Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Intertwine Gababutin-based Supramolecular Double Helix†

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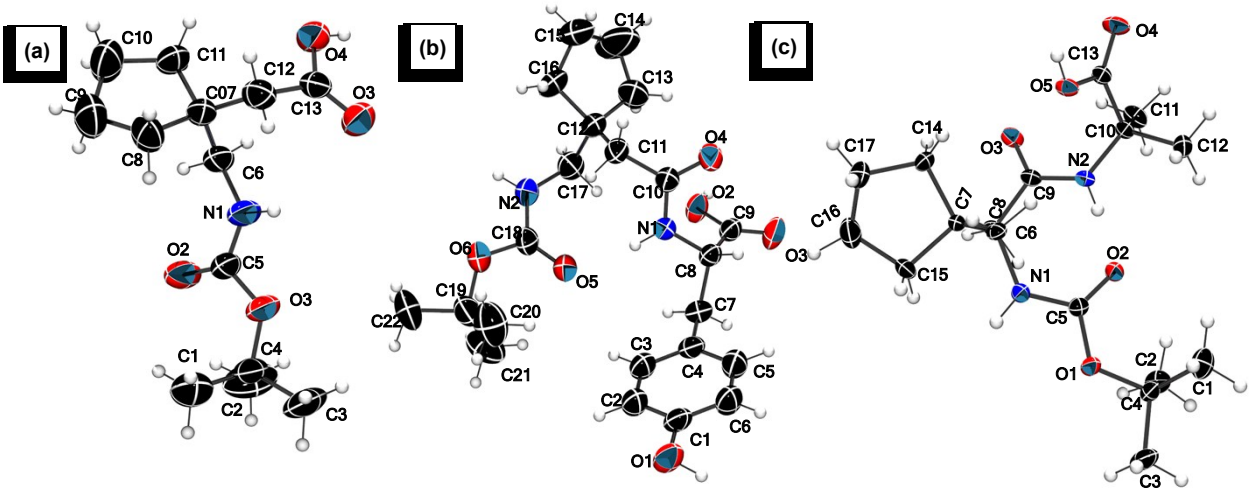


Fig. S1. ORTEP diagrams of (a) compound **1,** (b) compound **2** and (c) compound **3** with atomic numbering. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are not labeled for clarity.

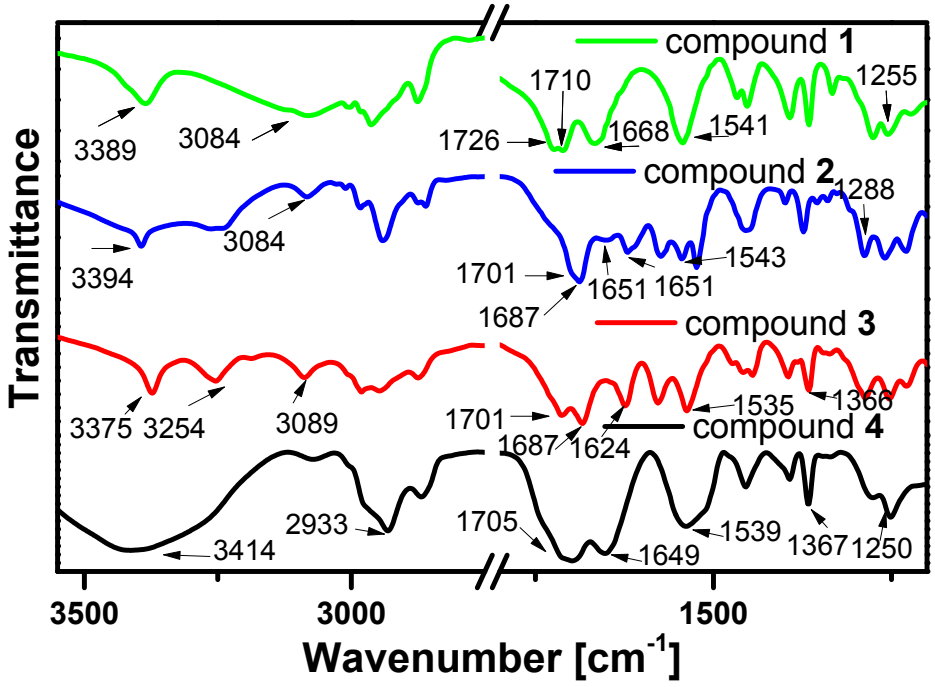


Fig. S2. The representative FT-IR spectra of compounds **1-4** and the informative amide A, amide I and II regions are shown.

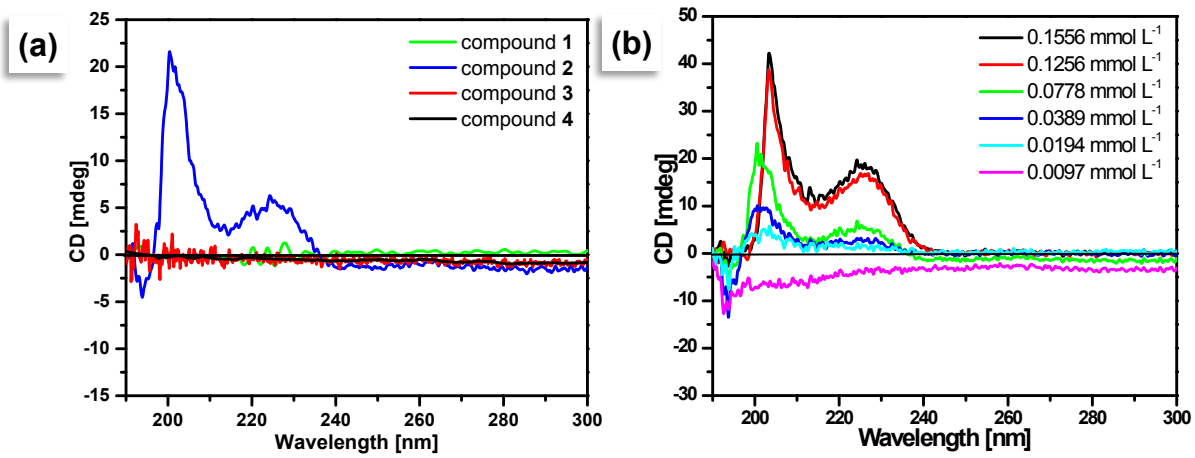


Fig. S3. Circular dichroism spectra of (a) compounds **1-4** in MeOH, c = 0.08 mmol L^{-1} at 25 °C, (b) CD spectra of compound **2** at different concentrations in MeOH.

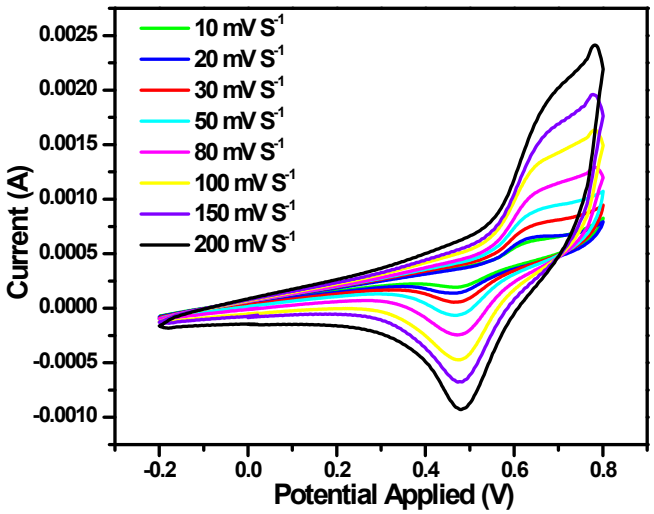


Fig. S4. Cyclic voltammograms of supramolecular double helix architecture **2** at various scan rates.

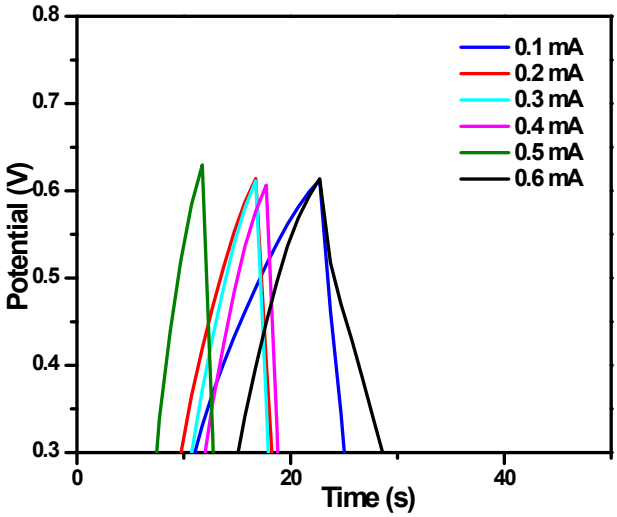


Fig. S5. Galvanostatic charge/discharge curves of double helix architecture of compound **2** at different current densities.

Table S1. Crystal and diffraction parameters of compounds **1-3**

	Compound 1	**Compound 2**	**Compound 3**
Empirical formula	$C_{13}H_{23}N_1O_4$	$C_{22}H_{32}N_2O_6$	$C_{17}H_{30}N_2O_5$
Crystal habit	Colorless hexagonal plates	Colorless rectangular	Colorless plates
Crystalizing solvent	Ethyl acetate	Methanol/DCM	Ethyl acetate/Hexane
Space group	$P\,2_1/c$	$P\,2_1\,2_1\,2_1$	$P\,2_1$
a (Å)	11.6825(7)	10.2051(2)	9.4628(15)
b (Å)	11.2969(5)	12.0183(3)	10.1211(16)
c (Å)	11.8091(8)	19.9352(4)	10.7468(17)
α (deg)	90.00	90.00	90.00
β (deg)	110.399(7)	90.00	108.784(4)
γ (deg)	90.00	90.00	90.00
Volume (Å^3)	1460.8	2445.01	974.444
Z	4	4	19
Molecules/asymmetric unit	1	1	1
Co-crystallized solvent	None	None	None
Molecular weight	257.32	420.22	342.21
Density (g/cm^3) (cal)	1.170	1.142	1.393
F (000)	560	904	418
θ Max. (˚)	24.99	71.48	32.12
R-factor	6.29	4.24	4.57
Goodness-of-fit (S)	1.056	1.064	1.004
λ (Å)	0.71073	1.5418	0.71073
Data/restraints/parameters	2567/0/167	4707/0/282	5327/0/223
CCDC	1501293	1815432	1845125

Table S2. Backbone dihedral angles of compounds **1-3**

Compound	Residue	Φ	θ_1	θ_2	Ψ	ω
1	Gbn (1)	131.1[3]	57.8[3]	45.3[3]	71.1[3]	-
2	Gbn (1)	-106.3[3]	65.4[3]	74.9[3]	-86.8[3]	172[2]
	Tyr (2)	-65.3[2]	-	-	-29.1[3]	-
3	Gbn (1)	104.5[2]	-67.7[2]	-74.6[2]	89.8[2]	-172[1]
	Aib (2)	61.0[2]	-	-	27.9[2]	-
[*] Values in parenthesis are the esd's of appropriate torsions						

Table S3. Hydrogen bond parameters of compounds **1-3**

Compound	Type of hydrogen-bond	D-H···A	H···A(Å)	D···A(Å)	∠D-H···A(°)
1	Intermolecular	N1-H1···O3	2.745[2]	3.292[3]	122.86[2]
		O4-H4···O2	1.858[3]	2.650[3]	161.87[2]
2	Intramolecular	N1-H1···O5	1.977[1]	2.837[2]	165.23[9]
	Intermolecular	N2-H2···O1	2.270[2]	2.974[2]	136.91[12]
		O1-H101···O3	1.779[3]	2.699[2]	164.27[3]
		O2-H···O4	1.525	2.524[3]	171.33[4]
3	Intramolecular	N2-H2···O2	2.006	2.828[2]	159.43
	Intermolecular	N1-H1···O4	2.224	3.044[2]	159.31
		O5-H5···O3	1.815	2.585[2]	155.75
[*] Values in parenthesis are the esd's of appropriate hydrogen bond lengths					

Table S4. Significant NOEs of compound **2** and **4** in DMSO-d_6

Intermolecular	**Intramolecular**
Compound **2**	
Gbn(1) $C^{\alpha}H$ ↔ Tyr(2) para H's	Tyr(2) OH ↔ Tyr(2) aromatic para H's
Gbn(1) $C^{\gamma}H$ ↔ Tyr(2) aromatic para H's	Gbn(1) $C^{\alpha}H$↔ Tyr(2) NH
Gbn(1) $C^{\gamma}H$ ↔ Tyr(2) aromatic ortho H's	Tyr(2) NH ↔ Tyr(2) $C^{\alpha}H$
Tyr(2) para H's ↔ Gbn(1) ring H's	Tyr(2) NH ↔ Tyr(2) $C^{\beta}H$
	Tyr(2) $C^{\alpha}H$ ↔ Tyr(2) aromatic ortho H's
	Tyr(2) $C^{\beta}H$ ↔ Tyr(2) aromatic ortho H's
	Tyr(2) NH ↔ Tyr(2) aromatic ortho H's
	Tyr(2) $C^{\beta}H$ ↔ Tyr(2) aromatic para H's
	Tyr(2) $C^{\alpha}H$ ↔ Tyr(2) $C^{\beta}H$
	Gbn(1) $C^{\gamma}H$ ↔ Tyr(2) $C^{\alpha}H$
	Boc CH's ↔ Tyr(2) aromatic ortho H's
	Boc CH's ↔ Tyr(2) aromatic para H's
Compound **4**	
	Gbn(1) $C^{\alpha}H$ ↔ Ser(2) NH
	Gbn(1) $C^{\gamma}H$ ↔ Ser(2) NH
	Gbn(1) $C^{\gamma}H$ ↔ Gbn(1) NH
	Gbn(1) $C^{\alpha}H$ ↔ Gbn(1) NH
	Ser(2) $C^{\alpha}H$ ↔ Ser(2) NH
	Ser(2) $C^{\beta}H$ ↔ Ser(2) NH

Experimental Section

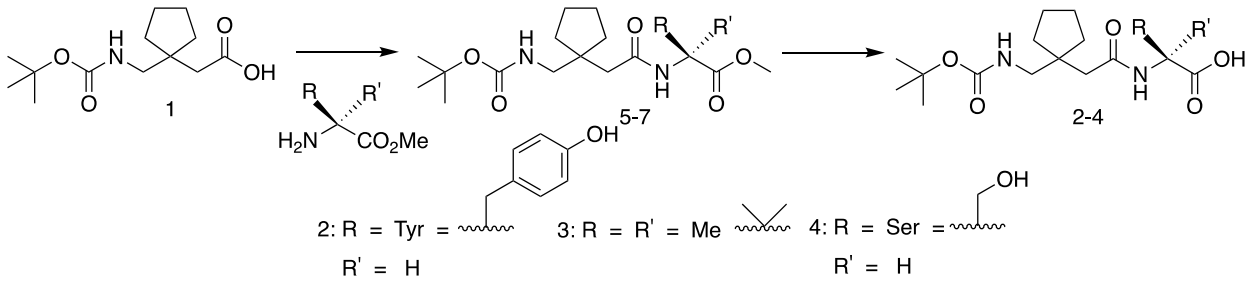
General Methods and Materials: α-Aminoisobutyric acid, L-tyrosine, L-serine, HOBt (1-hydroxybenzotriazole), DCC (*N*,*N*'-dicyclohexylcarbodiimide), polyvinylidene fluoride (average molecular weight Mw ~534,000) and acetylene black were obtained commercially. The precursor 1-(aminomethyl)cyclopentylacetic acid hydrochloride (gababutin; abbreviated as Gbn) was synthesized according to literature report (*Org. Biomol. Chem.*, 2018, **16**, 1728-1735). For chemical reactions and purification of peptides, methanol, dimethylformamide, ethyl acetate and

toluene were dried according to literature. Reactions were monitored by thin-layer chromatography (TLC). Visualization was attained with UV light and potassium permanganate stain followed by charring on hot-plate. All intermediates and final compounds were purified and well characterized by FT-IR, ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and mass spectral studies. The concentrations were in the range 1-10 mmol L^{-1} in $CDCl_3$ and DMSO-d_6 for ^{1}H and ^{13}C-NMR. Chemical shifts were expressed in parts per million (ppm, δ) relative to residual solvent protons as internal standards ($CHCl_3$: δ 7.26, DMSO: 2.50 for ^{1}H, $CHCl_3$: δ 77.00, DMSO: 39.50 for ^{13}C). ^{1}H-NMR multiplicities were designated as singlet (s), doublet (d), triplet (t), quartet (q) multiplet (m) and broad singlet (bs). ^{1}H NMR spectra assignments of all compounds were achieved by using a combination of 2D COSY and ROESY experiments. All 2D NMR experiments were recorded at 298 K with mixing time of 200 ms. FT-IR spectroscopic measurements were done with KBr pellet technique and scanned between 500 cm^{-1} to 4000 cm^{-1} over 64 scans at a resolution of 4 cm^{-1} and at an interval of 1 cm^{-1}. Mass spectra were recorded on a Bruker micrOTOF-Q II by positive-mode electrospray ionization. Cyclic voltammetry (CV) was performed using an AUTOLAB/PG STAT302N and a three-electrode cell equipped with platinum working, platinum counter and an Ag/AgCl reference electrodes. Aqueous Na_2SO_4 (0.5 N) solution was used as supporting electrolyte. For electrochemical study, a 70%: 25%: 5% proportions of peptide crystals, acetylene black (as a conductive agent) and polyvinylidene fluoride (as binder) were grinded in ethanol to form a paste. This active material was placed/dispersed on nickel foam (20 mm × 10 mm) plate and dried at 60 °C in incubator for an hour. This active material coated Ni-foam typically employed as a working electrode. Pt and Ag/AgCl were used as counter electrode and reference electrode respectively. The following equation 1 was used to calculate specific capacitance from galvanostatic charge/discharge curves.

$$C = \frac{I\Delta t}{m\Delta V}$$ ---------- Equation no. S1

Where C (F g^{-1}) is the specific capacitance; I(A) is the discharge current; Δt(s) is the discharge time; ΔV (V) is the potential window; and m (mg) is the mass of active materials loaded in working electrode.

Synthesis of Peptides



Scheme S1. Chemical structures and synthetic scheme of compounds. Reagents and conditions: (i) DCC, HOBt, DMF; (ii) 2N NaOH, MeOH.

Boc-Gbn-OH 1: 2.5 g (9.73 mmol) of Gababutin hydrochloride was added to a mixture of 1,4-dioxane : water (2:1 15 mL) and neutralized with 1M NaOH (20 mL). This mixture was stirred and cooled in an ice-water bath (the pH should be above 8). After 15 minutes, 2.33 g (10.70 mmol) of di-*tert*-butylpyrocarbonate was added and stirred overnight at room temperature. The solution was concentrated under *vacuo* to about 10-15 mL and it was cooled for 5 minutes in an ice-water bath. The cooled solution was covered with a layer of ethyl acetate (about 30 mL) and acidified with 1M $KHSO_4$ to pH 2-3. It was extracted with ethyl acetate (3 × 30 mL). The extracted ethyl acetate was dried over anhydrous Na_2SO_4 and evaporated in vacuo to yield **1** as white solid.

Yield 2.37 g (95%). FT-IR (KBr): $\tilde{\upsilon}$ = 3385, 2962, 1724, 1666, 1542, 1255 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 6.78 (m, 1H, NH of Gbn), 2.96 (d, J = 5.48 Hz, 2H, $C^{\gamma}Hs$ of Gbn), 2.19 (s, 2H, $C^{\alpha}Hs$ of Gbn), 1.55-1.49 (m, 4H), 1.45-1.40 (m, 4H), 1.36 (m, 9H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 173.51, 156.42, 77.68, 46.82, 45.42, 41.54, 34.41, 28.36, 24.45 ppm. HRMS (ESI-TOF) *m/z*: $(M + Na)^+$ calcd for $C_{13}H_{23}NO_4Na$ 280.1525; Found 280.1622.

General Procedure for Methyl Ester Hydrolysis:

Terminally protected dipeptide in methanol (20 mL/g) was taken in a round bottom flask (R.B) and 2N NaOH was added drop wise. The progress of hydrolysis was monitored by thin layer chromatography (TLC). The reaction was allowed for overnight. After completion of the reaction, 15 mL of distilled water was added to the reaction mixture and methanol was removed under vacuum. The aqueous part was washed with diethyl ether (2 × 30 mL). Then aqueous part

was cooled under ice-water bath for 15 minutes and then pH was adjusted to 2-3 by drop wise addition of 1M HCl. It was extracted with ethyl acetate (3 × 30 ml). The extracted ethyl acetate was dried over anhydrous Na_2SO_4 and evaporated under vacuum to yield corresponding carboxylic acid which was used for the next step without purification.

General Procedure for Peptide Coupling:

Boc-protected compound (1.0 equiv) was dissolved in dry-DMF (4 mL/g) and stirred on an ice-water bath. Methyl ester protected amino acid was isolated from its corresponding methyl ester hydrochloride (2.0 equiv) by neutralization and subsequently extracted twice with ethyl acetate (2 × 30 mL). The collected ethyl acetate extracts was dried over anhydrous Na_2SO_4 and concentrated to 6-8 mL. It was then added to the pre-cooled reaction mixture followed by addition of (1.0 equiv) HOBt, (1.1 equiv) dicyclohexylcarbodiimide (DCC). The reaction mixture was allowed to come to room temperature and stirred for 2 days. After completion of the reaction, ethyl acetate (40 mL) was added to the reaction mixture and dicyclohexylurea or diisopropylurea was filtered off. The organic layer was washed with 1M HCl (3 × 30 mL), brine (2 × 30 mL), 1M sodium carbonate (3 × 30 mL) and brine (2 × 30 mL) and dried over anhydrous Na_2SO_4 and evaporated in a vacuum. The purification was done by using silica gel column (100-200 mesh).

Boc-Gbn(1)-Tyr(2)-OMe 5:

5 was obtained as white fluffy solid. Purification was done by silica gel column (100-200 mesh) using ethyl acetate and toluene (3 : 7) as eluent. Yield 1.62 g (87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (m, 1H, NH of Tyr(2)), 7.04 (d, J = 7.86 Hz, 2H, ring protons of Tyr), 6.70 (d, J = 8.20 Hz, 2H, ring protons of Tyr), 5.05 (m, 1H, NH of Gbn(1)), 4.82 (m, 1H, C$^{\alpha}$H of Tyr), 3.73 (s, 3H, OC$\underline{H}_3$), 3.30-3.12 (m, 2H, C$^{\beta}$Hs of Tyr), 2.97-2.86 (m, 2H, C$^{\gamma}$Hs of Gbn), 2.06 (s, 2H, C$^{\alpha}$Hs of Gbn), 1.45 (s, 9H), 1.40-1.18 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.78, 171.98, 157.52, 155.59, 130.27, 127.90, 115.63, 79.88, 53.94, 52.43, 46.73, 42.42, 37.52, 36.95, 34.36, 33.83, 31.72, 28.52, 26.07, 22.78, 21.55, 14.25 ppm. HRMS (ESI-TOF) *m/z*: (M + Na)$^+$ calcd for $C_{23}H_{34}N_2O_6Na$ 457.2315; Found 457.2363.

Boc-Gbn(1)-Aib(2)-OMe 6:

6 obtained as white solid. Purification was done by silica gel column (100-200 mesh) using ethyl acetate and toluene (2 : 8) as eluent. Yield 1.37 g (90%). FT-IR (KBr): $\tilde{\upsilon}$ = 3301, 3258, 2933, 1744, 1687, 1645, 1558, 1364, 1285, 1150 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (s, 1H,

NH of Aib(2)), 5.07 (t, J = 6.48 Hz, 1H, NH of Gbn(1)), 3.71 (s, 3H, OC<u>H</u>$_3$), 3.14 (d, J = 7.04 Hz, 2H, C$^{\gamma}$Hs of Gbn), 2.11 (s, 2H, C$^{\alpha}$Hs of Gbn), 1.72-1.66 (m, 4H), 1.52 (s, 6H), 1.44 (s, 9H), 1.40-1.30 (m, 3H), 1.15-1.03 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.27, 171.07, 157.37, 79.76, 56.11, 52.47, 49.28, 47.15, 46.83, 43.28, 36.04, 34.08, 28.51, 25.74, 25.08, 23.98 ppm. HRMS (ESI-TOF) *m/z*: $(M + Na)^+$ calcd for $C_{18}H_{32}N_2O_5Na$ 379.2209; Found 379.2252.

Boc-Gbn(1)-Ser(2)-OMe 7:

7 was obtained as white fluffy solid. Purification was done by silica gel column (100-200 mesh) using ethyl acetate and toluene (3 : 7) as eluent. Yield 1.40 g (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (bs, 1H, OH of Ser(2)), 7.53 (d, J = 7.86 Hz, 1H, NH of Ser), 5.06 (m, 1H, NH of Gbn(1)), 4.61 (m, 2H, C$^{\beta}$H of Ser), 4.16-3.92 (m, 1H, C$^{\alpha}$H of Ser), 3.76 (s, 3H, OC<u>H</u>$_3$), 3.22-3.12 (m, 2H, C$^{\gamma}$Hs of Gbn), 2.21 (m, 2H, C$^{\alpha}$Hs of Gbn), 1.70-1.64 (m, 4H), 1.66-52 (m, 2H), 1.50 (s, 9H), 1.26-1.18 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.71, 171.53, 171.09, 171.06, 157.63, 157.52, 80.42, 63.46, 63.34, 55.23, 52.62, 47.13, 46.65, 43.07, 37.58, 36.16, 36.00, 35.97, 34.29, 34.22, 28.55, 29.81, 29.77, 28.53, 26.11, 24.14, 24.02, 21.53 ppm. HRMS (ESI-TOF) *m/z*: $(M + Na)^+$ calcd for $C_{17}H_{30}N_2O_6Na$ 381.2002; Found 381.2001.

Boc-Gbn(1)-Tyr(2)-OH 2:

2 was obtained as white crystalline solid. Yield 1.17 g (93%). FT-IR (KBr): $\tilde{\upsilon}$ = 3394, 3261, 3082, 1701, 1687, 1651, 1620, 1543, 1522, 1288 cm^{-1}. H NMR (400 MHz, DMSO-d_6): δ = 12.64 (bs, 1H, COO<u>H</u> of Tyr(2)), 9.18 (s, 1H, OH of Tyr), 8.24 (d, J = 7.88 Hz, 1H, NH of Tyr), 7.02 (d, J = 8.12 Hz, 2H, ring protons of Tyr), 6.64 (d, J = 8.20 Hz, 2H, ring protons of Tyr), 4.34 (m, 1H, NH of Gbn(1)), 2.99-2.88 (m, 2H, C$^{\gamma}$Hs of Gbn), 2.85-2.65 (m, 2H, C$^{\beta}$Hs of Tyr), 1.98 (d, J = 3.60 Hz, 2H, C$^{\alpha}$Hs of Gbn), 1.41-1.32 (m, 11H), 1.30-1.08 (m, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 173.36, 170.65, 156.29, 155.92, 129.95, 127.67, 114.93, 77.69, 53.73, 46.40, 41.85, 37.02, 35.99, 33.27, 32.85, 28.27, 25.70, 21.08 ppm. HRMS (ESI-TOF) *m/z*: $(M + H)^+$ calcd for $C_{22}H_{33}N_2O_6$ 421.2339; Found 421.2199.

Boc-Gbn(1)-Aib(2)-OH 3:

3 was obtained as white solid. Yield 0.88 g (91%). FT-IR (KBr): $\tilde{\upsilon}$ = 3373, 3254, 2980, 1713, 1684, 1623, 1578, 1366, 1253, 1167 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.16 (s, 1H, NH of Aib(2)), 6.80-6.73 (m, 1H, NH of Gbn(1)), 2.92 (d, J = 4.92 Hz, 2H, C$^{\gamma}$Hs of Gbn), 2.01 (s, 2H, C$^{\alpha}$Hs of Gbn), 1.56-1.40 (m, 7H), 1.40-1.34 (m, 11H), 1.30 (s, 6H) ppm. ^{13}C NMR (100

MHz, DMSO-d_6): δ = 175.75, 170.54, 156.50, 77.87, 54.75, 46.70, 46.47, 42.74, 34.65, 28.38, 25.00, 24.07 ppm. HRMS (ESI-TOF) *m/z*: $(M + Na)^+$ calcd for $C_{17}H_{30}N_2O_5Na$ 365.2052; Found 365.2093.

Boc-Gbn(1)-Ser(2)-OH 4:

4 was obtained as white solid. Yield 1.18 g (95%). FT-IR (KBr): $\tilde{\upsilon}$ = 3414, 2933, 1705, 1649, 1539, 1454, 1250 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 12.41 (bs, 1H, COOH of Ser(2)), 8.14 (d, J = 7.40 Hz, 1H, NH of Ser), 6.80 (m, 1H, NH of Gbn(1)), 4.89 (bs, 1H, OH of Ser), 4.29-4.25 (m, 1H, C^{α}Hs of Ser), 3.69-3.65 (m, C^{β}Hs of Ser), 3.05-2.88 (m, 2H, C^{γ}Hs of Gbn), 2.15-2.06 (m, 2H, C^{α}Hs of Gbn), 1.55-1.50 (m, 4H), 1.46-1.40 (m, 2H), 1.38 (s, 9H), 1.26-1.20 (m, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 172.55, 171.42, 171.17, 156.69, 156.55, 78.00, 61.87, 55.02, 54.96, 46.95, 46.72, 43.18, 37.58, 35.00, 33.97, 33.52, 29.49, 28.73, 26.20, 24.44, 22.20, 21.57, 14.37 ppm. HRMS (ESI-TOF) *m/z*: $(M + Na)^+$ calcd for $C_{16}H_{28}N_2O_6Na$ 367.1845; Found 367.1848.

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

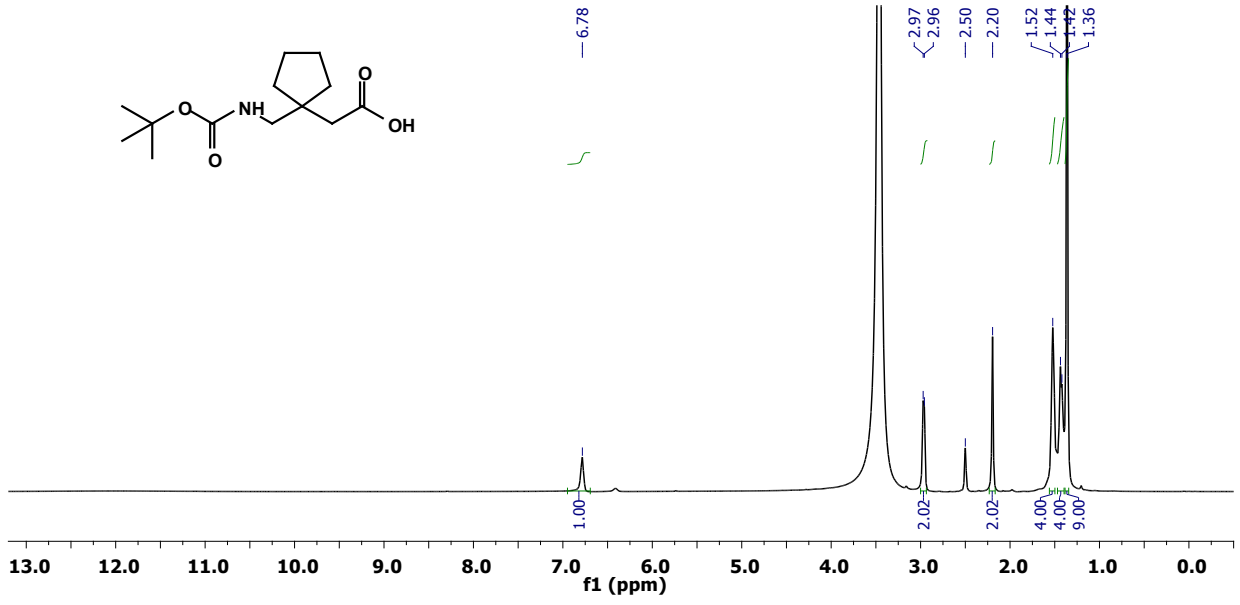


Fig. S6. ^1H NMR spectrum (400 MHz, DMSO-d_6) of Boc-Gbn(1)-OH **1**.

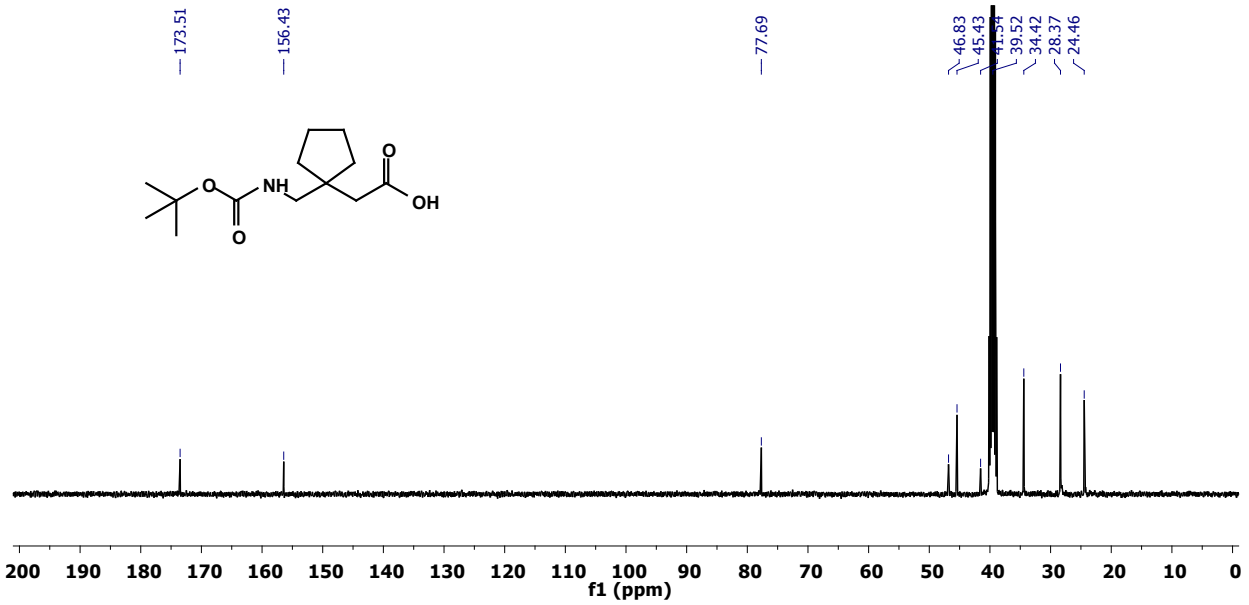


Fig. S7. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of Boc-Gbn(1)-OH **1**.

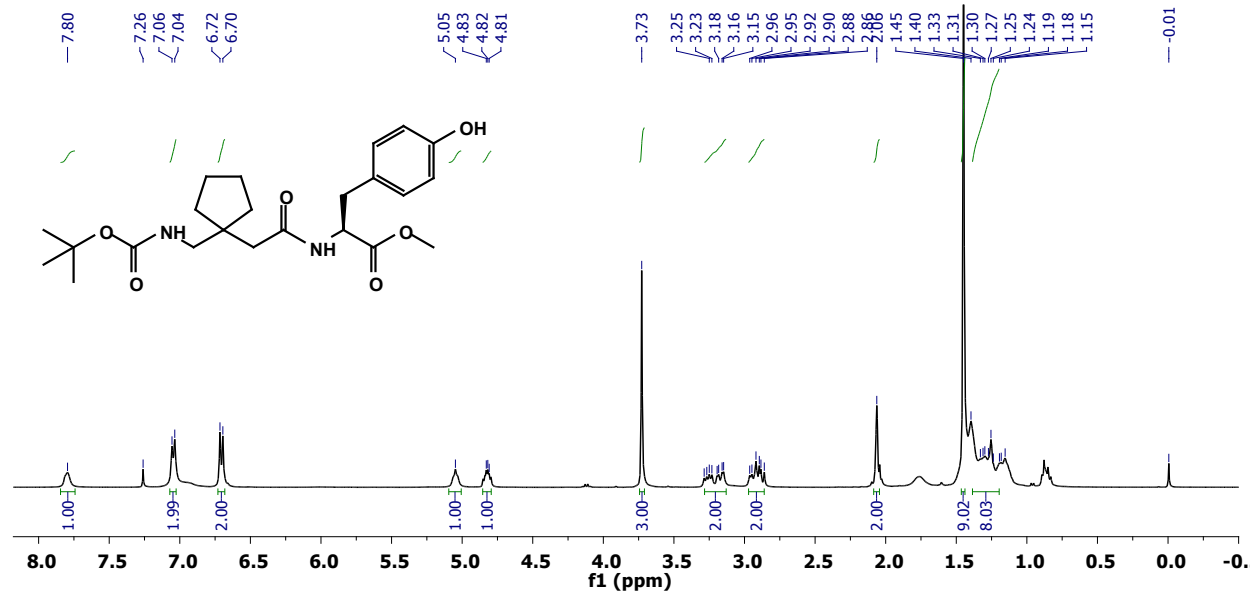


Fig. S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Boc-Gbn(1)-Tyr(2)-OMe **5**.

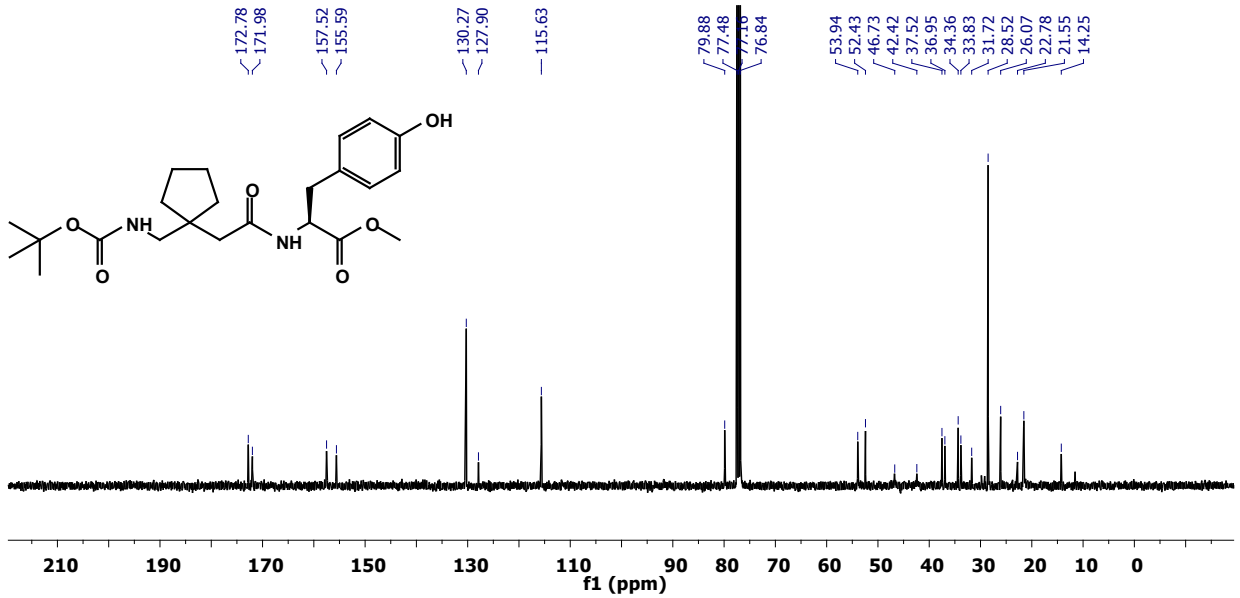


Fig. S9. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Boc-Gbn(1)-Tyr(2)-OMe **5**.

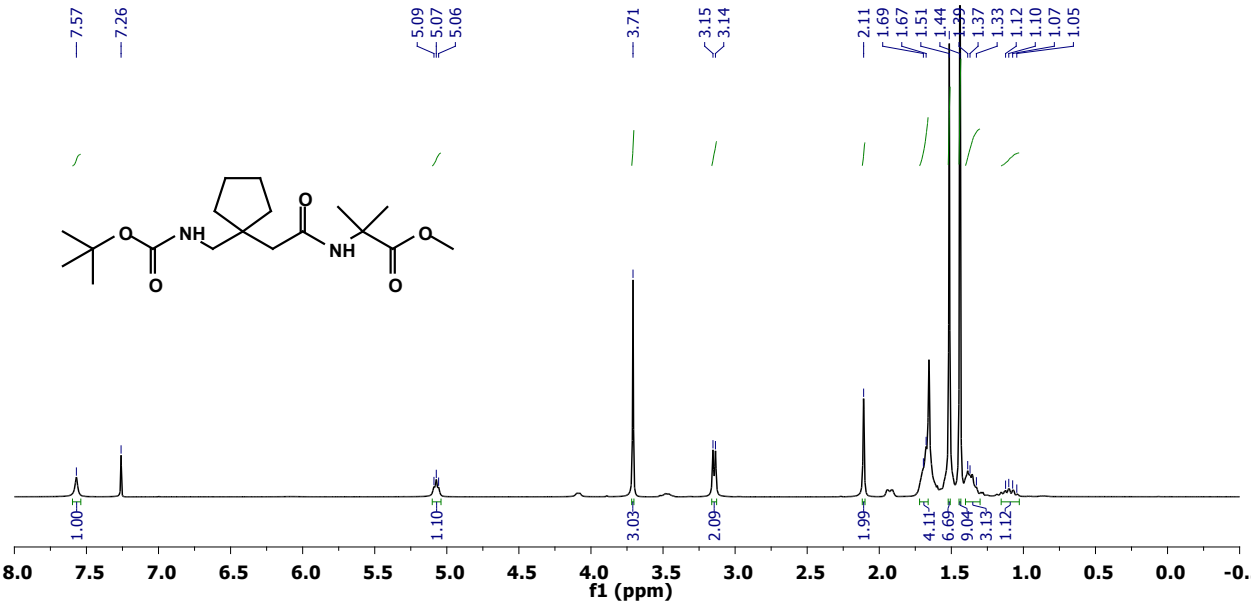


Fig. S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Boc-Gbn(1)-Aib(2)-OMe **6**.

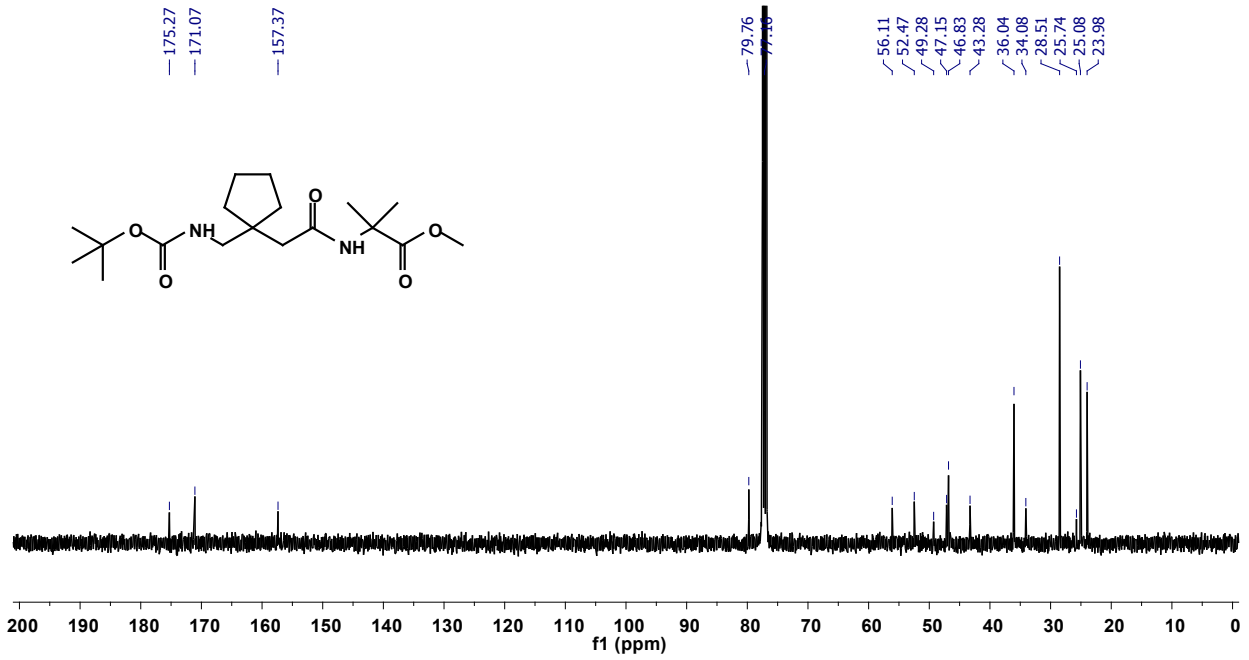


Fig. S11. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Boc-Gbn(1)-Aib(2)-OMe **6**.

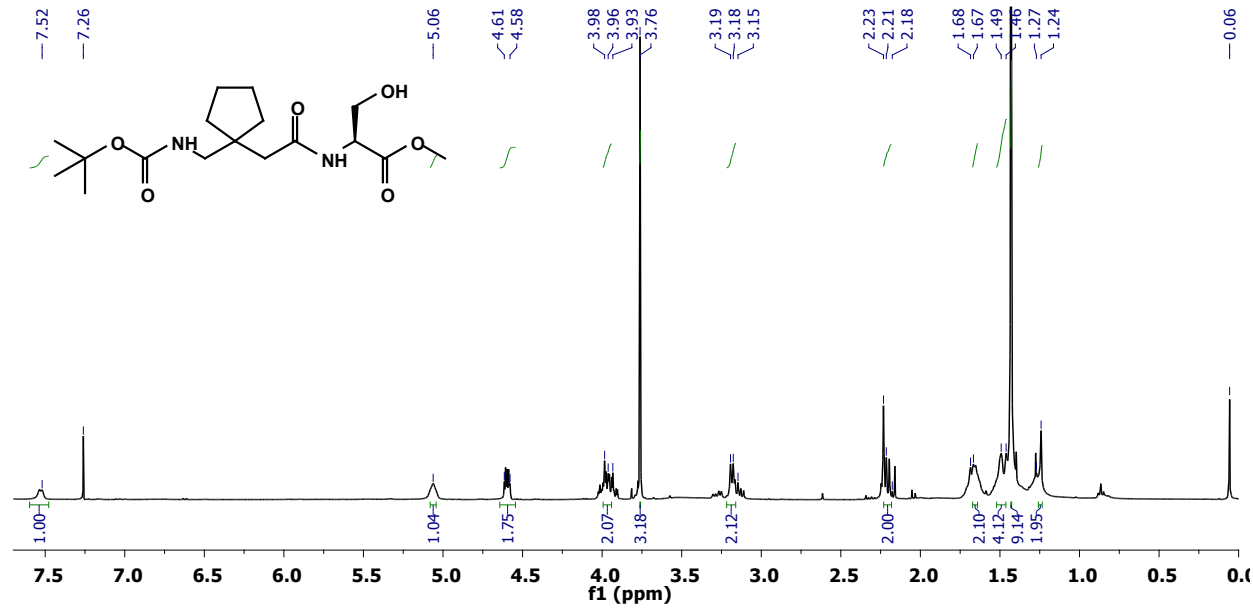


Fig. S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Boc-Gbn(1)-Ser(2)-OMe **7**.

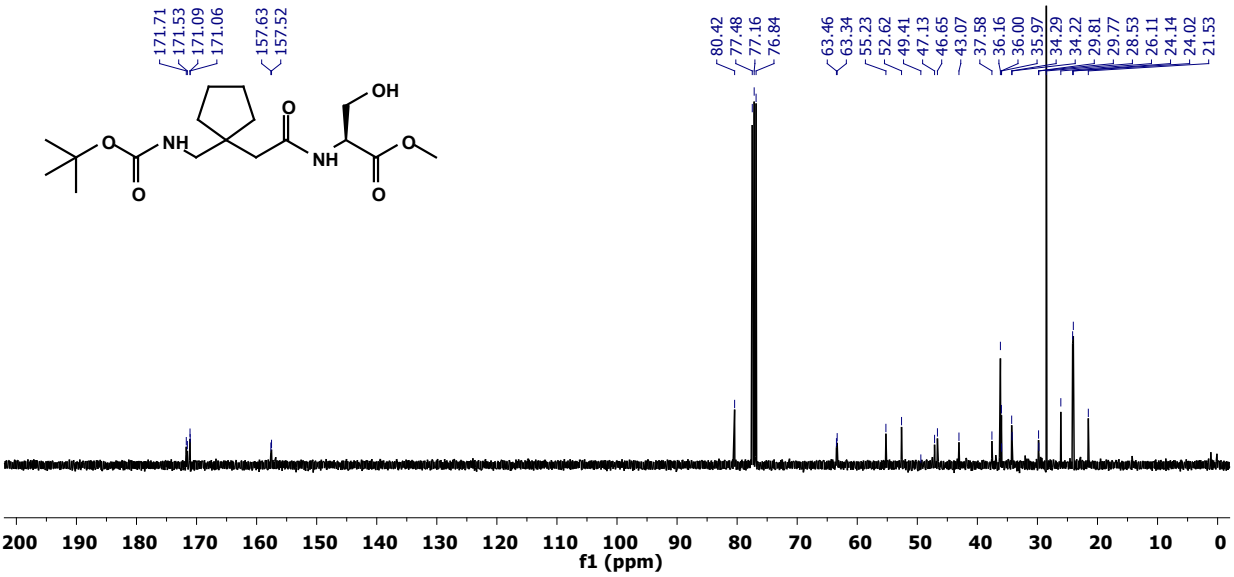


Fig. S13. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of Boc-Gbn(1)-Ser(2)-OMe **7**.

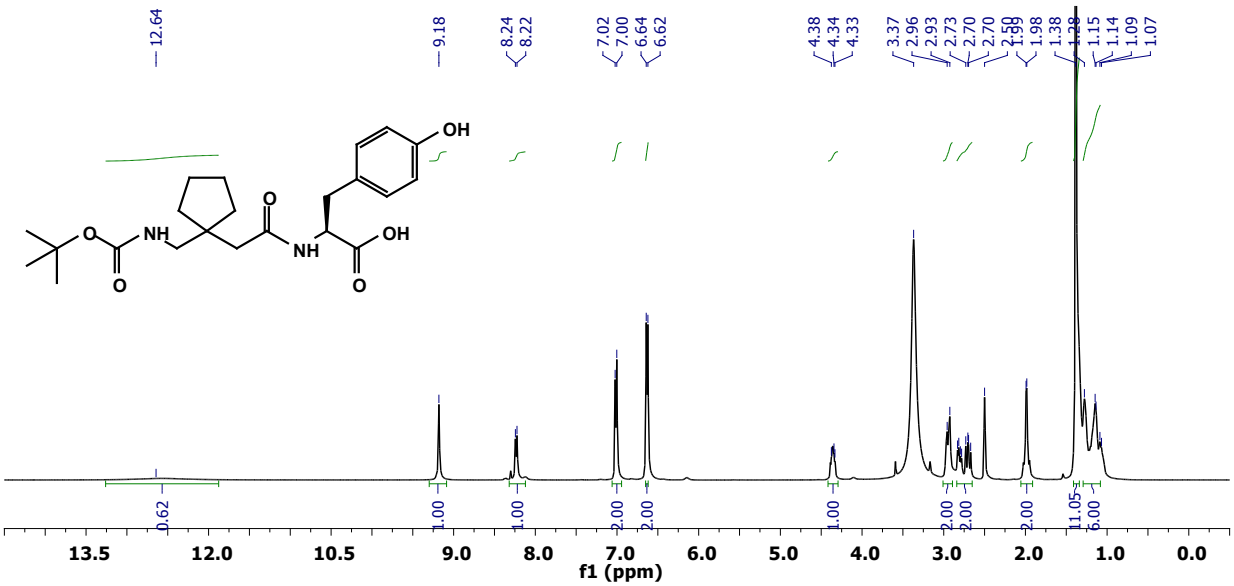


Fig. S14. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of Boc-Gbn(1)-Tyr(2)-OH **2**.

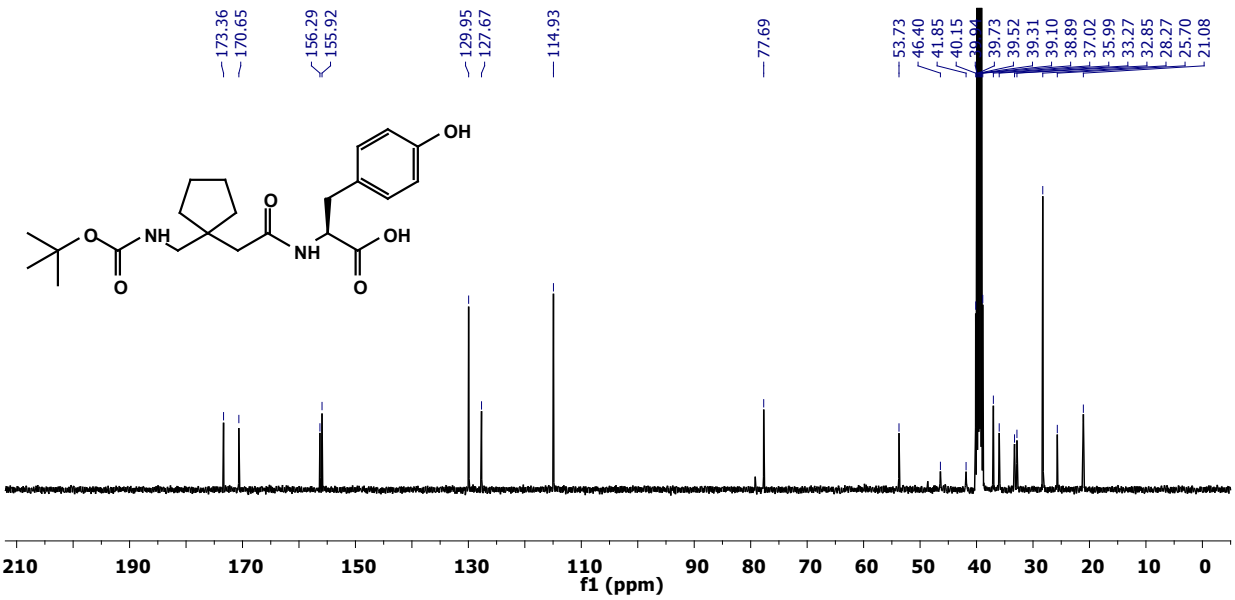


Fig. S15. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of Boc-Gbn(1)-Tyr(2)-OH **2**.

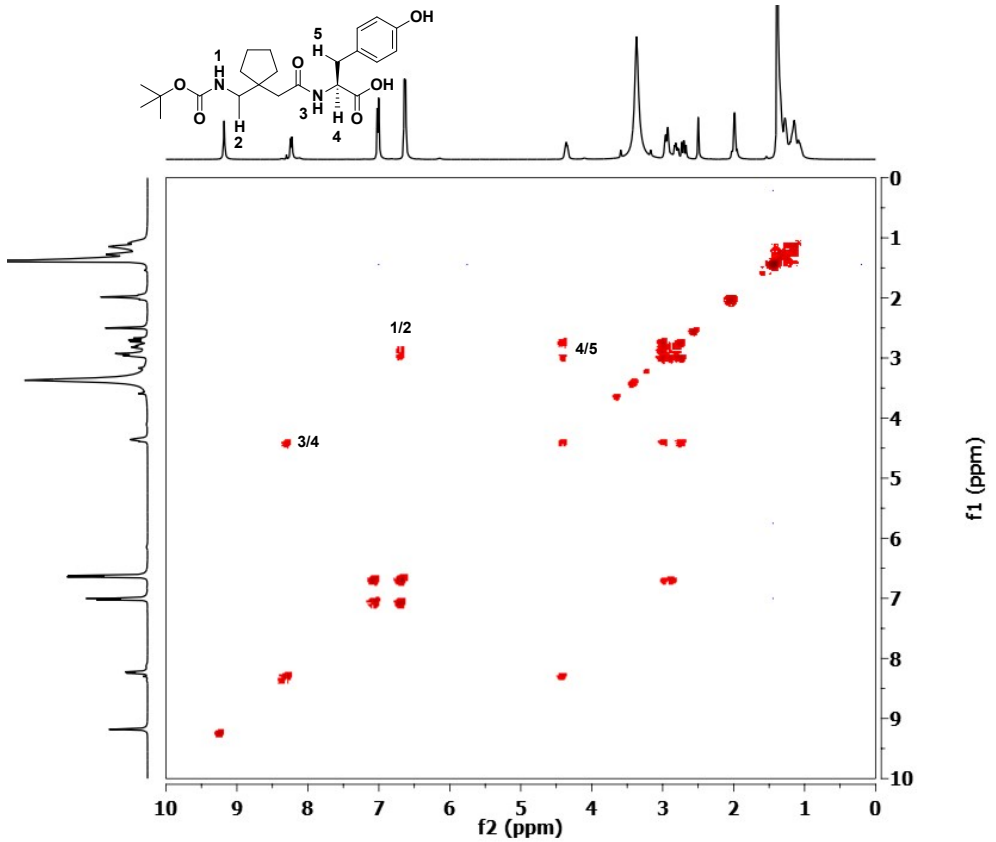


Fig. S16. ^{1}H-^{1}H COSY spectrum of Boc-Gbn(1)-Tyr(2)-OH **2** (400 MHz, DMSO-d_6 at 298 K).

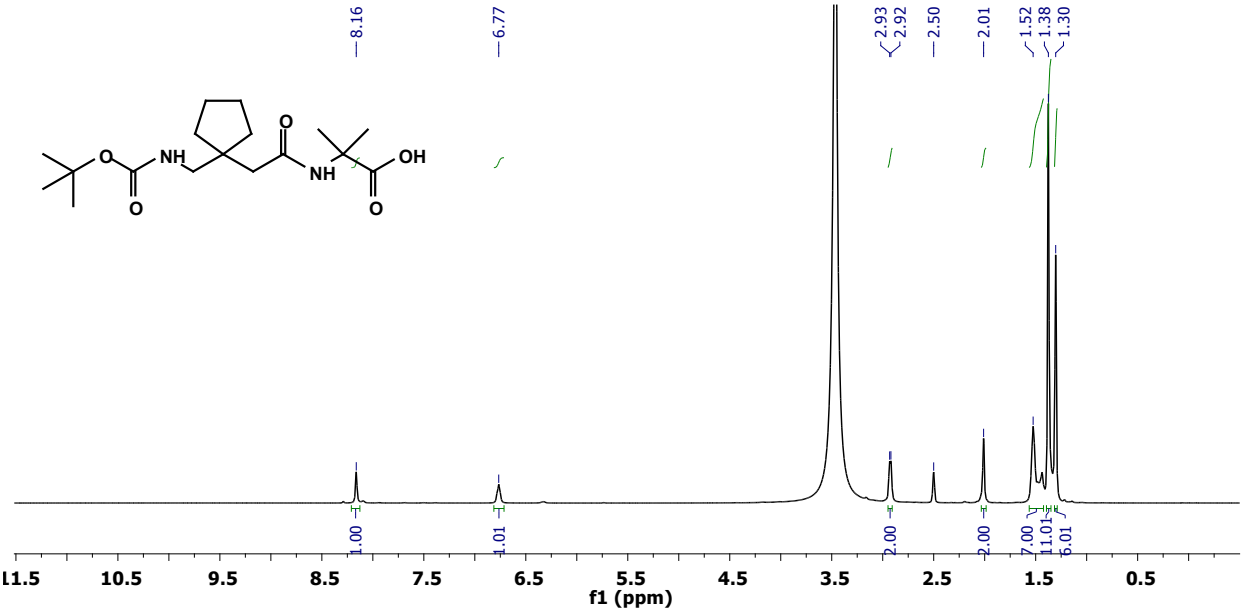


Fig. S17. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of Boc-Gbn(1)-Aib(2)-OH **3**.

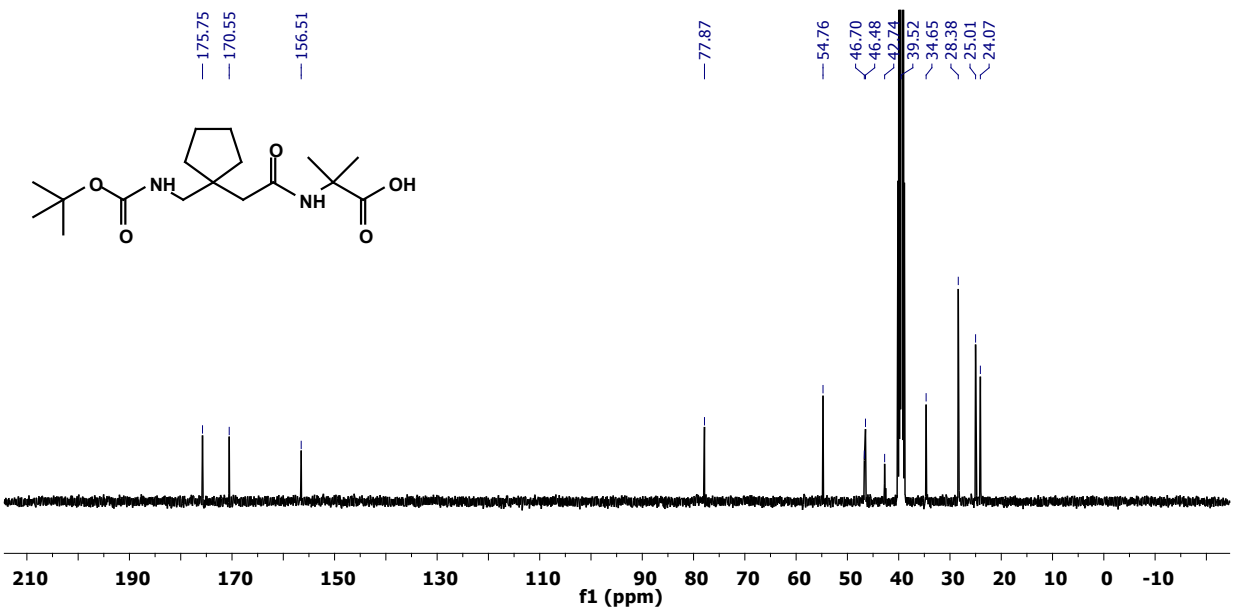


Fig. S18. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of Boc-Gbn(1)-Aib(2)-OH **3**.

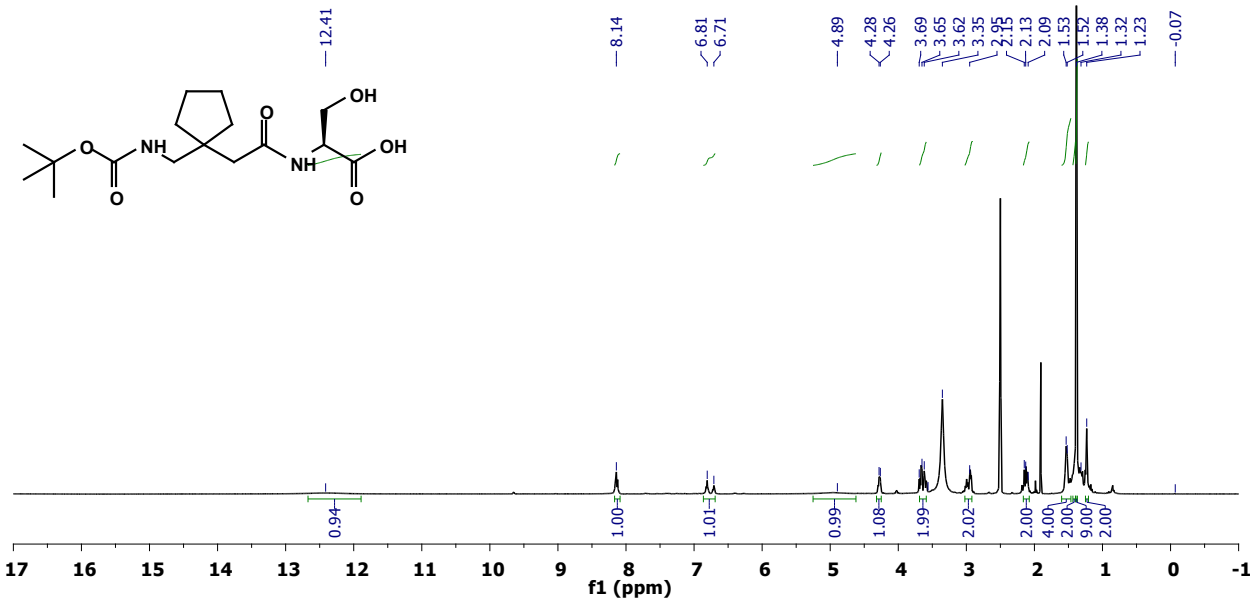


Fig. S19. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of Boc-Gbn(1)-Ser(2)-OH **4**.

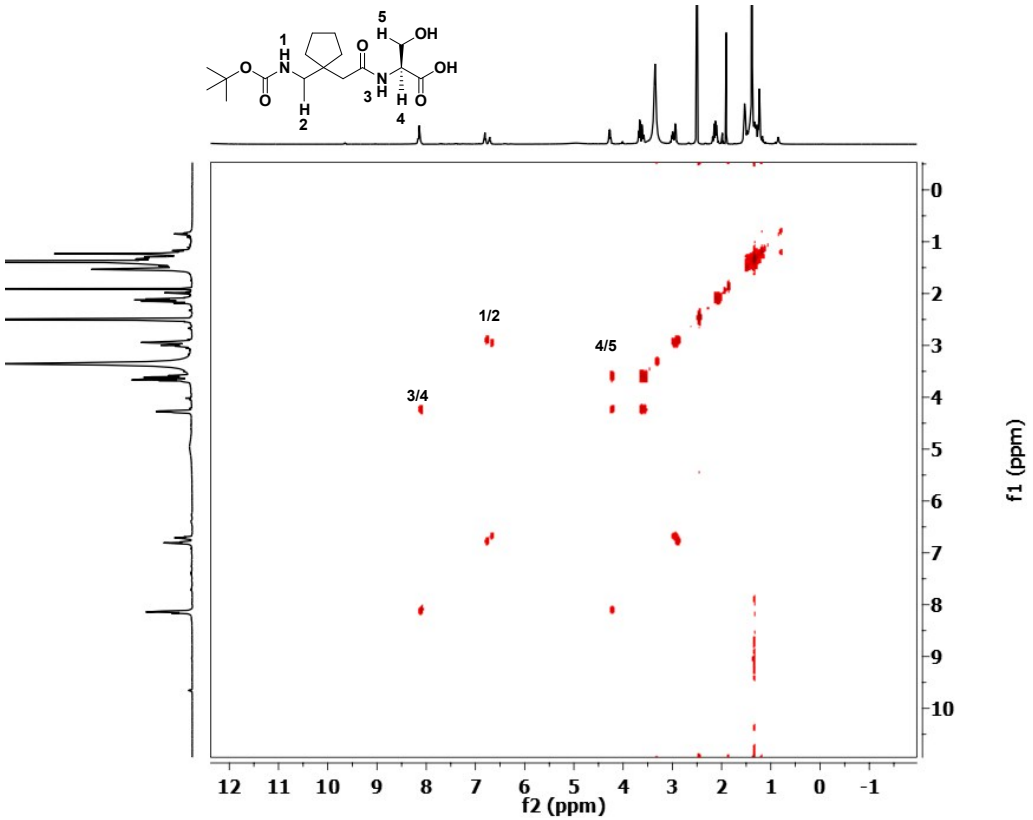


Fig. S20. ^{1}H-^{1}H COSY spectrum of Boc-Gbn(1)-Ser(2)-OH **4** (400 MHz, DMSO-d_6 at 298 K).

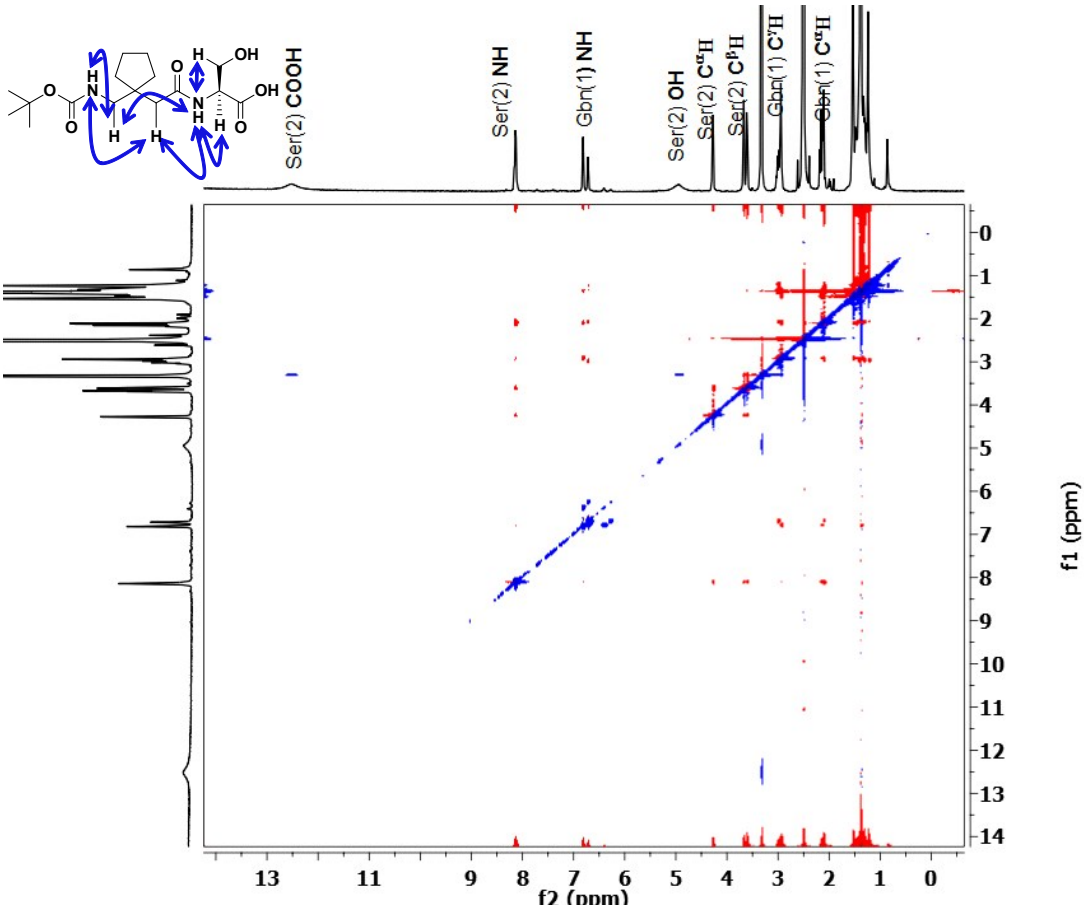


Fig. S21. ^{1}H-^{1}H ROESY spectrum of Boc-Gbn(1)-Ser(2)-OH **4** (400 MHz, DMSO-d_6 at 298 K, mixing time = 200 ms).

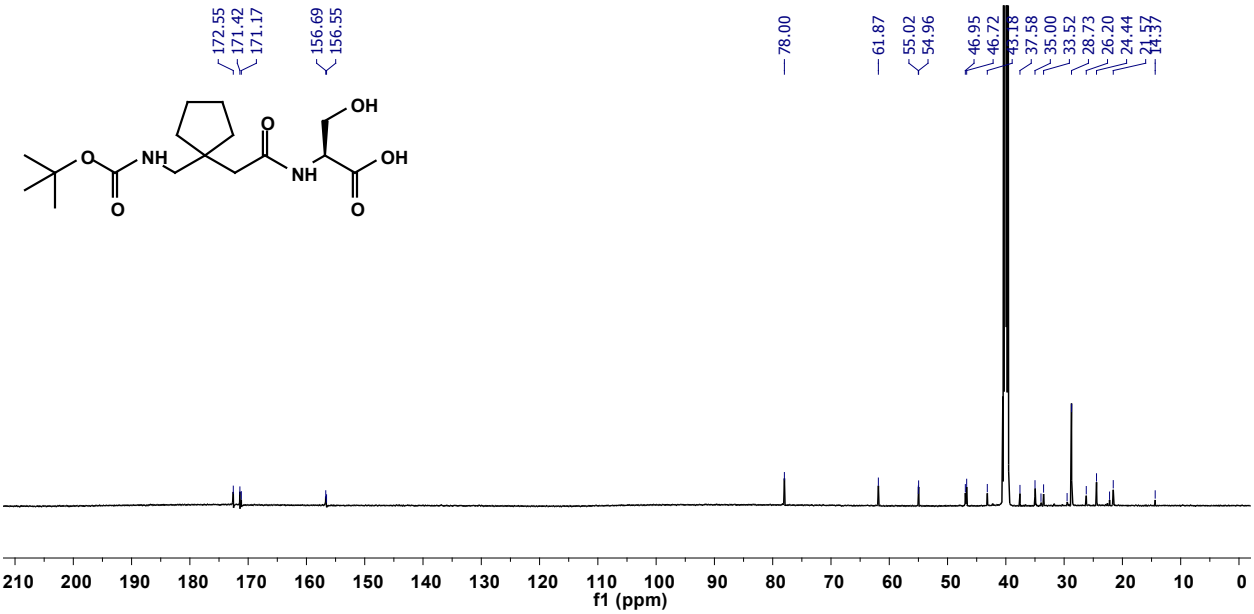


Fig. S22. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of Boc-Gbn(1)-Ser(2)-OH **4**.

Mass spectral Data

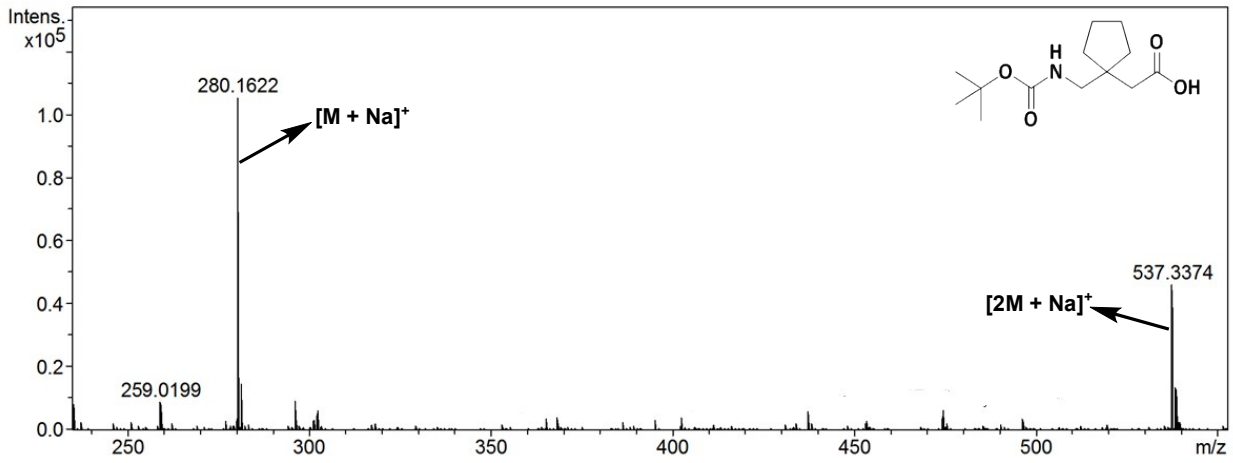


Fig. S23. HRMS spectrum of Boc-Gbn(1)-OH **1**.

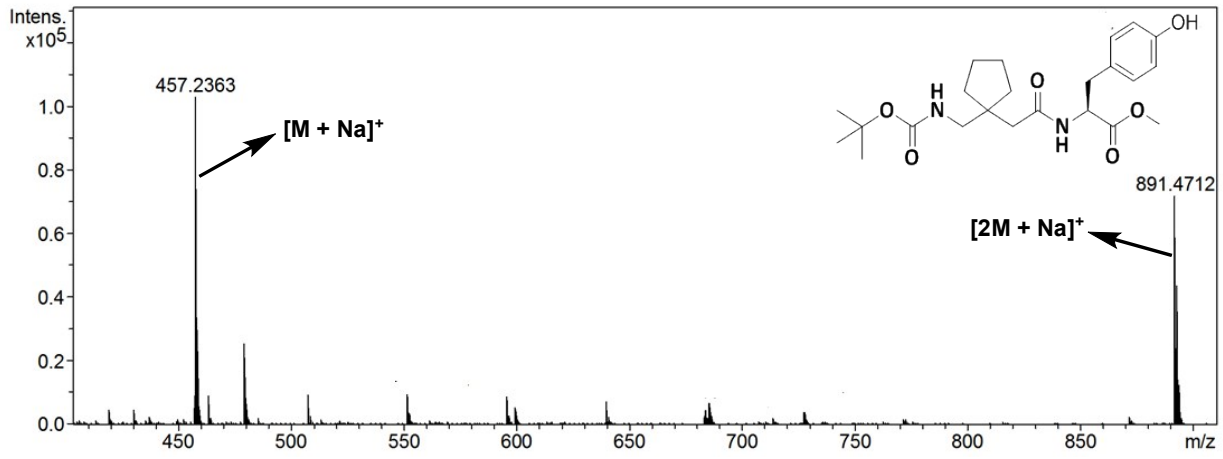


Fig. S24. HRMS spectrum of Boc-Gbn(1)-Tyr(2)-OMe **5**.

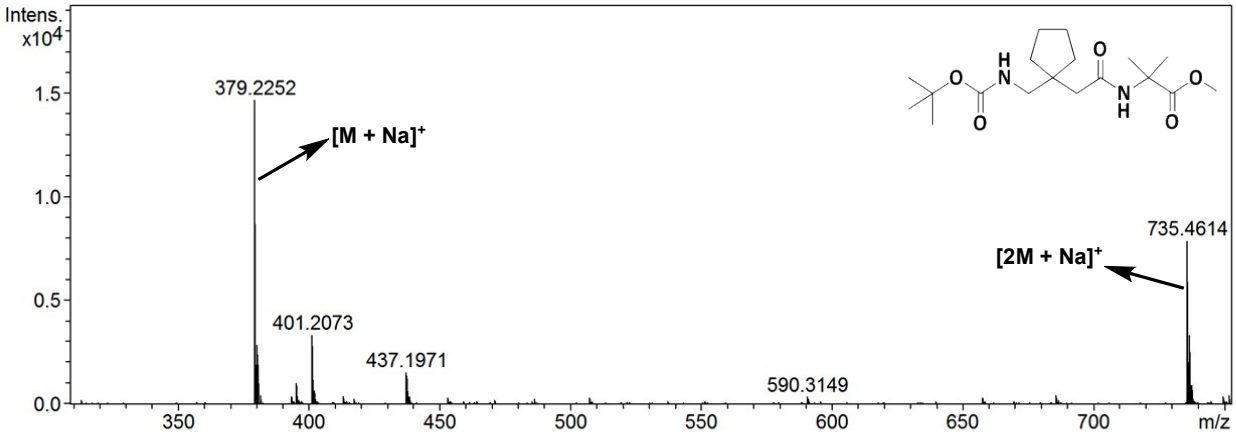


Fig. S25. HRMS spectrum of Boc-Gbn(1)-Aib(2)-OMe **6**.

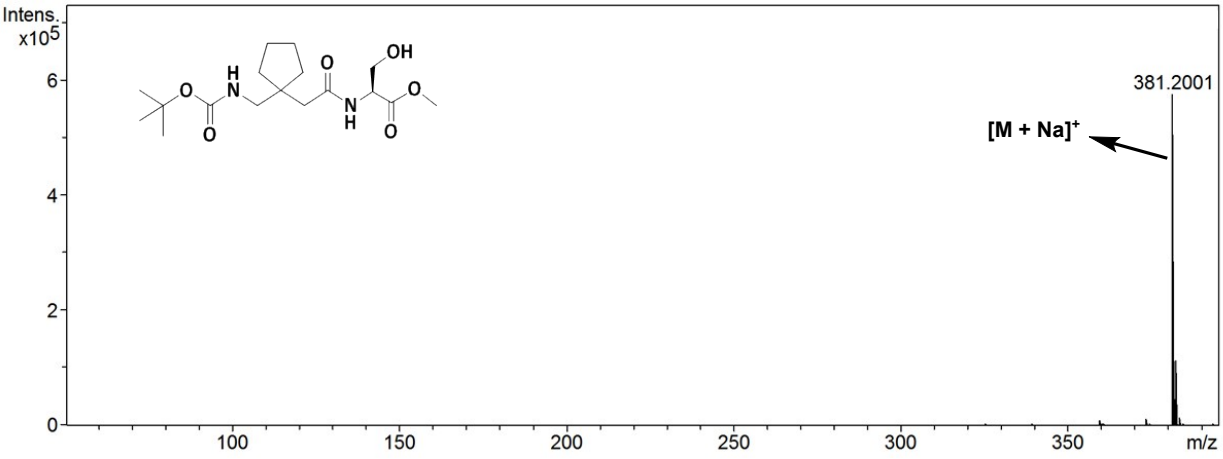


Fig. S26. HRMS spectrum of Boc-Gbn(1)-Ser(2)-OMe **7**.

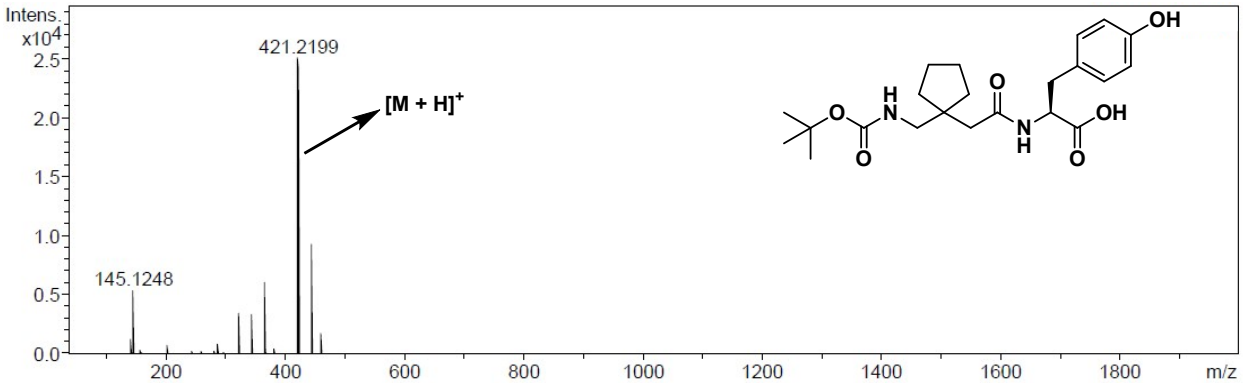


Fig. S27. HRMS spectrum of Boc-Gbn(1)-Tyr(2)-OH **2**.

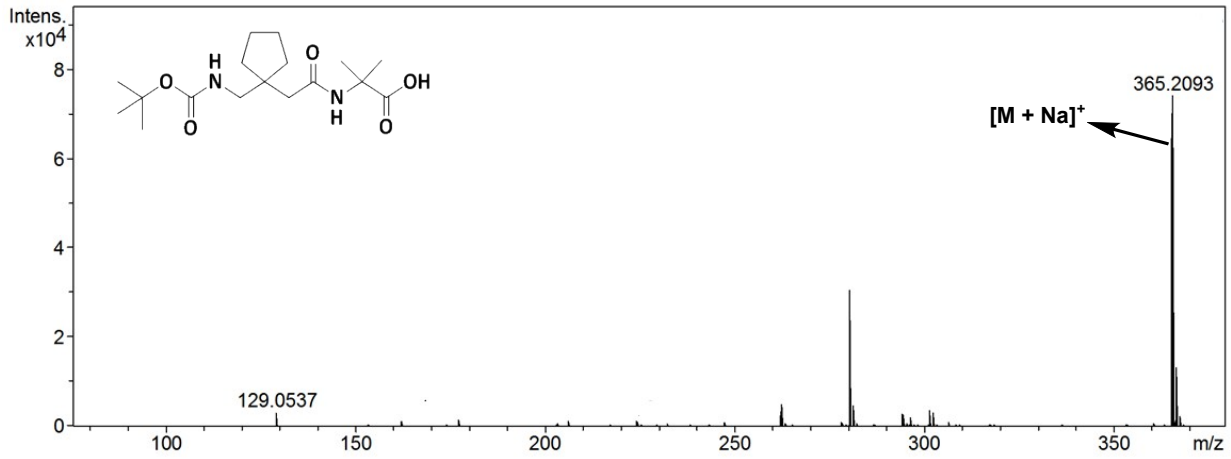


Fig. S28. HRMS spectrum of Boc-Gbn(1)-Aib(2)-OH **3**.

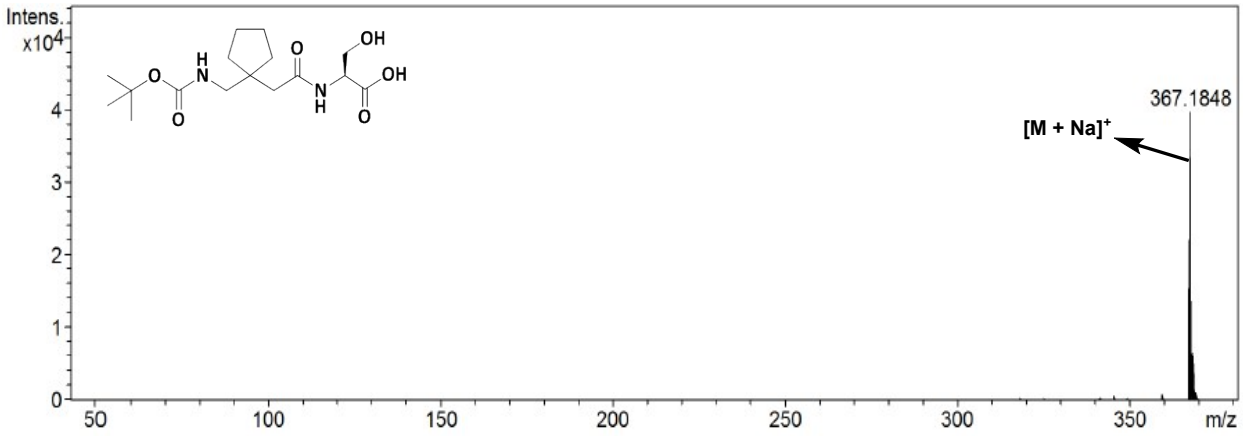


Fig. S29. HRMS spectrum of Boc-Gbn(1)-Ser(2)-OH **4**.