Supporting Information

Precise Functionalization of Peptides *via* Copper-catalyzed Ullmann Coupling

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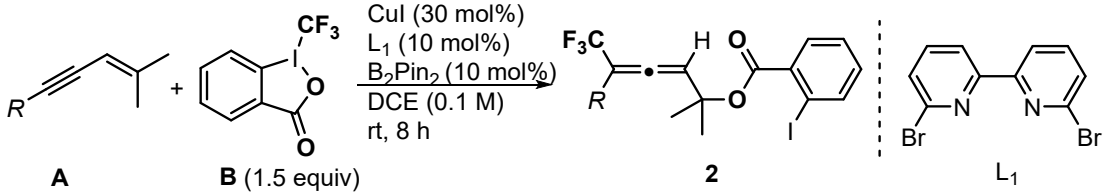
Instrumentation and Chemicals

NMR spectra were recorded on Bruker 400 and 600 M spectrometers and JEOL 400M spectrometers, operating at 400 and 600 MHz for ^{1}H NMR and 100 and 150 MHz for ^{13}C NMR spectrophotometer using $CDCl_3$ and TMS as the internal standard. Chemical shift values for ^{1}H and ^{13}C are referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^{1}H, 77.00 ppm for ^{13}C; 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 spectra (HRMS) were recorded on electron-spray ionization (ESI) technique.

Experimental Section

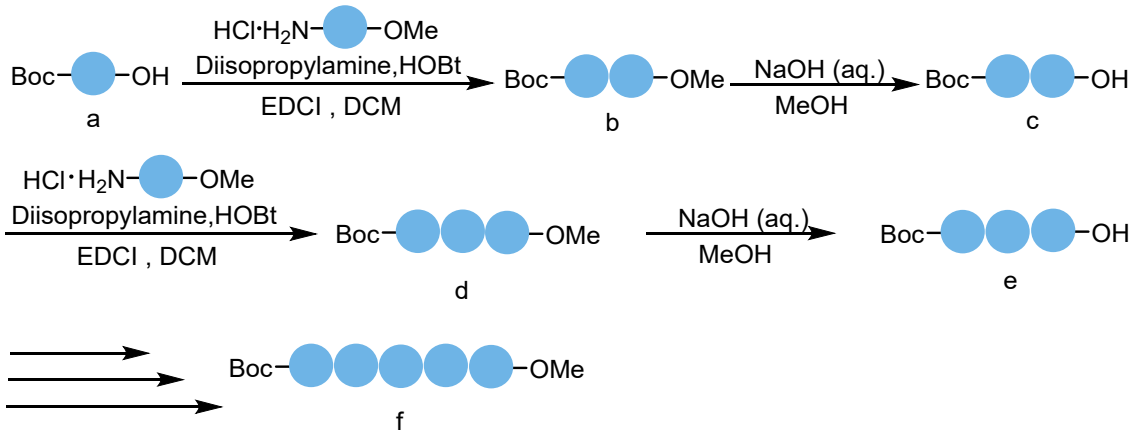
All reactions were carried out under nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard note procedures unless otherwise noted. CuI was purchased from Energy Chemical Reagent Co., Ltd., $Pd(PPh_3)_4$ was purchased from Energy Chemical Reagent Co., Ltd., DCE was freshly distilled over CaH_2 under N_2. Energy Chemical Reagent Co., Ltd. EDCI·HCl was the abbreviations of 1-(3-dimethylaminopropyl) -3-ethylcarbondiimide hydrochloride, it was purchased from Energy Chemical Reagent Co., Ltd.; HOBt was the abbreviations of 1-Hydroxybenzotriazole, it was was purchased from Energy Chemical Reagent Co., Ltd..

General synthesis of Trifluoromethyl-Substituted building blocks



The general procedure for allenes can be found in the references. [1] In an oven-dried 8 mL screwed-capped vial B_2Pin_2 (2.5 mg, 0.01 mmol, 10 mol%), 6,6'-dibromo-2,2'-bipyridine (3.1 mg, 0.01 mmol, 10 mol%), B (47.4 mg, 0.15 mmol, 1.5equiv.) were weighted. Then the vial was transferred into the glove-box, CuI (5.7 mg, 0.01 mmol, 30 mol%), A (13.6 mg, 0.1 mmol, 1.0 equiv.) and anhydrous DCE (1.0 mL) were added to the vial. The vial was sealed and moved outside of the glove-box. The vial was kept at 25 °C about 8 hours. After the reaction completion monitored by TLC (R_f = 0.3, PE), the reaction was quenched by brine (2 mL), and extracted with EtOAc (5 mL × 2), the organic solvent was filtrated through a pad of short anhrdrous Na_2SO_4 column. Evaporation and flash Silica gel column purification (petroleum as eluent) of the crude product provided 2 (33.0 mg) in 73% isolated yield.

General synthesis of peptides



The general synthesis of peptides can be found in the references. [2] Taking

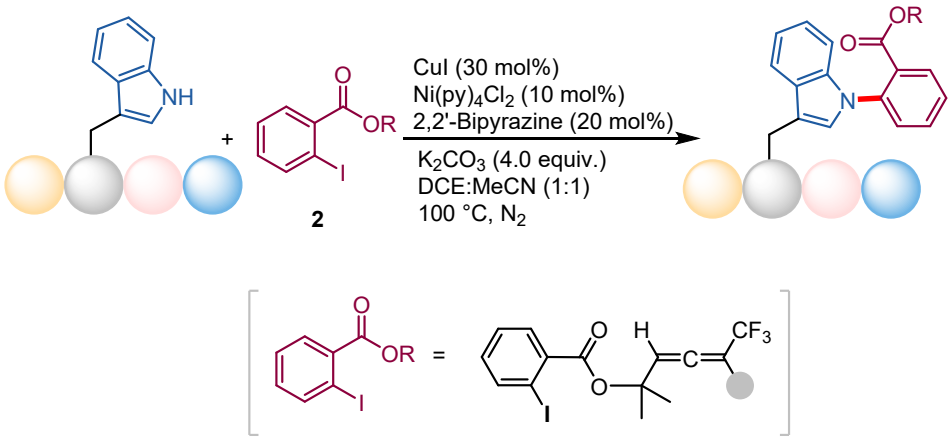
pentapeptide as an example: N-Boc-L-Trp-OH (a) (15 mmol, 1.0 equiv.) and amino acid methyl ester hydrochloride (1.0 equiv.) were added to a round bottom flask, and dichloromethane (100 mL) was added to it. Transfer the reaction into an ice bath, add diisopropylamine (2.5 equiv.) at 0 ℃, and stir for 15 minutes. Afterwards, keeping the temperature constant, HOBt (1.2 equiv.) was added and stirred for 30 minutes. Finally, EDCI (1.5 equiv.) was added and the reaction system was stirred at 0 ℃ for 3 hours. Then stir overnight at room temperature. Add water to the reaction system, separate the organic and aqueous phases in a separatory funnel, and extract the aqueous phase multiple times with dichloromethane (20 mL × 3). After merging the organic phases, wash the organic phases sequentially with 1M HCI aqueous solution (20 mL), saturated $NaHCO_3$ solution (20 mL), and saturated saline solution (20 mL). After washing, dry the organic phase with anhydrous Na_2SO_4, evaporate the solvent under reduced pressure, and then use column chromatography to obtain the dipeptide product (b) (60-88% yield).

Add the dipeptide product (b) to a round bottom flask, dissolve it in methanol, and then add 2 M NaOH aqueous solution (3.2 equiv.). Stir the reaction system at room temperature overnight. After the reaction is complete, use a rotary evaporator to remove methanol from the system, dilute the remaining reaction solution with water, acidify it with 1M HCl aqueous solution, and adjust the pH to 1. In a separatory funnel, extract the aqueous phase multiple times with ethyl acetate, dry the organic phase with anhydrous Na_2SO_4, and evaporate the solvent under reduced pressure to obtain crude product (c).

Repeat the above condensation and deprotection processes for the crude product (c) after demethylation. After the final condensation process is completed, water is added to the reaction system to stop the reaction. Separate the organic and aqueous phases in a separatory funnel, and extract the aqueous phase multiple times with dichloromethane (20 mL × 3). Combine the organic phases and wash them with 1 M HCl aqueous solution (20 mL), saturated $NaHCO_3$ solution (20 mL), and saturated saline solution (20 mL) in sequence. After washing, dry the organic phase with

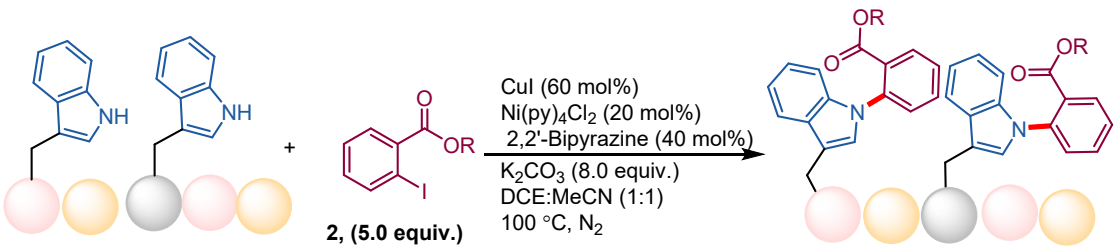
anhydrous Na_2SO_4, evaporate the solvent under reduced pressure, and finally use column chromatography to obtain the pentapeptide product (f) (yield of 40-55%).

General procedure of peptide modification



In an oven-dried 8 mL screwed-capped vial peptides (0.1 mmol, 1.0 equiv.), allenes **2** (0.25 mmol, 2.5 equiv.), CuI (5.7 mg, 0.03 mmol, 30 mol%), $Ni(py)_4Cl_2$ (4.4 mg, 0.01 mmol, 10 mol%), 2,2'-Bipyrazine (3 mg, 0.02 mmol, 20 mol%), K_2CO_3 (55.2 mg, 0.4 mmol, 4.0 equiv.) were weighted and anhydrous DCE: MeCN (1:1, 1.0 mL) were added to the vial. The reaction was kept at 100 °C about 10 hours in N_2. After the reaction completion monitored by TLC, the reaction was quenched by brine, and extracted with EtOAc, the organic solvent was filtrated through a pad of short anhrdrous Na_2SO_4 column. Evaporation and flash Silica gel column purification of the crude product provided modified peptides.

General procedure of peptide dimodification

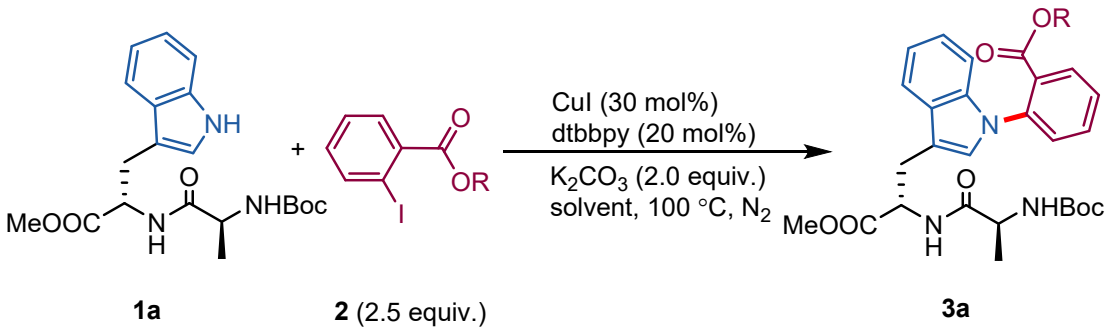


In an oven-dried 8 mL screwed-capped vial peptides (0.05 mmol, 1.0 equiv.),

allenes (0.25 mmol, 5 equiv.), CuI (5.7 mg, 0.03 mmol, 60 mol%), $Ni(py)_4Cl_2$ (4.4 mg, 0.01 mmol, 20 mol%), 2,2'-Bipyrazine (3 mg, 0.02 mmol, 40 mol%), K_2CO_3 (55.2 mg, 0.4 mmol, 8.0 equiv.) were weighted and anhydrous DCE: MeCN (1:1, 2.0 mL) were added to the vial. The reaction was kept at 100 °C about 10 hours in N_2. After the reaction completion monitored by TLC, the reaction was quenched by brine, and extracted with EtOAc, the organic solvent was filtrated through a pad of short anhrdrous Na_2SO_4 column. Evaporation and flash Silica gel column purification of the crude product provided modified peptides.

Optimization of reaction conditions

Table 1. Optimization of reaction solvent



1a **2** (2.5 equiv.) **3a**

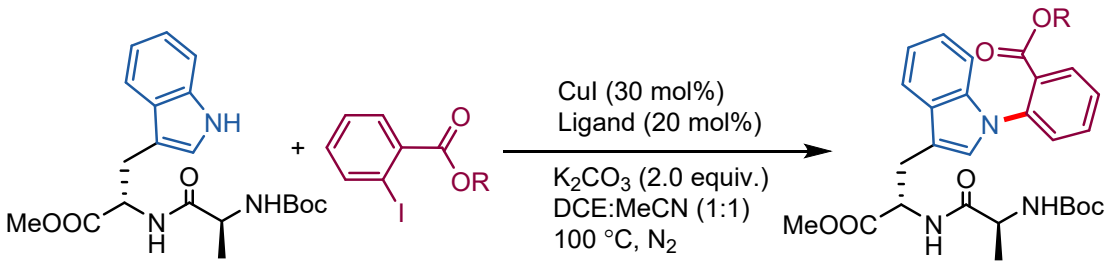
Entry	Solvent (1 mL)	Yield[ab] (%)
1	Toluene	8 %
2	1,4-Dioxane	N.P.
3	MeCN	15 %
4	DCE	16 %
5	THF	8 %
6	DMSO	N.P.
7	DMAC	N.P.
8	DMF	N.P.
9	NMP	N.P.
10	MeOH	N.P.

11	Isopropyl alcohol	N.P.
12	HFIP	N.P.
13	DCE: MeCN (9:1)	34 %
14	DCE: MeCN (8:2)	40 %
15	DCE: MeCN (7:3)	38 %
16	DCE: MeCN (6:4)	16 %
17	**DCE: MeCN (5:5)**	**45 %**
18	DCE: MeCN (4:6)	24 %

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

[b]The yield of the product was determined by 1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

Table 2. Optimization of ligands



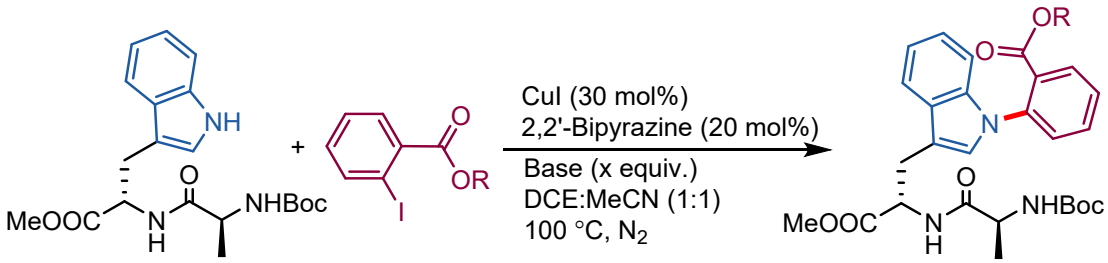
1a **2** (2.5 equiv.) **3a**

Entry	Ligand (20 mol%)	Yield[ab] (%)
19	dtbbpy	45%
20	6,6'-dibromo-2,2'-Bipyridyl	48%
21	**2,2'-Bipyrazine**	**56%**
22	2,2'-Bipyridine-4,4'-dicarboxylic acid	43%
23	L-Methionine	24%
24	L-Proline	27%

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

[b]The yield of the product was determined by 1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

Table 3. Optimization of base



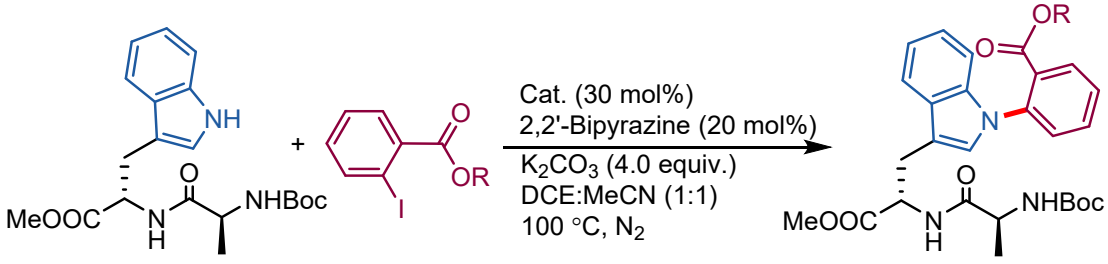
1a **2** (2.5 equiv.) **3a**

Entry	Base (x equiv)	Yield[ab] (%)
25	K_2CO_3 (2.0 equiv.)	56%
26	K_2CO_3 (3.0 equiv.)	60%
27	**K_2CO_3 (4.0 equiv.)**	**66%**
28	K_2CO_3 (5.0 equiv.)	61%
29	K_2CO_3 (6.0 equiv.)	62%
30	Na_2CO_3 (4.0 equiv.)	28%
31	$NaHCO_3$ (4.0 equiv.)	20%
32	NaOAc (4.0 equiv.)	N.P.
33	Ag_2CO_3 (4.0 equiv.)	trace
34	DBU (4.0 equiv.)	10%
35	ABCO (4.0 equiv.)	trace
36	DABCO (4.0 equiv.)	trace
37	Et_3N (4.0 equiv.)	trace
38	DIPEA (4.0 equiv.)	trace

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

[b]The yield of the product was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

Table 4. Optimization of catalyst



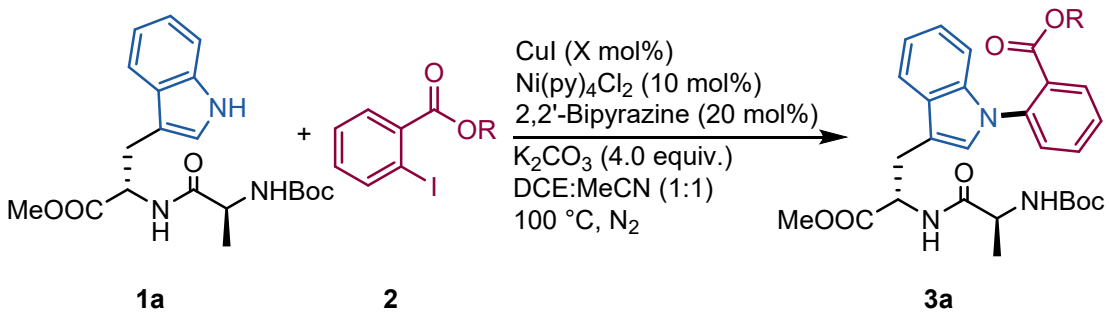
1a **2** (2.5 equiv.) **3a**

Entry	Catalyst (30 mol%)	Yield[ab] (%)
39	**CuI**	**66%**
40	CuBr	60%
41	CuCl	55%
42	Cu_2O	15%
43	Cu_2S	14%
44	$Cu(OAc)_2$	47%
45	$Cu(OTf)_2$	40%
46	$Cu(SO_4)_2 \cdot H_2O$	18%
47	$Cu(TFA)_2$	25%
48	Cu powder	60%

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

[b]The yield of the product was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

Table 5. Optimization of catalyst dosage



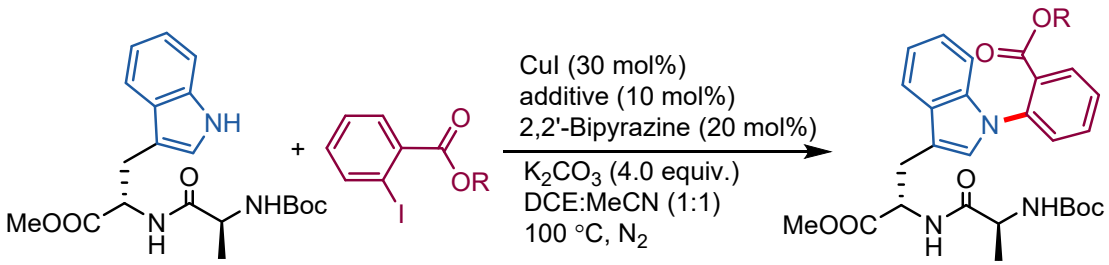
1a **2** **3a**

c	CuI (x mol%)	Yield[ab] (%)
49	10	65%
50	15	68%
51	20	73%
52	25	75%
53	**30**	**78%**

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

[b]This yield is the isolated yield.

Table 6. Optimization of additives



Entry	Additive (10 mol%)	Yield[ab] (%)
54	TBAB	N.P.
55	TBAC	N.P.
56	$Ni(acac)_2$	63%
57	$Ni(dppp)Cl_2$	62%
58	$NiBr_2$	61%
59	$NiF_2 \cdot H_2O$	58%
60	$Ni(PPh_3)_2Cl_2$	65%
61	$NiBr_2 \cdot glyme$	50%
62	$NiCl_2$	60%
63	**$Ni(py)_4Cl_2$**	**80% (78%)**

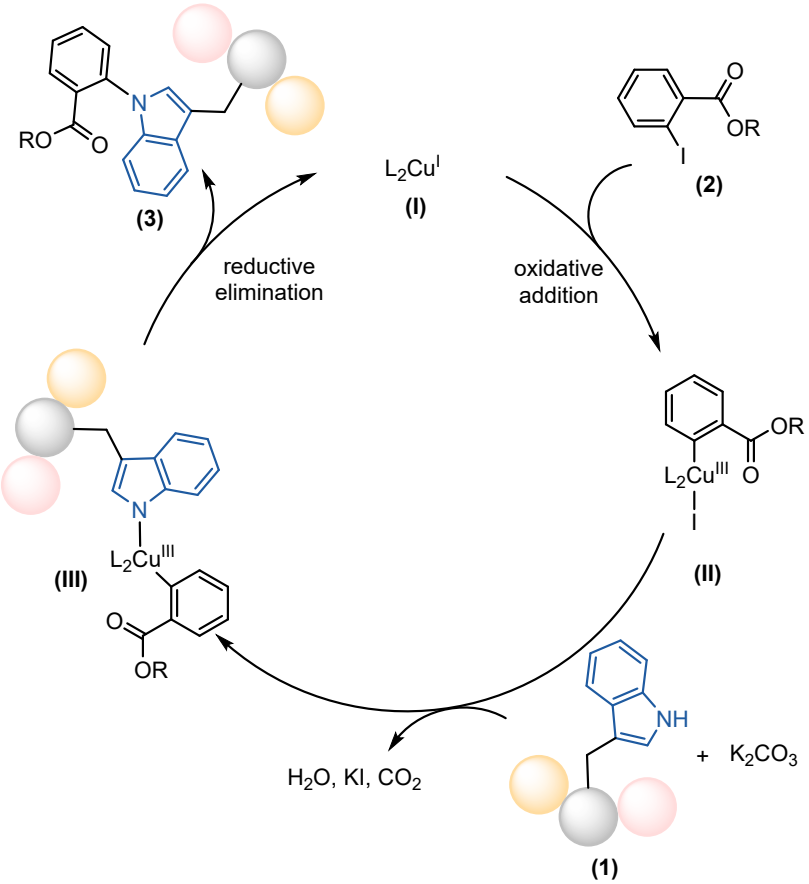
[a]The reaction was carried out on a scale of 0.1 mmol.

[b]The yield of the product was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The separation yield is indicated in parentheses.

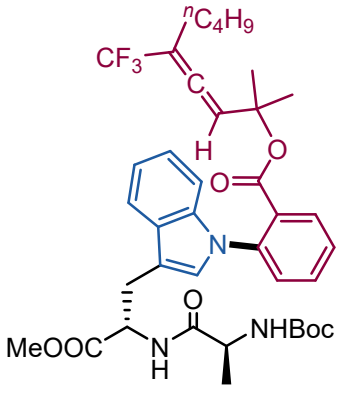
Proposed reaction mechanism

Based on literature reports [3,4] and classical Ullmann reactions, the proposed reaction mechanism proceeds as follows: Initially, 2,2'-bipiperazine and CuI are heated under reflux to form a copper complex (I). The trifluoromethyl structural unit **2** subsequently undergoes oxidative addition with the copper complex (I), generating complex (II). Complex (II) then reacts with the peptide substrate **2** and base (K_2CO_3) to yield complex (III). Finally, complex (III) undergoes a reductive elimination step, producing the desired product **3** and regenerating the starting copper complex (I),

thereby completing the catalytic cycle.



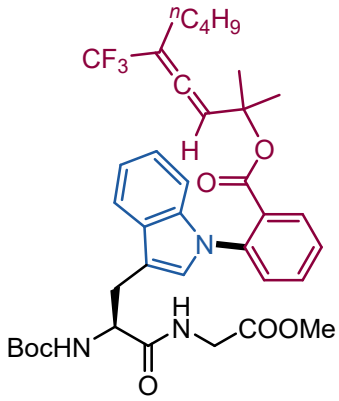
Characterization Data



3a

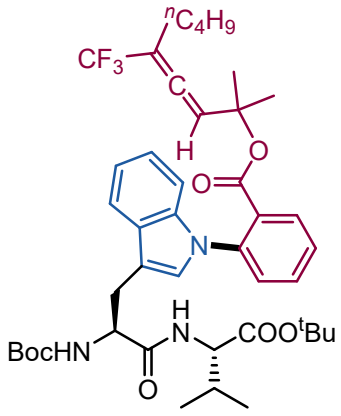
Faint yellow solid. **m.p.** 52.2-53.6 °C. 53.5 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.64 (td, *J* = 7.6, 1.3 Hz, 1H), 7.57-7.54 (m, 1H), 7.50 (td, *J* = 7.2, 0.6 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 4.2 Hz, 1H), 7.13 (d, *J* = 4.4 Hz, 1H), 7.08 (s, 1H), 7.05 (td, *J* = 5.1, 2.0 Hz, 1H), 6.65 (d, *J* = 7.4 Hz, 1H), 5.59 (s, 1H) , 4.98 (s, 1H), 4.94 (dd, *J* = 13.0, 5.5 Hz, 1H), 4.15 (s, 1H), 3.71

(s, 3H), 3.39-3.36 (m, 2H), 2.10-2.06 (m, 2H)，1.37 (s, 9H), 1.35-1.32 (m, 4H), 1.30 (d, J = 4.8 Hz, 3H), 1.03 (s, 3H), 0.98 (s, 3H), 0.87 (t, J = 7.1, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, J = 3.9 Hz), 172.4, 172.1, 165.3, 155.3, 137.9, 137.8, 132.7, 131.1, 130.6, 128.7, 128.3, 127.9, 127.7, 123.2 (q, J = 272 Hz), 122.7, 120.2, 118.8, 110.5, 110.3, 104.2, 102.2 (q, J = 33.7 Hz), 79.9, 79.7, 52.9, 52.5, 50.2, 29.4, 28.2, 27.6, 26.7, 26.0, 25.8, 22.2, 18.3, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.07 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{38}H_{46}F_3N_3NaO_7^+$, 736.3180; found, 736.3171. **IR** (KBr, cm^{-1}): ν 3325, 2978, 1715, 1601, 1497, 1293, 742.



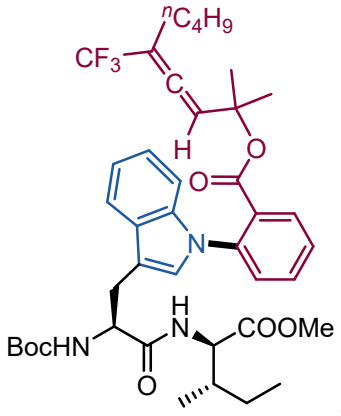
3b

Faint yellow solid. **m.p.** 50.4-51.1 ℃. 35.1 mg, 50% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.6 Hz, 1H), 7.71 (s, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.18-7.13 (m, 3H), 7.10-7.03 (m, 1H), 6.39 (s, 1H), 5.61 (s, 1H), 5.30 (s, 1H), 4.54 (s, 1H) , 3.94 (td, J = 18.1, 5.2 Hz, 1H), 3.86 (d, J = 17.6 Hz, 1H), 3.66 (s, 3H), 3.47-3.15 (m, 2H)，2.13-2.04 (m, 2H), 1.44 (s, 9H), 1.39-1.28 (m, 4H), 1.06(s, 3H), 1.02 (s, 3H), 0.87 (td, J = 7.0, 2.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, J = 4.1 Hz), 171.9, 169.9, 165.2, 155.6, 138.1, 137.9, 132.8, 131.2, 130.5, 128.7, 128.2, 128.0, 123.6 (q, J = 272 Hz), 122.8, 120.3, 119.2, 111.3, 110.2, 104.2, 102.3 (q, J = 33.6 Hz), 80.2, 79.8, 52.3, 52.3, 41.3, 29.8, 29.4, 28.4, 26.8, 26.7, 26.0, 22.2, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.08 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{37}H_{44}F_3N_3NaO_7^+$, 722.3024; found, 722.3038. **IR** (KBr, cm^{-1}): ν 3310, 2932, 1714, 1667, 1496, 1293, 1116, 741.



3c

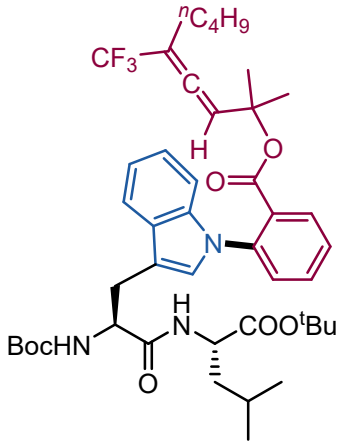
White solid. **m.p.** 53.2-54.5 ℃. 56.5 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.70 (s, 1H), 7.61 (td, *J* = 7.6, 1.1 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.17-7.11 (m, 3H), 7.08-7.04 (m, 1H), 6.49 (s, 1H), 5.54 (s, 1H), 5.19 (s, 1H), 4.52 (s, 1H), 4.37 (ddd, *J* = 8.3, 4.5 Hz, 1H), 3.40-3.22 (m, 2H)，2.11-2.05 (m, 3H), 1.43 (s, 9H), 1.40 (s, 9H), 1.36-1.27 (m, 4H), 0.94 (s, 6H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.83 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 3.3 Hz), 171.5, 170.6, 165.3, 155.6, 138.1, 137.9, 132.7, 131.3, 130.6, 128.7, 128.3, 127.9, 127.8, 123.6 (q, *J* = 273 Hz), 122.7, 120.2, 119.2, 111.3, 110.2, 104.2, 102.2 (q, *J* = 33.6 Hz), 82.0, 82.0, 79.7, 57.7, 57.7, 31.5, 29.4, 28.4, 28.1, 26.8, 26.0, 25.8, 22.2, 18.8, 17.8, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.08 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{43}H_{56}F_3N_3NaO_7^+$, 806.3963; found, 806.3983. **IR** (KBr, cm^{-1}): ν 3326, 2968, 2932, 1716, 1665, 1496, 1292, 1116, 742.



3d

White solid. **m.p.** 53.5-54.2 ℃. 54.4 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.69 (s, 1H), 7.63 (td, *J* = 7.7, 1.3 Hz, 1H), 7.49 (t, *J* =

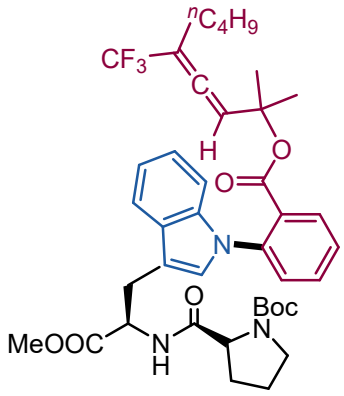
7.4 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.17-7.12 (m, 3H), 7.08-7.06 (m, 1H), 6.53 (s, 1H), 5.56 (s, 1H), 5.21 (s, 1H), 4.49-4.46 (m, 2H), 3.61 (s, 3H), 3.39-3.17 (m, 2H), 2.11-2.03 (m, 2H), 1.78 (s, 1H), 1.44 (s, 9H), 1.37-1.28 (m, 6H), 0.99 (s, 3H), 0.94 (s, 3H), 0.87 (t, J = 6.9 Hz, 3H) , 0.83 (t, J = 7.3 Hz, 3H), 0.76 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, J = 3.8 Hz), 171.8, 171.4, 165.3, 155.6, 138.1, 137.9, 132.7, 131.4, 130.6, 128.6, 128.2, 127.9, 127.8, 123.6 (q, J = 272 Hz), 122.8, 120.3, 119.1, 111.3, 110.2, 104.2, 102.2 (q, J = 33.6 Hz), 80.2, 79.7, 56.7, 56.6, 52.0, 37.9, 29.4, 28.4, 26.7, 26.0, 25.8, 25.2, 22.2, 15.3, 13.8, 11.6. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.09 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{41}H_{52}F_3N_3NaO_7^+$, 778.3650; found, 778.3667. **IR** (KBr, cm^{-1}): ν 3323, 2964, 1715, 1496, 1293, 1117, 739.



3e

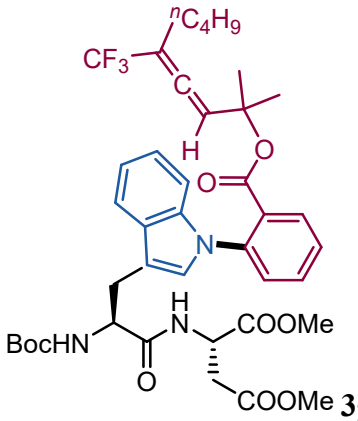
White solid. **m.p.** 54.6-56.2 °C. 60.0 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 1H), 7.70 (s, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.44 (s, 1H), 7.17-7.11 (m, 3H), 7.09-7.05 (m, 1H), 6.35 (s, 1H), 5.55 (s, 1H), 5.17 (s, 1H), 4.50 (s, 1H), 4.45 (dd, J = 13.3, 8.0 Hz, 1H), 3.32-3.28 (m, 2H), 2.10-2.15 (m, 2H), 1.64-1.65 (m, 2H), 1.57-1.50 (m, 1H) 1.43 (s, 9H), 1.40 (s, 9H), 1.35-1.28 (m, 4H), 0.99 (s, 3H), 0.95 (m, 3H) , 0.88-0.85 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, J = 4.8 Hz), 171.8, 171.2, 165.3, 155.6, 138.1, 137.9, 132.7, 131.3, 130.5, 128.7, 128.3, 127.9, 127.9, 123.6 (q, J = 272 Hz), 122.7, 120.3, 119.2, 111.2, 110.2, 104.2, 102.2 (q, J = 33.7 Hz), 81.9, 80.1, 79.7, 51.5, 51.5, 42.0, 29.4, 28.4, 28.0, 26.8, 26.0, 25.8, 24.8, 22.8, 22.2, 22.1, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.08 (s).

HRMS-ESI(m/z): $[M+Na]^+$ calcd. for $C_{44}H_{58}F_3N_3NaO_7^+$, 820.4119; found, 820.4140. **IR** (KBr, cm^{-1}): ν 3337, 2961, 1716, 1666, 1496, 1293, 1117, 741.



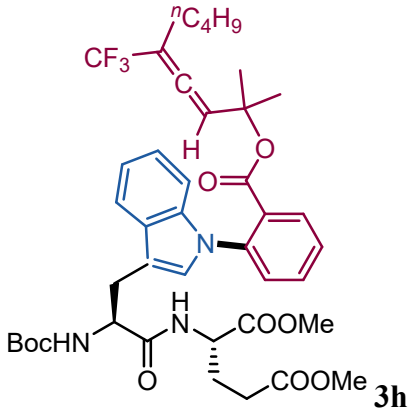
3f

White solid. **m.p.** 55.1-56.8 °C. 51.3 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.65-7.62 (m, 1H), 7.58-7.56 (m, 1H), 7.49(t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.14-7.10 (m, 2H), 7.08-7.00 (m, 2H), 6.58 (s, 1H), 5.58-5.48 (m, 1H), 4.92 (s, 1H), 4.23 (d, *J* = 34.0 Hz, 1H), 3.70 (s, 3H)，3.33-3.15 (m, 2H), 2.11-2.04 (m, 2H), 1.95-1.77 (m, 2H), 1.70-1.61 (m, 2H), 1.36 (s, 9H), 1.33-1.28 (m, 4H), 1.00 (s, 3H), 0.94 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 4.2 Hz), 172.5, 172.1, 165.3, 155.6, 138.0, 137.8, 132.8, 131.3, 130.6, 128.6, 128.4, 127.9, 127.3, 123.6 (q, *J* = 272 Hz), 122.7, 120.2, 118.8, 110.8, 110.3, 104.2, 102.2 (q, *J* = 33.5 Hz), 80.3, 79.7, 60.1, 52.7, 52.4, 47.1, 29.4, 28.2, 27.7, 26.7, 26.0, 25.8, 22.2, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.09 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{40}H_{48}F_3NaO_7^+$, 762.3337; found, 762.3343. **IR** (KBr, cm^{-1}): ν 3416, 2958, 1744, 1689, 1496, 1386, 1292, 1117, 741.



3g

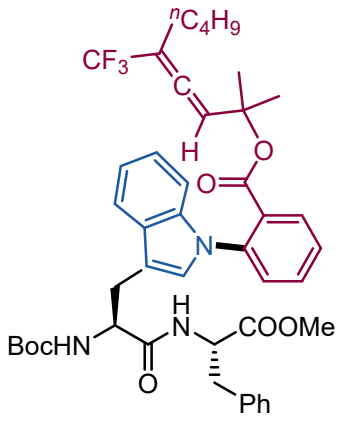
Faint yellow solid. **m.p.** 57.7-59.3 ℃. 61.4 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.64 (td, *J* = 7.5, 1.4 Hz, 2H), 7.52-7.49 (m, 1H), 7.46 (dd, *J* = 4.4, 3.4 Hz, 1H), 7.17-7.10 (m, 3H), 7.08-7.05 (m, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 5.57(s, 1H), 5.24 (s, 1H), 4.80 (dt, *J* = 7.8, 3.9 Hz, 1H), 4.51 (s, 1H), 3.64 (s, 3H), 3.49 (s, 3H), 3.40-3.20 (m, 2H), 2.79 (d, *J* = 16.7 Hz, 1H), 2.11-2.04 (m, 3H), 1.42 (s, 9H), 1.39-1.27 (m, 4H), 1.01 (s, 3H), 0.96 (s, 3H), 0.86 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 4.3 Hz), 171.4, 171.3, 170.9, 165.3, 155.5, 138.0, 137.8, 132.8, 131.4, 130.6, 128.7, 128.4, 128.0, 127.5, 123.6 (q, *J* = 272 Hz), 122.8, 120.3, 119.0, 111.2, 110.2, 104.2, 102.2 (q, *J* = 33.8 Hz), 80.2, 79.8, 52.8, 52.8, 51.9, 48.2, 29.4, 28.3, 28.2, 26.8, 26.0, 25.9, 22.2, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.08 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{40}H_{48}F_3N_3NaO_9^+$, 794.3235; found, 794.3234. **IR** (KBr, cm^{-1}): ν 3339, 2957, 1715, 1673, 1495, 1368, 1292, 1116, 742.



3h

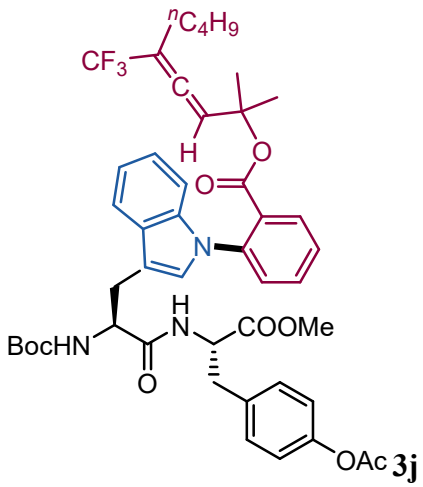
White solid. **m.p.** 58.3-60.1 ℃. 64.9 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.69-7.68 (m, 1H), 7.64 (td, *J* = 7.7, 1.4 Hz, 1H), 7.50 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.47 (t, *J* = 8.2 Hz, 1H), 7.16-7.11 (m, 3H), 7.08-7.05 (m, 1H), 6.55 (s, 1H), 5.59-5.56 (m, 1H), 5.22-5.21 (m, 1H), 4.52-4.47 (m, 1H), 3.62 (s, 3H), 3.60 (s, 3H), 3.37-3.20 (m, 2H), 2.31-2.19 (m, 2H), 2.17-2.10 (m, 1H), 2.10-2.04 (m, 2H), 1.88 (td, *J* = 13.9, 7.7 Hz, 2H), 1.43 (s, 9H), 1.40-1.26 (m, 4H), 1.00 (s, 3H), 0.95 (s, 3H), 0.86 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 3.3 Hz), 173.1, 171.7, 171.7, 165.3, 155.6, 138.0, 138.0, 132.7, 131.3, 130.6, 128.7, 128.2, 127.9, 127.8, 123.6 (q, *J* = 272 Hz), 122.8, 120.3, 119.1, 111.2, 110.2, 104.2, 102.2 (q,

J = 33.7 Hz), 80.3, 79.7, 52.5, 52.5, 51.8, 51.7, 29.8, 29.4, 28.4, 28.1, 26.7, 26.0, 25.9, 22.2, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.08 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{41}H_{50}F_3N_3NaO_9^+$, 808.3391; found, 808.3399. **IR** (KBr, cm^{-1}): ν 3321, 2957, 1741, 1496, 1293, 1117, 741.



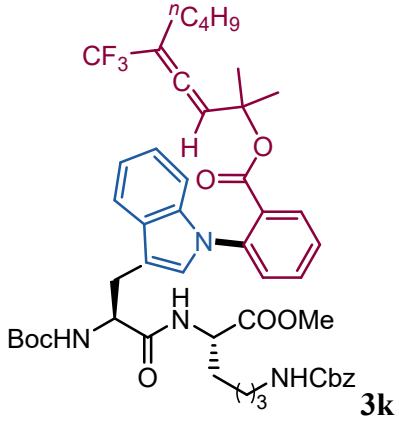
3i

White solid. **m.p.** 55.7-58.4℃. 60.5 mg, 75% yield.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 7.7, 1.2 Hz, 1H), 7.70 (s, 1H), 7.61 (td, J = 7.6, 1.2 Hz, 1H), 7.49 (td, J = 7.6, 0.8 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.18-7.10 (m, 5H), 7.08-7.04 (m, 2H), 6.87 (d, J = 4.5 Hz, 1H), 6.30 (s, 1H), 5.55 (s, 1H), 5.20 (s, 1H), 4.73 (s, 1H), 4.48 (s, 1H), 3.59 (s, 3H), 3.36-3.15 (m, 2H), 3.01-2.94 (m, 2H), 2.11-2.04 (m, 2H), 1.43 (s, 9H), 1.37-1.28 (m, 4H), 1.00 (s, 3H), 0.95 (s, 3H), 0.86 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, J = 4.2 Hz), 171.4, 171.2, 165.3, 155.4, 138.0, 138.0, 135.7, 132.7, 131.3, 130.6, 129.2, 128.6, 128.6, 128.0, 127.9, 127.1, 123.6 (q, J = 273 Hz), 122.8, 120.3, 119.2, 111.2, 110.2, 104.2, 102.2 (q, J = 33.5 Hz), 80.2, 79.8, 53.4, 53.4, 52.3, 38.0, 29.4, 28.4, 26.7, 26.0, 25.9, 22.2, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.08 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{44}H_{50}F_3N_3NaO_7^+$, 812.3493; found, 812.3514. **IR** (KBr, cm^{-1}): ν 3423, 2931, 1714, 1663, 1496, 1462, 1292, 1116, 741.



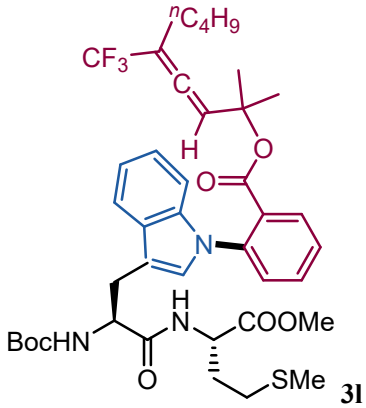
3j

White solid. **m.p.** 85.5-86.2 ℃. 48.4 mg, 56% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.70 (s, 1H), 7.61 (td, *J* = 7.5, 1.1 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.16-7.13 (m, 2H), 7.08-7.05 (m, 2H), 6.92-6.86 (m, 4H), 6.36 (s, 1H), 5.56 (s, 1H), 5.22 (s, 1H), 4.71 (s, 1H), 4.47 (s, 1H), 3.58 (s, 3H), 3.33-3.17 (m, 2H)，3.01-2.92 (m, 2H), 2.26 (s, 3H), 2.10-2.05 (m, 2H), 1.43 (s, 9H), 1.37-1.27 (m, 4H), 1.00 (s, 3H), 0.96 (s, 3H), 0.86 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 4.3 Hz), 171.3, 171.3, 169.4, 165.3, 155.5, 149.7, 138.0, 138.0, 133.4, 132.7, 131.3, 130.6, 130.3, 128.7, 128.0, 127.8, 123.6 (q, *J* = 272 Hz), 122.8, 121.6, 120.3, 119.2, 111.2, 110.2, 104.2, 102.2 (q, *J* = 33.6 Hz), 80.2, 79.7, 53.4, 52.3, 52.3, 37.4, 29.4, 28.4, 26.8, 26.7, 25.8, 22.2, 21.2, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.07 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{46}H_{52}F_3N_3NaO_9^+$, 870.3548; found, 870.3570. **IR** (KBr, cm^{-1}): ν 3326, 2931, 1713, 1601, 1502, 1463, 1368, 1293, 1198, 1116, 1018, 912, 852, 738.



3k

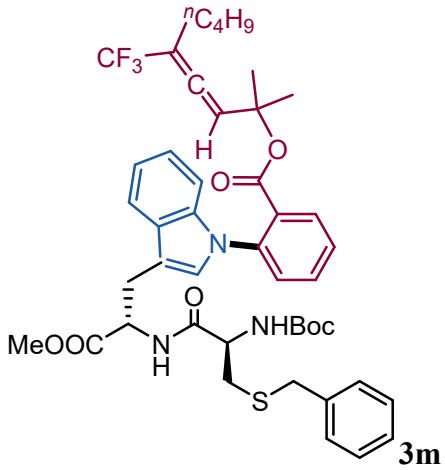
White solid. **m.p.** 53.6-54.9 ℃. 68.2 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.68 (s, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 3.8 Hz, 4H), 7.29 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.15-7.11(m, 2H), 7.10 (s, 1H), 7.08-7.04 (m, 1H), 6.55 (s, 1H) , 5.56 (s, 1H), 5.29(s, 1H), 5.11-5.01 (m, 2H) , 4.96 (s, 1H)， 4.53-4.44 (m, 2H), 3.61 (s, 3H), 3.34-3.21 (m, 2H), 3.14-3.02 (m, 2H), 2.11-2.03 (m, 2H), 1.88(s, 1H), 1.80-1.70 (m, 1H), 1.65-1.53 (m, 2H), 1.42 (s, 9H), 1.38-1.28 (m, 6H), 1.00 (s, 3H), 0.95 (s, 3H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 3.8 Hz), 172.3, 171.7, 165.3, 156.6, 155.6, 138.1, 137.9, 136.7, 132.7, 131.3, 130.6, 128.6, 128.6, 128.2, 128.2, 127.9, 127.8, 123.6 (q, *J* = 272 Hz), 122.8, 120.2, 119.2, 111.3, 110.2, 104.2, 102.2 (q, *J* = 33.6 Hz), 80.2, 79.7, 66.7, 52.4, 52.4, 52.0, 40.5, 32.0, 29.8, 29.4, 29.2, 28.4, 28.1, 26.8, 26.0, 25.9, 22.2, 22.1, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.06 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{49}H_{59}F_3N_4NaO_9^+$, 927.4126; found, 927.4130. **IR** (KBr, cm^{-1}): ν 3320, 2932, 1713, 1497, 1292, 1117, 739.6.



3l

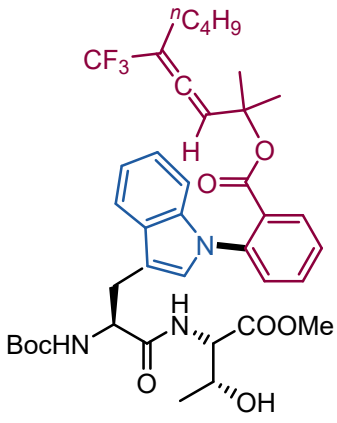
White solid. **m.p.** 49.6-51.1 ℃. 55.3 mg, 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.69 (s, 1H), 7.63 (td, *J* = 7.7, 1.3 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.17-7.11 (m, 3H), 7.10-7.02 (m, 1H), 6.57 (s, 1H), 5.57 (s, 1H), 5.23 (s, 1H), 4.59 (dd, *J* = 11.8, 6.5 Hz, 1H), 4.48 (s, 1H), 3.63 (s, 3H), 3.29 (ddd, *J* = 54.4, 14.0, 6.3 Hz, 2H), 2.35-2.29 (m, 2H), 2.11-2.02 (m, 3H), 1.98 (s, 3H), 1.89 (dt, *J* = 14.2, 7.1 Hz, 1H), 1.44 (s, 9H), 1.38-1.29 (m, 4H), 1.01 (s, 3H), 0.96 (s, 3H), 0.86 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 4.2 Hz), 171.9, 171.6, 165.2, 155.6, 138.0, 138.0, 132.8, 131.3, 130.6, 128.7, 128.2,

128.0, 127.8, 123.6 (q, J = 273 Hz), 122.8, 120.3, 119.1, 111.2, 110.2, 104.2, 102.2 (q, J = 34.0 Hz), 80.3, 79.7, 52.5, 52.4, 51.7, 31.7, 29.8, 29.4, 28.4, 28.1, 26.8, 26.0, 25.9, 22.2, 15.4, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.07 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{40}H_{50}F_3N_3NaO_7S^+$, 796.3214; found, 796.3233. **IR** (KBr, cm^{-1}): ν 3319, 2960, 1714, 1496, 1293, 1116, 741.



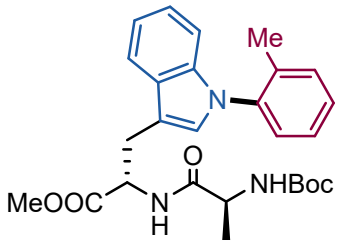
3m

White solid. **m.p.** 62.3-63.7 ℃. 61.3 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.5 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.59-7.55 (m, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.40 (d, J = 7.7 Hz, 1H), 7.25-7.23 (m, 4H), 7.21-7.19 (m, 1H), 7.15-7.13 (m, 2H), 7.08-7.05 (m, 2H), 6.82 (d, J = 6.6 Hz, 1H), 5.60-5.57 (m, 1H), 5.23 (s, 1H), 4.93 (dd, J = 12.6, 5.4 Hz, 1H), 4.24-4.22 (m, 1H), 3.70 (s, 3H)，3.66 (dd, J = 13.2, 8.5 Hz, 2H), 3.38-3.35 (m, 2H), 2.76-2.69 (m, 2H), 2.10-2.07 (m, 2H), 1.39 (s, 9H), 1.35-1.29 (m, 4H), 1.02 (s, 3H), 0.97 (s, 3H), 0.87 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.7 (q, J = 3.9 Hz), 171.9, 170.5, 165.3, 155.3, 137.9, 137.9, 132.8, 131.2, 130.7, 129.1, 128.7, 128.6, 128.3, 128.0, 127.6, 127.3, 123.6 (q, J = 273 Hz), 122.8, 120.3, 118.9, 110.5, 110.4, 104.2, 102.2 (q, J = 33.5 Hz), 80.3, 79.8, 53.8, 53.2, 52.5, 36.5, 33.8, 29.4, 28.3, 27.6, 26.7, 26.0, 25.9, 22.2, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.06 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{45}H_{52}F_3N_3NaO_7S^+$, 858.3370; found, 858.3390. **IR** (KBr, cm^{-1}): ν 3311, 2930, 1715, 1496, 1293, 1117, 741.



3n

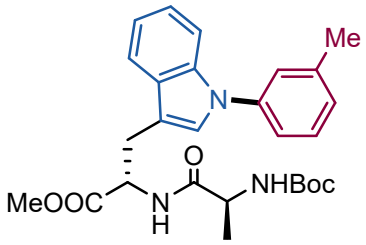
White solid. **m.p.** 62.9-64.7 ℃. 19.1 mg, 25% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.2 Hz, 1H), 7.72-7.69 (m, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.17-7.10 (m, 3H), 7.08-7.03 (m, 1H), 6.78-6.73 (m, 1H), 5.59 (s, 1H), 5.31 (d, *J* = 7.7 Hz, 1H), 4.54-4.51 (m, 2H), 4.25-4.17 (m, 1H), 3.65 (s, 3H), 3.37-3.27 (m, 2H), 2.72 (s, 1H), 2.12-2.02 (m, 2H), 1.42 (s, 9H), 1.37-1.29 (m, 4H), 1.09 (d, *J* = 5.9 Hz, 3H), 1.04(s, 3H), 0.99 (s, 3H), 0.86 (td, *J* = 7.0, 2.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 4.1 Hz), 172.3, 171.1, 165.4, 155.7, 138.1, 137.9, 132.8, 131.2, 130.4, 128.6, 128.3, 127.9, 127.8, 123.6 (q, *J* = 272 Hz), 122.8, 120.3, 119.2, 111.3, 110.2, 104.2, 102.3 (q, *J* = 33.6 Hz), 80.3, 79.8, 68.3, 57.6, 55.3, 52.5, 29.4, 28.4, 28.0, 26.8, 26.0, 25.9, 22.2, 19.9, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.07 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{39}H_{48}F_3N_3NaO_8^+$, 766.3286; found, 766.3323. **IR** (KBr, cm^{-1}): ν 3427, 2975, 1715, 1665, 1496, 1462, 1368, 1292, 1115, 743.



3o

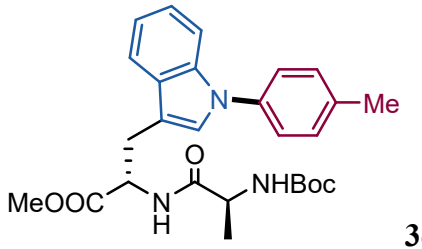
White solid. **m.p.** 95.9-96.7 ℃. 9.1 mg, 19% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.0 Hz, 1H), 7.43-7.28 (m, 4H), 7.22 - 7.10 (m, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 6.61 (d, *J* = 7.9 Hz, 1H), 5.06-4.76 (m, 2H), 4.15 (s, 1H), 3.69 (s, 3H), 3.38 (d, *J* = 6.2 Hz, 2H), 2.04 (s, 3H), 1.37 (s, 9H), 1.31 (d, *J* = 7.1 Hz, 4H). **^{13}C NMR** (100

MHz, $CDCl_3$) δ 172.3, 172.1, 155.3, 137.2, 135.8, 131.3, 128.4, 128.2, 128.1, 126.9, 122.5, 119.9, 118.9, 110.8, 110.0, 80.1, 53.2, 52.5, 50.3, 29.8, 28.3, 27.8, 18.5, 17.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{27}H_{33}N_3NaO_5^+$, 502.2312; found, 502.2313. **IR** (KBr, cm^{-1}): ν 3348, 2926, 1740, 1690, 1655, 1508, 1449, 1374, 1241, 1165, 1023, 742, 631.



3p

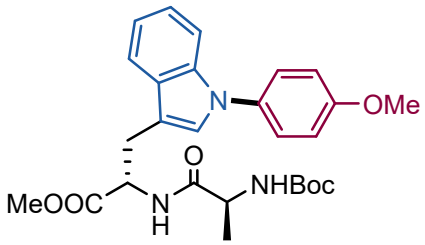
White solid. **m.p.** 92.7-93.8 °C. 16.8 mg, 35% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (t, *J* = 7.0 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 6.8 Hz, 2H), 6.63 (d, *J* = 7.7 Hz, 1H), 5.07-4.83 (m, 2H), 4.26-4.00 (m, 1H), 3.70 (s, 3H), 3.38 (d, *J* = 5.4 Hz, 2H), 2.44 (s, 3H), 1.38 (s, 9H), 1.32 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 172.1, 155.4, 139.7, 136.0, 129.5, 129.1, 127.3, 124.9, 122.7, 121.3, 120.3, 119.0, 110.9, 110.8, 80.1, 53.0, 52.6, 50.3, 29.8, 28.3, 27.6, 21.6, 18.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{27}H_{33}N_3NaO_5^+$, 502.2312; found, 502.2312. **IR** (KBr, cm^{-1}): ν 3311, 2977, 1669, 1601, 1499, 1457, 1369, 1247, 1167, 1019, 856, 788, 743, 697.



3q

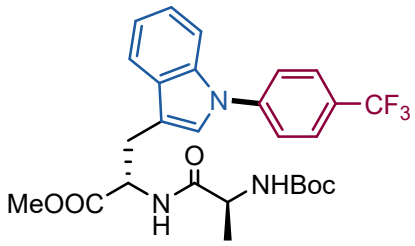
White solid. **m.p.** 128.4-129.6 °C. 32.6 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 21.9, 7.8 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.18 (dq, *J* = 14.8, 7.1 Hz, 3H), 6.63 (d, *J* = 7.8 Hz, 1H), 5.00-4.84 (m, 2H), 4.14 (s, 1H), 3.70 (s, 3H), 3.38 (d, *J* = 5.5 Hz, 2H), 2.43 (s, 3H), 1.38 (s, 9H), 1.31 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 172.1, 155.4, 137.1, 136.3, 136.1,

130.2, 129.0, 126.9, 124.2, 122.6, 120.2, 119.0, 110.8, 110.6, 80.1, 53.0, 52.6, 50.3, 28.3, 27.6, 21.2, 18.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{27}H_{33}N_3NaO_5^+$, 502.2312; found, 502.2315. **IR** (KBr, cm^{-1}): ν 3335, 2939, 1738, 1689, 1647, 1513, 1456, 1387, 1236, 1162, 1024, 851, 819, 729, 621.



3r

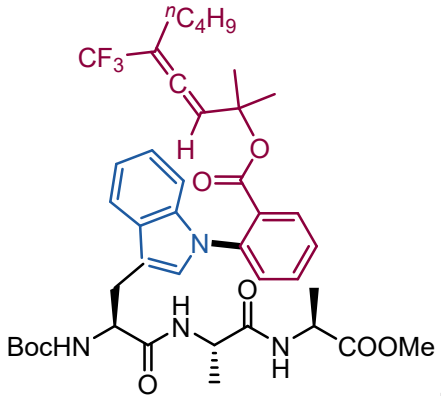
White solid. **m.p.** 73.2-74.9 °C. 19.4 mg, 39% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.17 (dt, *J* = 19.4, 7.1 Hz, 3H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 7.7 Hz, 1H), 5.03-4.78 (m, 2H), 4.14 (s, 1H), 3.88 (s, 3H), 3.70 (s, 3H), 3.38 (d, *J* = 5.6 Hz, 2H), 1.38 (s, 9H), 1.31 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 172.1, 158.2, 155.4, 136.5, 132.6, 128.8, 127.1, 125.9, 122.6, 120.1, 118.9, 114.8, 110.6, 110.3, 80.1, 55.7, 53.0, 52.5, 50.3, 29.8, 28.3, 27.6, 18.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{27}H_{33}N_3NaO_6^+$, 518.2262; found, 518.2264. **IR** (KBr, cm^{-1}): ν 3309, 2930, 1671, 1515, 1460, 1367, 1249, 1165, 1030, 836, 742, 574.



3s

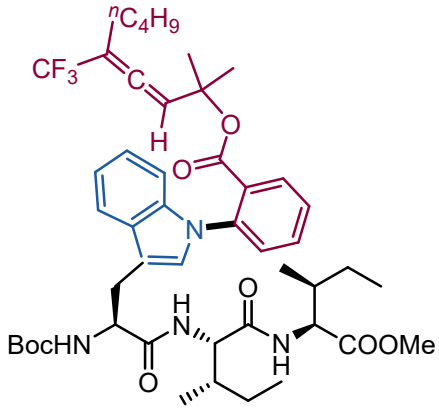
White solid. **m.p.** 52.9-53.8 °C. 40.5 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.58 (dd, *J* = 7.8, 2.9 Hz, 2H), 7.30 (d, *J* = 19.6 Hz, 1H), 7.21 (dd, *J* = 14.8, 7.2 Hz, 2H), 6.67 (d, *J* = 7.7 Hz, 1H), 5.04-4.85 (m, 2H), 4.24-4.05 (m, 1H), 3.70 (s, 3H), 3.46-3.31 (m, 2H), 1.38 (s, 9H), 1.34-1.29 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 172.0, 155.5, 142.6, 135.6, 129.6, 129.5, 127.0, 127.0, 127.0, 126.9, 126.4, 123.8, 123.3, 121.0, 119.3, 112.3, 110.6, 80.1, 76.8, 52.7, 52.6, 50.4, 28.3, 27.5, 18.2. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ = -62.12

(s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{27}H_{30}F_3N_3NaO_5^+$, 556.2030; found, 556.2033. **IR** (KBr, cm^{-1}): ν 3324, 2976, 1738, 1647, 1525, 1458, 1443, 1325, 1161, 1119, 1067, 846, 736, 609.



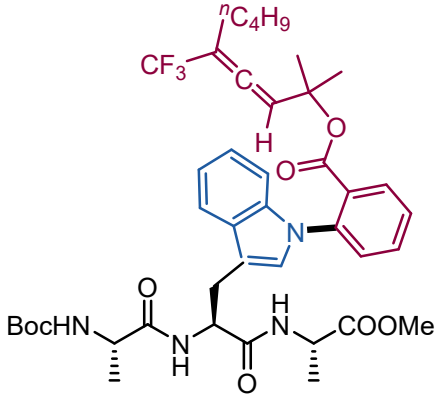
4a

White solid. **m.p.** 72.6-74.1 ℃. 56.1 mg, 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.69-7.67 (m, 1H), 7.63 (td, *J* = 7.6, 1.5 Hz, 1H), 7.49 (td, *J* = 7.6, 0.9 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.17-7.11 (m, 3H), 7.07-7.05 (m, 1H), 6.74 (s, 1H), 6.53 (s, 1H), 5.58 (s, 1H), 5.20 (s, 1H), 4.48-4.42 (m, 3H), 3.72 (s, 3H), 3.39-3.22 (m, 2H)，2.10-2.04 (m, 2H), 1.41 (s, 9H), 1.36-1.30 (m, 7H), 1.24 (d, *J* = 6.5 Hz, 3H), 1.02 (s, 3H), 0.97 (s, 3H), 0.86 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 3.9 Hz), 173.1, 171.6, 171.5, 165.2, 155.7, 138.0, 138.0, 132.8, 131.3, 130.5, 128.7, 128.1, 128.0, 127.8, 123.6 (q, *J* = 273 Hz), 122.9, 120.3, 119.2, 111.0, 110.3, 104.2, 102.3 (q, *J* = 33.5 Hz), 80.4, 79.7, 52.5, 52.5, 49.0, 48.2, 29.4, 28.3, 28.1, 26.8, 26.0, 25.9, 22.2, 18.2, 18.1, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.07 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{41}H_{51}F_3N_4NaO_8^+$, 807.3551; found, 807.3582. **IR** (KBr, cm^{-1}): ν 3301, 2933, 1716, 1645, 1496, 1293, 1117, 739.



4b

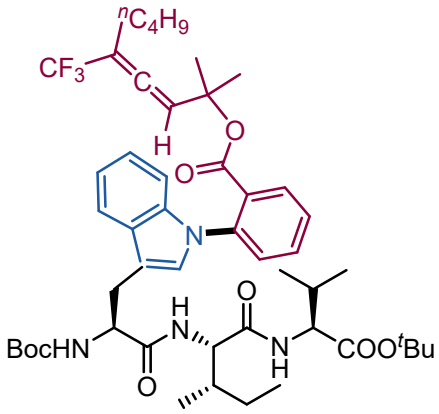
White solid. **m.p.** 75.5-76.0 ℃. 46.1 mg, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.69 (s, 1H), 7.63 (td, *J* = 7.7, 1.2 Hz, 1H), 7.50-7.42 (m, 2H), 7.16-7.12 (m, 2H), 7.09-7.05 (m, 2H), 6.61 (s, 1H), 6.50 - 6.48 (m, 1H), 5.57 (s, 1H), 5.19 (s, 1H), 4.52-4.48 (m, 2H), 4.28 (t, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 3.38-3.28 (m, 2H), 2.09-2.05 (m, 2H), 1.85-1.83 (m, 2H), 1.41 (s, 9H), 1.36-1.28 (m, 6H), 1.20-1.09 (m, 2H), 1.00 (s, 3H), 0.94 (s, 3H), 0.89-0.80 (m, 15H). **^{13}C NMR** (100 MHz, Acetone-D_6) δ 200.4 (q, *J* = 4.2 Hz), 171.8, 171.6, 171.3, 165.1, 155.5, 138.1, 137.8, 133.0, 131.0, 130.6, 128.9, 128.7, 127.9, 127.9, 123.9 (q, *J* = 273 Hz), 122.2, 119.7, 119.2, 112.3, 109.8, 104.7, 101.6 (q, *J* = 33.5 Hz), 79.0, 78.6, 57.2, 56.7, 55.2, 51.2, 37.7, 37.1, 27.8, 26.3, 25.7, 25.4, 25.1, 24.5, 21.9, 15.1, 14.9, 13.2, 11.0, 10.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.09 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{47}H_{63}F_3N_4NaO_8^+$, 891.4490; found, 891.4526. **IR** (KBr, cm^{-1}): ν 3307, 2965, 1713, 1646, 1462, 1293, 1117, 742.



4c

Faint yellow solid.. **m.p.** 73.7-74.0 ℃. 56.9 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.77 (s, 1H), 7.63 (td, *J* = 7.7, 1.5 Hz, 1H),

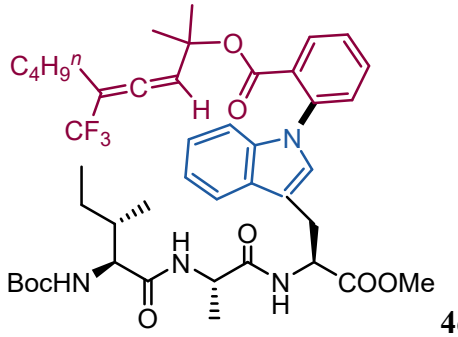
7.49 (td, J = 7.7, 0.8 Hz, 1H), 7.46 (d, J = 8.2 Hz, 1H), 7.18-7.12 (m, 3H), 7.07-7.03 (m, 1H), 6.89 (d, J = 6.9 Hz, 1H), 6.55 (s, 1H), 5.56 (s, 1H), 4.98 (s, 1H), 4.75 (dd, J = 12.7, 7.1 Hz, 1H), 4.51-4.40 (m, 1H), 4.18-4.10 (m, 1H)， 3.62 (s, 3H), 3.31 (ddd, J = 20.8, 13.9, 6.1 Hz, 2H), 2.11-2.05 (m, 2H), 1.38-1.29 (m, 16H), 1.27 (d, J = 7.3 Hz, 3H), 1.05 (s, 3H), 1.00 (s, 3H), 0.86 (td, J = 6.9, 1.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, J = 4.0 Hz), 172.8, 172.5, 170.6, 165.2, 155.6, 138.1, 138.0, 132.8, 131.2, 130.6, 128.6, 128.1, 128.1, 128.0, 123.6 (q, J = 272 Hz), 122.9, 120.4, 119.3, 111.1, 110.2, 104.2, 102.3 (q, J = 33.9 Hz), 80.3, 79.8, 53.5, 52.4, 50.7, 48.4, 29.4, 28.3, 28.0, 26.8, 26.0, 25.9, 22.2, 18.4, 18.0, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.08 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{41}H_{51}F_3N_4NaO_8^+$, 807.3551; found, 807.3572. **IR** (KBr, cm^{-1}): ν 3292, 2959, 1715, 1647, 1497, 1293, 1117, 743.



4d

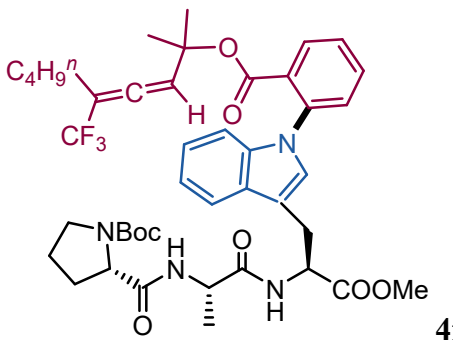
White solid. **m.p.** 85-85.5 ℃. 47.5 mg, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.7 Hz, 1H), 7.70 (s, 1H), 7.63 (t, J = 7.1 Hz, 1H), 7.48 (t, J = 7.3 Hz, 1H), 7.16-7.13 (m, 2H), 7.09-7.05 (m, 2H), 6.61 (s, 1H), 6.37-6.36 (m, 1H), 5.54 (s, 1H), 5.19 (s, 1H), 4.51 (s, 1H), 4.33 (dd, J = 8.6, 5.0 Hz, 1H), 4.28 (t, J = 7.4 Hz, 1H), 3.37-3.28 (m, 2H)， 2.09-2.05 (m, 3H), 1.79 (s, 1H), 1.45 (s, 9H), 1.41 (s, 9H), 1.36-1.29 (m, 6H), 0.97-0.94 (m, 6H), 0.87-0.85 (m, 6H), 0.85-0.82 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, J = 3.8 Hz), 171.7, 170.7, 170.7, 165.3, 155.7, 138.0, 138.0, 132.8, 131.3, 130.6, 128.8, 128.3, 127.9, 127.7, 123.6 (q, J = 273 Hz), 122.8, 120.3, 119.2, 111.3, 110.2, 104.2, 102.2 (q, J = 33.5 Hz), 82.0, 80.2, 79.7, 58.1, 58.1, 57.8, 37.2, 31.3, 29.4, 28.3, 28.1, 26.8, 26.0, 25.8, 25.0, 22.2, 18.9, 17.9, 15.3, 13.8,

11.4. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.08 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{49}H_{67}F_3N_4NaO_8^+$, 919.4803; found, 919.4825. **IR** (KBr, cm^{-1}): ν 3272, 2965, 1717, 1645, 1292, 1117, 740.



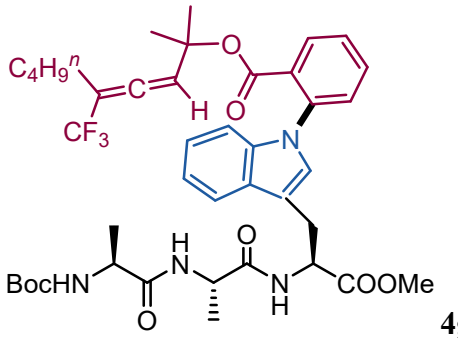
4e

White solid. **m.p.** 72.5-73.0 °C. 50.6 mg, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.64 (td, *J* = 7.7, 1.5 Hz, 1H), 7.56-7.43 (m, 3H), 7.17-7.03 (m, 4H), 6.64 (s, 1H), 6.54 (s, 1H), 5.55 (s, 1H), 5.02 (d, *J* = 7.3, 1H), 4.91 (dd, *J* = 13.1, 5.5 Hz, 1H), 4.46 (q, *J* = 7.0 Hz, 1H), 3.87 (s, 1H), 3.69 (s, 3H), 3.36-3.35 (m, 2H), 2.09-2.05 (m, 2H), 1.87-1.85 (m, 1H), 1.73-1.71 (m, 1H), 1.42 (s, 9H), 1.39-1.28 (m, 8H), 1.02 (s, 3H), 0.96 (s, 3H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.83 (t, *J* = 7.1 Hz, 3H), 0.80 (d, *J* = 5.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 4.3 Hz), 172.0, 171.7, 171.4, 165.3, 155.8, 137.9, 137.9, 132.8, 131.3, 130.6, 128.7, 128.2, 128.0, 127.8, 123.6 (q, *J* = 272 Hz), 122.8, 120.3, 118.8, 110.4, 110.4, 104.3, 102.2 (q, *J* = 33.6 Hz), 80.0, 79.8, 59.2, 53.1, 52.5, 48.9, 37.4, 29.4, 28.4, 27.6, 26.7, 26.0, 24.7, 22.2, 18.4, 15.6, 13.8, 11.5. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.09 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{44}H_{57}F_3N_4NaO_8^+$, 849.4021; found, 849.4039. **IR** (KBr, cm^{-1}): ν 3301, 2964, 1714, 1643, 1497, 1292, 1117, 739.



4f

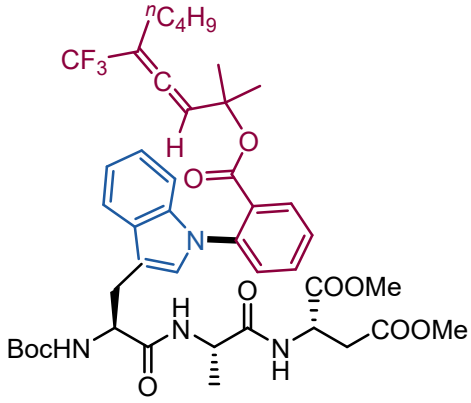
White solid. **m.p.** 67.8-69.5 ℃. 53.8 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.55 (m, 1H), 7.49-7.45 (m, 1H), 7.13-7.09 (m, 3H), 7.05-7.03 (m, 1H), 6.92 (s, 1H), 6.64 (s, 1H), 5.54 (s, 1H), 5.57 (s, 1H), 4.89 (dd, *J* = 12.0, 6.6 Hz, 1H), 4.41 (s, 1H), 4.11-4.08 (m, 1H), 3.68 (s, 3H), 3.40-3.27 (m, 4H), 2.09-2.02 (m, 4H), 1.84-1.75 (m, 2H), 1.42 (s, 9H), 1.35-1.24 (m, 7H), 1.00 (s, 3H), 0.95 (s, 3H), 0.85 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 4.2 Hz), 172.1, 172.0, 171.7, 165.3, 155.9, 138.0, 137.9, 132.8, 131.2, 130.6, 128.8, 128.3, 127.9, 127.7, 123.6 (q, *J* = 273 Hz), 122.7, 120.2, 118.9, 110.7, 110.3, 104.3, 102.2 (q, *J* = 34.4 Hz), 80.6, 79.7, 59.9, 53.0, 52.5, 49.0, 47.2, 29.4, 28.4, 28.1, 27.6, 26.7, 26.0, 25.8, 24.6, 22.2, 17.6, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.08 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{43}H_{53}F_3N_4NaO_8^+$, 833.3708; found, 833.3731. **IR** (KBr, cm^{-1}): ν 3306, 2933, 1693, 1498, 1292, 1118, 910, 734.



4g

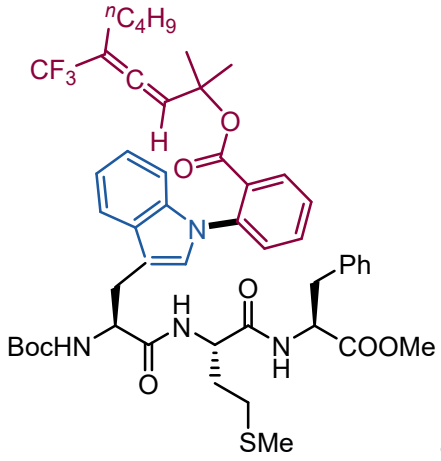
Faint yellow solid. **m.p.** 60.5-62.0 ℃. 48.9 mg, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.4 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.56-7.53 (m, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.15-7.11 (m, 2H), 7.07-7.05 (m, 2H), 6.66 (s, 2H), 6.53 (s, 1H), 5.57 (s, 1H), 5.70 (s, 1H), 4.91 (d, *J* = 12.8, 5.5 Hz, 1H), 4.49-4.37 (m, 1H), 4.03 (s, 1H), 3.70 (s, 3H), 3.41-3.34 (m, 2H), 2.10-0.06 (m, 2H), 1.42 (s, 9H), 1.36-1.30 (m, 7H), 1.20 (d, *J* = 5.3 Hz, 3H), 1.03 (s, 3H), 0.98 (s, 3H), 0.86 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 3.5 Hz), 172.6, 172.1, 171.9, 165.3, 155.5, 137.9, 137.8, 132.8, 131.2, 130.6, 128.7, 128.3, 128.0, 127.7, 123.6 (q, *J* = 272 Hz), 122.8, 120.3, 118.8, 110.5, 110.3, 104.3, 102.2 (q, *J* = 33.7 Hz), 80.2, 79.8, 53.0, 52.5, 50.0, 48.9, 29.4, 28.4, 27.6, 26.7, 26.0, 25.9, 22.2, 18.3, 18.2, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.08 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd.

for $C_{41}H_{51}F_3N_4NaO_8^+$, 807.3551; found, 807.3571. **IR** (KBr, cm^{-1}): ν 3306, 2978, 2933, 1713, 1499, 1292, 911, 737.



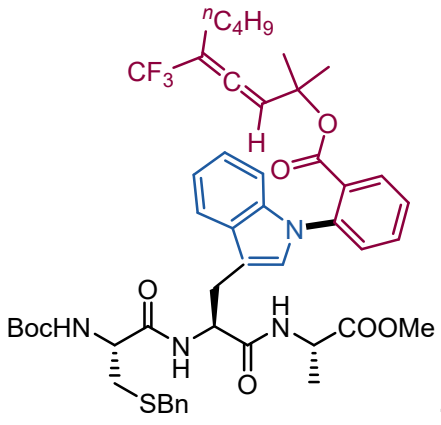
4h

White solid. **m.p.** 53.4-54.1 °C. 57.6 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.69 (s, 1H), 7.63 (td, *J* = 7.7, 1.0 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.17-7.03 (m, 4H), 6.95 (s, 1H), 6.57 (s, 1H), 5.58 (s, 1H), 5.20 (s, 1H), 4.78-4.71 (m, 1H), 4.56-4.29 (m, 2H), 3.73 (s, 3H), 3.68 (s, 3H), 3.39-3.21 (m, 2H), 2.86 (ddd, *J* = 81.3, 17.2, 4.4 Hz, 2H), 2.12-2.02 (m, 2H), 1.41 (s, 9H), 1.36-1.29 (m, 4H), 1.27 (d, *J* = 7.1 Hz, 3H), 1.01 (s, 3H), 0.96 (s, 3H), 0.86 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 4.3 Hz), 171.8, 171.5, 171.3, 170.9, 165.2, 155.6, 138.0, 138.0, 132.8, 131.3, 130.6, 128.7, 128.2, 128.0, 127.7, 123.6 (q, *J* = 273 Hz), 122.8, 120.2, 119.2, 111.2, 110.2, 104.3, 102.2 (q, *J* = 33.3 Hz), 80.3, 79.7, 52.9, 52.2, 49.0, 48.7, 48.6, 36.0, 29.4, 28.3, 26.8, 26.0, 25.9, 22.2, 18.5, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.08 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{43}H_{53}F_3N_4NaO_{10}^+$, 865.3606; found, 865.3596. **IR** (KBr, cm^{-1}): ν 3301, 2932, 1717, 1647, 1496, 1292, 1117, 739.



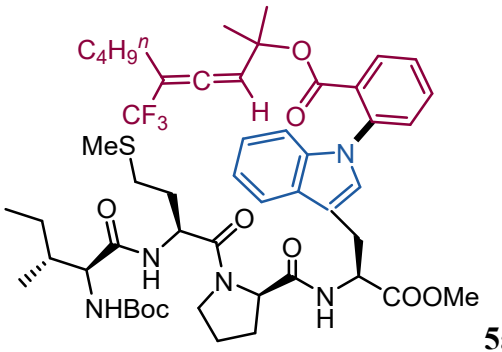
4i

White solid. **m.p.** 60.8-62.3 ℃. 65.6 mg, 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.69-7.67 (m, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51-7.46 (m, 2H), 7.29-7.20 (m, 3H), 7.15-7.12 (m, 2H), 7.09-7.05 (m, 3H), 7.02 (s, 1H), 6.76-6.72 (m, 2H), 5.59 (s, 1H), 5.18 (s, 1H), 4.71 (dd, *J* = 13.2, 6.4 Hz, 1H), 4.54-4.44 (m, 2H), 3.69 (s, 3H), 3.37-3.14 (m, 2H), 3.07-3.01(m, 2H), 2.42-2.37 (m, 2H), 2.10-2.04 (m, 2H), 1.93 (s, 3H), 1.87-1.80 (m, 2H), 1.42 (s, 9H), 1.36-1.28 (m, 4H), 1.01 (s, 3H), 0.96 (s, 3H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 3.8 Hz), 171.7, 171.6, 170.4, 165.3, 155.7, 138.0, 138.0, 135.8, 132.8, 131.4, 130.6, 129.3, 128.8, 128.1, 128.0, 127.8, 127.3, 123.6 (q, *J* = 274 Hz), 122.9, 120.3, 119.2, 111.1, 110.3, 104.2, 102.2 (q, *J* = 33.7 Hz), 80.4, 79.7, 53.5, 52.4, 52.4, 52.2, 37.8, 29.8, 29.4, 28.4, 26.8, 26.0, 25.9, 22.2, 14.9, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.05 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{49}H_{59}F_3N_4NaO_8S^+$, 943.3898; found, 943.3898. **IR** (KBr, cm^{-1}): ν 3291, 2930, 1714, 1644, 1496, 1293, 1116, 743.



4j

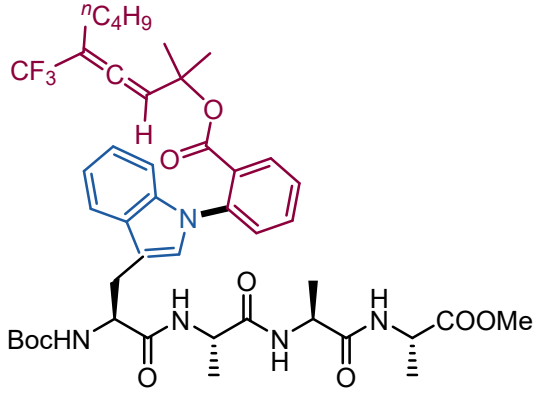
Faint yellow solid. **m.p.** 51.2-52.0 ℃. 67.4 mg, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.4 Hz, 1H), 7.78 (s, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.55-7.41 (m, 2H), 7.28-7.27 (m, 4H), 7.24-7.20 (m, 1H), 7.16-7.14 (m, 3H), 7.08-6.94 (m, 2H), 6.55 (m, 2H), 5.56 (s, 1H), 5.23 (s, 1H), 4.76 (dd, *J* = 12.4, 6.9 Hz, 1H), 4.48-4.44 (m, 1H), 4.22-4.21 (m, 1H), 3.67-3.61 (m, 5H), 3.48-3.43 (m, 1H), 3.22-3.16 (m, 1H), 2.79 (d, *J* = 6.0 Hz, 2H), 2.09-2.05 (m, 2H), 1.39-1.29 (m, 13H), 1.26 (d, *J* = 7.0 Hz, 3H), 1.03 (s, 3H), 0.98 (s, 3H), 0.86 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 3.9 Hz), 172.8, 170.5, 170.4, 165.2, 155.5, 138.0, 137.8, 132.8, 131.2, 130.6, 129.1, 128.7, 128.1, 128.0, 127.3, 124.6 (q, *J* = 274 Hz), 122.9, 120.4, 119.2, 111.0, 110.2, 104.2, 102.2 (q, *J* = 33.8 Hz), 80.4, 79.8, 60.5, 54.1, 52.4, 48.4, 36.5, 33.6, 29.4, 28.3, 28.2, 26.8, 26.0, 25.9, 22.2, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.05 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{48}H_{57}F_3N_4NaO_8S^+$, 929.3741; found, 929.3767. **IR** (KBr, cm^{-1}): ν 3296, 2933, 1714, 1643, 1495,1293, 1117, 737.



5a

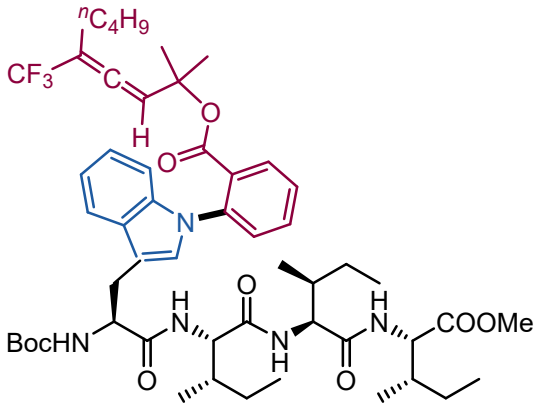
White solid. **m.p.** 96.0-96.7 ℃. 60.5 mg, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.65-7.61 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.19 (s, 1H), 7.13-7.10 (m, 2H), 7.07-7.05 (m, 1H), 6.97 (s, 2H), 5.58-5.54 (m, 1H), 5.37-5.35 (m, 1H), 4.92 (dd, *J* = 14.7, 7.2 Hz, 1H), 4.82 (dd, *J* = 13.1, 6.7 Hz, 1H), 4.44-4.41 (m, 1H), 4.05-3.98 (m, 1H), 3.70 (s, 3H), 3.66-3.63 (m, 1H), 3.53-3.47 (m, 1H), 3.42-3.27 (m, 2H), 2.51 (dd, *J* = 13.7, 6.8 Hz, 2H), 2.09-2.04 (m, 6H), 1.90-1.72 (m, 6H), 1.46-1.44 (m, 2H), 1.41 (s, 9H), 1.36-1.28 (m, 4H), 1.14-0.96 (m, 6H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.86 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 4.8 Hz), 172.8, 172.1, 171.2, 170.3, 165.4, 156.2, 138.1, 137.7, 132.7, 131.2, 130.6, 128.5, 128.4, 127.9, 127.7, 123.6 (q, *J* = 272 Hz), 122.6, 120.1, 119.0,

111.3, 110.2, 104.3, 102.2 (q, J = 34.0 Hz), 79.9, 79.7, 60.8, 59.0, 52.9, 52.5, 50.3, 47.2, 37.0, 30.9, 30.2, 29.4, 29.1, 28.4, 27.6, 26.7, 26.0, 25.8, 24.9, 24.4, 22.2, 15.8, 13.8, 11.5. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.09 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{51}H_{68}F_3N_5NaO_9S^+$, 1006.4582; found, 1006.4621. **IR** (KBr, cm^{-1}): ν 3302, 2964, 1714, 1498, 1292, 1117, 736.



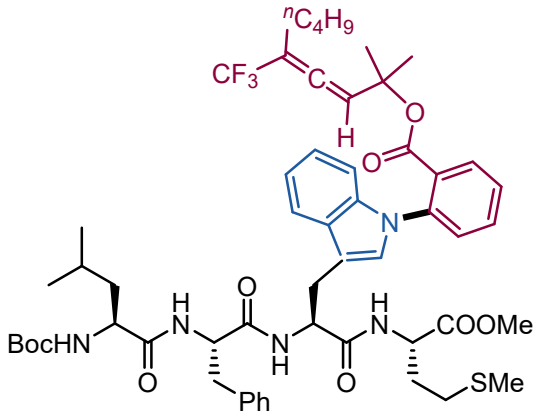
5b

White solid. **m.p.** 142.0-142.6 ℃. 33.2 mg, 38% yield. **^{1}H NMR** (400 MHz, Acetone-D_6) δ 7.89 (dd, J = 7.7, 1.1 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.70 (d, J = 9.5 Hz, 2H), 7.60-7.54 (m, 3H), 7.48 (d, J = 6.8 Hz, 1H), 7.29 (s, 1H), 7.17-7.13 (m, 5H), 7.12-7.08 (m, 2H), 7.00-6.98 (m, 1H), 6.22 (d, J = 5.9 Hz, 1H), 5.59 (s, 1H), 4.80 (dd, J = 14.0, 6.9 Hz, 1H), 4.70-4.67 (m, 1H), 4.62 (td, J = 8.4, 4.8 Hz, 1H), 4.05 (dd, J = 14.6, 7.2 Hz, 1H), 3.62 (s, 3H), 3.43-3.18 (m, 2H), 3.03 (ddd, J = 22.3, 14.1, 6.7 Hz, 2H), 2.90-2.85 (m, 2H), 2.28-2.48 (m, 2H), 2.09-2.06 (m, 1H), 2.03-2.02 (m, 1H), 2.01 (m, 3H), 1.62 (dt, J = 13.1, 6.5 Hz, 1H), 1.45 (t, J = 7.1 Hz, 2H), 1.34 (s, 9H), 1.31-1.26 (m, 4H), 1.00 (s, 3H), 0.93 (s, 3H), 0.86-0.81 (m, 9H). **^{13}C NMR** (100 MHz, Acetone-D_6) δ 205.7 (q, J = 4.5 Hz), 172.8, 172.3, 171.9, 171.9, 165.0, 156.0, 138.1, 137.8, 133.2, 131.0, 130.5, 128.8, 128.6, 128.0, 127.9, 123.9 (q, J = 272 Hz), 122.3, 119.8, 119.2, 112.1, 109.9, 104.7, 101.7 (q, J = 33.4 Hz), 79.0, 79.0, 55.7, 51.5, 49.5, 48.5, 48.0, 27.7, 27.6, 26.3, 25.7, 25.4, 21.9, 17.5, 17.0, 13.2. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.03 (d, J = 7.6 Hz). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{44}H_{56}F_3N_5NaO_9^+$, 878.3922; found, 878.3947. **IR** (KBr, cm^{-1}): ν 3275, 2931, 1709, 1631, 1460, 1291, 1117, 740.



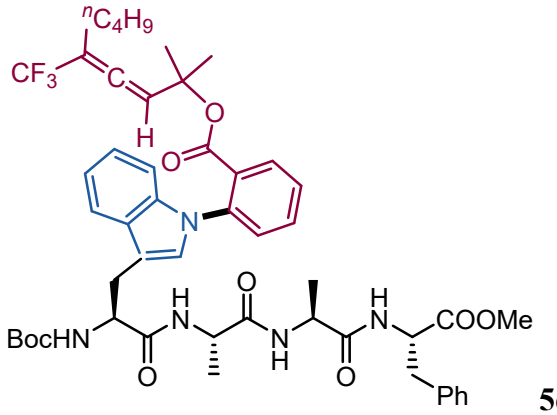
5c

White solid. **m.p.** 121.6-122.9 ℃. 60.9 mg, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.67-7.65 (m, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.16-7.11 (m, 2H), 7.09-7.06 (m, 2H), 6.84-6.76 (m, 3H), 5.58 (s, 1H), 5.24 (s, 1H), 4.57 (dd, *J* = 8.5, 5.5 Hz, 1H), 4.53-4.52 (m, 1H), 4.38 (t, *J* = 7.6 Hz, 1H), 4.33-4.28 (m, 1H), 3.72 (s, 3H), 3.33-3.24 (m, 2H)，2.09-2.04 (m, 2H), 1.90-1.84 (m, 3H), 1.38 (s, 9H), 1.34-1.27 (m, 6H), 1.21-1.12 (m, 4H), 1.07-0.97 (m, 6H), 0.91-0.86 (m, 12H), 0.84-0.79 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 3.6 Hz), 172.4, 172.1, 171.2, 171.1, 165.3, 155.9, 138.0, 137.9, 132.7, 131.4, 130.5 128.6, 128.3, 127.9, 127.7, 123.6 (q, *J* = 273 Hz), 122.8, 120.2, 119.1, 111.3, 110.2, 104.2, 102.2 (q, *J* = 33.4 Hz), 80.2, 79.6, 58.3, 58.0, 56.6, 52.2, 37.6, 37.2, 29.4, 28.3, 26.8, 26.0, 25.8, 25.2, 24.9, 22.2, 15.5, 15.4, 13.8, 11.6, 11.5, 11.4. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.09 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{53}H_{74}F_3N_5NaO_9^+$, 1004.5331; found, 1004.5363. **IR** (KBr, cm^{-1}): ν 3274, 2964, 1716, 1639, 1550, 1293, 1118, 740.



5d

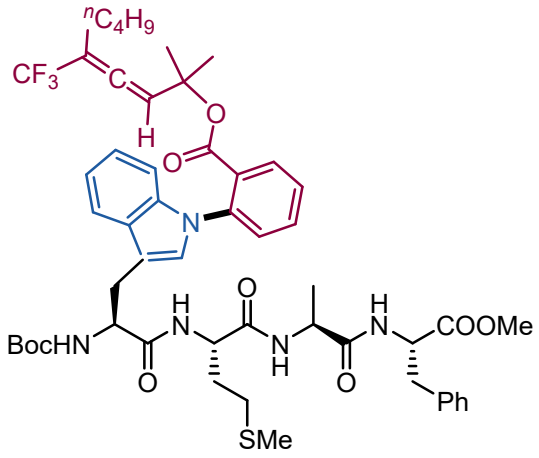
White solid. **m.p.** 139.6-140.0 °C. 52.5 mg, 50% yield. **^{1}H NMR** (400 MHz, Acetone-D_6) δ 7.90 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 9.5 Hz, 2H), 7.64-7.56 (m, 3H), 7.50 (d, *J* = 6.8 Hz, 1H), 7.32 (s, 1H), 7.19-7.16 (m, 5H), 7.15-7.11 (m, 2H), 7.03-7.01 (m, 1H), 6.25 (d, *J* = 5.9 Hz, 1H), 5.61 (s, 1H), 4.83 (dd, *J* = 14.0, 6.9 Hz, 1H), 4.70 (dd, *J* = 13.9, 8.9 Hz, 1H), 4.65 (td, *J* = 8.4, 4.8 Hz, 1H), 4.07 (dd, *J* = 14.6, 7.2 Hz, 1H), 3.65 (s, 3H), 3.46-3.21 (m, 2H), 3.05 (ddd, *J* = 22.3, 14.1, 6.7 Hz, 2H), 2.91-2.88 (m, 2H), 2.56-2.50 (m, 2H), 2.12-2.10 (m, 2H), 2.04 (s, 3H), 1.65 (dt, *J* = 13.1, 6.5 Hz, 1H), 1.48 (t, *J* = 7.1 Hz, 2H), 1.37 (s, 9H), 1.34-1.29 (m, 4H), 1.03-0.96 (m, 6H), 0.89-0.83 (m, 9H). **^{13}C NMR** (100 MHz, Acetone-D_6) δ 205.7 (q, *J* = 4.5 Hz), 178.4, 177.2, 176.3, 176.0, 170.3, 161.3, 143.3, 143.0, 142.7, 138.2, 136.1, 135.8, 134.6, 134.0, 133.9, 133.5, 133.1, 133.1, 131.7, 129.1 (q, *J* = 273 Hz), 127.4, 125.0, 124.4, 117.4, 115.0, 109.9, 106.8 (q, *J* = 33.3 Hz), 84.2, 84.1, 59.6, 59.1, 58.9, 56.8, 56.8, 46.2, 42.6, 36.5, 35.1, 33.1, 32.9, 31.5, 30.9, 30.5, 29.8, 27.7, 27.1, 26.6, 19.6, 18.4. **^{19}F NMR (**376 MHz, Acetone-D_6**)** δ= -64.07 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{55}H_{70}F_3N_5NaO_9S^+$, 1056.4739; found, 1056.4768. **IR** (KBr, cm^{-1}): ν 3288, 2958, 1713, 1637, 1498, 1292, 1117, 742, 699.



5e

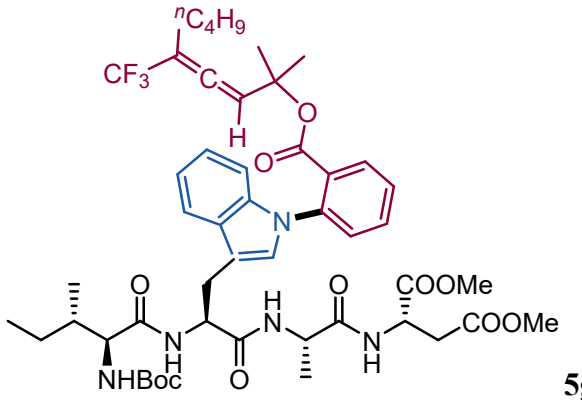
White solid. **m.p.** 74.6-75.5 °C. 61.6 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.5 Hz, 1H), 7.68-7.60 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 6.8 Hz, 2H), 7.20-7.06 (m, 8H), 7.00 (s, 1H), 6.48 (s, 1H), 5.60 (s, 1H), 5.23 (s, 1H), 4.82 (dd, *J* = 13.5, 7.4 Hz, 1H), 4.47-4.29 (m, 3H), 3.70 (s, 3H), 3.45-3.02 (m, 4H), 2.13-2.04 (m, 2H), 1.41 (s, 9H), 1.36-1.26 (m, 4H), 1.27 (d, *J* =

7.1 Hz, 3H), 1.21 (d, *J* = 6.0 Hz, 3H), 1.05 (s, 3H), 1.00 (s, 3H), 0.86 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.6 (q, *J* = 3.7 Hz), 172.4, 172.0, 171.9, 171.8, 165.2, 156.1, 138.0, 137.9, 136.5, 132.9, 131.4, 130.5, 129.4, 128.6, 128.5, 128.1, 127.8, 126.9, 123.6 (q, *J* = 274 Hz), 122.3, 120.4, 119.0, 110.8, 110.3, 104.2, 102.3 (q, *J* = 33.5 Hz), 80.7, 79.7, 55.8, 53.5, 52.4, 49.6, 49.2, 38.0, 29.4, 28.3, 27.9, 26.8, 26.0, 22.2, 18.1, 17.9, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.03 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{50}H_{60}F_3N_5NaO_9^+$, 954.4235; found, 954.4268. **IR** (KBr, cm^{-1}): ν 3290, 2931, 1713, 1635, 1495, 1292, 1117, 740.



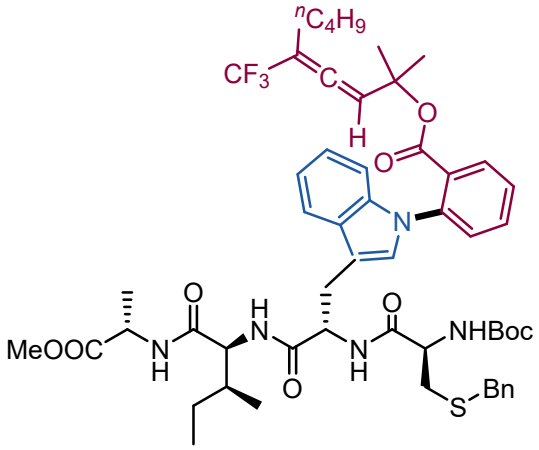
5f

White solid. **m.p.** 74.8-76.4 °C. 66.5 mg, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.66-7.63 (m, 2H), 7.55-7.43 (m, 2H), 7.24-7.07 (m, 11H), 7.00 (s, 1H), 5.64 (s, 1H), 5.17 (s, 1H), 4.81 (dd, *J* = 13.6, 7.7 Hz, 1H), 4.52-4.32 (m, 3H), 3.71 (s, 3H), 3.43-3.03 (m, 4H), 2.35-2.21 (m, 2H), 2.10-2.06 (m, 2H), 1.96-1.91 (m, 5H), 1.42 (s, 9H), 1.36-1.32 (m, 4H), 1.28 (d, *J* = 7.2 Hz, 3H), 1.06 (s, 3H), 1.01 (s, 3H), 0.86 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.6 (q, *J* = 4.1 Hz), 172.9, 171.9, 170.6, 165.1, 156.3, 138.0, 137.9, 136.6, 132.9, 134.6, 131.5, 130.4, 129.4, 128.6, 128.5, 128.1, 128.0, 127.8, 126.9, 123.6 (q, *J* = 274 Hz), 123.1, 120.5, 119.2, 110.6, 110.4, 104.2, 102.3 (q, *J* = 33.2 Hz), 81.0, 79.8, 55.9, 53.5, 52.4, 49.3, 38.0, 30.0, 29.4, 28.4, 27.7, 26.8, 26.0, 22.2, 17.8, 15.0, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.02 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{52}H_{64}F_3N_5NaO_9S^+$, 1014.4269; found, 1014.4302. **IR** (KBr, cm^{-1}): ν 3285, 2931, 1714, 1635, 1496, 1259, 1115, 803, 741.



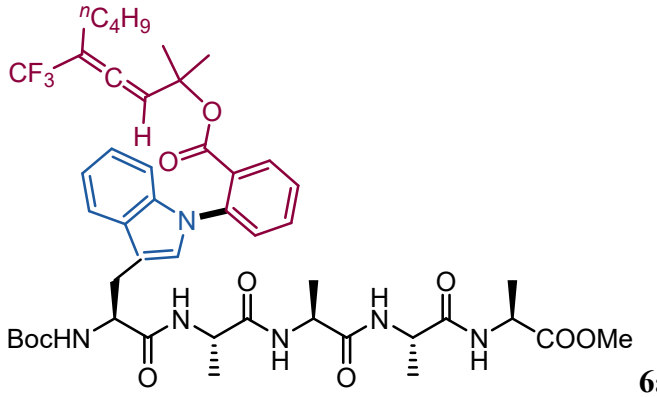
5g

White solid. **m.p.** 65.4-65.7 ℃. 58.3 mg, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.69 (s, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.38 (s, 1H), 7.19-7.11 (m, 4H), 7.08-7.03 (m, 1H), 6.99 (d, *J* = 5.7 Hz, 1H), 6.79 (d, *J* = 6.2 Hz, 1H), 5.53 (s, 1H), 4.86-4.81 (m, 2H), 4.70 (dd, *J* = 11.4, 5.7 Hz, 1H), 4.57-4.48 (m, 1H), 3.89 (t, *J* = 4.9 Hz, 1H), 3.73 (s, 3H), 3.65 (s, 3H), 3.43 (dd, *J* = 14.3, 4.0 Hz, 1H), 3.27 (dd, *J* = 14.5, 5.7 Hz, 1H), 2.93 (dd, *J* = 16.9, 5.8 Hz, 1H), 2.85 (dd, *J* = 16.9, 5.0 Hz, 1H), 2.09-2.05 (m, 2H), 1.87-1.82 (m, 1H), 1.32-1.24 (m, 18H), 1.03 (s, 3H), 0.97 (s, 3H), 0.88-0.84 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.6 (q, *J* = 4.1 Hz), 172.0, 172.0, 171.1, 171.1, 170.9, 165.1, 156.4, 138.1, 137.8, 132.9, 131.4, 130.6, 128.5, 128.1, 128.0, 127.8, 123.6 (q, *J* = 274 Hz), 123.2, 120.5, 118.8, 110.9, 110.4, 104.1, 102.3 (q, *J* = 33.4 Hz), 80.6, 79.8, 60.3, 52.8, 52.0, 49.0, 48.8, 36.8, 36.2, 29.8, 29.4, 28.1, 26.7, 26.0, 25.9, 24.7, 22.2, 17.8, 15.7, 13.8, 11.7. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.09 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{49}H_{64}F_3N_5NaO_{11}^+$, 978.4447; found, 978.4482. **IR** (KBr, cm^{-1}): ν 3281, 2931, 1718, 1634, 1116, 740.



5h

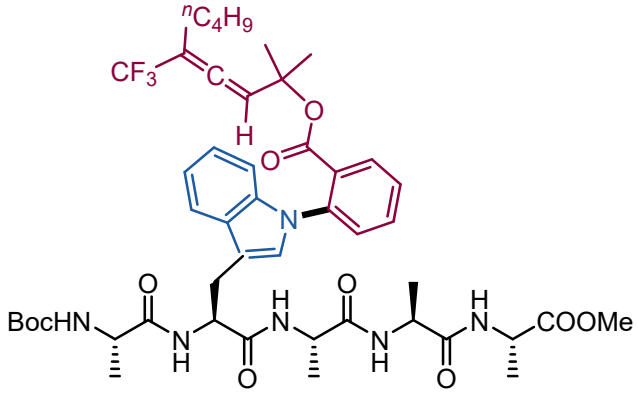
White solid. **m.p.** 90.3-91.9 ℃. 70.1 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.75 (s, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.53-7.39 (m, 2H), 7.26-7.19 (m, 5H), 7.19-7.11 (m, 3H), 7.09-7.00 (m, 2H), 6.72 (s, 1H), 6.62 (s, 1H), 5.55 (s, 1H), 5.23 (s, 1H), 4.75 (dd, *J* = 12.3, 6.0 Hz, 1H), 4.51-4.41 (m, 1H), 4.36-4.29 (m, 1H), 4.22-4.10 (m, 1H), 3.71 (s, 3H), 3.65-3.58 (m, 2H), 3.44-3.24 (m, 2H), 2.75 (s, 2H), 2.09-2.05 (m, 2H), 1.92-1.81 (m, 1H), 1.36 (d, *J* = 13.3 Hz, 6H), 1.33-1.29 (m, 12H), 1.01 (s, 3H), 0.95 (s, 3H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.83-0.76 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.6 (q, *J* = 2.9 Hz), 173.2, 171.0, 170.8, 170.4, 165.2, 155.6, 138.0, 137.9, 137.7, 132.8, 131.8, 130.7, 129.0, 128.7, 128.6, 128.0, 127.9, 127.4, 127.3, 123.6 (q, *J* = 274 Hz), 123.0, 122.9, 120.5, 110.4, 110.3, 104.2, 102.2 (q, *J* = 33.4 Hz), 80.5, 79.8, 58.1, 57.9, 54.1, 52.4, 48.1, 36.4, 33.6, 29.4 28.3, 28.2, 26.7, 26.0, 25.8, 24.8, 22.2, 18.0, 15.3, 13.8, 11.5. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.06 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{54}H_{68}F_3N_5NaO_9S^+$, 1042.4582; found, 1042.4627. **IR** (KBr, cm^{-1}): ν 3285, 2963, 1711, 1634, 1517, 1292, 1118, 738.



6a

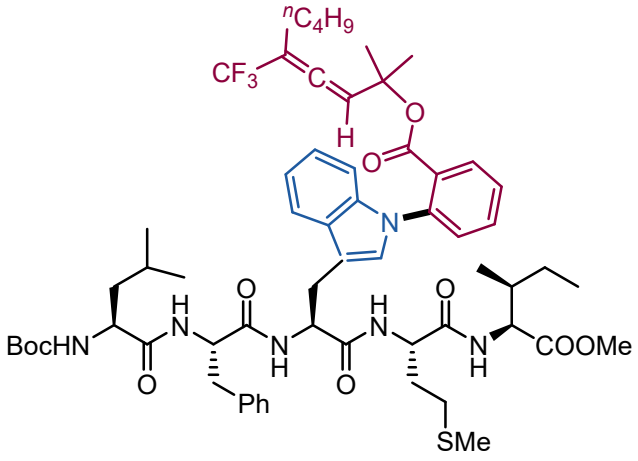
White solid. **m.p.** over 200 ℃. 33.1 mg, 35% yield. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 8.25 (d, *J* = 7.6 Hz, 1H), 8.11-8.06 (m, 2H), 7.88 (d, *J* = 7.4 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.80-7.76 (m, 1H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.30 (s, 1H), 7.12-7.10 (m, 2H), 6.98-6.97 (m, 1H), 6.92-6.88 (m, 1H), 5.76 (s, 1H), 4.33-4.22 (m, 5H), 4.06 (s, 1H), 3.61 (s, 3H), 3.18-2.97 (m, 2H)，2.08-2.04 (m, 2H), 1.28 (s, 9H), 1.26-1.17 (m, 16H), 0.89 (s, 3H), 0.85-0.79 (m, 6H). **^{13}C NMR** (100 MHz, DMSO-D_6) δ 200.4 (q, *J* = 4.1 Hz), 173.4, 172.5, 172.5, 172.2, 172.1, 165.3, 155.9, 137.9, 137.4, 133.8, 131.3, 130.1, 128.8, 128.7, 128.4, 128.3, 124.1 (q, *J* = 273

Hz), 122.6, 120.0, 119.8, 113.0, 110.0, 105.3, 101.4 (q, J = 33.0 Hz), 79.2, 78.6, 55.4, 52.4, 48.6, 48.6, 48.2, 48.0, 29.3, 28.6, 28.3, 27.9, 26.9, 25.7, 21.9, 18.8, 18.7, 18.5, 17.4, 14.0. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.02 (d, J = 12.3 Hz). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{47}H_{61}F_3N_6NaO_{10}^+$, 949.4293; found, 949.4311. **IR** (KBr, cm^{-1}): ν 3443, 1662, 1460, 1293, 761.



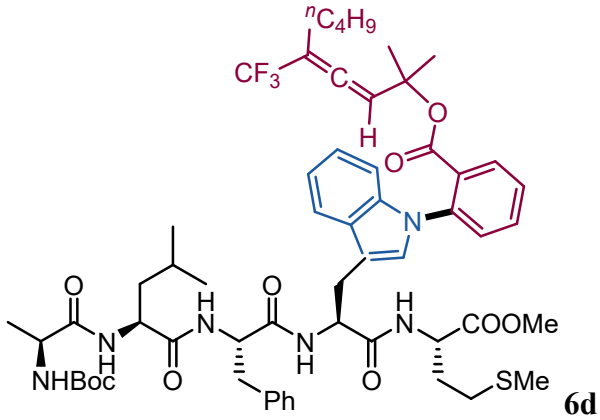
6b

White solid. **m.p.** over 200 ℃. 30.2 mg, 32% yield. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 8.25 (d, J = 7.0 Hz, 1H), 8.14-8.13 (m, 1H), 7.97 (d, J = 7.2 Hz, 1H), 7.92-7.91 (m, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.73-7.68 (m, 1H), 7.61-7.55 (m, 2H), 7.30 (s, 1H), 7.10-7.08 (m, 2H), 6.95-6.91 (m, 2H), 5.68 (s, 1H), 4.58 (dd, J = 12.0, 6.3 Hz, 1H), 4.33-4.23 (m, 3H), 3.99-3.89 (m, 1H), 3.61 (s, 3H), 3.22-3.02 (m, 2H)，2.08-2.04 (m, 2H), 1.29-1.26 (m, 16H), 1.19 (d, J = 6.3 Hz, 6H), 1.12 (d, J = 6.6 Hz, 3H), 0.91 (s, 6H), 0.81 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-D_6) δ 200.4 (q, J = 4.4 Hz), 173.4, 173.3, 172.5, 172.1, 171.4, 165.2, 155.6, 138.0, 137.4, 133.7, 131.2, 130.2, 128.9, 128.8, 128.3, 128.1, 124.1 (q, J = 273 Hz), 122.5, 120.0, 119.7, 112.4, 109.9, 105.3, 101.4 (q, J = 33.2 Hz), 79.1, 78.6, 53.2, 52.4, 50.4, 48.6, 48.2, 48.0, 29.3, 28.6, 27.8, 26.8, 26.1, 25.7, 21.9, 18.7, 18.7, 18.6, 17.4, 14.0. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.06 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{47}H_{61}F_3N_6NaO_{10}^+$, 949.4293; found, 949.4316. **IR** (KBr, cm^{-1}): ν 3449, 1662, 1460, 1293, 1116, 1027, 761.



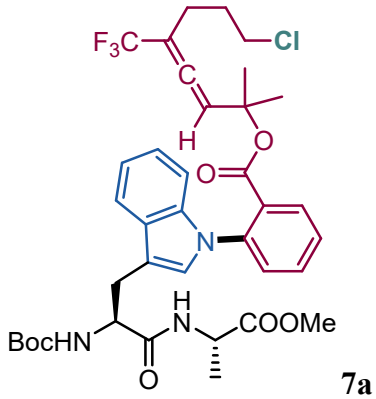
6c

White solid. **m.p.** 109.2-110.5 ℃. 57.1 mg, 49% yield. **^{1}H NMR** (400 MHz, Acetone-D_6) δ 7.90 (d, *J* = 7.8 Hz, 1H), 7.84-7.70 (m, 4H), 7.64-7.56 (m, 3H), 7.23-7.10 (m, 9H), 7.03-7.00 (m, 1H), 6.30 (d, *J* = 6.1 Hz, 1H), 5.65-5.61 (m, 1H), 4.81 (dd, *J* = 13.1, 7.6 Hz, 1H), 4.71-4.64 (m, 1H), 4.58 (s, 1H), 4.45-4.41 (m, 1H), 4.16-4.04 (m, 1H), 3.70 (s, 3H), 3.41-3.22 (m, 2H)，3.20-3.12 (m, 1H), 3.07-2.84 (m, 3H), 2.55-2.42 (m, 2H), 2.14-2.09 (m, 2H), 2.02 (s, 3H), 1.93-1.85 (m, 1H), 1.46-1.39 (m, 5H), 1.37 (s, 9H), 1.34-1.29 (m, 4H), 1.02 (s, 3H), 0.99 (s, 3H), 0.91 (t, *J* = 7.6 Hz, 6H), 0.87-0.85 (m, 9H). **^{13}C NMR** (100 MHz, Acetone-D_6) δ 200.5 (q, *J* = 3.6 Hz), 173.6, 171.7, 171.5, 171.3, 171.1, 165.0, 156.1, 138.6, 138.4, 137.8, 133.5, 131.5, 131.3, 130.0, 129.5, 129.2, 128.8, 128.6, 128.5, 127.0, 124.5 (q, *J* = 273 Hz), 122.9, 120.4, 119.8, 112.7, 110.4, 105.3, 102.2 (q, *J* = 33.3 Hz), 79.6, 79.4, 57.4, 55.7, 54.7, 54.3, 53.0, 51.9, 41.7, 37.8, 37.7, 32.4, 30.4, 28.4, 28.1, 26.9, 26.3, 25.9, 25.6, 25.1, 23.0, 22.5, 22.0, 15.8, 15.0, 13.8, 11.7. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.06 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{61}H_{81}F_3N_6NaO_{10}S^+$, 1169.5579; found, 1169.5596. **IR** (KBr, cm^{-1}): ν 3289, 2960, 1716, 1635, 1497, 1117, 742.



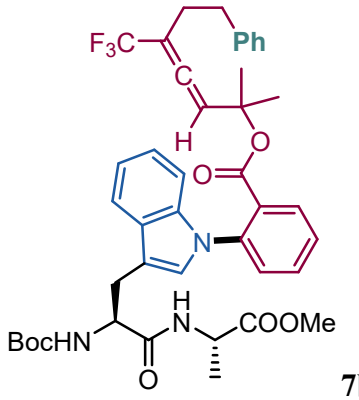
6d

White solid. **m.p.** over 200 ℃. 60.5 mg, 54% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 6.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.48-7.42 (m, 2H), 7.15-7.11 (m, 7H), 7.05-6.92 (m, 5H), 6.69 (s, 1H), 5.50 (s, 1H), 4.97-4.90 (m, 2H), 4.64-4.60 (m, 2H), 4.14-4.12 (m, 1H), 3.79-3.73 (m, 1H), 3.67 (s, 3H), 3.50-3.47 (m, 1H), 3.27 (dd, *J* = 13.7, 7.9 Hz, 1H), 3.16-3.12 (m, 1H), 2.91-2.80 (m, 1H), 2.53-2.47 (m, 2H), 2.17-2.06 (m, 3H), 2.04 (s, 3H), 2.02-1.85 (m, 2H), 1.60-1.45 (m, 2H), 1.36 (s, 9H), 1.33-1.28 (m, 4H), 1.19 (d, *J* = 4.9 Hz, 3H), 1.08-0.96 (m, 6H), 0.86-0.85 (m, 6H), 0.81 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 4.0 Hz), 173.7, 172.6, 171.9, 171.3, 171.0, 165.4, 156.1, 138.1, 137.8, 136.7, 132.7, 131.2, 130.6, 129.0, 128.5, 128.4, 127.7, 127.5, 126.8, 123.6 (q, *J* = 274 Hz), 122.5, 120.1, 119.2, 112.1, 110.1, 104.2, 102.1 (q, *J* = 34.0 Hz), 80.5, 79.6, 52.4, 52.4, 51.8, 51.8, 50.8, 50.8, 31.7, 30.0, 29.8, 29.4, 28.3, 26.6, 26.0, 25.8, 24.9, 22.9, 22.2, 22.2, 15.3, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.06 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{58}H_{75}F_3N_6NaO_{10}S^+$, 1127.5110; found, 1127.5173. **IR** (KBr, cm^{-1}): ν 2930, 1712, 1632, 1497, 1292, 1116, 740.



7a

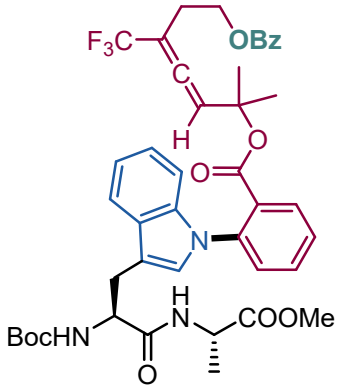
Faint yellow oil. 50.0 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.70 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.19-6.97 (m, 4H), 6.44 (m, 1H), 5.48 (s, 1H), 5.24 (s, 1H), 4.53-4.43 (m, 2H), 3.64 (s, 3H), 3.51 (t, *J* = 5.4 Hz, 2H), 3.39-3.19 (m, 2H), 2.35-2.17 (m, 2H), 1.87 (dt, *J* = 13.5, 6.7 Hz, 2H), 1.44 (s, 9H), 1.29 (d, *J* = 7.0 Hz, 3H), 1.01 (s, 3H), 0.95 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.4 (q, *J* = 3.1 Hz), 173.0, 171.2, 165.3, 155.5, 138.1, 138.0, 132.8, 131.3, 130.4, 128.7, 128.3, 128.0, 127.9, 123.4 (q, *J* = 274 Hz), 122.8, 120.3, 119.2, 111.3, 110.2, 104.9, 101.0 (q, *J* = 34.2 Hz), 80.2, 79.4, 52.4, 48.2, 44.0, 30.0, 28.4, 27.2, 25.5, 23.7, 18.4. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.15 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{37}H_{43}ClF_3N_3NaO_7^+$, 756.2634; found, 756.2668. **IR** (KBr, cm^{-1}): ν 3309, 2980, 1714, 1663, 1496, 1293, 1117, 742.



7b

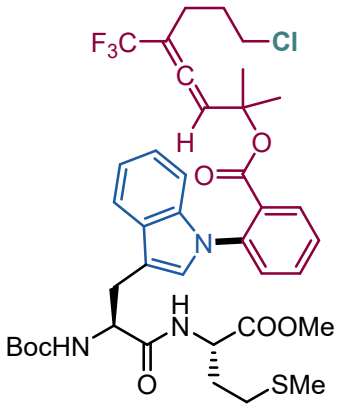
Faint yellow oil. 57.2 mg, 72% yield.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.70 (s, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.28-7.24 (m, 2H), 7.20 (d, *J* = 7.1 Hz, 1H), 7.15-7.07 (m, 6H), 6.43 (s, 1H), 5.52 (s, 1H), 5.23 (s, 1H), 4.53-4.43 (m, 2H), 3.63 (s, 3H), 3.39-3.18 (m, 2H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.43-2.37 (m, 2H), 1.44 (s, 9H), 1.28 (d, *J* = 7.0 Hz, 3H), 0.99 (s, 3H), 0.92 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.7 (q, *J* = 3.9 Hz), 173.0, 171.2, 165.2, 155.5, 140.7, 138.1, 138.0, 132.8, 131.3, 130.5, 128.6, 128.5, 128.4, 128.0, 127.9, 126.3, 123.5 (q, *J* = 274 Hz), 122.8, 120.3, 119.3, 111.3, 110.2, 104.7, 101.6 (q, *J* = 34.0 Hz), 80.2, 79.6, 60.5, 52.4, 48.2, 33.4, 28.4, 28.0, 26.8, 25.7, 18.4, 14.3. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -63.96 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd.

for $C_{42}H_{46}F_3N_3NaO_7^+$, 784.3180; found, 784.3215. **IR** (KBr, cm^{-1}): ν 3306, 2929, 1713, 1665, 1495, 1294, 1116, 743.



7c

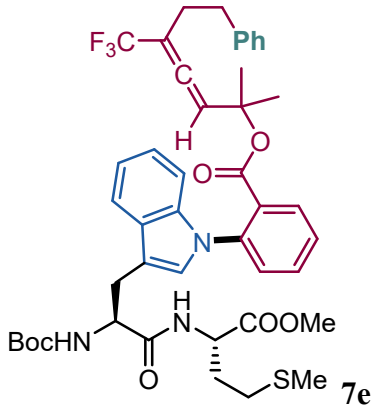
Faint yellow oil. 33.7 mg, 41% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.67 (s, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.43-7.39 (m, 3H), 7.14-6.98 (m, 4H), 6.46 (s, 1H), 5.53 (s, 1H), 5.24 (s, 1H), 4.47 (m, 2H), 4.36 (t, *J* = 6.4 Hz, 2H), 3.62 (s, 3H), 3.39-3.08 (m, 2H), 2.58 (td, *J* = 6.3, 2.7 Hz, 2H), 1.42 (s, 9H), 1.27 (d, *J* = 6.8 Hz, 3H), 0.98 (s, 3H), 0.91 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.0 (q, *J* = 4.8 Hz), 173.0, 171.2, 166.4, 165.3, 155.5, 138.0, 138.0, 133.2, 132.8, 131.4, 130.4, 130.0, 129.7, 128.6, 128.5, 128.0, 127.9, 123.3 (q, *J* = 273 Hz), 122.8, 120.3, 119.2, 111.3, 110.2, 105.0, 98.5 (q, *J* = 34.8 Hz), 80.2, 79.3, 62.3, 62.3, 52.4, 48.2, 28.4, 26.9, 25.5, 18.4. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.18 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{43}H_{46}F_3N_3NaO_9^+$, 828.3078; found, 828.3125. **IR** (KBr, cm^{-1}): ν 3310, 2980, 1719, 1496, 1275, 1293, 1117, 738.



7d

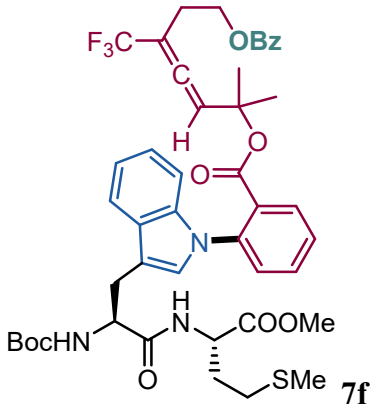
Faint yellow oil. 62.8 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.69 (s, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* =

8.0 Hz, 1H), 7.17-7.05 (m, 4H), 6.55 (s, 1H), 5.49 (s, 1H), 5.22 (s, 1H), 4.60-4.48 (m, 2H), 3.63 (s, 3H), 3.51 (td, J = 6.4, 1.6 Hz, 2H), 3.38-3.19 (m, 2H), 2.36-2.31 (m, 2H), 2.30-2.23 (m, 2H), 2.08-2.03 (m, 1H), 1.99 (s, 3H), 1.94-1.82 (m, 3H), 1.44 (s, 9H), 1.01 (s, 3H), 0.95 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.4 (q, J = 4.1Hz), 171.9, 171.6, 165.3, 155.6, 138.0, 138.0, 132.9, 131.3, 130.4, 128.7, 128.2, 128.0, 127.8, 123.4 (q, J = 274 Hz), 122.8, 120.3, 119.1, 111.2, 110.2, 104.9, 101.0 (q, J = 34.4 Hz), 80.3, 79.4, 52.5, 51.7, 44.0, 31.7, 30.0, 29.8, 28.4, 27.1, 25.5, 23.7, 15.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -64.14 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{39}H_{47}ClF_3N_3NaO_7S^+$, 816.2668; found, 816.2713. **IR** (KBr, cm^{-1}): ν 2925, 1713, 1496, 1294, 1162, 1117, 741.



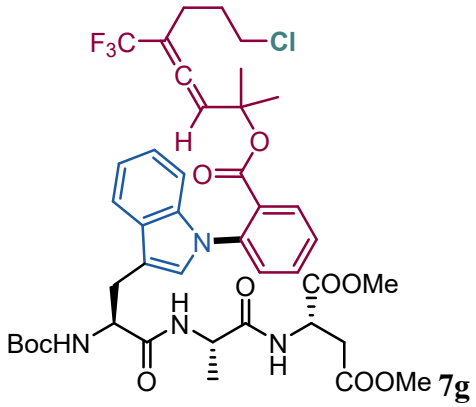
7e

Faint yellow oil. 69.2 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.7 Hz, 1H), 7. 69 (s, 1H), 7.64 (t, J = 7.1 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.28-7.24 (m, 2H), 7.20 (d, J = 7.2 Hz, 1H), 7.15-7.08 (m, 6H), 6.54 (s, 1H), 5.53 (s, 1H), 5.21 (s, 1H), 4.62-4.48 (m, 2H), 3.63 (s, 3H), 3.42-3.17 (m, 2H), 2.69 (t, J = 8.0 Hz, 2H), 2.45-2.29 (m, 4H), 2.09-2.01 (m, 1H), 1.99 (m, 3H), 1.92-1.83 (m, 1H), 1.44 (s, 9H), 0.99 (s, 3H), 0.92 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.8 (q, J = 3.8 Hz), 171.9, 171.6, 165.3, 155.6, 140.7, 138.0, 138.0, 132.8, 131.4, 130.5, 128.7, 128.5, 128.4, 128.0, 127.8, 126.3, 123.5 (q, J = 274 Hz), 122.8, 120.3, 119.2, 111.2, 110.2, 104.7, 101.6 (q, J = 33.7 Hz), 80.3, 79.6, 52.5, 51.7, 33.4, 31.7, 29.8, 28.4, 28.0, 26.8, 25.7, 15.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ= -63.94 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{44}H_{50}F_3N_3NaO_7S^+$, 844.3214; found, 844.3247. **IR** (KBr, cm^{-1}): ν 2926, 1714, 1496, 1295, 1166, 1116, 740.



7f

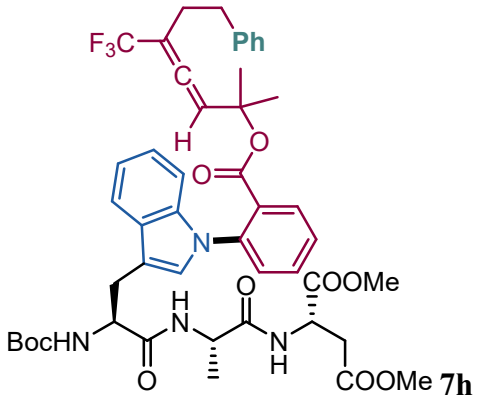
Faint yellow oil. 59.1 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.68 (s, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.51-7.39 (m, 4H), 7.13-7.02 (m, 4H), 6.57 (s, 1H), 5.53 (s, 1H), 5.22 (s, 1H), 4.59 (s, 1H), 4.48 (s, 1H), 4.38 (t, *J* = 6.5 Hz, 2H), 3.63 (s, 3H), 3.35-3.19 (m, 2H), 2.59 (td, *J* = 6.4, 2.7 Hz, 2H), 2.35 (s, 2H), 2.08-2.03 (m, 1H), 1.98 (s, 3H), 1.90-1.85 (m, 1H), 1.43 (s, 9H), 0.99 (s, 3H), 0.92 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.0 (q, *J* = 3.8 Hz), 171.9, 171.6, 166.4, 165.3, 155.6, 138.0, 137.9, 133.2, 132.8, 131.4, 130.4, 130.0, 129.7, 128.6, 128.5, 128.0, 127.8, 123.3 (q, *J* = 274 Hz), 122.8, 120.3, 119.1, 111.2, 110.2, 105.0, 98.5 (q, *J* = 34.6 Hz), 80.2, 79.3, 62.3, 62.3, 52.5, 51.7, 31.7, 28.8, 28.4, 26.9, 25.9, 25.5, 15.4. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.17 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{45}H_{50}F_3N_3NaO_9S^+$, 888.3112; found, 888.3152. **IR** (KBr, cm^{-1}): ν 3326, 2979, 1714, 1495, 1275, 1116, 738.



7g

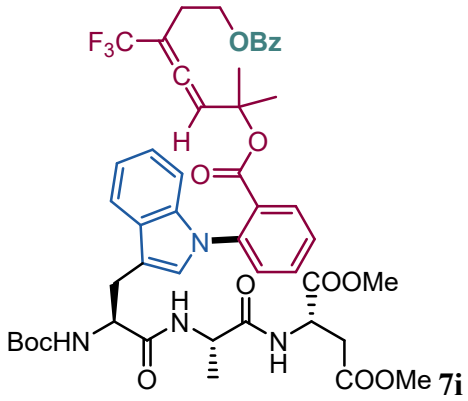
White solid. **m.p.**62.0-63.8 °C. 52.7 mg, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.0 Hz, 1H), 7.68 (s, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 6.9 Hz, 1H), 7.18-7.08 (m, 3H), 7.07-7.00 (m, 1H), 6.91 (s, 1H), 5.17 (s, 1H), 4.77-4.69 (m, 1H), 4.47-4.38 (m, 2H), 3.72 (s, 3H), 3.67 (s, 3H), 3.50 (t, *J* = 5.4

Hz, 2H), 3.38-3.21 (m, 2H), 3.04 -2.65 (m, 2H), 2.31-2.18 (m, 2H), 1.90-1.81 (m, 2H), 1.40 (s, 9H), 1.27 (d, J = 6.8 Hz, 3H), 1.00 (s, 3H), 0.93 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.4 (q, J = 3.7 Hz), 171.8, 171.5, 171.3, 170.9, 165.3, 155.6, 138.0, 138.0, 132.9, 131.3, 130.4, 128.7, 128.2, 128.0, 127.8, 123.4 (q, J = 274 Hz), 122.8, 120.3, 119.3, 111.2, 110.2, 104.9, 101.0 (q, J = 34.1 Hz), 80.3, 79.4, 52.9, 52.2, 49.0, 48.6, 44.0, 36.0, 30.0, 28.3, 27.2, 25.5, 23.7, 18.5. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.15 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{42}H_{50}ClF_3N_4NaO_{10}^+$, 885.3060; found, 885.3110. **IR** (KBr, cm^{-1}): ν 3306, 2980, 1714, 1648, 1496, 1293, 1117, 741.



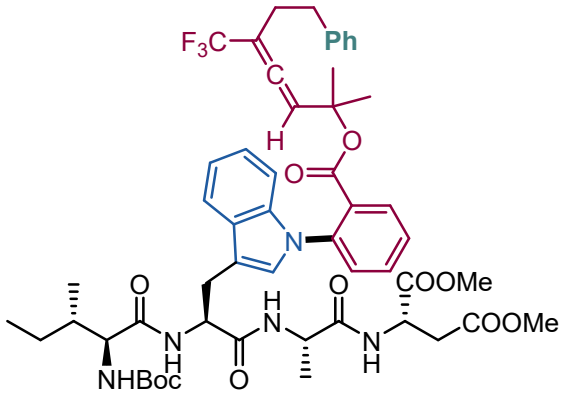
7h

White solid. **m.p.** 57.1-58.2 °C. 64.4 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 1H), 7. 68 (s, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.51-7.45 (m, 2H), 7.24-7.24 (m, 2H), 7.19 (d, J = 7.0 Hz, 1H), 7.15-7.05 (m, 6H), 7.00-6.96 (m, 1H), 6.58 (s, 1H), 5.52 (s, 1H), 5.21 (s, 1H), 4.78-4.73 (m, 1H), 4.48-4.41 (m, 2H), 3.73 (s, 3H), 3.68 (s, 3H), 3.38-3.22 (m, 2H), 2.96 (dd, J = 17.1, 4.2 Hz, 1H), 2.76 (dd, J = 17.2, 4.7 Hz, 1H), 2.69 (t, J = 7.9 Hz, 2H), 2.45-2.33 (m, 2H), 1.41 (s, 9H), 1.28 (d, J = 6.7 Hz, 3H), 0.99 (s, 3H), 0.92 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.7 (q, J = 3.9 Hz), 172.0, 171.7, 171.3, 171.0, 165.3, 155.7, 140.7, 138.1, 138.0, 132.8, 131.3, 130.5, 128.7, 128.5, 128.4, 128.0, 127.8, 126.3, 123.5 (q, J = 274 Hz), 122.8, 120.2, 119.3, 111.4, 110.2, 104.7, 101.5 (q, J = 33.9 Hz), 80.1, 79.5, 52.8, 52.1, 49.0, 48.7, 36.1, 33.4, 28.4, 28.0, 26.8, 25.7, 18.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -63.93 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{47}H_{53}F_3N_4NaO_{10}^+$, 913.3606; found, 913.3637. **IR** (KBr, cm^{-1}): ν 3302, 2932, 1715, 1648, 1496, 1294, 1167, 1117, 736.



7i

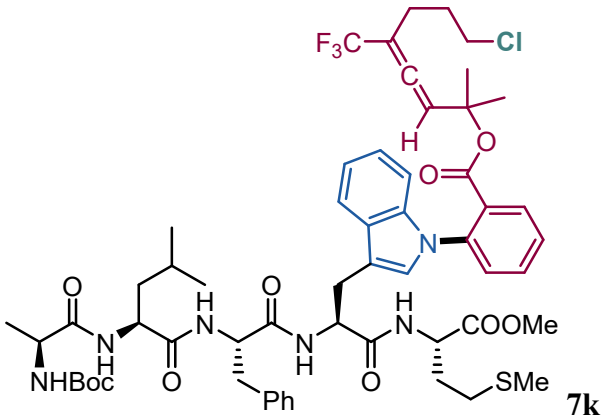
White solid. **m.p.** 53.8-55.3 ℃. 57.1 mg, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.67 (s, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.44-7.40 (m, 3H), 7.16-7.00 (m, 4H), 6.98 (s, 1H), 6.61 (s, 1H), 5.54 (s, 1H), 5.22 (s, 1H), 4.77-4.73 (m, 1H), 4.48-4.42 (m, 2H), 4.37 (t, *J* = 6.5 Hz, 2H), 3.73 (s, 3H), 3.67 (s, 3H), 3.36-3.20 (m, 2H), 2.96 (dd, *J* = 17.2, 3.9 Hz, 1H), 2.75 (dd, *J* = 17.1, 4.6 Hz, 1H), 2.59 (td, *J* = 6.2, 2.6 Hz, 2H), 1.41 (s, 9H), 1.27 (d, *J* = 6.4 Hz, 3H), 0.99 (s, 3H), 0.92 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.0 (q, *J* = 3.3 Hz), 171.9, 171.6, 171.3, 171.0, 166.3, 165.3, 155.7, 138.0, 137.9, 133.2, 132.9, 131.4, 130.4, 130.0, 129.7, 128.7, 128.5, 128.0, 127.8, 123.3 (q, *J* = 273 Hz), 122.8, 120.2, 119.2, 111.3, 110.2, 105.0, 98.5 (q, *J* = 34.8 Hz), 80.1, 79.2, 62.3, 62.3, 52.8, 52.1, 49.0, 48.7, 36.0, 28.3, 26.9, 25.9, 25.4, 18.7. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.17 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{48}H_{53}F_3N_4NaO_{12}^+$, 957.3504; found, 957.3546. **IR** (KBr, cm^{-1}): ν 3304, 2980, 1721, 1649, 1496, 1275, 1117, 736.



7j

White solid. **m.p.** 108.5-109.0 ℃. 67.3 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 4.7 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.51 (t, *J* =

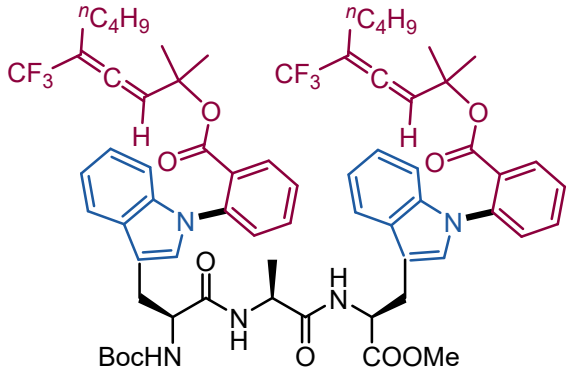
7.5 Hz, 1H), 7.40 (s, 1H), 7.28-7.24 (m, 2H), 7.20-7.13 (m, 7H), 7.07-6.98 (m, 2H), 6.83 (d, J = 6.3 Hz, 1H), 5.49 (s, 1H), 4.87-4.82 (m, 2H), 4.71 (dd, J = 11.2, 5.9 Hz, 1H), 4.58-4.52 (m, 1H), 3.92 (t, J = 4.7 Hz, 1H), 3.74 (s, 3H), 3.66 (s, 3H), 3.43 (dd, J = 14.6, 5.5 Hz, 1H), 3.26 (dd, J = 14.6, 6.0 Hz, 1H), 2.93 (dd, J = 16.9, 5.7 Hz, 1H), 2.85 (dd, J = 16.7, 4.9 Hz, 1H), 2.68 (t, J = 8.0 Hz, 2H), 2.44-2.37 (m, 2H), 1.87-1.81 (m, 1H), 1.36-1.16 (m, 14H), 0.99 (s, 3H), 0.92 (s, 3H), 0.87-0.82 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.7 (q, J = 4.0 Hz), 172.1, 172.1, 171.2, 171.1, 170.1, 165.2, 156.3, 140.6, 138.0, 137.9, 132.9, 131.4, 130.5, 128.5, 128.4, 128.1, 127.8, 126.3, 123.5 (q, J = 274 Hz), 123.0, 120.4, 118.9, 111.0, 110.4, 104.6, 101.6 (q, J = 34.0 Hz), 80.3, 79.6, 60.1, 52.8, 52.0, 49.0, 48.8, 37.1, 36.2, 33.4, 29.8, 28.2, 28.0, 26.7, 25.6, 24.7, 18.2, 15.7, 11.7. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -63.96 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{53}H_{64}F_3N_5NaO_{11}^+$, 1026.4447; found, 1026.4484. **IR** (KBr, cm^{-1}): ν 3254, 2931, 1711, 1496, 1633, 1293, 1116, 910, 736.



7k

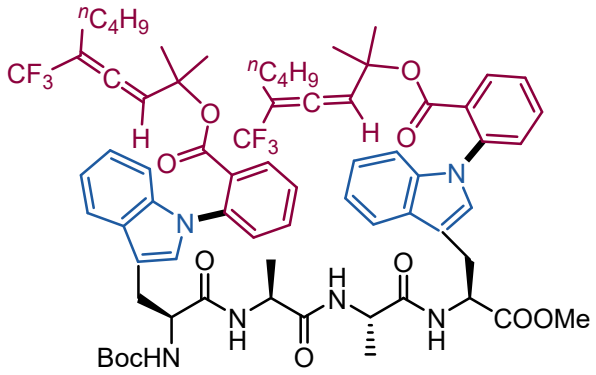
White solid. **m.p.** over 200 ℃. 68.1 mg, 58% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.6 Hz, 1H), 7.64 (s, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.49-7.42 (m, 2H), 7.15-7.11 (m, 7H), 7.06-7.00 (m, 5H), 6.92 (s, 1H), 6.68 (s, 1H), 4.95-4.90 (m, 2H), 4.63-4.61 (m, 2H), 4.12-4.07 (m, 1H), 3.75 (s, 1H), 3.68 (s, 3H), 3.52-3.46 (m, 3H), 3.35-3.08 (m, 2H), 2.88-2.86 (m, 1H), 2.51-2.44 (m, 2H), 2.27-2.23 (m, 2H), 2.19-2.08 (m, 1H), 2.04 (s, 3H), 1.89-1.84 (m, 2H), 1.60-1.45 (m, 2H), 1.36 (s, 9H), 1.28-1.19 (m, 5H), 1.01-0.97 (m, 6H), 0.86 (d, J = 6.2 Hz, 3H), 0.81 (d, J = 6.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.4 (q, J = 3.1 Hz), 173.8, 172.7, 172.0, 171.3,

171.0, 165.4, 156.2, 138.1, 137.9, 136.7, 132.8, 131.2, 130.5, 128.9, 128.7, 128.6, 128.4, 127.8, 126.9, 123.4 (q, J = 274 Hz), 122.6, 120.1, 119.2, 110.1, 104.9, 101.0 (q, J = 33.3 Hz), 80.9, 79.4, 52.5, 52.4, 51.8, 44.1, 44.0, 40.6, 31.6, 30.0, 30.0, 29.8, 28.3, 27.1, 25.4, 24.9, 23.7, 22.9, 22.0, 15.3. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.14 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{57}H_{72}ClF_3N_6NaO_{10}S^+$, 665.2809; found, 665.2804. **IR** (KBr, cm^{-1}): ν 3273, 2927, 1711, 1632, 1496, 1293, 1117, 738.



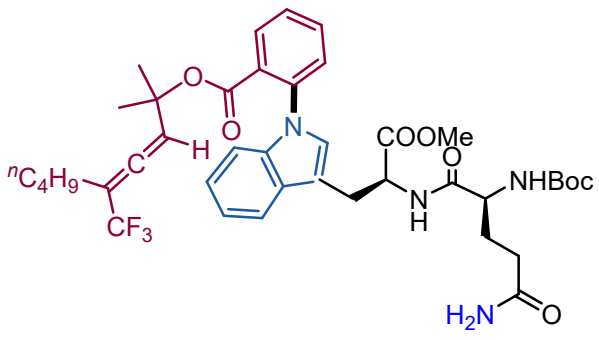
9

Faint yellow solid. **m.p.** 69.0-70.0 ℃. 75.4 mg, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 2H), 7.66-7.60 (m, 3H), 7.54-7.46 (m, 5H), 7.13-7.10 (m, 5H), 7.06-7.04 (m, 3H), 6.61-6.47 (m, 2H), 5.57 (s, 2H), 5.16 (s, 1H), 4.84 (dd, J = 12.2, 5.8 Hz, 1H), 4.41-4.36 (m, 2H), 4.30 (m, 1H), 3.68 (s, 3H), 3.31-3.10 (m, 4H), 2.10-2.05 (m, 4H), 1.41 (s, 9H), 1.36-1.31 (m, 8H), 1.20 (d, J = 4.9 Hz, 3H), 1.02 (s, 6H), 0.97 (s, 6H), 0.86 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, J = 3.8 Hz), 172.1, 171.6, 171.5, 165.3, 165.2, 155.5, 138.0, 137.9, 132.8, 131.3, 131.3, 130.6, 130.6, 128.8, 128.1, 128.0, 127.9, 127.9, 123.6 (q, J = 272 Hz), 122.8, 122.8, 120.3, 120.3, 119.2, 118.8, 111.1, 110.3, 110.2, 104.3, 104.2, 102.2 (q, J = 33.3 Hz), 80.2, 79.8, 79.6, 53.0, 52.5, 49.0, 29.4, 28.4, 27.6, 26.7, 26.0, 25.9, 22.2, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.07 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{67}H_{75}F_6N_5NaO_{10}^+$, 1246.5310; found, 1246.5324. **IR** (KBr, cm^{-1}): ν 3307, 2932, 1715, 1646, 1496, 1292, 1116, 741.



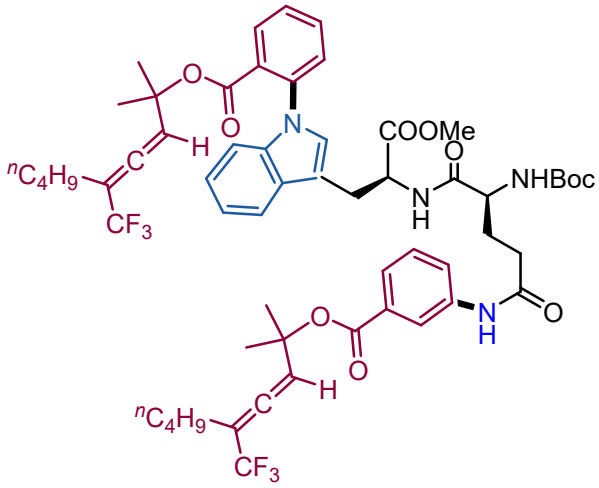
11

Faint yellow solid. **m.p.** 91.0-92.2 ℃. 75.7 mg, 57% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.62-7.56 (m, 4H), 7.50-7.40 (m, 4H), 7.16-7.04 (m, 8H), 6.93 (s, 2H), 6.40 (s, 1H), 5.60-5.70 (m, 2H), 5.18-5.15 (m, 1H), 4.91 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.39-4.37 (m, 1H), 4.30 (m, 1H), 4.26-4.24 (m,1H), 3.71 (s, 3H), 3.45-3.36 (m, 2H), 3.27-3.17 (m, 2H), 2.10-2.05 (m, 4H), 1.38 (s, 9H), 1.36-1.26 (m, 14H), 1.12 (s, 6H), 1.00 (s, 6H), 0.86 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 3.4 Hz), 200.6 (q, *J* = 4.0 Hz), 172.2, 172.2, 172.0, 171.7, 165.4, 165.1, 156.0, 138.1, 138.0, 137.9, 137.8, 132.9, 132.7, 131.4, 131.2, 130.6, 130.4, 128.7, 128.6, 128.4, 128.1, 128.0, 127.9, 127.8, 127.6, 123.6 (q, *J* = 272 Hz), 123.6 (q, *J* = 272 Hz), 123.0, 122.7, 120.4, 120.2, 119.1, 119.0, 111.2, 110.7, 110.3, 110.2, 104.3, 104.2, 102.4 (q, *J* = 34.0 Hz), 102.2 (q, *J* = 33.2 Hz), 80.8, 79.8, 79.8, 55.6, 53.1, 52.5, 49.6, 49.2, 29.4, 28.3, 27.6, 26.8, 26.0, 25.9, 22.2, 17.7, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.05 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{70}H_{80}F_6N_6NaO_{11}^+$, 1317.5681; found, 1317.5692. **IR** (KBr, cm^{-1}): ν 3287, 2932, 1714, 1634, 1497, 1292, 1116, 738.



13

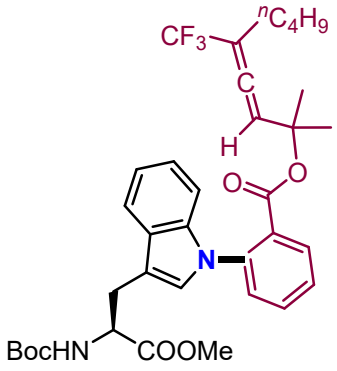
Faint yellow solid. **m.p. 60.3-61.2** ℃. 48.0 mg, 61% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.7, Hz, 1H), 7.59-7.57 (m, 1H), 7.47 (dd, *J* = 16.1, 7.9 Hz, 2H), 7.17-7.10 (m, 4H), 7.08-7.03 (m, 1H), 6.30 (s, 1H), 5.73 (s, 1H), 5.60-5.49 (m, 2H), 4.98-4.85 (m, 1H), 4.17 (s, 1H) , 3.72 (s, 3H), 3.36-3.33 (m, 2H), 2.36-2.22 (m, 2H)，2.15-2.06 (m, 2H), 2.06-1.97 (m, 2H), 1.96-1.90 (m, 2H), 1.37 (s, 3H), 1.33-1.28 (m, 4H), 1.02 (s, 2H), 0.97 (s, 3H), 0.87 (t, *J* = 7.0, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, *J* = 3.9 Hz), 175.6, 172.7, 171.7, 165.4, 155.8, 137.9, 137.8, 132.7, 131.2, 128.8, 128.2, 127.9, 127.6, 122.6 (q, *J* = 272 Hz), 122.8, 120.2, 118.8, 110.7, 110.3, 104.2, 102.2 (q, *J* = 33.5 Hz), 80.1, 79.8, 53.4, 53.1, 52.6, 31.7, 29.8, 29.4, 28.3, 27.6, 26.7, 26.0, 25.8, 22.2, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.06 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{40}H_{49}F_3N_4NaO_8^+$, 793.3395; found, 793.3398. **IR** (KBr, cm^{-1}): ν 3428, 2928, 1713, 1665, 1496, 1116, 742.



15

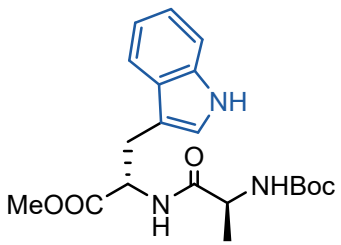
Faint yellow solid. **m.p.** 51.0-51.8 ℃. 32.7 mg, 29% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.11 (s, 1H), 8.59 (d, *J* = 8.3 Hz, 1H), 7.94 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.88 (d, *J* = 7.4 Hz, 1H), 7.60-7.53 (m, 2H), 7.58-7.39 (m, 3H), 7.35 (d, *J* = 5.8 Hz, 1H), 7.15 (s, 1H), 7.14-7.09 (m, 2H), 7.06-7.01 (m, 2H), 6.17 (dd, *J* = 6.4, 3.2 Hz, 1H), 5.50 (s, 2H), 4.92 (dd, *J* = 13.1, 6.5 Hz, 1H), 4.27 (d, *J* = 4.6 Hz, 1H), 3.68 (s, 3H), 3.46-3.33 (m, 2H), 2.66-2.52 (m, 2H), 2.18-2.13 (m, 3H), 2.08-2.01 (m, 3H), 1.69 (d, *J* = 4.6 Hz, 6H), 1.42 (dd, *J* = 14.9, 7.6 Hz, 2H), 1.37-1.26 (m, 15H), 0.97 (s, 3H), 0.93 (s, 3H), 0.87-0.82 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.0 (q, *J* = 4.2 Hz), 200.6 (q, *J* = 3.8 Hz), 172.2, 171.8, 171.6, 167.3, 165.4, 155.6, 141.5, 138.0, 137.9,

134.5, 132.8, 131.2, 131.0, 130.6, 128.9, 128.2, 127.9, 127.7, 127.6, 123.6 (q, J = 272 Hz), 122.7, 122.6, 120.6, 120.2, 118.9, 115.9, 110.6, 110.3, 104.6, 104.3, 102.9 (q, J = 33.7 Hz), 102.2 (q, J = 33.3 Hz), 80.5, 79.9, 79.7, 53.7, 53.1, 52.5, 34.3, 29.5, 29.4, 28.8, 28.3, 27.7, 27.6, 27.5, 27.0, 26.9, 26.7, 26.1, 26.0, 25.8, 22.2, 22.2,13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.09 (d, J = 11.1 Hz). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{58}H_{68}F_6N_4NaO_{10}^+$, 1117.4732; found, 1117.4728. **IR** (KBr, cm^{-1}): ν 3310, 2932, 1712, 1686, 1524, 1256, 1118, 742.



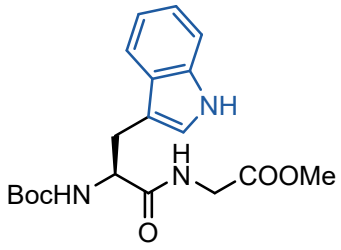
16

Yellow oil. 48.8 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 1H), 7.66-7.57 (m, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.17-7.11 (m, 2H), 7.09-7.06 (m, 2H), 5.57 (s, 1H), 5.15 (d, J = 7.9 Hz, 1H), 4.70 (dd, J = 12.6, 5.2 Hz, 1H), 3.72 (s, 3H), 3.43-3.27 (m, 2H), 2.12-2.03 (m, 2H), 1.42 (s, 9H), 1.00 (s, 3H), 0.95 (s, 3H), 0.87 (t, J = 7.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.6 (q, J = 3.9 Hz), 172.8, 165.4, 155.4, 138.0, 137.9, 132.8, 131.4, 130.6, 128.6, 128.5, 128.0, 127.3, 123.7 (q, J = 272 Hz), 122.8, 120.2, 119.0, 111.0, 110.3, 104.3, 102.2 (q, J = 33.6 Hz), 79.9, 79.7, 54.2, 52.4, 29.4, 28.4, 27.9, 26.8, 26.0, 25.8, 22.2, 13.8. **^{19}F NMR (**376 MHz, $CDCl_3$**)** δ= -64.08 (s). **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{35}H_{41}F_3N_2NaO_6^+$, 665.2809; found, 665.2804. **IR** (KBr, cm^{-1}): ν 2960, 1716, 1496, 1463, 1293, 1157, 1117, 743.



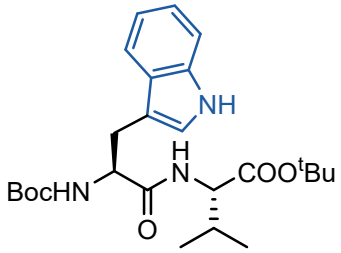
SM-3a

Yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.11 (dt, *J* = 26.6, 7.4 Hz, 2H), 6.96 (s, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 5.11 (d, *J* = 7.8 Hz, 1H), 4.87 (q, *J* = 6.0 Hz, 1H), 4.23-4.08 (m, 1H), 3.62 (s, 3H), 3.29 (d, *J* = 5.4 Hz, 2H), 1.40 (s, 9H), 1.27 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 172.3, 155.5, 136.2, 127.6, 123.3, 122.2, 119.6, 118.5, 111.5, 109.6, 80.1, 76.9, 53.1, 52.5, 50.2, 28.4, 27.6, 18.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{20}H_{27}N_3NaO_5^+$, 412.1843; found, 412.1849.



SM-3b

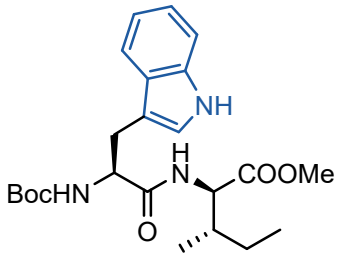
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.07 (dd, *J* = 16.6, 9.4 Hz, 2H), 6.52 (t, *J* = 5.4 Hz, 1H), 5.25 (d, *J* = 8.0 Hz, 1H), 4.50 (d, *J* = 7.2 Hz, 1H), 3.86 (t, *J* = 5.8 Hz, 2H), 3.64 (s, 3H), 3.33-3.14 (m, 2H), 1.40 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 169.9, 155.5, 136.1, 127.4, 123.4, 121.9, 119.3, 118.5, 111.2, 109.9, 80.1, 55.0, 52.2, 41.0, 28.1. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{19}H_{25}N_3NaO_5^+$, 398.1686; found, 398.1681.



SM-3c

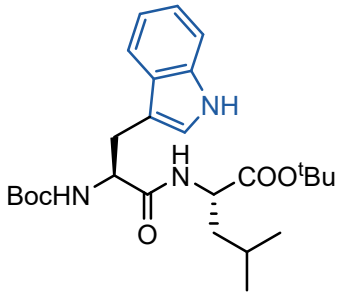
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.02 (s, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 5.19 (d, *J* = 7.8 Hz, 1H), 4.48 (q, *J* = 7.4, 6.8 Hz, 1H), 4.33 (dd, *J* = 8.6, 4.6 Hz, 1H), 3.24 (q, *J* = 14.4, 10.8 Hz, 2H), 2.05 (dd, *J* = 12.2, 6.4 Hz, 1H), 1.41 (s, 18H), 0.80 (dd, *J* = 7.0, 2.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

171.5, 170.4, 155.4, 136.1, 127.4, 123.3, 121.9, 119.3, 118.6, 111.2, 110.1, 81.8, 79.9, 57.5, 55.1, 31.2, 28.2, 27.9, 18.5, 17.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{37}N_3NaO_5^+$, 482.2625; found, 482.2625.



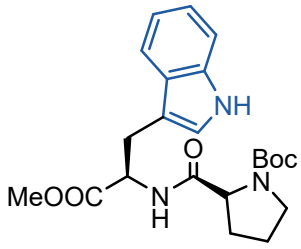
SM-3d

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.02 (s, 1H), 6.47 (d, *J* = 8.4 Hz, 1H), 5.30 (d, *J* = 7.6 Hz, 1H), 4.53-4.41 (m, 2H), 3.58 (s, 3H), 3.33-3.13 (m, 2H), 1.72 (d, *J* = 7.6 Hz, 1H), 1.42 (s, 9H), 1.34-1.22 (m, 1H), 1.08-0.93 (m, 1H), 0.81 (t, *J* = 7.4 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 155.4, 136.1, 127.3, 123.3, 121.8, 119.3, 118.5, 111.2, 109.9, 79.9, 56.4, 55.1, 51.8, 37.6, 28.1, 24.9, 15.0, 11.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{33}N_3NaO_5^+$, 454.2312; found, 454.2309.



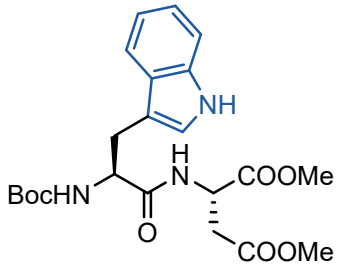
SM-3e

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.00 (s, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 5.24 (d, *J* = 8.0 Hz, 1H), 4.59-4.36 (m, 2H), 3.24 (s, 2H), 1.60-1.47 (m, 2H), 1.40 (s, 19H), 0.85 (d, *J* = 5.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 171.4, 155.4, 136.1, 127.4, 123.3, 121.8, 119.2, 118.6, 111.2, 109.9, 81.6, 79.8, 54.9, 51.4, 41.5, 28.1, 27.8, 24.5, 22.5, 22.0. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{26}H_{39}N_3NaO_5^+$, 496.2782; found, 496.2786.



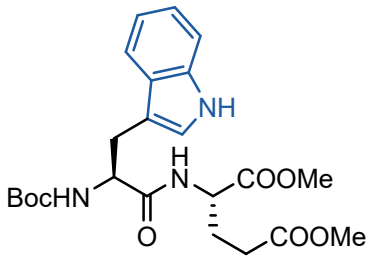
SM-3f

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.30 (d, *J* = 39.2 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 13.0 Hz, 1H), 6.57 (d, *J* = 8.2 Hz, 1H), 4.86 (d, *J* = 8.0 Hz, 1H), 4.31-4.06 (m, 1H), 3.60 (d, *J* = 32.0 Hz, 3H), 3.33-3.10 (m, 4H), 1.91 (d, *J* = 40.8 Hz, 2H), 1.76-1.41 (m, 2H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 172.0, 171.9, 171.8, 155.0, 154.2, 136.0, 127.3, 127.1, 123.0, 122.8, 121.6, 121.4, 119.0, 118.8, 117.9, 117.7, 111.3, 108.9, 108.7, 80.3, 79.9, 60.6, 59.8, 53.0, 52.5, 51.9, 50.0, 46.7, 46.4, 30.4, 28.5, 27.9, 27.7, 27.4, 27.2, 24.0, 23.0. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{22}H_{29}N_3NaO_5^+$, 438.1999; found, 438.1996.



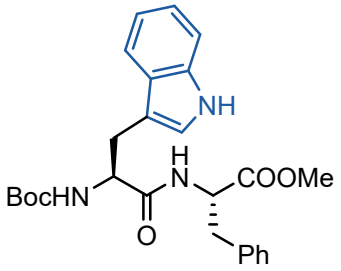
SM-3g

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.02 (s, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 5.31 (d, *J* = 7.4 Hz, 1H), 4.80 (d, *J* = 4.6 Hz, 1H), 4.50 (d, *J* = 7.4 Hz, 1H), 3.62 (s, 3H), 3.54 (s, 3H), 3.35-3.13 (m, 2H), 2.79 (dd, *J* = 17.4, 4.6 Hz, 1H), 2.35 (dd, *J* = 17.4, 5.0 Hz, 1H), 1.41 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.5, 171.1, 170.8, 155.3, 136.1, 127.3, 123.1, 121.9, 119.4, 118.5, 111.2, 110.0, 79.9, 55.2, 52.6, 51.8, 47.9, 35.4, 28.1. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{22}H_{29}N_3NaO_7^+$, 470.1898; found, 470.1895.



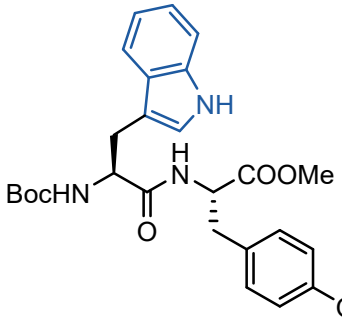
SM-3h

White solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.13-7.02 (m, 2H), 6.55 (s, 1H), 5.21 (d, *J* = 7.4 Hz, 1H), 4.58-4.42 (m, 2H), 3.62 (s, 6H), 3.32 (dd, *J* = 15.4, 5.4 Hz, 1H), 3.21-3.14 (m, 1H), 2.27-2.02 (m, 3H), 1.89-1.80 (m, 1H), 1.43 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1, 171.7, 171.5, 155.4, 136.1, 127.4, 123.3, 122.0, 119.5, 118.6, 111.2, 110.0, 80.1, 55.3, 52.4, 51.7, 51.5, 29.5, 28.2, 28.0, 27.2. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{31}N_3NaO_7^+$, 484.2054; found, 484.2056.



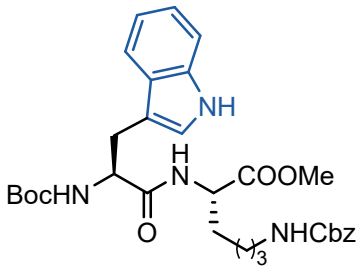
SM-3i

White solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.22-7.08 (m, 5H), 6.98 (s, 1H), 6.79 (d, *J* = 7.4 Hz, 2H), 6.27 (d, *J* = 7.4 Hz, 1H), 5.22-5.12 (m, 1H), 4.72 (q, *J* = 6.4 Hz, 1H), 4.52-4.41 (m, 1H), 3.58 (s, 3H), 3.30 (d, *J* = 17.4 Hz, 1H), 3.16-3.10 (m, 1H), 2.92 (d, *J* = 6.0 Hz, 2H), 1.41 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 155.3, 136.2, 135.5, 129.0, 128.4, 127.3, 126.9, 123.3, 122.1, 119.5, 118.7, 111.2, 110.1, 80.0, 55.1, 53.1, 52.1, 37.7, 28.2. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{26}H_{31}N_3NaO_5^+$, 488.2156; found, 488.2152.



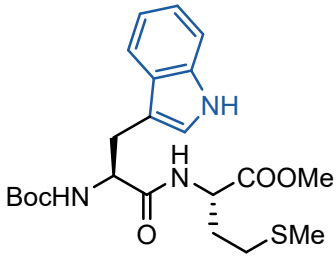
SM-3j

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.19-7.07 (m, 2H), 6.93-6.71 (m, 5H), 6.25 (d, *J* = 8.0 Hz, 1H), 5.33-5.20 (m, 1H), 4.79 (q, *J* = 6.0 Hz, 1H), 4.48 (s, 1H), 3.63 (s, 3H), 3.38-3.28 (m, 1H), 3.10-2.98 (m, 1H), 2.98-2.85 (m, 2H), 2.32 (s, 3H), 1.44 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 171.4, 170.4, 155.5, 149.6, 136.3, 133.6, 130.2, 127.4, 123.6, 122.1, 121.8, 119.6, 118.9, 111.4, 109.9, 80.1, 55.0, 52.9, 52.4, 37.0, 28.5, 28.4, 21.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{28}H_{33}N_3NaO_7^+$, 546.2211; found, 546.2210.



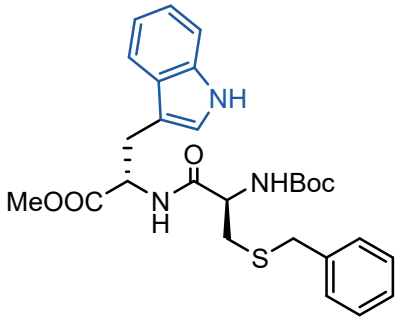
SM-3k

White solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.42-7.29 (m, 6H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 6.62-6.54 (m, 1H), 5.22-5.13 (m, 2H), 5.10 (d, *J* = 12.2 Hz, 1H), 4.61-4.43 (m, 2H), 3.63 (s, 3H), 3.49-3.38 (m, 1H), 3.19-3.07 (m, 2H), 3.05-2.96 (m, 1H), 1.77 (s, 1H), 1.66-1.48 (m, 2H), 1.44 (s, 10H), 1.39-1.32 (m, 1H), 1.22 (t, *J* = 7.0 Hz, 1H), 1.02-0.91 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 171.4, 156.8, 155.4, 136.4, 136.2, 128.5, 128.1, 127.6, 123.6, 121.8, 119.5, 118.4, 111.5, 109.4, 80.2, 66.8, 55.5, 52.3, 51.9, 40.8, 31.6, 29.60, 28.2, 27.6, 21.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{31}H_{40}N_4NaO_7^+$, 603.2789; found, 603.2801.



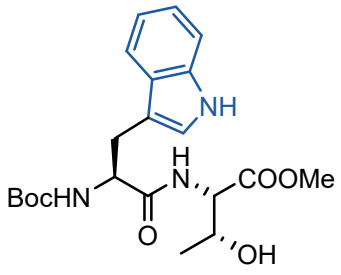
SM-3l

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.02 (s, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 5.26 (d, *J* = 7.8 Hz, 1H), 4.56 (q, *J* = 6.6 Hz, 1H), 4.46 (q, *J* = 7.0 Hz, 1H), 3.60 (s, 3H), 3.34-3.25 (m, 1H), 3.21-3.11 (m, 1H), 2.24 (t, *J* = 7.8 Hz, 2H), 1.95 (s, 4H), 1.88-1.75 (m, 1H), 1.42 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 155.4, 136.1, 127.3, 123.3, 121.9, 119.4, 118.5, 111.17, 109.8, 80.0, 55.1, 52.3, 51.4, 31.1, 29.3, 28.1, 27.9, 15.1. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{22}H_{31}N_3NaO_5S^+$, 472.1877; found, 472.1869.



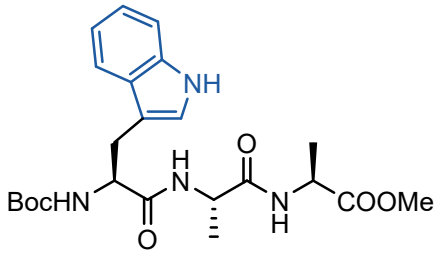
SM-3m

White solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 4.8 Hz, 4H), 7.23 (q, *J* = 4.0 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 2.6 Hz, 1H), 6.83 (d, *J* = 5.8 Hz, 1H), 5.25-5.16 (m, 1H), 4.91-4.87 (m, 1H), 4.21 (s, 1H), 3.66 (s, 3H), 3.33 (d, *J* = 5.6 Hz, 3H), 2.76 (s, 1H), 2.72-2.66 (m, 1H), 1.58 (s, 2H), 1.42 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.8, 170.2, 137.9, 136.1, 129.0, 128.6, 127.6, 127.2, 122.9, 122.3, 119.7, 118.6, 111.3, 109.9, 80.2, 53.7, 53.1, 52.4, 36.4, 33.7, 28.2, 27.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{27}H_{33}N_3NaO_5S^+$, 534.2033; found, 534.2032.



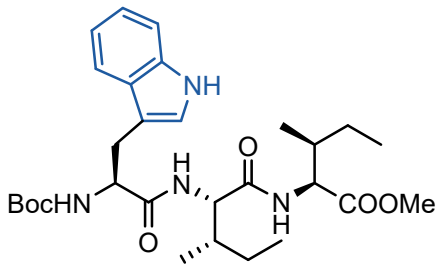
SM-3n

White solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.05 (s, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 5.40 (d, *J* = 8.0 Hz, 1H), 4.52 (d, *J* = 8.8 Hz, 2H), 4.25-4.17 (m, 1H), 3.59 (s, 3H), 3.24 (t, *J* = 6.2 Hz, 2H), 1.40 (s, 9H), 1.06 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 171.0, 155.7, 136.1, 127.5, 123.4, 121.8, 119.3, 118.6, 111.2, 109.9, 80.2, 68.0, 57.5, 55.3, 52.4, 28.2, 19.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{21}H_{29}N_3NaO_6^+$, 442.1949; found, 442.1945.



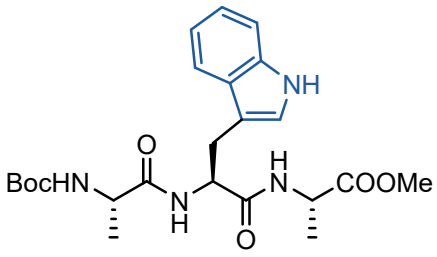
SM-4a

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.15 (q, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.03 (s, 1H), 6.75 (d, *J* = 7.4 Hz, 1H), 5.30 (d, *J* = 7.4 Hz, 1H), 4.49 (p, *J* = 7.4 Hz, 2H), 4.44-4.37 (m, 1H), 3.70 (s, 3H), 3.32-3.17 (m, 2H), 1.41 (s, 9H), 1.30 (d, J = 7.4 Hz, 3H), 1.23 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, DMSO-D_6) δ 173.4, 172.6, 172.0, 155.7, 136.5, 127.9, 124.2, 121.3, 119.0, 118.6, 111.7, 110.7, 79.7, 78.6, 55.6, 52.4, 48.2, 48.0, 28.6, 28.1, 18.9, 17.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{32}N_4NaO_6^+$, 483.2214; found, 483.2207.



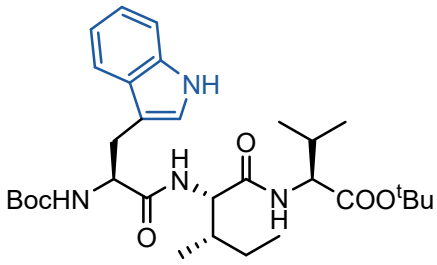
SM-4b

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.70 (d, *J* = 8.6 Hz, 1H), 5.30 (d, *J* = 7.6 Hz, 1H), 4.55-4.45 (m, 2H), 4.34 (t, *J* = 7.6 Hz, 1H), 3.68 (s, 3H), 3.30-3.16 (m, 2H), 1.81 (t, *J* = 7.4 Hz, 2H), 1.38 (s, 11H), 1.21-1.07 (m, 1H), 1.04-0.92 (m, 1H), 0.91-0.72 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 172.0, 171.0, 155.8, 136.4, 127.6, 123.4, 122.2, 119.6, 118.9, 111.4, 110.3, 80.2, 58.1, 56.7, 55.3, 52.1, 37.6, 37.1, 28.3, 27.8, 25.3, 24.9, 15.5, 15.2, 11.6, 11.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{29}H_{44}N_4NaO_6^+$, 567.3153; found, 567.3167.



SM-4c

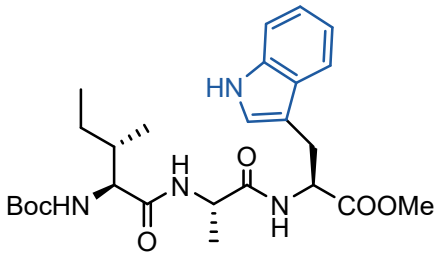
White solid. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 10.85 (s, 1H), 8.44 (d, *J* = 7.4 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.97 (q, *J* = 7.6 Hz, 2H), 4.57 (q, *J* = 8.2 Hz, 1H), 4.35-4.24 (m, 1H), 4.00-3.89 (m, 1H), 3.61 (s, 3H), 3.18-3.09 (m, 1H), 2.97 (dd, *J* = 15.0, 8.0 Hz, 1H), 1.36 (s, 9H), 1.27 (d, *J* = 7.4 Hz, 3H), 1.12 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-D_6) δ 173.4, 173.0, 171.8, 155.6, 136.6, 128.0, 124.2, 121.4, 119.0, 118.7, 111.8, 110.2, 78.7, 53.3, 52.4, 50.5, 48.2, 28.7, 28.3, 18.7, 17.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{32}N_4NaO_6^+$, 483.2214; found, 483.2208.



SM-4d

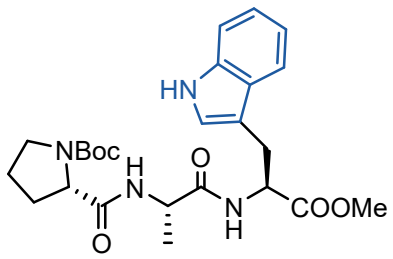
White solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H),

7.33 (d, J = 8.2 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 7.03 (s, 1H), 6.70 (d, J = 8.8 Hz, 1H), 6.65 (d, J = 8.4 Hz, 1H), 5.32 (d, J = 7.6 Hz, 1H), 4.50 (s, 1H), 4.39-4.31 (m, 2H), 3.24 (dt, J = 14.8, 7.2 Hz, 2H), 2.16-2.04 (m, 1H), 1.80 (s, 1H), 1.46 (s, 9H), 1.40 (s, 10H), 1.04-0.96 (m, 1H), 0.94-0.85 (m, 6H), 0.85-0.76 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 170.7, 170.6, 155.5, 136.2, 127.4, 123.2, 121.9, 119.4, 118.7, 111.2, 110.2, 81.8, 79.9, 58.0, 57.7, 55.1, 37.0, 31.1, 28.2, 27.9, 24.7, 18.8, 17.8, 15.1, 11.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{31}H_{48}N_4NaO_6^+$, 595.3466; found, 595.3473.



SM-4e

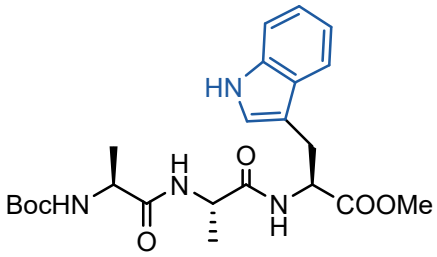
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.08-7.00 (m, 2H), 6.95 (s, 1H), 6.88 (d, J = 7.6 Hz, 1H), 5.31 (d, J = 8.8 Hz, 1H), 4.85 (q, J = 6.0 Hz, 1H), 4.50 (t, J = 7.2 Hz, 1H), 4.02-3.93 (m, 1H), 3.62 (s, 3H), 3.24 (t, J = 5.4 Hz, 2H), 1.81-1.69 (m, 1H), 1.42 (s, 9H), 1.26 (d, J = 7.2 Hz, 3H), 1.08-0.99 (m, 1H), 0.90-0.74 (m, 7H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 172.0, 171.8, 156.1, 136.2, 127.5, 123.6, 122.0, 119.5, 118.4, 111.5, 109.3, 80.2, 59.5, 53.0, 52.5, 48.8, 37.3, 28.4, 27.6, 24.6, 18.3, 15.6, 11.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{26}H_{38}N_4NaO_6^+$, 525.2684; found, 525.2680.



SM-4f

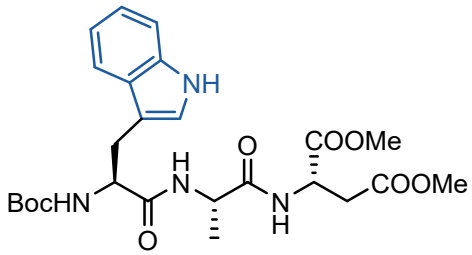
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, J = 41.8 Hz, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.21-7.08 (m, 2H), 7.07-6.97 (m, 1H), 6.93 (d, J =

11.0 Hz, 1H), 6.67 (dd, *J* = 17.2, 7.8 Hz, 1H), 4.95-4.77 (m, 1H), 4.52-4.34 (m, 1H), 4.20-4.03 (m, 1H), 3.64 (d, *J* = 6.8 Hz, 3H), 3.46-3.30 (m, 2H), 3.29-3.16 (m, 2H), 2.05 (d, *J* = 14.4 Hz, 1H), 1.97-1.72 (m, 3H), 1.43 (d, *J* = 23.0 Hz, 9H), 1.26 (d, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 171.9, 155.6, 136.0, 127.4, 123.3, 121.8, 119.3, 118.3, 111.3, 109.3, 80.5, 60.6, 60.0, 52.8, 52.3, 48.6, 47.2, 28.7, 28.3, 27.4, 24.4, 23.6, 18.7, 17.9. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{34}N_4NaO_6^+$, 509.2371; found, 509.2358.



SM-4g

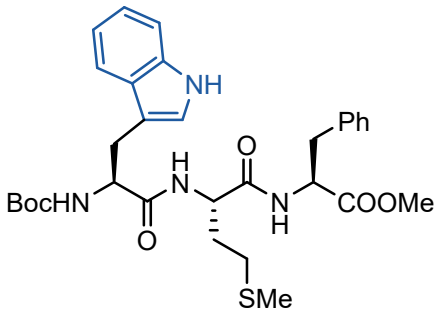
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 2H), 7.05 (dd, *J* = 15.0, 7.6 Hz, 3H), 6.95 (s, 1H), 5.37 (d, *J* = 7.8 Hz, 1H), 4.92-4.80 (m, 1H), 4.58-4.43 (m, 1H), 4.21-4.06 (m, 1H), 3.64 (s, 3H), 3.27 (d, *J* = 6.0 Hz, 2H), 1.43 (s, 10H), 1.26 (d, *J* = 7.4 Hz, 3H), 1.19 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 172.1, 171.9, 155.5, 136.0, 127.3, 123.4, 121.8, 119.3, 118.2, 111.4, 109.1, 80.2, 52.8, 52.4, 50.1, 48.7, 28.3, 27.3, 18.3, 18.1. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{23}H_{32}N_4NaO_6^+$, 483.2214; found, 483.2220.



SM-4h

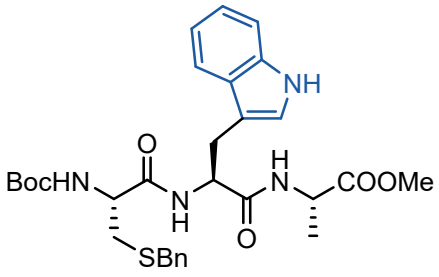
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.22-7.12 (m, 2H), 7.10-7.00 (m, 2H), 6.58 (d, *J* = 7.4 Hz, 1H), 5.31 (d, *J* = 7.6 Hz, 1H), 4.77-4.69 (m, 1H), 4.45 (p, *J* = 7.0 Hz, 2H), 3.70 (s, 3H), 3.66 (s, 3H), 3.33-3.23 (m, 1H), 3.18 (dd, *J* = 14.2, 6.8 Hz, 1H), 2.90 (dd, *J* =

17.4, 5.0 Hz, 1H), 2.83-2.73 (m, 1H), 1.39 (s, 9H), 1.21 (d, J = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 171.7, 171.4, 171.0, 155.7, 136.3, 127.6, 123.5, 122.2, 119.6, 118.9, 111.4, 110.3, 80.2, 76.9, 55.2, 52.9, 52.3, 49.0, 48.8, 36.0, 28.4, 18.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{34}N_4NaO_8^+$, 541.2269; found, 541.2264.



SM-4i

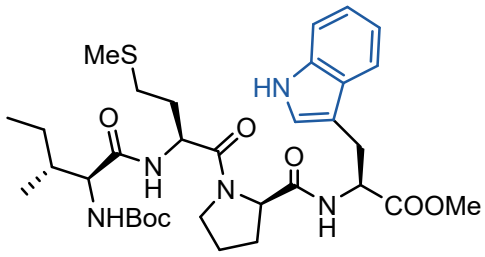
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 3.0 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.29-7.23 (m, 2H), 7.21 (d, *J* = 7.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 3H), 7.00-6.90 (m, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 5.30 (d, *J* = 7.2 Hz, 1H), 4.71 (q, *J* = 7.0 Hz, 1H), 4.53 (q, *J* = 6.8 Hz, 1H), 4.46 (q, *J* = 6.8 Hz, 1H), 3.64 (d, *J* = 3.4 Hz, 3H), 3.33-3.23 (m, 1H), 3.21-3.11 (m, 1H), 3.10-3.01 (m, 1H), 3.00-2.88 (m, 1H), 2.27 (t, *J* = 7.4 Hz, 2H), 1.89 (s, 3H), 1.86-1.70 (m, 2H), 1.41 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 171.8, 170.6, 155.7, 136.4, 136.0, 129.3, 128.8, 128.7, 127.5, 127.3, 123.5, 122.3, 119.7, 118.9, 111.5, 110.1, 80.3, 76.9, 55.4, 53.6, 52.5, 52.4, 37.8, 30.9, 29.6, 28.4, 28.22, 14.9. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{31}H_{40}N_4NaO_6S^+$, 619.2561; found, 619.2567.



SM-4j

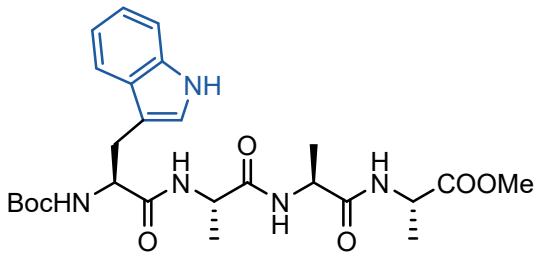
White solid. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 10.85 (d, *J* = 2.8 Hz, 1H), 8.48 (d, *J* = 7.0 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 4.6 Hz, 4H), 7.27-7.20 (m, 2H), 7.16 (d, *J* = 2.8 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.99 (d, *J* = 3.8 Hz, 1H), 6.96 (d, *J* = 7.4 Hz, 1H), 4.60 (q, *J* = 8.0 Hz, 1H), 4.32-4.23 (m, 1H), 4.22-4.14 (m, 1H), 3.72 (s, 2H),

3.60 (s, 3H), 3.18-3.08 (m, 1H), 3.02-2.92 (m, 1H), 2.73-2.63 (m, 1H), 2.49-2.44 (m, 1H), 1.39 (s, 9H), 1.24 (d, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-D_6) δ 173.4, 171.6, 170.8, 155.8, 138.9, 136.5, 129.4, 128.9, 127.9, 127.4, 124.2, 121.4, 119.0, 118.7, 111.8, 110.1, 78.9, 54.4, 53.5, 52.4, 48.2, 35.7, 34.2, 28.7, 28.4, 17.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{30}H_{38}N_4NaO_6S^+$, 605.2404; found, 605.2400.



SM-5a

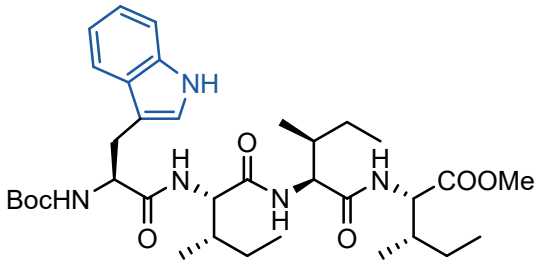
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.27 (s, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 6.92 (d, J = 2.4 Hz, 1H), 6.65 (d, J = 7.4 Hz, 1H), 5.35 (d, J = 9.2 Hz, 1H), 4.95-4.84 (m, 1H), 4.50-4.39 (m, 2H), 4.12-4.02 (m, 1H), 3.78 (s, 3H), 3.51-3.43 (m, 1H), 3.31-3.17 (m, 2H), 3.10 (t, J = 8.8 Hz, 1H), 2.49-2.28 (m, 3H), 2.04 (s, 3H), 2.02-1.95 (m, 1H), 1.86-1.69 (m, 7H), 1.47 (s, 9H), 1.17-1.05 (m, 1H), 0.97 (d, J = 7.0 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 170.9, 170.0, 169.9, 156.5, 135.8, 127.9, 122.6, 121.6, 118.9, 118.1, 111.3, 109.3, 80.4, 60.3, 58.8, 52.8, 52.5, 50.2, 46.8, 37.9, 31.1, 29.5, 27.2, 26.5, 24.4, 24.3, 15.8, 15.5, 11.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{33}H_{49}N_5NaO_7S^+$, 682.3245; found, 682.3245.



SM-5b

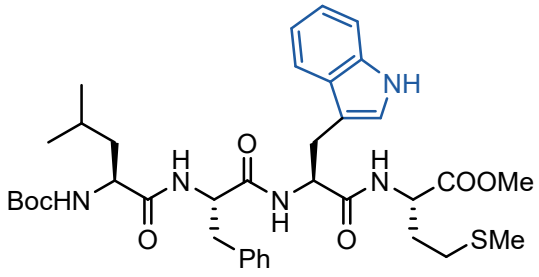
White solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.20 (t, J = 7.0 Hz, 2H), 7.15-7.10 (m, 3H), 7.08 (s, 2H), 6.42 (d, J = 7.2 Hz, 1H), 5.22 (d, J = 5.6 Hz, 1H), 4.56-4.47 (m, 3H), 4.42-4.33 (m, 3H), 3.73 (s, 3H), 3.26-3.23 (m, 2H), 1.44 (d, J = 7.2 Hz, 3H), 1.41 (s, 9H), 1.34 (d, J

= 7.4 Hz, 3H), 1.22 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, DMSO-D_6) δ 173.5, 172.5, 172.2, 172.2, 155.8, 136.6, 127.9, 124.2, 121.3, 119.0, 118.6, 111.8, 110.8, 78.6, 60.9, 55.6, 52.4, 48.5, 48.2, 48.0, 28.6, 28.1, 18.8, 18.7, 17.4, 14.5. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{26}H_{37}N_5NaO_7^+$, 554.2585; found, 554.2578.



SM-5c

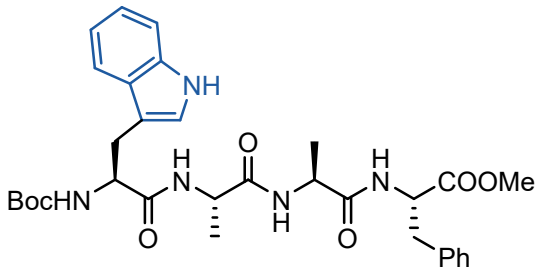
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.98 (s, 1H), 5.56 (s, 1H), 4.75-4.65 (m, 1H), 4.64-4.44 (m, 4H), 3.71 (s, 3H), 3.35-3.10 (m, 2H), 1.93-1.75 (m, 3H), 1.37 (s, 10H), 0.90 (t, *J* = 6.0 Hz, 9H), 0.83 (d, *J* = 7.4 Hz, 4H), 0.79 (d, *J* = 6.4 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 172.2, 171.5, 171.3, 155.6, 136.1, 127.6, 123.1, 121.9, 119.4, 118.8, 111.2, 110.4, 79.8, 58.0, 57.8, 56.6, 55.2, 52.0, 37.3, 36.6, 28.2, 25.1, 24.9, 24.7, 15.3, 15.2, 11.5, 11.4, 11.2. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{35}H_{55}N_5NaO_7^+$, 680.3994; found, 680.3995.



SM-5d

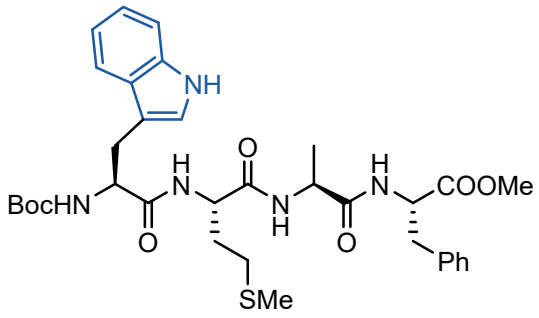
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 10.2 Hz, 1H), 7.24 (d, *J* = 6.0 Hz, 1H), 7.19-7.14 (m, 5H), 7.11 (d, *J* = 7.4 Hz, 3H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.74 (s, 1H), 5.15-5.05 (m, 1H), 4.99 (d, *J* = 7.4 Hz, 1H), 4.82 (s, 1H), 4.58-4.51 (m, 1H), 4.05 (s, 1H), 3.63 (s, 3H), 3.19 (d, *J* = 7.4 Hz, 2H), 3.01-3.93 (m, 2H), 2.27 (t, *J* = 7.8 Hz, 2H), 2.09-1.99 (m, 2H), 1.98 (s, 3H), 1.92-1.82 (m, 2H), 1.62-1.51 (m, 1H), 1.42 (s, 9H), 0.87 (d, *J* = 6.4 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 171.7, 171.1, 170.6, 155.7,

136.2, 136.0, 129.2, 128.6, 127.4, 127.0, 123.1, 121.8, 119.2, 118.6, 111.1, 110.1, 80.5, 54.3, 53.5, 53.3, 52.3, 51.5, 40.8, 37.6, 31.4, 29.5, 28.3, 24.7, 22.8, 21.8, 15.1. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{37}H_{51}N_5NaO_7S^+$, 732.3401; found, 732.3404.



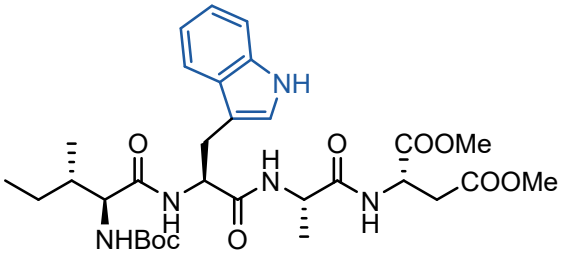
SM-5e

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.30-7.13 (m, 8H), 7.05 (t, *J* = 7.0 Hz, 2H), 6.54 (d, *J* = 6.4 Hz, 1H), 5.35 (d, *J* = 5.4 Hz, 1H), 4.84-4.76 (m, 1H), 4.51-4.30 (m, 3H), 3.65 (s, 3H), 3.28-3.04 (m, 4H), 1.39 (s, 9H), 1.25 (d, *J* = 7.2 Hz, 3H), 1.15 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8, 172.4, 172.1, 172.0, 156.2, 136.6, 136.5, 129.4, 128.5, 127.4, 127.0, 123.7, 122.4, 119.7, 118.7, 111.6, 109.6, 80.8, 56.0, 53.6, 52.4, 49.8, 49.2, 37.9, 28.3, 27.9, 17.8, 17.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{32}H_{41}N_5NaO_7^+$, 630.2898; found, 630.2909.



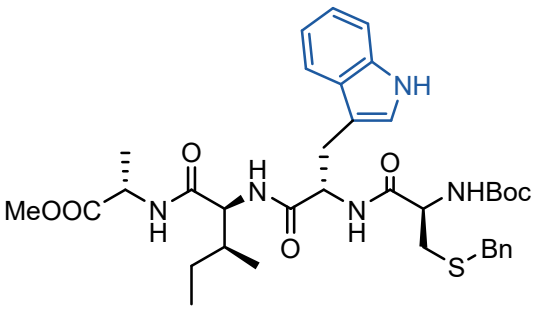
SM-5f

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.32-7.12 (m, 9H), 7.07 (s, 2H), 5.24 (s, 1H), 4.79 (d, *J* = 7.2 Hz, 1H), 4.54-4.34 (m, 2H), 4.28 (s, 1H), 3.67 (s, 3H), 3.34-3.03 (m, 4H), 2.33-2.06 (m, 2H), 1.97-1.75 (m, 5H), 1.40 (s, 9H), 1.25 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.3, 172.3, 172.0, 170.8, 156.4, 136.7, 136.5, 129.5, 128.6, 128.5, 127.4, 126.9, 123.7, 122.5, 119.8, 118.8, 111.7, 109.5, 81.0, 56.1, 54.0, 53.7, 52.4, 49.3, 37.9, 29.9, 29.0, 28.4, 27.6, 17.6, 14.8. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{34}H_{45}N_5NaO_7S^+$, 690.2932; found, 690.2928.



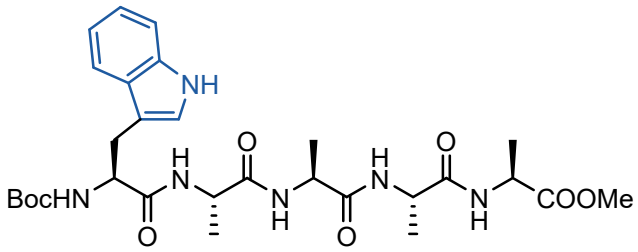
SM-5g

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 5.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.13-7.06 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 6.8 Hz, 1H), 5.01 (d, *J* = 5.0 Hz, 1H), 4.88-4.80 (m, 1H), 4.68-4.60 (m, 1H), 4.59-4.49 (m, 1H), 3.85 (t, *J* = 5.0 Hz, 1H), 3.71 (s, 3H), 3.64 (s, 3H), 3.45-3.36 (m, 1H), 3.23-3.14 (m, 1H), 2.89 (d, *J* = 6.0 Hz, 2H), 1.41-1.30 (m, 2H), 1.25-1.16 (m, 12H), 1.09-0.97 (m, 1H), 0.85 (t, *J* = 6.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 172.3, 171.3, 171.2, 171.01, 156.6, 136.5, 127.4, 123.6, 122.4, 119.8, 118.4, 111.7, 109.6, 80.7, 60.5, 54.2, 52.8, 52.1, 49.0, 48.9, 36.6, 36.2, 28.1, 27.0, 24.9, 17.6, 15.7, 11.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{31}H_{45}N_5NaO_9^+$, 654.3109; found, 654.3113.



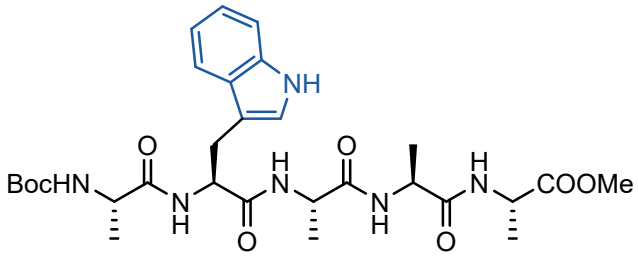
SM-5h

Yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.91 (d, *J* = 48.6 Hz, 1H), 7.56 (t, *J* = 9.4 Hz, 2H), 7.46 (s, 1H), 7.18 (d, *J* = 9.6 Hz, 3H), 7.12 (t, *J* = 7.6 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 3H), 5.86 (s, 1H), 5.12 (s, 1H), 4.60-4.40 (m, 3H), 3.65 (d, *J* = 7.8 Hz, 5H), 3.31-3.08 (m, 2H), 2.86-2.66 (m, 2H), 1.79 (d, *J* = 21.0 Hz, 1H), 1.46 (d, *J* = 12.4 Hz, 2H), 1.40 (s, 9H), 1.27 (d, *J* = 7.8 Hz, 3H), 0.82 (d, *J* = 7.0 Hz, 3H), 0.72 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1, 171.2, 170.8, 155.5, 137.8, 136.0, 128.9, 128.5, 127.4, 127.1, 123.5, 121.8, 119.4, 118.4, 111.2, 109.7, 80.0, 57.7, 53.9, 53.7, 52.2, 47.9, 37.2, 36.4, 34.2, 28.2, 24.8, 17.6, 15.0, 11.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{36}H_{49}N_5NaO_7S^+$, 718.3245; found, 718.3243.



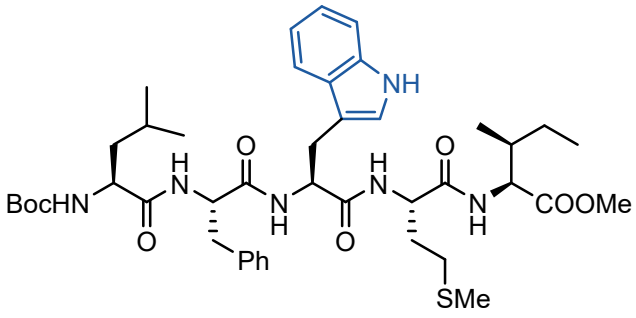
SM-6a

White solid. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 10.82 (t, *J* = 7.0 Hz, 1H), 8.28 (d, *J* = 7.0 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.13 (s, 1H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 4.30-4.22 (m, 4H), 4.21-4.15 (m, 1H), 3.60 (s, 3H), 3.13-3.03 (m, 1H), 2.92-2.79 (m, 1H), 1.29 (s, 9H), 1.20 (t, *J* = 6.2 Hz, 12H). **^{13}C NMR** (100 MHz, DMSO-D_6) δ 173.5, 172.6, 172.5, 172.3, 172.1, 155.8, 136.6, 127.9, 124.3, 121.3, 119.1, 118.7, 111.8, 110.8, 78.6, 55.6, 52.4, 48.5, 48.2, 48.1, 28.7, 28.3, 28.1, 18.8, 18.8, 18.6, 17.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{29}H_{42}N_6NaO_8^+$, 625.2956; found, 625.2956.



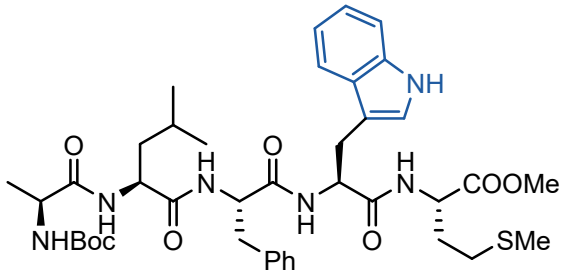
SM-6b

White solid. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 10.82 (s, 1H), 8.27 (d, *J* = 7.0 Hz, 1H), 8.08 (d, *J* = 7.4 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.95 (q, *J* = 6.4 Hz, 2H), 4.55-4.47 (m, 1H), 4.31-4.21 (m, 3H), 3.91 (t, *J* = 7.4 Hz, 1H), 3.61 (s, 3H), 3.11 (dd, *J* = 15.0, 4.8 Hz, 1H), 3.00-2.92 (m, 1H), 1.34 (s, 9H), 1.28 (d, *J* = 7.4 Hz, 3H), 1.21 (d, *J* = 7.4 Hz, 3H), 1.15 (d, *J* = 5.0 Hz, 3H), 1.11 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, DMSO-D_6) δ 173.4, 173.1, 172.5, 172.1, 171.5, 155.6, 136.5, 127.9, 124.1, 121.3, 118.9, 118.6, 111.7, 110.2, 78.7, 53.5, 52.4, 50.4, 48.6, 48.2, 48.0, 28.7, 18.6, 18.5, 18.5, 17.4. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{29}H_{42}N_6NaO_8^+$, 625.2956; found, 625.2956.



SM-6c

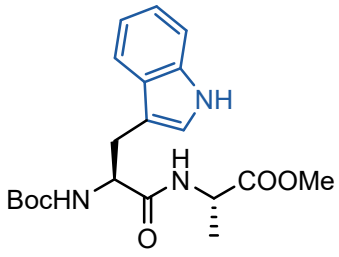
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.23 (s, 3H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 6.4 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 2H), 6.89 (s, 1H), 5.40 (s, 1H), 4.79 (s, 1H), 4.67 (s, 1H), 4.57-4.43 (m, 2H), 4.07 (s, 1H), 3.72 (s, 3H), 3.25 (s, 1H), 3.15-2.95 (m, 2H), 2.86 (dd, *J* = 14.0, 5.2 Hz, 1H), 2.25 (t, *J* = 7.6 Hz, 2H), 2.05-1.95 (m, 1H), 1.93 (s, 3H), 1.88 (d, *J* = 7.0 Hz, 2H), 1.42 (s, 9H), 1.40 (s, 2H), 1.27 (dd, *J* = 10.2, 4.6 Hz, 2H), 1.17 (dd, *J* = 15.8, 7.2 Hz, 1H), 0.93-0.87 (m, 6H), 0.84 (d, *J* = 6.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.2, 172.2 171.5, 171.2, 170.7, 155.8, 136.4, 136.0, 129.3, 128.4, 127.4, 126.9, 123.1, 121.9, 119.4, 118.5, 111.3, 109.7, 79.9, 56.7, 54.8, 52.7, 52.1, 51.9, 41.0, 37.3, 29.6, 28.3, 24.9, 24.5, 22.8, 21.9, 15.5, 14.9, 11.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{43}H_{62}N_6NaO_8S^+$, 845.4242; found, 845.4251.



SM-6d

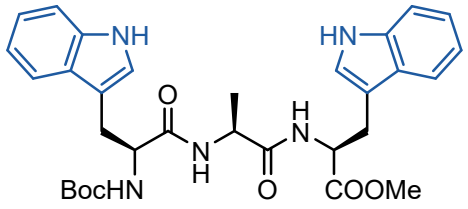
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.22-7.11 (m, 5H), 7.11-7.01 (m, 4H), 7.00 (d, *J* = 11.4 Hz, 1H), 6.88 (s, 1H), 5.19 (s, 1H), 4.94 (s, 1H), 4.71 (s, 1H), 4.57 (s, 1H), 4.24 (d, *J* = 67.8 Hz, 1H), 4.00 (s, 1H), 3.67 (s, 3H), 3.25 (d, *J* = 7.0 Hz, 2H), 3.12-2.86 (m, 2H), 2.34 (d, *J* = 7.8 Hz, 2H), 2.12-2.03 (m, 1H), 2.01 (s, 3H), 1.97-1.85 (m, 2H), 1.44 (s, 9H), 1.23 (d, *J* = 7.4 Hz, 3H), 0.82 (dd, *J* = 12.4, 6.0 Hz, 6H). **^{13}C NMR** (150 MHz, DMSO-D_6) δ 172.9, 172.5, 172.2, 171.9, 171.0, 155.6, 138.0, 136.5, 129.7, 128.4, 127.9, 126.6, 124.0, 121.3, 118.8, 118.7, 111.7, 110.2, 78.6, 53.9, 53.7, 52.4, 51.4,

50.1, 41.4, 37.9, 31.1, 29.9, 28.7, 24.4, 23.5, 22.1, 18.4, 15.1. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{40}H_{56}N_6NaO_8S^+$, 803.3773; found, 803.3778.



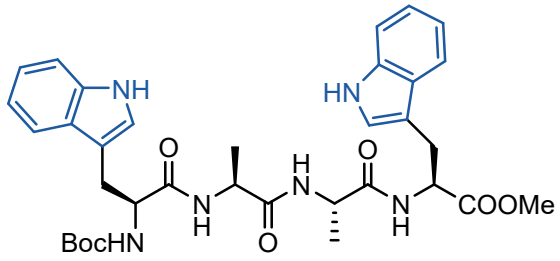
SM-7a

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.08 (dd, *J* = 15.0, 7.6 Hz, 2H), 6.44 (d, *J* = 7.2 Hz, 1H), 5.23 (d, *J* = 8.2 Hz, 1H), 4.55-4.36 (m, 2H), 3.62 (s, 3H), 3.37-3.08 (m, 2H), 1.41 (s, 9H), 1.23 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8, 171.2, 155.4, 136.1, 127.4, 123.3, 122.0, 119.5, 118.8, 111.1, 110.3, 80.0, 55.0, 52.3, 48.0, 28.2, 18.2. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{20}H_{27}N_3NaO_5^+$, 412.1843; found, 412.1829.



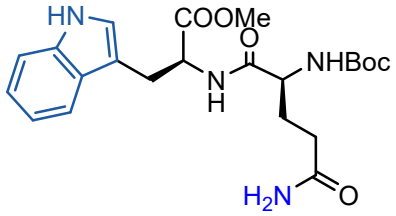
SM-8

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.22 (s, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.24 (s, 1H), 7.14 (q, *J* = 7.2 Hz, 2H), 7.07 (td, *J* = 7.6, 3.2 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.87 (s, 1H), 6.78 (s, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.30 (d, *J* = 7.8 Hz, 1H), 4.80 (q, *J* = 6.0 Hz, 1H), 4.48-4.36 (m, 2H), 3.63 (s, 3H), 3.27 (dd, *J* = 15.2, 5.0 Hz, 1H), 3.19 (dd, *J* = 15.0, 6.6 Hz, 2H), 3.08 (dd, *J* = 14.4, 6.6 Hz, 1H), 1.40 (s, 9H), 1.04 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 171.7, 171.6, 155.6, 136.1, 136.0, 127.3, 123.5, 123.2, 122.1, 121.9, 119.5, 119.3, 118.7, 118.3, 111.5, 111.3, 109.8, 109.3, 80.3, 55.0, 52.8, 52.4, 48.8, 28.2, 27.3, 17.7. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{31}H_{37}N_5NaO_6^+$, 598.2636; found, 598.2634.



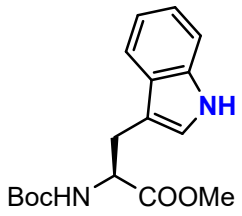
SM-10

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.70 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 2H), 7.09-7.00 (m, 4H), 6.98 (s, 1H), 6.76 (s, 1H), 6.70 (d, *J* = 7.0 Hz, 1H), 5.47 (d, *J* = 7.0 Hz, 1H), 4.86 (q, *J* = 6.2 Hz, 1H), 4.47 (t, *J* = 7.4 Hz, 1H), 4.39 (t, *J* = 7.6 Hz, 2H), 3.60 (s, 3H), 3.37-3.21 (m, 2H), 3.19-3.08 (m, 2H), 1.40 (s, 9H), 1.20 (d, *J* = 7.4 Hz, 3H), 1.06 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 172.1, 172.0, 155.8, 136.1, 136.0, 127.3, 127.2, 123.5, 123.3, 122.0, 121.8, 119.4, 119.2, 118.5, 118.3, 111.4, 109.7, 109.4, 80.4, 55.5, 52.9, 52.4, 49.1, 48.9, 28.2, 27.4, 18.2, 17.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{34}H_{42}N_6NaO_7^+$, 669.3007; found, 669.3013.



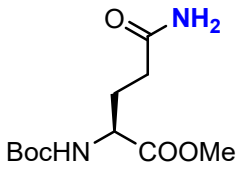
SM-12

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.27 (s, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 2H), 6.24 (s, 2H), 5.80 (d, *J* = 7.8 Hz, 1H), 4.85 (q, *J* = 6.4 Hz, 1H), 4.26 (q, *J* = 7.4 Hz, 1H), 3.65 (s, 3H), 3.32-3.23 (m, 2H), 2.22 (q, *J* = 6.6 Hz, 2H), 2.03-1.83 (m, 2H), 1.41 (s, 9H). **^{13}C NMR** (150 MHz, DMSO-D_6) δ 174.4, 172.7, 172.5, 155.7, 136.6, 127.6, 124.2, 121.5, 119.0, 118.5, 111.9, 109.6, 79.7, 78.6, 54.3, 53.5, 52.3, 32.0, 28.7, 28.3, 27.6. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{22}H_{30}N_4NaO_6^+$, 469.2058; found, 469.2064.



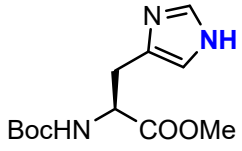
SM-16

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.15 (dt, *J* = 27.2, 7.4 Hz, 2H), 6.95 (s, 1H), 5.13 (d, *J* = 8.2 Hz, 1H), 4.65 (d, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 3.28 (d, *J* = 4.2 Hz, 2H), 1.43 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 155.5, 136.3, 127.7, 123.0, 122.2, 119.6, 118.8, 111.4, 110.0, 80.1, 54.3, 52.4, 28.4, 28.0. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{17}H_{22}N_2NaO_4^+$, 341.1472; found, 341.1459.



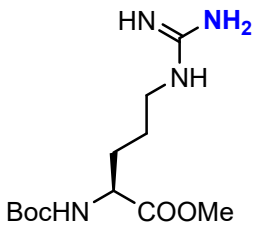
SM-17

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.44 (s, 1H), 6.27 (s, 1H), 5.63 (d, *J* = 8.2 Hz, 1H), 4.20 (dt, *J* = 8.8, 4.6 Hz, 1H), 3.65 (s, 3H), 2.30-2.19 (m, 2H), 2.14-1.99 (m, 1H), 1.93-1.76 (m, 1H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.9, 172.7, 155.7, 79.8, 52.9, 52.2, 31.6, 28.1, 27.0. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{11}H_{20}N_2NaO_5^+$, 283.1264; found, 283.1256.



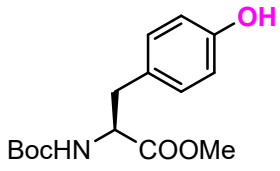
SM-18

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 6.81 (s, 1H), 5.88 (d, *J* = 8.2 Hz, 1H), 4.61-4.50 (m, 1H), 3.72 (s, 1H), 3.70 (s, 3H), 3.13-3.03 (m, 2H), 1.43 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 155.6, 135.2, 116.0, 114.5, 79.9, 53.6, 52.3, 29.6, 28.3. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{12}H_{19}N_3NaO_4^+$, 292.1268; found, 292.1263.



SM-19

White solid. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 7.99 (t, *J* = 5.8 Hz, 1H), 7.51 (s, 2H), 7.33 (s, 1H), 7.15 (s, 2H), 3.97-3.88 (m, 1H), 3.61 (s, 3H), 3.06 (q, *J* = 7.2 Hz, 2H), 1.73-1.62 (m, 1H), 1.61-1.53 (m, 1H), 1.52-1.47 (m, 2H), 1.36 (s, 9H). **^{13}C NMR** (150 MHz, DMSO-D_6) δ 173.5, 157.6, 156.1, 79.8, 78.8, 53.7, 52.3, 40.7, 28.7, 28.3, 25.8. **HRMS-ESI**(m/z): $[M+H]^+$ calcd. for $C_{12}H_{25}N_4O_4^+$, 289.1870; found, 289.1868.



SM-20

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 7.8 Hz, 2H), 5.15 (d, *J* = 8.2 Hz, 1H), 4.53 (q, *J* = 6.4 Hz, 1H), 3.69 (s, 3H), 3.06-2.92 (m, 2H), 1.42 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 155.4, 155.4, 130.2, 126.8, 115.4, 80.3, 54.5, 52.2, 37.3, 28.2. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{15}H_{21}NNaO_5^+$, 318.1312; found, 318.1305.

References

1. Li, S. et al. Synthesis of trifluoromethyl-substituted allenols via catalytic trifluoromethylbenzoxylation of 1,3-enynes, *ACS Catal.*, **13**, 2142-2148 (2023).
2. Han, Y. et al. Selective editing of a peptide skeleton via C-N bond formation at N-terminal aliphatic side chains, *Chem. Sci.*, **13**, 14382-14386 (2022).
3. Periasamy, M. et al. New Diimine-Copper Complexes: An Efficient and Simple Catalyst System for Buchwald N-Arylation of Indole. *Organometallics*, **27**, 1963-1966 (2008).
4. Sarkar, G. et al. An Efficient 2-(2-Pyridyl)imidazole Based Copper Catalyst for

N-Arylation of N-Heterocycles. *Mol. Catal.*, **545**, 113212-113219 (2023).

5. Merriam, J. S. et al. Polarized Electronic Spectra and Electronic Energy Levels of Some Tetragonal Nickel(II) Complexes. *J. Phys. Chem.*, **79**, 142-149 (1975).
6. Noa, F. M. A. et al. Secondary Interactions in Halogenated Werner Clathrates. *Cryst. Growth Des.*, **17**, 1876-1883 (2017).
7. M. Malinowski, et al. A. Ferry. Glycosamine Derivatives through Metal-Catalyzed C-N Bond Formation on Protected and Unprotected 2-Iodoglycals. *Eur. J. Org. Chem.*, **2021**, 1521-1524 (2021).

NMR Spectra

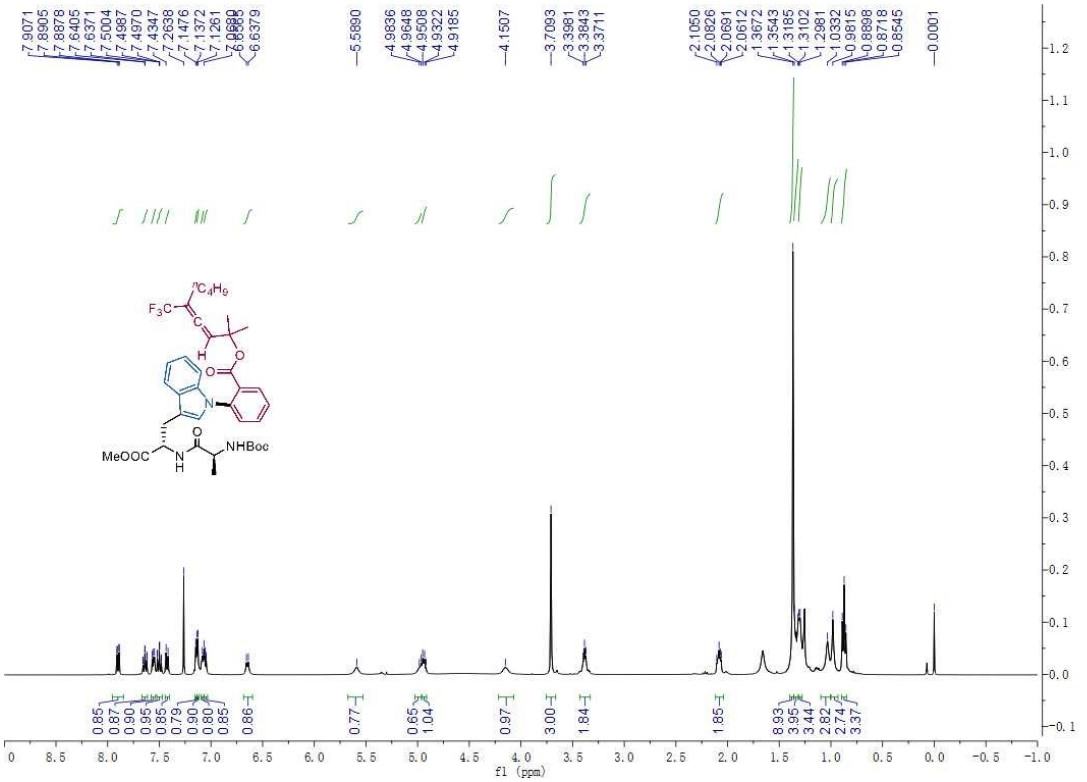


Fig 1. ^{1}H NMR of (**3a**)

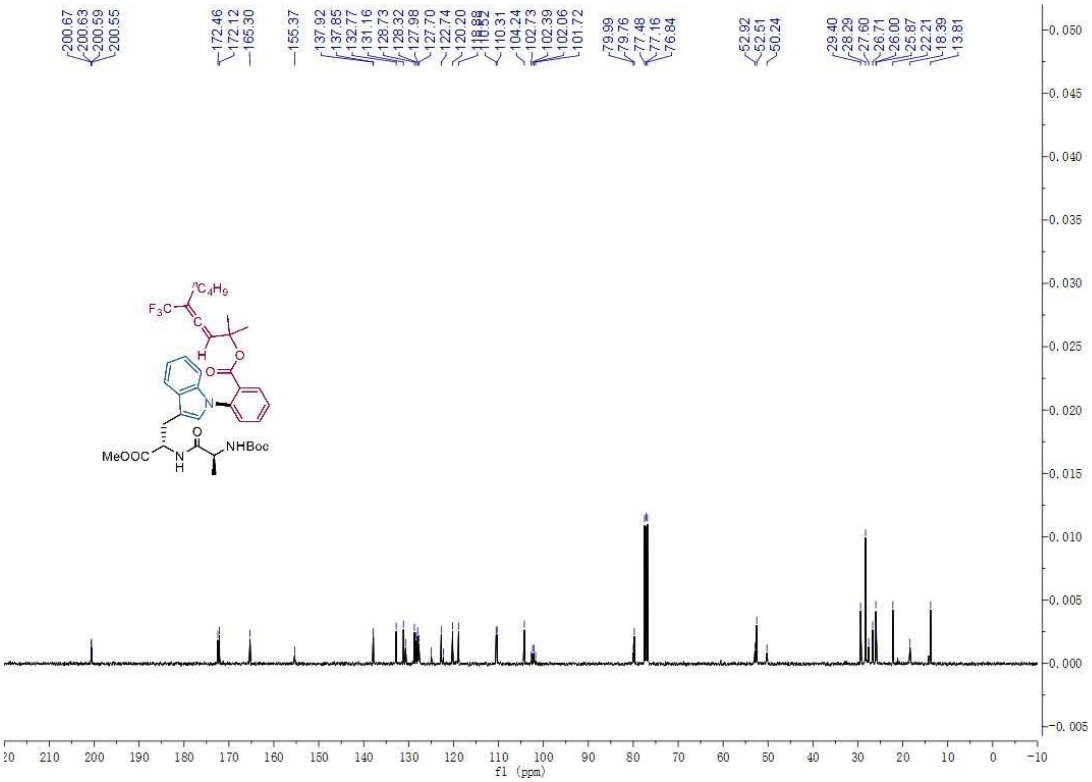


Fig 2. ^{13}C NMR of (**3a**)

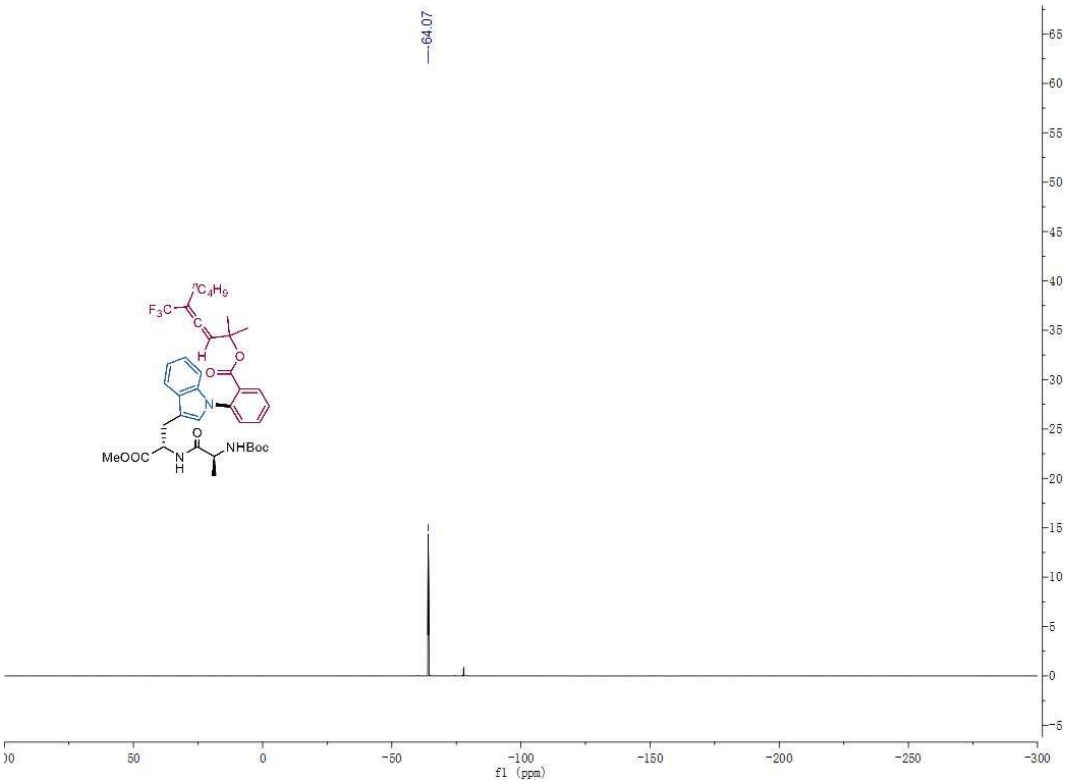


Fig 3. ^{19}F NMR of (**3a**)

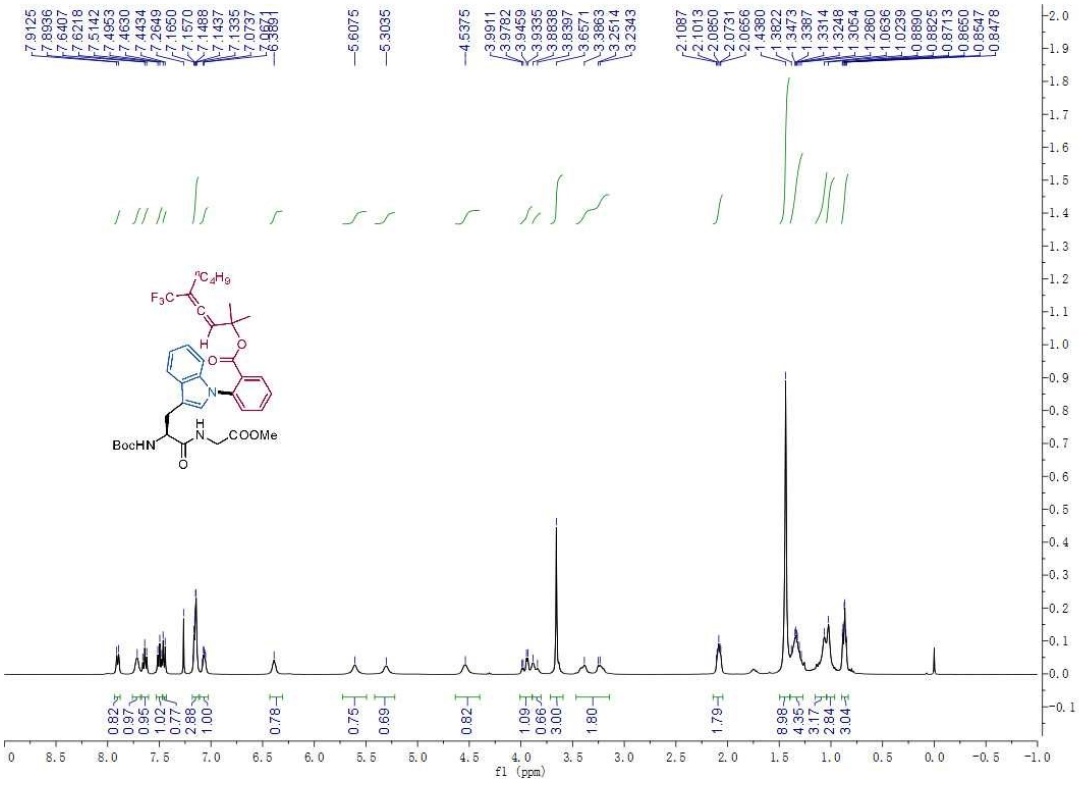


Fig 4. ^{1}H NMR of (**3b**)

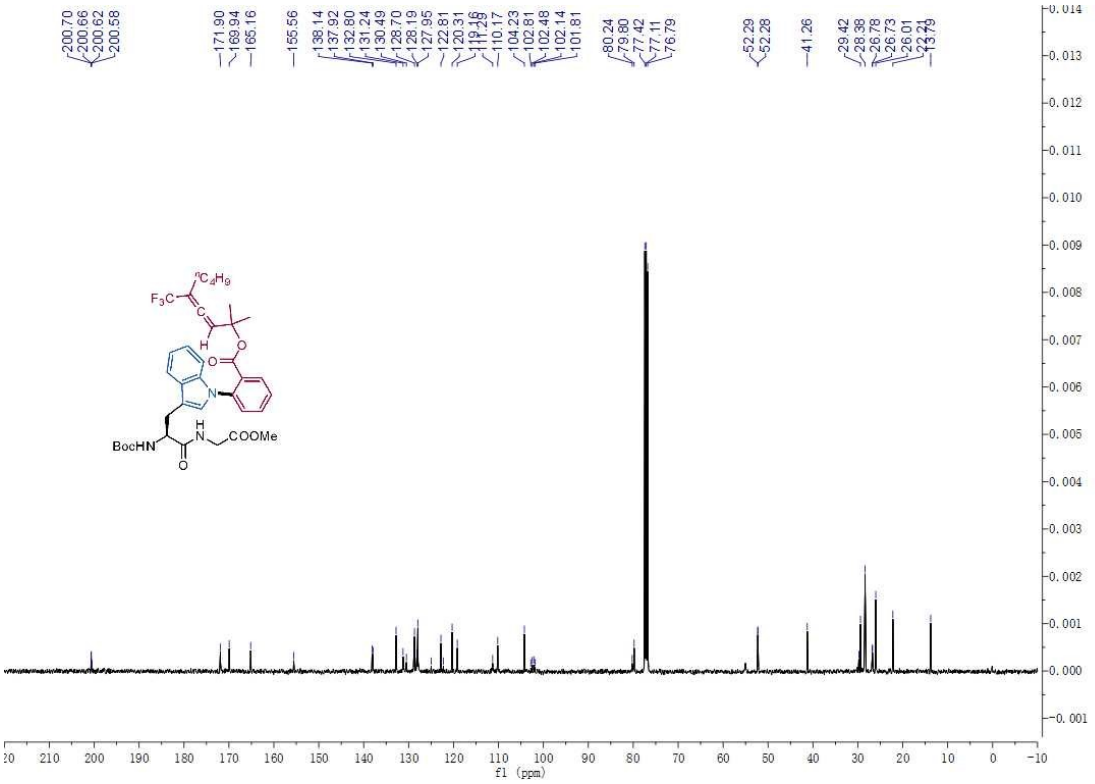


Fig 5. ^{13}C NMR of (**3b**)

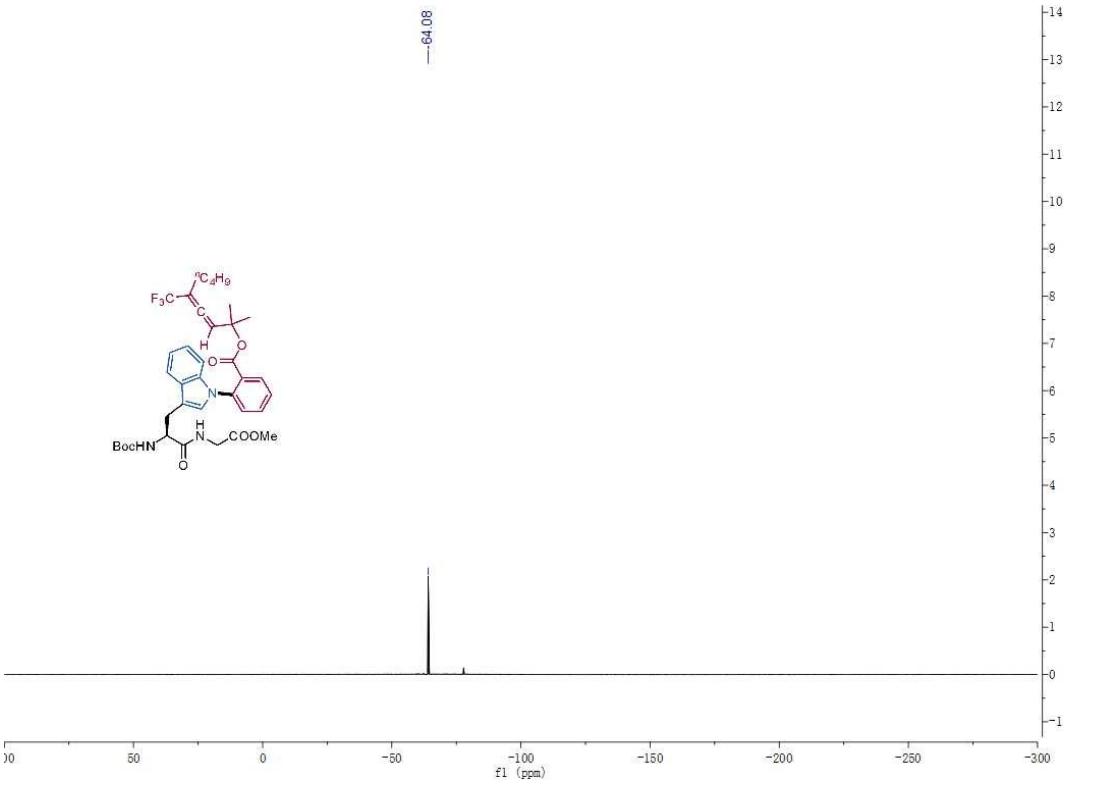


Fig 6. ^{19}F NMR of (**3b**)

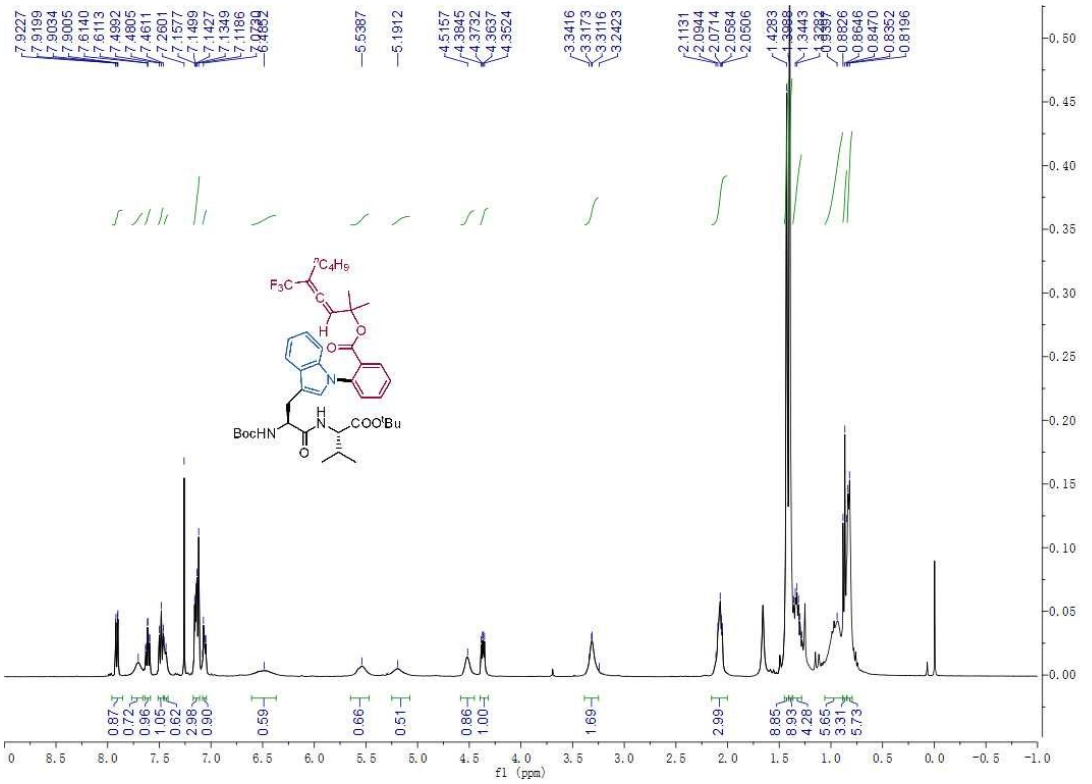


Fig 7. ^{1}H NMR of (**3c**)

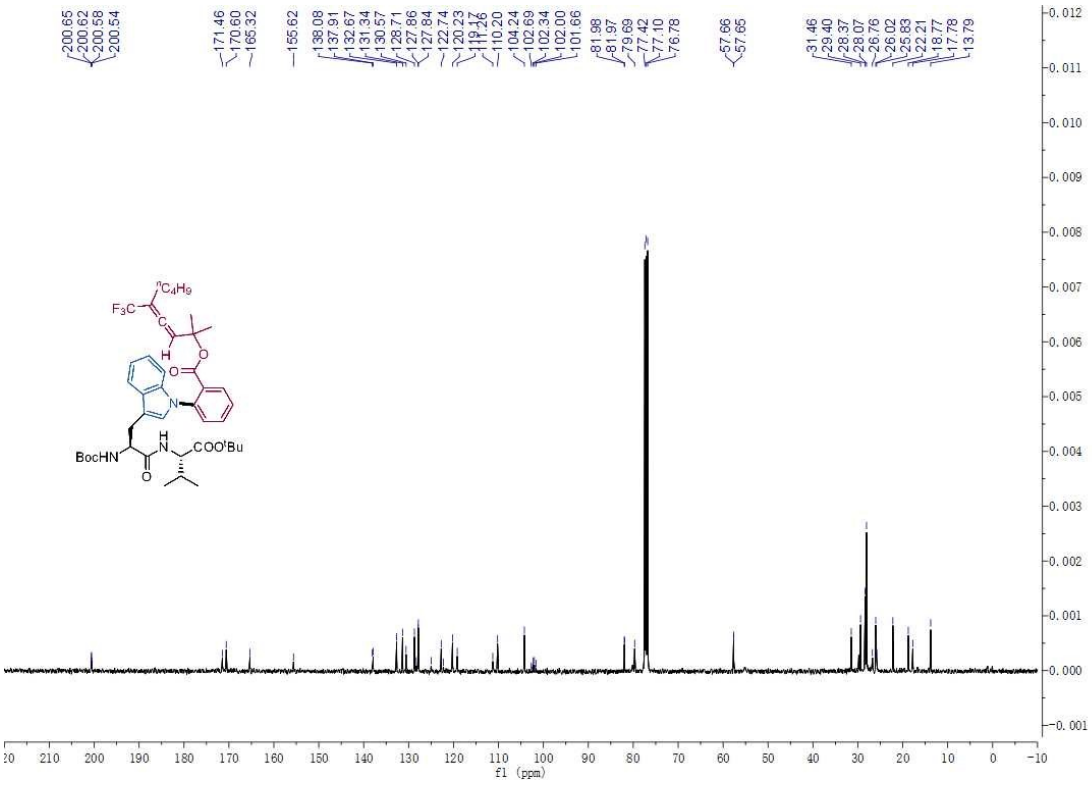


Fig 8. ^{13}C NMR of (**3c**)

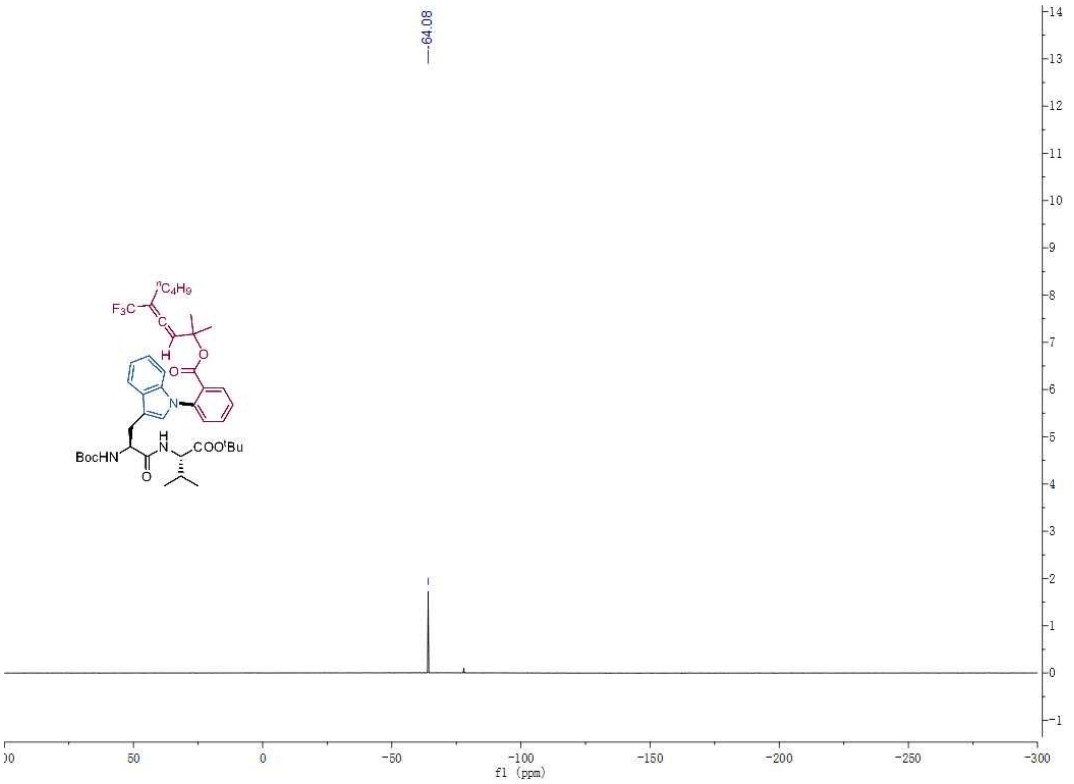


Fig 9. ^{19}F NMR of (**3c**)

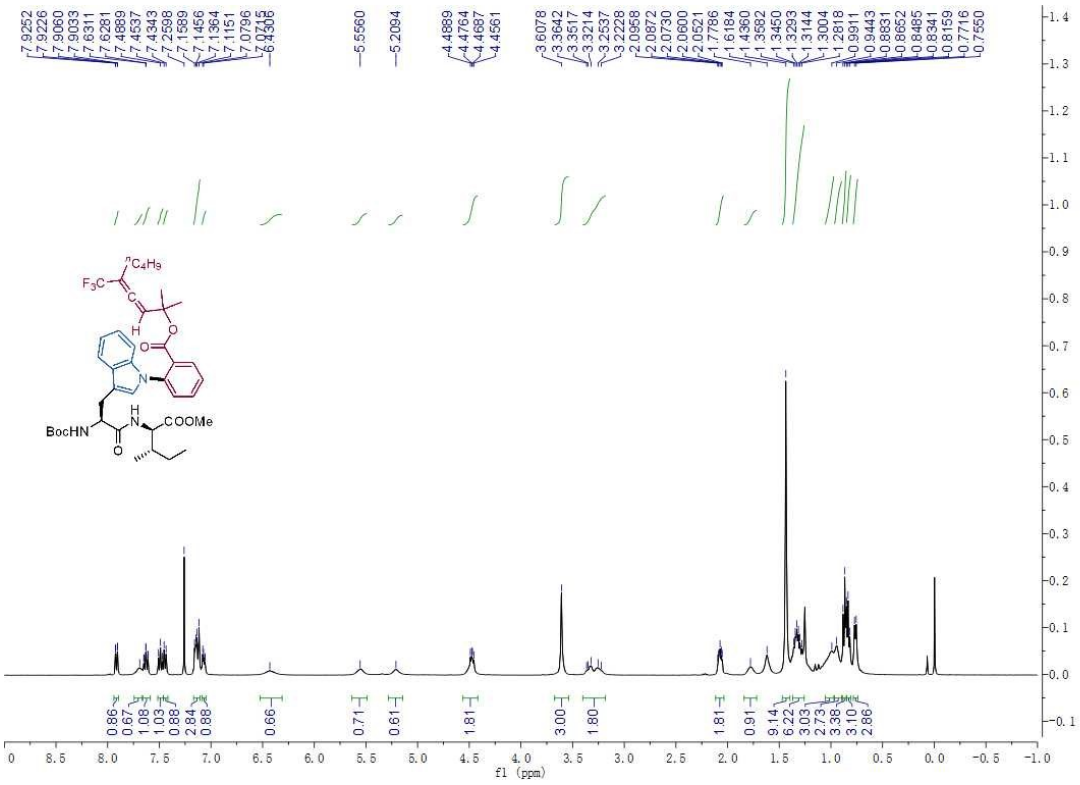


Fig 10. ^{1}H NMR of (**3d**)

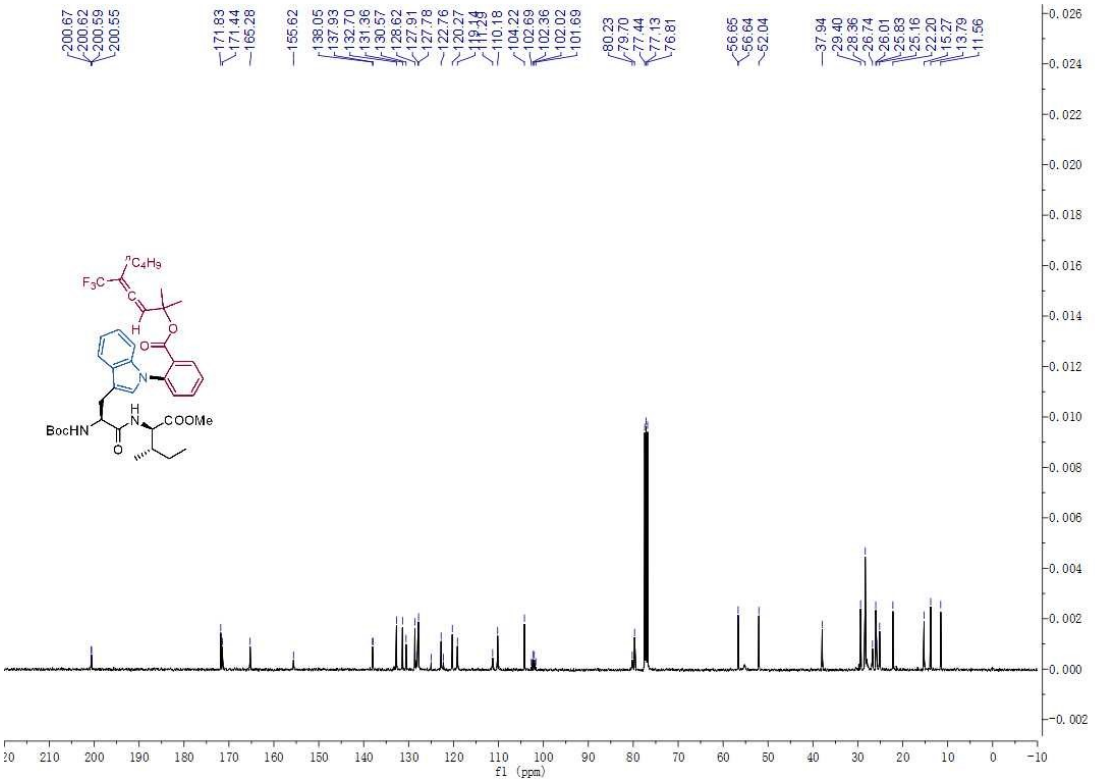


Fig 11. ^{13}C NMR of (**3d**)

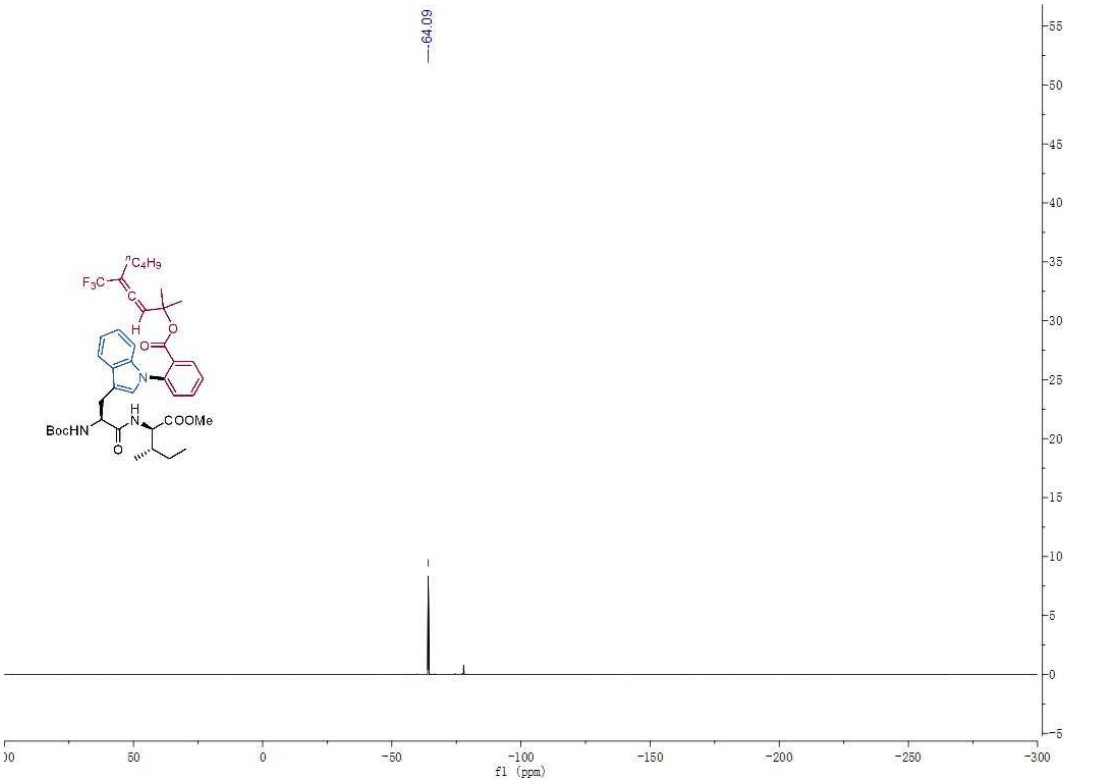


Fig 12. ^{19}F NMR of (**3d**)

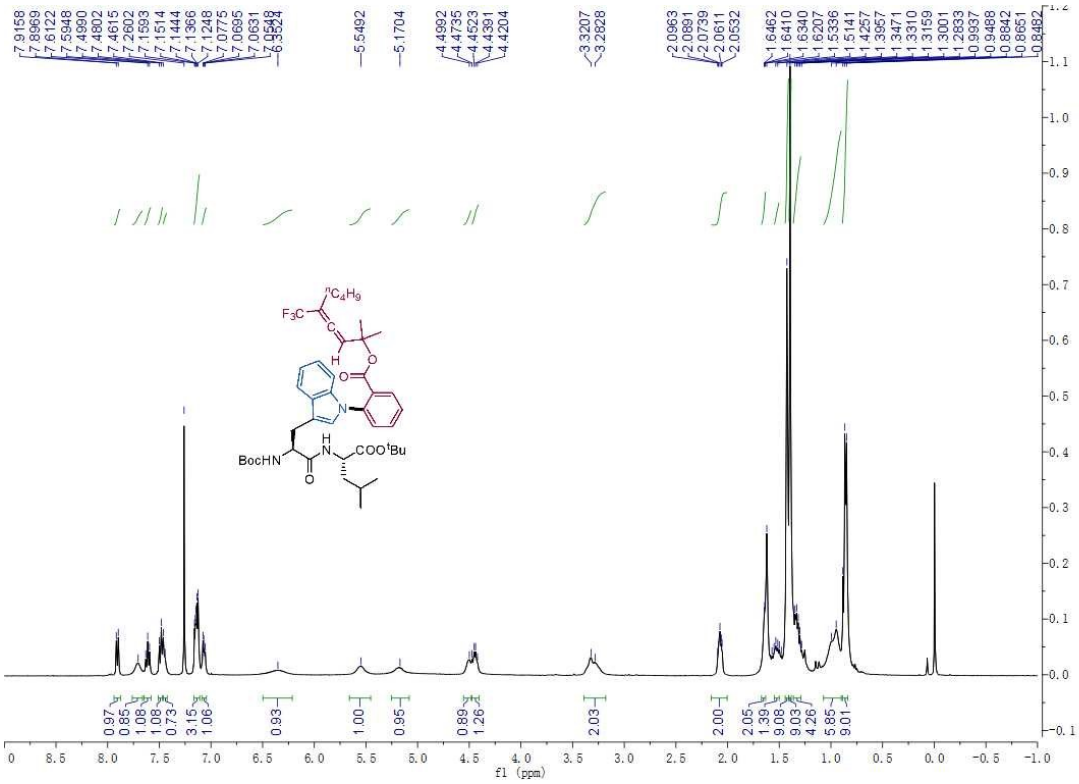


Fig 13. ^{1}H NMR of (**3e**)

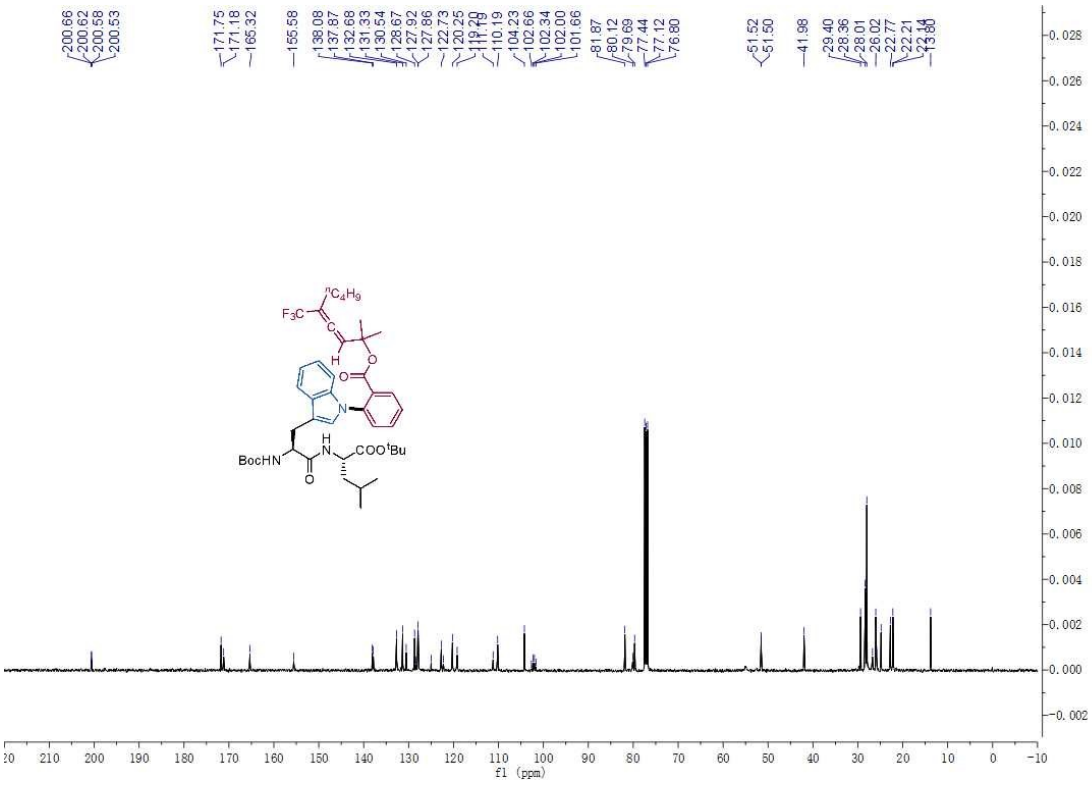


Fig 14. ^{13}C NMR of (**3e**)

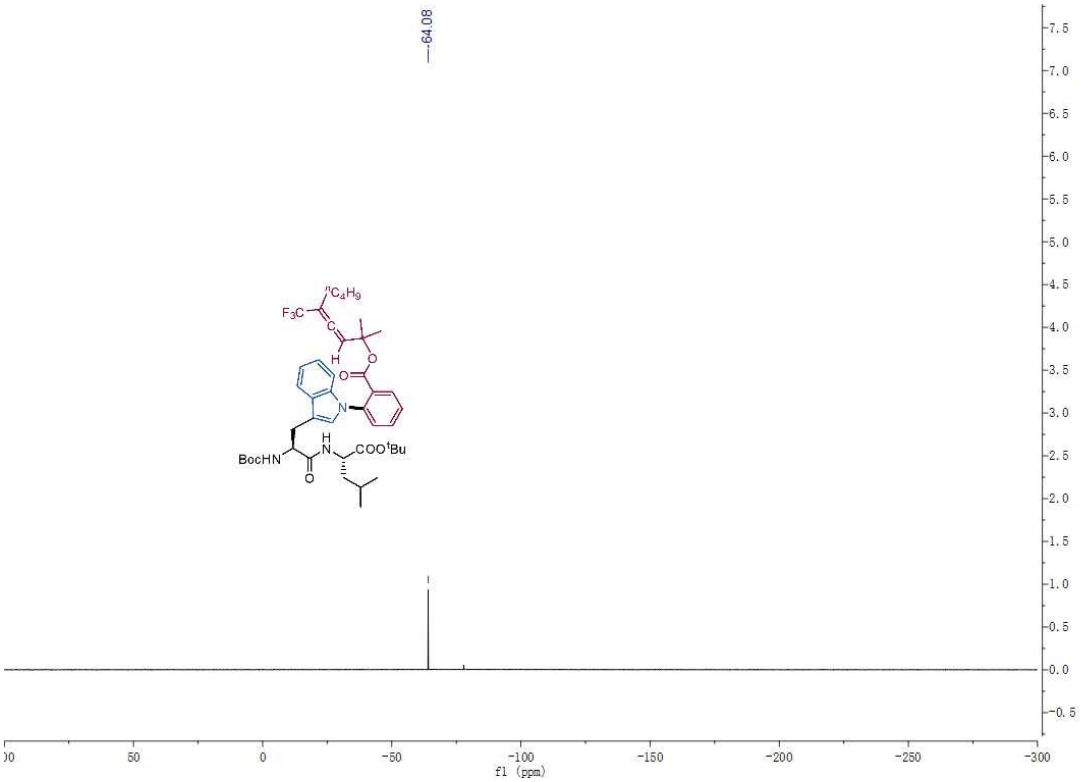


Fig 15. ^{19}F NMR of (**3e**)

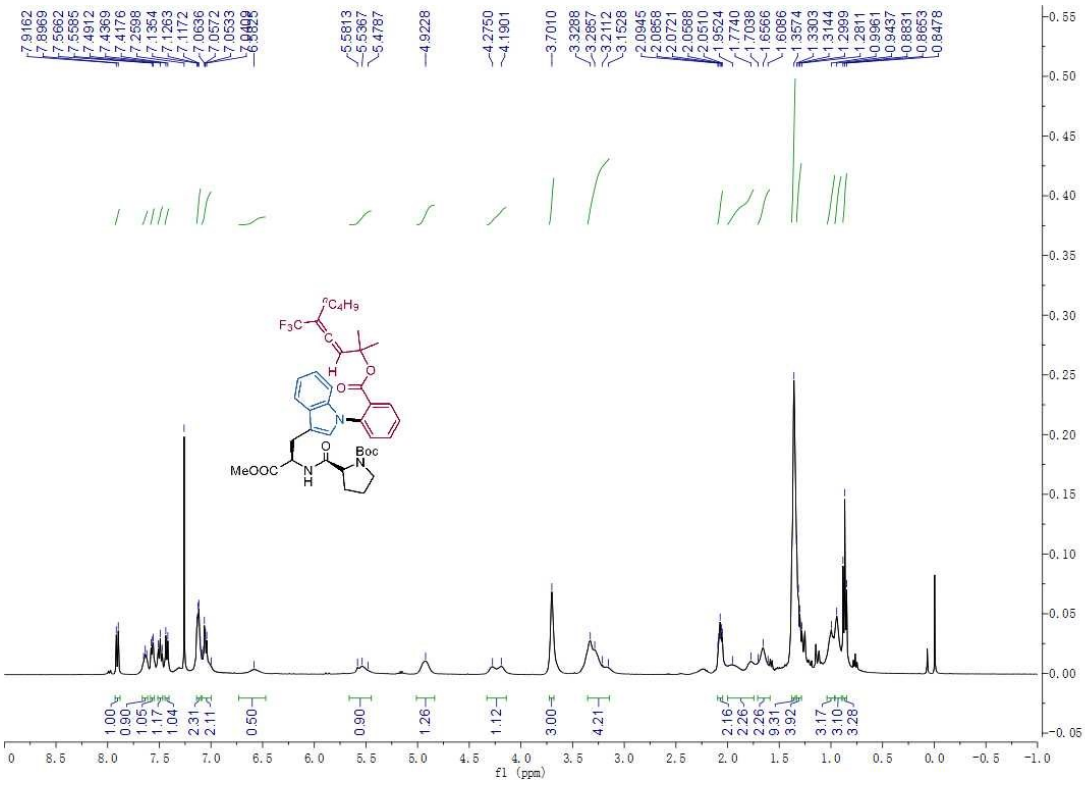


Fig 16. ^{1}H NMR of (**3f**)

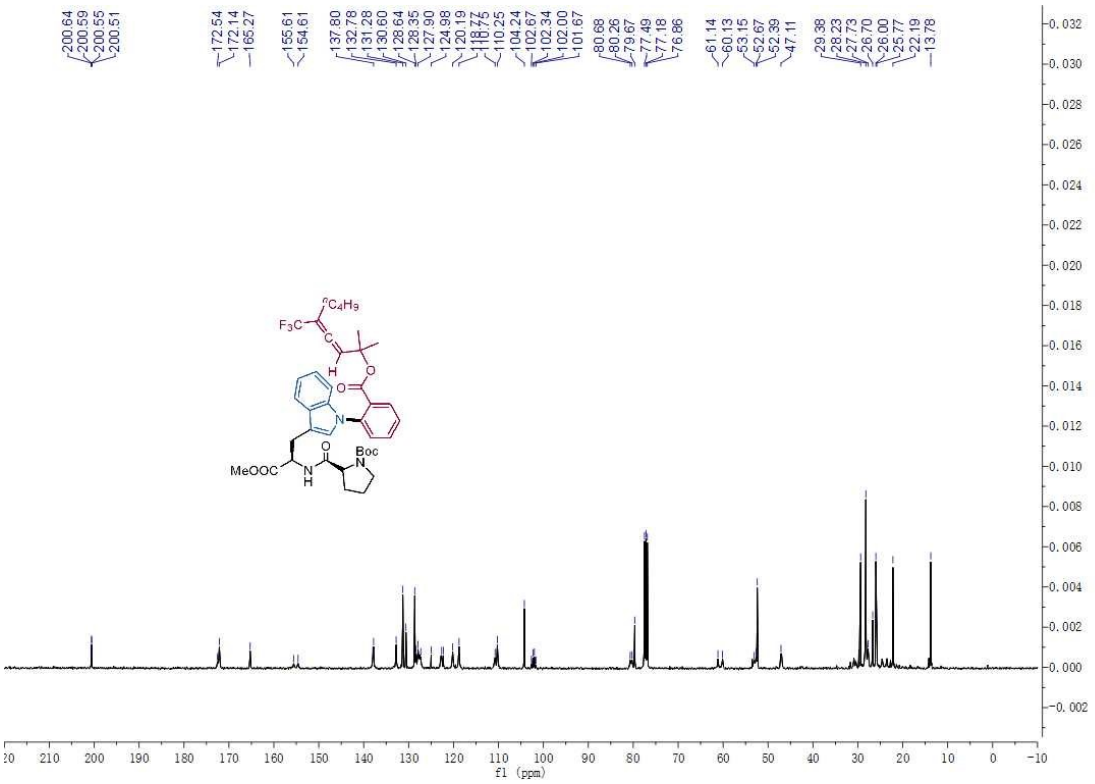


Fig 17. ^{13}C NMR of (**3f**)

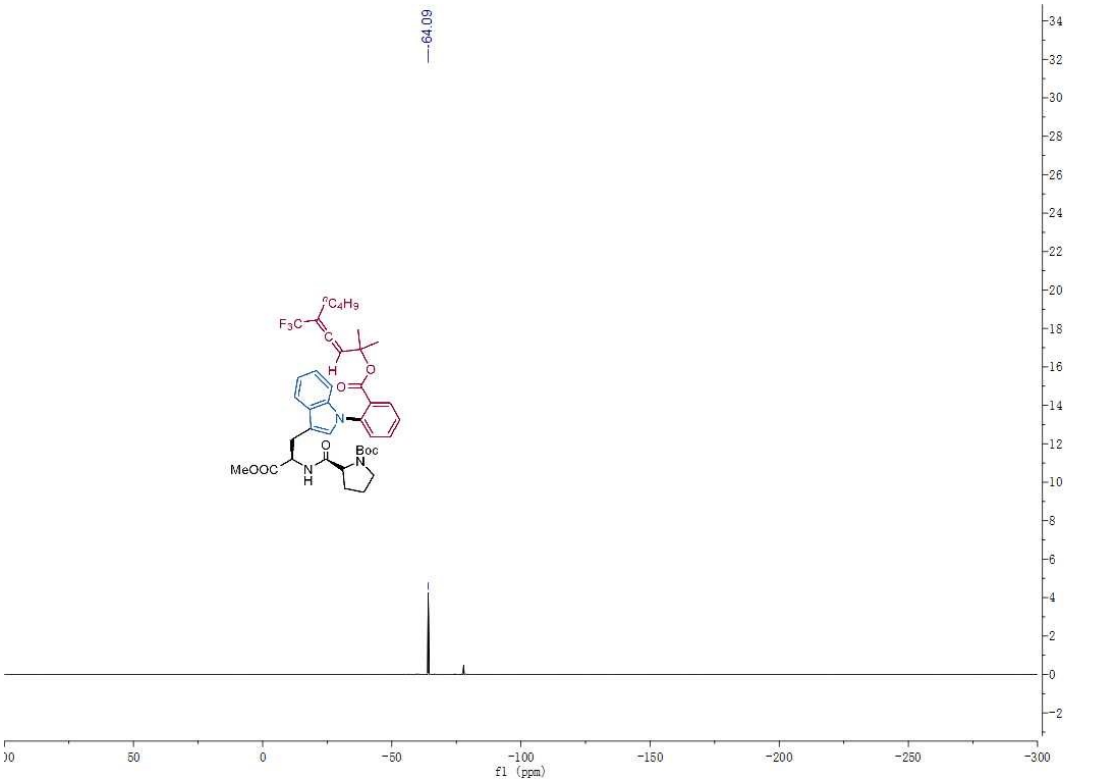


Fig 18. ^{19}F NMR of (**3f**)

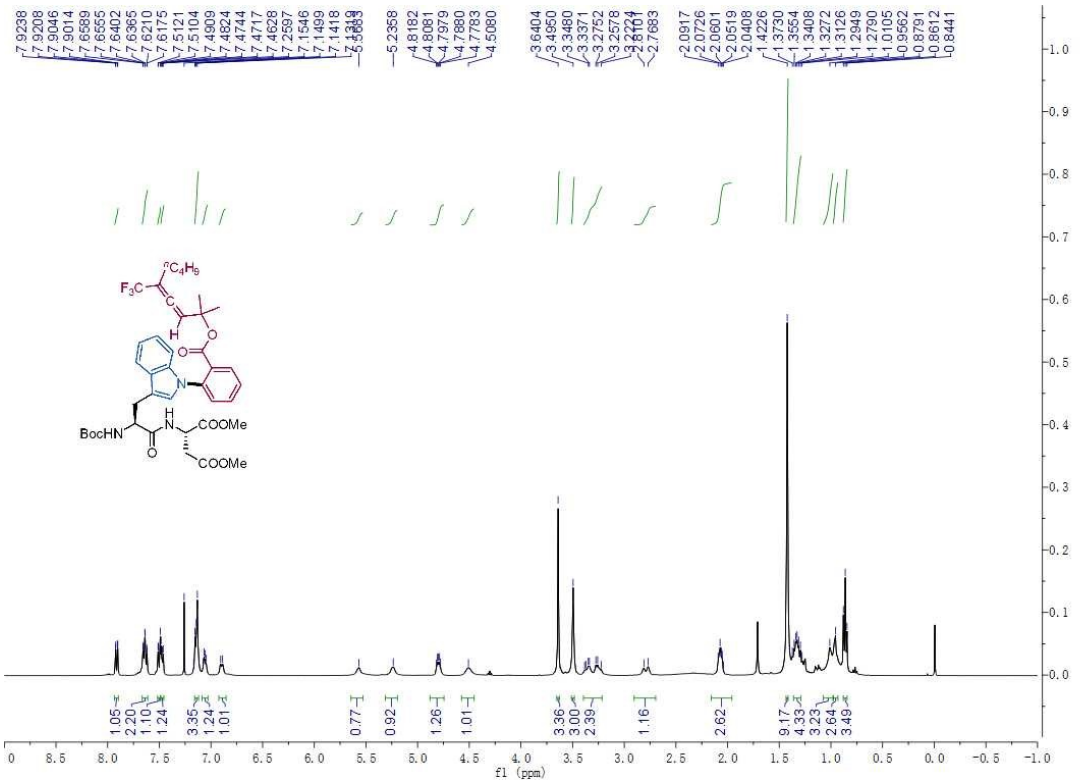


Fig 19. ^{1}H NMR of (**3g**)

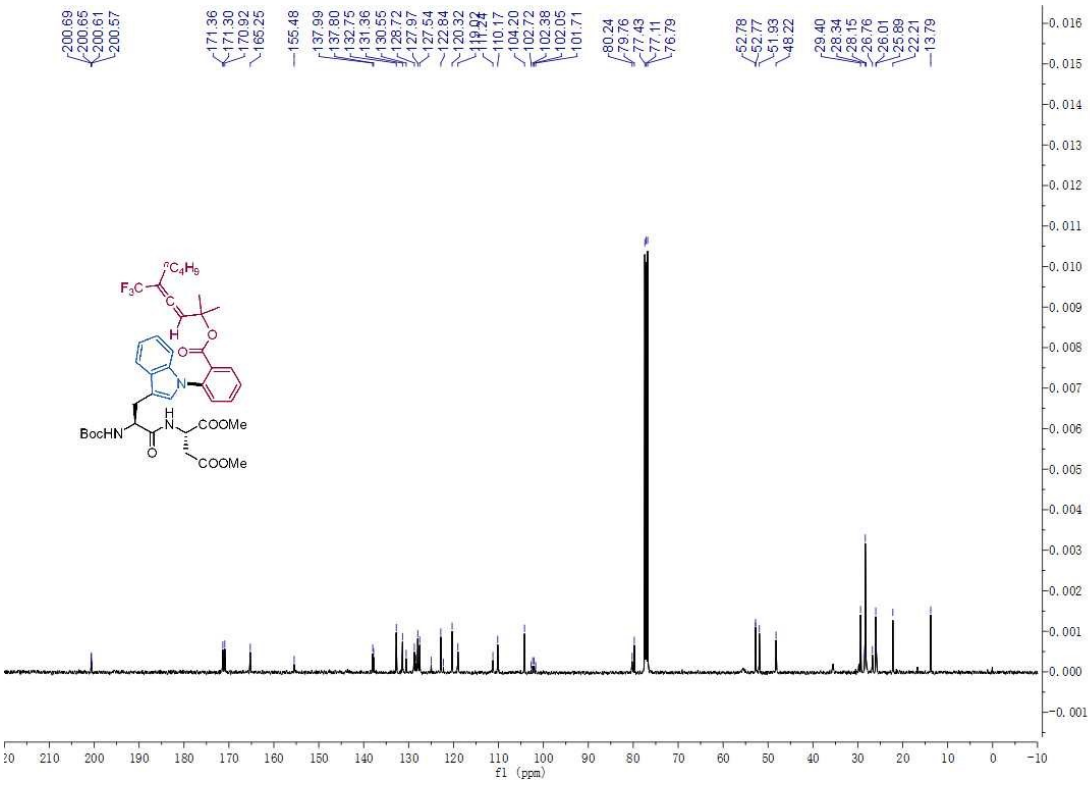


Fig 20. ^{13}C NMR of (**3g**)

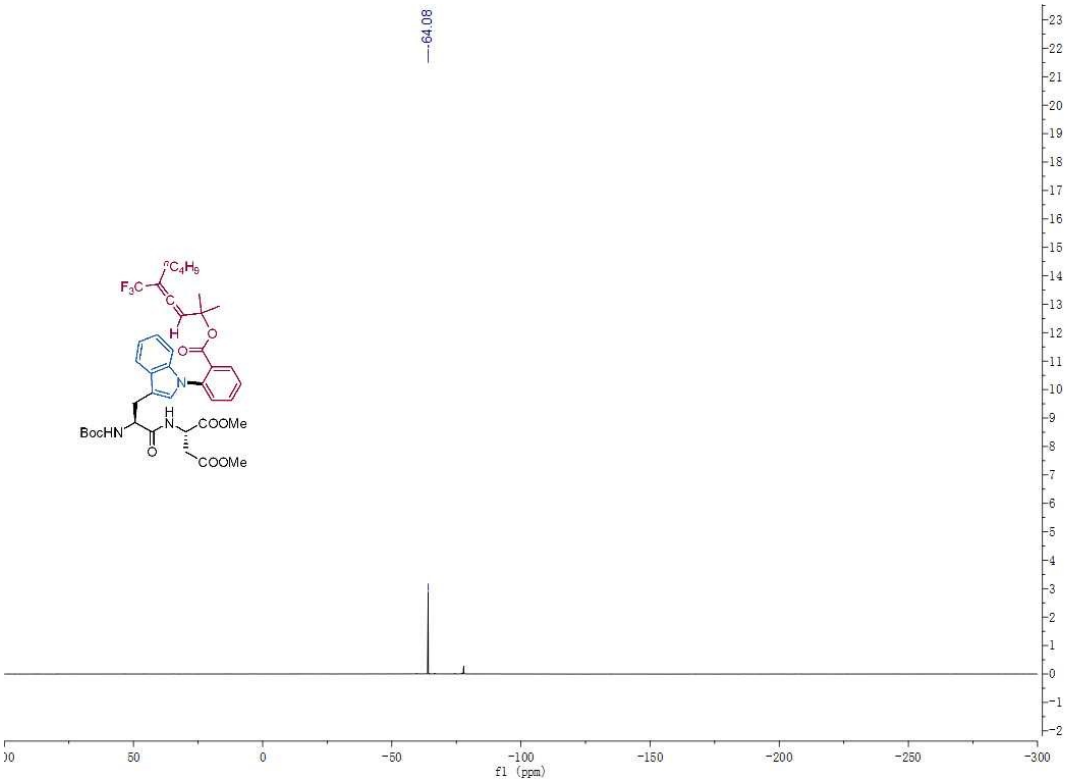


Fig 21. ^{19}F NMR of (**3g**)

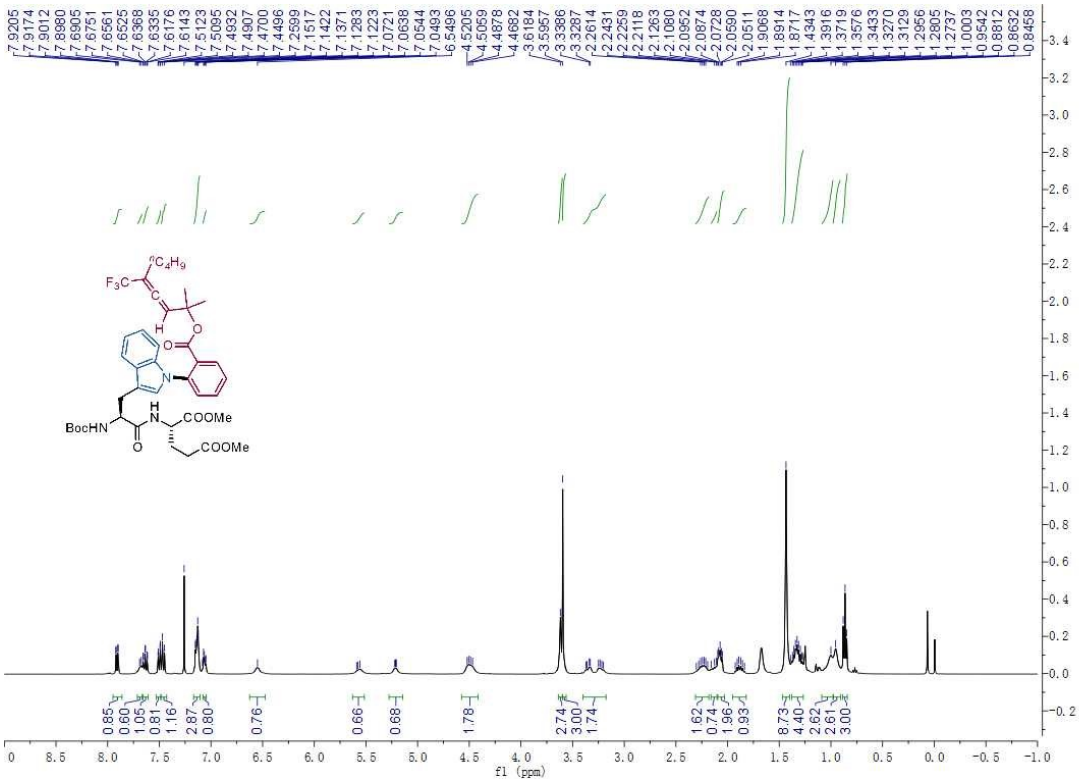


Fig 22. ^{1}H NMR of (**3h**)

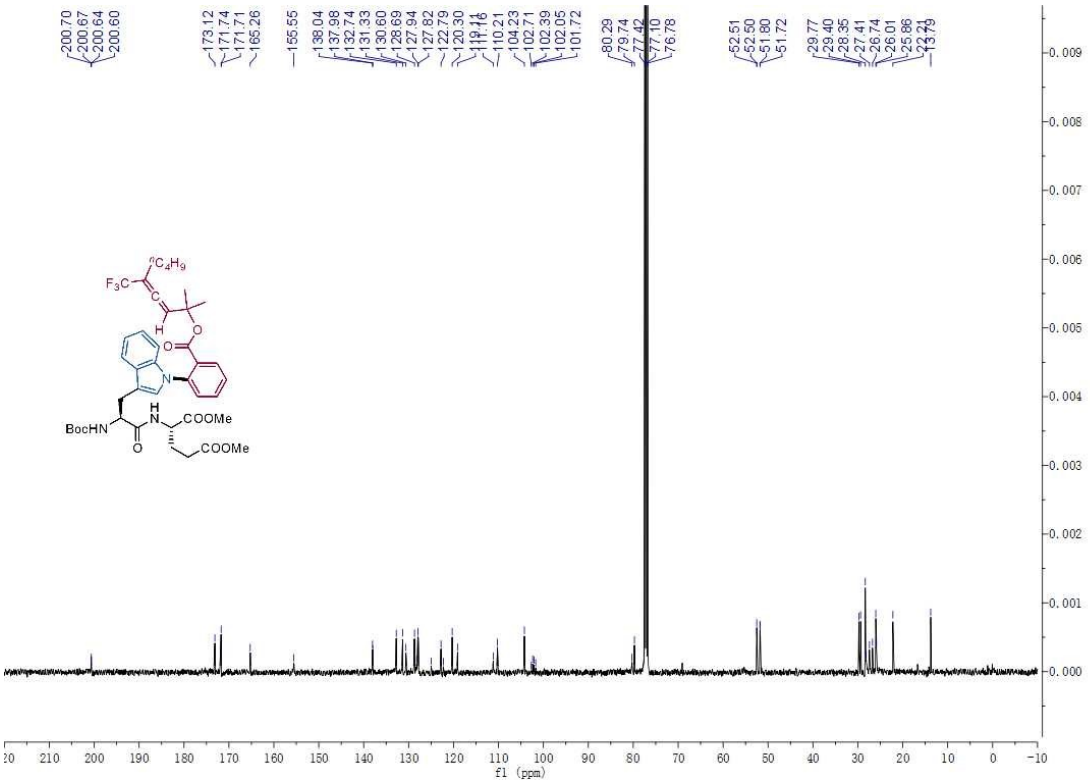


Fig 23. ^{13}C NMR of (**3h**)

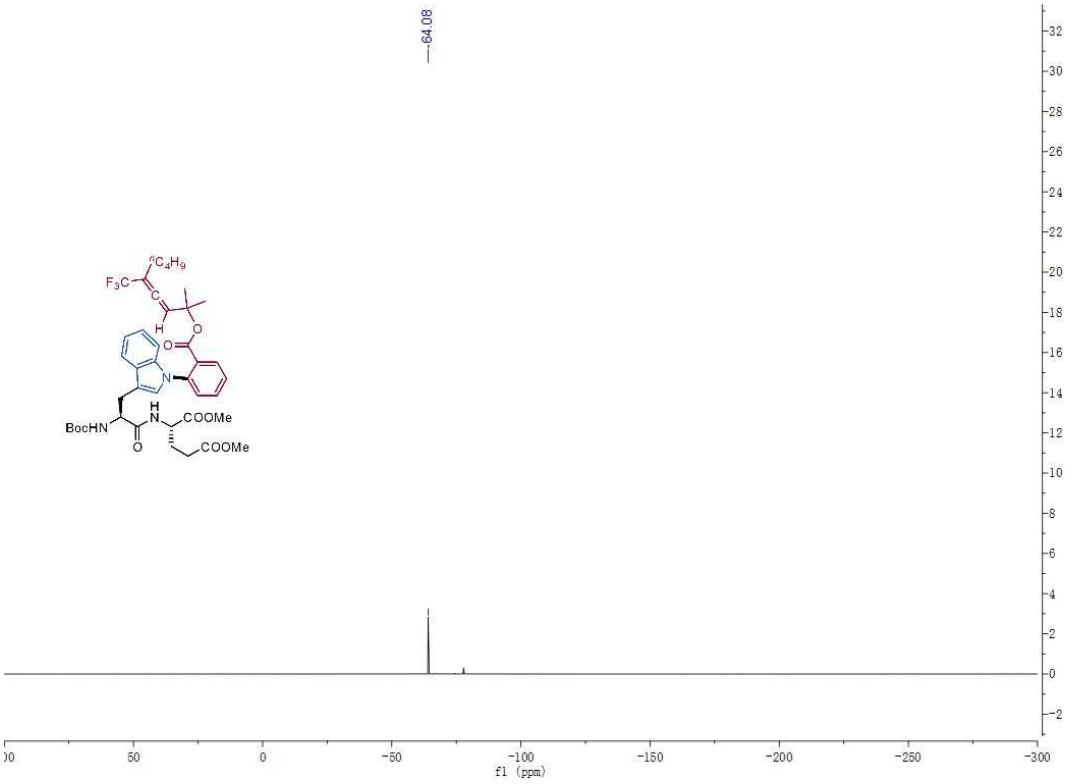


Fig 24. ^{19}F NMR of (**3h**)

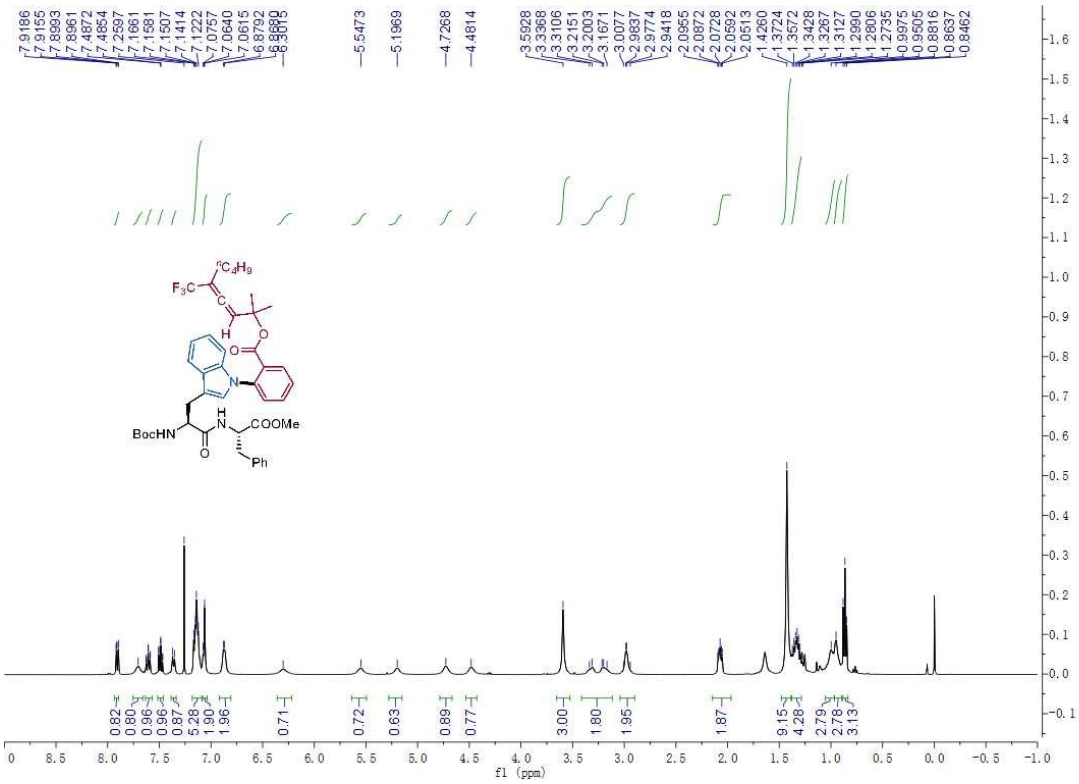


Fig 25. ^{1}H NMR of (**3i**)

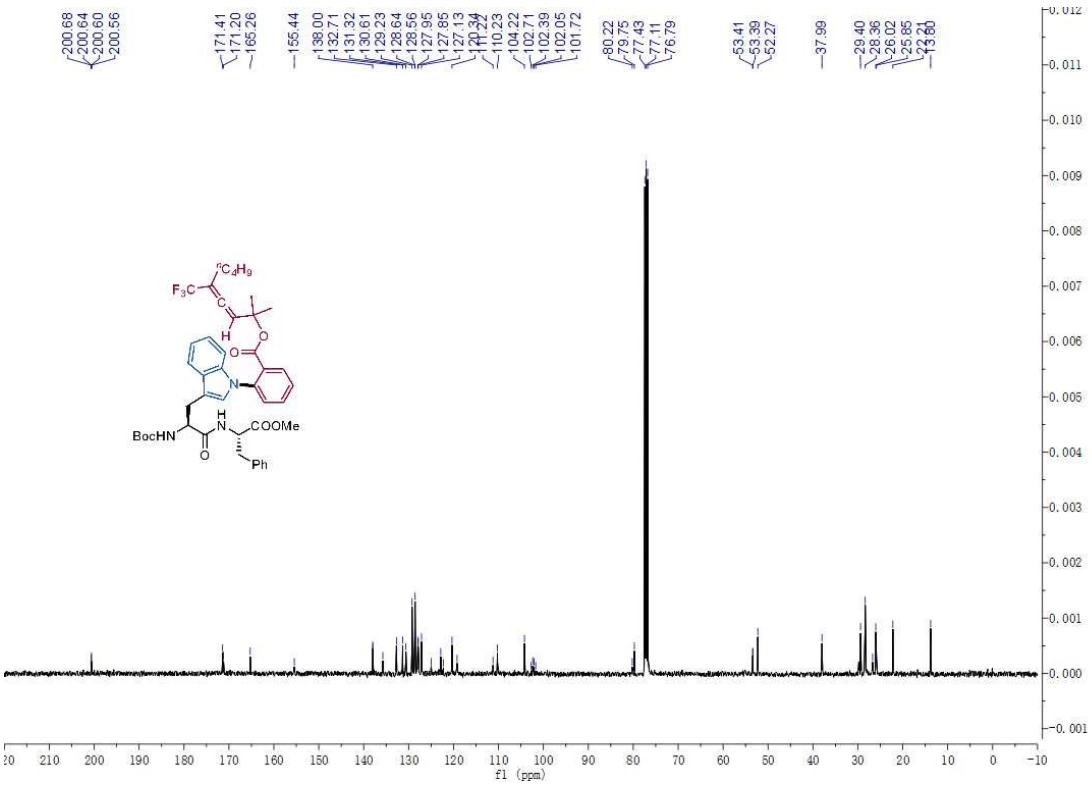


Fig 26. ^{13}C NMR of (**3i**)

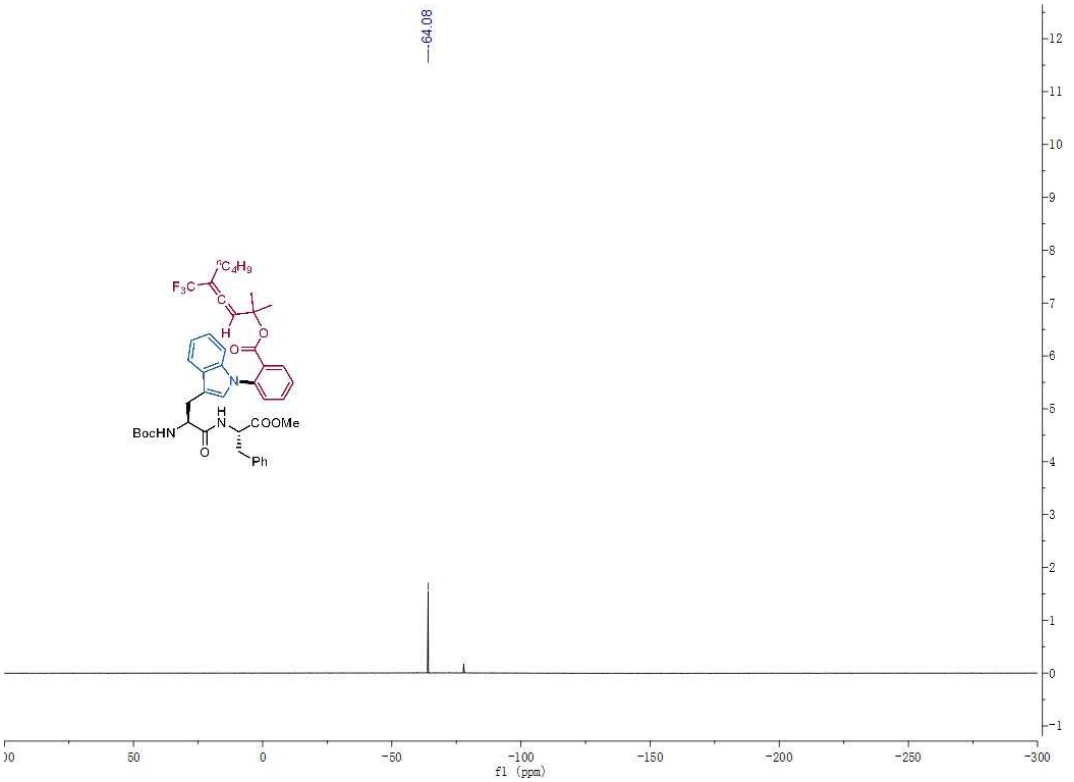


Fig 27. ^{19}F NMR of (**3i**)

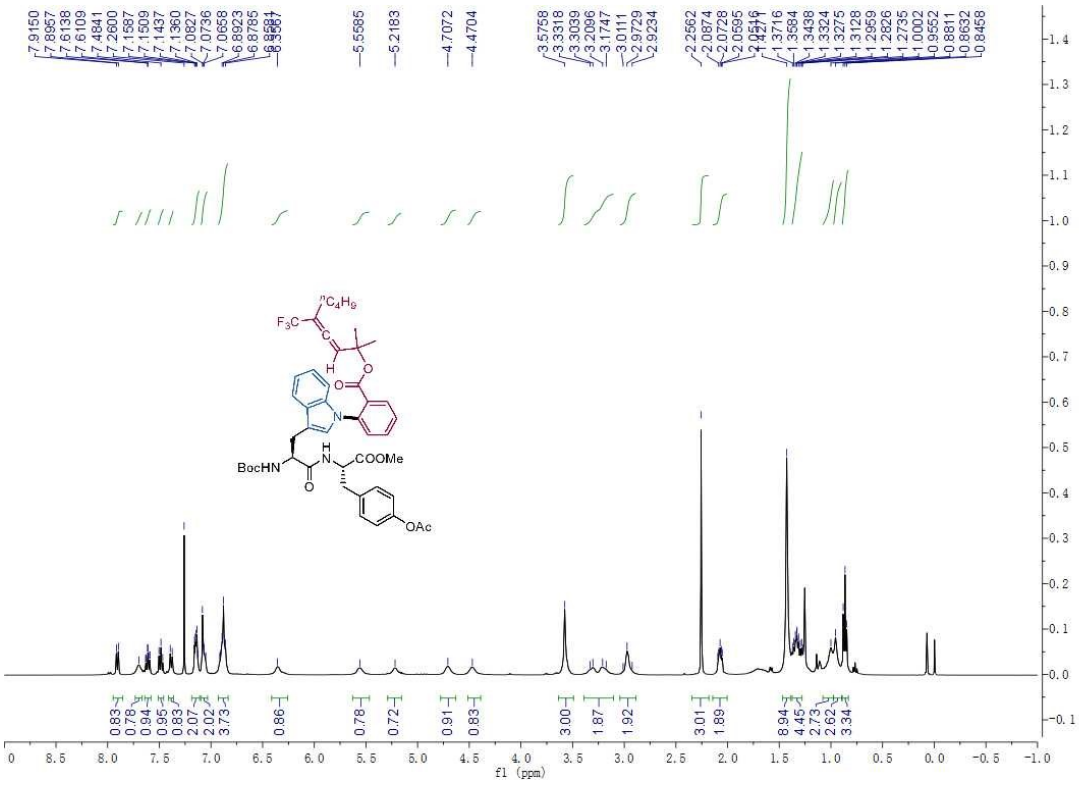


Fig 28. ^{1}H NMR of (**3j**)

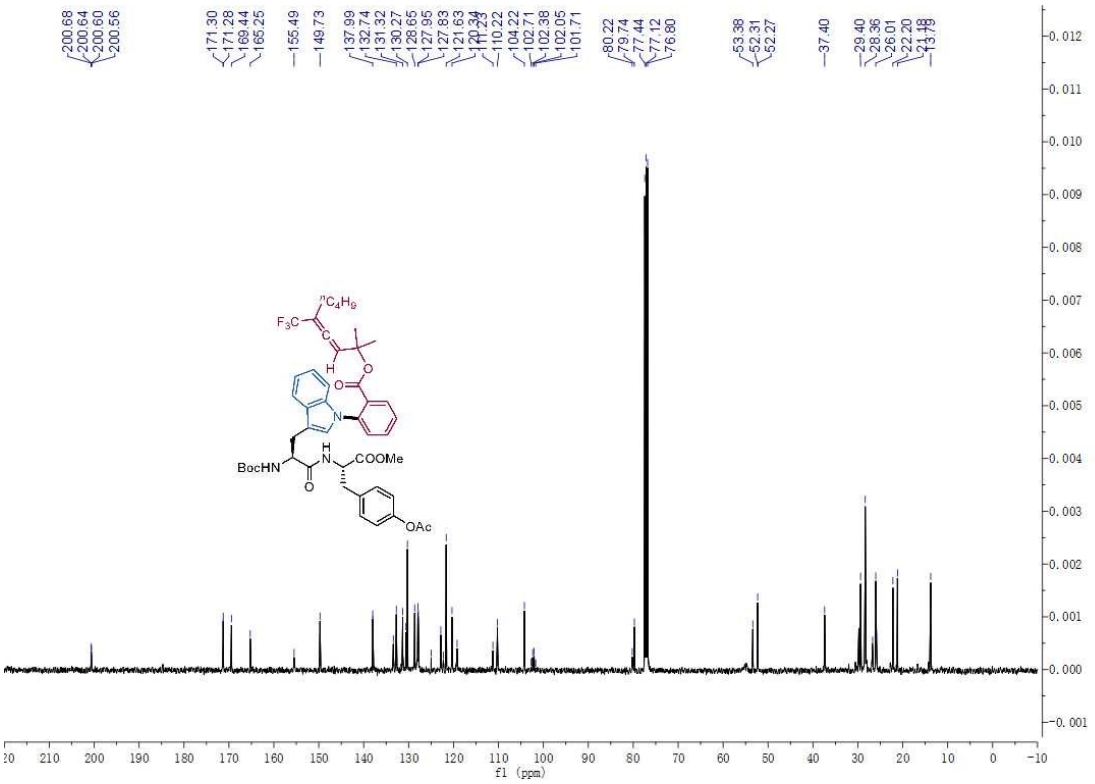


Fig 29. ^{13}C NMR of (**3j**)

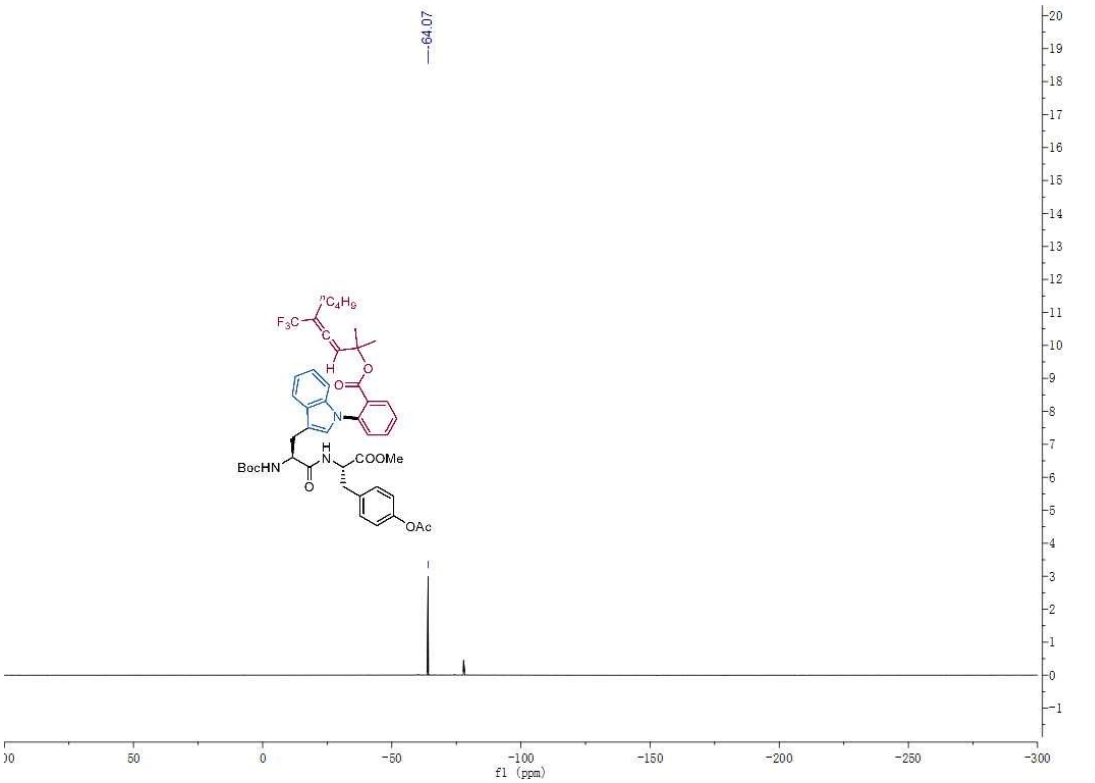


Fig 30. ^{19}F NMR of (**3j**)

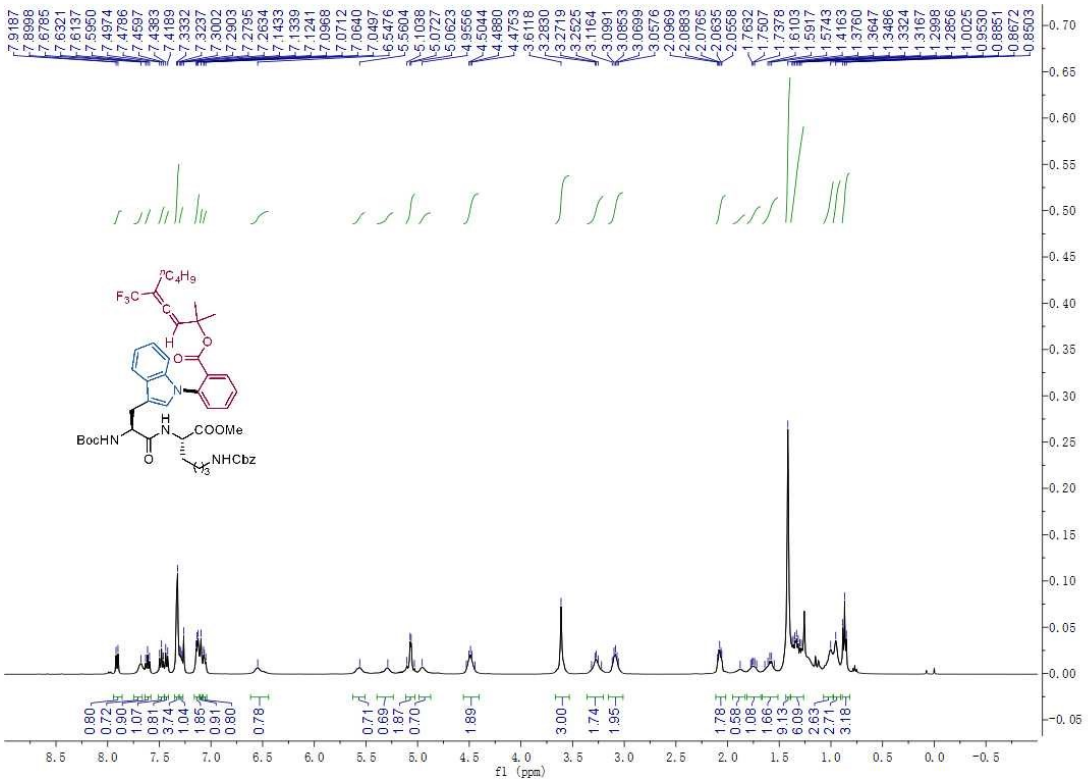


Fig 31. ^{1}H NMR of (**3k**)

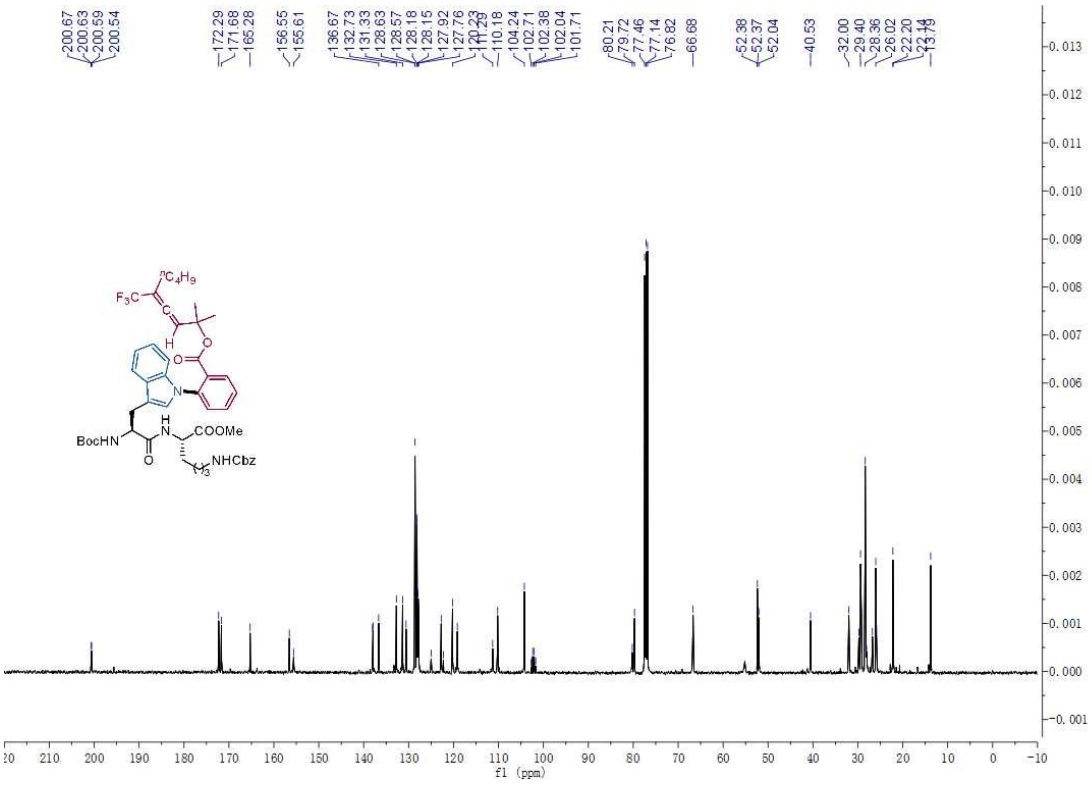


Fig 32. ^{13}C NMR of (**3k**)

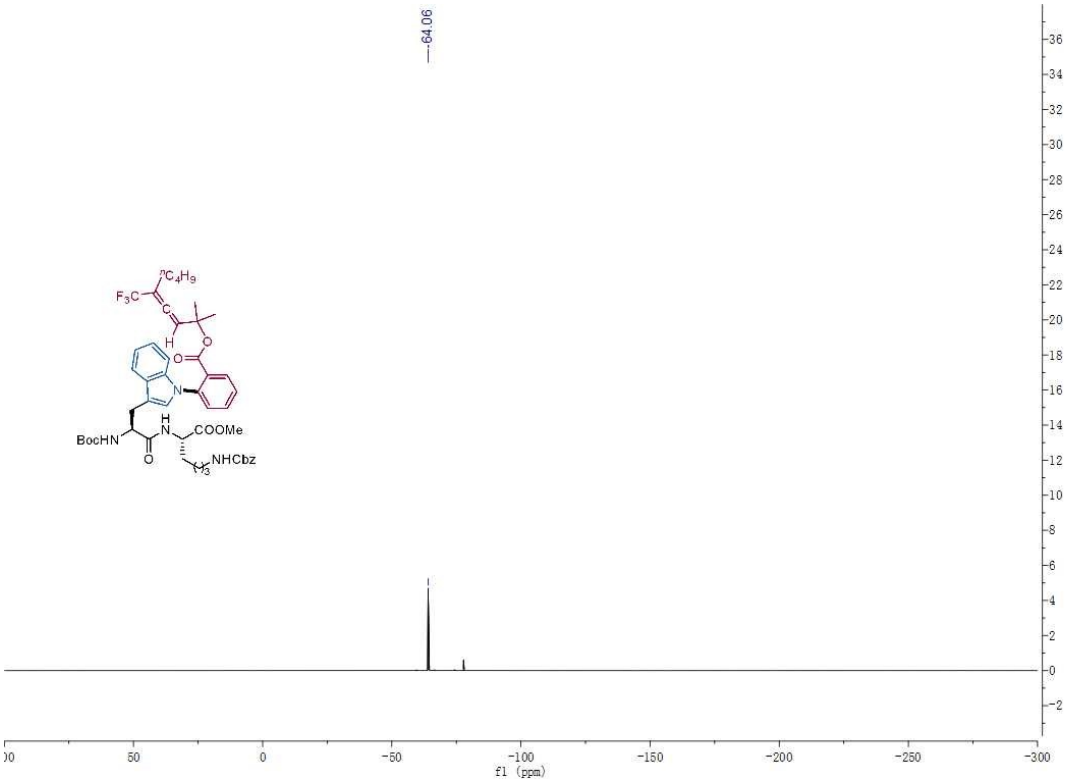


Fig 33. ^{19}F NMR of (**3k**)

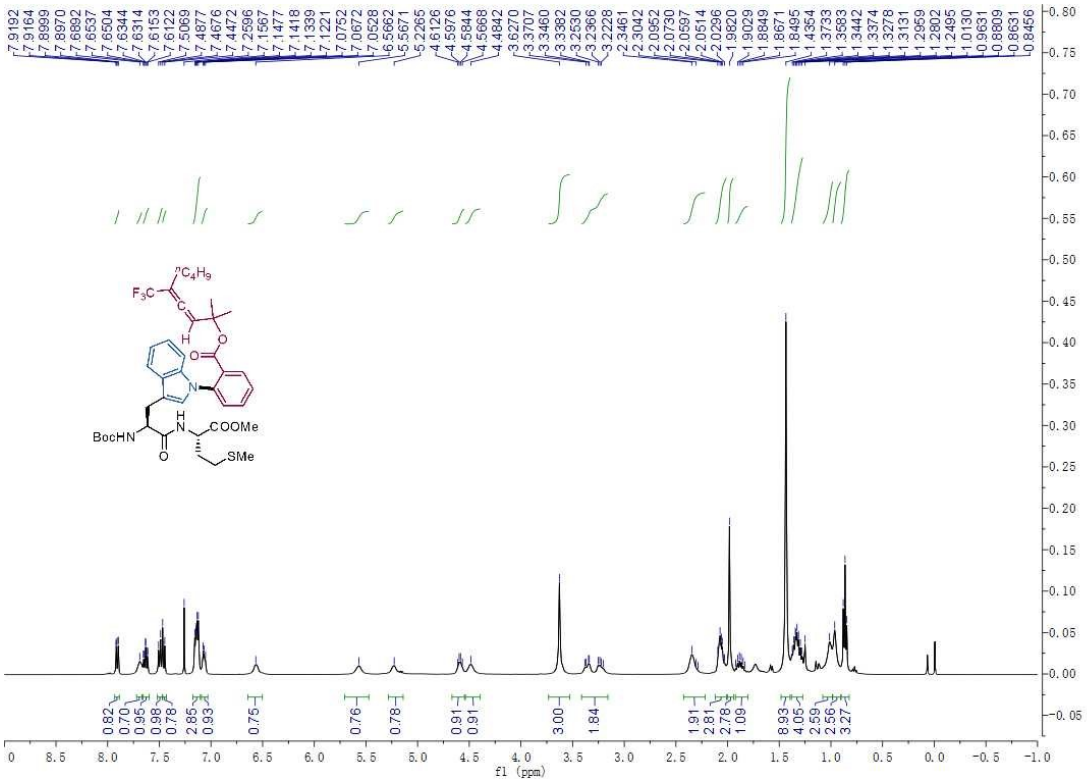


Fig 34. ^{1}H NMR of (**3l**)

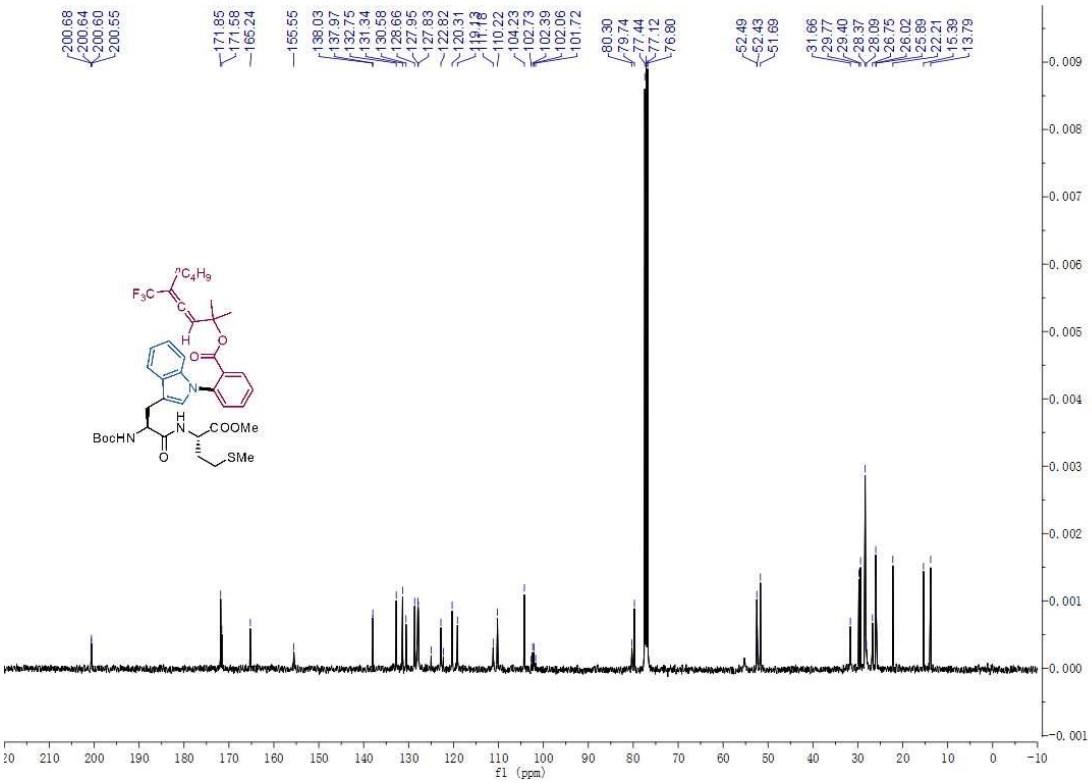


Fig 35. ^{13}C NMR of (**3l**)

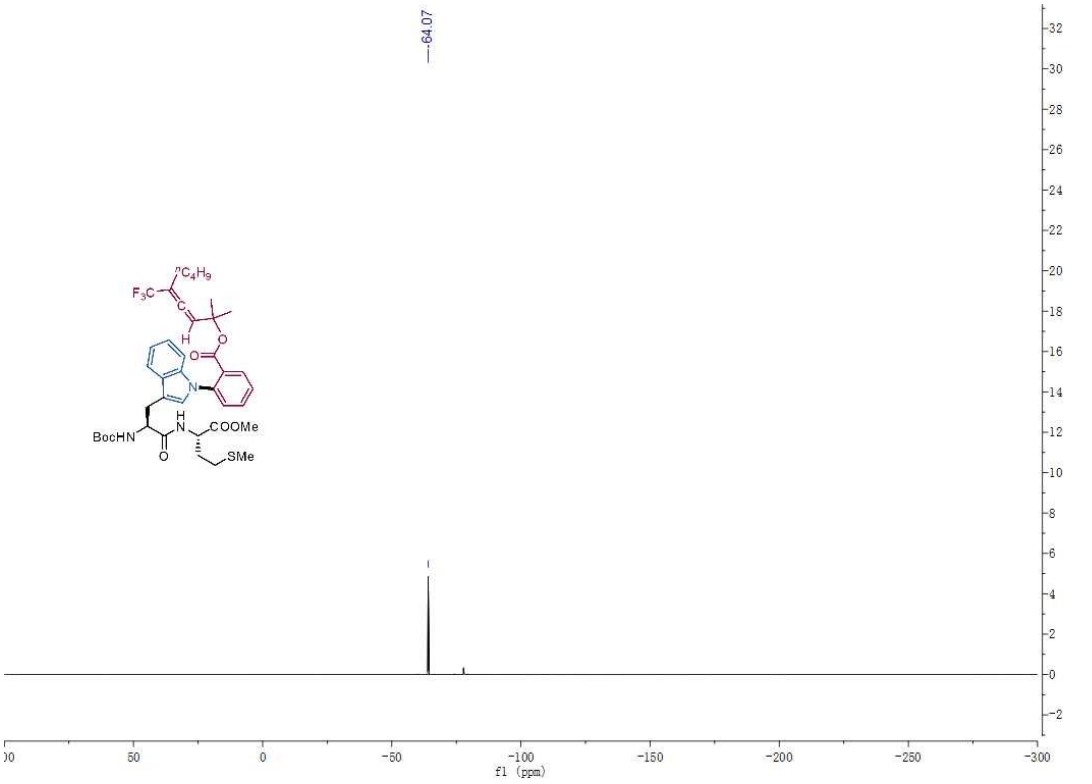


Fig 36. ^{19}F NMR of (**3l**)

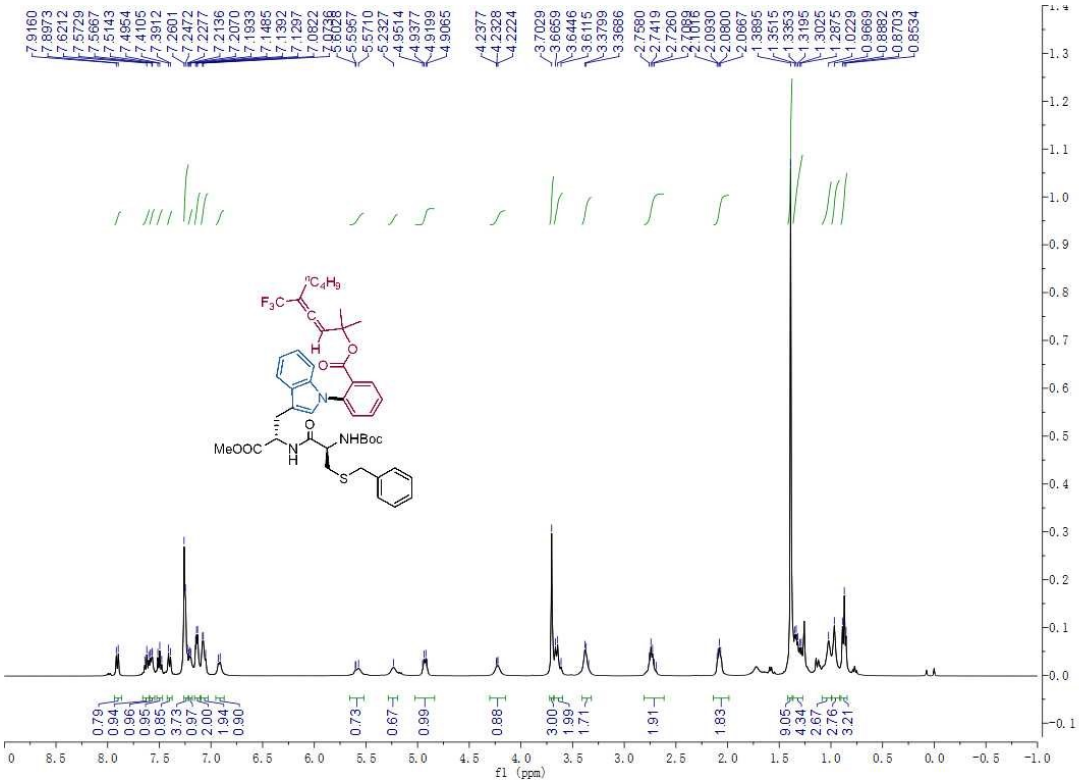


Fig 37. ^{1}H NMR of (**3m**)

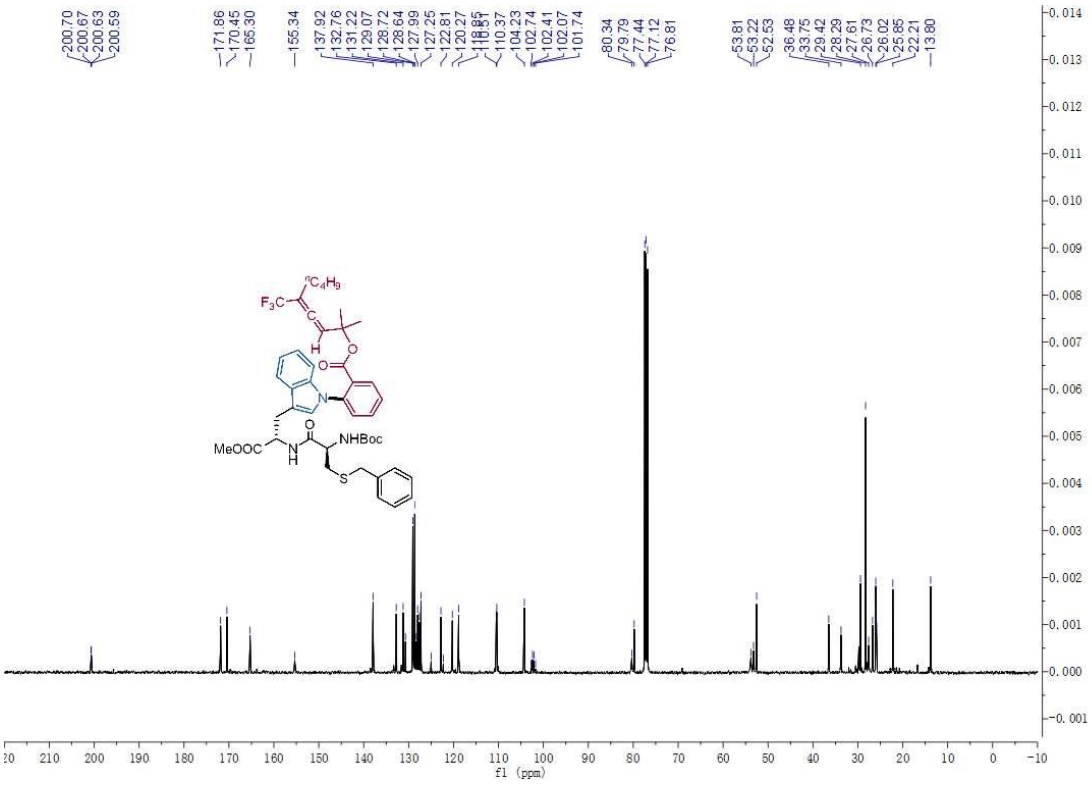


Fig 38. ^{13}C NMR of (**3m**)

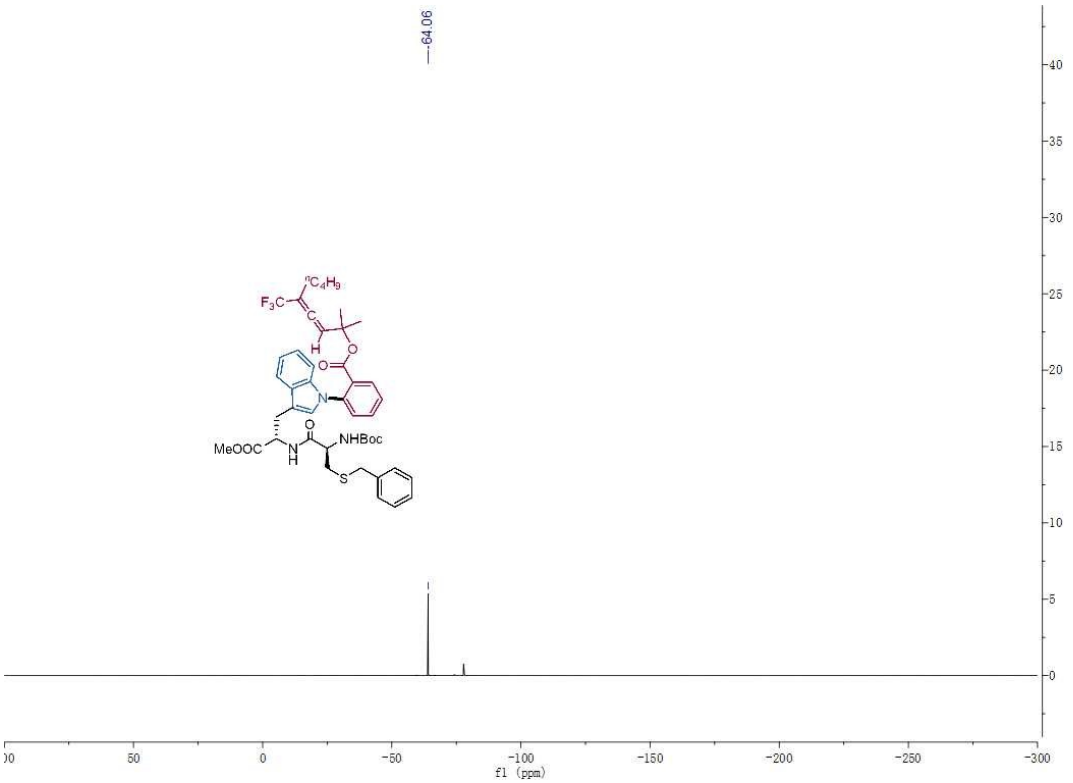


Fig 39. ^{19}F NMR of (**3m**)

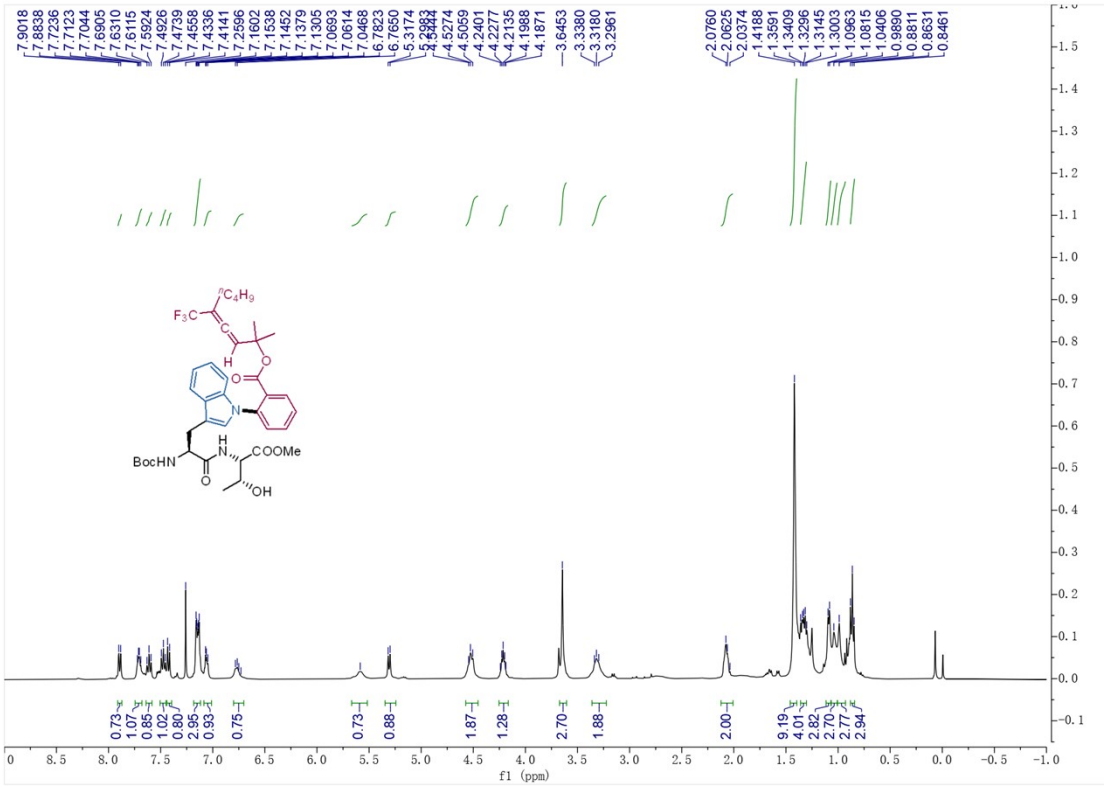


Fig 40. ^{1}H NMR of (**3n**)

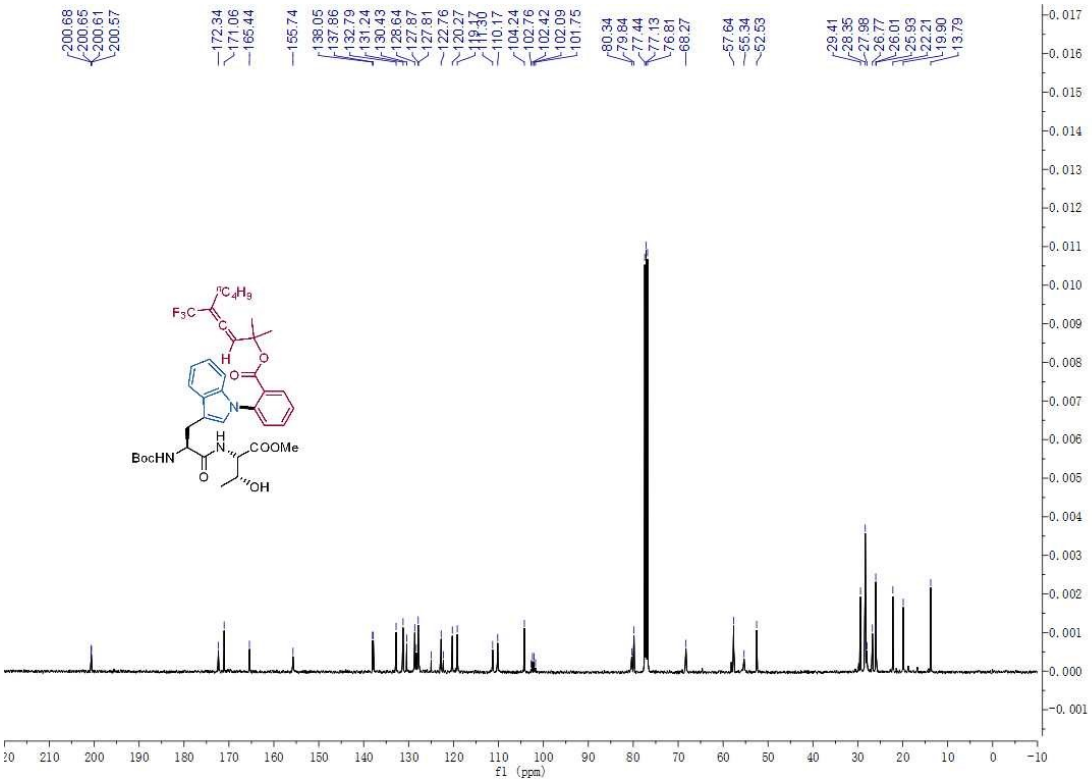


Fig 41. ^{13}C NMR of (**3n**)

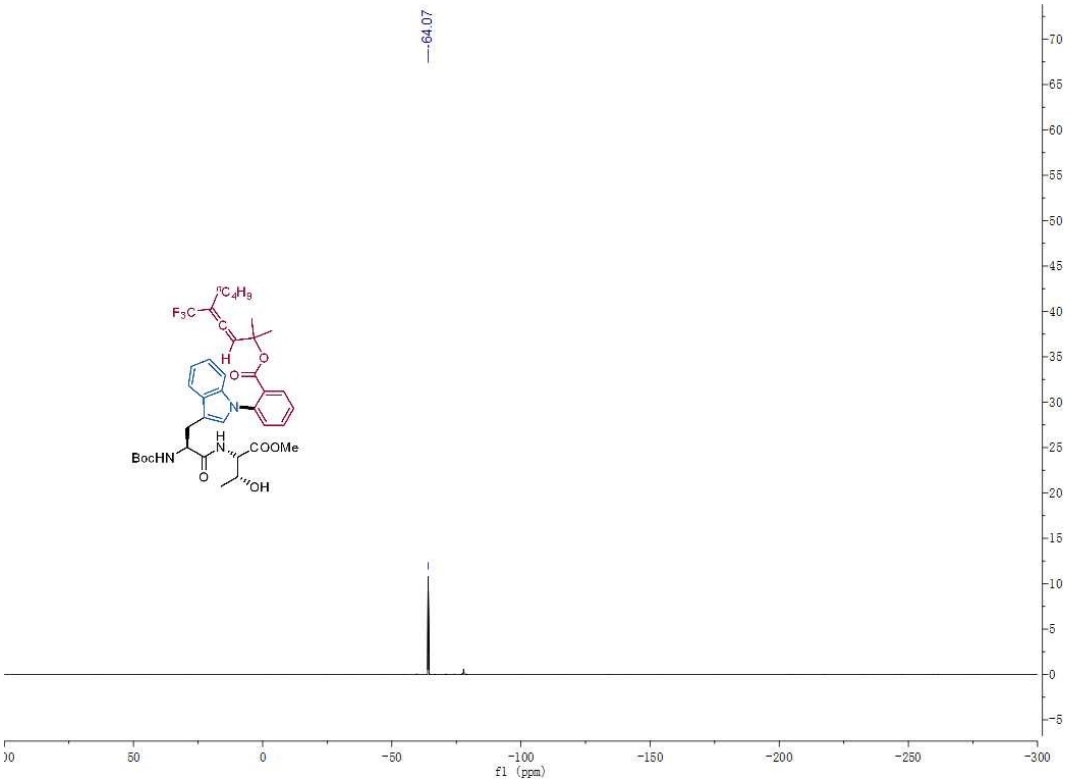


Fig 42. ^{19}F NMR of (**3n**)

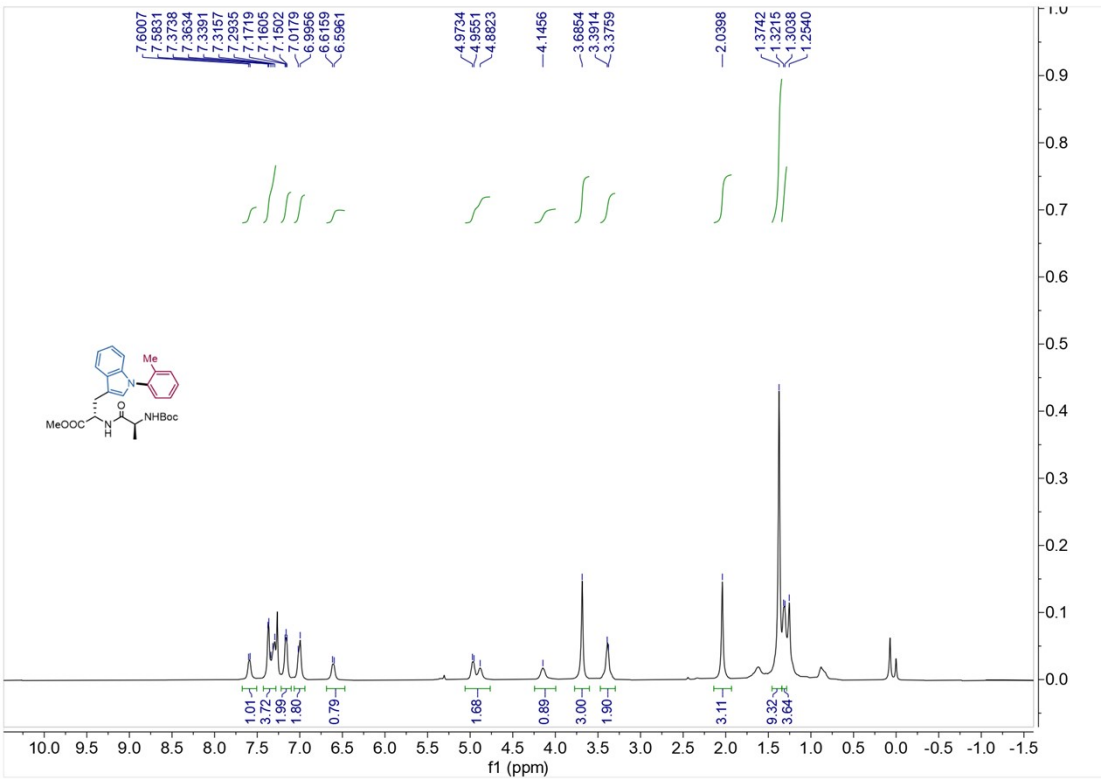


Fig 43. ^{1}H NMR of (**3o**)

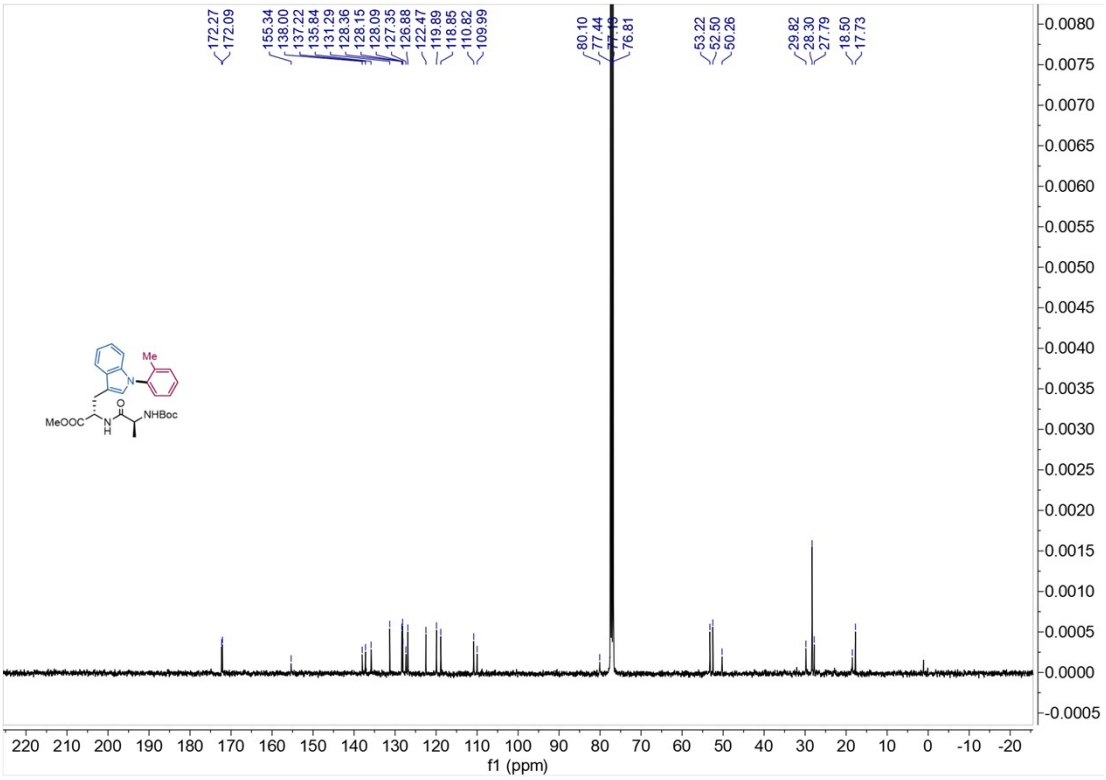


Fig 44. ^{13}C NMR of (**3o**)

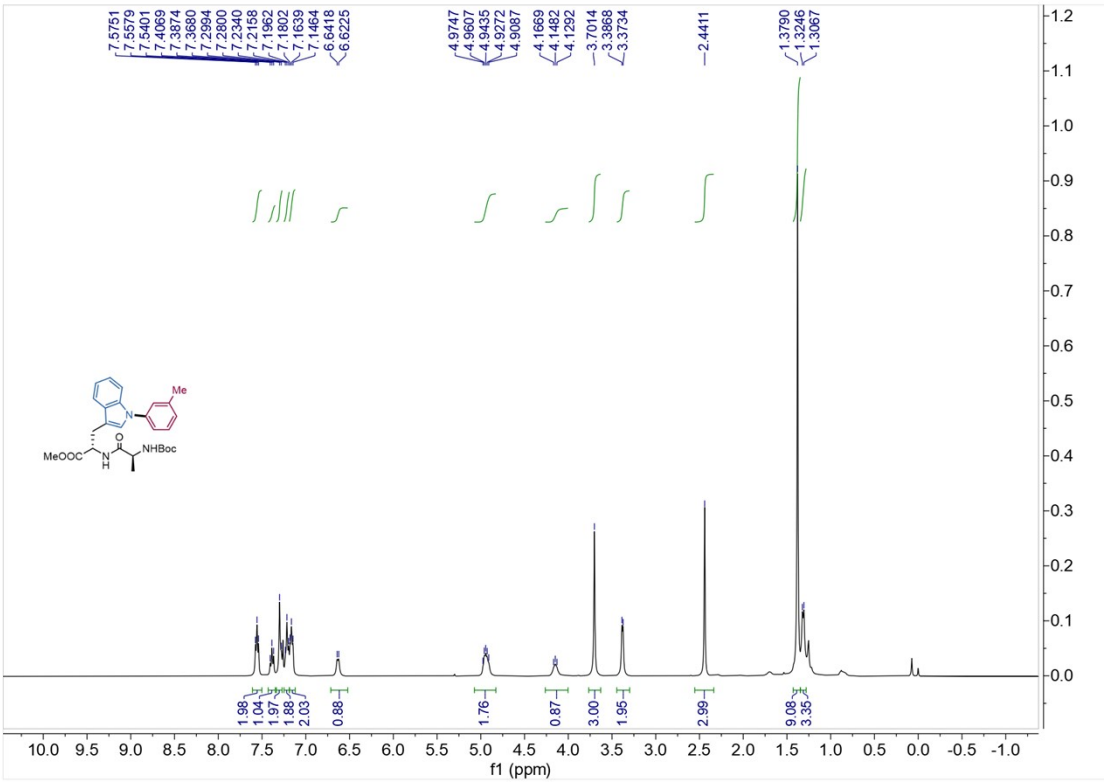


Fig 45. ^{1}H NMR of (**3p**)

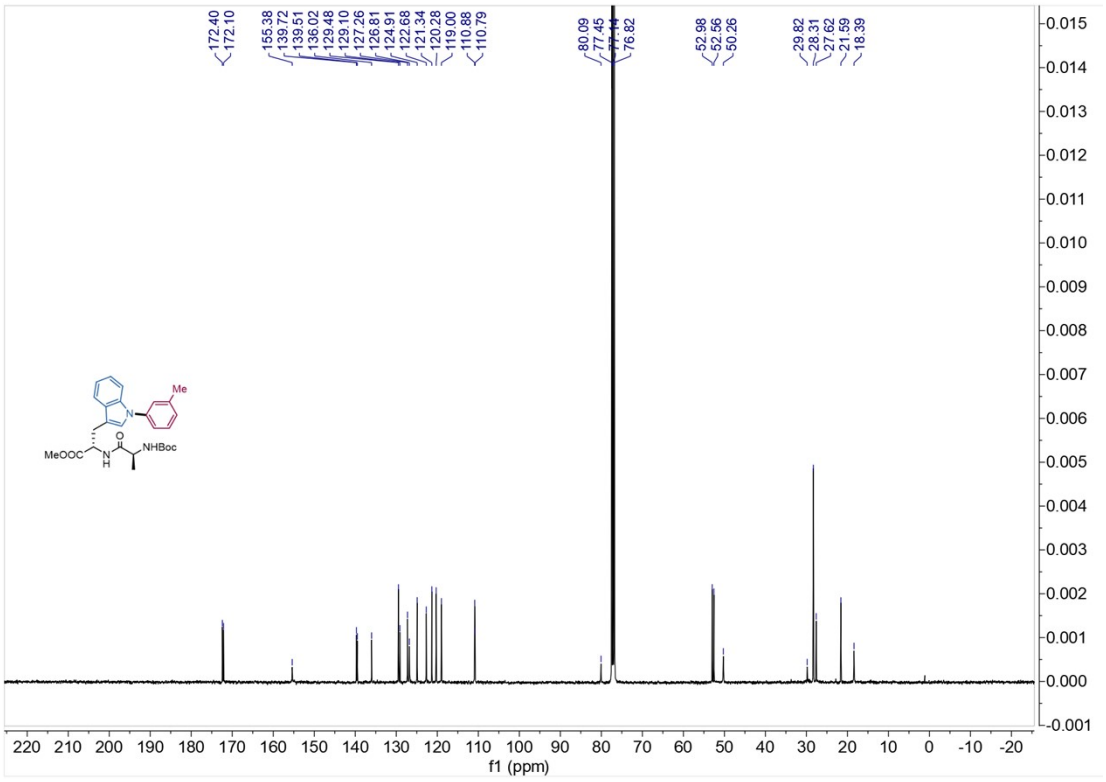


Fig 46. ^{13}C NMR of (**3p**)

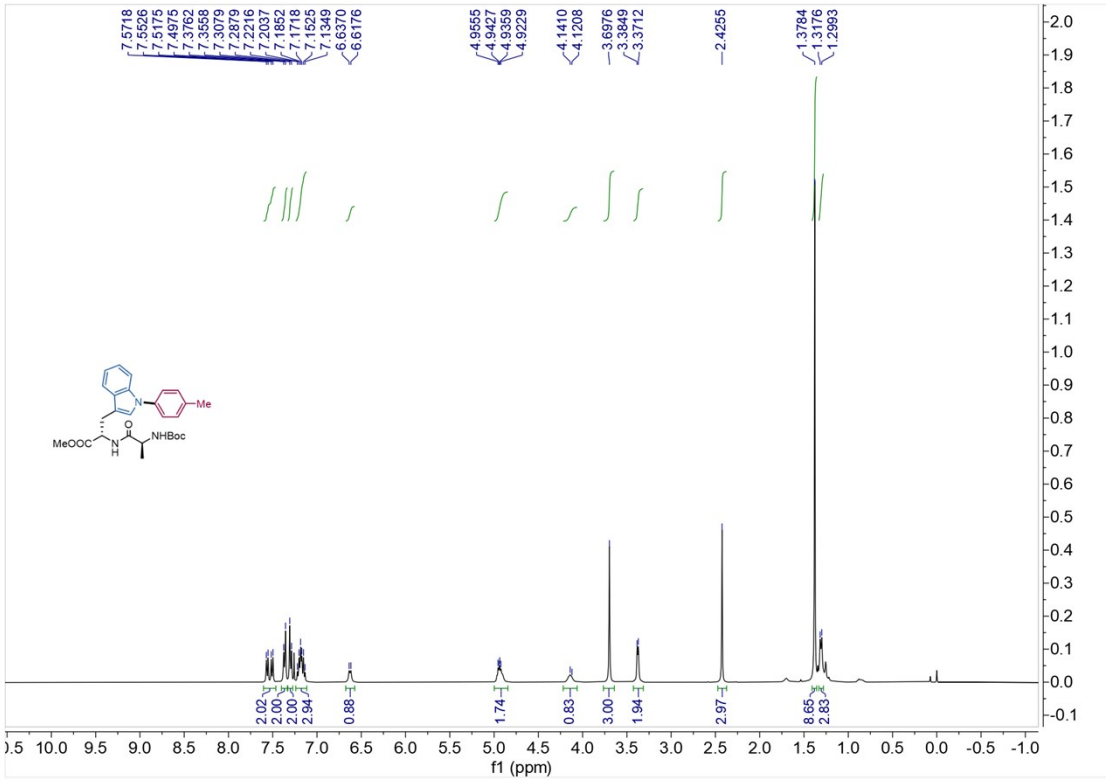


Fig 47. ^{1}H NMR of (**3q**)

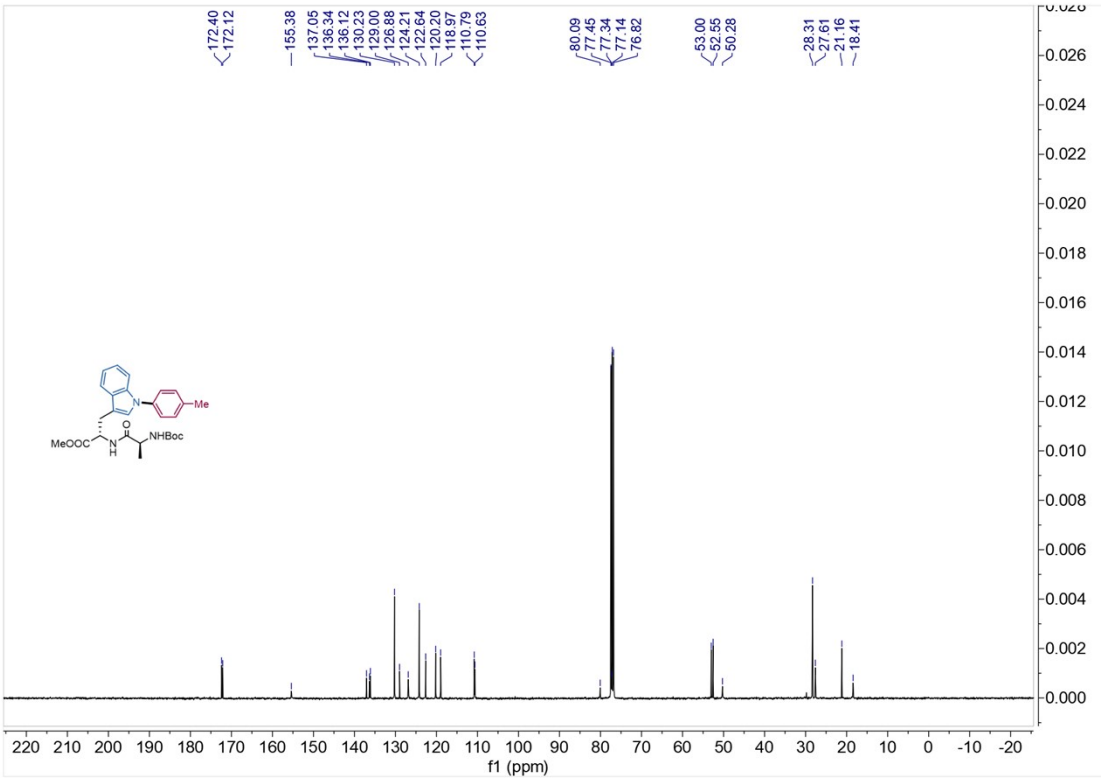


Fig 48. ^{13}C NMR of (**3q**)

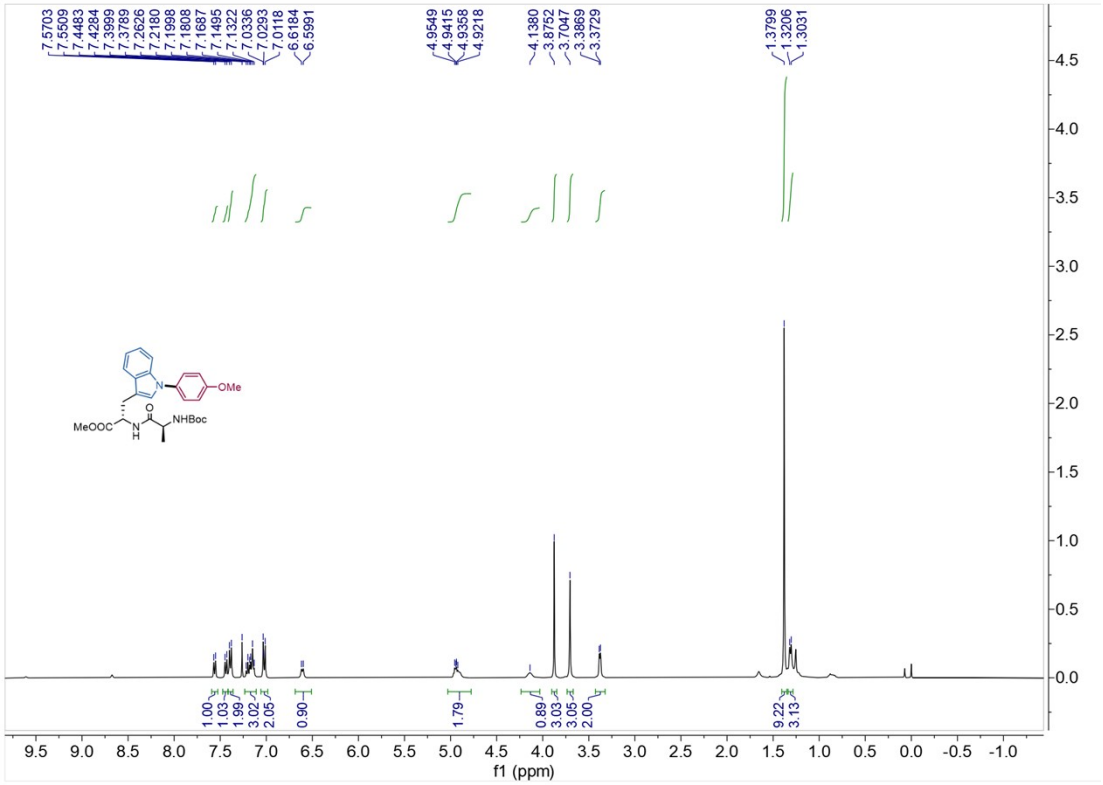


Fig 49. ^{1}H NMR of (**3r**)

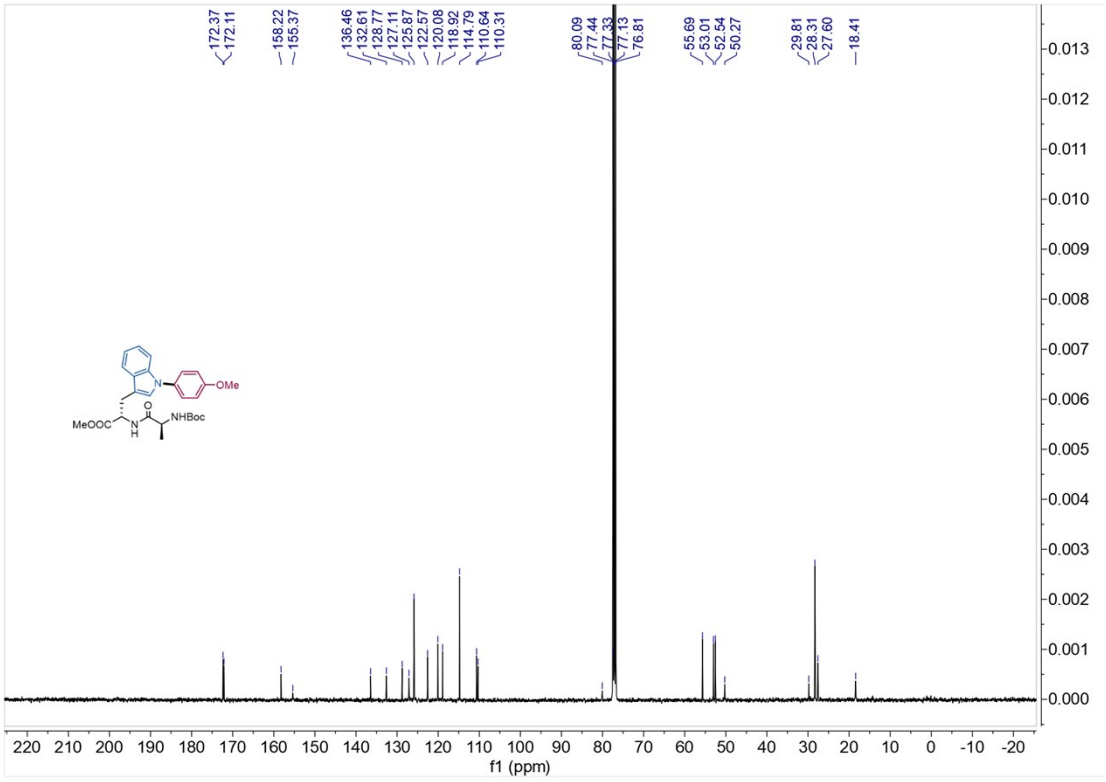


Fig 50. ^{13}C NMR of (**3r**)

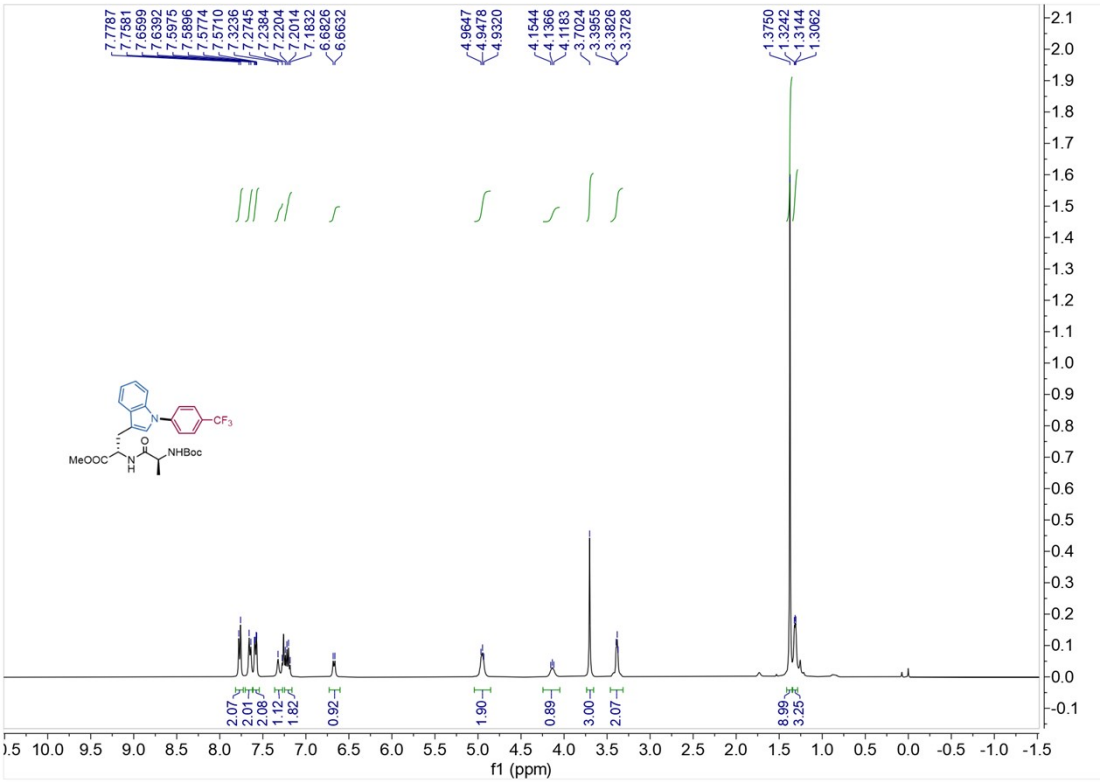


Fig 51. ^{1}H NMR of (**3s**)

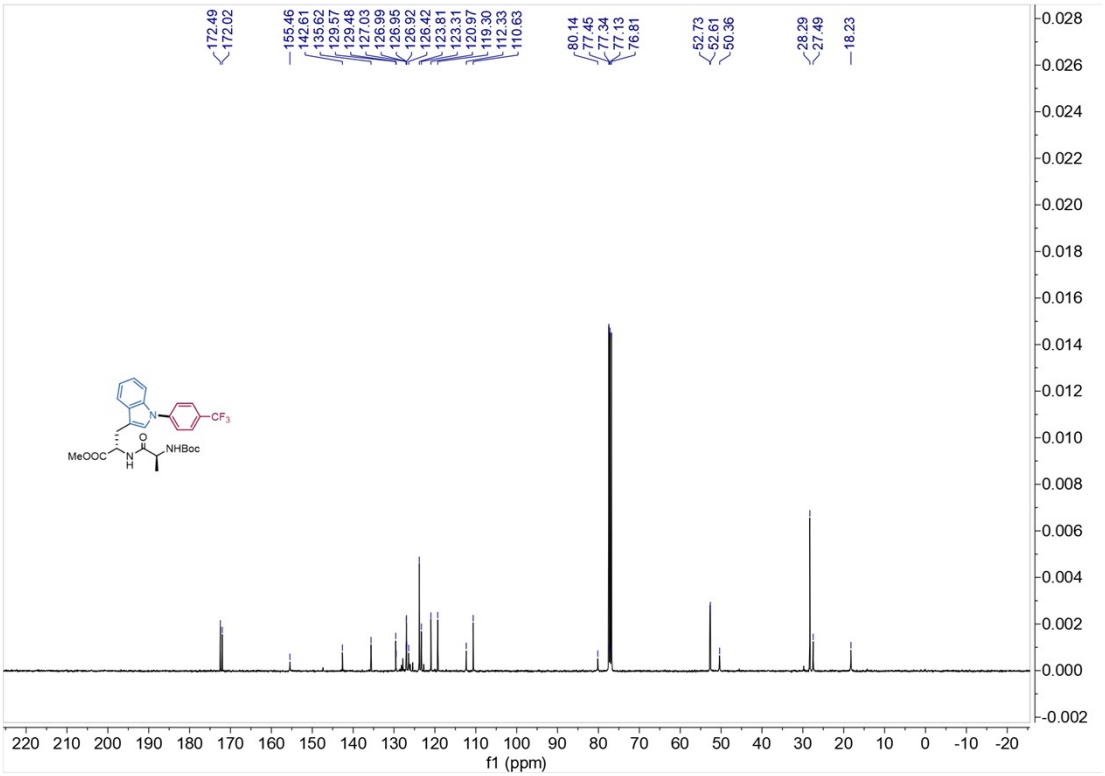


Fig 52. ^{13}C NMR of (**3s**)

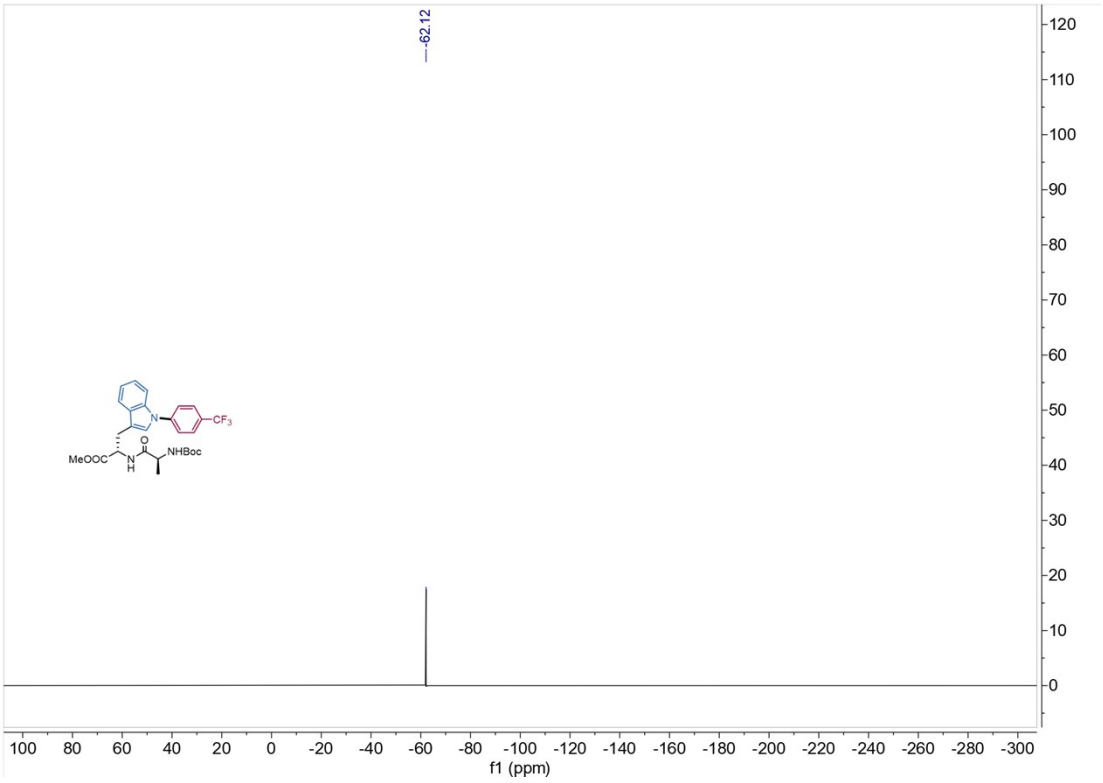


Fig 53. ^{19}F NMR of (**3s**)

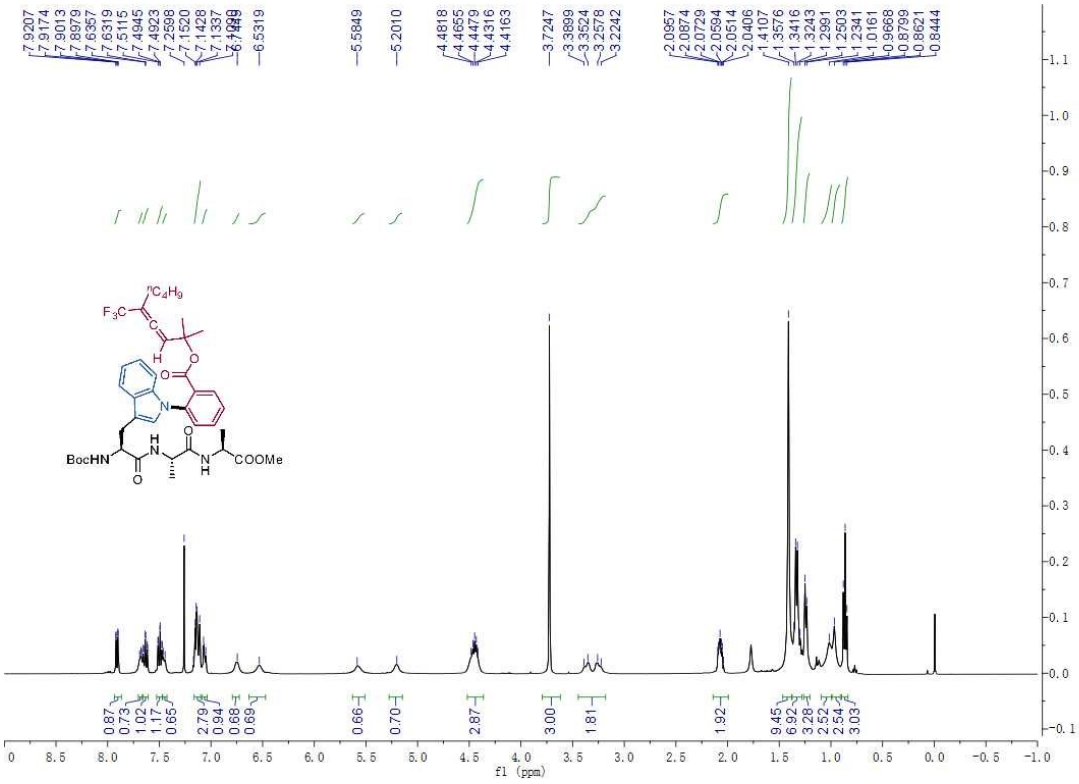


Fig 54. ^{1}H NMR of (**4a**)

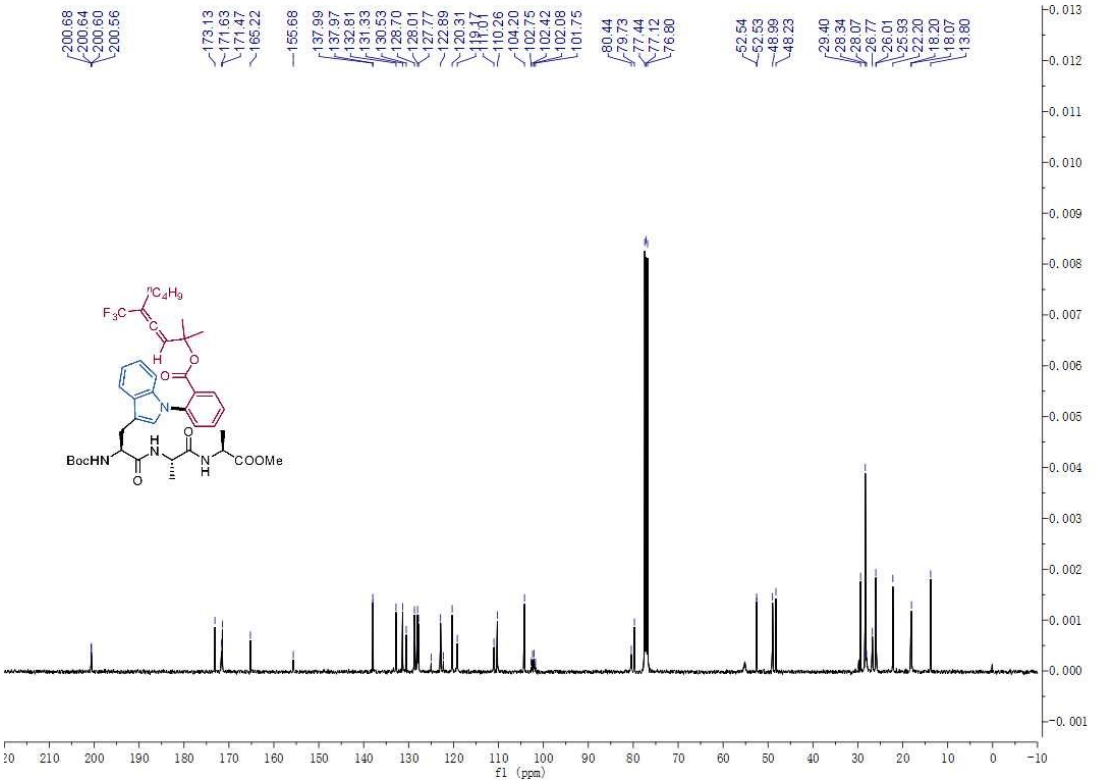


Fig 55. ^{13}C NMR of (**4a**)

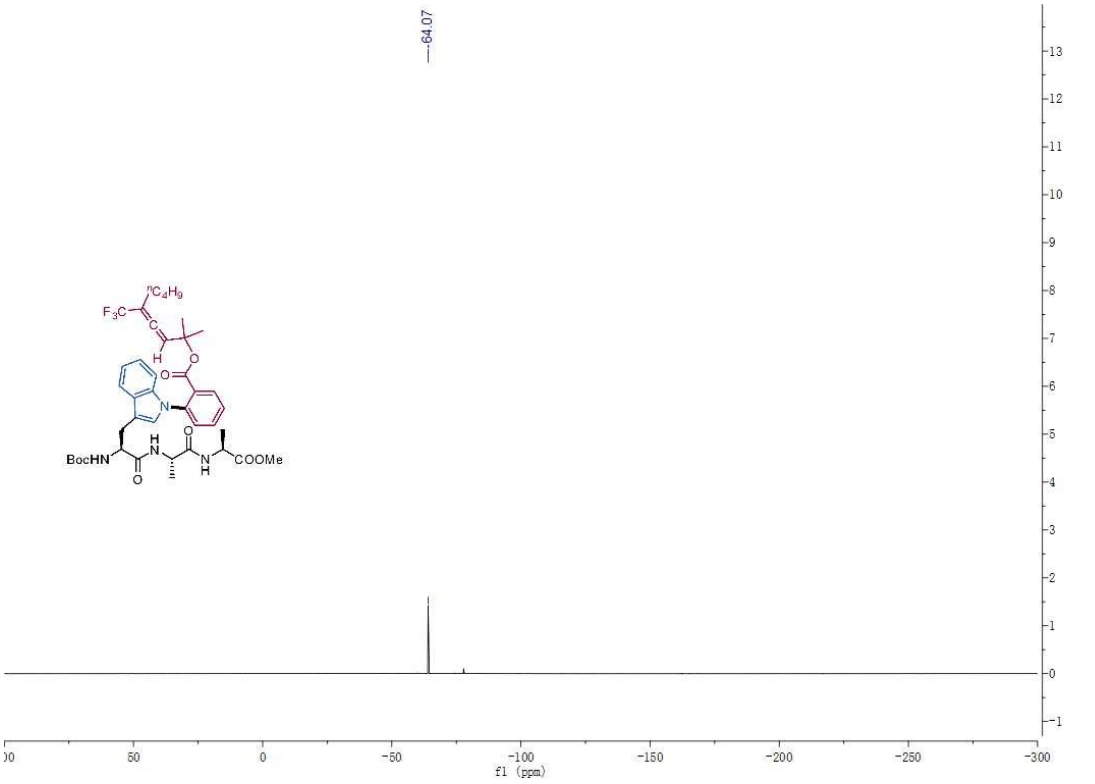


Fig 56. ^{19}F NMR of (**4a**)

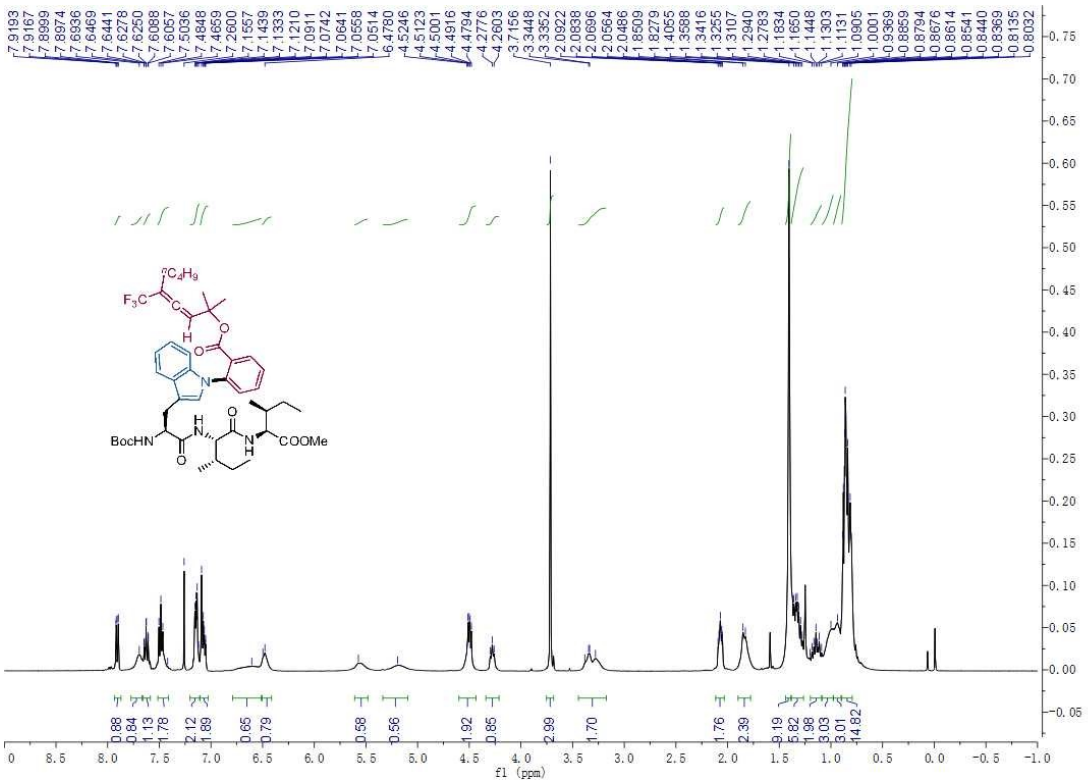


Fig 57. ^{1}H NMR of (**4b**)

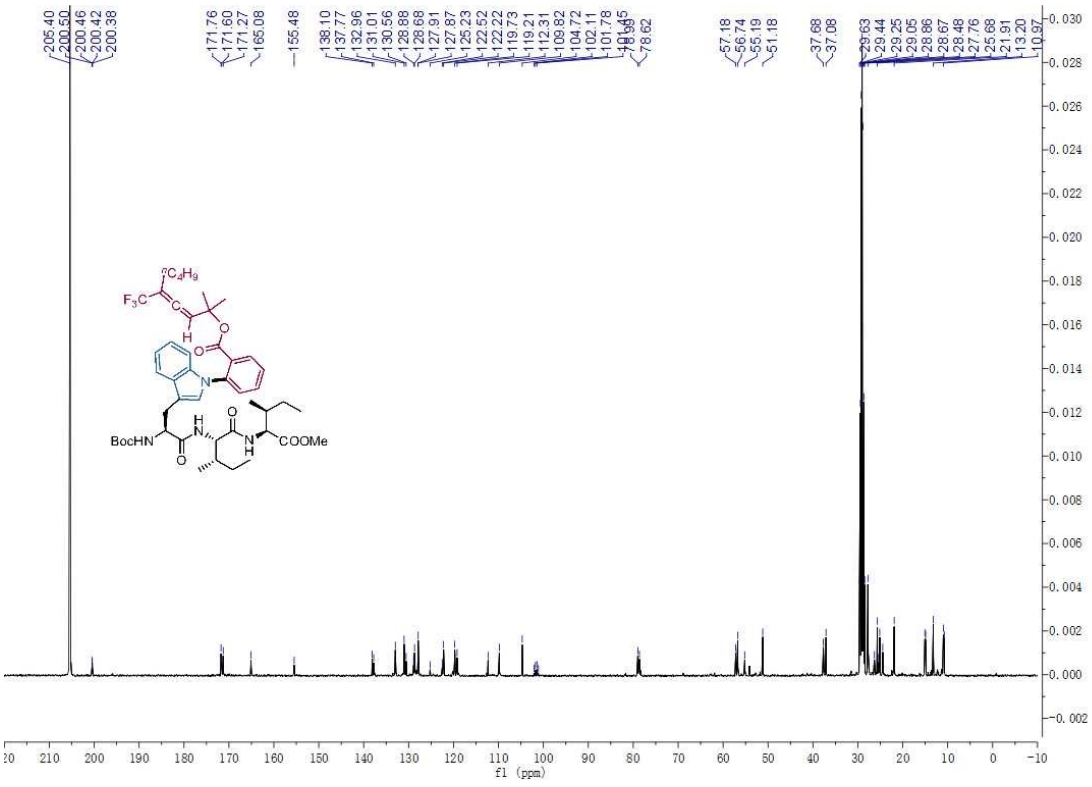


Fig 58. ^{13}C NMR of (**4b**)

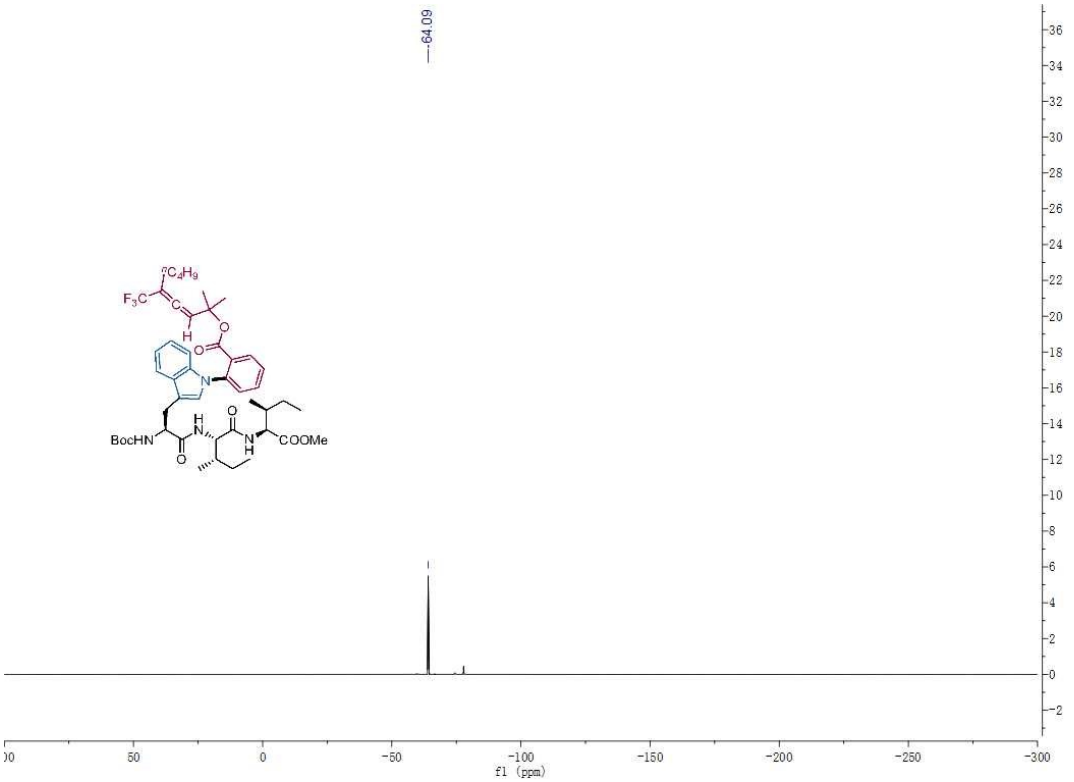


Fig 59. ^{19}F NMR of (**4b**)

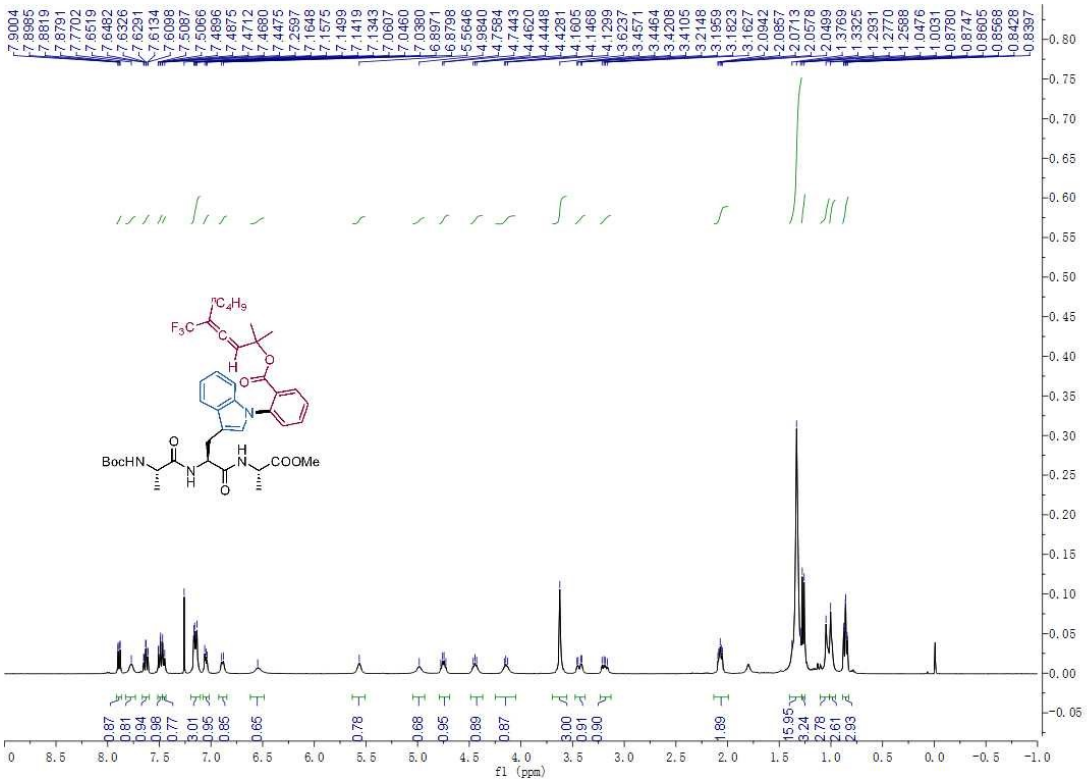


Fig 60. ^{1}H NMR of (**4c**)

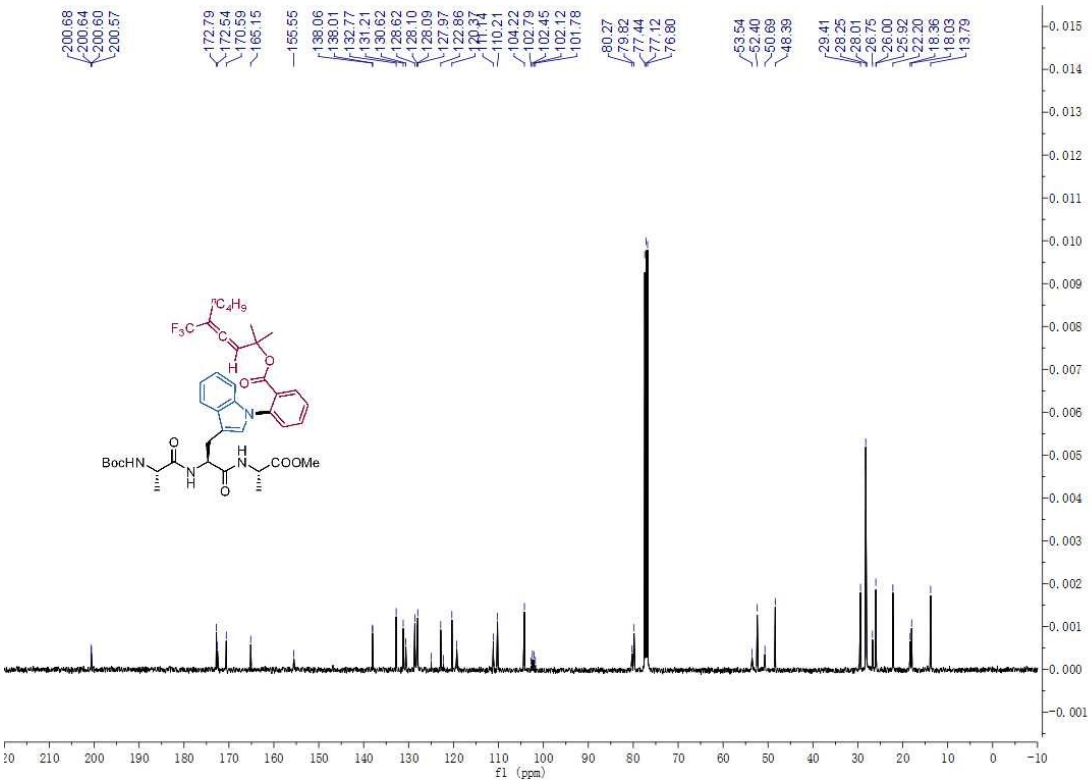


Fig 61. ^{13}C NMR of (**4c**)

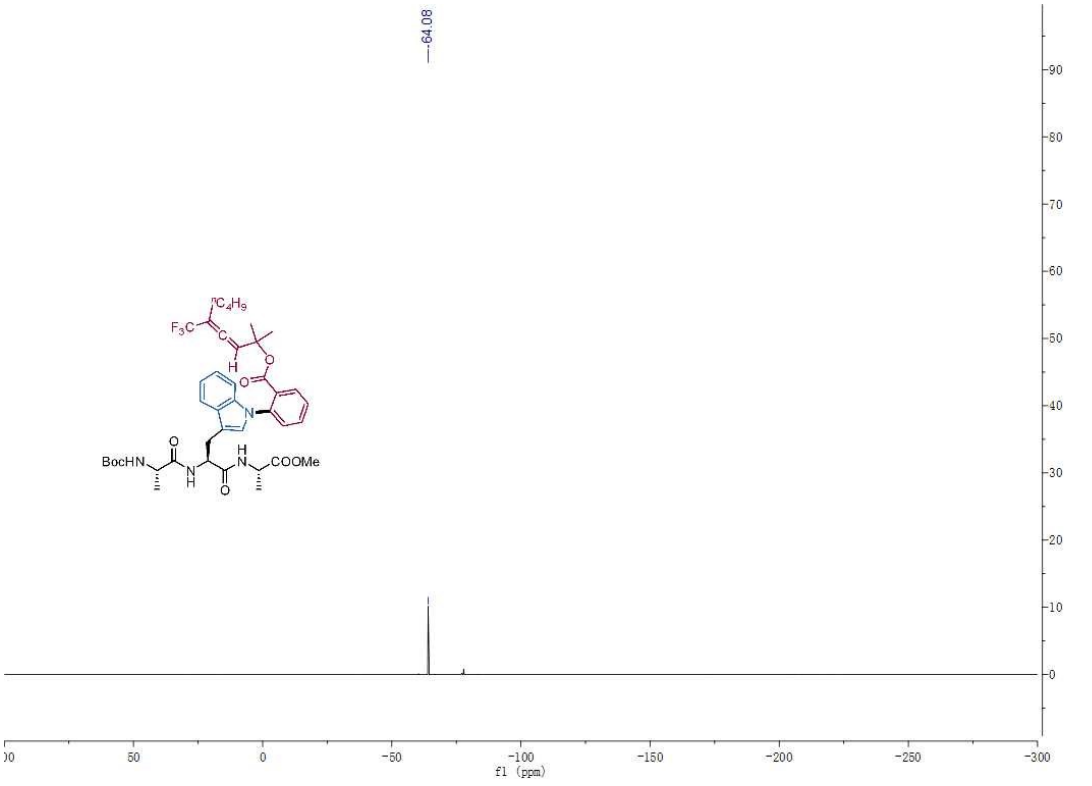


Fig 62. ^{19}F NMR of (**4c**)

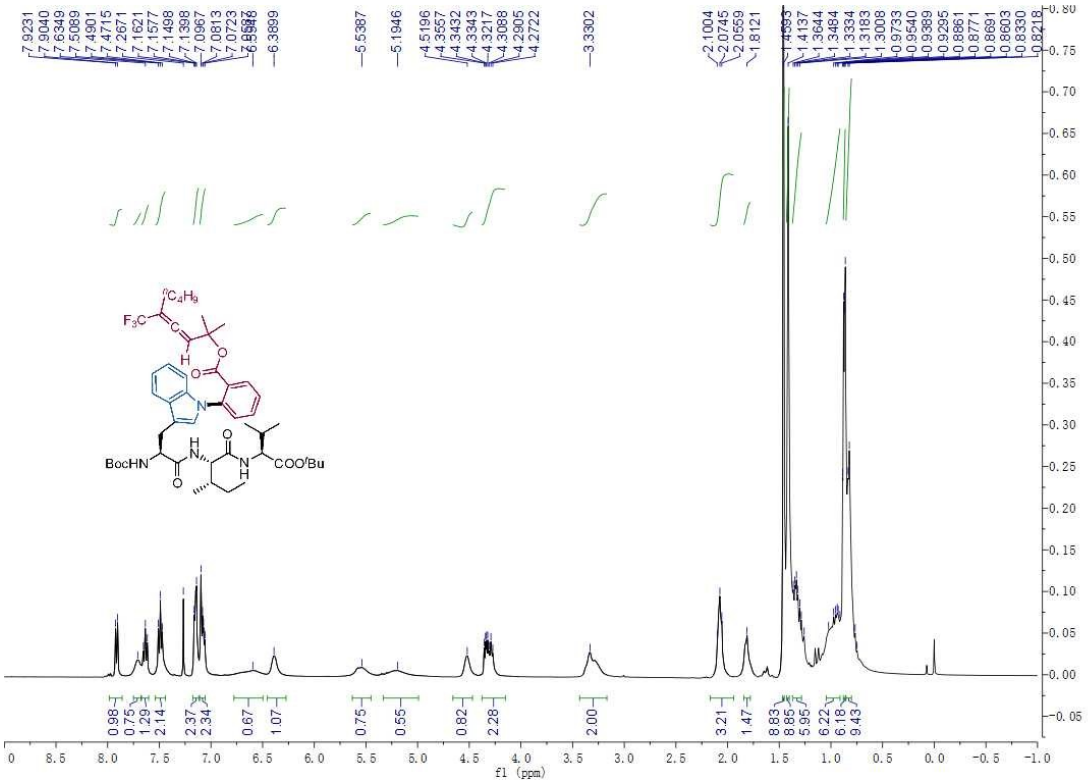


Fig 63. ^{1}H NMR of (**4d**)

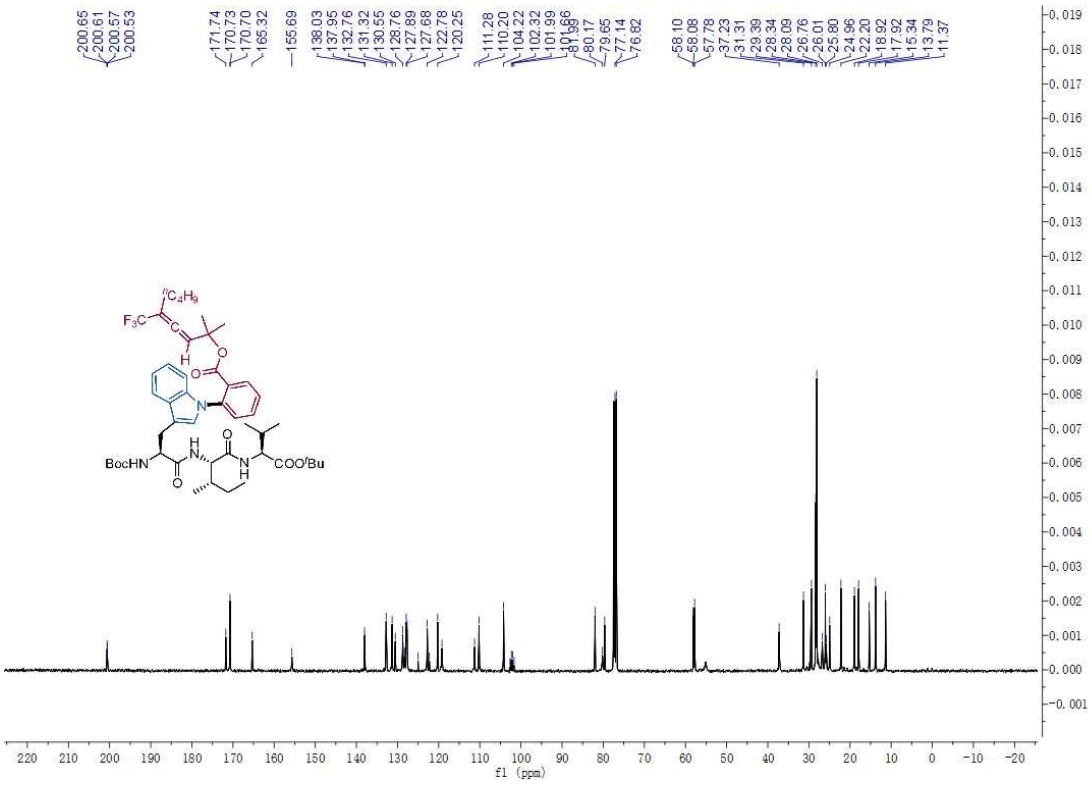


Fig 64. ^{13}C NMR of (**4d**)

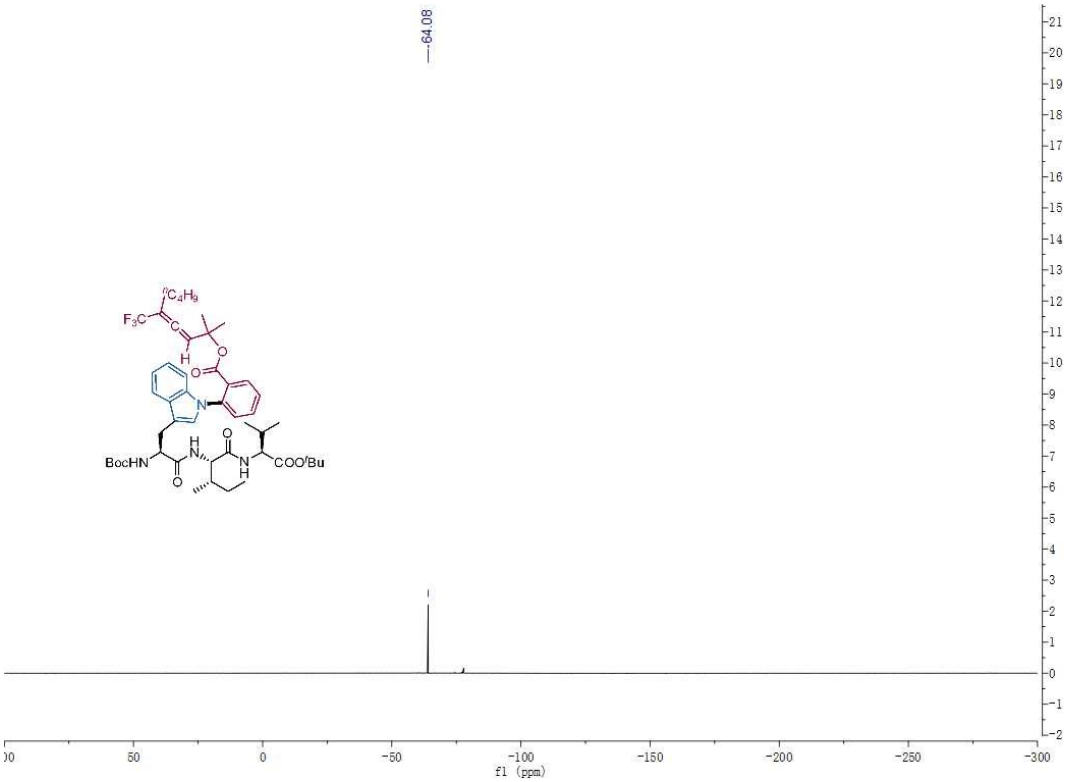


Fig 65. ^{19}F NMR of (**4d**)

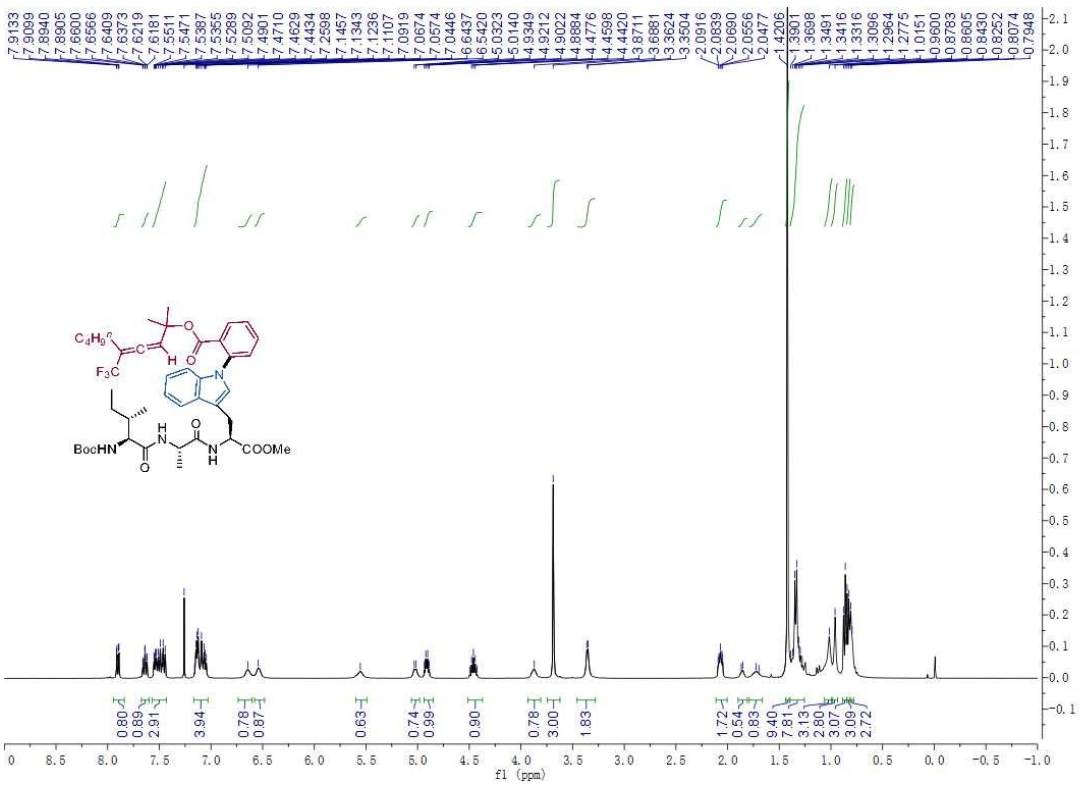


Fig 66. ^{1}H NMR of (**4e**)

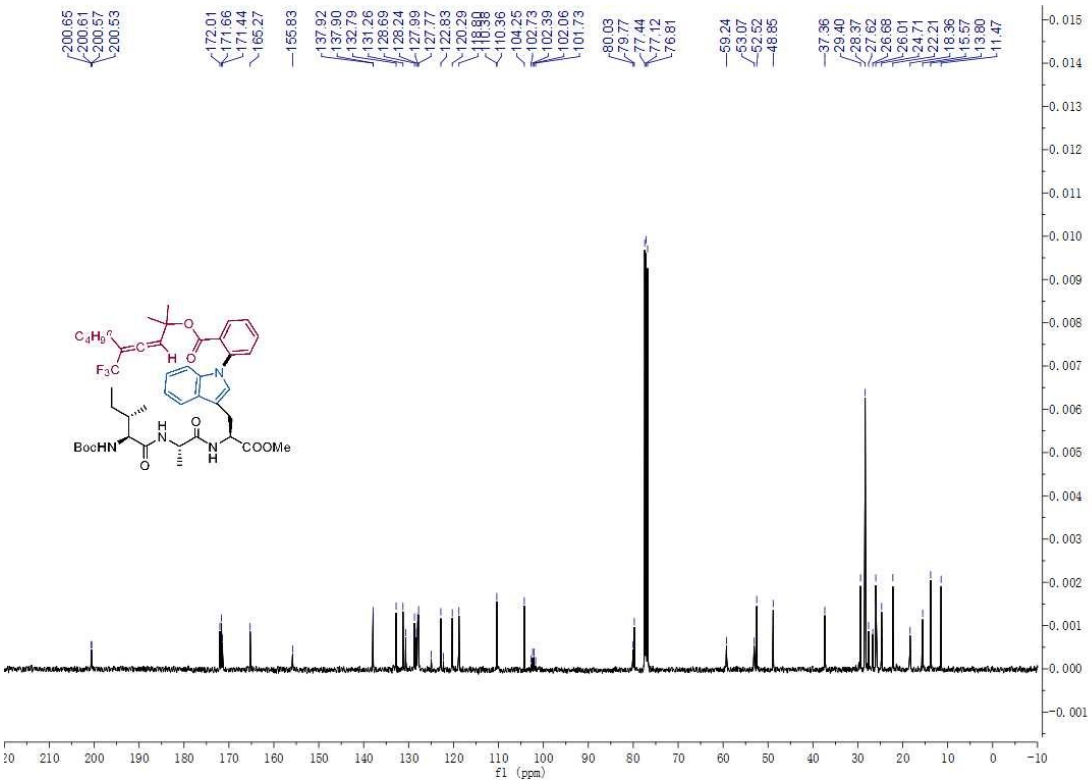


Fig 67. ^{13}C NMR of (**4e**)

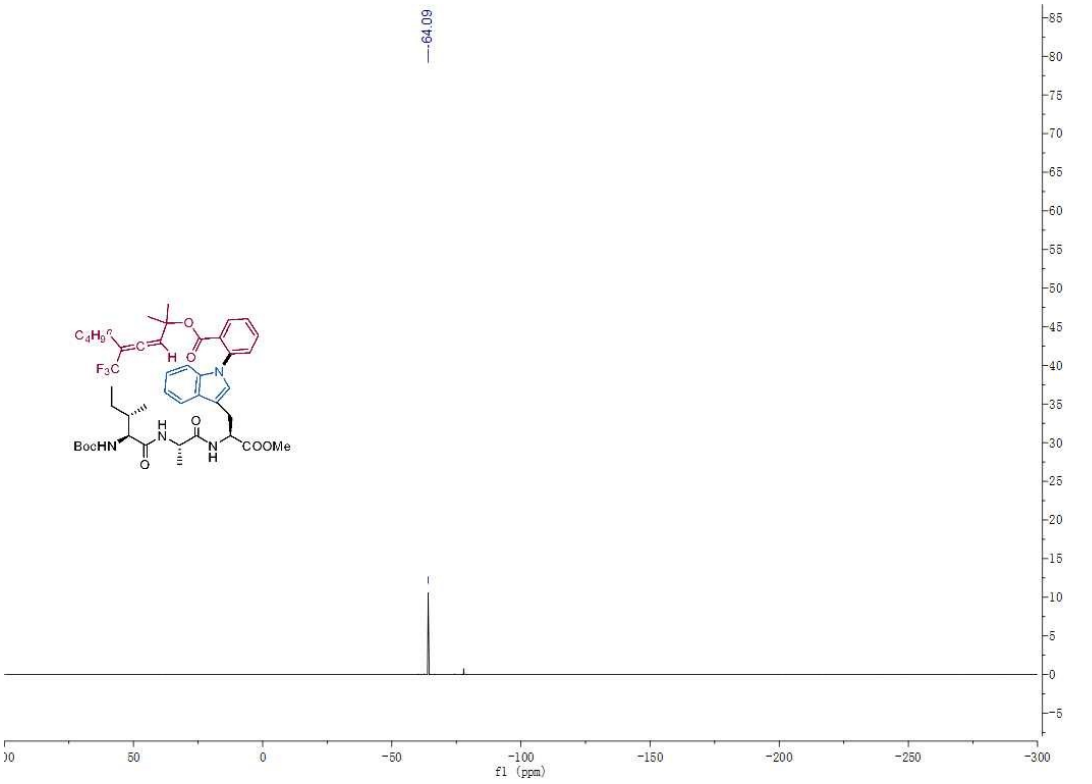


Fig 68. ^{19}F NMR of (**4e**)

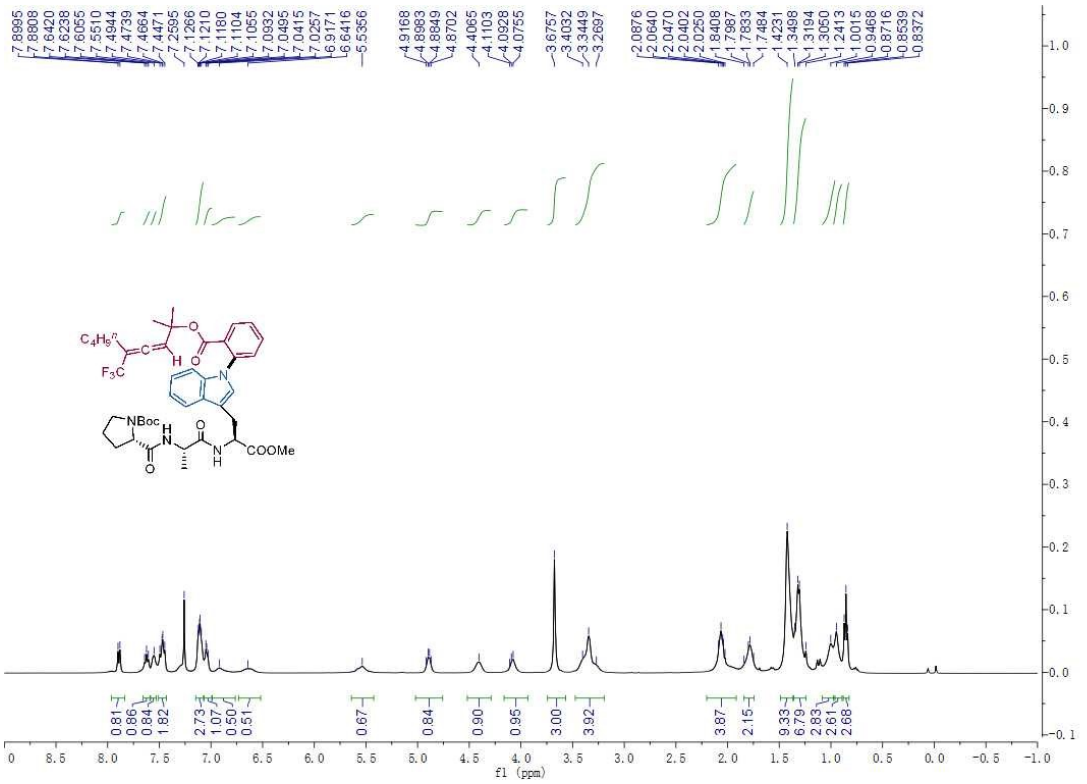


Fig 69. ^{1}H NMR of (**4f**)

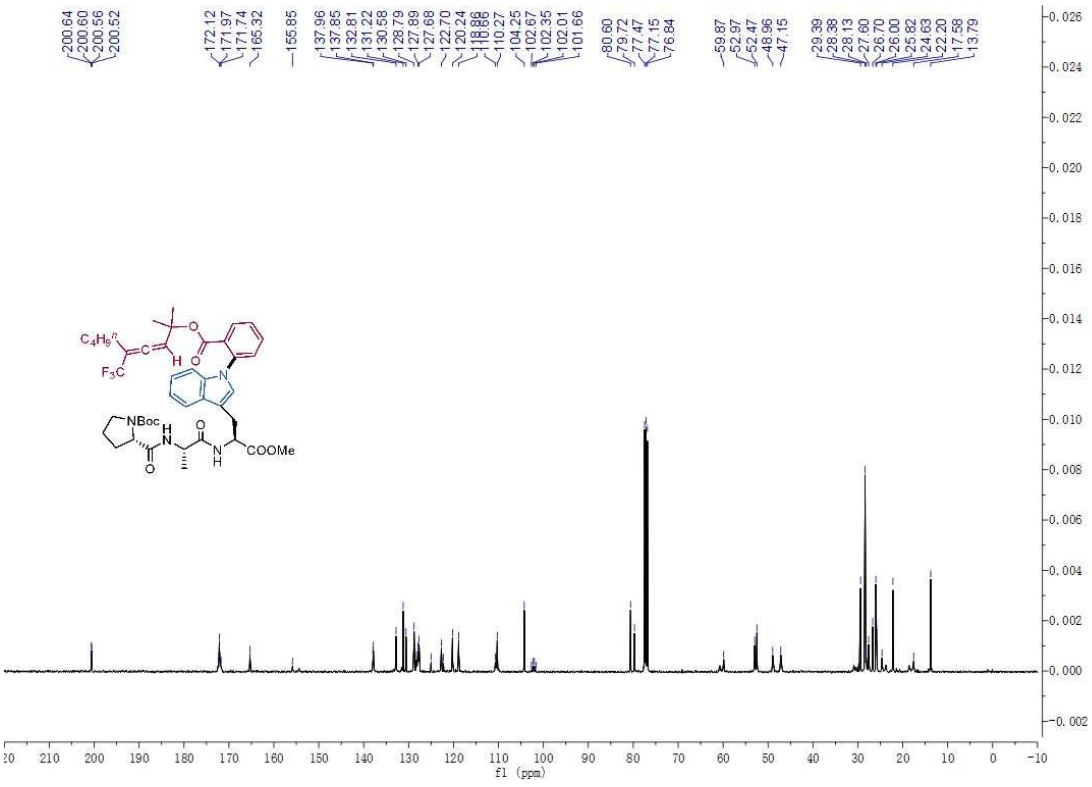


Fig 70. ^{13}C NMR of (**4f**)

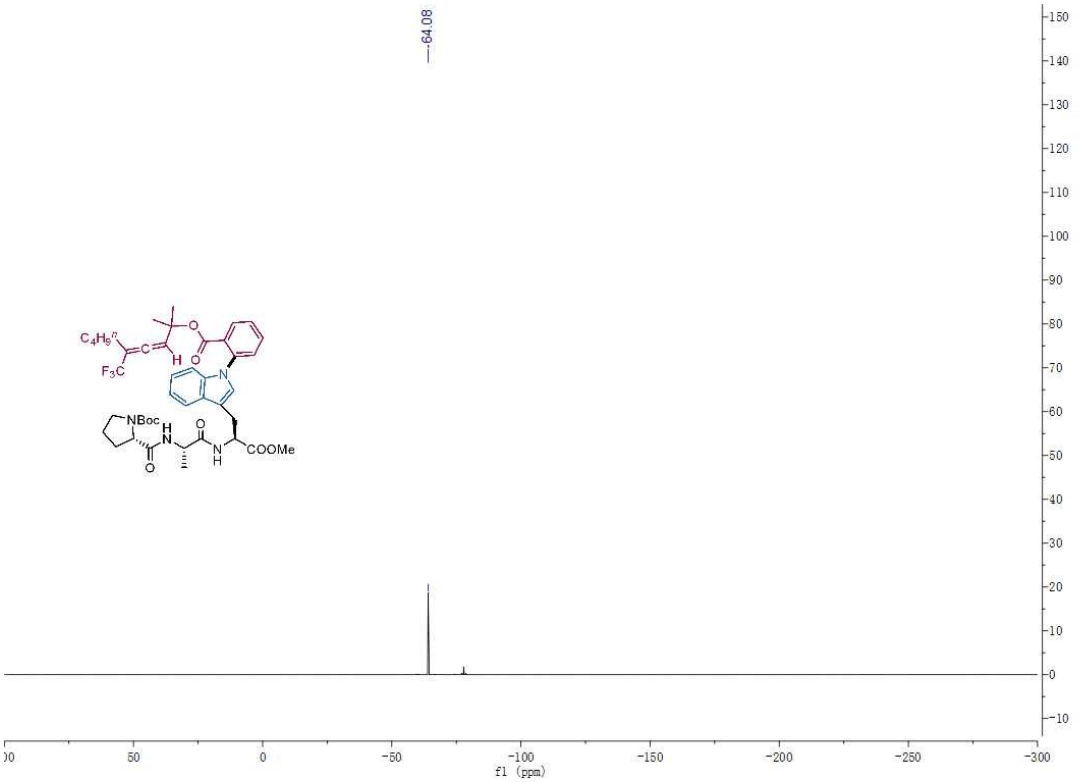


Fig 71. ^{19}F NMR of (**4f**)

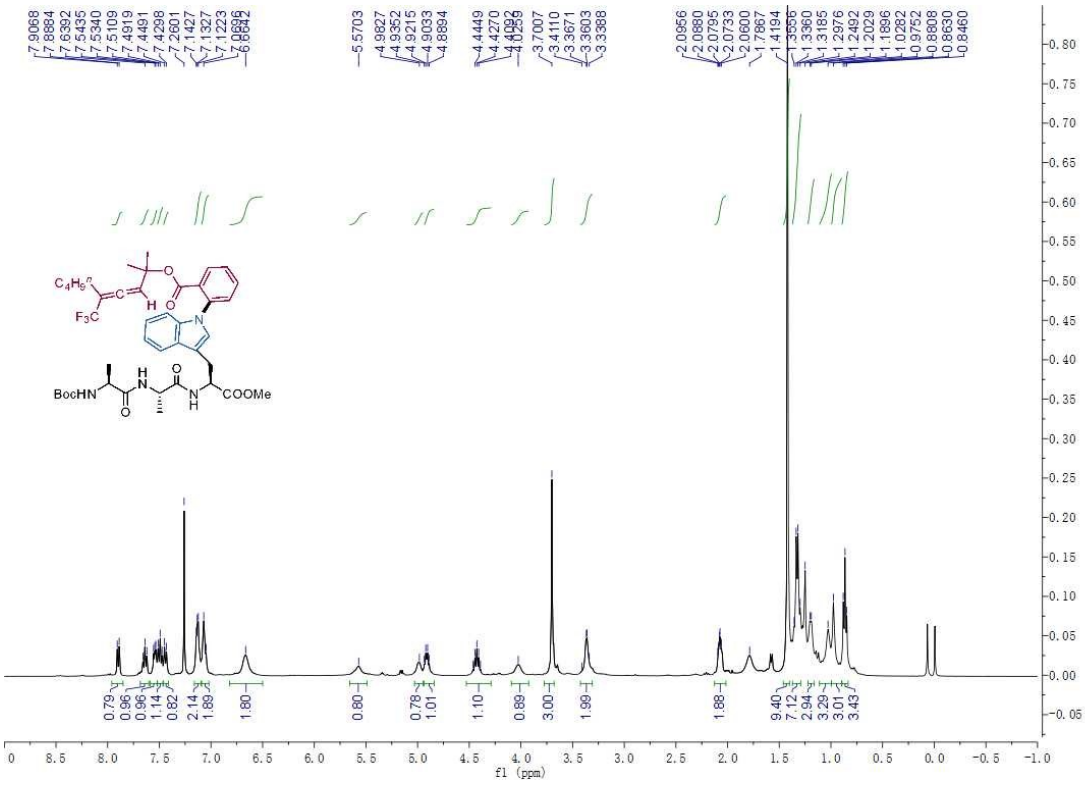


Fig 72. ^{1}H NMR of (**4g**)

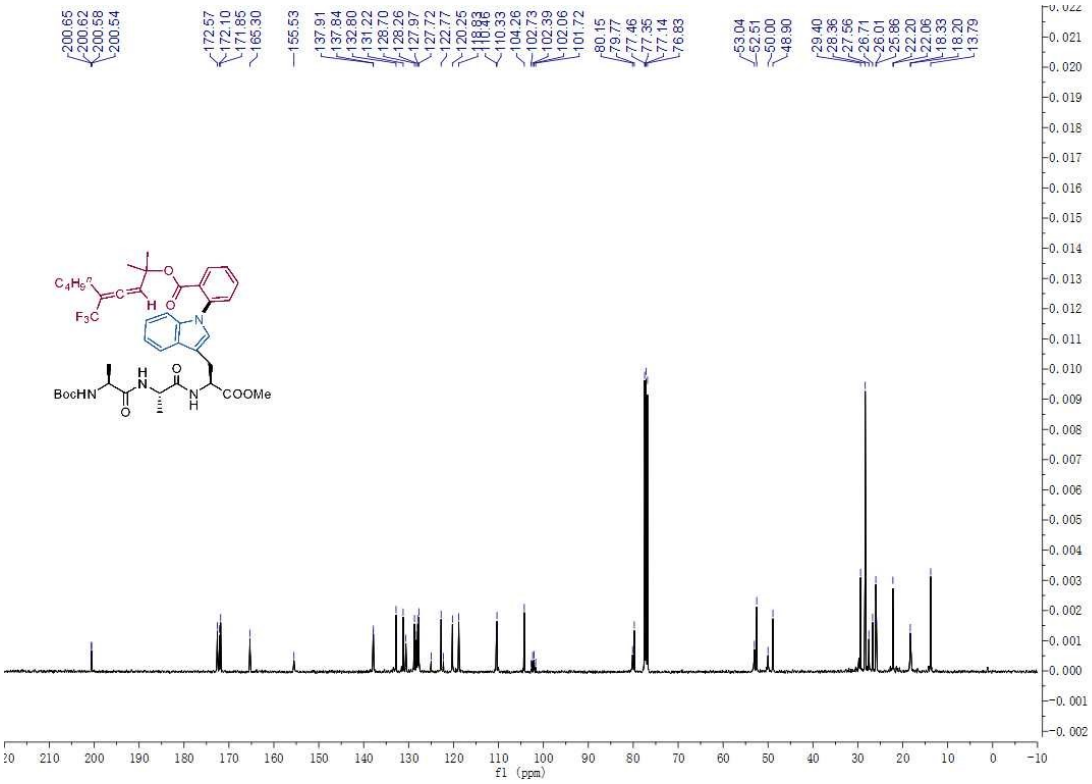


Fig 73. ^{13}C NMR of (**4g**)

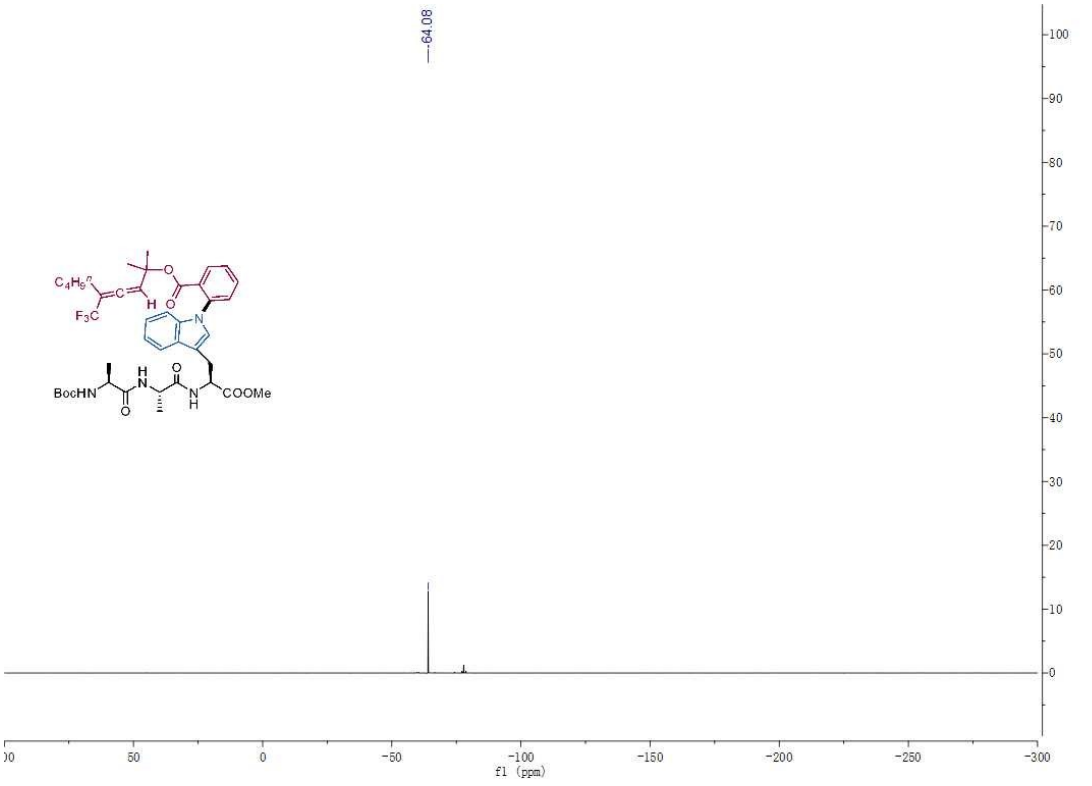


Fig 74. ^{19}F NMR of (**4g**)

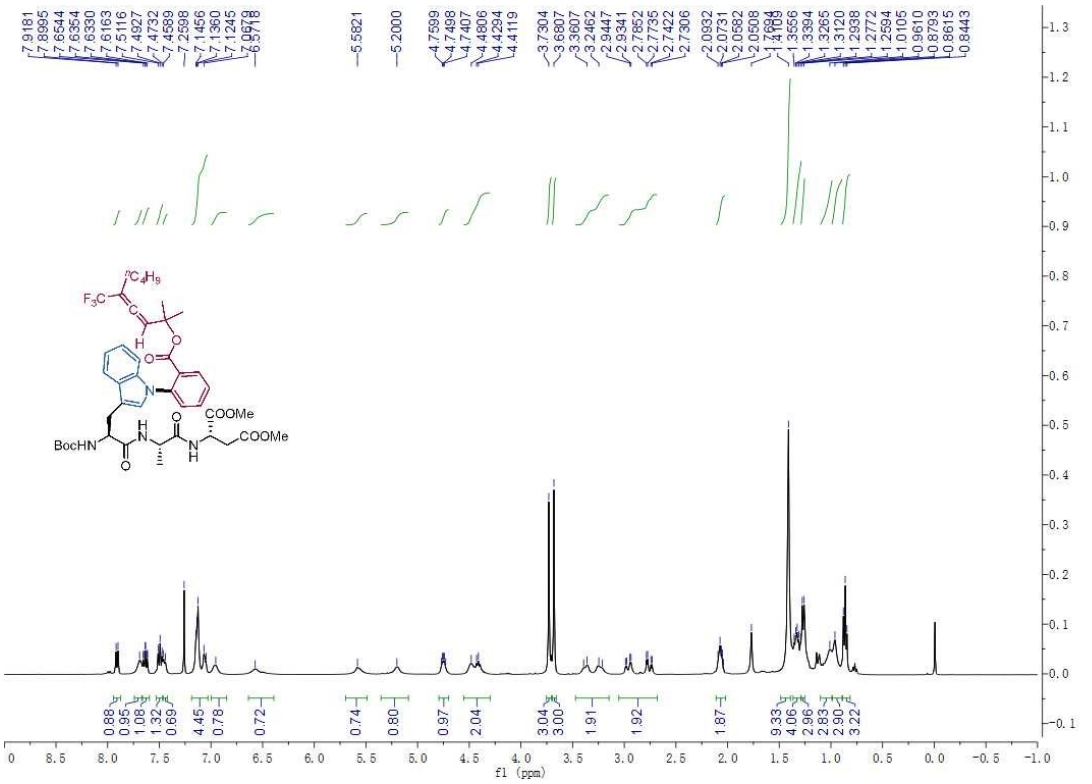


Fig 75. ^{1}H NMR of (**4h**)

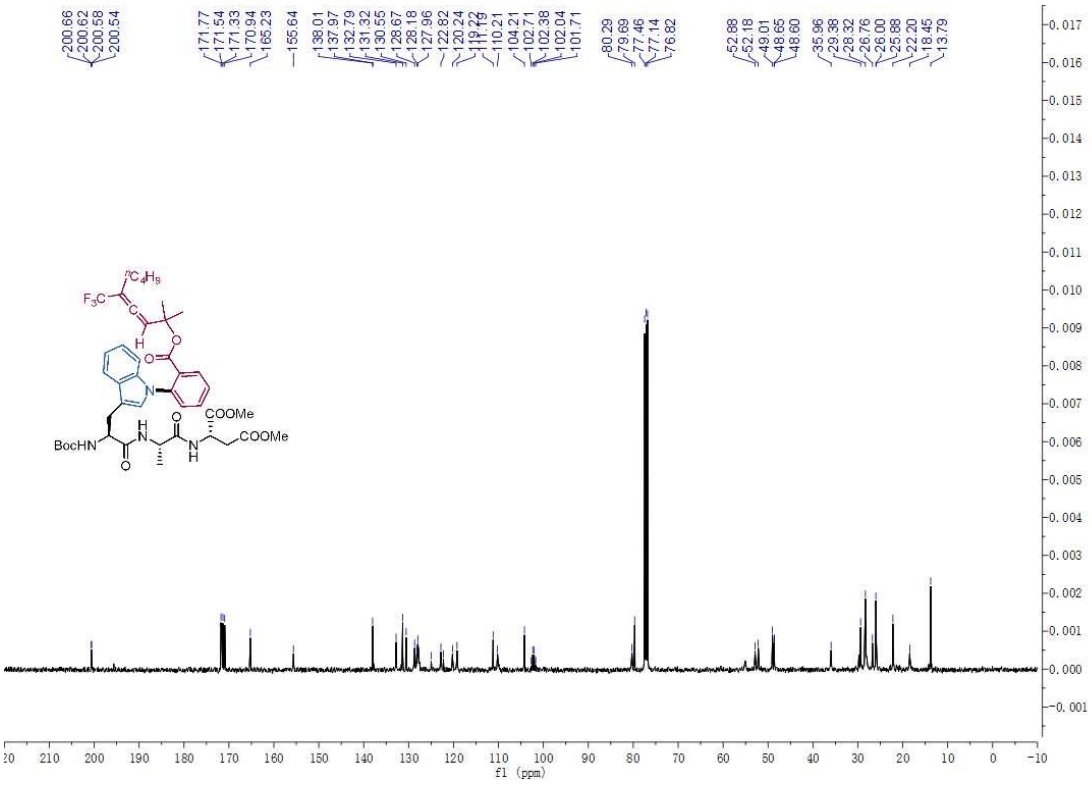


Fig 76. ^{13}C NMR of (**4h**)

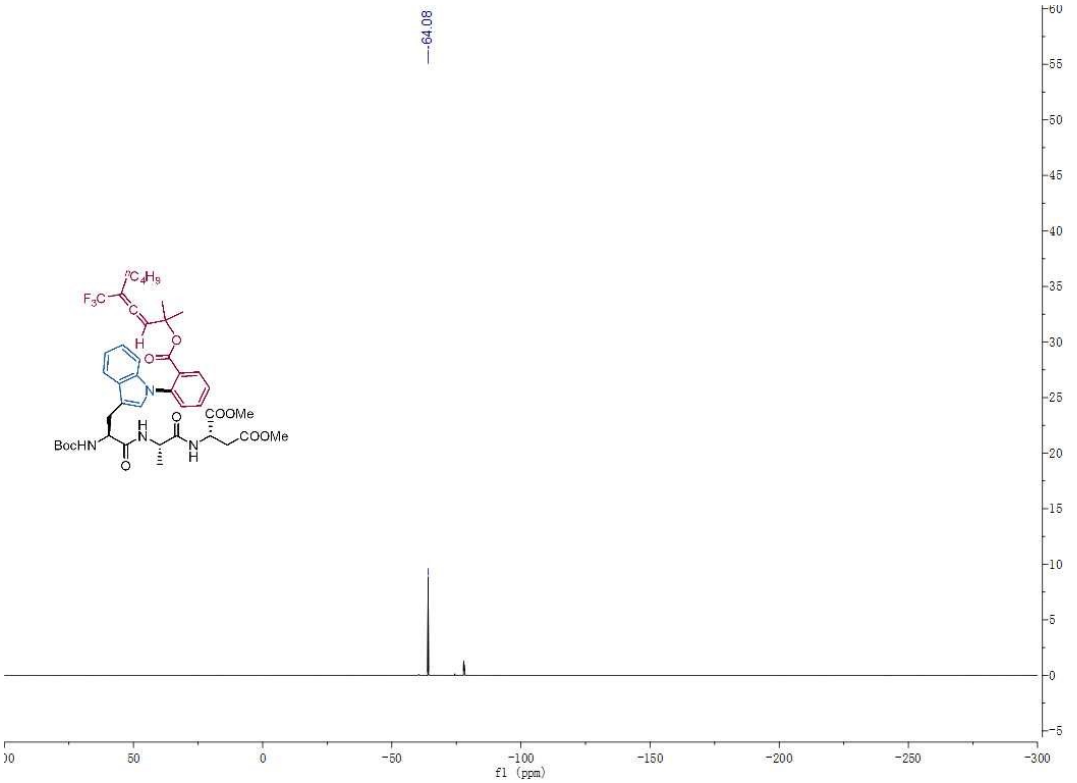


Fig 77. ^{19}F NMR of (**4h**)

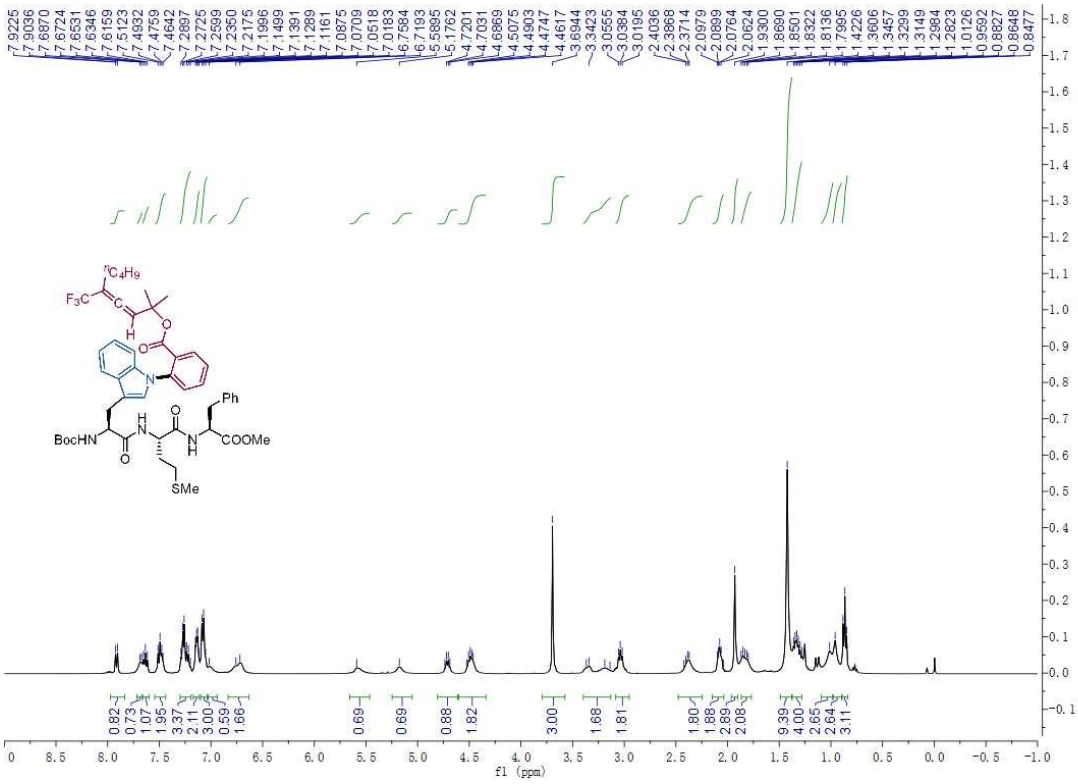


Fig 78. ^{1}H NMR of (**4i**)

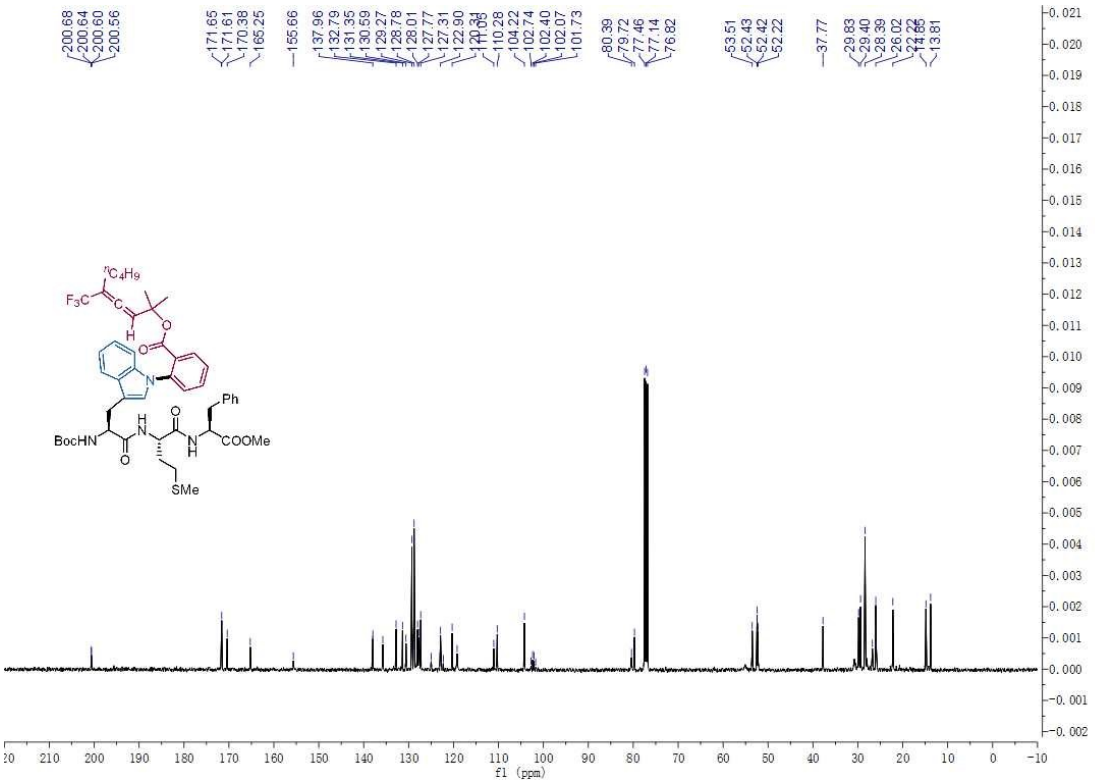


Fig 79. ^{13}C NMR of (**4i**)

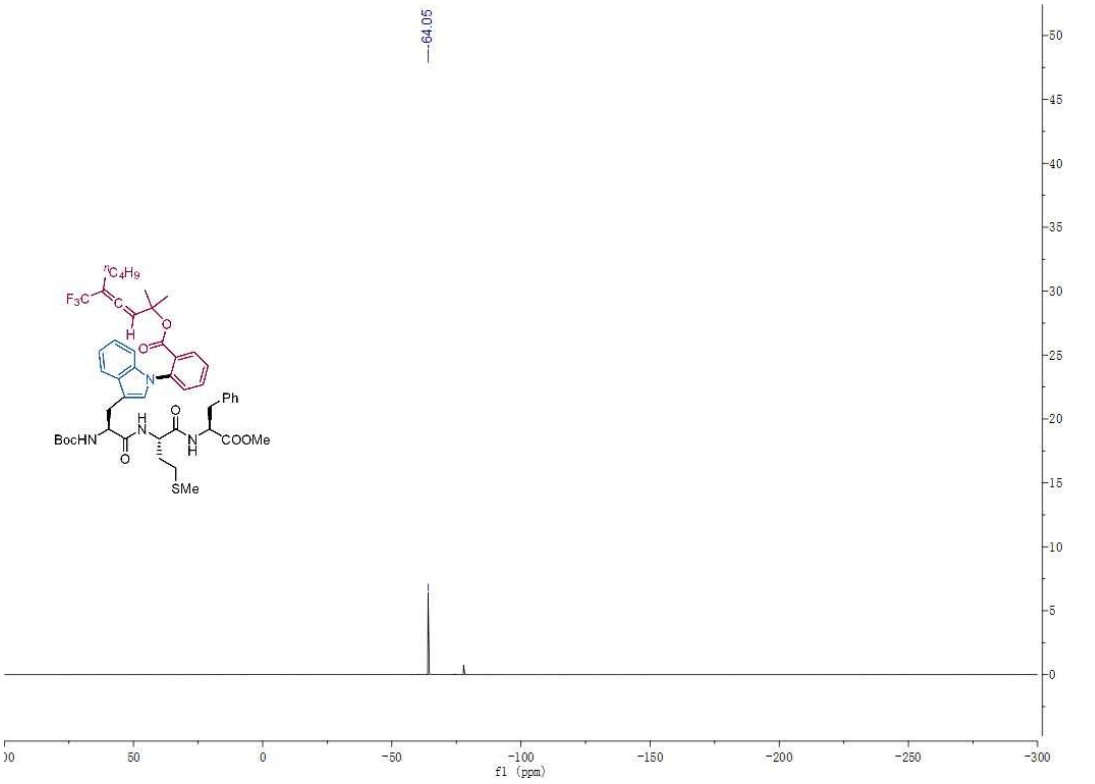


Fig 80. ^{19}F NMR of (**4i**)

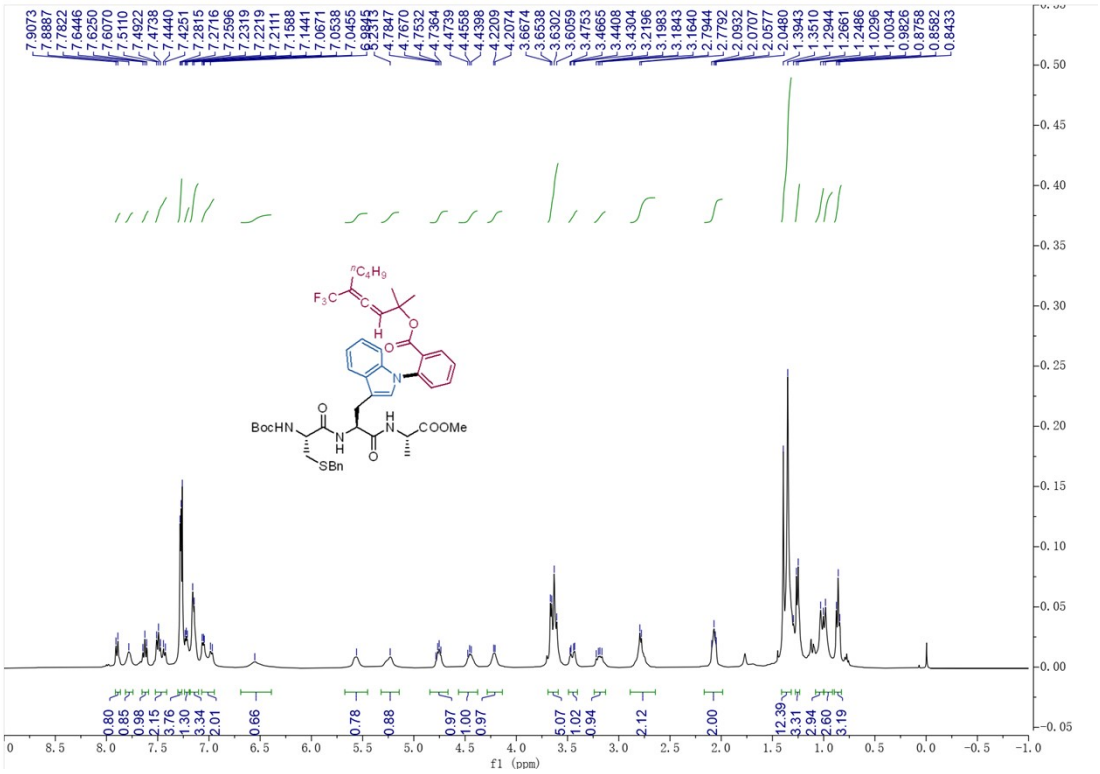


Fig 81. ^{1}H NMR of (**4j**)

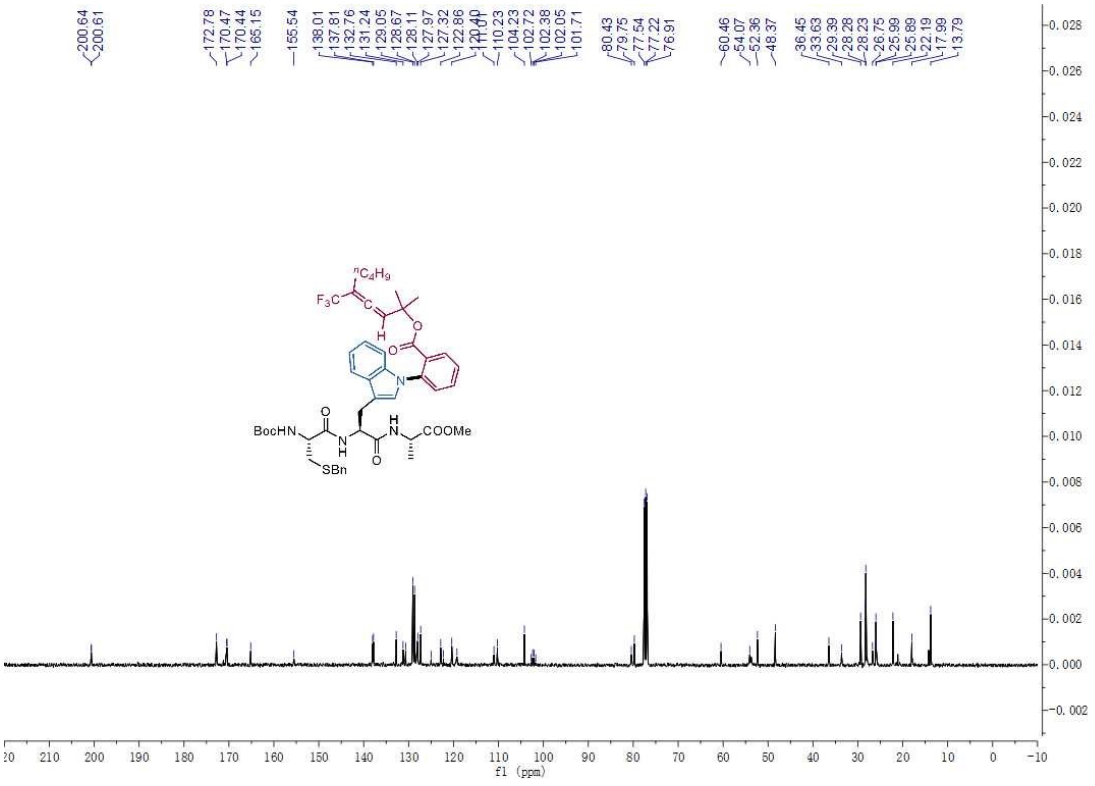


Fig 82. ^{13}C NMR of (**4j**)

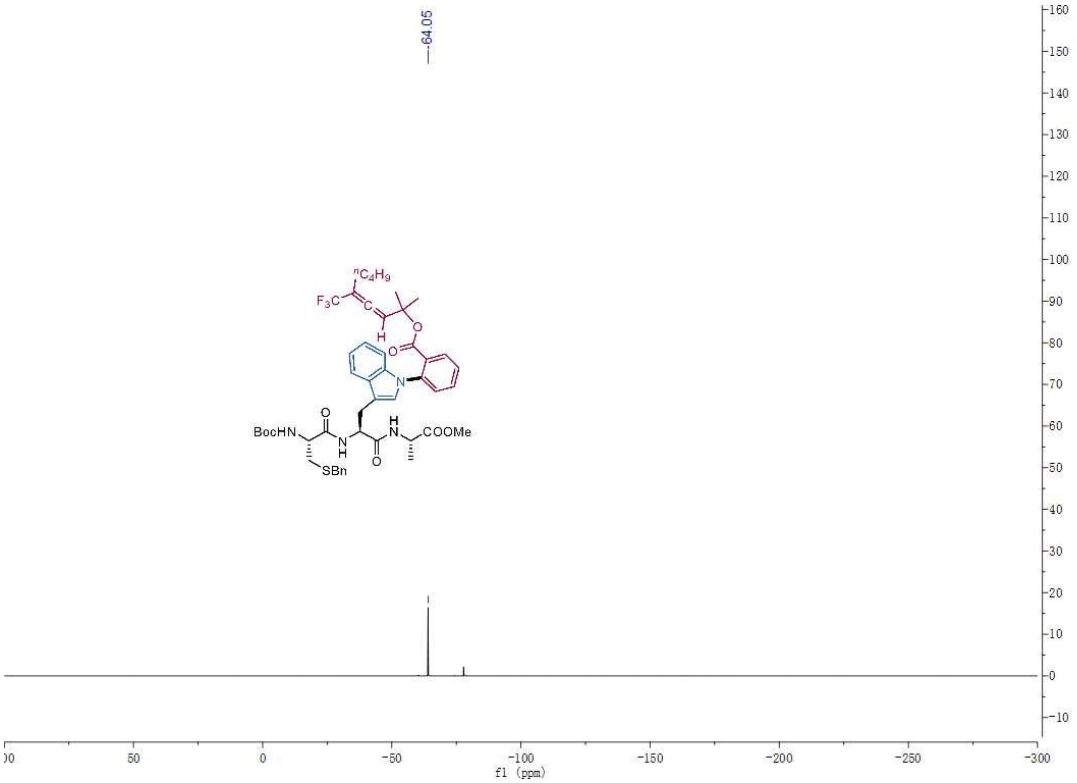


Fig 83. ^{19}F NMR of (**4j**)

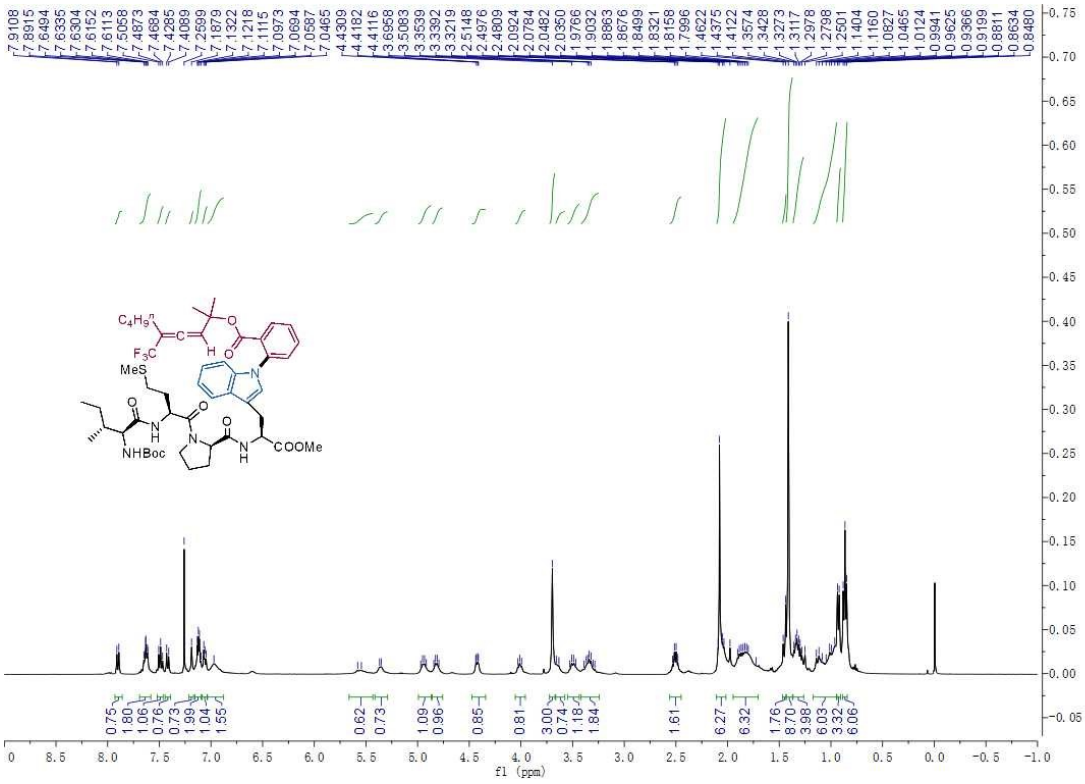


Fig 84. ^{1}H NMR of (**5a**)

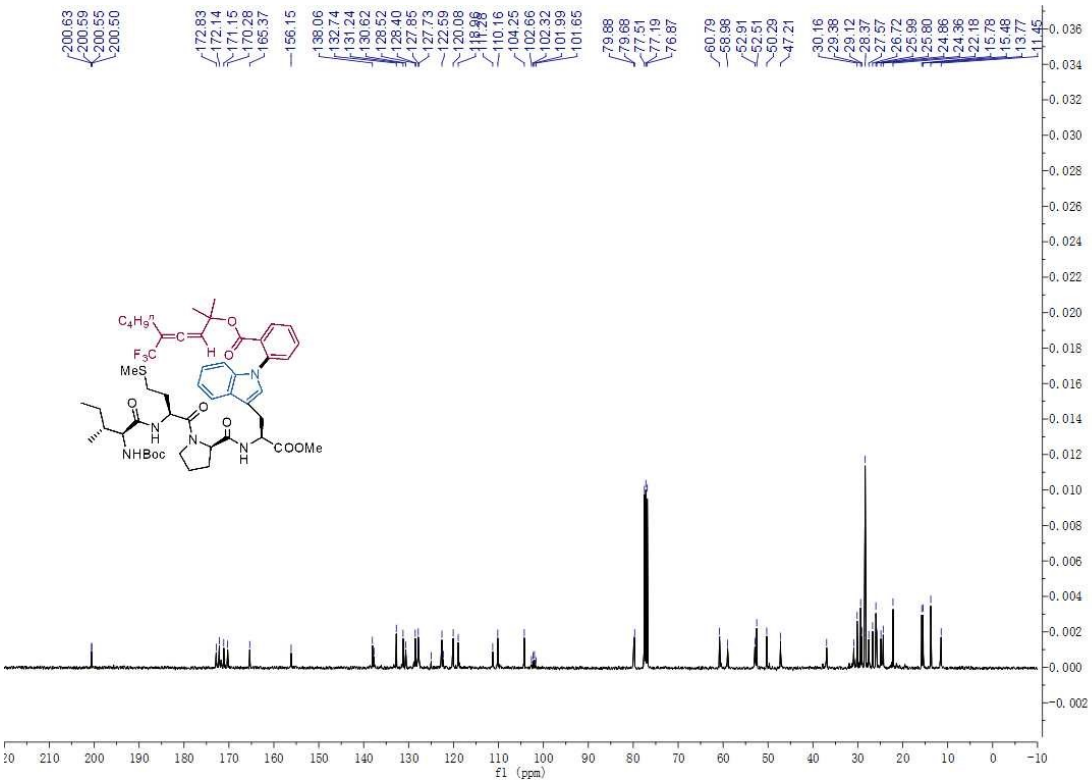


Fig 85. ^{13}C NMR of (**5a**)

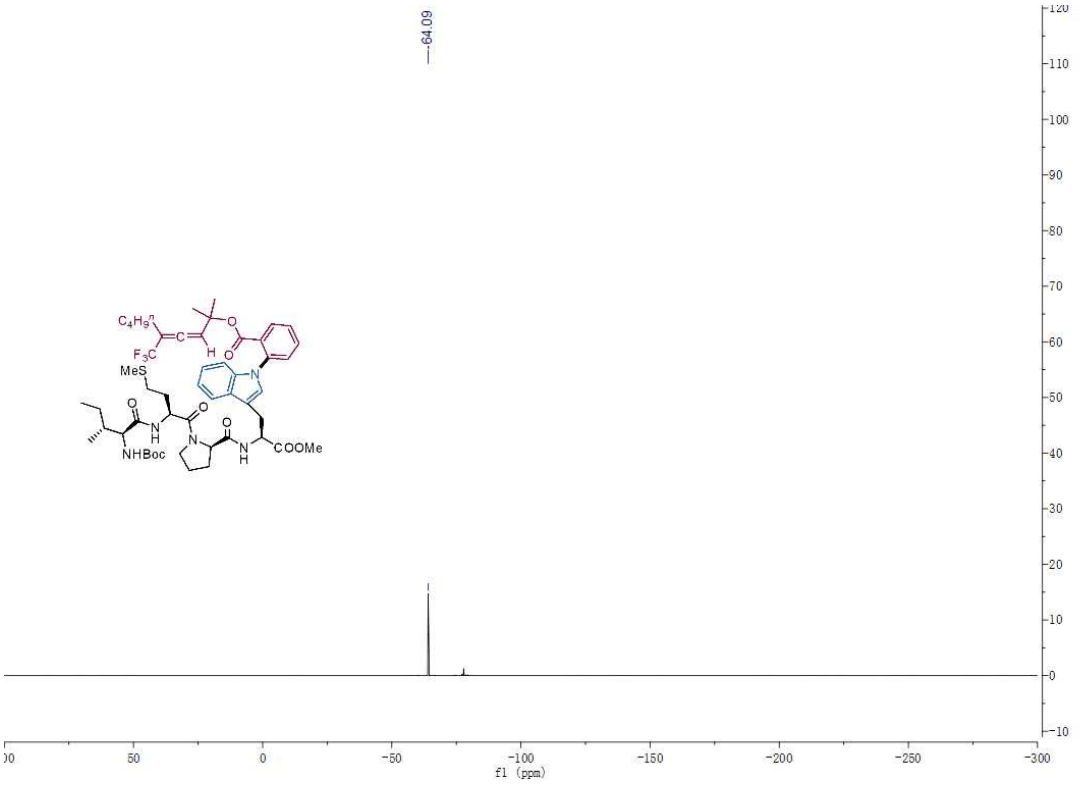


Fig 86. ^{19}F NMR of (**5a**)

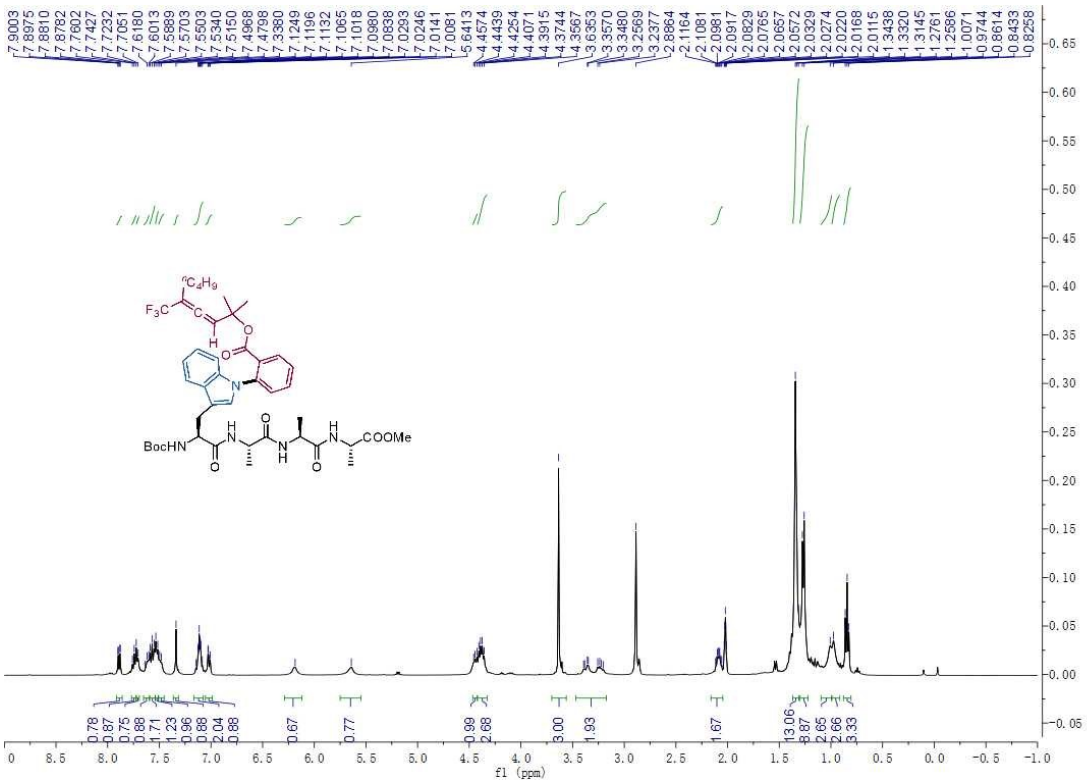


Fig 87. ^{1}H NMR of (**5b**)

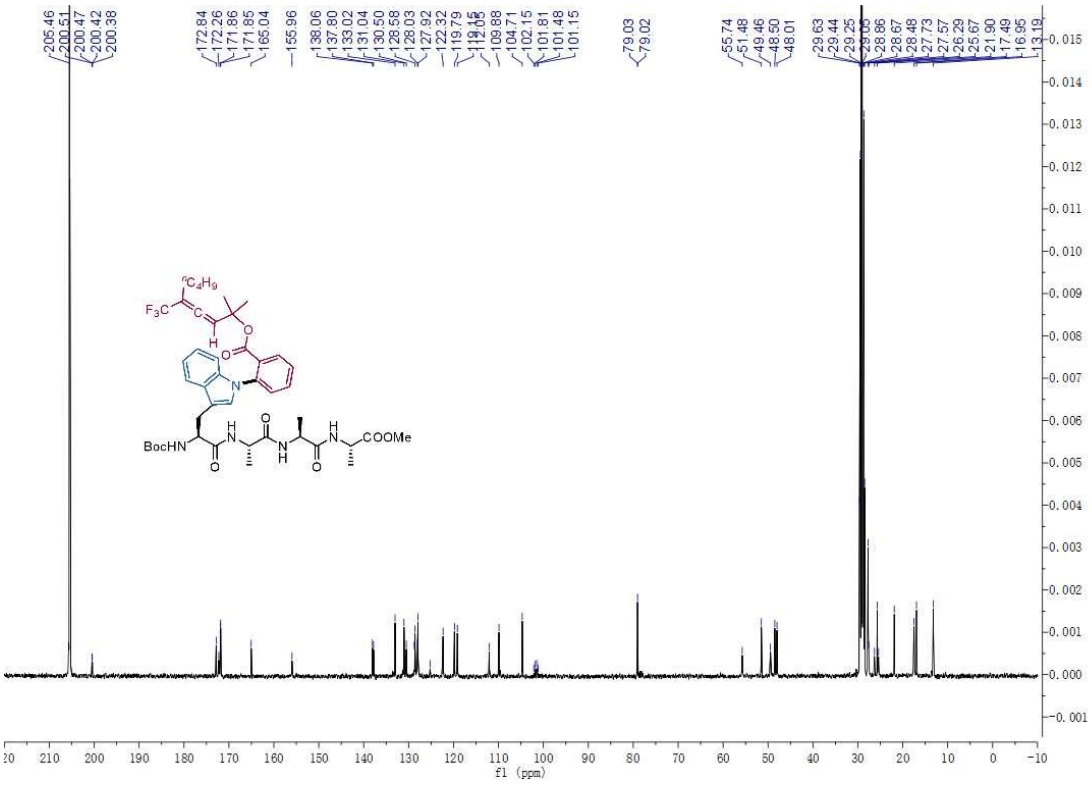


Fig 88. ^{13}C NMR of (**5b**)

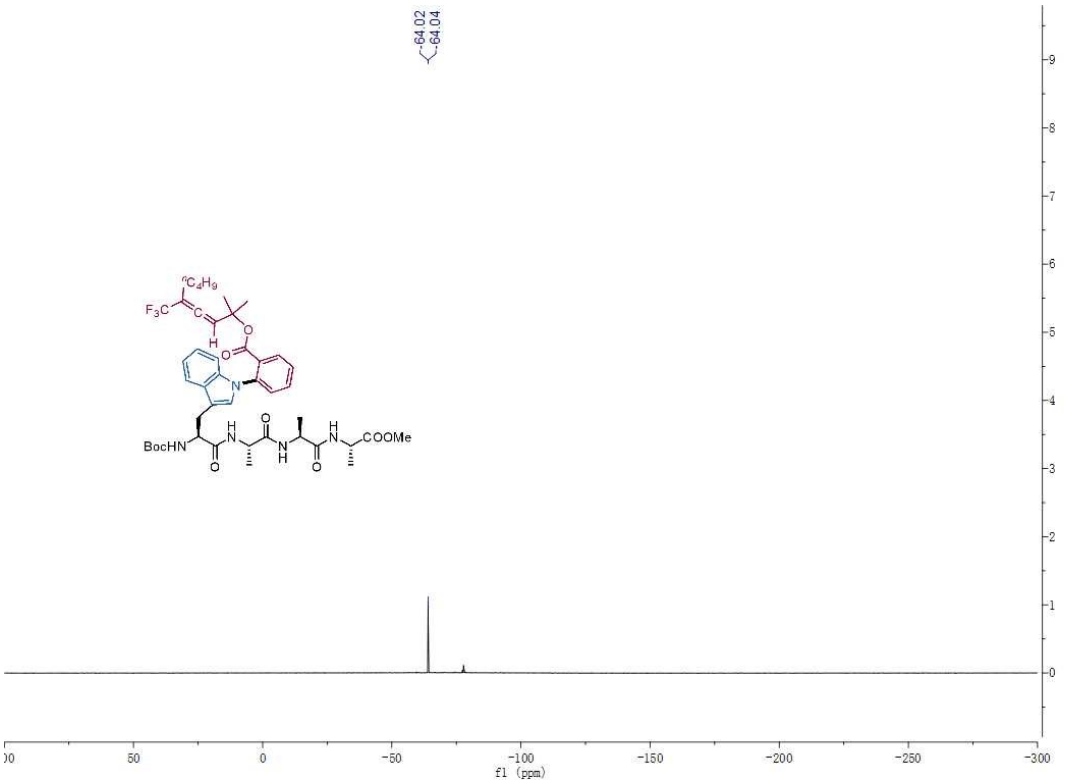


Fig 89. ^{19}F NMR of (**5b**)

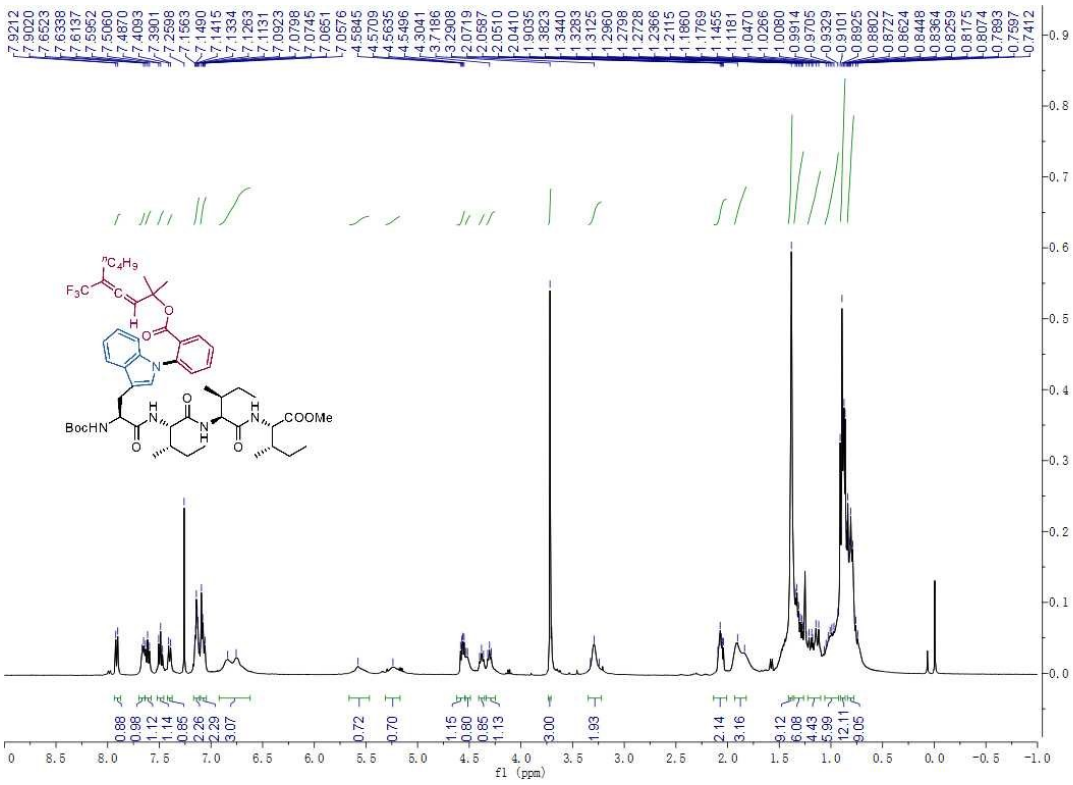


Fig 90. ^{1}H NMR of (**5c**)

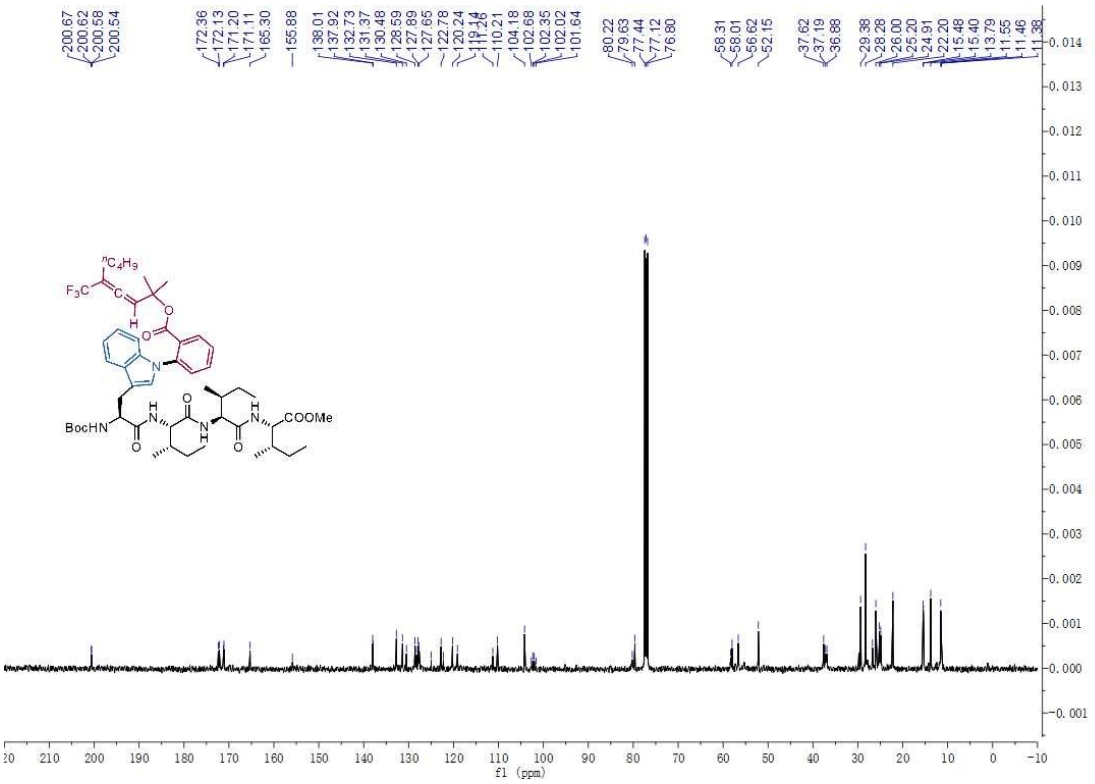


Fig 91. ^{13}C NMR of (**5c**)

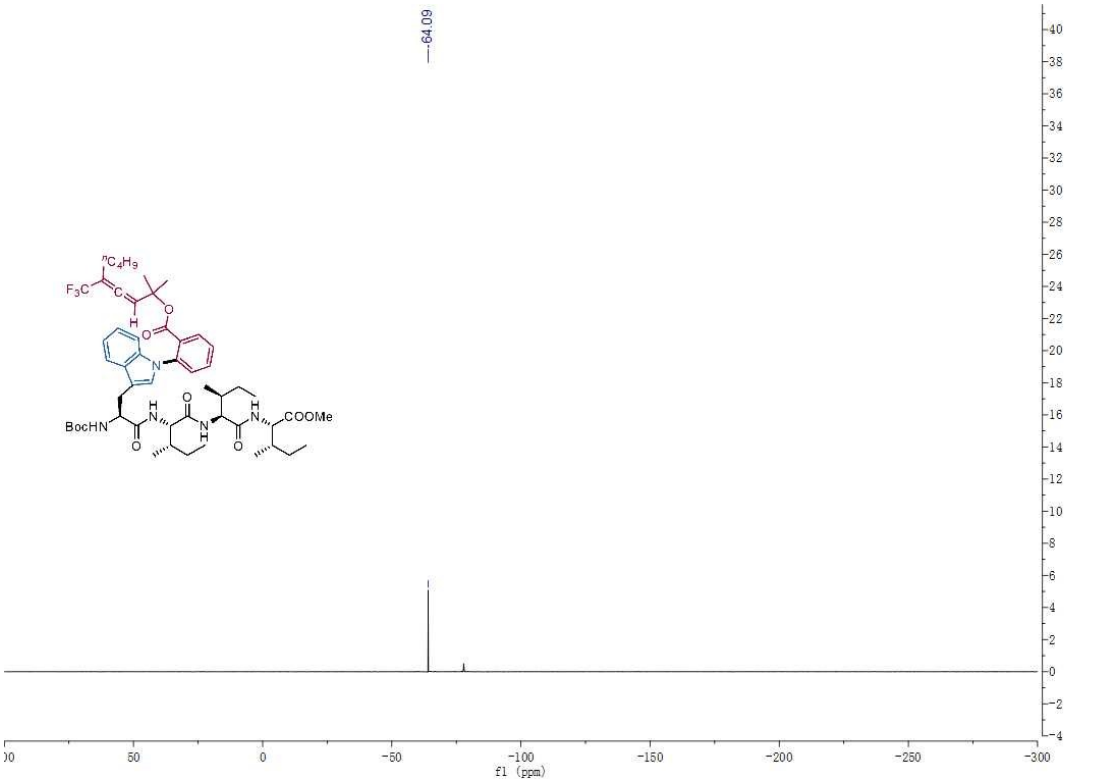


Fig 92. ^{19}F NMR of (**5c**)

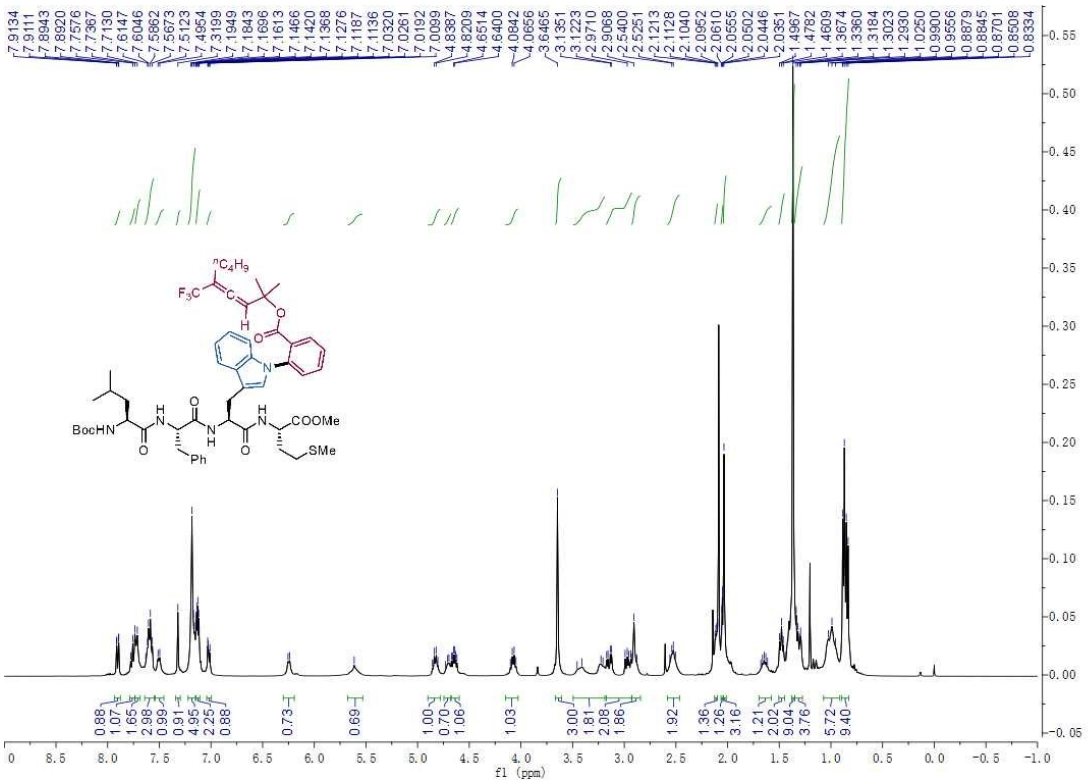


Fig 93. ^{1}H NMR of (**5d**)

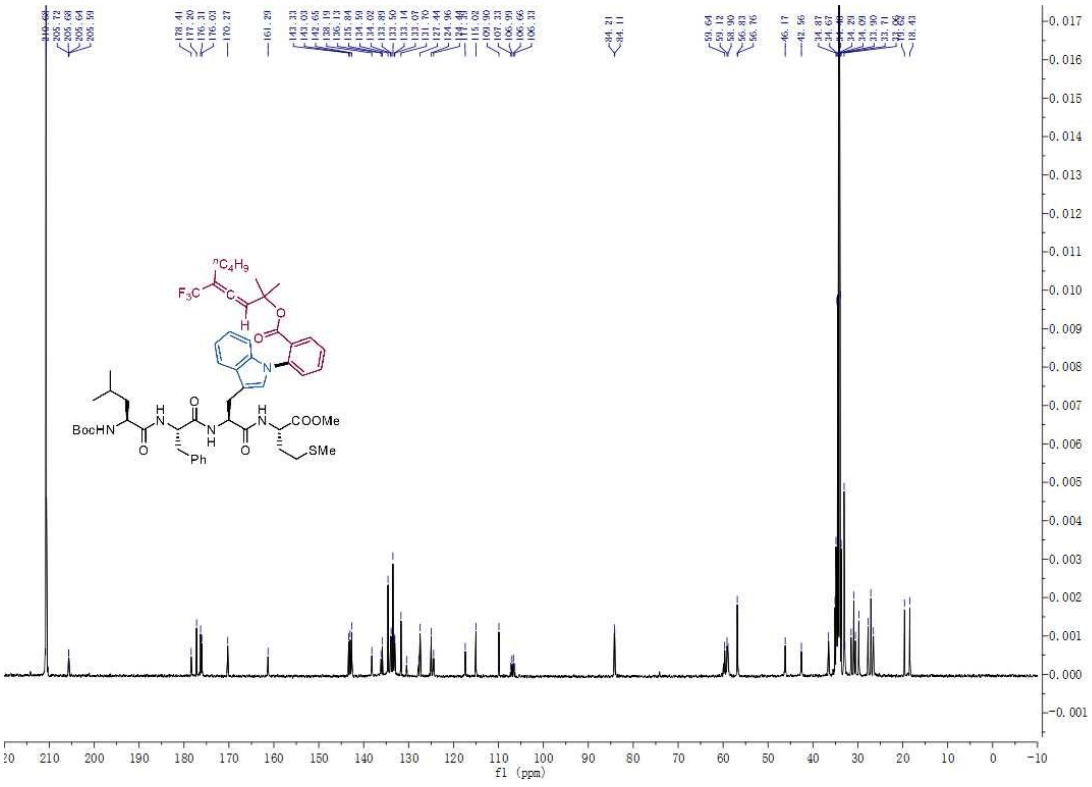


Fig 94. ^{13}C NMR of (**5d**)

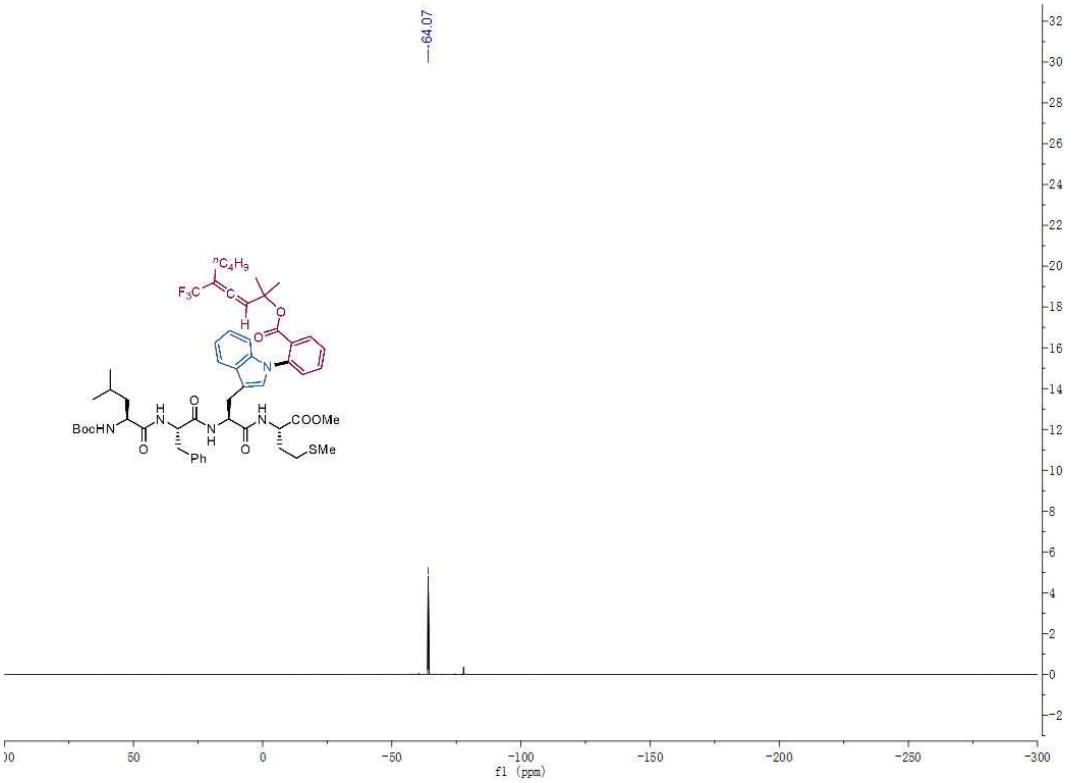


Fig 95. ^{19}F NMR of (**5d**)

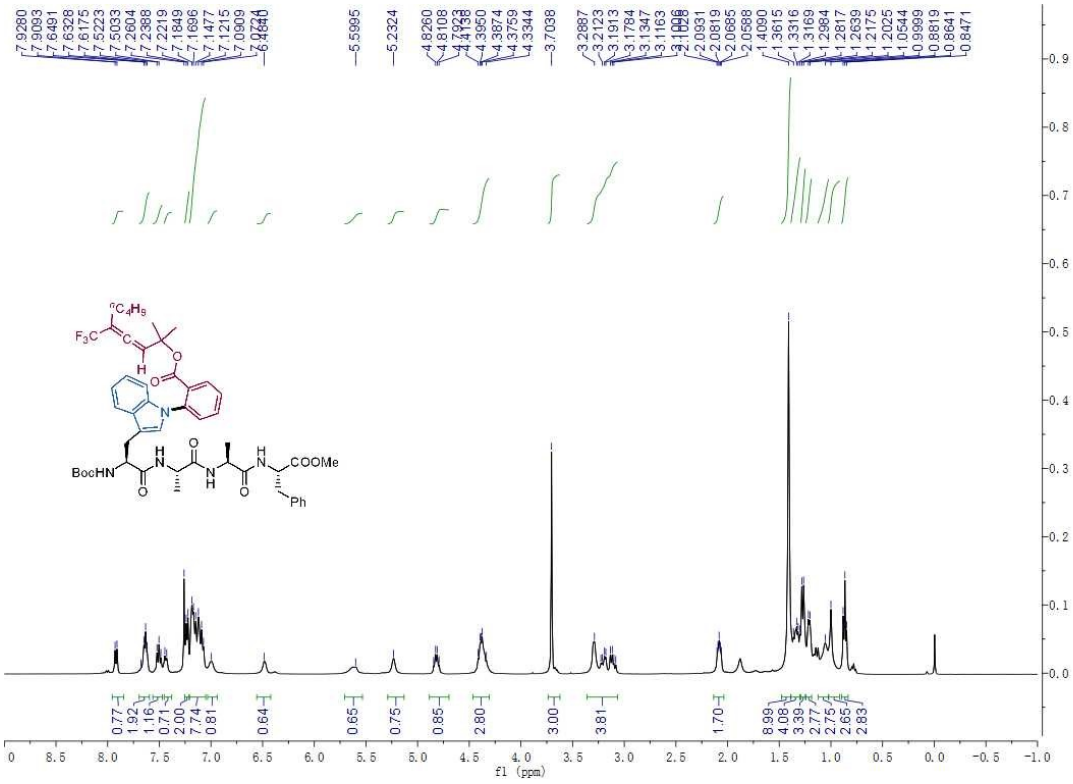


Fig 96. ^{1}H NMR of (**5e**)

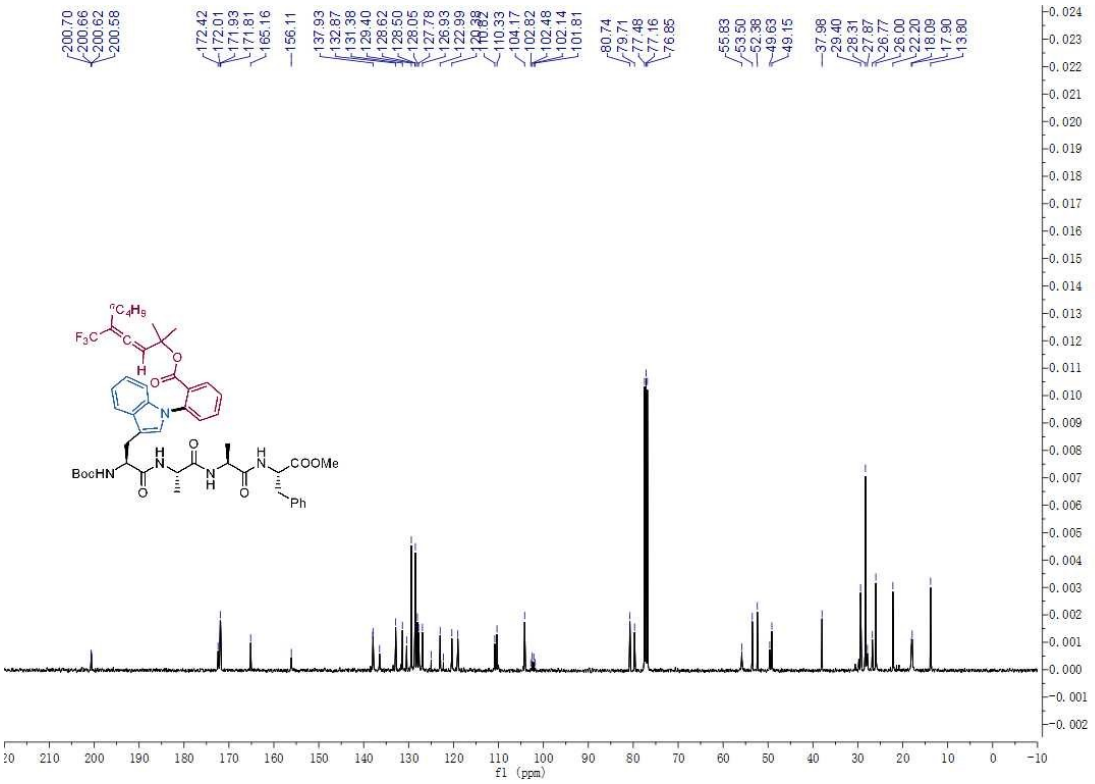


Fig 97. ^{13}C NMR of (**5e**)

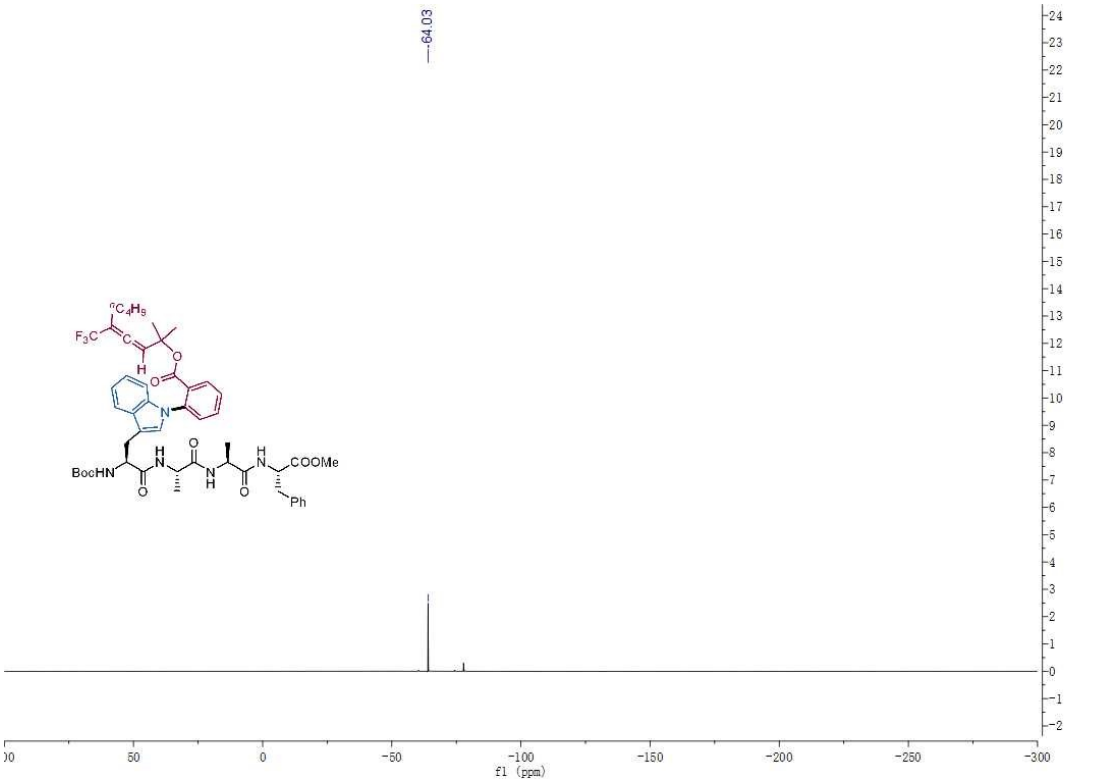


Fig 98. ^{19}F NMR of (**5e**)

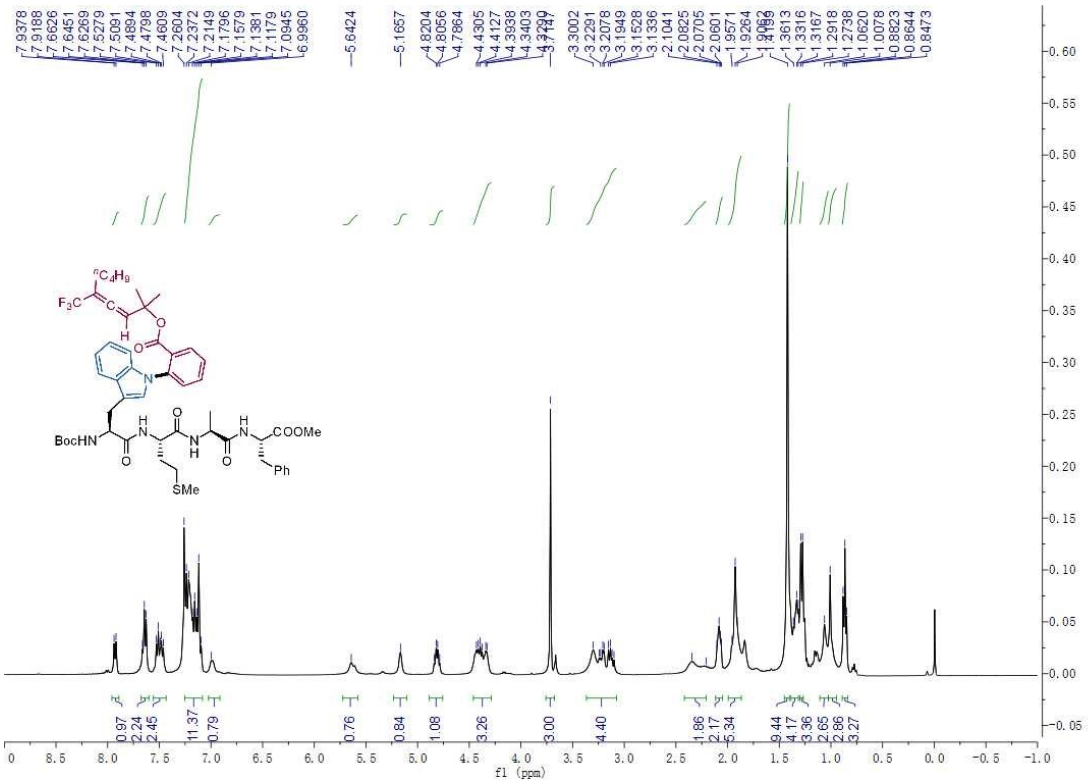


Fig 99. ^{1}H NMR of (**5f**)

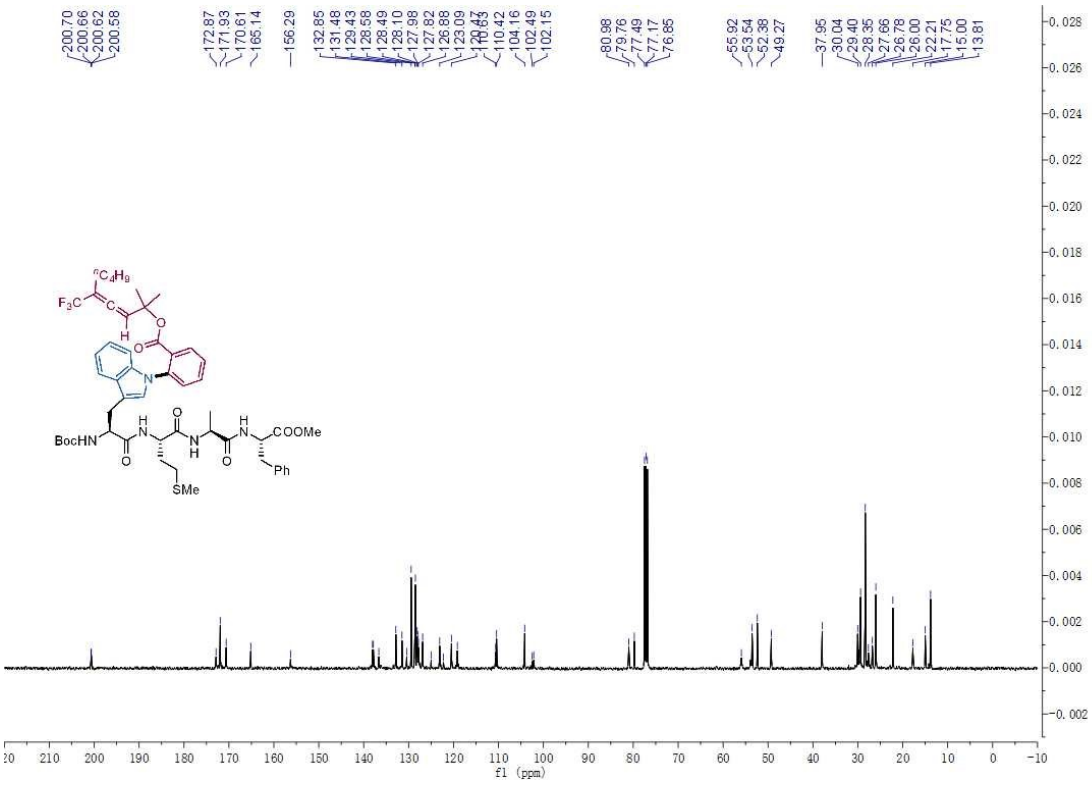


Fig 100. ^{13}C NMR of (**5f**)

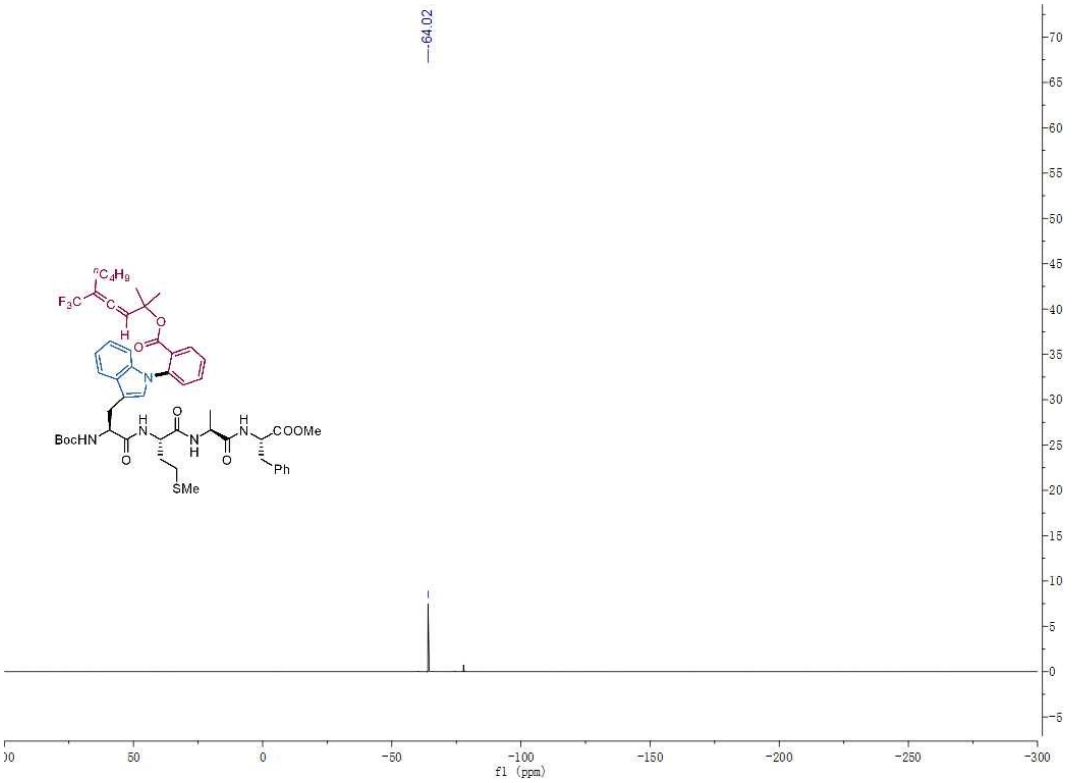


Fig 101. ^{19}F NMR of (**5f**)

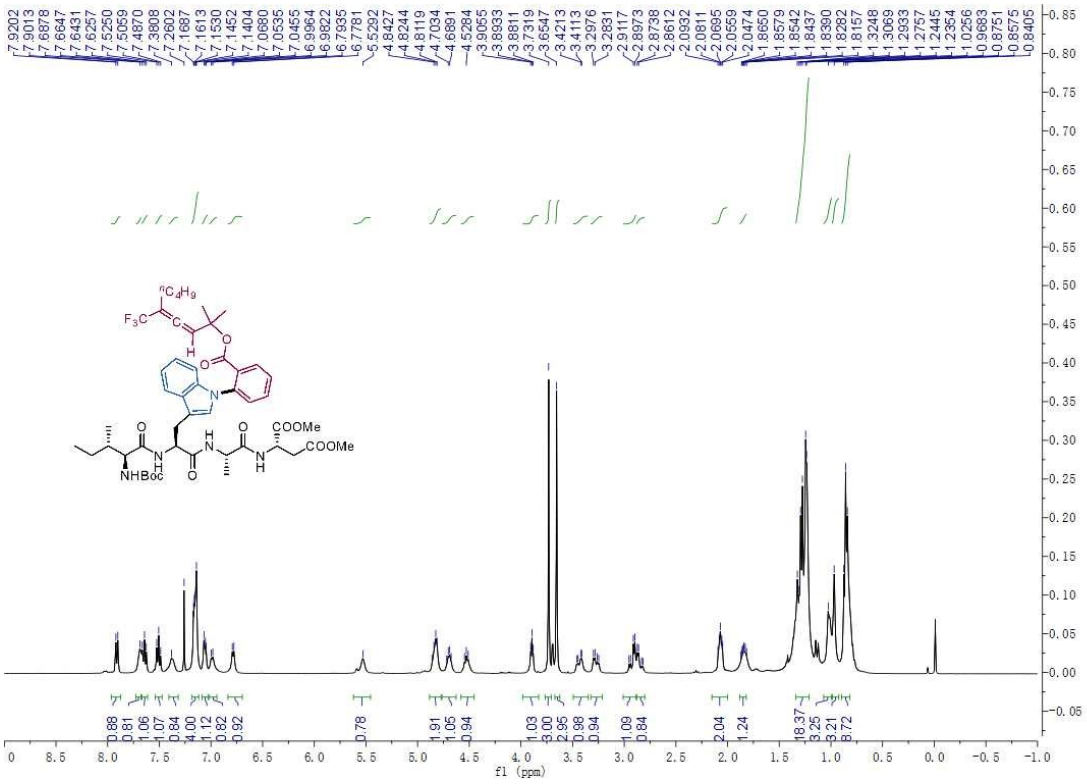


Fig 102. ^{1}H NMR of (**5g**)

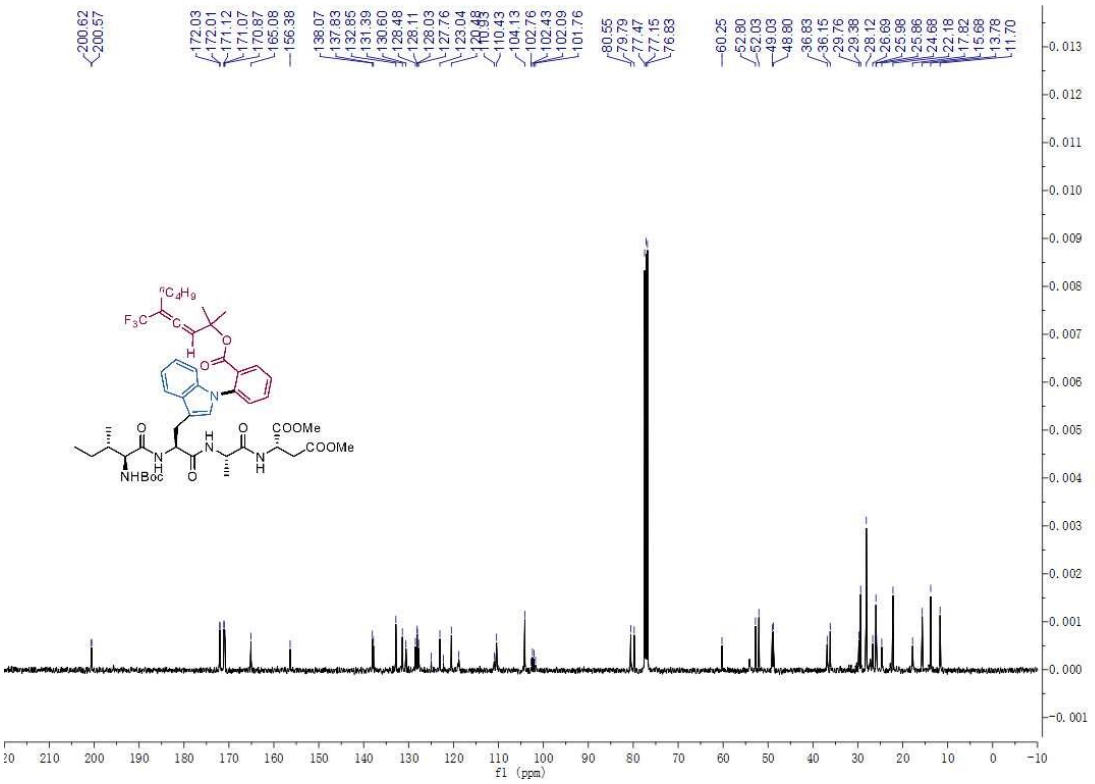


Fig 103. ^{13}C NMR of (**5g**)

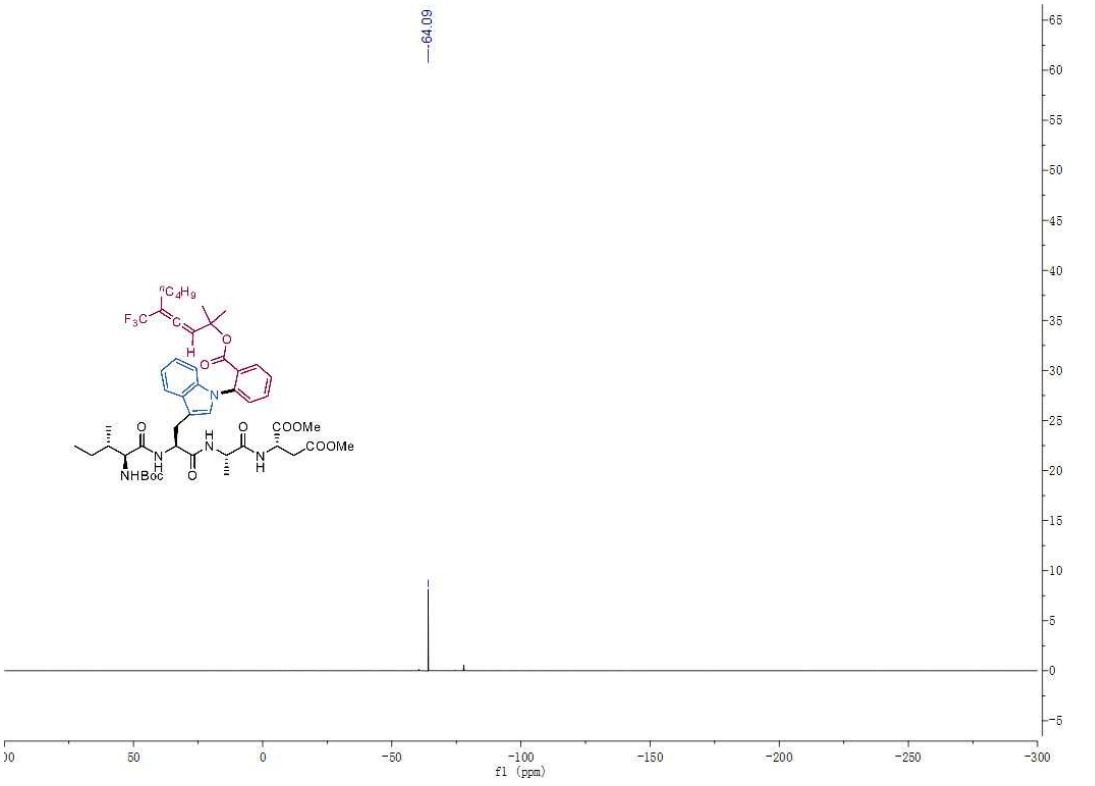


Fig 104. ^{19}F NMR of (**5g**)

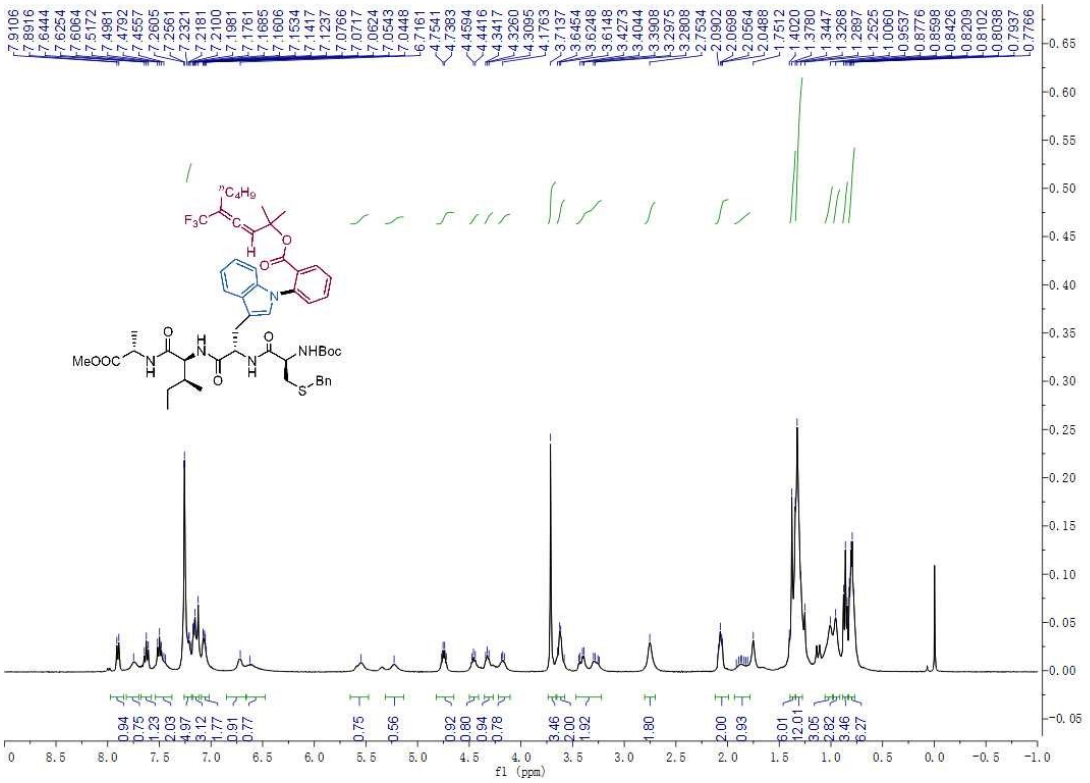


Fig 105. ^{1}H NMR of (**5h**)

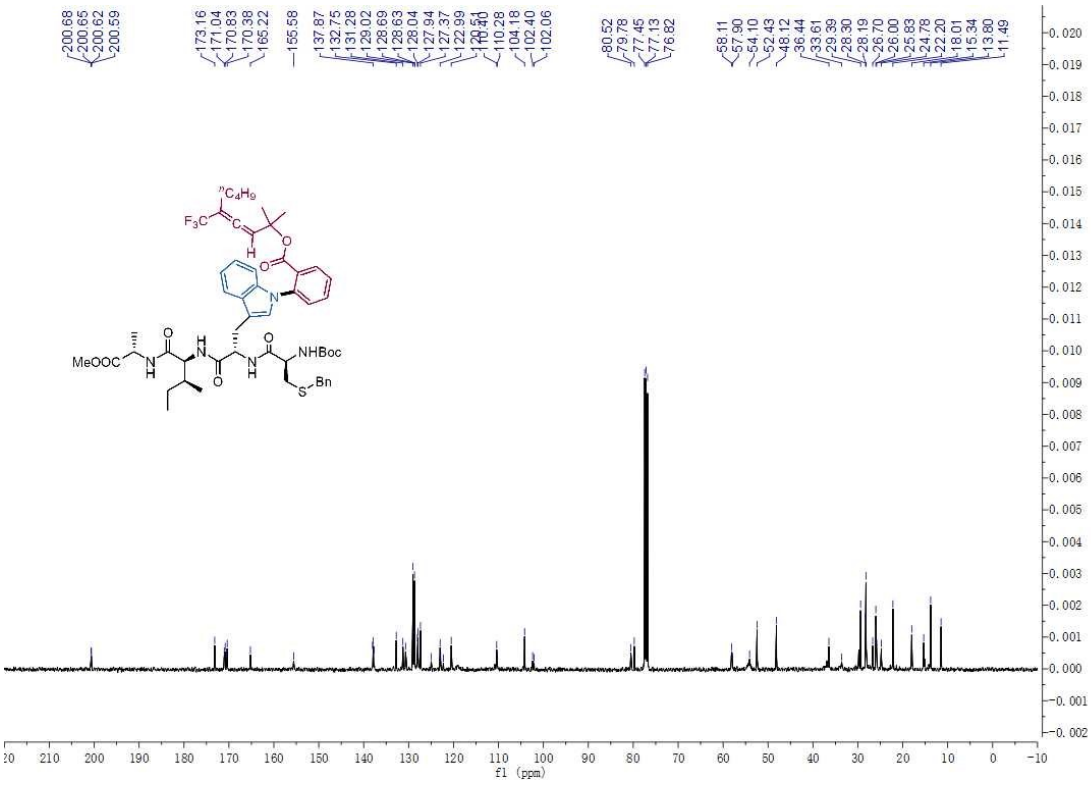


Fig 106. ^{13}C NMR of (**5h**)

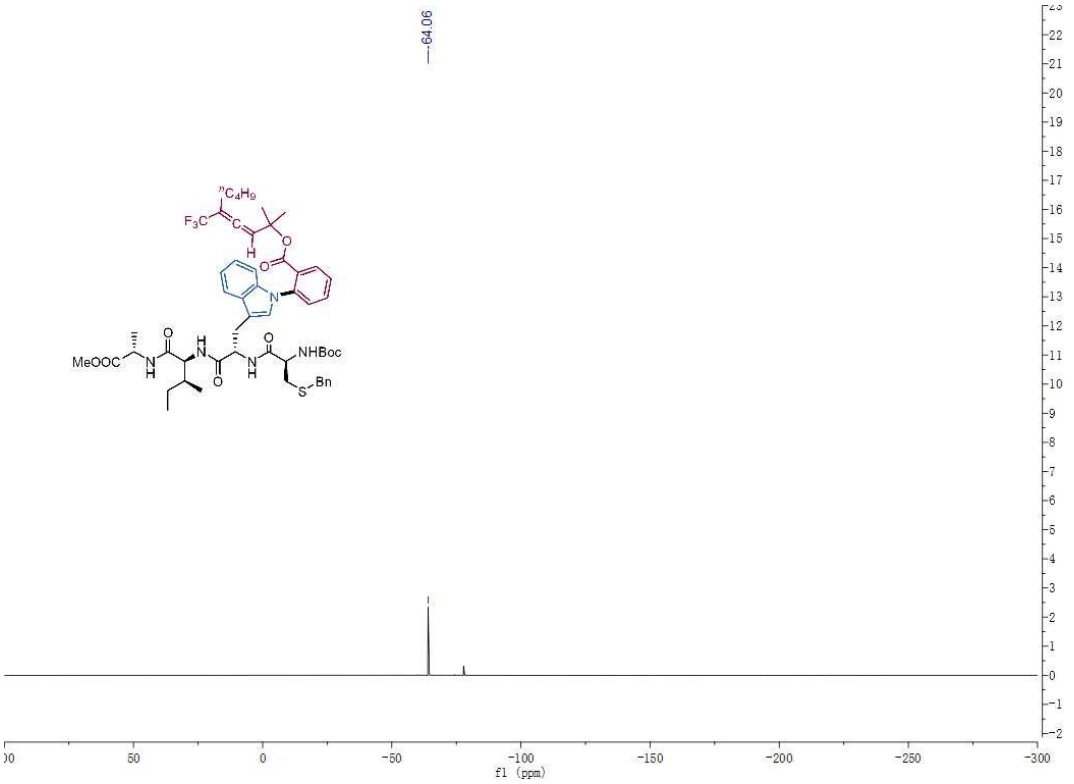


Fig 107. ^{19}F NMR of (**5h**)

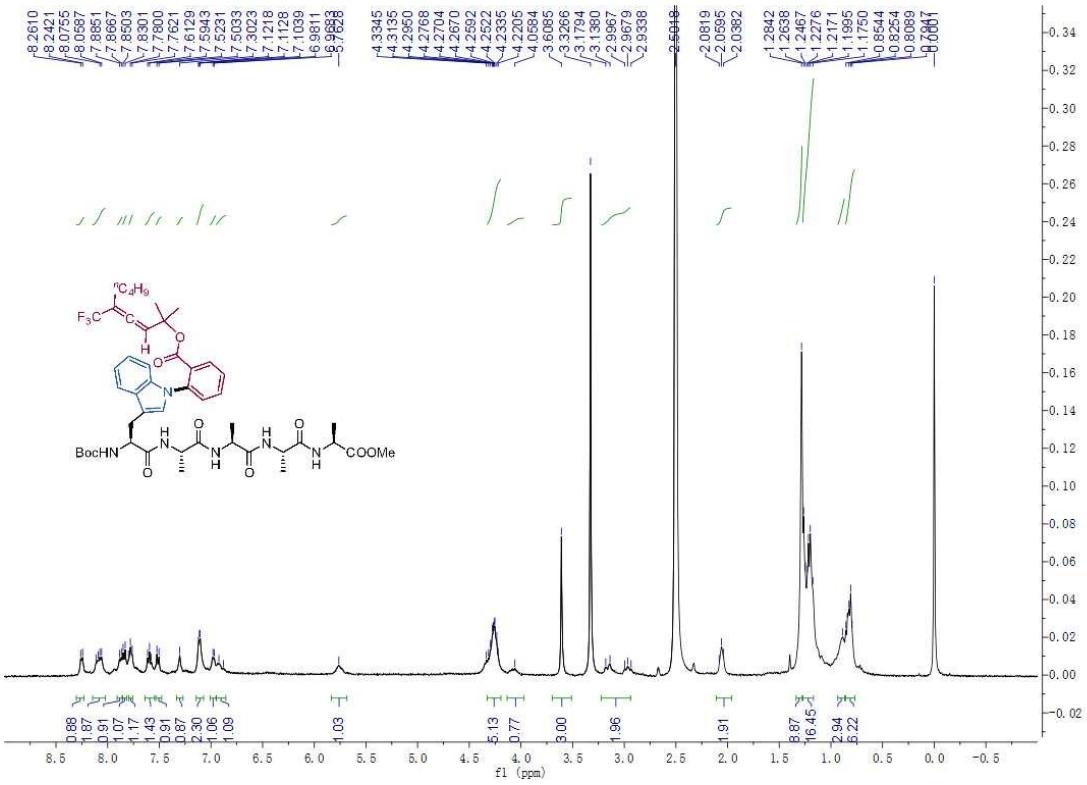


Fig 108. ^{1}H NMR of (**6a**)

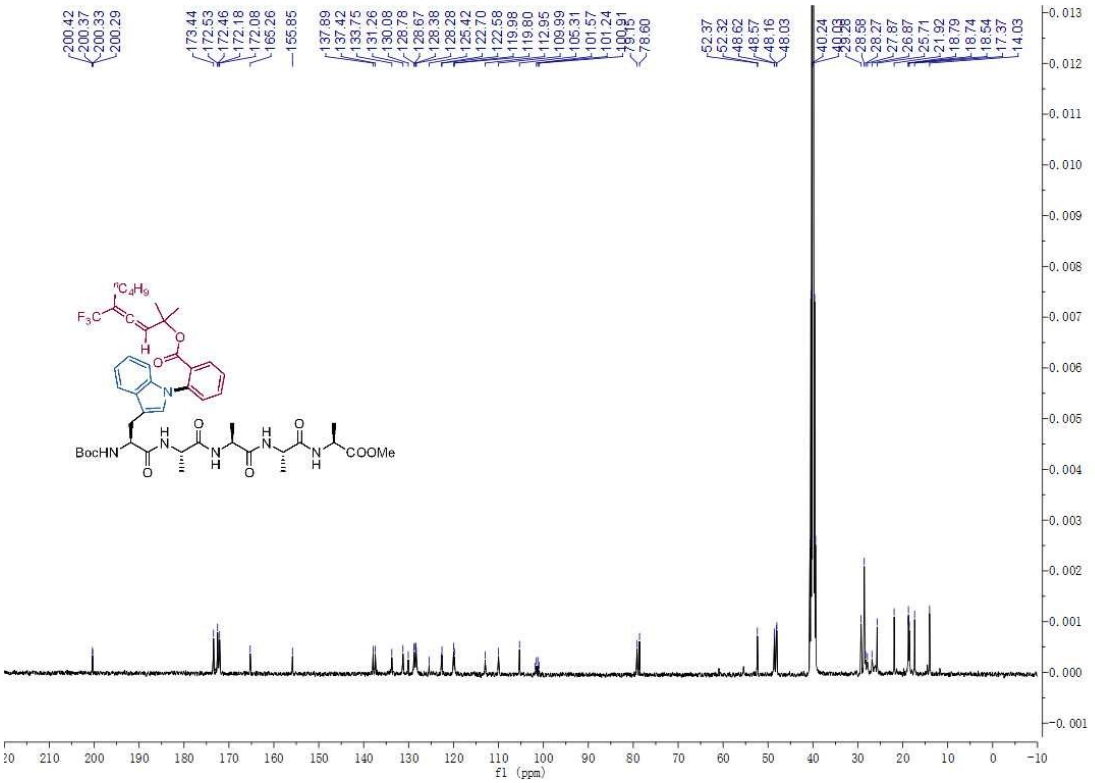


Fig 109. ^{13}C NMR of (**6a**)

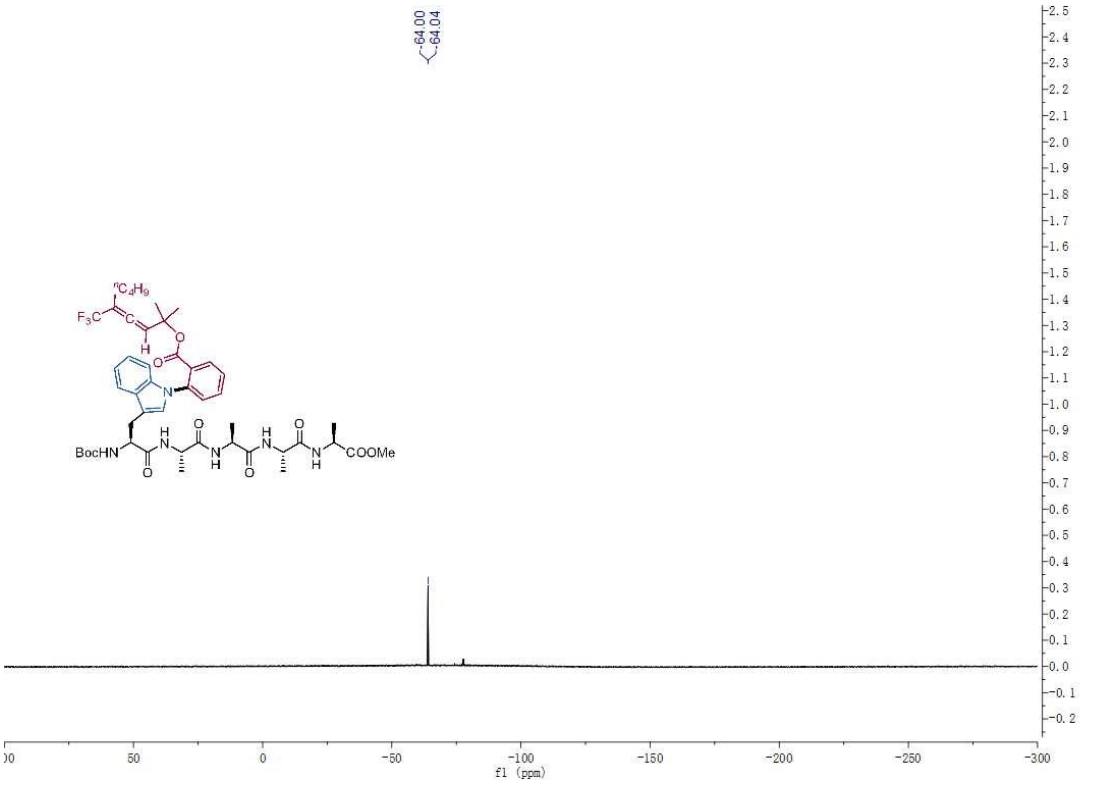


Fig 110. ^{19}F NMR of (**6a**)

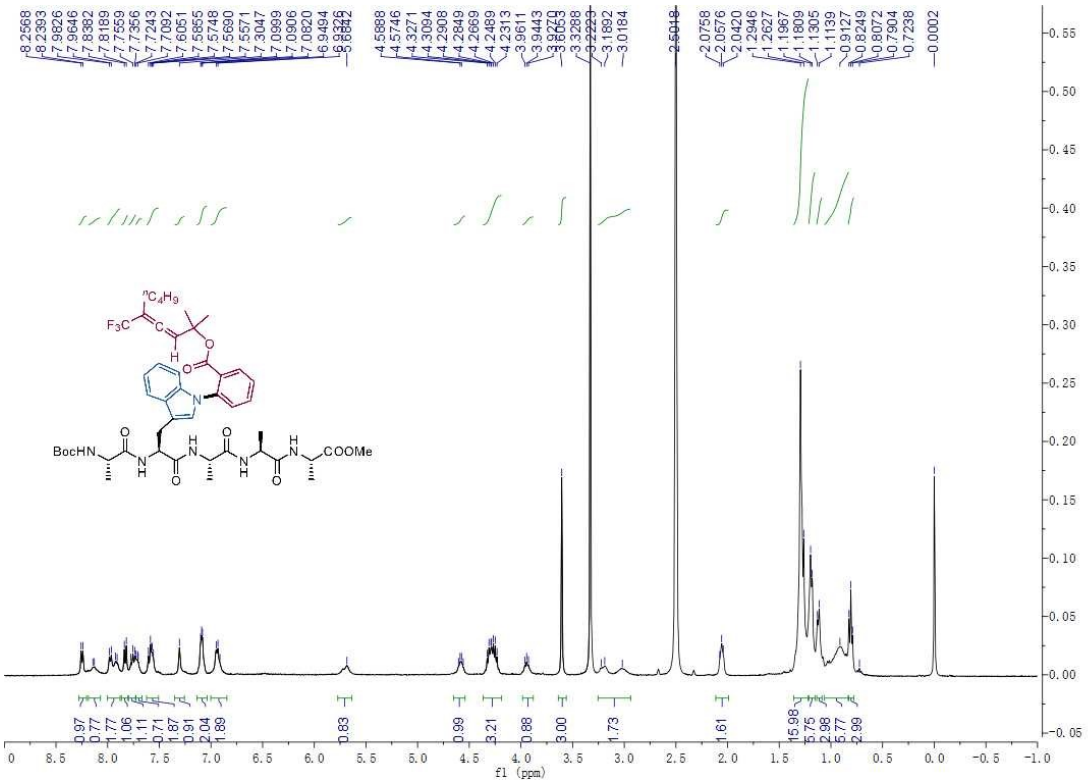


Fig 111. ^{1}H NMR of (**6b**)

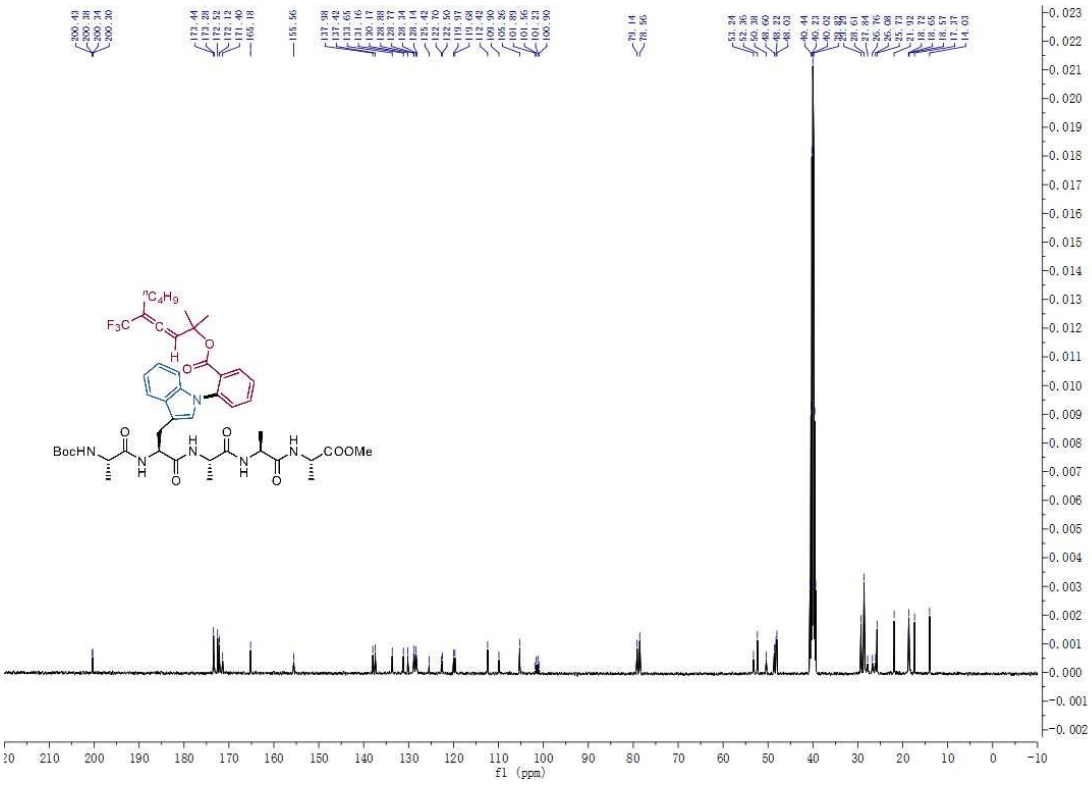


Fig 112. ^{13}C NMR of (**6b**)

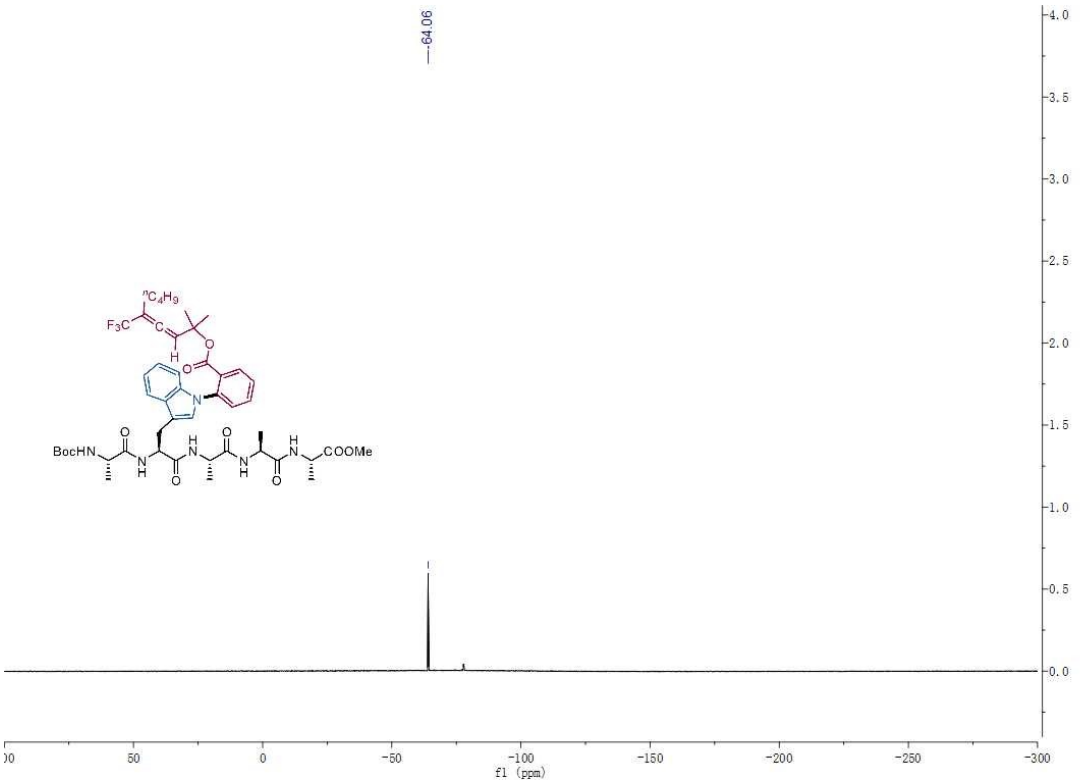


Fig 113. ^{19}F NMR of (**6b**)

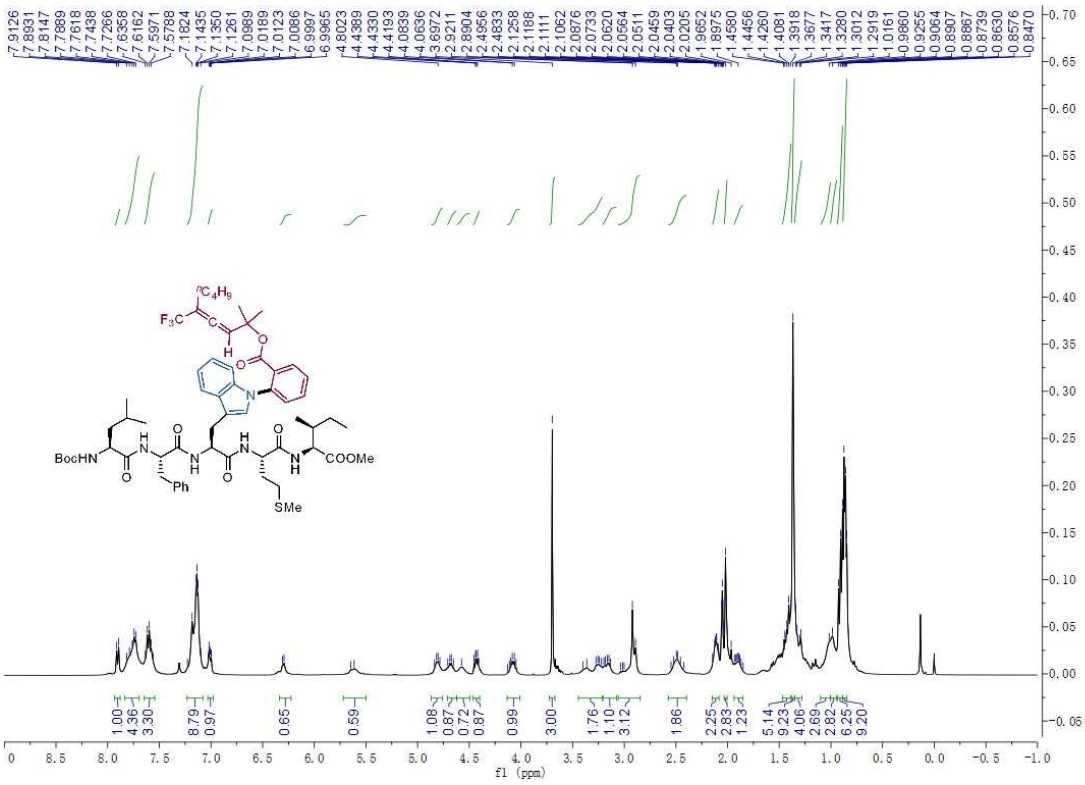


Fig 114. ^{1}H NMR of (**6c**)

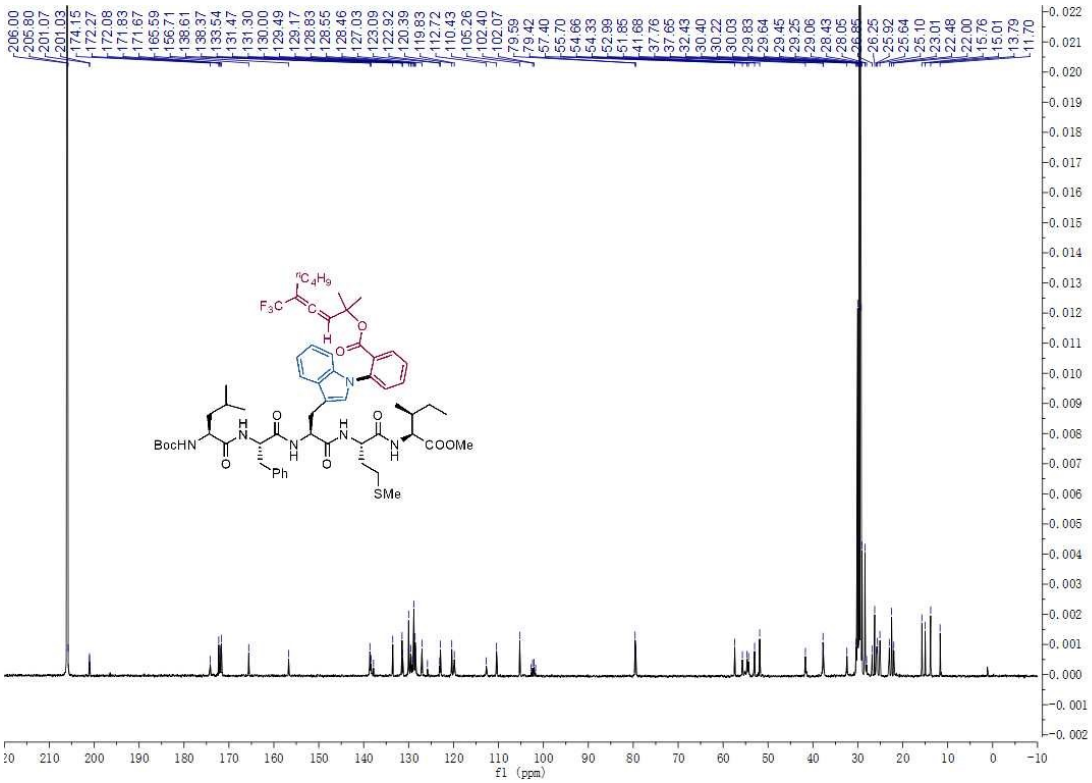


Fig 115. ^{13}C NMR of (**6c**)

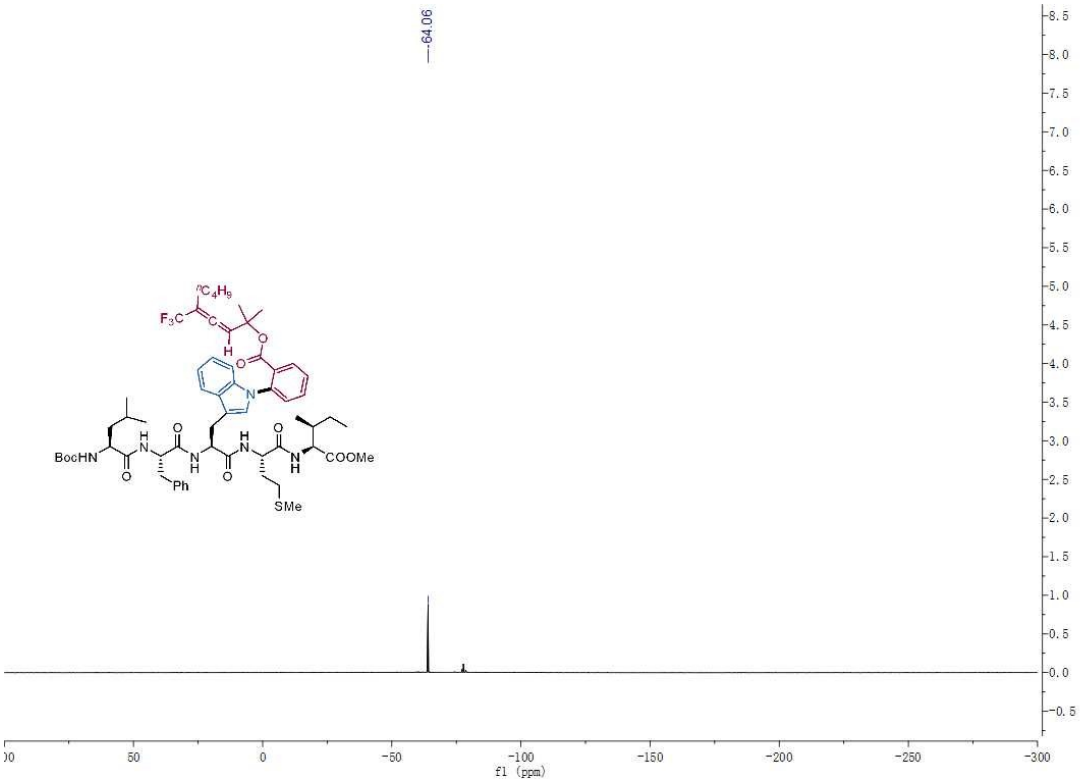


Fig 116. ^{19}F NMR of (**6c**)

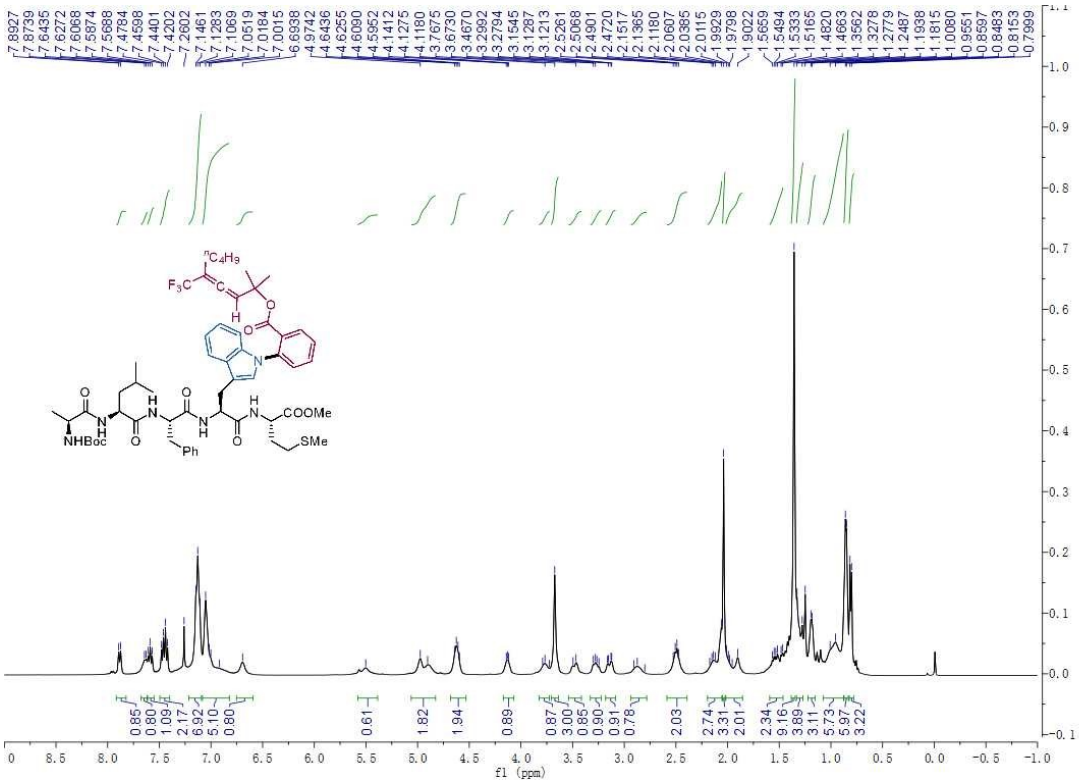


Fig 117. ^{1}H NMR of (**6d**)

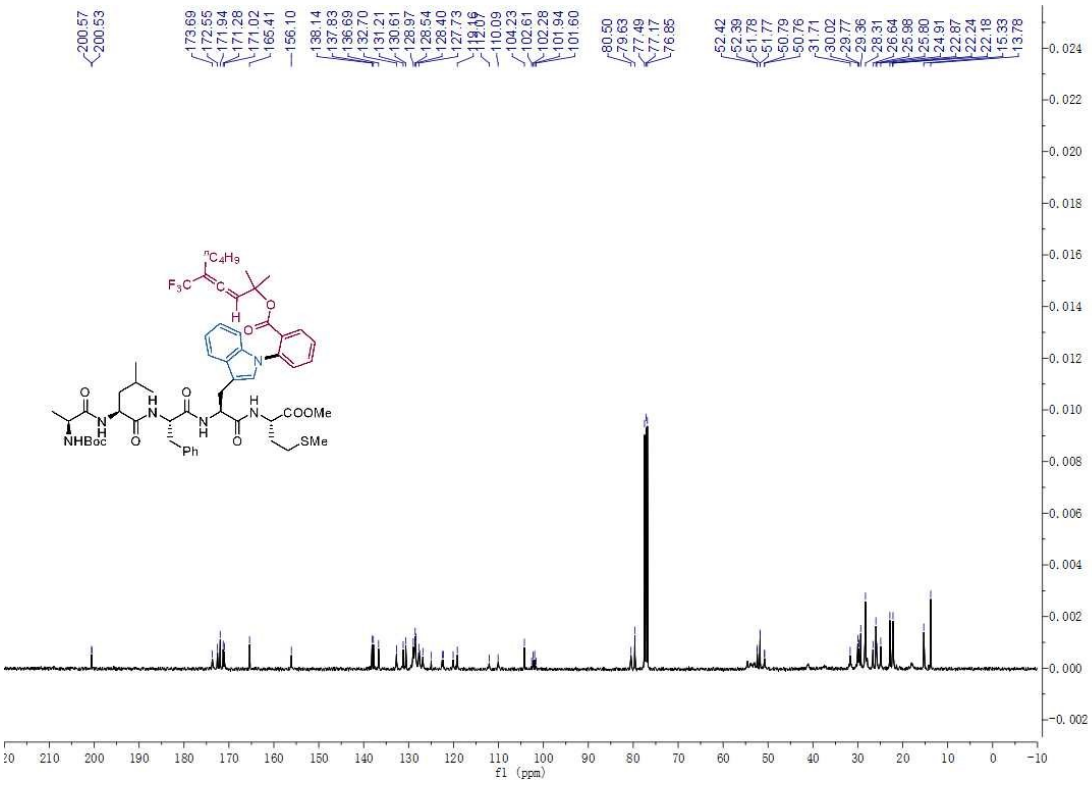


Fig 118. ^{13}C NMR of (**6d**)

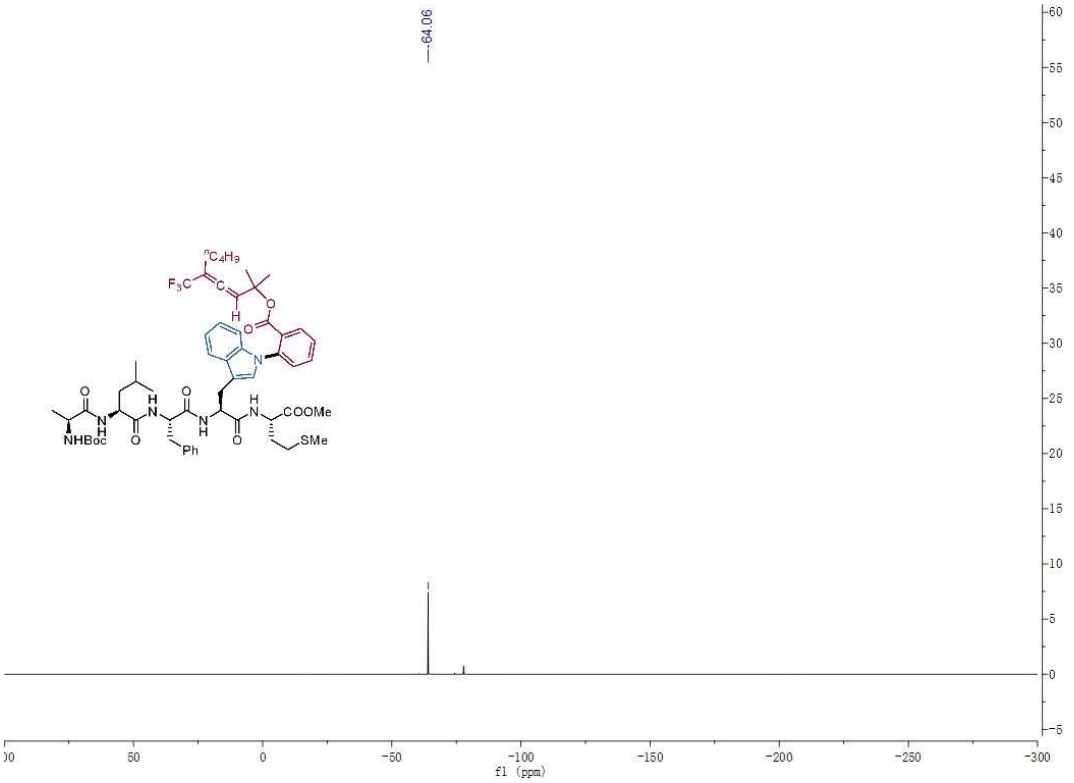


Fig 119. ^{19}F NMR of (**6d**)

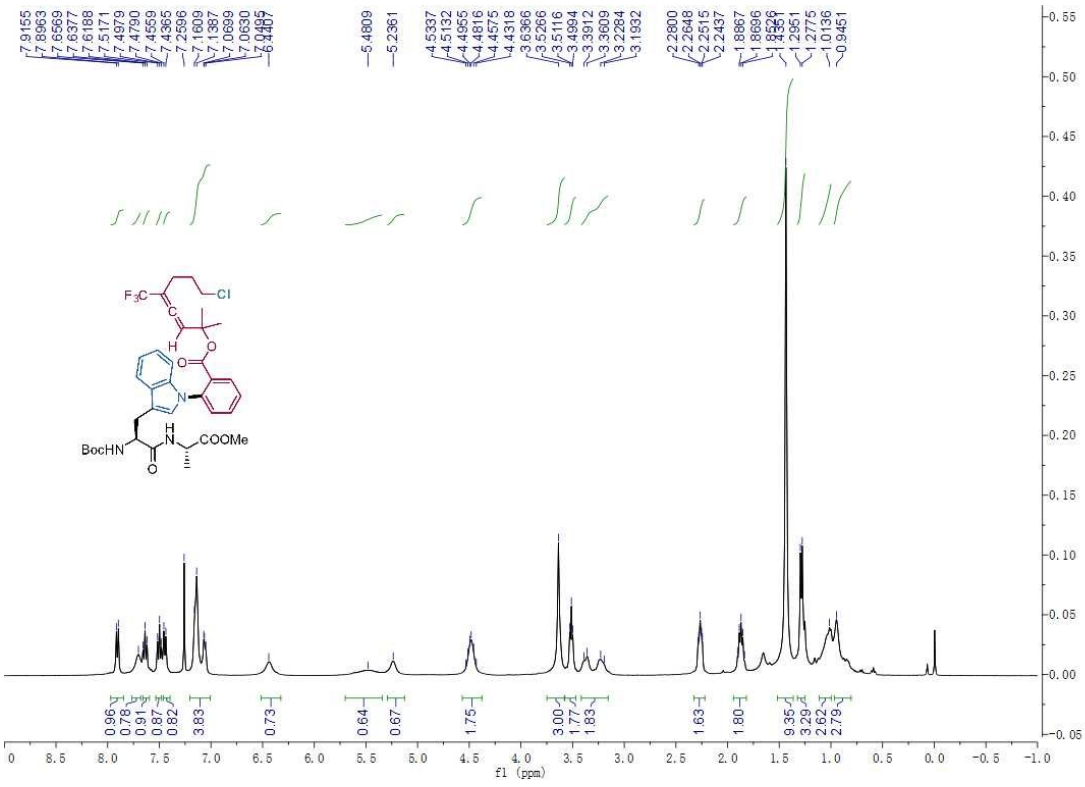


Fig 120. ^{1}H NMR of (**7a**)

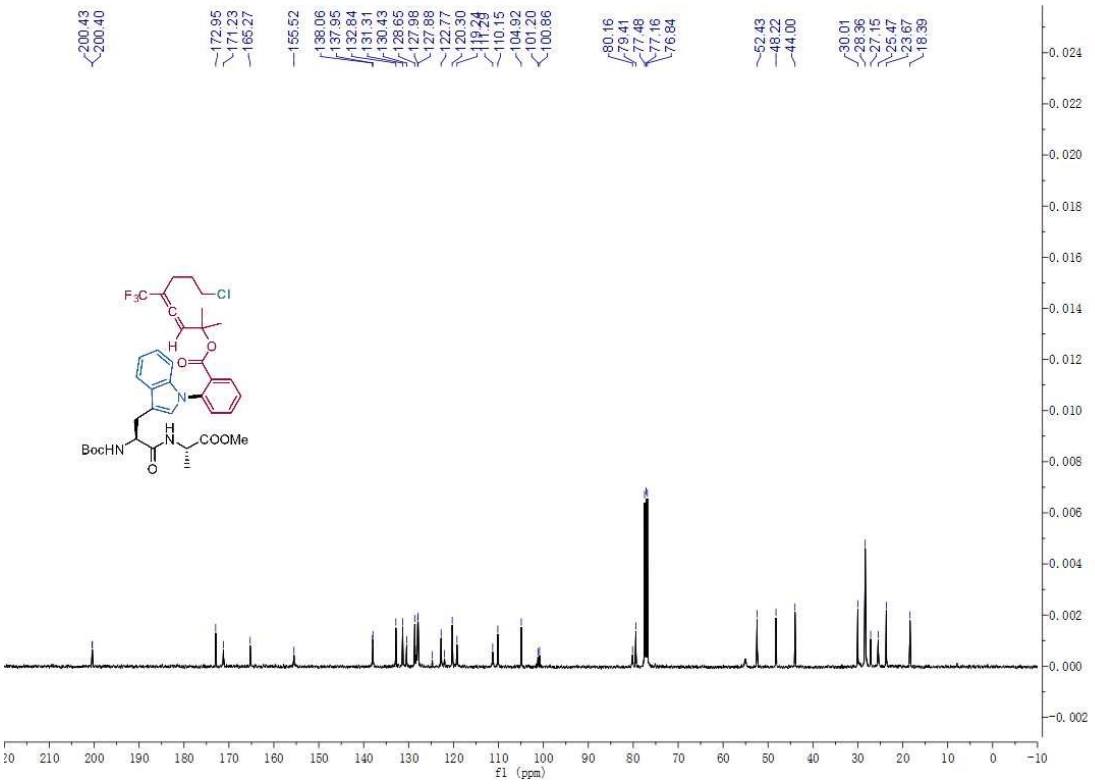


Fig 121. ^{13}C NMR of (**7a**)

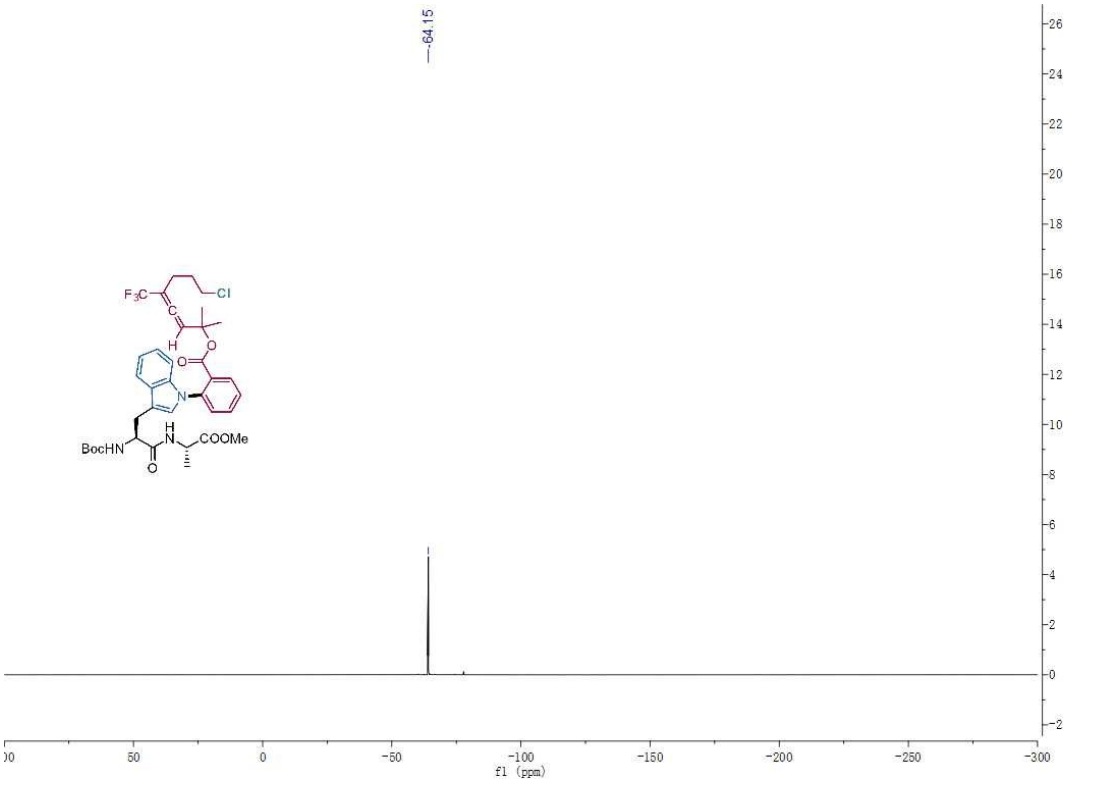


Fig 122. ^{19}F NMR of (**7a**)

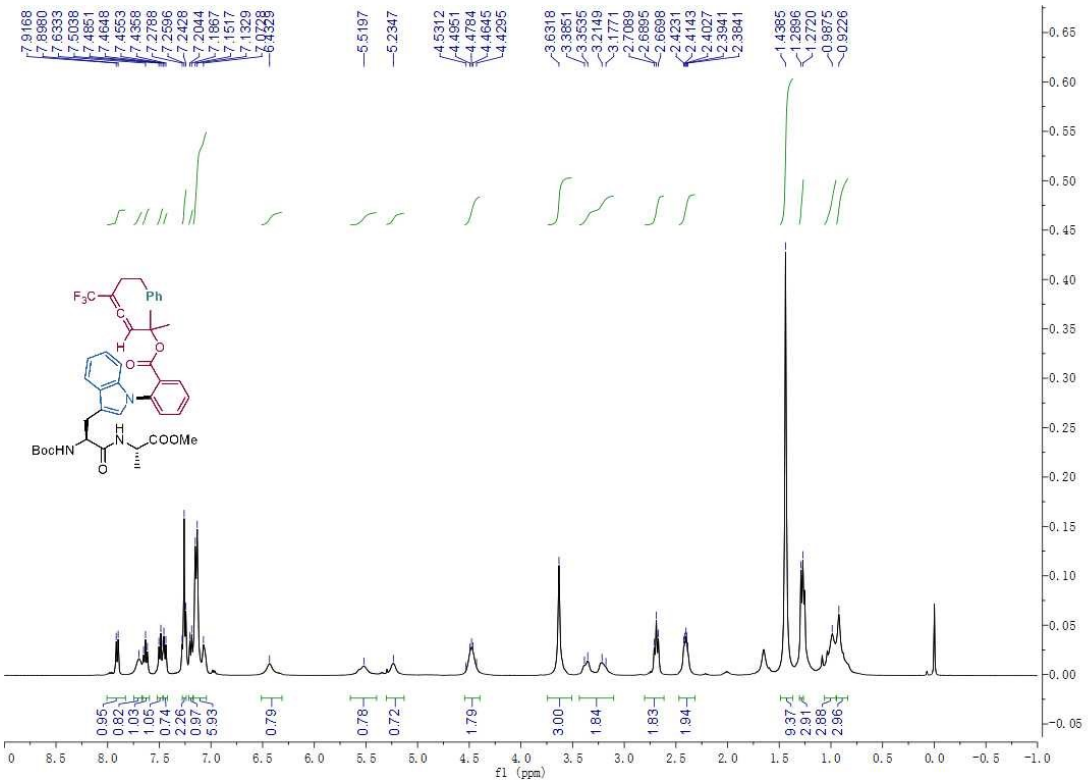


Fig 123. ^{1}H NMR of (**7b**)

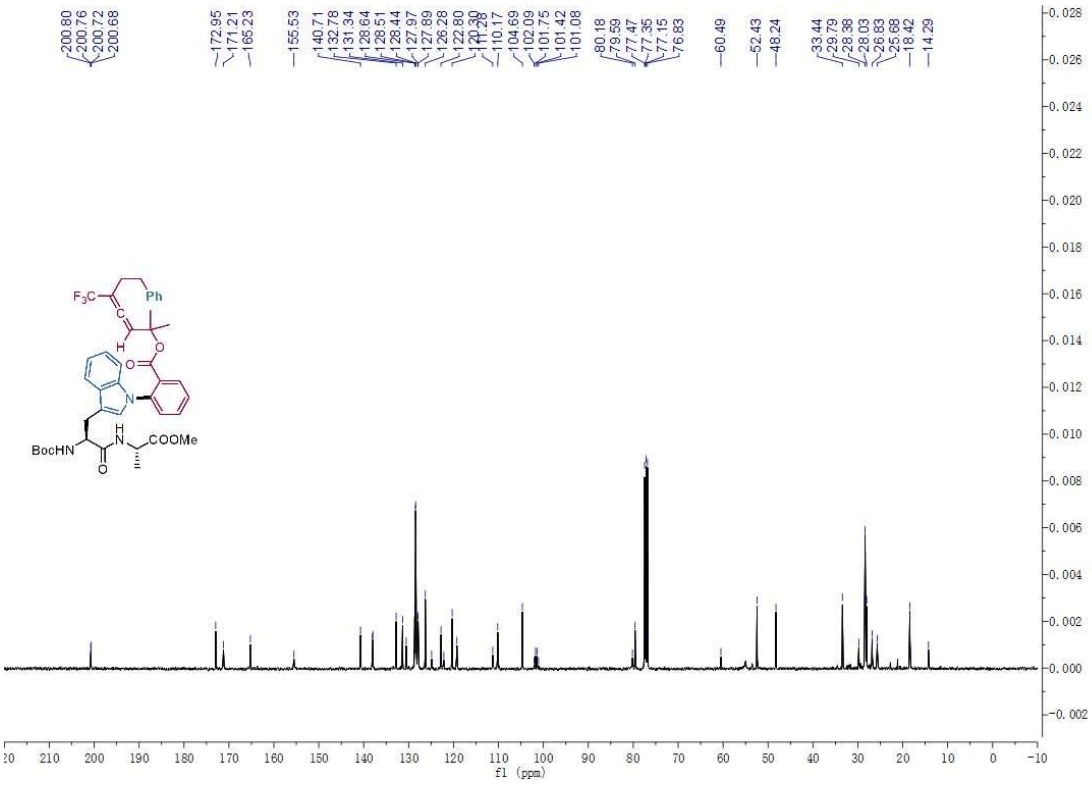


Fig 124. ^{13}C NMR of (**7b**)

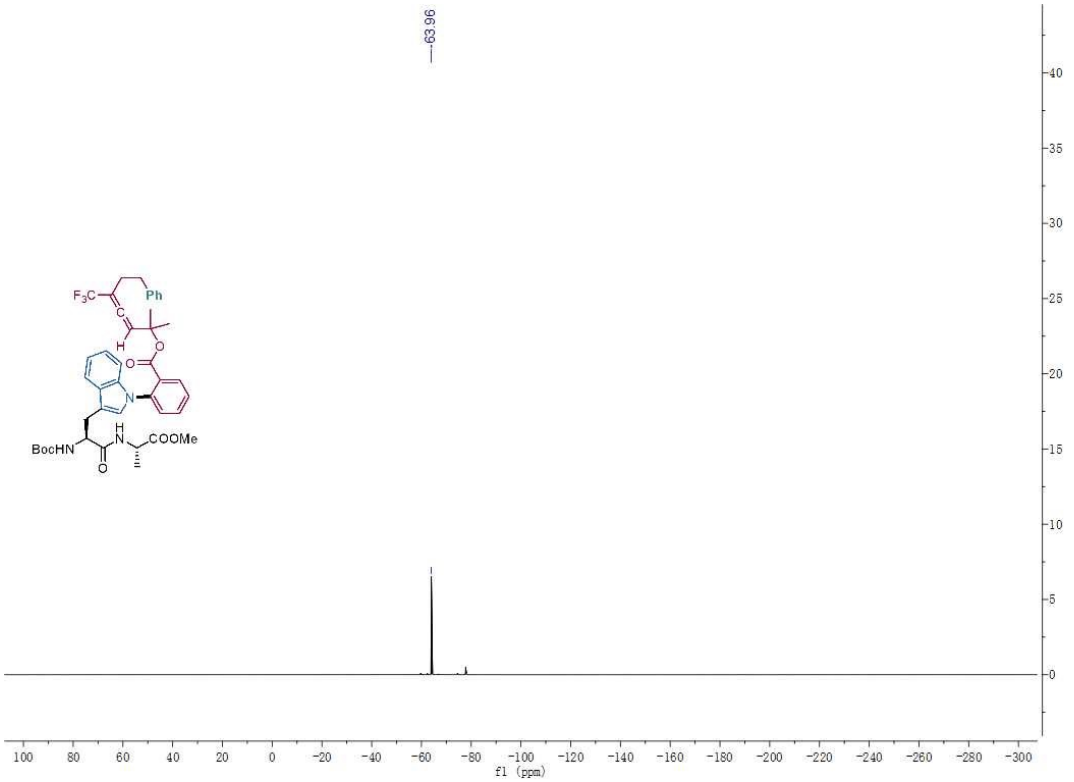


Fig 125. ^{19}F NMR of (**7b**)

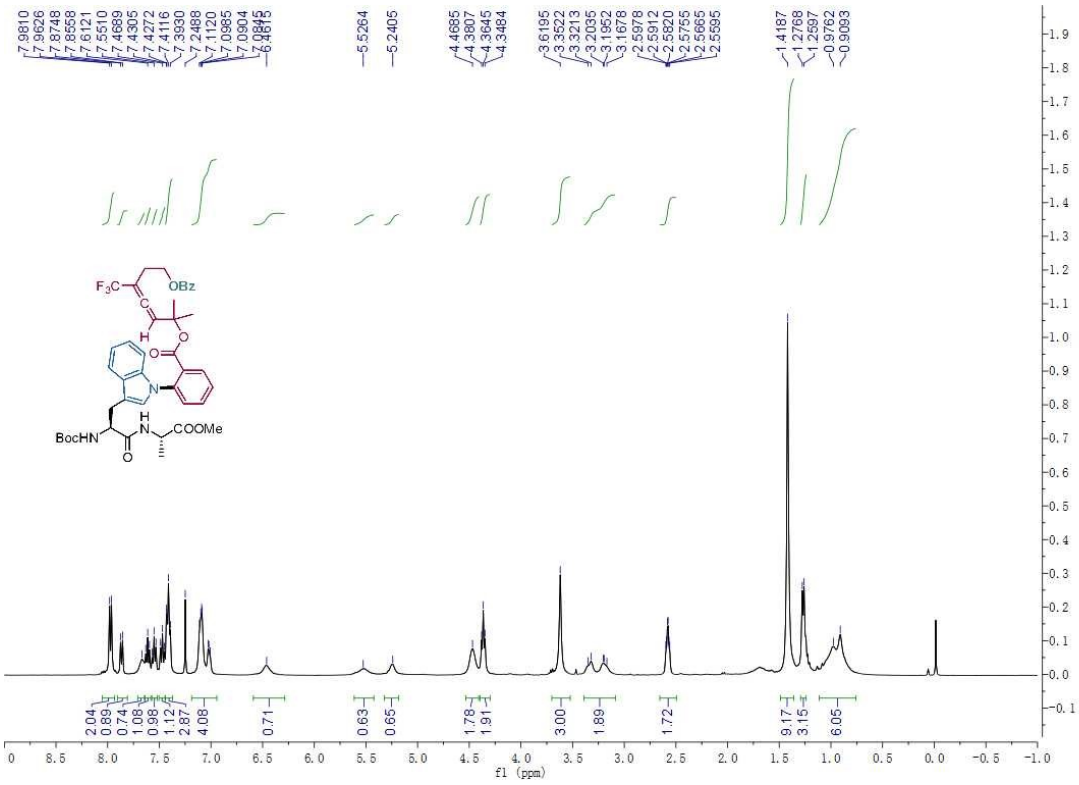


Fig 126. ^{1}H NMR of (**7c**)

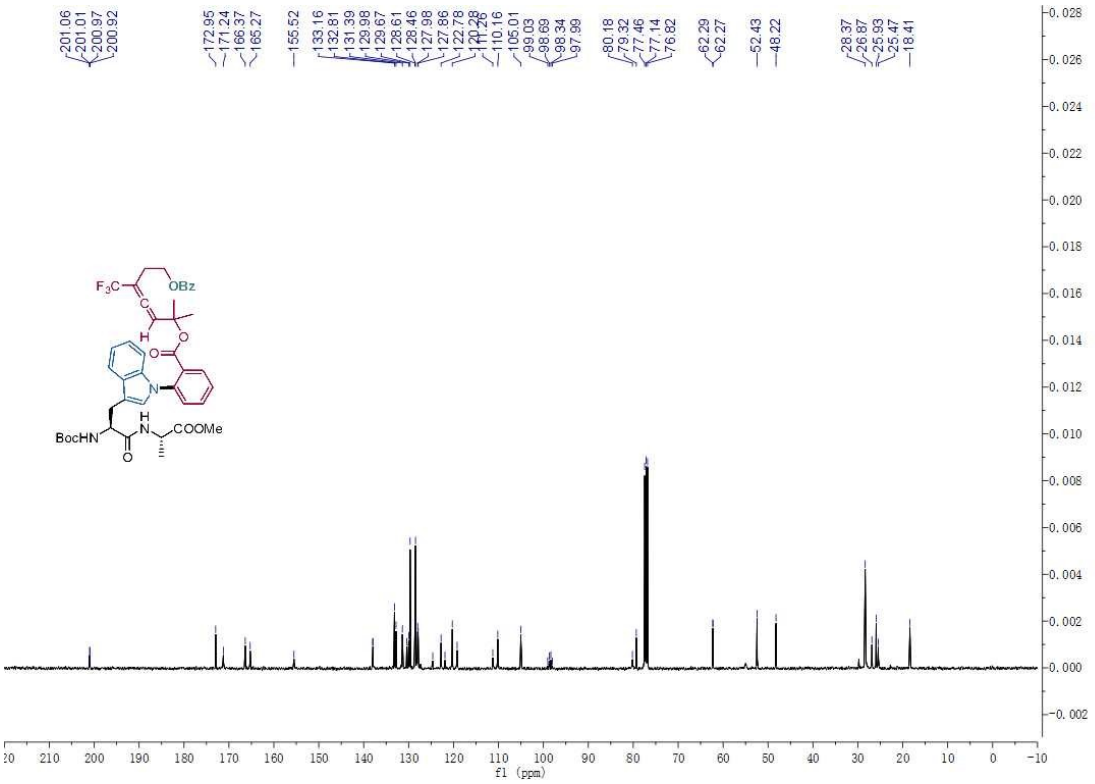


Fig 127. ^{13}C NMR of (**7c**)

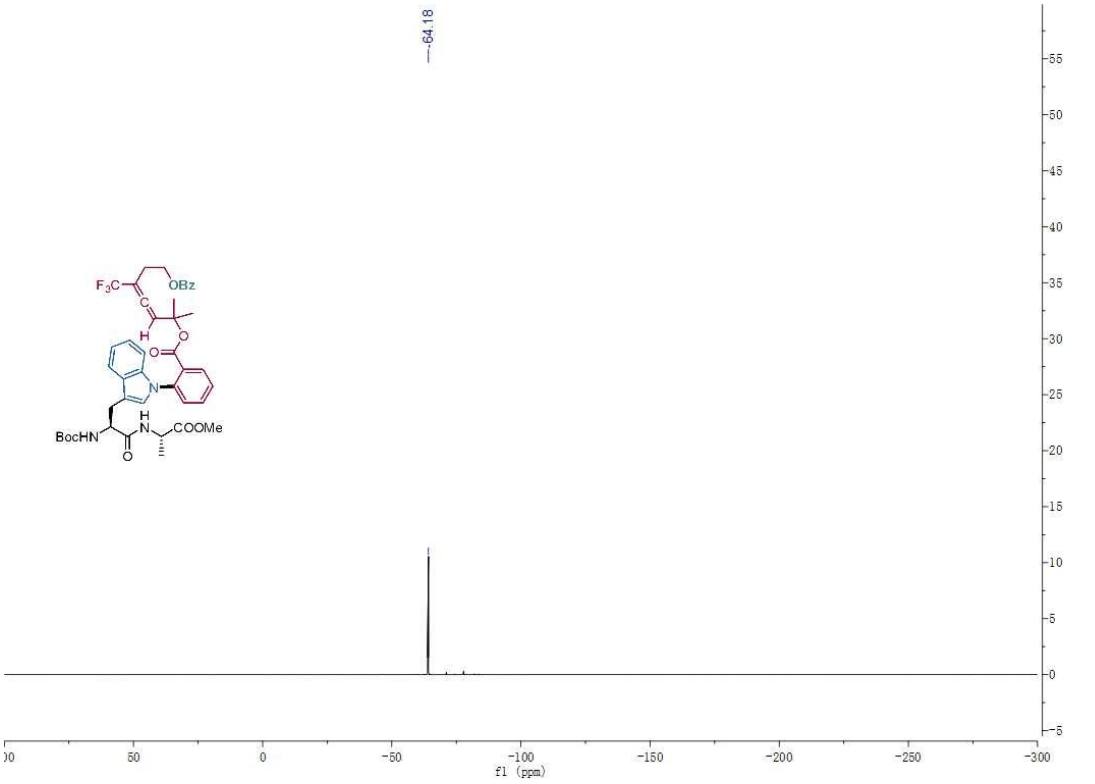


Fig 128. ^{19}F NMR of (**7c**)

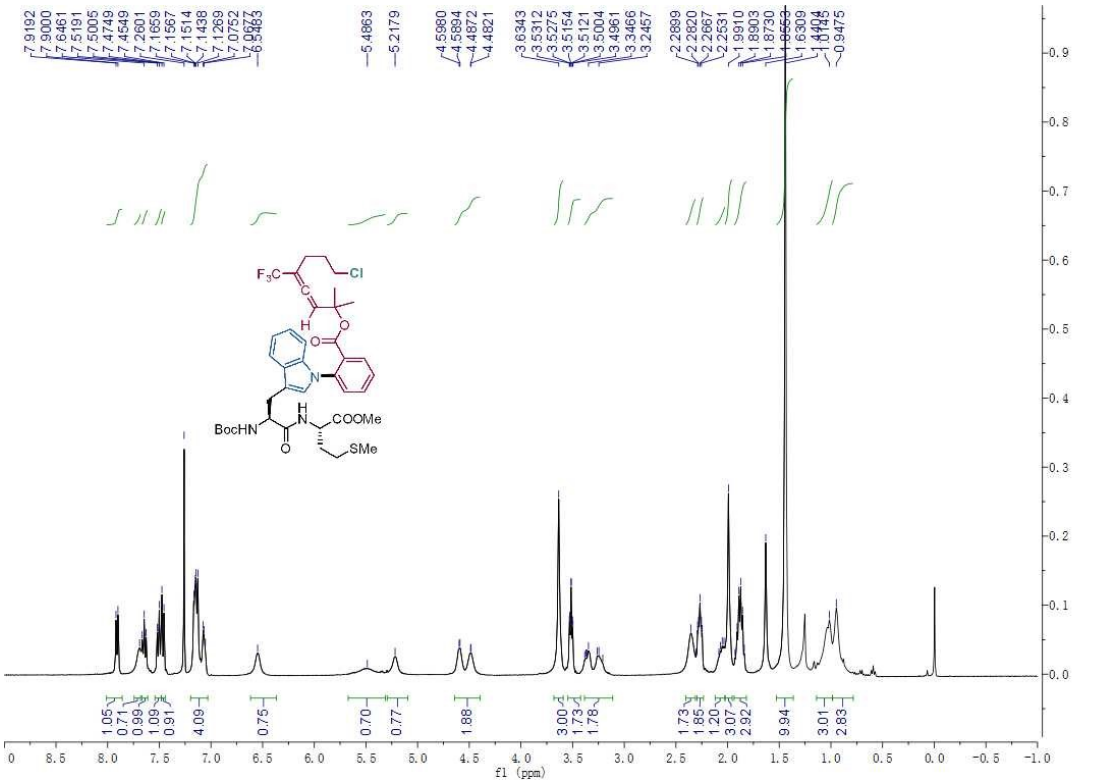


Fig 129. ^{1}H NMR of (**7d**)

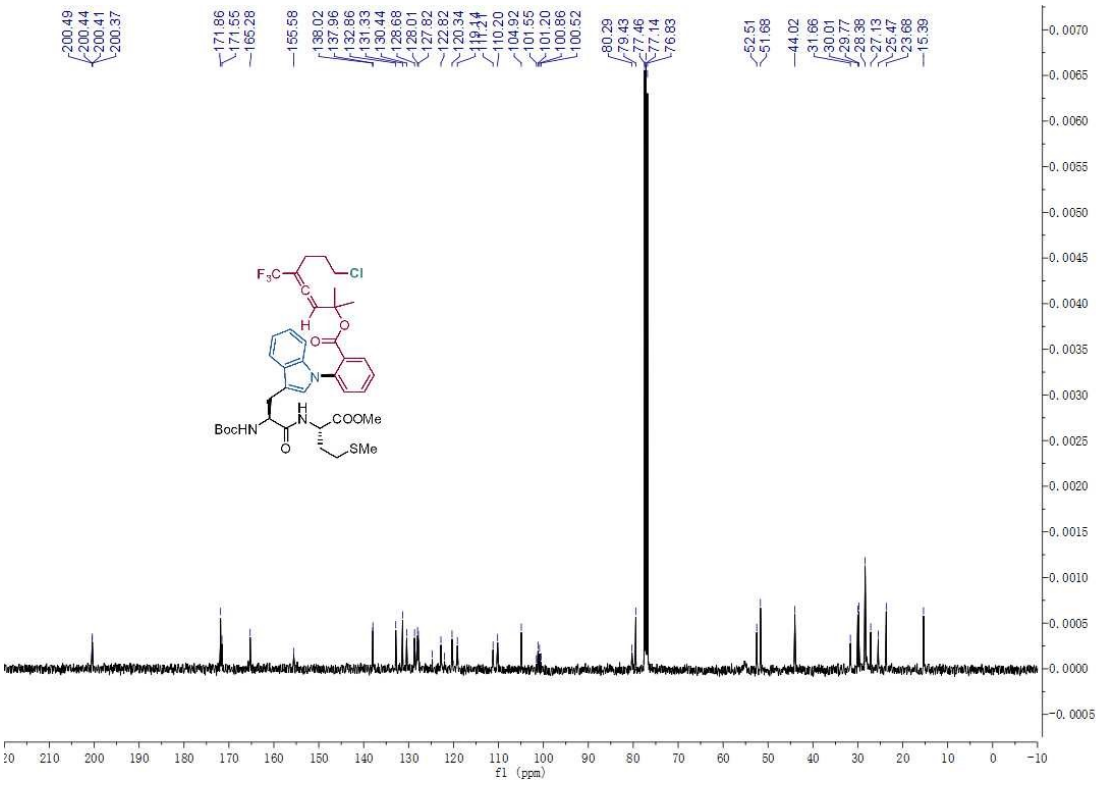


Fig 130. ^{13}C NMR of (**7d**)

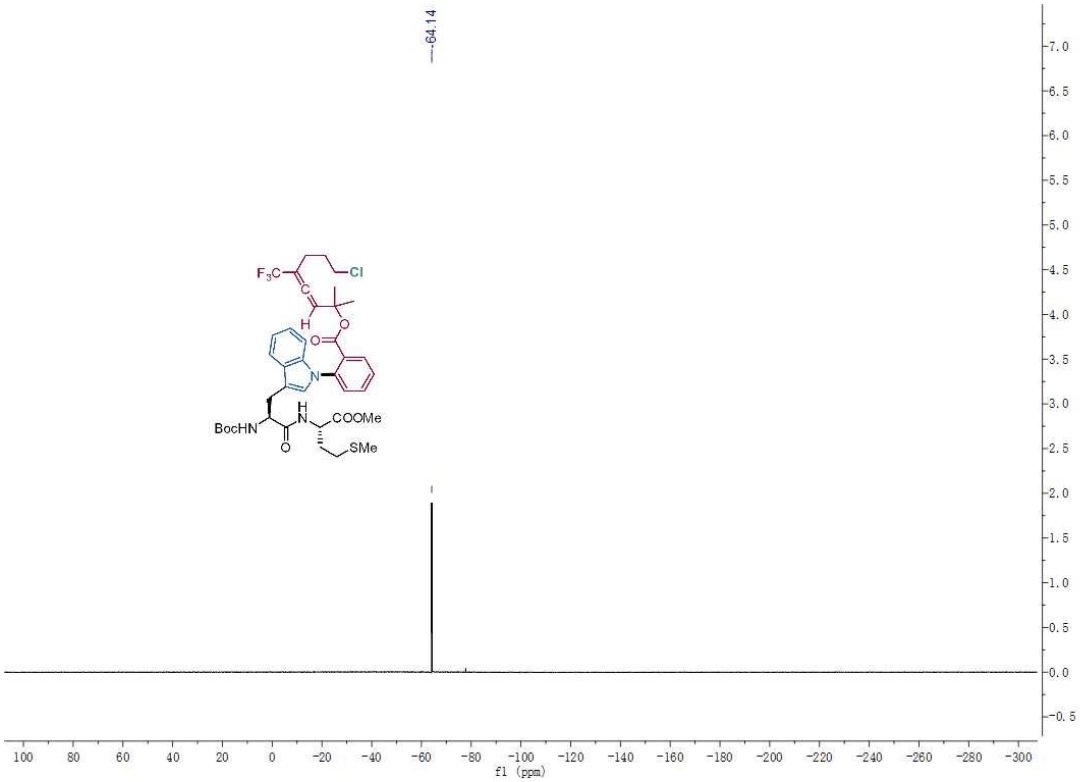


Fig 131. ^{19}F NMR of (**7d**)

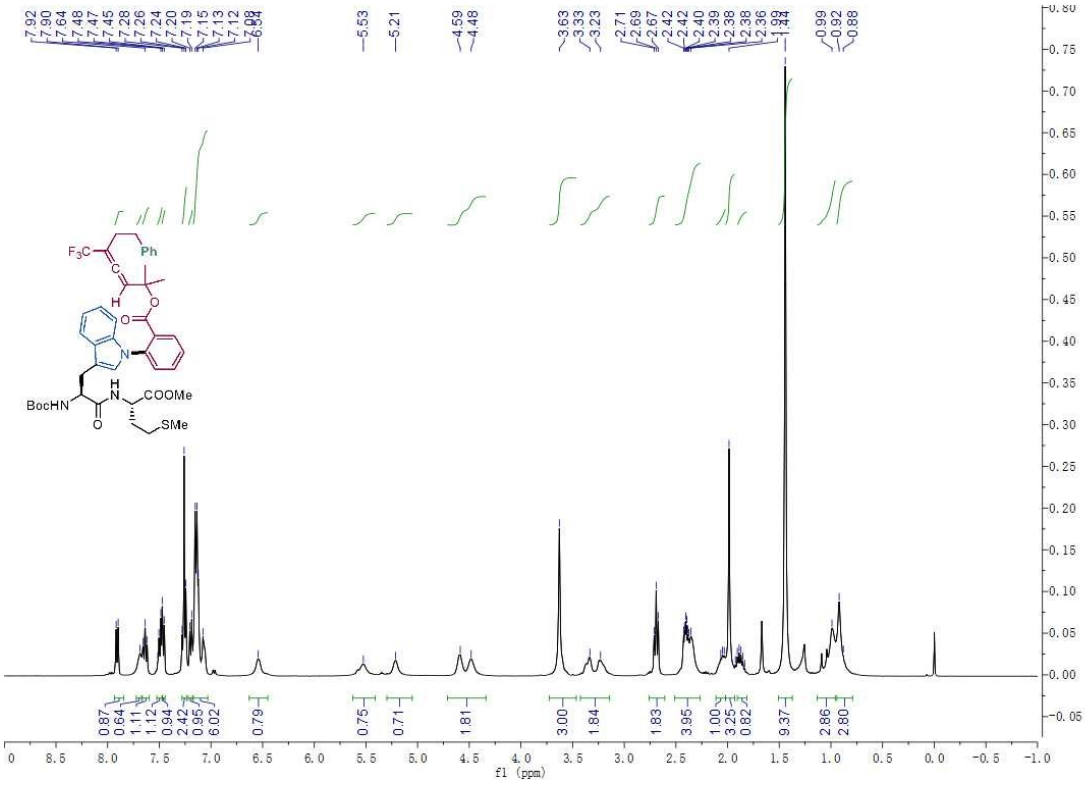


Fig 132. ^{1}H NMR of (**7e**)

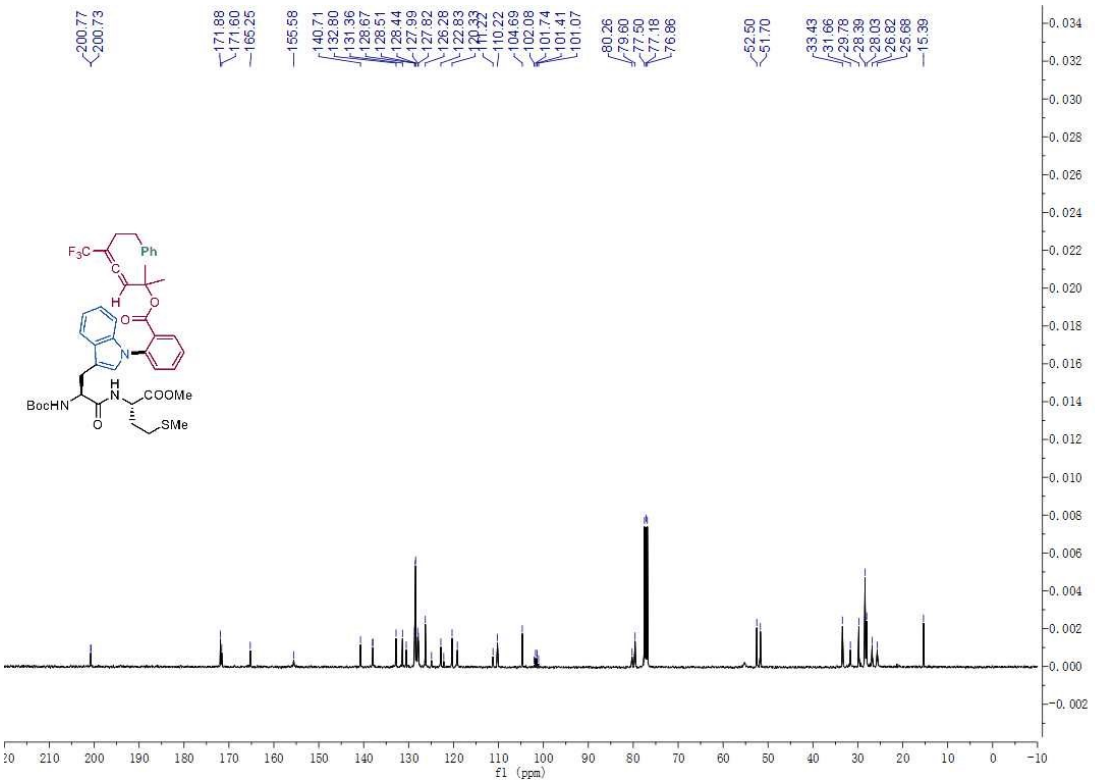


Fig 133. ^{13}C NMR of (**7e**)

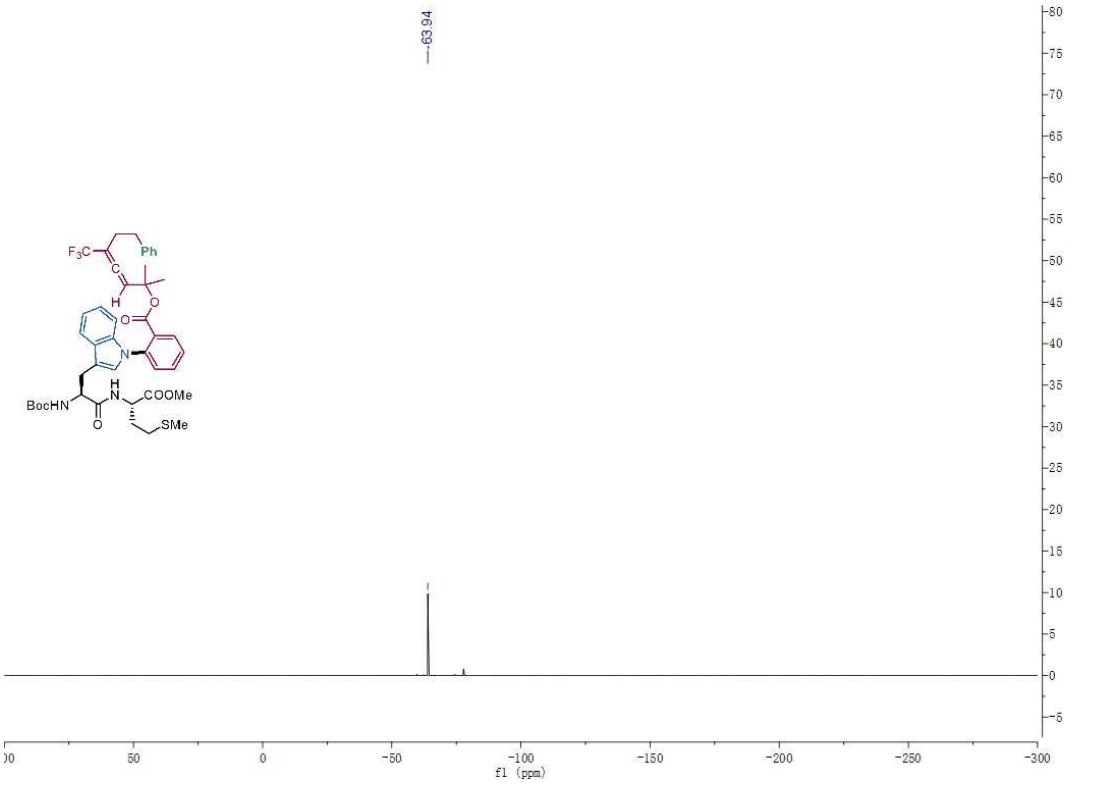


Fig 134. ^{19}F NMR of (**7e**)

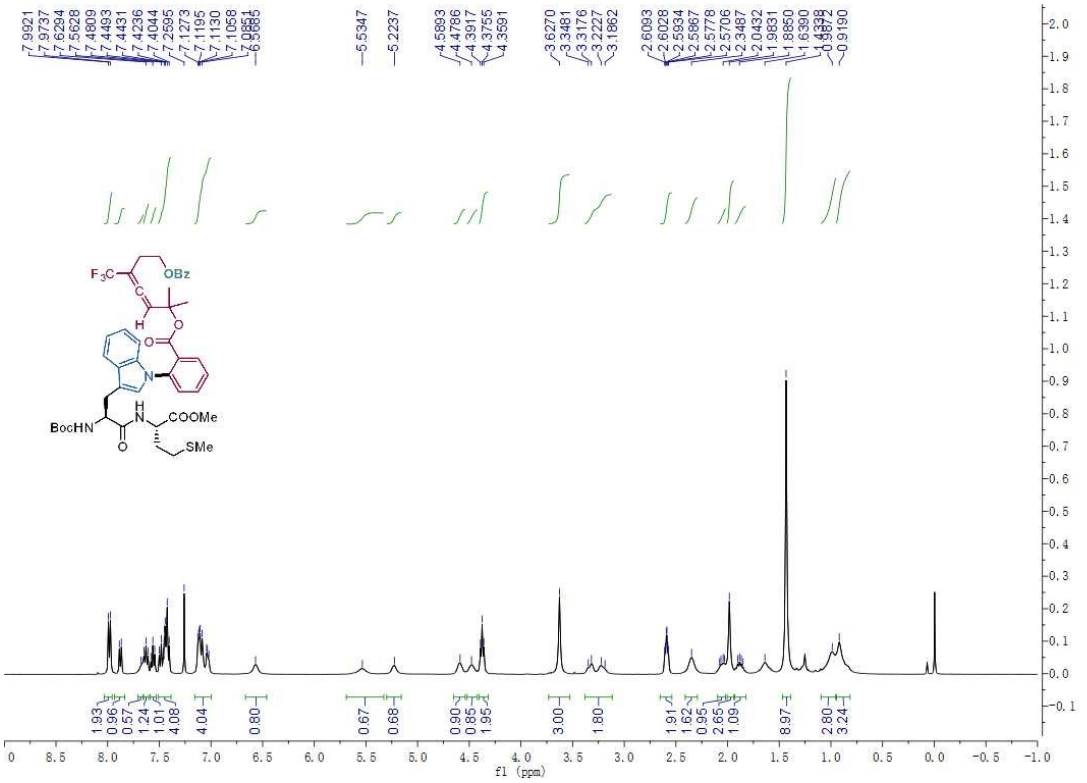


Fig 135. ^{1}H NMR of (**7f**)

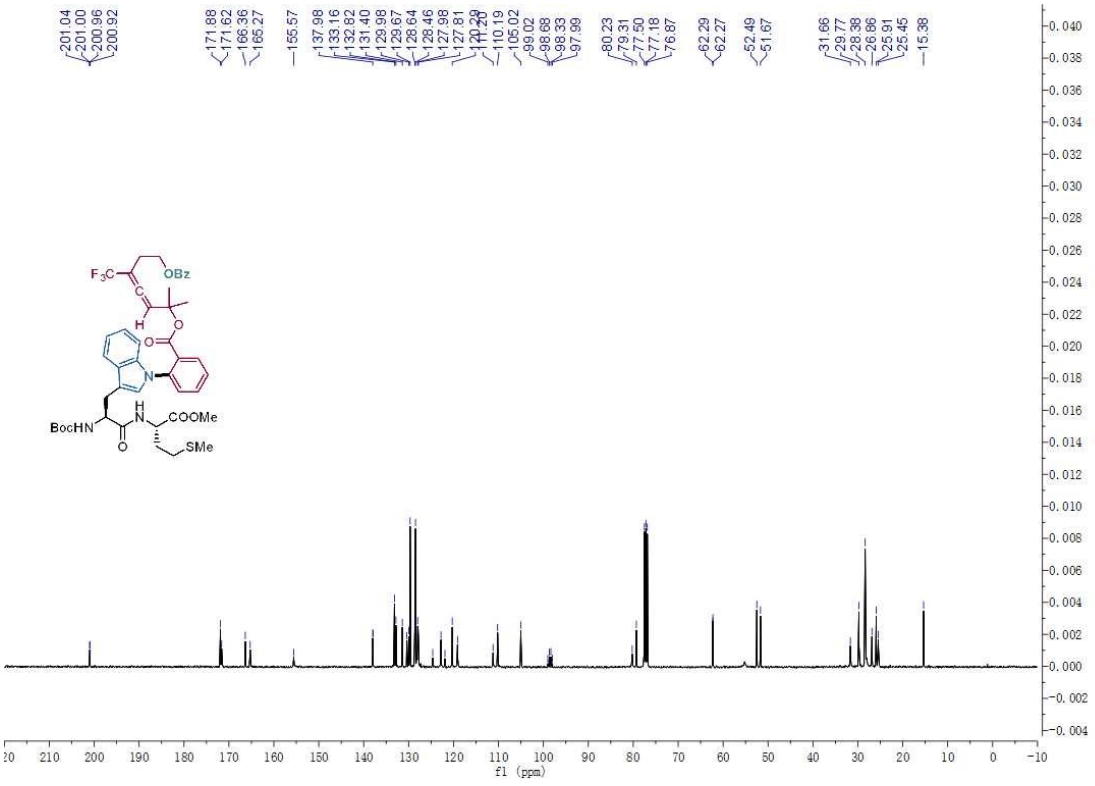


Fig 136. ^{13}C NMR of (**7f**)

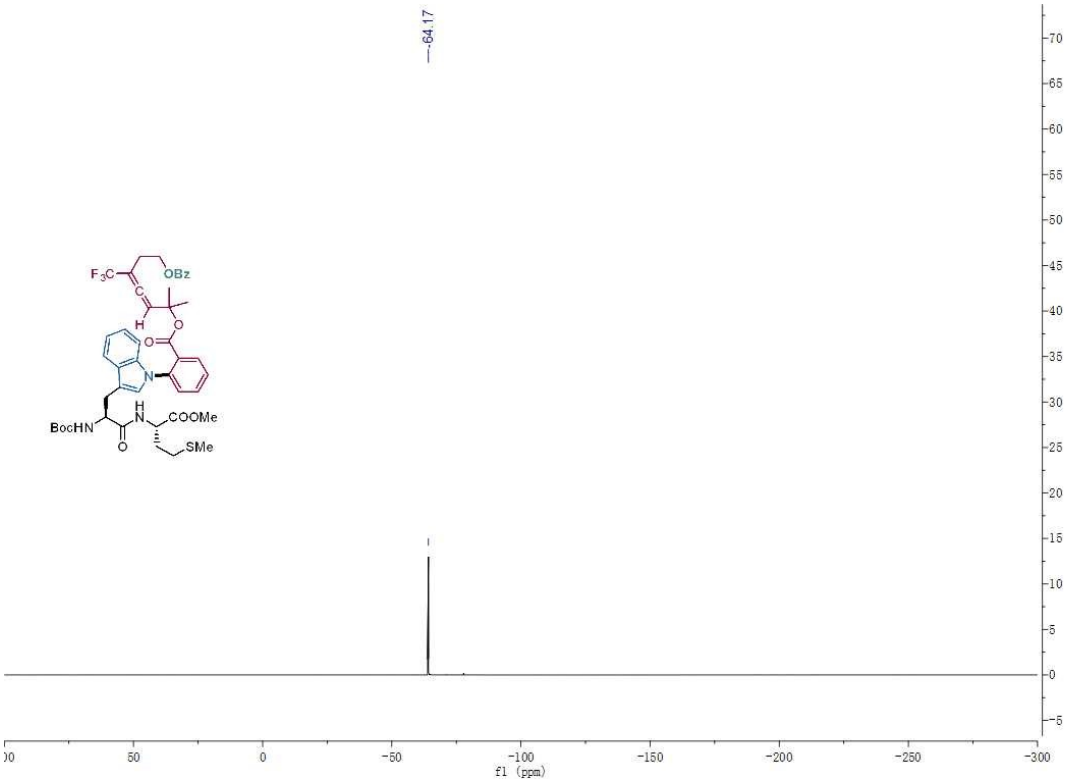


Fig 137. ^{19}F NMR of (**7f**)

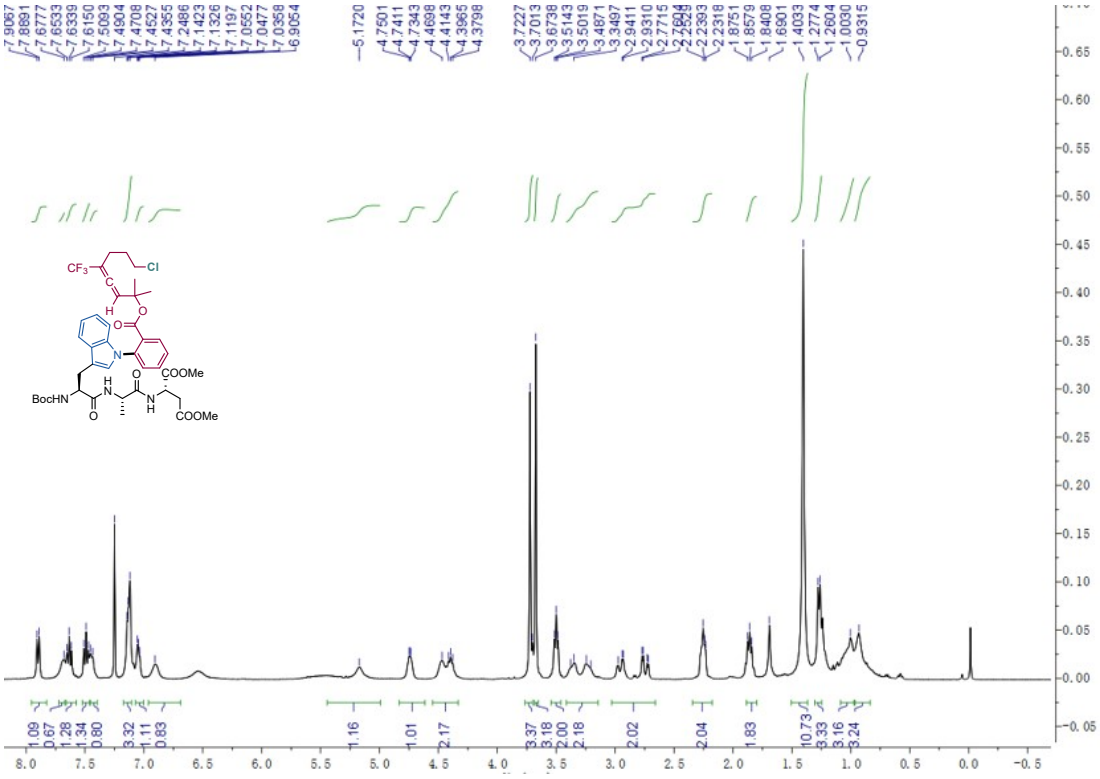


Fig 138. ^{1}H NMR of (**7g**)

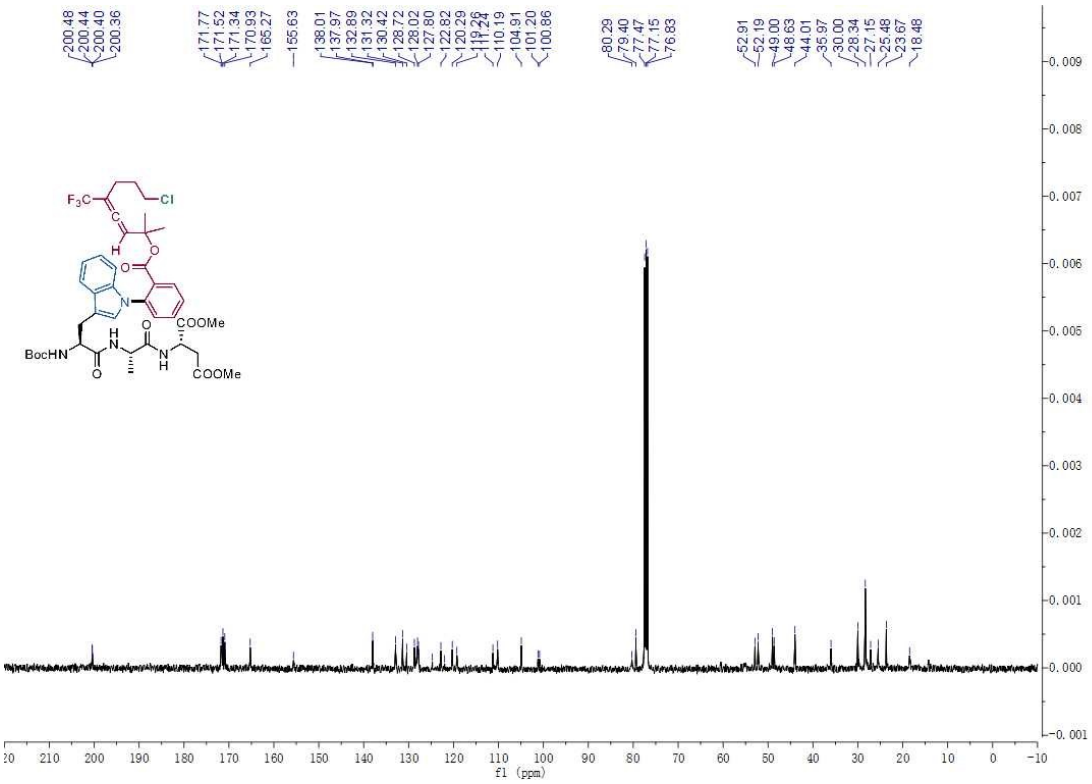


Fig 139. ^{13}C NMR of (**7g**)

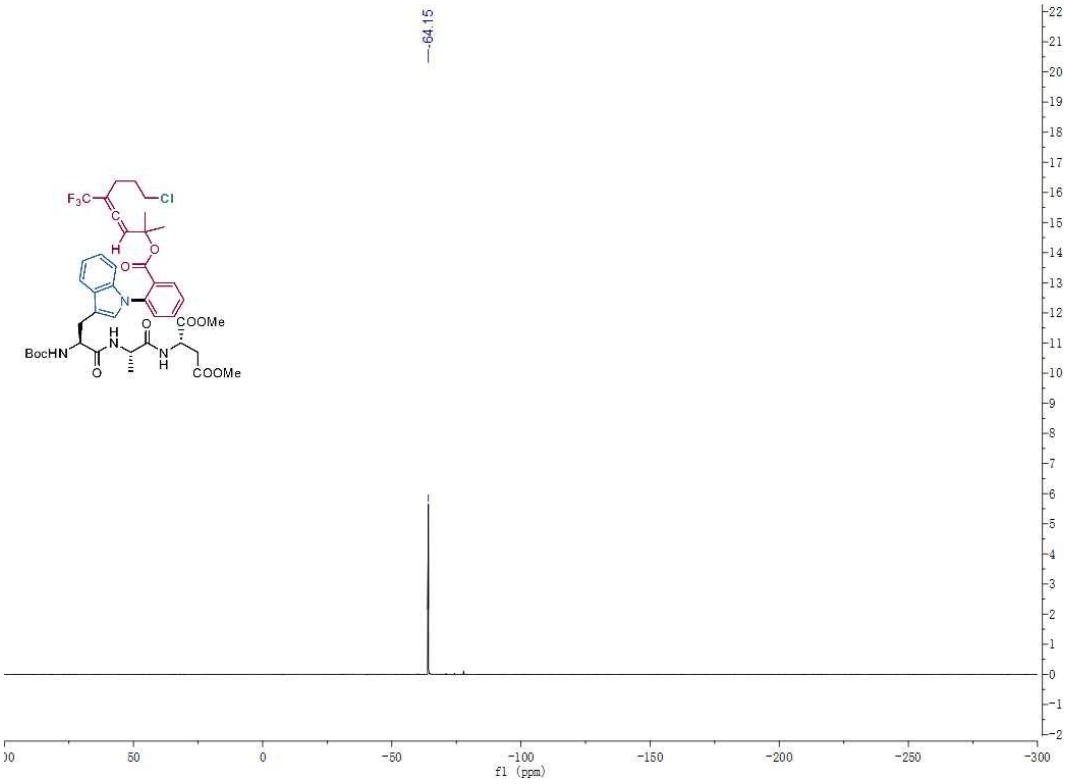


Fig 140. ^{19}F NMR of (**7g**)

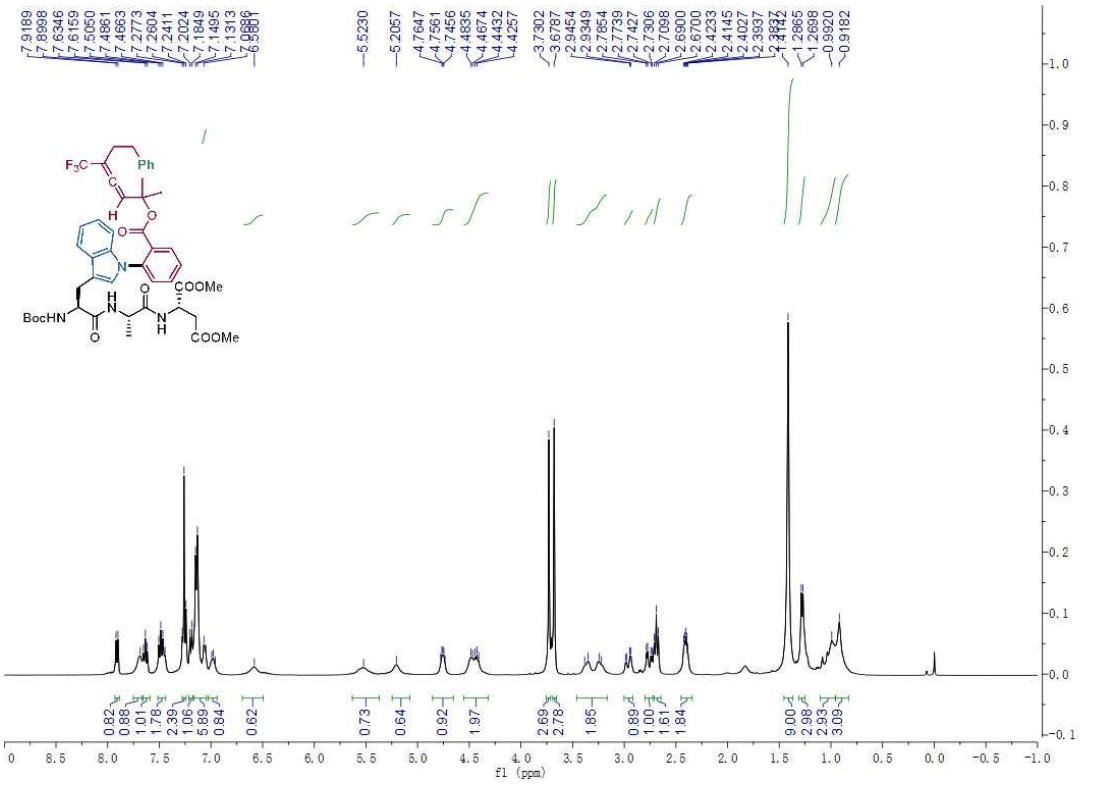


Fig 141. ^{1}H NMR of (**7h**)

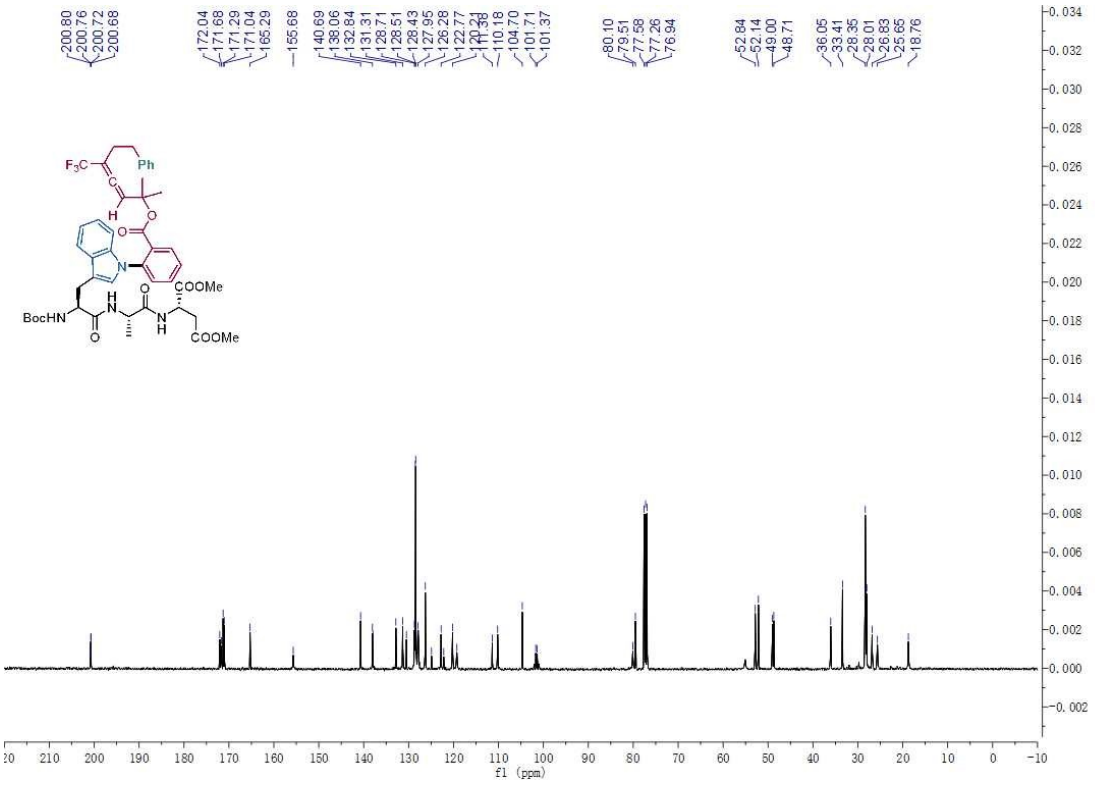


Fig 142. ^{13}C NMR of (**7h**)

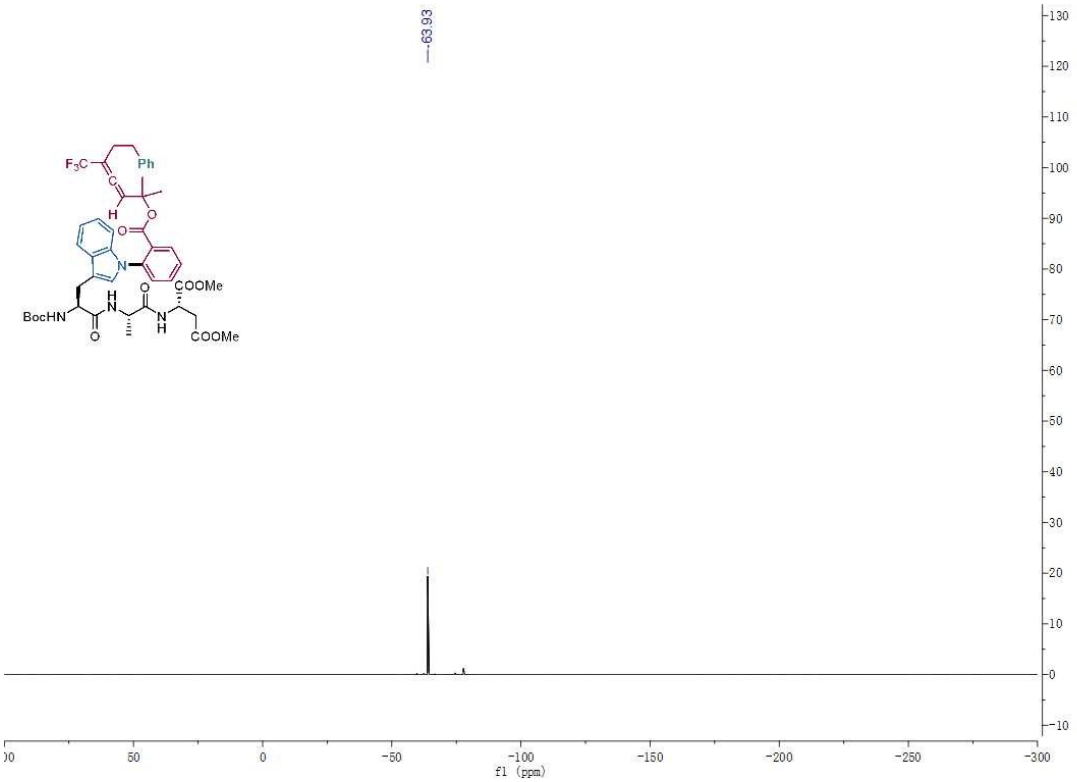


Fig 143. ^{19}F NMR of (**7h**)

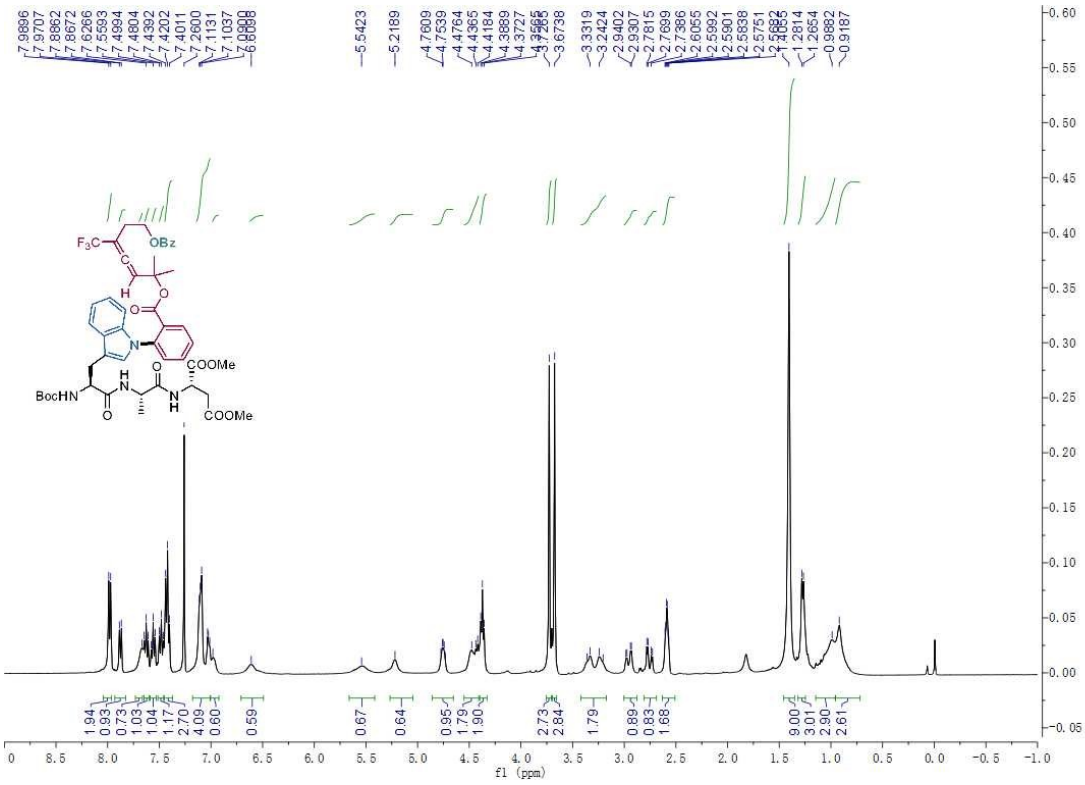


Fig 144. ^{1}H NMR of (**7i**)

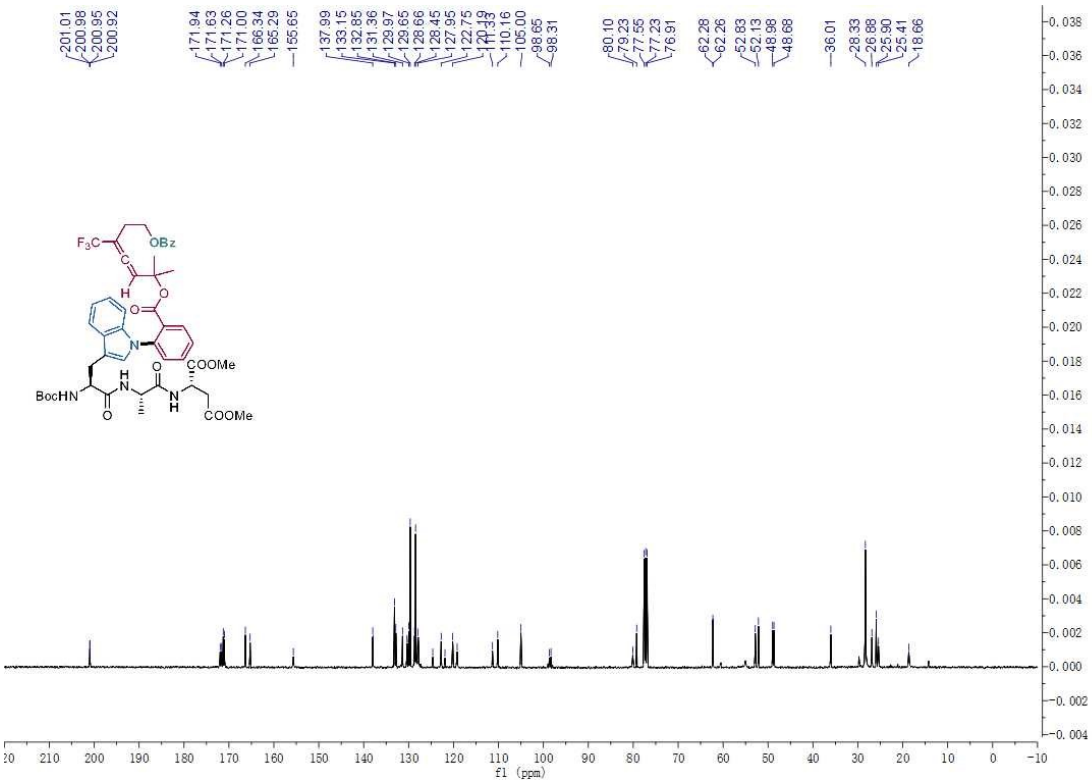


Fig 145. ^{13}C NMR of (**7i**)

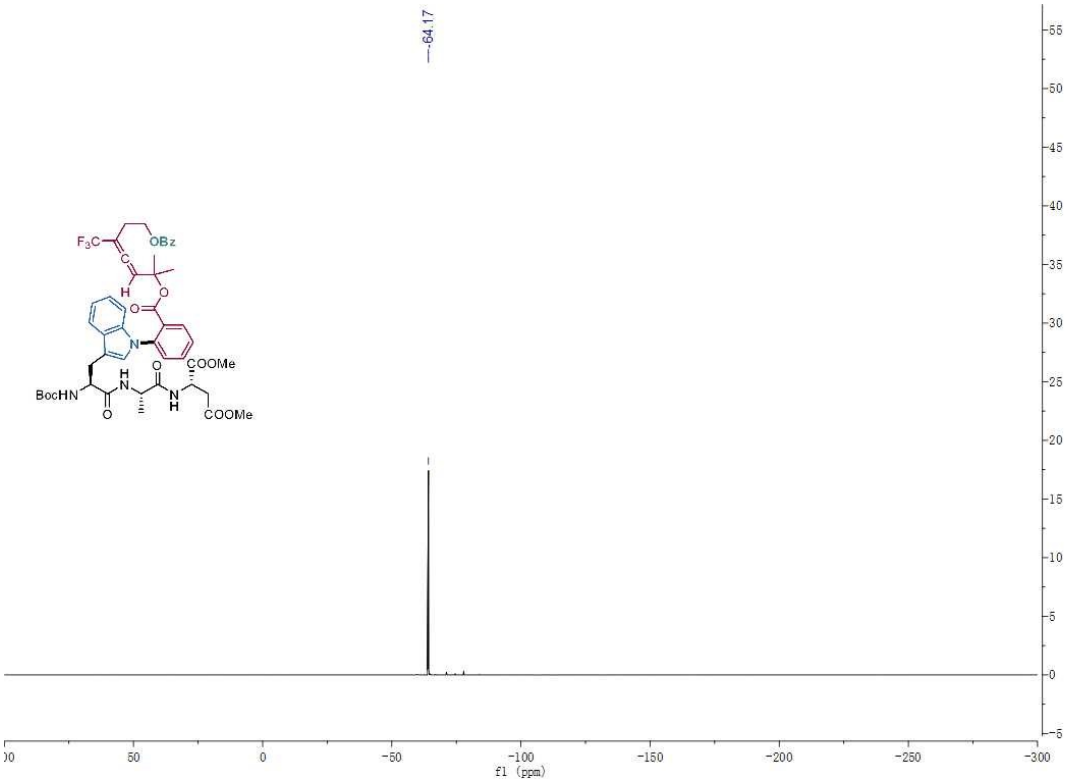


Fig 146. ^{19}F NMR of (**7i**)

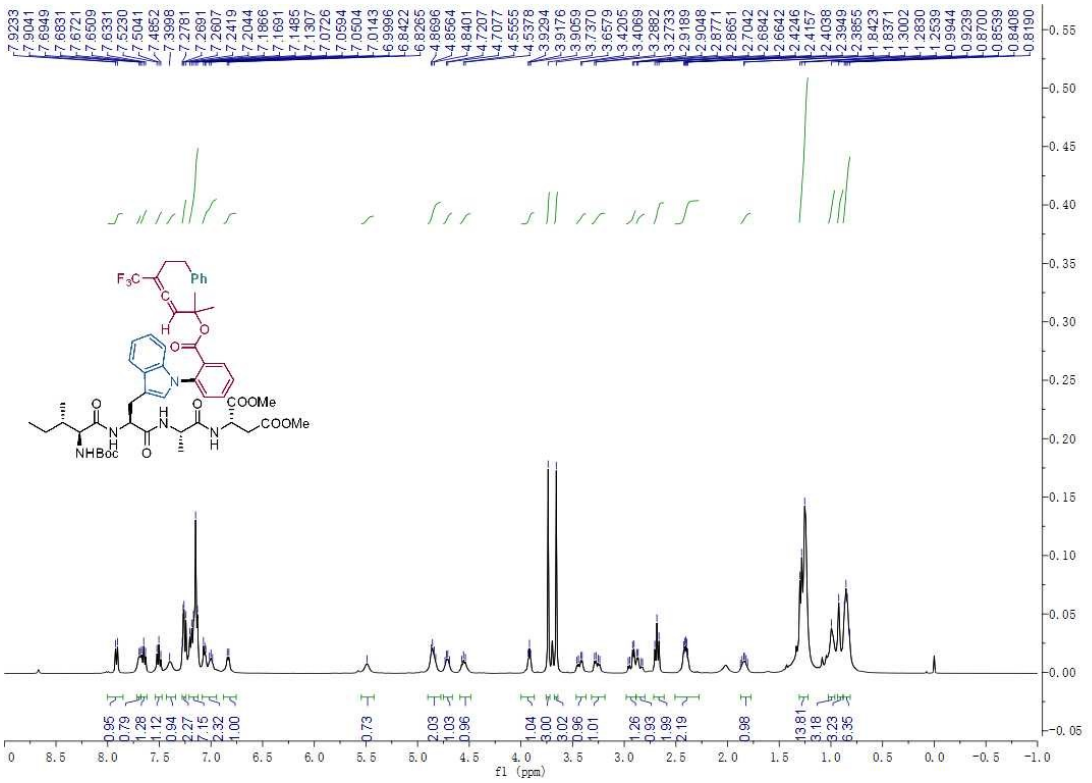


Fig 147. ^{1}H NMR of (**7j**)

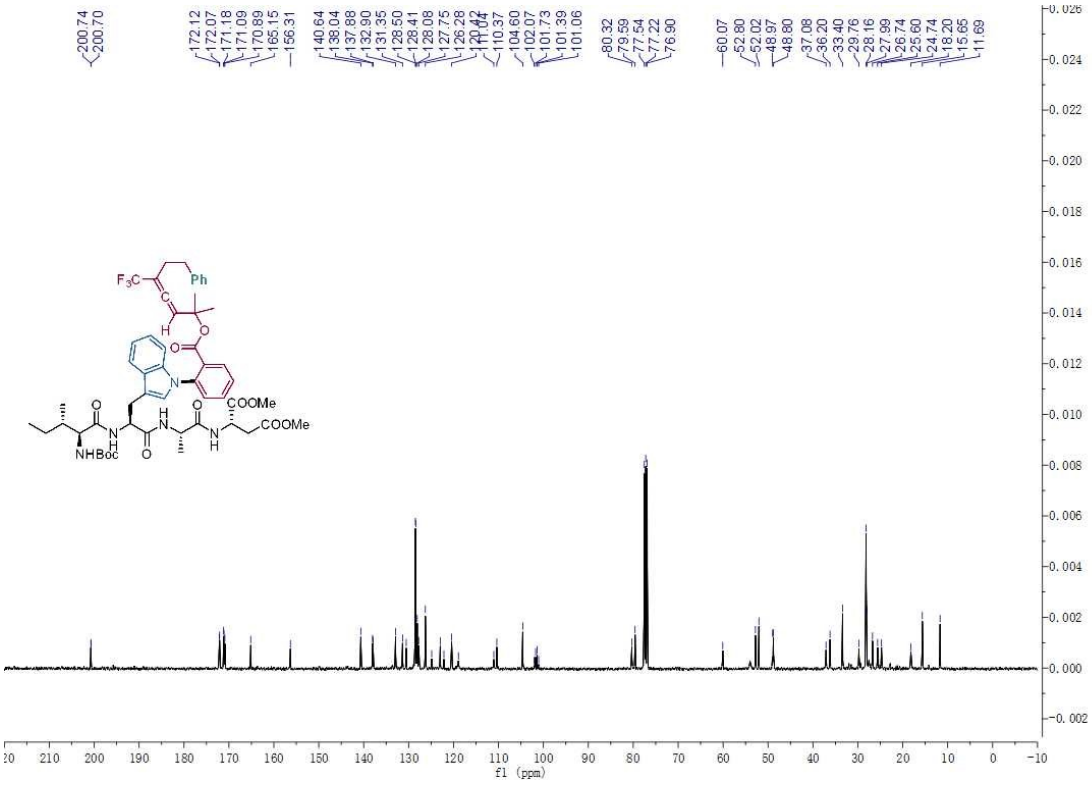


Fig 148. ^{13}C NMR of (**7j**)

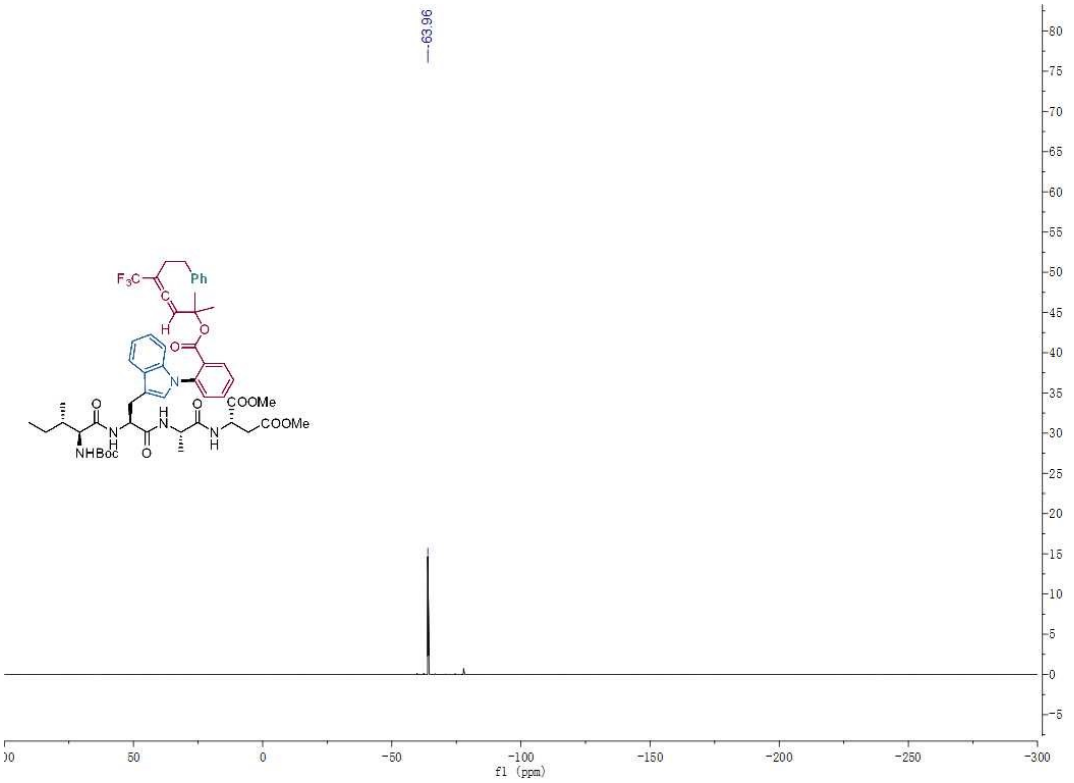


Fig 149. ^{19}F NMR of (**7j**)

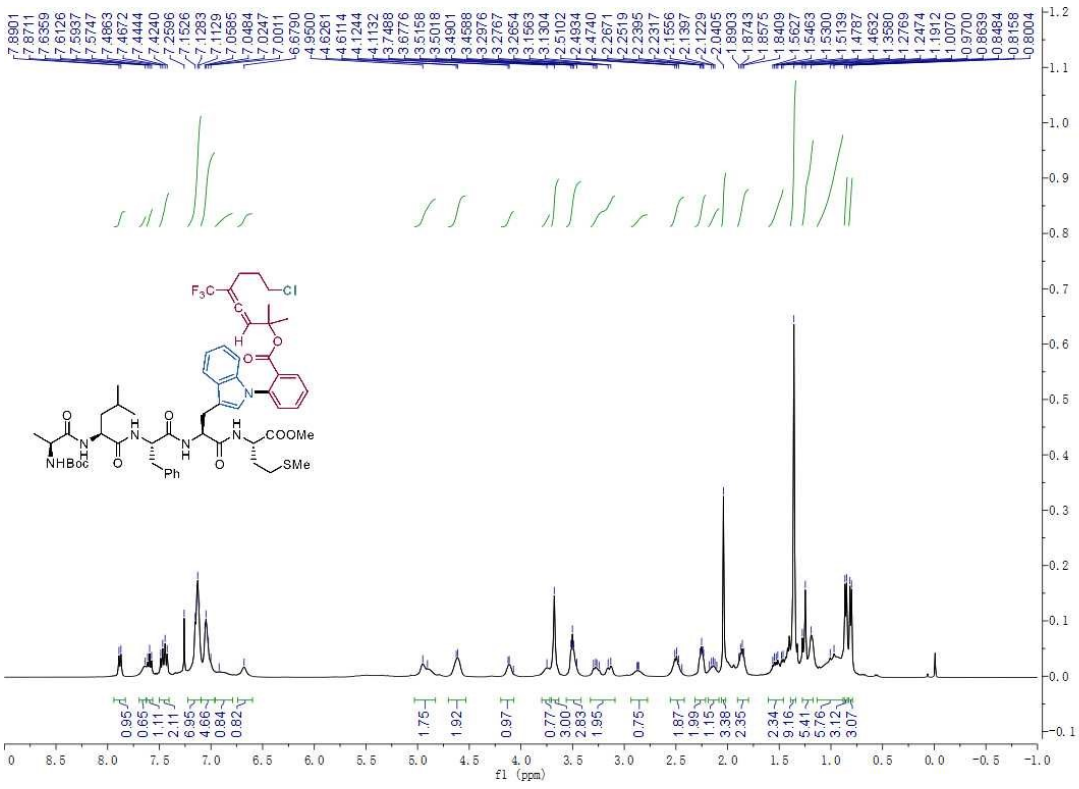


Fig 150. ^{1}H NMR of (**7k**)

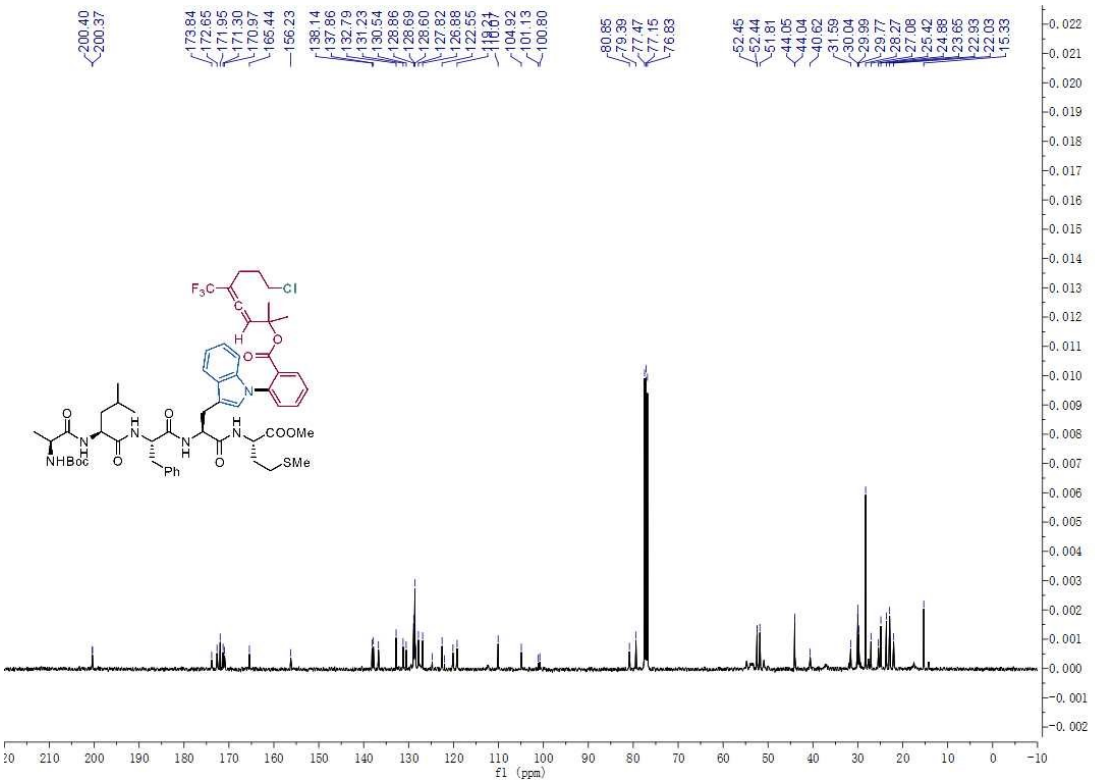


Fig 151. ^{13}C NMR of (**7k**)

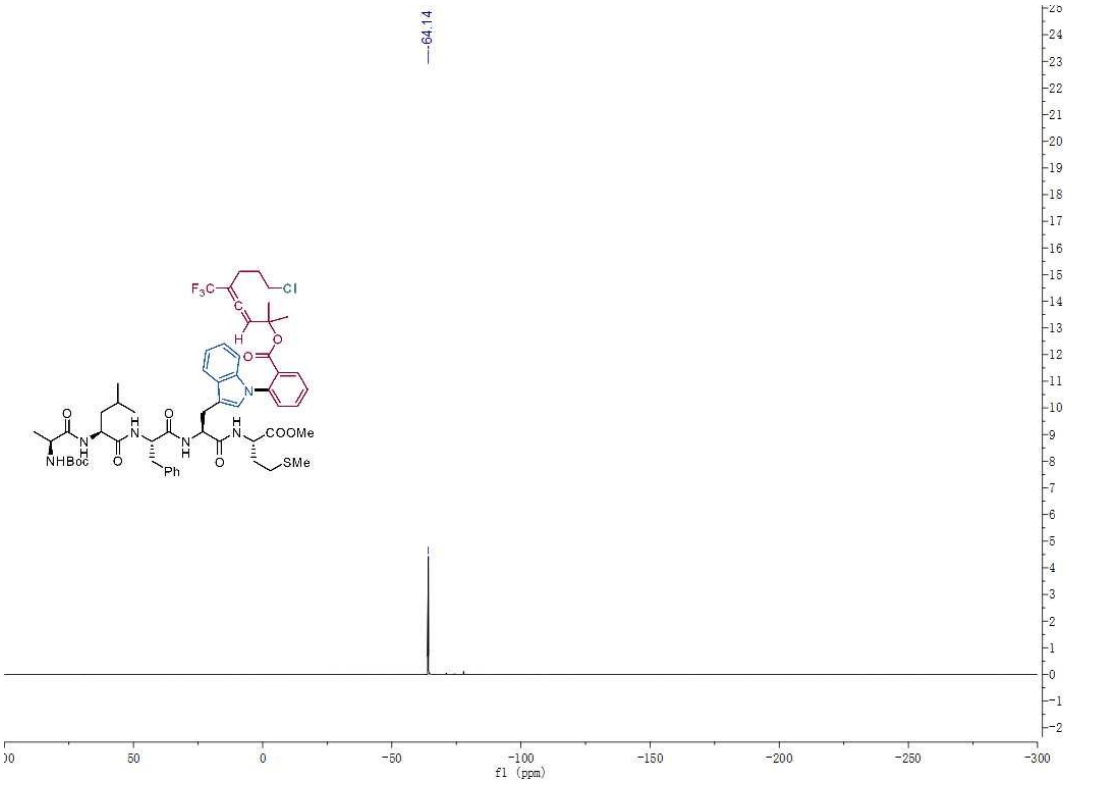


Fig 152. ^{19}F NMR of (**7k**)

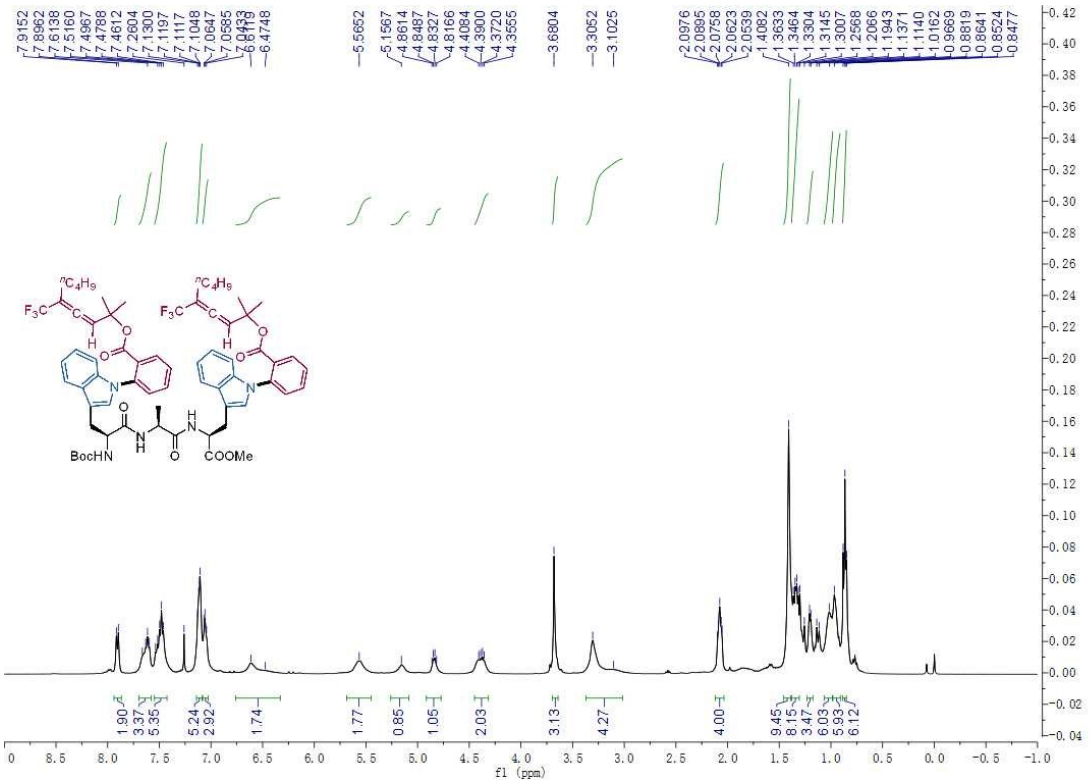


Fig 153. ^{1}H NMR of (**9**)

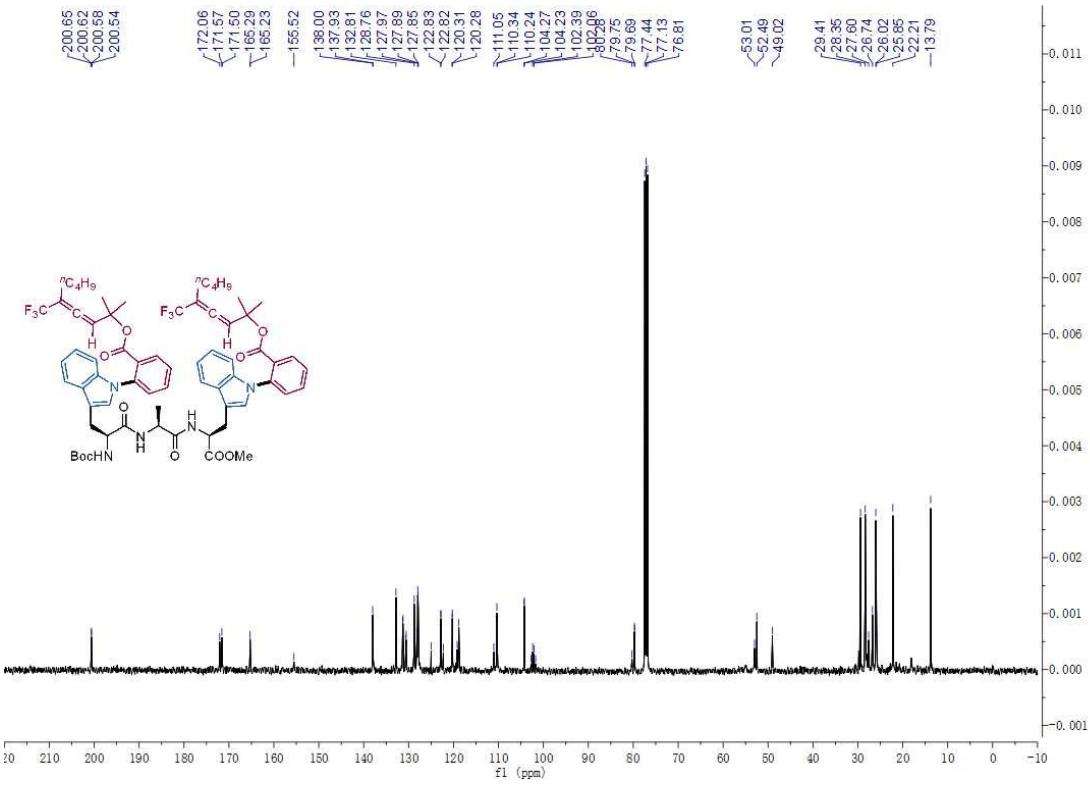


Fig 154. ^{13}C NMR of (**9**)

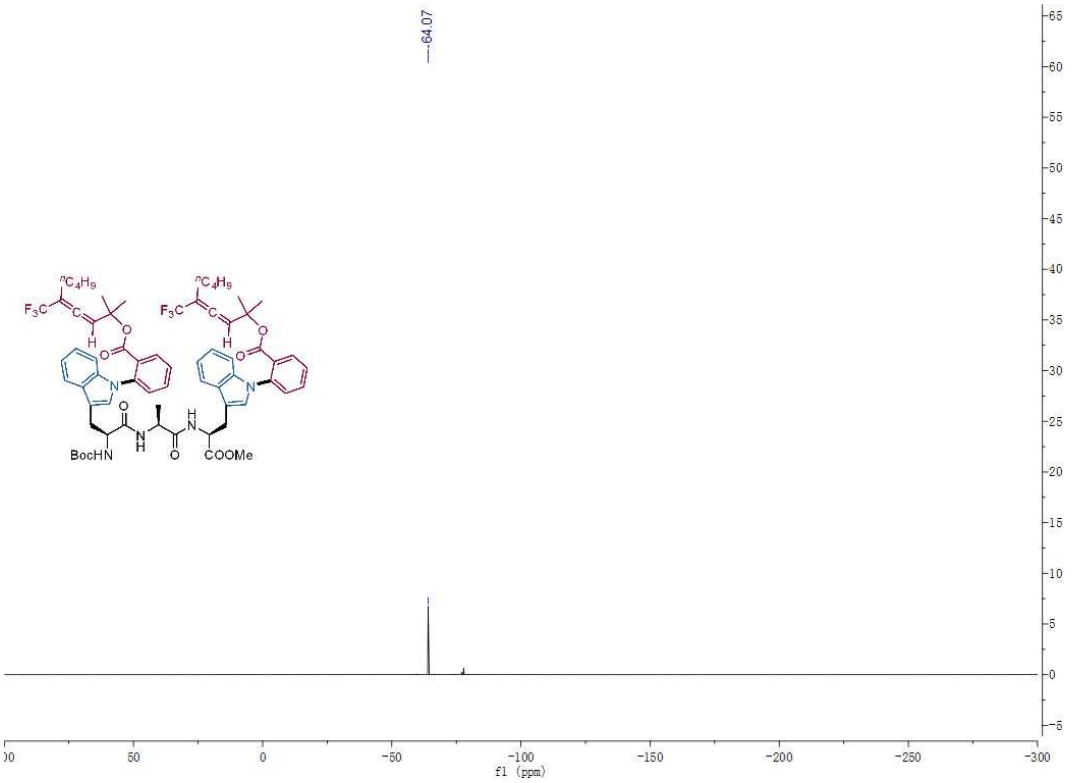


Fig 155. ^{19}F NMR of (**9**)

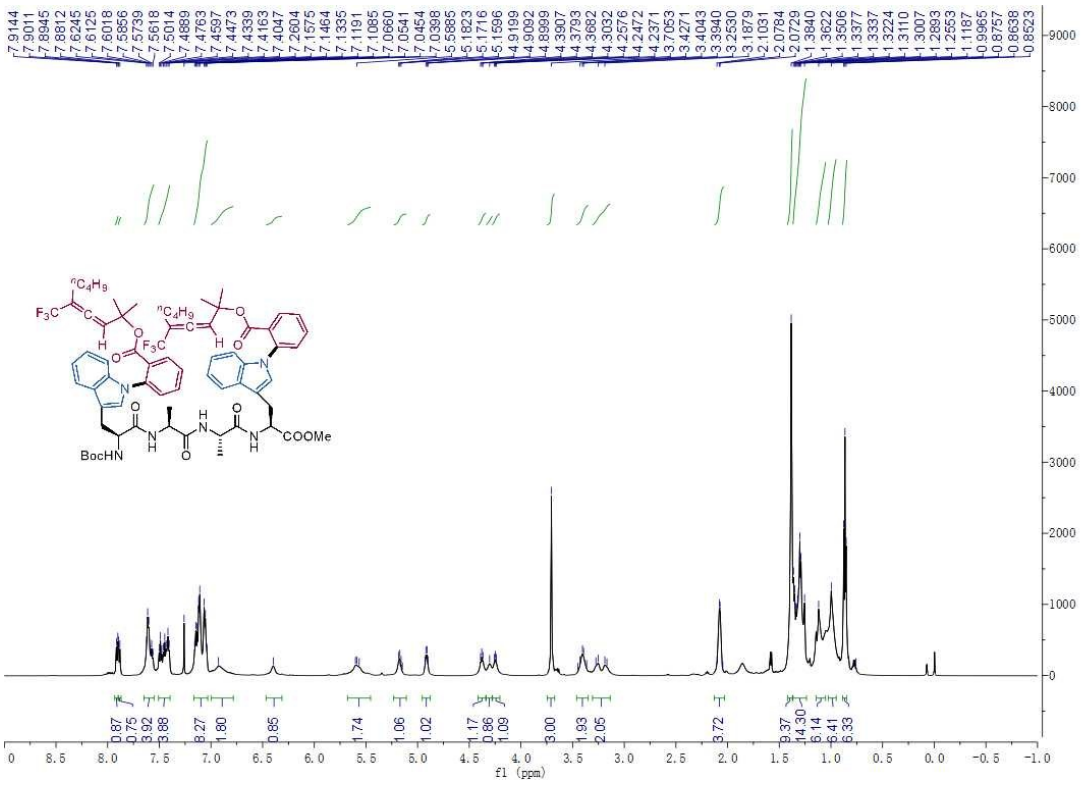


Fig 156. ^{1}H NMR of (**11**)

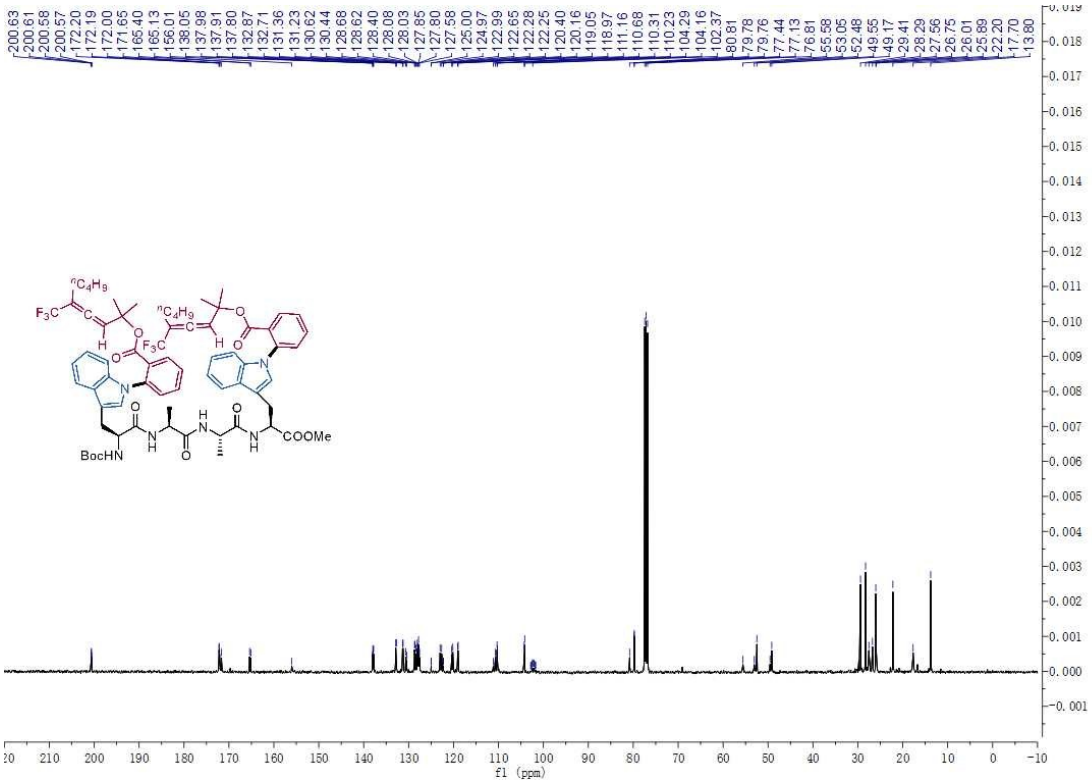


Fig 157. ^{13}C NMR of (**11**)

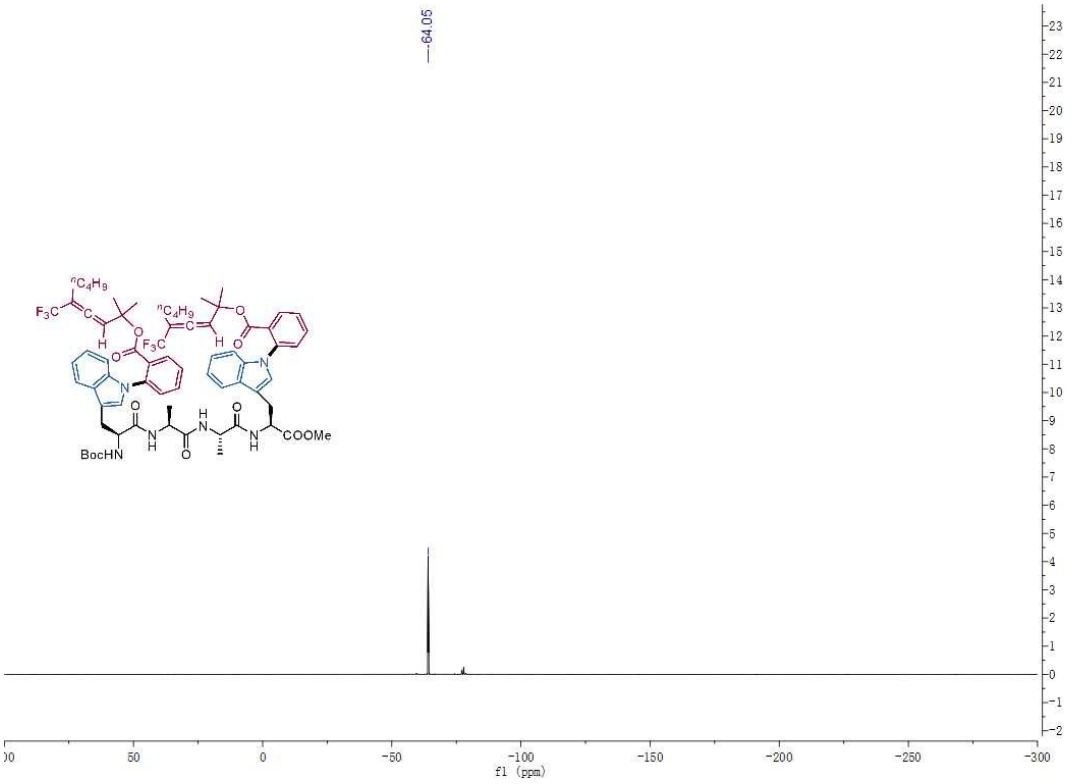


Fig 158. ^{19}F NMR of (**11**)

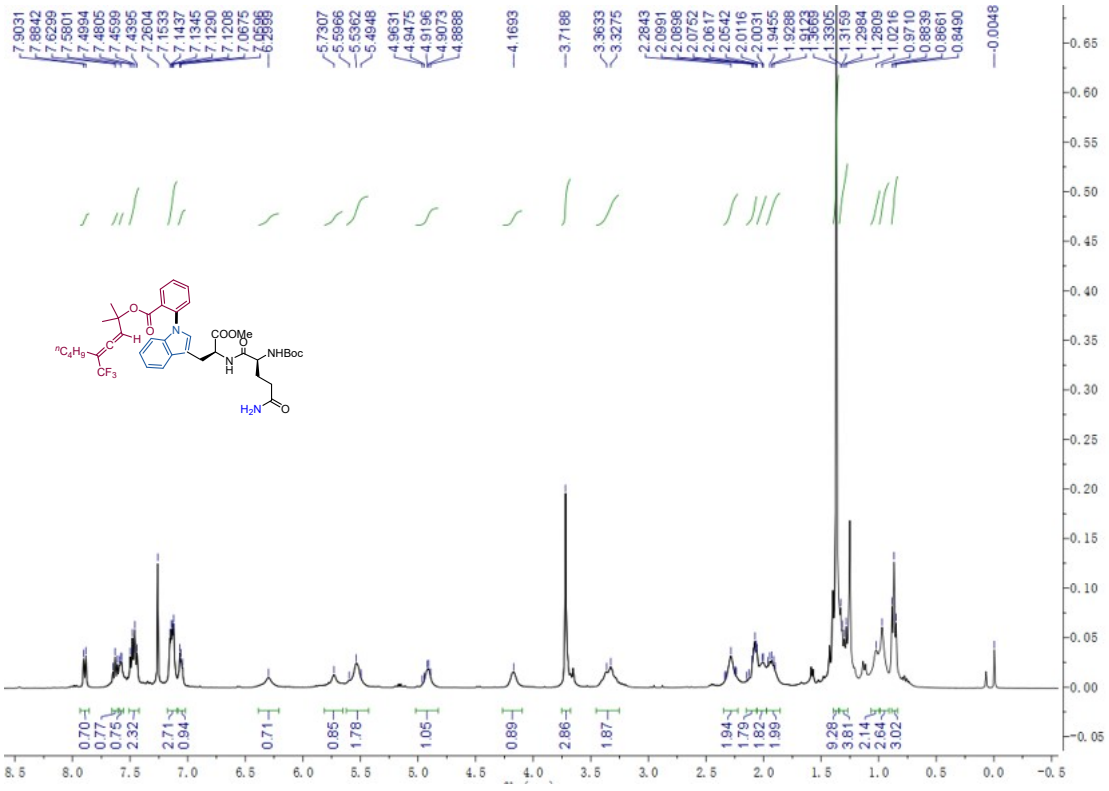


Fig 159. ^{1}H NMR of (**13**)

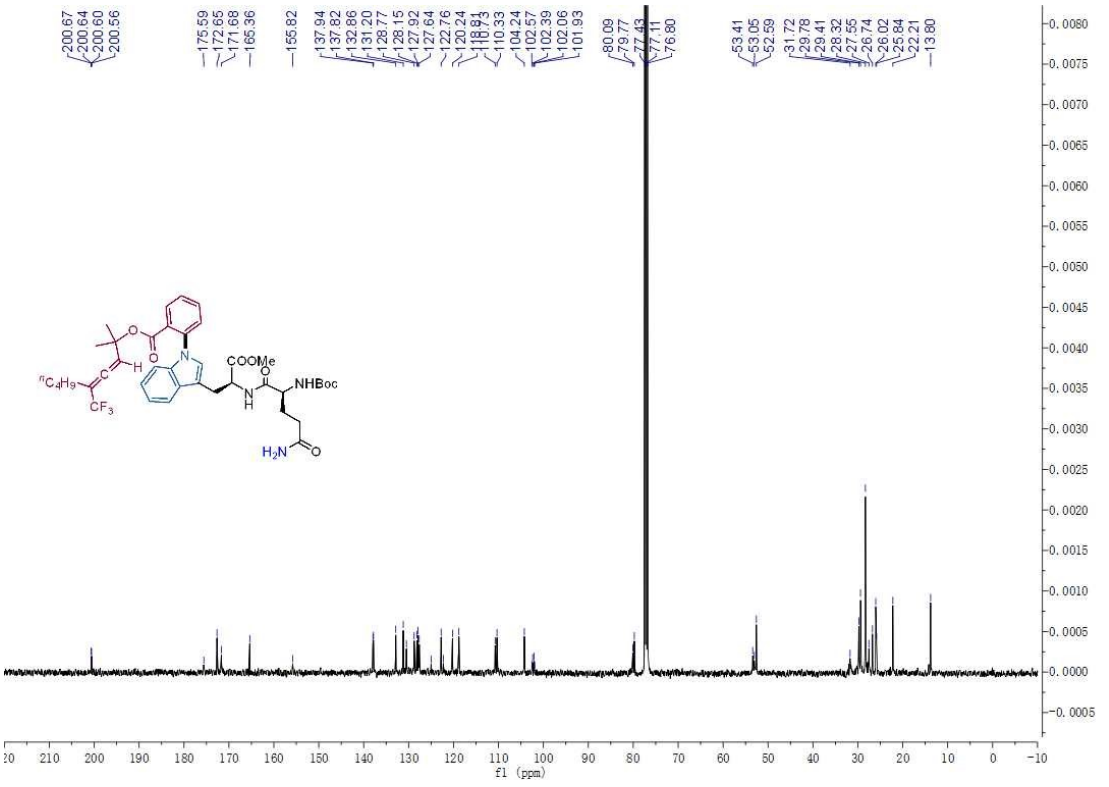


Fig 160. ^{13}C NMR of (**13**)

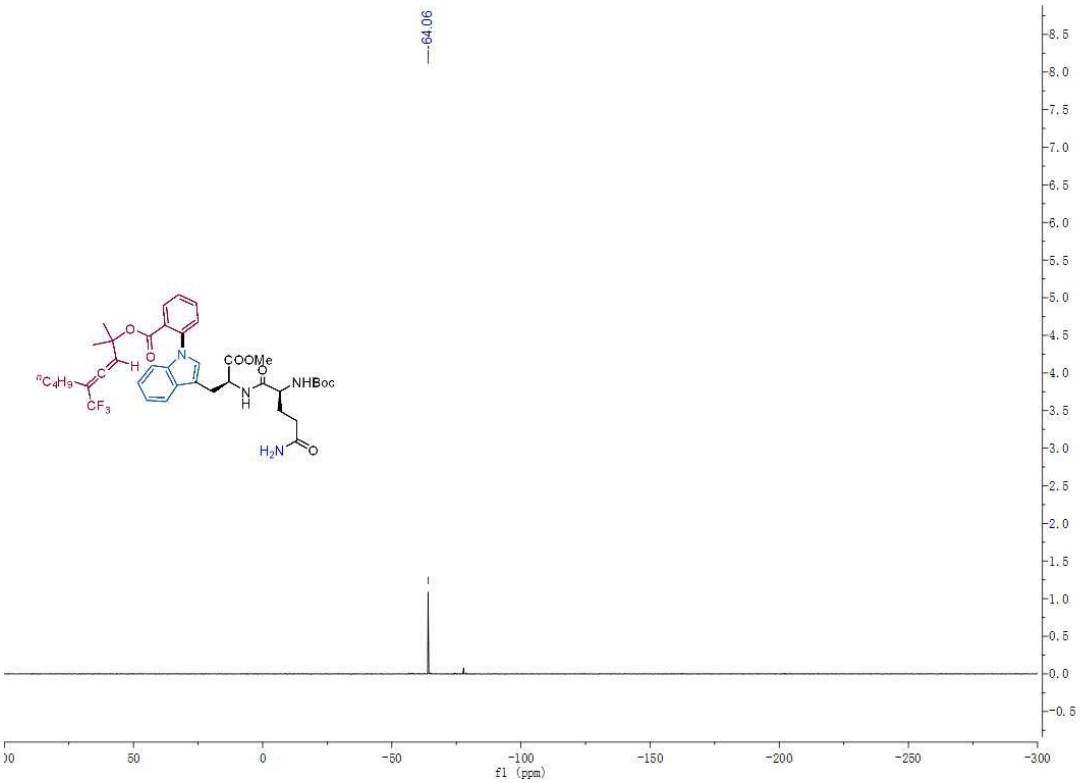


Fig 161. ^{19}F NMR of (**13**)

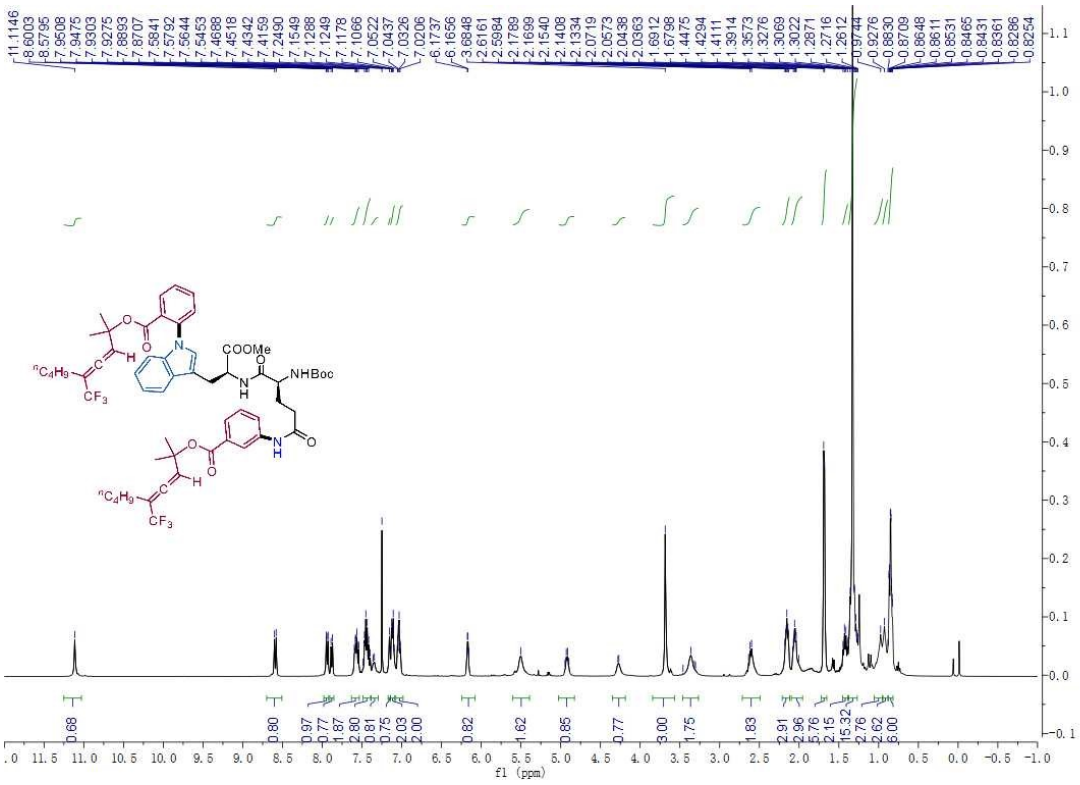


Fig 162. ^{1}H NMR of (**15**)

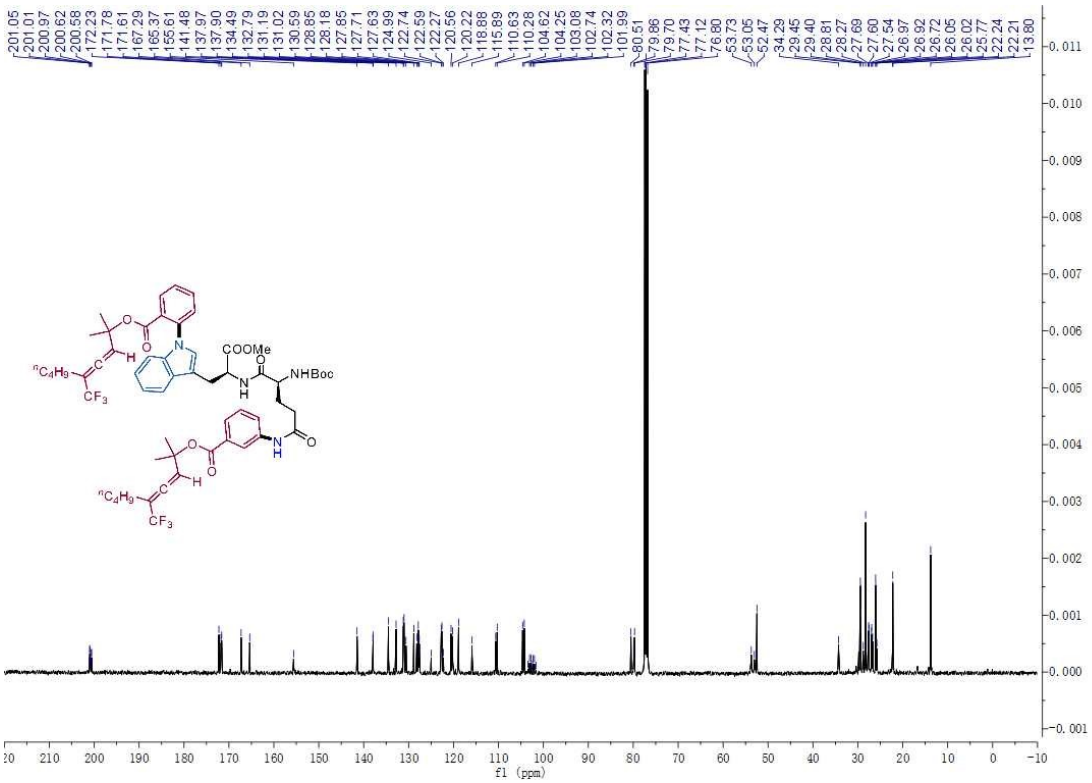


Fig 163. ^{13}C NMR of (**15**)

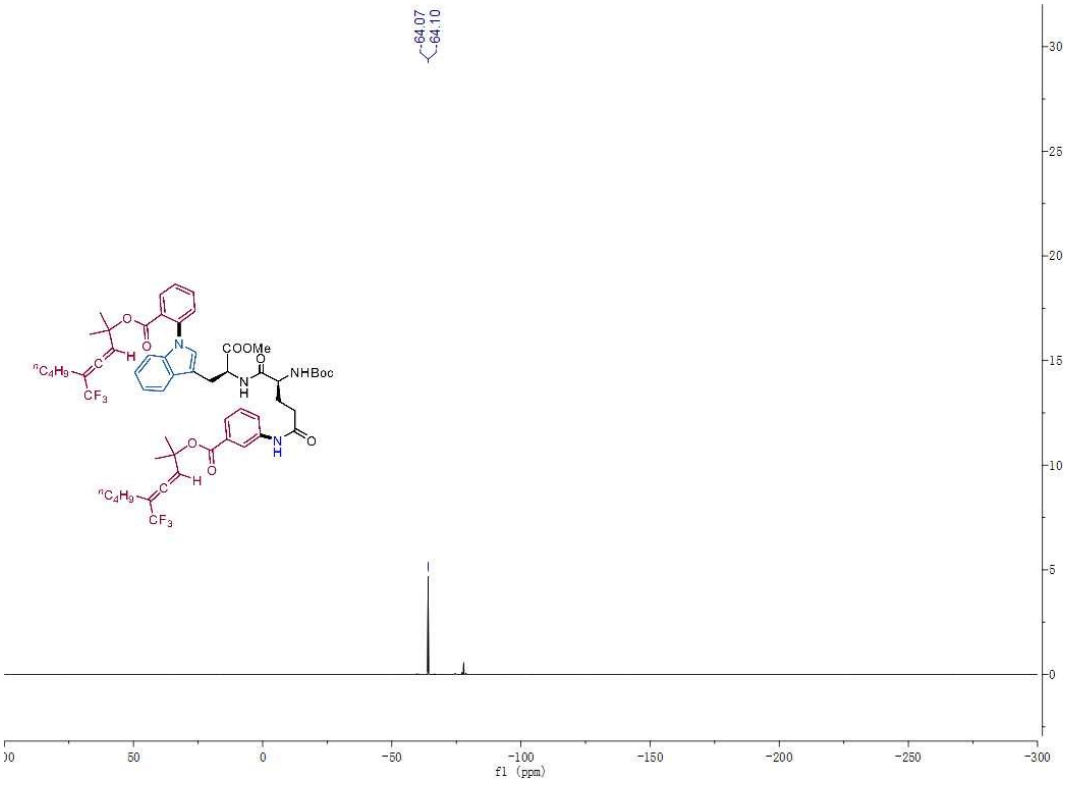


Fig 164. ^{19}F NMR of (**15**)

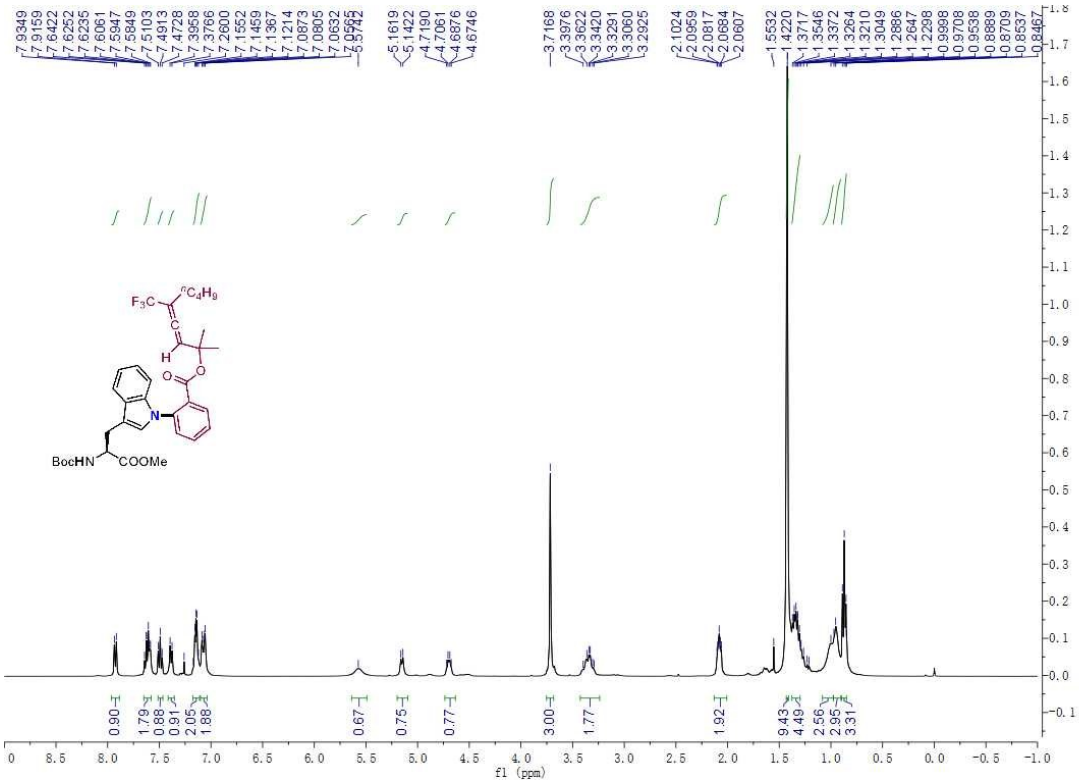


Fig 165. ^{1}H NMR of (**16**)

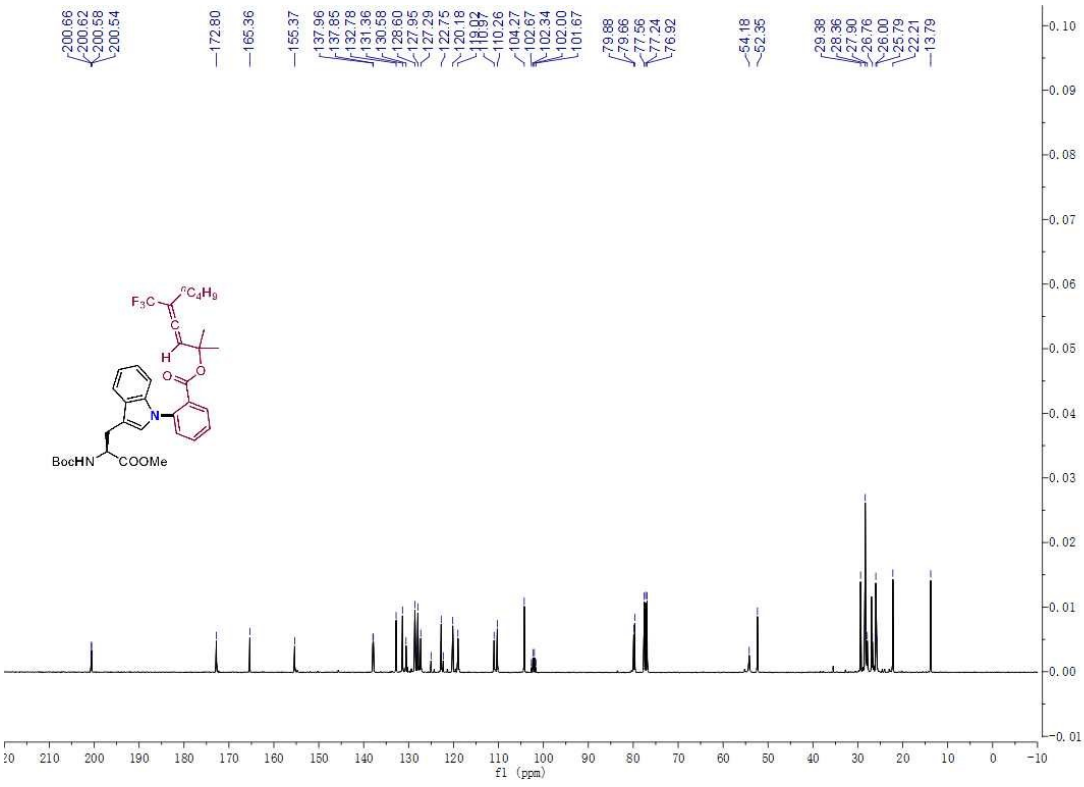


Fig 166. ^{13}C NMR of (**16**)

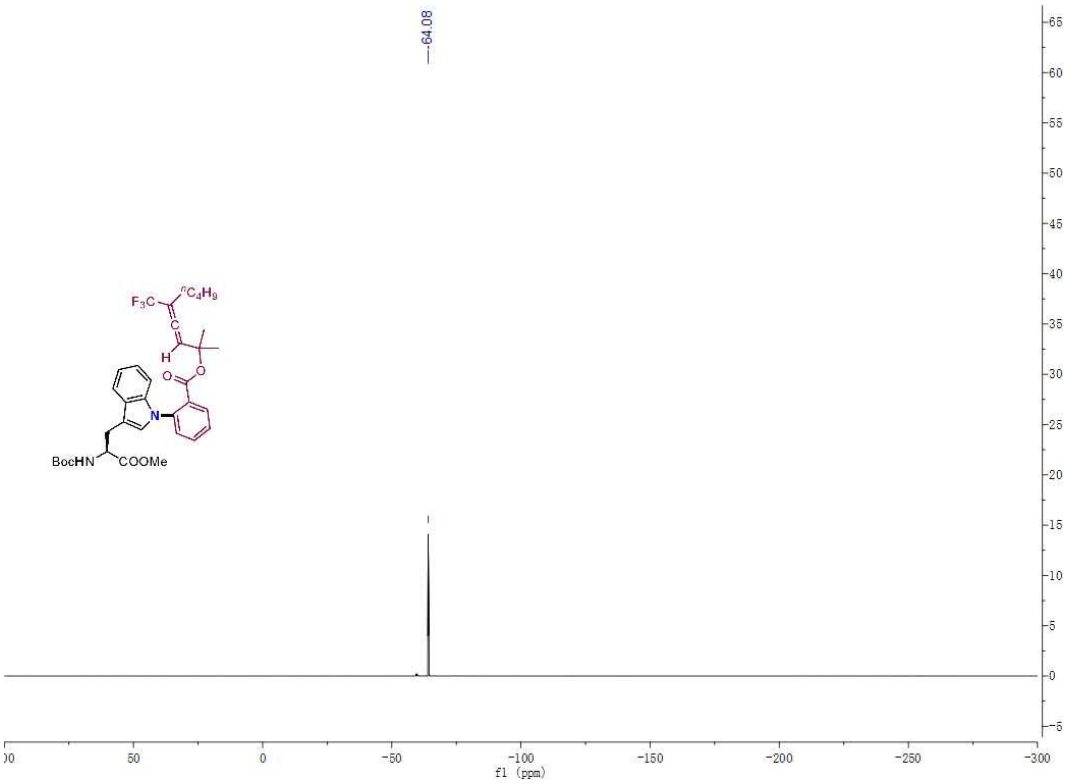


Fig 167. 19F NMR of (16)

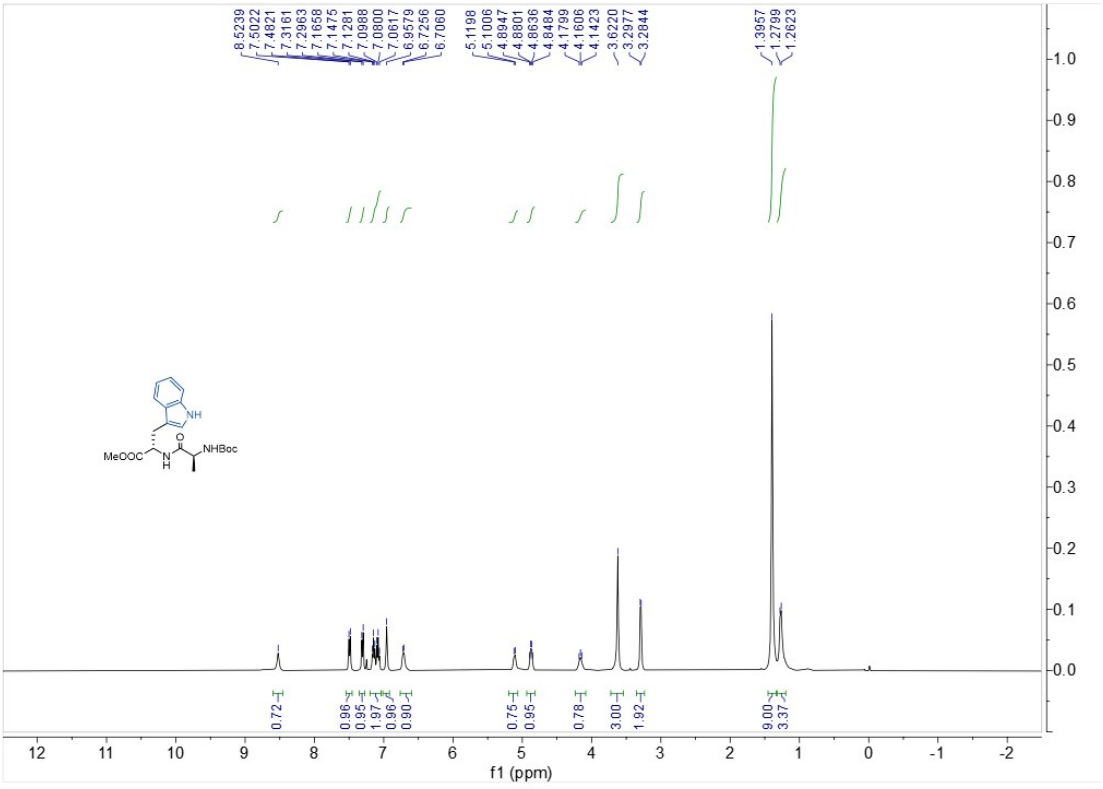


Fig 168. ^{1}H NMR of (**SM-3a**)

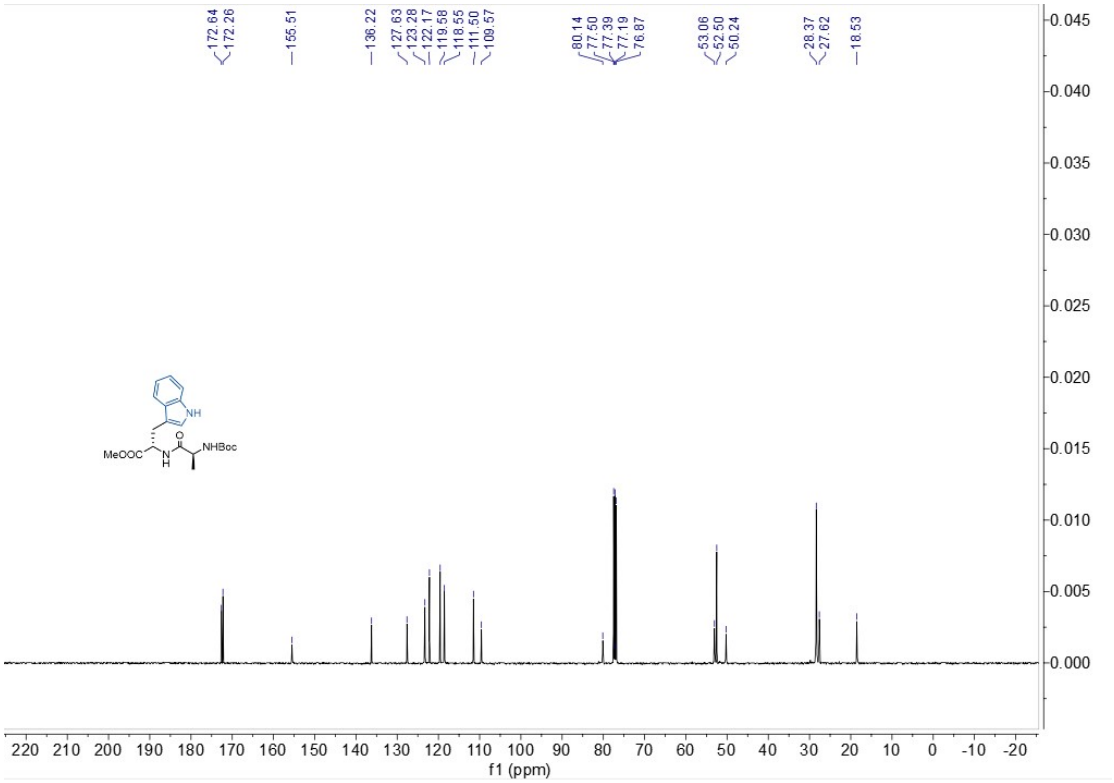


Fig 169. ^{13}C NMR of (**SM-3a**)

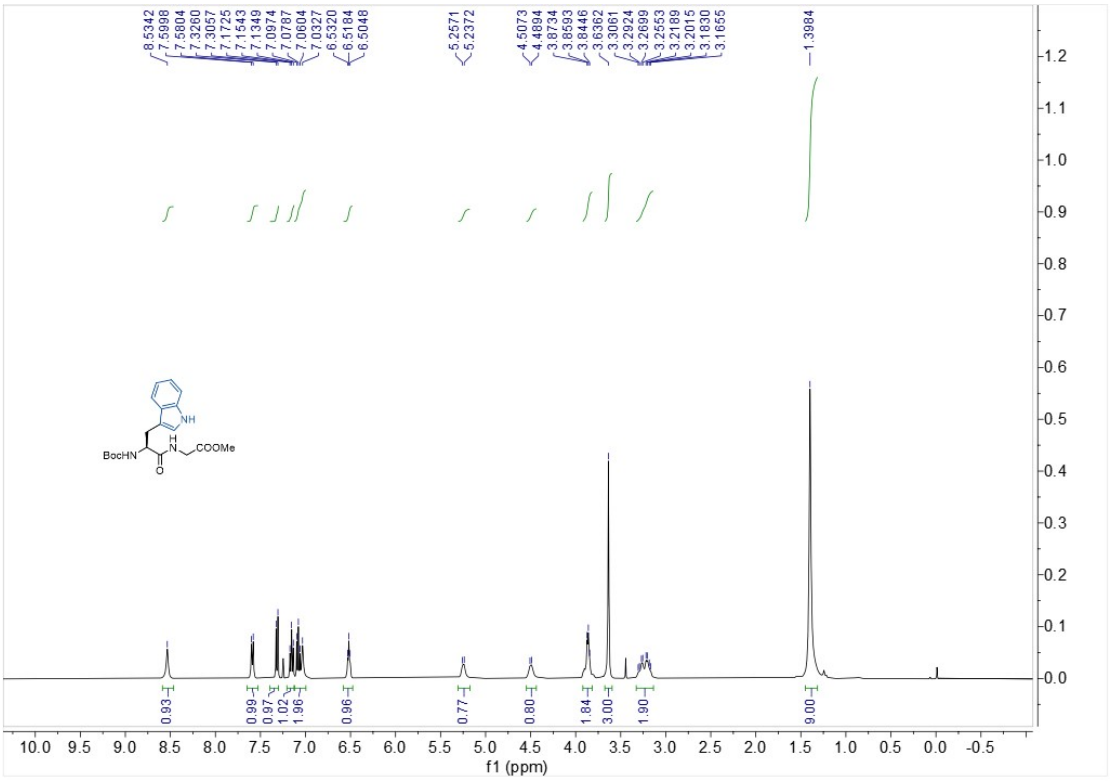


Fig 170. ^{1}H NMR of (**SM-3b**)

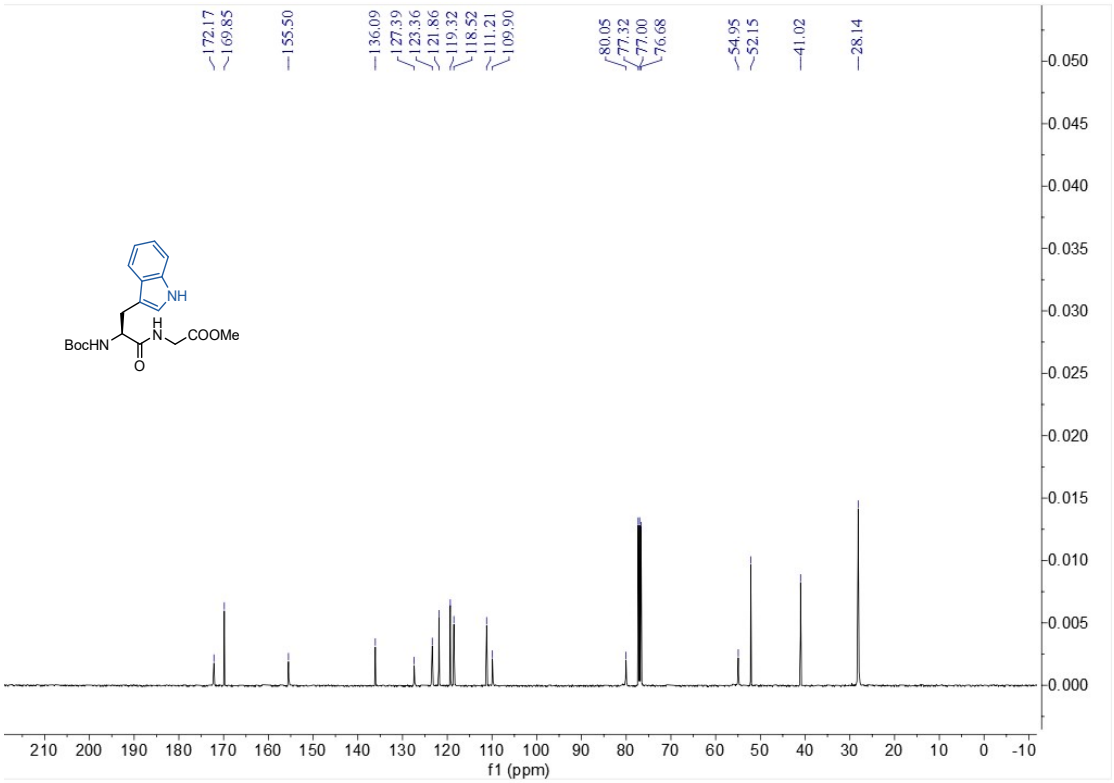


Fig 171. ^{13}C NMR of (**SM-3b**)

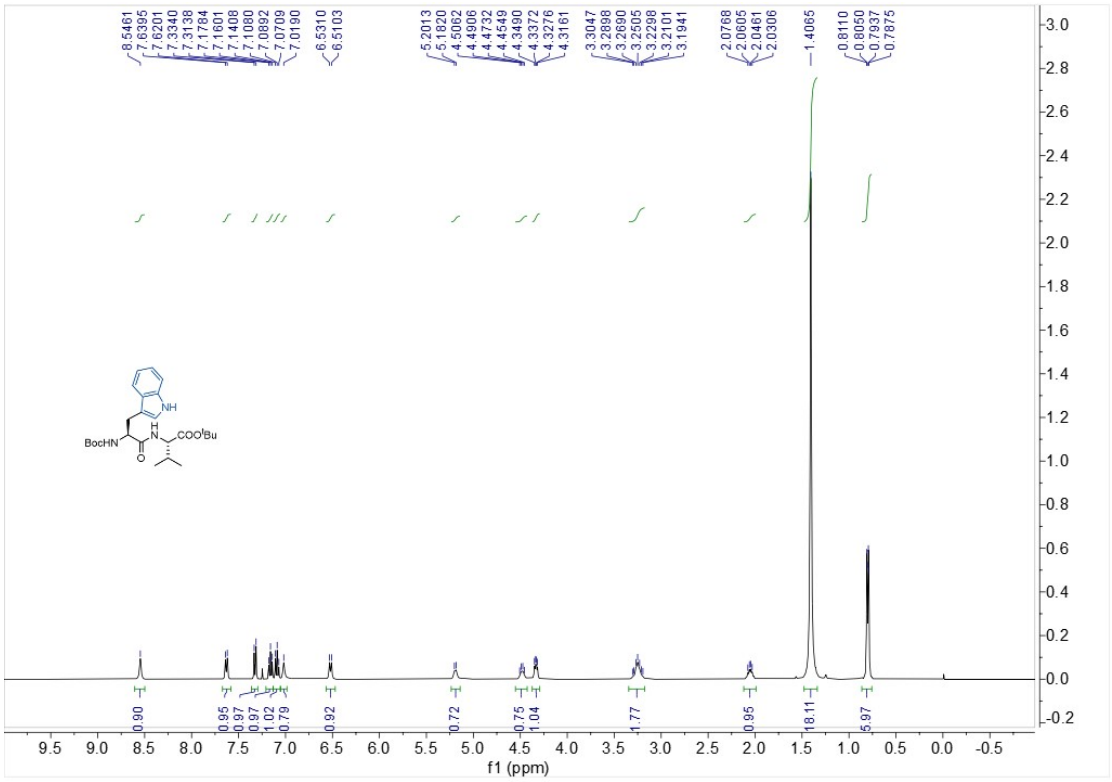


Fig 172. ^{1}H NMR of (**SM-3c**)

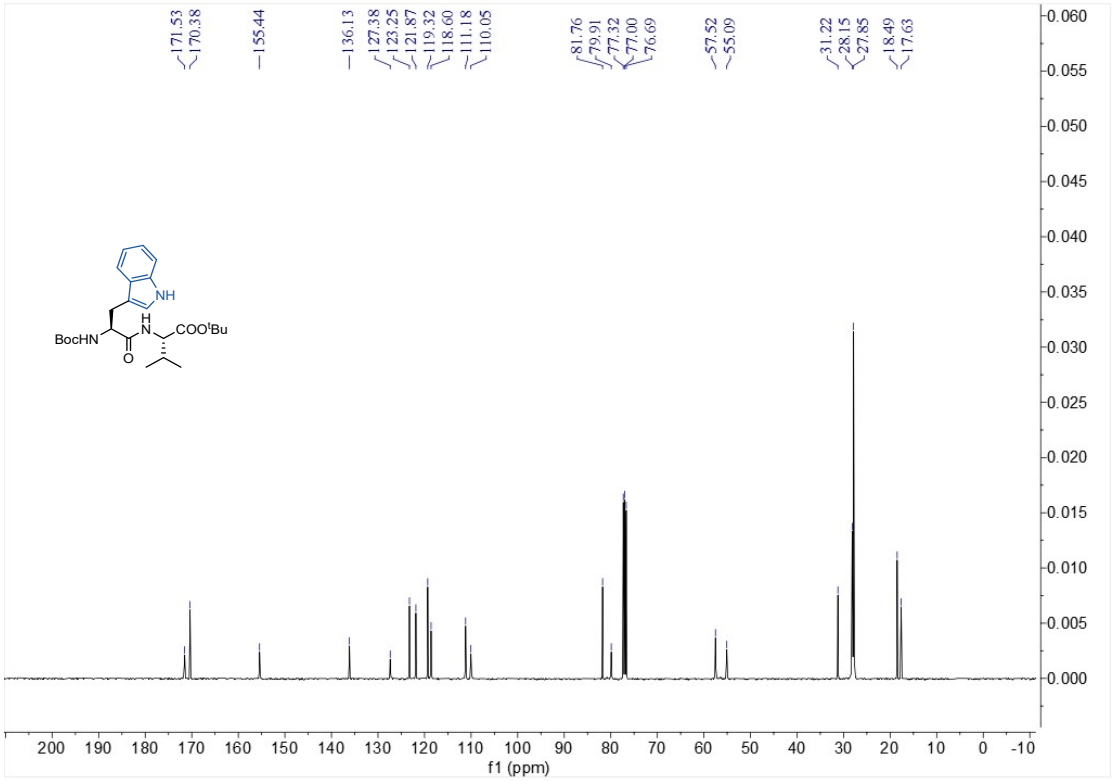


Fig 173. ^{13}C NMR of (**SM-3c**)

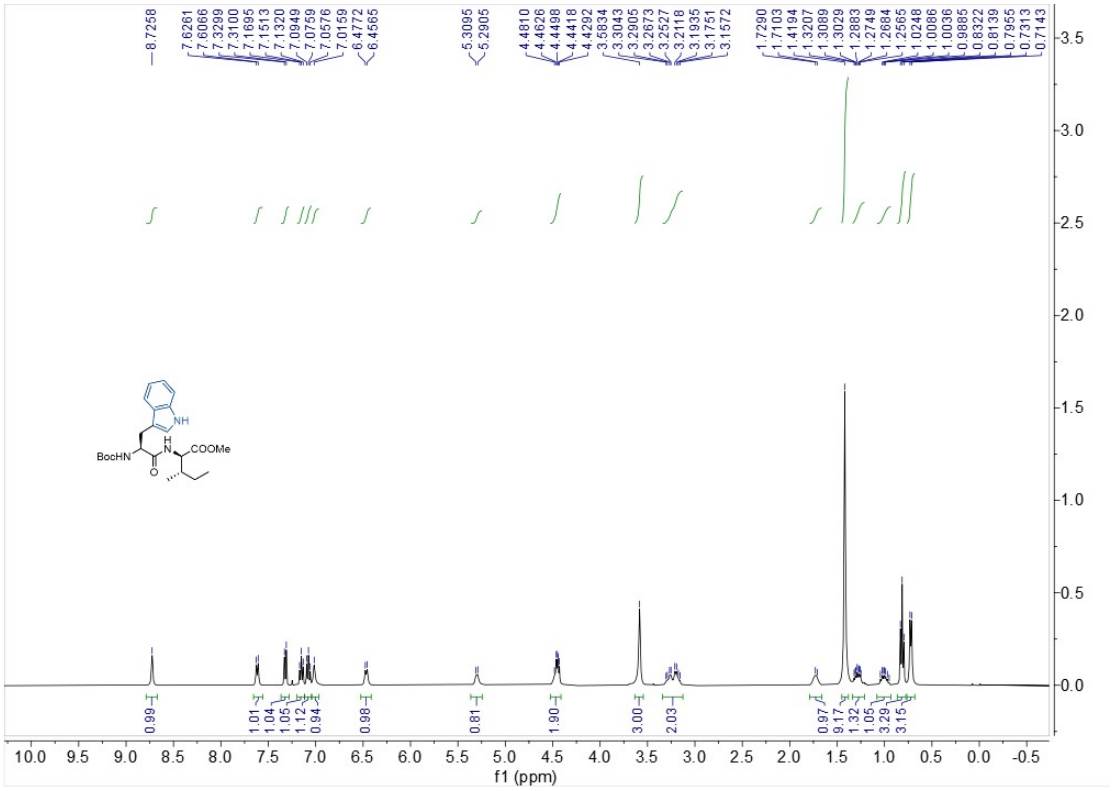


Fig 174. ^{1}H NMR of (**SM-3d**)

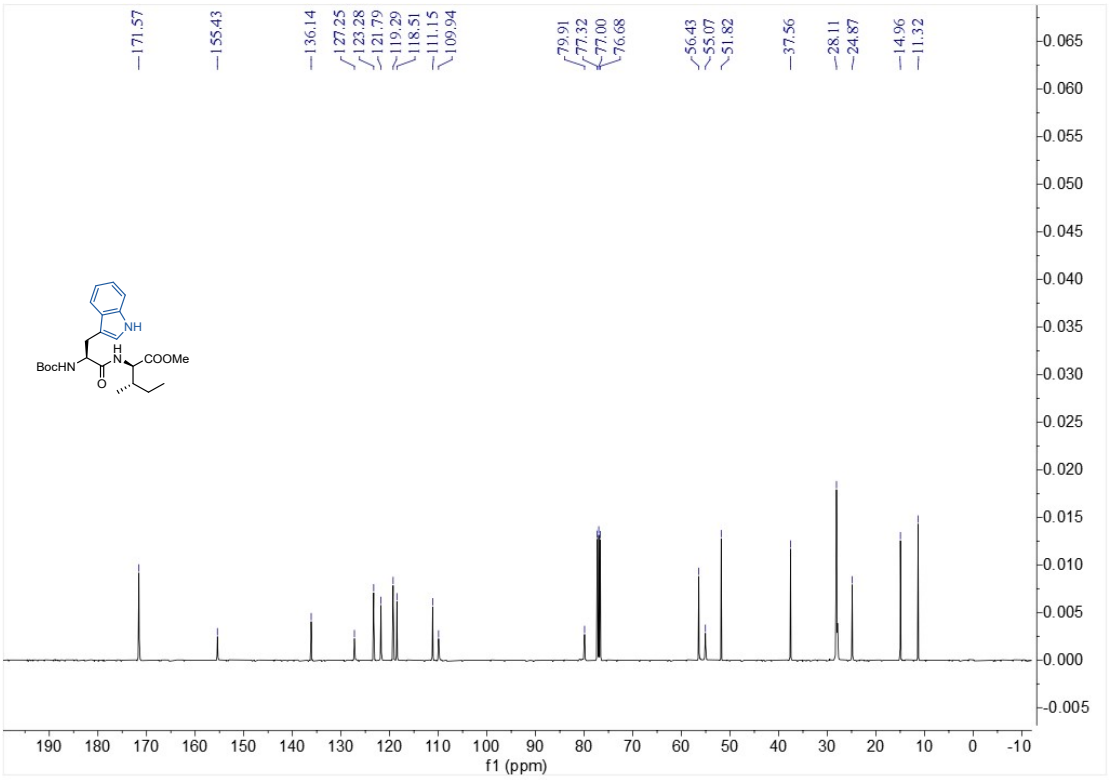


Fig 175. ^{13}C NMR of (**SM-3d**)

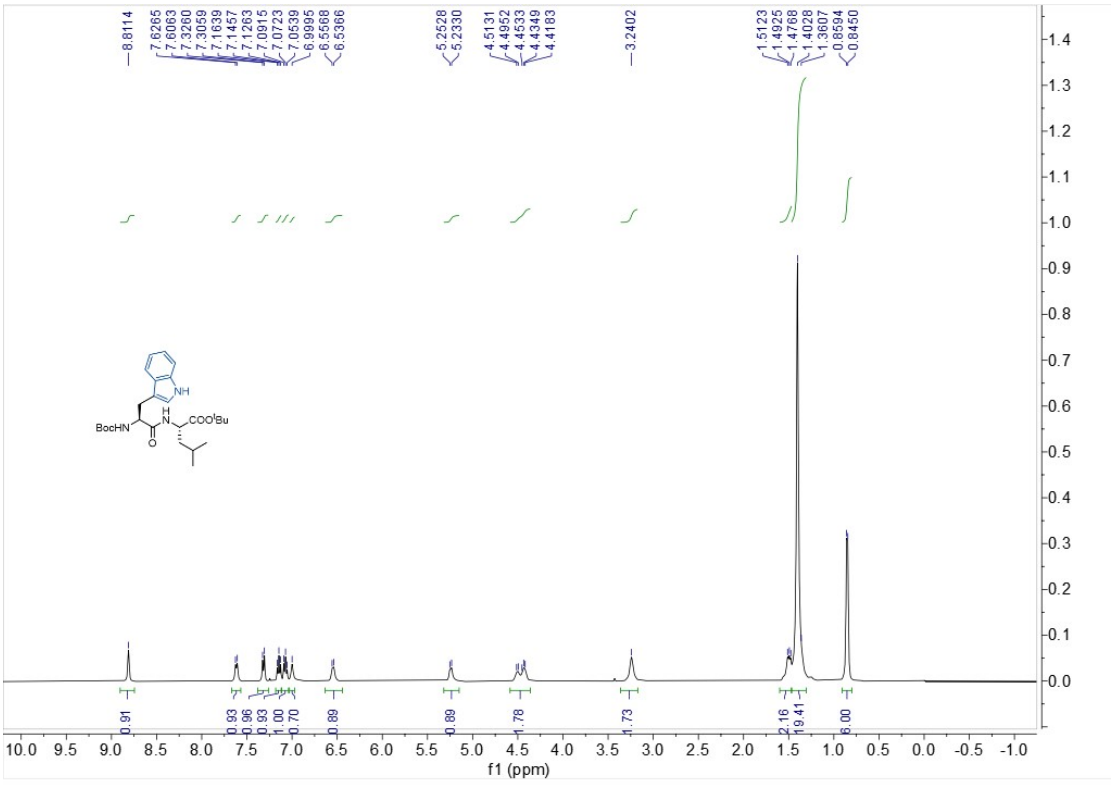


Fig 176. ^{1}H NMR of (**SM-3e**)

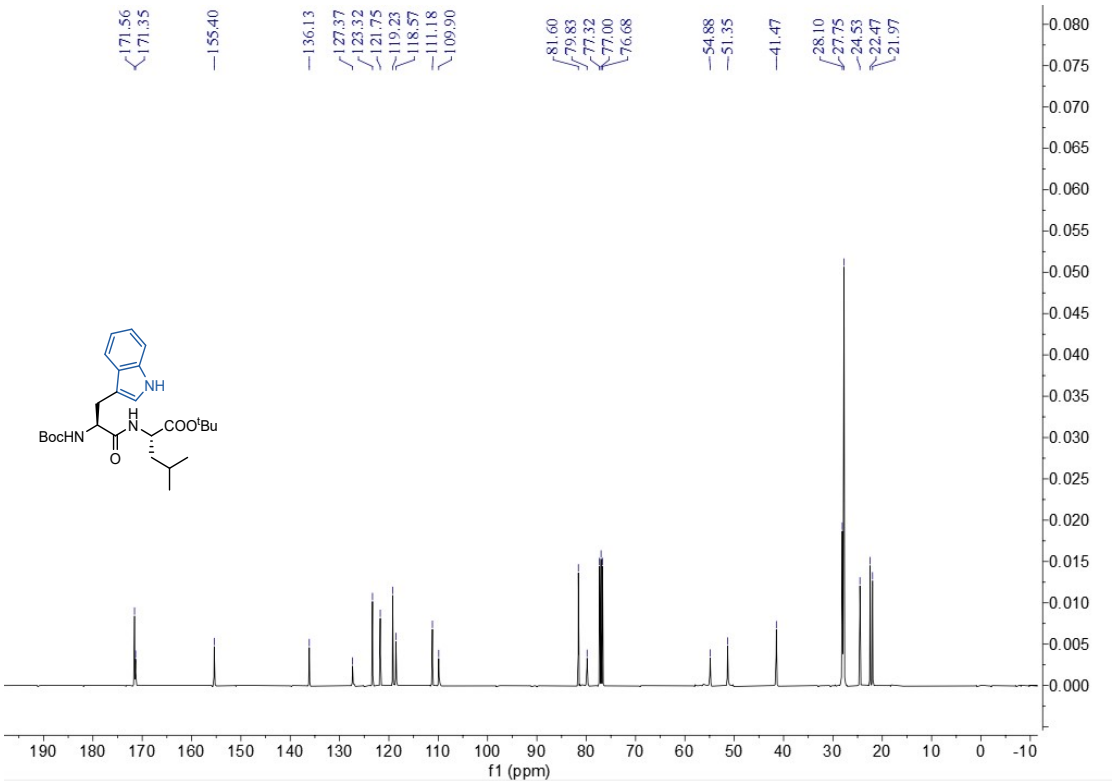


Fig 177. ^{13}C NMR of (**SM-3e**)

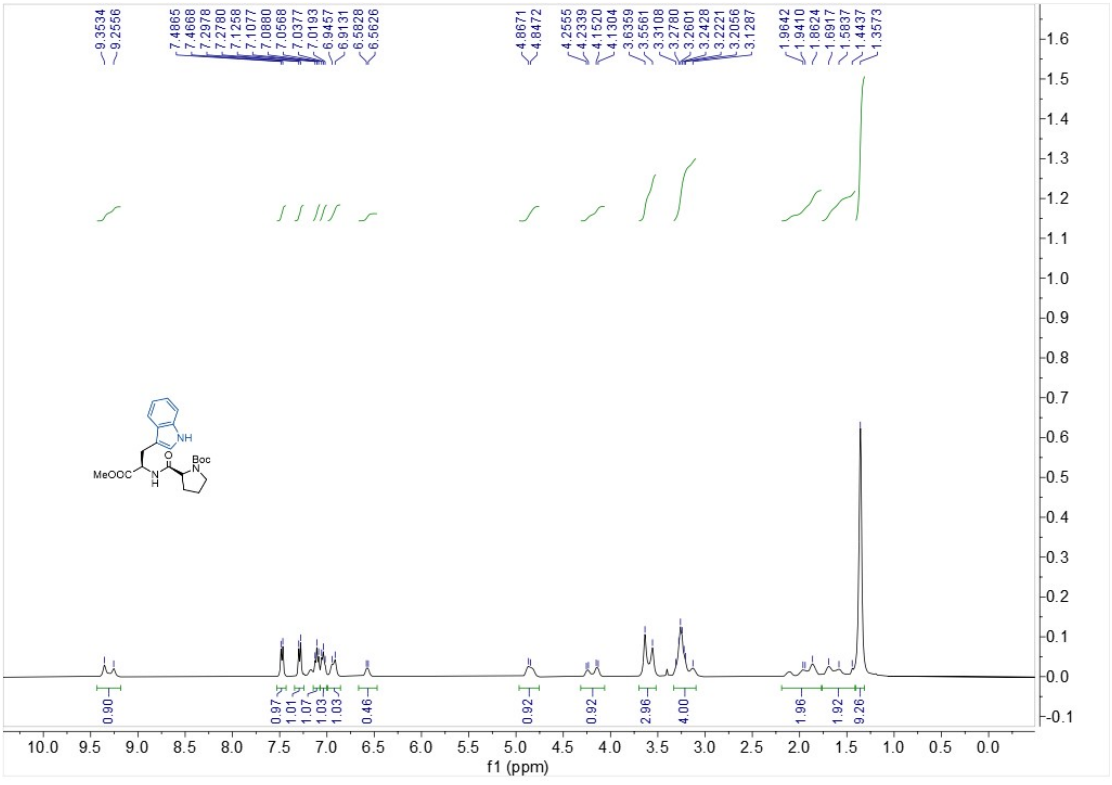


Fig 178. ^{1}H NMR of (**SM-3f**)

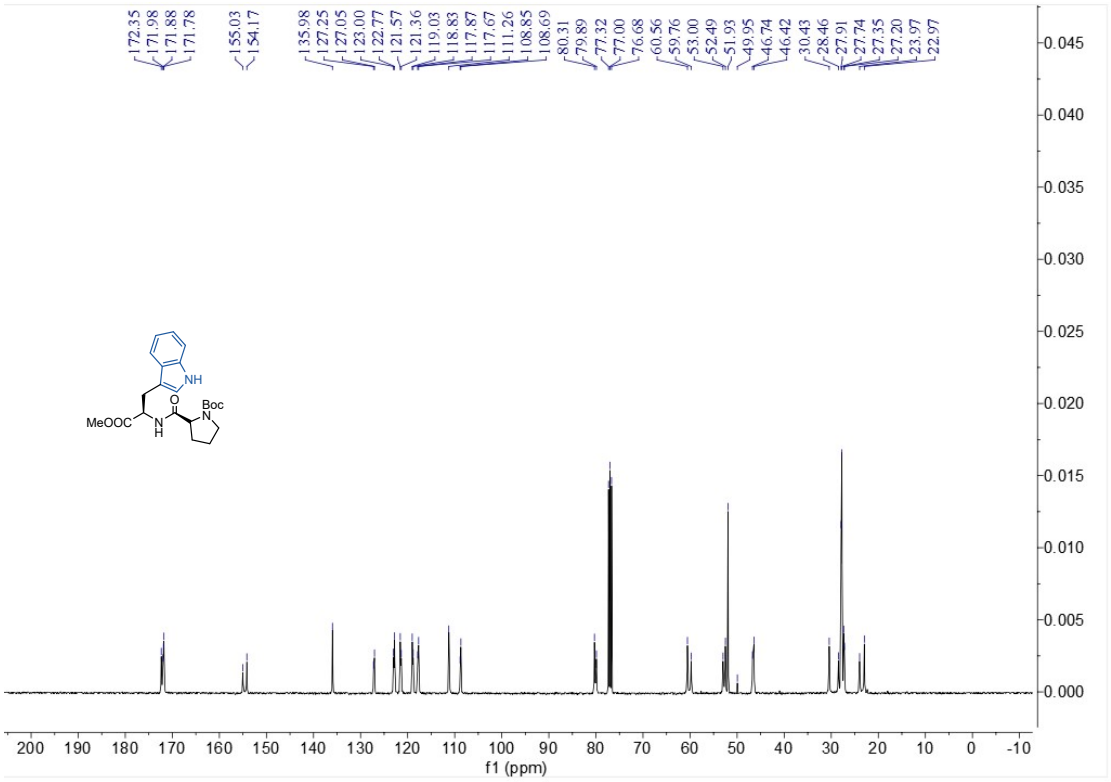


Fig 179. ^{13}C NMR of (**SM-3f**)

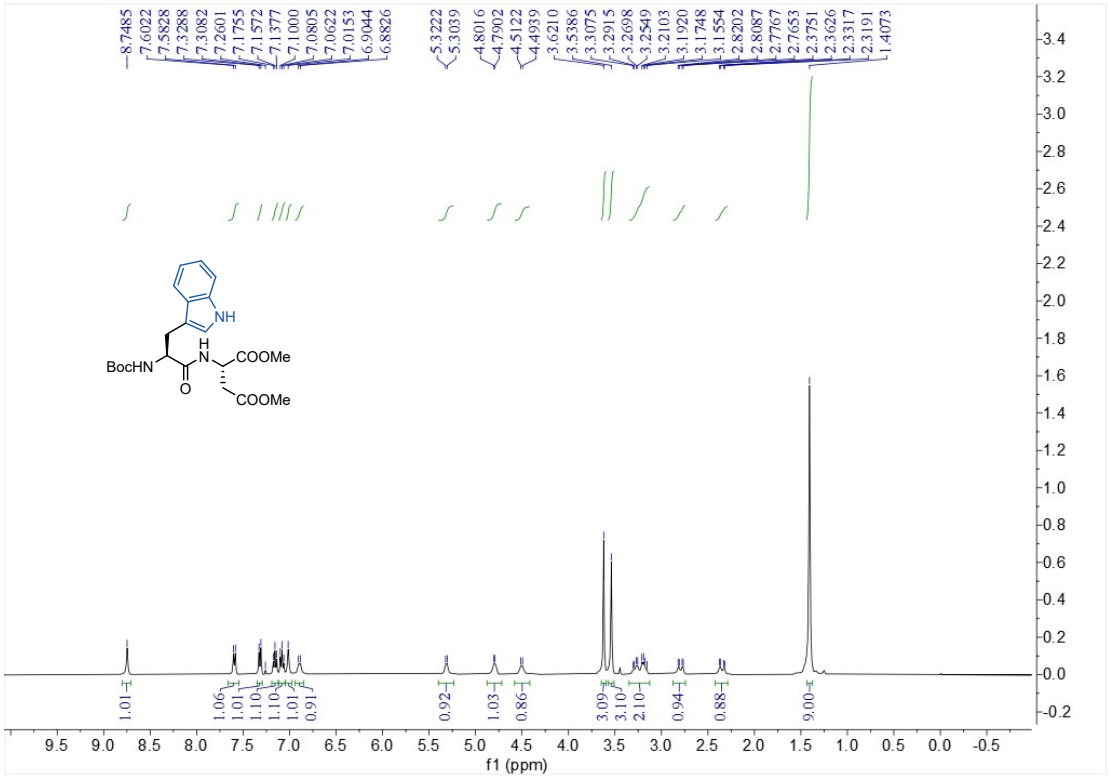


Fig 180. ^{1}H NMR of (**SM-3g**)

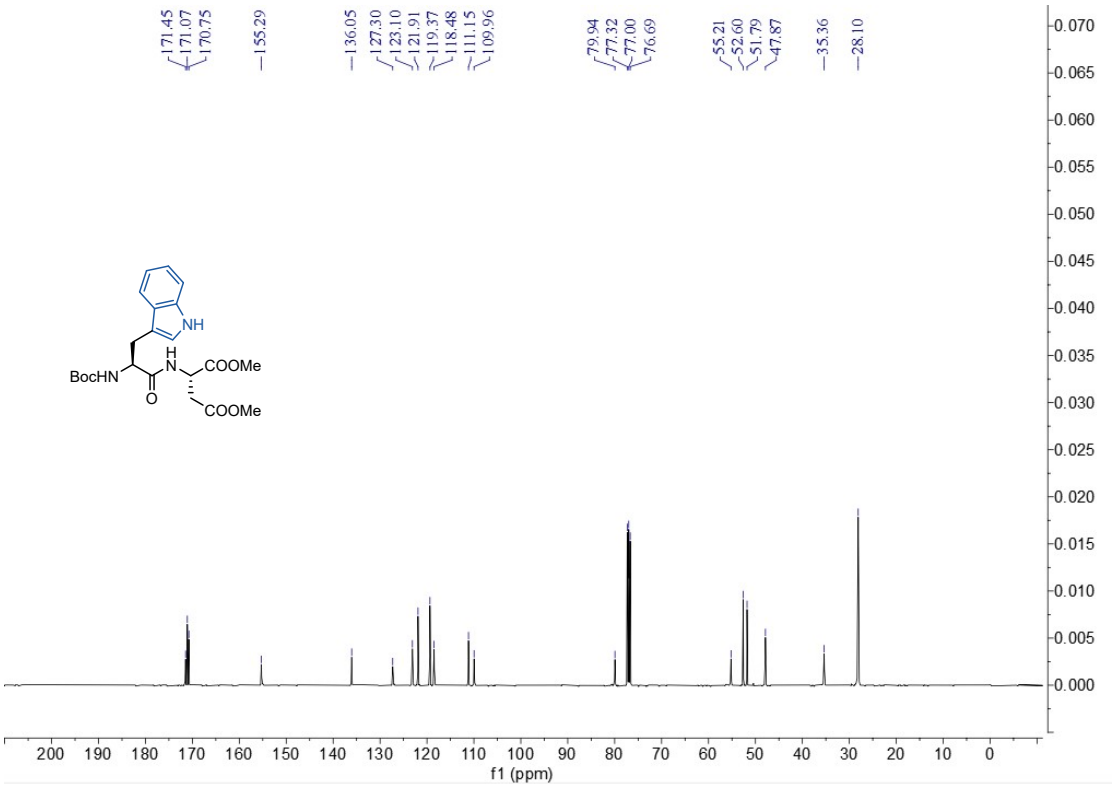


Fig 181. ^{13}C NMR of (**SM-3g**)

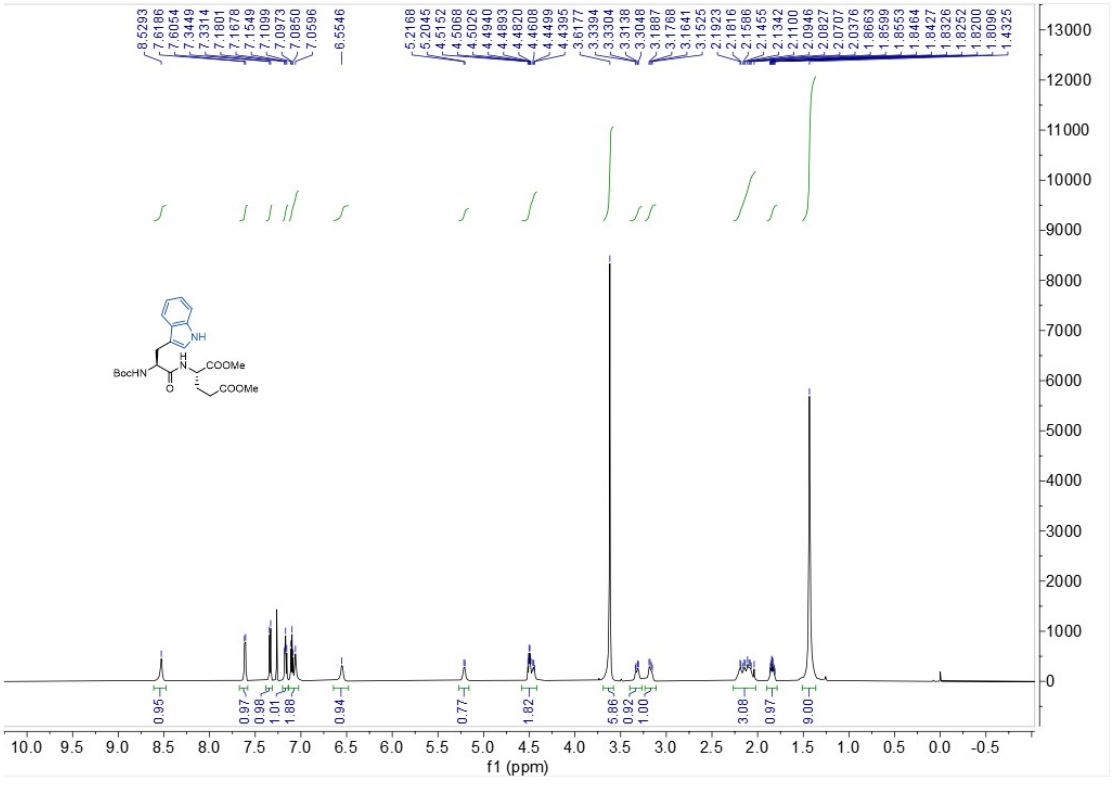


Fig 182. ^{1}H NMR of (**SM-3h**)

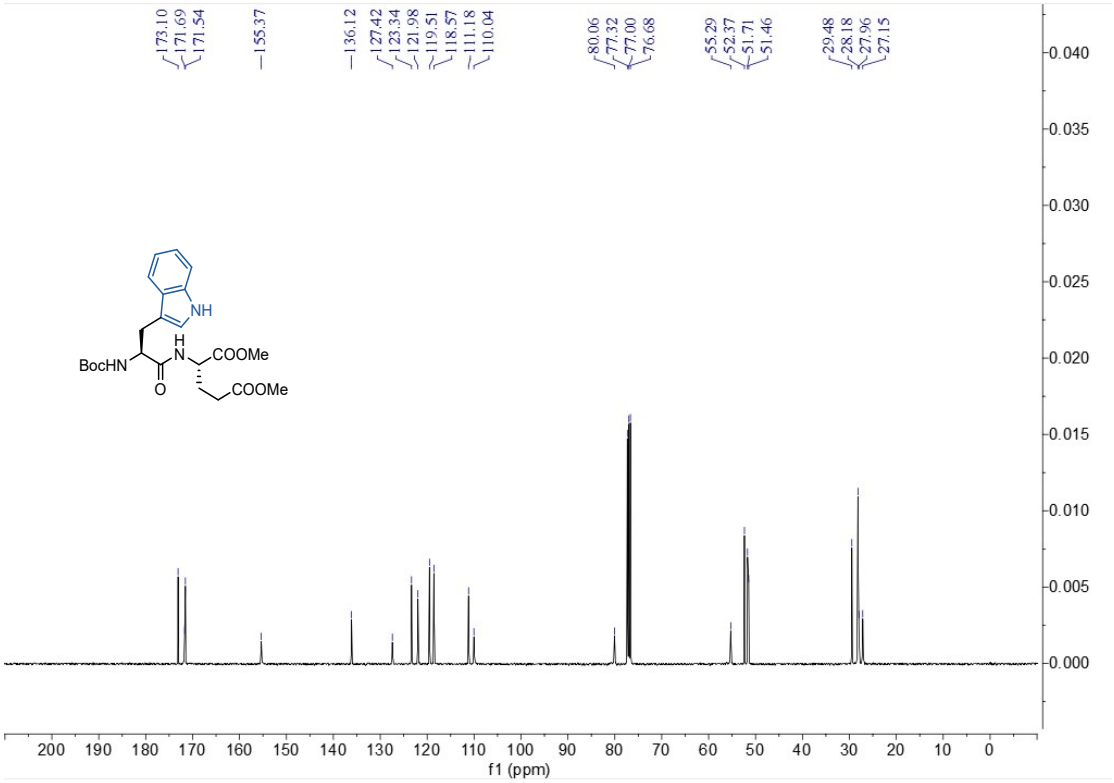


Fig 183. ^{13}C NMR of (**SM-3h**)

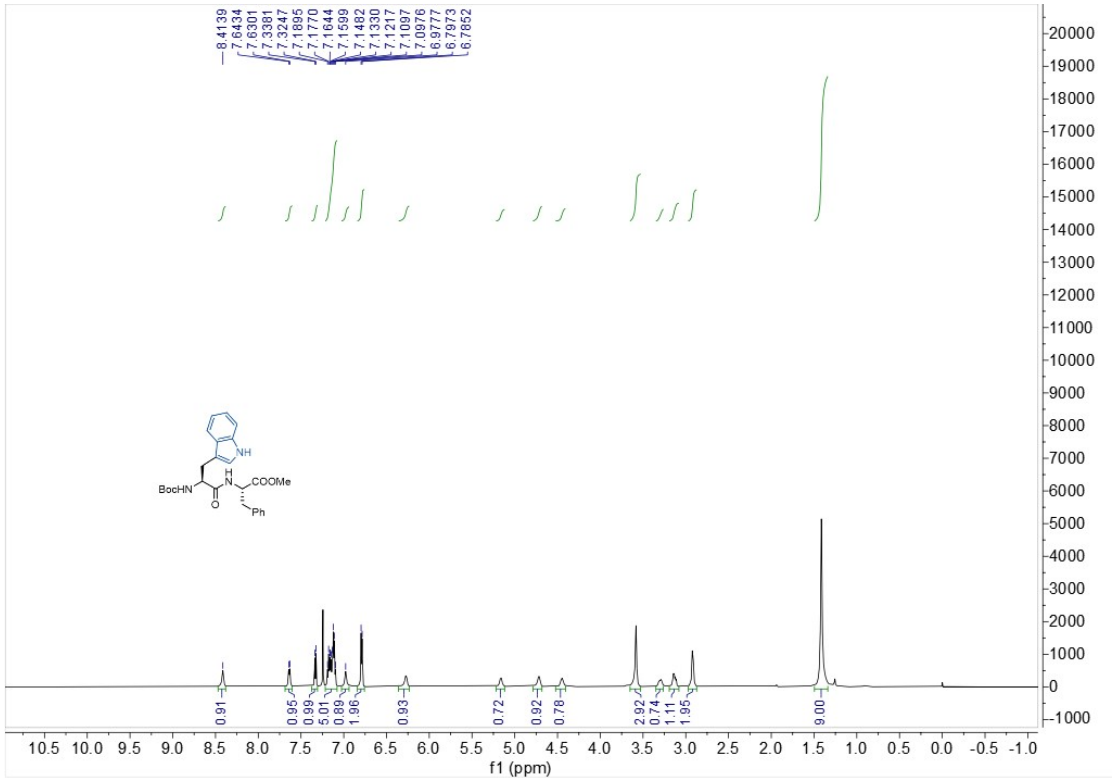


Fig 184. ^{1}H NMR of (**SM-3i**)

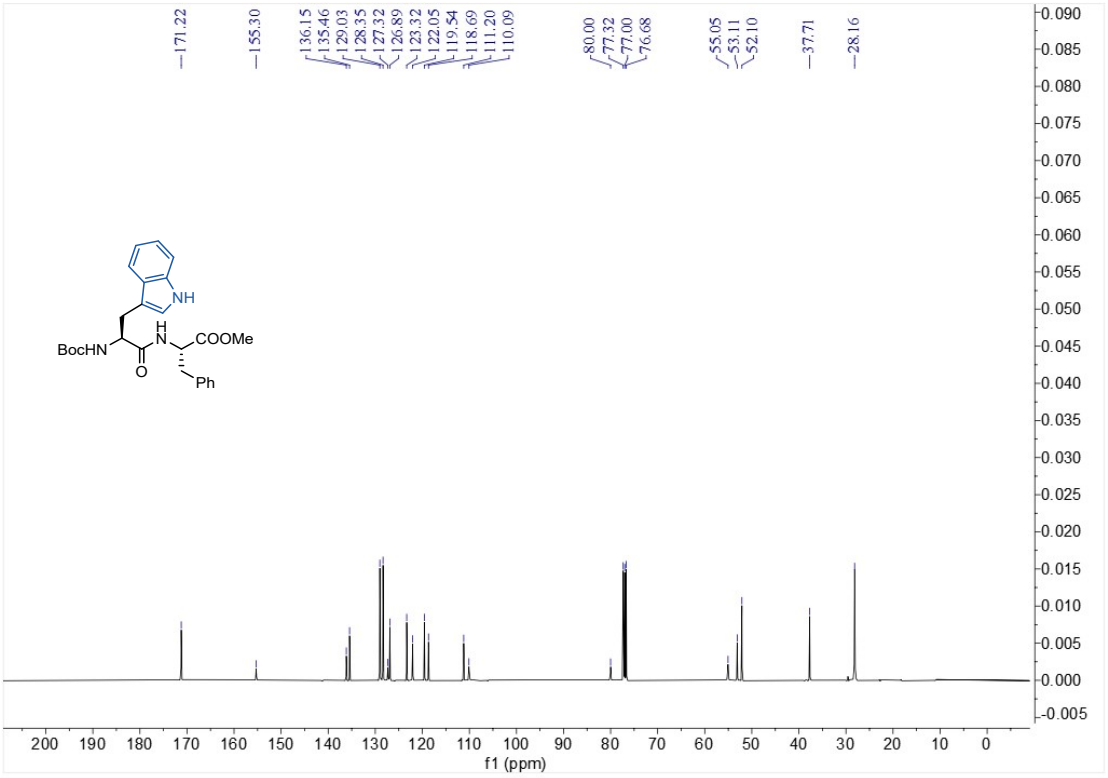


Fig 185. ^{13}C NMR of (**SM-3i**)

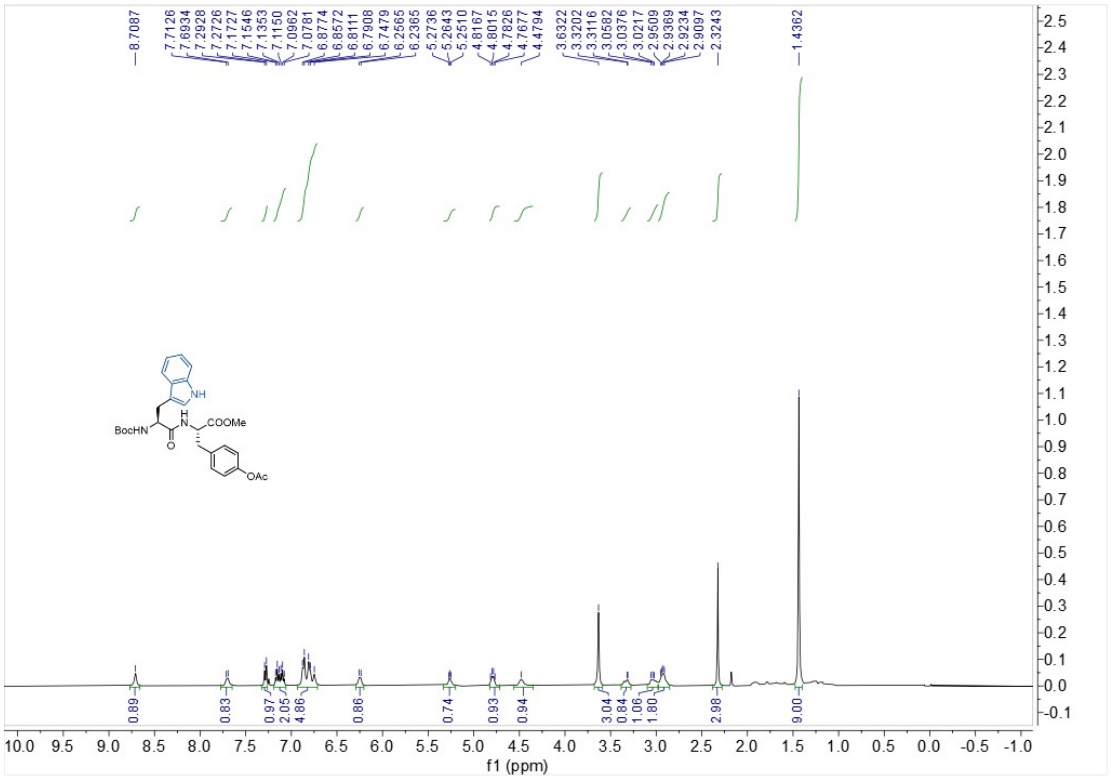


Fig 186. ^{1}H NMR of (**SM-3j**)

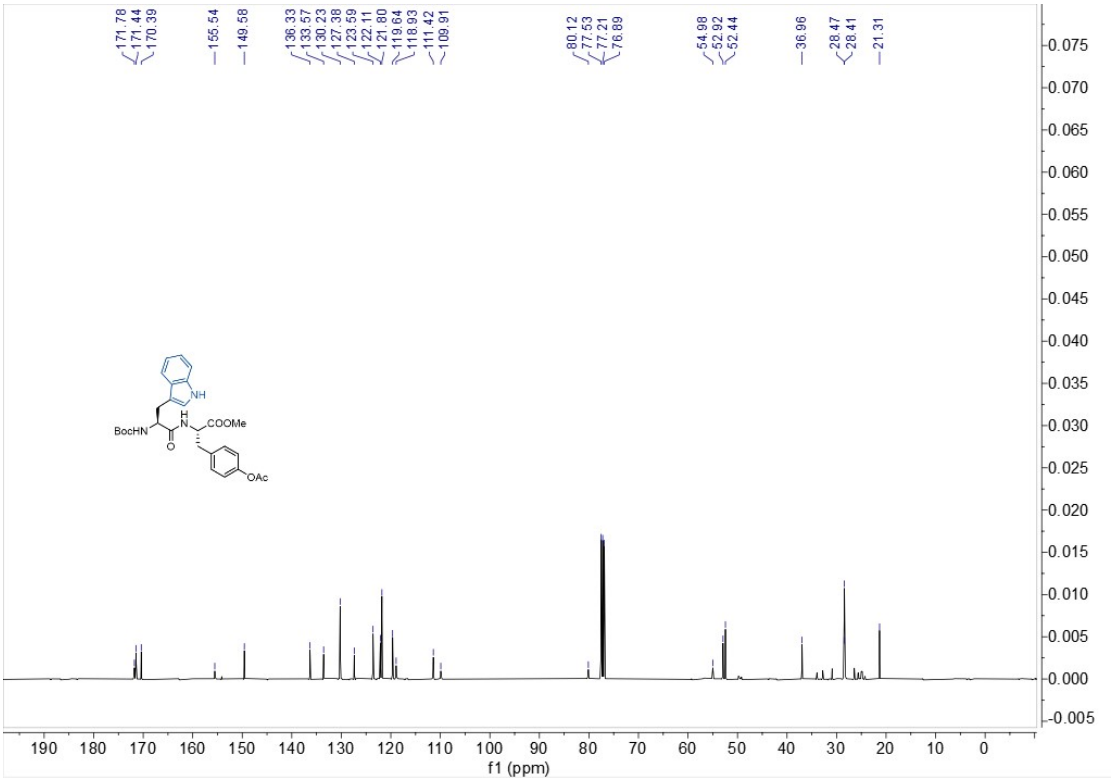


Fig 187. ^{13}C NMR of (**SM-3j**)

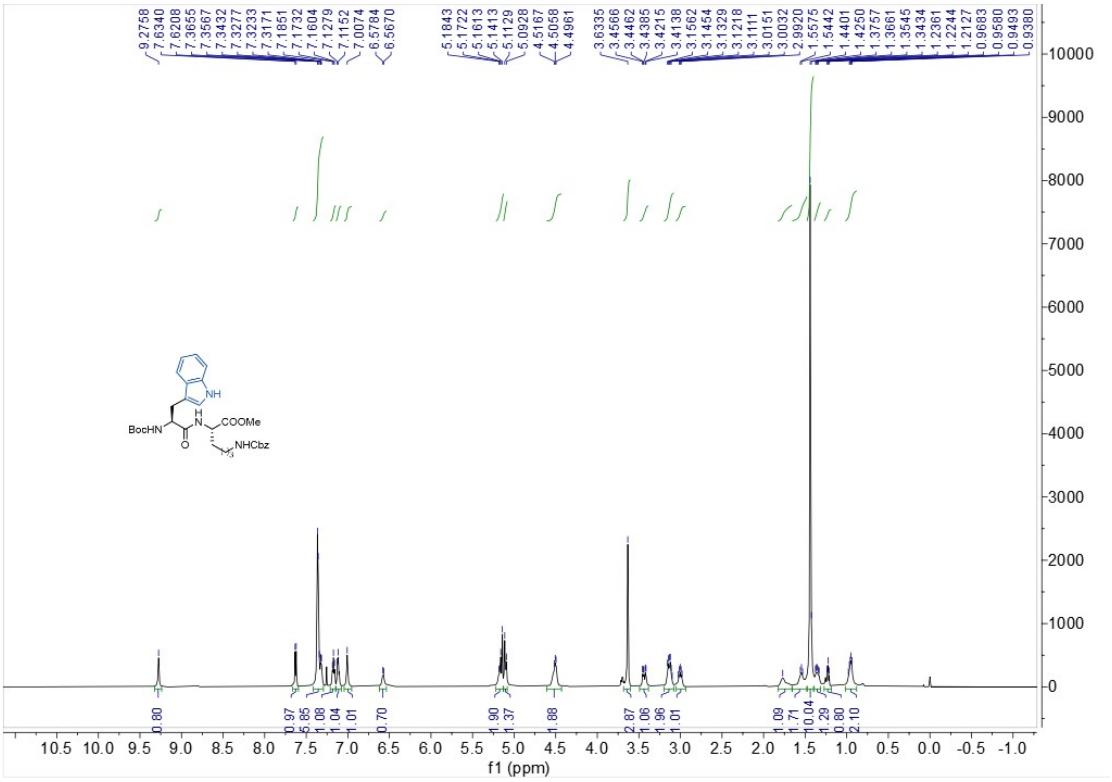


Fig 188. ^{1}H NMR of (**SM-3k**)

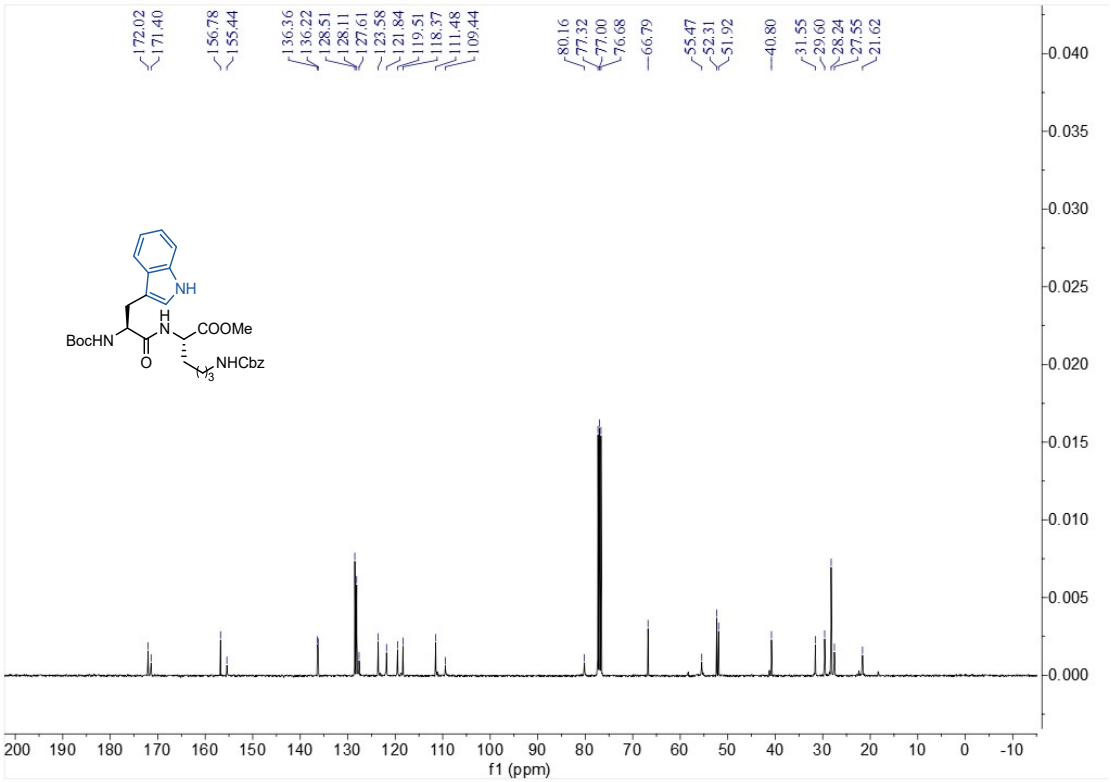


Fig 189. ^{13}C NMR of (**SM-3k**)

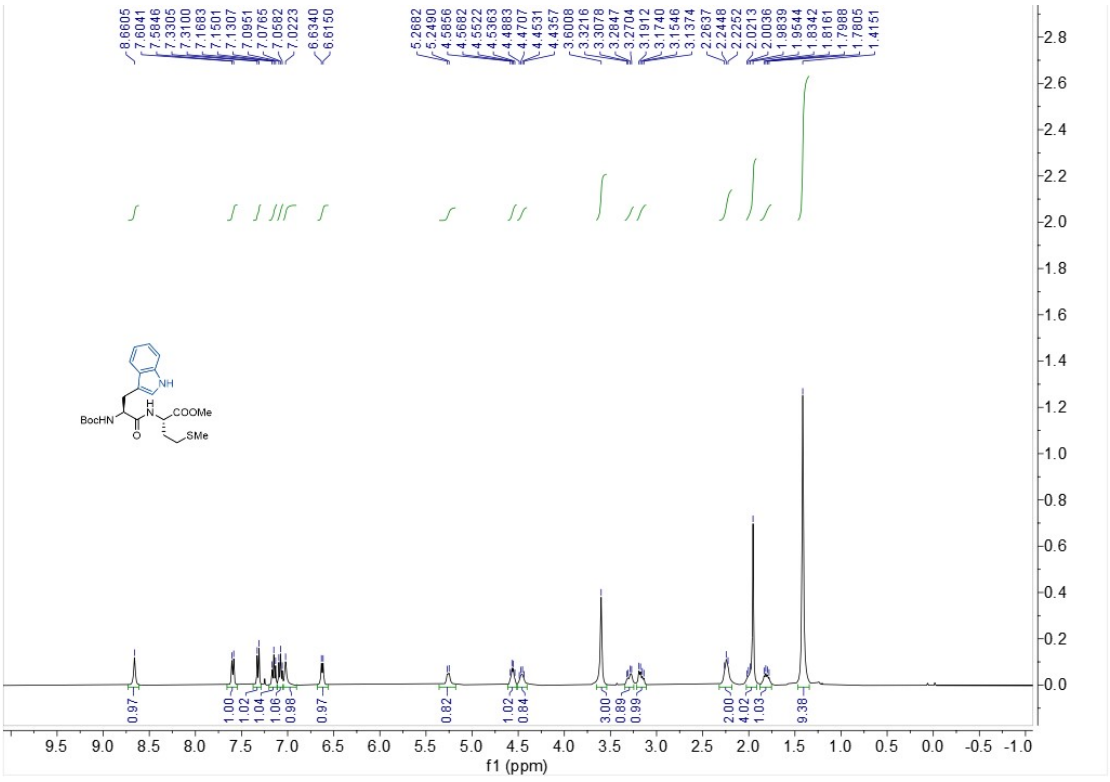


Fig 190. ^{1}H NMR of (**SM-3l**)

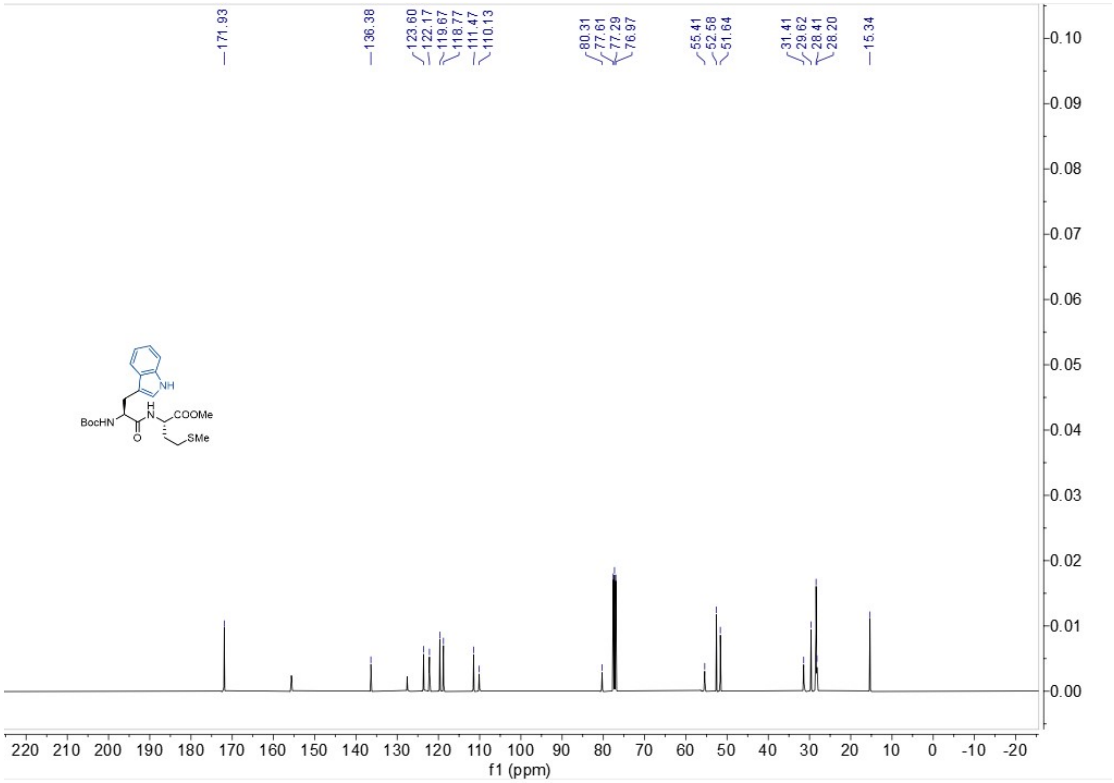


Fig 191. ^{13}C NMR of (**SM-3l**)

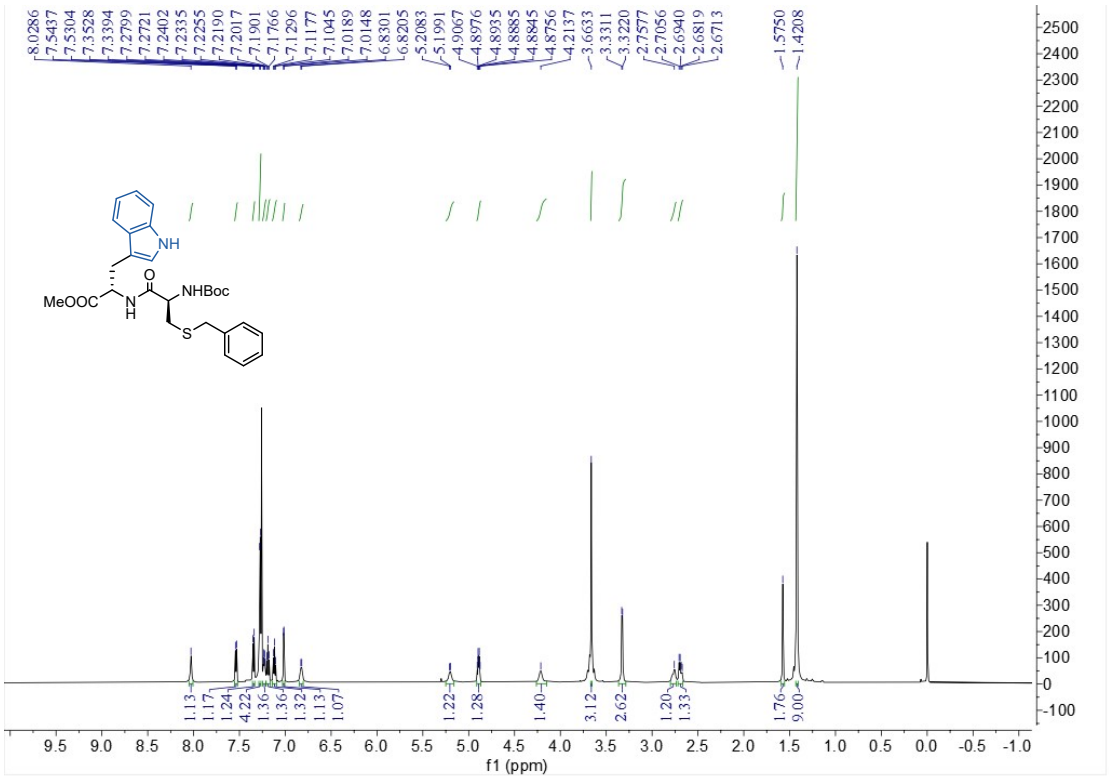


Fig 192. ^{1}H NMR of (**SM-3m**)

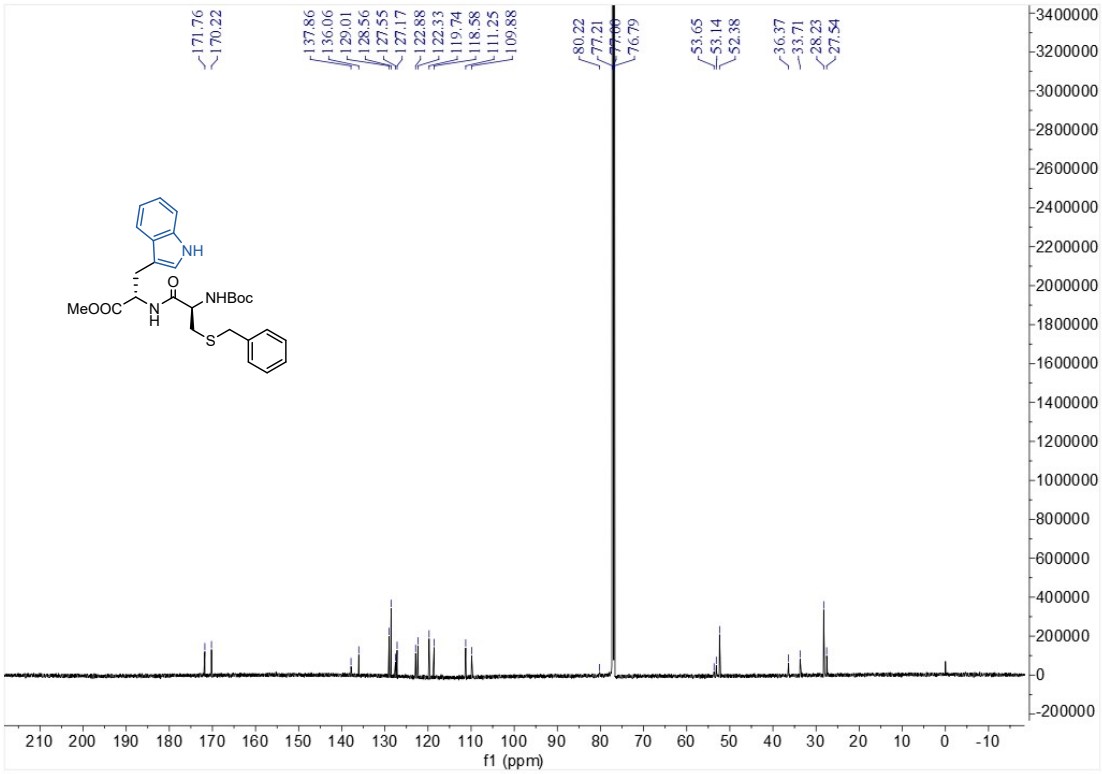


Fig 193. ^{13}C NMR of (**SM-3m**)

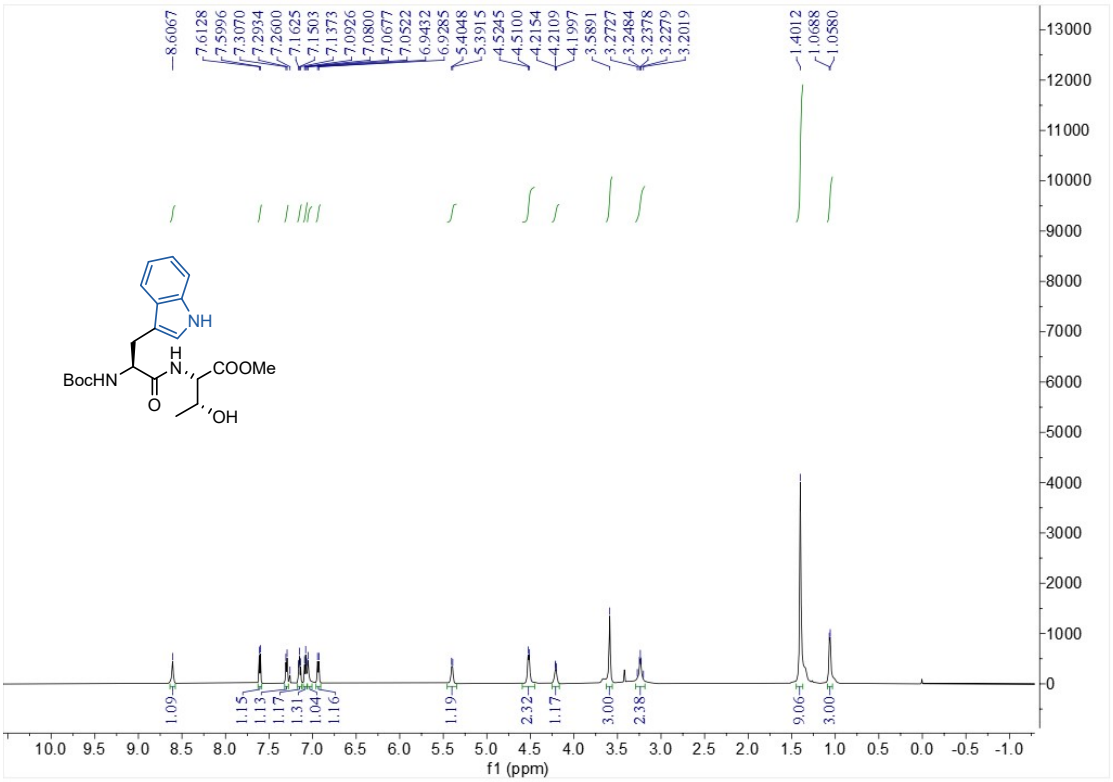


Fig 194. ^{1}H NMR of (**SM-3n**)

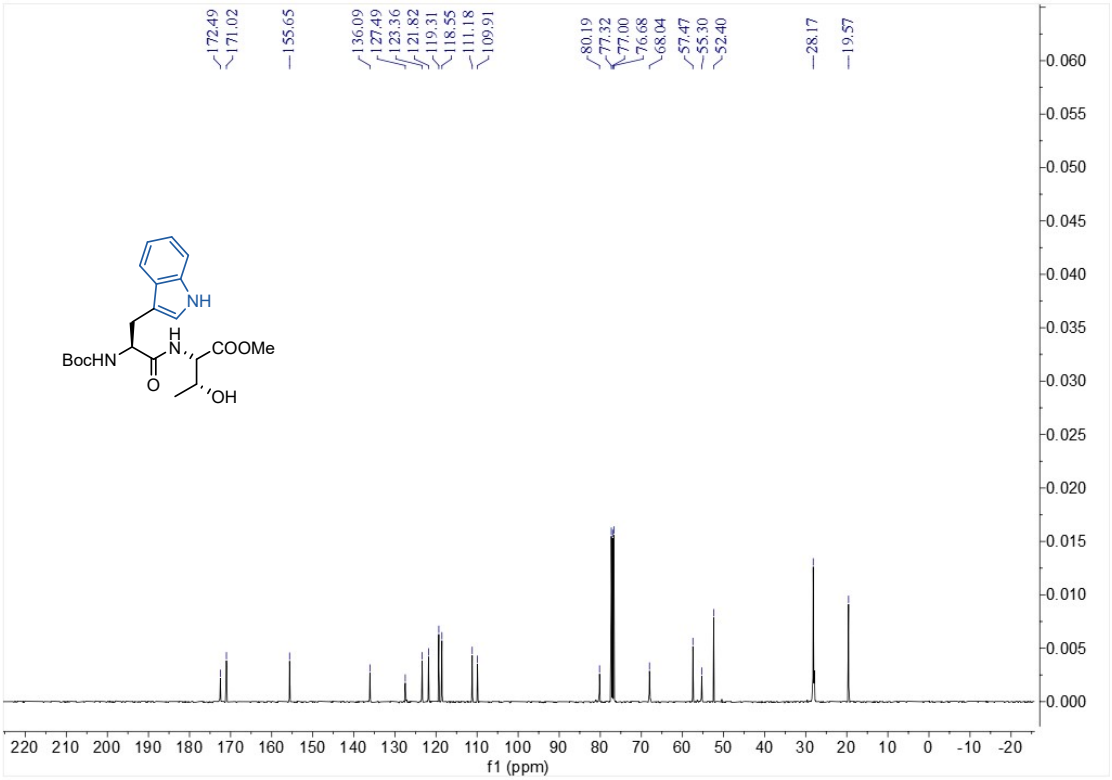


Fig 195. ^{13}C NMR of (**SM-3n**)

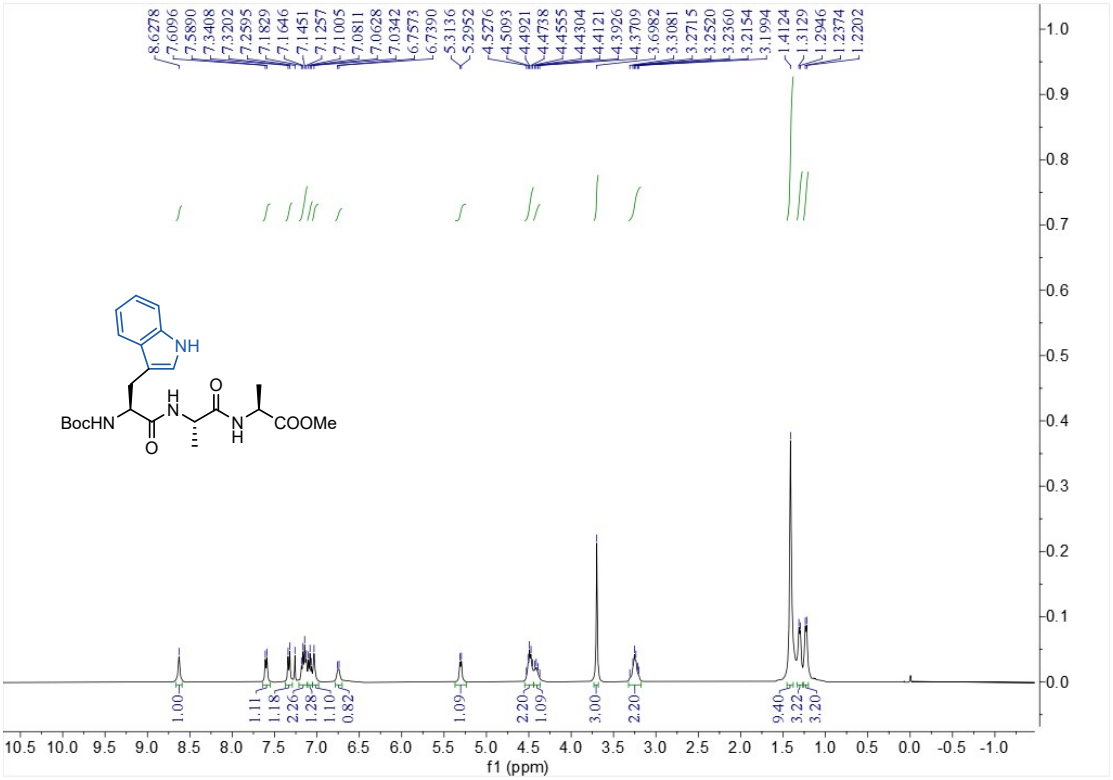


Fig 196. ^{1}H NMR of (**SM-4a**)

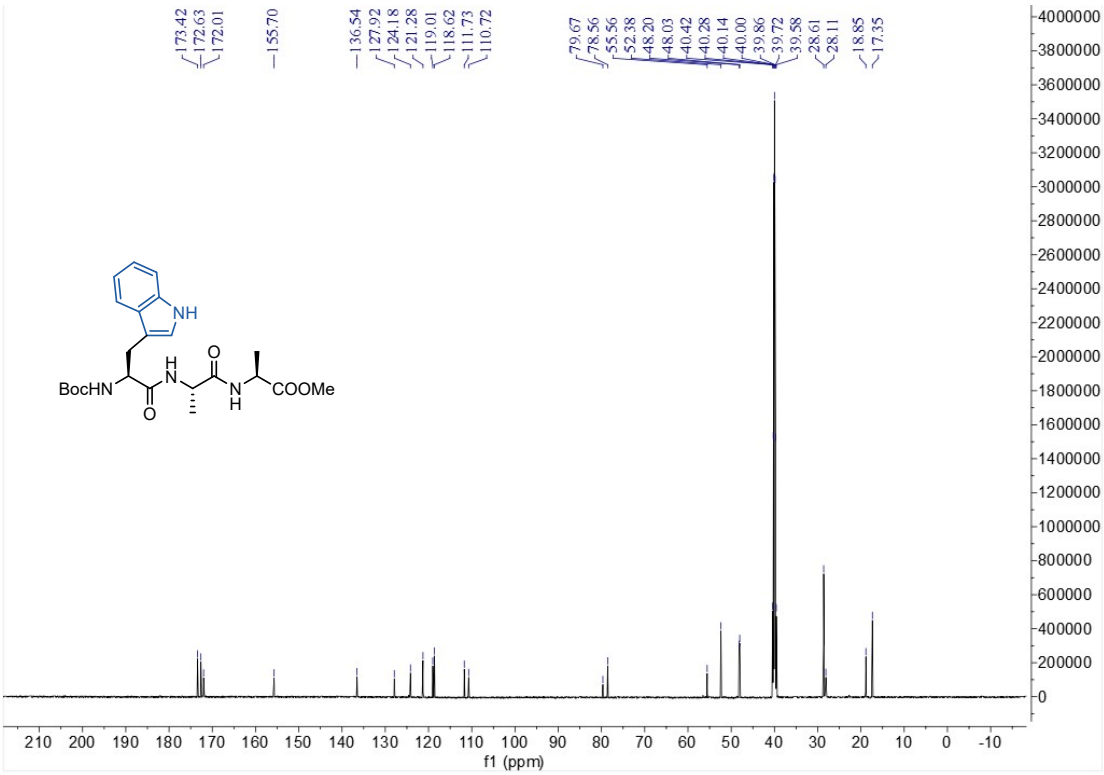


Fig 197. ^{13}C NMR of (**SM-4a**)

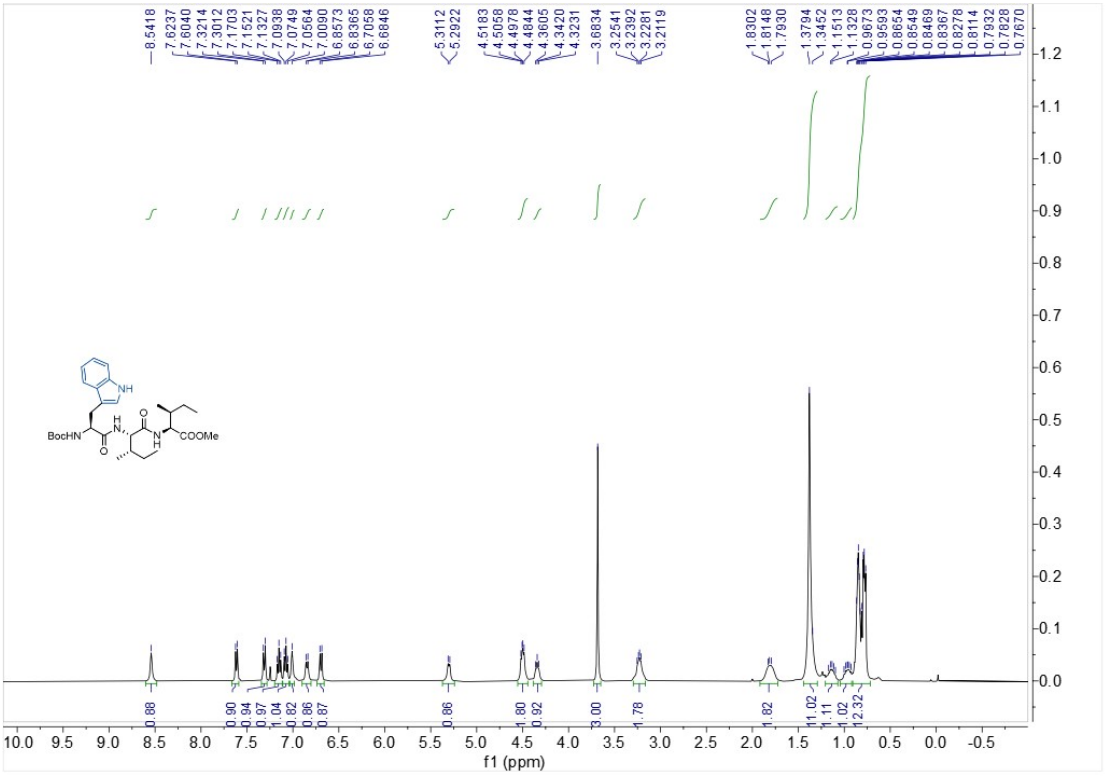


Fig 198. ^{1}H NMR of (**SM-4b**)

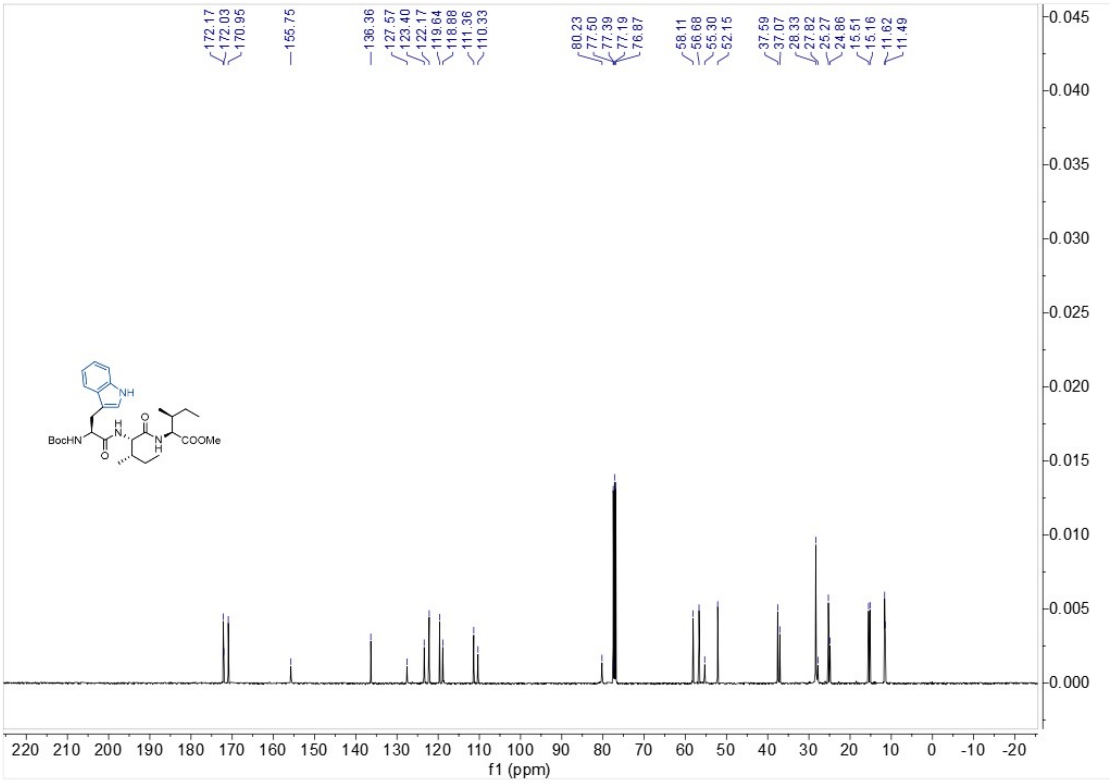


Fig 199. ^{13}C NMR of (**SM-4b**)

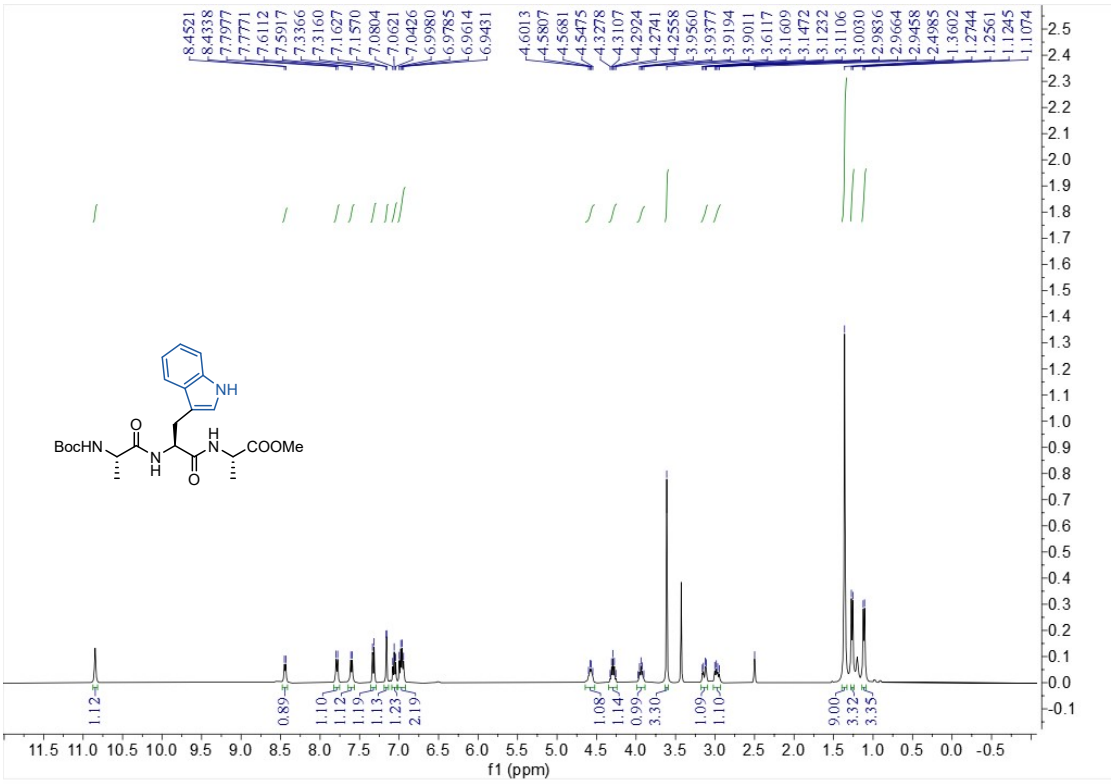


Fig 200. ^{1}H NMR of (**SM-4c**)

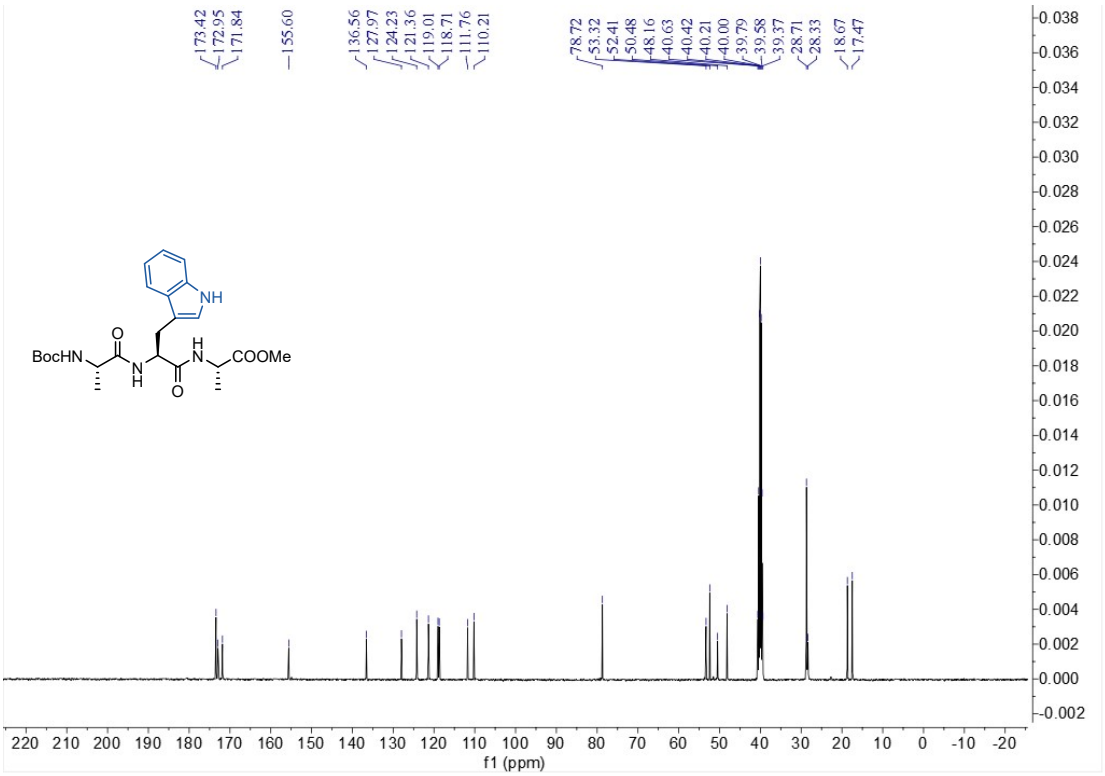


Fig 201. ^{13}C NMR of (**SM-4c**)

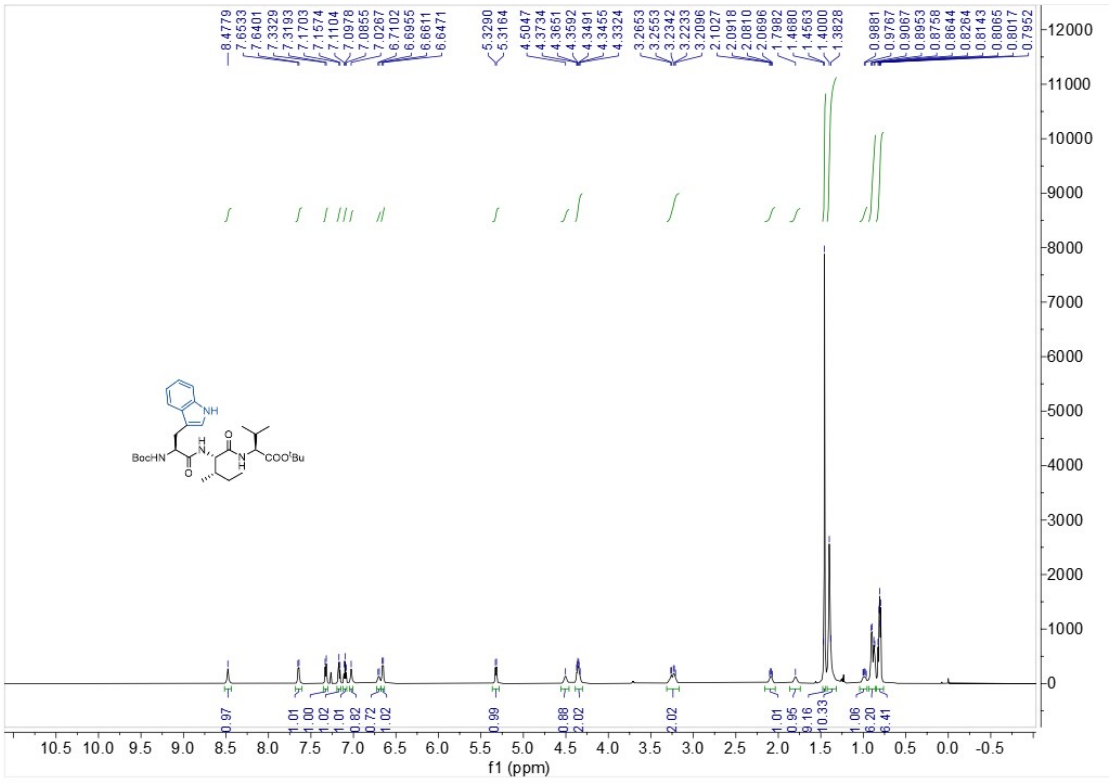


Fig 202. ^{1}H NMR of (**SM-4d**)

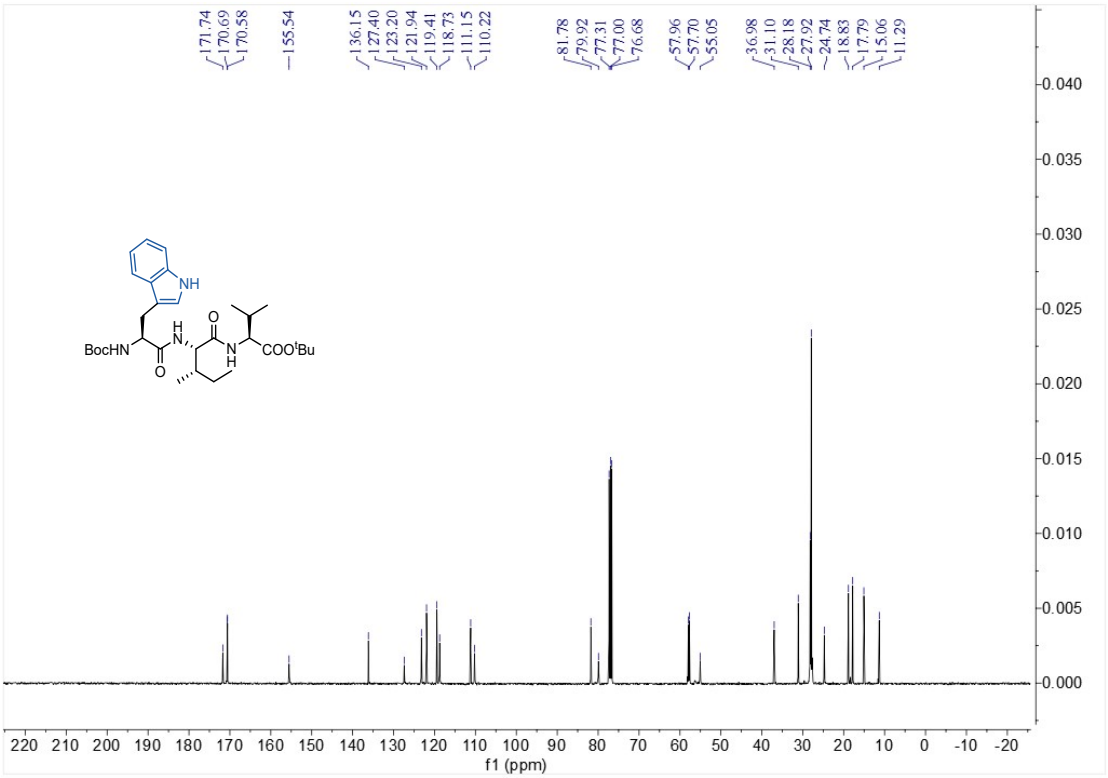


Fig 203. ^{13}C NMR of (**SM-4d**)

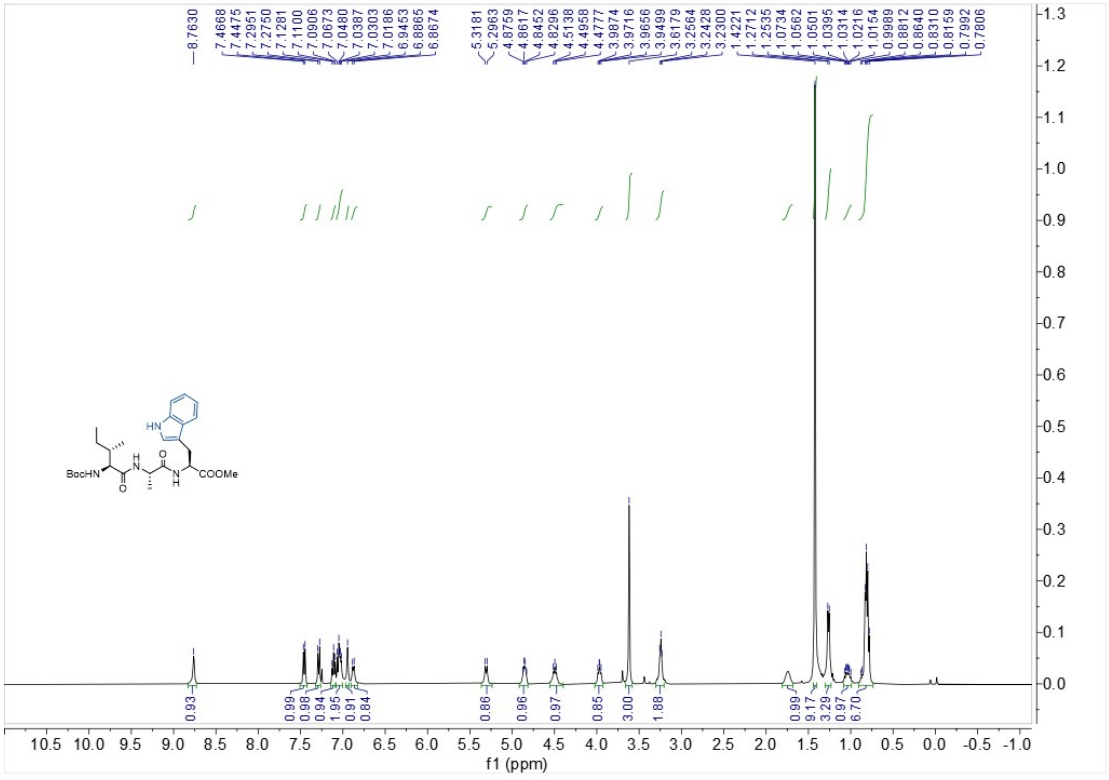


Fig 204. ^{1}H NMR of (**SM-4e**)

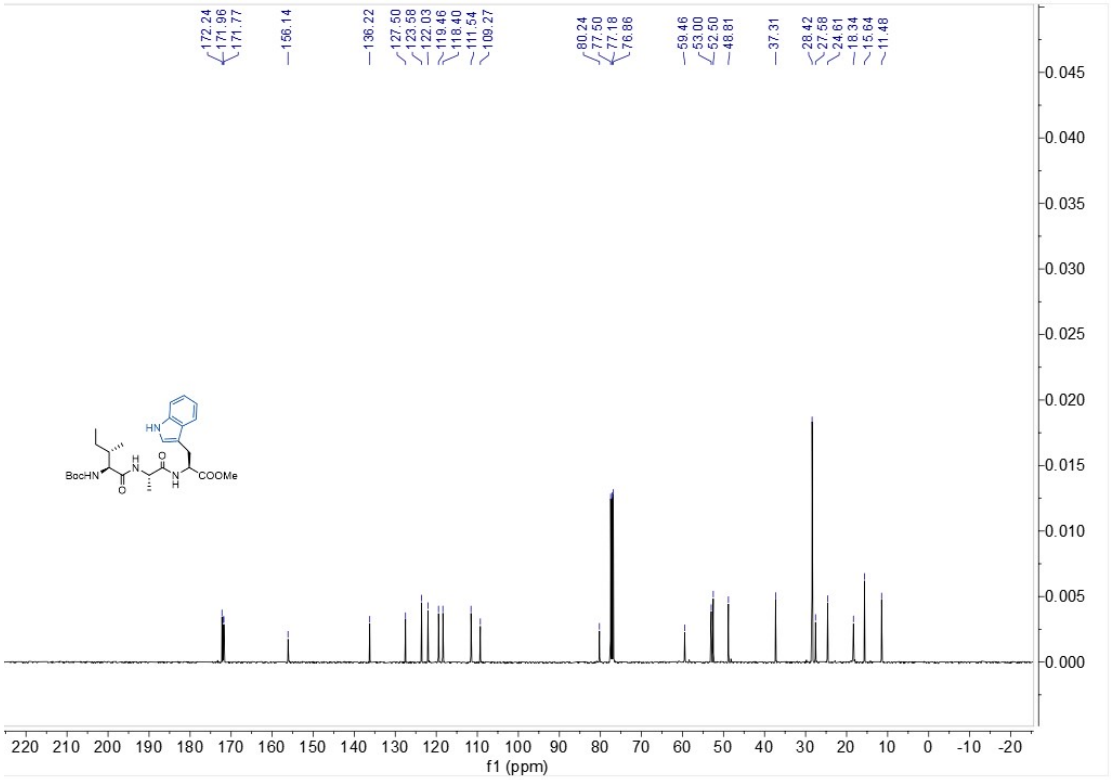


Fig 205. ^{13}C NMR of (**SM-4e**)

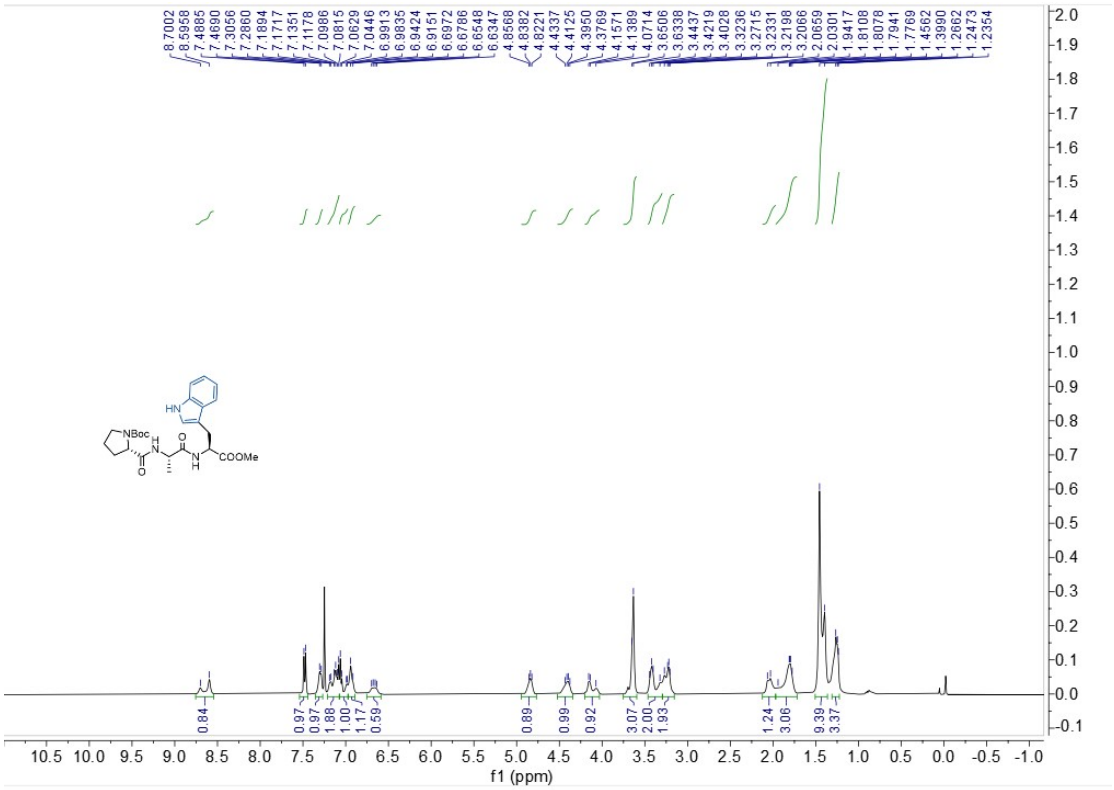


Fig 206. ^{1}H NMR of (**SM-4f**)

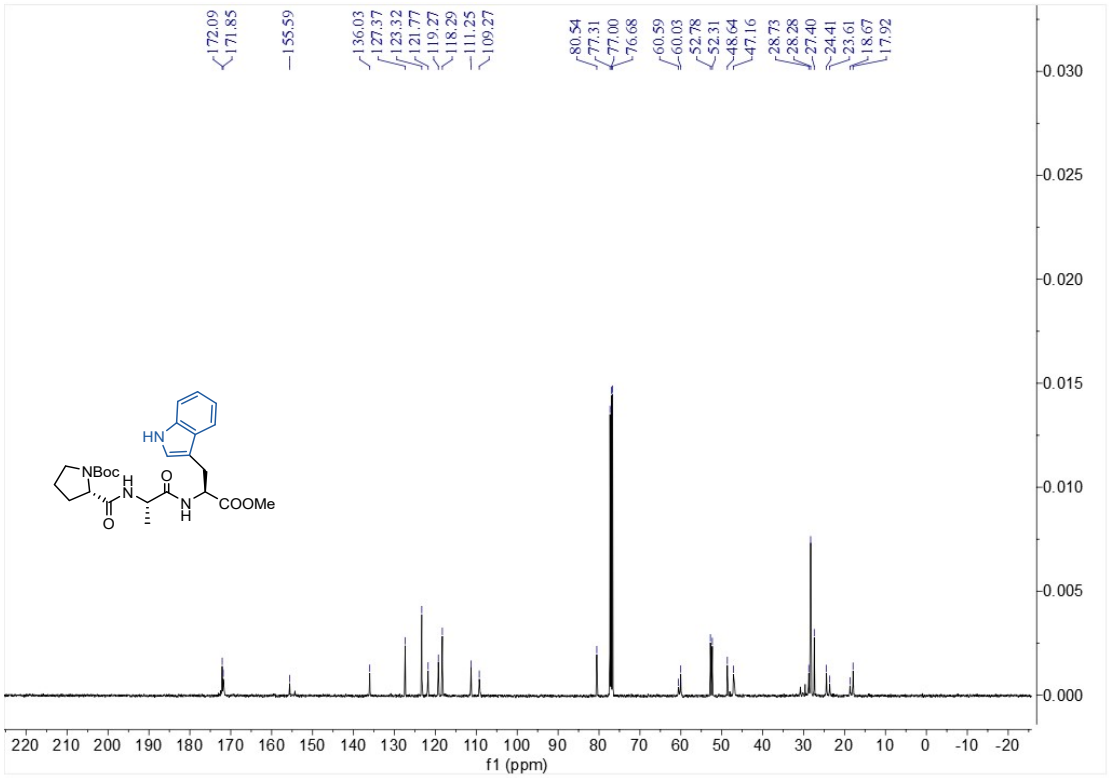


Fig 207. ^{13}C NMR of (**SM-4f**)

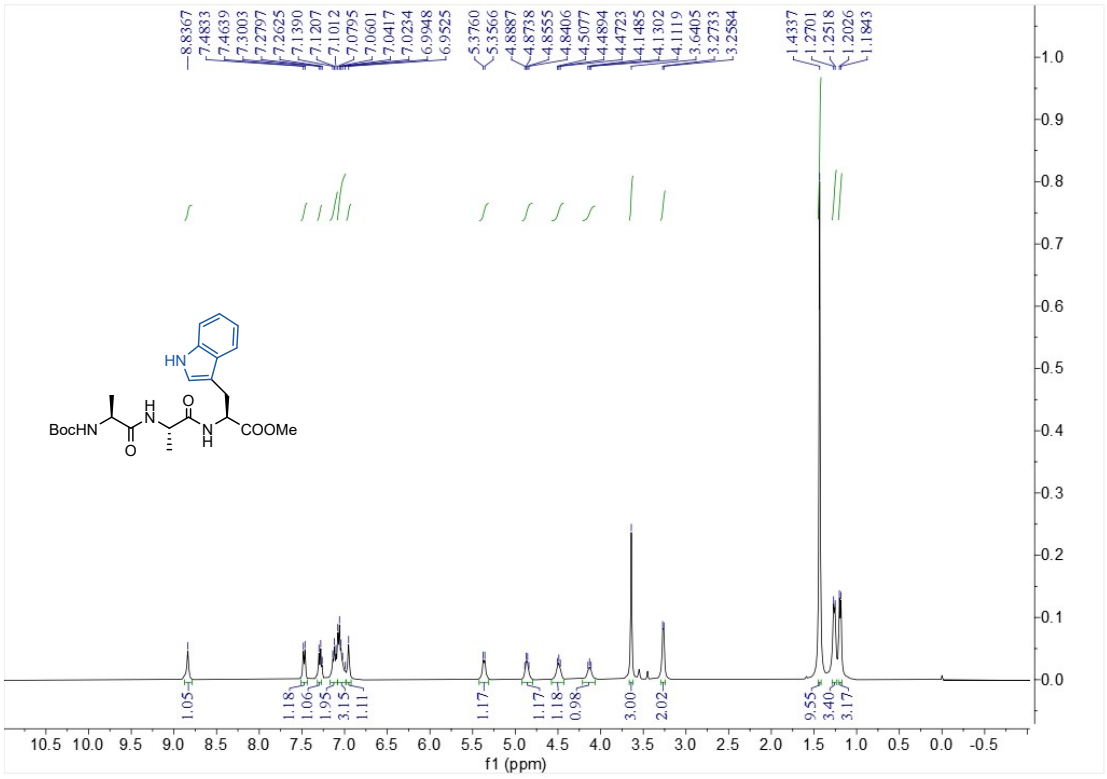


Fig 208. ^{1}H NMR of (**SM-4g**)

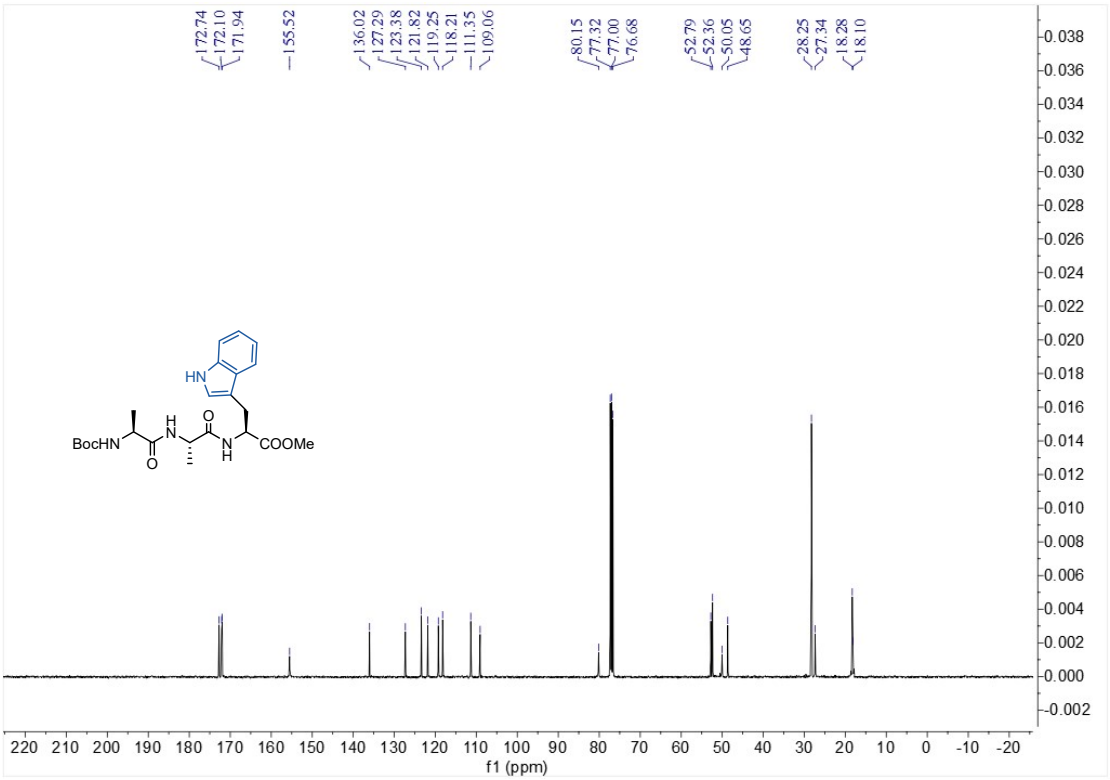


Fig 209. ^{13}C NMR of (**SM-4g**)

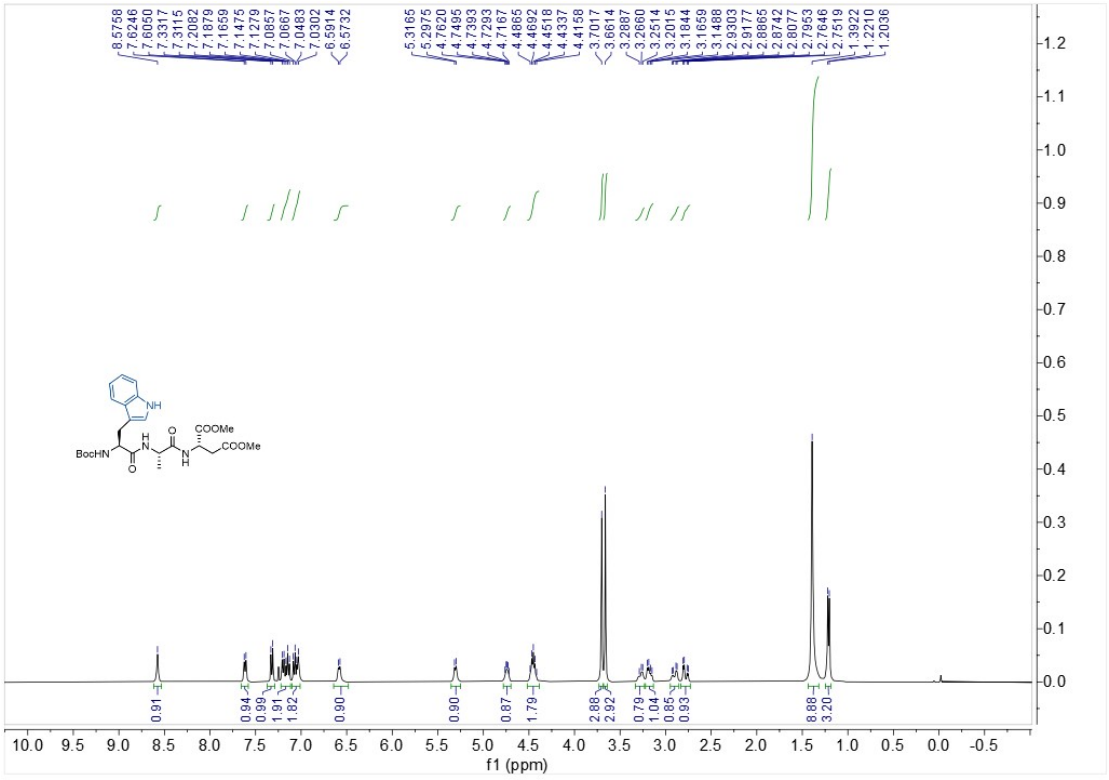


Fig 210. ^{1}H NMR of (**SM-4h**)

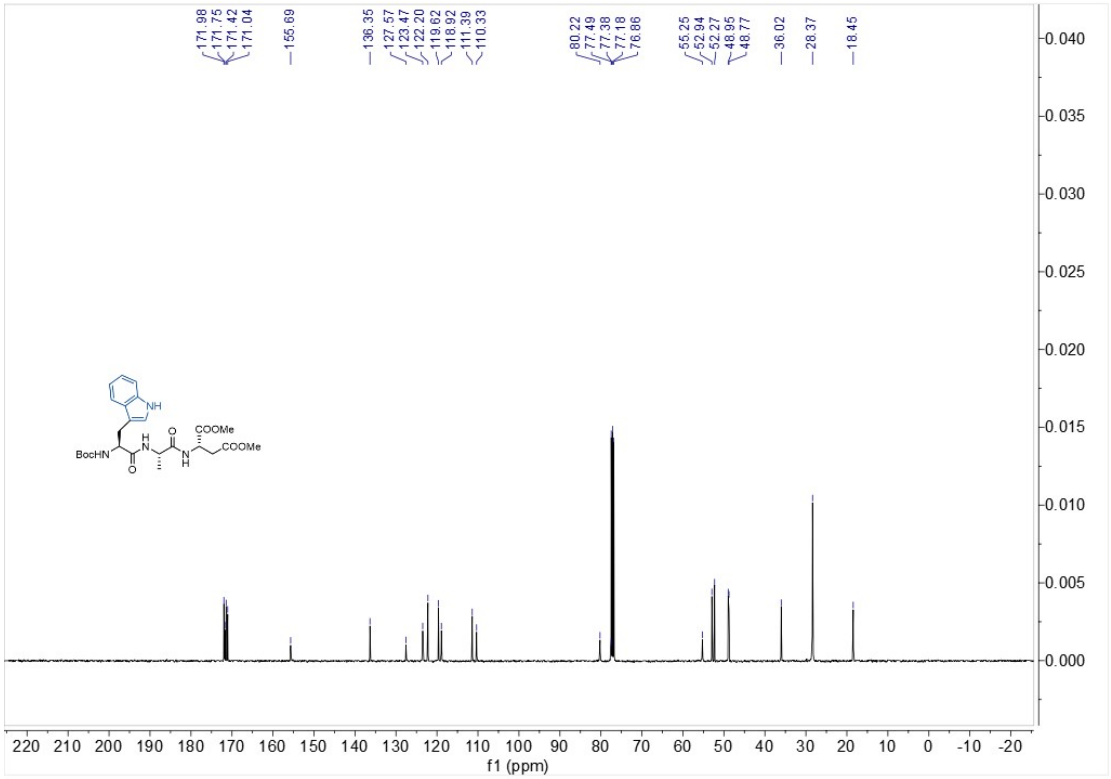


Fig 211. ^{13}C NMR of (**SM-4h**)

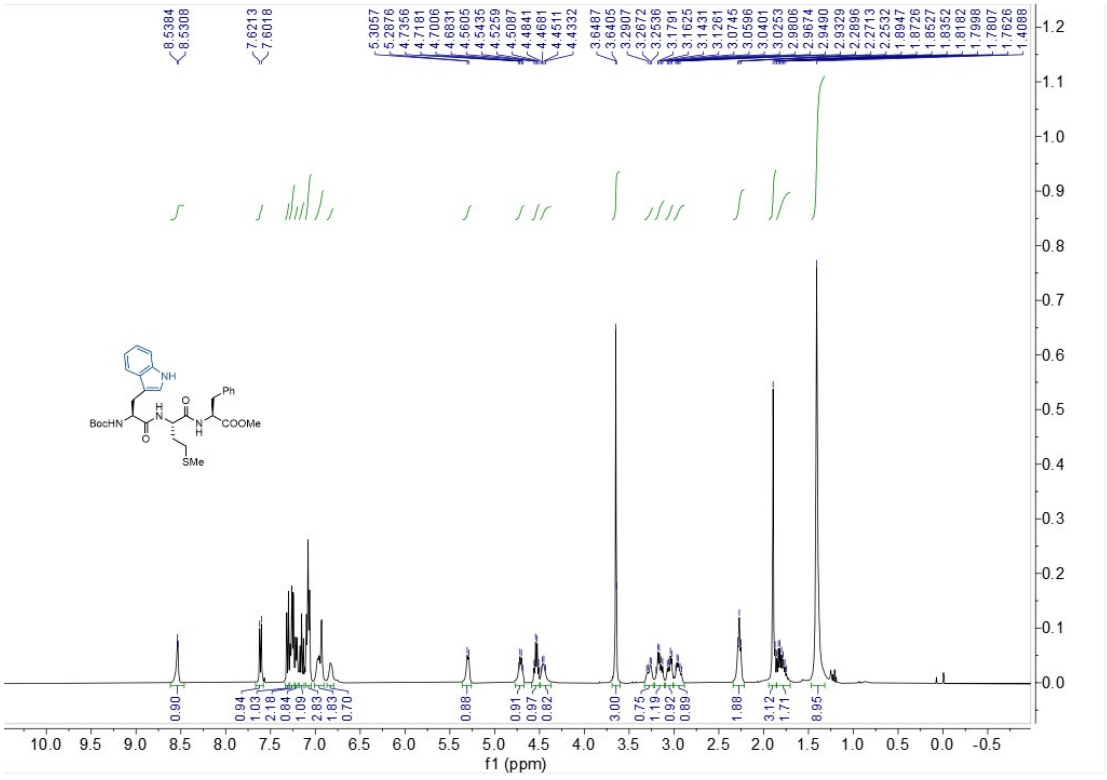


Fig 212. ^{1}H NMR of (**SM-4i**)

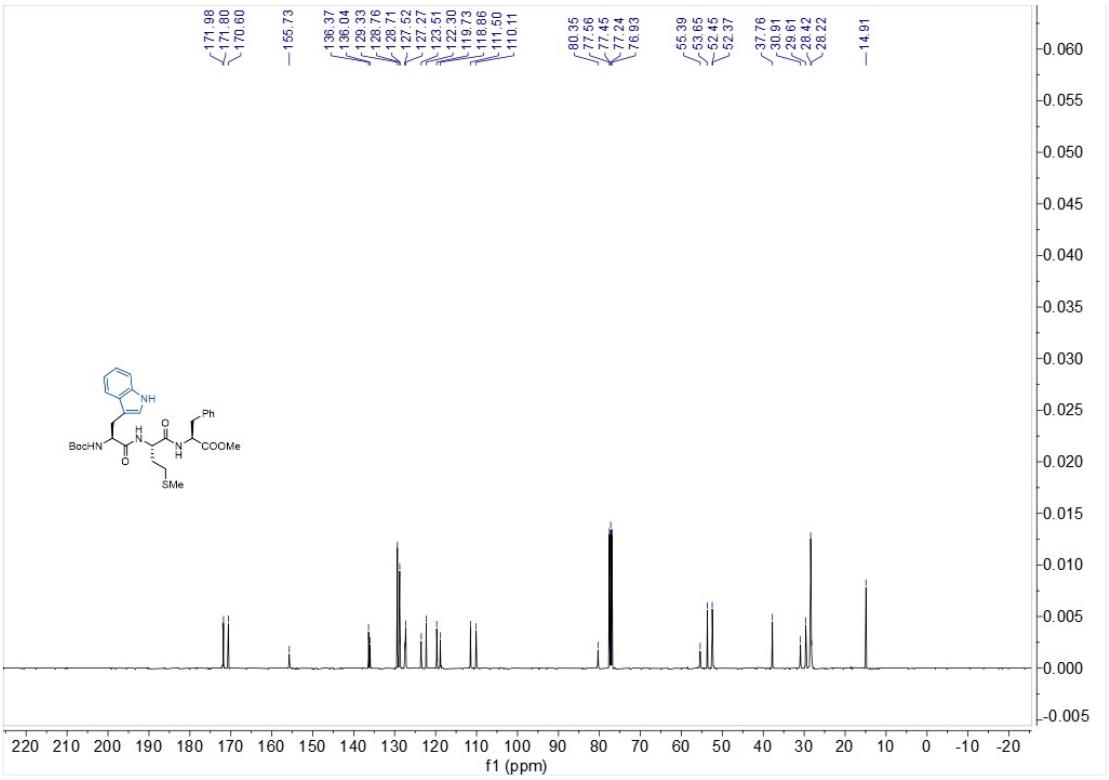


Fig 213. ^{13}C NMR of (**SM-4i**)

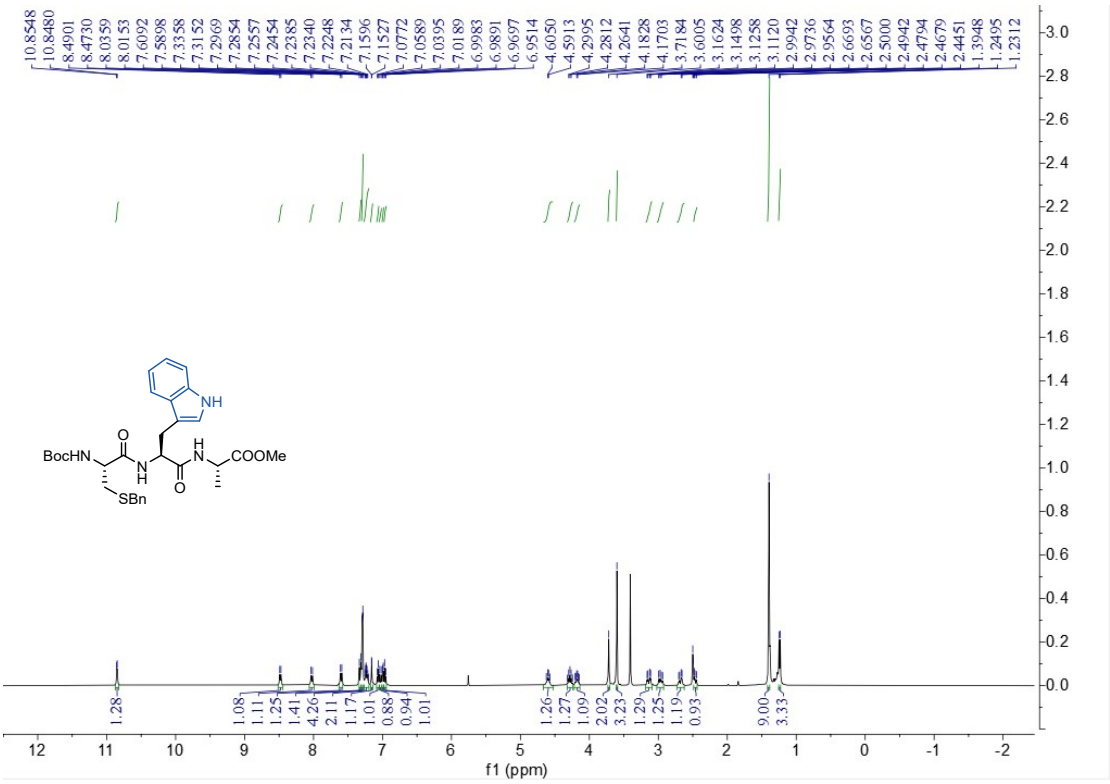


Fig 214. ^{1}H NMR of (**SM-4j**)

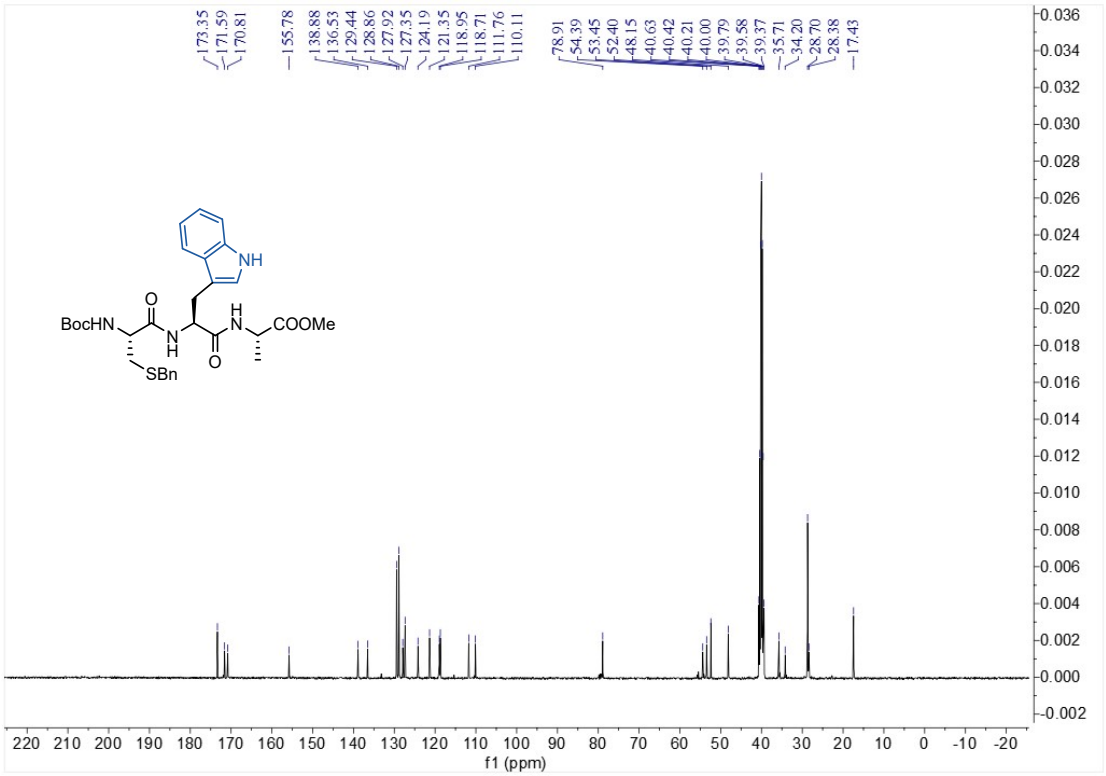


Fig 215. ^{13}C NMR of (**SM-4j**)

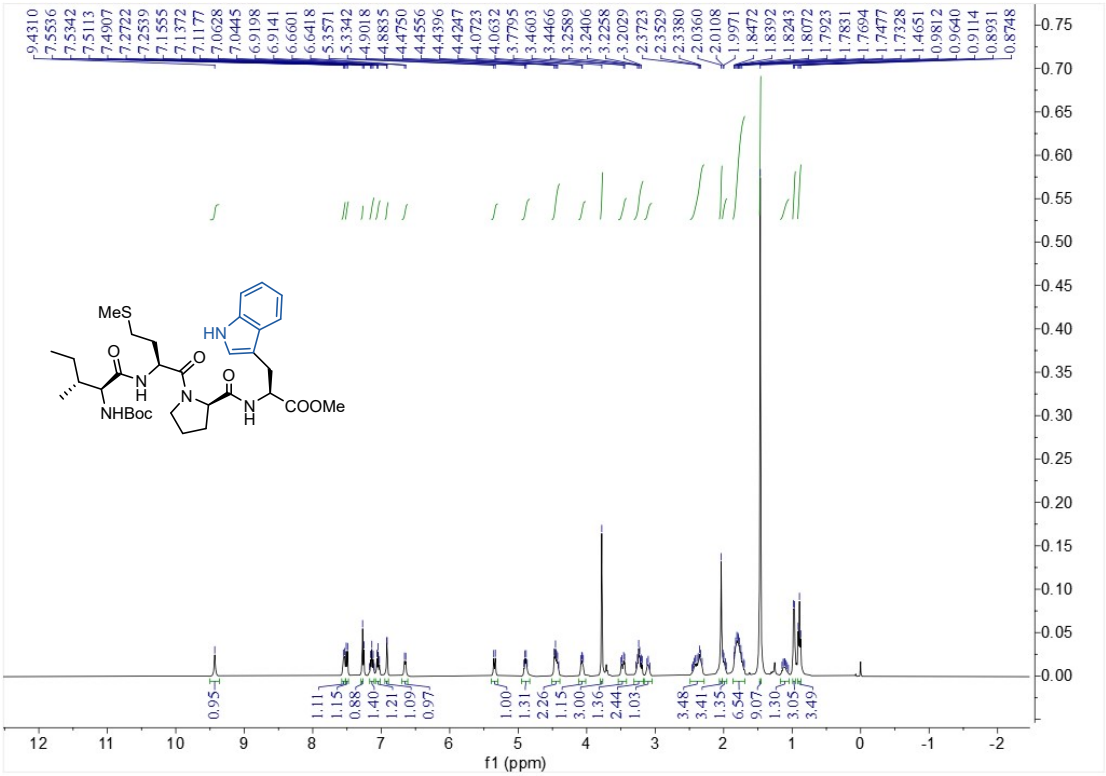


Fig 216. ^{1}H NMR of (**SM-5a**)

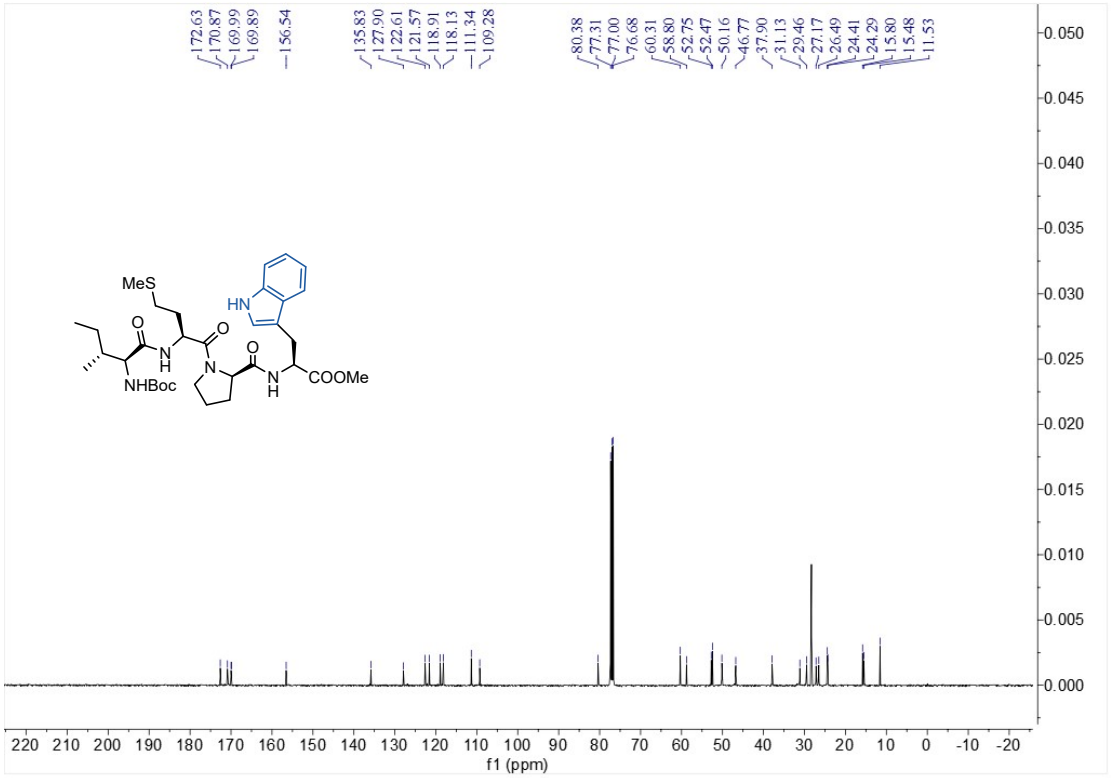


Fig 217. ^{13}C NMR of (**SM-5a**)

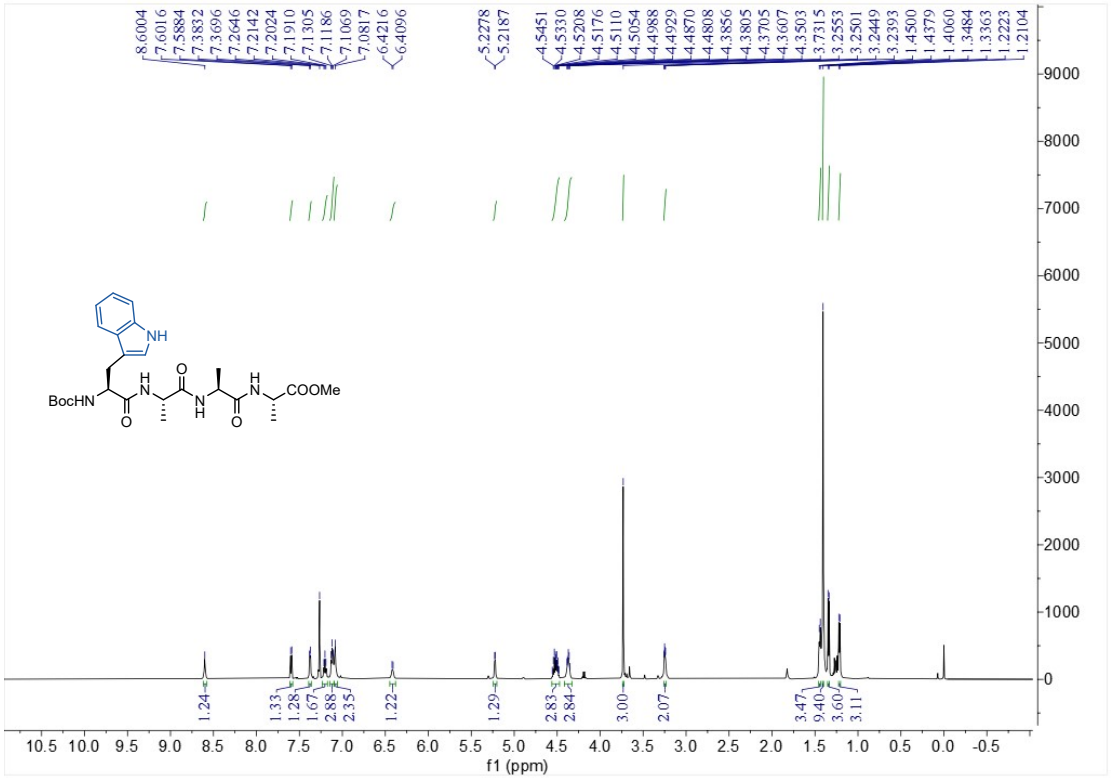


Fig 218. ^{1}H NMR of (**SM-5b**)

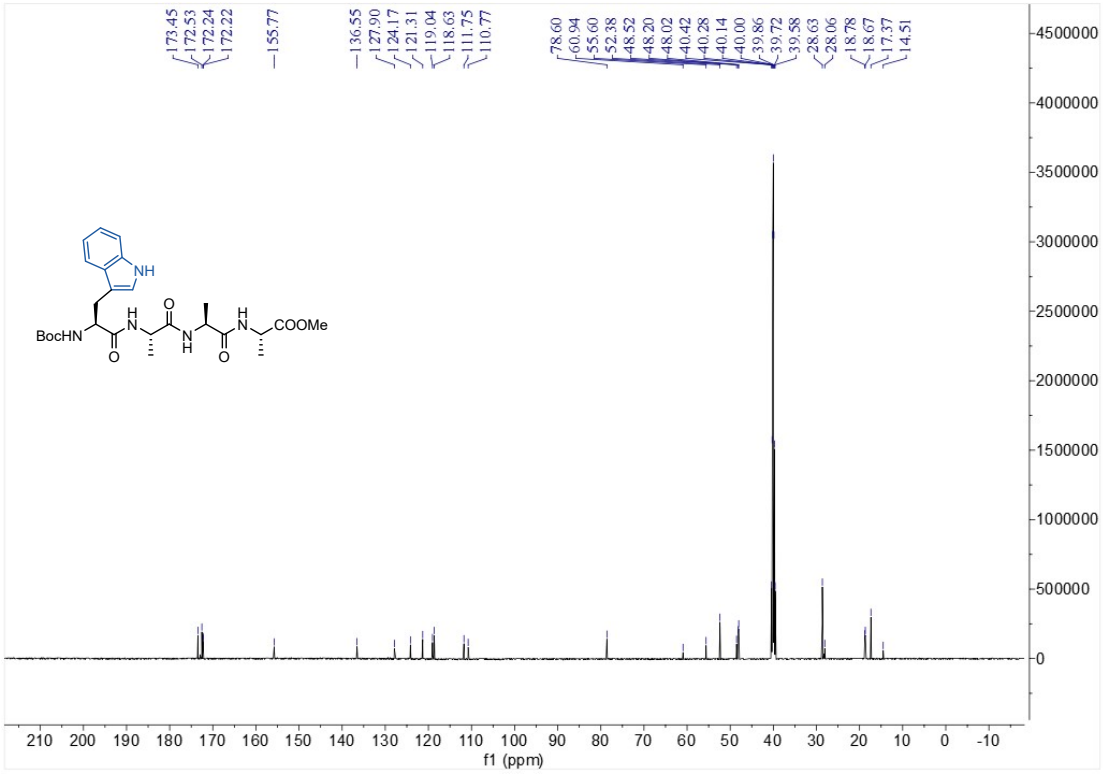


Fig 219. ^{13}C NMR of (**SM-5b**)

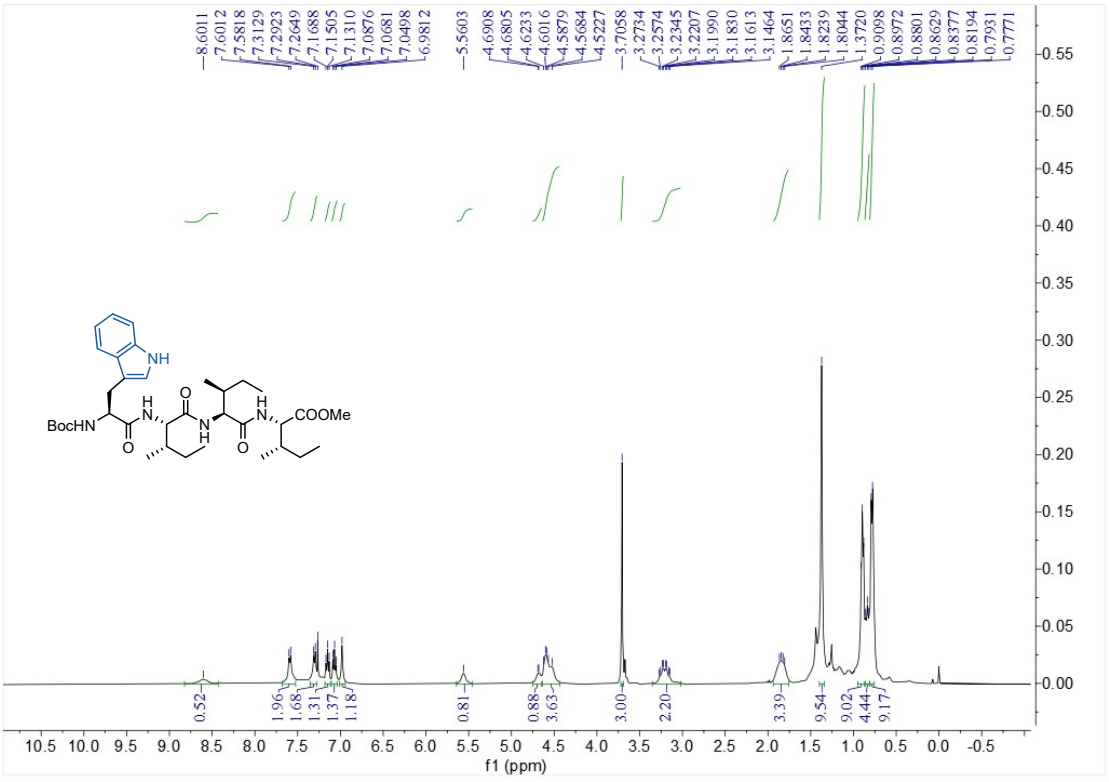


Fig 220. ^{1}H NMR of (**SM-5c**)

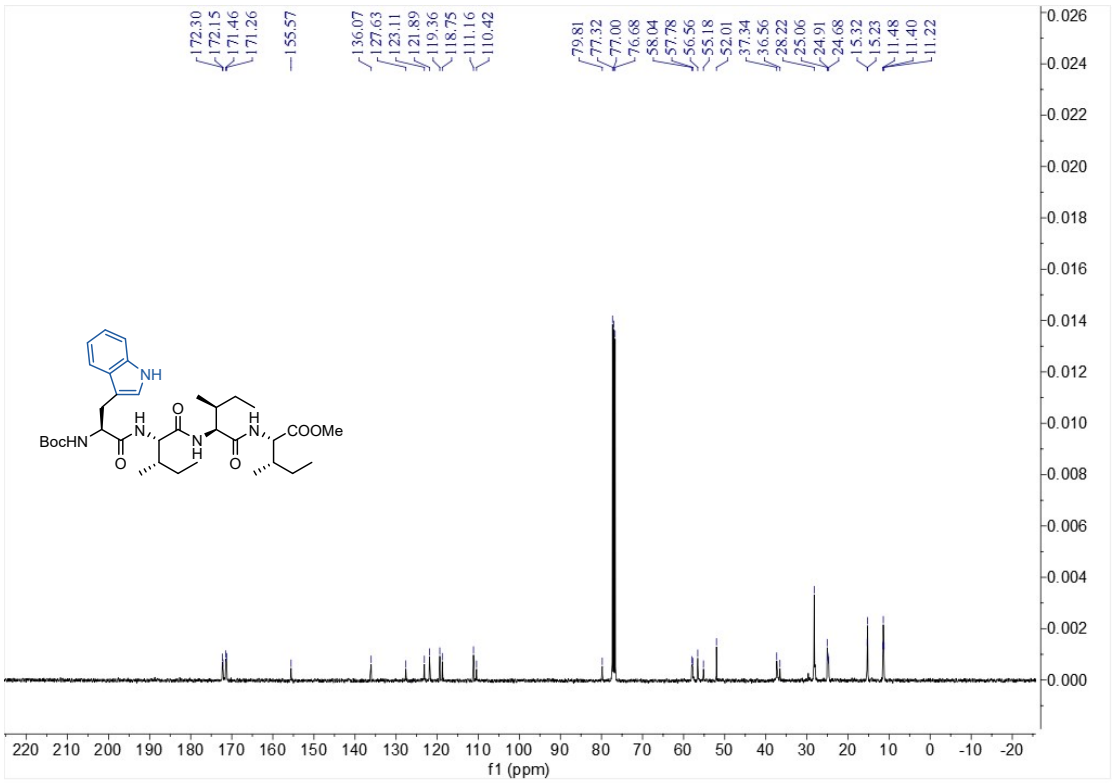


Fig 221. ^{13}C NMR of (**SM-5c**)

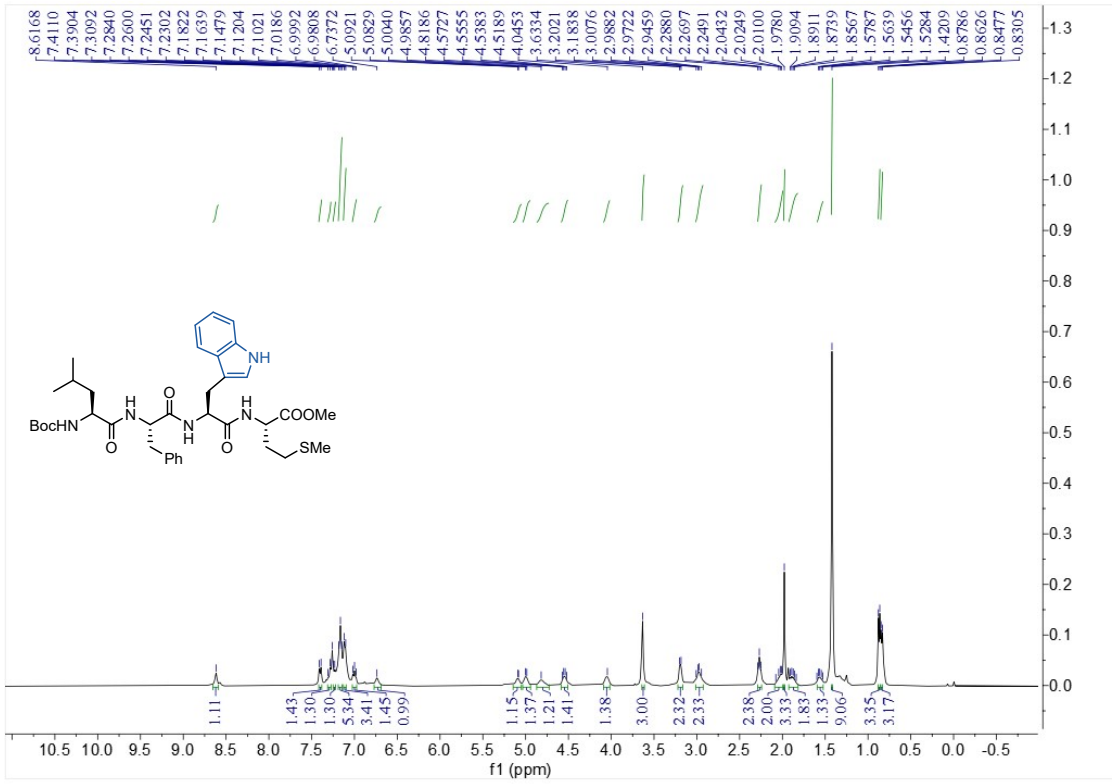


Fig 222. ^{1}H NMR of (**SM-5d**)

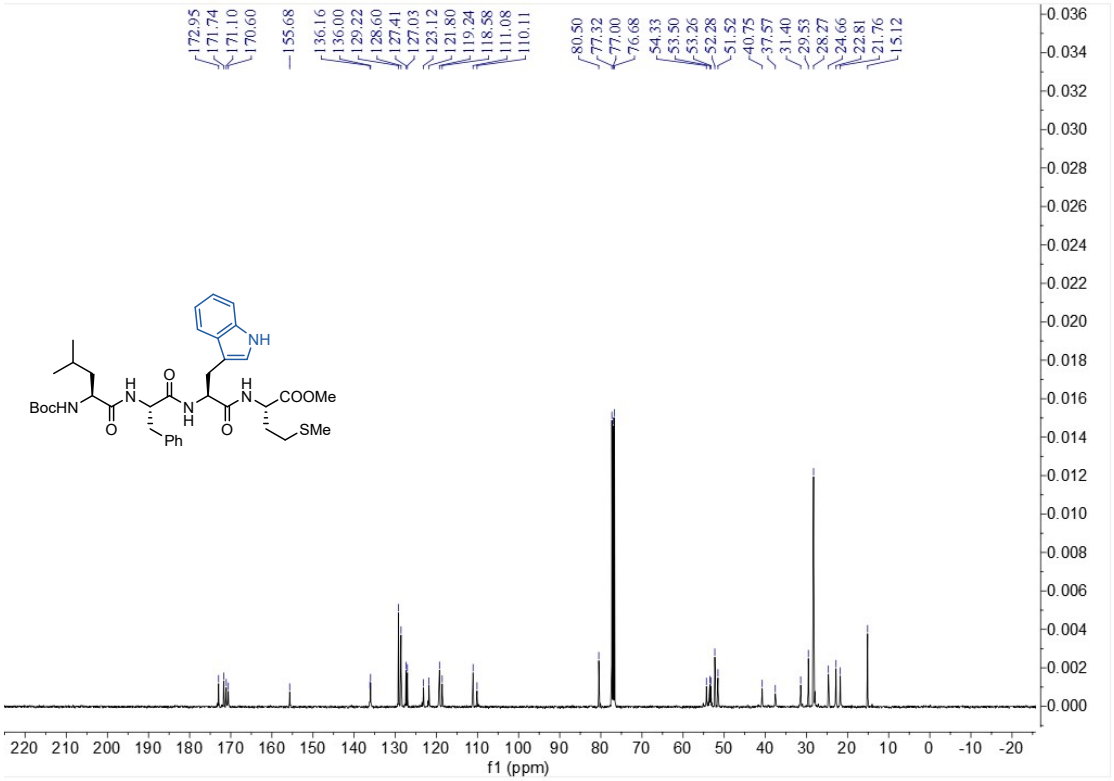


Fig 223. ^{13}C NMR of (**SM-5d**)

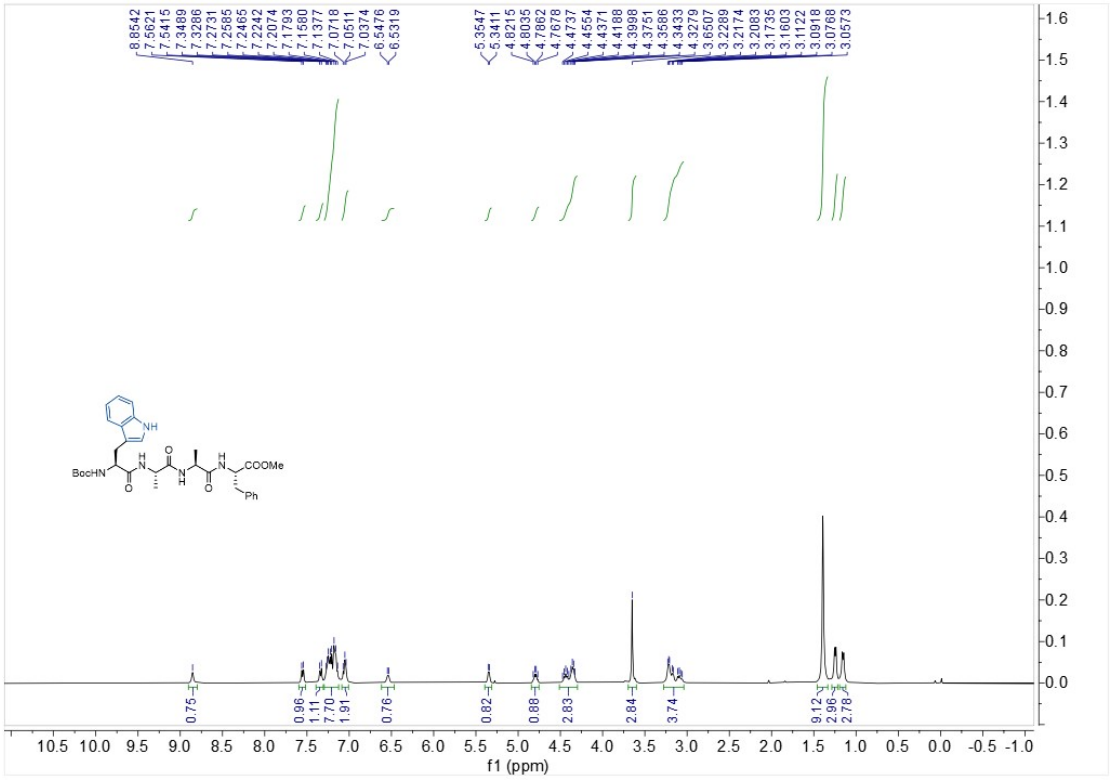


Fig 224. ^{1}H NMR of (**SM-5e**)

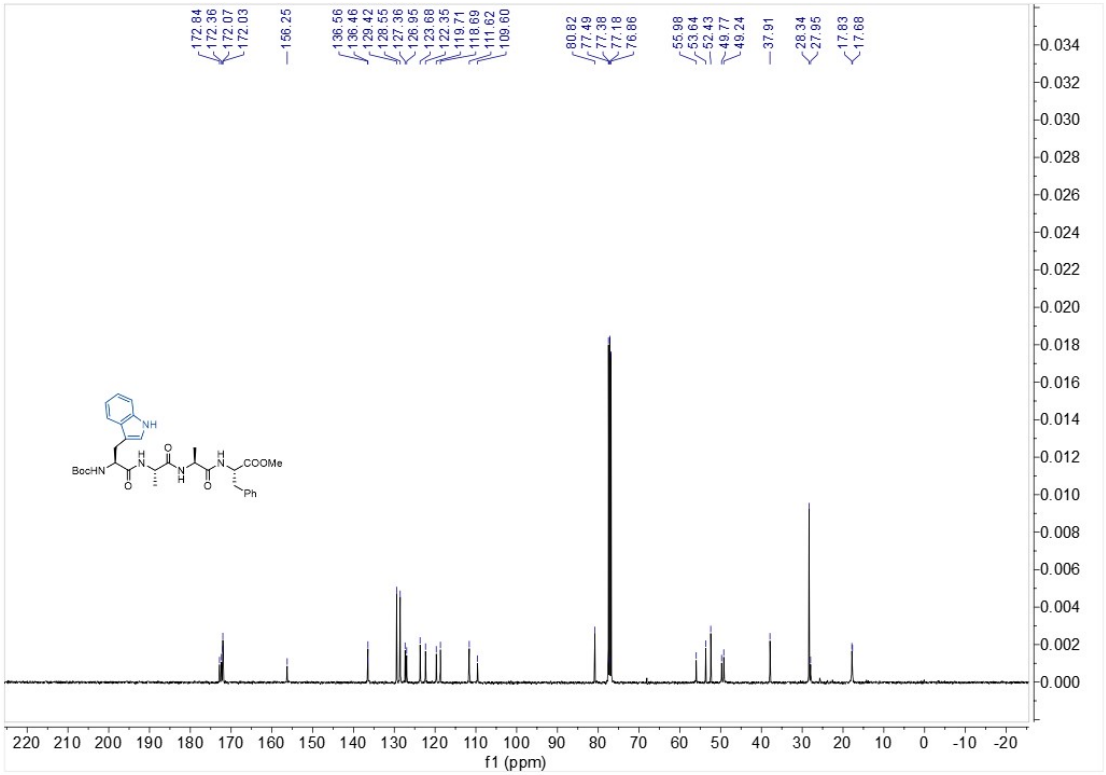


Fig 225. ^{13}C NMR of (**SM-5e**)

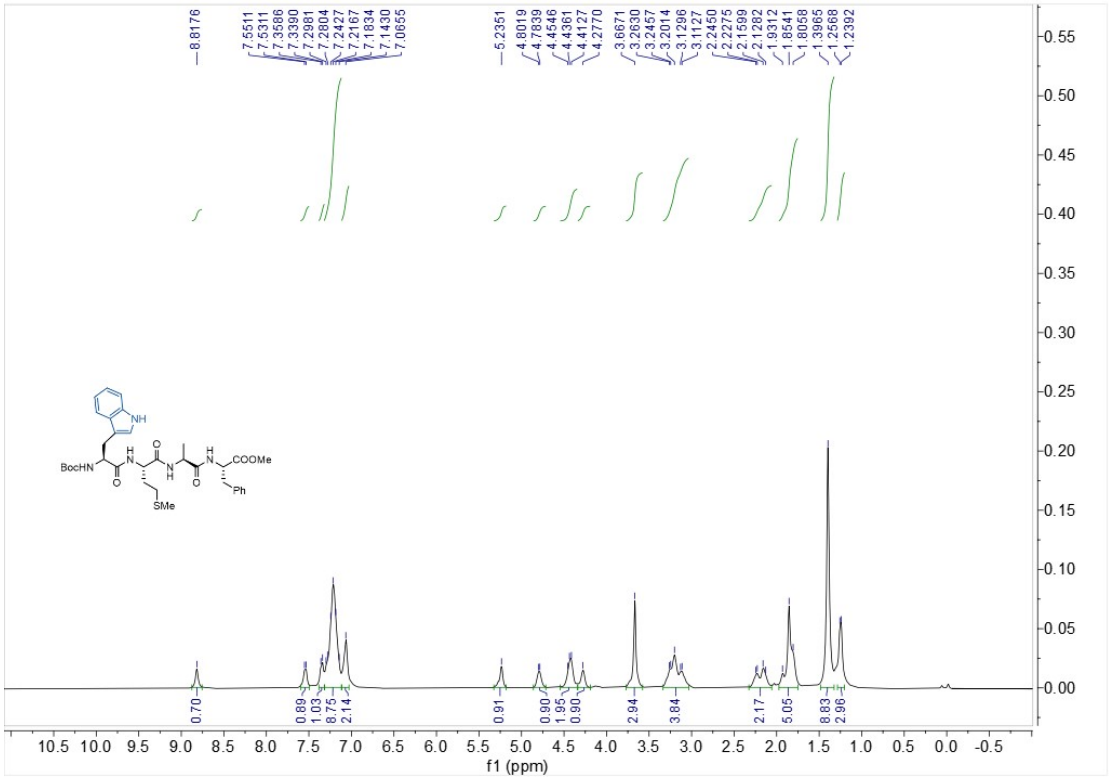


Fig 226. ^{1}H NMR of (**SM-5f**)

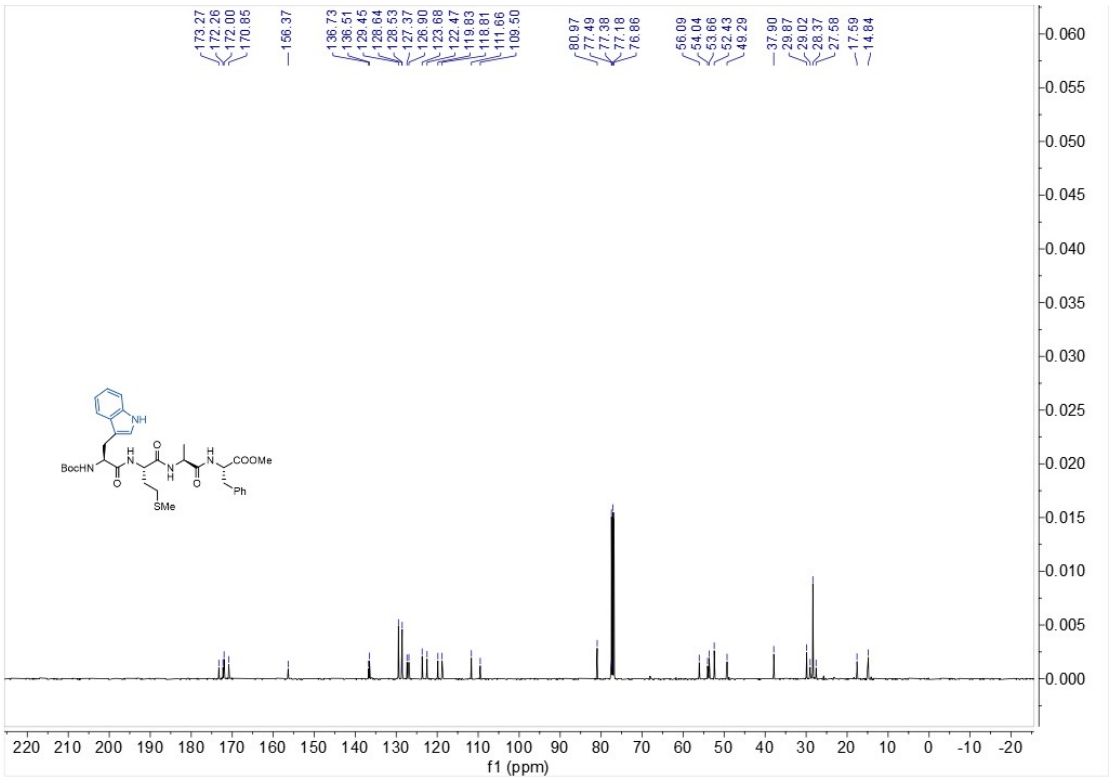


Fig 227. ^{13}C NMR of (**SM-5f**)

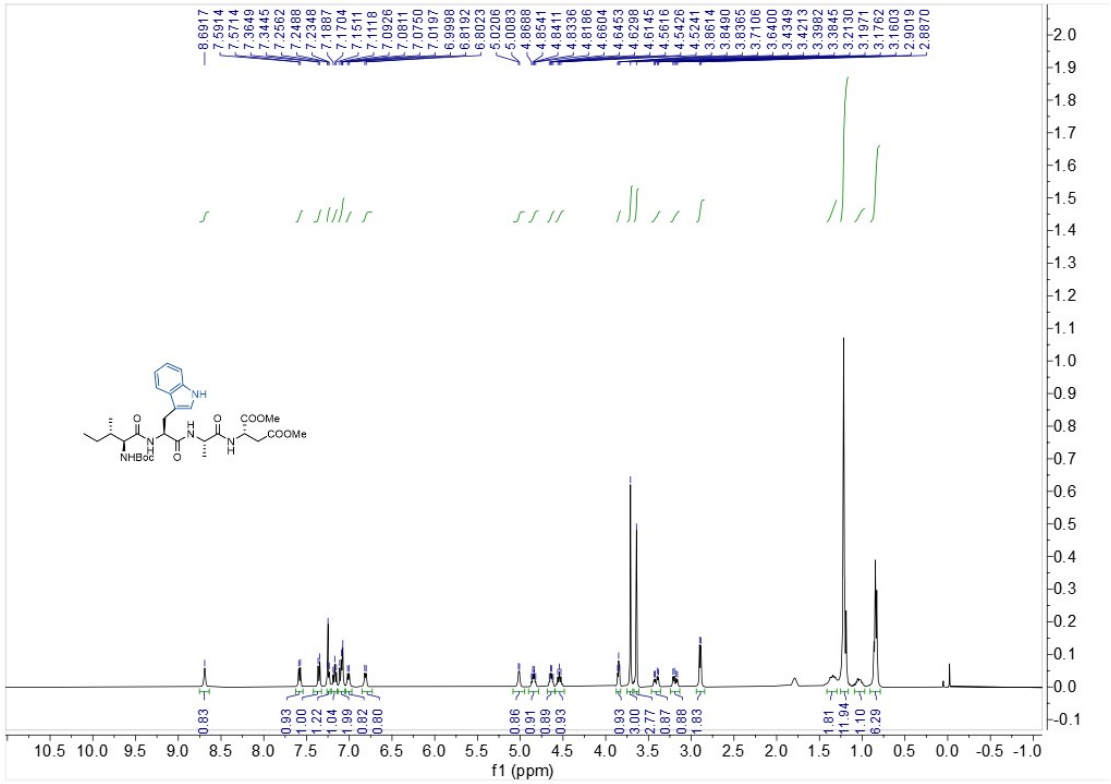


Fig 228. ^{1}H NMR of (**SM-5g**)

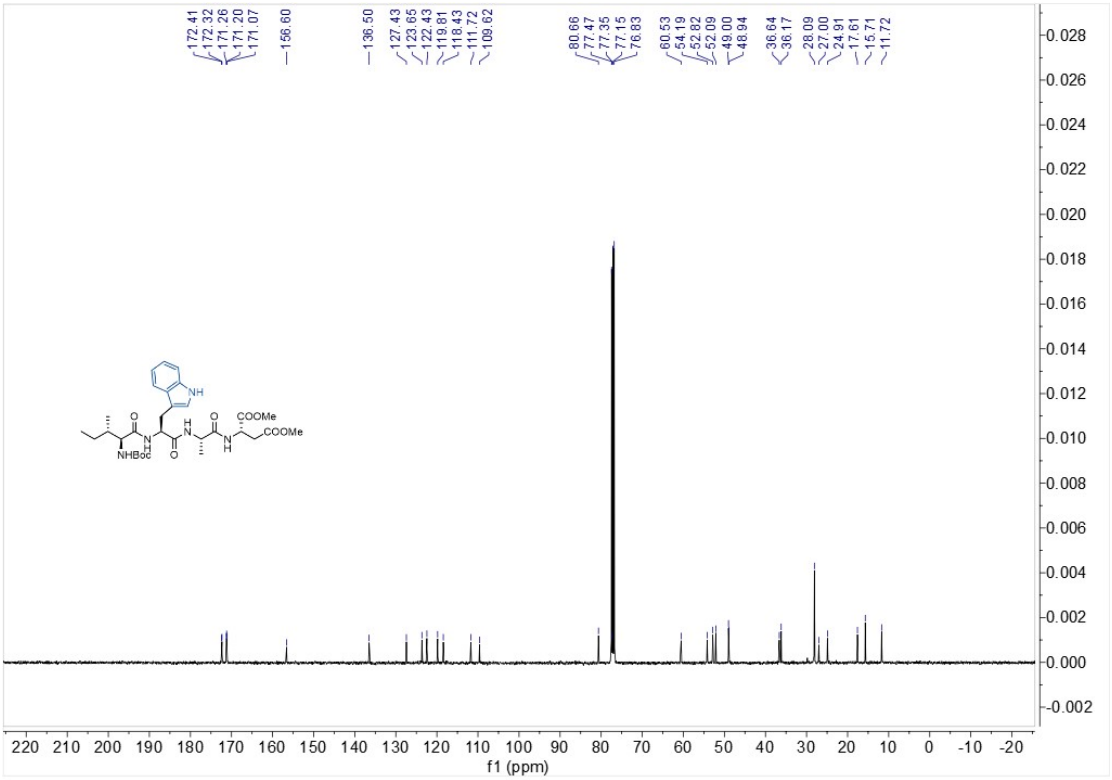


Fig 229. ^{13}C NMR of (**SM-5g**)

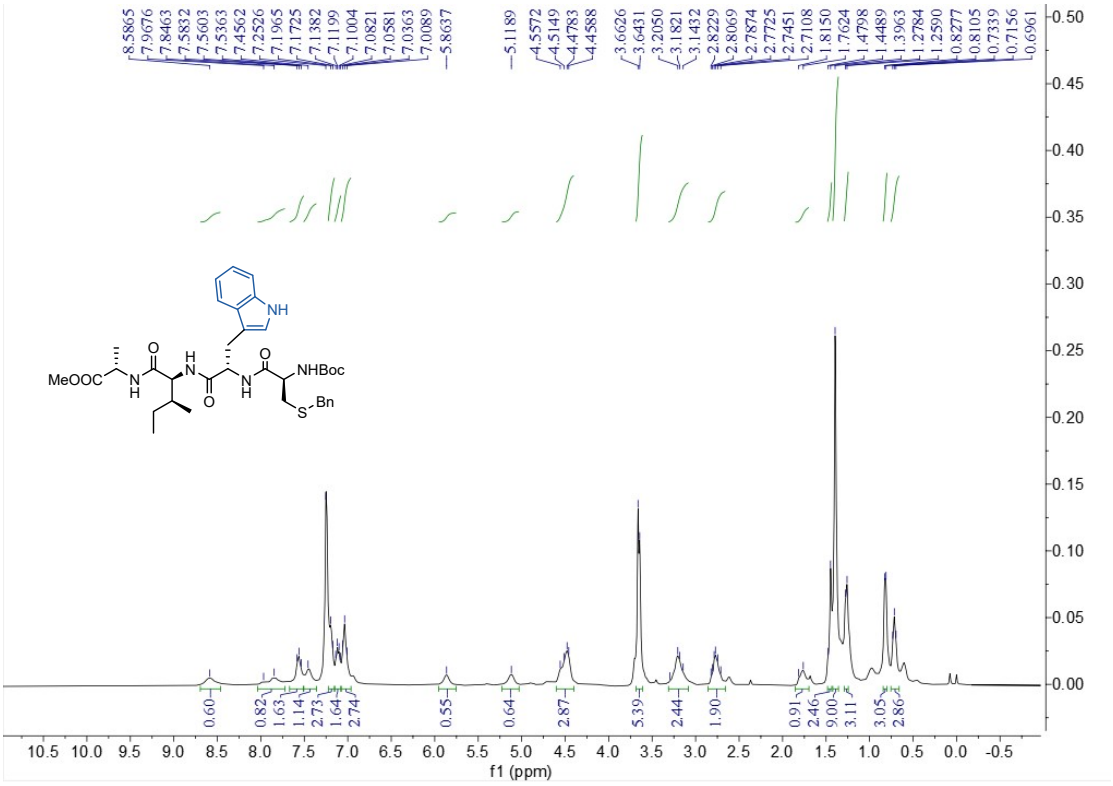


Fig 230. ^{1}H NMR of (**SM-5h**)

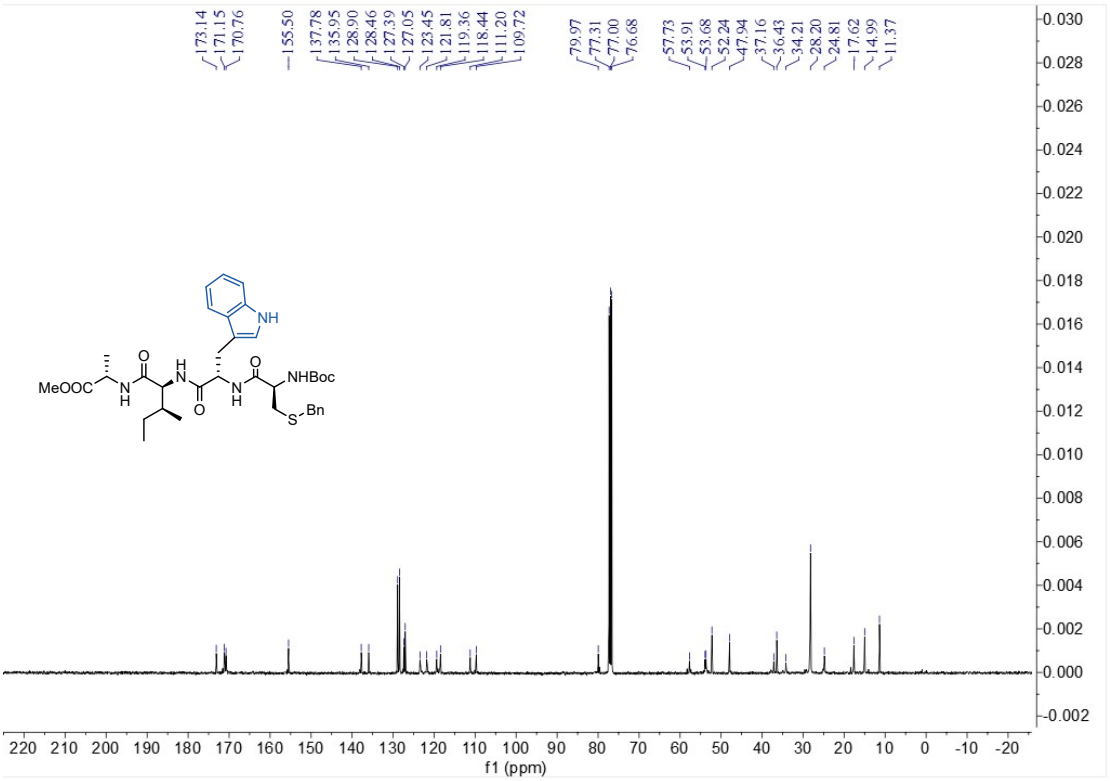


Fig 231. ^{13}C NMR of (**SM-5h**)

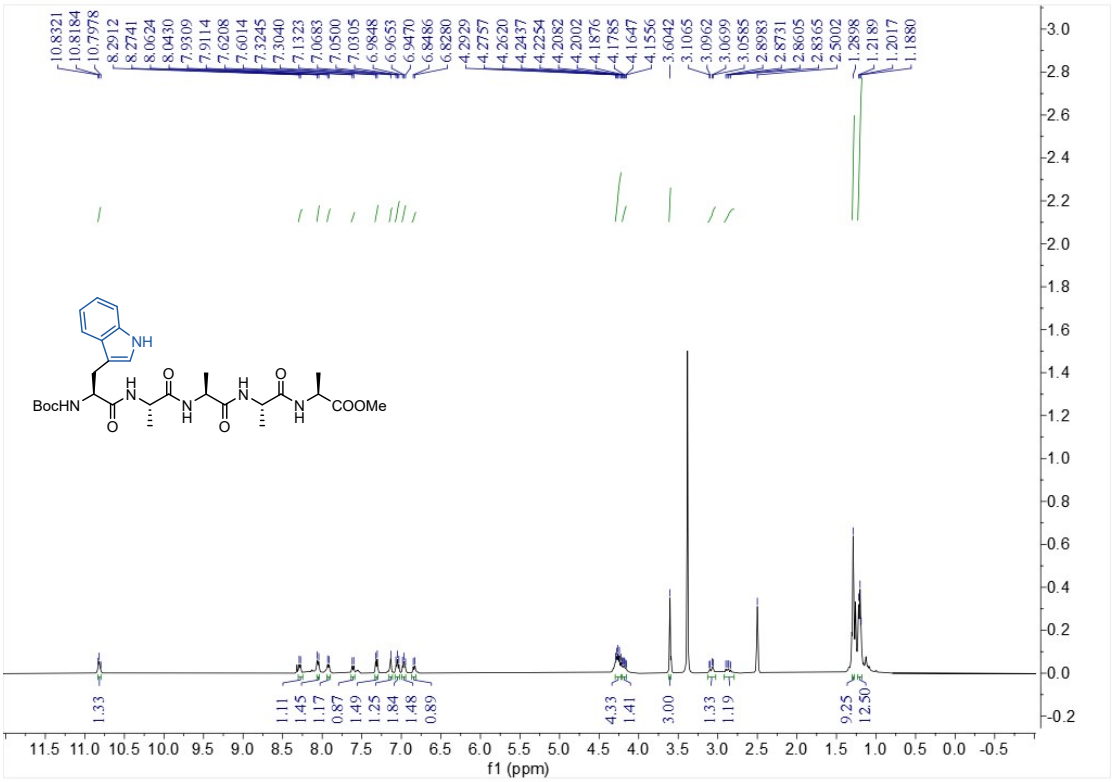


Fig 232. ^{1}H NMR of (**SM-6a**)

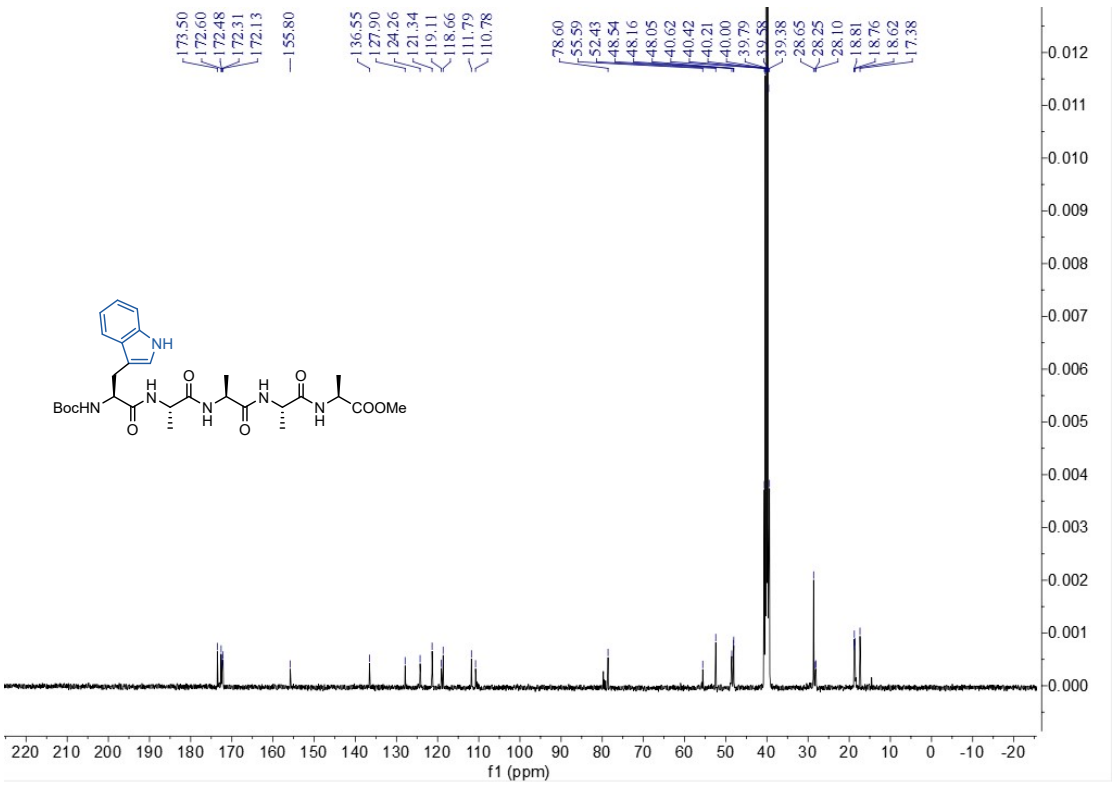


Fig 233. ^{13}C NMR of (**SM-6a**)

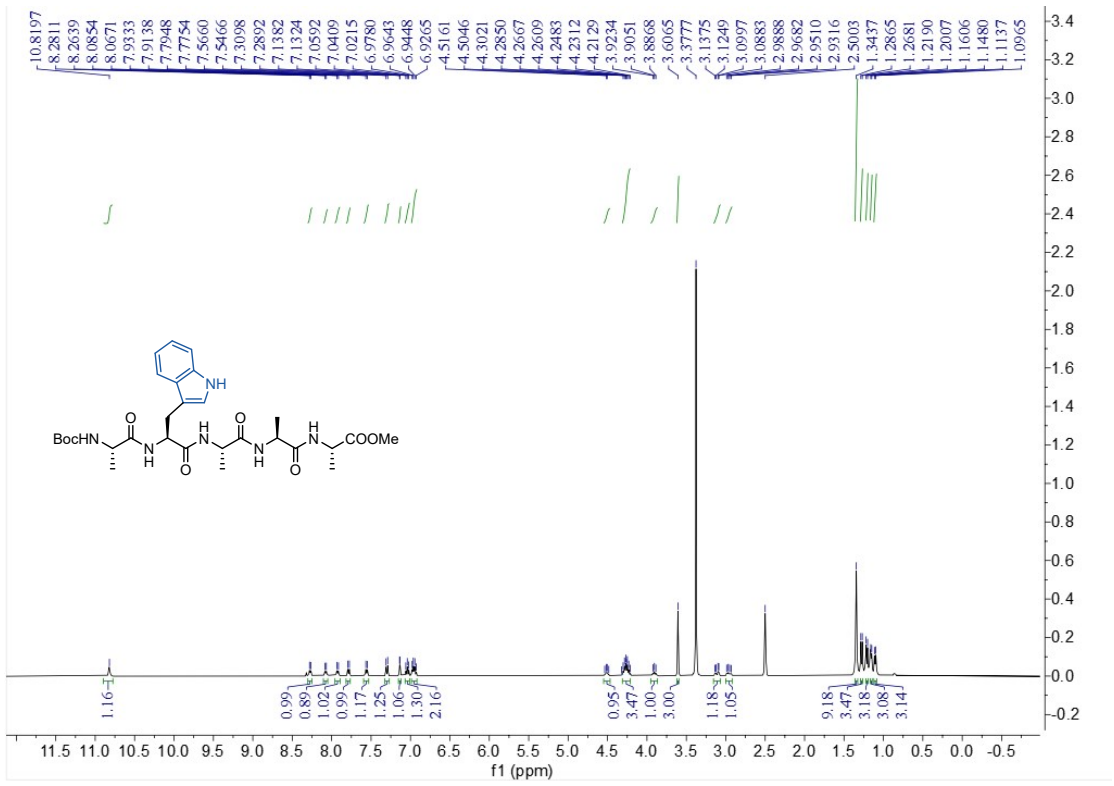


Fig 234. ^{1}H NMR of (**SM-6b**)

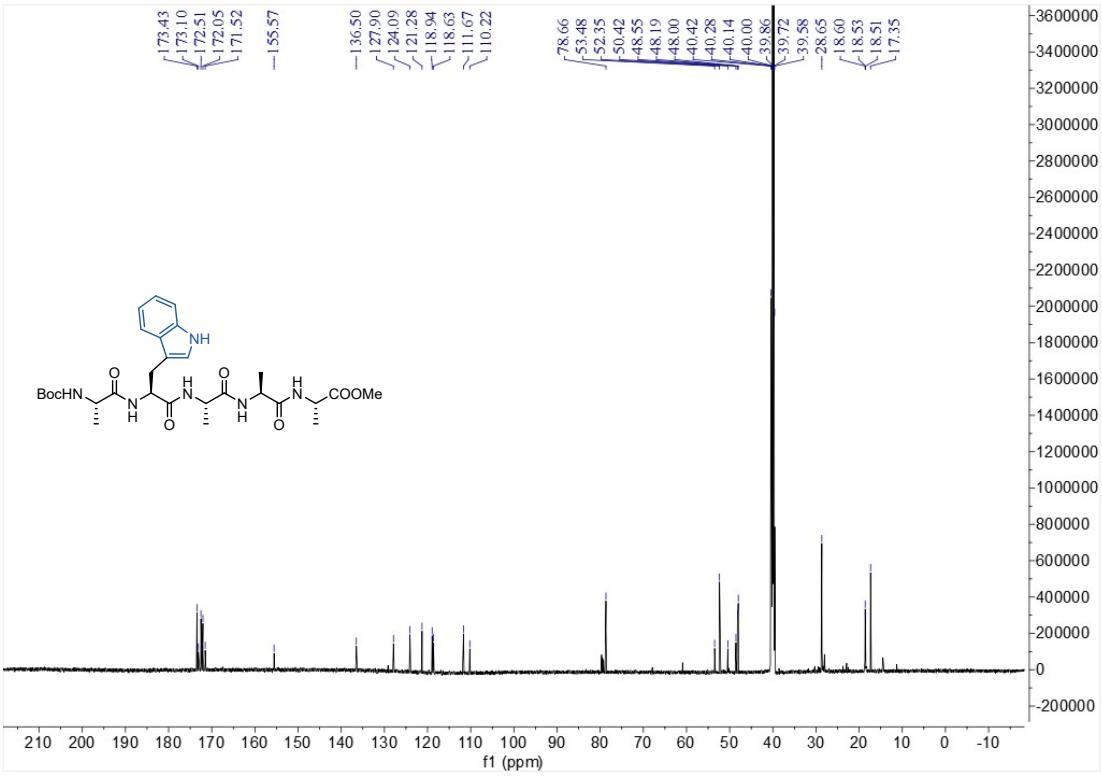


Fig 235. ^{13}C NMR of (**SM-6b**)

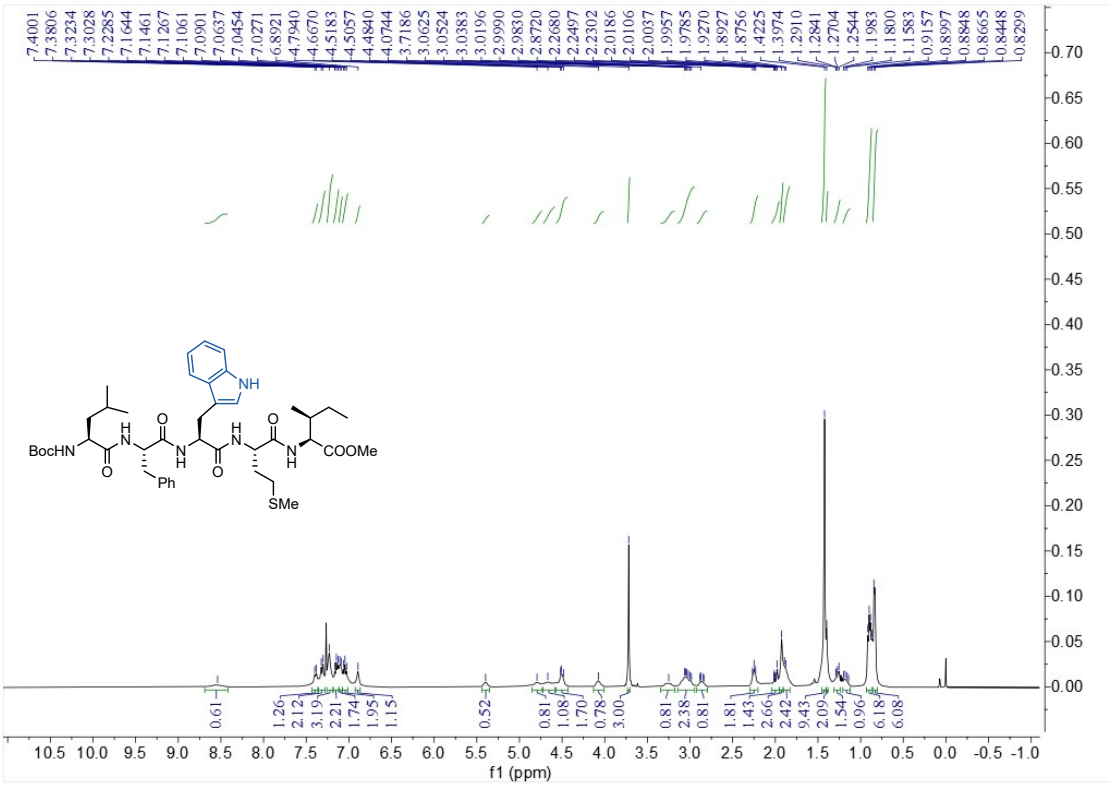


Fig 236. ^{1}H NMR of (**SM-6c**)

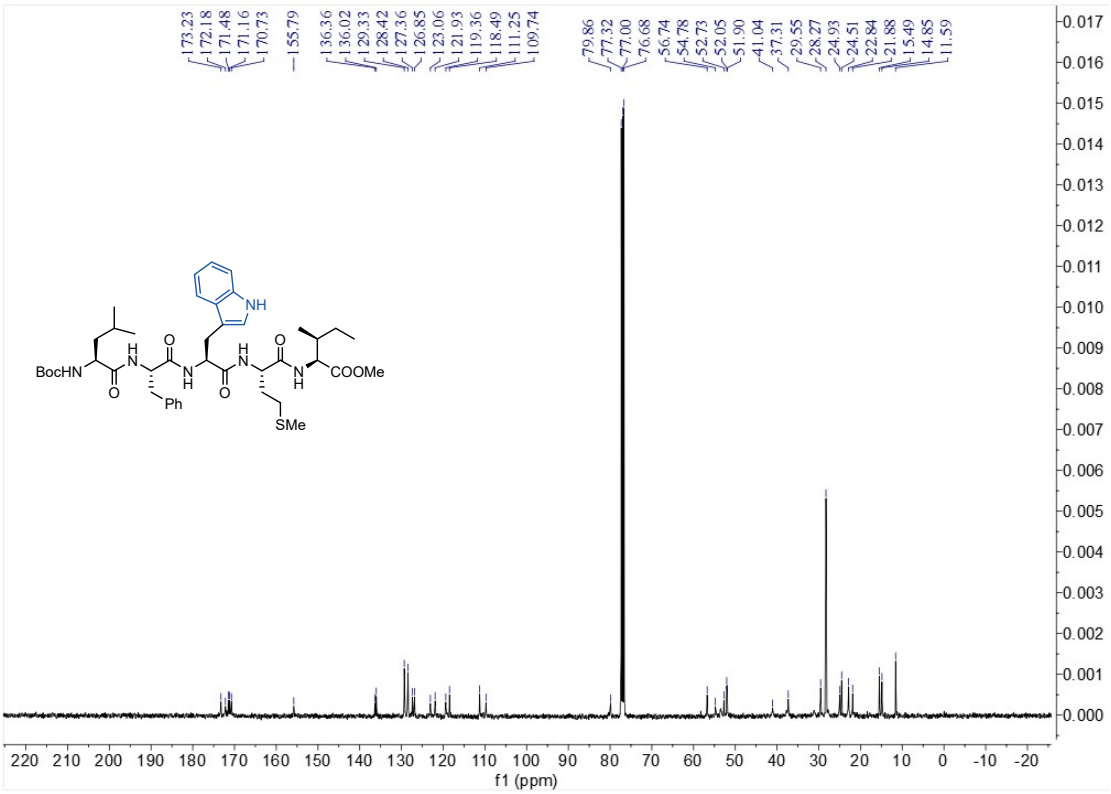


Fig 237. ^{13}C NMR of (**SM-6c**)

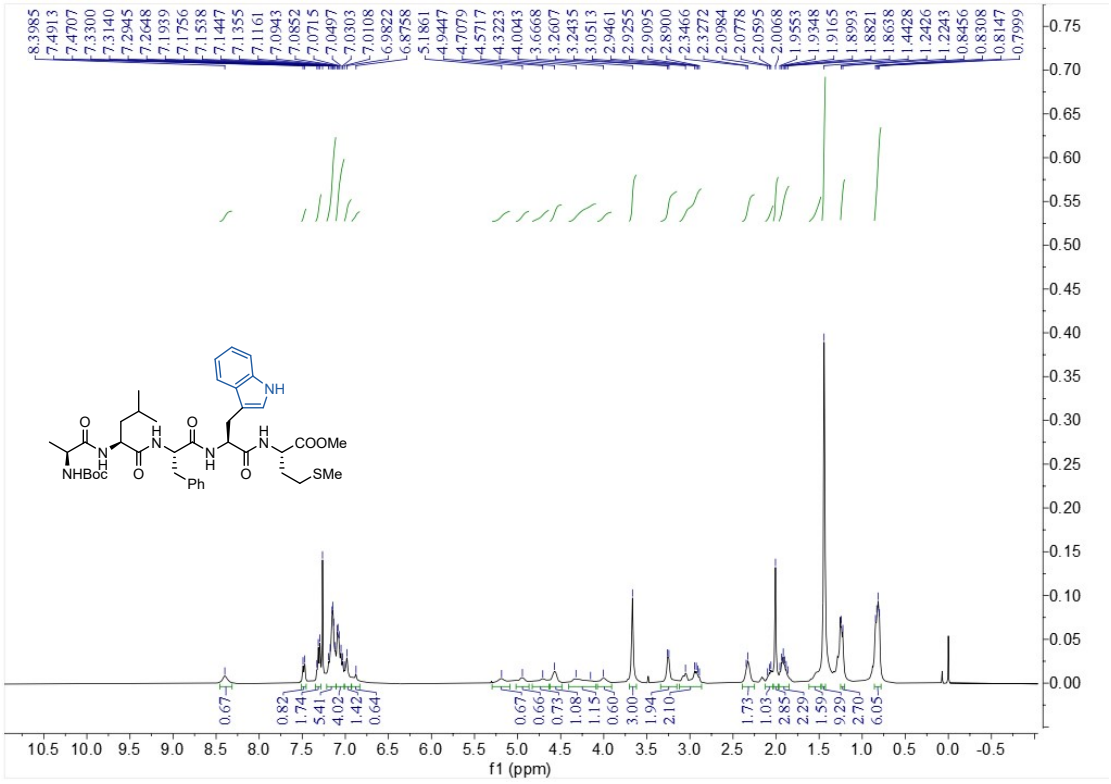


Fig 238. ^{1}H NMR of (**SM-6d**)

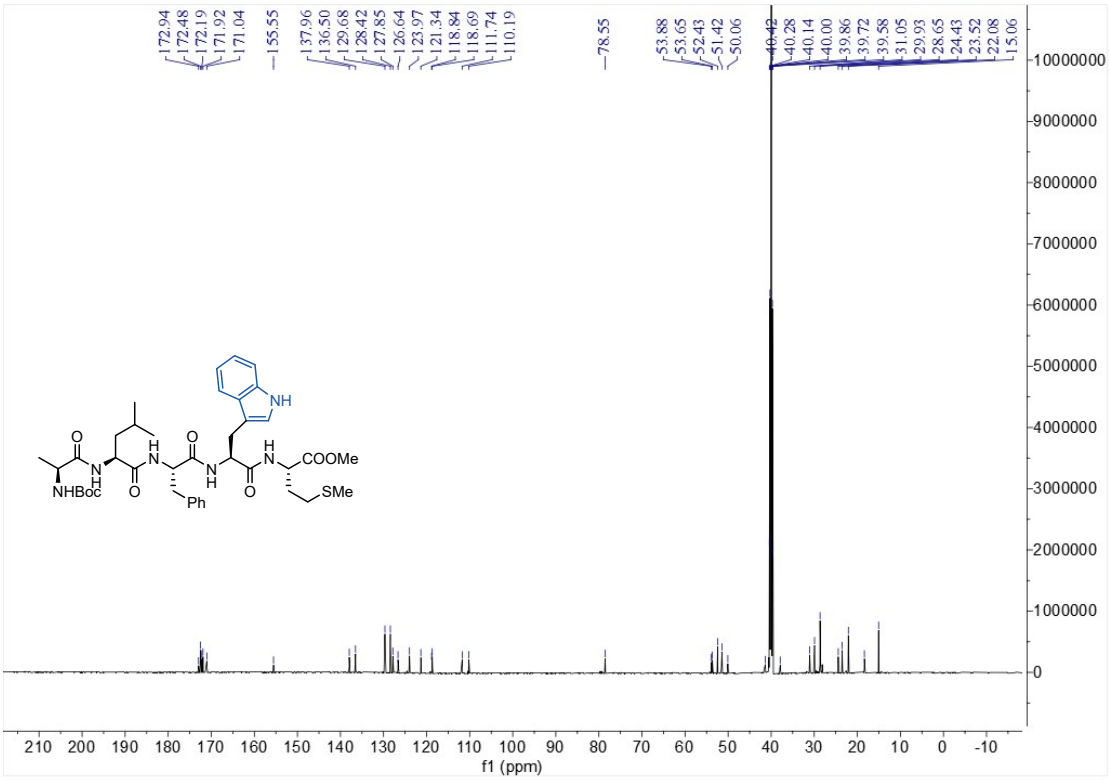


Fig 239. ^{13}C NMR of (**SM-6d**)

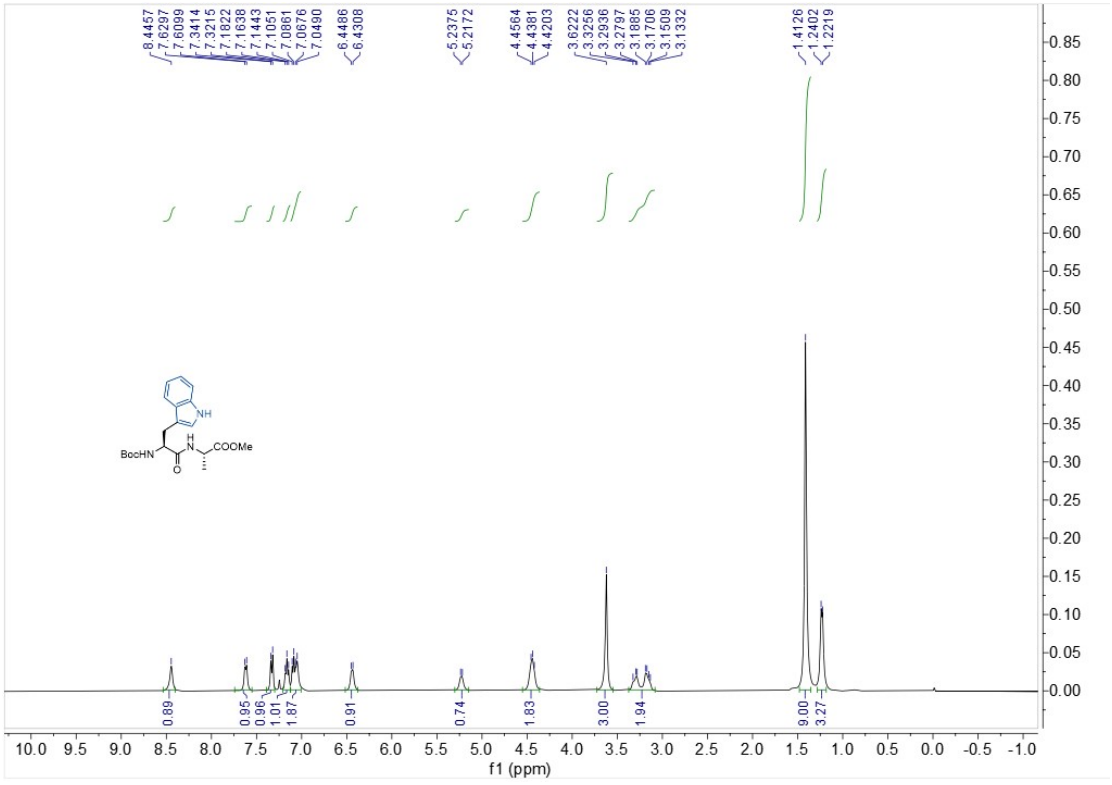


Fig 240. ^{1}H NMR of (**SM-7a**)

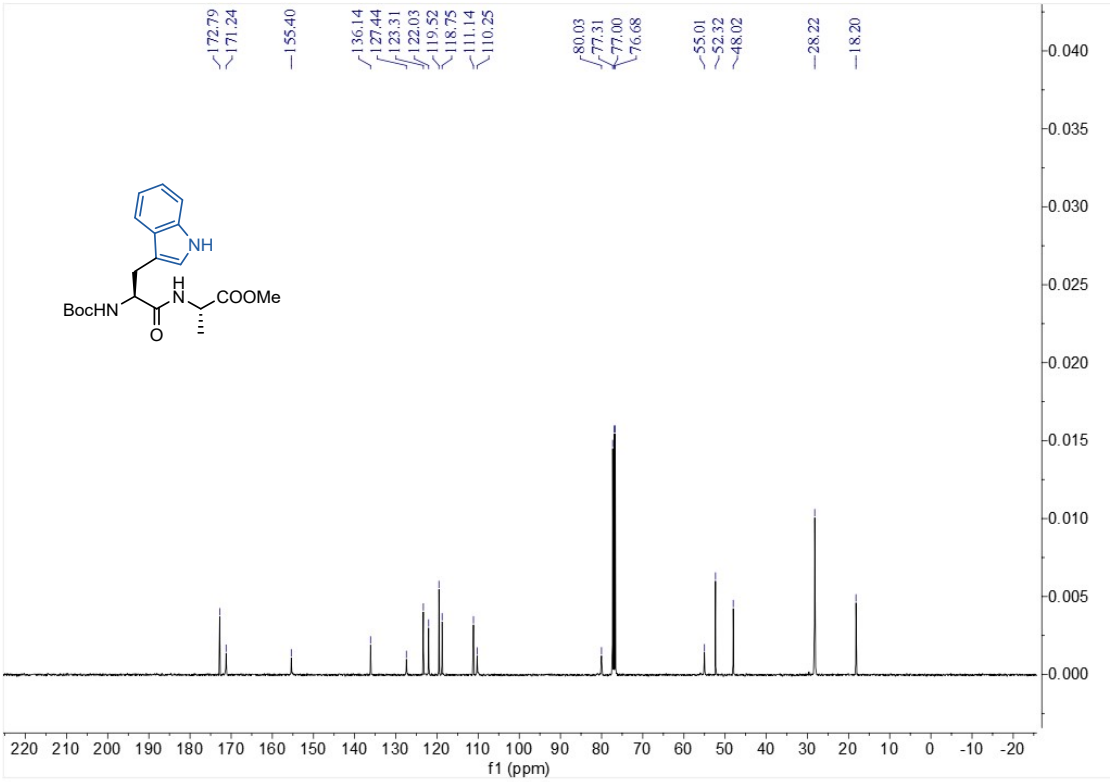


Fig 241. ^{13}C NMR of (**SM-7a**)

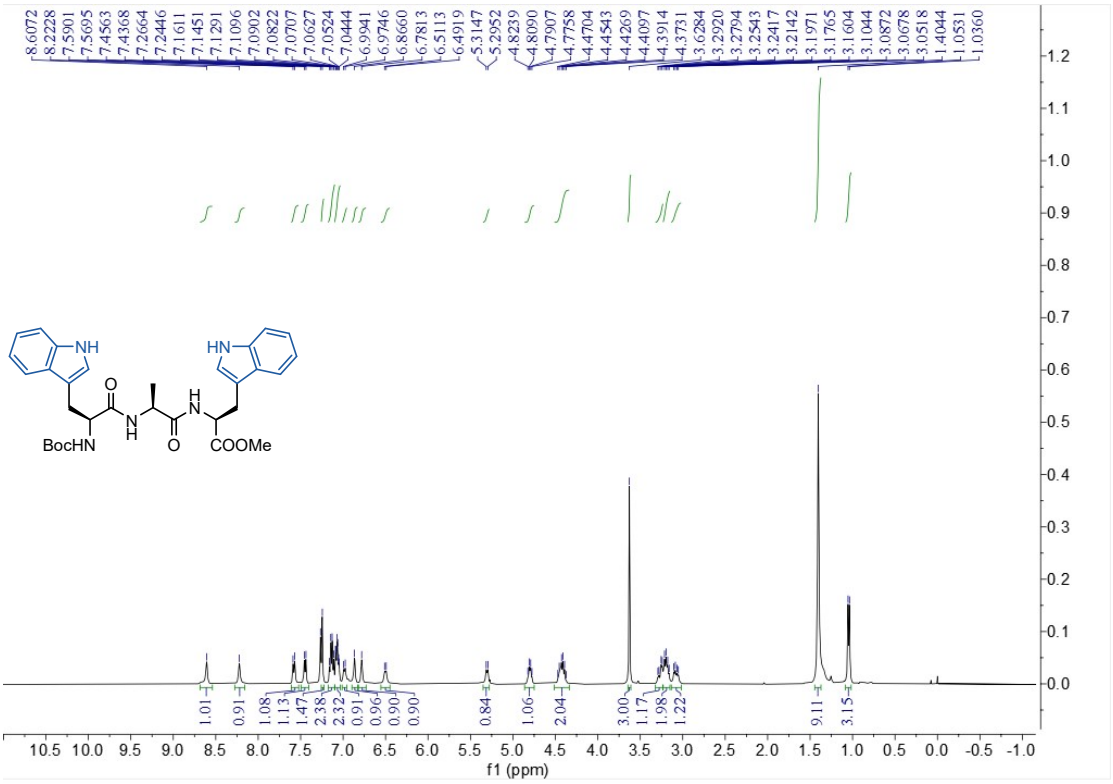


Fig 242. ^{1}H NMR of (**SM-8**)

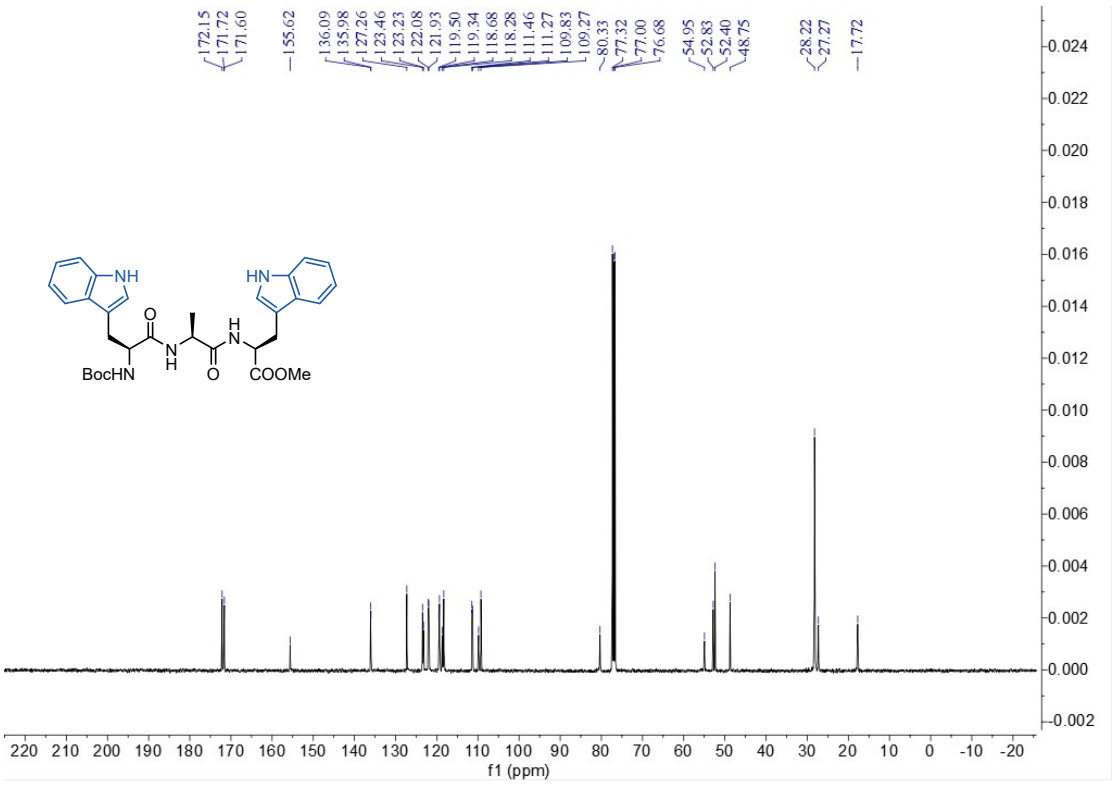


Fig 243. ^{13}C NMR of (**SM-8**)

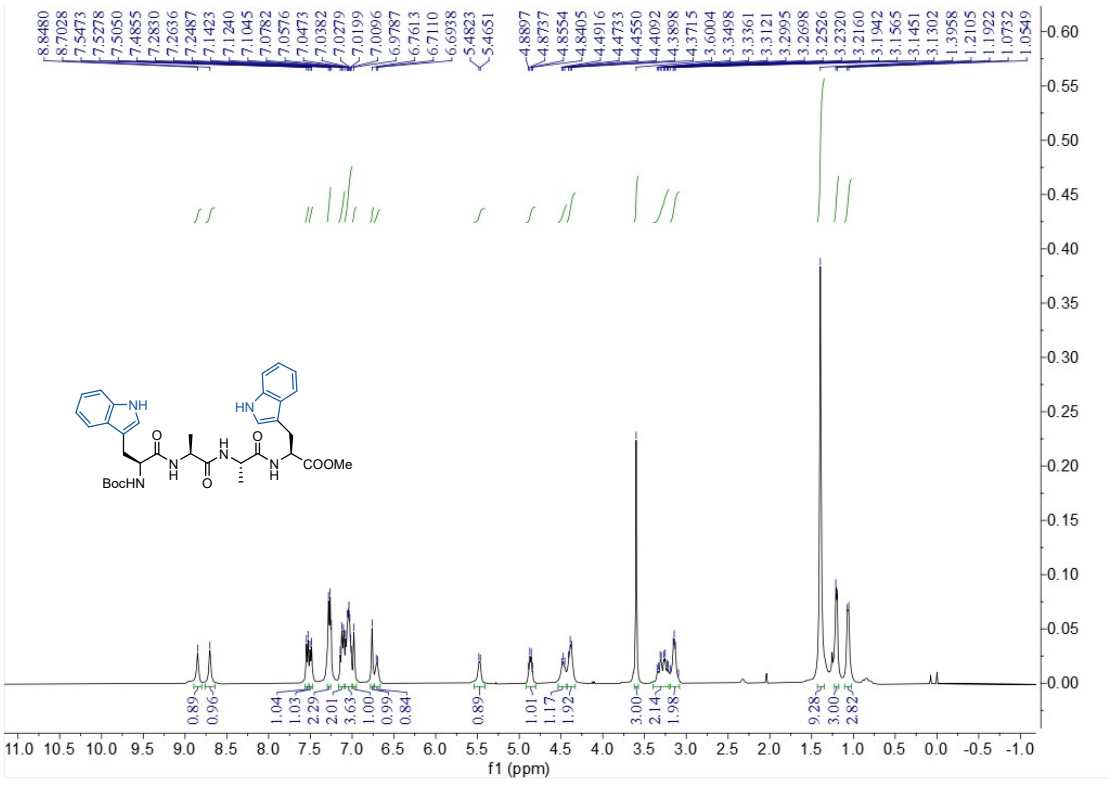


Fig 244. ^{1}H NMR of (**SM-10**)

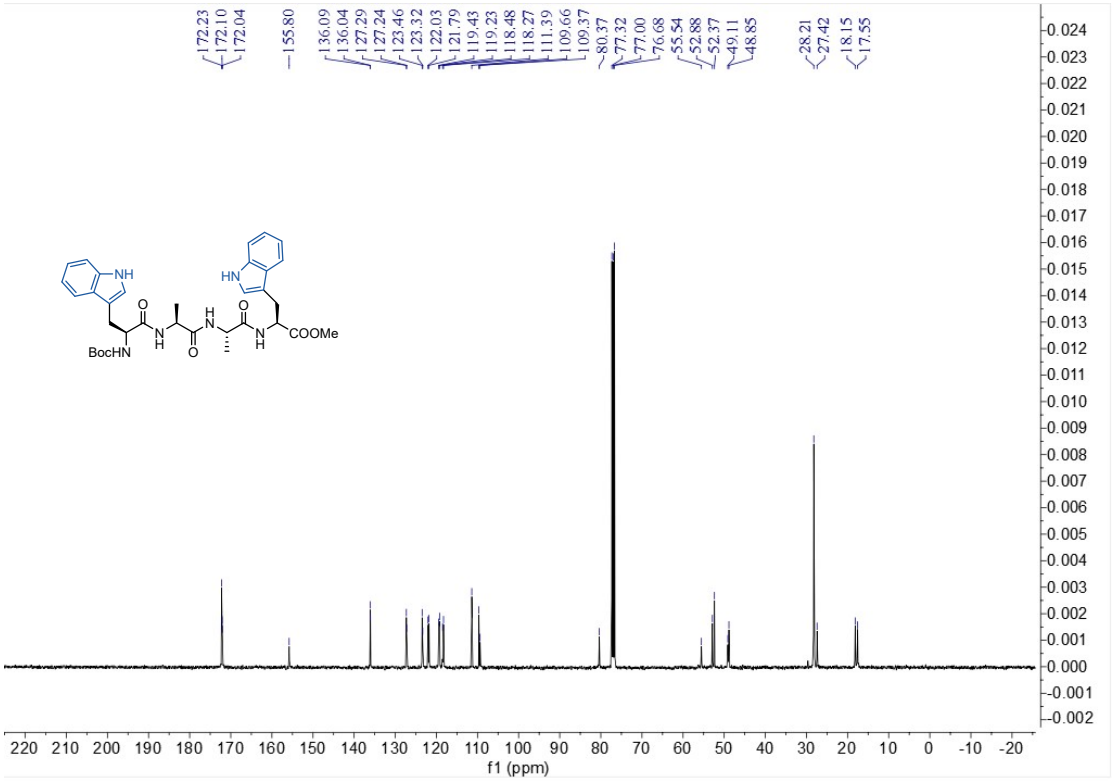


Fig 245. ^{13}C NMR of (**SM-10**)

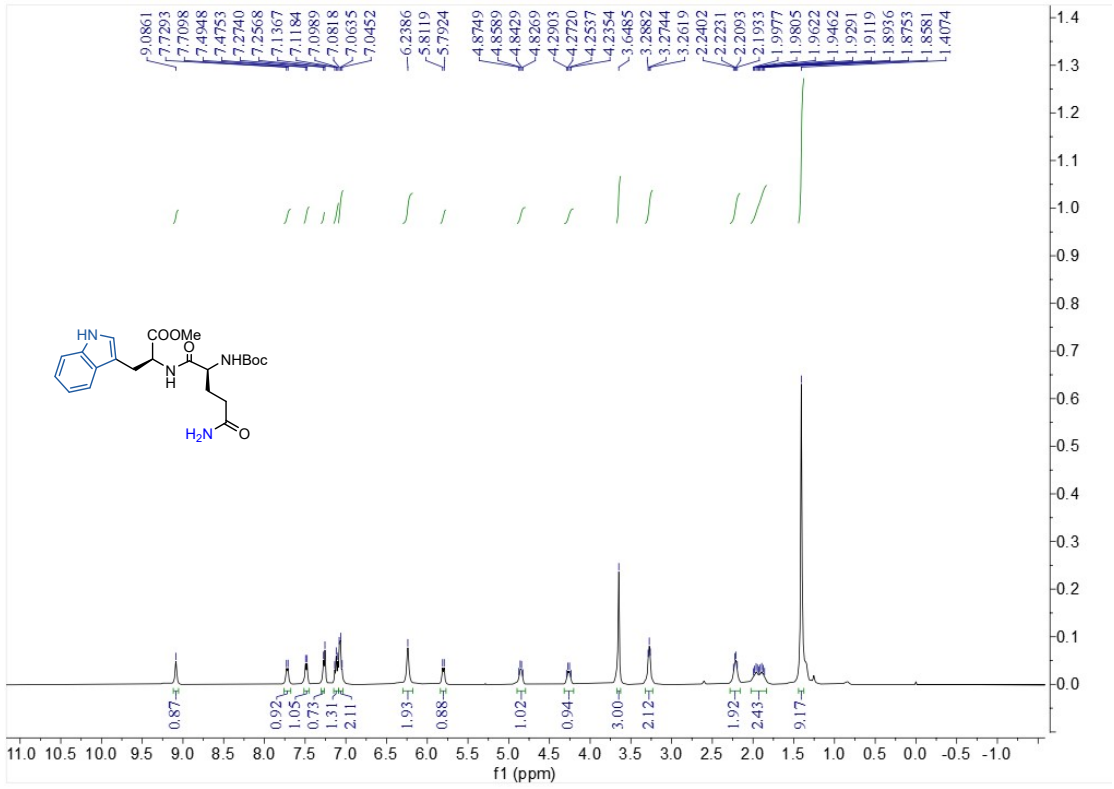


Fig 246. ^{1}H NMR of (**SM-12**)

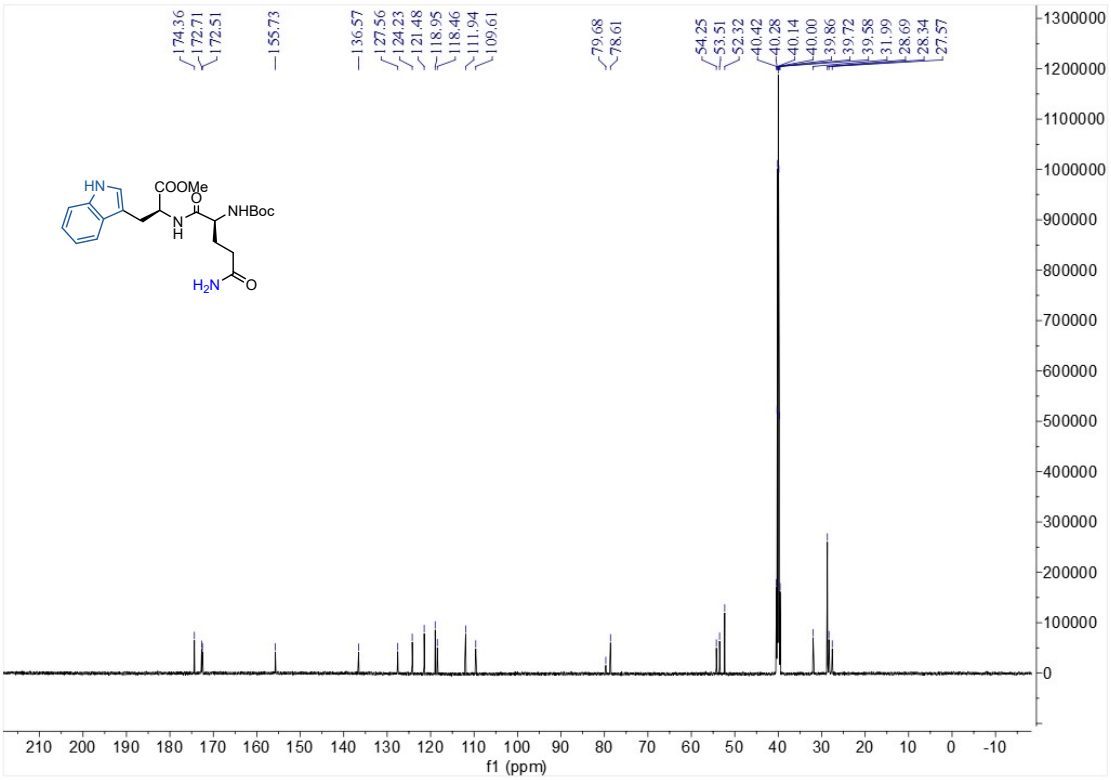


Fig 247. ^{13}C NMR of (**SM-12**)

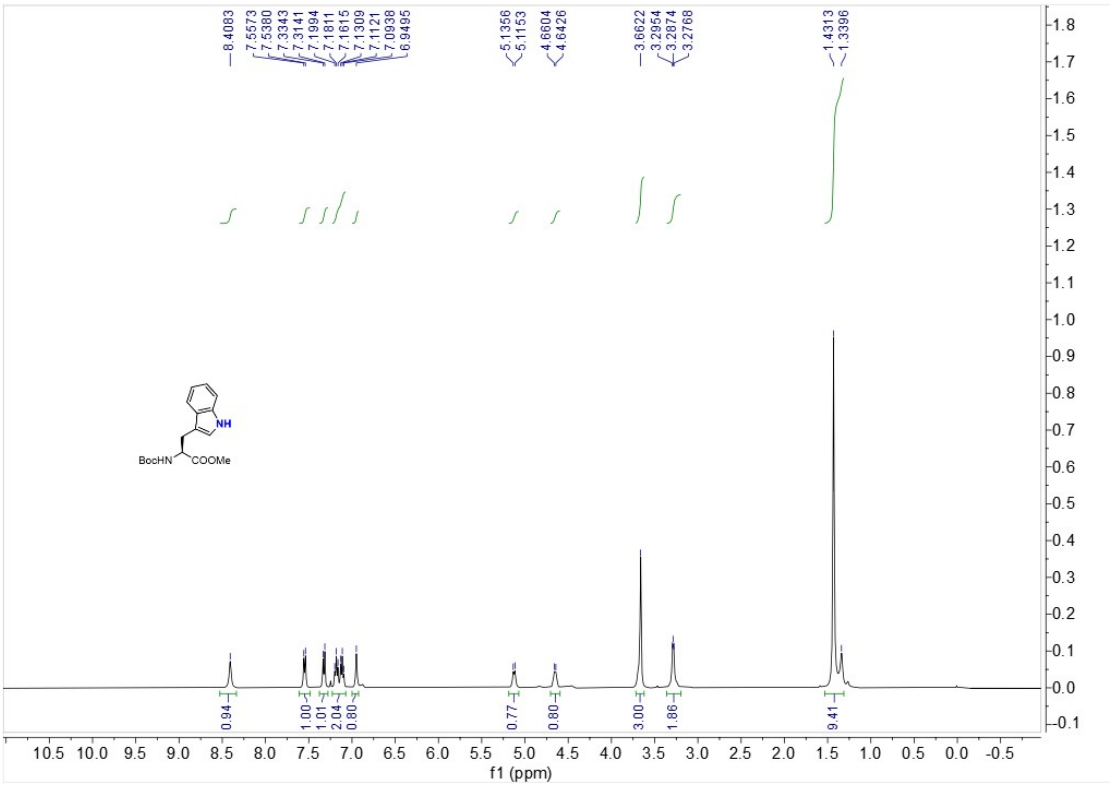


Fig 248. ^{1}H NMR of (**SM-16**)

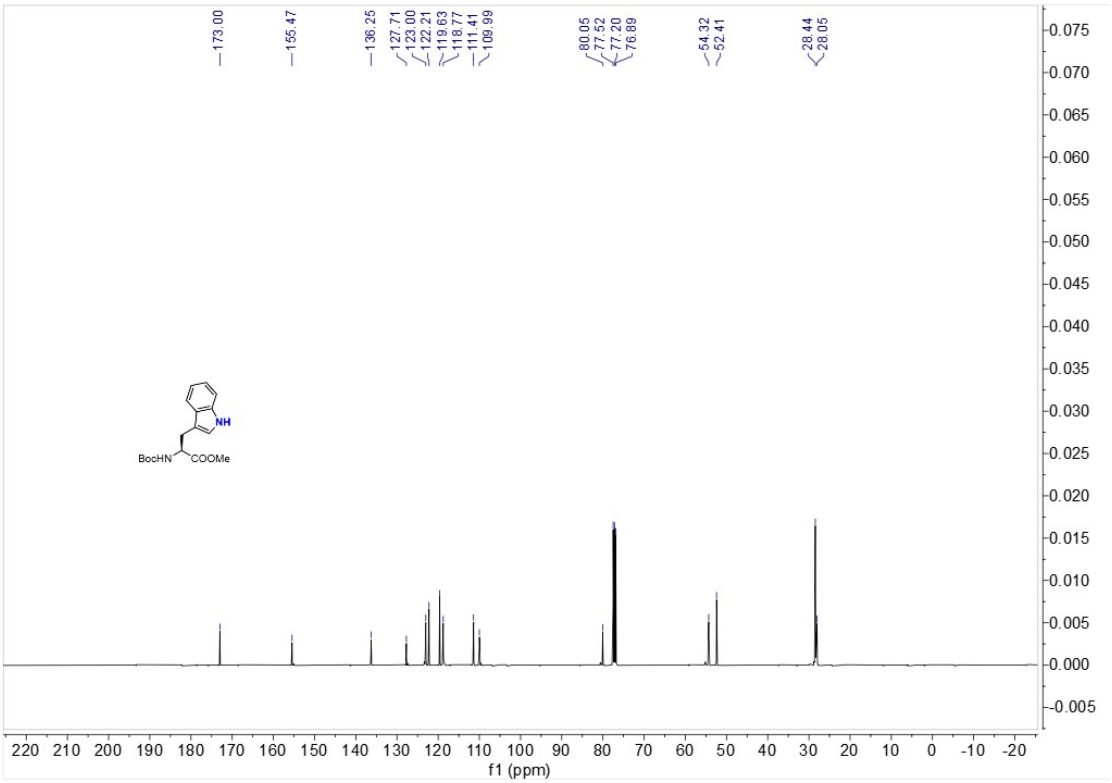


Fig 249. ^{13}C NMR of (**SM-16**)

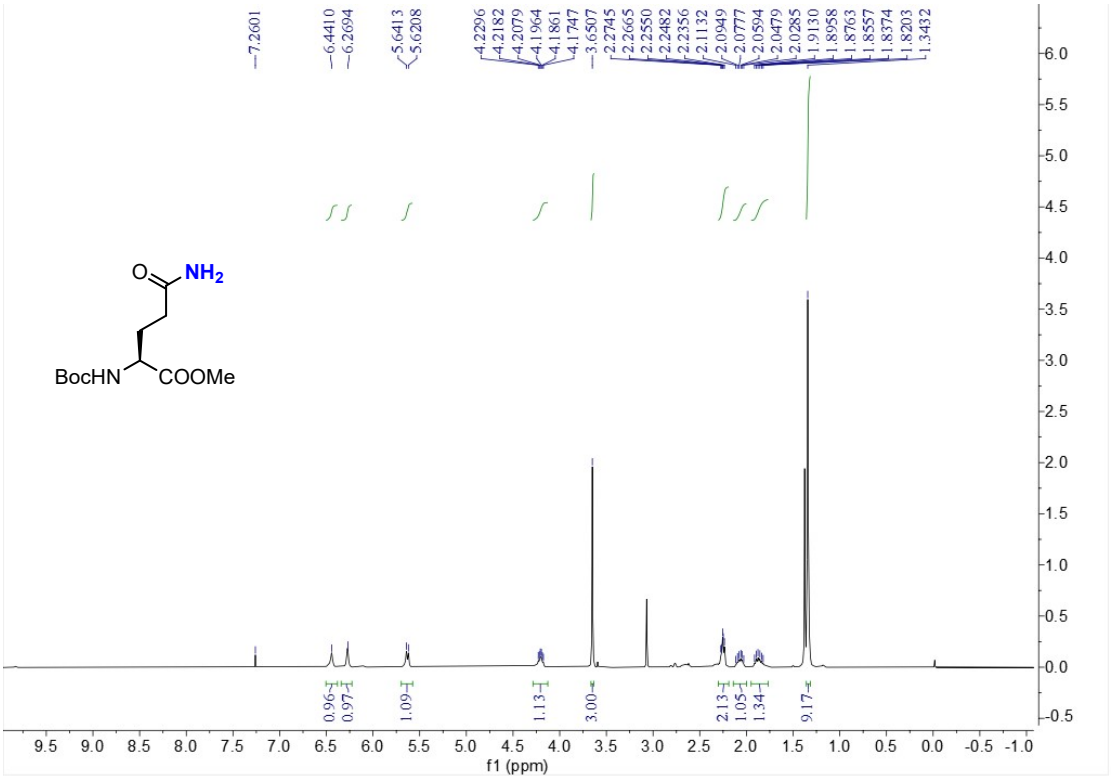


Fig 250. ^{1}H NMR of (**SM-17**)

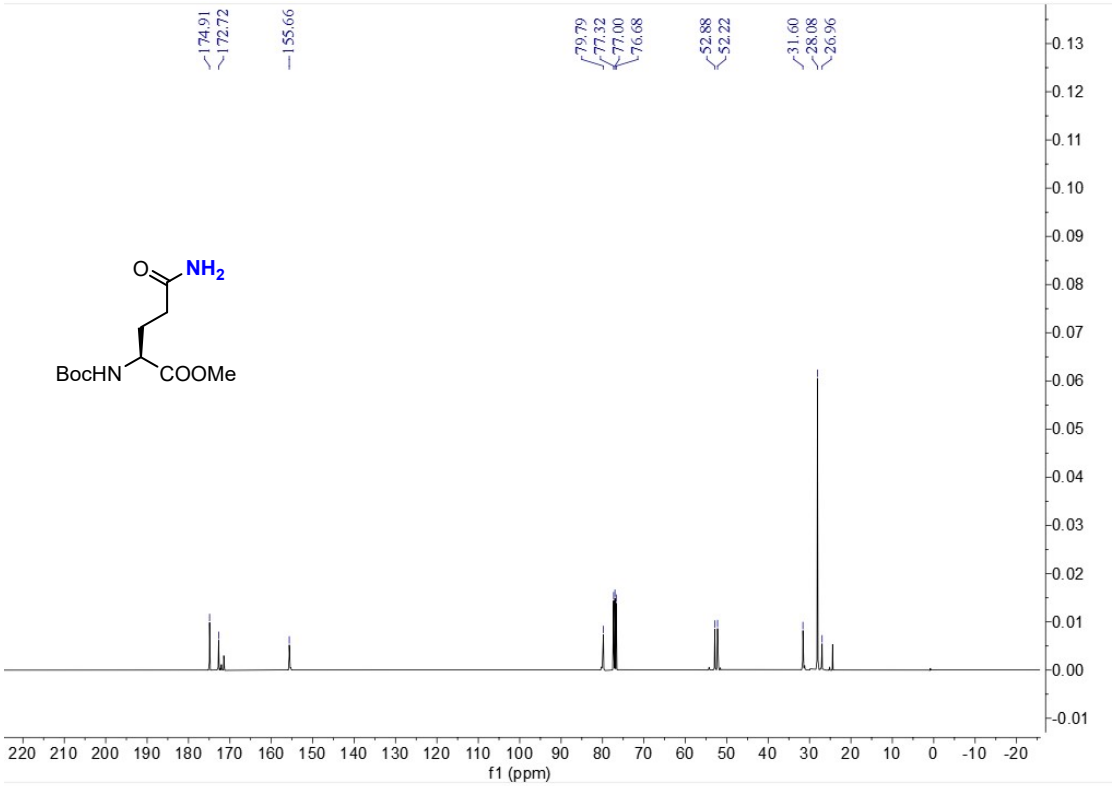


Fig 251. ^{13}C NMR of (**SM-17**)

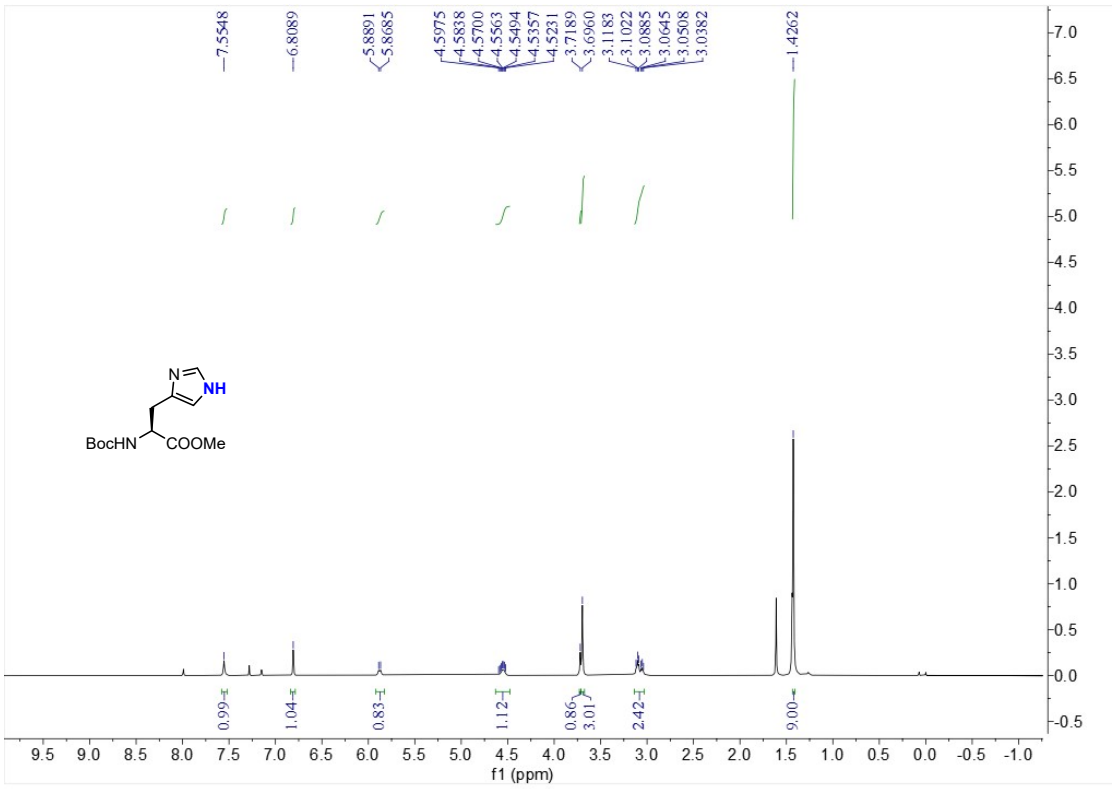


Fig 252. ^{1}H NMR of (**SM-18**)

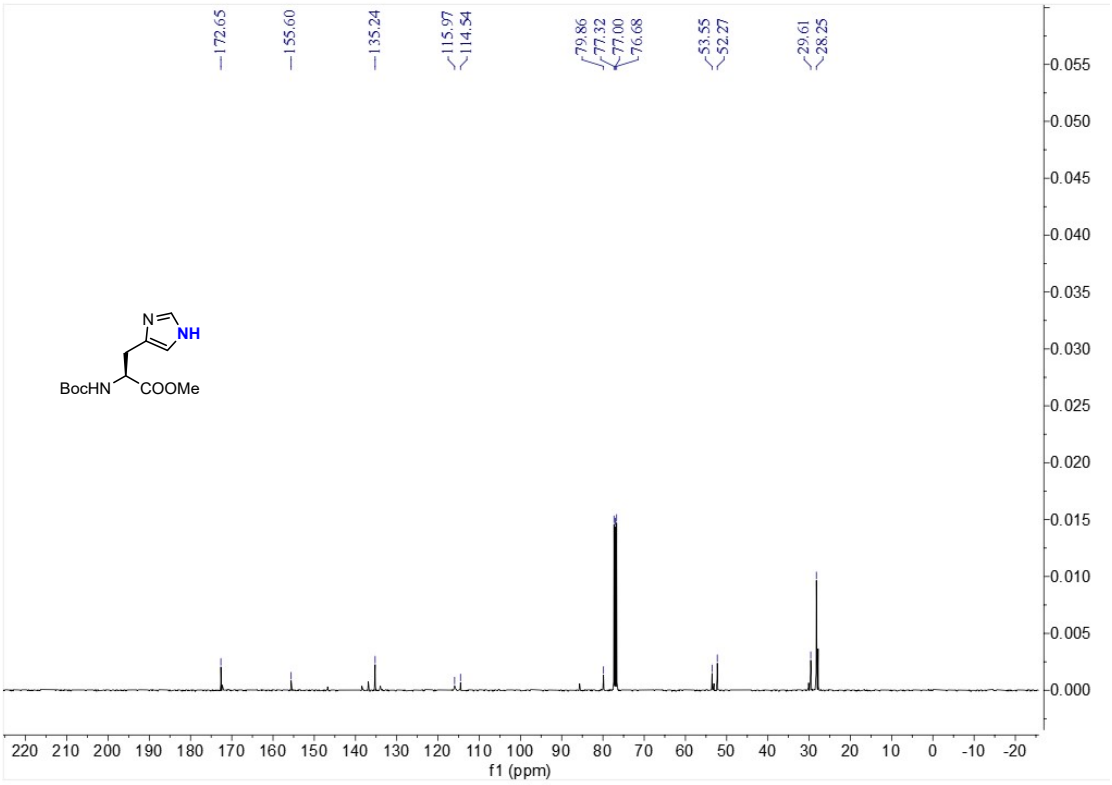


Fig 253. ^{13}C NMR of (**SM-18**)

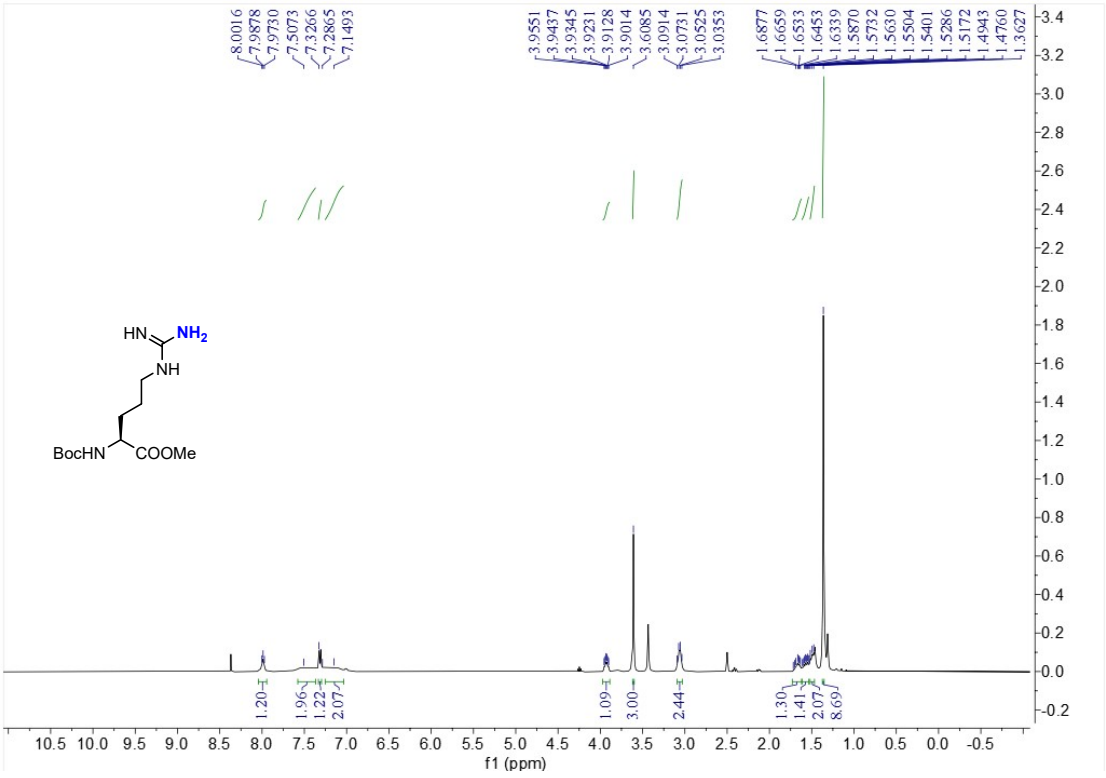


Fig 254. ^{1}H NMR of (**SM-19**)

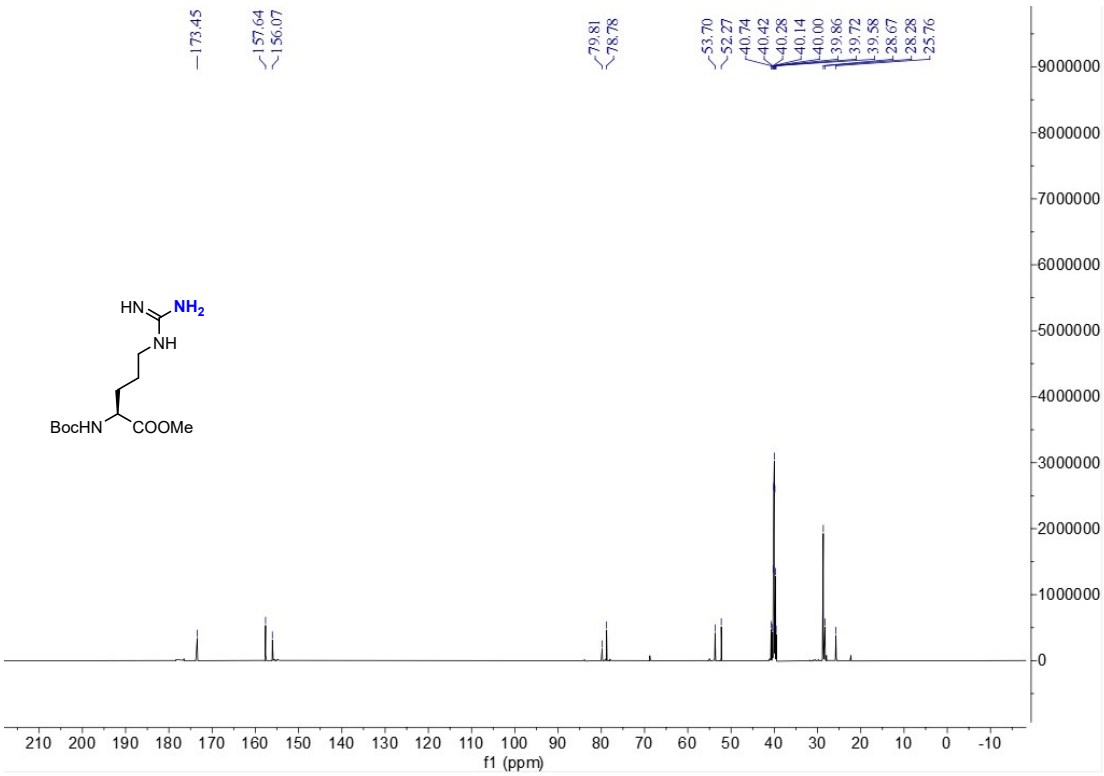


Fig 255. ^{13}C NMR of (**SM-19**)

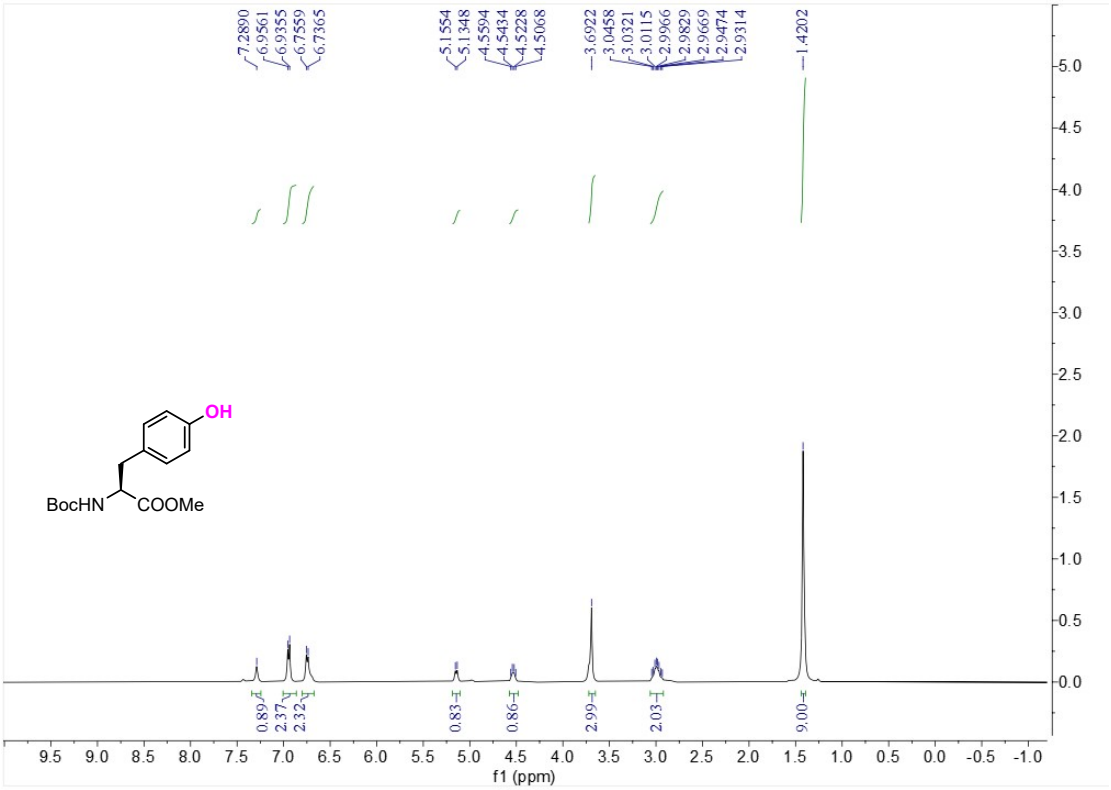


Fig 256. ^{1}H NMR of (**SM-20**)

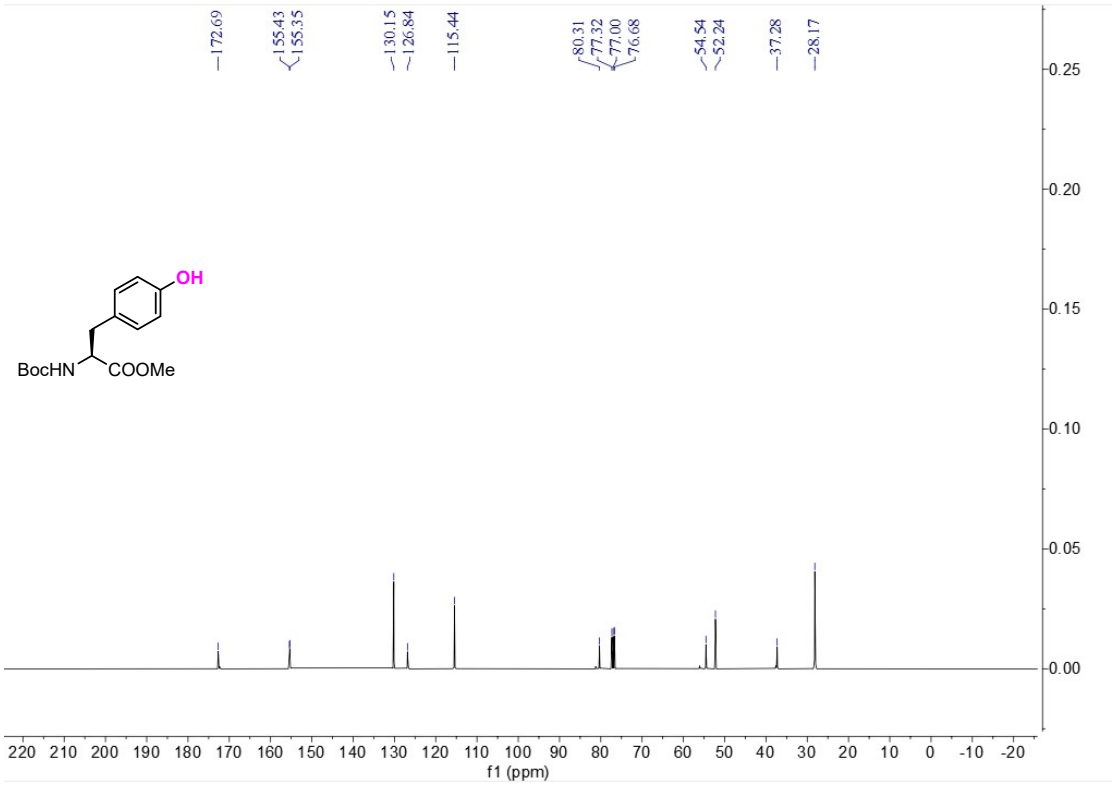


Fig 257. ^{13}C NMR of (**SM-20**)