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One stone two birds, diverse glycopeptides synthesis via radical Ullmann coupling from serine

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Supporting Information

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General Information

^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 and 600 M spectrometers and JEOL 400M spectrometers using $CDCl_3$. Chemical shift values for ^{1}H and ^{13}C are referenced to residual solvent peaks ($CDCl_3$: 7.26 ppm for ^{1}H NMR, 77.0 ppm for ^{13}C NMR; Chemical shifts are reported in δ ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz) and integration. Column chromatography was performed on silica gel 200-300 mesh. High resolution mass spectrometry (HRMS) was performed on a Waters Premier GC-TOF MS instrument with electron impact (EI) ionization mode.

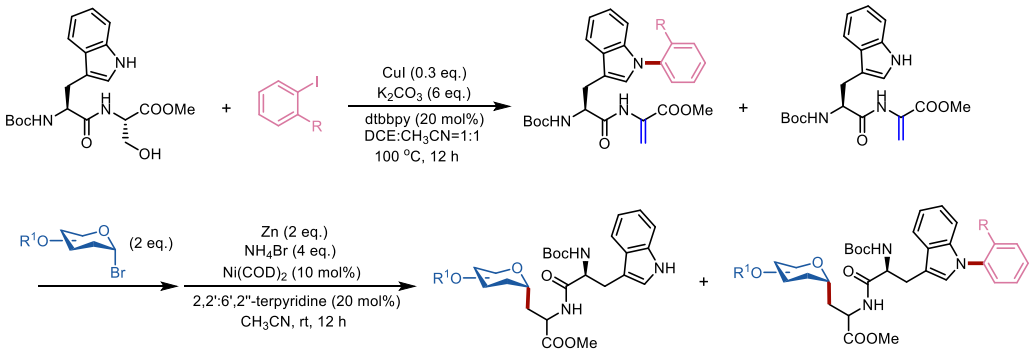
Experimental Section

All reactions were carried out under a nitrogen atmosphere. Unless otherwise specified, materials are obtained from commercial suppliers or prepared according to standard annotation procedures. HBr (33% in AcOH) was purchased from Shanghai Honghu Biopharmaceutical Technology Co., Ltd., Ni $(COD)_2$ was purchased from Suzhou Xinjiayuan Chemical Technology Co., Ltd., 2,2 ': 6', 2 " - Tripyridine was purchased from Shanghai Honghu Biopharmaceutical Technology Co., Ltd., EDCI·HCl is the abbreviation of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, purchased from Shanghai Honghu Biopharmaceutical Technology Co., Ltd., and HOBt is the abbreviation of 1-hydroxybenzotriazole, purchased from Shanghai Honghu Biopharmaceutical Technology Co., Ltd.

Dulbecco's modified eagle medium (DMEM), fetal bovine serum (FBS), Penicillin-Streptomycin (P/S) and 0.25% (1×) Trypsin were obtained from Gibco. 10× phosphate buffer solution (PBS) were purchased from Sangon Biotech Co. Ltd (Shanghai, China). The absorbance in the MTT assay was measured on a microplate reader (SpectraMax M5).

Optimization of reaction conditions

General procedure for the initial optimization reactions：

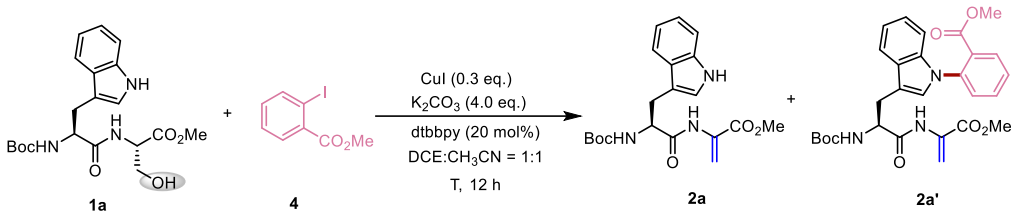


In a dry 8 mL screw cap vial, peptide (0.1 mmol, 1.0 eq.), o-iodobenzoate (0.15 mmol, 1.5 eq.), CuI (5.7 mg, 0.03 mmol, 30 mol%), dtbbpy (5.2 mg, 0.02 mmol, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol, 6.0 eq.), then 1 mL of anhydrous DCE/MeCN (1:1) was added. The reaction was kept in nitrogen at 100 °C (oil bath) for about 10 hours. After the completion of the reaction was monitored by TLC, the reaction was quenched with brine, extracted with EtOAc, and the organic solvent was filtered through a short, stiff Na_2SO_4 column pad. After rotary drying, the crude product was rapidly purified using a silica gel column to obtain the modified peptide.

Then, the modified peptide (0.1 mmol, 1.0 eq.) was added to an 8 mL screw-capped vial, and brominated sugar (0.2 mmol, 2.0 eq.), Zn (13 mg, 0.2 mmol, 2.0 eq.), NH_4Br (20 mg, 0.4 mmol, 4.0 eq.), $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 10 mol%), 2,2':6',2''-terpyridine (4.7 mg, 0.02 mmol, 20 mol%) were added to it, and 1 mL of anhydrous CH_3CN was added.The reaction was carried out under nitrogen atmosphere for 12 h at room temperature. After the completion of the reaction was monitored by TLC, the reaction was quenched with brine, after which the mixture was extracted with dichloromethane (3×5 mL), dried with anhydrous Na_2SO_4, filtered, concentrated by rotary evaporator, and then purified by flash column chromatography to give the final product.

Optimization of reaction conditions for Dha derivative

Table S1. Screening of reaction temperatures

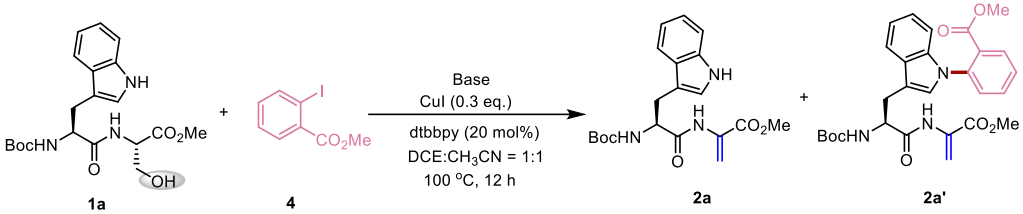


Entry	T	**2a** Yield[ab]	**2a'** Yield[ab]
1	40 °C	N.P.	N.P.
2	60 °C	N.P.	N.P.
3	80 °C	12%	25%
4	100 °C	19%	29%

[a]The reaction was carried out on a scale of 0.1 mmol.

[b]This yield is the isolated yield.

Table S2. Screening of bases

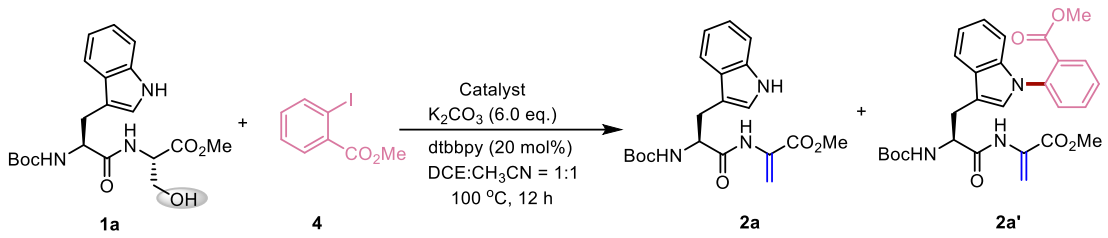


Entry	Base (x eq.)	**2a** Yield[ab]	**2a'** Yield[ab]
1	K_2CO_3 (4.0 eq.)	19%	29%
2	K_2CO_3 (5.0 eq.)	21%	34%
3	K_2CO_3 (6.0 eq.)	25%	38%
4	K_2CO_3 (7.0 eq.)	16%	22%
5	K_2CO_3 (8.0 eq.)	10%	17%
6	Na_2CO_3 (6.0 eq.)	18%	23%
7	$NaHCO_3$ (6.0 eq.)	11%	17%
8	Cs_2CO_3 (6.0 eq.)	20%	28%
9	Na_3PO_4 (6.0 eq.)	trace	trace
10	DMAP (6.0 eq.)	trace	trace
11	DBU (6.0 eq.)	trace	trace
12	DIPEA (6.0 eq.)	trace	trace

[a]The reaction was carried out on a scale of 0.1 mmol.

[b]This yield is the isolated yield.

Table S3. Screening of catalysts

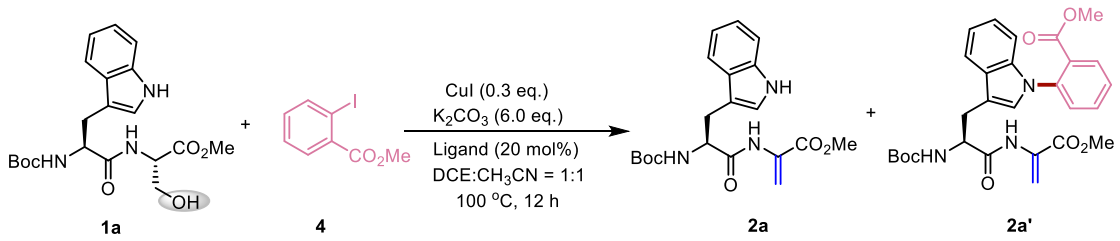


Entry	Catalyst (30 mol%)	**2a** Yield[ab]	**2a'** Yield[ab]
1	CuI	25%	38%
2	CuCl	13%	19%
3	CuBr	10%	17%
4	Cu_2O	9%	16%
5	$CuCl_2$	trace	trace
6	$Cu(OAc)_2$	trace	trace
7	$Cu(OTf)_2$	trace	trace

[a]The reaction was carried out on a scale of 0.1 mmol.

[b]This yield is the isolated yield.

Table S4. Screening of ligands

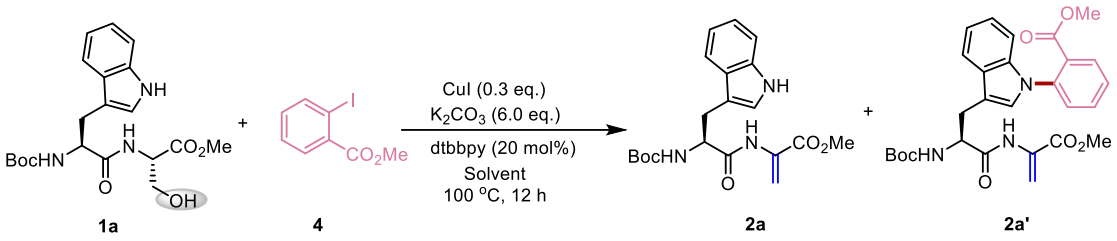


Entry	Ligand (20 mol%)	**2a** Yield[ab]	**2a'** Yield[ab]
1	dtbbpy	25%	38%
2	2,2'-Bipyridine	25%	16%
3	4,4'-Dimethyl-2,2'-bipyridyl	28%	14%
4	4,4'-Dibromo-2,2'-bipyridine	14%	34%
5	1,10-Phen	8%	trace
6	Bathophenanthroline	24%	30%
7	4,7-Dichloro-1,10-phenanthroline	22%	23%
8	4,7-Dimethyl-1,10-phenanthroline	23%	23%

[a]The reaction was carried out on a scale of 0.1 mmol.

[b]This yield is the isolated yield.

Table S5. Screening of solvents



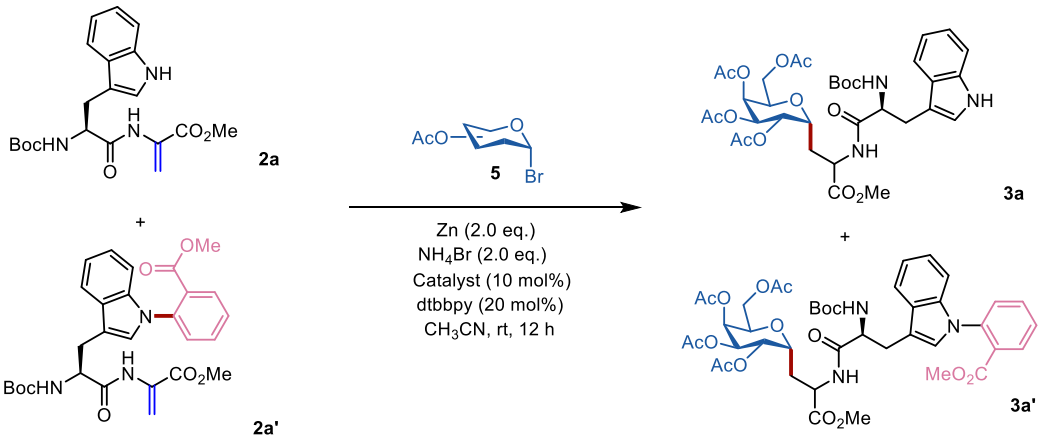
Entry	Solvent	**2a** Yield[ab]	**2a'** Yield[ab]
1	DCE	12%	17%
2	CH_3CN	10%	12%
3	THF	18%	20%
4	1,4-Dioxane	23%	24%
5	DMAc	13%	11%
6	DMF	12%	9%
7	DMSO	trace	trace
8	Toluene	15%	12%
9	DCE:CH_3CN (1:1)	25%	38%

[a]The reaction was carried out on a scale of 0.1 mmol.

[b]This yield is the isolated yield.

Optimization of reaction conditions for the coupling

Table S6. Screening of catalysts

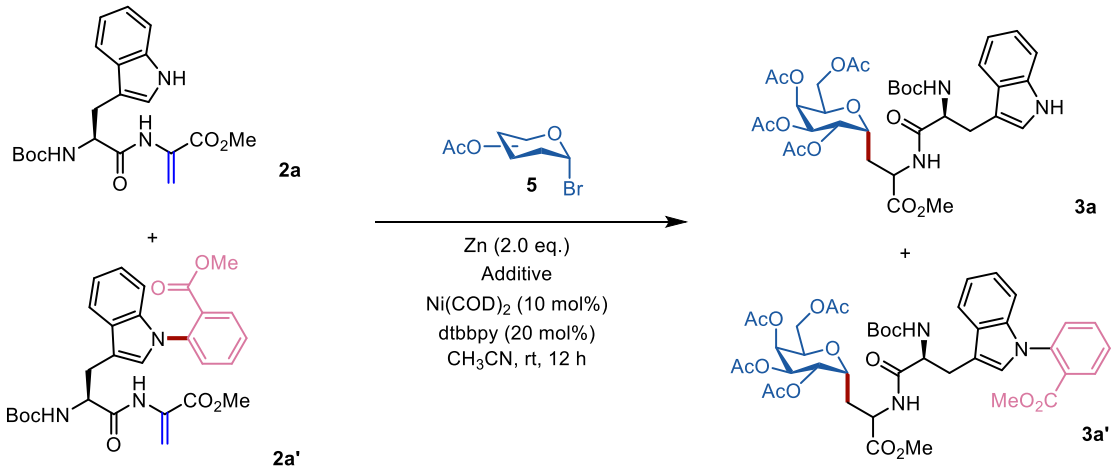


Entry	Catalyst (10 mol%)	**3a** Yield[ab]	**3a'** Yield[ab]
1	$Ni(COD)_2$	47%, d.r. = 1:1.4	58%, d.r. = 1:1.5
2	$NiBr_2$·DME	40%, d.r. = 1:1.4	53%, d.r. = 1:1.3
3	$NiCl_2$·DME	38%, d.r. = 1:1.2	49%, d.r. = 1:1.3
4	$Ni(OAc)_2$	26%, d.r. = 1:1.0	34%, d.r. = 1:1.2
5	$Ni(Py)_4Cl_2$	22%, d.r. = 1:1.0	33%, d.r. = 1:1.0
6	$Ni(acac)_2$	30%, d.r. = 1:1.1	39%, d.r. = 1:1.1
7	$Ni(dppp)Cl_2$	20%, d.r. = 1:1.2	31%, d.r. = 1:1.2
8	$Ni(PPh_3)_2Cl_2$	31%, d.r. = 1:1.2	39%, d.r. = 1:1.0

[a]The reaction was carried out on a scale of 0.1 mmol.

[b]This yield is the isolated yield.

Table S7. Screening of additives

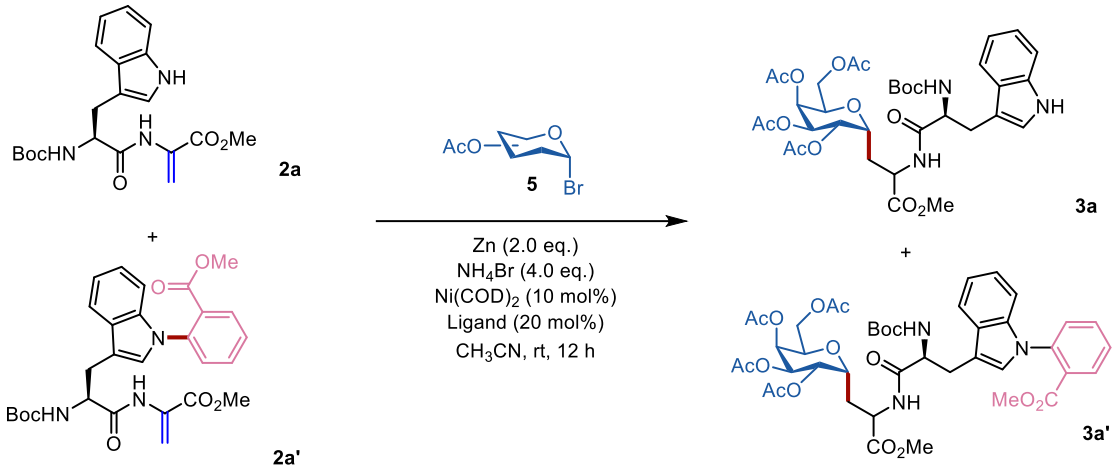


Entry	Additive	**3a** Yield[ab]	**3a'** Yield[ab]
1	NH_4Br (2.0 eq.)	47%, d.r. = 1:1.4	58%, d.r. = 1:1.5
2	NH_4Br (3.0 eq.)	52%, d.r. = 1:1.4	60%, d.r. = 1:1.3
3	NH_4Br (4.0 eq.)	58%, d.r. = 1:1.7	66%, d.r. = 1:2.0
4	H_2O (4.0 eq.)	21%, d.r. = 1:1.1	35%, d.r. = 1:1.0
5	HFIP (4.0 eq.)	34%, d.r. = 1:1.0	45%, d.r. = 1:2.0
6	*t*-BuOH (4.0 eq.)	27%, d.r. = 1:1.1	37%, d.r. = 1:1.0
7	CH_3OH (4.0 eq.)	28%, d.r. = 1:1.1	41%, d.r. = 1:1.5

[a]The reaction was carried out on a scale of 0.1 mmol.

[b]This yield is the isolated yield.

Table S8. Screening of ligands

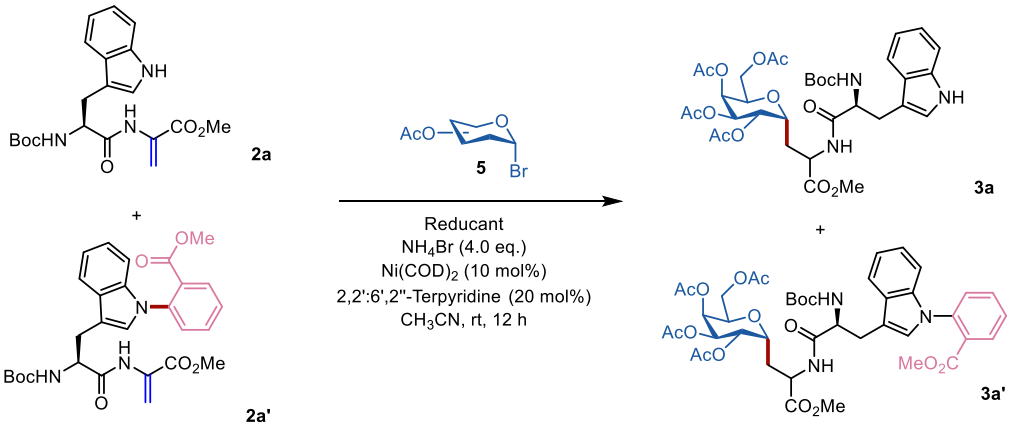


Entry	Ligand (20 mol%)	**3a** Yield[ab]	**3a'** Yield[ab]
1	2-Chloropyridine	31%, d.r. = 1:1.3	40%, d.r. = 1:1.2
2	dtbbpy	58%, d.r. = 1:1.7	66%, d.r. = 1:2.0
3	2,2':6',2"-Terpyridine	67%, d.r. = 1:1.5	74%, d.r. = 1:1.4
4	1,10-Phen	27%, d.r. = 1:1.4	34%, d.r. = 1:1.5
5	Dppp	16%, d.r. = 1:1.4	21%, d.r. = 1:1.7

[a]The reaction was carried out on a scale of 0.1 mmol.

[b]This yield is the isolated yield.

Table S9. Screening of reducants

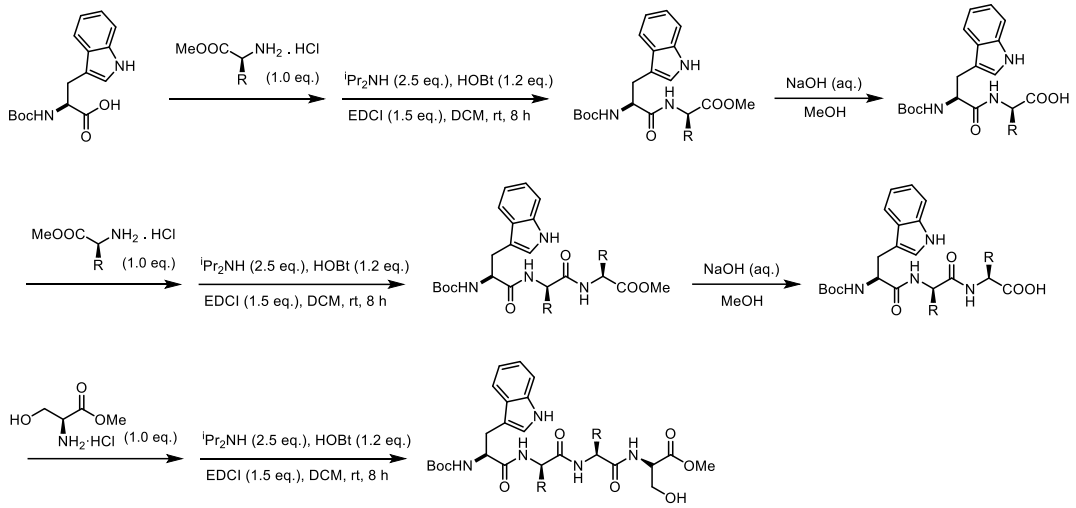


Entry	Reducant (2.0 equiv.)	**3a** Yield[ab]	**3a'** Yield[ab]
1	Zn	67%, d.r. = 1:1.5	74%, d.r. = 1:1.4
2	Mn	38%, d.r. = 1:1.2	49%, d.r. = 1:1.1
3	Mg	15%, d.r. = 1:1.2	21%, d.r. = 1:1.1
4	In	60%, d.r. = 1:1.2	68%, d.r. = 1:1.3
5	Fe	18%, d.r. = 1:1.0	23%, d.r. = 1:1.0
6	Pinacolborane	29%, d.r. = 1:1.1	37%, d.r. = 1:1.2
7	$(MeO)_3SiH$	N.P.	N.P.

[a]The reaction was carried out on a scale of 0.1 mmol.

[b]This yield is the isolated yield.

General procedure for the synthesis of peptides

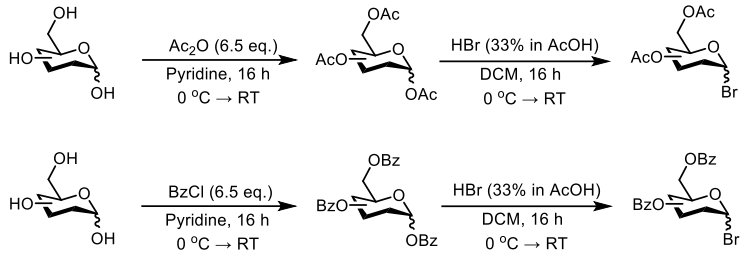


The general synthesis of peptides can be found in the references.[1]

The synthesis steps of peptides: Place Boc protected amino acids (3.04 g, 10 mmol) and amino acid methyl ester hydrochloride (10 mmol) in a round bottom flask and dissolve in dry DCM (100 mL). Subsequently, $^{i}Pr_2NH$ (25 mmol) was added to the reaction solution and stirred for 15 minutes. HOBt (12 mmol) was added to an ice water bath and allowed to react for 30 minutes. Finally, EDCI (15 mmol) was added, and the ice bath was removed and stirred at room temperature for 8 hours. Monitor the reaction progress using TLC. After the reaction is complete, extract with DCM (3 × 20 mL), wash with saturated NaCl, combine the organic phases, dry with anhydrous Na_2SO_4, spin dry to remove the solvent, and obtain the crude product.

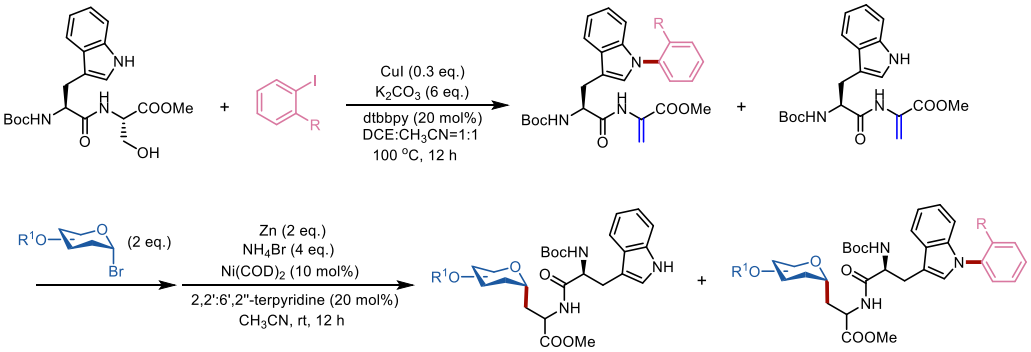
The synthesis steps of peptide demethylation: Dissolve the synthesized dipeptide in methanol (20 mL), then add NaOH aqueous solution (2M, 3.2 eq.) and react for 8 hours. After the reaction is complete, place it in a rotary evaporator to spin out most of the solvent, then add 1M HCl aqueous solution to the reaction system to make the pH of the solution acidic. Pour the solution into a separatory funnel, extract the organic phase with EtOAc (3 × 20 mL), dry with anhydrous Na_2SO_4, spin dry, and obtain the crude product.

Procedure for preparation of protected sugars



The synthesis of protected sugars can be found in the references.[2] Dissolve unprotected sugar (1.8 g, 10 mmol, 1.0 eq.) in pyridine (40 mL), cool to 0 °C, then add acetic anhydride/benzoyl chloride (6.5 eq.) dropwise, heat the solution to room temperature, and stir overnight. After the reaction is complete, add ice water (10 mL) to the reaction solution, stir for 15 minutes, extract the organic phase with EtOAc (3 × 20 mL), wash with citric acid, saturated $NaHCO_3$ solution, saturated NaCl solution, dry with anhydrous Na_2SO_4, spin dry to obtain the crude product. Dissolve fully protected sugar (10 mmol, 1.0 eq.) in DCM (40 mL), cool to 0 °C, add HBr (33% in AcOH) dropwise, heat to room temperature, and stir overnight. After the reaction is complete, add ice water (10 mL) to the reaction solution, stir for 15 minutes, extract with DCM (3 × 20 mL), wash with saturated NaCl, combine the organic phases, dry with anhydrous Na_2SO_4, spin dry to obtain the crude product.

General procedure for glycopeptide modification

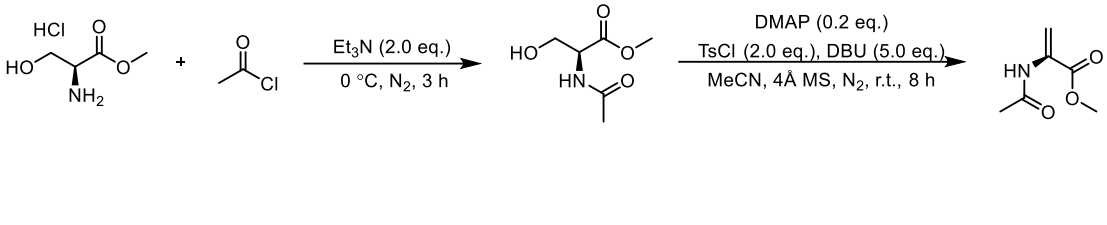


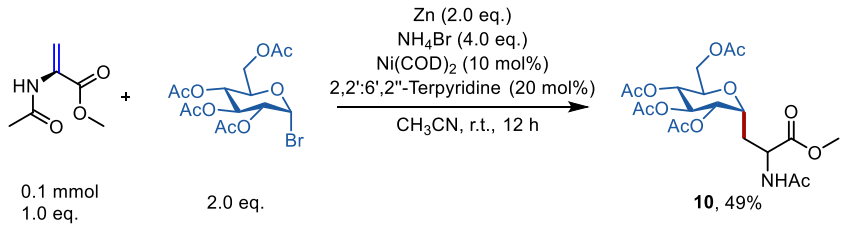
In a dry 8 mL screw cap vial, peptide (0.1 mmol, 1.0 eq.), o-iodobenzoate (0.15 mmol, 1.5 eq.), CuI (5.7 mg, 0.03 mmol, 30 mol%), dtbbpy (5.2 mg, 0.02 mmol, 20 mol%), K_2CO_3 (82.8 mg, 0.6 mmol, 6.0 eq.), then 1 mL of anhydrous DCE/MeCN

(1:1) was added. The reaction was kept in nitrogen at 100 °C (oil bath) for about 10 hours. After the completion of the reaction was monitored by TLC, the reaction was quenched with brine, extracted with EtOAc, and the organic solvent was filtered through a short, stiff Na_2SO_4 column pad. After rotary drying, the crude product was rapidly purified using a silica gel column to obtain the modified peptide.

Then, the modified peptide (0.1 mmol, 1.0 eq.) was added to an 8 mL screw-capped vial, and brominated sugar (0.2 mmol, 2.0 eq.), Zn (13 mg, 0.2 mmol, 2.0 eq.), NH_4Br (20 mg, 0.4 mmol, 4.0 eq.), $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 10 mol%), 2,2':6',2''-terpyridine (4.7 mg, 0.02 mmol, 20 mol%) were added to it, and 1 mL of anhydrous CH_3CN was added.The reaction was carried out under nitrogen atmosphere for 12 h at room temperature. After the completion of the reaction was monitored by TLC, the reaction was quenched with brine, after which the mixture was extracted with dichloromethane (3 x 5 mL), dried with anhydrous Na_2SO_4, filtered, concentrated by rotary evaporator, and then purified by flash column chromatography to give the final product.

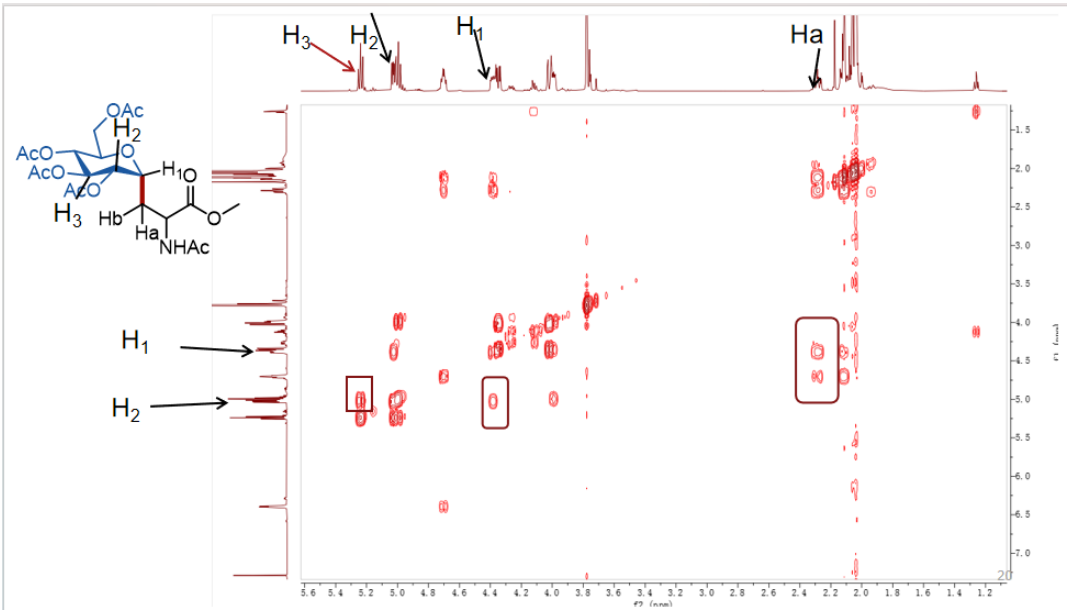
Determination of the Configuration of Glycosyl Compounds

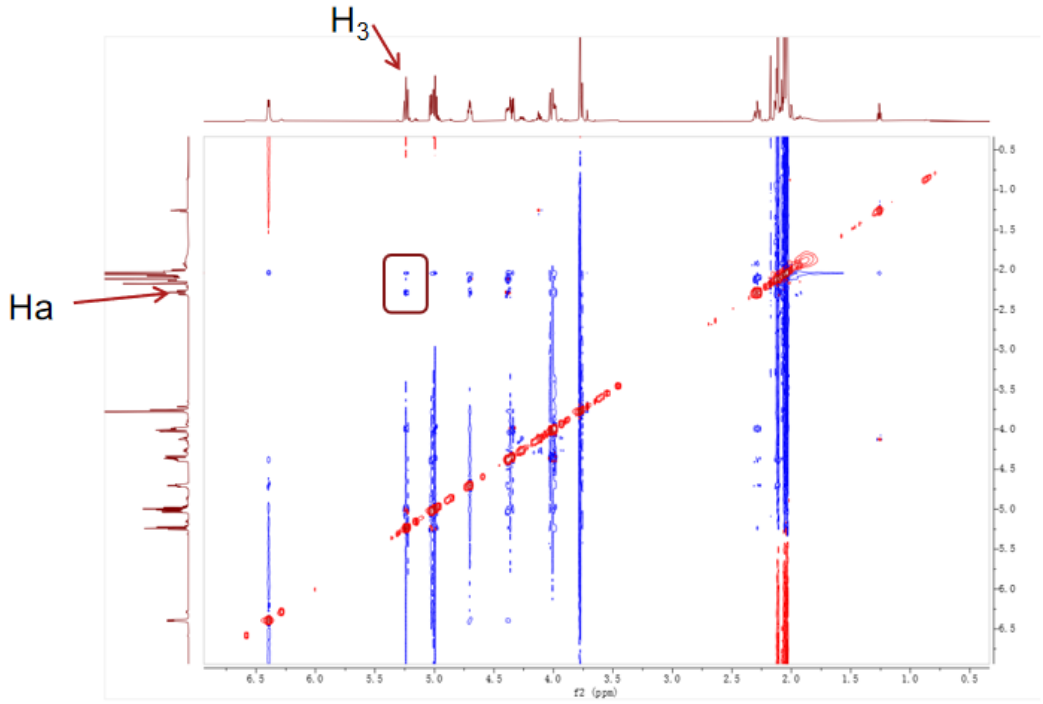




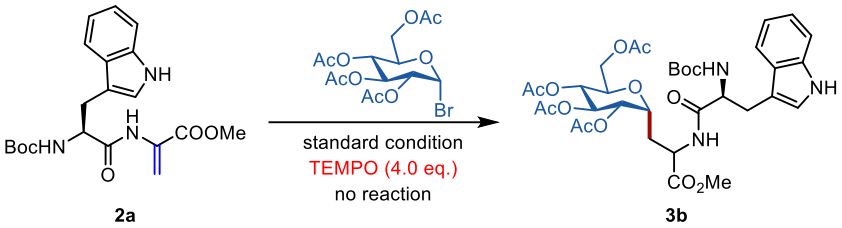
To determine the stereochemistry of the C-glycosylation products, we synthesized Ac-Ser-OMe following a literature procedure and subsequently converted it into the corresponding dehydroalanine derivative.[3-4] The Methyl 2-acetamidoacrylate (0.1 mmol, 1.0 eq.) was added to an 8 mL screw-capped vial, and 2,3,4,6-Tetra-O-acetyl-alpha-D-glucopyranosyl bromide (0.2 mmol, 2.0 eq.), Zn (13

mg, 0.2 mmol, 2.0 eq.), NH_4Br (20 mg, 0.4 mmol, 4.0 eq.), $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 10 mol%), 2,2':6',2"-terpyridine (4.7 mg, 0.02 mmol, 20 mol%) were added to it, and 1 mL of anhydrous CH_3CN was added.The reaction was carried out under nitrogen atmosphere for 12 h at room temperature. After the completion of the reaction was monitored by TLC, the reaction was quenched with brine, after which the mixture was extracted with dichloromethane (3 x 5 mL), dried with anhydrous Na_2SO_4, filtered, concentrated by rotary evaporator. The filtrate collected was concentrated under reduced pressure and purified by silica gel column chromatography using petroleum ether/ethyl acetate to abtain 10 (49%) as Colorless oil. Based on the COSY spectrum of 10, the protons on the sugar ring were assigned unambiguously. The proton at the anomeric position (C1-H) is adjacent to Ha and Hb, as evidenced by the observed cross-peaks between C1-H and Ha/Hb, allowing its identification as the anomeric proton. The proton at C2 (C2-H) shows a correlation with C1-H, and the proton at C3 (C3-H) is similarly assigned based on the sequential correlations. Furthermore, the NOESY correlation between H_3 and Ha for compound 10 indicates that H_3 and Ha are spatially close, meaning these protons lie on the same face of the sugar ring. Collectively, the two-dimensional NMR analysis of 10 supports the assignment of the α-configuration for this compound.



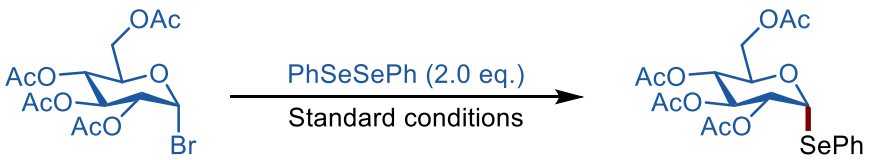


Mechanistic study



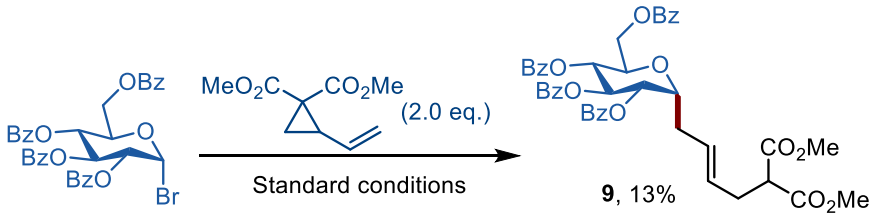
The 2a (0.1 mmol, 1.0 eq.) was added to an 8 mL screw-capped vial, and 2,3,4,6-Tetra-O-acetyl-alpha-D-glucopyranosyl bromide (0.2 mmol, 2.0 eq.), Zn (13 mg, 0.2 mmol, 2.0 eq.), NH_4Br (20 mg, 0.4 mmol, 4.0 eq.), $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 10 mol%), 2,2':6',2''-terpyridine (4.7 mg, 0.02 mmol, 20 mol%) and TEMPO (0.4 mmol, 4.0 eq.) were added to it, and 1 mL of anhydrous CH_3CN was added.The reaction was carried out under nitrogen atmosphere for 12 h at room temperature. After the completion of the reaction was monitored by TLC, the reaction was quenched with brine, after which the mixture was extracted with dichloromethane (3 x 5 mL), dried with anhydrous Na_2SO_4, filtered, concentrated by rotary evaporator. The filtrate collected was concentrated under reduced pressure and purified by silica gel column chromatography using petroleum ether/ethyl acetate. It indicated that no

product was obtain and most of starting material was remaining, with 2a being recovered in 78.59% yield.



8, 56%

The 2,3,4,6-Tetra-O-acetyl-alpha-D-glucopyranosyl bromide (0.2 mmol, 1.0 eq.) was added to an 8 mL screw-capped vial, and diphenyl diselenide (PhSeSePh) (0.4 mmol, 2.0 eq.), Zn (13 mg, 0.2 mmol, 2.0 eq.), NH_4Br (20 mg, 0.4 mmol, 4.0 eq.), $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 10 mol%), 2,2':6',2"-terpyridine (4.7 mg, 0.02 mmol, 20 mol%) were added to it, and 1 mL of anhydrous CH_3CN was added.The reaction was carried out under nitrogen atmosphere for 12 h at room temperature. After the completion of the reaction was monitored by TLC, the reaction was quenched with brine, after which the mixture was extracted with dichloromethane (3 x 5 mL), dried with anhydrous Na_2SO_4, filtered, concentrated by rotary evaporator. The filtrate collected was concentrated under reduced pressure and purified by silica gel column chromatography using petroleum ether/ethyl acetate (3:1) to abtain 8 (56%) as white solid.



9, 13%

The 2,3,4,6-Tetra-O-benzoyl-α-D-glucopyranosyl bromide (0.2 mmol, 1.0 eq.) was added to an 8 mL screw-capped vial, and 2-Vinylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.4 mmol, 2.0 eq.), Zn (13 mg, 0.2 mmol, 2.0 eq.), NH_4Br (20 mg, 0.4 mmol, 4.0 eq.), $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 10 mol%), 2,2':6',2"-terpyridine (4.7 mg, 0.02 mmol, 20 mol%) were added to it, and 1 mL of anhydrous CH_3CN was added.The reaction was carried out under nitrogen atmosphere for 12 h at room temperature. After the completion of the reaction was monitored by TLC, the reaction was quenched with brine, after which the mixture was extracted with dichloromethane

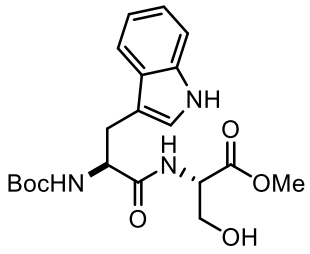
(3 x 5 mL), dried with anhydrous Na_2SO_4, filtered, concentrated by rotary evaporator. The filtrate collected was concentrated under reduced pressure and purified by silica gel column chromatography using petroleum ether/ethyl acetate(3:1) to abtain 9 (13%).[5]

Cytotoxicity by MTT assay

The cytotoxicity of compounds 3a', 3b', 3e, 3k, 7h', 7k' on 3T3 cells was evaluated by MTT assay.[6] In short, cells were seeded in a 96 well plate with a density of 10000 cells per well. After 24 hours of incubation, replace the incubation medium with compounds 3a', 3b', 3e, 3k, 7h', 7k' at different concentrations, and then incubate the cells for another 24 hours. Add MTT (5 mg/mL, 10 μL) to each well, incubate for 4 hours, then remove the culture medium containing MTT and add DMSO (100 μL) to each well to dissolve the generated formazan. After shaking the plate for 10 minutes, measure the absorbance at 490 nm using a microplate reader.

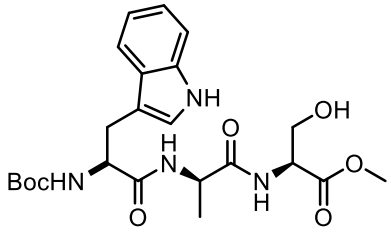
Characterization Data

Raw Material Data Characterization：



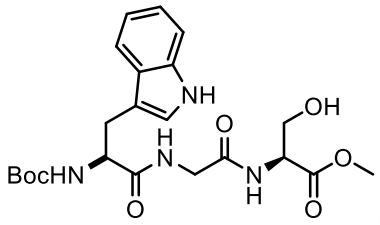
1a

Purification by column chromatography resulted in a white solid product (PE/EA/DCM = 1:2:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.06 (s, 1H), 6.97 – 6.79 (m, 1H), 5.34 (s, 1H), 4.55 – 4.36 (m, 2H), 3.78 (s, 2H), 3.64 (s, 3H), 3.35 – 3.09 (m, 2H), 2.21 (s, 1H), 1.40 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.2, 170.5, 155.7, 136.2, 127.4, 123.4, 122.1, 119.5, 118.6, 111.3, 110.0, 80.4, 62.5, 55.3, 54.9, 52.6, 28.2, 27.9. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{20}H_{27}N_3NaO_6^+$, 428.1792, found, 428.1790.



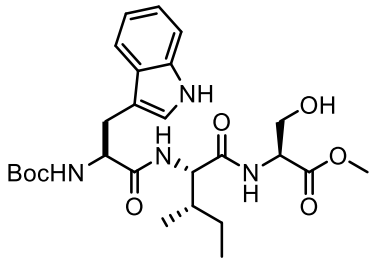
SM-1

Purification by column chromatography resulted in a white solid product (DCM/MeOH = 30:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.68 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.03 (s, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 5.44 (d, *J* = 6.4 Hz, 1H), 4.50 (m, 3H), 3.87 (d, *J* = 11.6 Hz, 1H), 3.71 (s, 3H), 3.56 (d, *J* = 11.2 Hz, 1H), 3.46 (s, 1H), 3.25 (m, 2H), 1.42 (s, 9H), 1.26 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 172.5, 171.6, 171.0, 155.3, 136.1, 127.4, 123.8, 120.8, 118.6, 118.2, 111.3, 110.3, 78.1, 61.2, 55.1, 54.6, 52.0, 47.8, 28.2, 27.6, 18.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{32}N_4NaO_7^+$, 499.2163, found, 499.2159.



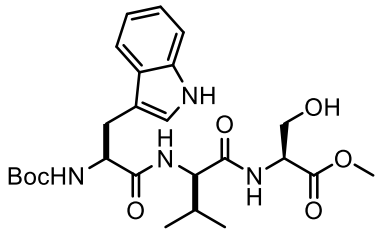
SM-2

Purification by column chromatography resulted in a white solid product (DCM/MeOH = 30:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.73 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.11 – 7.02 (m, 2H), 6.88 (q, *J* = 6.6, 6.0 Hz, 1H), 5.36 (d, *J* = 6.4 Hz, 1H), 4.62 – 4.50 (m, 1H), 4.33 (d, *J* = 6.8 Hz, 1H), 3.99 – 3.86 (m, 2H), 3.82 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.71 (d, *J* = 2.4 Hz, 3H), 3.46 (s, 2H), 3.20 (d, *J* = 6.6 Hz, 2H), 1.39 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.0, 171.0, 169.4, 155.9, 136.1, 127.3, 123.6, 121.9, 119.3, 118.4, 111.4, 109.5, 80.4, 62.2, 55.5, 54.7, 52.6, 42.8, 28.2, 27.8. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{22}H_{30}N_4NaO_7^+$, 485.2007, found, 485.2001.



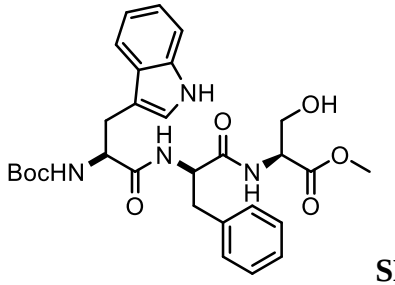
SM-3

Purification by column chromatography resulted in a white solid product (DCM/MeOH = 30:1, R_f = 0.5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.06 (s, 1H), 6.54 (d, *J* = 8.2 Hz, 1H), 5.29 (d, *J* = 7.0 Hz, 1H), 4.48 (m, 2H), 4.34 (t, *J* = 7.6 Hz, 1H), 3.88 (s, 1H), 3.75 (s, 3H), 3.64 (s, 1H), 3.57 (s, 1H), 3.26 (m, 2H), 1.80 (s, 1H), 1.73 (s, 1H), 1.44 (s, 9H), 0.99 (m, 1H), 0.84 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 171.6, 171.2, 170.9, 155.2, 136.0, 127.4, 123.6, 120.8, 118.5, 118.2, 111.3, 110.3, 78.1, 61.2, 56.2, 55.4, 54.7, 51.8, 37.4, 28.1, 27.7, 27.4, 24.0, 15.1, 11.1. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{26}H_{38}N_4NaO_7^+$, 541.2633, found, 541.2637.



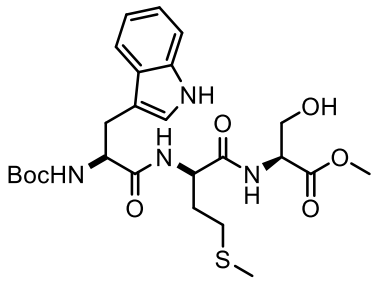
SM-4

Purification by column chromatography resulted in a white solid product (EA, R_f = 0.3). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.81 (d, J = 3.0 Hz, 1H), 8.42 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 7.8 Hz, 1H), 7.11 (d, J = 2.2 Hz, 1H), 7.05 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 5.08 (t, J = 5.8 Hz, 1H), 4.40 – 4.32 (m, 2H), 4.22 (m, 1H), 3.72 (q, J = 5.6 Hz, 1H), 3.67 – 3.63 (m, 1H), 3.62 (s, 3H), 3.08 (m, 1H), 2.90 (m, 1H), 2.04 – 1.94 (m, 1H), 1.29 (s, 9H), 0.88 (m, 6H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 171.8, 171.2, 170.9, 155.3, 136.1, 127.4, 123.6, 120.8, 118.5, 118.2, 111.3, 110.4, 78.2, 61.2, 56.9, 55.5, 54.8, 51.8, 31.4, 28.1, 27.8, 27.5, 19.1, 17.9. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{36}N_4NaO_7^+$, 527.2476, found, 527.2465.



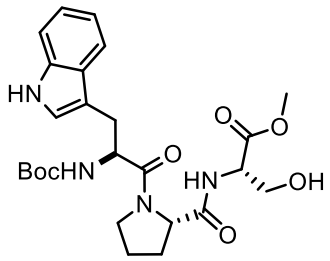
SM-5

Purification by column chromatography resulted in a white solid product (EA, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.50 (s, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.17 (q, J = 11.6, 8.8 Hz, 6H), 6.97 (s, 1H), 6.90 (s, 2H)，6.44 (d, J = 7.8 Hz, 1H), 5.18 (d, J = 6.2 Hz, 1H), 4.72 (d, J = 7.2 Hz, 1H), 4.56 – 4.46 (m, 1H), 4.37 (d, J = 6.0 Hz, 1H), 4.12 (q, J = 7.2 Hz, 1H), 3.86 (s, 1H), 3.71 (s, 3H), 3.68 (s, 1H), 3.17 (d, J = 6.2 Hz, 2H), 3.04 – 2.92 (m, 1H), 2.86 (d, J = 7.2 Hz, 1H), 1.35 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 171.9, 171.2, 170.7, 170.4, 155.7, 136.2, 136.0, 129.3, 128.5, 127.3, 126.9, 123.4, 122.3, 119.7, 118.7, 111.4, 109.7, 80.7, 62.5, 60.4, 55.4, 54.8, 53.6, 52.6, 37.1, 28.2, 27.8. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{29}H_{36}N_4NaO_7^+$, 575.2476, found, 575.2465.



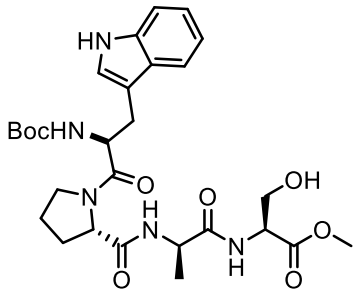
SM-6

Purification by column chromatography resulted in a white solid product (DCM/MeOH = 30:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.81 (s, 1H), 7.63 – 7.47 (m, 2H), 7.36 – 7.18 (m, 2H), 7.10 (m, 2H), 7.00 (s, 1H), 5.46 (d, *J* = 6.8 Hz, 1H), 4.76 – 4.60 (m, 1H), 4.55 – 4.40 (m, 2H), 3.86 (d, *J* = 11.0 Hz, 1H), 3.68 (s, 3H), 3.57 (d, *J* = 11.4 Hz, 1H), 3.42 (s, 1H), 3.23 (d, *J* = 5.8 Hz, 2H), 2.34 (s, 2H), 1.96 (s, 5H), 1.40 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.3, 170.9, 170.5, 155.7, 136.2, 127.4, 123.5, 122.0, 119.5, 118.5, 111.3, 109.5, 80.6, 62.1, 55.5, 54.7, 52.5, 52.2, 50.5, 31.1, 29.3, 28.2, 27.9, 15.0. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{36}N_4NaO_7S^+$, 559.2197, found, 559.2187.



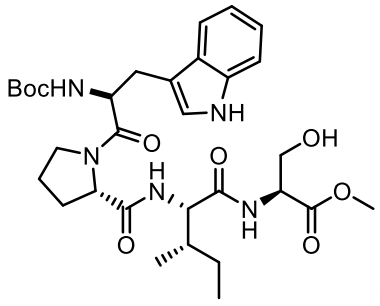
SM-7

Purification by column chromatography resulted in a white solid product (EA, R_f = 0.2). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.98 (d, *J* = 10.4 Hz, 1H), 7.63 (t, *J* = 9.4 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.8 Hz, 1H), 7.12 (p, *J* = 7.8 Hz, 3H), 5.59 (d, *J* = 8.2 Hz, 1H), 4.76 (d, *J* = 7.2 Hz, 1H), 4.69 – 4.58 (m, 1H), 4.43 (m, *J* = 20.6, 6.2 Hz, 1H), 3.92 (m, 2H), 3.72 (d, *J* = 10.6 Hz, 3H), 3.54 (d, *J* = 8.2 Hz, 1H), 3.44 (s, 2H), 3.31 – 3.18 (m, 1H), 3.17 – 3.07 (m, 2H), 2.08 – 1.84 (m, 2H), 1.77 (s, 1H), 1.41 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.0, 171.4, 170.8, 155.9, 136.0, 127.6, 124.1, 122.3, 119.7, 118.4, 111.4, 109.8, 80.5, 62.2, 60.4, 55.5, 53.7, 52.5, 47.4, 30.4, 28.6, 28.2, 24.9. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{34}N_4NaO_7^+$, 525.2320, found, 525.2315.



SM-8

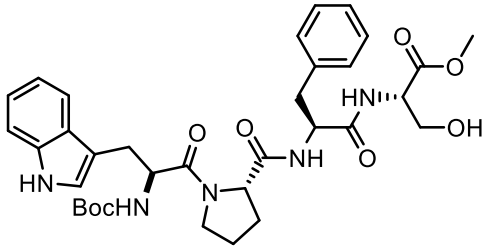
Purification by column chromatography resulted in a white solid product (DCM/MeOH = 30:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.17 – 7.11 (m, 1H), 7.09 (d, *J* = 2.3 Hz, 1H), 6.44 (d, *J* = 8.2 Hz, 1H), 5.35 – 5.26 (m, 1H), 4.84 – 4.75 (m, 1H), 4.68 (m, 1H), 4.60 – 4.38 (m, 3H), 4.02 – 3.86 (m, 2H), 3.78 (d, *J* = 4.0 Hz, 3H), 3.49 (s, 2H), 3.28 – 3.12 (m, 2H), 3.00 – 2.90 (m, 1H), 2.13 – 2.02 (m, 1H), 1.90 – 1.80 (m, 1H), 1.65 – 1.58 (m, 1H), 1.43 (s, 9H), 1.30 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 172.6, 171.3, 171.0, 170.9, 155.4, 136.1, 127.3, 124.2, 120.9, 118.4, 118.4, 111.4, 110.1, 78.0, 61.2, 59.4, 54.7, 53.1, 52.0, 47.9, 46.9, 29.0, 28.2, 27.8, 26.5, 24.6, 18.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{28}H_{39}N_5NaO_8^+$, 596.2691, found, 596.2693.



SM-9

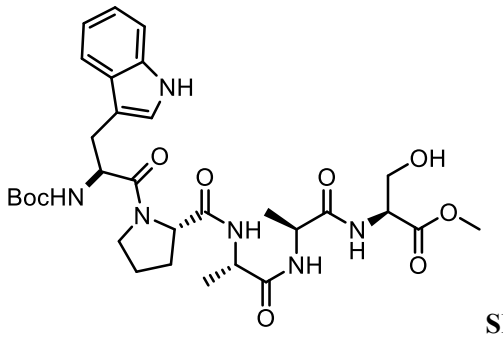
Purification by column chromatography resulted in a white solid product (DCM/MeOH = 30:1, R_f = 0.3. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.17 (m, 2H), 7.09 (s, 1H), 6.33 (d, *J* = 8.6 Hz, 1H), 5.33 (d, *J* = 7.8 Hz, 1H), 4.82 (d, *J* = 6.8 Hz, 1H), 4.69 (m, *J* = 7.8, 3.6 Hz, 1H), 4.47 (dd, *J* = 8.6, 4.8 Hz, 1H), 4.32 (t, *J* = 8.2 Hz, 1H), 4.16 (d, *J* = 7.2 Hz, 1H), 3.97 (t, *J* = 4.6 Hz, 2H), 3.79 (s, 3H), 3.49 (t, *J* = 8.8 Hz, 1H), 3.17 (m, 2H), 2.89 (q, *J* = 7.2 Hz, 1H), 2.11 – 1.84 (m, 3H), 1.65 (q, *J* = 7.4, 6.4 Hz, 2H), 1.43 (s, 9H), 1.35 (s, 2H), 1.25 (s, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.83 (t, *J* = 7.2 Hz, 3H). **^{13}C**

NMR (100 MHz, Chloroform-*d*) δ 173.0, 172.0, 171.2, 170.6, 155.3, 136.1, 127.2, 123.8, 122.2, 119.7, 118.5, 111.4, 109.5, 80.0, 62.5, 61.1, 57.7, 54.9, 52.8, 52.6, 47.6, 35.4, 29.7, 28.9, 28.3, 24.9, 24.6, 15.7, 10.9. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{31}H_{45}N_5NaO_8^+$, 638.3160, found, 638.3161.



SM-10

Purification by column chromatography resulted in a white solid product (DCM/MeOH = 40:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.89 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.16 – 7.06 (m, 4H), 6.80 – 6.75 (m, 1H), 5.68 (d, *J* = 8.8 Hz, 1H), 5.29 (d, *J* = 8.2 Hz, 1H), 4.95 – 4.84 (m, 1H), 4.76 – 4.62 (m, 2H), 4.54 (s, 1H), 4.27 (dd, *J* = 8.8, 4.2 Hz, 1H), 4.05 – 3.88 (m, 2H), 3.76 (s, 3H), 3.55 (d, *J* = 8.8 Hz, 1H), 3.29 (m, 1H), 3.21 – 3.08 (m, 2H), 2.87 (m, 1H), 2.72 (m, 1H), 1.83 (m, 1H), 1.48 (s, 2H), 1.42 (s, 9H), 1.26 (s, 1H), 1.10 (t, *J* = 8.0 Hz, 1H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 171.4, 171.1, 170.9, 170.2, 155.3, 137.7, 136.1, 129.3, 127.9, 127.2, 126.2, 124.0, 120.8, 118.3, 111.4, 110.1, 78.0, 61.2, 59.7, 54.7, 54.6, 53.5, 51.9, 46.8, 37.2, 28.3, 28.1, 27.7, 24.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{34}H_{43}N_5NaO_8^+$, 672.3004, found, 672.3001.

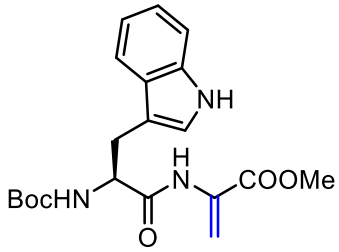


SM-11

Purification by column chromatography resulted in a white solid product (DCM/MeOH = 30:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.32 – 9.13 (m, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.47 (q, *J* = 3.8 Hz, 1H), 7.39

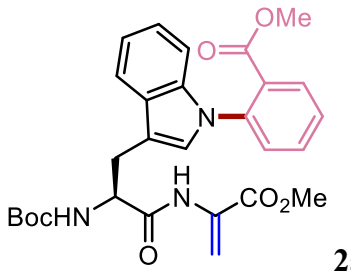
(d, *J* = 8.0 Hz, 1H), 7.25 – 7.14 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 5.45 (d, *J* = 4.8 Hz, 1H), 4.76 – 4.61 (m, 3H), 4.56 (d, *J* = 5.4 Hz, 1H), 4.32 (t, *J* = 7.0 Hz, 1H), 4.27 (t, *J* = 7.6 Hz, 1H), 4.14 – 4.02 (m, 1H), 3.95 (m, 1H), 3.74 (d, *J* = 8.8 Hz, 3H), 3.47 (s, 1H), 3.24 (t, *J* = 7.4 Hz, 2H), 3.04 (q, *J* = 3.8 Hz, 1H), 2.12 (q, *J* = 8.4 Hz, 1H), 1.68 (t, *J* = 5.8 Hz, 2H), 1.51 (d, *J* = 7.0 Hz, 2H), 1.44 (s, 3H), 1.43 – 1.31 (m, 12H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.2, 172.8, 172.6, 172.5, 170.6, 156.0, 136.5, 126.9, 123.6, 122.3, 119.6, 118.5, 111.6, 109.0, 80.7, 62.8, 62.4, 55.2, 52.4, 50.4, 48.7, 47.6, 46.8, 28.4, 28.2, 27.1, 25.3, 17.2, 16.9. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{31}H_{44}N_6NaO_9^+$, 667.3062, found, 667.3052.

Product data characterization:



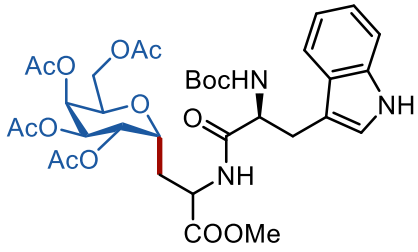
2a

Purification by column chromatography afforded product in 25% yield (9.7 mg) as a colorless sticky oil (PE/EA = 2:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 8.13(s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.05 (s, 1H), 6.60 (s, 1H), 5.86 (s, 1H), 5.14 (s, 1H), 4.54 (s, 1H), 3.72 (s, 3H), 3.34 (s, 1H), 3.24 (dd, *J* = 14.2, 6.8 Hz, 1H), 1.42 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.8, 163.9, 155.5, 136.3, 130.7, 127.4, 123.1, 122.3, 119.8, 118.8, 111.2, 110.3, 109.3, 80.4, 55.9, 52.8, 28.2, 28.0. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{20}H_{25}N_3NaO_5^+$, 410.1686, found, 410.1703.



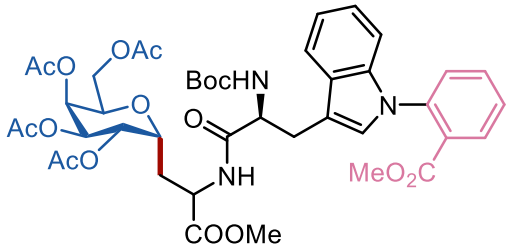
2a'

Purification by column chromatography afforded product in 38% yield (19.8 mg) as a colorless sticky oil (PE/EA = 2:1, R_f = 0.5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 2H), 7.54 – 7.42 (m, 2H), 7.16 (q, *J* = 6.8 Hz, 2H), 7.12 – 7.04 (m, 2H), 6.59 (s, 1H), 5.87 (s, 1H), 5.21 (s, 1H), 4.58 (s, 1H), 3.72 (s, 3H), 3.47 (s, 3H), 3.41 (s, 1H), 3.29 (m, 1H), 1.43 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.7, 166.5, 164.0, 155.5, 138.5, 137.6, 132.9, 131.4, 130.7, 128.7, 128.6 127.9, 127.7, 122.7, 120.2, 119.1, 110.9, 109.9, 109.3, 80.4, 52.8, 52.3, 29.7, 28.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{28}H_{31}N_3NaO_7^+$, 544.2054, found, 544.2052.



3a

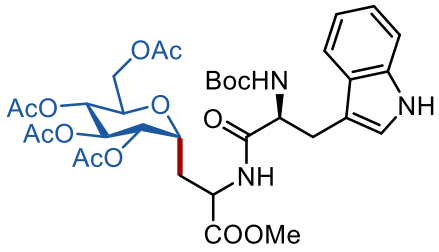
Purification by column chromatography afforded product in 74% yield (53.2 mg, d.r. = 1:1.5) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.3). Contains isomers. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.05 (s, 2/5H), 8.67 (s, 3/5H), 7.76 (d, *J* = 8.0 Hz, 3/5H), 7.63 (d, *J* = 7.8 Hz, 3/5H), 7.41 (d, *J* = 8.0 Hz, 2/5H), 7.37 (d, *J* = 8.2 Hz, 3/5H), 7.21 (d, *J* = 6.8 Hz, 2/5H), 7.17 (d, *J* = 7.0 Hz, 3/5H), 7.12 (dd, *J* = 7.6, 4.2 Hz, 2/5×2H), 7.08 (s, 3/5×2H), 6.92 (d, *J* = 7.2 Hz, 3/5H), 6.88 (s, 2/5H), 5.54 – 5.27 (m, 3/5×4H), 5.20 – 5.08 (m, 2/5×4H), 4.98 (d, *J* = 11.6 Hz, 3/5H), 4.83 (d, *J* = 10.4 Hz, 2/5H), 4.52 – 4.33 (m, 3/5×4H), 4.23 – 4.06 (m, 2/5×4H), 3.84 (d, *J* = 11.0 Hz, 3/5H), 3.80 (s, 2/5H), 3.68 (s, 3/5×3H), 3.67 (s, 2/5×3H), 3.28 – 3.24 (m, 3/5×2H), 3.22 (d, *J* = 9.6 Hz, 2/5×2H), 2.08 (d, *J* = 6.2 Hz, 3/5×12H), 2.06 (d, *J* = 4.6 Hz, 2/5×12H), 2.00 (s, 3/5×2H), 1.92 (m, 2/5×2H), 1.46 (s, 2/5×9H), 1.42 (s, 3/5×9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.5, 171.3, 171.1, 171.0, 170.5, 170.4, 170.2, 170.0, 169.9, 169.8, 169.7, 169.5, 155.4, 154.9, 136.1, 136.0, 127.5, 127.3, 123.2, 122.1, 120.0, 119.6, 118.7, 118.5, 111.7, 111.3, 111.0, 110.3, 95.8, 90.5, 80.0, 79.8, 70.8, 70.4, 68.7, 68.3, 68.2, 67.7, 67.2, 66.9, 66.8, 66.0, 61.7, 61.4, 55.3, 52.5, 52.4, 49.4, 48.4, 28.2, 20.8, 20.7, 20.7, 20.7, 20.7, 20.6, 20.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{34}H_{45}N_3NaO_{14}^+$, 742.2794, found, 742.2808.



3a'

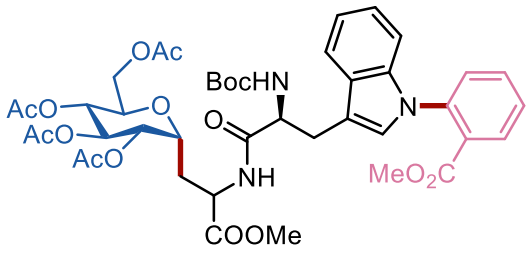
Purification by column chromatography afforded product in 67% yield (57.2 mg, d.r. = 1:1.4) as a white solid (PE/EA = 1:1, R_f = 0.4). mp 130.7 - 131.6 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.67 (m, 2H), 7.57 – 7.46 (m, 2H),

7.21 – 7.15 (m, 2H), 7.13 (d, *J* = 9.0 Hz, 2H), 6.72 (s, 1H), 5.37 (s, 1H), 5.28 (t, *J* = 3.2 Hz, 1H), 5.02 (s, 2H), 4.56 – 4.41 (m, 2H), 4.20 (d, *J* = 10.8 Hz, 1H), 4.03 (d, *J* = 4.8 Hz, 1H), 4.00 (d, *J* = 4.6 Hz, 1H), 3.92 (s, 1H), 3.64 (s, 3H), 3.55 (s, 3H), 3.43 – 3.31 (m, 1H), 3.20 (dd, *J* = 14.4, 8.2 Hz, 1H), 2.09 (s, 3H), 2.02 (d, *J* = 6.4 Hz, 6H), 1.97 (s, 3H), 1.78 (s, 1H), 1.59 (s, 1H), 1.43 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.8, 171.4, 170.8, 169.9, 169.6, 169.4, 166.3, 155.3, 138.7, 137.2, 133.0, 131.4, 128.5, 128.2, 127.8, 127.6, 122.7, 120.2, 119.0, 111.6, 109.8, 80.0, 69.1, 68.2, 67.8, 67.6, 66.7, 60.6, 55.6, 52.4, 49.5, 28.2, 24.8, 20.7, 20.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{42}H_{51}N_3NaO_{16}^+$, 876.3162, found, 876.3178.



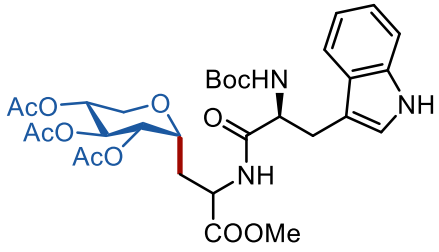
3b

Purification by column chromatography afforded product in 53% yield (38.1 mg, d.r. = 1:1.1) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.56 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.19 (m, 2H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.06 (d, *J* = 8.4 Hz, 1H), 5.17 (m, 2H), 4.95 (m, 2H), 4.60 – 4.40 (m, 2H), 4.14 (m, 1H), 3.99 (d, *J* = 12.4 Hz, 1H), 3.87 (s, 1H), 3.66 (s, 3H), 3.54 (s, 1H), 3.33 (d, *J* = 13.6 Hz, 1H), 3.11 (m, 1H), 2.09 (d, *J* = 4.6 Hz, 6H), 2.06 (s, 6H), 1.58 (s, 2H), 1.44 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.7, 171.5, 170.8, 170.4, 169.5, 169.4, 155.3, 136.2, 127.3, 123.2, 122.3, 119.9, 118.8, 111.4, 110.6, 80.1, 76.8, 70.2, 69.6, 69.4, 69.0, 68.1, 61.7, 55.0, 52.6, 49.0, 29.7, 29.1, 28.3, 27.7, 20.7, 20.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{34}H_{45}N_3NaO_{14}^+$, 742.2794, found, 742.2808.



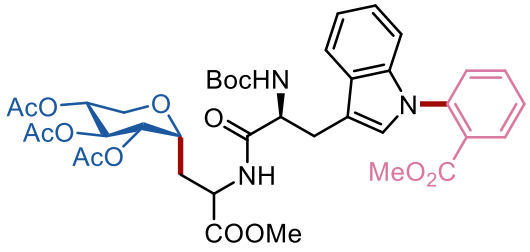
3b'

Purification by column chromatography afforded product in 68% yield (58.0 mg, d.r. = 1:1.1) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.63 (m, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.17 (m, 2H), 7.11 (m, 2H), 6.68 (d, *J* = 6.6 Hz, 1H), 5.35 (s, 1H), 5.19 (t, *J* = 8.8 Hz, 1H), 4.99 – 4.92 (m, 2H), 4.60 - 4.40 (m, 1H), 4.47 (s, 1H), 4.36 – 4.19 (m, 2H), 4.02 – 3.83 (m, 2H), 3.58 (s, 3H), 3.52 (s, 3H), 3.26 (m, 2H), 2.08 (s, 3H), 2.04 (s, 3H), 2.02 (s, 6H), 1.97 (d, *J* = 5.8 Hz, 2H), 1.43 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.4, 171.3, 170.9, 169.9, 169.5, 166.4, 155.4, 138.6, 137.5, 132.9, 131.4, 128.6, 128.5, 128.1, 127.8, 127.7, 122.7, 120.1, 119.1, 111.4, 109.8, 80.1, 70.0, 69.7, 69.6, 68.6, 68.1, 61.6, 55.3, 52.5, 52.3, 49.0, 28.3, 28.1, 20.8, 20.7, 20.6, 20.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{42}H_{51}N_3NaO_{16}^+$, 876.3162, found, 876.3181.



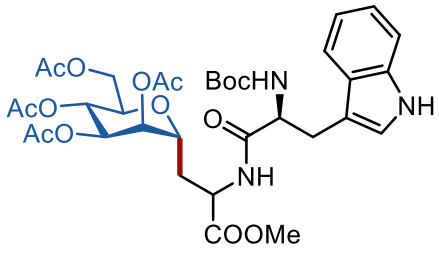
3c

Purification by column chromatography afforded product in 66% yield (42.7 mg, d.r. = 1:1.1) as a colorless sticky oil (PE/EA/DCM = 1:1:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 34.6 Hz, 1H), 7.63 (t, *J* = 10.6, 7.8 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.20 (m, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.07 (s, *J* = 2.8 Hz, 1H), 6.73 – 6.57 (m, 1H), 5.47 – 5.30 (m, 1H), 5.17 – 5.01 (m, 1H), 4.97 (t, *J* = 4.6 Hz, 1H), 4.77 – 4.64 (m, 2H), 4.49 (s, 1H), 3.91 (d, *J* = 13.2 Hz, 1H), 3.82 – 3.74 (m, 1H), 3.72 (d, *J* = 10.4 Hz, 1H), 3.64 (d, *J* = 11.4 Hz, 3H), 3.45 – 3.26 (m, 1H), 3.18 (m, 1H), 2.22 (t, *J* = 7.6 Hz, 1H), 2.13 – 2.10 (m, 6H), 2.05 – 1.98 (m, 3H), 1.94 (q, *J* = 4.4 Hz, 1H), 1.42 (d, *J* = 17.2 Hz, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.0, 171.5, 169.9, 169.8, 168.8, 155.5, 136.2, 129.9, 123.2, 122.3, 119.8, 118.6, 111.3, 111.2, 80.2, 71.3, 70.9, 68.3, 66.4, 65.5, 52.5, 50.9, 49.9, 35.9, 31.9, 29.3, 28.3, 27.2, 21.0, 20.9, 20.8. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{31}H_{41}N_3NaO_{12}^+$, 670.2582, found, 670.2594.



3c'

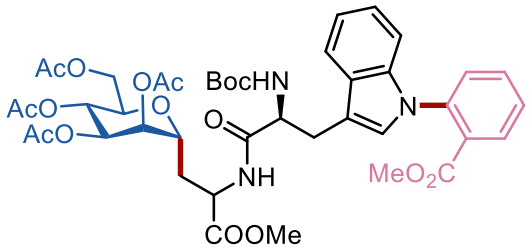
Purification by column chromatography afforded product in 55% yield (43.0 mg, d.r. = 1:1.4) as a colorless sticky oil (PE/EA/DCM = 1:1:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.66 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.15 (m, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.78 (s, 1H), 5.23 (s, 1H), 4.94 (s, 1H), 4.66 (d, *J* = 14.2 Hz, 2H), 4.58 (s, 1H), 4.48 (s, 1H), 3.92 (d, *J* = 13.4 Hz, 1H), 3.77 (d, *J* = 13.4 Hz, 1H), 3.66 (s, 1H), 3.60 (s, 3H), 3.53 (s, 3H), 3.39 (s, 1H), 3.25 (m, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.02 – 1.89 (m, 2H), 1.41 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.0, 171.8, 169.7, 168.6, 166.3, 155.4, 138.6, 137.4, 133.0, 131.4, 128.6, 128.4, 128.0, 127.7, 122.6, 120.1, 119.0, 111.1, 109.8, 80.1, 71.2, 68.3, 66.5, 66.2, 66.0, 55.3, 52.4, 52.3, 49.7, 33.2, 28.2, 27.7, 21.0, 20.8, 20.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{39}H_{47}N_3NaO_{14}^+$, 804.2950, found, 804.2955.



3d

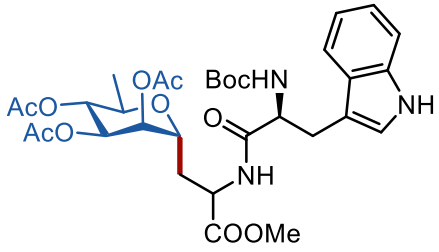
Purification by column chromatography afforded product in 68% yield (48.9 mg, d.r. = 1:2) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.79 – 8.65 (m, 1H), 7.63 (dd, *J* = 11.4, 7.8 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.22 – 7.09 (m, 2H), 7.06 (dd, *J* = 10.0, 2.4 Hz, 1H), 6.67 (m, 1H), 5.47 – 5.29 (m, 1H), 5.29 – 5.22 (m, 1H), 5.22 – 5.14 (m, 1H), 5.11 (d, *J* = 4.4 Hz, 1H), 5.05 – 4.95 (m, 1H), 4.66 – 4.46 (m, 2H), 4.27 (m, 1H), 4.17 – 4.00 (m, 1H), 3.99 – 3.80 (m, 1H), 3.65 (d, *J* = 5.4 Hz, 3H), 3.42 – 3.26 (m, 1H), 3.17 (m, 1H), 2.15 (s, 1H), 2.12 – 2.05 (m, 12H), 2.00 (s, 1H), 1.42 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.4, 170.8, 170.1, 169.9, 169.7, 169.4, 155.3, 136.1, 127.4, 123.3, 122.0, 119.5,

118.3, 111.2, 110.1, 91.9, 79.9, 70.8, 70.2, 69.9, 68.9, 68.2, 66.7, 62.4, 61.6, 52.4, 49.1, 30.5, 28.1, 20.5, 20.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{34}H_{45}N_3NaO_{14}^+$, 742.2794, found, 742.2841.



3d'

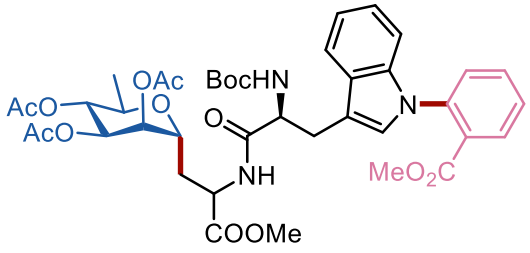
Purification by column chromatography afforded product in 77% yield (65.7 mg, d.r. = 1:1.2) as a white solid (PE/EA = 1:1, R_f = 0.4). mp 85.8 - 87.1 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.0 Hz, 2H), 7.51 (t, *J* = 8.4 Hz, 2H), 7.18 – 7.13 (m, 2H), 7.11 (s, 2H), 6.62 (s, 1H), 5.35 (s, 1H), 5.06 (d, *J* = 5.8 Hz, 2H), 4.92 (d, *J* = 4.0 Hz, 1H), 4.56 (s, 1H), 4.46 (s, 1H), 4.28 (m, 1H), 4.04 (dd, *J* = 12.2, 3.4 Hz, 1H), 3.92 – 3.69 (m, 2H), 3.64 (s, 3H), 3.55 (s, 3H), 3.37 (s, 1H), 3.21 (d, *J* = 11.6 Hz, 1H), 2.04 (t, *J* = 6.0 Hz, 12H), 1.69 (s, 2H), 1.42 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.7, 171.4, 170.8, 169.9, 169.6, 169.5, 166.2, 155.4, 138.8, 137.3, 133.0, 131.5, 128.7, 128.4, 128.3, 127.9, 127.7, 122.7, 120.2, 119.0, 111.5, 109.9, 79.9, 71.1, 70.3, 69.8, 68.2, 67.1, 61.7, 52.5, 52.4, 49.5, 28.3, 20.8, 20.7, 20.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{42}H_{51}N_3NaO_{16}^+$, 876.3162, found, 876.3162.



3e

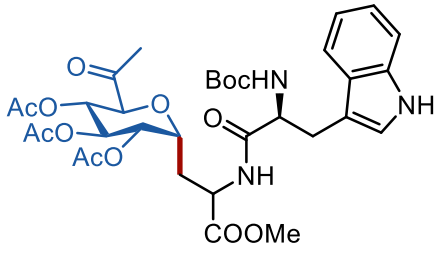
Purification by column chromatography afforded product in 88% yield (58.2 mg, d.r. = 1:4) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.07 (s, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 5.13 (d, *J* = 7.4 Hz, 1H), 5.04 (dd, *J* = 8.2, 3.4 Hz, 1H), 5.00 – 4.88 (m, 2H), 4.62 (q, *J*

= 6.6, 5.6 Hz, 1H), 4.47 (s, 1H), 3.83 (m, 1H), 3.67 (s, 3H), 3.58 (t, *J* = 6.6 Hz, 1H), 3.33 (d, *J* = 12.8 Hz, 1H), 3.16 (m, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.71 (m, 2H), 1.40 (s, 9H), 1.14 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.5, 171.0, 170.2, 170.1, 169.8, 155.3, 136.1, 123.5, 122.2, 119.5, 118.6, 111.4, 111.2, 91.9, 80.0, 71.1, 70.4, 68.9, 68.7, 68.2, 66.1, 52.5, 49.6, 48.3, 29.6, 28.2, 20.8, 20.7, 20.6, 17.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{32}H_{43}N_3NaO_{12}^+$, 684.2739, found, 684.2754.



3e'

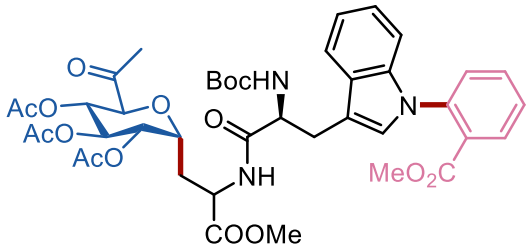
Purification by column chromatography afforded product in 83% yield (66.0 mg, d.r. = 1:4) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.0, 1H), 7.81 – 7.60 (m, 2H), 7.51 (m, 2H), 7.19 – 7.07 (m, 4H), 6.59 (s, 1H), 5.36 (s, 1H), 5.09 – 4.86 (m, 3H), 4.70 – 4.35 (m, 2H), 3.94 – 3.79 (m, 1H), 3.75 – 3.64 (m, 1H), 3.64 – 3.47 (m, 6H), 3.41 (s, 1H), 3.19 (m, 1H), 2.25 – 2.10 (m, 1H), 2.07 (d, *J* = 8.2 Hz, 3H), 2.04 (s, 3H), 1.99 (d, *J* = 5.6 Hz, 3H), 1.76 (s, 1H), 1.43 (s, 9H), 1.17 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.6, 170.0, 169.9, 169.8, 166.1, 155.3, 138.6, 137.5, 133.0, 131.6, 128.7, 128.6, 128.2, 127.9, 127.7, 127.6, 122.8, 120.1, 118.9, 109.9, 80.0, 71.3, 70.6, 70.5, 68.9, 68.8, 52.4, 49.6, 28.5, 28.2, 20.8, 20.8, 20.6, 17.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{40}H_{49}N_3NaO_{14}^+$, 818.3107, found, 818.3118.



3f

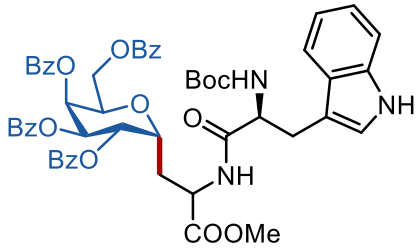
Purification by column chromatography afforded product in 73% yield (50.3 mg, d.r. = 1:2.3) as a colorless sticky oil (PE/EA/DCM = 1:4:1, R_f = 0.4). **^{1}H NMR** (400 MHz,

Chloroform-*d*) δ 8.33 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.15 – 7.05 (m, 2H), 5.21 (t, *J* = 3.0 Hz, 1H), 5.15 – 5.06 (m, 1H), 5.01 (t, *J* = 4.0 Hz, 1H), 4.62 (s, 2H), 4.59 (s, 1H), 4.32 (s, 1H), 4.13 (d, *J* = 9.8 Hz, 1H), 3.70 (s, 3H), 3.60 (s, 3H), 3.31 (m, 2H), 2.12 (d, *J* = 6.0 Hz, 6H), 1.99 (s, 3H), 1.87 – 1.70 (m, 2H), 1.36 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.6, 169.8, 169.3, 168.9, 168.3, 155.3, 136.1, 127.9, 123.4, 122.0, 119.5, 118.8, 111.1, 79.9, 73.3, 68.1, 67.6, 66.2, 65.8, 55.0, 52.5, 52.4, 50.0, 31.2, 28.2, 27.9, 20.8, 20.6, 20.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{33}H_{43}N_3NaO_{13}^+$, 712.2688, found, 712.2689.



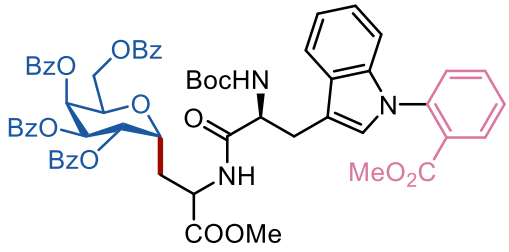
3f'

Purification by column chromatography afforded product in 75% yield (61.7 mg, d.r. = 1:3) as a colorless sticky oil (PE/EA = 1:2, R_f = 0.5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (t, *J* = 6.6 Hz, 1H), 7.73 (m, 1H), 7.64 (q, *J* = 6.0, 4.2 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.49 (m, 2H), 7.13 (m, 4H), 5.46 – 5.29 (m, 1H), 5.21 (d, *J* = 16.0 Hz, 1H), 5.02 (m, 1H), 4.78 (q, *J* = 7.2 Hz, 1H), 4.67 (m, 2H), 4.28 (d, *J* = 10.8 Hz, 1H), 4.21 (d, *J* = 9.8 Hz, 1H), 3.74 – 3.56 (m, 6H), 3.48 (d, *J* = 5.0 Hz, 3H), 3.42 – 3.22 (m, 2H), 2.12 (t, *J* = 10.8 Hz, 6H), 2.00 (s, 3H), 1.81 (s, 2H), 1.40 (d, *J* = 6.4 Hz, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.0, 169.8, 169.4, 168.1, 166.6, 155.4, 137.4, 132.7, 131.3, 129.9, 128.7, 128.6, 128.4, 128.1, 127.5, 122.5, 119.9, 119.2, 111.6, 109.7, 79.8, 73.3, 67.5, 67.0, 66.4, 65.5, 54.9, 52.7, 52.3, 50.0, 31.5, 29.7, 28.2, 20.9, 20.7, 20.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{41}H_{49}N_3NaO_{15}^+$, 846.3058, found, 846.3062.



3g

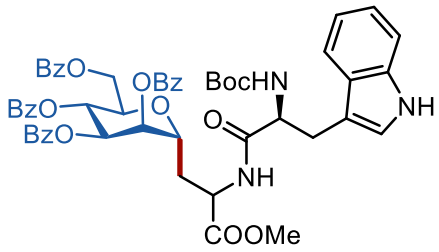
Purification by column chromatography afforded product in 71% yield (68.7 mg, d.r. = 1:2) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.04 (dd, *J* = 13.4, 8.2 Hz, 4H), 7.99 (d, *J* = 3.8 Hz, 1H), 7.97 (s, 1H), 7.89 (m, 2H), 7.61 (dd, *J* = 12.4, 7.0 Hz, 2H), 7.57 – 7.51 (m, 2H), 7.48 (d, *J* = 9.6 Hz, 2H), 7.45 (s, 2H), 7.43 (s, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.03 (m, 1H), 6.83 (d, *J* = 6.8 Hz, 1H), 5.96 (s, 1H), 5.75 (d, *J* = 10.6 Hz, 2H), 5.20 (s, 1H), 4.85 (s, 1H), 4.61 (d, *J* = 13.0 Hz, 1H), 4.57 – 4.36 (m, 2H), 4.24 (dd, *J* = 11.6, 5.4 Hz, 1H), 3.75 – 3.64 (m, 1H), 3.61 (s, 3H), 3.34 (s, 1H), 3.21 – 3.03 (m, 1H), 2.17 – 1.90 (m, 2H), 1.42 (d, *J* = 4.8 Hz, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.4, 171.2, 166.5, 166.0, 165.5, 165.4, 155.4, 136.2, 133.7, 133.6, 133.2, 129.9, 129.8, 129.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 127.7, 123.3, 122.6, 119.8, 118.6, 111.3, 110.4, 80.1, 69.5, 68.9, 68.2, 61.5, 55.5, 52.6, 49.2, 29.3, 28.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{54}H_{53}N_3NaO_{14}^+$, 990.3420, found, 990.3430.



3g'

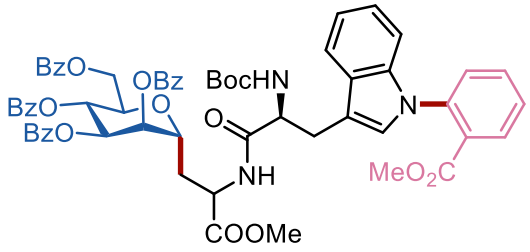
Purification by column chromatography afforded product in 68% yield (74.9 mg, d.r. = 1:1) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.06 – 8.01 (m, 3H), 8.01 – 7.93 (m, 2H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.78 (s, 1H), 7.71 – 7.66 (m, 1H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.59 (d, *J* = 3.4 Hz, 1H), 7.57 – 7.43 (m, 7H), 7.39 (q, *J* = 7.0 Hz, 4H), 7.31 (q, *J* = 8.6, 7.8 Hz, 3H), 7.21 – 7.12 (m, 2H), 7.07 (q, *J* = 9.8, 8.8 Hz, 2H), 6.87 – 6.55 (m,

1H), 5.91 (d, *J* = 21.0 Hz, 1H), 5.72 (d, *J* = 2.6 Hz, 1H), 5.57 (s, 1H), 5.37 (m, 1H), 4.67 (s, 2H), 4.56 – 4.46 (m, 1H), 4.45 – 4.35 (m, 1H), 4.25 (d, *J* = 12.6 Hz, 1H), 3.56 (s, 3H), 3.48 (s, 3H), 3.30 (s, 1H), 3.21 (m, 1H), 2.35 – 2.04 (m, 2H), 1.40 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.7, 171.4, 166.5, 166.3, 165.4, 165.3, 155.4, 138.7, 137.5, 133.6, 133.4, 133.2, 133.0, 131.4, 129.9, 129.8, 129.8, 128.9, 128.6, 128.5, 128.5, 128.4, 127.8, 122.8, 120.1, 119.2,109.9, 79.9, 69.5, 69.0, 68.9, 68.5, 68.2, 61.6, 52.5, 52.3, 49.2, 31.9, 29.3, 28.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{62}H_{59}N_3NaO_9^+$, 1124.3788, found, 1124.3791.



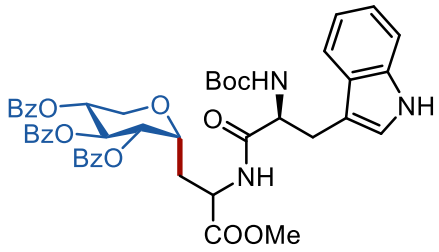
3h

Purification by column chromatography afforded product in 64% yield (61.9 mg, d.r. = 1:1) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.81 (s, 1H), 8.13 (d, *J* = 7.6 Hz, 2H), 8.00 (dd, *J* = 11.4, 7.8 Hz, 4H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.74 (s, 1H), 7.63 – 7.53 (m, 3H), 7.51 – 7.39 (m, 5H), 7.33 (m, 5H), 7.17 (q, *J* = 5.6, 3.8 Hz, 2H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.04 (q, *J* = 8.6, 8.0 Hz, 2H), 5.62 (dd, *J* = 9.4, 3.2 Hz, 1H), 5.46 (d, *J* = 3.2 Hz, 1H), 5.30 (d, *J* = 8.2 Hz, 1H), 4.65 (d, *J* = 12.4 Hz, 1H), 4.62 – 4.45 (m, 2H), 4.36 (dd, *J* = 12.4, 4.0 Hz, 1H), 4.05 (d, *J* = 11.0 Hz, 1H), 3.97 (s, 1H), 3.68 (s, 3H), 3.38 (d, *J* = 14.0 Hz, 1H), 3.07 (m, 1H), 1.74 (s, 2H), 1.43 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.6, 171.4, 170.9, 166.2, 166.0, 165.8, 165.6, 165.3, 155.3, 136.3, 133.6, 133.6, 133.6, 133.2, 129.9, 129.9, 129.8, 129.8, 129.2, 129.0, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 127.3, 123.5, 122.3, 120.0, 118.9, 111.4, 110.6, 80.0, 72.4, 71.6, 70.6, 70.1, 66.9, 62.4, 54.9, 52.8, 49.5, 30.3, 29.6, 28.4, 28.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{54}H_{53}N_3NaO_{14}^+$, 990.3420, found, 990.3425.



3h'

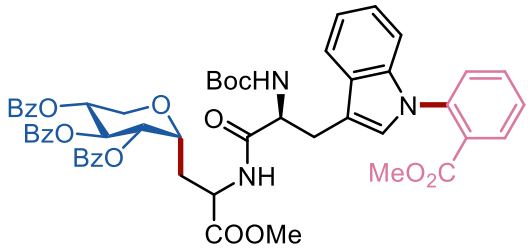
Purification by column chromatography afforded product in 47% yield (51.7 mg, d.r. = 1:1.2) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.4). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.12 – 8.09 (m, 2H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.94 – 7.91 (m, 2H), 7.84 – 7.77 (m, 2H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.44 – 7.40 (m, 3H), 7.36 (m, 4H), 7.29 – 7.25 (m, 3H), 7.16 (q, *J* = 6.8 Hz, 1H), 7.13 – 7.06 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 6.05 – 5.99 (m, 1H), 5.93 (t, *J* = 8.8 Hz, 1H), 5.68 – 5.54 (m, 1H), 5.50 (s, 1H), 5.39 (m, 1H), 4.79 – 4.71 (m, 1H), 4.64 – 4.57 (m, 1H), 4.50 (dd, *J* = 12.2, 4.0 Hz, 1H), 4.44 – 4.38 (m, 1H), 4.32 – 4.22 (m, 1H), 4.14 (s, 1H), 3.70 – 3.47 (m, 6H), 3.39 (m, 1H), 3.21 (t, *J* = 6.8 Hz, 1H), 1.98 – 1.70 (m, 2H), 1.39 (d, *J* = 7.8 Hz, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.6, 171.2, 166.3, 166.2, 165.5, 165.4, 165.3, 165.3, 155.4, 138.8, 137.5, 133.5, 133.3, 133.1, 131.6, 129.9, 129.8, 129.7, 129.4, 129.4, 129.1, 129.0, 128.9, 128.7, 128.5, 128.5, 128.4, 128.0, 127.7, 122.8, 120.3, 119.3, 109.9, 92.4, 80.1, 71.4, 70.9, 69.8, 68.9, 67.3, 66.9, 62.8, 62.7, 52.6, 52.5, 49.9, 28.5, 28.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{62}H_{59}N_3NaO_9^+$, 1124.3788, found, 1124.3779.



3i

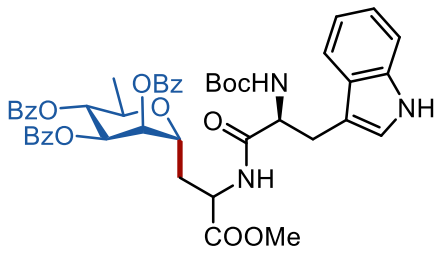
Purification by column chromatography afforded product in 72% yield (60.0 mg, d.r. = 1:2) as a colorless sticky oil (PE/EA = 2:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.01 (s, 1H), 8.01 – 7.97 (m, 2H), 7.91 (t, *J* = 8.2 Hz, 4H), 7.84 (d, *J* = 5.6 Hz, 1H), 7.63 (d, *J* = 6.6 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 2H), 7.47 (d, *J* = 1.8 Hz,

2H), 7.44 (d, *J* = 7.6 Hz, 3H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.17 (dd, *J* = 6.0, 3.2 Hz, 2H), 6.99 (d, *J* = 2.2 Hz, 1H), 6.24 (d, *J* = 6.2 Hz, 1H), 5.71 (t, *J* = 9.8 Hz, 1H), 5.38 (m, 1H), 5.20 (m, 2H), 5.09 (t, *J* = 9.8 Hz, 1H), 4.68 (s, 1H), 4.50 (dd, *J* = 6.2, 3.8 Hz, 1H), 3.82 (dd, *J* = 11.0, 5.6 Hz, 1H), 3.63 (s, 3H), 3.29 (m, 1H), 3.08 (m, 1H), 2.03 – 1.98 (m, 2H), 1.46 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.6, 170.9, 167.1, 165.7, 165.3, 155.1, 136.3, 133.6, 133.5, 129.8, 129.7, 129.6, 129.1, 129.0, 128.8, 128.7, 128.6, 128.4, 127.1, 123.2, 122.4, 120.1, 119.3, 111.9, 110.8, 80.0, 74.2, 73.5, 72.2, 69.5, 66.5, 54.8, 52.5, 49.1, 32.0, 29.3, 28.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{46}H_{47}N_3NaO_{12}^+$, 856.3052, found, 856.3055.



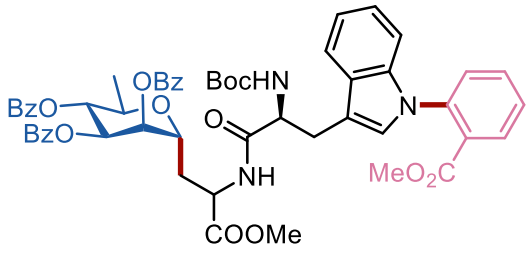
3i'

Purification by column chromatography afforded product in 56% yield (54.2 mg, d.r. = 1:1.3) as a colorless sticky oil (PE/EA = 2:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (m, 3H), 7.84 (dd, *J* = 12.4, 7.2 Hz, 4H), 7.76 – 7.56 (m, 2H), 7.51 (q, *J* = 7.8 Hz, 3H), 7.47 – 7.32 (m, 6H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.22 – 7.15 (m, 2H), 7.15 – 7.07 (m, 2H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.73 (s, 1H), 5.70 (m, 1H), 5.33 (m, 1H), 5.29 – 5.10 (m, 2H), 4.54 (s, 1H), 4.47 (s, 1H), 4.16 (dd, *J* = 11.6, 6.0 Hz, 1H), 3.64 (s, 4H), 3.49 (s, 3H), 3.27 – 3.04 (m, 2H), 2.01 (d, *J* = 7.0 Hz, 2H), 1.45 (d, *J* = 11.0 Hz, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.8, 171.6, 165.8, 165.8, 165.5, 165.4, 138.7, 137.5, 133.4, 133.4, 133.1, 133.0, 131.5, 130.1, 129.9, 129.8, 129.8, 129.6, 129.1, 128.9, 128.7, 128.4, 128.3, 127.9, 127.6, 122.8, 120.4, 120.2, 119.3, 119.0, 110.1, 109.8, 80.1, 75.5, 73.6, 72.2, 72.1, 70.2, 66.6, 52.3, 52.3, 35.9, 31.9, 31.9, 29.3, 28.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{54}H_{53}N_3NaO_{14}^+$, 990.3420, found, 990.3439.



3j

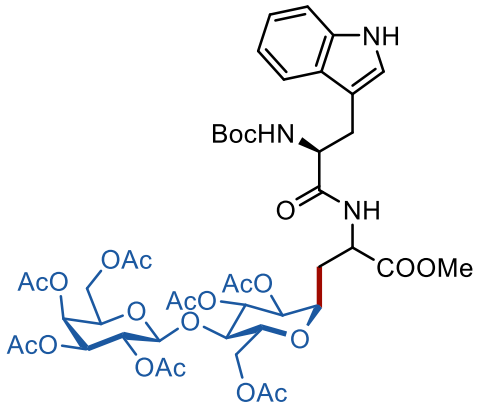
Purification by column chromatography afforded product in 52% yield (44.0 mg, d.r. = 1:1.1) as a colorless sticky oil (PE/EA/DCM = 1:2:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.77 (s, 1H), 8.07 (d, *J* = 7.6 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.71 (t, *J* = 4.6 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (m, 4H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.30 (dd, *J* = 10.2, 5.8 Hz, 3H), 7.18 – 7.13 (m, 2H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.30 (d, *J* = 7.6 Hz, 1H), 5.66 – 5.53 (m, 2H), 5.41 (s, 1H), 5.25 (s, 1H), 4.67 (s, 1H), 4.58 (s, 1H), 4.11 (t, *J* = 7.0 Hz, 1H), 4.03 (d, *J* = 12.2 Hz, 1H), 3.68 (s, 3H), 3.37 (m, 1H), 3.16 (m, 1H), 2.04 (q, *J* = 9.4, 6.2 Hz, 2H), 1.44 (s, 9H), 1.35 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.3, 171.1, 166.1, 165.9, 165.7, 155.3, 136.4, 133.6, 133.5, 133.5, 129.9, 129.8, 129.7, 129.4, 129.2, 128.9, 128.6, 128.5, 128.4, 127.3, 122.9, 122.5, 119.9, 118.8, 111.5, 110.6, 80.1, 72.0, 71.7, 70.2, 68.5, 54.9, 52.7, 48.5, 30.7, 29.3, 28.3, 27.2, 22.7, 17.9. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{47}H_{49}N_3NaO_{12}^+$, 870.3208, found, 870.3217.



3j'

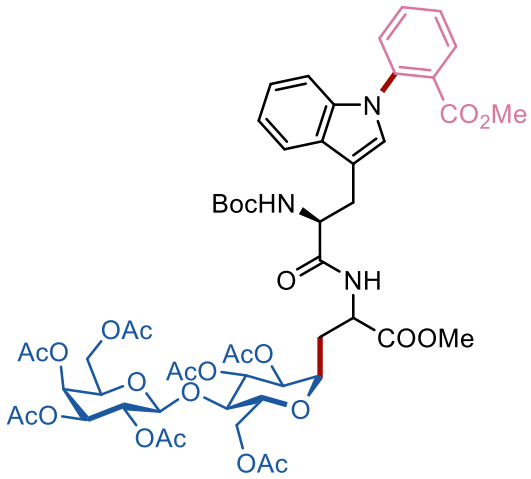
Purification by column chromatography afforded product in 64% yield (62.8 mg, d.r. = 1:1.2) as a colorless sticky oil (PE/EA/DCM = 1:1:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (q, *J* = 7.8 Hz, 5H), 7.81 (t, *J* = 6.8 Hz, 2H), 7.74 (s, 1H), 7.66 (d, *J* = 11.8 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.56 – 7.49 (m, 2H), 7.47 (s, 1H), 7.46 – 7.40 (m, 4H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.23 – 7.09 (m, 3H), 7.03 (s, 1H), 6.68 (s, 1H), 5.62 – 5.46 (m, 2H), 5.43 (d, *J* = 3.2 Hz, 2H), 4.75 (s, 1H), 4.53 (m, 1H), 4.13 (s, 1H), 3.95 (s, 1H), 3.65 (s, 3H), 3.48 (s, 3H), 3.41 (s, 1H), 3.23

(m, 1H), 2.38 (s, 1H), 1.99 (s, 1H), 1.40 (s, 9H), 1.30 (d, J = 6.4 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.7, 166.4, 165.6, 165.6, 165.5, 155.4, 138.7, 137.5, 133.4, 133.3, 132.9, 131.3, 129.9, 129.7, 129.7, 129.4, 129.2, 129.0, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 127.7, 120.2, 119.3, 119.0, 111.4, 110.1, 109.8, 80.0, 72.0, 71.7, 69.8, 68.8, 55.0, 52.5, 52.4, 49.9, 31.9, 30.6, 29.7, 28.3, 17.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{55}H_{55}N_3NaO_{14}^+$, 1004.3576, found, 1004.3581.



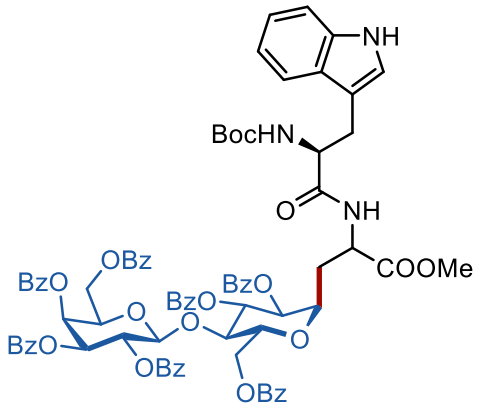
3k

Purification by column chromatography afforded product in 32% yield (32.2 mg, d.r. = 1:1.2) as a colorless sticky oil (PE/EA = 1:3, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.94 (s, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 6.0 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 6.2 Hz, 1H), 6.15 (d, J = 8.4 Hz, 1H), 5.38 (q, J = 7.2, 5.6 Hz, 2H), 5.20 (p, J = 8.8, 7.4 Hz, 2H), 5.05 – 4.99 (m, 1H), 4.75 (d, J = 7.4 Hz, 1H), 4.55 (m, 2H), 4.46 (d, J = 7.8 Hz, 1H), 4.38 (q, J = 7.6, 7.0 Hz, 1H), 4.28 – 4.15 (m, 2H), 4.15 – 4.10 (m, 2H), 4.08 (d, J = 6.0 Hz, 1H), 3.91 (t, J = 6.8 Hz, 1H), 3.80 (s, 1H), 3.65 (d, J = 9.6 Hz, 3H), 3.40 – 3.31 (m, 1H), 3.09 (m, 1H), 2.18 (s, 3H), 2.14 (d, J = 2.8 Hz, 3H), 2.12 (s, 3H), 2.10 (s, 6H), 2.06 (s, 3H), 2.00 (s, 3H), 1.80 (s, 2H), 1.45 (d, J = 5.0 Hz, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.5 171.3, 170.6, 170.4, 170.1, 170.0, 169.7, 169.3, 155.2, 136.3, 136.2, 124.0, 123.1, 122.2, 119.8, 118.6, 118.2, 111.7, 101.5, 101.2, 79.9, 75.8, 75.6, 70.8, 70.7, 69.2, 66.6, 61.4, 60.8, 60.7, 55.4, 52.5, 52.4, 49.5, 48.0, 29.6, 28.3, 20.9, 20.7, 20.7, 20.6, 20.6, 20.5, 20.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{46}H_{61}N_3NaO_{22}^+$, 1030.3639, found, 1030.3638.



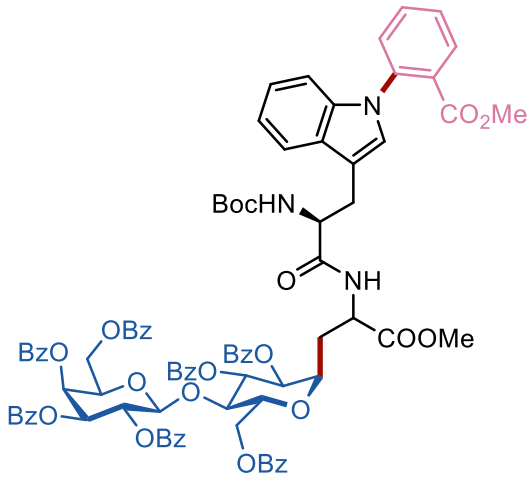
3k'

Purification by column chromatography afforded product in 46% yield (52.5 mg, d.r. = 1:1.4) as a colorless sticky oil (PE/EA = 1:2, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.67 (dd, *J* = 10.0, 6.2 Hz, 2H), 7.55 – 7.45 (m, 2H), 7.15 (q, *J* = 4.8 Hz, 2H), 7.10 (d, *J* = 5.6 Hz, 2H), 6.61 (d, *J* = 6.8 Hz, 1H), 5.39 (d, *J* = 3.4 Hz, 1H), 5.28 (s, 1H), 5.25 – 5.18 (m, 1H), 5.00 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.88 (dd, *J* = 9.8, 6.2 Hz, 1H), 4.52 (dd, *J* = 7.8, 4.2 Hz, 2H), 4.45 (s, 1H), 4.16 (d, *J* = 5.4 Hz, 2H), 4.14 (s, 1H), 4.10 (d, *J* = 11.4 Hz, 1H), 4.03 (s, 1H), 4.00 (d, *J* = 5.6 Hz, 1H), 3.76 – 3.63 (m, 2H), 3.59 (q, *J* = 6.2 Hz, 3H), 3.48 (s, 3H), 3.42 (d, *J* = 14.6 Hz, 1H), 3.34 – 3.16 (m, 2H), 2.17 (s, 3H), 2.11 (d, *J* = 4.2 Hz, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.05 (d, *J* = 2.7 Hz, 3H), 1.98 (s, 6H), 1.70 (s, 2H), 1.42 (d, *J* = 2.6 Hz, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.3, 170.7, 170.5, 170.0, 170.0, 169.9, 169.5, 166.4, 155.4, 138.7, 137.5, 133.0, 131.4, 128.6, 128.5, 127.9, 127.7, 122.7, 120.2, 119.1, 111.4, 109.8, 101.9, 82.7, 80.1, 71.4, 71.3, 70.9, 70.0, 69.0, 68.8, 68.7, 66.8, 62.4, 61.7, 52.5, 52.4, 49.3, 29.7, 28.3, 22.7, 20.9, 20.8, 20.6, 20.6, 20.5, 20.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{54}H_{67}N_3NaO_{24}^+$, 1164.4007, found, 1164.4010.



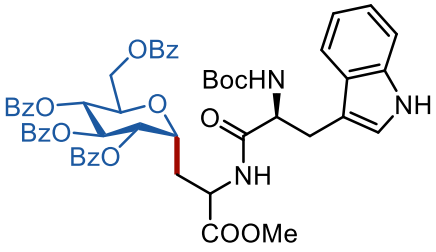
3l

Purification by column chromatography afforded product in 43% yield (62.0 mg, d.r. = 1:1.3) as a colorless sticky oil (PE/EA/DCM = 1:2:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 2.4 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 2H), 7.98 (m, 6H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 3H), 7.57 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.45 (m, 7H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 9.6 Hz, 2H), 7.25 (s, 2H), 7.23 (s, 1H), 7.19 (d, *J* = 7.6 Hz, 3H), 7.16 (s, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.98 (s, 1H), 6.09 – 5.94 (m, 3H), 5.65 (dd, *J* = 10.4, 3.5 Hz, 1H), 5.37 – 5.26 (m, 1H), 5.11 (dd, *J* = 9.8, 6.0 Hz, 1H), 5.04 (d, *J* = 8.0 Hz, 1H), 4.69 (d, *J* = 7.8 Hz, 1H), 4.58 (s, 1H), 4.45 (d, *J* = 7.4 Hz, 3H), 4.25 (s, 1H), 4.17 (d, *J* = 11.8 Hz, 1H), 4.00 (d, *J* = 12.2 Hz, 1H), 3.87 (t, *J* = 9.2 Hz, 1H), 3.80 (s, 1H), 3.72 (t, *J* = 9.0 Hz, 1H), 3.52 (s, 3H), 3.26 (d, *J* = 14.0 Hz, 1H), 3.07 (d, *J* = 8.6 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.41 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.8, 171.4, 166.2, 166.0, 165.5, 165.5, 165.4, 165.3, 155.1, 136.0, 134.0, 133.9, 133.5, 133.5, 133.3, 133.2, 130.0, 129.8, 129.8, 129.6, 129.6, 129.5, 129.3, 128.8, 128.7, 128.7, 128.7, 128.5, 128.5, 128.4, 128.4, 128.3, 128.1, 123.3, 122.2, 119.7, 118.9, 111.6, 110.9, 102.2, 82.9, 79.8, 72.6, 71.4, 71.3, 70.2, 70.2, 69.8, 68.6, 68.0, 62.9, 62.0, 56.1, 52.4, 49.9, 29.6, 28.3, 25.9. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{81}H_{75}N_3NaO_{22}^+$, 1464.4734, found, 1464.4735.



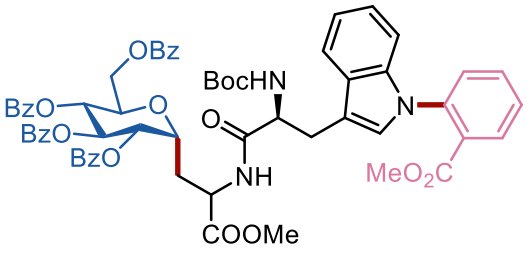
3l'

Purification by column chromatography afforded product in 48% yield (75.6 mg, d.r. = 1:1.1) as a colorless sticky oil (PE/EA/DCM = 1:1:1, R_f = 0.5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 3H), 7.97 – 7.91 (m, 4H), 7.90 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.0 Hz, 3H), 7.59 – 7.53 (m, 2H), 7.53 – 7.43 (m, 7H), 7.42 (s, 1H), 7.40 (s, 1H), 7.38 (s, 1H), 7.36 (s, 1H), 7.34 (s, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.21 (m, 3H), 7.21 – 7.10 (m, 6H), 7.09 – 7.04 (m, 1H), 7.01 (s, 1H), 6.61 (d, *J* = 6.6 Hz, 1H), 5.97 (d, *J* = 3.4 Hz, 1H), 5.92 (dd, *J* = 10.5, 7.9 Hz, 1H), 5.57 (dd, *J* = 10.4, 3.4 Hz, 1H), 5.20 (dd, *J* = 10.0, 6.4 Hz, 2H), 5.03 (d, *J* = 7.8 Hz, 1H), 4.65 (t, *J* = 8.4 Hz, 1H), 4.54 – 4.47 (m, 2H), 4.42 (d, *J* = 8.6 Hz, 2H), 4.39 – 4.32 (m, 2H), 4.23 (s, 1H), 4.12 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.06 (t, *J* = 8.8 Hz, 1H), 3.90 – 3.79 (m, 2H), 3.44 (s, 3H), 3.41 (s, 3H), 3.19 (s, 1H), 3.09 (dd, *J* = 14.6, 7.2 Hz, 1H), 2.13 – 2.02 (m, 2H), 1.38 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.2, 166.3, 166.2, 165.5, 165.5, 165.4, 165.2, 155.4, 138.7, 137.5, 133.8, 133.5, 133.4, 133.3, 133.1, 133.0, 131.5, 130.0, 129.8, 129.7, 129.7, 129.5, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.1, 127.8, 127.7, 122.7, 120.2, 119.2, 111.5, 109.8, 102.3, 82.8, 80.1, 72.5, 71.6, 71.6, 70.5, 69.5, 69.5, 69.1, 68.0, 62.8, 62.2, 55.2, 52.4, 52.3, 49.4, 29.3, 28.2, 27.3, 27.2. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{89}H_{81}N_3NaO_{22}^+$, 1598.5102, found, 1598.5105.



3m

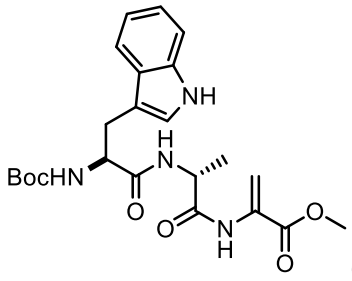
Purification by column chromatography afforded product in 50% yield (48.4 mg, d.r. = 1:1.4) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.69 (s, 1H), 8.07 (d, *J* = 7.6 Hz, 2H), 8.00 – 7.88 (m, 6H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.53 (m, 4H), 7.43 (m, 4H), 7.35 (m, 5H), 7.17 (m, 2H), 6.99 (d, *J* = 2.2 Hz, 1H), 6.14 (d, *J* = 8.4 Hz, 1H), 5.80 (t, *J* = 8.6 Hz, 1H), 5.59 (t, *J* = 8.2 Hz, 1H), 5.38 (dd, *J* = 8.8, 5.2 Hz, 1H), 5.24 (s, 1H), 4.54 (p, *J* = 8.8, 7.6 Hz, 3H), 4.40 (dd, *J* = 12.2, 5.0 Hz, 1H), 4.23 (d, *J* = 10.8 Hz, 1H), 4.02 (dd, *J* = 8.6, 4.4 Hz, 1H), 3.62 (s, 3H), 3.34 (d, *J* = 14.2 Hz, 1H), 3.08 (m, 1H), 1.86 (s, 1H), 1.73 (d, *J* = 8.8 Hz, 1H), 1.41 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.8, 171.4, 166.2, 166.0, 165.3, 165.1, 155.3, 136.3, 133.7, 133.6, 133.5, 133.2, 129.8, 129.8, 129.5, 128.8, 128.7, 128.6, 128.5, 128.4, 127.2, 123.2, 122.3, 120.0, 118.9, 111.3, 110.6, 80.0, 70.4, 70.3, 70.2, 69.3, 68.5, 62.4, 54.8, 52.6, 49.2, 29.2, 28.3, 28.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{54}H_{53}N_3NaO_{14}^+$, 990.3420, found, 990.3443.



3m'

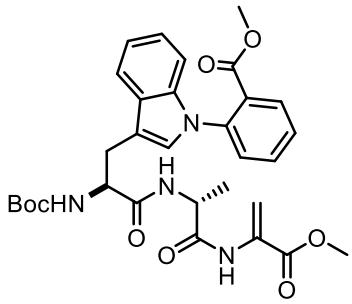
Purification by column chromatography afforded product in 48% yield (52.8 mg, d.r. = 1:1.5) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.8 Hz, 2H), 8.00 – 7.91 (m, 1H), 7.87 (q, *J* = 5.4 Hz, 4H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.57 – 7.45 (m, 5H), 7.42 (t, *J* = 7.8 Hz, 4H), 7.31 (dd, *J* = 10.6, 7.8 Hz, 5H), 7.21 – 7.11 (m, 2H), 7.06 (d, *J* = 9.8 Hz, 2H), 6.80 – 6.53 (m, 1H), 5.87 – 5.68 (m, 1H), 5.60 – 5.34 (m, 2H), 5.27 (d, *J* = 21.6 Hz, 1H), 4.73 – 4.53 (m, 2H), 4.52 – 4.33 (m, 2H), 4.20 (s, 1H), 3.62 (s, 3H),

3.50 (s, 3H), 3.44 (s, 1H), 3.30 (s, 1H), 3.18 (m, 1H), 2.11 – 1.71 (m, 2H), 1.39 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.7, 171.3, 166.3, 166.2, 165.5, 165.2, 155.3, 138.9, 137.5, 133.3, 133.3, 133.1, 133.0, 131.6, 129.8, 129.8, 129.7, 129.6, 128.9, 128.8, 128.4, 128.4, 128.3, 128.3, 127.7, 127.4, 122.8, 120.4, 120.1, 119.2, 118.9, 109.9, 79.8, 70.4, 70.2, 69.8, 62.8, 52.4, 49.4, 31.9, 29.7, 28.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{62}H_{59}N_3NaO_9^+$, 1124.3788, found, 1124.3779.



6a

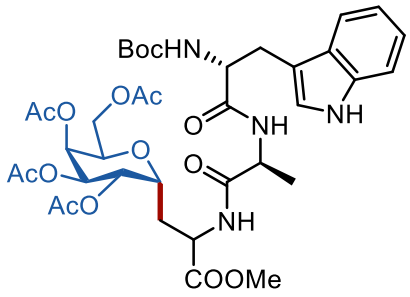
Purification by column chromatography afforded product in 16% yield (7.3mg) as a colorless sticky oil (PE/EA/DCM = 1:2:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 8.22 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.51 (s, 1H), 6.39 (s, 1H), 5.90 (s, 1H), 5.26 (s, 1H), 4.47 (m, 2H), 3.84 (s, 3H), 3.32 (m, 1H), 3.18 (dd, *J* = 14.6, 7.0 Hz, 1H), 1.42 (s, 9H), 1.24 – 1.15 (m, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.0, 170.4, 164.1, 155.5, 136.2, 131.0, 127.4, 123.2, 122.3, 119.8, 118.8, 111.2, 110.5, 109.5, 80.2, 55.0, 53.0, 49.7, 29.7, 28.3, 28.3, 17.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{30}N_4NaO_6^+$, 481.2058, found, 481.2056.



6a'

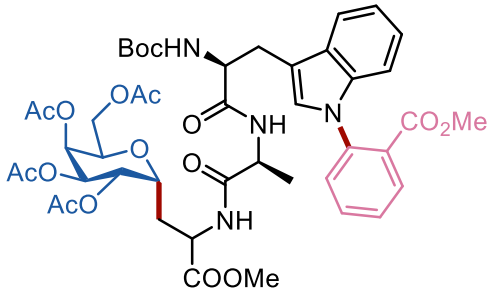
Purification by column chromatography afforded product in 28% yield (116.6 mg) as a colorless sticky oil (PE/EA = 1:2:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.68 (q, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.16 – 7.11 (m, 2H), 7.05 (s, 2H), 6.40 (s, 1H), 6.30 (d, *J* = 6.4 Hz, 1H), 5.79 (s,

1H), 5.38 (s, 1H), 4.52 (s, 1H), 4.38 (s, 1H), 3.82 (s, 3H), 3.52 (s, 3H), 3.45 (s, 1H), 3.17 (m, 1H), 1.43 (s, 9H), 1.27 (d, *J* = 11.8 Hz, 3H) **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.1, 170.3, 164.1, 155.4, 138.8, 137.6, 133.1, 131.5, 131.0, 128.8, 128.3, 128.1, 128.0, 127.8, 122.7, 120.2, 119.2, 111.1, 109.8, 109.2, 80.2, 64.6, 54.9, 52.9, 52.4, 49.8, 28.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{31}H_{36}N_4NaO_8^+$, 615.2425, found, 615.2426.



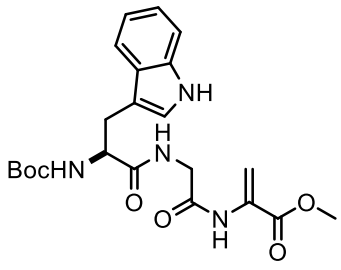
7a

Purification by column chromatography afforded product in 38% yield (30.0 mg, d.r. = 1:1.3) as a colorless sticky oil (DCM/MeOH = 40:1, R_f = 0.3). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 12.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.10 (s, 1H), 6.99 (d, *J* = 9.4 Hz, 1H), 6.17 (d, *J* = 7.4 Hz, 1H), 5.41 (t, *J* = 3.0 Hz, 1H), 5.18 (m, 2H), 5.13 – 5.06 (m, 1H), 4.58 (m, 1H), 4.41 – 4.32 (m, 3H), 4.27 (m, 1H), 4.16 (m, 2H), 3.70 (s, 3H), 3.26 (t, *J* = 6.8 Hz, 2H), 2.17 (m, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 1.87 (m, 1H), 1.40 (s, 9H), 1.20 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.2, 171.9, 171.7, 171.1, 170.0, 169.9, 169.8, 156.1, 136.3, 127.3, 123.3, 122.5, 119.9, 118.9, 111.3, 110.1, 80.9, 69.5, 68.8, 67.9, 67.0, 60.9, 55.5, 52.5, 49.10, 48.90, 28.3, 20.8, 20.8, 20.8, 20.7, 17.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{37}H_{50}N_4NaO_{15}^+$, 813.3165 found, 813.3179.



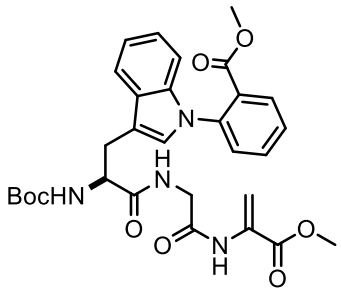
7a'

Purification by column chromatography afforded product in 48% yield (35.1 mg) as a colorless sticky oil (DCM/MeOH = 40:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.63 (m, 2H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.19 – 7.10 (m, 4H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.61 (s, 1H), 5.37 (t, *J* = 3.8 Hz, 1H), 5.29 – 5.13 (m, 2H), 5.08 (dd, *J* = 7.0, 3.8 Hz, 1H), 4.75 – 4.57 (m, 2H), 4.51 (s, 1H), 4.41 (s, 1H), 4.32 (d, *J* = 10.8 Hz, 1H), 4.12 (m, 1H), 3.95 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.71 (s, 3H), 3.52 (s, 3H), 3.42 (s, 1H), 3.24 (d, *J* = 14.4 Hz, 1H), 2.17 (s, 1H), 2.12 (s, 3H), 2.10 (s, 6H), 2.01 – 1.93 (m, 1H), 2.08 (s, 3H), 1.42 (s, 9H), 1.26 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.8, 171.7, 169.8, 169.7, 169.6, 166.3, 138.7, 137.6, 133.0, 131.5, 128.7, 128.5, 128.3, 128.0, 127.8, 122.7, 120.1, 119.3, 111.1, 109.8, 70.4, 68.8, 67.4, 66.6, 59.8, 54.9, 52.5, 52.4, 49.2, 49.1, 29.7, 28.3, 21.1, 20.9, 20.8, 20.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{45}H_{56}N_4NaO_{17}^+$, 947.3533, found, 947.3567.



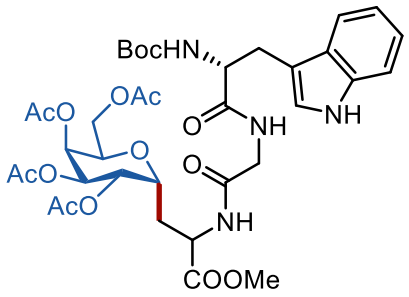
6b

Purification by column chromatography afforded product in 38% yield (16.9 mg) as a colorless sticky oil (DCM/MeOH = 40:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 8.30 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.76 (s, 1H), 6.48 (s, 1H), 5.88 (s, 1H), 5.29 (s, 1H), 4.50 (d, *J* = 7.6 Hz, 1H), 3.85 (d, *J* = 5.6 Hz, 1H), 3.81 (s, 4H), 3.32 – 3.14 (m, 2H), 1.39 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.7, 167.3, 164.1, 155.6, 136.2, 130.7, 127.4, 123.2, 122.3, 119.7, 118.7, 111.2, 110.3, 109.8, 80.3, 55.2, 53.0, 44.1, 29.7, 28.2. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{22}H_{28}N_4NaO_6^+$, 467.1906, found, 467.1902.



6b'

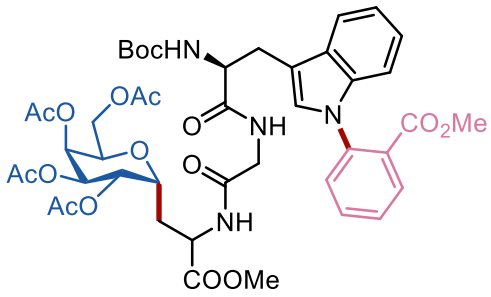
Purification by column chromatography afforded product in 25% yield (14.5 mg) as a white solid (DCM/MeOH = 40:1, R_f = 0.4). mp 65.3 - 65.9 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.28 (s, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.66 (q, *J* = 6.4, 5.2 Hz, 2H), 7.50 (q, *J* = 7.6 Hz, 2H), 7.20 – 7.10 (m, 3H), 7.03 (dd, *J* = 6.6, 2.8 Hz, 1H), 6.50 (t, 1H), 6.44, (s, 1H), 5.82 (s, 1H), 5.62 – 5.48 (m, 1H), 4.51 (s, 1H), 3.88 – 3.82 (m, 1H), 3.80 (s, 3H), 3.63 (t, *J* = 5.8 Hz, 1H), 3.54 (s, 3H), 3.45 (s, 1H), 3.16 (m, 1H), 1.45 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.6, 167.6, 166.0, 164.1, 155.4, 138.8, 137.5, 133.2, 131.5, 130.7, 128.9, 128.3, 127.9, 122.8, 120.2, 119.0, 118.8, 111.4, 109.7, 109.3, 80.0, 52.9, 52.4, 44.3, 41.1, 28.3, 28.2. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{30}H_{34}N_4NaO_8^+$, 601.2269, found, 601.2277.



7b

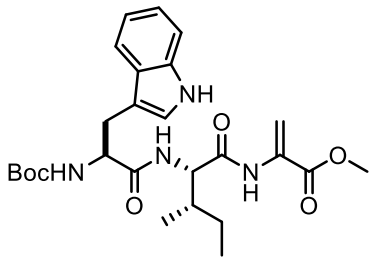
Purification by column chromatography afforded product in 73% yield (56.6 mg, d.r. = 1:1.5) as a white solid (PE/EA/DCM = 1:1:1, R_f = 0.3). mp 101.8 - 102.1 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.16 – 7.07 (m, 2H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.64 (s, 1H), 5.44 – 5.36 (m, 1H), 5.16 (d, *J* = 8.8 Hz, 3H), 4.68 – 4.57 (m, 1H), 4.40 (m, 2H), 4.25 (d, *J* = 11.2 Hz, 1H), 4.19 – 4.02 (m, 2H), 3.87 (t, *J* = 6.2 Hz, 2H), 3.70 (s, 3H), 3.25 (d, *J* = 6.6 Hz, 2H), 2.18 (m, 1H), 2.09 (d, *J* = 4.6 Hz, 6H), 2.06 (d, *J* = 6.0 Hz, 6H), 1.85 (m, 1H), 1.39 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.4, 172.0, 171.2, 169.9, 169.8, 169.0, 156.2, 136.3, 127.3, 123.3, 122.4, 119.8, 119.8,

118.7, 111.4, 110.1, 80.7, 69.6, 68.8, 67.8, 66.9, 60.8, 55.7, 52.5, 49.0, 43.0, 28.3, 20.8, 20.7, 20.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{36}H_{48}N_4NaO_{15}^+$, 799.3008, found, 799.3005.



7b'

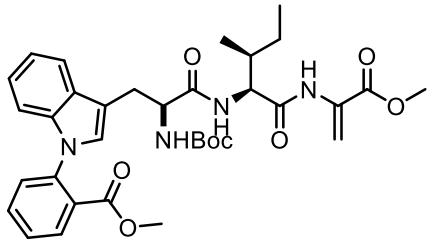
Purification by column chromatography afforded product in 84% yield (76.4 mg, d.r. = 1:1.1) as a white solid (PE/EA/DCM = 1:1:1, R_f = 0.4). mp 96.7 - 97.3 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 2H), 7.56 – 7.47 (m, 2H), 7.21 – 7.14 (m, 2H), 7.13 – 7.04 (m, 3H), 6.56 (t, *J* = 5.8 Hz, 1H), 5.44 – 5.32 (m, 2H), 5.17 (q, *J* = 5.6, 4.0 Hz, 2H), 4.59 – 4.50 (m, 1H), 4.49 – 4.33 (m, 2H), 4.26 (d, *J* = 11.2 Hz, 1H), 4.12 (m, 2H), 3.76 (d, *J* = 10.4 Hz, 2H), 3.67 (s, 3H), 3.56 (s, 3H), 3.32 (s, 1H), 3.23 (m, 1H), 2.21 (d, *J* = 3.4 Hz, 1H), 2.10 (s, 3H), 2.07 (d, *J* = 3.4 Hz, 9H), 1.89 (m, 1H), 1.41 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.3, 171.9, 171.1, 169.9, 169.8, 169.1, 166.0, 156.1, 138.6, 137.6, 133.1, 131.5, 128.8, 128.4, 128.0, 128.0, 127.8, 122.9, 120.3, 119.0 110.8, 109.9, 80.5, 69.7, 68.7, 67.7, 67.1, 66.8, 60.7, 55.8, 52.4, 52.4, 48.9, 43.1, 28.3, 20.8, 20.7, 20.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{44}H_{54}N_4NaO_{17}^+$, 933.3376, found, 933.3380.



6c

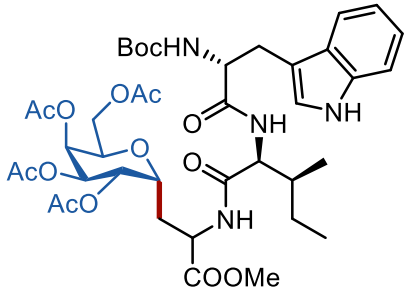
Purification by column chromatography afforded product in 25% yield (12.5 mg) as a white solid (PE/EA/DCM = 1:2:1, R_f = 0.3). mp 68.9 - 69.3 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 8.05 (s, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.32 (s, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.03 (s, 1H), 6.51 (s, 1H), 6.45 (d, *J* = 8.2

Hz, 1H), 5.88 (d, *J* = 4.0 Hz, 1H), 5.24 (d, *J* = 7.4 Hz, 1H), 4.54 – 4.40 (m, 1H), 4.24 (t, *J* = 7.2 Hz, 1H), 3.82 (d, *J* = 7.0 Hz, 3H), 3.33 – 3.23 (m, 1H), 3.18 (dd, *J* = 14.6, 7.4 Hz, 1H), 1.77 (s, 2H), 1.40 (d, *J* = 11.0 Hz, 10H), 0.85 – 0.75 (m, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.4, 171.9, 169.5, 164.2, 155.6, 136.2, 130.6, 127.3, 123.2, 122.2, 119.7, 118.8, 111.2, 109.6, 80.1, 58.6, 57.4, 55.1, 53.0, 36.9, 28.2, 28.2, 24.6, 15.2, 11.6, 11.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{26}H_{36}N_4NaO_6^+$, 523.2526, found, 523.2526.



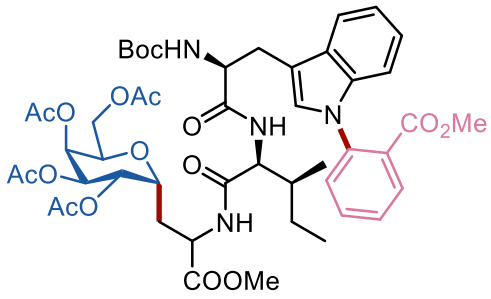
6c'

Purification by column chromatography afforded product in 30% yield (19.0 mg) as a colorless sticky oil (PE/EA/DCM = 1:2:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.66 (m, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.12 (m, 2H), 7.07 (d, *J* = 4.2 Hz, 2H), 6.55 (d, *J* = 8.0 Hz, 1H), 6.44 (s, 1H), 5.81 (s, 1H), 5.31 (s, 1H), 4.52 (s, 1H), 4.22 (s, 1H), 3.85 – 3.71 (m, 3H), 3.53 – 3.44 (m, 3H), 3.39 (d, *J* = 5.4 Hz, 1H), 3.24 (m, 1H), 1.79 (s, 1H), 1.67 (s, 2H), 1.43 (s, 9H), 0.79 (d, *J* = 7.6 Hz, 3H), 0.77 – 0.71 (m, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.9, 169.5, 166.4, 164.1, 163.3, 155.6, 138.6, 137.4, 132.9, 131.4, 130.6, 128.7, 128.5, 128.0, 127.7, 127.6, 122.6, 120.2, 119.2, 109.8, 109.4, 80.2, 65.4, 58.7, 53.0, 52.3, 36.8, 28.3, 28.2, 24.7, 15.1, 11.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{34}H_{42}N_4NaO_8^+$, 657.2895, found, 657.2893.



7c

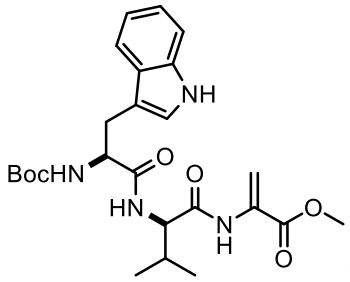
Purification by column chromatography afforded product in 63% yield (52.4 mg, d.r. = 1:1.1) as a colorless sticky oil (PE/EA/DCM = 1:1:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 9.4 Hz, 2H), 6.20 (d, *J* = 7.4 Hz, 1H), 5.41 (t, *J* = 3.0 Hz, 1H), 5.19 (m, 2H), 5.12 (d, *J* = 4.8 Hz, 1H), 4.61 (s, 1H), 4.51 – 4.32 (m, 2H), 4.29 (d, *J* = 11.6 Hz, 1H), 4.26 – 4.23 (m, 1H), 4.22 – 4.12 (m, 2H), 3.69 (s, 3H), 3.34 – 3.20 (m, 2H), 2.25 – 2.14 (m, 1H), 2.14 – 2.07 (m, 9H), 2.05 (s, 3H), 1.89 (m, 2H), 1.72 (s, 2H), 1.40 (s, 9H), 0.84 (t, *J* = 7.0 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.3, 171.7, 171.1, 170.8, 170.1, 169.9, 169.8, 156.3, 136.4, 136.3, 127.2, 123.2, 122.5, 120.0, 118.8, 111.3, 109.9, 81.1, 69.5, 68.8, 67.9, 67.0, 61.0, 58.2, 55.8, 52.3, 48.7, 36.1, 29.7, 28.3, 27.4, 24.2, 20.8, 20.8, 20.7, 15.6, 11.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{40}H_{56}N_4NaO_{15}^+$, 855.3634, found, 855.3635.



7c'

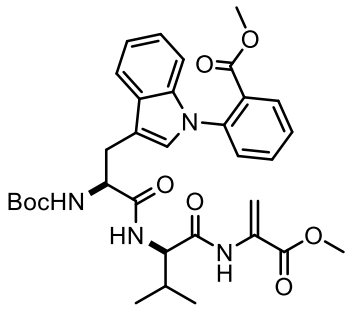
Purification by column chromatography afforded product in 52% yield (50.2 mg, d.r. = 1:1.3) as a colorless sticky oil (PE/EA/DCM = 1:1:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (t, *J* = 6.8 Hz, 1H), 7.74 – 7.63 (m, 2H), 7.50 (t, *J* = 6.8 Hz, 2H), 7.20 – 7.13 (m, 2H), 7.13 – 7.02 (m, 3H), 6.70 (d, *J* = 8.6 Hz, 1H), 5.44 – 5.33 (m, 1H), 5.27 – 5.14 (m, 2H), 5.13 – 5.01 (m, 1H), 4.78 (s, 1H), 4.64 (q, *J* = 6.6 Hz, 1H), 4.50 (d, *J* = 8.0 Hz, 1H), 4.39 – 4.24 (m, 2H), 4.21 – 4.08 (m, 1H), 3.96 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.70 (s, 3H), 3.48 (s, 3H), 3.37 (m, 1H), 3.32 – 3.22 (m, 1H), 2.11 (d, *J* = 4.8 Hz, 9H), 2.08 (s, 3H), 2.04 (s, 2H), 1.95 (s, 1H), 1.72 (s, 2H), 1.41 (s, 9H), 0.79 (t, *J* = 7.4 Hz, 3H), 0.74 (d, *J* = 7.8 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.3, 171.7, 171.7, 170.5, 169.8, 169.6, 169.5, 166.6, 155.7, 138.7, 137.6, 132.9, 131.5, 128.6, 128.0, 127.7, 122.7, 122.6, 120.2, 119.3, 111.2, 109.8, 80.3, 70.7, 68.9,

67.3, 66.4, 59.7, 58.0, 52.5, 52.3, 49.0, 37.1, 29.7, 28.3, 28.2, 24.8, 21.0, 20.9, 20.7, 20.7, 15.1, 11.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{48}H_{62}N_4NaO_{17}^+$, 989.4002, found, 989.3988.



6d

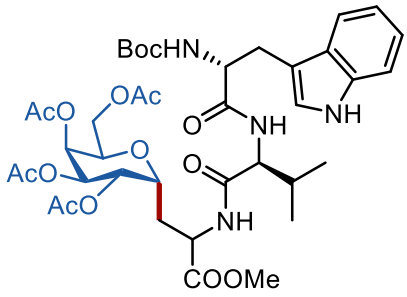
Purification by column chromatography afforded product in 32% yield (15.5 mg) as a white solid (PE/EA/DCM = 1:1:1, R_f = 0.3). mp 60.8 - 61.8 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 8.09 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.04 (s, 1H), 6.64 – 6.45 (m, 2H), 5.90 (s, 1H), 5.27 (d, *J* = 7.2 Hz, 1H), 4.55 – 4.42 (m, 1H), 4.23 (t, *J* = 7.4 Hz, 1H), 3.84 (s, 3H), 3.29 (t, *J* = 10.4 Hz, 1H), 3.20 (dd, *J* = 14.8, 7.0 Hz, 1H), 2.13 – 1.96 (m, 1H), 1.43 (s, 9H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.1, 169.6, 169.6, 164.2, 155.6, 136.2, 130.7, 127.3, 123.2, 122.1, 119.7, 118.7, 111.2, 110.4, 109.7, 80.2, 59.3, 55.2, 53.0, 30.6, 28.2, 19.0, 17.1. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{34}N_4NaO_6^+$, 509.2371, found, 509.2370.



6d'

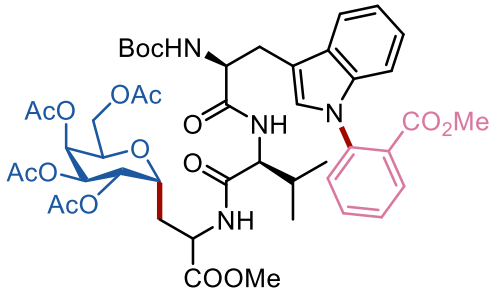
Purification by column chromatography afforded product in 22% yield (13.6 mg) as a white solid (PE/EA/DCM = 1:1:1, R_f = 0.4). mp 92.1 - 92.8 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.72 – 7.59 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.12 (m, 2H), 7.06 (s, 2H), 6.54 (d, *J* = 8.0 Hz, 1H), 6.44 (s, 1H), 5.81 (s, 1H), 5.30 (s, 1H), 4.52 (s, 1H), 4.17 (d, *J* = 8.8 Hz, 1H), 3.82 (s, 3H), 3.48 (d, *J* =

6.6 Hz, 3H), 3.42 – 3.35 (m, 1H), 3.25 (dd, *J* = 14.6, 7.0 Hz, 1H), 2.05 (s, 1H), 1.43 (s, 9H), 0.77 (d, *J* = 7.8 Hz, 6H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.0, 169.5, 166.4, 164.1, 155.6, 138.7, 137.6, 132.9, 131.4, 130.6, 128.7, 128.5, 128.0, 127.6, 122.6, 120.1, 119.2, 109.8, 109.4, 80.2, 59.4, 53.0, 52.3, 30.4, 29.7, 28.3, 28.3, 19.0, 17.8. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{33}H_{40}N_4NaO_8^+$, 643.2738, found, 643.2735.



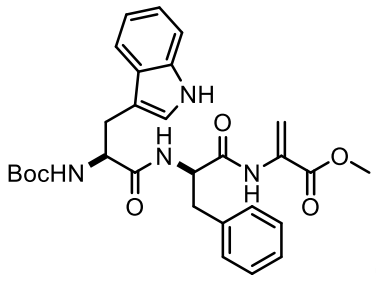
7d

Purification by column chromatography afforded product in 66% yield (54.0 mg, d.r. = 1:2.6) as a white solid (PE/EA/DCM = 1:3:1, R_f = 0.4). mp 112.5 - 113.6 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.12 (dd, *J* = 14.8, 7.4 Hz, 3H), 6.23 (d, *J* = 7.6 Hz, 1H), 5.41 (t, *J* = 3.0 Hz, 1H), 5.20 (m, 3H), 4.62 (d, *J* = 8.2 Hz, 1H), 4.42 – 4.26 (m, 3H), 4.20 (t, *J* = 3.8 Hz, 1H), 4.17 (q, *J* = 4.2 Hz, 2H), 3.69 (s, 3H), 3.28 (d, *J* = 3.0 Hz, 2H), 2.33 – 2.22 (m, 1H), 2.19 (d, *J* = 11.8 Hz, 1H), 2.12 – 2.06 (m, 9H), 2.04 (s, 3H), 1.88 (d, *J* = 13.4 Hz, 1H), 1.40 (s, 9H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.3, 171.8, 171.0, 170.0, 169.9, 169.7, 156.4, 136.4, 127.2, 123.3, 122.4, 119.9, 118.7, 111.3, 109.6, 81.1, 69.3, 68.7, 67.9, 67.1, 61.0, 58.5, 55.8, 52.3, 48.6, 29.4, 28.2, 27.3, 20.8, 20.7, 20.6, 19.1, 16.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{39}H_{54}N_4NaO_{15}^+$, 841.3478, found, 841.3471.



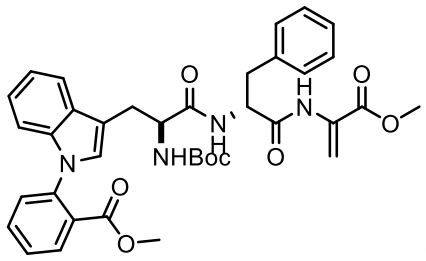
7d'

Purification by column chromatography afforded product in 75% yield (71.4 mg, d.r. = 1:1.3) as a colorless sticky oil (PE/EA/DCM = 1:3:1, R_f = 0.5). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.62 (m, 2H), 7.53 (t, *J* = 8.8 Hz, 2H), 7.15 (q, *J* = 6.8, 5.4 Hz, 3H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.23 (s, 1H), 5.41 (t, *J* = 3.2 Hz, 1H), 5.37 – 5.24 (m, 2H), 5.20 (dd, *J* = 8.2, 3.2 Hz, 1H), 4.65 (t, *J* = 9.0 Hz, 1H), 4.41 – 4.20 (m, 4H), 4.15 (m, 2H), 3.67 (s, 3H), 3.57 (s, 3H), 3.31 (s, 2H), 2.22 (d, *J* = 13.8 Hz, 2H), 2.12 (d, *J* = 8.2 Hz, 9H), 2.03 (s, 3H), 1.92 (m, 1H), 1.40 (s, 9H), 0.95 – 0.36 (m, 6H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.5, 172.0, 171.1, 171.0, 170.1, 170.0, 169.7, 156.6, 138.7, 137.7, 133.1, 131.6, 128.8, 128.1, 128.0, 127.9, 123.0, 120.5, 119.3, 110.2, 109.9, 81.2, 68.6, 67.2, 61.2, 58.6, 55.7, 52.3, 52.2, 48.5, 29.7, 28.3, 20.8, 20.7, 16.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{47}H_{60}N_4NaO_{17}^+$, 975.3846, found, 975.3839.



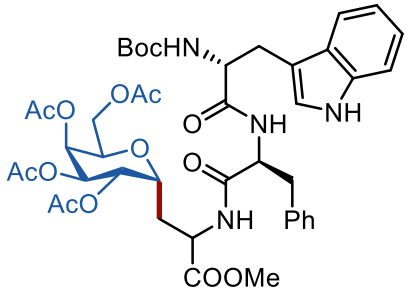
6e

Purification by column chromatography afforded product in 28% yield (15.0 mg) as a colorless sticky oil (PE/EA = 2:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 7.6 Hz, 1H), 8.01 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.20 – 7.11 (m, 5H), 6.97 (s, 1H), 6.92 (s, 2H), 6.47 (s, 1H), 6.35 (d, *J* = 6.4 Hz, 1H), 5.87 (s, 1H), 5.14 (s, 1H), 4.59 (q, *J* = 7.2 Hz, 1H), 4.41 (m, 1H), 3.78 (s, 3H), 3.30 (s, 1H), 3.13 (m, 1H), 2.95 – 2.78 (m, 2H), 1.39 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.9, 169.2, 163.8, 155.4, 136.2, 135.9, 130.7, 129.1, 128.6, 127.3, 127.0, 123.3, 122.3, 119.7, 118.8, 111.3, 110.3, 109.8, 80.1, 55.0, 52.9, 37.6, 28.3, 28.2. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{29}H_{34}N_4NaO_6^+$, 557.2371, found, 557.2375.



6e'

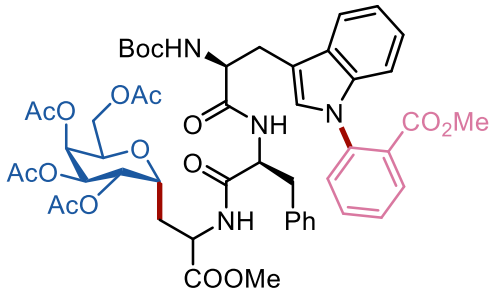
Purification by column chromatography afforded product in 17% yield (11.4 mg) as a white solid (PE/EA = 2:1, R_f = 0.4). mp 70.2 - 72.1 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 – 7.97 (m, 2H), 7.77 – 7.70 (m, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.18 – 7.12 (m, 5H), 7.09 – 7.05 (m, 1H), 7.00 (s, 1H), 6.95 (d, *J* = 6.0 Hz, 2H), 6.41 (d, *J* = 7.4 Hz, 2H), 5.79 (s, 1H), 5.32 (s, 1H), 4.53 (m, 2H), 3.76 (s, 3H), 3.51 (s, 3H), 3.41 (s, 1H), 3.14 (m, 1H), 2.86 (d, *J* = 8.2 Hz, 2H), 1.41 (d, *J* = 6.6 Hz, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.9, 169.1, 166.2, 163.7, 155.3, 138.7, 137.6, 136.1, 133.0, 131.5, 130.7, 129.1, 128.7, 128.6, 128.3, 128.0, 128.0, 127.7, 126.9, 122.7, 120.2, 119.3, 111.0, 109.9, 109.4, 80.1, 55.4, 54.8, 52.8, 52.4, 37.3, 28.2. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{37}H_{40}N_4NaO_8^+$, 691.2738, found, 691.2737.



7e

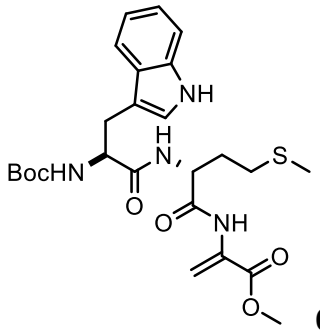
Purification by column chromatography afforded product in 58% yield (50.2 mg, d.r. = 1:1.5) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.12 (m, 5H), 7.04 (s, 1H), 6.97 (d, *J* = 5.8 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.28 (d, *J* = 7.6 Hz, 1H), 5.37 (q, *J* = 6.8, 5.4 Hz, 1H), 5.21 – 5.05 (m, 3H), 4.71 – 4.50 (m, 3H), 4.45 – 4.34 (m, 1H), 4.26 (dd, *J* = 9.4, 5.0 Hz, 1H), 4.09 (m, 1H), 3.95 (dd, *J* = 12.0, 4.2 Hz, 1H), 3.70 (s, 3H), 3.29 – 3.10 (m, 2H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.12 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.01 (d, *J* = 7.8 Hz, 3H), 1.99 – 1.90 (m, 2H), 1.40 (s,

9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.6, 171.4, 171.4, 170.3, 169.9, 169.9, 169.7, 155.3, 136.3, 136.2, 129.2, 128.6, 127.0, 123.4, 119.7, 119.0, 111.3, 110.4, 80.9, 80.9, 80.0, 68.8, 67.5, 66.7, 60.1, 55.1, 54.4, 52.6, 49.0, 41.4, 37.9, 31.9, 29.7, 28.3, 21.0, 20.8, 20.7, 20.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{43}H_{54}N_4NaO_{15}^+$, 889.3478, found, 889.3488.



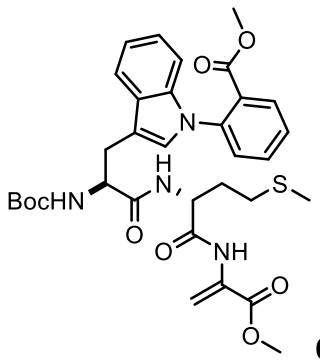
7e'

Purification by column chromatography afforded product in 50% yield (50.0 mg, d.r. = 1:1) as a colorless sticky oil (PE/EA = 1:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.77 – 7.70 (m, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.14 (m, 6H), 7.01 (s, 2H), 6.92 (s, 2H), 6.54 (d, *J* = 7.2 Hz, 1H), 5.36 (t, *J* = 3.8 Hz, 1H), 5.16 (d, *J* = 3.0 Hz, 1H), 5.14 (d, *J* = 3.0 Hz, 1H), 5.11 (s, 1H), 4.68 – 4.57 (m, 2H), 4.55 (dd, *J* = 7.4, 3.4 Hz, 1H), 4.45 (d, *J* = 6.2 Hz, 1H), 4.29 (q, *J* = 4.2 Hz, 1H), 4.09 (m, 1H), 3.98 (dd, *J* = 11.8, 4.4 Hz, 1H), 3.68 (s, 3H), 3.51 (s, 3H), 3.33 (s, 1H), 3.22 – 3.10 (m, 1H), 2.94 (s, 1H), 2.87 (s, 1H), 2.09 (d, *J* = 2.6 Hz, 12H), 2.03 (s, 1H), 1.94 (m, 1H), 1.36 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.6, 171.3, 170.2, 169.9, 169.6, 169.6, 138.6, 137.6, 136.4, 133.0, 131.5, 129.3, 128.6, 128.5, 128.1, 127.7, 126.9, 122.8, 120.2, 119.4, 111.1, 109.9, 80.9, 80.2, 68.6, 67.4, 66.7, 60.1, 54.4, 52.5, 52.4, 49.0, 28.2, 29.7, 21.0, 20.9, 20.8, 20.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{51}H_{60}N_4NaO_{17}^+$, 1023.3846, found, 1023.3855.



6f

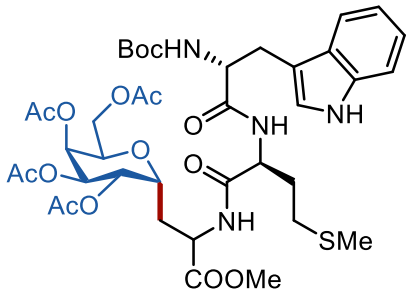
Purification by column chromatography afforded product in 27% yield (14.0 mg) as a colorless sticky oil (PE/EA/DCM = 1:1:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 8.27 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.48 (s, 1H), 5.91 (s, 1H), 5.23 (s, 1H), 4.52 (m, 2H), 3.84 (s, 3H), 3.26 (m, 2H), 2.42 – 2.21 (m, 2H), 1.99 (s, 3H), 1.95 – 1.74 (m, 2H), 1.42 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.2, 169.4, 164.0, 155.5, 136.3, 131.0, 127.3, 123.2, 122.3, 119.8, 118.8, 111.3, 110.3, 109.9, 80.3, 55.2, 53.0, 53.0, 40.1, 30.5, 29.7, 28.3, 28.2, 15.0. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{34}N_4NaO_6S^+$, 541.2091, found, 541.2093.



6f'

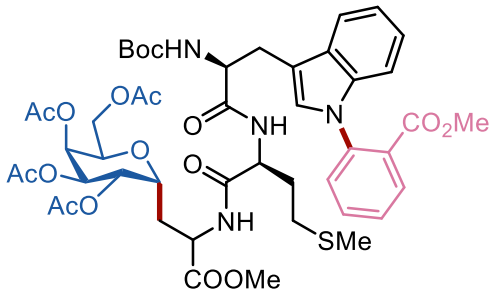
Purification by column chromatography afforded product in 23% yield (15.0 mg) as a colorless sticky oil (PE/EA/DCM = 1:1:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 8.02 (d, *J* = 7.4 Hz, 1H), 7.79 – 7.60 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.14 (dd, *J* = 6.0, 3.4 Hz, 2H), 7.06 (d, *J* = 6.0 Hz, 2H), 6.58 (d, *J* = 7.4 Hz, 1H), 6.39 (s, 1H), 5.82 (d, *J* = 7.2 Hz, 1H), 5.38 (s, 1H), 4.51 (s, 2H), 3.82 (s, 3H), 3.53 (s, 3H), 3.46 (s, 1H), 3.24 – 3.12 (m, 1H), 2.27 (s, 2H), 1.94 (s, 3H), 1.67 (s, 2H), 1.43 (d, *J* = 3.4 Hz, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.2, 169.3, 166.1,

164.0, 155.5, 138.8, 133.0, 131.6, 130.9, 128.8, 128.3, 128.1, 128.0, 127.8, 122.8, 120.2, 119.2, 109.9, 109.6, 80.2, 55.0, 53.1, 53.0, 52.4, 30.2, 29.8, 29.7, 28.3, 28.2, 15.0. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{33}H_{40}N_4NaO_8S^+$, 675.2459, found, 675.2455.



7f

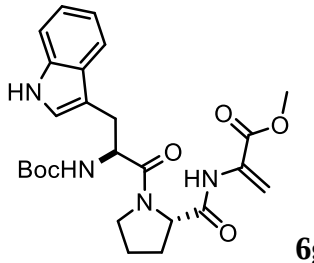
Purification by column chromatography afforded product in 61% yield (51.8 mg, d.r. = 1:1.7) as a colorless sticky oil (PE/EA/DCM = 1:3:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.8 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.17 – 7.09 (m, 2H), 5.41 (t, *J* = 3.2 Hz, 1H), 5.21 (m, 2H), 5.08 (d, *J* = 4.6 Hz, 1H), 4.62 (t, *J* = 8.6 Hz, 1H), 4.50 (q, *J* = 6.2 Hz, 1H), 4.32 (m, 3H), 4.19 (m, 2H), 3.67 (s, 3H), 3.38 – 3.31 (m, 1H), 3.21 (m, 1H), 2.38 (dd, *J* = 9.2, 5.0 Hz, 1H), 2.33 – 2.17 (m, 2H), 2.13 – 2.08 (m, 9H), 2.06 (s, 3H), 1.94 (q, *J* = 12.8 Hz, 2H), 1.79 (s, 3H), 1.70 (dd, *J* = 9.6, 4.8 Hz, 1H), 1.39 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.2, 172.0, 171.0, 171.0, 170.1, 170.0, 169.7, 156.4, 136.5, 127.3, 123.3, 122.6, 120.0, 119.0, 111.4, 109.9, 81.1, 69.4, 68.7, 68.0, 67.1, 61.0, 55.6, 53.5, 52.4, 48.7, 29.6, 28.4, 28.1, 27.4, 20.8, 20.8, 20.8, 20.7, 14.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{39}H_{54}N_4NaO_{15}S^+$, 873.3199, found, 873.3197.



7f'

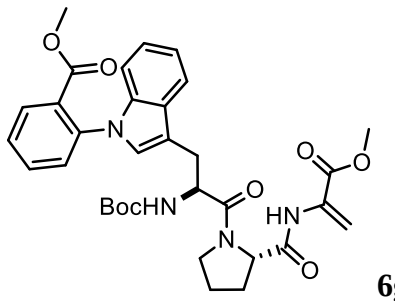
Purification by column chromatography afforded product in 34% yield (33.4mg, d.r. = 1:2) as a colorless sticky oil (PE/EA/DCM = 1:3:1, R_f = 0.4). **^{1}H NMR** (600 MHz, Chloroform-*d*) 8.05 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz,

1H), 7.52 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 4.4 Hz, 1H), 7.14 (d, *J* = 10.2 Hz, 2H), 7.10 (s, 1H), 5.42 (d, *J* = 3.6 Hz, 1H), 5.26 (dd, *J* = 8.4, 4.2 Hz, 1H), 5.21 (dd, *J* = 8.2, 3.0 Hz, 1H), 5.19 – 5.07 (m, 1H), 4.68 – 4.61 (m, 1H), 4.48 (d, *J* = 5.8 Hz, 1H), 4.32 (d, *J* = 6.6 Hz, 2H), 4.25 (dd, *J* = 11.6, 4.4 Hz, 1H), 4.17 (m, 1H), 3.70 (d, *J* = 5.3 Hz, 1H), 3.66 (s, 3H), 3.54 (d, *J* = 7.8 Hz, 1H), 3.47 (s, 2H), 3.32 – 3.13 (m, 2H), 2.24 (t, *J* = 14.0 Hz, 2H), 2.12 (d, *J* = 5.6 Hz, 6H), 2.10 (s, 6H), 2.05 (s, 3H), 1.96 (d, *J* = 13.0 Hz, 2H), 1.84 (s, 2H), 1.40 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.3, 171.1, 171.0, 170.1, 169.6, 156.6, 138.6, 137.7, 133.1, 131.7, 128.6, 127.9, 127.8, 123.0, 120.3, 119.5, 110.3, 110.0, 110.0, 81.0, 69.2, 68.6, 68.0, 67.1, 61.0, 55.3, 53.7, 52.4, 52.3, 48.6, 29.7, 28.4, 28.3, 20.8, 20.8, 20.8, 20.7, 14.1. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{47}H_{60}N_4NaO_{17}S^+$, 1007.3566, found, 1007.3562.



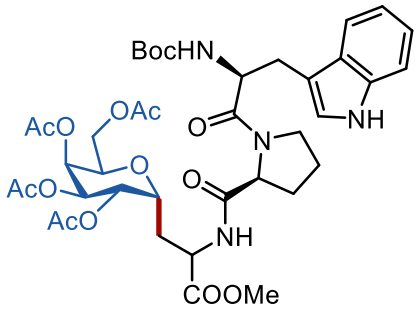
6g

Purification by column chromatography afforded product in 23% yield (11.1 mg) as a colorless sticky oil (PE/EA/DCM = 1:2:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.23 (s, 1H), 8.16 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.56 (s, 1H), 5.92 (s, 1H), 5.47 (d, *J* = 8.6 Hz, 1H), 4.77 (t, *J* = 7.6 Hz, 1H), 4.69 – 4.60 (m, 1H), 3.84 (s, 3H), 3.45 (q, *J* = 8.4 Hz, 1H), 3.19 (d, *J* = 6.8 Hz, 2H), 2.87 (m, 1H), 2.31 (s, 1H), 1.81 (q, *J* = 7.8, 6.4 Hz, 3H), 1.42 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.8, 169.5, 164.1, 155.2, 136.0, 131.5, 127.5, 123.2, 122.0, 119.6, 118.5, 111.1, 109.9, 109.1, 79.6, 60.5, 52.9, 52.4, 47.2, 29.2, 28.3, 26.6, 25.0. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{32}N_4NaO_6^+$, 507.2214, found, 507.2223.



6g'

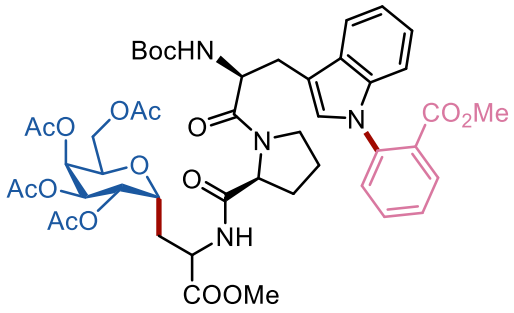
Purification by column chromatography afforded product in 35% yield (21.6 mg) as a colorless sticky oil (PE/EA/DCM=1:2:1, R_f =0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 7.99 (m, 1H), 7.68 (q, *J* = 8.2, 7.6 Hz, 2H), 7.47 (m, 2H), 7.20 – 7.05 (m, 4H), 6.54 (s, 1H), 5.86 (s, 1H), 5.46 – 5.33 (m, 1H), 4.57 (s, 1H), 4.51 – 4.41 (m, 1H), 3.84 (s, 3H), 3.70 – 3.63 (m, 1H), 3.61 (s, 1H), 3.47 (s, 3H), 3.25 (d, *J* = 7.4 Hz, 2H), 1.64 (s, 4H), 1.41 (d, *J* = 8.2 Hz, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.9, 169.4, 164.1, 155.2, 137.3, 132.9, 131.2, 130.9, 128.6, 128.3, 127.8, 127.4, 122.5, 122.5, 120.1, 118.8, 118.7, 110.8, 109.8, 108.9, 79.7, 65.2, 60.6, 52.8, 52.3, 52.1, 47.3, 41.1, 29.7, 28.3, 24.9. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. For $C_{33}H_{38}N_4NaO_8^+$, 641.2582, found, 641.2583.



7g

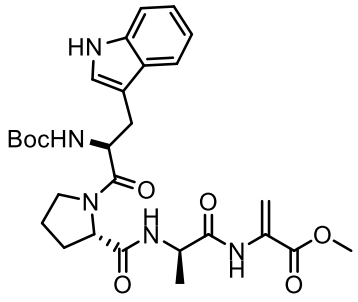
Purification by column chromatography afforded product in 53% yield (43.2 mg, d.r. = 1:1.5) as a colorless sticky oil (PE/EA/DCM = 1:3:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.14 – 7.08 (m, 2H), 5.40 (d, *J* = 4.0 Hz, 1H), 5.31 (d, *J* = 8.0 Hz, 1H), 5.13 (s, 2H), 4.78 (t, *J* = 7.0 Hz, 1H), 4.53 (d, *J* = 7.6 Hz, 2H), 4.38 (d, *J* = 8.4 Hz, 1H), 4.26 (d, *J* = 11.2 Hz, 1H), 4.14 (m, 1H), 4.04 (dd, *J* = 11.8, 4.2 Hz, 1H), 3.74 (s, 3H), 3.52 (q, *J* = 8.0 Hz, 1H), 3.28 (m, 1H), 3.23 – 3.10 (m, 2H), 2.16 – 2.02 (m, 12H), 1.96 (s, 4H), 1.85 (m, 2H), 1.42 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.1, 172.0, 171.4, 171.1, 170.2, 169.9, 169.8, 155.2,

136.1, 127.8, 123.7, 122.0, 119.6, 118.7, 111.3, 109.8, 79.7, 70.3, 69.0, 67.9, 66.8, 60.8, 60.1, 52.8, 52.5, 49.5, 47.5, 28.4, 27.5, 25.1, 20.9, 20.9, 20.6, 20.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{39}H_{52}N_4NaO_{15}^+$, 839.3321, found, 839.3316.



7g'

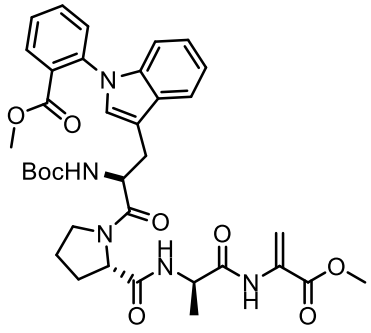
Purification by column chromatography afforded product in 43% yield (40.8 mg, d.r. = 1:2.5) as a colorless sticky oil (PE/EA/DCM = 1:3:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.06 – 7.92 (m, 1H), 7.79 – 7.60 (m, 2H), 7.60 – 7.37 (m, 3H), 7.21 – 7.01 (m, 3H), 5.50 – 5.32 (m, 2H), 5.15 (d, *J* = 13.4 Hz, 2H), 4.85 – 4.71 (m, 1H), 4.68 – 4.52 (m, 2H), 4.47 – 4.25 (m, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 4.07 – 3.95 (m, 1H), 3.70 (s, 3H), 3.63 (d, *J* = 6.0 Hz, 1H), 3.60 (s, 1H), 3.44 (d, *J* = 12.8 Hz, 3H), 3.34 – 3.09 (m, 2H), 2.19 – 2.04 (m, 12H), 2.03 – 1.96 (m, 4H), 1.91 (q, *J* = 11.6, 9.4 Hz, 2H), 1.44 – 1.32 (m, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.3, 171.8, 171.5, 171.3, 169.9, 169.7, 166.9, 155.4, 138.7, 137.4, 132.8, 131.3, 128.6, 128.5, 127.9, 127.3, 122.4, 120.0, 119.4, 119.0, 109.9, 109.8, 79.5, 68.6, 67.6, 66.6, 64.7, 60.3, 60.1, 52.5, 52.2, 49.4, 47.5, 41.4, 29.7, 28.4, 28.3, 25.3, 21.0, 20.9, 20.8, 20.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{47}H_{58}N_4NaO_{17}^+$, 973.3689, found, 973.3685.



6h

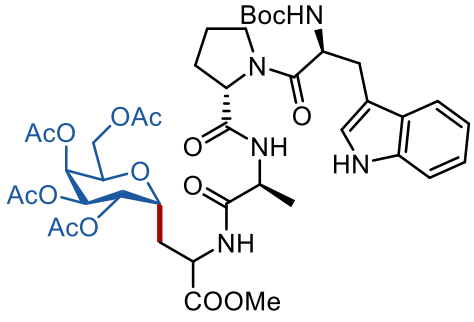
Purification by column chromatography afforded product in 38% yield (21.1 mg) as a colorless sticky oil (PE/EA/DCM=1:2:1, R_f =0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.52 (d, 14.0 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.17 (m, 2H), 7.12 – 6.96 (m, 2H), 6.57 (s, 1H), 5.88 (s, 1H), 5.38 (s, 1H), 4.81 (q, *J* = 7.4 Hz,

1H), 4.55 (dd, *J* = 8.2, 3.6 Hz, 1H), 4.47 (q, *J* = 6.8, 5.8 Hz, 1H), 3.83 (d, *J* = 10.0 Hz, 3H), 3.50 (m, 1H), 3.39 – 3.29 (m, 1H), 3.19 (d, *J* = 7.4 Hz, 2H), 1.98 – 1.73 (m, 4H), 1.40 (s, 9H), 1.28 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.6, 171.1, 164.3, 156.2, 136.1, 131.1, 127.5, 123.4, 122.1, 119.7, 118.6, 111.4, 109.9, 109.7, 80.5, 60.1, 53.0, 52.8, 49.9, 47.5, 28.4, 28.3, 27.9, 25.0, 17.2. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{28}H_{37}N_5NaO_7^+$, 578.2585, found, 578.2590.



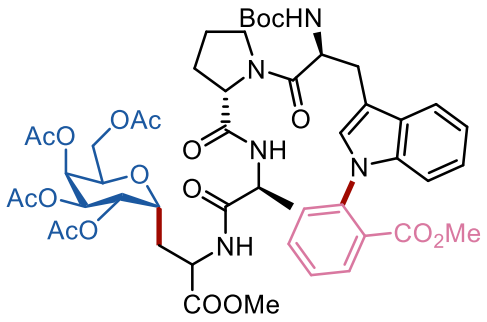
6h'

Purification by column chromatography afforded product in 25% yield (17.2 mg) as a colorless sticky oil (PE/EA/DCM=1:2:1, R_f =0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.72 (s, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.13 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.09 – 6.92 (m, 2H), 6.34 (s, 1H), 5.65 (s, 1H), 5.45 (d, *J* = 8.6 Hz, 1H), 4.85 (q, *J* = 7.6 Hz, 1H), 4.68 (d, *J* = 6.8 Hz, 1H), 4.47 – 4.28 (m, 1H), 3.77 (s, 3H), 3.68 (m, 1H), 3.58 (s, 1H), 3.42 (d, *J* = 4.8 Hz, 3H), 3.26 (s, 2H), 2.35 (d, *J* = 9.0 Hz, 1H), 1.81 (s, 3H), 1.64 (s, 2H), 1.44 (s, 9H), 1.26 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.7, 171.1, 166.3, 164.3, 155.3, 137.4, 133.2, 133.0, 131.4, 131.2, 130.9, 128.9, 128.6, 127.9, 127.7, 122.9, 122.7, 120.2, 119.4, 109.9, 108.9, 79.8, 54.6, 52.9, 52.8, 52.3, 47.6, 29.7, 28.3, 28.3, 25.2, 21.8, 16.9. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{36}H_{43}N_5NaO_9^+$, 712.2953, found, 712.2958.



7h

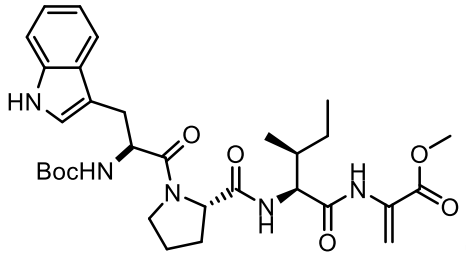
Purification by column chromatography afforded product in 57% yield (50.6 mg, d.r. = 1:4) as a colorless sticky oil (EA, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.63 (s, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.25 – 7.12 (m, 3H), 5.79 (m, 1H), 5.48 – 5.37 (m, 2H), 5.30 – 5.15 (m, 2H), 4.90 (m, 1H), 4.74 – 4.60 (m, 1H), 4.52 – 4.30 (m, 4H), 4.20 (m, 2H), 3.98 (dd, *J* = 11.8, 5.0 Hz, 1H), 3.76 (d, *J* = 8.8 Hz, 3H), 3.68 (m, 1H), 3.22 (m, 2H), 3.01 (d, *J* = 8.8 Hz, 1H), 2.33 – 2.19 (m, 2H), 2.10 (d, *J* = 6.0 Hz, 9H), 2.06 (d, *J* = 4.6 Hz, 3H), 1.88 (dd, *J* = 12.8, 6.4 Hz, 2H), 1.76 (d, *J* = 7.6 Hz, 2H), 1.44 (s, 9H), 1.26 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-d) δ 172.9, 172.5, 172.2, 171.8, 171.5, 171.0, 170.0, 169.8, 155.4, 136.4, 127.4, 123.6, 122.2, 119.7, 118.7, 111.3, 79.8, 69.6, 68.9, 68.1, 67.0, 61.6, 60.7, 60.3, 52.6, 49.1, 48.7, 47.5, 29.7, 28.9, 28.4, 28.3, 25.0, 20.9, 20.8, 20.8, 20.7, 16.9. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{42}H_{57}N_5NaO_{16}^+$, 910.3693, found, 910.3704.



7h'

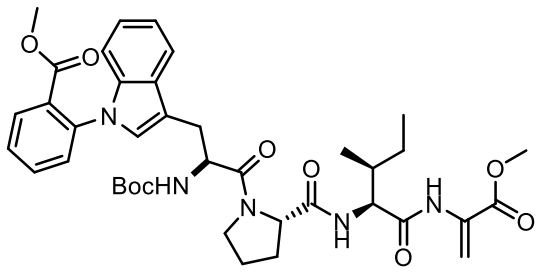
Purification by column chromatography afforded product in 52% yield (53.1 mg, d.r. = 1:2) as a white solid (EA, R_f = 0.4). mp 101.4 - 102.5 ℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.58 (s, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.18 (p, *J* = 7.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.24 (s, 1H), 5.81 (s, 1H), 5.44 (t, *J* = 3.8 Hz, 1H), 5.30 (dd, *J* = 6.4, 3.4 Hz, 1H), 5.25 – 5.09 (m, 2H), 4.66 (m, 1H), 4.44 (d, *J* = 11.0 Hz, 1H), 4.37 – 4.28 (m, 2H), 4.28 – 4.20 (m, 2H), 4.08 (s, 1H), 3.75 (s, 3H), 3.65 (s, 1H), 3.56 (s, 3H), 3.49 (s, 1H), 3.35 (d, *J* = 14.2 Hz, 1H), 3.21 (t, *J* = 12.4 Hz, 1H), 2.48 (s, 1H), 2.38 – 2.16 (m, 2H), 2.14 (d, *J* = 2.4 Hz, 6H), 2.08 (d, *J* = 13.6 Hz, 6H), 1.90 (s, 1H), 1.73 (s, 2H), 1.49 (s, 9H), 1.27 (d, *J* = 12.2 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 174.0, 173.2, 172.2, 171.4, 171.1, 170.1, 170.0, 169.9, 166.8, 155.5, 138.4, 137.8, 133.7, 129.9, 129.2, 128.6, 128.4, 128.0, 126.6, 122.9, 120.6, 119.4,

111.8, 109.4, 79.9, 70.5, 70.0, 68.5, 66.8, 66.2, 63.5, 60.5, 52.3, 52.3, 49.0, 48.6, 47.9, 29.7, 28.4, 25.0, 21.0, 20.9, 20.8, 20.7, 15.8. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{50}H_{63}N_5NaO_{18}^+$, 1044.4060, found, 1044.4072.



6i

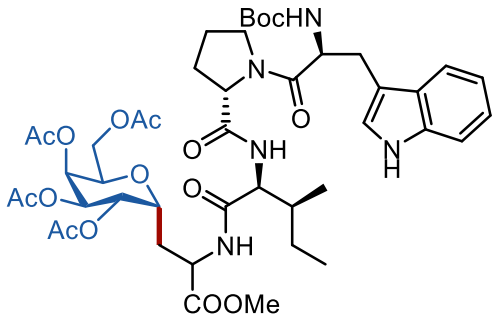
Purification by column chromatography afforded product in 47% yield (28.1 mg) as a colorless sticky oil (PE/EA/DCM=1:2:1, R_f =0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.53 – 8.34 (m, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.02 (m, 4H), 6.63 (s, 1H), 5.93 (s, 1H), 5.38 (m, 1H), 4.80 (q, *J* = 7.4 Hz, 1H), 4.61 (dd, *J* = 7.6, 3.4 Hz, 1H), 4.30 (m, 1H), 3.81 (s, 3H), 3.56 (m, 1H), 3.46 – 3.29 (m, 1H), 3.23 – 2.97 (m, 3H), 2.27 – 2.16 (m, 1H), 2.04 – 1.95 (m, 1H), 1.87 (m, 4H), 1.40 (s, 9H), 0.92 (m, 6H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.7, 171.7, 170.1, 164.3, 155.3, 136.1, 131.4, 130.8, 127.6, 123.4, 122.1, 119.6, 118.5, 111.3, 110.1, 109.6, 79.7, 60.2, 59.1, 54.6, 53.0, 52.8, 47.5, 36.5, 28.3, 28.2, 25.1, 24.7, 15.7, 11.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{31}H_{43}N_5NaO_7^+$, 620.3055, found, 620.3058.



6i'

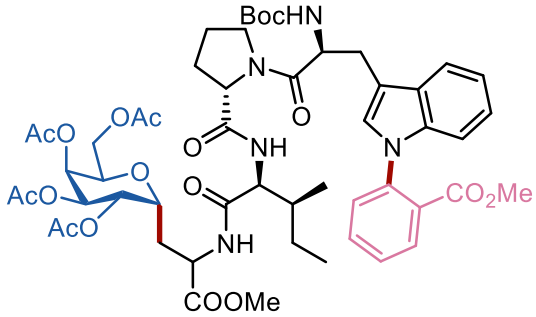
Purification by column chromatography afforded product in 37% yield (27.0 mg) as a colorless sticky oil (PE/EA/DCM=1:2:1, R_f =0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.98 (t, *J* = 7.4 Hz, 1H), 7.68 (m, 2H), 7.50 (q, *J* = 8.2 Hz, 2H), 7.40 (t, *J* = 10.2 Hz, 1H), 7.21 – 7.04 (m, 4H), 6.58 (s, 1H), 5.86 (s, 1H), 5.40 (m, 1H), 4.63 (t, *J* = 4.8 Hz, 1H), 4.37 – 4.22 (m, 1H), 3.77 (m, 4H), 3.67 – 3.55 (m, 2H), 3.45 (s, 3H), 3.35 – 3.12 (m, 3H), 2.35 – 2.06 (m, 1H), 2.05 – 1.84 (m, 3H), 1.43 (s, 2H), 1.38 (d, *J* = 3.0 Hz, 9H), 0.87 (m, 6H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.8, 171.3,

169.9, 166.4, 164.4, 155.3, 138.6, 137.4, 133.2, 131.3, 130.6, 128.6, 128.6, 127.9, 127.5, 122.6, 120.2, 119.4, 109.9, 109.3, 79.7, 59.0, 53.0, 52.2, 47.6, 36.8, 28.3, 28.2, 25.3, 24.8, 21.8, 15.9, 11.2. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{39}H_{49}N_5NaO_9^+$, 754.3422, found, 754.3424.



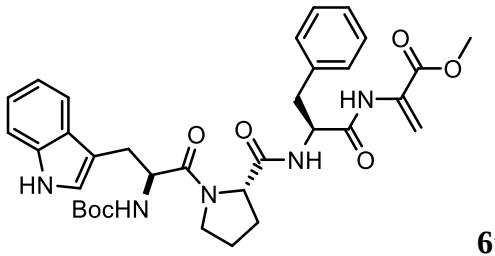
7i

Purification by column chromatography afforded product in 51% yield (47.4 mg, d.r. = 1:2.6) as a colorless sticky oil (PE/EA/DCM = 1:1:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 7.70 (dd, *J* = 11.6, 7.8 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.19 (dd, *J* = 7.8, 4.2 Hz, 1H), 7.15 (d, *J* = 6.6 Hz, 2H), 7.12 – 7.09 (m, 1H), 6.30 (d, *J* = 8.2 Hz, 1H), 5.42 (h, *J* = 5.0 Hz, 2H), 5.28 – 5.23 (m, 1H), 5.22 – 5.16 (m, 1H), 4.87 (q, *J* = 7.6 Hz, 1H), 4.77 – 4.66 (m, 1H), 4.62 (m, 1H), 4.49 – 4.34 (m, 2H), 4.28 (t, *J* = 7.0 Hz, 1H), 4.23 – 4.13 (m, 2H), 3.75 (d, *J* = 11.6 Hz, 3H), 3.69 (s, 1H), 3.66 – 3.50 (m, 1H), 3.31 (m, 1H), 3.23 – 3.06 (m, 3H), 2.31 – 2.17 (m, 2H), 2.11 – 2.07 (m, 12H), 2.04 – 1.91 (m, 5H), 1.41 (s, 9H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 173.2, 172.5, 171.8, 171.4, 171.1, 170.7, 170.0, 169.8, 155.4, 136.2, 127.5, 123.4, 122.3, 119.7, 119.0, 118.6, 111.4, 109.9, 80.8, 80.0, 69.8, 68.9, 68.0, 66.9, 61.4, 60.8, 58.1, 52.6, 49.1, 47.7, 35.7, 29.7, 29.3, 28.8, 28.3, 25.1, 24.6, 20.9, 20.8, 20.8, 20.7, 15.8, 11.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{45}H_{63}N_5NaO_{16}^+$, 952.4162, found, 952.4177.



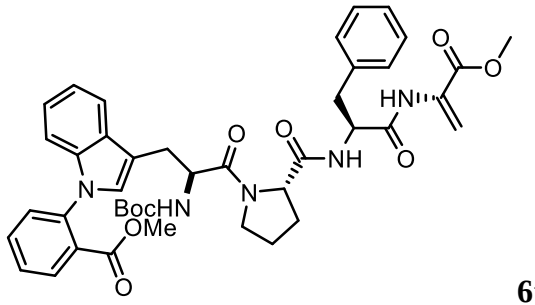
7i'

Purification by column chromatography afforded product in 68% yield (72.3 mg, d.r. = 1:1.2) as a colorless sticky oil (PE/EA/DCM = 1:1:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (m, 1H), 7.76 (s, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.54 (m, 1H), 7.47 (m, 2H), 7.24 (s, 1H), 7.20 – 7.14 (m, 2H), 7.09 (m, 2H), 5.63 – 5.37 (m, 2H), 5.32 – 5.13 (m, 2H), 4.89 (d, *J* = 7.8 Hz, 1H), 4.63 (m, 1H), 4.36 (m, 3H), 4.26 – 4.15 (m, 2H), 4.09 (d, *J* = 7.6 Hz, 1H), 3.73 (s, 3H), 3.67 (d, *J* = 4.2 Hz, 2H), 3.52 (s, 3H), 3.38 – 3.06 (m, 3H), 2.27 – 2.13 (m, 3H), 2.10 (d, *J* = 5.0 Hz, 12H), 2.05 – 1.89 (m, 5H), 1.42 (d, *J* = 13.0 Hz, 9H), 0.95 – 0.74 (m, 6H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 173.4, 172.5, 171.4, 171.0, 170.0, 169.8, 169.7, 166.5, 155.5, 138.5, 137.6, 133.0, 131.2, 128.9, 128.7, 128.2, 127.8, 127.7, 127.3, 122.8, 120.3 111.2, 109.8, 79.8, 69.9, 69.1, 68.0, 66.8, 60.6, 57.8, 53.0, 52.3, 52.2, 48.9, 47.8, 35.9, 29.7, 29.3, 28.3, 28.2, 25.2, 24.5, 20.8, 20.8,, 20.7, 15.7, 11.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{53}H_{69}N_5NaO_{18}^+$, 1086.4530, found, 1086.4528.



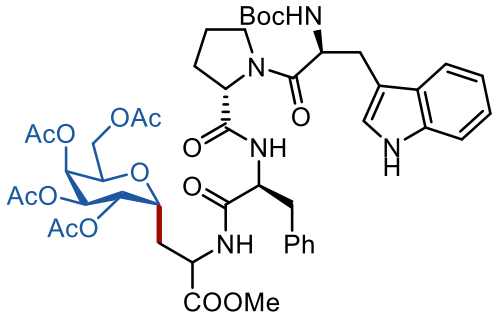
6j

Purification by column chromatography afforded product in 21% yield (13.3 mg) as a colorless sticky oil (PE/EA/DCM=1:2:1, R_f =0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 8.36 – 8.25 (m, 1H), 7.47 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.0 Hz, 2H), 7.14 (m, 4H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.69 (s, 1H), 6.61 (d, *J* = 12.0 Hz, 1H), 5.97 (d, *J* = 6.6 Hz, 1H), 5.86 (s, 1H), 5.27 (m, 1H), 4.58 (m, 1H), 4.52 (q, *J* = 6.8, 5.6 Hz, 1H), 4.38 (m, 1H), 3.83 (s, 3H), 3.59 (m, 1H), 3.46 – 3.27 (m, 1H), 3.14 (m, 2H), 3.07 – 2.93 (m, 1H), 2.88 (m, 1H), 1.84 – 1.61 (m, 4H), 1.43 (d, *J* = 4.6 Hz, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.2, 171.2, 169.9, 164.5, 156.5, 137.6, 136.1, 130.8, 128.9, 128.5, 126.7, 123.5, 122.6, 119.9, 118.9, 111.2, 110.1, 108.9, 80.6, 60.2, 56.7, 54.9, 52.8, 46.6, 36.4, 29.7, 29.5, 28.3, 21.1. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{34}H_{41}N_5NaO_7^+$, 654.2898, found, 654.2915.



6j'

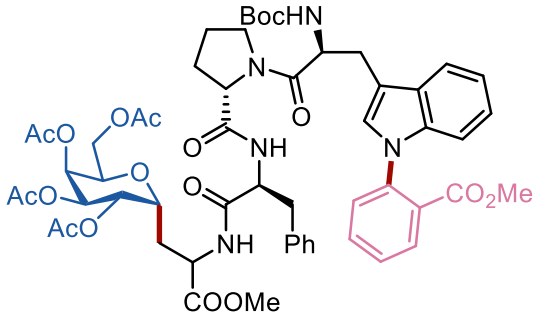
Purification by column chromatography afforded product in 36% yield (27.5 mg) as a colorless sticky oil (PE/EA/DCM=1:2:1, R_f =0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 8.07 (s, 1H), 7.96 (m, 1H), 7.77 – 7.60 (m, 2H), 7.51 (m, 2H), 7.39 (s, 1H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.20 (s, 2H), 7.18 – 7.16 (m, 1H), 7.15 (d, *J* = 4.0 Hz, 1H), 7.11 – 7.07 (m, 1H), 7.05 (t, *J* = 6.4 Hz, 2H), 6.58 (s, 1H), 5.86 (s, 1H), 5.34 (d, *J* = 5.8 Hz, 1H), 4.57 (m, 1H), 4.45 (m, 1H), 3.74 (s, 4H), 3.64 (d, *J* = 8.0 Hz, 1H), 3.54 (s, 3H), 3.42 (m, 2H), 3.30 – 3.15 (m, 2H), 3.03 (t, *J* = 12.8 Hz, 2H), 1.78 (d, *J* = 13.2 Hz, 2H), 1.42 (d, *J* = 6.4 Hz, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.9, 171.3, 170 .0, 164.0, 156.3, 137.4, 133.1, 131.3, 130.8, 129.0, 128.6, 128.6, 127.9, 127.7, 126.7, 122.9, 120.2, 119.2, 109.9, 108.9, 79.8, 60.3, 55.9, 54.6, 52.7, 46.7, 36.6, 29.7, 28.3, 21.2. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{42}H_{47}N_5NaO_9^+$, 788.3266, found, 788.3273.



7j

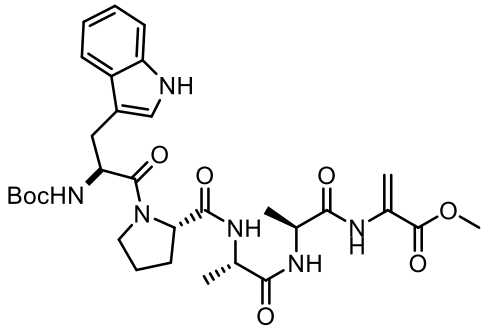
Purification by column chromatography afforded product in 34% yield (32.7 mg, d.r. = 1:1.6) as a colorless sticky oil (PE/EA/DCM = 1:4:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.85 (s, 1H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.26 – 7.18 (m, 4H), 7.12 (dd, *J* = 11.0, 5.6 Hz, 2H), 7.06 (d, *J* = 4.8 Hz, 2H), 6.78 – 6.52 (m, 2H), 5.42 (m, 2H), 5.31 – 5.26 (m, 1H), 5.20 (dd, *J* = 7.8, 3.6 Hz, 1H), 4.94 (m, 1H), 4.71 – 4.62 (m, 1H), 4.55 (q, *J* = 10.0, 7.6 Hz, 1H), 4.39 (m, 1H), 4.35 – 4.23 (m, 2H), 4.18 (t, *J* = 6.2 Hz, 2H), 3.80 (s, 3H), 3.73 (d, *J* = 5.4 Hz, 1H), 3.68 – 3.58 (m, 1H),

3.27 (dd, *J* = 14.0, 5.0 Hz, 1H), 3.21 – 3.11 (m, 3H), 3.08 – 2.78 (m, 2H), 2.42 – 2.31 (m, 1H), 2.29 – 2.19 (m, 1H), 2.11 (d, *J* = 5.6 Hz, 9H), 2.07 (s, 3H), 2.03 (s, 2H), 1.44 (d, *J* = 5.8 Hz, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 173.0, 172.4, 171.5, 171.0, 171.0, 170.0, 169.9, 169.8, 155.3, 136.3, 128.7, 128.5, 127.5, 126.9, 123.9, 122.6, 120.0, 118.7, 111.8, 109.9, 80.8, 80.1, 69.6, 68.7, 67.0, 61.3, 60.8, 53.9, 52.7, 52.0, 49.2, 47.8, 36.3, 29.7, 29.0, 28.4, 28.3, 24.2, 20.9, 20.8, 20.8, 20.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{48}H_{61}N_5NaO_{16}^+$, 986.4006, found, 986.4018.



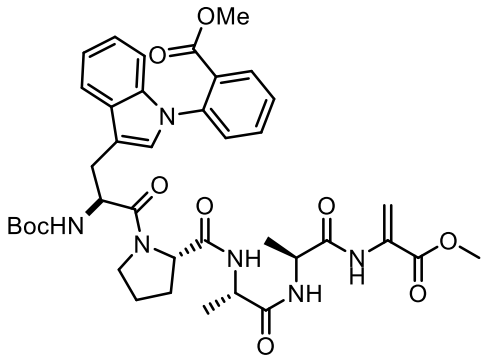
7j'

Purification by column chromatography afforded product in 51% yield (55.9 mg, d.r. = 1:1.2) as a colorless sticky oil (PE/EA/DCM = 1:4:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (m, 1H), 7.87 – 7.77 (m, 1H), 7.67 (q, *J* = 6.6, 5.8 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.49 – 7.44 (m, 2H), 7.21 – 7.15 (m, 5H), 7.11 – 7.05 (m, 2H), 6.93 (s, 1H), 6.33 (d, *J* = 8.6 Hz, 1H), 5.51 – 5.35 (m, 2H), 5.24 (m, 2H), 4.75 (s, 1H), 4.64 (m, 1H), 4.48 – 4.28 (m, 3H), 4.18 (d, *J* = 13.2 Hz, 2H), 4.06 (t, *J* = 12.4 Hz, 1H), 3.73 (s, 3H), 3.62 (m, 4H), 3.44 (s, 1H), 3.32 (s, 2H), 3.22 (t, *J* = 6.8 Hz, 2H), 3.09 (m, 2H), 3.00 (q, *J* = 12.8, 9.8 Hz, 2H), 2.11 (d, *J* = 6.8 Hz, 9H), 2.06 (s, 3H), 1.95 (d, *J* = 10.4 Hz, 2H), 1.41 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.5, 171.0, 170.7, 170.1, 169.9, 169.9, 169.7, 166.5, 155.6, 138.5, 137.7, 133.2, 133.0, 131.2, 129.2, 129.0, 128.9, 128.7, 128.6, 128.5, 128.3, 127.7, 122.8, 120.3, 119.2, 109.8, 79.8, 68.3, 67.9, 66.9, 61.3, 60.6, 54.4, 52.6, 52.4, 52.1, 49.0, 47.7, 29.7, 28.7, 28.4, 28.3, 25.0, 20.9, 20.8, 20.7, 20.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{56}H_{67}N_5NaO_{18}^+$, 1120.4373, found, 1120.4378.



6k

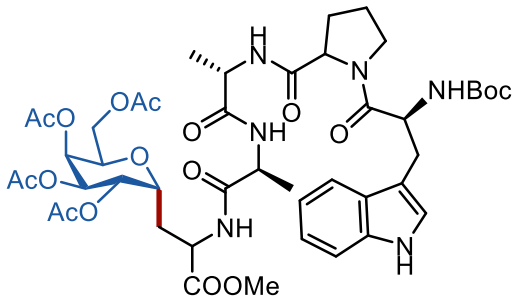
Purification by column chromatography afforded product in 28% yield (17.5 mg) as a colorless sticky oil (DCM/MeOH=30:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.98 (s, 1H), 8.57 (s, 1H), 7.67 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.15 – 7.09 (m, 2H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 3.6 Hz, 1H), 5.92 (d, *J* = 3.6 Hz, 1H), 5.38 (d, *J* = 7.2 Hz, 1H), 4.76 (q, *J* = 7.0 Hz, 1H), 4.61 – 4.44 (m, 3H), 3.83 (s, 3H), 3.45 (m, 1H), 3.20 (t, *J* = 7.6 Hz, 2H), 3.03 – 2.92 (m, 1H), 2.01 (m, 2H), 1.72 (m, 1H), 1.62 (m, 1H), 1.45 (d, *J* = 7.4 Hz, 3H), 1.42 (s, 9H), 1.32 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.9, 172.5, 171.6, 171.1, 164.3, 155.4, 136.3, 131.1, 127.3, 123.6, 122.1, 119.6, 118.5, 111.4, 109.8, 109.5, 80.0, 61.0, 53.5, 52.9, 50.0, 48.9, 47.5, 28.4, 28.3, 25.0, 17.5, 17.1. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{31}H_{42}N_6NaO_8^+$, 649.2956, found, 649.2973.



6k'

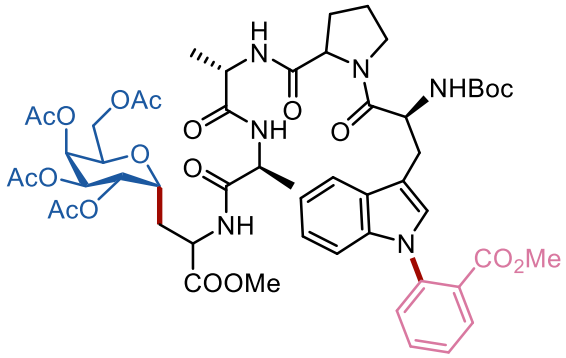
Purification by column chromatography afforded product in 12% yield (9.1 mg) as a colorless sticky oil (DCM/MeOH=30:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 7.99 (m, 1H), 7.69 (m, 2H), 7.60 – 7.37 (m, 3H), 7.17 (m, 2H), 7.09 (m, 2H), 6.54 (s, 1H), 5.91 (s, 1H), 5.36 (s, 1H), 4.83 (s, 1H), 4.59 – 4.51 (m, 1H), 4.49 (d, *J* = 11.2 Hz, 1H), 4.35 (m, 2H), 3.82 (s, 3H), 3.68 – 3.60 (m, 1H), 3.56 (s, 3H), 3.43 (s,

1H), 3.31 (d, *J* = 19.8 Hz, 1H), 3.25 (t, *J* = 7.4 Hz, 1H), 1.84 (s, 4H), 1.55 (d, *J* = 7.0 Hz, 3H), 1.44 (s, 9H), 1.35 – 1.23 (m, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 172.7, 171.5, 171.1, 166.5, 164.1, 155.6, 138.4, 137.6, 133.3, 131.4, 128.9, 128.6, 128.0, 128.0, 127.9, 123.1, 120.5, 120.2, 119.3, 109.9, 109.5, 80.3, 54.7, 52.8, 52.3, 50.1, 49.1, 47.8, 46.8, 28.4, 28.3, 25.2, 17.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{39}H_{48}N_6NaO_{10}^+$, 783.3324, found, 783.3332.



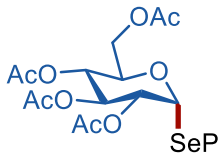
7k

Purification by column chromatography afforded product in 32% yield (30.7 mg, d.r. = 1:1.5) as a colorless sticky oil (DCM/MeOH = 30:1, R_f = 0.3). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.86 – 8.72 (m, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.58 – 7.45 (m, 1H), 7.40 (t, *J* = 7.0 Hz, 1H), 7.22 – 7.15 (m, 3H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.05 (s, 1H), 5.51 – 5.28 (m, 2H), 5.28 – 5.12 (m, 2H), 4.72 – 4.63 (m, 1H), 4.56 (q, *J* = 6.6 Hz, 1H), 4.44 (t, *J* = 7.4 Hz, 1H), 4.36 (m, 2H), 4.22 (d, *J* = 4.5 Hz, 1H), 4.20 – 4.09 (m, 2H), 4.07 – 3.98 (m, 1H), 3.75 (s, 3H), 3.65 (s, 1H), 3.60 (d, *J* = 4.6 Hz, 1H), 3.42 (t, *J* = 10.8 Hz, 1H), 3.24 (d, *J* = 7.6 Hz, 1H), 3.18 (d, *J* = 8.2 Hz, 1H), 3.04 (m, 1H), 2.19 (dd, *J* = 14.4, 4.8 Hz, 2H), 2.09 (d, *J* = 8.6 Hz, 9H), 2.04 (d, *J* = 6.8 Hz, 3H), 1.85 – 1.70 (m, 2H), 1.47 (d, *J* = 9.8 Hz, 3H), 1.41 (d, *J* = 6.0 Hz, 9H), 1.26 (d, *J* = 4.4 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-d) δ 173.1, 172.7, 172.5, 172.1, 171.7, 171.0, 170.1, 169.9, 155.8, 136.4, 127.1, 123.1, 122.4, 119.9, 118.6, 111.6, 109.7, 80.5, 68.7, 68.0, 67.2, 61.9, 61.1, 60.3, 54.9, 52.4, 51.2, 49.6, 49.1, 47.6, 41.4, 29.7, 29.3, 28.4, 28.3, 25.4, 22.5, 22.5, 20.9, 20.8, 20.7, 17.3, 16.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{45}H_{62}N_6NaO_{17}^+$, 981.4064, found, 981.4076.



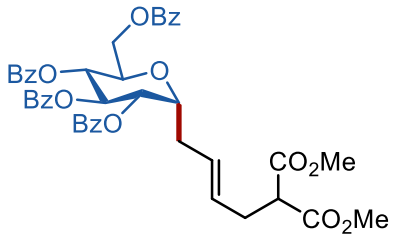
7k'

Purification by column chromatography afforded product in 57% yield (62.2 mg, d.r. = 1:1.5) as a colorless sticky oil (DCM/MeOH = 30:1, R_f = 0.4). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.80 (s, 1H), 7.68 (dd, *J* = 13.4, 10.6 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.19 (q, *J* = 7.4, 5.8 Hz, 3H), 7.06 (d, *J* = 7.4 Hz, 2H), 6.82 (s, 1H), 5.38 (s, 1H), 5.26 – 5.14 (m, 2H), 4.57 (d, *J* = 11.0 Hz, 2H), 4.46 (dd, *J* = 7.0, 6.8 Hz, 1H), 4.38 (t, *J* = 8.0 Hz, 1H), 4.28 – 4.11 (m, 5H), 4.01 (t, *J* = 7.0 Hz, 1H), 3.74 (s, 3H), 3.59 (s, 3H), 3.40 (s, 2H), 3.25 (m, 2H), 2.09 (s, 9H), 2.04 (s, 3H), 2.02 (s, 4H), 1.92 (s, 2H), 1.57 (d, *J* = 7.4 Hz, 3H), 1.46 (s, 9H), 1.26 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 173.0, 172.9, 172.3, 171.0, 170.2, 170.0, 169.9, 155.7, 137.7, 133.5, 128.7, 128.2, 127.9, 123.2, 120.7, 109.8, 80.3, 68.8, 68.6, 68.1, 67.4, 67.2, 61.2, 52.4, 52.3, 49.4, 48.6, 47.9, 29.7, 28.8, 28.4, 28.4, 27.2, 20.9, 20.8, 20.7, 17.6, 16.0. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{53}H_{68}N_6NaO_{19}^+$, 1115.4431, found, 1115.4426.



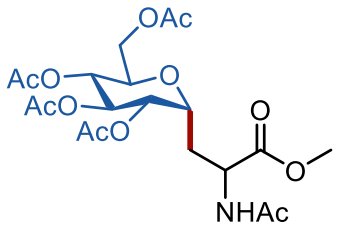
8

Purification by column chromatography afforded product in 56% yield as a white solid (PE/EA = 3:1, R_f = 0.3). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.38 – 7.33 (m, 1H), 7.32 – 7.29 (m, 2H), 5.20 (t, *J* = 9.3 Hz, 1H), 5.01 (ddd, *J* = 14.9, 10.1, 9.3 Hz, 2H), 4.90 (d, *J* = 10.2 Hz, 1H), 4.25 – 4.13 (m, 2H), 3.70 (ddd, *J* = 10.1, 4.8, 2.6 Hz, 1H), 2.07 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H).



9

Compound **9** is known in the literature[5]. The crude yield was determined to be 13% by ^{1}H NMR spectroscopic analysis.



10

Purification by column chromatography afforded product in 49% yield as Colorless oil (PE/EA = 1:1, R_f = 0.3).[7] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.39 (d, J = 6.9 Hz, 1H), 5.28 – 5.19 (m, 1H), 5.02 (dd, J = 9.1, 5.7 Hz, 1H), 4.99 (t, J = 8.6 Hz, 1H), 4.70 (td, J = 7.6, 3.9 Hz, 1H), 4.41 – 4.37 (m, 1H), 4.35 (dd, J = 12.2, 4.6 Hz, 1H), 4.04 – 4.00 (m, 1H), 3.99 (tt, J = 4.7, 2.3 Hz, 1H), 3.78 (s, 3H), 2.29 (ddd, J = 15.1, 11.3, 4.0 Hz, 1H), 2.15 – 2.12 (m, 1H), 2.11 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.04 (s, 6H).

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NMR Spectra

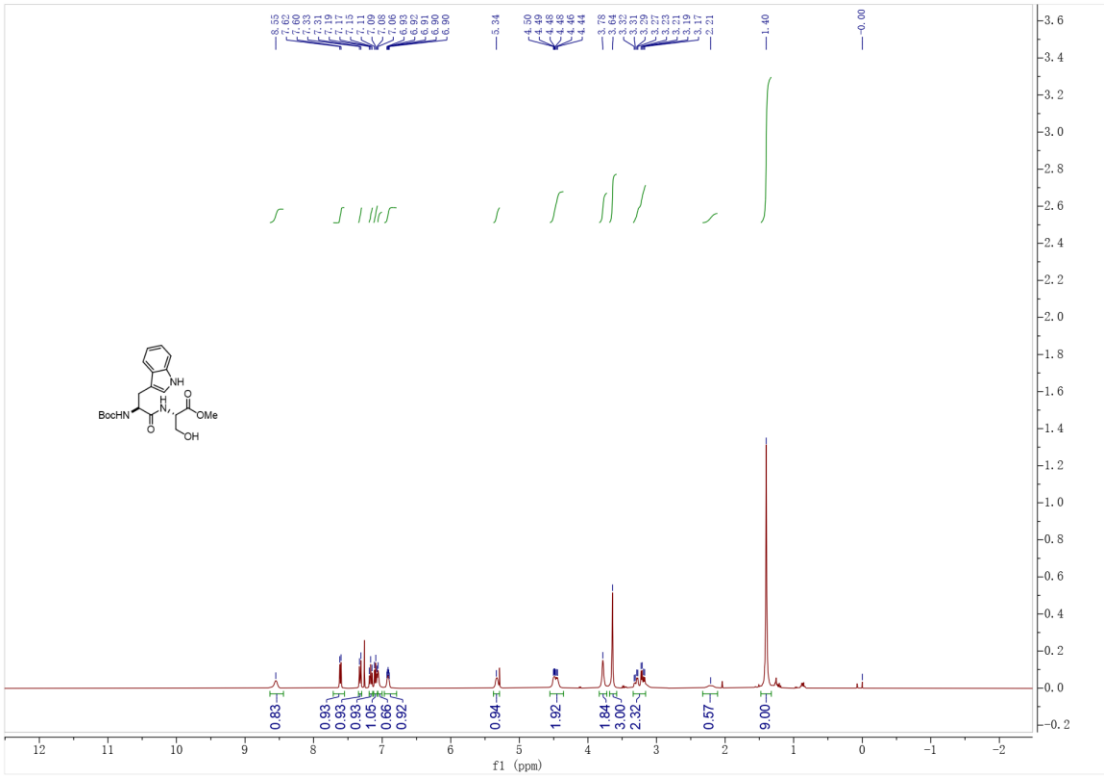

Fig 1. ^{1}H NMR of (**1a**) (400 MHz, $CDCl_3$)

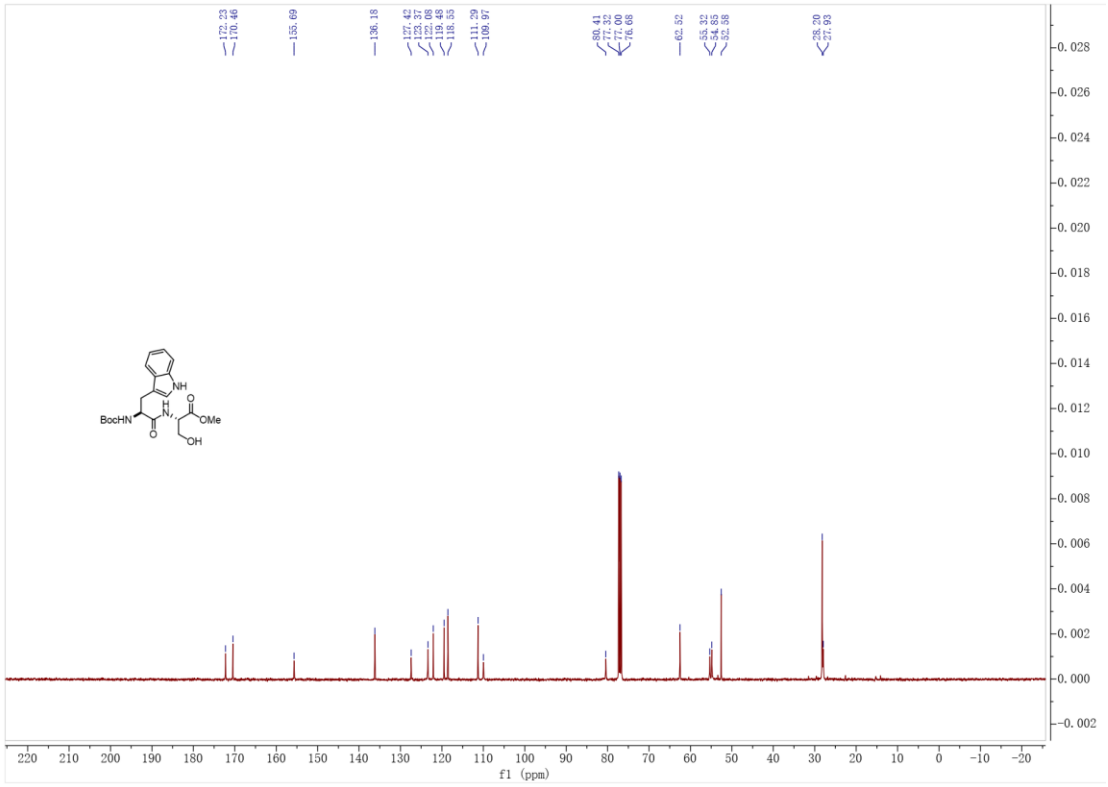

Fig 2. ^{13}C NMR of (**1a**) (100 MHz, $CDCl_3$)

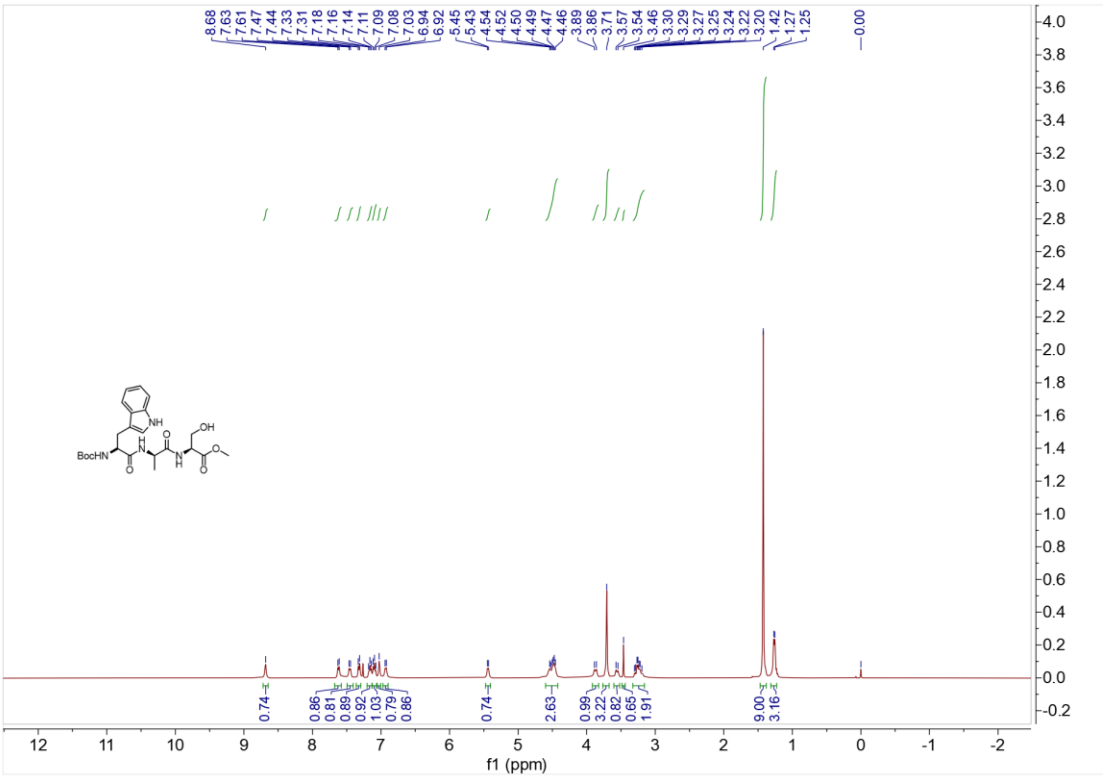

Fig 3. ^{1}H NMR of (**SM-1**) (400 MHz, $CDCl_3$)

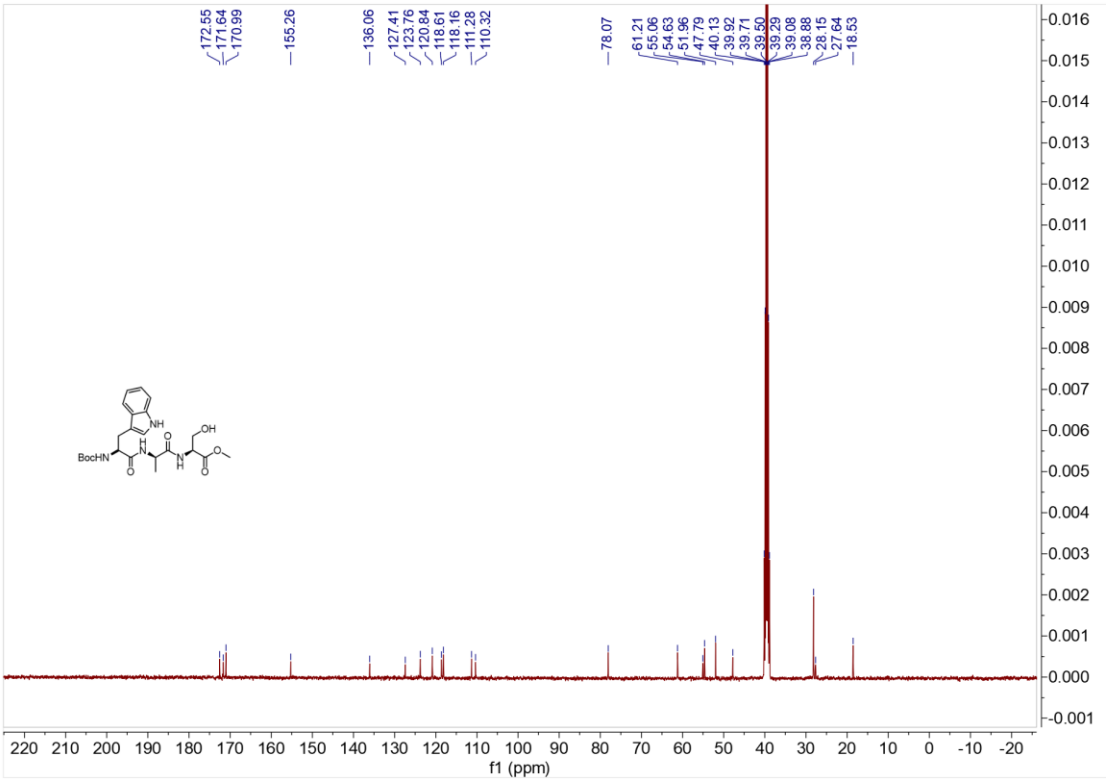

Fig 4. ^{13}C NMR of (**SM-1**) (100 MHz, DMSO-d_6)

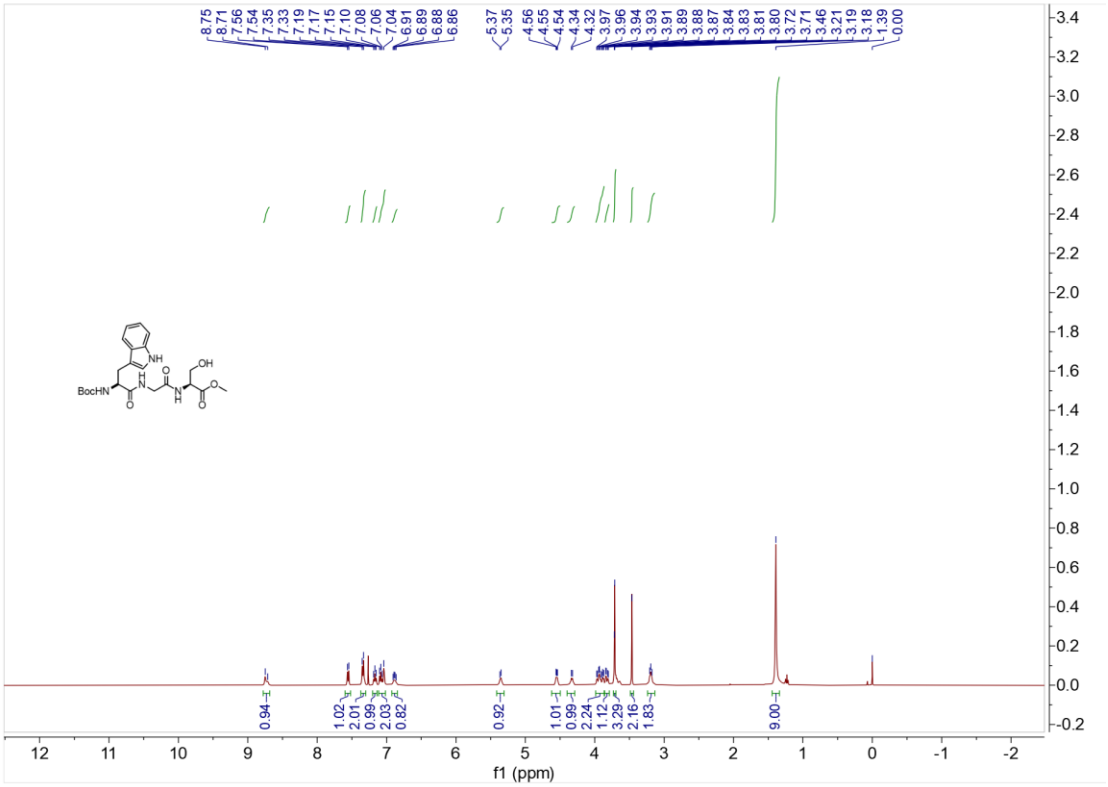

Fig 5. ^{1}H NMR of (**SM-2**) (400 MHz, $CDCl_3$)

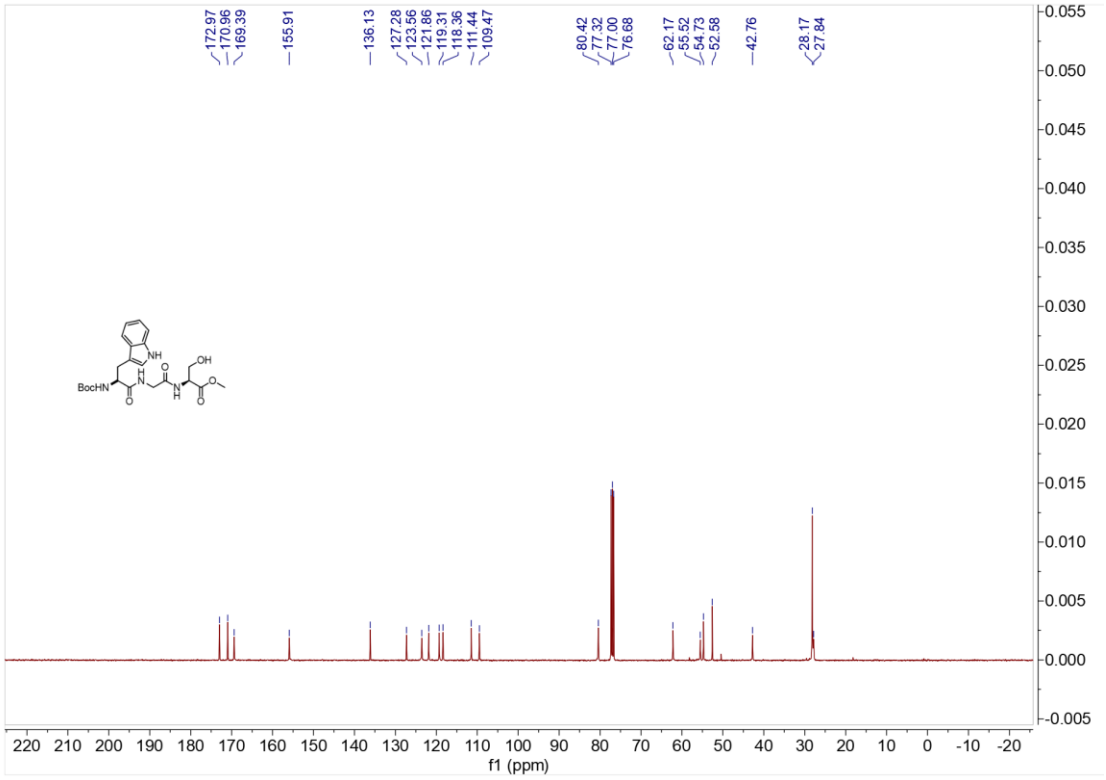

Fig 6. ^{13}C NMR of (**SM-2**) (100 MHz, $CDCl_3$)

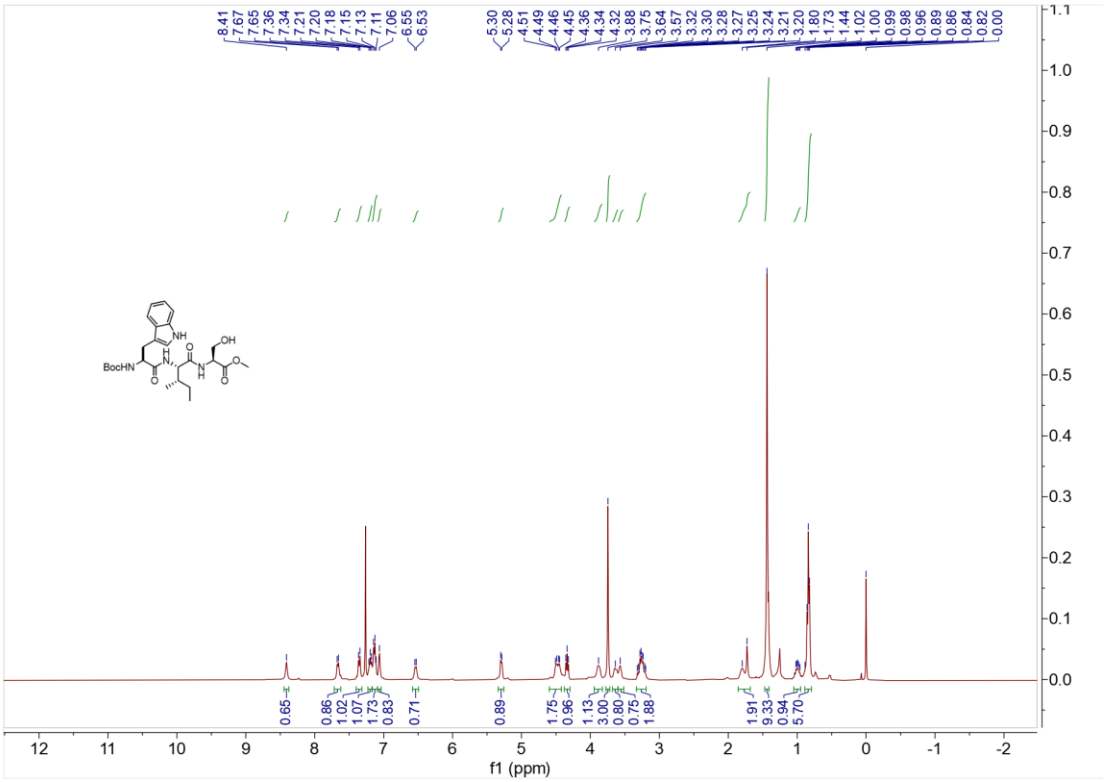

Fig 7. ^{1}H NMR of (**SM-3**) (400 MHz, $CDCl_3$)

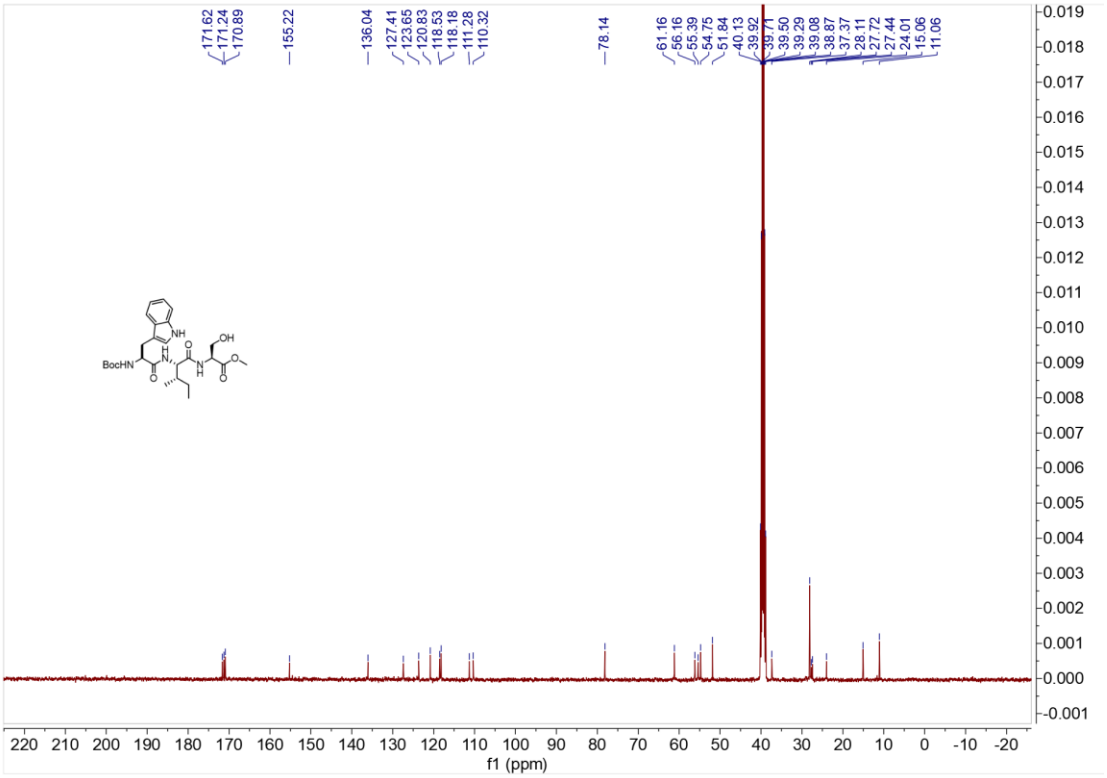

Fig 8. ^{13}C NMR of (**SM-3**) (100 MHz, DMSO-d_6)

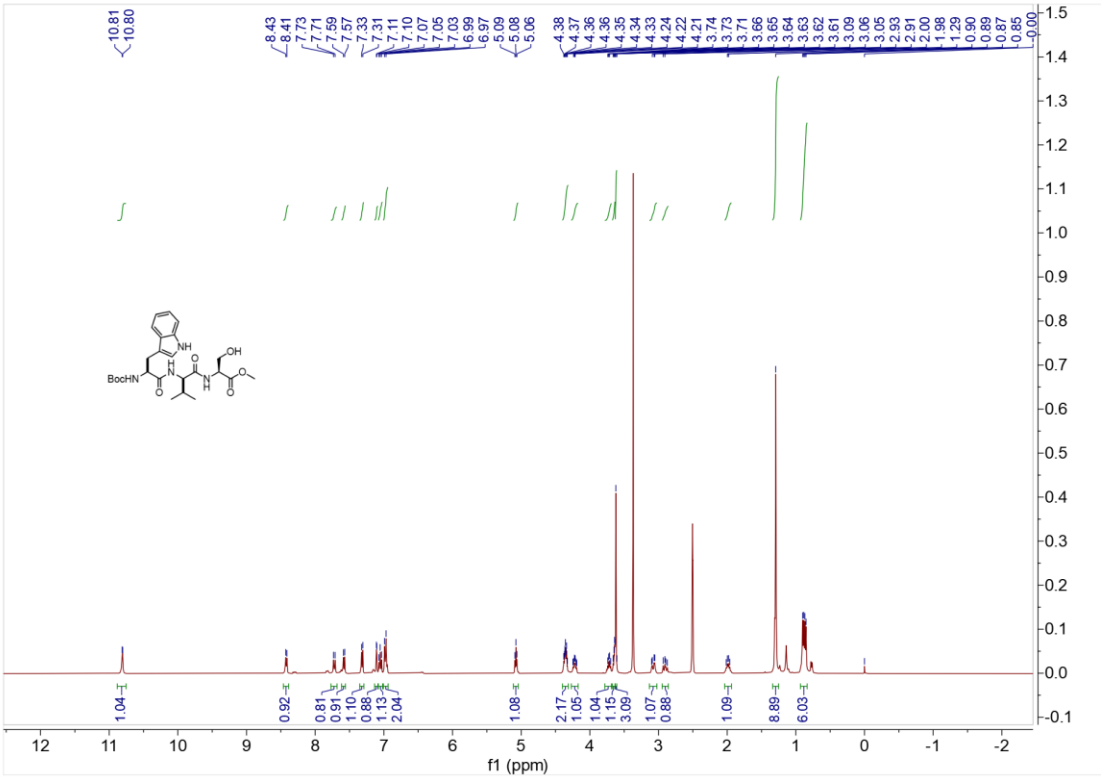

Fig 9. ^{1}H NMR of (**SM-4**) (400 MHz, DMSO-d_6)

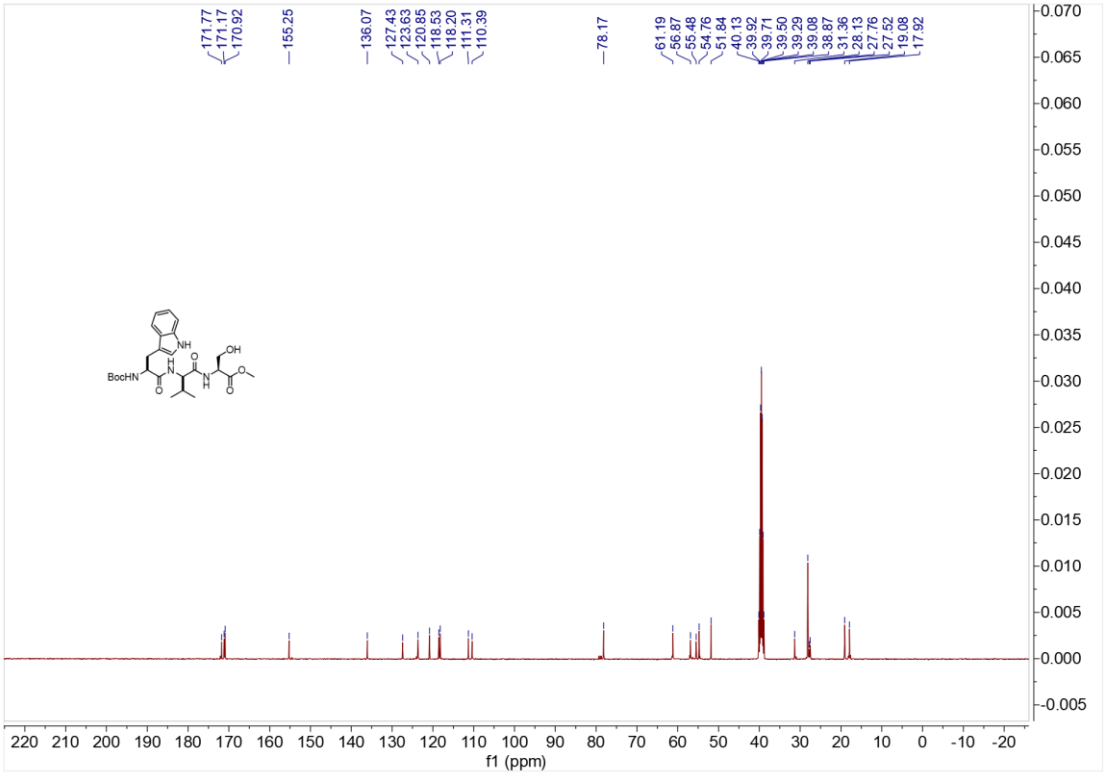

Fig 10. ^{13}C NMR of (**SM-4**) (100 MHz, DMSO-d_6)

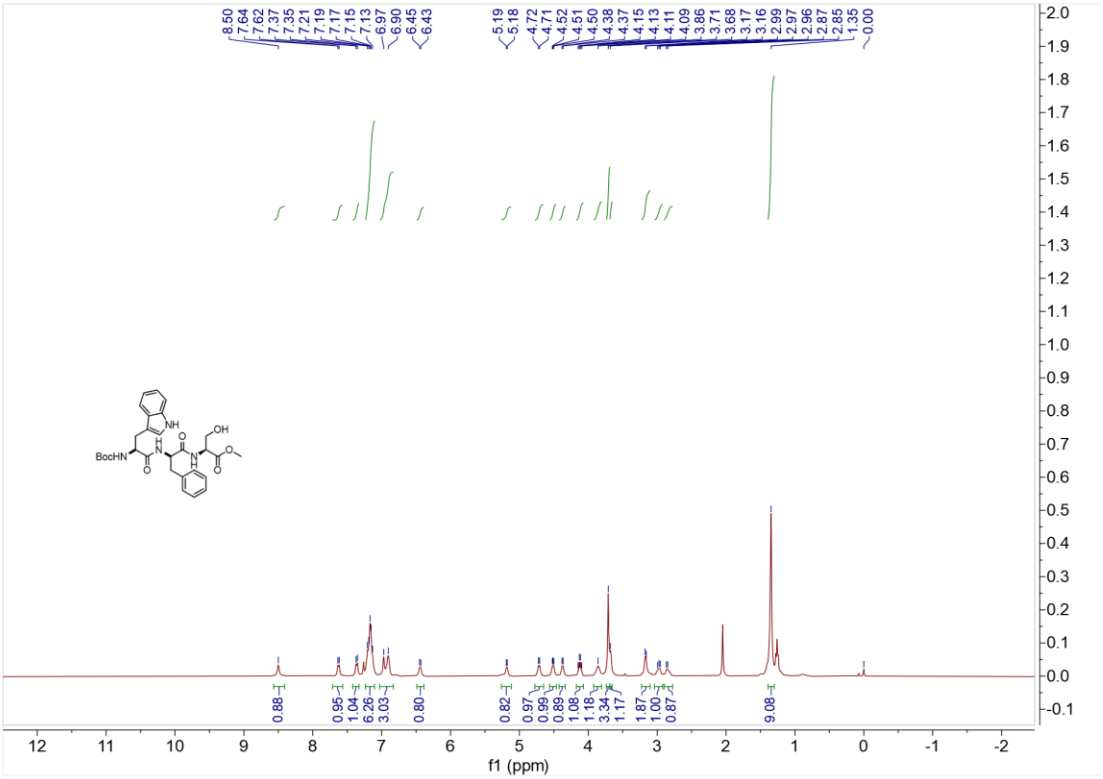

Fig 11. ^{1}H NMR of (**SM-5**) (400 MHz, $CDCl_3$)

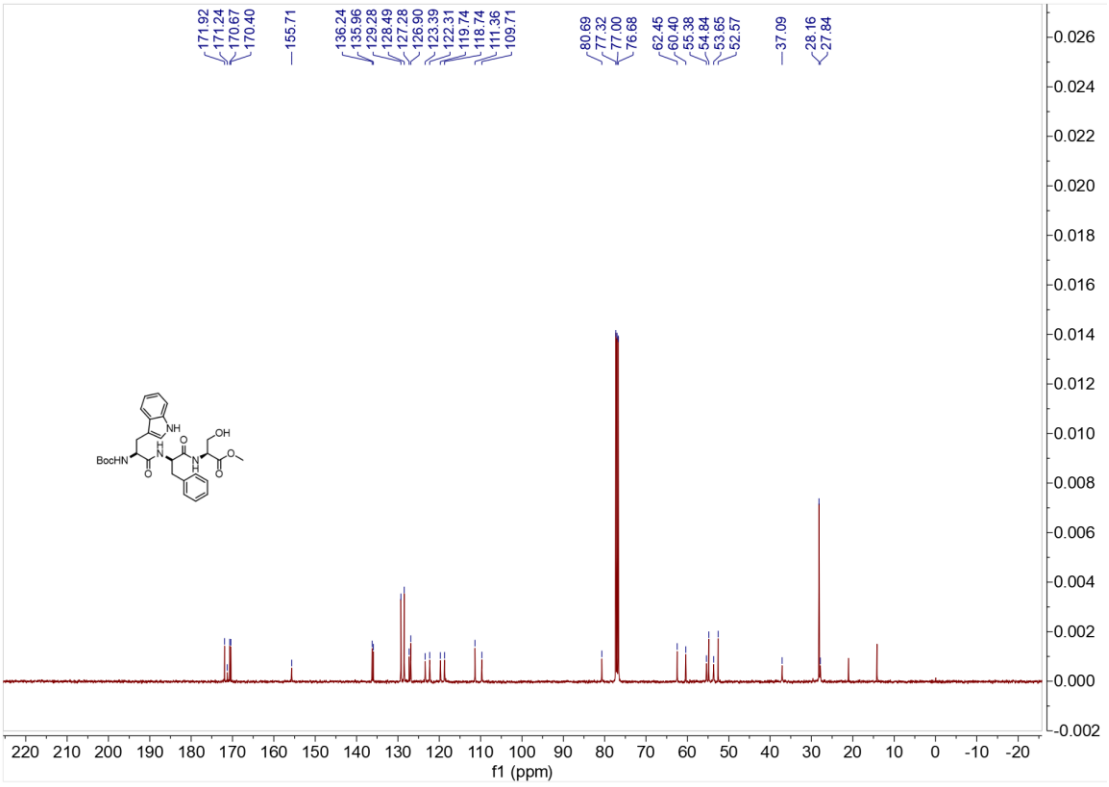

Fig 12. ^{13}C NMR of (**SM-5**) (100 MHz, $CDCl_3$)

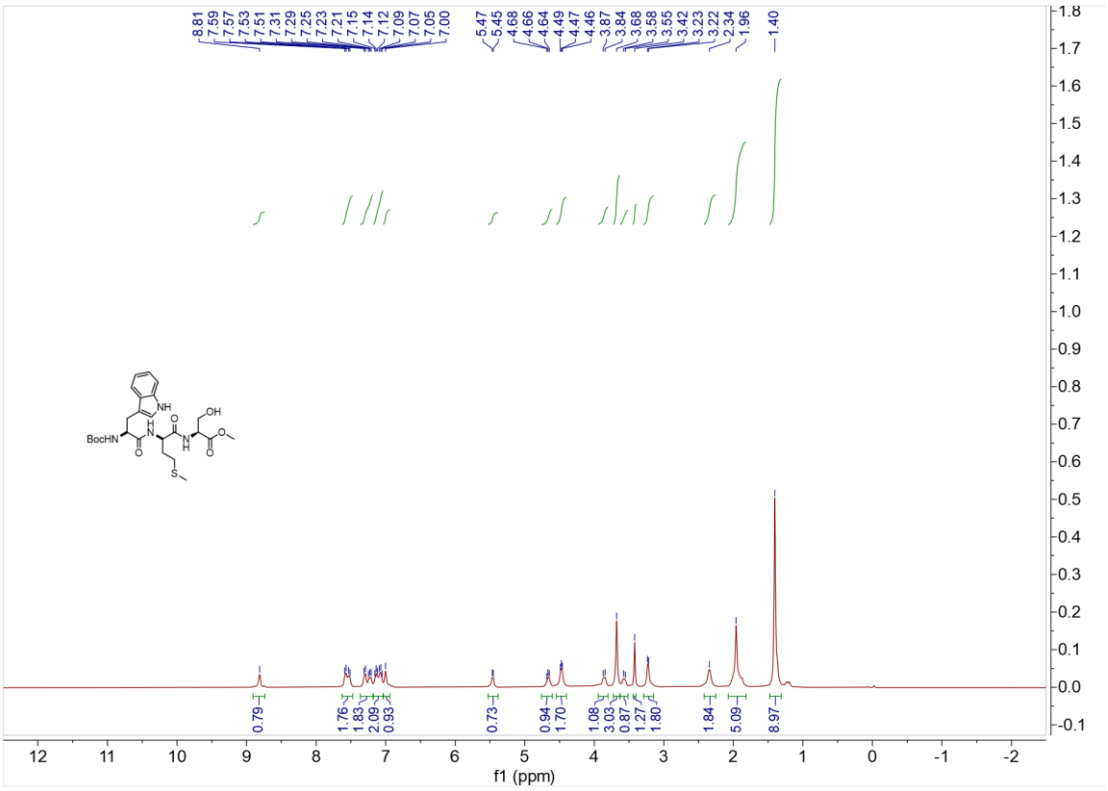

Fig 13. ^{1}H NMR of (**SM-6**) (400 MHz, $CDCl_3$)

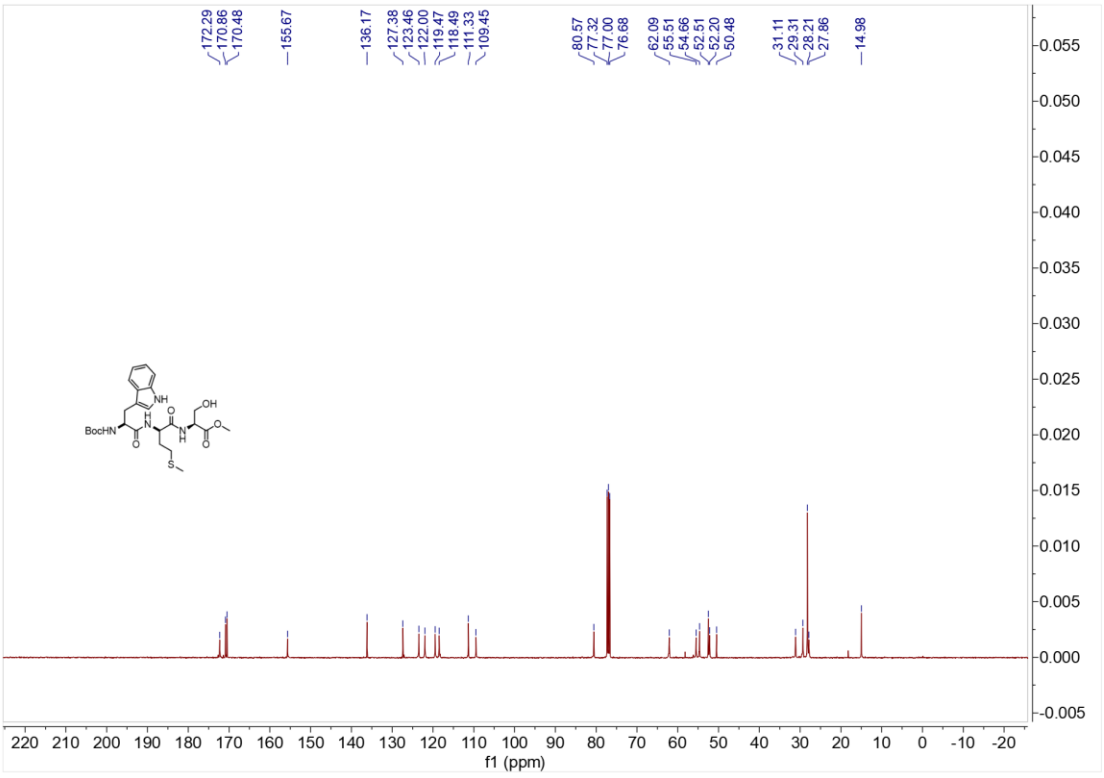

Fig 14. ^{13}C NMR of (**SM-6**) (100 MHz, $CDCl_3$)

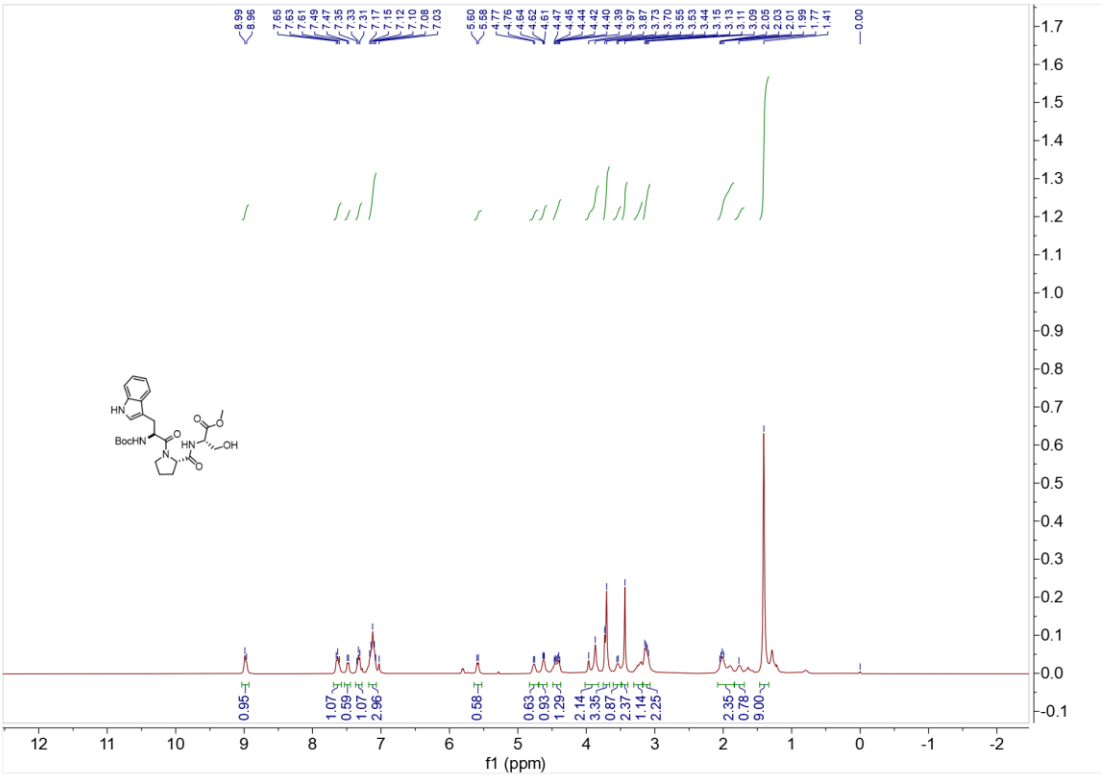

Fig 15. ^{1}H NMR of (**SM-7**) (400 MHz, $CDCl_3$)

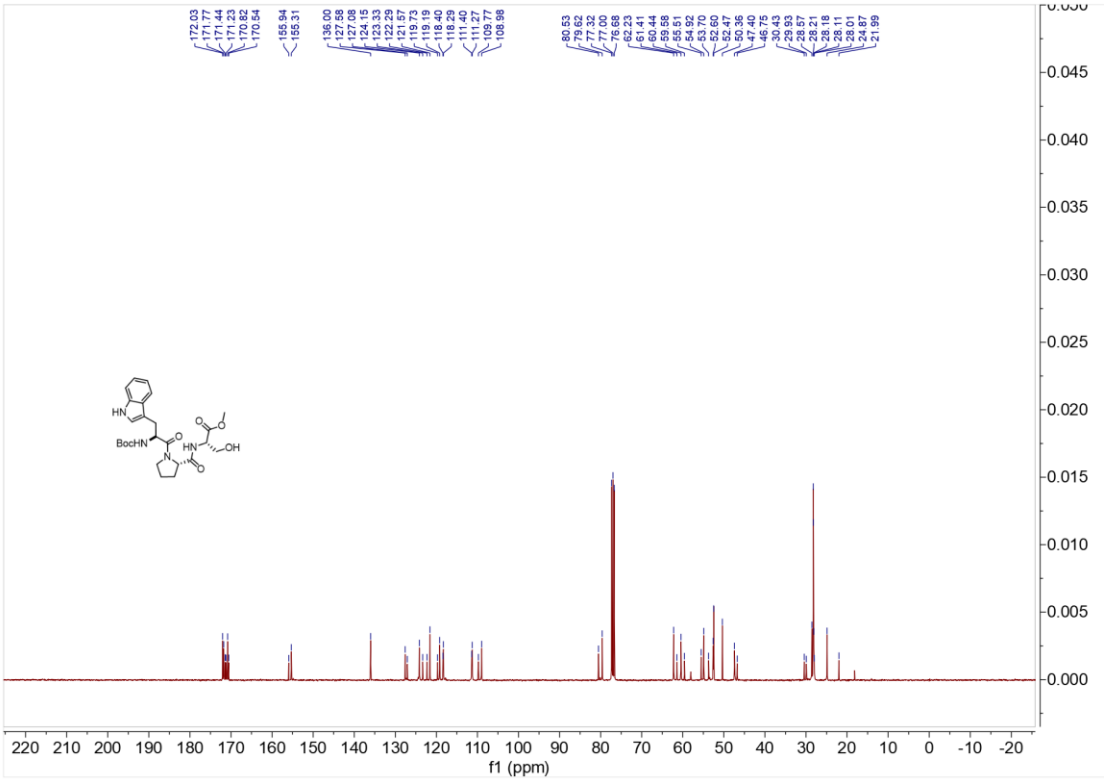

Fig 16. ^{13}C NMR of (**SM-7**) (100 MHz, $CDCl_3$)

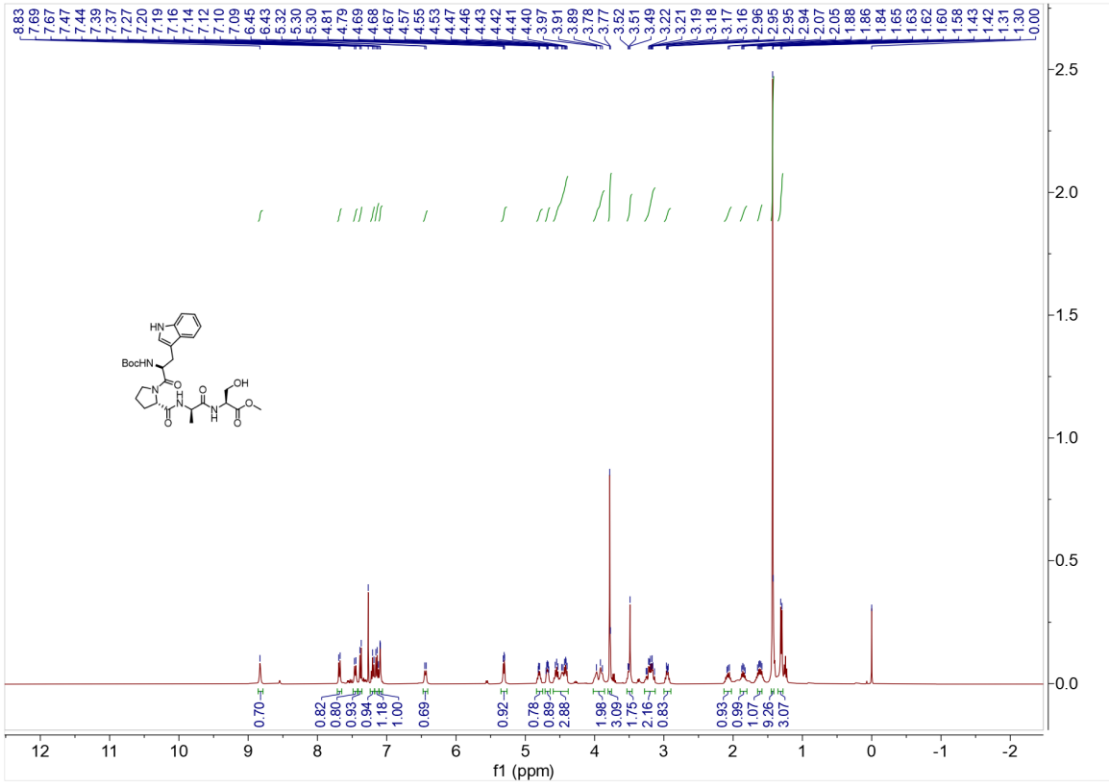

Fig 17. ^{1}H NMR of (**SM-8**) (400 MHz, $CDCl_3$)

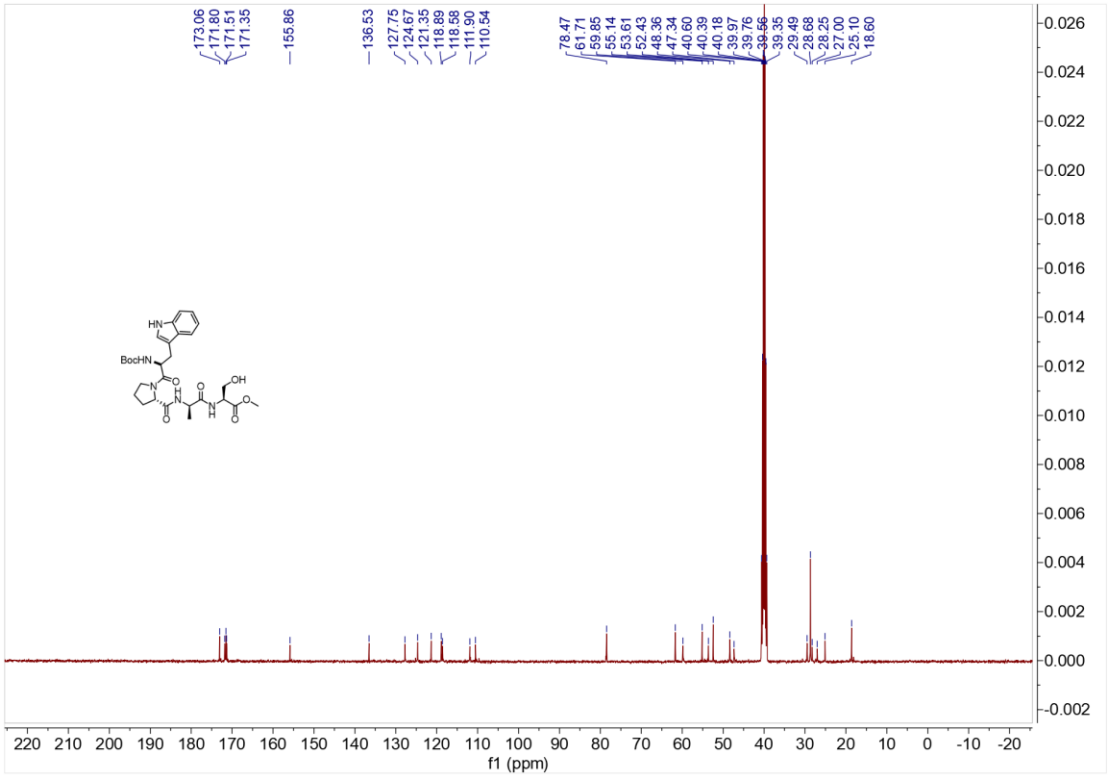

Fig 18. ^{13}C NMR of (**SM-8**) (100 MHz, DMSO-d_6)

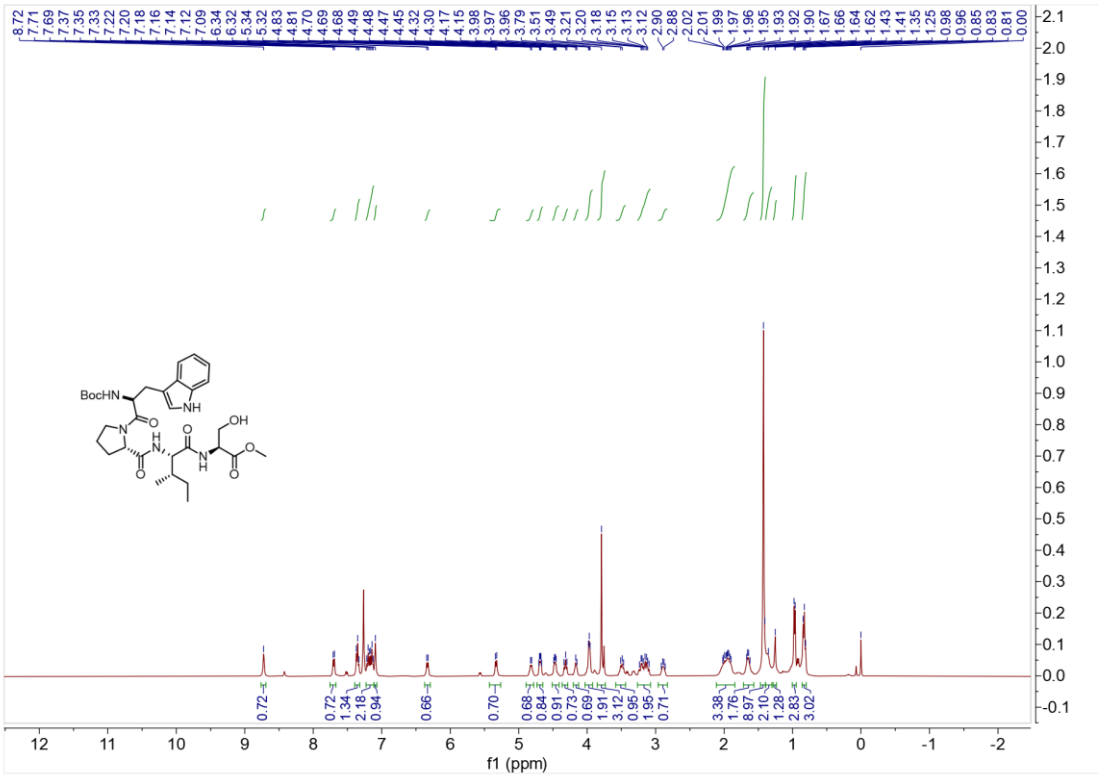

Fig 19. ^{1}H NMR of (**SM-9**) (400 MHz, $CDCl_3$)

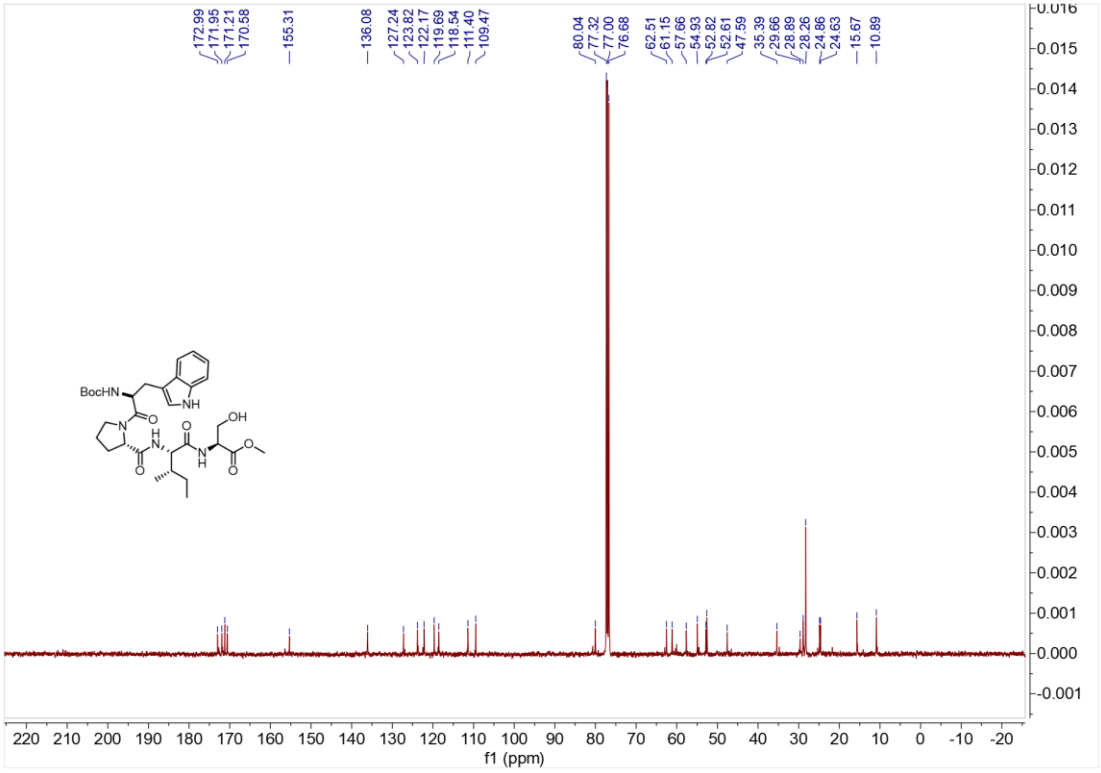

Fig 20. ^{13}C NMR of (**SM-9**) (100 MHz, $CDCl_3$)

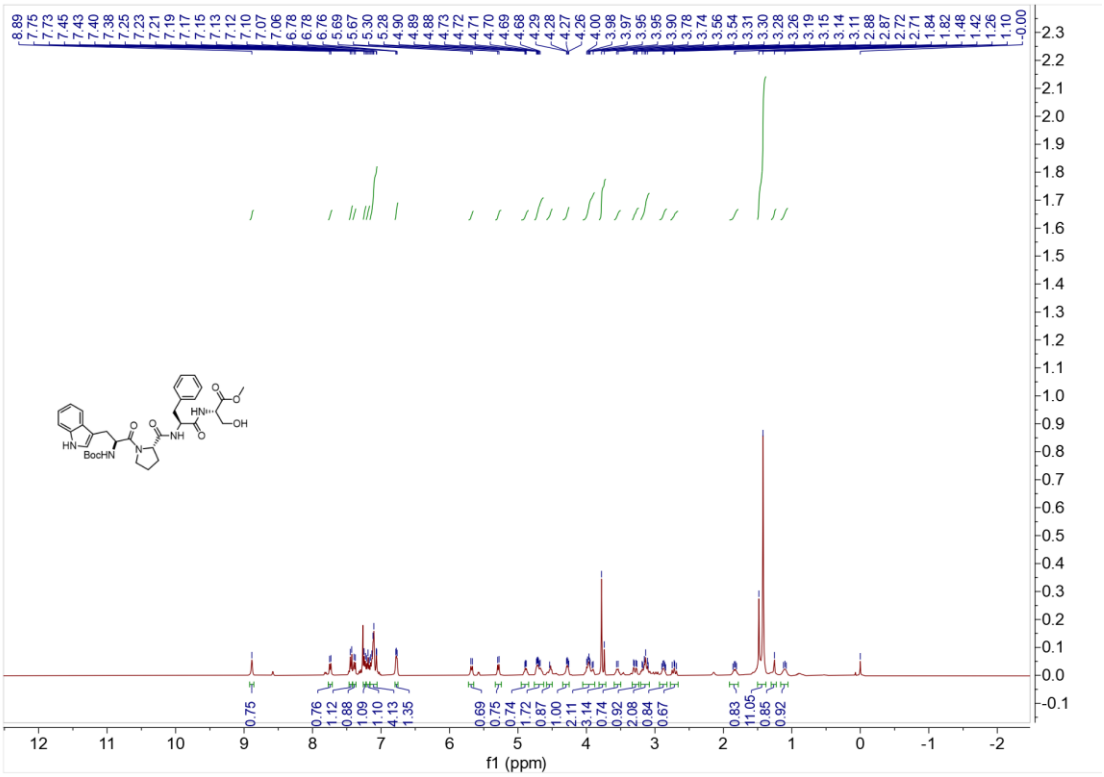

Fig 21. ^{1}H NMR of (**SM-10**) (400 MHz, $CDCl_3$)

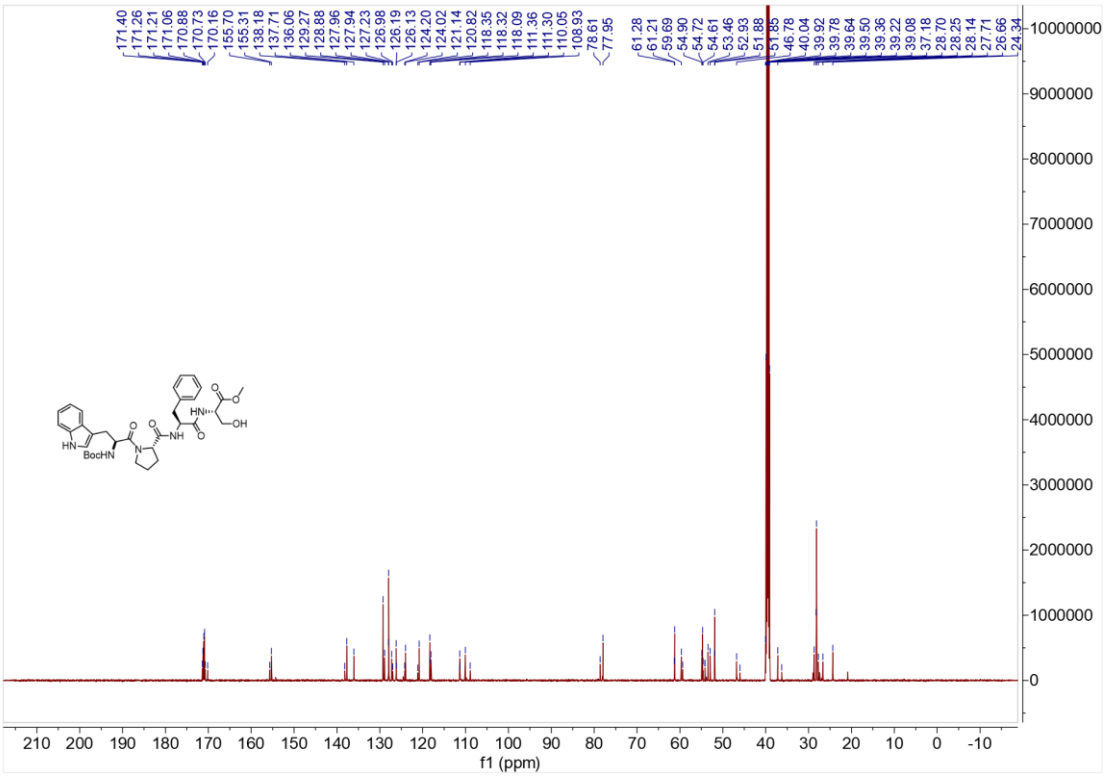

Fig 22. ^{13}C NMR of (**SM-10**) (150 MHz, DMSO-d_6)

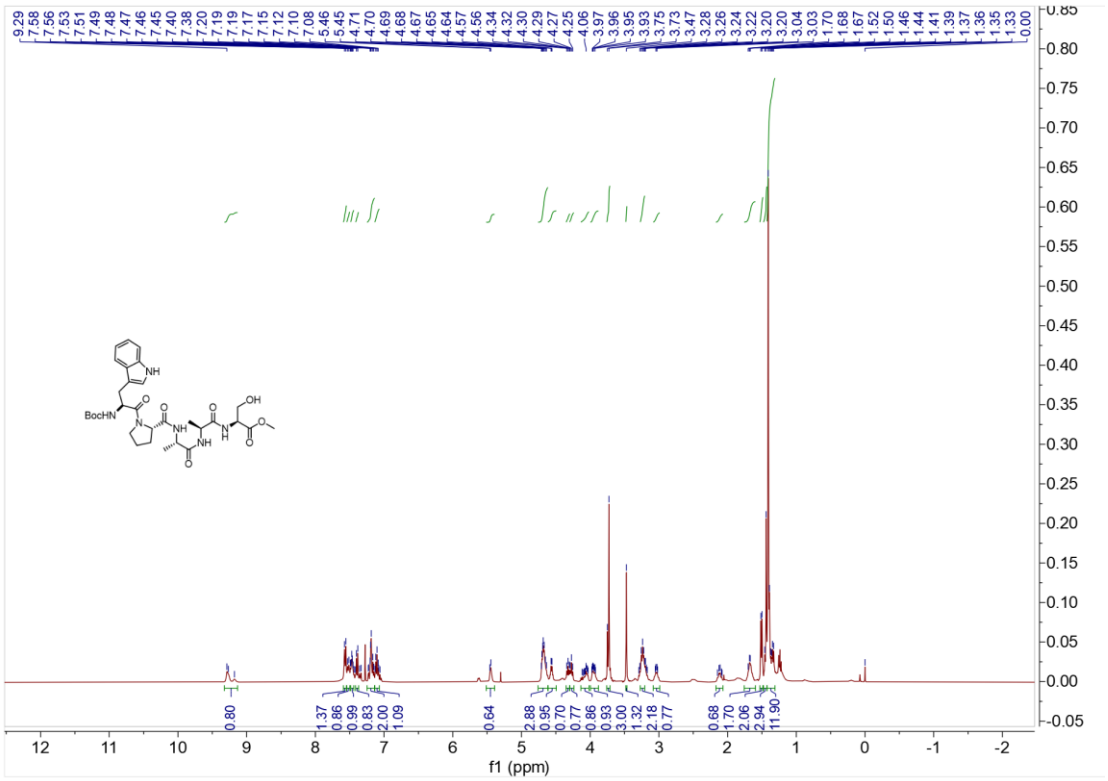

Fig 23. ^{1}H NMR of (**SM-11**) (400 MHz, $CDCl_3$)

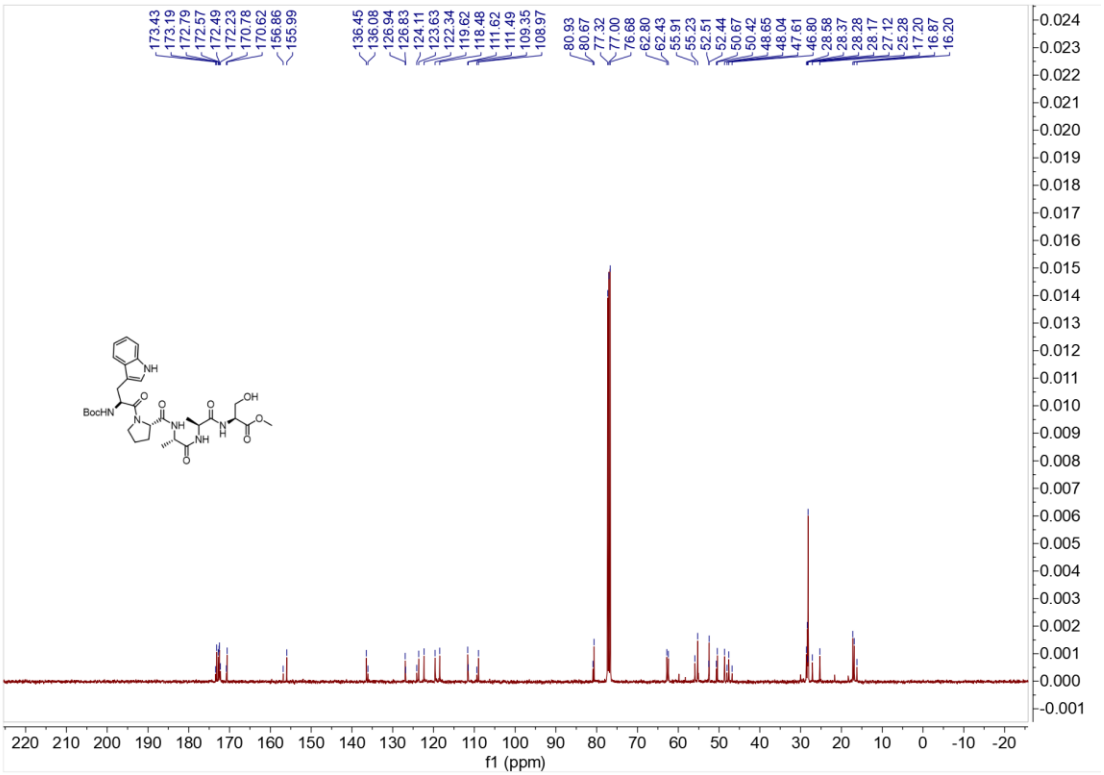

Fig 24. ^{13}C NMR of (**SM-11**) (150 MHz, $CDCl_3$)

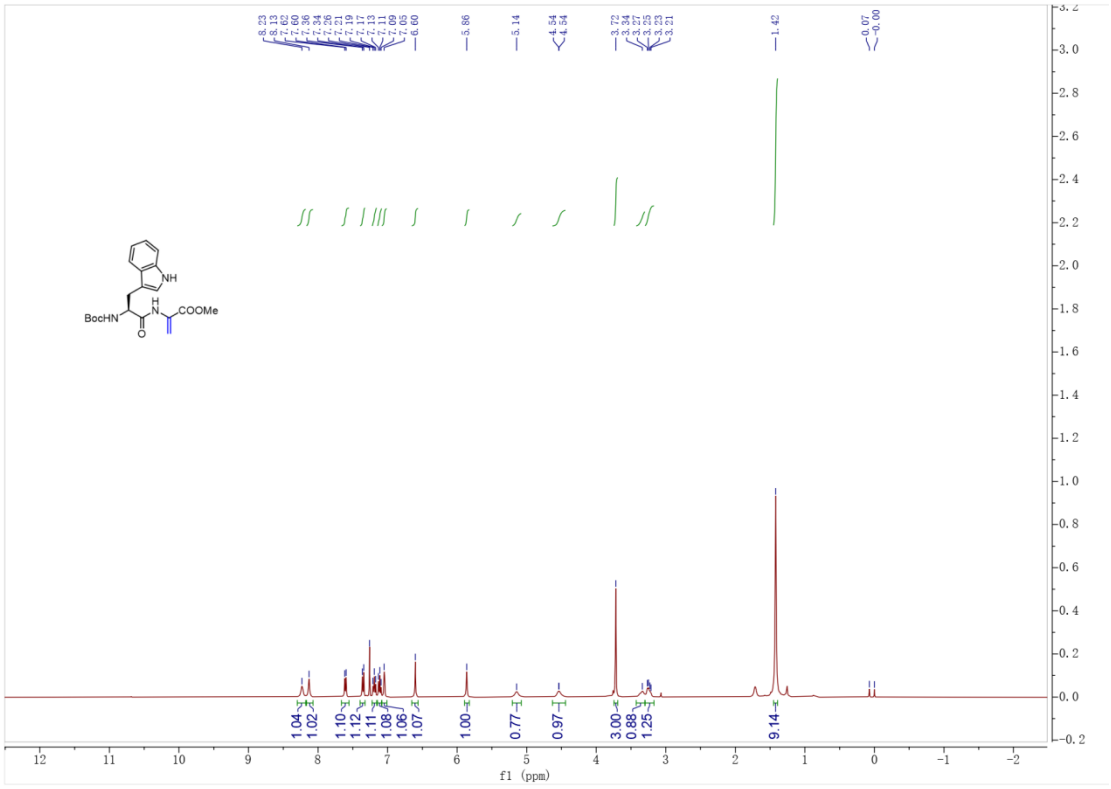

Fig 25. ^{1}H NMR of (**2a**) (400 MHz, $CDCl_3$)

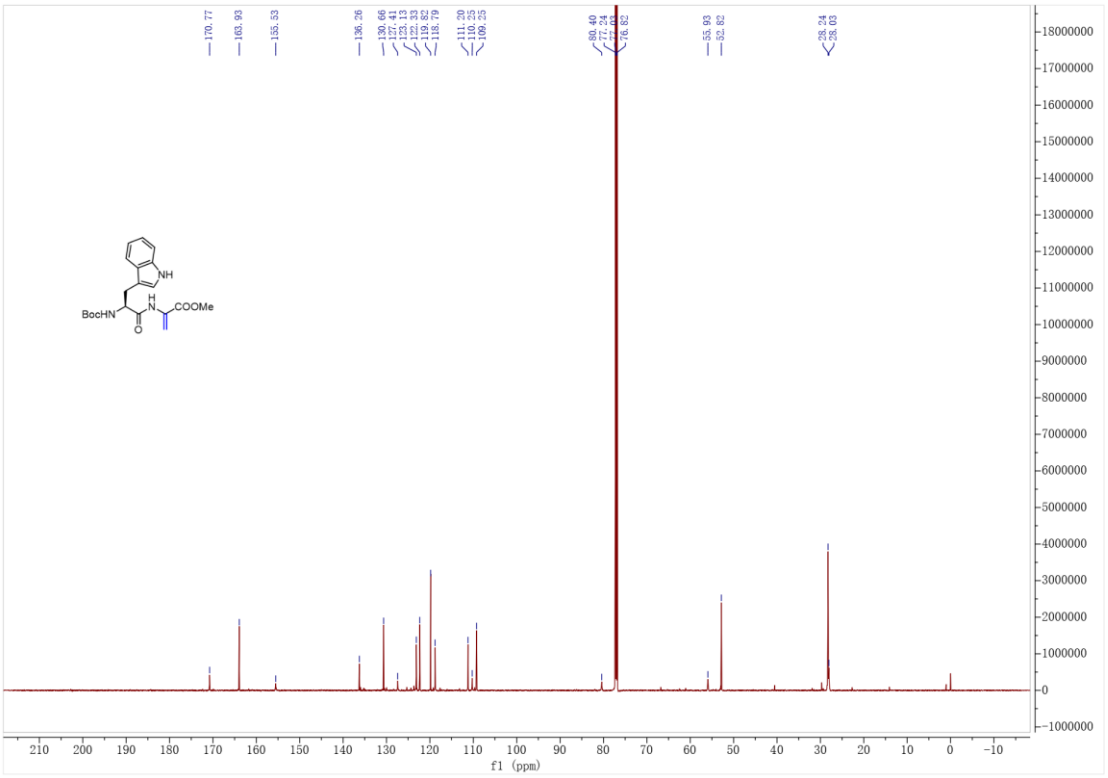

Fig 26. ^{13}C NMR of (**2a**) (150 MHz, $CDCl_3$)

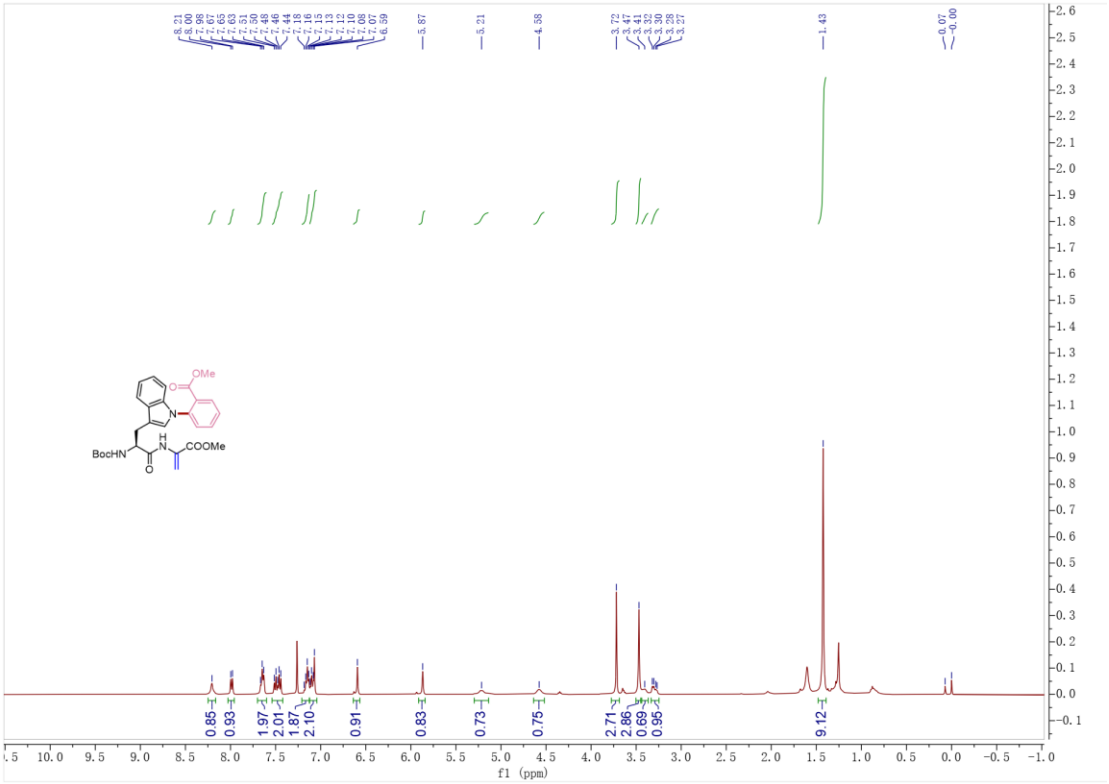

Fig 27. ^{1}H NMR of (**2a'**) (400 MHz, $CDCl_3$)

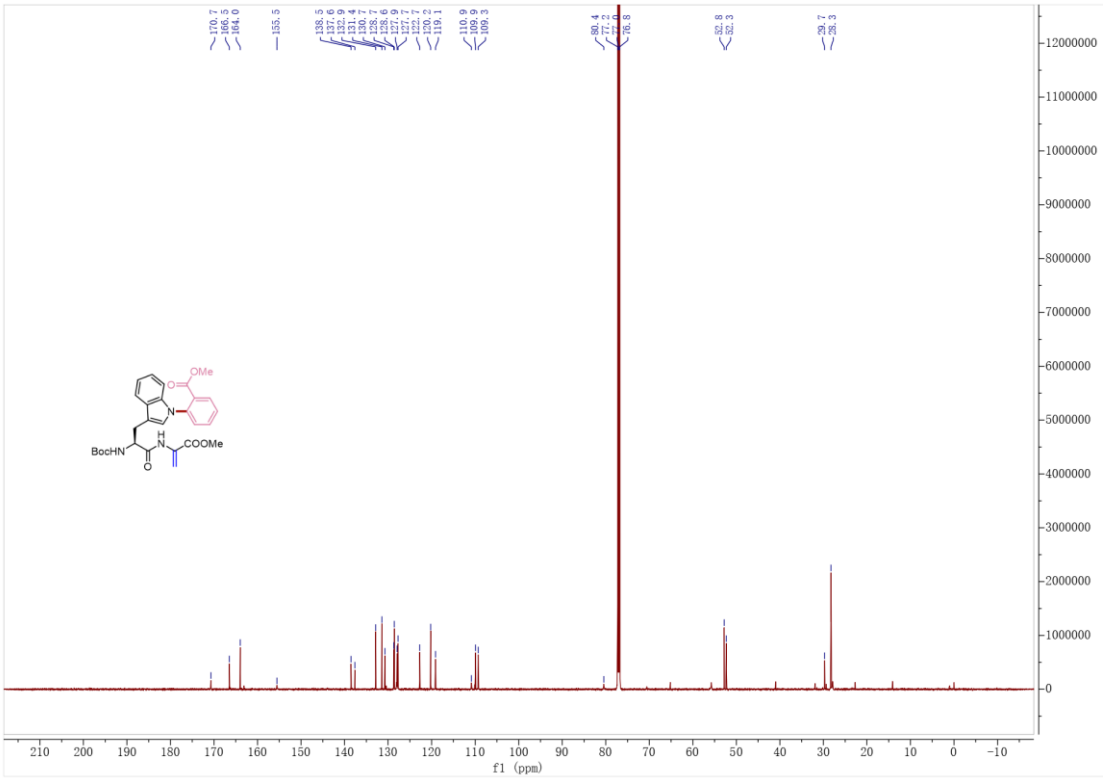

Fig 28. ^{13}C NMR of (**2a'**) (150 MHz, $CDCl_3$)

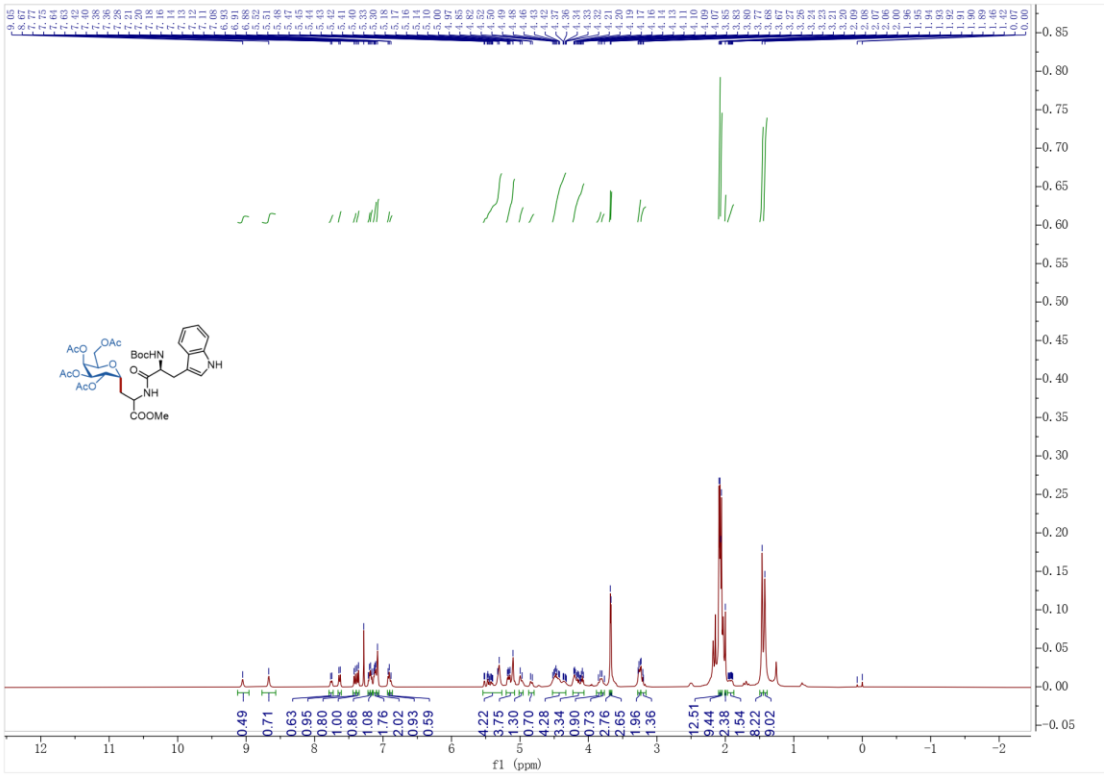

Fig 29. ^{1}H NMR of (**3a**) (400 MHz, $CDCl_3$)

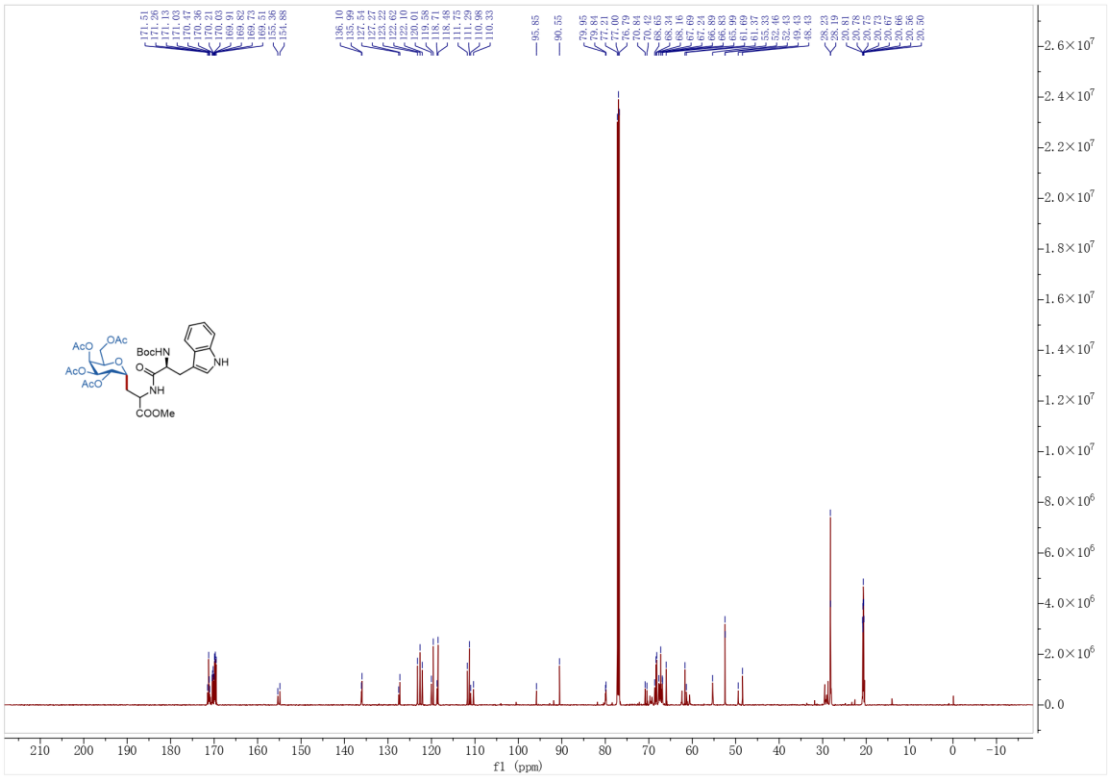

Fig 30. ^{13}C NMR of (**3a**) (150 MHz, $CDCl_3$)

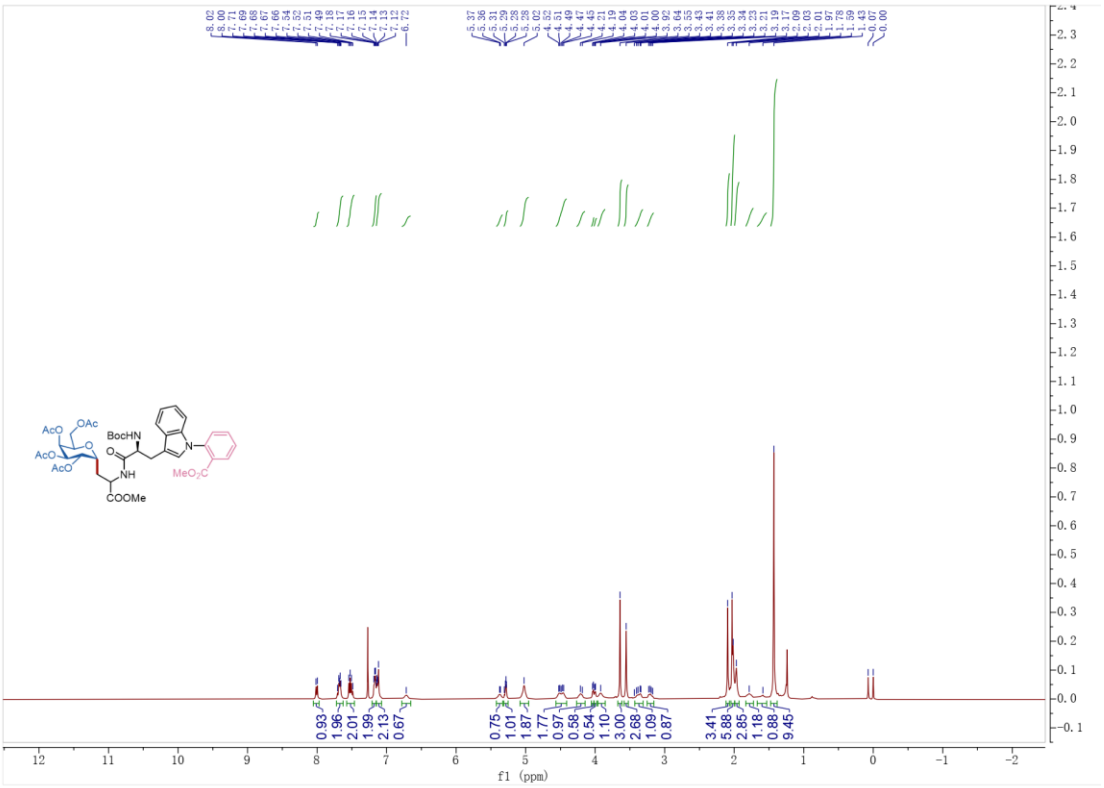

Fig 31. ^{1}H NMR of (**3a'**) (400 MHz, $CDCl_3$)

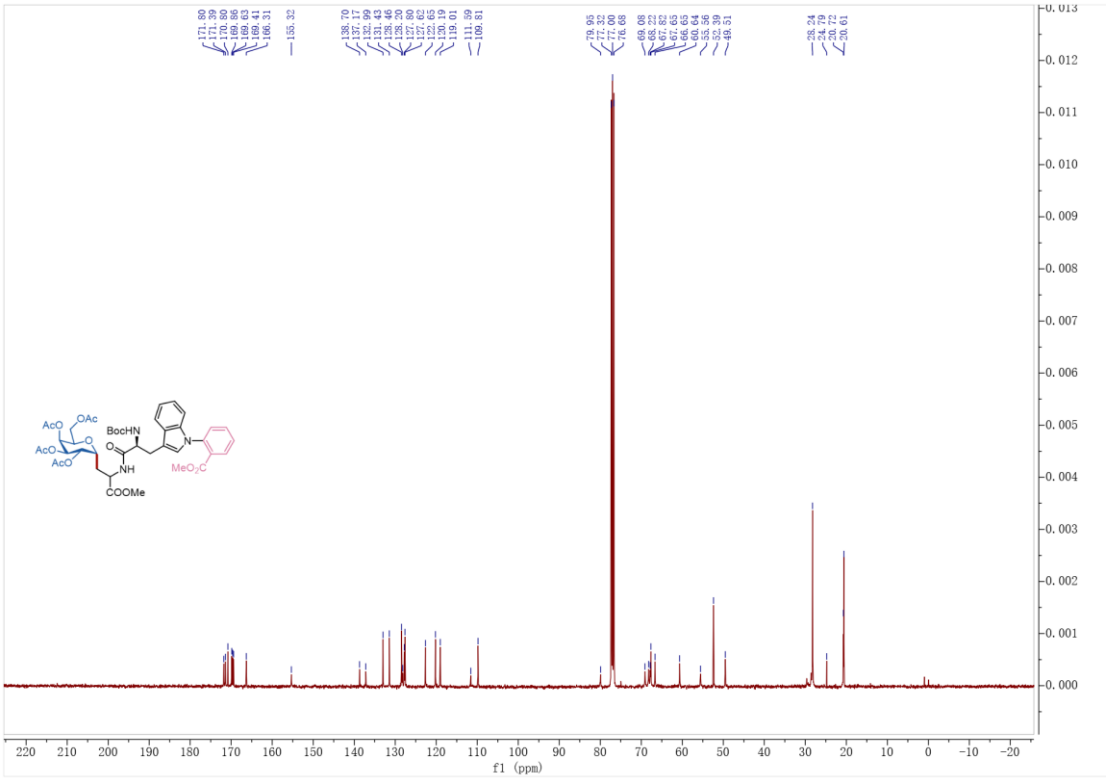

Fig 32. ^{13}C NMR of (**3a'**) (100 MHz, $CDCl_3$)

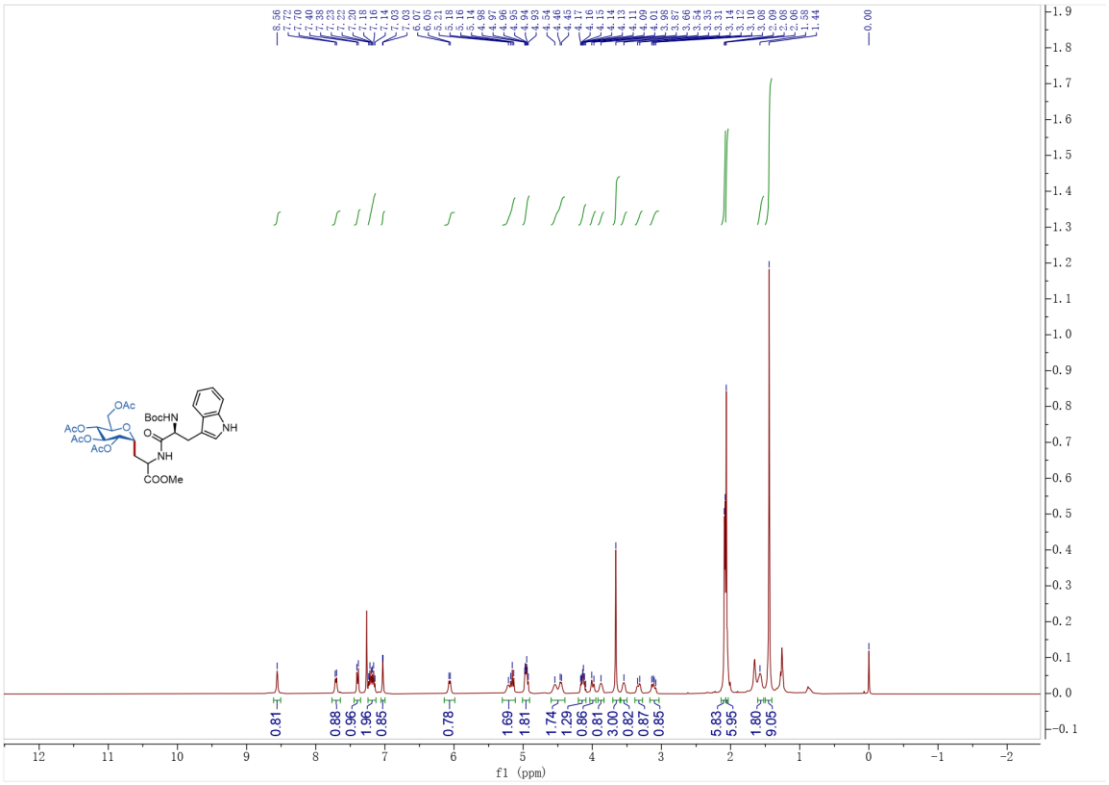

Fig 33. ^{1}H NMR of (**3b**) (400 MHz, $CDCl_3$)

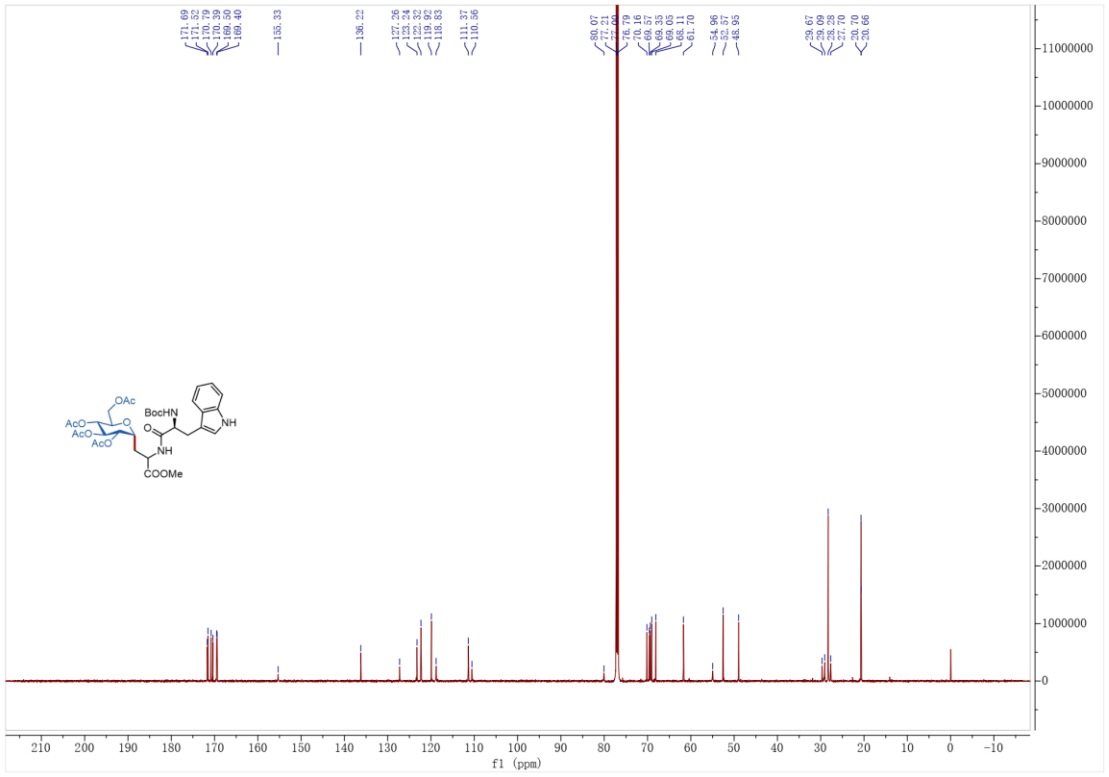

Fig 34. ^{13}C NMR of (**3b**) (150 MHz, $CDCl_3$)

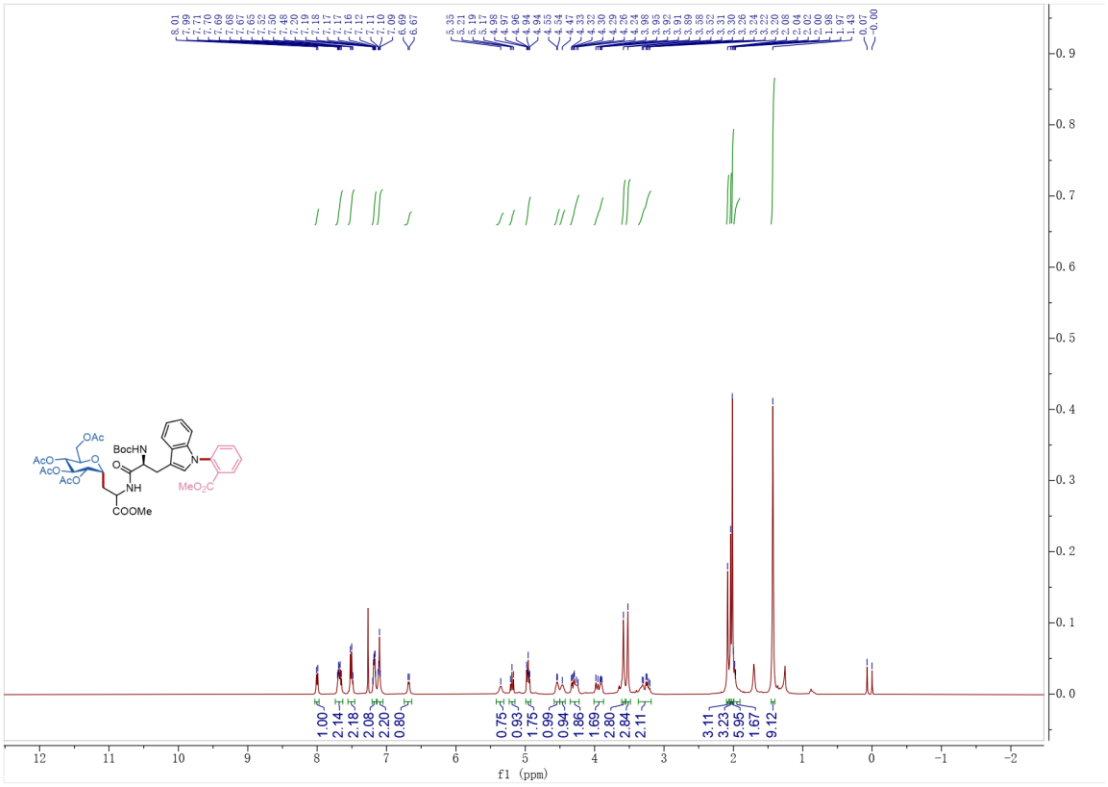

Fig 35. ^{1}H NMR of (**3b'**) (400 MHz, $CDCl_3$)

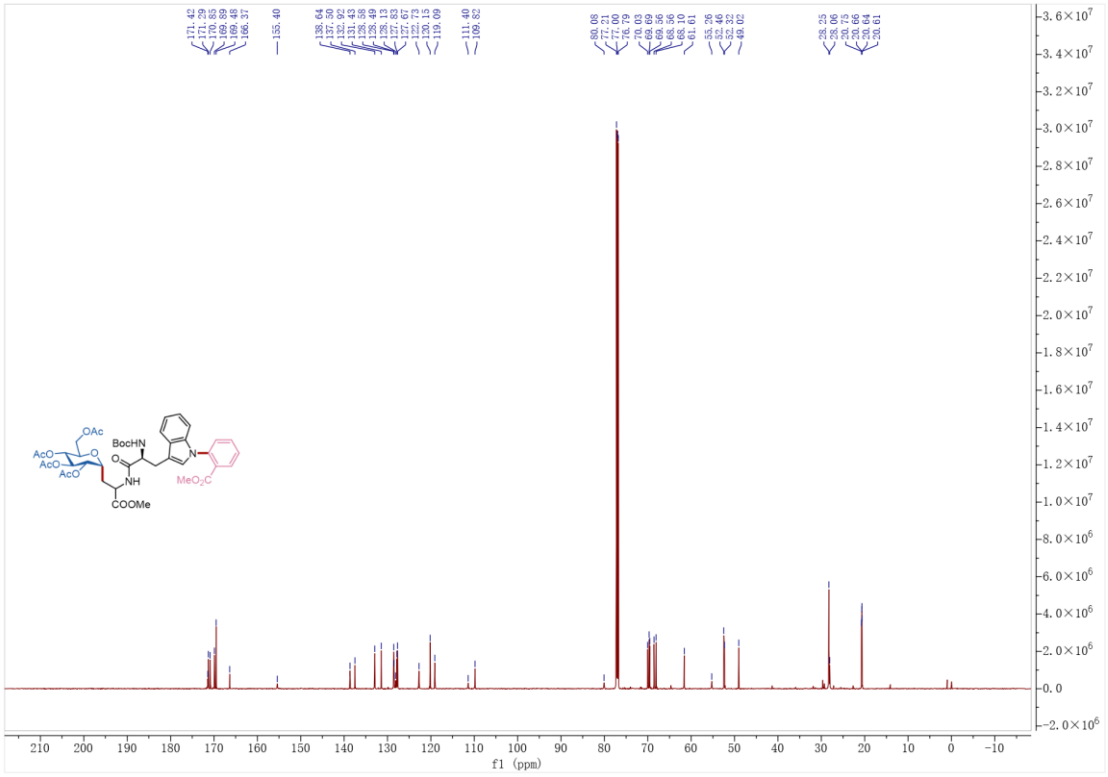

Fig 36. ^{13}C NMR of (**3b'**) (150 MHz, $CDCl_3$)

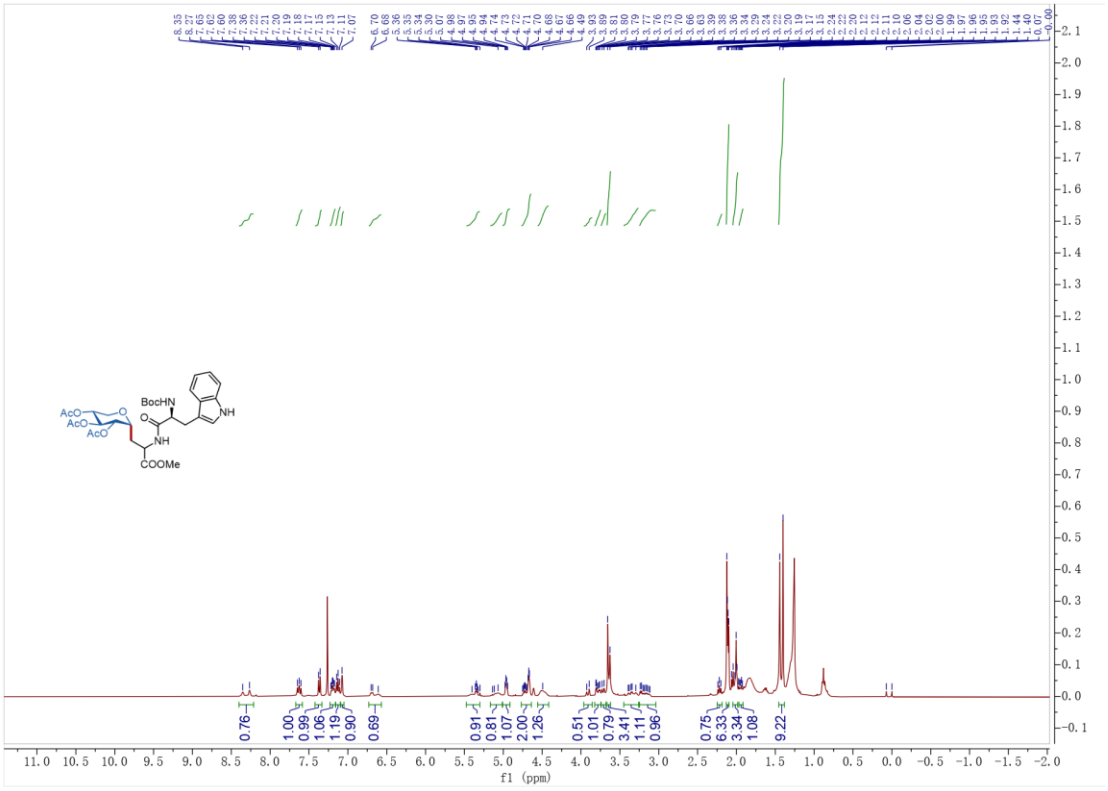

Fig 37. ^{1}H NMR of (**3c**) (400 MHz, $CDCl_3$)

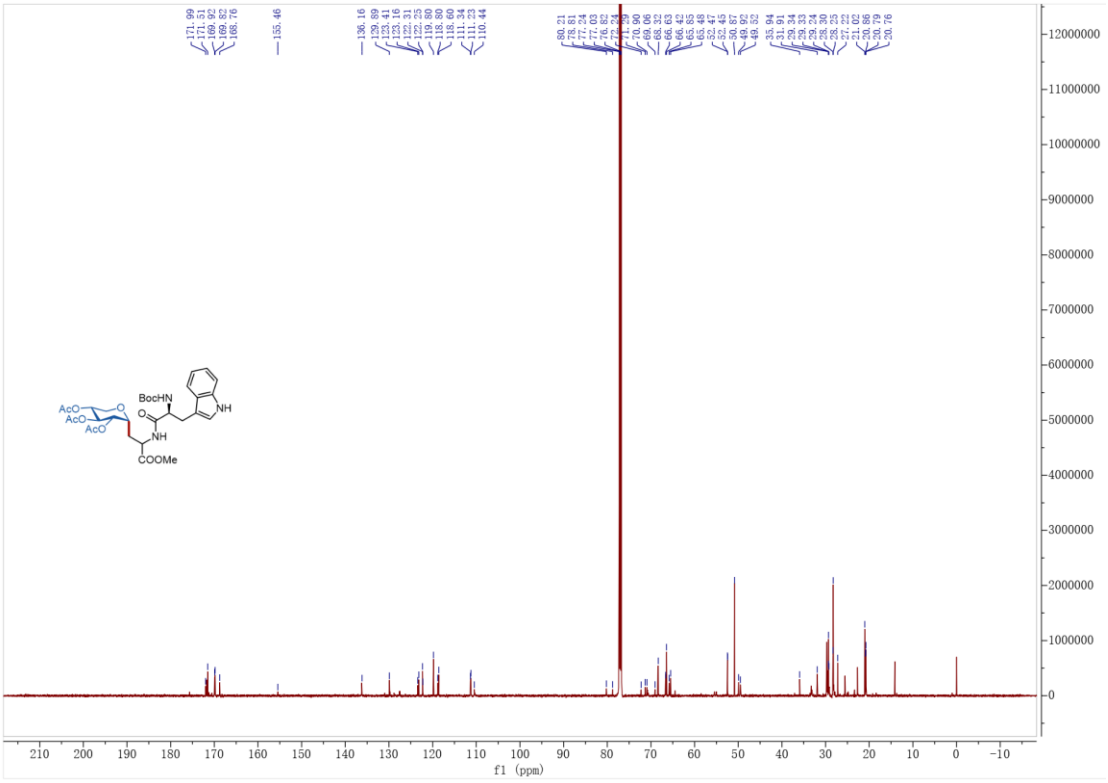

Fig 38. ^{13}C NMR of (**3c**) (150 MHz, $CDCl_3$)

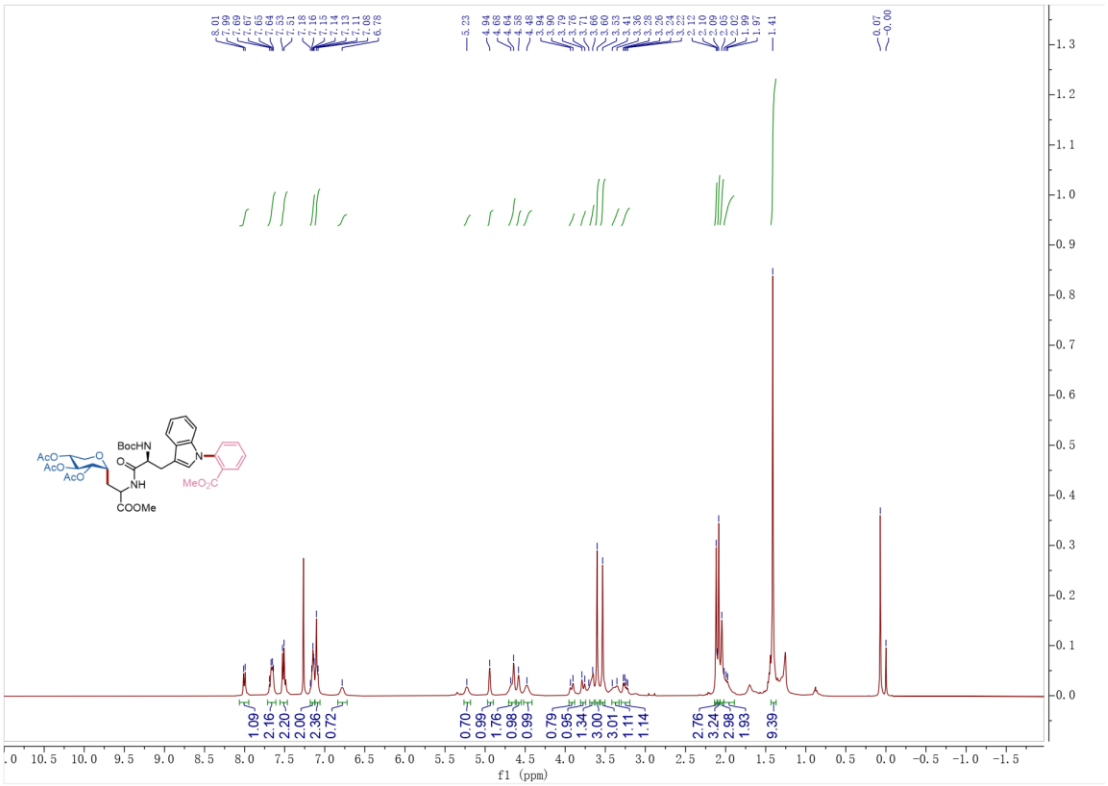

Fig 39. ^{1}H NMR of (**3c'**) (400 MHz, $CDCl_3$)

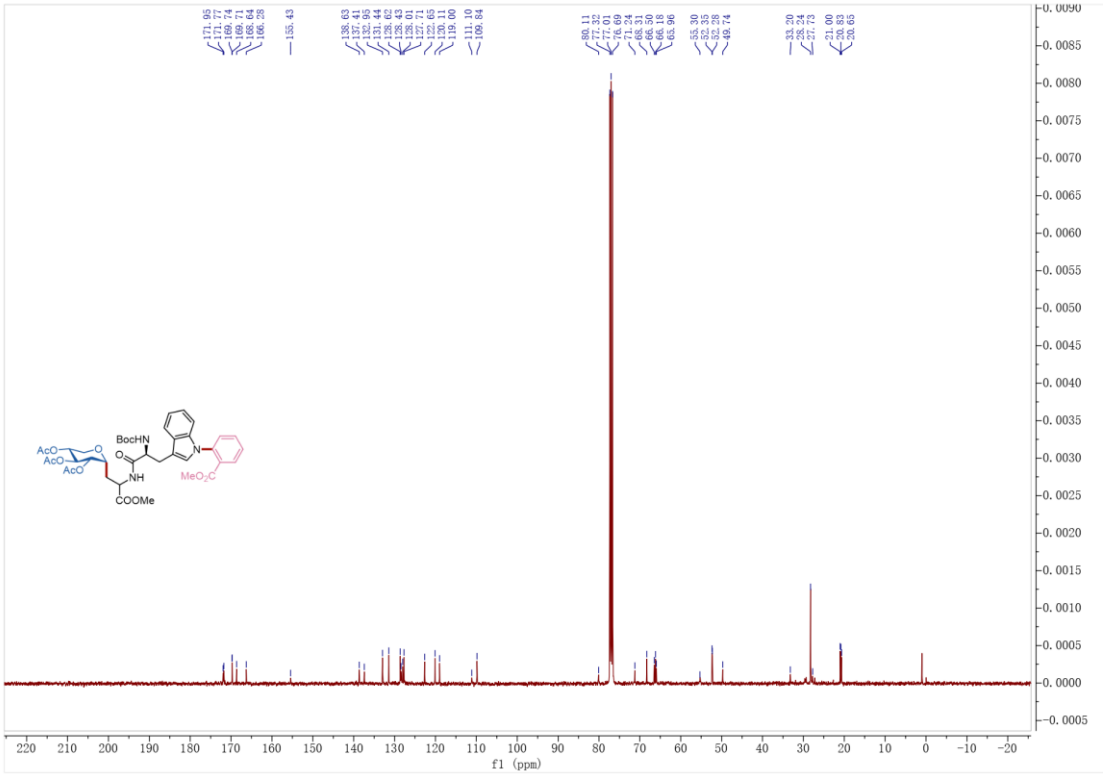

Fig 40. ^{13}C NMR of (**3c'**) (100 MHz, $CDCl_3$)

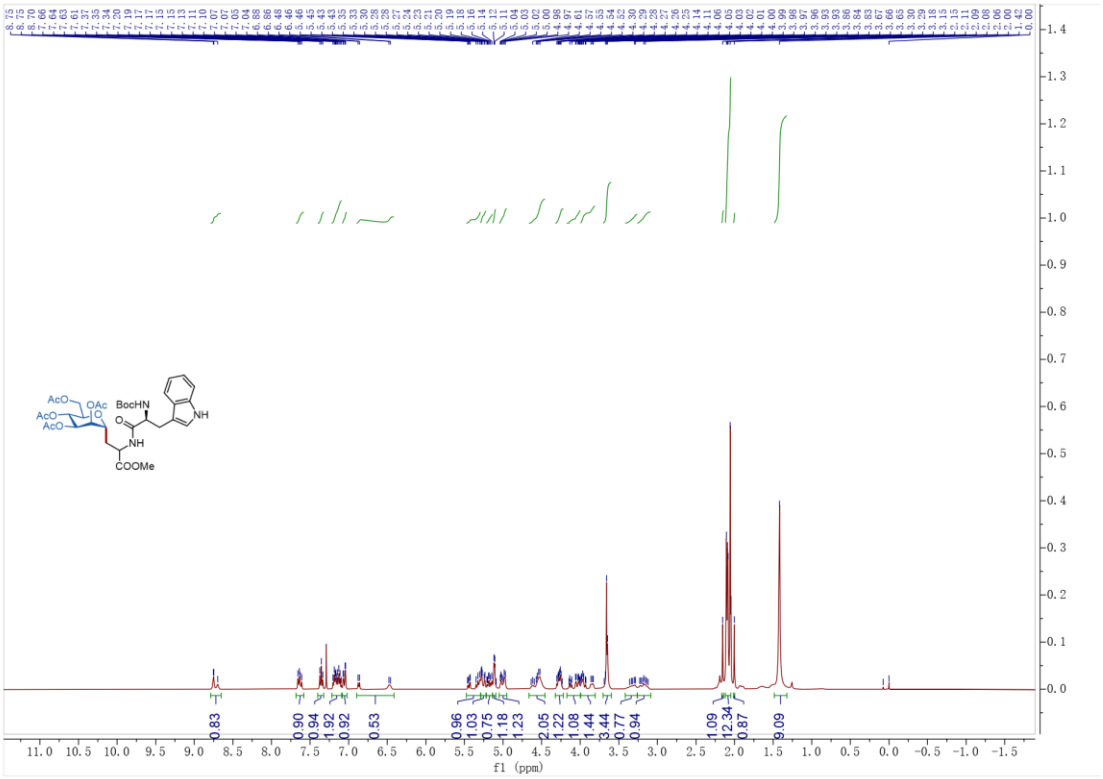

Fig 41. ^{1}H NMR of (**3d**) (400 MHz, $CDCl_3$)

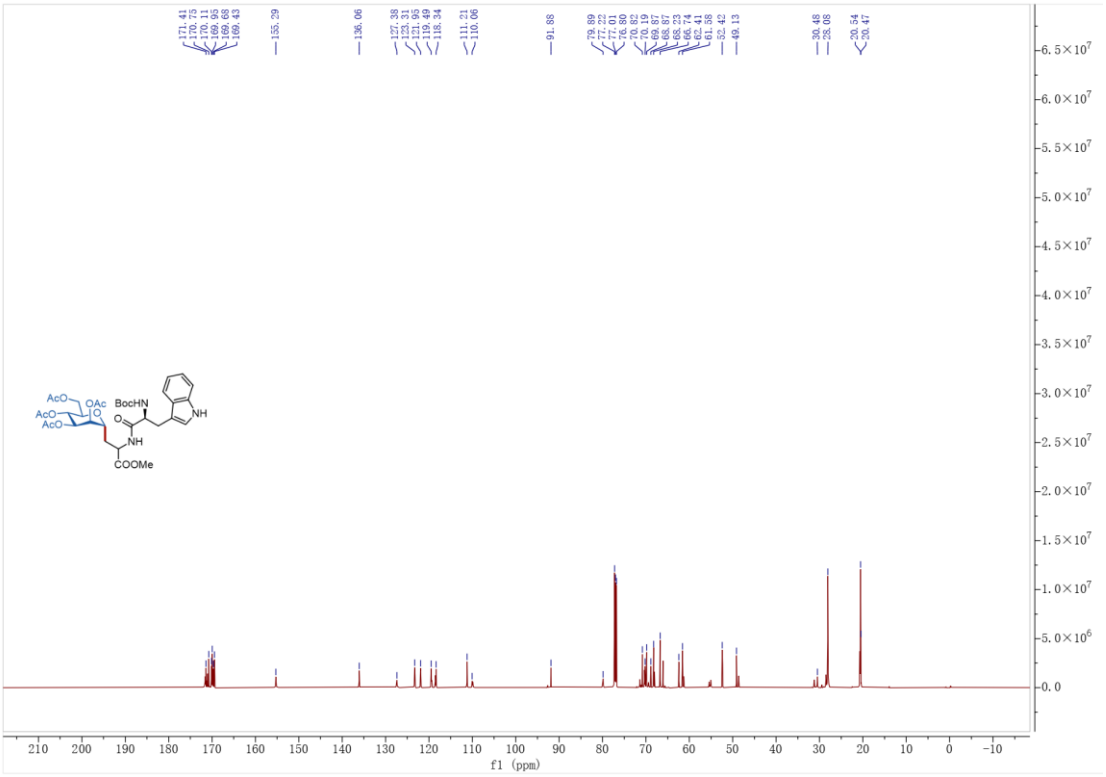

Fig 42. ^{13}C NMR of (**3d**) (150 MHz, $CDCl_3$)

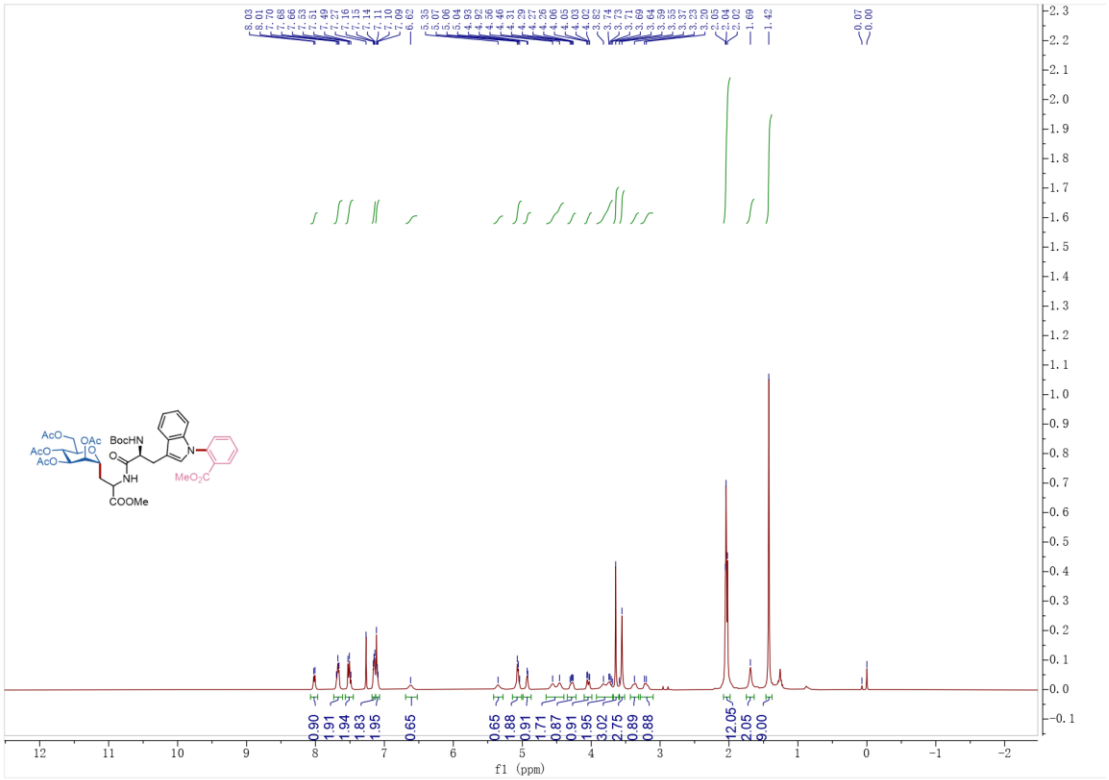

Fig 43. ^{1}H NMR of (**3d'**) (400 MHz, $CDCl_3$)

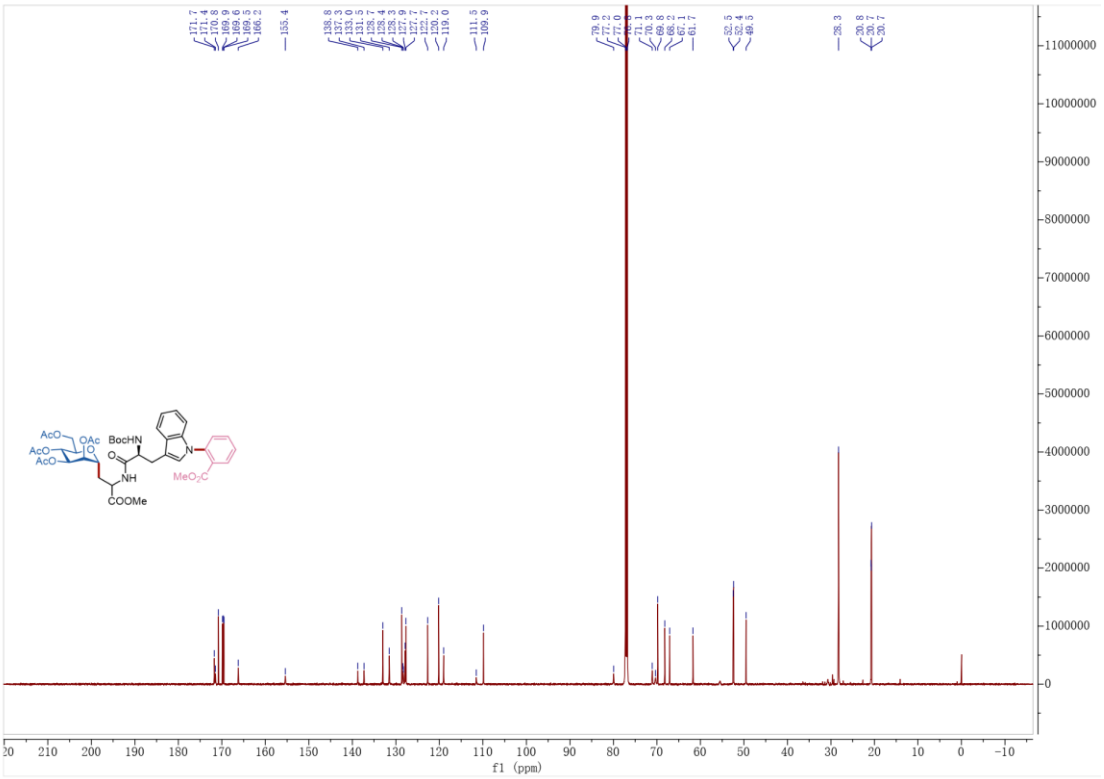

Fig 44. ^{13}C NMR of (**3d'**) (150 MHz, $CDCl_3$)

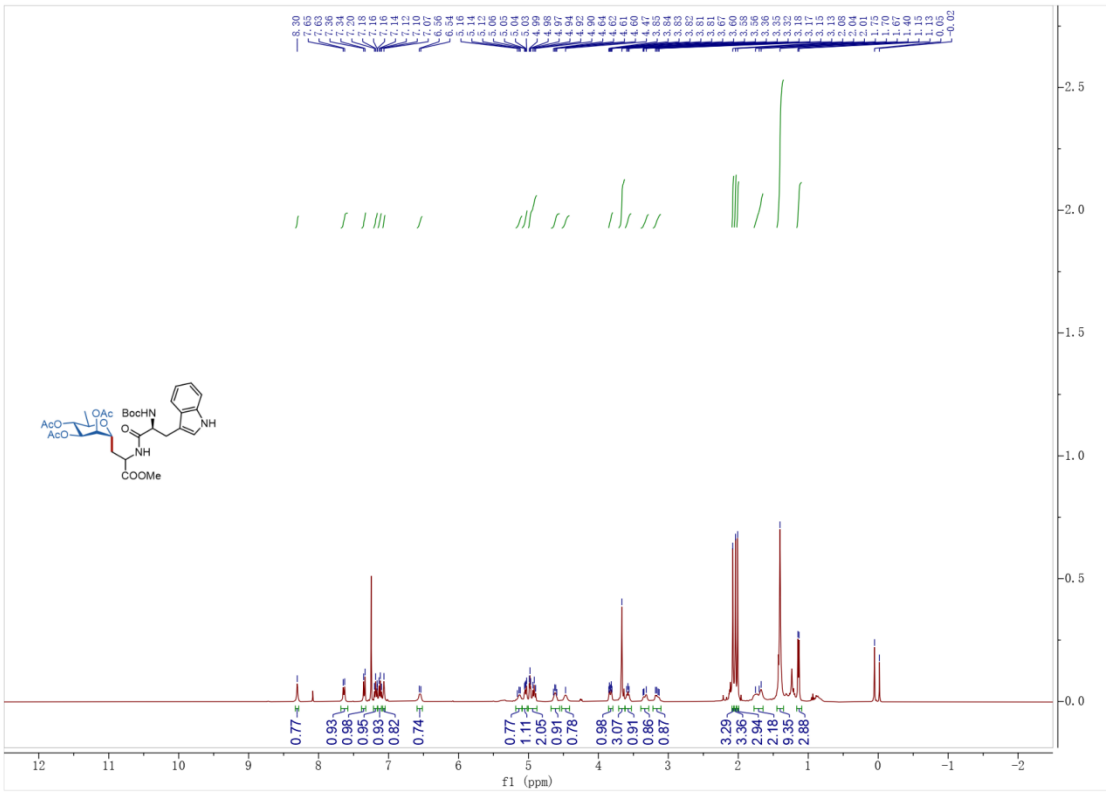

Fig 45. ^{1}H NMR of (**3e**) (400 MHz, $CDCl_3$)

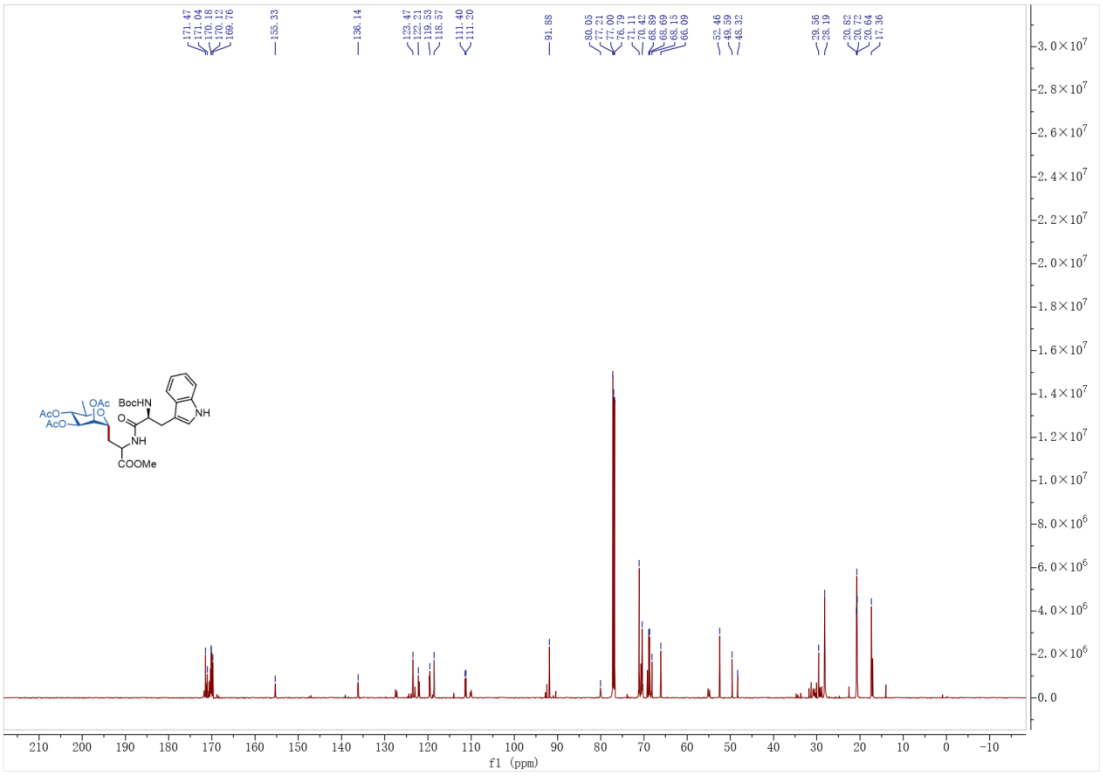

Fig 46. ^{13}C NMR of (**3e**) (150 MHz, $CDCl_3$)

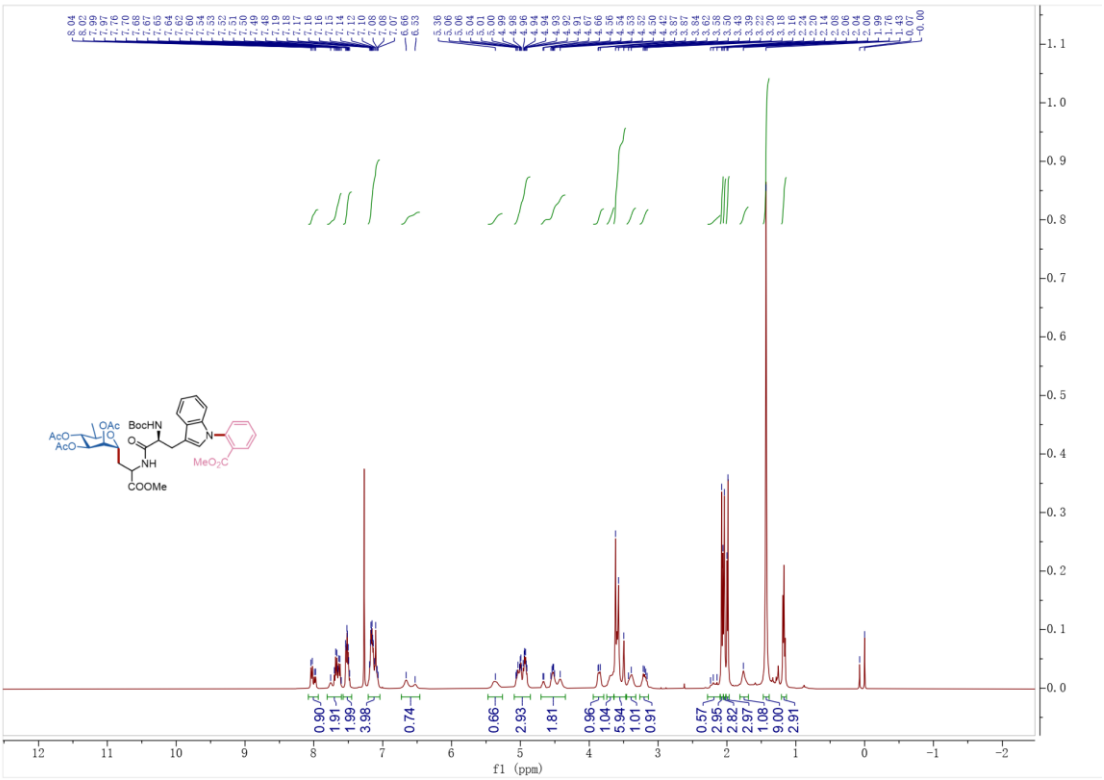

Fig 47. ^{1}H NMR of (**3e'**) (400 MHz, $CDCl_3$)

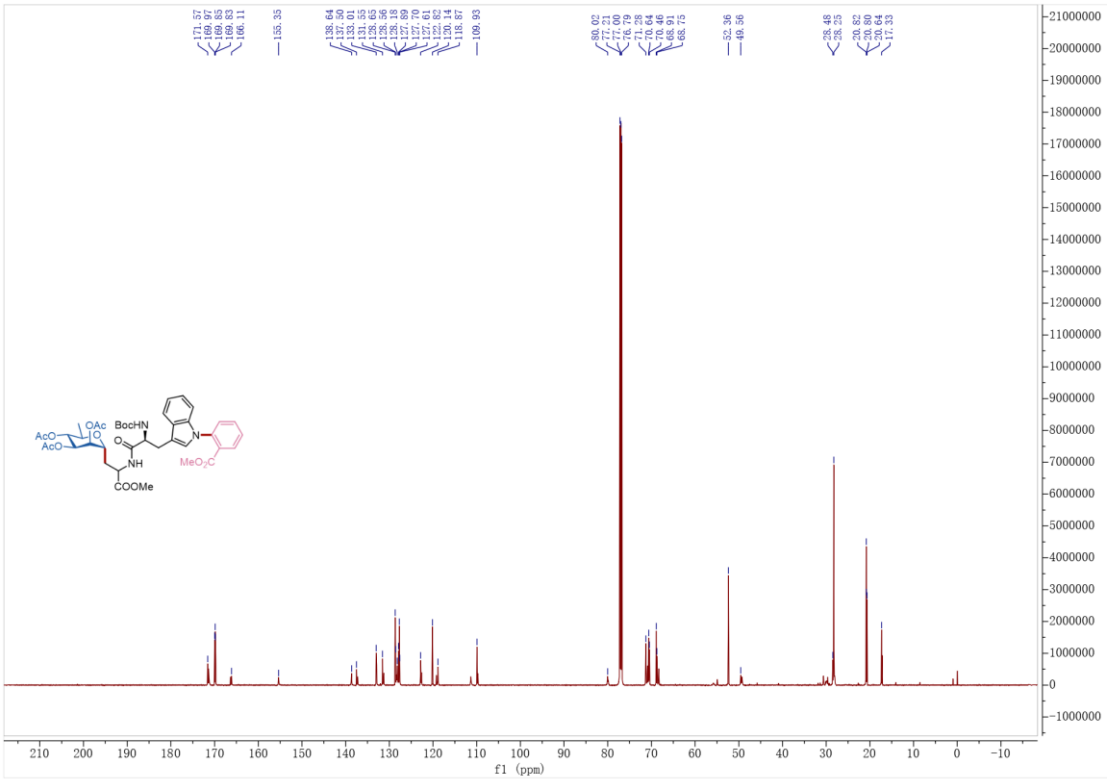

Fig 48. ^{13}C NMR of (**3e'**) (150 MHz, $CDCl_3$)

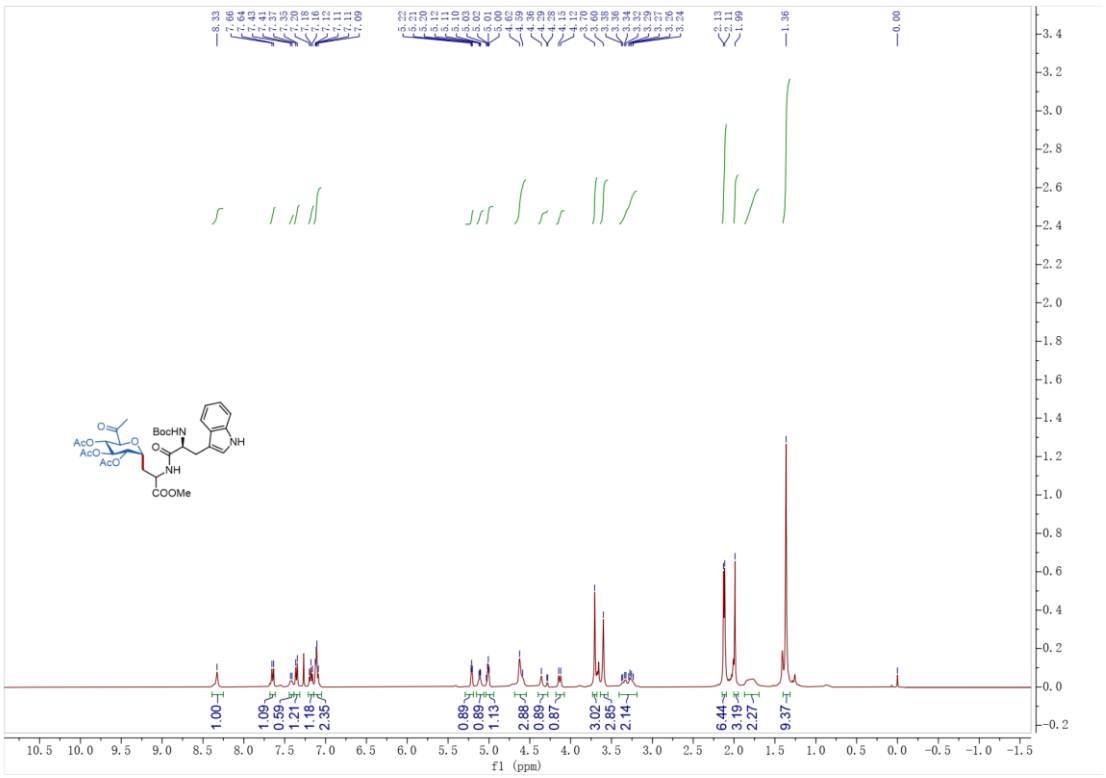

Fig 49. ^{1}H NMR of (**3f**) (400 MHz, $CDCl_3$)

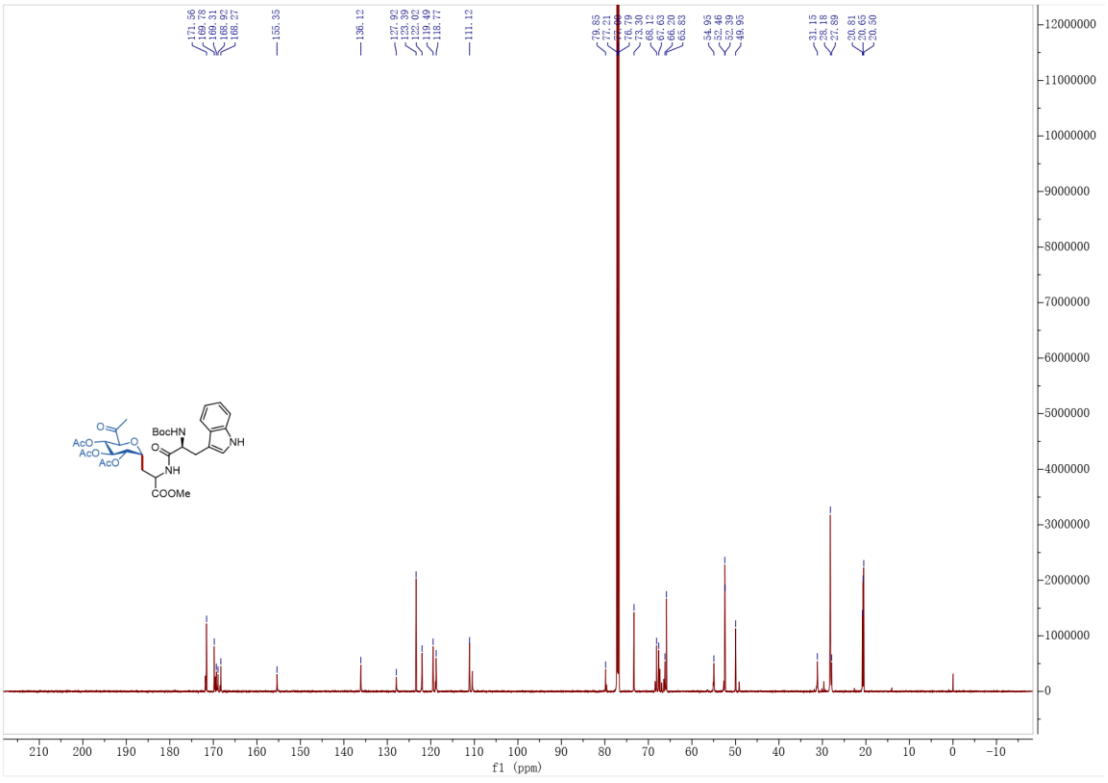

Fig 50. ^{13}C NMR of (**3f**) (150 MHz, $CDCl_3$)

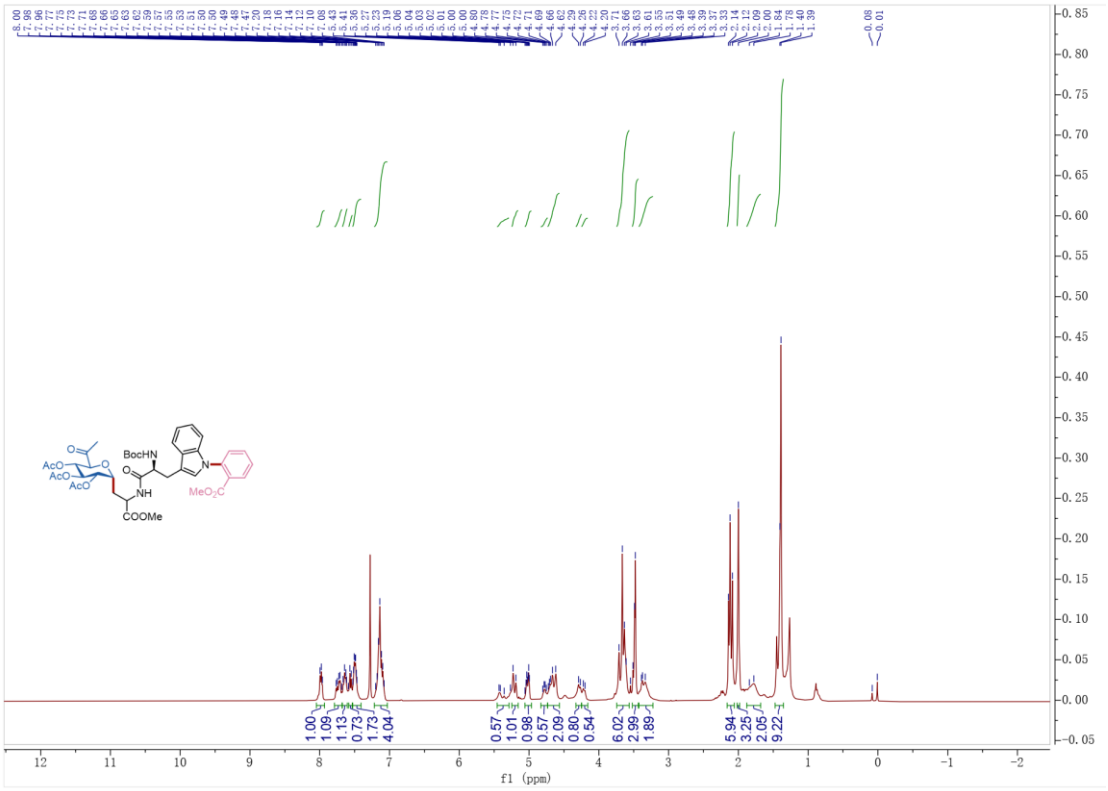

Fig 51. ^{1}H NMR of (**3f'**) (400 MHz, $CDCl_3$)

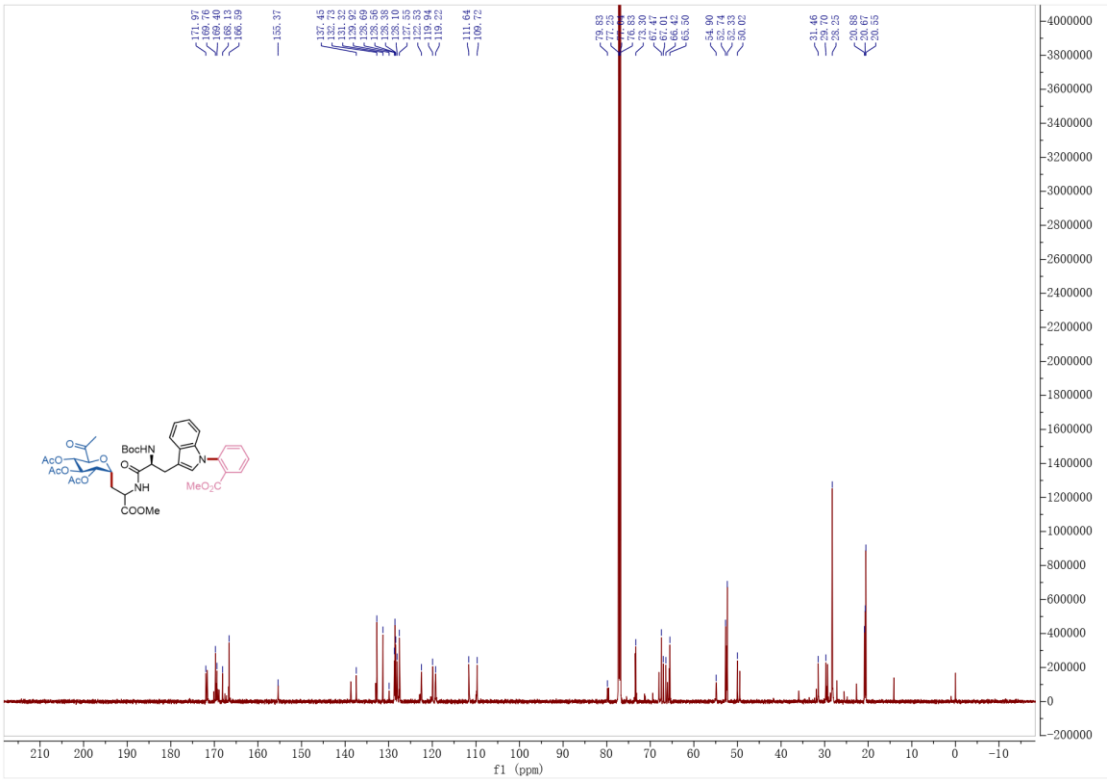

Fig 52. ^{13}C NMR of (**3f'**) (150 MHz, $CDCl_3$)

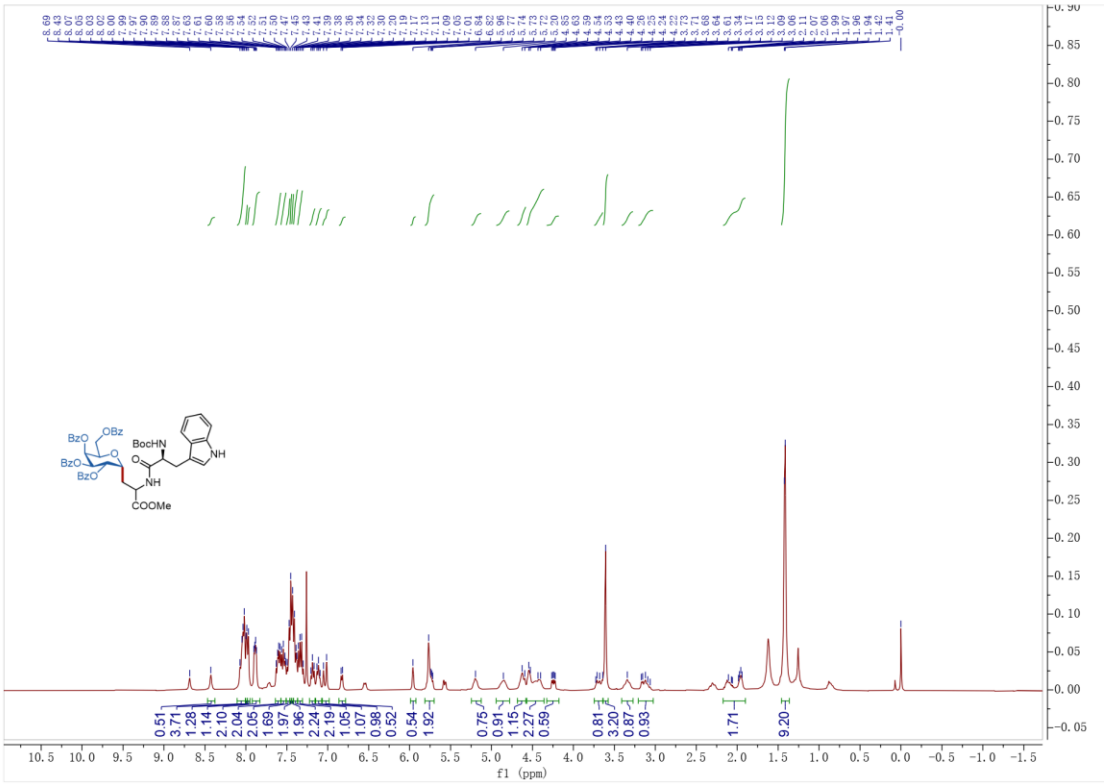

Fig 53. ^{1}H NMR of (**3g**) (400 MHz, $CDCl_3$)

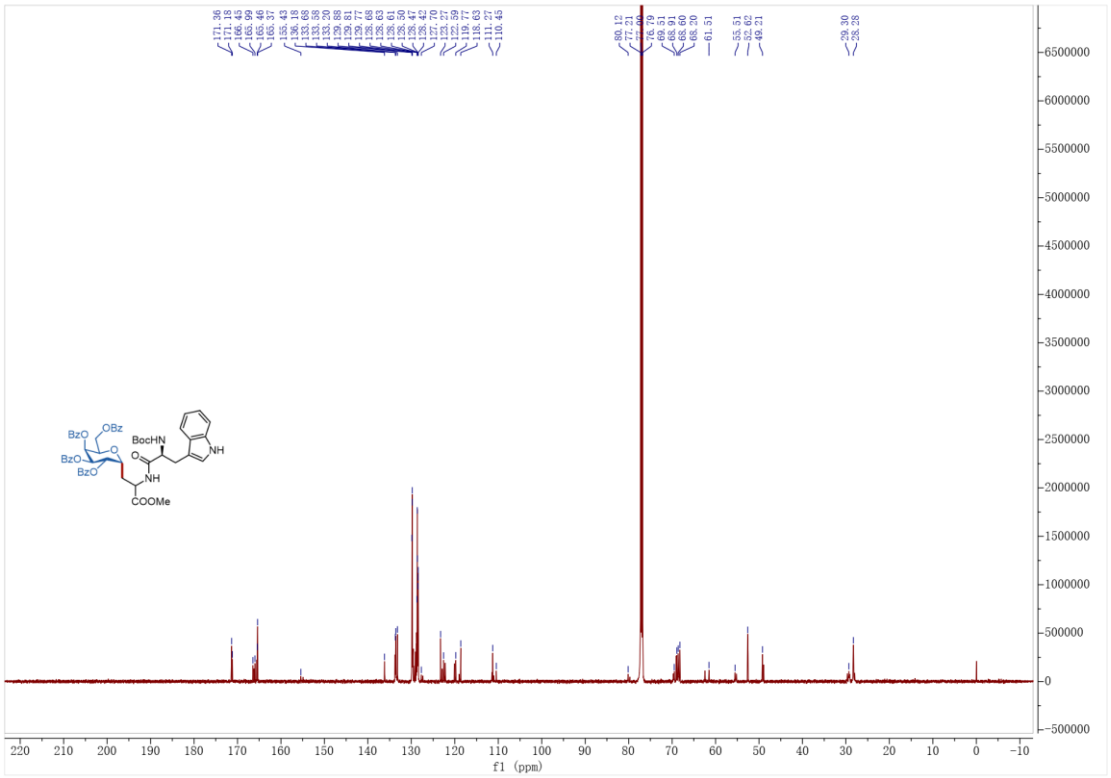

Fig 54. ^{13}C NMR of (**3g**) (150 MHz, $CDCl_3$)

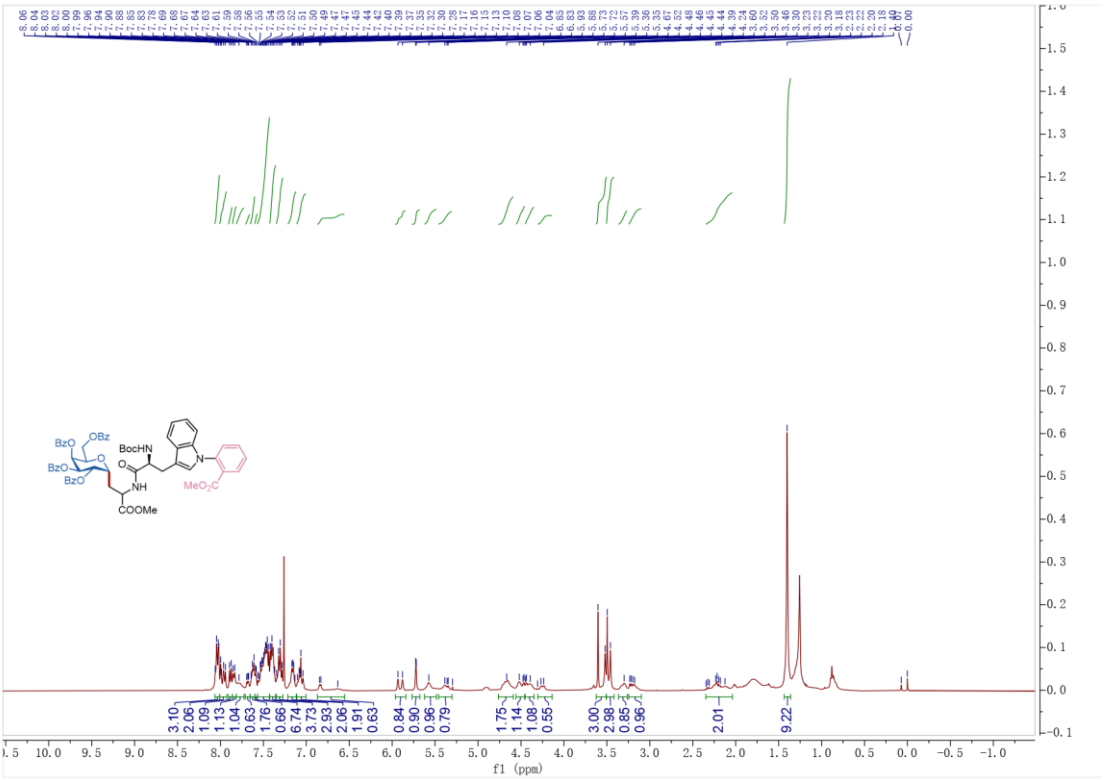

Fig 55. ^{1}H NMR of (**3g'**) (400 MHz, $CDCl_3$)

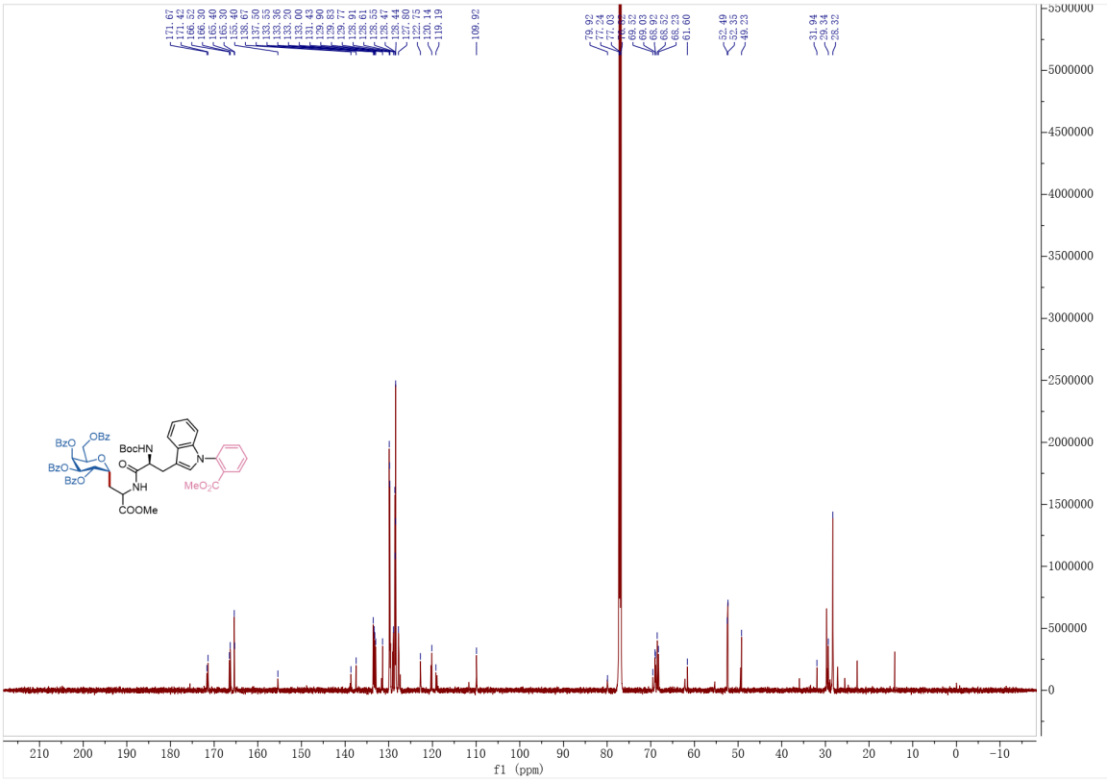

Fig 56. ^{13}C NMR of (**3g'**) (150 MHz, $CDCl_3$)

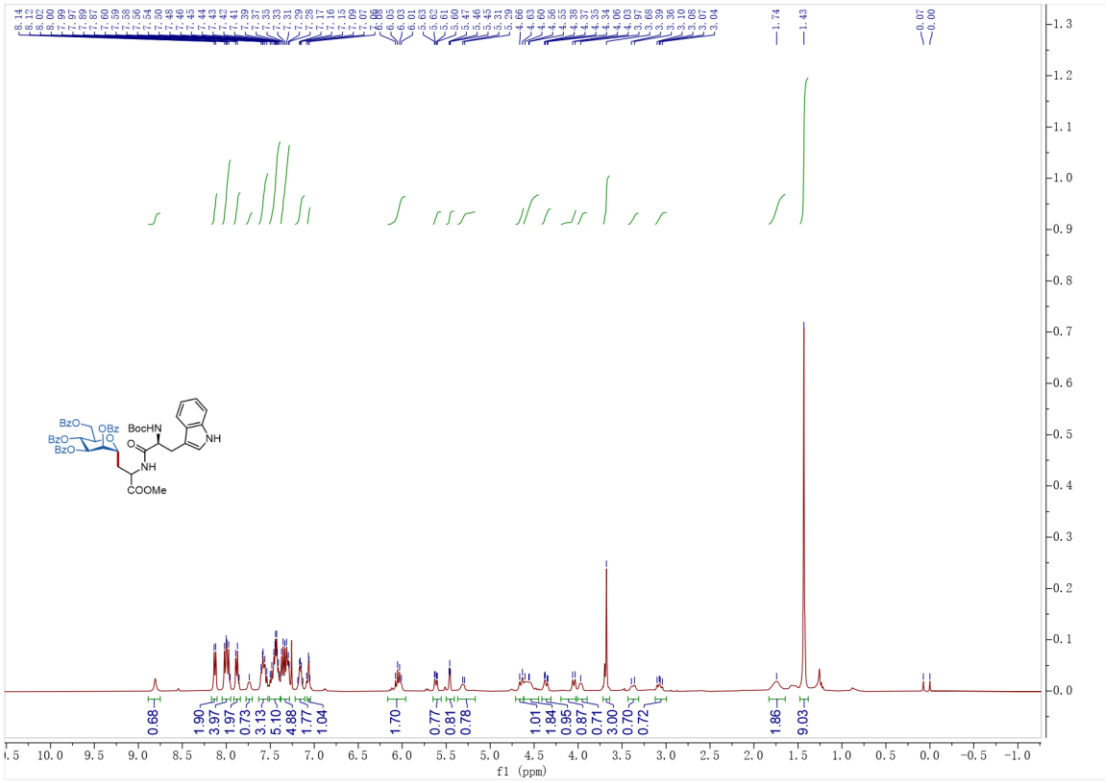

Fig 57. ^{1}H NMR of (**3h**) (400 MHz, $CDCl_3$)

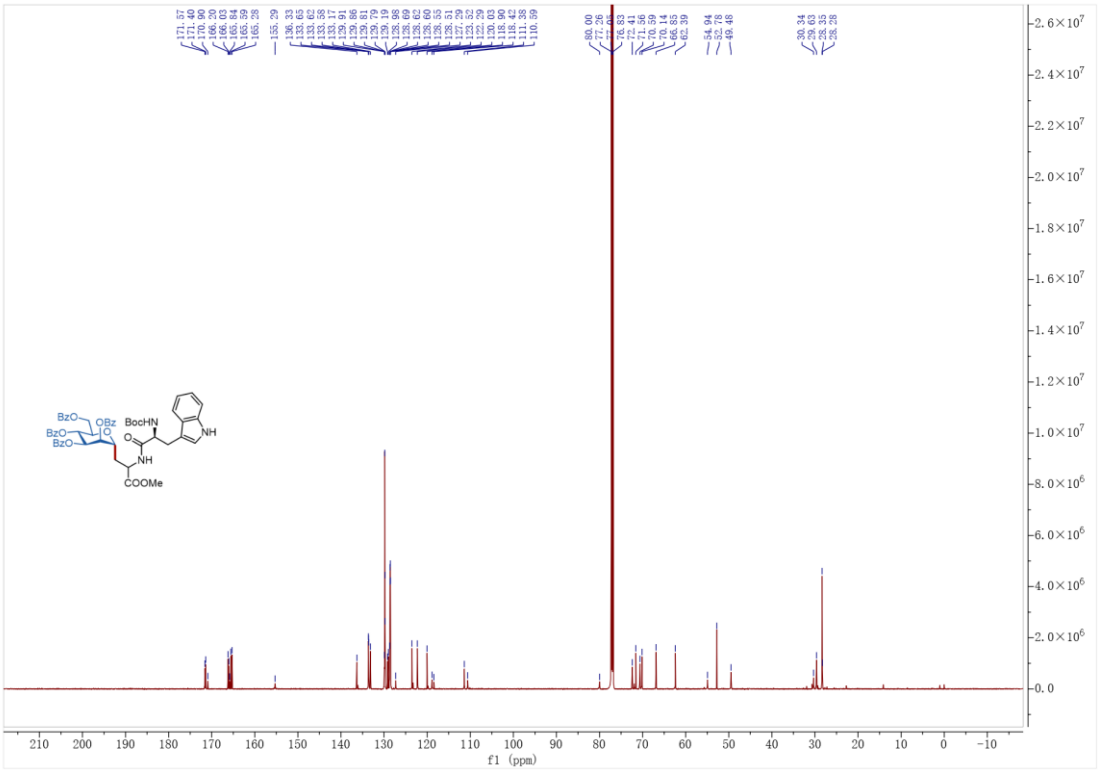

Fig 58. ^{13}C NMR of (**3h**) (150 MHz, $CDCl_3$)

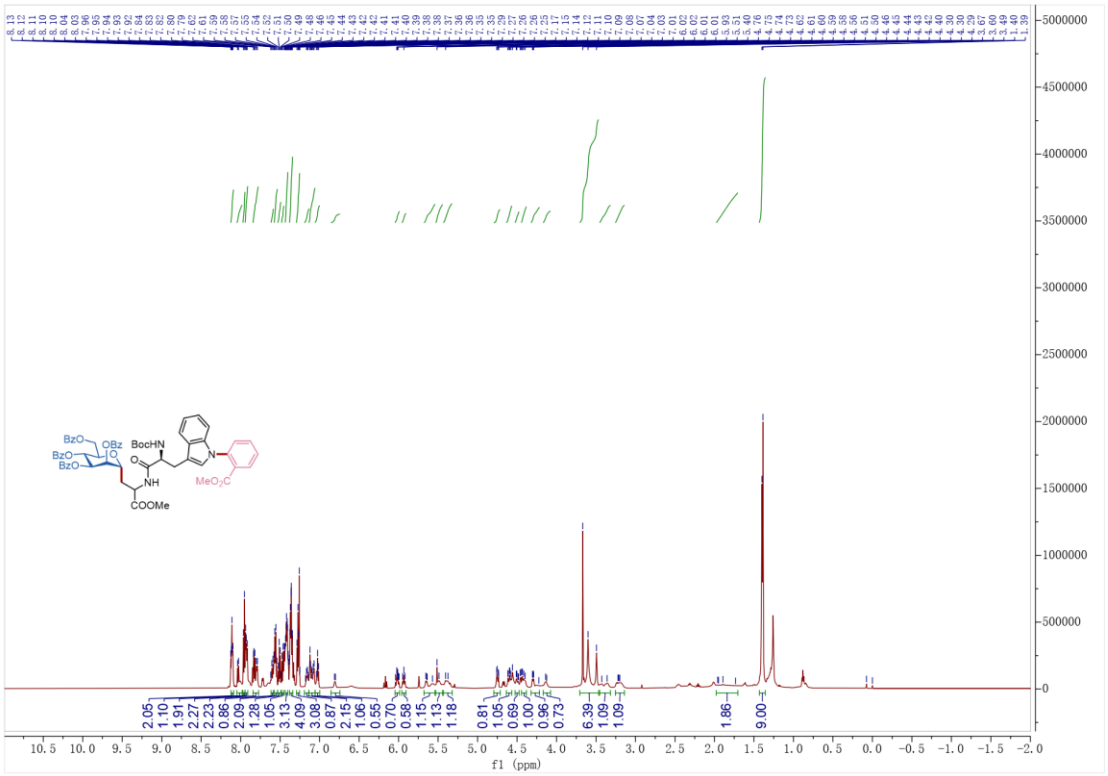

Fig 59. ^{1}H NMR of (**3h'**) (600 MHz, $CDCl_3$)

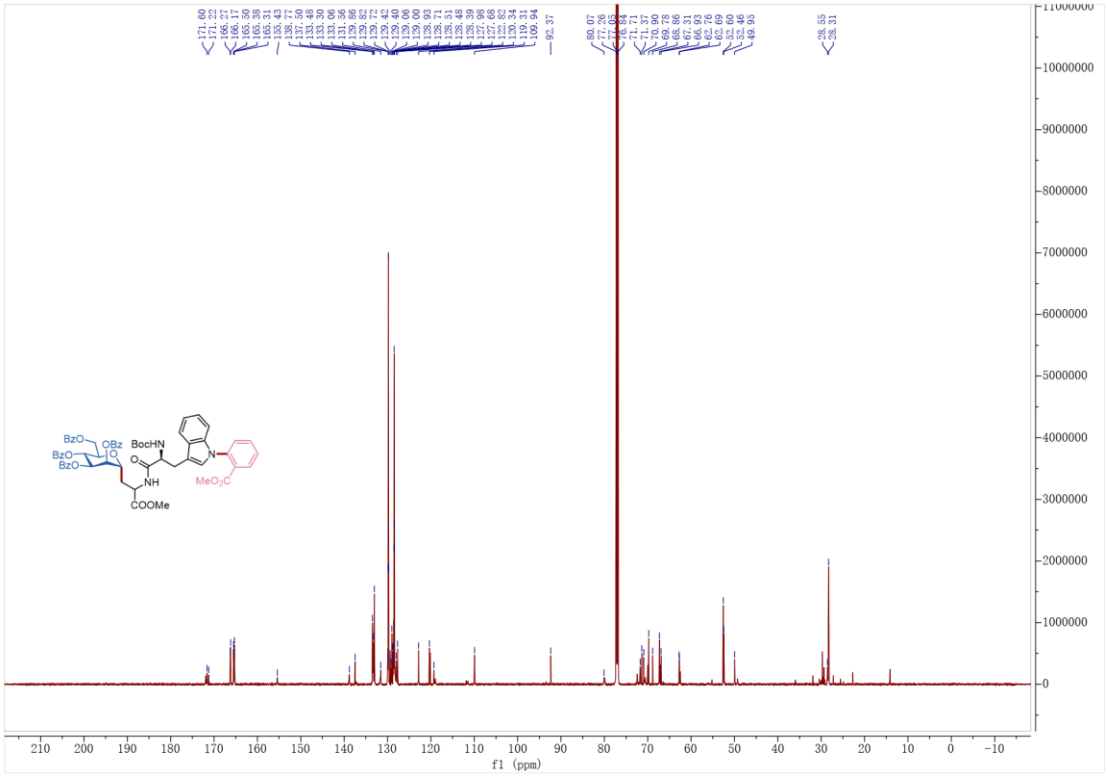

Fig 60. ^{13}C NMR of (**3h'**) (150 MHz, $CDCl_3$)

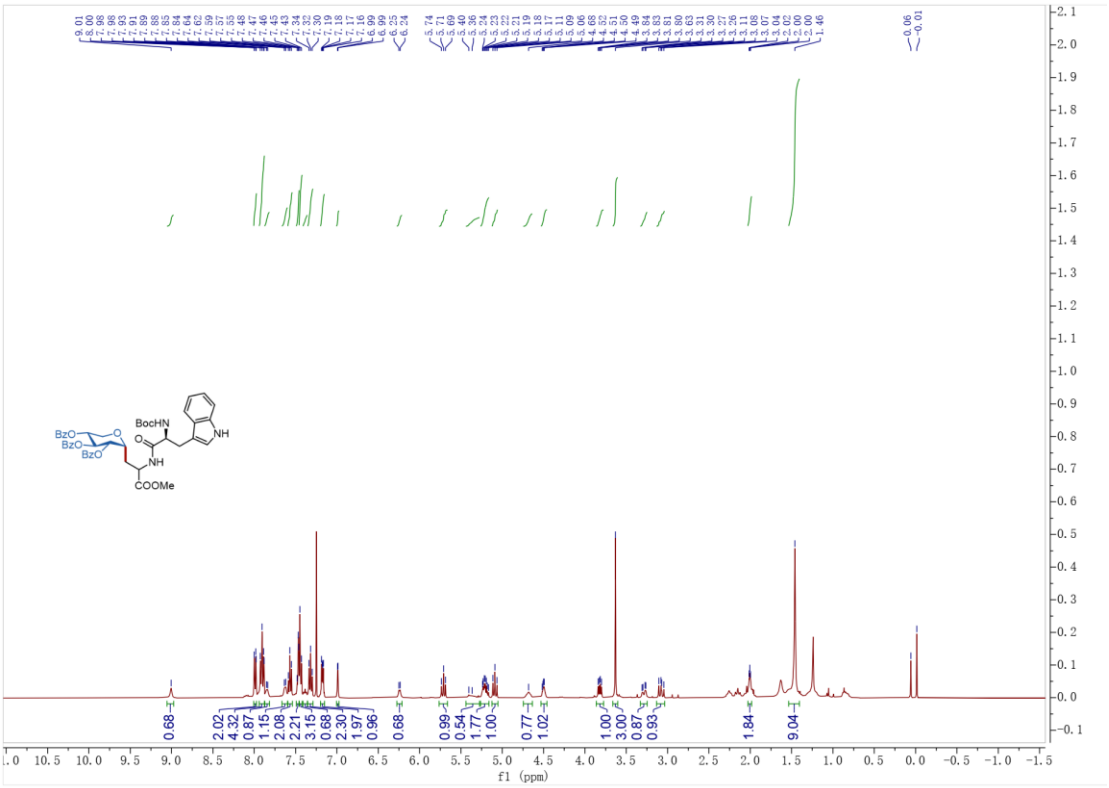

Fig 61. ^{1}H NMR of (**3i**) (400 MHz, $CDCl_3$)

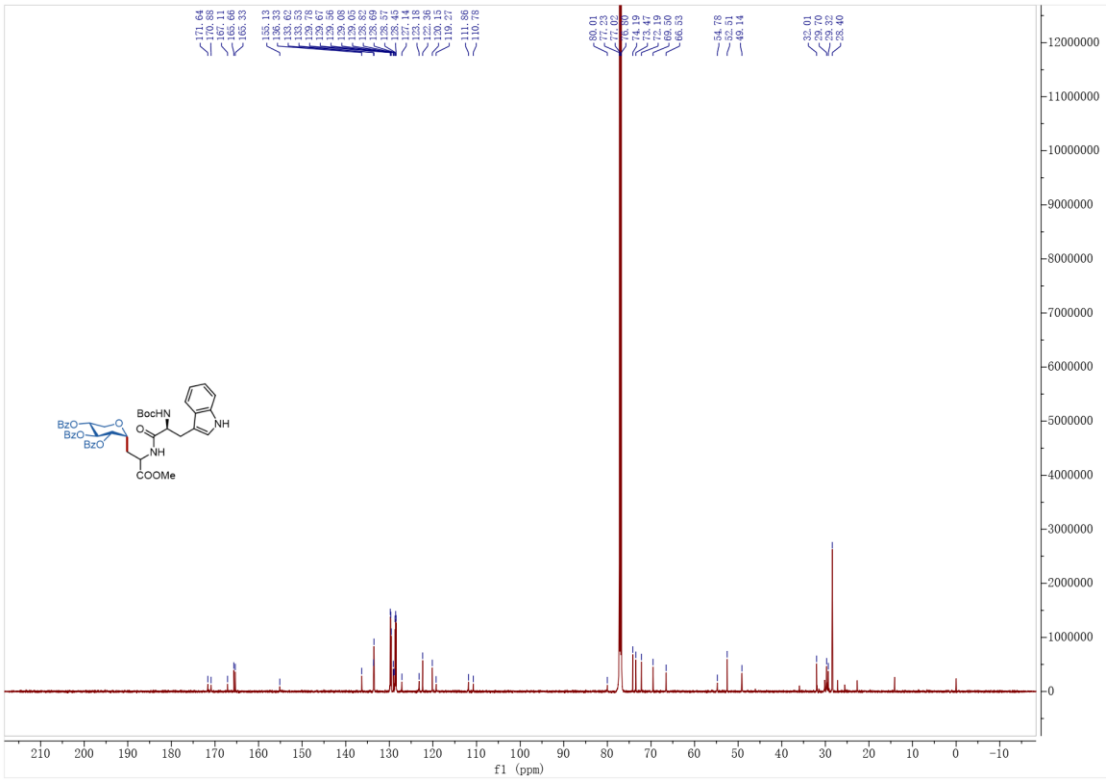

Fig 62. ^{13}C NMR of (**3i**) (150 MHz, $CDCl_3$)

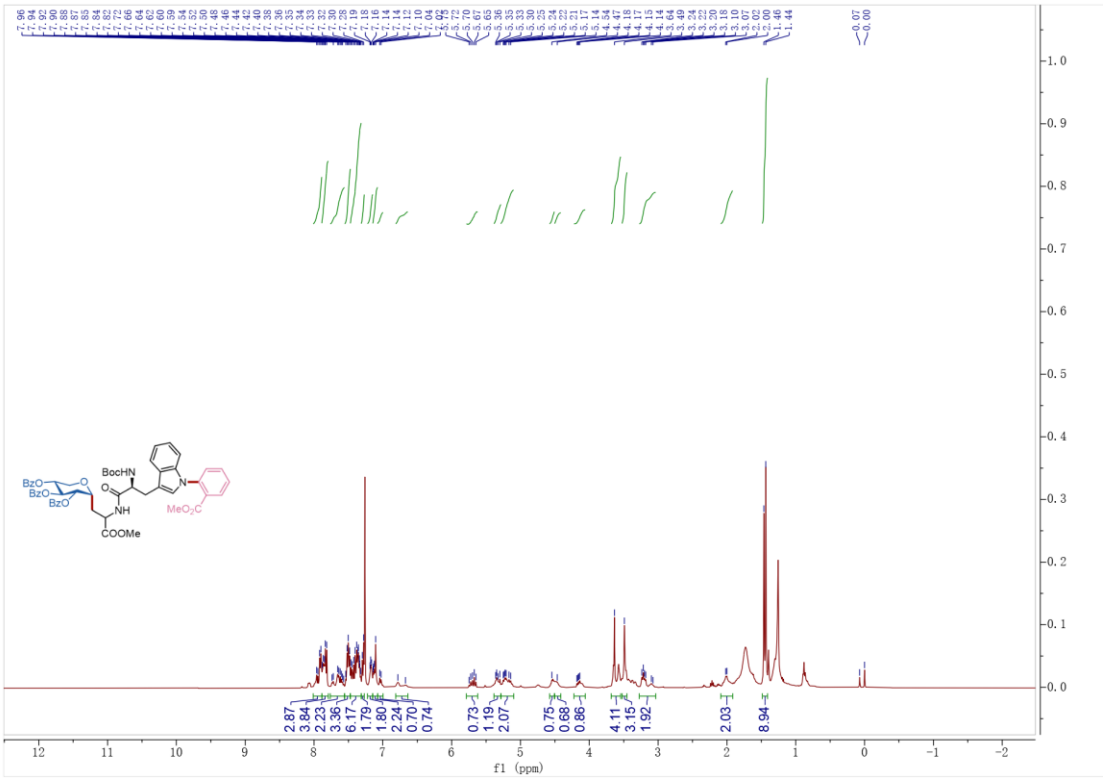

Fig 63. ^{1}H NMR of (**3i'**) (400 MHz, $CDCl_3$)

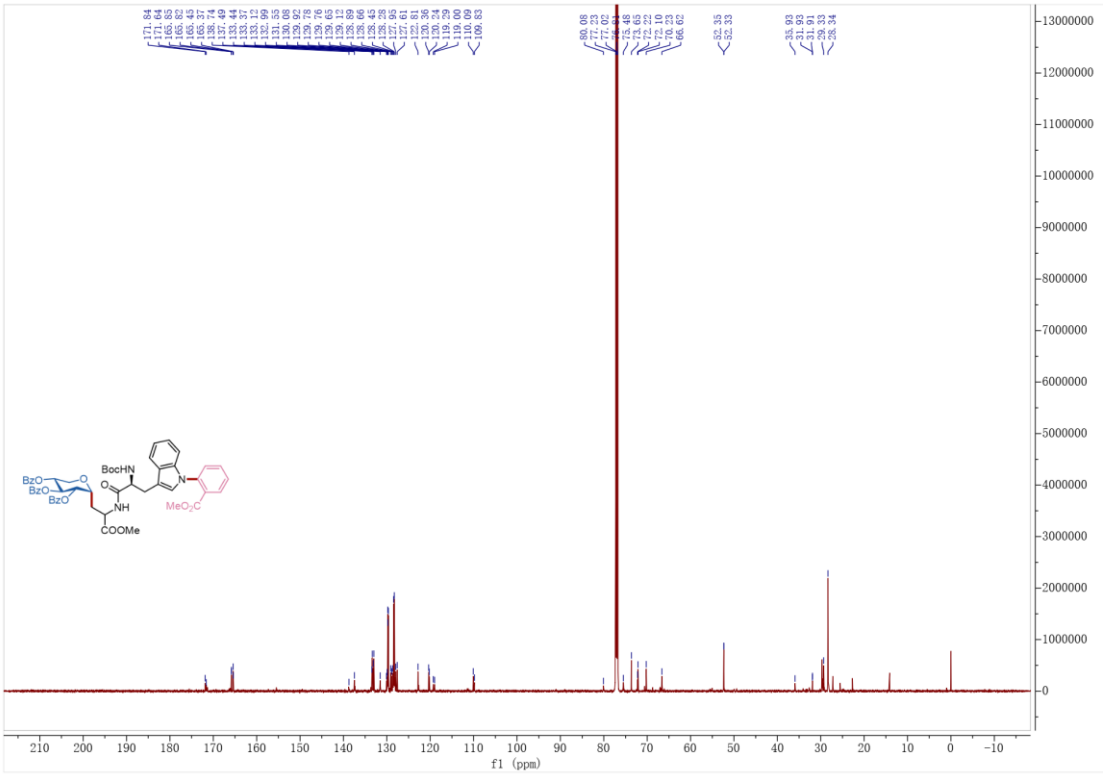

Fig 64. ^{13}C NMR of (**3i'**) (150 MHz, $CDCl_3$)

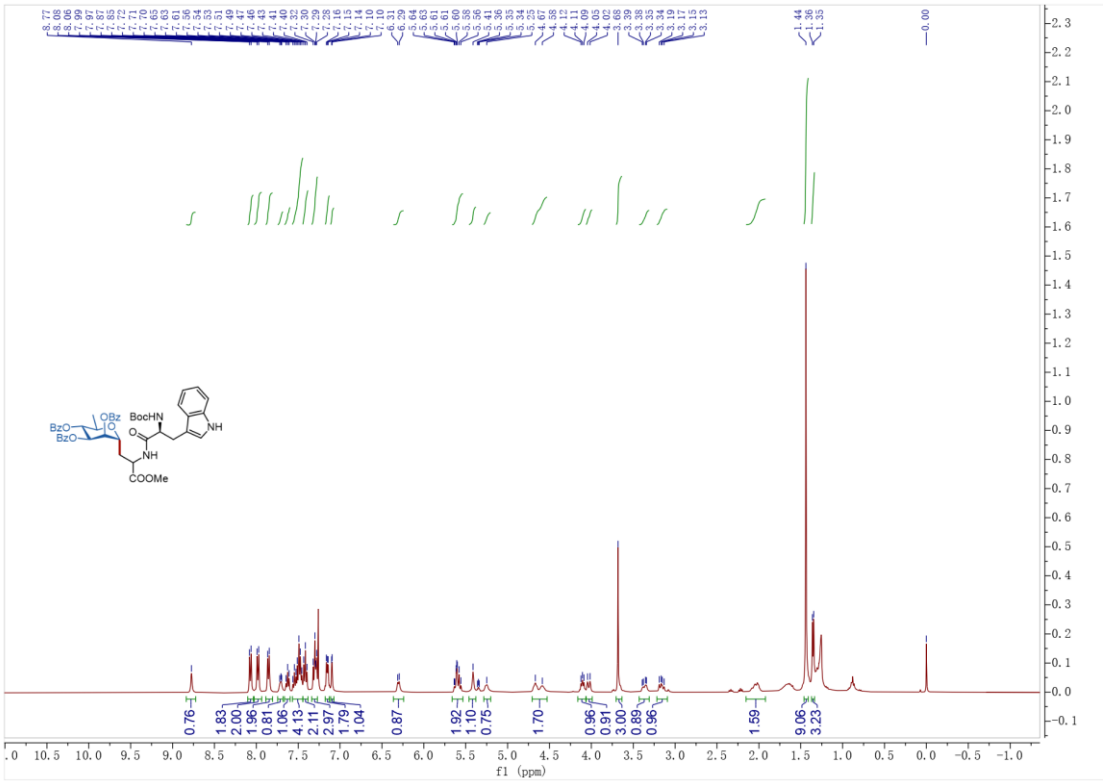

Fig 65. ^{1}H NMR of (**3j**) (400 MHz, $CDCl_3$)

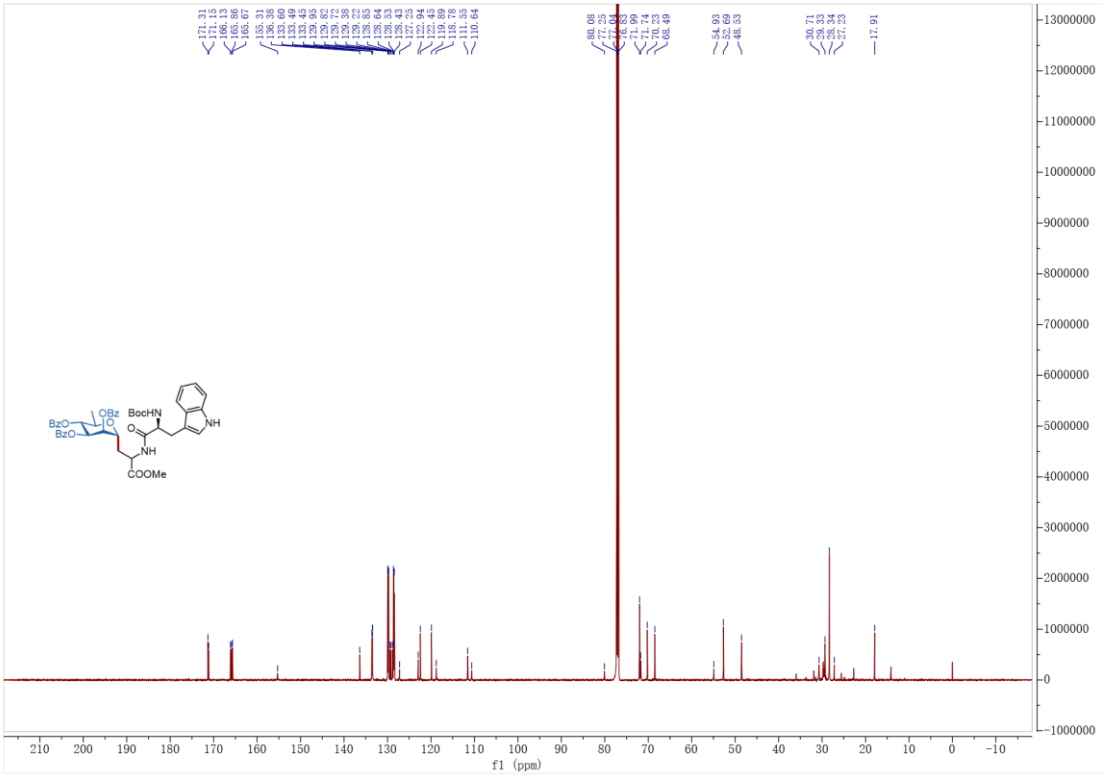

Fig 66. ^{13}C NMR of (**3j**) (150 MHz, $CDCl_3$)

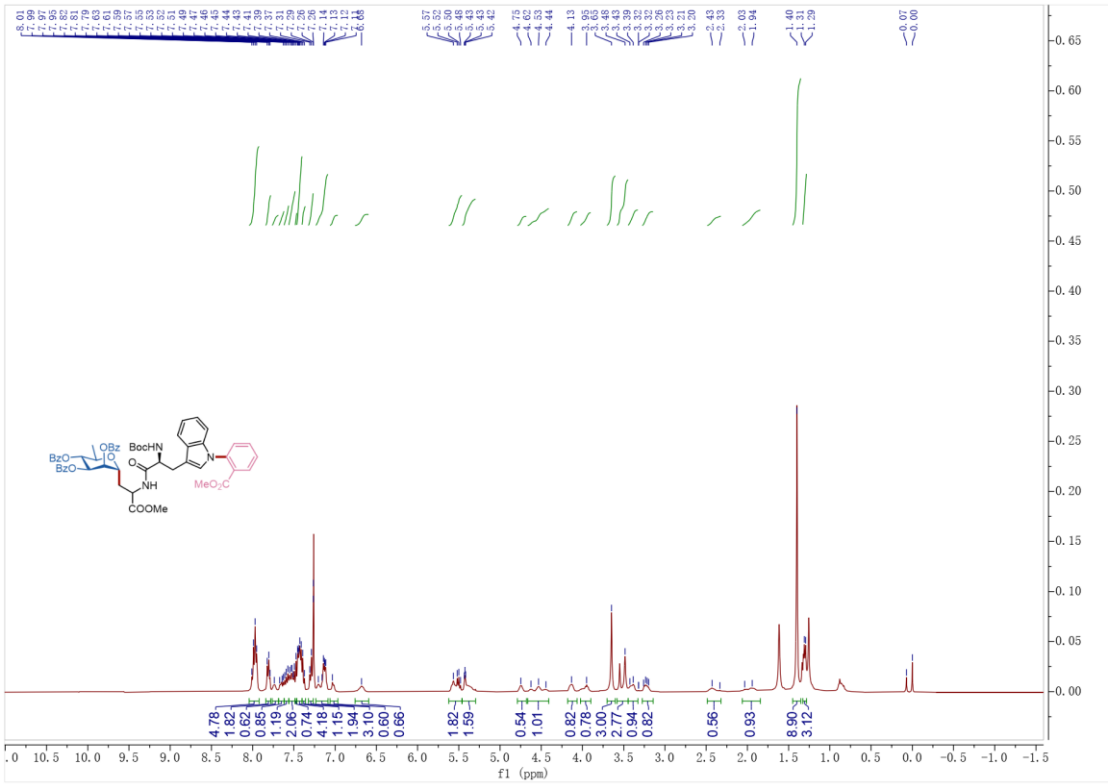

Fig 67. ^{1}H NMR of (**3j'**) (400 MHz, $CDCl_3$)

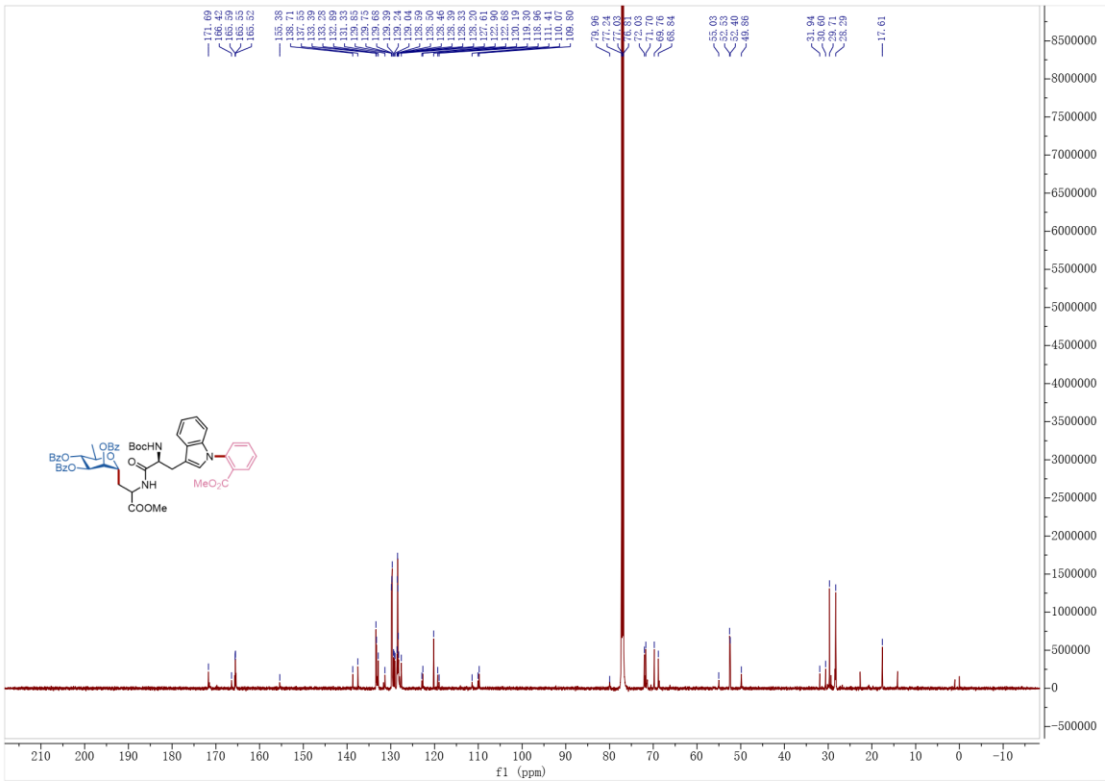

Fig 68. ^{13}C NMR of (**3j'**) (150 MHz, $CDCl_3$)

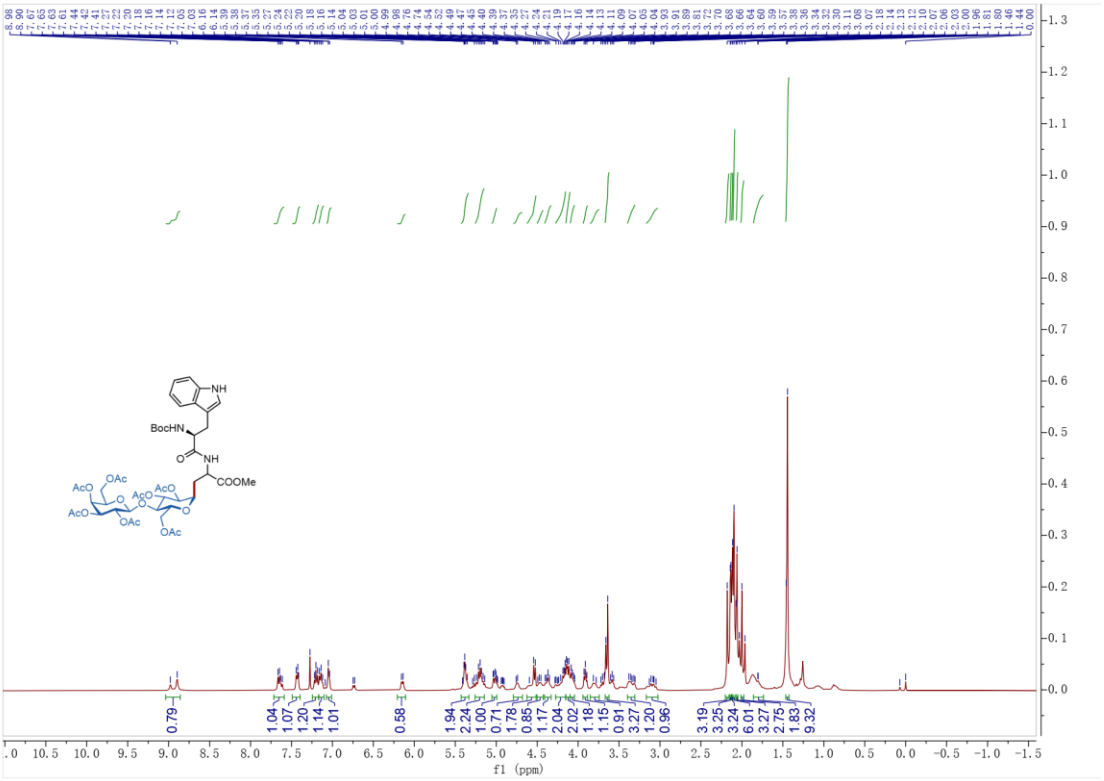

Fig 69. ^{1}H NMR of (**3k**) (400 MHz, $CDCl_3$)

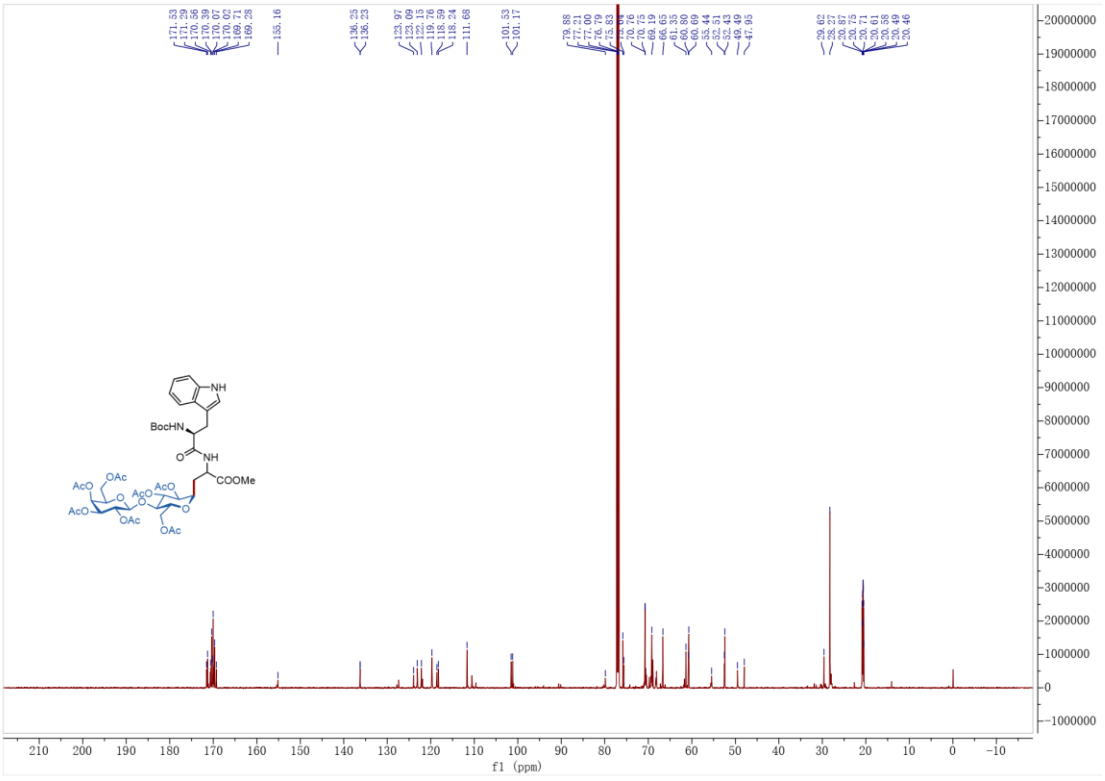

Fig 70. ^{13}C NMR of (**3k**) (150 MHz, $CDCl_3$)

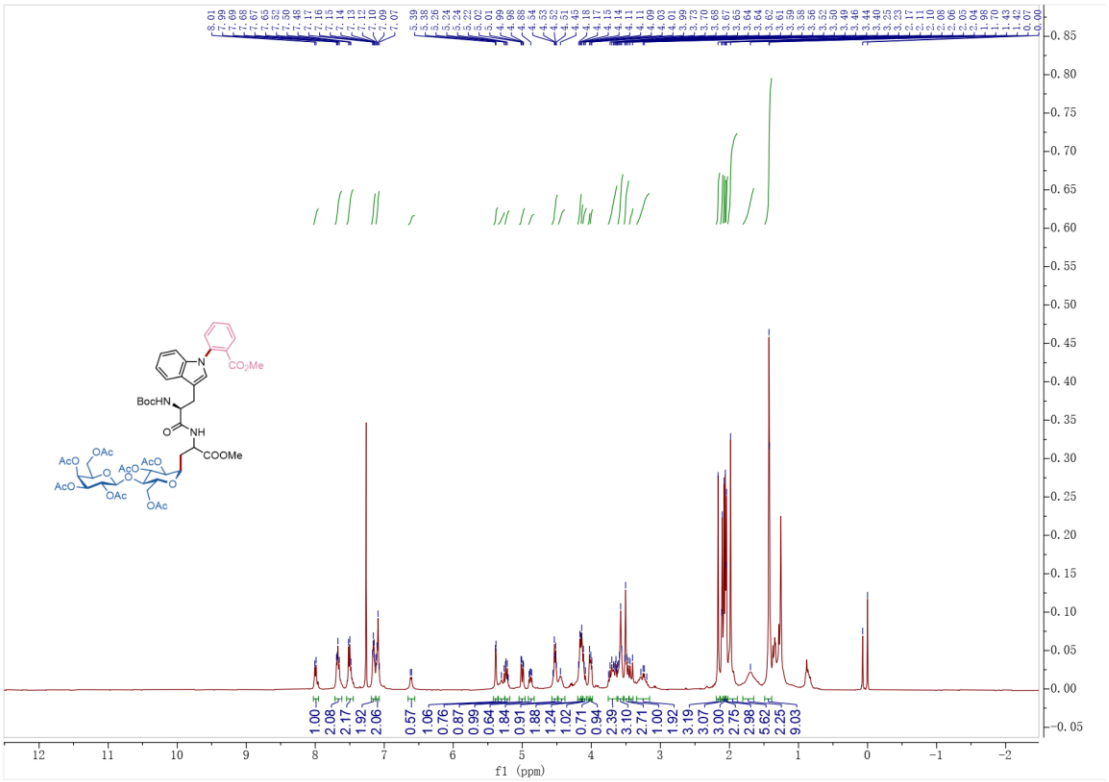

Fig 71. ^{1}H NMR of (**3k'**) (400 MHz, $CDCl_3$)

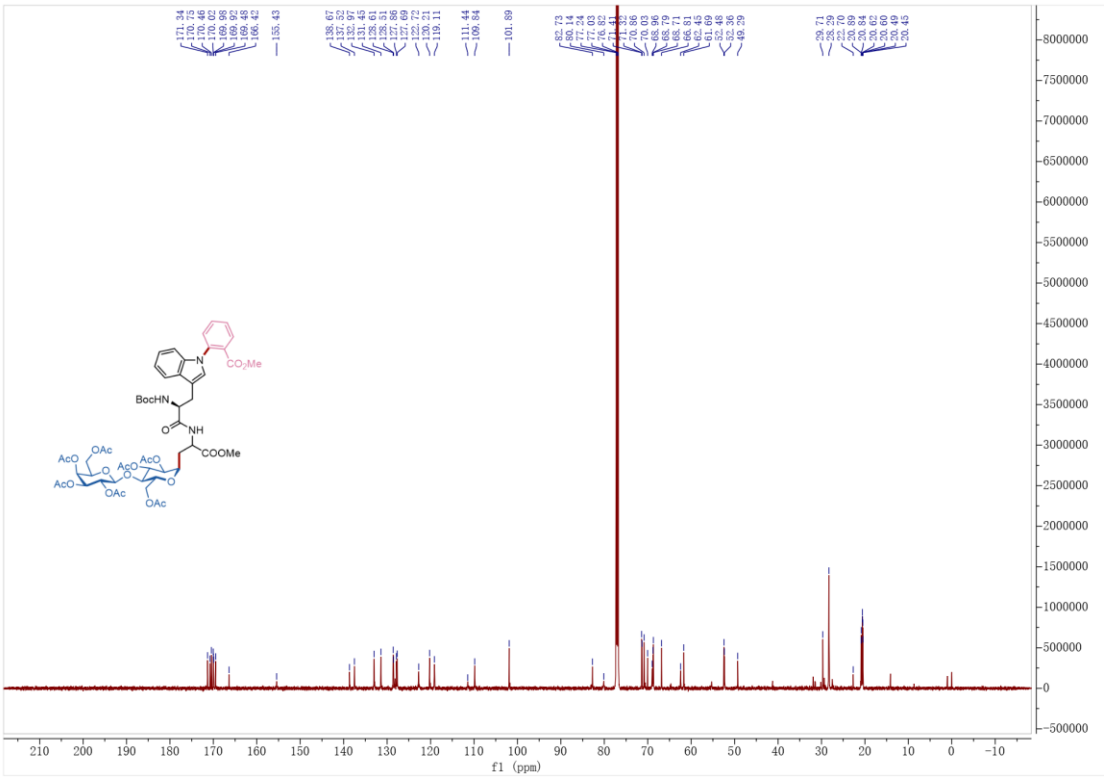

Fig 72. ^{13}C NMR of (**3k'**) (150 MHz, $CDCl_3$)

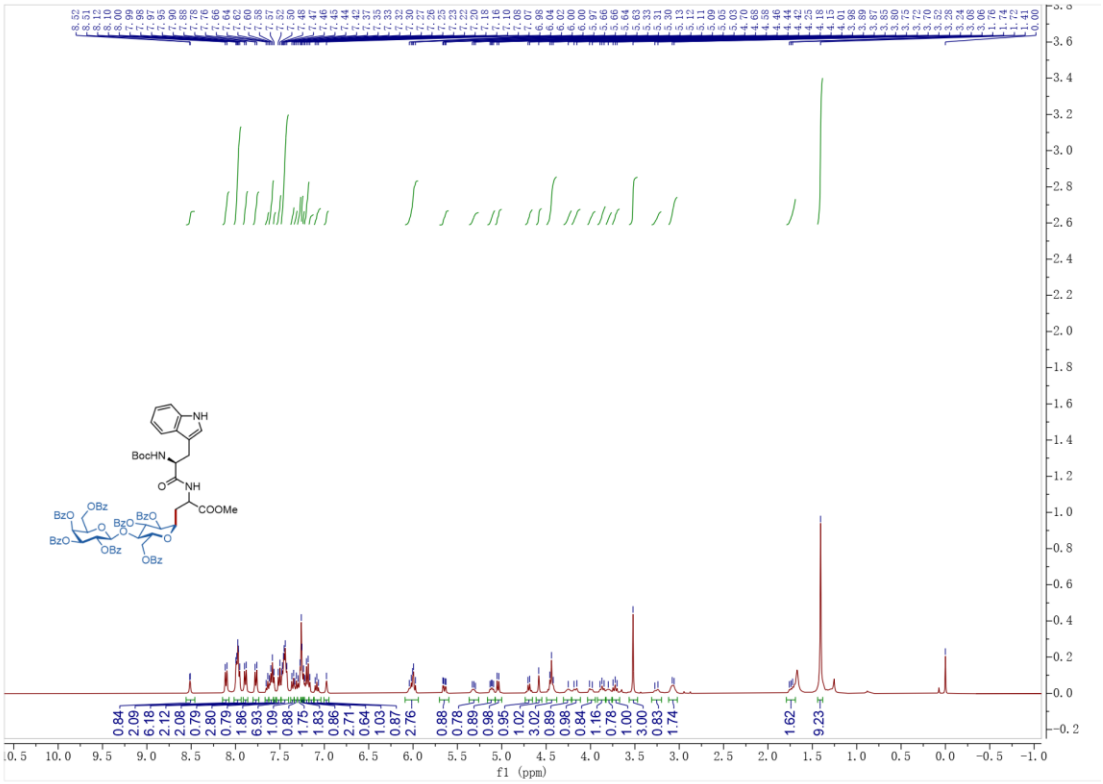

Fig 73. ^{1}H NMR of (**3l**) (400 MHz, $CDCl_3$)

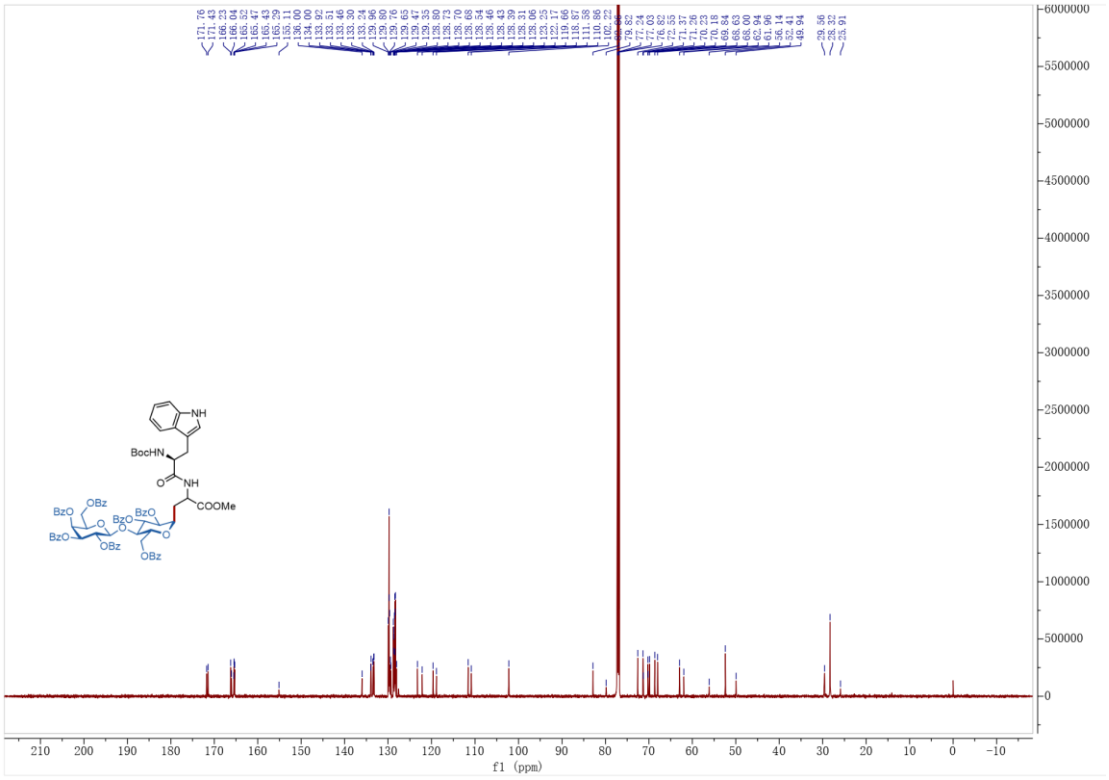

Fig 74. ^{13}C NMR of (**3l**) (150 MHz, $CDCl_3$)

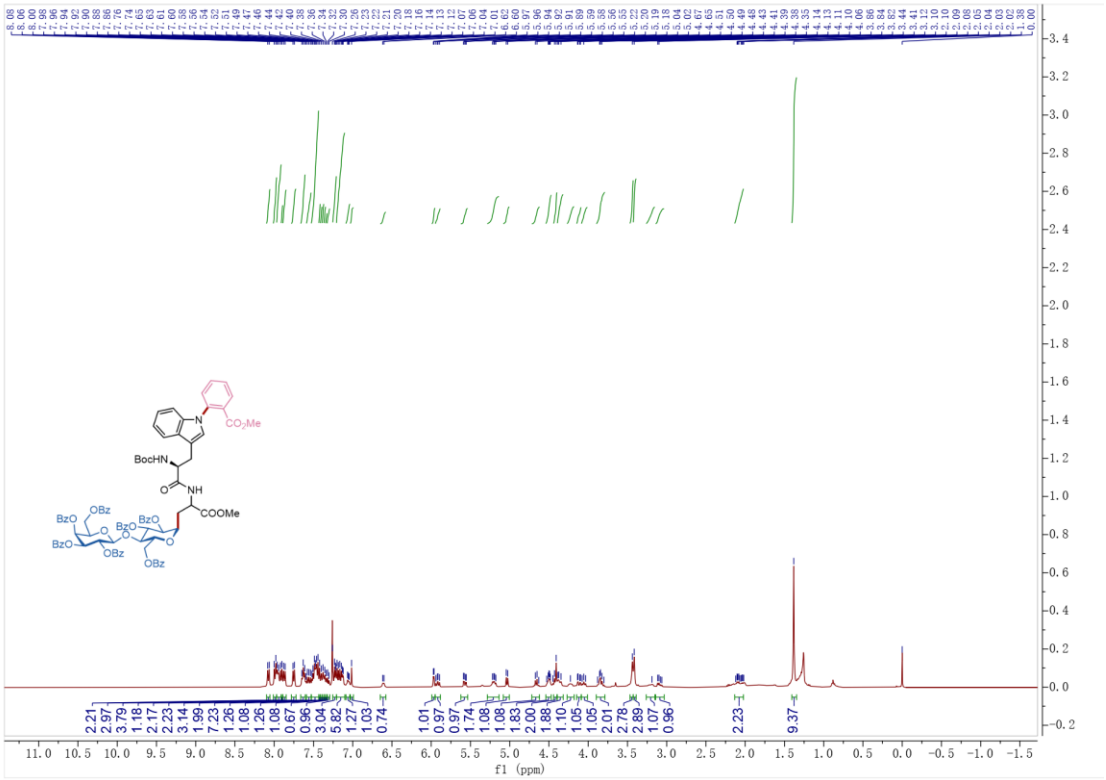

Fig 75. ^{1}H NMR of (**3l'**) (400 MHz, $CDCl_3$)

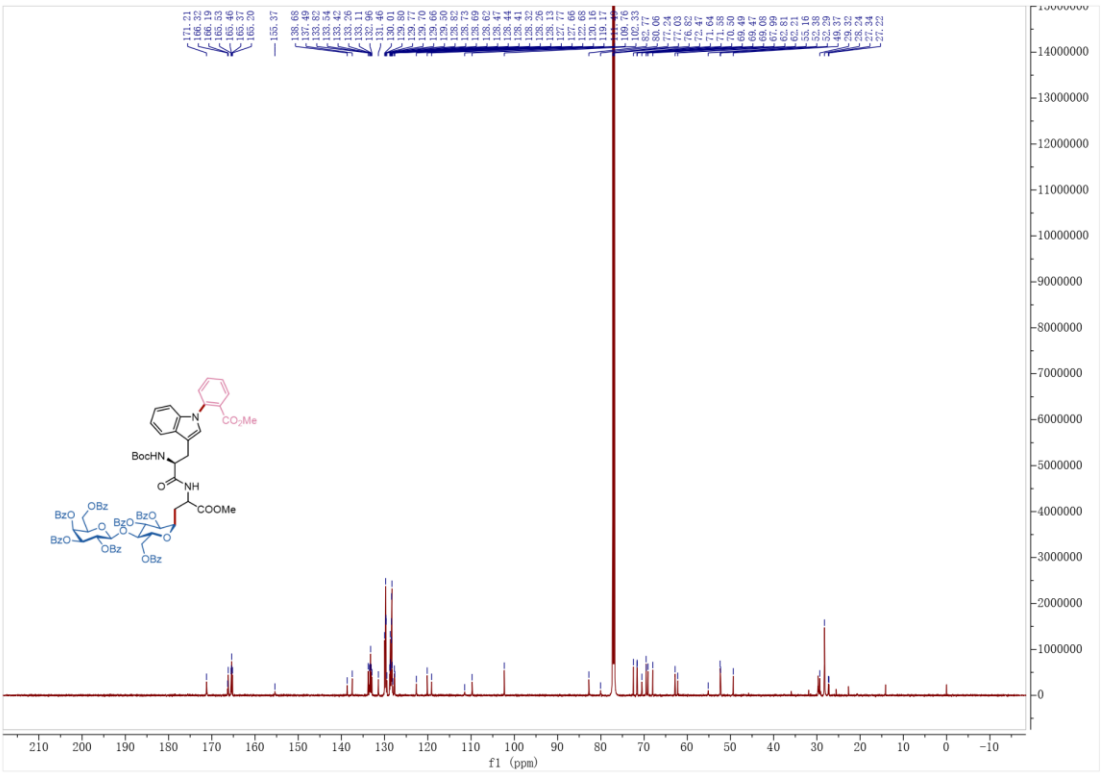

Fig 76. ^{13}C NMR of (**3l'**) (150 MHz, $CDCl_3$)

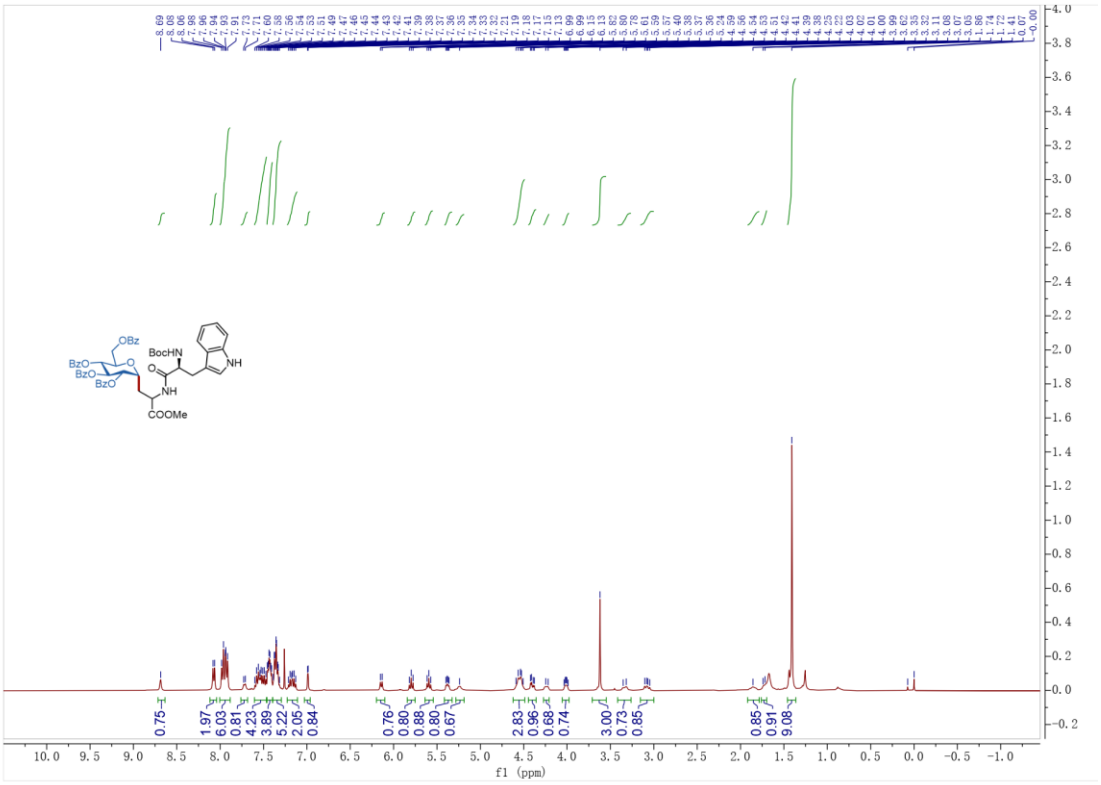

Fig 77. ^{1}H NMR of (**3m**) (400 MHz, $CDCl_3$)

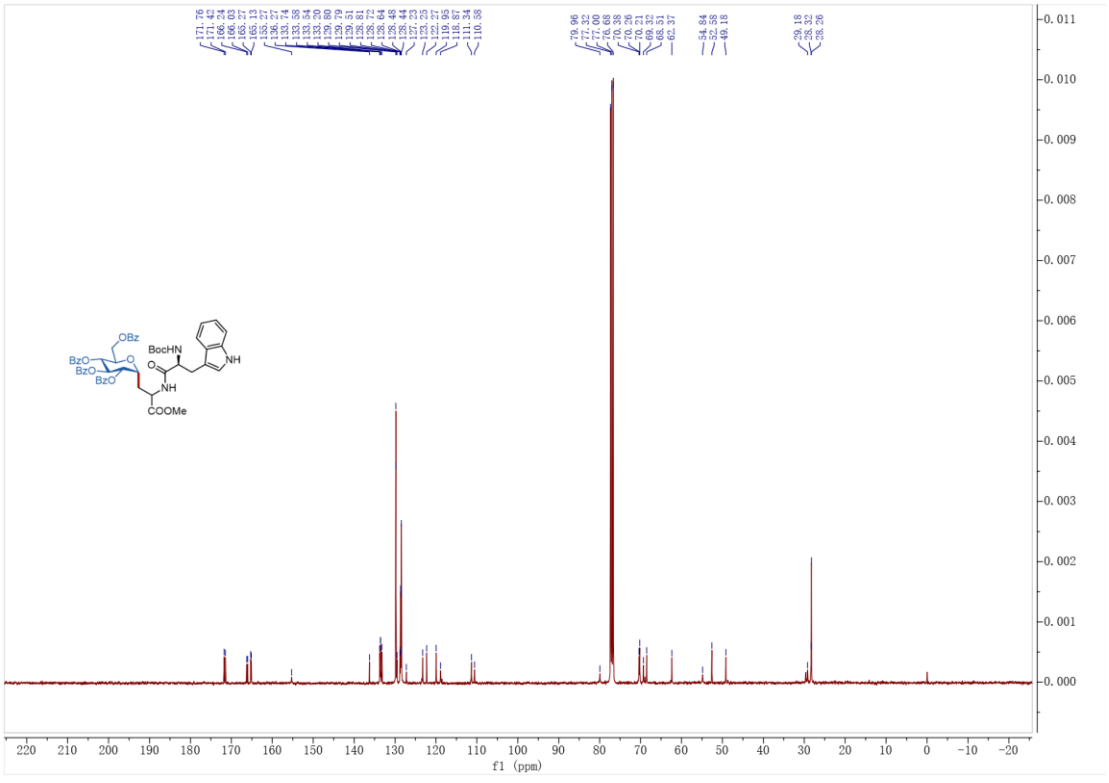

Fig 78. ^{13}C NMR of (**3m**) (100 MHz, $CDCl_3$)

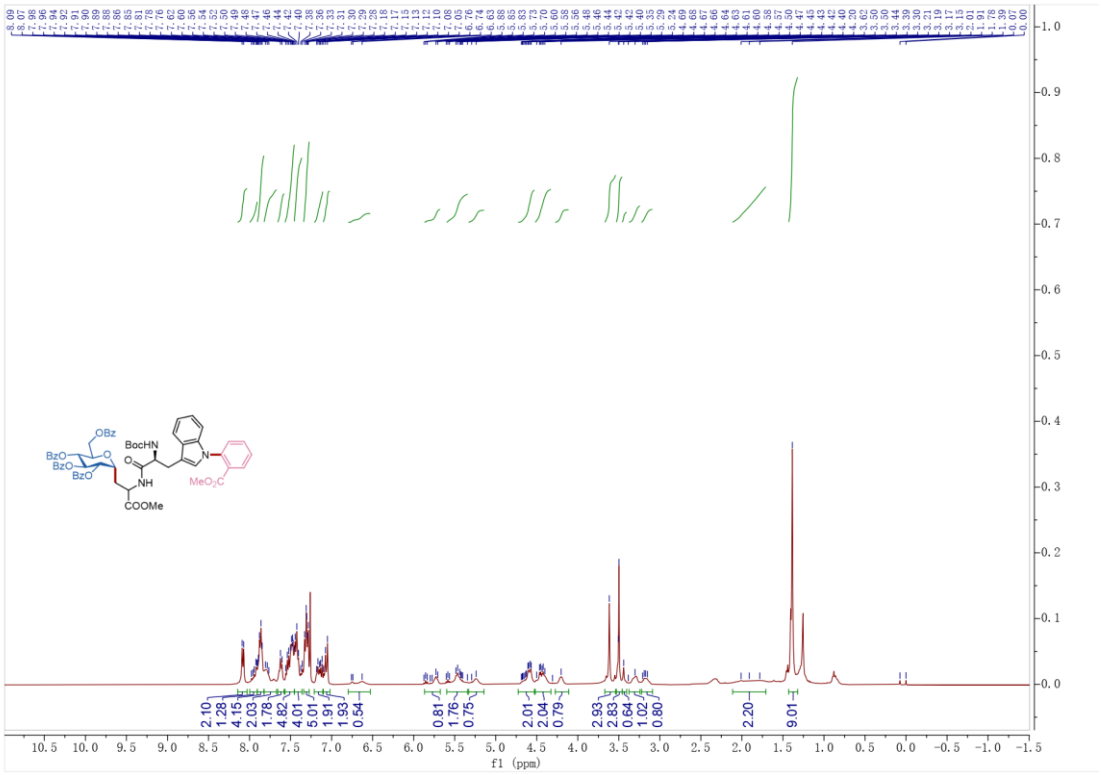

Fig 79. ^{1}H NMR of (**3m'**) (400 MHz, $CDCl_3$)

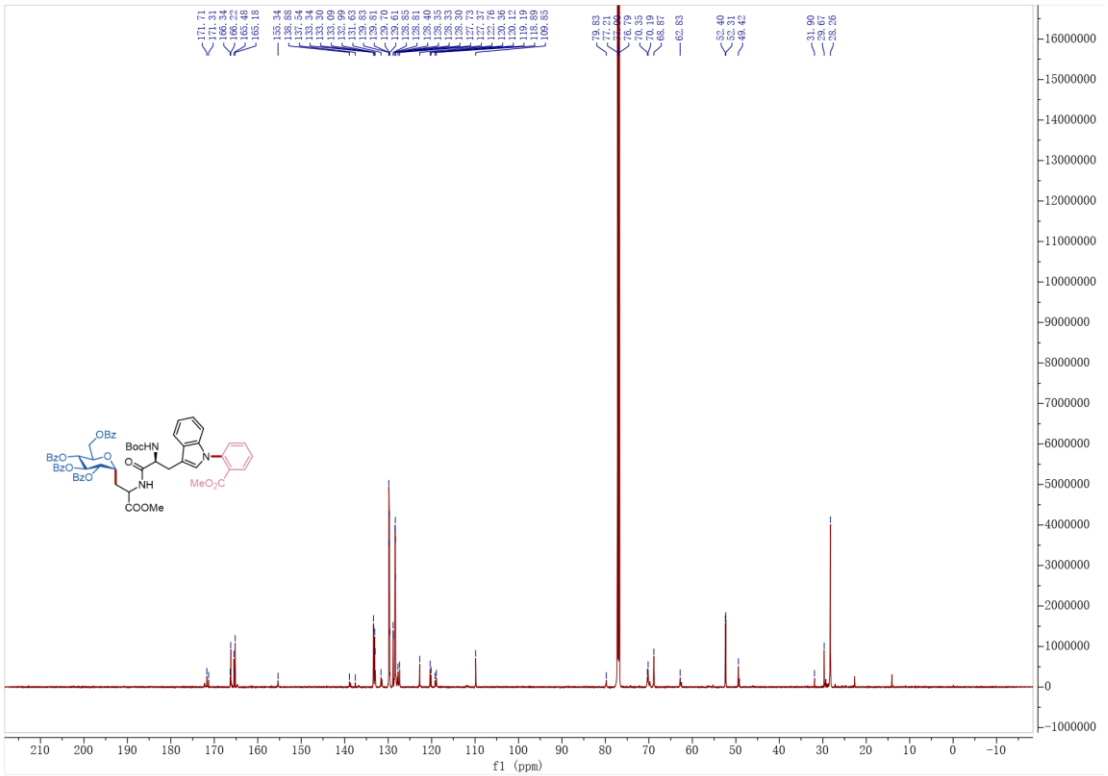

Fig 80. ^{13}C NMR of (**3m'**) (150 MHz, $CDCl_3$)

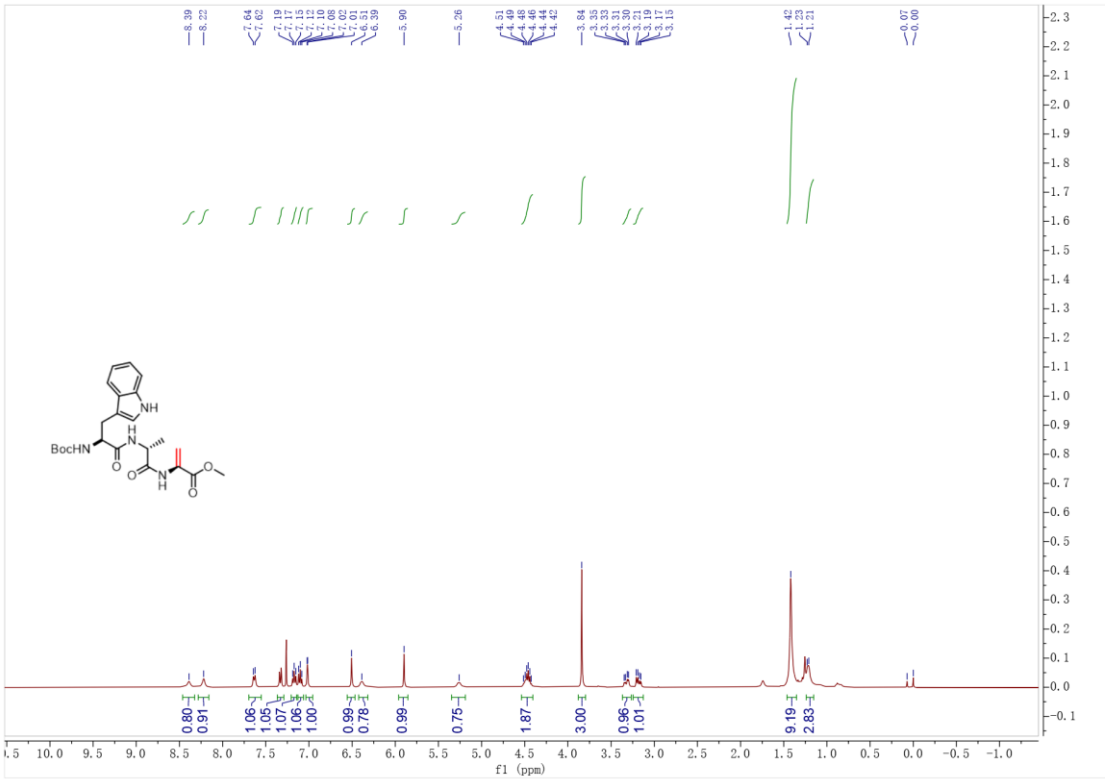

Fig 81. ^{1}H NMR of (**6a**) (400 MHz, $CDCl_3$)

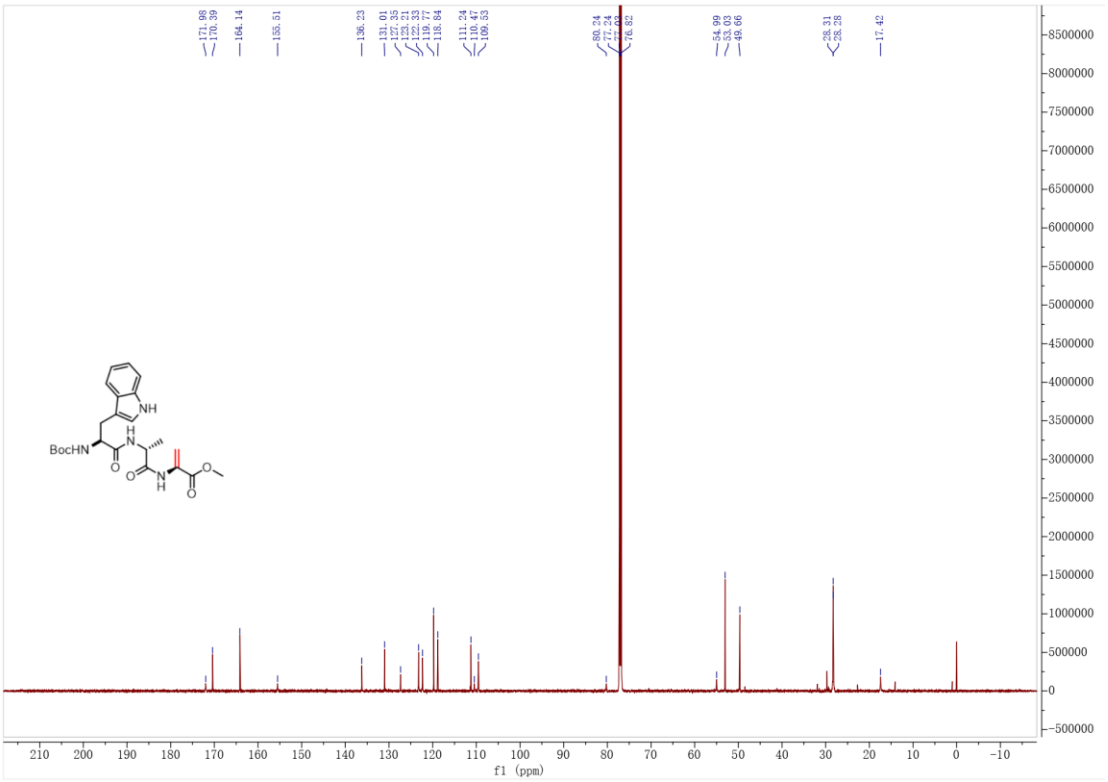

Fig 82. ^{13}C NMR of (**6a**) (150 MHz, $CDCl_3$)

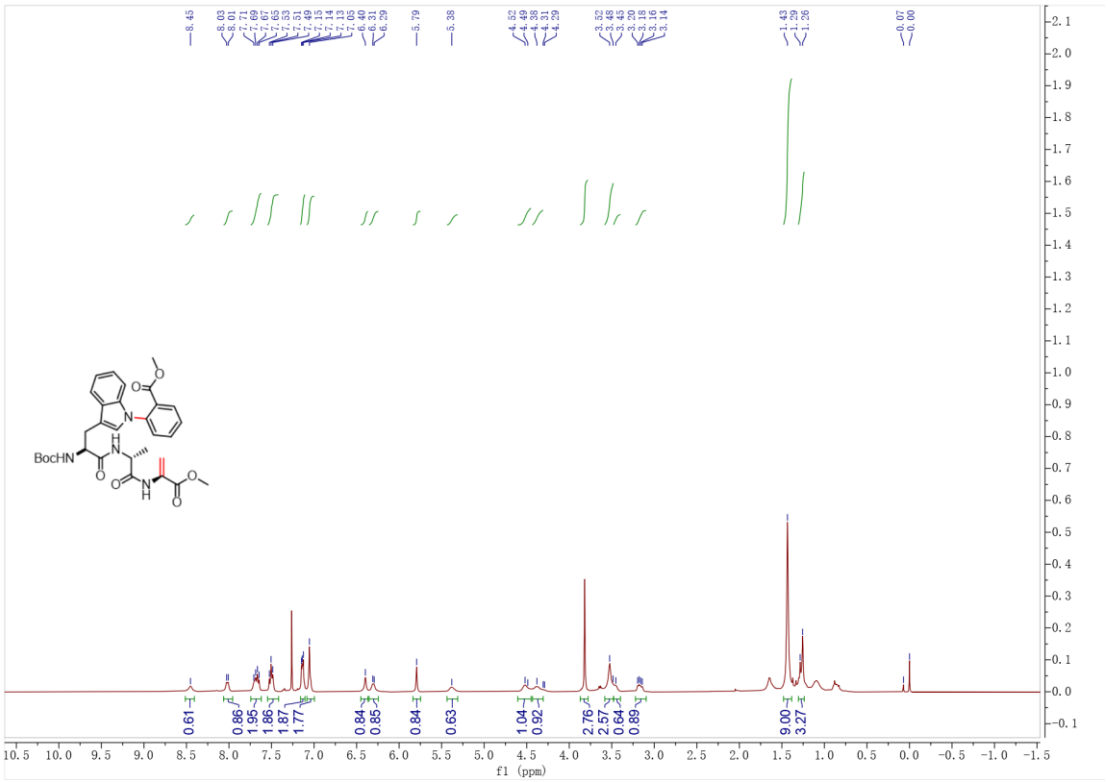

Fig 83. ^{1}H NMR of (**6a'**) (400 MHz, $CDCl_3$)

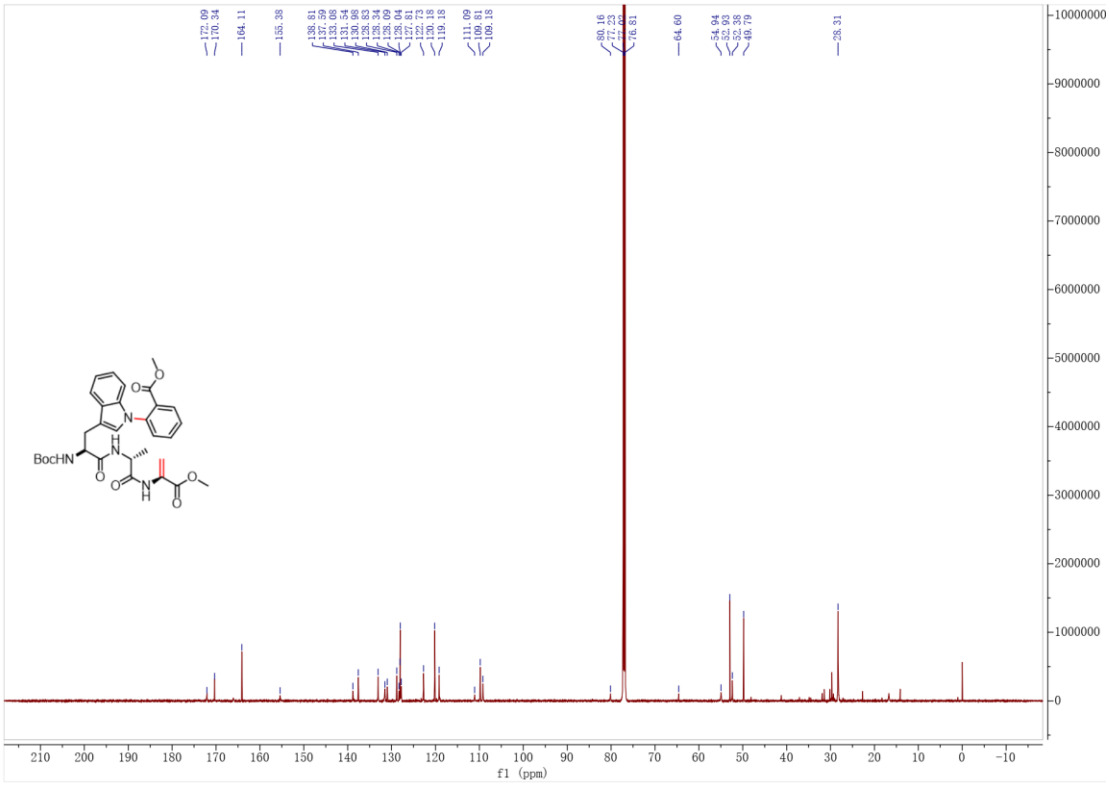

Fig 84. ^{13}C NMR of (**6a'**) (150 MHz, $CDCl_3$)

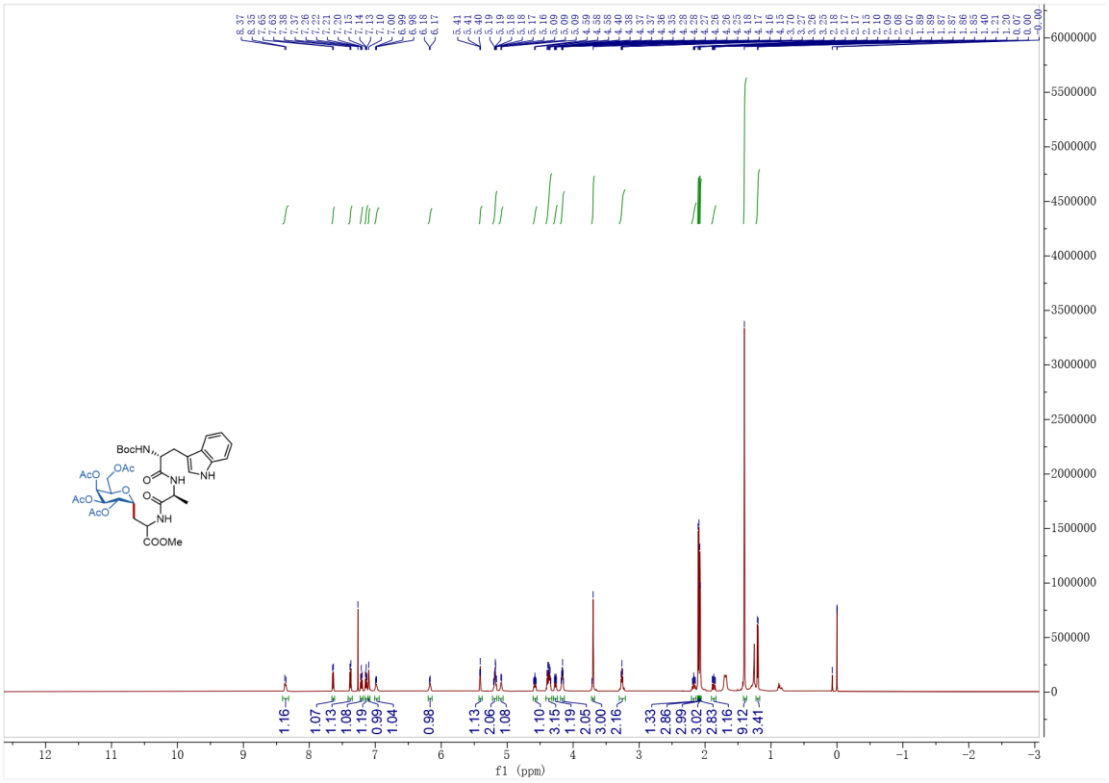

Fig 85. ^{1}H NMR of (**7a**) (600 MHz, $CDCl_3$)

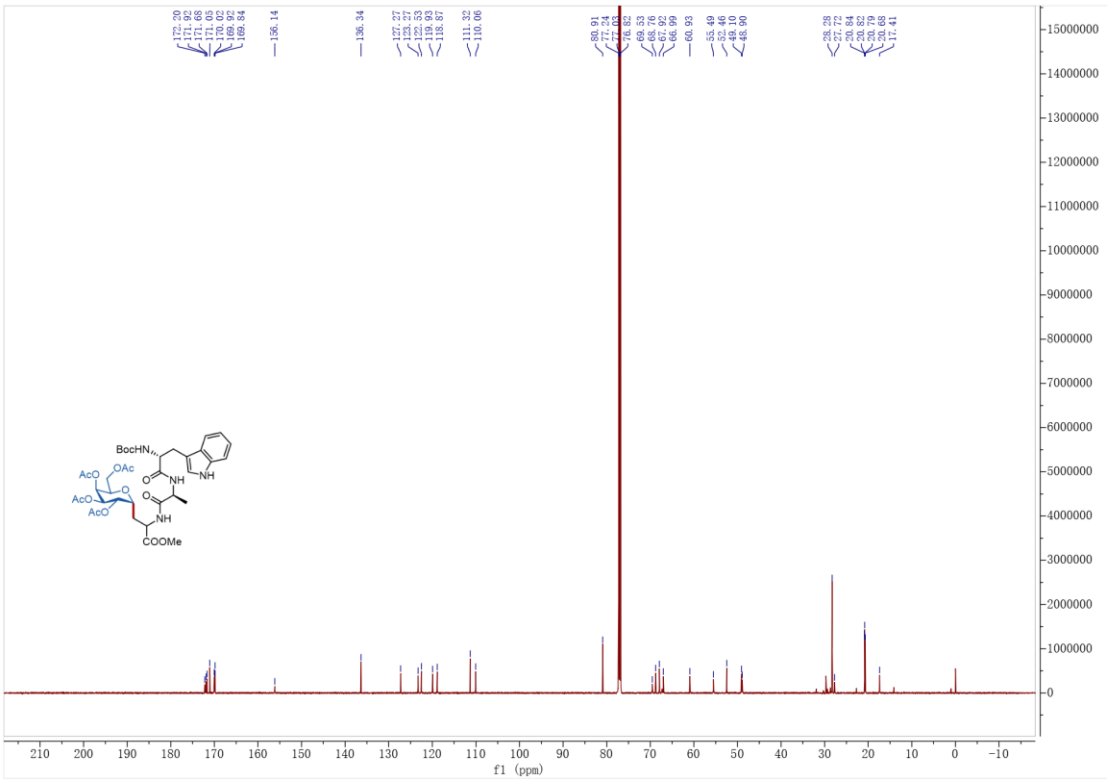

Fig 86. ^{13}C NMR of (**7a**) (150 MHz, $CDCl_3$)

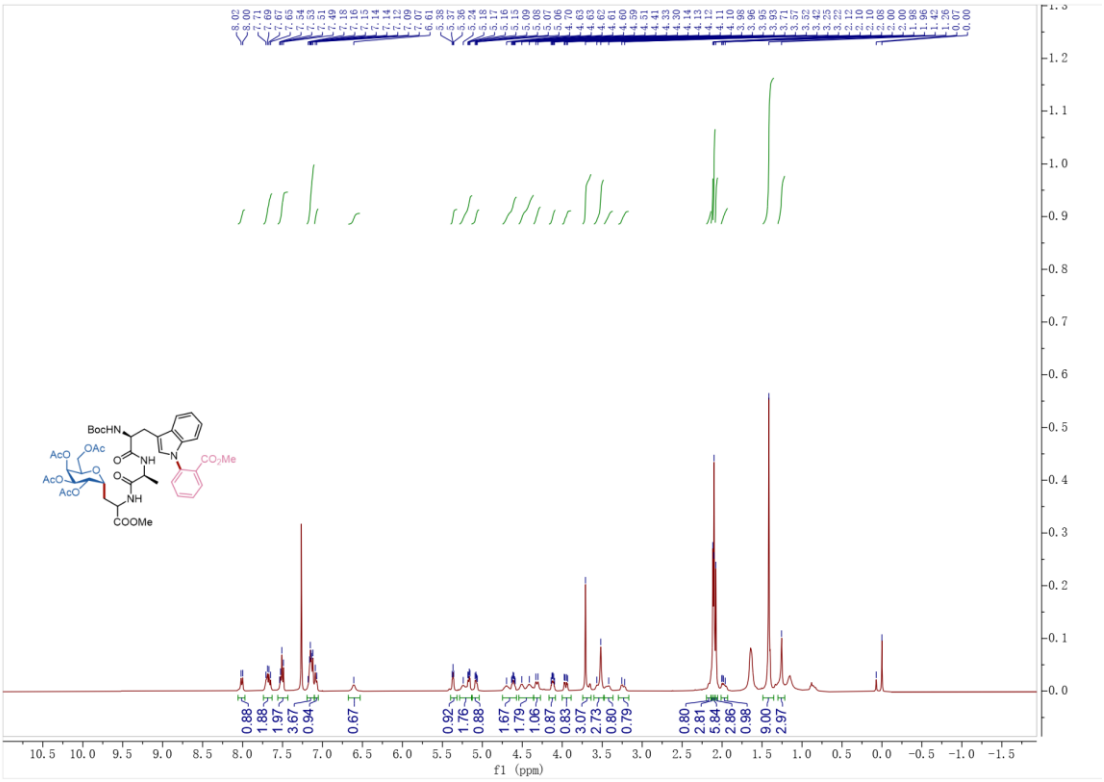

Fig 87. ^{1}H NMR of (**7a'**) (400 MHz, $CDCl_3$)

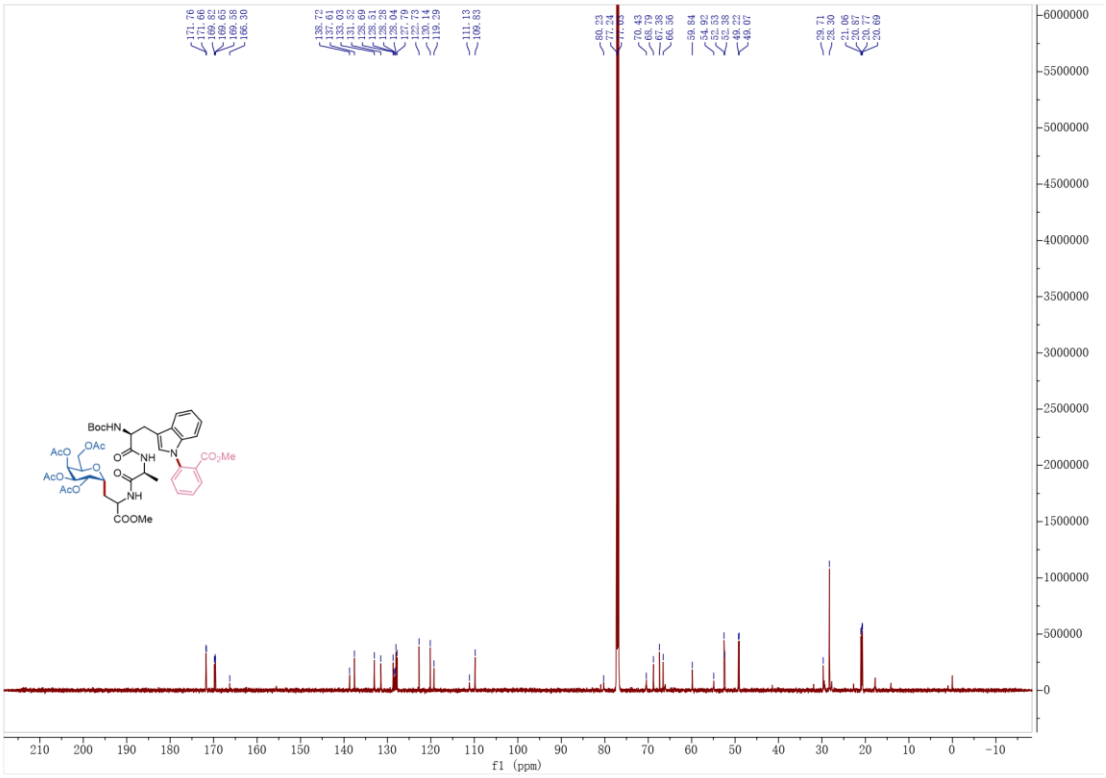

Fig 88. ^{13}C NMR of (**7a'**) (150 MHz, $CDCl_3$)

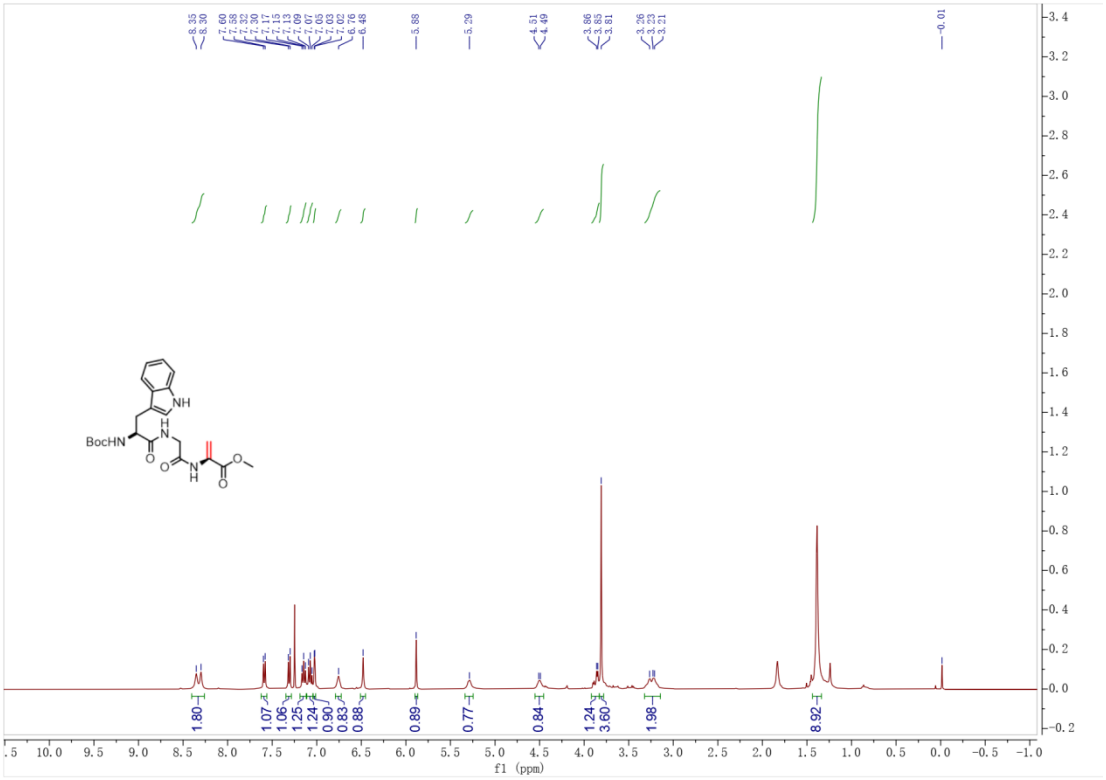

Fig 89. ^{1}H NMR of (**6b**) (400 MHz, $CDCl_3$)

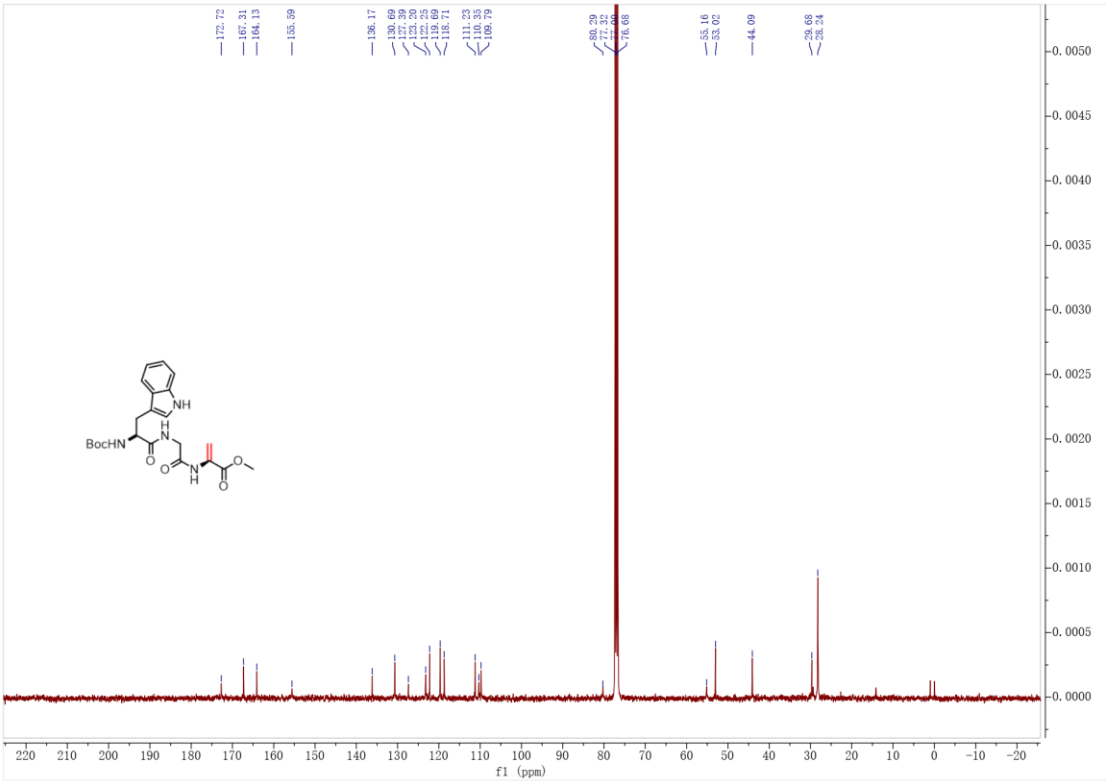

Fig 90. ^{13}C NMR of (**6b**) (150 MHz, $CDCl_3$)

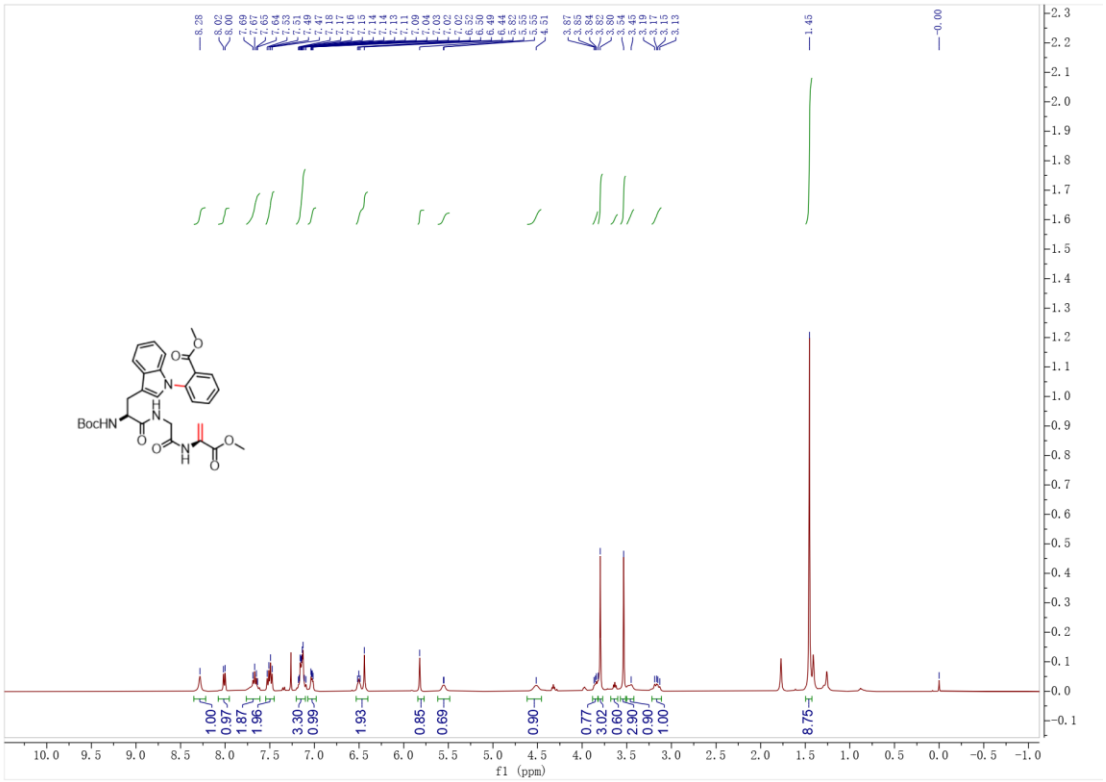

Fig 91. ^{1}H NMR of (**6b'**) (400 MHz, $CDCl_3$)

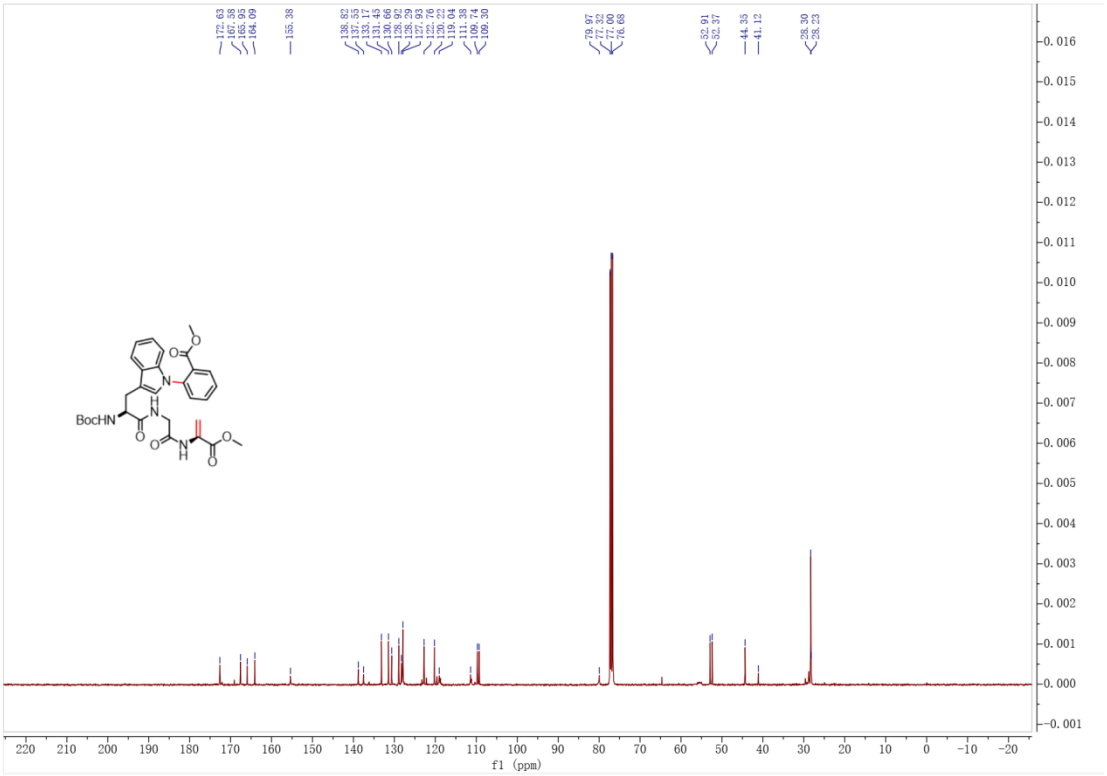

Fig 92. ^{13}C NMR of (**6b'**) (100 MHz, $CDCl_3$)

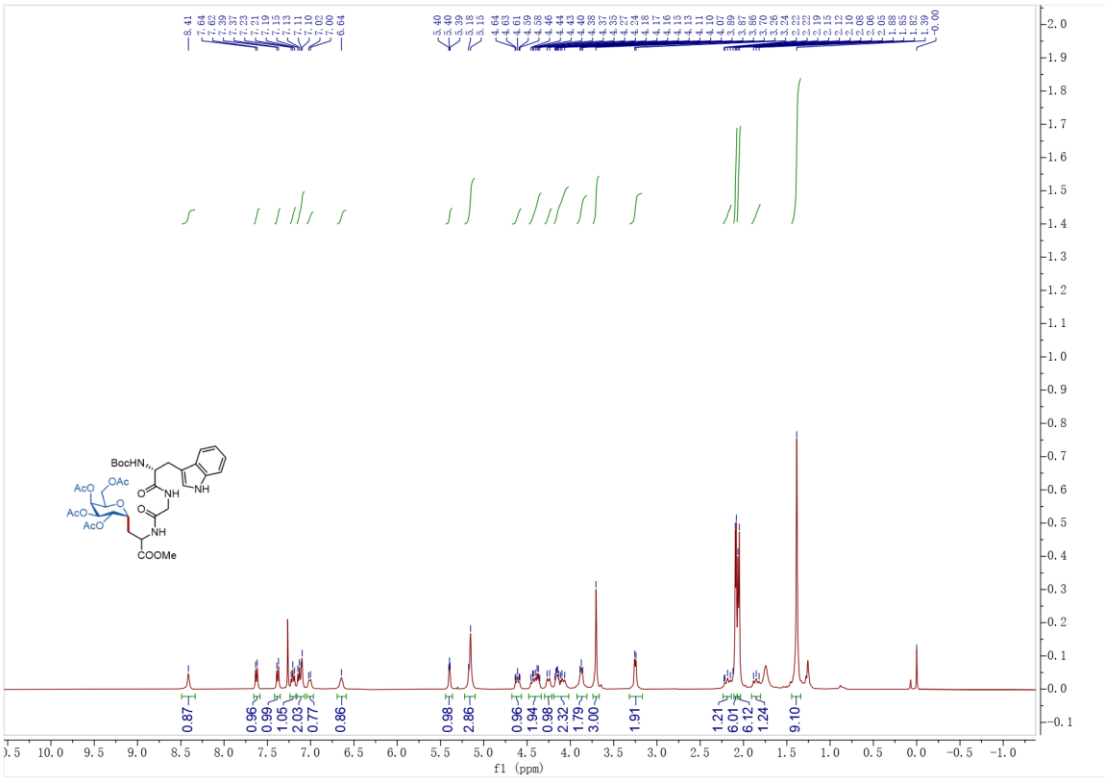

Fig 93. ^{1}H NMR of (**7b**) (400 MHz, $CDCl_3$)

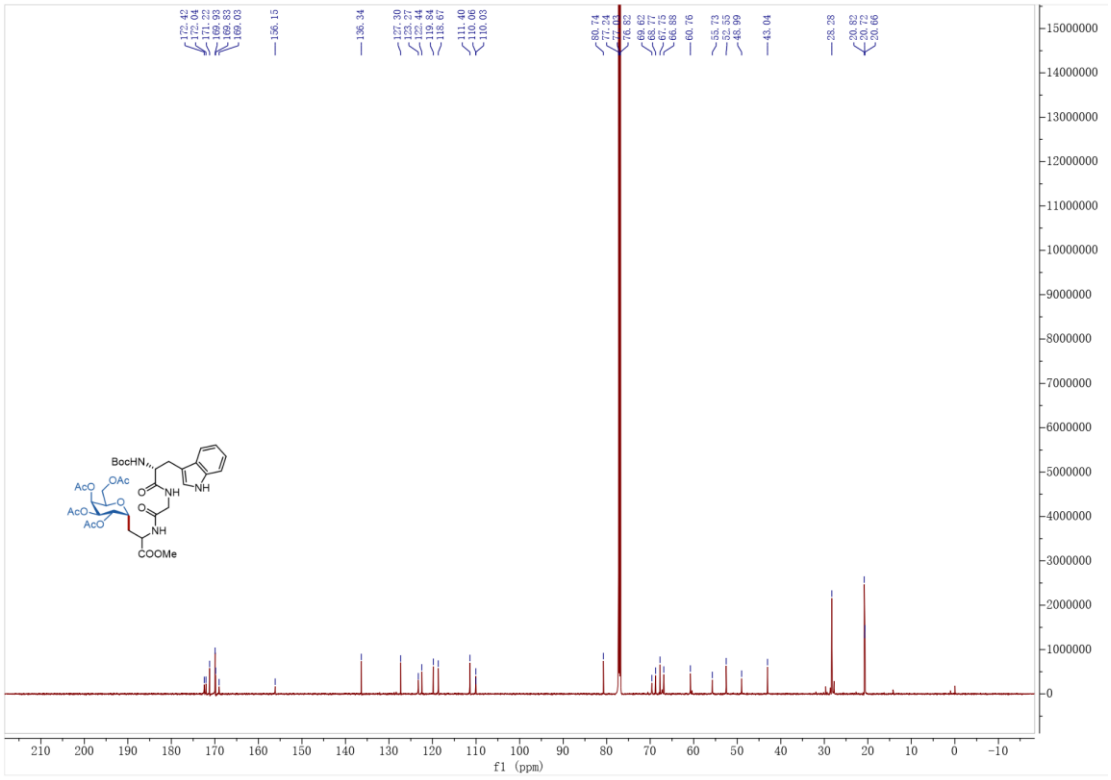

Fig 94. ^{13}C NMR of (**7b**) (150 MHz, $CDCl_3$)

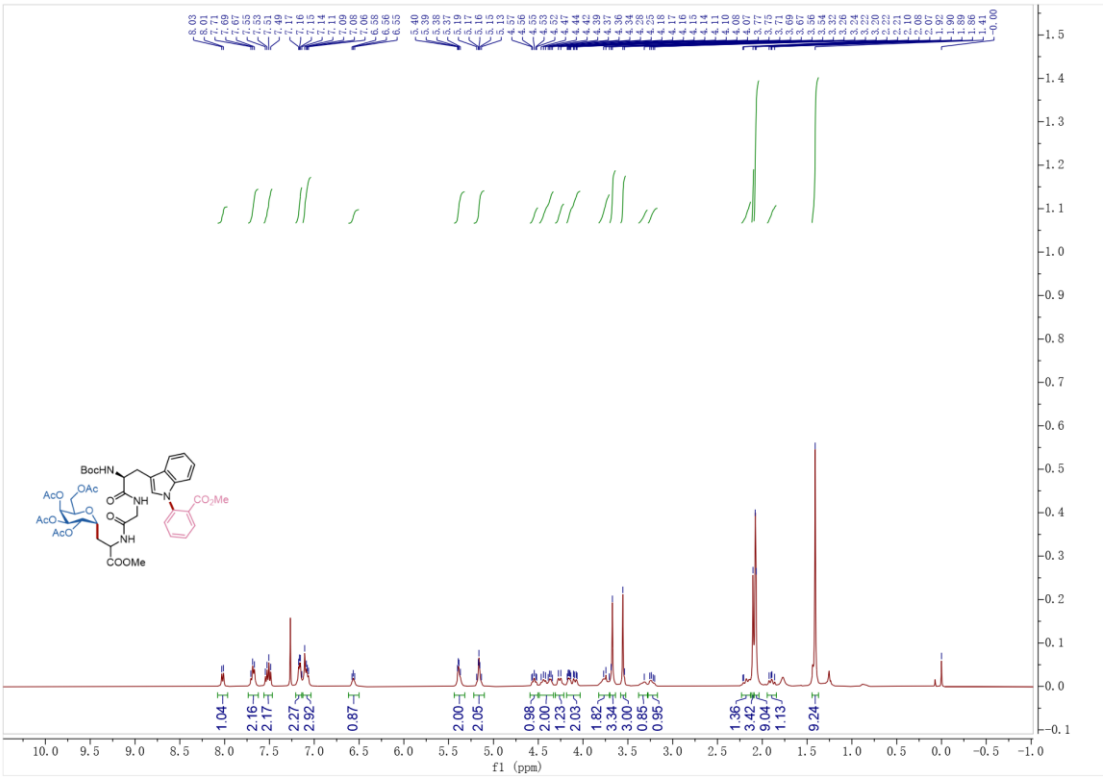

Fig 95. ^{1}H NMR of (**7b'**) (400 MHz, $CDCl_3$)

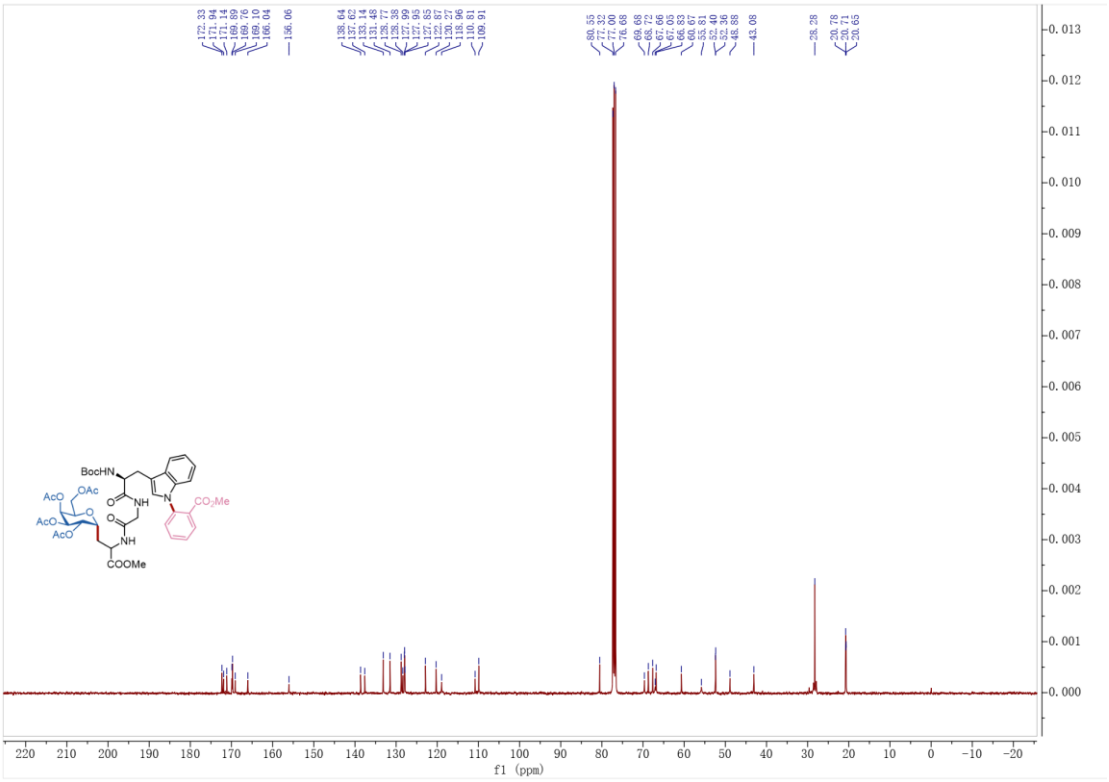

Fig 96. ^{13}C NMR of (**7b'**) (100 MHz, $CDCl_3$)

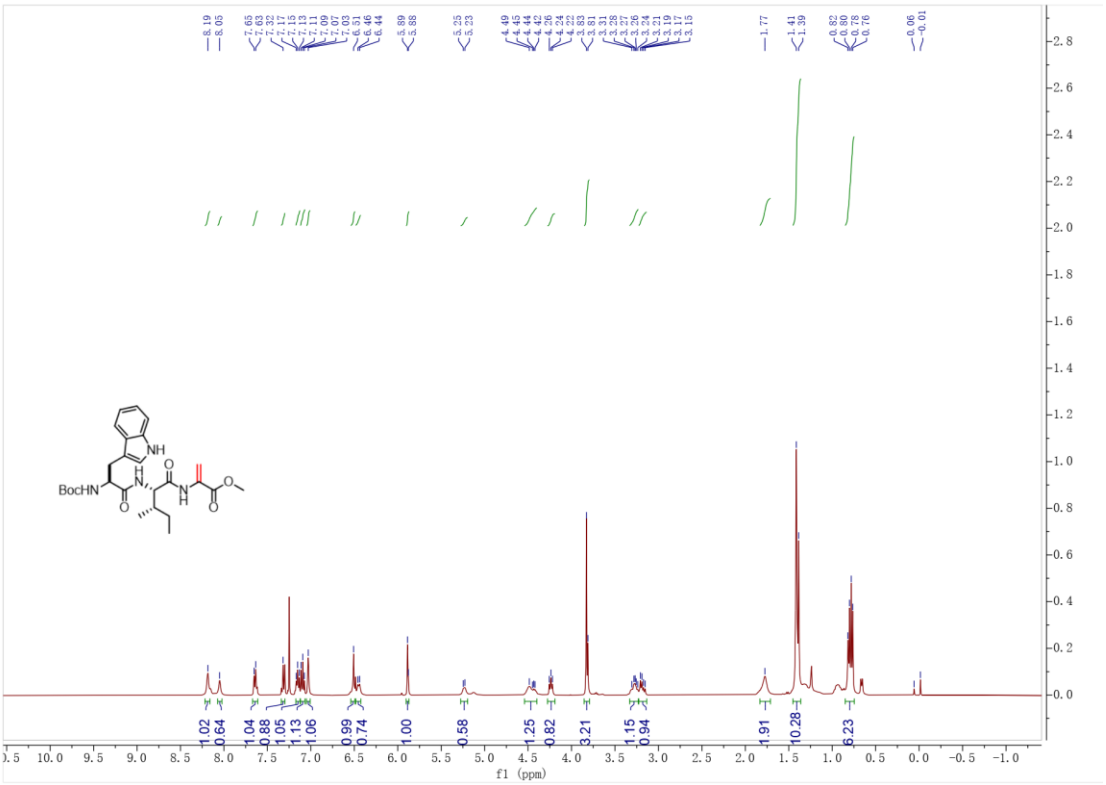

Fig 97. ^{1}H NMR of (**6c**) (400 MHz, $CDCl_3$)

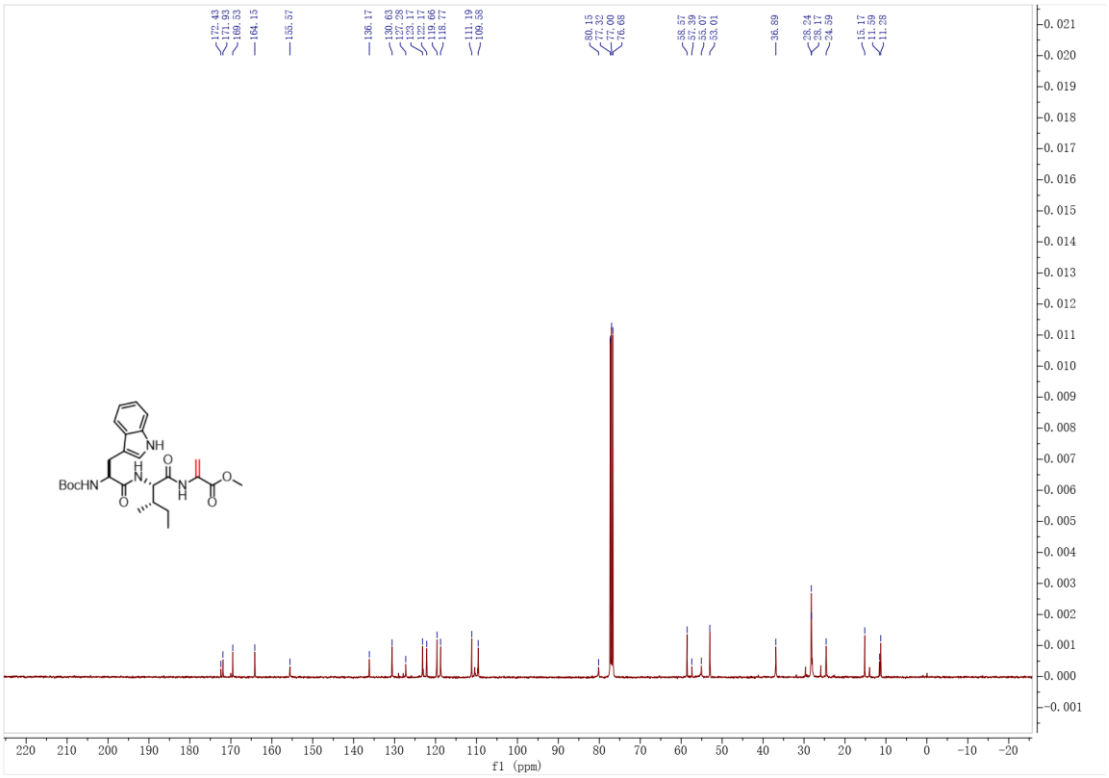

Fig 98. ^{13}C NMR of (**6c**) (100 MHz, $CDCl_3$)

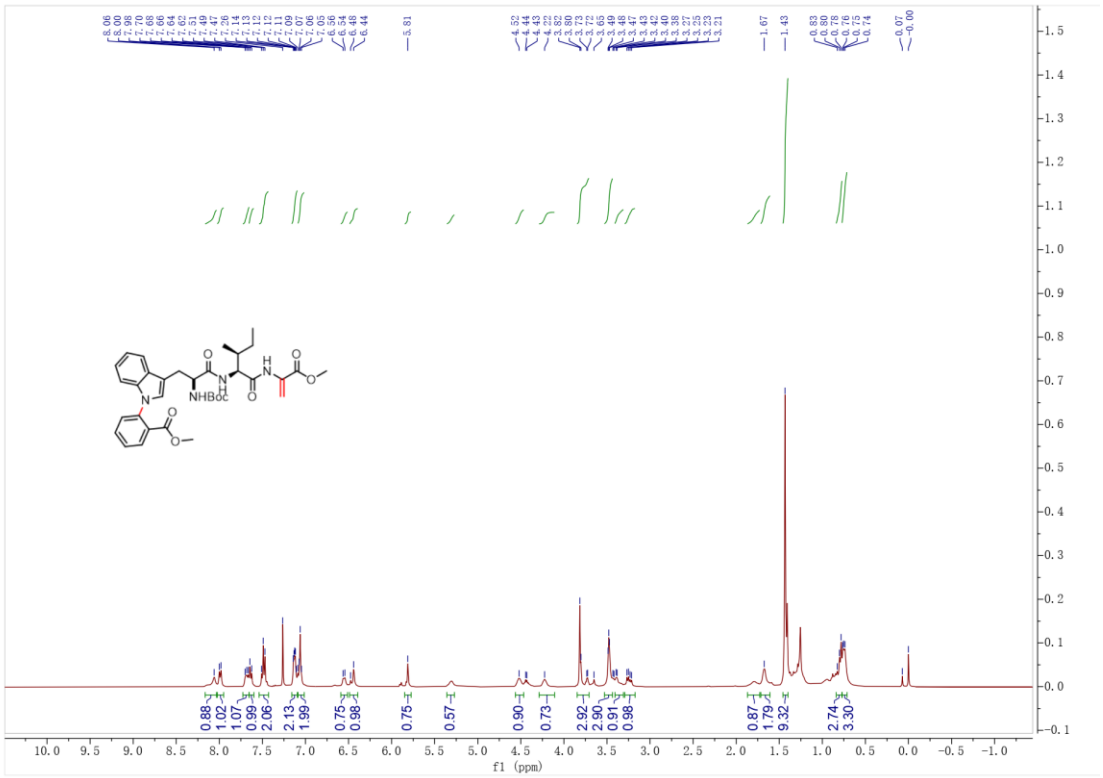

Fig 99. ^{1}H NMR of (**6c'**) (400 MHz, $CDCl_3$)

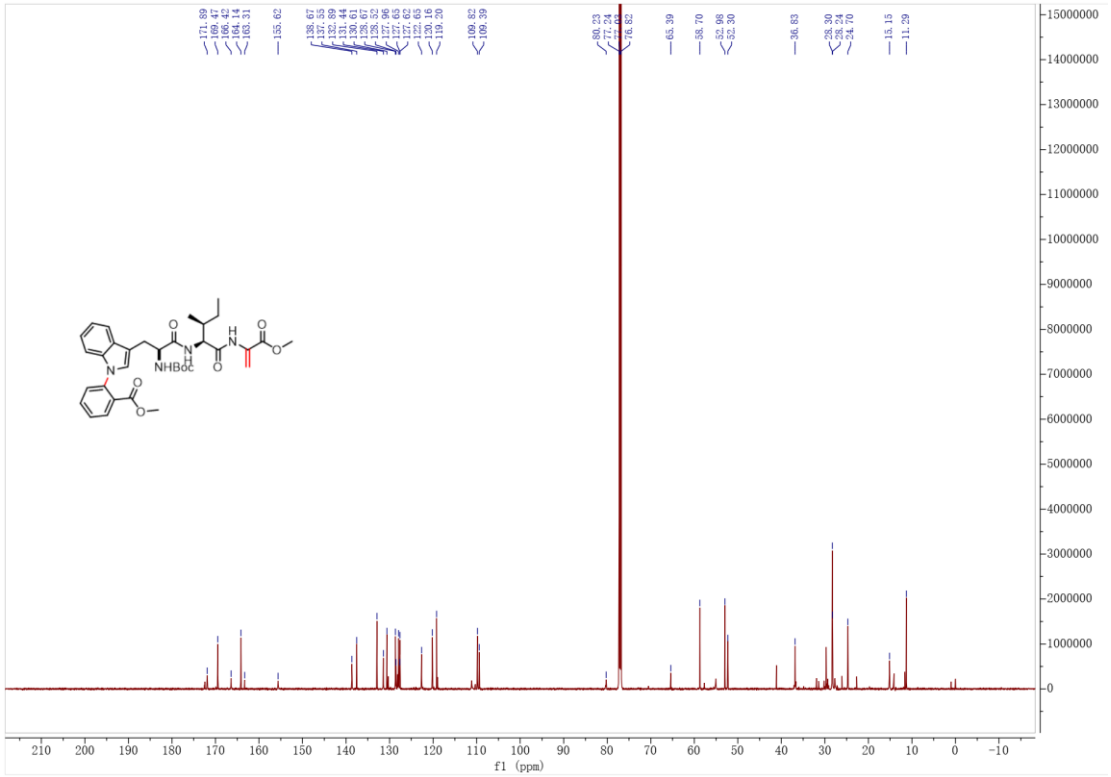

Fig 100. ^{13}C NMR of (**6c'**) (150 MHz, $CDCl_3$)

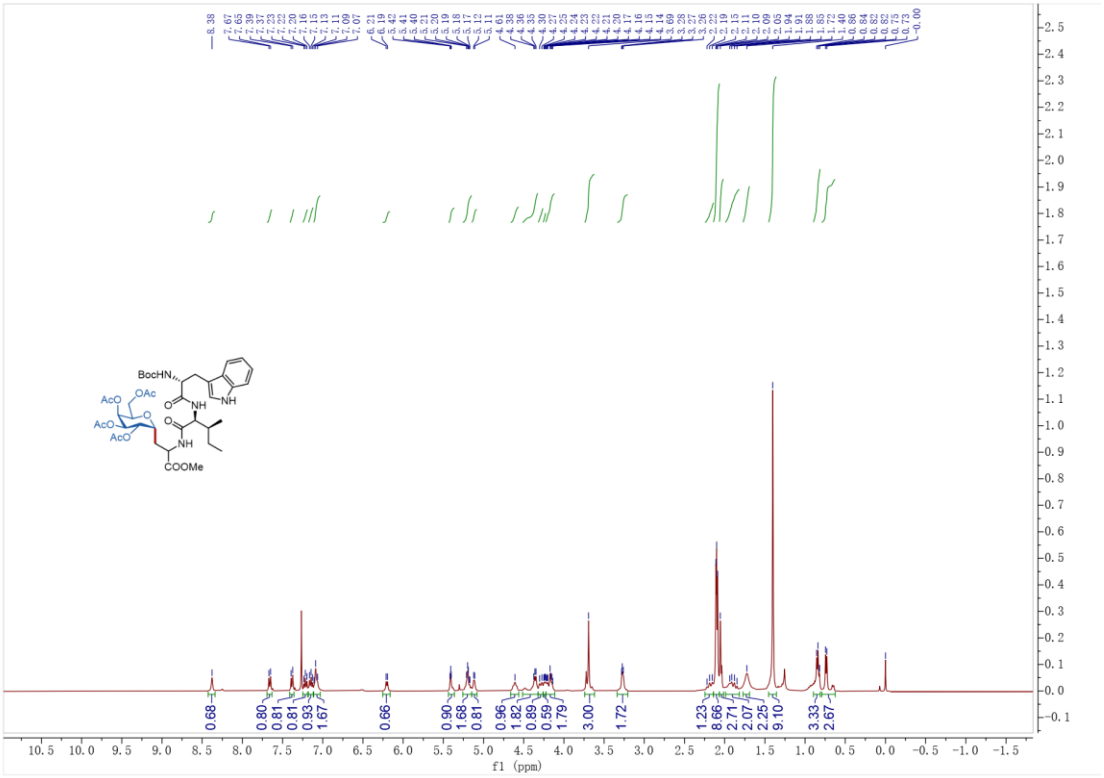

Fig 101. ^{1}H NMR of (**7c**) (400 MHz, $CDCl_3$)

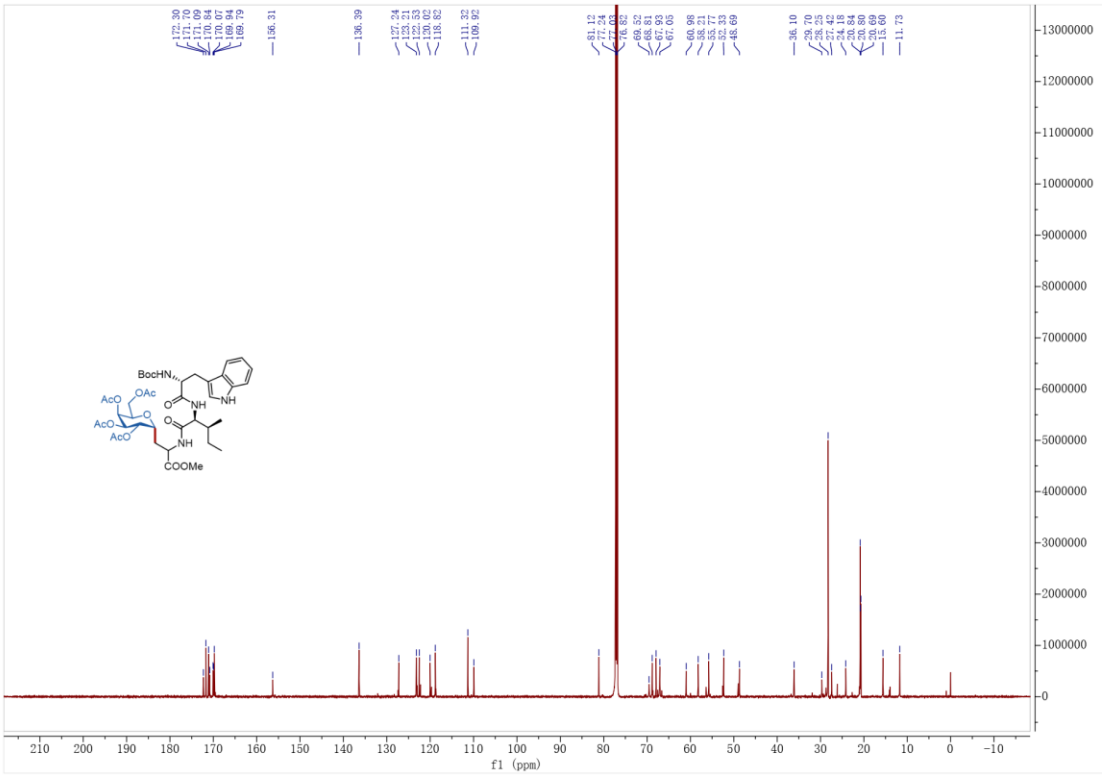

Fig 102. ^{13}C NMR of (**7c**) (150 MHz, $CDCl_3$)

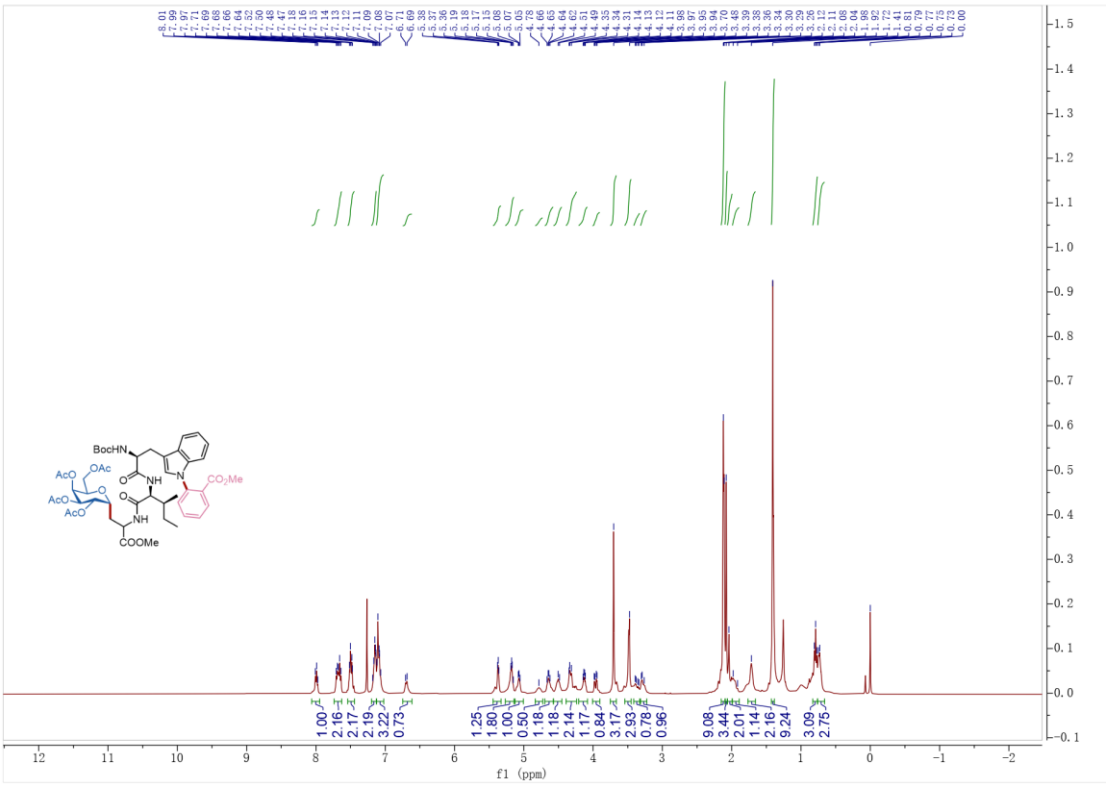

Fig 103. ^{1}H NMR of (**7c'**) (400 MHz, $CDCl_3$)

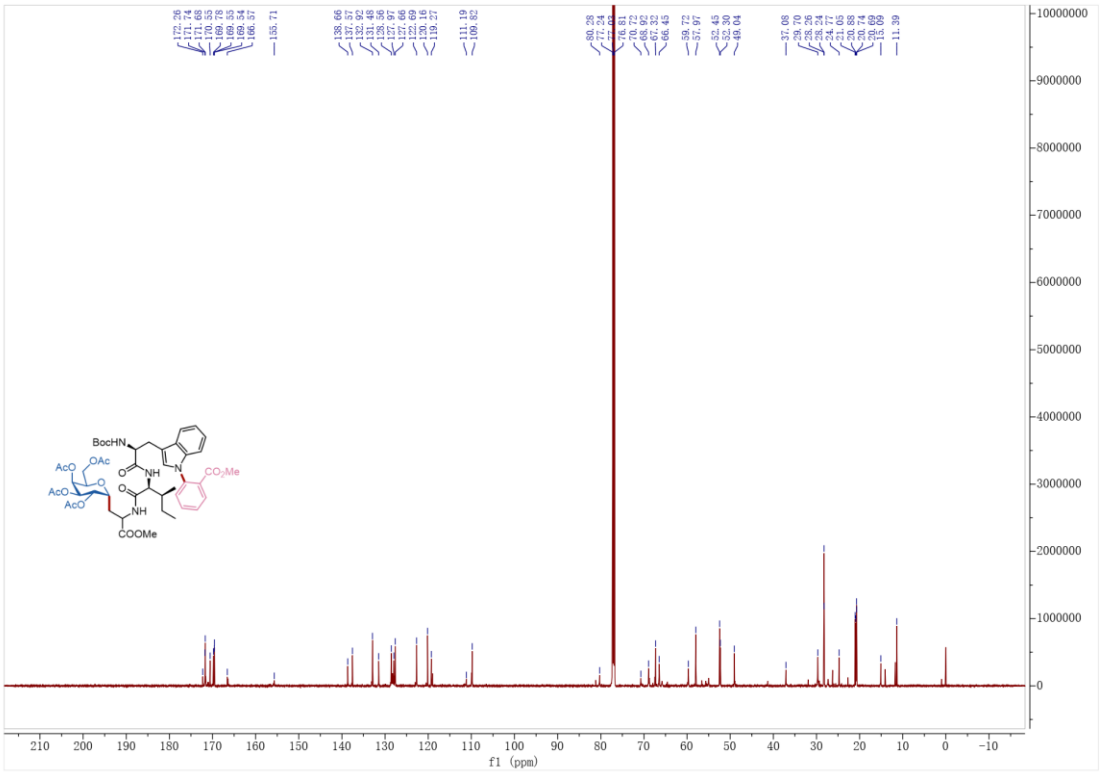

Fig 104. ^{13}C NMR of (**7c'**) (150 MHz, $CDCl_3$)

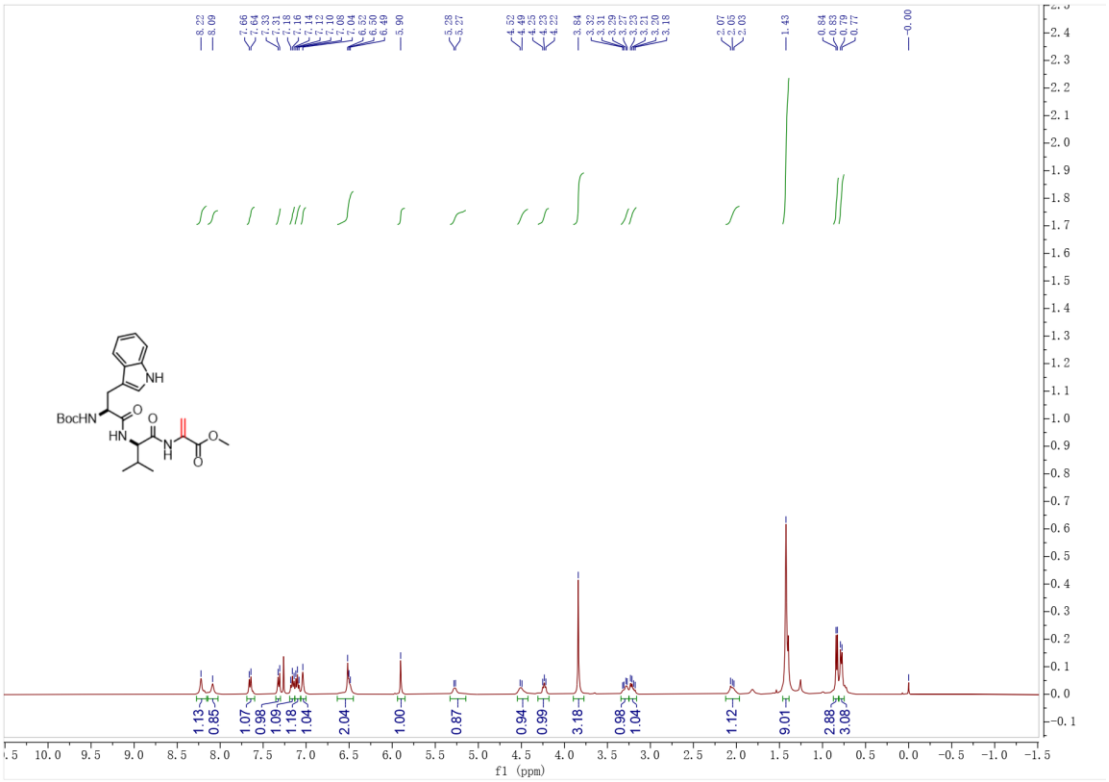

Fig 105. ^{1}H NMR of (**6d**) (400 MHz, $CDCl_3$)

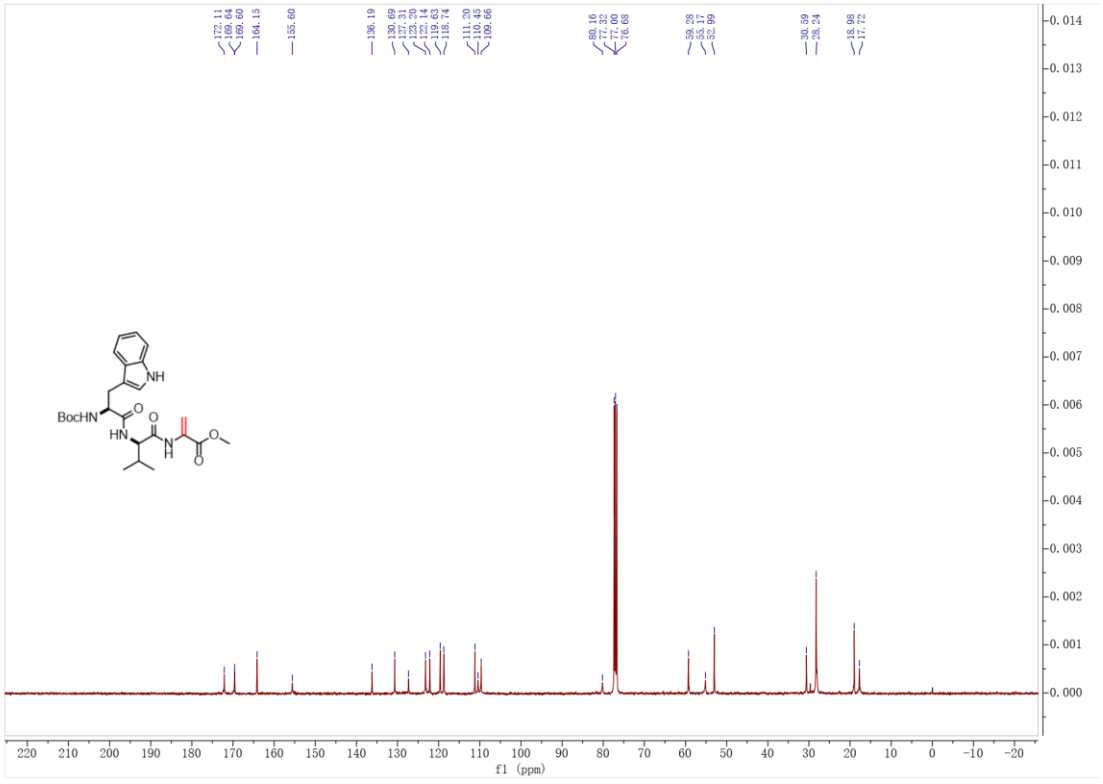

Fig 106. ^{13}C NMR of (**6d**) (100 MHz, $CDCl_3$)

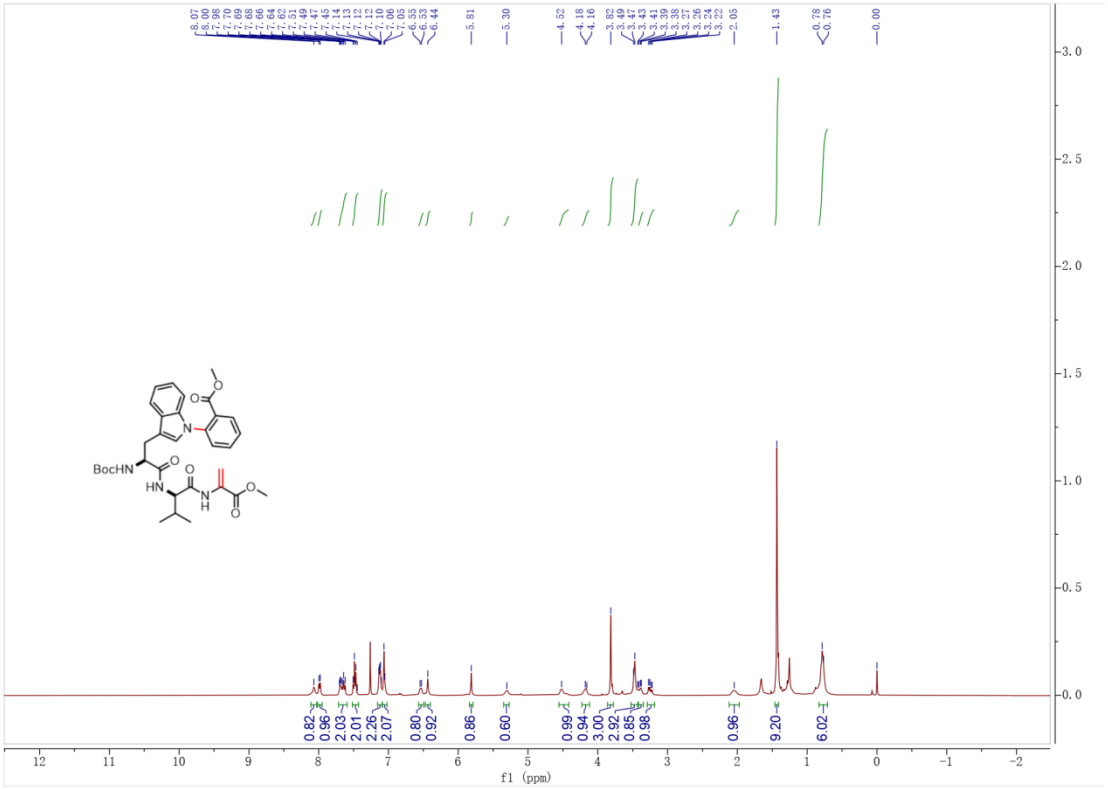

Fig 107. ^{1}H NMR of (**6d'**) (400 MHz, $CDCl_3$)

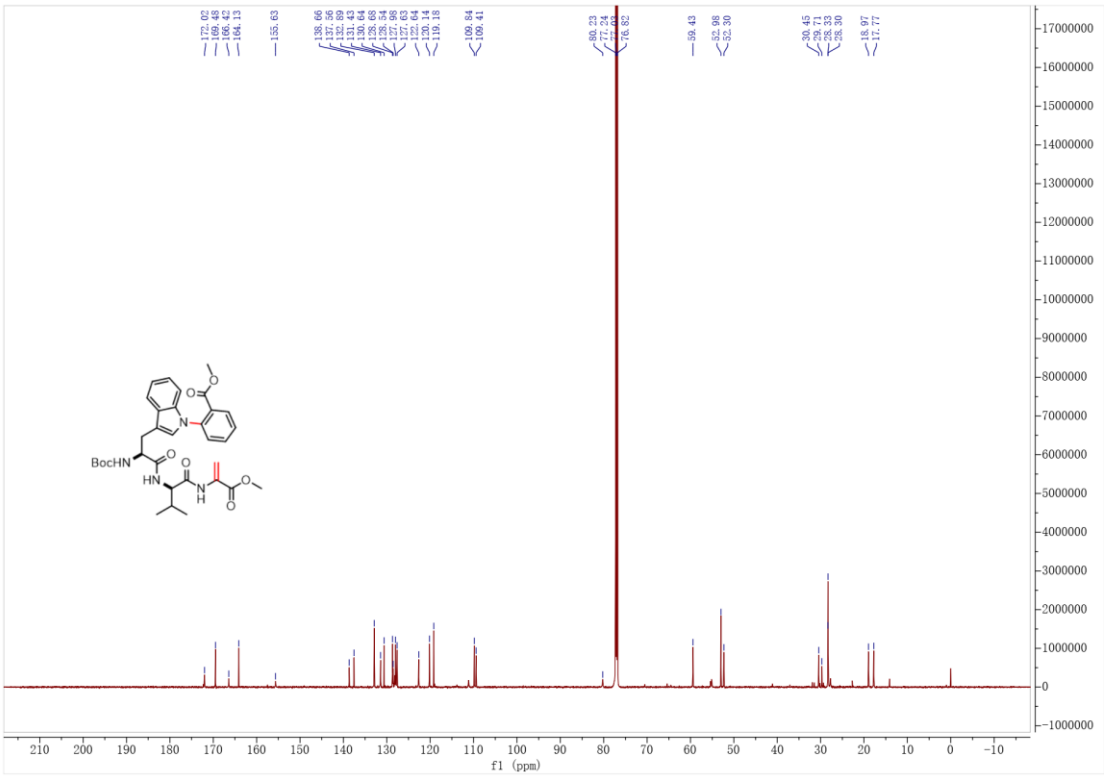

Fig 108. ^{13}C NMR of (**6d'**) (150 MHz, $CDCl_3$)

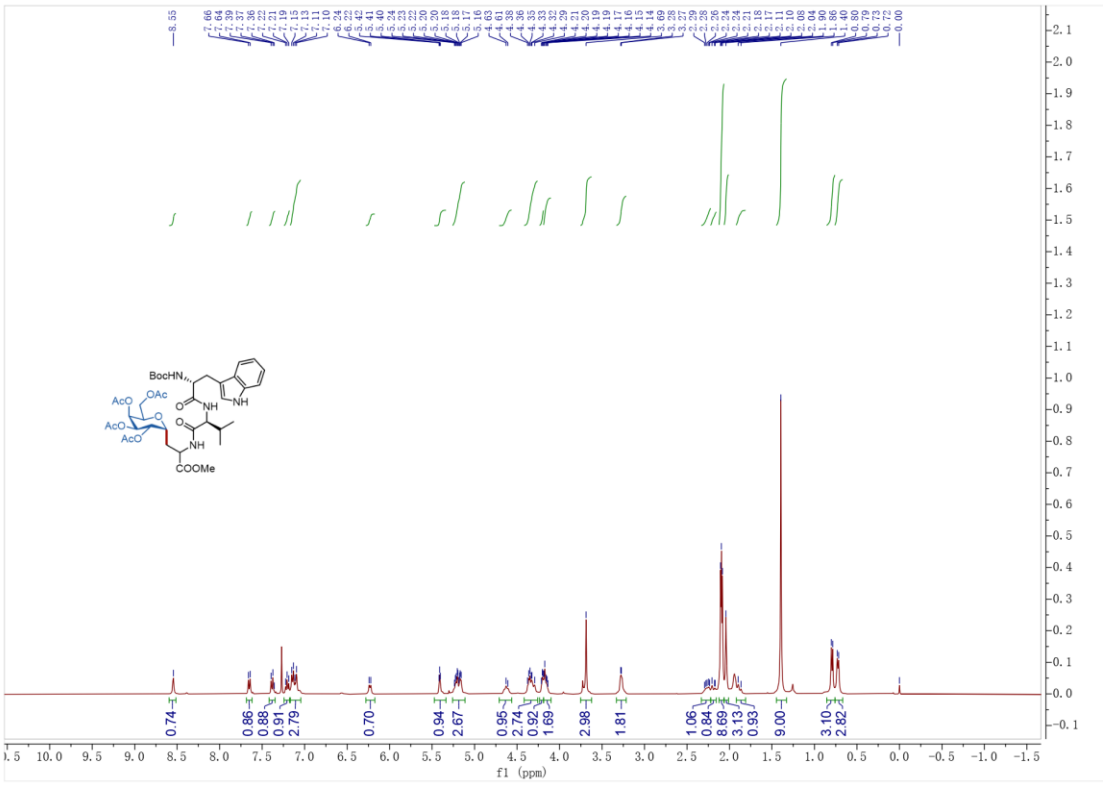

Fig 109. ^{1}H NMR of (**7d**) (400 MHz, $CDCl_3$)

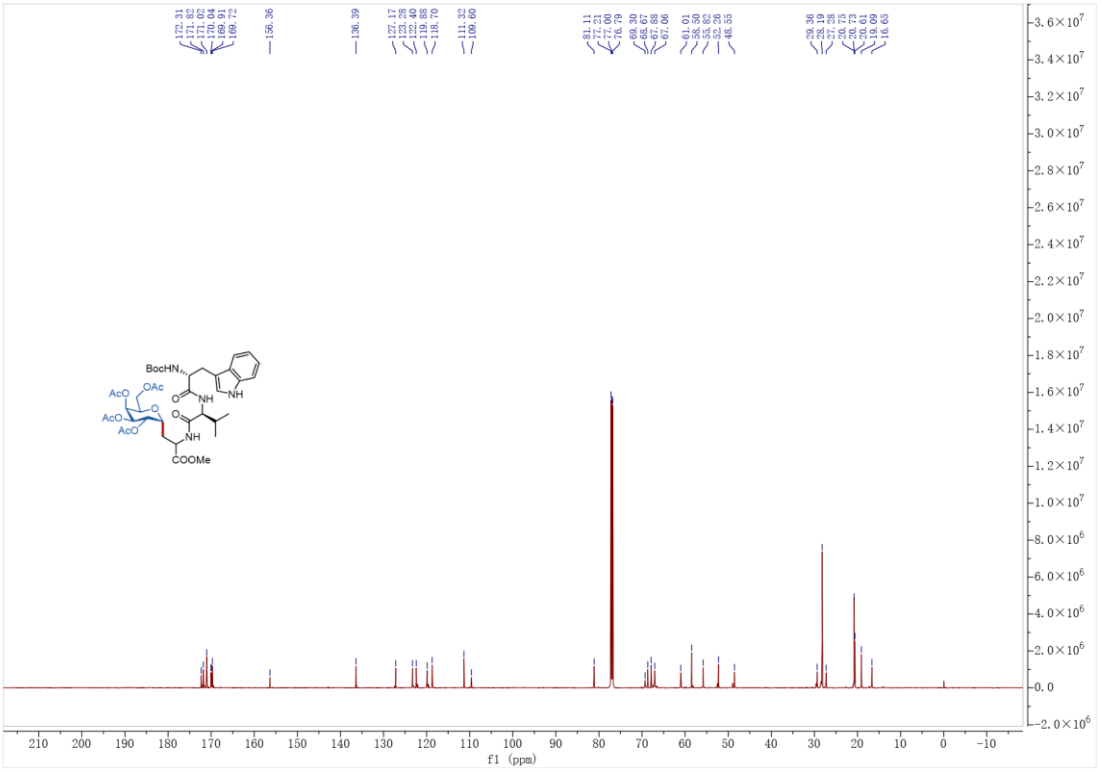

Fig 110. ^{13}C NMR of (**7d**) (150 MHz, $CDCl_3$)

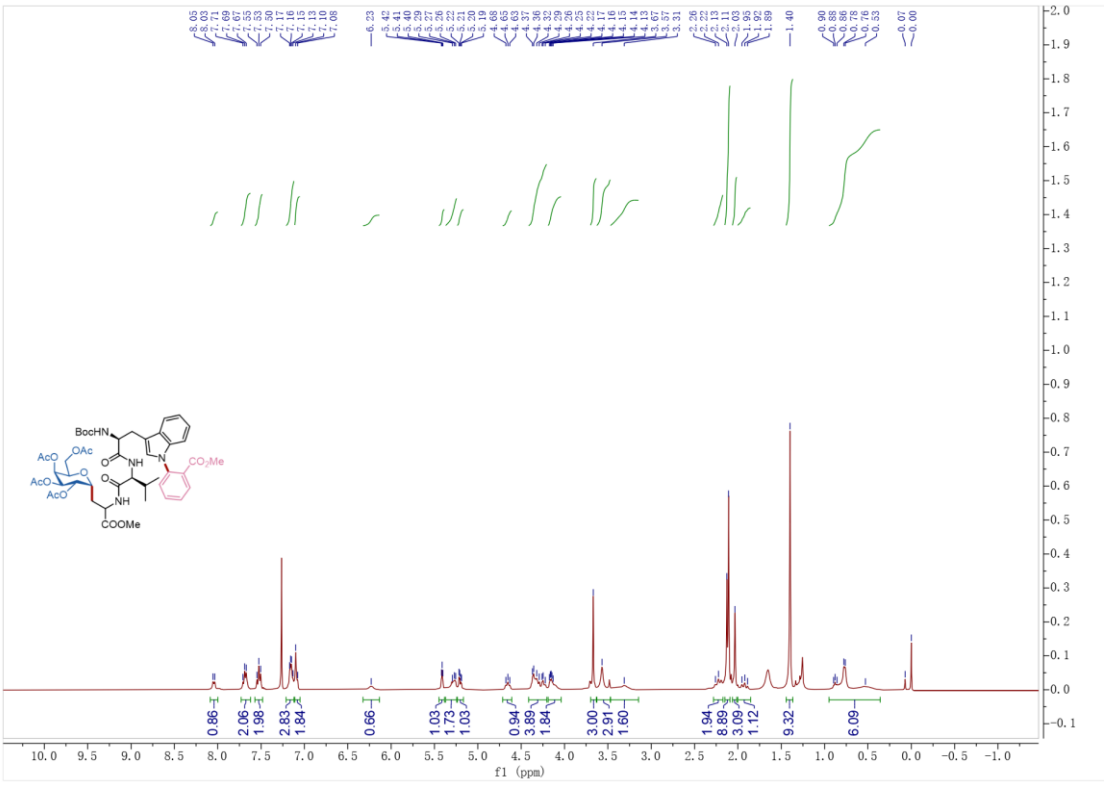

Fig 111. ^{1}H NMR of (**7d'**) (400 MHz, $CDCl_3$)

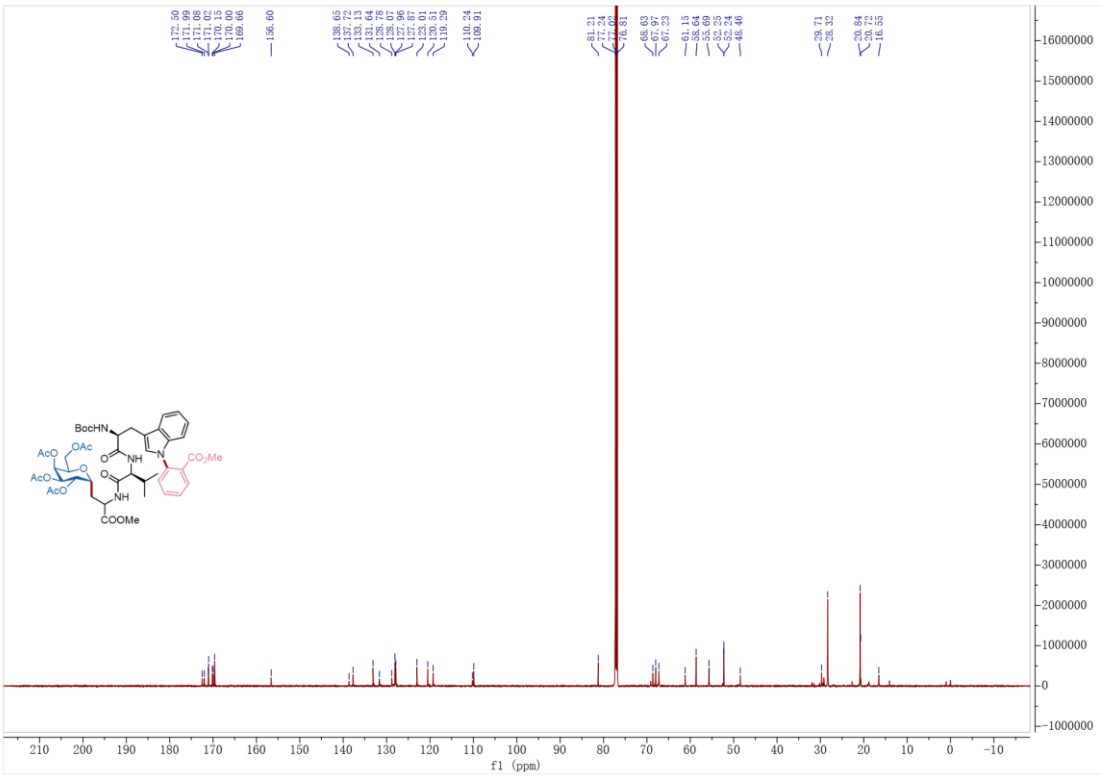

Fig 112. ^{13}C NMR of (**7d'**) (150 MHz, $CDCl_3$)

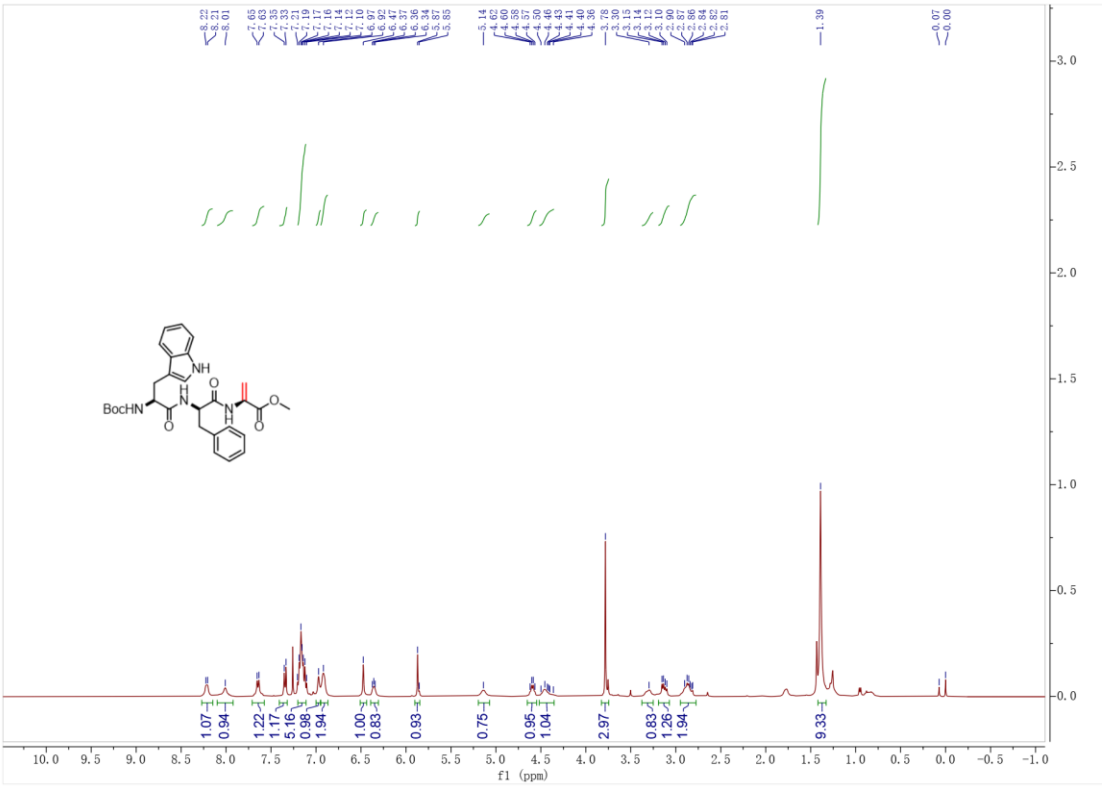

Fig 113. ^{1}H NMR of (**6e**) (400 MHz, $CDCl_3$)

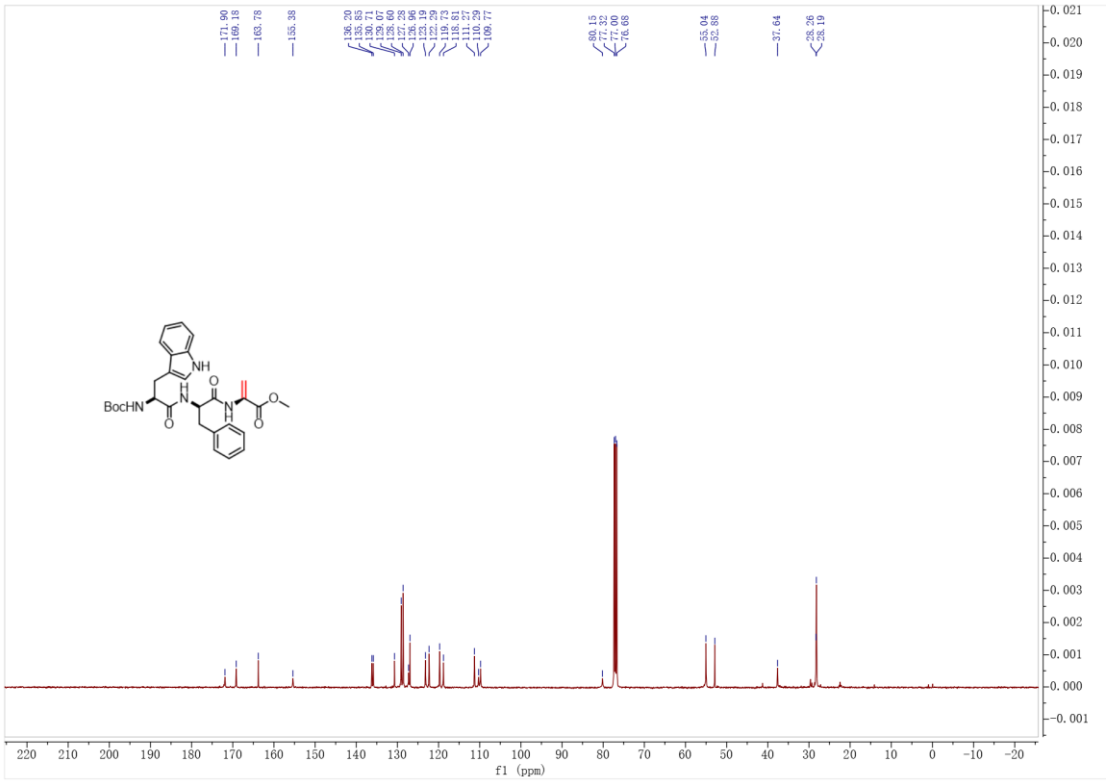

Fig 114. ^{13}C NMR of (**6e**) (100 MHz, $CDCl_3$)

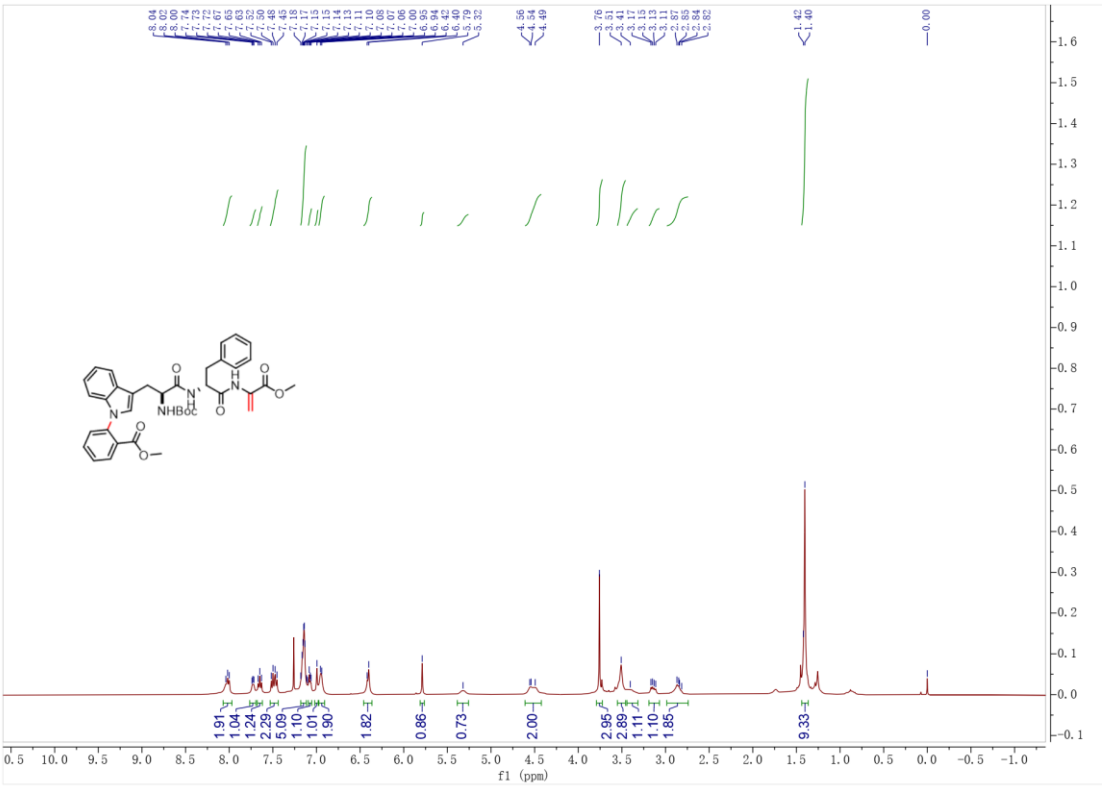

Fig 115. ^{1}H NMR of (**6e'**) (400 MHz, $CDCl_3$)

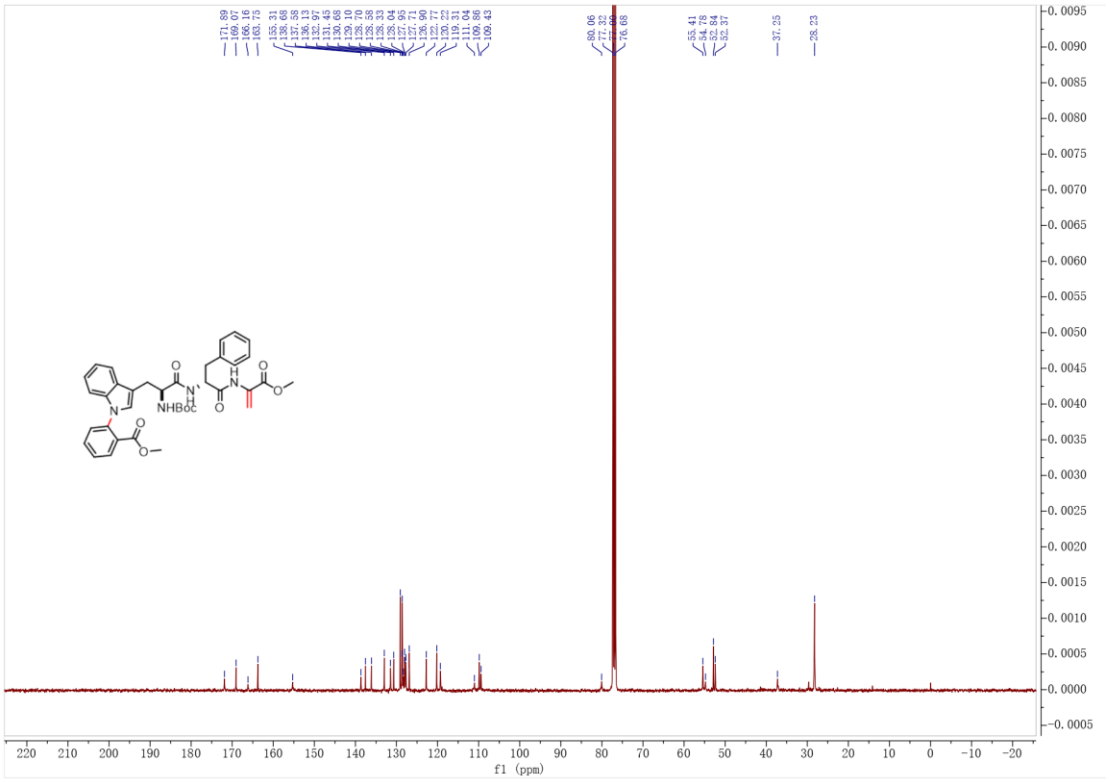

Fig 116. ^{13}C NMR of (**6e'**) (100 MHz, $CDCl_3$)

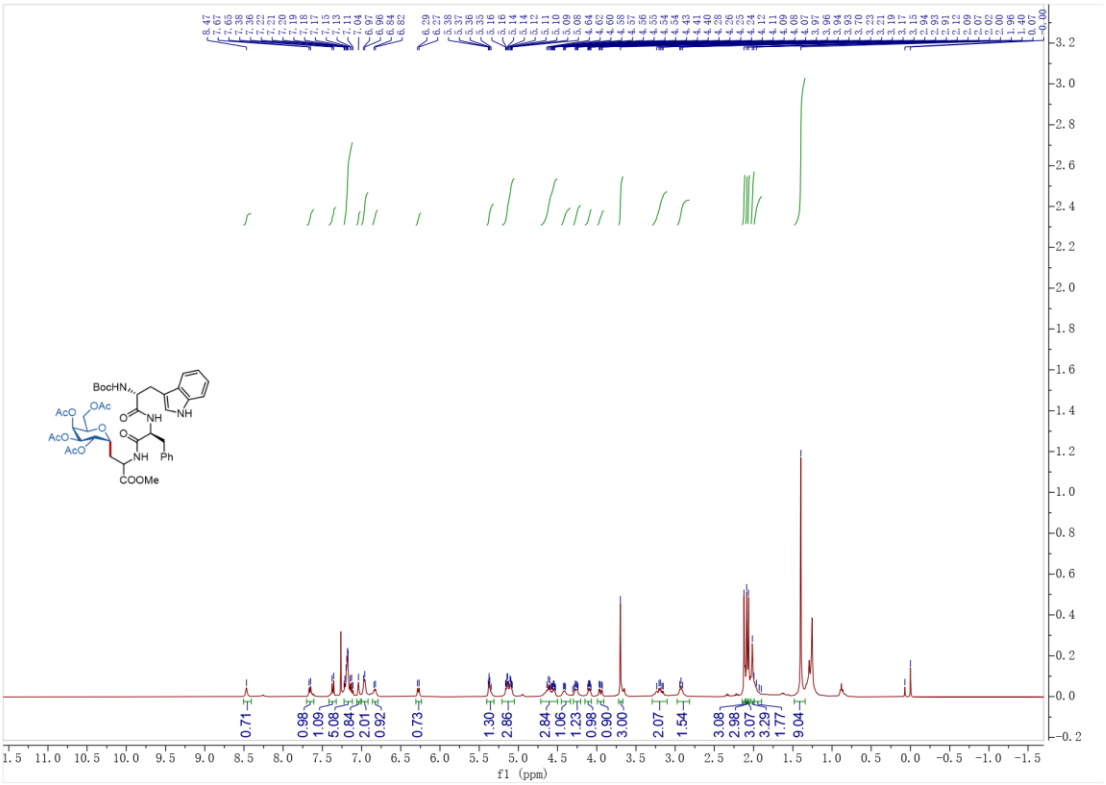

Fig 117. ^{1}H NMR of (**7e**) (400 MHz, $CDCl_3$)

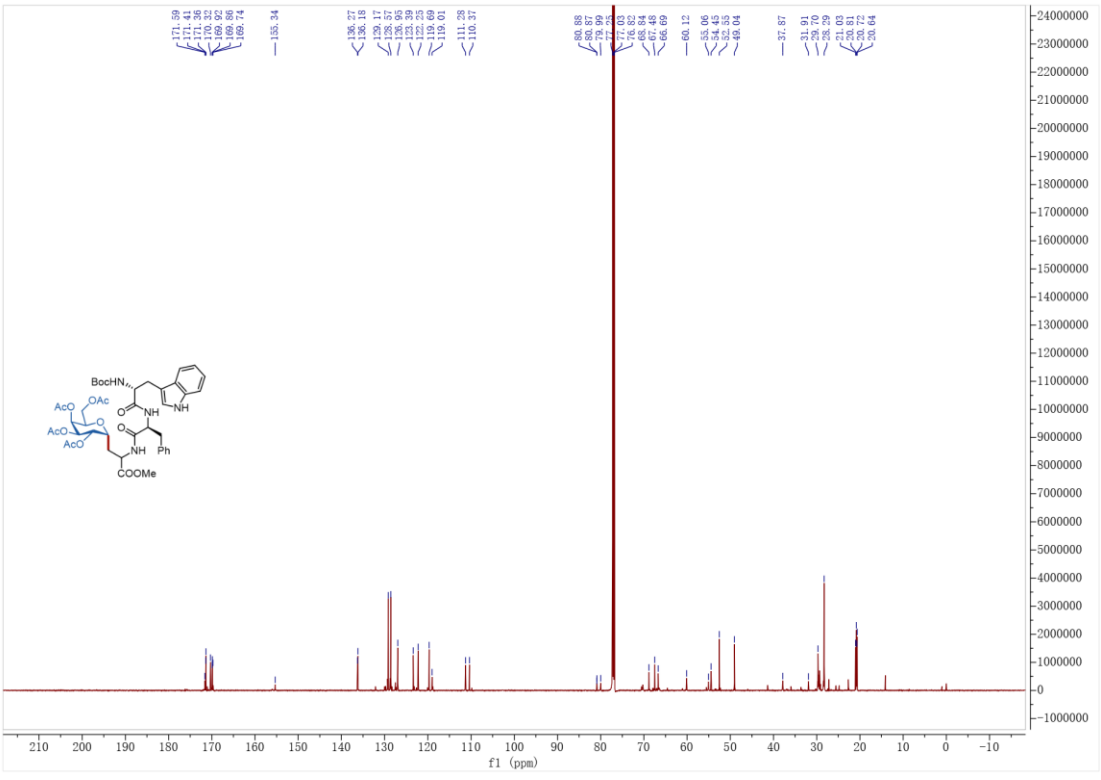

Fig 118. ^{13}C NMR of (**7e**) (150 MHz, $CDCl_3$)

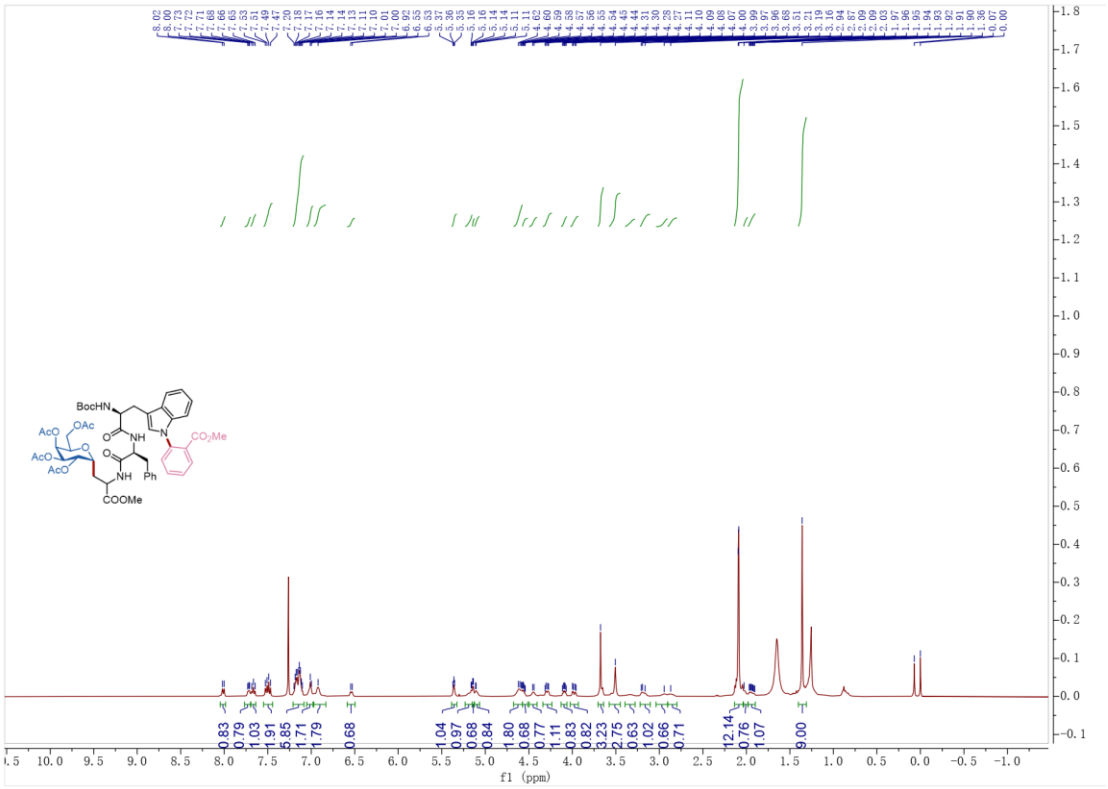

Fig 119. ^{1}H NMR of (**7e'**) (400 MHz, $CDCl_3$)

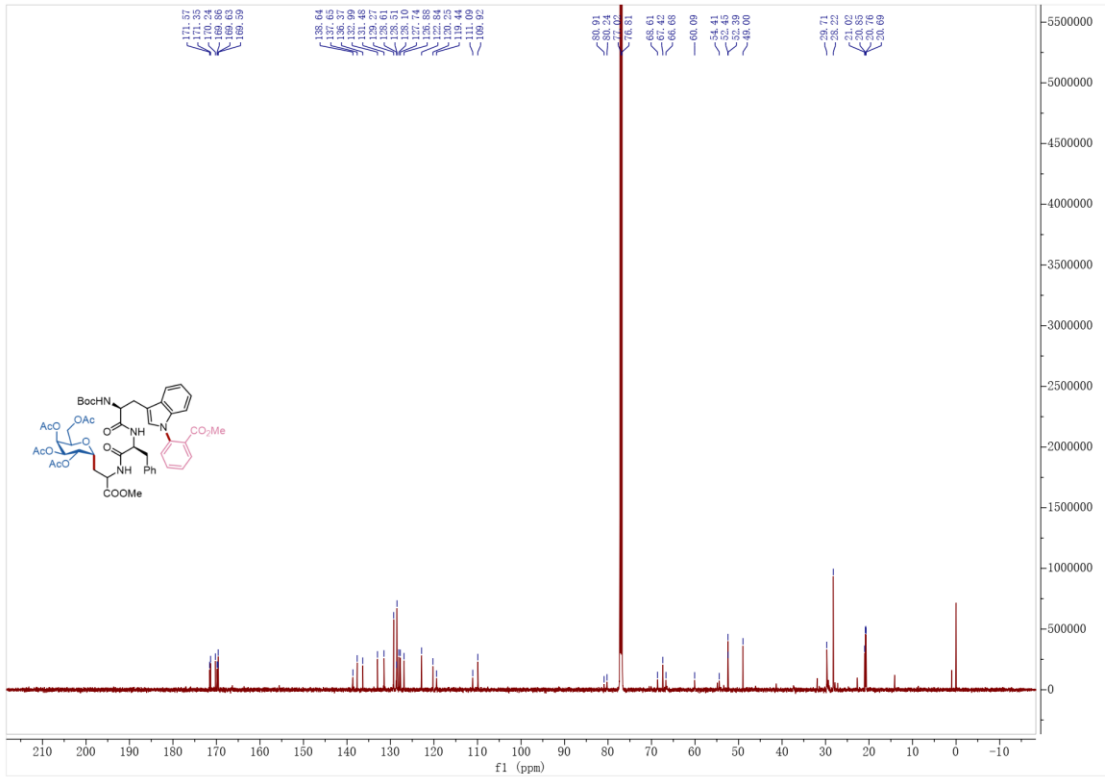

Fig 120. ^{13}C NMR of (**7e'**) (150 MHz, $CDCl_3$)

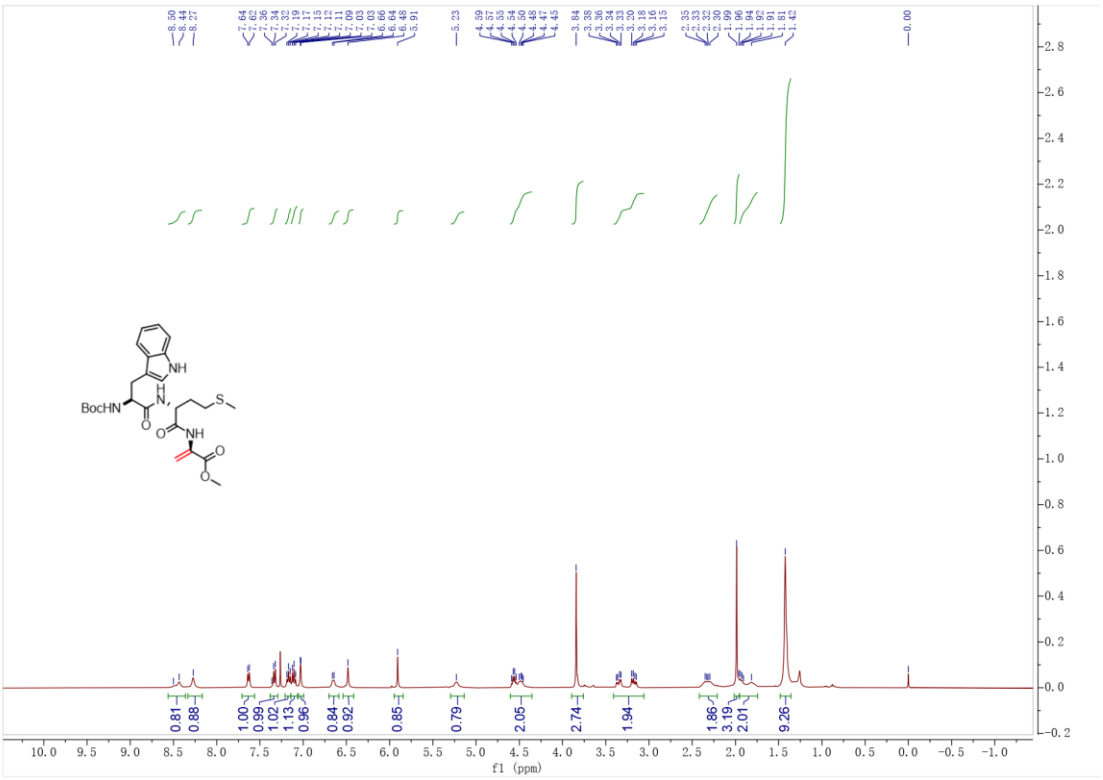

Fig 121. ^{1}H NMR of (**6f**) (400 MHz, $CDCl_3$)

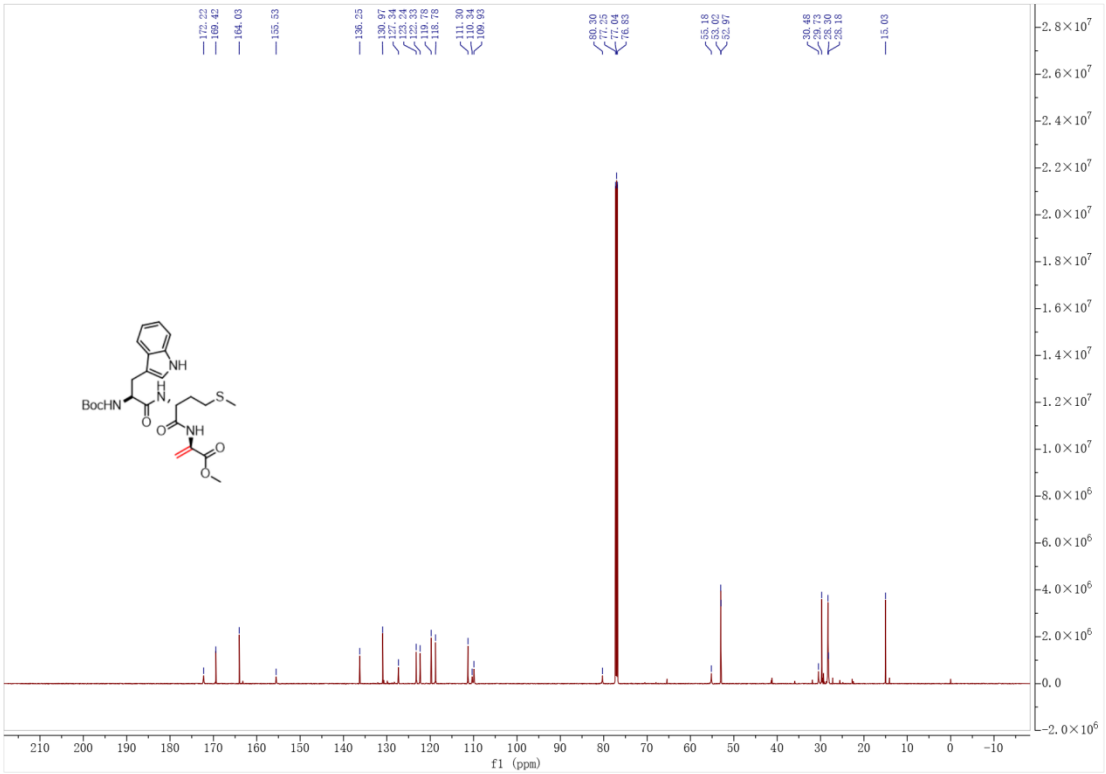

Fig 122. ^{13}C NMR of (**6f**) (150 MHz, $CDCl_3$)

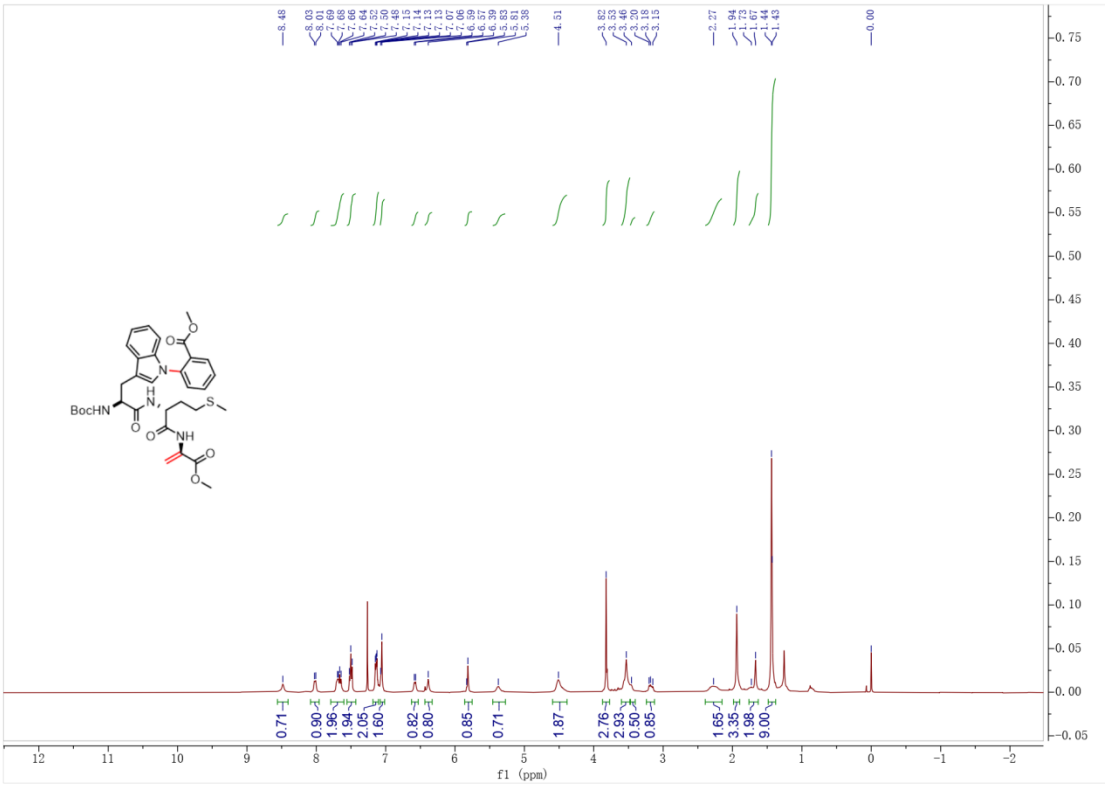

Fig 123. ^{1}H NMR of (**6f'**) (400 MHz, $CDCl_3$)

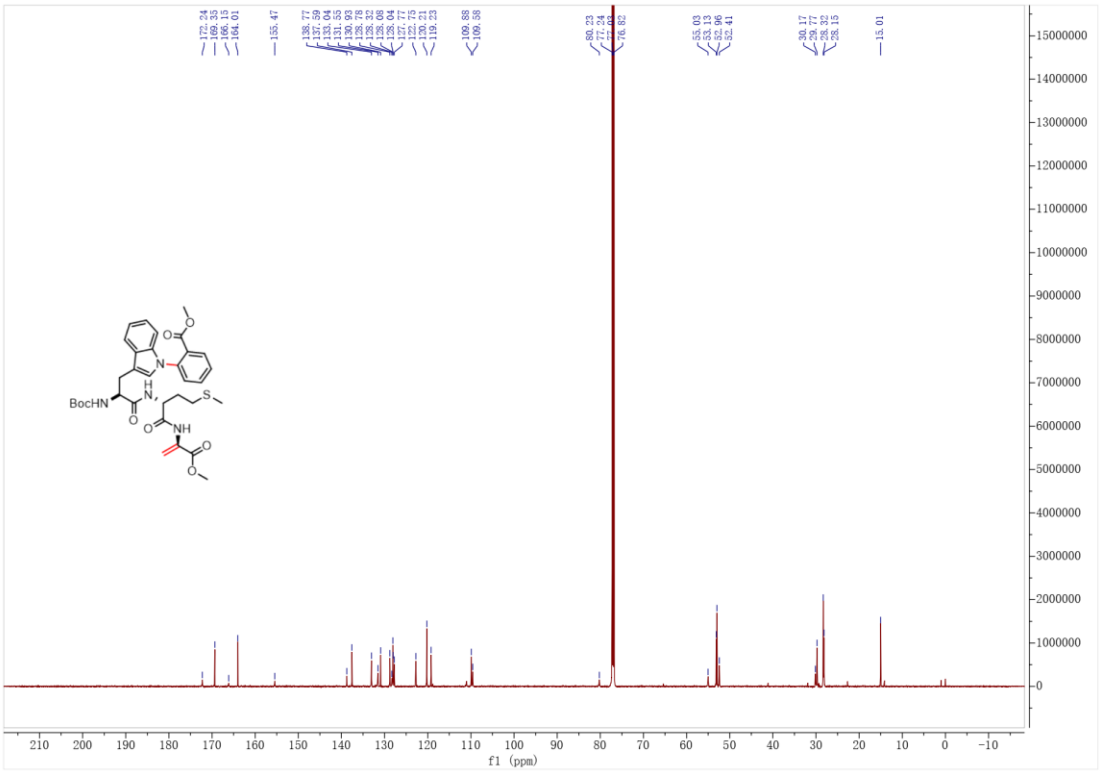

Fig 124. ^{13}C NMR of (**6f'**) (150 MHz, $CDCl_3$)

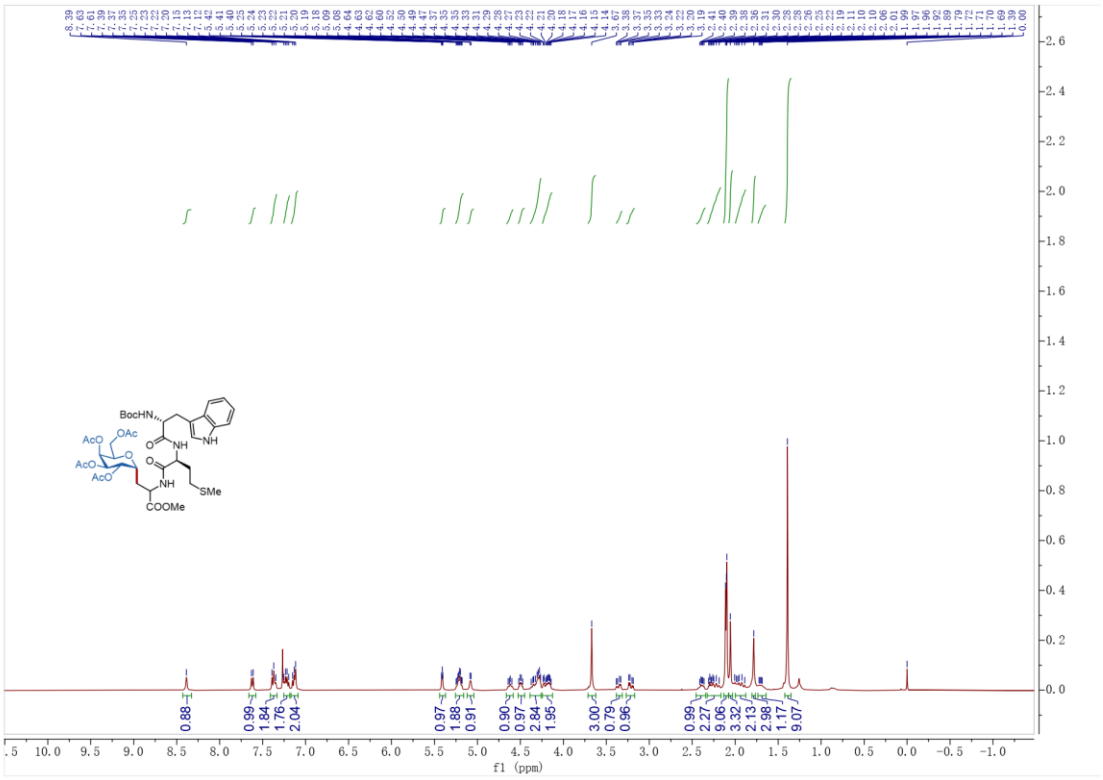

Fig 125. ^{1}H NMR of (**7f**) (400 MHz, $CDCl_3$)

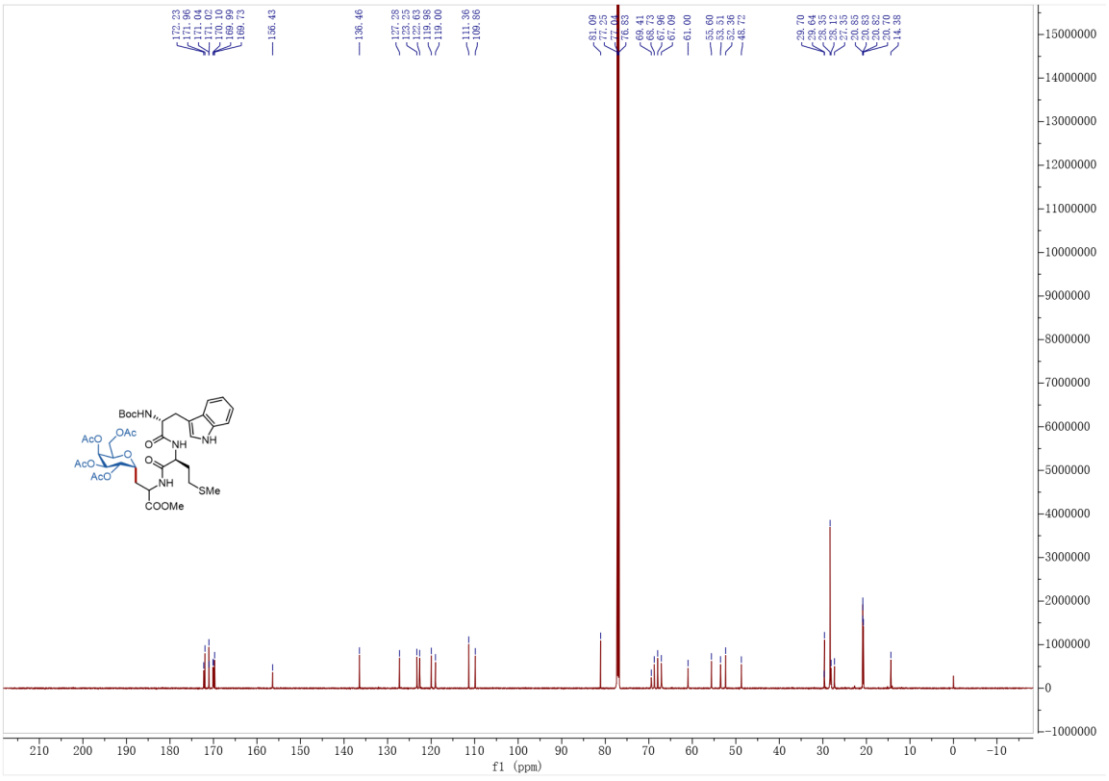

Fig 126. ^{13}C NMR of (**7f**) (150 MHz, $CDCl_3$)

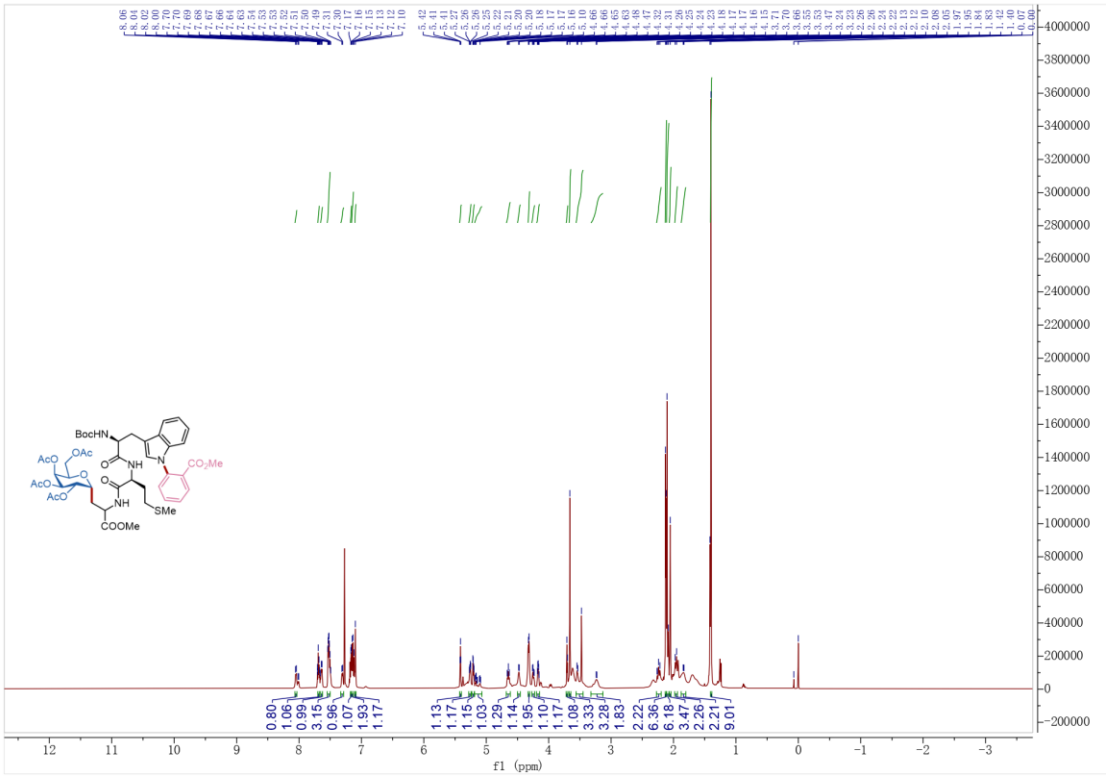

Fig 127. ^{1}H NMR of (**7f'**) (600 MHz, $CDCl_3$)

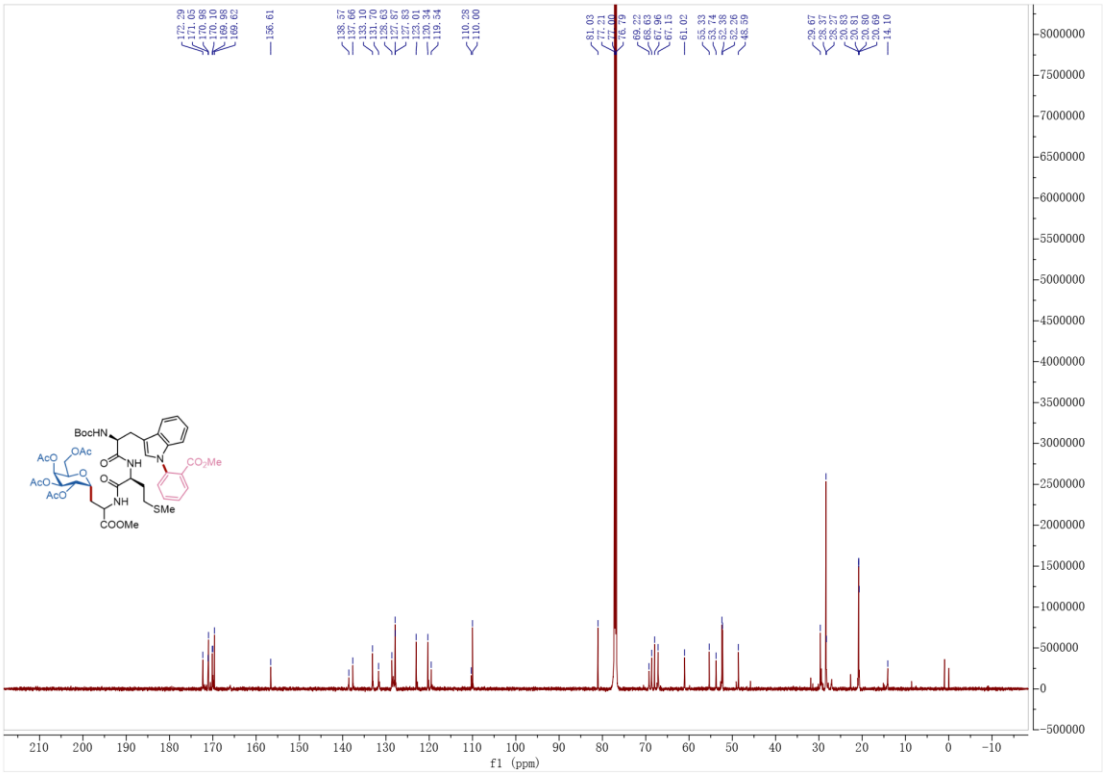

Fig 128. ^{13}C NMR of (**7f'**) (150 MHz, $CDCl_3$)

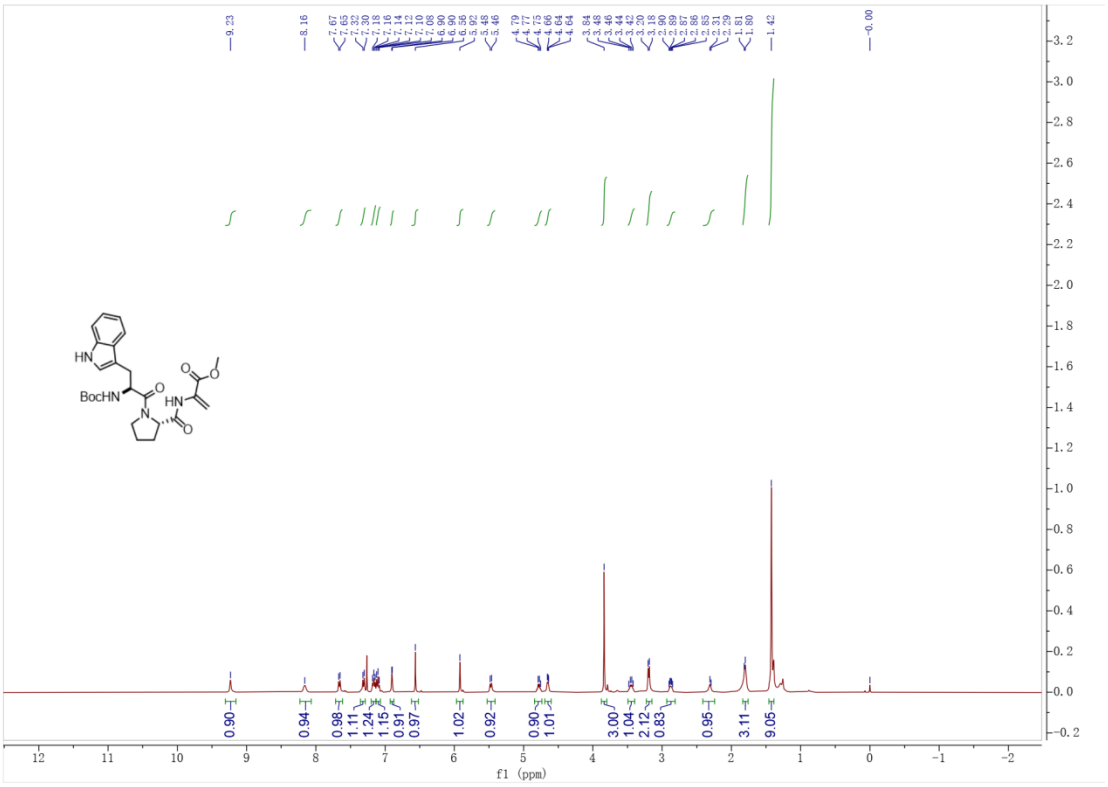

Fig 129. ^{1}H NMR of (**6g**) (400 MHz, $CDCl_3$)

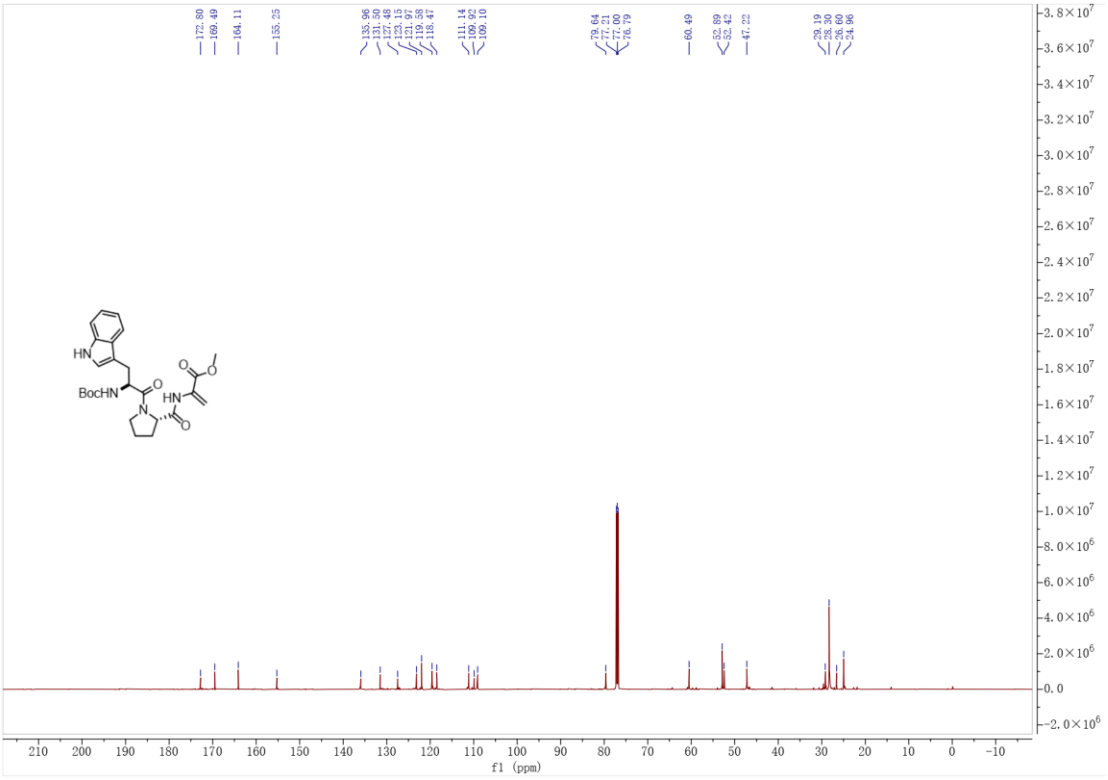

Fig 130. ^{13}C NMR of (**6g**) (150 MHz, $CDCl_3$)

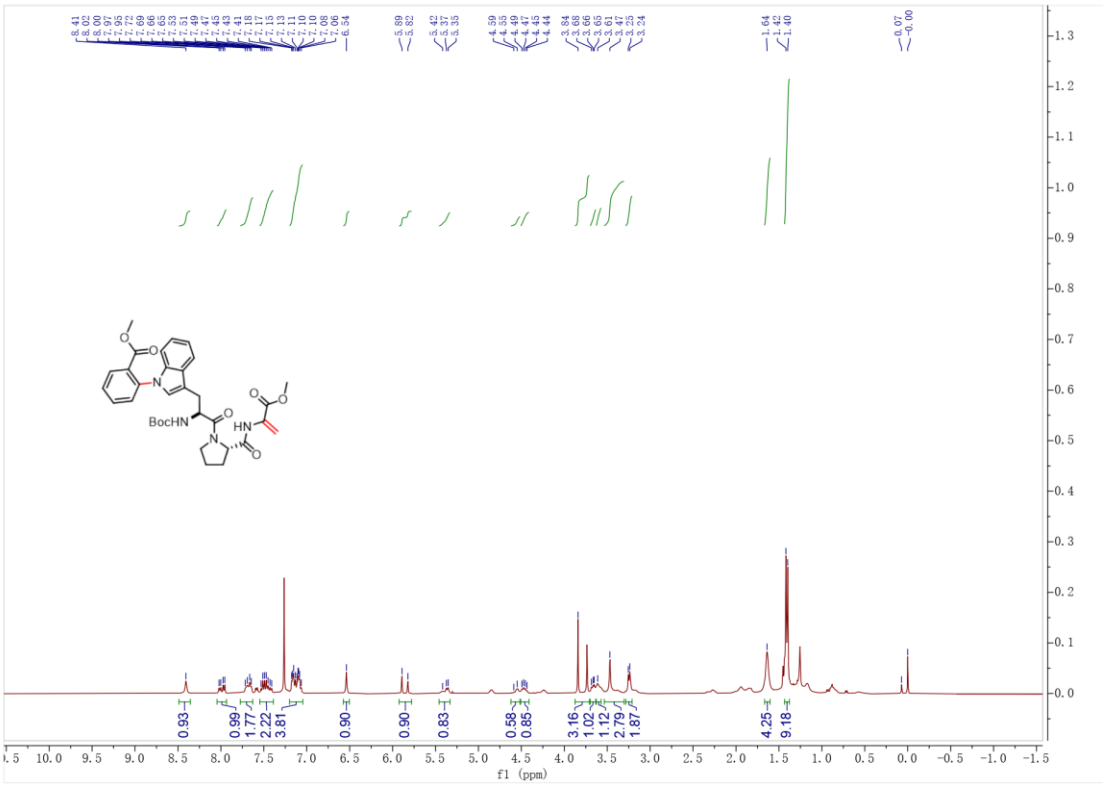

Fig 131. ^{1}H NMR of (**6g'**) (400 MHz, $CDCl_3$)

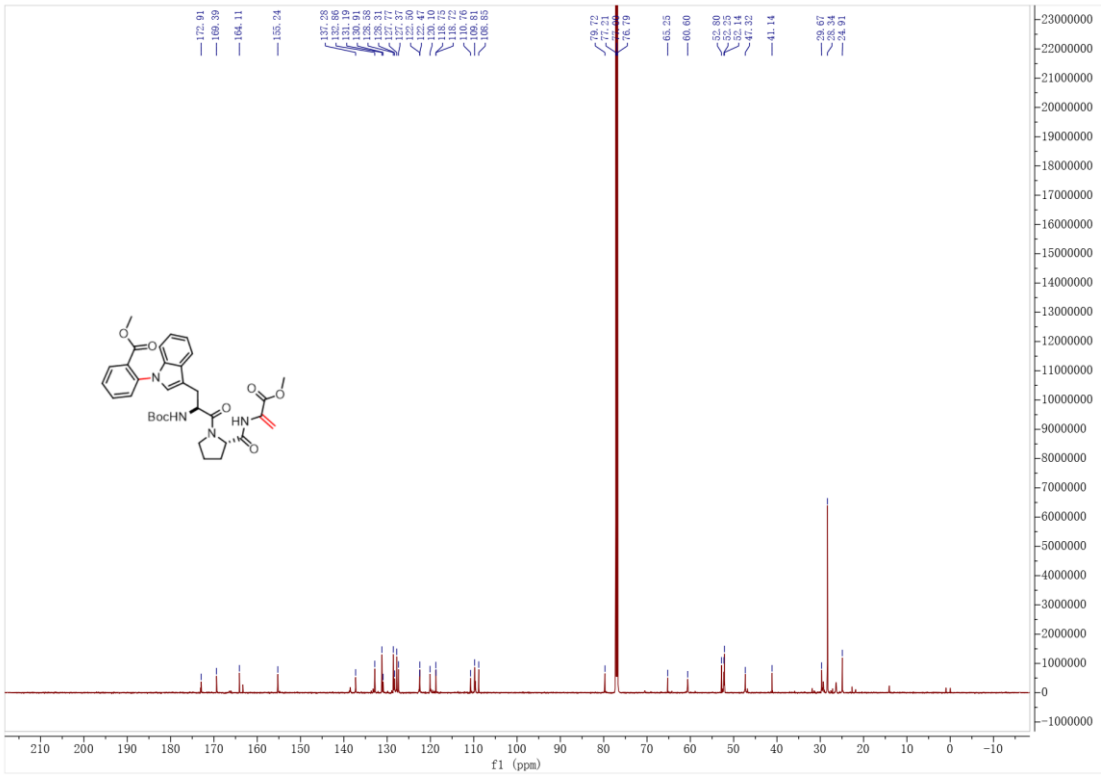

Fig 132. ^{13}C NMR of (**6g'**) (150 MHz, $CDCl_3$)

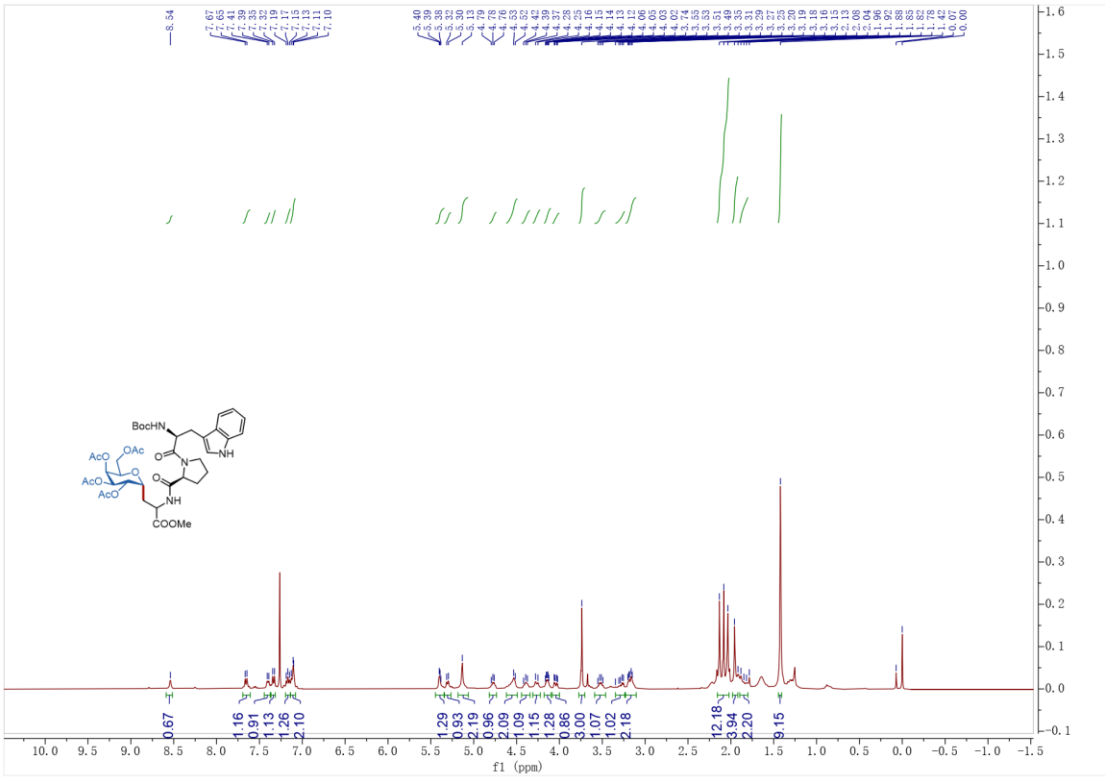

Fig 133. ^{1}H NMR of (**7g**) (400 MHz, $CDCl_3$)

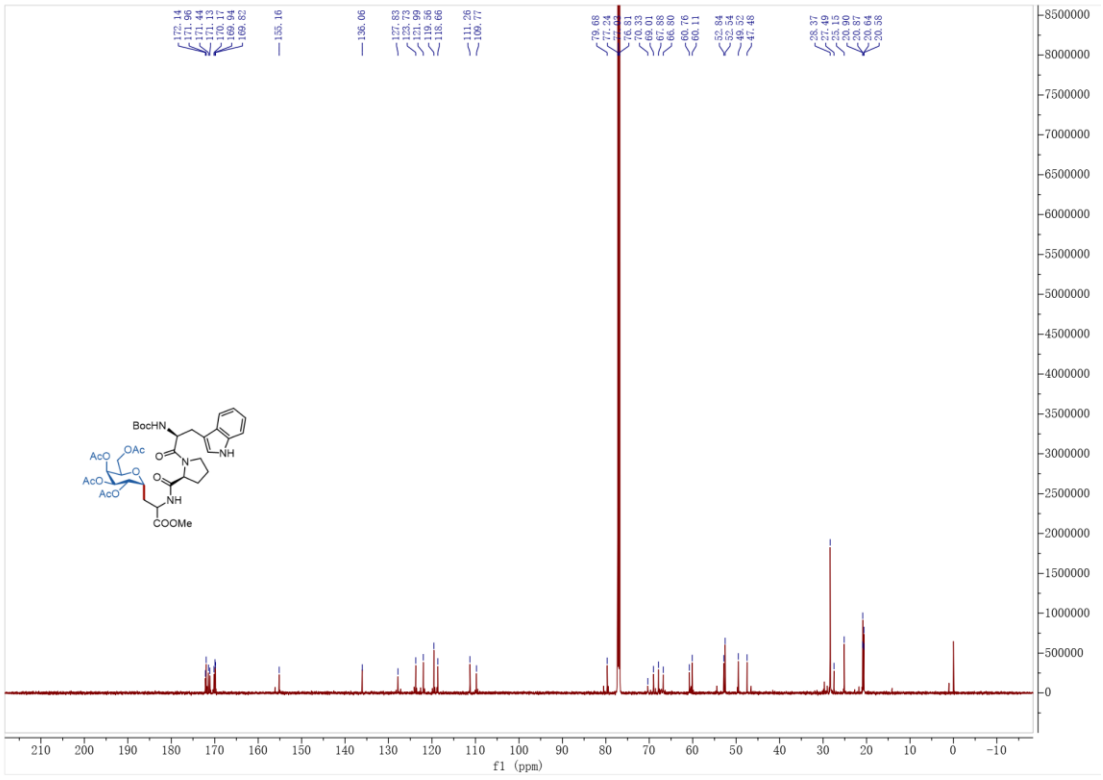

Fig 134. ^{13}C NMR of (**7g**) (150 MHz, $CDCl_3$)

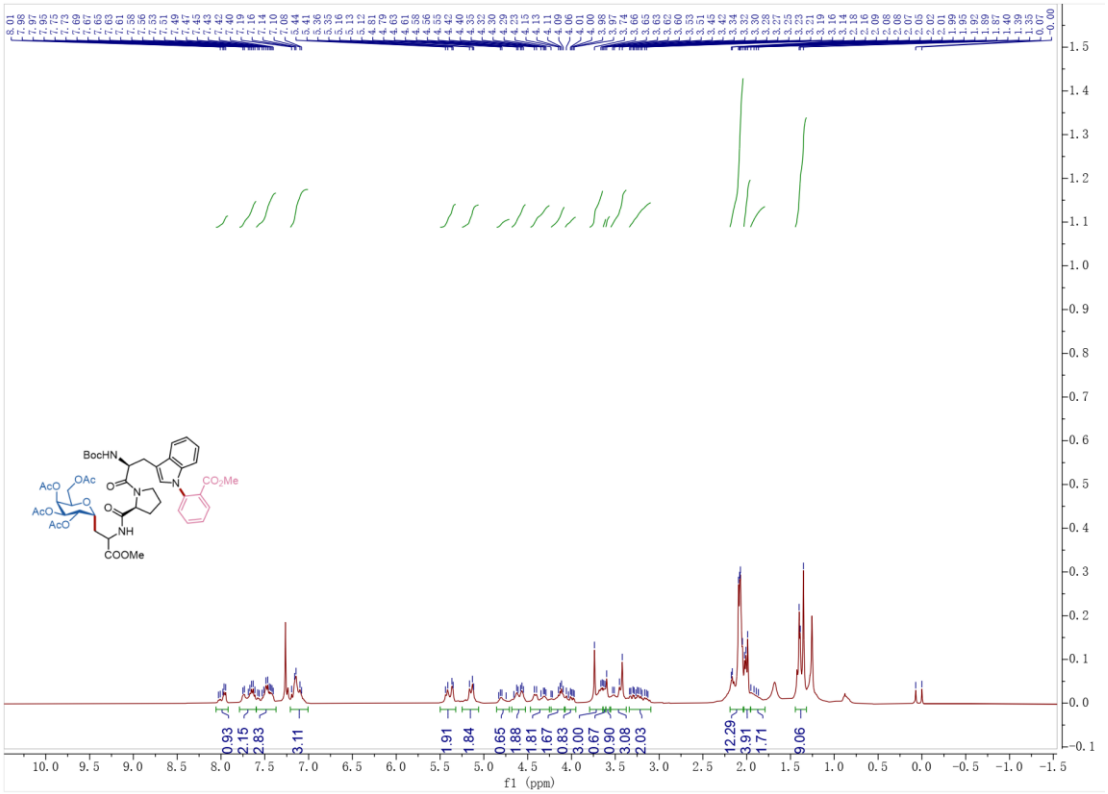

Fig 135. ^{1}H NMR of (**7g'**) (400 MHz, $CDCl_3$)

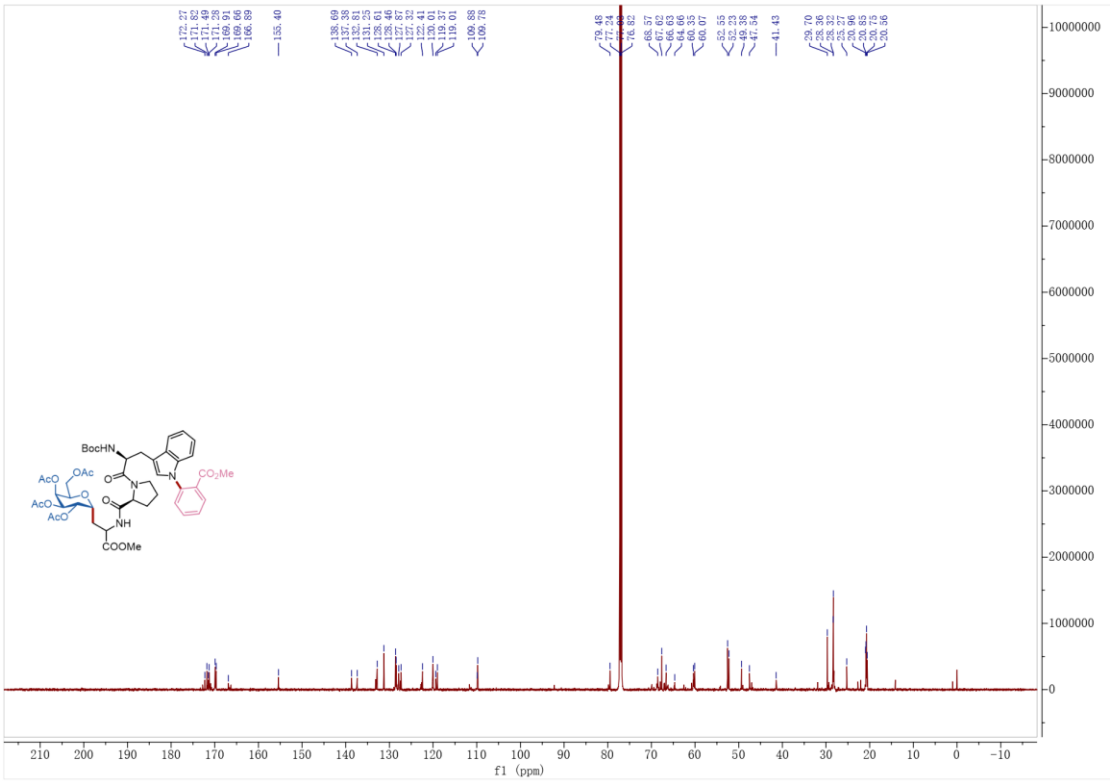

Fig 136. ^{13}C NMR of (**7g'**) (150 MHz, $CDCl_3$)

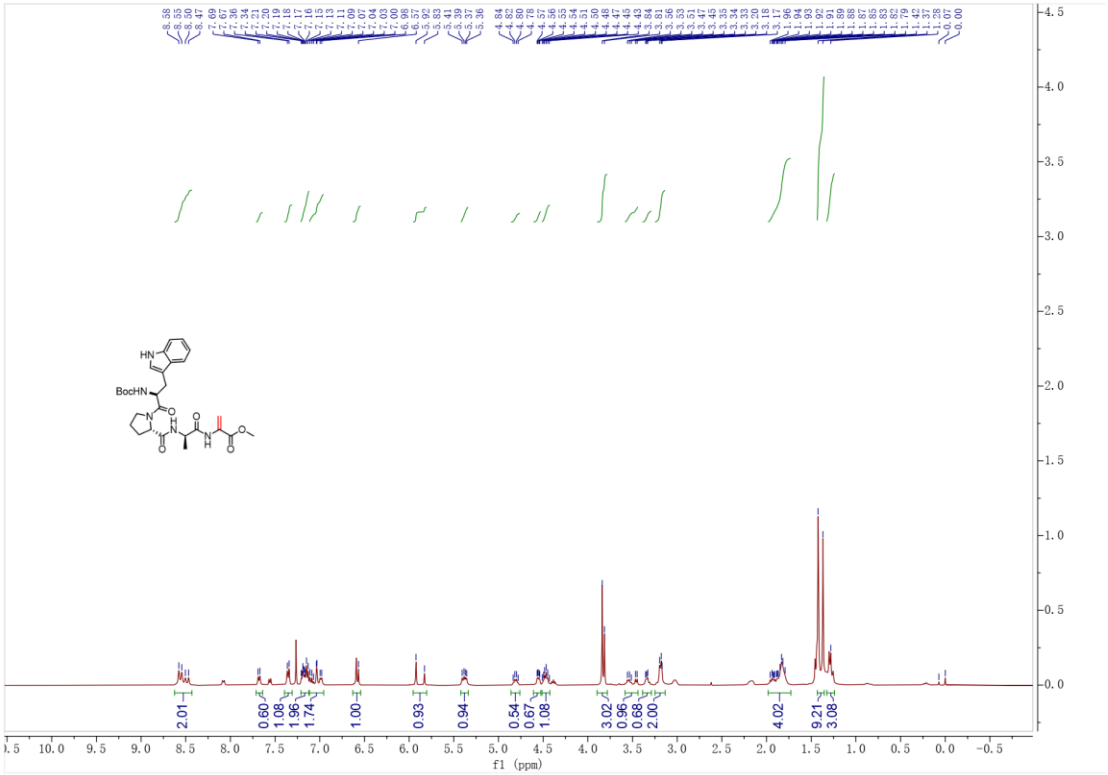

Fig 137. ^{1}H NMR of (**6h**) (400 MHz, $CDCl_3$)

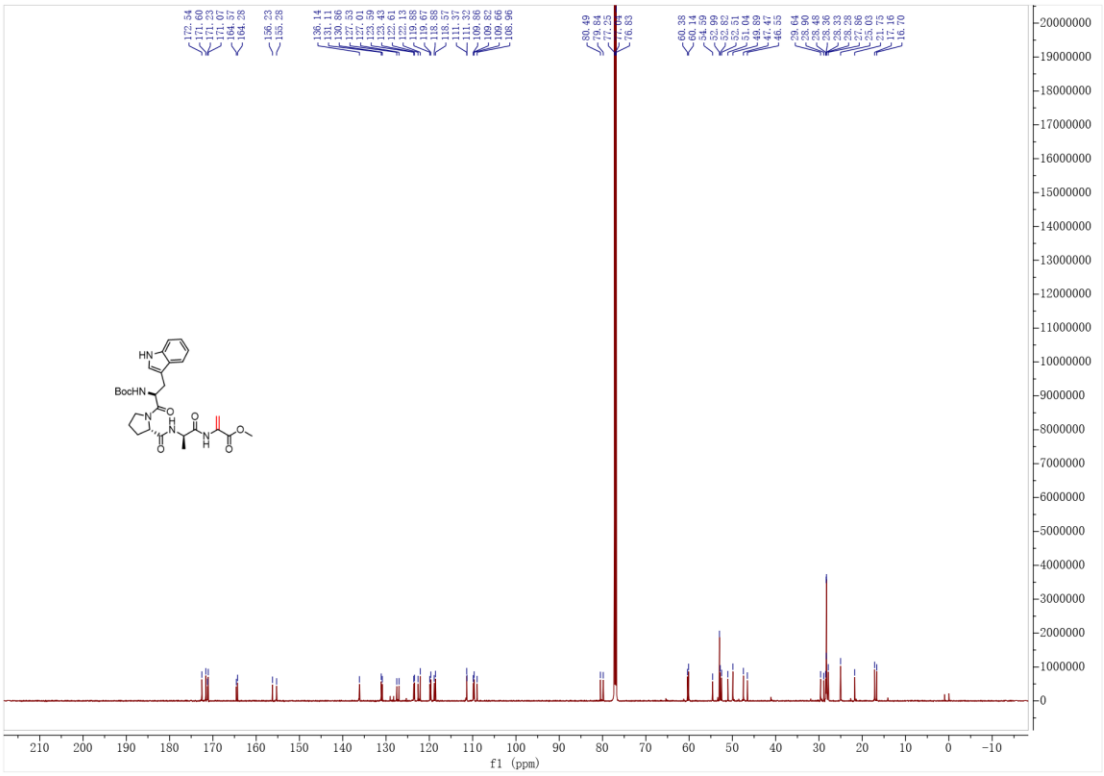

Fig 138. ^{13}C NMR of (**6h**) (150 MHz, $CDCl_3$)

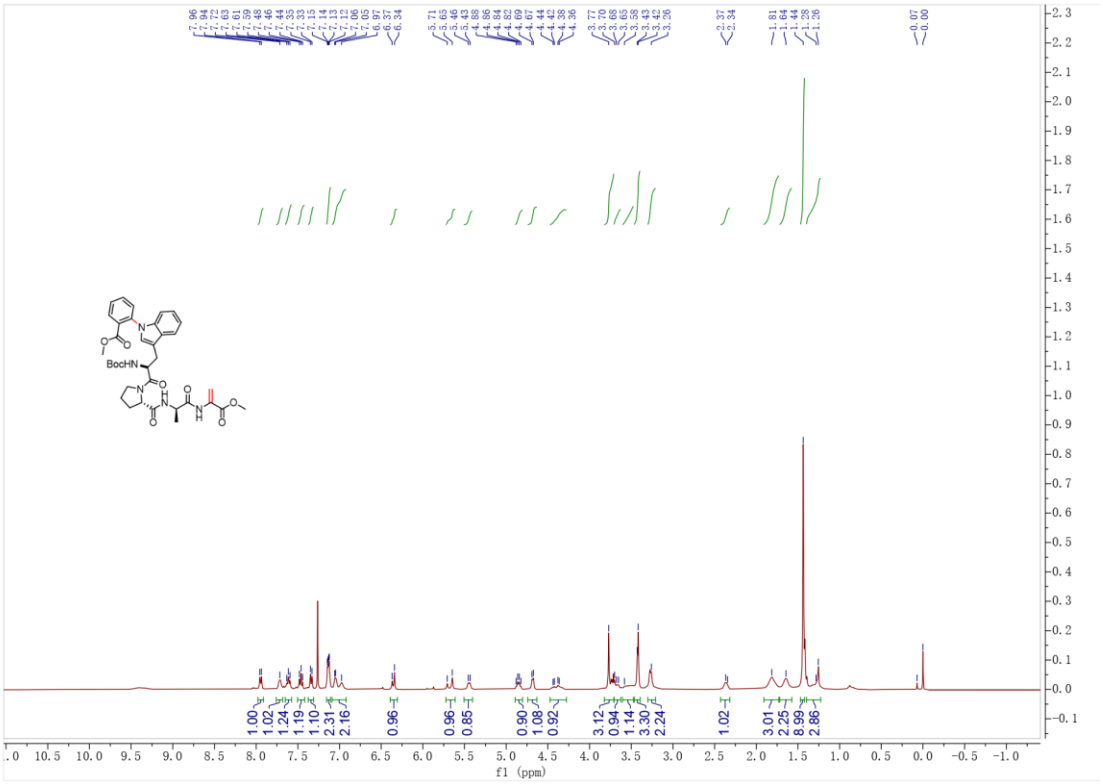

Fig 139. ^{1}H NMR of (**6h'**) (400 MHz, $CDCl_3$)

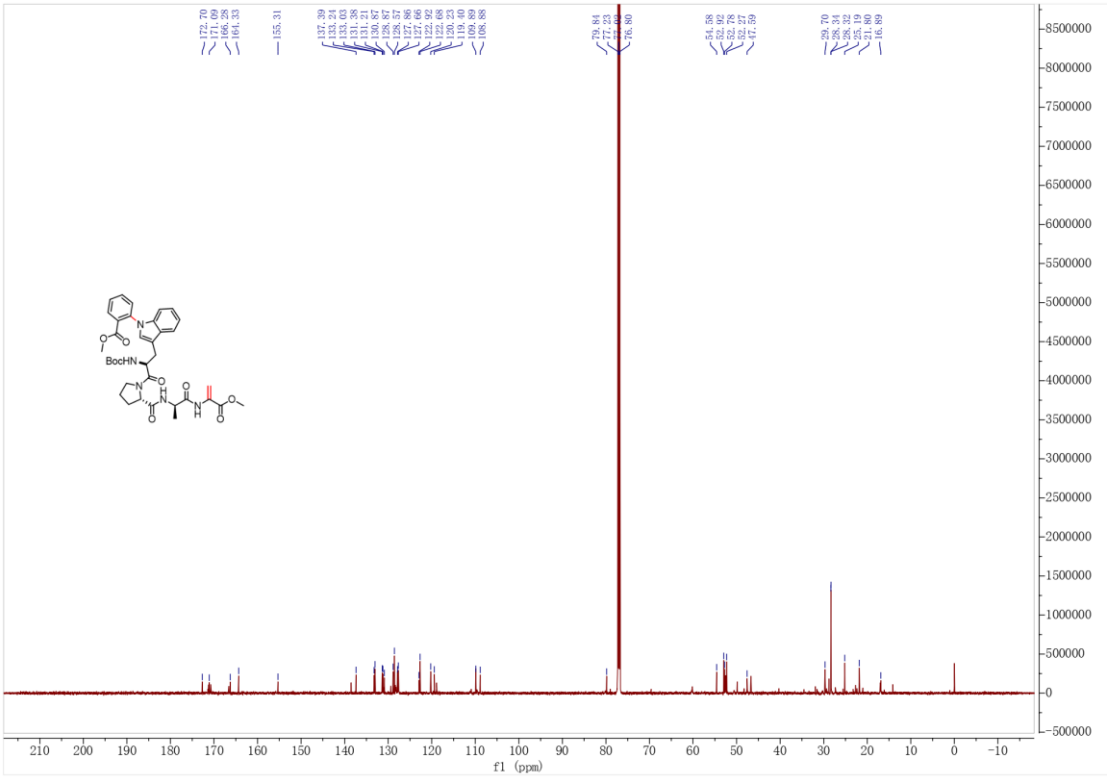

Fig 140. ^{13}C NMR of (**6h'**) (150 MHz, $CDCl_3$)

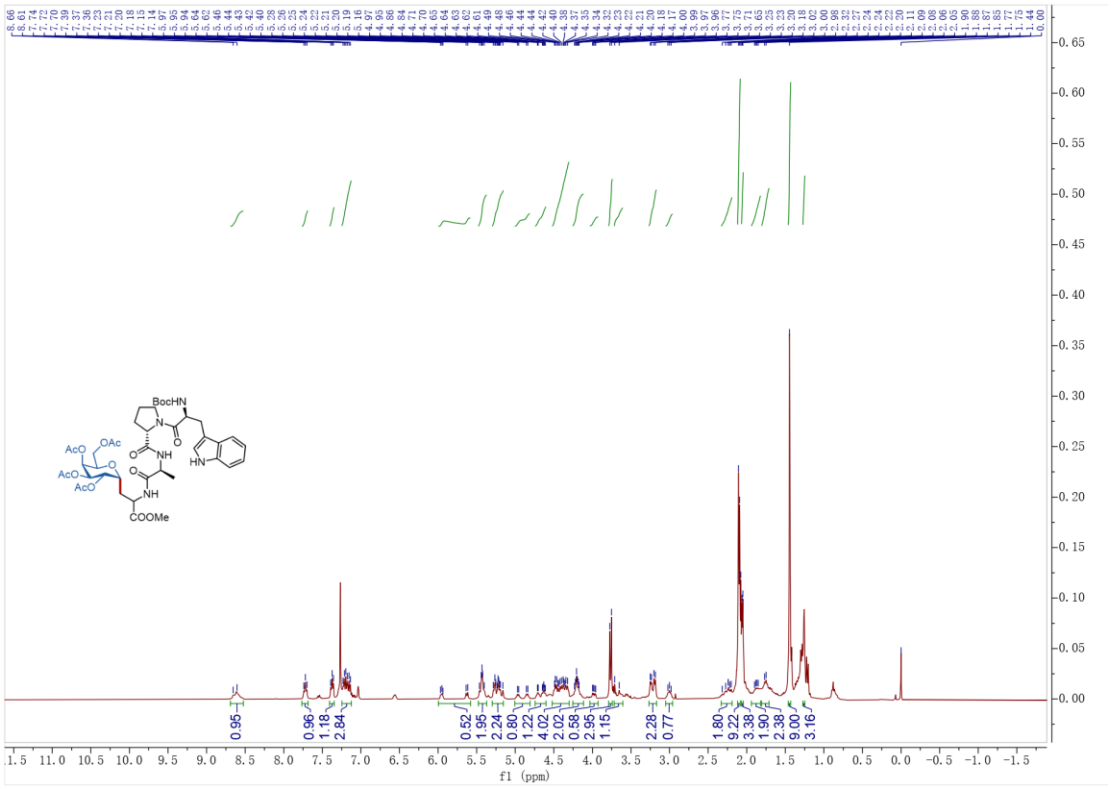

Fig 141. ^{1}H NMR of (**7h**) (400 MHz, $CDCl_3$)

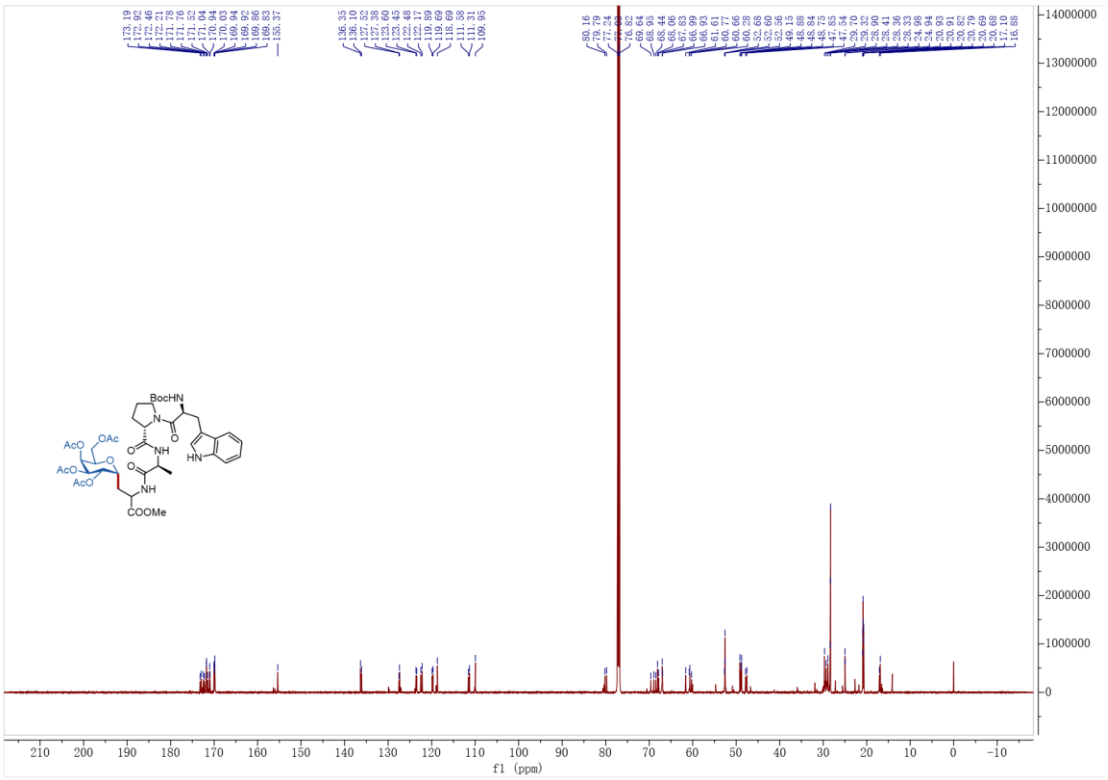

Fig 142. ^{13}C NMR of (**7h**) (150 MHz, $CDCl_3$)

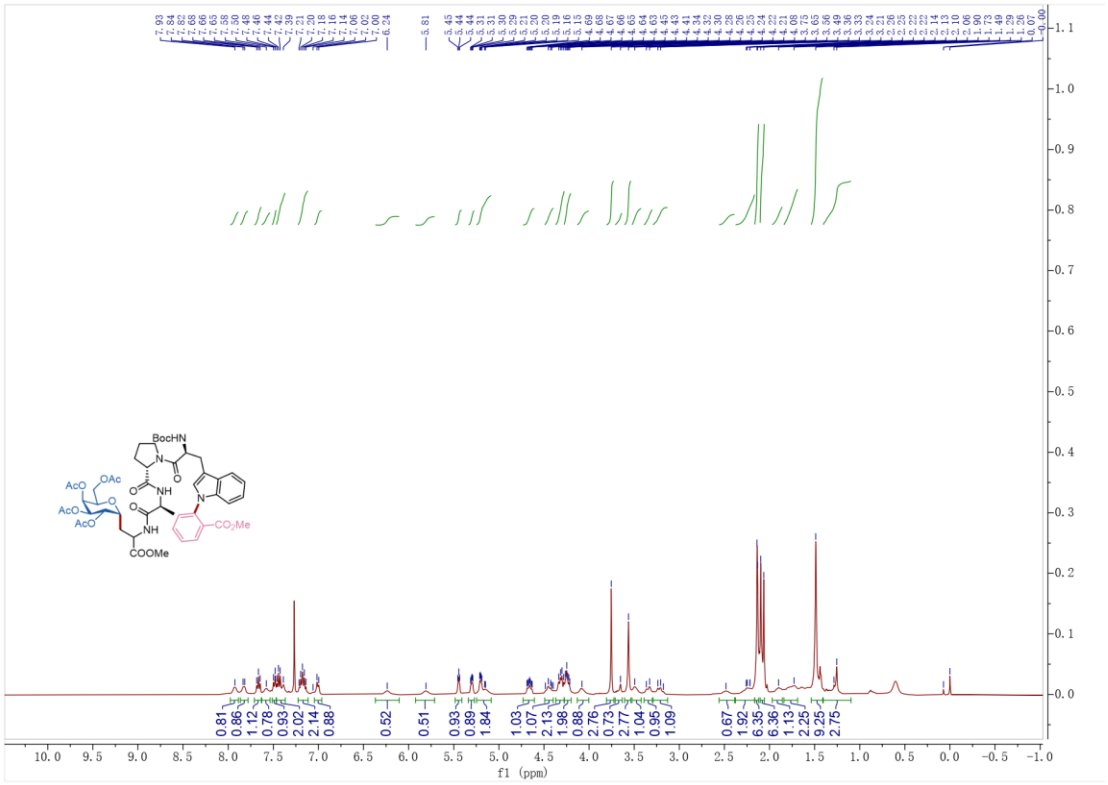

Fig 143. ^{1}H NMR of (**7h'**) (400 MHz, $CDCl_3$)

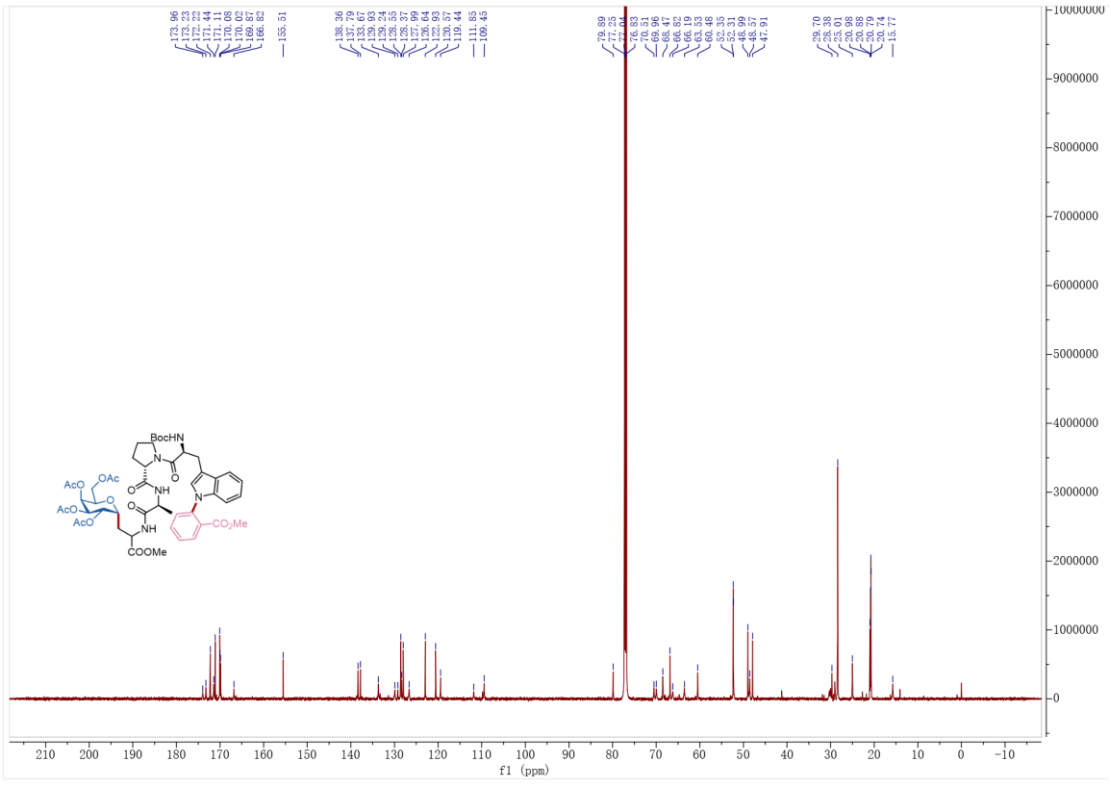

Fig 144. ^{13}C NMR of (**7h'**) (150 MHz, $CDCl_3$)

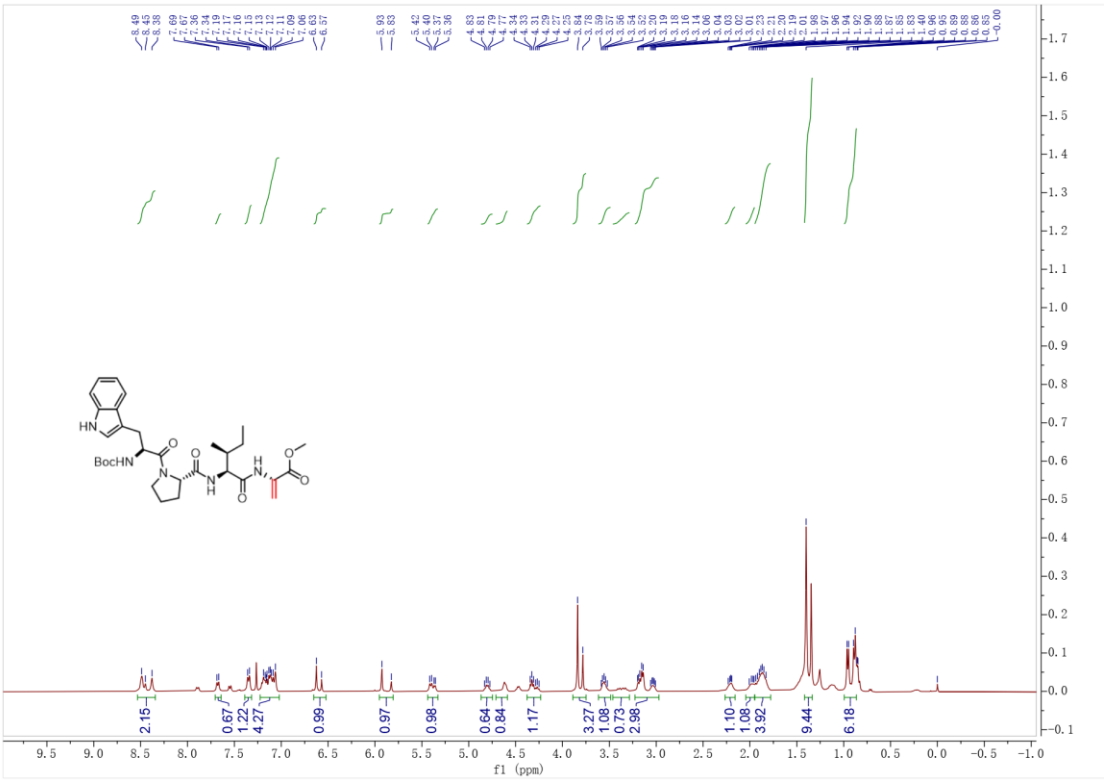

Fig 145. ^{1}H NMR of (**6i**) (400 MHz, $CDCl_3$)

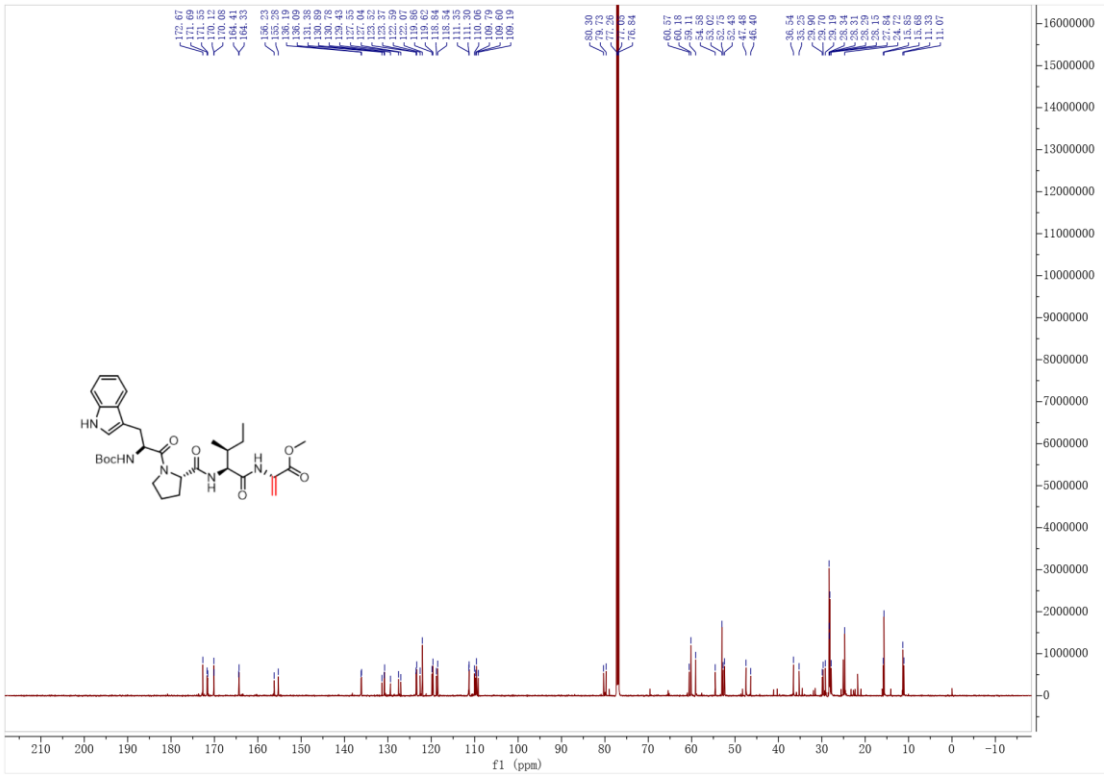

Fig 146. ^{13}C NMR of (**6i**) (150 MHz, $CDCl_3$)

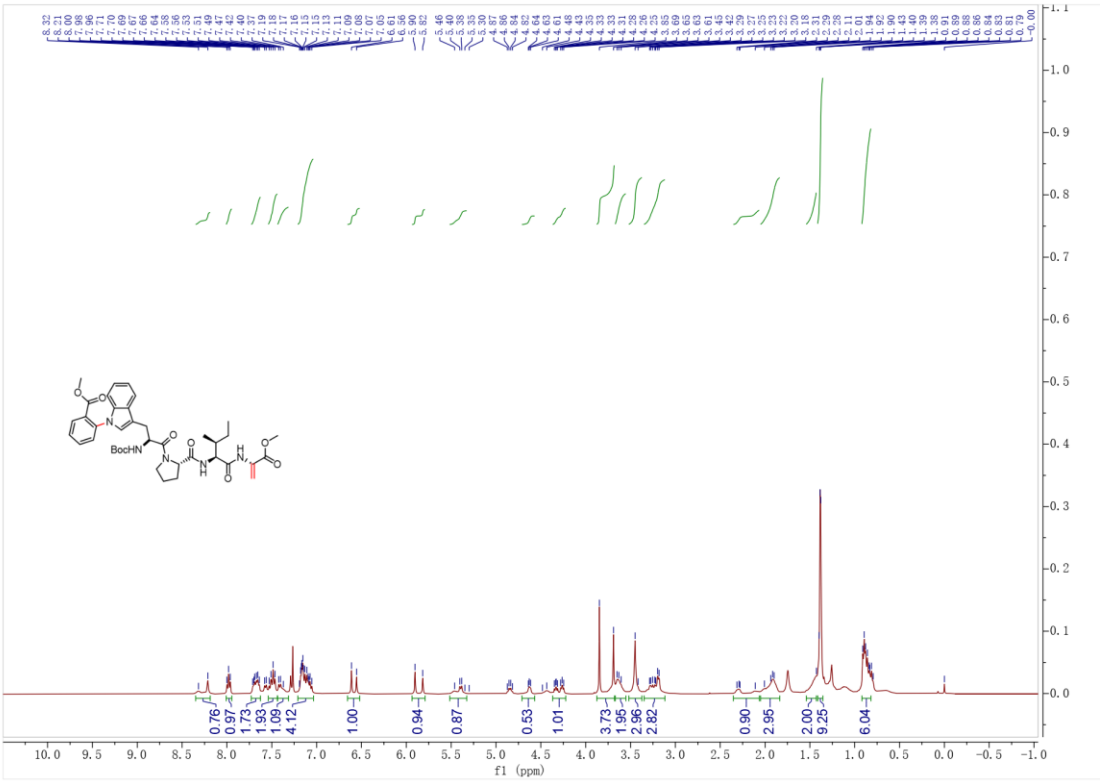

Fig 147. ^{1}H NMR of (**6i'**) (400 MHz, $CDCl_3$)

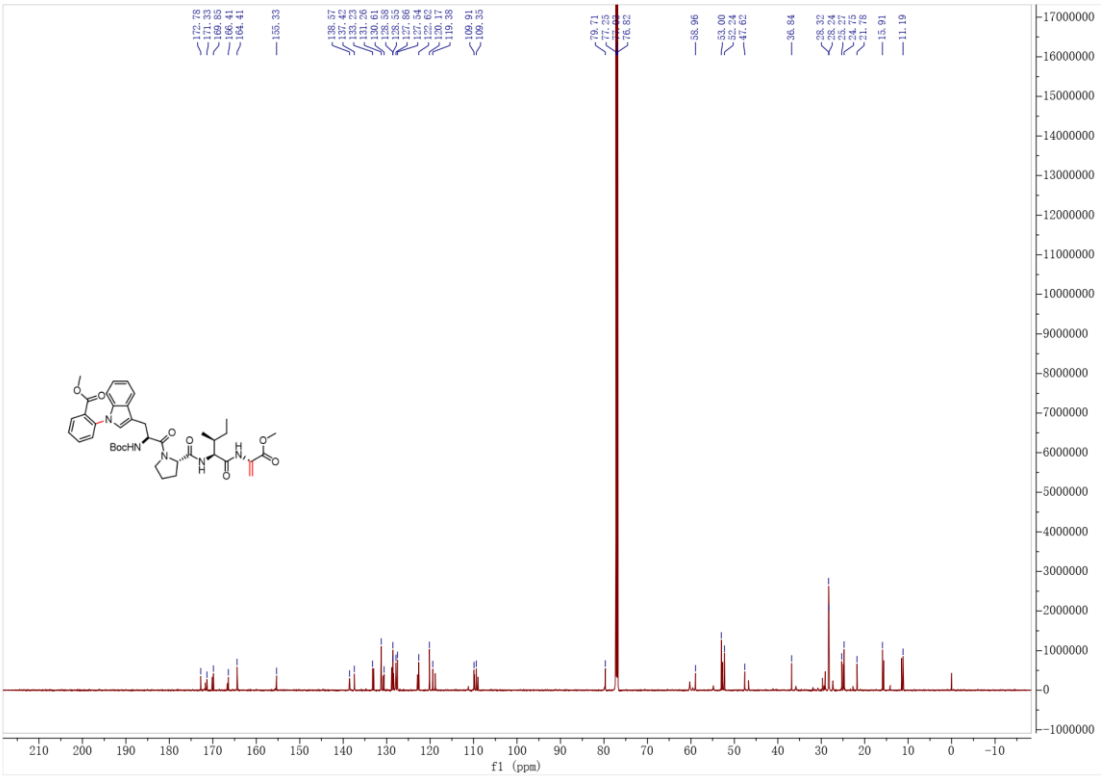

Fig 148. ^{13}C NMR of (**6i'**) (150 MHz, $CDCl_3$)

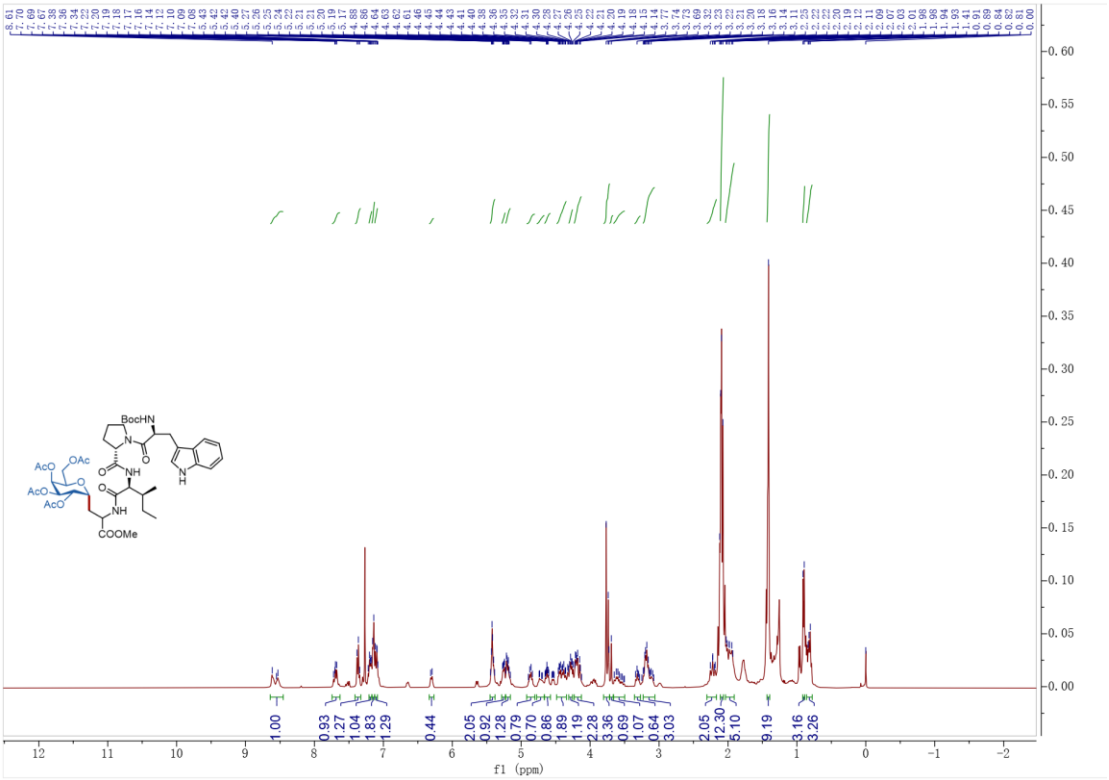

Fig 149. ^{13}C NMR of (**7i**) (400 MHz, $CDCl_3$)

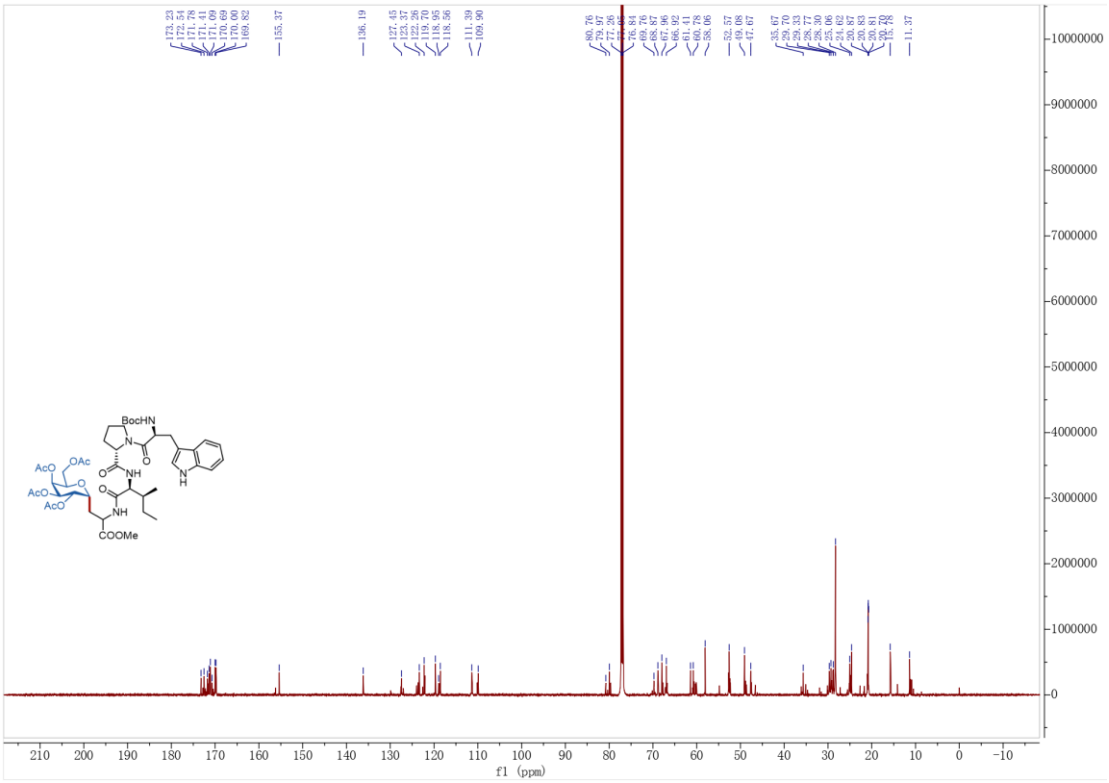

Fig 150. ^{13}C NMR of (**7i**) (150 MHz, $CDCl_3$)

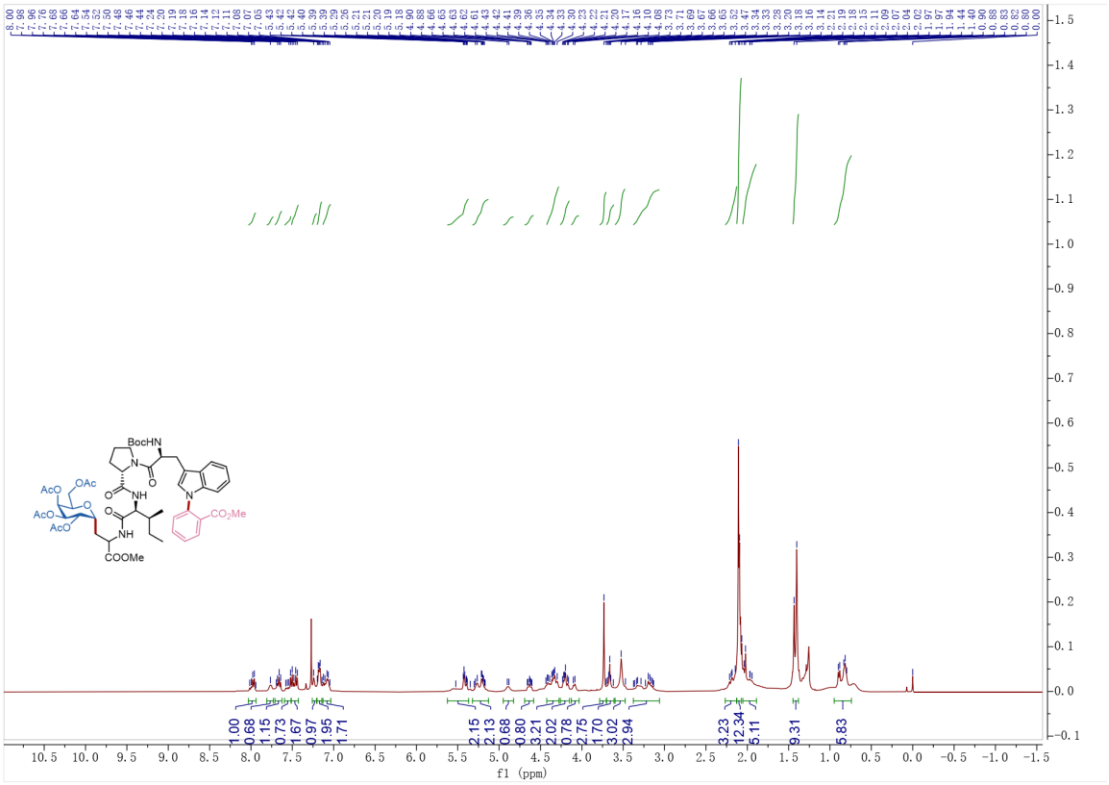

Fig 151. ^{1}H NMR of (**7i'**) (400 MHz, $CDCl_3$)

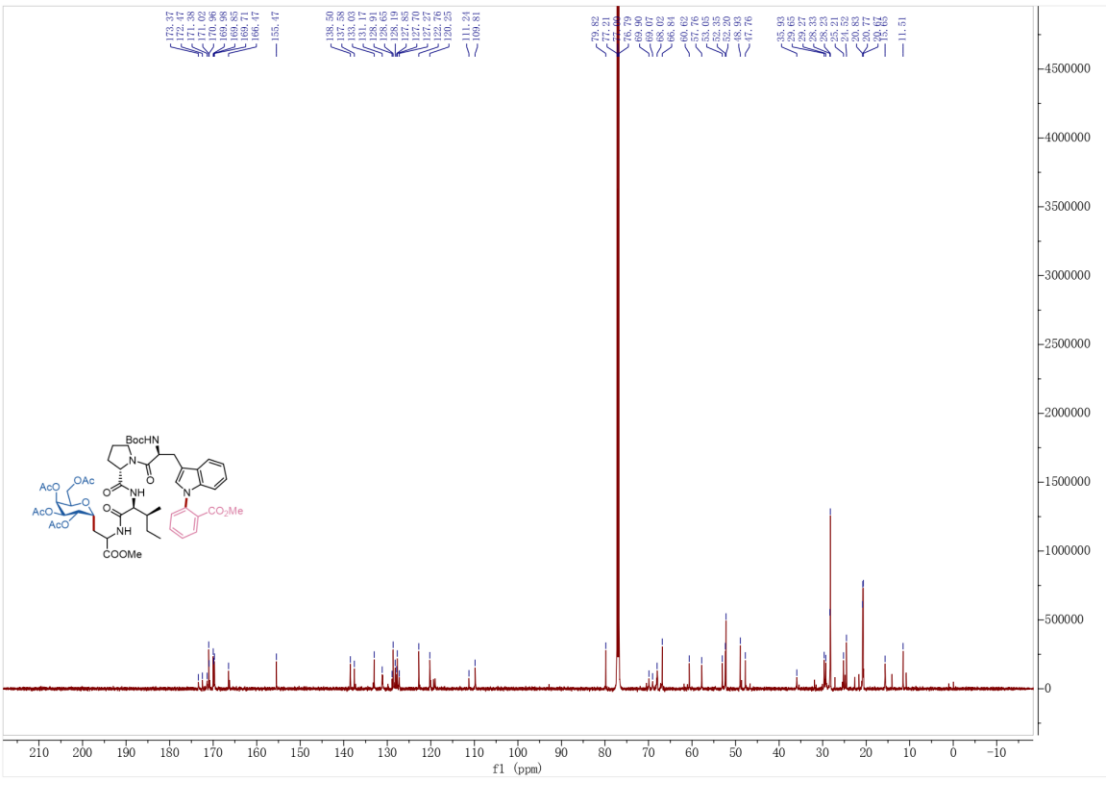

Fig 152. ^{13}C NMR of (**7i'**) (150 MHz, $CDCl_3$)

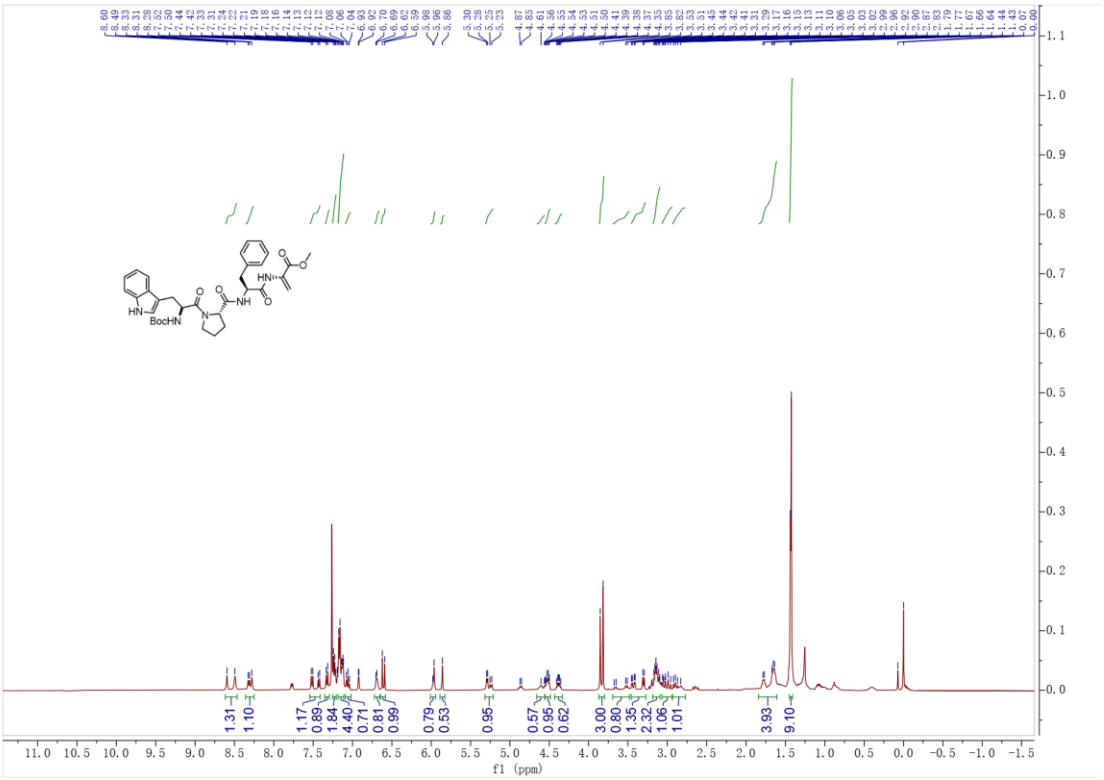

Fig 153. ^{1}H NMR of (**6j**) (400 MHz, $CDCl_3$)

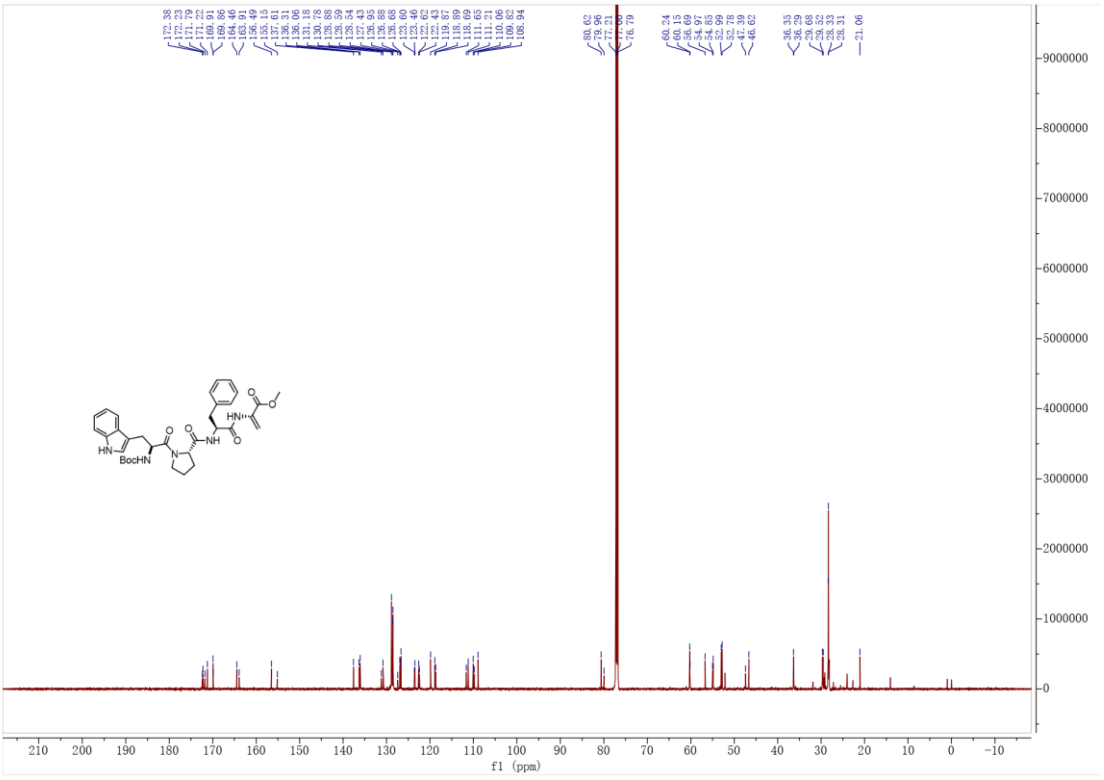

Fig 154. ^{13}C NMR of (**6j**) (150 MHz, $CDCl_3$)

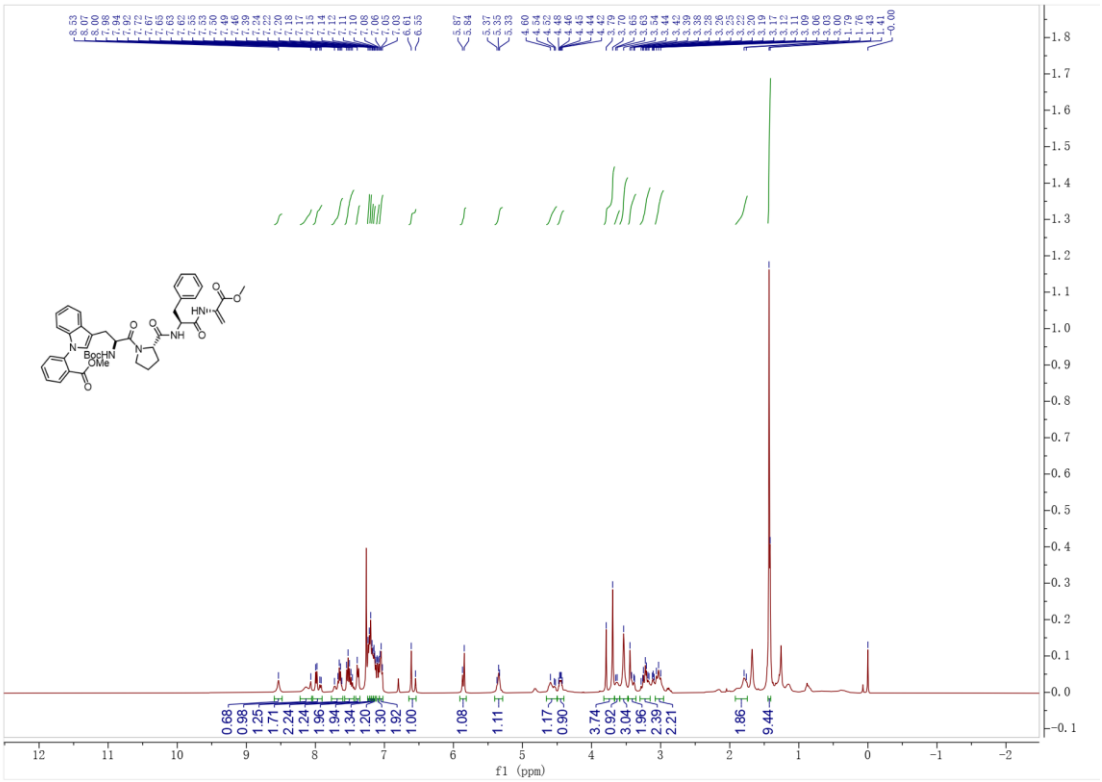

Fig 155. ^{1}H NMR of (**6j'**) (400 MHz, $CDCl_3$)

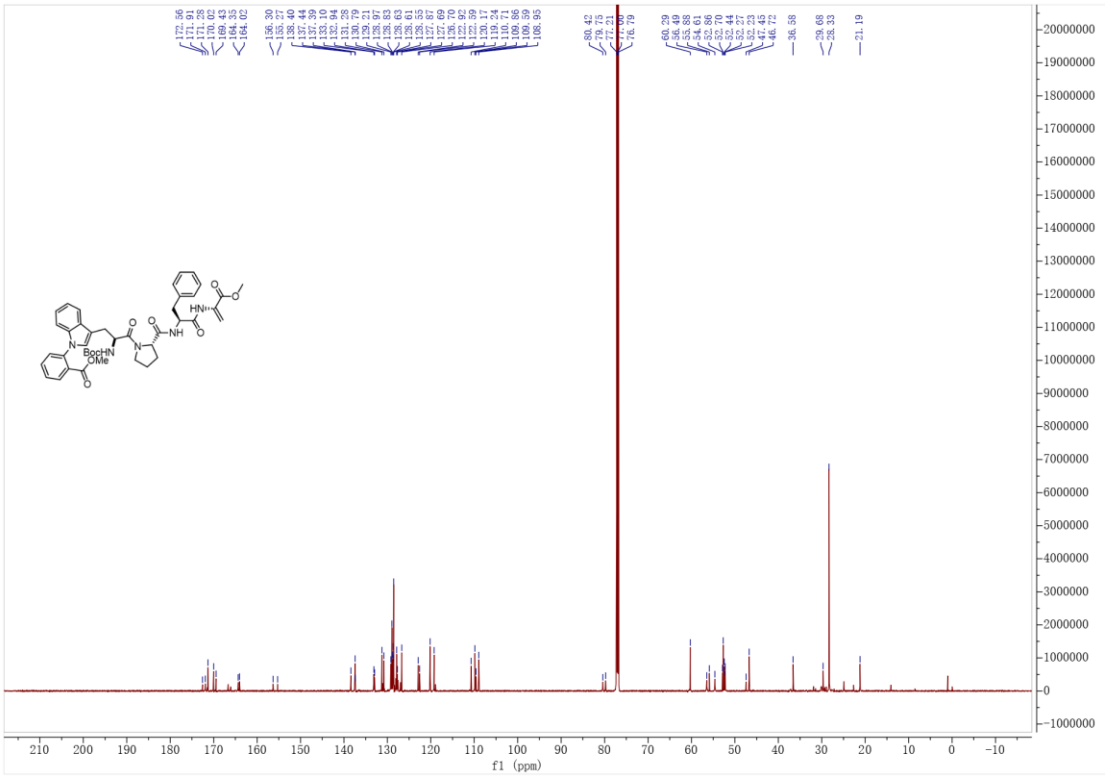

Fig 156. ^{13}C NMR of (**6j'**) (150 MHz, $CDCl_3$)

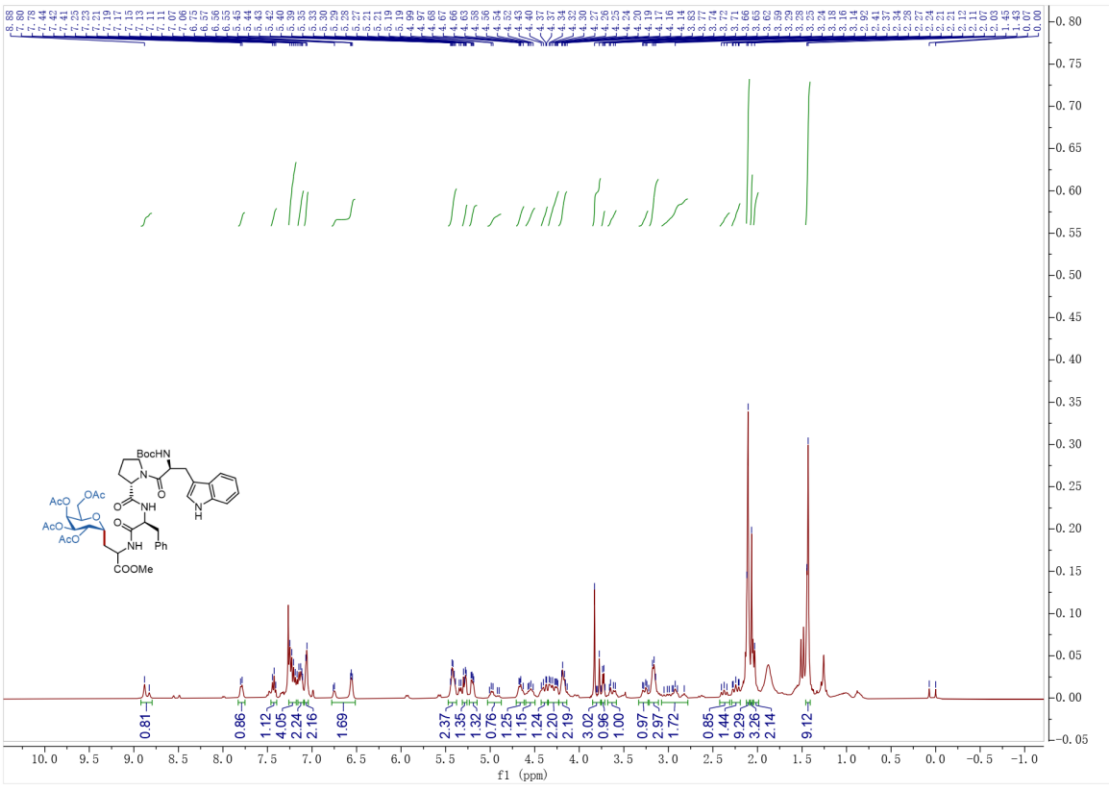

Fig 157. ^{1}H NMR of (**7j**) (400 MHz, $CDCl_3$)

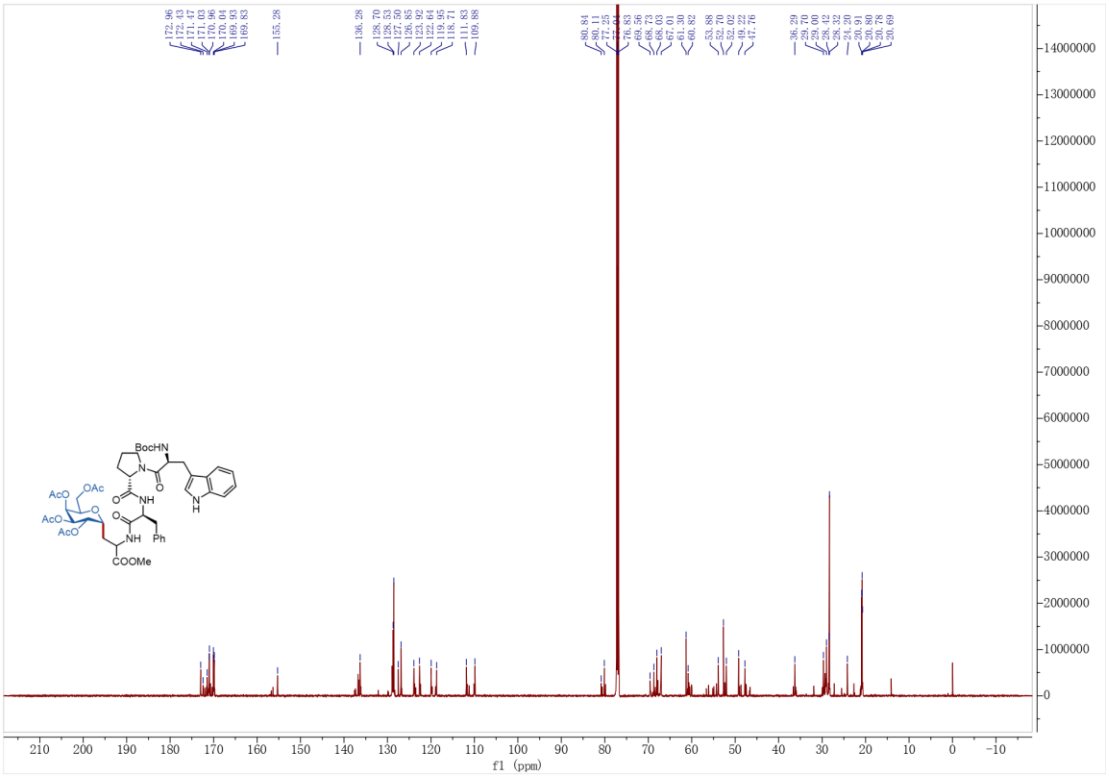

Fig 158. ^{13}C NMR of (**7j**) (150 MHz, $CDCl_3$)

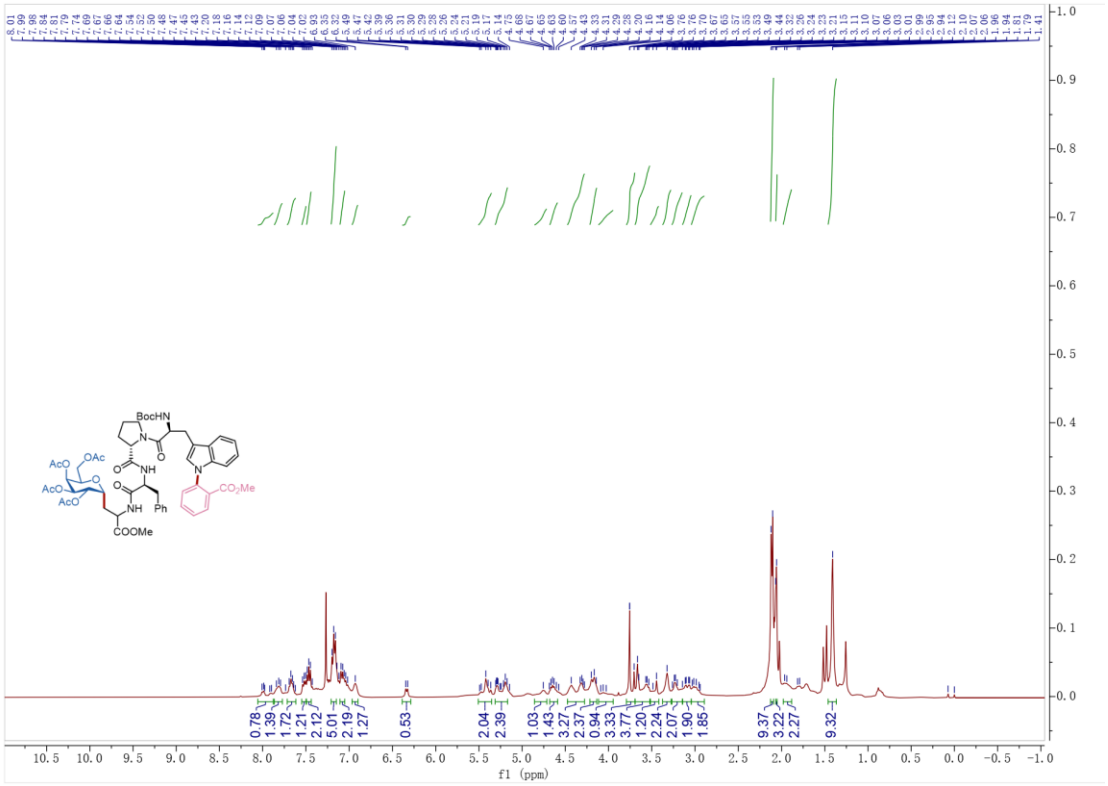

Fig 159. ^{1}H NMR of (**7j'**) (400 MHz, $CDCl_3$)

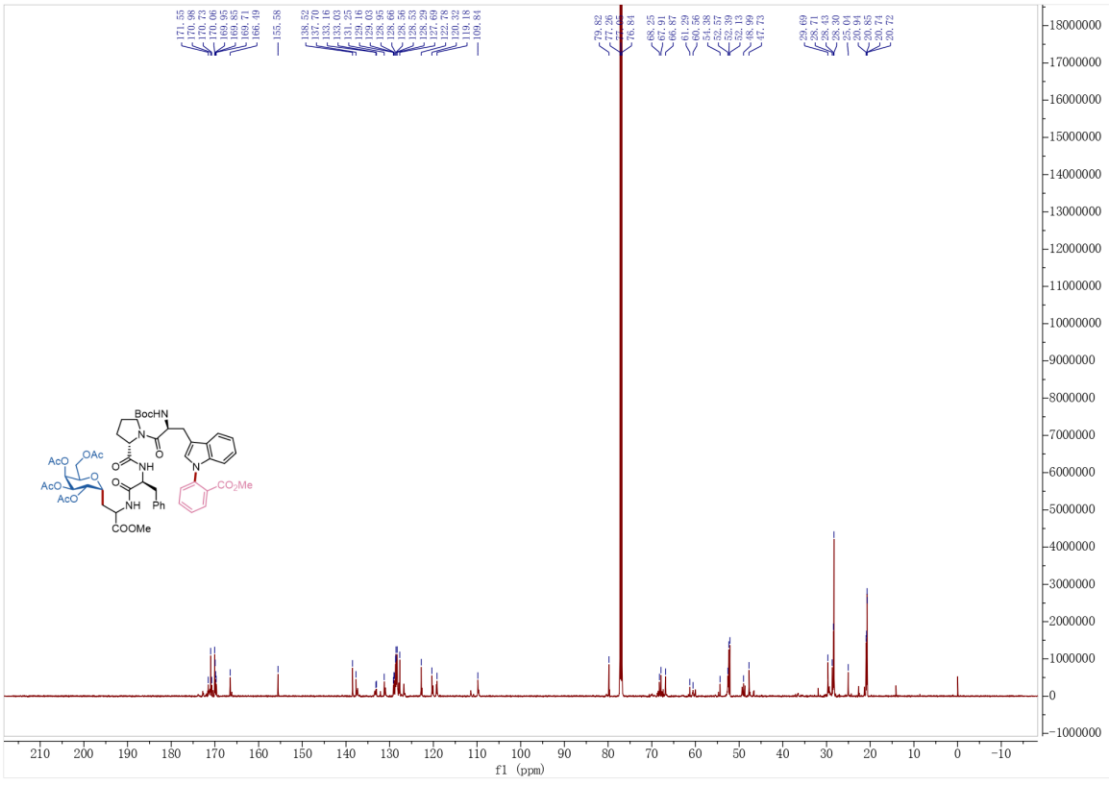

Fig 160. ^{13}C NMR of (**7j'**) (150 MHz, $CDCl_3$)

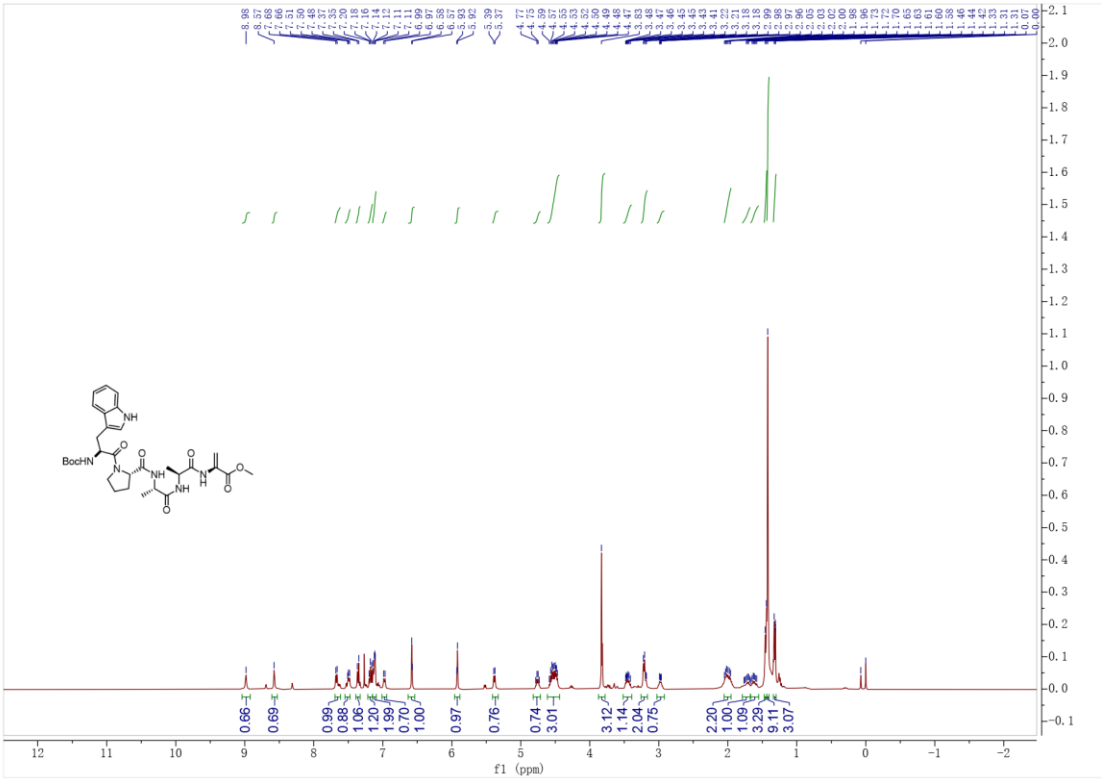

Fig 161. ^{1}H NMR of (**6k**) (400 MHz, $CDCl_3$)

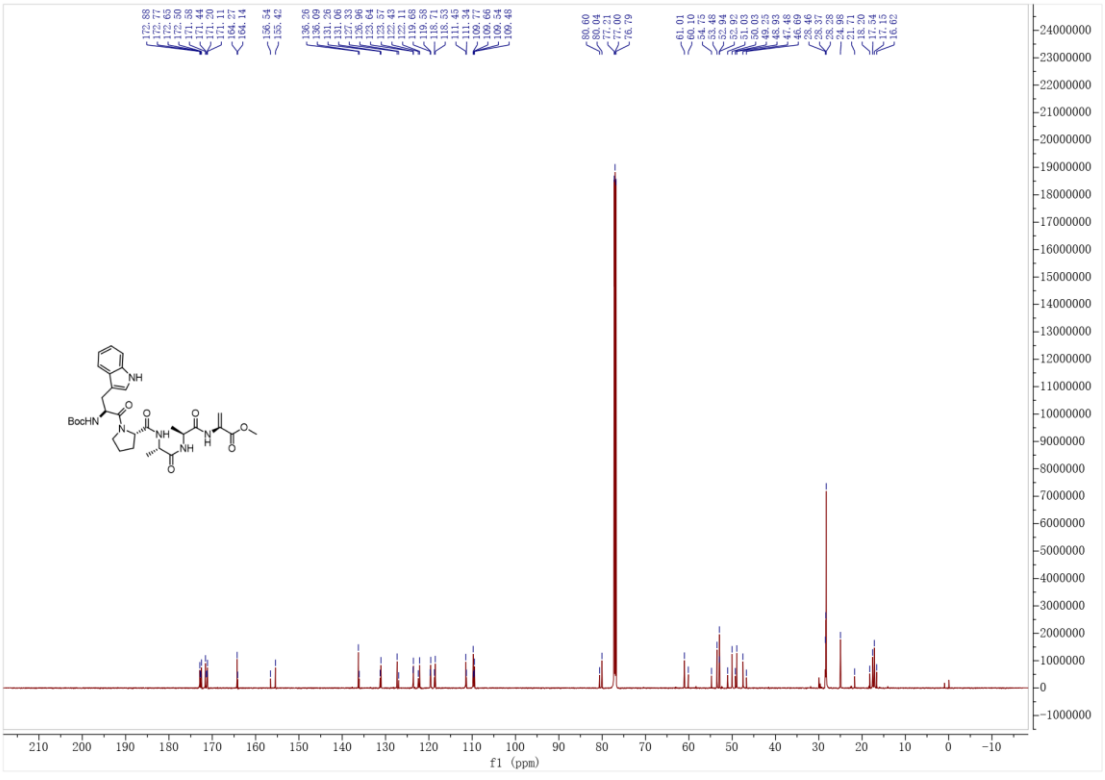

Fig 162. ^{13}C NMR of (**6k**) (150 MHz, $CDCl_3$)

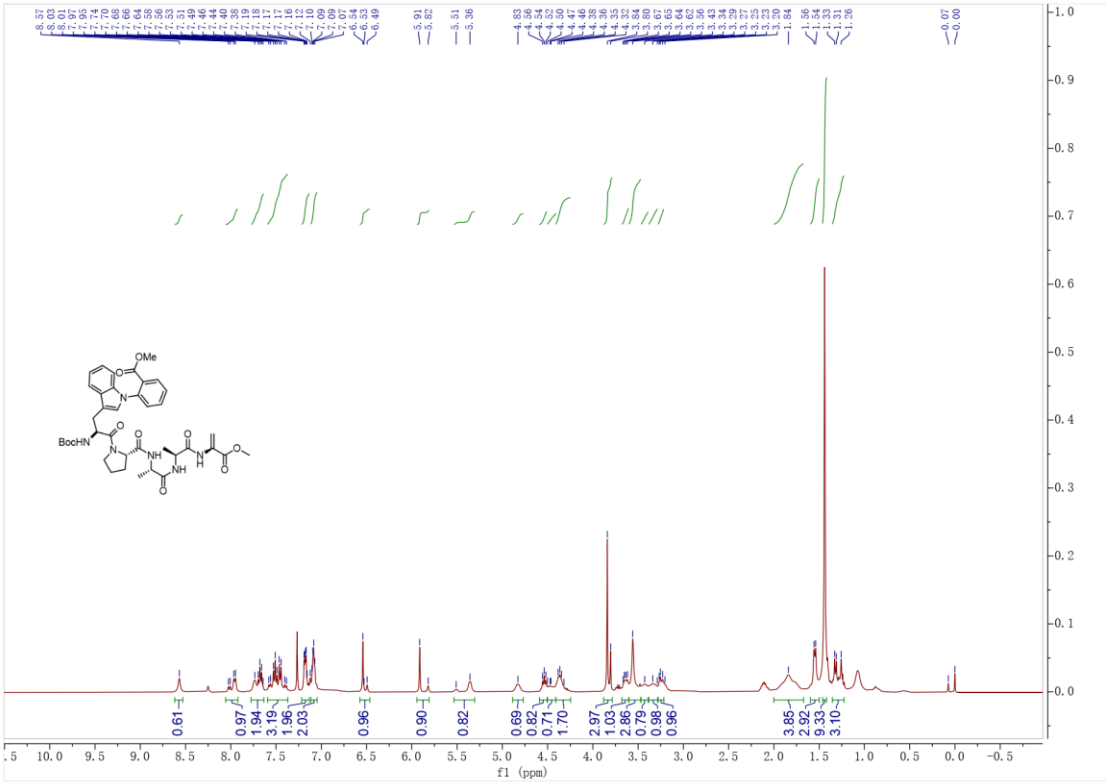

Fig 163. ^{1}H NMR of (**6k'**) (400 MHz, $CDCl_3$)

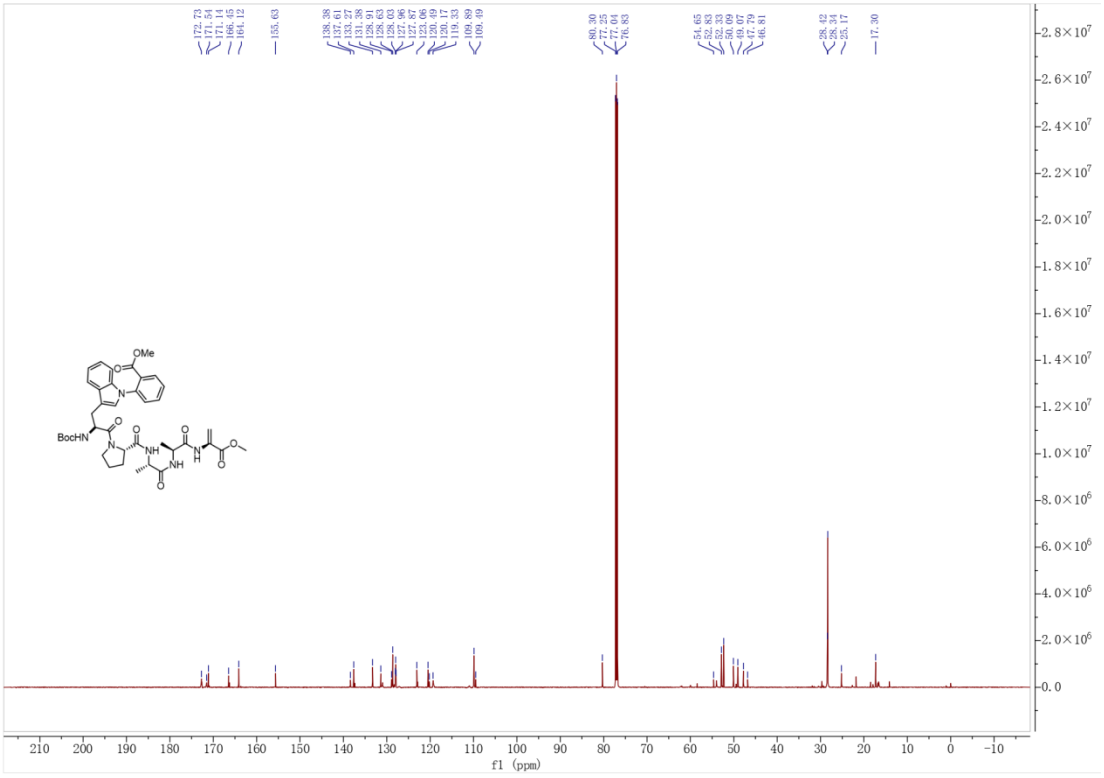

Fig 164. ^{13}C NMR of (**6k'**) (150 MHz, $CDCl_3$)

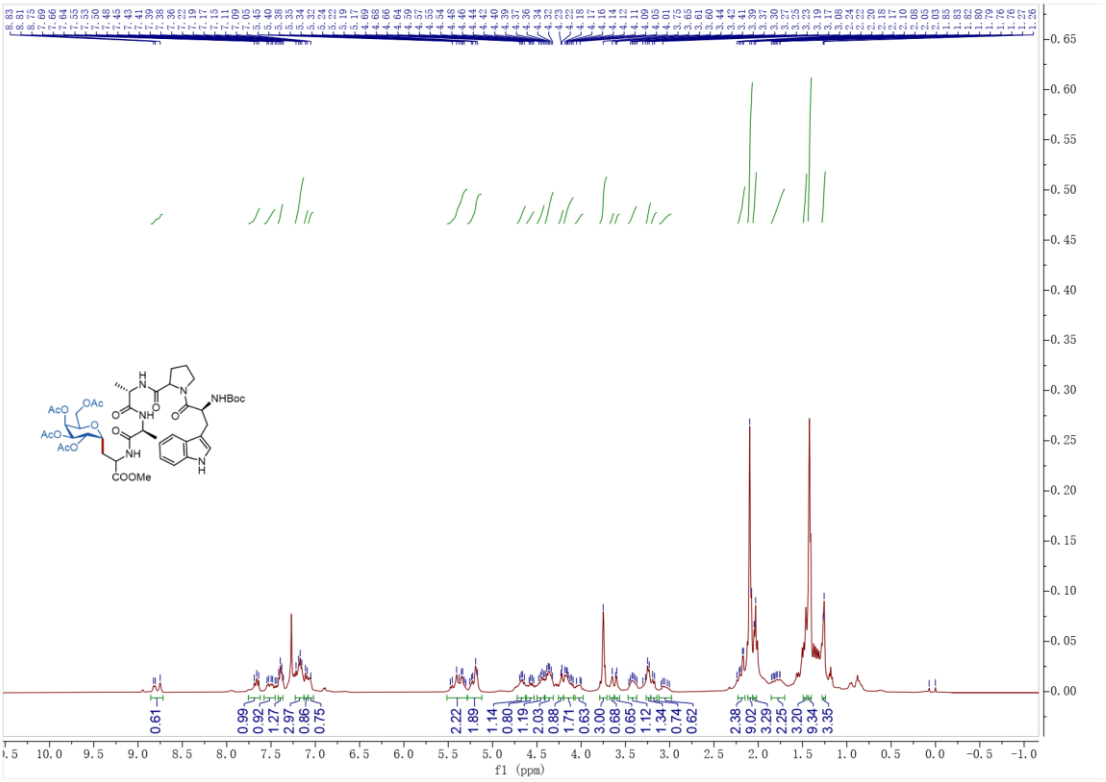

Fig 165. ^{1}H NMR of (**7k**) (400 MHz, $CDCl_3$)

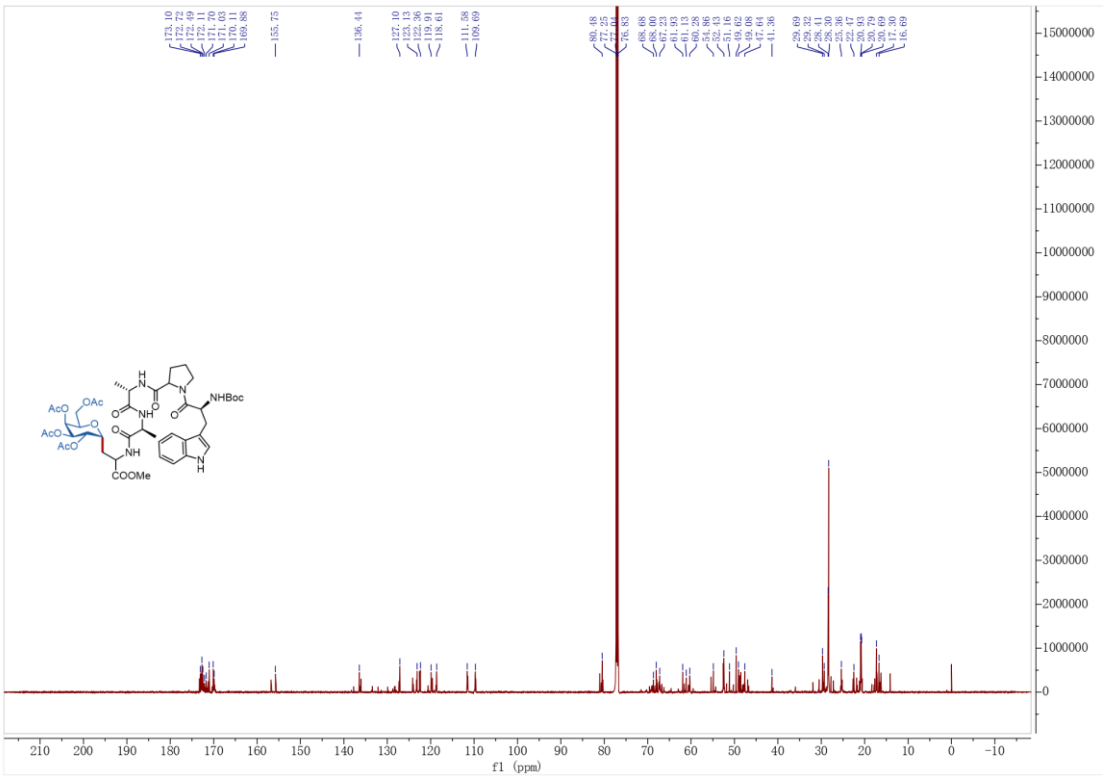

Fig 166. ^{13}C NMR of (**7k**) (150 MHz, $CDCl_3$)

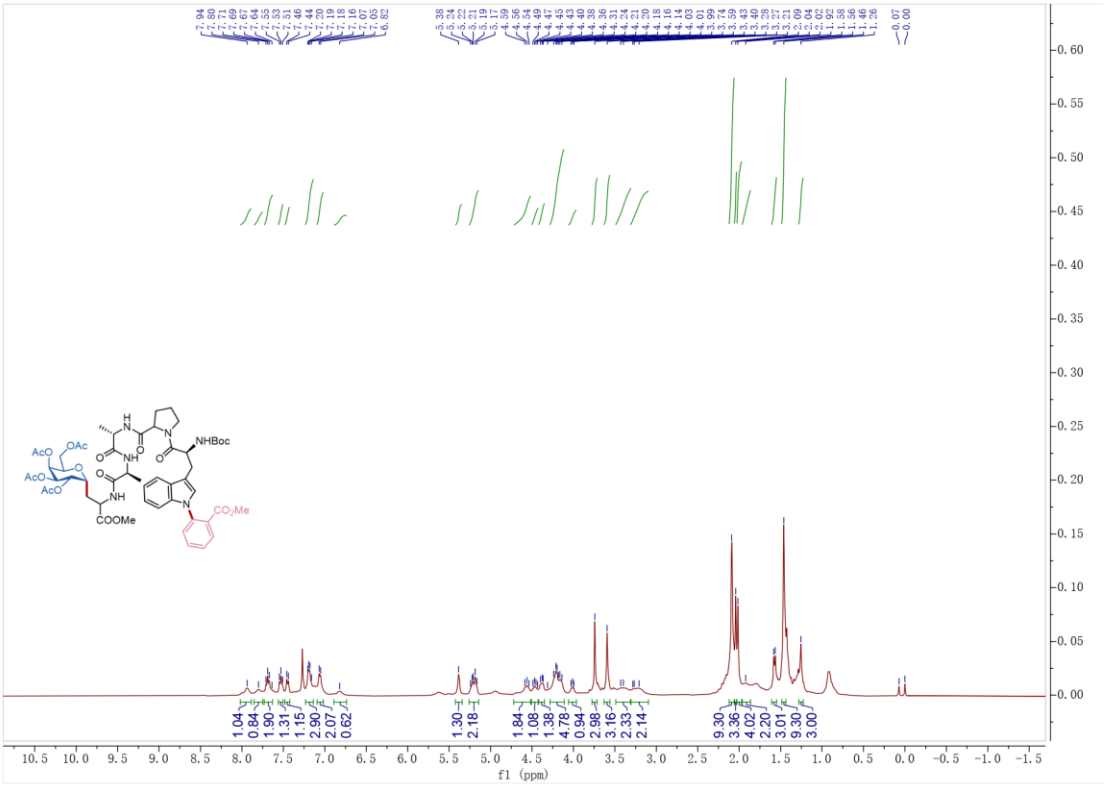

Fig 167. ^{1}H NMR of (**7k'**) (400 MHz, $CDCl_3$)

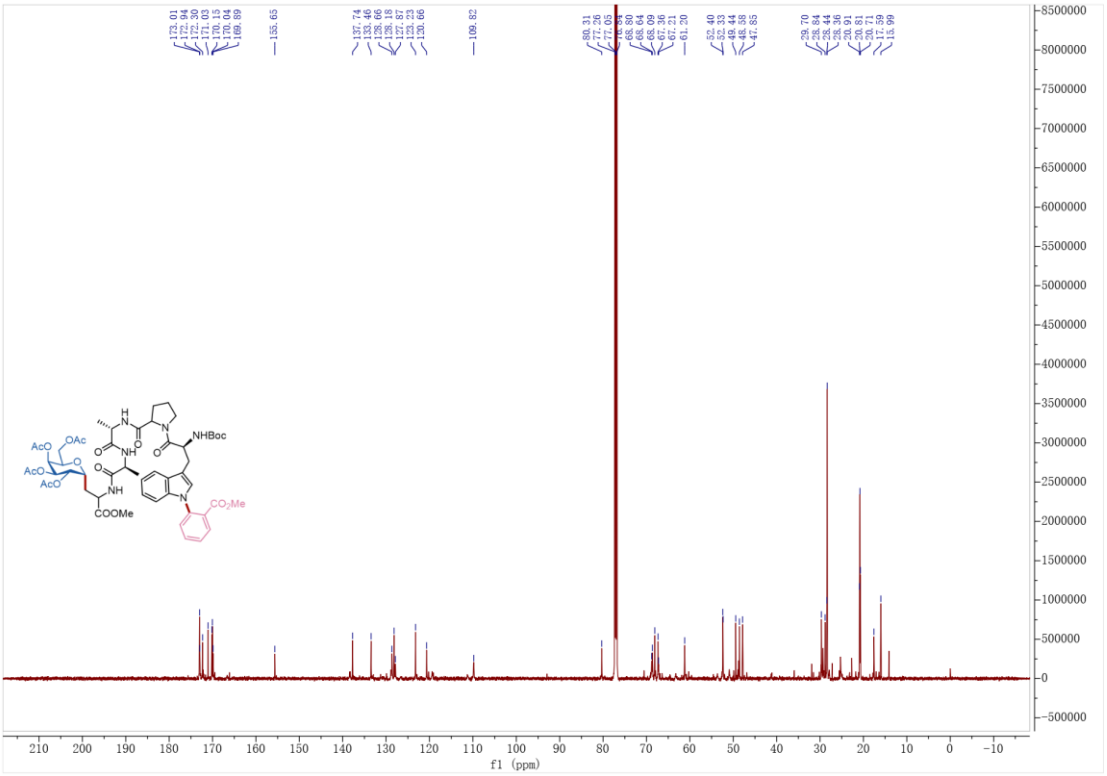

Fig 168. ^{13}C NMR of (**7k'**) (150 MHz, $CDCl_3$)

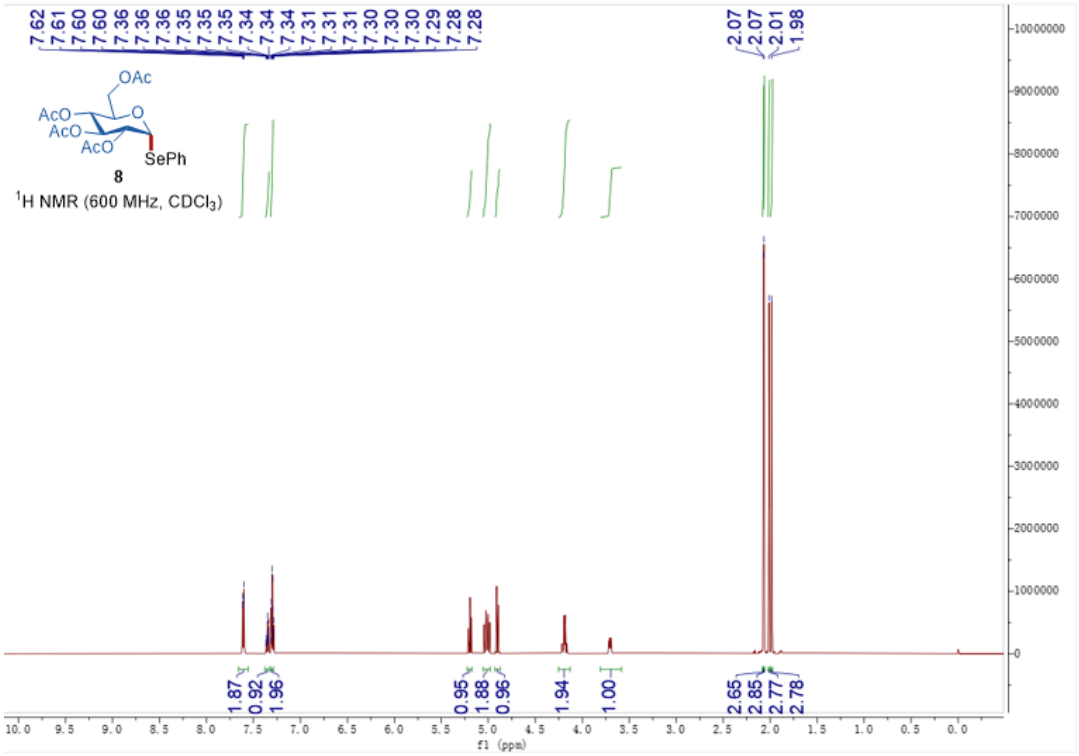

Fig 169. ^{1}H NMR of **8** (600 MHz, $CDCl_3$)

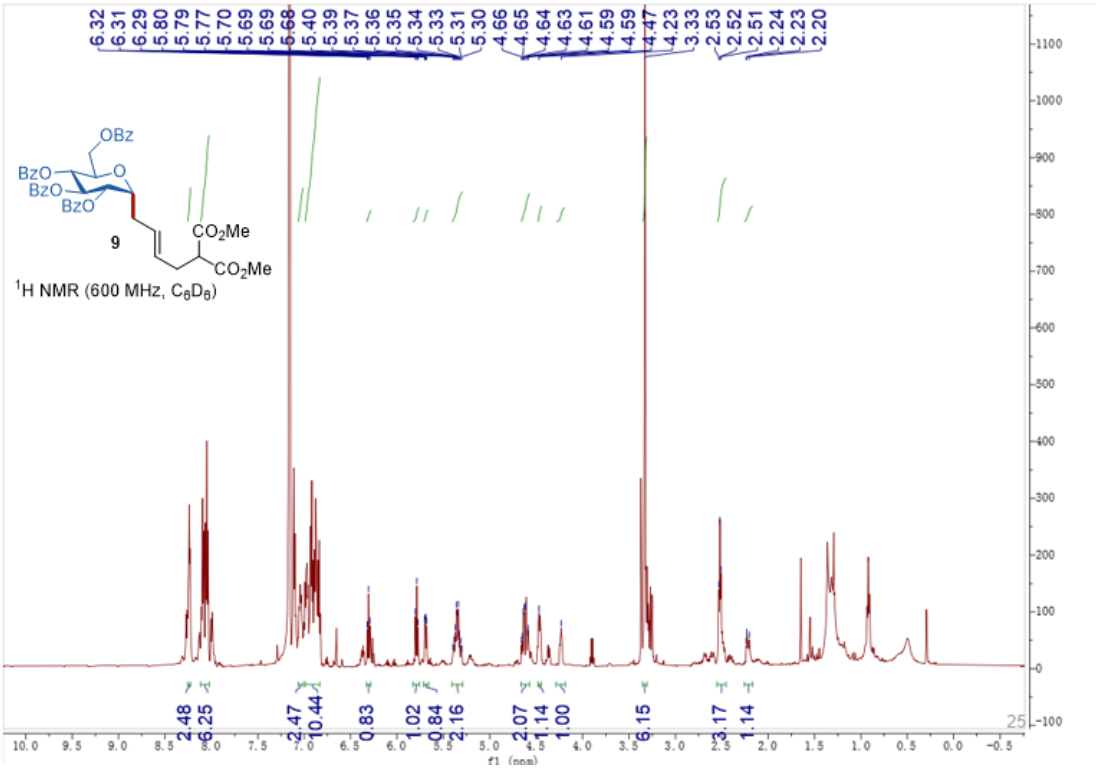

Fig 169. ^{1}H NMR of **9** (600 MHz, C_6D_6)

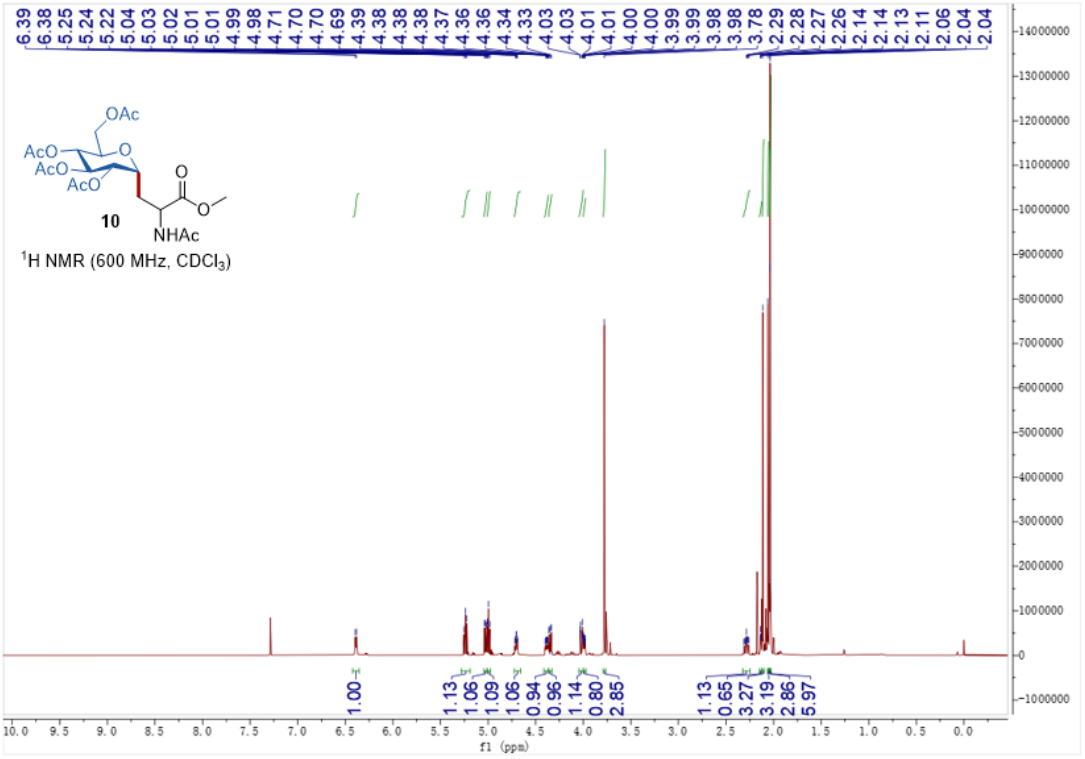

Fig 170. ^{1}H NMR of **10** (600 MHz, $CDCl_3$)

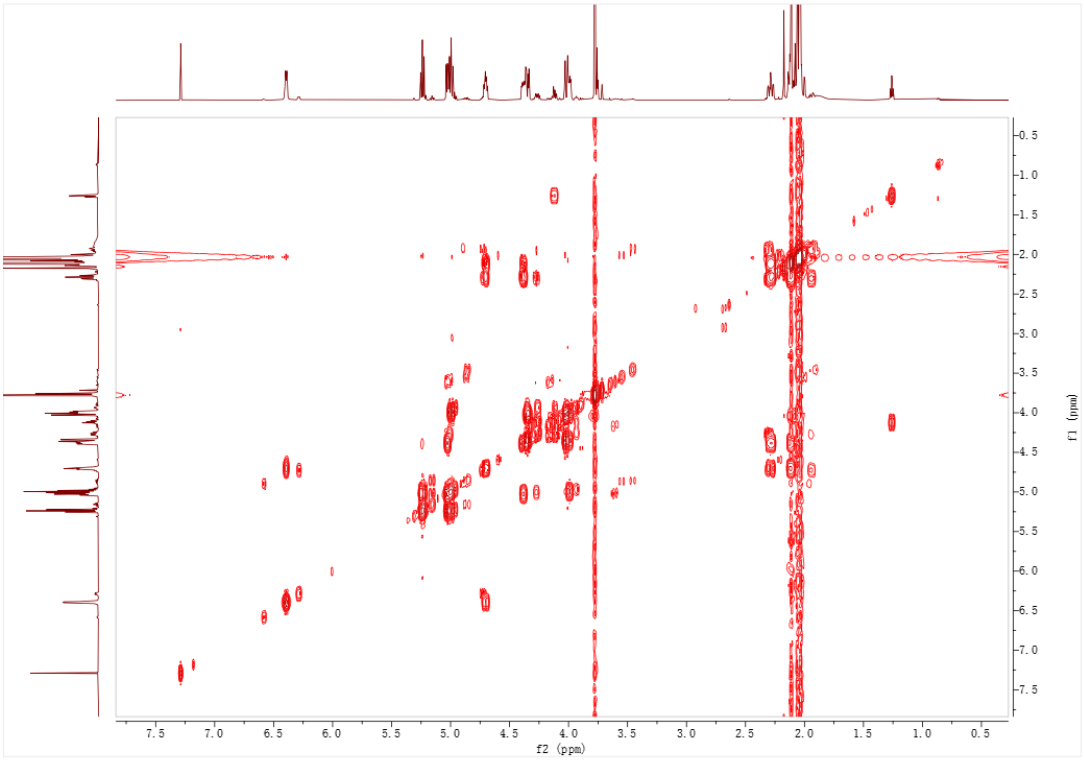

Fig 171. COSY of **10**

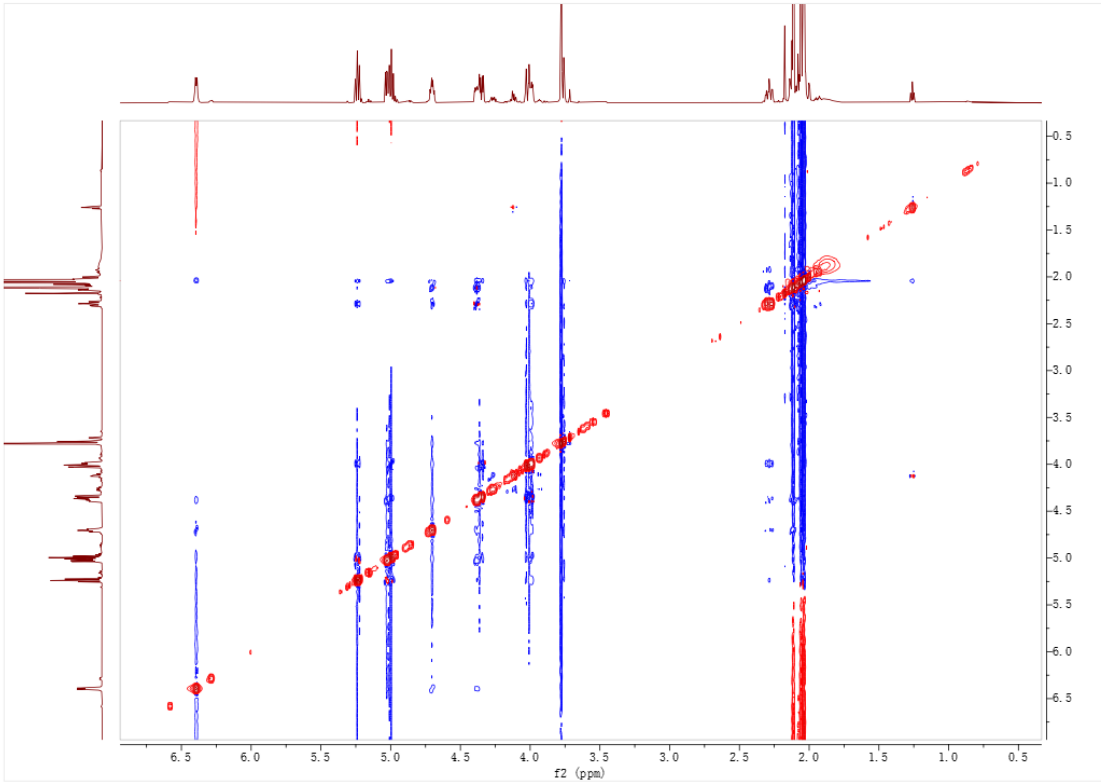

Fig 172. NOESY of **10**