Supporting Information

Natural product cercosporin as a biomimic photocatalyst for the synthesis of peptides containing kynurenine via energy transfer mechanism

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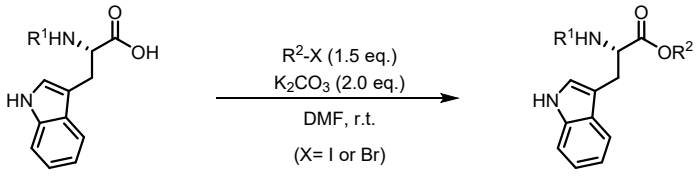
1. General Information

^{1}H, ^{13}C and ^{19}F NMR spectra were collected on a 400 or 600 MHz spectrometer using $CDCl_3$, DMSO-d_6 or Methanol-d_4 as solvents. Chemical shifts of ^{1}H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. High Resolution Mass measurement was performed with Electron Spray Ionization (ESI) method on a Q-TOF mass spectrometer operating in positive-ion mode. Melting point (m.p.) was measured on a microscopic melting point apparatus. PE refers to petroleum ether (b.p. 60–90 °C), EA refers to ethyl acetate, and DCM refers to dichloromethane. Flash column chromatography was carried out using commercially available 200–300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA. Cercosporin was biosynthesized from microbial fermentation,[1] and purified through column chromatography (Sephadex LH-20)[2] according to our previous report. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

Photochemical reactions were carried out in a borosilicate glass bottle with PHILIPS household CFLs as light sources at room temperature. The sample was placed at an approximate distance of 5 cm to the lamp. The intensity of irradiation was measured by an FZ-A radiometer (Photoelectric Instrument Factory of Beijing Normal University) equipped with a 400–1000 nm sensor. The light intensity was measured as follows: 20.6 mW cm^{-2} for 15 W CFL, 32.5 mW cm^{-2} for 23 W CFL, and 33.3 mW cm^{-2} for 32 W CFL.

2. General procedure for preparation of substrates

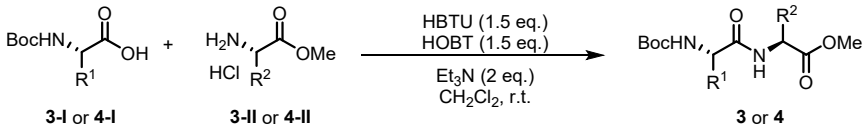
2.1 General procedure for the synthesis of 1c–1h



1-I **1**

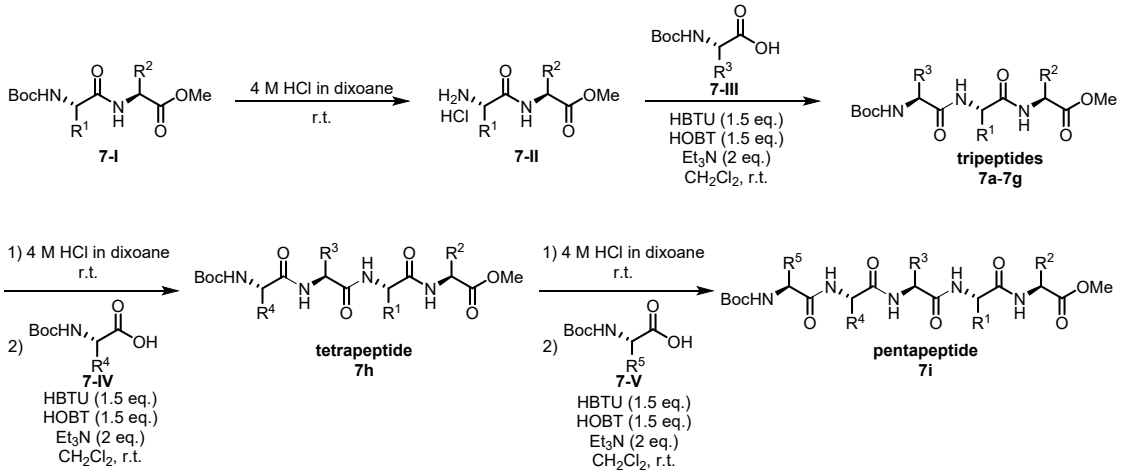
To a solution of **1-I** (5 mmol) in DMF (10 mL), K_2CO_3 (10 mmol, 2 equiv) was added and stirred for 15 min at room temperature. After that, corresponding halides (7.5 mmol, 1.5 equiv) was added. The mixture was stirred at room temperature for 1 h. After dilution with H_2O, the mixture was extracted with EA for 3 times. The combined organic layers were washed with water and brine sequentially, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel (200–300 mesh) (PE/EA) to afford the corresponding products **1**.[3]

2.2 General procedure for the synthesis of 3 and 4[4]



In a round-bottomed flask (250 mL), equipped with a stir bar, acids **3-I** or **4-I** (5 mmol), HBTU (*O*-benzotriazole-*N,N,N′,N′*-tetramethyl-uronium-hexafluorophosphate) (7.5 mmol, 1.5 equiv), HOBT (1-hydroxybenzotriazole) (7.5 mmol, 1.5 equiv), dichloromethane (50 mL) and triethylamine (5 mmol, 1 equiv) were combined and added. The mixture was stirred for 30 min at room temperature, and then, amino acids methyl ester hydrochlorides **3-II** or **4-II** (5 mmol, 1 equiv) and triethylamine (5 mmol, 1 equiv) were added to the solution for stirring overnight. After dilution with H_2O, the mixture was extracted with CH_2Cl_2 for 3 times, and washed by saturated $NaHCO_3$ solution (100 mL × 3), 2 M hydrochloric acid solution (100 mL × 3), H_2O (100 mL × 3) and saturated NaCl solution (100 mL). The organic layers were combined, dried with Na_2SO_4, and concentrated for purification by flash column chromatography on silica gel (200–300 mesh) (PE/EA) to afford corresponding dipeptides **3** or **4**.

2.3 General procedure for the synthesis of 7[5]



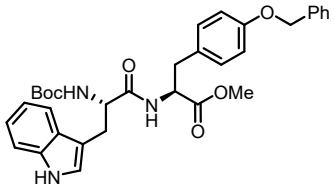
The *N*-Boc protected dipeptide ester **7-I** (5 mmol) was dissolved in 4 M HCl in dioxane and stirred at room temperature for 3 h. The reaction mixture was diluted with dichloromethane and concentrated in vacuo for the preparation of the dipeptide ester hydrochloride, which was subsequently used without further purification.

In a round-bottomed flask (250 mL), equipped with a stir bar, acids **7-III** (5 mmol), HBTU (7.5 mmol, 1.5 equiv), HOBT (7.5 mmol, 1.5 equiv), dichloromethane (50 mL) and triethylamine (5 mmol, 1 equiv) were combined and added. The mixture was stirred for 30 min at room temperature, and then, amino acids methyl ester hydrochlorides **7-II** (5 mmol, 1 equiv) in the previous step and triethylamine (5 mmol, 1 equiv) were added to the solution for stirring overnight. After dilution with H_2O, the mixture was extracted with CH_2Cl_2 for 3 times, and washed by saturated $NaHCO_3$ solution (100 mL × 3), 2 M hydrochloric acid solution (100 mL × 3), H_2O (100 mL × 3) and saturated NaCl solution (100 mL). The organic layers were combined, dried with Na_2SO_4, and

concentrated for purification by flash column chromatography on silica gel (200–300 mesh) (PE/EA) to afford corresponding tripeptides **7a-7g**.

For the synthesis of tetrapeptides **7h** and pentapeptide **7i**, deprotection with 4 M HCl in dioxane and coupling with *N*-Boc-protected amino acid were repeated for one and two times, respectively. Purification by column chromatography on silica gel (200–300 mesh) (PE/EA) afforded the desired polypeptides.

2.4 Characterization of new substrates



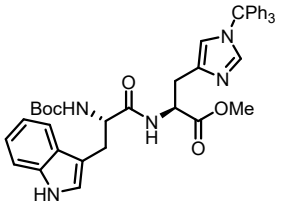
methyl (S)-3-(4-(benzyloxy)phenyl)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-(1H-indol-3-yl)propanamido)propanoate (3h)

White solid, m.p. 72 – 74 °C; [α]20 D = –16 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.36 (m, 4H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.19 (td, *J* = 8.2, 7.8, 1.3 Hz, 1H), 7.13 (td, *J* = 7.5, 7.0, 1.1 Hz, 1H), 6.99 (s, 1H), 6.70 (q, *J* = 8.6, 8.6, 7.2 Hz, 4H), 6.20 (d, *J* = 7.5 Hz, 1H), 5.11 (s, 1H), 4.98 (s, 2H), 4.69 (d, *J* = 6.8 Hz, 1H), 4.44 (s, 1H), 3.62 (s, 3H), 3.32 (d, *J* = 14.9 Hz, 1H), 3.12 (dd, *J* = 14.6, 7.2 Hz, 1H), 2.89 – 2.87 (m, 2H), 1.42 (s, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 171.3, 157.8, 155.4, 137.0, 136.3, 130.2, 128.6, 128.0, 127.9, 127.5, 123.4, 122.3, 119.8, 118.9, 114.8, 111.3, 110.5, 80.1, 70.0, 55.2, 53.4, 52.2, 37.0, 28.3, 28.3 ppm.

HRMS calcd for $C_{33}H_{37}N_3O_6$ $[M + H]^+$ 572.2755, found 572.2761.



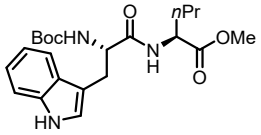
methyl N^{α}-((tert-butoxycarbonyl)-L-tryptophyl)-N^{τ}-trityl-L-histidinate (3i)

White solid, m.p. 98 – 100 °C; [α]20 D = –10 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.30 (m, 9H), 7.23 (s, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.06 (ddd, *J* = 7.4, 4.8, 2.6 Hz, 9H), 6.38 (d, *J* = 1.4 Hz, 1H), 5.28 (d, *J* = 7.5 Hz, 1H), 4.74 (dt, *J* = 7.7, 4.9 Hz, 1H), 4.52 (s, 1H), 3.53 (s, 3H), 3.23 (d, *J* = 6.8 Hz, 1H), 2.95 (dd, *J* = 14.6, 4.9 Hz, 1H), 2.82 (d, *J* = 10.6 Hz, 1H), 1.36 (s, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 171.4, 155.3, 142.3, 138.6, 136.2, 129.8, 128.1, 128.1, 123.5, 121.9, 119.6, 119.4, 119.0, 111.1, 110.4, 79.6, 75.2, 55.0, 52.6, 52.1, 29.9, 28.5, 28.3 ppm.

HRMS calcd for $C_{42}H_{43}N_5O_5$ $[M + H]^+$ 698.3337, found 698.3339.



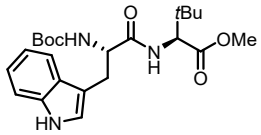
methyl (S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-(1H-indol-3-yl)propanamido)pentanoate (3p)

White solid, m.p. 70 – 72 °C; [α]20 D = –22 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.14 – 7.10 (m, 1H), 7.10 (s, 1H), 6.28 (d, *J* = 7.8 Hz, 1H), 5.18 (s, 1H), 4.50 – 4.43 (m, 2H), 3.64 (s, 3H), 3.31 (dd, *J* = 14.5, 5.6 Hz, 1H), 3.17 (dd, *J* = 14.6, 7.4 Hz, 1H), 1.72 – 1.66 (m, 1H), 1.55 – 1.48 (m, 1H), 1.43 (s, 9H), 1.18 – 1.13 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 171.6, 155.5, 136.3, 127.5, 123.4, 122.1, 119.6, 118.8, 111.2, 110.4, 80.1, 55.2, 52.2, 52.1, 34.4, 28.3, 18.4, 13.6 ppm.

HRMS calcd for $C_{22}H_{31}N_3O_5$ $[M + H]^+$ 418.2336, found 418.2330.



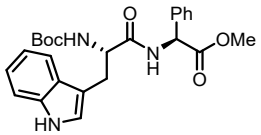
methyl (S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-(1H-indol-3-yl)propanamido)-3,3-dimethylbutanoate (3q)

White solid, m.p. 67 – 69 °C; [α]20 D = –20 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.19 (td, *J* = 8.3, 6.9, 1.0 Hz, 1H), 7.12 (td, *J* = 7.5, 7.0, 1.1 Hz, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 6.38 (d, *J* = 9.0 Hz, 1H), 5.19 (s, 1H), 4.43 (s, 1H), 4.32 (d, *J* = 9.1 Hz, 1H), 3.60 (s, 3H), 3.27 (dd, *J* = 14.2, 5.9 Hz, 1H), 3.19 (dd, *J* = 14.5, 7.6 Hz, 1H), 1.43 (s, 9H), 0.85 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 171.4, 155.6, 136.3, 127.4, 123.3, 122.1, 119.7, 118.8, 111.2, 110.5, 80.2, 60.2, 55.4, 51.7, 34.6, 28.3, 28.0, 26.4 ppm.

HRMS calcd for $C_{23}H_{33}N_3O_5$ $[M + H]^+$ 432.2493, found 432.2498.



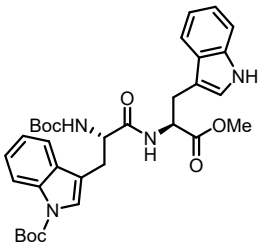
methyl (S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-(1H-indol-3-yl)propanamido)-2-phenylacetate (3r)

White solid, m.p. 126 – 128 °C; [α]20 D = +52 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.27 (m, 3H), 7.21 – 7.17 (m, 2H), 7.11 (td, *J* = 7.5, 7.0, 1.1 Hz, 1H), 6.99 (s, 1H), 6.79 (d, *J* = 4.1 Hz, 2H), 5.41 (d, *J* = 6.8 Hz, 1H), 5.17 (s, 1H), 4.49 (s, 1H), 3.63 (s, 3H), 3.33 (d, *J* = 14.8 Hz, 1H), 3.17 (dd, *J* = 14.6, 7.5 Hz, 1H), 1.42 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 170.7, 155.5, 136.2, 128.9, 128.5, 127.6, 127.2, 123.5, 122.2, 119.8, 118.7, 111.2, 110.3, 80.2, 56.5, 55.3, 52.7, 28.3, 28.2 ppm.

HRMS calcd for $C_{25}H_{29}N_3O_5$ $[M + H]^+$ 452.2180, found 452.2173.



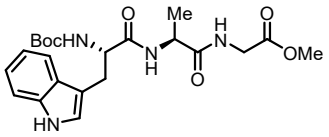
tert-butyl 3-((S)-3-(((S)-3-(1H-indol-3-yl)-1-methoxy-1-oxopropan-2-yl)amino)-2-((tert-butoxycarbonyl)amino)-3-oxopropyl)-1H-indole-1-carboxylate (4b)

White solid, m.p. 92 – 94 °C; [α]20 D = +14 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.07 (m, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.43 (s, 1H), 7.33 – 7.27 (m, 3H), 7.24 – 7.20 (m, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.71 (s, 1H), 6.39 (d, *J* = 7.7 Hz, 1H), 5.07 (s, 1H), 4.81 (q, *J* = 5.5 Hz, 1H), 4.43 (s, 1H), 3.57 (s, 3H), 3.23 – 3.06 (m, 4H), 1.62 (s, 9H), 1.37 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 170.9, 155.3, 149.6, 136.0, 135.5, 130.3, 127.5, 124.6, 124.5, 122.8, 122.7, 122.2, 119.5, 119.2, 118.3, 115.5, 115.2, 111.3, 109.5, 83.7, 80.1, 54.5, 53.0, 52.3, 28.2, 27.6 ppm.

HRMS calcd for $C_{33}H_{40}N_4O_7$ $[M + H]^+$ 605.2970, found 605.2964.



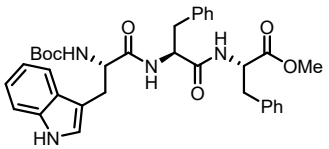
methyl (tert-butoxycarbonyl)-L-tryptophyl-L-alanylglycinate (7a)

White solid, m.p. 74 – 76 °C; [α]20 D = –19 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.10 – 7.06 (m, 2H), 6.93 (s, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 5.47 (d, *J* = 7.2 Hz, 1H), 4.50 (t, *J* = 7.2 Hz, 2H), 3.82 (dd, *J* = 17.6, 5.6 Hz, 1H), 3.72 – 3.68 (m, 4H), 3.24 (d, *J* = 6.6 Hz, 2H), 1.42 (s, 9H), 1.22 (d, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 172.0, 170.2, 155.8, 136.3, 127.4, 123.6, 122.1, 119.6, 118.7, 111.4, 110.0, 80.4, 55.5, 52.3, 48.8, 41.0, 28.3, 18.0 ppm.

HRMS calcd for $C_{22}H_{30}N_4O_6$ $[M + H]^+$ 447.2238, found 447.2231.

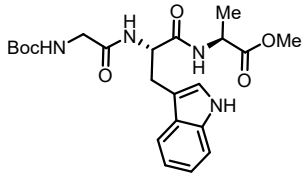


methyl (tert-butoxycarbonyl)-L-tryptophyl-L-phenylalanylphenylalaninate (7b)

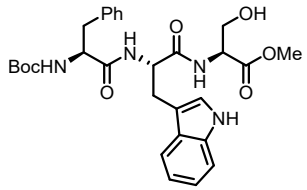
White solid, m.p. 143 – 145 °C; [α]20 D = –26 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.21 – 7.17 (m, 1H), 7.14 – 7.10 (m, 4H), 6.99 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.88 – 6.85 (m, 3H), 6.39 (d, *J* = 7.6 Hz, 1H), 6.22 (d, *J* = 7.6 Hz, 1H), 5.09 (d, *J* = 6.6 Hz, 1H), 4.68 (q, *J* = 6.5 Hz, 1H), 4.52 (q, *J* = 6.9 Hz, 1H), 4.40 (d, *J* = 6.6 Hz, 1H), 3.65 (s, 3H), 3.26 (d, *J* = 10.4 Hz, 1H), 3.11 – 3.01 (m, 2H), 2.94 – 2.75 (m, 3H), 1.38 (s, 9H) ppm.

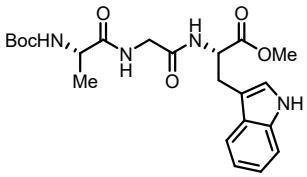
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 171.4, 170.1, 155.5, 136.3, 136.1, 135.9, 129.3, 128.6, 127.3, 127.1, 126.9, 123.3, 122.4, 119.8, 118.9, 111.4, 110.3, 80.3, 60.4, 55.1, 54.2, 53.6, 52.3, 37.8, 37.6, 28.3 ppm.
HRMS calcd for $C_{35}H_{40}N_4O_6$ $[M + H]^+$ 613.3021, found 613.3008.



methyl (tert-butoxycarbonyl)glycyl-L-tryptophyl-L-alaninate (7c)
White solid, m.p. 180 – 182 °C; [α]20 D = –13 (*c* = 0.10, DMSO).
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.82 (s, 1H), 8.47 (d, *J* = 7.0 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 7.08 – 7.04 (m, 1H), 7.00 – 6.97 (m, 1H), 6.90 (t, *J* = 6.0 Hz, 1H), 4.59 (q, *J* = 8.2, 7.7, 4.7 Hz, 1H), 4.31 (p, *J* = 7.2 Hz, 1H), 3.62 (s, 4H), 3.45 (dd, *J* = 16.7, 5.9 Hz, 1H), 3.13 (dd, *J* = 14.7, 4.9 Hz, 1H), 2.93 (dd, *J* = 14.7, 8.5 Hz, 1H), 1.37 (s, 9H), 1.29 (d, *J* = 7.2 Hz, 3H) ppm.
^{13}C NMR (151 MHz, DMSO-d_6) δ 173.3, 171.8, 169.5, 156.2, 136.5, 127.8, 124.1, 121.3, 118.9, 118.7, 111.7, 110.2, 78.5, 53.3, 52.3, 48.1, 43.6, 28.6, 28.3, 17.3 ppm.
HRMS calcd for $C_{22}H_{30}N_4O_6$ $[M + H]^+$ 447.2238, found 447.2230.

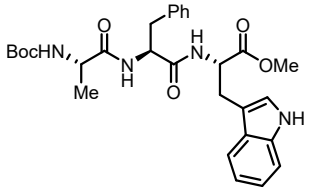


methyl (tert-butoxycarbonyl)-L-phenylalanyl-L-tryptophyl-L-serinate (7d)
White solid, m.p. 88 – 90 °C; [α]20 D = –15 (*c* = 0.10, MeOH).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.5 Hz, 1H), 7.29 (dd, *J* = 15.6, 7.9 Hz, 6H), 7.13 (d, *J* = 7.3 Hz, 3H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.94 (s, 1H), 6.89 (d, *J* = 7.9 Hz, 1H), 5.03 (d, *J* = 6.7 Hz, 1H), 4.83 (d, *J* = 6.8 Hz, 1H), 4.52 – 4.50 (m, 1H), 4.31 (d, *J* = 6.7 Hz, 1H), 3.81 (d, *J* = 9.3 Hz, 1H), 3.72 – 3.65 (m, 4H), 3.59 (s, 1H), 3.31 (dd, *J* = 14.7, 5.5 Hz, 1H), 3.09 (dd, *J* = 14.8, 6.2 Hz, 1H), 2.99 (dd, *J* = 14.0, 5.3 Hz, 1H), 2.91 (d, *J* = 7.4 Hz, 1H), 1.23 (s, 9H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 171.5, 170.5, 155.7, 136.2, 136.2, 129.3, 128.8, 127.6, 127.2, 123.9, 122.1, 119.6, 118.3, 111.5, 109.6, 80.7, 62.6, 55.9, 55.0, 54.0, 52.6, 37.6, 28.0, 27.3 ppm.
HRMS calcd for $C_{29}H_{36}N_4O_7$ $[M + H]^+$ 553.2657, found 553.2652.

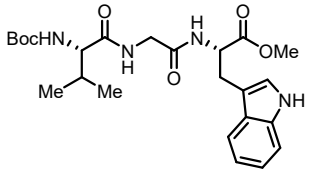


methyl (tert-butoxycarbonyl)-L-alanylglycyl-L-tryptophanate (7e)
Yellow solid, m.p. 80 – 82 °C; [α]20 D = –8 (*c* = 0.10, MeOH).

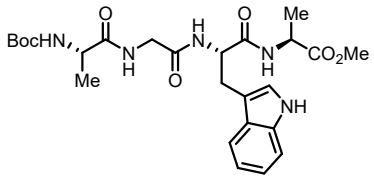
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 2.6 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.10 – 7.04 (m, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 2.4 Hz, 1H), 5.34 (d, *J* = 7.4 Hz, 1H), 4.85 – 4.80 (m, 1H), 4.16 – 4.13 (m, 1H), 3.79 (dd, *J* = 15.7, 4.0 Hz, 1H), 3.70 – 3.63 (m, 4H), 3.32 – 3.22 (m, 2H), 1.43 (s, 9H), 1.25 (d, *J* = 7.3 Hz, 3H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 172.3, 168.9, 155.8, 136.2, 127.3, 123.7, 122.0, 119.4, 118.3, 111.5, 109.1, 80.4, 52.6, 52.5, 50.2, 42.8, 28.4, 27.3, 18.5 ppm.
H HRMS calcd for $C_{22}H_{30}N_4O_6$ $[M + H]^+$ 447.2238, found 447.2231.



methyl (tert-butoxycarbonyl)-L-alanyl-L-phenylalanyl-L-tryptophanate (7f)
Yellow solid, m.p. 86 – 88 °C; [α]20 D = –16 (*c* = 0.10, MeOH).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.4 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.18 (m, 3H), 7.15 – 7.12 (m, 3H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 2.4 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 5.03 (d, *J* = 7.1 Hz, 1H), 4.83 (dd, *J* = 13.3, 5.6 Hz, 1H), 4.69 (q, *J* = 7.1 Hz, 1H), 4.04 (t, *J* = 7.4 Hz, 1H), 3.61 (s, 3H), 3.21 (d, *J* = 5.6 Hz, 2H), 3.06 – 2.95 (m, 2H), 1.42 (s, 9H), 1.11 (d, *J* = 7.1 Hz, 3H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 171.8, 170.3, 155.5, 136.4, 136.1, 129.4, 128.6, 127.4, 127.0, 123.3, 122.0, 119.5, 118.3, 111.4, 109.3, 80.4, 54.0, 52.9, 52.4, 50.4, 37.9, 28.3, 27.5, 18.3 ppm.
HRMS calcd for $C_{29}H_{36}N_4O_6$ $[M + H]^+$ 537.2708, found 537.2698.



methyl (tert-butoxycarbonyl)-L-valylglycyl-L-tryptophanate (7g)
White solid, m.p. 154 – 156 °C; [α]20 D = +7 (*c* = 0.10, MeOH).
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.88 (d, *J* = 2.5 Hz, 1H), 8.25 (d, *J* = 7.5 Hz, 1H), 8.08 (t, *J* = 5.7 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 2.3 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 8.7 Hz, 1H), 4.54 (q, *J* = 7.1 Hz, 1H), 3.82 (dd, *J* = 8.6, 6.6 Hz, 1H), 3.75 (dd, *J* = 5.9, 2.5 Hz, 2H), 3.56 (s, 3H), 3.16 (dd, *J* = 14.6, 6.1 Hz, 1H), 3.06 (dd, *J* = 14.6, 7.6 Hz, 1H), 1.94 (q, *J* = 6.7 Hz, 1H), 1.38 (s, 9H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H) ppm.
^{13}C NMR (101 MHz, DMSO-d_6) δ 172.6, 172.1, 169.2, 156.0, 136.6, 127.5, 124.3, 121.4, 118.9, 118.4, 111.9, 109.6, 78.5, 60.2, 53.6, 52.3, 42.1, 30.8, 28.7, 27.7, 19.7, 18.5 ppm.
HRMS calcd for $C_{24}H_{34}N_4O_6$ $[M + H]^+$ 475.2551, found 475.2553.



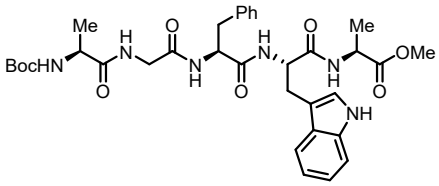
methyl (tert-butoxycarbonyl)-L-alanylglycyl-L-tryptophyl-L-alaninate (7h)

Light yellow solid, m.p. 194 – 196 °C; [α]20 D = –13 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.59 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.14 (s, 1H), 7.10 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.02 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 4.72 (dd, *J* = 7.8, 5.8 Hz, 1H), 4.40 (q, *J* = 7.3 Hz, 1H), 4.04 (q, *J* = 7.0 Hz, 1H), 3.87 (d, *J* = 16.7 Hz, 1H), 3.78 (d, *J* = 16.9 Hz, 1H), 3.67 (s, 3H), 3.37 – 3.31 (m, 1H), 3.16 (dd, *J* = 14.8, 7.7 Hz, 1H), 1.43 (s, 9H), 1.33 (d, *J* = 7.3 Hz, 3H), 1.28 (d, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Methanol-d_4) δ 175.1, 172.9, 172.2, 169.9, 156.5, 136.6, 127.5, 123.3, 121.0, 118.4, 117.9, 110.9, 109.4, 79.4, 53.9, 51.3, 50.5, 48.2, 42.3, 27.4, 16.7, 16.0 ppm.

HRMS calcd for $C_{25}H_{35}N_5O_7$ $[M + H]^+$ 518.2609, found 518.2620.



methyl (tert-butoxycarbonyl)-L-alanylglycyl-L-phenylalanyl-L-tryptophyl-L-alaninate (7i)

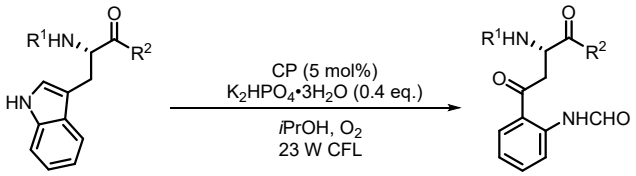
Yellow solid, m.p. 201 – 203 °C; [α]20 D = –13 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.59 (d, *J* = 7.9 Hz, 1H), 7.21 – 7.15 (m, 3H), 7.17 (dd, *J* = 10.2, 7.1 Hz, 3H), 7.14 (s, 1H), 7.12 – 7.09 (m, 3H), 7.05 – 7.01 (m, 1H), 4.69 (dd, *J* = 8.3, 5.7 Hz, 1H), 4.57 (dd, *J* = 8.5, 5.5 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 1H), 3.81 (d, *J* = 16.7 Hz, 1H), 3.68 (s, 3H), 3.33 – 3.29 (m, 1H), 3.15 (dd, *J* = 14.7, 8.3 Hz, 1H), 3.05 (dd, *J* = 14.0, 5.6 Hz, 1H), 2.84 (dd, *J* = 14.1, 8.6 Hz, 1H), 1.45 (s, 9H), 1.32 (dd, *J* = 7.3, 3.3 Hz, 6H) ppm.

^{13}C NMR (101 MHz, Methanol-d_4) δ 175.1, 172.9, 172.1, 171.6, 170.2, 156.5, 136.8, 136.6, 128.8, 128.0, 127.5, 126.3, 123.5, 121.0, 118.4, 118.0, 110.9, 109.4, 79.4, 55.0, 53.9, 51.4, 50.6, 48.1, 42.2, 37.0, 27.4, 16.8, 16.1 ppm.

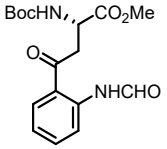
HRMS calcd for $C_{34}H_{44}N_6O_8$ $[M + H]^+$ 665.3293, found 665.3297.

3. General procedure for cercosporin-catalyzed synthesis of kynurenine (Kyn) derivatives and Kyn-contained peptides



1, 3, 4, 7 **2, 5, 6, 8**

A sealed oven-dried Schlenk tube was charged with the substrates **1**, **3**, **4** or **7** (0.1 mmol, 1 equiv), cercosporin (5 mol%), and $K_2HPO_4 \cdot 3H_2O$ (0.4 equiv). The vial is thoroughly flushed with O_2, and *i*PrOH (0.0125 M) was added under O_2 atmosphere. The mixtures were stirred at room temperature and irradiated with 23 W CFL under O_2 atmosphere. After completion, the solution was concentrated *in vacuo* and purified by chromatography on silica gel (200–300 mesh) (PE/EA or DCM/MeOH) to afford the desired products.



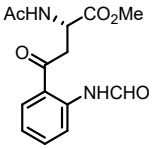
methyl (S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoate (2a)

26.2 mg, 75% yield; R_f = 0.3 (PE/EA = 2/1); white solid, m.p. 93 – 95 °C; [α]20 D = –10 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.40 (s, 1H), 8.76 (d, *J* = 8.4 Hz, 1H), 8.48 (s, 1H), 7.92 (d, *J* = 7.3 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 5.55 (d, *J* = 8.2 Hz, 1H), 4.72 – 4.70 (m, 1H), 3.81 – 3.77 (m, 4H), 3.64 (dd, *J* = 18.0, 4.2 Hz, 1H), 1.45 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 172.0, 159.9, 155.5, 140.1, 135.8, 131.0, 123.2, 121.7, 121.1, 80.3, 52.8, 49.5, 42.3, 28.3 ppm.

HRMS calcd for $C_{17}H_{22}N_2O_6$ $[M + H]^+$ 351.1551, found 351.1550.



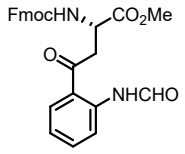
methyl (S)-2-acetamido-4-(2-formamidophenyl)-4-oxobutanoate (2b)

25.2 mg, 86% yield; R_f = 0.1 (PE/EA = 1/1); white solid, m.p. 102 – 104 °C; [α]20 D = +37 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.38 (s, 1H), 8.74 (d, *J* = 8.5 Hz, 1H), 7.92 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 4.98 (dt, *J* = 7.8, 3.8 Hz, 2H), 3.83 – 3.69 (m, 5H), 2.04 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 171.7, 170.1, 159.9, 140.1, 135.9, 131.0, 123.3, 121.7, 121.0, 52.8, 48.2, 41.8, 23.1 ppm.

HRMS calcd for $C_{14}H_{16}N_2O_5$ $[M + H]^+$ 293.1132, found 293.1134.



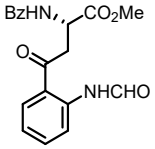
methyl (S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoate (2c)

38.2 mg, 81% yield; R_f = 0.4 (PE/EA = 2/1); light yellow solid, m.p. 62 – 64 °C; [α]20 D = –11 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.35 (s, 1H), 8.75 (d, *J* = 8.5 Hz, 1H), 8.45 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 8.2 Hz, 2H), 7.58 – 7.57 (m, 3H), 7.38 – 7.25 (m, 5H), 7.15 (t, *J* = 7.7 Hz, 1H), 5.89 (d, *J* = 8.5 Hz, 1H), 4.76 – 4.74 (m, 1H), 4.43 (q, *J* = 9.3, 8.1 Hz, 1H), 4.19 (t, *J* = 7.0 Hz, 1H), 3.80 – 3.75 (m, 4H), 3.63 (dd, *J* = 18.2, 4.1 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 171.6, 159.9, 156.1, 143.8, 143.6, 141.3, 141.3, 140.2, 135.9, 131.0, 127.8, 127.1, 127.0, 125.1, 123.3, 121.8, 121.0, 120.0, 120.0, 67.1, 52.9, 50.0, 47.2, 42.1 ppm.

HRMS calcd for $C_{27}H_{24}N_2O_6$ $[M + H]^+$ 473.1707, found 473.1710.



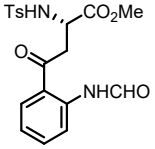
methyl (S)-2-benzamido-4-(2-formamidophenyl)-4-oxobutanoate (2d)

29.3 mg, 83% yield; R_f = 0.3 (PE/EA = 1/1); light yellow solid, m.p. 59 – 61 °C; [α]20 D = –15 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.38 (s, 1H), 8.73 (d, *J* = 8.5 Hz, 1H), 8.47 (d, *J* = 1.9 Hz, 1H), 7.93 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.81 (d, *J* = 7.0 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 5.18 (dt, *J* = 8.0, 4.2 Hz, 1H), 3.92 – 3.85 (m, 2H), 3.79 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.0, 171.7, 167.0, 159.8, 140.1, 135.8, 133.6, 131.9, 131.0, 128.6, 127.1, 123.3, 121.7, 121.0, 52.9, 48.8, 41.8 ppm.

HRMS calcd for $C_{19}H_{18}N_2O_5$ $[M + H]^+$ 355.1288, found 355.1297.

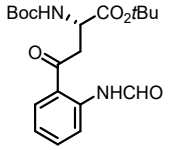


methyl (S)-4-(2-formamidophenyl)-2-((4-methylphenyl)sulfonamido)-4-oxobutanoate (2e)

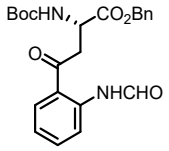
30.0 mg, 74% yield; R_f = 0.4 (PE/EA = 1/1); white solid, m.p. 115 – 116 °C; [α]20 D = +4 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.24 (s, 1H), 8.73 (d, *J* = 8.5 Hz, 1H), 8.46 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.27 – 7.25 (m, 2H), 7.14 (t, *J* = 7.7 Hz, 1H), 5.85 (d, *J* = 7.7 Hz, 1H), 4.27 (dt, *J* = 8.0, 4.3 Hz, 1H), 3.69 (d, *J* = 4.2 Hz, 2H), 3.61 (s, 3H), 2.38 (s, 3H) ppm.

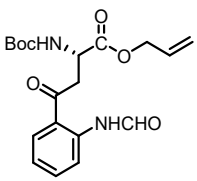
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 170.8, 159.9, 143.8, 140.1, 136.8, 135.8, 130.8, 129.7, 127.2, 123.2, 121.7, 120.9, 53.0, 51.6, 43.1, 21.5 ppm.
HRMS calcd for $C_{19}H_{20}N_2O_6S$ $[M + H]^+$ 405.1115, found 405.1109.



tert-butyl (S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoate (2f)
29.5 mg, 75% yield; R_f = 0.5 (PE/EA = 3/1); light pink solid, m.p. 111 – 113 °C; [α]20 D = –8 (*c* = 0.10, MeOH).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.45 (s, 1H), 8.76 (d, *J* = 8.5 Hz, 1H), 8.48 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 5.53 (d, *J* = 8.3 Hz, 1H), 4.57 (dd, *J* = 8.6, 4.3 Hz, 1H), 3.72 (dd, *J* = 17.8, 4.3 Hz, 1H), 3.57 (dd, *J* = 17.8, 4.3 Hz, 1H), 1.44 (s, 18H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 170.3, 159.8, 155.6, 140.0, 135.6, 131.0, 123.2, 121.7, 121.3, 82.3, 80.0, 50.3, 42.4, 28.3, 27.9 ppm.
HRMS calcd for $C_{20}H_{28}N_2O_6$ $[M + H]^+$ 393.2020, found 393.2031.



benzyl (S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoate (2g)
30.0 mg, 70% yield; R_f = 0.6 (PE/EA = 2/1); brown oil; [α]20 D = –8 (*c* = 0.10, MeOH).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.29 (s, 1H), 8.75 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.30 (s, 5H), 7.16 (t, *J* = 7.6 Hz, 1H), 5.58 (d, *J* = 8.6 Hz, 1H), 5.19 (q, *J* = 12.3 Hz, 2H), 4.74 (dt, *J* = 8.7, 4.1 Hz, 1H), 3.80 (dd, *J* = 18.1, 4.3 Hz, 1H), 3.62 (dd, *J* = 18.1, 4.1 Hz, 1H), 1.43 (s, 9H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 171.4, 159.9, 155.5, 140.1, 135.8, 135.3, 131.0, 128.5, 128.4, 128.3, 123.2, 121.7, 120.9, 80.3, 67.4, 49.7, 42.3, 28.3 ppm.
HRMS calcd for $C_{23}H_{26}N_2O_6$ $[M + H]^+$ 427.1864, found 427.1877.

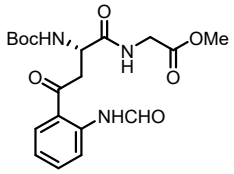


allyl (S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoate (2h)
29.8 mg, 79% yield; R_f = 0.5 (PE/EA = 2/1); light orange solid, m.p. 62 – 64 °C; [α]20 D = –9 (*c* = 0.10, MeOH).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.38 (s, 1H), 8.75 (d, *J* = 8.5 Hz, 1H), 8.48 (d, *J* = 1.9 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 5.88 (ddt, *J* = 16.4, 11.0, 5.7 Hz, 1H), 5.61 (d, *J* = 8.5 Hz, 1H), 5.31 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.23 (d, *J* = 10.4 Hz, 1H),

4.74 (dt, *J* = 8.8, 4.3 Hz, 1H), 4.66 (dd, *J* = 5.8, 1.5 Hz, 2H), 3.80 (dd, *J* = 17.9, 4.4 Hz, 1H), 3.64 (dd, *J* = 17.9, 4.3 Hz, 1H), 1.45 (s, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 201.9, 171.1, 159.8, 155.5, 140.1, 135.7, 131.5, 130.9, 123.2, 121.7, 121.2, 118.7, 80.2, 66.2, 49.7, 42.2, 28.3 ppm.

HRMS calcd for $C_{19}H_{24}N_2O_6$ $[M + H]^+$ 377.1707, found 377.1700.



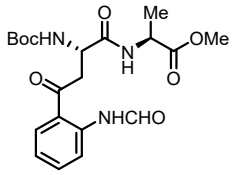
methyl (S)-(2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)glycinate (5a)

30.9 mg, 76% yield; R_f = 0.4 (PE/EA = 1/1); yellow solid, m.p. 74 – 76 °C; [α]20 D = –12 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.70 (d, *J* = 8.5 Hz, 1H), 8.46 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.20 – 7.13 (m, 2H), 5.77 (d, *J* = 9.2 Hz, 1H), 4.79 (s, 2H), 4.12 – 3.99 (m, 4H), 3.80 – 3.74 (m, 4H), 3.46 (dd, *J* = 18.0, 3.3 Hz, 1H), 1.46 (s, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.6, 171.5, 170.1, 160.0, 155.6, 139.8, 135.5, 130.9, 123.2, 121.6, 121.6, 80.7, 52.4, 50.5, 41.6, 41.4, 28.3 ppm.

HRMS calcd for $C_{19}H_{25}N_3O_7$ $[M + H]^+$ 408.1765, found 408.1773.



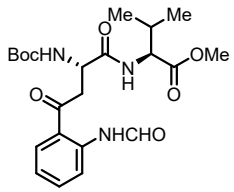
methyl ((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-alaninate (5b)

29.1 mg, 69% yield; R_f = 0.6 (PE/EA = 1/1); light yellow solid, m.p. 110 – 112 °C; [α]20 D = –9 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.71 (d, *J* = 8.5 Hz, 1H), 8.47 (d, *J* = 1.9 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 2H), 5.71 (d, *J* = 9.0 Hz, 1H), 4.75 (s, 1H), 4.55 (t, *J* = 7.2 Hz, 1H), 3.79 – 3.72 (m, 4H), 3.43 (dd, *J* = 18.8, 5.3 Hz, 1H), 1.46 (s, 9H), 1.43 (d, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.7, 173.0, 170.7, 159.9, 155.5, 139.8, 135.5, 130.9, 123.2, 121.6, 80.6, 52.5, 50.5, 48.3, 41.8, 28.3, 18.2 ppm.

HRMS calcd for $C_{20}H_{27}N_3O_7$ $[M + H]^+$ 422.1922, found 422.1902.



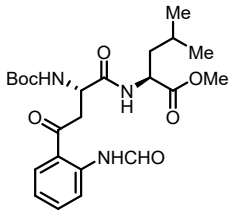
methyl ((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-valinate (5c)

26.8 mg, 60% yield; R_f = 0.6 (PE/EA = 1/1); light yellow solid, m.p. 118 – 120 °C; [α]20 D = –10 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.29 (s, 1H), 8.72 (d, *J* = 8.4 Hz, 1H), 8.47 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 5.70 (d, *J* = 8.3 Hz, 1H), 4.75 (s, 1H), 4.50 (dd, *J* = 8.8, 4.8 Hz, 1H), 3.76 (dd, *J* = 18.0, 4.6 Hz, 1H), 3.71 (s, 3H), 3.43 (dd, *J* = 17.9, 6.3 Hz, 1H), 2.20 (dq, *J* = 13.8, 6.8 Hz, 1H), 1.52 – 1.44 (m, 9H), 0.95 (t, *J* = 7.2 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 172.0, 171.0, 159.8, 155.5, 139.7, 135.5, 130.8, 123.2, 121.7, 80.7, 57.4, 52.2, 50.7, 41.5, 31.3, 28.3, 18.9, 17.7 ppm.

HRMS calcd for $C_{22}H_{31}N_3O_7$ $[M + H]^+$ 450.2235, found 450.2241.



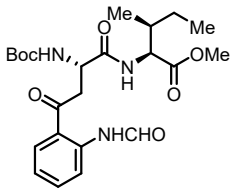
methyl ((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-leucinate (5d)

25.1 mg, 54% yield; R_f = 0.5 (PE/EA = 1/1); light yellow solid, m.p. 107 – 109 °C; [α]20 D = –11 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.30 (s, 1H), 8.71 (d, *J* = 8.4 Hz, 1H), 8.47 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 5.72 (d, *J* = 8.7 Hz, 1H), 4.75 (s, 1H), 4.54 (dd, *J* = 8.7, 4.9 Hz, 1H), 3.70 (s, 4H), 3.44 (dd, *J* = 17.9, 6.3 Hz, 1H), 1.92 (ddd, *J* = 9.4, 6.8, 4.7 Hz, 1H), 1.47 (s, 10H), 1.26 – 1.15 (m, 1H), 0.92 (t, *J* = 7.0 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.8, 171.9, 170.8, 159.8, 155.5, 139.7, 135.5, 130.8, 123.2, 121.7, 121.7, 80.6, 56.7, 52.1, 50.6, 41.5, 37.8, 28.3, 25.0, 15.4, 11.5 ppm.

HRMS calcd for $C_{23}H_{33}N_3O_7$ $[M + H]^+$ 464.2391, found 464.2393.



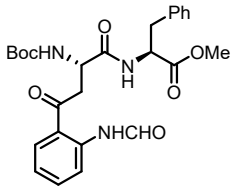
methyl (2S)-2-((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanamido)-3-methylpentanoate (5e)

33.0 mg, 71% yield; R_f = 0.5 (PE/EA = 1/1); light yellow solid, m.p. 122 – 124 °C; [α]20 D = –13 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 8.71 (d, *J* = 8.5 Hz, 1H), 8.47 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 5.71 (d, *J* = 8.9 Hz, 1H), 4.75 (s, 1H), 4.59 (d, *J* = 4.8 Hz, 1H), 3.77 – 3.69 (m, 4H), 3.45 (dd, *J* = 18.0, 6.1 Hz, 1H), 1.75 – 1.57 (m, 3H), 1.46 (s, 9H), 0.94 (t, *J* = 6.4 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.8, 173.0, 170.9, 159.8, 155.5, 139.7, 135.5, 130.9, 123.2, 121.7, 121.6, 80.6, 52.3, 50.9, 50.6, 41.6, 41.4, 28.3, 24.7, 22.8, 21.8 ppm.

HRMS calcd for $C_{23}H_{33}N_3O_7$ $[M + H]^+$ 464.2391, found 464.2387.



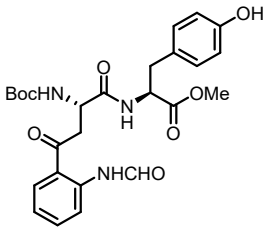
methyl ((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-phenylalaninate (5f)

38.1 mg, 77% yield; R_f = 0.2 (PE/EA = 2/1); light yellow solid, m.p. 137 – 139 °C; [α]20 D = –2 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.23 (s, 1H), 8.71 (d, *J* = 8.5 Hz, 1H), 8.43 (d, *J* = 2.0 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.33 – 7.23 (m, 3H), 7.18 – 7.12 (m, 3H), 7.04 (d, *J* = 8.1 Hz, 1H), 5.62 (d, *J* = 8.9 Hz, 1H), 4.82 (d, *J* = 6.9 Hz, 1H), 4.73 (s, 1H), 3.74 (d, *J* = 17.6 Hz, 1H), 3.66 (s, 3H), 3.38 (dd, *J* = 18.0, 6.1 Hz, 1H), 3.18 – 3.09 (m, 2H), 1.44 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 171.5, 170.7, 159.8, 155.4, 139.8, 135.8, 135.5, 130.9, 129.3, 128.6, 127.1, 123.2, 121.7, 121.5, 80.6, 53.4, 52.3, 50.5, 41.8, 37.9, 28.3 ppm.

HRMS calcd for $C_{26}H_{31}N_3O_7$ $[M + H]^+$ 498.2235, found 498.2239.



methyl ((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-tyrosinate (5g)

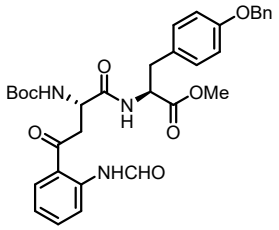
32.7 mg, 64% yield; R_f = 0.2 (PE/EA = 1/1); yellow solid, m.p. 75 – 77 °C; [α]20 D = –3 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 0.6H), 10.93 (d, *J* = 11.2 Hz, 0.3H), 8.93 (d, *J* = 11.2 Hz, 0.4H), 8.68 (d, *J* = 8.4 Hz, 0.6H), 8.43 (d, *J* = 1.9 Hz, 0.6H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.70 (s, 0.3H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 0.4H), 7.20 – 7.09 (m, 2H), 7.00 (dd, *J* = 24.7, 8.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.69 (d, *J* = 8.7 Hz, 0.6H), 5.56 (d, *J* = 9.2 Hz, 0.4H), 4.80 – 4.64 (m, 2H), 3.83 – 3.66 (m, 4H), 3.40 – 2.86 (m, 3H), 1.47 – 1.45 (m, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, ***major***) δ 202.5, 171.7, 171.0, 160.4, 155.6, 139.7, 135.5, 130.9, 130.4, 123.3, 121.5, 115.5, 77.3, 53.5, 52.4, 41.9, 28.3 ppm.

^{13}C NMR (101 MHz, $CDCl_3$, ***minor***) δ 201.9, 171.9, 170.8, 162.6, 156.0, 139.2, 135.3, 131.8, 126.9, 123.9, 121.7, 116.0, 80.8, 53.3, 50.4, 40.9, 37.0 ppm.

HRMS calcd for $C_{26}H_{31}N_3O_8$ $[M + H]^+$ 514.2184, found 514.2176.



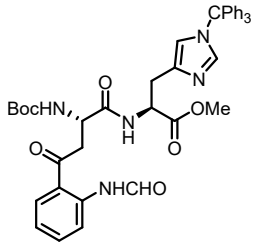
methyl (S)-3-(4-(benzyloxy)phenyl)-2-((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanamido)propanoate (5h)

47.5 mg, 79% yield; R_f = 0.5 (PE/EA = 1/1); white solid, m.p. 100 – 102 °C; [α]20 D = +6 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.23 (s, 1H), 8.71 (d, *J* = 8.4 Hz, 1H), 8.43 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 6.9 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 2H), 5.61 (d, *J* = 8.7 Hz, 1H), 5.02 (s, 2H), 4.79 – 4.75 (m, 2H), 3.75 – 3.65 (m, 4H), 3.37 (dd, *J* = 18.0, 6.1 Hz, 1H), 3.07 (dd, *J* = 5.8, 2.0 Hz, 2H), 1.44 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 171.6, 170.7, 159.9, 158.0, 155.4, 139.8, 136.9, 135.6, 130.9, 130.4, 128.6, 128.0, 127.5, 123.2, 121.7, 121.6, 115.0, 80.6, 70.0, 53.6, 52.3, 50.5, 41.8, 37.1, 28.3 ppm.

HRMS calcd for $C_{33}H_{37}N_3O_8$ $[M + H]^+$ 604.2653, found 604.2655.



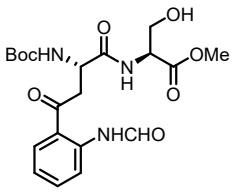
methyl N^{α}-((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-N^{τ}-trityl-L-histidinate (5i)

23.8 mg, 33% yield; R_f = 0.4 (PE/EA = 1/1); yellow solid, m.p. 84 – 86 °C; [α]20 D = +18 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.25 (s, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.26 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.34 – 7.33 (m, 10H), 7.11 – 7.10 (m, 7H), 6.59 (s, 1H), 6.00 (d, *J* = 8.8 Hz, 1H), 4.79 (dt, *J* = 8.4, 4.6 Hz, 2H), 3.80 (dd, *J* = 17.8, 2.7 Hz, 1H), 3.56 (s, 3H), 3.43 (dd, *J* = 18.1, 5.6 Hz, 1H), 3.06 (s, 2H), 1.38 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 171.3, 170.8, 159.9, 155.3, 142.3, 139.7, 138.6, 136.3, 135.3, 130.8, 129.7, 128.1, 123.1, 121.8, 121.6, 119.9, 80.1, 75.3, 52.8, 52.2, 50.6, 42.0, 29.7, 28.3 ppm.

HRMS calcd for $C_{42}H_{43}N_5O_7$ $[M + H]^+$ 730.3235, found 730.3230.



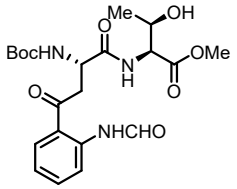
methyl ((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-serinate (5j)

29.7 mg, 68% yield; R_f = 0.2 (PE/EA = 1/1); yellow oil; [α]20 D = +13 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.26 (s, 1H), 8.69 (d, *J* = 8.5 Hz, 1H), 8.46 (d, *J* = 2.0 Hz, 1H), 7.90 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 5.85 (dd, *J* = 37.0, 8.7 Hz, 1H), 4.77 (s, 1H), 4.64 – 4.62 (m, 1H), 3.97 (s, 2H), 3.75 (s, 4H), 3.54 – 3.45 (m, 2H), 1.45 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 171.3, 170.7, 160.2, 155.7, 139.7, 135.5, 130.9, 123.3, 121.8, 80.9, 62.6, 55.0, 52.8, 50.6, 42.0, 28.3 ppm.

HRMS calcd for $C_{20}H_{27}N_3O_8$ $[M + H]^+$ 438.1871, found 438.1863.



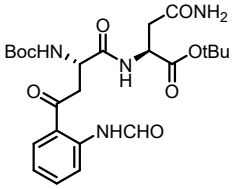
methyl ((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-threoninate (5k)

31.8 mg, 70% yield; R_f = 0.2 (PE/EA = 1/1); yellow oil; [α]20 D = +1 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.28 (s, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.46 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 5.77 (d, *J* = 8.8 Hz, 1H), 4.82 (s, 1H), 4.58 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.37 (d, *J* = 6.9 Hz, 1H), 3.80 – 3.71 (m, 4H), 3.49 (dd, *J* = 18.0, 6.0 Hz, 1H), 3.07 (s, 1H), 1.45 (s, 9H), 1.25 (d, *J* = 6.5 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 171.6, 171.1, 160.1, 155.5, 139.6, 135.5, 130.8, 123.3, 121.8, 121.7, 80.7, 68.1, 57.6, 52.6, 50.7, 41.9, 28.3, 19.9 ppm.

HRMS calcd for $C_{21}H_{29}N_3O_8$ $[M + H]^+$ 452.2027, found 452.2032.



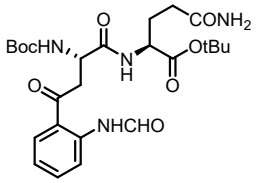
tert-butyl ((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-asparaginate (5l)

30.1 mg, 59% yield; R_f = 0.2 (PE/EA = 1/2); yellow solid, m.p. 90 – 92 °C; [α]20 D = +10 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.59 (d, *J* = 8.4 Hz, 1H), 8.45 (s, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 4.72 (t, *J* = 6.3 Hz, 1H), 4.61 (t, *J* = 5.3 Hz, 1H), 3.62 – 3.50 (m, 2H), 2.85 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.74 (dd, *J* = 16.0, 5.0 Hz, 1H), 1.46 (s, 9H), 1.45 (s, 9H) ppm.

^{13}C NMR (101 MHz, Methanol-d_4) δ 201.2, 173.6, 172.4, 169.8, 161.1, 156.3, 138.6, 134.3, 130.7, 123.3, 123.1, 121.3, 81.8, 79.6, 50.6, 49.8, 41.6, 36.0, 27.3, 26.8 ppm.

HRMS calcd for $C_{24}H_{34}N_4O_8$ $[M + H]^+$ 507.2449, found 507.2460.



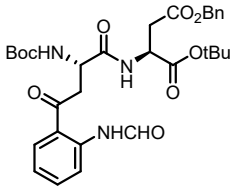
tert-butyl ((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-glutaminate (5m)

31.6 mg, 61% yield; R_f = 0.2 (PE/EA = 1/2); white solid, m.p. 167 – 169 °C; [α]20 D = –6 (*c* = 0.10, DMSO).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.11 (s, 1H), 8.47 (s, 2H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.78 (s, 1H), 4.53 (d, *J* = 6.5 Hz, 1H), 4.10 (d, *J* = 5.1 Hz, 1H), 2.13 (t, *J* = 7.9 Hz, 2H), 1.99 – 1.87 (m, 1H), 1.83 – 1.74 (m, 1H), 1.40 (s, 9H), 1.37 (s, 9H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6) δ 200.9, 173.9, 171.9, 171.3, 161.7, 155.7, 138.5, 134.6, 131.2, 124.3, 123.8, 121.6, 81.2, 78.7, 52.9, 50.8, 42.1, 31.6, 28.6, 28.1, 27.3 ppm.

HRMS calcd for $C_{25}H_{36}N_4O_8$ $[M + H]^+$ 521.2606, found 521.2612.



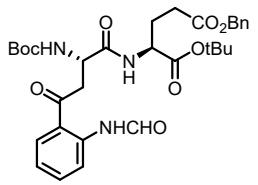
4-benzyl 1-(tert-butyl) ((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-aspartate (5n)

45.5 mg, 76% yield; R_f = 0.5 (PE/EA = 1/2); orange oil; [α]20 D = +6 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.19 (s, 1H), 8.71 (d, *J* = 8.5 Hz, 1H), 8.38 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.32 (m, 5H), 7.14 (t, *J* = 7.7 Hz, 1H), 5.59 (d, *J* = 8.4 Hz, 1H), 5.21 – 5.11 (m, 2H), 4.75 (s, 1H), 4.68 (dt, *J* = 8.4, 4.5 Hz, 1H), 3.78 (d, *J* = 16.8 Hz, 1H), 3.40 (dd, *J* = 18.1, 5.9 Hz, 1H), 3.02 (dd, *J* = 17.0, 4.4 Hz, 1H), 2.89 (dd, *J* = 16.9, 4.8 Hz, 1H), 1.47 (s, 9H), 1.38 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 170.9, 170.6, 169.1, 160.0, 155.3, 139.7, 135.5, 135.4, 130.8, 128.6, 128.5, 128.4, 123.1, 121.8, 121.7, 82.7, 80.6, 66.8, 50.4, 49.5, 42.3, 36.3, 28.3, 27.8 ppm.

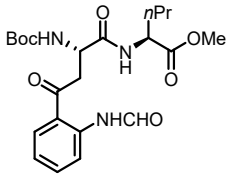
HRMS calcd for $C_{31}H_{39}N_3O_9$ $[M + H]^+$ 598.2759, found 598.2787.



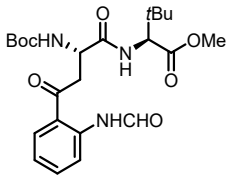
5-benzyl 1-(tert-butyl) ((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-glutamate (5o)

42.9 mg, 70% yield; R_f = 0.5 (PE/EA = 1/2); orange solid, m.p. 113 – 115 °C; [α]20 D = –4 (*c* = 0.10, MeOH).

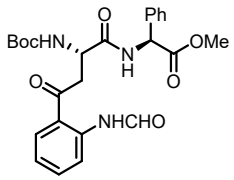
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.24 (s, 1H), 8.71 (d, *J* = 8.5 Hz, 1H), 8.38 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.33 (s, 5H), 7.15 (dd, *J* = 7.8, 2.7 Hz, 2H), 5.59 (d, *J* = 8.9 Hz, 1H), 5.12 (s, 2H), 4.71 (s, 1H), 4.51 (td, *J* = 7.9, 4.7 Hz, 1H), 3.85 (dd, *J* = 18.1, 4.3 Hz, 1H), 3.39 (dd, *J* = 18.1, 5.3 Hz, 1H), 2.53 (ddd, *J* = 16.1, 9.6, 6.4 Hz, 1H), 2.47 – 2.39 (m, 1H), 2.27 (tt, *J* = 11.2, 6.0 Hz, 1H), 2.05 – 1.98 (m, 1H), 1.46 (s, 9H), 1.45 (s, 9H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 172.7, 170.8, 170.5, 160.1, 155.4, 139.9, 135.7, 135.6, 130.9, 128.6, 128.3, 128.2, 123.2, 121.7, 121.5, 82.6, 80.8, 66.5, 52.3, 50.6, 41.8, 30.1, 28.3, 28.0, 27.7 ppm.
HRMS calcd for $C_{32}H_{41}N_3O_9$ $[M + H]^+$ 612.2916, found 612.2913.



methyl (S)-2-((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanamido)pentanoate (5p)
34.6 mg, 77% yield; R_f = 0.4 (PE/EA = 2/1); yellow solid, m.p. 123 – 125 °C; [α]20 D = –17 (*c* = 0.10, MeOH).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 8.71 (d, *J* = 8.4 Hz, 1H), 8.47 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 5.71 (d, *J* = 8.7 Hz, 1H), 4.75 (s, 1H), 4.56 (q, *J* = 7.6 Hz, 1H), 3.78 – 3.71 (m, 4H), 3.44 (dd, *J* = 18.0, 6.1 Hz, 1H), 1.88 – 1.79 (m, 1H), 1.73 – 1.62 (m, 1H), 1.47 (s, 9H), 1.42 – 1.34 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 172.6, 170.8, 159.8, 155.5, 139.8, 135.5, 130.9, 123.2, 121.7, 80.6, 52.3, 52.2, 50.6, 41.6, 34.4, 28.3, 18.5, 13.6 ppm.
HRMS calcd for $C_{22}H_{31}N_3O_7$ $[M + H]^+$ 450.2235, found 450.2246.



methyl (S)-2-((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanamido)-3,3-dimethylbutanoate (5q)
38.7 mg, 83% yield; R_f = 0.6 (PE/EA = 2/1); yellow oil; [α]20 D = –7 (*c* = 0.10, MeOH).
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.28 (s, 1H), 8.70 (d, *J* = 8.4 Hz, 1H), 8.47 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 2H), 5.77 (d, *J* = 8.5 Hz, 1H), 4.74 (s, 1H), 4.39 (d, *J* = 9.3 Hz, 1H), 3.77 – 3.69 (m, 4H), 3.43 (dd, *J* = 17.9, 6.2 Hz, 1H), 1.47 (s, 9H), 1.00 (s, 9H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 171.5, 170.7, 159.8, 155.6, 139.7, 135.4, 130.8, 123.2, 121.8, 121.7, 80.7, 60.4, 51.8, 51.8, 50.8, 41.2, 34.8, 28.3, 26.5 ppm.
HRMS calcd for $C_{23}H_{33}N_3O_7$ $[M + H]^+$ 464.2391, found 464.2388.



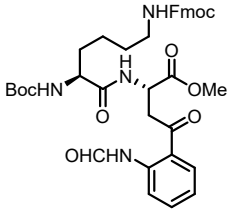
methyl (S)-2-((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanamido)-2-phenylacetate (5r)

37.5 mg, 76% yield; R_f = 0.4 (PE/EA = 2/1); yellow solid, m.p. 95 – 97 °C ; [α]20 D = +56 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.23 (s, 1H), 8.69 (d, *J* = 8.5 Hz, 1H), 8.41 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.68 (s, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.39 (m, 2H), 7.34 – 7.31 (m, 2H), 7.12 (t, *J* = 7.7 Hz, 1H), 5.71 (d, *J* = 8.8 Hz, 1H), 5.52 (d, *J* = 7.2 Hz, 1H), 4.80 (s, 1H), 3.74 – 3.70 (m, 4H), 3.44 (dd, *J* = 18.1, 6.0 Hz, 1H), 1.45 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 170.9, 170.5, 159.9, 155.6, 139.7, 136.2, 135.5, 130.8, 128.9, 128.6, 127.2, 123.2, 121.7, 121.6, 80.7, 56.7, 52.9, 52.8, 50.5, 41.6, 28.3 ppm.

HRMS calcd for $C_{25}H_{29}N_3O_7$ $[M + H]^+$ 484.2078, found 484.2087.



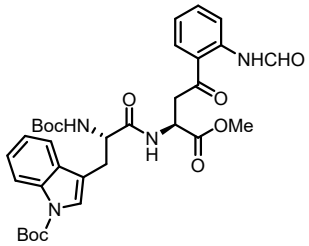
methyl (S)-2-((S)-6-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-2-((tert-butoxycarbonyl)amino)hexanamido)-4-(2-formamidophenyl)-4-oxobutanoate (6a)

36.0 mg, 51% yield; R_f = 0.4 (PE/EA = 1/1); yellow solid, m.p. 88 – 90 °C; [α]20 D = +11 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.73 (d, *J* = 8.5 Hz, 1H), 8.43 (s, 1H), 7.86 (d, *J* = 7.4 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.60 – 7.54 (m, 3H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.16 – 7.12 (m, 2H), 5.27 (d, *J* = 7.6 Hz, 1H), 5.12 (s, 1H), 4.99 – 4.97 (m, 1H), 4.40 (p, *J* = 10.2, 9.3 Hz, 4H), 4.20 (t, *J* = 6.9 Hz, 1H), 4.15 – 4.10 (m, 1H), 3.81 – 3.74 (m, 4H), 3.65 (dd, *J* = 18.3, 4.2 Hz, 1H), 3.19 – 3.06 (m, 2H), 1.86 – 1.83 (m, 1H), 1.69 – 1.62 (m, 1H), 1.53 – 1.52 (m, 2H), 1.37 (s, 10H), 1.27 (t, *J* = 3.5 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.6, 172.2, 171.5, 160.0, 156.7, 155.6, 144.0, 144.0, 141.3, 140.0, 135.8, 130.9, 127.7, 127.1, 125.1, 123.2, 121.7, 121.0, 120.0, 80.0, 66.5, 54.3, 52.9, 48.1, 47.3, 41.7, 40.4, 31.9, 29.4, 28.2, 22.4 ppm.

HRMS calcd for $C_{38}H_{44}N_4O_9$ $[M + H]^+$ 701.3181, found 701.3188.



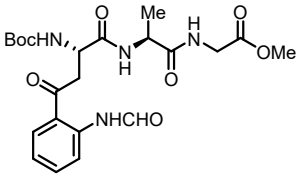
tert-butyl 3-((S)-2-((tert-butoxycarbonyl)amino)-3-(((S)-4-(2-formamidophenyl)-1-methoxy-1,4-dioxobutan-2-yl)amino)-3-oxopropyl)-1H-indole-1-carboxylate (6b)

49.6 mg, 78% yield; R_f = 0.3 (PE/EA = 1/1); yellow solid, m.p. 132 – 134 °C; [α]20 D = +22 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.19 (s, 1H), 8.72 (d, *J* = 8.5 Hz, 1H), 8.45 (s, 1H), 8.06 (d, *J* = 5.7 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.50 (m, 3H), 7.24 – 7.12 (m, 3H), 6.95 (d, *J* = 7.9 Hz, 1H), 5.30 (s, 1H), 4.87 – 4.85 (m, 1H), 4.49 (d, *J* = 7.3 Hz, 1H), 3.74 – 3.69 (m, 4H), 3.52 (d, *J* = 14.6 Hz, 1H), 3.27 – 3.14 (m, 2H), 1.65 (s, 9H), 1.38 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 171.3, 171.0, 160.0, 155.3, 149.6, 140.1, 135.7, 135.5, 131.0, 130.2, 124.6, 124.5, 123.1, 122.6, 121.6, 120.8, 119.1, 115.4, 115.2, 83.7, 80.2, 80.2, 54.3, 52.8, 48.2, 41.5, 28.2, 28.2 ppm.

HRMS calcd for $C_{33}H_{40}N_4O_9$ $[M + H]^+$ 637.2868, found 637.2867.



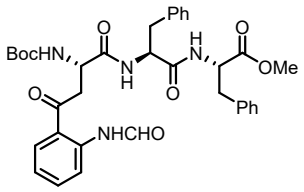
methyl ((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-alanylglycinate (8a)

31.6 mg, 66% yield; R_f = 0.3 (DCM/MeOH = 20/1); white solid, m.p. 151 – 153 °C; [α]20 D = –8 (*c* = 0.10, DMSO).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.30 (s, 1H), 8.70 (d, *J* = 8.5 Hz, 1H), 8.48 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.14 (t, *J* = 7.3 Hz, 2H), 5.68 (d, *J* = 8.9 Hz, 1H), 4.70 (s, 1H), 4.55 (t, *J* = 7.2 Hz, 1H), 4.06 (dd, *J* = 18.2, 5.6 Hz, 1H), 3.96 (dd, *J* = 18.2, 5.1 Hz, 1H), 3.70 – 3.66 (m, 4H), 3.54 (dd, *J* = 17.7, 6.4 Hz, 1H), 1.45 – 1.41 (m, 12H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 172.3, 171.2, 170.3, 160.2, 155.6, 139.8, 135.5, 131.0, 123.2, 121.7, 121.6, 80.8, 52.3, 50.7, 49.0, 41.7, 41.2, 28.3, 17.9 ppm.

HRMS calcd for $C_{22}H_{30}N_4O_8$ $[M + H]^+$ 479.2136, found 479.2136.



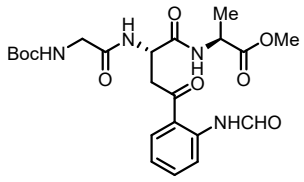
methyl ((S)-2-((tert-butoxycarbonyl)amino)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-phenylalanylphenylalaninate (8b)

46.1 mg, 72% yield; R_f = 0.4 (PE/EA = 1/1); light yellow solid, m.p. 148 – 150 °C; [α]20 D = –9 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.17 (s, 1H), 8.71 (d, *J* = 8.4 Hz, 1H), 8.42 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.29 – 7.13 (m, 9H), 6.96 (t, *J* = 8.7 Hz, 3H), 6.57 (d, *J* = 7.8 Hz, 1H), 5.39 (d, *J* = 9.1 Hz, 1H), 4.79 (q, *J* = 6.5 Hz, 1H), 4.61 (d, *J* = 7.1 Hz, 2H), 3.69 – 3.15 (m, 4H), 3.41 (dd, *J* = 17.9, 6.3 Hz, 1H), 3.18 – 2.95 (m, 4H), 1.46 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 171.5, 171.0, 170.0, 160.2, 155.4, 139.9, 136.5, 135.6, 130.9, 129.5, 129.2, 128.7, 128.5, 127.1, 127.0, 123.2, 121.7, 121.4, 80.8, 54.5, 53.4, 52.3, 50.7, 41.6, 38.0, 37.6, 28.3 ppm.

HRMS calcd for $C_{35}H_{40}N_4O_8$ $[M + H]^+$ 645.2919, found 645.2915.



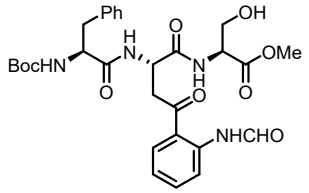
methyl ((S)-2-(2-((tert-butoxycarbonyl)amino)acetamido)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-alaninate (8c)

33.8 mg, 71% yield; R_f = 0.2 (PE/EA = 1/2); yellow solid, m.p. 139 – 141 °C; [α]20 D = –7 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.26 (s, 1H), 8.70 (d, *J* = 8.4 Hz, 1H), 8.47 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 5.38 (t, *J* = 5.7 Hz, 1H), 5.07 (s, 1H), 4.51 (p, *J* = 6.9 Hz, 1H), 3.85 – 3.81 (m, 3H), 3.69 (s, 3H), 3.40 (dd, *J* = 18.1, 6.1 Hz, 1H), 1.44 – 1.43 (m, 12H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 172.9, 170.2, 169.7, 159.9, 156.4, 139.7, 135.6, 130.9, 123.3, 121.7, 121.6, 80.6, 52.4, 48.9, 48.5, 44.7, 41.5, 28.3, 17.8 ppm.

HRMS calcd for $C_{22}H_{30}N_4O_8$ $[M + H]^+$ 479.2136, found 479.2140.



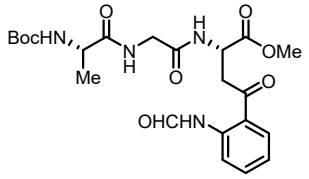
methyl ((S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-serinate (8d)

31.7 mg, 54% yield; R_f = 0.2 (PE/EA = 1/2); yellow solid, m.p. 165 – 167 °C; [α]20 D = +8 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.45 (d, *J* = 8.4 Hz, 1H), 8.30 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.14 – 7.12 (m, 5H), 7.06 – 7.04 (m, 1H), 4.91 (t, *J* = 6.4 Hz, 1H), 4.42 (t, *J* = 4.3 Hz, 1H), 4.23 (dd, *J* = 9.4, 5.0 Hz, 1H), 3.81 (dd, *J* = 11.3, 4.5 Hz, 1H), 3.72 (dd, *J* = 11.3, 4.1 Hz, 1H), 3.60 (s, 3H), 3.52 (dd, *J* = 17.9, 5.8 Hz, 1H), 3.44 (dd, *J* = 18.1, 6.5 Hz, 1H), 3.03 (dd, *J* = 13.9, 5.1 Hz, 1H), 2.73 (dd, *J* = 13.9, 9.4 Hz, 1H), 1.22 (s, 9H) ppm.

^{13}C NMR (101 MHz, Methanol-d_4) δ 200.9, 173.0, 171.6, 170.7, 161.0, 156.4, 138.5, 137.2, 134.3, 130.6, 129.0, 128.0, 126.3, 123.4, 123.2, 121.4, 79.4, 61.3, 56.0, 55.0, 51.5, 49.3, 41.1, 37.5, 27.2 ppm.

HRMS calcd for $C_{29}H_{36}N_4O_9$ $[M + H]^+$ 585.2555, found 585.2554.



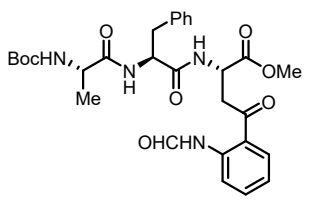
methyl (6S,12S)-12-(2-(2-formamidophenyl)-2-oxoethyl)-2,2,6-trimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-oate (8e)

42.0 mg, 88% yield; R_f = 0.1 (PE/EA = 1/2);yellow solid, m.p. 74 – 76 °C; [α]20 D = +19 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 8.72 (d, *J* = 8.4 Hz, 1H), 8.48 (s, 1H), 7.90 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 5.4 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 5.35 (s, 1H), 5.00 – 4.98 (m, 1H), 4.22 (t, *J* = 7.2 Hz, 1H), 4.04 (dd, *J* = 17.3, 5.6 Hz, 1H), 3.97 (dd, *J* = 16.8, 5.3 Hz, 1H), 3.79 – 3.65 (m, 5H), 1.41 (s, 9H), 1.36 (d, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 173.5, 171.3, 168.9, 160.1, 155.6, 139.9, 135.7, 130.9, 123.2, 121.7, 121.2, 80.2, 52.9, 52.8, 50.2, 48.2, 43.0, 41.7, 28.3, 28.3, 18.4 ppm.

HRMS calcd for $C_{22}H_{30}N_4O_8$ $[M + H]^+$ 479.2136, found 393.2134.



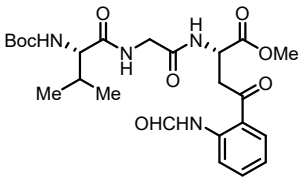
methyl (6S,9S,12S)-9-benzyl-12-(2-(2-formamidophenyl)-2-oxoethyl)-2,2,6-trimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-oate (8f)

38.3 mg, 67% yield; R_f = 0.6 (PE/EA = 1/2); white solid, m.p. 194 – 196 °C; [α]20 D = +17 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.07 (s, 1H), 8.48 (d, *J* = 6.7 Hz, 3H), 8.03 (d, *J* = 7.4 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 4.4 Hz, 3H), 7.18 – 7.15 (m, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 4.79 (q, *J* = 6.5 Hz, 1H), 4.54 (q, *J* = 8.4 Hz, 2H), 3.90 (t, *J* = 7.3 Hz, 1H), 3.63 (s, 3H), 3.57 – 3.48 (m, 2H), 3.01 (dd, *J* = 13.9, 4.9 Hz, 1H), 2.81 (dd, *J* = 13.9, 8.6 Hz, 1H), 1.36 (s, 9H), 1.07 (d, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6) δ 200.5, 172.8, 172.0, 171.3, 161.8, 155.4, 138.7, 137.8, 135.0, 131.5, 129.8, 128.4, 126.7, 123.8, 123.7, 121.6, 78.6, 53.5, 52.6, 50.3, 48.4, 41.6, 38.3, 28.6, 18.6 ppm.

HRMS calcd for $C_{29}H_{36}N_4O_8$ $[M + H]^+$ 569.2606, found 569.2600.



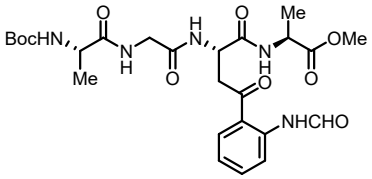
methyl (6S,12S)-12-(2-(2-formamidophenyl)-2-oxoethyl)-6-isopropyl-2,2-dimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-oate (8g)

43.4 mg, 86% yield; R_f = 0.1 (PE/EA = 1/1);brown oil; [α]20 D = +15 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.72 (d, *J* = 8.5 Hz, 1H), 8.48 (s, 1H), 7.90 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.32 (s, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 5.39 (d, *J* = 8.5 Hz, 1H), 5.02 – 5.00 (m, 1H), 4.03 (s, 3H), 3.80 – 3.64 (m, 5H), 2.11 (q, *J* = 6.7 Hz, 1H), 1.41 (s, 9H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 172.6, 171.3, 169.0, 160.2, 156.0, 139.9, 135.7, 130.9, 123.2, 121.7, 121.2, 79.9, 59.8, 52.8, 52.8, 48.2, 43.0, 41.7, 31.0, 28.3, 19.3, 17.8 ppm.

HRMS calcd for $C_{24}H_{34}N_4O_8$ $[M + H]^+$ 507.2449, found 507.2447.



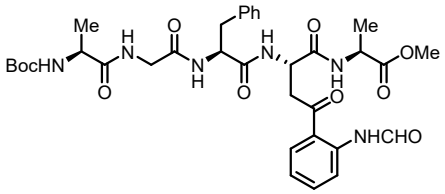
methyl ((S)-2-(2-((S)-2-((tert-butoxycarbonyl)amino)propanamido)acetamido)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-alaninate (8h)

39.5 mg, 72% yield; R_f = 0.1 (PE/EA = 1/6); yellow solid, m.p. 116 – 118 °C; [α]20 D = –10 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.47 (d, *J* = 8.4 Hz, 1H), 8.33 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.49 (td, *J* = 8.5, 7.2, 1.1 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 4.92 (t, *J* = 6.3 Hz, 1H), 4.31 (q, *J* = 7.3 Hz, 1H), 3.91 (q, *J* = 7.1 Hz, 1H), 3.76 (s, 2H), 3.61 – 3.55 (m, 4H), 3.46 (dd, *J* = 17.9, 7.1 Hz, 1H), 1.33 (d, *J* = 7.3 Hz, 3H), 1.27 (s, 9H), 1.21 (d, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Methanol-d_4) δ 200.6, 175.4, 173.0, 171.6, 170.3, 161.1, 156.7, 138.6, 134.3, 130.6, 123.3, 123.0, 121.4, 79.4, 51.4, 50.7, 49.2, 48.4, 42.5, 41.0, 27.3, 16.4, 15.9 ppm.

HRMS calcd for $C_{25}H_{35}N_5O_9$ $[M + H]^+$ 550.2508, found 550.2513.



methyl ((S)-2-((S)-2-(2-((S)-2-((tert-butoxycarbonyl)amino)propanamido)acetamido)-3-phenylpropanamido)-4-(2-formamidophenyl)-4-oxobutanoyl)-L-alaninate (8i)

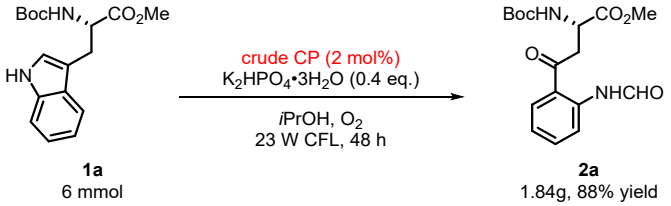
48.1 mg, 69% yield; R_f = 0.2 (DCM/MeOH = 20/1); brown solid, m.p. 186 – 188 °C; [α]20 D = – 24 (*c* = 0.10, MeOH).

^{1}H NMR (400 MHz, Methanol-d_4) δ 8.48 (d, *J* = 8.4 Hz, 1H), 8.33 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.49 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H), 7.16 – 7.06 (m, 5H), 7.03 – 6.99 (m, 1H), 4.80 (s, 1H), 4.47 (dd, *J* = 8.7, 5.7 Hz, 1H), 4.28 (q, *J* = 7.3 Hz, 1H), 3.84 (q, *J* = 7.2 Hz, 1H), 3.73 (d, *J* = 16.7 Hz, 1H), 3.64 (d, *J* = 16.8 Hz, 1H), 3.59 (s, 3H), 3.20 (p, *J* = 1.7 Hz, 1H), 3.10 (dd, *J* = 14.2, 5.6 Hz, 1H), 2.86 (dd, *J* = 14.1, 8.8 Hz, 1H), 1.30 – 1.28 (m, 12H), 1.14 (d, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Methanol-d_4) δ 200.6, 175.3, 173.1, 172.0, 171.4, 170.6, 161.1, 156.6, 138.6, 136.8, 134.3, 130.7, 128.8, 128.1, 126.4, 123.4, 123.1, 121.4, 79.4, 55.1, 51.4, 50.7, 49.3, 48.5, 48.4, 42.4, 36.7, 27.4, 16.6, 16.0 ppm.

HRMS calcd for $C_{34}H_{44}N_6O_{10}$ $[M + H]^+$ 697.3192, found 697.3207.

4. General procedure for the gram-scale synthesis of 2a



1a
6 mmol

2a
1.84g, 88% yield

The crude cercosporin was used directly after extraction and concentration from the fermentation broth of *Cercospora* without further purification for the convenience in the gram-scale synthesis. A sealed oven-dried three-necked bottle was charged with the substrate **1a** (6 mmol, 1 equiv), crude cercosporin (2 mol%), and $K_2HPO_4 \cdot 3H_2O$ (0.4 equiv). The vial is thoroughly flushed with O_2, and *i*PrOH (0.05 M) was added under O_2 atmosphere. The mixtures were stirred at room temperature and irradiated with two 23 W CFL under O_2 atmosphere. After completion, the solution was concentrated *in vacuo* and purified by chromatography on silica gel (200–300 mesh) (PE/EA or DCM/MeOH) to afford the desired product **2a** (1.84 g) in 88% yield.

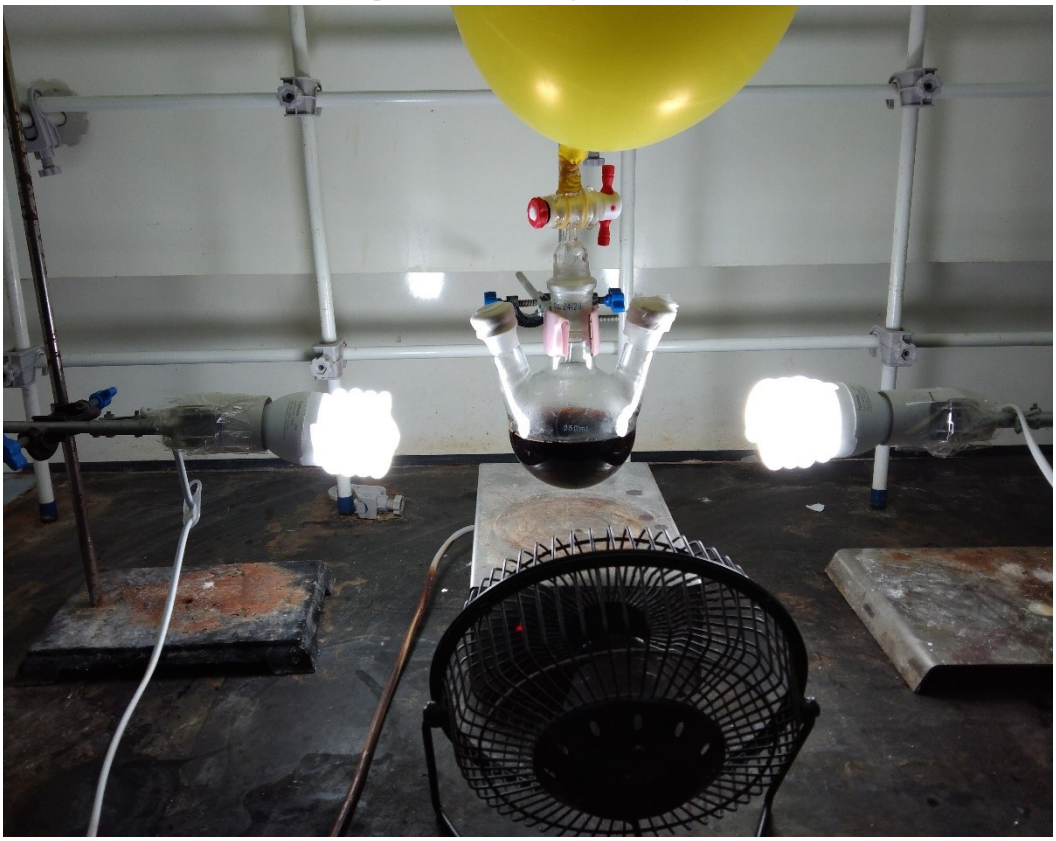
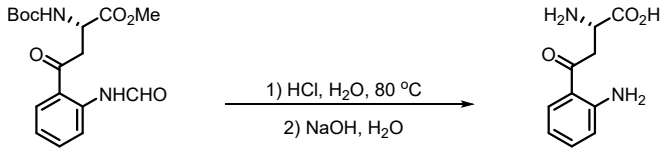


Figure S1. Photochemical reaction set up for the gram-scale synthesis

5. General procedure for synthesis of kynurenine 9



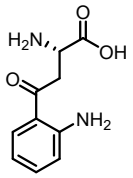
2a **9**

2a (0.1 mmol), water (1 mL), and concentrated HCl (0.6 mmol, 6 equiv) were charged to an oven-dried Schlenk tube with a mechanical stirrer. The mixture was heated to 70°C for 4 h. After

completion, the reaction mixture slowly cooled to room temperature. The cooled reaction mixture was basified to pH 12 with 50% sodium hydroxide, and stirred for 6 h at room temperature. The basic aqueous solution was washed with DCM (3 x 2 mL), ethyl acetate (3 x 2 mL), and MTBE (3 x 2 mL). Concentrated HCl was added in portions to the aqueous reaction mixture to adjust to pH 6.[6] The crude product was purified by semi-preparative high performance liquid chromatograph after dissolving in 3% (v/v) aqueous MeCN containing0.1%(v/v) TFA. The separation method was listed in Table S1 according to the literature.[7]

Table S1 HPLC conditions for preparation of kynurenine.

Stationary phase		Thermo Fisher GOLD HILIC 250*4.6 mm, 5 μm		
Mobile phase		0.1% TFA in H_2O	MeOH	MeCN
Gradient	0 min	95%	5%	0%
	-10 min	86%	14%	0%
	-30 min	46%	14%	40%
Flow		3 mL/min		
Temperature		30°C		
Detection		UV, 260 nm		



(S)-2-amino-4-(2-aminophenyl)-4-oxobutanoic acid (9)

10.8 mg, 52% yield; white solid, m.p. 182 – 184 °C; [α]20 D = –64 (*c* = 0.10, MeOH).

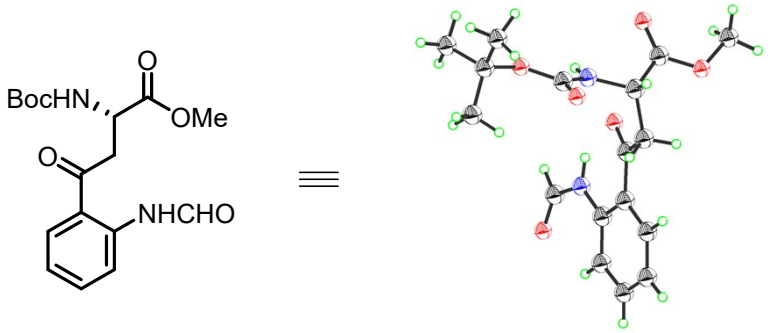
^{1}H NMR (400 MHz, DMSO-d_6 + 1% TFA) δ 7.70 (d, *J* = 8.1 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.56 (t, *J* = 7.5 Hz, 1H), 4.14 (t, *J* = 5.1 Hz, 1H), 3.56 (d, *J* = 4.5 Hz, 3H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6 + 1% TFA) δ 198.0, 171.2, 151.8, 135.2, 131.5, 117.5, 116.1, 115.1, 49.0, 39.4 ppm.

HRMS calcd for $C_{10}H_{12}N_2O_3$ $[M + H]^+$ 209.0921, found 209.0917.

HPLC for preparation: t_R = 18.2 min (conditions in Table S1).

6. Crystal Structure of 2a



2a **CCDC 2131727**

Figure S2. ORTEP plot of the crystal structure of 2a

Table S2 X-ray crystallographic data of **2a**

CCDC number	2131727		
Empirical formula	$C_{17}H_{22}N_2O_6$		
Formula weight	350.36		
Temperature	301 K		
Wavelength	1.54178 Å		
Space group	C 1 2 1		
Unit cell dimensions	a= 20.3983(8)	Å	=90º
	b= 8.6680(3)	Å	=90º
	c= 14.0946(6)	Å	=90º
Volume	2016.20(14) $Å^3$		
Z	4		
F(000)	744.0		
Completeness to theta = 66.680°	1.86/1.00		
Max. and min. transmission	0.860 and 0.660		
R indices (all data)	R= 0.0596(3362) wR2(reflections)= 0.1829(3580)		
S	1.179		

7. References

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Org. Chem., 2019, **2019**, 7596-7605.

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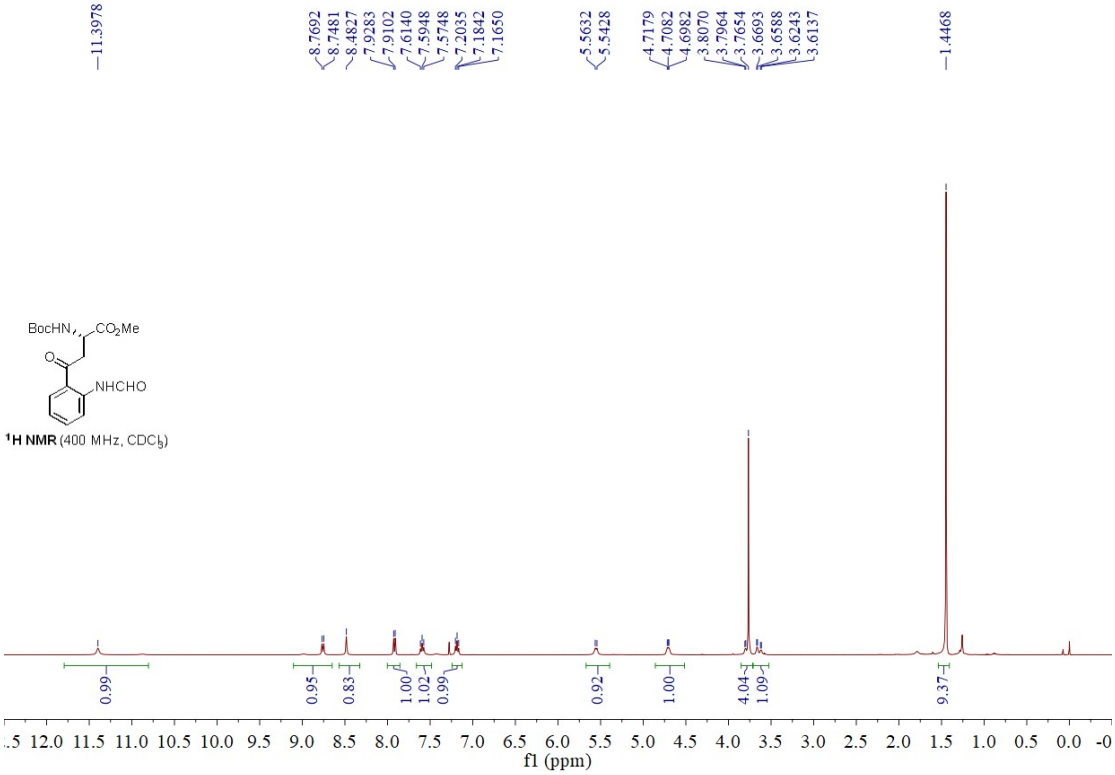
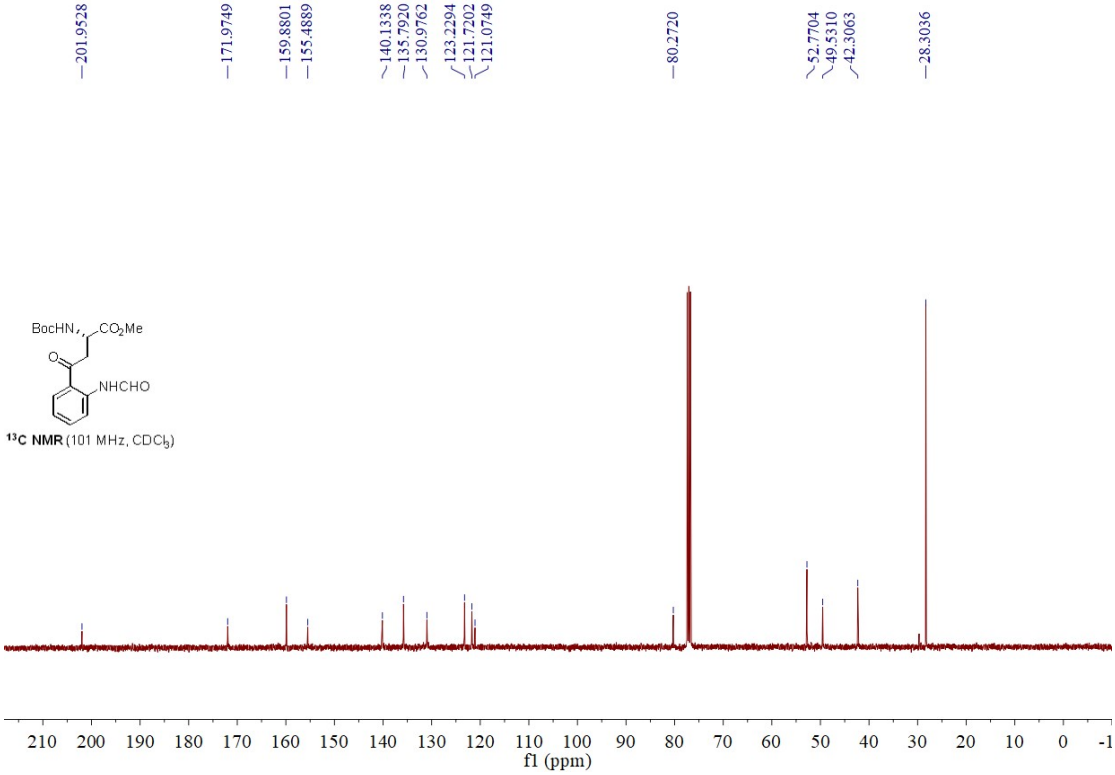
7. T. Simat, K. Meyer and H. Steinhart, *J. Chromatogr. A*, 1994, **661**, 93-99.

8. NMR spectra

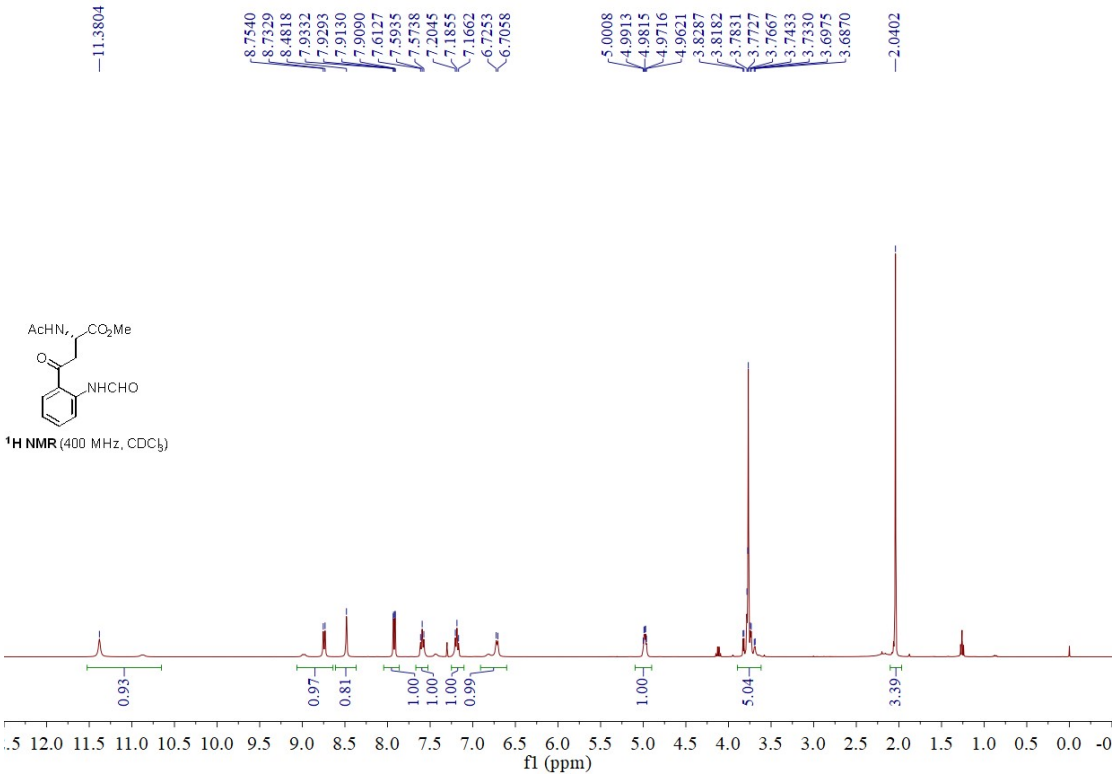
^{1}H NMR of **2a**



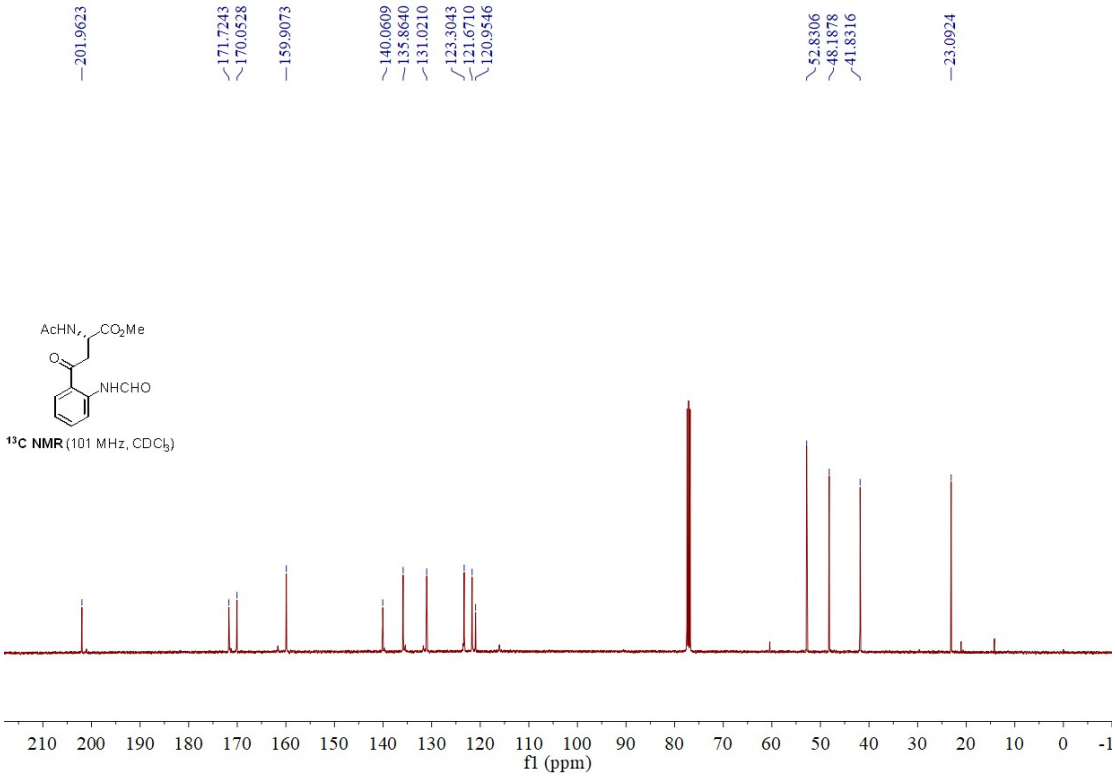
^{13}C NMR of **2a**



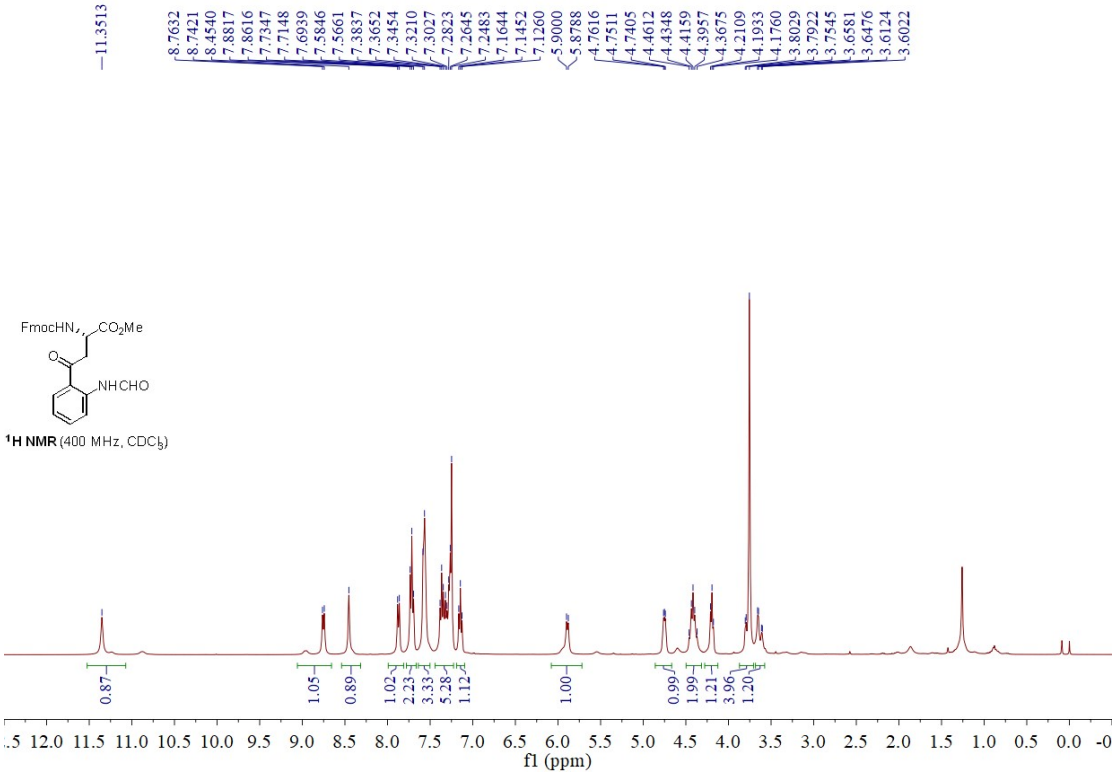
^{1}H NMR of **2b**



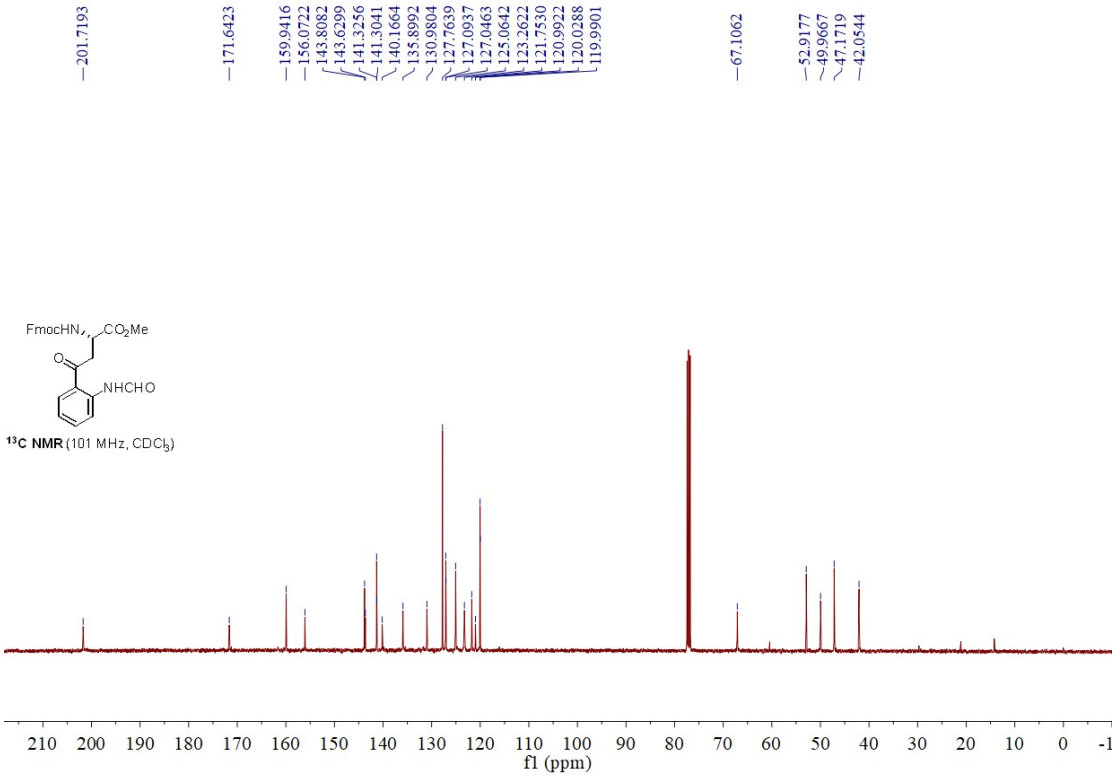
^{13}C NMR of **2b**



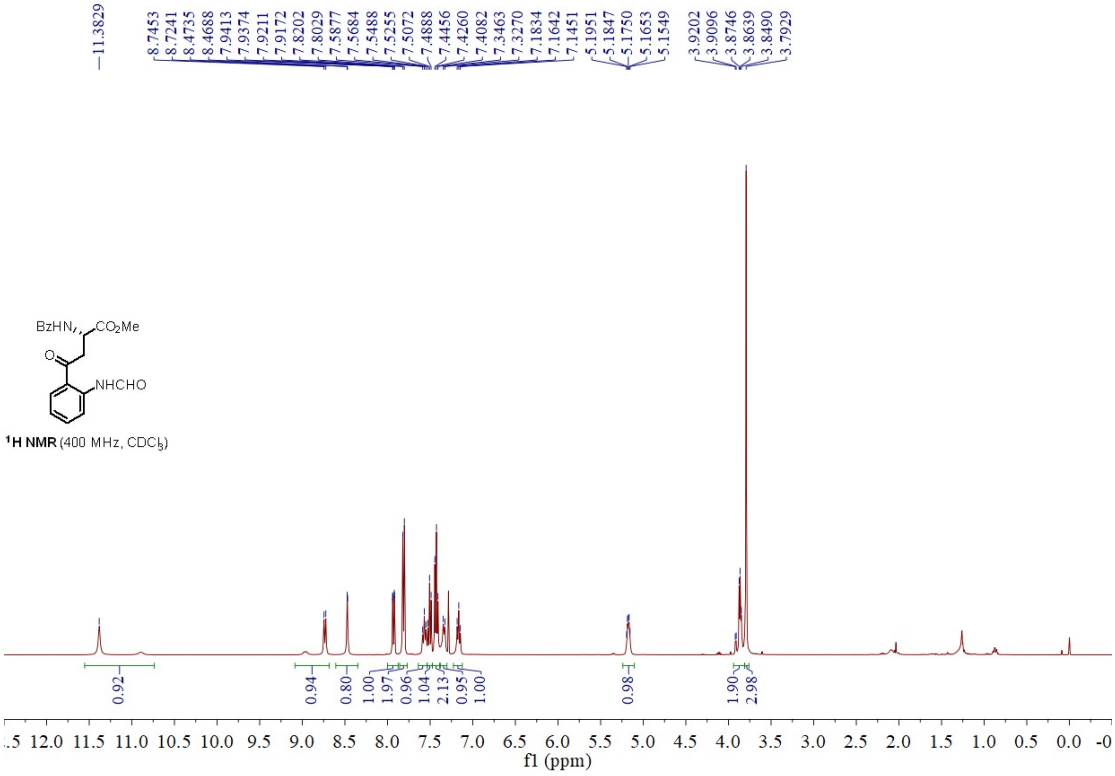
^{1}H NMR of **2c**



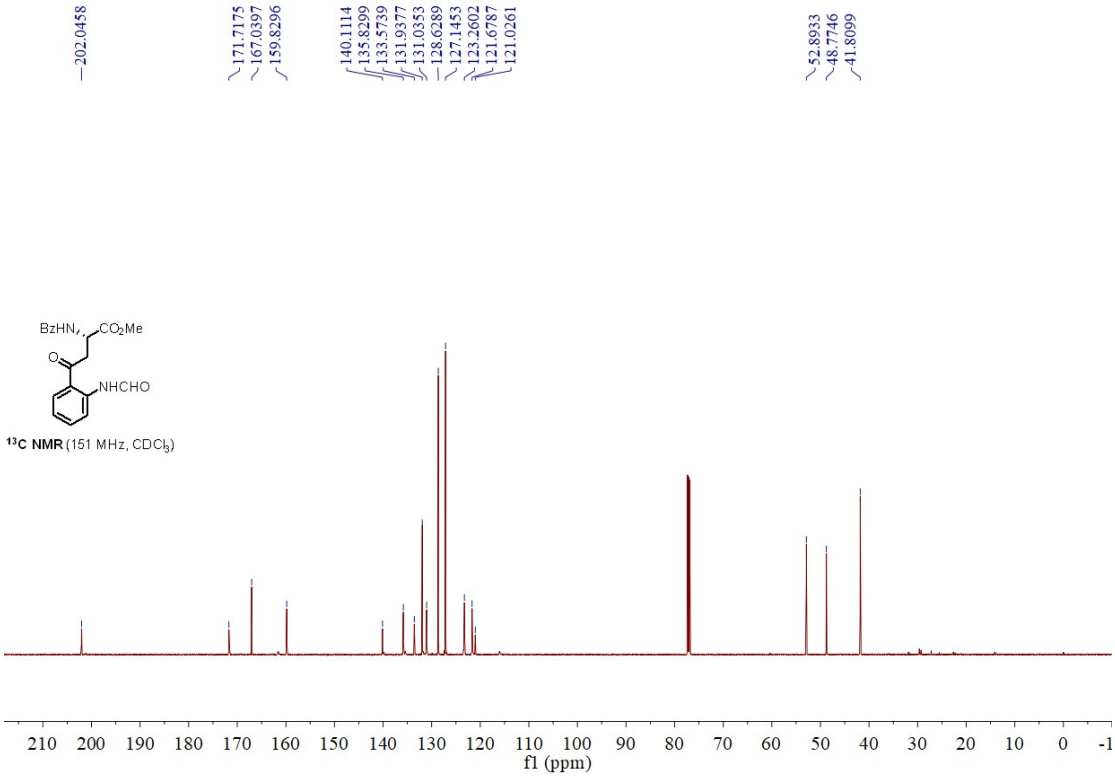
^{13}C NMR of **2c**



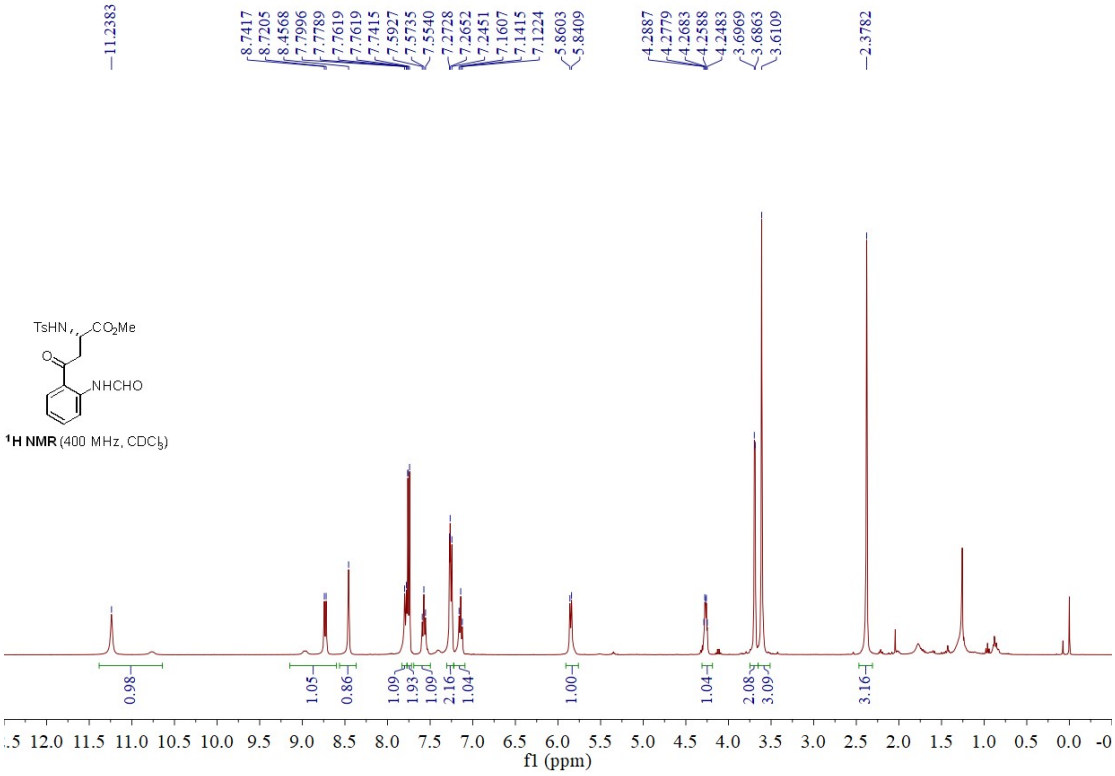
^{1}H NMR of **2d**



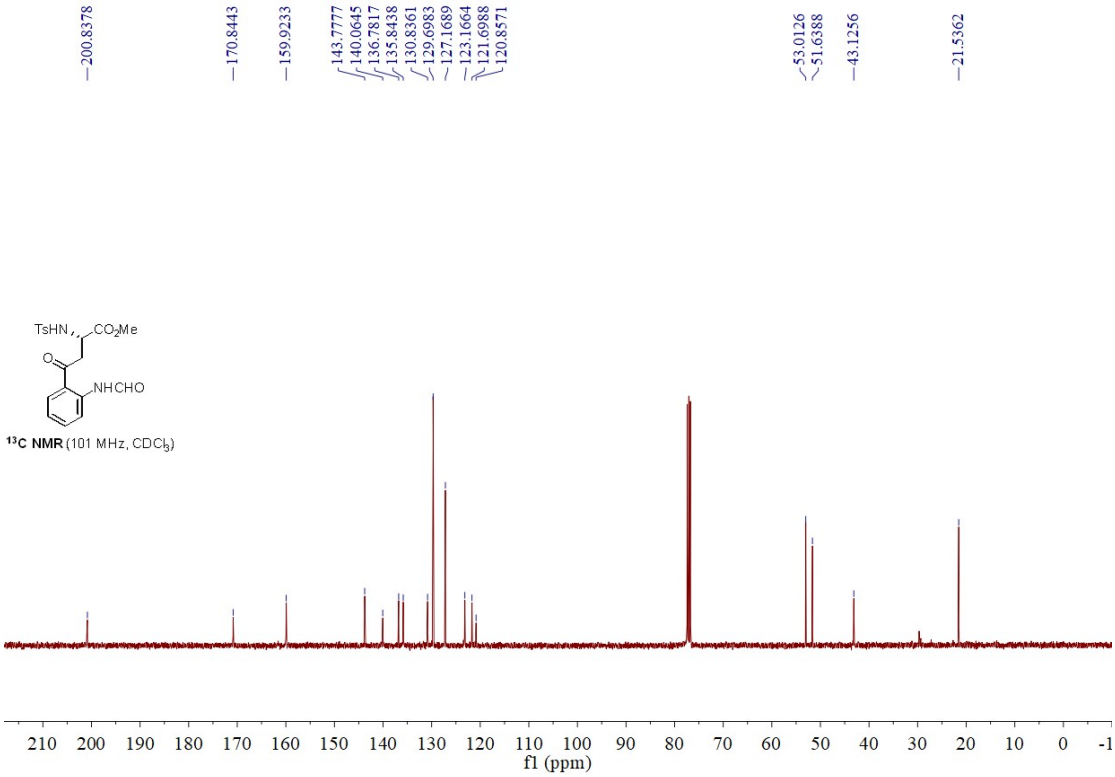
^{13}C NMR of **2d**



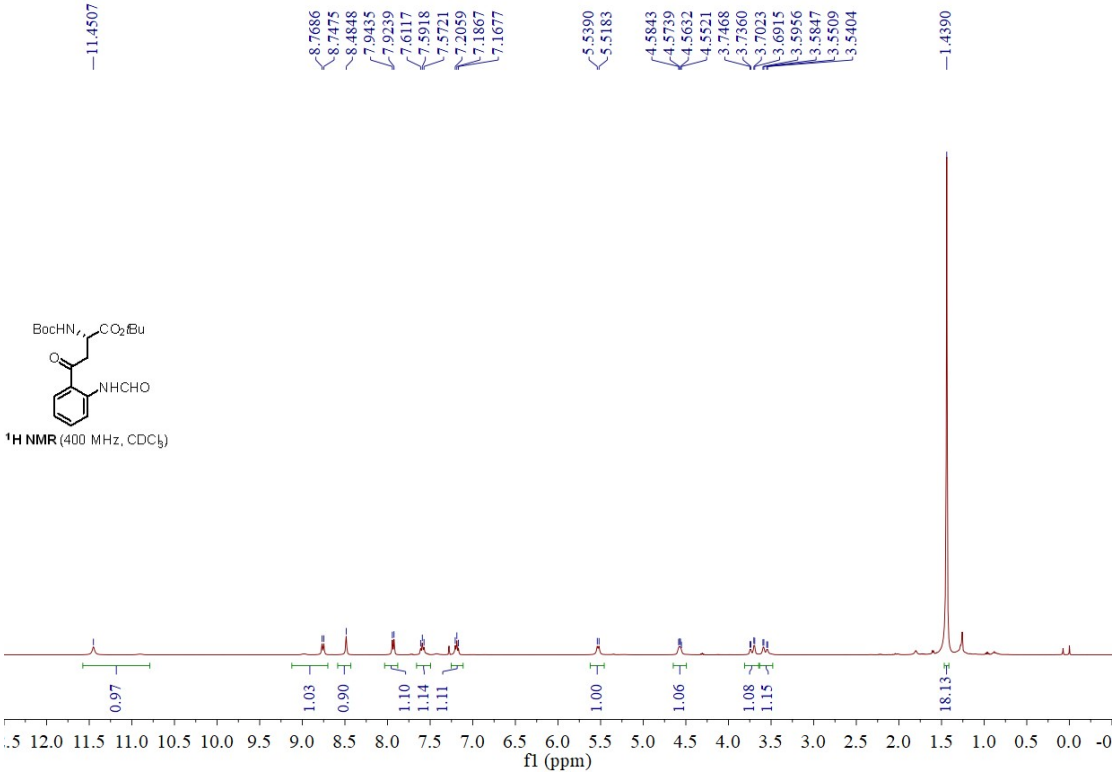
^{1}H NMR of **2e**



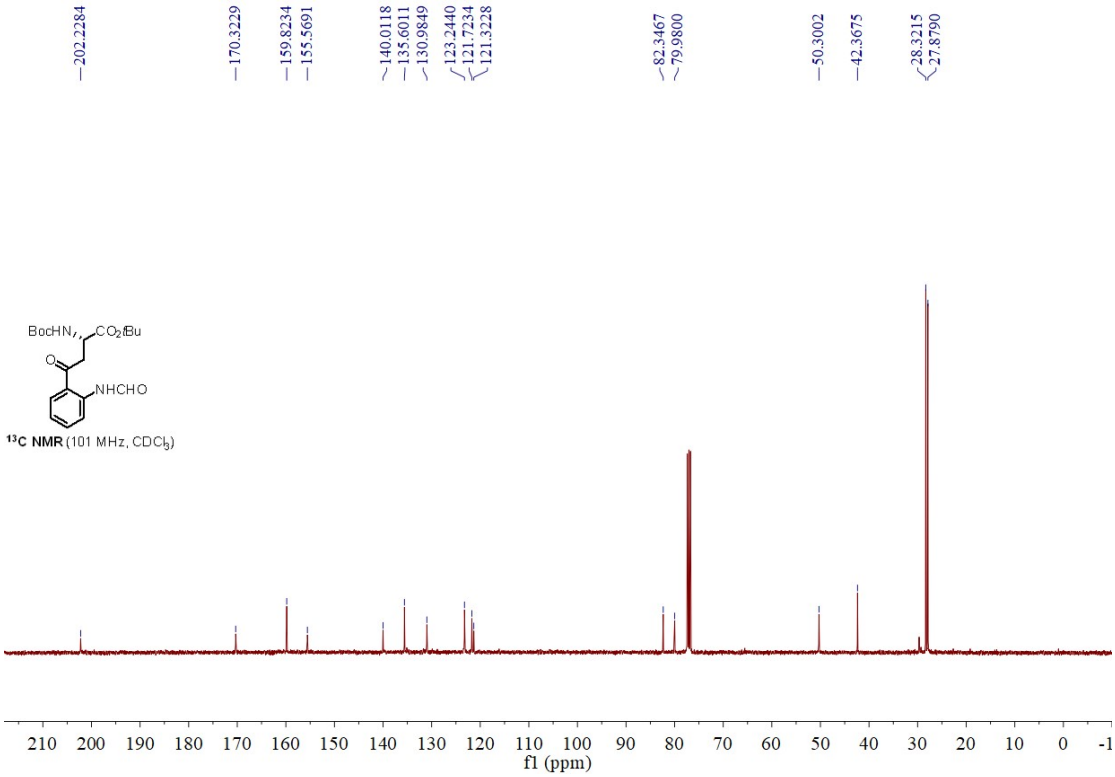
^{13}C NMR of **2e**



^{1}H NMR of **2f**



^{13}C NMR of **2f**



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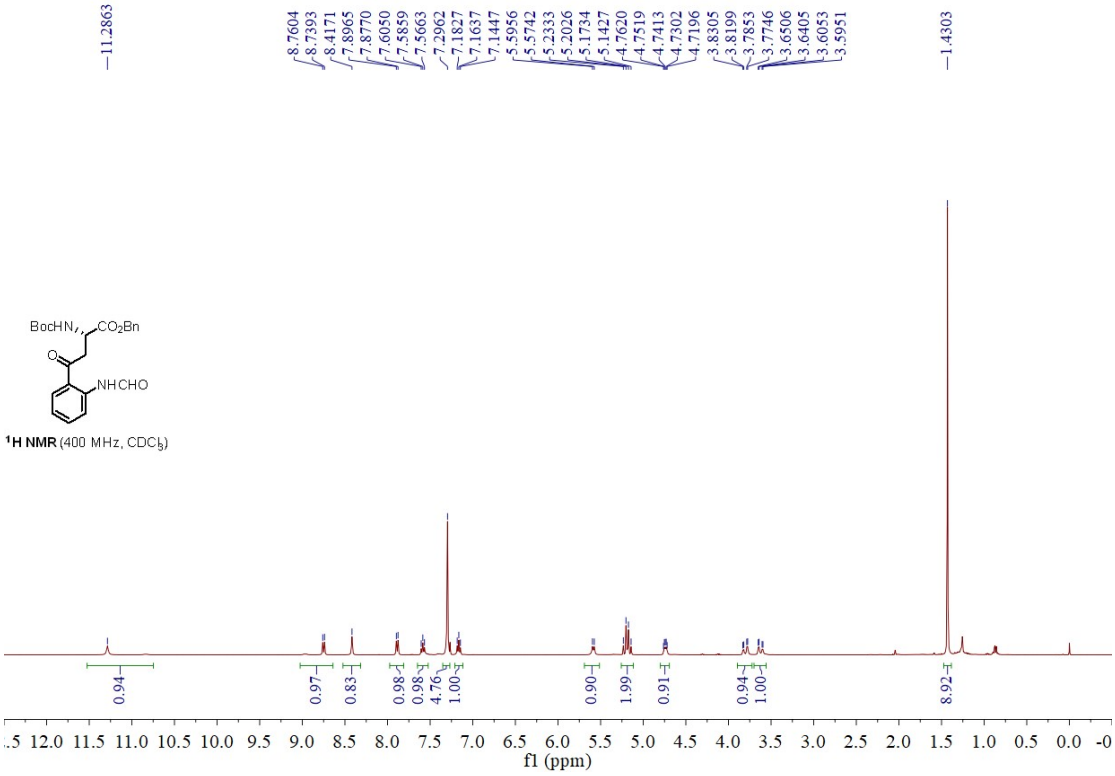

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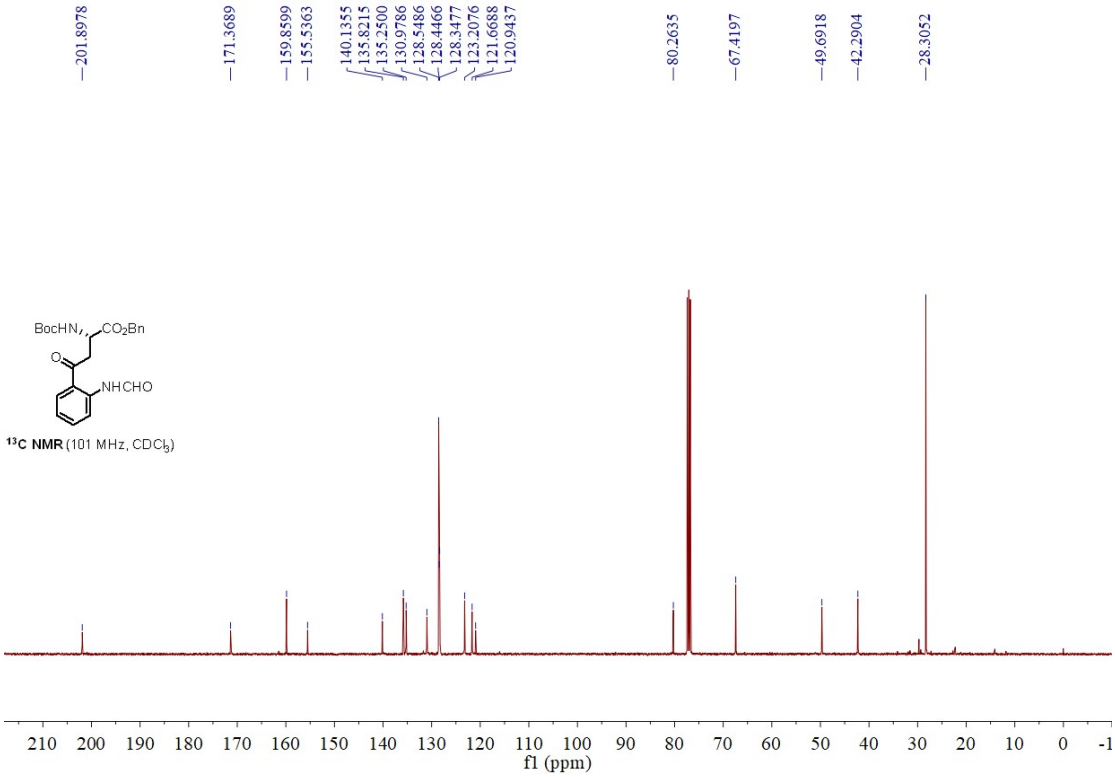

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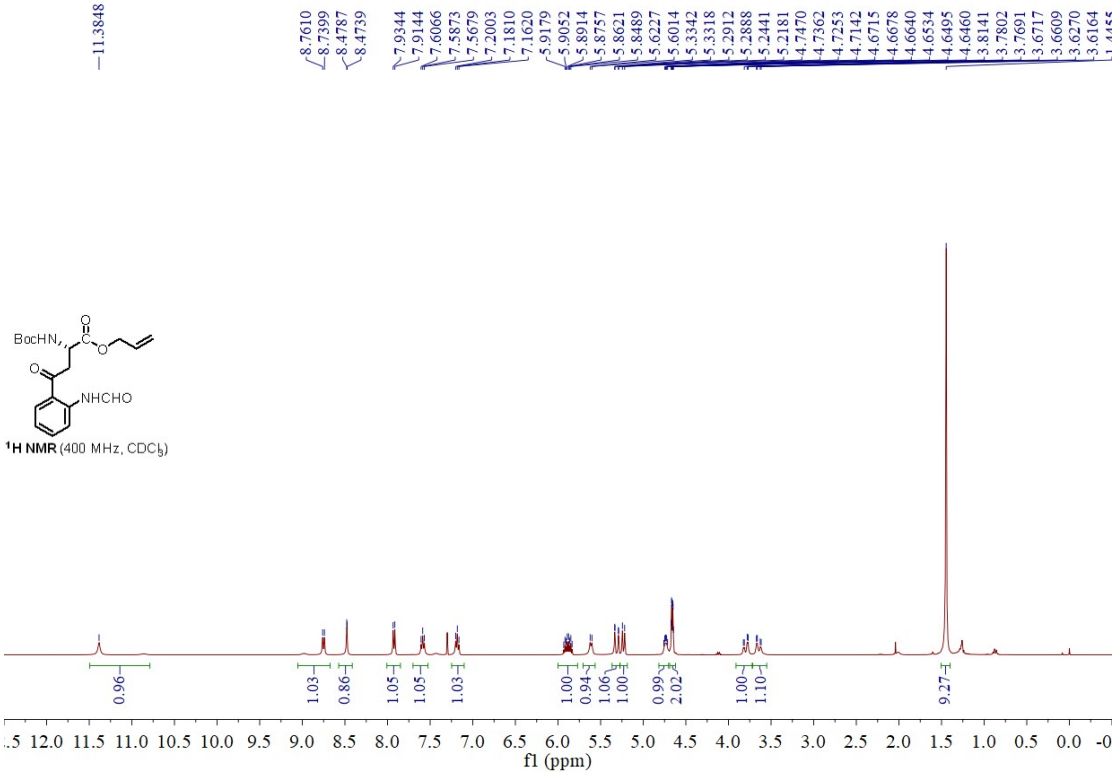

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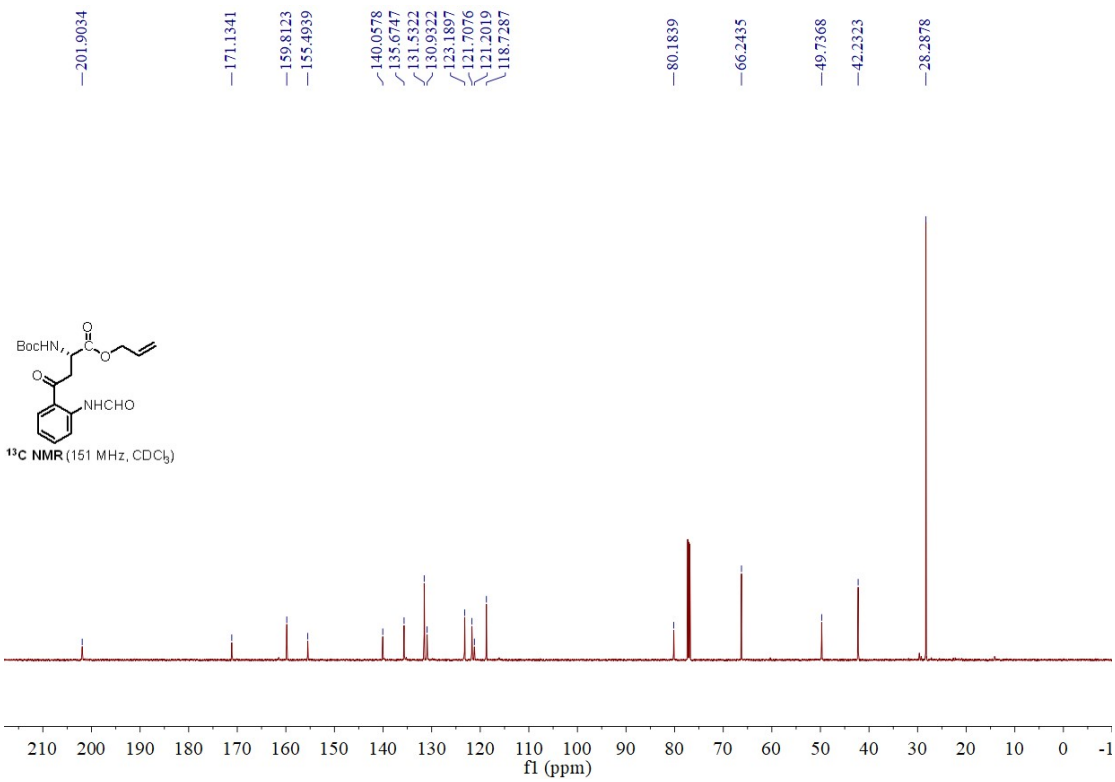

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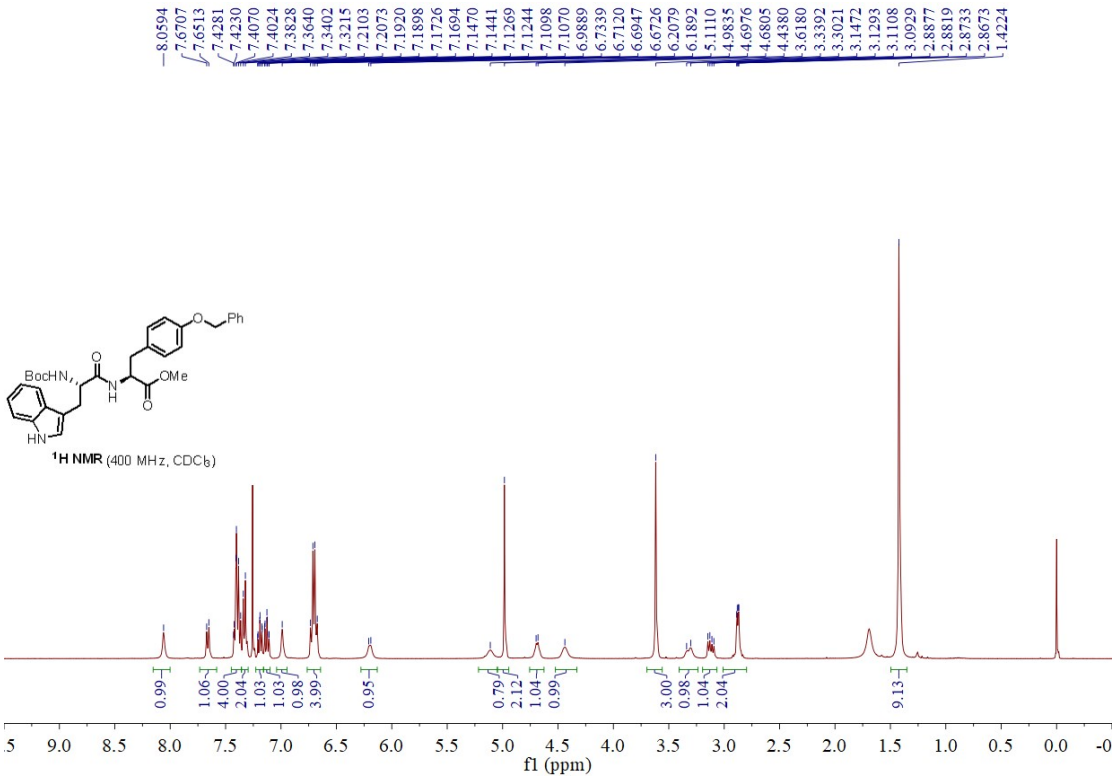

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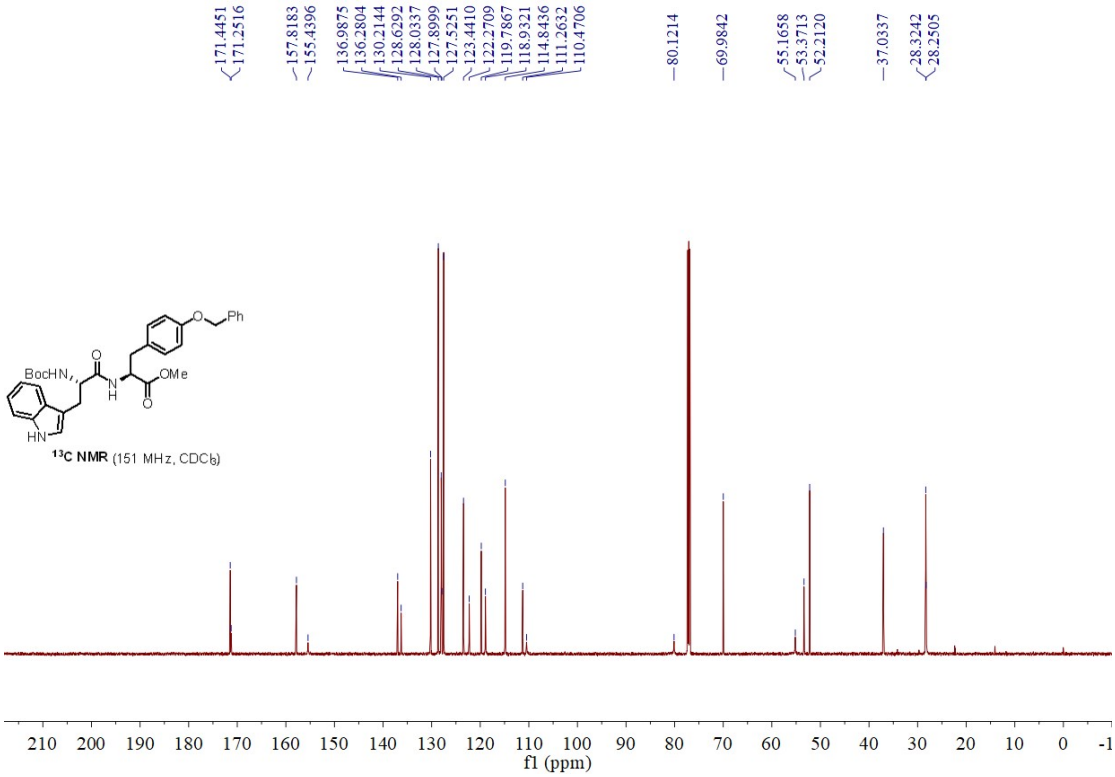
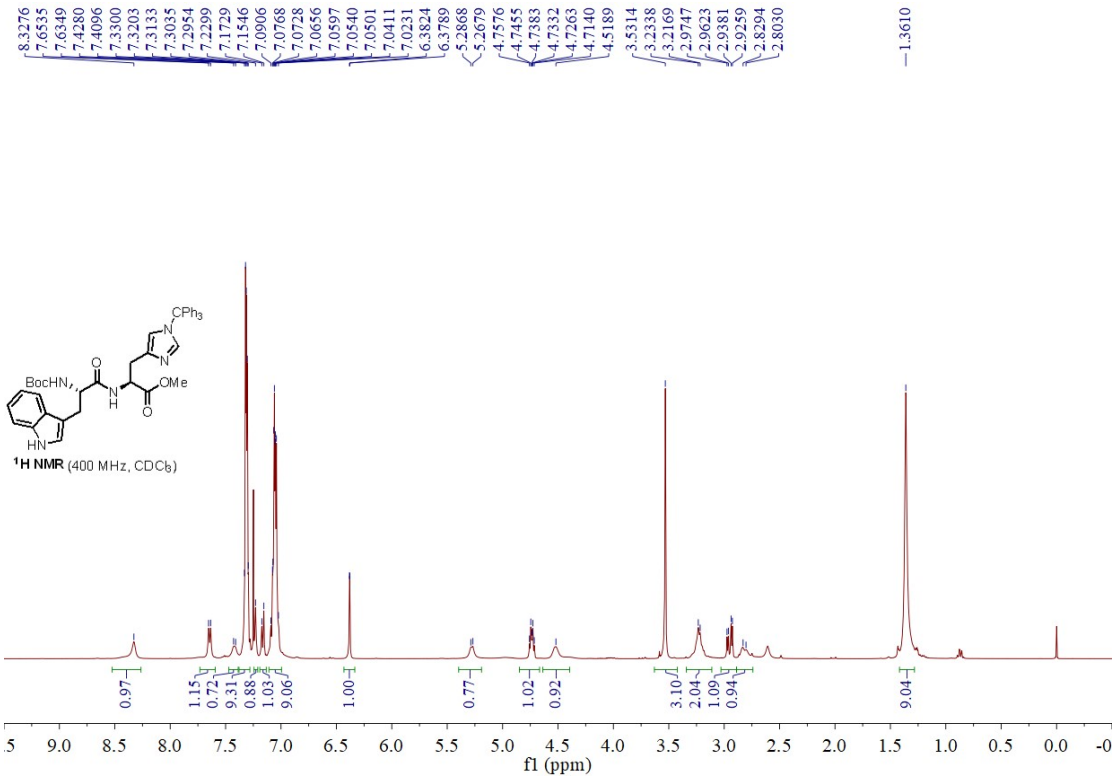


^{1}H NMR of **3i**



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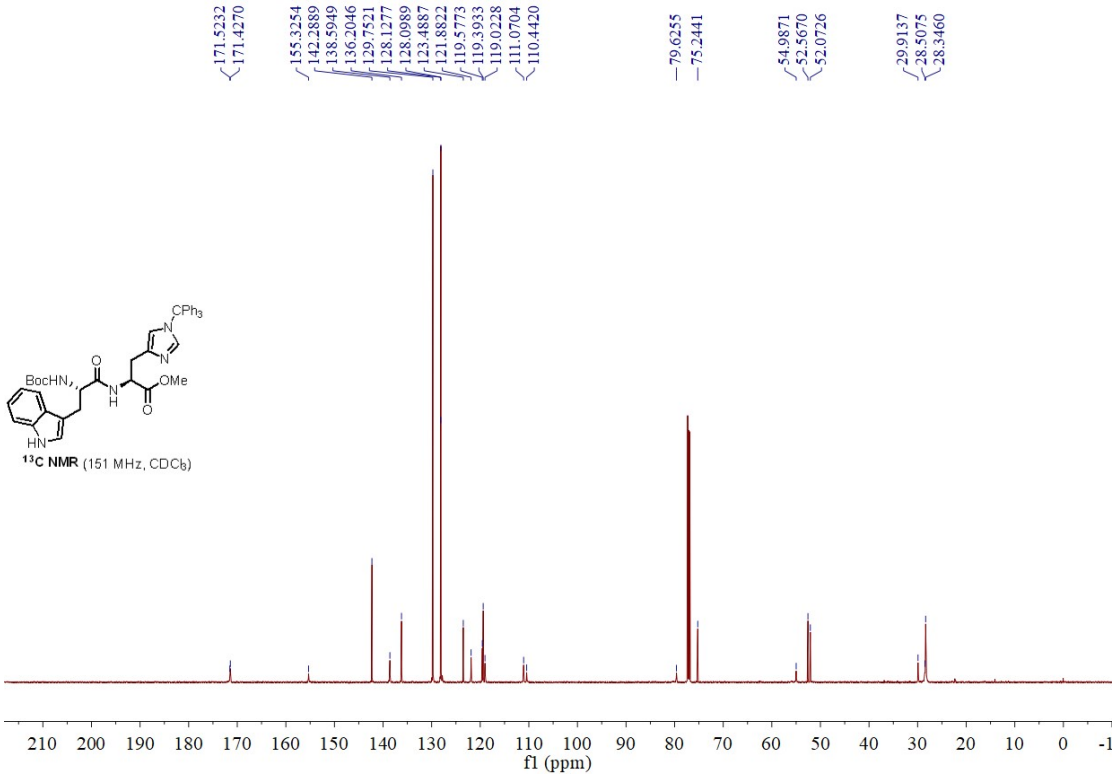

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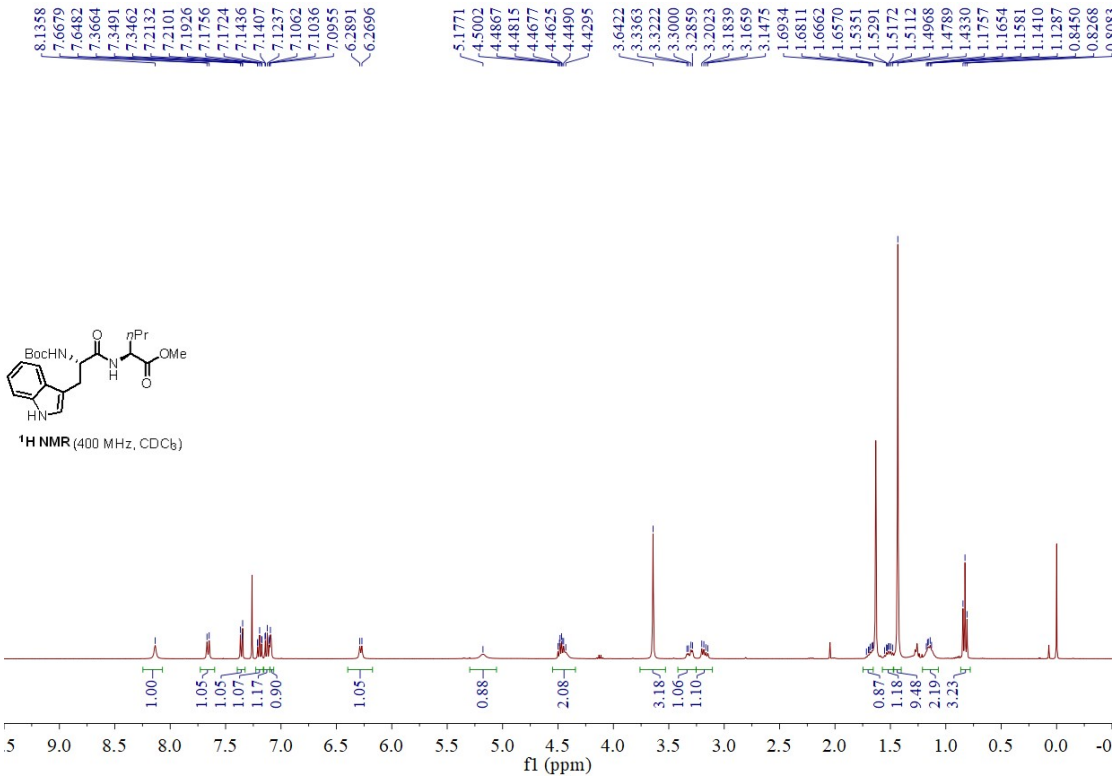

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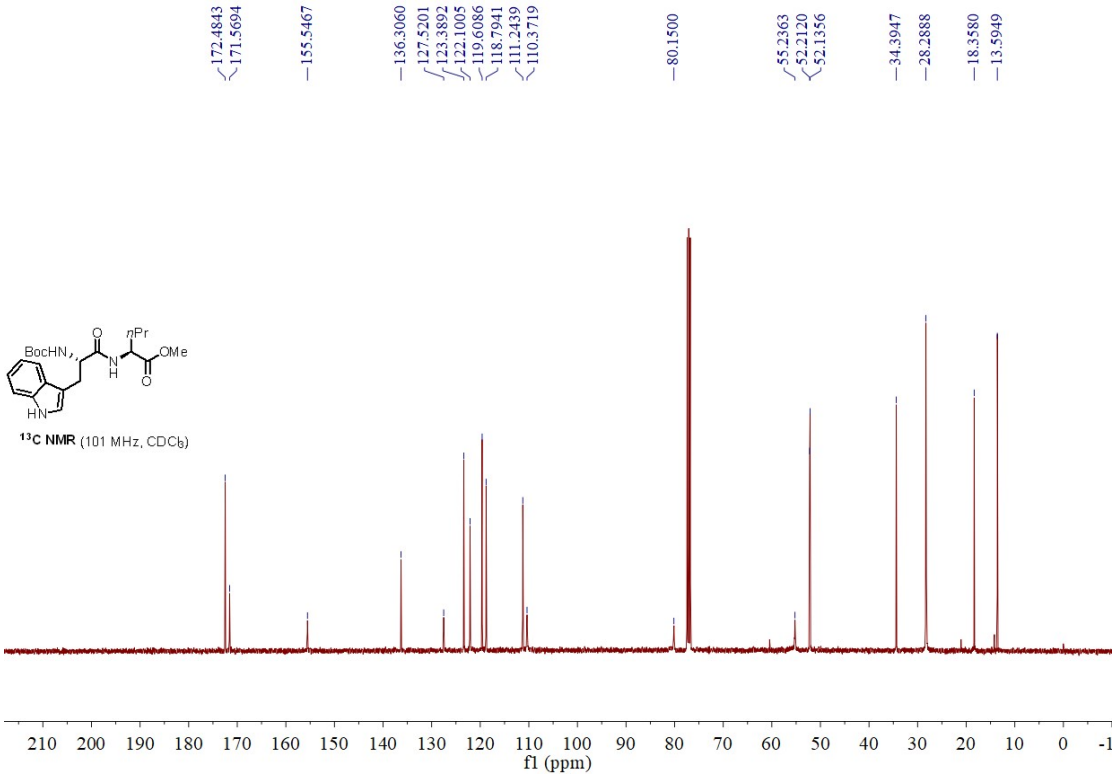

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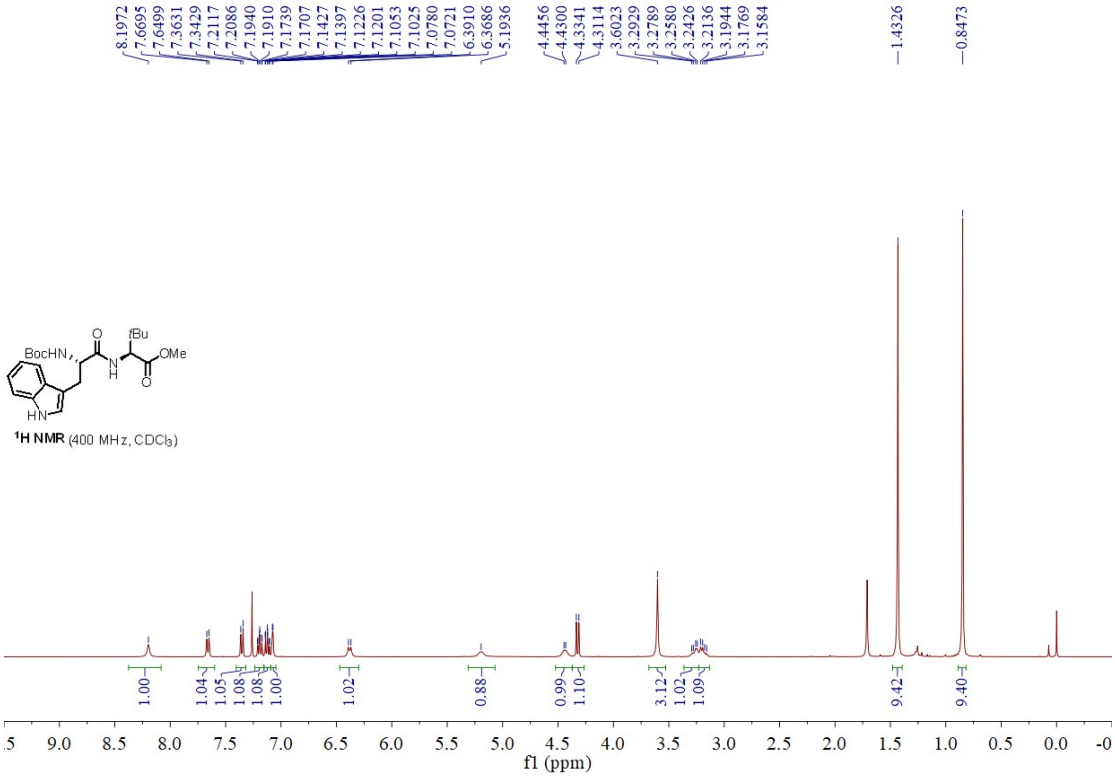

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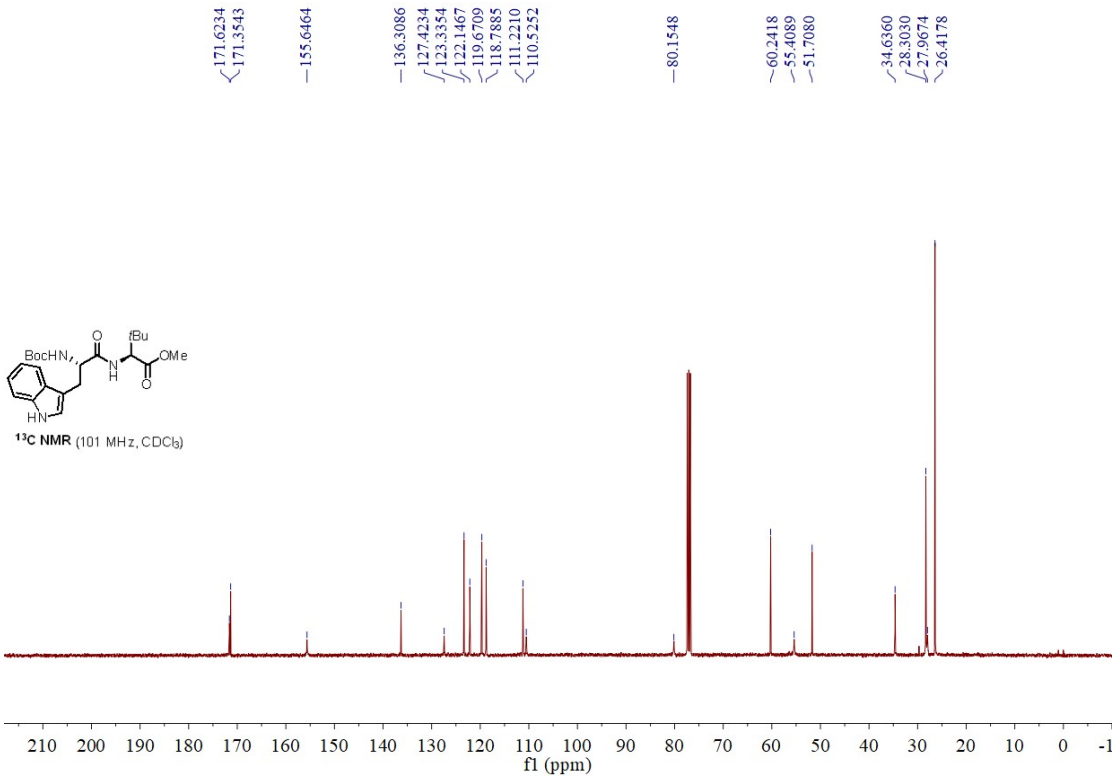

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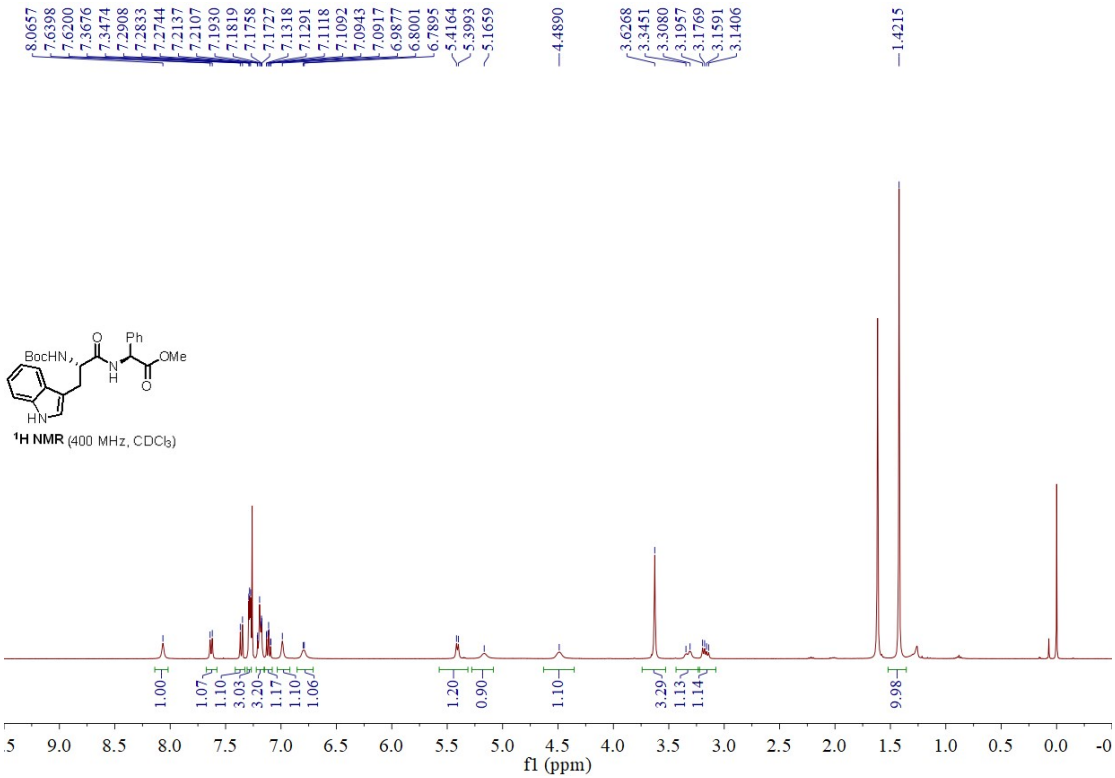

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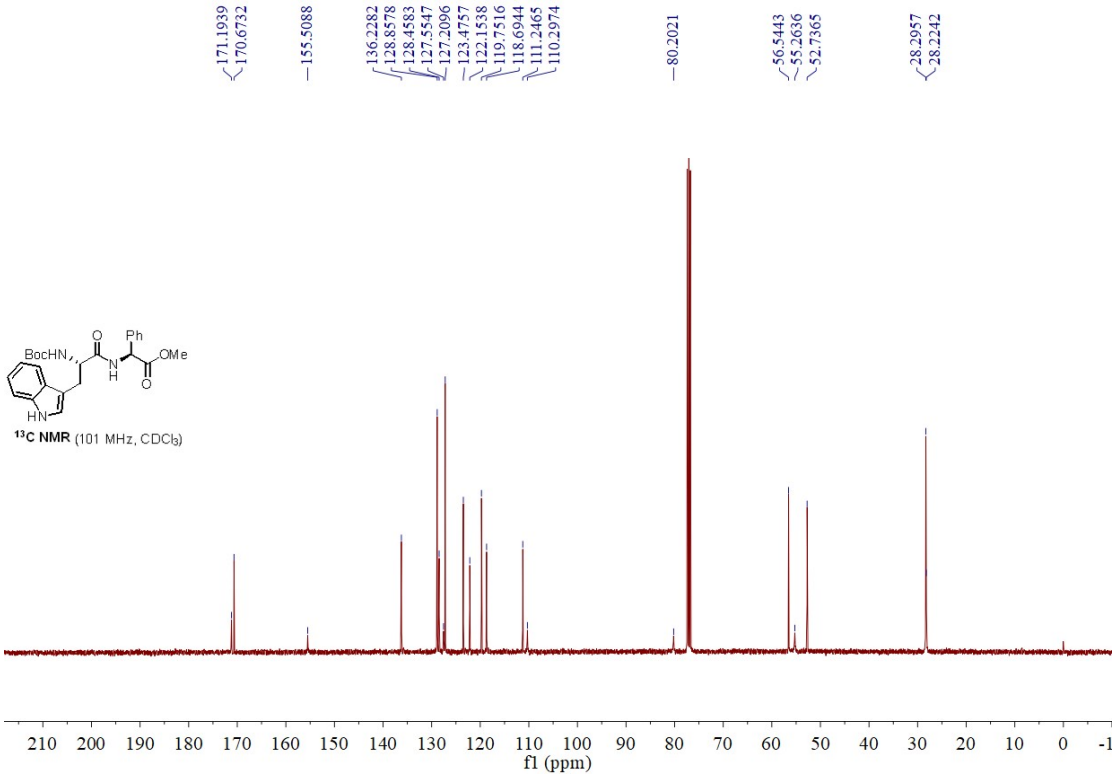

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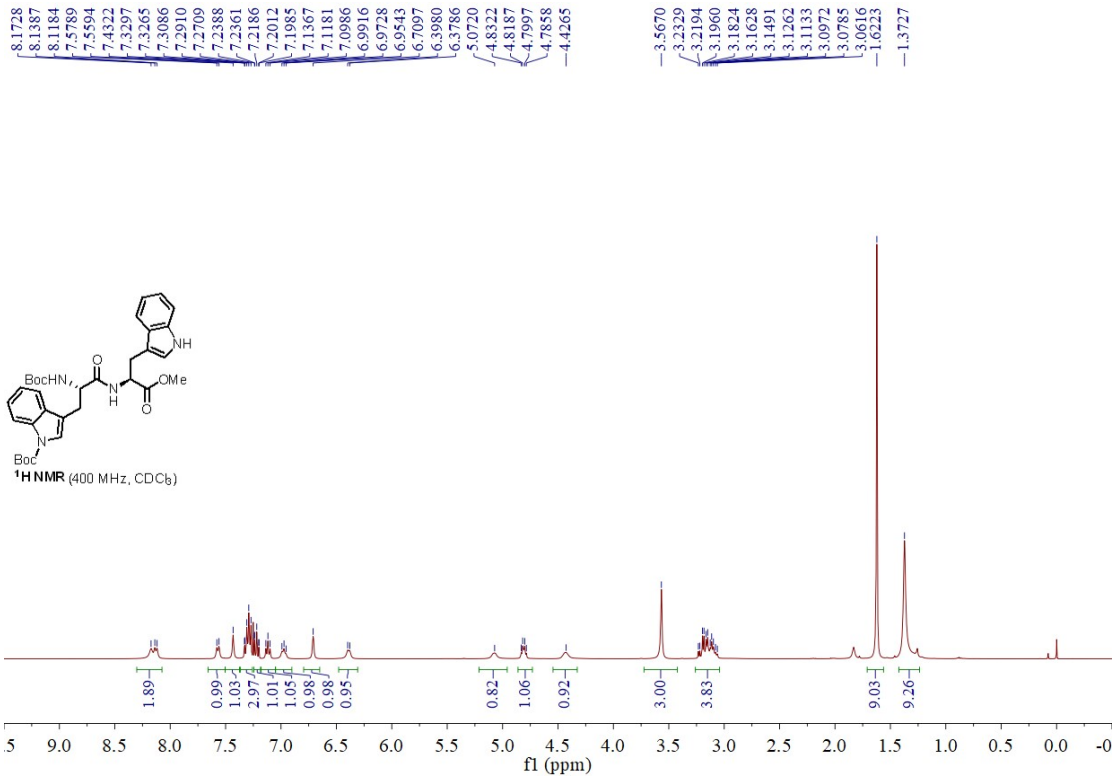
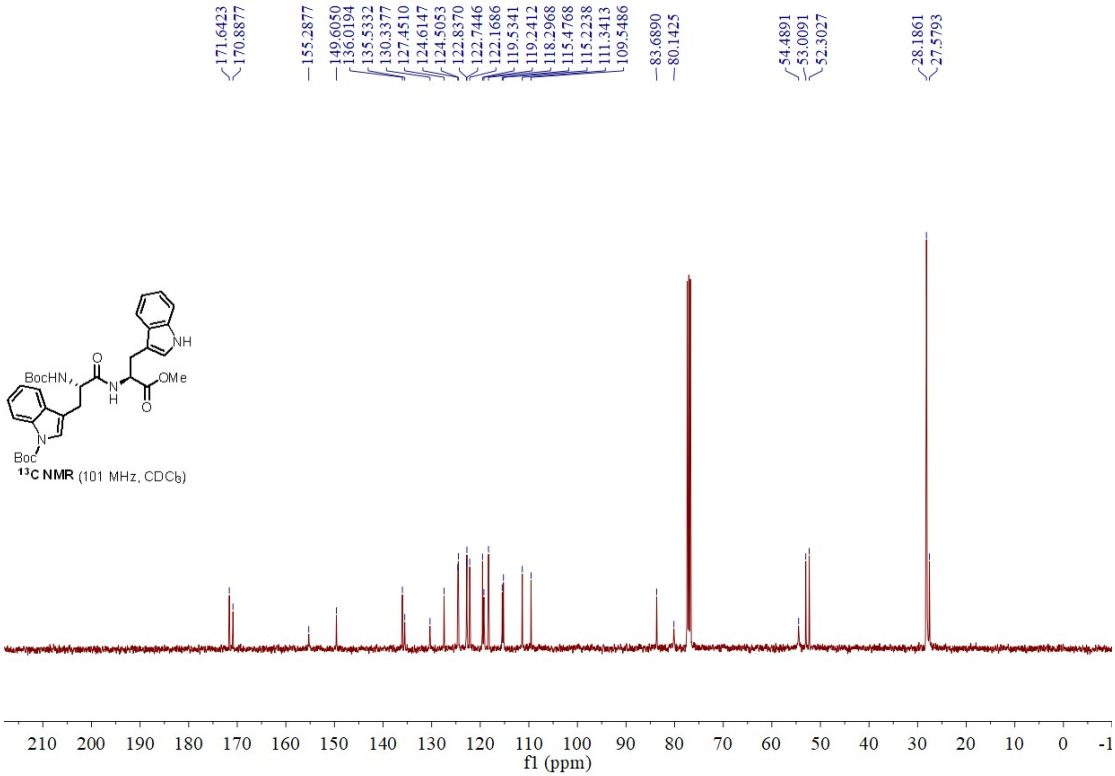
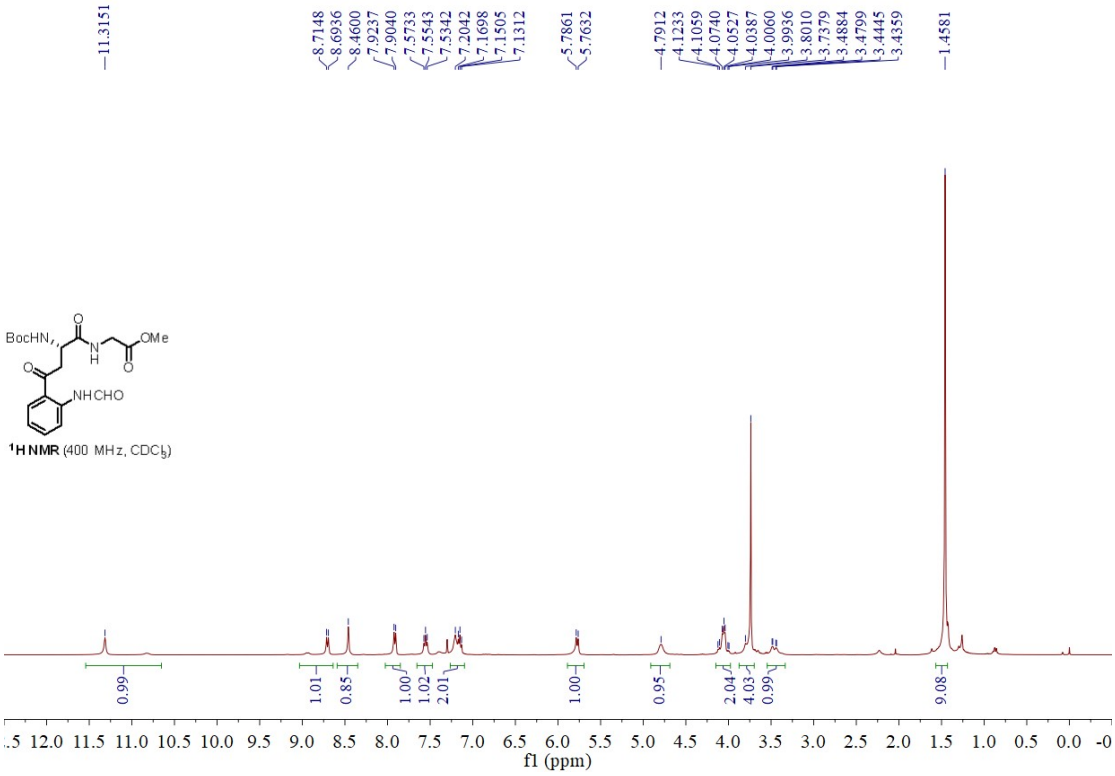


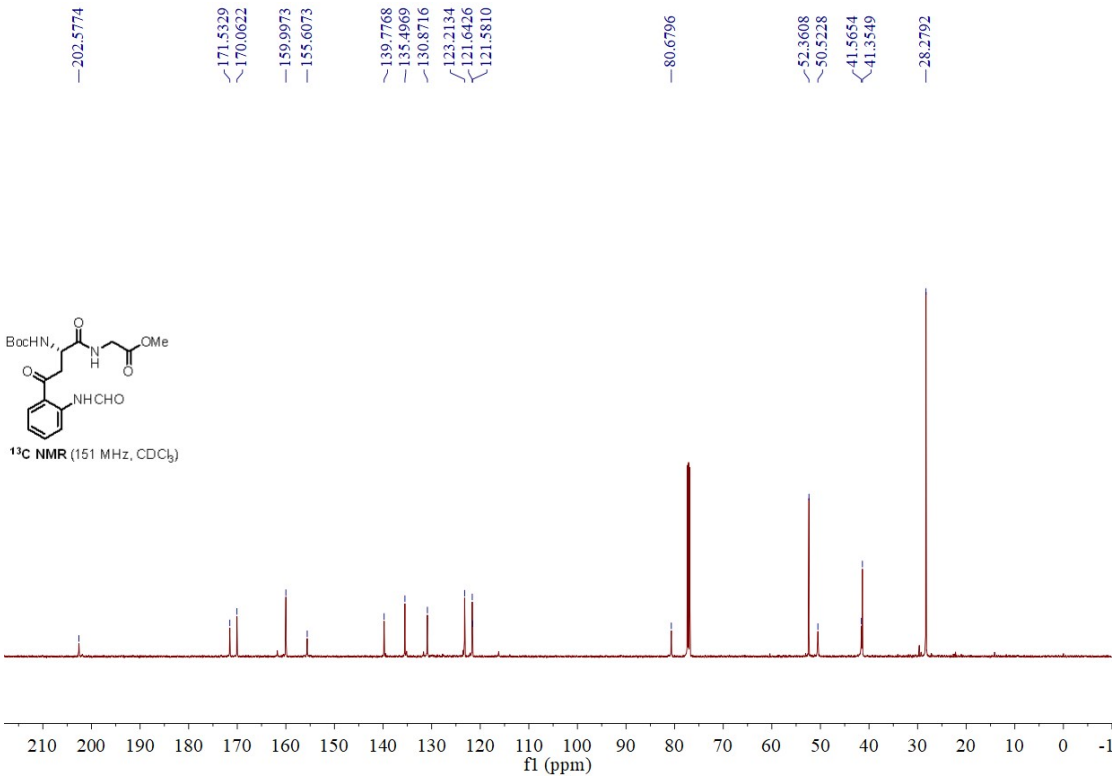
^{13}C NMR of **4b**



^{1}H NMR of **5a**



^{13}C NMR of **5a**



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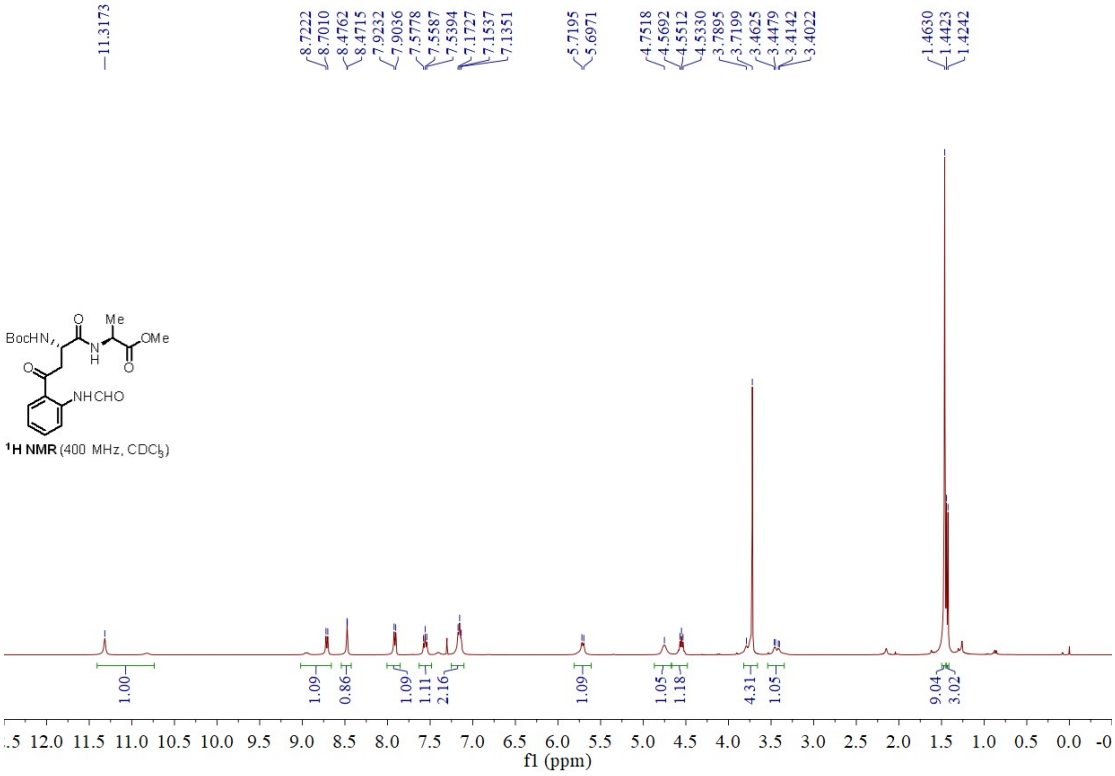

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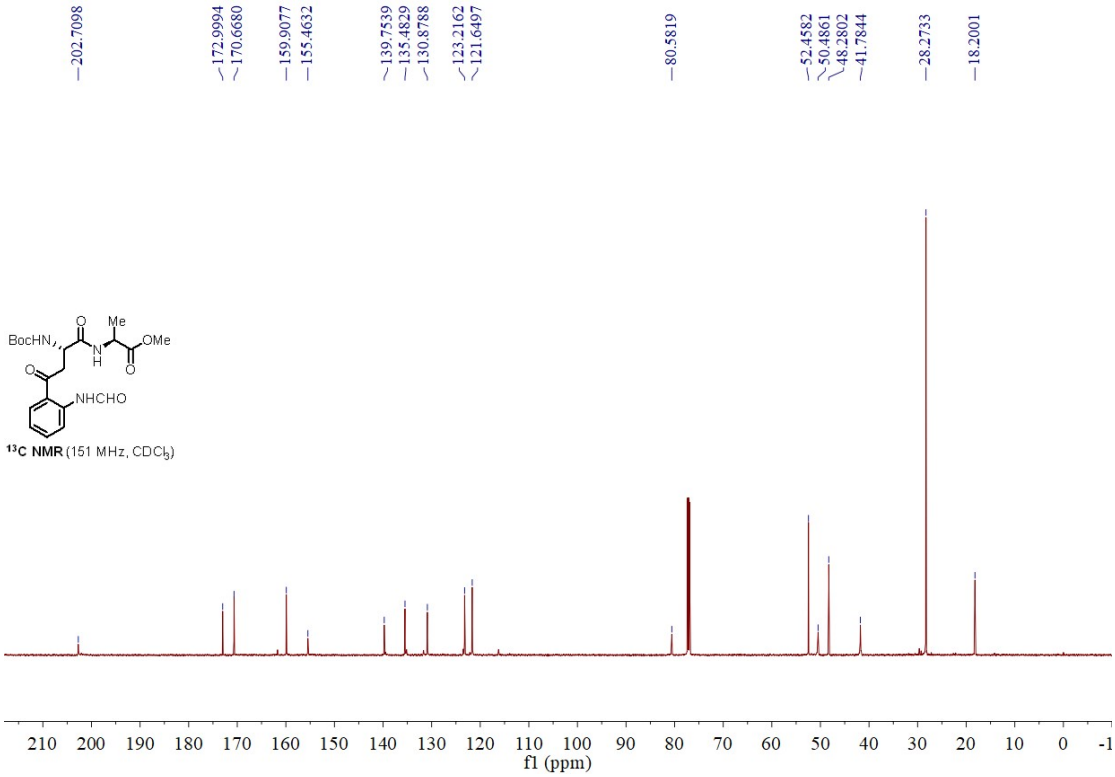

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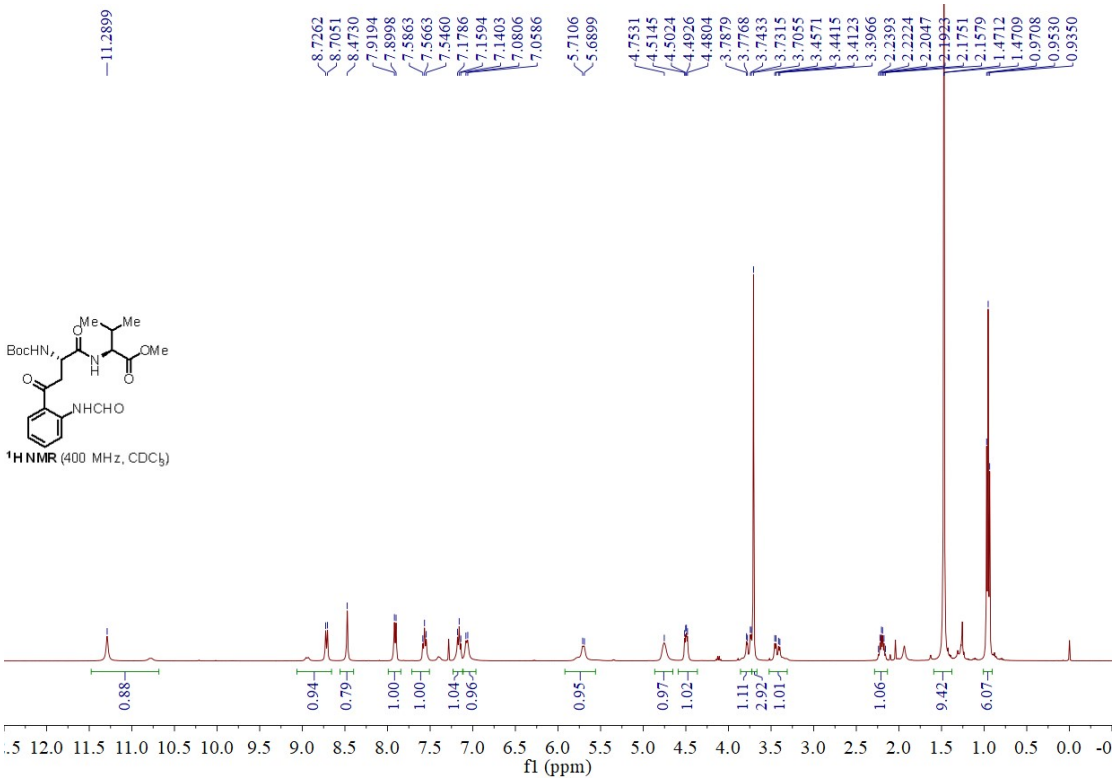

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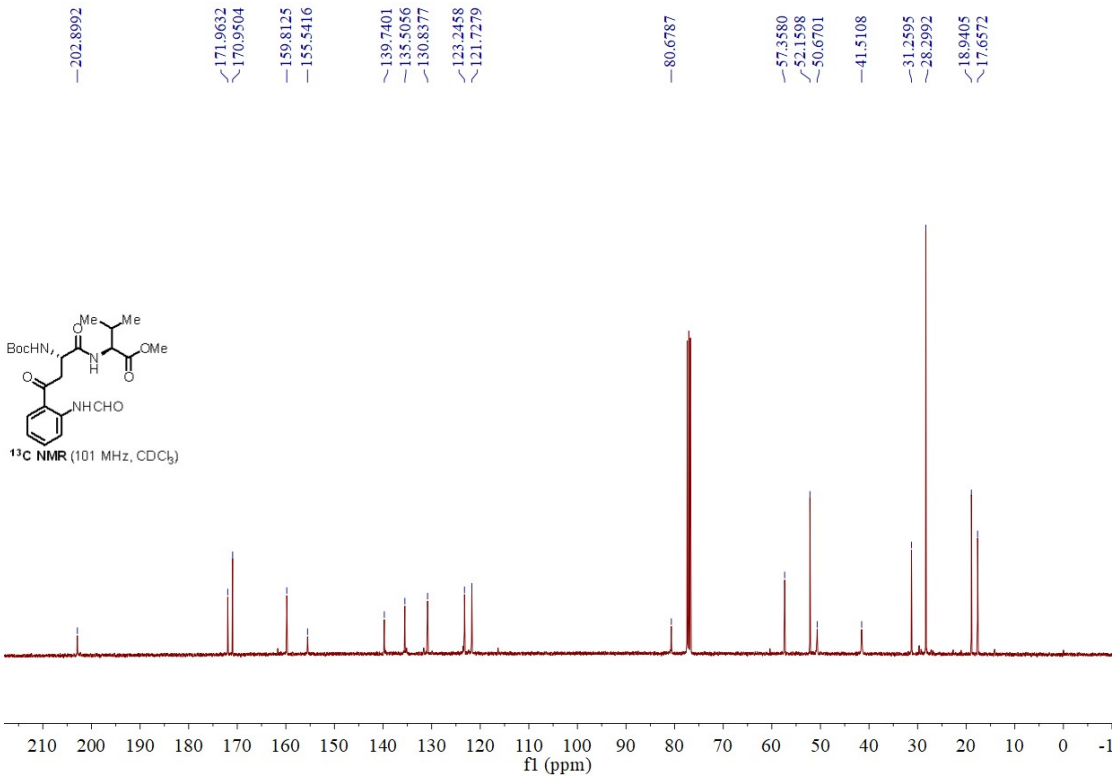

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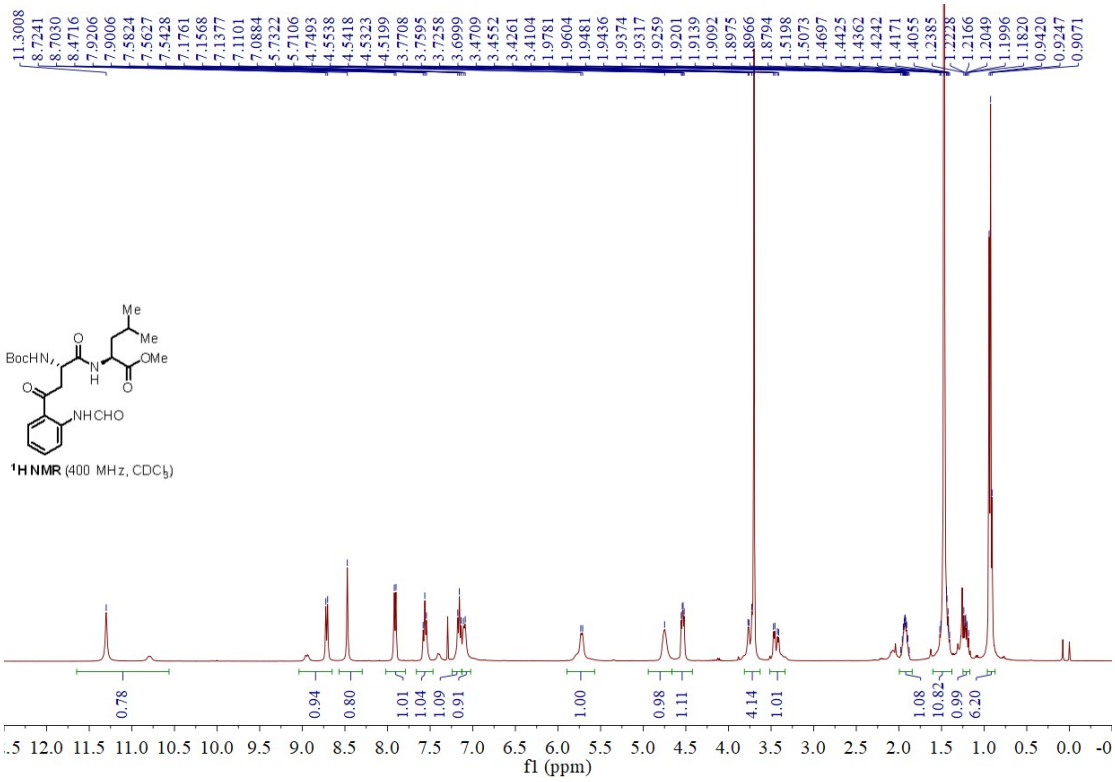

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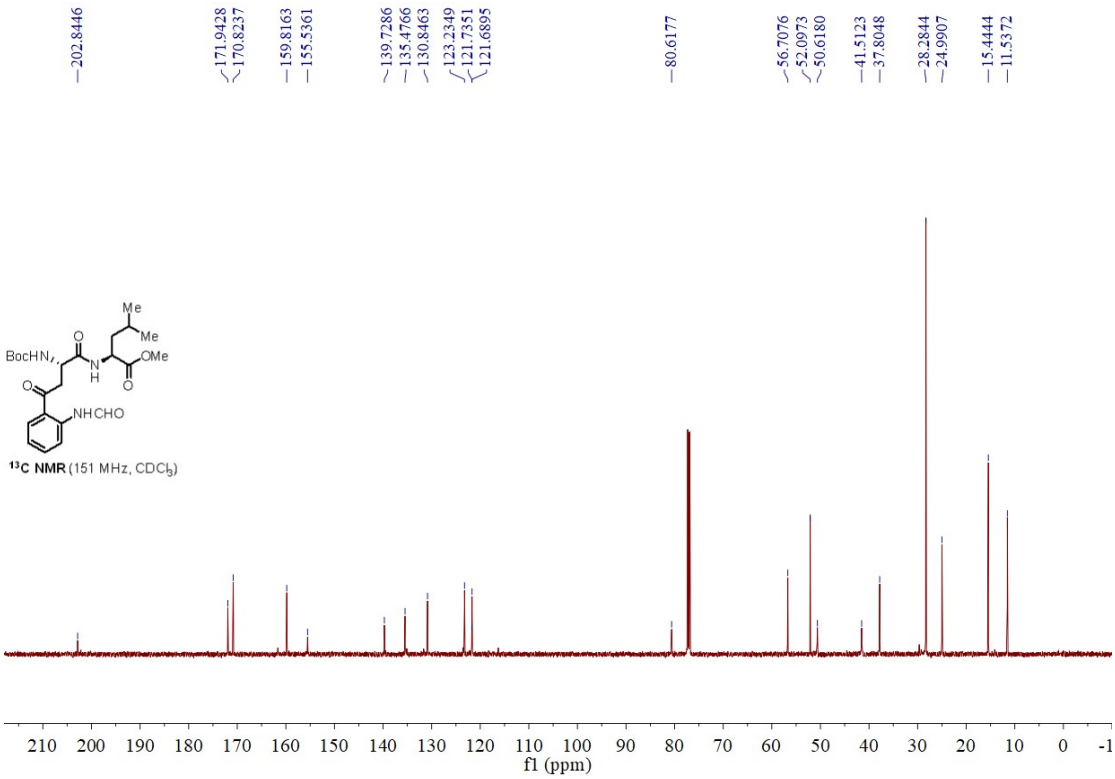

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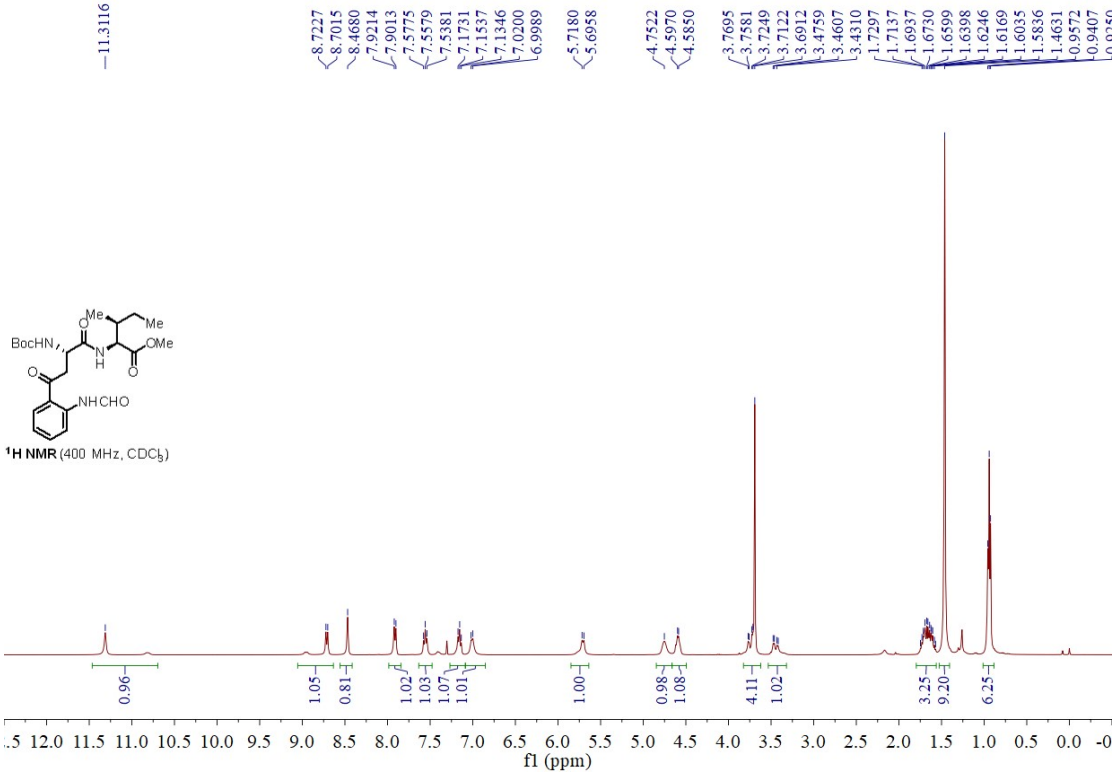

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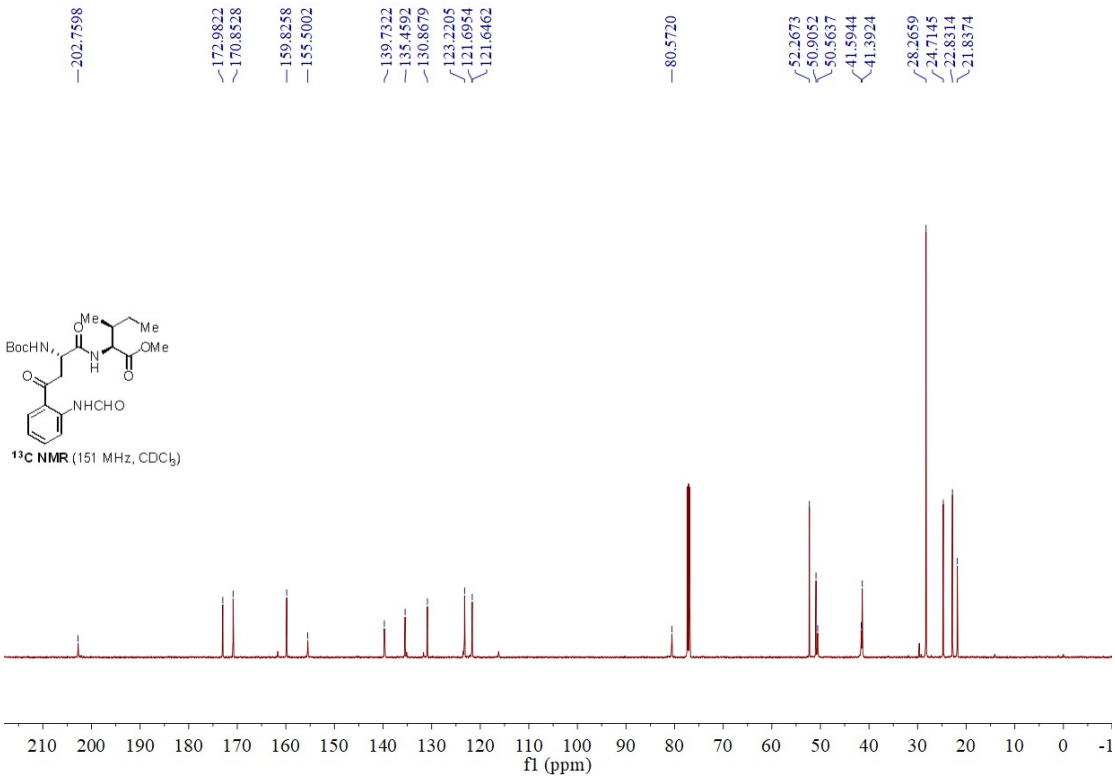

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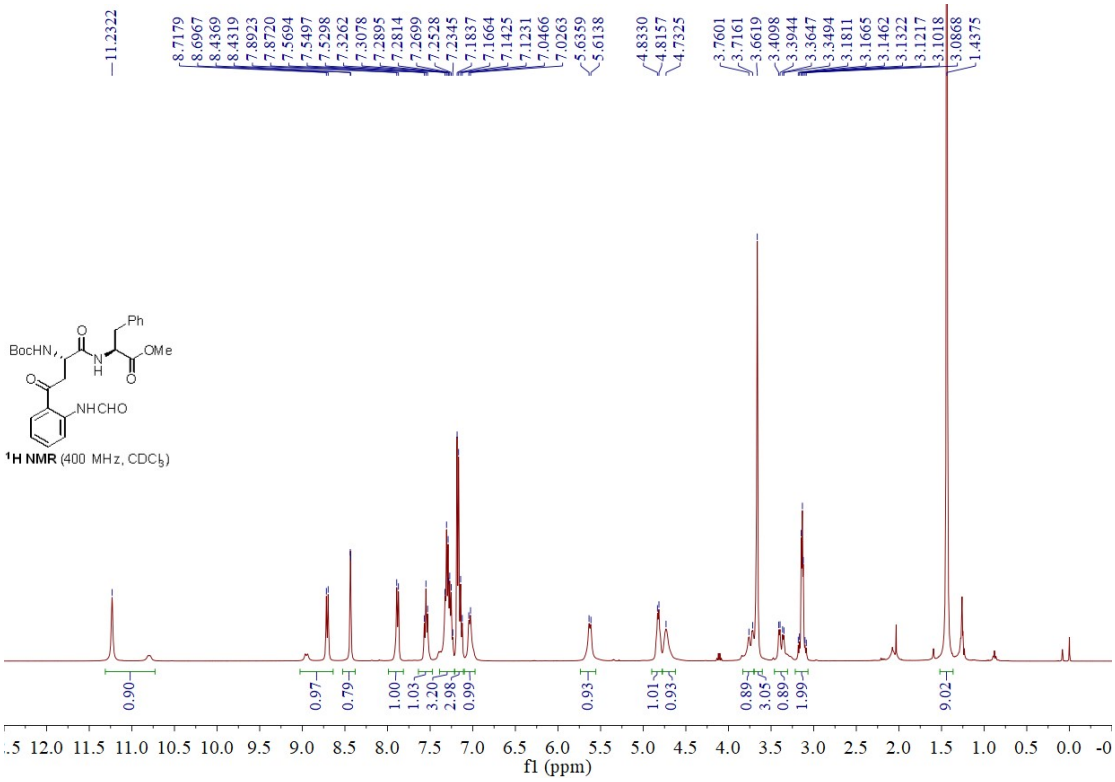

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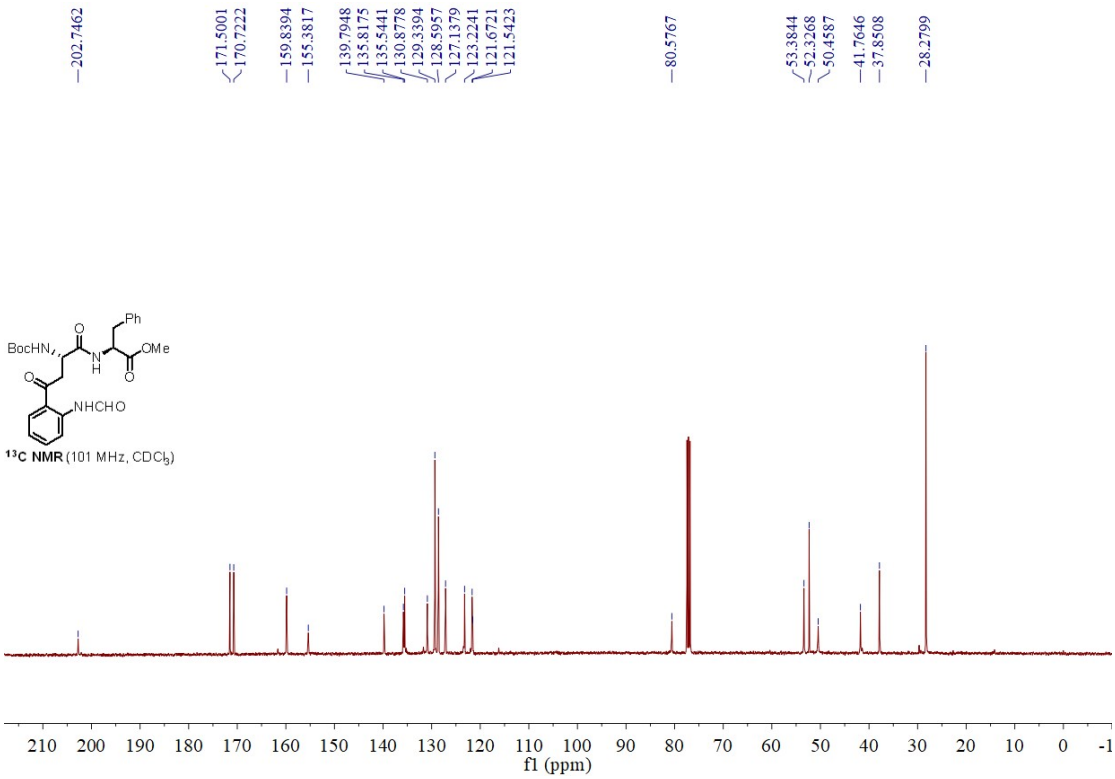

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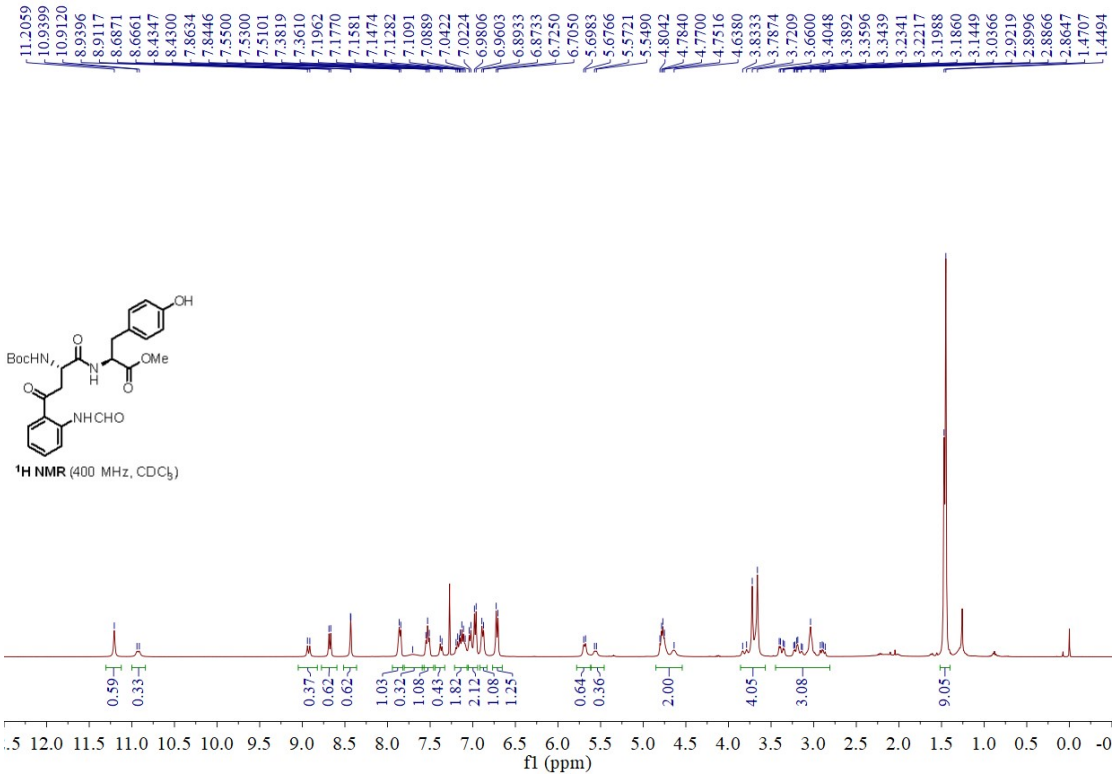

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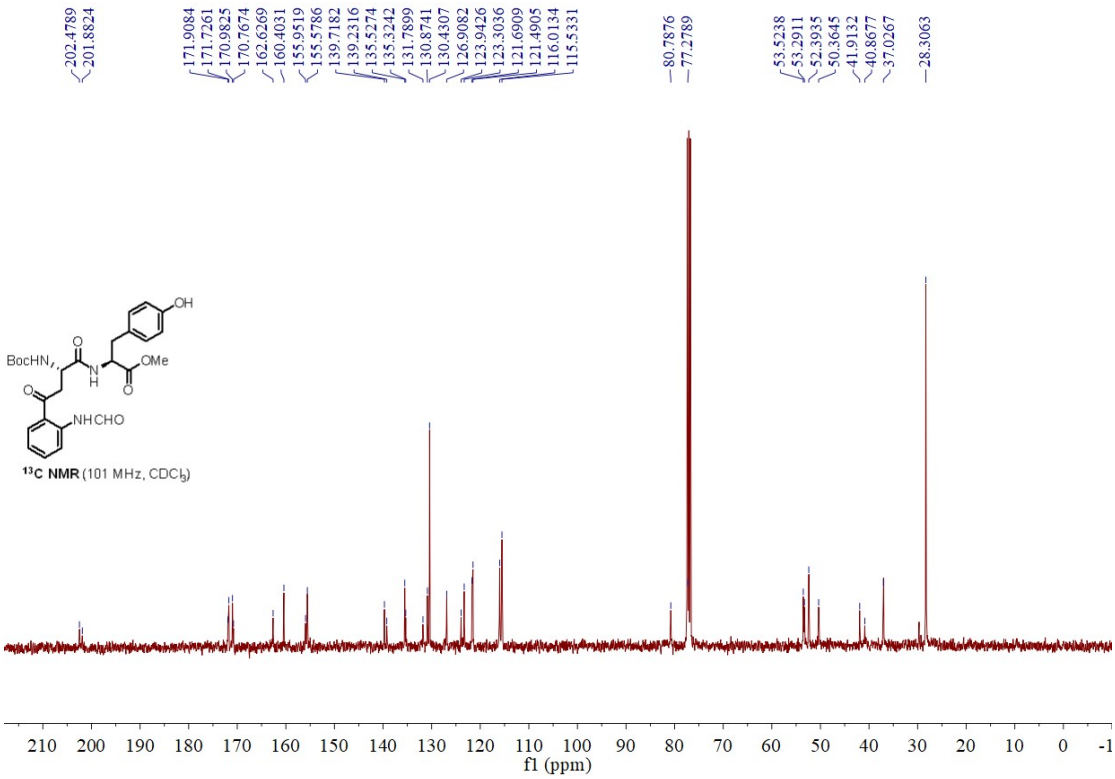

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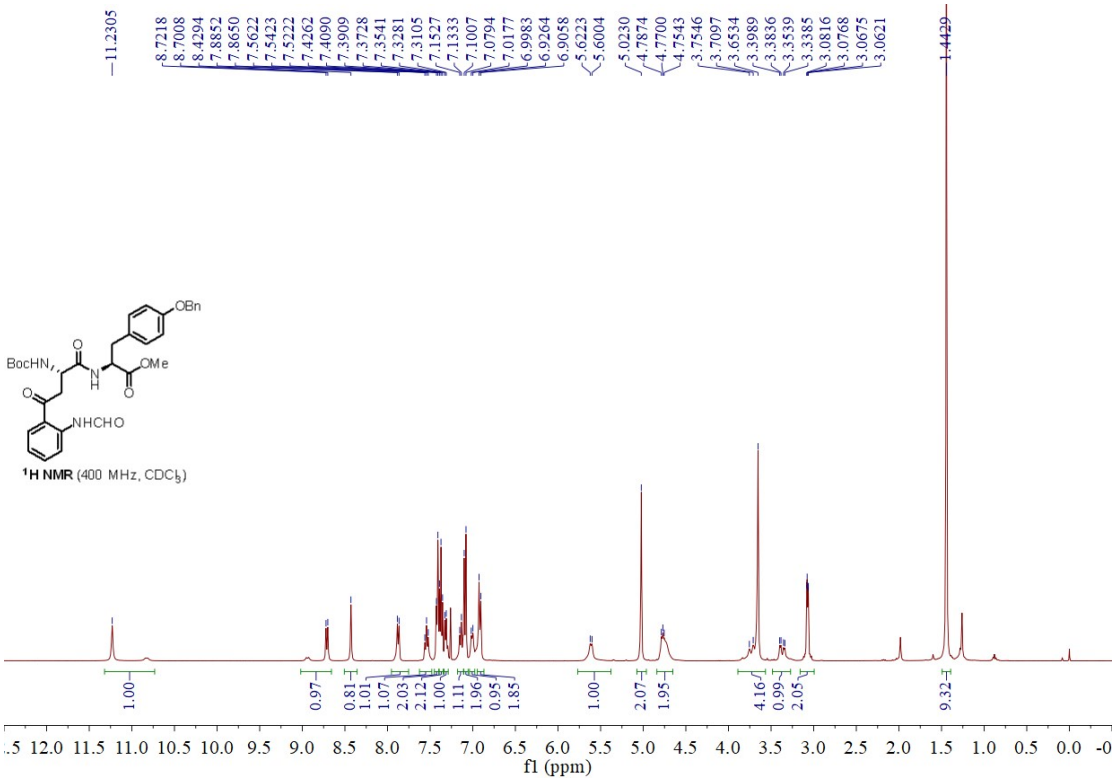

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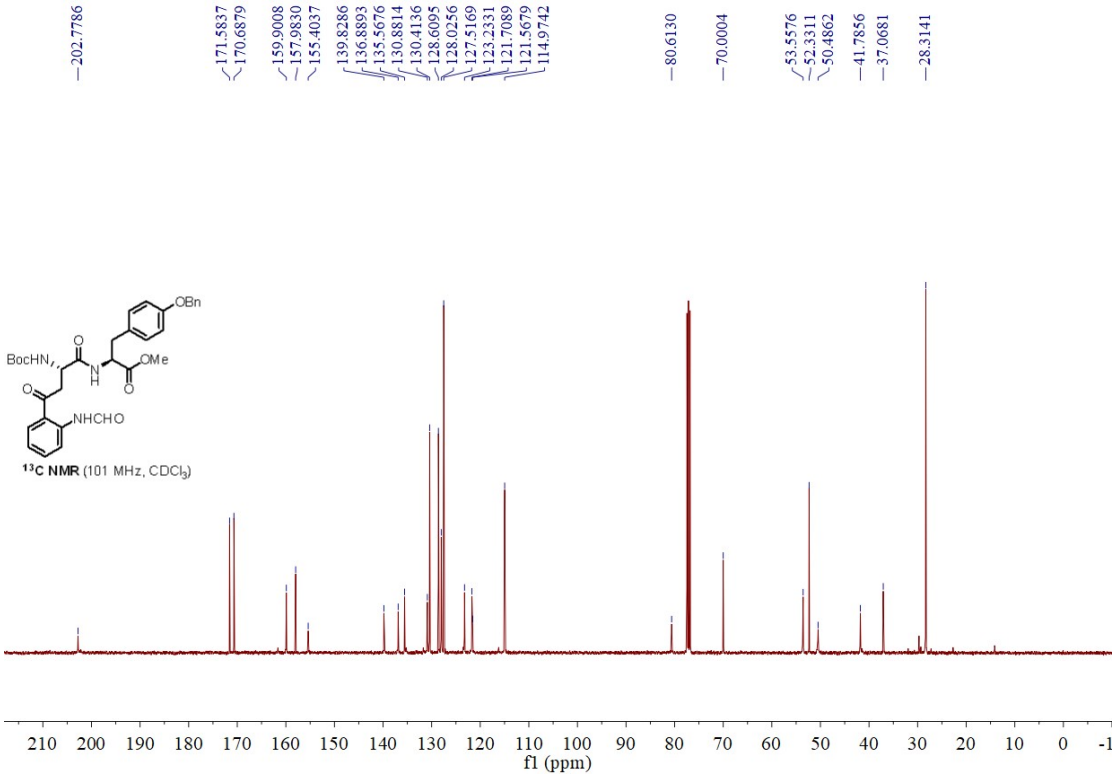

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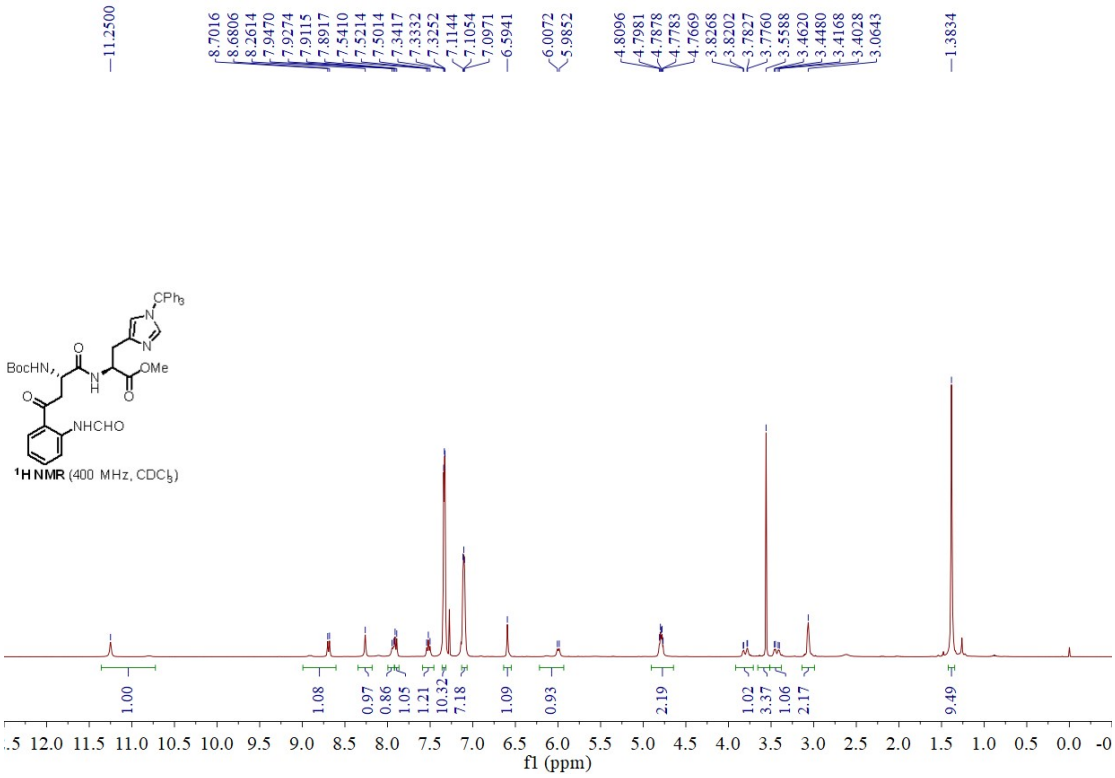

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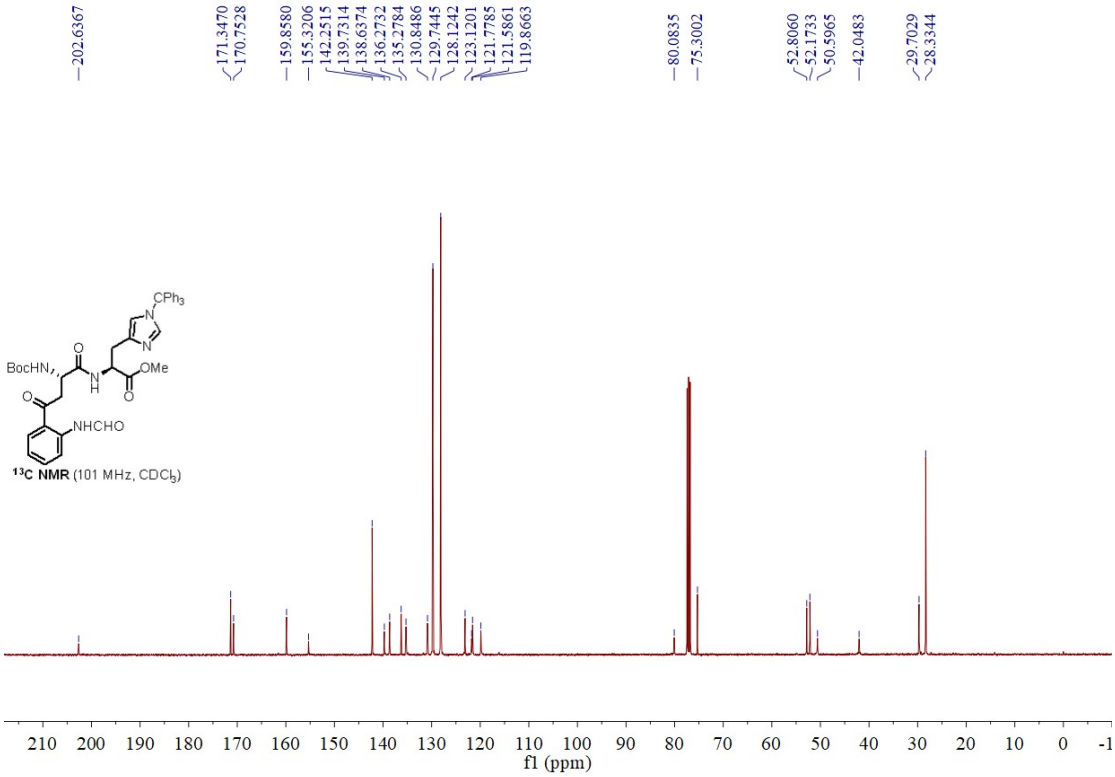

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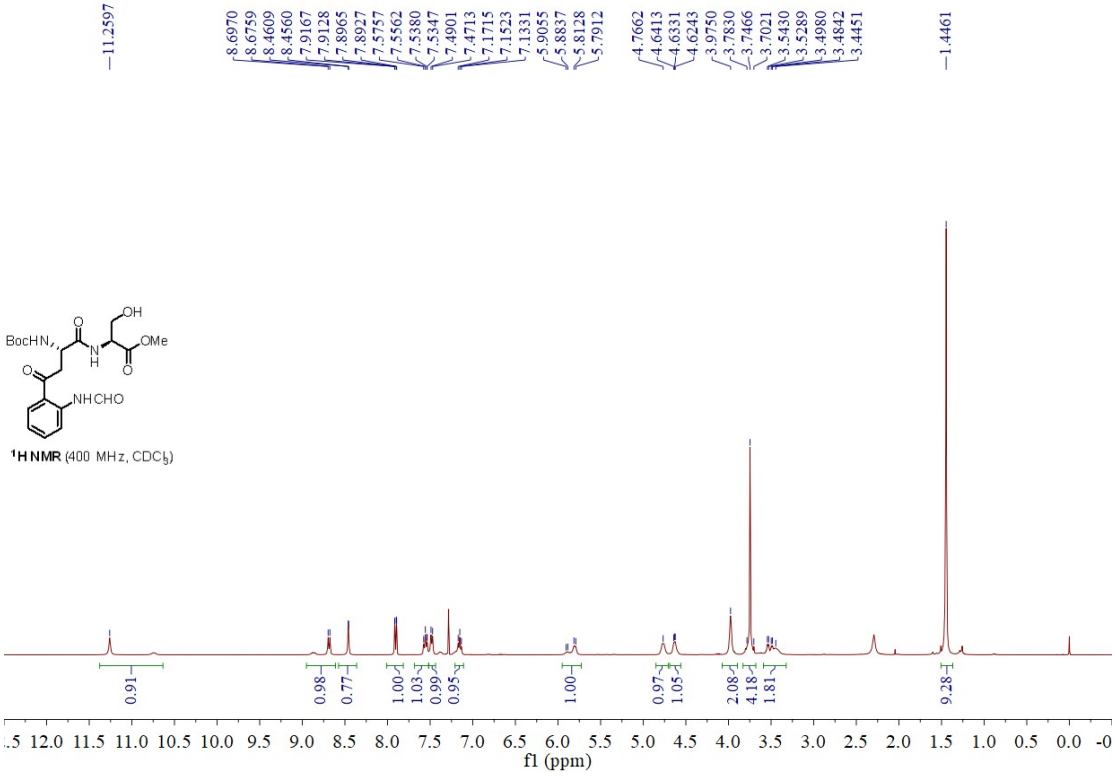

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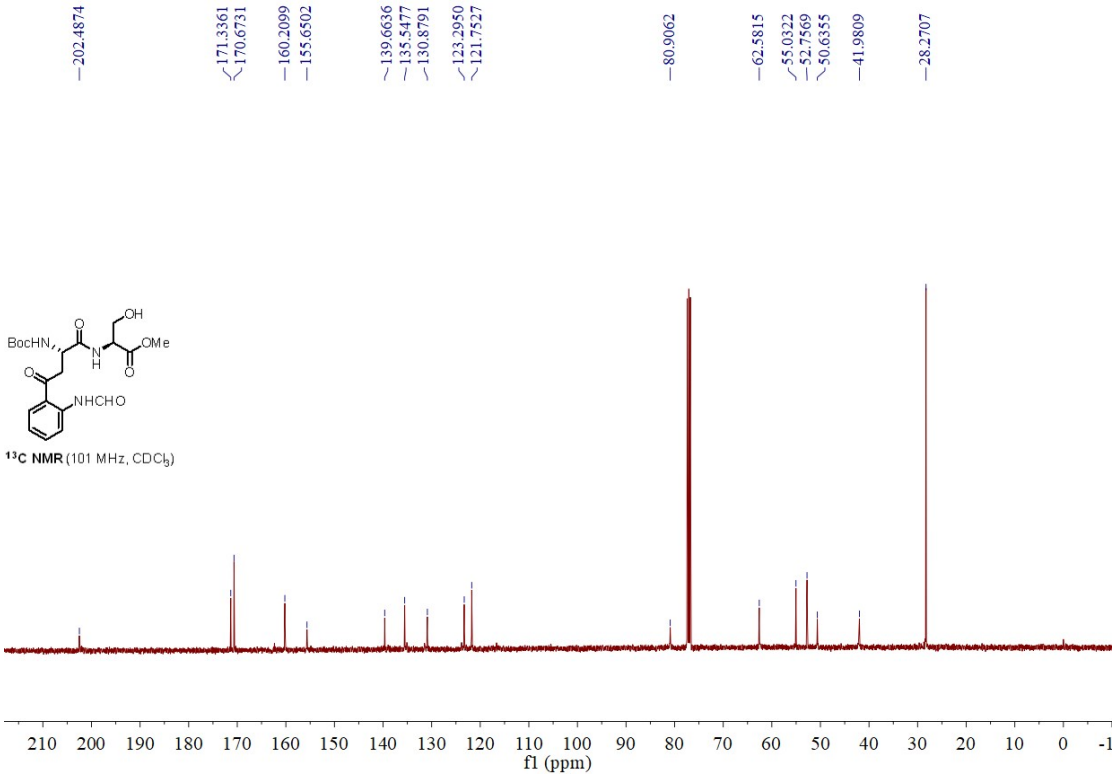

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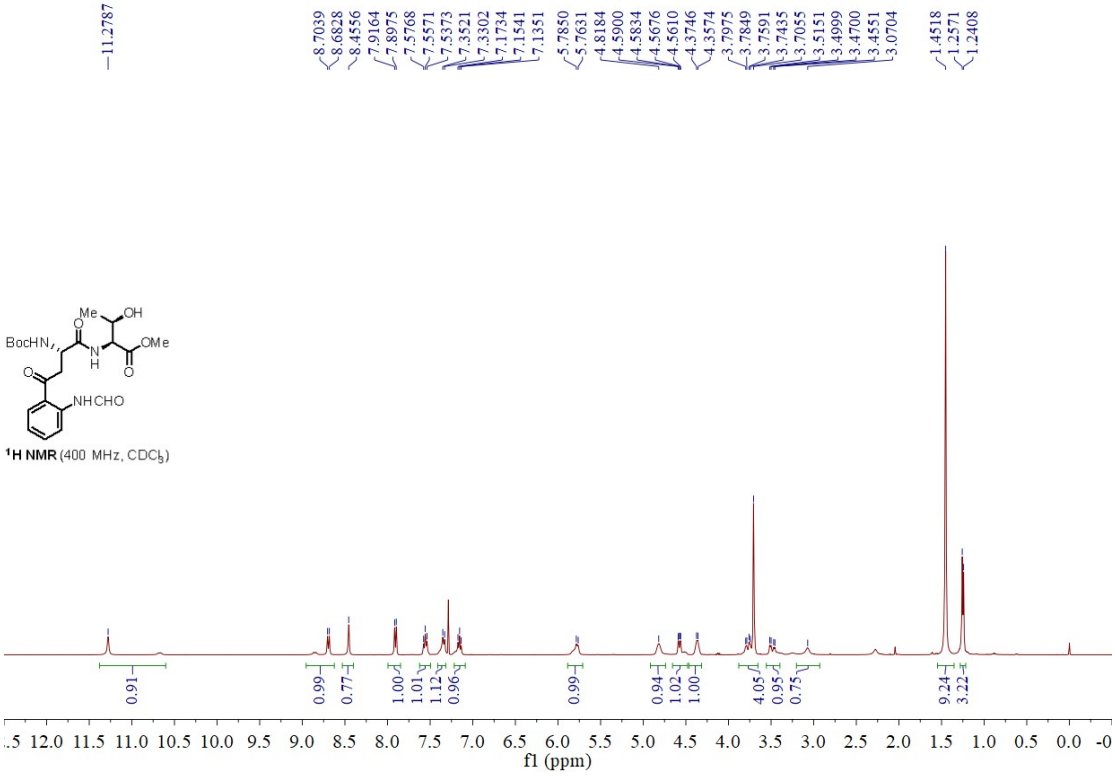

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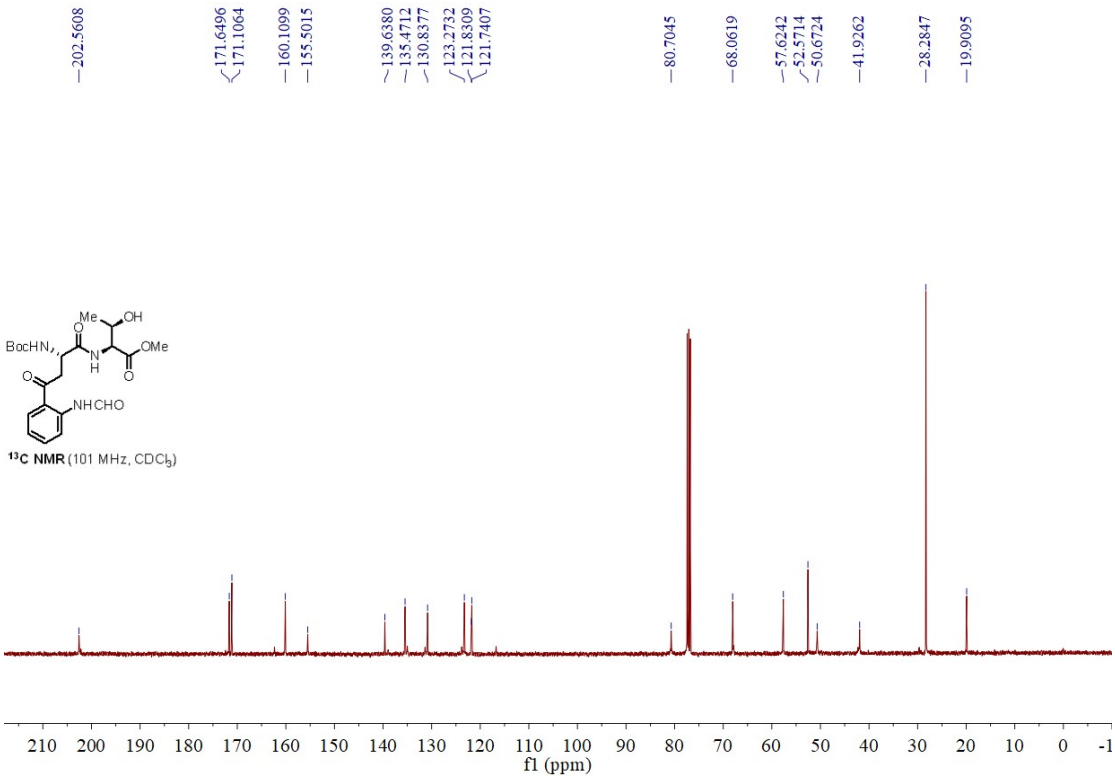

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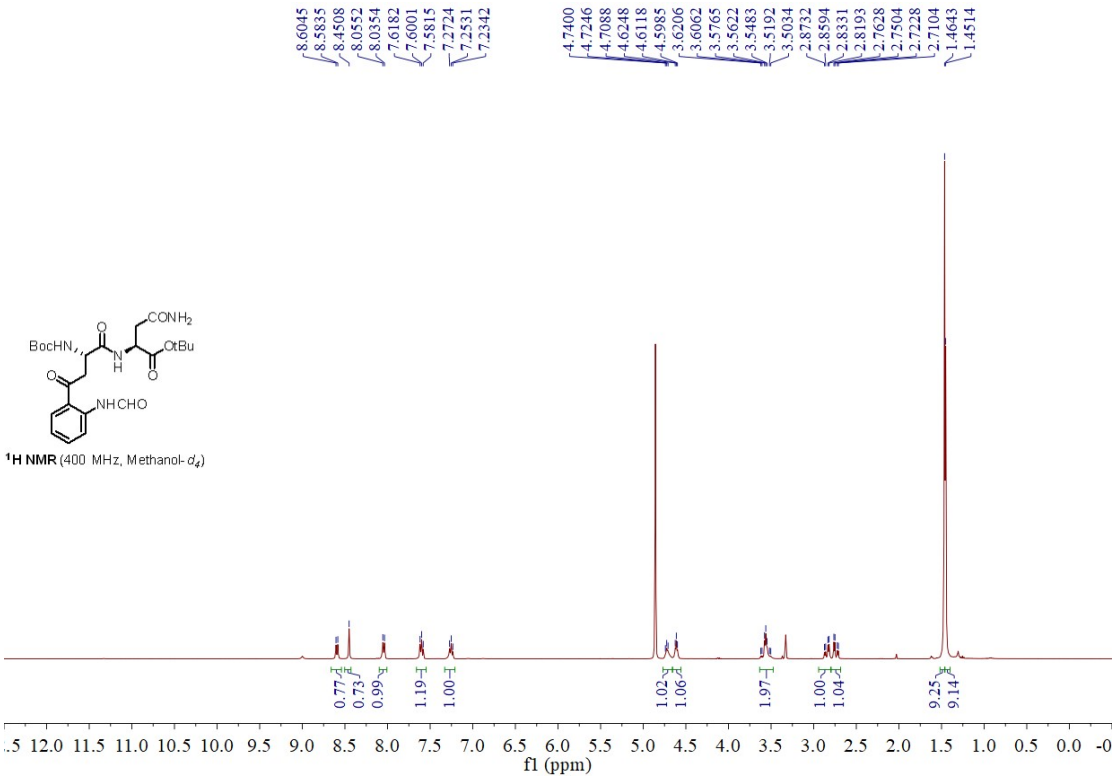

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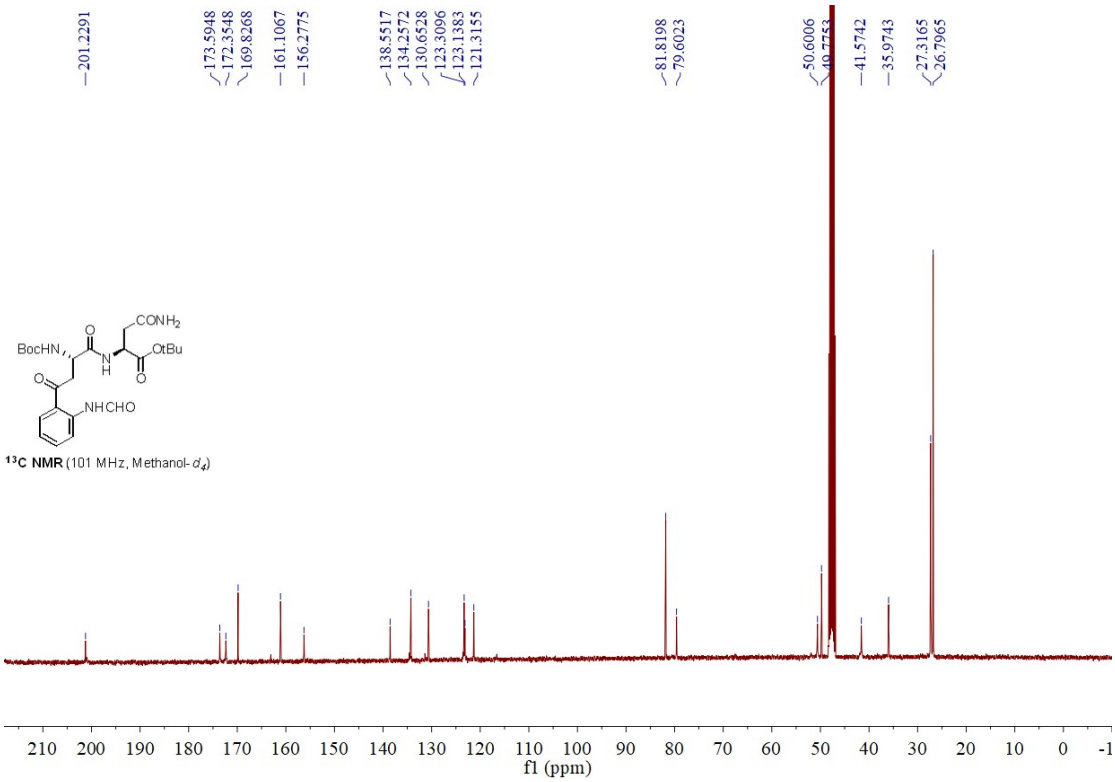
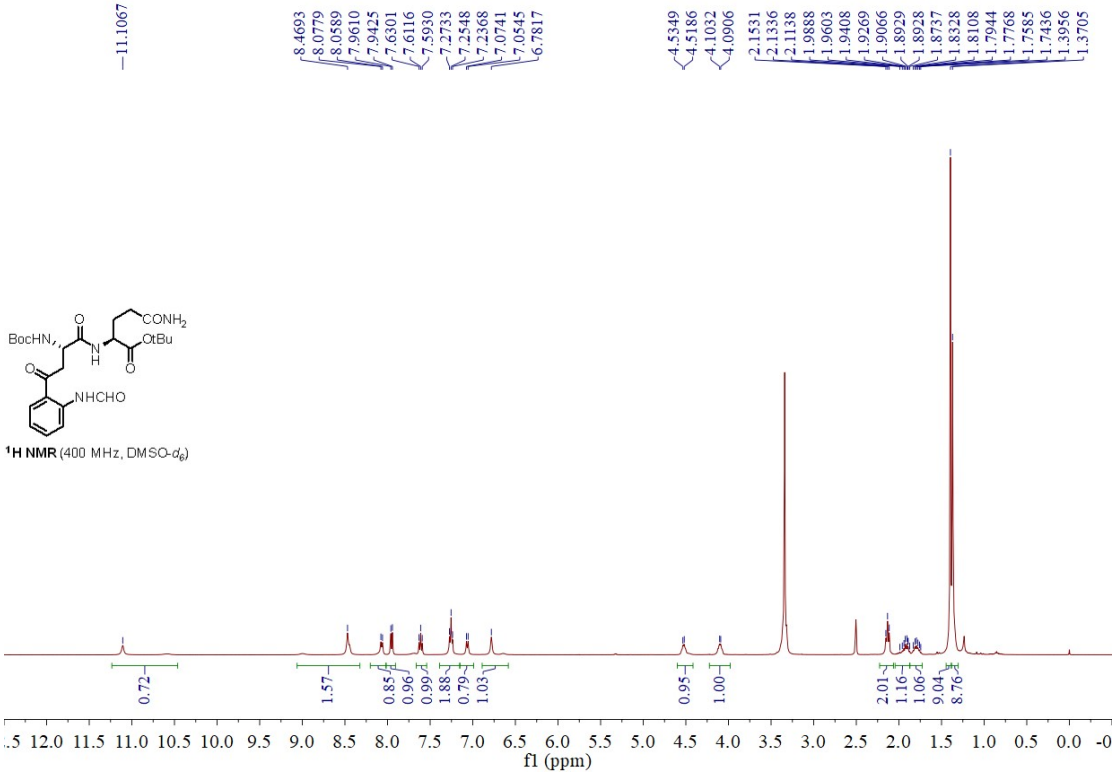
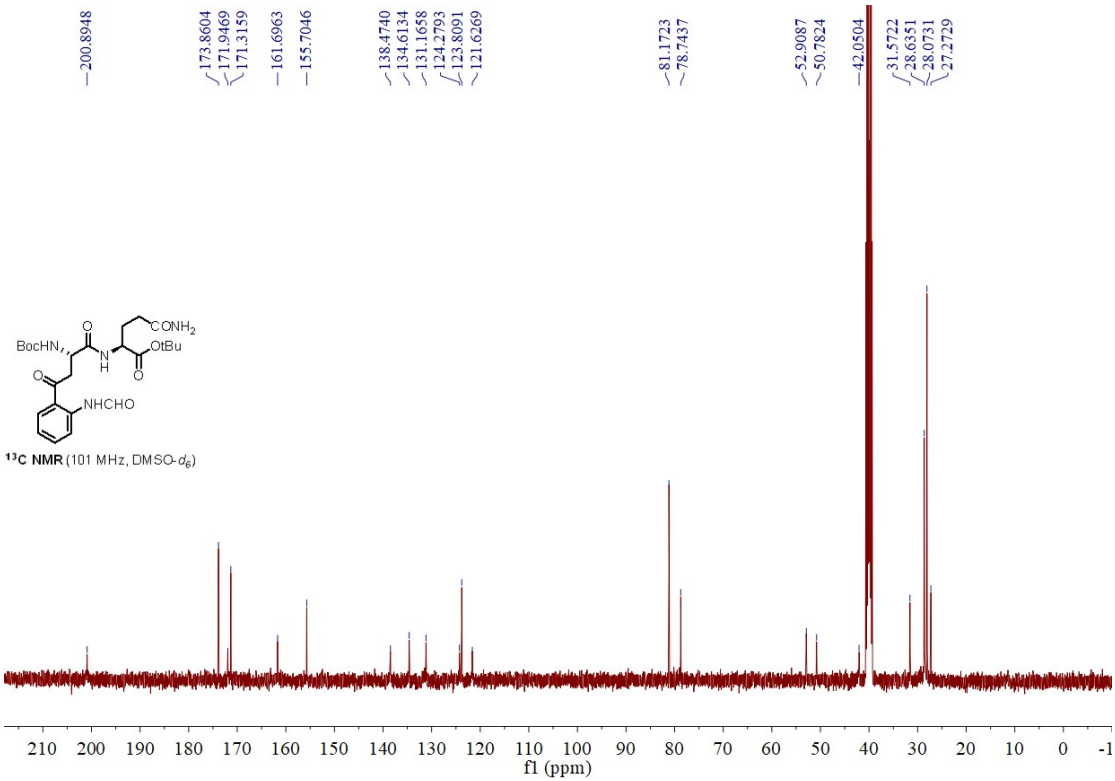


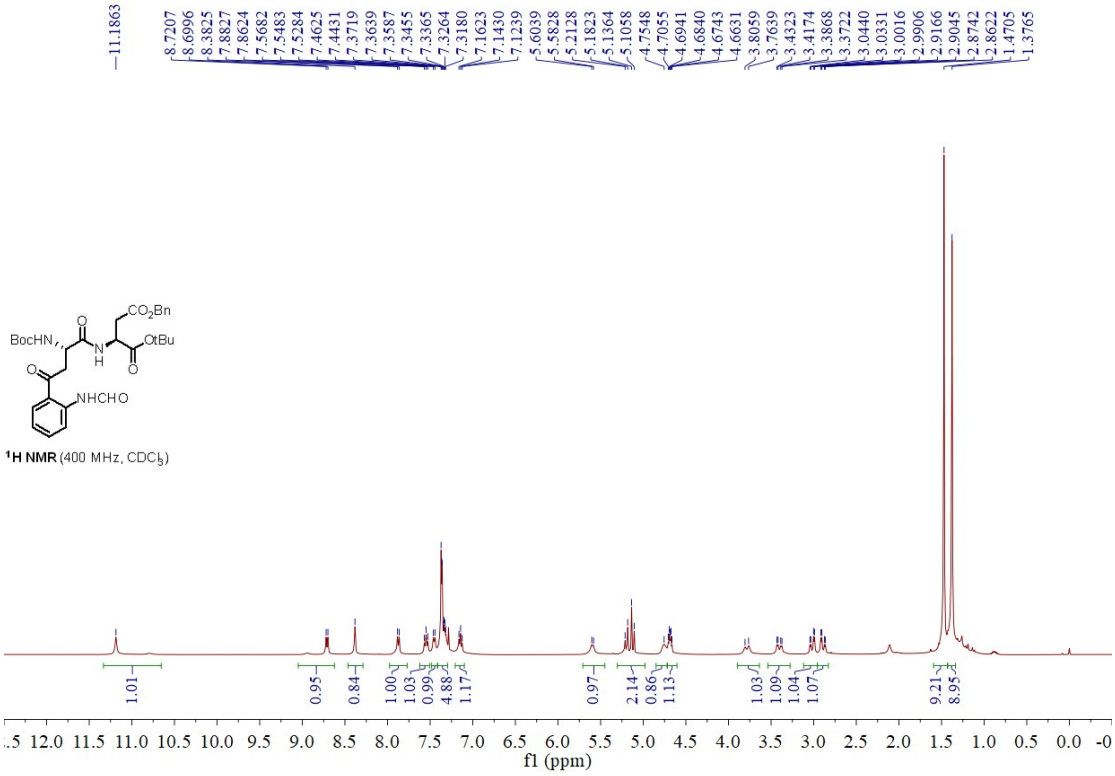
^{1}H NMR of **5m**



^{13}C NMR of **5m**



^{1}H NMR of **5n**



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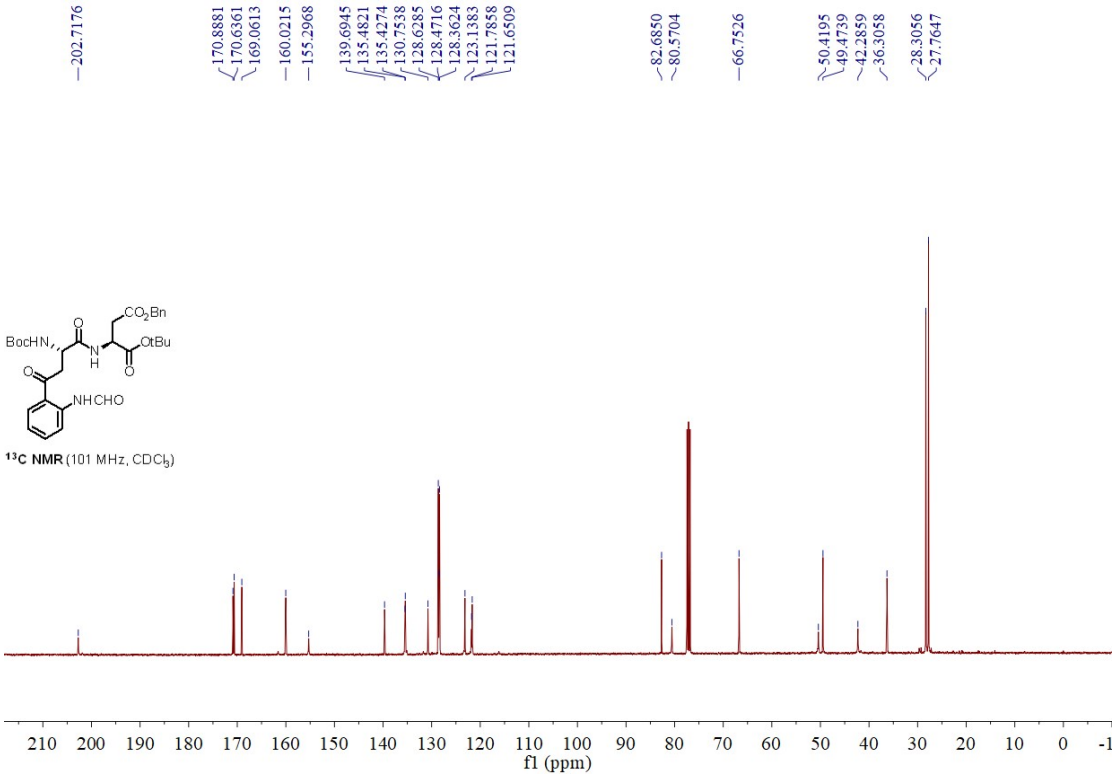

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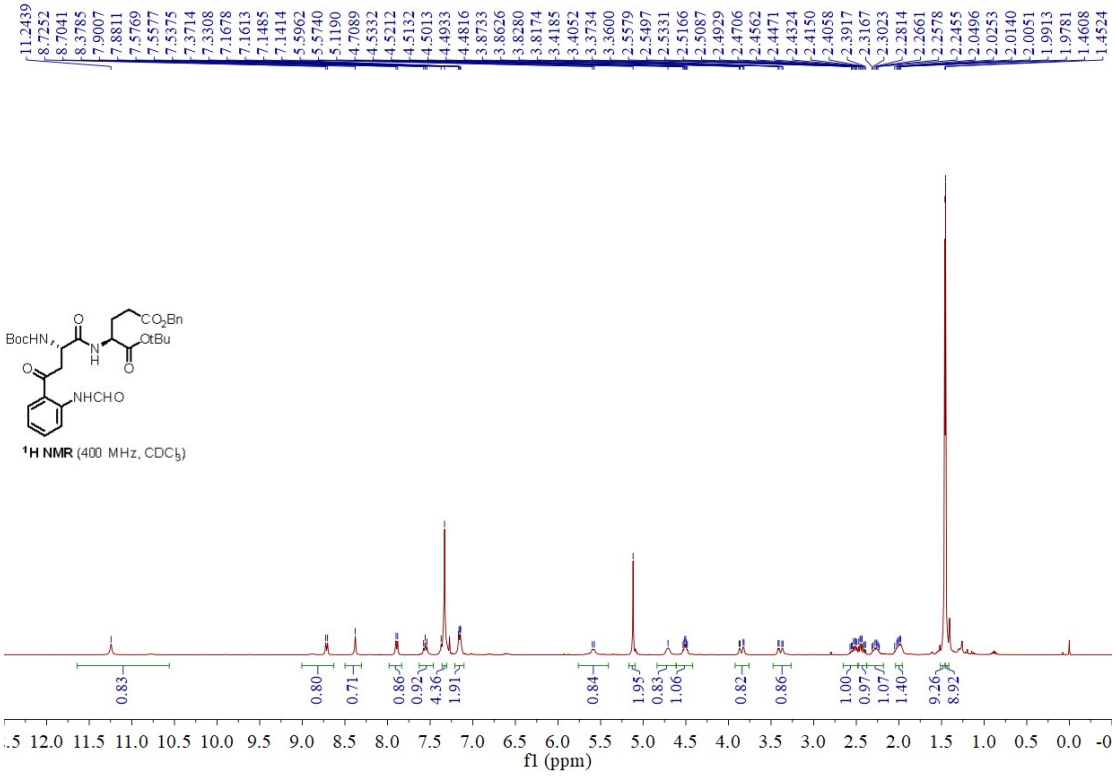

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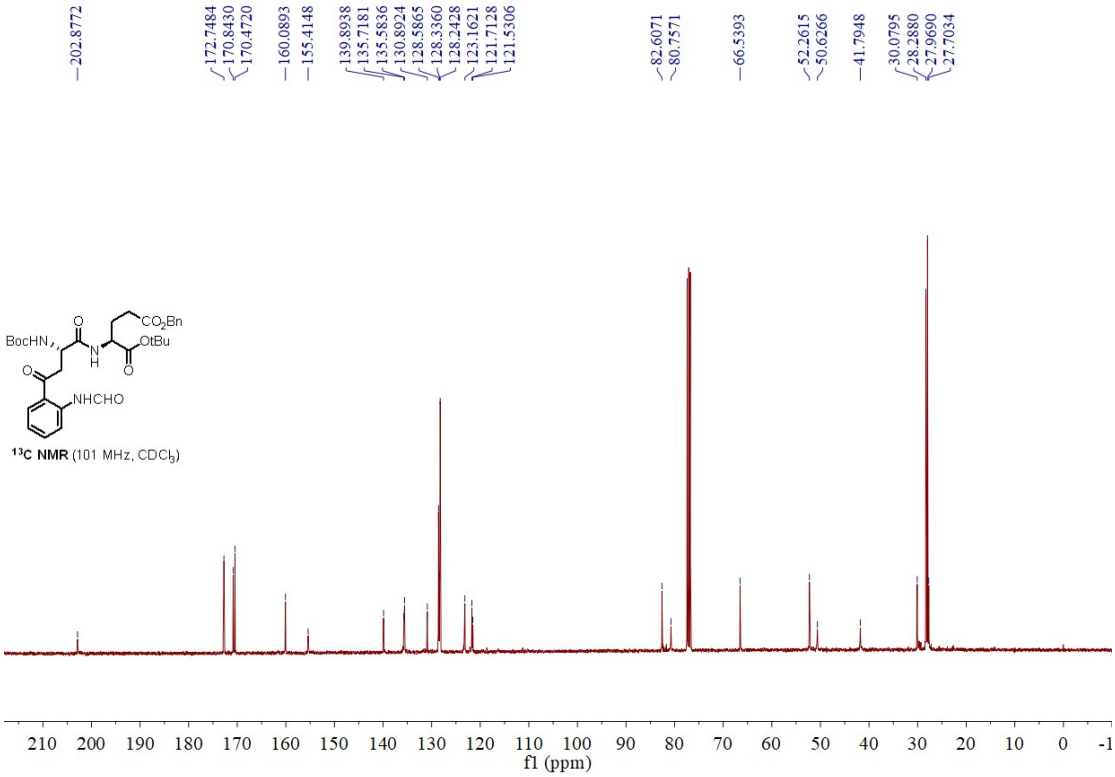

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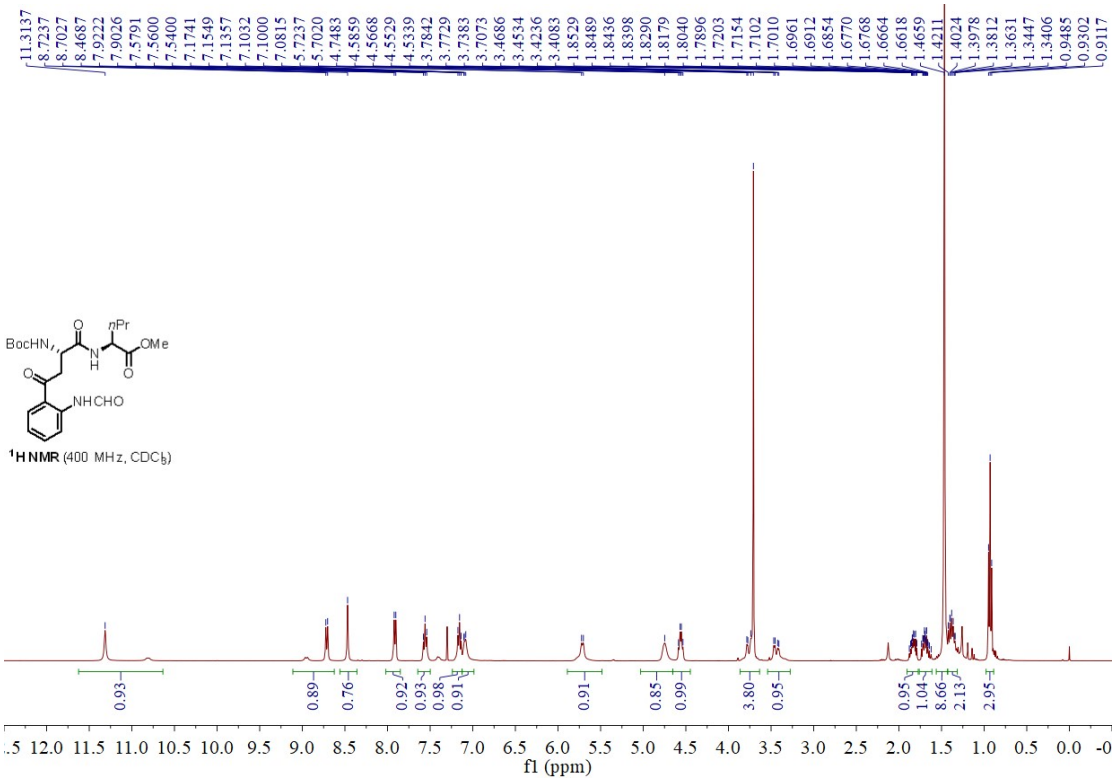

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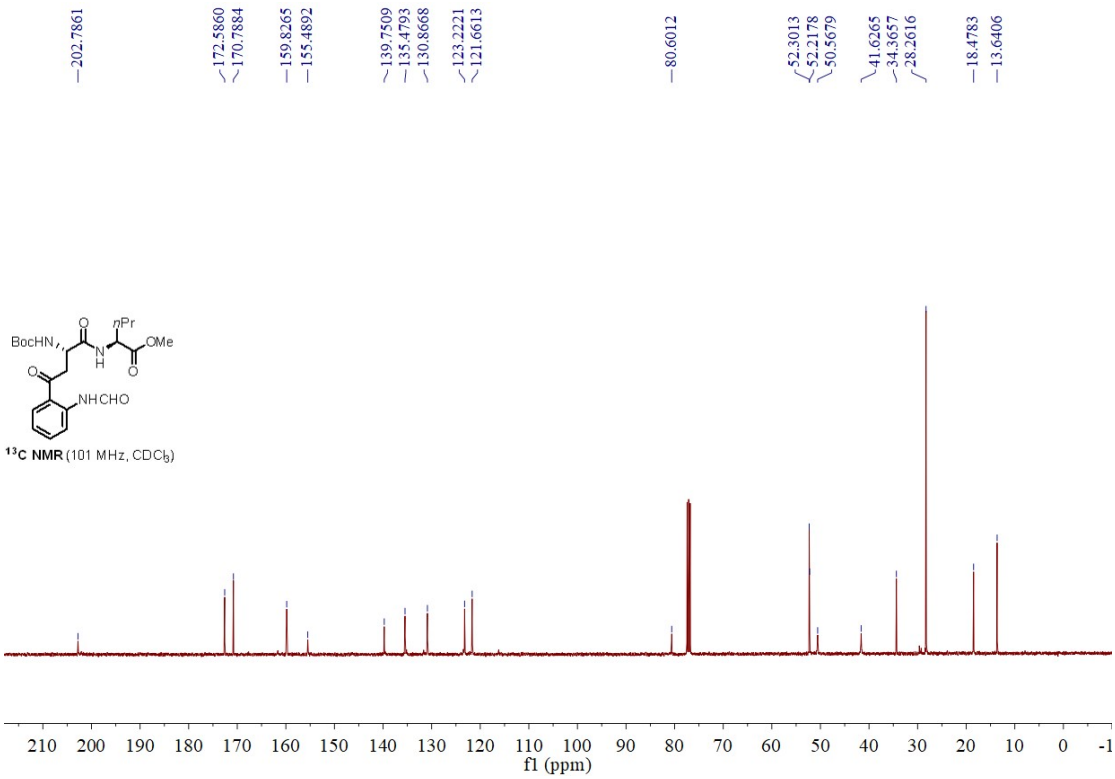

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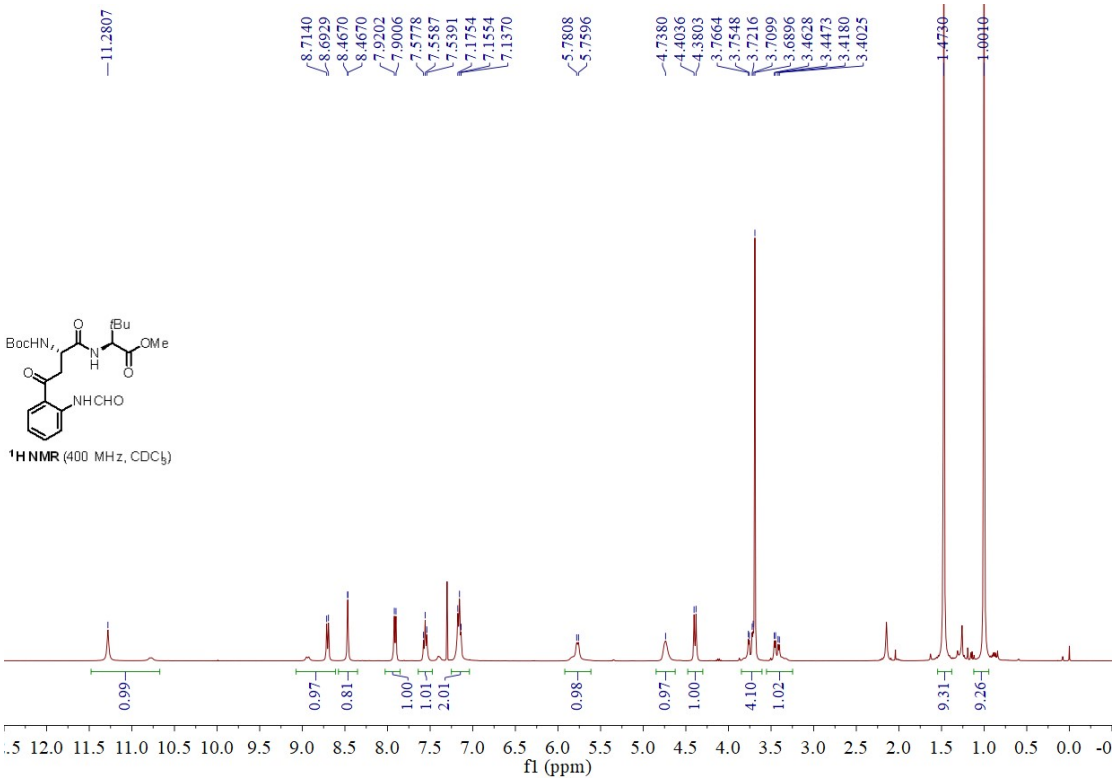

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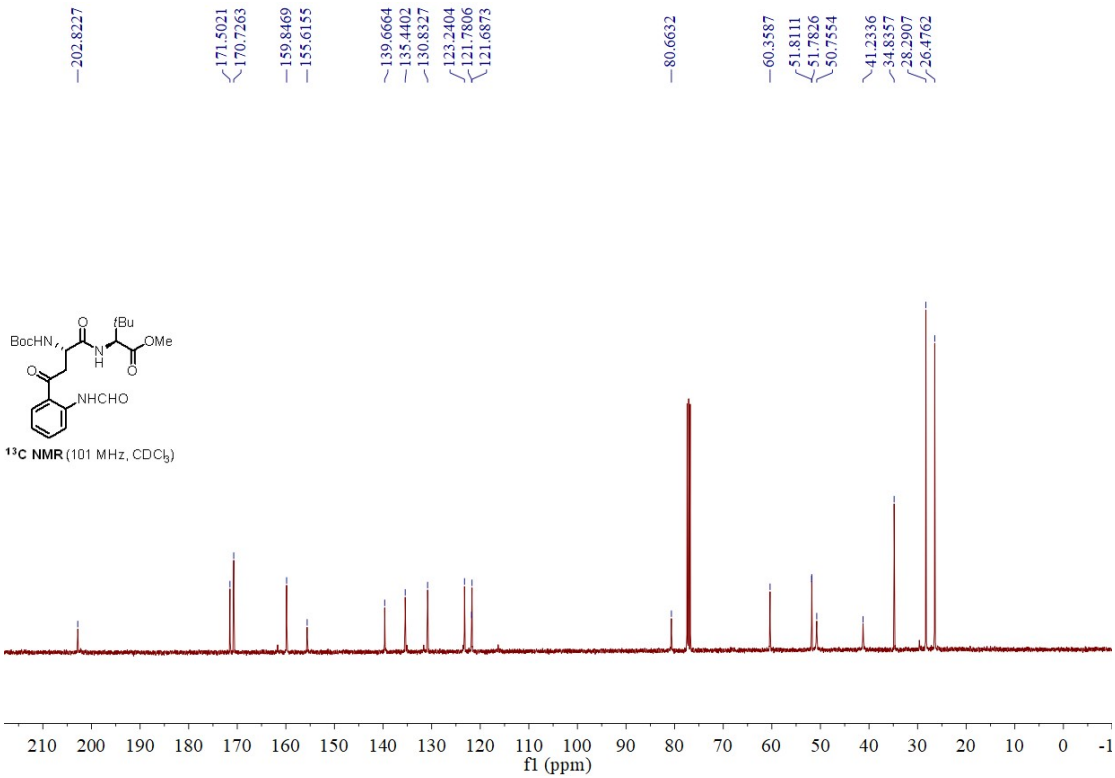

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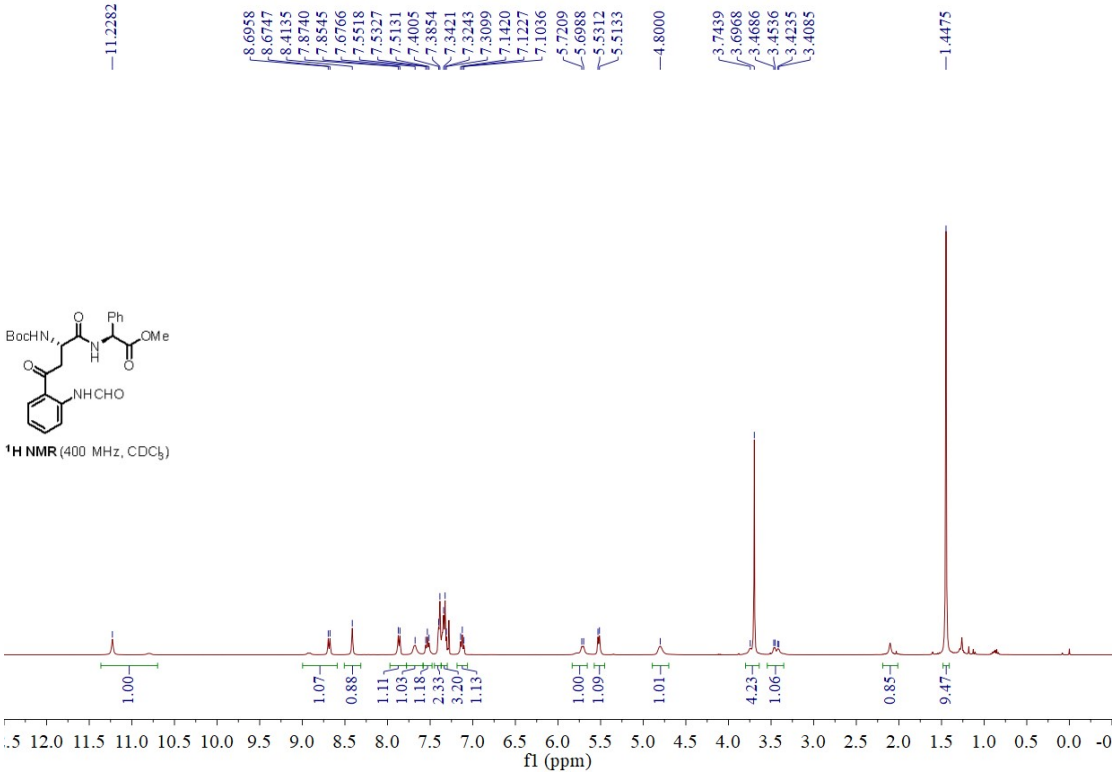

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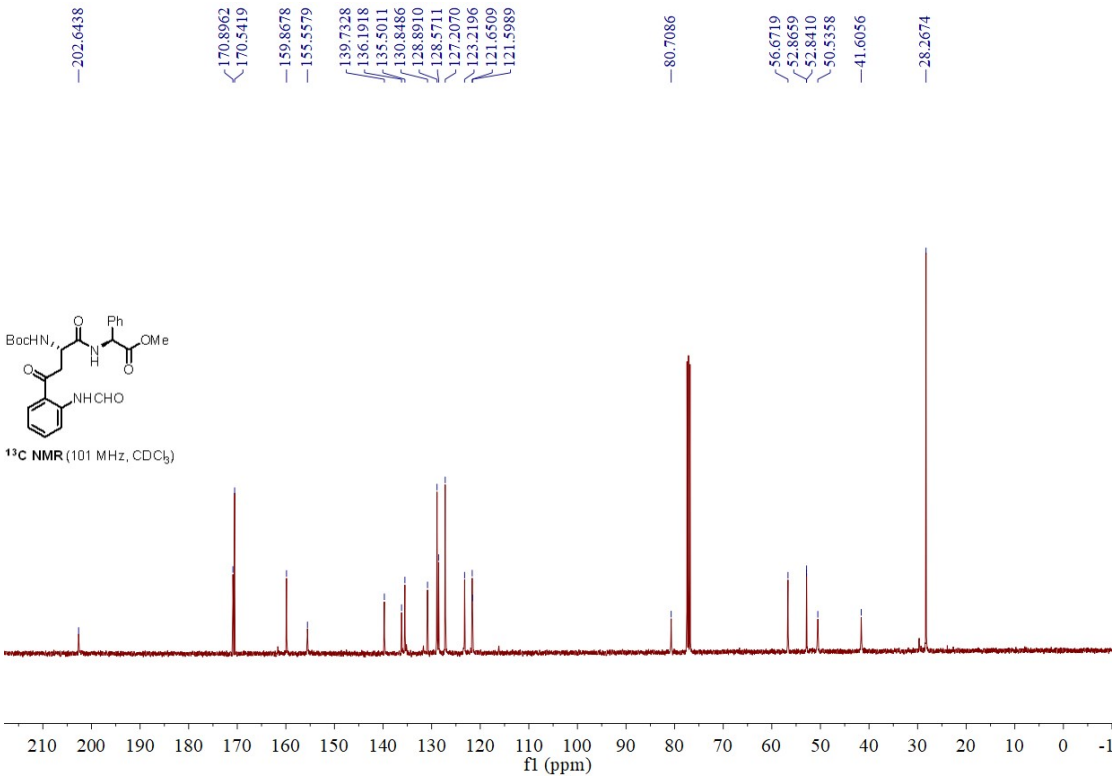
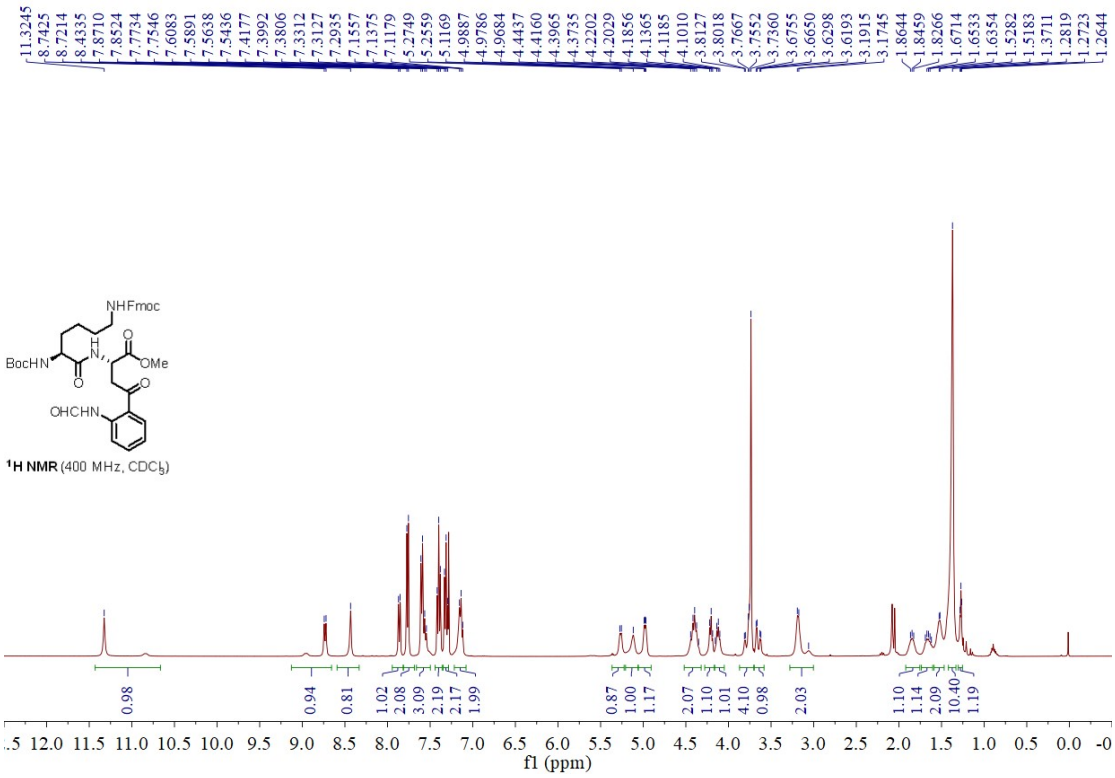
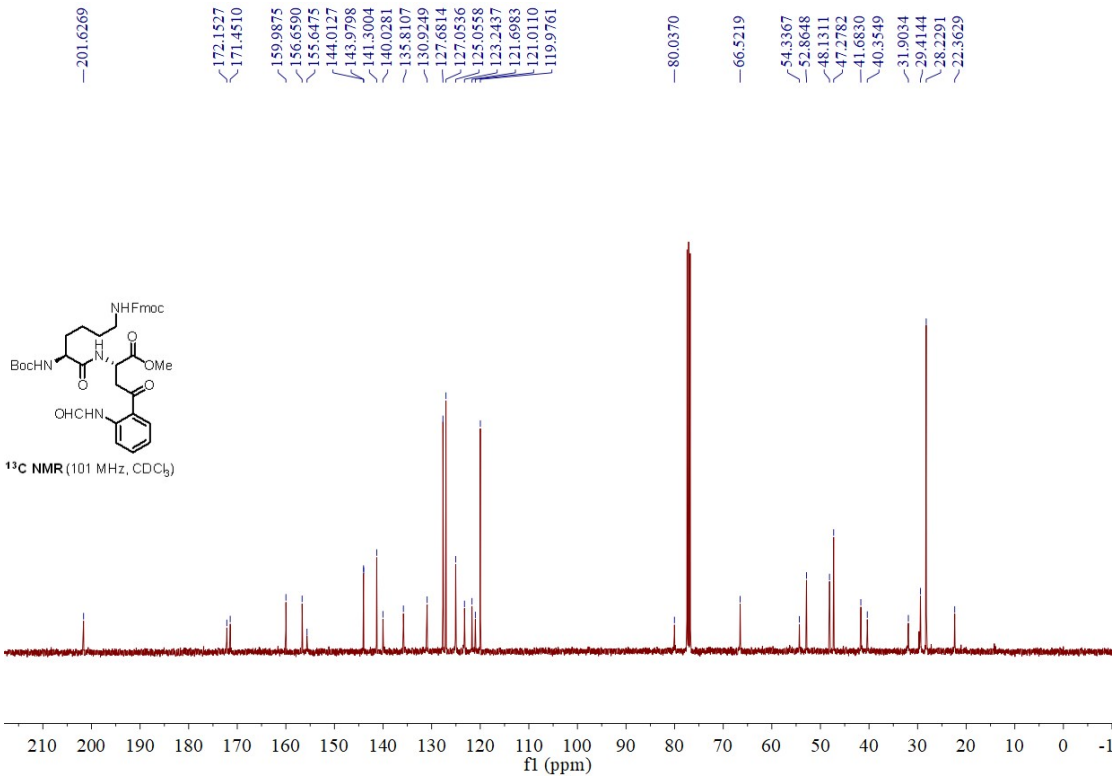


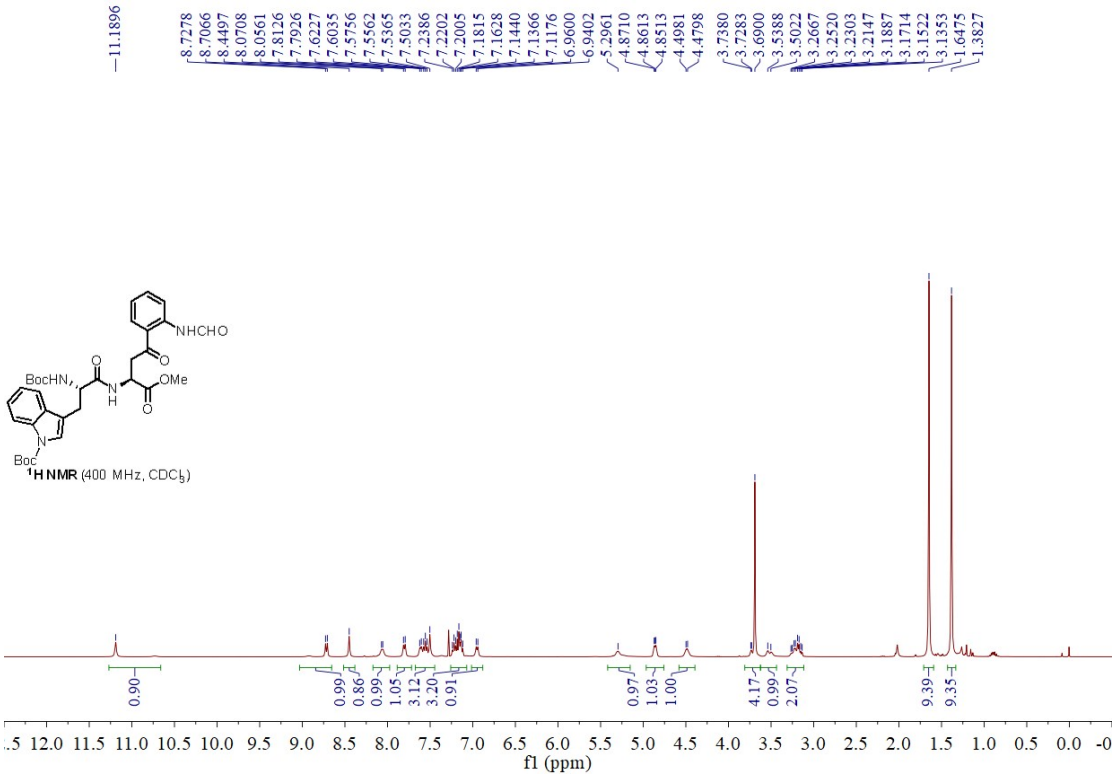
^{1}H NMR of **6a**



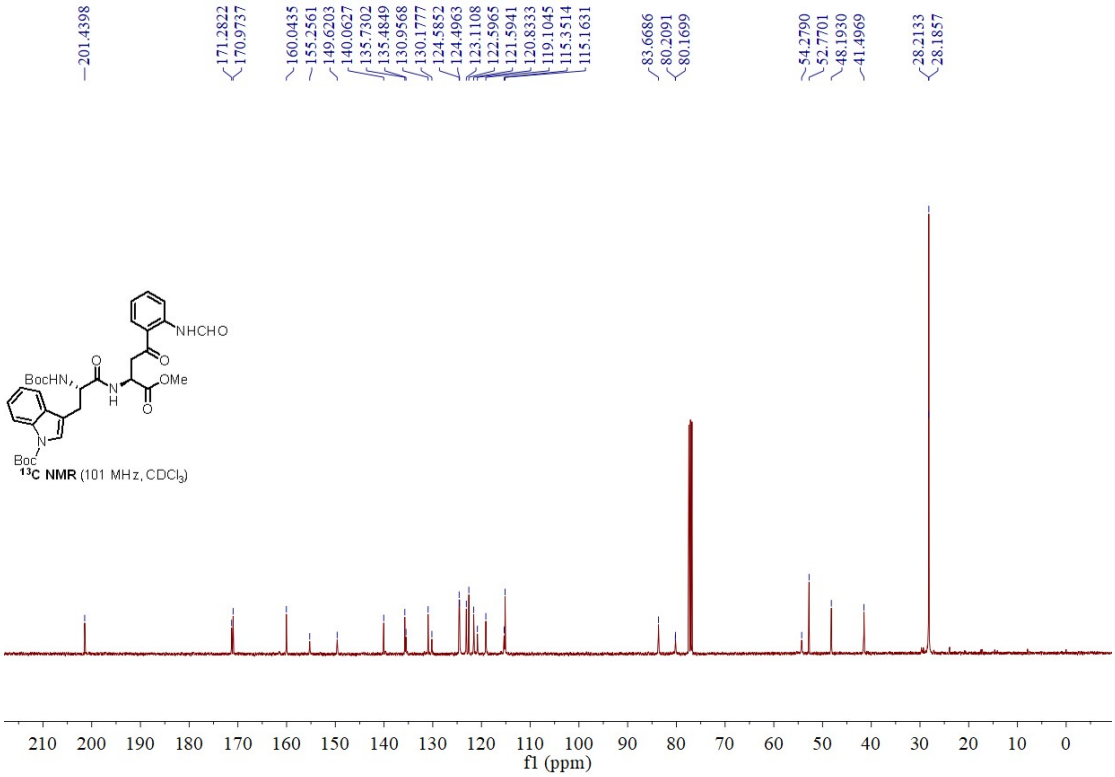
^{13}C NMR of **6a**



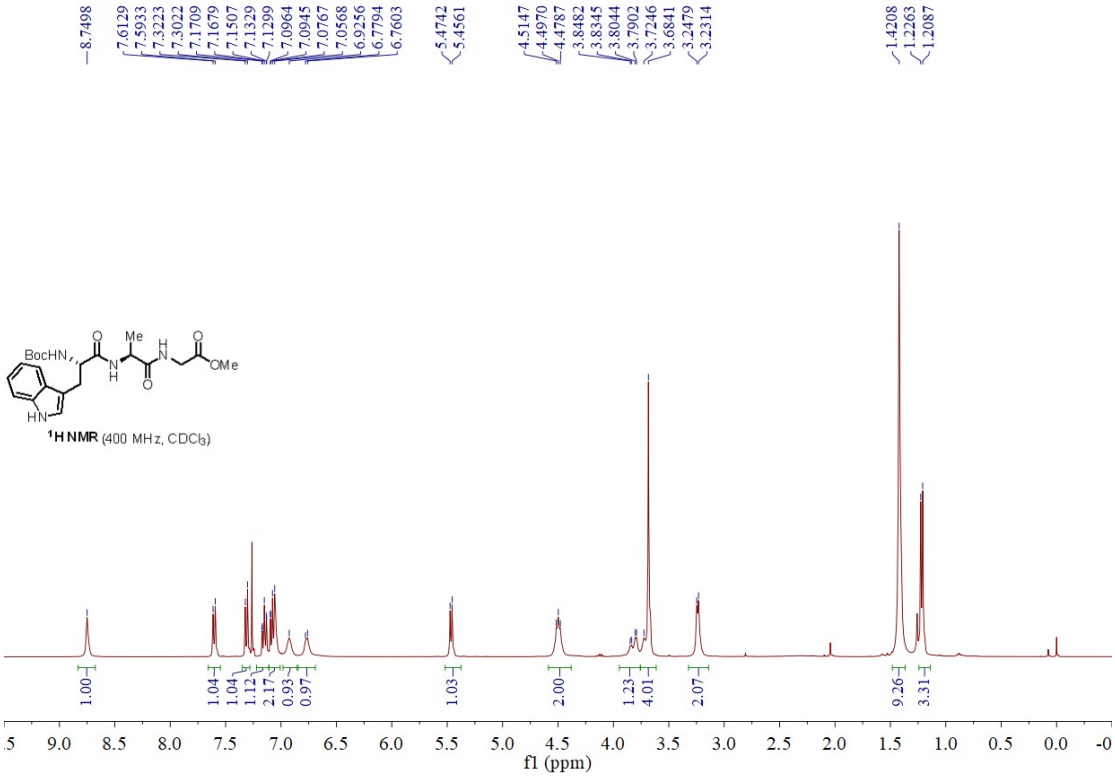
^{1}H NMR of **6b**



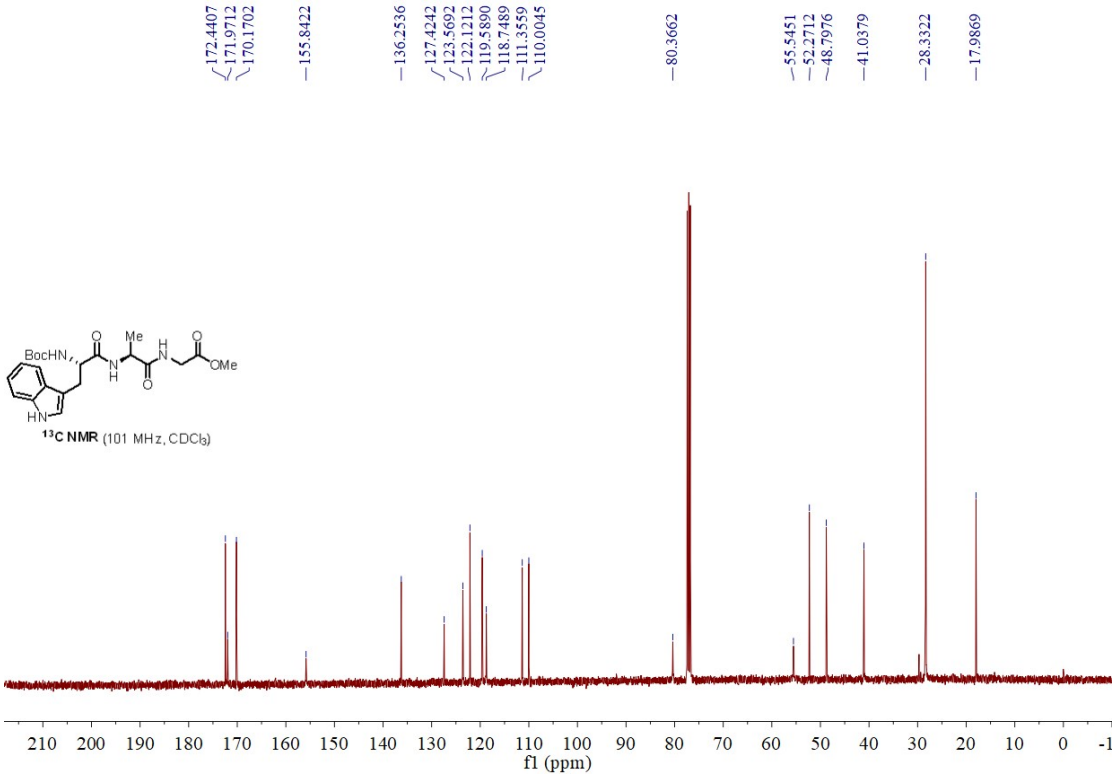
^{13}C NMR of **6b**



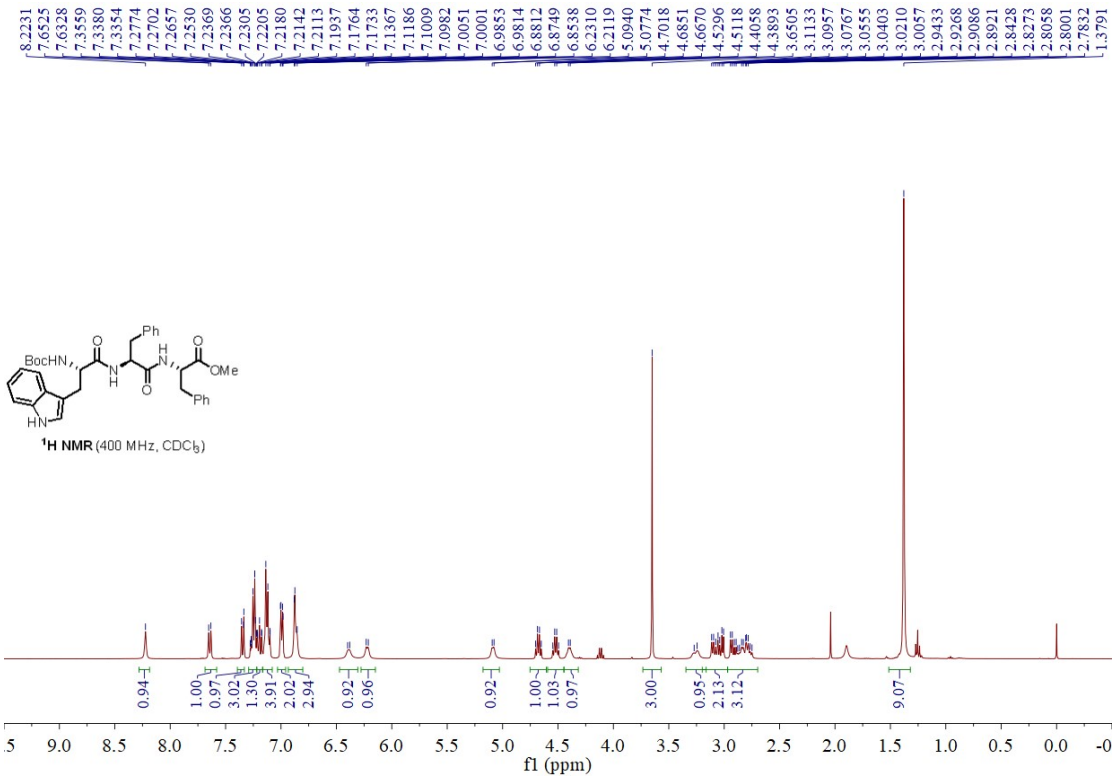
^{1}H NMR of **7a**



^{13}C NMR of **7a**



^{1}H NMR of **7b**



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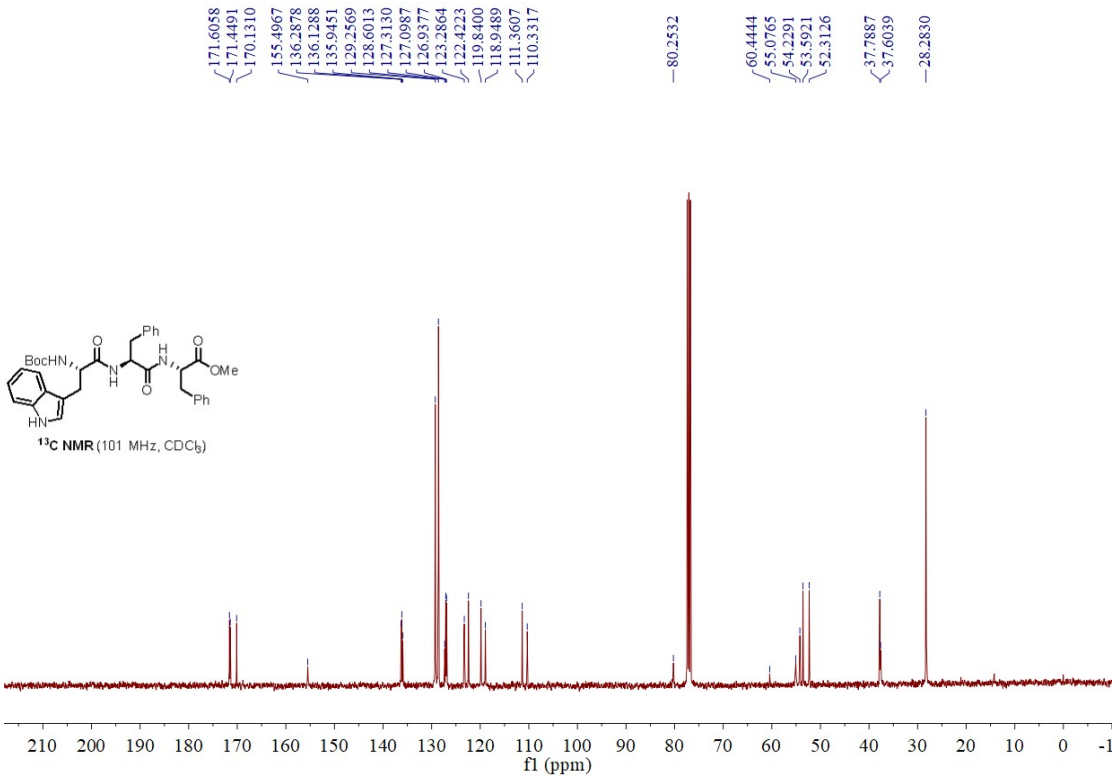
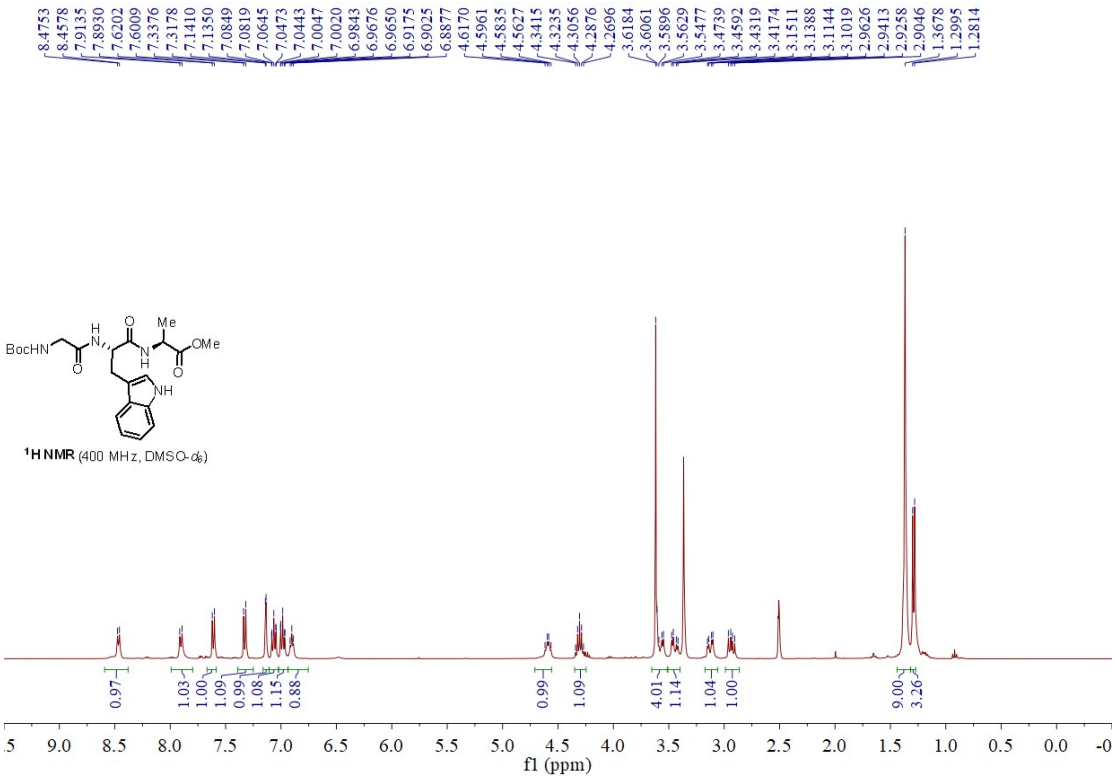
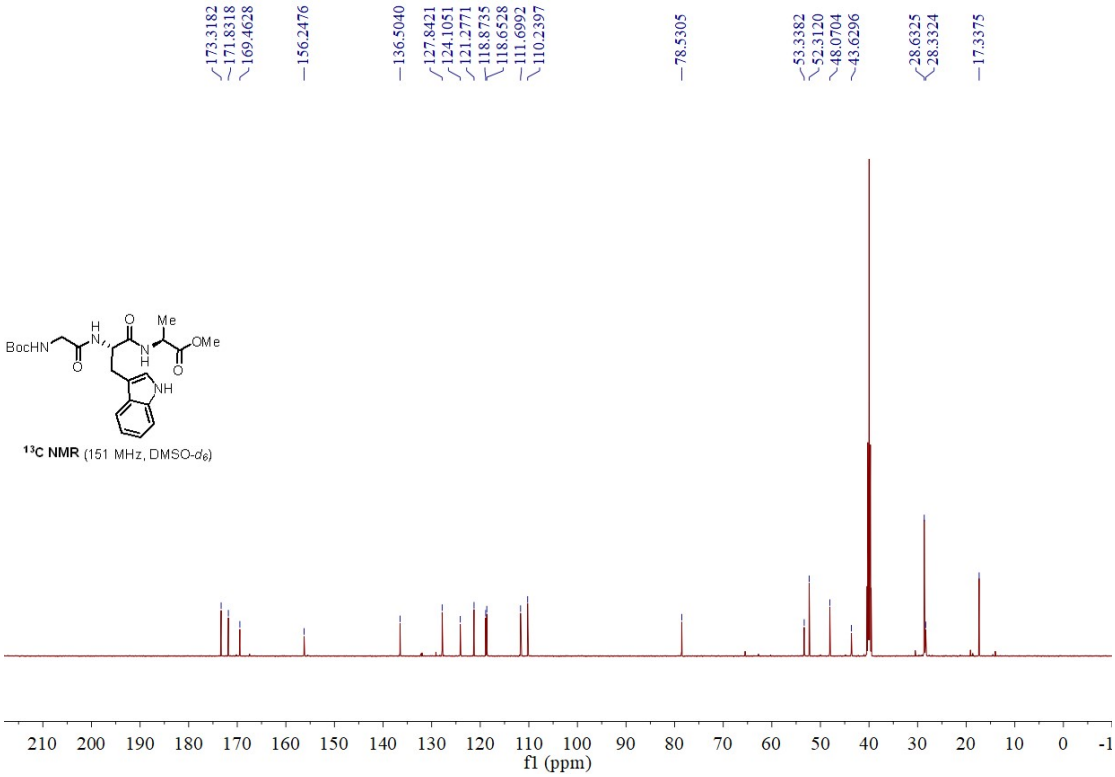


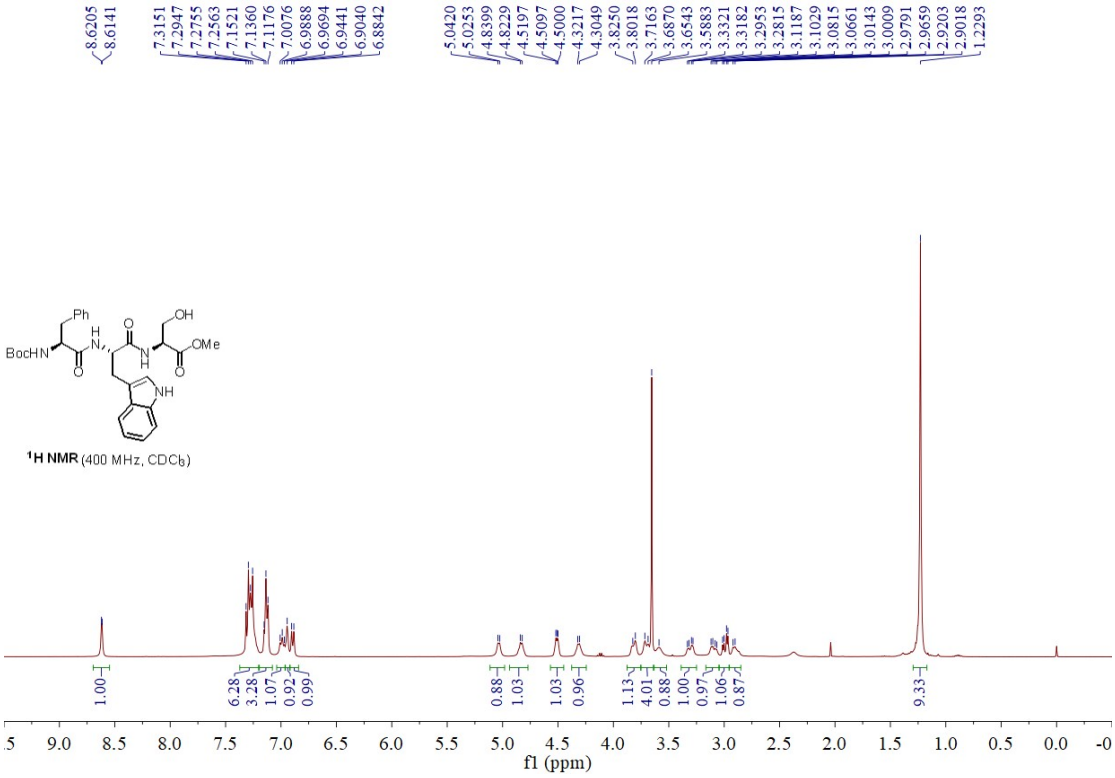
^{1}H NMR of **7c**



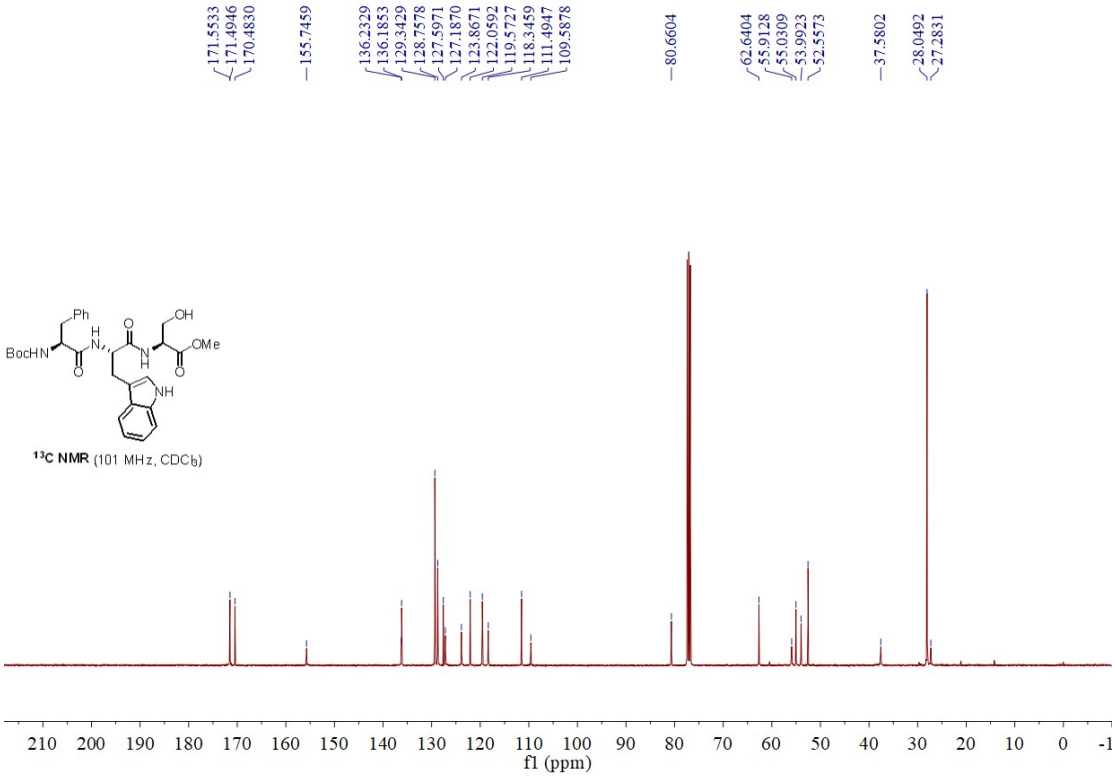
^{13}C NMR of **7c**



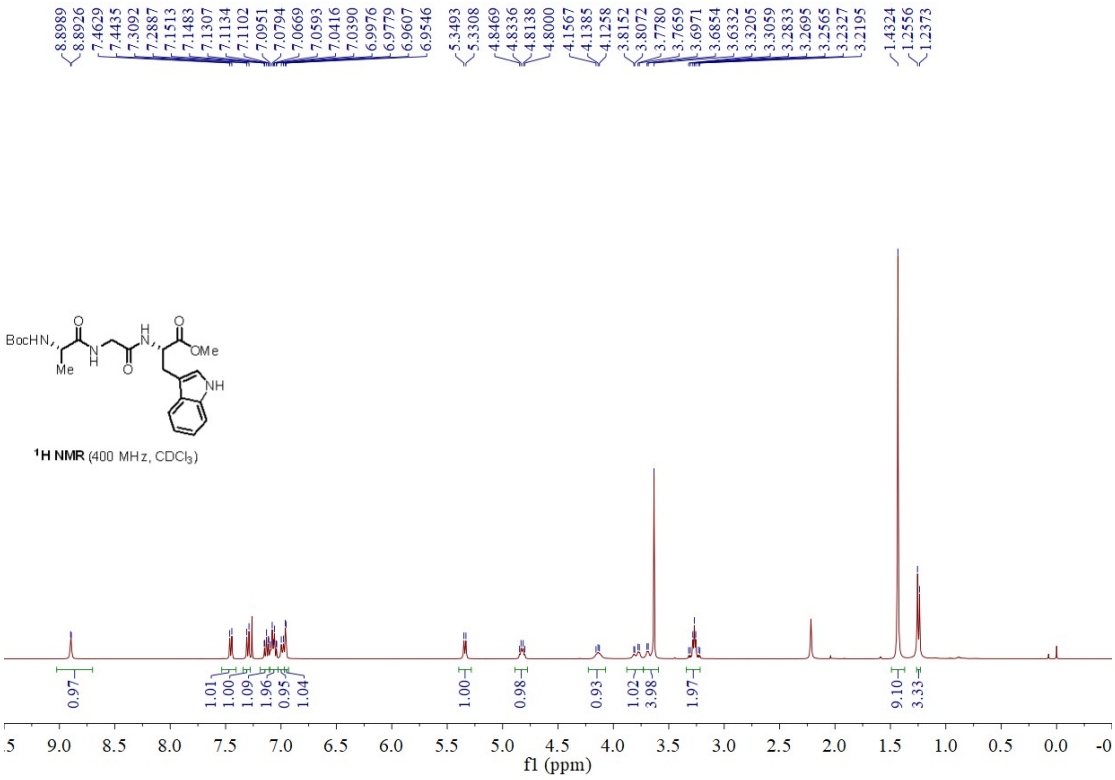
^{1}H NMR of **7d**



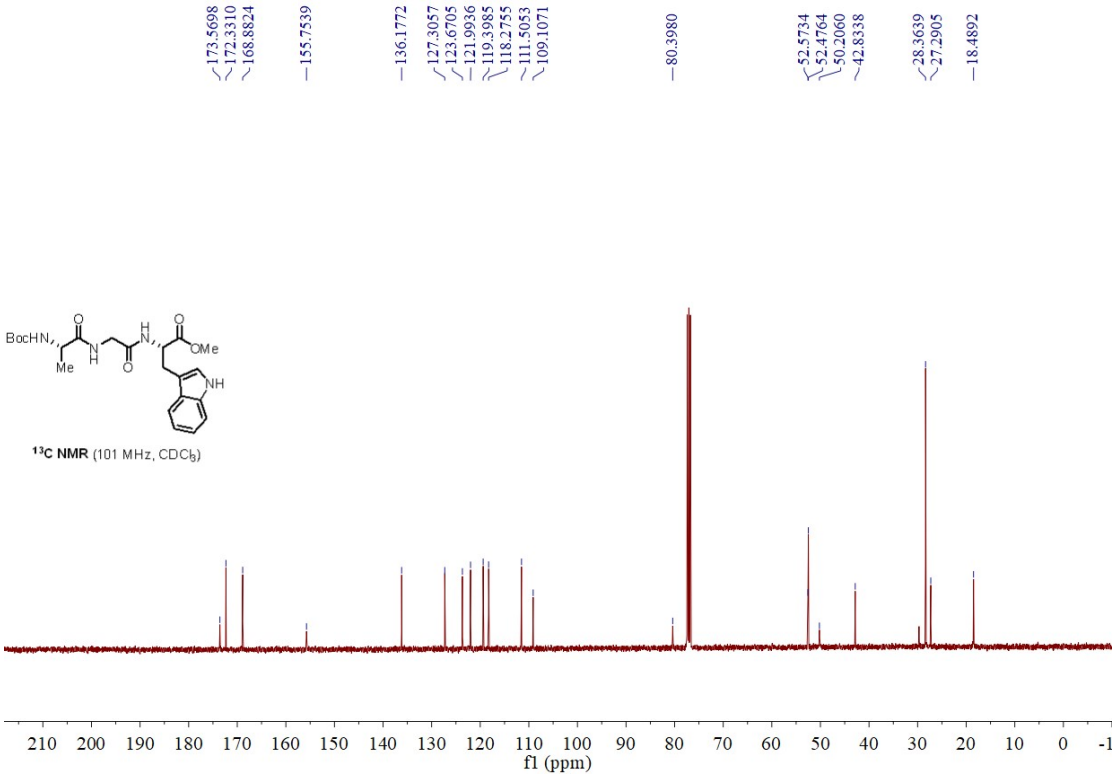
^{13}C NMR of **7d**



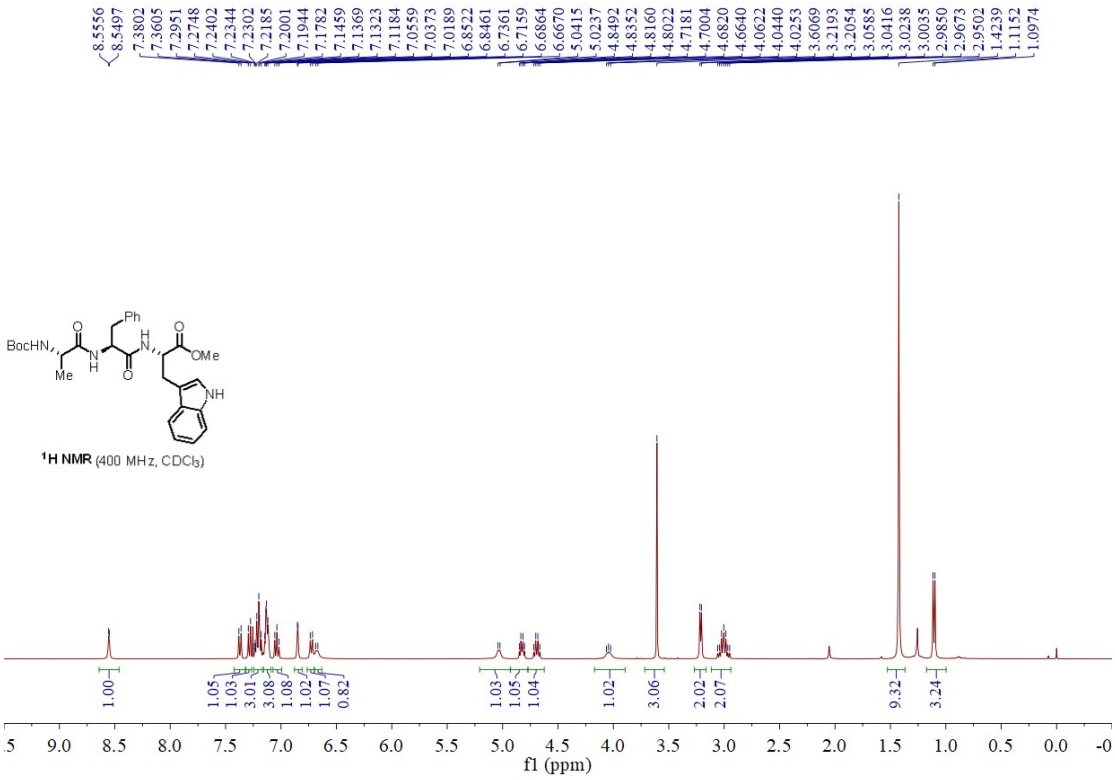
^{1}H NMR of **7e**



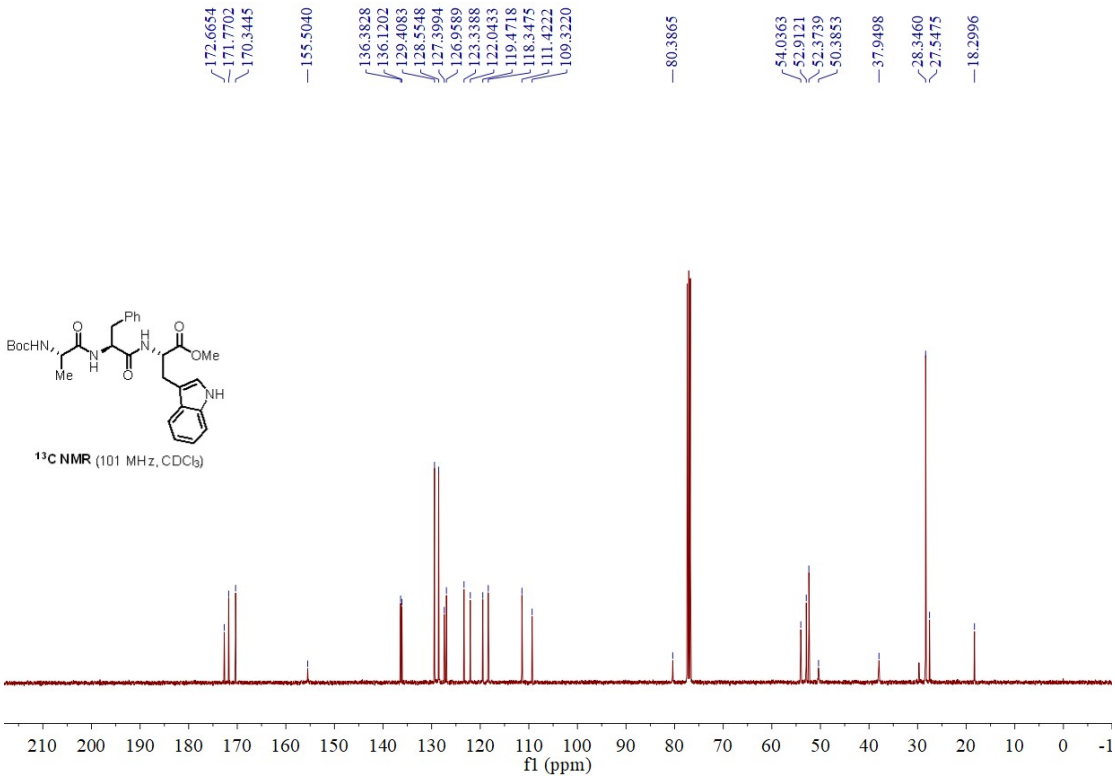
^{13}C NMR of **7e**



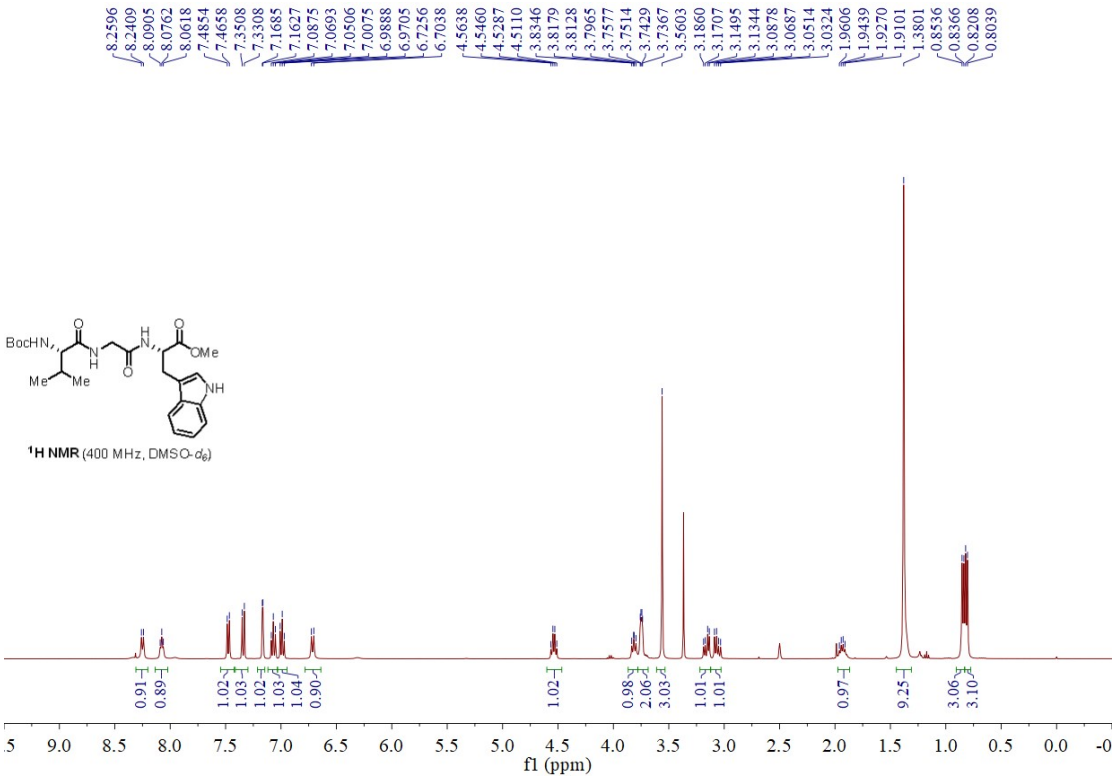
^{1}H NMR of **7f**



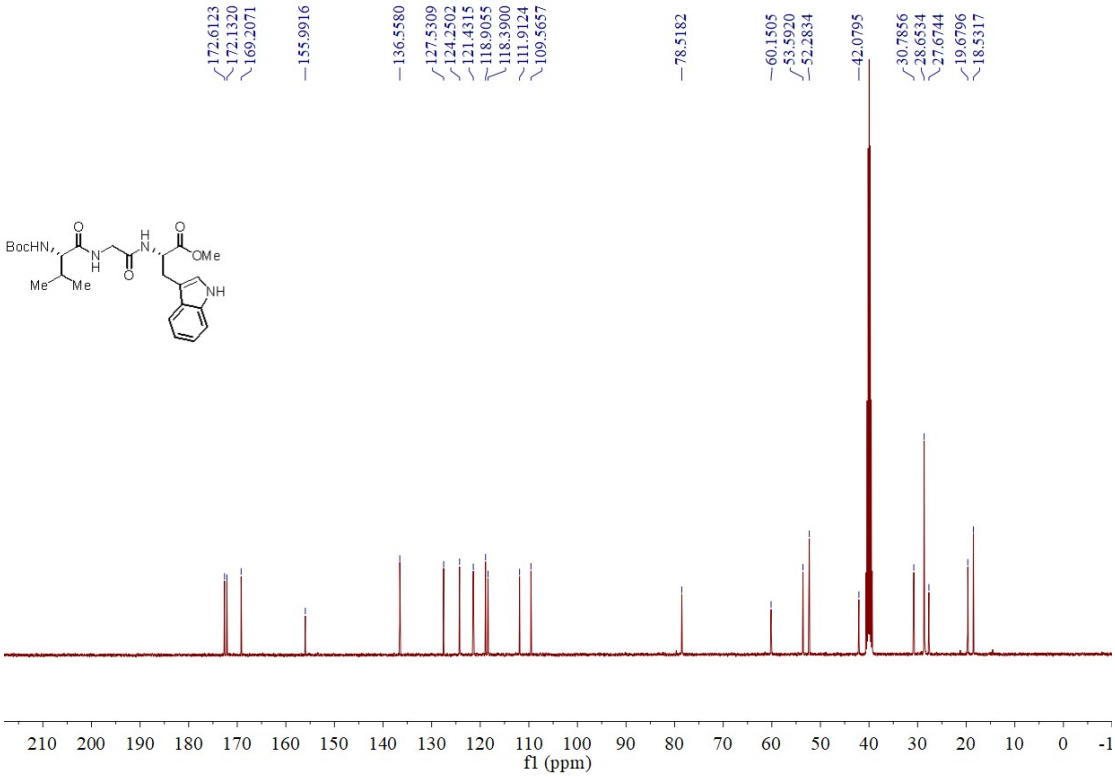
^{13}C NMR of **7f**



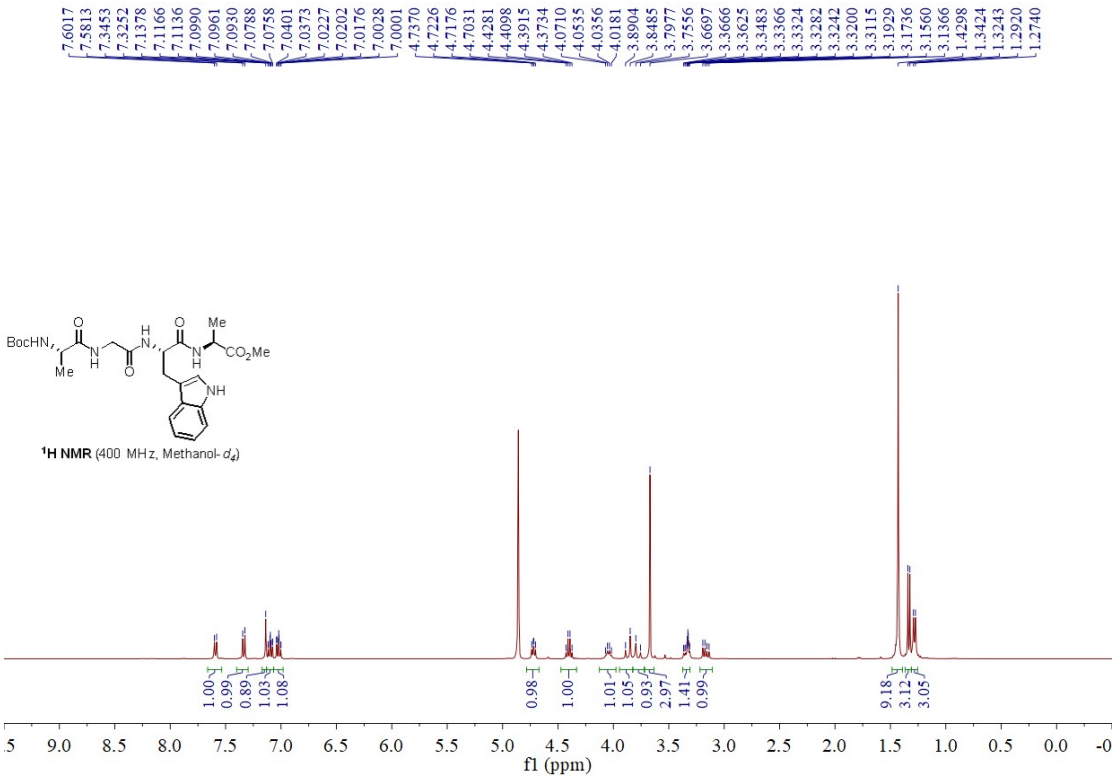
^{1}H NMR of **7g**



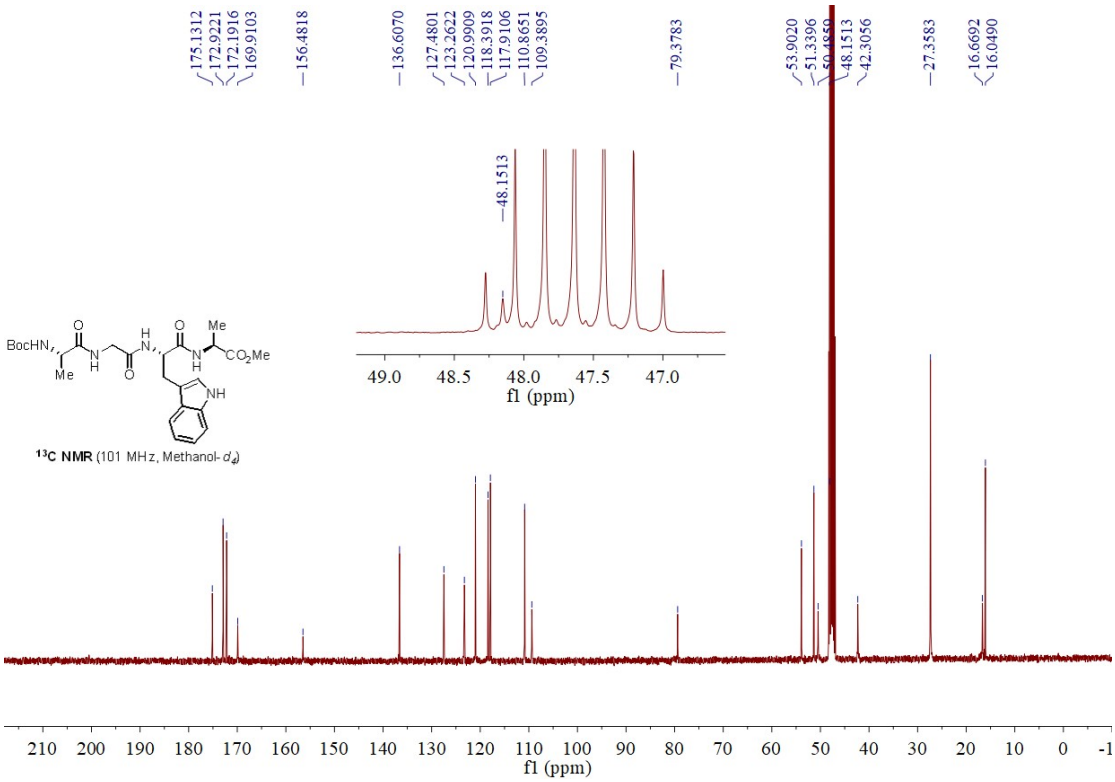
^{13}C NMR of **7g**



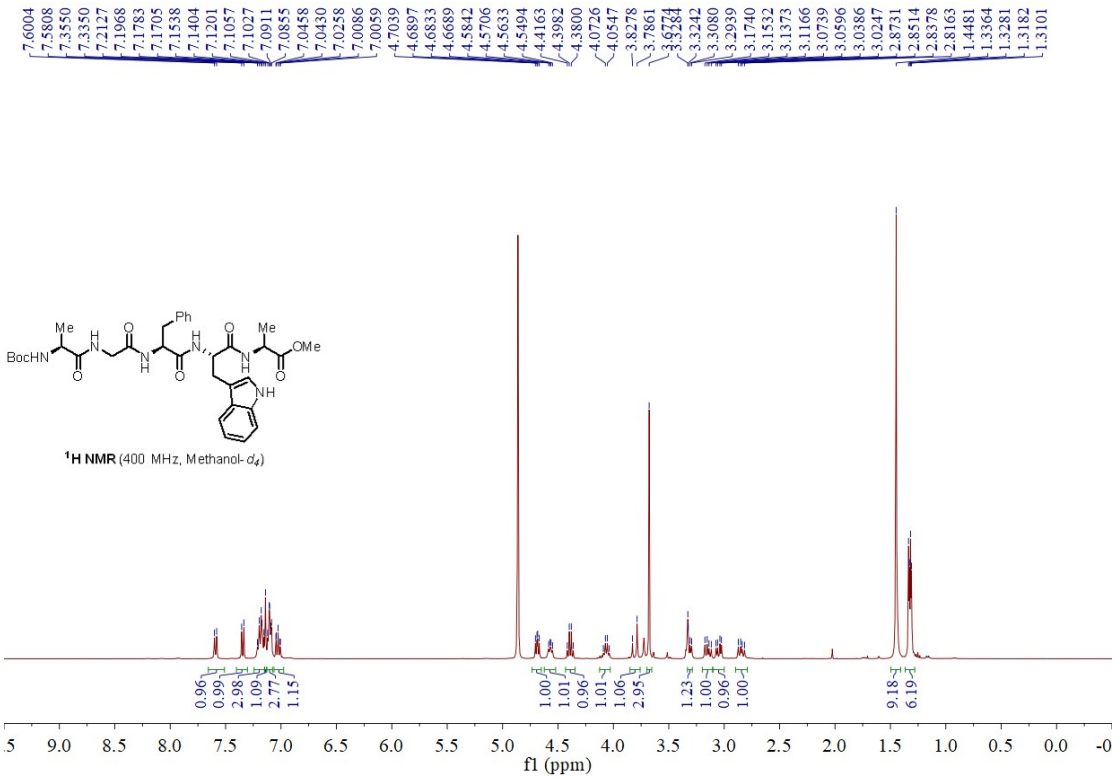
^{1}H NMR of **7h**



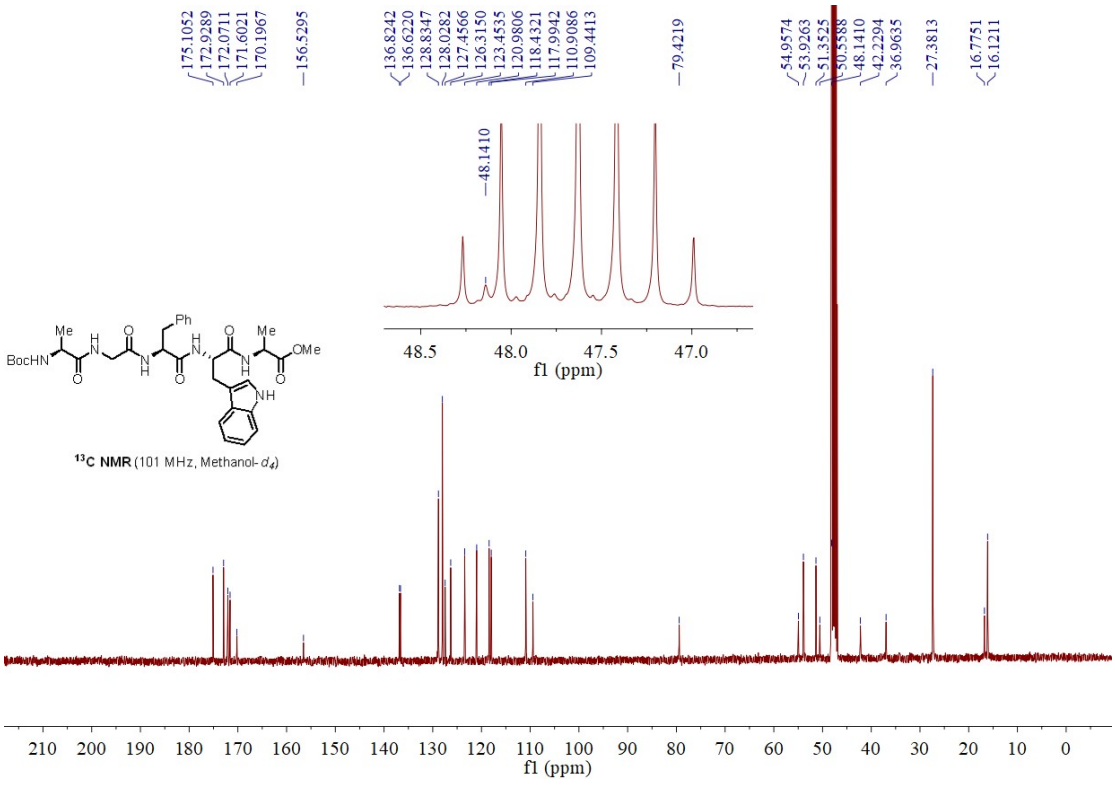
^{13}C NMR of **7h**



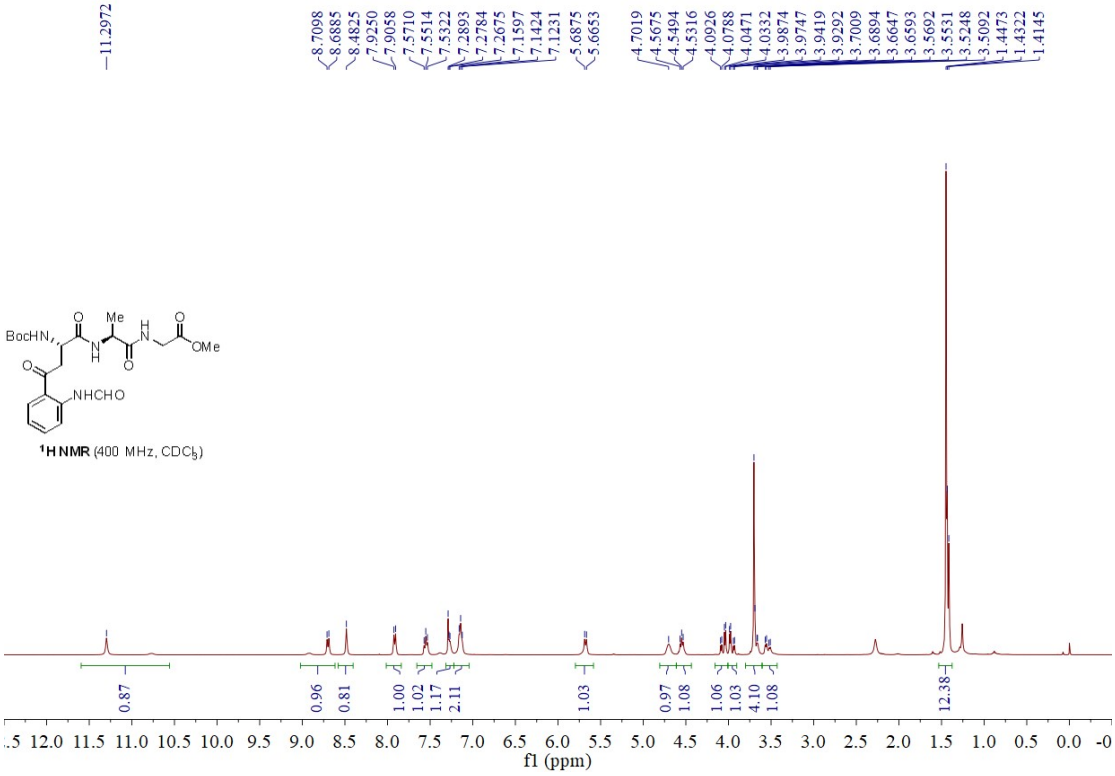
^{1}H NMR of **7i**



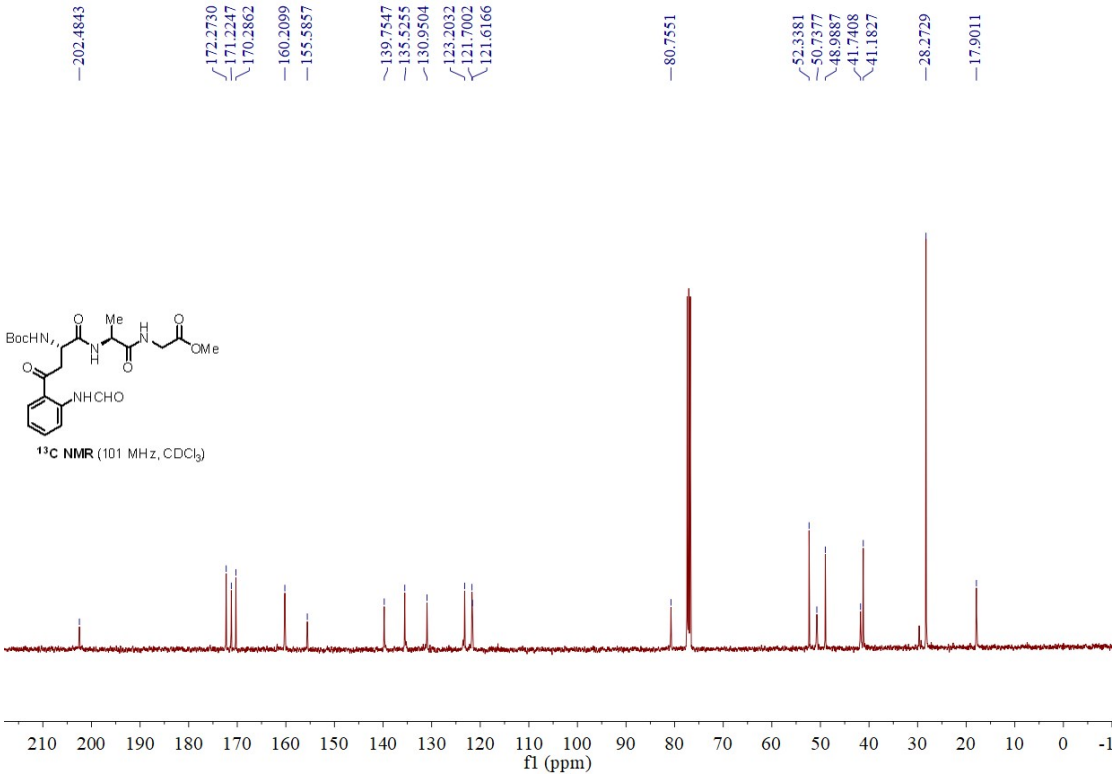
^{13}C NMR of **7i**



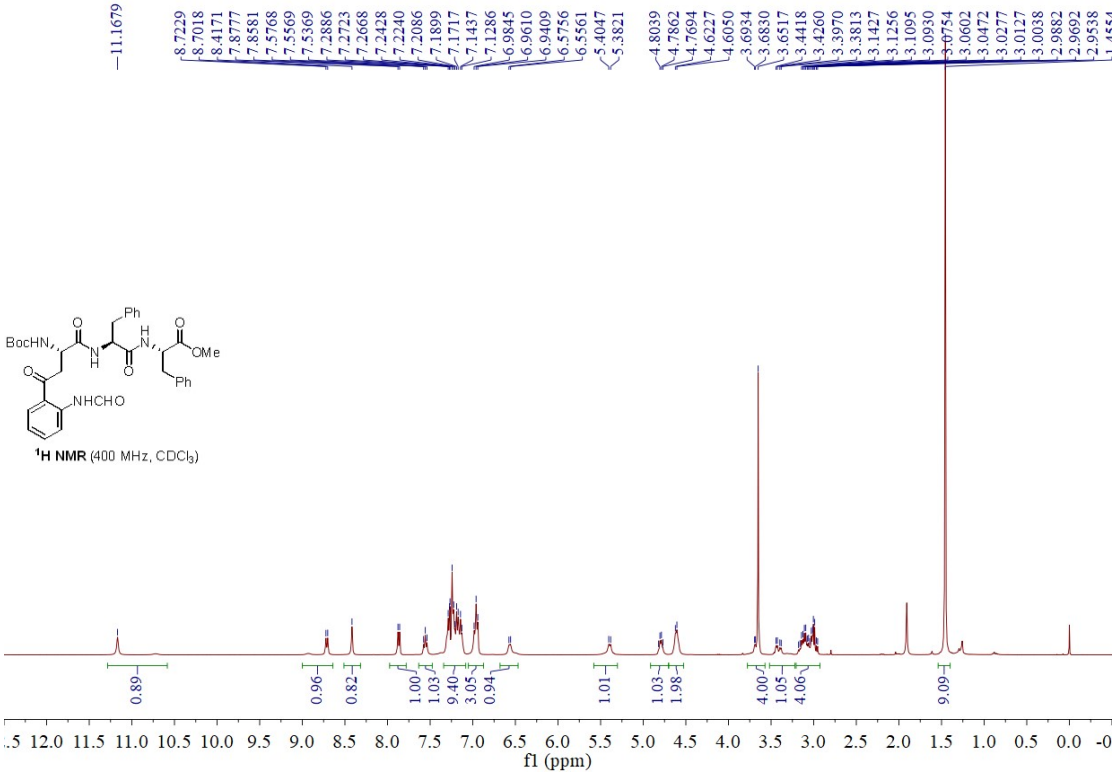
^{1}H NMR of **8a**



^{13}C NMR of **8a**



^{1}H NMR of **8b**



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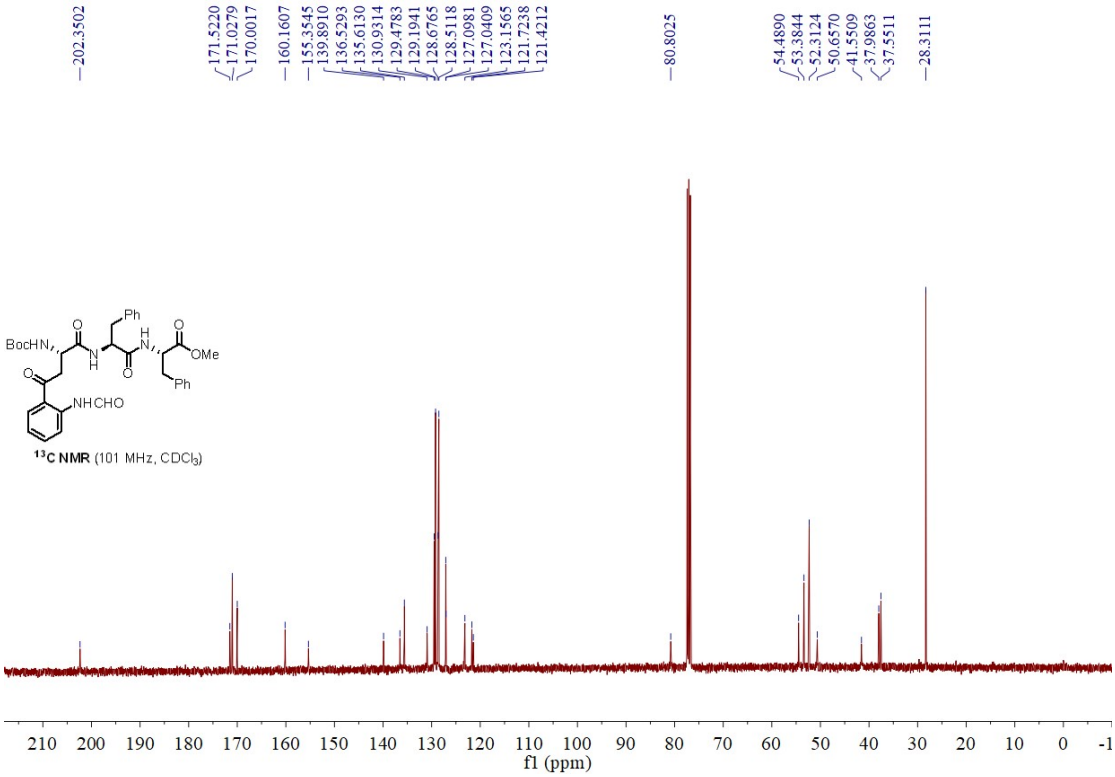
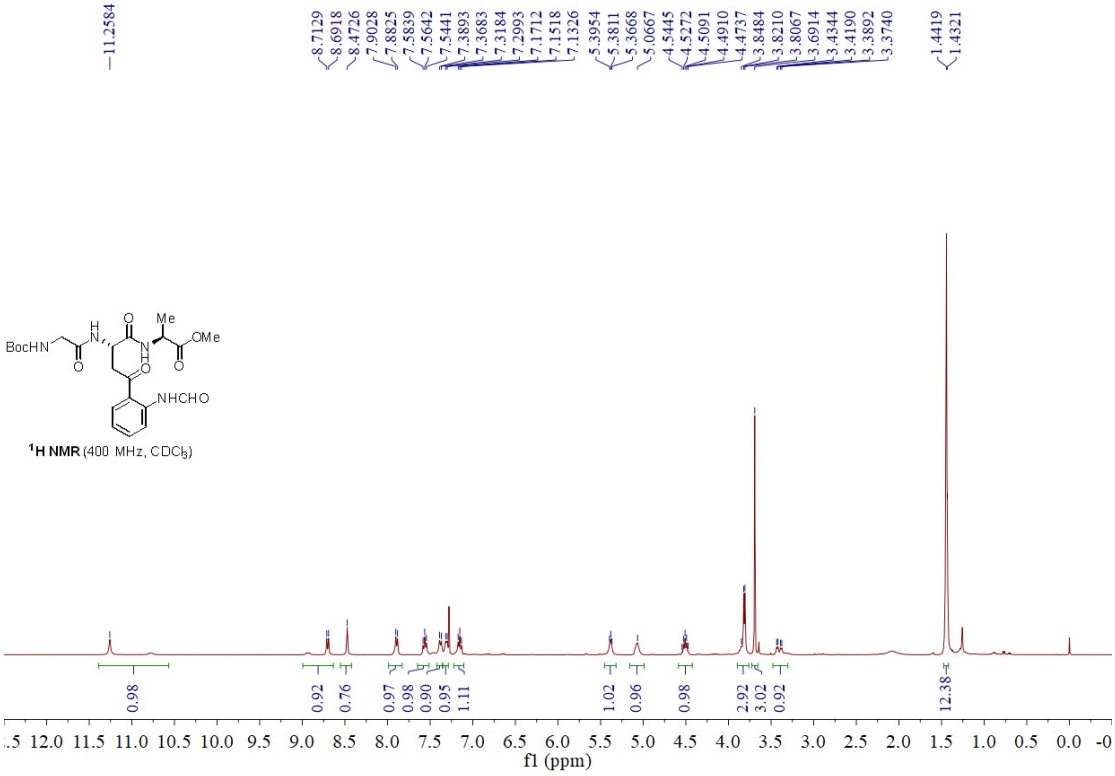
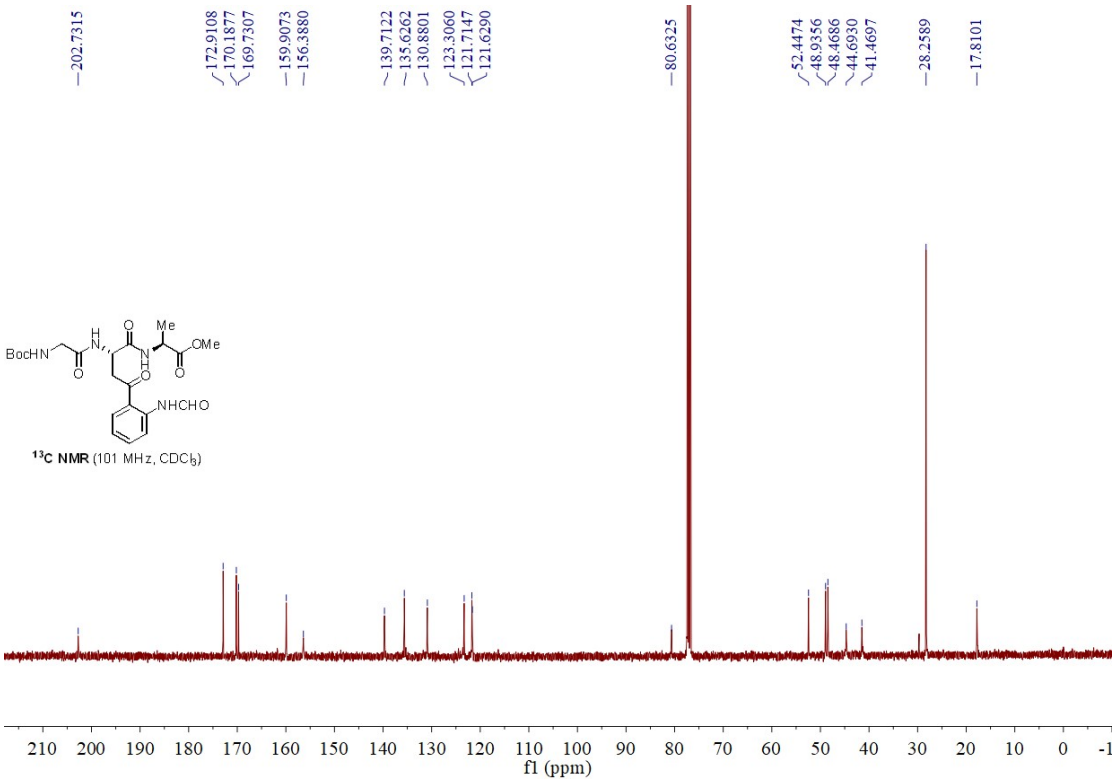


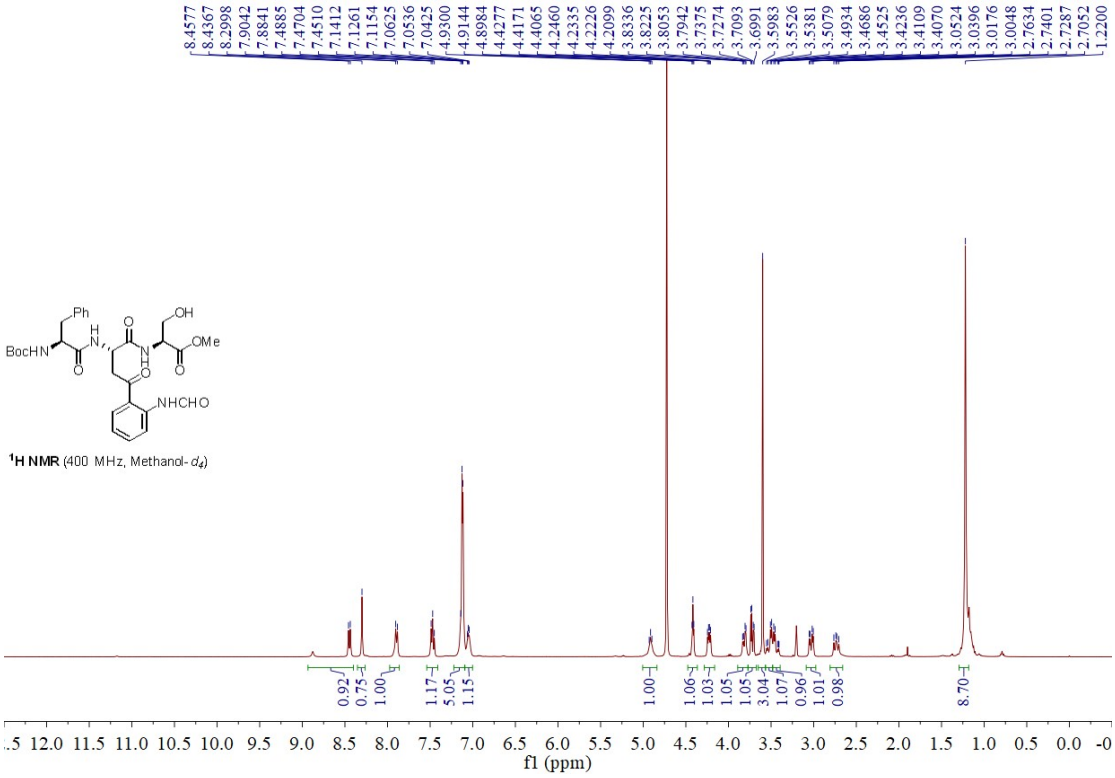
^{1}H NMR of **8c**



^{13}C NMR of **8c**

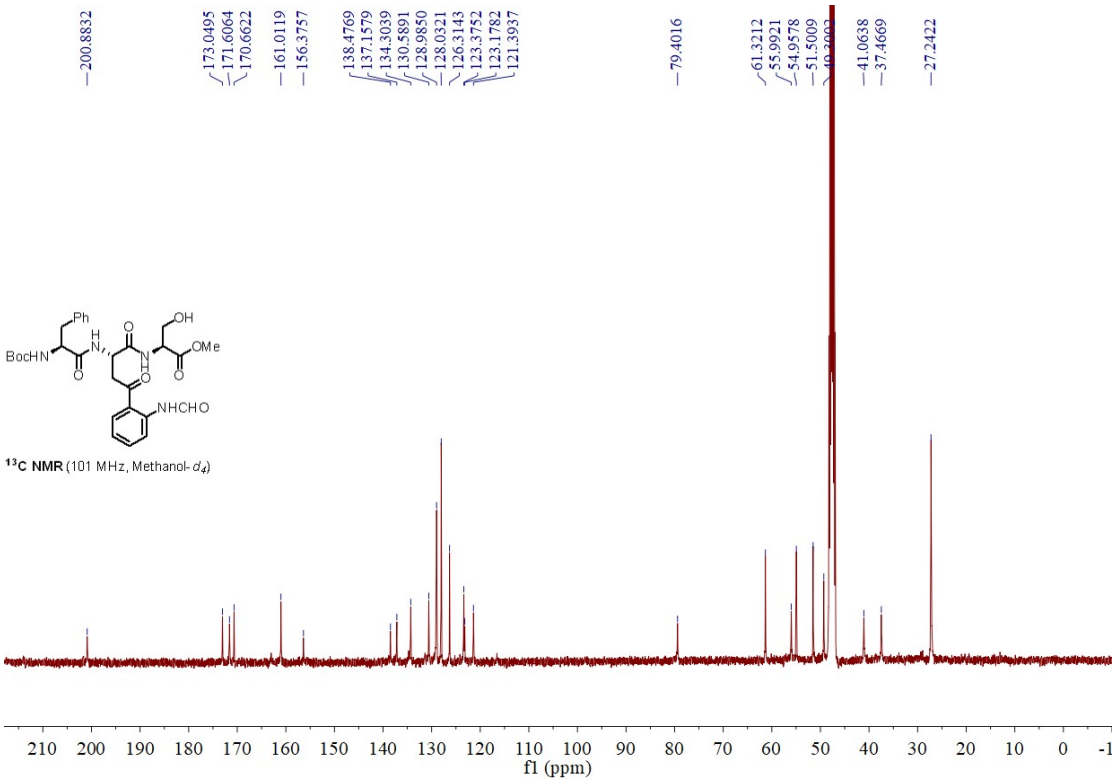


^{1}H NMR of **8d**



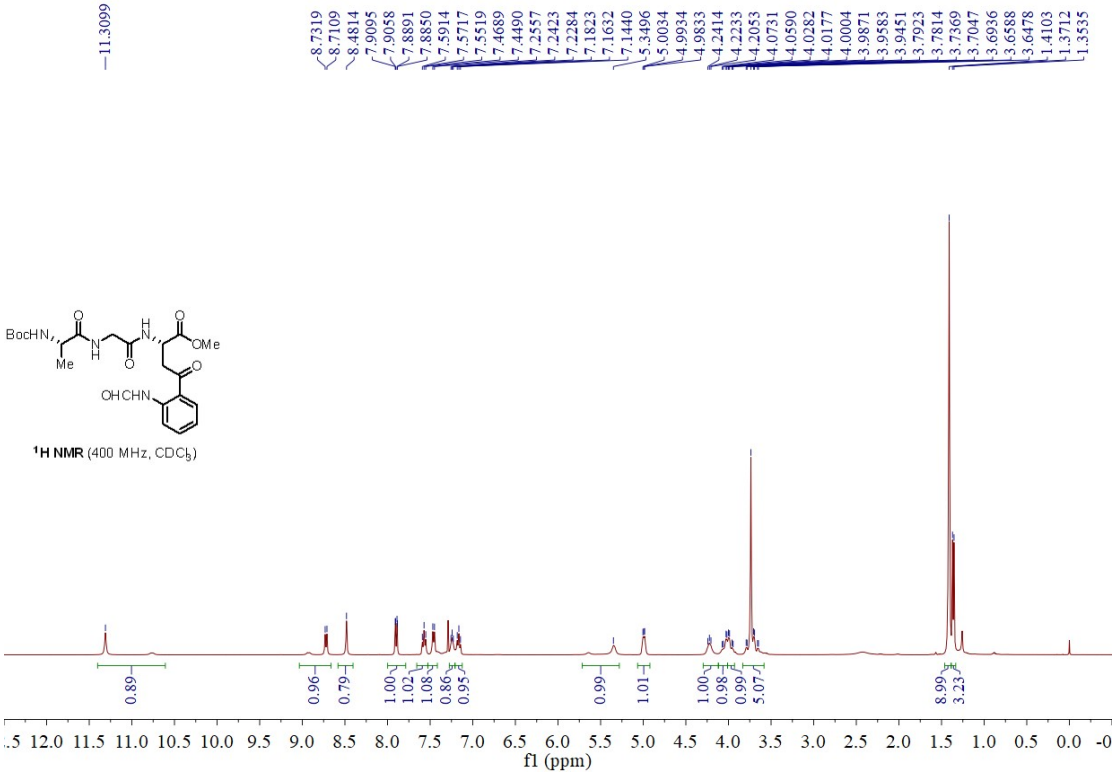
^{1}H NMR (400 MHz, Methanol-d_4)

^{13}C NMR of **8d**

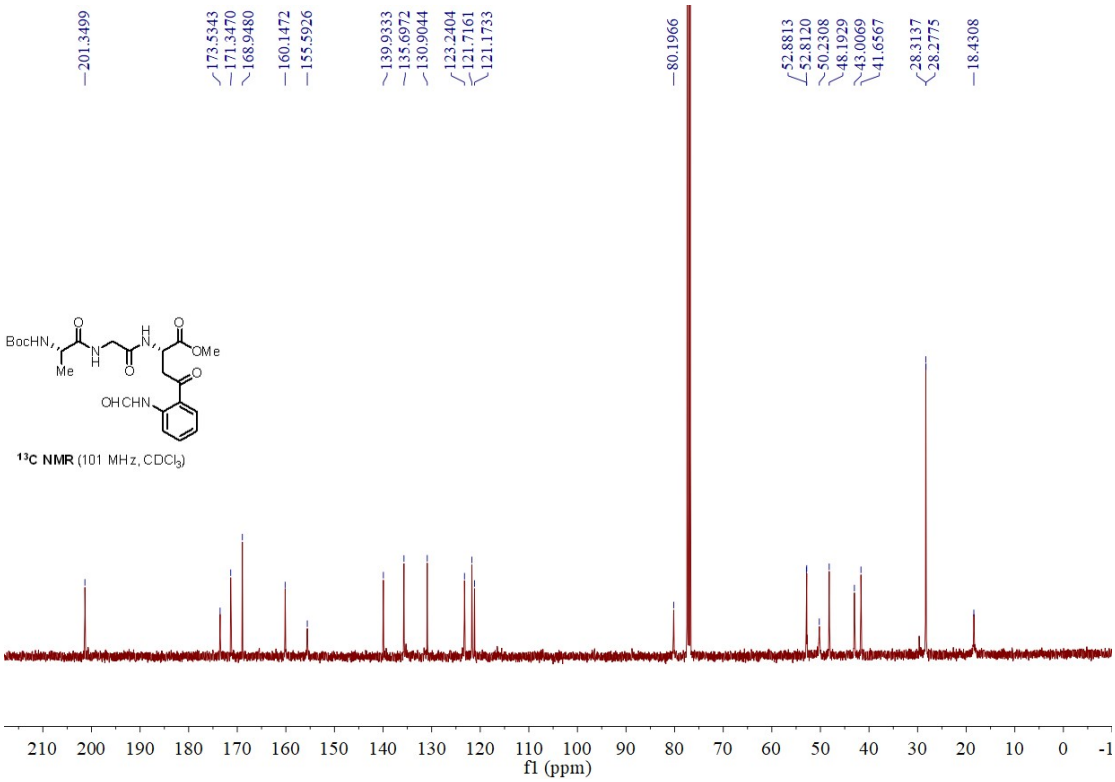


^{13}C NMR (101 MHz, Methanol-d_4)

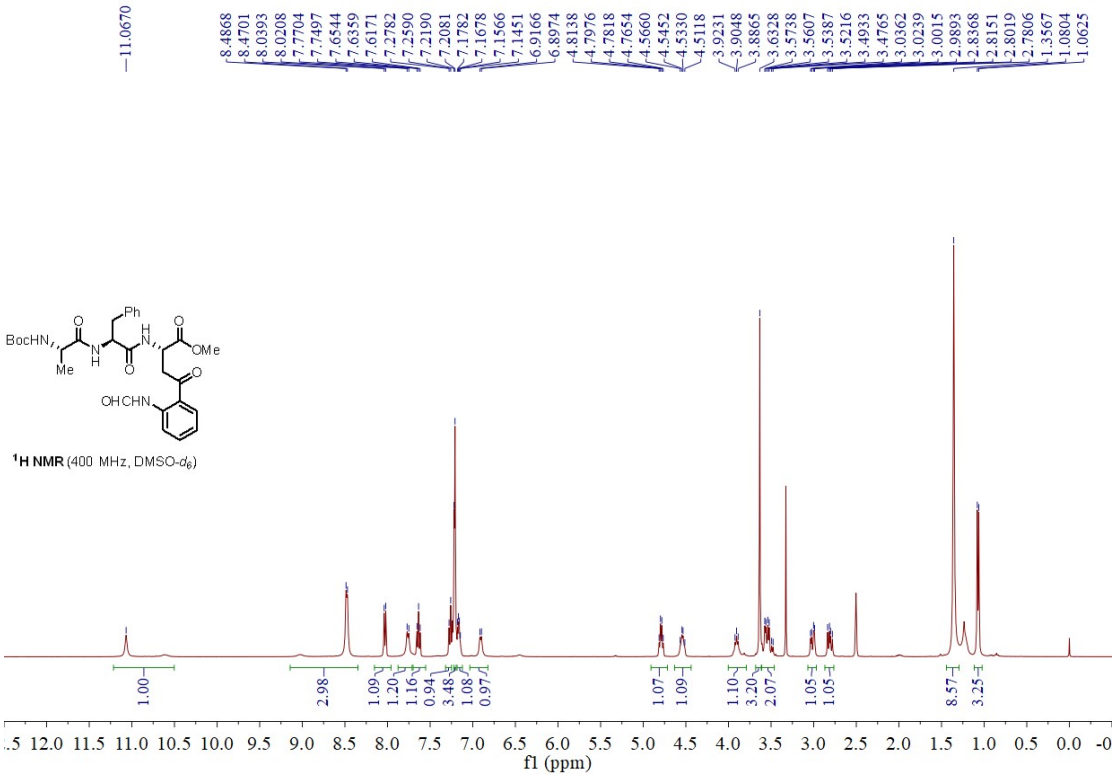
^{1}H NMR of **8e**



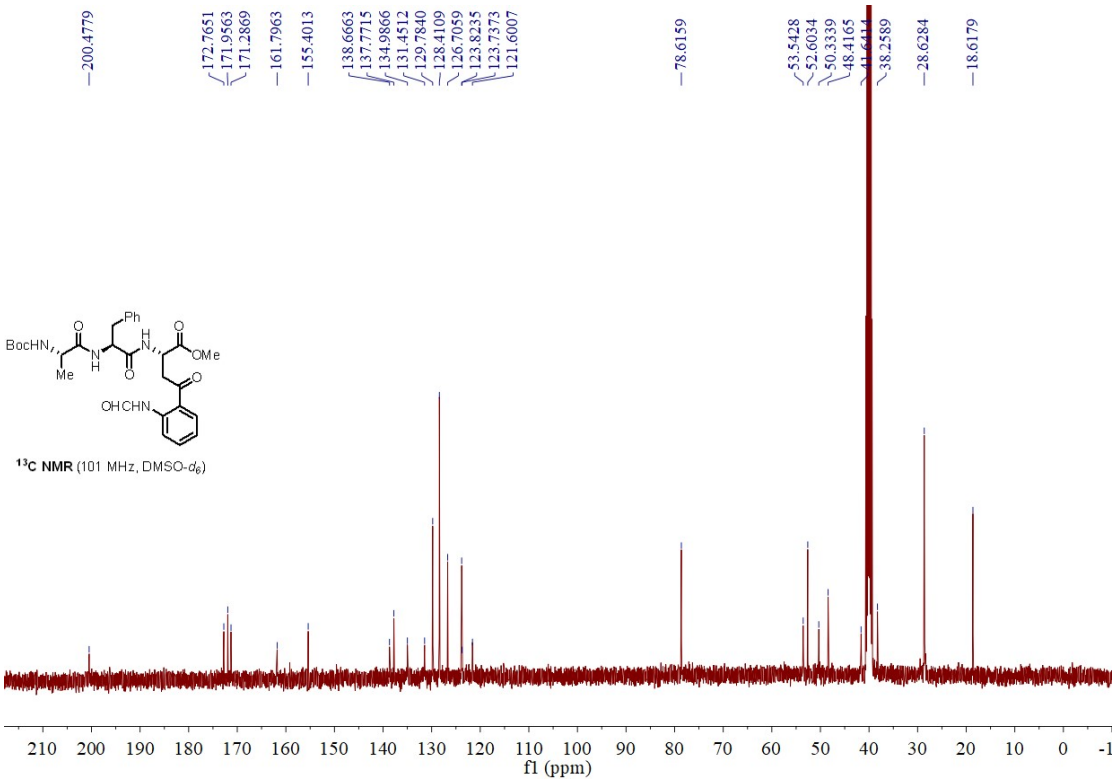
^{13}C NMR of **8e**



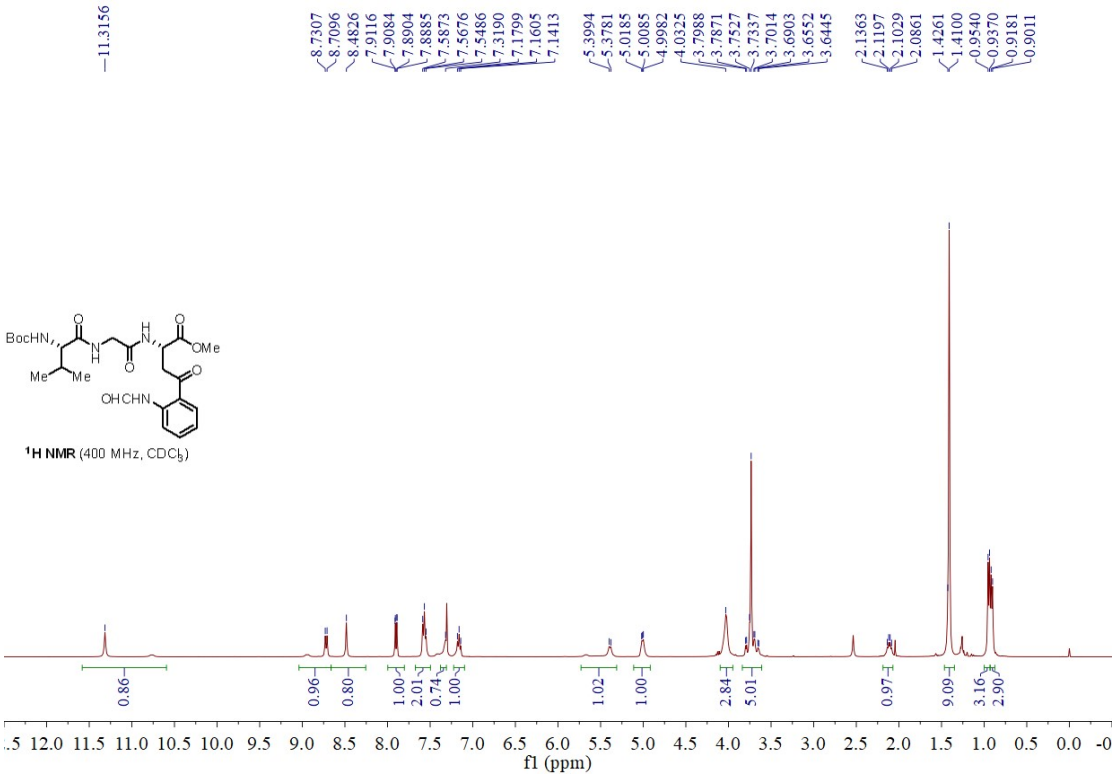
^{1}H NMR of **8f**



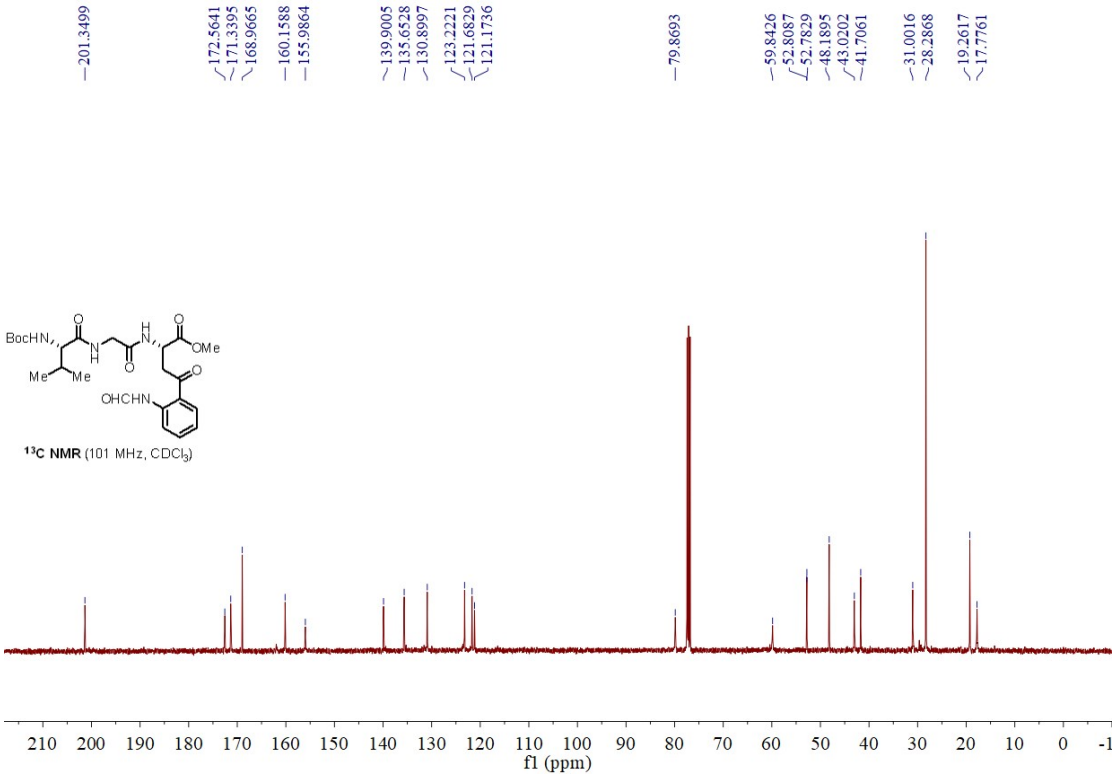
^{13}C NMR of **8f**



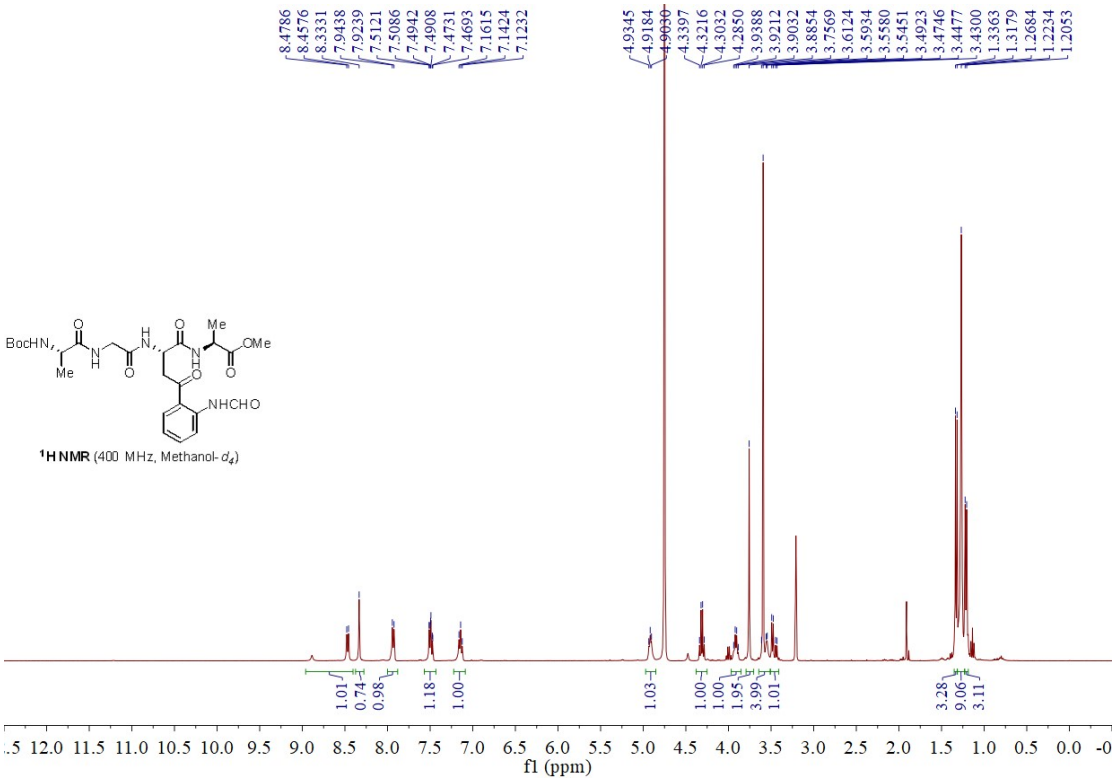
^{1}H NMR of **8g**



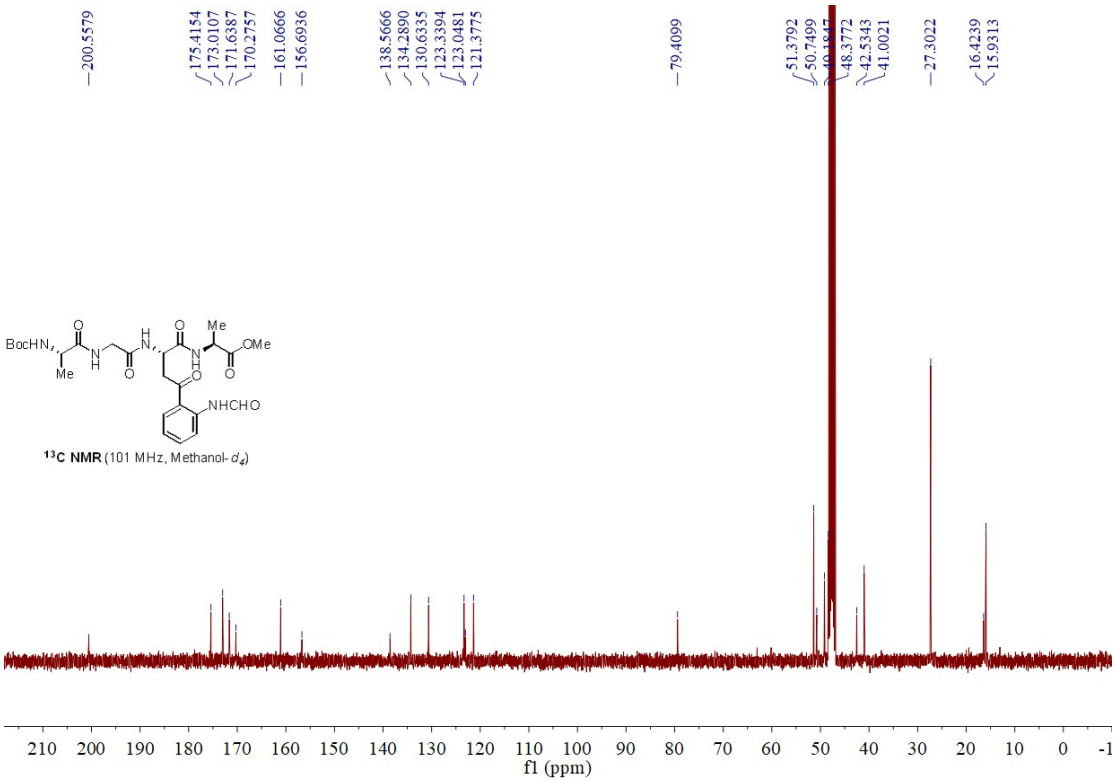
^{13}C NMR of **8g**



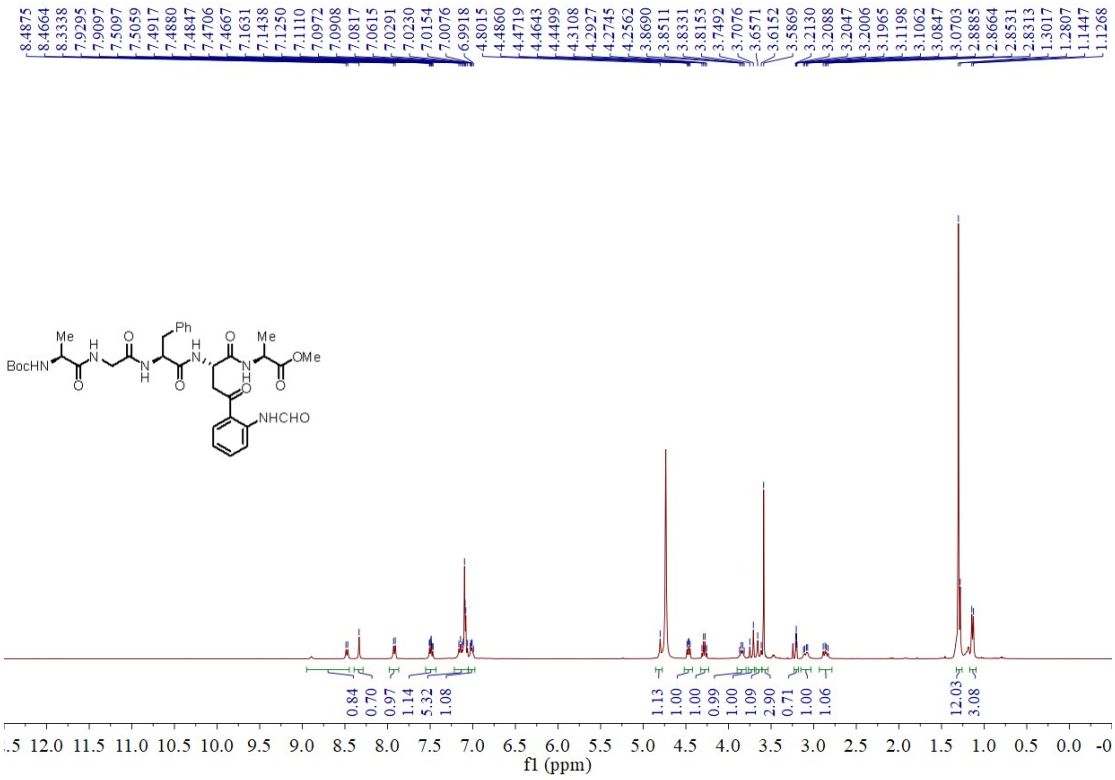
^{1}H NMR of **8h**



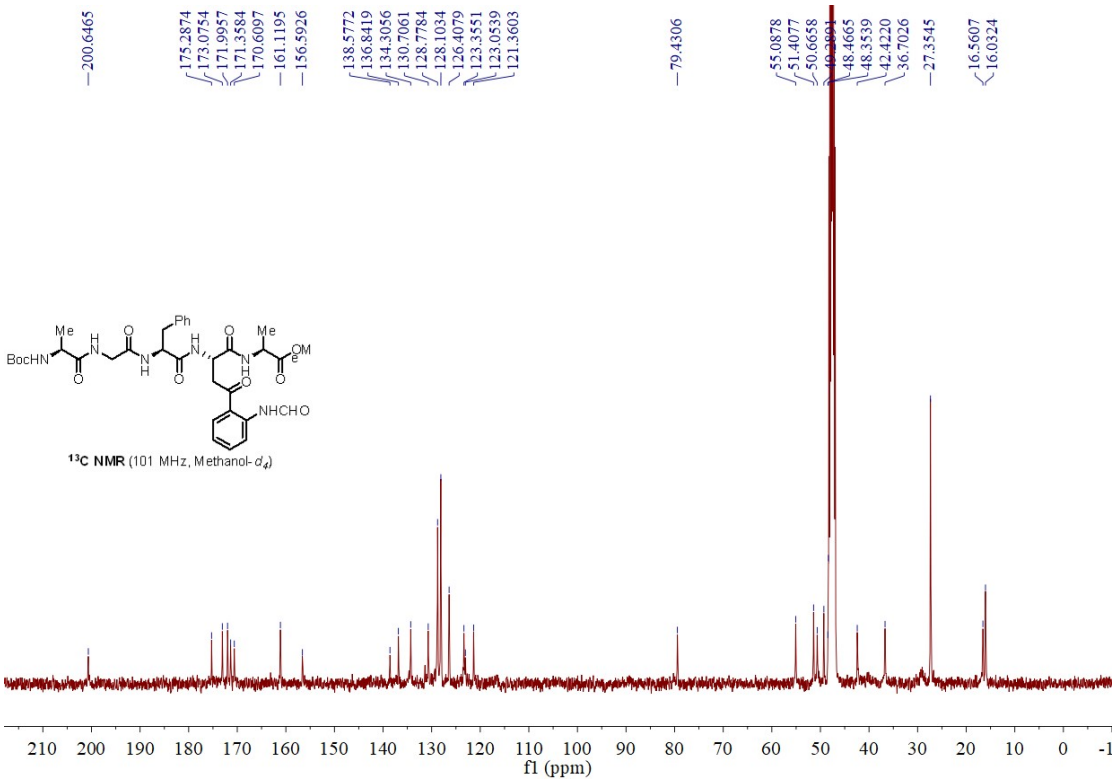
^{13}C NMR of **8h**



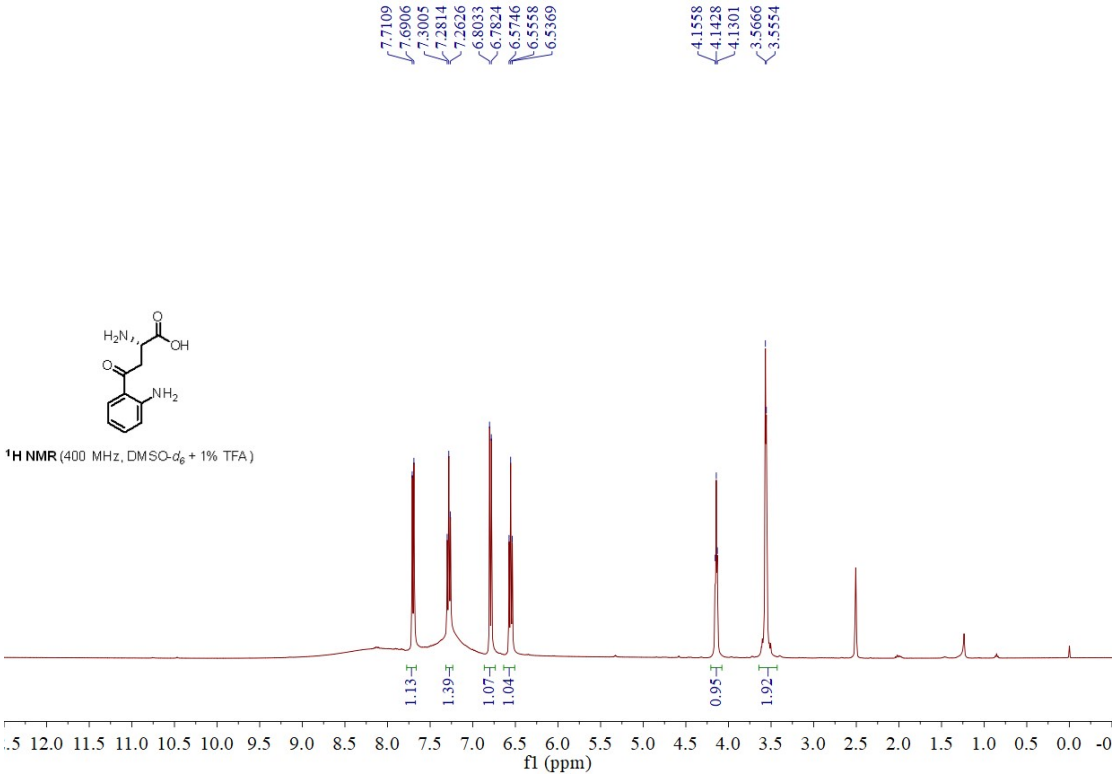
^{1}H NMR of **8i**



^{13}C NMR of **8i**



^{1}H NMR of **9**



^{13}C NMR of **9**