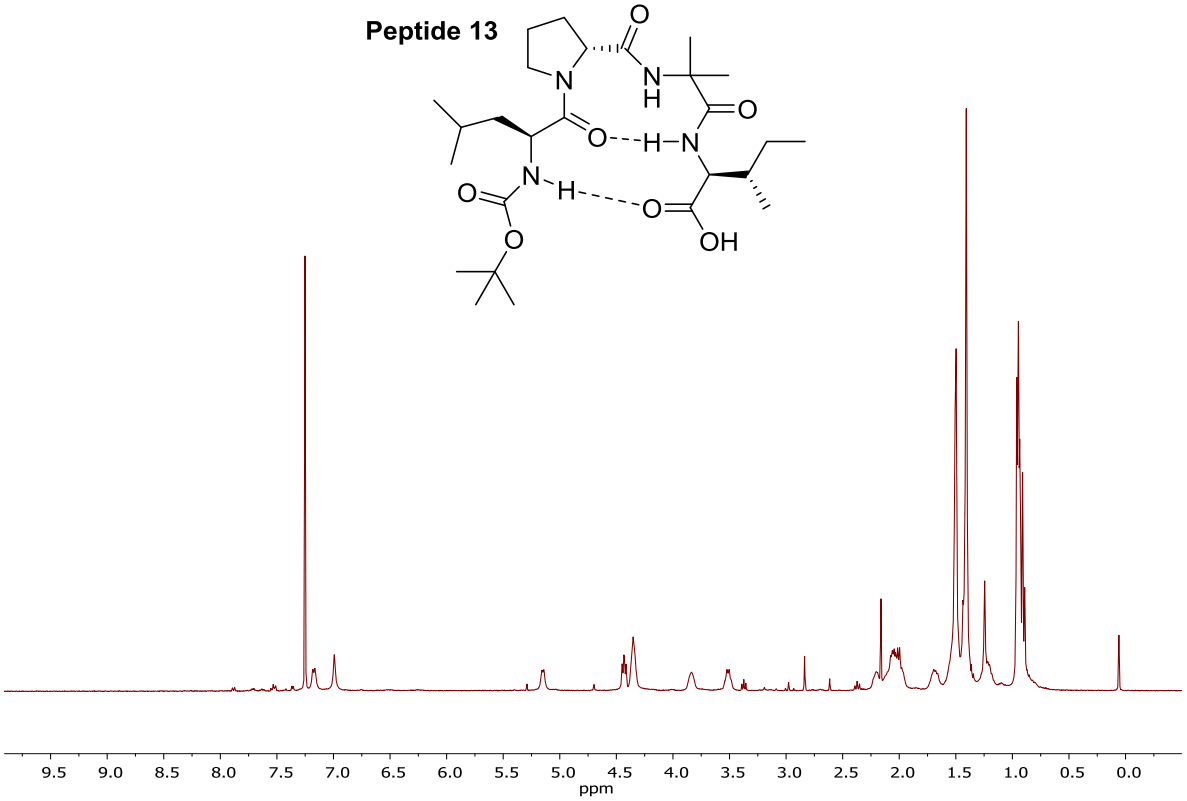
Peptide 11



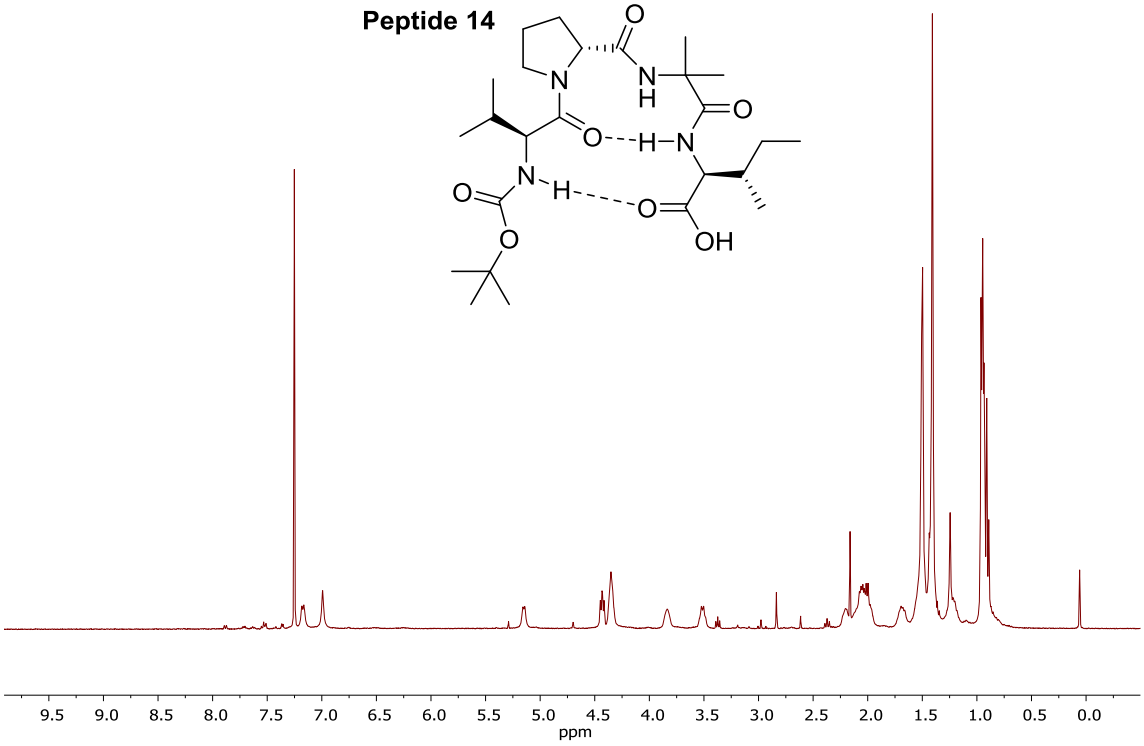
Peptide 12



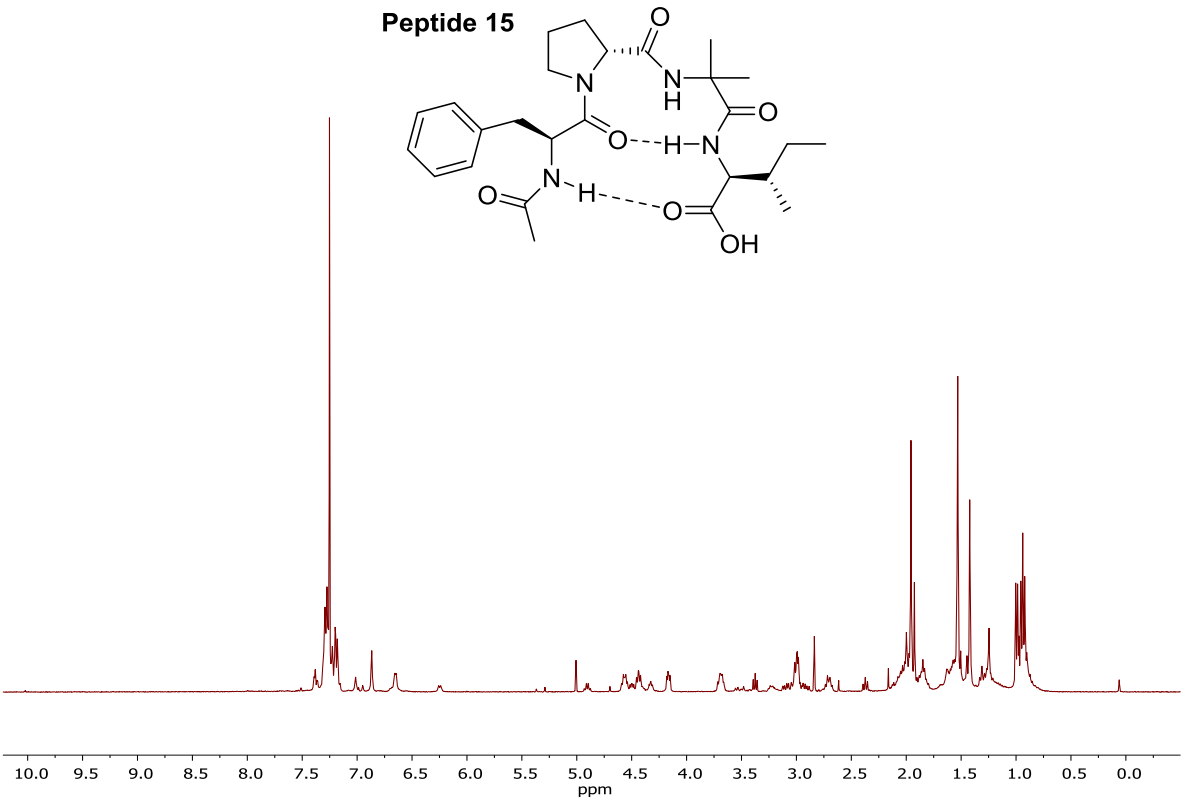
Peptide 13



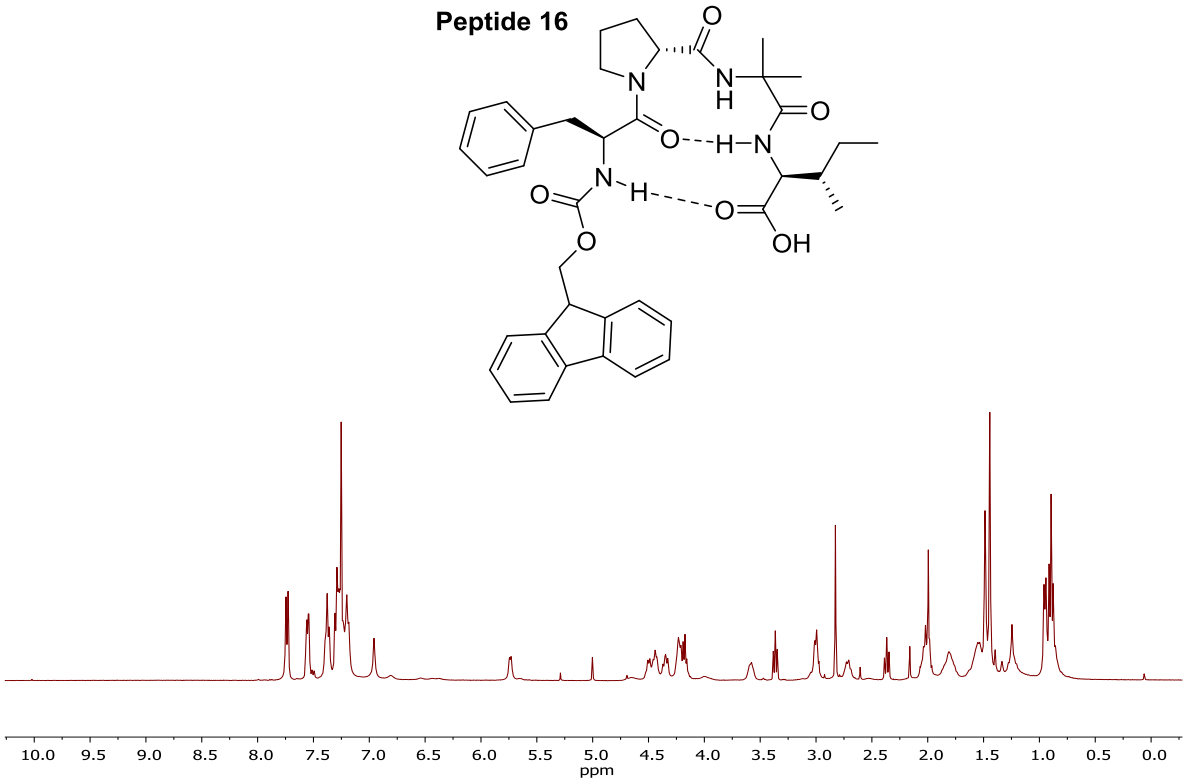
Peptide 14



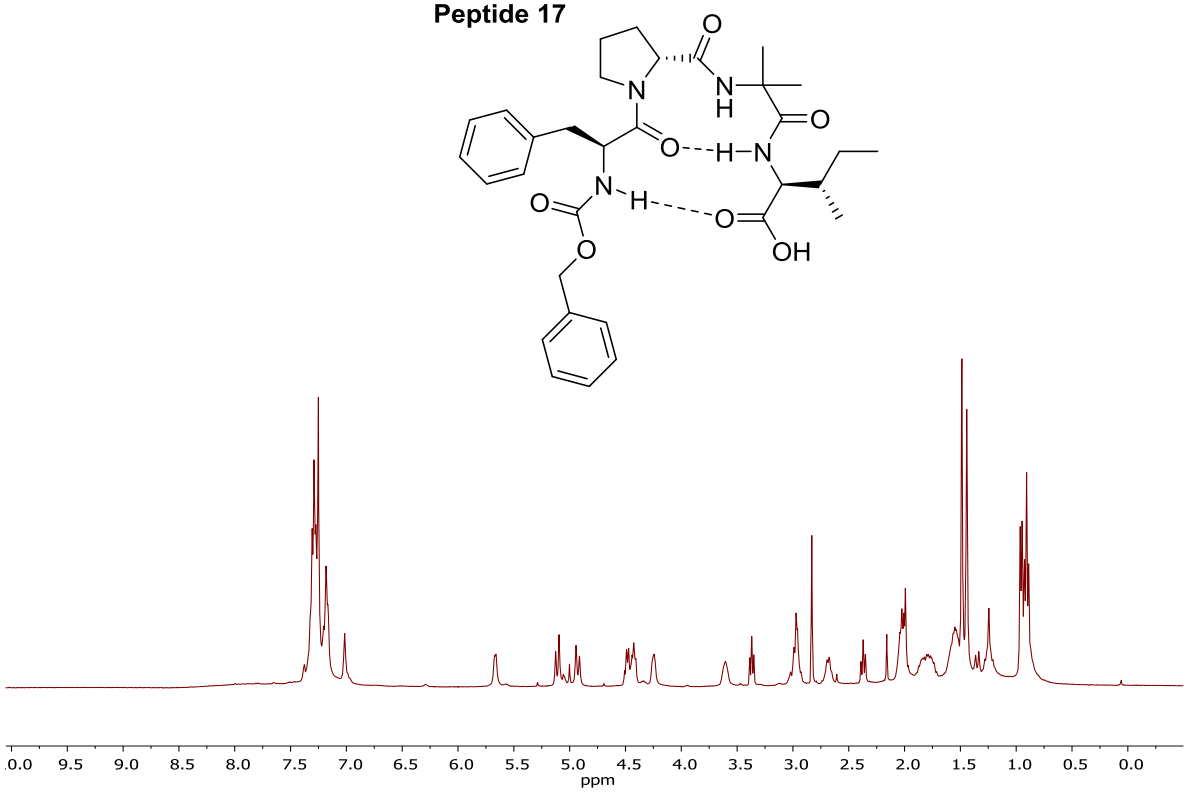
Peptide 15



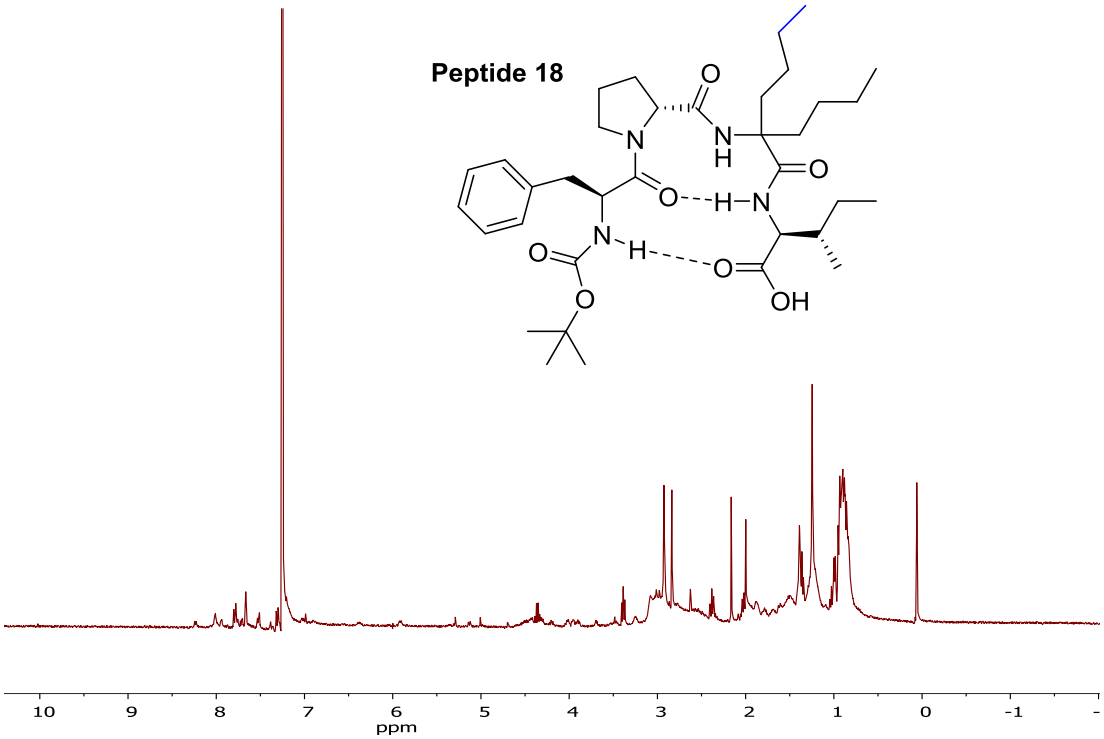
Peptide 16



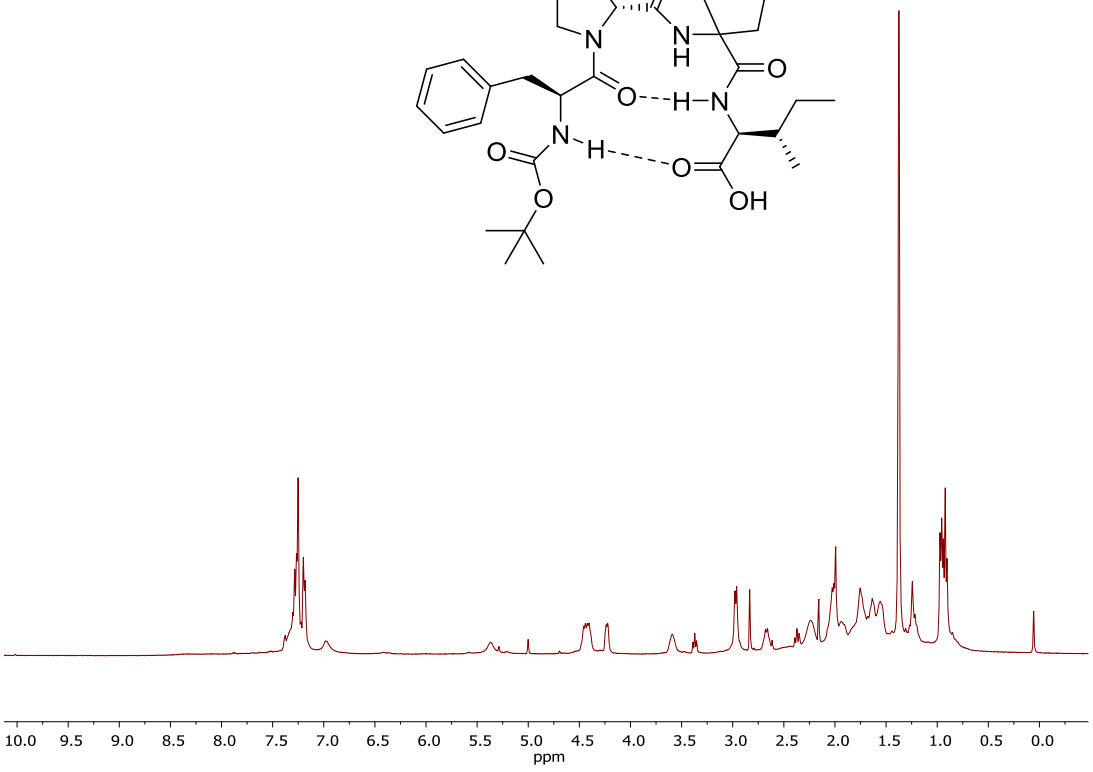
Peptide 17



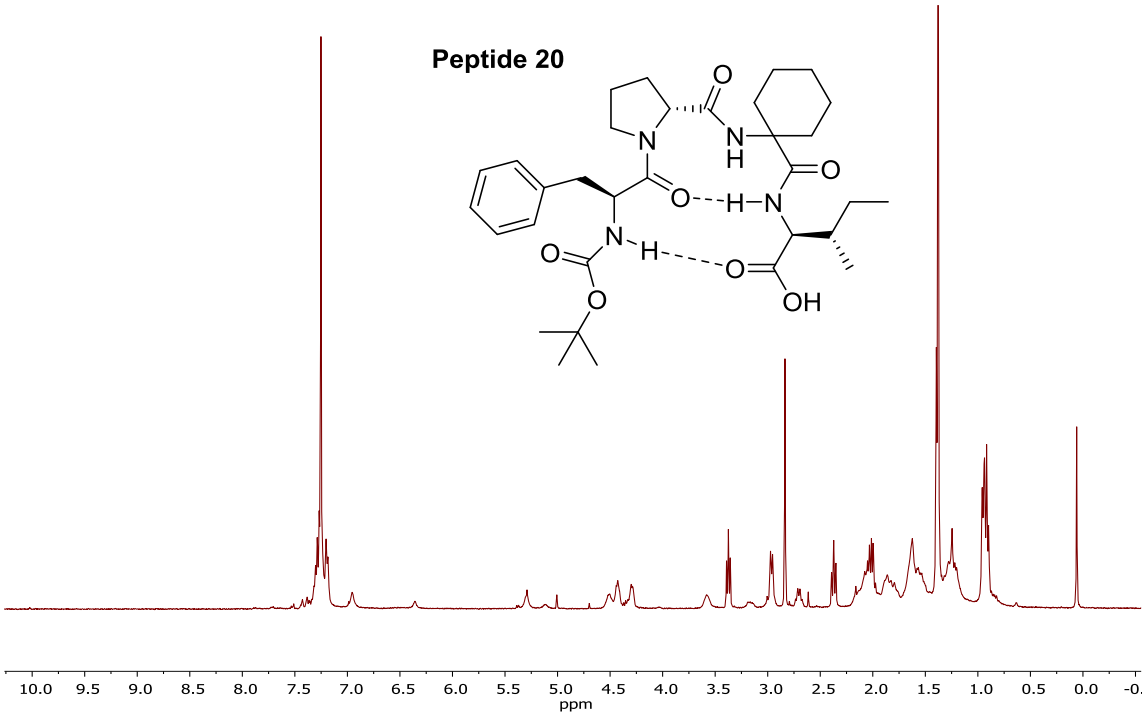
Peptide 18



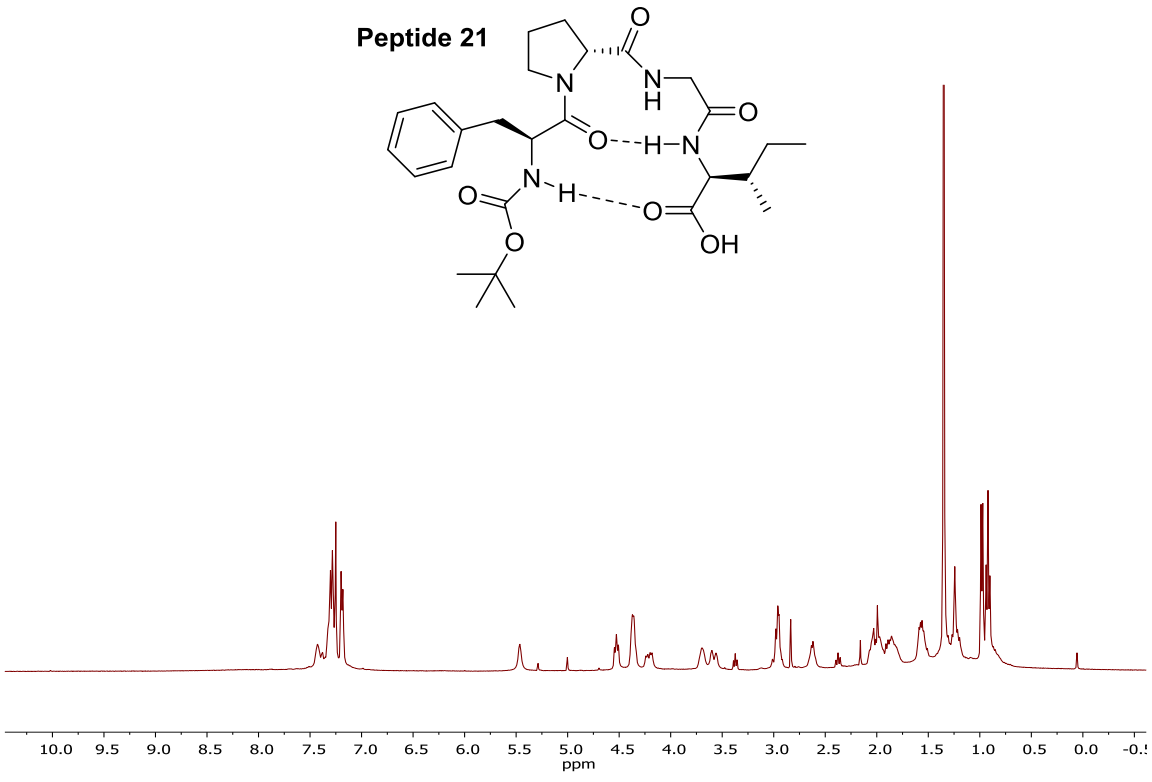
Peptide 19



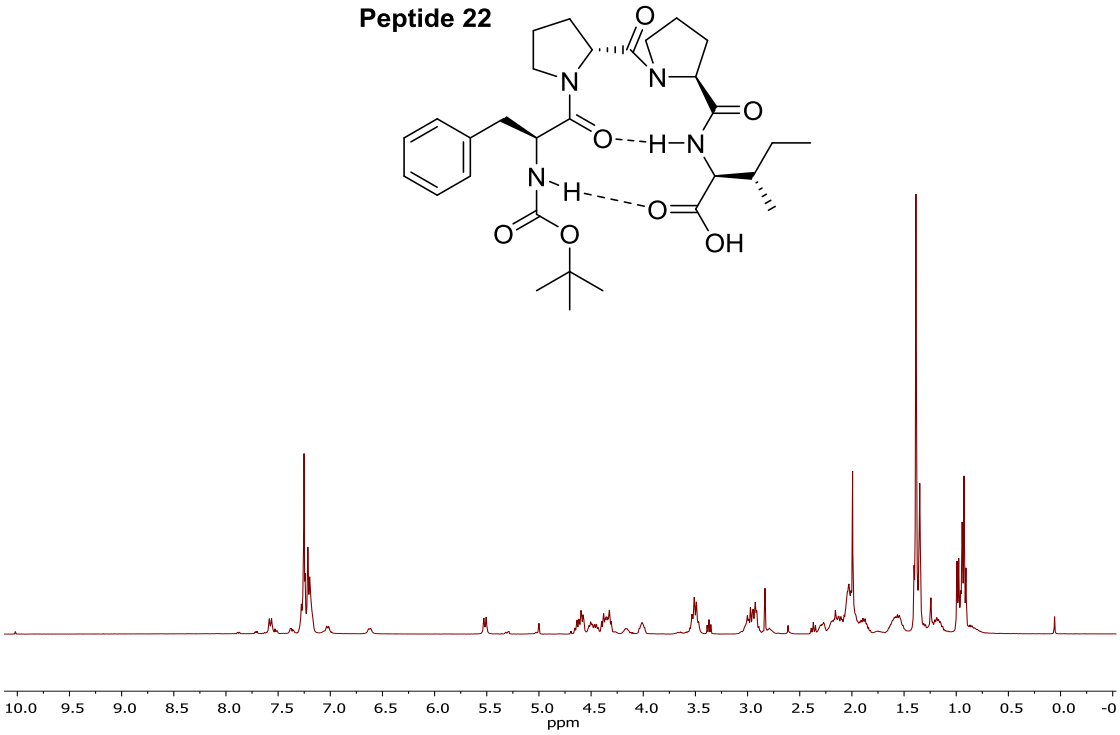
Peptide 20



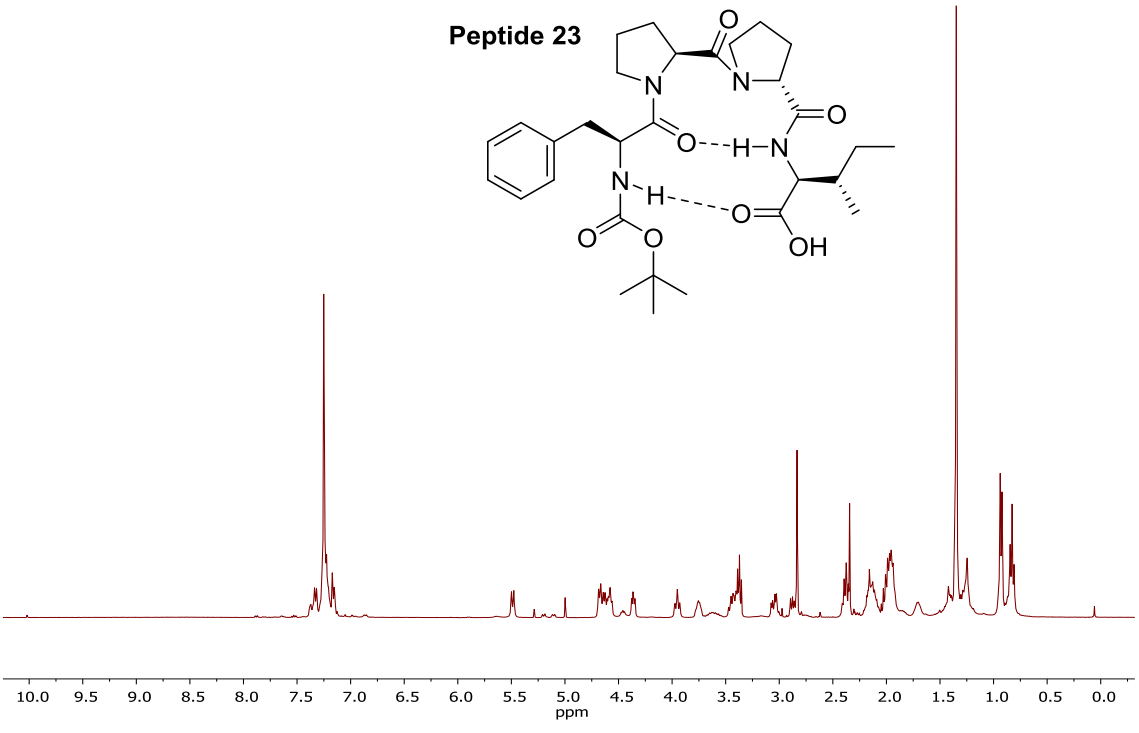
Peptide 21



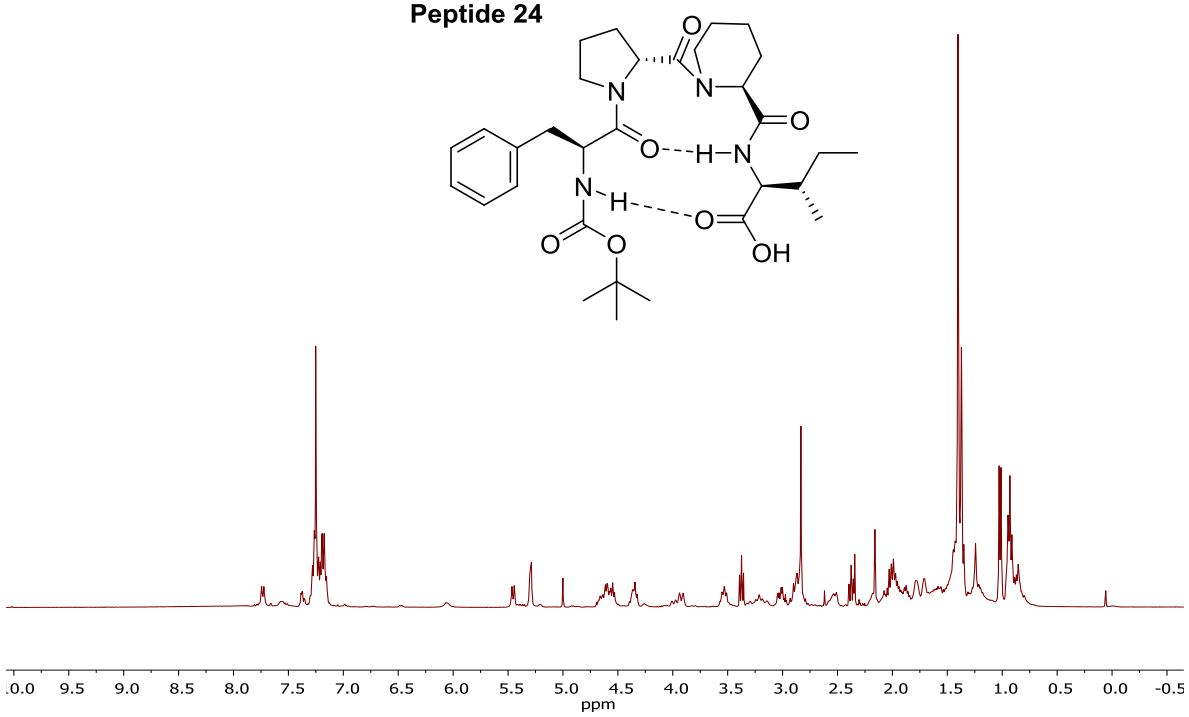
Peptide 22



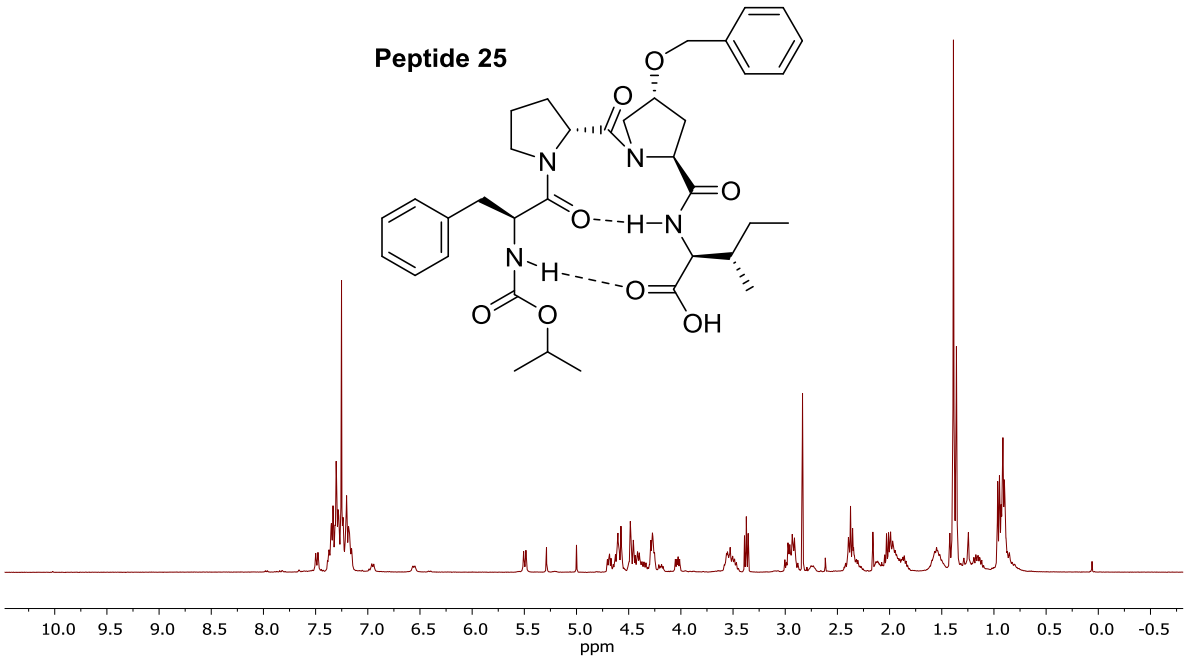
Peptide 23



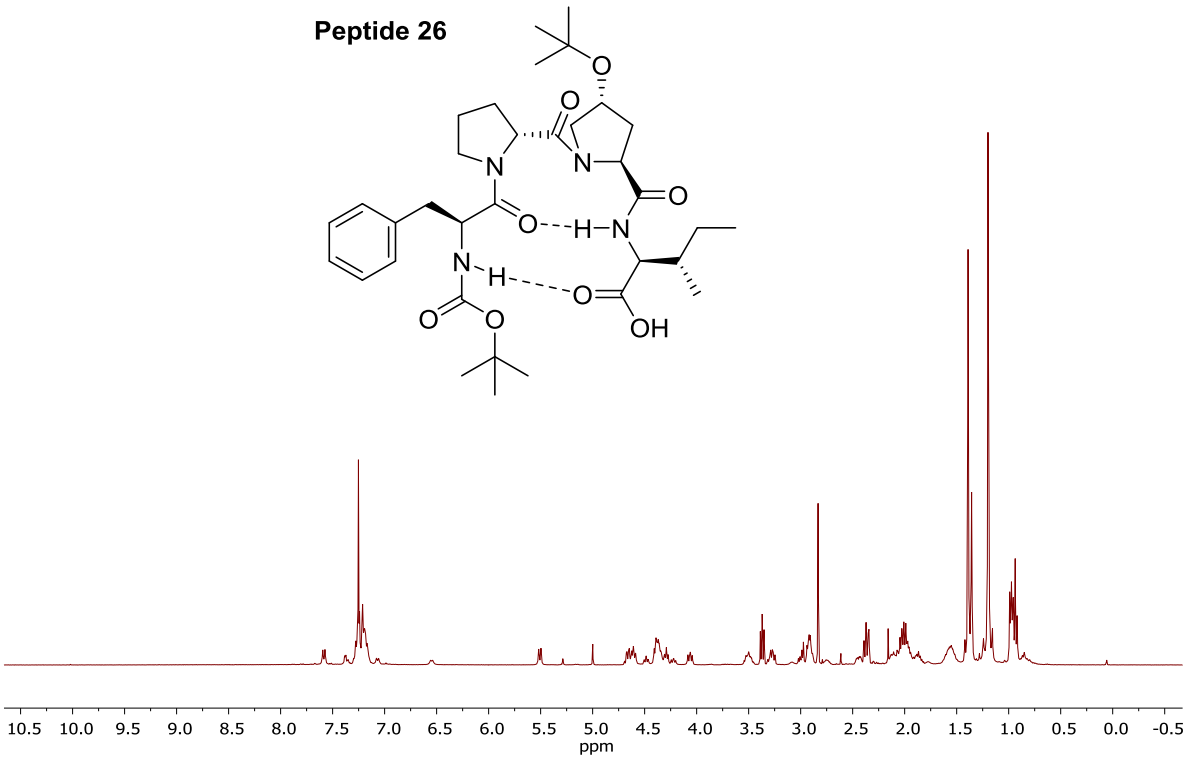
Peptide 24



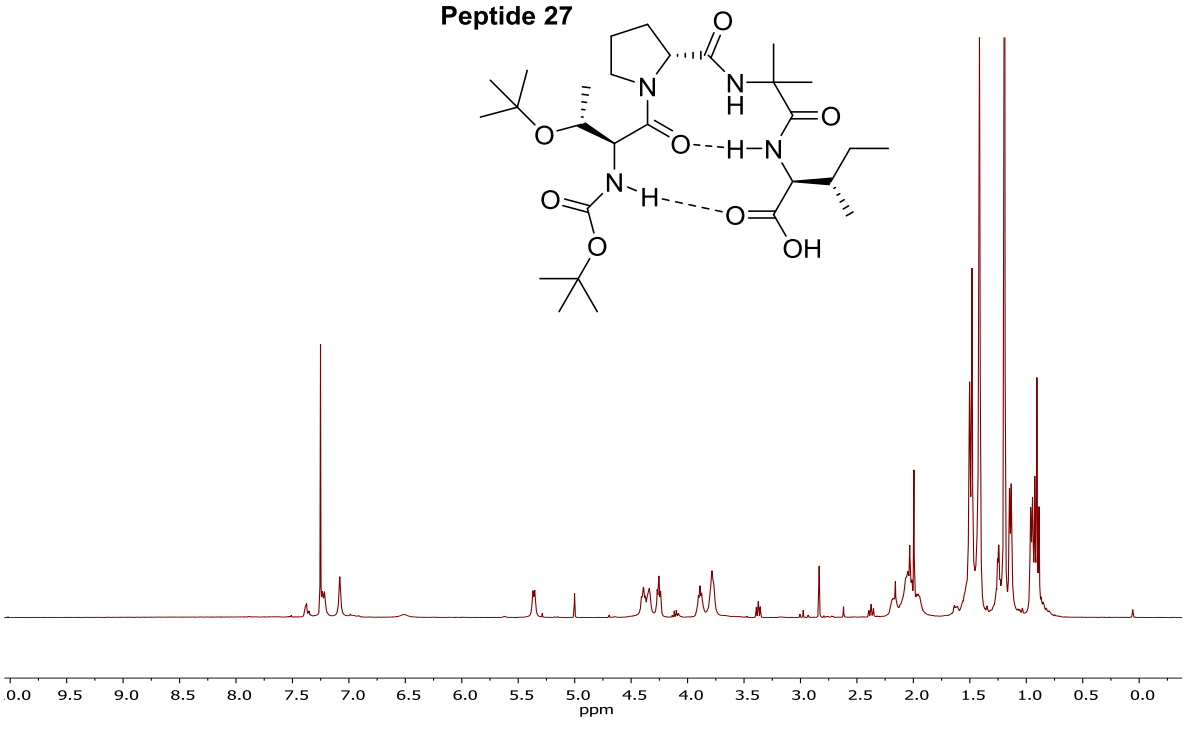
Peptide 25



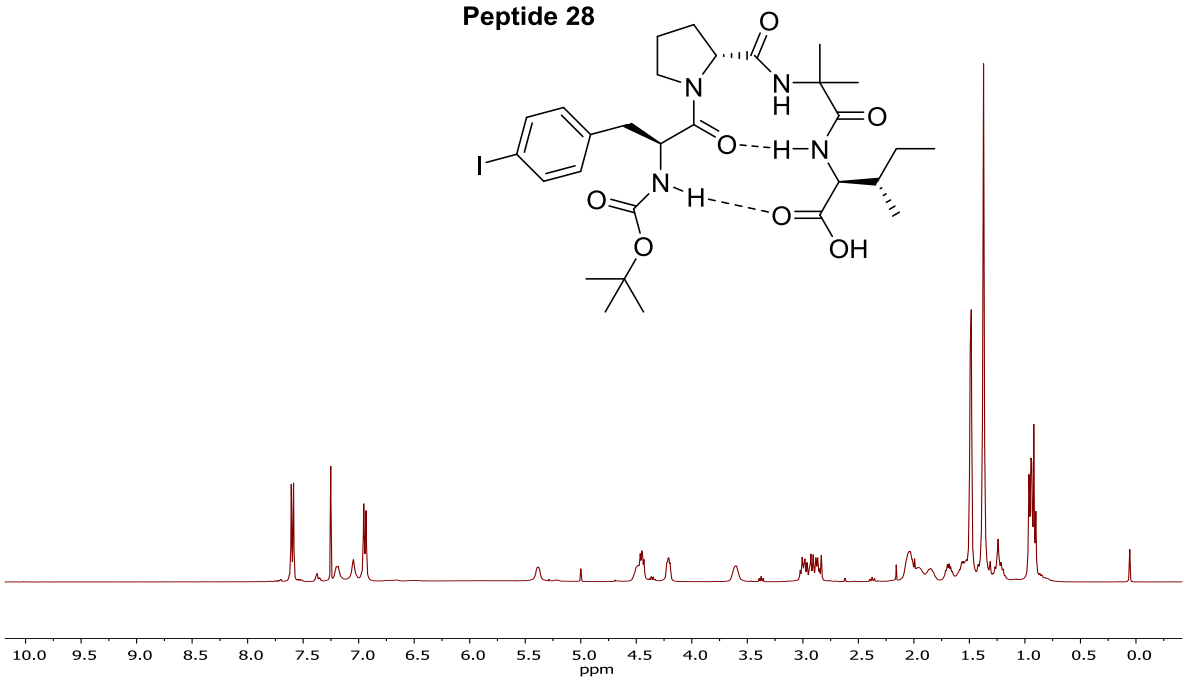
Peptide 26



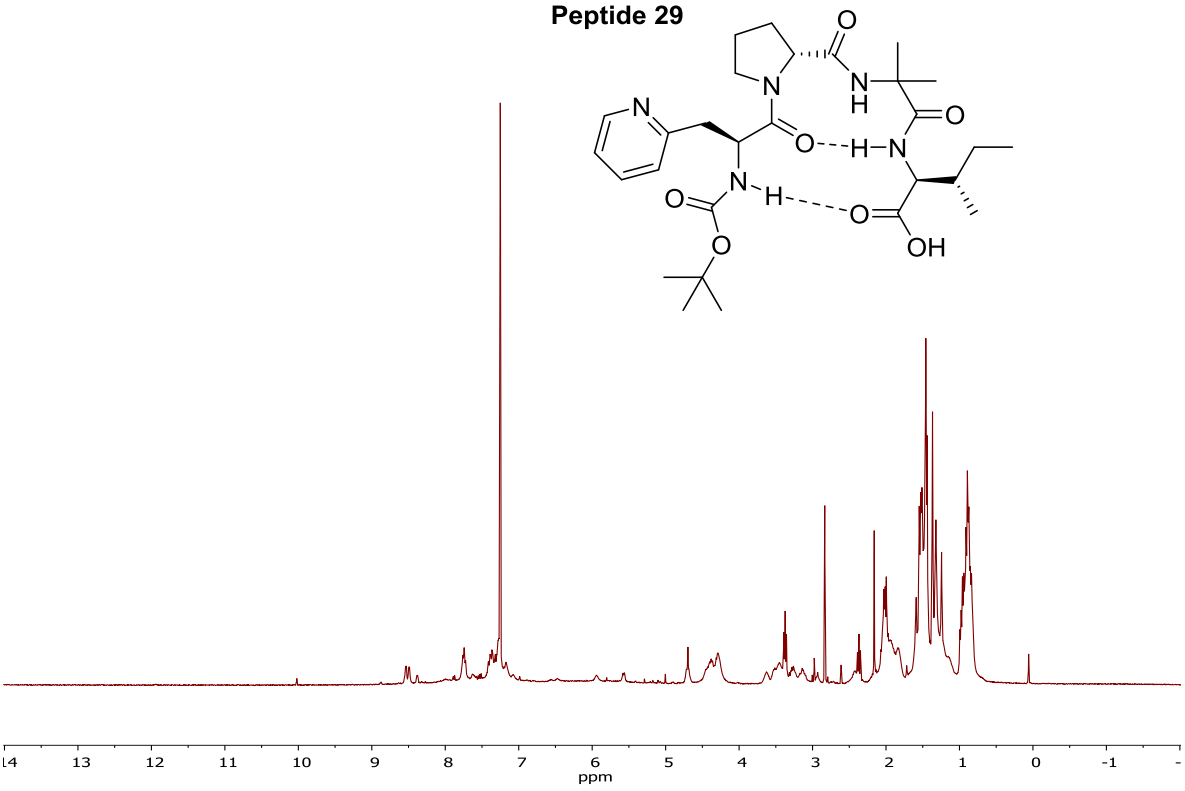
Peptide 27



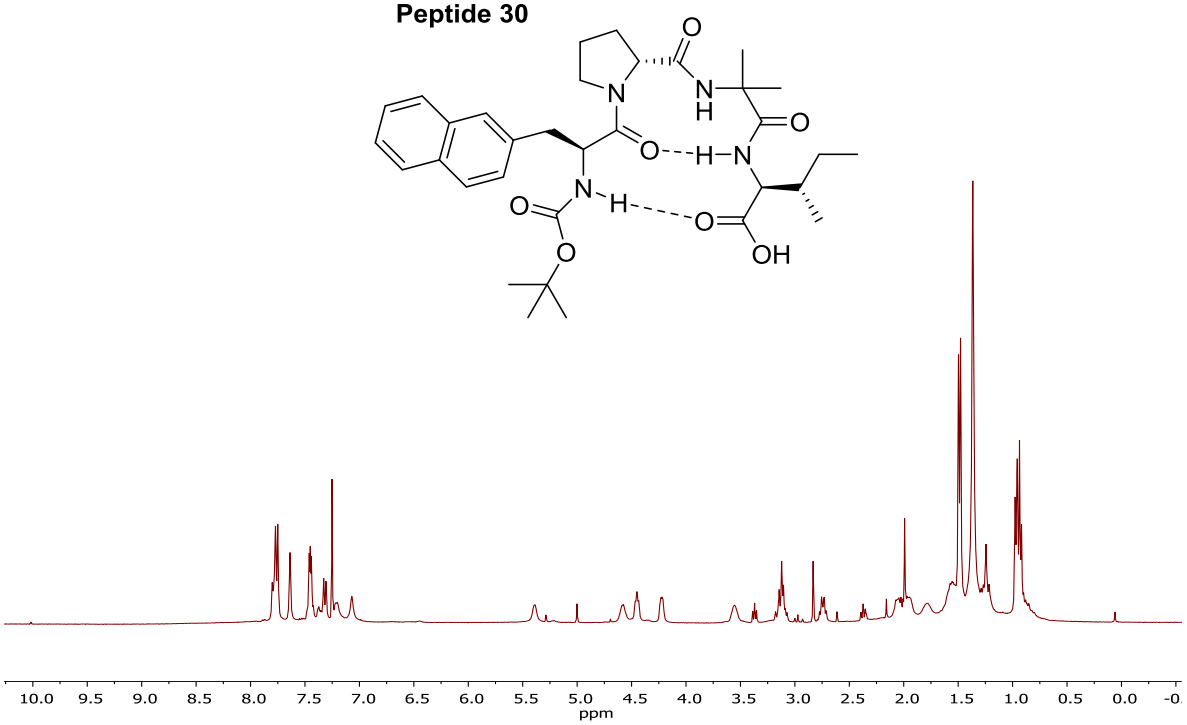
Peptide 28



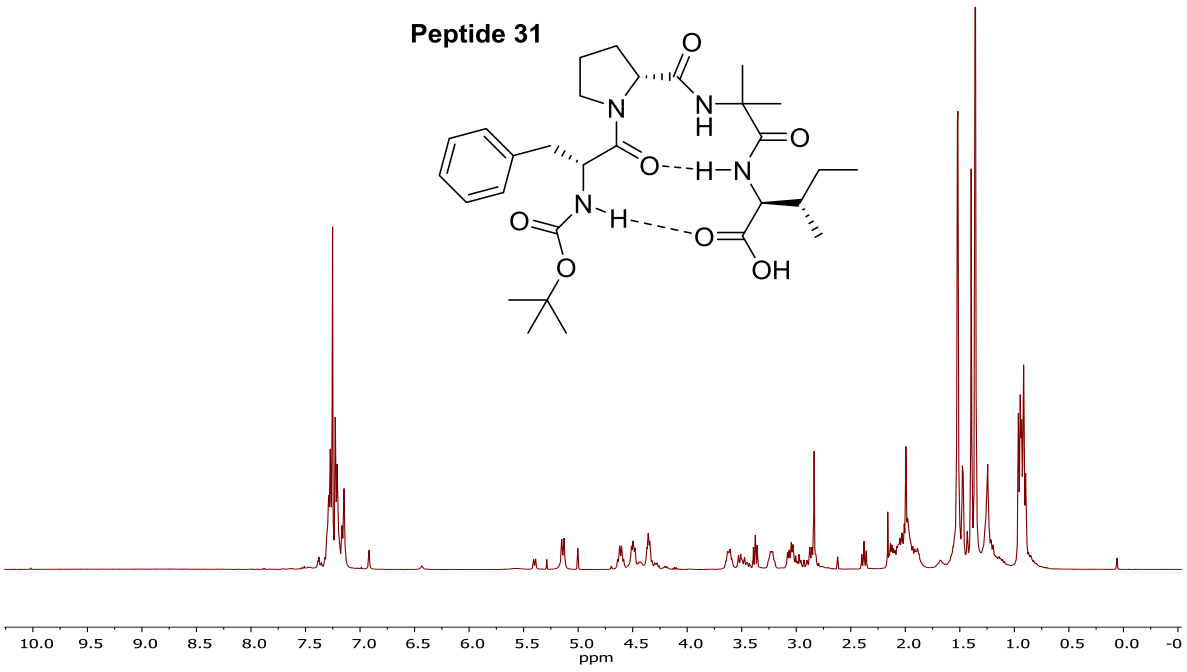
Peptide 29



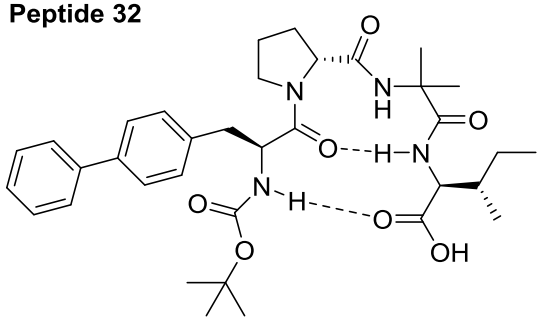
Peptide 30



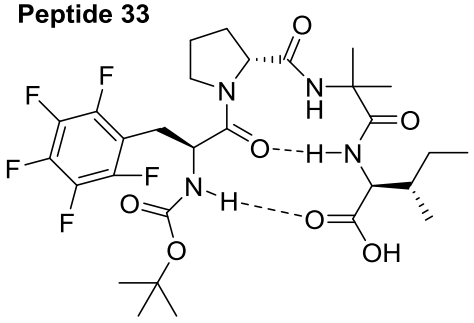
Peptide 31



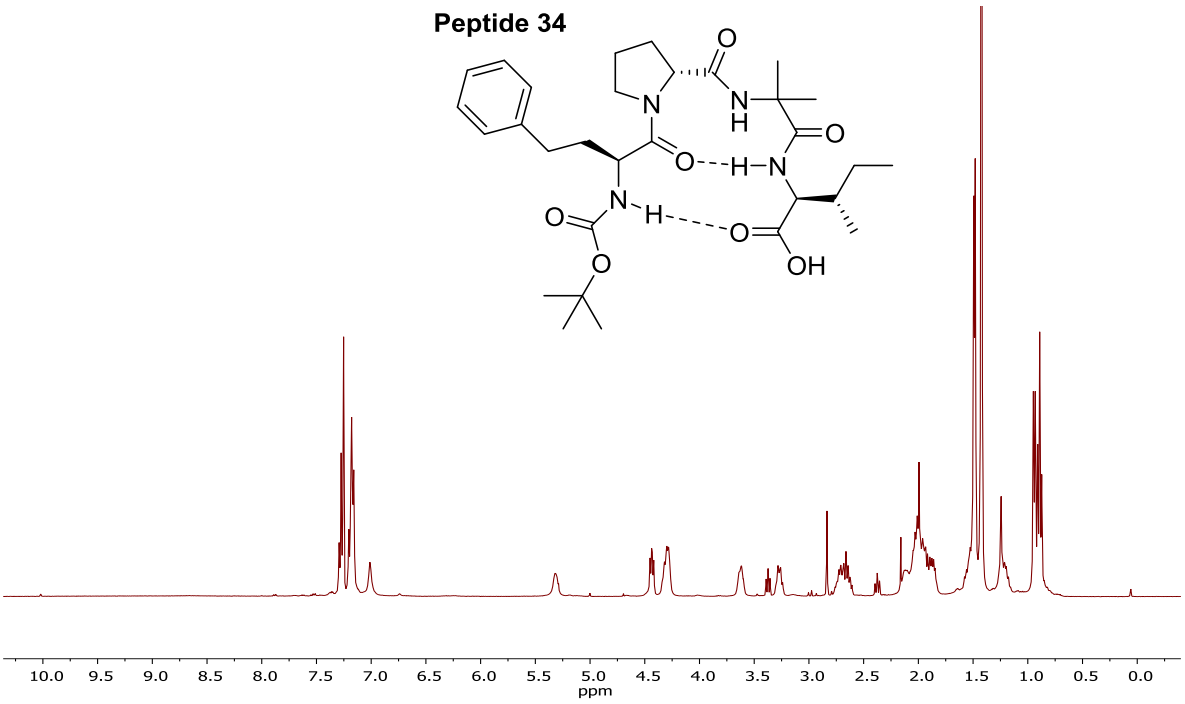
Peptide 32



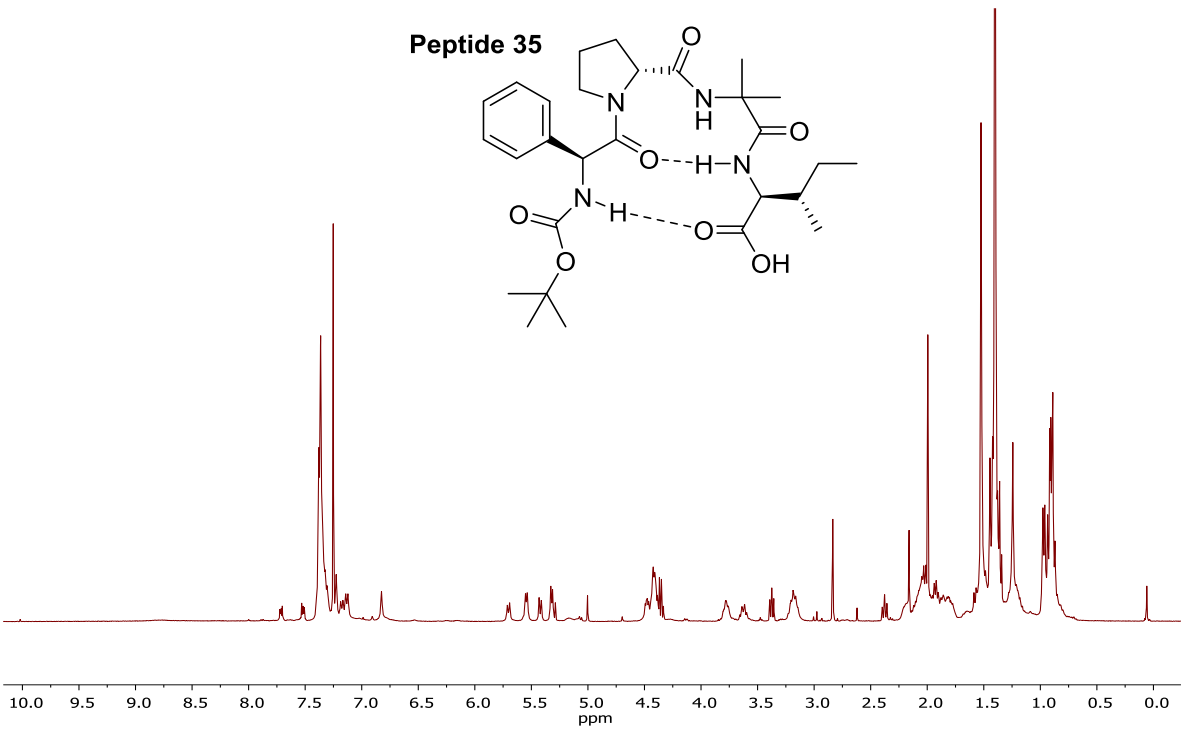
Peptide 33



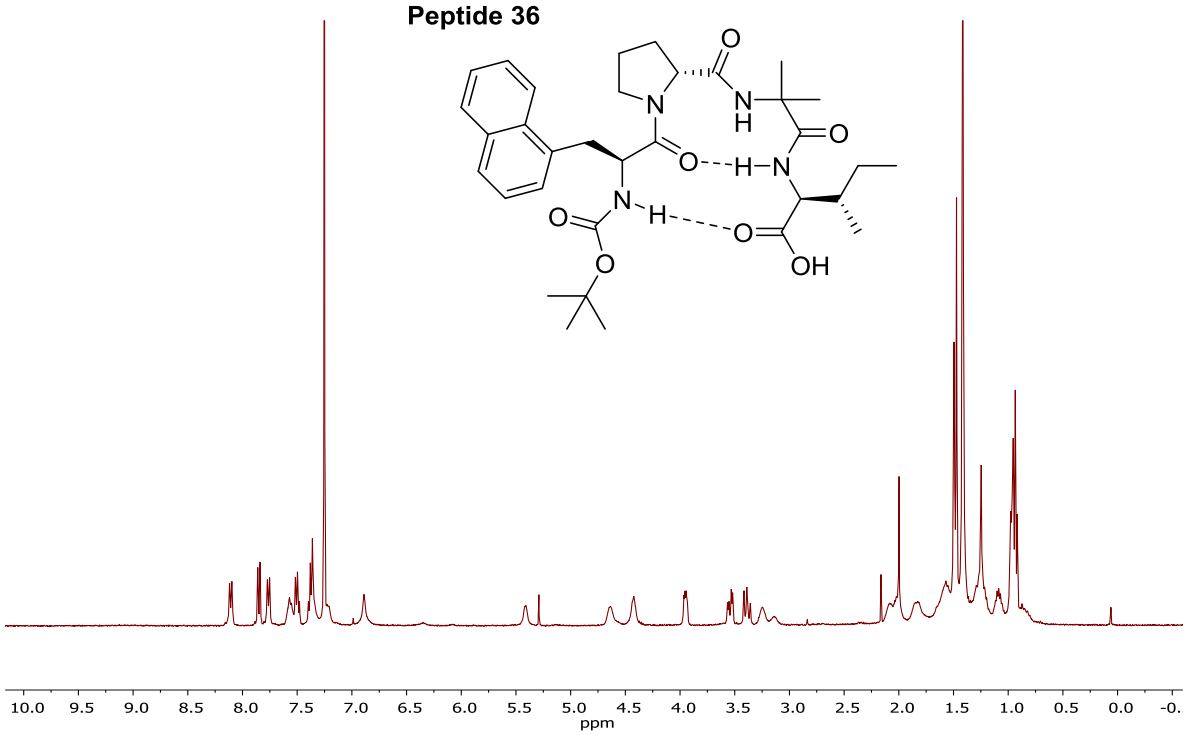
Peptide 34



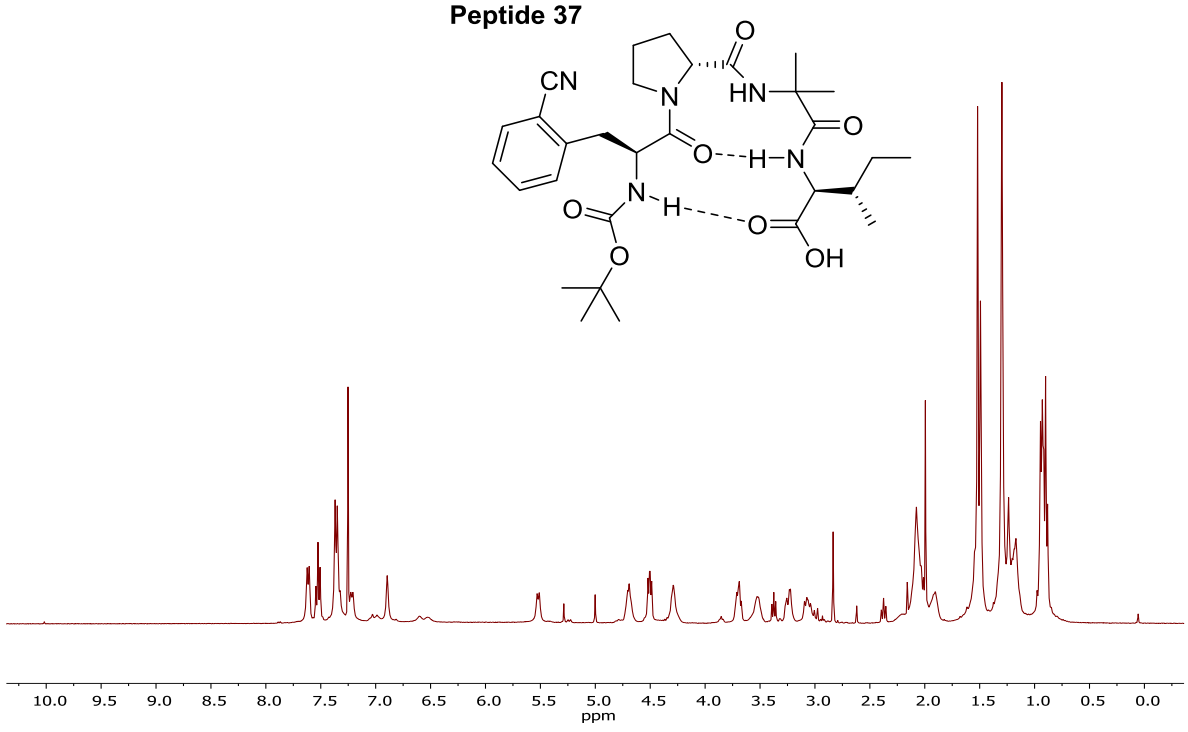
Peptide 35



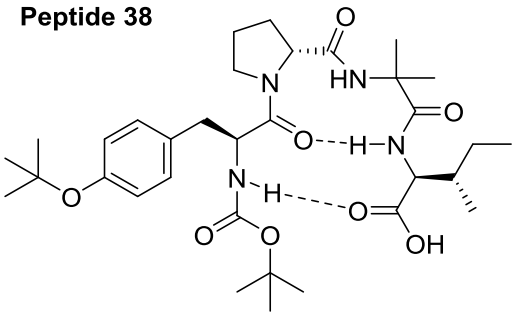
Peptide 36



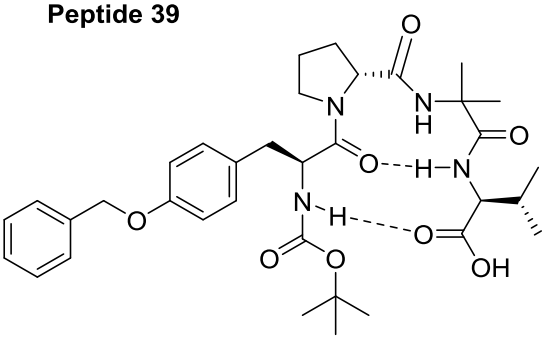
Peptide 37



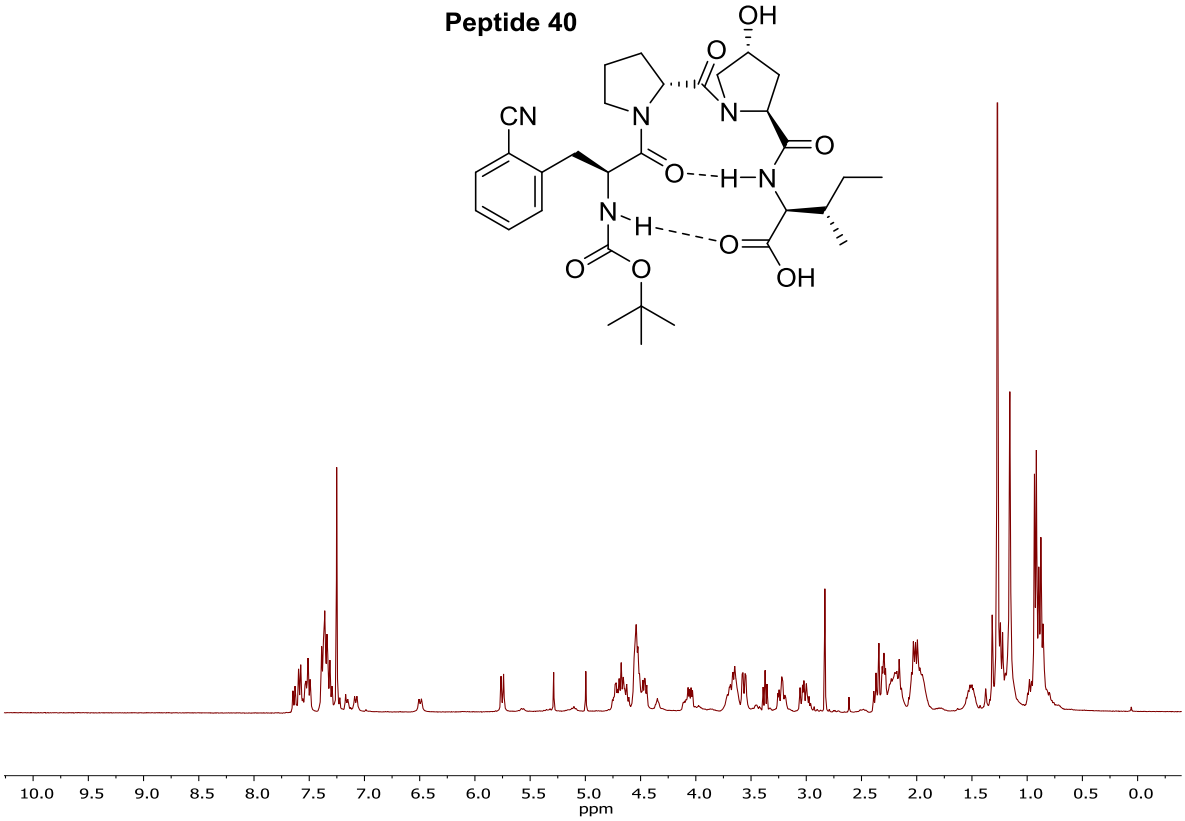
Peptide 38



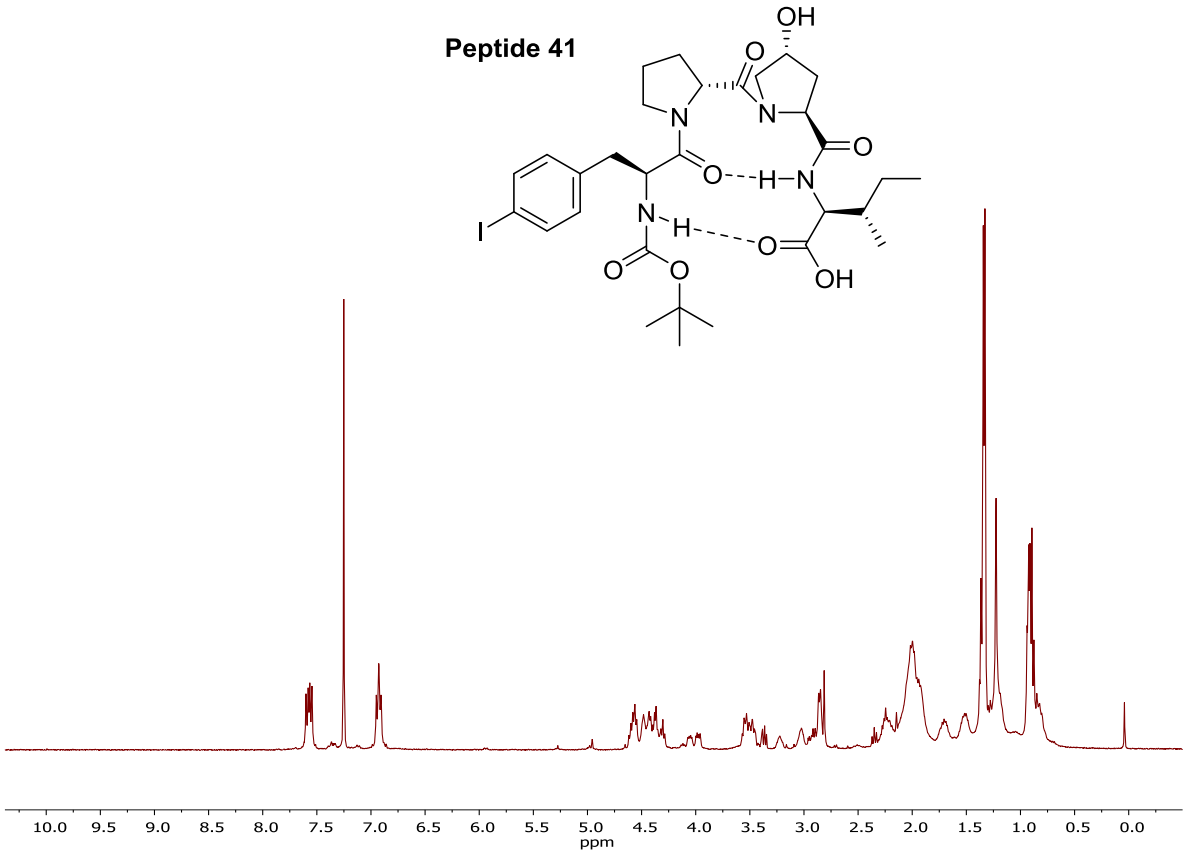
Peptide 39



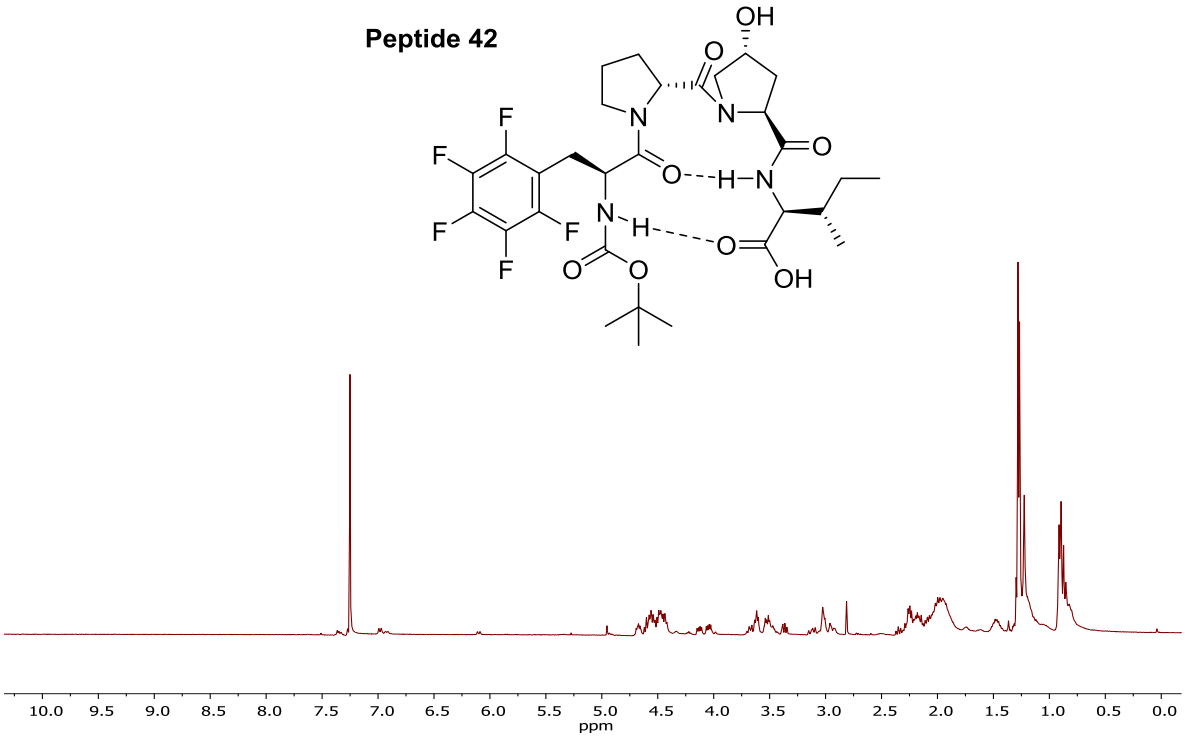
Peptide 40



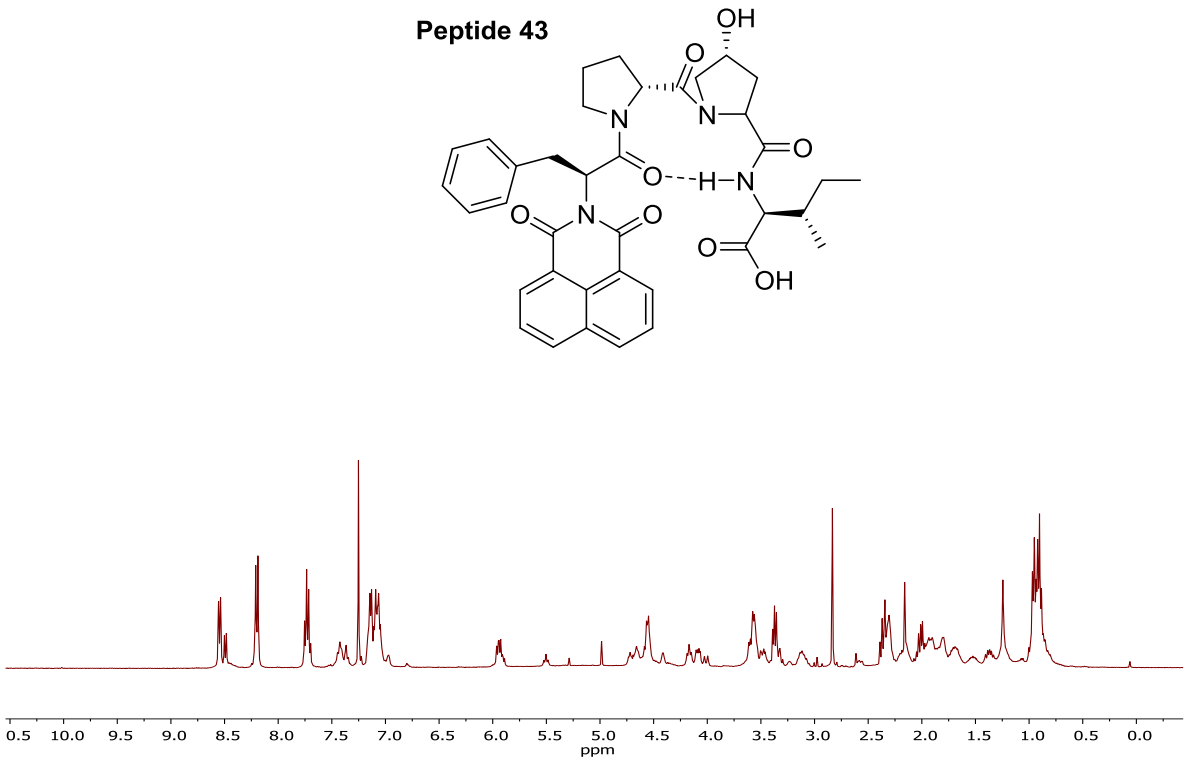
Peptide 41



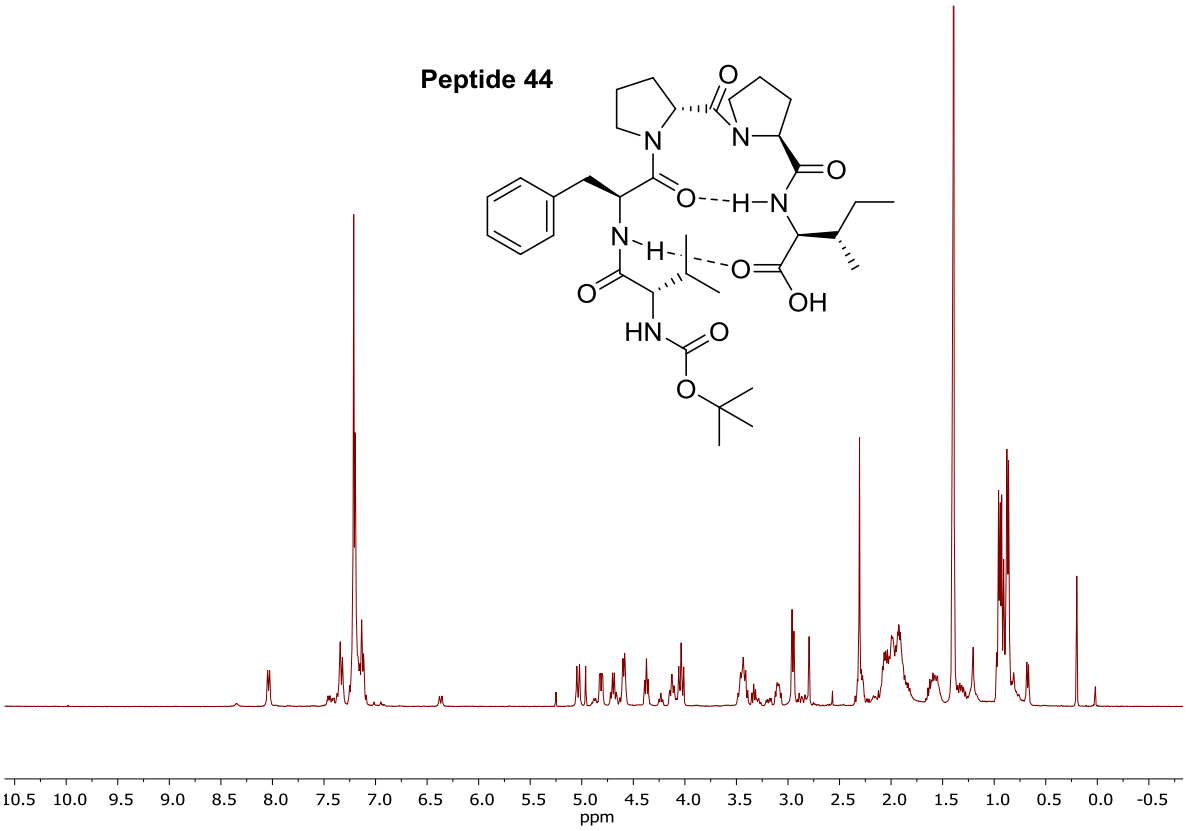
Peptide 42



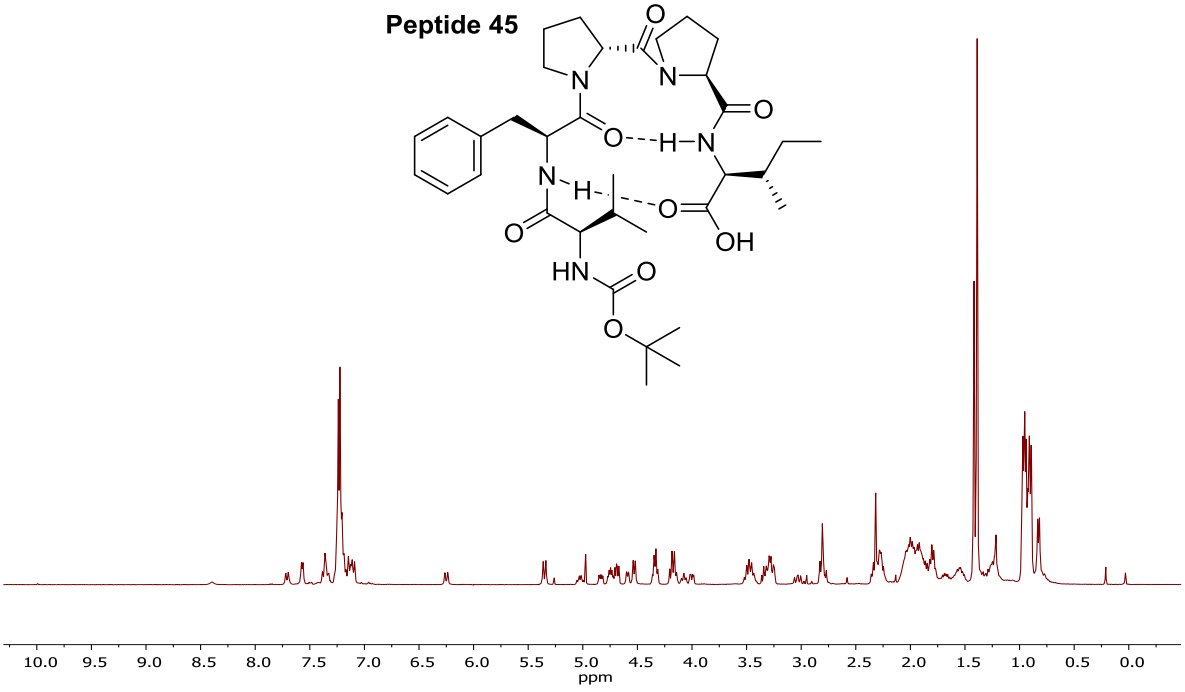
Peptide 43



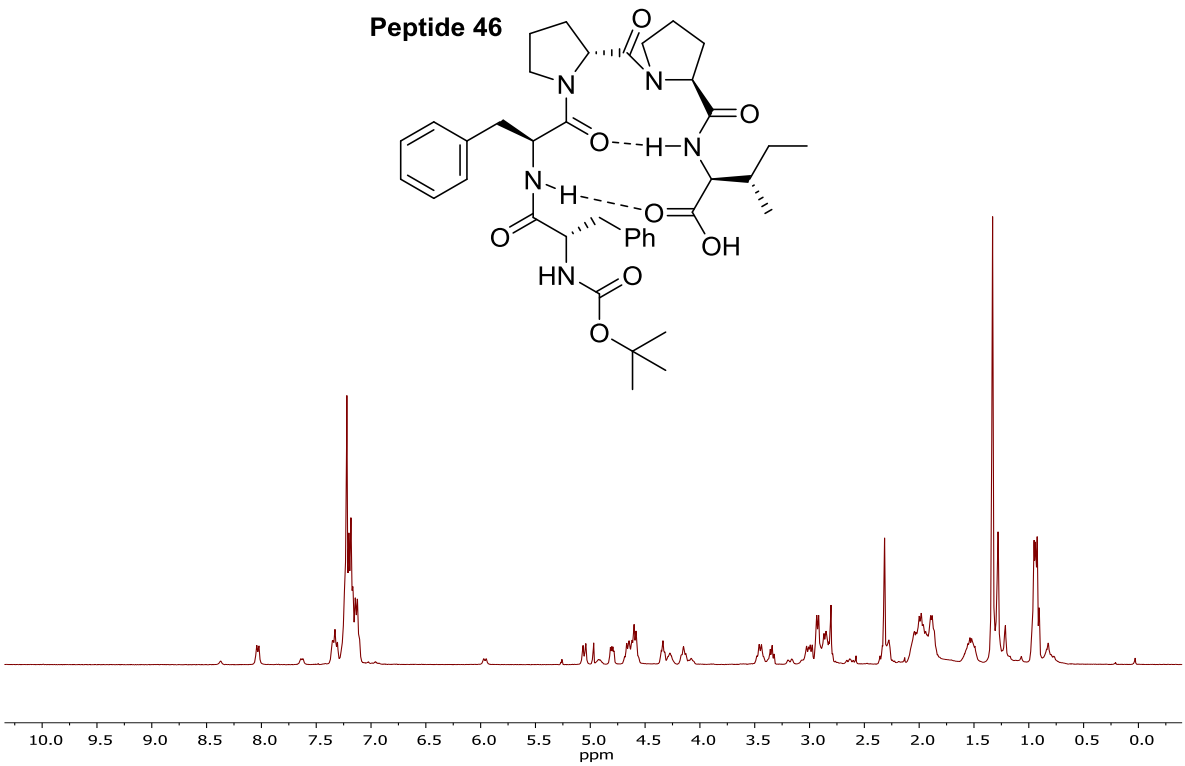
Peptide 44



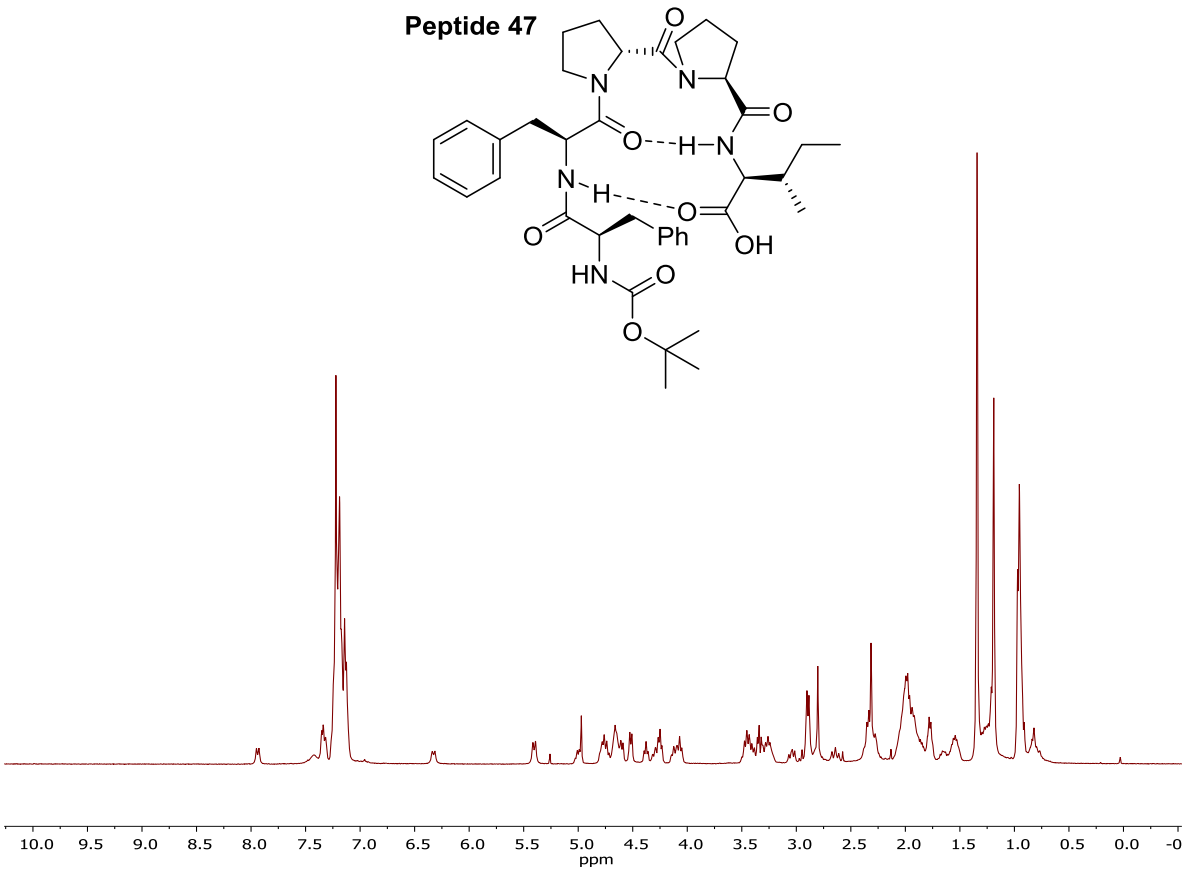
Peptide 45

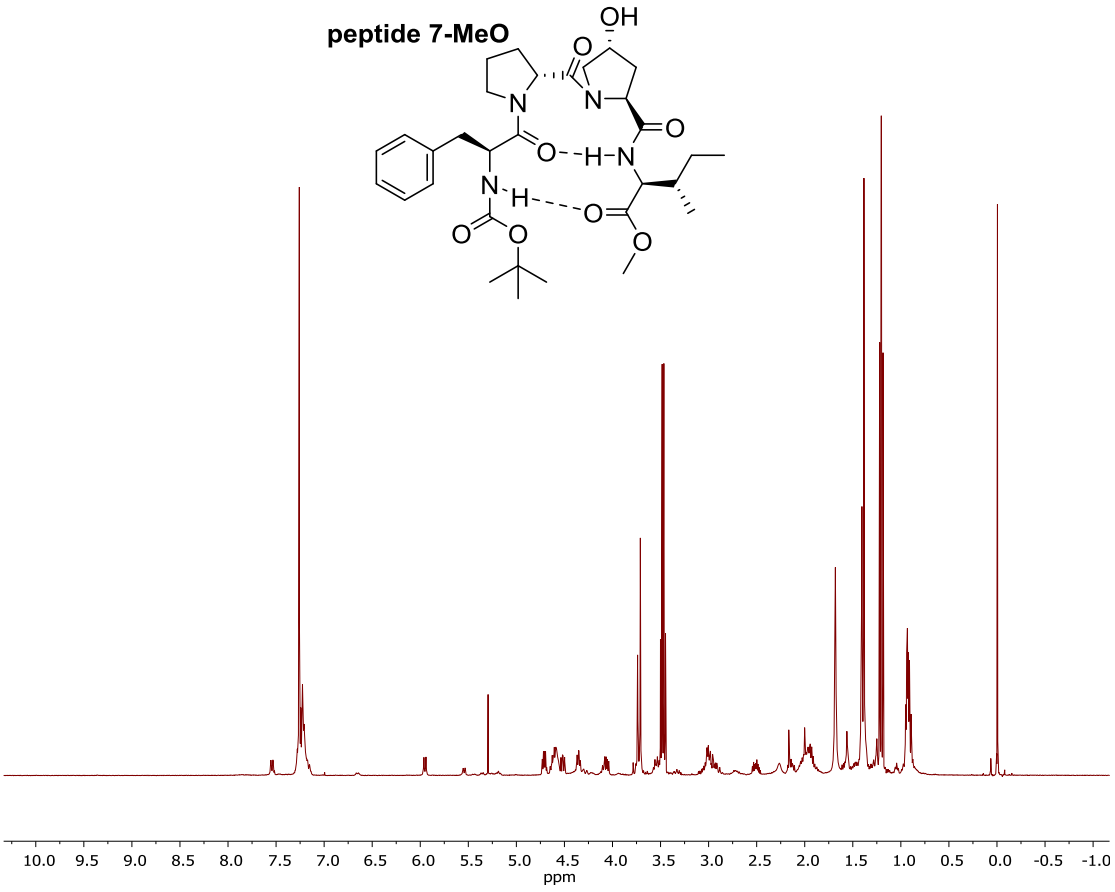


Peptide 46



Peptide 47




peptide 7-MeO
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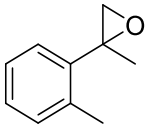
O
N
N
O
O
H
N
N
H
O
O
O
O
O
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

A4) GC spectra of epoxides



Rac

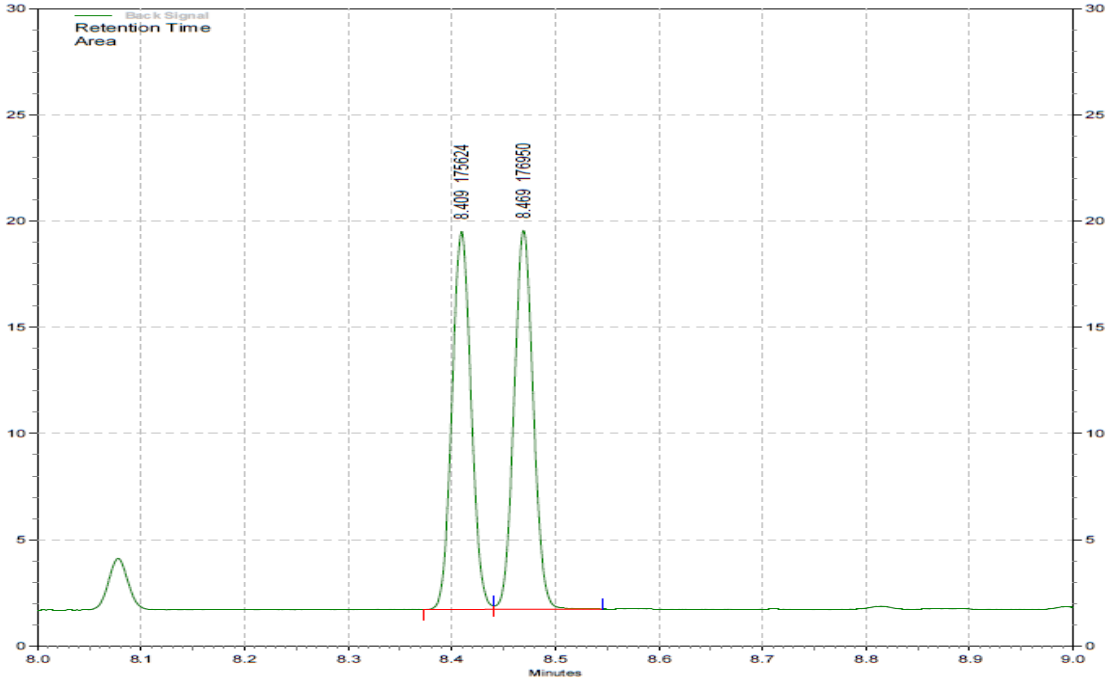
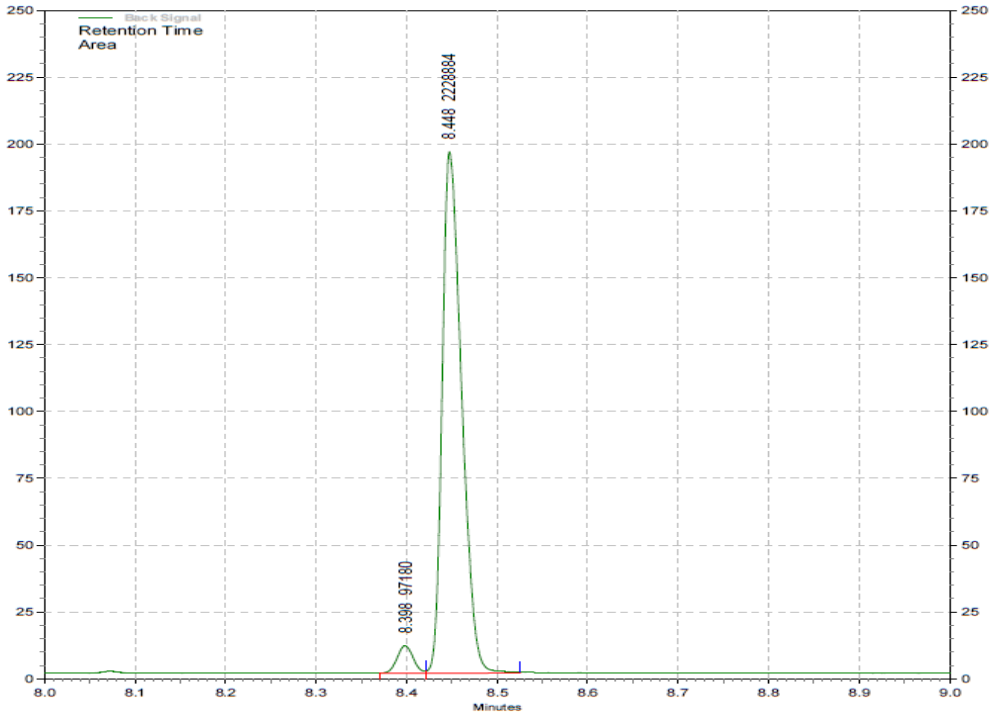
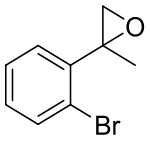


Table 2 entry 4





Rac

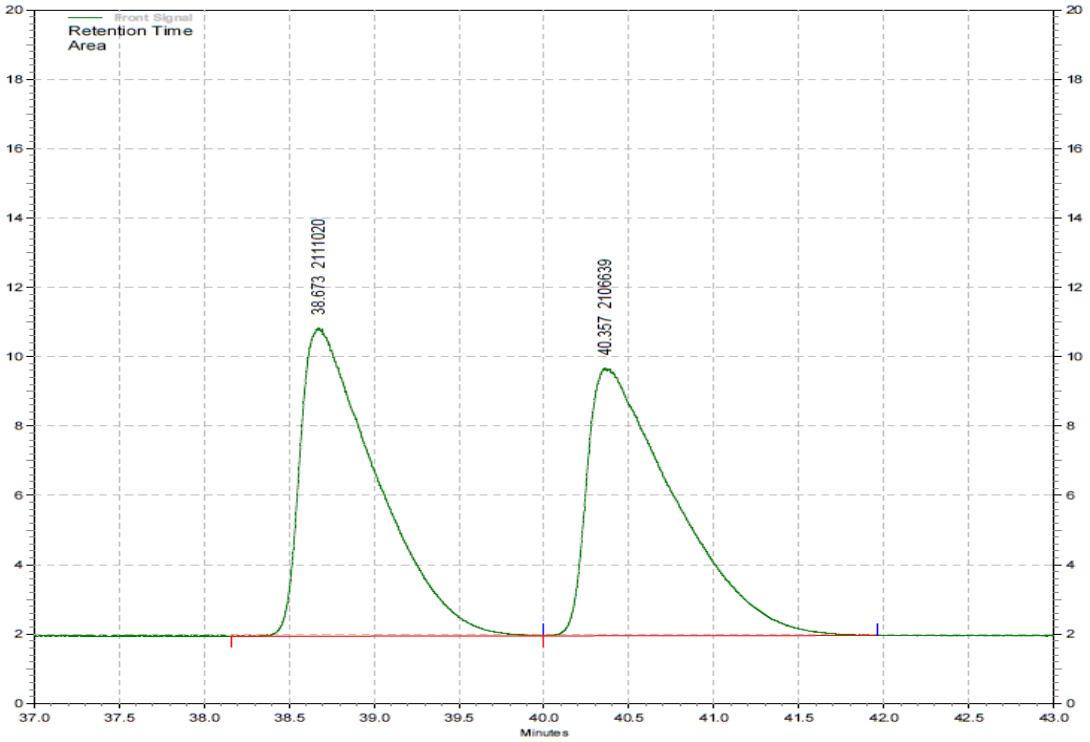
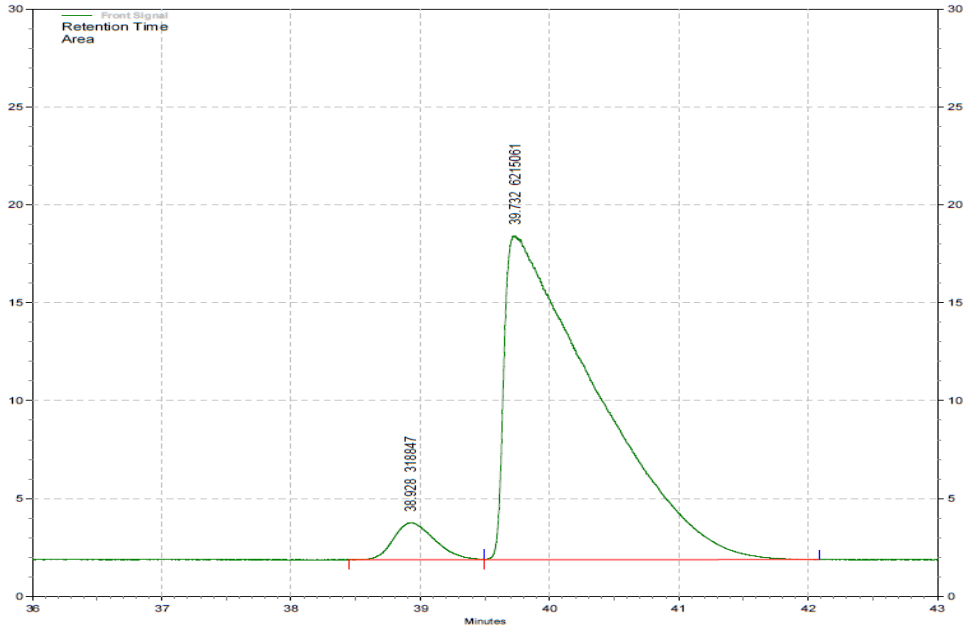
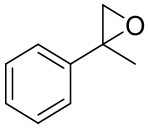


Table 3 entry 3

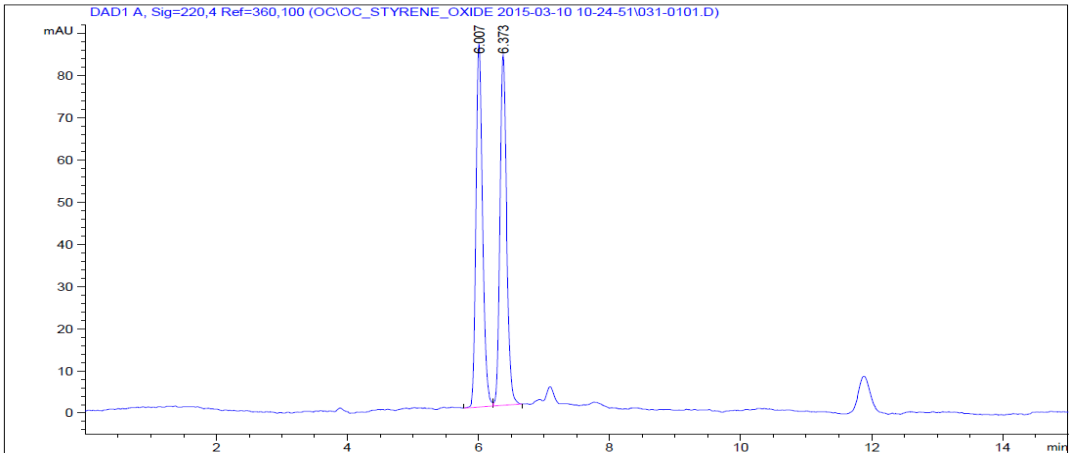


A5) HPLC spectra of epoxides

HPLC-separation conditions: Chiralpack IC 25ºC, 220 nm, 98/2 hexane/*i*-PrOH, 1.0 mL/min; r.t.(major) = 5.7 min, r.t.(minor) = 6.1 min

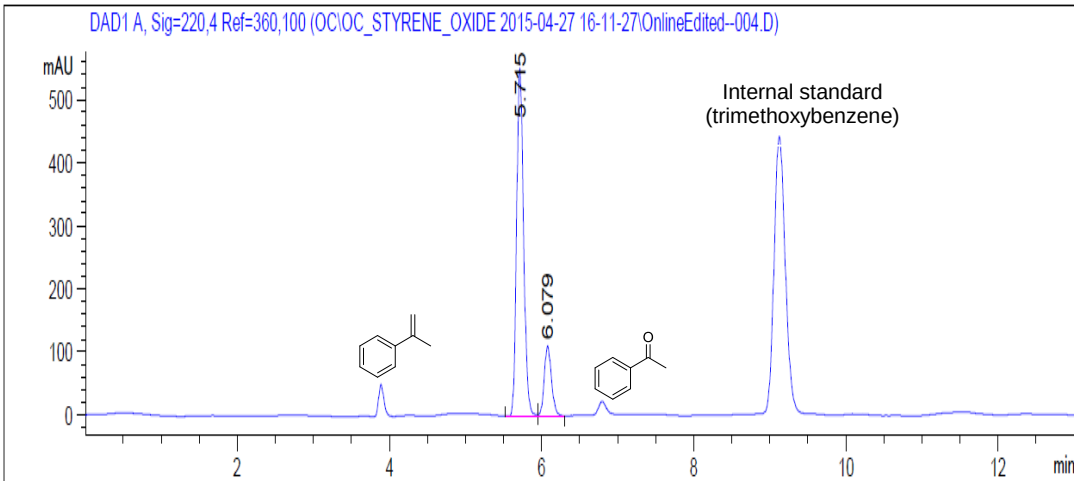


Rac



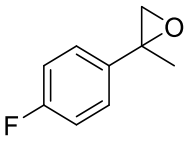
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.007	BV	0.1056	589.17432	86.32866	49.8558
2	6.373	VB	0.1091	592.58350	83.19460	50.1442

Table 2 entry 1

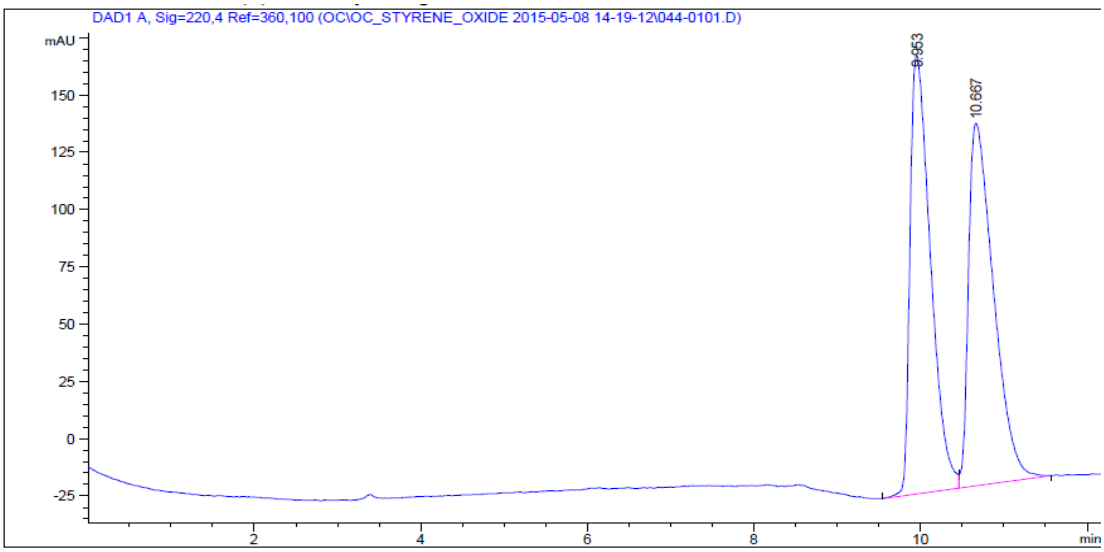


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.715	BV	0.0981	3506.15771	551.81085	82.6699
2	6.079	VB	0.1011	734.99506	111.21644	17.3301

HPLC-separation conditions: Chiralpack IC 25ºC, 220 nm, 99.9/0.1 hexane/*i*-PrOH, 1.0 mL/min; r.t.(major) = 10.4 min, r.t.(minor) = 11.3 min

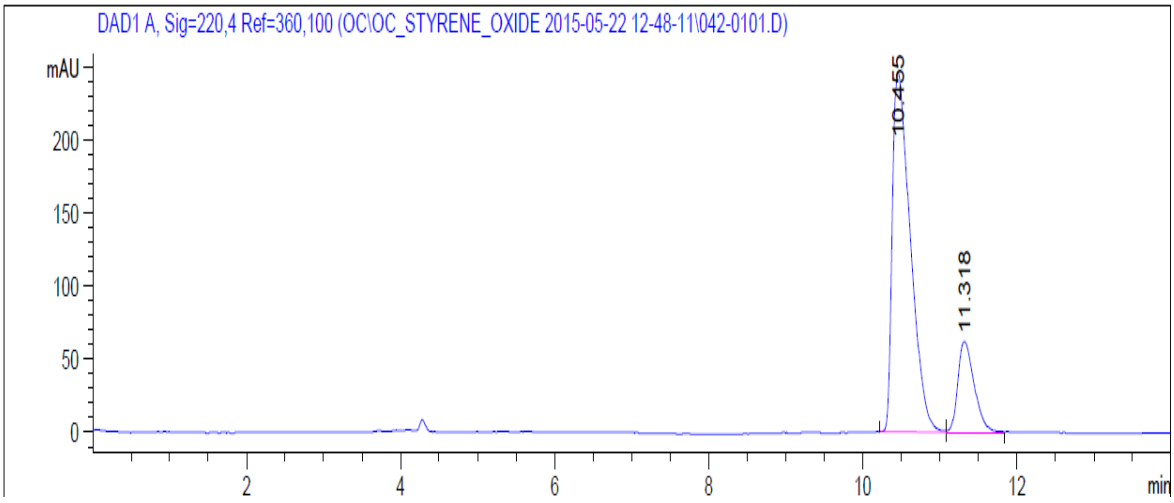


Rac



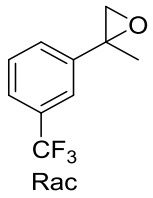
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.953	BV	0.2633	3271.98999	191.50729	49.7036
2	10.667	VB	0.3198	3311.02051	158.42682	50.2964

Table 2 entry 2

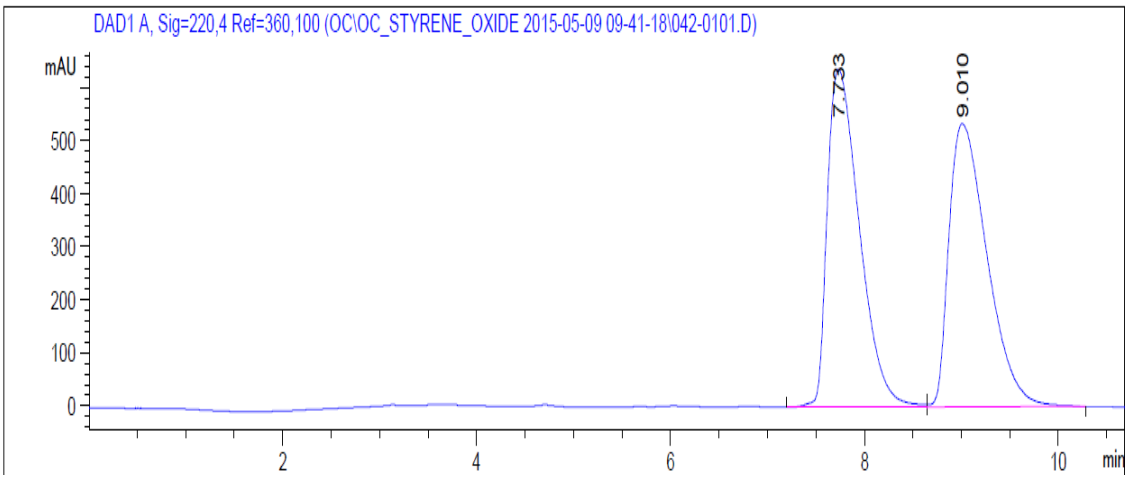


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.455	BV	0.2455	4005.81982	246.64026	81.4983
2	11.318	VB	0.2254	909.39874	61.91505	18.5017

HPLC-separation conditions: Chiralpack OB-H 25ºC, 220 nm, 99.9/0.1 hexane/*i*-PrOH, 1.0 mL/min; r.t.(major) = 8.7 min, r.t.(minor) = 10.2 min

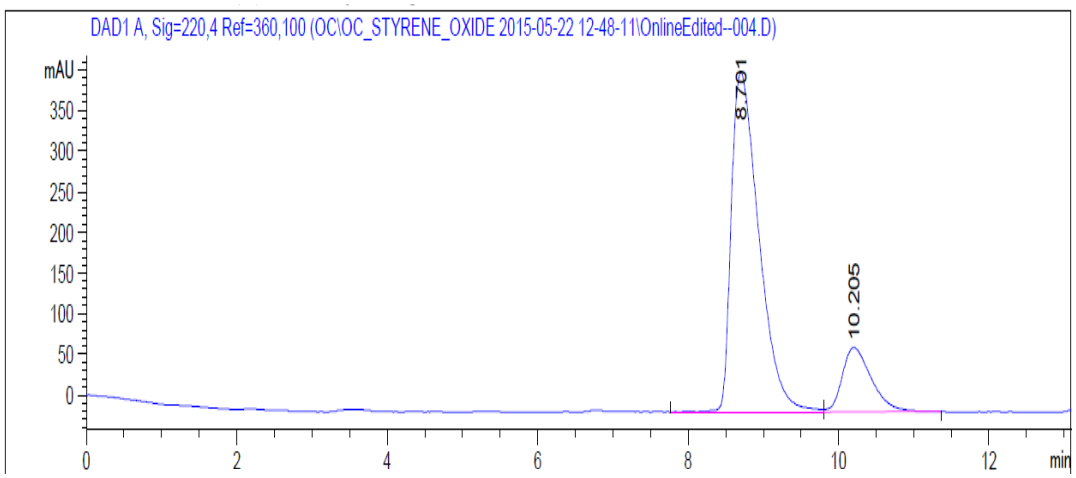


Rac



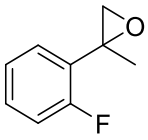
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.733	BV	0.3581	1.46402e4	637.02472	50.1391
2	9.010	VB	0.4186	1.45590e4	533.17413	49.8609

Table 2 entry 3

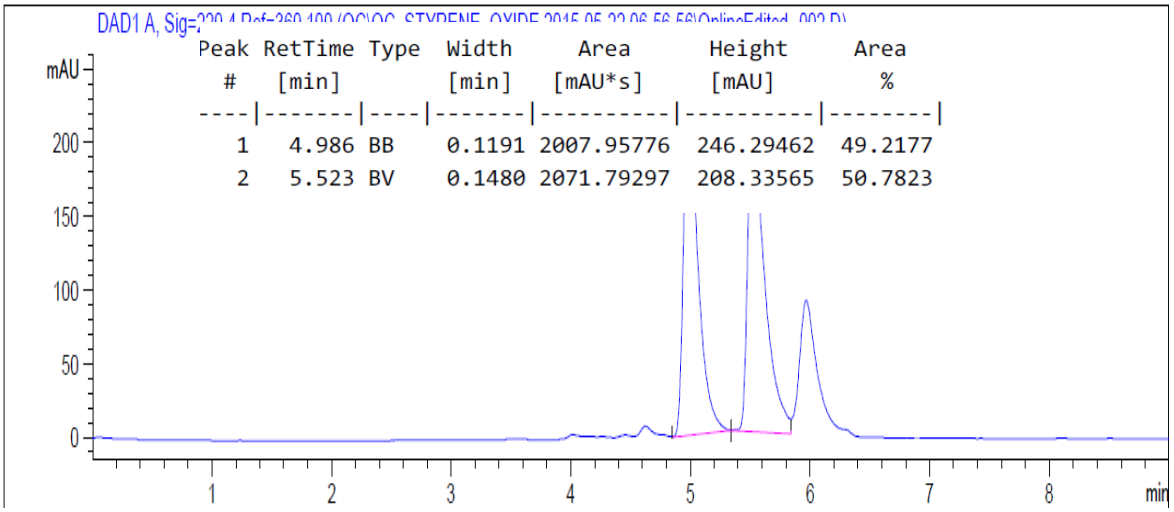


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.701	VV R	0.3934	1.06244e4	416.74301	83.3828
2	10.205	VV R	0.3946	2117.31421	79.01508	16.6172

HPLC-separation conditions: Chiralpack OD-H 25ºC, 254nm, 99.4/0.6 hexane/*i*-PrOH, 1.0 mL/min; r.t.(minor) = 5.0 min, r.t.(major) = 5.6 min

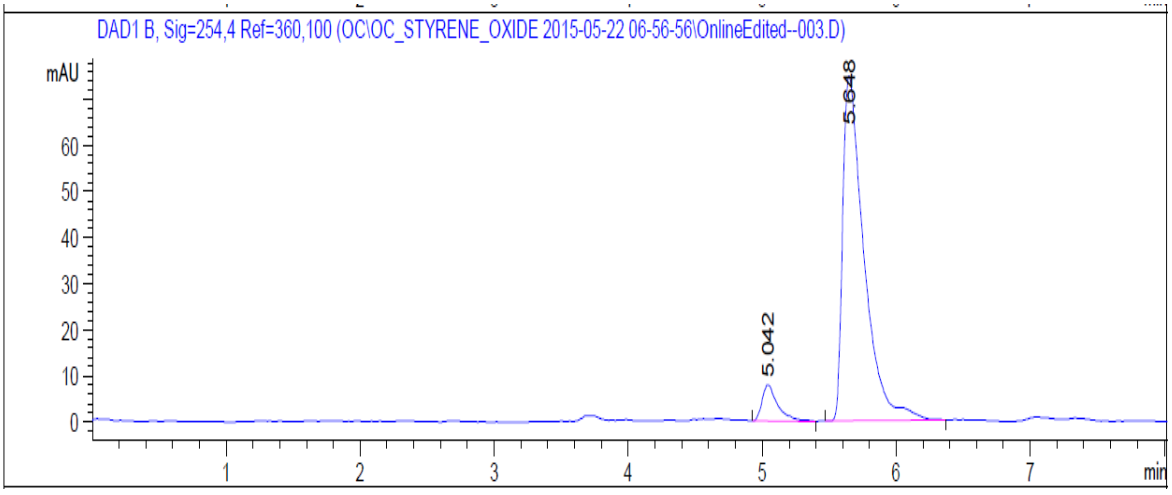


Rac



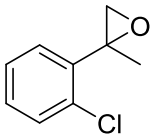
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.986	BB	0.1191	2007.95776	246.29462	49.2177
2	5.523	BV	0.1480	2071.79297	208.33565	50.7823

Table 3 entry 1



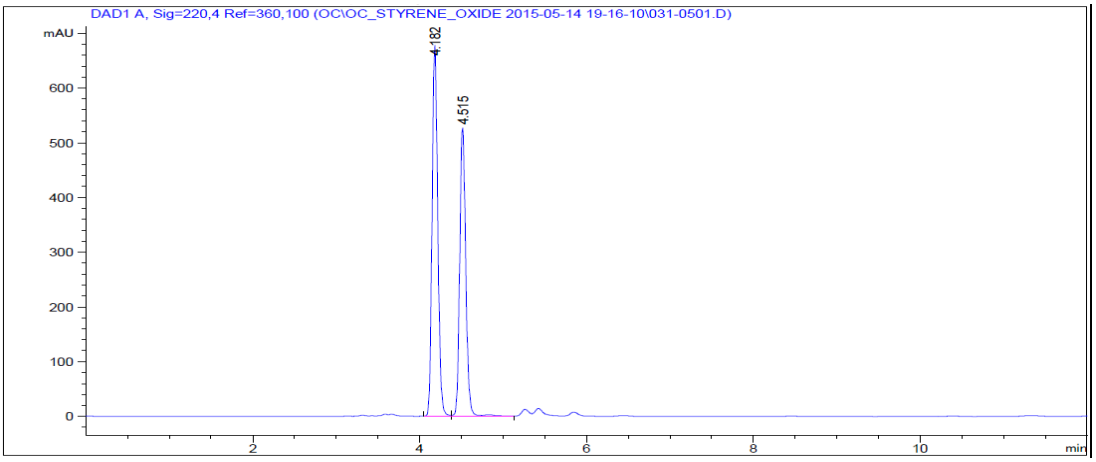
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.042	BB	0.1195	64.59106	7.89121	7.2430
2	5.648	BB	0.1628	827.18713	74.91674	92.7570

HPLC-separation conditions: Chiralpack IB 25ºC, 220nm, 98/2 hexane/*i*-PrOH, 1.0 mL/min; r.t.(minor) = 4.5 min, r.t.(major) = 4.8 min



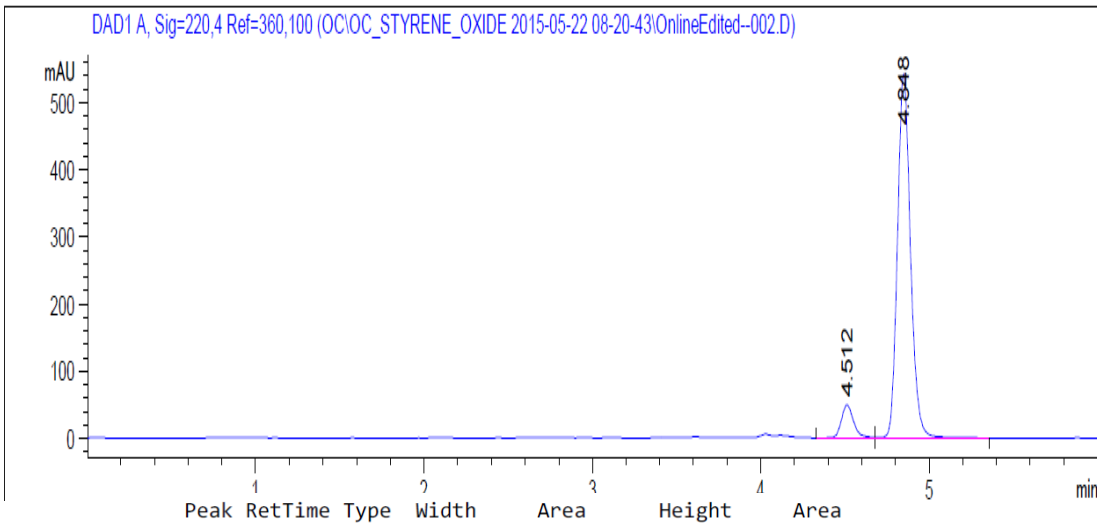
Rac

The racemic epoxide was obtained mixing (S,S') and (R,R') catalysts (1/1)



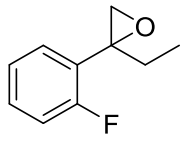
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.182	BV	0.0730	3198.84399	677.94733	54.6530
2	4.515	VV R	0.0761	2654.16479	527.20892	45.3470

Table 3 entry 2

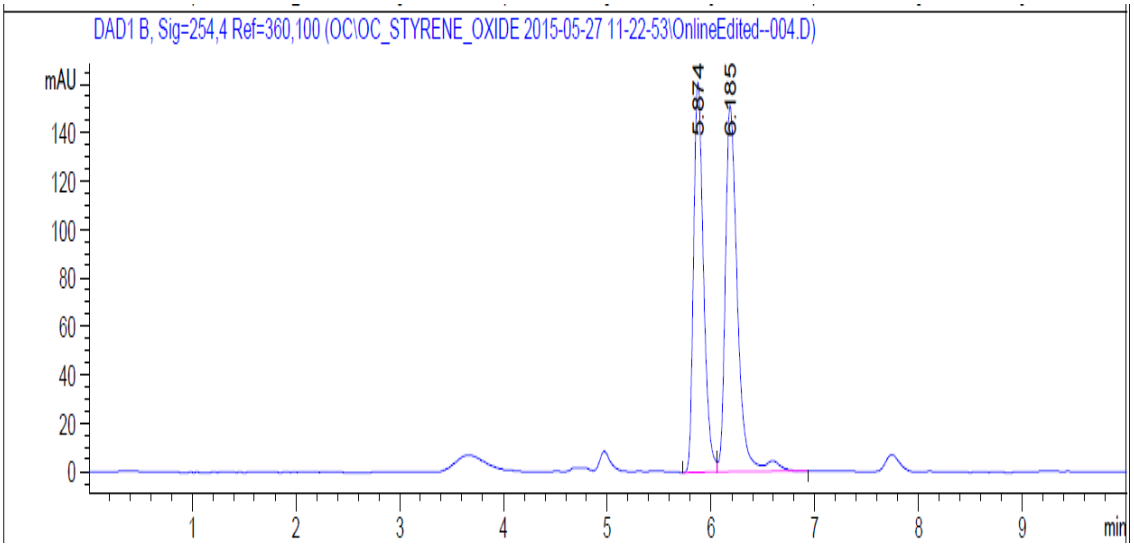


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.512	BV	0.0772	249.62737	49.19366	7.8790
2	4.848	VB	0.0828	2918.64746	542.63934	92.1210

HPLC-separation conditions: Chiralpack AS-H 25ºC, 254nm, 99.6/0.4 hexane/*i*-PrOH, 1.0 mL/min; r.t.(major) = 5.6 min, r.t.(minor) = 5.9 min

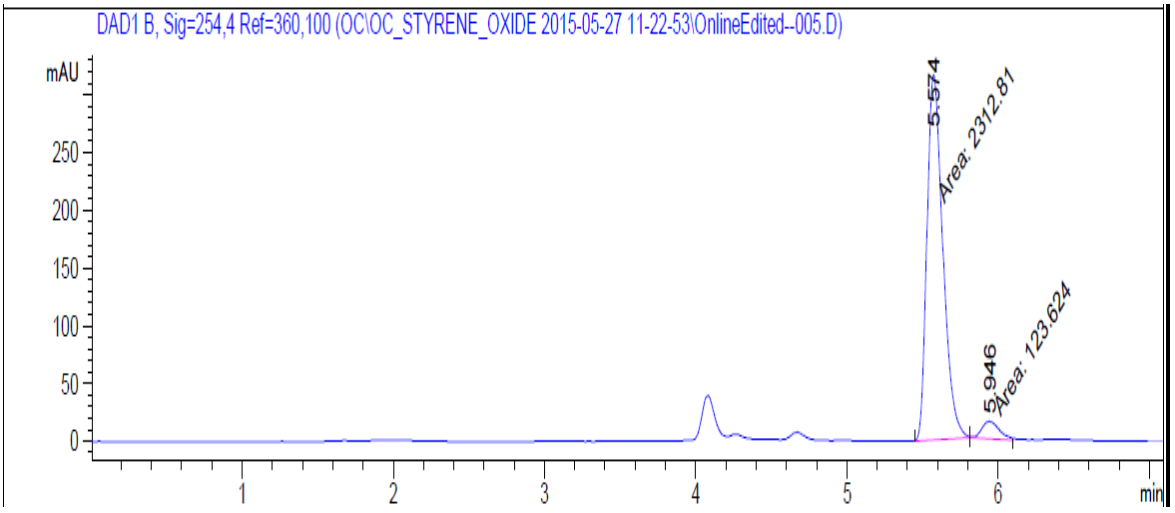


Rac



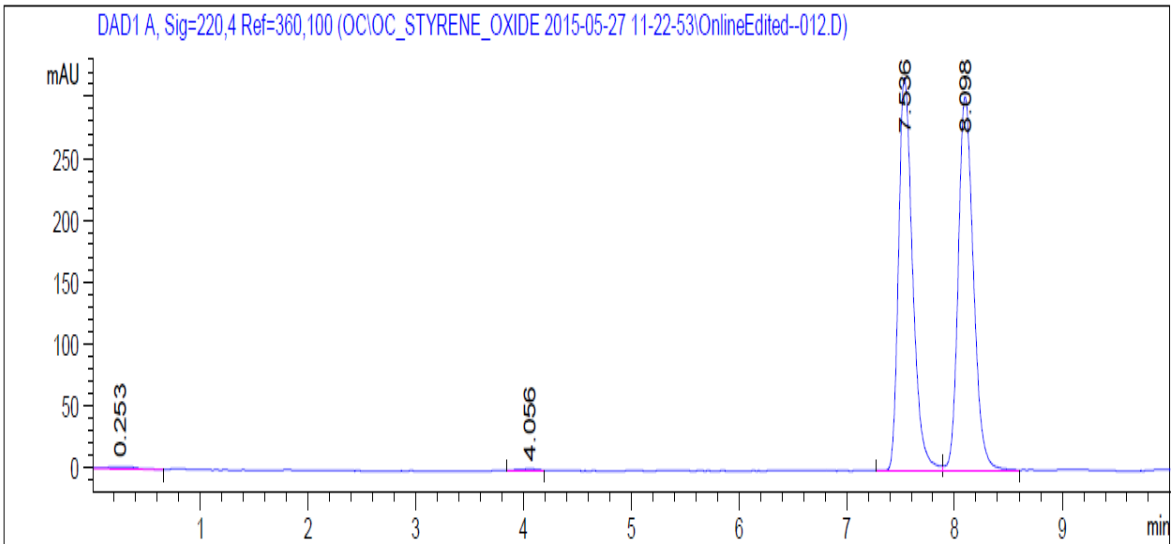
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.874	BV	0.1010	1064.74548	161.30972	46.3207
2	6.185	VV R	0.1192	1233.89160	151.35045	53.6793

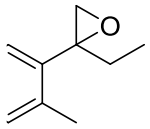
Table 3 entry 4



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.574	MM	0.1217	2312.80811	316.79874	94.9260
2	5.946	MM	0.1383	123.62414	14.90095	5.0740

HPLC-separation conditions: Chiralpack OJ-H 25ºC, 220nm, 99.8/0.2 hexane/*i*-PrOH, 1.0 mL/min; r.t.(major) = 7.8 min, r.t.(minor) = 8.4 min

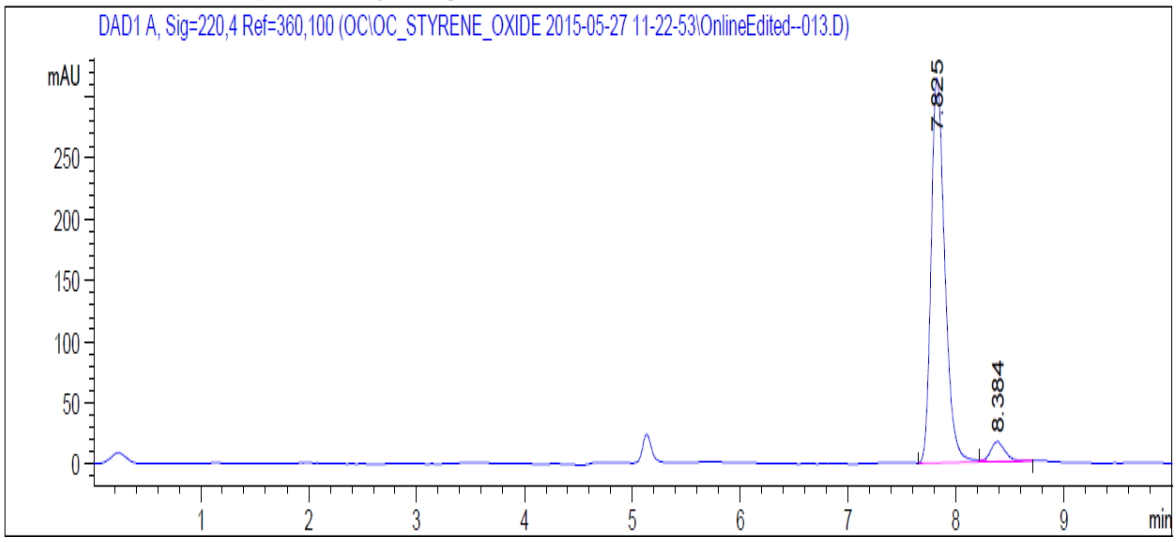




Rac

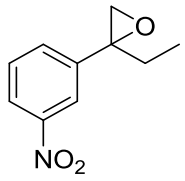
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
3	7.536	BV	0.1400	2886.33130	317.81555	48.9063
4	8.098	VB	0.1500	2955.83423	302.48767	50.0840

Table 3 entry 5

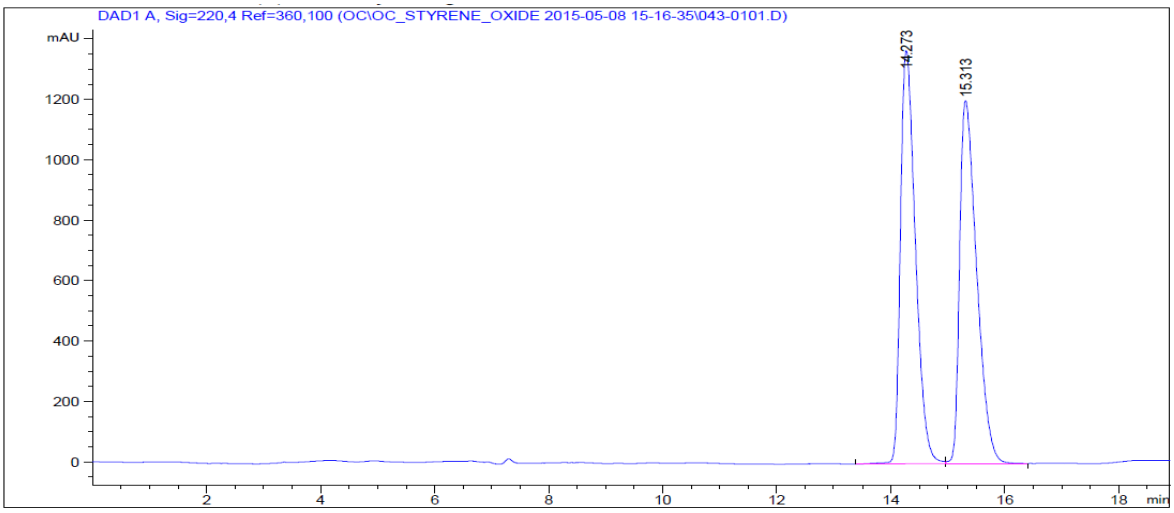


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.825	BV R	0.1372	2784.27295	314.71735	94.9409
2	8.384	VB E	0.1438	148.36496	16.05228	5.0591

HPLC-separation conditions: Chiralpack IC 25ºC, 220nm, 99/1 hexane/*i*-PrOH, 1.0 mL/min; r.t.(minor) = 12.7 min, r.t.(major) = 13.2 min

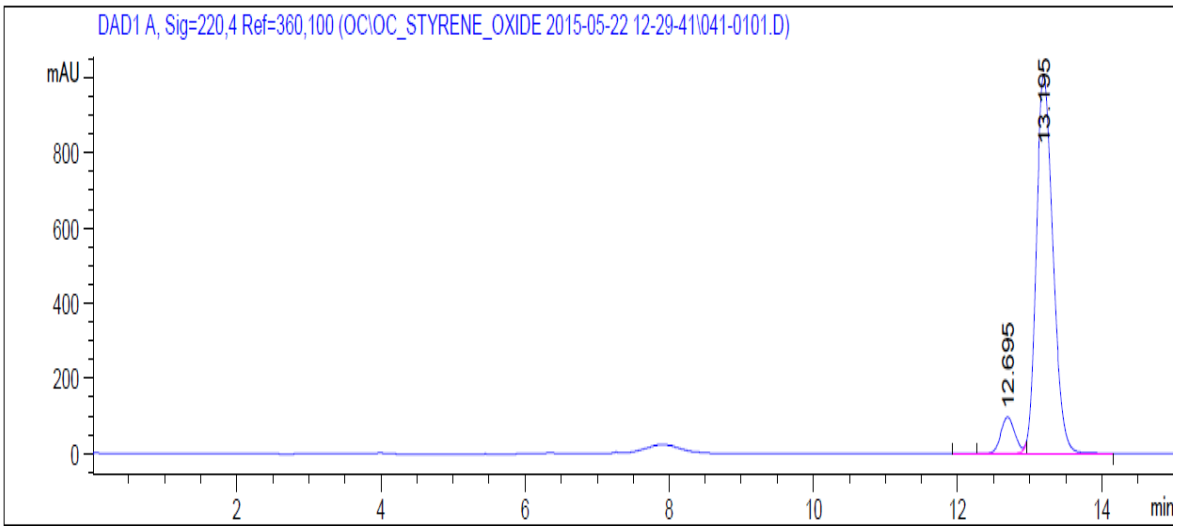


Rac



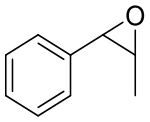
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.273	BV	0.2828	2.49392e4	1367.08350	50.0461
2	15.313	VB	0.3178	2.48932e4	1200.85046	49.9539

Table 3 entry 6

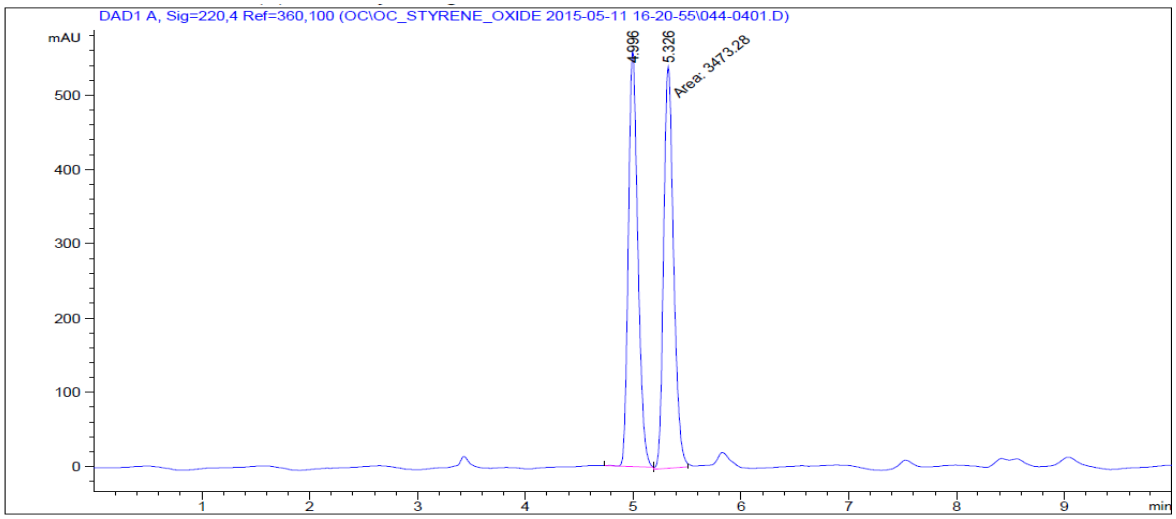


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.695	VV E	0.2086	1298.99988	96.74610	7.4257
2	13.195	VV R	0.2519	1.61943e4	1005.60919	92.5743

HPLC-separation conditions: Chiralpack IC 25ºC, 220nm, 98/2 hexane/*i*-PrOH, 1.0 mL/min; r.t.(minor) = 4.9 min, r.t.(major) = 5.3 min

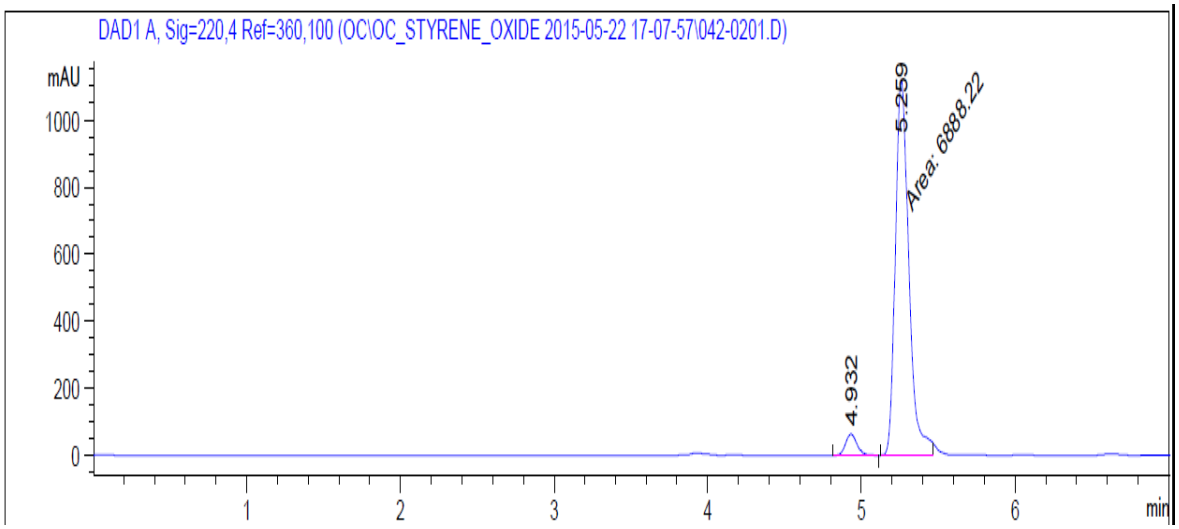


Rac



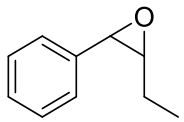
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.996	VB R	0.0934	3423.52515	559.61566	49.6393
2	5.326	MM	0.1068	3473.28149	541.96600	50.3607

Table 3 entry 7

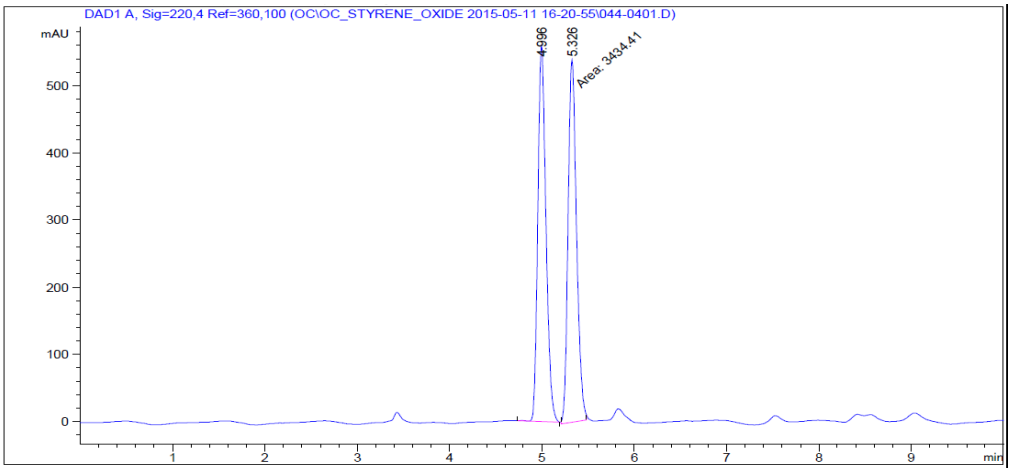


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.932	BV	0.0811	336.48401	64.28787	4.6574
2	5.259	MM	0.1022	6888.21533	1123.17126	95.3426

HPLC-separation conditions: Chiralpack IC 25ºC, 220nm, 98/2 hexane/*i*-PrOH, 1.0 mL/min; r.t.(major) = 5.6 min, r.t.(minor) = 5.9 min

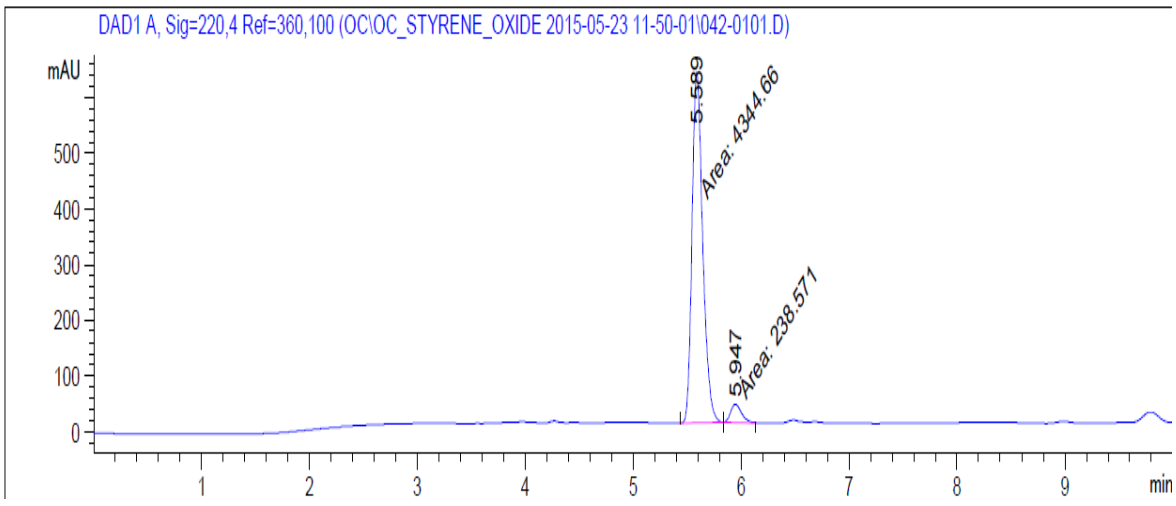


Rac



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.996	VB R	0.0934	3423.52515	559.61566	49.9207
2	5.326	MM	0.1059	3434.40649	540.71307	50.0793

Table 3 entry 8



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.589	MM	0.1148	4344.66309	630.71265	94.7947
2	5.947	MM	0.1187	238.57077	33.48513	5.2053