Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Formation of Supramolecular Single and Double Helix-like Structures by Designed Tripeptides

Rajat Subhra Giri and Bhubaneswar Mandal*

Department of Chemistry, Laboratory of Peptide and Amyloid Research, Indian Institute of Technology Guwahati, Assam- 781039, India

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Crystal images:

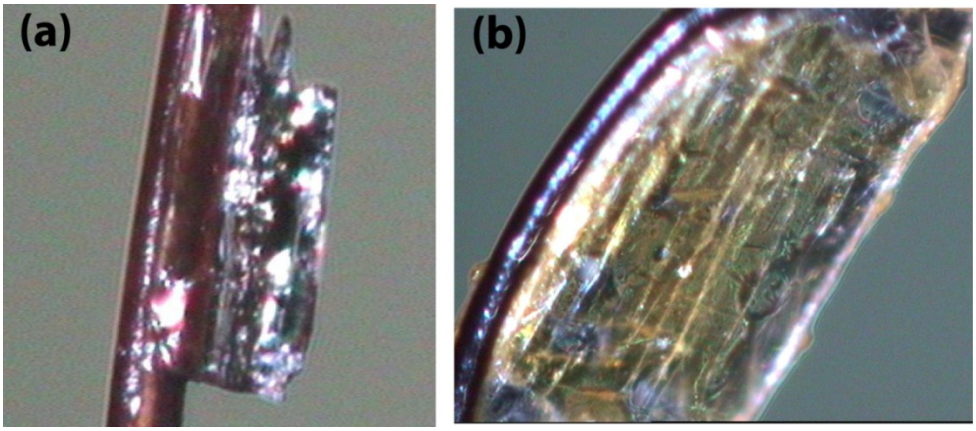


Fig. S1: Block shape crystal structure of (a) Boc-Gly-L-Phg-D-Phe-OMe (**1**) and Boc-Gly-L-Phg-D-Phg-OMe (**2**)

Table S1: Compares the torsional angles (deg) of L/L and D/L tripeptides

Entry	Peptides		ϕ1	ψ1	ϕ2 (L)	ψ2 (L)	ϕ3 (L)	ψ3 (L)	Conformations	Ref
1	**Boc-Gly-L-Phg-L-Phe-OMe**		126.2 (3)	-121.4 (3)	-127.6 (3)	124.4 (3)	-159.9 (3)	-179.0 (3)	Parallel β-sheet	1
					ϕ (L)	**ψ (L)**	**ϕ (D)**	**ψ (D)**		
2	**β-helix peptide**				-133	117	118	-130	β-helix	2,3
3	**Boc-Gly-L-Phg-D-Phe-OMe (1)**	**Molecule A**	-59.8 (4)	150.1 (3)	-141.4 (3)	112.7 (3)	141.1 (3)	8.0 (5)	Anti-parallel β-sheet	This work
		Molecule B	155.7 (3)	-143.2 (3)	-128.7 (3)	140.9 (3)	133.6 (3)	-109.7 (3)		
4	**Boc-Gly-L-Phg-D-Phg-OMe (2)**		172.9 (3)	-175.1 (3)	-138.0 (3)	141.3 (3)	142.3 (3)	18.1 (4)	Anti-parallel β-sheet	This work

Table S2: Hydrogen bonding distances (Å) and Bond angles (º) of peptide **1** and **2**

molecule	D−H···A	*d*(D···H) /Å	*d*(H···A) /Å	*d*(D···A) /Å	<D−H··· A/°	symmetry operation
Boc-Gly-L-Phg-D-Phe-OMe (**1**)	N1-H1···O11	0.86	2.39	3.009(2)	130	x,-1+y,z
	N2-H2···O10	0.86	2.09	2.906(2)	158	
	N3-H3···O9	0.86	2.05	2.899(2)	168	x,-1+y,z
	N4-H4···O6	0.86	2.56	3.390(2)	163	x,1+y,z
	N5-H5 O4	0.86	2.03	2.870(2)	164	
	N6-H6 O3	0.86	2.01	2.850(2)	166	x,1+y,z
	C8-H8 O9	0.98	2.53	3.400(2)	149	x,-1+y,z
	C17-H17B O8	0.97	2.57	3.179(2)	121	
	C20-H20 O5	0.93	2.58	3.336(2)	139	-1+x,y,z
	C31-H31A O4	0.97	2.43	3.278(2)	145	
	C33-H33 O3	0.98	2.39	3.213(2)	142	x,1+y,z
	C37-H37 O3	0.93	2.59	3.432(3)	152	-1+x,1+y,z
	C50-H50B O2	0.96	2.51	3.367(2)	148	1+x,y,z
Boc-Gly-L-Phg-D-Phg-OMe (**2**)	N1-H1 O4	0.86	2.18	3.021(1)	164	1/2-x,-1/2+y,1-z
	N2-H2 O3	0.86	2.09	2.927(1)	164	1/2-x,1/2+y,1-z
	N3-H3 O2	0.86	2.12	2.968(1)	167	1/2-x,-1/2+y,1-z
	C6-H6B O5	0.97	2.41	3.308(1)	155	1/2+x,1/2+y,z
	C14-H14 O2	0.93	2.45	3.296(1)	151	1/2-x,-1/2+y,1-z

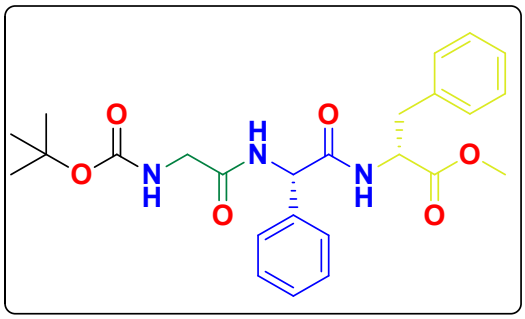
2D NMR and titration data:

Table S3. Proton chemical shifts (ppm) for peptide **1**

Amino acid	HN	Hα	Hβ	Others
Gly	5.24	3.81		Boc CH_3 1.43
Phg	7.41	5.50		OCH_3 3.70
Phe	6.55	4.90-4.85	2.97-2.95	

Table S4. Titration of peptide **1** in $CDCl_3$ with d_6-DMSO

Sl. No.	The volume of d_6-DMSO added (µL)	Chemical shifts δ (ppm)					
		NH of L-Phg	Δδ(NH) of L-Phg	NH of D-Phe	Δδ(NH) of D-Phe	NH of Gly	Δδ(NH) of Gly
1	0	7.410		6.550		5.238	
2	5	7.452		6.630		5.285	
3	10	7.485		6.783		5.341	
4	15	7.549		6.900		5.435	
5	20	7.649	0.239	7.036	0.486	5.674	0.436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O
N
H
H
N
O
O
N
H
O
O

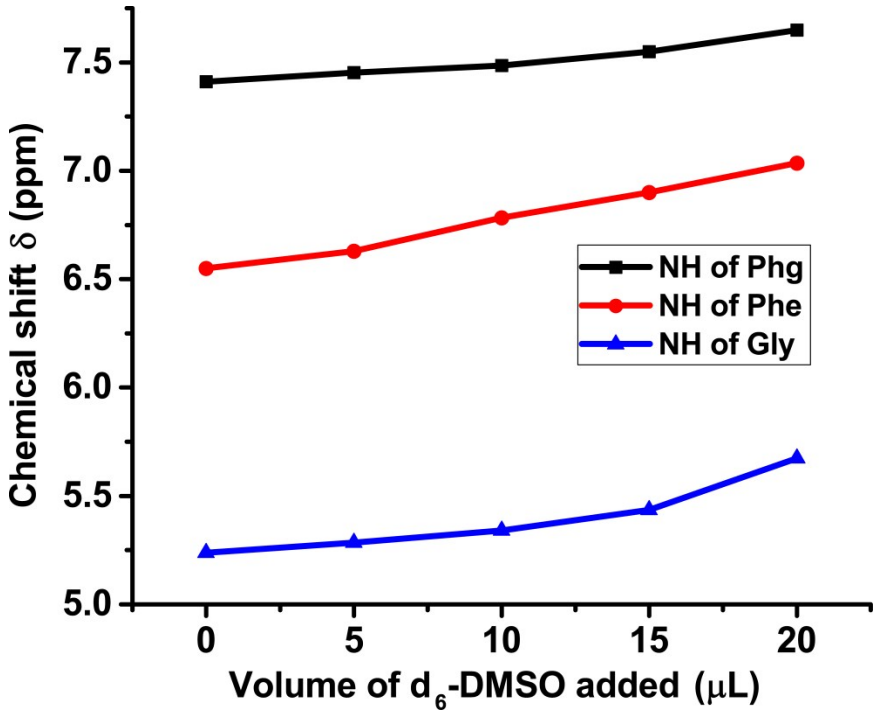

Chemical shift δ (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
0
5
10
15
20
Volume of d6-DMSO added (μL)
NH of Phg
NH of Phe
NH of Gly

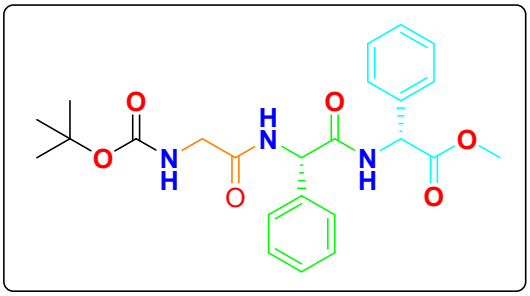
Table S5. Proton chemical shifts (ppm) for peptide **2**

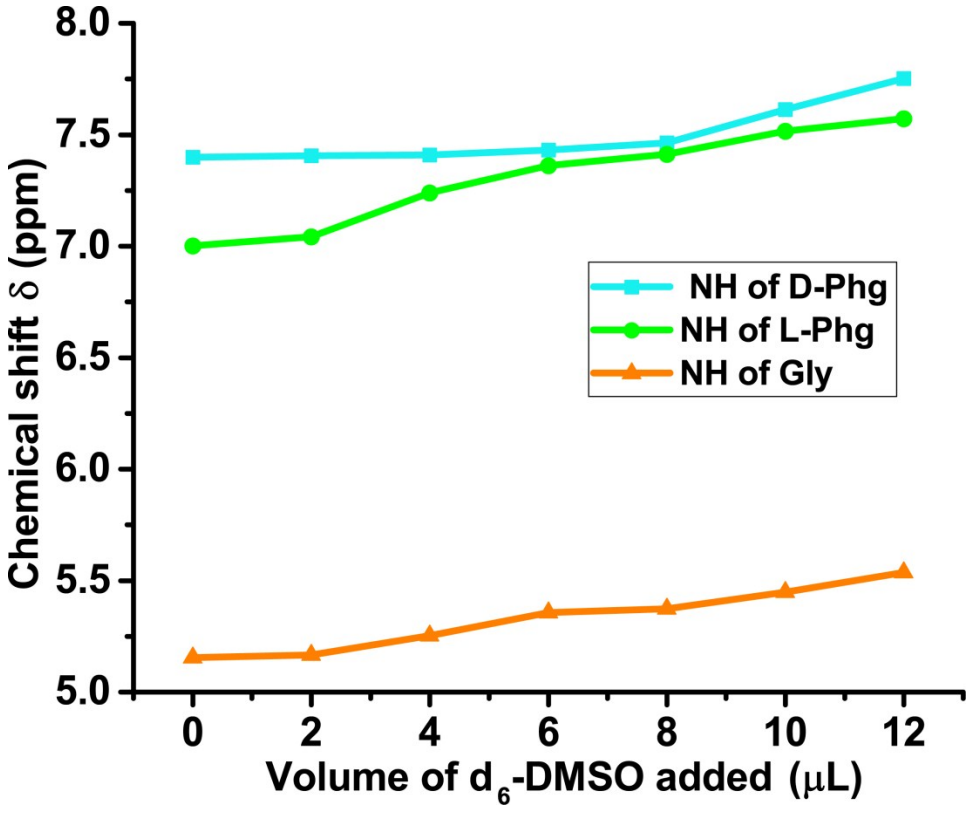
Amino acid	**HN**	**Hα**	**Others**
Gly	5.20	3.82	Boc CH_3 1.41
L-Phg	7.39	5.66	OCH_3 3.70
D-Phg	7.00	5.52-5.51	

Table S6. Titration of peptide **2** in $CDCl_3$ with d_6-DMSO

Sl. No.	**The volume of d_6-DMSO added (µL)**	**Chemical shifts δ (ppm)**					
		NH of D-Phg	**Δδ(NH) of D-Phg**	**NH of L-Phg**	**Δδ(NH) of L-Phg**	**NH of Gly**	**Δδ(NH) of Gly**
1	0	7.002		7.399		5.154	
2	2	7.0042		7.406		5.167	
3	4	7.239		7.409		5.253	
4	6	7.361		7.432		5.357	
5	8	7.412		7.463		5.374	

6	10	7.516		7.613		5.449	
7	12	7.573	0.571	7.752	0.353	5.536	0.382





Spectra of peptide 1:

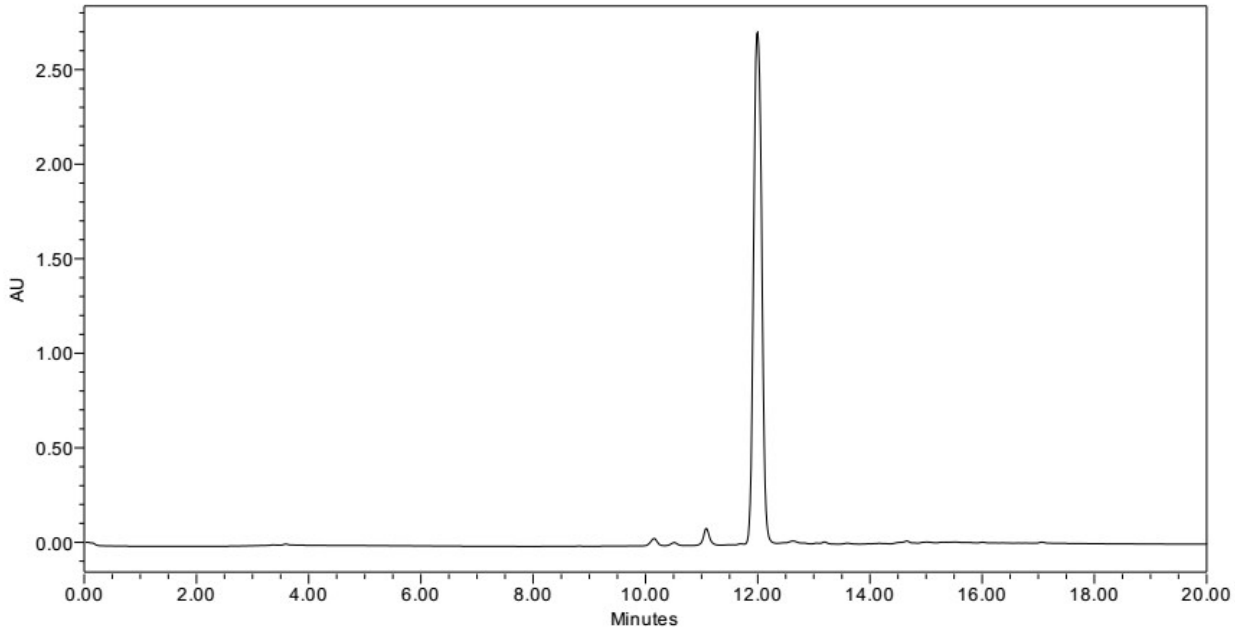


Fig. S2: HPLC profile picture of purified peptide **1**

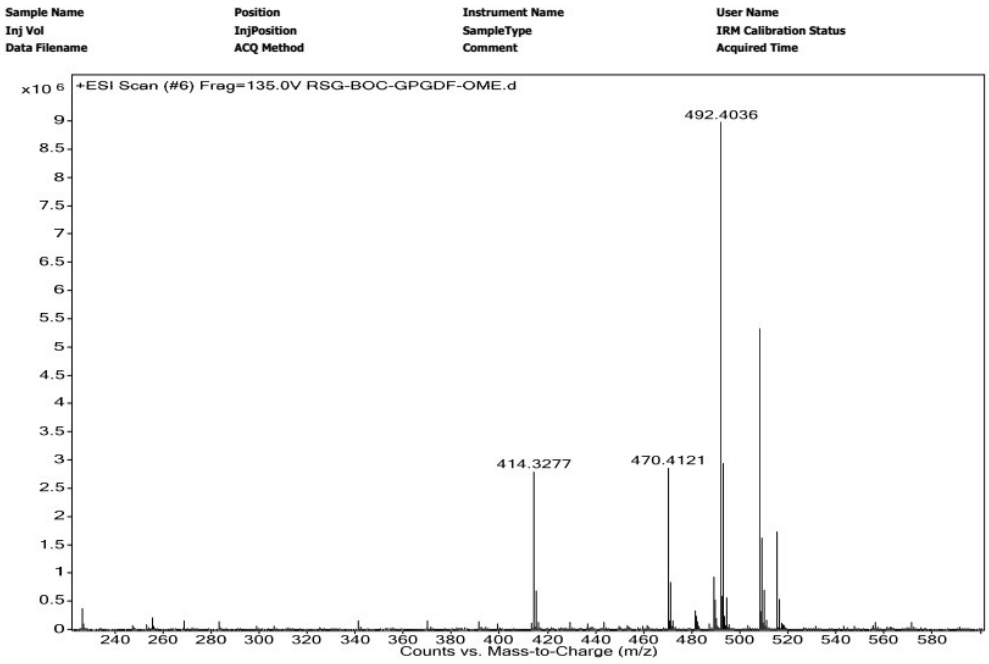


Fig. S3: MS spectra of peptide **1**

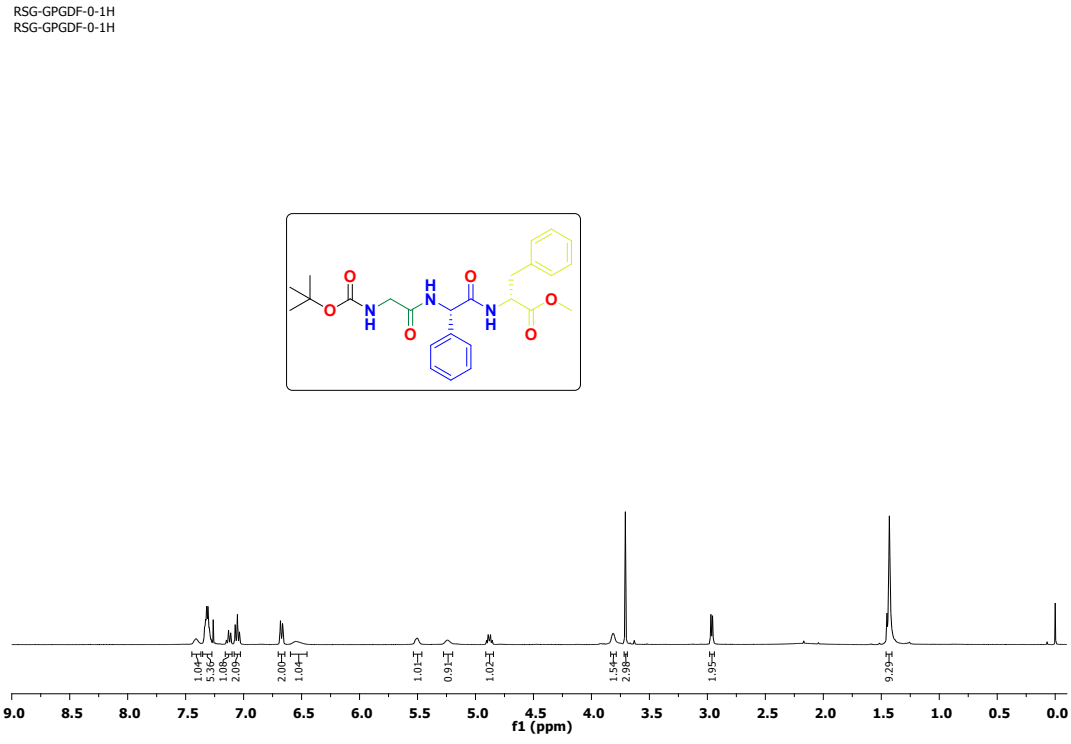


Fig. S4: ^{1}H NMR spectra of peptide **1**

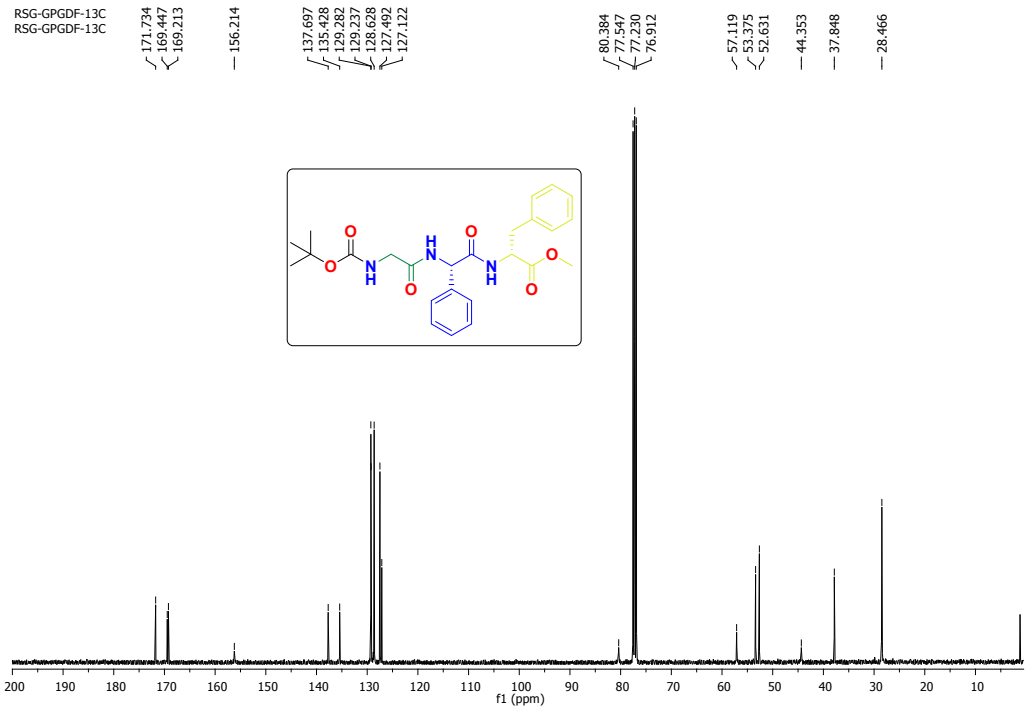


Fig. S5: ^{13}C NMR spectra of peptide **1**

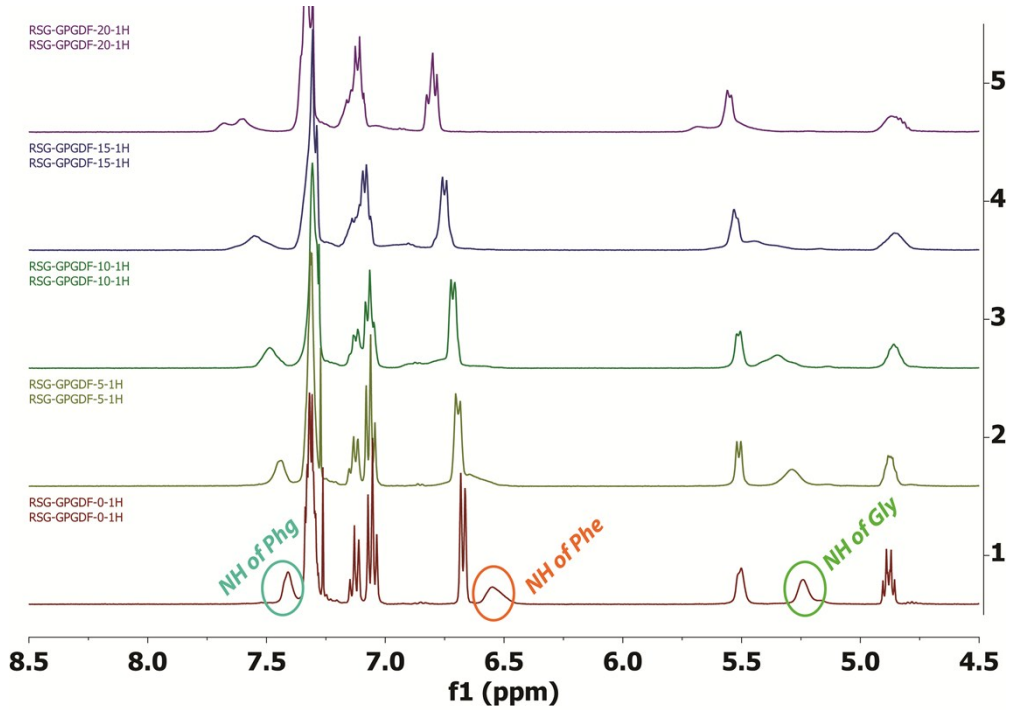


Fig. S6: Partial titration spectra of peptide **1** in $CDCl_3$ with d_6-DMSO

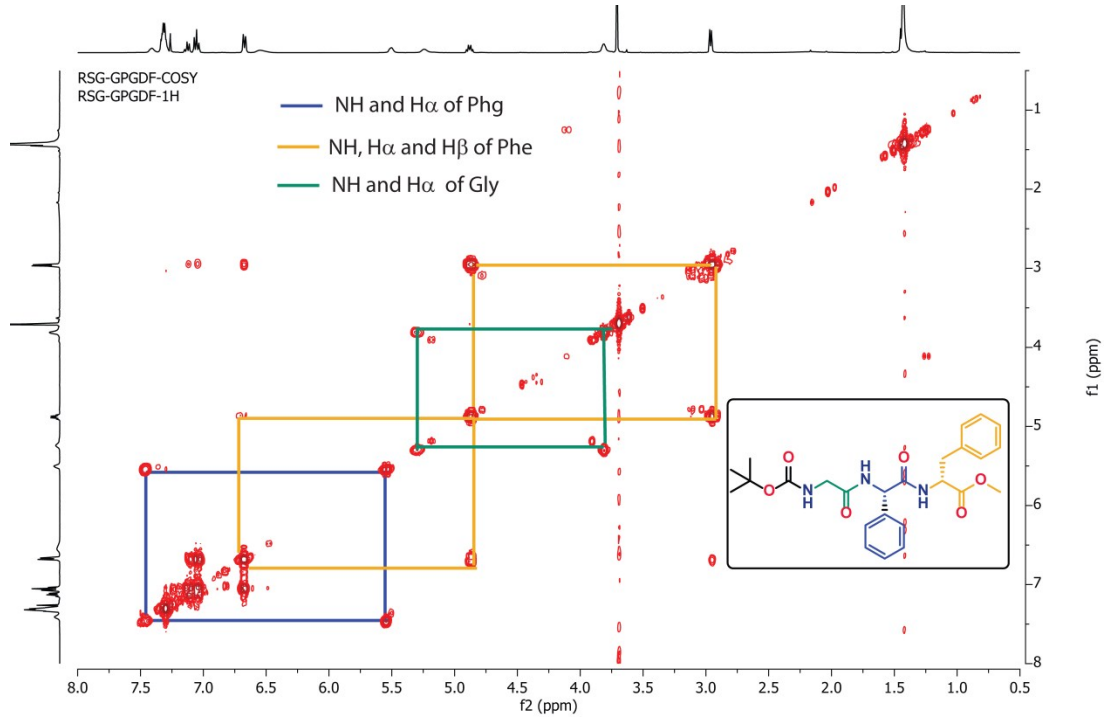


Fig. S7: COSY spectra of peptide **1**

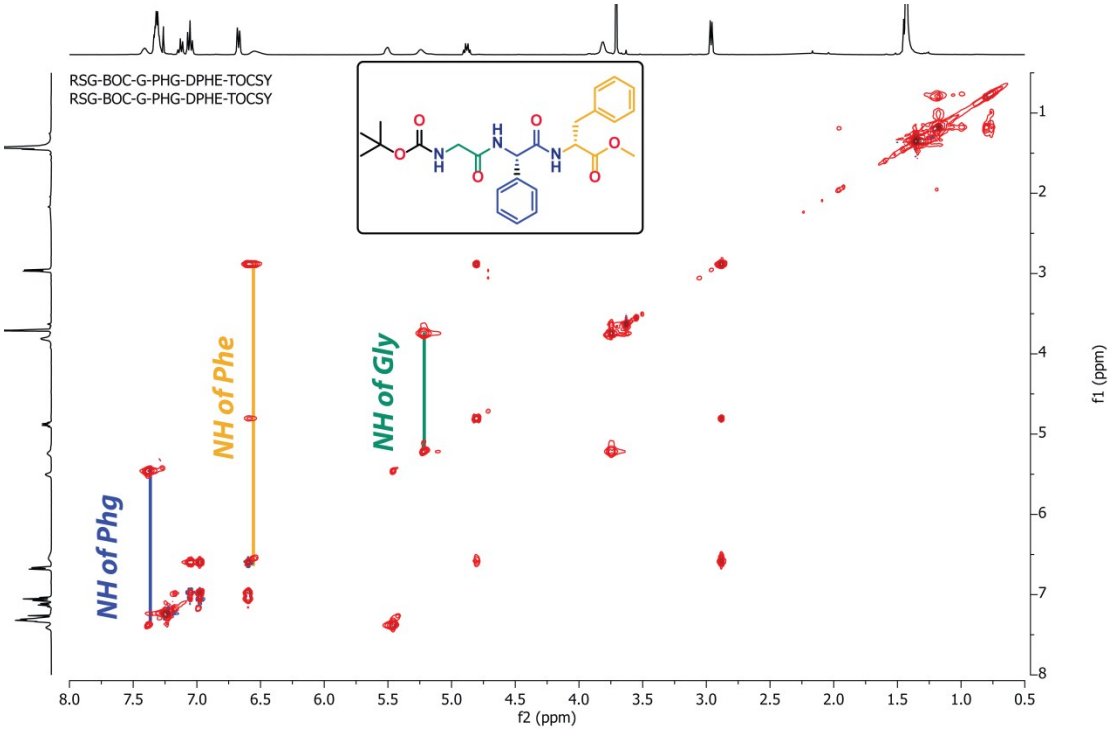


Fig. S8: TOCSY spectra of peptide **1**

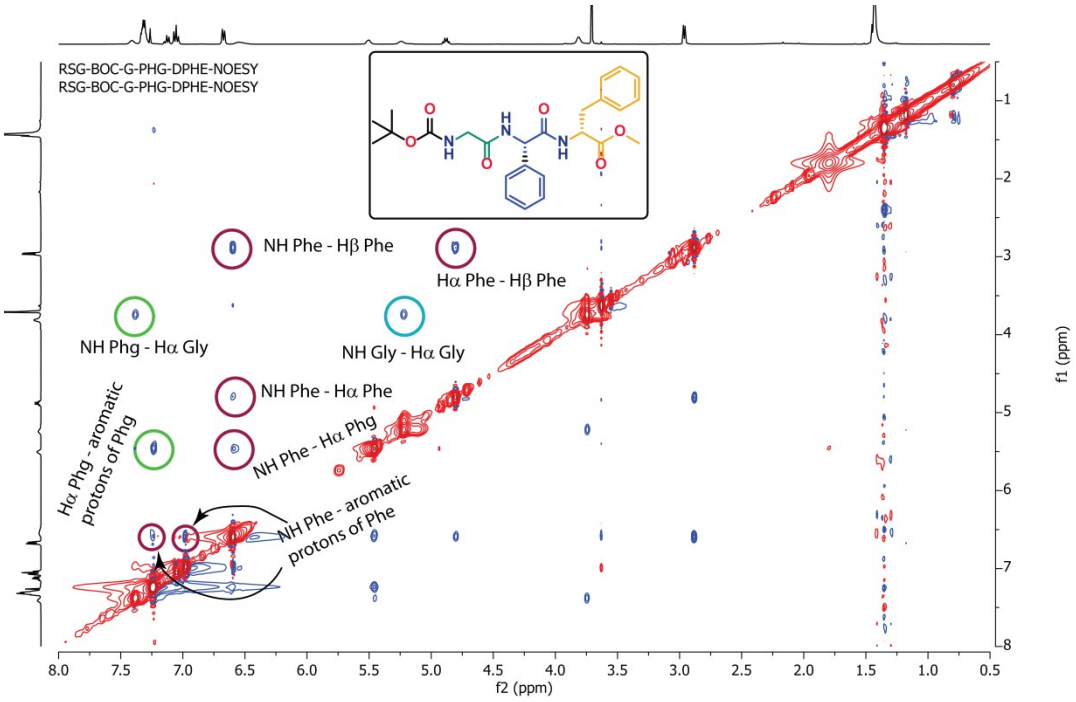


Fig. S9: NOESY spectra of peptide **1**

Spectra of peptide 2:

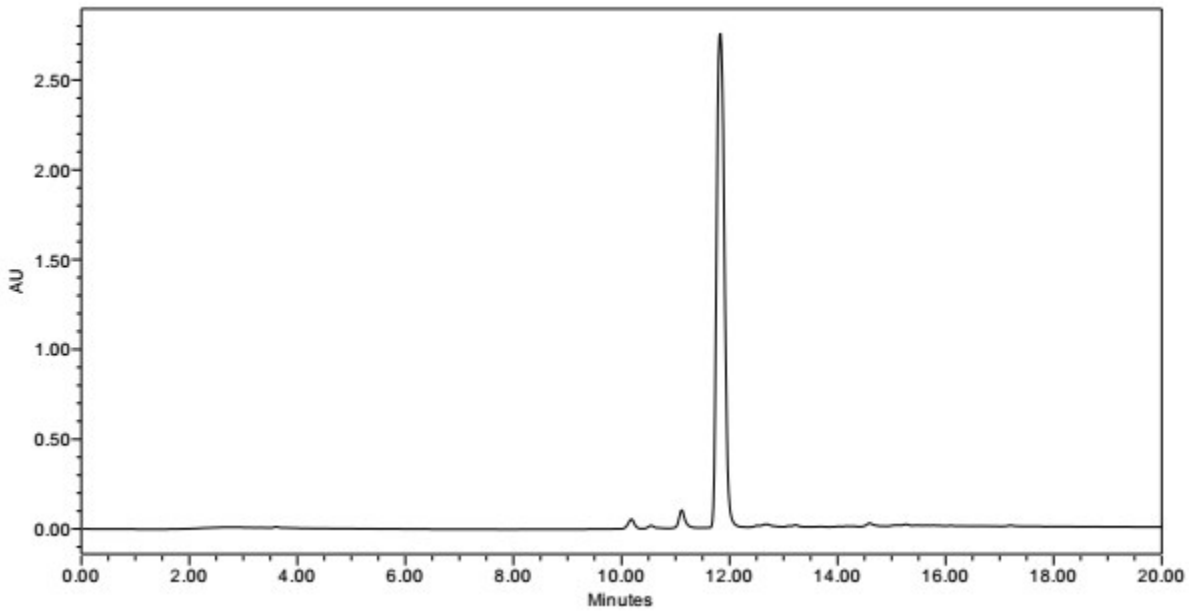


Fig. S10: HPLC profile picture of purified peptide **2**

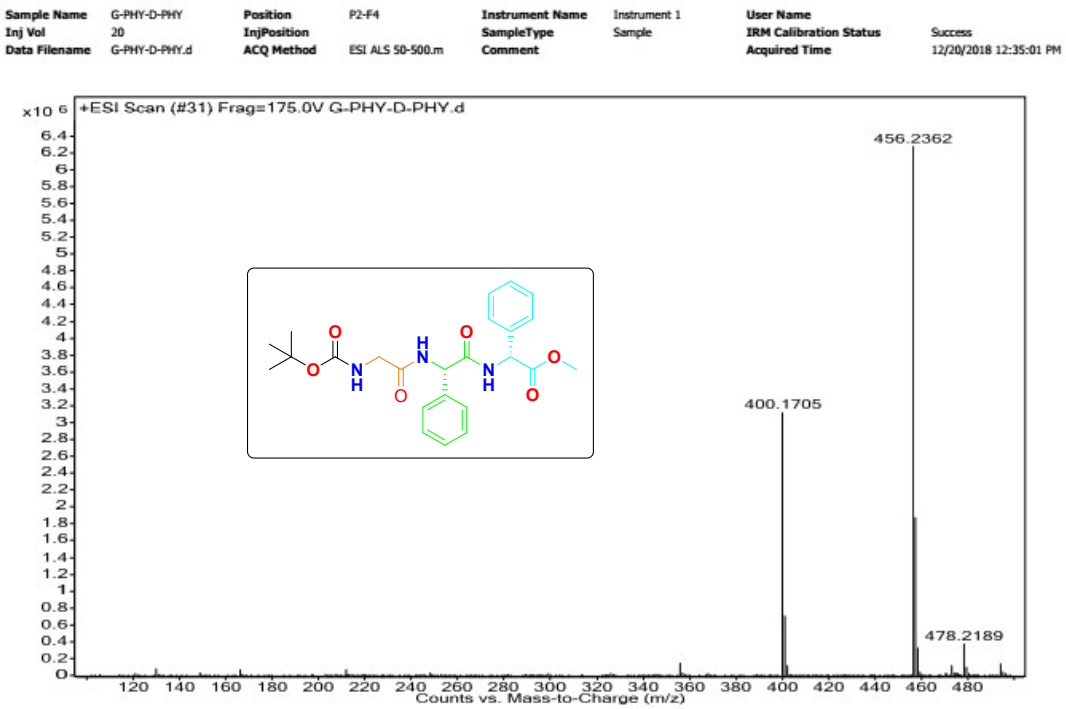


Fig. S11: MS spectra of peptide **2**

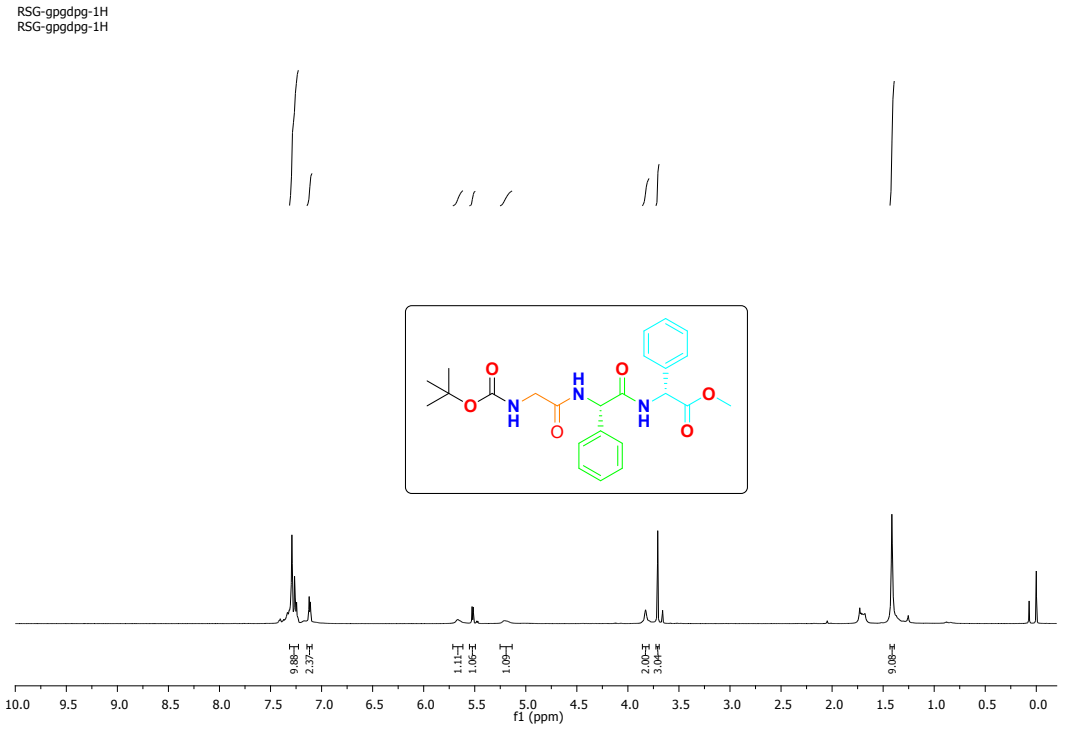


Fig. S12: ^{1}H NMR spectra of peptide **2**

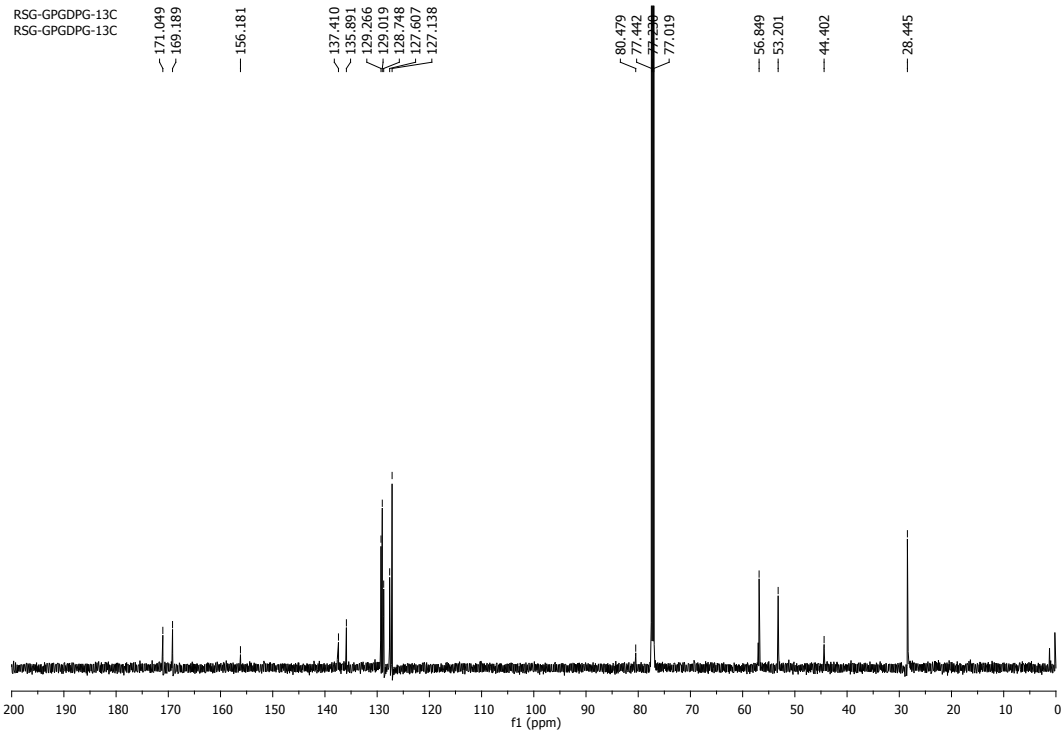


Fig. S13: ^{13}C NMR spectra of peptide **2**

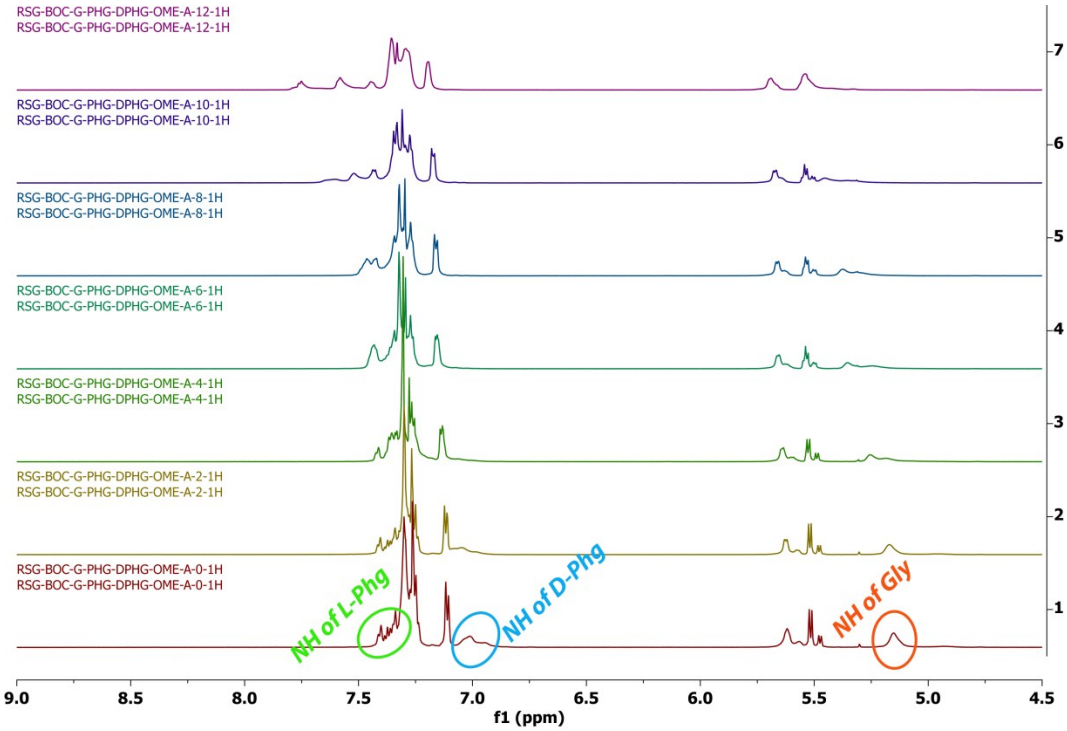


Fig. S14: Partial titration spectra of peptide **2** in $CDCl_3$ with d_6-DMSO

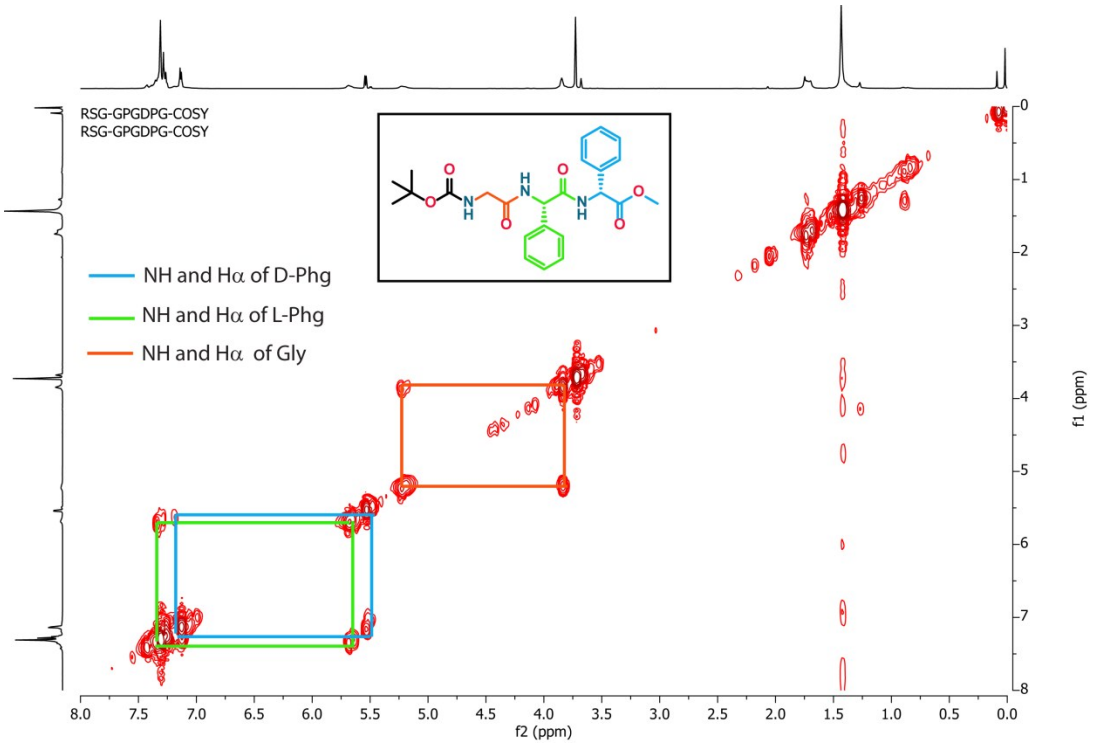


Fig. S15: COSY spectra of peptide **2**

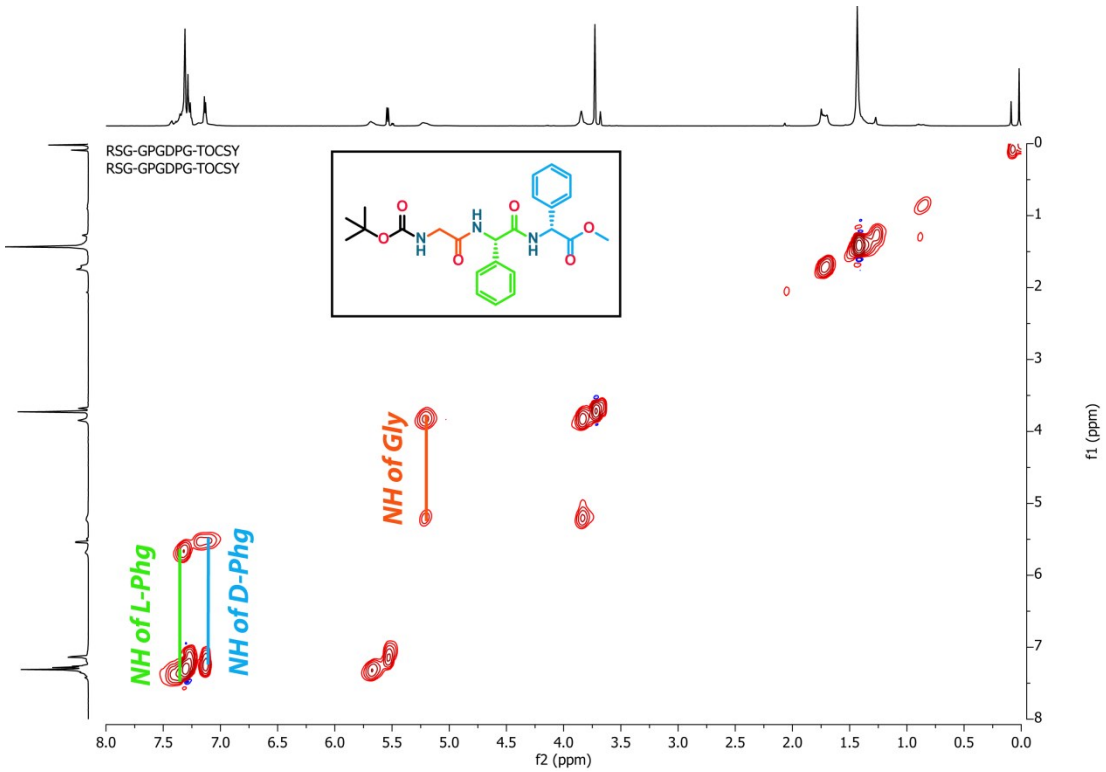


Fig. S16: TOCSY spectra of peptide **2**

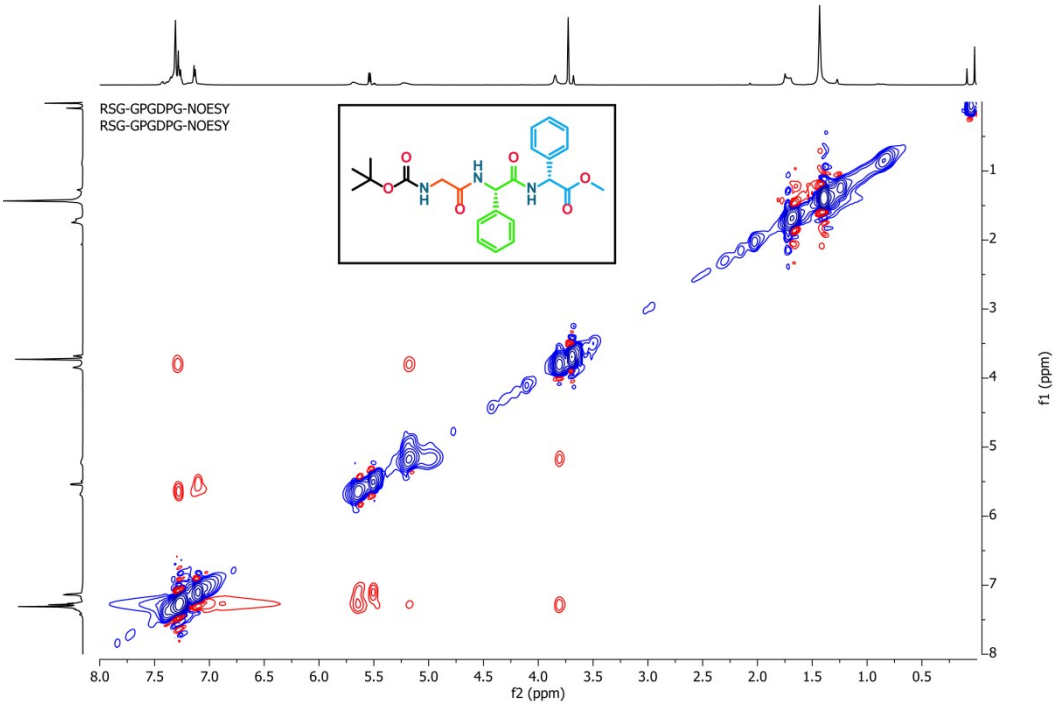


Fig. S17: NOESY spectra of peptide **2**

References:

1**.** R. S. Giri and B. Mandal, *CrystEngComm*, 2019, **21**, 236–243.

2. P. De Santis, S. Morosetti and R. Rizzo, *Macromolecules,* 1974, **7**, 52–58.

3. D. T. Bong, T. D. Clark, J. R. Granja and M. R. Ghadiri, *Angew. Chem. Int. Ed.,* 2001, **40**, 988–1011.