Stereoselective Peptide Catalysis in Complex Environments – From River Water to Cell Lysates

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Supporting Information

Contents

1. General Aspects and Materials

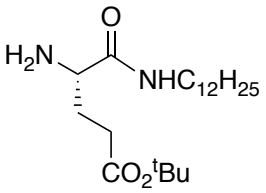
Reagents and materials were of the highest commercially available grade and used without further purification. Reactions were monitored by thin layer chromatography using Merck silica gel 60 F254 aluminium sheets. Visualization of the compounds was achieved by UV-Vis or $KMnO_4$. Flash chromatography and plug filtrations were performed using silica gel 60 (particle size 0.040 – 0.063 mm, 200 – 400 mesh) manufactured by Fluka. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 400, a Bruker AV III 400 (400 MHz/100 MHz) or a Bruker AV III 600 (600 MHz/150 MHz). All spectra were recorded at 25 °C, unless stated otherwise. Chemical shifts (δ) are reported in parts per million (ppm) relative to the signal of tetramethylsilane (TMS) using the residual solvent signals. SFC analyses were performed on an analytical SFC with a diode array detector ACQUITY-UPLC-PDA from Waters using chiral stationary phase columns (Trefoil, AS, AD, IA, Whelk, IC, OD, OJ) (150 mm x 30 mm) from Daicel or Waters under the reported conditions. HPLC analyses were performed on an analytical Ultimate 3000 HPLC system from Dionex with a diode array detector and chiral stationary phase columns (Daicel AD-H, Daicel AS-H, AY-H, OD-H or Daicel OJ-H). High-resolution electron ionization (HR-EI) mass spectra were measured on a Waters Micromass AutoSpec Ultima spectrometer. High-resolution MALDI spectra were acquired on a Bruker solariX 94 (ESI/MALDI-FT-ICR) and a Bruker Ultra-Flex II (MALDI-TOF) spectrometer.

2. Synthesis and Analytical Data of the Peptides

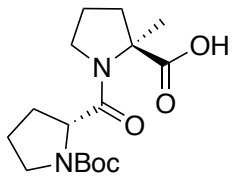
Peptide Synthesis

Peptides **1** and **2** were prepared by solution peptide synthesis, peptide **1a** and **2b** by solid phase peptide synthesis. The syntheses of **1**[1] and **1a**[2] have been previously described.

Procedure for the synthesis of H-Glu(O^{t}Bu)-NHC$_{12}$H$_{25}$: *Z-Glu(O^{t}Bu)-OH* (5.0 g, 14.8 mmol, 1 equiv.), dodecylamine (2.75 g, 14.82 mmol, 1.0 equiv.) and EDC•HCl (3.4 g, 17.8 mmol, 1.2 equiv.) were suspended in EtOAc (75 mL) and stirred at room temperature overnight. The mixture was diluted with EtOAc (350 mL) and washed with 0.1 M HCl (3x 100 mL), aq. 5% w/w Na_2CO_3 (2x 100 mL) and brine (150 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting colorless solid was purified by flash column chromatography on silica gel eluting with 1-5% MeOH in CH_2Cl_2. The colorless solid was then dissolved in MeOH (20 mL). Pd/C (10 % w/w) was added and the mixture was stirred under a hydrogen atmosphere (balloon) at room temperature overnight. The reaction mixture was filtered over a pad of celite, which was washed with MeOH (3x 10 mL). Removal of all volatiles yielded the desired product as colorless solid (3.95 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 (s, J = 3.1 Hz, 1H), 3.37 (dd, J = 7.5, 5.0 Hz, 1H), 3.23 (td, J = 7.2, 5.9 Hz, 2H), 2.36 (m, 1H), 2.08 (dtd, J = 14.1, 7.5, 5.0 Hz, 1H), (dtd, J = 14.3, 7.7, 6.8 Hz, 1H), 1.55 – 1.45 (m, 2H), 1.43 (s, 9H), 1.36 – 1.17 (m, 20H), 0.86 (t, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 174.3, 173.0, 80.7, 54.8, 39.3, 32.2, 32.05, 30.55, 29.9, 29.8, 29.73, 29.69, 29.5, 29.4, 28.2, 27.1, 22.8, 14.2. The spectroscopic data are in agreement with published data.[1]



Procedure for the synthesis of Boc-DPro-MePro-OH: Boc-DPro-OH (9.5 g, 44.1 mmol, 1.0 equiv.) and EDC•HCl (10.2 g, 53.0 mmol, 1.2 equiv.) were dissolved in EtOAc (110 mL). ^{i}Pr$_2$NEt (15.0 mL 88.3 mmol, 2.2 equiv.) was added and the mixture was stirred for 5 min before addition of H-MePro-OMe•HCl (6.3 g, 44.1 mmol, 1.0 equiv.). The reaction mixture was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc and subsequently washed with 1 M aq. HCl (100 mL), H_2O (100 mL), sat. aq. $NaHCO_3$ solution (100 mL) and brine (100 mL). The combined aqueous layers were then reextracted with EtOAc (10x). The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product (colorless solid, 5.7 g) was purified by flash column chromatography on silica gel eluting with 1-5% MeOH in CH_2Cl_2. The resulting colorless solid was dissolved in THF/MeOH 1:1 (20 mL) and NaOH (1.33 g, 2 equiv.) and water (1 mL) was added. The reaction mixture was stirred for 1.5-2 h, acidified with concentrated HCl (pH ≈ 2) and extracted with CH_2Cl_2 (3x). The combined organic layers were dried over $MgSO_4$. Removal of all volatiles yielded the desired product as colorless solid (5.20 g, 37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.44 (m, 1H), 4.05 – 3.77 (m, 1H), 3.67 – 3.39 (m, 3H), 2.85 – 2.58 (m, 1H), 2.32 – 1.78 (m, 3H), 1.67 and 1.65 (2 s, 3H), 1.44 and 1.40 (2 s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 176.6, 174.3, 173.8, 173.4, 80.8, 80.6, 69.9, 68.9, 58.5, 58.0, 49.6, 49.4, 47.1, 46.9, 38.2, 37.6, 30.6, 29.5, 28.6, 28.3, 24.8, 23.9, 23.7, 23.5, 22.4, 22.2. [M + H]$^+$ $C_{16}H_{27}N_2O_5^+$: 327.1923; found: 327.1830.



***Procedure for solution peptide synthesis of H-DPro-MePro-Glu-NHC$_{12}$H$_{25}$ 2*:** Boc-DPro-MePro-OH (0.88 g, 2.40 mmol, 1.0 equiv) and EDC•HCl (0.57 g, 2.96 mmol, 1.2 equiv.) were suspended in EtOAc (30 mL) and ^{i}Pr$_2$NEt (0.92 mL, 2.2 equiv.). After stirring for 5 min at room temperature H-Glu-NHC$_{12}$H$_{25}$ (1.00 g, 2.70 mmol, 1.0 equiv.) was added and the suspension was stirred at room temperature overnight. The reaction mixture was diluted with EtOAc (20 mL), washed with 0.1 M HCl (2x 5 mL), 5% w/w aq. Na_2CO_3 (5 mL) and brine (5 mL). The solution was dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a yellowish oil which was purified by flash column chromatography on silica gel eluting with 1-5% MeOH in CH_2Cl_2. The protected peptide was dissolved in TFA/CH_2Cl_2 2:1 (14 mL) and the mixture was stirred at room temperature for 30 min. Removal of all volatiles and precipitation from cold Et_2O yielded the desired product as a colorless solid (0.91 mg, 56 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.84 (d, J = 7.1 Hz, 1H), 6.82 (t, J = 5.6 Hz, 1H), 4.80 – 4.71 (m, 1H), 4.44 – 4.35 (m, 1H), 3.95 – 3.85 (m, 1H), 3.81 – 3.70 (m, 1H), 3.65 – 3.54 (m, 1H), 3.42 – 3.31 (m, 1H), 3.30 – 3.14 (m, 1H), 2.64 – 2.21 (m, 6H), 2.15 – 1.86 (m, 4H), 1.83 – 1.72 (m, 1H), 1.64 (s, 3H), 1.53 – 1.42 (m, 2H), 1.33 – 1.19 (brs, 20H), 0.87 (td, J = 7.0, 2.3 Hz, 3H) (Mixture of *trans*/*cis* conformers in a ratio of > 30:1). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 179.9, 171.2, 170.1, 168.7, 77.5, 77.2, 76.8, 69.7, 59.8, 53.6, 49.1, 47.0, 39.7, 39.6, 32.1, 30.2, 30.1, 29.8, 29.8, 29.8, 29.6, 29.5, 29.1, 27.1, 25.7, 25.0, 23.6, 22.8, 21.9, 14.3. HRMS (ESI): m/z calcd. for $[M + H]^+$ $C_{28}H_{51}N_4O_5^+$: 523.3854; found: 523.3850.

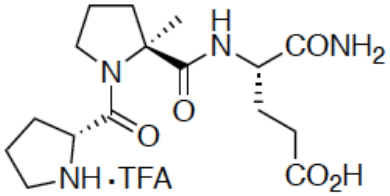
Peptide **2a** was prepared on solid phase using Rink Amide resin. The general protocol for Fmoc/*t*Bu peptide synthesis was followed according to the general procedures below:

General procedure for peptide couplings: ^{i}Pr$_2$NEt (6 equiv.) was added to a solution of Fmoc-Xaa-OH (3 equiv.) and HATU (3 equiv.) in DMF. The solution of the activated amino acid (≈ 100 mM) was added to the amino-functionalized resin (preswollen in CH_2Cl_2) and the mixture was agitated for 1 h before washing with DMF (3x) and CH_2Cl_2 (3x).

General procedure for Fmoc-deprotections: A solution of 20% piperidine in DMF was added to the resin (preswollen in CH_2Cl_2) and the reaction mixture was agitated for 10 min, drained and the piperidine treatment was repeated for 10 min. Finally, the resin was washed with DMF (3x) and CH_2Cl_2 (3x).

General procedure for side chain deprotection and cleavage of the peptides from the solid support: The peptides were side-chain deprotected and cleaved from the resin by shaking in a mixture of TFA/TIS/H_2O (95:2.5:2.5) for 1 h and a second time for 30 min. Pooling of the filtrates and removal of all volatiles under reduced pressure followed by precipitation and thorough washing with Et_2O afforded the peptides as their TFA-salts. The peptides were redissolved in MeCN/H_2O 1:1, dried by lyophilisation and used without further purification.

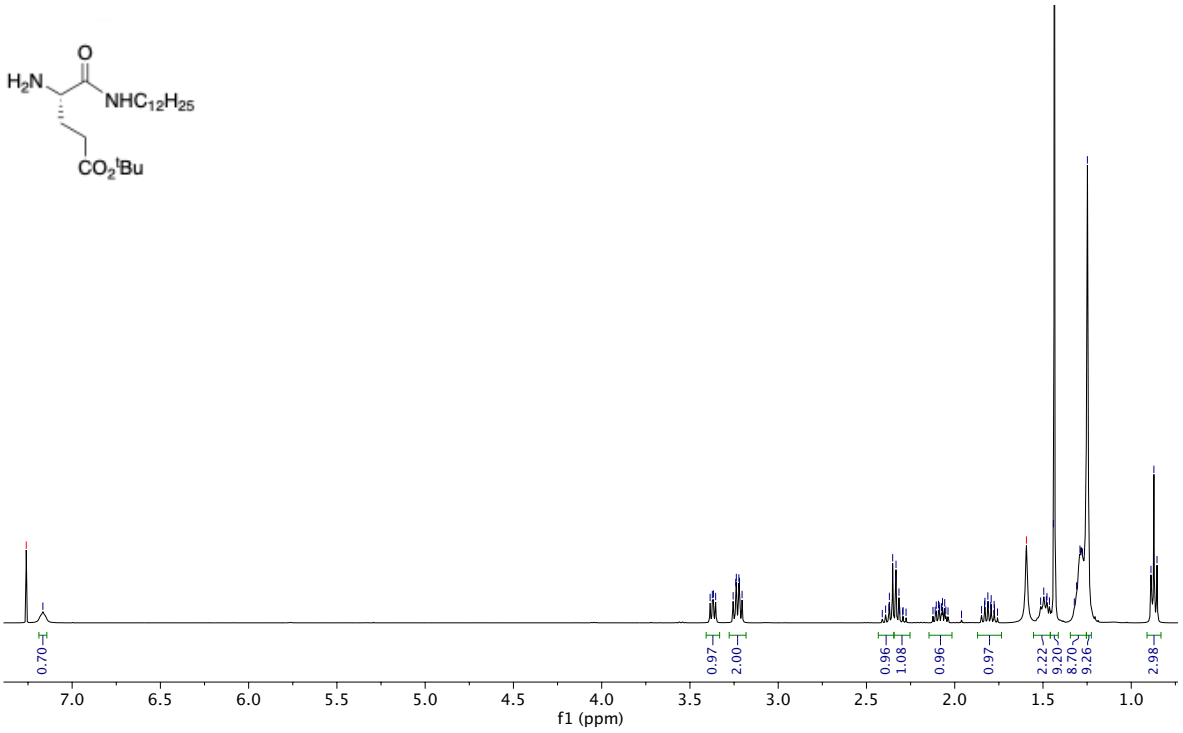
H-DPro-MePro-Glu-NH$_2$•TFA (2a): Only the signals of the *trans* isomer are reported.



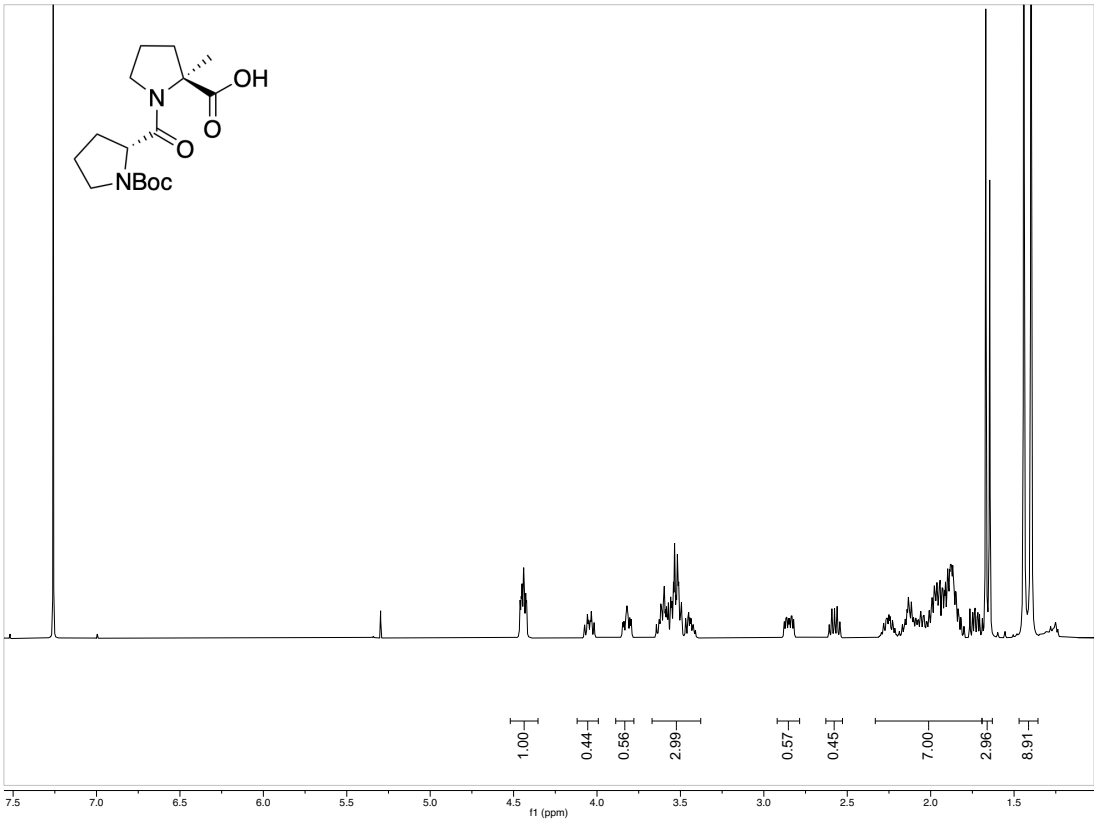
^{1}H NMR (400 MHz, $CDCl_3/CD_3OH$ 9:1) δ = 8.83 (d, *J* = 7.0 Hz, 1H), 7.14 (s, 1H), 6.28 (s, 1H), 4.71 (dd, *J* = 8.9, 6.7 Hz, 1H), 4.35 (td, *J* = 7.2, 2.8 Hz, 1H), 3.92 (dt, *J* = 10.2, 6.2 Hz, 1H), 3.60 (dt, *J* = 10.0, 7.2 Hz, 1H), 3.54 (dt, J = 11.2, 6.8 Hz, 1H), 3.41 – 3.32 (m, 1H), 2.68 – 2.44 (m, 3H), 2.30 (q, J = 5.8 Hz, 1H), 2.24 – 2.14 (m, 2H), 2.13 – 1.82 (m, 6H), 1.59 (s, 3H). 13C NMR (101 MHz, $CDCl_3/CD_3OH$ 9:1) *δ* = 178.7, 174.8, 173.0, 168.5, 68.8, 59.4, 53.6, 48.7, 46.8, 39.4, 30.2, 29.1, 25.0, 24.8, 23.7, 21.2. HRMS (MALDI): m/z calcd. for $[M + H]^+$ $C_{16}H_{27}N_4O_5^+$: 355.1976; found: 355.1976.

^{1}H and ^{13}C NMR Spectra

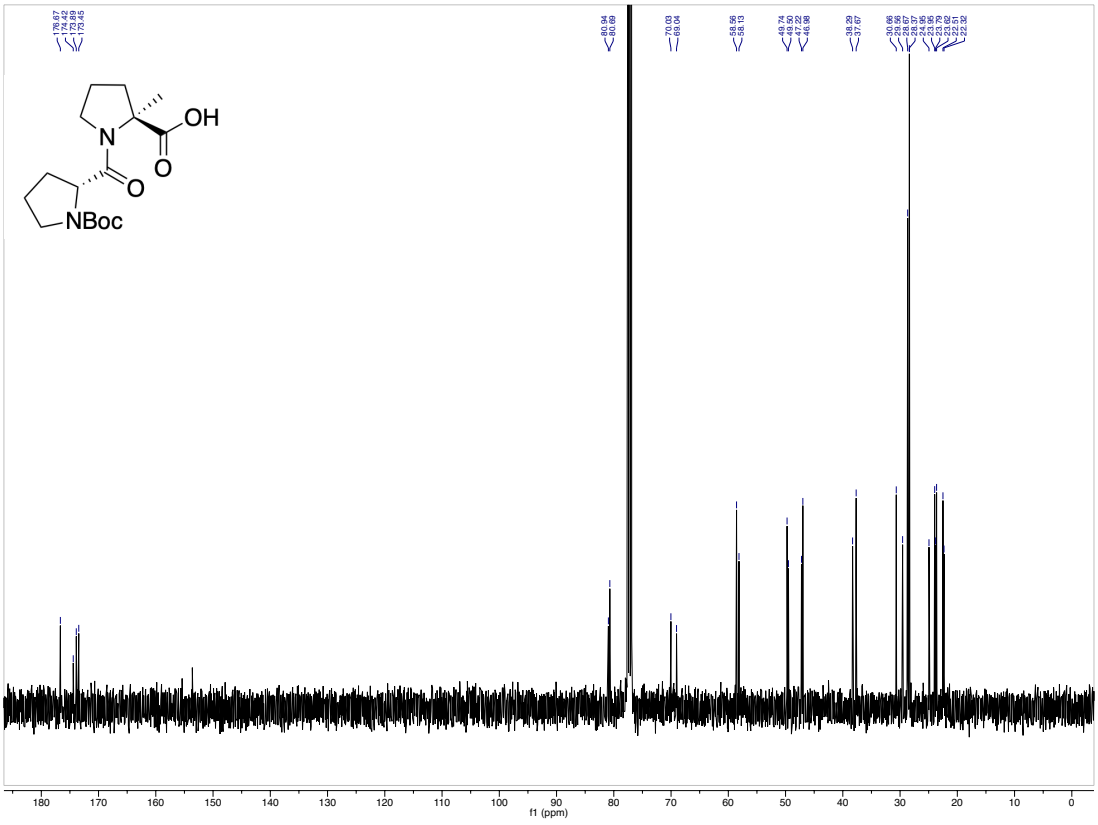
^{1}H NMR Spectrum (400 MHz) of H-Glu(O^{t}Bu)-$NHC_{12}H_{25}$ recorded in $CDCl_3$:



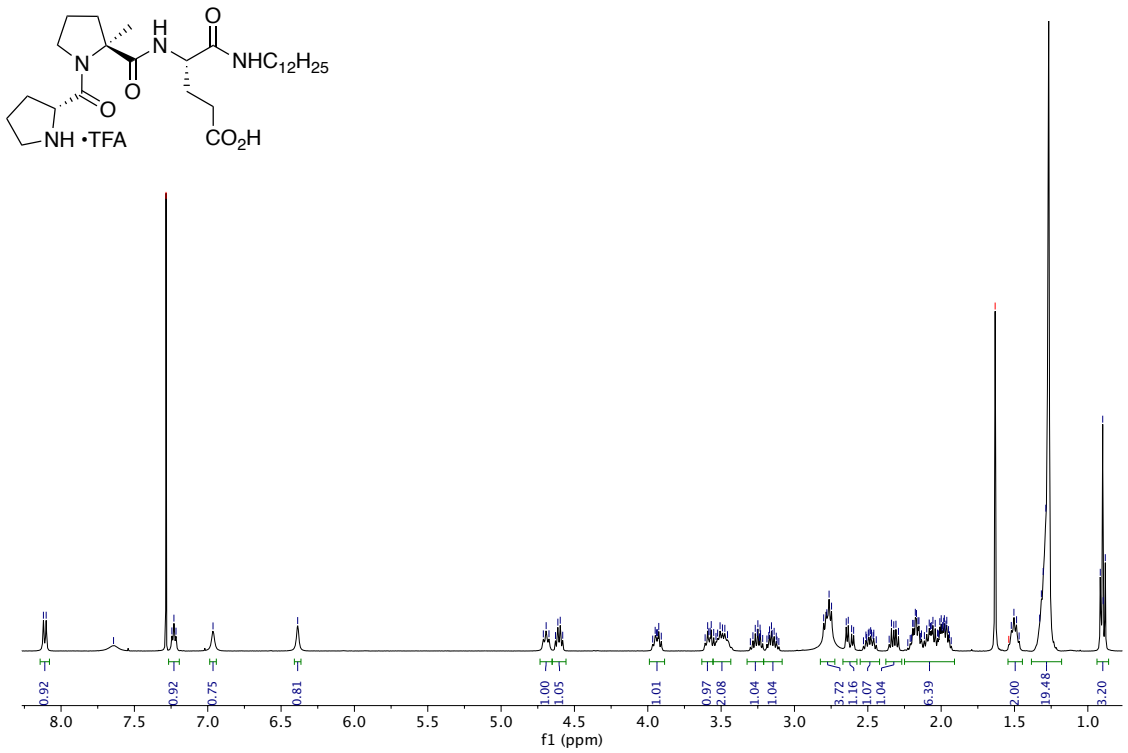
^{1}H NMR Spectrum (400 MHz) of Boc-DPro-MePro-OH recorded in $CDCl_3$:



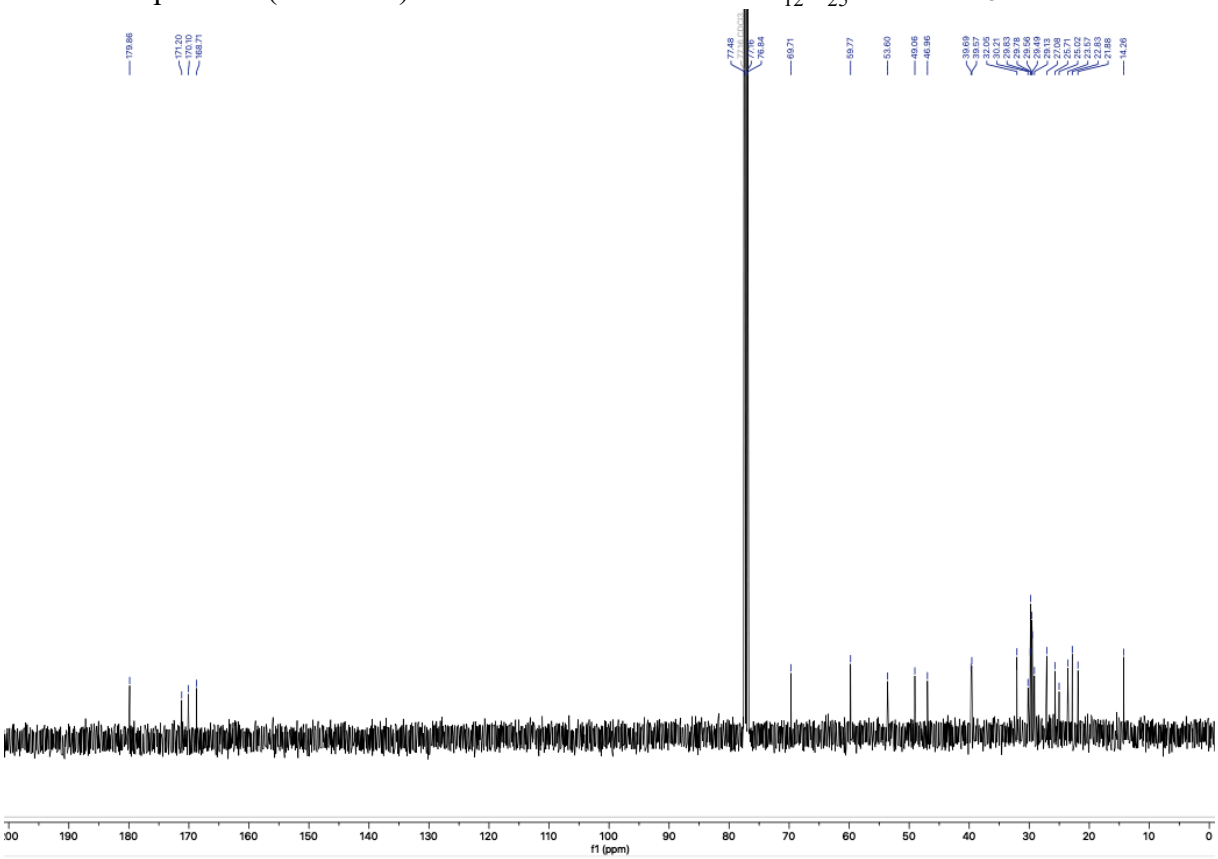
^{13}C NMR Spectrum (126 MHz) of Boc-DPro-MePro-OH recorded in $CDCl_3$:



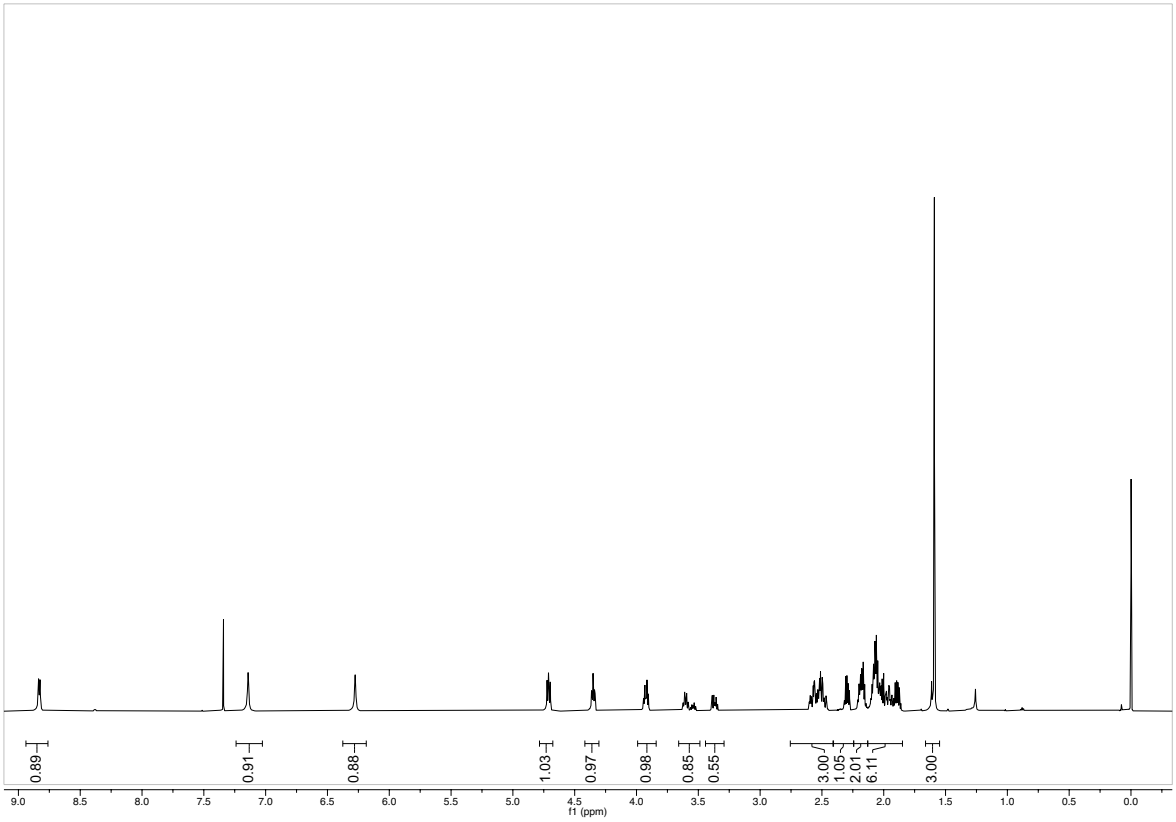
^{1}H NMR Spectrum (400 MHz) of H-DPro-MePro-Glu-NHC$_{12}$H$_{25}$ **2** in CDCl$_3$:



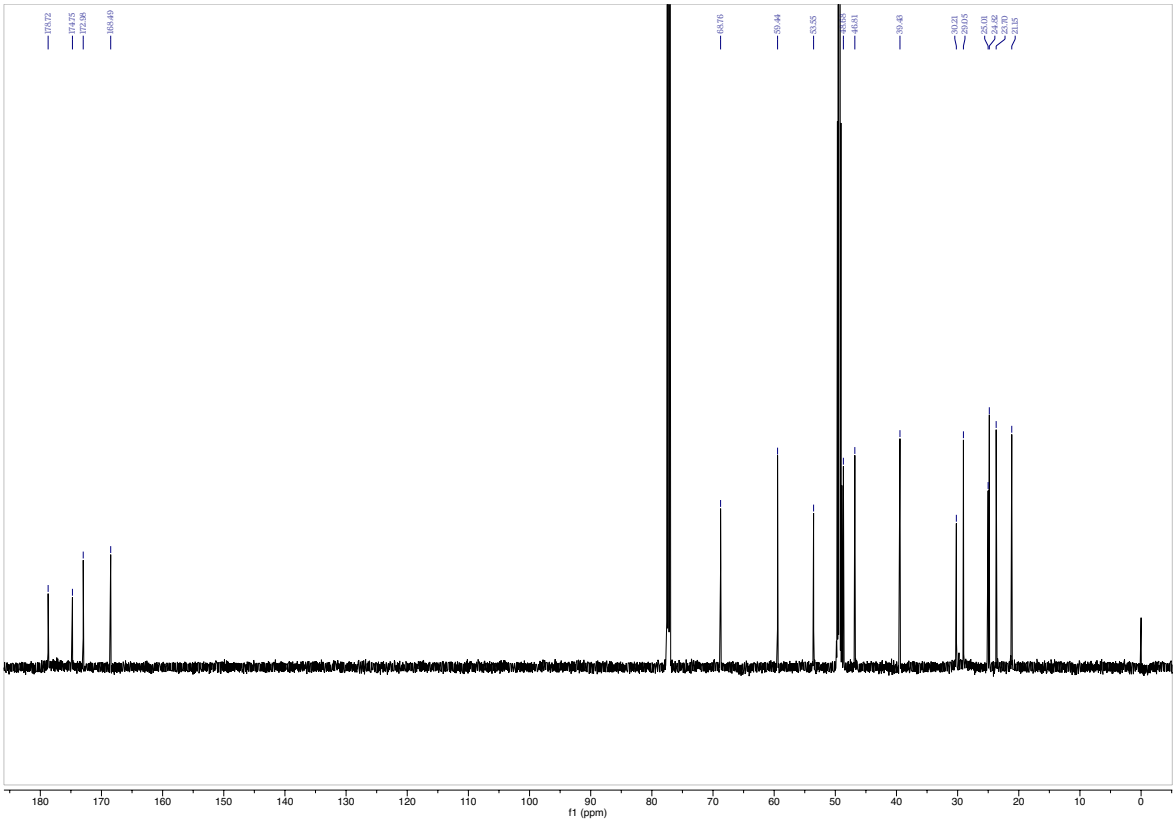
^{13}C NMR Spectrum (125 MHz) of H-DPro-MePro-Glu-NHC$_{12}$H$_{25}$ **2** in CDCl$_3$:



^{1}H NMR Spectrum (400 MHz) of H-DPro-MePro-Glu-NH_2 recorded in $CDCl_3/CD_3OH$ 9:1: (the peak of $CD_3O\underline{H}$ was supressed)

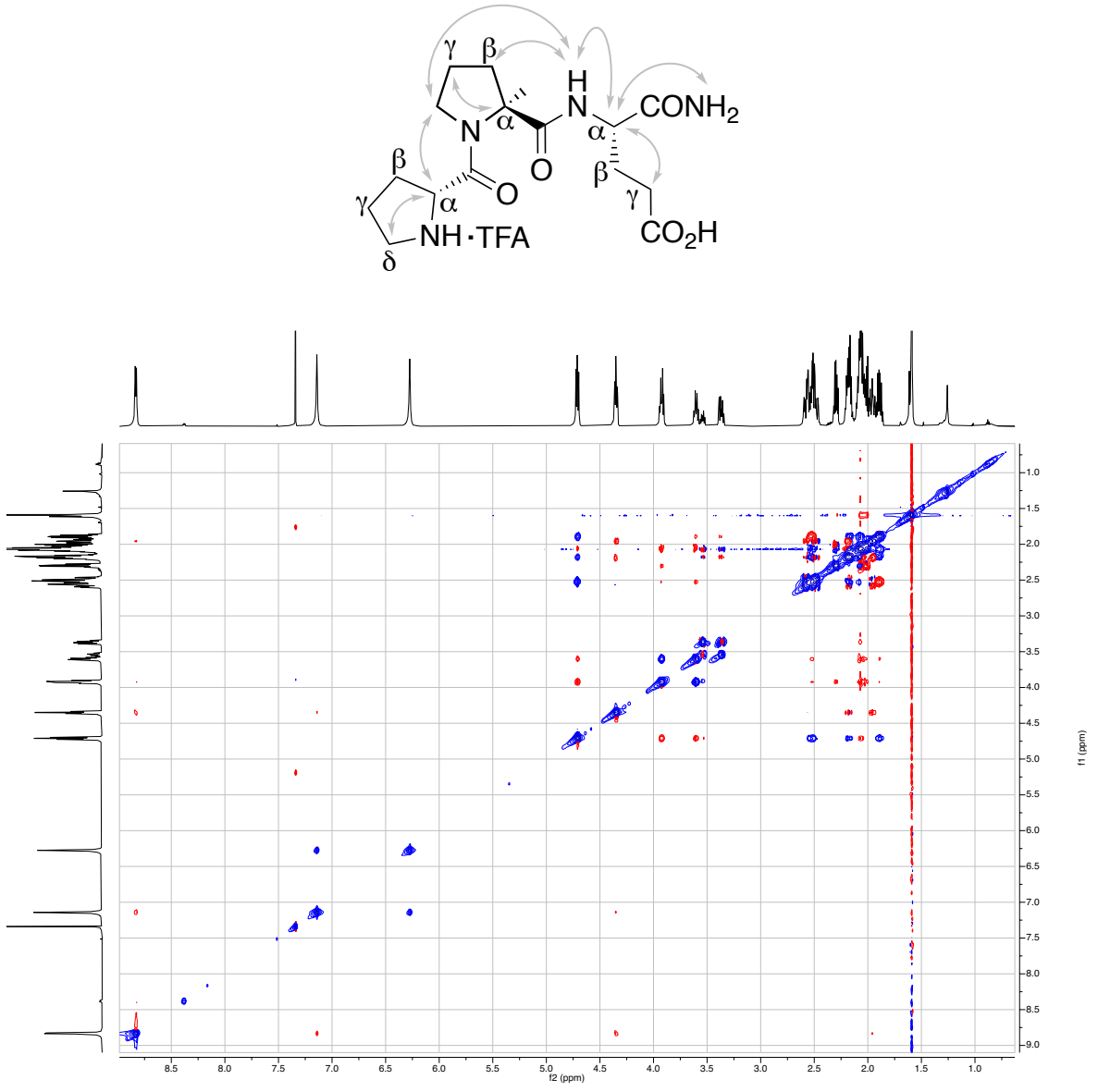


^{13}C NMR Spectrum (150 MHz) of H-DPro-MePro-Glu-NH_2 recorded in $CDCl_3/CD_3OH$ 9:1:



3. ROESY spectrum of 2a

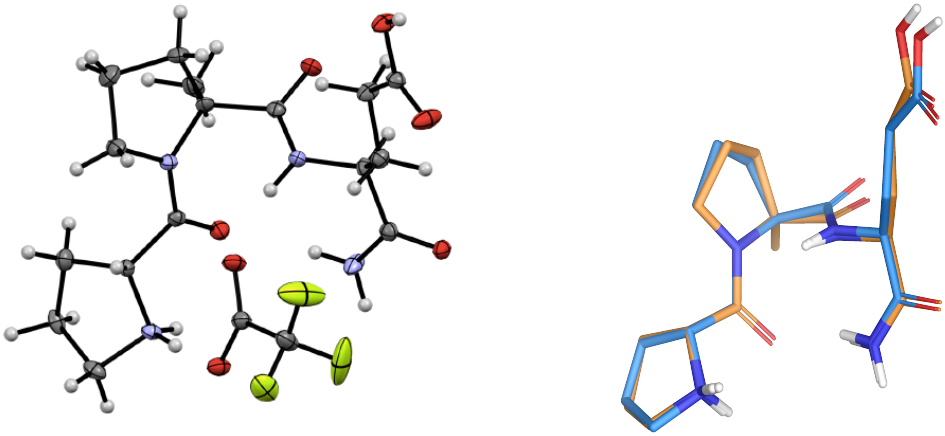
The ROESY NMR spectrum of peptide **2a** was recorded in $CDCl_3/CD_3OH$ 9:1, a solvent in which the population of the minor (*cis*) conformer is low and in which only the characteristic cross peaks for the major (*trans*) conformer are clearly visible. Note, **1a** has been intensively studied in this solvent mixture,[3] allowing for comparison of the conformation of **1a** and **2a**.



4. Crystal Structure of H-DPro-MePro-Glu-NH_2 (2a)

Single crystals of **2a** were obtained by vapor diffusion with MeOH as the solvent and THF as the antisolvent. A suitable crystal was selected and measured on a Bruker/Nonius ApexII diffractometer. The crystal was kept at 100.0(2) K during data collection. Using Olex2,[4] the structure was solved with the XT[5] structure solution program using Charge Flipping and refined with the XL[6] refinement package using Least Squares minimization.
Deposit number in CCSD: 2152664.

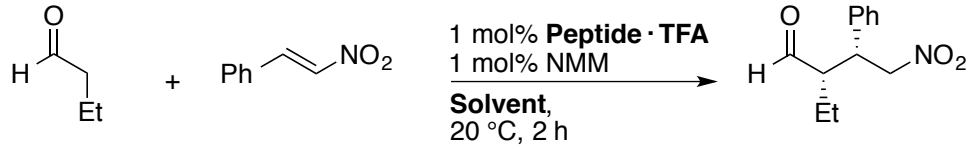
Left: ORTEP representation of the crystal structure of **2a**. Right: Overlay of the crystal structures of **1a**[7] and **2a**.



Identification code w021016_2_1
Empirical formula C18H27F3N4O7
Formula weight 468.43
Temperature/K 100.0(1)
Crystal system monoclinic
Space group P21
a/ 18.0201(3)
b/ 14.3179(2)
c/ 18.0259(3)
α/ 90
β/ 111.0260(10)
γ/ 90
Volume/ 3 4341.20(12)
Z 8
ρcalcg/cm3 1.433
μ/mm-1 1.096
F(000) 1968.0
Crystal size/mm3 0.12 0.1 0.08
Radiation CuKα (λ = 1.54178)
2Θ range for data collection/ 5.252 to 133.404
Index ranges -18 ≤ h ≤ 21, -16 ≤ k ≤ 17, -21 ≤ l ≤ 18
Reflections collected 57508
Independent reflections 14865 [Rint = 0.0336, Rsigma = 0.0287]
Data/restraints/parameters 14865/193/1253
Goodness-of-fit on F2 1.016
Final R indexes [I>=2σ (I)] R1 = 0.0273, wR2 = 0.0699
Final R indexes [all data] R1 = 0.0277, wR2 = 0.0703
Largest diff. peak/hole / e -3 0.36/-0.22
Flack parameter 0.08(4)

5. Conjugate Addition Reaction with Peptides 1a and 2a in Organic Solvents

Reaction procedure: The peptide-TFA salt (1 mol%, 2.5 µmol) was added to a solution of *N*-methylmorpholine (1 mol%, 2.5 µmol), (*E*)-nitrostyrene (1 equiv., 250 µmol, 37.3 mg) and butanal (1.5 equiv., 375 µmol, 33.8 µl) in the respective solvent (0.5 ml). The reaction mixture was stirred for 2 h. The conversion and diastereoisomeric ratio were determined by ^{1}H NMR spectroscopy of the crude mixture by comparison of the aldehyde R-C<u>H</u>O signals. The enantiomeric excess was determined by chiral stationary phase SFC (AD-3, 5% MeOH, 2.0 ml/min, 40° C, 214 nm, 1.00 min (*syn,* minor), 1.21 min (*syn,* major)).

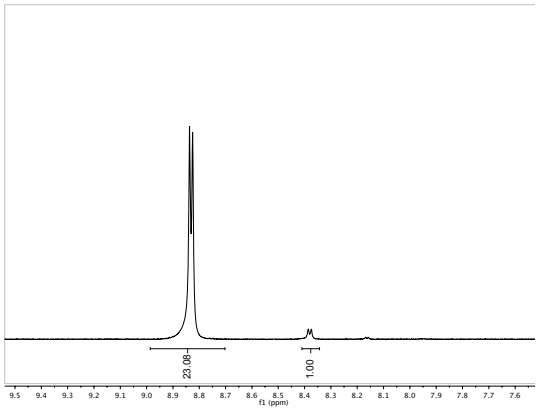


Solvent	Peptide	*trans* population[a]	d.r.[b]	*ee* (%)[c]	conv. (%)[b]
CH_2Cl_2	**1a**	91	18:1	89	23
	2a	95	34:1	98	27
THF	**1a**	88	31:1	84	6
	2a	96	36:1	95	18
Dioxane	**1a**	89	17:1	85	20
	2a	95	29:1	96	33
MeOH	**1a**	94	17:1	70	36
	2a	95	29:1	85	71
MeCN	**1a**	95	19:1	80	36
	2a	96	22:1	87	64
DMF	**1a**	78	15:1	63	20
	2a	97	22:1	74	42
DMSO	**1a**	78	8:1	40	60
	2a	96	14:1	77	8
$CHCl_3$/^{i}PrOH 9:1	**1a**	98	35:1	97	quant.
	2a	96	54:1	98	quant.

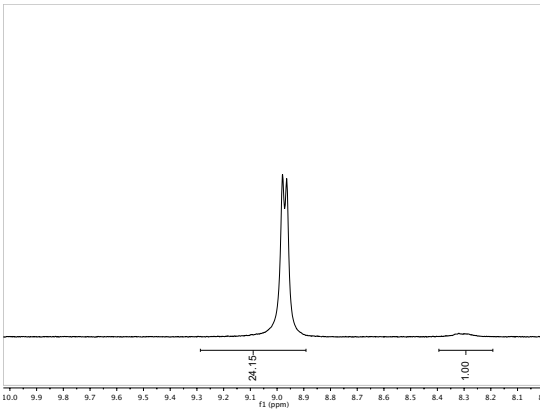
[a] Determined by ^{1}H NMR spectroscopic analysis in the corresponding anhydrous deuterated solvent. Note: The *trans*/*cis* ratio depends on the water content of the deuterated solvent. [b] Determined after 2 hours by ^{1}H NMR spectroscopic analysis of the crude product and comparison of the aldehyde signals. [c] Determined by chiral stationary phase SFC analysis. The *trans*/*cis* ratios of **1a** have been previously reported in ref 7.

^{1}H NMR spectroscopic analysis of *cis*/*trans* ratios: ^{1}H NMR spectra of peptides **2a** were recorded at a concentration of ~5 mM, the concentration used in the conjugate addition reactions, or, in case of low solubility of the peptide in a saturated solution. No evidence for peptide aggregation was observed. The samples were equilibrated for at least 2 h and no changes of the *trans*/*cis* ratios over time were observed. The *trans*/*cis* ratios were determined by manual integration of baseline separated signals of the two spin systems.

$CDCl_3/CD_3OH$ 9:1:



CD_2Cl_2:



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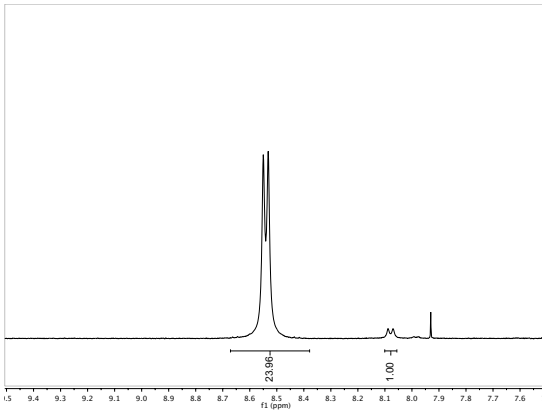

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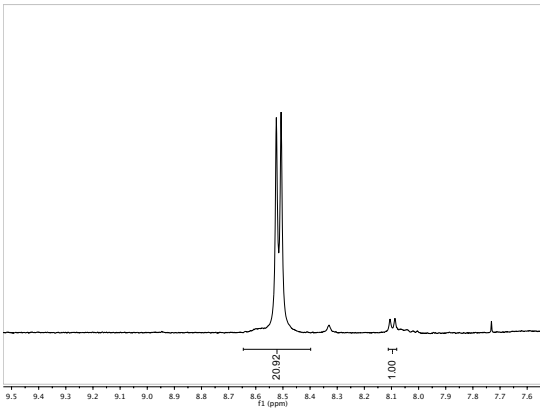

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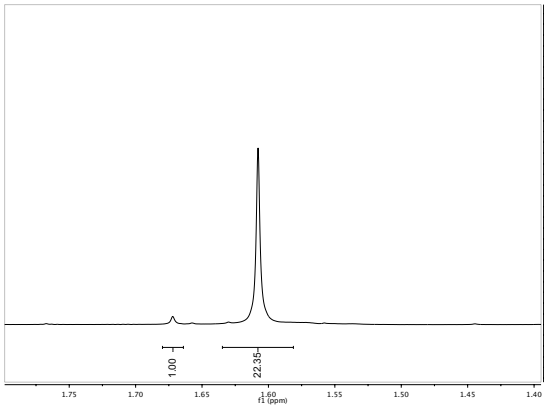
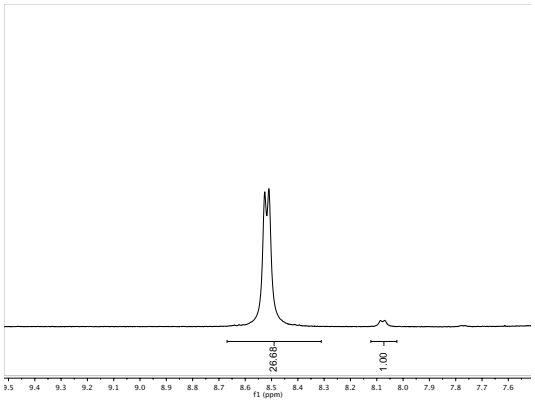


CD_3CN:



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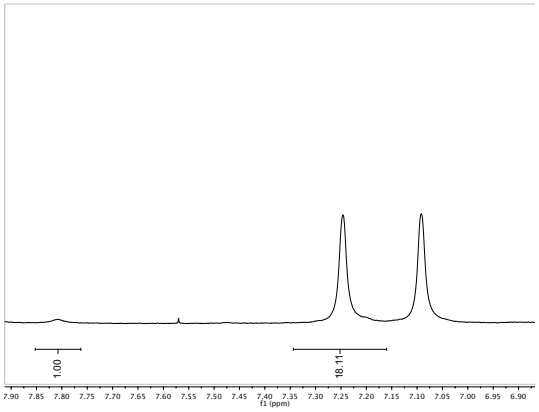
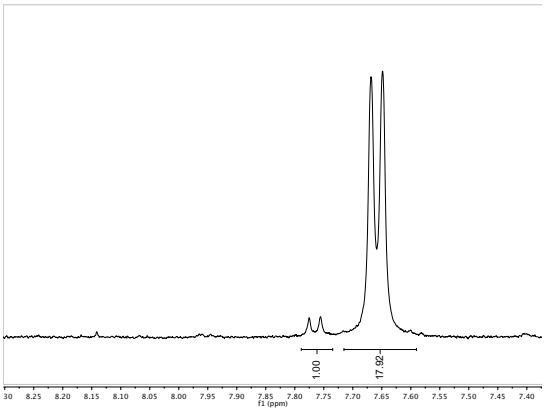


d^6-DMSO



6. Conjugate Addition Reaction in the Presence of Additives

The peptide TFA salt (3 mol%) was added to a solution of *N*-methylmorpholine (3 mol%, 1.45 μL), (*E*)-nitrostyrene (2 equiv., 0.88 mmol, 65.6 mg) and butanal (1.0 equiv., 0.44 mmol, 99.1 μL) in the respective solutions (1.0 mL, complex mixture or additive solution in water). The reaction mixture was sonicated until no more solid (nitroolefin) was observed and a stable emulsion was obtained (approximately 2 min). The resulting emulsion was vigorously stirred at room temperature. The conversion and diastereoisomeric ratio were determined by ^{1}H NMR spectroscopic analysis of the crude mixture by comparison of the aldehyde R-C<u>H</u>O signals. The enantiomeric excess was determined by chiral stationary phase SFC (AD-3, 5% MeOH, 2.0 mL/min, 40 °C, 214 nm, 1.00 min (*syn*, minor), 1.21 min (*syn*, major)).

Results of the reactions in the presence of additives:

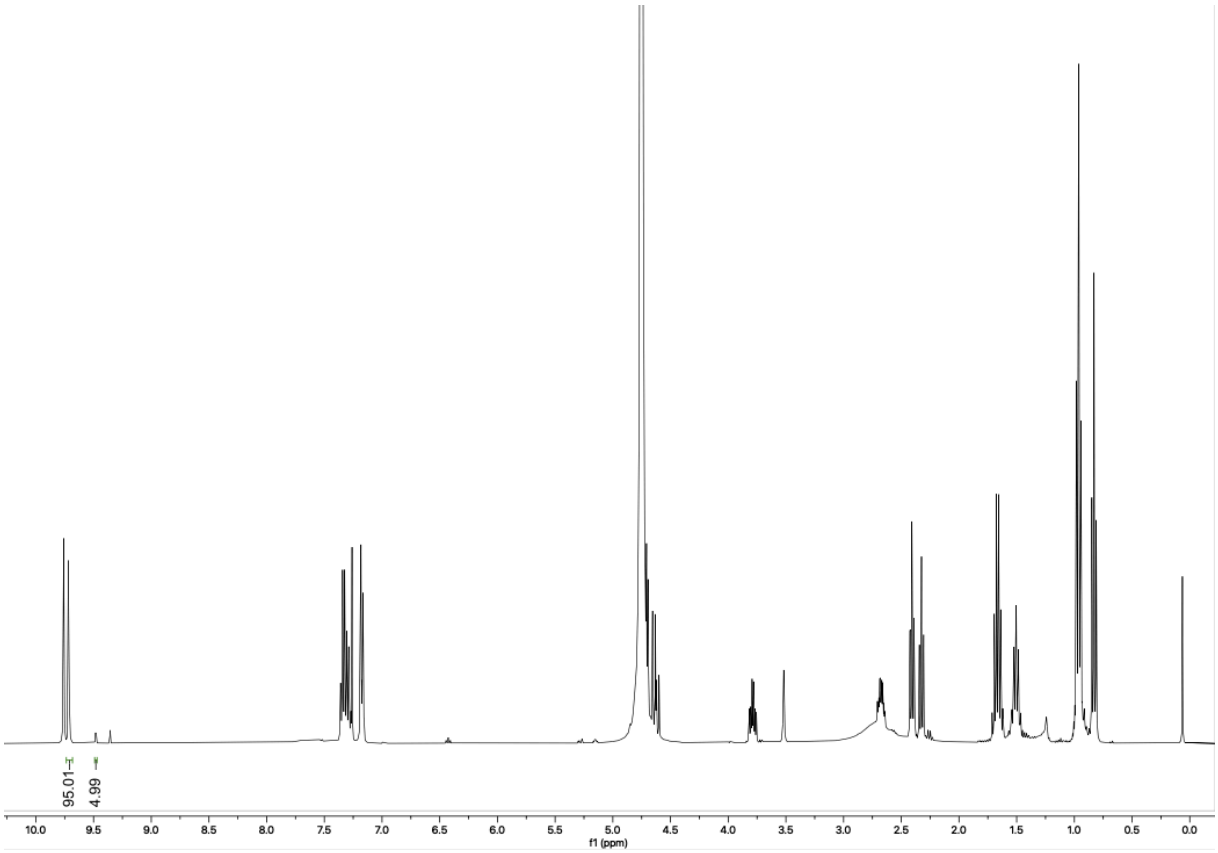
Additives	**Conversion[a] (%)**				**Major diastereomer[a] (%)**				***ee*[b] (%)**			
	Amount of additive (mol%)				**Amount of additive (mol%)**				**Amount of additive (mol%)**			
	3	10	50	100	3	10	50	100	3	10	50	100
No additive	>95	-	-	-	98	-	-	-	91	-	-	-
A	>95	>95	>95	>95	96	96	95	95	91	89	90	91
B	>95	>95	>95	>95	95	91	68	66	91	90	88	88
C	>95	>95	>95	>95	97	96	96	96	91	91	91	90
D	>95	>95	>95	>95	97	96	97	96	90	90	91	91
E	>95	>95	>95	>95	96	97	96	96	91	91	90	91
F	>95	>95	>95	>95	96	96	95	96	90	91	91	91
G	>95	>95	>95	>95	97	96	97	97	91	91	91	91
H	>95	>95	>95	>95	96	95	93	94	91	89	88	87
I	>95	>95	>95	>95	96	96	96	94	90	90	90	90
J	>95	>95	>95	>95	96	96	96	96	90	90	89	88
K	>95	>95	>95	>95	96	97	97	97	90	92	91	91
L	>95	>95	>95	>95	97	97	98	98	90	90	91	91
M	>95	>95	>95	>95	96	97	97	96	92	91	89	88
N	>95	93	56	36	97	97	98	98	90	90	90	90
O	81	84	37	24	98	98	98	98	91	91	92	92
P	>95	>95	>95	>95	94	92	85	78	89	90	90	83

[a]Determined by ^{1}H NMR spectroscopic analysis of the crude mixture. [b]Determined by chiral stationary phase SFC analysis.

^{1}H NMR spectra:

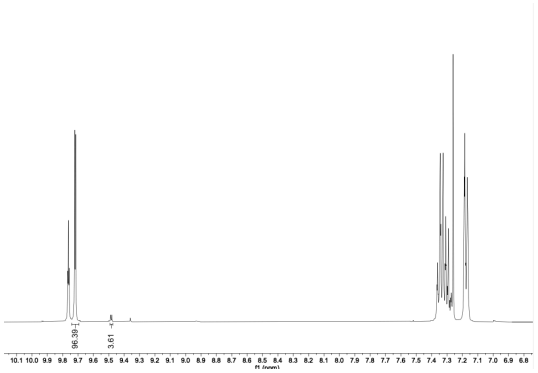
A sample of 50 µL from the crude reaction mixture was added to an NMR tube that contained 600 µL $CDCl_3$. Vigorous shaking / vortexing ensured extraction of the reaction products from the mixture. Conversion was determined by comparing the integrals of the olefinic signal of nitrostyrene and the RCHO signals of the γ-nitroaldehyde. The diastereomeric ratio was determined by integration of the RCHO signals of the γ-nitroaldehyde. Below an exemplary spectrum of the reaction with glycine is listed, for all other additives only a section.

Exemplary spectrum of the reaction with 100 mol% glycine:

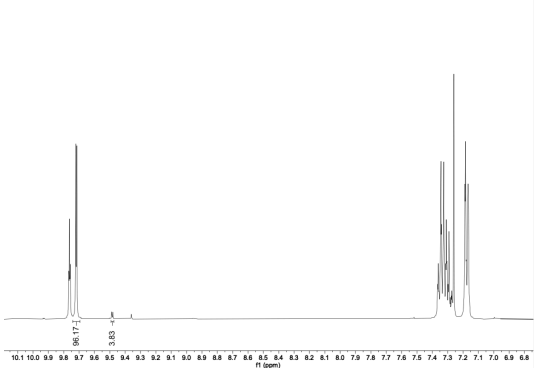


Additive A (Glycine):

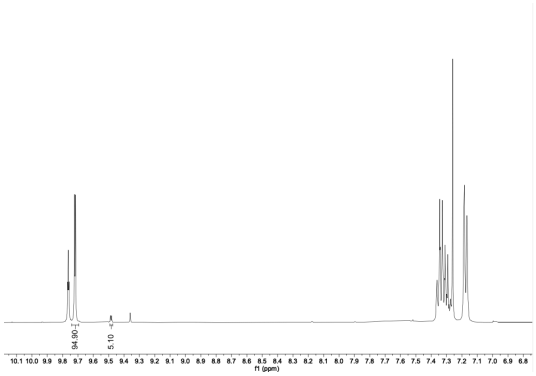
3 mol%:



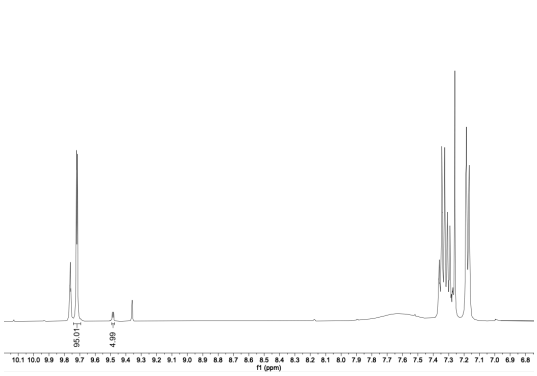
10 mol%:



50 mol%:

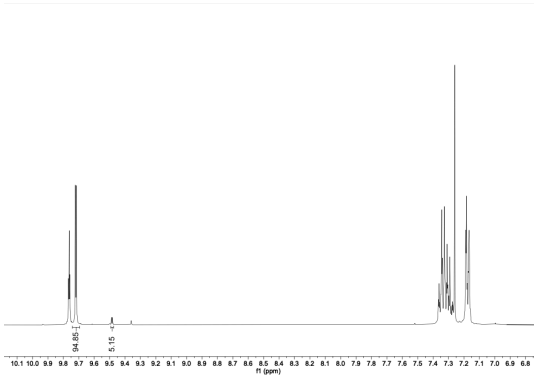


100 mol%:

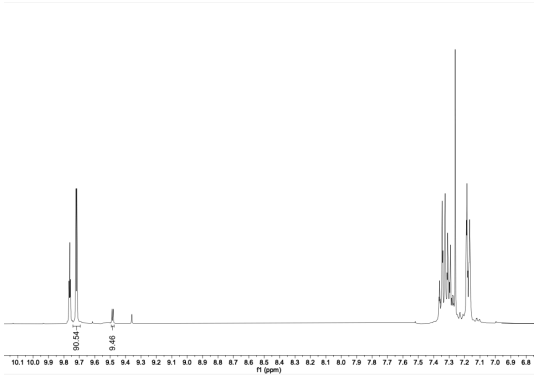


Additive B (Phenylalanine):

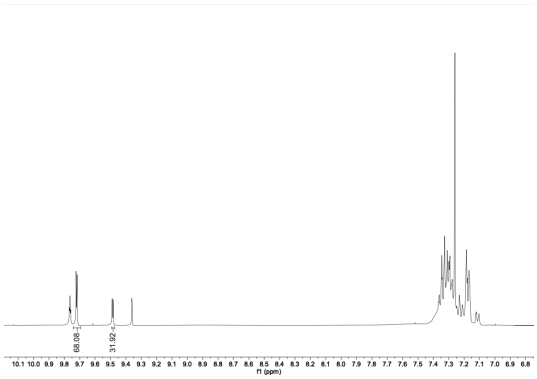
3 mol%:



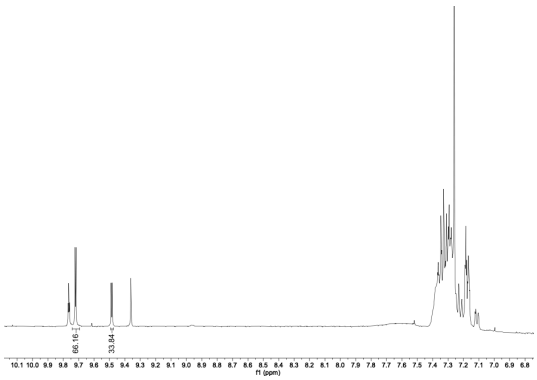
10 mol%:



50 mol%:

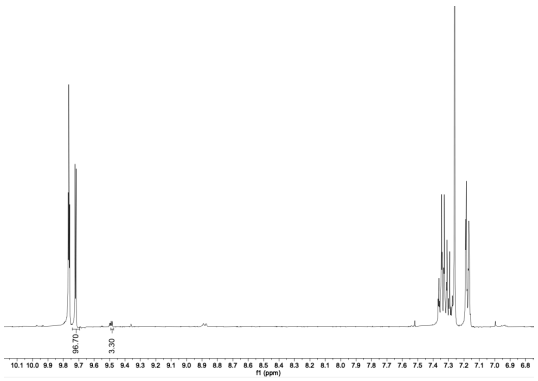


100 mol%:

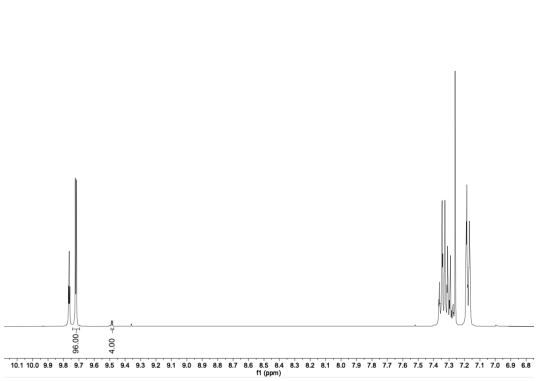


Additive C (Glucose):

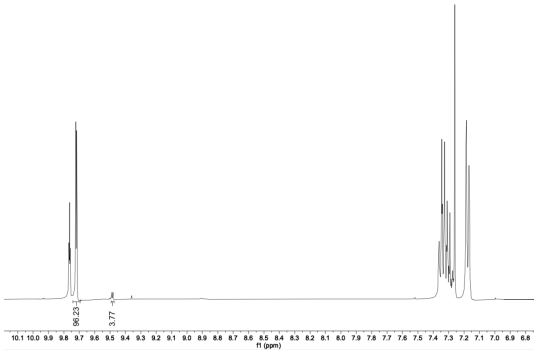
3 mol%:



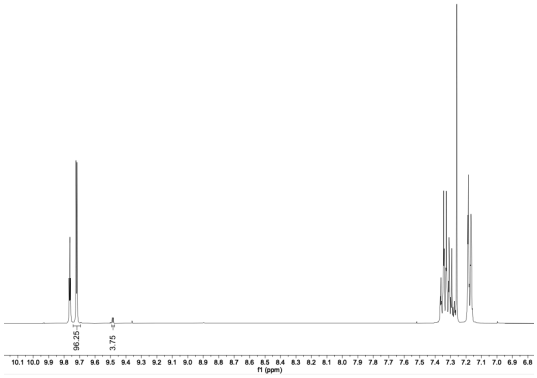
10 mol%:



50 mol%:

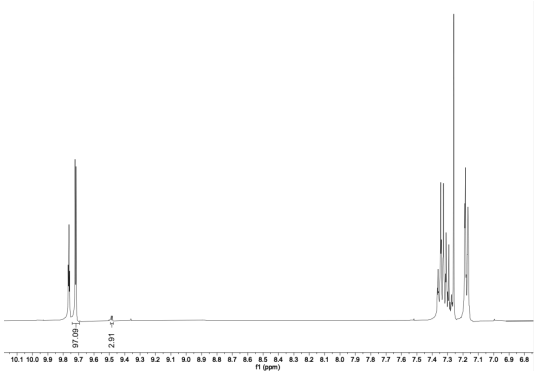


100 mol%:

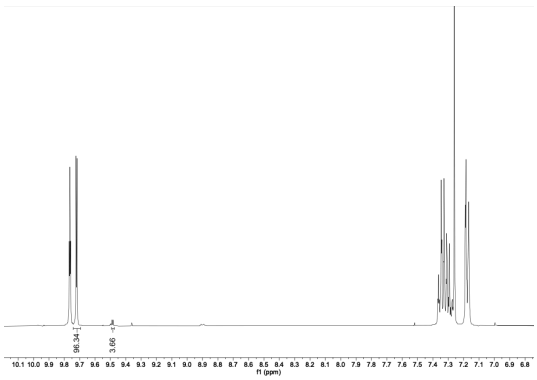


Additive D (Fructose):

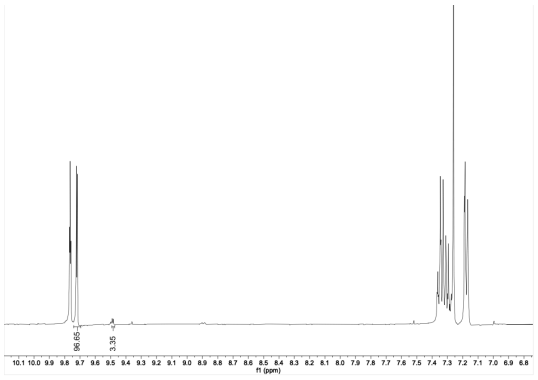
3 mol%:



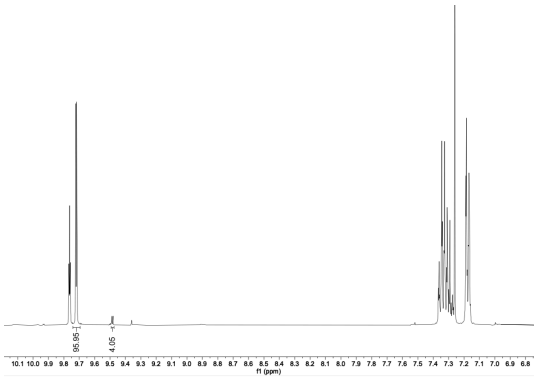
10 mol%:



50 mol%:

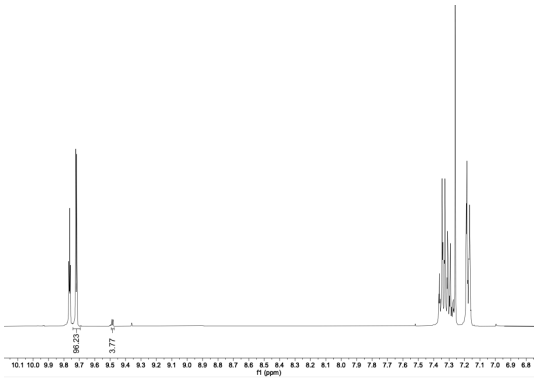


100 mol%:

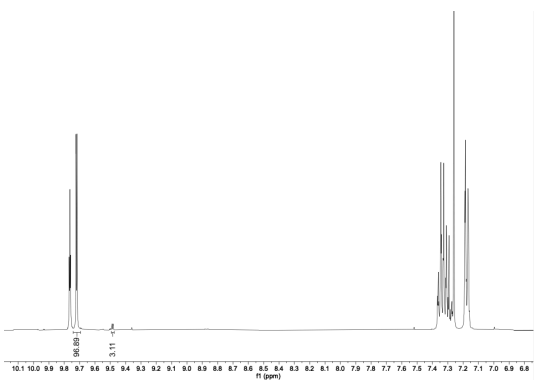


Additive E (Lactose):

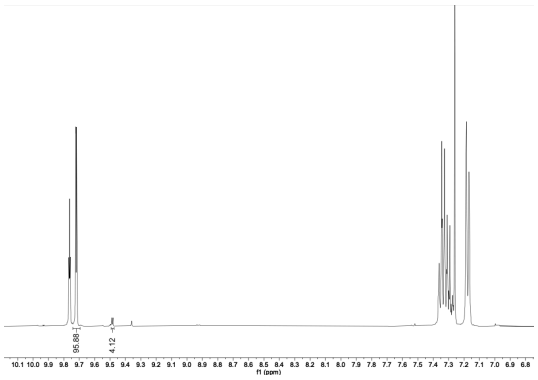
3 mol%:



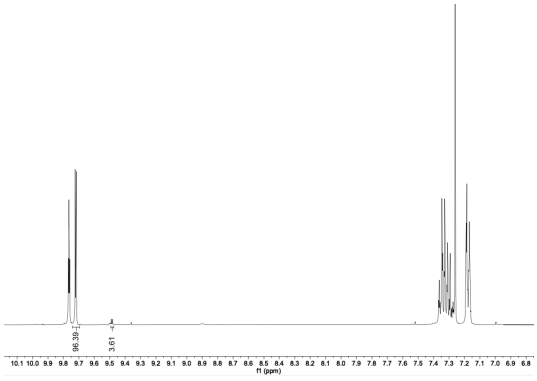
10 mol%:



50 mol%:

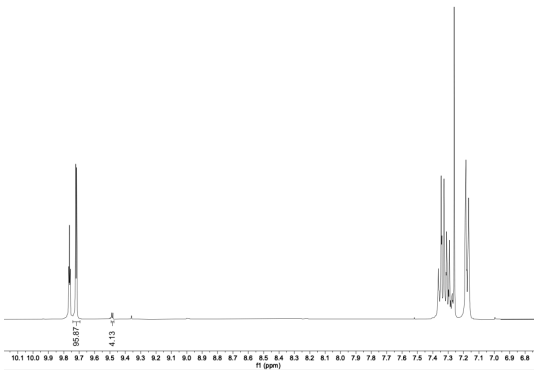


100 mol%:

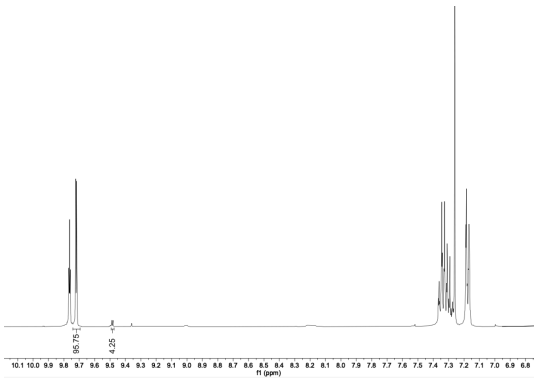


Additive F (Adenine):

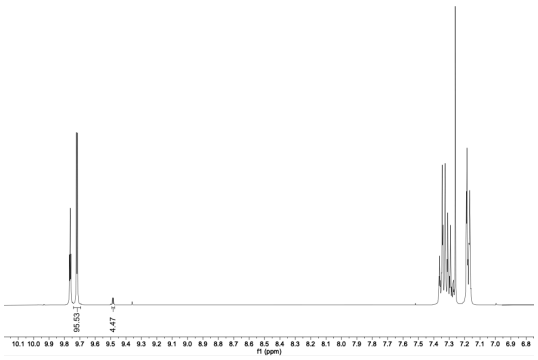
3 mol%:



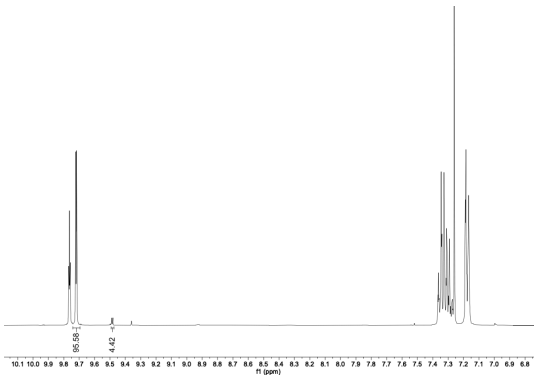
10 mol%:



50 mol%:

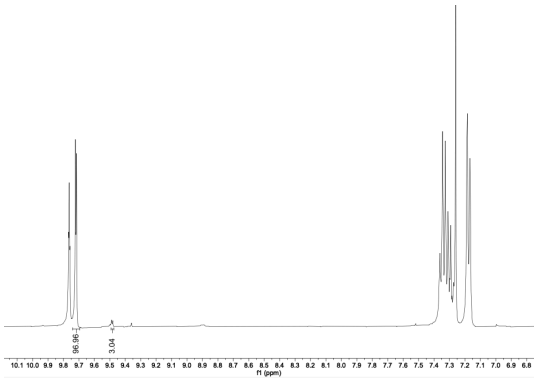


100 mol%:

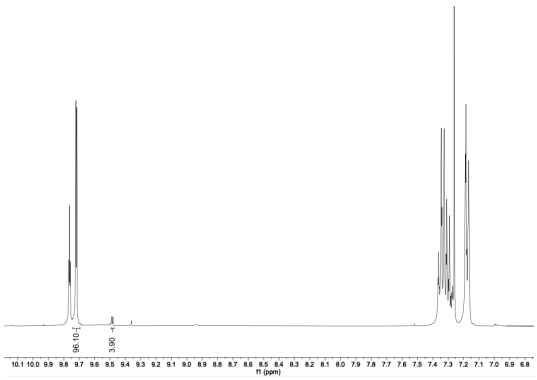


Additive G (Guanosine):

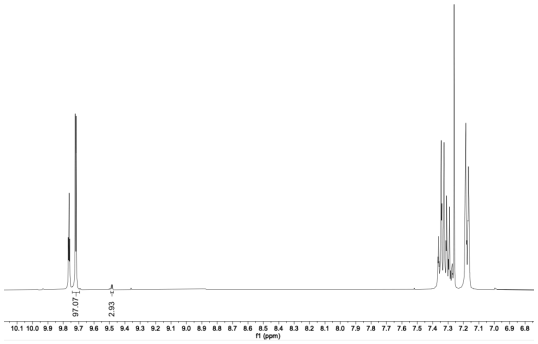
3 mol%:



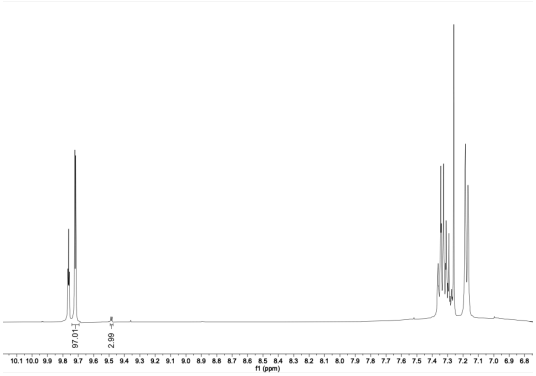
10 mol%:



50 mol%:

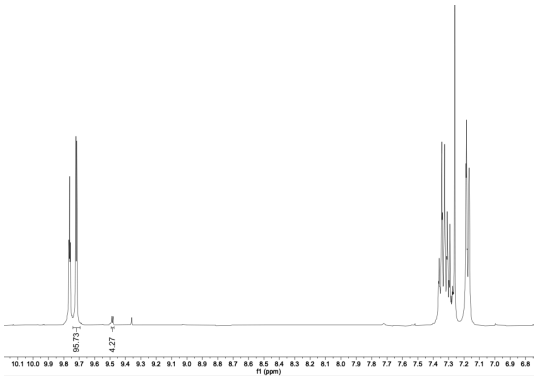


100 mol%:

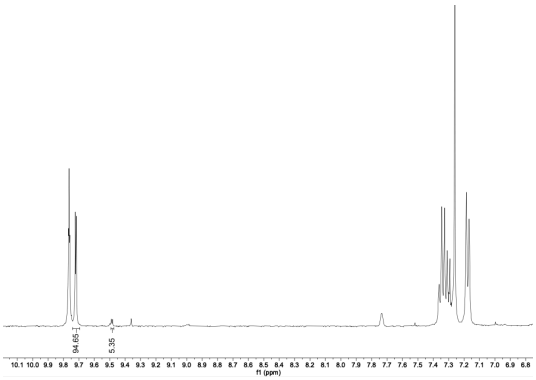


Additive H (Thymidine-5`-monophosphoric acid):

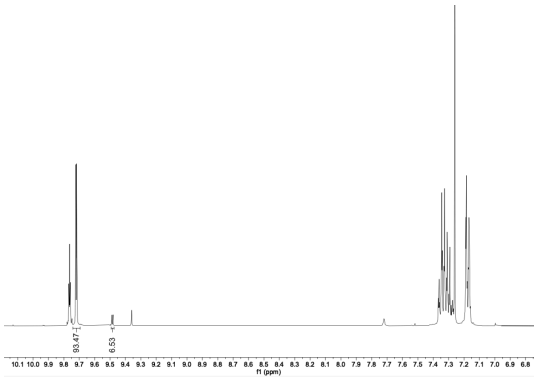
3 mol%:



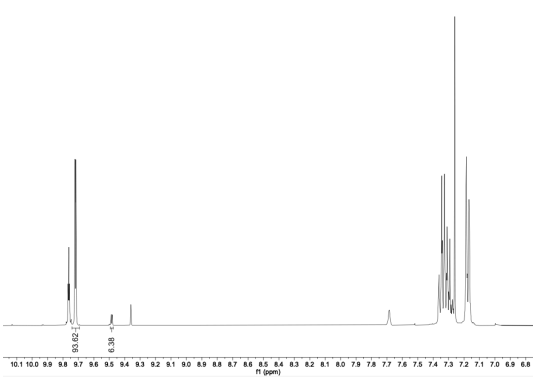
10 mol%:



50 mol%:

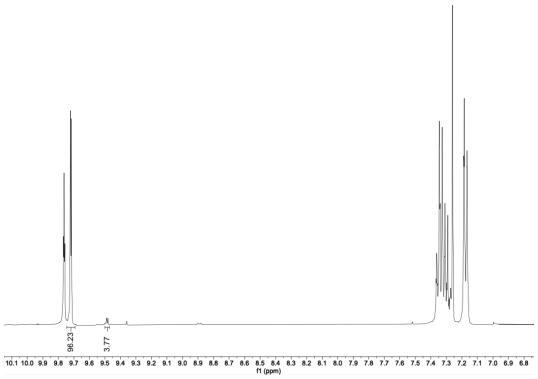


100 mol%:

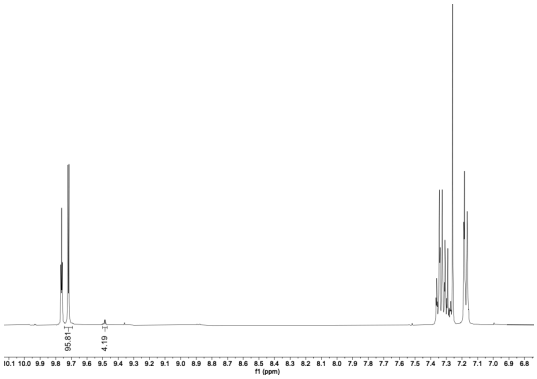


Additive I (Tristearine):

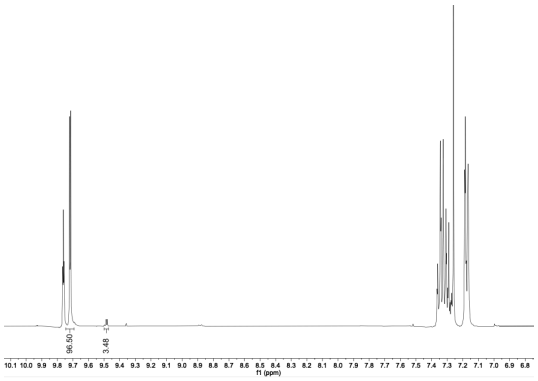
3 mol%:



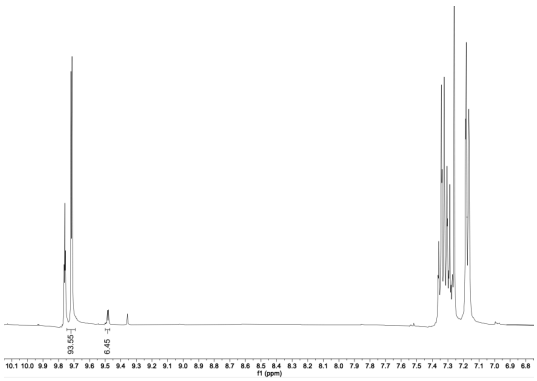
10 mol%:



50 mol%:

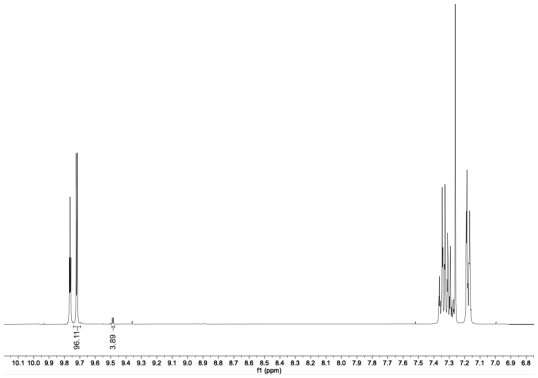


100 mol%:

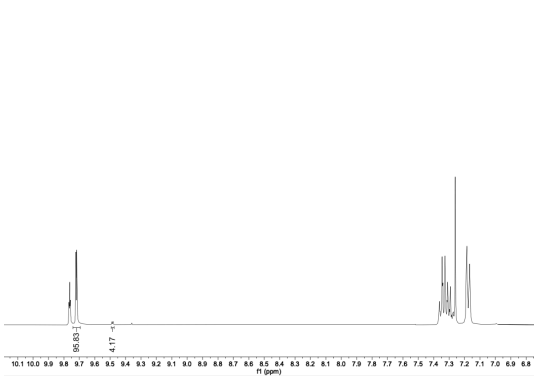


Additive J (Squalene):

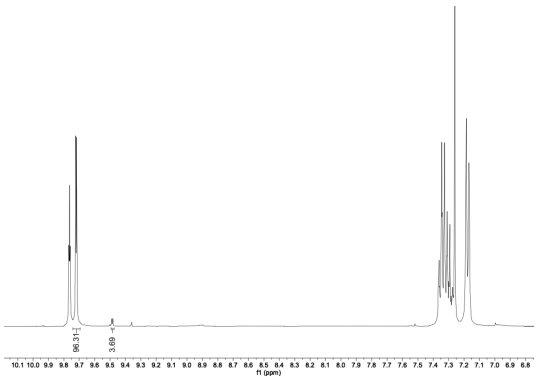
3 mol%:



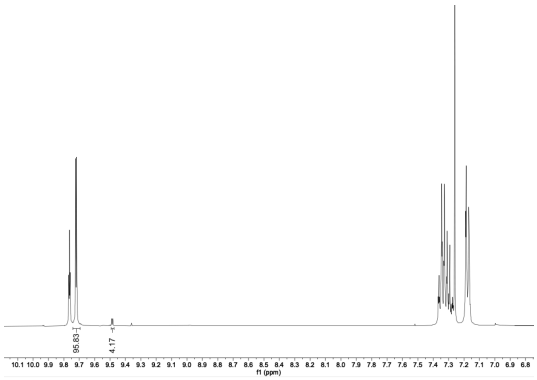
10 mol%:



50 mol%:

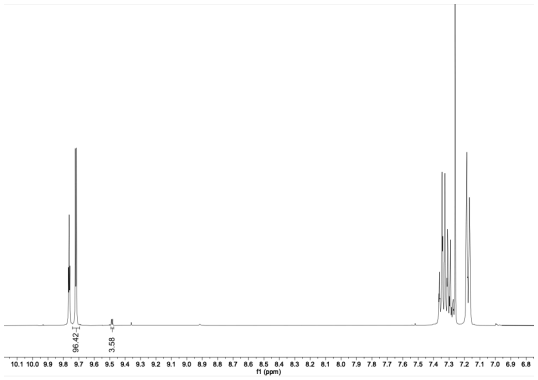


100 mol%:

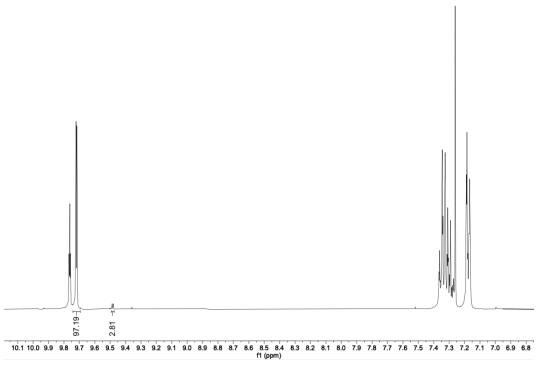


Additive K (Cholesterol):

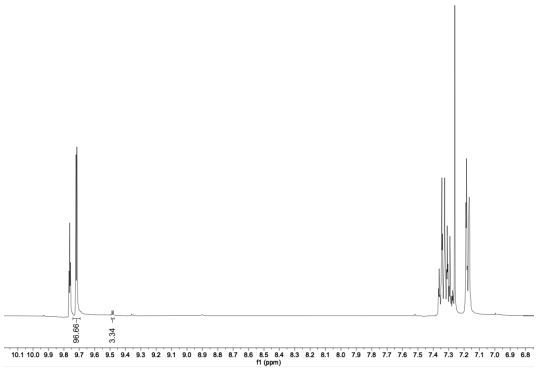
3 mol%:



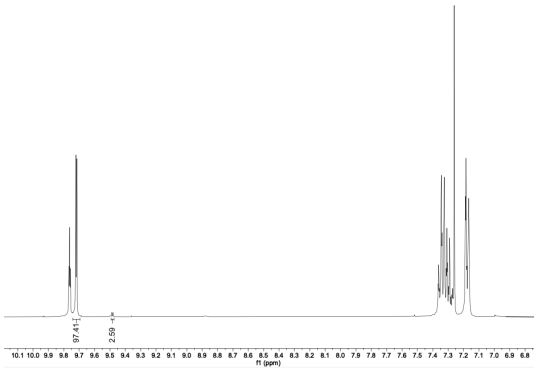
10 mol%:



50 mol%:

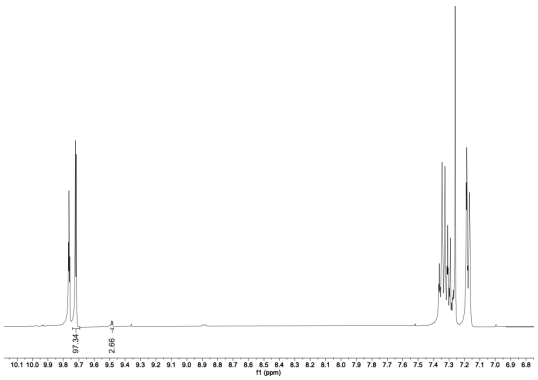


100 mol%:

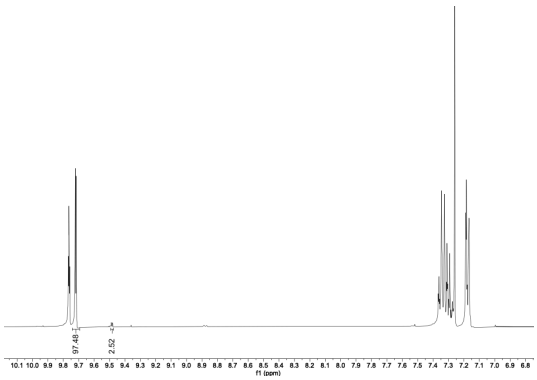


Additive L (Ascorbic acid):

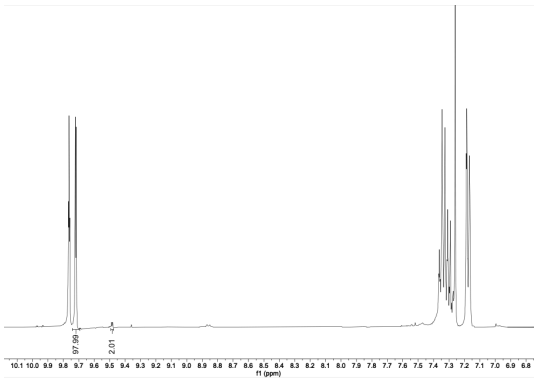
3 mol%:



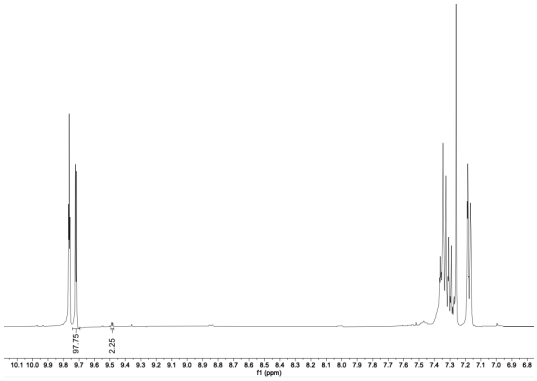
10 mol%:



50 mol%:

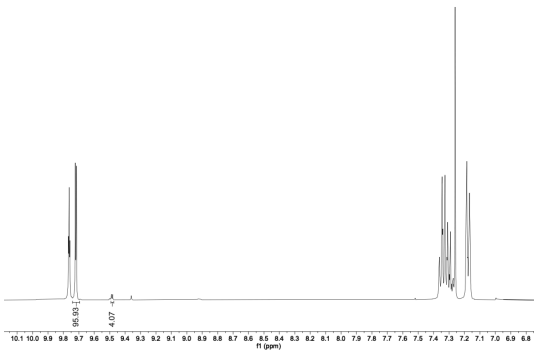


100 mol%:

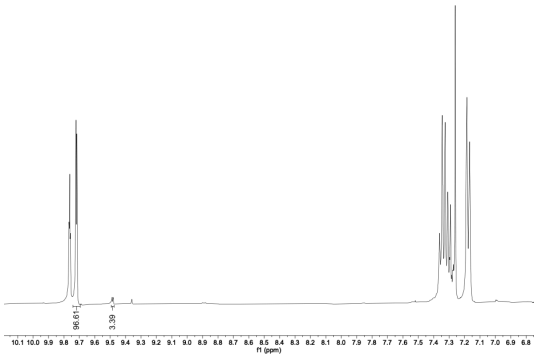


Additive M (Vitamine B_{12}):

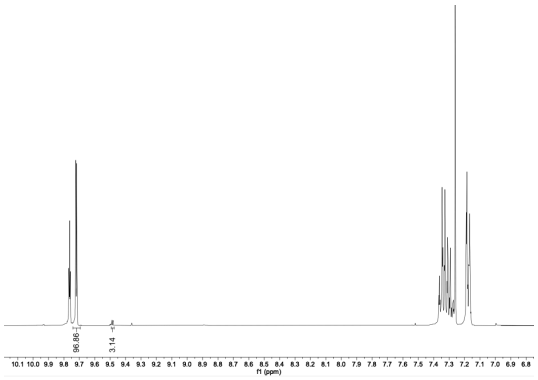
3 mol%:



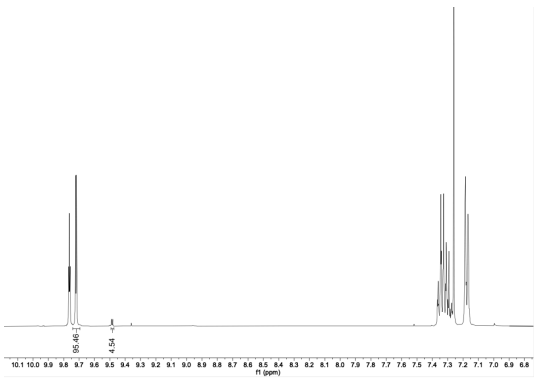
10 mol%:



50 mol%:

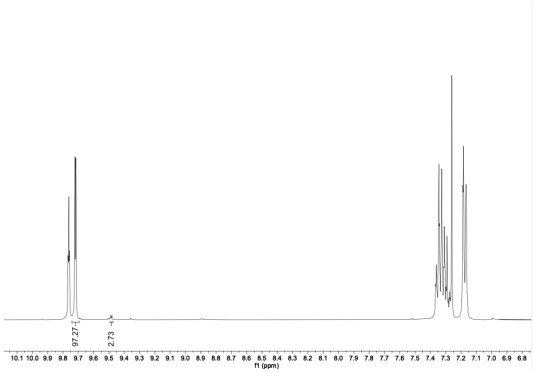


100 mol%:

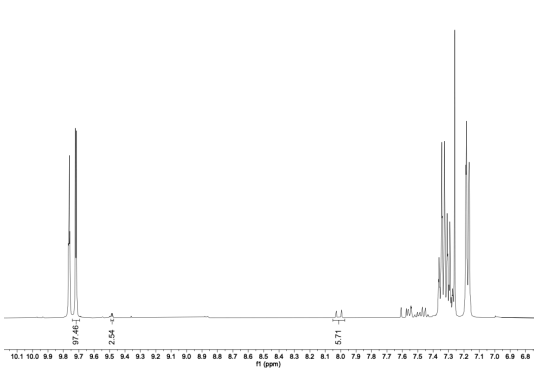


Additive N (Citric Acid):

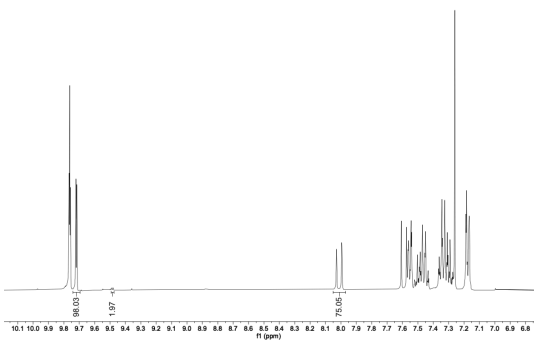
3 mol%:



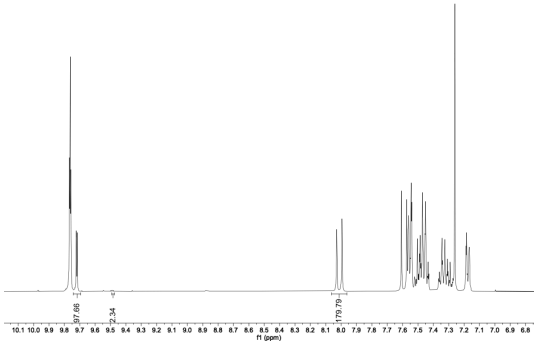
10 mol%:



50 mol%:

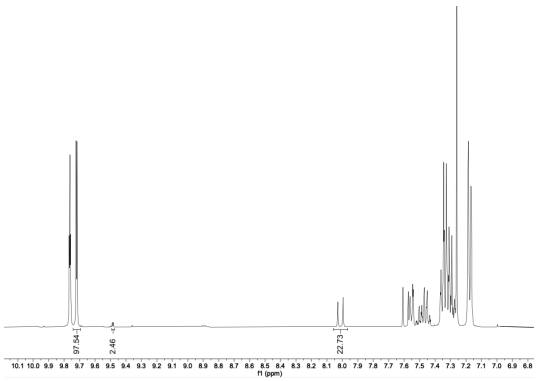


100 mol%:

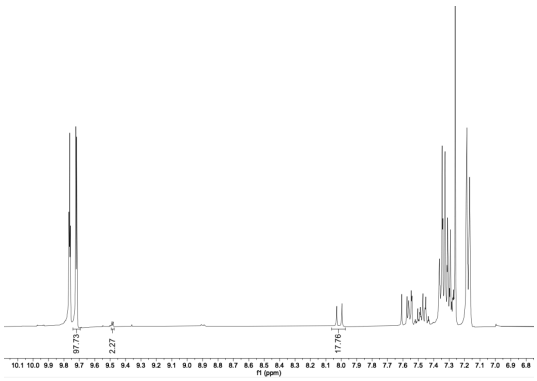


Additive O (Pyruvic acid):

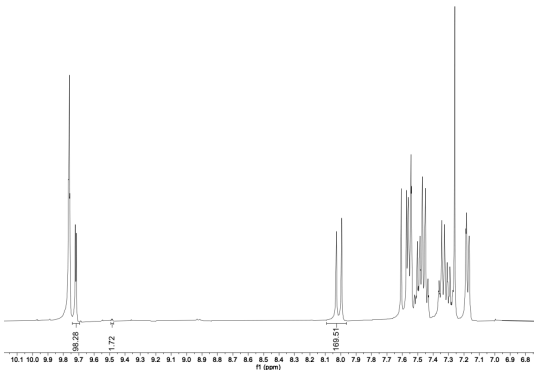
3 mol%:



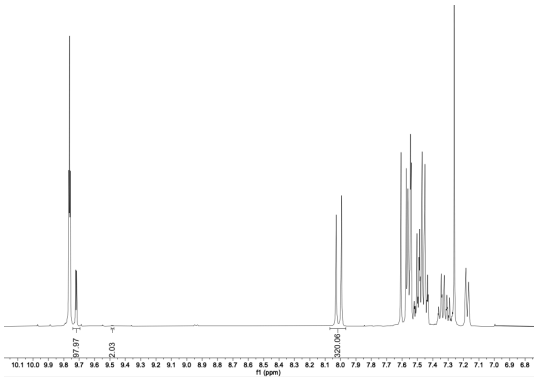
10 mol%:



50 mol%:

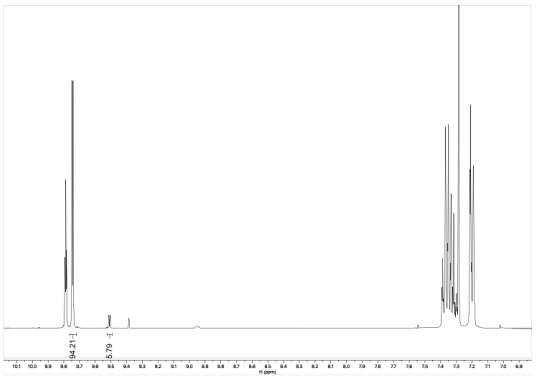


100 mol%:

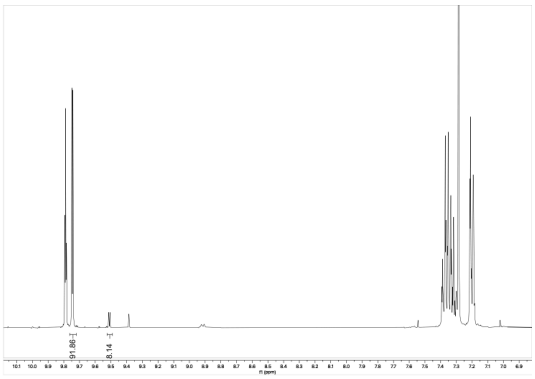


Additive P (Glutathione):

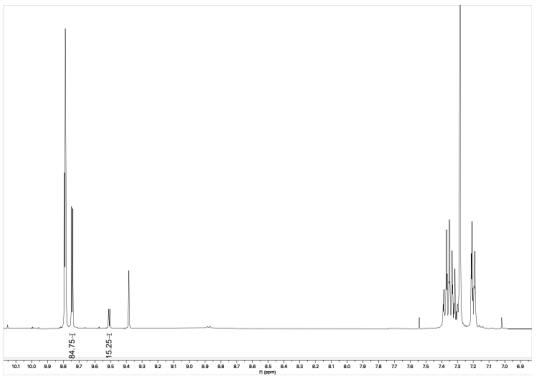
3 mol%:



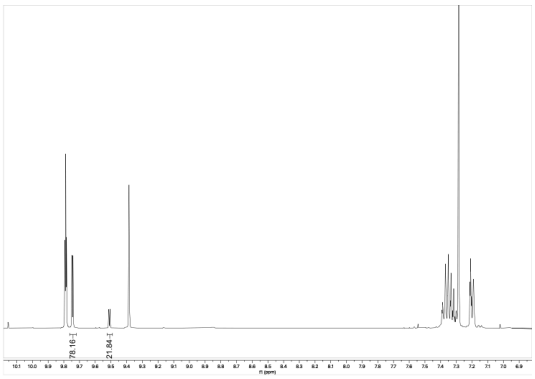
10 mol%:



50 mol%:

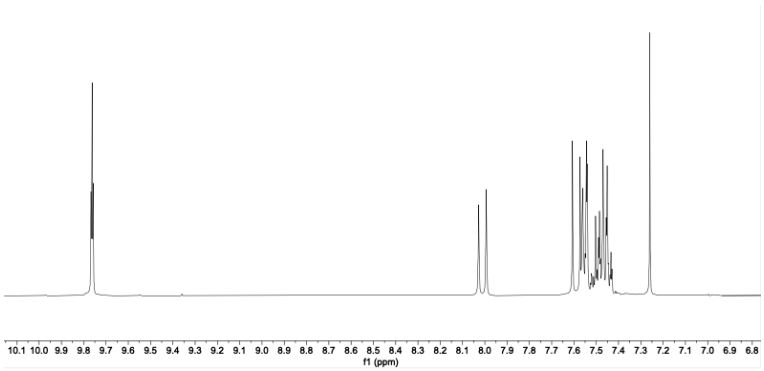


100 mol%:

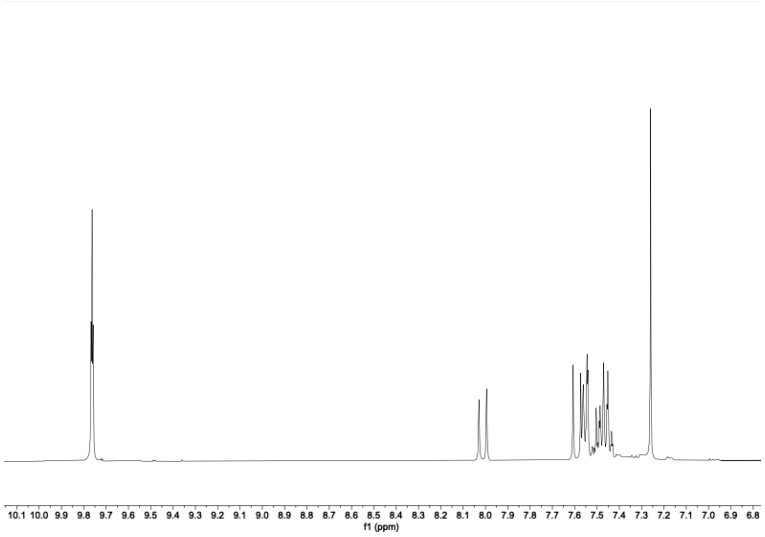


Control Experiments in the Absence of Catalyst (100 mol% additive)

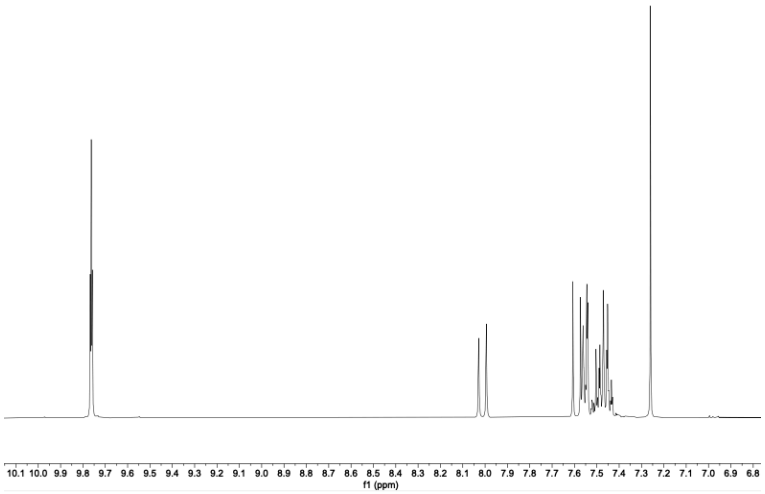
Additive A (Glycine):



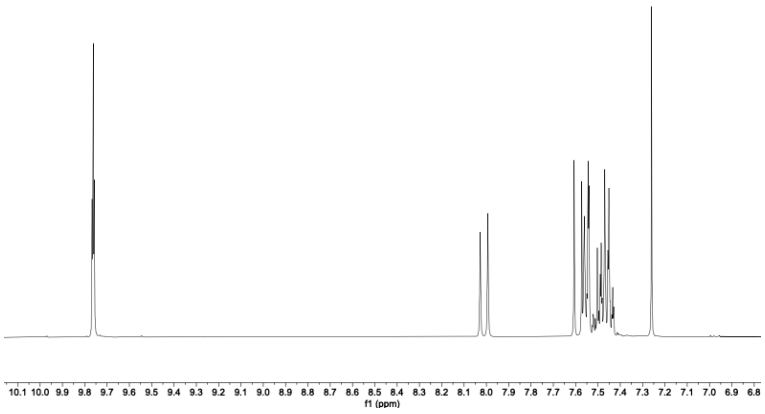
Additive B (Phenylalanine):



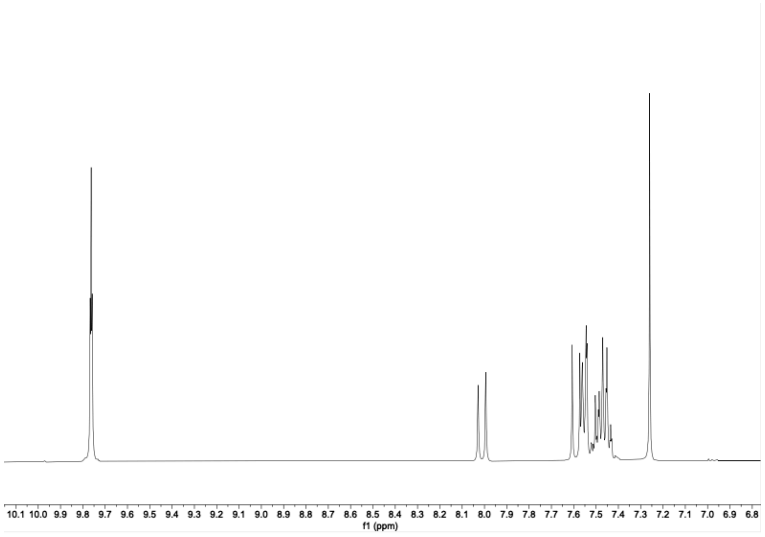
Additive C (Glucose):



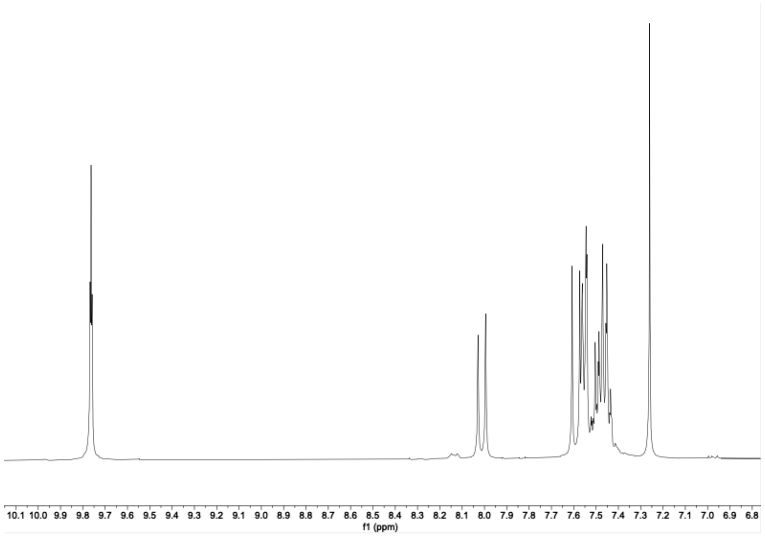
Additive D (Fructose):



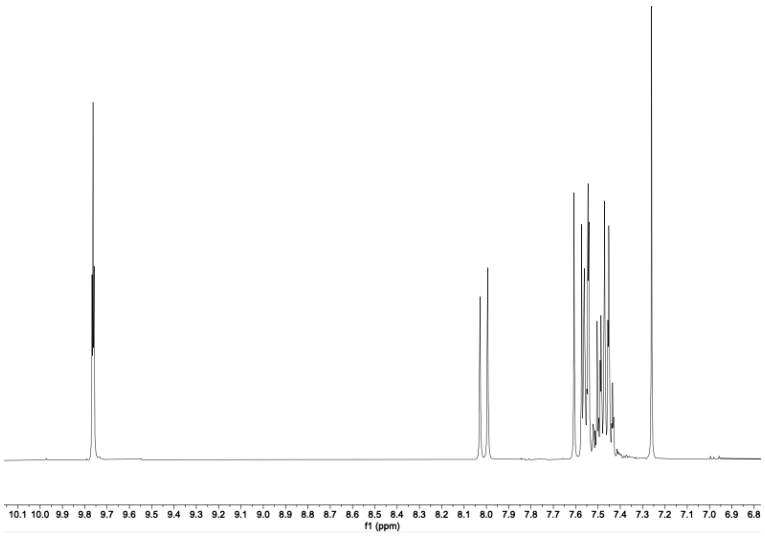
Additive E (Lactose):



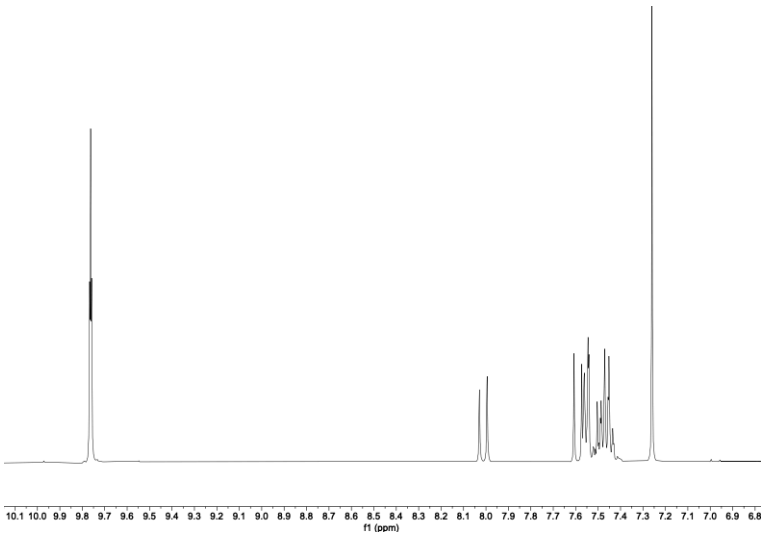
Additive F (Adenine):



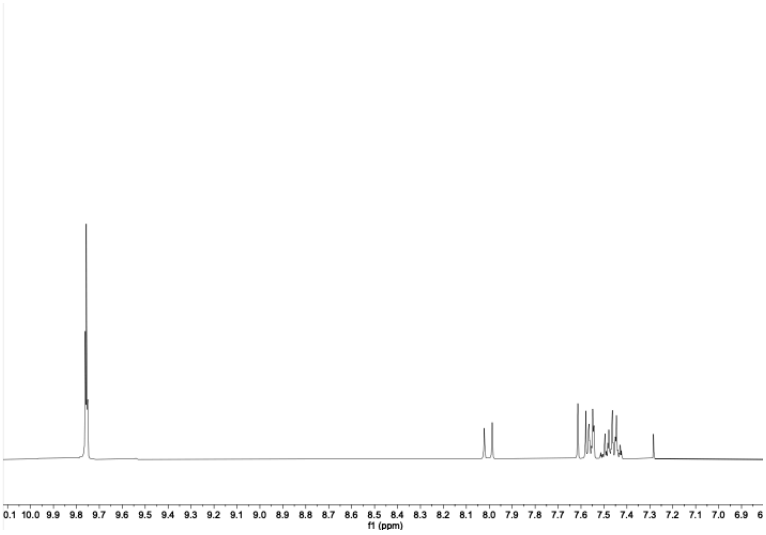
Additive G (Guanosine):



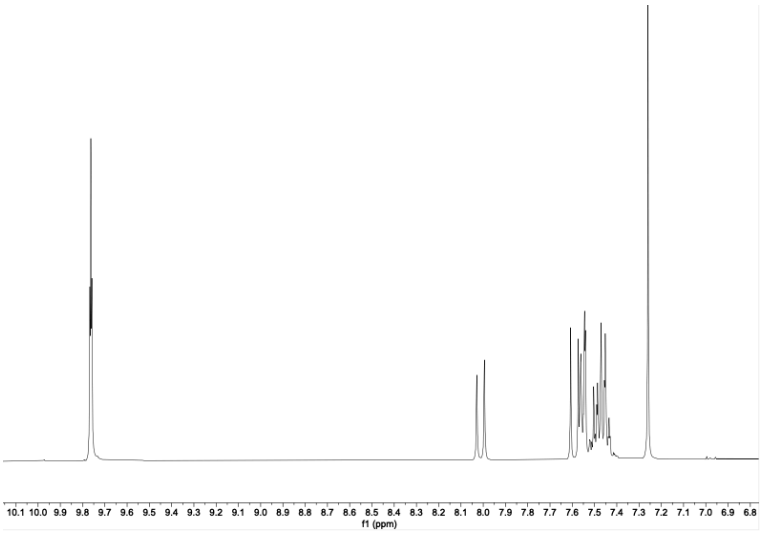
Additive H (Thymidine-5`-monophosphoric acid):



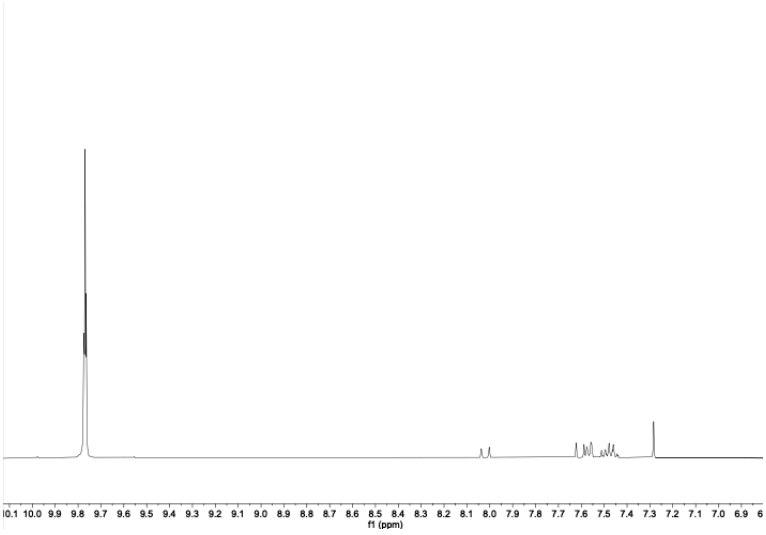
Additive I (Tristearine):



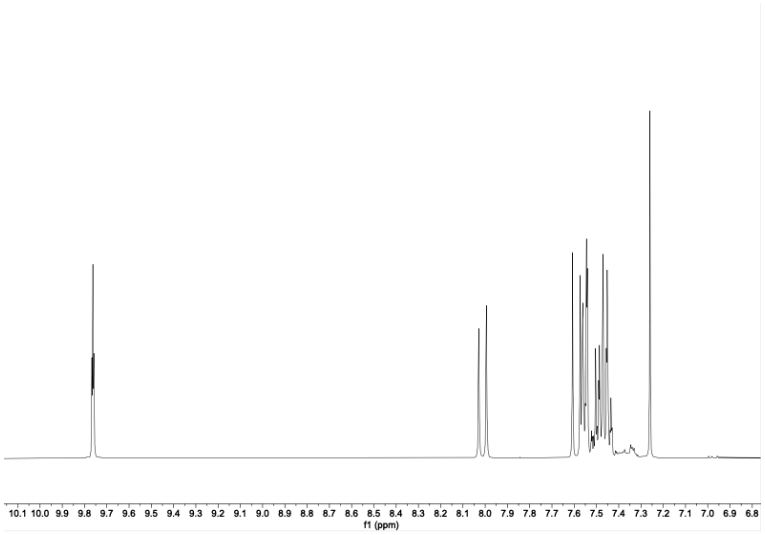
Additive J (Squalene):



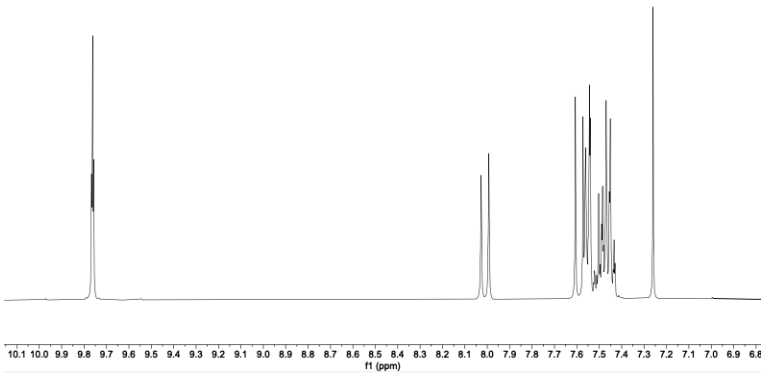
Additive K (Cholesterol):



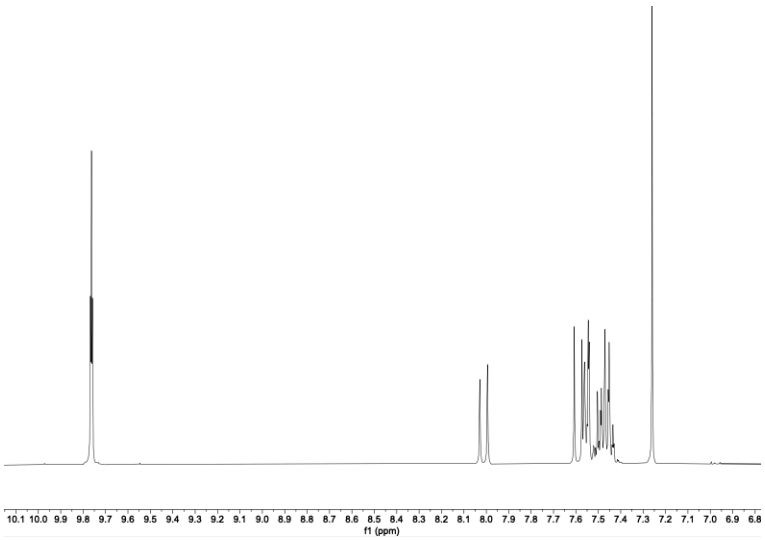
Additive L (Ascorbic acid):



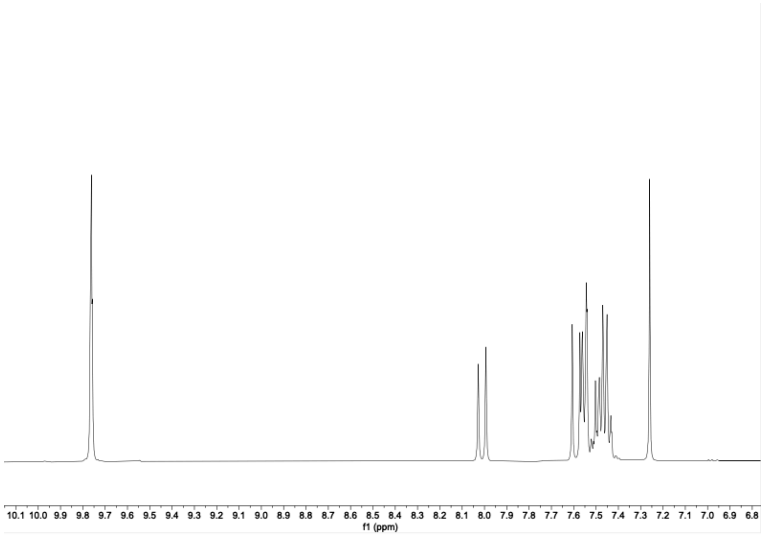
Additive M (Vitamine B_{12}):



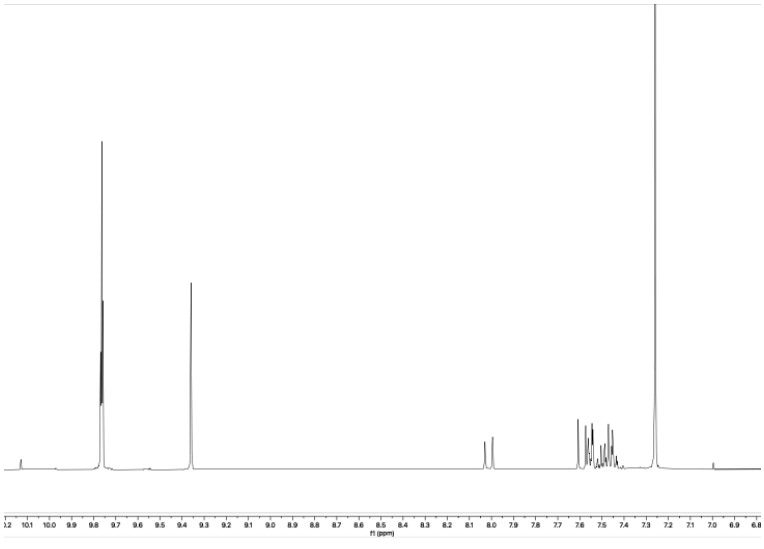
Additive N (Citric Acid):



Additive O (Pyruvic acid):

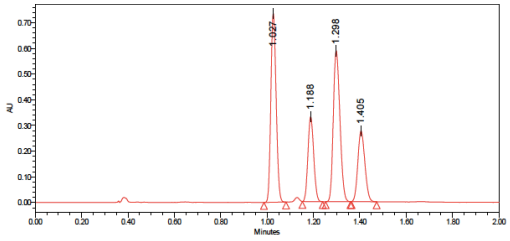


Additive P (Glutathione):



SFC chromatograms:

Racemate:

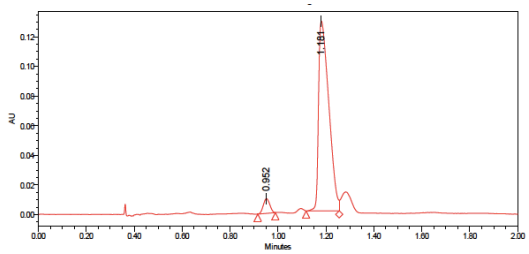


Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.027	1161127	33.42	734743
2	1	1.405	578245	16.64	275064
3	1	1.298	1162526	33.46	587304
4	1	1.188	572390	16.48	330553
Mean		1.229			
Std. Dev.		0.162			
% RSD		13.15			

Additive A (Glycine):

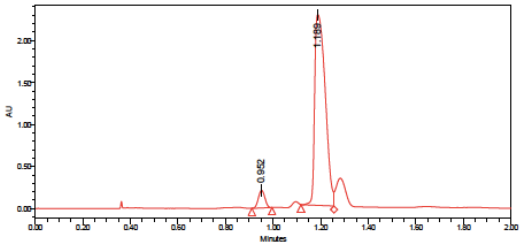
3 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.181	379485	95.32	128031
2	1	0.952	18614	4.68	9909
Mean		1.067			
Std. Dev.		0.162			
% RSD		15.20			

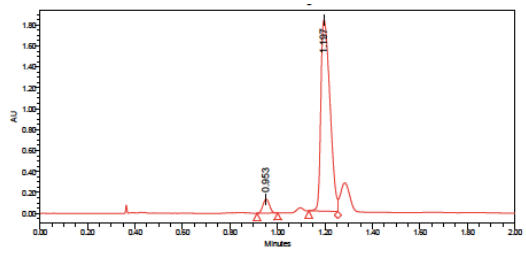
10 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.189	7002699	94.61	2269307
2	1	0.952	398621	5.39	208969
Mean		1.070			
Std. Dev.		0.167			
% RSD		15.65			

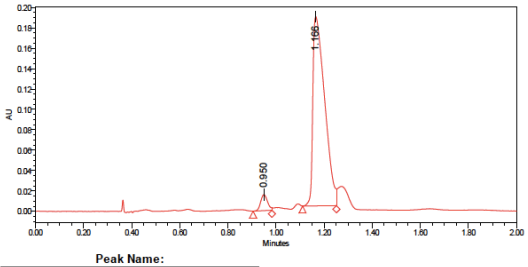
50 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.197	4865208	95.04	1827103
2	1	0.953	254167	4.96	132643
Mean		1.075			
Std. Dev.		0.173			
% RSD		16.05			

100 mol%:

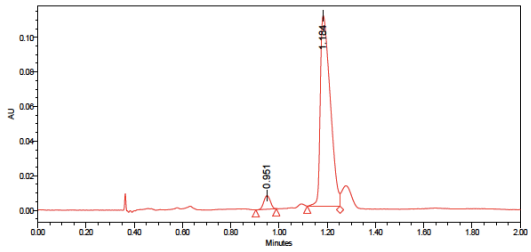


Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.166	632808	95.36	185628
2	1	0.950	30804	4.64	15586
Mean		1.058			
Std. Dev.		0.153			
% RSD		14.43			

Additive B (Phenylalanine):

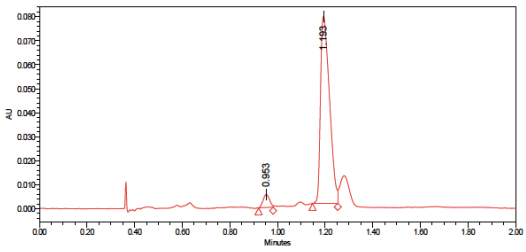
3 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.184	315585	95.57	110230
2	1	0.951	14615	4.43	7833
Mean		1.067			
Std. Dev.		0.165			
% RSD		15.43			

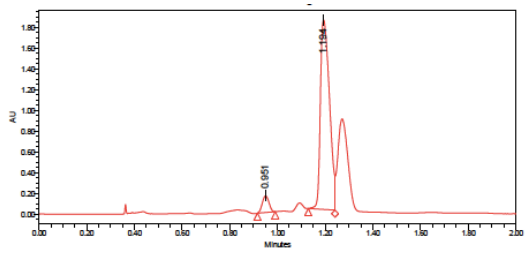
10 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.193	204101	95.24	77903
2	1	0.953	10194	4.76	5368
Mean		1.073			
Std. Dev.		0.170			
% RSD		15.81			

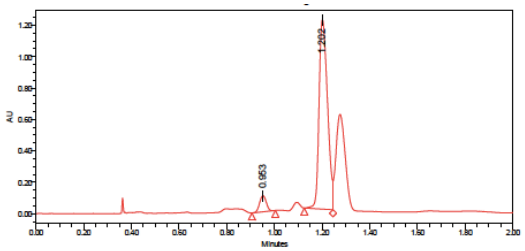
50 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.194	4845038	93.94	1826353
2	1	0.951	312786	6.06	160143
Mean		1.072			
Std. Dev.		0.172			
% RSD		16.05			

100 mol%:

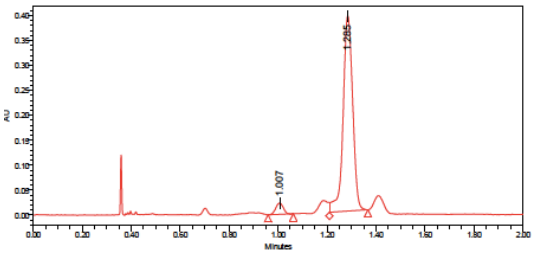


Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.202	2966630	93.75	1205529
2	1	0.953	197924	6.25	101890
Mean		1.077			
Std. Dev.		0.176			
% RSD		16.35			

Additive C (Glucose):

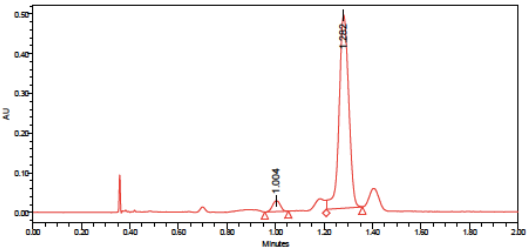
3 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.007	48327	4.34	22729
2	PDA Ch2 214nm@1.2nm	1.285	1066391	95.66	391067

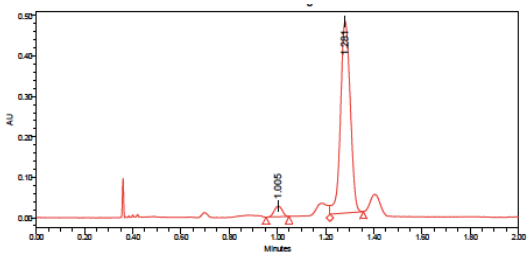
10 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.004	60469	4.30	27101
2	PDA Ch2 214nm@1.2nm	1.282	1344439	95.70	486621

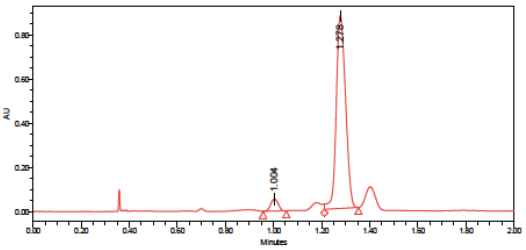
50 mol%:



Processed Channel: PDA Ch2
214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.005	60734	4.36	26936
2	PDA Ch2 214nm@1.2nm	1.281	1331102	95.64	474201

100 mol%:

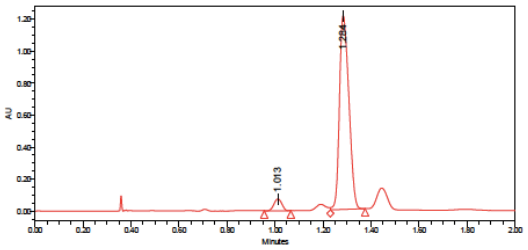


Processed Channel: PDA Ch2
214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.004	117396	4.76	53701
2	PDA Ch2 214nm@1.2nm	1.278	2349658	95.24	871500

Additive D (Fructose):

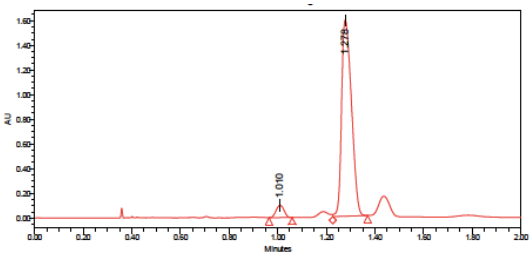
3 mol%:



Processed Channel: PDA Ch2
214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.013	167770	4.83	73446
2	PDA Ch2 214nm@1.2nm	1.284	3302658	95.17	1209592

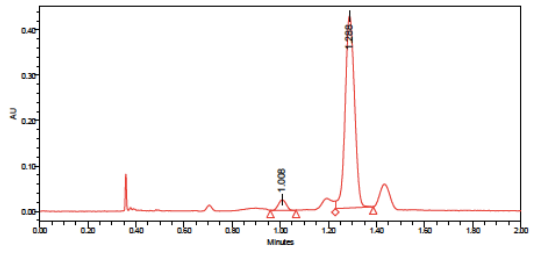
10 mol%:



Processed Channel: PDA Ch2
214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.010	227760	4.83	100419
2	PDA Ch2 214nm@1.2nm	1.278	4485253	95.17	1589897

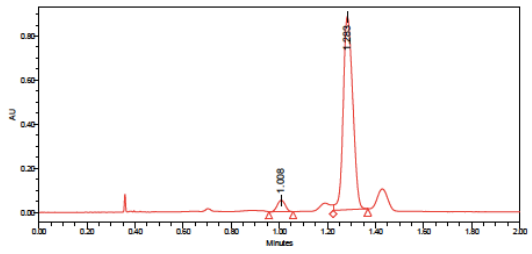
50 mol%:



Processed Channel: PDA Ch2
214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.008	51425	4.30	22857
2	PDA Ch2 214nm@1.2nm	1.288	1143656	95.70	422990

100 mol%:

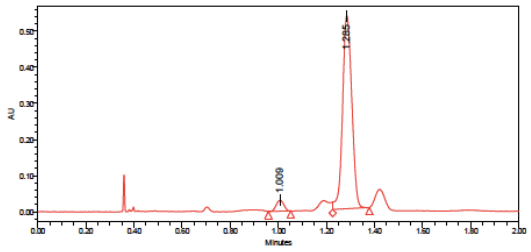


Processed Channel: PDA Ch2
214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.008	118427	4.67	51707
2	PDA Ch2 214nm@1.2nm	1.283	2416827	95.33	875765

Additive E (Lactose):

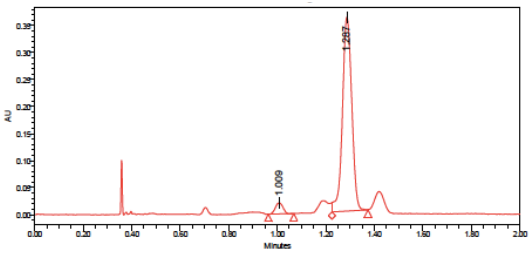
3 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.009	65757	4.41	30038
2	PDA Ch2 214nm@1.2nm	1.285	1424943	95.59	533388

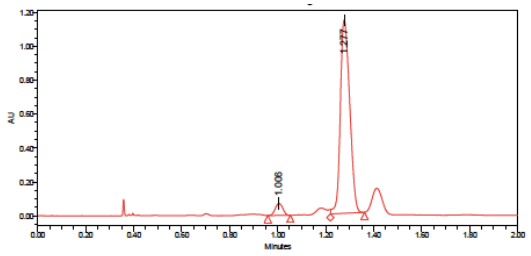
10 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.009	44605	4.44	20408
2	PDA Ch2 214nm@1.2nm	1.287	959046	95.56	358841

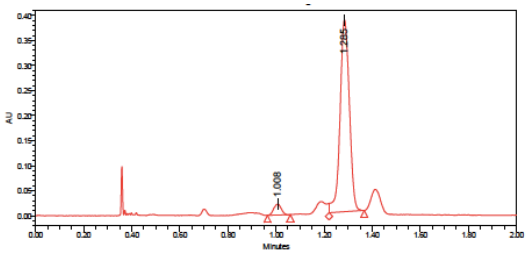
50 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.006	154755	4.77	70578
2	PDA Ch2 214nm@1.2nm	1.277	3088109	95.23	1139085

100 mol%:

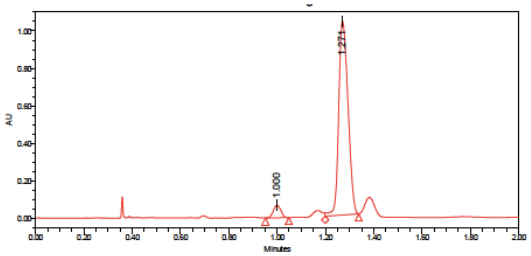


Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.008	46996	4.36	21419
2	PDA Ch2 214nm@1.2nm	1.285	1030216	95.64	382467

Additive F (Adenine):

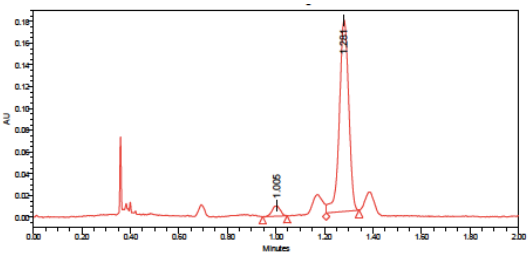
3 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.000	143954	4.94	66514
2	PDA Ch2 214nm@1.2nm	1.271	2769006	95.06	1033932

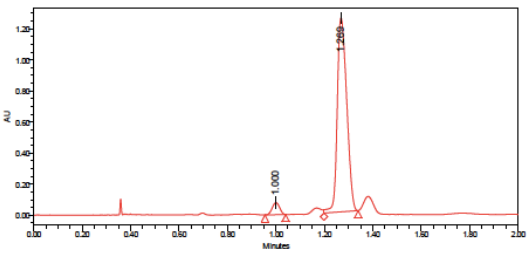
10 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

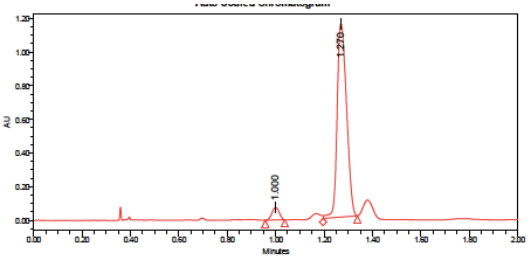
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.005	22378	4.52	9405
2	PDA Ch2 214nm@1.2nm	1.281	472210	95.48	175851

50 mol%: 100 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.000	165287	4.65	77867
2	PDA Ch2 214nm@1.2nm	1.269	3388757	95.35	1249762

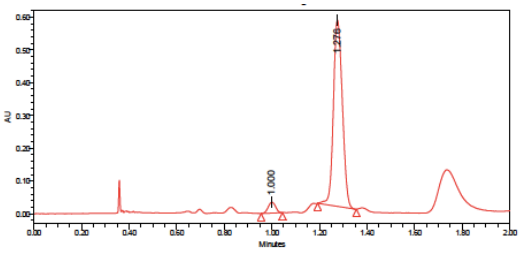


Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.000	153113	4.72	72978
2	PDA Ch2 214nm@1.2nm	1.270	3094224	95.28	1148178

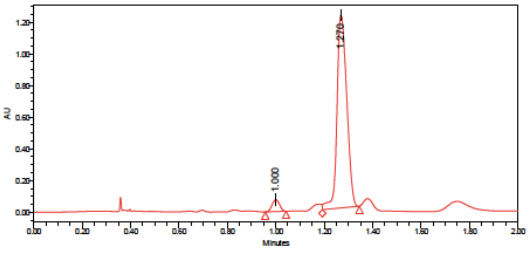
Additive G (Guanosine):

3 mol%: 10 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

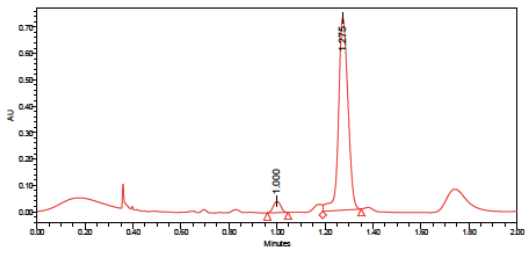
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.000	71835	4.61	33144
2	PDA Ch2 214nm@1.2nm	1.276	1484825	95.39	568103



Processed Channel: PDA Ch2 214nm@1.2nm

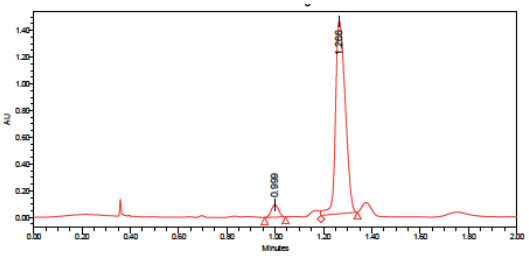
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.000	160477	4.49	75323
2	PDA Ch2 214nm@1.2nm	1.270	3417569	95.51	1219734

50 mol%: 100 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.000	92127	4.40	42680
2	PDA Ch2 214nm@1.2nm	1.275	2001791	95.60	729620

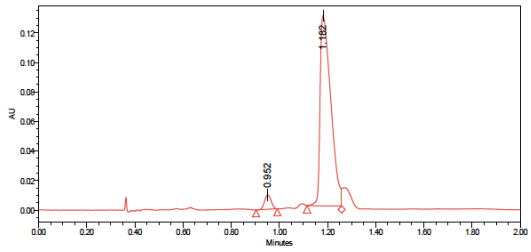


Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	0.999	193776	4.58	91872
2	PDA Ch2 214nm@1.2nm	1.266	4037925	95.42	1439697

Additive H (Thymidine-5`-monophosphoric acid):

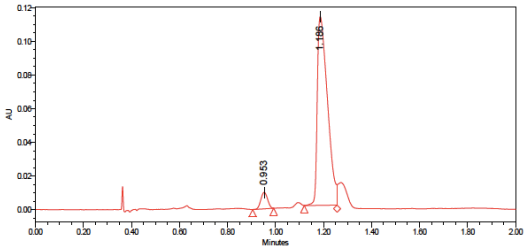
3 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.182	396760	95.57	128709
2	1	0.952	18405	4.43	9720
Mean		1.067			
Std. Dev.		0.162			
% RSD		15.21			

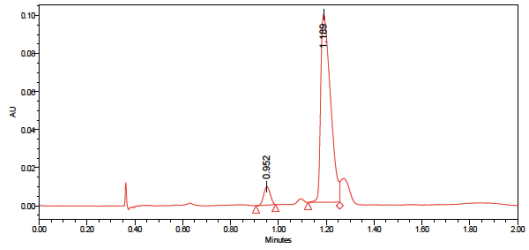
10 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.186	330145	94.55	112047
2	1	0.953	19046	5.45	9804
Mean		1.070			
Std. Dev.		0.165			
% RSD		15.43			

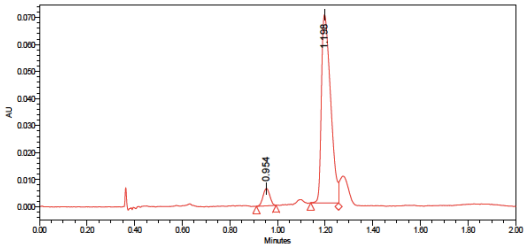
50 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.189	280949	93.78	98629
2	1	0.952	18627	6.22	9663
Mean		1.071			
Std. Dev.		0.168			
% RSD		15.67			

100 mol%:

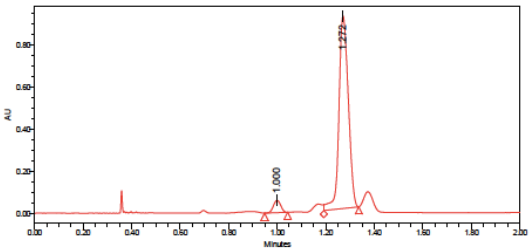


Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.198	186237	93.63	69616
2	1	0.954	12670	6.37	6381
Mean		1.076			
Std. Dev.		0.172			
% RSD		16.02			

Additive I (Tristearine):

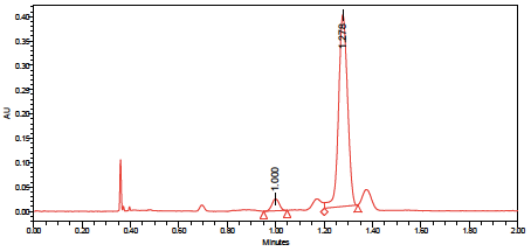
3 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.000	121585	4.71	58089
2	PDA Ch2 214nm@1.2nm	1.272	2463472	95.29	914943

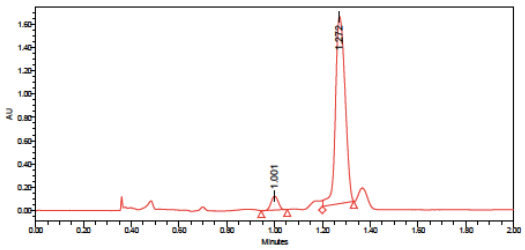
10 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.000	51515	4.82	34132
2	PDA Ch2 214nm@1.2nm	1.278	1017360	95.18	393607

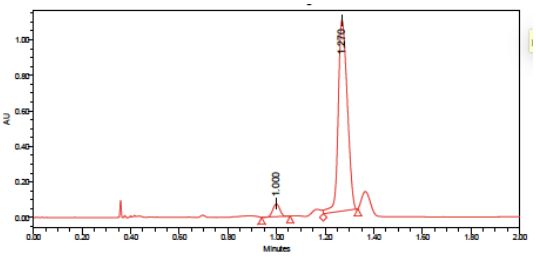
50 mol%:



Processed Channel: PDA 205.6 nm (190-400)nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 205.6 nm (190-400)nm	1.001	245466	5.17	117648
2	PDA 205.6 nm (190-400)nm	1.272	4502436	94.83	1603583

100 mol%:

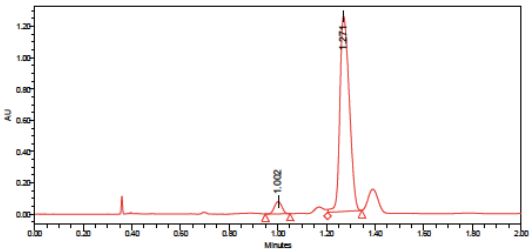


Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.000	141752	4.83	70864
2	PDA Ch2 214nm@1.2nm	1.270	2792984	95.17	1072878

Additive J (Squalene):

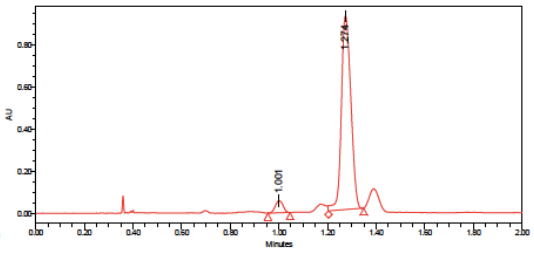
3 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.002	167946	4.76	78312
2	PDA Ch2 214nm@1.2nm	1.271	3363738	95.24	1248839

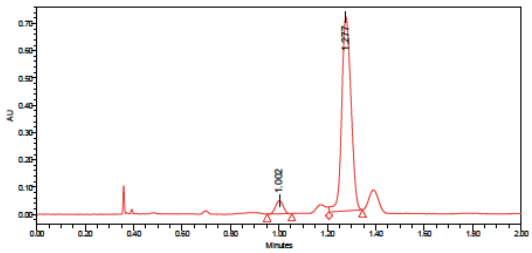
10 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.001	126364	4.83	57353
2	PDA Ch2 214nm@1.2nm	1.274	2490308	95.17	916066

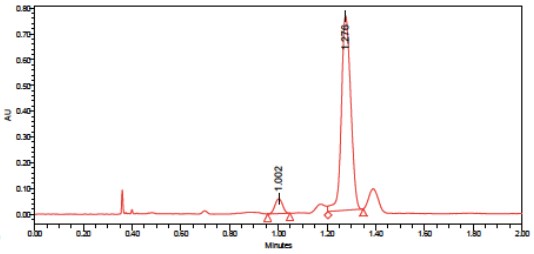
50 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.002	105441	5.27	48071
2	PDA Ch2 214nm@1.2nm	1.277	1894788	94.73	711006

100 mol%:

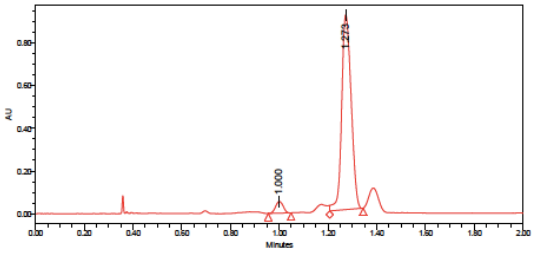


Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.002	124102	5.80	57230
2	PDA Ch2 214nm@1.2nm	1.276	2016829	94.20	754030

Additive K (Cholesterol):

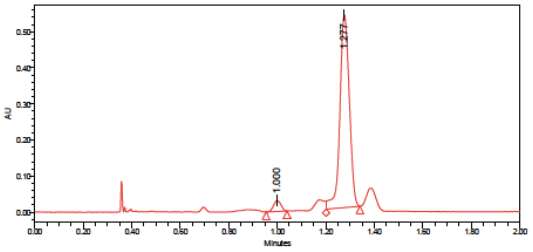
3 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.000	11908	4.62	5498
2	PDA Ch2 214nm@1.2nm	1.273	245846	95.38	91128

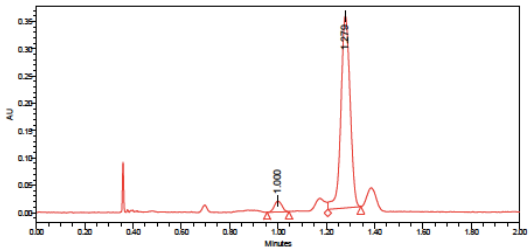
10 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.000	63238	4.19	29893
2	PDA Ch2 214nm@1.2nm	1.277	1446318	95.81	533977

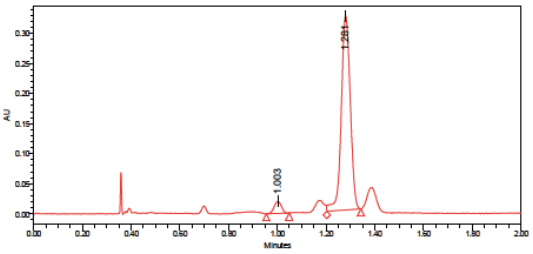
50 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.000	42549	4.40	19676
2	PDA Ch2 214nm@1.2nm	1.279	932699	95.60	351330

100 mol%:

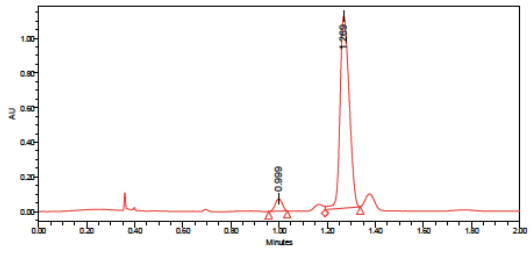


Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.003	40913	4.71	20037
2	PDA Ch2 214nm@1.2nm	1.281	828188	95.29	322548

Additive L (Ascorbic acid):

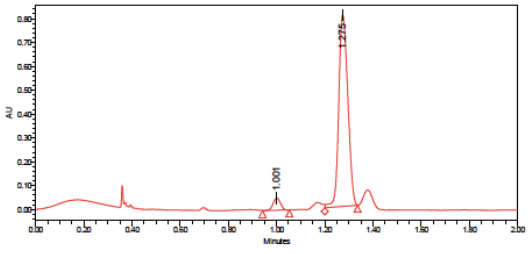
3 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	0.999	146024	4.72	71250
2	PDA Ch2 214nm@1.2nm	1.269	2947663	95.28	1105049

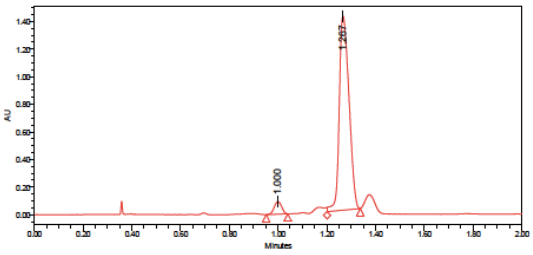
10 mol%:



Processed Channel: PDA 214.0 nm (190-400)nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 214.0 nm (190-400)nm	1.001	107220	4.86	50462
2	PDA 214.0 nm (190-400)nm	1.275	2100819	95.14	803233

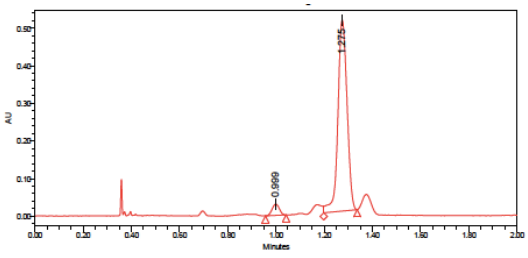
50 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.000	191067	4.66	90214
2	PDA Ch2 214nm@1.2nm	1.267	3907559	95.34	1405807

100 mol%:

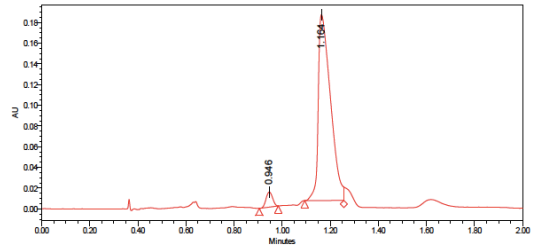


Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	0.999	62688	4.47	29890
2	PDA Ch2 214nm@1.2nm	1.275	1340198	95.53	508199

Additive M (Vitamine B_{12}):

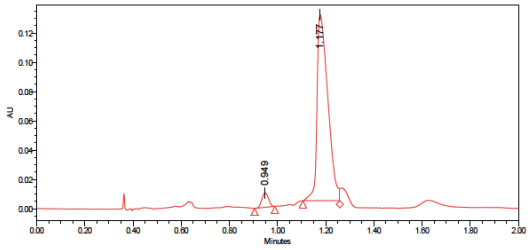
3 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.164	634214	95.85	179477
2	1	0.946	27493	4.15	14578
Mean		1.055			
Std. Dev.		0.154			
% RSD		14.56			

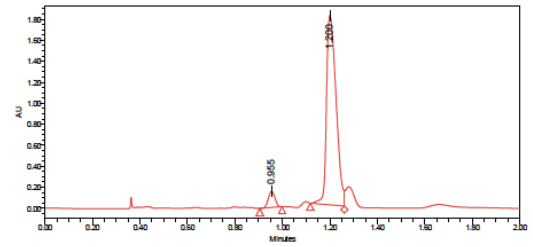
10 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.177	397625	95.46	127048
2	1	0.949	18898	4.54	9871
Mean		1.063			
Std. Dev.		0.162			
% RSD		15.20			

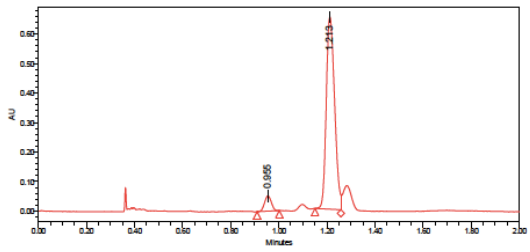
50 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.200	5064167	94.49	1804288
2	1	0.955	295089	5.51	151944
Mean		1.078			
Std. Dev.		0.174			
% RSD		16.12			

100 mol%:

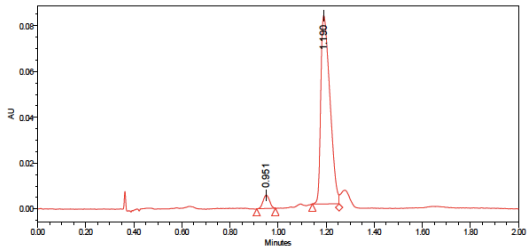


Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.213	1566339	93.95	652231
2	1	0.955	100821	6.05	51718
Mean		1.084			
Std. Dev.		0.182			
% RSD		16.81			

Additive N (Citric Acid):

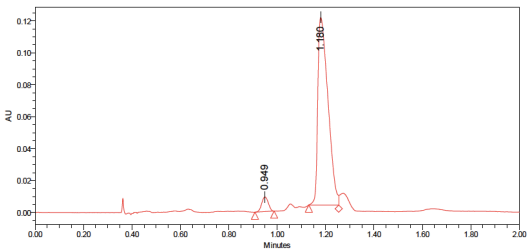
3 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.190	217647	95.24	82259
2	1	0.951	10878	4.76	5876
Mean		1.071			
Std. Dev.		0.169			
% RSD		15.80			

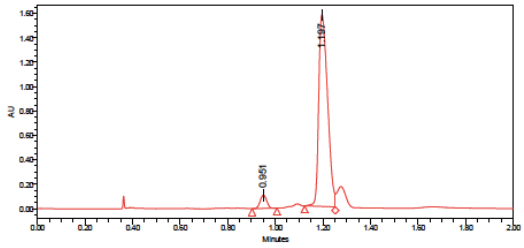
10 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.180	342601	95.24	117486
2	1	0.949	17137	4.76	9132
Mean		1.065			
Std. Dev.		0.163			
% RSD		15.32			

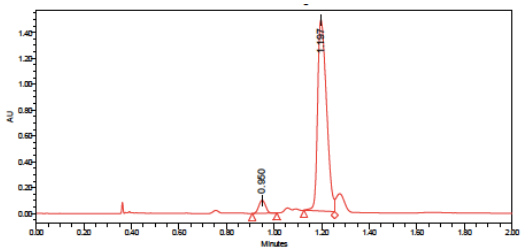
50 mol%:



Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.197	4073488	95.14	1571183
2	1	0.951	208127	4.86	107751
Mean		1.074			
Std. Dev.		0.174			
% RSD		16.20			

100 mol%:

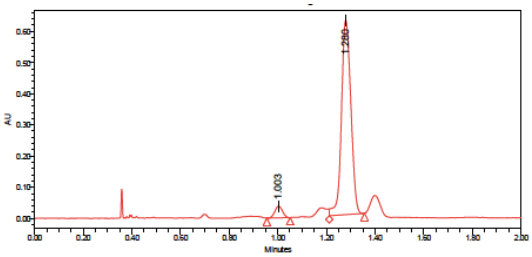


Peak Name:

	Injection	RT	Area	% Area	Height
1	1	1.197	3837368	95.13	1478489
2	1	0.950	196554	4.87	100340
Mean		1.074			
Std. Dev.		0.175			
% RSD		16.29			

Additive O (Pyruvic acid):

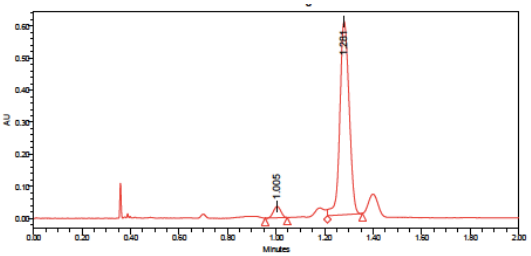
3 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.003	81830	4.65	37041
2	PDA Ch2 214nm@1.2nm	1.280	1679716	95.35	623672

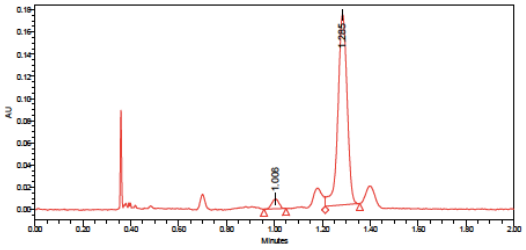
10 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.006	74555	4.45	34880
2	PDA Ch2 214nm@1.2nm	1.281	1602552	95.55	602861

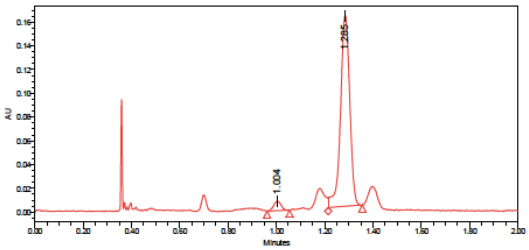
50 mol%:



Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.006	18398	3.88	8886
2	PDA Ch2 214nm@1.2nm	1.285	456304	96.12	171045

100 mol%:

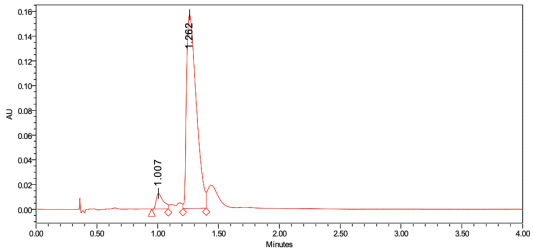


Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.004	17022	3.84	8097
2	PDA Ch2 214nm@1.2nm	1.285	426746	96.16	160415

Additive P (Glutathione):

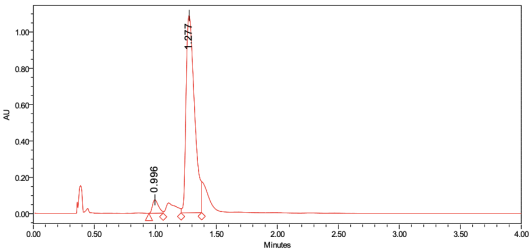
3 mol%:



Peak Results

	Name	RT	Start Time (min)	Height	Area	% Area
1		1.007	0.951	12564	49997	5.40
2		1.262	1.208	156515	876019	94.60

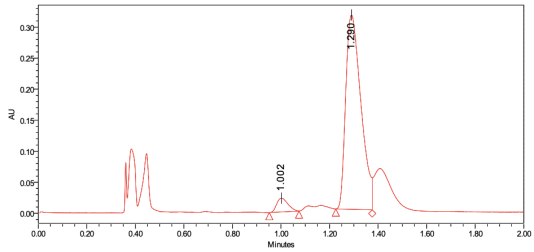
10 mol%:



Peak Results

	Name	RT	Start Time (min)	Height	Area	% Area
1		0.996	0.948	74092	253561	4.64
2		1.277	1.212	1086319	5206870	95.36

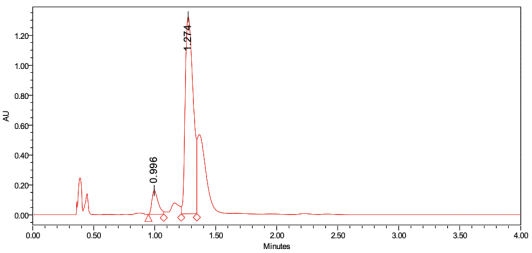
50 mol%:



Peak Results

	Name	RT	Start Time (min)	Height	Area	% Area
1		1.002	0.952	22281	71184	4.96
2		1.290	1.226	313223	1363816	95.04

100 mol%:



Peak Results

	Name	RT	Start Time (min)	Height	Area	% Area
1		0.996	0.948	158189	553881	8.48
2		1.274	1.217	1314848	5977596	91.52

7. Conjugate Addition Reaction in Complex Mixtures

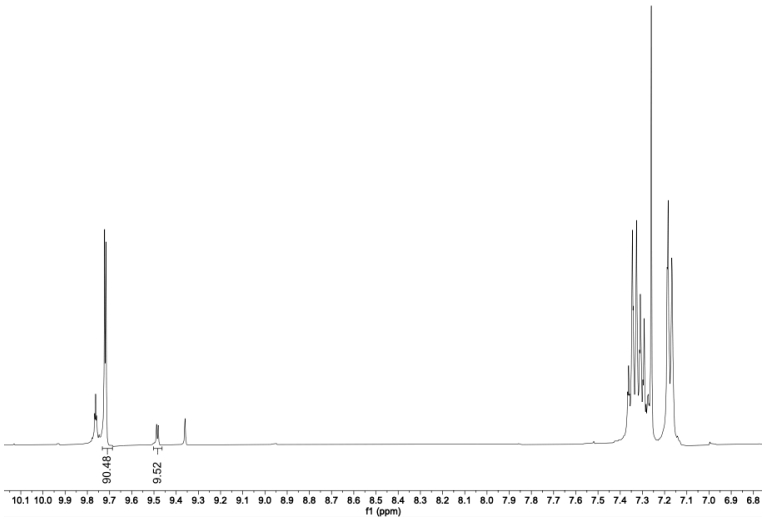
Solvent	Conversion[a] (%)		Major diastereomer[a] (%)		*ee*[b] (%)		Solvent	Conversion[a] (%)		Major diastereomer[a] (%)		*ee*[b] (%)	
Cat:	**1**	**2**	**1**	**2**	**1**	**2**		**1**	**2**	**1**	**2**	**1**	**2**
S1	>95	>95	90	90	85	96	**S19**	>95	>95	90	94	86	96
S2	>95	>95	90	90	84	96	**S20**	>95	>95	91	91	86	96
S3	>95	>95	90	89	85	96	**S21**	>95	>95	90	89	71	96
S4	>95	>95	89	90	84	96	**S22**	>95	>95	90	91	75	96
S5	>95	>95	91	87	88	96	**S23**	>95	>95	92	91	86	96
S6	>95	>95	91	87	88	96	**S24**	>95	>95	96	90	84	95
S7	>95	>95	90	89	87	96	**S25**	>95	>95	91	93	84	96
S8	>95	>95	90	89	86	96	**S26**	>95	>95	88	89	87	97
S9	>95	>95	91	91	86	96	**S27**	>95	>95	92	94	90	96
S10	>95	>95	92	93	89	96	**S28**	>95	>95	88	91	87	95
S11	>95	>95	92	95	80	96	**S29**	>95	>95	90	89	82	95
S12	>95	>95	92	94	89	96	**S30**	>95	>95	90	95	83	96
S13	>95	>95	88	89	88	96	**S31**	>95	>95	90	95	84	95
S14	>95	>95	89	91	87	96	**S32**	>95	>95	90	95	83	95
S15	>95	>95	87	91	86	96	**S33**	>95	>95	90	94	86	96
S16	>95	>95	92	90	88	96	**S34**	>95	>95	96	94	84	95
S17	>95	>95	90	91	79	96	**S35**	>95	>95	96	94	90	96
S18	>95	>95	90	90	83	96	**S36**	>95	>95	88	88	89	96

[a]Determined by ^{1}H NMR spectroscopic analysis of the crude mixture. [b]Determined by chiral stationary phase HPLC analysis.

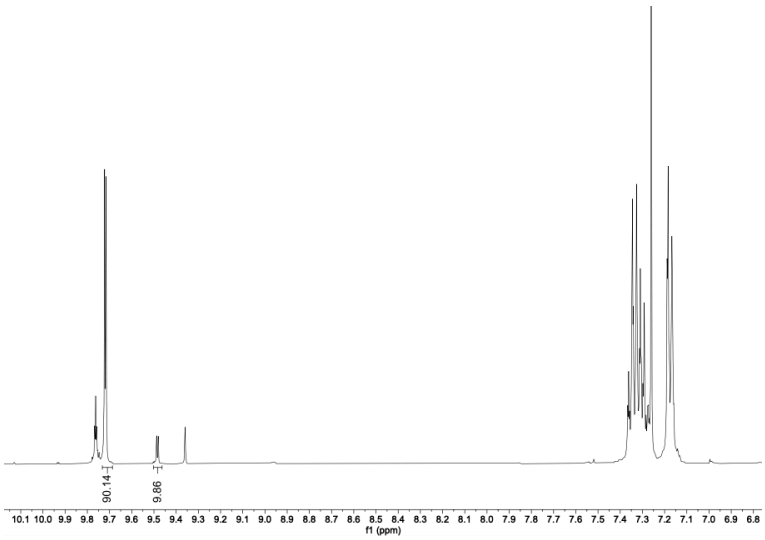
^{1}H NMR spectra of the reactions in the presence of H-DPro-Pro-Glu-NH_2 1:

A sample of 50 μL from the crude reaction mixture was added to an NMR tube that contained 600 μL $CDCl_3$. Vigorous shaking or vortexing ensured extraction of the reaction products from the mixture. Conversion was determined by comparing the integrals of the olefinic signal of nitrostyrene and the RCHO signals of the γ-nitroaldehyde. The diastereomeric ratio was determined by integration of the RCHO signals of the γ-nitroaldehyde.

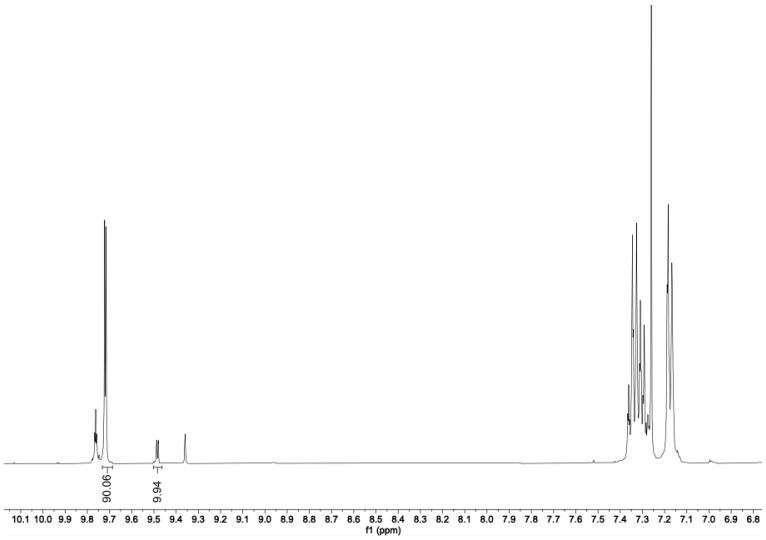
MilliQ water (S1):



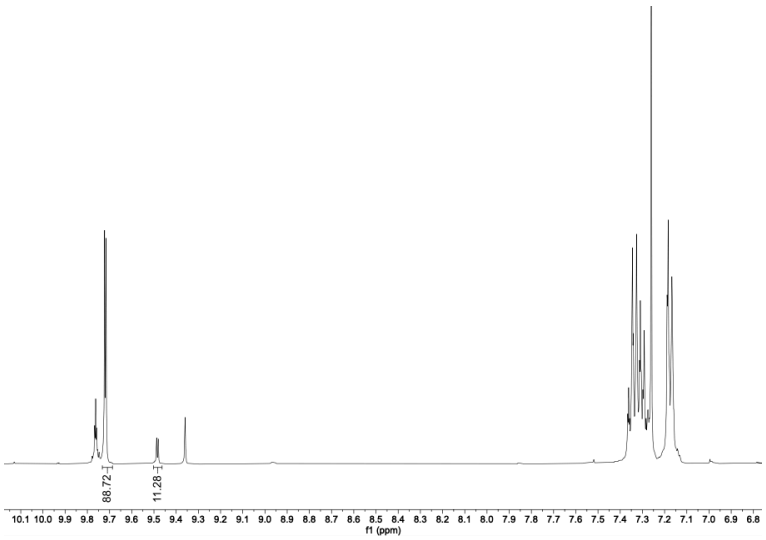
Tab water (S2):



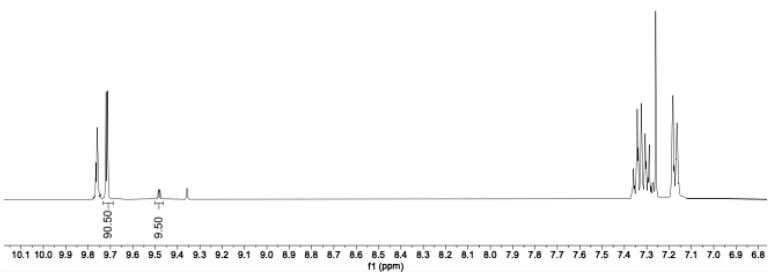
Lake Zürich water (S3):



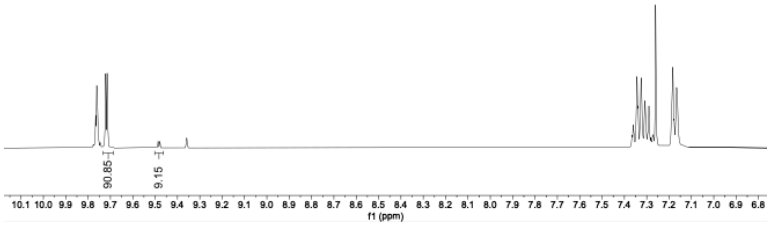
River Limmat water (S4):



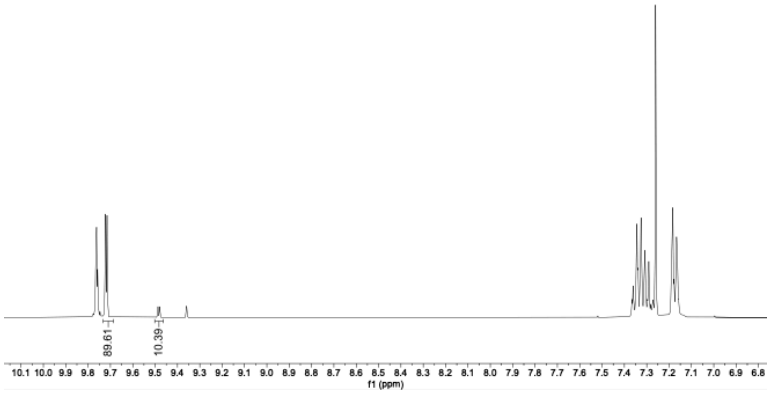
Milk (S5):



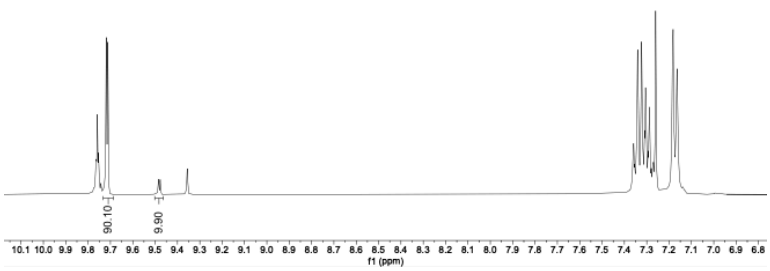
Low fat milk (S6):



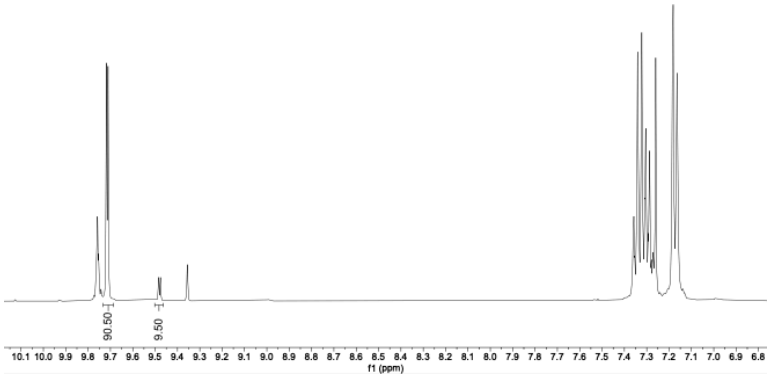
Soya milk (S7):



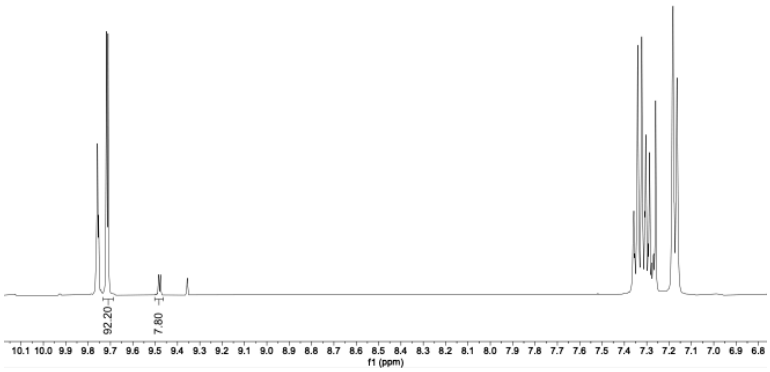
Almond milk (S8):



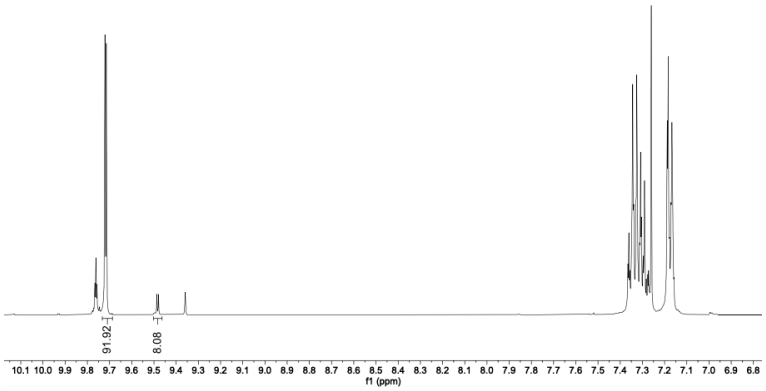
Rice milk (S9):



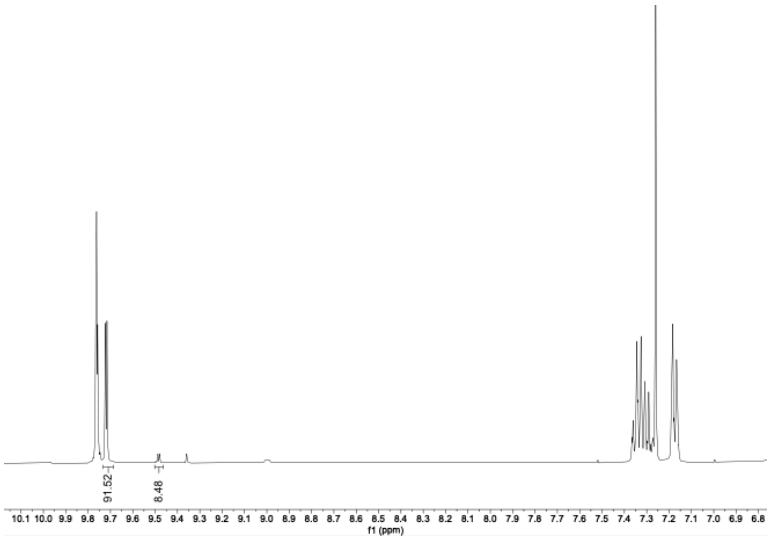
Orange juice (S10):



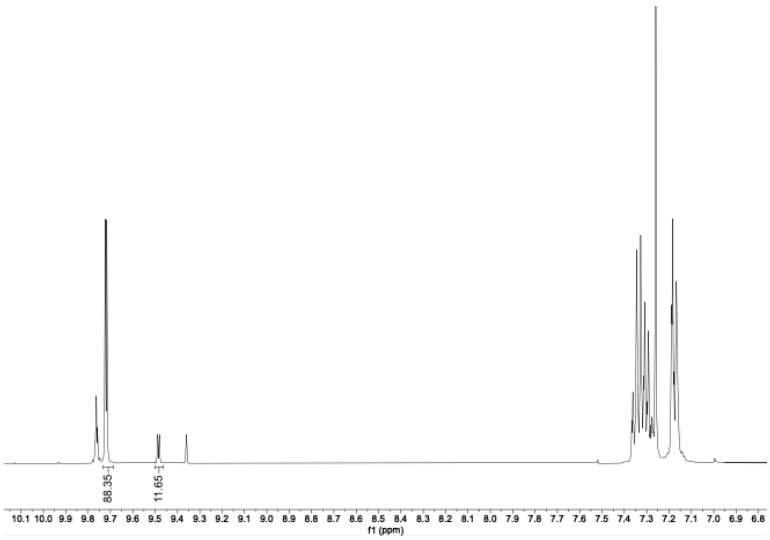
Blood orange juice (S11):



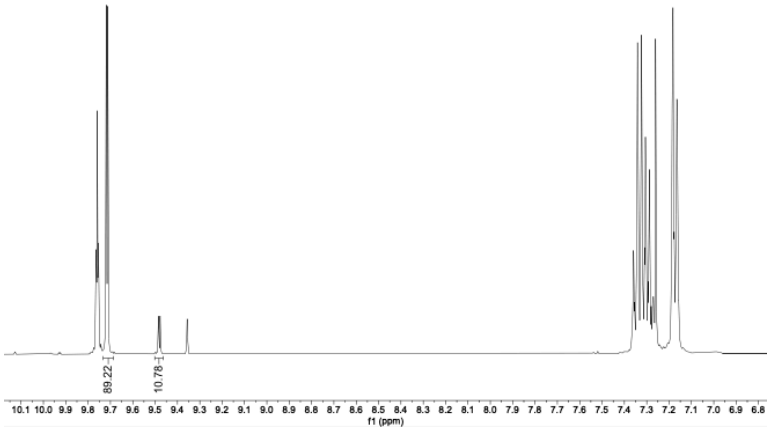
Apple juice (S12):



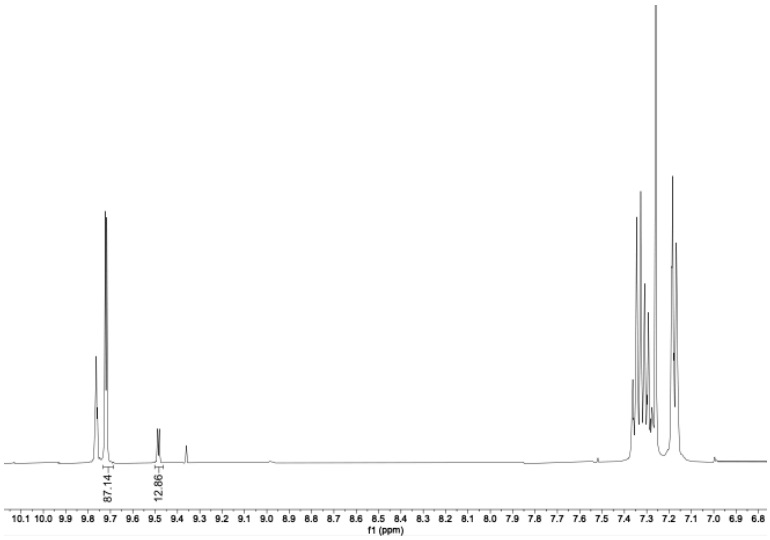
Coconut water (S13):



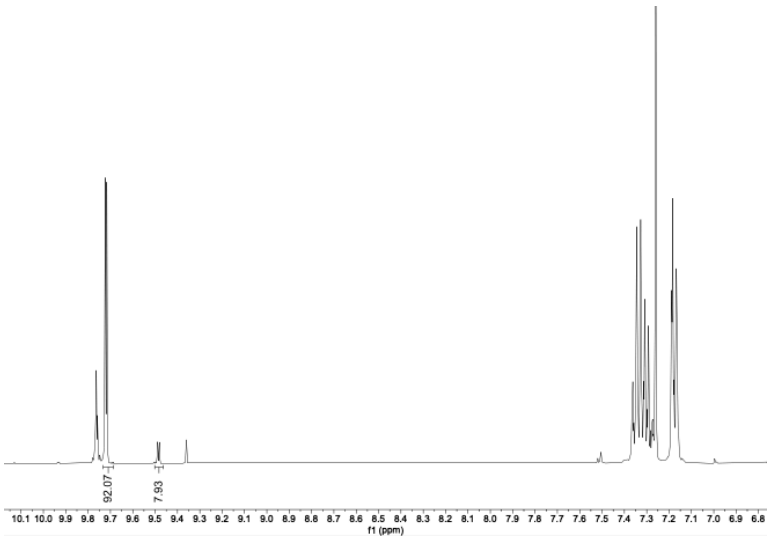
Carrot juice (S14):



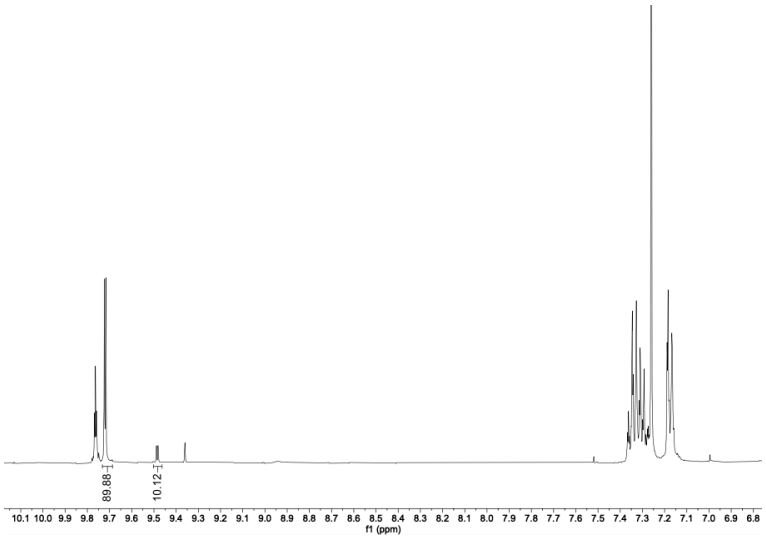
Beetroot juice (S15):



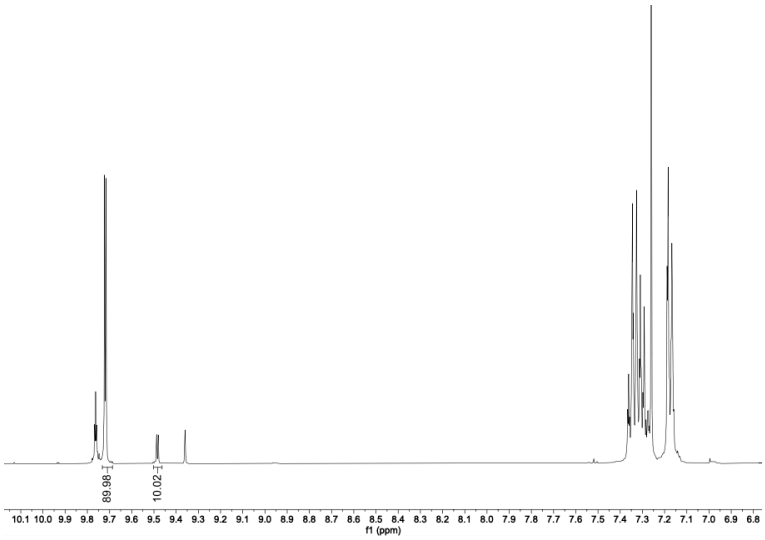
Coffee (S16):



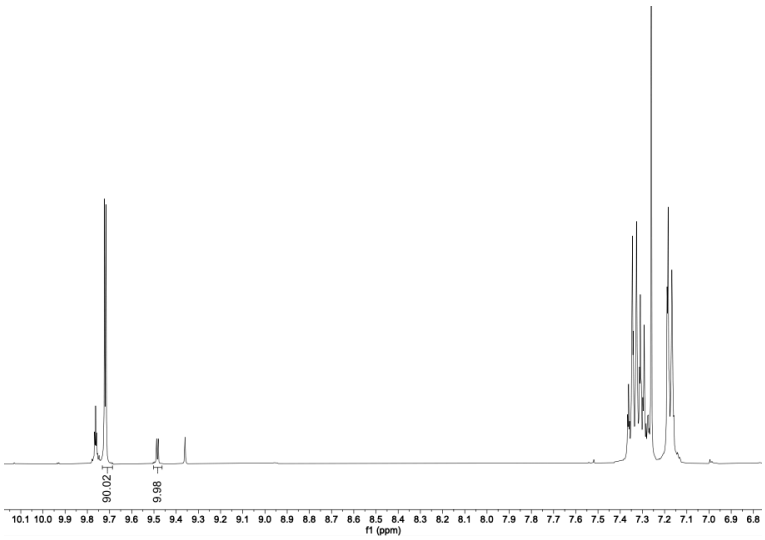
Green tea (S17):



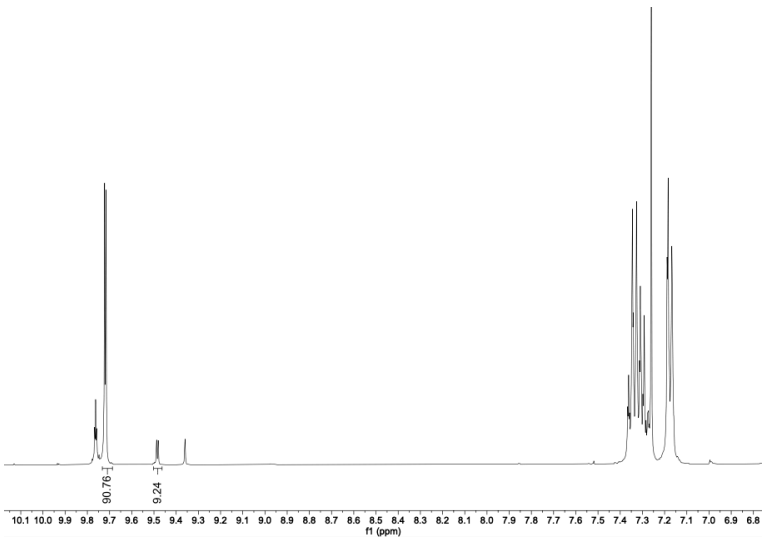
Black tea (S18):



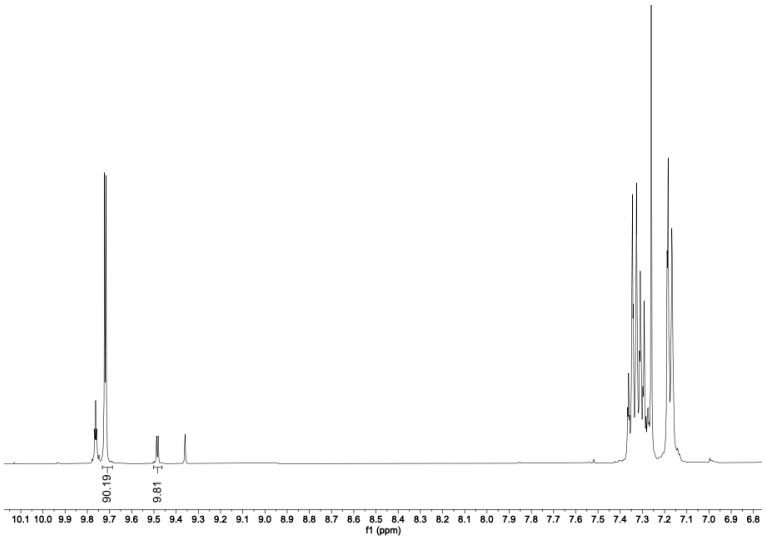
Peppermint tea (S19):



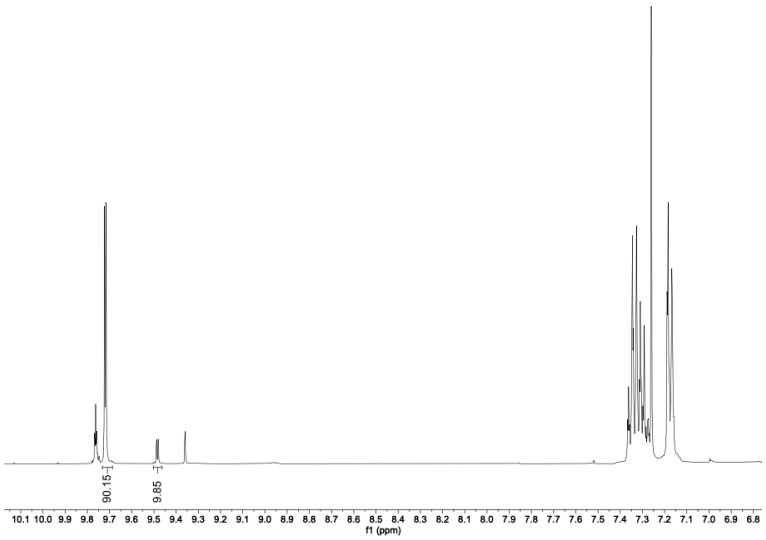
Fruit tea (S20):



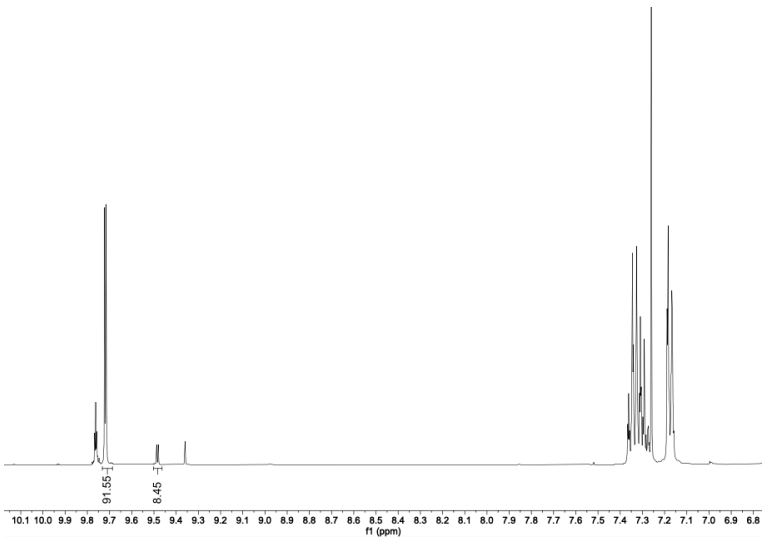
Honey solution 5 wt% (S21):



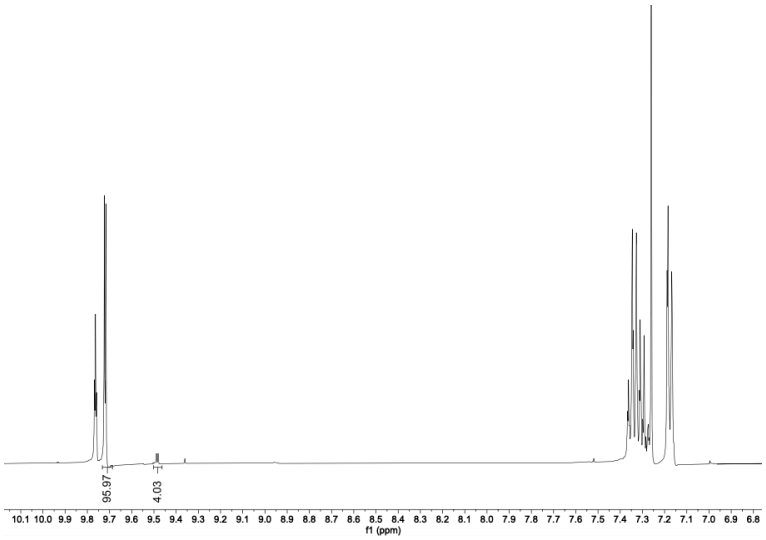
Coke (S22):



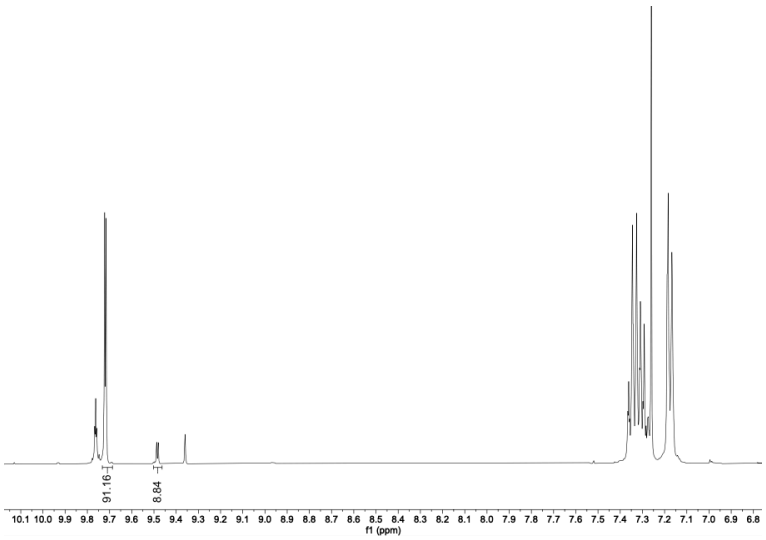
Rivella (S23):



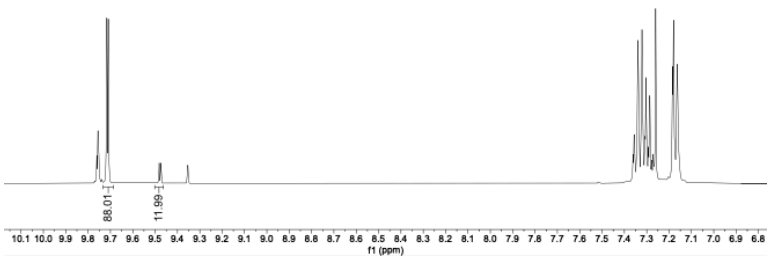
Diet Rivella (S24):



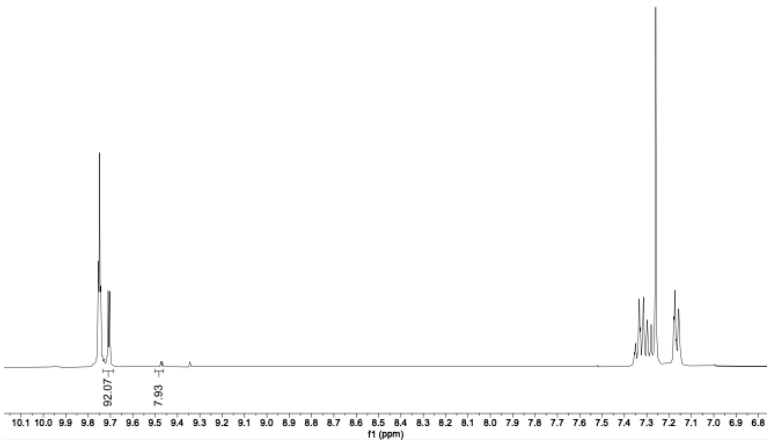
Ice tea (S25):



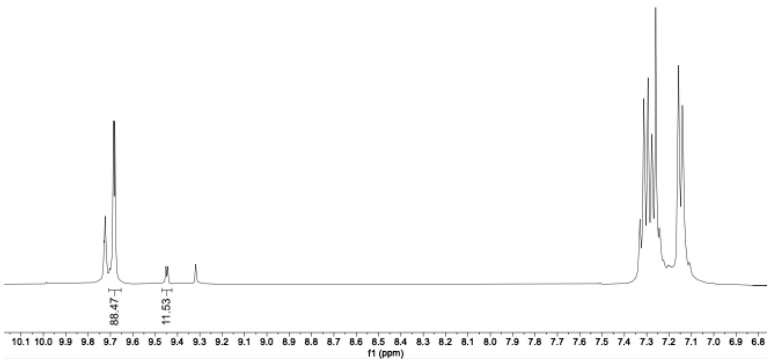
Beer (S26):



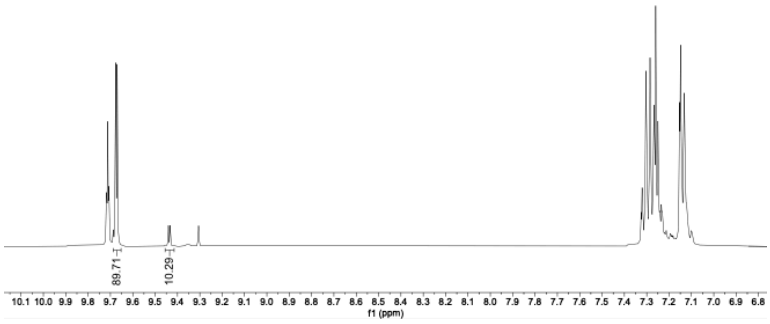
Red wine (S27):



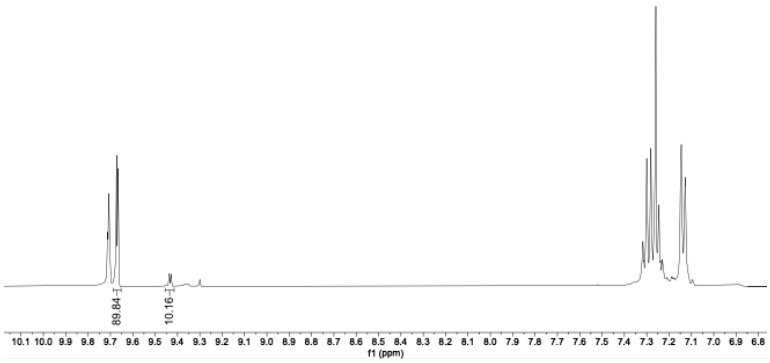
Amaretto (S28):



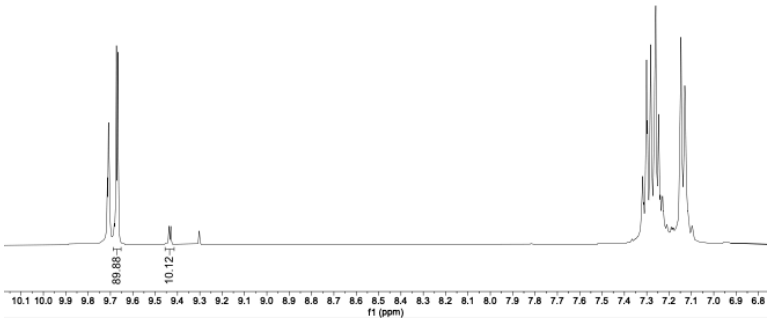
Herb Liqueur – "Jägermeister" (S29):



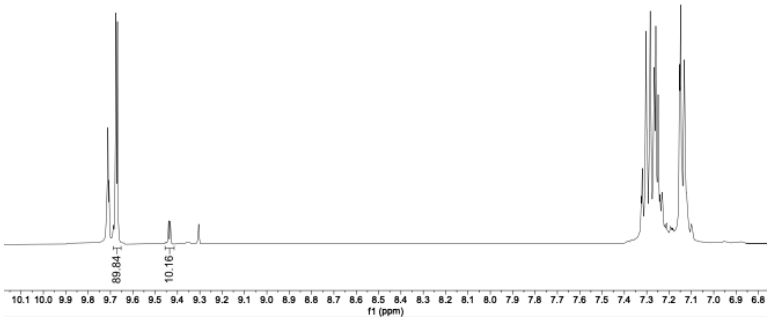
Scotch Whisky – Aberlour 18 y (S30):



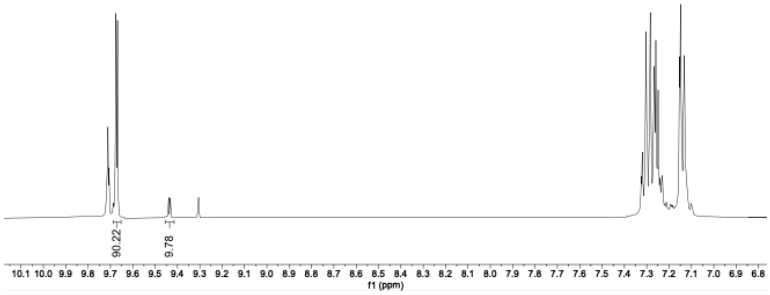
Vodka (S31):



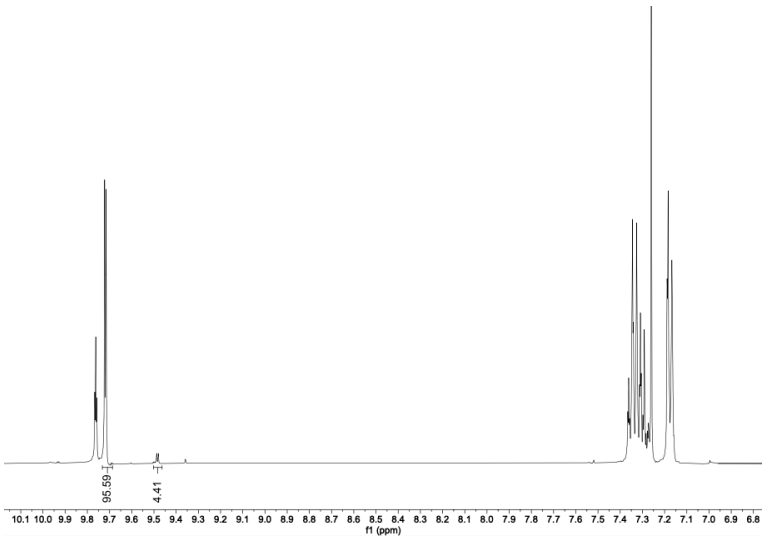
Gin (S32):



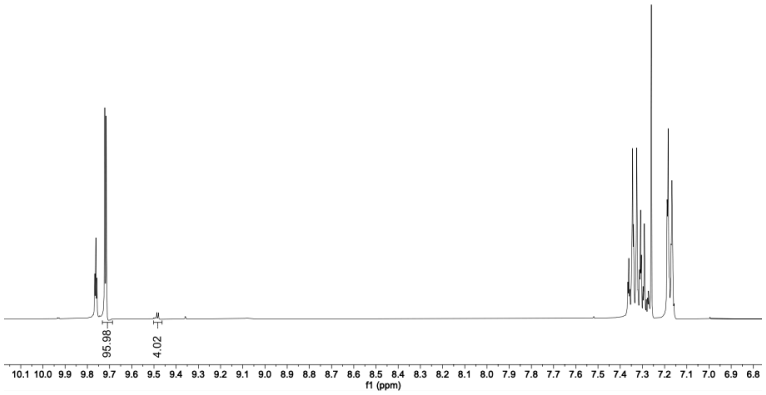
Rum (S33):



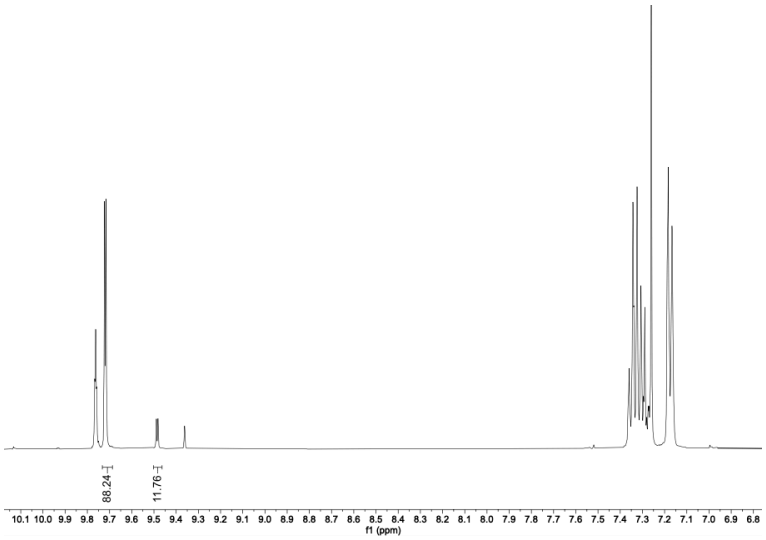
Aceto balsamico (S34):



Herb vinegar (S35):

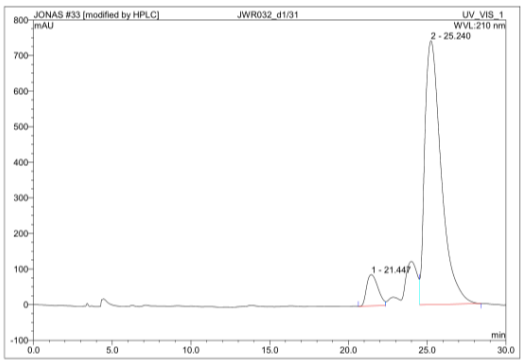


Olive oil (S36):



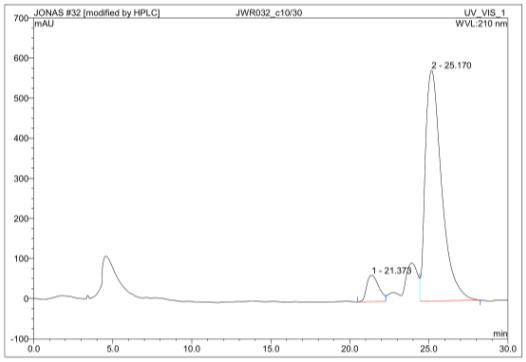
HPLC chromatograms of the reactions in presence of H-DPro-Pro-Glu-NH_2 1:

MilliQ water (S1):



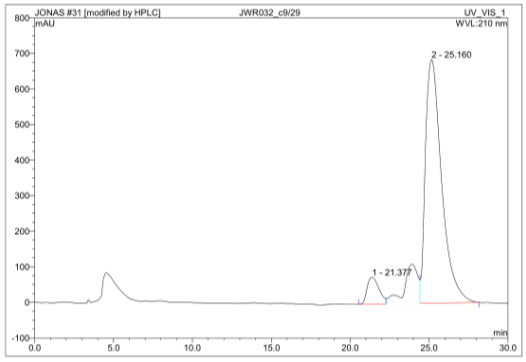
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.45	n.a.	87.969	74.077	7.62	n.a.	BM *
2	25.24	n.a.	741.386	898.663	92.38	n.a.	MB*
Total:			829.355	972.740	100.00	0.000	

Tab water (S2):



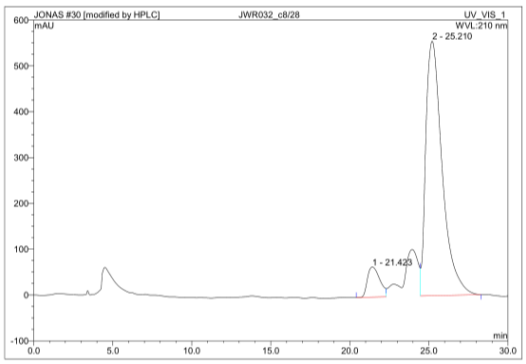
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.37	n.a.	65.737	58.222	7.79	n.a.	BM *
2	25.17	n.a.	575.397	689.270	92.21	n.a.	MB*
Total:			641.134	747.493	100.00	0.000	

Lake Zürich water (S3):



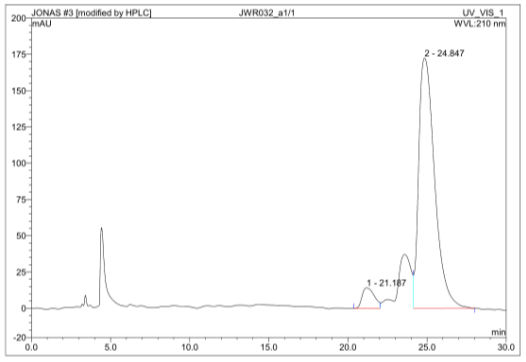
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.38	n.a.	75.305	65.313	7.40	n.a.	BM *
2	25.16	n.a.	685.146	817.527	92.60	n.a.	MB*
Total:			760.451	882.840	100.00	0.000	

River Limmat water (S4):



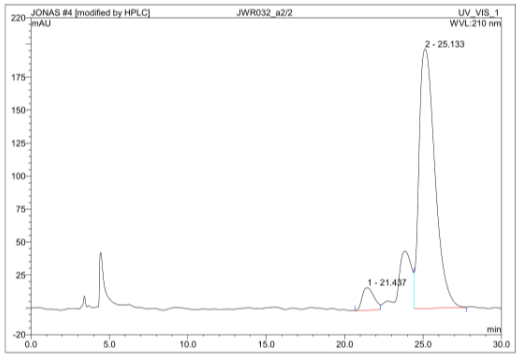
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.42	n.a.	65.450	59.417	8.17	n.a.	BM *
2	25.21	n.a.	555.413	667.520	91.83	n.a.	MB*
Total:			620.862	726.936	100.00	0.000	

Milk (S5):



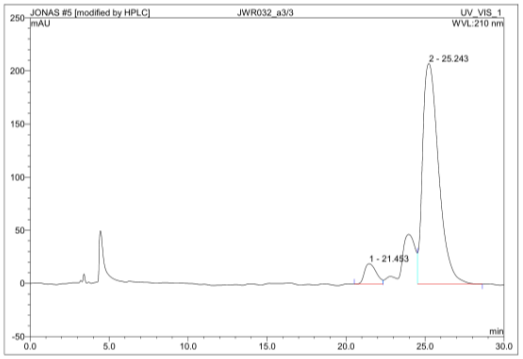
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.19	n.a.	14.084	12.667	5.92	n.a.	BM *
2	24.85	n.a.	172.321	201.237	94.08	n.a.	MB*
Total:			186.406	213.905	100.00	0.000	

Low fat milk (S6):



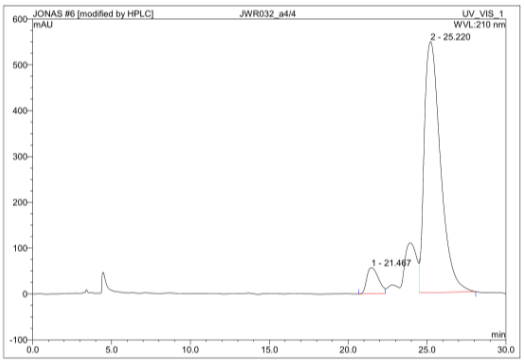
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.44	n.a.	17.120	14.889	6.05	n.a.	BM *
2	25.13	n.a.	196.662	231.112	93.95	n.a.	MB*
Total:			213.782	246.000	100.00	0.000	

Soya milk (S7):



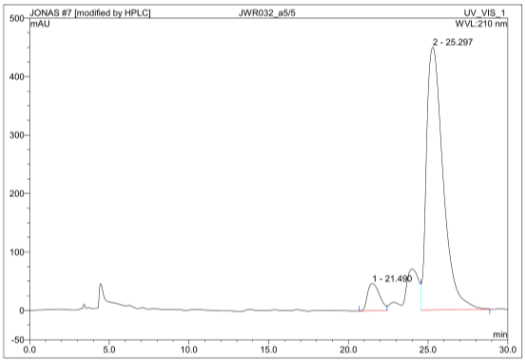
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.45	n.a.	19.129	16.606	6.35	n.a.	BM *
2	25.24	n.a.	207.667	245.039	93.65	n.a.	MB*
Total:			226.796	261.645	100.00	0.000	

Almond milk (S8):



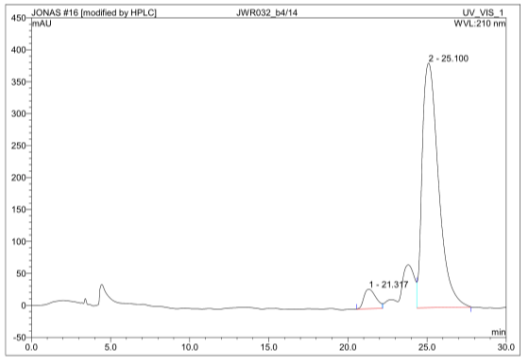
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.47	n.a.	56.763	49.016	6.96	n.a.	BM *
2	25.22	n.a.	547.828	655.391	93.04	n.a.	MB*
Total:			604.591	704.407	100.00	0.000	

Rice milk (S9):



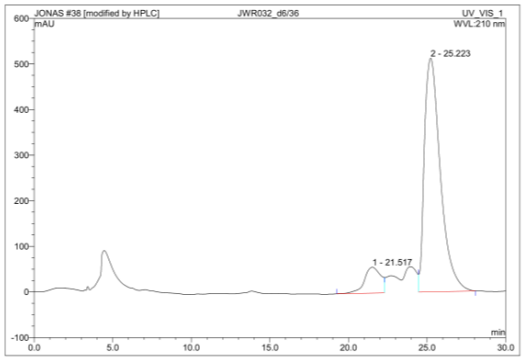
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.49	n.a.	46.640	40.858	7.00	n.a.	BM *
2	25.30	n.a.	449.498	543.122	93.00	n.a.	MB*
Total:			496.138	583.980	100.00	0.000	

Orange juice (S10):



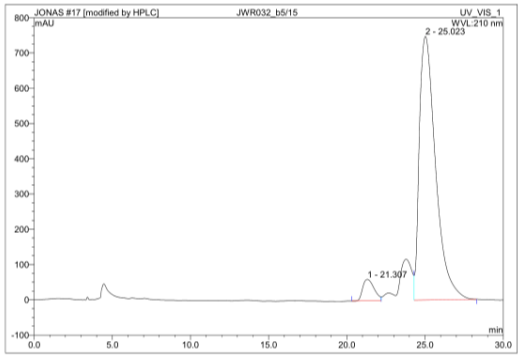
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.32	n.a.	30.577	26.968	5.56	n.a.	BM *
2	25.10	n.a.	382.973	458.421	94.44	n.a.	MB*
Total:			413.550	485.389	100.00	0.000	

Blood orange juice (S11):



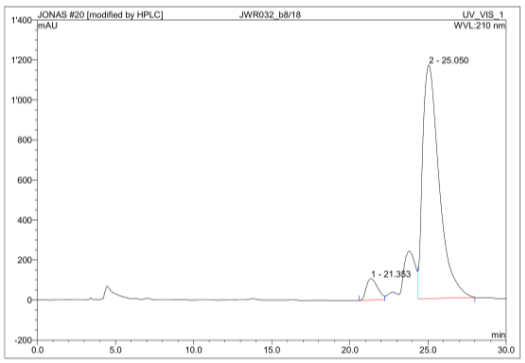
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.52	n.a.	56.764	68.128	10.12	n.a.	BM *
2	25.22	n.a.	512.496	605.138	89.88	n.a.	MB*
Total:			569.260	673.266	100.00	0.000	

Apple juice (S12):



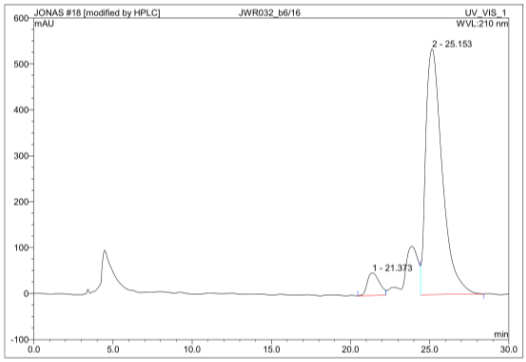
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.31	n.a.	60.740	51.595	5.41	n.a.	BM *
2	25.02	n.a.	747.797	902.339	94.59	n.a.	MB*
Total:			808.537	953.934	100.00	0.000	

Coconut water (S13):



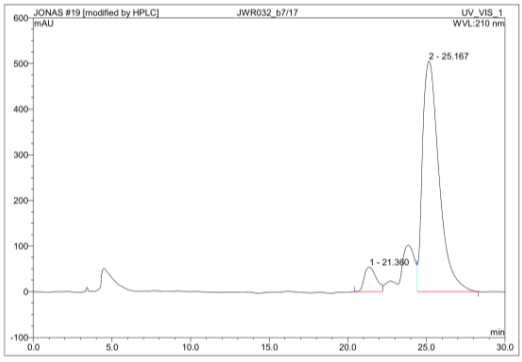
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.35	n.a.	105.833	89.275	5.85	n.a.	BM *
2	25.05	n.a.	1167.053	1437.061	94.15	n.a.	MB*
Total:			1272.887	1526.336	100.00	0.000	

Carrot juice (S14):



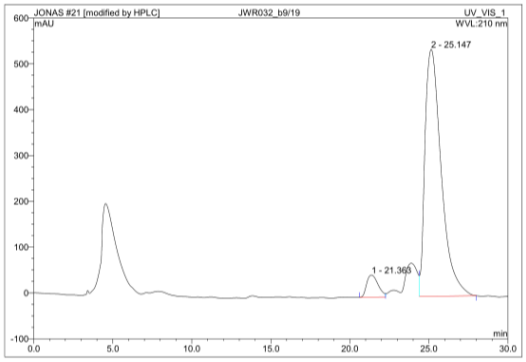
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.37	n.a.	49.223	43.482	6.30	n.a.	BM *
2	25.15	n.a.	534.889	647.107	93.70	n.a.	MB*
Total:			584.112	690.589	100.00	0.000	

Beetroot juice (S15):



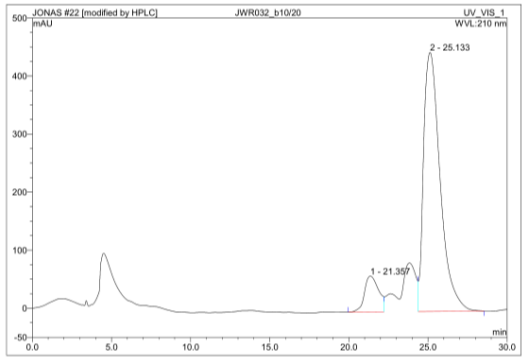
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.36	n.a.	53.774	47.670	7.16	n.a.	BM *
2	25.17	n.a.	505.052	617.841	92.84	n.a.	MB*
Total:			558.826	665.511	100.00	0.000	

Coffee (S16):



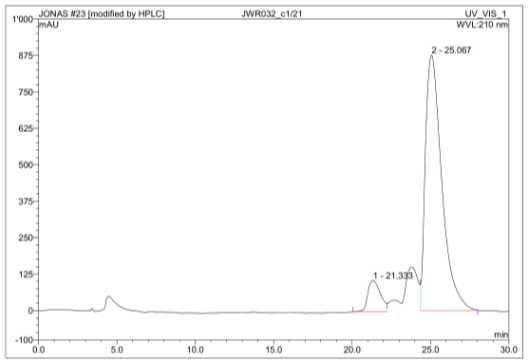
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.36	n.a.	48.078	40.295	5.89	n.a.	BM *
2	25.15	n.a.	538.978	643.817	94.11	n.a.	MB*
Total:			587.056	684.112	100.00	0.000	

Green tea (S17):



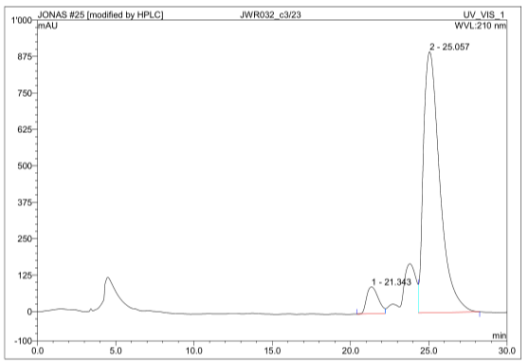
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.36	n.a.	61.641	63.923	10.55	n.a.	BM *
2	25.13	n.a.	446.142	542.205	89.45	n.a.	MB*
Total:			507.783	606.128	100.00	0.000	

Black tea (S18):



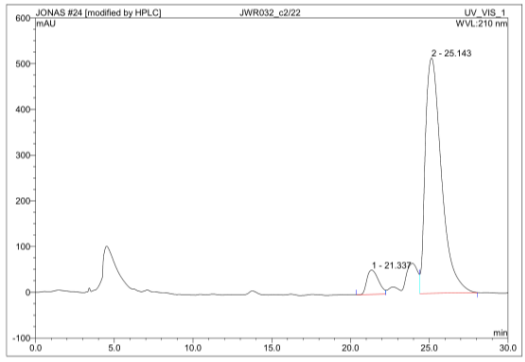
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.33	n.a.	106.545	99.556	8.56	n.a.	BM *
2	25.07	n.a.	876.880	1063.783	91.44	n.a.	MB*
Total:			983.425	1163.340	100.00	0.000	

Peppermint tea (S19):



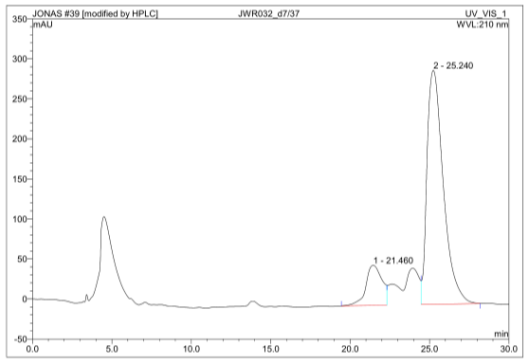
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.34	n.a.	91.867	79.718	6.82	n.a.	BM *
2	25.06	n.a.	895.273	1089.884	93.18	n.a.	MB*
Total:			987.140	1169.602	100.00	0.000	

Fruit tea (S20):



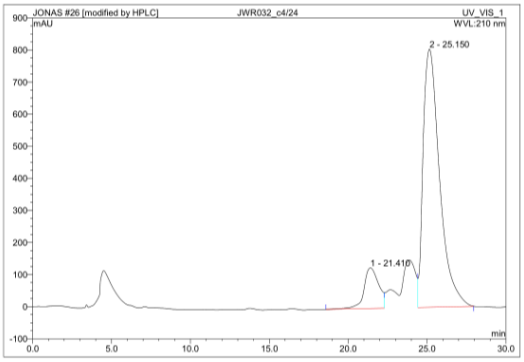
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.34	n.a.	53.026	45.408	6.90	n.a.	BM *
2	25.14	n.a.	514.646	612.285	93.10	n.a.	MB*
Total:			567.672	657.692	100.00	0.000	

Honey solution 5 wt% (S21):



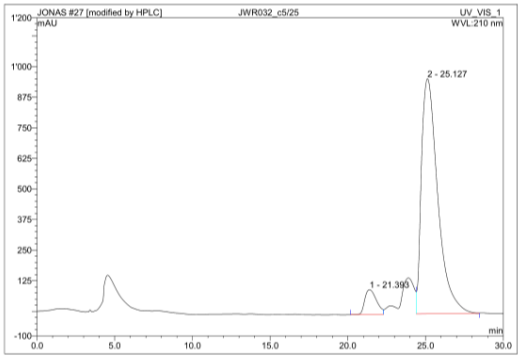
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.46	n.a.	50.044	59.132	14.50	n.a.	BM *
2	25.24	n.a.	292.524	348.797	85.50	n.a.	MB*
Total:			342.569	407.929	100.00	0.000	

Coke (S22):



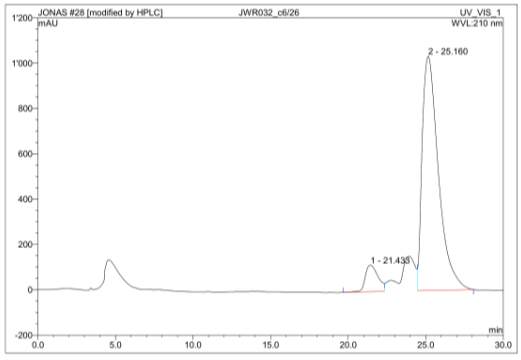
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.41	n.a.	126.247	136.346	12.28	n.a.	BM *
2	25.15	n.a.	804.296	973.627	87.72	n.a.	MB*
Total:			930.543	1109.973	100.00	0.000	

Rivella (S23):



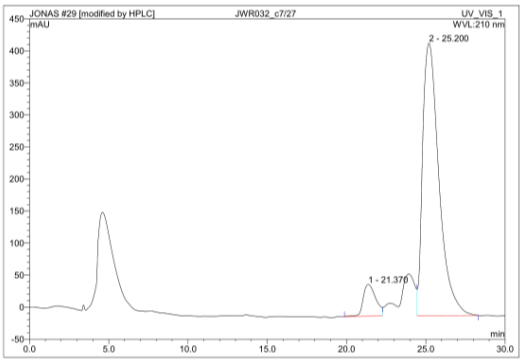
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.39	n.a.	101.090	88.544	7.02	n.a.	BM *
2	25.13	n.a.	960.501	1172.134	92.98	n.a.	MB*
Total:			1061.591	1260.678	100.00	0.000	

Diet Rivella (S24):



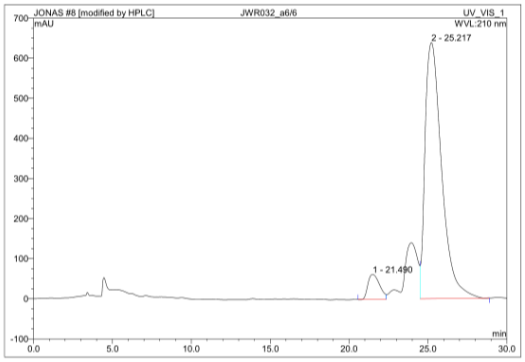
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.43	n.a.	116.778	111.964	8.18	n.a.	BM *
2	25.16	n.a.	1033.797	1256.250	91.82	n.a.	MB*
Total:			1150.575	1368.214	100.00	0.000	

Ice tea (S25):



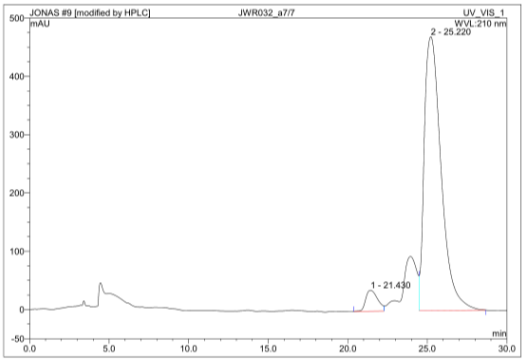
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.37	n.a.	49.374	45.422	8.21	n.a.	BM *
2	25.20	n.a.	425.564	507.889	91.79	n.a.	MB*
Total:			474.938	553.311	100.00	0.000	

Beer (S26):



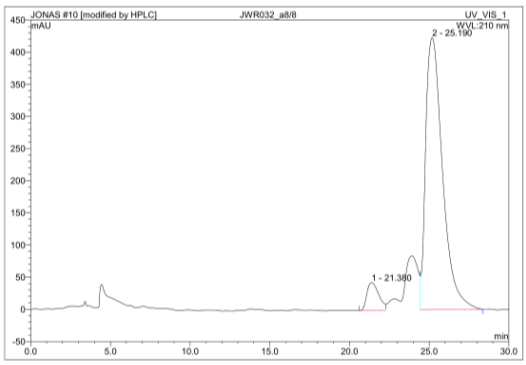
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.49	n.a.	62.261	53.409	6.41	n.a.	BM *
2	25.22	n.a.	638.841	779.374	93.59	n.a.	MB*
Total:			701.101	832.784	100.00	0.000	

Red wine (S27):



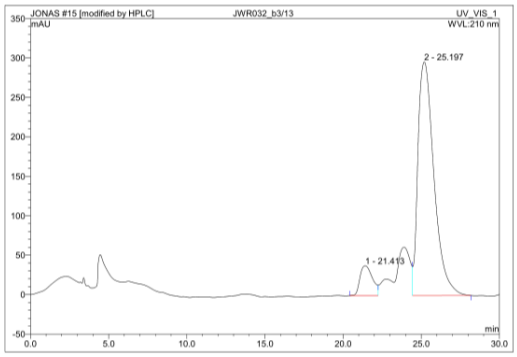
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.43	n.a.	35.883	31.276	5.12	n.a.	BM *
2	25.22	n.a.	469.928	579.639	94.88	n.a.	MB*
Total:			505.811	610.915	100.00	0.000	

Amaretto (S28):



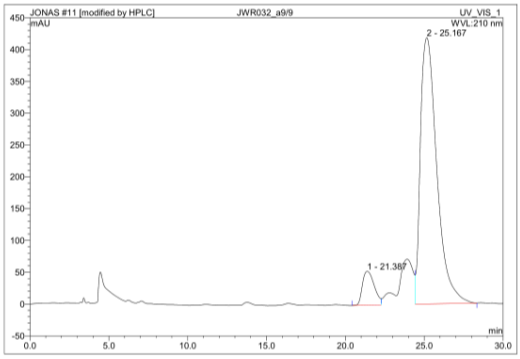
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.38	n.a.	42.868	36.878	6.63	n.a.	BM *
2	25.19	n.a.	423.162	519.656	93.37	n.a.	MB*
Total:			466.031	556.535	100.00	0.000	

Herb Liqueur – “Jägermeister” (S29):



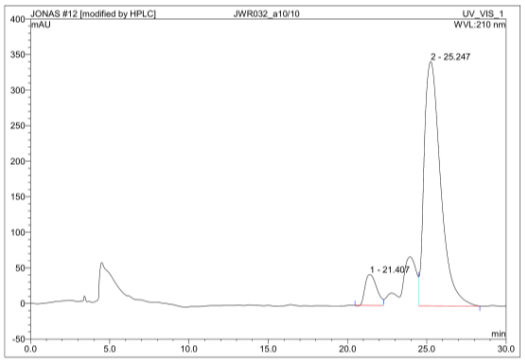
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.41	n.a.	37.863	35.148	9.07	n.a.	BM *
2	25.20	n.a.	296.222	352.573	90.93	n.a.	MB*
Total:			334.085	387.721	100.00	0.000	

Scotch Whisky – Aberlour 18 y (S30):



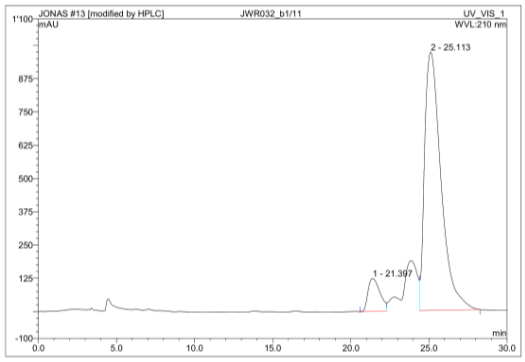
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.39	n.a.	53.174	46.364	8.42	n.a.	BM *
2	25.17	n.a.	418.639	504.577	91.58	n.a.	MB*
Total:			471.812	550.940	100.00	0.000	

Vodka (S31):



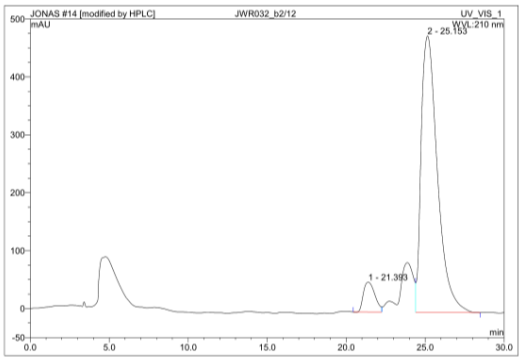
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.41	n.a.	43.667	37.241	8.24	n.a.	BM *
2	25.25	n.a.	343.580	414.642	91.76	n.a.	MB*
Total:			387.247	451.883	100.00	0.000	

Gin (S32):



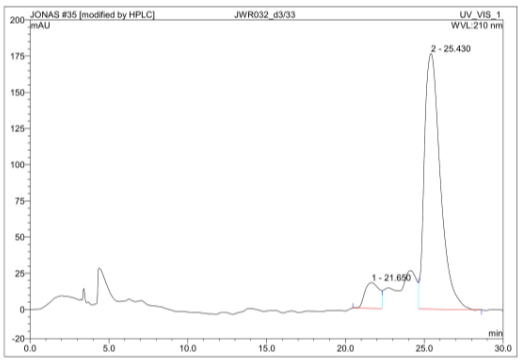
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.40	n.a.	123.539	109.900	8.49	n.a.	BM *
2	25.11	n.a.	971.086	1185.002	91.51	n.a.	MB*
Total:			1094.625	1294.903	100.00	0.000	

Rum (S33):



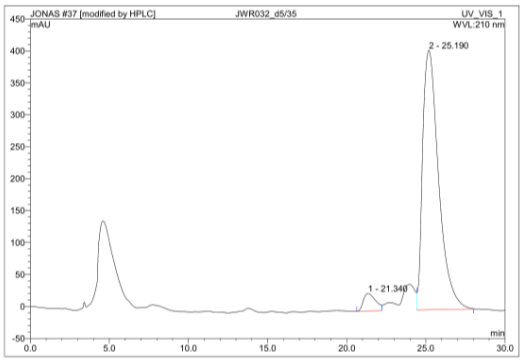
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.39	n.a.	51.471	43.657	7.09	n.a.	BM *
2	25.15	n.a.	477.146	572.121	92.91	n.a.	MB*
Total:			528.617	615.777	100.00	0.000	

Aceto balsamico (S34):



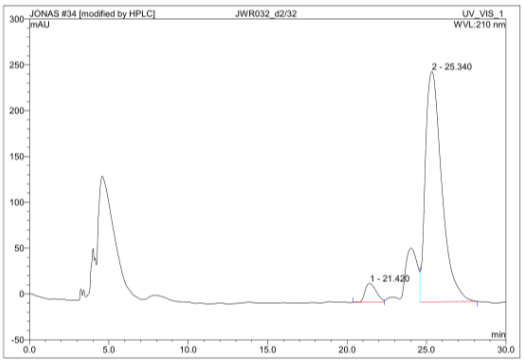
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.65	n.a.	17.721	18.636	8.23	n.a.	BM *
2	25.43	n.a.	176.518	207.815	91.77	n.a.	MB*
Total:			194.239	226.451	100.00	0.000	

Herb vinegar (S35):



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.34	n.a.	27.153	24.680	4.93	n.a.	BM *
2	25.19	n.a.	406.388	475.913	95.07	n.a.	MB*
Total:			433.541	500.593	100.00	0.000	

Olive oil (S36):

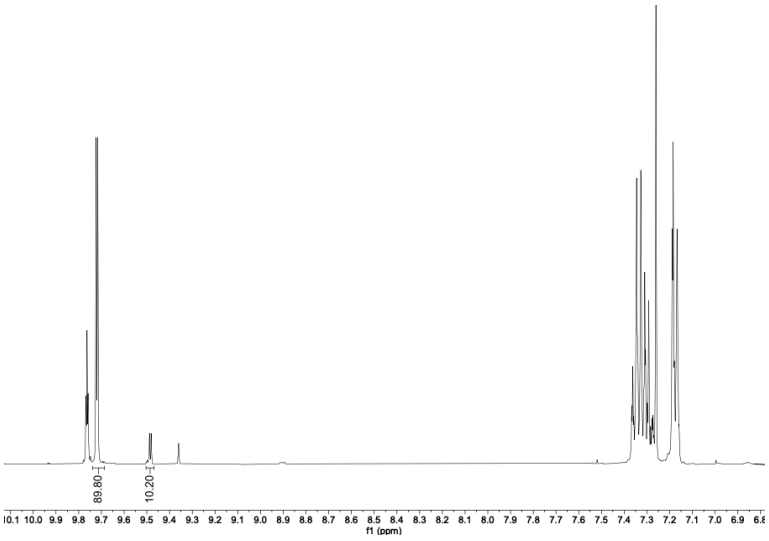


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.42	n.a.	20.477	16.950	5.33	n.a.	BM *
2	25.34	n.a.	251.399	301.333	94.67	n.a.	MB*
Total:			271.876	318.284	100.00	0.000	

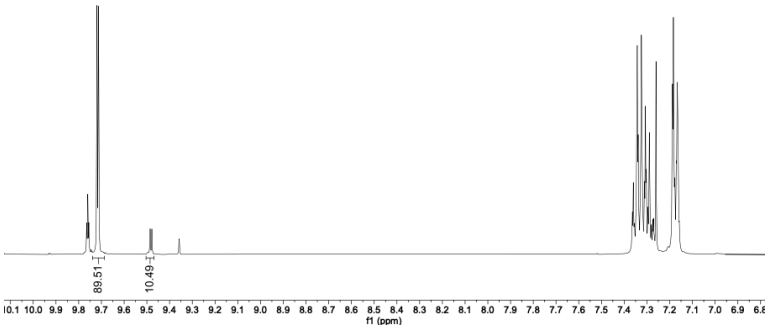
^{1}H NMR spectra of the reactions in the presence of H-DPro-MePro-Glu-NH_2 2:

A sample of 50 μL from the crude reaction mixture was added to an NMR tube that contained 600 μL $CDCl_3$. Vigorous shaking or vortexing ensured extraction of the reaction products from the mixture. Conversion was determined by comparing the integrals of the olefinic signal of nitrostyrene and the RCHO signals of the γ-nitroaldehyde. The diastereomeric ratio was determined by integration of the RCHO signals of the γ-nitroaldehyde.

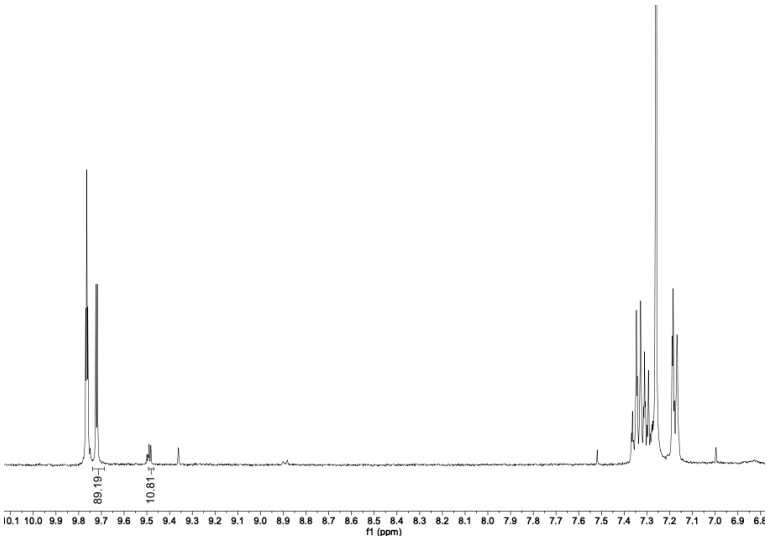
MilliQ water (S1):



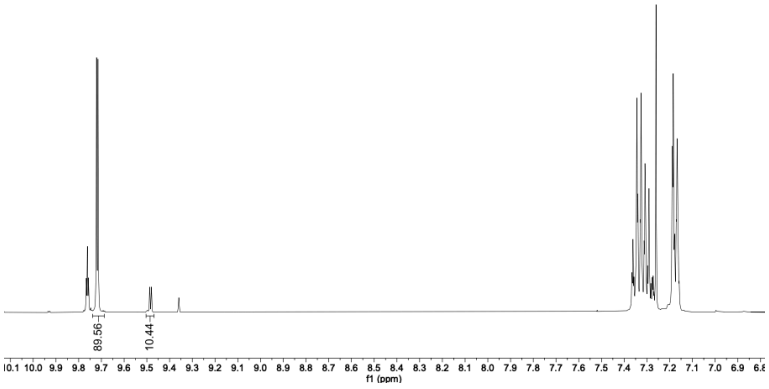
Tab water (S2):



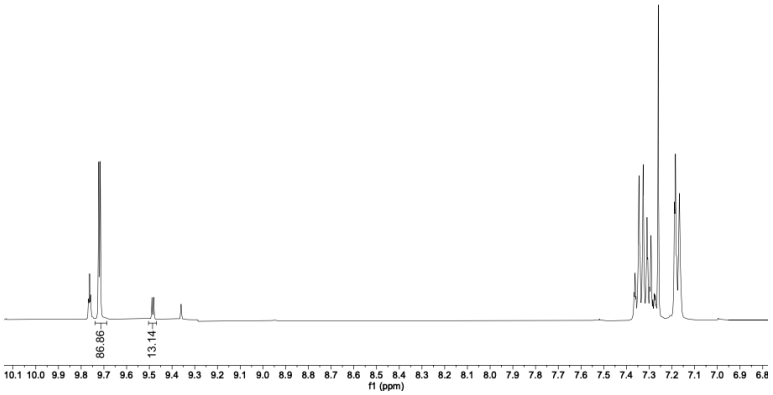
Lake Zürich water (S3):



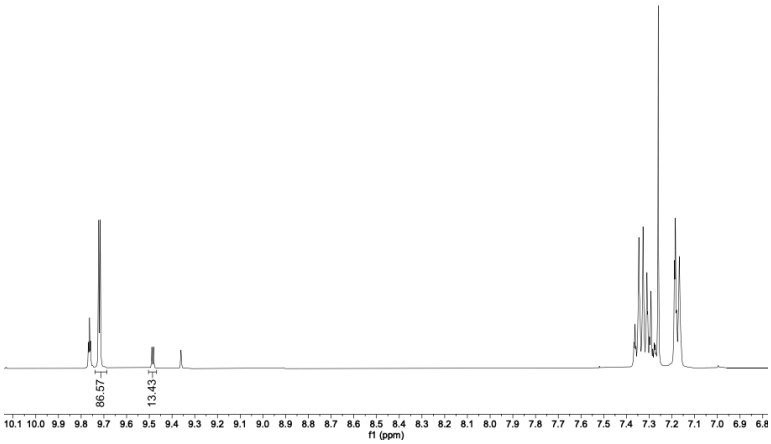
River Limmat water (S4):



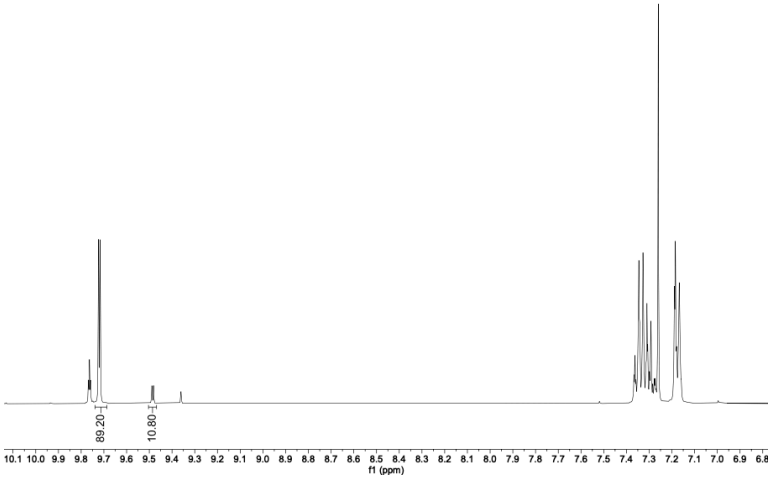
Milk (S5):



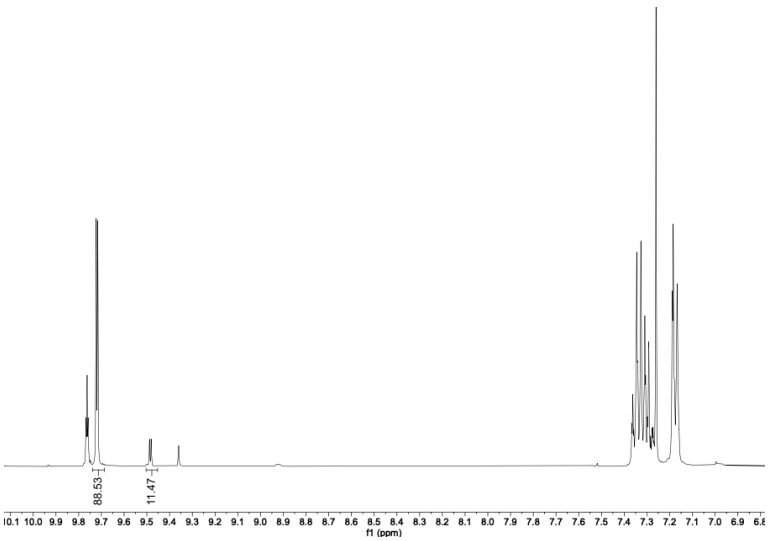
Low fat milk (S6):



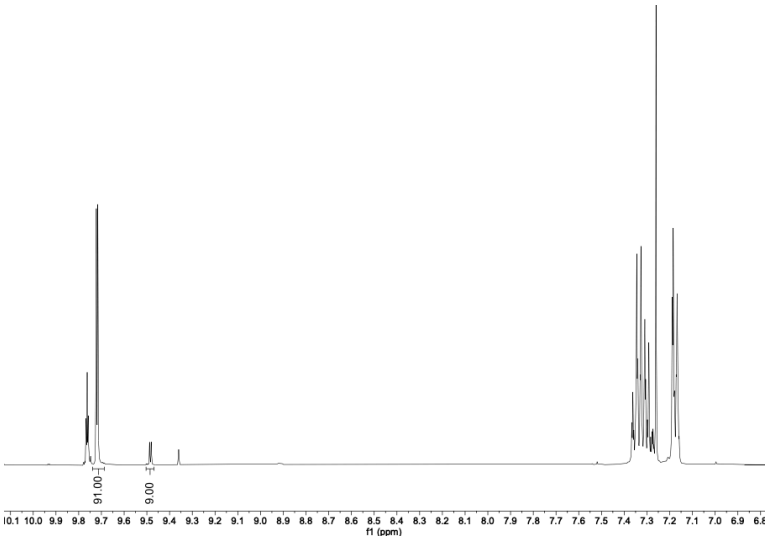
Soya milk (S7):



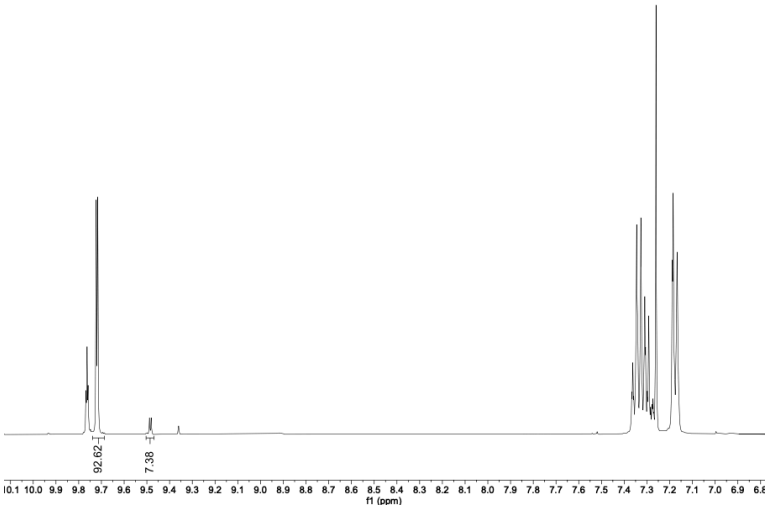
Almond milk (S8):



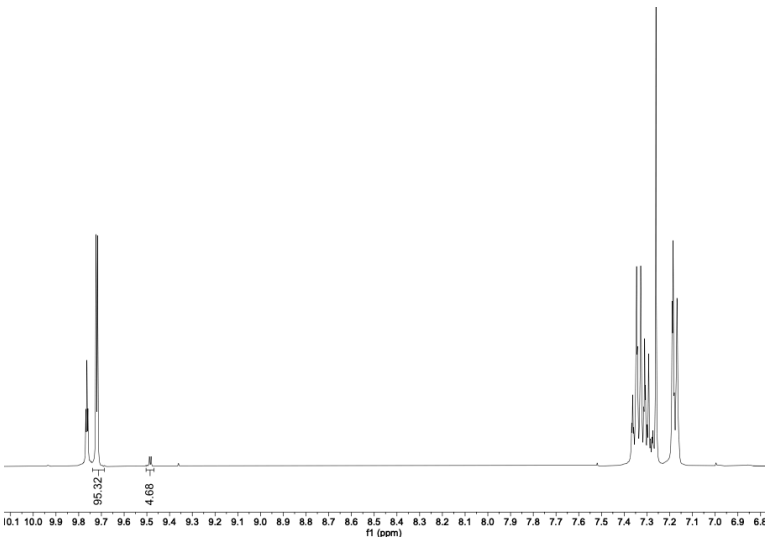
Rice milk (S9):



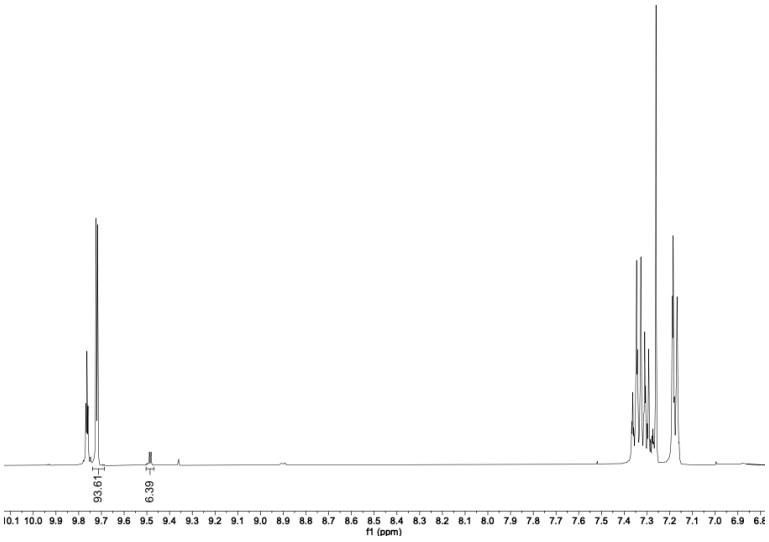
Orange juice (S10):



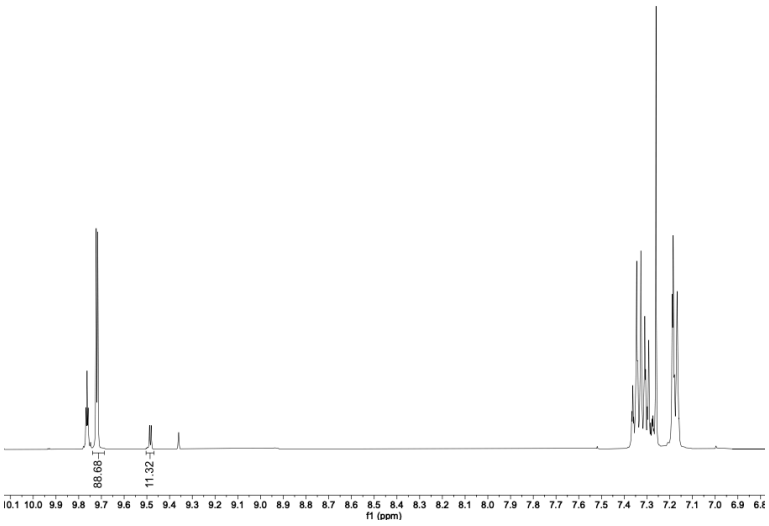
Blood orange juice (S11):



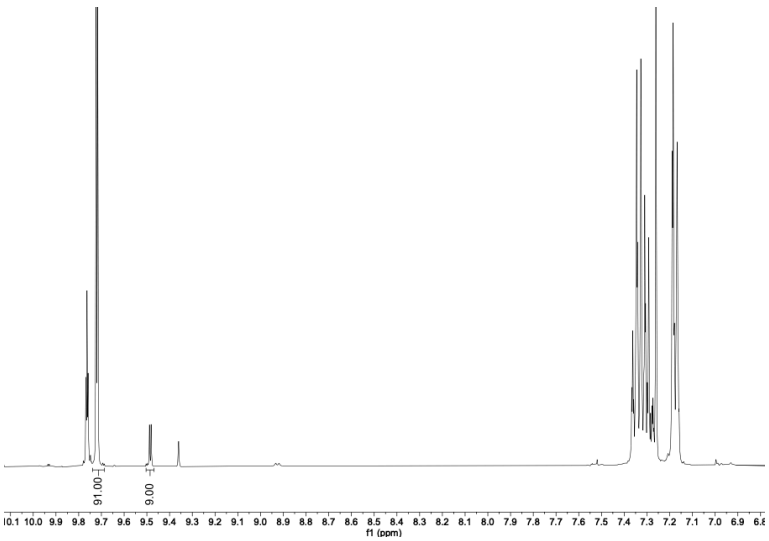
Apple juice (S12):



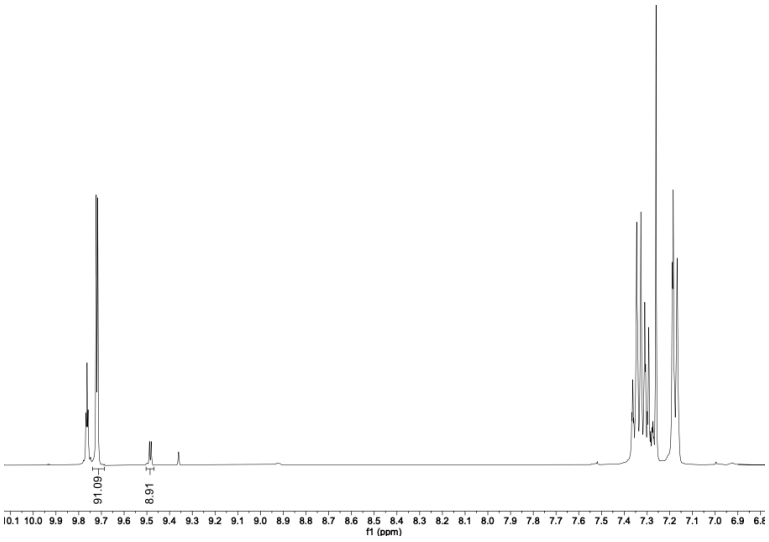
Coconut water (S13):



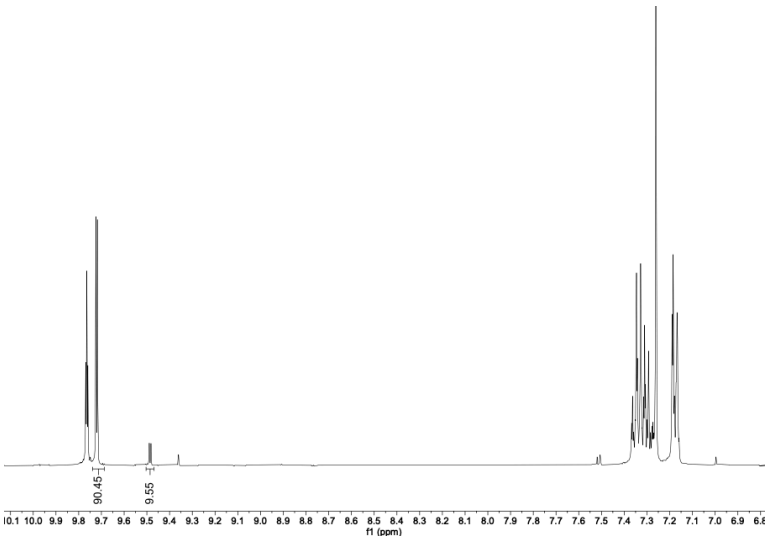
Carrot juice (S14):



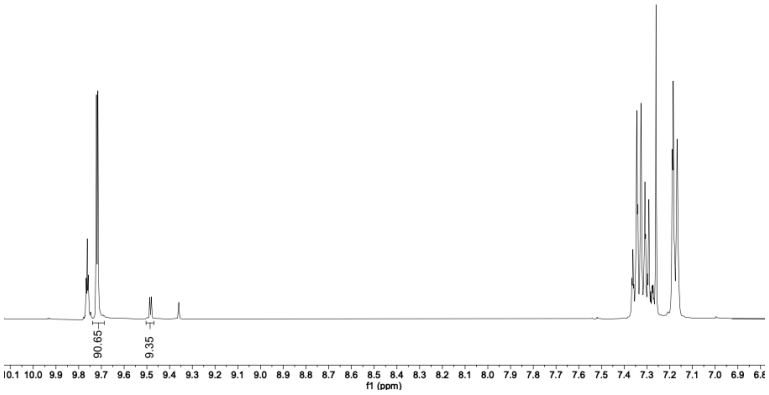
Beetroot juice (S15):



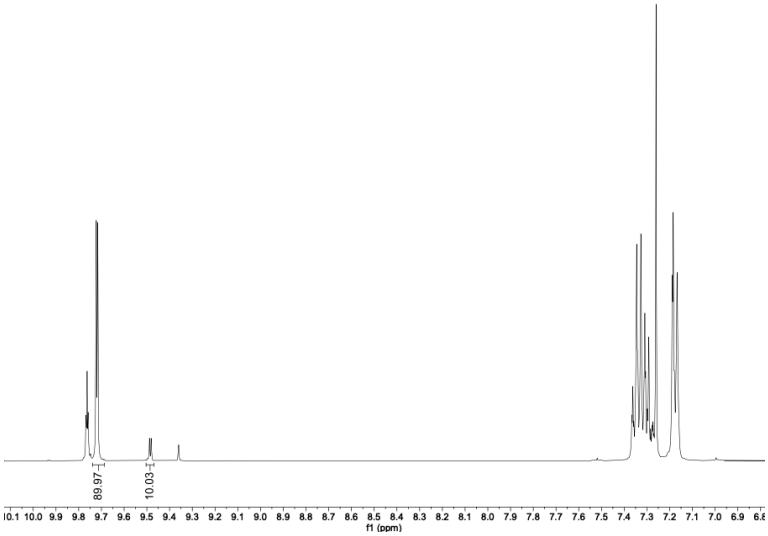
Coffee (S16):



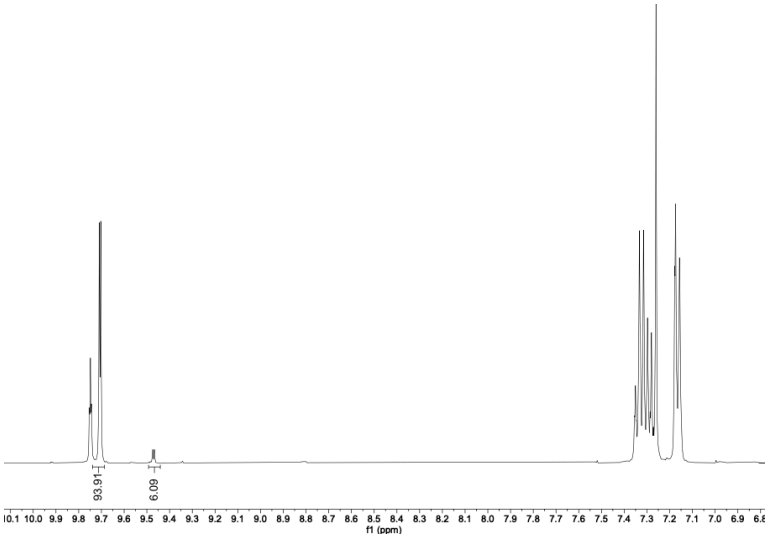
Green tea (S17):



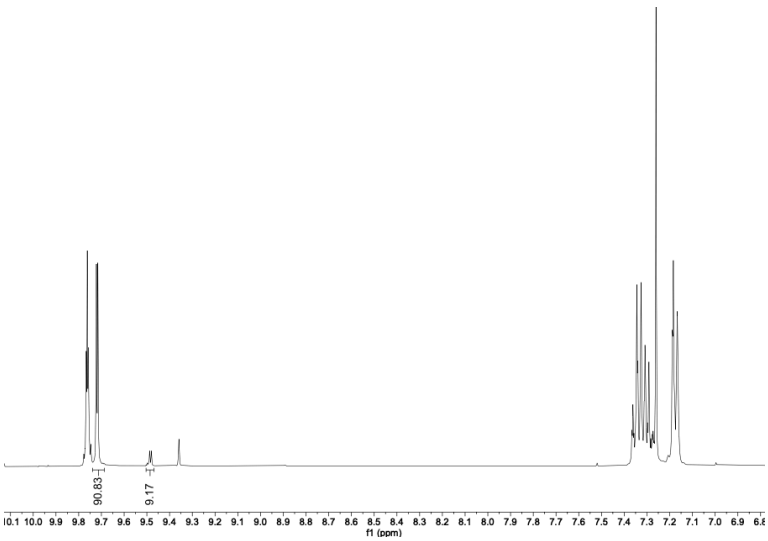
Black tea (S18):



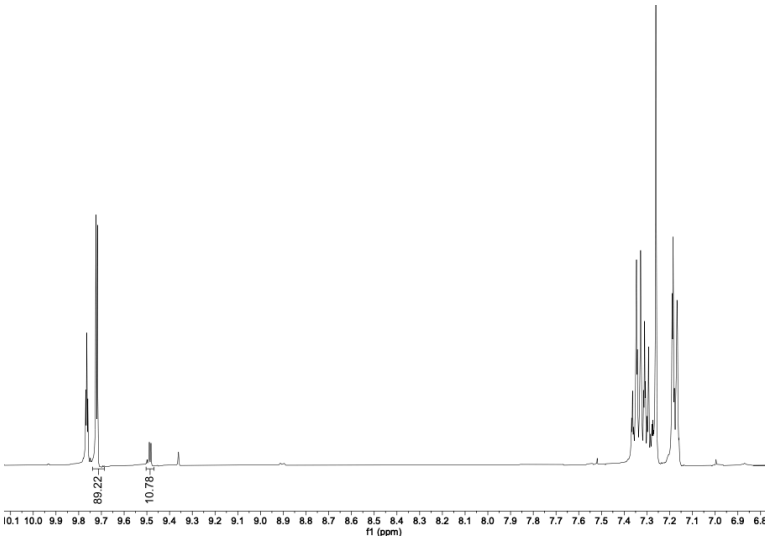
Peppermint tea (S19):



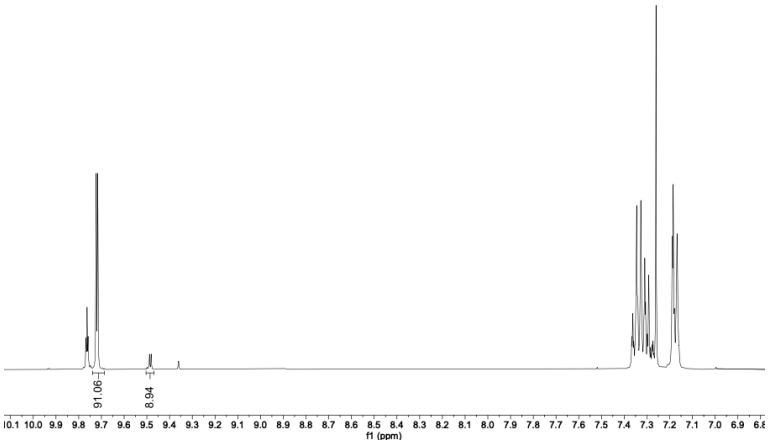
Fruit tea (S20):



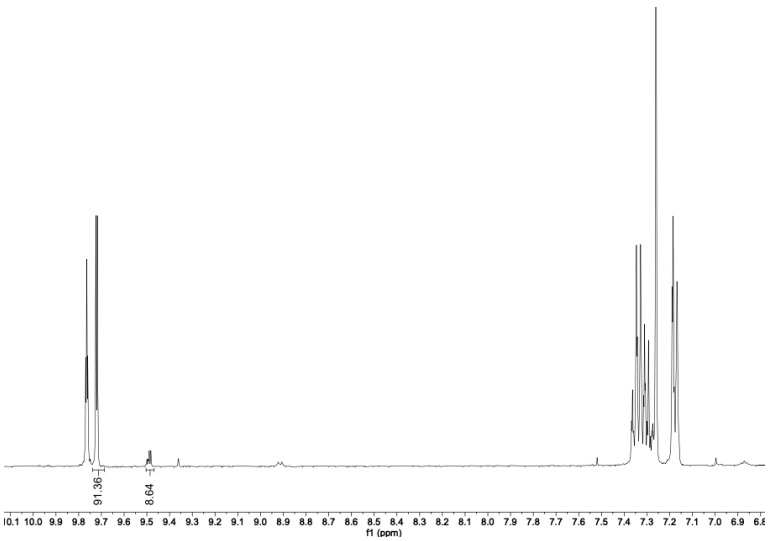
Honey solution 5 wt% (S21):



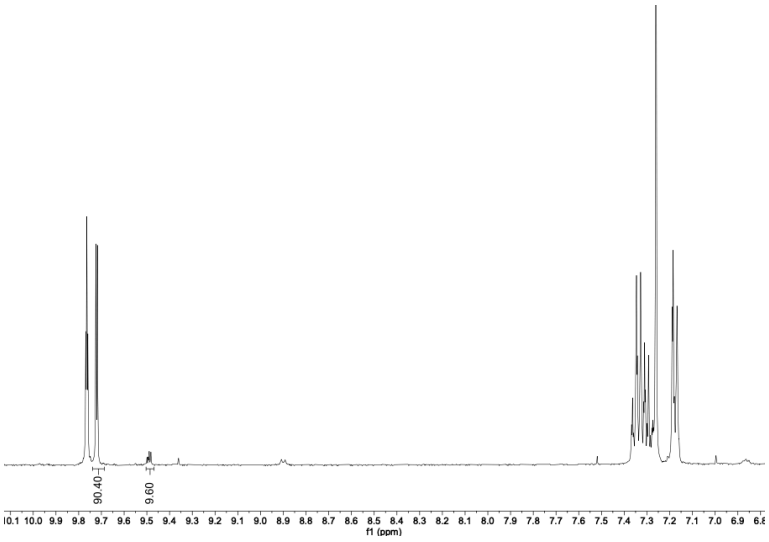
Coke (S22):



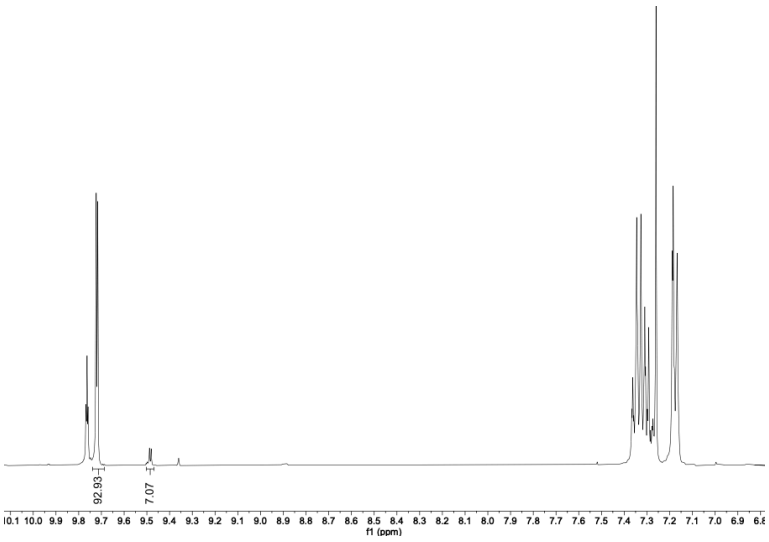
Rivella (S23):



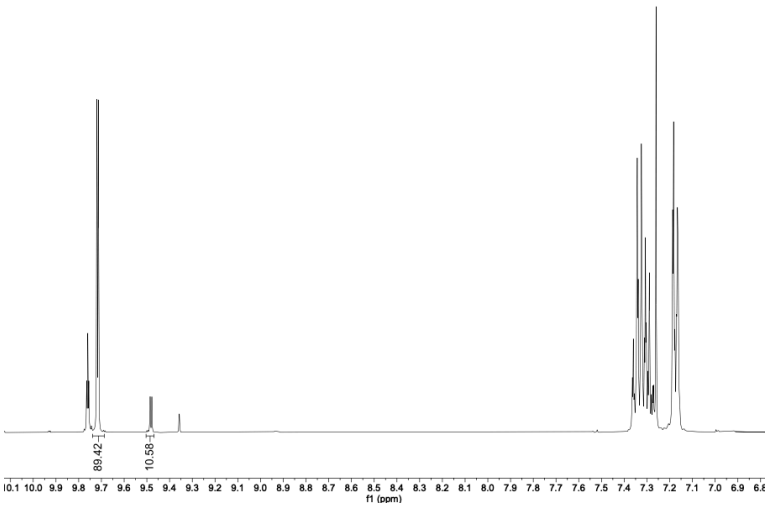
Diet Rivella (S24):



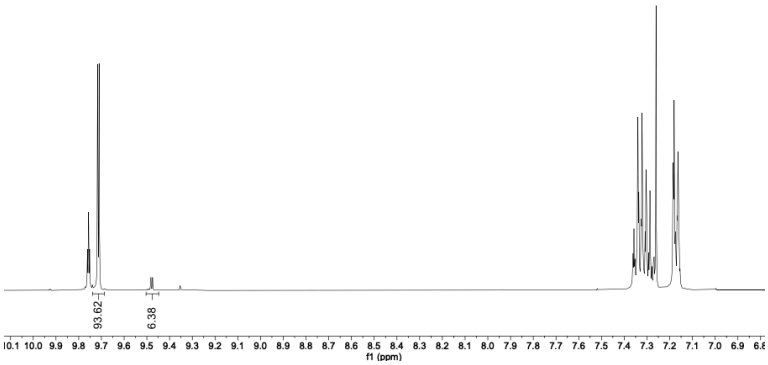
Ice tea (S25):



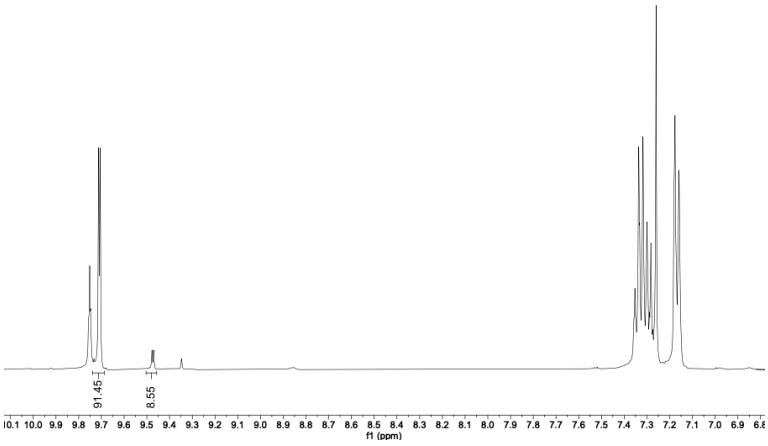
Beer (S26):



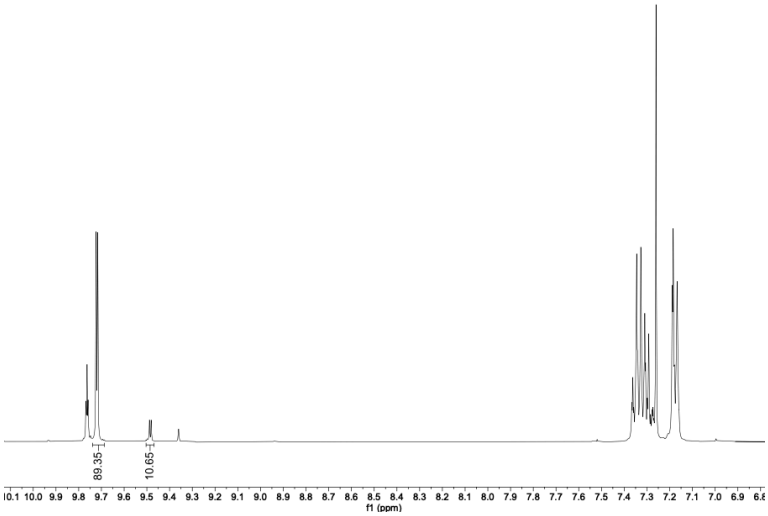
Red wine (S27):



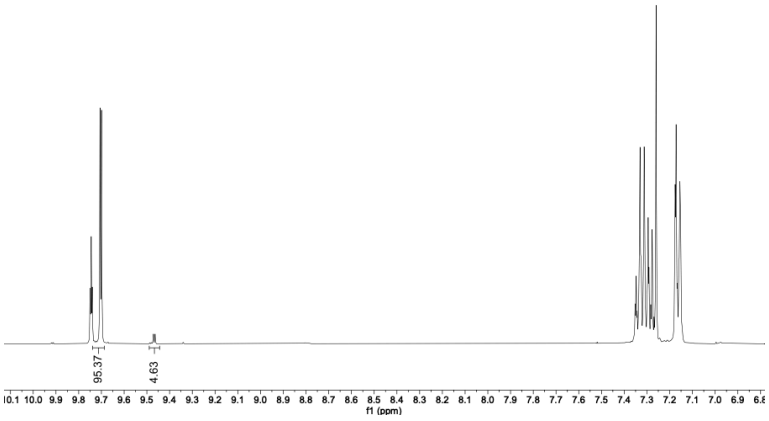
Amaretto (S28):



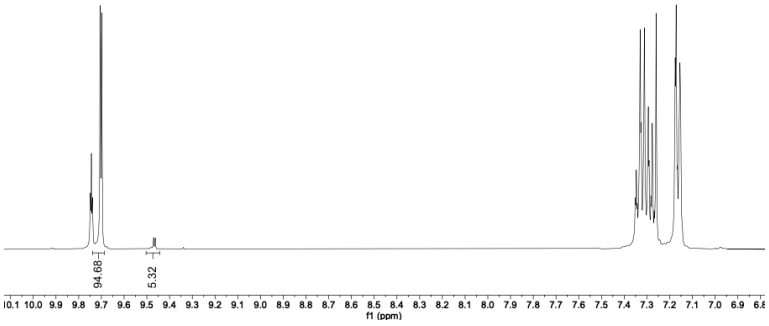
Herb Liqueur – "Jägermeister" (S29):



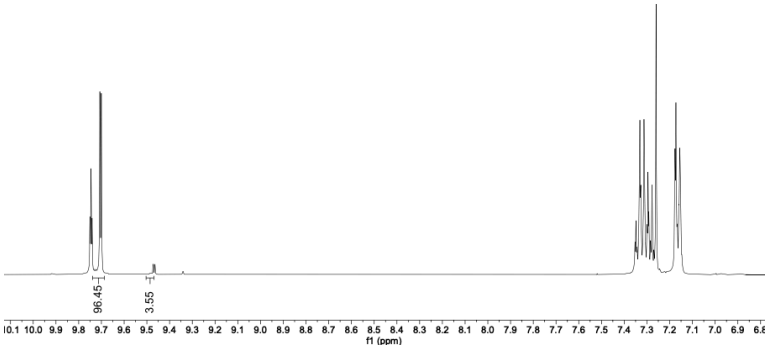
Scotch Whisky – Aberlour 18 y (S30):



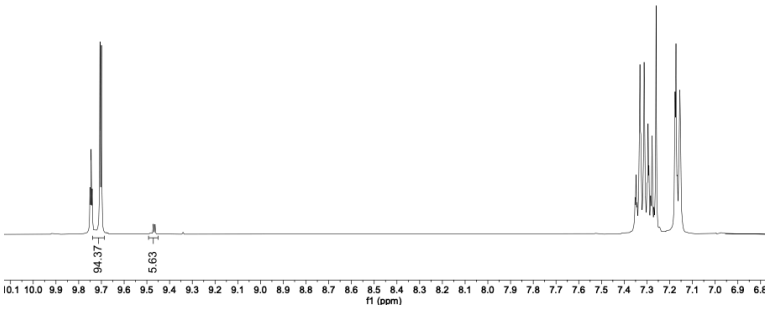
Vodka (S31):



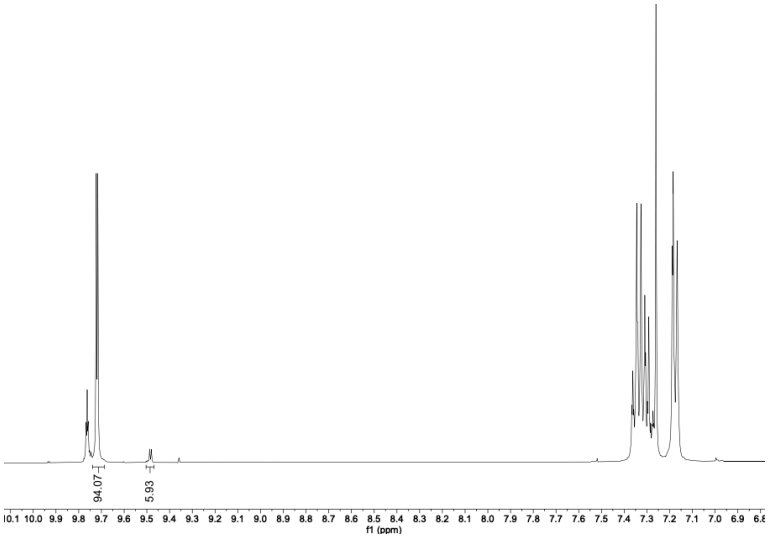
Gin (S32):



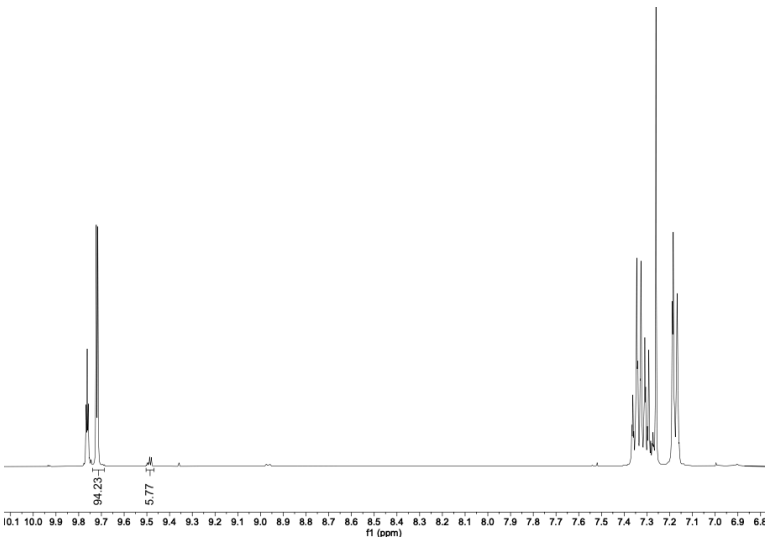
Rum (S33):



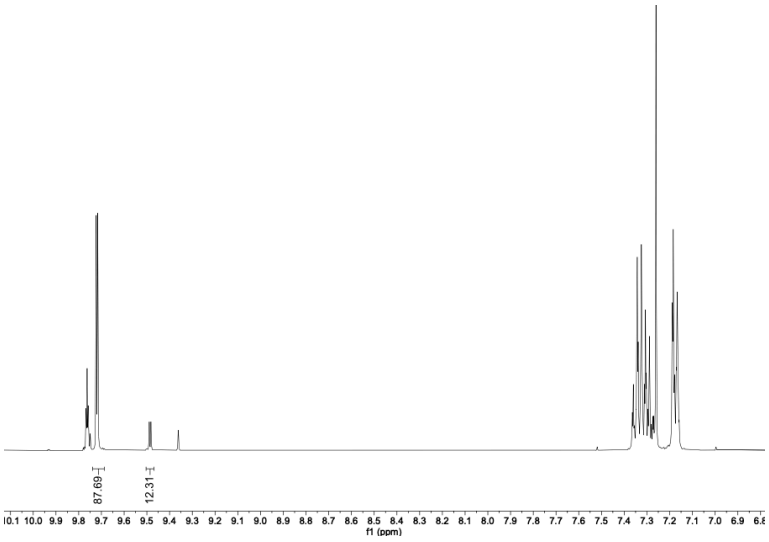
Aceto balsamico (S34):



Herb vinegar (S35):



Olive oil (S36):

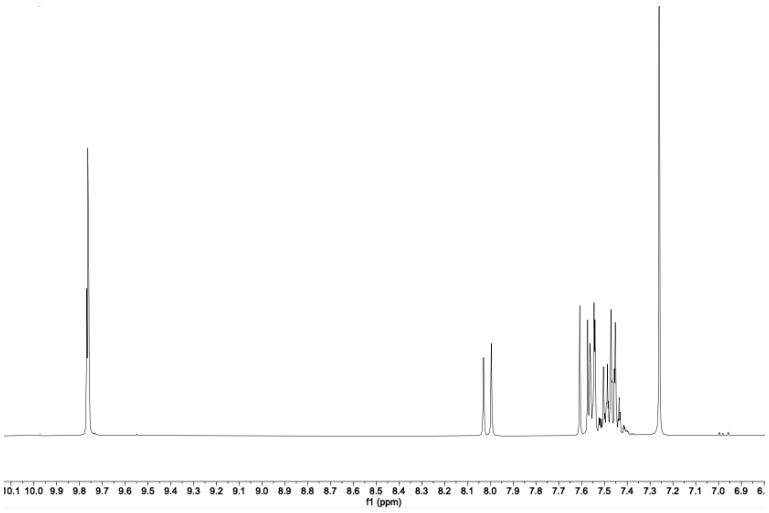


Control Experiments (Reaction without Catalyst in complex mixtures):

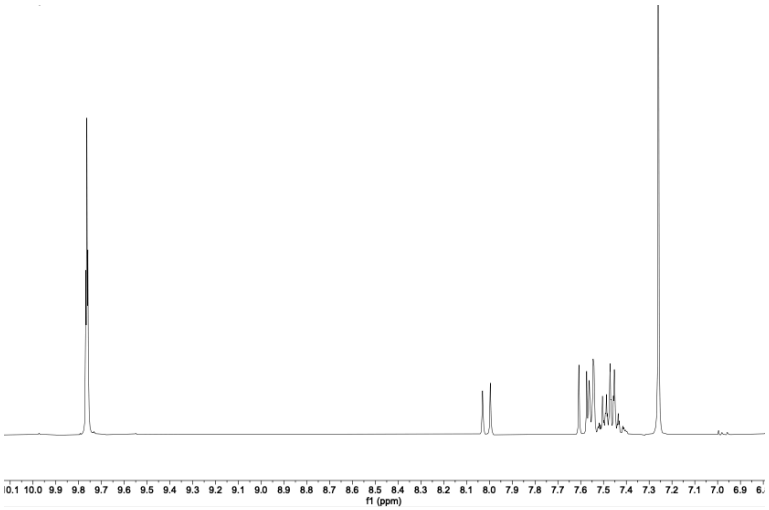
MilliQ water (S1):

See ref 1.

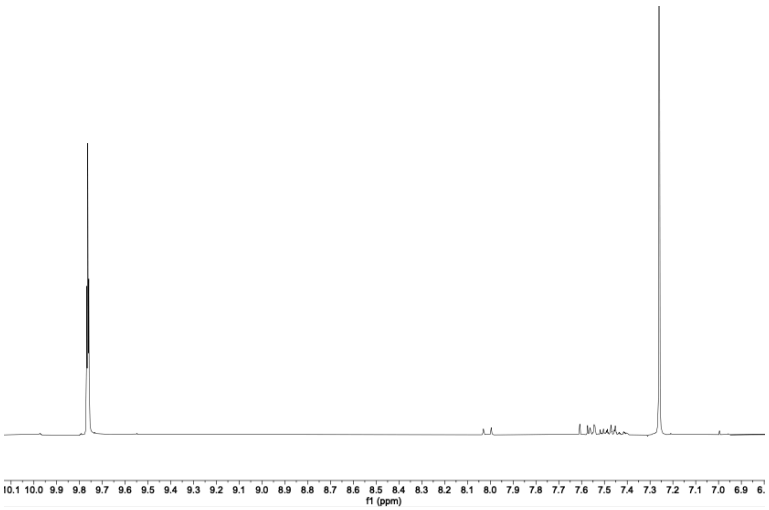
Tab water (S2):



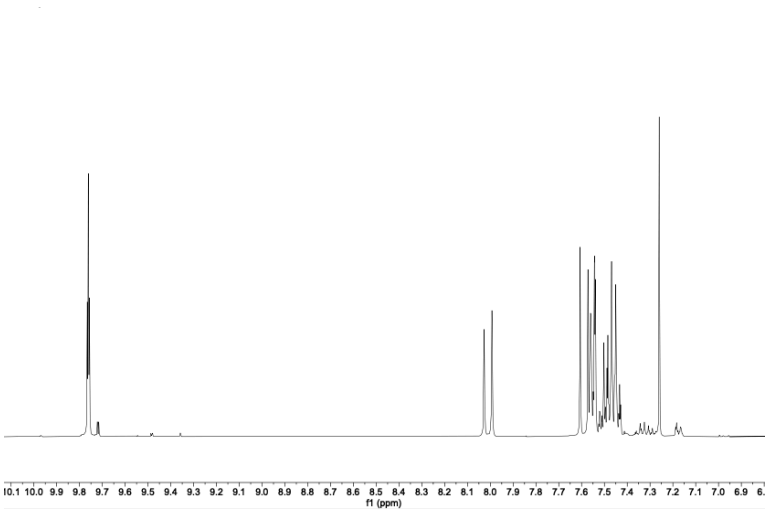
Lake Zürich water (S3):



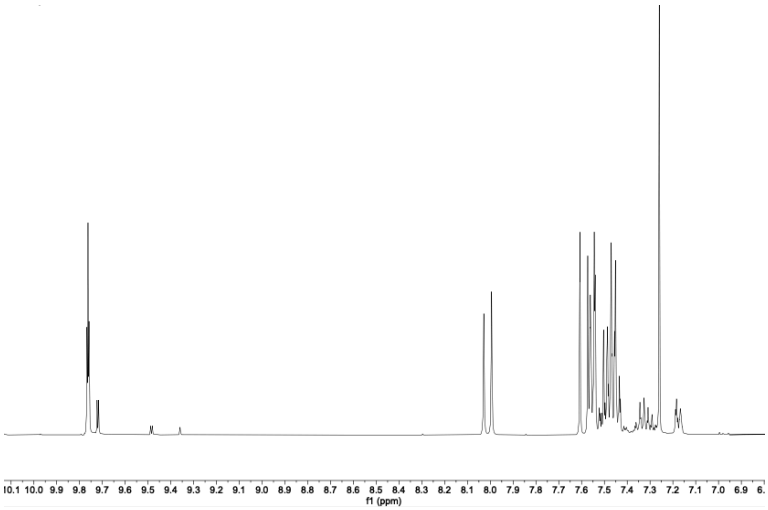
River Limmat water (S4):



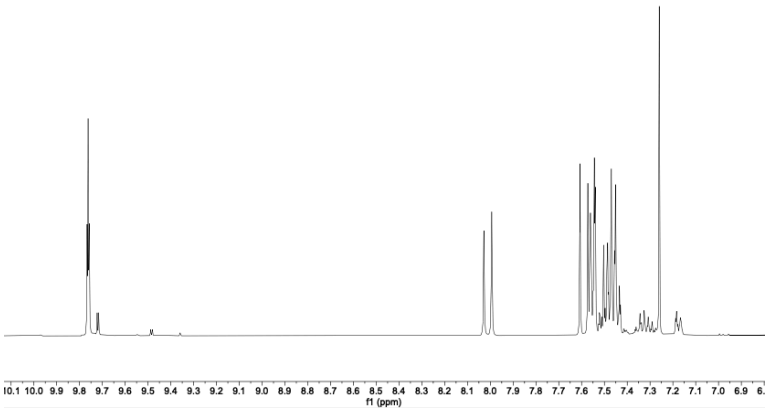
Milk (S5):



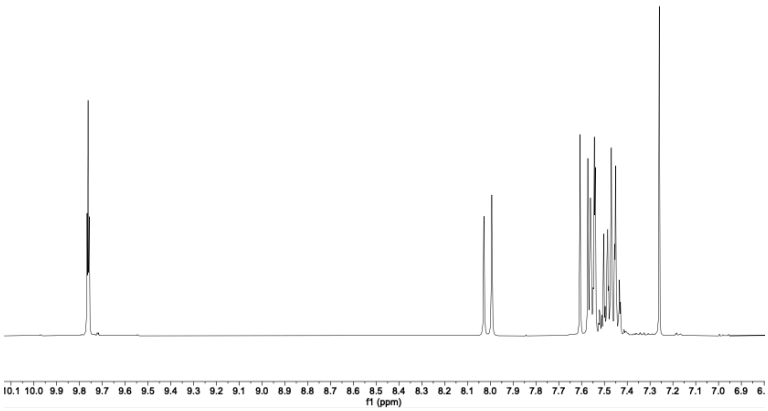
Low fat milk (S6):



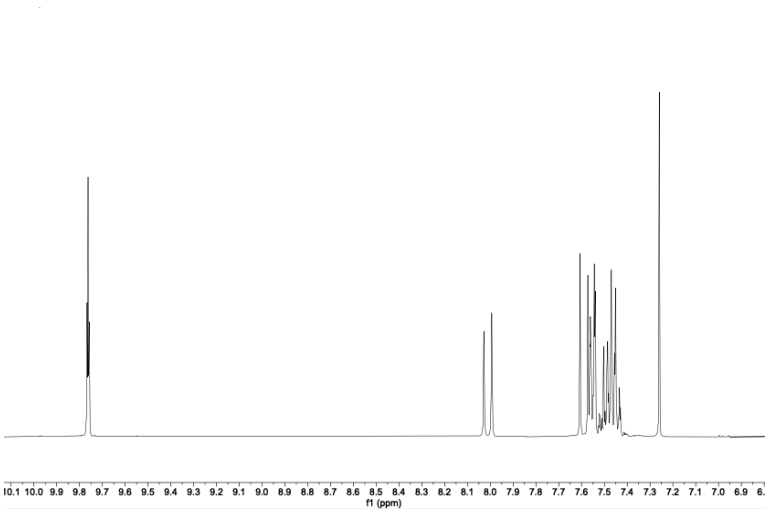
Soya milk (S7):



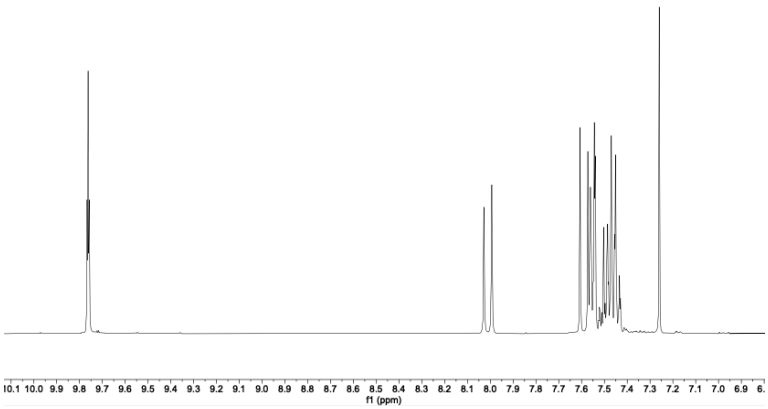
Almond milk (S8):



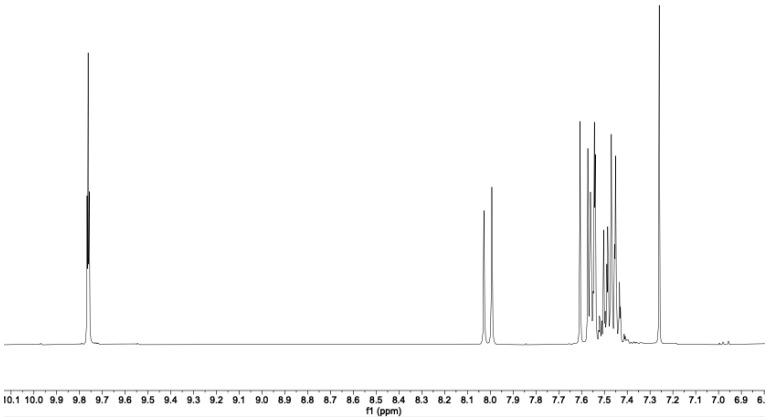
Rice milk (S9):



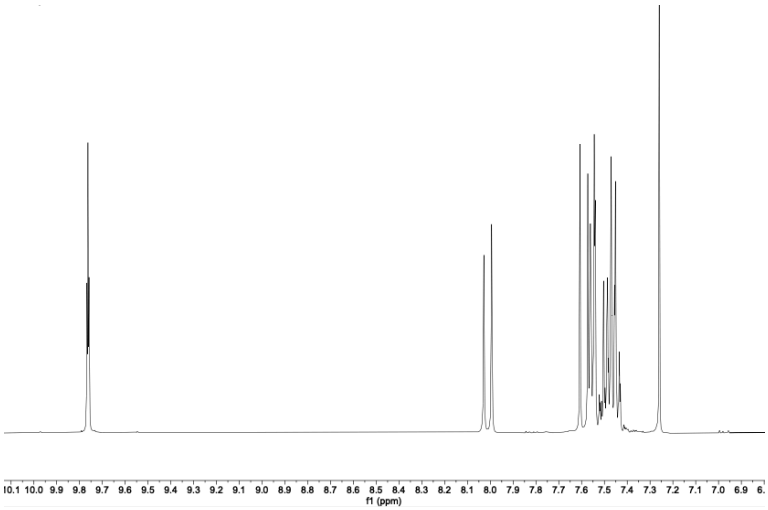
Orange juice (S10):



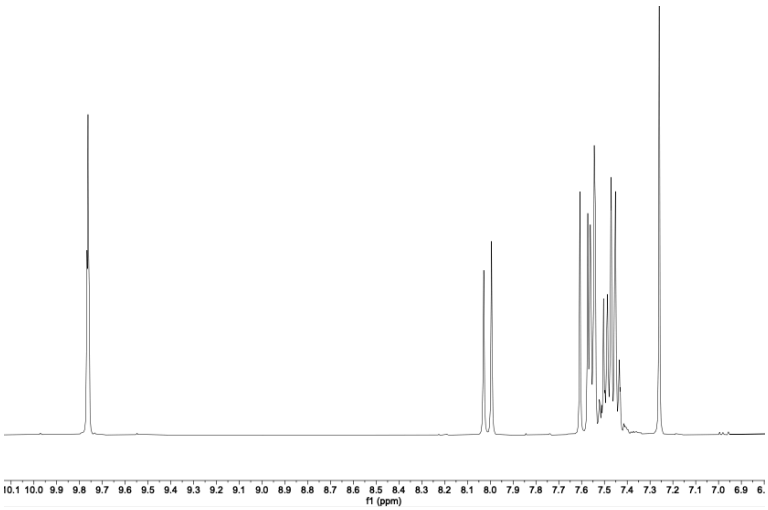
Blood orange juice (S11):



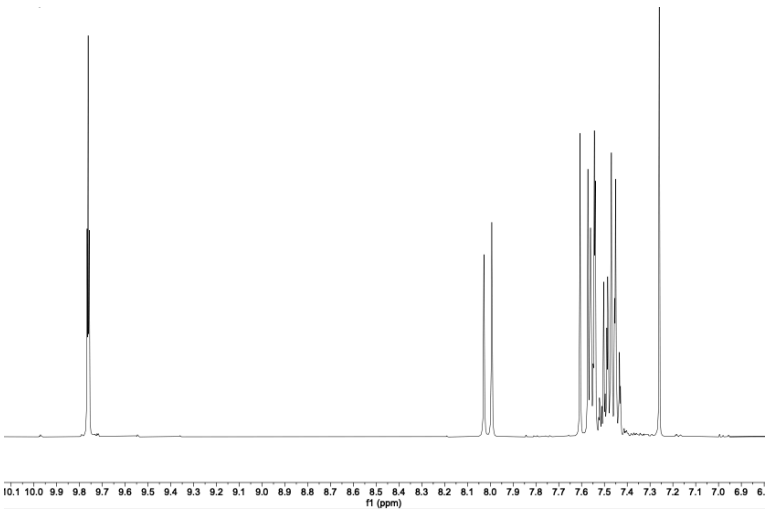
Apple juice (S12):



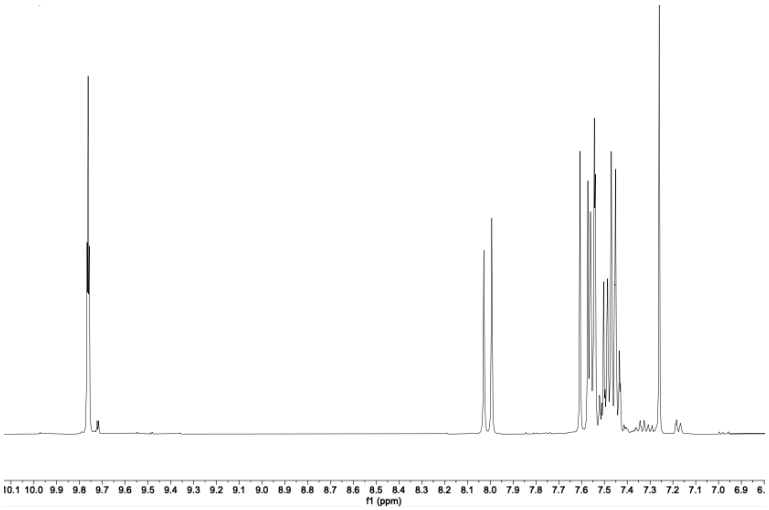
Coconut water (S13):



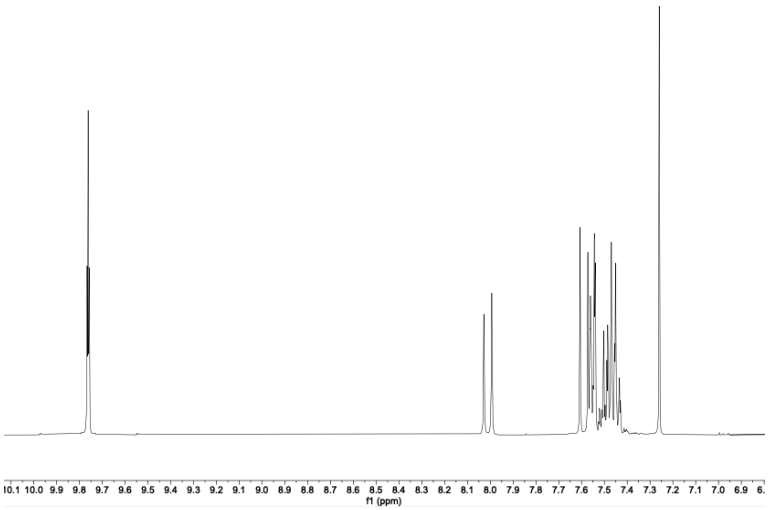
Carrot juice (S14):



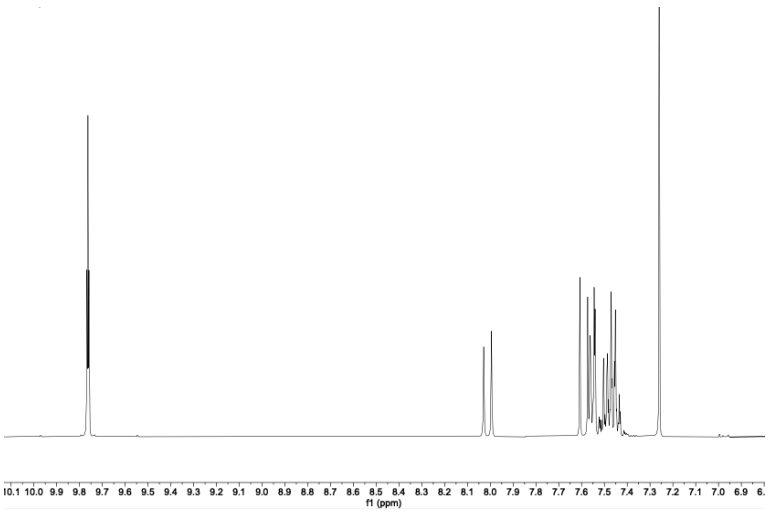
Beetroot juice (S15):



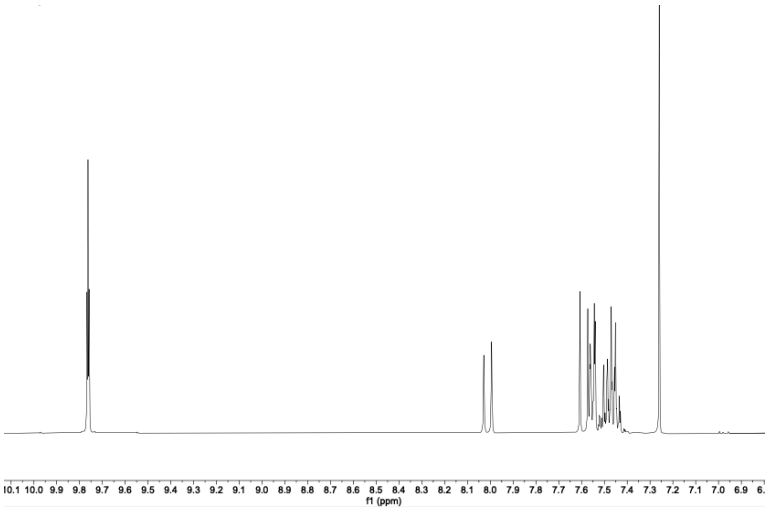
Coffee (S16):



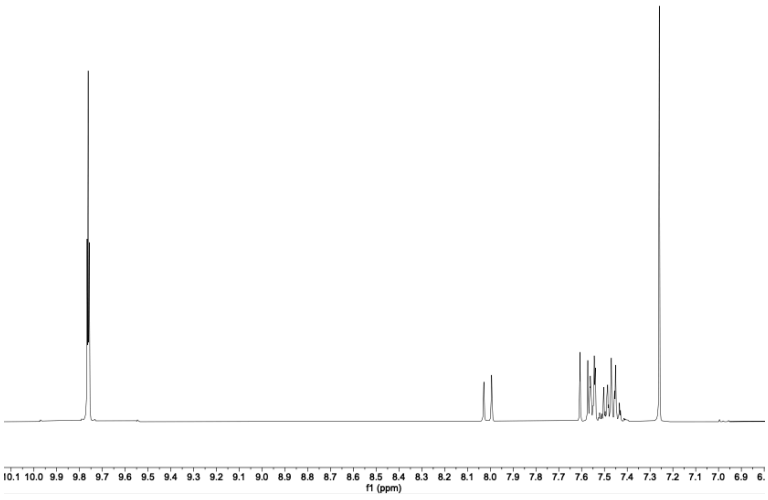
Green tea (S17):



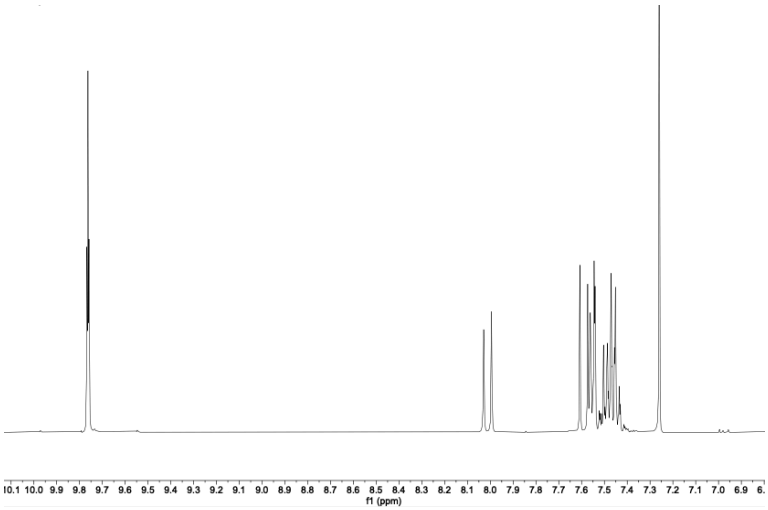
Black tea (S18):



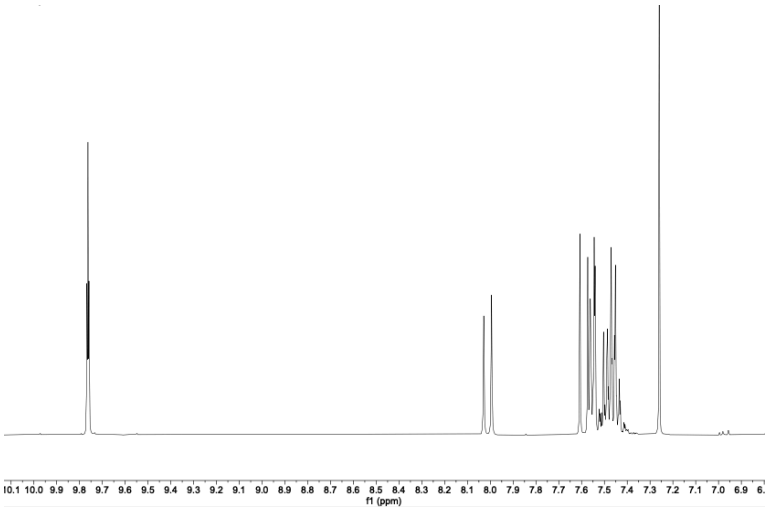
Peppermint tea (S19):



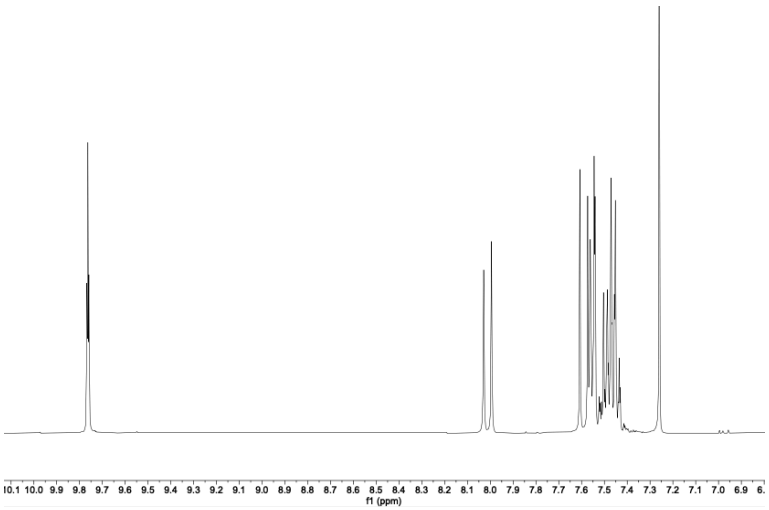
Fruit tea (S20):



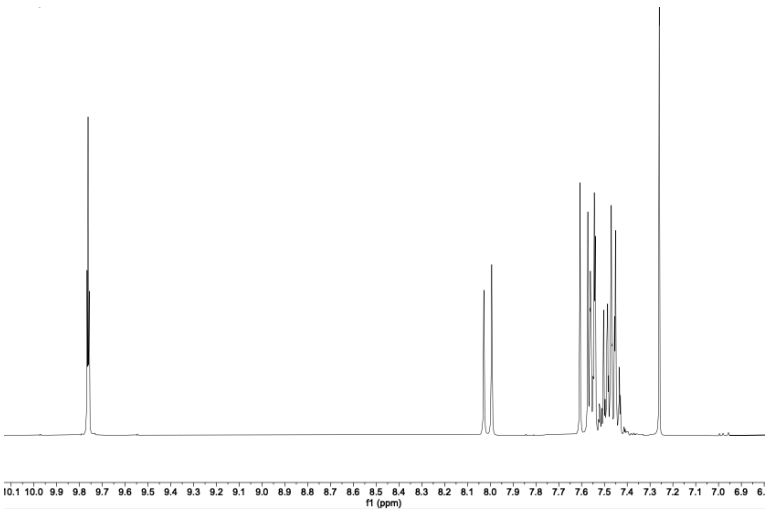
Honey solution 5 wt% (S21):



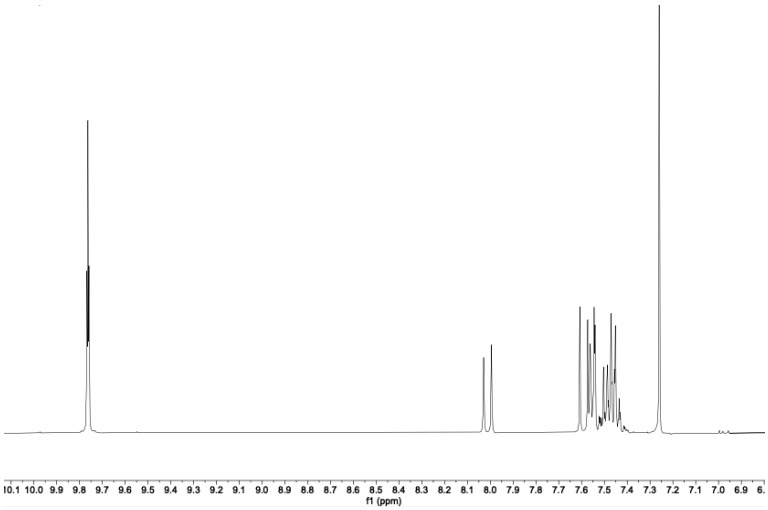
Coke (S22):



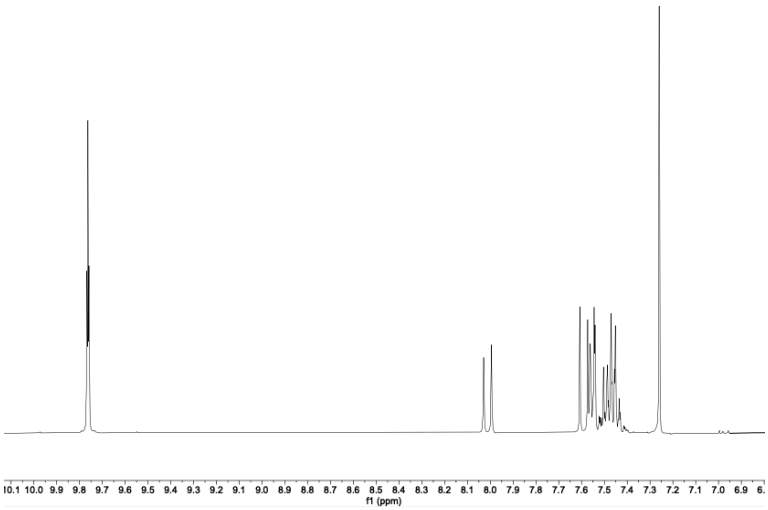
Rivella (S23):



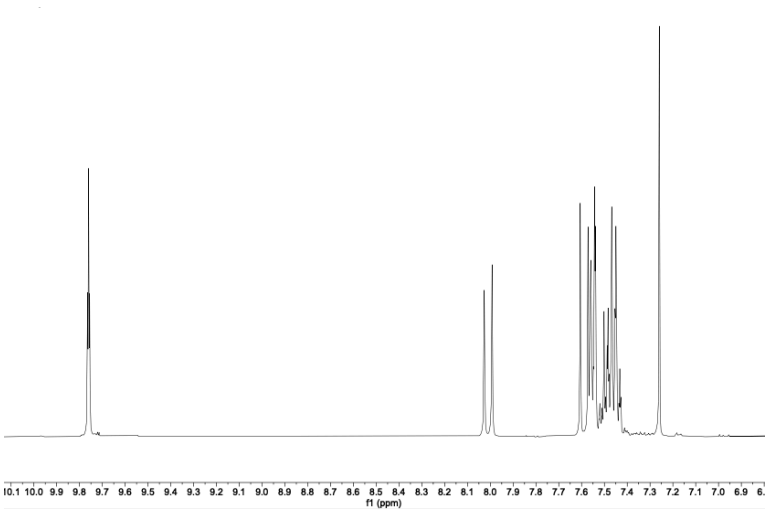
Diet Rivella (S24):



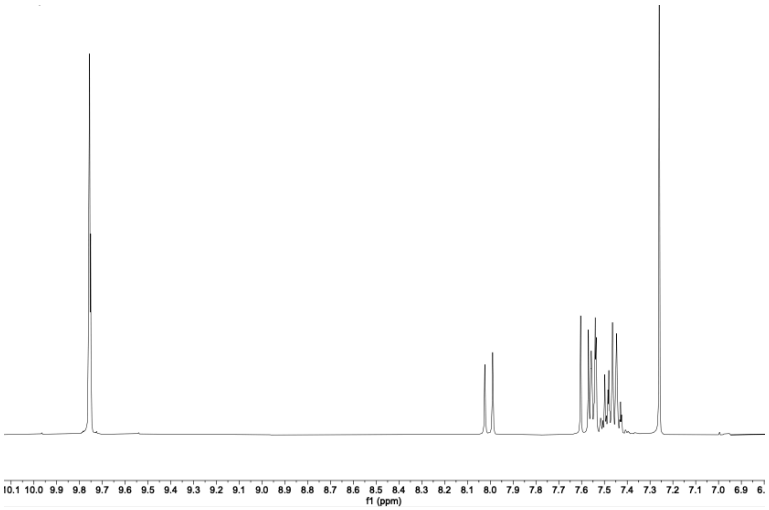
Ice tea (S25):



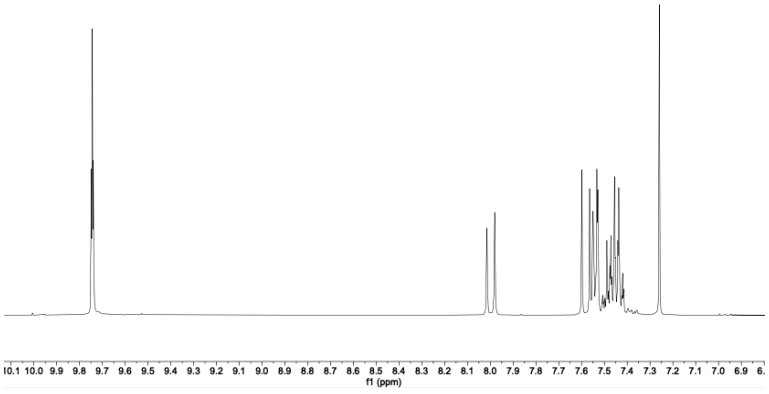
Beer (S26):



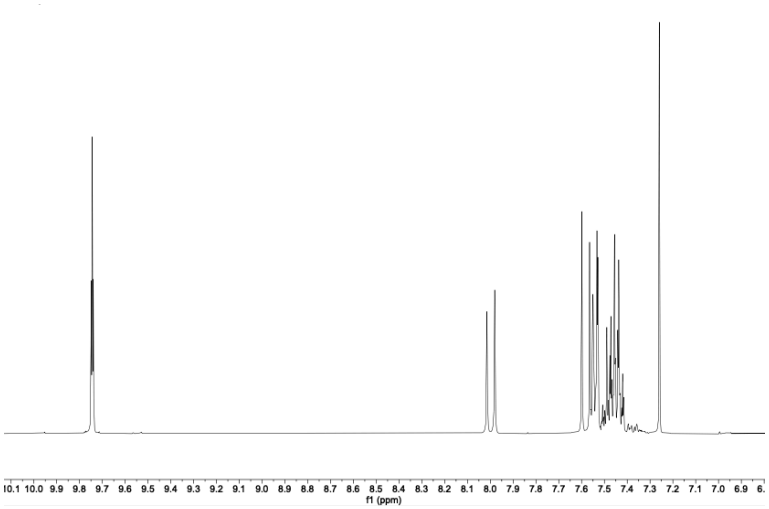
Red wine (S27):



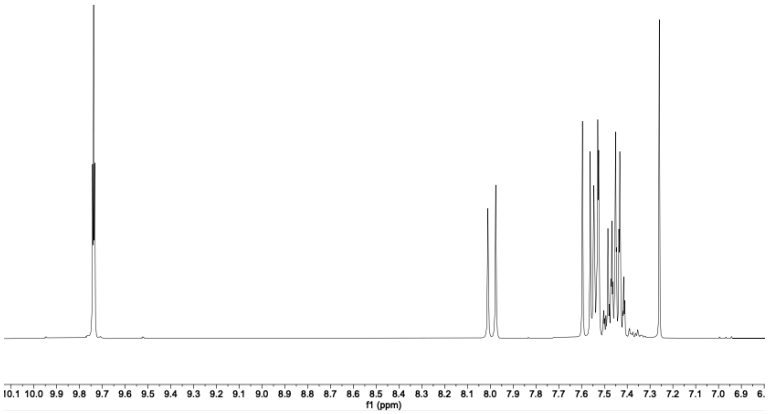
Amaretto (S28):



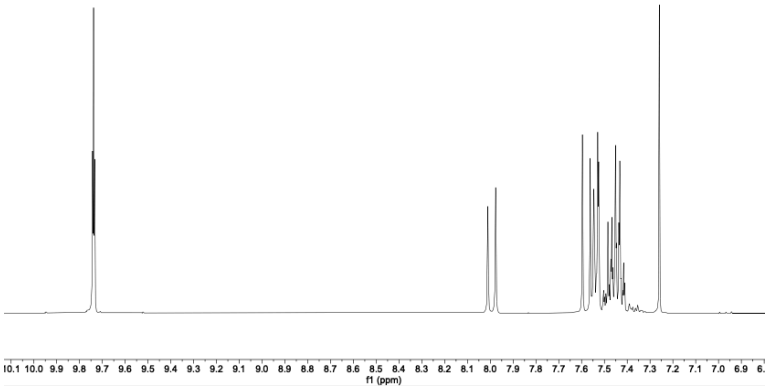
Herb Liqueur – "Jägermeister" (S29):



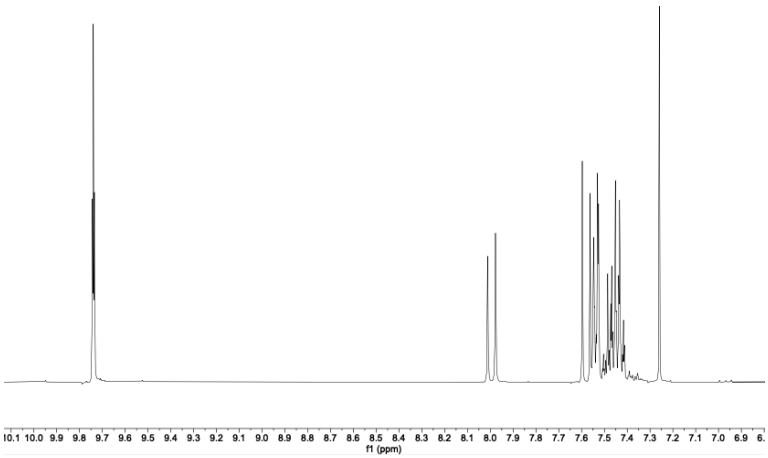
Scotch Whisky – Aberlour 18 y (S30):



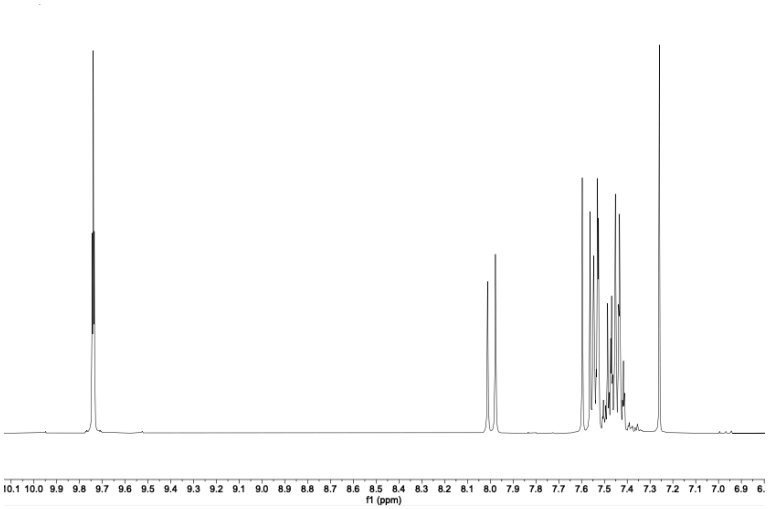
Vodka (S31):



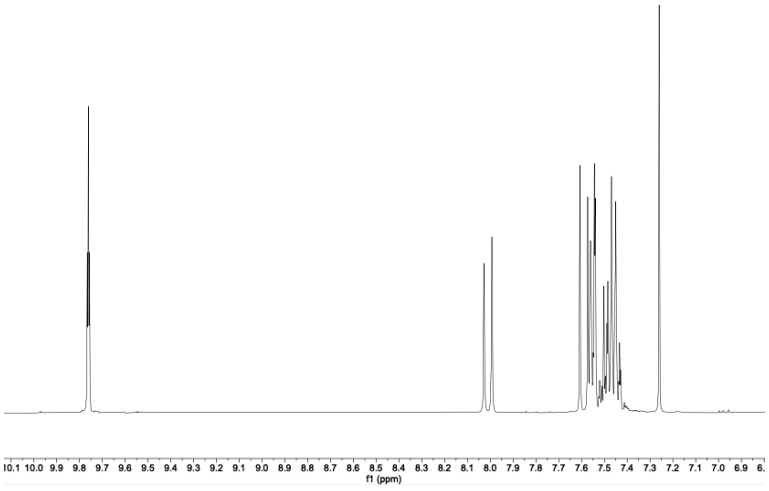
Gin (S32):



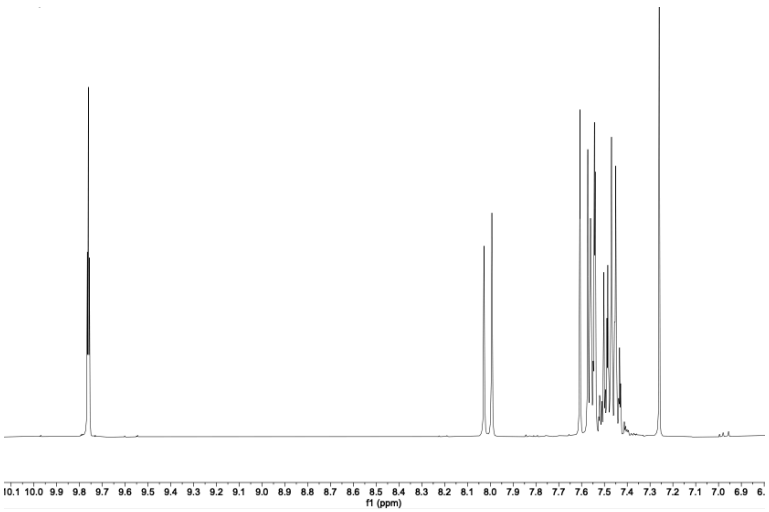
Rum (S33):



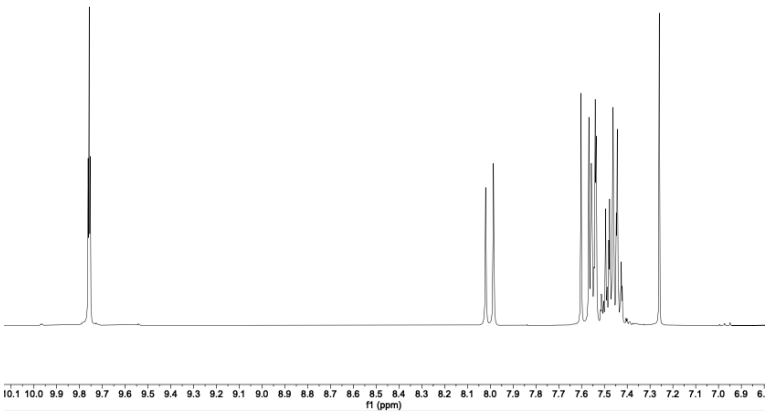
Aceto balsamico (S34):



Herb vinegar (S35):

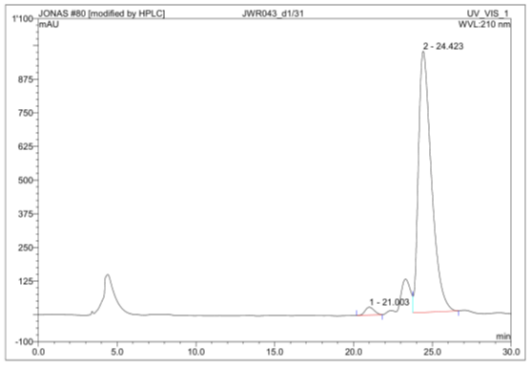


Olive oil (S36):



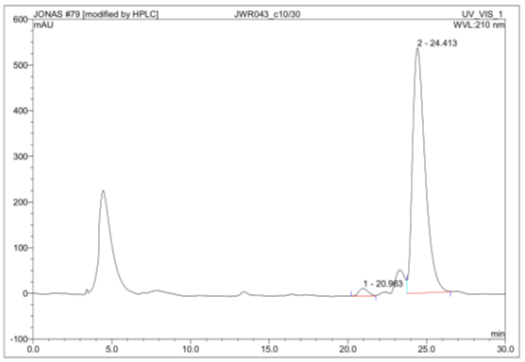
HPLC chromatograms of the reactions in the presence of H-DPro-MePro-Glu-NH_2 2:

MilliQ water (S1):



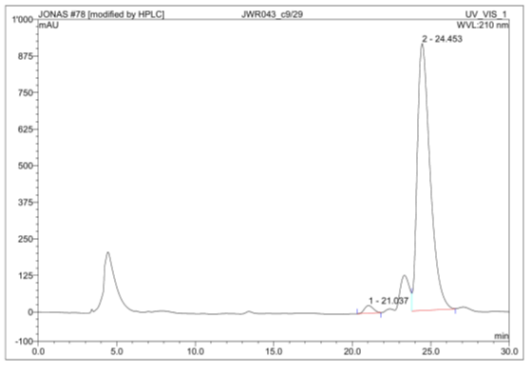
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.00	n.a.	29.210	19.385	2.05	n.a.	BMb*
2	24.42	n.a.	970.010	927.759	97.95	n.a.	MB*
Total:			999.220	947.144	100.00	0.000	

Tab water (S2):



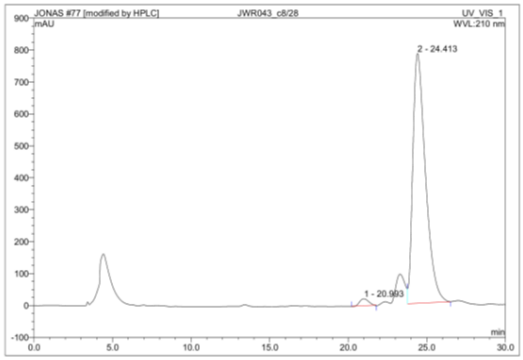
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.96	n.a.	16.378	11.290	2.23	n.a.	BM *
2	24.41	n.a.	536.467	495.298	97.77	n.a.	MB*
Total:			552.845	506.588	100.00	0.000	

Lake Zürich water (S3):



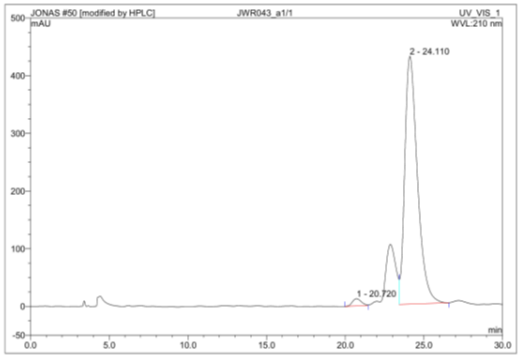
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.04	n.a.	25.973	16.668	1.89	n.a.	BM *
2	24.45	n.a.	911.933	864.343	98.11	n.a.	MB*
Total:			937.905	881.011	100.00	0.000	

River Limmat water (S4):



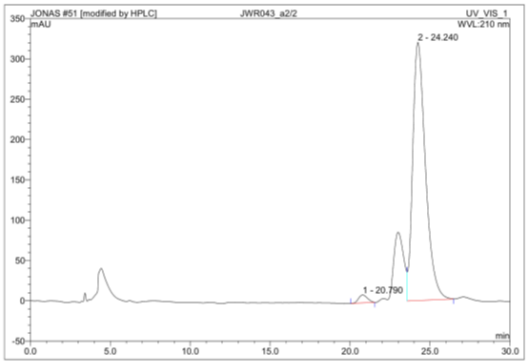
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.99	n.a.	21.947	14.071	1.89	n.a.	BM *
2	24.41	n.a.	782.243	729.215	98.11	n.a.	MB*
Total:			804.191	743.286	100.00	0.000	

Milk (S5):



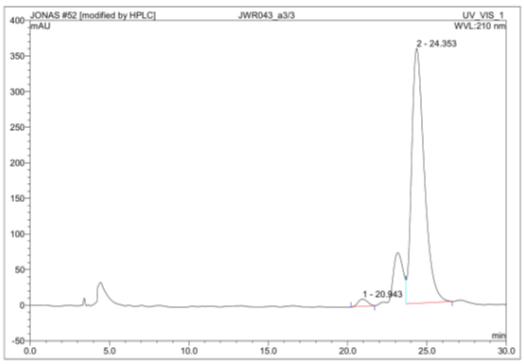
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.72	n.a.	12.654	8.399	2.06	n.a.	BM *
2	24.11	n.a.	429.742	400.276	97.94	n.a.	MB*
Total:			442.397	408.675	100.00	0.000	

Low fat milk (S6):



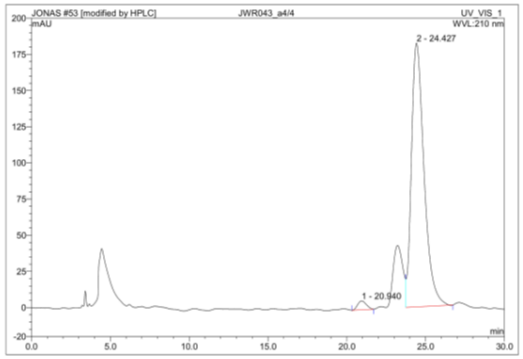
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.79	n.a.	9.737	6.217	2.05	n.a.	BM *
2	24.24	n.a.	320.170	296.910	97.95	n.a.	MB*
Total:			329.906	303.127	100.00	0.000	

Soya milk (S7):



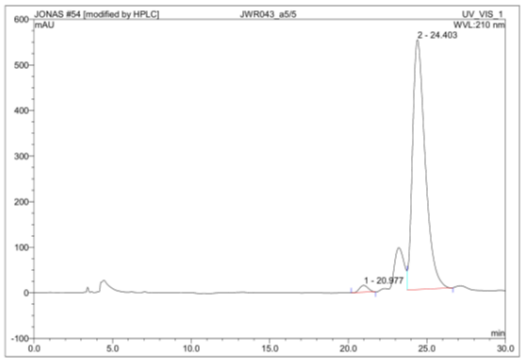
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.94	n.a.	10.075	6.822	2.03	n.a.	BM *
2	24.35	n.a.	357.946	329.730	97.97	n.a.	MB*
Total:			368.021	336.552	100.00	0.000	

Almond milk (S8):



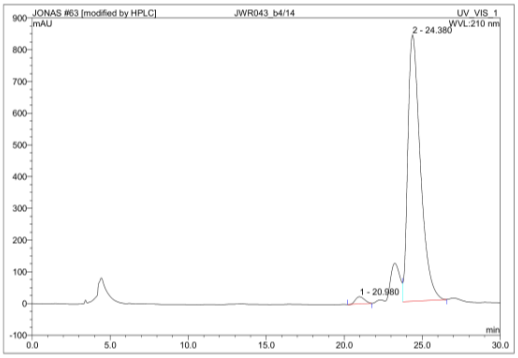
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.94	n.a.	6.085	3.852	2.23	n.a.	BM *
2	24.43	n.a.	182.319	169.099	97.77	n.a.	MB*
Total:			188.404	172.951	100.00	0.000	

Rice milk (S9):



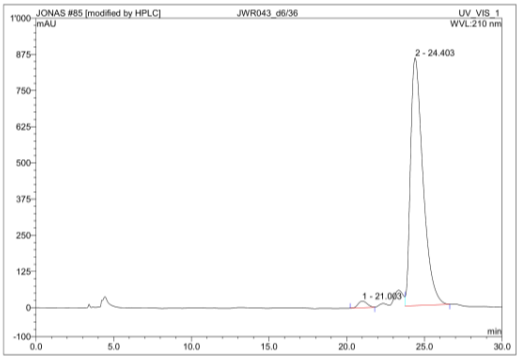
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.98	n.a.	14.830	9.099	1.75	n.a.	BM *
2	24.40	n.a.	547.501	511.252	98.25	n.a.	MB*
Total:			562.331	520.351	100.00	0.000	

Orange juice (S10):



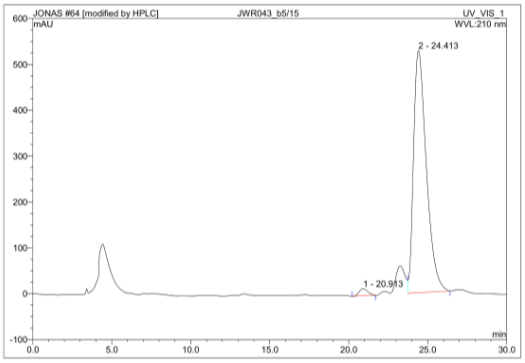
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.98	n.a.	22.640	15.048	1.89	n.a.	BM *
2	24.38	n.a.	839.987	782.223	98.11	n.a.	MB*
Total:			862.627	797.271	100.00	0.000	

Blood orange juice (S11):



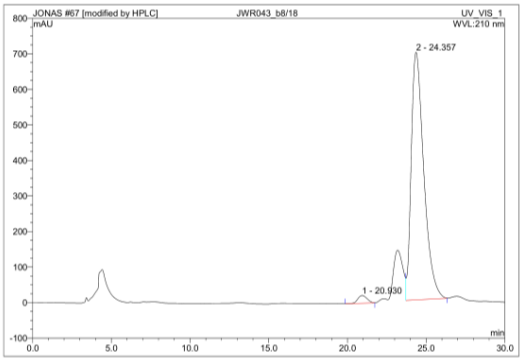
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.00	n.a.	23.124	15.466	1.90	n.a.	BM *
2	24.40	n.a.	856.129	799.582	98.10	n.a.	MB*
Total:			879.253	815.049	100.00	0.000	

Apple juice (S12):



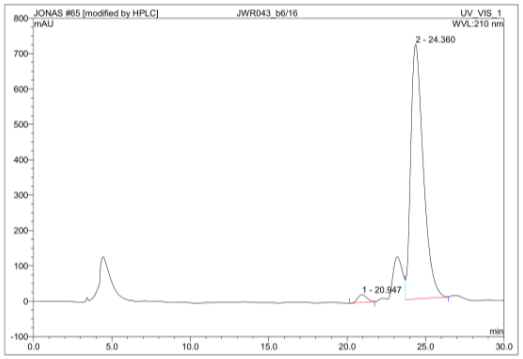
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.91	n.a.	14.801	9.042	1.79	n.a.	BM *
2	24.41	n.a.	527.873	495.119	98.21	n.a.	MB*
Total:			542.674	504.160	100.00	0.000	

Coconut water (S13):



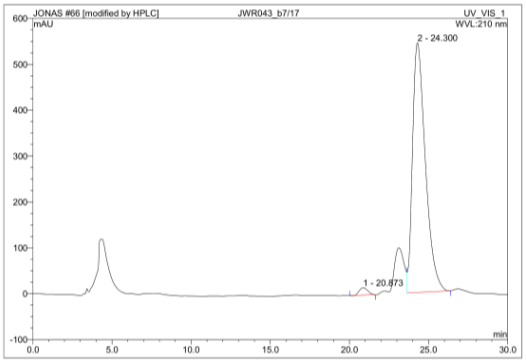
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.93	n.a.	21.620	14.532	2.20	n.a.	BMb*
2	24.36	n.a.	696.821	645.004	97.80	n.a.	MB*
Total:			718.442	659.536	100.00	0.000	

Carrot juice (S14):



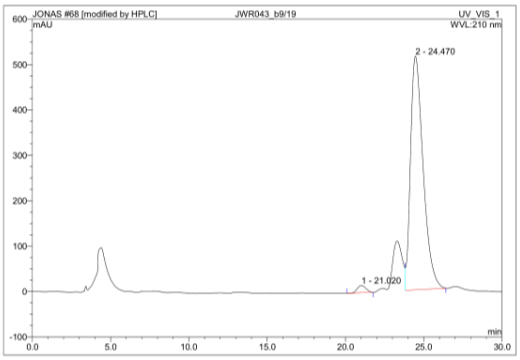
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.95	n.a.	21.606	14.331	2.10	n.a.	BM *
2	24.36	n.a.	719.542	667.189	97.90	n.a.	MB*
Total:			741.148	681.520	100.00	0.000	

Beetroot juice (S15):



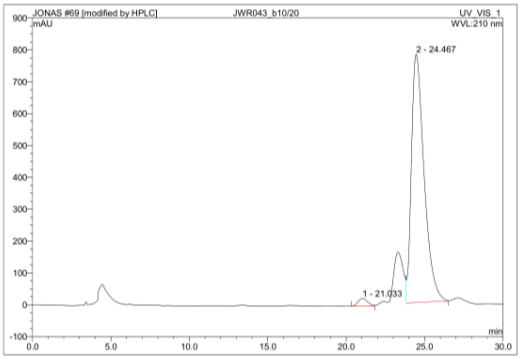
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.87	n.a.	15.857	9.741	1.86	n.a.	BM *
2	24.30	n.a.	543.804	513.048	98.14	n.a.	MB*
Total:			559.661	522.789	100.00	0.000	

Coffee (S16):



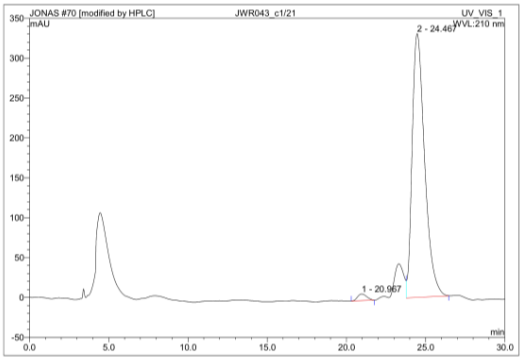
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.02	n.a.	15.732	9.719	1.98	n.a.	BM *
2	24.47	n.a.	514.141	480.802	98.02	n.a.	MB*
Total:			529.873	490.521	100.00	0.000	

Green tea (S17):



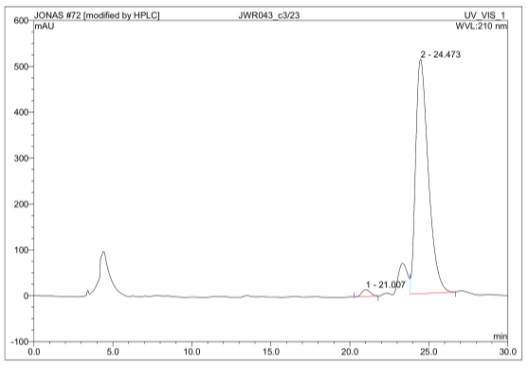
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.03	n.a.	23.191	16.494	2.21	n.a.	BM *
2	24.47	n.a.	779.537	731.374	97.79	n.a.	MB*
Total:			802.729	747.869	100.00	0.000	

Black tea (S18):



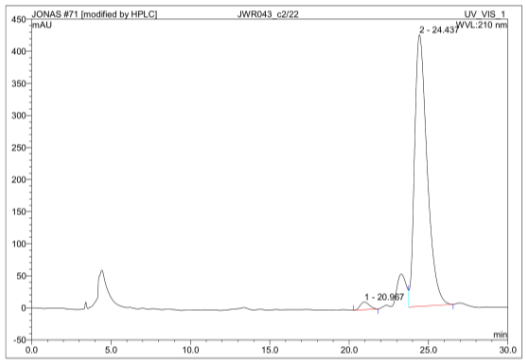
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.97	n.a.	8.321	5.478	1.78	n.a.	BMb*
2	24.47	n.a.	330.712	302.249	98.22	n.a.	MB*
Total:			339.033	307.726	100.00	0.000	

Peppermint tea (S19):



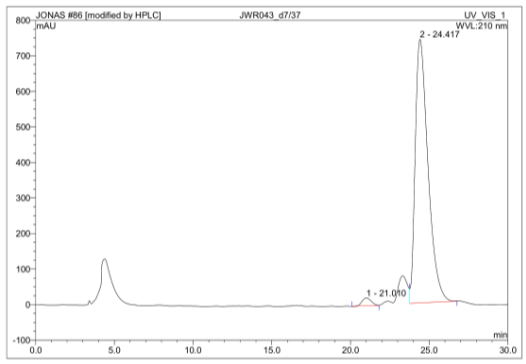
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.01	n.a.	14.384	8.735	1.80	n.a.	BM *
2	24.47	n.a.	510.826	476.276	98.20	n.a.	MB*
Total:			525.210	485.011	100.00	0.000	

Fruit tea (S20):



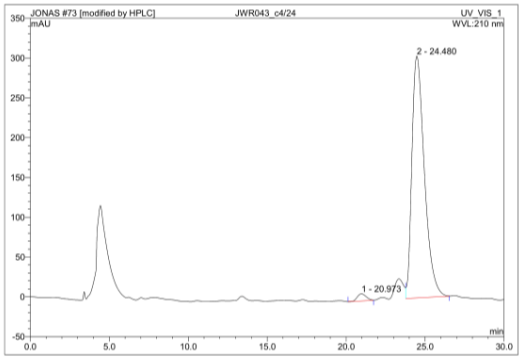
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.97	n.a.	11.957	7.747	1.96	n.a.	BM *
2	24.44	n.a.	423.507	387.196	98.04	n.a.	MB*
Total:			435.463	394.943	100.00	0.000	

Honey solution 5 wt% (S21):



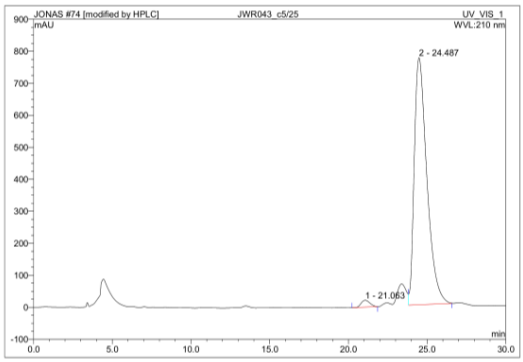
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.01	n.a.	21.903	14.502	2.04	n.a.	BMb*
2	24.42	n.a.	741.871	697.140	97.96	n.a.	MB*
Total:			763.774	711.642	100.00	0.000	

Coke (S22):



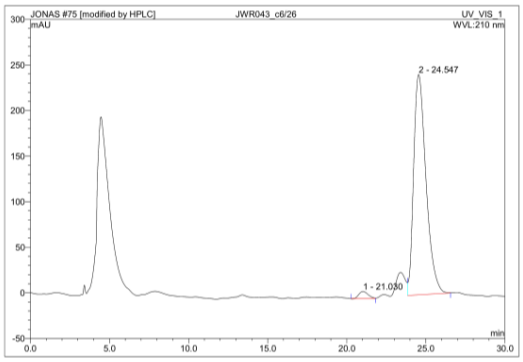
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.97	n.a.	8.942	5.858	2.06	n.a.	BM *
2	24.48	n.a.	303.729	279.025	97.94	n.a.	MB*
Total:			312.672	284.883	100.00	0.000	

Rivella (S23):



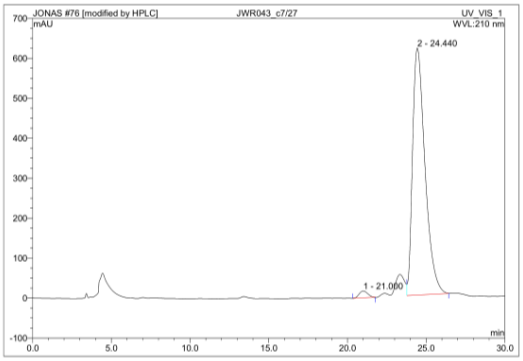
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.06	n.a.	21.416	13.640	1.87	n.a.	BM *
2	24.49	n.a.	772.117	717.078	98.13	n.a.	MB*
Total:			793.533	730.718	100.00	0.000	

Diet Rivella (S24):



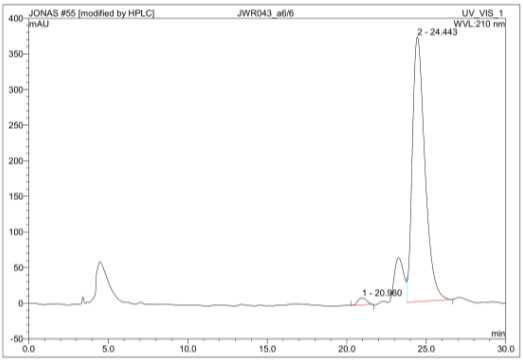
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.03	n.a.	7.957	5.493	2.45	n.a.	BM *
2	24.55	n.a.	241.584	218.486	97.55	n.a.	MB*
Total:			249.541	223.979	100.00	0.000	

Ice tea (S25):



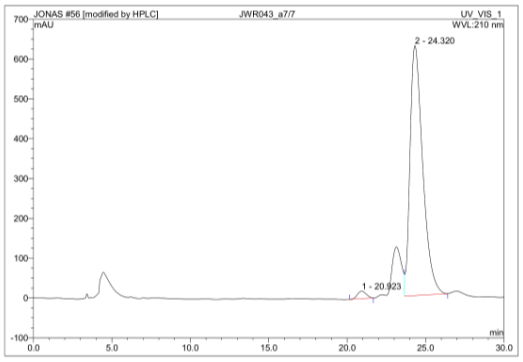
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.00	n.a.	16.980	10.524	1.82	n.a.	BM *
2	24.44	n.a.	617.923	567.100	98.18	n.a.	MB*
Total:			634.903	577.624	100.00	0.000	

Beer (S26):



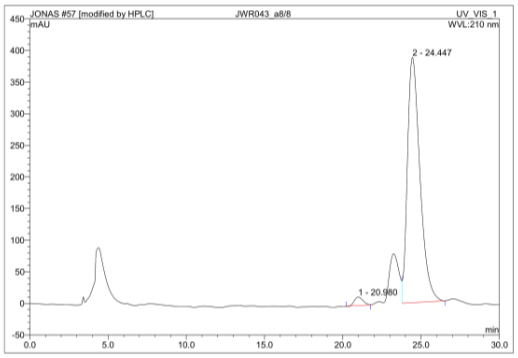
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.96	n.a.	9.718	5.920	1.71	n.a.	BM *
2	24.44	n.a.	371.655	339.861	98.29	n.a.	MB*
Total:			381.373	345.780	100.00	0.000	

Red wine (S27):



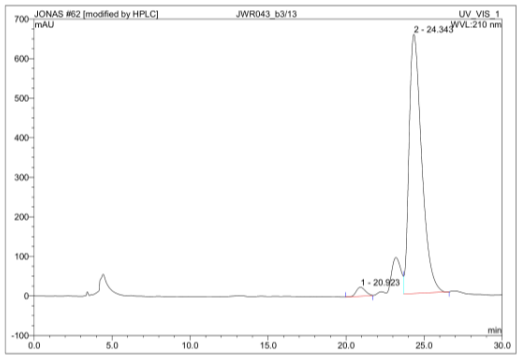
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.92	n.a.	18.580	11.995	2.00	n.a.	BM *
2	24.32	n.a.	627.586	588.543	98.00	n.a.	MB*
Total:			646.166	600.537	100.00	0.000	

Amaretto (S28):



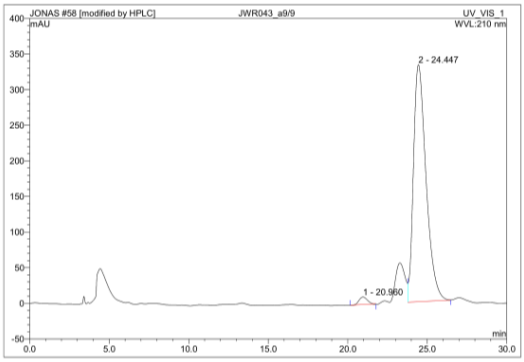
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.98	n.a.	13.345	8.611	2.33	n.a.	BM *
2	24.45	n.a.	387.959	361.102	97.67	n.a.	MB*
Total:			401.304	369.713	100.00	0.000	

Herb Liqueur – “Jägermeister” (S29):



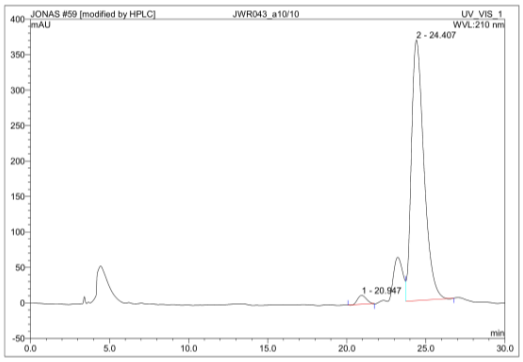
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.92	n.a.	22.721	15.510	2.46	n.a.	BM *
2	24.34	n.a.	655.145	614.155	97.54	n.a.	MB*
Total:			677.866	629.665	100.00	0.000	

Scotch Whisky – Aberlour 18 y (S30):



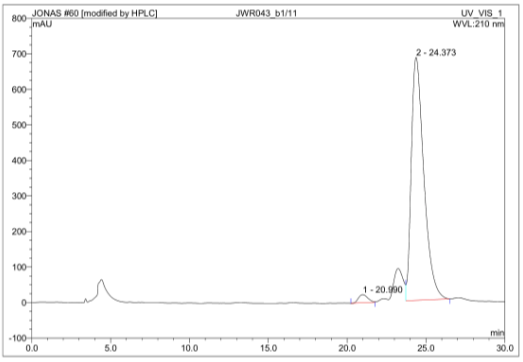
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.96	n.a.	10.425	6.040	1.94	n.a.	BM *
2	24.45	n.a.	332.624	304.990	98.06	n.a.	MB*
Total:			343.049	311.030	100.00	0.000	

Vodka (S31):



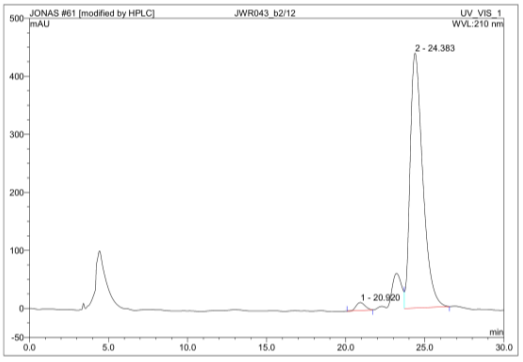
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.95	n.a.	12.410	7.755	2.26	n.a.	BM *
2	24.41	n.a.	367.373	336.060	97.74	n.a.	MB*
Total:			379.782	343.815	100.00	0.000	

Gin (S32):



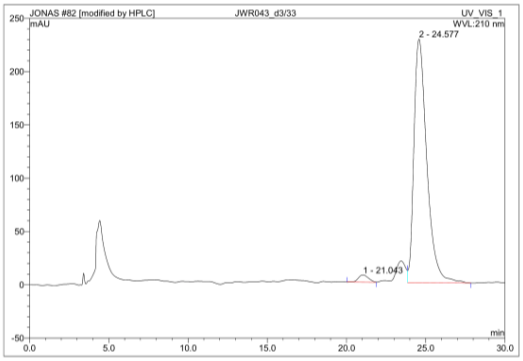
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.99	n.a.	22.852	15.414	2.38	n.a.	BM *
2	24.37	n.a.	683.924	631.365	97.62	n.a.	MB*
Total:			706.777	646.778	100.00	0.000	

Rum (S33):



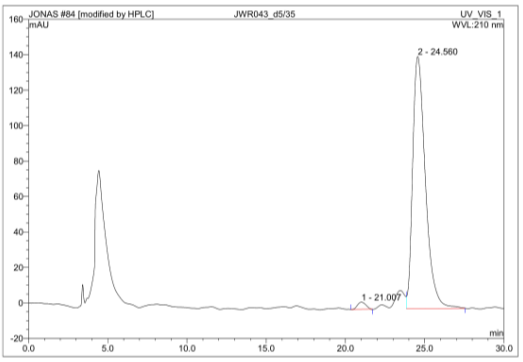
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.92	n.a.	13.664	8.889	2.14	n.a.	BM *
2	24.38	n.a.	439.257	406.511	97.86	n.a.	MB*
Total:			452.921	415.400	100.00	0.000	

Aceto balsamico (S34):



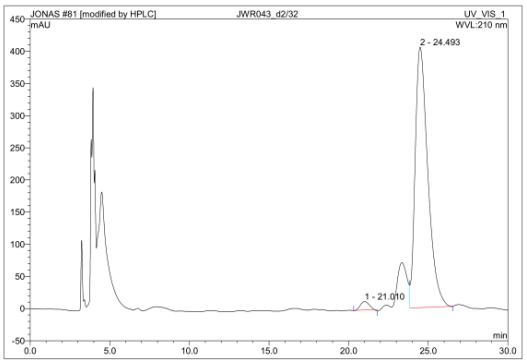
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.04	n.a.	6.799	5.014	2.27	n.a.	BM *
2	24.58	n.a.	228.498	215.640	97.73	n.a.	MB*
Total:			235.296	220.654	100.00	0.000	

Herb vinegar (S35):



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.01	n.a.	3.982	2.393	1.78	n.a.	BM *
2	24.56	n.a.	142.201	132.381	98.22	n.a.	MB*
Total:			146.183	134.773	100.00	0.000	

Olive oil (S36):



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.01	n.a.	13.226	8.155	2.14	n.a.	BM *
2	24.49	n.a.	405.240	373.412	97.86	n.a.	MB*
Total:			418.466	381.568	100.00	0.000	

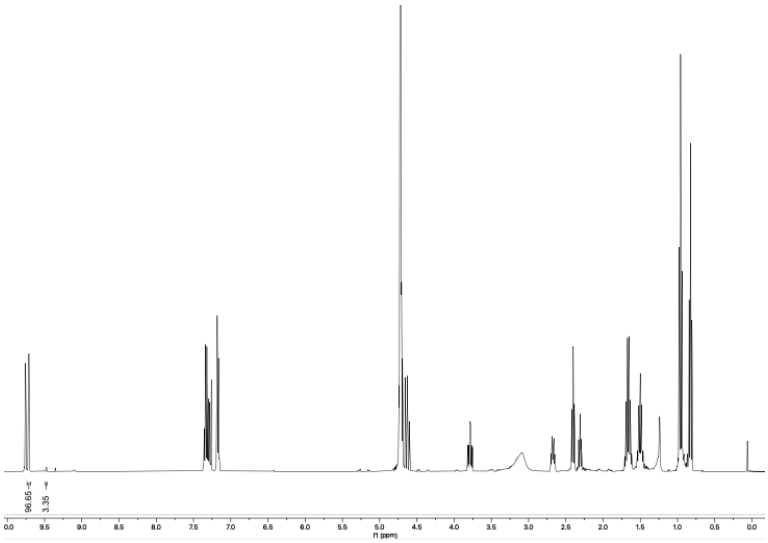
8. Conjugate Addition Reaction in Cell Lysate:

Preparation of the cell lysate:

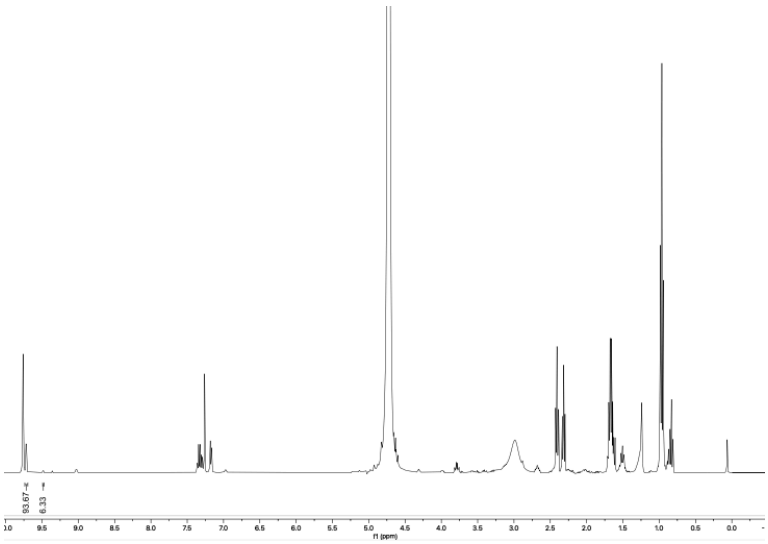
Hep G2 cells were seeded in a *TPP® Tissue Culture Flask 300* culture plate and grown to approximately 80% confluence in a cell culture incubator at 37 °C and 5% CO_2. The cells were washed three times with phosphate-buffered saline (PBS), then harvested off the bottom of the flask by cell scrapers into PBS buffer. The solution was transferred into conical *Falcon®* tubes. The collected cells were sonicated using a *Branson SFX 250 Sonifier®* while kept in an ice bath through the whole process. The cell lysate protein concentration was quantified at $\lambda = 280$ nm using a *NanoDrop™* spectrophotometer.

^{1}H NMR spectra:

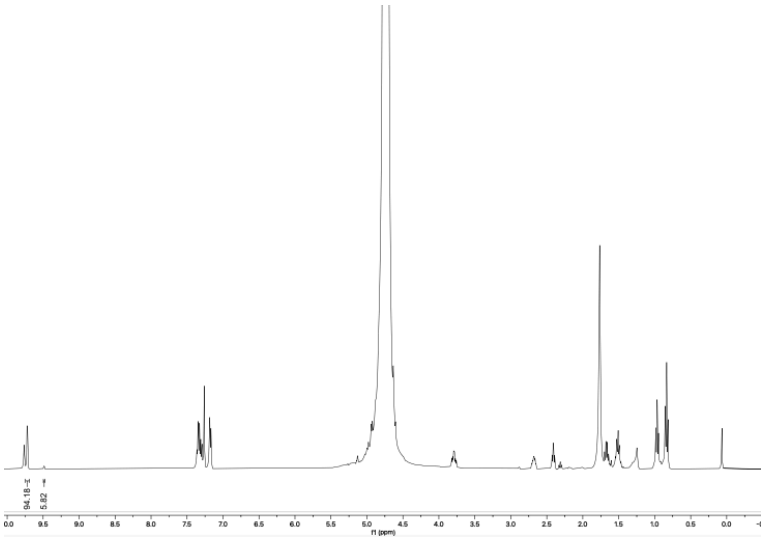
*Reaction with H-DPro-Pro-Glu-NH_2 **1** (440 mM nitrostyrene)*



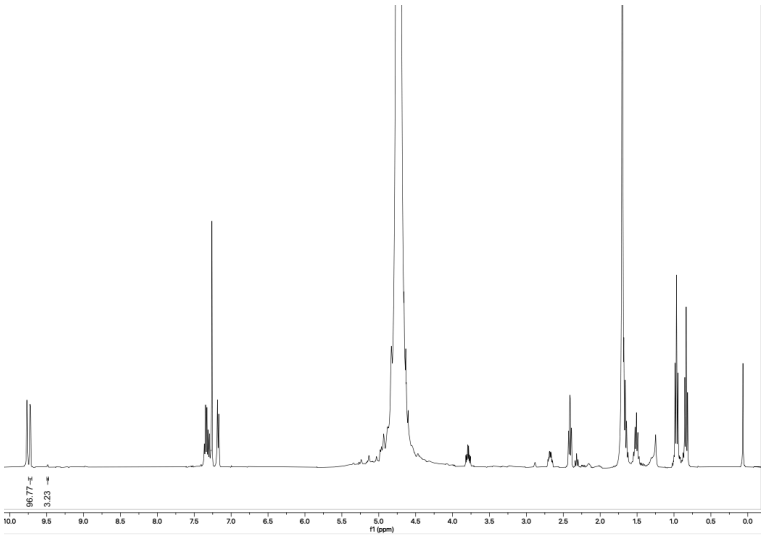
*Reaction with H-DPro-MePro-Glu-NH_2 **2** (440 mM nitrostyrene)*



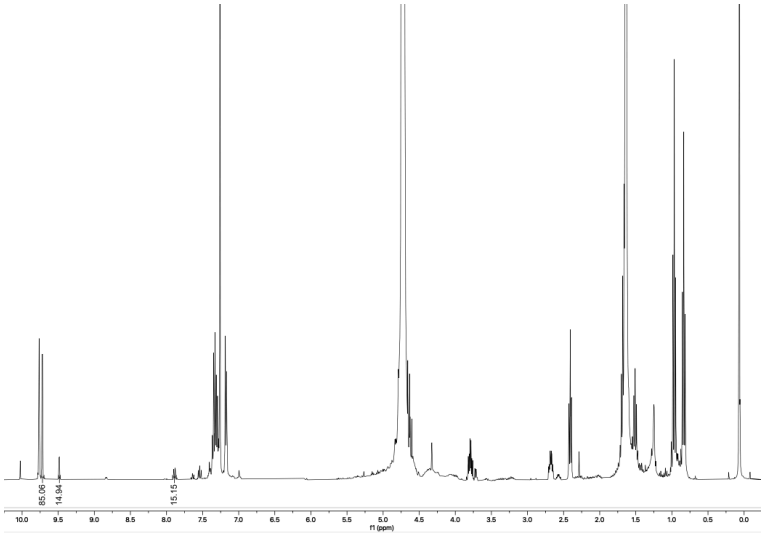
*Reaction with H-DPro-Pro-Glu-NH_2 **1** (44 mM nitrostyrene)*



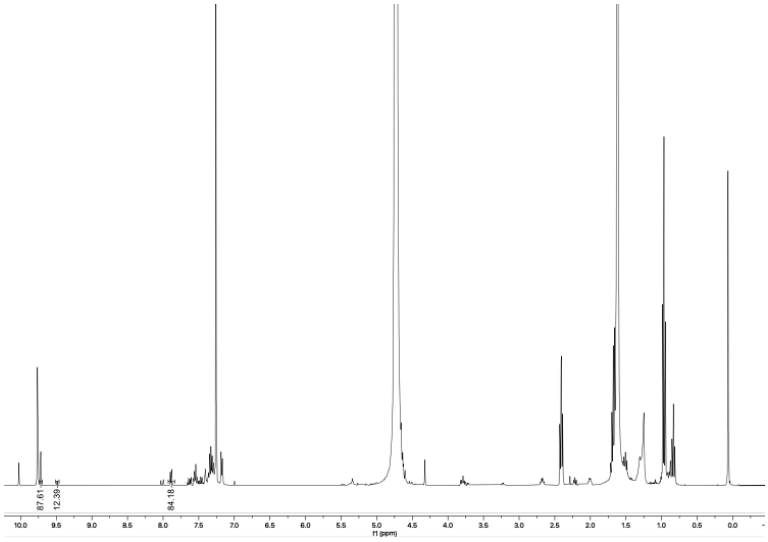
*Reaction with H-DPro-MePro-Glu-NH_2 **2** (44 mM nitrostyrene)*



*Reaction with H-DPro-Pro-Glu-NH_2 **1** (4 mM nitrostyrene)*

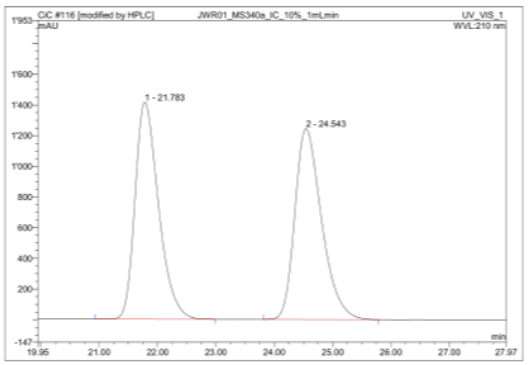


*Reaction with H-DPro-MePro-Glu-NH_2 **2** (4 mM nitrostyrene)*



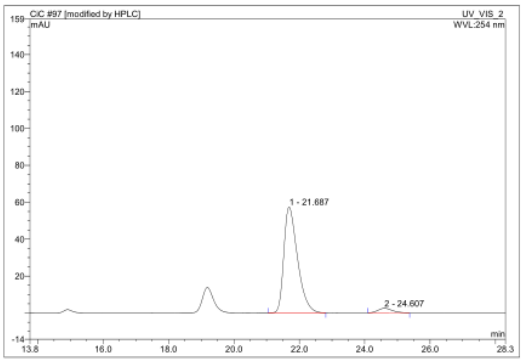
HPLC chromatograms:

Racemic sample:



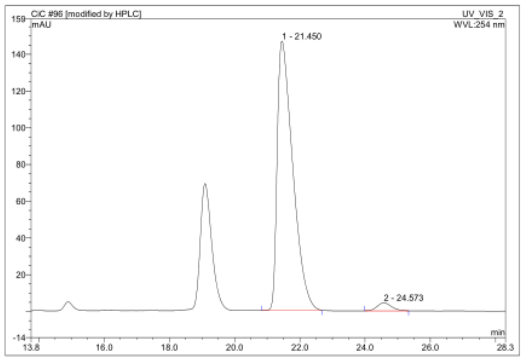
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.78	n.a.	1414.984	661.951	50.03	n.a.	BMB*
2	24.54	n.a.	1244.489	661.053	49.97	n.a.	BMB*
Total:			2659.472	1323.004	100.00	0.000	

*Reaction with H-DPro-Pro-Glu-NH_2 **1** (440 mM nitrostyrene)*



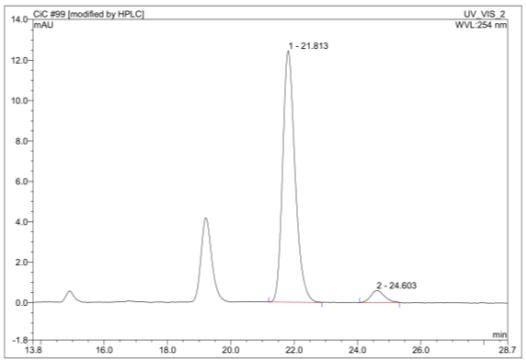
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.69	n.a.	57.307	27.691	95.72	n.a.	BMB*
2	24.61	n.a.	2.470	1.238	4.28	n.a.	BMB*
Total:			59.777	28.929	100.00	0.000	

*Reaction with H-DPro-MePro-Glu-NH_2 **2** (440 mM nitrostyrene)*



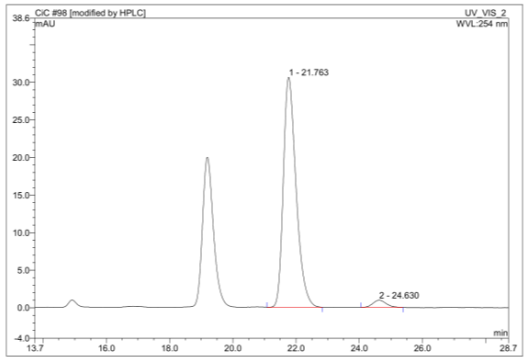
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.45	n.a.	146.607	81.173	97.36	n.a.	BMB*
2	24.57	n.a.	4.359	2.204	2.64	n.a.	BMB*
Total:			150.966	83.377	100.00	0.000	

Reaction with H-DPro-Pro-Glu-NH_2 ***1*** *(44 mM nitrostyrene)*



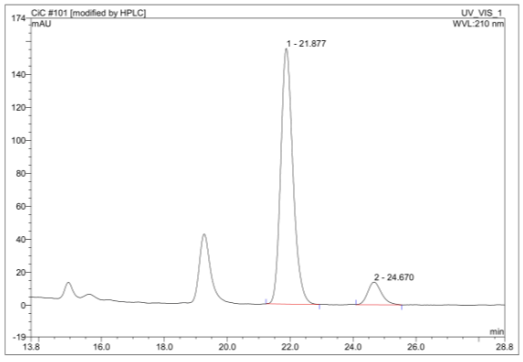
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.81	n.a.	12.434	5.652	94.90	n.a.	BMB*
2	24.60	n.a.	0.600	0.304	5.10	n.a.	BMB*
Total:			13.034	5.956	100.00	0.000	

Reaction with H-DPro-MePro-Glu-NH_2 ***2*** *(44 mM nitrostyrene)*



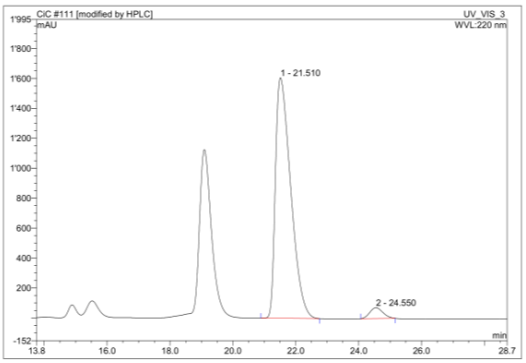
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.76	n.a.	30.608	14.280	96.80	n.a.	BMB*
2	24.63	n.a.	0.963	0.473	3.20	n.a.	BMB*
Total:			31.571	14.753	100.00	0.000	

Reaction with H-DPro-Pro-Glu-NH_2 ***1*** *(4 mM nitrostyrene)*



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.88	n.a.	155.009	69.924	90.90	n.a.	BMB*
2	24.67	n.a.	13.774	7.000	9.10	n.a.	BMB*
Total:			168.782	76.924	100.00	0.000	

Reaction with H-DPro-MePro-Glu-NH_2 ***2*** *(4 mM nitrostyrene)*



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.51	n.a.	1607.298	905.346	96.27	n.a.	BMB*
2	24.55	n.a.	72.930	35.093	3.73	n.a.	BMB*
Total:			1680.228	940.439	100.00	0.000	

9. References

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