

Supporting Information

Conformational Heterogeneity and Self-Assembly of α,β,γ -Hybrid Peptides Containing Fenamic Acid: Multi-Stimuli Responsive Phase Selective Gelation

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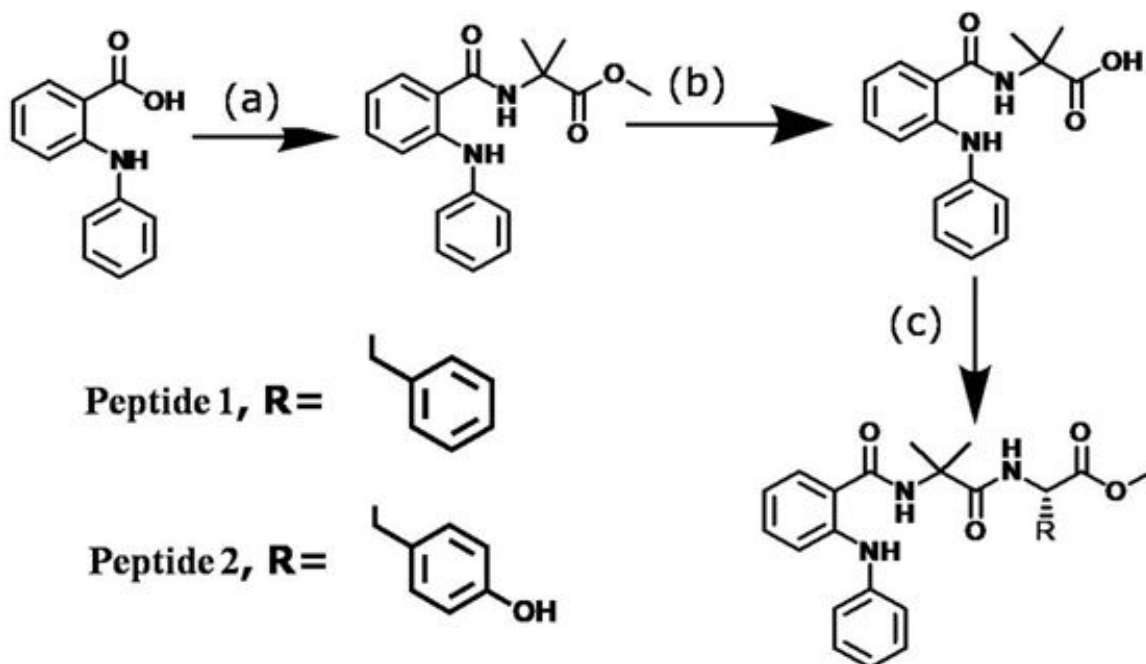
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(A) For Peptide 1 and Peptide 2



(B) For Peptide 3

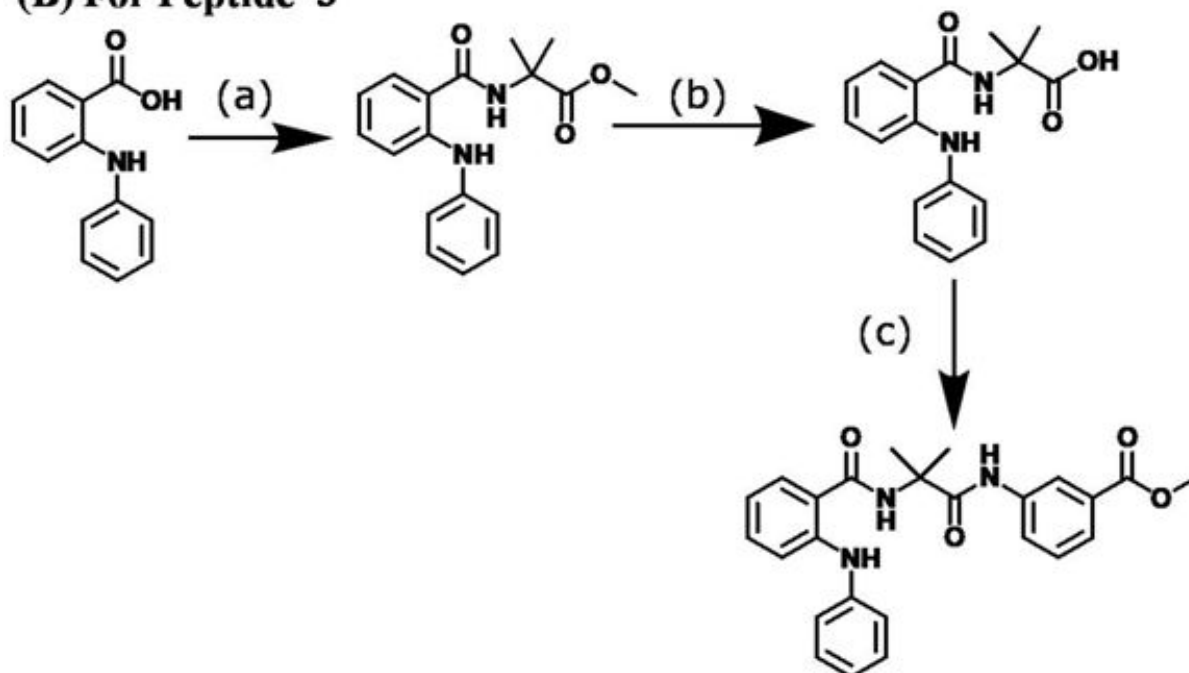


Figure S1 (A): Synthetic route of Peptide 1 and Peptide 2. (a) Dry DCM, H-Aib-OMe, DCC, 48h, rt; (b) 2(N) NaOH, MeOH, 12h, rt; (c) Dry DCM, DCC, HOBT, H-Phe-OMe, 48h, rt (for peptide 1), H-Tyr-OMe (for peptide 2). **(B):** Synthetic route of Peptide 3 (B). (a) Dry DCM, H-Aib-OMe, DCC, 48h, rt; (b) 2(N) NaOH, MeOH, 12h, rt; (c) Dry DCM, DCC, 48h, rt, Maba-OMe (for peptide 3).

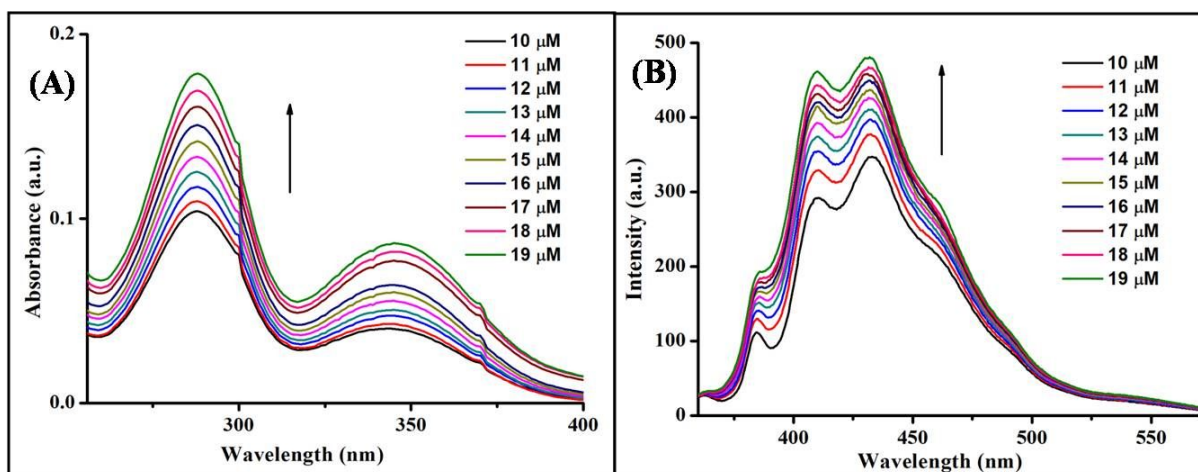


Figure S2 : (A) Concentration dependent UV-Vis spectra and (B) Concentration dependent Fluorescence spectra [excitation at 346 nm] in MeOH of Peptide 1.

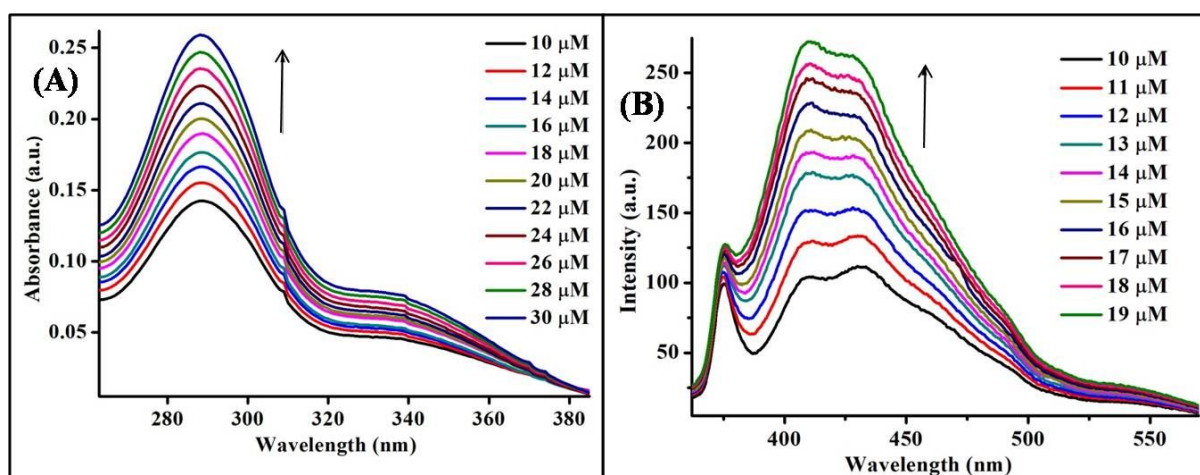


Figure S3 : (A) Concentration dependent UV-Vis spectra and (B) Concentration dependent Fluorescence spectra [excitation at 338 nm] in MeOH of Peptide 2.

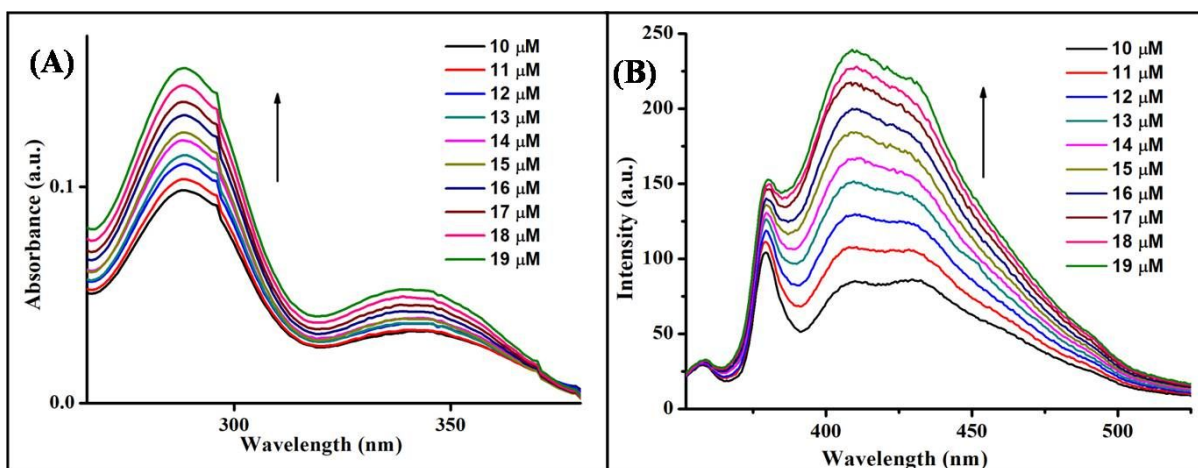


Figure S4 : (A) Concentration dependent UV-Vis spectra and (B) Concentration dependent Fluorescence spectra [excitation at 342 nm] in MeOH of Peptide 3.

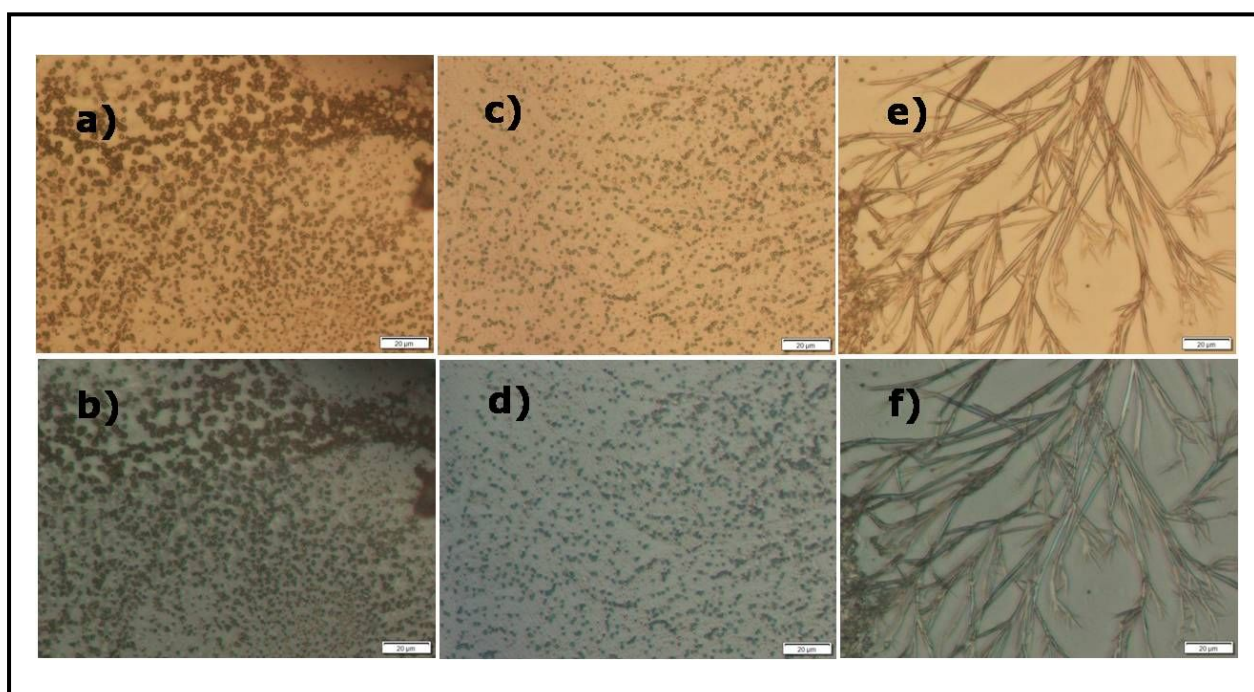


Figure S5: POM image of peptide 1 (a) without polarizer and (b) with polarizer; POM image of peptide 2 (c) without polarizer and (d) with polarizer, POM image of peptide 3 (e) without polarizer and (f).with polarizer.

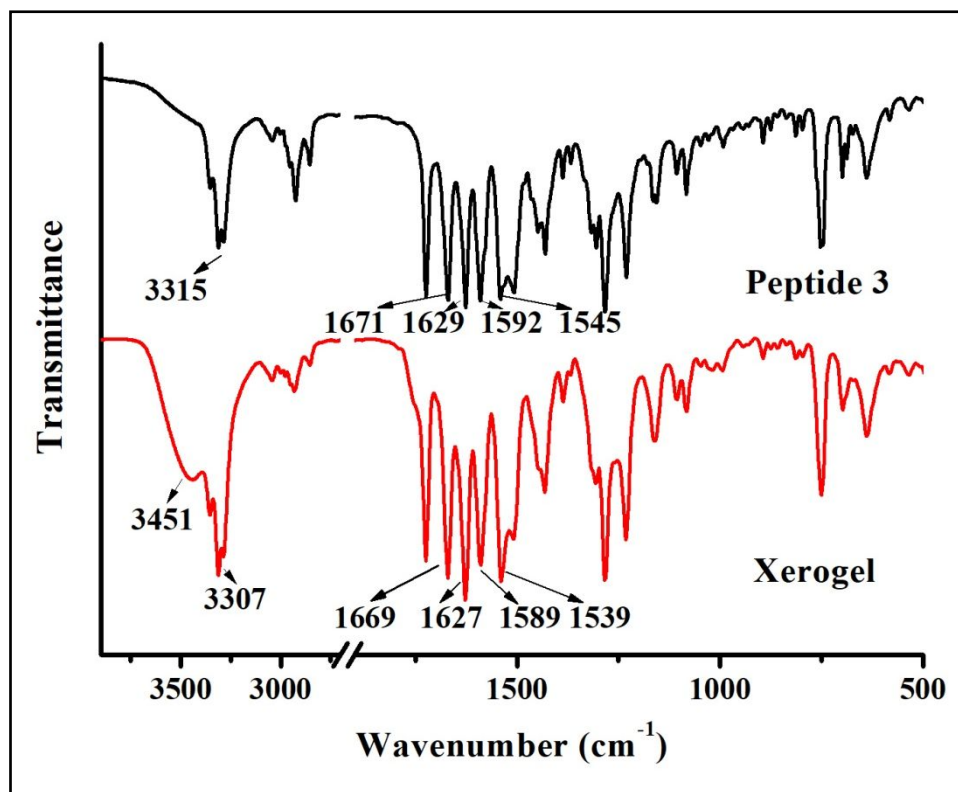


Figure S6: FT-IR Spectra of Peptide 3 and its xerogel.

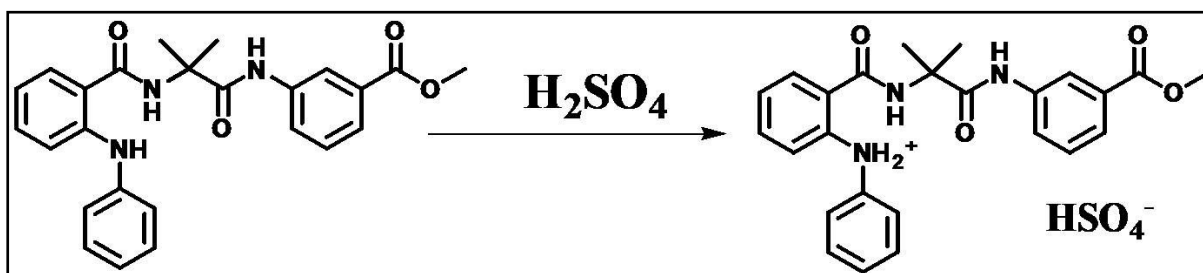


Figure S7: The plausible effect of H_2SO_4 on peptide 3 gel to sol transition and phase transfer.

Table S1. Crystal data and structure refinement for Peptide 1.

Identification code	NPAP
Empirical formula	$\text{C}_{27} \text{H}_{29} \text{N}_3 \text{O}_4$
Formula weight	459.53
Temperature/K	298
Crystal system	monoclinic
Space group	P 1 21 1
a/Å	6.9113
b/Å	18.1972
c/Å	10.1370
$\alpha/^\circ$	90

$\beta/^\circ$	105.648
$\gamma/^\circ$	90
Volume/ \AA^3	1227.64
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.243
μ/mm^{-1}	0.084
F(000)	488.0
Crystal size/ mm^3	$0.2458 \times 0.2358 \times 0.1587$
Radiation	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/ $^\circ$	4.172 to 50.044
Index ranges	$-8 \leq h \leq 8, -21 \leq k \leq 21, -12 \leq l \leq 12$
Reflections collected	10027
Independent reflections	4315 [$R_{\text{int}} = 0.0331, R_{\text{sigma}} = 0.0427$]
Data/restraints/parameters	4315/1/310
Goodness-of-fit on F^2	1.088
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0470, wR_2 = 0.1506$
Final R indexes [all data]	$R_1 = 0.0534, wR_2 = 0.1574$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.21/-0.17
Flack parameter	0.25(3)

Table S2. Crystal data and structure refinement for Peptide **2**.

Identification code	NPAT
Empirical formula	$\text{C}_{27} \text{H}_{29} \text{N}_3 \text{O}_5$
Formula weight	475.53
Temperature/K	100.01
Crystal system	monoclinic
Space group	P 1 21 1
a/ \AA	6.9049
b/ \AA	17.9673
c/ \AA	10.1305
$\alpha/^\circ$	90
$\beta/^\circ$	106.637
$\gamma/^\circ$	90
Volume/ \AA^3	1204.20
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.311
μ/mm^{-1}	0.091
F(000)	506.0
Crystal size/ mm^3	$0.248 \times 0.187 \times 0.107$
Radiation	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/ $^\circ$	4.196 to 50.04

Index ranges	$-8 \leq h \leq 7, -21 \leq k \leq 10, -4 \leq l \leq 12$
Reflections collected	3435
Independent reflections	2739 [$R_{\text{int}} = 0.0337, R_{\text{sigma}} = 0.0502$]
Data/restraints/parameters	2739/1/320
Goodness-of-fit on F^2	0.971
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0423, wR_2 = 0.1229$
Final R indexes [all data]	$R_1 = 0.0455, wR_2 = 0.1275$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.49/-0.37
Flack parameter	-1.0(10)

Table S3. Crystal data and structure refinement for Peptide **3**.

Identification code	NPAM
Empirical formula	$C_{25} H_{25} N_3 O_4$
Formula weight	431.48
Temperature/K	273
Crystal system	monoclinic
Space group	P 1 21/c 1
a/ \AA	13.2844
b/ \AA	9.4272
c/ \AA	36.075
$\alpha/^\circ$	90
$\beta/^\circ$	93.302
$\gamma/^\circ$	90
Volume/ \AA^3	4510.4
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.271
μ/mm^{-1}	0.709
F(000)	1824
Crystal size/ mm^3	-
Radiation	CuK α ($\lambda = 1.54178$)
Theta Min-Max / $^\circ$	2.5, 68.0
Dataset	-15: 15 ; -10: 11 ; -43: 43
Tot., Uniq. Data, R(int)	49064, 8166, 0.153
Observed data [$I > 2.0 \text{ sigma}(I)$]	5419
Nref, Npar	8166, 584
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1315, wR_2 = 0.3302$
Final R indexes [all data]	$R_1 = 0.1735, wR_2 = 0.3429$
Min. and Max. Resd. Dens. [$e/\text{\AA}^3$]	-0.64, 0.83

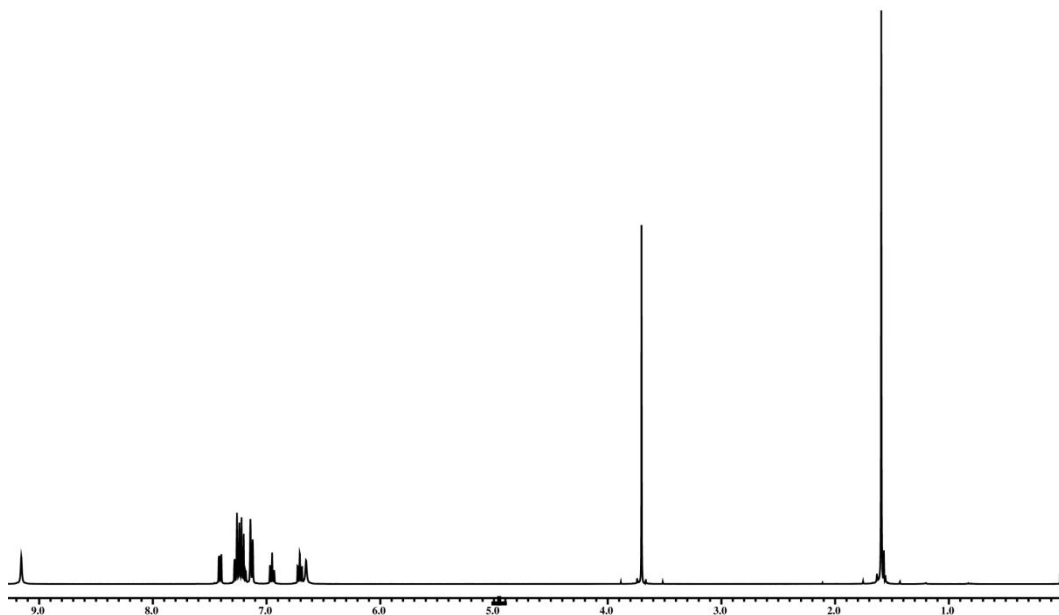


Figure S8. ¹H NMR (400 MHz, CDCl₃) spectrum of Fenamic acid- Aib OMe (NPA-Aib-OMe) 4.

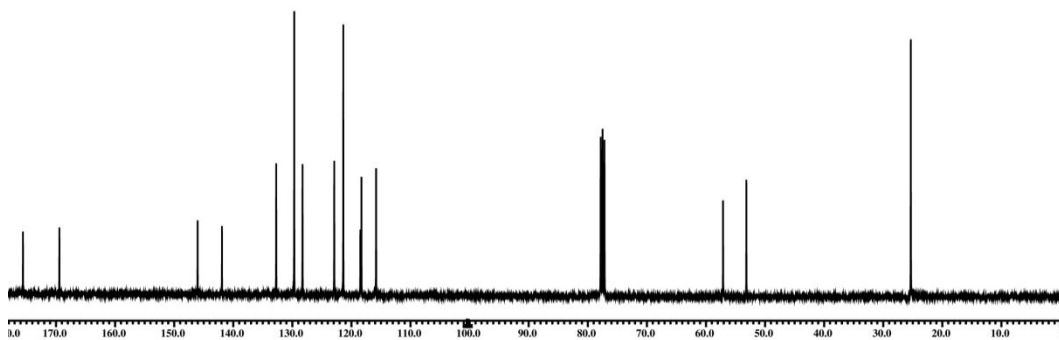


Figure S9. ¹³C NMR (100 MHz, CDCl₃) spectrum of Fenamic acid- Aib OMe (NPA-Aib-OMe) 4.

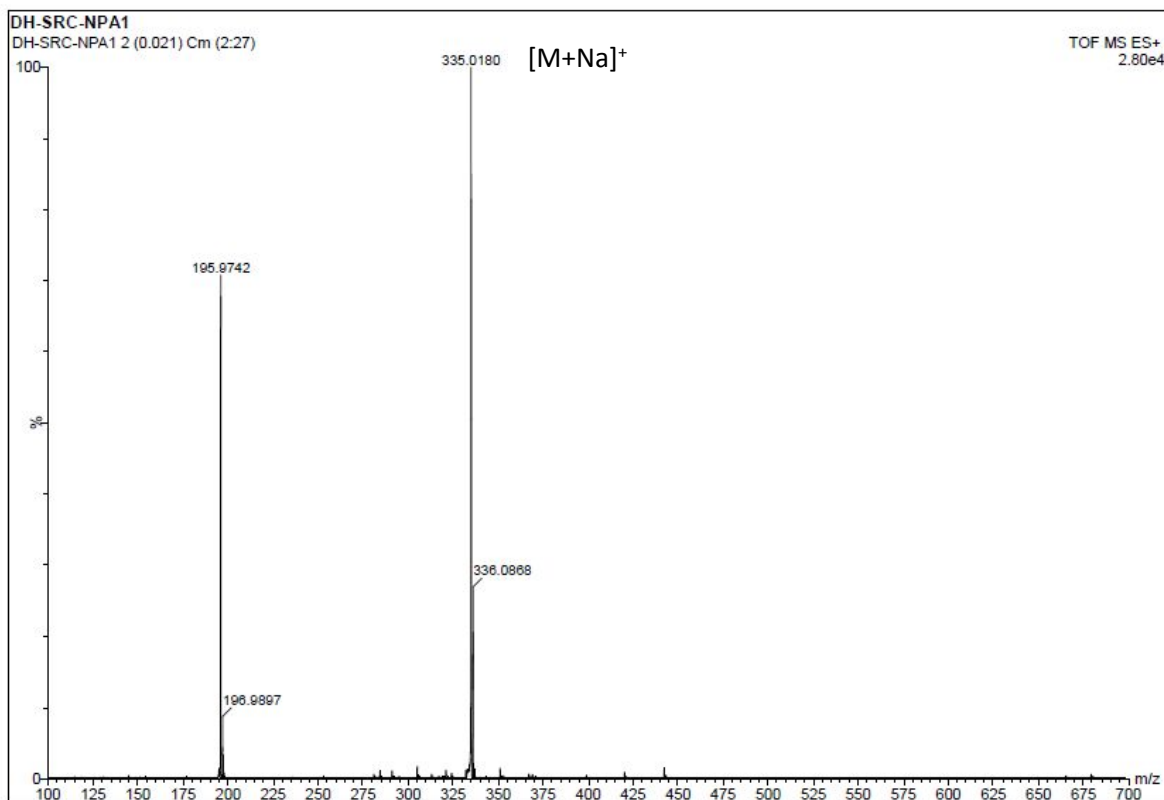


Figure S10. Mass spectrum of Fenamic acid- Aib OMe (NPA-Aib-OMe) 4.

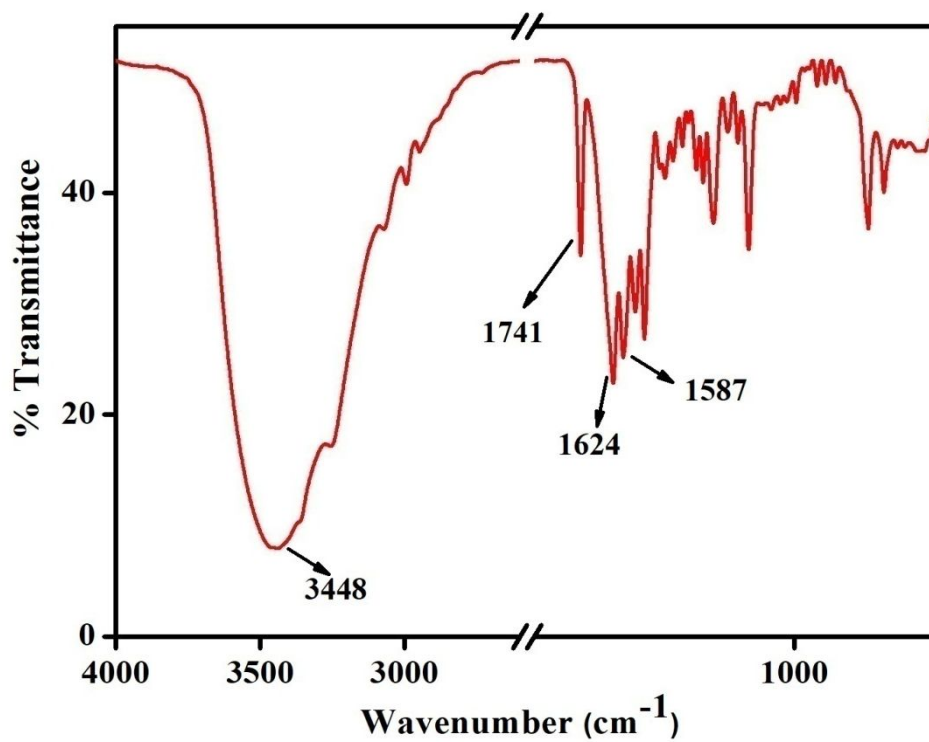


Figure S11. FT-IR spectrum of Fenamic acid- Aib OMe (NPA-Aib-OMe) 4.

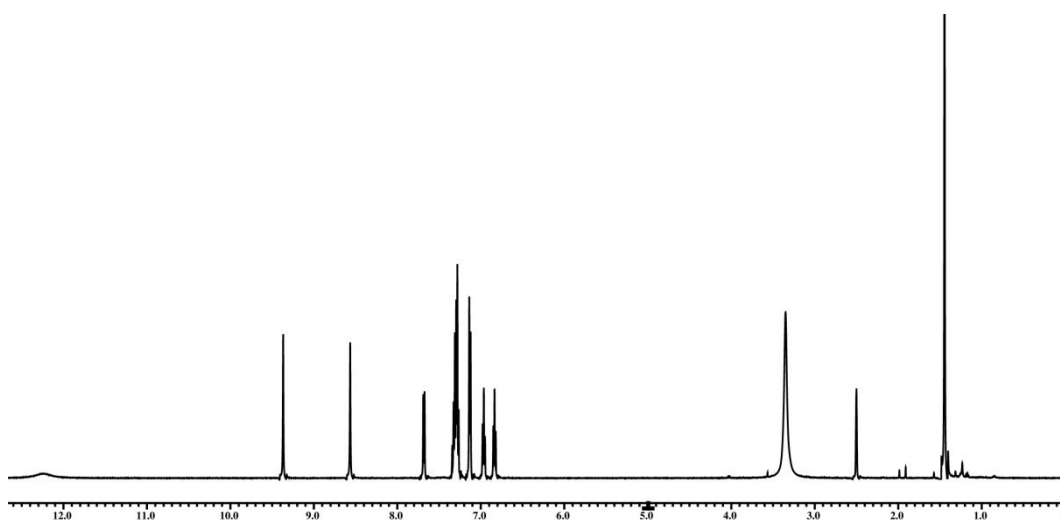


Figure S12. ¹H NMR (500 MHz, DMSO-d₆) spectrum of Fenamic acid- Aib OH (NPA-Aib-OH) 5.

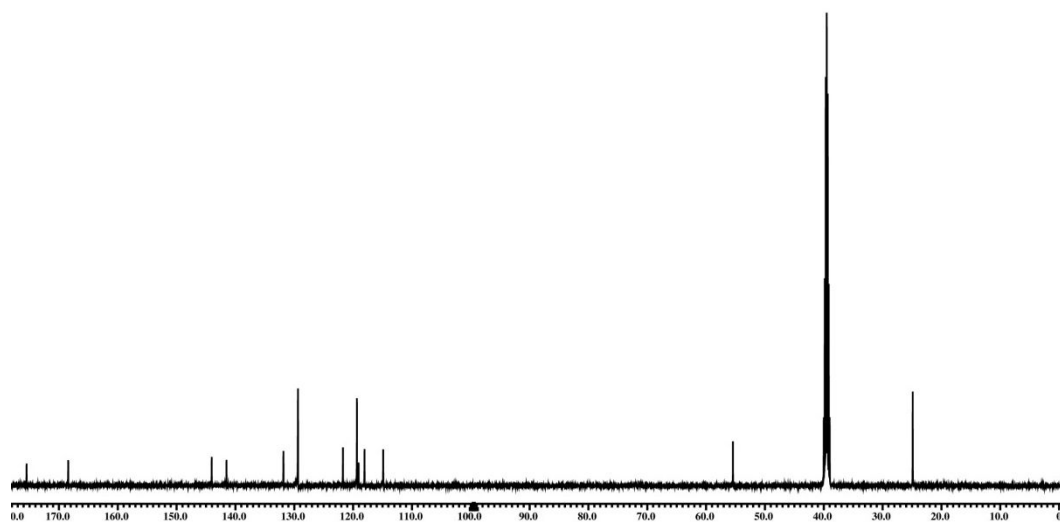


Figure S13. ¹³C NMR (125 MHz, DMSO-d₆) spectrum of Fenamic acid- Aib OH (NPA-Aib-OH) 5.

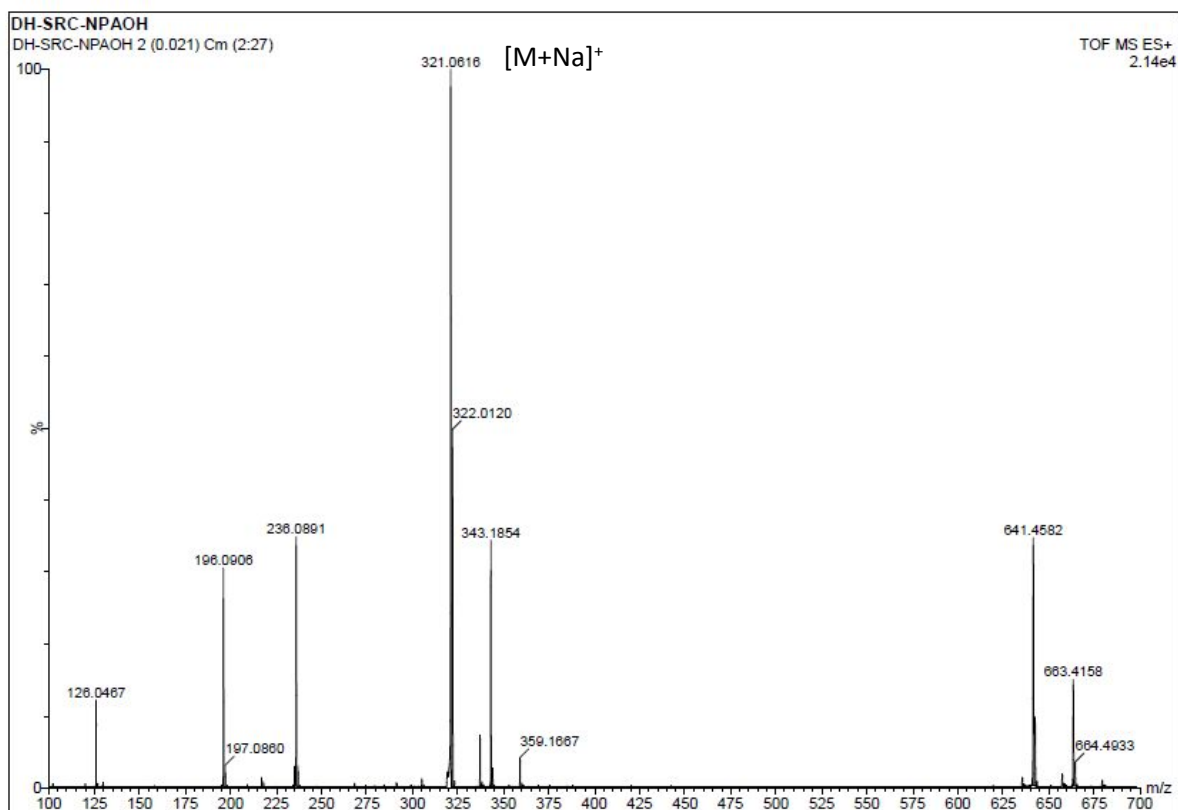


Figure S14. Mass spectrum of Fenamic acid- Aib OH (NPA-Aib-OH) 5.

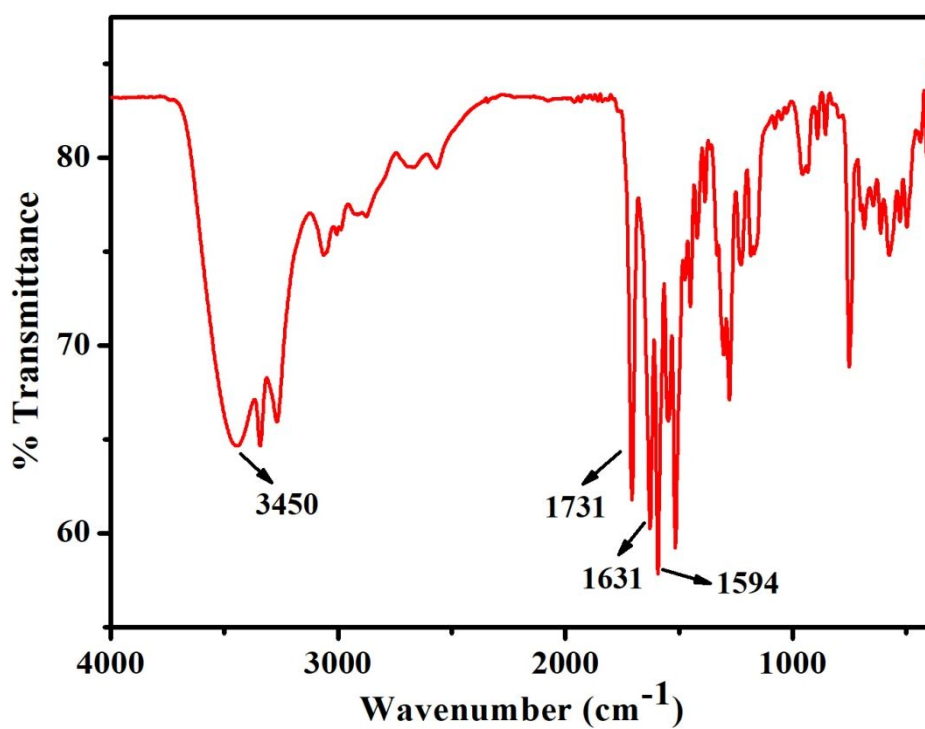


Figure S15. FT-IR spectrum of Fenamic acid- Aib OH (NPA-Aib-OH) 5.

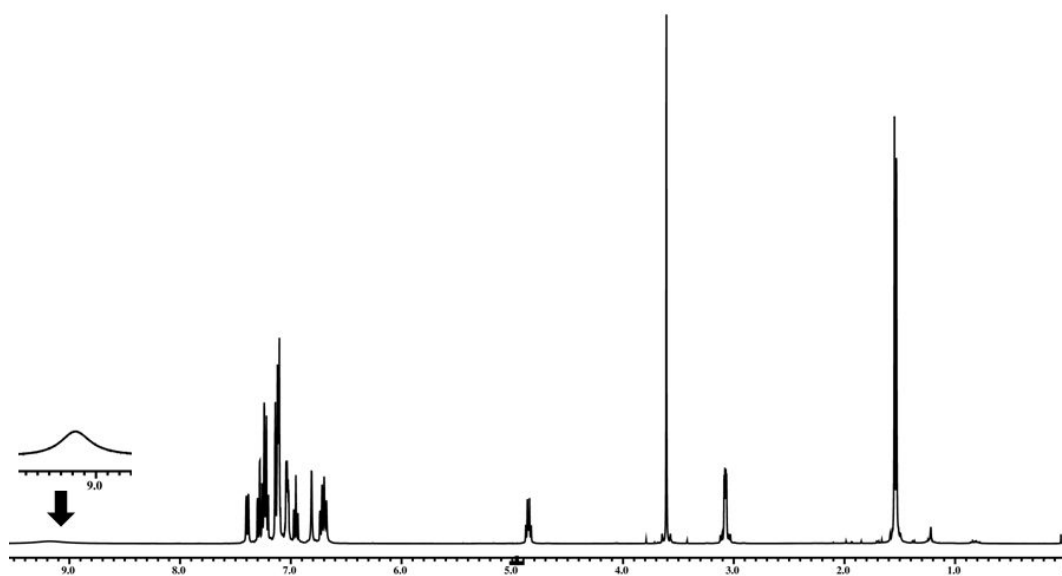


Figure S16. ^1H NMR (400 MHz, CDCl_3) spectrum of Fenamic acid- Aib-Phe OMe 1.

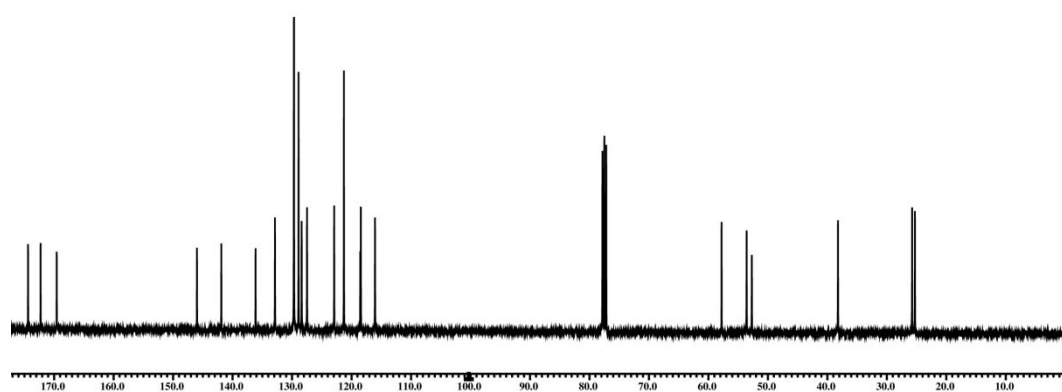


Figure S17. ^{13}C NMR (100 MHz, CDCl_3) spectrum of Fenamic acid- Aib-Phe OMe 1.

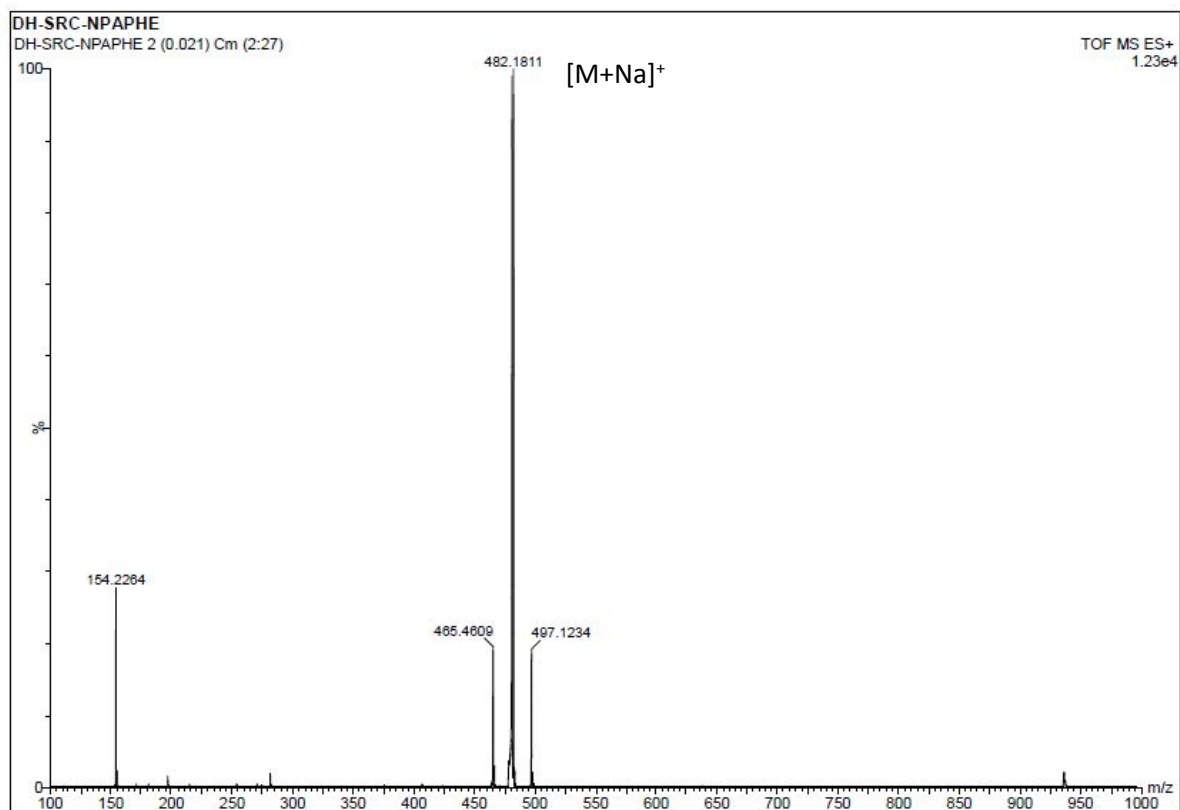


Figure S18. Mass spectrum of Fenamic acid- Aib-Phe OMe 1.

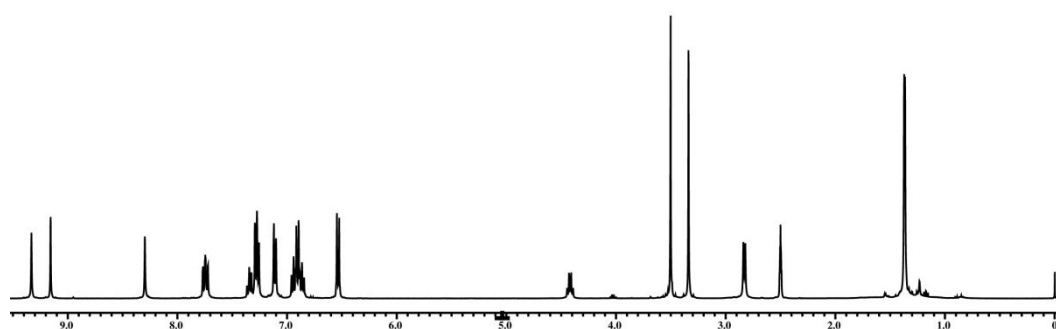


Figure S19. ^1H NMR (400 MHz, DMSP- d_6) spectrum of Fenamic acid- Aib-Tyr OMe 2.

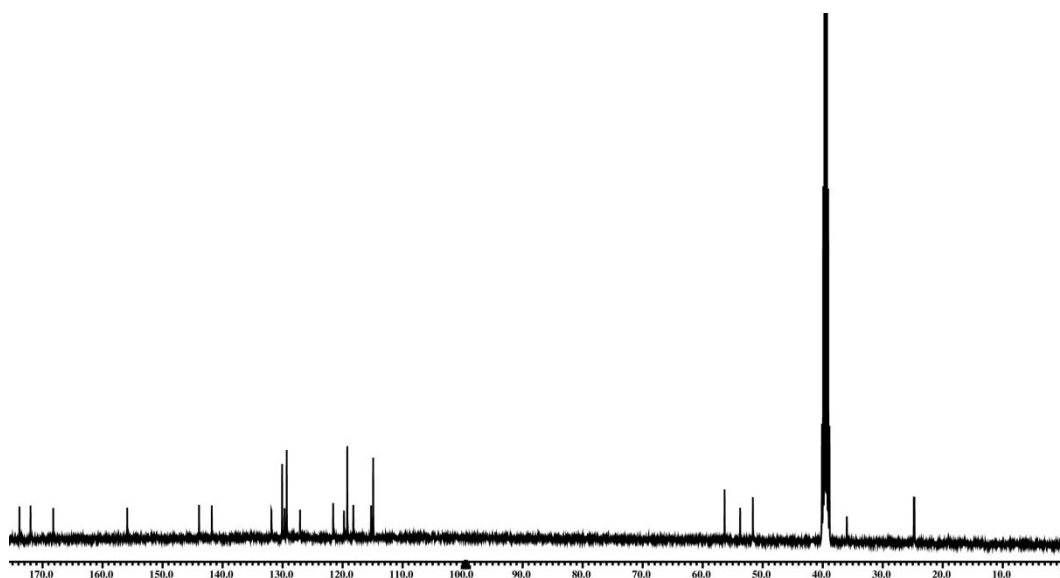


Figure S20. ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of Fenamic acid- Aib-Tyr OMe 2.

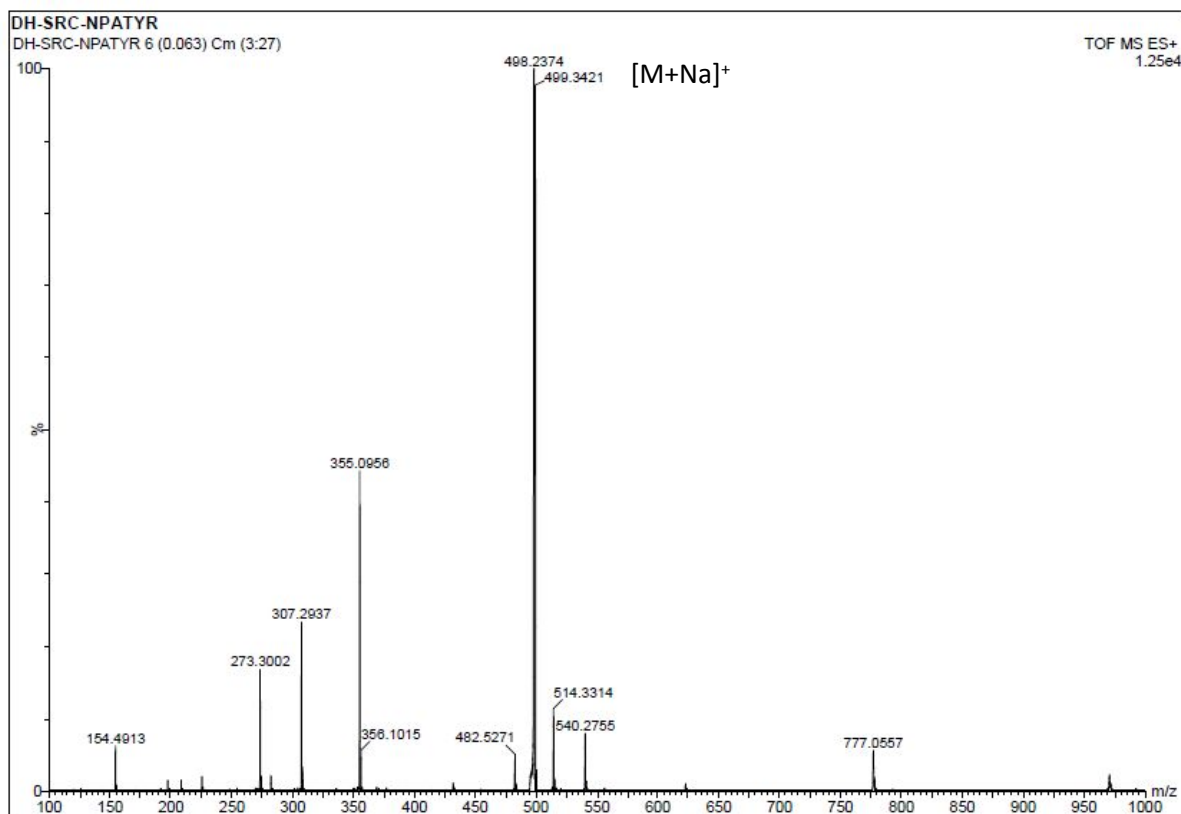


Figure S21. Mass spectrum of Fenamic acid- Aib-Tyr OMe 2.

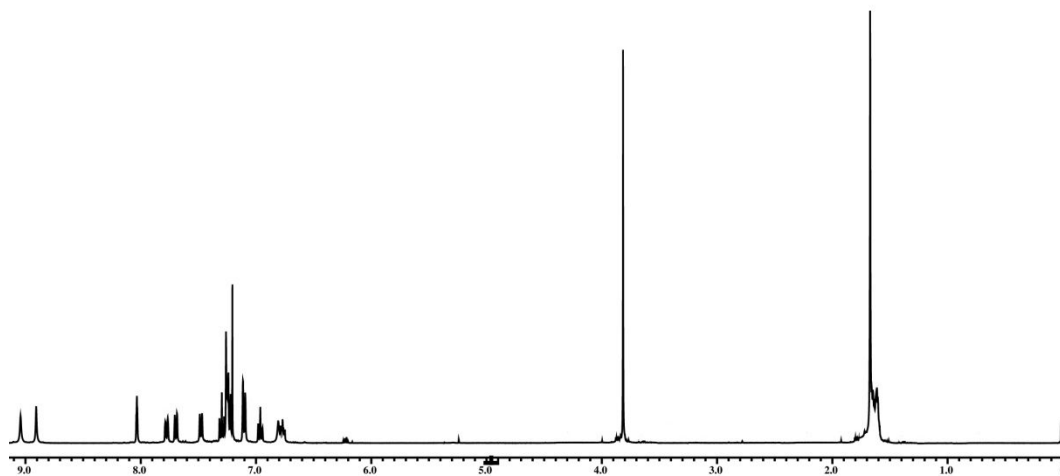


Figure S22. ¹H NMR (400 MHz, CDCl₃) spectrum of Fenamic acid- Aib-Maba OMe **3**.

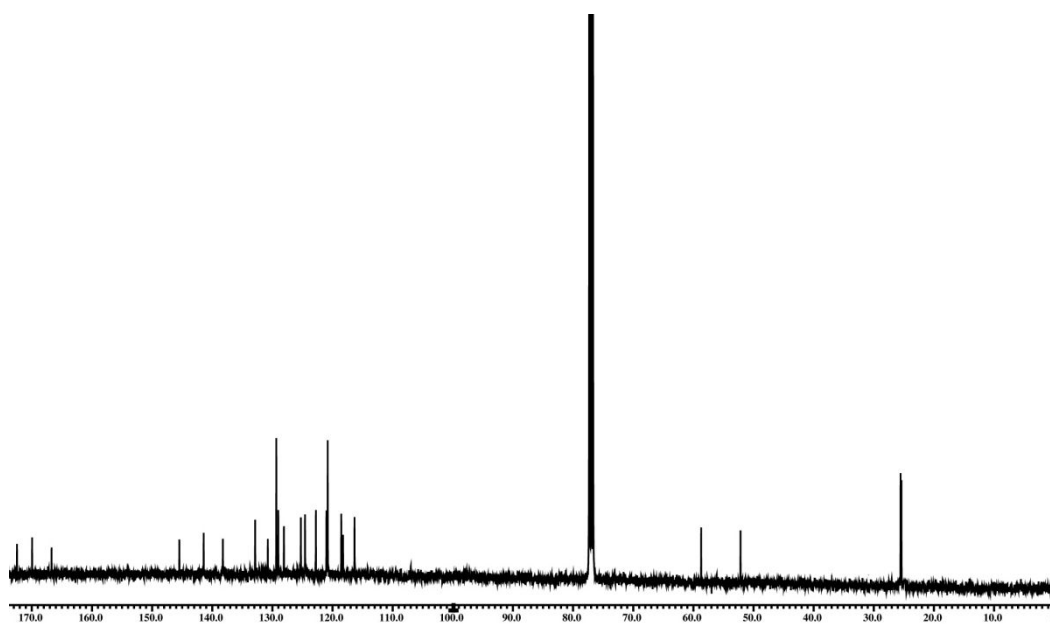


Figure S23. ¹³C NMR (100 MHz, CDCl₃) spectrum of Fenamic acid- Aib-Maba OMe **3**.

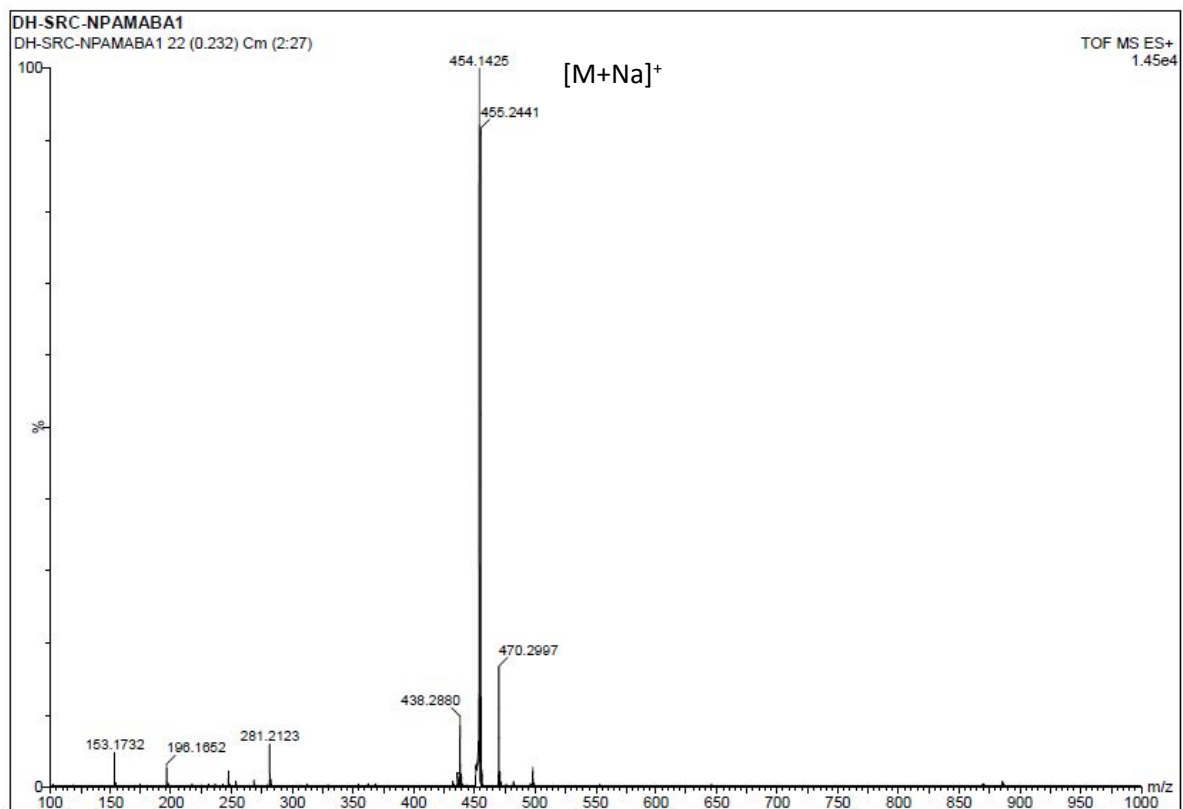


Figure S24. Mass spectrum of Fenamic acid- Aib-Maba OMe **3**.