# Supporting Information

# A step-economic and one-pot access to chiral $C^{\alpha}$-tetrasubstituted α-amino acid derivatives via a bicyclic imidazole-catalyzed direct enantioselective C-acylation

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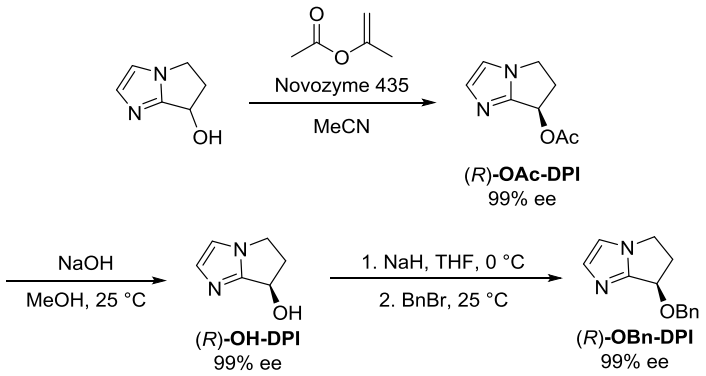
# 1. General Details

All air- and moisture-sensitive manipulations were carried out under a nitrogen atmosphere. The solvents used in the reactions were distilled under nitrogen after dehydration. All other chemicals and solvents were purchased from commercial company and used as received. The NMR spectra were recorded on a Bruker Avance III HD (400 MHz, $^{1}H$; 100 MHz, $^{13}C$) spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvents or the internal standard tetramethylsilane. Mass spectrometry analysis was carried out using a Waters Micromass Q-TOF Premier Mass Spectrometer at the Instrumental Analysis Center of Shanghai Jiao Tong University. Melting points were measured with SGW X-4 micro melting point apparatus. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm. Chiral HPLC analyses were performed using a Shimadzu LC-10Avp system using isopropanol-hexane mobile phase and UV detection.

# 2. Preparation of Catalysts



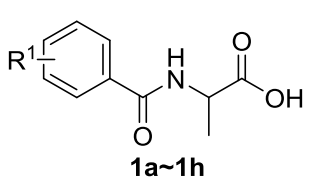

**(*R*)-7-Benzyloxy-6,7-dihydro-5*H*-pyrrolo[1,2-a]imidazole ((*R*)-OBn-DPI)**[1-4]

A solution of racemic 6,7-dihydro-5*H*-pyrrolo[1,2-*a*]imidazol-7-ol (620.7 mg, 5 mmol,), isopropenyl acetate (0.65mL, 6 mmol) and NOV435 (620.7 mg) in 3.0 mL acetonitrile was stirred gently at 35 ℃ for 3 h in a 10 mL two-necked flask. The reaction mixture was filtrated and MeCN was removed. The residue was purified by column chromatography (EtOAc/MeOH = 30/1, Rf = 0.38) to give (*R*)-**OAc-DPI** (340.7 mg, 41% yield) as a colorless oil. **HPLC analysis:** 99.9% ee [Daicel CHIRALPAK OJ column; solvent system: 10% isopropanol/90% hexane; 0.5 mL/min; retention times: 39.0 min (major), 41.6 min (minor)].

A solution of (*R*)-**OAc-DPI** (830.9 mg, 5 mmol) and NaOH (300.0 mg, 7.5 mmol) in 30 mL MeOH was stirred gently at 25 ℃ for 3 h in a 100 mL two-necked flask. The reaction mixture was filtrated and MeOH was removed. The residue was purified by column chromatography (EtOAc/MeOH = 4/1, Rf = 0.30) to give (*R*)-**OH-DPI** (505.0 mg, 81% yield) as a white solid. **HPLC analysis:** 99.9% ee [Daicel CHIRALPAK OJ column; solvent system: 10% isopropanol/90% hexane; 0.5 mL/min; retention times: 39.0 min (major), 41.6 min (minor)].

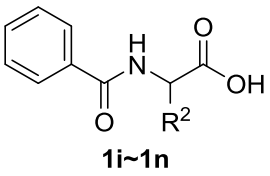
In a dry two-necked flask, a solution of (*R*)-**OH-DPI** (100.0 mg, 0.8 mmol) in THF (15 mL) was treated with NaH (48.0 mg, 1.2 mmol) for 2 h at 0 ℃, then BnBr (0.15 mL, 1.3 mmol) was added dropwise and stirred for 16 h at 25 ℃. The solvent was acidized with 1 M HCl (10 mL) then basified with 2 M NaOH and extracted with EtOAc (30 mL × 3). The crude product was purified by flash chromatography on silica gel (EtOAc/MeOH = 20/1, Rf = 0.38) to give 125.3 mg of (*R*)-**OBn-DPI** as yellow oil (73% yield). **HPLC analysis:** 99.9% ee [Daicel CHIRALPAK IE column; solvent system: 30% isopropanol/70% hexane; 0.5 mL/min; retention times: 18.7 min (major)]. $[\alpha]_D^{14}$ = 55.0 (*c* 0.13, MeOH). **$^1$H NMR ($CDCl_3$, 400 MHz):** $\delta$ 7.41-7.27 (m, 5 H), 7.16 (d, *J* = 1.2 Hz, 1 H), 6.93 (d, *J* = 1.2 Hz, 1 H), 4.83 (dd, *J* = 7.2 Hz, 2.0 Hz, 1 H), 4.81 (dd, *J* = 67.6 Hz, 11.6 Hz, 2 H), 4.21-4.13 (m, 1 H), 3.96-3.89 (m, 1 H), 2.92-2.82 (m, 1 H), 2.67-2.59 (m, 1 H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** $\delta$ 153.5, 137.9, 133.8, 128.4, 128.1, 127.7, 115.0, 71.1, 70.8, 43.1, 35.3. **HRMS (ESI):** calcd. for $C_{13}H_{15}N_2O$ $(M+H)^+$ 215.1179, found 215.1184.

# 3. Preparation of Substrates



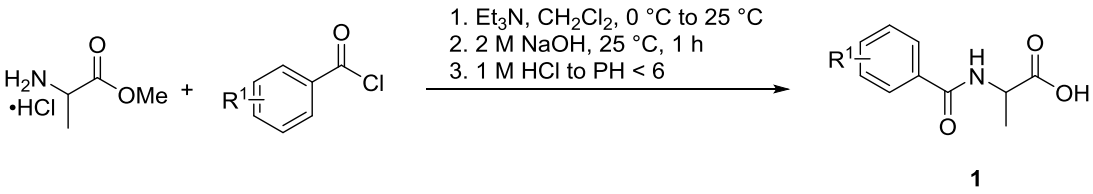
**1a~1h**

**1a:** $R^1$ = 4-MeO
**1b:** $R^1$ = 3-MeO
**1c:** $R^1$ = 2-MeO
**1d:** $R^1$ = 4-Me
**1e:** $R^1$ = 4-*t*Bu
**1f:** $R^1$ = 4-F
**1g:** $R^1$ = 4-Cl
**1h:** $R^1$ = None



**1i~1n**

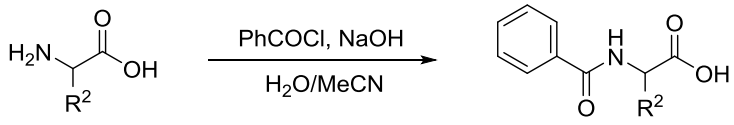
**1i:** $R^2$ = Et
**1j:** $R^2$ = *n*Pr
**1k:** $R^2$ = *n*Bu
**1l:** $R^2$ = *i*Bu
**1m:** $R^2$ = Bn
**1n:** $R^2$ = Ph




**1**

**General procedure A:**[5]

(DL)-Alanine methyl ester hydrochloride (10 mmol) were dissolved in $CH_2Cl_2$ (50 mL) in a flask and $Et_3N$ (25 mmol) were added. The resulting slurry was cooled to 0 ℃, and the corresponding benzoyl chloride (10 mmol) in $CH_2Cl_2$ (10 mL) was added by cannula over 15 minutes. After 75 minutes, the ice bath was removed, and the mixture was stirred at room temperature for 6 hours. The mixture was then washed with 1 M HCl (30 mL × 2), saturated $NaHCO_3$ (30 mL × 2), and saturated NaCl (30 mL). The $CH_2Cl_2$ layer was dried over $MgSO_4$, and the solvent was removed by rotary evaporation, providing the *N*-acyl-(DL)-alanine methyl ester as a white solid. This solid was dissolved in methanol (30 mL), and 2 M aqueous NaOH (6 mL) was added. The resulting mixture was stirred for 20 minutes, and then the methanol was removed by rotary evaporation. Water was added until the aqueous solution was homogeneous, and then the aqueous solution was washed with $CH_2Cl_2$ (20 mL × 2). The aqueous layer was made acidic with 1M HC1, giving a white precipitate, which was filtered, washed with several portions of water, and dried with a flow of air through a filter.



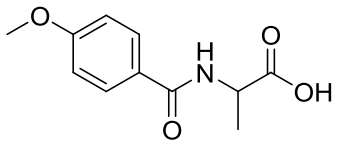

**1**

**General procedure B:**[6]

The corresponding racemic amino acid (10 mmol) and NaOH (40 mmol) were dissolved in $H_2O/CH_3CN$ (75/25, 50 mL). After cooling to 0 ℃, benzoyl chloride (11 mmol) was added dropwise at this temperature. After the addition was complete, the mixture was stirred for additional 2 h at 0 ℃. Subsequently, the mixture was allowed to warm to room temperature and was stirred for one additional hour. All volatiles were then removed under reduced pressure before conc. HCl was added to cause

precipitation. The mixture was filtered and the filter cake was washed with ice-cold diethyl ether and dried with a flow of air through a filter.

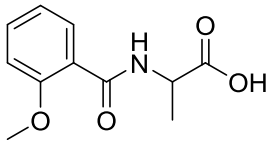
Substrates **1a-1g** were prepared via general procedure A, while substrates **1i-1m** were prepared via general procedure B according to the literature's methods. Substrates **1b**, **1h**, **1l** and **1n** were commercially available. The following substrates **1a**-**1m** are known compounds, and their characterization data were in agreement with reported values.[5-9]



**1a**

**(4-Methoxybenzoyl)alanine (1a)**[5]

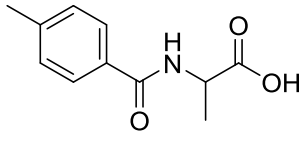
**$^1$H NMR (DMSO, 400 MHz):** δ 12.46 (br s, 1H), 8.49 (d, *J* = 7.0 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.43 – 4.34 (m, 1H), 3.81 (s, 3H), 1.38 (d, *J* = 7.2 Hz, 3H).



**1c**

**(2-Methoxybenzoyl)alanine (1c)**[7]

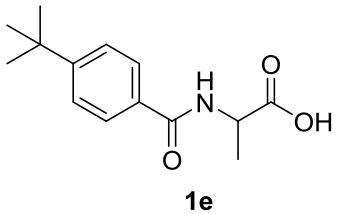
**$^1$H NMR ($CDCl_3$, 400 MHz):** δ 10.67 (s, 1H), 8.81 (d, *J* = 6.6 Hz, 1H), 8.17 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.50 – 7.39 (m, 1H), 7.11 – 6.90 (m, 2H), 4.87 – 4.78 (m, 1H), 3.95 (s, 3H), 1.58 (d, *J* = 7.2 Hz, 3H).



**1d**

**(4-Methylbenzoyl)alanine (1d)**[8]

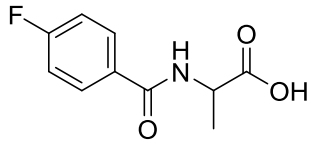
**$^1$H NMR (DMSO, 400 MHz):** δ 8.58 (d, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 4.39 – 4.36 (m, 1H), 2.34 (s, 3H), 1.37 (d, *J* = 7.2 Hz, 3H).



**1e**

**(4-(*tert*-Butyl)benzoyl)alanine (1e)**[8]

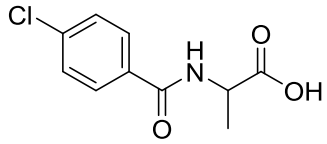
**$^1$H NMR (DMSO, 400 MHz):** δ 12.59 (br s, 1H), 8.57 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 4.46 – 4.35 (m, 1H), 1.38 (d, *J* = 7.4 Hz, 3H), 1.30 (s, 9H).




**1f**

**(4-Fluorobenzoyl)alanine (1f)**[8]

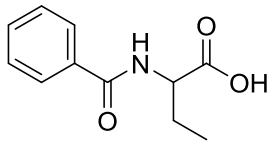
**$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.84 – 7.81 (m, 2H), 7.16 – 7.12 (m, 2H), 6.61 (d, *J* = 4.0 Hz, 1H), 4.82 – 4.77 (m, 1H), 1.59 (d, *J* = 4.8 Hz, 3H).




**1g**

**(4-Chlorobenzoyl)alanine (1g)**[8]

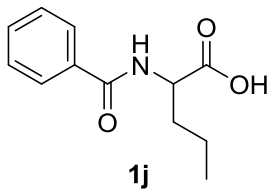
**$^1$H NMR (DMSO, 400 MHz):** δ 8.74 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 4.39 – 4.33 (m, 1H), 1.37 (d, *J* = 7.2 Hz, 3H).




**1i**

**2-Benzamidobutanoic acid (1i)**[9]

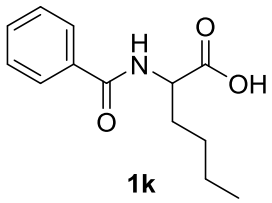
**$^1$H NMR (DMSO, 400 MHz):** δ 12.59 (br s, 1H), 8.54 (d, *J* = 7.2 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.57 – 7.43 (m, 3H), 4.33 – 4.25 (m, 1H), 1.92 – 1.71 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).




**1j**

**2-Benzamidopentanoic acid (1j)**[9]

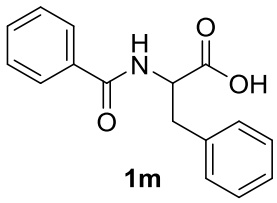
**$^1$H NMR (DMSO, 400 MHz):** δ 12.53 (br s, 1H), 8.56 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.4 Hz, 2H), 7.57 – 7.42 (m, 3H), 4.42 – 4.33 (m, 1H), 1.82 – 1.72 (m, 2H), 1.49 – 1.30 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H).




1k

**2-Benzamidohexanoic acid (1k)**[9]

**$^1$H NMR (DMSO, 400 MHz):** δ 12.56 (br s, 1H), 8.57 (d, *J* = 7.6 Hz, 1H), 7.93 – 7.85 (m, 2H), 7.58 – 7.43 (m, 3H), 4.39 – 4.31 (m, 1H), 1.87 – 1.70 (m, 2H), 1.46 – 1.24 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H).




1m

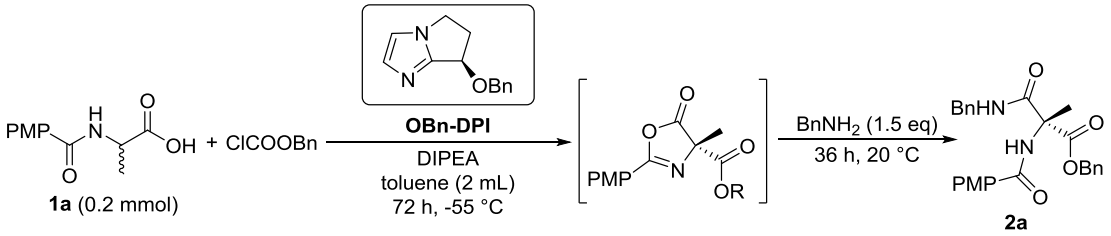
**Benzoylphenylalanine (1m)**[6]

**$^1$H NMR (DMSO, 400 MHz):** δ 8.69 (d, *J* = 6.2 Hz, 1H), 7.83 – 7.72 (m, 2H), 7.56 – 7.39 (m, 3H), 7.35 – 7.10 (m, 5H), 4.65 – 4.57 (m, 1H), 3.21 – 3.03 (m, 2H).

The other analytical data are in accordance with the literature.

# 4. Optimization of Conditions

**Table S1. The Effect of the Usage of Each Components**



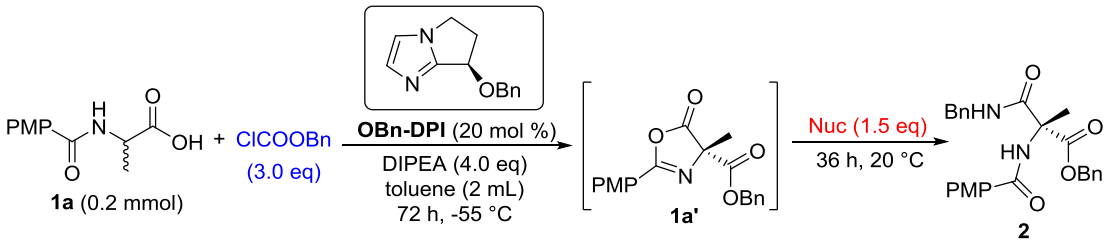

| entry [a] | loading of ClCOOBn (eq) | loading of DIPEA (eq) | yield (%) [b] | ee (%) [c] |
|---|---|---|---|---|
| 1 | 3.5 | 4.0 | 78 | 99 |
| 2 | 2.5 | 4.0 | 75 | 99 |
| 3 | 3.0 | 4.0 | 78 | 99 |
| 4 | 4.0 | 4.0 | 76 | 98 |
| 5 | 3.0 | 3.5 | 76 | 99 |
| 6 | 3.0 | 4.5 | 73 | 98 |
| 7 [d] | 3.0 | 4.0 | 56 | 99 |

a) **1a** (0.1 M), **OBn-DPI** (20 mol %), toluene (2 mL), −55 ℃, 72 h, unless otherwise noted. b) Yields were calculated from $^1$H NMR spectra. c) The ee values were calculated from HPLC spectra. d) **OBn-DPI** (10 mol %).

The effect of reagent equivalents was investigated (Table S1). Changing the usage of benzyl chloroformate has almost no effect on results (entries 1-4). Only when the usage was increased to 4.0 equivalents, the ee value of product was slightly decreased to 98% (entry 4). Decreasing the usage of DIPEA to 3.5 equivalents will slightly reduce the yield (entry 5), while increasing the usage to 4.5 equivalents decreased the ee value to 98% (entry 6). Decreasing the loading of catalyst to 10 mol % dramatically reduced the yield, though the enantioselectivity was remained at 99% ee (entry 7).

# 5. Asymmetric Reactions

**Different Nucleophiles:**



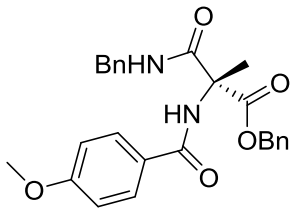

**The steps to 1a':** Under a $N_2$ atmosphere, the substrate **1a** (0.2 mmol, 44.7 mg), the catalyst **OBn-DPI** (0.04 mmol, 8.6 mg) and DIPEA (0.8 mmol, 132.2 μL) were dissolved in anhydrous toluene (2 mL) and cooled to −55 ℃ in a dry two-necked flask. ClCOOallyl (0.6 mmol, 84.5 μL) was then added and the vial was sealed with a septum. The reaction mixture was stirred at −55 ℃ for 72 h and then the temperature was gradually raised to 20 ℃.

**The step to 2a~2e:** Following the steps to **1a'**, the corresponding amines (0.3 mmol) was added to the vial and the reaction mixture was was stirred at 20 ℃ for 36 h.

**The step to 2f:** Following the steps to **1a'**, 1 mL methanol was added to the vial and the reaction mixture was stirred at 20 ℃ for 36 h.

**The step to 2g~2r:** Following the steps to **1a'**, the corresponding amino acid methyl ester hydrochloride (0.3 mmol) and DIPEA (0.3 mmol, 49.6 μL) were dissolved in anhydrous toluene (1 mL) in another dry flask and stirred for 10 min. Then the mixture was transferred into the former reaction flask and the reaction mixture was stirred at 20 ℃ for 36 h.

The reaction mixture was quenched with 0.2 M HCl (5 mL) and extracted with DCM (5 mL × 3). The combined organic phases were dried over $Na_2SO_4$. After filtration, the residue was purified by column chromatography (petroleum ether/ethyl acetate) to give the corresponding product **2**.

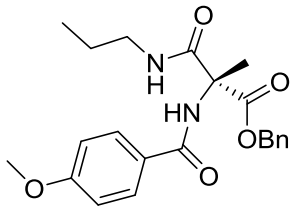



**2a**

**Benzyl (*R*)-3-(benzylamino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanoate (2a)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a white solid (66.9 mg, 75% yield). **M.p.:** 130.6-131.6 ℃. **HPLC analysis:** 99% ee [Daicel CHIRALPAK OD-H column; solvent system: 20% isopropanol/80% hexane; 0.5 mL/min; retention times: 28.8 min (minor), 33.2 min (major)]. **$[\alpha]^{25}_D$** = 4.9 (*c* 0.55, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.82 – 7.77 (m, 2H), 7.74 (s, 1H), 7.33 – 7.22 (m, 8H), 7.18 – 7.12 (m, 2H), 6.96 – 6.90 (m, 2H), 6.55 (t, *J* = 5.2 Hz, 1H), 5.19 (s, 2H), 4.45 (dd, *J* = 14.8, 5.6 Hz, 1H), 4.36 (dd, *J* =

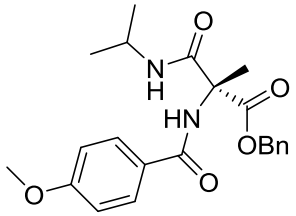
14.8, 5.6 Hz, 1H), 3.86 (s, 3H), 1.92 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 170.7, 167.9, 165.8, 162.5, 137.1, 135.0, 129.0, 128.8, 128.5, 128.3, 128.1, 127.7, 127.4, 125.8, 113.7, 68.1, 63.1, 55.4, 44.1, 22.3. **IR (thin film):** ν 3715, 3647, 3482, 2923, 2848, 1743, 1646, 1486, 1384, 1258, 1179, 1118, 1029, 845, 697 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{26}H_{26}N_2O_5$ $(M+H)^+$ 447.1914, found 447.1913.




**2b**

**Benzyl (*R*)-2-(4-methoxybenzamido)-2-methyl-3-oxo-3-(propylamino)propanoate (2b)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a colorless oil (62.0 mg, 78% yield). **HPLC analysis:** 99% ee [Daicel CHIRALPAK OD-H column; solvent system: 35% isopropanol/65% hexane; 0.3 mL/min; retention times: 19.0 min (major), 21.2 min (minor)]. **$[\alpha]^{25}_D$** = 12.8 (*c* 0.55, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.83 – 7.76 (m, 3H), 7.28 (s, 5H), 6.95 – 6.90 (m, 2H), 6.17 (t, *J* = 5.2 Hz, 1H), 5.22 (d, *J* = 12.0 Hz, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 3.85 (s, 3H), 3.25 – 3.10 (m, 2H), 1.90 (s, 3H), 1.47 – 1.37 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 170.8, 167.8, 165.7, 162.4, 135.1, 129.0, 128.4, 128.3, 128.2, 126.0, 113.7, 68.0, 63.0, 55.4, 41.8, 22.4, 22.4, 11.1. **IR (thin film):** ν 3736, 3481, 3420, 2963, 2923, 2850, 1740, 1646, 1607, 1536, 1483, 1384, 1257, 1178, 1118, 1030, 845, 769, 602 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{22}H_{26}N_2O_5$ $(M+H)^+$ 399.1914, found 399.1914.

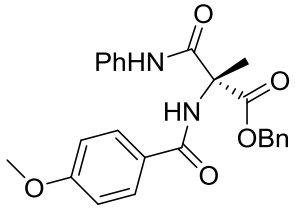



**2c**

**Benzyl (*R*)-3-(isopropylamino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanoate (2c)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a light yellow oil (51.5 mg, 65% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK OD-H column; solvent system: 20% isopropanol/80% hexane; 0.1 mL/min; retention times: 92.7 min (minor), 99.6 min (major)]. **$[\alpha]^{25}_D$** = -10.4 (*c* 0.10, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.84 – 7.77 (m, 3H), 7.32 – 7.28 (m, 5H), 6.95 – 6.90 (m, 2H), 5.81 (d, *J* = 7.6 Hz, 1H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.16 (d, *J* = 12.0 Hz, 1H), 4.03 – 3.92 (m, 1H), 3.86 (s, 3H), 1.88 (s, 3H), 1.11 (d, *J* = 6.4 Hz,

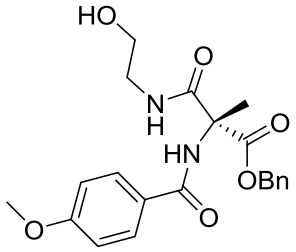
3H), 0.95 (d, $J$ = 6.8 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 170.8, 167.0, 165.7, 162.5, 135.3, 129.0, 128.5, 128.4, 128.4, 126.0, 113.7, 67.9, 63.0, 55.4, 42.5, 22.4, 22.3, 22.0. **IR (thin film):** ν 3714, 3648, 3481, 2920, 2854, 1748, 1647, 1558, 1384, 1261, 596 cm$^{-1}$. **HRMS (ESI):** calcd. for $C_{22}H_{26}N_2O_5$ $(M+H)^+$ 399.1914, found 399.1914.




**2d**

**Benzyl (*R*)-2-(4-methoxybenzamido)-2-methyl-3-oxo-3-(phenylamino)propanoate (2d)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a yellow oil (59.4 mg, 69% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK OD-H column; solvent system: 10% isopropanol/90% hexane; 0.5 mL/min; retention times: 44.8 min (minor), 49.4 min (major)]. **$[\alpha]^{25}_D$** = -2.0 (*c* 0.40, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 8.42 (s, 1H), 7.83 – 7.79 (m, 2H), 7.60 (s, 1H), 7.44 – 7.22 (m, 9H), 7.16 – 7.11 (m, 1H), 6.96 – 6.93 (m, 2H), 5.26 (s, 2H), 3.86 (s, 3H), 2.00 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 170.8, 166.3, 166.1, 162.7, 137.0, 134.9, 129.1, 129.0 128.5, 128.4, 128.1, 125.6, 124.9, 120.2, 113.8, 68.3, 63.9, 55.4, 22.2. **IR (thin film):** ν 3363, 3063, 3034, 2961, 2921, 2851, 1738, 1689, 1635, 1605, 1543, 1500, 1444, 1380, 1316, 1259, 1178, 1123, 1029, 845, 756, 696, 601 cm$^{-1}$. **HRMS (ESI):** calcd. for $C_{25}H_{25}N_2O_5$ $(M+H)^+$ 433.1758, found 433.1760.

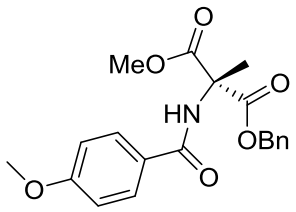



**2e**

**Benzyl (*R*)-3-((2-hydroxyethyl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanoate (2e)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 1/2) afforded the product as a colorless oil (61.5 mg, 77% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK OD-H column; solvent system: 20% isopropanol/80% hexane; 0.7 mL/min; retention times: 19.0 min (major), 25.0 min (minor)]. **$[\alpha]^{25}_D$** = 20.7 (*c* 0.45, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.83 – 7.76 (m, 2H), 7.65 (s, 1H), 7.41 – 7.30 (m, 5H), 6.98 – 6.88 (m, 2H), 6.72 (t, $J$ = 5.2 Hz, 1H), 5.26 (d, $J$ = 12.4 Hz, 1H), 5.19 (d, $J$ = 12.4 Hz, 1H), 3.86 (s, 3H), 3.61 (t, $J$ = 5.2 Hz, 2H), 3.46 – 3.27 (m, 2H),

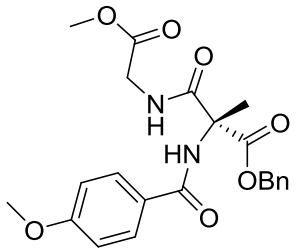
1.89 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 170.8, 168.6, 166.2, 162.7, 135.1, 129.1, 128.5, 128.5, 128.3, 125.6, 113.8, 68.1, 63.2, 61.2, 55.5, 42.7, 21.9. **IR (thin film):** ν 3481, 2960, 2923, 2851, 1744, 1643, 1607, 1537, 1485, 1384, 1259, 1177, 1121, 1029, 800 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{21}H_{25}N_2O_6$ $(M+H)^+$ 401.1707, found 401.1707.




**2f**

**1-Benzyl 3-methyl (*R*)-2-(4-methoxybenzamido)-2-methylmalonate (2f)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a colorless oil (53.6 mg, 72% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK OD-H column; solvent system: 20% isopropanol/80% hexane; 0.3 mL/min; retention times: 31.9 min (major), 36.9 min (minor)]. **$[\alpha]^{25}_D$** = 18.1 (*c* 0.30, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.83 – 7.73 (m, 2H), 7.45 (s, 1H), 7.37 – 7.28 (m, 5H), 6.98 – 6.89 (m, 2H), 5.27 (d, *J* = 12.4 Hz, 1H), 5.23 (d, *J* = 12.4 Hz, 1H), 3.86 (s, 3H), 3.73 (s, 3H), 1.88 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 169.3, 168.7, 165.5, 162.5, 135.0, 129.0, 128.5, 128.4, 128.0, 125.6, 113.8, 68.0, 63.2, 55.4, 53.4, 21.1. **IR (thin film):** ν 3486, 3419, 2918, 2847, 1743, 1658, 1488, 1384, 1276, 1259, 1221, 1126, 1113, 1029, 843, 765, 750 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{20}H_{22}NO_6$ $(M+H)^+$ 372.1442, found 372.1443.

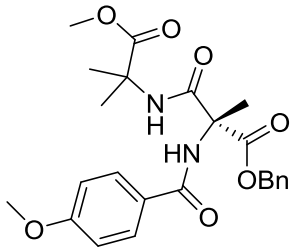



**2g**

**Benzyl (*R*)-3-((2-methoxy-2-oxoethyl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanoate (2g)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 1/1) afforded the product as a colorless oil (67.1 mg, 78% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK OD-H column; solvent system: 20% isopropanol/80% hexane; 0.5 mL/min; retention times: 31.9 min (minor), 39.1 min (major)]. **$[\alpha]^{25}_D$** = 8.4 (*c* 0.30, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.82 – 7.75 (m, 2H), 7.60 (s, 1H), 7.32 – 7.27 (m, 5H), 6.95 – 6.86 (m, 3H), 5.23 (s, 2H), 4.08 (dd, *J* = 18.0, 5.6 Hz, 1H), 3.91 (dd, *J* = 18.0, 5.2 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 1.94 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 170.4, 169.3, 168.4, 165.9, 162.5, 135.0, 129.0, 128.4, 128.3, 128.1,

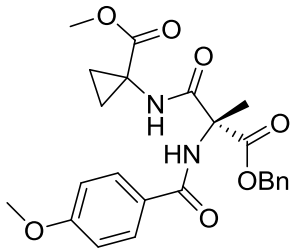
125.7, 113.7, 68.2, 63.1, 55.4, 52.5, 41.6, 22.1. **IR (thin film):** ν 3482, 2960, 2920, 2850, 1746, 1640, 1529, 1485, 1384, 1259, 1215, 1121, 1023, 768, 747, 601 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{22}H_{25}N_2O_7$ $(M+H)^+$ 429.1656, found 429.1651.



**2h**

**Benzyl (*R*)-3-((1-methoxy-2-methyl-1-oxopropan-2-yl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanoate (2h)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a colorless oil (68.5 mg, 75% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK OD-H column; solvent system: 20% isopropanol/80% hexane; 0.5 mL/min; retention times: 21.7 min (minor), 25.2 min (major)]. **$[\alpha]^{25}_D$** = 13.3 (*c* 0.25, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.82 – 7.77 (m, 2H), 7.67 (s, 1H), 7.36 – 7.27 (m, 5H), 6.95 – 6.89 (m, 2H), 6.69 (s, 1H), 5.28 (d, *J* = 12.4 Hz, 1H), 5.19 (d, *J* = 12.4 Hz, 1H), 3.85 (s, 3H), 3.69 (s, 3H), 1.91 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 174.1, 170.4, 167.1, 165.6, 162.4, 135.2, 129.0, 128.5, 128.4, 128.3, 125.9, 113.7, 68.0, 63.0, 57.0, 55.4, 52.8, 24.5, 24.1, 22.2. **IR (thin film):** ν 3481, 2920, 2847, 1743, 1639, 1484, 1385, 1260, 1123, 1030, 704, 625, 601 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{24}H_{29}N_2O_7$ $(M+H)^+$ 457.1969, found 457.1972.

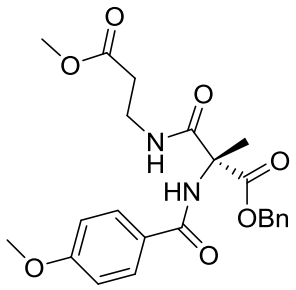


**2i**

**Methyl (*R*)-1-(3-(benzyloxy)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanamido)cyclopropane-1-carboxylate (2i)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a colorless oil (60.7 mg, 67% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK OD-H column; solvent system: 20% isopropanol/80% hexane; 0.5 mL/min; retention times: 23.5 min (minor), 28.6 min (major)]. **$[\alpha]^{25}_D$** = 8.8 (*c* 0.30, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.83 – 7.76 (m, 2H), 7.68 (s, 1H), 7.29 (s, 5H), 6.97 – 6.89 (m, 2H), 6.73 (s, 1H), 5.25 (d, *J* = 12.4 Hz, 1H), 5.16 (d, *J* = 12.0 Hz, 1H), 3.86 (s, 3H), 3.63 (s, 3H), 1.93 (s, 3H), 1.60 – 1.54 (m, 1H), 1.49 – 1.42 (m, 1H), 1.06 – 0.99 (m, 1H), 0.91 – 0.85 (m, 1H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.0,

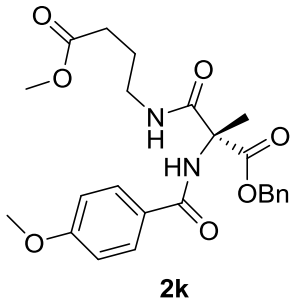
170.4, 169.2, 165.8, 162.5, 135.2, 129.0, 128.5, 128.4, 128.3, 125.8, 113.8, 68.0, 63.1, 55.4, 52.6, 33.8, 22.1, 17.6, 17.3. **IR (thin film):** ν 3848, 3715, 3648, 3481, 2950, 2918, 2845, 1738, 1639, 1488, 1384, 1340, 1259, 1125, 1029, 750, 602 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{24}H_{27}N_2O_7$ $(M+H)^+$ 455.1813, found 455.1812.



**2j**

**Benzyl (*R*)-3-((3-methoxy-3-oxopropyl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanoate (2j)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 1/1) afforded the product as a colorless oil (71.9 mg, 81% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK OD-H column; solvent system: 10% isopropanol/90% hexane; 0.5 mL/min; retention times: 32.4 min (major), 45.9 min (minor)]. $[\alpha]^{25}_D$ = -0.8 (*c* 0.25, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.83 – 7.75 (m, 2H), 7.68 (s, 1H), 7.29 (s, 5H), 6.98 – 6.88 (m, 2H), 6.77 (t, *J* = 5.6 Hz, 1H), 5.23 (d, *J* = 12.4 Hz, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 3.85 (s, 3H), 3.64 (s, 3H), 3.51 – 3.45 (m, 2H), 2.53 – 2.39 (m, 2H), 1.88 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.3, 170.4, 167.9, 165.7, 162.5, 135.1, 129.0, 128.4, 128.3, 128.1, 125.9, 113.7, 68.0, 63.1, 55.4, 51.8, 35.6, 33.2, 22.0. **IR (thin film):** ν 3482, 3419, 2918, 2850, 1738, 1640, 1533, 1488, 1384, 1258, 1177, 1121, 1029, 845, 700, 588 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{23}H_{27}N_2O_7$ $(M+H)^+$ 443.1813, found 443.1814.

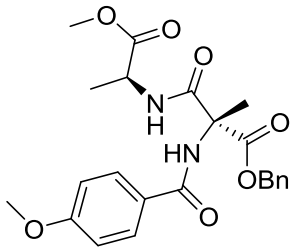


**2k**

**Methyl (*R*)-4-(3-(benzyloxy)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanamido)butanoate (2k)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 1/1) afforded the product as a colorless oil (72.7 mg, 80% yield). **HPLC analysis:** 97% ee [Daicel CHIRALPAK OD-H column; solvent system: 10% isopropanol/90% hexane; 0.5 mL/min; retention times: 33.9 min (major), 39.8 min (minor)]. $[\alpha]^{25}_D$ = 7.8 (*c* 0.35, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.82 – 7.76 (m, 2H), 7.71 (s, 1H), 7.29 (s, 5H), 6.96 – 6.90 (m, 2H), 6.46 (t, *J* = 5.2 Hz, 1H), 5.23 (d, *J* = 12.4 Hz, 1H), 5.19 (d,

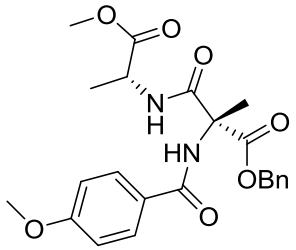
*J* = 12.4 Hz, 1H), 3.86 (s, 3H), 3.67 (s, 3H), 3.34 – 3.18 (m, 2H), 2.27 (t, *J* = 7.2 Hz, 2H), 1.89 (s, 3H), 1.78 – 1.70 (m, 2H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 173.4, 170.6, 168.1, 165.8, 162.5, 135.1, 129.0, 128.4, 128.3, 128.2, 125.9, 113.7, 68.0, 63.1, 55.4, 51.7, 39.5, 31.1, 24.2, 22.2. **IR (thin film):** ν 3707, 3646, 3482, 2922, 2850, 1738, 1647, 1558, 1489, 1384, 1259, 1175, 1119, 1023, 851, 806, 602 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{24}H_{29}N_2O_7$ $(M+H)^+$ 457.1969, found 457.1970.



**2l**

**Benzyl (*R*)-3-(((*S*)-1-methoxy-1-oxopropan-2-yl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanoate (2l)**

1H NMR analysis of the crude mixture showed a dr of >99:1. Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a colorless oil (69.8 mg, 79% yield). **$[\alpha]^{25}_D$** = 3.2 (*c* 0.25, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.82 – 7.75 (m, 2H), 7.63 (s, 1H), 7.34 – 7.27 (m, 5H), 6.95 – 6.90 (m, 2H), 6.87 (d, *J* = 7.2 Hz, 1H), 5.26 (d, *J* = 12.4 Hz, 1H), 5.22 (d, *J* = 12.4 Hz, 1H), 4.55 – 4.45 (m, 1H), 3.85 (s, 3H), 3.70 (s, 3H), 1.93 (s, 3H), 1.40 (d, *J* = 7.2 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.3, 170.3, 167.6, 165.9, 162.5, 135.1, 129.0, 128.4, 128.2, 128.1, 125.9, 113.7, 68.1, 63.2, 55.4, 52.5, 48.7, 22.1, 17.9. **IR (thin film):** ν 3481, 3416, 2953, 2921, 2847, 1743, 1639, 1529, 1484, 1384, 1258, 1210, 1173, 1123, 603, 570 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{23}H_{27}N_2O_7$ $(M+H)^+$ 443.1813, found 443.1815.

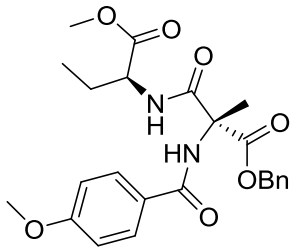


**2m**

**Benzyl (*R*)-3-(((*R*)-1-methoxy-1-oxopropan-2-yl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanoate (2m)**

1H NMR analysis of the crude mixture showed a dr of >99:1. Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a colorless oil (71.0 mg, 80% yield). **$[\alpha]^{25}_D$** = 6.0 (*c* 0.20, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.82 – 7.77 (m, 2H), 7.66 (s, 1H), 7.34 – 7.27 (m, 5H), 6.96 – 6.90 (m, 2H), 6.67 (d, *J* = 7.2 Hz, 1H), 5.27 (d, *J* = 12.0 Hz, 1H), 5.18 (d, *J* = 12.4 Hz, 1H),

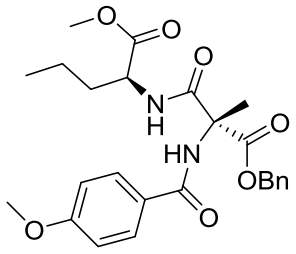
4.53 – 4.43 (m, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 1.93 (s, 3H), 1.22 (d, *J* = 7.2 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.4, 170.3, 167.6, 165.7, 162.5, 135.1, 129.0, 128.8, 128.5, 128.4, 125.8, 113.7, 68.0, 63.0, 55.4, 52.6, 48.6, 22.1, 17.6. **IR (thin film):** ν 3382, 3065, 3034, 2958, 2922, 2851, 1747, 1647, 1608, 1526, 1488, 1455, 1380, 1299, 1260, 1215, 1178, 1125, 1029, 846, 800, 770, 751, 699, 601 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{23}H_{27}N_2O_7$ $(M+H)^+$ 443.1813, found 443.1813.



**2n**

**Methyl (*S*)-2-((*R*)-3-(benzyloxy)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanamido)butanoate (2n)**

1H NMR analysis of the crude mixture showed a dr of >99:1. Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a colorless oil (71.0 mg, 78% yield). **$[\alpha]^{25}_D$** = 2.8 (*c* 0.50, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.82 – 7.75 (m, 2H), 7.64 (s, 1H), 7.33 – 7.27 (m, 5H), 6.95 – 6.90 (m, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 5.24 (s, 2H), 4.50 (td, *J* = 7.2, 5.2 Hz, 1H), 3.85 (s, 3H), 3.70 (s, 3H), 1.94 (s, 3H), 1.93 – 1.86 (m, 1H), 1.78 – 1.67 (m, 1H), 0.88 (t, *J* = 7.6 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 171.7, 170.4, 167.9, 165.9, 162.5, 135.1, 129.0, 128.5, 128.3, 128.1, 125.9, 113.8, 68.2, 63.4, 55.4, 53.9, 52.5, 25.3, 22.3, 9.4. **IR (thin film):** ν 3363, 3065, 3034, 2961, 2923, 2851, 1744, 1659, 1647, 1607, 1577, 1532, 1500, 1488, 1381, 1299, 1259, 1211, 1179, 1125, 1029, 846, 802, 770, 699, 596 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{24}H_{29}N_2O_7$ $(M+H)^+$ 457.1969, found 457.1971.

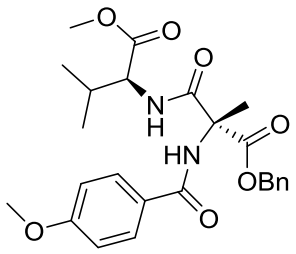


**2o**

**Methyl (*S*)-2-((*R*)-3-(benzyloxy)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanamido)pentanoate (2o)**

1H NMR analysis of the crude mixture showed a dr of >99:1. Purification by flash chromatography (petroleum ether/ethyl acetate = 5/2) afforded the product as a colorless oil (69.5 mg, 74% yield). **$[\alpha]^{25}_D$** = 4.0 (*c* 0.15, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.82 – 7.75 (m, 2H), 7.63 (s, 1H), 7.33 – 7.27 (m, 5H), 6.95 – 6.90 (m, 2H), 6.81 (d, *J* = 7.6 Hz, 1H), 5.25 (d, *J* = 12.4 Hz, 1H), 5.22 (d, *J* = 12.4 Hz, 1H),

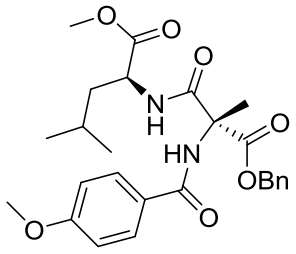
4.53 (td, *J* = 7.6, 5.2 Hz, 1H), 3.85 (s, 3H), 3.69 (s, 3H), 1.94 (s, 3H), 1.88 – 1.77 (m, 1H), 1.70 – 1.60 (m, 1H), 1.38 – 1.25 (m, 2H), 0.91 (t, *J* = 7.6 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 171.9, 170.3, 167.9, 165.9, 162.5, 135.0, 129.0, 128.4, 128.2, 128.1, 125.9, 113.7, 68.2, 63.3, 55.4, 52.7, 52.4, 34.1, 22.2, 18.5, 13.6. **IR (thin film):** ν 3408, 3005, 2959, 2921, 2850, 1744, 1659, 1647, 1607, 1532, 1488, 1471, 1379, 1301, 1259, 1209, 1181, 1114, 1030, 801, 769, 739, 699 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{25}H_{31}N_2O_7$ $(M+H)^+$ 471.2126, found 471.2123.



**2p**

**Methyl ((*R*)-3-(benzyloxy)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanoyl)-*L*-valinate (2p)**

1H NMR analysis of the crude mixture showed a dr of >99:1. Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a colorless oil (74.0 mg, 79% yield). **$[\alpha]^{25}_D$** = 4.6 (*c* 1.0, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.84 – 7.73 (m, 2H), 7.64 (s, 1H), 7.34 – 7.27 (m, 5H), 6.97 – 6.87 (m, 3H), 5.24 (s, 2H), 4.50 (dd, *J* = 8.8, 4.8 Hz, 1H), 3.85 (s, 3H), 3.68 (s, 3H), 2.24 – 2.13 (m, 1H), 1.95 (s, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 171.3, 170.4, 168.1, 166.0, 162.5, 135.0, 129.0, 128.4, 128.2, 128.1, 125.9, 113.7, 68.2, 63.4, 57.7, 55.4, 52.2, 31.2, 22.3, 18.9, 17.5. **IR (thin film):** ν 3345, 3064, 3034, 2963, 2935, 2875, 2850, 1743, 1682, 1607, 1532, 1504, 1373, 1302, 1259, 1210, 1180, 1124, 1029, 846, 770, 737, 699, 595 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{25}H_{31}N_2O_7$ $(M+H)^+$ 471.2126, found 471.2137.

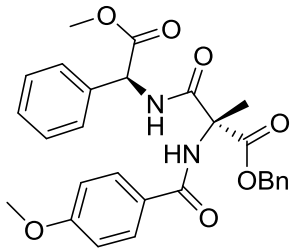


**2q**

**Methyl ((*R*)-3-(benzyloxy)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanoyl)-*L*-leucinate (2q)**

1H NMR analysis of the crude mixture showed a dr of >99:1. Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (77.8 mg, 80% yield). **$[\alpha]^{25}_D$** = 0.9 (*c* 0.45, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.82 – 7.76 (m, 2H), 7.63 (s, 1H), 7.33 – 7.27 (m, 5H), 6.96 – 6.88 (m, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.26 (d, *J* = 12.4 Hz, 1H), 5.21 (d, *J* = 12.4 Hz, 1H),

4.57 (td, *J* = 8.4, 5.2 Hz, 1H), 3.85 (s, 3H), 3.67 (s, 3H), 1.93 (s, 3H), 1.71 – 1.50 (m, 3H), 0.93 (d, *J* = 6.0 Hz, 6H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.3, 170.4, 168.0, 166.0, 162.5, 135.1, 129.0, 128.5, 128.3, 128.1, 125.9, 113.8, 68.2, 63.3, 55.4, 52.4, 51.4, 41.1, 24.9, 22.8, 22.2, 21.8. **IR (thin film):** ν 3714, 3647, 3360, 3065, 3034, 2958, 2925, 2871, 2853, 1747, 1688, 1660, 1607, 1577, 1532, 1488, 1441, 1372, 1258, 1208, 1122, 1029, 770, 698 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{26}H_{33}N_2O_7$ $(M+H)^+$ 485.2282, found 485.2285.

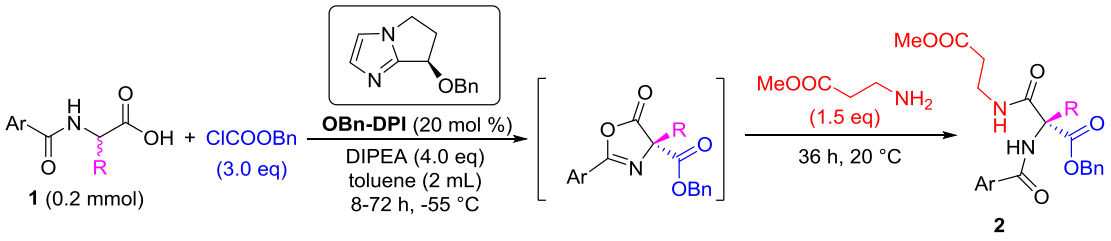


**2r**

**Benzyl (*R*)-3-(((*S*)-2-methoxy-2-oxo-1-phenylethyl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanoate (2r)**

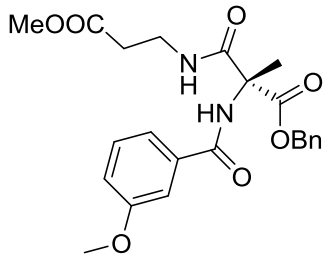
1H NMR analysis of the crude mixture showed a dr of >99:1. Purification by flash chromatography (petroleum ether/ethyl acetate = 5/2) afforded the product as a colorless oil (76.3 mg, 76% yield). **$[\alpha]^{25}_D$** = 42.9 (*c* 0.90, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.81 – 7.74 (m, 2H), 7.60 (s, 1H), 7.46 (d, *J* = 6.4 Hz, 1H), 7.38 – 7.27 (m, 10H), 6.94 – 6.86 (m, 2H), 5.44 (d, *J* = 6.8 Hz, 1H), 5.27 (d, *J* = 12.4 Hz, 1H), 5.22 (d, *J* = 12.4 Hz, 1H), 3.84 (s, 3H), 3.69 (s, 3H), 1.90 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 170.3, 170.3, 167.5, 166.0, 162.5, 135.8, 135.1, 129.1, 129.0, 128.8, 128.5, 128.3, 128.2, 127.0, 125.9, 113.7, 68.3, 63.2, 57.1, 55.4, 53.0, 22.1. **IR (thin film):** ν 3390, 3064, 3033, 3007, 2955, 2921, 2849, 1743, 1680, 1648, 1607, 1522, 1499, 1456, 1439, 1380, 1320, 1300, 1259, 1214, 1176, 1124, 1029, 769, 736, 698 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{28}H_{29}N_2O_7$ $(M+H)^+$ 505.1969, found 505.1962.

**Different Substrates:**




Under a $N_2$ atmosphere, the substrate **1** (0.2 mmol, 44.7 mg), the catalyst **OBn-DPI** (0.04 mmol, 8.6 mg) and DIPEA (0.8 mmol, 132.2 μL) were dissolved in anhydrous toluene (2 mL) and cooled to −55 ℃ in a dry two-necked flask. ClCOOBn (0.6 mmol, 84.5 μL) was then added and the vial was sealed with a septum. The reaction mixture was stirred at −55 ℃ for 8-72 h (Reaction time for **2s-v** was 72 h, reaction time for

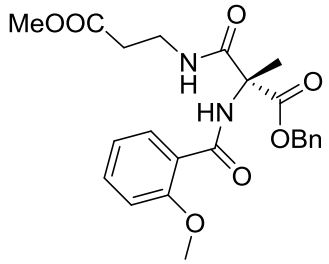
**2w-x** was 8 h, reaction time for **2y-ad** was 10 h) and then the temperature was gradually raised to 20 ℃. Methyl 3-aminopropionate hydrochloride (0.3 mmol, 41.9 mg) and DIPEA (0.3 mmol, 49.6 μL) were dissolved in anhydrous toluene (1 mL) in another dry flask and stirred for 10 min. Then the mixture was transferred into the former reaction flask and the reaction mixture was stirred at 20 ℃ for 36 h. The reaction mixture was quenched with 0.2 M HCl (5 mL) and extracted with DCM (5 mL × 3). The combined organic phases were dried over $Na_2SO_4$. After filtration, the residue was purified by column chromatography (petroleum ether/ethyl acetate) to give the corresponding product **2**. The ee value was determined by chiral HPLC analysis after purification by column chromatography (petroleum ether/ethyl acetate).




**2s**

**Benzyl (*R*)-3-((3-methoxy-3-oxopropyl)amino)-2-(3-methoxybenzamido)-2-methyl-3-oxopropanoate (2s)**

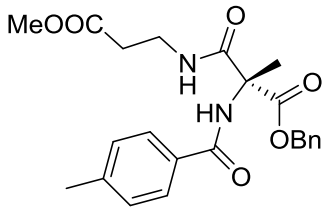
Purification by flash chromatography (petroleum ether/ethyl acetate = 3/2) afforded the product as a colorless oil (73.3 mg, 83% yield). **HPLC analysis:** 97% ee [Daicel CHIRALPAK AS-H column; solvent system: 20% isopropanol/80% hexane; 1.0 mL/min; retention times: 13.8 min (minor), 36.9 min (major)]. **$[\alpha]^{25}_{D}$** = 2.9 (*c* 0.70, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.79 (s, 1H), 7.41 – 7.27 (m, 8H), 7.09 – 7.02 (m, 1H), 6.76 (t, *J* = 5.6 Hz, 1H), 5.24 (d, *J* = 12.0 Hz, 1H), 5.19 (d, *J* = 12.0 Hz, 1H), 3.84 (s, 3H), 3.65 (s, 3H), 3.51 – 3.45 (m, 2H), 2.55 – 2.38 (m, 2H), 1.89 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.4, 170.3, 167.8, 166.1, 159.8, 135.1, 135.1, 129.6, 128.5, 128.4, 128.2, 119.0, 118.4, 112.2, 68.1, 63.2, 55.5, 51.9, 35.7, 33.3, 21.9. **IR (thin film):** ν 3372, 3066, 3034, 3002, 2955, 2922, 2851, 1744, 1731, 1659, 1583, 1506, 1481, 1373, 1262, 1225, 1122, 1044, 800, 758, 698 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{23}H_{27}N_2O_7$ $(M+H)^+$ 443.1813, found 443.1811.




**2t**

**Benzyl (*R*)-3-((3-methoxy-3-oxopropyl)amino)-2-(2-methoxybenzamido)-2-methyl-3-oxopropanoate (2t)**

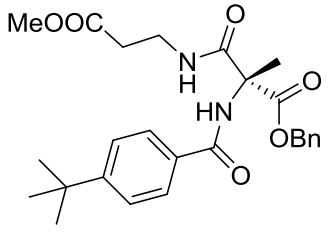
Purification by flash chromatography (petroleum ether/ethyl acetate = 3/2) afforded the product as a colorless oil (67.1 mg, 76% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK AS-H column; solvent system: 20% isopropanol/80% hexane; 0.5 mL/min; retention times: 26.1 min (minor), 30.4 min (major)]. **$[\alpha]^{25}_{D}$** = 0.9 (*c* 0.70, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 9.45 (s, 1H), 8.15 (dd, *J* = 8.0, 5.6 Hz, 1H), 7.52 – 7.43 (m, 1H), 7.35 – 7.27 (m, 5H), 7.11 – 7.04 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.84 (t, *J* = 5.6 Hz, 1H), 5.25 (d, *J* = 12.4 Hz, 1H), 5.20 (d, *J* = 12.0 Hz, 1H), 4.01 (s, 3H), 3.61 (s, 3H), 3.54 – 3.41 (m, 2H), 2.54 – 2.40 (m, 2H), 1.88 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.5, 170.6, 168.2, 164.2, 158.0, 135.3, 133.3, 132.1, 128.5, 128.3, 128.1, 121.1, 120.8, 111.4, 67.9, 63.8, 56.0, 51.8, 35.5, 33.4, 21.9. **IR (thin film):** ν 3360, 3067, 3033, 2922, 2850, 1738, 1688, 1647, 1601, 1516, 1483, 1440, 1373, 1301, 1262, 1241, 1178, 1103, 1048, 1021, 801, 758, 699, 608 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{23}H_{27}N_2O_7$ $(M+H)^+$ 443.1813, found 443.1815.




**2u**

**Benzyl (*R*)-3-((3-methoxy-3-oxopropyl)amino)-2-methyl-2-(4-methylbenzamido)-3-oxopropanoate (2u)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/2) afforded the product as a colorless oil (63.2 mg, 74% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK AS-H column; solvent system: 20% isopropanol/80% hexane; 1.0 mL/min; retention times: 11.2 min (minor), 21.3 min (major)]. **$[\alpha]^{25}_{D}$** = -0.8 (*c* 0.25, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.81 – 7.67 (m, 3H), 7.29 (s, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.76 (t, *J* = 5.6 Hz, 1H), 5.23 (d, *J* = 12.4 Hz, 1H), 5.18 (d, *J* = 12.4 Hz, 1H), 3.64 (s, 3H), 3.51 – 3.45 (m, 2H), 2.53 – 2.42 (m, 2H), 2.40 (s, 3H), 1.88 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.4, 170.4, 167.9, 166.1, 142.3, 135.1, 130.7, 129.2, 128.4, 128.3, 128.1, 127.1, 68.0, 63.1, 51.8, 35.6, 33.2, 21.9, 21.5. **IR (thin film):** ν 3475, 3414, 2960, 2922, 2851, 1738, 1644, 1524, 1487, 1384, 1262, 1122, 799, 753, 698, 602 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{23}H_{27}N_2O_6$ $(M+H)^+$ 427.1864, found 427.1860.

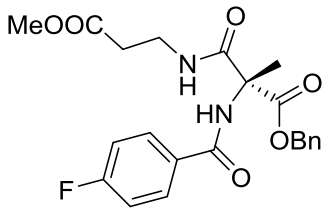



**2v**

**Benzyl (*R*)-2-(4-(*tert*-butyl)benzamido)-3-((3-methoxy-3-oxopropyl)amino)-2-**

**methyl-3-oxopropanoate (2v)**

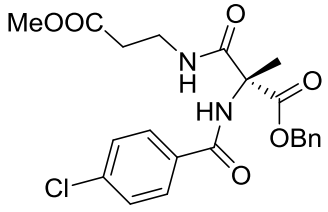
Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a colorless oil (73.2 mg, 78% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK AS-H column; solvent system: 20% isopropanol/80% hexane; 1.0 mL/min; retention times: 7.6 min (minor), 10.8 min (major)]. **$[\alpha]^{25}_{D}$** = 2.7 (*c* 0.15, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.81 – 7.72 (m, 3H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.29 (s, 5H), 6.75 (t, *J* = 5.6 Hz, 1H), 5.24 (d, *J* = 12.0 Hz, 1H), 5.17 (d, *J* = 12.0 Hz, 1H), 3.64 (s, 3H), 3.51 – 3.45 (m, 2H), 2.55 – 2.38 (m, 2H), 1.88 (s, 3H), 1.34 (s, 9H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.3, 170.4, 167.9, 166.1, 155.4, 135.1, 130.7, 128.4, 128.3, 128.1, 127.0, 125.4, 68.0, 63.1, 51.8, 35.6, 34.9, 33.3, 31.1, 21.9. **IR (thin film):** ν 3481, 3416, 2962, 2922, 2852, 1738, 1647, 1526, 1488, 1384, 1261, 1118, 1018, 801, 697, 602 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{26}H_{33}N_2O_6$ $(M+H)^+$ 469.2333, found 469.2332.




**2w**

**Benzyl (*R*)-2-(4-fluorobenzamido)-3-((3-methoxy-3-oxopropyl)amino)-2-methyl-3-oxopropanoate (2w)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 3/2) afforded the product as a colorless oil (65.8 mg, 76% yield). **HPLC analysis:** 97% ee [Daicel CHIRALPAK AS-H column; solvent system: 20% isopropanol/80% hexane; 1.0 mL/min; retention times: 10.6 min (minor), 36.7 min (major)]. **$[\alpha]^{25}_{D}$** = 4.4 (*c* 0.5, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.85 – 7.79 (m, 2H), 7.77 (s, 1H), 7.29 (s, 5H), 7.14 – 7.07 (m, 2H), 6.78 (t, *J* = 5.7 Hz, 1H), 5.23 (d, *J* = 12.3 Hz, 1H), 5.19 (d, *J* = 12.3 Hz, 1H), 3.65 (s, 3H), 3.52 – 3.45 (m, 2H), 2.55 – 2.38 (m, 2H), 1.88 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.4, 170.2, 167.8, 165.2, 165.0 (d, *J* = 250.9 Hz), 135.0, 129.8 (d, *J* = 3.0 Hz), 129.5 (d, *J* = 9.0 Hz), 128.5, 128.4, 128.2, 115.6 (d, *J* = 21.8 Hz), 68.1, 63.2, 51.9, 35.7, 33.2, 21.9. **IR (thin film):** ν 3648, 3481, 2960, 2920, 2850, 1738, 1659, 1605, 1533, 1488, 1471, 1384, 1262, 1127, 852, 802, 700 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{22}H_{24}FN_2O_6$ $(M+H)^+$ 431.1613, found 431.1614.

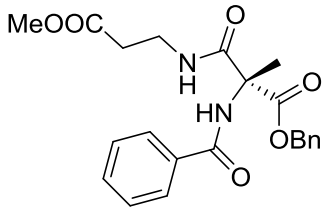



**2x**

**Benzyl (*R*)-2-(4-chlorobenzamido)-3-((3-methoxy-3-oxopropyl)amino)-2-methyl-**

**3-oxopropanoate (2x)**

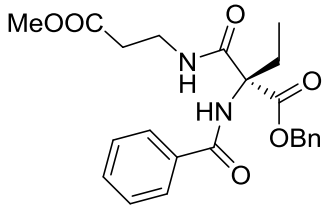
Purification by flash chromatography (petroleum ether/ethyl acetate = 3/2) afforded the product as a light yellow oil (65.1 mg, 73% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK AS-H column; solvent system: 20% isopropanol/80% hexane; 1.0 mL/min; retention times: 11.7 min (minor), 35.7 min (major)]. **$[\alpha]^{25}_{D}$** = -0.8 (*c* 0.25, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.82 – 7.72 (m, 3H), 7.44 – 7.38 (m, 2H), 7.32 – 7.27 (m, 5H), 6.74 (t, *J* = 5.6 Hz, 1H), 5.22 (d, *J* = 12.0 Hz, 1H), 5.18 (d, *J* = 12.4 Hz, 1H), 3.66 (s, 3H), 3.52 – 3.44 (m, 2H), 2.54 – 2.38 (m, 2H), 1.88 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.3, 170.1, 167.6, 165.1, 138.1, 135.0, 132.0, 128.8, 128.5, 128.5, 128.4, 128.2, 68.1, 63.2, 51.9, 35.7, 33.2, 21.9. **IR (thin film):** ν 3481, 2960, 2920, 2850, 1738, 1659, 1647, 1541, 1472, 1384, 1263, 1123, 1093, 1014, 800, 701 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{22}H_{24}ClN_2O_6$ $(M+H)^+$ 447.1317, found 447.1318.




**2y**

**Benzyl (*R*)-2-benzamido-3-((3-methoxy-3-oxopropyl)amino)-2-methyl-3-oxopropanoate (2y)**

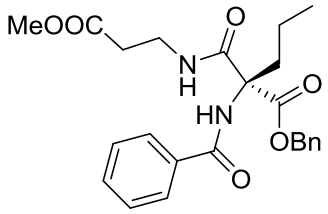
Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a colorless oil (66.3 mg, 80% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK AS-H column; solvent system: 20% isopropanol/80% hexane; 1.0 mL/min; retention times: 11.6 min (minor), 32.3 min (major)]. **$[\alpha]^{25}_{D}$** = 0.7 (*c* 0.55, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.89 – 7.78 (m, 3H), 7.55 – 7.49 (m, 1H), 7.48 – 7.40 (m, 2H), 7.29 (s, 5H), 6.77 (t, *J* = 5.6 Hz, 1H), 5.24 (d, *J* = 12.0 Hz, 1H), 5.19 (d, *J* = 12.4 Hz, 1H), 3.65 (s, 3H), 3.52 – 3.45 (m, 2H), 2.54 – 2.38 (m, 2H), 1.89 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.3, 170.3, 167.8, 166.2, 135.0, 133.6, 131.8, 128.5, 128.4, 128.3, 128.1, 127.1, 68.1, 63.2, 51.8, 35.6, 33.2, 21.9. **IR (thin film):** ν 3481, 3420, 2962, 2925, 2852, 1731, 1647, 1580, 1539, 1472, 1384, 1261, 1110, 1025, 801, 697, 602 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{22}H_{25}N_2O_6$ $(M+H)^+$ 413.1707, found 413.1703.




**2z**

**Benzyl (*R*)-2-benzamido-2-((3-methoxy-3-oxopropyl)carbamoyl)butanoate (2z)**

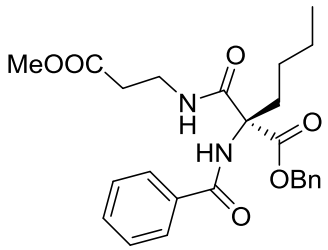
Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a colorless oil (66.1 mg, 78% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK AS-H column; solvent system: 20% isopropanol/80% hexane; 1.0 mL/min; retention times: 10.2 min (minor), 14.1 min (major)]. **$[\alpha]^{25}_{D}$** = -1.8 (*c* 0.55, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.88 – 7.80 (m, 2H), 7.75 (s, 1H), 7.57 – 7.49 (m, 1H), 7.48 – 7.41 (m, 2H), 7.29 (s, 5H), 6.78 (t, *J* = 5.6 Hz, 1H), 5.24 (d, *J* = 12.0 Hz, 1H), 5.18 (d, *J* = 12.4 Hz, 1H), 3.65 (s, 3H), 3.54 – 3.43 (m, 2H), 2.78 – 2.66 (m, 1H), 2.56 – 2.39 (m, 2H), 2.34 – 2.23 (m, 1H), 0.79 (t, *J* = 7.6 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.4, 170.1, 166.8, 166.1, 135.1, 133.7, 131.8, 128.6, 128.5, 128.4, 128.2, 127.1, 68.0, 67.3, 51.9, 35.6, 33.3, 26.6, 7.7. **IR (thin film):** ν 3400, 3063, 3032, 2960, 2922, 2851, 1738, 1659, 1648, 1580, 1507, 1475, 1384, 1259, 1220, 1089, 1028, 802, 698 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{23}H_{27}N_2O_6$ $(M+H)^+$ 427.1864, found 427.1861.




**2aa**

**Benzyl (*R*)-2-benzamido-2-((3-methoxy-3-oxopropyl)carbamoyl)pentanoate (2aa)**

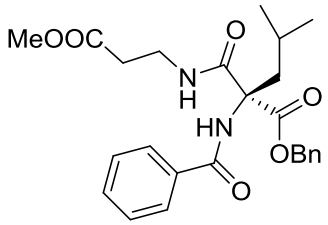
Purification by flash chromatography (petroleum ether/ethyl acetate = 5/2) afforded the product as a colorless oil (67.7 mg, 77% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK AS-H column; solvent system: 20% isopropanol/80% hexane; 1.0 mL/min; retention times: 9.2 min (minor), 12.3 min (major)]. **$[\alpha]^{25}_{D}$** = -0.8 (*c* 0.50, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.85 – 7.80 (m, 2H), 7.76 (s, 1H), 7.55 – 7.49 (m, 1H), 7.48 – 7.41 (m, 2H), 7.29 (s, 5H), 6.78 (t, *J* = 5.6 Hz, 1H), 5.24 (d, *J* = 12.0 Hz, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 3.65 (s, 3H), 3.56 – 3.41 (m, 2H), 2.70 – 2.58 (m, 1H), 2.57 – 2.37 (m, 2H), 2.26 – 2.14 (m, 1H), 1.30 – 1.17 (m, 1H), 1.16 – 1.02 (m, 1H), 0.88 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.4, 170.1, 166.9, 166.1, 135.1, 133.7, 131.8, 128.6, 128.5, 128.4, 128.2, 127.1, 68.0, 66.9, 51.9, 35.6, 35.4, 33.3, 17.0, 13.8. **IR (thin film):** ν 3714, 3648, 3377, 3065, 3033, 2960, 2923, 2874, 2851, 1738, 1659, 1506, 1476, 1368, 1281, 1218, 1178, 1028, 803, 698, 601 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{24}H_{29}N_2O_6$ $(M+H)^+$ 441.2020, found 441.2016.




**2ab**

**Benzyl (*R*)-2-benzamido-2-((3-methoxy-3-oxopropyl)carbamoyl)hexanoate (2ab)**

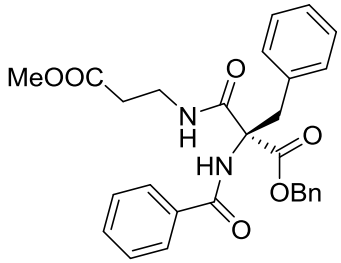
Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (67.0 mg, 74% yield). **HPLC analysis:** 99% ee [Daicel CHIRALPAK OD-H column; solvent system: 20% isopropanol/80% hexane; 1.0 mL/min; retention times: 7.8 min (minor), 11.1 min (major)]. **$[\alpha]^{25}_{D}$** = -1.2 (*c* 0.50, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.86 – 7.80 (m, 2H), 7.75 (s, 1H), 7.56 – 7.49 (m, 1H), 7.48 – 7.41 (m, 2H), 7.29 (s, 5H), 6.79 (t, *J* = 5.6 Hz, 1H), 5.24 (d, *J* = 12.4 Hz, 1H), 5.17 (d, *J* = 12.4 Hz, 1H), 3.65 (s, 3H), 3.56 – 3.41 (m, 2H), 2.70 – 2.60 (m, 1H), 2.57 – 2.39 (m, 2H), 2.28 – 2.16 (m, 1H), 1.34 – 1.22 (m, 2H), 1.22 – 1.10 (m, 1H), 1.09 – 0.97 (m, 1H), 0.82 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.4, 170.1, 167.0, 166.0, 135.1, 133.7, 131.8, 128.6, 128.5, 128.4, 128.2, 127.2, 68.0, 66.8, 51.8, 35.6, 33.3, 33.1, 25.7, 22.4, 13.8. **IR (thin film):** ν 3390, 3063, 2959, 2924, 2853, 1738, 1659, 1580, 1507, 1472, 1376, 1264, 1214, 1111, 800, 696 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{25}H_{31}N_2O_6$ $(M+H)^+$ 455.2177, found 455.2172.




**2ac**

**Benzyl (*R*)-2-benzamido-2-((3-methoxy-3-oxopropyl)carbamoyl)-4-methylpentanoate (2ac)**

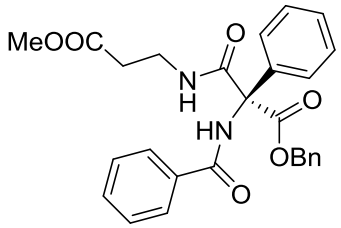
Purification by flash chromatography (petroleum ether/ethyl acetate = 3/1) afforded the product as a colorless oil (67.9 mg, 75% yield). **HPLC analysis:** 99% ee [Daicel CHIRALPAK AS-H column; solvent system: 20% isopropanol/80% hexane; 1.0 mL/min; retention times: 7.6 min (minor), 9.0 min (major)]. **$[\alpha]^{25}_{D}$** = -0.9 (*c* 0.45, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.92 – 7.78 (m, 3H), 7.55 – 7.49 (m, 1H), 7.48 – 7.41 (m, 2H), 7.29 (s, 5H), 6.75 (t, *J* = 5.2 Hz, 1H), 5.21 (d, *J* = 12.4 Hz, 1H), 5.17 (d, *J* = 12.4 Hz, 1H), 3.65 (s, 3H), 3.53 – 3.40 (m, 2H), 2.67 (dd, *J* = 14.8, 6.4 Hz, 1H), 2.56 – 2.38 (m, 2H), 2.19 (dd, *J* = 14.8, 6.4 Hz, 1H), 1.60 – 1.52 (m, 1H), 0.87 (d, *J* = 7.2 Hz, 3H), 0.85 (d, *J* = 7.2 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.4, 170.4, 167.3, 166.1, 135.0, 133.8, 131.8, 128.6, 128.5, 128.4, 128.3, 127.1, 68.1, 66.5, 51.9, 41.1, 35.6, 33.1, 24.5, 23.5, 23.3. **IR (thin film):** ν 3378, 3065, 3033, 2957, 2925, 2871, 2852, 1738, 1659, 1580, 1506, 1476, 1443, 1368, 1261, 1216, 1178, 1076, 1028, 803, 697 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{25}H_{31}N_2O_6$ $(M+H)^+$ 455.2177, found 455.2175.




**2ad**

**Benzyl (*R*)-2-benzamido-2-benzyl-3-((3-methoxy-3-oxopropyl)amino)-3-oxopropanoate (2ad)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a colorless oil (80.3 mg, 82% yield). **HPLC analysis:** 97% ee [Daicel CHIRALPAK OD-H column; solvent system: 10% isopropanol/90% hexane; 1.0 mL/min; retention times: 23.5 min (minor), 35.2 min (major)]. **$[\alpha]^{25}_{D}$** = -5.5 (*c* 0.80, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.76 – 7.67 (m, 2H), 7.55 – 7.38 (m, 4H), 7.38 – 7.30 (m, 5H), 7.23 – 7.10 (m, 3H), 6.97 – 6.92 (m, 2H), 6.83 (t, *J* = 5.6 Hz, 1H), 5.29 (d, *J* = 12.0 Hz, 1H), 5.22 (d, *J* = 12.0 Hz, 1H), 3.93 (d, *J* = 14.0 Hz, 1H), 3.65 (s, 3H), 3.62 (d, *J* = 14.4 Hz, 1H), 3.57 – 3.39 (m, 2H), 2.47 (t, *J* = 6.0 Hz, 2H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.7, 169.6, 166.4, 166.0, 134.9, 134.9, 133.7, 131.9, 129.9, 128.6, 128.6, 128.5, 128.3, 127.2, 127.1, 68.3, 67.5, 51.9, 38.3, 35.6, 33.2. **IR (thin film):** ν 3648, 3390, 3064, 3032, 2954, 2924, 2853, 1738, 1683, 1660, 1580, 1506, 1476, 1445, 1374, 1281, 1202, 1117, 1084, 1049, 748, 701 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{28}H_{29}N_2O_6$ $(M+H)^+$ 489.2020, found 489.2026.




**2ae**

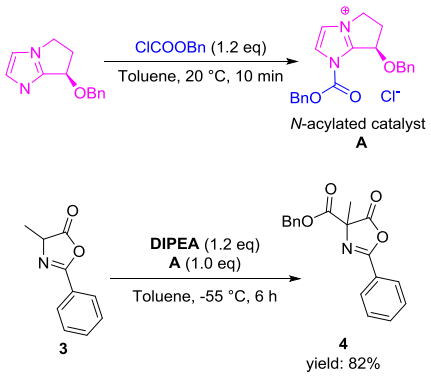
**Benzyl (*R*)-2-benzamido-3-((3-methoxy-3-oxopropyl)amino)-3-oxo-2-phenylpropanoate (2ae)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a white oil (69.5 mg, 73% yield). **HPLC analysis:** 57% ee [Daicel CHIRALPAK OD-H column; solvent system: 20% isopropanol/80% hexane; 1.0 mL/min; retention times: 10.7 min (major), 31.5 min (minor)]. **$[\alpha]^{25}_{D}$** = -22.0 (*c* 0.10, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.96 (s, 1H), 7.85 – 7.80 (m, 2H), 7.62 – 7.49 (m, 4H), 7.46 – 7.40 (m, 2H), 7.37 – 7.31 (m, 3H), 7.29 – 7.26 (m, 3H), 7.24 – 7.20 (m, 2H), 5.28 (d, *J* = 12.4 Hz, 1H), 5.24 (d, *J* = 12.4 Hz, 1H), 3.61 (s, 3H), 3.59 – 3.52 (m, 2H), 2.58 – 2.44 (m, 2H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.1, 169.4, 167.3, 166.5, 136.1, 134.9, 133.5, 132.0, 128.7, 128.6, 128.4, 128.3, 128.0, 127.4, 127.3, 69.6, 68.4, 51.8, 35.9, 33.4. **IR (thin film):** ν 3365, 3195, 3062, 3030, 2961, 2921, 2851, 1729, 1660, 1602, 1517, 1471, 1370, 1261, 1200, 1149, 1089, 1026, 939,

801, 697, 561 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{27}H_{26}N_2NaO_6$ $(M+Na)^+$ 497.1683, found 497.1698.

# 6. Effect of N-Acylated Catalyst

Under a $N_2$ atmosphere, azlactone **3** (0.2 mmol) and DIPEA (0.24 mmol) were dissolved in anhydrous toluene (1 mL) and cooled to −55 °C in a dry flask. The catalyst **OBn-DPI** (0.2 mmol) and ClCOOBn (0.24 mmol) were dissolved *in anhydrous toluene (1 mL)* in another dry flask and stirred for 10 min to form active species **A**. Then the mixture of the catalyst and ClCOOBn was transferred into the former reaction flask and the reaction mixture was stirred at −55 °C for 6 h. *C*-acylated product **4** was obtained in 82% yield (calculated from $^1$H NMR spectra).



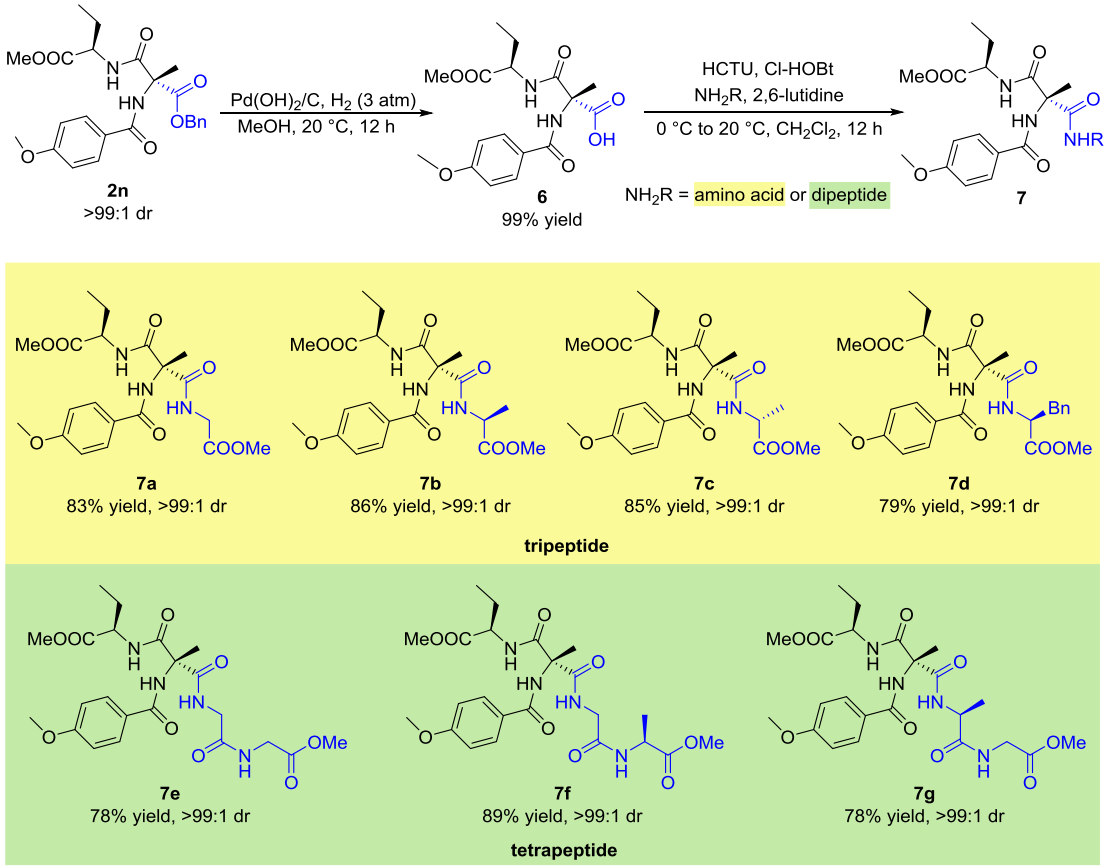

Effect of *N*-acylated catalyst

Because active species **A** can quickly turn into BnOH in the air, we made $^1$H NMR spectra of **A** by taking catalyst **OBn-DPI** (0.1 mmol) and ClCOOBn (0.12 mmol) with *solvent* $CDCl_3$ in a NMR tube and tested this sample immediately. Then the sample was transferred into a reaction flask, which contains azlactone **3** (0.1 mmol), DIPEA (0.12 mmol) and anhydrous toluene (0.5 mL) at −55 °C. This reaction mixture was stirred at −55 °C for 6 h and the *C*-acylated product **4** was obtained in 78% yield (calculated from $^1$H NMR spectra).

Here is the $^1$H NMR spectra of active species **A**. **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 8.10 (d, *J* = 2.1 Hz, 1H), 7.74 (d, *J* = 2.1 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.44 – 7.36 (m, 4H), 7.32 – 7.29 (m, 2H), 7.19 – 7.11 (m, 2H), 5.66 (d, *J* = 6.7 Hz, 1H), 5.57 (d, *J* = 11.5 Hz, 1H), 5.49 (d, *J* = 11.5 Hz, 1H), 4.83 – 4.75 (m, 1H), 4.48 (d, *J* = 11.0 Hz, 1H), 4.43 (d, *J* = 11.0 Hz, 1H), 4.44 – 4.39 (m, 1H), 3.43 – 3.32 (m, 1H), 2.62 – 2.54 (m, 1H).

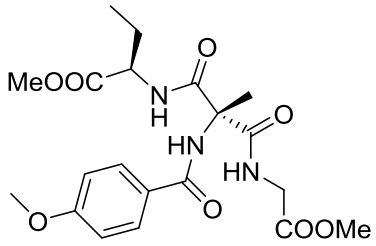
# 7. Synthetic Applications

## Synthesis of small peptides




Substrate **2n** (0.78 mmol, 356 mg) and $Pd(OH)_2/C$ (274 mg) were charged in an autoclave. The system was evacuated and filled with hydrogen. Then anhydrous MeOH (10 mL) was added and the hydrogen pressure was adjusted to 3 atm. After vigorous stirring at 20 ℃ for 12 h, the reaction mixture was filtered and evaporated under reduced pressure to give **6** (285 mg, 99% yield).

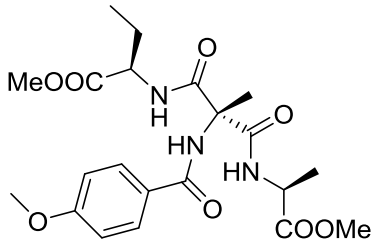
Compound **6** (0.2 mmol, 73.3 mg), *O*-(6-chloro-1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HCTU, 83.0 mg, 0.2 mmol), 6-chloro-1-hydroxybenzotriazole (Cl-HOBt, 85.0 mg, 0.5 mmol) and 2,6-lutidine (70 μL, 0.6 mmol) were dissolved in dry dichloromethane (10 mL). The solution was cooled in an ice bath and treated with a solution of amino acid methyl ester hydrochloride (0.2 mmol) and 2,6-lutidine (24 μL, 0.2 mmol) in dichloromethane (3 mL). The reaction mixture was stirred at 0 ℃ for 2 h and gradually raised to 20 ℃ for another 12 h. Subsequently, the solution was washed thrice with 1M HCl and the aqueous phase was extracted with dichloromethane. After drying over $Mg_2SO_4$, the combined organic phases were filtered and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel to give the corresponding small peptide product **7**.



**7a**

**Methyl (*R*)-2-((*S*)-3-((2-methoxy-2-oxoethyl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanamido)butanoate (7a)**

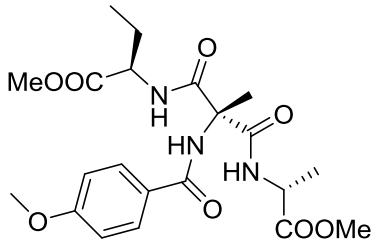
Purification by flash chromatography (petroleum ether/ethyl acetate = 1/2) afforded the product as a colorless oil (72.6 mg, 83% yield). $[\alpha]^{25}_{D}$ = 3.3 (*c* 1.2, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.87 – 7.81 (m, 3H), 7.69 – 7.62 (m, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 6.97 – 6.91 (m, 2H), 4.51 (td, *J* = 7.2, 5.5 Hz, 1H), 4.12 (dd, *J* = 18.1, 5.6 Hz, 1H), 4.02 (dd, *J* = 18.1, 5.2 Hz, 1H), 3.86 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 1.94 (s, 3H), 1.99 – 1.87 (m, 1H), 1.81 – 1.69 (m, 1H), 0.90 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 171.9, 170.6, 170.2, 169.5, 166.6, 162.8, 129.2, 125.7, 113.9, 63.3, 55.5, 54.1, 52.4, 52.4, 41.8, 25.2, 23.0, 9.5. **IR (thin film):** ν 3353, 3061, 2957, 2927, 2850, 1747, 1682, 1647, 1607, 1505, 1441, 1373, 1295, 1259, 1212, 1179, 1110, 1026, 983, 848, 795, 595 cm$^{-1}$. **HRMS (ESI):** calcd. for $C_{20}H_{27}N_3NaO_8$ $(M+Na)^+$ 460.1690, found 460.1695.



**7b**

**Methyl (*R*)-2-((*S*)-3-(((*S*)-1-methoxy-1-oxopropan-2-yl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanamido)butanoate (7b)**

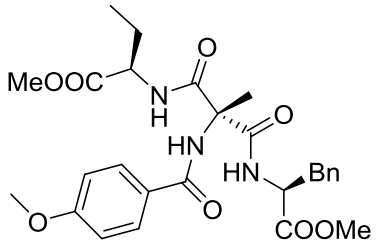
Purification by flash chromatography (petroleum ether/ethyl acetate = 1/2) afforded the product as a colorless oil (77.8 mg, 86% yield). $[\alpha]^{25}_{D}$ = -1.0 (*c* 0.6, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.87 – 7.83 (m, 2H), 7.82 (s, 1H), 7.53 (d, *J* = 7.1 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 6.97 – 6.92 (m, 2H), 4.62 – 4.47 (m, 2H), 3.86 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H), 1.98 – 1.89 (m, 1H), 1.93 (s, 3H), 1.79 – 1.68 (m, 1H), 1.43 (d, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.6, 171.9, 170.2, 169.6, 166.4, 162.7, 129.2, 125.8, 113.8, 63.2, 55.5, 53.9, 52.5, 52.4, 48.8, 25.2, 22.7, 17.7, 9.5. **IR (thin film):** ν 3379, 2955, 2878, 2847, 1744, 1661, 1607, 1506, 1376, 1296, 1257, 1211, 1178, 1029, 847, 772, 602 cm$^{-1}$. **HRMS (ESI):** calcd. for $C_{21}H_{29}N_3NaO_8$ $(M+Na)^+$ 474.1847, found 474.1850.



**7c**

**Methyl (*R*)-2-((*S*)-3-(((*R*)-1-methoxy-1-oxopropan-2-yl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanamido)butanoate (7c)**

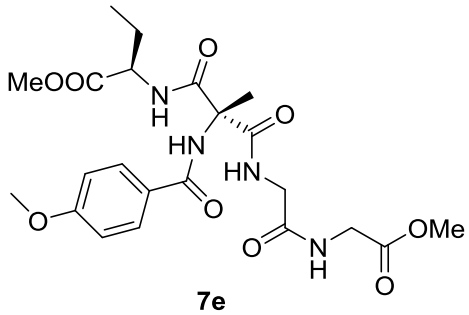
Purification by flash chromatography (petroleum ether/ethyl acetate = 1/2) afforded the product as a white solid (76.5 mg, 85% yield). **M.p.:** 135.2-136.0 ℃. **$[\alpha]^{25}_{D}$** = -10.3 (*c* 0.7, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.90 (s, 1H), 7.87 – 7.81 (m, 2H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 6.96 – 6.91 (m, 2H), 4.60 – 4.48 (m, 2H), 3.86 (s, 3H), 3.72 (s, 3H), 3.72 (s, 3H), 1.99 – 1.88 (m, 1H), 1.93 (s, 3H), 1.81 – 1.69 (m, 1H), 1.43 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.5, 171.8, 170.0, 169.8, 166.3, 162.7, 129.1, 125.8, 113.8, 63.3, 55.4, 54.0, 52.5, 52.4, 48.8, 25.2, 22.7, 17.9, 9.5. **IR (thin film):** ν 3481, 2962, 2925, 2854, 1747, 1681, 1647, 1608, 1507, 1455, 1376, 1263, 1209, 1030, 798, 601 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{21}H_{29}N_3NaO_8$ $(M+Na)^+$ 474.1847, found 474.1848.



**7d**

**Methyl (*R*)-2-((*R*)-3-(((*S*)-1-methoxy-1-oxo-3-phenylpropan-2-yl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanamido)butanoate (7d)**

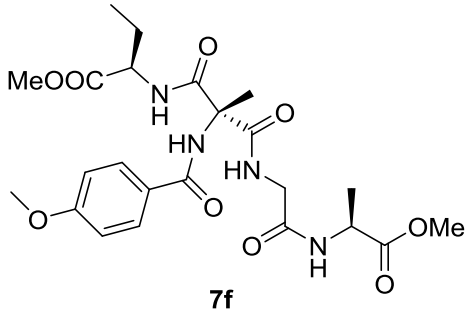
Purification by flash chromatography (petroleum ether/ethyl acetate = 1/1) afforded the product as a colorless oil (83.3 mg, 79% yield). **$[\alpha]^{25}_{D}$** = 29.5 (*c* 1.2, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.86 – 7.80 (m, 2H), 7.78 – 7.75 (m, 1H), 7.40 (d, *J* = 7.1 Hz, 2H), 7.18 – 7.09 (m, 5H), 6.97 – 6.92 (m, 2H), 4.84 (dt, *J* = 7.5, 6.0 Hz, 1H), 4.47 (td, *J* = 7.1, 5.6 Hz, 1H), 3.87 (s, 3H), 3.71 (s, 3H), 3.67 (s, 3H), 3.14 (dd, *J* = 13.7, 6.1 Hz, 1H), 3.09 (dd, *J* = 13.7, 5.6 Hz, 1H), 1.90 (s, 3H), 1.88 – 1.80 (m, 1H), 1.77 – 1.65 (m, 1H), 0.86 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 171.8, 171.2, 169.8, 169.8, 166.2, 162.8, 135.5, 129.2, 129.2, 128.6, 127.1, 125.7, 113.8, 63.3, 55.5, 54.0, 53.8, 52.4, 52.3, 37.7, 25.2, 22.7, 9.5. **IR (thin film):** ν 3374, 3062, 3030, 2954, 2879, 2842, 1747, 1689, 1608, 1516, 1362, 1295, 1258, 1212, 1029, 847, 772, 736, 702, 595 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{27}H_{33}N_3NaO_8$ $(M+Na)^+$ 550.2160, found 550.2163.



7e

**Methyl (*R*)-2-((*S*)-3-((2-((2-methoxy-2-oxoethyl)amino)-2-oxoethyl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanamido)butanoate (7e)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 1/7) afforded the product as a white solid (77.0 mg, 78% yield). **M.p.:** 179.0-179.8 ℃. **[α]$^{25}_{D}$** = -6.6 (*c* 0.7, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.98 (s, 1H), 7.85 – 7.79 (m, 2H), 7.66 – 7.59 (m, 1H), 7.59 – 7.52 (m, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 6.97 – 6.90 (m, 2H), 4.46 (td, *J* = 7.5, 5.2 Hz, 1H), 4.27 (dd, *J* = 17.2, 7.5 Hz, 1H), 4.17 (dd, *J* = 17.7, 6.4 Hz, 1H), 3.93 (dd, *J* = 17.7, 5.4 Hz, 1H), 3.86 (s, 3H), 3.80 (dd, *J* = 17.2, 5.2 Hz, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 1.99 – 1.92 (m, 1H), 1.92 (s, 3H), 1.81 – 1.71 (m, 1H), 0.93 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 171.8, 170.6, 170.2, 169.6, 169.2, 167.2, 163.1, 129.3, 125.0, 113.9, 63.3, 55.5, 54.1, 52.5, 52.1, 43.4, 41.0, 25.0, 22.8, 9.6. **IR (thin film):** ν 3648, 3481, 2955, 2921, 2850, 1747, 1660, 1647, 1607, 1506, 1296, 1259, 1211, 1184, 1082, 1026, 970, 844, 601 cm$^{-1}$. **HRMS (ESI):** calcd. for $C_{22}H_{30}N_4NaO_9$ $(M+Na)^+$ 517.1905, found 517.1904.

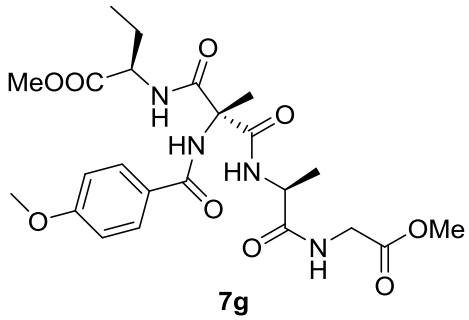


7f

**Methyl (*R*)-2-((*S*)-3-((2-(((*S*)-1-methoxy-1-oxopropan-2-yl)amino)-2-oxoethyl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanamido)butanoate (7f)**

Purification by flash chromatography (ethyl acetate) afforded the product as a white solid (90.2 mg, 89% yield). **M.p.:** 152.5-153.5 ℃. **[α]$^{25}_{D}$** = 20.7 (*c* 0.8, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.98 (s, 1H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.28 (s, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 4.59 – 4.50 (m, 1H), 4.47 (td, *J* = 7.5, 5.4 Hz, 1H), 4.39 (dd, *J* = 17.2, 8.0 Hz, 1H), 3.87 (s, 3H), 3.74 (s, 3H), 3.68 (s, 3H), 3.64 (dd, *J* = 17.4, 4.8 Hz, 1H), 2.00 – 1.93 (m, 1H), 1.92 (s, 3H), 1.83 – 1.71 (m, 1H), 1.52 (d, *J* = 7.3 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 173.5, 171.7, 170.3, 169.6, 168.6, 167.0, 163.1, 129.4, 125.1, 114.0, 63.3, 55.5, 54.1, 52.5, 52.3, 48.2, 43.3, 25.0, 22.8, 17.2, 9.6. **IR (thin film):** ν 3314, 3062, 2955, 2924, 2851, 1743, 1646, 1607, 1538, 1505, 1376, 1259, 1211, 1161,

1109, 1025, 849, 798, 736, 602 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{23}H_{32}N_4NaO_9$ $(M+Na)^+$ 531.2061, found 531.2068.

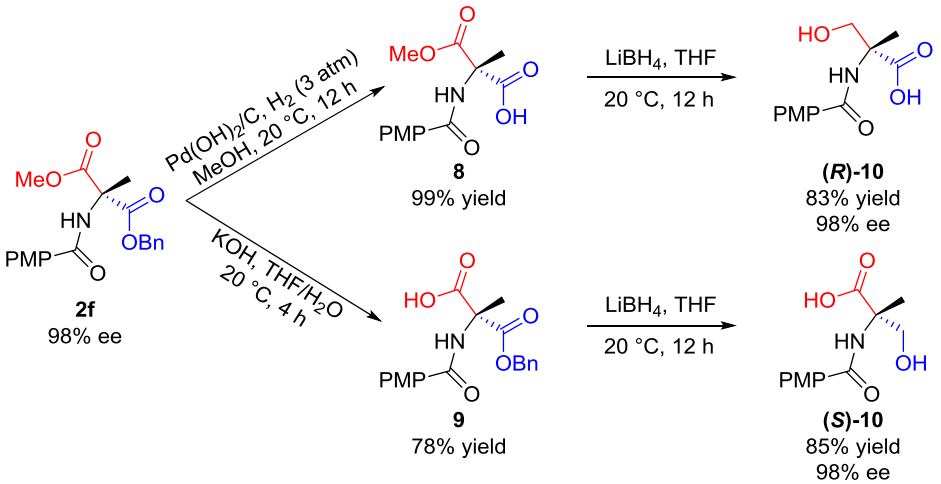


**7g**

**Methyl (*R*)-2-((*S*)-3-(((*S*)-1-((2-methoxy-2-oxoethyl)amino)-1-oxopropan-2-yl)amino)-2-(4-methoxybenzamido)-2-methyl-3-oxopropanamido)butanoate (7g)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 1/20) afforded the product as a colorless oil (79.6 mg, 78% yield). **$[\alpha]^{25}_D$** = -5.3 (*c* 0.3, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.87 – 7.81 (m, 2H), 7.76 (s, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 7.07 – 7.02 (m, 1H), 6.98 – 6.92 (m, 2H), 4.57 – 4.49 (m, 1H), 4.47 (td, *J* = 7.6, 5.0 Hz, 1H), 4.07 (dd, *J* = 17.9, 5.8 Hz, 1H), 3.96 (dd, *J* = 17.9, 5.5 Hz, 1H), 3.87 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H), 1.98 – 1.89 (m, 1H), 1.93 (s, 3H), 1.80 – 1.72 (m, 1H), 1.41 (d, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 172.4, 171.8, 170.5, 170.4, 169.8, 166.4, 162.9, 129.2, 125.4, 114.0, 63.4, 55.5, 54.1, 52.4, 52.2, 49.7, 41.2, 24.8, 22.7, 17.1, 9.8. **IR (thin film):** ν 3840, 3740, 3352, 2954, 2925, 2854, 1744, 1659, 1607, 1506, 1458, 1376, 1259, 1209, 1181, 1098, 1026, 848, 795, 701, 594 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{23}H_{32}N_4NaO_9$ $(M+Na)^+$ 531.2061, found 531.2061.

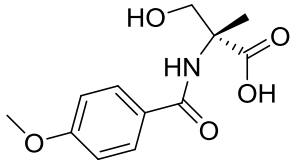
**Synthesis of α-Alkyl Serine:**




Substrate **2f** (0.41 mmol, 151 mg) and $Pd(OH)_2/C$ (100 mg) were charged in an autoclave. The system was evacuated and filled with hydrogen. Then anhydrous MeOH (2 mL) was added and the hydrogen pressure was adjusted to 3 atm. After vigorous stirring at 20 ℃ for 12 h, the reaction mixture was filtered and evaporated

under reduced pressure to give **8** (113 mg, 99% yield). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.77 (d, *J* = 8.7 Hz, 2H), 7.62 (s, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 1.84 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 171.1, 170.1, 166.8, 162.8, 129.2, 124.9, 113.8, 63.2, 55.4, 53.6, 21.1.

**8** (0.4 mmol, 113 mg) was dissolved in anhydrous THF (5 mL) in a dry two-necked flask at 20 ℃, $LiBH_4$ (2 M solution in THF, 0.6 mmol, 0.3 mL) was then added dropwise. The reaction mixture was stirred at 20 ℃ for 12 h. The solvent was acidized with 0.1 M HCl (8 mL) and extracted with EtOAc (10 mL × 4). The crude product was purified by flash chromatography on silica gel to give **(*R*)-10**.



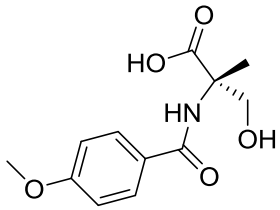
**(*R*)-10**

**(*R*)-3-Hydroxy-2-(4-methoxybenzamido)-2-methylpropanoic acid ((*R*)-10)**

Purification by flash chromatography (ethyl acetate/methanol = 5/1, added 0.5% AcOH) afforded the product as a white solid (71.2 mg, 83% yield). **M.p.:** 49.5-50.5 ℃. **HPLC analysis:** 98% ee [Daicel CHIRALPAK AS-H column; solvent system: 5% ethanol/95% hexane, added 0.5% AcOH; 0.5 mL/min; retention times: 46.7 min (minor), 52.1 min (major)]. **$[\alpha]^{25}_D$** = -0.6 (*c* 0.3, MeOH). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.74 (d, *J* = 8.7 Hz, 2H), 7.28 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.77 (brs, 1H), 4.05 – 3.95 (m, 2H), 3.81 (s, 3H), 1.60 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 175.4, 168.7, 162.7, 129.2, 125.5, 113.8, 66.2, 62.0, 55.4, 19.7. **IR (thin film):** ν 3411, 2955, 2917, 2849, 1715, 1640, 1608, 1540, 1504, 1463, 1305, 1259, 1180, 1120, 1052, 1030, 845, 769, 599 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{12}H_{15}NNaO_5$ $(M+Na)^+$ 276.0842, found 276.0847.

Substrate **2f** (0.43 mmol, 160 mg) was dissolved in THF (5 mL) in two-necked flask at 20 ℃. KOH (0.43 mmol, 24.1 mg) was dissolved in $H_2O$ (5 mL) and added dropwise into the flask. The reaction mixture was stirred at 20 ℃ for 4 h. The solvent was acidized with 0.1 M HCl to PH < 6 and extracted with EtOAc (10 mL × 4). The crude product was purified by flash chromatography on silica gel (ethyl acetate/methanol = 10/1, added 0.5% AcOH) to give **9** (120.5 mg, 78% yield). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.75 (d, *J* = 8.7 Hz, 2H), 7.47 (s, 1H), 7.29 (s, 5H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.24 (s, 2H), 3.83 (s, 3H), 1.86 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 170.9, 169.5, 167.0, 162.8, 134.8, 129.2, 128.5, 128.4, 128.0, 124.8, 113.9, 68.3, 63.4, 55.4, 21.2.

**9** (0.2 mmol, 71.5 mg) was dissolved in anhydrous THF (3 mL) in a dry two-necked flask at 20 ℃, $LiBH_4$ (2M solution in THF, 0.3 mmol, 0.15 mL) was then added dropwise. The reaction mixture was stirred at 20 ℃ for 12 h. The solvent was acidized with 0.1 M HCl (5 mL) and extracted with EtOAc (6 mL × 4). The crude product was purified by flash chromatography on silica gel to give **(*S*)-10**.

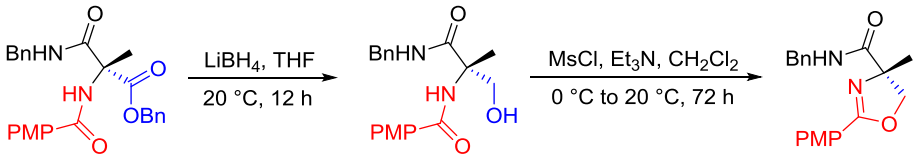


**(*S*)-10**

**(*S*)-3-Hydroxy-2-(4-methoxybenzamido)-2-methylpropanoic acid ((*S*)-10)**

Purification by flash chromatography (ethyl acetate/methanol = 5/1, added 0.5% AcOH) afforded the product as a white solid (43.1 mg, 85% yield). **M.p.:** 49.5-50.5 ℃. **HPLC analysis:** 98% ee [Daicel CHIRALPAK AS-H column; solvent system: 5% ethanol/95% hexane, added 0.5% AcOH; 0.5 mL/min; retention times: 46.1 min (major), 53.9 min (minor)]. **$[\alpha]^{25}_{D}$** = 0.7 (*c* 0.3, MeOH). **$^{1}$H NMR ($CDCl_3$, 400 MHz):** δ 7.74 (d, *J* = 8.7 Hz, 2H), 7.28 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.77 (brs, 1H), 4.05 – 3.95 (m, 2H), 3.81 (s, 3H), 1.60 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 175.4, 168.7, 162.7, 129.2, 125.5, 113.8, 66.2, 62.0, 55.4, 19.7. **HRMS (ESI):** calcd. for $C_{12}H_{15}NNaO_5$ $(M+Na)^+$ 276.0842, found 276.0847.

**Synthesis of Substituted 2-Oxazolines:**



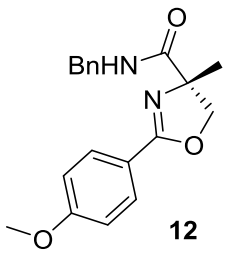

**2a**
99% ee

**11**
79% yield

**12**
94% yield
98% ee

Under a $N_2$ atmosphere, the compound **2a** (0.35 mmol, 156.3 mg) was dissolved in anhydrous THF (6 mL) in a dry two-necked flask at 20 ℃. $LiBH_4$ (2 M solution in THF, 0.53 mmol, 0.26 mL) was then added dropwise. The reaction mixture was stirred at 20 ℃ for 12 h. The solvent was acidized with 0.1 M HCl (6 mL) and extracted with EtOAc (10 mL × 4). The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 1/2, added 0.5% AcOH) to give **11** (94.6 mg, 79% yield). **$^{1}$H NMR ($CDCl_3$, 400 MHz):** δ 8.11 – 8.04 (m, 1H), 7.78 – 7.72 (m, 2H), 7.35 – 7.28 (m, 3H), 7.28 – 7.23 (m, 2H), 6.96 – 6.89 (m, 2H), 4.53 – 4.42 (m, 2H), 4.28 – 4.20 (m, 1H), 3.86 (s, 3H), 3.68 – 3.61 (m, 1H), 1.69 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 173.9, 168.2, 162.6, 138.0, 129.0, 128.7, 127.4, 127.3, 126.3, 113.9, 67.7, 61.1, 55.5, 43.5, 20.2. **HRMS (ESI):** calcd. for $C_{19}H_{23}N_2O_4$ $(M+H)^+$ 343.1652, found 343.1649.

Under a $N_2$ atmosphere, the compound **11** (0.16 mmol, 55.0 mg) and $Et_3N$ (0.4 mmol, 56 μL) was dissolved in DCM (10 mL) in a dry two-necked flask and cooled to 0 ℃. MsCl (0.4 mmol, 31 μL) was added dropwise at 0 ℃. Then the ice bath was removed, and the mixture was stirred at 20 ℃ for 72 hours. The solvent was acidized with 0.1 M HCl (5 mL) and extracted with EtOAc (8 mL × 4). The combined organic phases were dried over $Na_2SO_4$. After filtration, the residue was purified by column chromatography to give **12**.




12

**(*S*)-*N*-Benzyl-2-(4-methoxyphenyl)-4-methyl-4,5-dihydrooxazole-4-carboxamide (12)**

Purification by flash chromatography (petroleum ether/ethyl acetate = 2/1) afforded the product as a white oil (49.2 mg, 94% yield). **HPLC analysis:** 98% ee [Daicel CHIRALPAK AS-H column; solvent system: 20% isopropanol/80% hexane; 0.5 mL/min; retention times: 15.9 min (minor), 20.2 min (major)]. **$[\alpha]^{25}_{D}$** = -15.8 (*c* 1.0, $CH_2Cl_2$). **$^1$H NMR ($CDCl_3$, 400 MHz):** δ 7.88 (d, *J* = 8.9 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 3H), 7.18 – 7.09 (m, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.67 (d, *J* = 8.9 Hz, 1H), 4.57 (dd, *J* = 14.9, 6.5 Hz, 1H), 4.37 (dd, *J* = 15.0, 5.5 Hz, 1H), 4.27 (d, *J* = 8.9 Hz, 1H), 3.85 (s, 3H), 1.61 (s, 3H). **$^{13}$C NMR ($CDCl_3$, 100 MHz):** δ 175.1, 164.4, 162.5, 138.1, 130.2, 128.7, 127.6, 127.4, 119.6, 113.8, 76.5, 74.6, 55.4, 43.0, 26.7. **IR (thin film):** ν 3840, 3739, 3648, 3393, 3064, 3031, 2960, 2928, 2867, 1724, 1668, 1641, 1610, 1579, 1512, 1455, 1423, 1354, 1307, 1258, 1171, 1076, 1029, 841, 745, 699, 685 $cm^{-1}$. **HRMS (ESI):** calcd. for $C_{19}H_{21}N_2O_3$ $(M+H)^+$ 325.1547, found 325.1543.

# 8. Reference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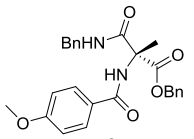
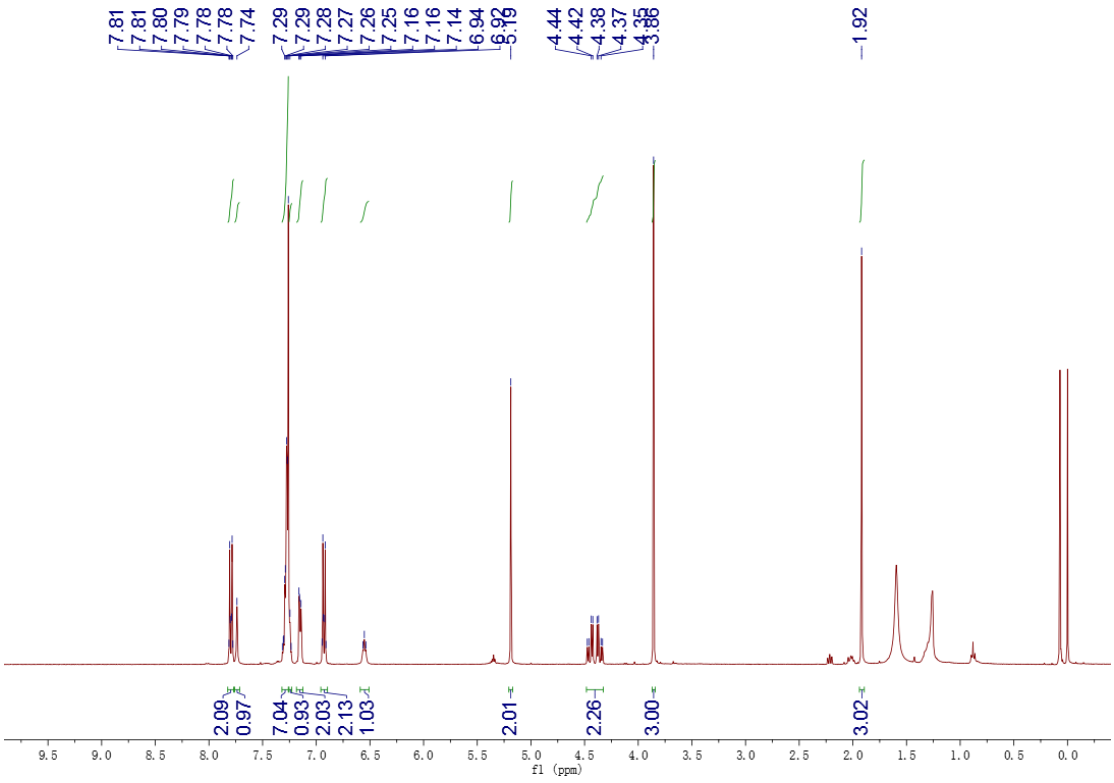
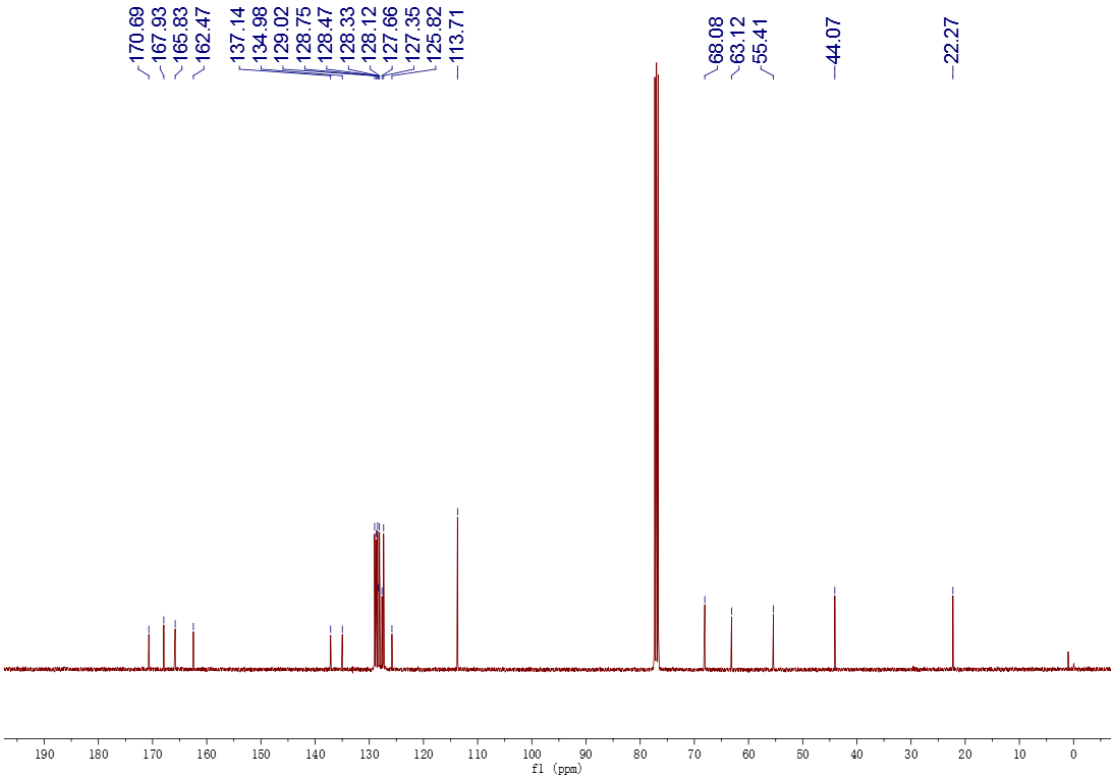
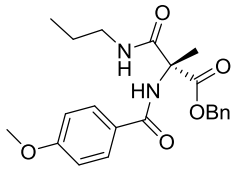
# 9. NMR Spectra



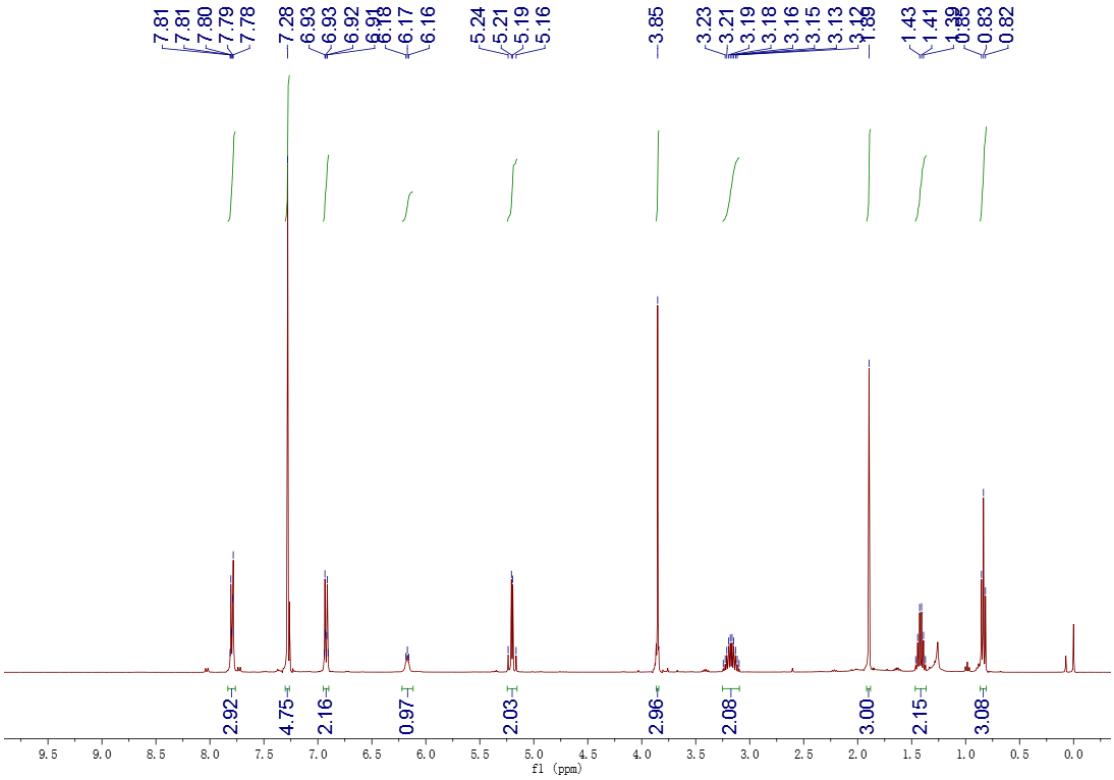

**2a**




O
N
H
HN
O
OBn
O
O

**2b**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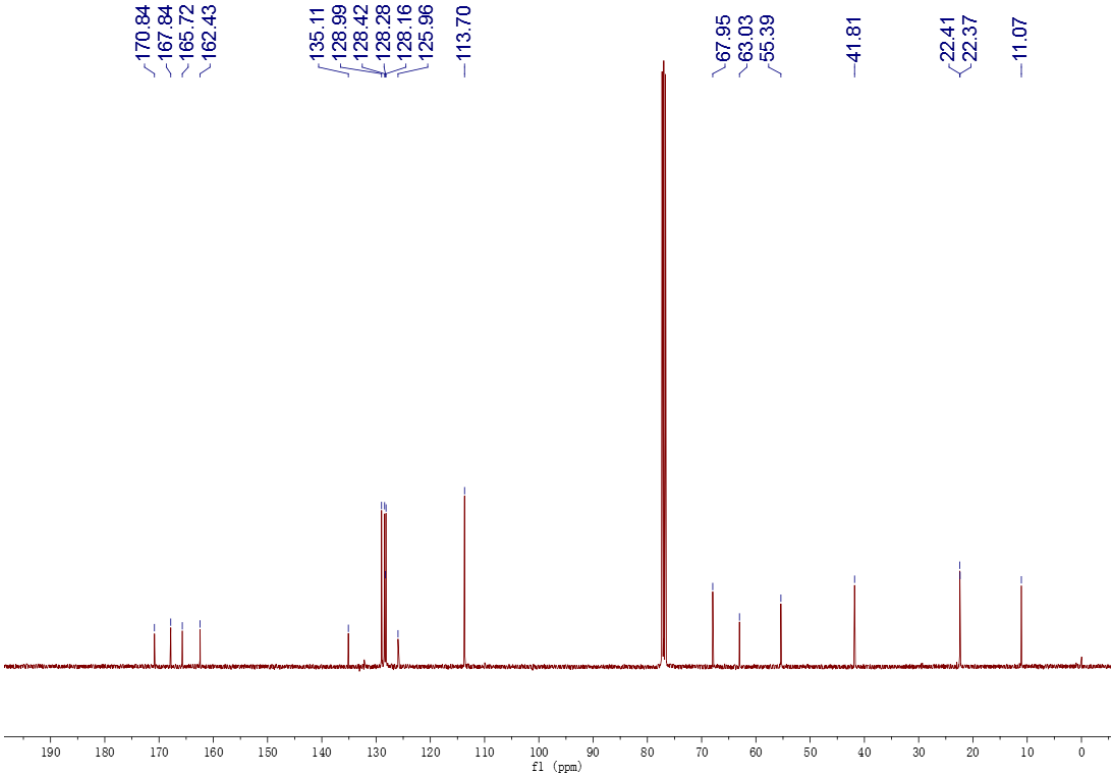
7.79
7.78
7.28
6.93
6.93
6.92
6.17
6.16
5.24
5.21
5.19
5.16
3.85
3.23
3.21
3.19
3.18
3.16
3.15
3.13
1.43
1.41
0.83
0.82
2.92
4.75
2.16
0.97
2.03
2.96
2.08
3.00
2.15
3.08
f1 (ppm)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167.84
165.72
162.43
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128.99
128.42
128.28
128.16
125.96
113.70
67.95
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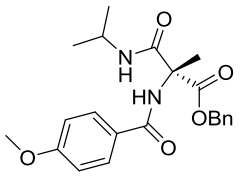
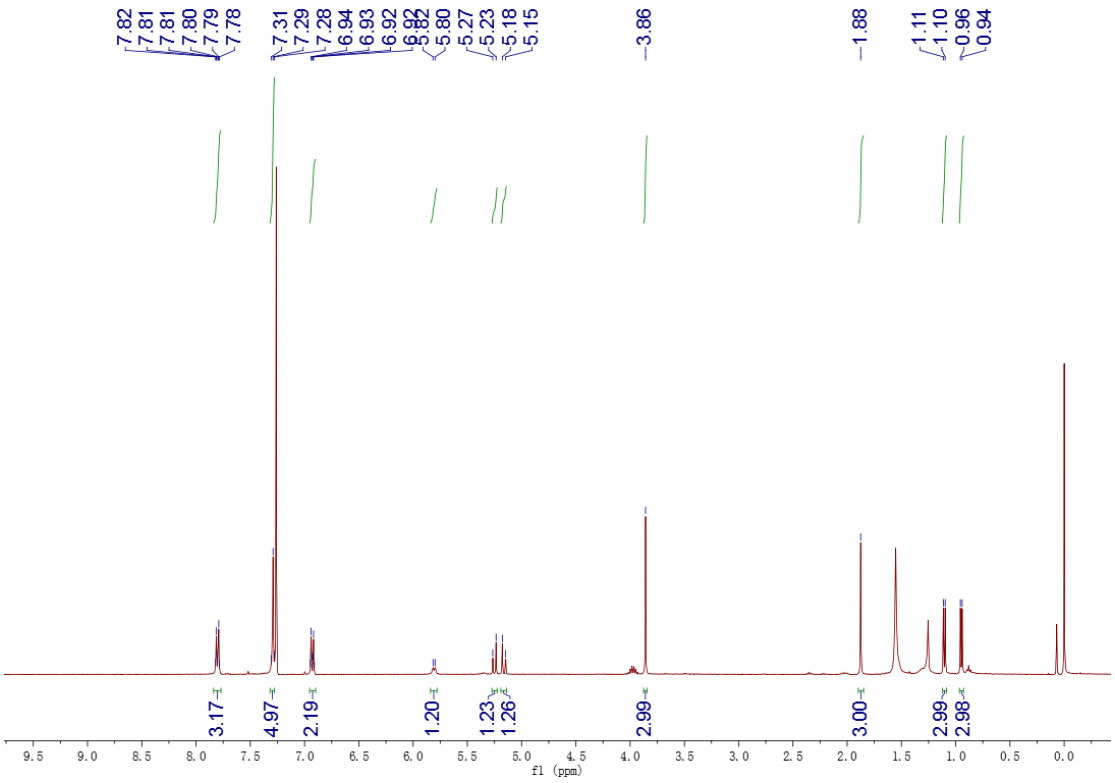
41.81
22.41
22.37
11.07
f1 (ppm)



**2c**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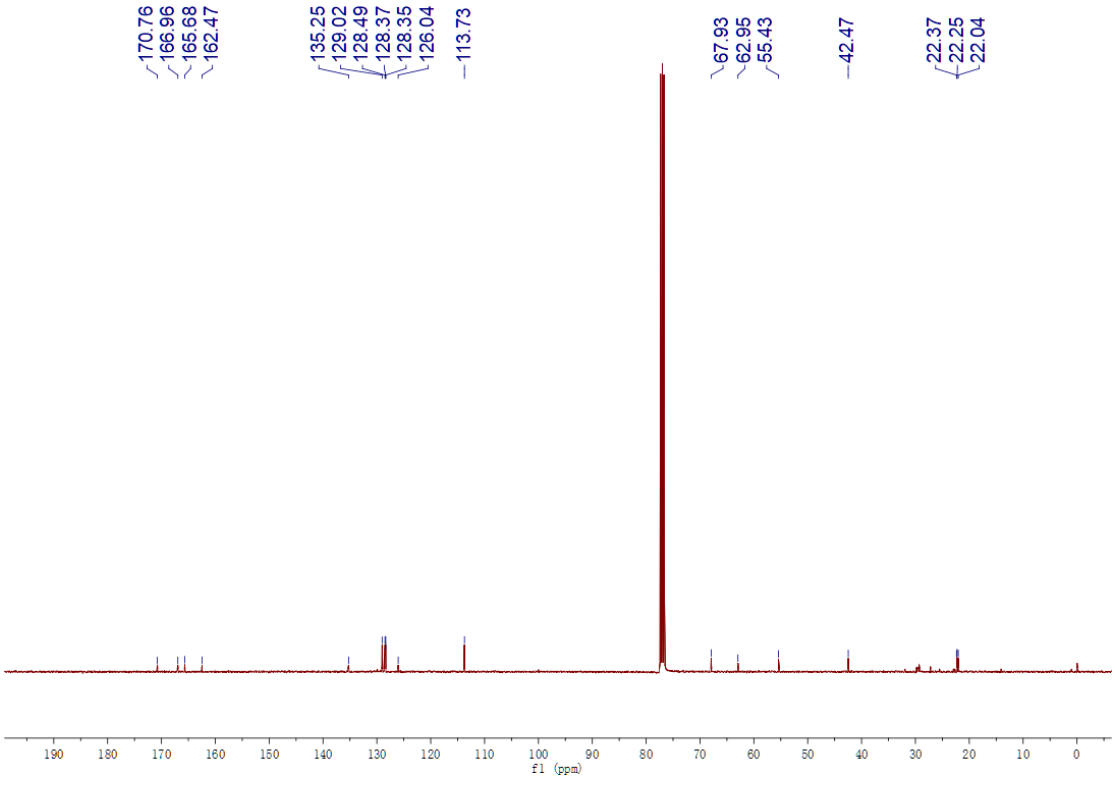
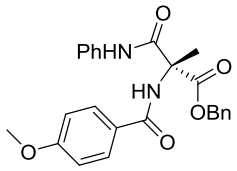
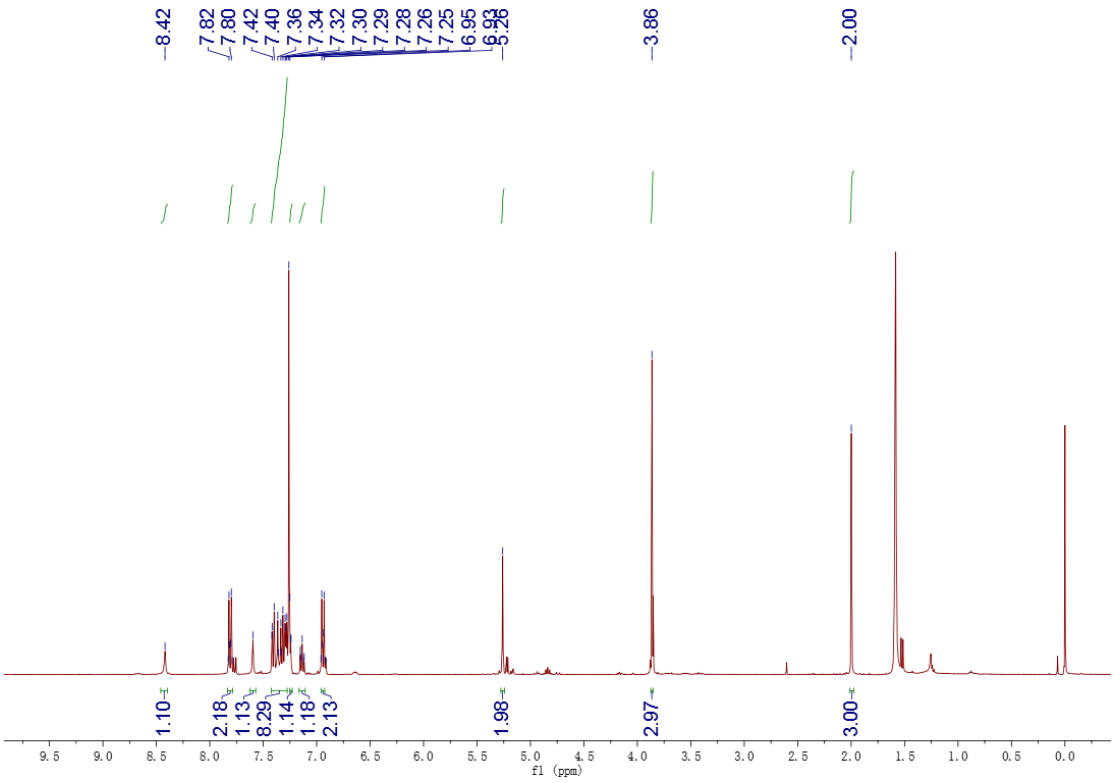
7.81
7.81
7.80
7.79
7.78
7.31
7.29
7.28
6.94
6.93
6.92
5.82
5.80
5.27
5.23
5.18
5.15
3.86
1.88
1.11
1.10
0.96
0.94
3.17
4.97
2.19
1.20
1.23
1.26
2.99
3.00
2.99
2.98
f1 (ppm)


170.76
166.96
165.68
162.47
135.25
129.02
128.49
128.37
128.35
126.04
113.73
67.93
62.95
55.43
42.47
22.37
22.25
22.04
f1 (ppm)


O
PhHN
HN
O
OBn
O
O

**2d**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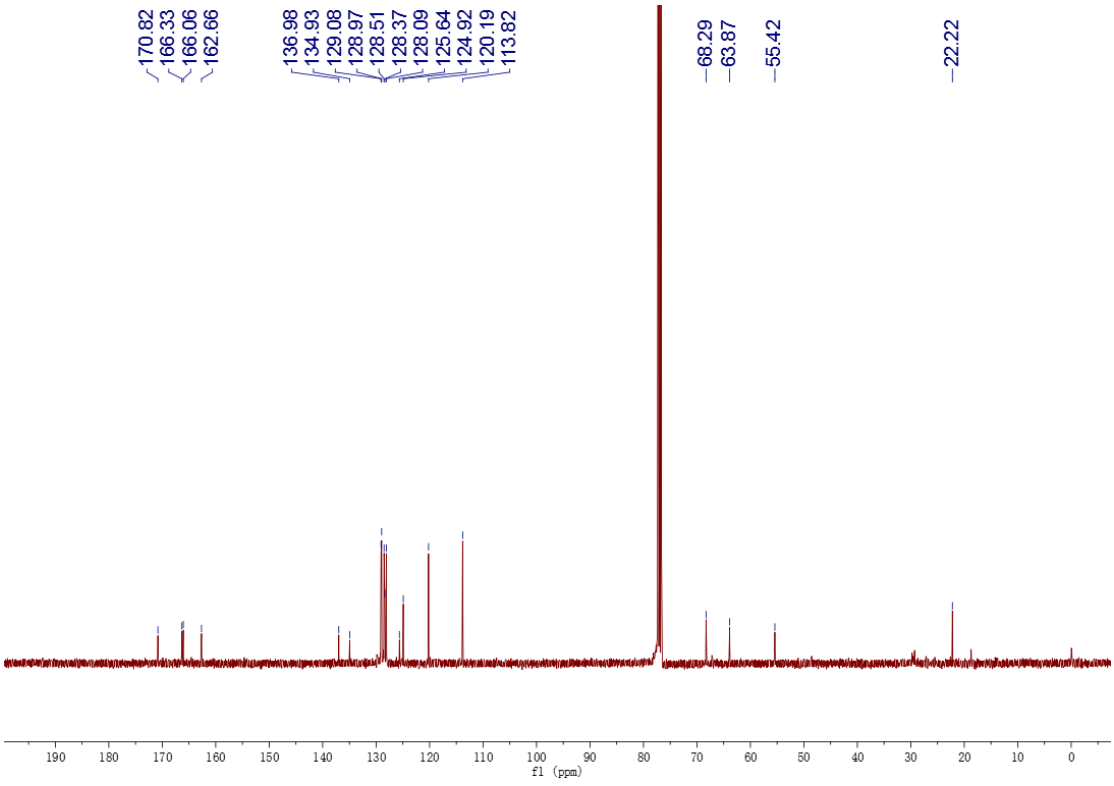
7.42
7.40
7.36
7.34
7.32
7.30
7.29
7.28
7.26
7.25
6.95
6.93
3.86
2.00
1.10
2.18
1.13
8.29
1.14
1.18
2.13
1.98
2.97
3.00
f1 (ppm)


170.82
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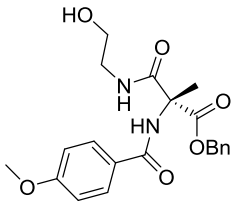
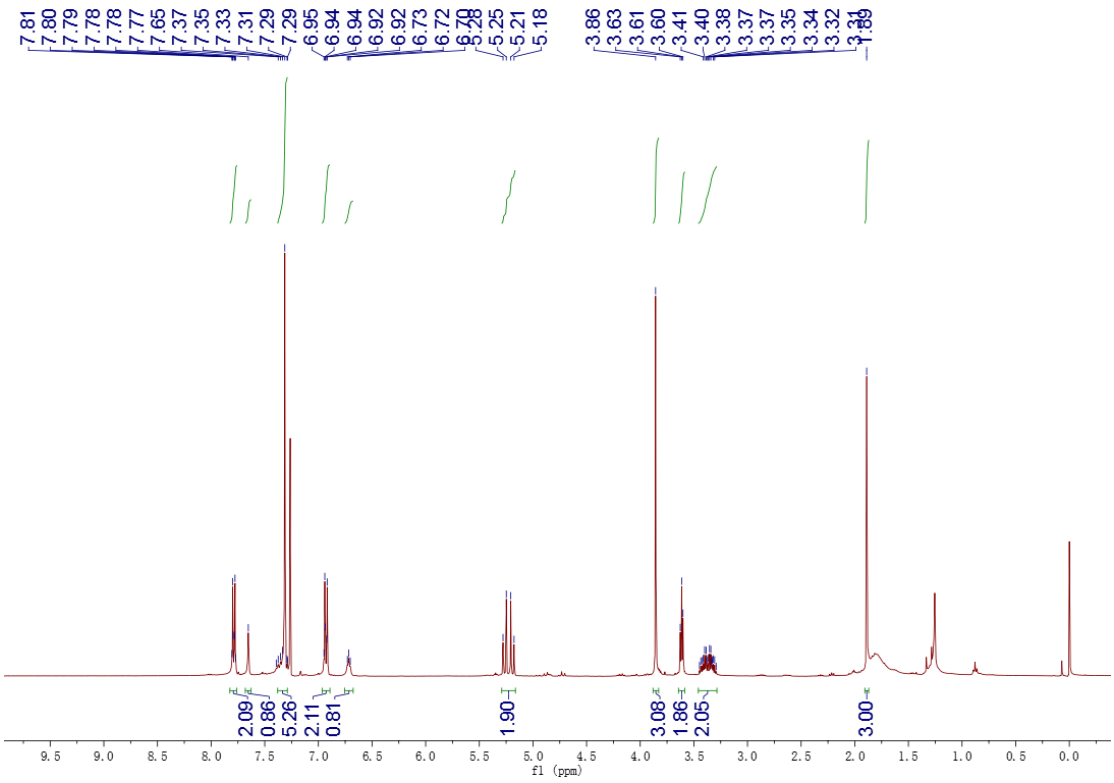
166.06
162.66
136.98
134.93
129.08
128.97
128.51
128.37
128.09
125.64
124.92
120.19
113.82
68.29
63.87
55.42
22.22
f1 (ppm)


HO
O
N
H
HN
O
OBn
O
O

**2e**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7.80
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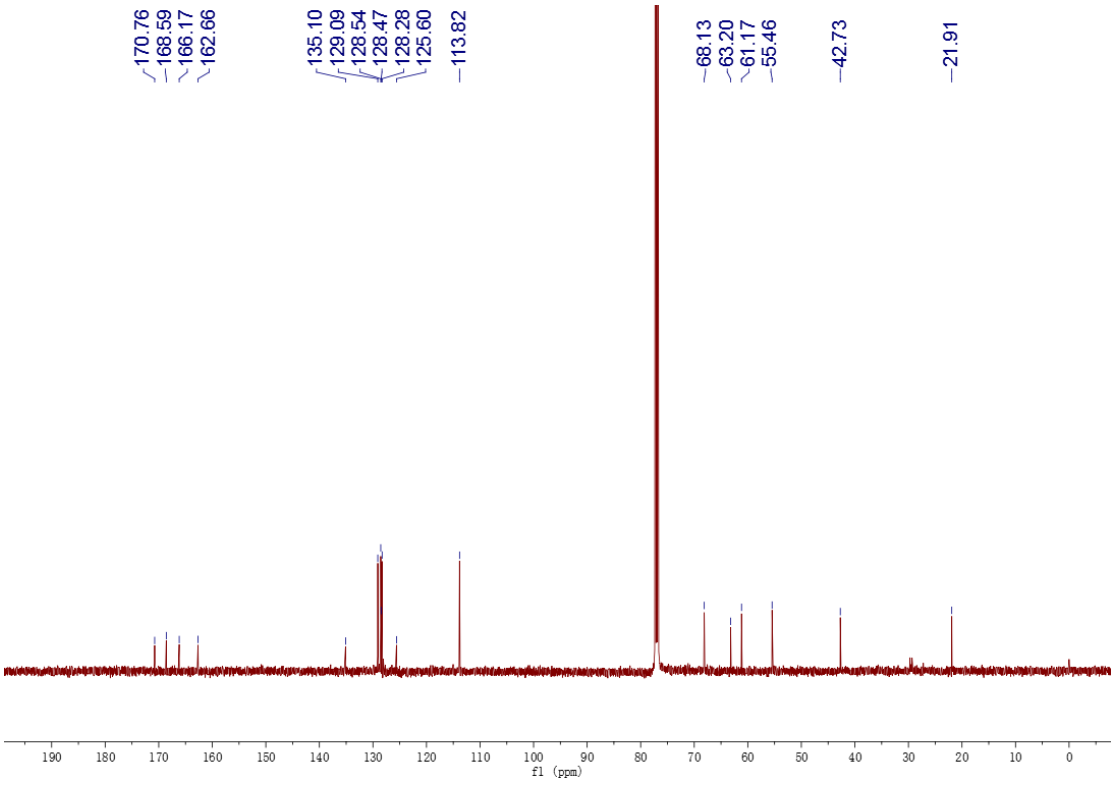
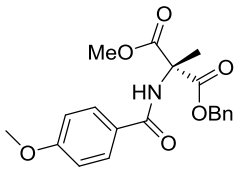
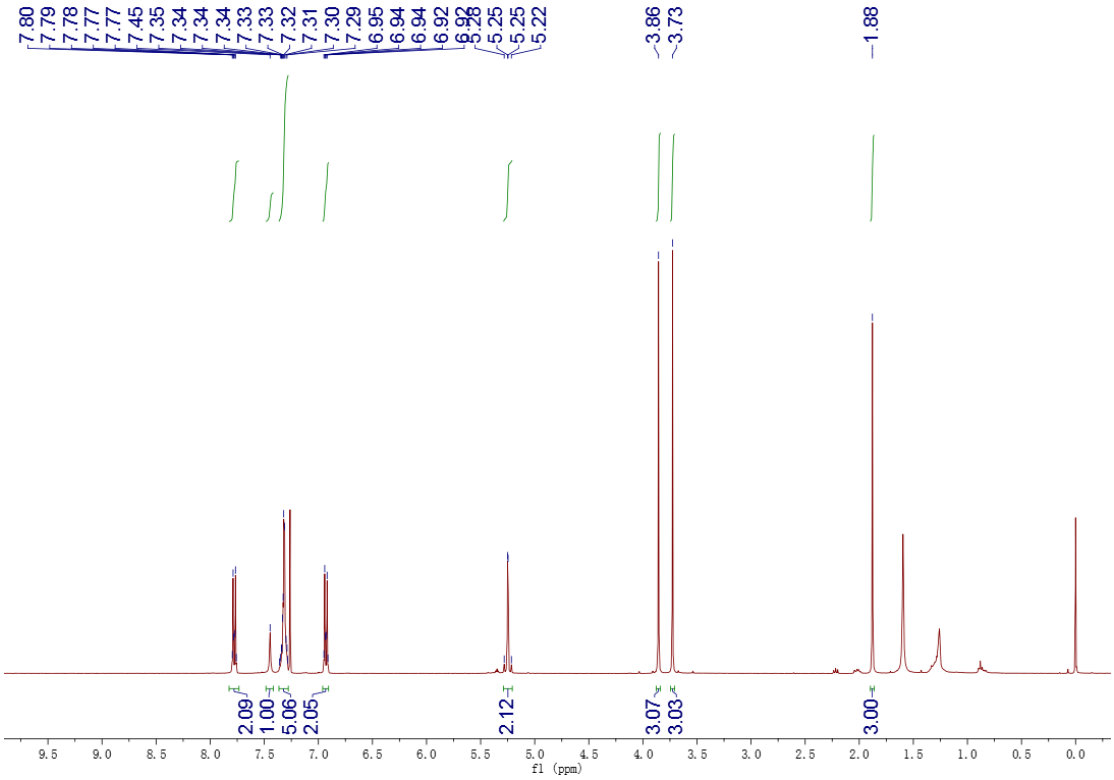
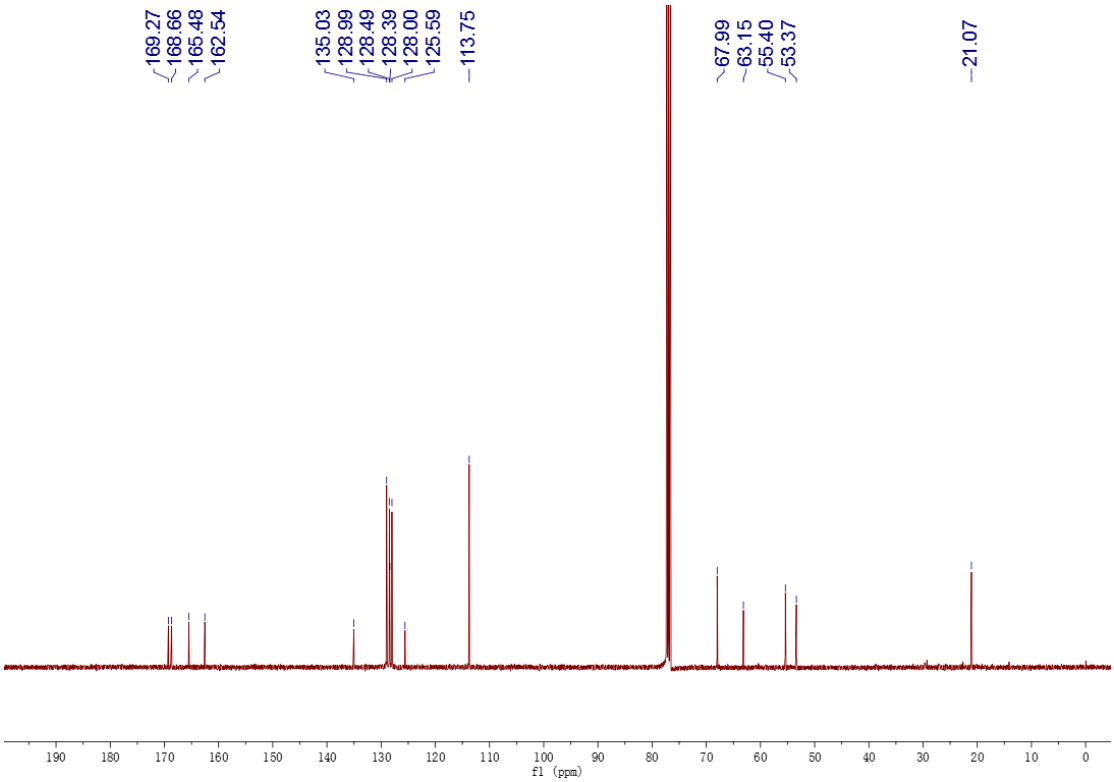
7.78
7.77
7.65
7.37
7.35
7.33
7.31
7.29
7.29
6.95
6.94
6.94
6.92
6.92
6.73
6.72
6.70
5.28
5.25
5.21
5.18
3.86
3.63
3.61
3.60
3.41
3.40
3.38
3.37
3.37
3.35
3.34
3.32
3.31
1.89
2.09
0.86
5.26
2.11
0.81
1.90
3.08
1.86
2.05
3.00
f1 (ppm)

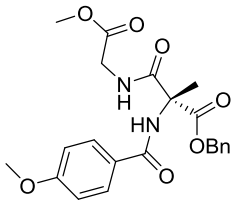

170.76
168.59
166.17
162.66
135.10
129.09
128.54
128.47
128.28
125.60
113.82
68.13
63.20
61.17
55.46
42.73
21.91
f1 (ppm)


O
MeO
O
HN
O
OBn
O

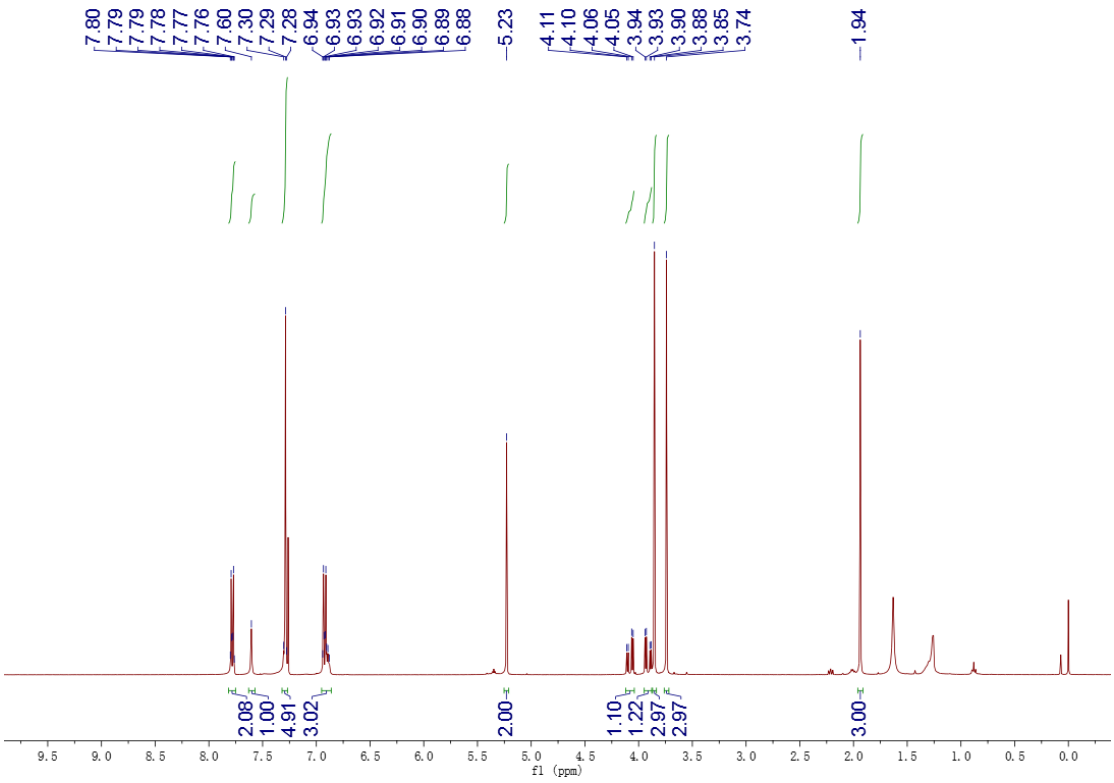
**2f**


7.80
7.79
7.78
7.77
7.77
7.45
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.31
7.30
7.29
6.95
6.94
6.94
6.92
6.92
5.28
5.25
5.25
5.22
3.86
3.73
1.88
2.09
1.00
5.06
2.05
2.12
3.07
3.03
3.00
f1 (ppm)


169.27
168.66
165.48
162.54
135.03
128.99
128.49
128.39
128.00
125.59
113.75
67.99
63.15
55.40
53.37
21.07
f1 (ppm)



**2g**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7.79
7.79
7.78
7.77
7.76
7.60
7.30
7.29
7.28
6.94
6.93
6.93
6.92
6.91
6.90
6.89
6.88
5.23
4.11
4.10
4.06
4.05
3.94
3.93
3.90
3.88
3.85
3.74
1.94
2.08
1.00
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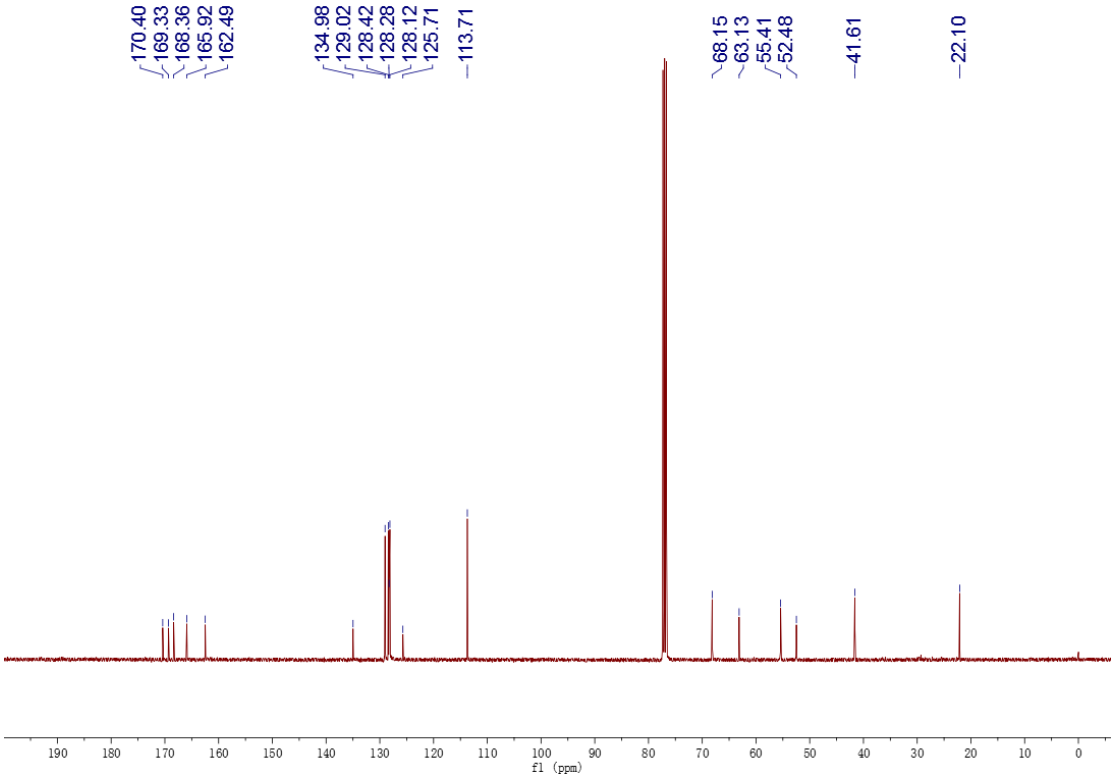
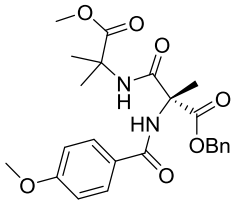
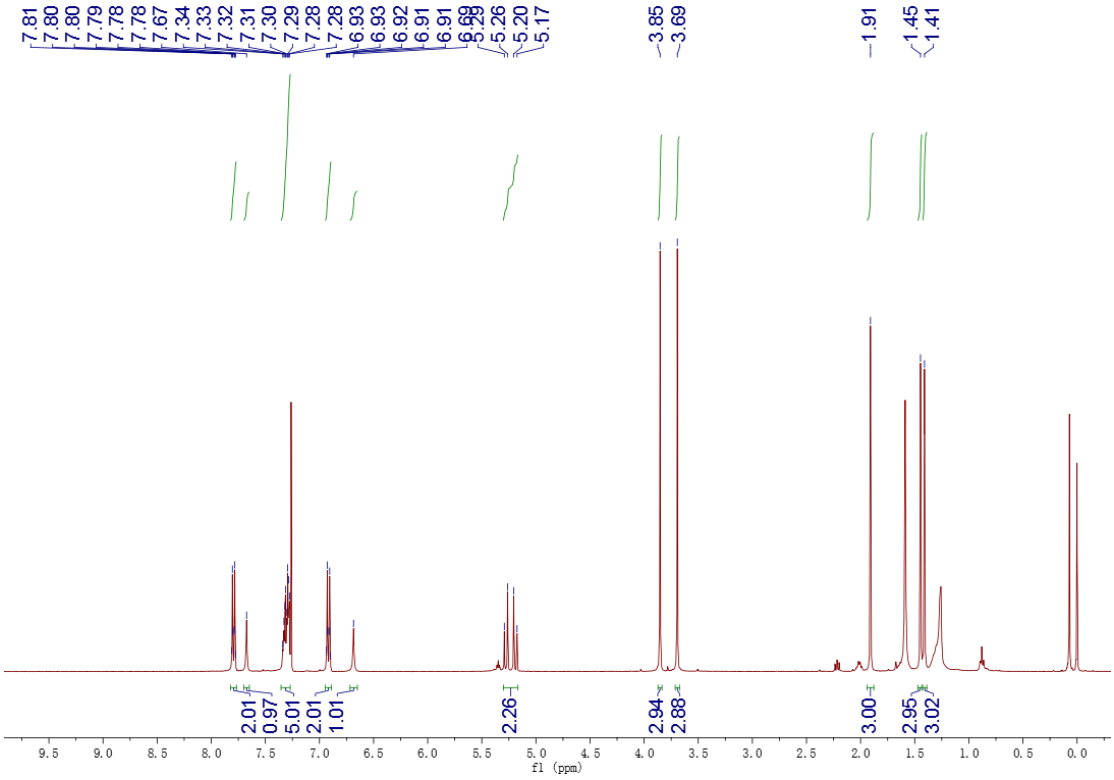
1.22
2.97
2.97
3.00
f1 (ppm)


170.40
169.33
168.36
165.92
162.49
134.98
129.02
128.42
128.28
128.12
125.71
113.71
68.15
63.13
55.41
52.48
41.61
22.10
f1 (ppm)



**2h**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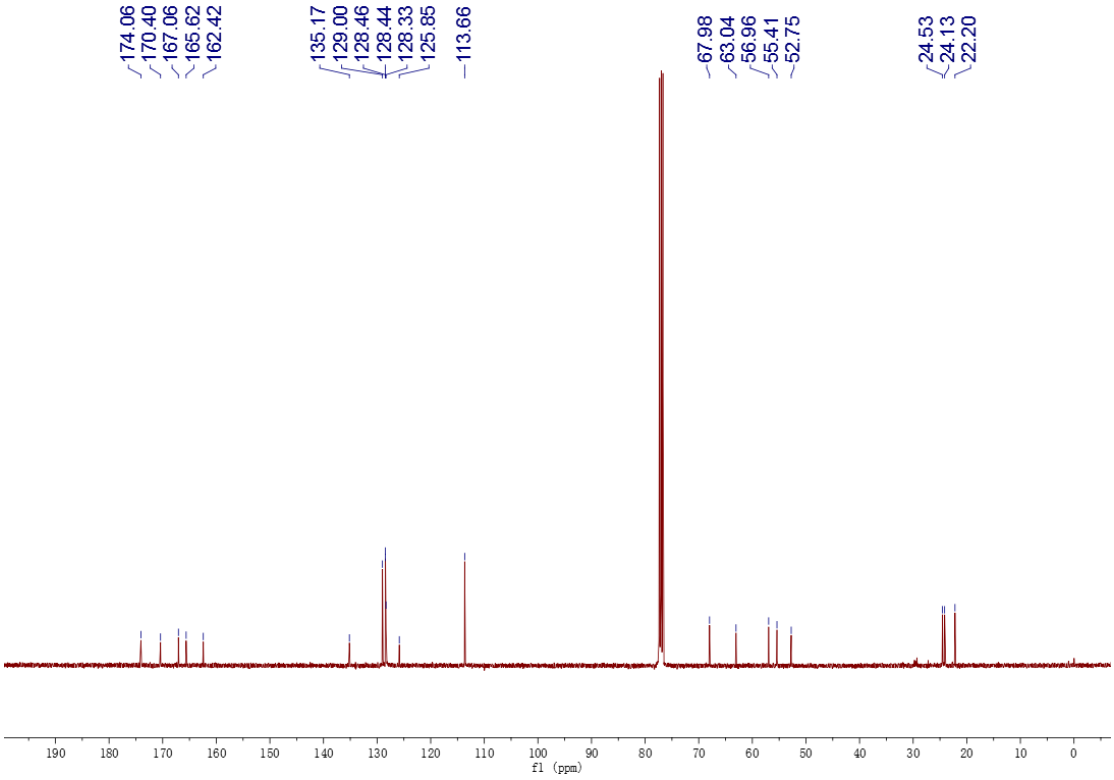
7.80
7.79
7.78
7.78
7.67
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.28
6.93
6.93
6.92
6.91
6.91
5.26
5.20
5.17
3.85
3.69
1.91
1.45
1.41
2.01
0.97
5.01
2.01
1.01
2.26
2.94
2.88
3.00
2.95
3.02
f1 (ppm)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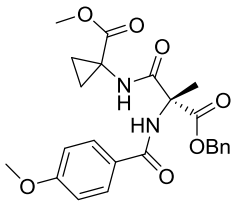
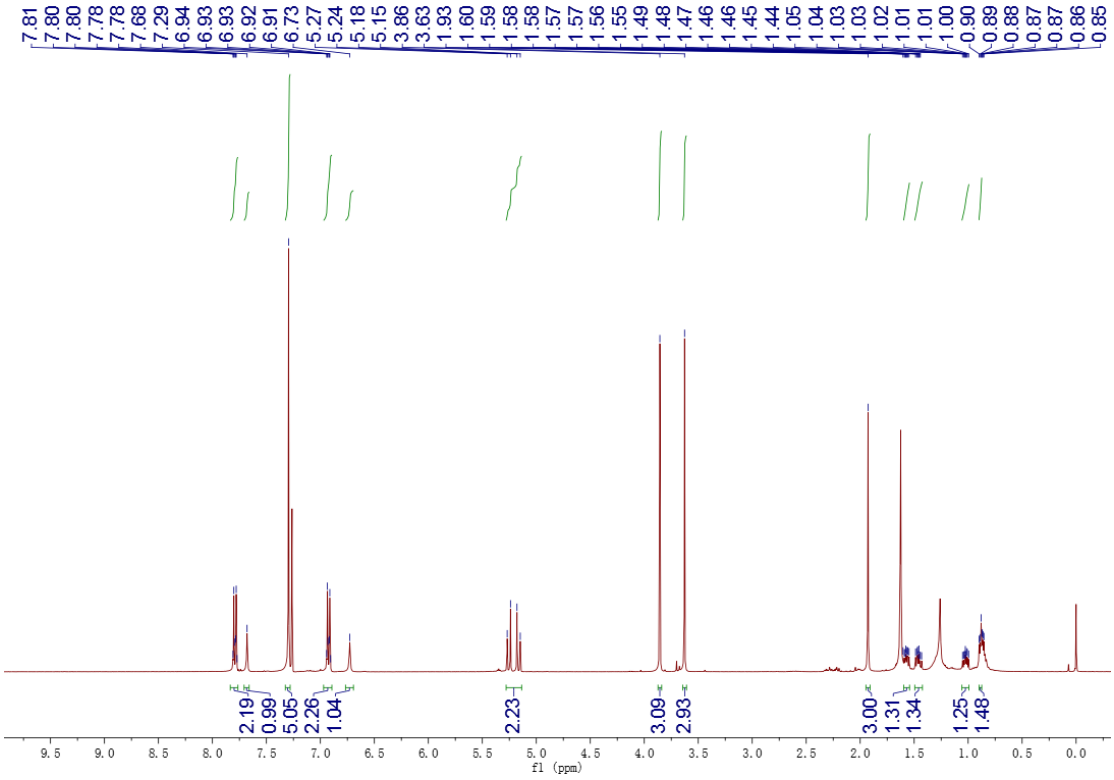
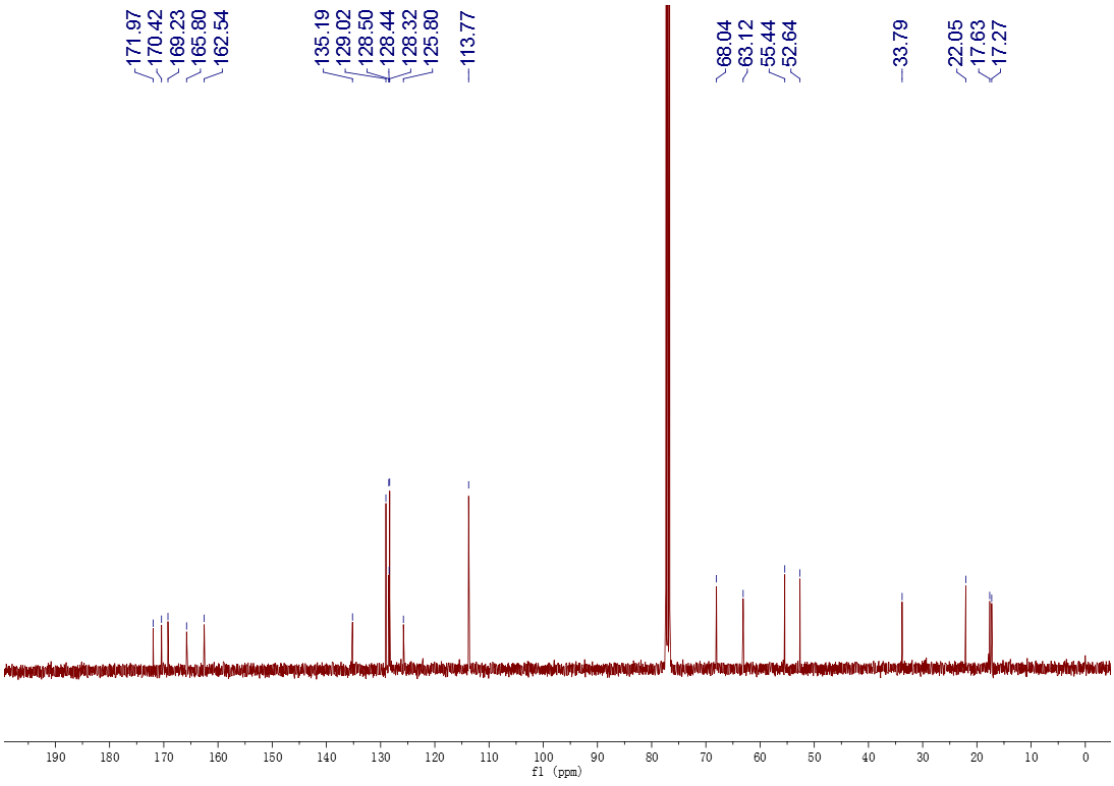
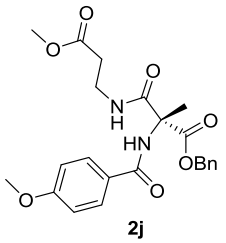
167.06
165.62
162.42
135.17
129.00
128.46
128.44
128.33
125.85
113.66
67.98
63.04
56.96
55.41
52.75
24.53
24.13
22.20
f1 (ppm)



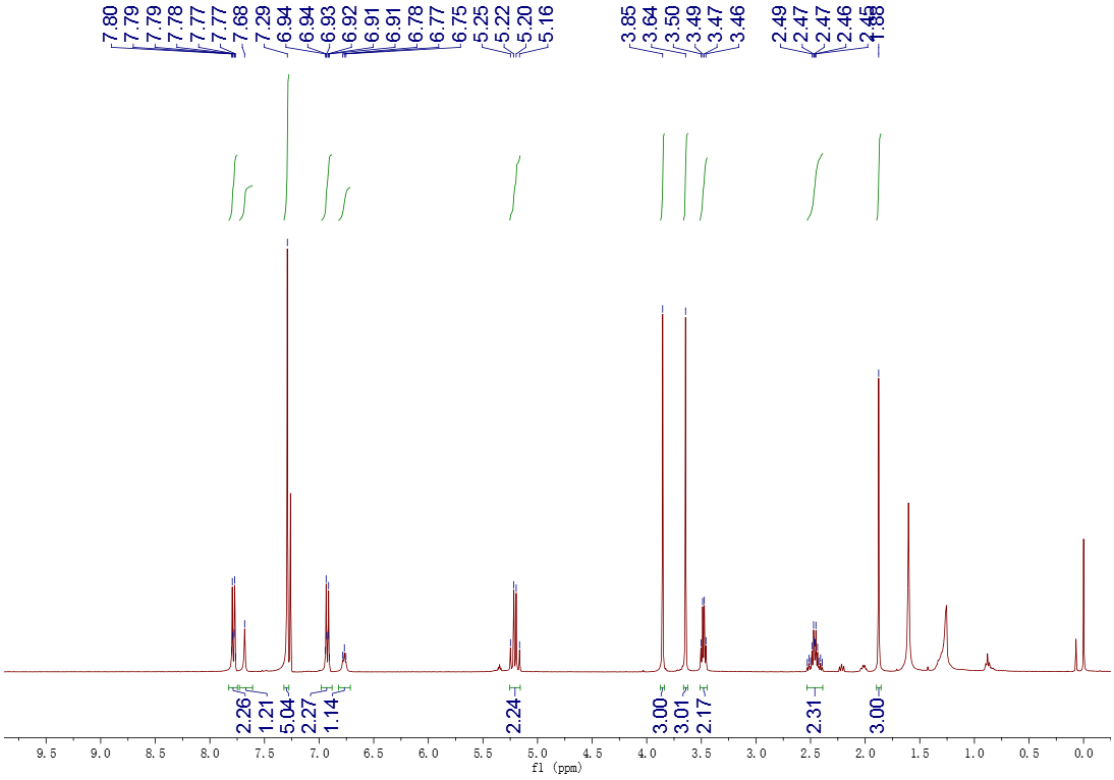
**2i**


7.81 7.80 7.80 7.78 7.78 7.68 7.29 6.94 6.93 6.93 6.92 6.91 6.73 5.27 5.24 5.18 5.15 3.86 3.63 1.93 1.60 1.59 1.58 1.58 1.57 1.57 1.56 1.55 1.49 1.48 1.47 1.46 1.46 1.45 1.44 1.05 1.04 1.03 1.03 1.02 1.01 1.01 1.00 0.90 0.89 0.88 0.87 0.87 0.86 0.85
2.19 0.99 5.05 2.26 1.04 2.23 3.09 2.93 3.00 1.31 1.34 1.25 1.48
f1 (ppm)


171.97 170.42 169.23 165.80 162.54 135.19 129.02 128.50 128.44 128.32 125.80 113.77 68.04 63.12 55.44 52.64 33.79 22.05 17.63 17.27
f1 (ppm)



**2j**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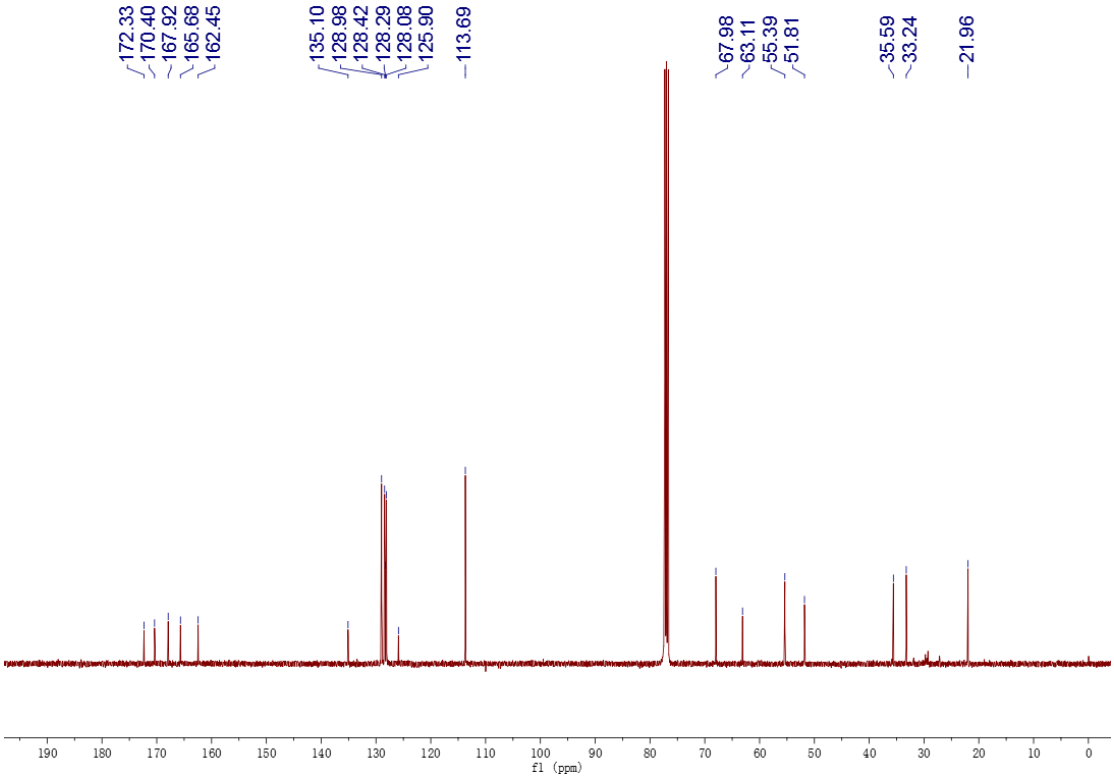
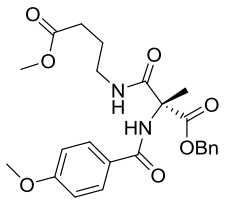
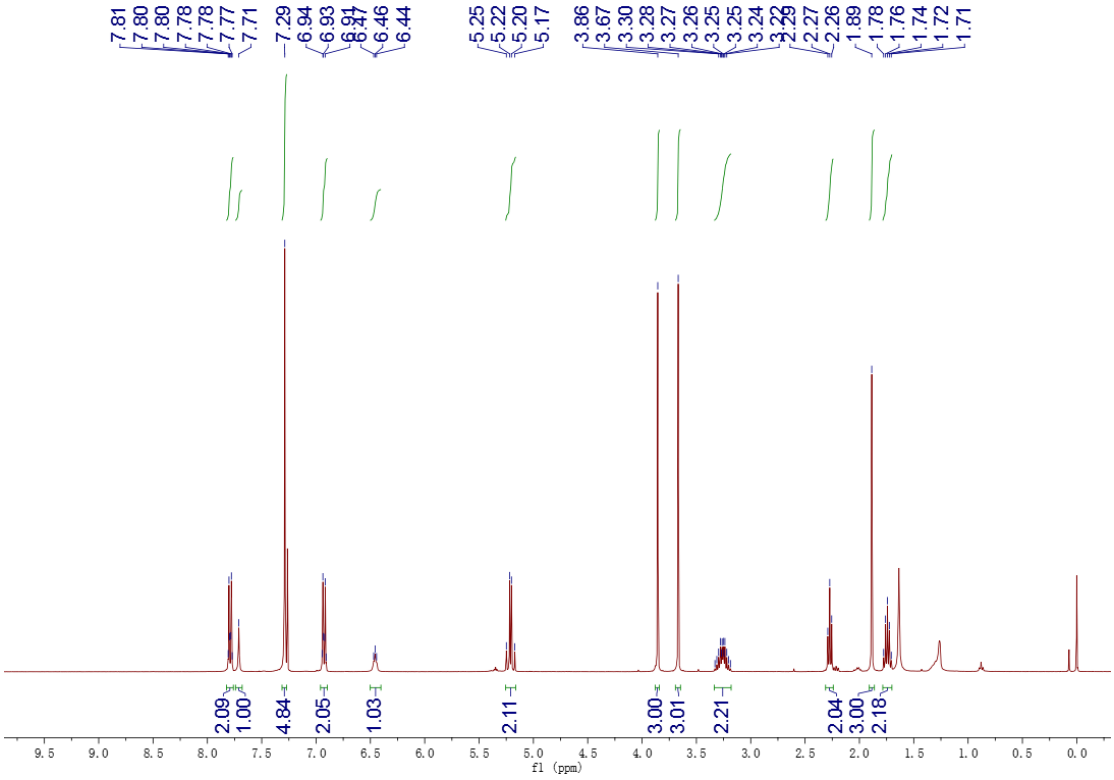
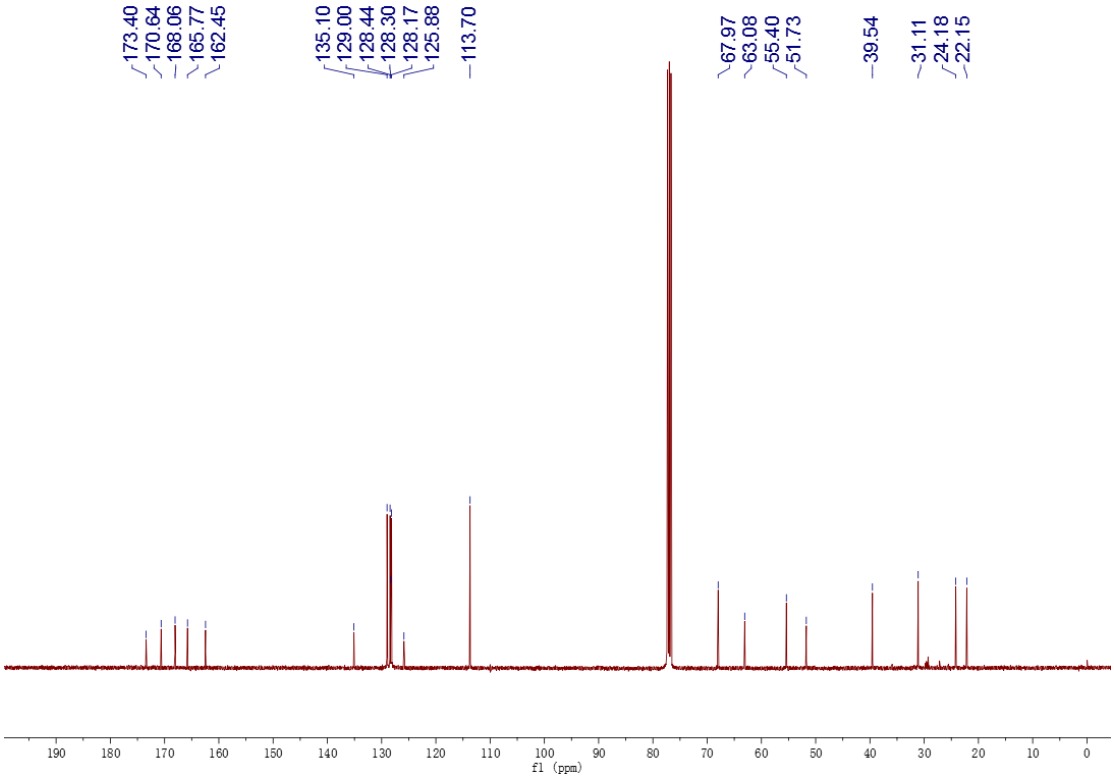
7.78
7.77
7.77
7.68
7.29
6.94
6.94
6.93
6.92
6.91
6.91
6.78
6.77
6.75
5.25
5.22
5.20
5.16
3.85
3.64
3.50
3.49
3.47
3.46
2.49
2.47
2.47
2.46
2.45
2.26
1.21
5.04
2.27
1.14
2.24
3.00
3.01
2.17
2.31
3.00
f1 (ppm)

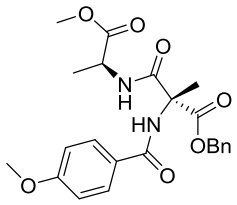

172.33
170.40
167.92
165.68
162.45
135.10
128.98
128.42
128.29
128.08
125.90
113.69
67.98
63.11
55.39
51.81
35.59
33.24
21.96
f1 (ppm)



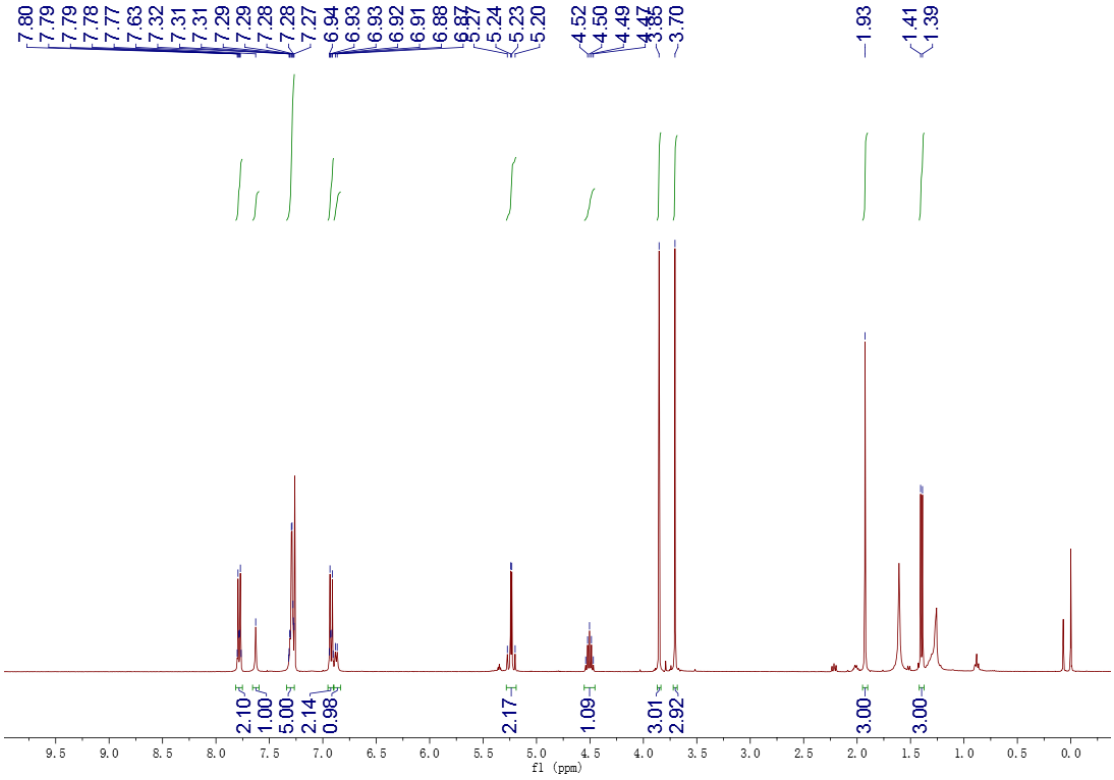
**2k**

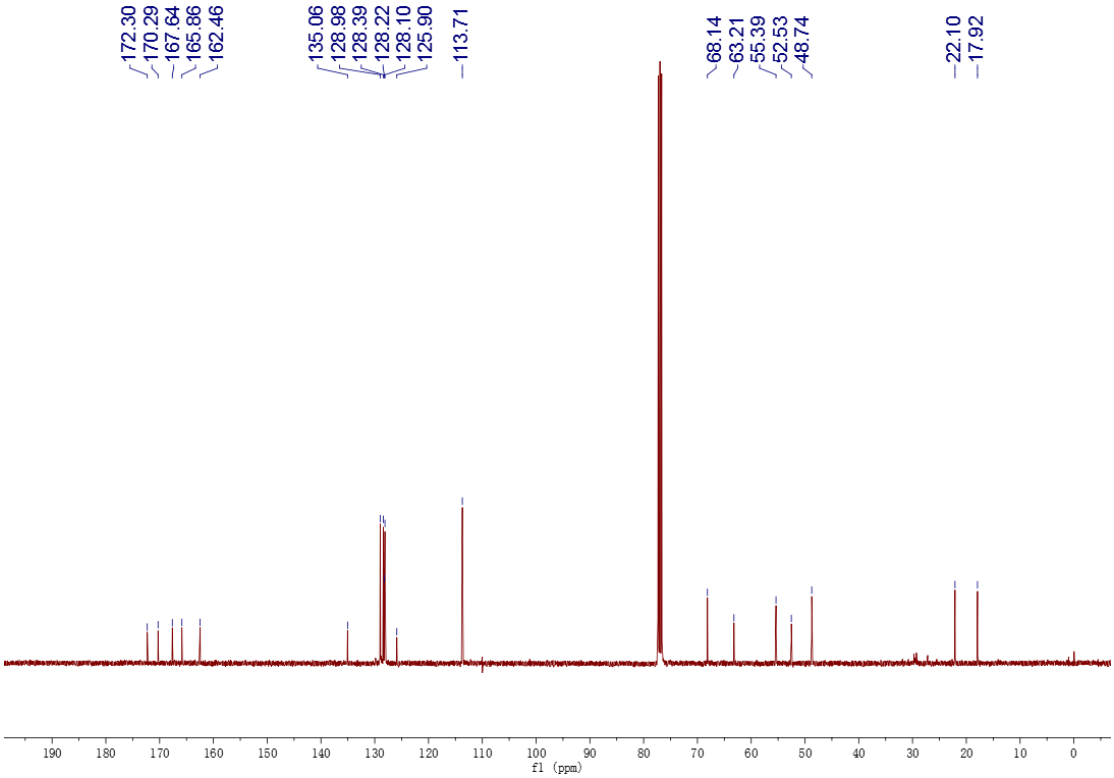

7.81
7.80
7.80
7.78
7.78
7.77
7.71
7.29
6.94
6.93
6.46
6.44
5.25
5.22
5.20
5.17
3.86
3.67
3.30
3.28
3.27
3.26
3.25
3.25
3.24
2.27
2.26
1.89
1.78
1.76
1.74
1.72
1.71
2.09
1.00
4.84
2.05
1.03
2.11
3.00
3.01
2.21
2.04
3.00
2.18
f1 (ppm)

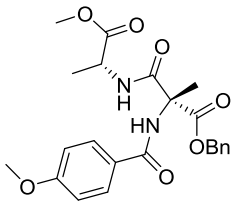

173.40
170.64
168.06
165.77
162.45
135.10
129.00
128.44
128.30
128.17
125.88
113.70
67.97
63.08
55.40
51.73
39.54
31.11
24.18
22.15
f1 (ppm)



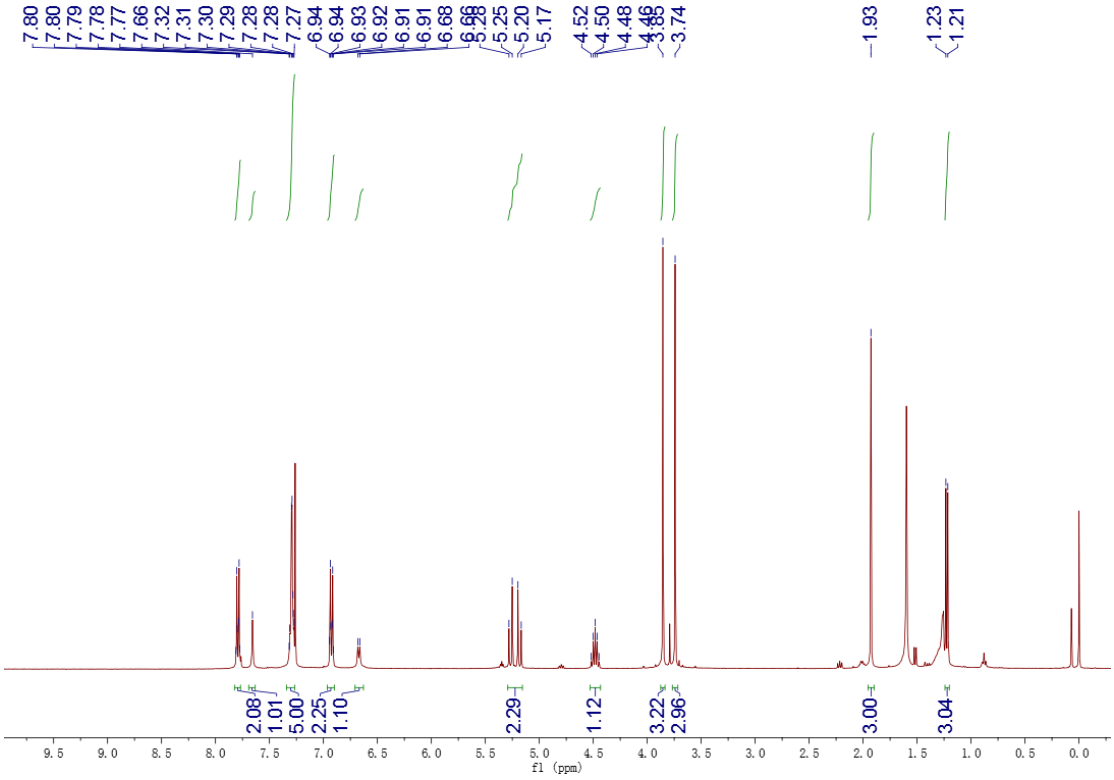
**2l**


7.80
7.79
7.79
7.78
7.77
7.63
7.32
7.31
7.31
7.29
7.29
7.28
7.28
7.27
6.94
6.93
6.93
6.92
6.91
6.88
5.24
5.23
5.20
4.52
4.50
4.49
3.70
1.93
1.41
1.39
2.10
1.00
5.00
2.14
0.98
2.17
1.09
3.01
2.92
3.00
3.00
f1 (ppm)


172.30
170.29
167.64
165.86
162.46
135.06
128.98
128.39
128.22
128.10
125.90
113.71
68.14
63.21
55.39
52.53
48.74
22.10
17.92
f1 (ppm)



**2m**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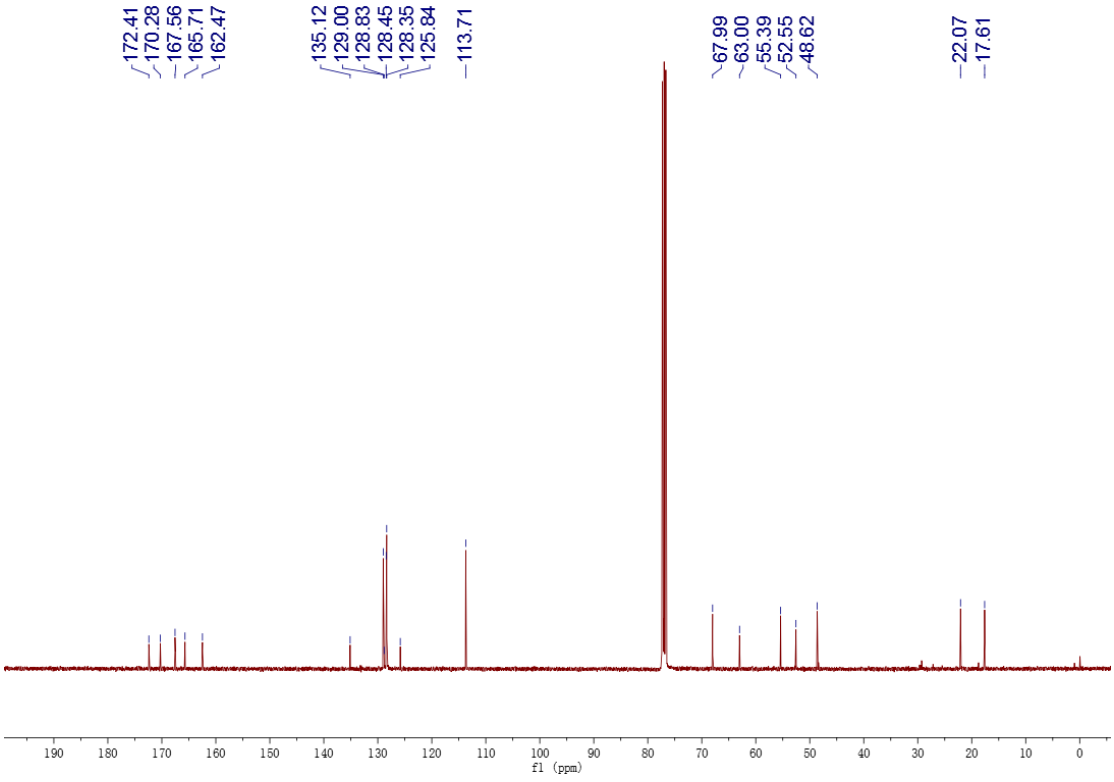
7.31
7.30
7.29
7.28
7.28
7.27
6.94
6.94
6.93
6.92
6.91
6.91
6.68
5.28
5.25
5.20
5.17
4.52
4.50
4.48
3.74
1.93
1.23
1.21
2.08
1.01
5.00
2.25
1.10
2.29
1.12
3.22
2.96
3.00
3.04
f1 (ppm)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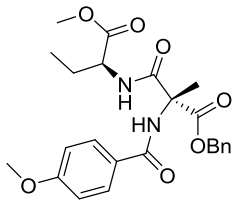
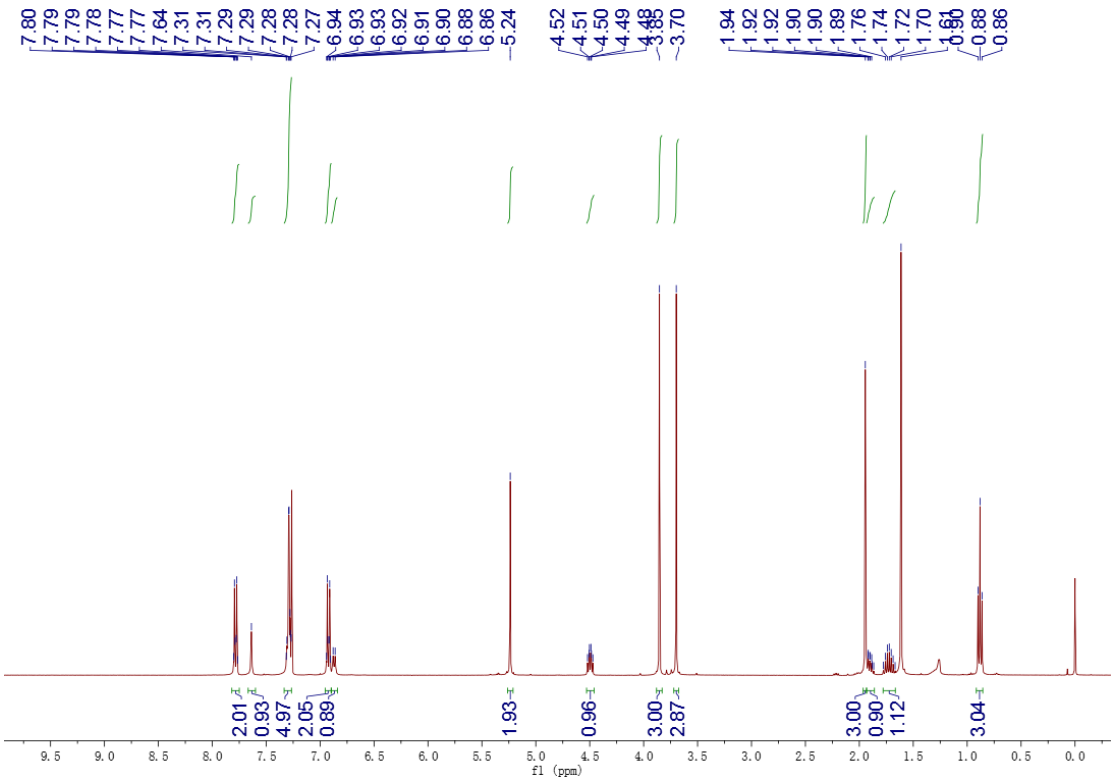
129.00
128.83
128.45
128.35
125.84
113.71
67.99
63.00
55.39
52.55
48.62
22.07
17.61
f1 (ppm)



**2n**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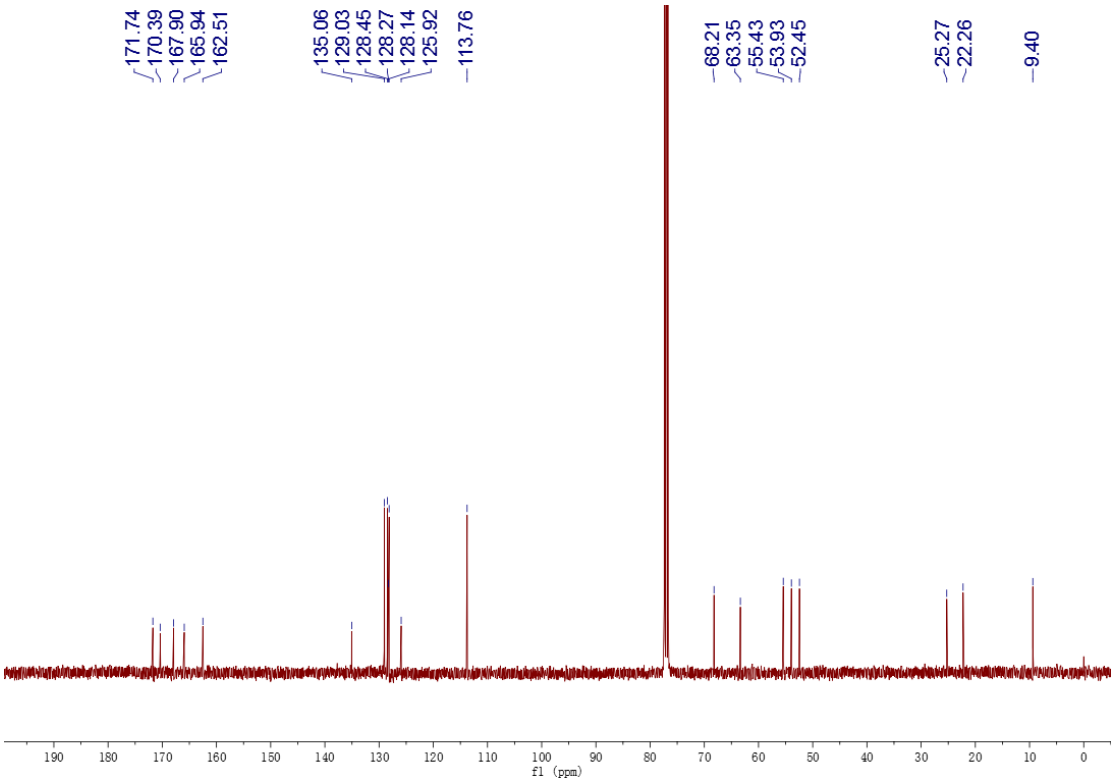
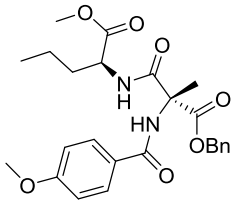
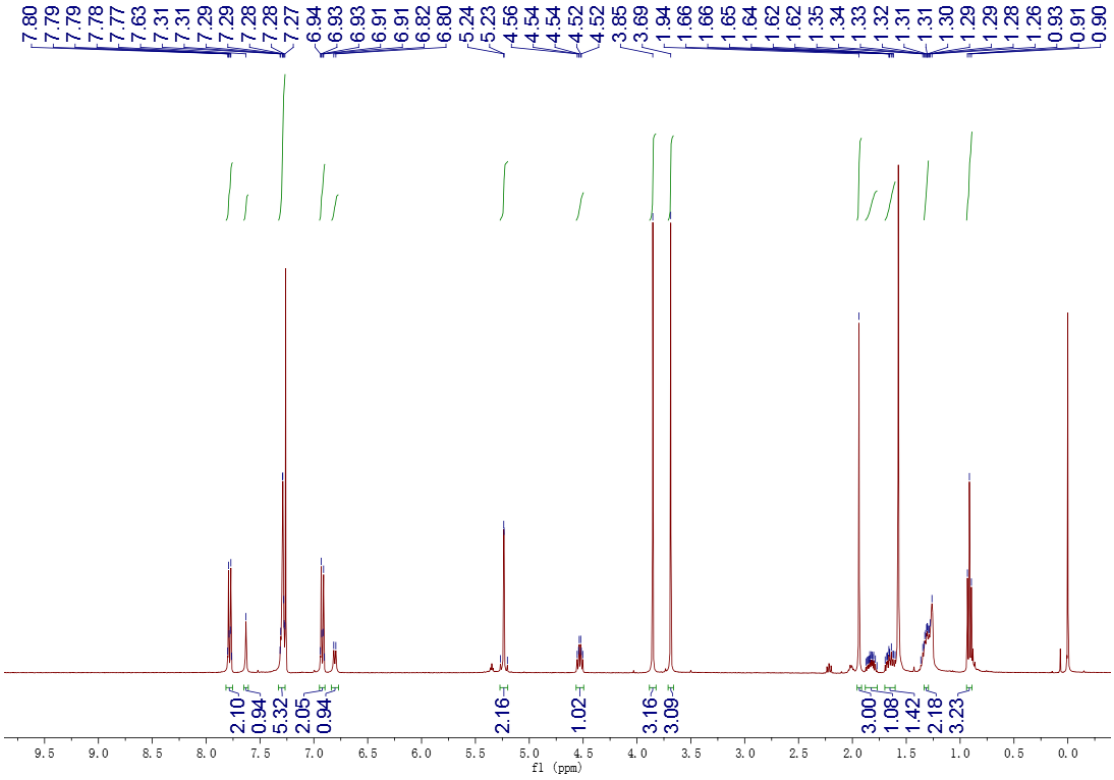
2.01 0.93 4.97 2.05 0.89 1.93 0.96 3.00 2.87 3.00 0.90 1.12 3.04
f1 (ppm)


171.74 170.39 167.90 165.94 162.51 135.06 129.03 128.45 128.27 128.14 125.92 113.76 68.21 63.35 55.43 53.93 52.45 25.27 22.26 9.40
f1 (ppm)



**2o**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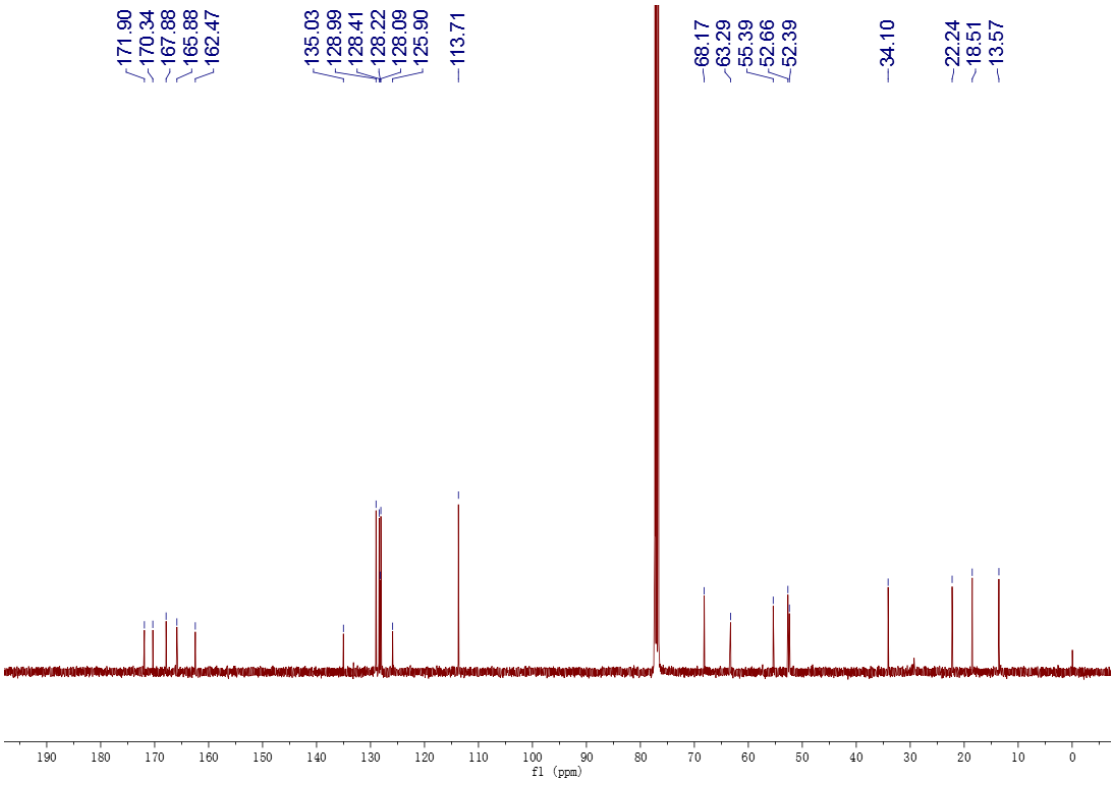
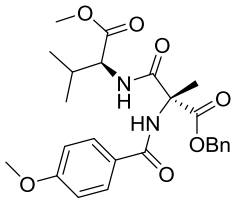
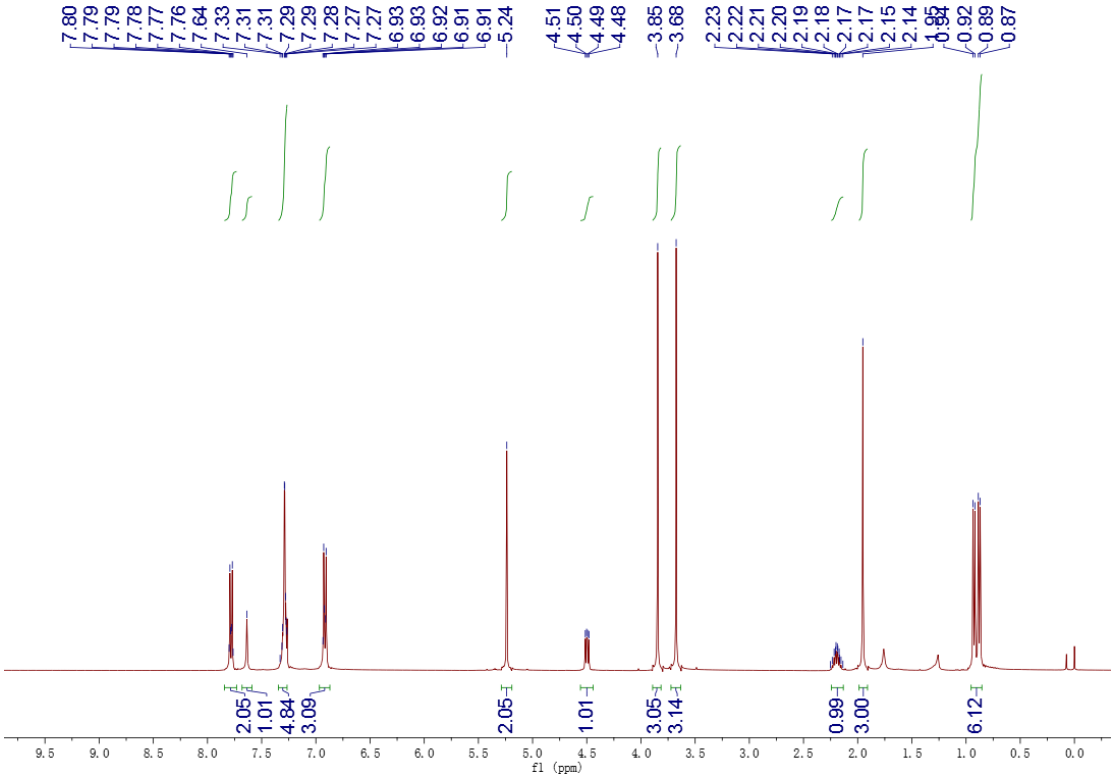
2.10 0.94 5.32 2.05 0.94 2.16 1.02 3.16 3.09 3.00 1.08 1.42 2.18 3.23
f1 (ppm)


171.90 170.34 167.88 165.88 162.47 135.03 128.99 128.41 128.22 128.09 125.90 113.71 68.17 63.29 55.39 52.66 52.39 34.10 22.24 18.51 13.57
f1 (ppm)



**2p**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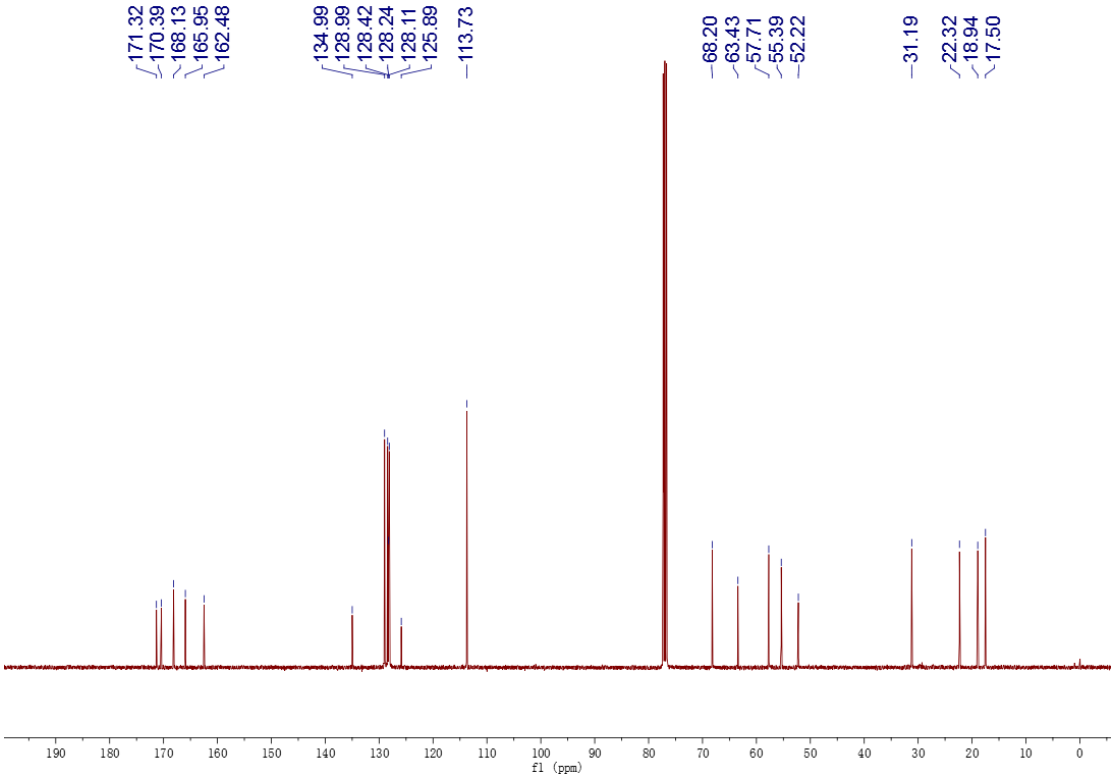
7.79
7.79
7.78
7.77
7.76
7.64
7.33
7.31
7.31
7.29
7.29
7.28
7.27
7.27
6.93
6.93
6.92
6.91
6.91
5.24
4.51
4.50
4.49
4.48
3.85
3.68
2.23
2.22
2.21
2.20
2.19
2.18
2.17
2.17
2.15
2.14
0.92
0.89
0.87
2.05
1.01
4.84
3.09
2.05
1.01
3.05
3.14
0.99
3.00
6.12
f1 (ppm)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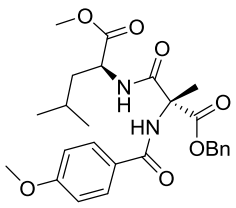
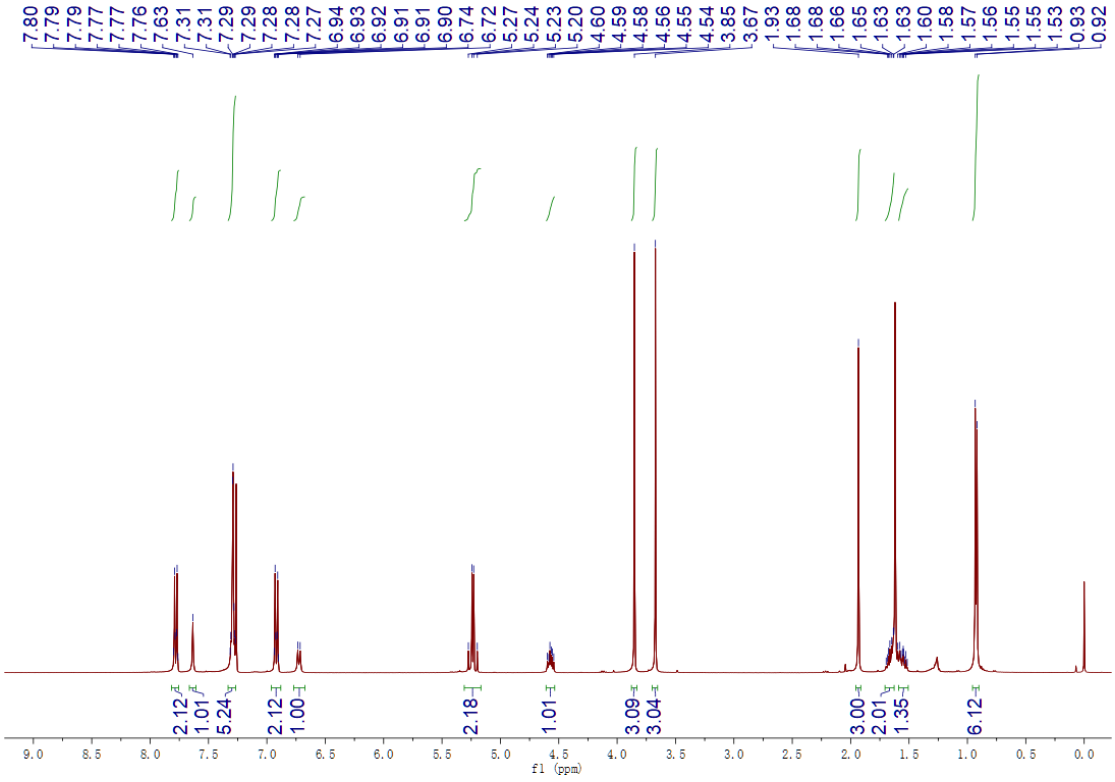
170.39
168.13
165.95
162.48
134.99
128.99
128.42
128.24
128.11
125.89
113.73
68.20
63.43
57.71
55.39
52.22
31.19
22.32
18.94
17.50
f1 (ppm)



**2q**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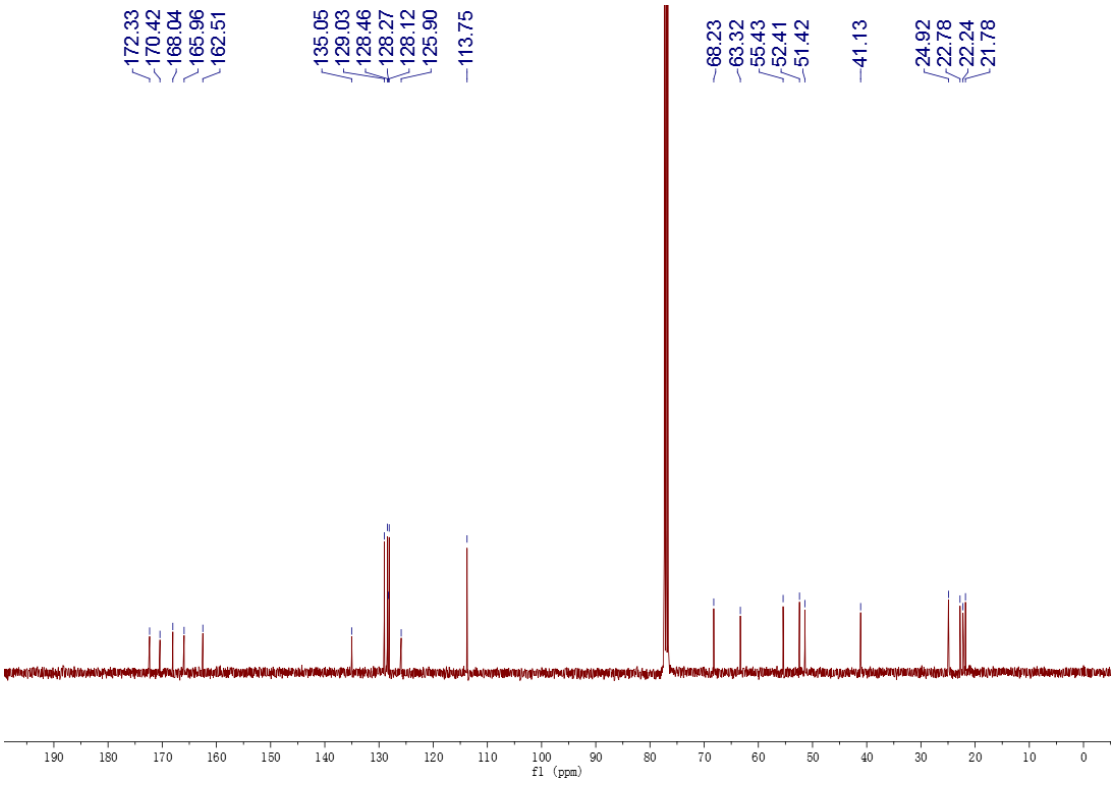
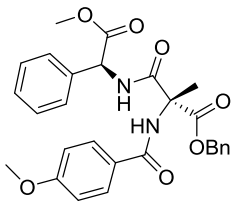
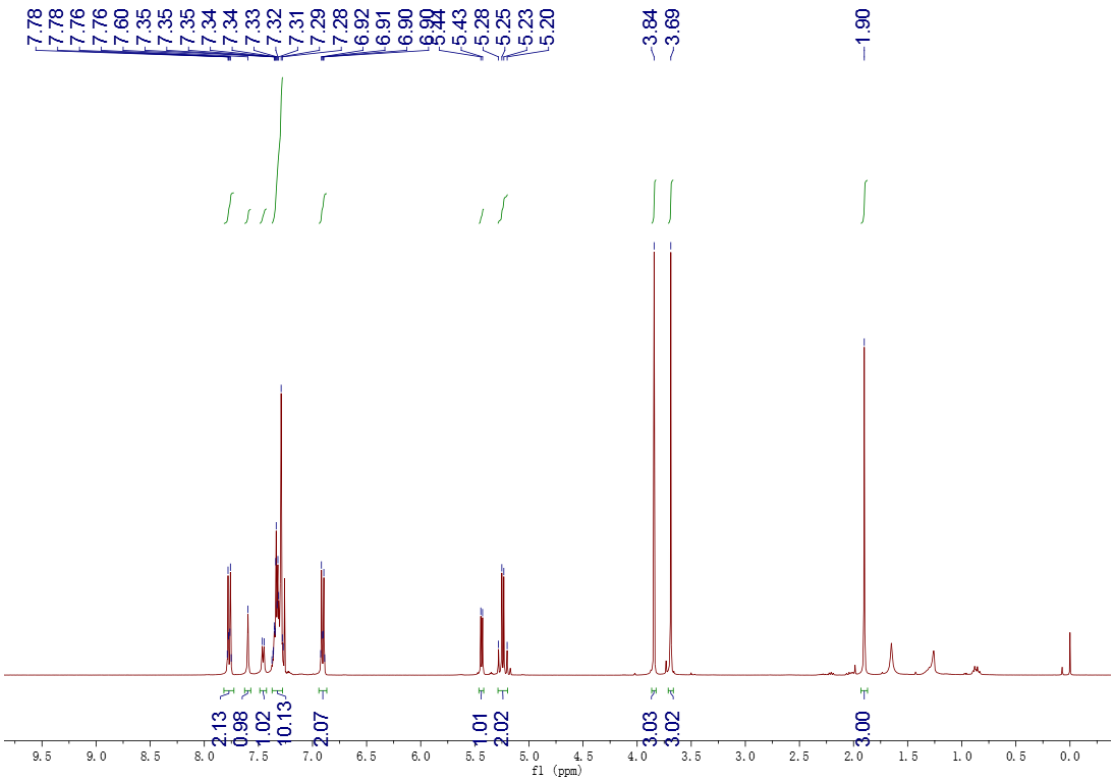
2.12 1.01 5.24 2.12 1.00 2.18 1.01 3.09 3.04 3.00 2.01 1.35 6.12
f1 (ppm)


172.33 170.42 168.04 165.96 162.51 135.05 129.03 128.46 128.27 128.12 125.90 113.75 68.23 63.32 55.43 52.41 51.42 41.13 24.92 22.78 22.24 21.78
f1 (ppm)



**2r**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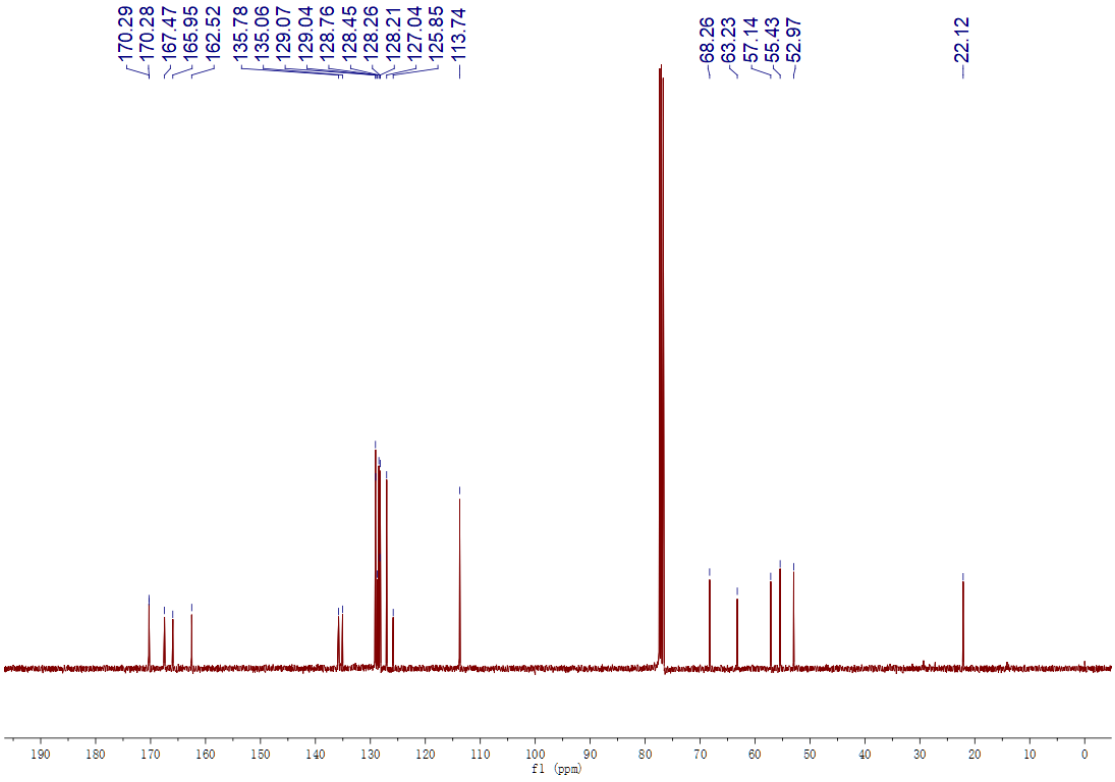
7.35
7.35
7.34
7.34
7.33
7.32
7.31
7.29
7.28
6.92
6.91
6.90
5.43
5.28
5.25
5.23
5.20
3.84
3.69
1.90
2.13
0.98
1.02
10.13
2.07
1.01
2.02
3.03
3.02
3.00
f1 (ppm)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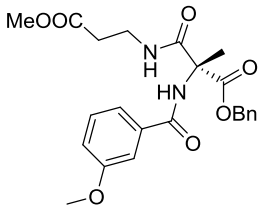
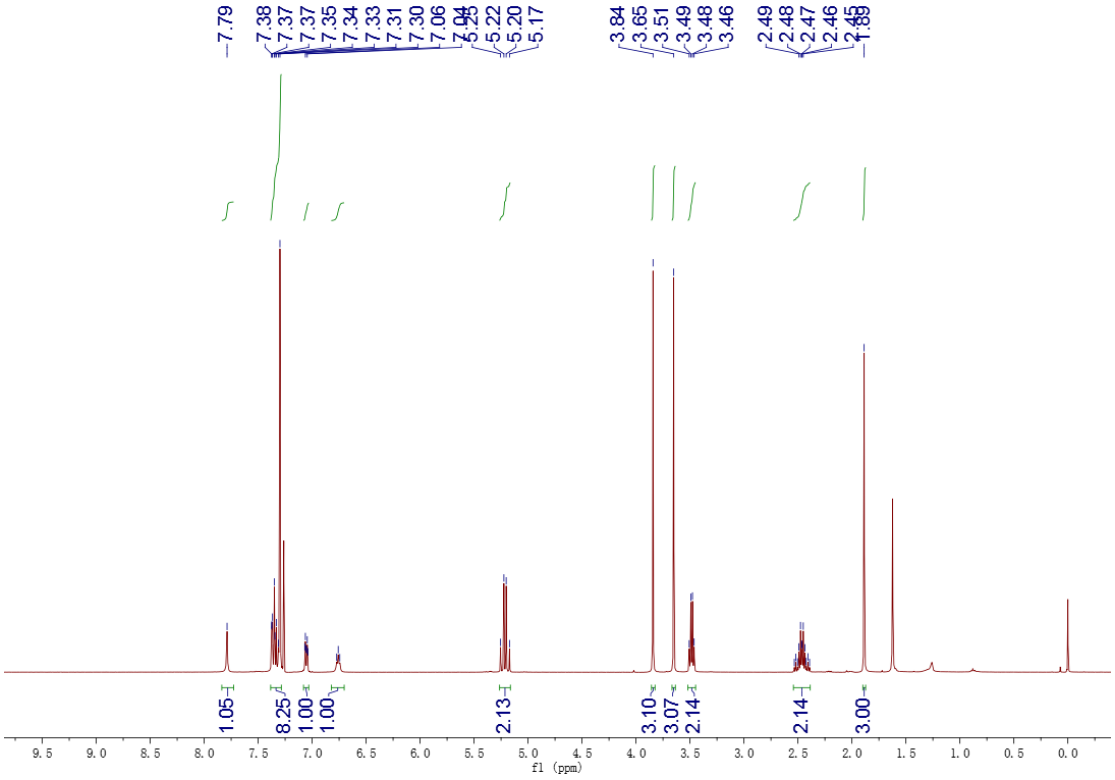
165.95
162.52
135.78
135.06
129.07
129.04
128.76
128.45
128.26
128.21
127.04
125.85
113.74
68.26
63.23
57.14
55.43
52.97
22.12
f1 (ppm)


MeOOC
N
H
HN
O
O
O
OBn
O
O

**2s**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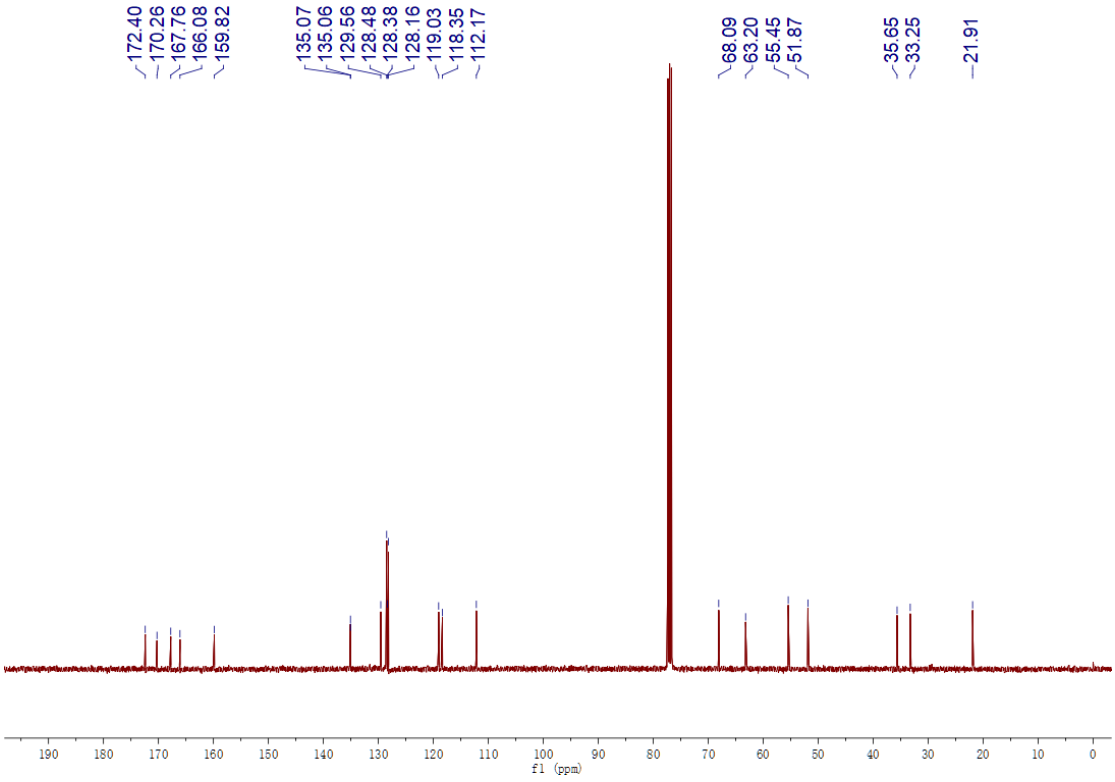
7.34
7.33
7.31
7.30
7.06
5.22
5.20
5.17
3.84
3.65
3.51
3.49
3.48
3.46
2.49
2.48
2.47
2.46
1.88
1.05
8.25
1.00
1.00
2.13
3.10
3.07
2.14
2.14
3.00
f1 (ppm)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166.08
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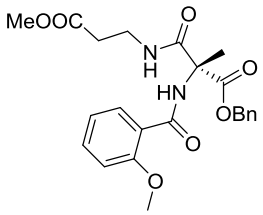
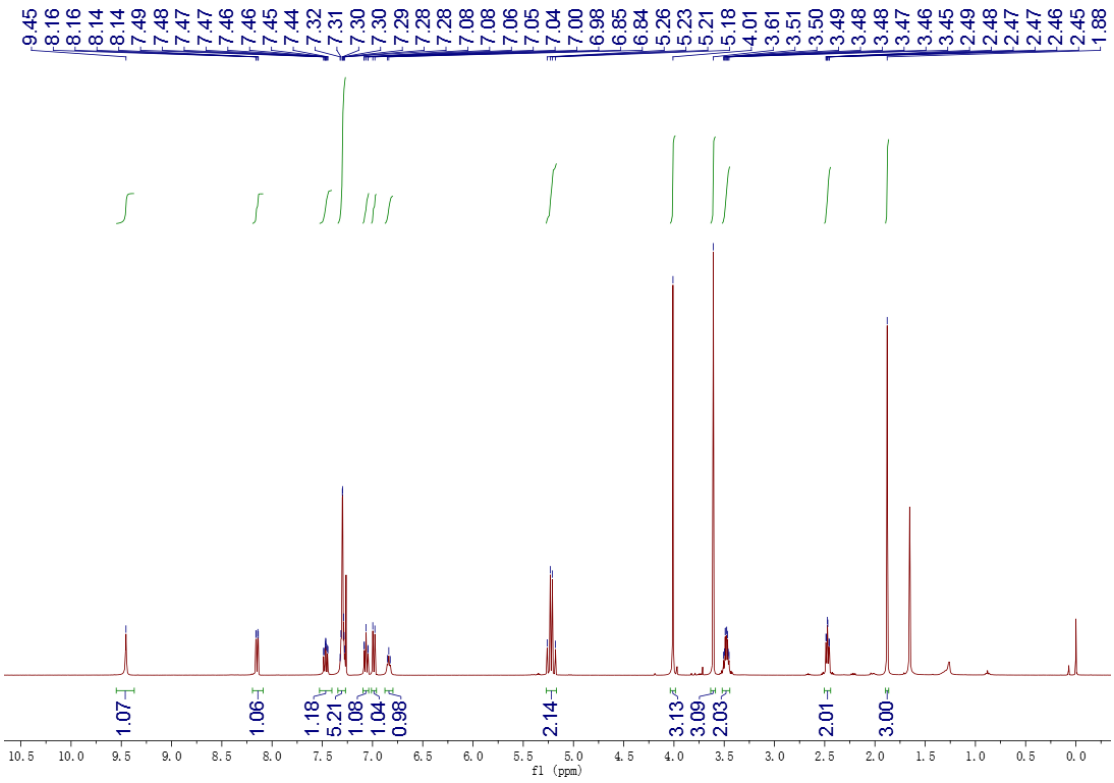
135.06
129.56
128.48
128.38
128.16
119.03
118.35
112.17
68.09
63.20
55.45
51.87
35.65
33.25
21.91
f1 (ppm)


MeOOC
N
H
O
HN
O
OBn
O
O

**2t**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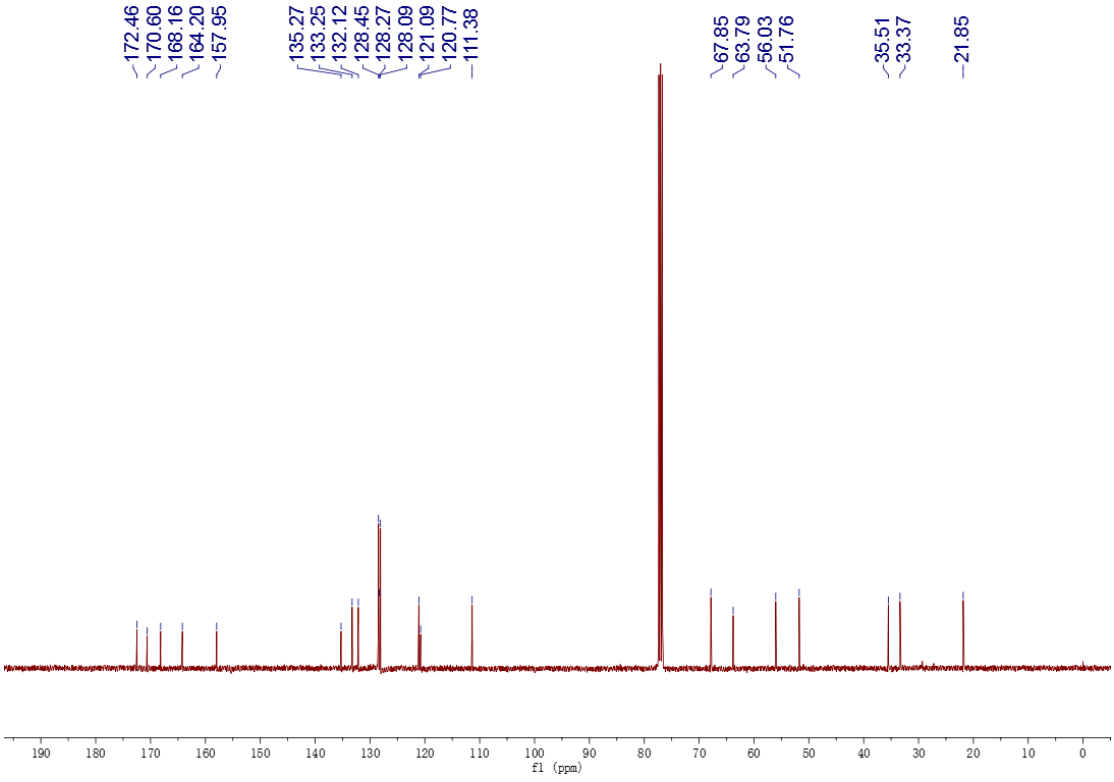
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.08
7.08
7.06
7.05
7.04
7.00
6.98
6.85
6.84
5.26
5.23
5.21
5.18
4.01
3.61
3.51
3.50
3.49
3.48
3.48
3.47
3.46
3.45
2.49
2.48
2.47
2.47
2.46
2.45
1.88
1.07
1.06
1.18
5.21
1.08
1.04
0.98
2.14
3.13
3.09
2.03
2.01
3.00
f1 (ppm)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157.95
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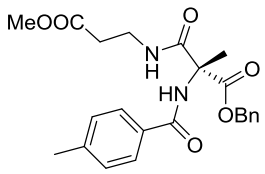
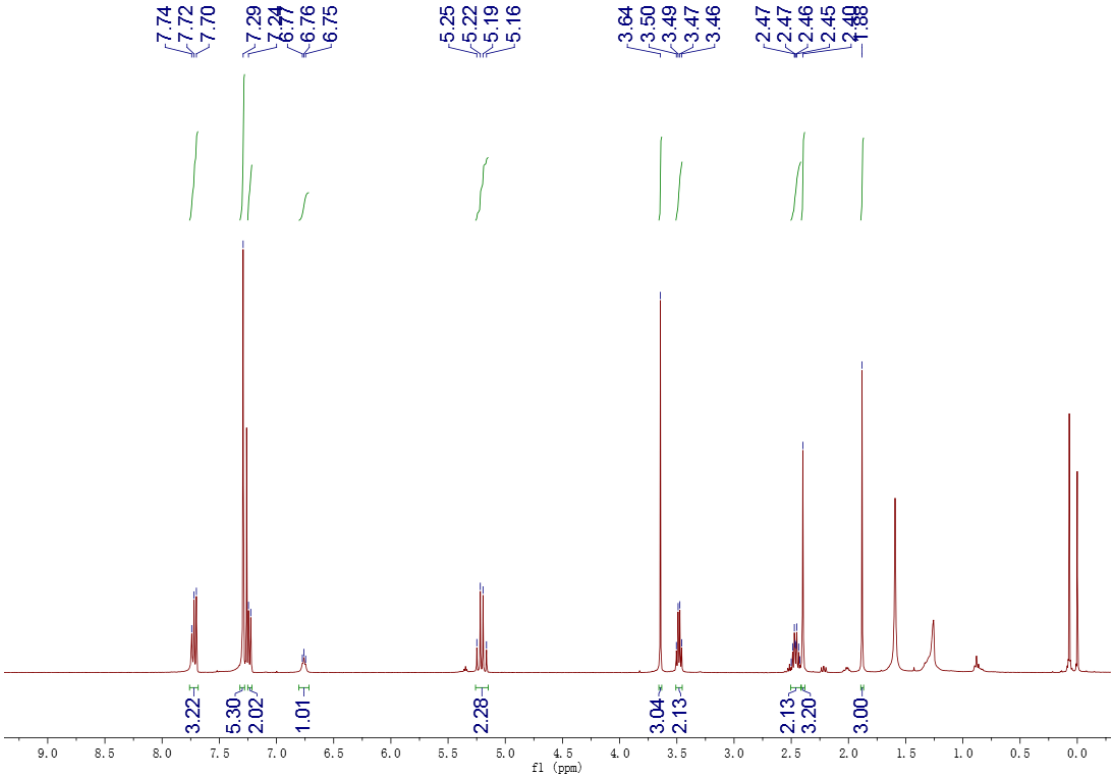
133.25
132.12
128.45
128.27
128.09
121.09
120.77
111.38
67.85
63.79
56.03
51.76
35.51
33.37
21.85
f1 (ppm)


MeOOC
O
N
H
HN
O
OBn
O

**2u**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6.75
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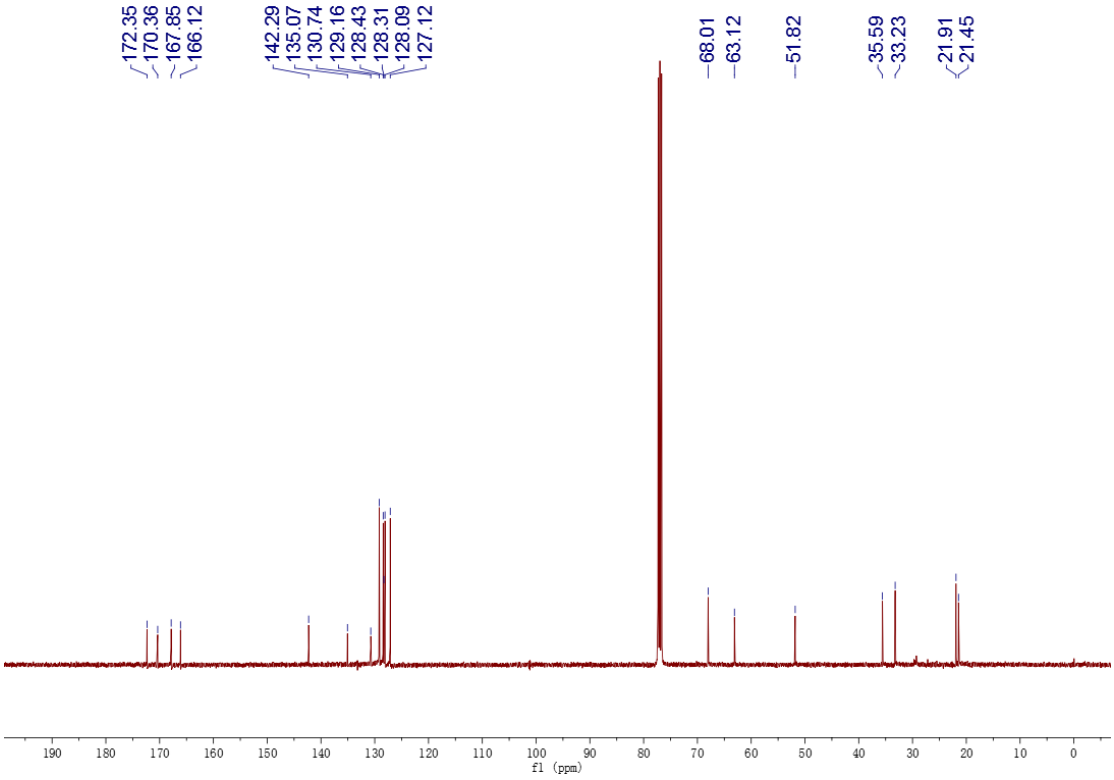
5.22
5.19
5.16
3.64
3.50
3.49
3.47
3.46
2.47
2.47
2.46
2.45
1.88
3.22
5.30
2.02
1.01
2.28
3.04
2.13
2.13
3.20
3.00
f1 (ppm)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135.07
130.74
129.16
128.43
128.31
128.09
127.12
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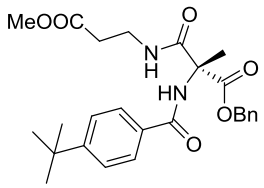
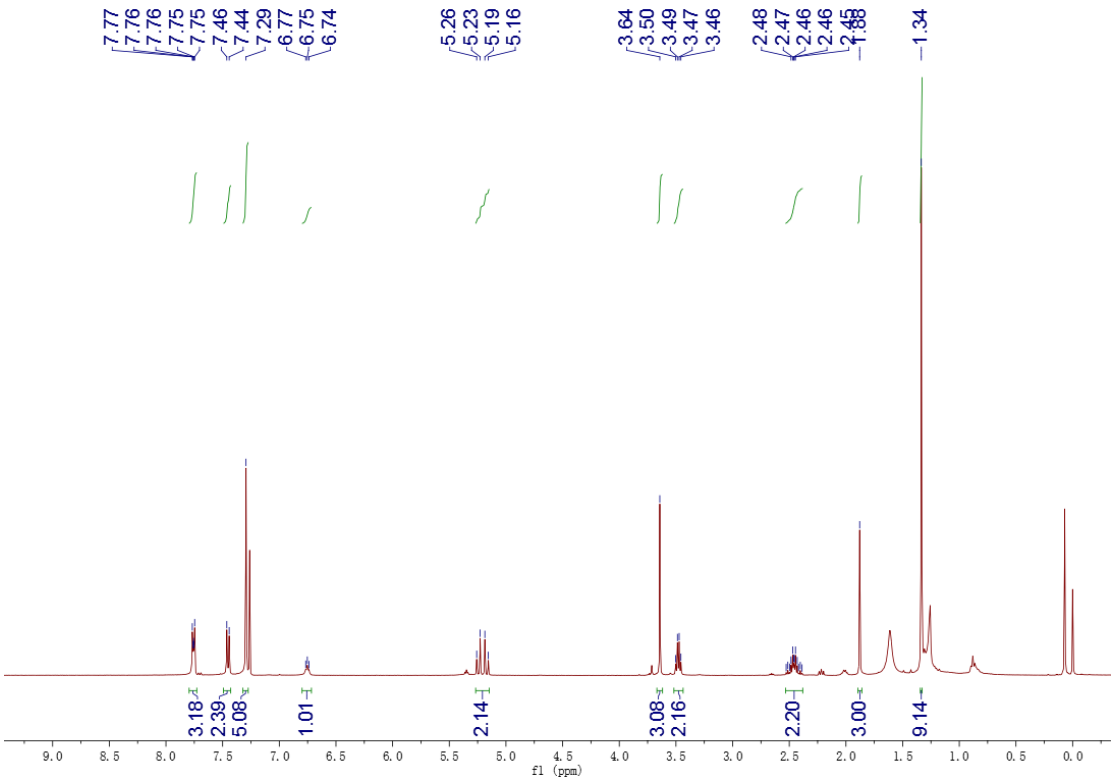
35.59
33.23
21.91
21.45
f1 (ppm)


MeOOC
N
H
HN
O
O
OBn
O
O

**2v**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7.76
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7.46
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6.77
6.75
6.74
5.26
5.23
5.19
5.16
3.64
3.50
3.49
3.47
3.46
2.48
2.47
2.46
2.46
1.34
3.18
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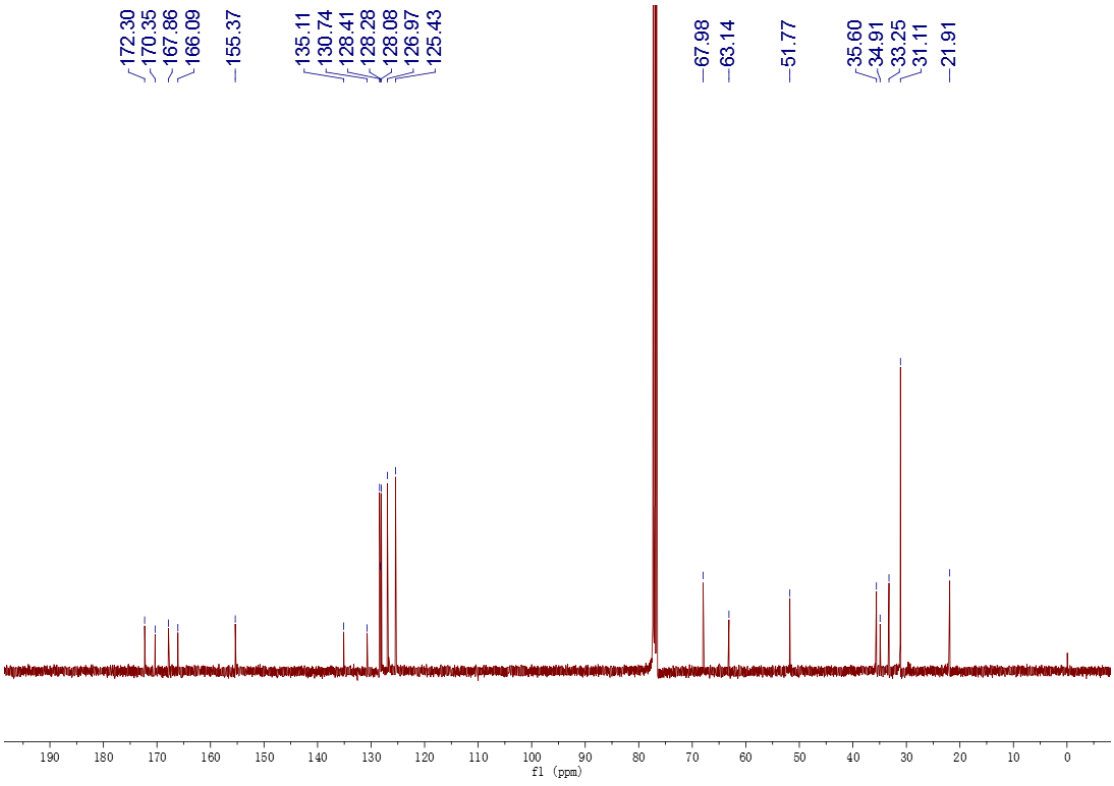
2.16
2.20
3.00
9.14
f1 (ppm)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135.11
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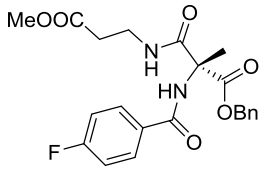
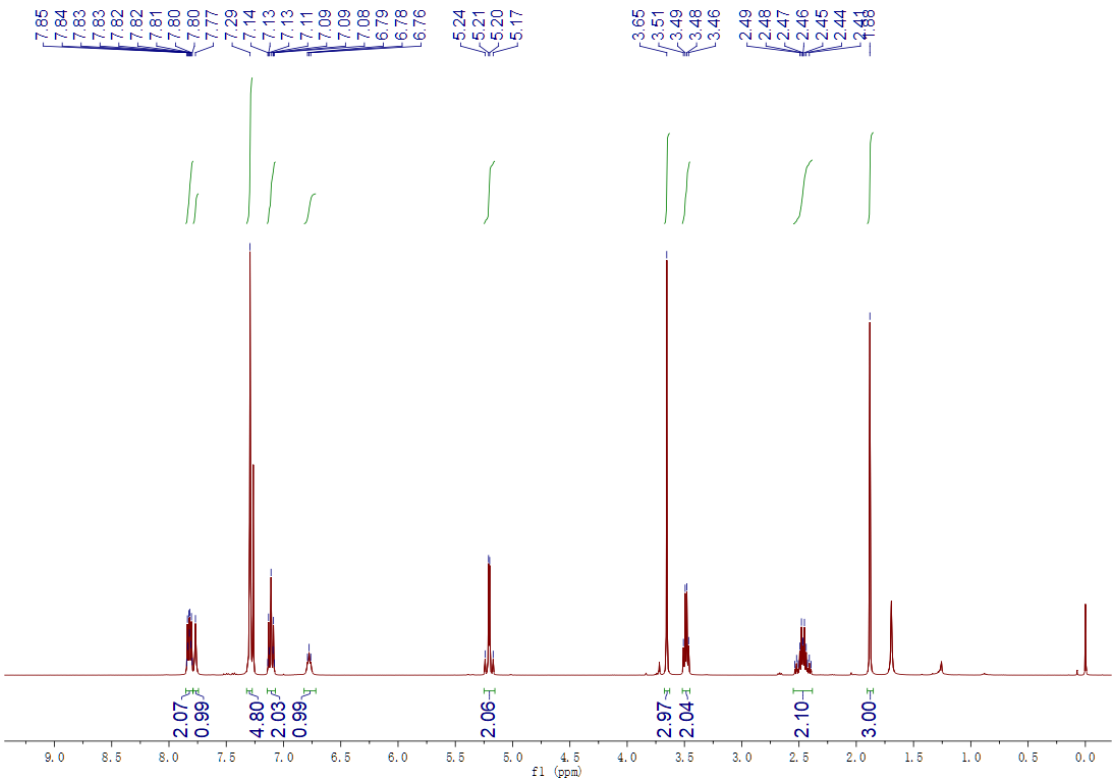
128.41
128.28
128.08
126.97
125.43
67.98
63.14
51.77
35.60
34.91
33.25
31.11
21.91
f1 (ppm)


MeOOC
O
N
H
HN
O
OBn
F
O

**2w**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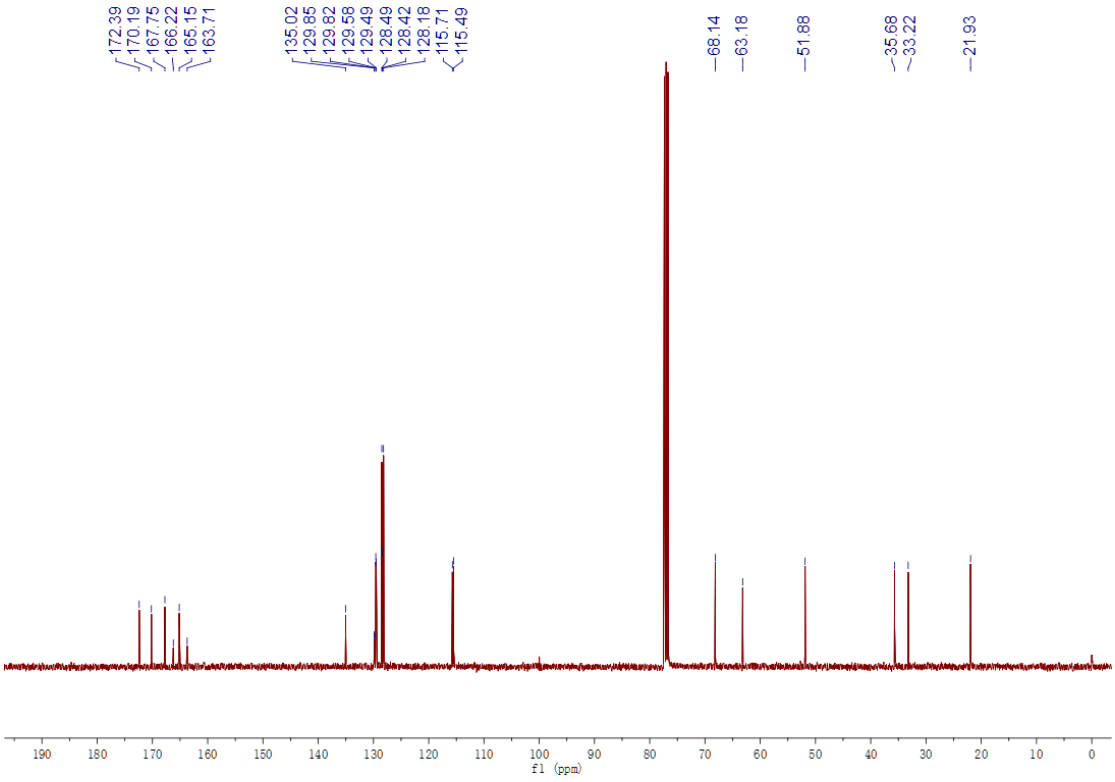
7.84
7.83
7.83
7.82
7.82
7.81
7.80
7.80
7.77
7.29
7.14
7.13
7.13
7.11
7.09
7.09
7.08
6.79
6.78
6.76
5.24
5.21
5.20
5.17
3.65
3.51
3.49
3.48
3.46
2.49
2.48
2.47
2.46
2.45
2.44
1.88
2.07
0.99
4.80
2.03
0.99
2.06
2.97
2.04
2.10
3.00
f1 (ppm)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165.15
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135.02
129.85
129.82
129.58
129.49
128.49
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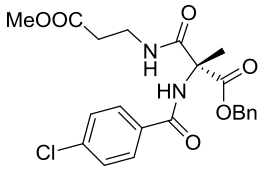
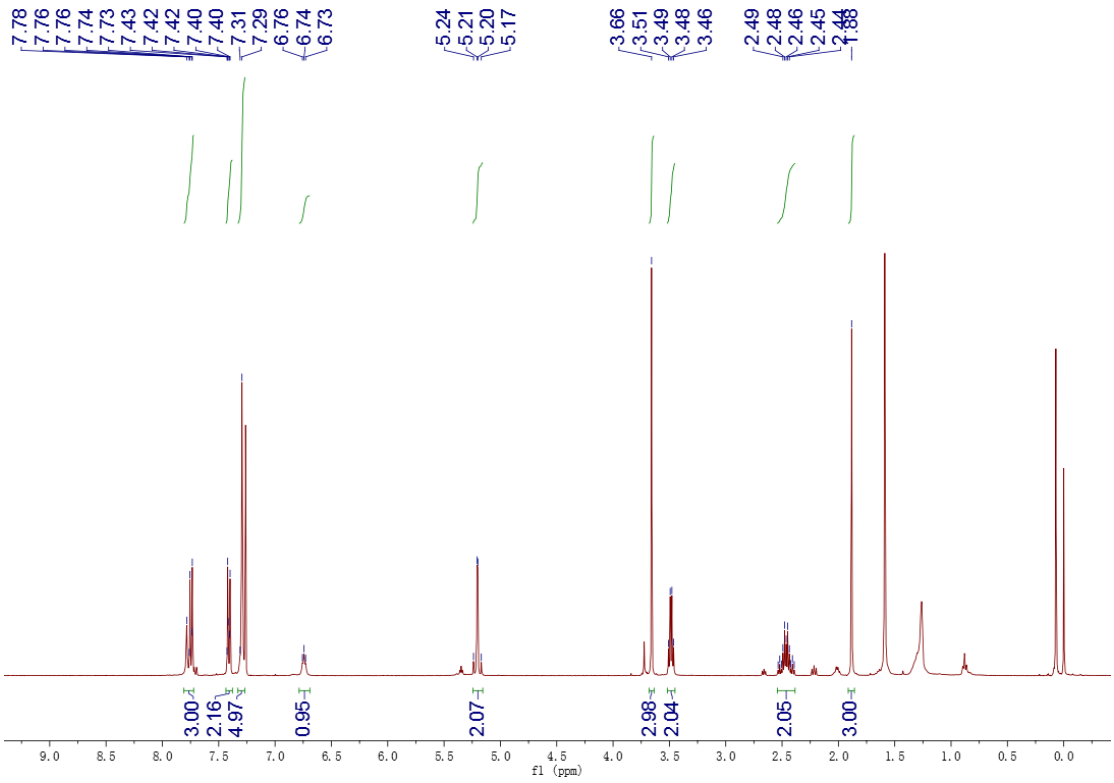
63.18
51.88
35.68
33.22
21.93
f1 (ppm)


MeOOC
O
N
H
HN
O
OBn
Cl
O

**2x**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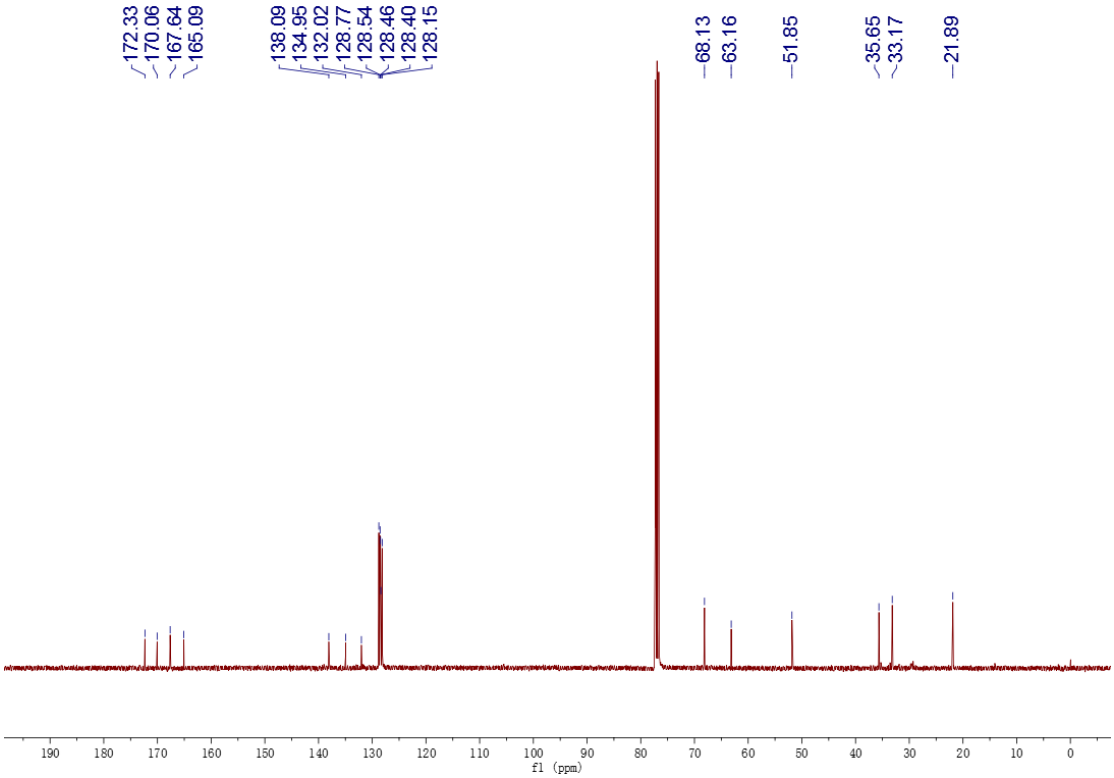
7.43
7.42
7.42
7.40
7.40
7.31
7.29
6.76
6.74
6.73
5.24
5.21
5.20
5.17
3.66
3.51
3.49
3.48
3.46
2.49
2.48
2.46
2.45
3.00
2.16
4.97
0.95
2.07
2.98
2.04
2.05
3.00
f1 (ppm)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165.09
138.09
134.95
132.02
128.77
128.54
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128.40
128.15
68.13
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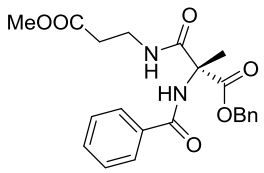
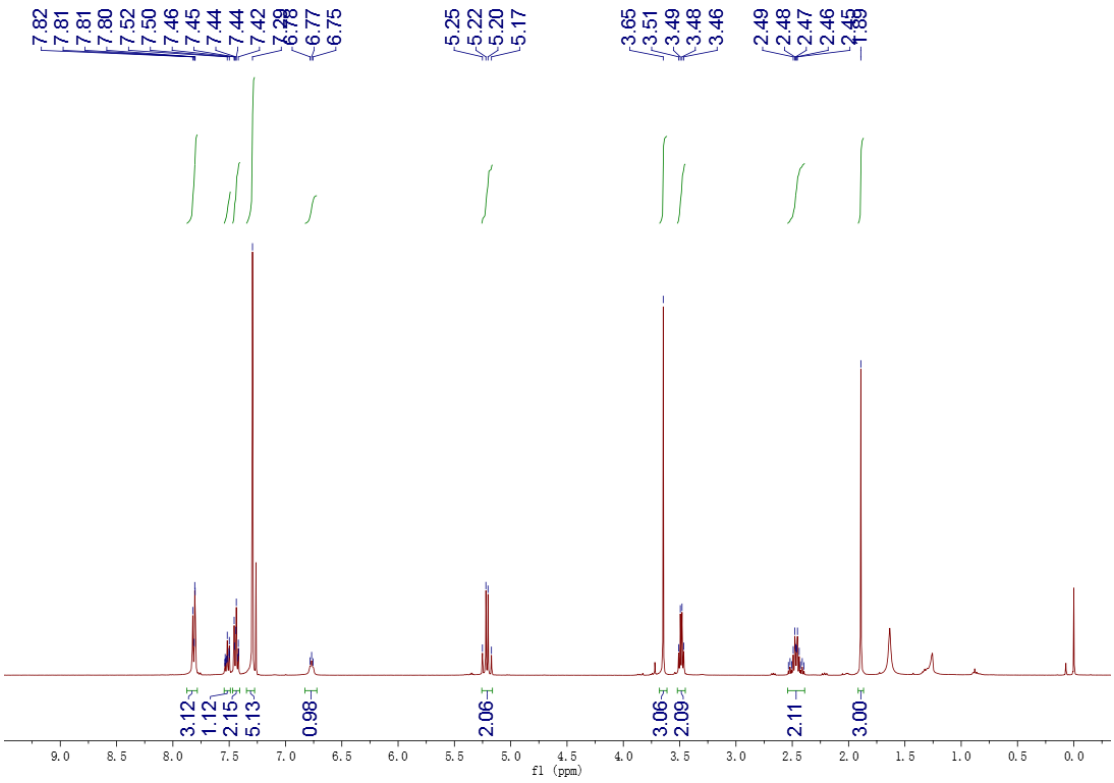
51.85
35.65
33.17
21.89
f1 (ppm)


MeOOC
O
N
H
HN
O
OBn
O

**2y**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7.45
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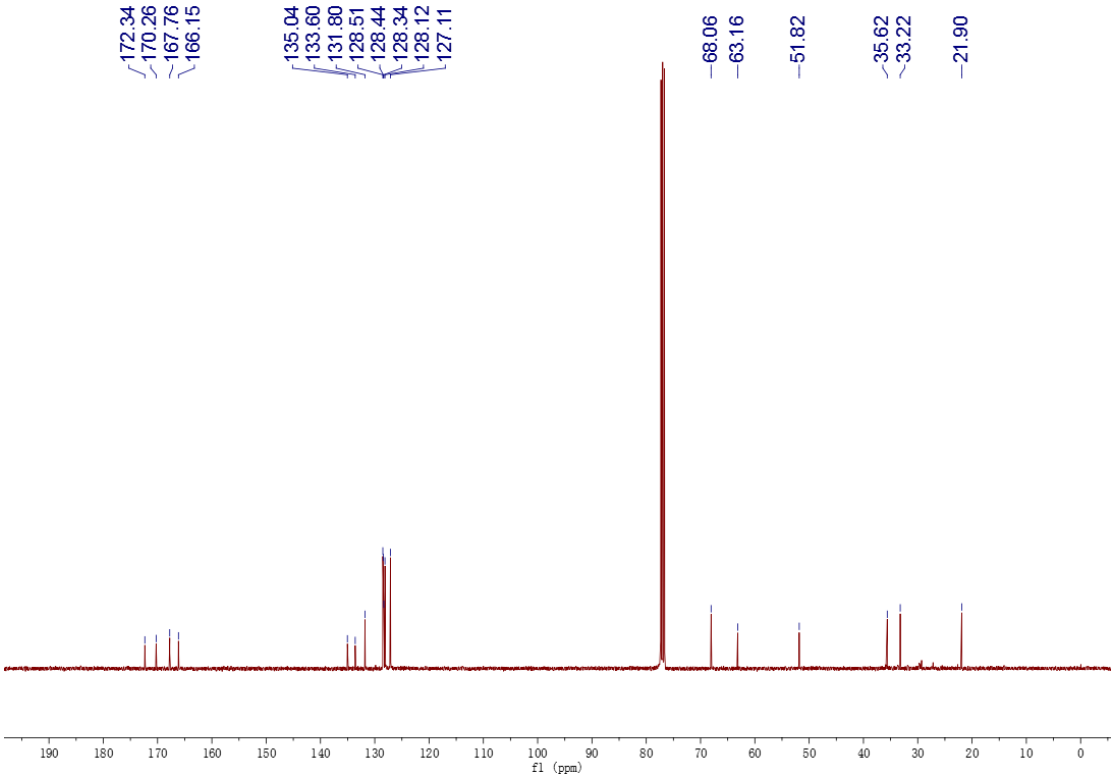
7.44
7.42
6.77
6.75
5.25
5.22
5.20
5.17
3.65
3.51
3.49
3.48
3.46
2.49
2.48
2.47
2.46
3.12
1.12
2.15
5.13
0.98
2.06
3.06
2.09
2.11
3.00
f1 (ppm)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133.60
131.80
128.51
128.44
128.34
128.12
127.11
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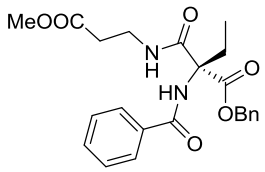
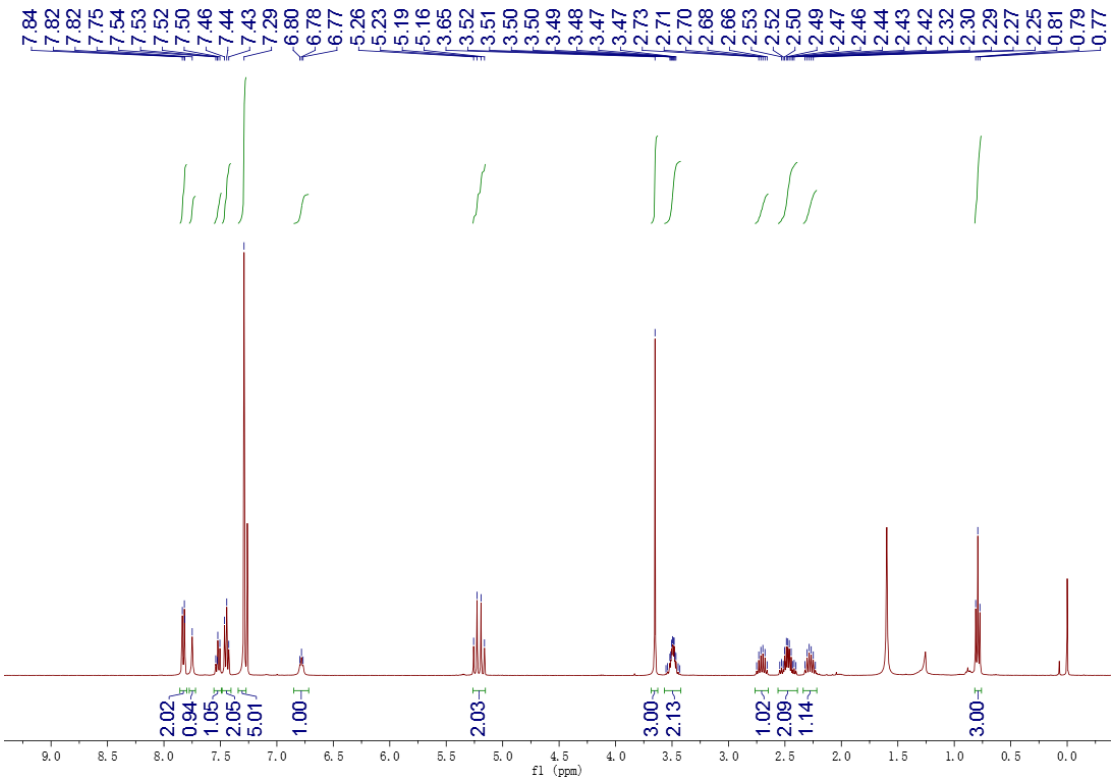
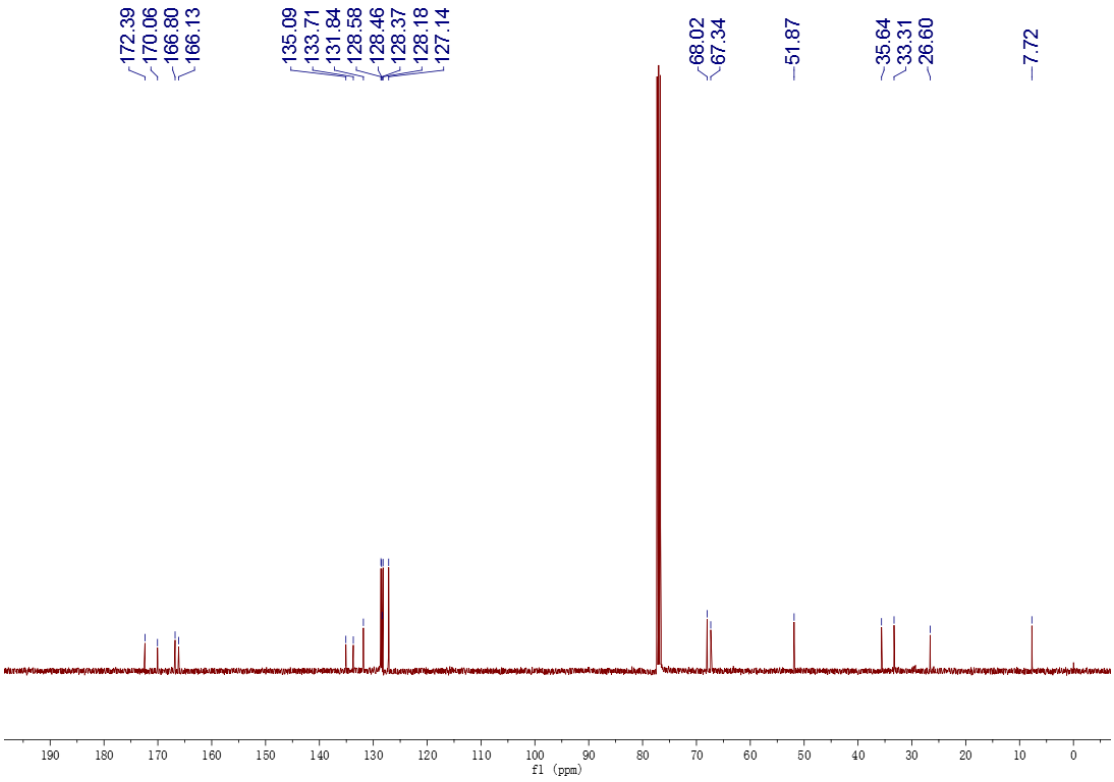
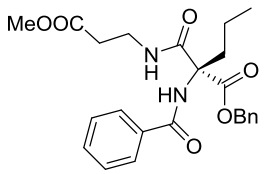
51.82
35.62
33.22
21.90
f1 (ppm)


MeOOC
N
H
O
HN
O
OBn
O

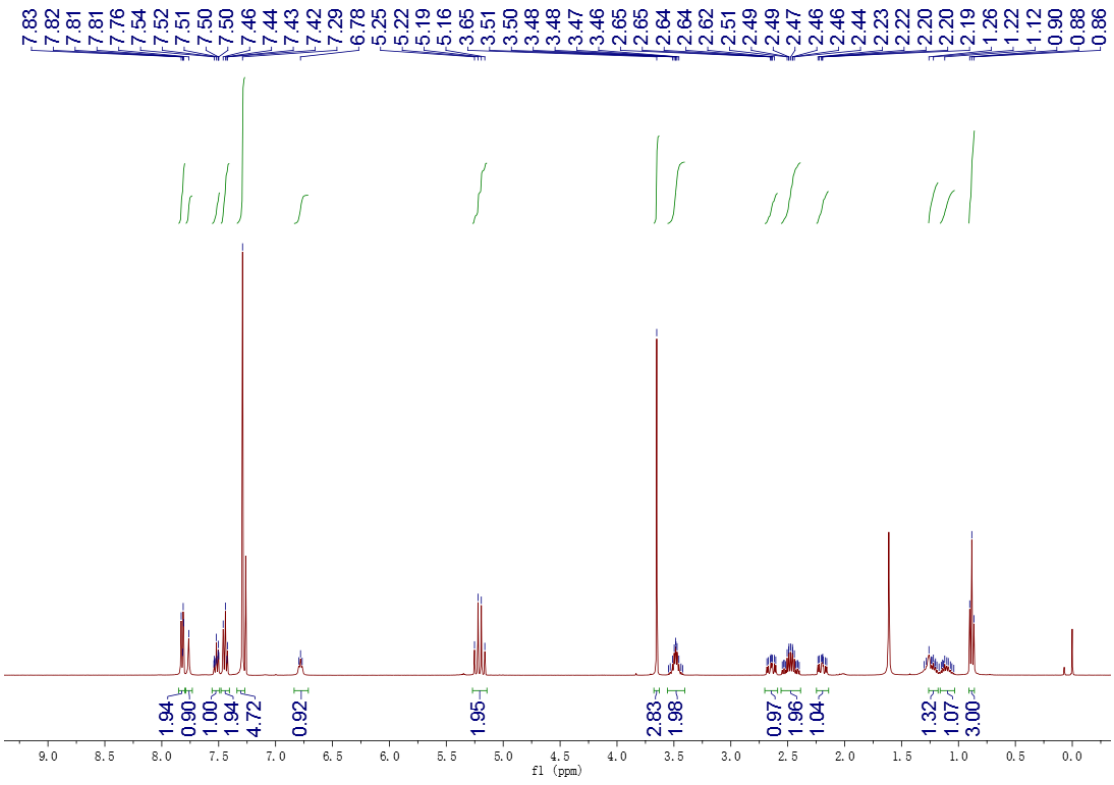
**2z**


7.84 7.82 7.82 7.75 7.54 7.53 7.52 7.50 7.46 7.44 7.43 7.29 6.80 6.78 6.77 5.26 5.23 5.19 5.16 3.65 3.52 3.51 3.50 3.50 3.49 3.48 3.47 3.47 2.73 2.71 2.70 2.68 2.66 2.53 2.52 2.50 2.49 2.47 2.46 2.44 2.43 2.42 2.32 2.30 2.29 2.27 2.25 0.81 0.79 0.77
2.02 0.94 1.05 2.05 5.01 1.00 2.03 3.00 2.13 1.02 2.09 1.14 3.00
f1 (ppm)


172.39 170.06 166.80 166.13 135.09 133.71 131.84 128.58 128.46 128.37 128.18 127.14 68.02 67.34 51.87 35.64 33.31 26.60 7.72
f1 (ppm)


MeOOC
N
H
O
HN
O
OBn
O

**2aa**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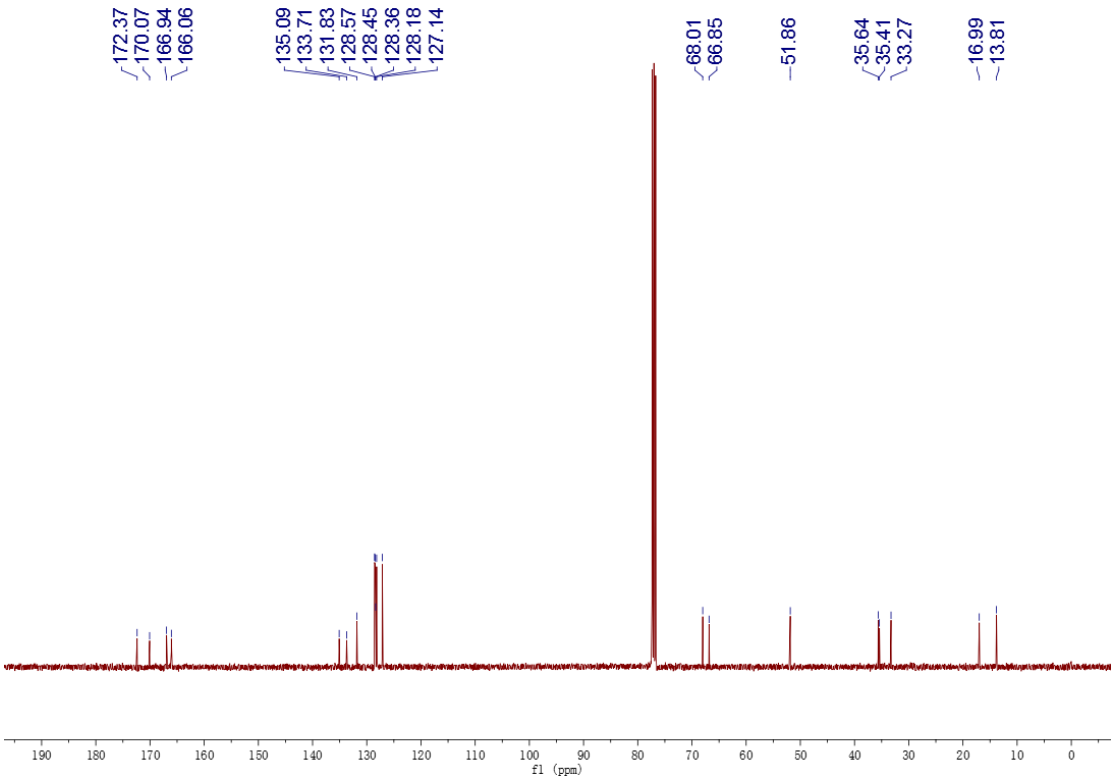
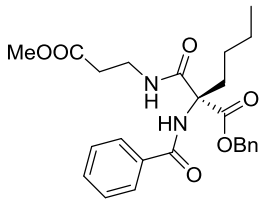
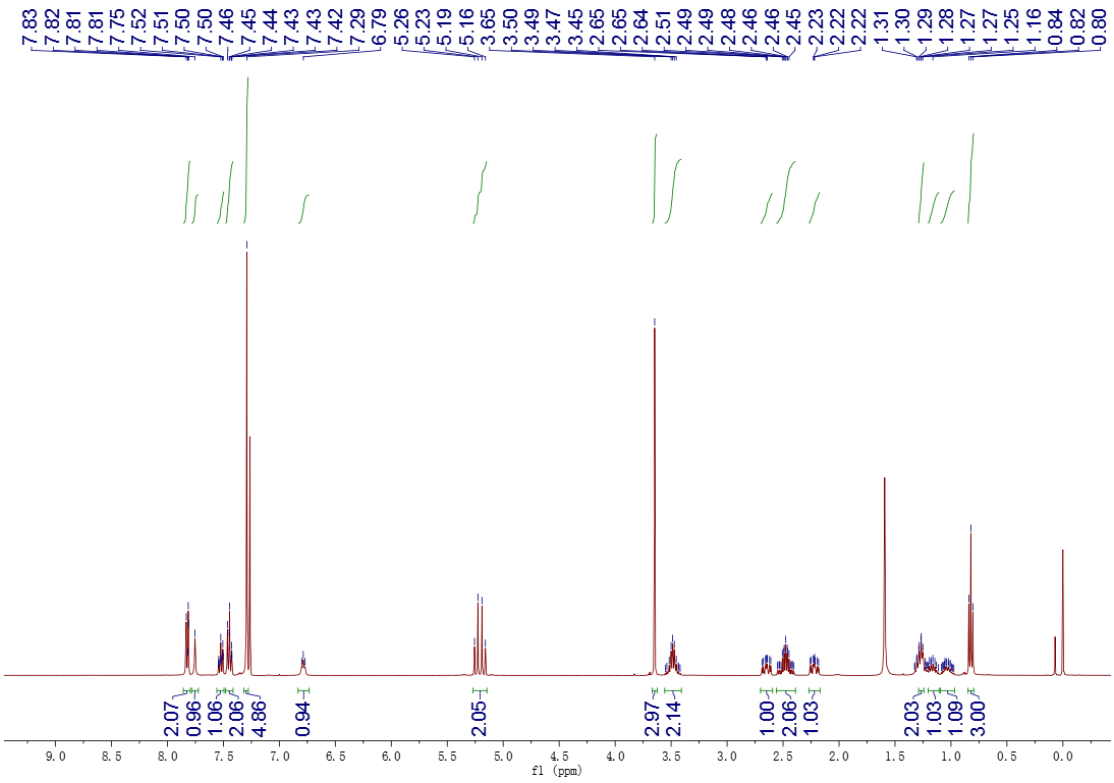
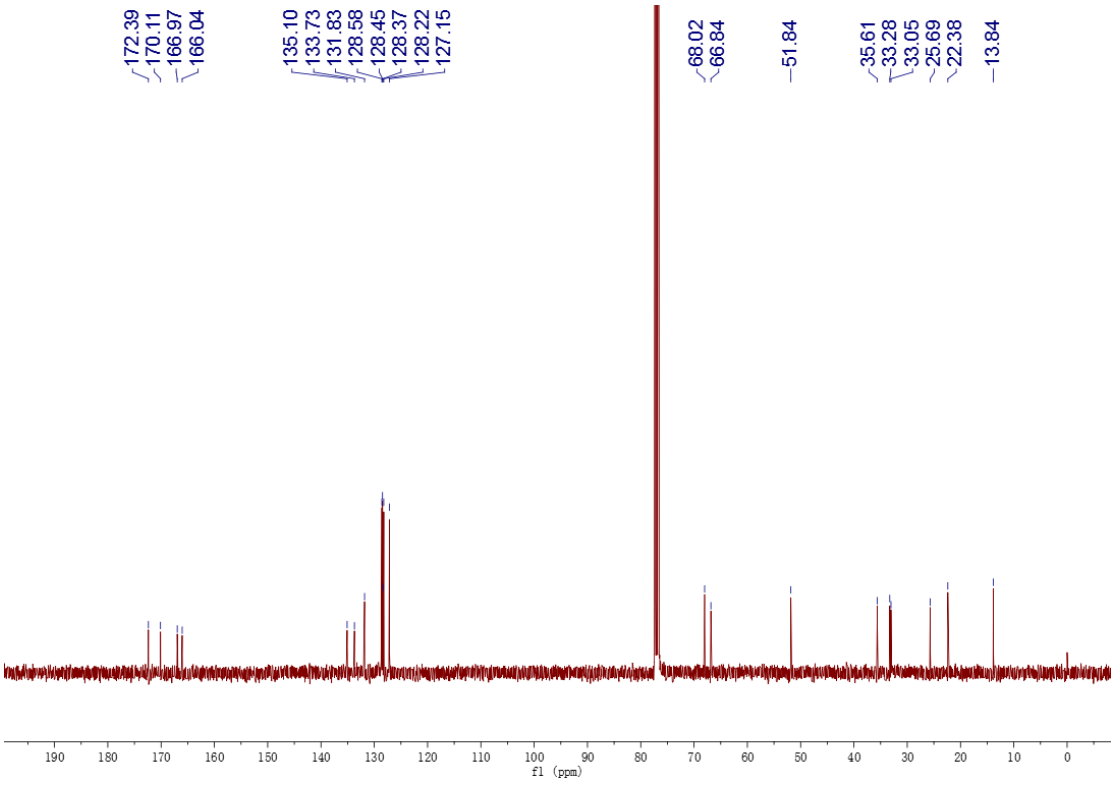
7.81
7.76
7.54
7.52
7.51
7.50
7.50
7.46
7.44
7.43
7.42
7.29
6.78
5.25
5.22
5.19
5.16
3.65
3.51
3.50
3.48
3.48
3.47
3.46
2.65
2.65
2.64
2.64
2.62
2.51
2.49
2.49
2.47
2.46
2.46
2.44
2.23
2.22
2.20
2.20
2.19
1.26
1.22
1.12
0.90
0.88
0.86
1.94
0.90
1.00
1.94
4.72
0.92
1.95
2.83
1.98
0.97
1.96
1.04
1.32
1.07
3.00
f1 (ppm)

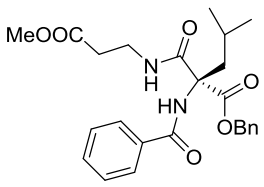

172.37
170.07
166.94
166.06
135.09
133.71
131.83
128.57
128.45
128.36
128.18
127.14
68.01
66.85
51.86
35.64
35.41
33.27
16.99
13.81
f1 (ppm)


MeOOC
N
H
O
HN
O
OBn
O

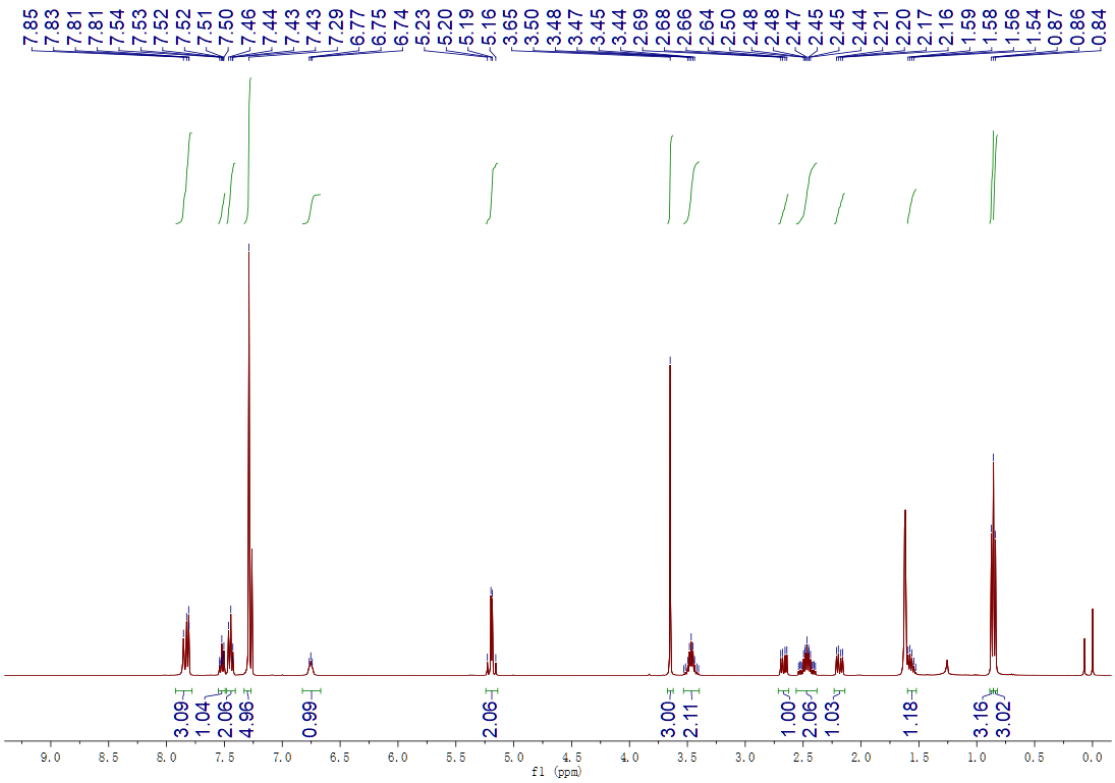
**2ab**


7.83 7.82 7.81 7.81 7.75 7.52 7.51 7.50 7.50 7.46 7.45 7.44 7.43 7.43 7.42 7.29 6.79
5.26 5.23 5.19 5.16 3.65 3.50 3.49 3.47 3.45 2.65 2.65 2.64 2.51 2.49 2.49 2.48 2.46 2.46 2.45 2.23 2.22 2.22 1.31 1.30 1.29 1.28 1.27 1.27 1.25 1.16 0.84 0.82 0.80
2.07 0.96 1.06 2.06 4.86 0.94 2.05 2.97 2.14 1.00 2.06 1.03 2.03 1.03 1.09 3.00
f1 (ppm)


172.39 170.11 166.97 166.04
135.10 133.73 131.83 128.58 128.45 128.37 128.22 127.15
68.02 66.84
51.84
35.61 33.28 33.05 25.69 22.38
13.84
f1 (ppm)


MeOOC
O
N
H
HN
O
OBn
O

**2ac**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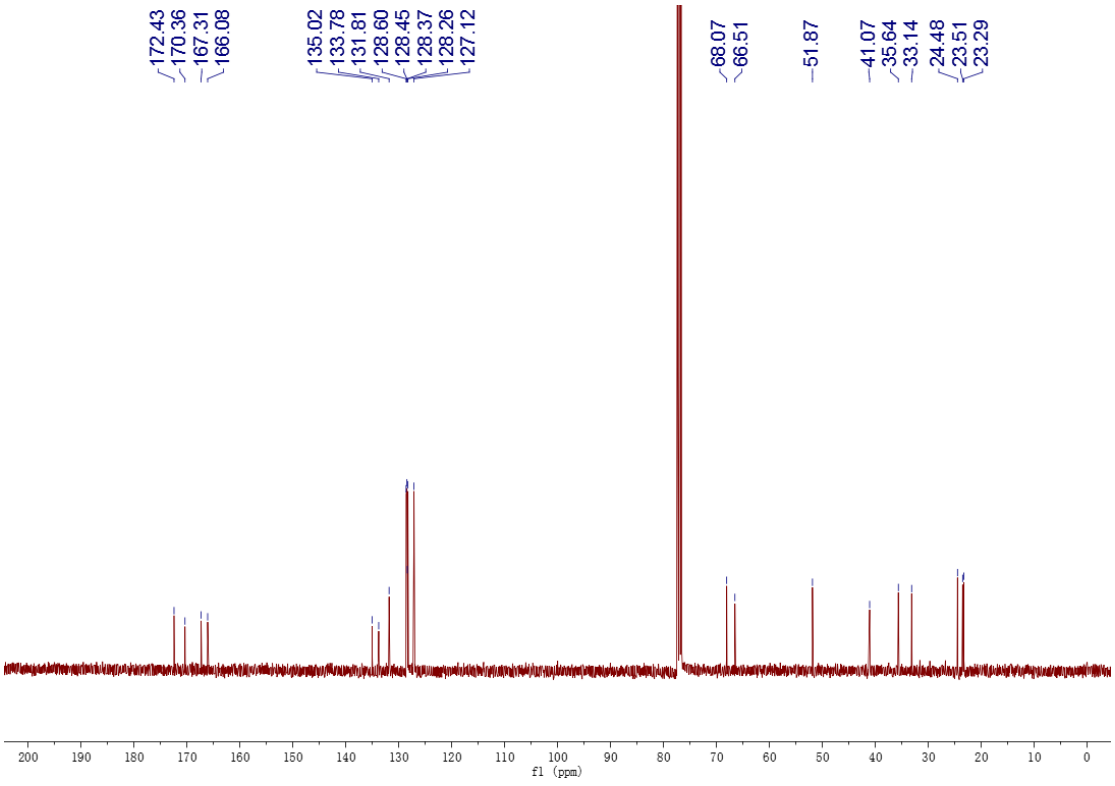
7.52
7.52
7.51
7.50
7.46
7.44
7.43
7.43
7.29
6.77
6.75
6.74
5.23
5.20
5.19
5.16
3.65
3.50
3.48
3.47
3.45
3.44
2.69
2.68
2.66
2.64
2.50
2.48
2.48
2.47
2.45
2.45
2.44
2.21
2.20
2.17
2.16
1.59
1.58
1.56
1.54
0.87
0.86
0.84
3.09
1.04
2.06
4.96
0.99
2.06
3.00
2.11
1.00
2.06
1.03
1.18
3.16
3.02
f1 (ppm)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133.78
131.81
128.60
128.45
128.37
128.26
127.12
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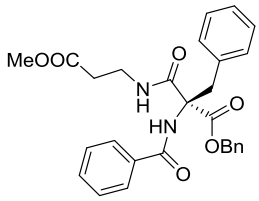
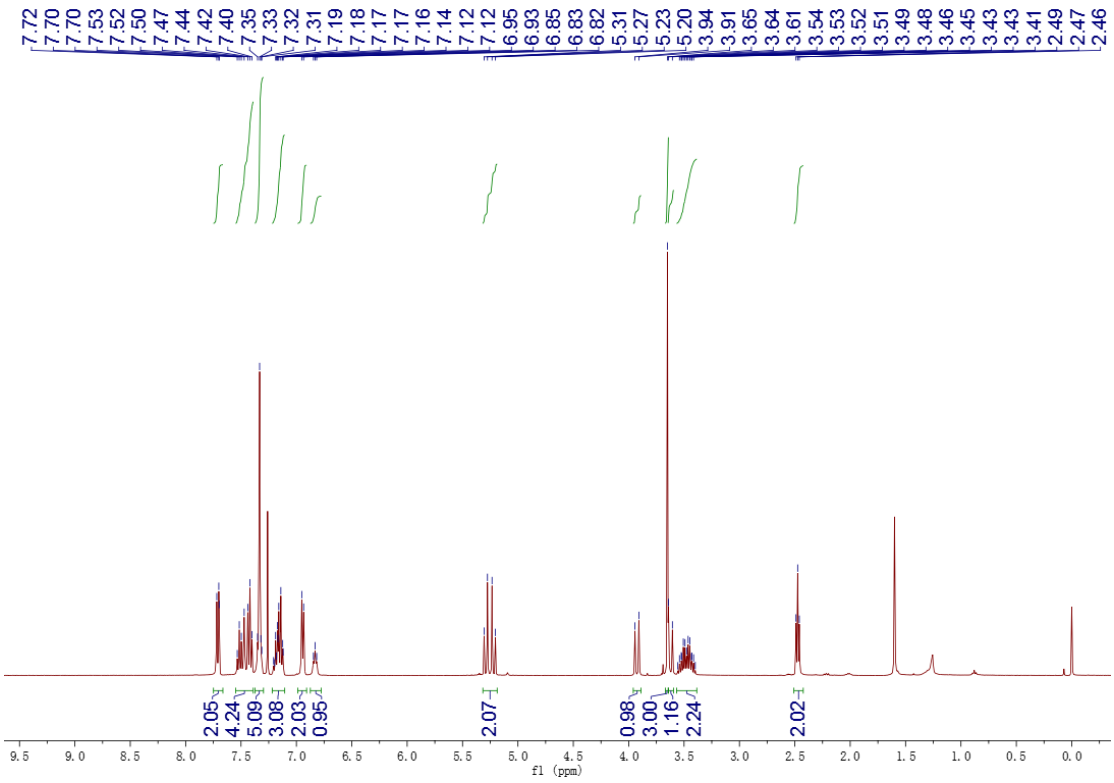
66.51
51.87
41.07
35.64
33.14
24.48
23.51
23.29
f1 (ppm)


MeOOC
N
H
O
HN
O
OBn
O

**2ad**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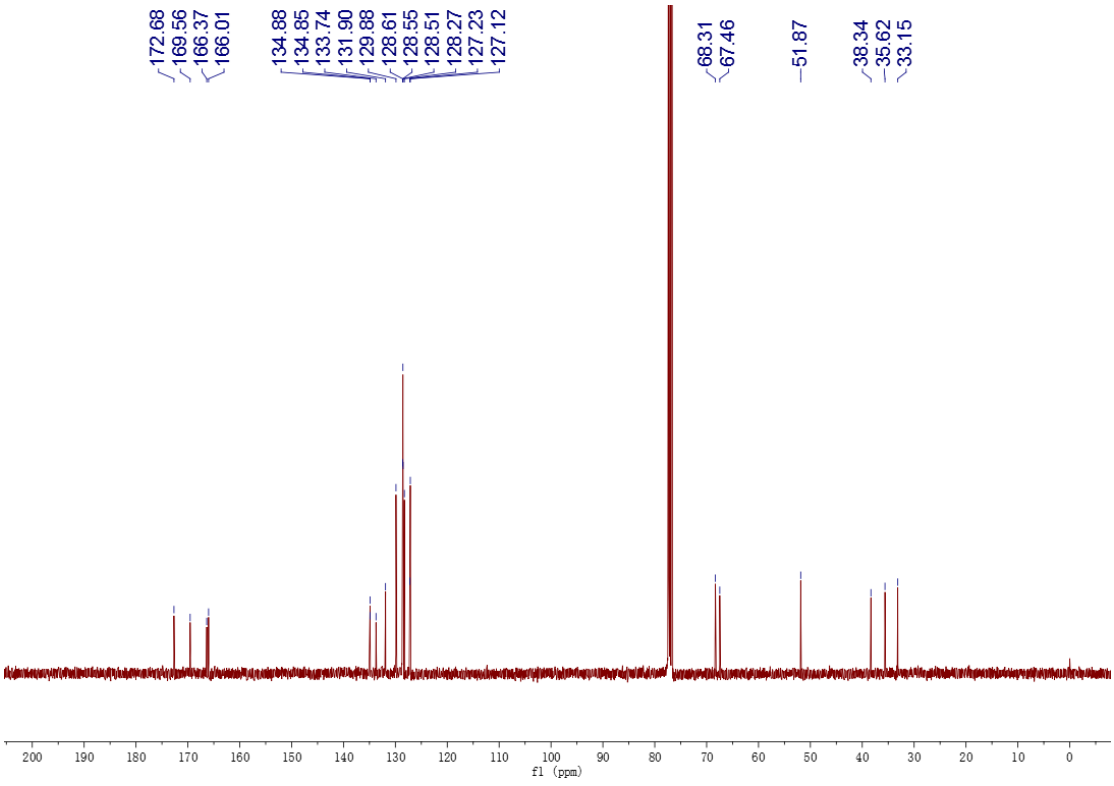
7.35
7.33
7.32
7.31
7.19
7.18
7.17
7.17
7.16
7.14
7.12
7.12
6.95
6.93
6.85
6.83
6.82
5.31
5.27
5.23
5.20
3.94
3.91
3.65
3.64
3.61
3.54
3.53
3.52
3.51
3.49
3.48
3.46
3.45
3.43
3.43
3.41
2.49
2.47
2.46
2.05
4.24
5.09
3.08
2.03
0.95
2.07
0.98
3.00
1.16
2.24
2.02
f1 (ppm)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134.85
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131.90
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128.61
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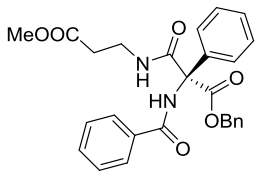
128.51
128.27
127.23
127.12
68.31
67.46
51.87
38.34
35.62
33.15
f1 (ppm)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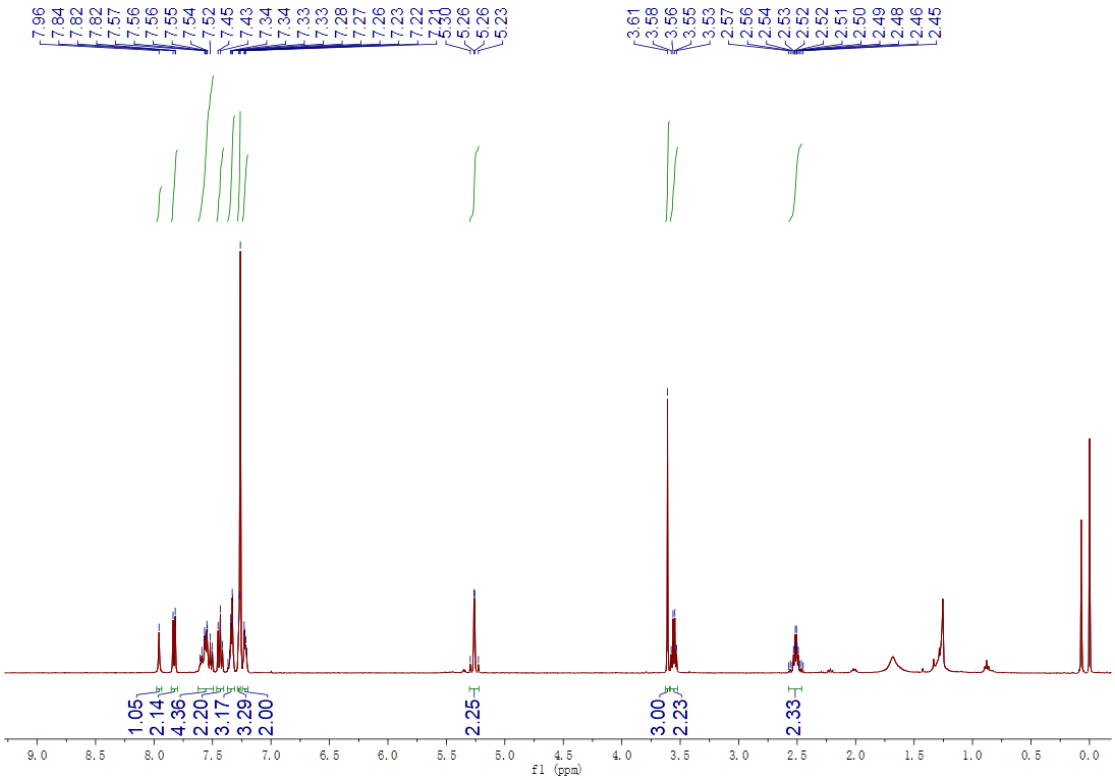
O
N
H
HN
O
O
OBn
O

**2ae**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7.52
7.45
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7.34
7.34
7.33
7.33
7.28
7.27
7.26
7.23
7.22
7.21
5.30
5.26
5.26
5.23
3.61
3.58
3.56
3.55
3.53
2.57
2.56
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2.53
2.52
2.52
2.51
2.50
2.49
2.48
2.46
2.45
1.05
2.14
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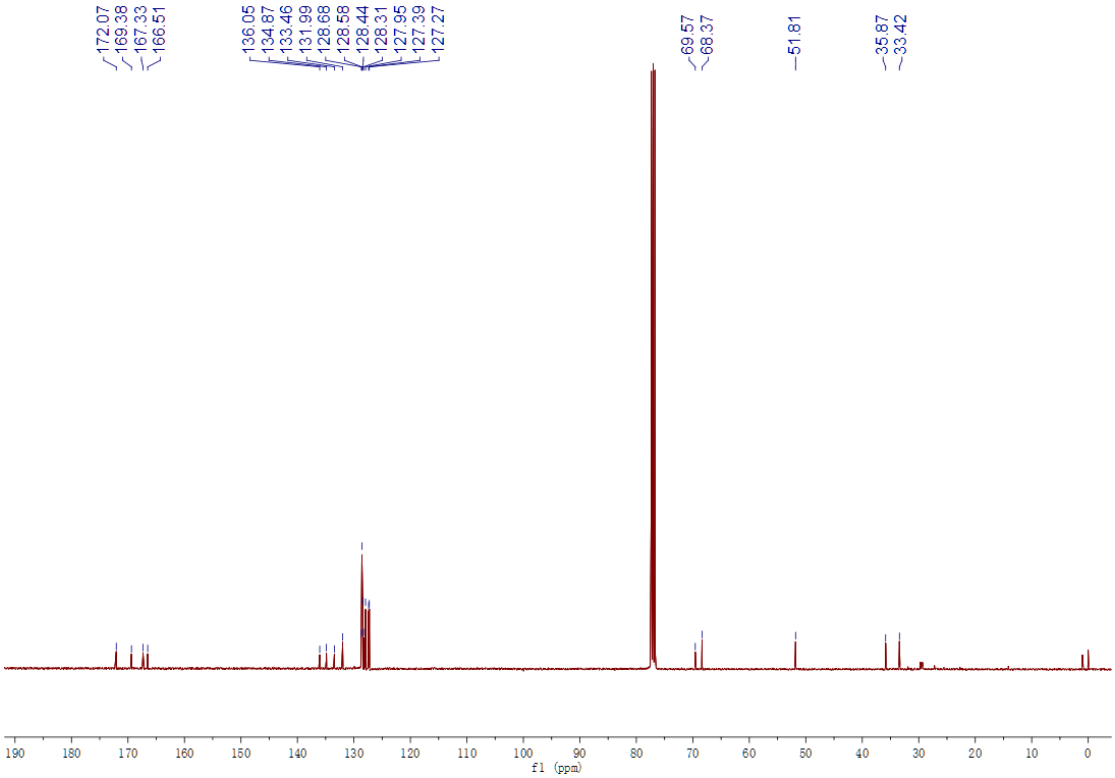
2.20
3.17
3.29
2.00
2.25
3.00
2.23
2.33
f1 (ppm)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169.38
167.33
166.51
136.05
134.87
133.46
131.99
128.68
128.58
128.44
128.31
127.95
127.39
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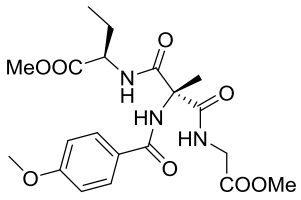
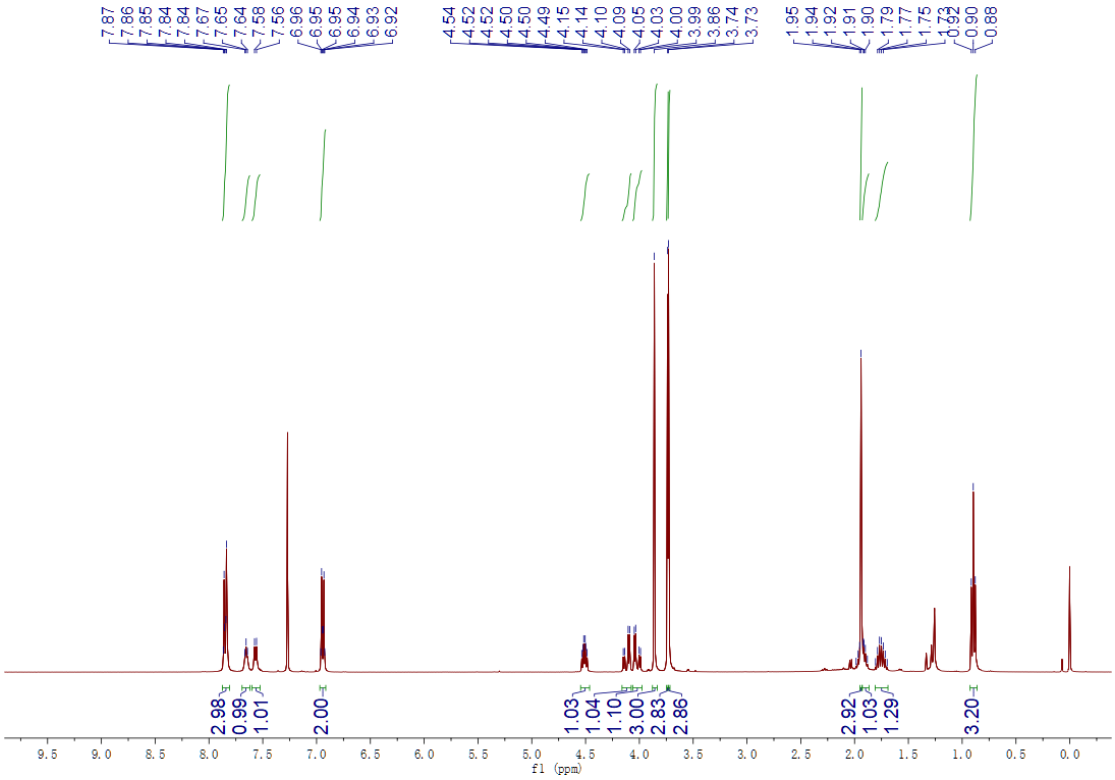
68.37
51.81
35.87
33.42
f1 (ppm)


MeOOC
N
H
O
HN
O
HN
O
O
COOMe

**7a**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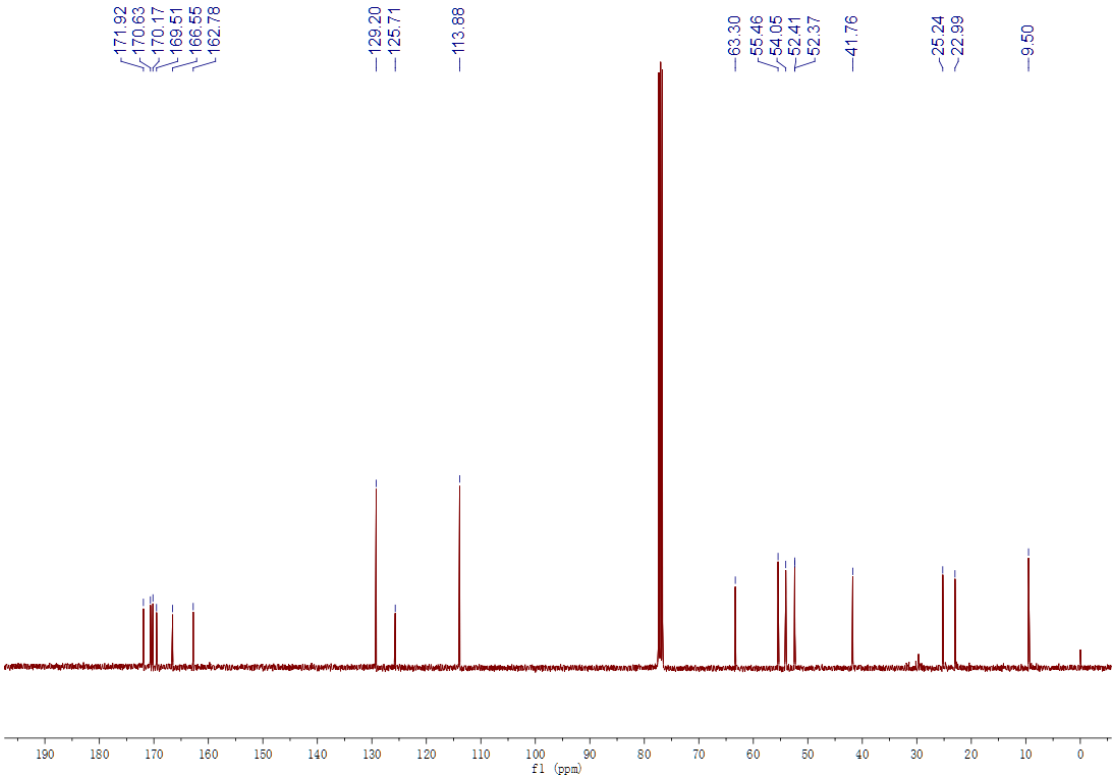
6.96
6.95
6.95
6.94
6.93
6.92
4.54
4.52
4.52
4.50
4.50
4.49
4.15
4.14
4.10
4.09
4.05
4.03
4.00
3.99
3.86
3.74
3.73
1.95
1.94
1.92
1.91
1.90
1.79
1.77
1.75
0.92
0.90
0.88
2.98
0.99
1.01
2.00
1.03
1.04
1.10
3.00
2.83
2.86
2.92
1.03
1.29
3.20
f1 (ppm)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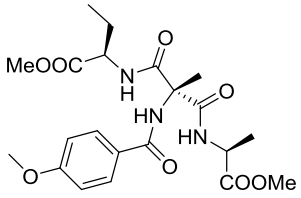
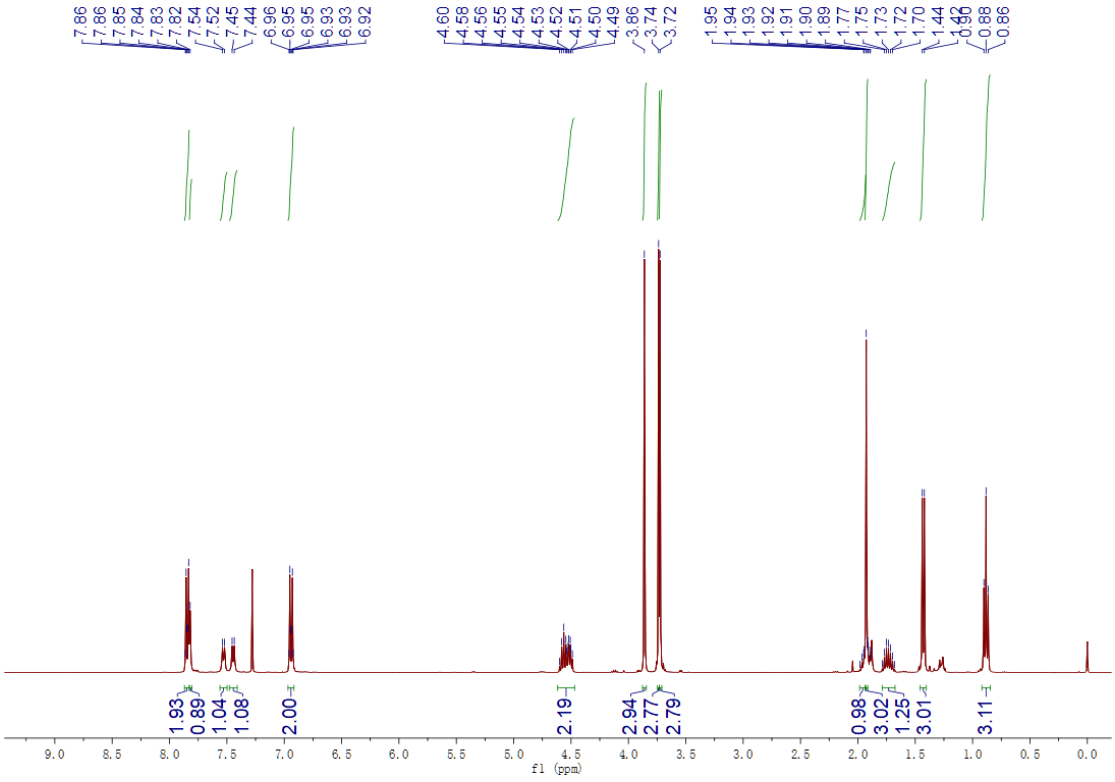
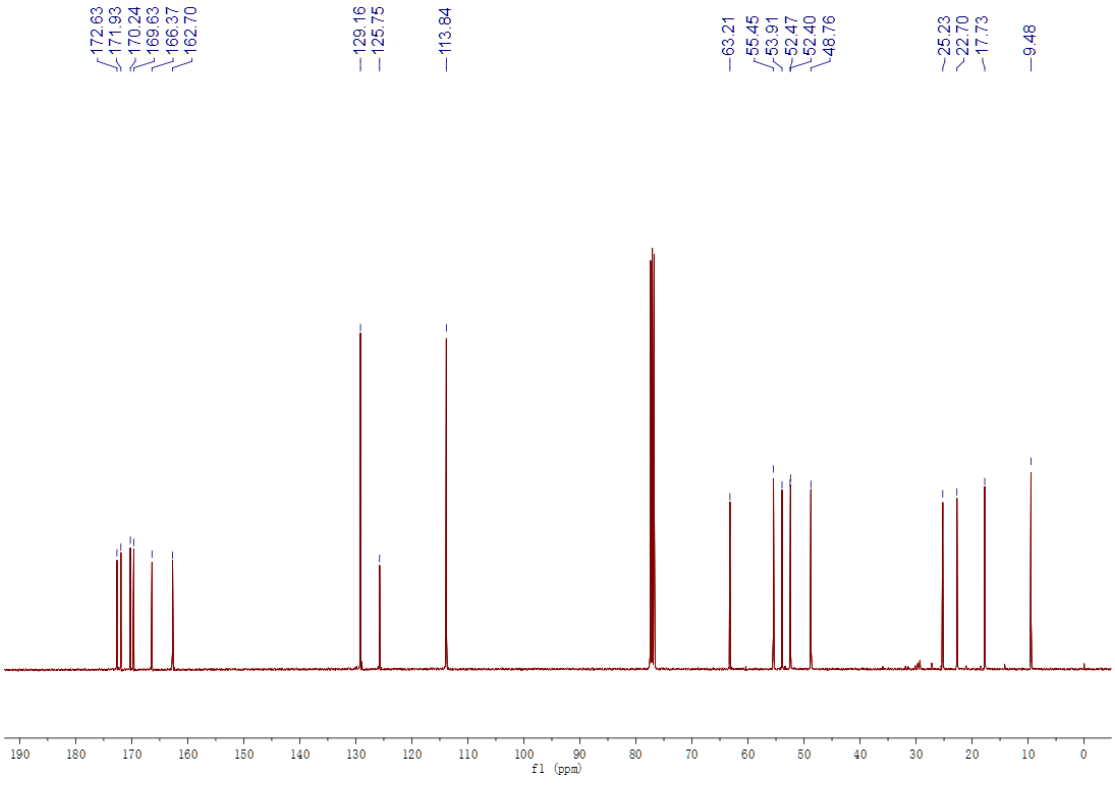
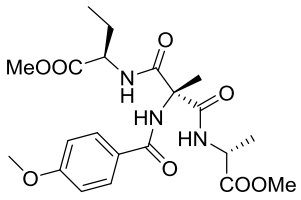
170.63
170.17
169.51
166.55
162.78
129.20
125.71
113.88
63.30
55.46
54.05
52.41
52.37
41.76
25.24
22.99
9.50
f1 (ppm)


MeOOC
N
H
O
HN
O
HN
O
O
COOMe

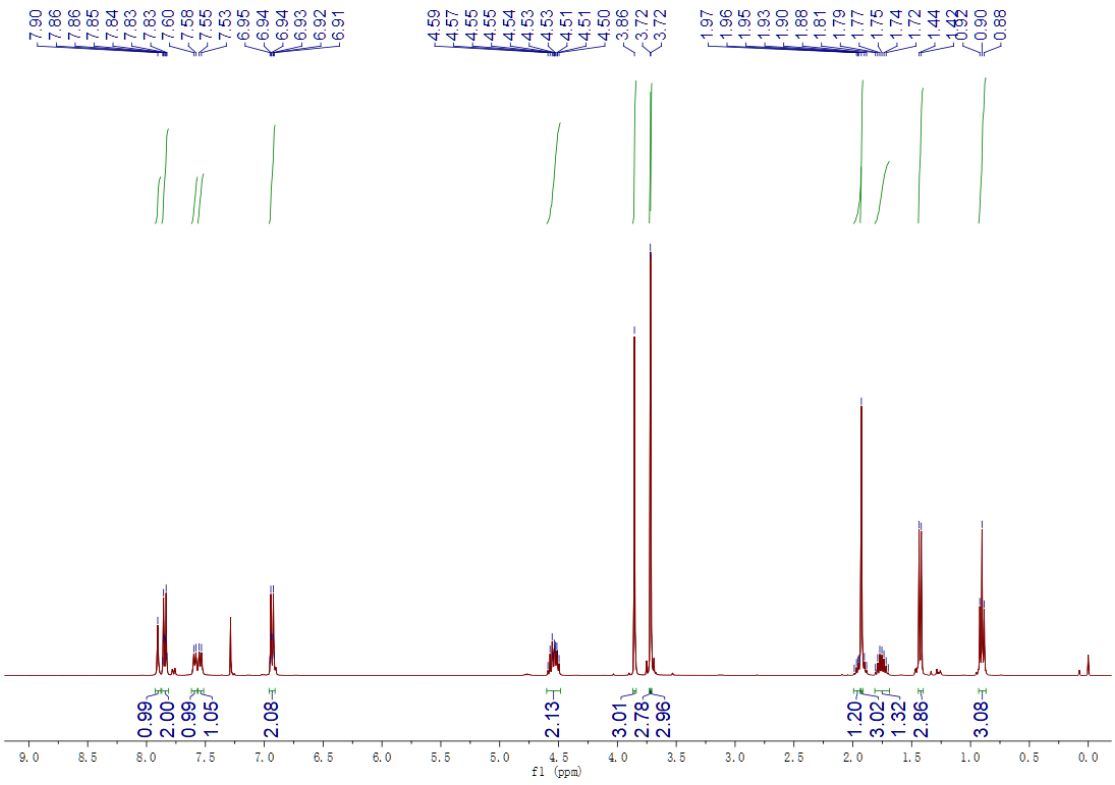
**7b**

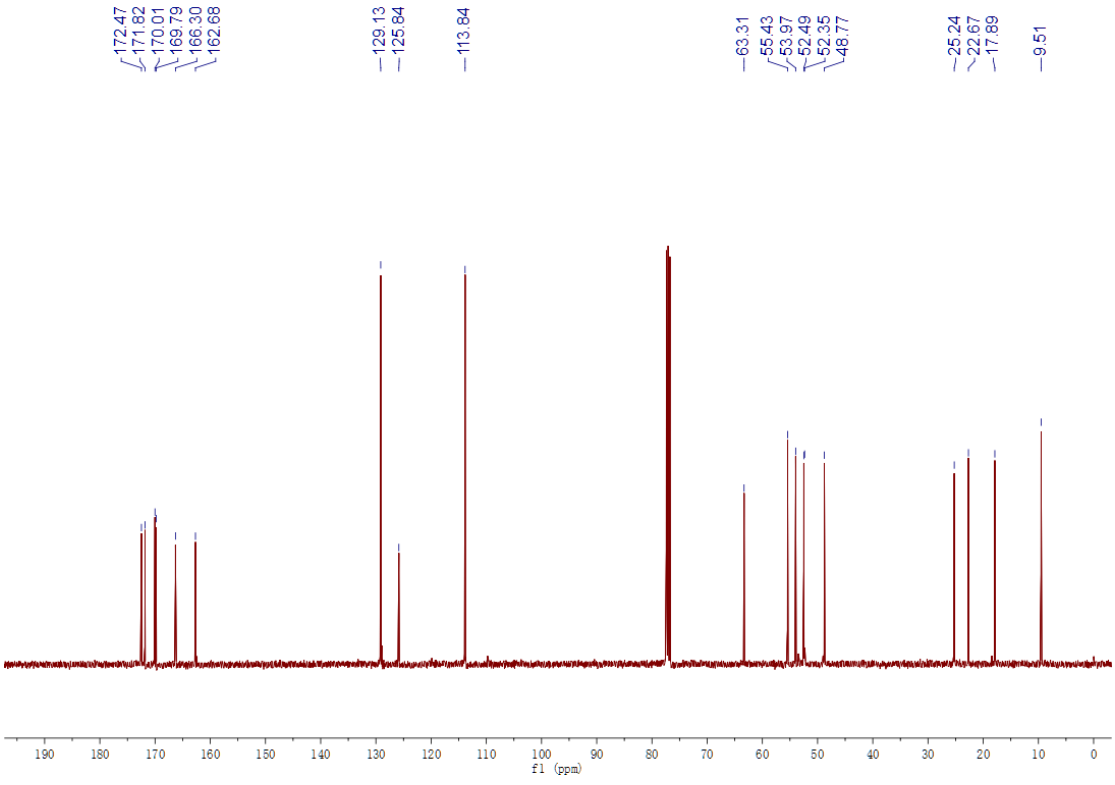

7.86
7.86
7.85
7.84
7.83
7.82
7.54
7.52
7.45
7.44
6.96
6.95
6.95
6.93
6.93
6.92
4.60
4.58
4.56
4.55
4.54
4.53
4.52
4.51
4.50
4.49
3.86
3.74
3.72
1.95
1.94
1.93
1.92
1.91
1.90
1.89
1.77
1.75
1.73
1.72
1.70
1.44
0.90
0.88
0.86
1.93
0.89
1.04
1.08
2.00
2.19
2.94
2.77
2.79
0.98
3.02
1.25
3.01
3.11
f1 (ppm)

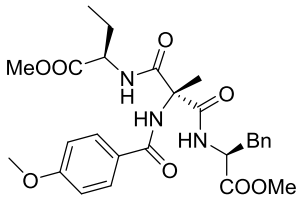

172.63
171.93
170.24
169.63
166.37
162.70
129.16
125.75
113.84
63.21
55.45
53.91
52.47
52.40
48.76
25.23
22.70
17.73
9.48
f1 (ppm)


MeOOC
N
H
O
HN
O
HN
O
O
COOMe

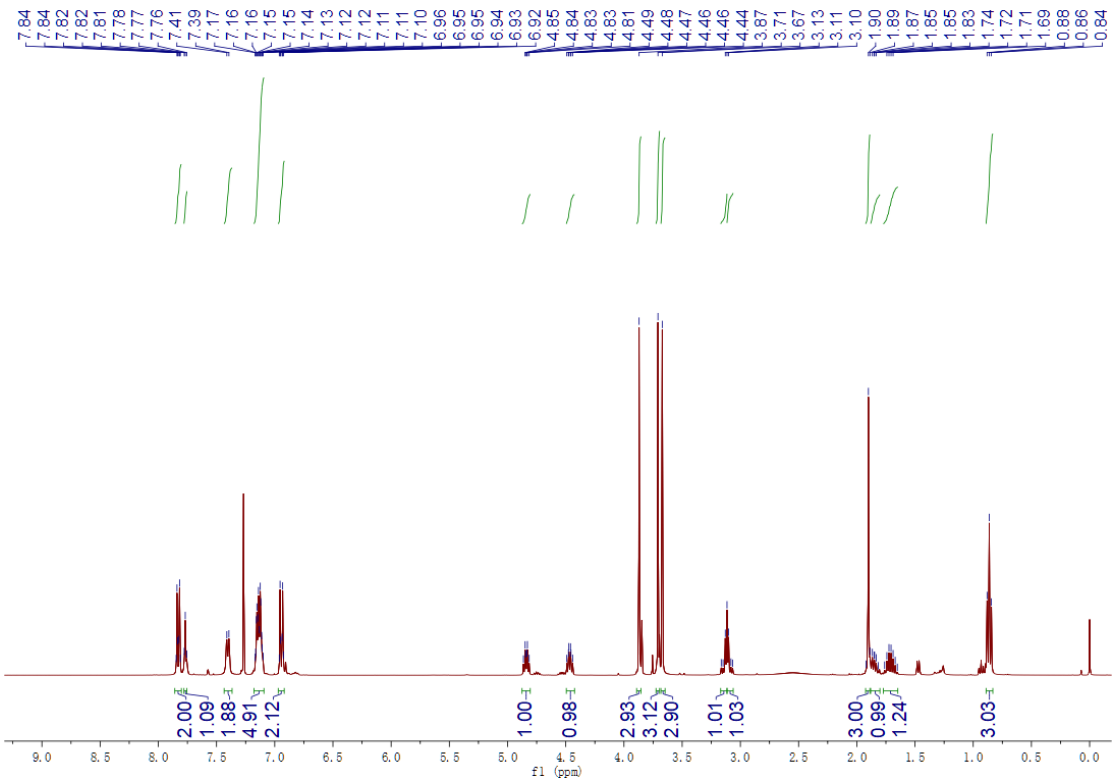
**7c**

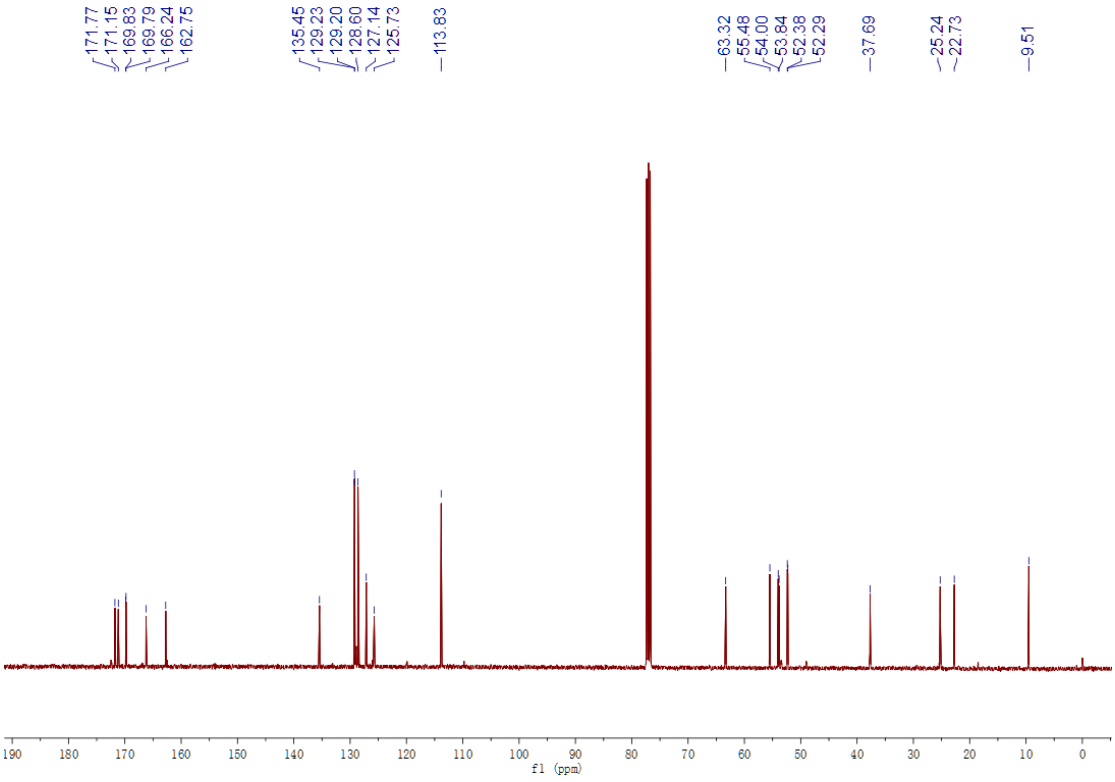

7.90
7.86
7.86
7.85
7.84
7.83
7.83
7.60
7.58
7.55
7.53
6.95
6.94
6.94
6.93
6.92
6.91
4.59
4.57
4.55
4.55
4.54
4.53
4.53
4.51
4.51
4.50
3.86
3.72
3.72
1.97
1.96
1.95
1.93
1.90
1.88
1.81
1.79
1.77
1.75
1.74
1.72
1.44
0.92
0.90
0.88
0.99
2.00
0.99
1.05
2.08
2.13
3.01
2.78
2.96
1.20
3.02
1.32
2.86
3.08
f1 (ppm)

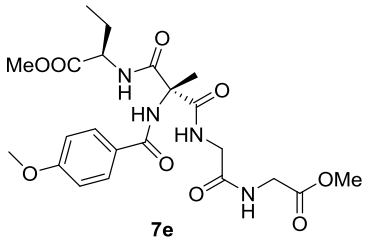

172.47
171.82
170.01
169.79
166.30
162.68
129.13
125.84
113.84
63.31
55.43
53.97
52.49
52.35
48.77
25.24
22.67
17.89
9.51
f1 (ppm)


MeOOC
N
H
O
HN
O
HN
Bn
O
O
COOMe

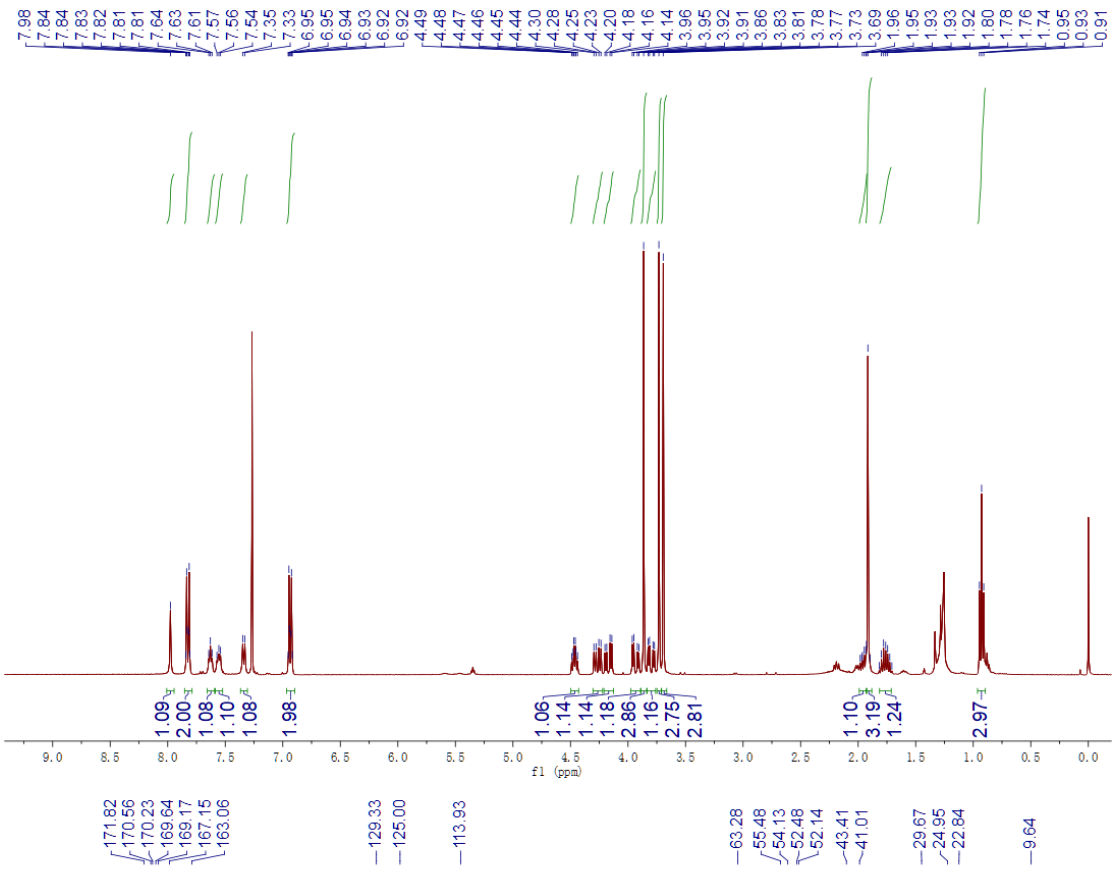
**7d**


7.84 7.84 7.82 7.82 7.81 7.78 7.77 7.76 7.41 7.39 7.17 7.16 7.16 7.15 7.15 7.14 7.13 7.12 7.12 7.11 7.11 7.10 6.96 6.95 6.95 6.94 6.93 6.92 4.85 4.84 4.83 4.83 4.81 4.49 4.48 4.47 4.46 4.46 4.44 3.87 3.71 3.67 3.13 3.11 3.10 1.90 1.89 1.87 1.85 1.85 1.83 1.74 1.72 1.71 1.69 0.88 0.86 0.84
2.00 1.09 1.88 4.91 2.12 1.00 0.98 2.93 3.12 2.90 1.01 1.03 3.00 0.99 1.24 3.03
f1 (ppm)

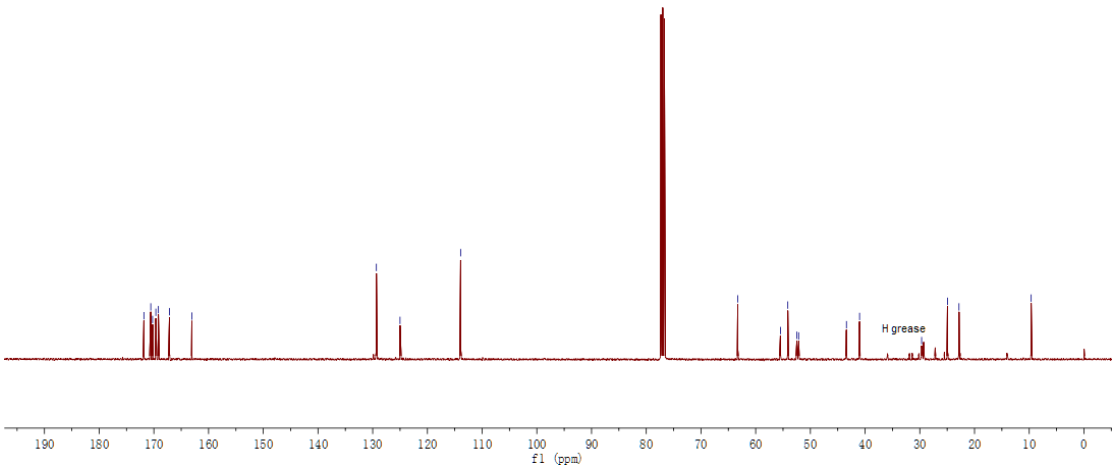

171.77 171.15 169.83 169.79 166.24 162.75 135.45 129.23 129.20 128.60 127.14 125.73 113.83 63.32 55.48 54.00 53.84 52.38 52.29 37.69 25.24 22.73 9.51
f1 (ppm)

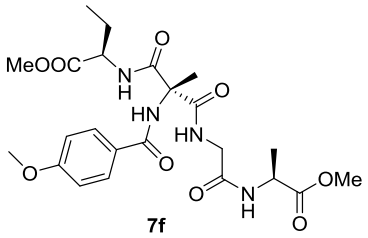

MeOOC
O
N
H
HN
O
HN
O
O
O
N
H
OMe
O

**7e**

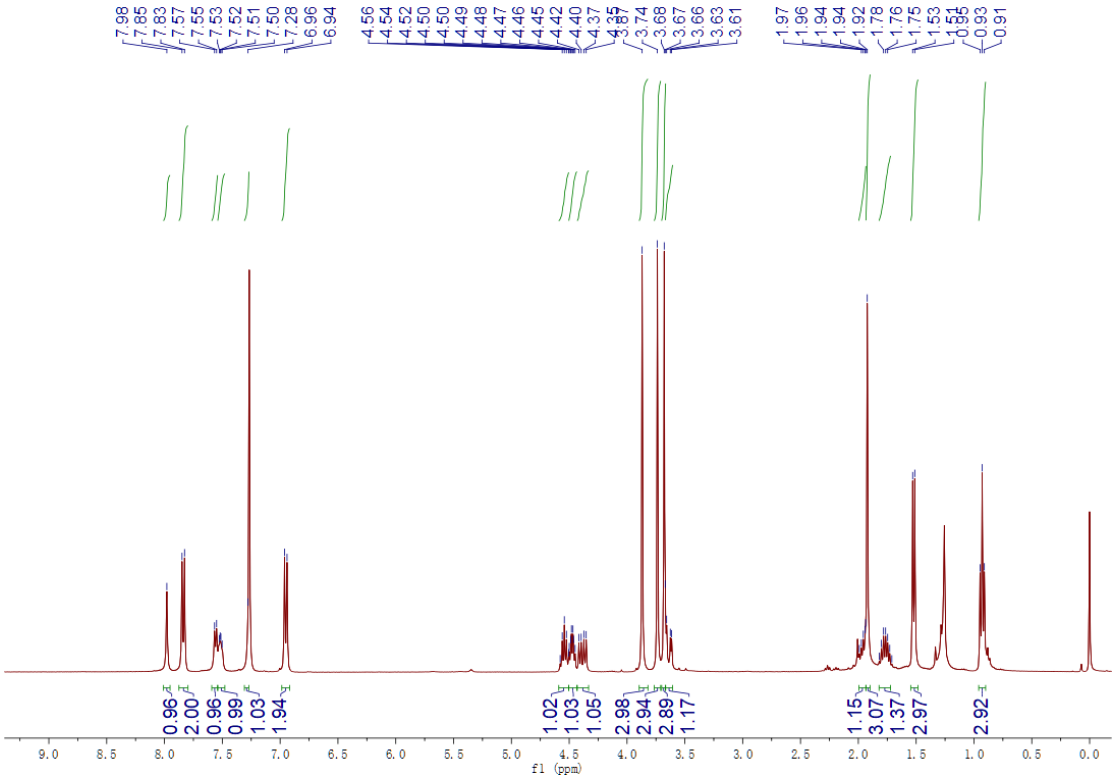

7.98 7.84 7.84 7.83 7.82 7.81 7.81 7.64 7.63 7.61 7.57 7.56 7.54 7.35 7.33 6.95 6.95 6.94 6.93 6.92 6.92
4.49 4.48 4.47 4.46 4.45 4.44 4.30 4.28 4.25 4.23 4.20 4.18 4.16 4.14 3.96 3.95 3.92 3.91 3.86 3.83 3.81 3.78 3.77 3.73 3.69 1.96 1.95 1.93 1.93 1.92 1.80 1.78 1.76 1.74 0.95 0.93 0.91
1.09 2.00 1.08 1.10 1.08 1.98
1.06 1.14 1.14 1.18 2.86 1.16 2.75 2.81
1.10 3.19 1.24
2.97
f1 (ppm)

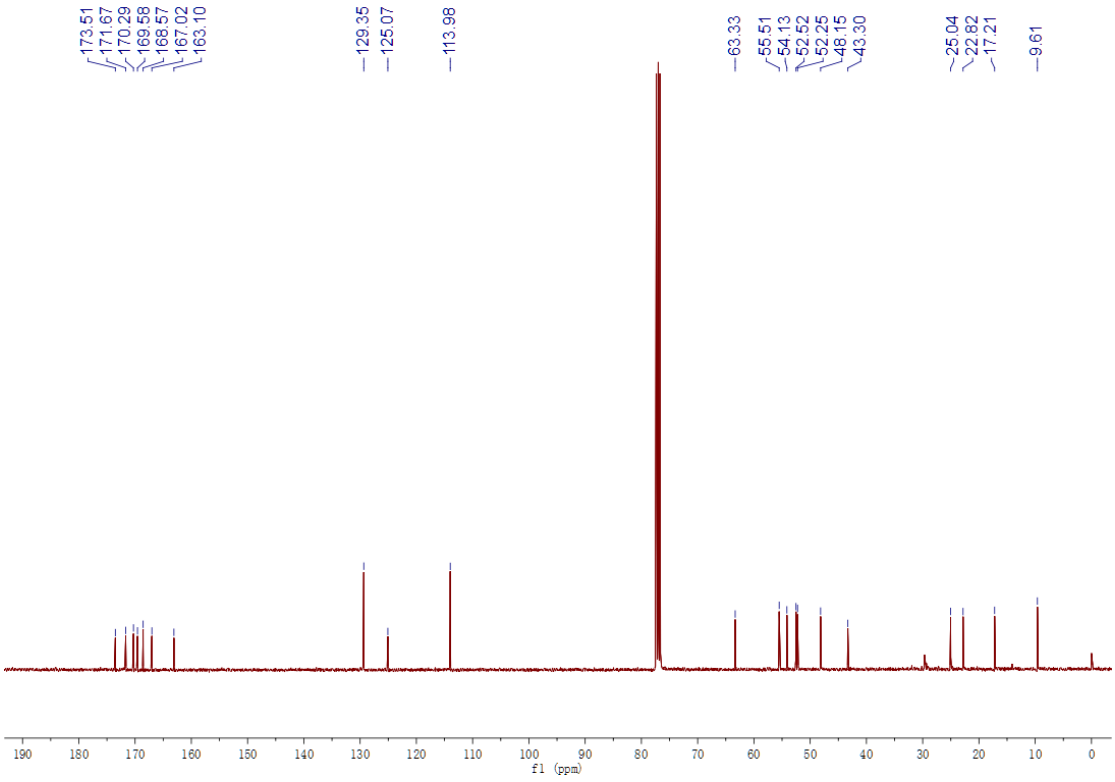

171.82 170.56 170.23 169.64 169.17 167.15 163.06
129.33 125.00 113.93
63.28 55.48 54.13 52.48 52.14 43.41 41.01
29.67 24.95 22.84
9.64

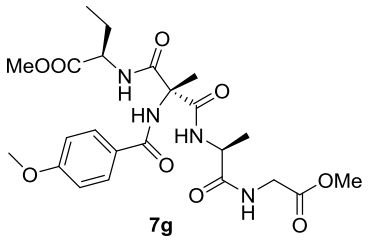

H grease
f1 (ppm)


MeOOC
N
H
O
HN
O
HN
O
O
N
H
OMe
O
O

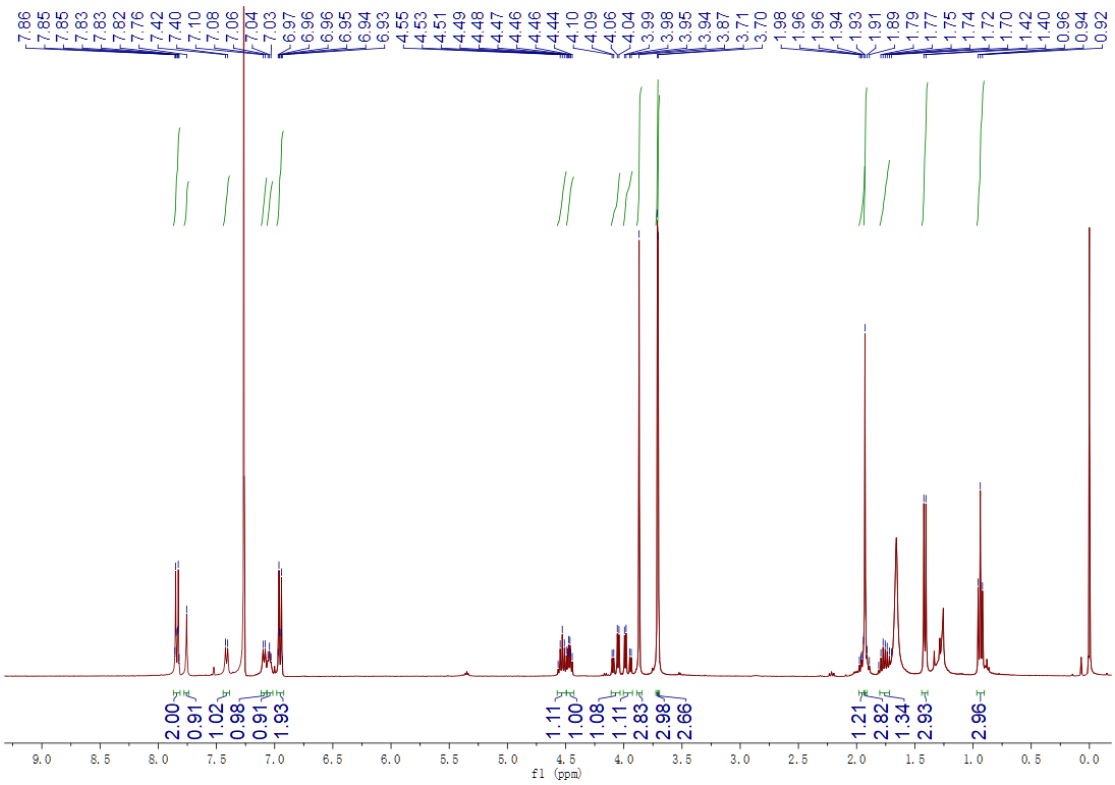
**7f**

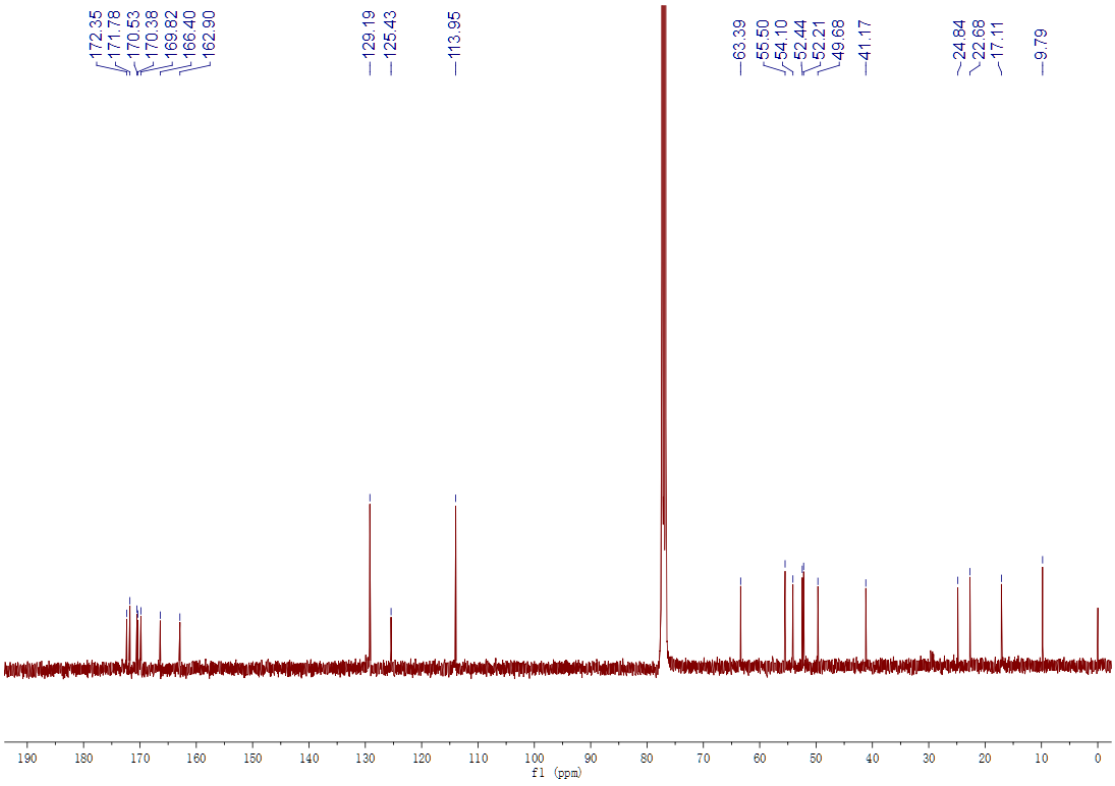

7.98
7.85
7.83
7.57
7.55
7.53
7.52
7.51
7.50
7.28
6.96
6.94
4.56
4.54
4.52
4.50
4.50
4.49
4.48
4.47
4.46
4.45
4.42
4.40
4.37
3.74
3.68
3.67
3.66
3.63
3.61
1.97
1.96
1.94
1.94
1.92
1.78
1.76
1.75
1.53
0.95
0.93
0.91
0.96
2.00
0.96
0.99
1.03
1.94
1.02
1.03
1.05
2.98
2.94
2.89
1.17
1.15
3.07
1.37
2.97
2.92
f1 (ppm)

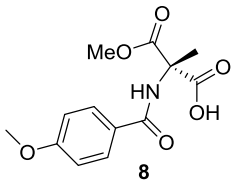

173.51
171.67
170.29
169.58
168.57
167.02
163.10
129.35
125.07
113.98
63.33
55.51
54.13
52.52
52.25
48.15
43.30
25.04
22.82
17.21
9.61
f1 (ppm)


MeOOC
N
H
O
HN
O
HN
O
O
O
N
H
OMe
O

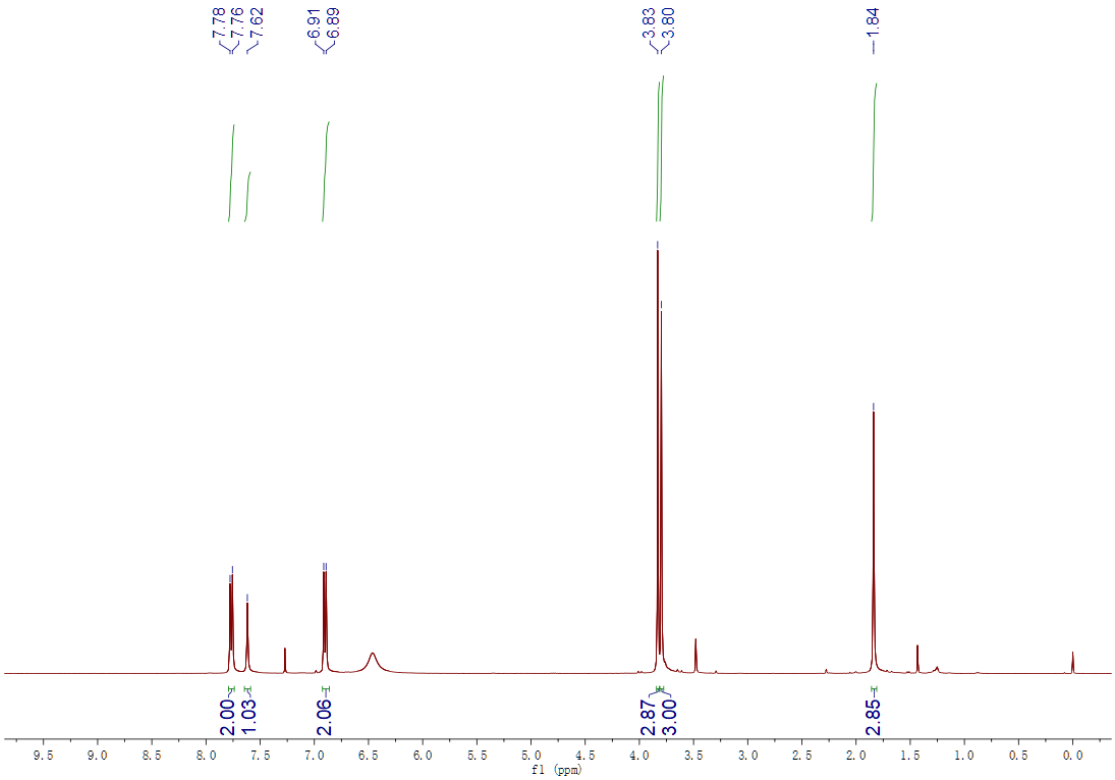
**7g**

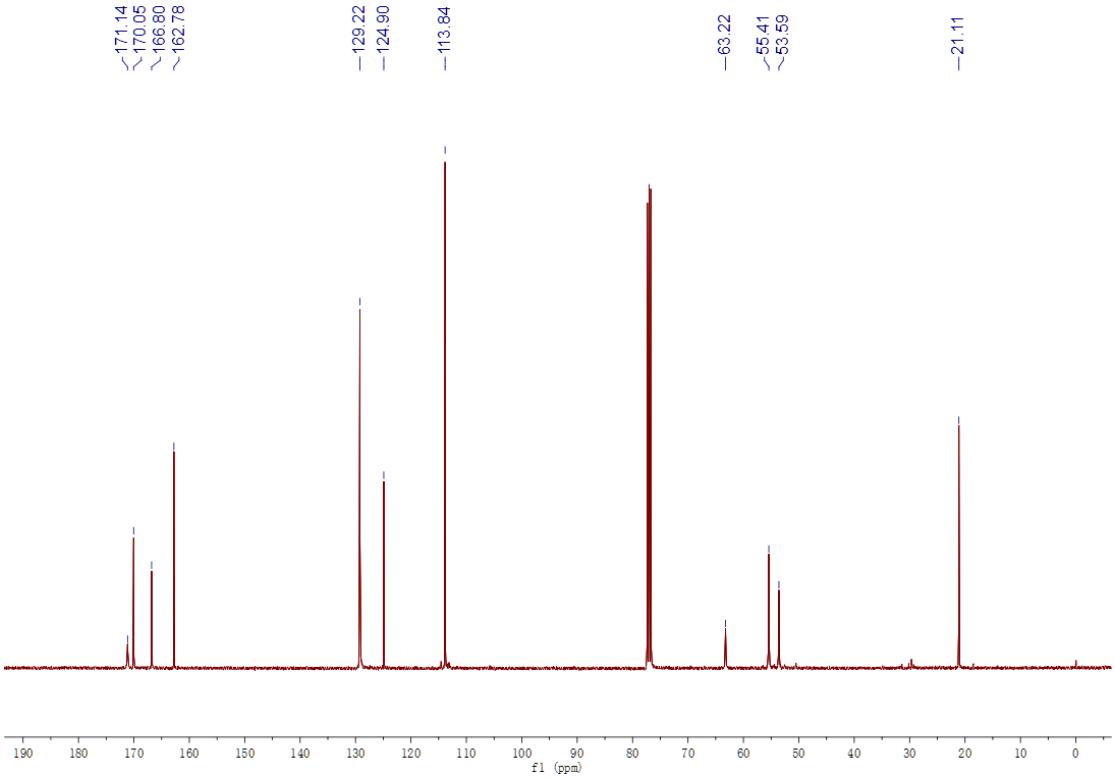

7.86 7.85 7.85 7.83 7.83 7.82 7.76 7.42 7.40 7.10 7.08 7.06 7.04 7.03 6.97 6.96 6.96 6.95 6.94 6.93
4.55 4.53 4.51 4.49 4.48 4.47 4.46 4.46 4.44 4.10 4.09 4.06 4.04 3.99 3.98 3.95 3.94 3.87 3.71 3.70
1.98 1.96 1.96 1.94 1.93 1.91 1.89 1.79 1.77 1.75 1.74 1.72 1.70 1.42 1.40 0.96 0.94 0.92
2.00 0.91 1.02 0.98 0.91 1.93 1.11 1.00 1.08 1.11 2.83 2.98 2.66 1.21 2.82 1.34 2.93 2.96
f1 (ppm)

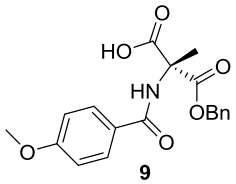

172.35 171.78 170.53 170.38 169.82 166.40 162.90
129.19 125.43 113.95
63.39 55.50 54.10 52.44 52.21 49.68 41.17
24.84 22.68 17.11 9.79
f1 (ppm)


MeO
O
HN
O
OH
O
O

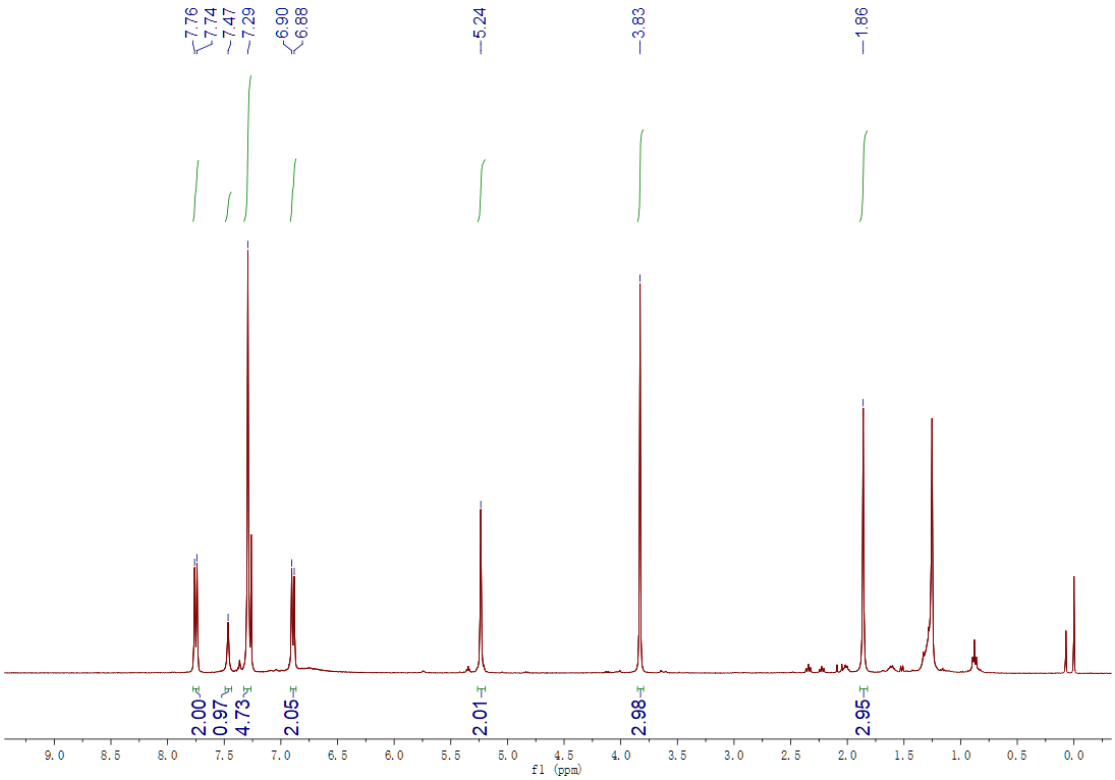
**8**

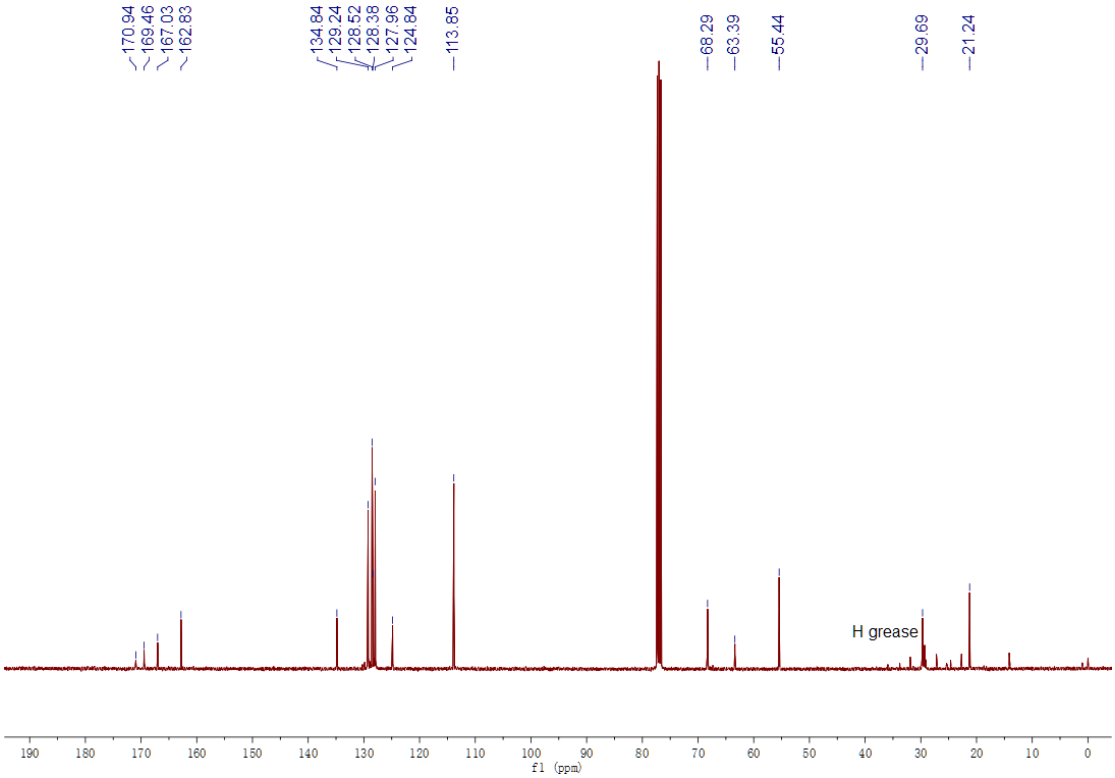

7.78
7.76
7.62
6.91
6.89
3.83
3.80
1.84
2.00
1.03
2.06
2.87
3.00
2.85
f1 (ppm)

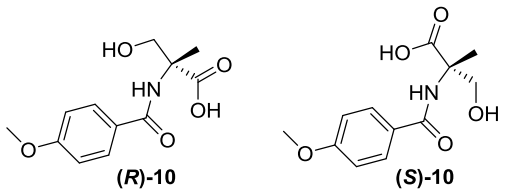

171.14
170.05
166.80
162.78
129.22
124.90
113.84
63.22
55.41
53.59
21.11
f1 (ppm)

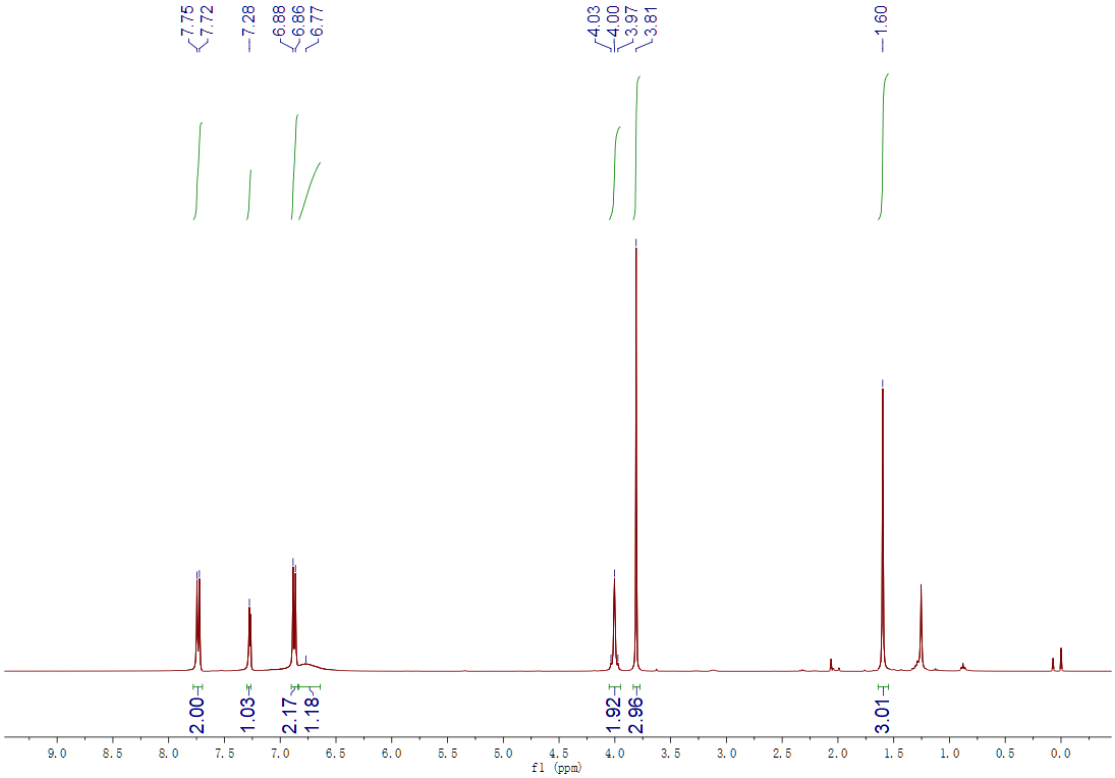

HO
O
HN
O
OBn
O
O

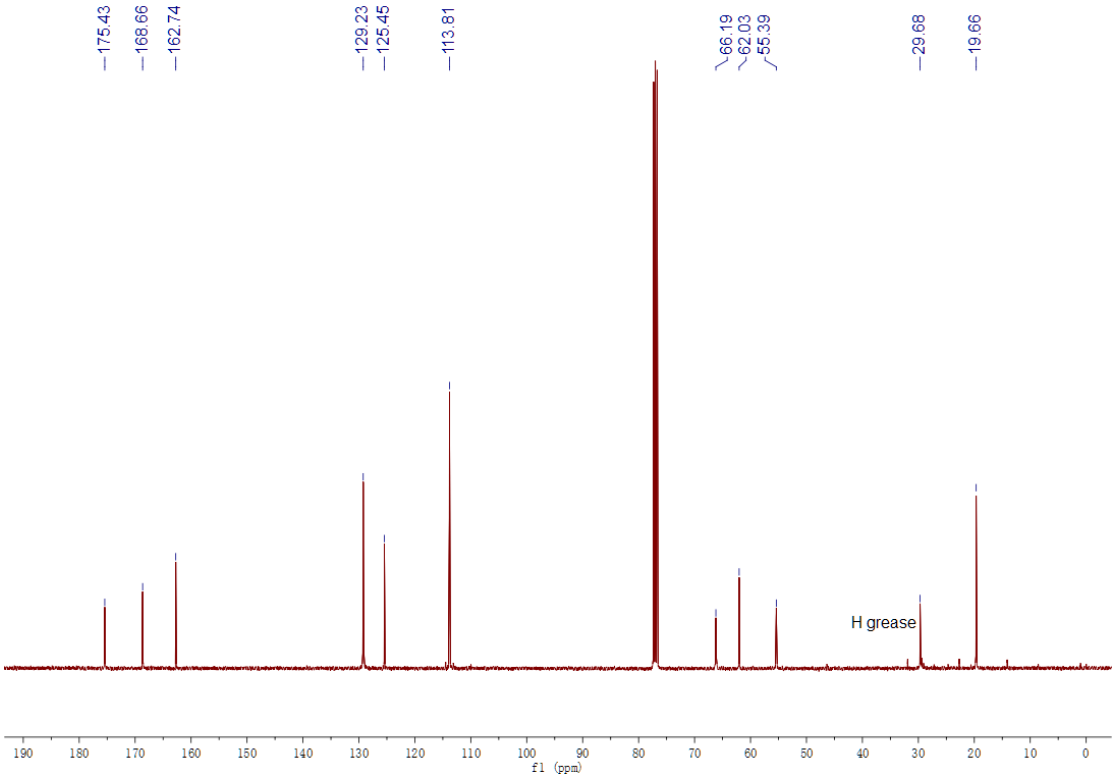
**9**

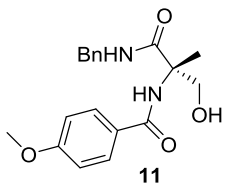

7.76
7.74
7.47
7.29
6.90
6.88
5.24
3.83
1.86
2.00
0.97
4.73
2.05
2.01
2.98
2.95
f1 (ppm)


170.94
169.46
167.03
162.83
134.84
129.24
128.52
128.38
127.96
124.84
113.85
68.29
63.39
55.44
29.69
21.24
H grease
f1 (ppm)

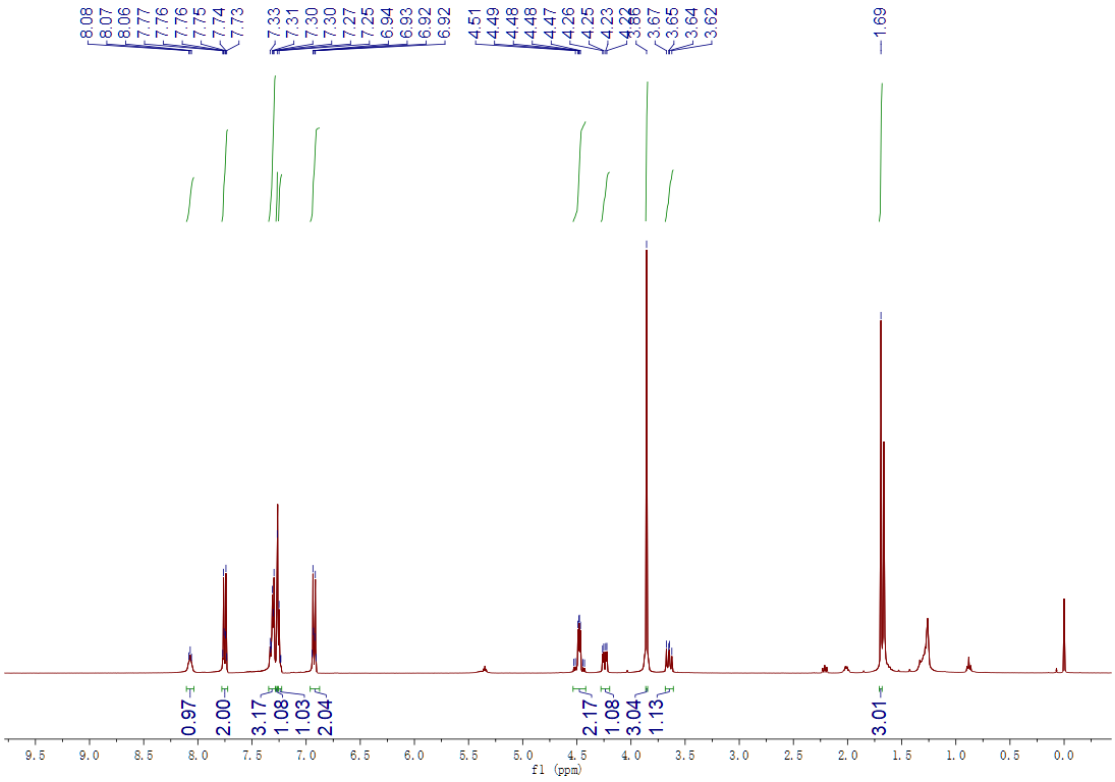

HO
HN
O
OH
O
O
(R)-10
HO
O
HN
OH
O
O
(S)-10

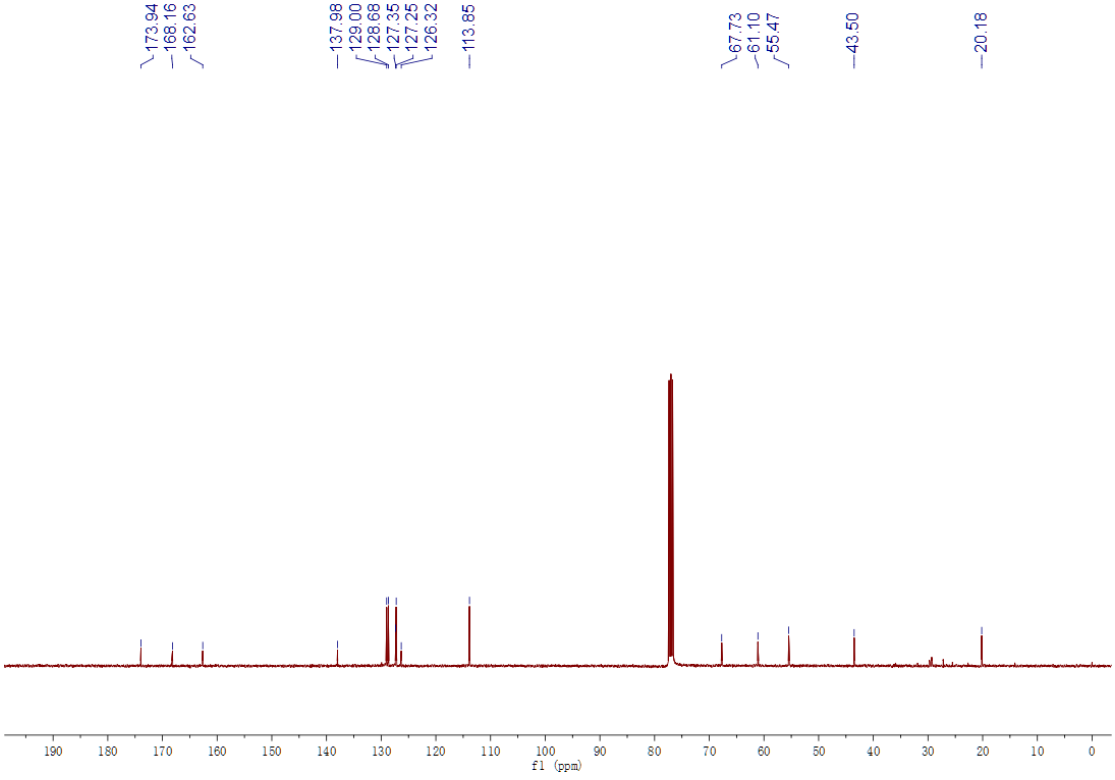

7.75
7.72
7.28
6.88
6.86
6.77
4.03
4.00
3.97
3.81
1.60
2.00
1.03
2.17
1.18
1.92
2.96
3.01
f1 (ppm)

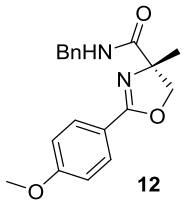

175.43
168.66
162.74
129.23
125.45
113.81
66.19
62.03
55.39
29.68
19.66
H grease
f1 (ppm)


O
BnHN
HN
OH
O
O

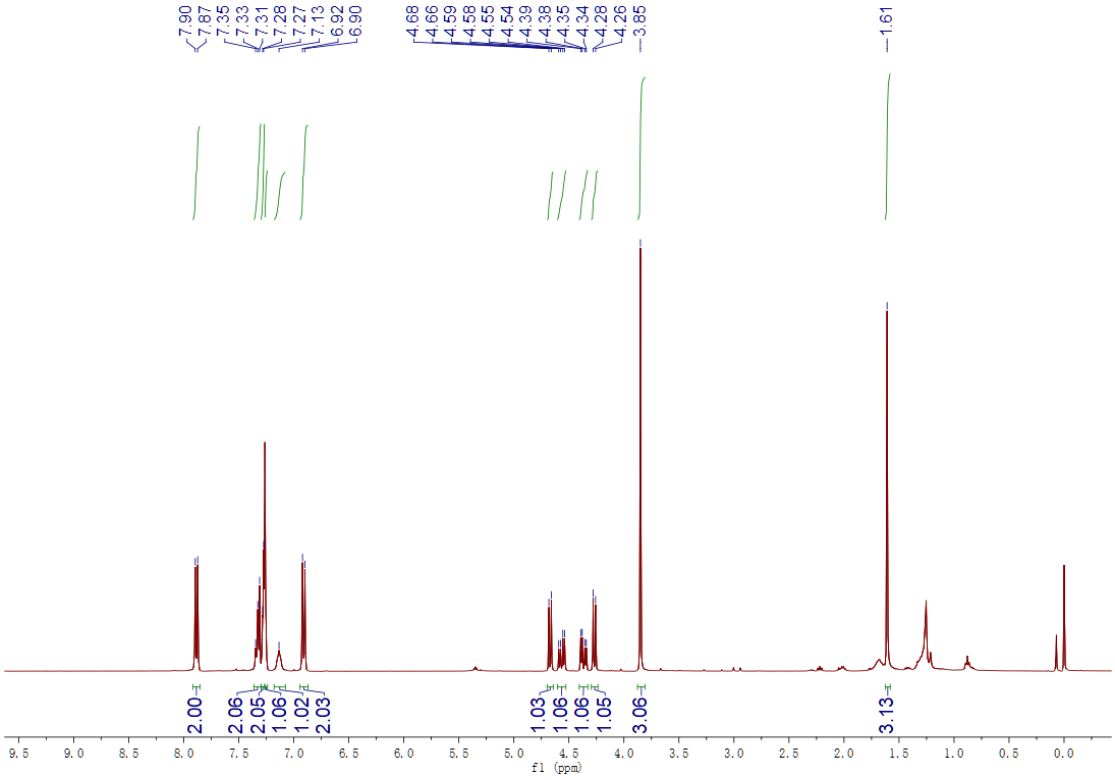
**11**

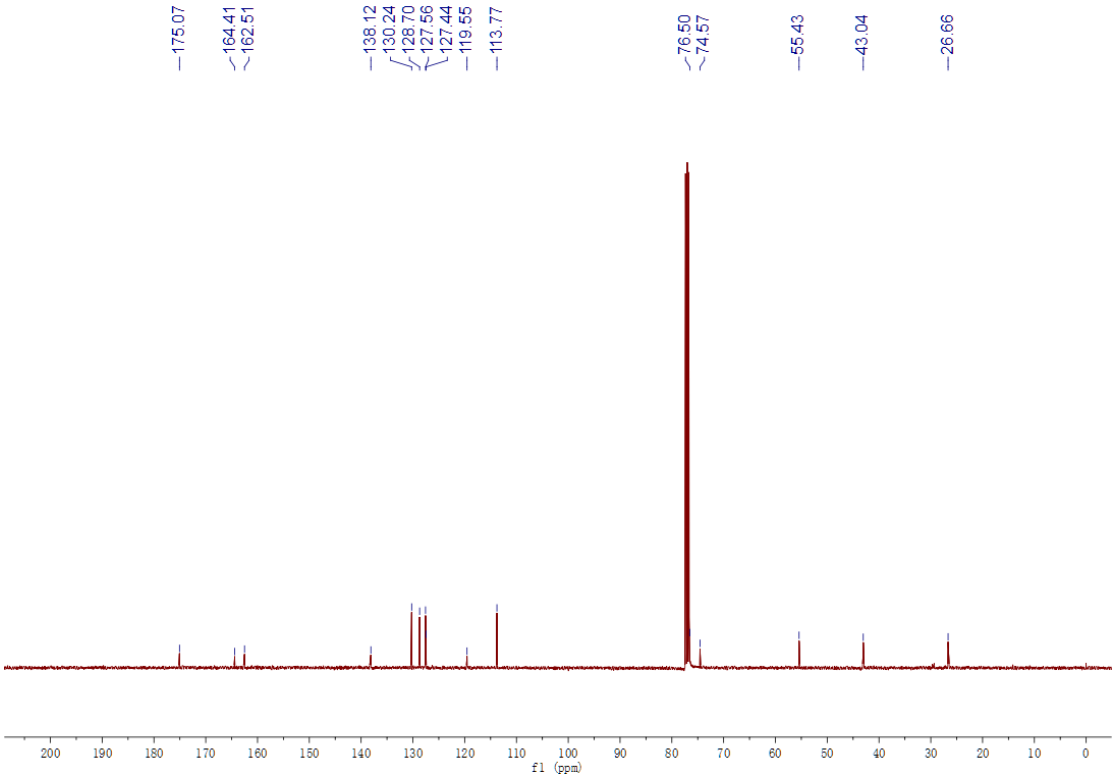

8.08
8.07
8.06
7.77
7.76
7.76
7.75
7.74
7.73
7.33
7.31
7.30
7.30
7.27
7.25
6.94
6.93
6.92
6.92
4.51
4.49
4.48
4.48
4.47
4.26
4.25
4.23
3.67
3.65
3.64
3.62
1.69
0.97
2.00
3.17
1.08
1.03
2.04
2.17
1.08
3.04
1.13
3.01
f1 (ppm)

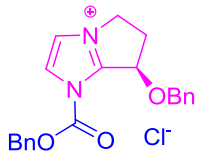

173.94
168.16
162.63
137.98
129.00
128.68
127.35
127.25
126.32
113.85
67.73
61.10
55.47
43.50
20.18
f1 (ppm)


BnHN
O
N
O
O

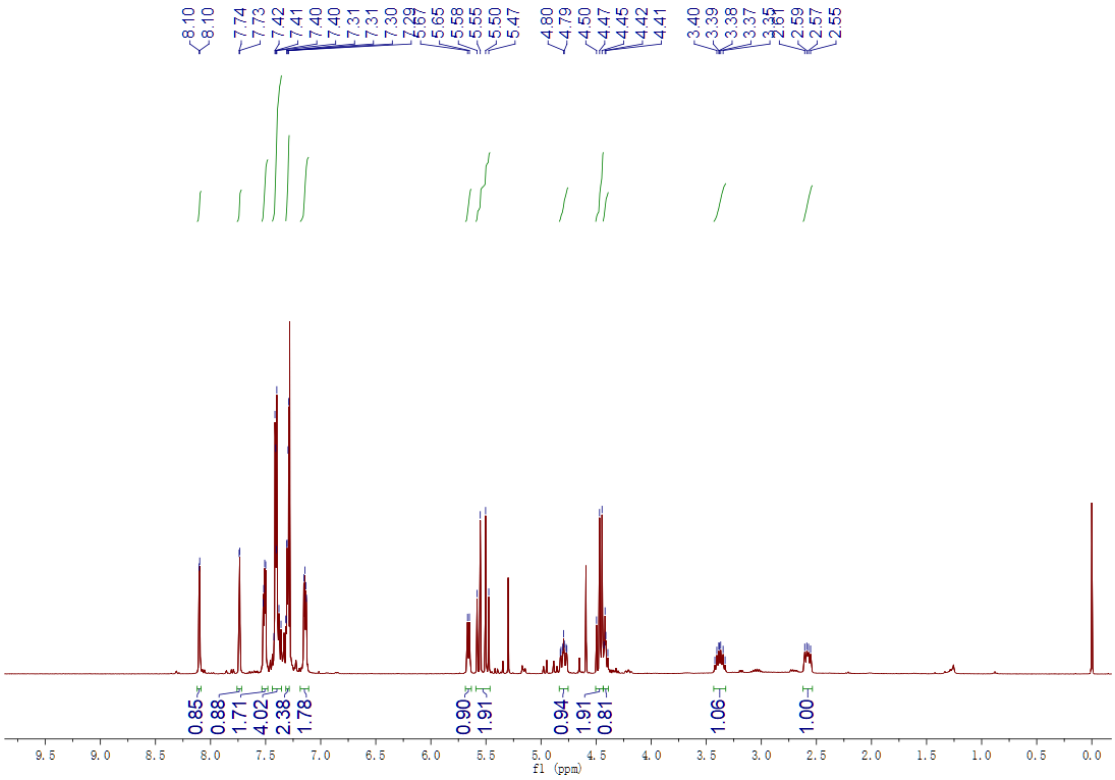
**12**


7.90
7.87
7.35
7.33
7.31
7.28
7.27
7.13
6.92
6.90
4.68
4.66
4.59
4.58
4.55
4.54
4.39
4.38
4.35
4.34
4.28
4.26
3.85
1.61
2.00
2.06
2.05
1.06
1.02
2.03
1.03
1.06
1.06
1.05
3.06
3.13
f1 (ppm)

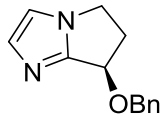

175.07
164.41
162.51
138.12
130.24
128.70
127.56
127.44
119.55
113.77
76.50
74.57
55.43
43.04
26.66
f1 (ppm)


N
N
OBn
BnO
O
Cl-

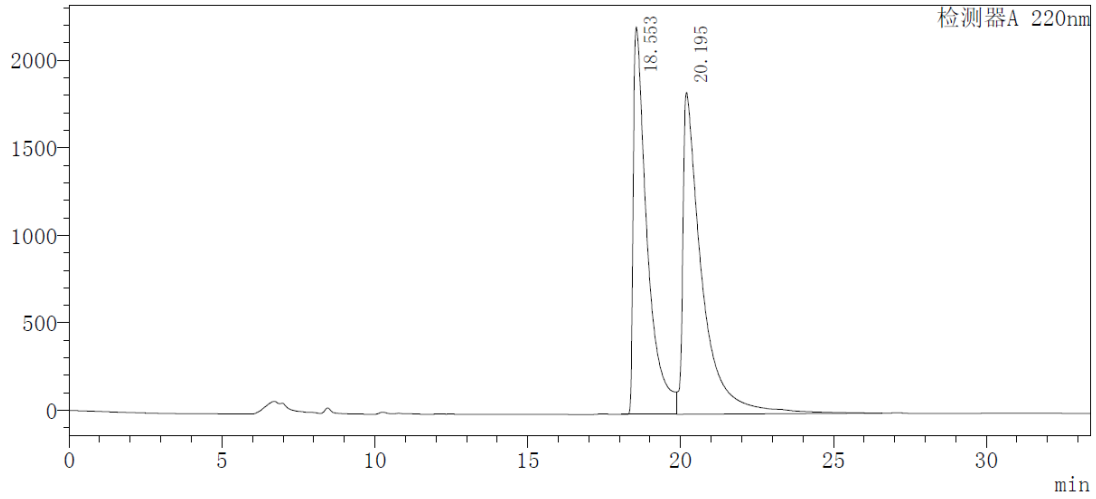
**A**


8.10
8.10
7.74
7.73
7.42
7.41
7.40
7.40
7.31
7.31
7.30
7.29
5.67
5.65
5.58
5.55
5.50
5.47
4.80
4.79
4.50
4.47
4.45
4.42
4.41
3.40
3.39
3.38
3.37
3.35
2.61
2.59
2.57
2.55
0.85
0.88
1.71
4.02
2.38
1.78
0.90
1.91
0.94
1.91
0.81
1.06
1.00
f1 (ppm)

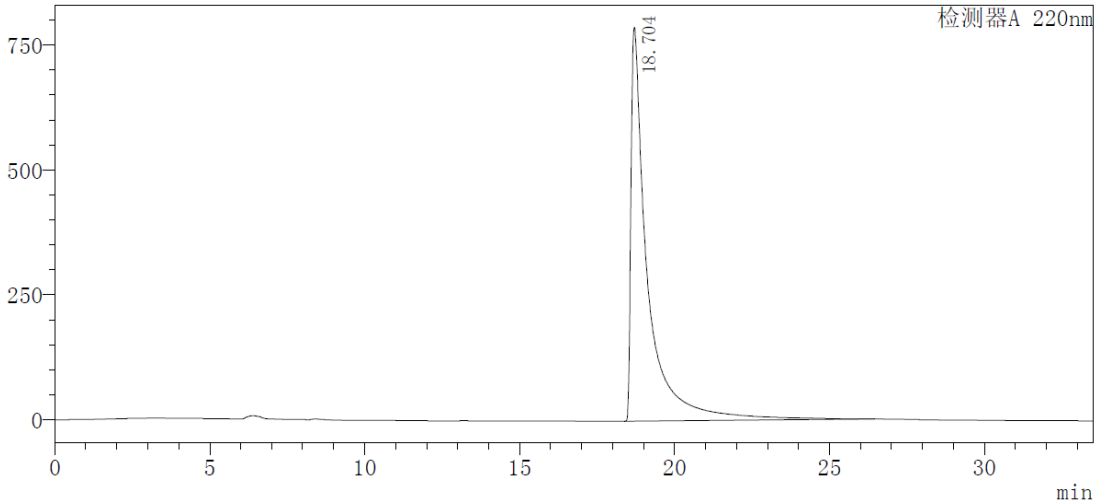
# 10. HPLC Charts



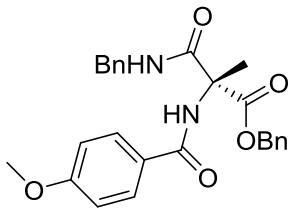

(*R*)-**OBn-DPI**



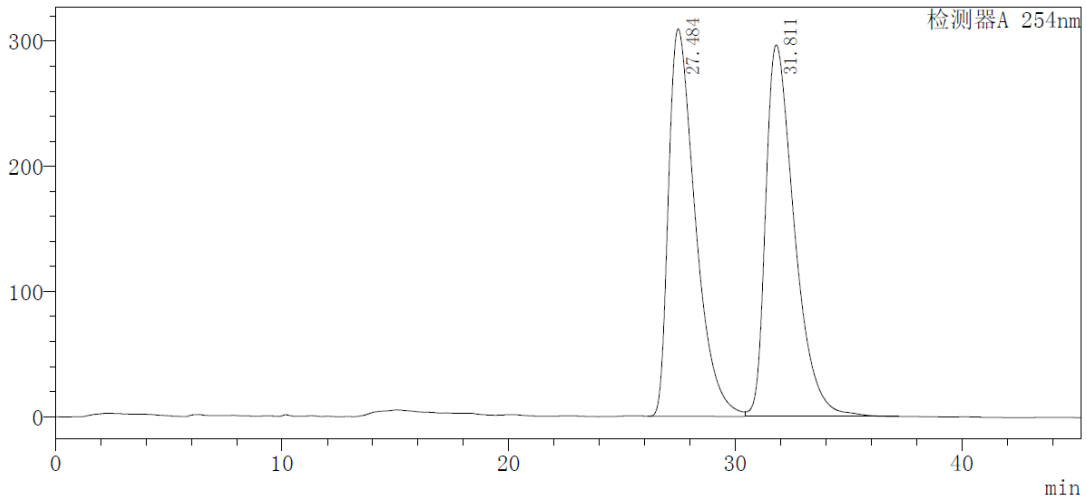

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 18.553 | 46.721 |
| 2 | 20.195 | 53.279 |



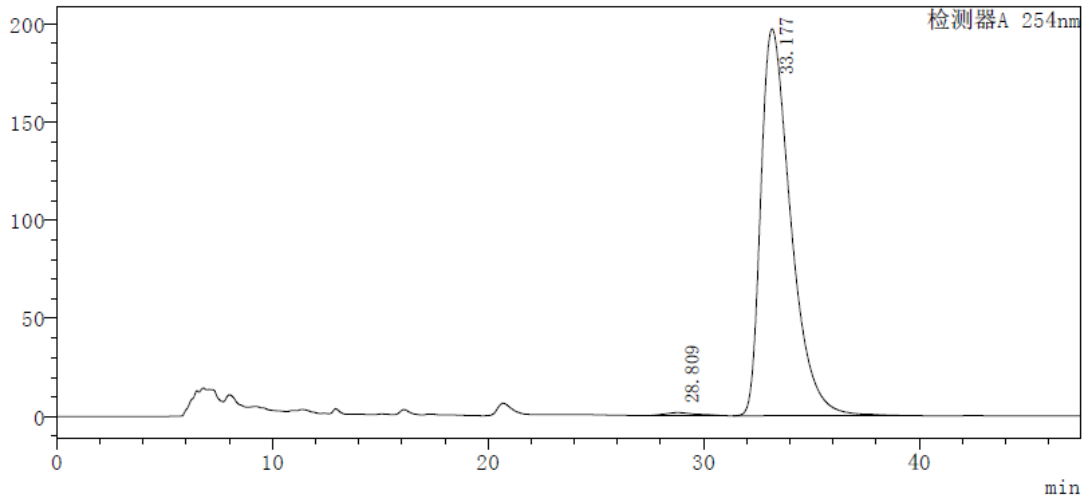

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 18.704 | 100.000 | 100 |



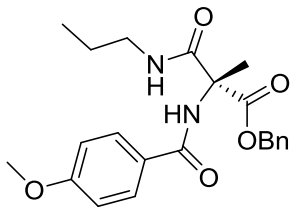

**2a**



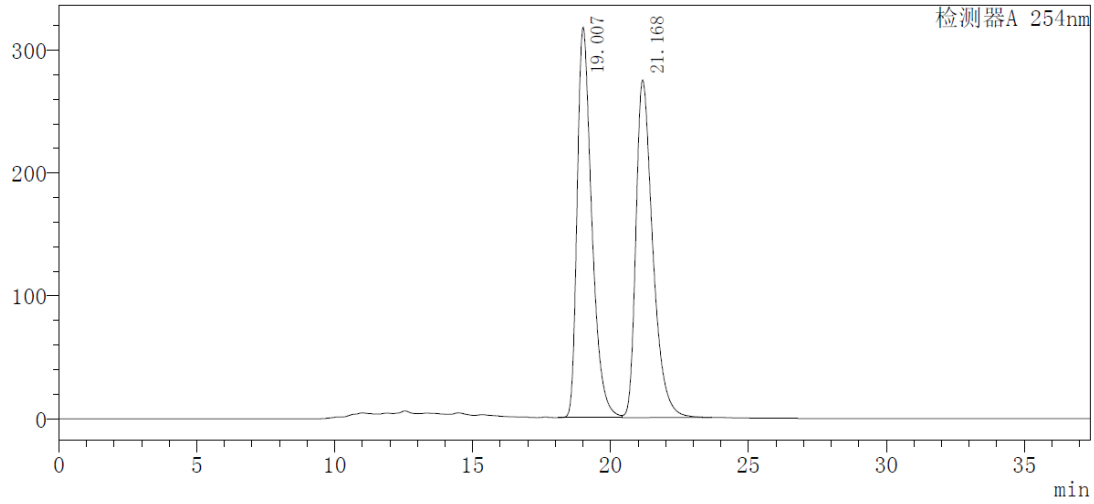

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 27.484 | 49.318 |
| 2 | 31.811 | 50.682 |



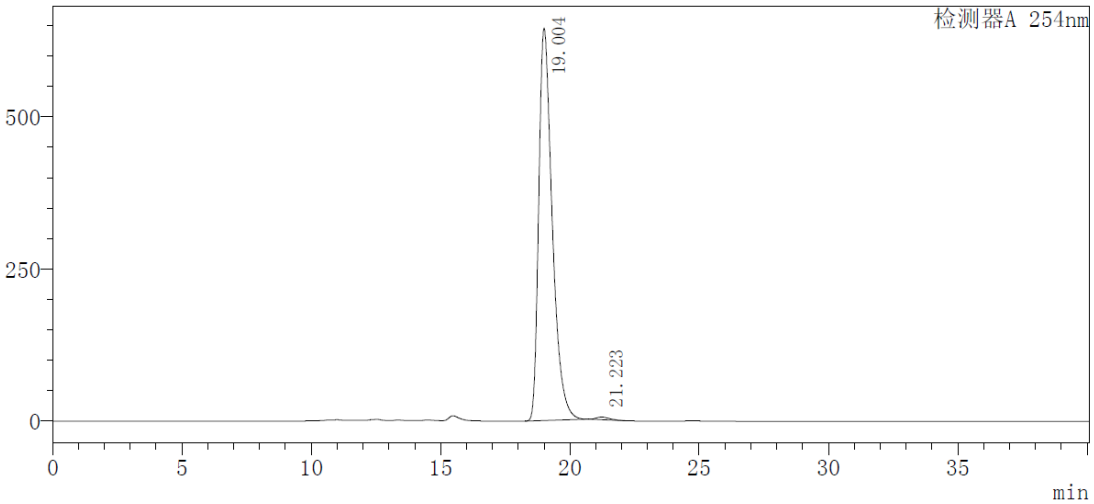

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 28.809 | 0.719 | |
| 2 | 33.177 | 99.281 | 99 |



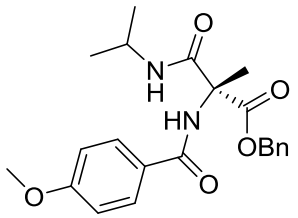
**2b**



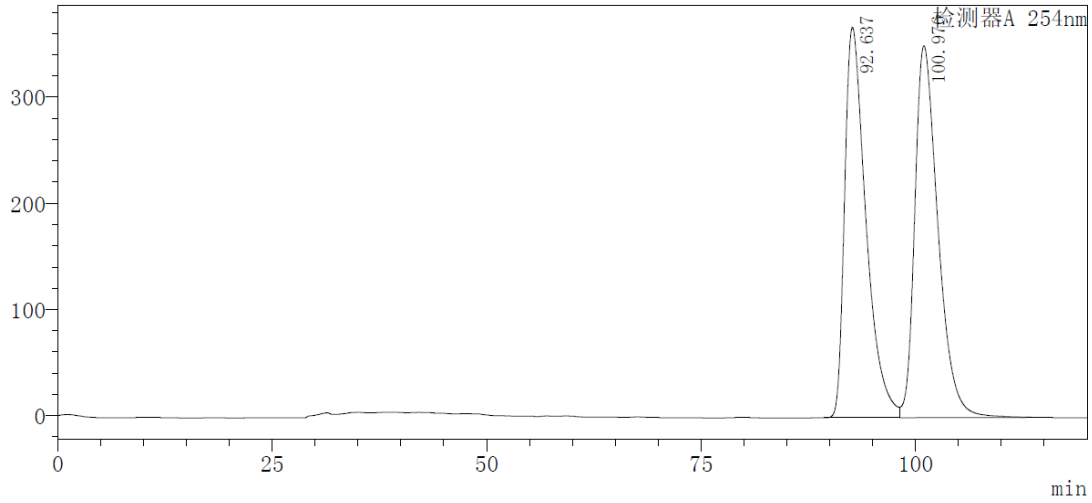

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 19.007 | 50.033 |
| 2 | 21.168 | 49.967 |



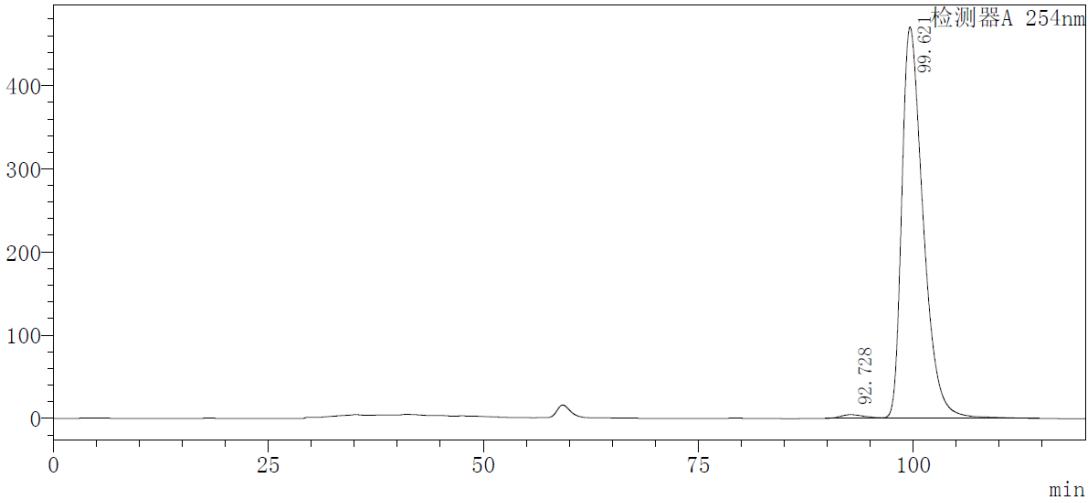

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 19.004 | 99.334 | 99 |
| 2 | 21.223 | 0.666 | |



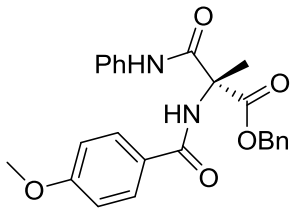

**2c**



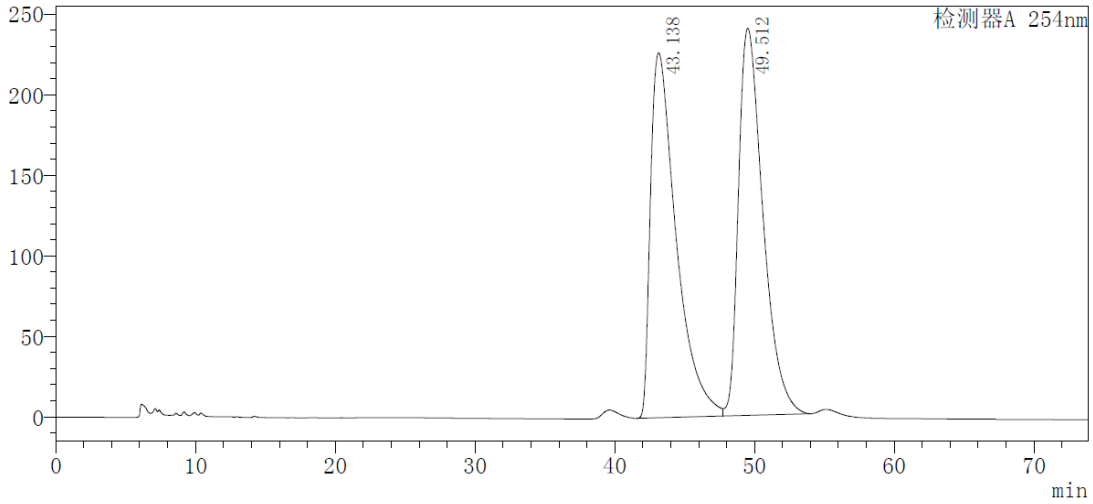

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 92.637 | 49.171 |
| 2 | 100.976 | 50.829 |



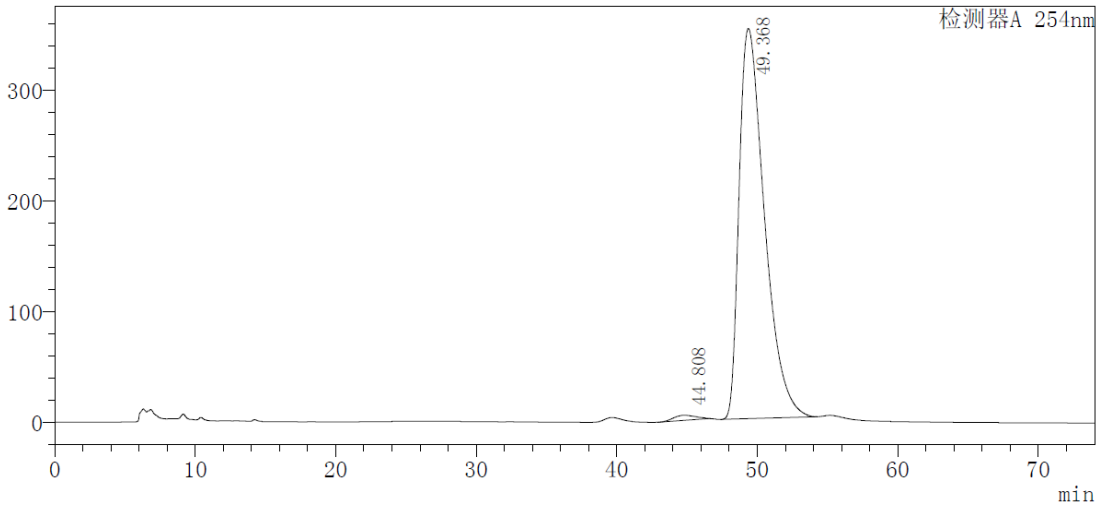

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 92.728 | 1.078 | |
| 2 | 99.621 | 98.922 | 98 |



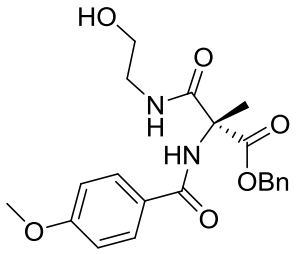

**2d**



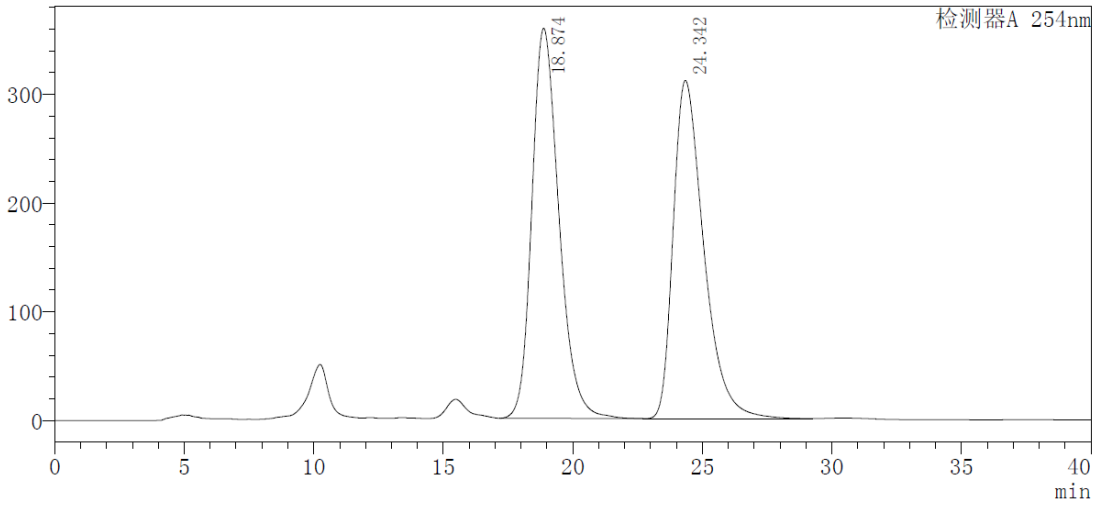

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 43.138 | 49.685 |
| 2 | 49.512 | 50.315 |



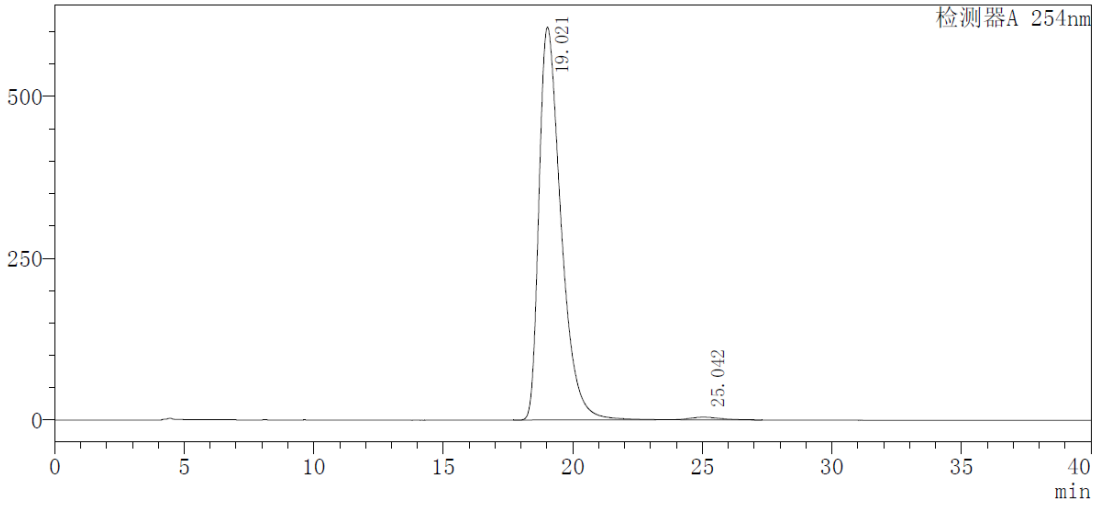

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 44.808 | 1.163 | |
| 2 | 49.368 | 98.837 | 98 |



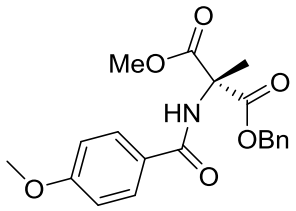

**2e**



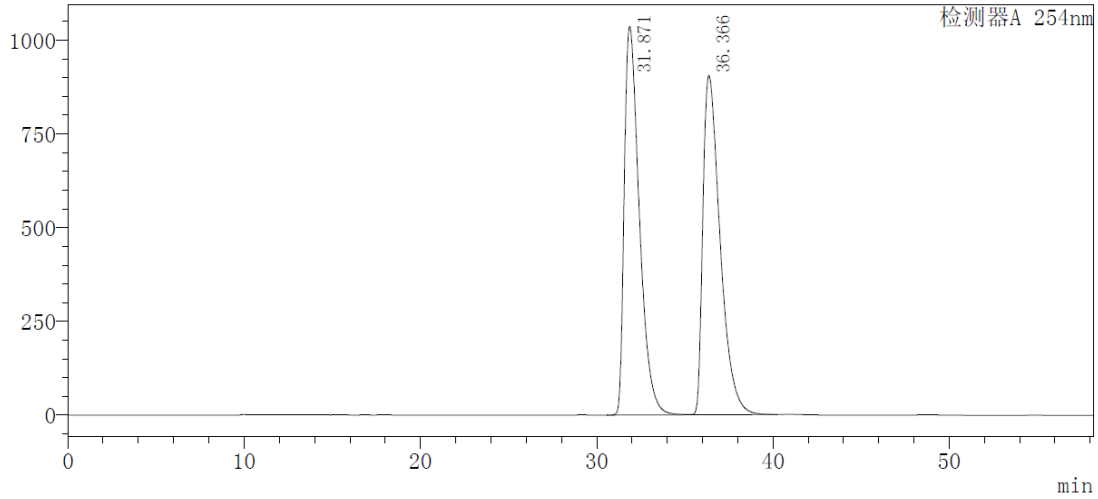

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 18.874 | 50.587 |
| 2 | 24.342 | 49.413 |



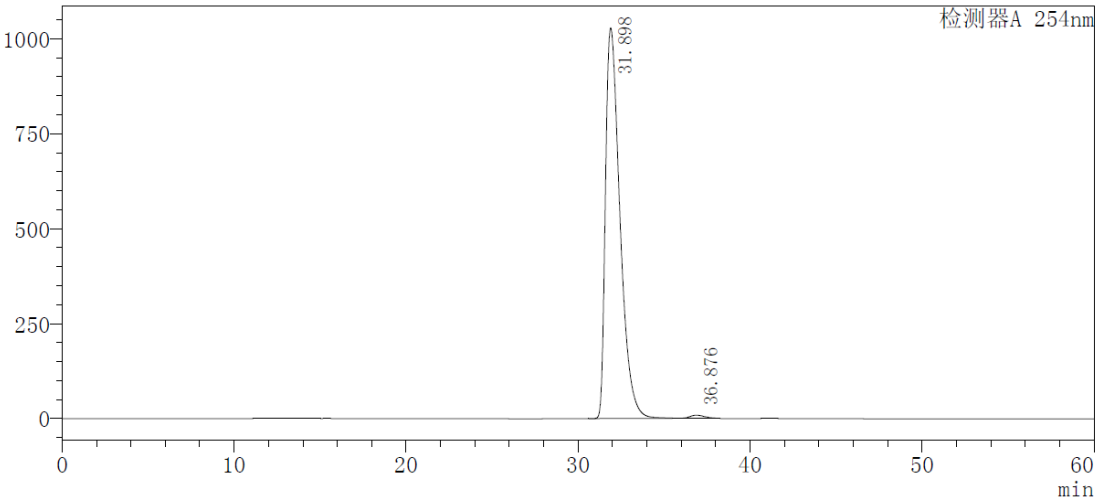

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 19.021 | 99.127 | 98 |
| 2 | 25.042 | 0.873 | |



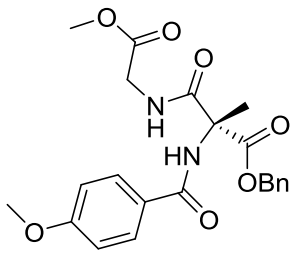

**2f**



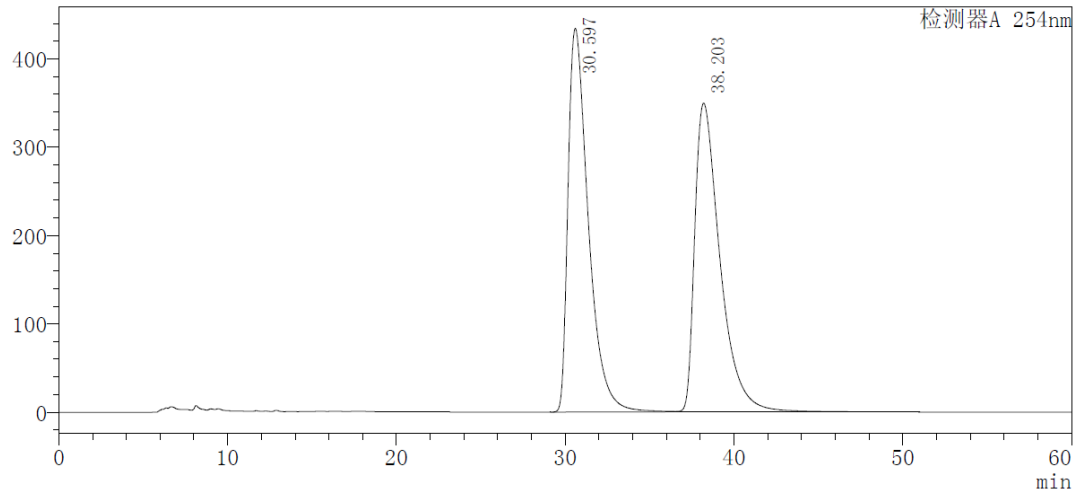

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 31.871 | 50.030 |
| 2 | 36.366 | 49.970 |



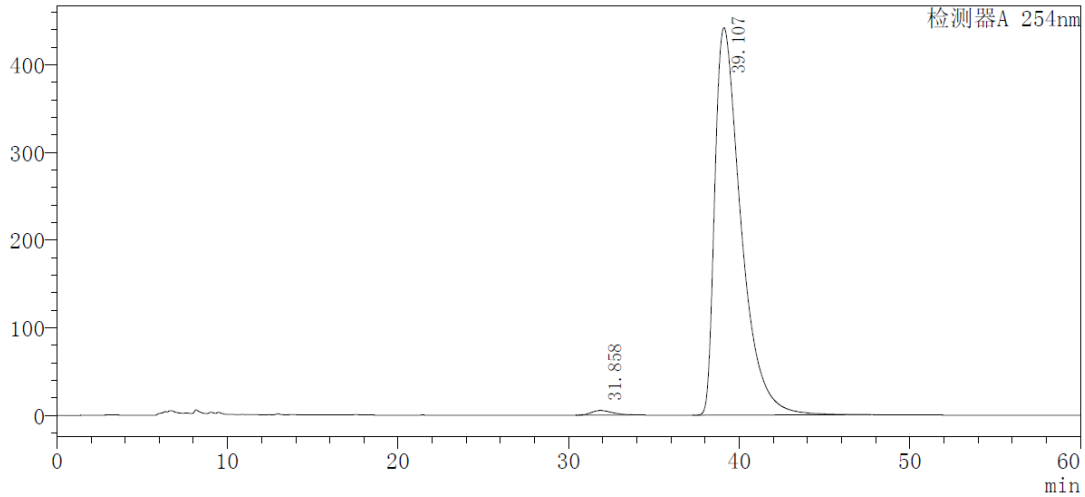

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 31.898 | 99.230 | 98 |
| 2 | 36.876 | 0.770 | |



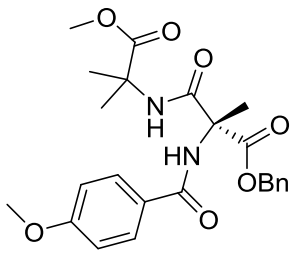
**2g**



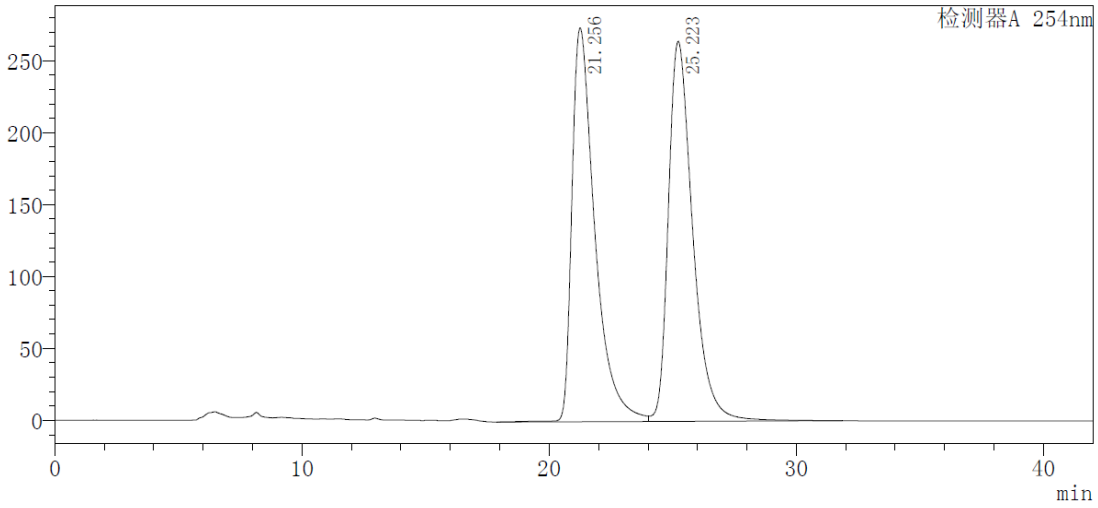

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 30.597 | 49.979 |
| 2 | 38.203 | 50.021 |



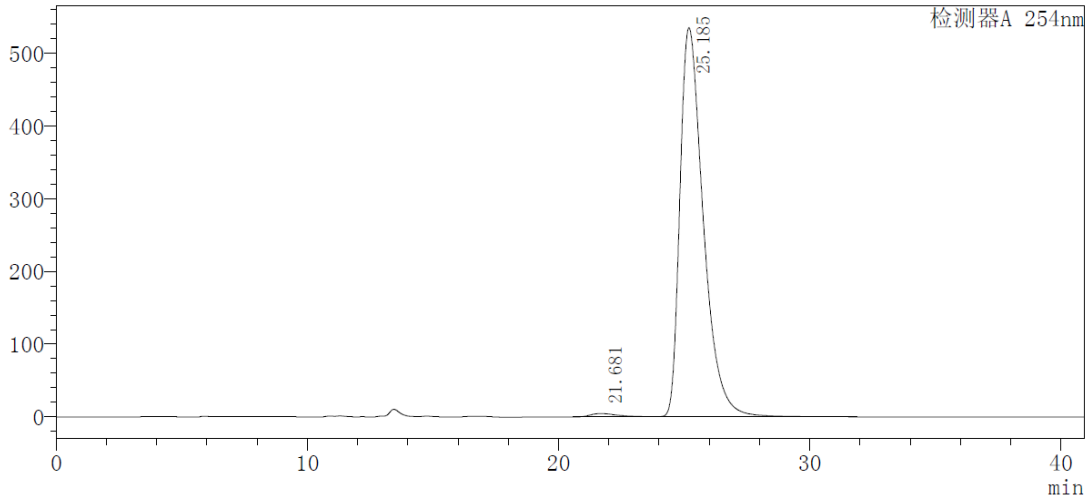

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 31.858 | 0.923 | |
| 2 | 39.107 | 99.077 | 98 |



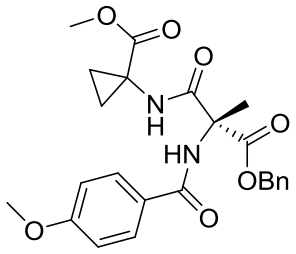
**2h**



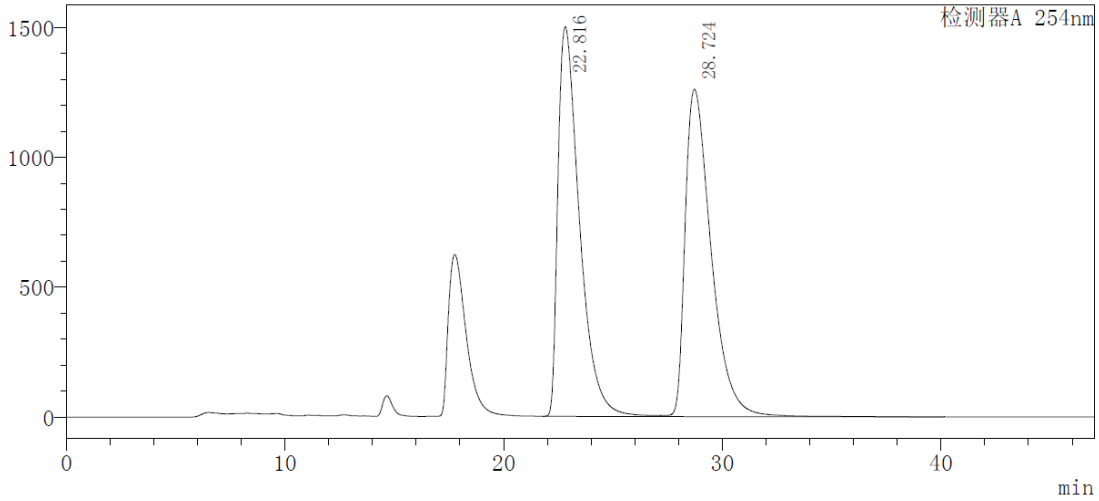

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 21.256 | 49.374 |
| 2 | 25.223 | 50.626 |



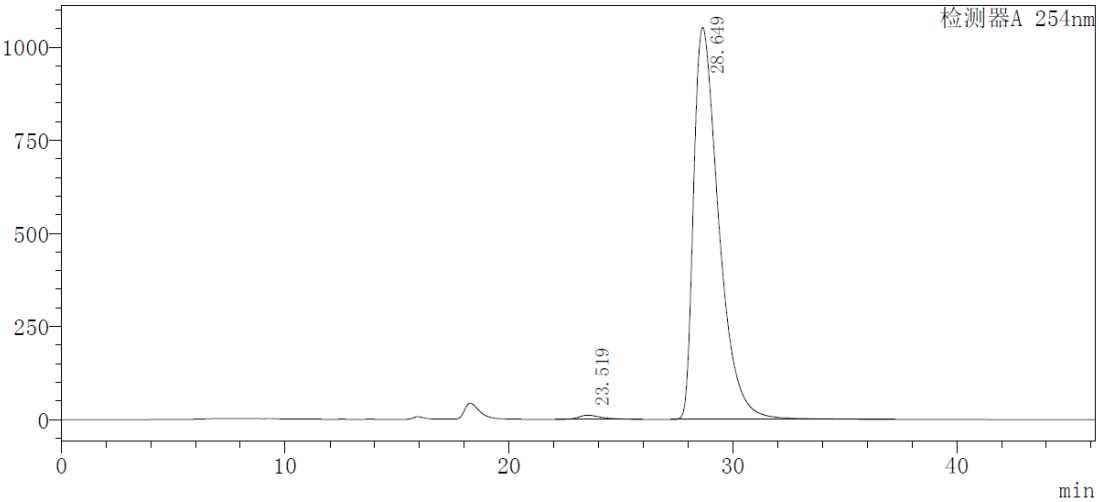

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 21.681 | 1.030 | |
| 2 | 25.185 | 98.970 | 98 |



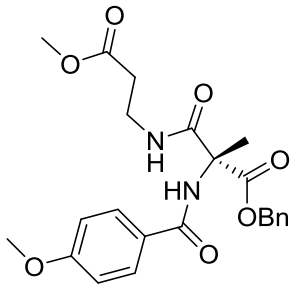
**2i**



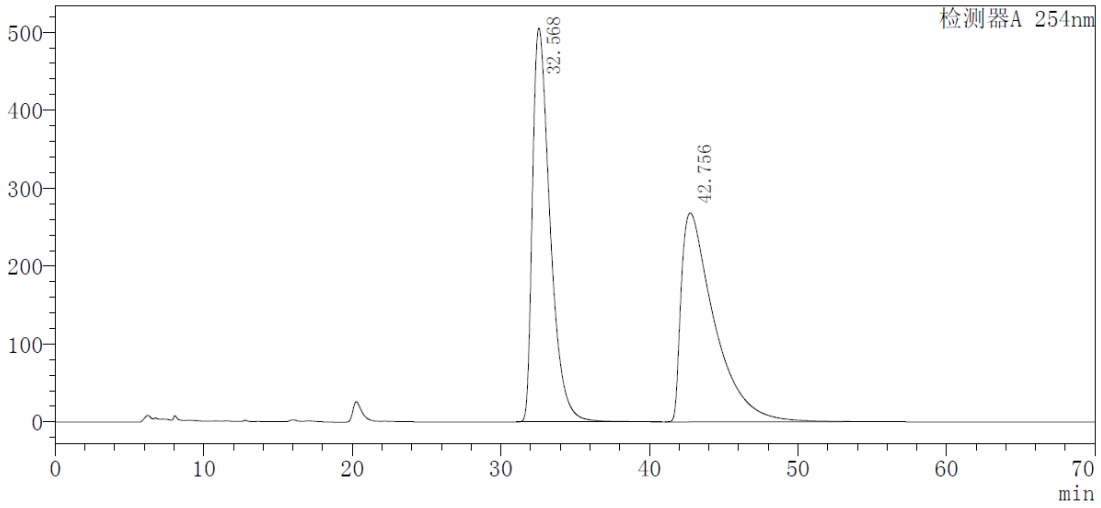

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 22.816 | 49.643 |
| 2 | 28.724 | 50.357 |



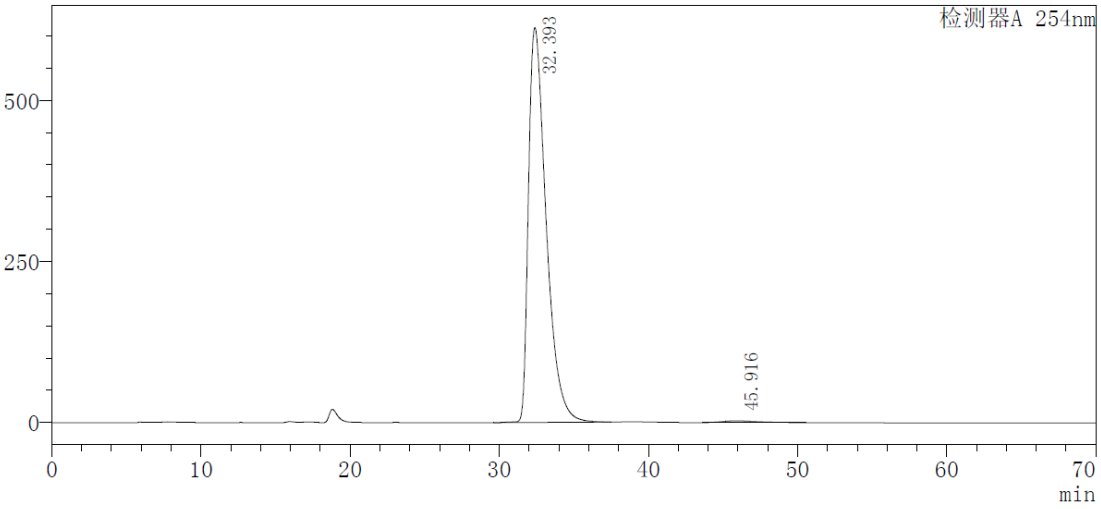

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 23.519 | 0.959 | |
| 2 | 28.649 | 99.041 | 98 |



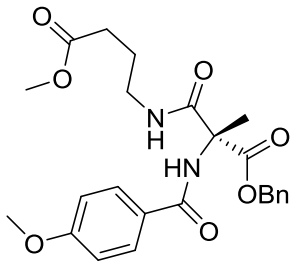
**2j**



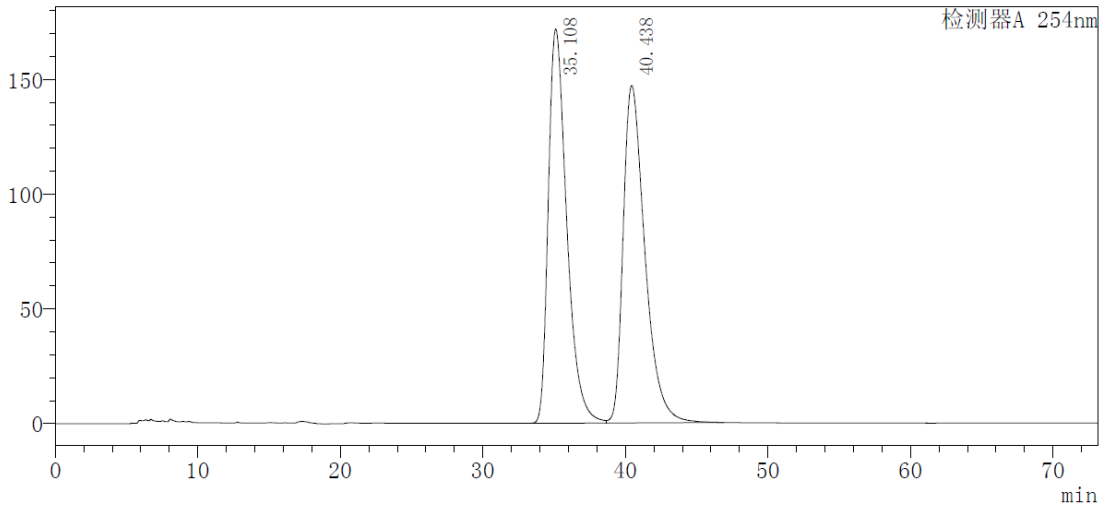

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 32.568 | 50.129 |
| 2 | 42.756 | 49.871 |



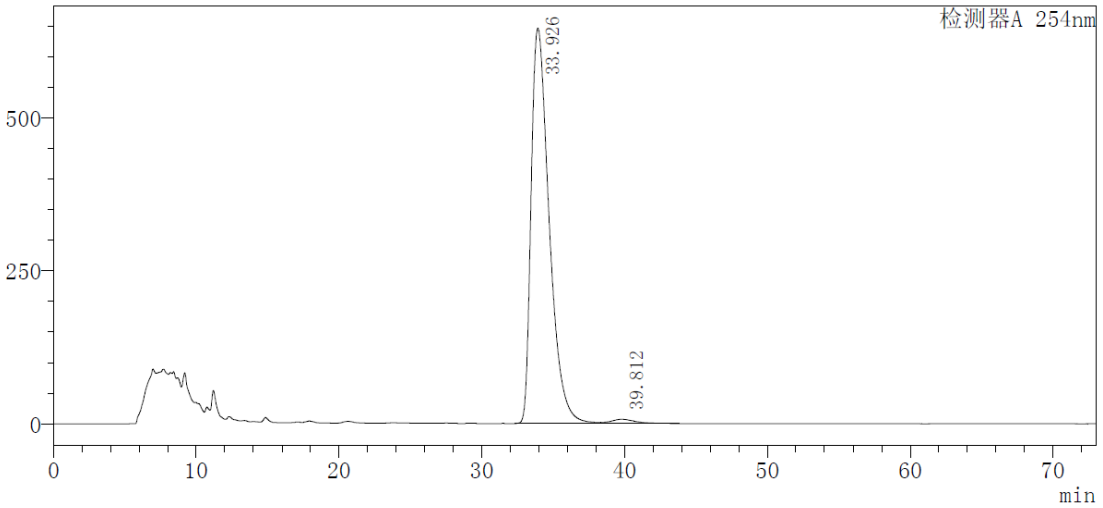

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 32.393 | 99.110 | 98 |
| 2 | 45.916 | 0.890 | |



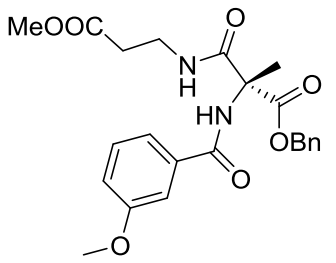
**2k**



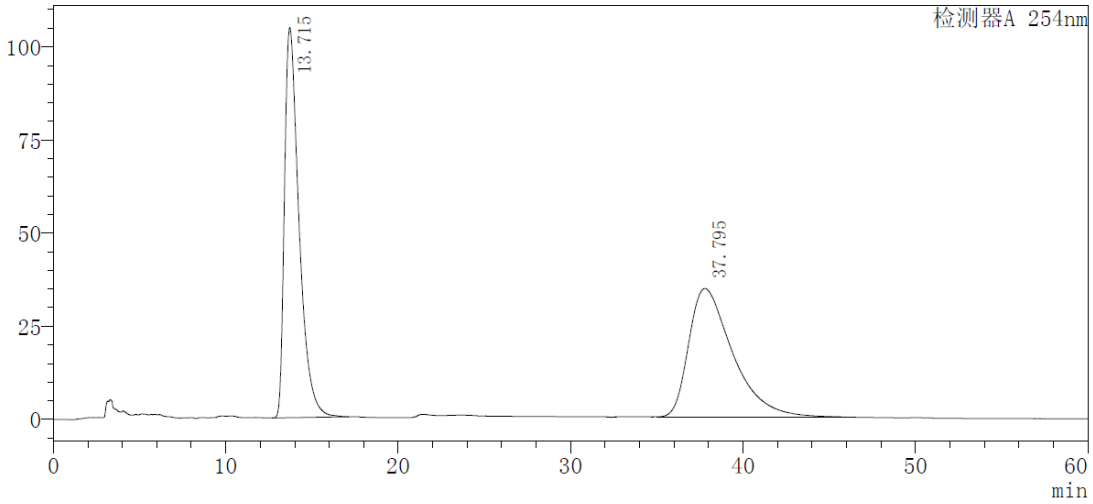

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 35.108 | 49.799 |
| 2 | 40.438 | 50.201 |



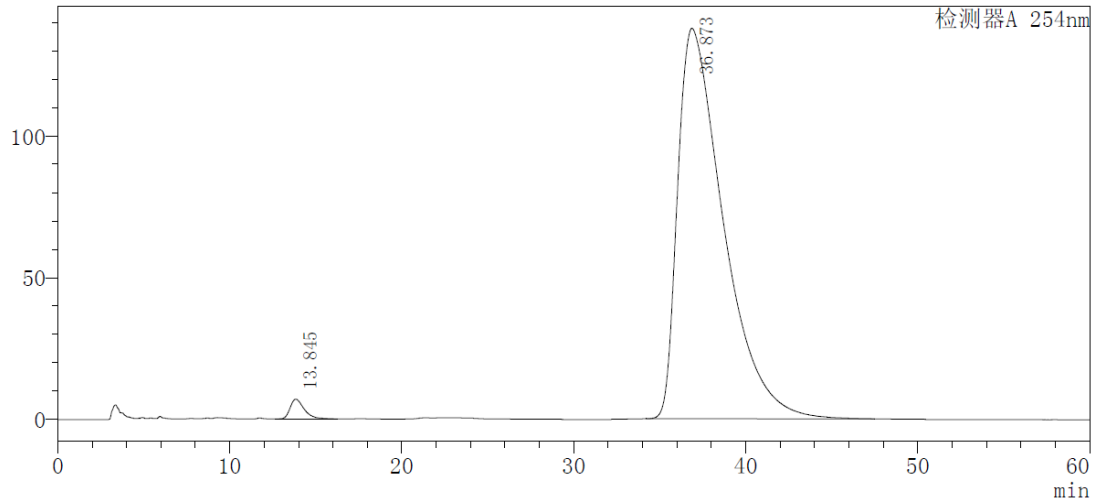

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 33.926 | 98.596 | 97 |
| 2 | 39.812 | 1.404 | |



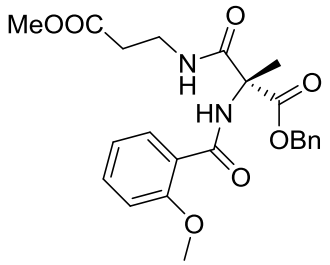

**2s**



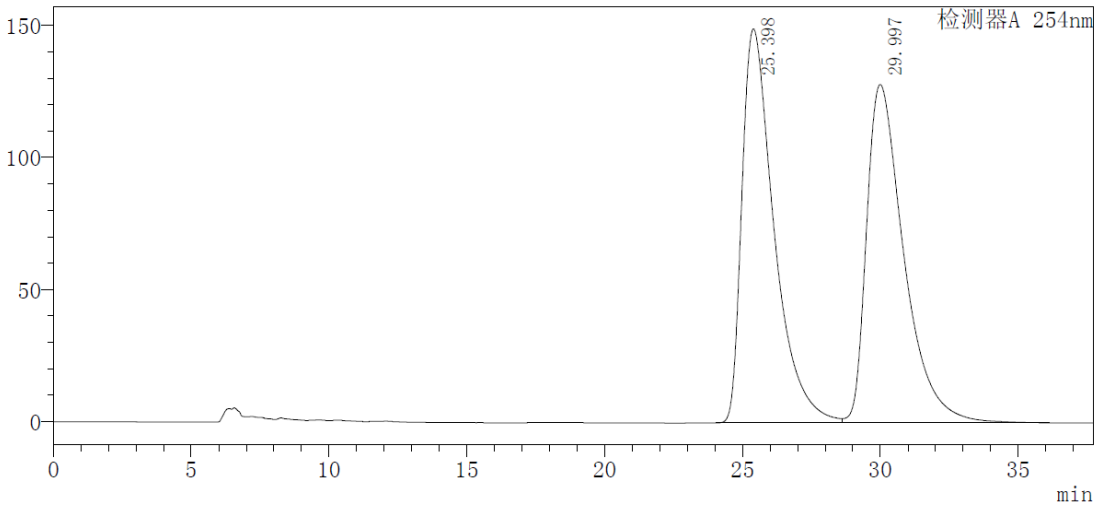

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 13.715 | 50.187 |
| 2 | 37.795 | 49.813 |



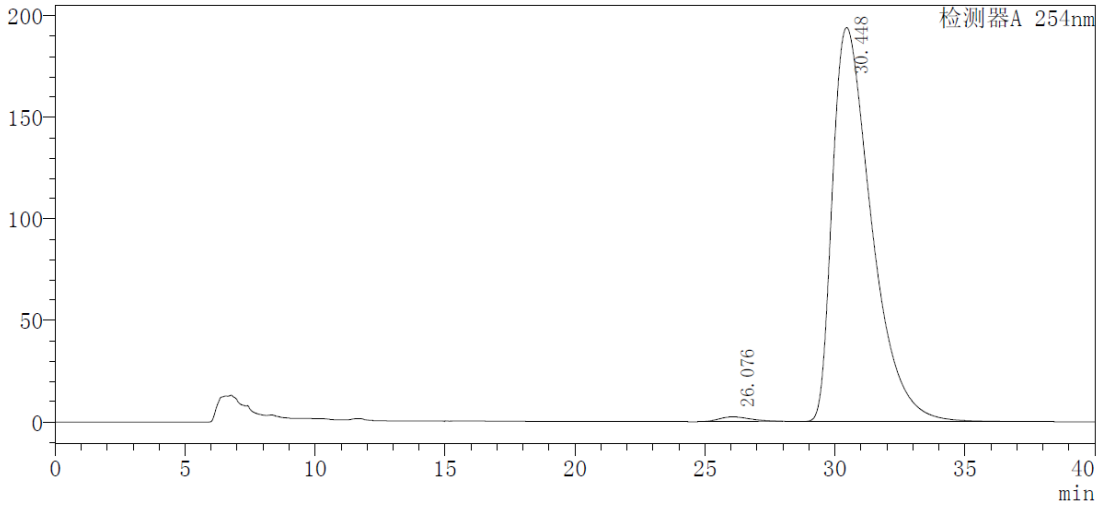

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 13.845 | 1.545 | |
| 2 | 36.873 | 98.455 | 97 |



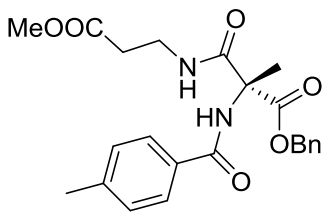

**2t**



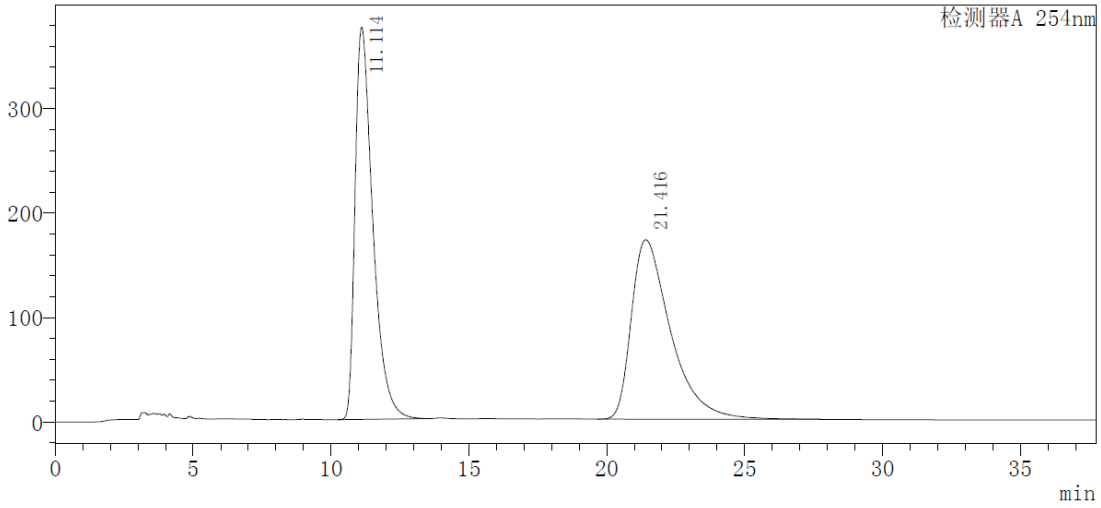

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 25.398 | 50.002 |
| 2 | 29.997 | 49.998 |



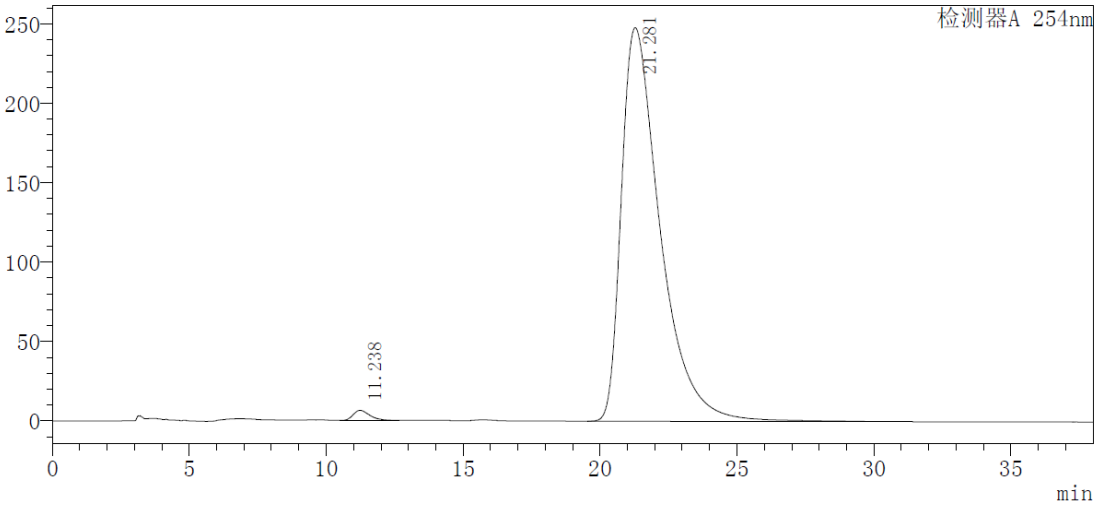

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 26.076 | 0.938 | |
| 2 | 30.448 | 99.062 | 98 |



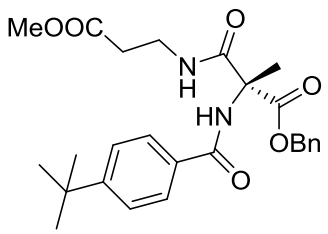

**2u**



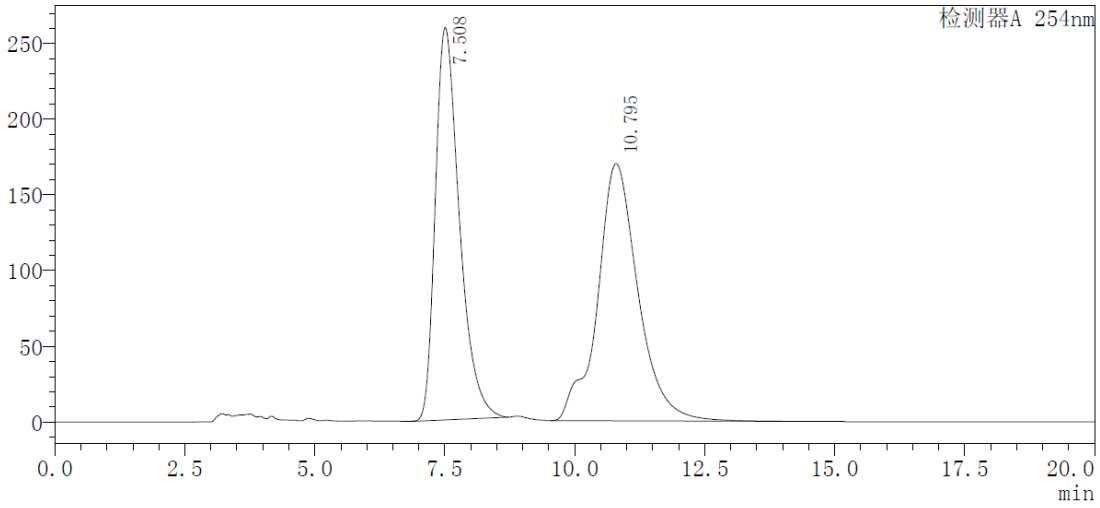

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 11.114 | 49.621 |
| 2 | 21.416 | 50.379 |



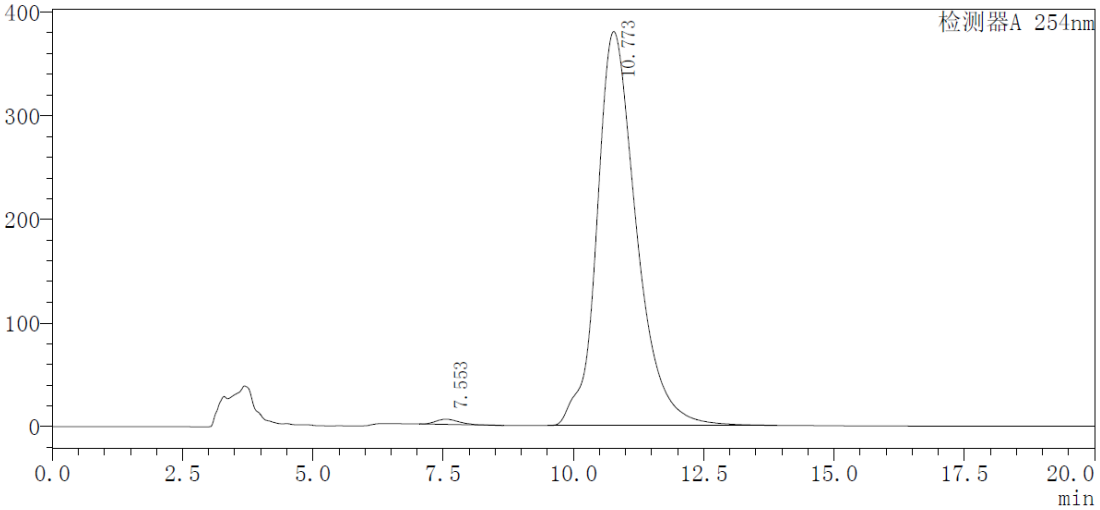

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 11.238 | 1.088 | |
| 2 | 21.281 | 98.912 | 98 |



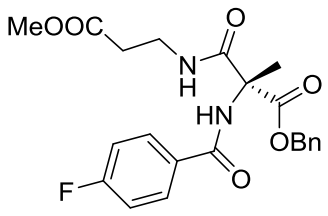

**2v**



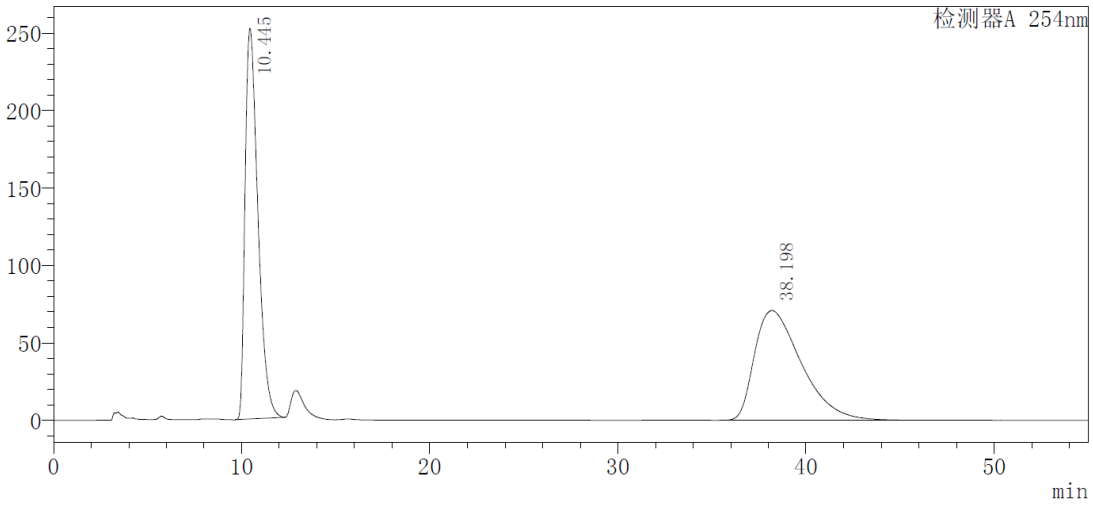

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 7.508 | 47.488 |
| 2 | 10.795 | 52.512 |



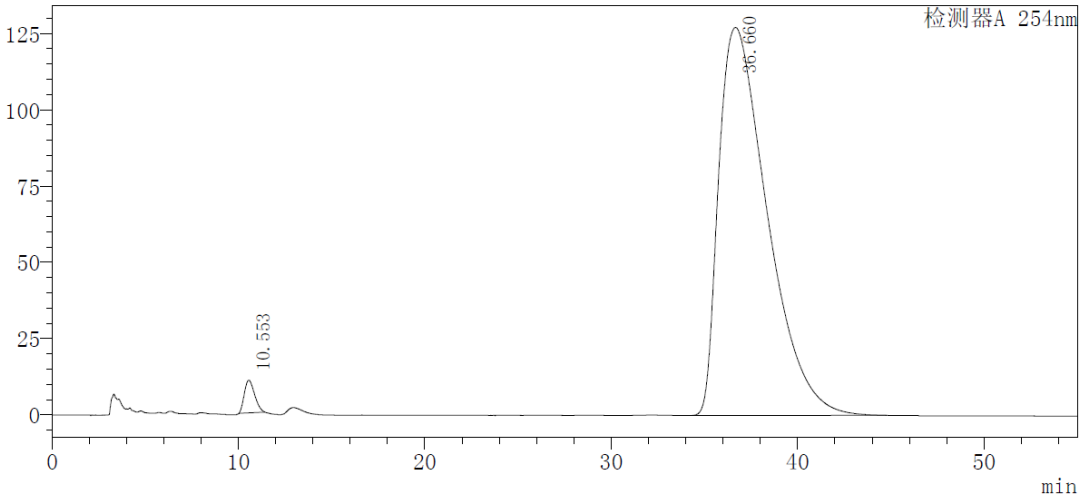

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 7.553 | 0.804 | |
| 2 | 10.773 | 99.196 | 98 |



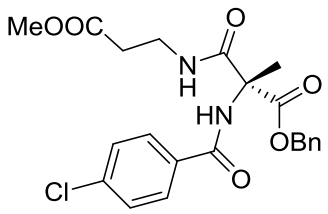

**2w**



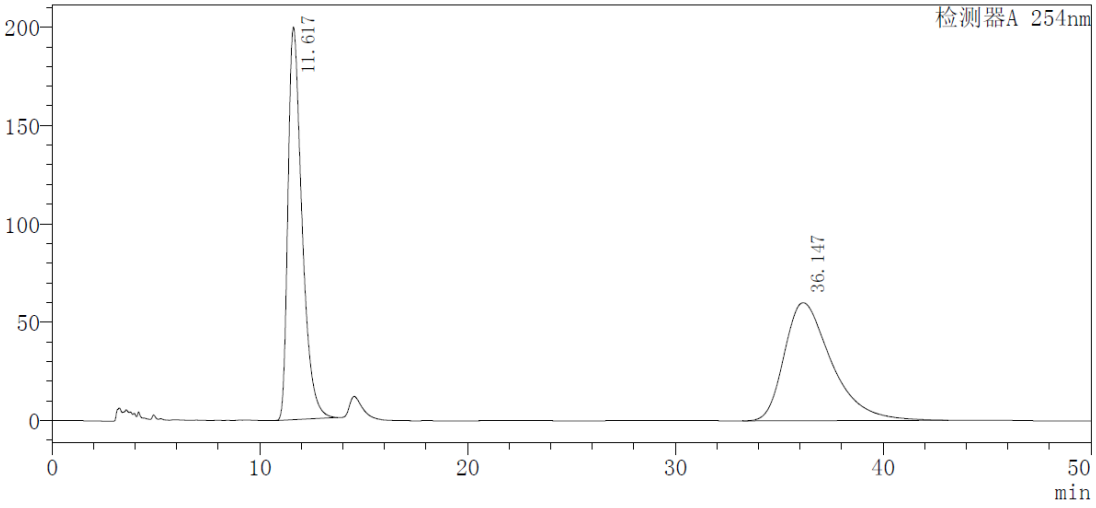

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 10.445 | 49.398 |
| 2 | 38.198 | 50.602 |



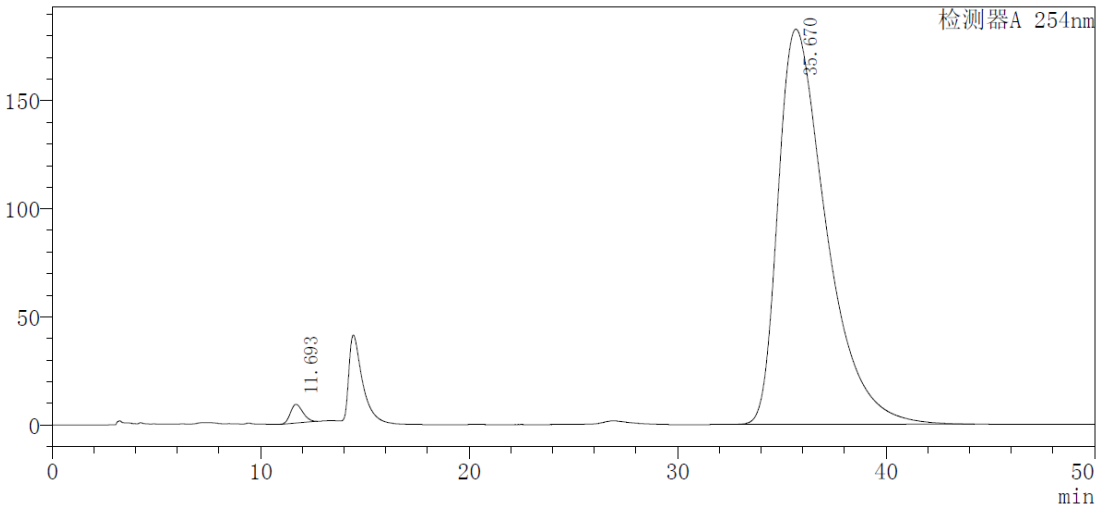

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 10.553 | 1.746 | |
| 2 | 36.660 | 98.254 | 97 |



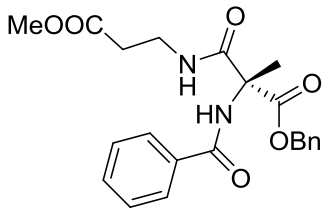

**2x**



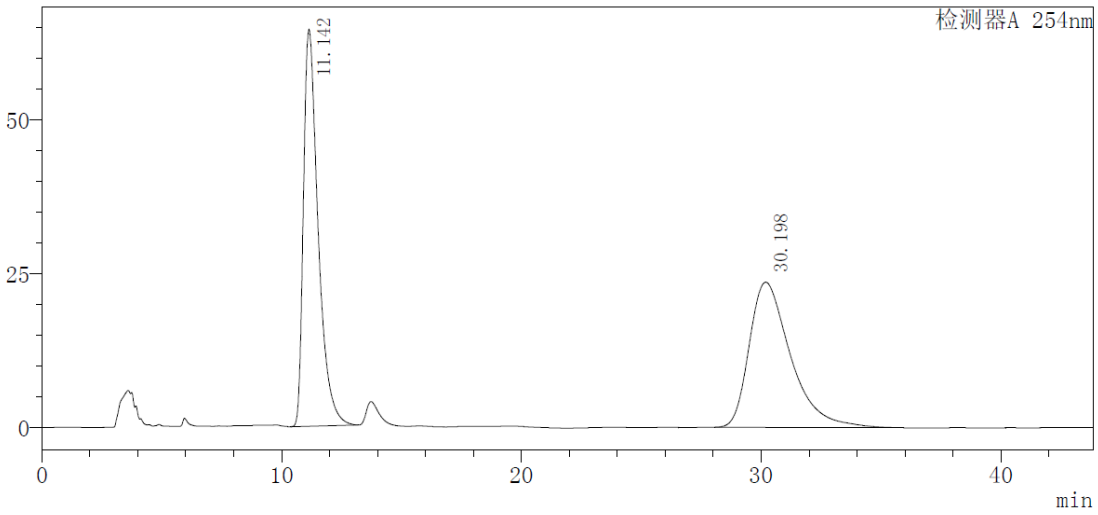

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 11.617 | 49.723 |
| 2 | 36.147 | 50.277 |



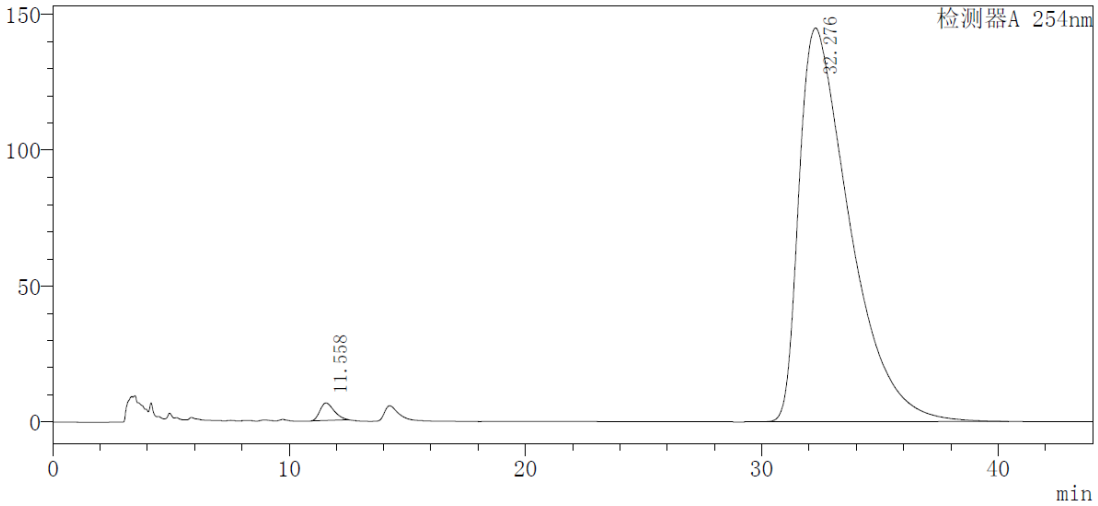

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 11.693 | 1.205 | |
| 2 | 35.670 | 98.795 | 98 |



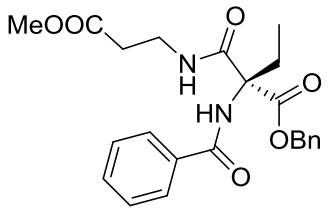

**2y**



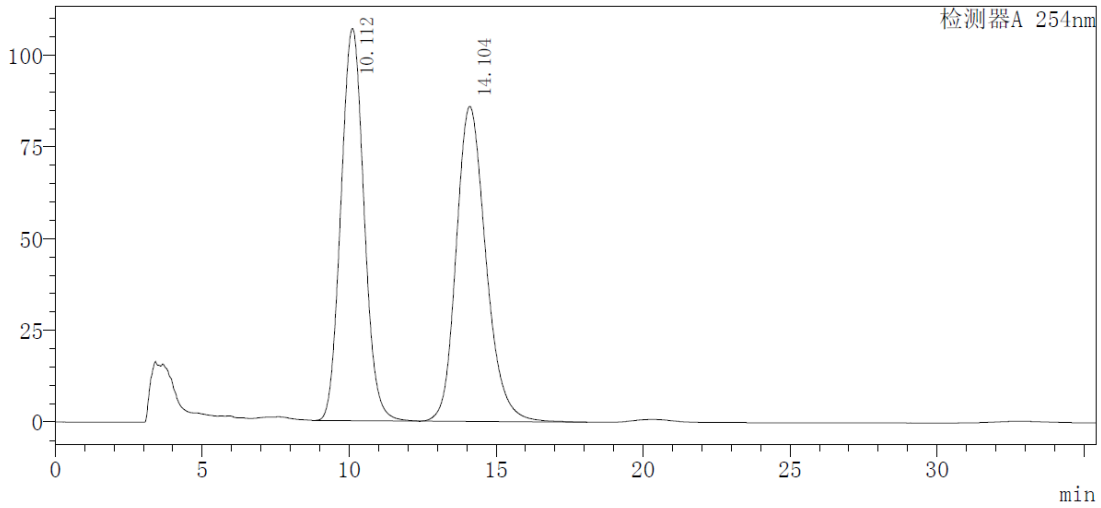

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 11.142 | 49.296 |
| 2 | 30.198 | 50.704 |



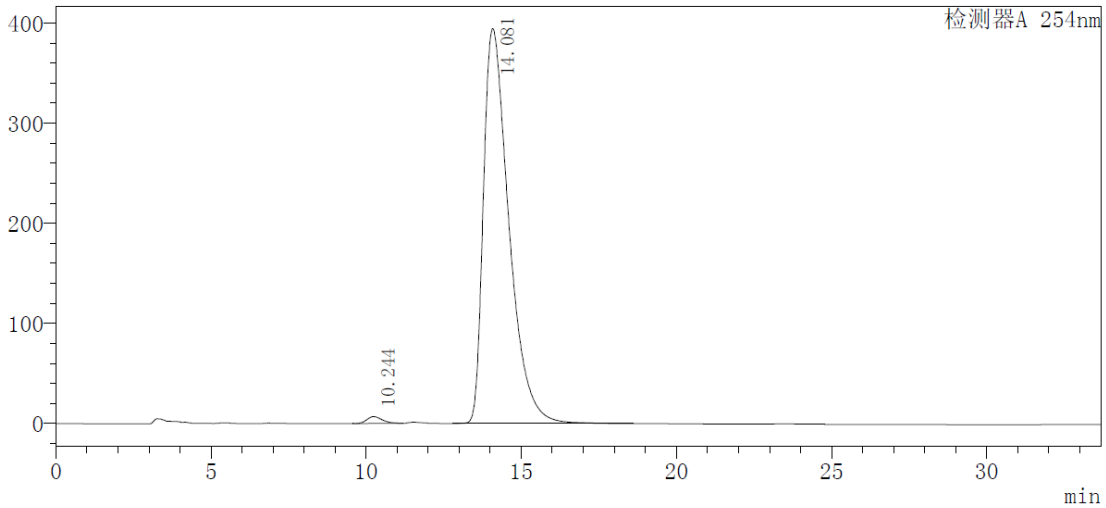

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 11.558 | 1.221 | |
| 2 | 32.276 | 98.779 | 98 |



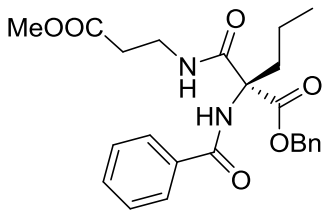

**2z**



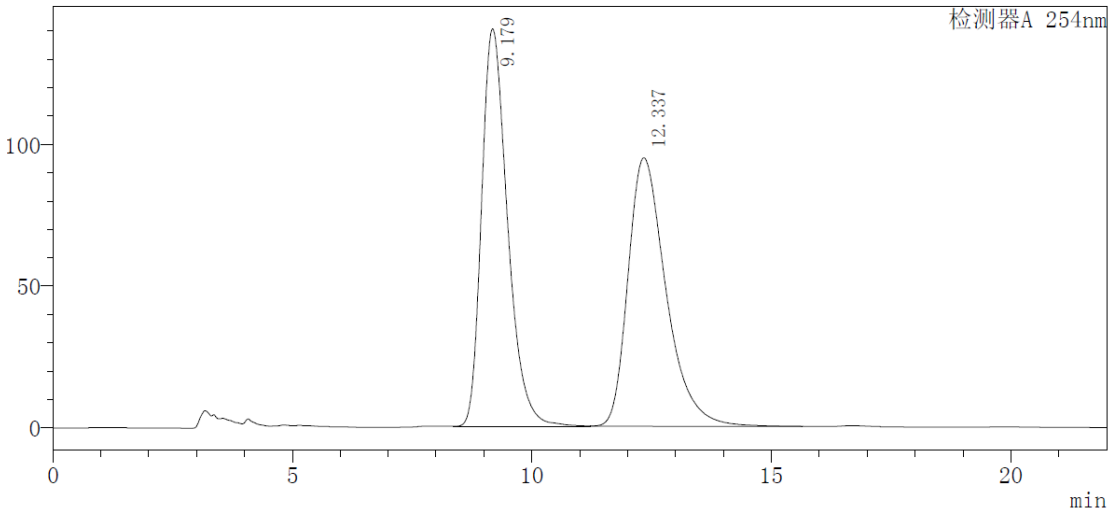

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 10.112 | 49.198 |
| 2 | 14.104 | 50.802 |



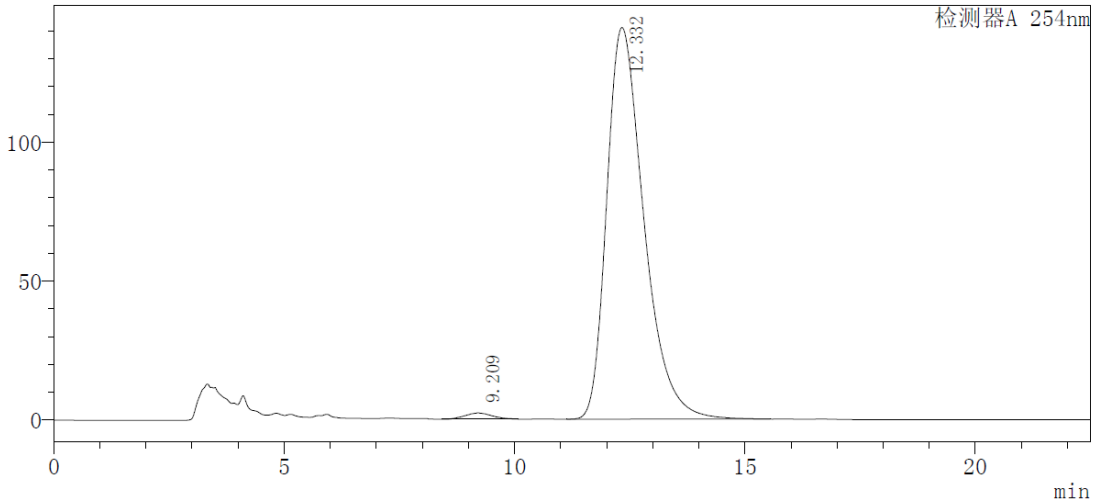

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 10.244 | 1.021 | |
| 2 | 14.081 | 98.979 | 98 |



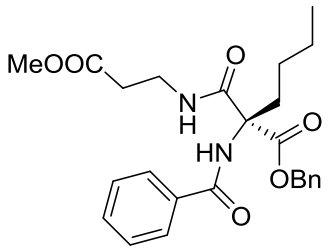

**2aa**



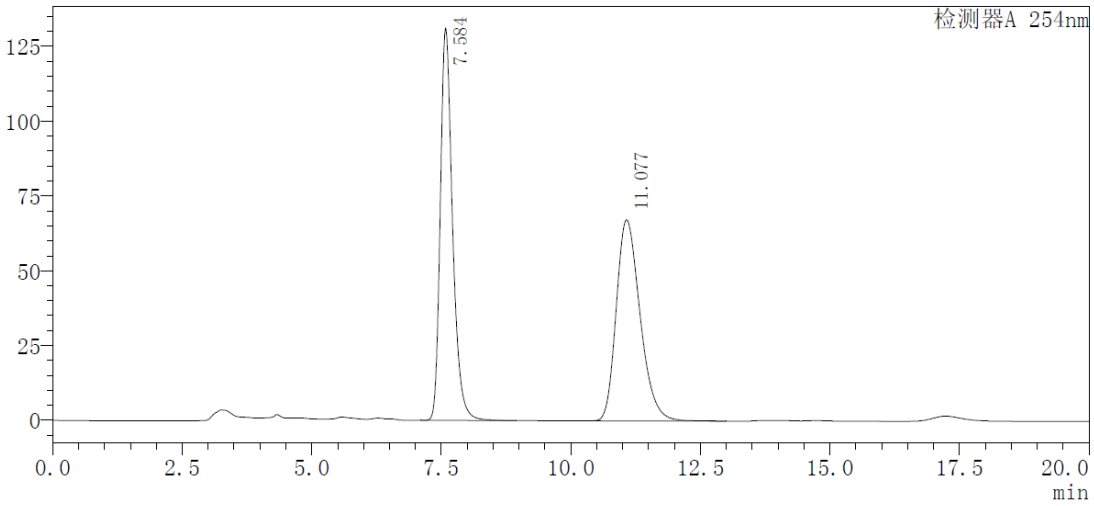

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 9.179 | 50.262 |
| 2 | 12.337 | 49.738 |



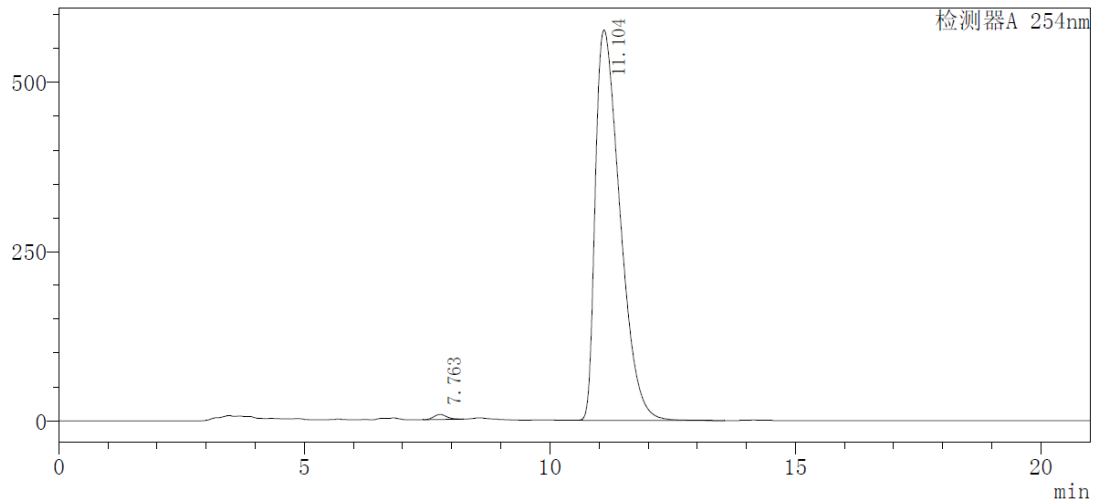

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 9.209 | 1.160 | |
| 2 | 12.332 | 98.840 | 98 |



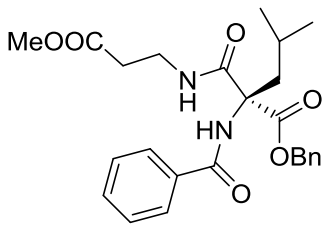

**2ab**



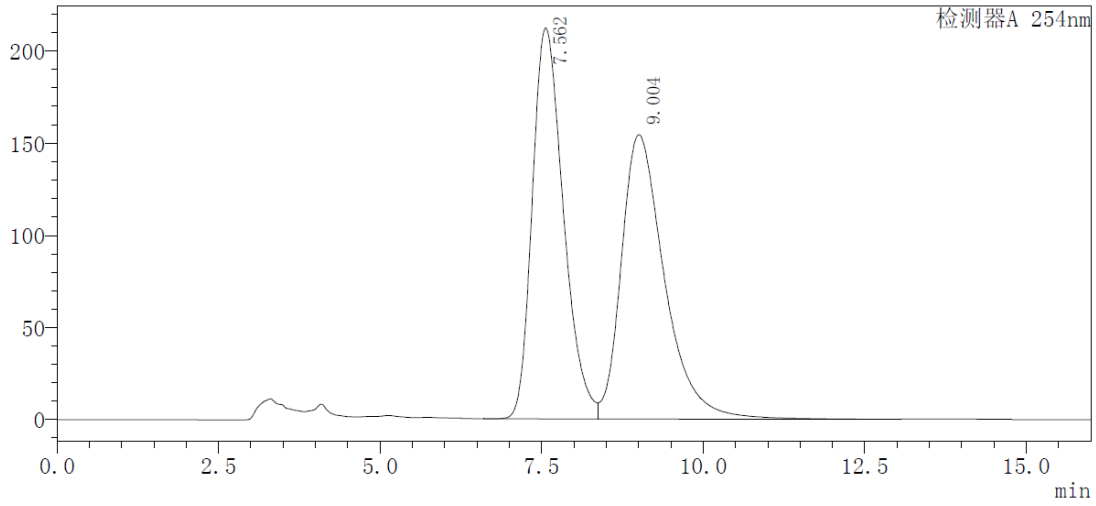

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 7.584 | 50.033 |
| 2 | 11.077 | 49.967 |



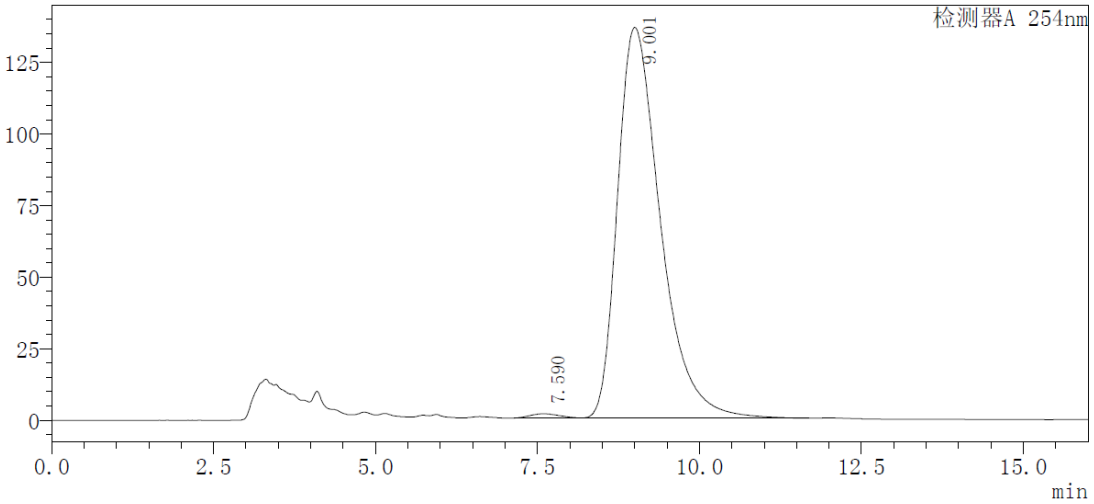

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 7.763 | 0.669 | |
| 2 | 11.104 | 99.331 | 99 |



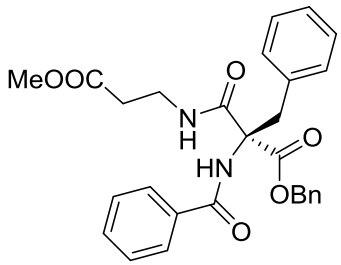

**2ac**



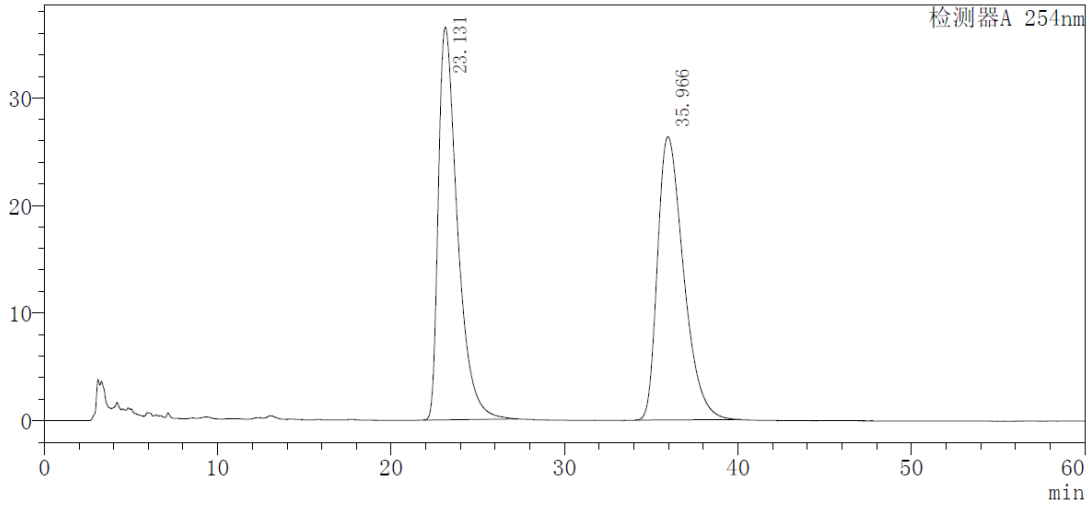

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 7.562 | 49.817 |
| 2 | 9.004 | 50.183 |



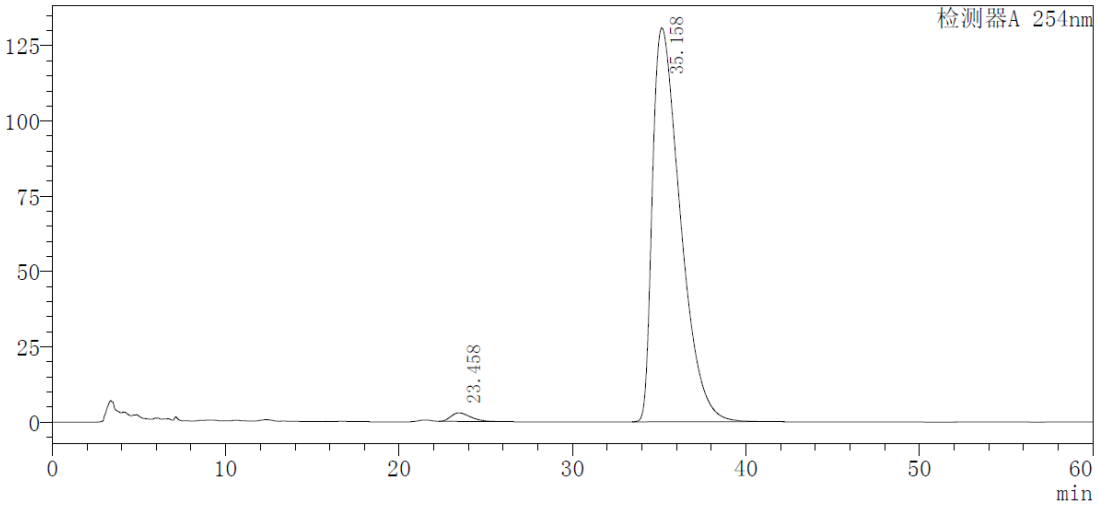

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 7.590 | 0.726 | |
| 2 | 9.001 | 99.274 | 99 |



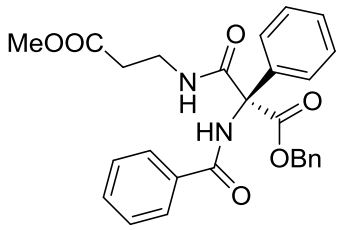

**2ad**



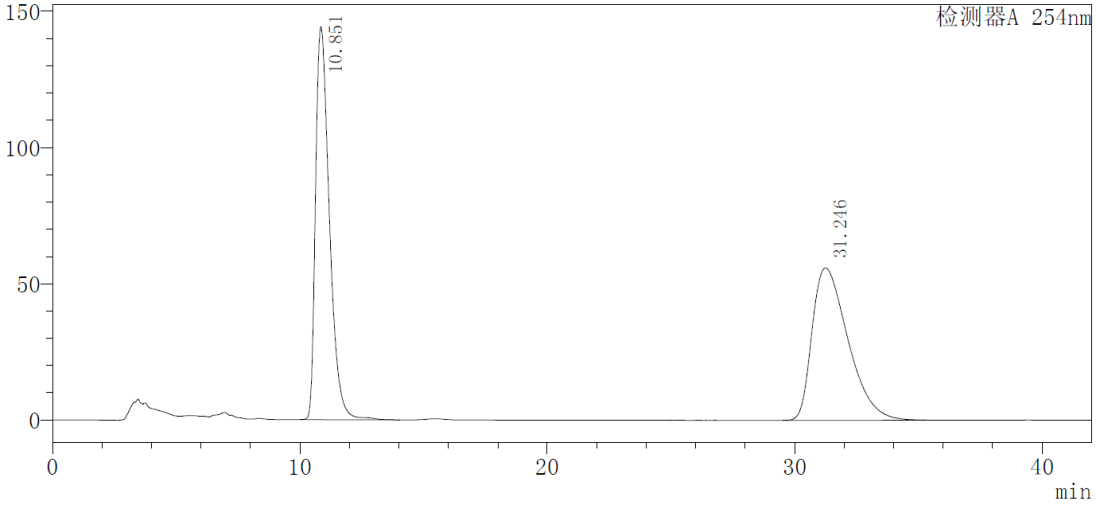

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 23.131 | 50.455 |
| 2 | 35.966 | 49.545 |



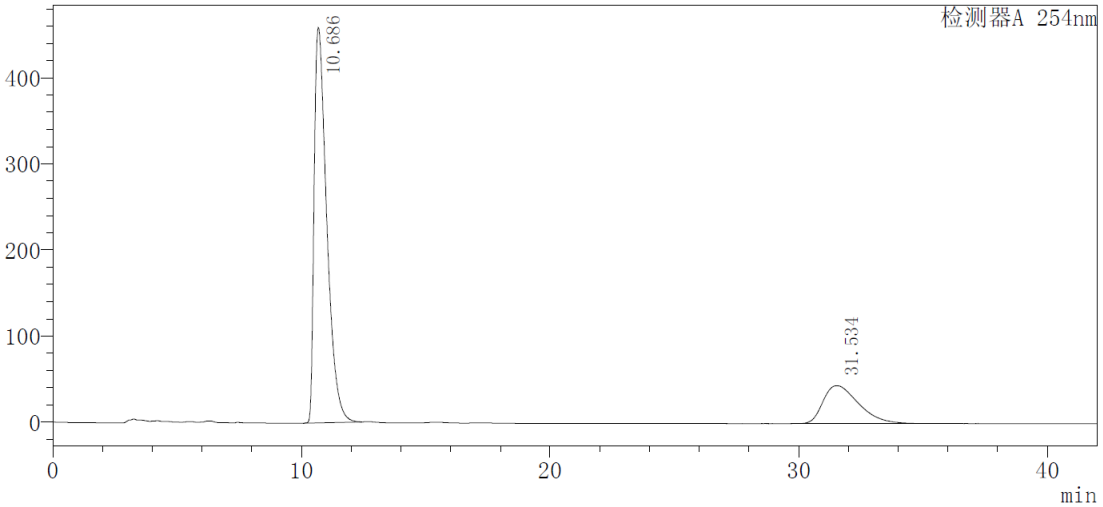

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 23.458 | 1.506 | |
| 2 | 35.158 | 98.494 | 97 |



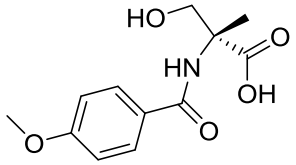

**2ae**



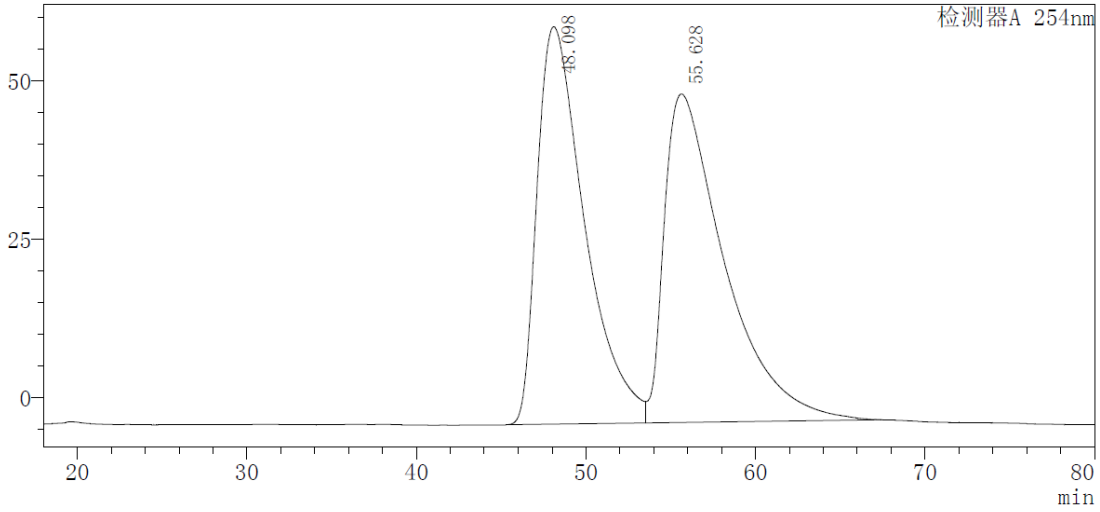

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 10.851 | 49.854 |
| 2 | 31.246 | 50.146 |



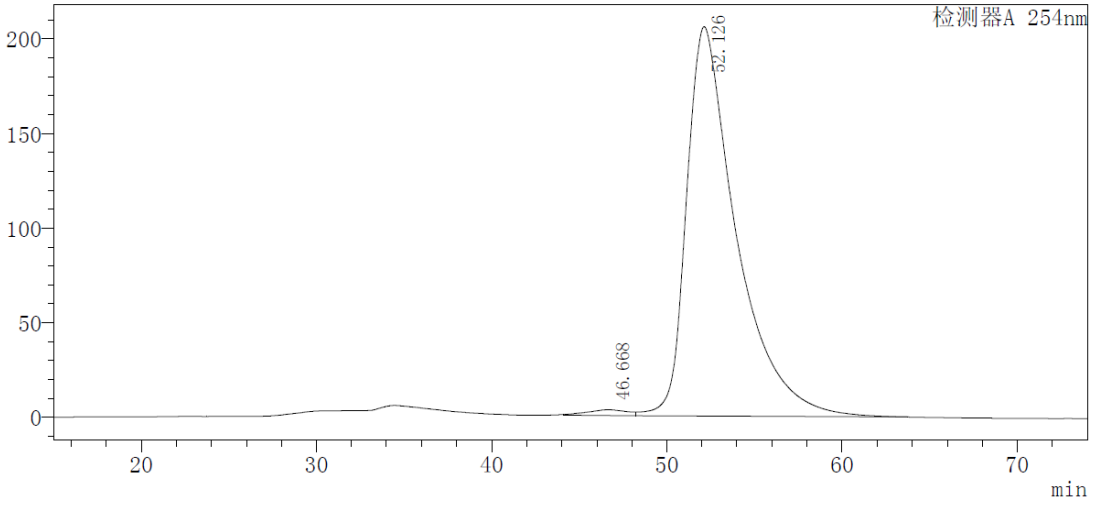

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 10.686 | 78.617 | 57 |
| 2 | 31.534 | 21.383 | |



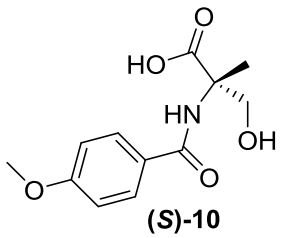

(*R*)-10



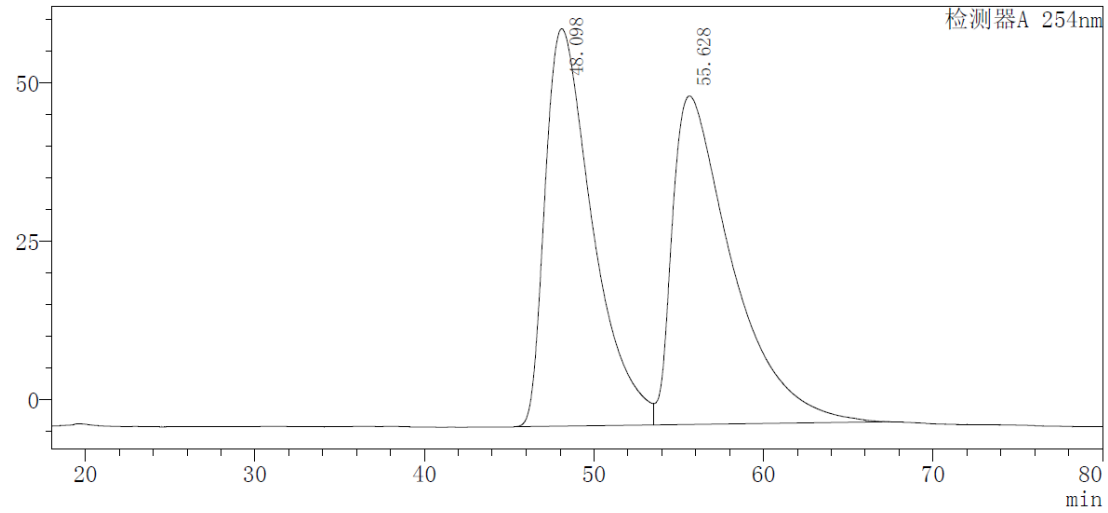

| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 48.098 | 48.860 |
| 2 | 55.628 | 51.140 |



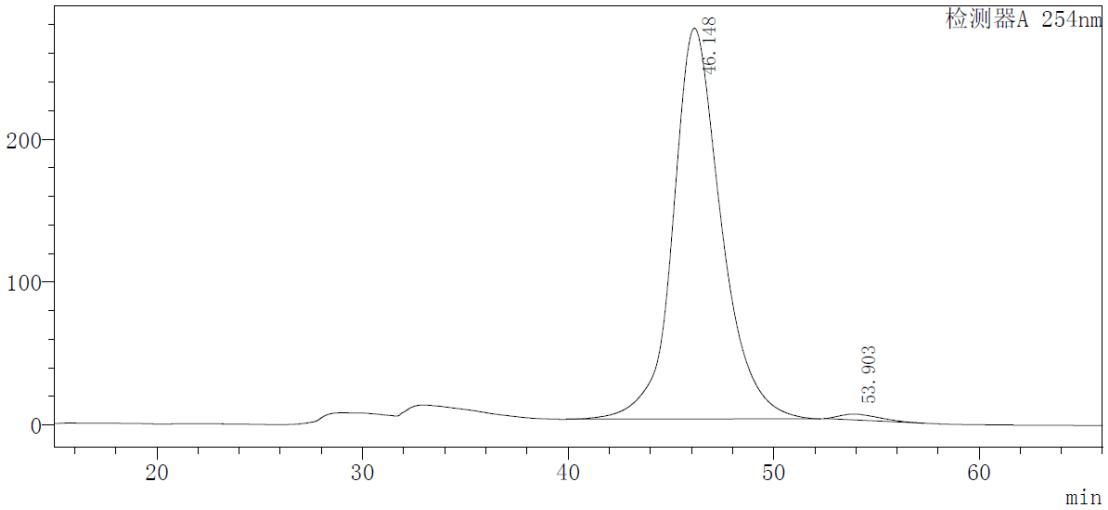

| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 46.668 | 1.182 | |
| 2 | 52.126 | 98.818 | 98 |



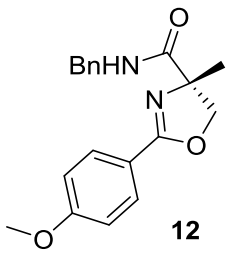

**(*S*)-10**




| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 48.098 | 48.860 |
| 2 | 55.628 | 51.140 |




| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 46.148 | 98.774 | 98 |
| 2 | 53.903 | 1.226 | |

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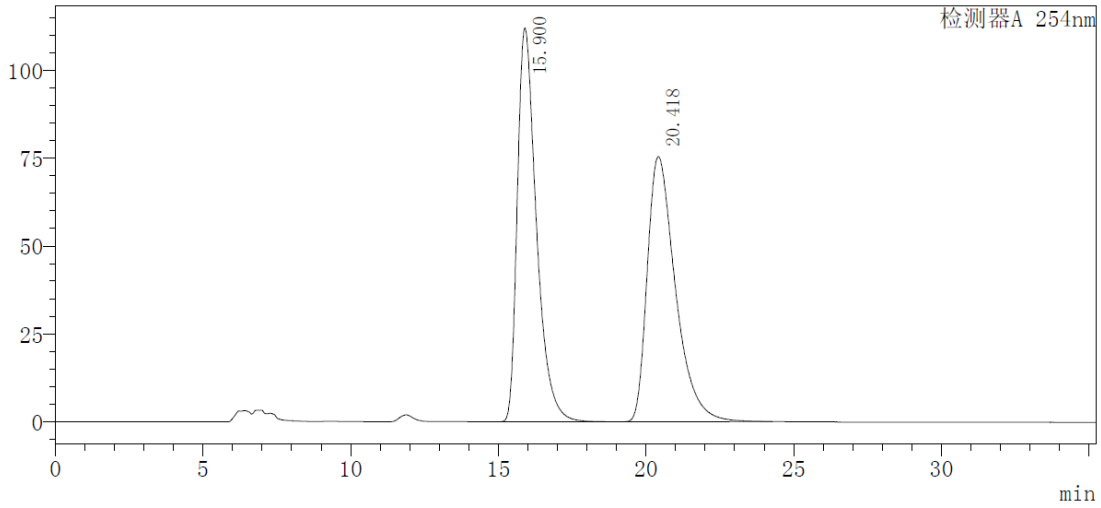
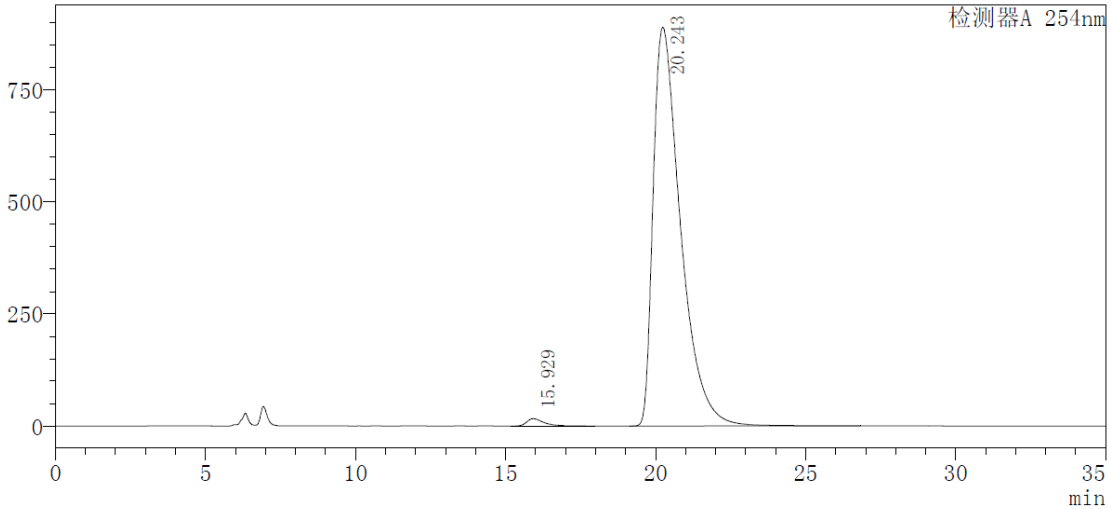



| Peak | Ret. Time | Area % |
|---|---|---|
| 1 | 15.900 | 50.147 |
| 2 | 20.418 | 49.853 |




| Peak | Ret. Time | Area % | Ee |
|---|---|---|---|
| 1 | 15.929 | 1.118 | |
| 2 | 20.243 | 98.882 | 98 |