Supporting Information

Total Synthesis and Stereochemical Assignment of Rakicidin F

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Author Contributions

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1. General Information

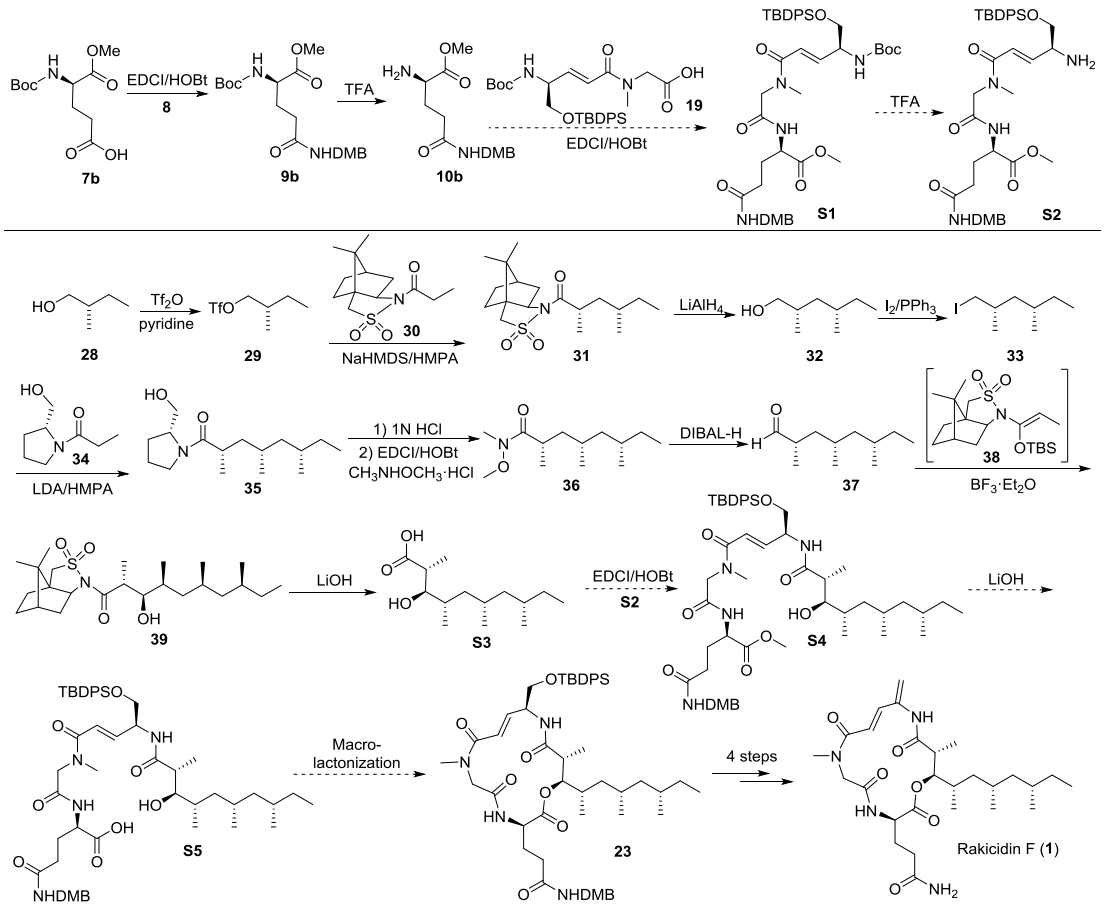
High-resolution mass spectra (HRMS) were obtained with a Thermo Scientific^{TM} Q Exactive Focus mass spertrometer (Orbitrap spec). IR spectra were recorded on a Bruker Tensor 27 instrument. Optical rotations were recorded on an Insmark IP 120 digital polarimeter. Elemental analysis data was obtained with a CHONS Elemental Analyzer (Vario EL cube).

^{1}H NMR spectra were recorded on a Bruker AV 400 spectrometer (400 MHz) using $CDCl_3$, MeOD-d_4 or DMSO-d_6 as the solvents. Chemical shifts are reported in parts per million (ppm) relative to either a tetramethylsilane internal standard or solvent signals. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, h = heplet, m = multiplet), coupling constants and integration. ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer (100 MHz) using $CDCl_3$, MeOD-d_4 or DMSO-d_6 as the solvents. Chemical shifts (δ) are reported in ppm measured relative to the solvent peak.

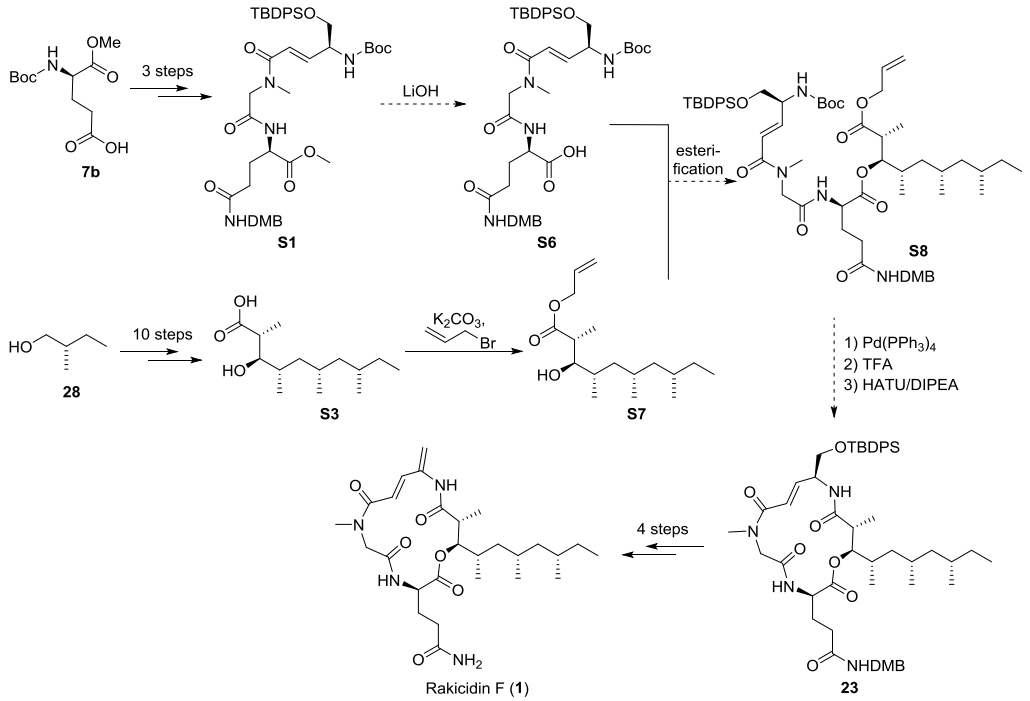
HPLC level solvent such as tetrahydrofuran (THF), dimethylformamide (DMF) and dichloromethane (DCM) were purified by solvent purification system (Innovative Technology) and stored with 4 Å molecular sieves under an argon atmosphere. Reagents were purchased from Experimental Reagents and Technology Management Platform of Nankai University without further purification, unless otherwise stated. Yields refer to chromatographically unless otherwise stated. Silica gel (200 – 300 or 100 – 200 mesh) and TLC plates were bought from Shanghai Haohong Scientific Co., Ltd.

2. Hypothetic Routes of Rakicidin F Macrocyclized at Different Sites

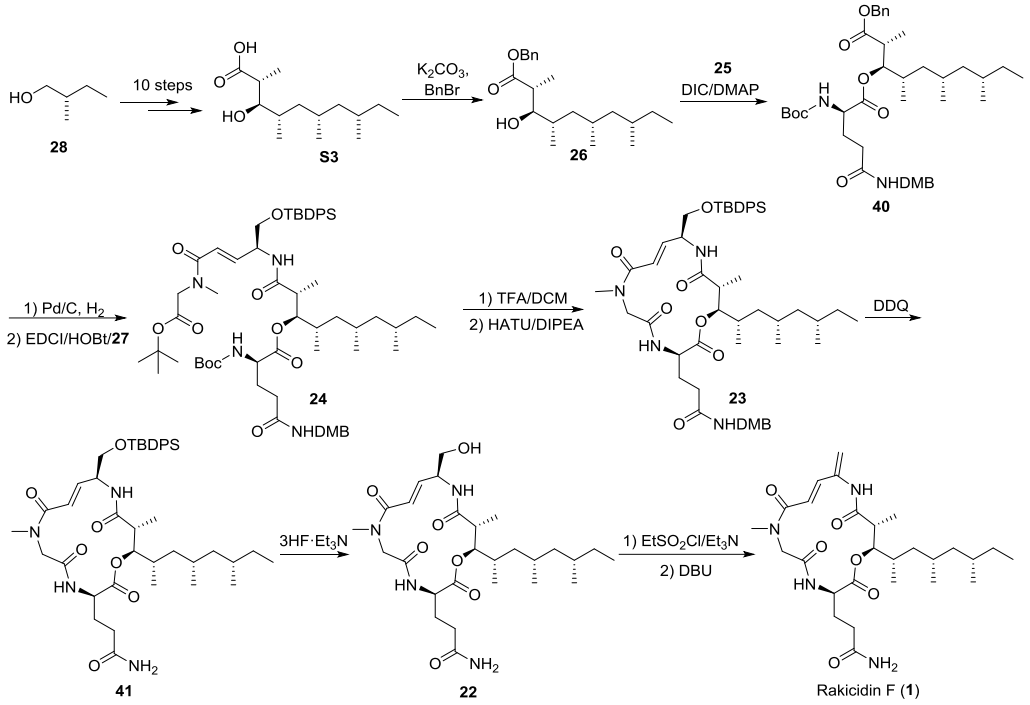
1) Macrocyclization at D site (17 LLS)



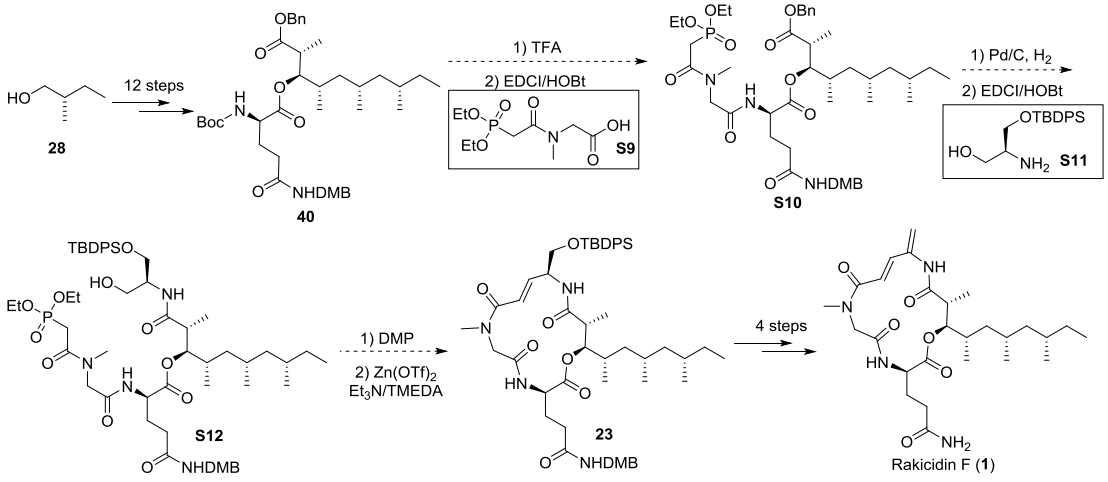
2) Macrocyclization at E site (19 LLS)



3) Macrocyclization at C site (20 LLS)



4) Macrocyclization at A site (22 LLS)



5) Macrocyclization at B site (20 LLS)

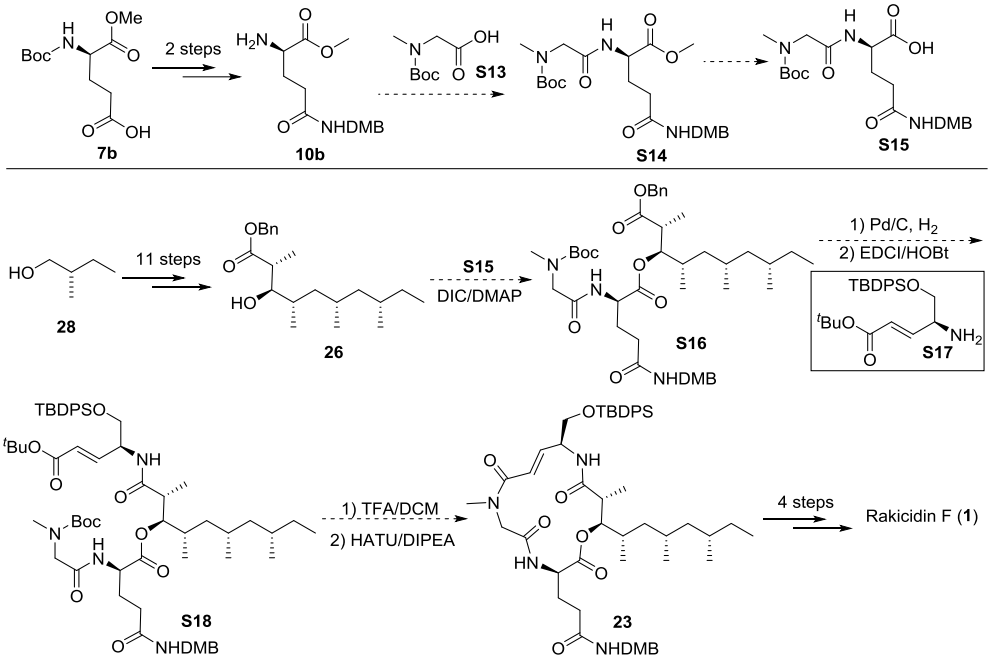
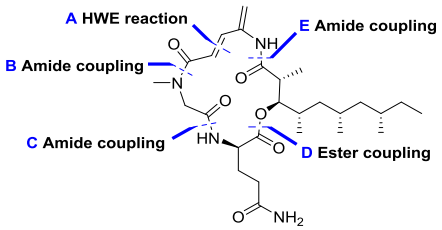


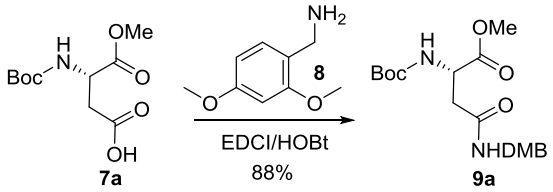
Table S1 Comparison of the five different macrocyclization sites of rakicidin F



Macrocyclization site	Estimated longest linear sequence (LLS)	Estimated total steps from commercial materials	Comparison
A	22	28	the longest LLS and epimerization might occur during the macrocyclization
B	20	27	secondary amine of **S18** was not suitable for macrocyclization
C	20	27	reported macrocyclization site
D	17	27	the shortest LLS and without any report
E	19	29	the second short LLS and without any report

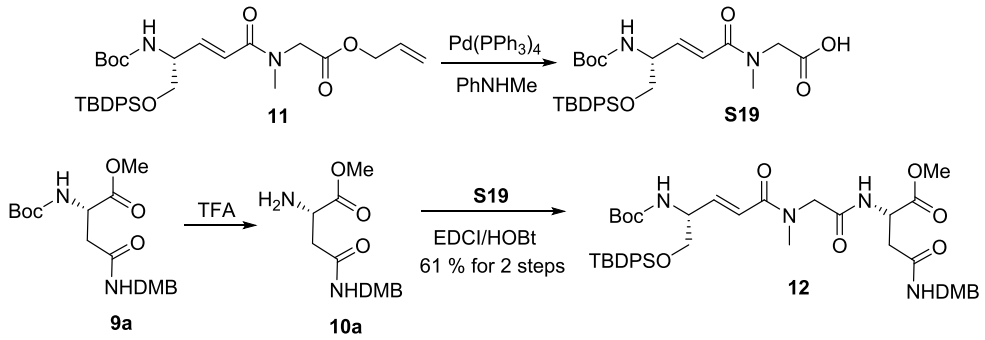
3. Synthesis of Compounds

Preparation of 9a.



To a solution of **7a** (3.85 g, 15.61 mmol) and **8** (3.13 g, 18.73 mmol) in DCM (150 mL) was added EDCI (3.59 g, 18.73 mmol) and HOBt (2.32 g, 17.17 mmol) at room temperature (r.t.). The reaction mixture was stirred for 12 h, then quenched with 5% $NaHSO_4$ (200 mL) and separated. The aqueous phase was extracted with ethyl acetate (2 × 100 mL). The combined organic phases were washed with brine (100 mL), dried (Na_2SO_4) and concentrated under reduced pressure to obtain **9a** (5.45 g, 88%) as a white solid. Melting point: 76 – 79 ℃; $[\alpha]_D^{15}$ = + 11.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.2 Hz, 1H), 6.47 – 6.35 (m, 2H), 6.04 (t, *J* = 5.6 Hz, 1H), 5.77 (d, *J* = 8.5 Hz, 1H), 4.47 (dt, *J* = 9.1, 4.5 Hz, 1H), 4.39 – 4.22 (m, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 3.69 (s, 3H), 2.86 (dd, *J* = 15.6, 4.6 Hz, 1H), 2.63 (dd, *J* = 15.6, 4.5 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 169.4, 160.7, 158.7, 155.8, 130.6, 118.6, 104.1, 98.7, 79.9, 55.5, 55.5, 52.6, 50.6, 39.1, 38.0, 28.4; ν_{max} (neat): 3333, 2975, 2839, 1714, 1654, 1615, 1508, 1461, 1291, 1209, 1163, 1037, 834, 736 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{29}N_2O_7^+$ $[M + H]^+$: 397.1970, found: 397.1973.

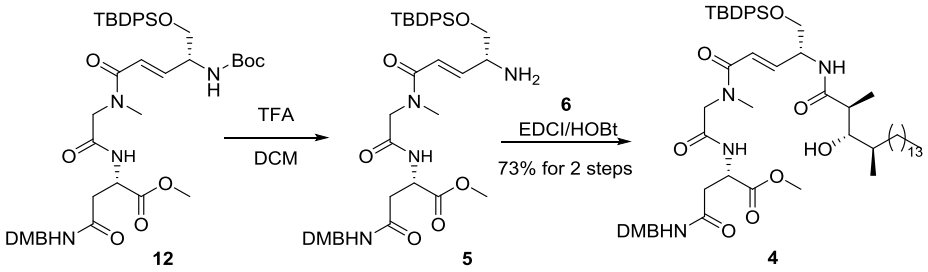
Preparation of 12.



To a solution of compound **9a** (1.6 g, 4.10 mmol) in DCM (19 mL) was added TFA (2 mL) dropwisely. The reaction mixture was stirred for 2 h at r.t., diluted with toluene (50 mL) and concentrated under reduced pressure to remove excess TFA. The crude product **10a** was used for the next step directly. To a solution of **11** (2.00 g, 3.45 mmol) in anhydrous THF (34 mL) were added $Pd(PPh_3)_4$ (398 mg, 0.35 mmol) and *N*-methylaniline (746 μL, 6.90 mmol). The reaction mixture was stirred for 1 h at r.t., and diluted with ethyl acetate (200 mL). The organic phase was separated and washed by 1 % HCl (2 × 60 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 20: 1 to 1: 1) to afford acid **S19**. The above-obtained acid **S19** and amine **10a** (4.10 mmol) were dissolved in anhydrous DCM (17 mL). To the mixture, HOBt (513 mg, 3.80 mmol) and EDCI (749 mg, 3.80 mmol) were added successively. The reaction

mixture was stirred for 18 h and the solvent was removed under reduced pressure. The residue was diluted with DCM (100 mL) and washed successively with 1 % HCl, saturated aqueous $NaHCO_3$, brine, dried over Na_2SO_4 and filtrated. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 2: 1) to obtain compound **12** (1.72 g, 61 % for 2 steps) as a colorless oil. $[\alpha]_D^{15}$ = + 21.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 4H), 7.46 – 7.31 (m, 6H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.80 (dd, *J* = 15.5, 5.3 Hz, 1H), 6.46 – 6.29 (m, 3H), 4.98 – 4.91 (m, 1H), 4.75 (dt, *J* = 8.2, 4.6 Hz, 1H), 4.39 (s, 1H), 4.27 (d, *J* = 5.7 Hz, 2H), 4.09 – 3.93 (m, 2H), 3.74 (d, *J* = 8.1 Hz, 7H), 3.65 (s, 3H), 3.05 (s, 3H), 2.83 (dd, *J* = 15.7, 4.6 Hz, 1H), 2.65 (dd, *J* = 16.0, 4.8 Hz, 1H), 1.42 (s, 9H), 1.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 169.2, 168.5, 166.8, 160.5, 158.5, 155.2, 143.8, 135.6, 135.5, 133.0, 132.8, 130.3, 129.9, 129.9, 127.8, 127.8, 120.8, 118.5, 104.0, 98.5, 79.6, 65.5, 55.3, 53.6, 52.6, 51.5, 49.1, 38.7, 37.3, 36.6, 28.3, 26.8, 19.2; ν_{max} (neat): 3310, 3070, 2934, 2859, 1745, 1665, 1617, 1510, 1465, 1430, 1395, 1288, 1209, 1163, 1113, 1041, 977, 825, 738, 705, 613, 506 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{43}H_{58}N_4O_{10}SiNa^+$ $[M + Na]^+$: 841.3815, found: 841.3820.

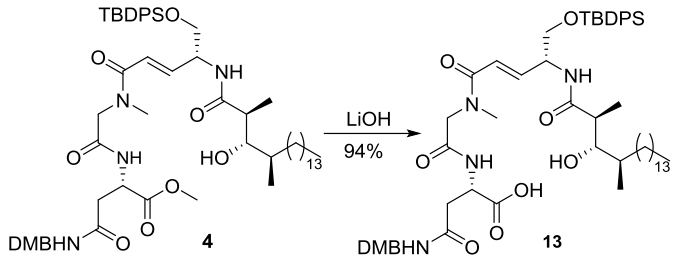
Preparation of 4.



To a solution of compound **12** (1.00 g, 1.22 mmol) in DCM (10 mL) was added TFA (1.5 mL) dropwisely. The reaction mixture was stirred for 2 h at r.t., diluted with toluene (50 mL) and concentrated under reduced pressure to remove excess TFA. The crude product **5** was used for the next step directly. The acid **6** (400 mg, 1.22 mmol) was dissolved in anhydrous DCM (10 mL). To the mixture were added HOBt (181 mg, 1.34 mmol), and EDCI (287 mg, 1.50 mmol). The reaction mixture was stirred for 0.5 h followed by addition of compound **5** (1.22 mmol). The reaction mixture was stirred for another 12 h, quenched with NH_4Cl (100 mL) and separated. The aqueous phase was extracted with ethyl acetate (2 × 100 mL). The combined organic phases were washed with 5% $NaHSO_4$ (100 mL), $NaHCO_3$ (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 1 : 1) to obtain compound **4** (955 mg, 73% for 2 steps) as a yellow oil. $[\alpha]_D^{15}$ = + 22.9 (*c* = 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.56 (m, 4H), 7.48 – 7.34 (m, 6H), 7.31 (t, *J* = 5.1 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 7.04 (d, *J* = 9.0 Hz, 1H), 6.68 (dd, *J* = 14.9, 2.9 Hz, 1H), 6.46 – 6.31 (m, 2H), 6.24 (dd, *J* = 14.8, 2.2 Hz, 1H), 5.91 (d, *J* = 8.2 Hz, 1H), 4.84 (dt, *J* = 8.7, 4.1 Hz, 1H), 4.31 (dd, *J* = 14.3, 5.6 Hz, 1H), 4.27 – 4.06 (m, 3H), 3.78 (dd, *J* = 15.6, 5.2 Hz, 2H), 3.75 (s, 3H), 3.72 (s, 3H), 3.68 (s, 3H), 3.65 – 3.50 (m, 3H), 3.11 (s, 2H), 3.06 (s, 1H), 2.89 (dd, *J* = 15.3, 4.0 Hz, 1H), 2.62 (dd, *J* = 15.3, 4.5 Hz, 1H), 2.17 – 2.05 (m, 1H), 1.56 (dq, *J* = 13.2, 6.6, 5.8 Hz, 1H), 1.25 (s, 26H), 1.04 (d, *J* = 5.6 Hz, 9H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 171.3, 169.7, 169.1,

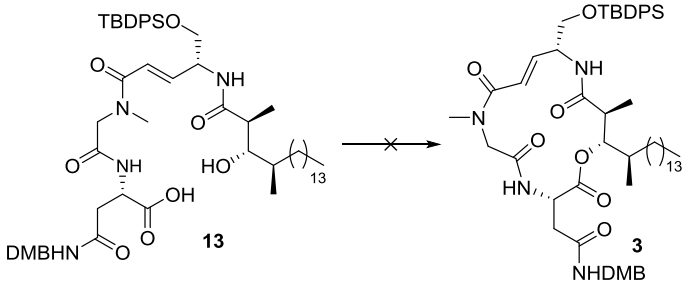
166.2, 160.5, 158.7, 144.9, 135.7, 135.6, 133.1, 132.84, 130.7, 130.1, 128.0, 119.3, 118.7, 103.8, 98.6, 75.1, 65.2, 55.5, 55.4, 55.3, 53.7, 52.8, 52.5, 48.9, 45.4, 38.7, 37.8, 36.8, 34.1, 32.0, 30.0, 29.9, 29.8, 29.7, 29.4, 27.5, 26.9, 22.8, 19.4, 14.2, 13.9, 11.9; ν_{max} (neat): 3299, 3071, 2927, 2855, 1746, 1656, 1617, 1537, 1510, 1463, 1431, 1289, 1209, 1113, 1039, 979，825, 743, 705, 506 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{58}H_{89}N_4O_{10}Si^+$ $[M + H]^+$: 1029.6343, found: 1029.6348.

Preparation of 13.



To a solution of compound **4** (600 mg, 0.58 mmol) in THF/ MeOH/ H_2O (*v*/ *v*/ *v* = 3 mL/ 1 mL/ 1 mL) was added LiOH (17 mg, 0.70 mmol). After stirred for 3 h, the reaction mixture was acidified to pH = 3.0 with 10% aqueous $NaHSO_4$ and extracted with ethyl acetate (2 × 50 mL). The organic phase was evaporated to obtain compound **13** (558 mg, 94%) as a yellow oil. $[\alpha]_D^{20}$ = + 2.4 (*c* = 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6, including rotamer 2:1) δ 12.60 (s, 1H), 8.17 (dd, *J* = 14.5, 7.0 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.63 (t, *J* = 6.3 Hz, 4H), 7.42 (q, *J* = 10.9, 9.2 Hz, 6H), 7.07 (t, *J* = 6.3 Hz, 1H), 6.87 – 6.58 (m, 2H), 6.56 – 6.38 (m, 2H), 4.79 – 4.47 (m, 3H), 4.15 (d, *J* = 5.6 Hz, 2H), 4.09 – 3.98 (m, 2H), 3.77 (s, 3H), 3.73 (s, 3H), 3.67 (t, *J* = 6.0 Hz, 2H), 3.47 (d, *J* = 7.2 Hz, 1H), 2.99 (s, 2H), 2.81 (d, *J* = 3.9 Hz, 1H), 2.63 (pd, *J* = 14.7, 12.2, 6.3 Hz, 2H), 2.46 – 2.32 (m, 1H), 1.47 (q, *J* = 7.0 Hz, 1H), 1.23 (s, 26H), 0.99 (d, *J* = 4.6 Hz, 9H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.84 (t, *J* = 6.6 Hz, 3H), 0.77 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100MHz, DMSO-d_6, including rotamer) δ 175.2, 172.7, 169.1, 168.0, 165.4, 159.6, 157.6, 142.7, 135.1, 132.8, 129.9, 128.8, 128.7, 127.9, 121.2, 118.8, 104.3, 98.1, 73.8, 65.2, 55.3, 55.1, 51.5, 49.9, 48.9, 43.8, 37.0, 36.8, 35.9, 34.1, 33.6, 31.3, 29.3, 29.1, 29.1, 29.0, 28.7, 26.8, 26.6, 22.1, 18.8, 14.9, 13.9, 12.8; ν_{max} (KBr): 3303, 2926, 2854, 1727, 1655, 1617, 1540, 1510, 1463, 1289, 1263, 1209, 1112, 1037, 977, 825, 741, 704, 611,505 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{57}H_{86}N_4O_{10}NaSi^+$ $[M + Na]^+$: 1037.6006, found: 1037.6005.

Unsuccessful synthesis of 3.



entry	reaction conditions	Solvent	yield/%
1	HATU, DMAP	THF	nd[b]
2	2,4,6-trichlorobenzoyl chloride, DMAP	Toluene	nd[b]
3	MYTsA, PTSA·H_2O	DCM	nd[b]

[a] Reaction conditions: compound **13** (10 mg), solvent (10 mL), concentration (1.0 mM). [b] nd = not detected (by TLC analysis). MYTsA = N-methyl ynetoluenesulfonamide; PTSA·H_2O = *p*-toluenesulfonic acid monohydrate.

Entry 1:

The solution of **13** (10 mg, 0.01 mmol) in THF (5 mL) was added to a suspension of HATU (38 mg, 0.10 mmol) and DMAP (14 mg, 0.10 mmol) in 5 mL of THF via a micro syringe pump (1.0 mL/h). The reaction mixture was stirred for another 24 h at r.t.. No compound **3** was detected through TLC analysis.

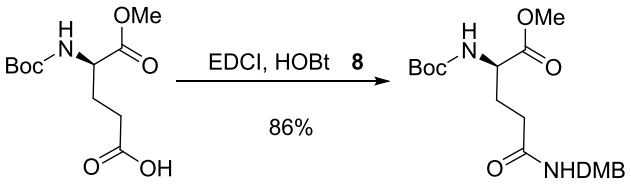
Entry 2:

To a solution of **13** (10 mg, 0.01 mmol) in toluene (0.5 mL) were added 2,4,6-trichlorobenzoyl chloride (2.6 mg, 0.015 mmol) and TEA (2.0 mg, 0.02 mmol). After stirring under Ar atmosphere at r.t. for 1 h, the reaction mixture was added with 5 mL of toluene. The solution obtained was then added to a suspension of DMAP (14 mg, 0.10 mmol in 4.5 mL of toluene) via a micro syringe pump (1.0 mL/h). The reaction mixture was stirred for another 12 h at r.t.. No compound **3** was detected through TLC analysis.

Entry 3:

To a solution of **13** (10 mg, 0.01 mmol) in DCM (0.5 mL) was added MYTsA (2.3 mg, 0.011 mmol). The reaction mixture was stirred under Ar atmosphere at r.t. overnight. TLC showed compound **13** was consumed out. The reaction mixture was added with 5 mL of DCM. The solution obtained was then added to a suspension of PTSA·H_2O (0.2 mg in 4.5 mL of DCM) via a micro syringe pump (1.0 mL/h). The reaction mixture was stirred for another 12 h at r.t.. No compound **3** was detected through TLC analysis.

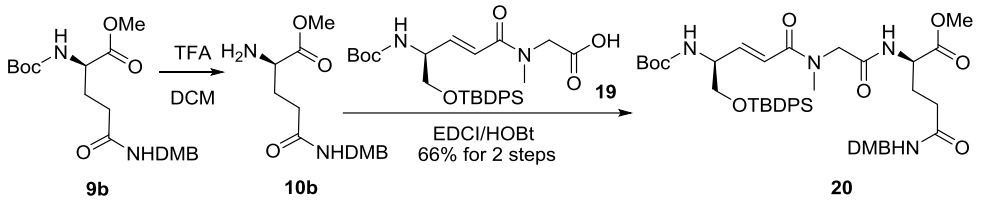
Preparation of 9b.



The titled compound **9b** was obtained following the procedure described for **9a**. (1.35 g, 86%) as a white solid. Melting point: 80 – 83 ℃; $[\alpha]_D^{15}$ = – 6.6 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.1 Hz, 1H), 6.42 (d, *J* = 2.3 Hz, 1H), 6.39 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.28 (s, 1H), 5.39 (d, *J* = 8.2 Hz, 1H), 4.32 (d, *J* = 5.7 Hz, 2H), 4.24 (td, *J* = 8.6, 4.4 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.69 (s, 3H), 2.22 (td, *J* = 7.1, 6.6, 2.4 Hz, 2H), 2.13 (dtd, *J* = 14.9, 7.5, 7.0, 4.5 Hz, 1H), 1.98 – 1.85 (m, 1H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 171.4, 160.6, 158.6, 155.8, 130.6, 118.9, 104.0, 98.6, 80.0, 55.5, 55.4, 53.2, 52.4, 39.1, 32.7, 28.7, 28.4; ν_{max} (neat): 3316, 2931, 1712, 1510, 1457, 1366, 1289, 1258, 1209, 1162, 1037,

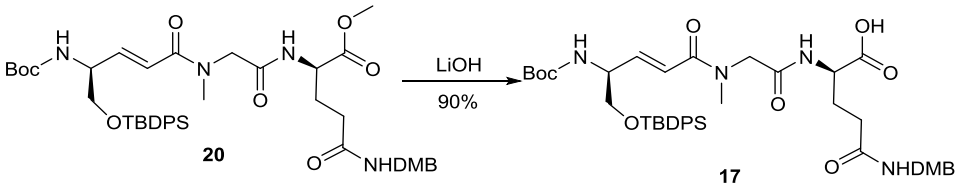
933, 834, 737, 638 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{31}N_2O_7^+$ $[M + H]^+$: 411.2126, found: 411.2128.

Preparation of 20.



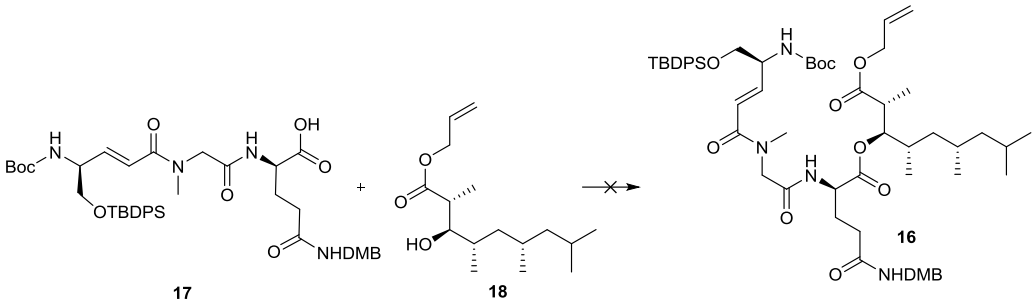
The titled compound **20** was obtained following the procedure described for **12**. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 2: 1) to obtain compound **20** (1.32 g, 66% for 2 steps) as a colorless oil. $[\alpha]_D^{15}$ = – 9.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, including rotamer = 3:1) δ 7.70 – 7.58 (m, 4H), 7.47 – 7.33 (m, 6H), 7.16 (t, *J* = 8.1 Hz, 2H), 6.81 (dd, *J* = 15.3, 5.6 Hz, 1H), 6.49 – 6.36 (m, 3H), 6.31 – 6.21 (m, 1H), 5.10 (s, 0.25H), 4.88 (s, 0.75H), 4.49 (d, *J* = 9.3 Hz, 1H), 4.38 (s, 1H), 4.31 (d, *J* = 5.7 Hz, 2H), 4.17 (d, *J* = 15.8 Hz, 1H), 3.94 (d, *J* = 15.6 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.74 – 3.71 (m, 1H), 3.69 (s, 3H), 3.68 – 3.59 (m, 1H), 3.12 (s, 2.25H), 3.08 (s, 0.75H), 2.21 (p, *J* = 8.2, 6.6 Hz, 3H), 1.98 (p, *J* = 9.1, 7.9 Hz, 1H), 1.43 (d, *J* = 5.5 Hz, 9H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, including rotamer) δ 172.2, 171.6, 169.0, 167.0, 160.6, 158.6, 155.4, 144.2, 135.7, 135.6, 133.1, 132.9, 130.5, 130.0, 128.0, 120.8, 118.9, 104.0, 98.7, 79.8, 65.6, 55.5, 55.4, 53.7, 52.6, 52.3, 52.1, 39.1, 37.0, 32.4, 28.5, 27.0, 19.4; ν_{max} (neat): 3302, 2934, 2859, 1744, 1711, 1661, 1616, 1509, 1463, 1264, 1208, 1163, 1113, 1039, 824, 741, 705, 613, 506 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{44}H_{61}N_4O_{10}Si^+$ $[M + H]^+$: 833.4152, found: 833.4159.

Preparation of 17.



The titled compound **17** was obtained following the procedure described for **13**. The solvent was evaporated to obtain compound **17** (140 mg, 90%) as a yellow oil. $[\alpha]_D^{20}$ = – 1.1 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6, including rotamer = 2:1) δ 8.19 (s, 1H), 7.61 (dt, *J* = 7.6, 4.1 Hz, 4H), 7.43 (tq, *J* = 10.5, 5.6 Hz, 6H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.66 (dt, *J* = 11.1, 5.4 Hz, 1H), 6.59 – 6.37 (m, 3H), 4.38 (dd, *J* = 15.9, 8.6 Hz, 1H), 4.13 (d, *J* = 5.6 Hz, 2H), 4.02 (dd, *J* = 14.0, 7.0 Hz, 2H), 3.75 (s, 3H), 3.71 (s, 3H), 3.60 (dd, *J* = 11.5, 6.4 Hz, 2H), 3.03 (s, 2H), 2.84 (s, 1H), 2.15 (s, 2H), 1.97 (s, 1H), 1.81 (s, 1H), 1.37 (d, *J* = 9.6 Hz, 9H), 0.98 (d, *J* = 3.6 Hz, 9H); ^{13}C NMR (100 MHz, DMSO-d_6, including rotamer) δ 172.4, 167.1, 166.9, 166.1, 165.5, 159.5, 157.5, 155.2, 142.5, 141.7, 135.1, 132.9, 129.8, 128.5, 127.8, 121.2, 119.3, 104.2, 98.1, 77.9, 65.7, 65.5, 55.3, 55.1, 53.5, 52.2, 50.5, 36.7, 36.2, 32.4, 29.2, 28.2, 26.6, 18.8; ν_{max} (KBr): 3300, 2934, 1664, 1529, 1463, 1420, 1367, 1289, 1260, 1209, 1162, 1115, 1041, 971, 825, 742, 704, 612, 506 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{43}H_{58}N_4O_{10}NaSi^+$ $[M + Na]^+$: 841.3815, found: 841.3810.

Unsuccessful synthesis of 16.



entry	reaction conditions	Solvent	yield/%
1	DIC, DMAP	DCM	nd[a]
2	MYTsA, TEA	ACN	nd[a]

[a] nd = not detected (by TLC analysis). MYTsA = N-methyl ynetoluenesulfonamide; PTSA·H_2O = *p*-toluenesulfonic acid monohydrate.

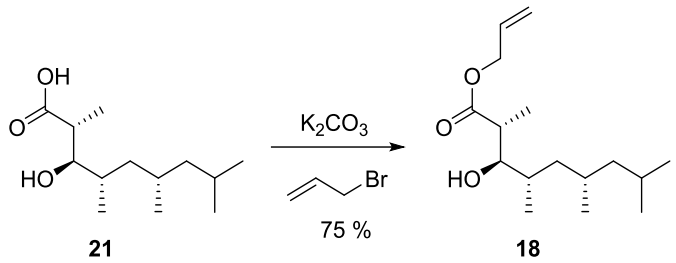
Entry 1:

To a solution of compound **17** (100 mg, 0.12 mmol) and **18** (32 mg, 0.12 mmol) in DCM (240 μL) were added DMAP (1.2 mg, 0.01 mmol) and DIC (20 μL, 0.13 mmol) at 0 ℃. The reaction mixture was stirred for 3 h, and diluted with DCM (20 mL). The suspension was filtered through a pad of celite and the filter cake was washed with DCM (3 × 10 mL). The combined filtrates were concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 3:1) to obtain a new product. However, considerable racemization at the α-position of acid fragment **17** was observed.

Entry 2:

The solution of compound **17** (100 mg, 0.12 mmol) and MYTsA (27.6 mg, 0.13 mmol) in DCM (1.2 mL) was stirred ar r.t. overnight. TLC analysis showed compound **17** was consumed out. The reaction mixture was concentrated under reduced pressure followed by addition of ACN (1.2 mL) and TEA (12 mg, 0.12 mmol). The reaction mixture was stirred for another 12 h at r.t.. No new compound was detected through TLC analysis.

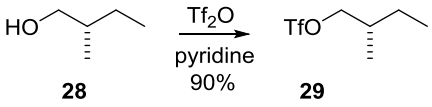
Preparation of 18.



To a solution of known acid **21** (100 mg, 0.43 mmol) in DMF (4 mL) were added K_2CO_3 (119 mg, 0.86 mmol) and 3-bromoprop-1-ene (77 mg, 0.65 mmol) at r.t.. The mixture was stirred for 10 h followed by addition of H_2O (10mL). The resultant mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed by brine (4 × 50 mL), dried

over $MgSO_4$, filtered and concentrated under reduced pressure. The crude was purified with column chromatography on silica gel (petroleum ether/ ethyl acetate = 30:1) to afford compound **18** (87 mg, 75 %) as a colorless oil. $[\alpha]_D^{15}$ = – 20.4 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (ddtd, *J* = 16.4, 10.9, 5.7, 2.3 Hz, 1H), 5.38 – 5.28 (m, 1H), 5.27 – 5.20 (m, 1H), 4.61 (dd, *J* = 5.5, 2.2 Hz, 2H), 3.59 (ddt, *J* = 8.6, 5.8, 2.7 Hz, 1H), 2.66 (pd, *J* = 7.3, 2.2 Hz, 1H), 2.42 (dd, *J* = 6.2, 2.4 Hz, 1H), 1.77 – 1.59 (m, 2H), 1.62 – 1.50 (m, 1H), 1.38 (dtd, *J* = 13.8, 6.9, 2.3 Hz, 1H), 1.17 (dd, *J* = 7.2, 2.3 Hz, 3H), 1.14 – 0.97 (m, 2H), 1.01 – 0.88 (m, 1H), 0.89 – 0.77 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 132.1, 118.6, 75.5, 65.4, 46.7, 43.4, 42.0, 32.0, 27.5, 25.3, 23.8, 22.2, 20.4, 14.5, 13.3; ν_{max} (neat): 3530, 2957, 1724, 1461, 1382, 1259, 1173, 1035, 985, 930, 751 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{30}O_3Na^+$ [M + Na]$^+$: 293.2088, found: 293.2091.

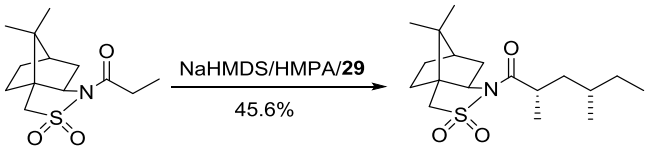
Preparation of 29.



28 **29**

To a suspension of pyridine (28.6 mL, 354.45 mmol) and Tf_2O (100 g, 354.45 mmol) in 300 mL of DCM was added compound **28** (40.5 mL, 372.17 mmol) under Ar atmosphere at 0 ℃. The reaction mixture was stirred for 2 h and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether) to obtain compound **29** (8.6 g, 90 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (dd, *J* = 9.5, 5.7 Hz, 1H), 4.34 (dd, *J* = 9.5, 6.4 Hz, 1H), 1.93 – 1.83 (m, 1H), 1.55 – 1.43 (m, 1H), 1.27 (dt, *J* = 13.5, 7.5 Hz, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.8 (d, *J* = 319.5 Hz), 81.8, 34.9, 25.3, 15.8, 11.1; ^{19}F NMR (375 MHz, $CDCl_3$) δ -74.75. The spectroscopic data were identical with those reported in the literature (*J. Org. Chem*. **2002**, 67, 5176–5183)

Preparation of 31.

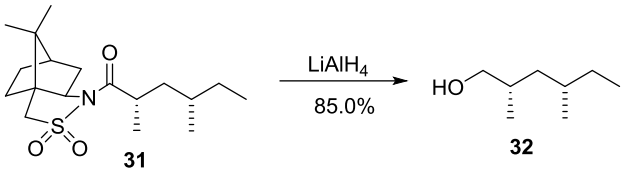


30 **31**

To a solution of compound **30** (96.2 g, 354.45 mmol) and HMPA (69.9 mL, 389.90 mmol) in THF (500 mL) was added NaHMDS (177.2 mL, 354.45 mmol, 2 M in THF) under Ar atmosphere at –78 ℃. The reaction mixture was stirred for 0.5 h followed by addition of compound **29** (8.6 g) over 30 min. The reaction mixture was stirred for another 8 h at –78 ℃, quenched with NH_4Cl (100 mL) and separated. The aqueous phase was extracted with ethyl acetate (2 × 300 mL). The combined organic phases were washed with 5% $NaHSO_4$ (400 mL) and brine (200 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 35:1) to obtain compound **31** (49.6 g, 45.6 %) as a white solid. Melting point: 68 – 71 ℃; $[\alpha]_D^{15}$ = – 74.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (dd, *J* = 7.4, 5.1 Hz, 1H), 3.43 (d, *J* = 13.8 Hz, 1H), 3.35 (d, *J* = 13.8 Hz, 1H), 3.10 (ddq, *J* = 11.8, 9.1, 6.4 Hz, 1H), 2.01 –

1.88 (m, 2H), 1.88 – 1.71 (m, 3H), 1.69 (td, *J* = 9.0, 4.5 Hz, 1H), 1.36 – 1.28 (m, 1H), 1.27 – 1.18 (m, 2H), 1.17 – 1.10 (m, 1H), 1.10 – 0.97 (m, 8H), 0.87 (s, 3H), 0.80 (d, *J* = 6.3 Hz, 3H), 0.73 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 65.1, 53.0, 48.1, 47.6, 44.6, 42.6, 38.5, 37.6, 32.7, 32.4, 29.5, 26.3, 20.6, 19.8, 18.9, 17.7, 11.1; ν_{max} (neat): 2961, 1695, 1460, 1390, 1331, 1268, 1211, 1133, 1061, 1037, 769, 540 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{32}NO_3S^+$ $[M + H]^+$: 342.2098, found: 342.2101.

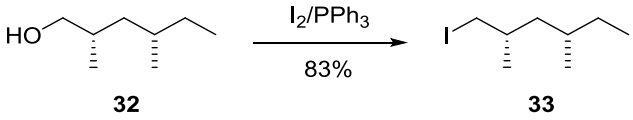
Preparation of 32.



31 **32**

To a suspension of $LiAlH_4$ (2.7 g, 71.3 mmol) in THF (100 mL) was added compound **31** (20.3 g, 59.4 mmol, in 150 mL of THF) at 0 ℃. After stirred for 30 min, the reaction mixture was warmed to r.t.. The reaction mixture was stirred for another 3 h, quenched with H_2O (2.7 mL), 15% NaOH (aq., m/v, 8.1 mL), and H_2O (2.7 mL) successively. The resulting suspension was added with anhydrous $MgSO_4$, and stirred for 20 min. The solid was removed by filtration and the residue was washed with DCM (3 × 400 mL). The combined organic phases were concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (petroleum ether (30–60 boiling range)/ ethyl acetate = 20:1) to obtain compound **32** (6.5 g, 85.0%) as colorless liquid. $[\alpha]_D^{15}$ = – 4.0 (*c* = 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (dd, *J* = 10.5, 5.2 Hz, 1H), 3.33 (dd, *J* = 10.5, 6.8 Hz, 1H), 1.90 – 1.81 (m, 1H), 1.75 – 1.61 (m, 1H), 1.45 – 1.33 (m, 2H), 1.32 – 1.24 (m, 2H), 1.04 (dq, *J* = 13.1, 7.4 Hz, 1H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.88 – 0.79 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.4, 40.7, 33.2, 31.7, 29.1, 19.9, 17.4, 11.2; ν_{max} (neat): 2959, 2925, 1721, 1461, 1379, 1264, 1167, 1034, 750 cm^{-1}. The spectroscopic data and physical properties of **32** were identical with those reported in the literature (*Angew. Chem. Int. Ed.* **2017**, *56*, 7525-7530).

Preparation of 33.

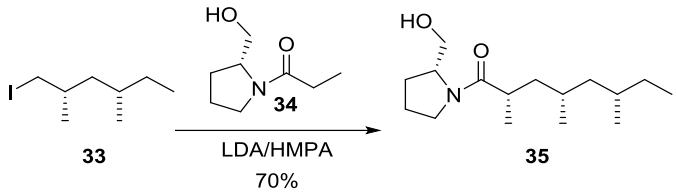


32 **33**

To a solution of I_2 (12.9 g, 50.8 mmol), imidazole (3.5 g, 50.8 mmol) and PPh_3 (13.3 g, 50.8 mmol, 1.1 eq) in DCM (250 mL) was added compound **32** (6.0 g in 100 mL of DCM, 50.8 mmol) under Ar atmosphere at 0 ℃. The reaction mixture was stirred for 2 h and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-pentane) to obtain compound **33** (10.1 g, 83%) as a light-yellow liquid. $[\alpha]_D^{15}$ = + 5.1 (*c* = 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.25 (dd, *J* = 9.6, 4.1 Hz, 1H), 3.13 (dd, *J* = 9.6, 6.0 Hz, 1H), 1.50 (dtd, *J* = 13.0, 6.8, 4.3 Hz, 1H), 1.42 – 1.27 (m, 3H), 1.23 – 1.03 (m, 1H), 1.05 – 0.97 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.88 (dd, *J* = 8.3, 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.7, 32.0, 31.7, 29.5, 21.5, 19.5, 18.5, 11.3; ν_{max} (neat): 2960, 2923, 1698, 1460, 1378, 1316,

1194, 1137, 766, 605 cm^{-1}; Elem. Anal.: calcd for $C_8H_{17}I$: C, 40.02; H, 7.14; I, 52.85, found: C, 40.78; H, 6.96; I, 52.26.

Preparation of 35.



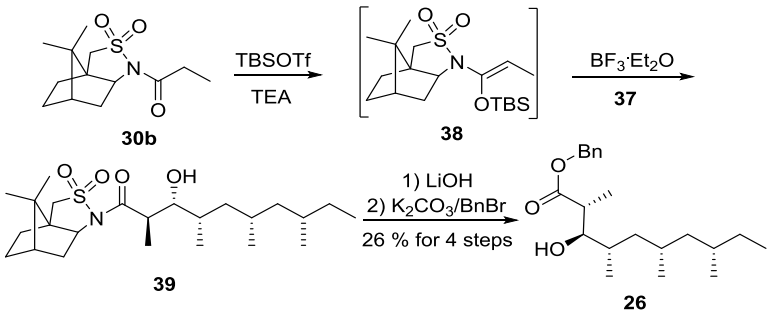
To the solution of diisopropylamine (1.35 mL, 9.58 mmol) in THF (8 mL) was added *n*-BuLi (2.5 M, 3.82 mL, 9.16 mmol) dropwise at –10 ℃ under Ar atmosphere. The reaction mixture was warmed to r.t., stirred for 40 min, and then cooled back to –10 ℃ followed by addition of compound **34** (983 mg, 6.25mmol) dropwise. After stirred for 1 h, HMPA (1.72 g, 9.58 mmol) was added to the mixture. The reaction mixture was cooled to –78 ℃ followed by addition of compound **33** (1.00 g, 4.16 mmol, in 5 mL of THF) dropwise. After stirred for 10 h at –78 ℃, the reaction was quenched with saturated aqueous NH_4Cl (30 mL), EtOAc (50 mL) and separated. The organic phase was washed with brine (3 × 20 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated and purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 5:1) to obtain compound **35** (785 mg, 70%) as a colorless oil. $[\alpha]_D^{15}$ = + 54.0 (*c* = 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (s, 1H), 4.21 (dq, *J* = 11.2, 3.9, 3.1 Hz, 1H), 3.66 – 3.51 (m, 3H), 3.54 – 3.43 (m, 1H), 2.65 (h, *J* = 6.7 Hz, 1H), 2.09 – 1.94 (m, 1H), 1.88 (ddq, *J* = 26.0, 13.2, 6.5 Hz, 2H), 1.72 (ddd, *J* = 13.7, 8.5, 5.4 Hz, 1H), 1.57 (dq, *J* = 11.7, 6.0 Hz, 1H), 1.52 – 1.36 (m, 2H), 1.31 (ddd, *J* = 12.7, 6.8, 5.0 Hz, 1H), 1.16 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.03 (dq, *J* = 14.3, 7.2 Hz, 2H), 0.87 (dd, *J* = 15.1, 8.4 Hz, 1H), 0.85 – 0.78 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 67.8, 61.1, 47.9, 44.8, 41.1, 35.7, 31.5, 29.1, 28.3, 28.1, 24.6, 20.9, 19.8, 18.5, 11.3; ν_{max} (neat): 3392, 2960, 2927, 2875, 1619, 1462, 1434, 1377, 1335, 1188, 1055, 753 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{32}NO_2^+$ $[M + H]^+$: 270.2428, found: 270.2431.

Preparation of 36.

The solution of compound **35** (2.5 g, 9.28 mmol) in 1 N HCl (90 mL) was stirred at 90 ℃ for 6 h. The aqueous phase was extracted with ethyl acetate (3 × 80 mL). The combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The above-obtained acid crude was dissolved in anhydrous DCM (46 mL) followed by addition of HOBt (1.25 g, 9.28 mmol), EDCI (1.77 g, 9.28 mmol), DIPEA (1.80 g, 13.92 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride (1.36 g, 13.92 mmol). The reaction mixture was stirred for another 12 h, quenched with NH_4Cl (100 mL). and separated. The aqueous phase was extracted with ethyl acetate (2 ×100 mL). The combined organic phases were washed with 5% $NaHSO_4$ (100 mL), $NaHCO_3$ (100 mL) and brine (100 mL), dried over

Na_2SO_4, filtered and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 20:1) to obtain compound **36** (1.47 g, 69% for 2 steps) as a yellow oil. $[\alpha]_D^{15}$ = + 16.9 (*c* = 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 3.15 (s, 3H), 3.03 – 2.93 (m, 1H), 1.75 (ddd, *J* = 13.8, 9.2, 4.9 Hz, 1H), 1.50 – 1.35 (m, 2H), 1.38 – 1.20 (m, 1H), 1.17 (dt, *J* = 14.2, 7.0 Hz, 1H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.00 (tdd, *J* = 13.7, 8.8, 4.1 Hz, 2H), 0.92 – 0.86 (m, 1H), 0.88 – 0.77 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 61.5, 45.0, 41.4, 32.8, 32.5, 31.6, 29.3, 28.3, 20.7, 19.8, 18.5, 11.3; ν_{max} (neat): 2961, 2929, 1735, 1669, 1462, 1413, 1381, 1305, 1176, 998, 753, 601 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{28}NO_2^+$ $[M + H]^+$: 230.2115, found: 230.2116.

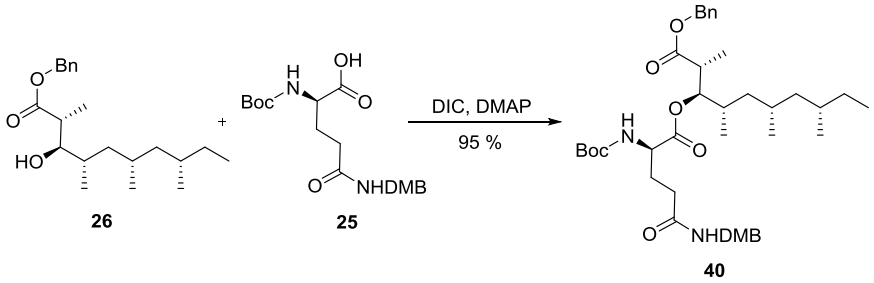
Preparation of 26.



To a solution of compound **38** (18.3 mmol) in DCM (30 mL) was added aldehyde **37** (6.10 mmol in 20 mL of DCM) at –78 ℃ under Ar atmosphere. After stirred for 30 min, the reaction mixture was added with BF_3·Et_2O (866 mg, 6.10 mmol). The reaction mixture was stirred at –78 ℃ for 3 h before saturated aqueous Na_2CO_3 (30 mL) was added. The resulting mixture was separated and the aqueous phase was extracted with ethyl acetate (2 × 50 mL). The combined organic phases were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 15:1) to obtain crude **39**. The above-obtained compound **39** was dissolved in THF/ MeOH/ H_2O (*v*/ *v*/ *v* = 36 mL/ 12 mL/ 12 mL) followed by addition of LiOH (438 mg, 18.30 mmol). After stirred for 4 h, the reaction mixture was acidified to pH = 3.0 with aqueous 10% $NaHSO_4$, extracted with ethyl acetate (2 × 100 mL) and separated. The organic phase was evaporated, and the resulting colorless oil was directly used for the next step without further purification. The above-obtained colorless oil was dissolved in DMF (30 mL) followed by addition of K_2CO_3 (2.53 g, 18.30 mmol) and BnBr (2.07 g, 12.2 mmol) at r.t.. The mixture was stirred for 10 h, added with H_2O (10 mL). The resultant mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed by brine (4 × 50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude was purified with column chromatography on silica gel (petroleum ether/ ethyl acetate = 35:1) to afford compound **26** (489 mg, 26 % for 4 steps) as a colorless oil. $[\alpha]_D^{15}$ = – 32.1 (*c* = 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 3.4 Hz, 5H), 5.19 (d, *J* = 12.4 Hz, 1H), 5.14 (d, *J* = 12.4 Hz, 1H), 3.65 (ddd, *J* = 8.8, 5.9, 3.1 Hz, 1H), 2.69 (p, *J* = 7.4 Hz, 1H), 2.38 (d, *J* = 5.9 Hz, 1H), 1.72 (hd, *J* = 6.8, 3.0 Hz, 1H), 1.59 (dd, *J* = 13.8, 7.1 Hz, 1H), 1.50 – 1.40 (m, 2H), 1.40 – 1.30 (m, 1H), 1.24 – 1.19 (m, 1H), 1.17 (d, *J* = 7.1 Hz, 3H), 1.11 – 0.89 (m, 3H), 0.89 – 0.80 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 136.0, 128.7, 128.4, 128.3, 75.2, 66.5, 44.9, 43.6, 41.6, 31.9, 31.7, 29.1, 27.4, 20.8, 20.0, 14.5, 13.5, 11.3; ν_{max} (neat): 2958, 2926,

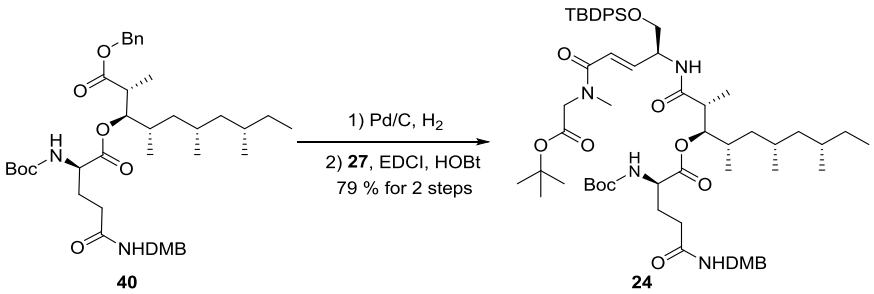
1736, 1620, 1459, 1380, 1261, 1170, 1131, 984, 749, 698 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{34}O_3Na^+$ [M + Na]$^+$: 357.2401, found: 357.2395.

Preparation of 40.



To a solution of compound **25** (1.31 g, 3.59 mmol) and **26** (400 mg, 1.19 mmol) in DCM (1.20 mL) were added DMAP (14.7 mg, 0.12 mmol) and DIC (612 μL, 3.95 mmol) at 0 ℃. The reaction mixture was stirred for 1.5 h, diluted with DCM (50 mL). The suspension was filtered through a pad of celite and the filter cake was washed with DCM (3 × 10 mL). The combined filtrates were concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 20 to 10:1) to obtain compound **40** (768 mg, 95 %) as a colorless oil. $[\alpha]_D^{15}$ = – 9.4 (*c* = 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5H), 7.16 (d, *J* = 8.2 Hz, 1H), 6.50 – 6.31 (m, 3H), 5.21 (d, *J* = 8.2 Hz, 1H), 5.14 (dd, *J* = 8.9, 3.1 Hz, 1H), 4.99 (q, *J* = 12.3 Hz, 2H), 4.35 (d, *J* = 5.6 Hz, 2H), 4.22 (td, *J* = 8.0, 4.5 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.81 (p, *J* = 7.5 Hz, 1H), 2.26 – 2.05 (m, 3H), 1.93 – 1.75 (m, 2H), 1.61 (dq, *J* = 13.7, 6.5 Hz, 1H), 1.42 (s, 9H), 1.35 (ddt, *J* = 11.6, 6.8, 3.8 Hz, 2H), 1.28 – 1.19 (m, 3H), 1.14 (d, *J* = 7.2 Hz, 3H), 1.00 (dp, *J* = 13.9, 7.4, 6.9 Hz, 2H), 0.95 – 0.71 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 171.7, 171.6, 160.6, 158.7, 155.6, 135.8, 130.6, 128.6, 128.5, 128.4, 119.1, 104.0, 98.7, 79.9, 77.9, 66.7, 55.5, 55.4, 53.1, 44.6, 42.3, 41.5, 39.0, 32.6, 31.5, 31.1, 28.8, 28.7, 28.4, 27.1, 20.6, 20.1, 14.3, 13.9, 11.2; ν_{max} (neat): 2960, 2927, 2361, 1747, 1714, 1655, 1509, 1458, 1369, 1239, 1162, 1079, 1042, 750 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{40}H_{61}N_2O_9^+$ [M + H]$^+$:713.4372, found: 713.4381.

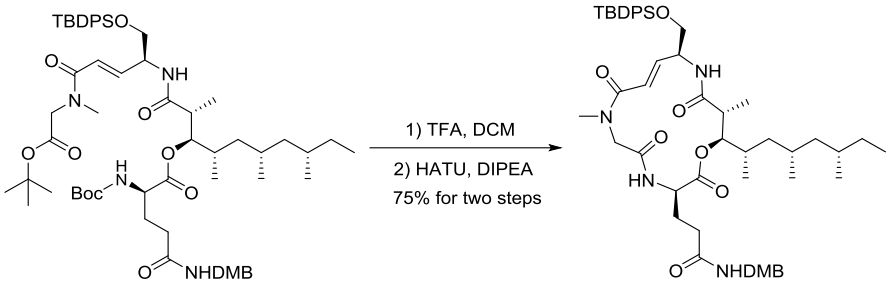
Preparation of 24.



To a solution of compound **40** (721 mg, 1.06 mmol) in MeOH (20 mL) was added Pd/C (10%, 72 mg) under Ar atmosphere. The suspension was degassed under vacuum and purged with H_2 for three times. The mixture was stirred under H_2 balloon at 20 ℃ for 2 h. The resulting mixture was filtered through a short pad of silica gel, washed with MeOH (2 × 30 mL). The filtrates were concentrated under reduced pressure. The crude product was used directly for the next step. To a solution of the acid obtained above (0.53 mmol) and **27** (398 mg, 0.80 mmol) in

DCM (5 mL) were added EDCI (123 mg, 0.64 mmol) and HOBt (79 mg, 0.59 mmol) at r.t.. The reaction mixture was stirred for 12 h, quenched with 1% HCl (10 mL) and separated. The aqueous phase was extracted with ethyl acetate (2 × 10 mL). The combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 8:1 to 2:1) to obtain **24** (450 mg, 79 % for 2 steps) as a colorless oil. $[\alpha]_D^{15}$ = + 12.0 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, including rotamer, 3:1) δ 7.67 – 7.59 (m, 4H), 7.45 – 7.32 (m, 6H), 7.14 (d, *J* = 8.3 Hz, 1H), 6.78 (dd, *J* = 15.1, 7.7 Hz, 1H), 6.74 – 6.63 (m, 2H), 6.48 (d, *J* = 15.2 Hz, 0.75H), 6.44 – 6.33 (m, 2H), 6.25 (d, *J* = 15.1 Hz, 0.25H), 5.50 (d, J = 8.1 Hz, 0.75H), 5.44 (d, J = 8.2 Hz, 0.25H), 5.09 – 5.01 (m, 1H), 4.65 (td, *J* = 7.9, 4.1 Hz, 1H), 4.39 (dd, *J* = 14.5, 6.4 Hz, 1H), 4.25 (dd, *J* = 14.5, 5.5 Hz, 1H), 4.18 – 4.02 (m, 2H), 3.94 (d, *J* = 17.1 Hz, 0.75H), 3.85 (d, *J* = 18.2 Hz, 0.25H), 3.77 (s, 3H), 3.74 (s, 3H), 3.71 (t, *J* = 6.8 Hz, 2H), 3.06 (s, 2.25H), 2.93 (s, 0.75H), 2.35 (dt, *J* = 9.5, 6.8 Hz, 1H), 2.30 – 2.13 (m, 2H), 2.15 – 2.01 (m, 1H), 1.86 (hept, *J* = 7.8, 7.0 Hz, 2H), 1.57 (p, *J* = 8.1, 7.4 Hz, 1H), 1.42 (s, 9H), 1.40 (s, 9H), 1.37 – 1.22 (m, 4H), 1.15 – 1.07 (m, 2H), 1.07 (d, *J* = 6.9 Hz, 3H), 1.04 (s, 9H), 1.03 – 0.92 (m, 1H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.84 – 0.74 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, including rotamer) δ 173.4, 173.3, 172.4, 170.8, 170.6, 168.4, 168.1, 166.8, 166.7, 160.4, 160.4, 158.6, 158.5, 156.1, 142.6, 142.3, 135.7, 133.2, 133.1, 130.2, 130.1, 129.9, 127.9, 122.6, 122.5, 119.2, 119.1, 103.9, 98.5, 82.5, 81.8, 79.6, 79.5, 65.4, 65.3, 55.4, 55.4, 53.8, 52.5, 52.2, 50.4, 45.1, 43.8, 41.4, 38.8, 38.7, 36.6, 35.0, 33.4, 31.5, 30.6, 28.8, 28.4, 28.1, 28.1, 27.7, 26.9, 26.8, 20.8, 20.0, 19.4, 14.1, 14.0, 13.6, 11.2; ν_{max} (neat): 3307, 2961, 2932, 1741, 1659, 1616, 1590, 1509, 1460, 1368, 1256, 1228, 1209, 1160, 1112, 1039, 975, 827, 745, 704, 506 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{61}H_{93}N_4O_{12}Si^+$ $[M + H]^+$: 1101.6554, found: 1101.6552.

Preparation of 23.

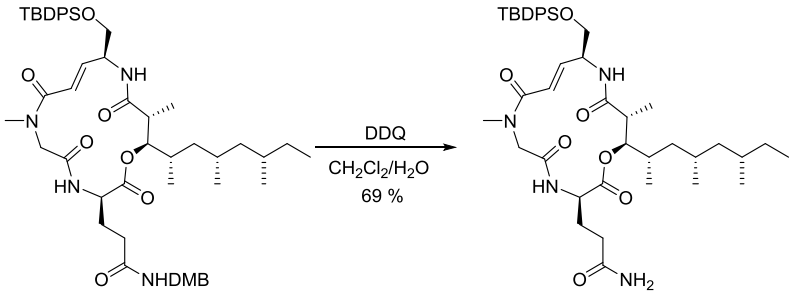


24 **23**

To a solution of **24** (900 mg, 0.84 mmol) in DCM (7 mL) was added trifluoroacetic acid (1.7 mL) at 0 ℃. After stirred for 4 h, the reaction mixture was diluted with toluene (7 mL) and concentrated under reduced pressure. The resulting white solid was dissolved in THF (20 mL), and the solution was added to a suspension of HATU (4.81 g, 12.66 mmol) and DIPEA (4 mL, 25.32 mmol) in THF (850 mL) via a micro syringe pump (1 mL/h). The reaction was stirred for another 24 h at r.t.. After that, the reaction mixture was evaporated, diluted with MeOH and ethyl acetate (*v*/ *v* = 2:1, 150 mL) and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (300 mL), washed with 1 % HCl (50 mL), saturated $NaHCO_3$ (60 mL), and brine (60 mL). The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (5% MeOH in DCM) to obtain **23** (570 mg,

75% for two steps) as an off-white solid. Melting point: 96 – 99 ℃; $[\alpha]_D^{15}$ = + 45.4 (*c* = 2.0, DMSO); ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.39 (d, *J* = 9.4 Hz, 1H), 8.05 (t, *J* = 5.8 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.62 (td, *J* = 7.3, 6.7, 1.7 Hz, 4H), 7.44 (qdd, *J* = 8.4, 5.6, 2.1 Hz, 6H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.72 (dd, *J* = 14.9, 2.9 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.44 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.02 (dd, *J* = 14.9, 2.2 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.65 (dtd, *J* = 11.9, 6.2, 5.7, 2.8 Hz, 1H), 4.38 – 4.30 (m, 2H), 4.13 (d, *J* = 5.7 Hz, 2H), 3.85 (d, *J* = 18.0 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.64 (dd, *J* = 10.1, 5.6 Hz, 1H), 3.57 (dd, *J* = 9.9, 7.6 Hz, 1H), 2.96 (s, 3H), 2.87 – 2.76 (m, 1H), 2.22 (t, *J* = 8.0 Hz, 2H), 2.02 – 1.77 (m, 3H), 1.71 (dt, *J* = 7.6, 4.2 Hz, 1H), 1.41 – 1.30 (m, 2H), 1.27 – 1.08 (m, 5H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.98 (s, 9H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.82 (t, *J* = 6.0 Hz, 9H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 173.0, 170.9, 169.7, 167.8, 165.4, 159.6, 157.6, 142.2, 135.1, 135.1, 132.8, 132.7, 129.9, 129.9, 128.6, 127.9, 119.1, 119.0, 104.2, 98.1, 75.4, 65.2, 55.3, 55.2, 52.1, 52.0, 51.2, 44.7, 41.6, 41.4, 36.8, 36.4, 31.8, 30.9, 30.2, 29.4, 28.2, 26.6, 26.4, 20.0, 20.0, 18.8, 15.7, 13.8, 10.8; ν_{max} (neat): 3292, 2958, 2928, 2857, 2361, 1739, 1658, 1617, 1549, 1509, 1462, 1395, 1261, 1208, 1112, 1039, 971, 824, 747, 704, 506 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{52}H_{75}N_4O_9Si^+$ $[M + H]^+$: 927.5298, found: 927.5301.

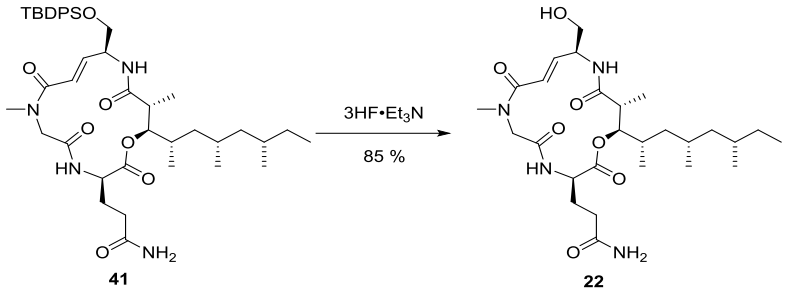
Preparation of 41.



23 **41**

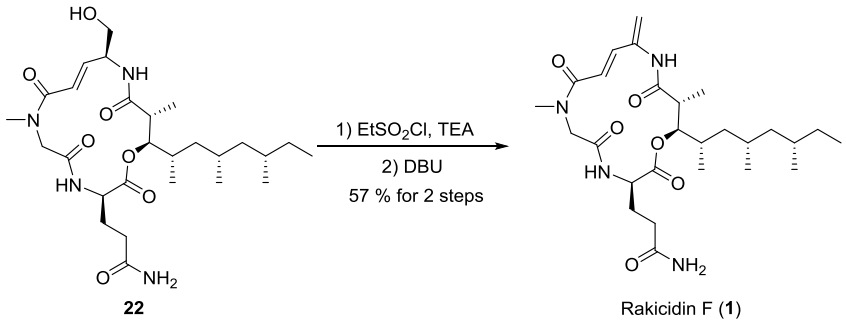
To a solution of compound **23** (200 mg, 0.22 mmol) in DCM/H_2O (2 mL/0.2 mL) was added DDQ (59 mg, 0.26 mmol). The mixture was stirred at r.t. for 1.5 h, diluted with ethyl acetate (50 mL) and separated. The organic phase was washed with saturated $NaHCO_3$ (2 × 30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (7% MeOH in DCM) to obtain **41** (116 mg, 69 %) as an off-white solid. $[\alpha]_D^{15}$ = + 53.3 (*c* = 1.0, DMSO); ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.38 (d, *J* = 9.4 Hz, 1H), 7.98 (d, *J* = 8.9 Hz, 1H), 7.66 – 7.58 (m, 4H), 7.51 – 7.37 (m, 6H), 7.27 (s, 1H), 6.78 (s, 1H), 6.71 (dd, *J* = 14.9, 3.0 Hz, 1H), 6.03 (dd, *J* = 15.0, 2.3 Hz, 1H), 5.19 (d, *J* = 10.4 Hz, 1H), 4.64 (ddt, *J* = 8.8, 5.6, 3.0 Hz, 1H), 4.39 – 4.27 (m, 2H), 3.86 (d, *J* = 17.9 Hz, 1H), 3.64 (dd, *J* = 10.1, 5.6 Hz, 1H), 3.56 (dd, *J* = 10.0, 7.6 Hz, 1H), 2.96 (s, 3H), 2.88 – 2.75 (m, 1H), 2.13 (t, *J* = 7.9 Hz, 2H), 1.97 – 1.82 (m, 2H), 1.82 – 1.65 (m, 2H), 1.44 – 1.27 (m, 2H), 1.29 – 1.07 (m, 5H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.98 (s, 9H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.89 – 0.78 (m, 9H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 173.0, 173.0, 169.7, 167.8, 165.4, 142.2, 135.1, 135.0, 132.8, 132.7, 129.9, 129.9, 127.9, 119.1, 75.3, 65.2, 52.1, 52.0, 51.2, 44.7, 41.6, 41.3, 36.4, 31.5, 30.9, 30.2, 29.1, 28.2, 26.6, 26.4, 20.0, 18.8, 15.7, 13.8, 10.9; ν_{max} (neat): 3306, 2958, 2926, 2855, 2361, 2338, 1735, 1669, 1618, 1543, 1461, 1396, 1263, 1111, 970, 823, 750, 704 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{43}H_{64}N_4O_7SiNa^+$ $[M + Na]^+$: 799.4437, found: 799.4441.

Preparation of 22.



To a solution of compound **41** (110 mg, 0.14 mmol) in THF (2.8 mL) was added 3HF·Et_3N (68 mg, 0.42 mmol). The mixture was stirred at r.t. for 24 h. The precipitate was filtered and washed with DCM (4 × 10 mL). The filtrate was concentrated under reduced pressure to remove most of the solvent, and then filtered and washed with DCM (2 × 5 mL). The precipitates were combined to obtain **22** (64 mg, 85 %) as a white powder. $[\alpha]_D^{15}$ = + 7.3 (*c* = 0.10, DMSO); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 (d, *J* = 9.4 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.25 (s, 1H), 6.82 – 6.70 (m, 2H), 5.94 (dd, *J* = 14.9, 2.3 Hz, 1H), 5.16 (d, *J* = 10.4 Hz, 1H), 4.89 (t, *J* = 5.7 Hz, 1H), 4.41 (qd, *J* = 6.7, 3.9 Hz, 1H), 4.37 – 4.25 (m, 2H), 3.84 (d, *J* = 17.9 Hz, 1H), 3.40 (dq, *J* = 10.7, 5.7 Hz, 2H), 2.95 (s, 3H), 2.80 (dq, *J* = 14.2, 7.3 Hz, 1H), 2.12 (t, *J* = 7.9 Hz, 2H), 1.94 – 1.83 (m, 2H), 1.81 – 1.62 (m, 2H), 1.36 (qq, *J* = 12.0, 7.3, 6.7 Hz, 2H), 1.24 – 1.04 (m, 5H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.87 – 0.76 (m, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.0, 172.9, 169.7, 167.9, 165.5, 143.8, 118.4, 75.4, 63.0, 52.0, 52.0, 51.6, 44.7, 41.5, 41.3, 36.4, 31.5, 30.9, 30.3, 29.0, 28.2, 26.4, 20.1, 20.0, 15.9, 13.8, 10.9; ν_{max} (KBr): 3337, 2962, 2926, 2483, 1725, 1668, 1543, 1459, 1266, 1115, 1078, 1055, 972, 738, 558 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{47}N_4O_7^+$ $[M + H]^+$: 539.3440, found: 539.3445.

Preparation of rakicidin F (1).

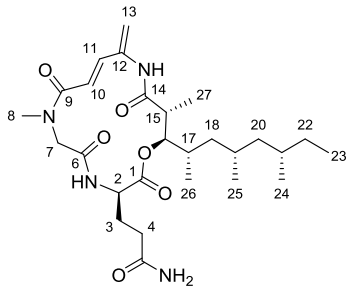


To a solution of compound **22** (50 mg, 0.09 mmol) in DCM (1 mL) and THF (1 mL) were added triethylamine (23 mg, 0.23 mmol) and $EtSO_2Cl$ (23 mg, 0.18 mmol) at 0 ℃. After stirred for 2 h, the reaction mixture was quenched by addition of water (0.10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was dissolved in THF (2 mL) followed by addition of DBU (109 mg, 0.72 mmol) at r.t.. After stirred for 4 h, the mixture was dissolved in ethyl acetate (80 mL) and washed successively with 1% HCl (20 mL), saturated aqueous $NaHCO_3$ (20 mL) and brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure carefully. The crude product was purified by column chromatography on silica gel (DCM: MeOH = 50:1 to 25:1). *t*-BuOH (30 mL) was added to the eluent. The final concentration to remove DCM and MeOH was stopped when about 5 mL solvent remained in the round bottle. The residual solution was lyophilized to give **1** (27 mg, 57 % for 2 steps) as a

white solid. $[\alpha]_D^{15}$ = + 83.7 (*c* = 0.20, MeOH); ^{1}H NMR (400 MHz, MeOD-d_4) δ 7.11 (d, *J* = 14.9 Hz, 1H), 6.24 (d, *J* = 15.0 Hz, 1H), 5.53 (s, 1H), 5.47 (s, 1H), 5.37 (dd, *J* = 10.3, 1.7 Hz, 1H), 4.60 (dd, *J* = 10.2, 4.5 Hz, 1H), 4.54 (d, *J* = 15.3 Hz, 1H), 4.00 (d, *J* = 17.8 Hz, 1H), 3.14 (s, 3H), 3.04 – 2.94 (m, 1H), 2.30 (t, *J* = 7.6 Hz, 2H), 2.24 – 2.06 (m, 1H), 2.06 – 1.98 (m, 1H), 1.98 – 1.89 (m, 1H), 1.82 – 1.74 (m, 1H), 1.49 – 1.31 (m, 2H), 1.30 – 1.23 (m, 1H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.21 – 1.13 (m, 1H), 1.13 – 1.05 (m, 1H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.98 – 0.91 (m, 2H), 0.91 – 0.83 (m, 9H); ^{13}C NMR (100 MHz, MeOD-d_4) δ 177.2, 175.7, 171.0, 170.2, 168.8, 141.2, 139.4, 120.3, 119.0, 78.2, 54.0, 53.8, 48.3, 44.2, 43.4, 37.6, 32.9, 32.1, 30.8, 28.3, 26.4, 24.3, 22.4, 20.1, 15.8, 14.1; ν_{max} (neat): 3364, 2961, 2925, 2875, 2854, 2508, 2363, 2239, 2073, 1723, 1646, 1613, 1433, 1262, 1104, 1016, 980, 801, 752 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{45}N_4O_6^+$ $[M + H]^+$: 521.3334, found: 521.3332.

4. Data Comparison of Synthesized and Natural Rakicidin F

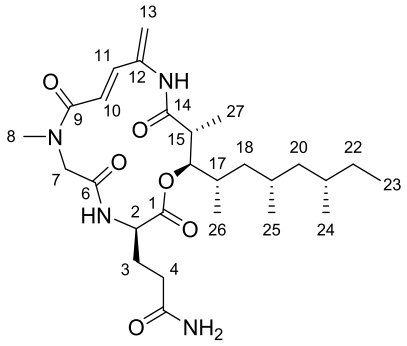
Table S2. ^{1}H NMR Data Comparison (MeOH-d_4)



position	Natural Rakicidin F[a] δ_H mult (*J* in Hz) (600 MHz)	Synthetic Rakicidin F [b] δ_H mult (*J* in Hz) (400 MHz)	Δδ/ppm[b]	Synthetic Rakicidin F[c] δ_H mult (*J* in Hz) (400 MHz)	Δδ/ppm[c]
2, CH	4.59, dd (10.2, 4.2)	4.59, dd (10.4, 4.6)	0.00	4.60, dd (10.2, 4.5)	-0.01
3, CH_2	2.12, m; 1.96, m	2.12, m; 1.95, m	0.00; 0.01	2.13, m; 1.95, m	-0.01; 0.01
4, CH_2	2.29, t (7.8)	2.30, t (7.7)	-0.01	2.30, t (7.6)	-0.01
7, CH_2	4.47, d (17.4); 3.99, d (18.0)	4.50, d (17.8); 3.99, d (17.9)	-0.03; 0.00	4.54, d (15.3); 4.00, d (17.8)	-0.07; -0.01
8, CH_3	3.13, s	3.13, s	0.00	3.14, s	-0.01
10, CH	6.20, d (15.0)	6.22, d (15.0)	-0.02	6.24, d (15.0)	-0.04
11, CH	7.12, d (14.4)	7.12, d (14.4)	0.00	7.11, d (14.9)	0.01
13, CH_2	5.54, s; 5.46,s	5.53, s; 5.47,s	0.01, -0.01	5.53, s; 5.47s	0.01, -0.01
15, CH	2.92, m	2.95, dq (10.1, 7.0)	-0.03	2.98, m	-0.07
16, CH	5.38, dd (10.2, 1.2)	5.37, dd (10.4, 1.7)	0.01	5.37, dd (10.3, 1.7)	0.01
17, CH	2.02, m	2.03, m	-0.01	2.02, m	0.00
18, CH_2	1.28, m; 0.92, m	1.26, m; 0.93, m	0.02; -0.01	1.26, m; 0.93, m	0.02; -0.01
19, CH	1.79, m	1.79, m	0.00	1.78, m	0.01
20, CH_2	1.18, m; 0.92, m	1.17, m; 0.94, m	0.01; -0.02	1.,17 m; 0.93, m	0.01; -0.01
21, CH	1.42, m	1.41, m	0.01	1.41, m	0.01
22, CH_2	1.42, m; 1.07, m	1.41, m; 1.08, m	0.01; -0.01	1.41, m; 1.08, m	0.01; -0.01
23, CH_3	0.88, m	0.88, m	0.00	0.88, m	0.00
24, CH_3	0.88, m	0.88, m	0.00	0.88, m	0.00
25, CH_3	0.88, m	0.88, m	0.00	0.88, m	0.00
26, CH_3	1.04, d (6.6)	1.04, d (6.8)	0.00	1.05, d (6.8)	-0.01
27, CH_3	1.22, d (7.2)	1.22, d (6.9)	0.00	1.22, d (7.0)	0.00

[a] *J. Antibiot.* **2018,** *71,* 139–141. [b] obtained via one-time column chromatography [c] obtained via two-time column chromatography followed by lyophilization

Table S3. ^{13}C NMR Data Comparison (MeOH-d_4)



position	Natural Rakicidin F[a] δ_C (125 MHz)	Synthetic Rakicidin F[b] δ_C (100 MHz)	Δδ/ppm
1	171.1	171.0	0.1
2	53.9	53.8	0.1
3	31.0	30.9	0.1
4	33.1	32.8	0.3
5	177.3	177.2	0.1
6	170.3	170.4	-0.1
7	54.1	54.0	0.1
8	37.8	37.6	0.2
9	168.9	168.8	0.1
10	119.0	119.0	0.0
11	141.4	141.2	0.2
12	139.5	139.3	0.2
13	120.5	120.3	0.2
14	175.9	175.8	0.1
15	44.3	44.1	0.2
16	78.1	78.1	0.0
17	32.2	32.1	0.1
18	43.3	43.2	0.1
19	28.3	28.2	0.1
20	46.6	46.5	0.1
21	32.9	32.8	0.1
22	30.0	29.8	0.2
23	11.7	11.5	0.2
24	20.72	20.59	0.13
25	20.77	20.62	0.15
26	14.4	14.2	0.2
27	16.0	15.8	0.2

[a] *J. Antibiot.* **2018,** *71,* 139–141. [b] obtained via two-time column chromatography followed by lyophilization

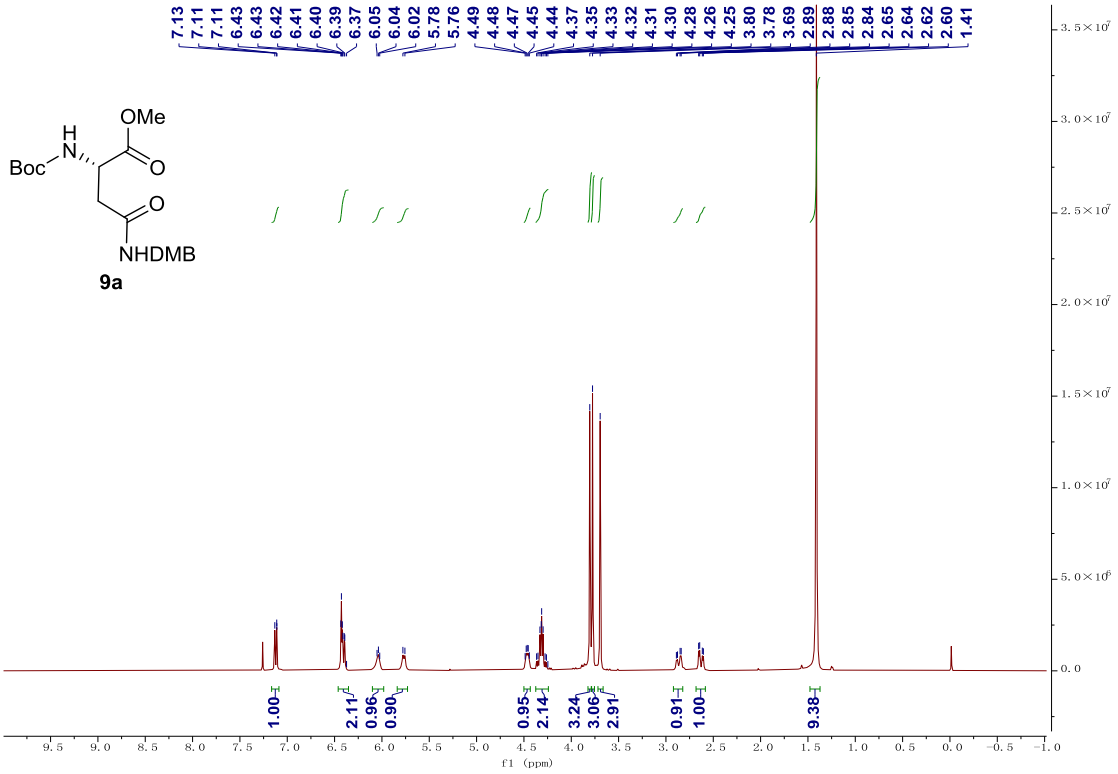
Table S4. IR, HRMS, $[\alpha]_D$ Data Comparison

	Natural rakicidin F[a]	Synthetic rakicidin F (**1**)
Appearance	white powder	white powder
HRMS (*m/z*) Calcd for: $C_{27}H_{45}N_4O_6^+$ $[M+H]^+$	521.3334	
found	521.3345(FAB)	521.3332 (ESI)
$[\alpha]_D$ (MeOH)	+ 108 (*c* = 0.21)	+ 83.7 (*c* = 0.20)
IR (neat) cm^{-1}	3372, 2962, 1655, 1616	3368, 2961, 1646, 1613

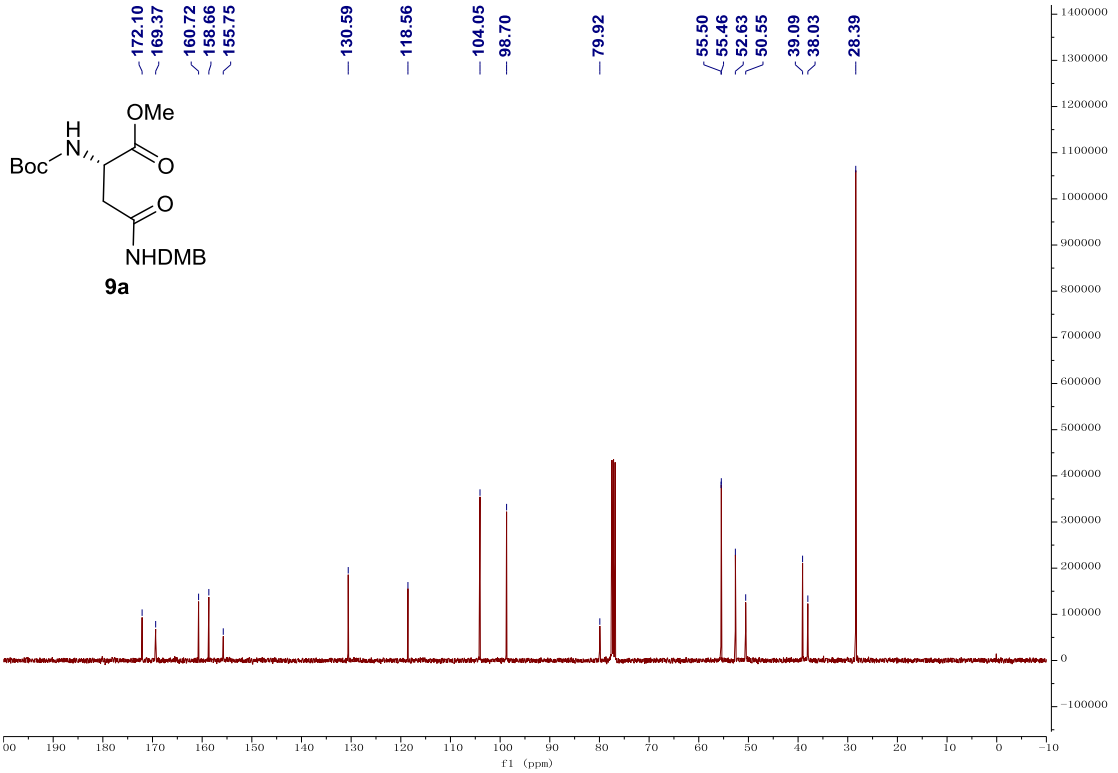
[a] *J. Antibiot.* **2018,** *71,* 139–141.

5. Copies of NMR Spectrum

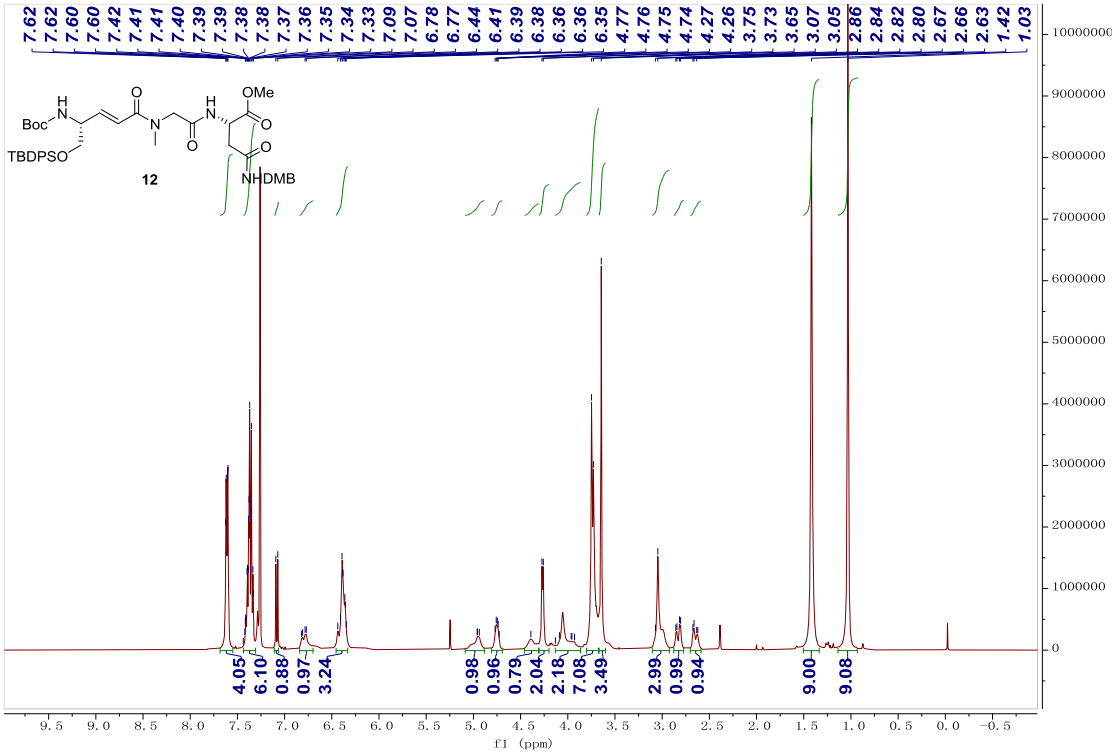
^{1}H NMR spectrum of compound 9a in $CDCl_3$ (400 MHz)



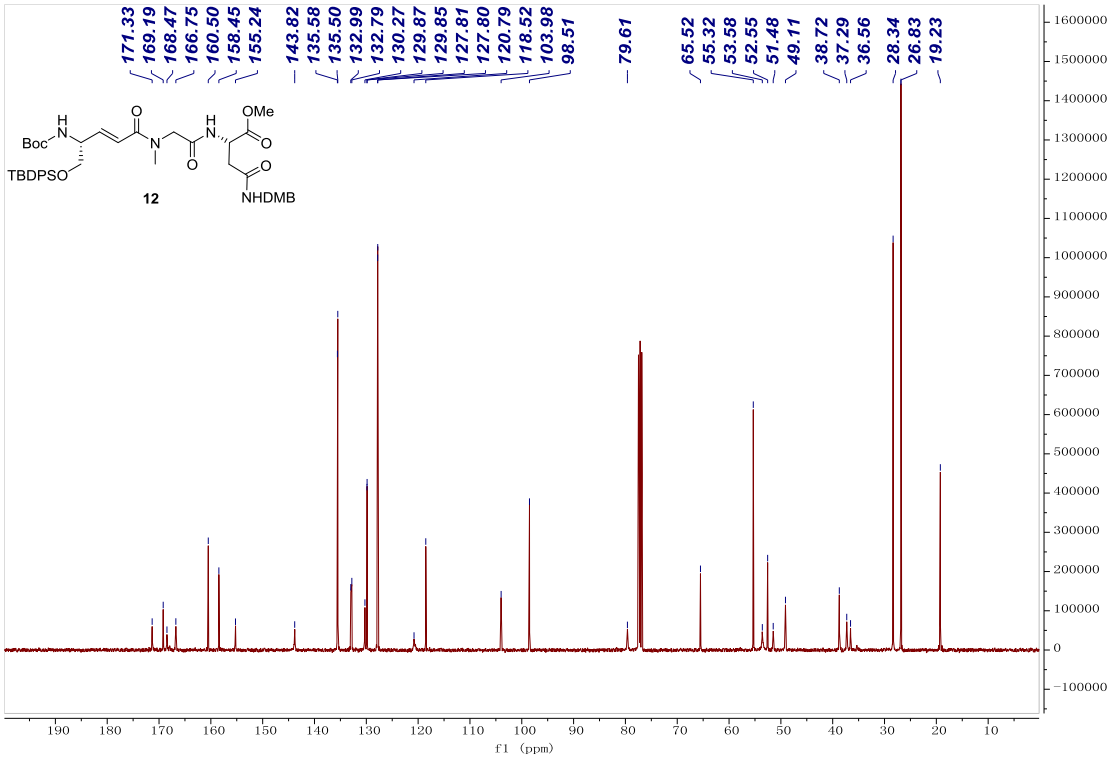
^{13}C NMR spectrum of compound 9a in $CDCl_3$ (100 MHz)



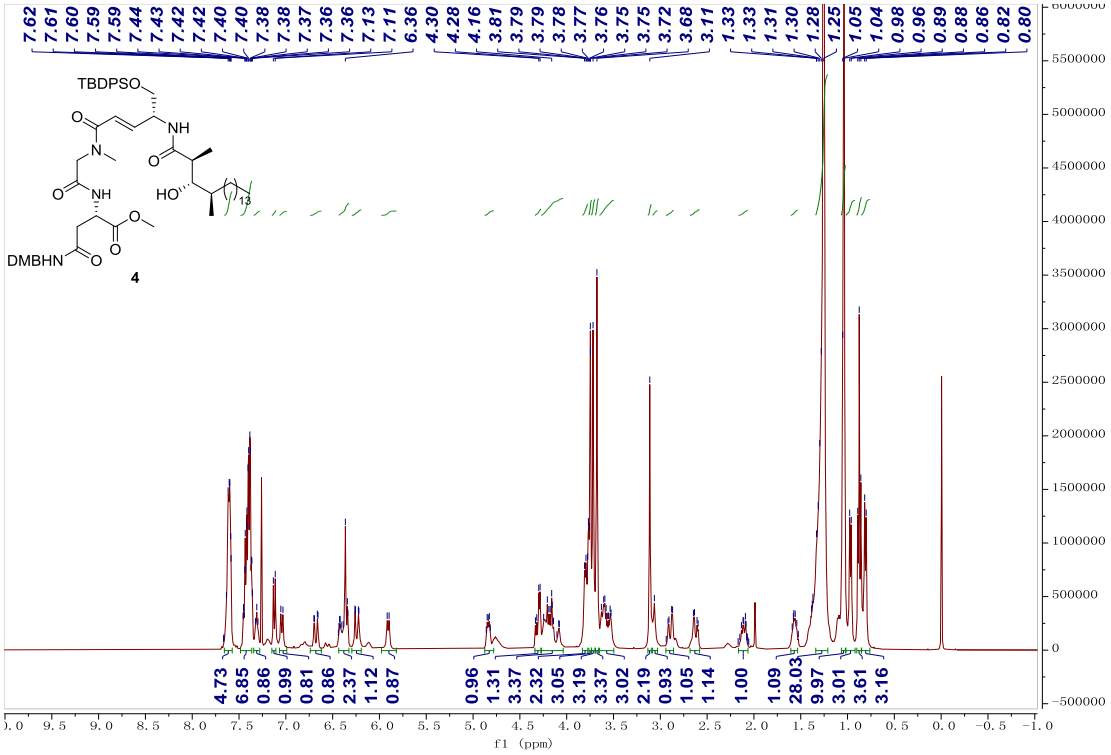
^{1}H NMR spectrum of compound 12 in $CDCl_3$ (400 MHz).



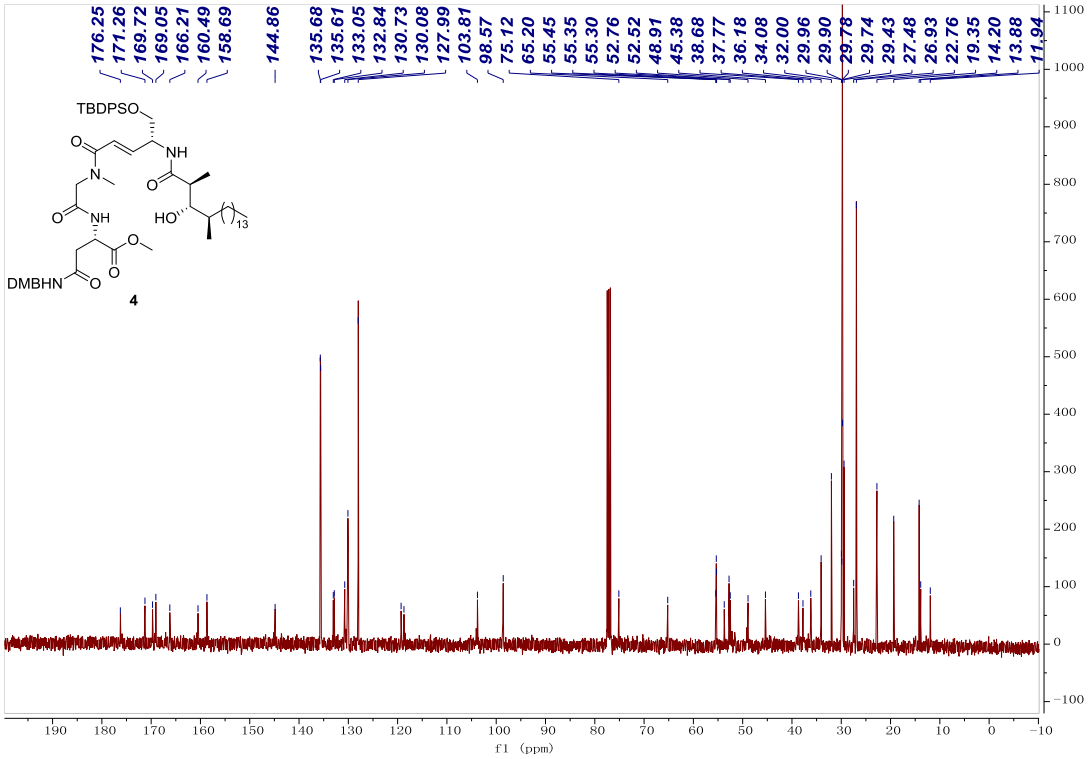
^{13}C NMR spectrum of compound 12 in $CDCl_3$ (100 MHz).



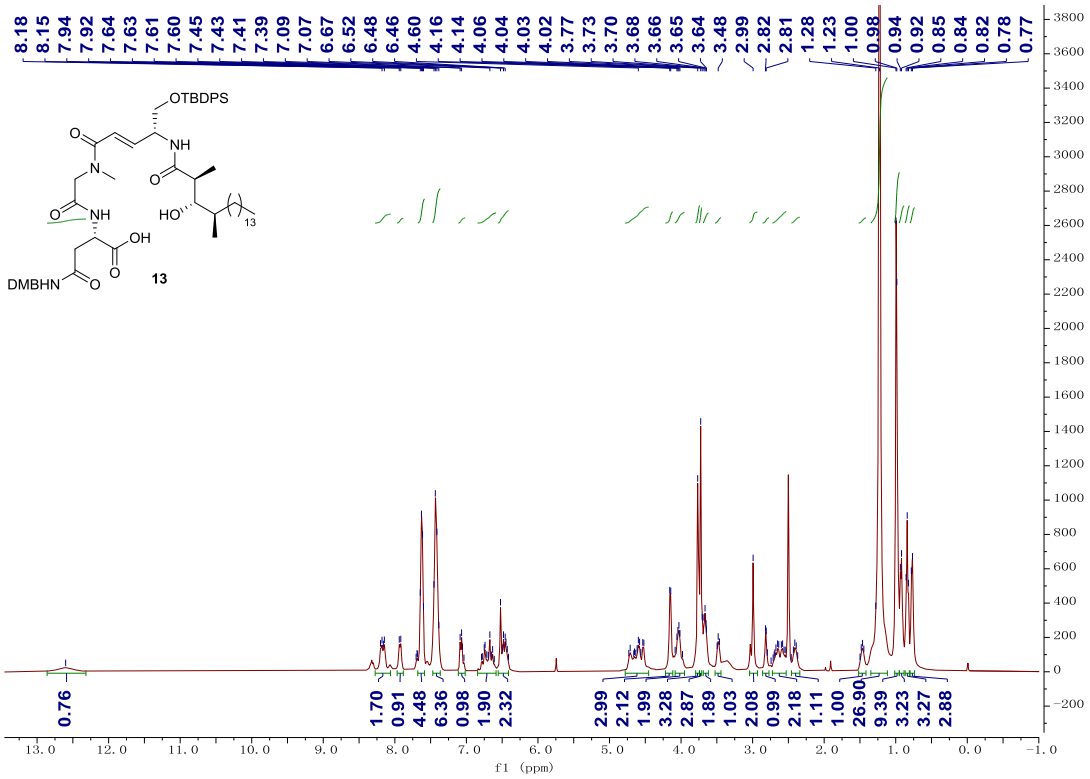
^{1}H NMR spectrum of compound 4 in $CDCl_3$ (400 MHz).



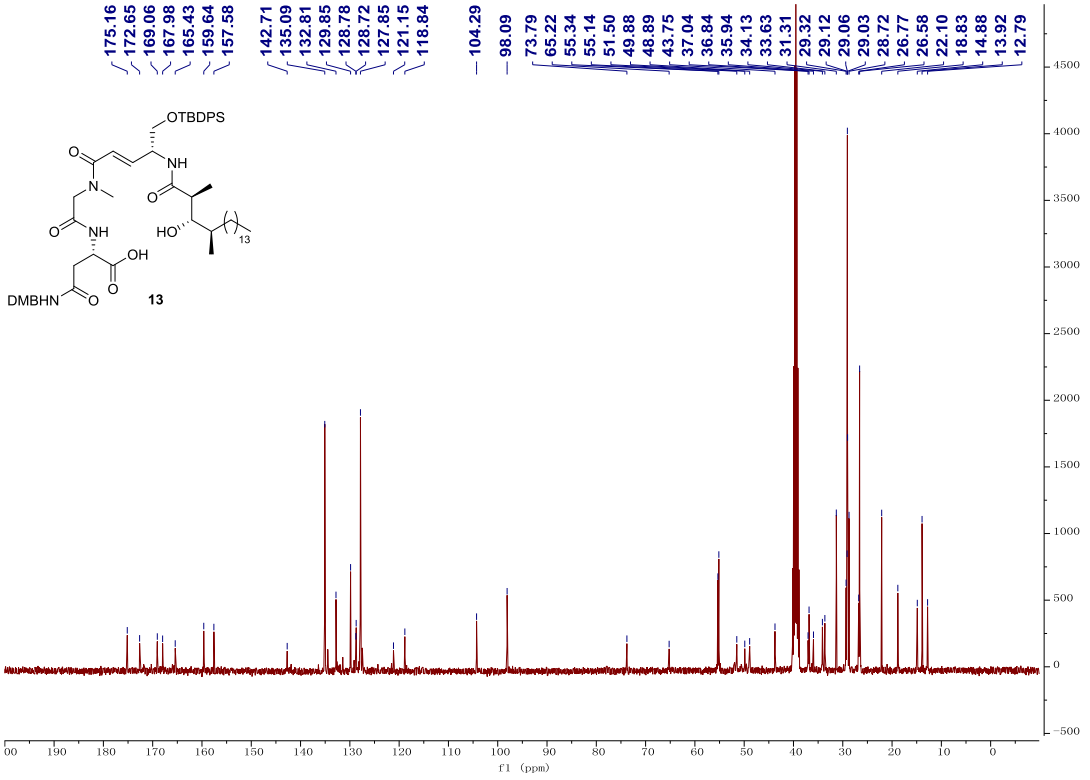
^{13}C NMR spectrum of compound 4 in $CDCl_3$ (100 MHz).



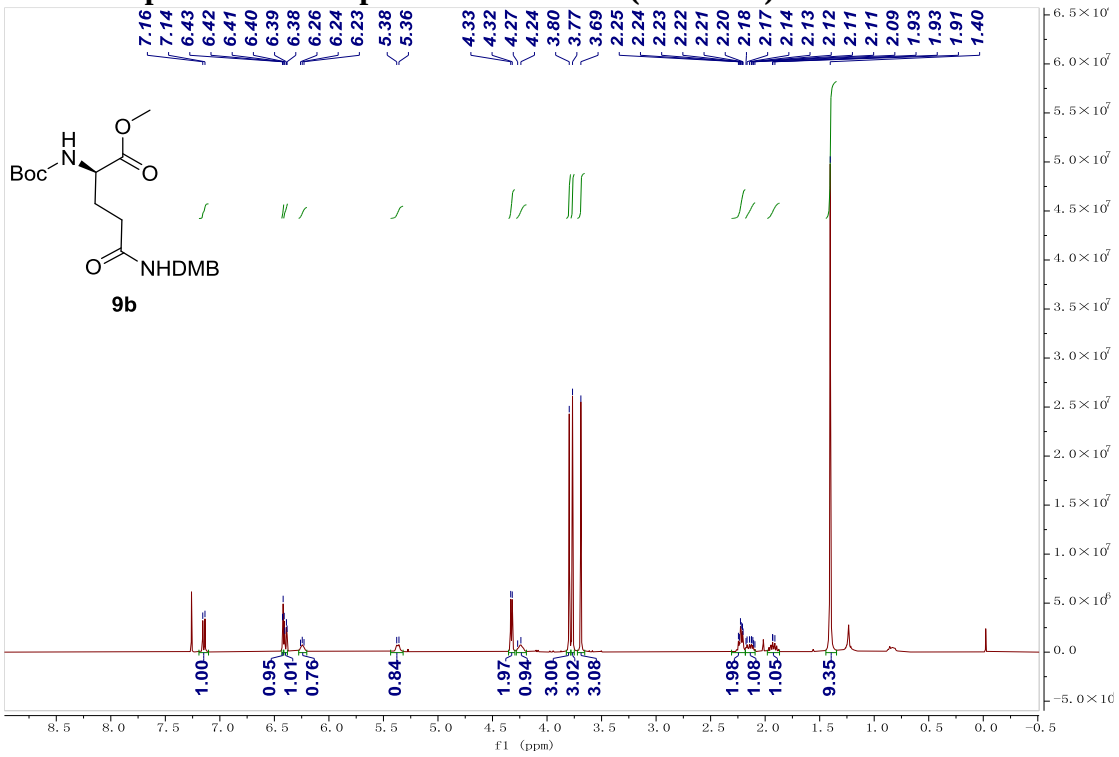
^{1}H NMR spectrum of compound 13 in DMSO-d_6 (400 MHz).



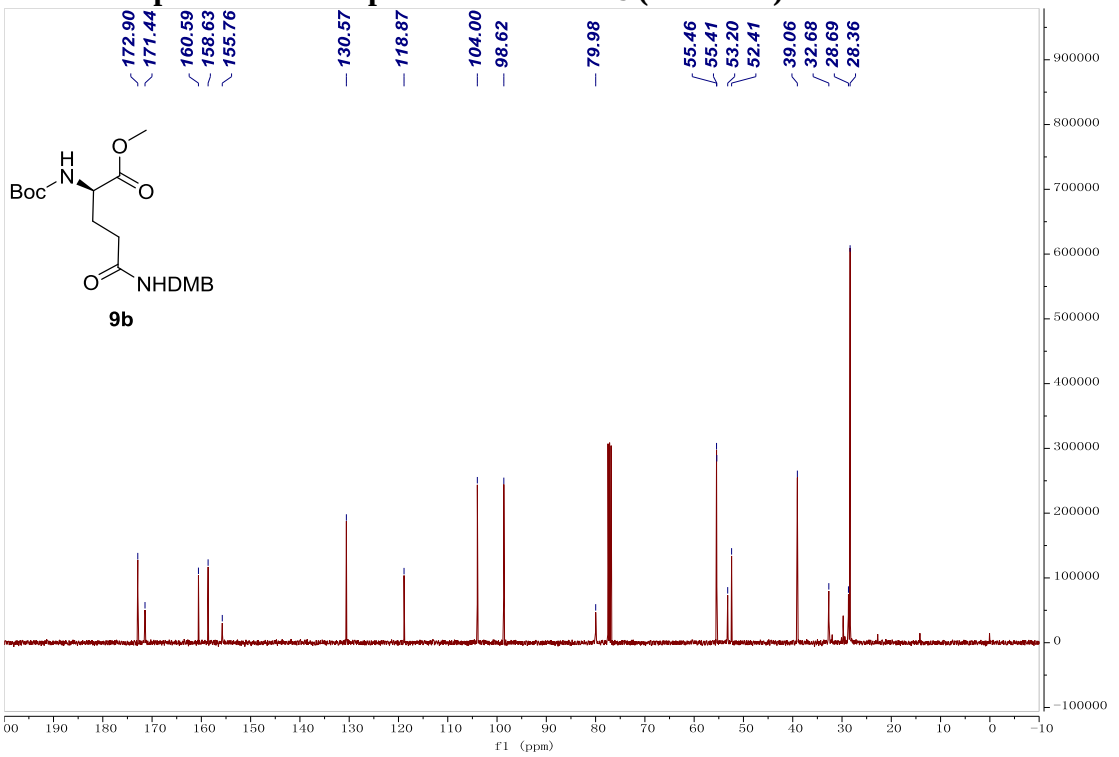
^{13}C NMR spectrum of compound 13 in DMSO-d_6 (100 MHz).



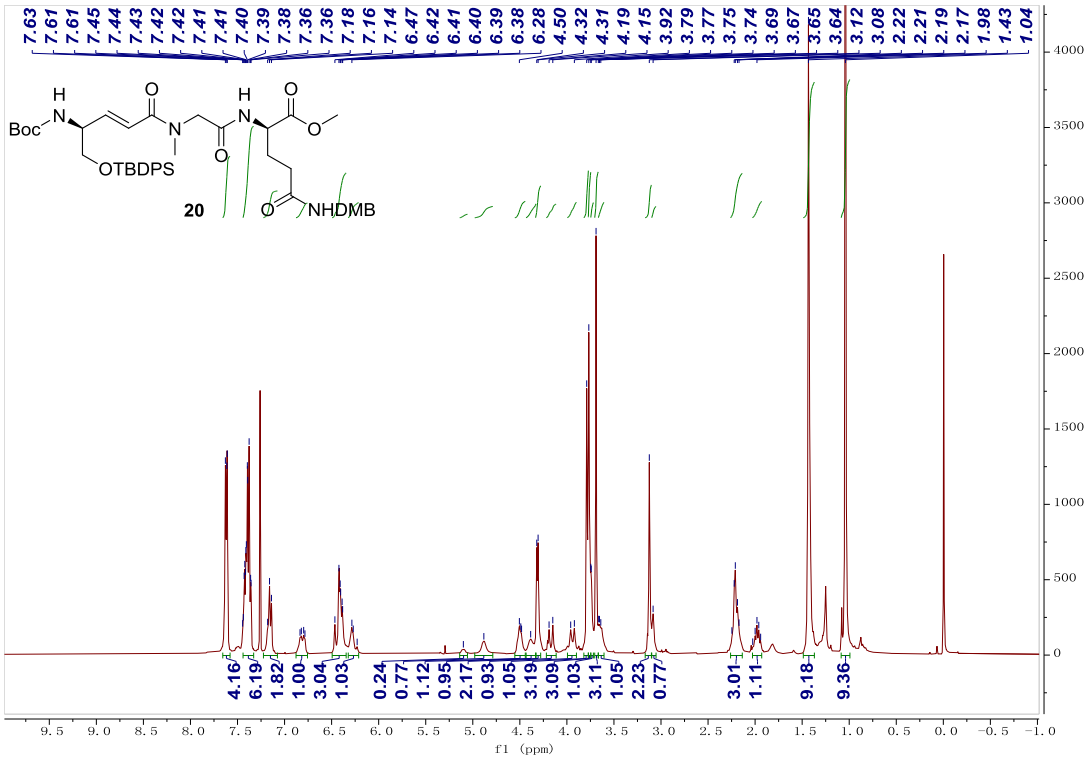
^{1}H NMR spectrum of compound 9b in $CDCl_3$ (400 MHz)



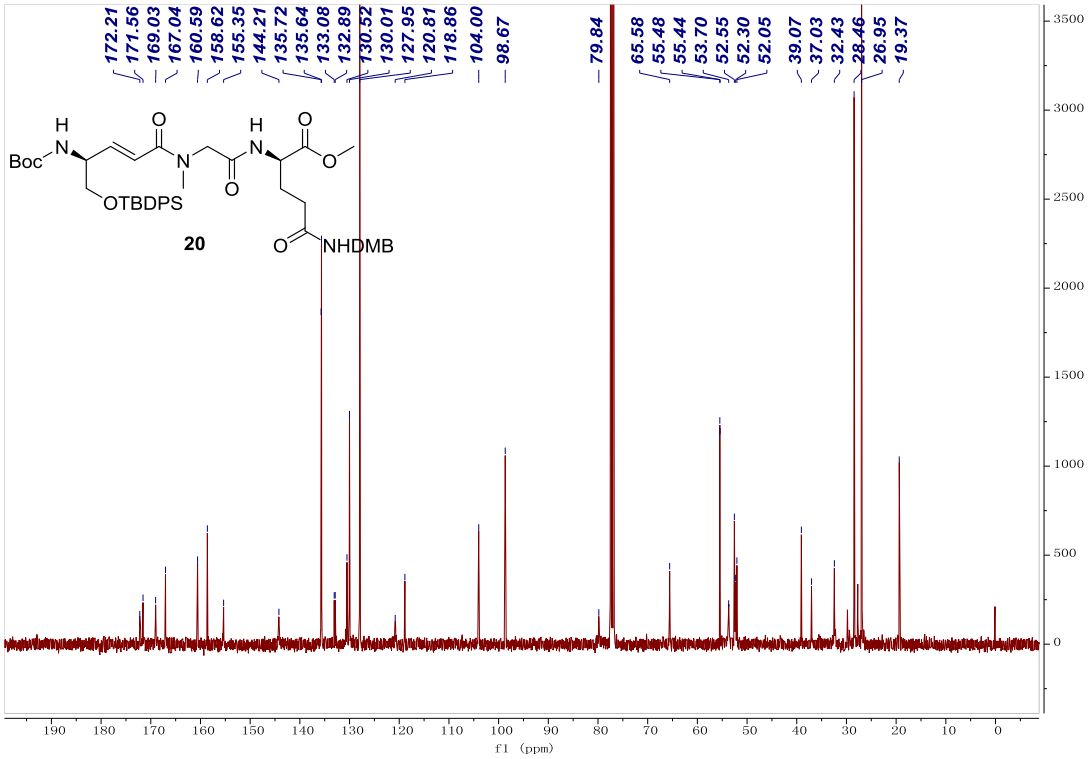
^{13}C NMR spectrum of compound 9b in $CDCl_3$ (100 MHz)



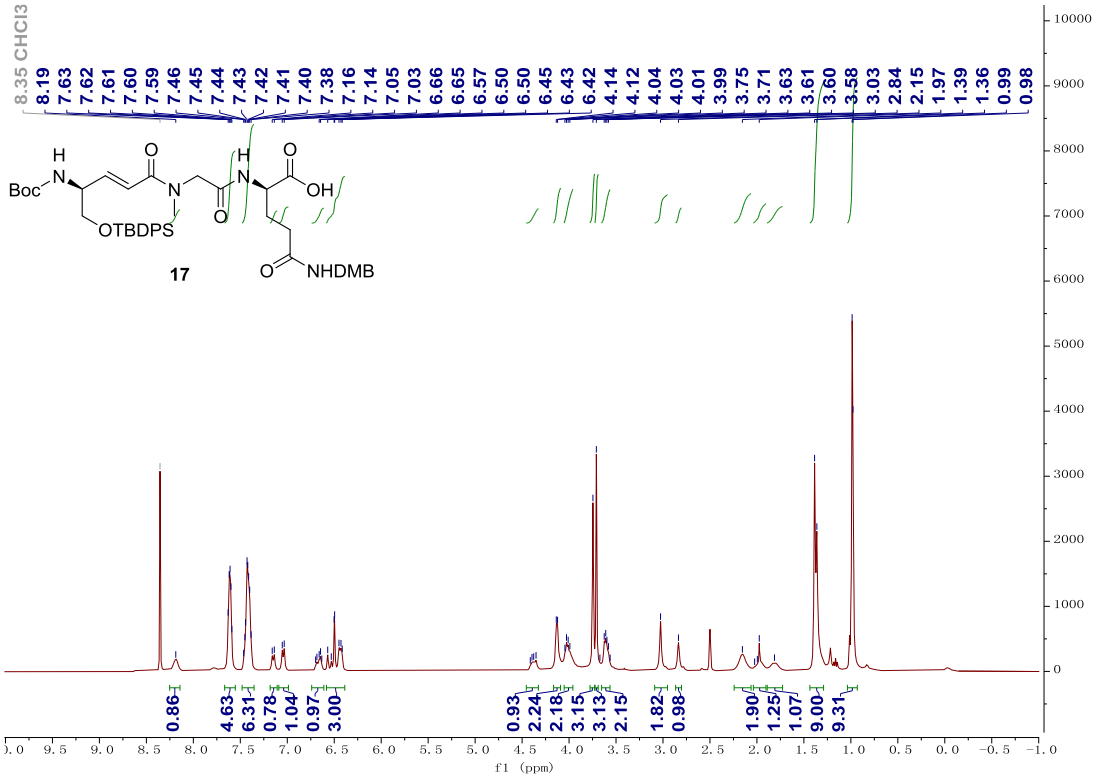
^{1}H NMR spectrum of compound 20 in $CDCl_3$ (400 MHz).



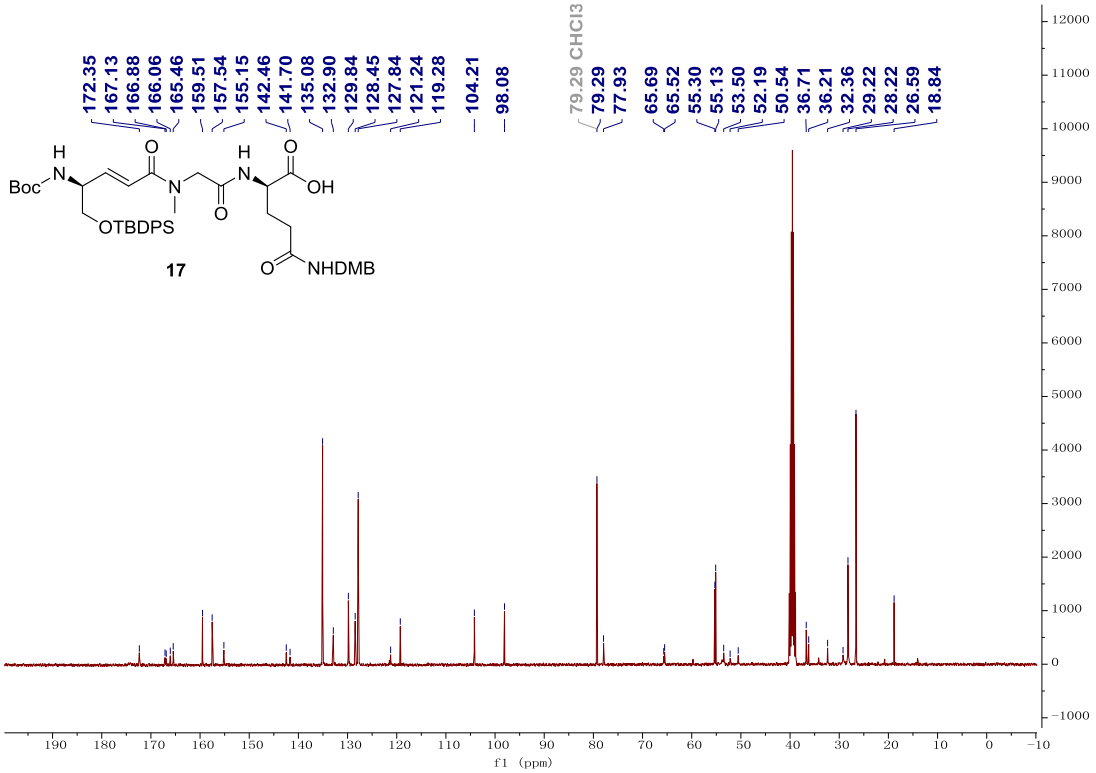
^{13}C NMR spectrum of compound 20 in $CDCl_3$ (100 MHz).



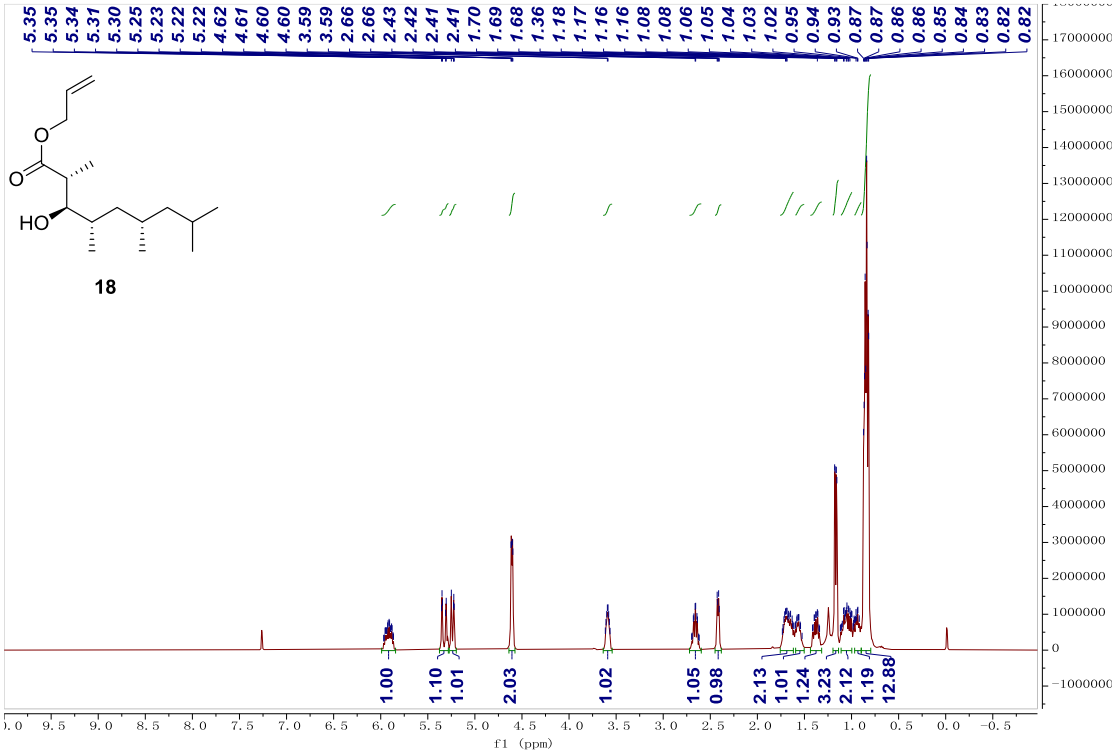
^{1}H NMR spectrum of compound 17 in DMSO-d_6 (400 MHz).



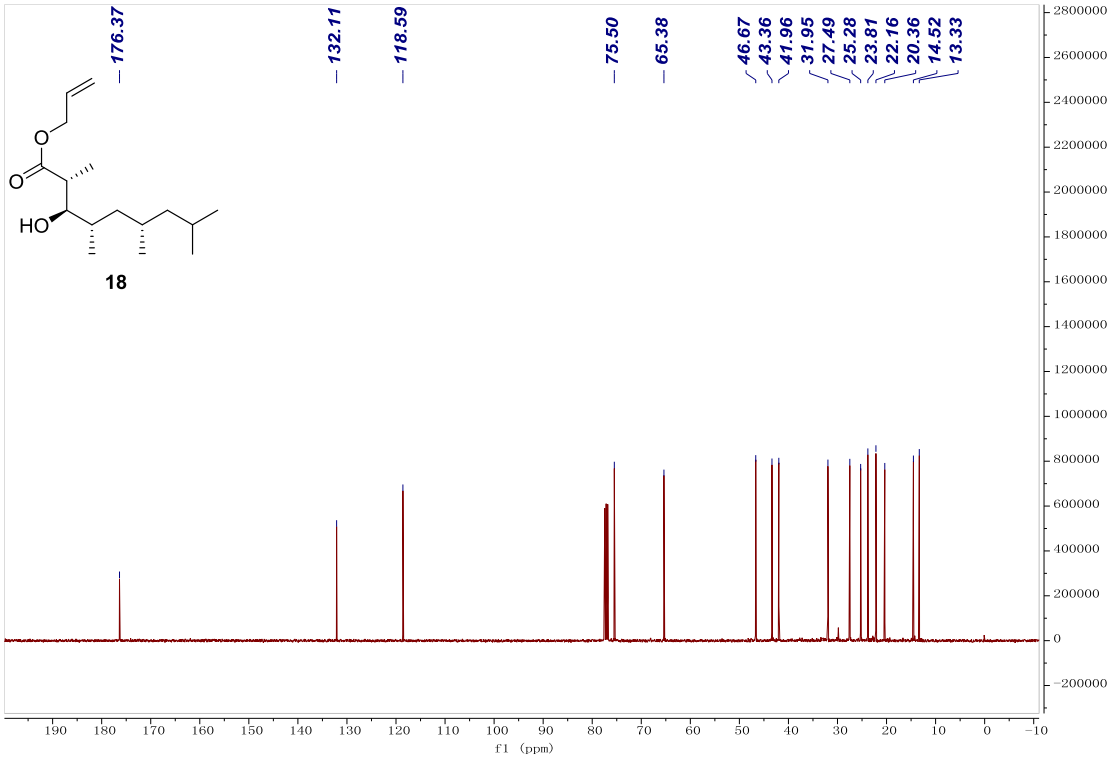
^{13}C NMR spectrum of compound 17 in DMSO-d_6 (100 MHz).



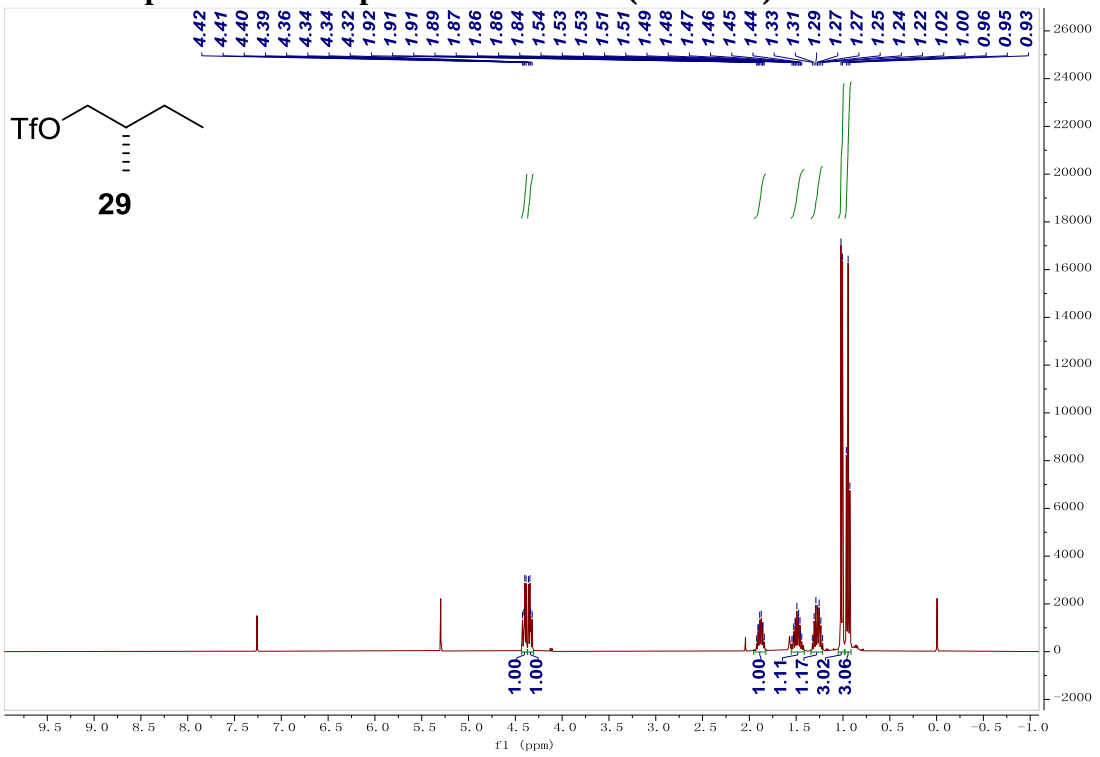
^{1}H NMR spectrum of compound 18 in $CDCl_3$ (400 MHz).



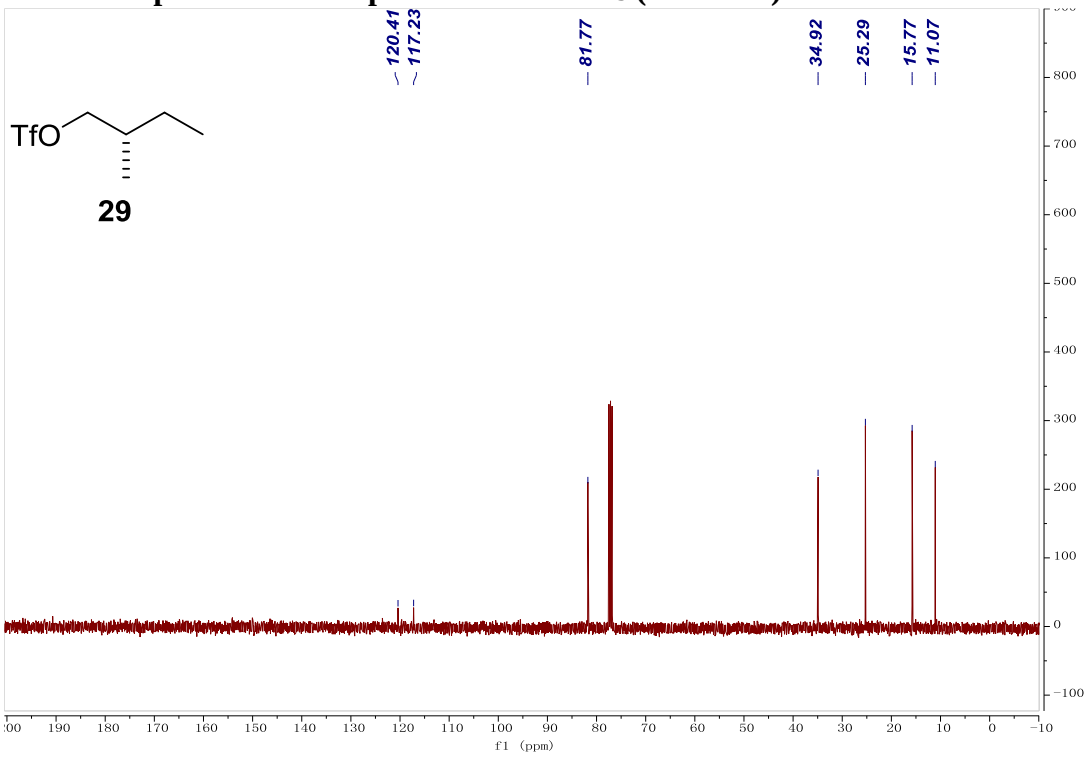
^{13}C NMR spectrum of compound 18 in $CDCl_3$ (100 MHz)



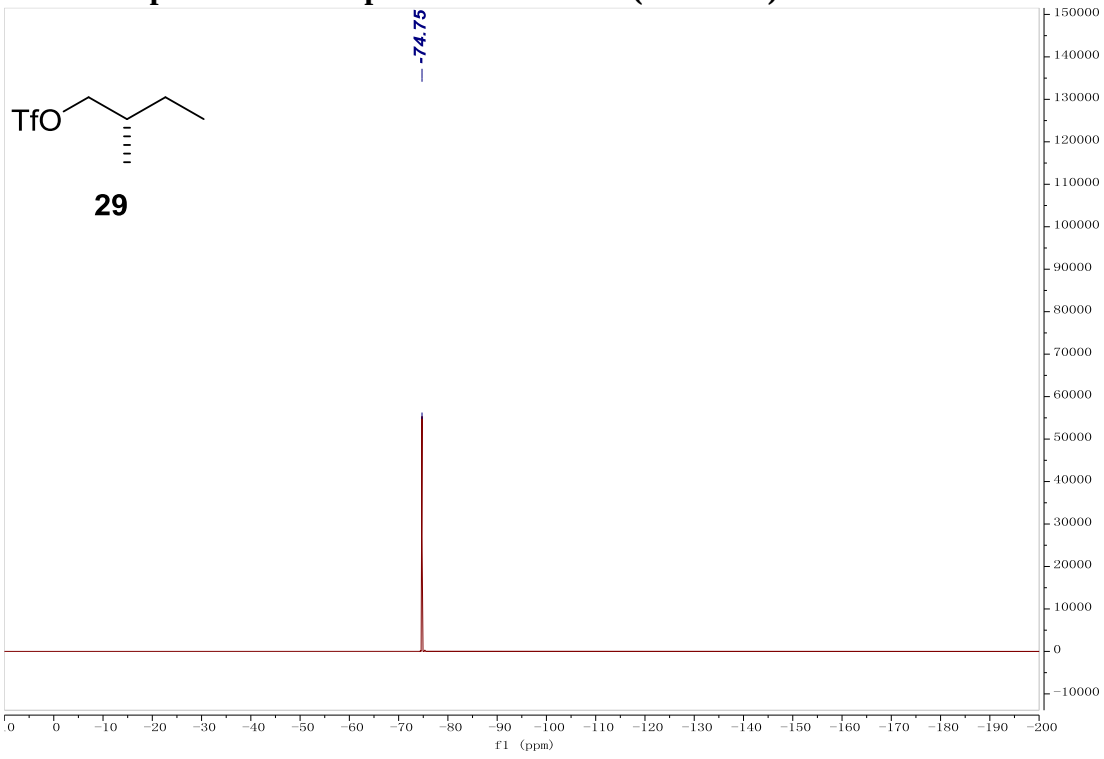
^{1}H NMR spectrum of compound 29 in $CDCl_3$ (400 MHz)



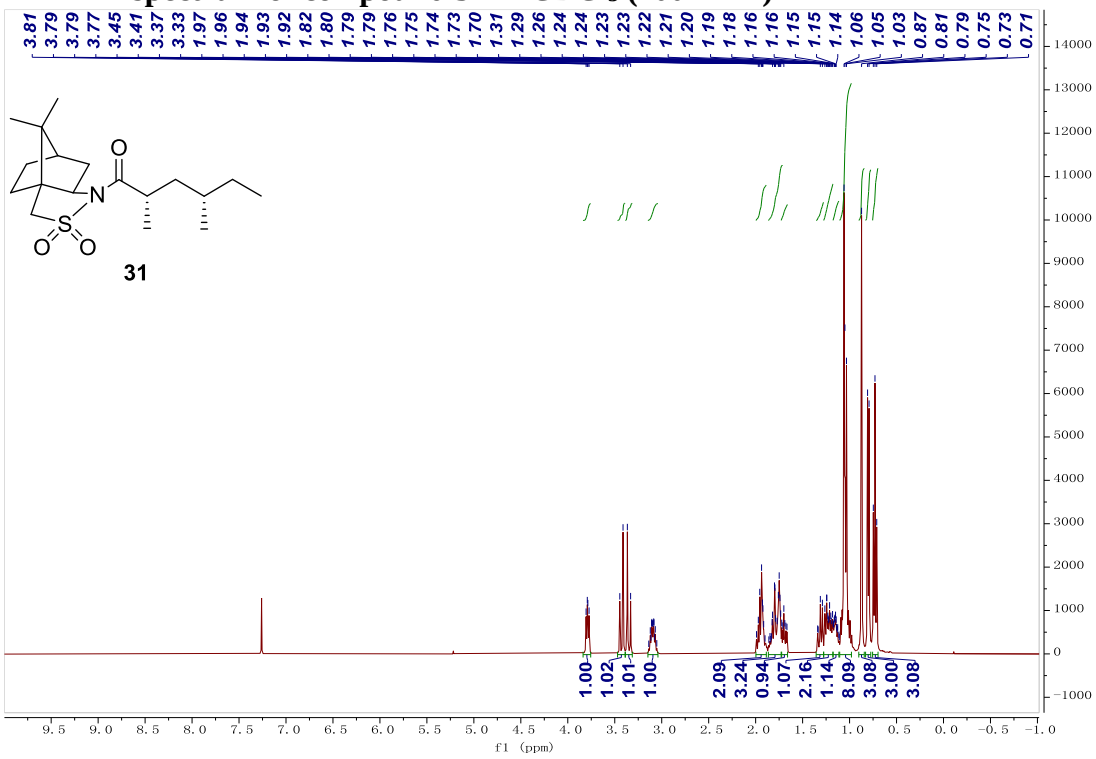
^{13}C NMR spectrum of compound 29 in $CDCl_3$ (100 MHz)

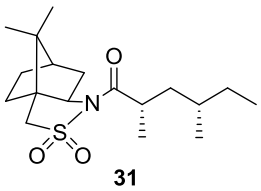


^{19}F NMR spectrum of compound 29 in $CDCl_3$ (375 MHz)



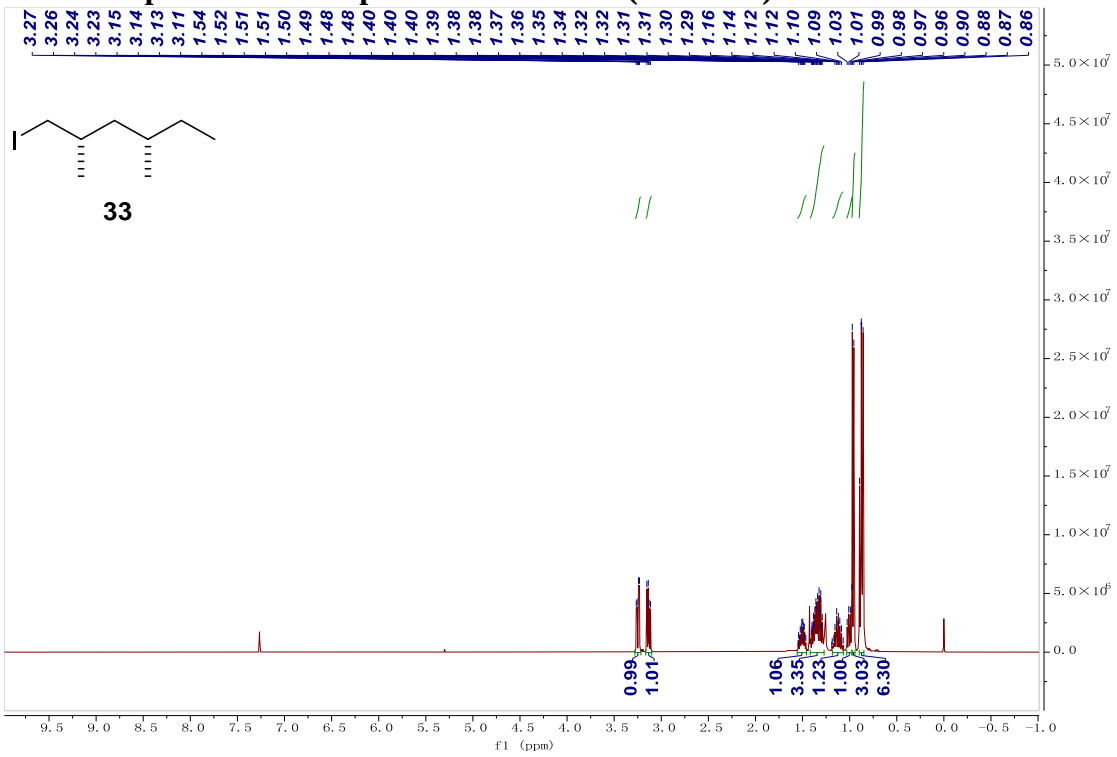
^{1}H NMR spectrum of compound 31 in $CDCl_3$ (400 MHz)



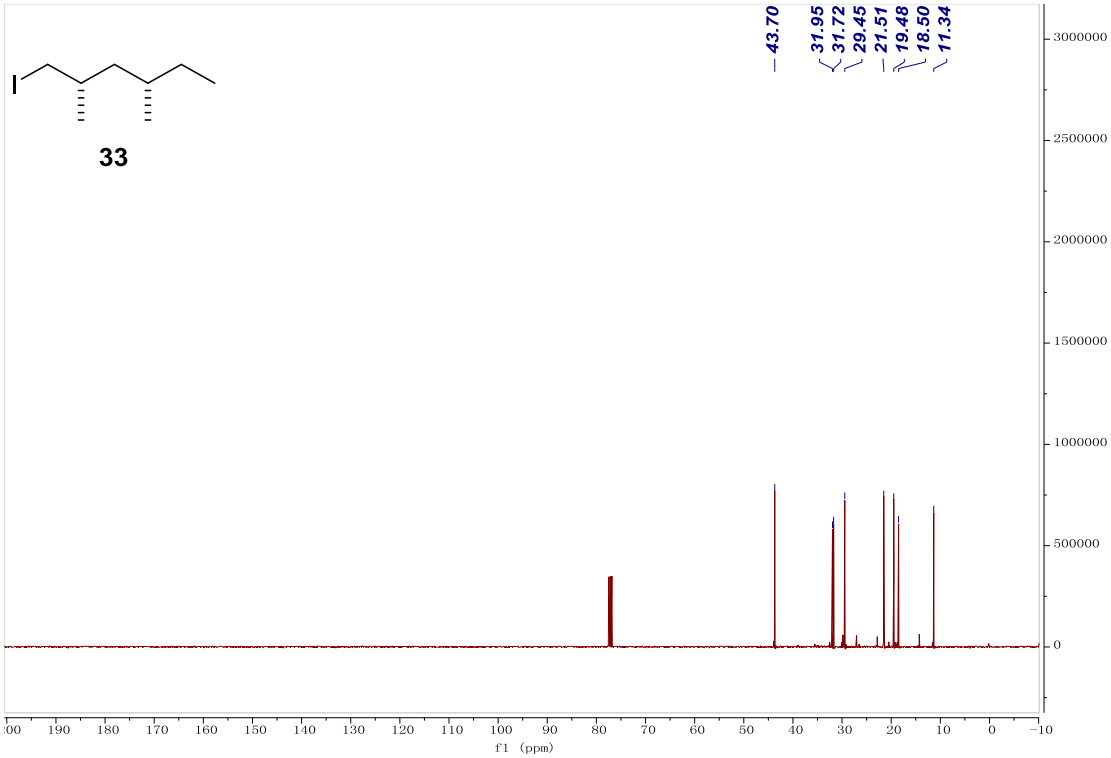


^{13}C NMR spectrum of compound 31 in $CDCl_3$ (100 MHz)

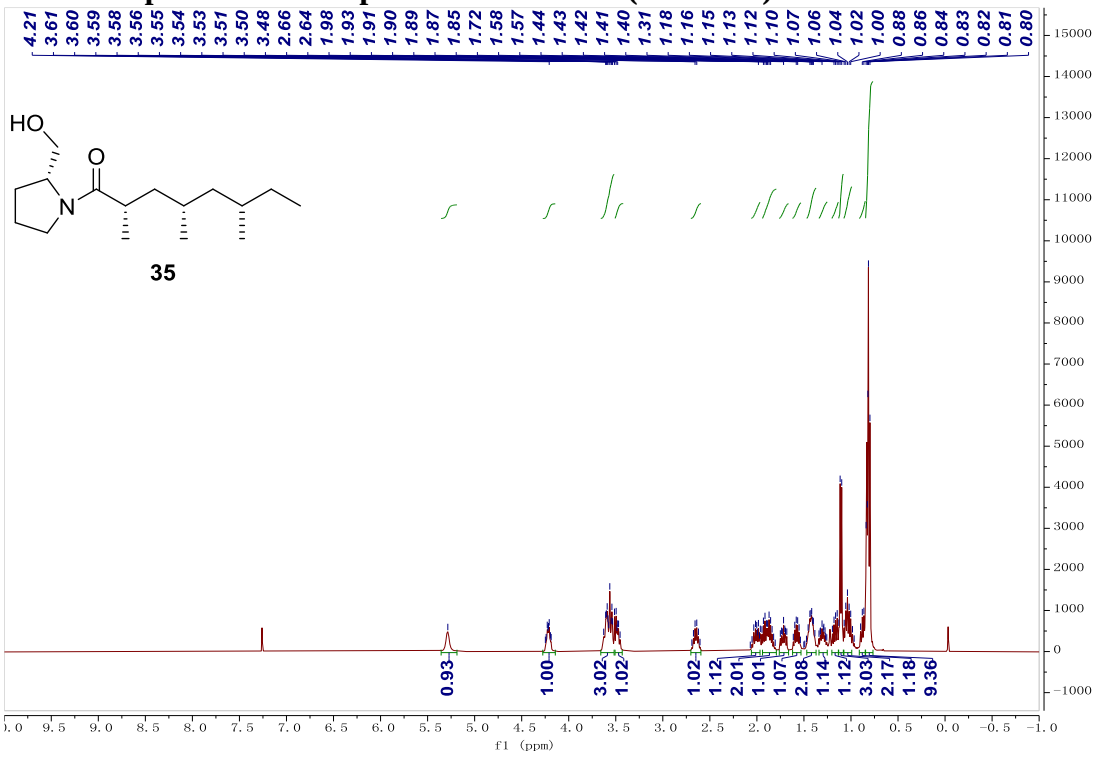
^{1}H NMR spectrum of compound 33 in $CDCl_3$ (400 MHz)



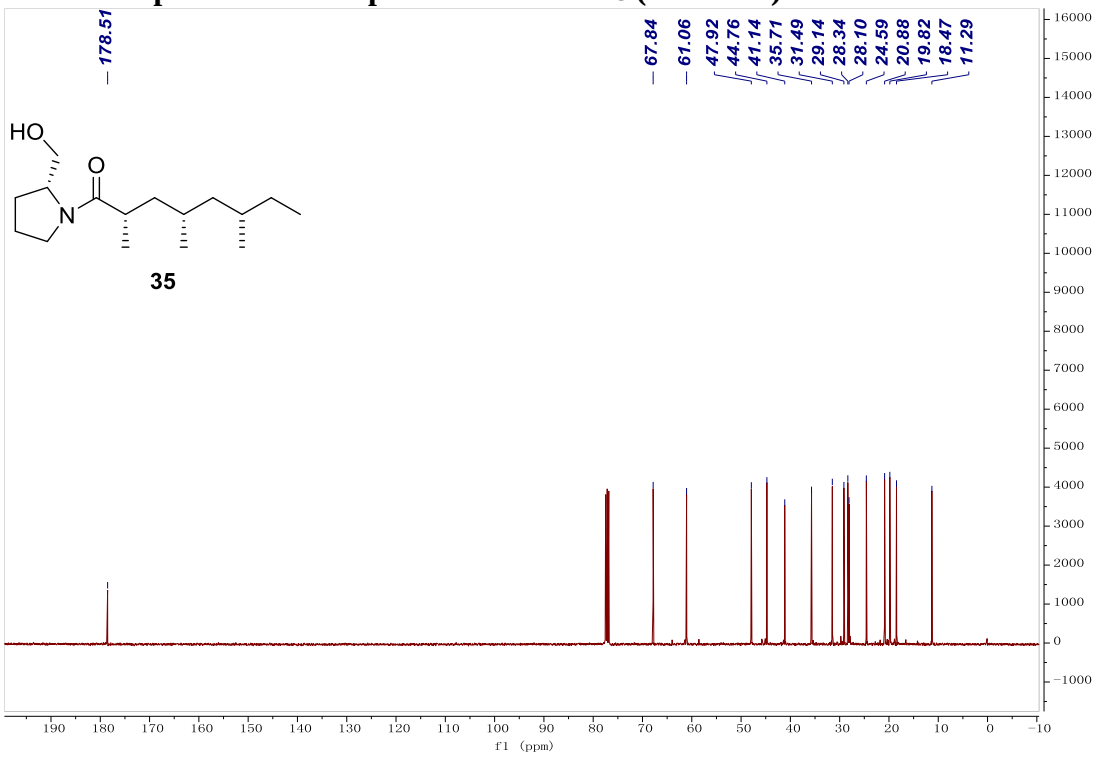
^{13}C NMR spectrum of compound 33 in $CDCl_3$ (100 MHz)



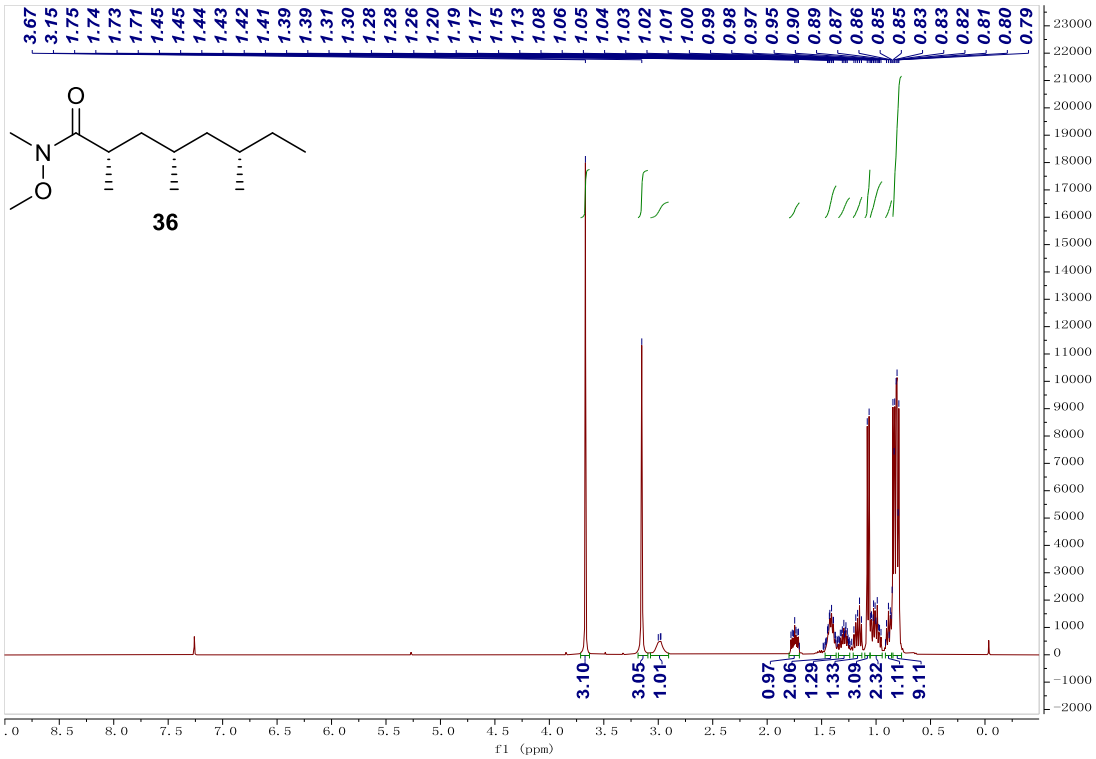
^{1}H NMR spectrum of compound 35 in $CDCl_3$ (400 MHz)



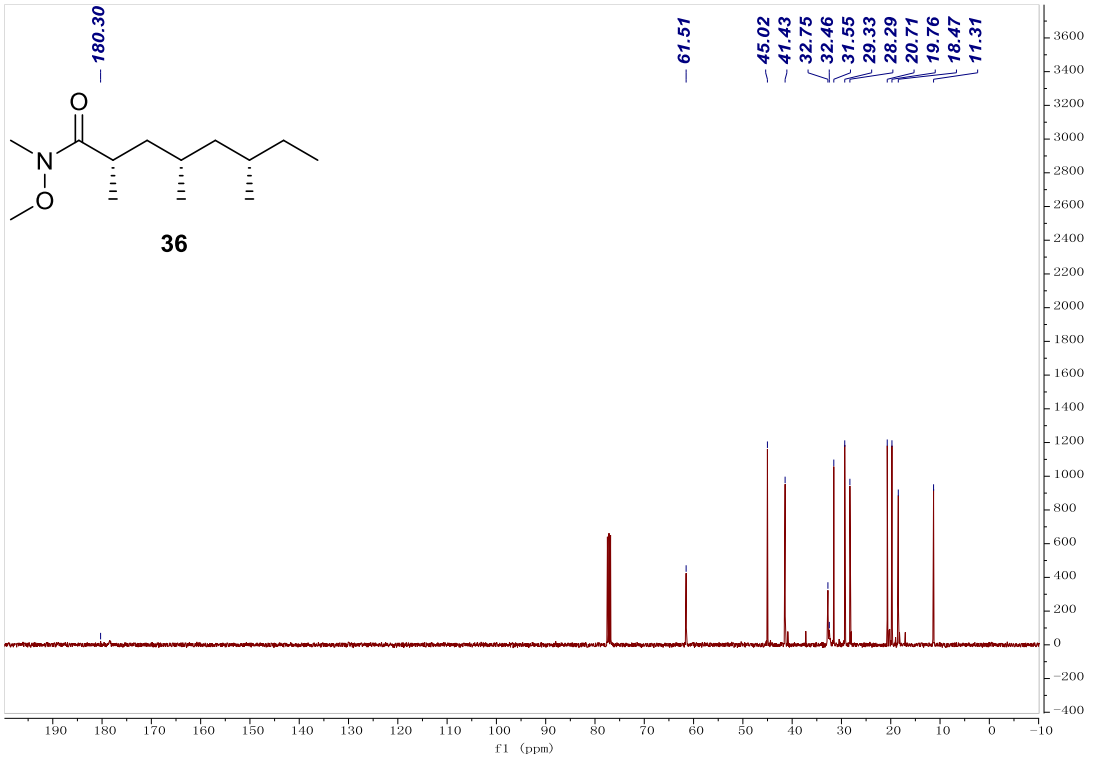
^{13}C NMR spectrum of compound 35 in $CDCl_3$ (100 MHz)



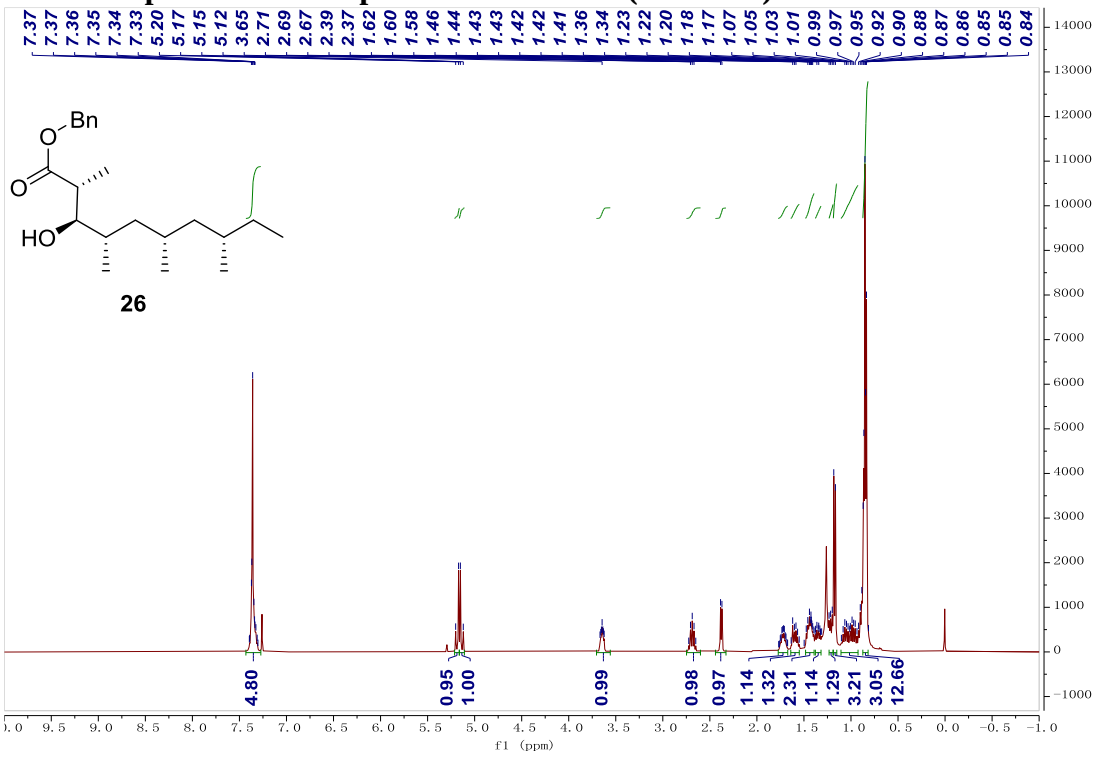
^{1}H NMR spectrum of compound 36 in $CDCl_3$ (400 MHz).



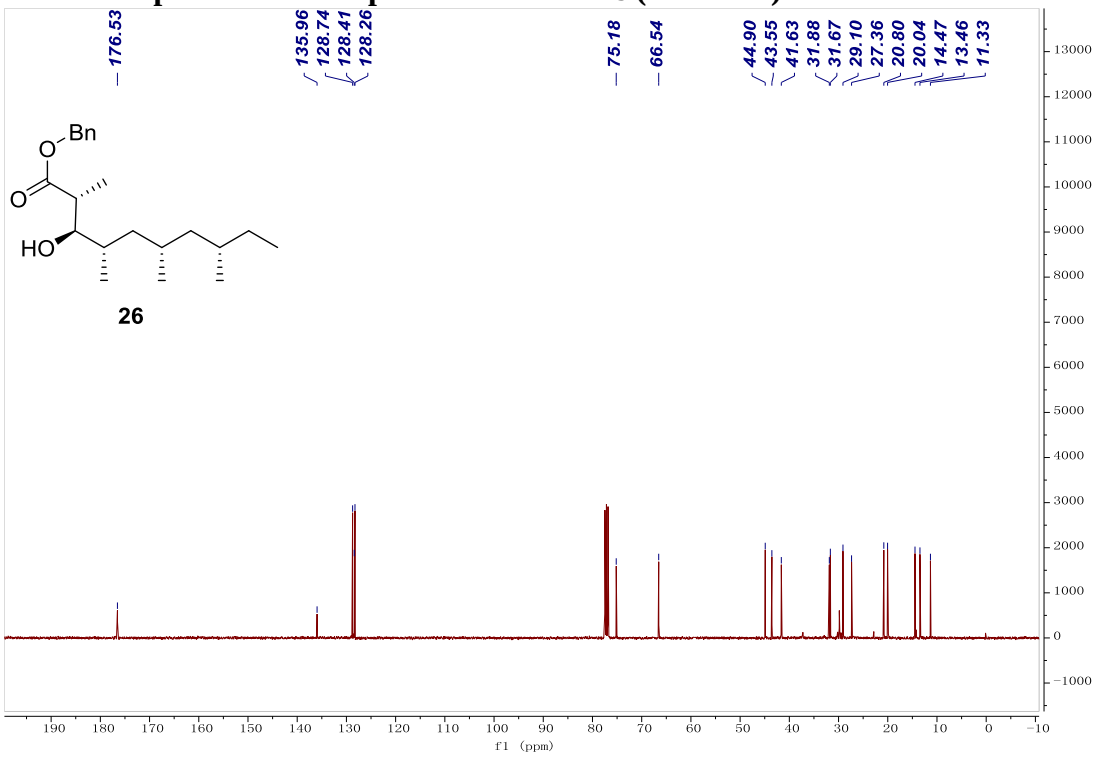
^{13}C NMR spectrum of compound 36 in $CDCl_3$ (100 MHz).



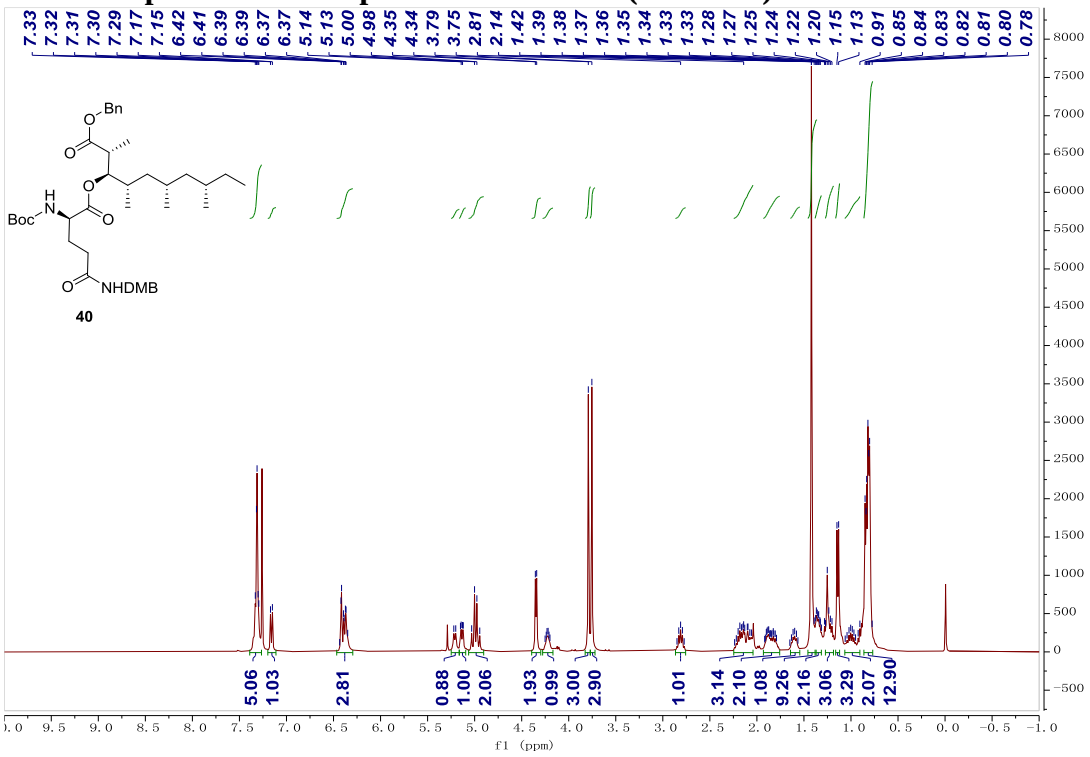
^{1}H NMR spectrum of compound 26 in $CDCl_3$ (400 MHz)



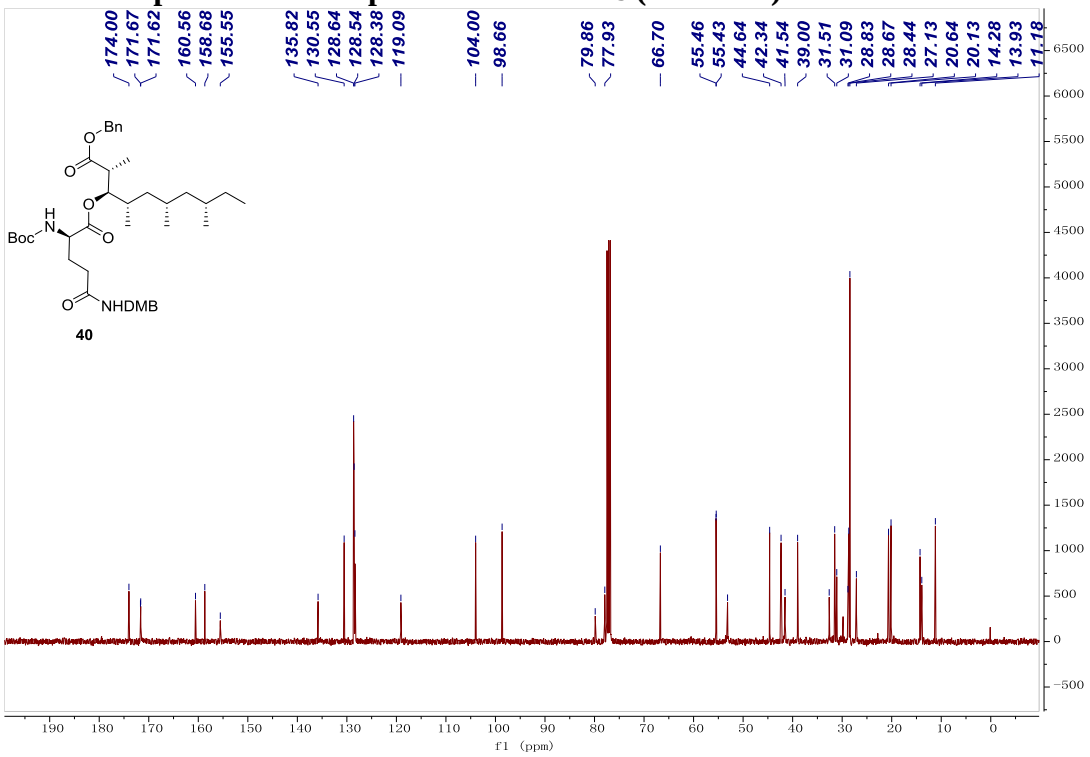
^{13}C NMR spectrum of compound 26 in $CDCl_3$ (100 MHz)



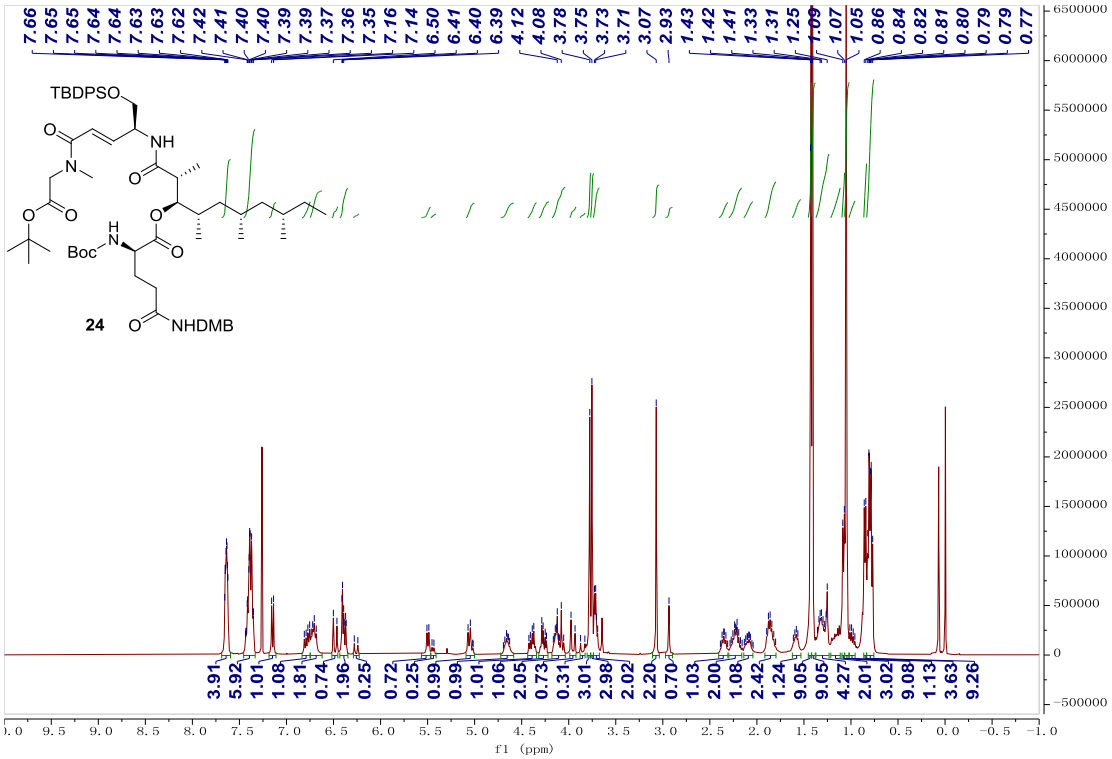
^{1}H NMR spectrum of compound 40 in $CDCl_3$ (400 MHz)



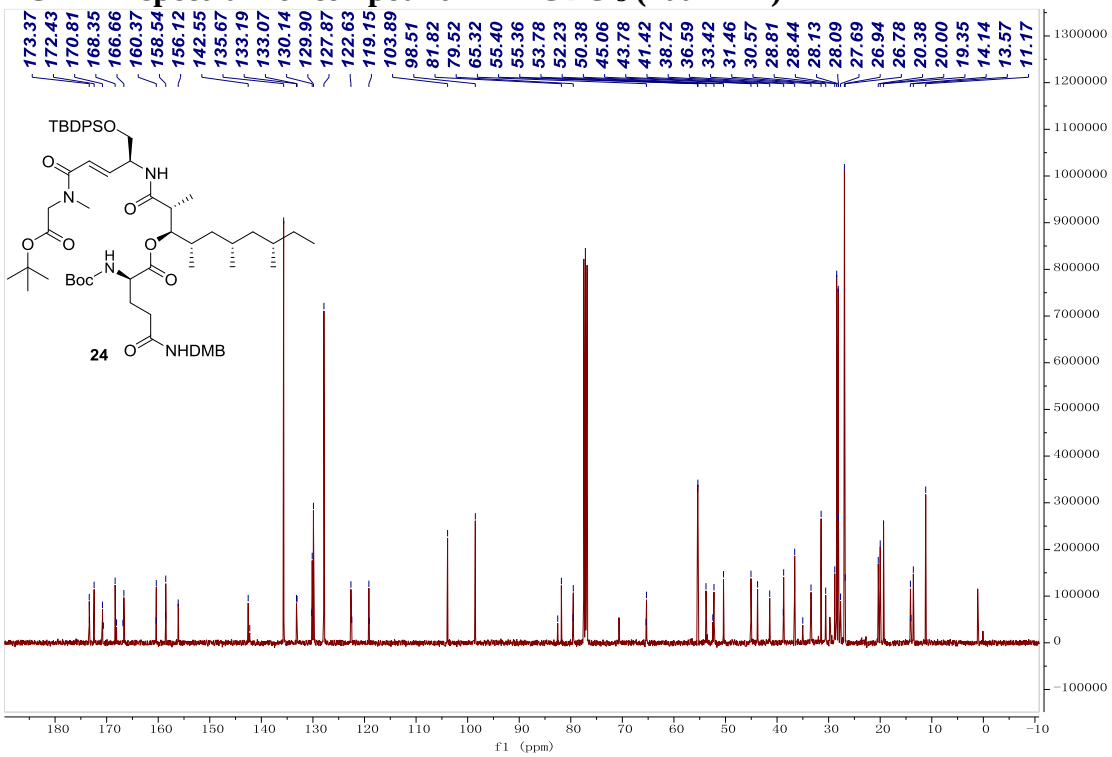
^{13}C NMR spectrum of compound 40 in $CDCl_3$ (100 MHz)



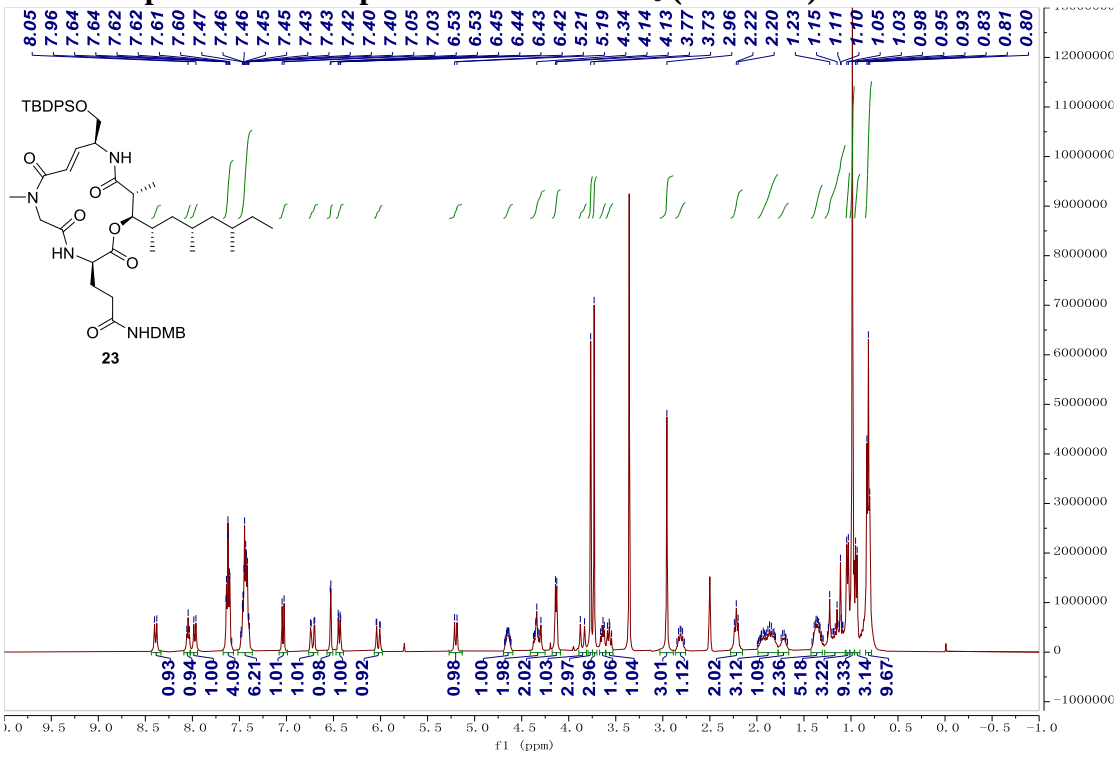
^{1}H NMR spectrum of compound 24 in $CDCl_3$ (400 MHz)



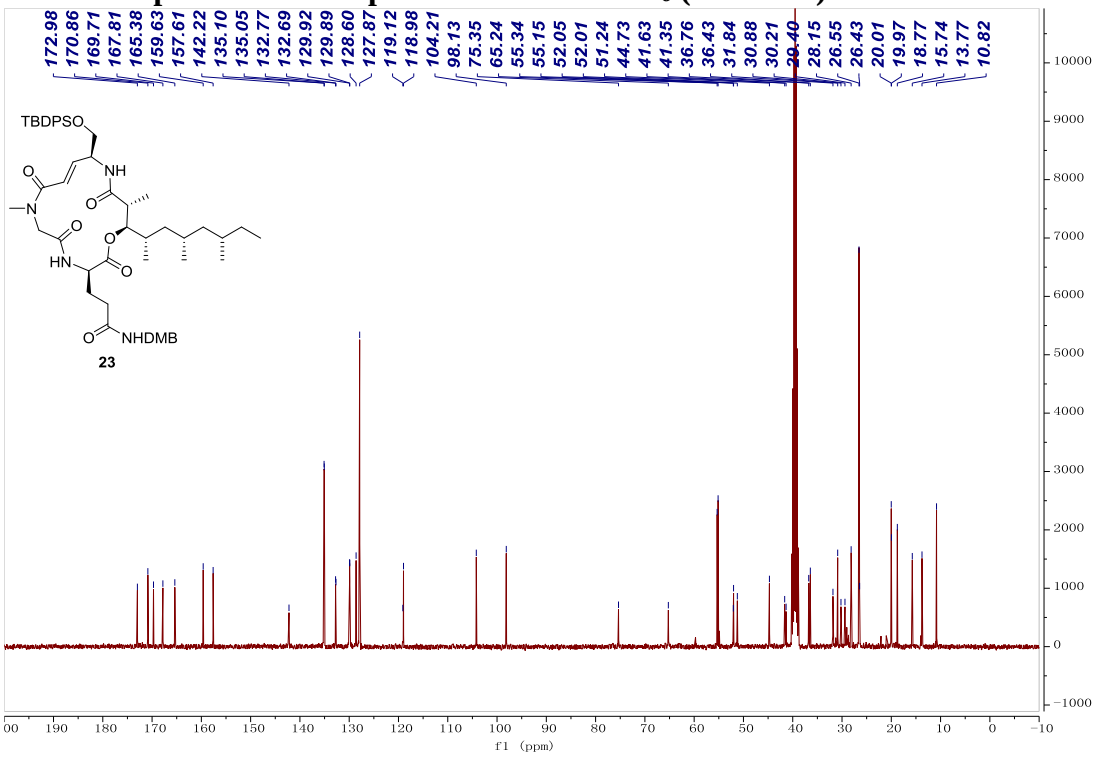
^{13}C NMR spectrum of compound 24 in $CDCl_3$ (100 MHz)



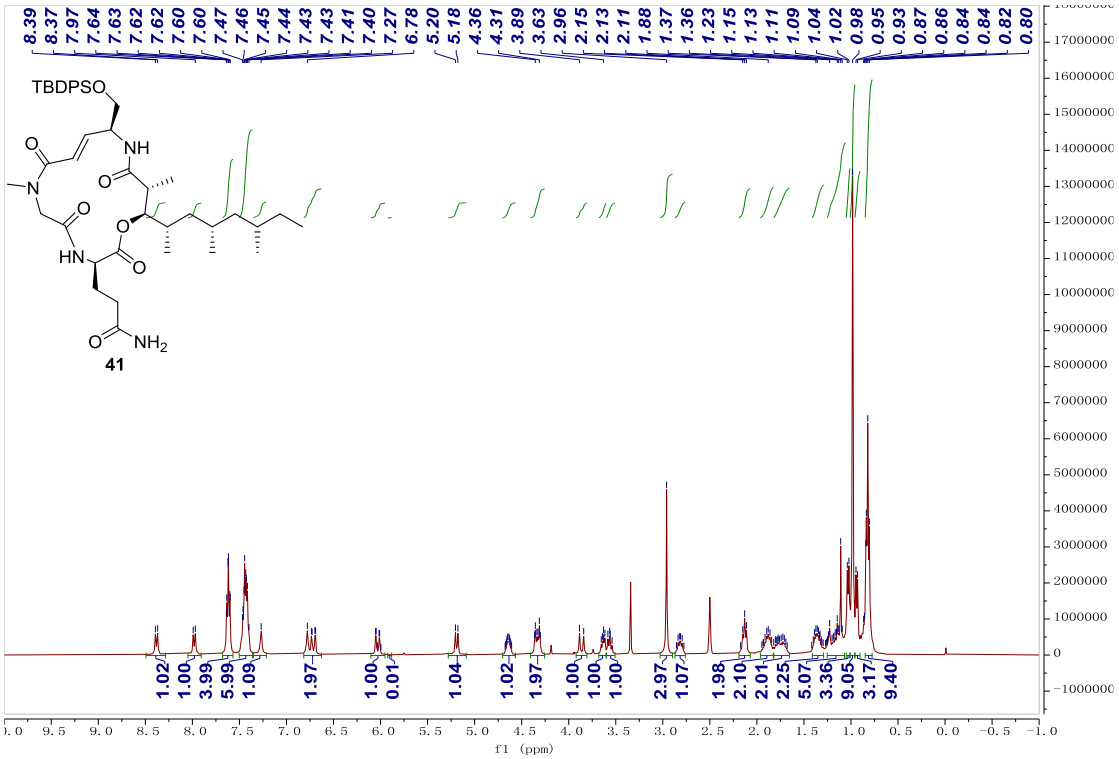
^{1}H NMR spectrum of compound 23 in DMSO-d_6 (400 MHz)



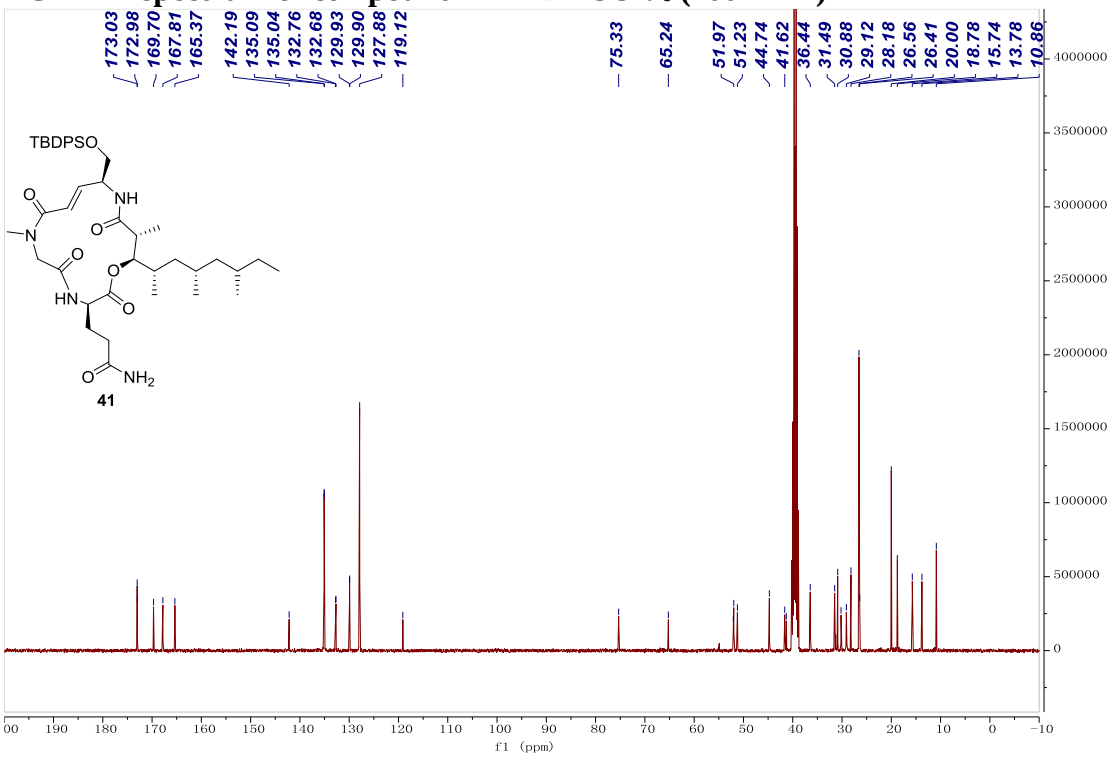
^{13}C NMR spectrum of compound 23 in DMSO-d_6 (100 MHz)



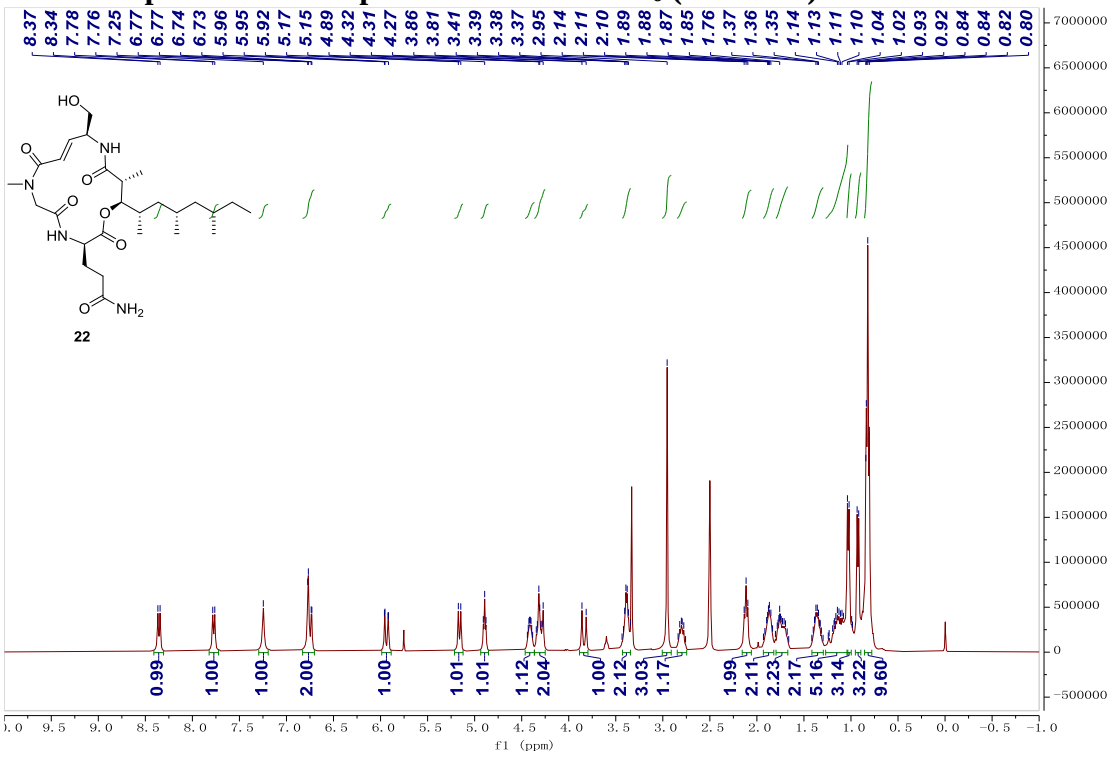
^{1}H NMR spectrum of compound 41 in DMSO-d_6 (400 MHz)



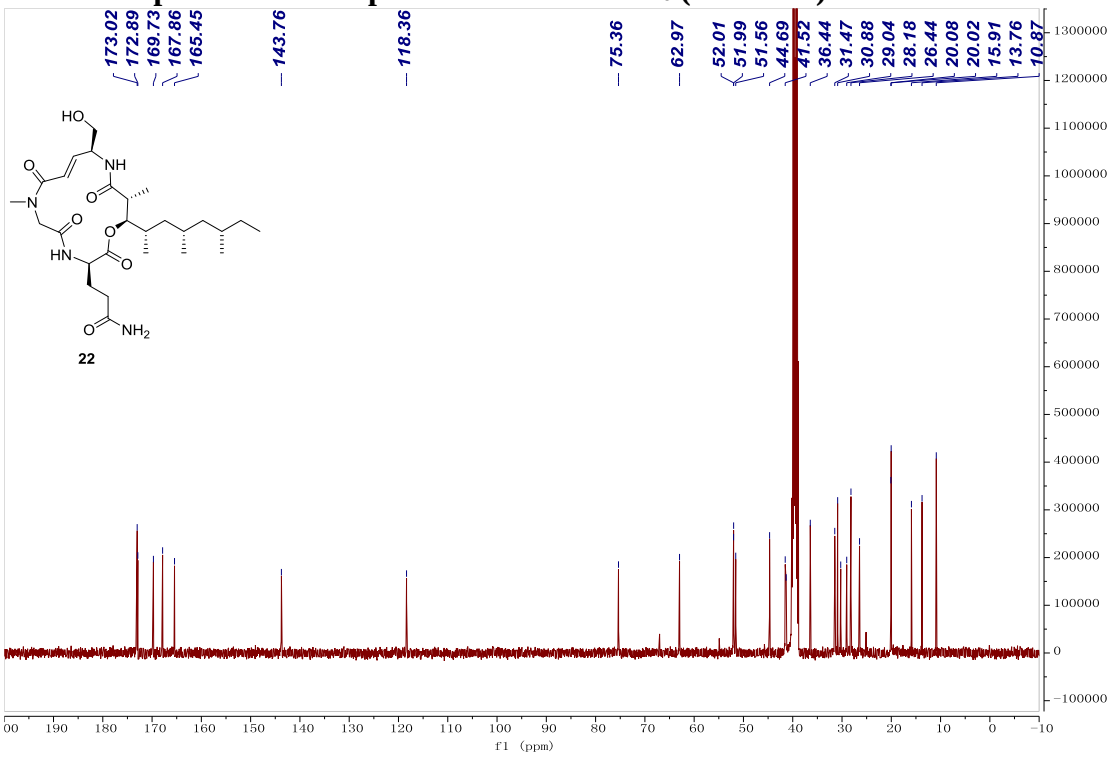
^{13}C NMR spectrum of compound 41 in DMSO-d_6 (100 MHz)



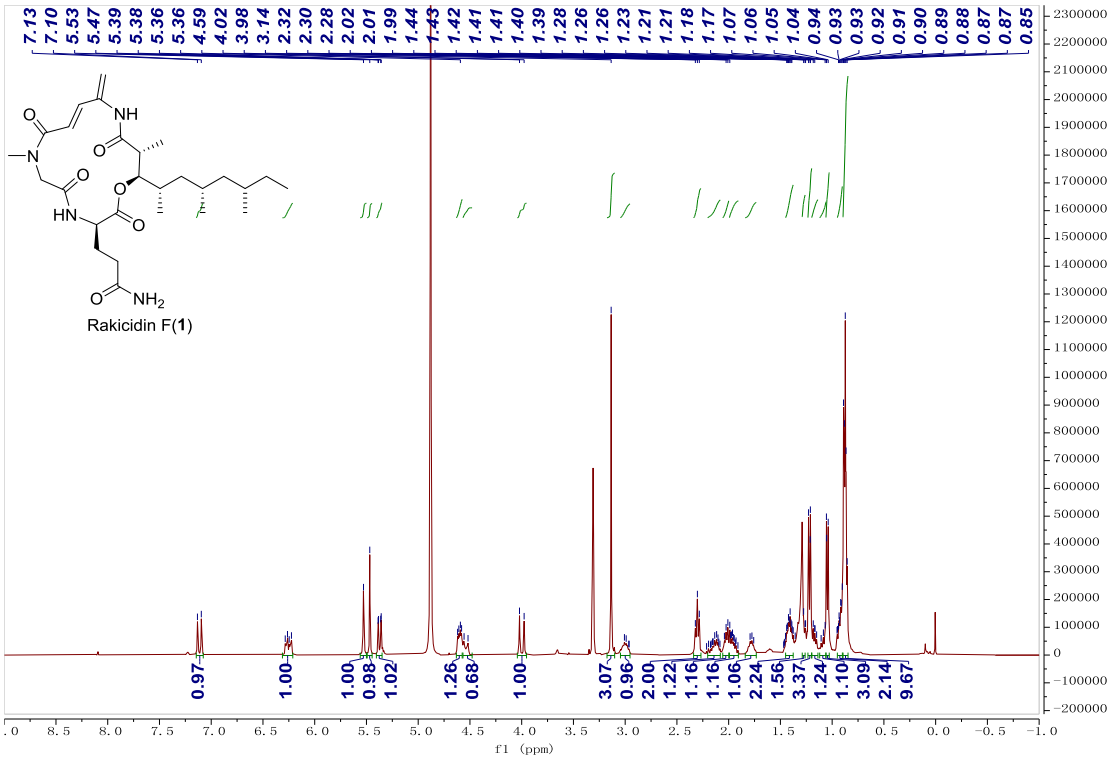
^{1}H NMR spectrum of compound 22 in DMSO-d_6 (400 MHz)



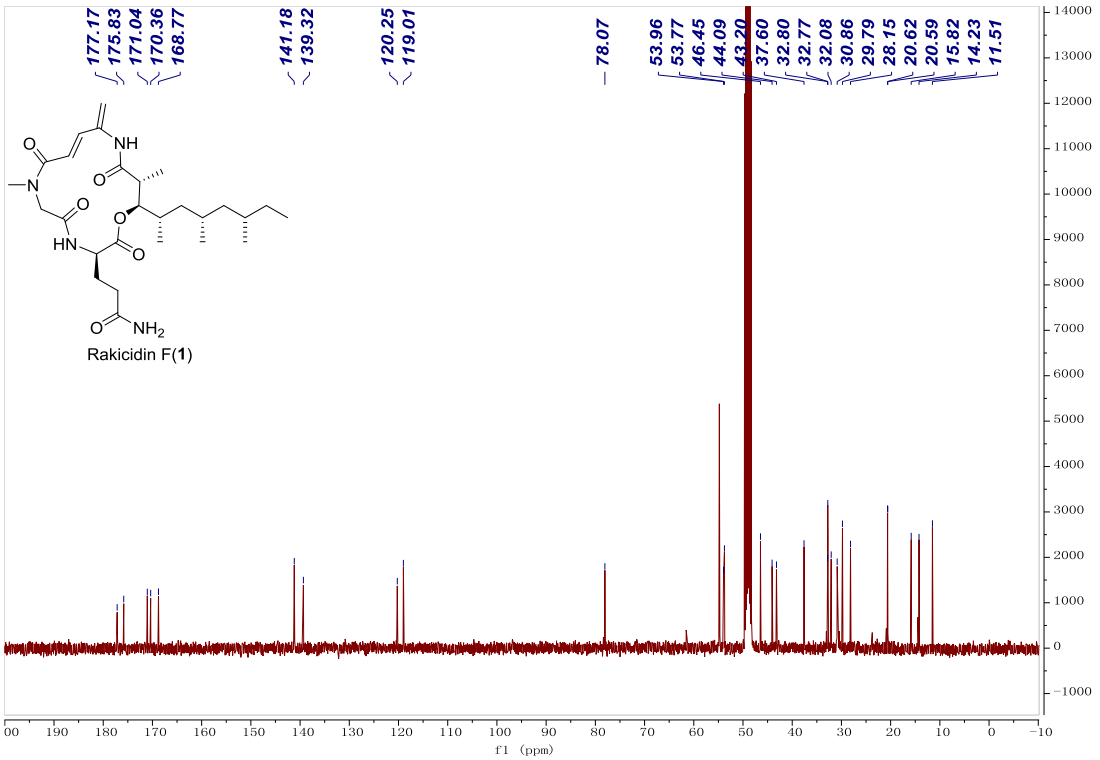
^{13}C NMR spectrum of compound 22 in DMSO-d_6 (100 MHz)



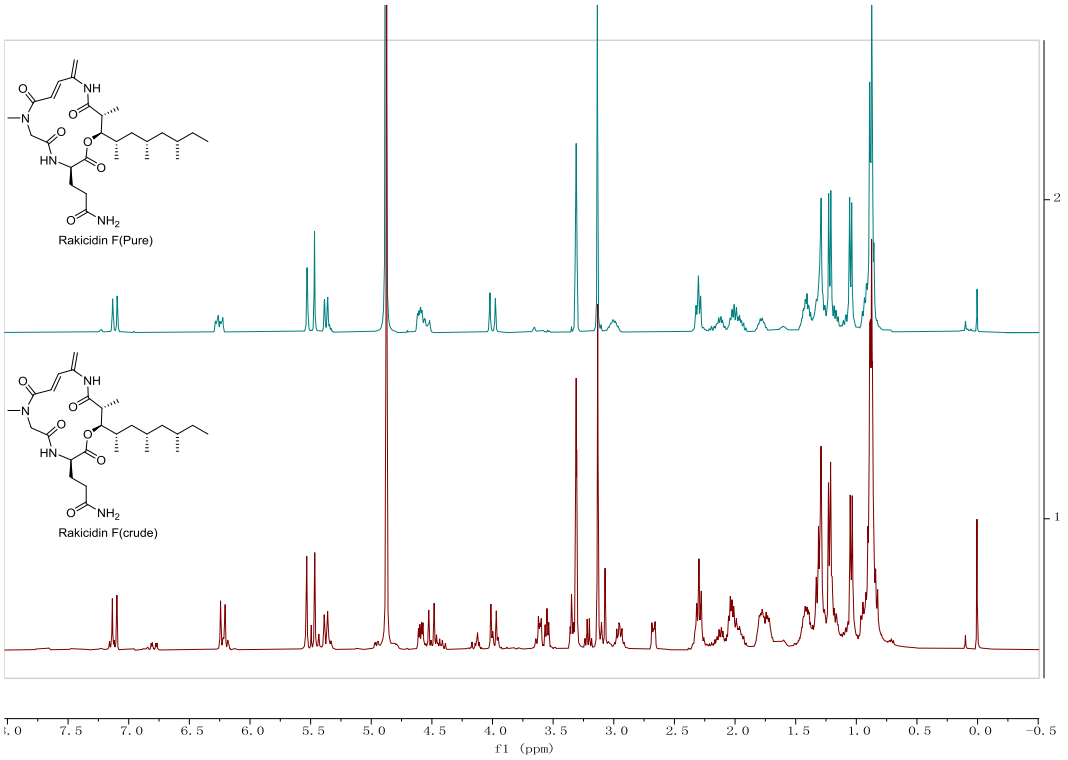
^{1}H NMR spectrum of rakicidin F (1) in MeOD-d_4 (400 MHz)



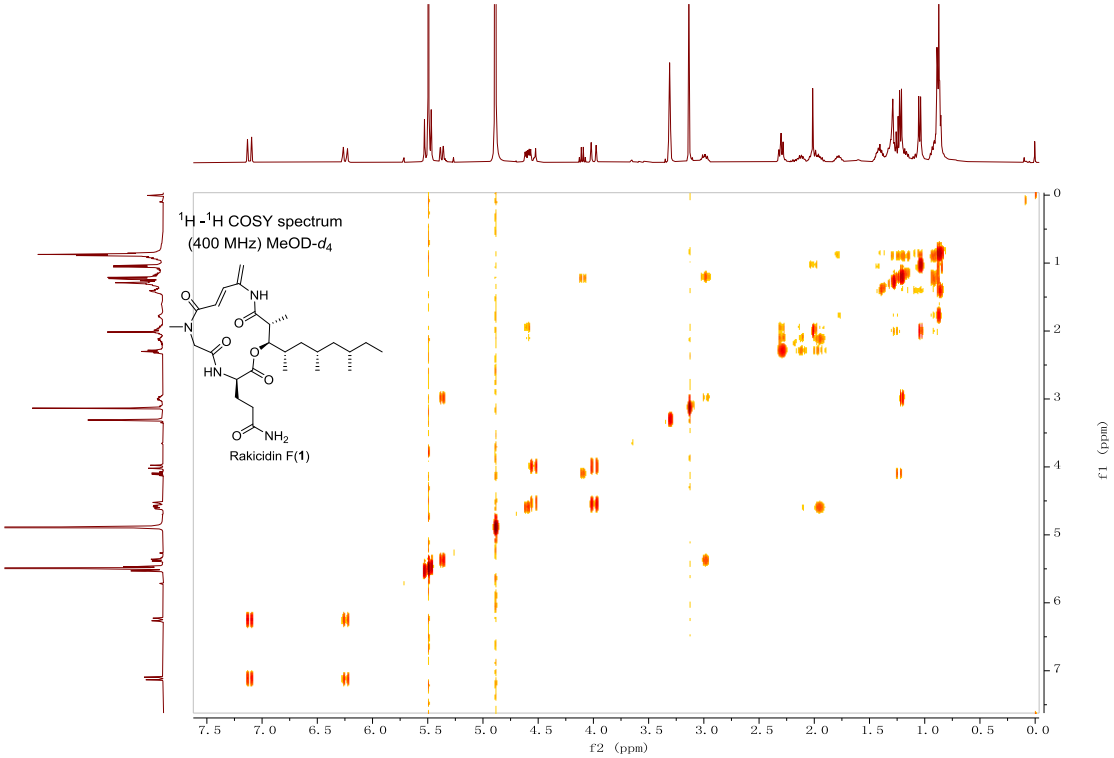
^{13}C NMR spectrum of rakicidin F (1) in MeOD-d_4 (100 MHz)



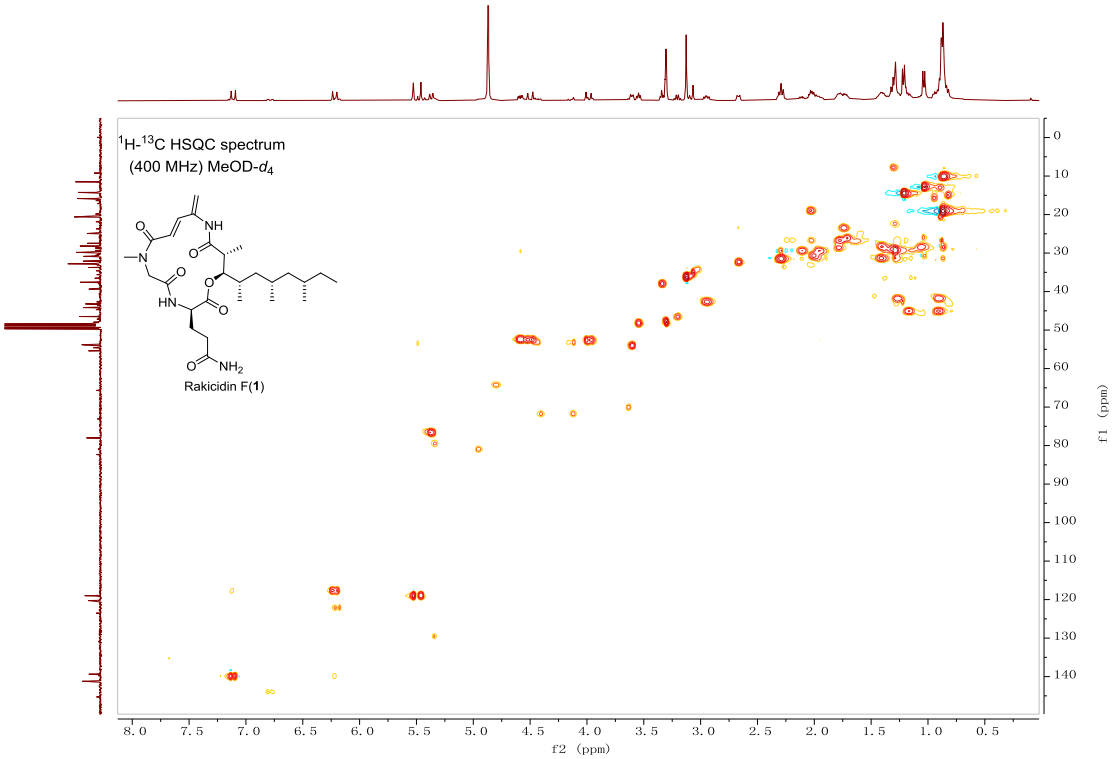
^{1}H NMR spectrum comparison of pure and crude rakicidin F (1) in MeOD-*d*$_4$ (400 MHz)



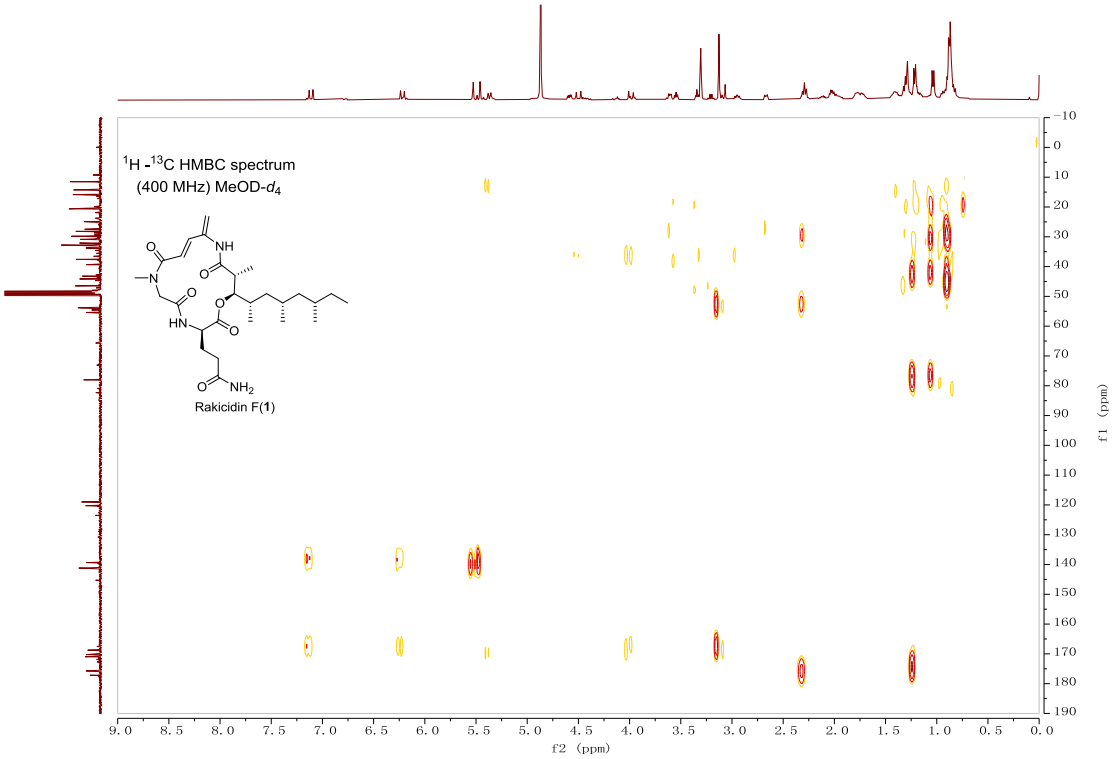
COSY spectrum of rakicidin F (1) in MeOD-*d*$_4$



HSQC spectrum of rakicidin F (1) in MeOD-*d*4

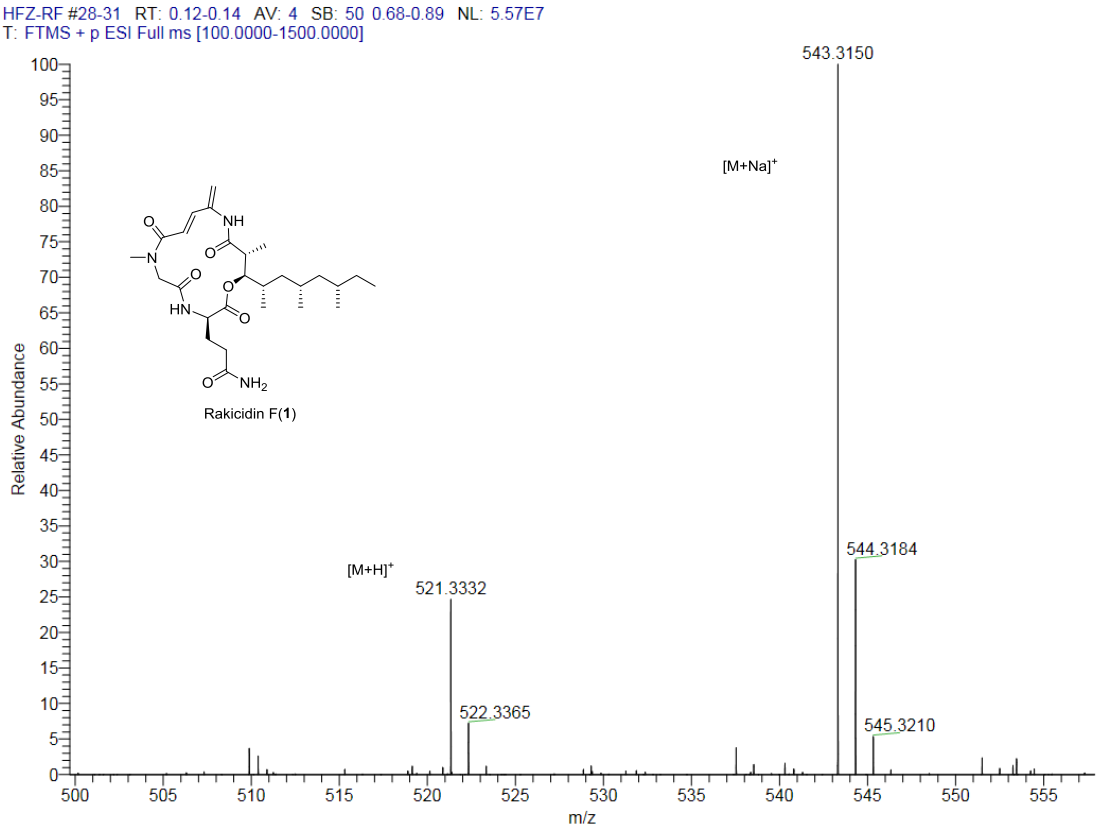


HMBC spectrum of rakicidin F (1) in MeOD-*d*4

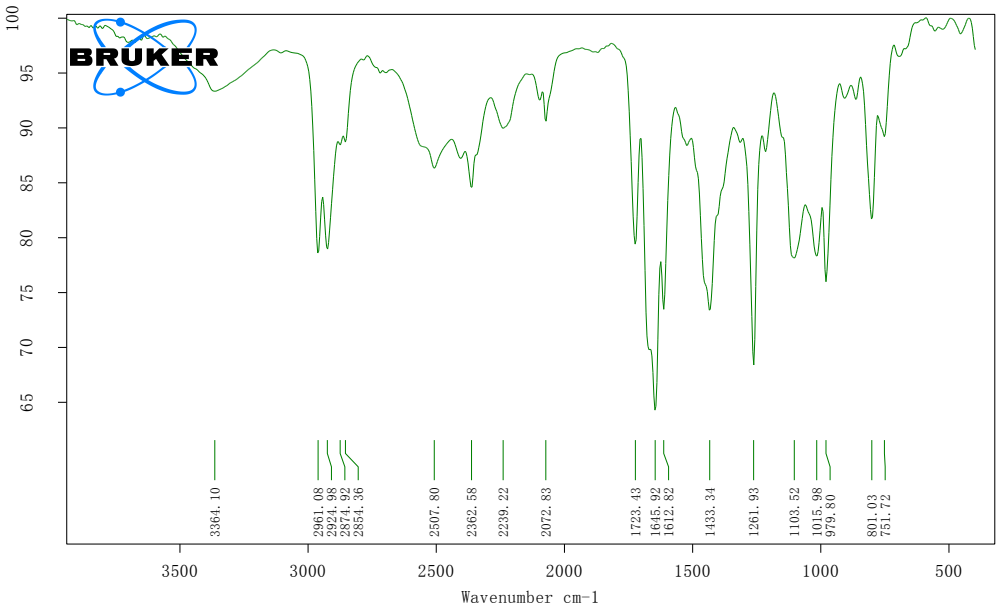


6. Copies of IR and HRMS Spectrum for Rakicidin F

HRMS Spectrum for Rakicidin F (1)



IR Spectrum for Rakicidin F (1)



D:\原始数据\中红外原始数据\韩方智\RF\Rakicidin F.1	Rakicidin F	Instrument type and / or accessory	2022/3/2

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