Supporting information

Total synthesis of callipeltin B and M, peptidyl marine natural products

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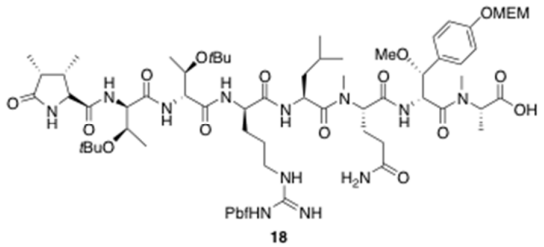
Contents

General information

All solvents were reagent grade. CH_2Cl_2 was distilled from CaH_2. All commercial reagents were of the highest purity available. ^1H (500 or 800 MHz) and ^{13}C NMR (125 or 200 MHz) spectra were recorded on either a JNM-ECX500 or JNM-ECA800. Chemical shifts are expressed in ppm relative to CH_3OH (3.31 ppm for ^1H and 49.0 ppm for ^{13}C). Analytical HPLC was carried out with a COSMOSIL $5C_{18}$-AR-II column (4.6ID×150 mm) with a linear gradient of MeCN (0.1% TFA) in H_2O (0.1% TFA) at a run time of 30 min (flow rate of 1 mL/min), on a SHIMADZU SPD-10A as a UV-Vis detector, HITACHI L-6000 Pump and HITACHI L-6200 Intelligent Pump. Preparative HPLC was performed with a COSMOSIL $5C_{18}$-AR-II column (10ID×250 mm) with a linear gradient of MeCN (0.1% TFA) in H_2O (0.1% TFA) at a run time of 30 min (flow rate of 2 mL/min), on a SHIMADZU SPD-10A*i* as a UV-Vis detector and HITACHI L-6200 Intelligent Pump. UV measurement was recorded at a wavelength of 220 nm. High-resolution mass spectra (HRMS) were obtained using a JEOL AccuTOF JMS-T100LC (ESIMS).

Experimental procedures

pDME-D-*a*Thr(*t*Bu)-D-*a*Thr(*t*Bu)-D-Arg(Pbf)-Leu-MeGln-βMeOTyr(MEM)-MeAla-OH (18)



18

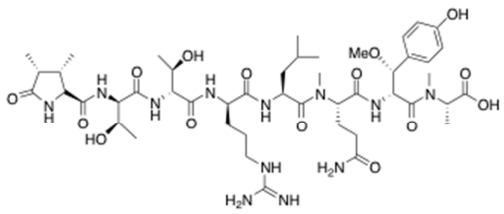
2-Chlorotrityl chloride resin (161 mg, 100-200 mesh, 1% DVB, 1.60 mmol/g) was swelled in DMF (2.5 mL) for 40 min. Fmoc-MeAla-OH (167 mg, 514 μmol) and *i*-Pr_2NEt (133 μL, 771 μmol) were dissolved in DMF (2.5 mL) and added to the preactivated resin, through the reaction for 2 h. The solvent was removed by filtration and the resin washed sequentially with DMF. The resin was treated with a 20% piperidine/DMF solution (2.5 mL) for 30 min. The solvent was removed by filtration and the resin was washed with DMF. Fmoc-βMeOTyr(MEM)-OH (268 mg, 514 μmol), PyBOP (401 mg, 771 μmol), HOBt·H_2O (118 mg, 771 μmol), *i*-Pr_2NEt (177 μL, 1.03 mmol) dissolved in DMF (2.5 mL) were added to the resin and agitated for 4 h. The solvent was removed by filtration, and the resin was washed with DMF. This procedure was repeated (2 times). The resin was treated with a 20% piperidine/DMF solution (2.5 mL) for 30 min. Fmoc-MeGln-OH (197 mg, 514 μmol), PyBOP (401 mg, 771 μmol), HOBt·H_2O (118 mg, 771 μmol), *i*-Pr_2NEt (177 μL, 1.03 mmol) dissolved in DMF (2.5 mL) were added to the resin and agitated for 4 h. The solvent was removed by filtration, and the resin was washed with DMF. The resin was treated with a 20% piperidine/DMF solution (2.5 mL) for 30 min. Fmoc-Leu-OH (454 mg, 1.29 mmol), COMU (440 mg, 1.03 mmol), HOAt (140 mg, 1.03 mmol), *i*-Pr_2NEt (266 μL, 1.54 mmol), dissolved in

DMF (2.5 mL) were added to the resin and agitated for 5 h. The solvent was removed by filtration, and the resin was washed with DMF. The resin was treated with a 20% piperidine/DMF solution (2.5 mL) for 30 min. Fmoc-D-Arg(Pbf)-OH (365 mg, 514 μmol), PyBOP (401 mg, 771 μmol), HOBt·H_2O (118 mg, 771 μmol), *i*-Pr_2NEt (177 μL, 1.03 mmol) dissolved in DMF (2.5 mL) were added to the resin and agitated for 3 h. The solvent was removed by filtration, and the resin was washed with DMF. The resin was treated with a 20% piperidine/DMF solution (2.5 mL) for 30 min. Fmoc-D-*a*Thr(*t*Bu)-OH (204 mg, 514 μmol), PyBOP (401 mg, 771 μmol), HOBt·H_2O (118 mg, 771 μmol), *i*-Pr_2NEt (177 μL, 1.03 mmol) dissolved in DMF (2.5 mL) were added to the resin and agitated for 2 h. The solvent was removed by filtration, and the resin was washed with DMF. The resin was treated with a 20% piperidine/DMF solution (2.5 mL) for 30 min.

To the resin (128 μmol) in DMF (2 mL) was added Fmoc-D-*a*Thr(*t*Bu)-OH (102 mg, 256 μmol) using PyBOP (200 mg, 384 μmol), HOBt·H_2O (58.8 mg, 384 μmol), *i*-Pr_2NEt (88 μL, 512 μmol) and agitated for 4 h. The solvent was removed by filtration, and the resin was washed with DMF. The resin was treated with a 20% piperidine/DMF solution (2 mL) for 30 min. pDME (30.2 mg, 192 μmol), PyBOP (200 mg, 384 μmol), HOBt·H_2O (58.8 mg, 384 μmol), *i*-Pr_2NEt (88 μL, 512 μmol) dissolved in DMF (2 mL) were added to the resin and agitated for 4 h. The solvent was removed by filtration, and the resin was washed with DMF and Et_2O. The product was cleaved from the resin with a 20% HFIP/CH_2Cl_2 (3.5 mL) for 2.5 h. The mixture was filtrated and evaporated under reduced pressure. To the residue in Et_2O was centrifuged and decanted. The crude product was purified with RP-HPLC (linear gradient from 40% to 80% MeCN) and lyophilized to afford protected callipeltin M (**18**) (7.9 mg, 5.26 μmol, 4%) as a white powder. **18**: ^1H NMR (500 MHz, CD_3OD) δ 7.30 (d, J = 8.5 Hz, 2H),

7.04 (d, *J* = 9.0 Hz, 2H), 5.25, (m, 2H), 5.20 (d, *J* = 9.0 Hz, 1H), 5.12 (q, *J* = 7.5 Hz, 1H), 4.88 (overlapped, 1H), 4.73 (m, 1H), 4.43-4.32 (m, 4H), 4.12 (m, 1H), 4.05 (t, *J* = 6.5 Hz, 1H), 3.86 (d, *J* = 3.5 Hz, 1H), 3.79 (t, *J* = 5.0 Hz, 2H), 3.55 (t, *J* = 5.0 Hz, 2H), 3.33 (s, 3H), 3.18 (m, 2H), 3.14 (s, 3H), 3.09 (s, 2H), 3.01 (s, 3H), 2.83 (s, 3H), 2.67-2.62 (m, 2H), 2.57 (s, 3H), 2.51 (s, 3H), 2.09 (s, 3H), 1.96-1.79 (m, 5H), 1.67-1.59 (m, 6H), 1.46 (s, 6H), 1.40 (d, *J* = 7.5 Hz, 3H), 1.19 (s, 9H), 1.18 (overlapped, 3H), 1.17 (s, 9H), 1.11 (d, *J* = 7.5 Hz, 3H), 1.05 (d, *J* = 7.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 183.3, 175.1, 174.3, 172.4, 170.9, 159.0, 132.1, 130.4, 117.3, 94.7, 85.2, 75.9, 75.9, 72.8, 68.8, 68.2, 63.6, 60.5, 59.1, 57.2, 54.1, 43.9, 40.3, 39.9, 32.7, 32.6, 31.3, 28.7, 26.0, 25.1, 23.8, 21.7, 19.9, 19.6, 18.4, 14.7, 14.7, 12.5, 10.5; HRMS (ESI) *m/z*: calcd. for $C_{72}H_{117}N_{12}O_{20}S$ $[M+H]^+$ 1501.8228, found 1501.8207; RP-HPLC: t_R = 22.2 min (linear gradient from 10% to 90% MeCN).

pDME-D-*a*Thr-D-*a*Thr-D-Arg-Leu-MeGln-βMeOTyr-MeAla-OH; callipeltin M (4)

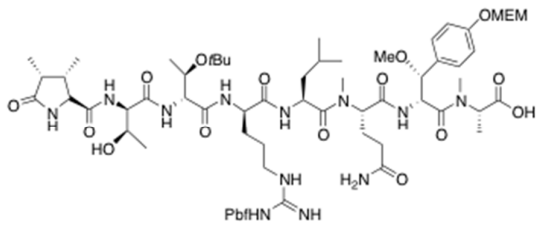


4

Protected callipeltin M (**18**) (7.9 mg, 5.26 μmol) was added 50% TFA/CH_2Cl_2 (1 mL) and stirred for 2 h. To the mixture in Et_2O was centrifuged and decanted. The crude material was purified with RP-HPLC (linear gradient from 20% to 90% MeCN) and lyophilized to afford **4** (1.6 mg, 1.53 μmol, 29%) as a white powder. ^{1}H NMR (500 MHz, CD_3OD) δ 7.19 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 5.21 (t, *J* = 9.0 Hz, 1H), 5.13 (q, *J* = 7.5 Hz, 1H), 4.88 (overlapped, 1H), 4.73 (m, 1H),

4.36-4.32 (m, 3H), 4.22 (d, J = 6.5 Hz, 1H), 4.09-4.01 (m, 2H), 3.81 (d, J = 4.0 Hz, 1H), 3.16 (m, 2H), 3.13 (s, 3H), 3.10 (s, 3H), 2.83 (s, 3H), 2.66 (m, 1H), 2.57 (m, 1H), 1.99-1.88 (m, 3H), 1.72-1.61 (m, 7H), 1.47 (m, 1H), 1.40 (d, J = 7.5 Hz, 3H), 1.28 (m, 6H), 1.12 (d, J = 7.0 Hz, 3H), 1.07 (d, J = 7.5 Hz, 3H), 0.95 (d, J = 6.0 Hz, 3H), 0.92 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 180.6, 177.6, 174.6, 174.0, 173.6, 172.8, 172.8, 171.0, 169.8, 163.2, 162.9, 130.5, 116.2, 85.3, 68.6, 68.5, 63.9, 61.3, 61.2, 57.4, 57.1, 54.2, 53.8, 48.2, 41.8, 40.6, 40.3, 39.9, 32.6, 32.5, 30.7, 29.4, 26.2, 25.9, 24.9, 23.7, 21.6, 20.7, 20.4, 14.9, 14.7, 10.5; HRMS (ESI) *m/z*: calcd. for $C_{47}H_{77}N_{12}O_{15}$ $[M+H]^+$ 1049.5631, found 1049.5672; RP-HPLC: t_R = 10.6 min (linear gradient from 10% to 90% MeCN).

pDME-D-*a*Thr-D-*a*Thr(*t*Bu)-D-Arg(Pbf)-Leu-MeGln-βMeOTyr(MEM)-MeAla-OH (19)



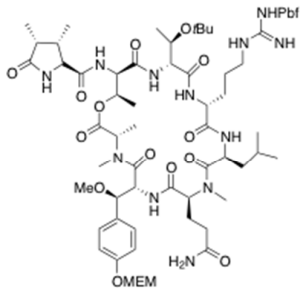
19

2-Chlorotrityl chloride resin (111 mg, 100-200 mesh, 1% DVB, 1.60 mmol/g) was swelled in DMF (2.5 mL) for 40 min. Fmoc-MeAla-OH (115 mg, 354 μmol) and *i*-Pr_2NEt (91 μL, 531 μmol) were dissolved in DMF (2 mL) and added to the preactivated resin, through the reaction for 2 h. The solvent was removed by filtration and the resin washed sequentially with DMF. The resin was treated with a 20% piperidine/DMF solution (2 mL) for 30 min. The solvent was removed by filtration and the resin washed with DMF. Fmoc-βMeOTyr(MEM)-OH (185 mg, 354 μmol), HATU

(202 mg, 531 μmol), HOAt (72.3 mg, 531 μmol), *i*-Pr_2NEt (122 μL, 708 μmol) dissolved in DMF (2 mL) were added to the resin and agitated for 4 h. The solvent was removed by filtration, and the resin was washed with DMF. The resin was treated with a 20% piperidine/DMF solution (2 mL) for 30 min. Fmoc-MeGln-OH (135 mg, 354 μmol), PyBOP (276 mg, 531 μmol), HOBt･H_2O (81.3 mg, 531 μmol), *i*-Pr_2NEt (122 μL, 708 μmol) dissolved in DMF (2 mL) were added to the resin and agitated for 4 h. The solvent was removed by filtration, and the resin was washed with DMF. The resin was treated with a 20% piperidine/DMF solution (2 mL) for 30 min. Fmoc-Leu-OH (313 mg, 885 μmol), PyBOP (368 mg, 708 μmol), HOBt･H_2O (108 mg, 708 μmol), *i*-Pr_2NEt (183 μL, 1.06 mmol), dissolved in DMF (2 mL) were added to the resin and agitated for 5 h. The solvent was removed by filtration, and the resin was washed with DMF. The resin was treated with a 20% piperidine/DMF solution (2 mL) for 30 min. Fmoc-D-Arg(Pbf)-OH (251 mg, 354 μmol), PyBOP (276 mg, 531 μmol), HOBt･H_2O (81.3 mg, 531 μmol), *i*-Pr_2NEt (122 μL, 708 μmol) dissolved in DMF (2 mL) were added to the resin and agitated for 3 h. The solvent was removed by filtration, and the resin was washed with DMF. The resin was treated with a 20% piperidine/DMF solution (2 mL) for 30 min. Fmoc-D-*a*Thr(*t*Bu)-OH (141 mg, 354 μmol), PyBOP (276 mg, 531 μmol), HOBt･H_2O (81.3 mg, 531 μmol), *i*-Pr_2NEt (122 μL, 708 μmol) dissolved in DMF (2 mL) were added to the resin and agitated for 2 h. The solvent was removed by filtration, and the resin was washed with DMF. The resin was treated with a 20% piperidine/DMF solution (2 mL) for 30 min. Fmoc-D-*a*Thr-OH (121 mg, 354 μmol), PyBOP (276 mg, 531 μmol), HOBt･H_2O (81.3 mg, 531 μmol), *i*-Pr_2NEt (122 μL, 708 μmol) dissolved in DMF (2 mL) were added to the resin and agitated for 4 h. The solvent was removed by filtration, and the resin was washed with DMF. The resin was treated with a 20% piperidine/DMF solution (2 mL) for 30 min. pDME (30.6 mg, 195

μmol), PyBOP (276 mg, 531 μmol), HOBt·H_2O (81.3 mg, 531 μmol), *i*-Pr_2NEt (122 μL, 708 μmol) dissolved in DMF (2 mL) were added to the resin and agitated for 2 h. The solvent was removed by filtration, and the resin was washed with DMF and Et_2O. The product was cleaved from the resin with a 20% HFIP/CH_2Cl_2 (4 mL) for 2.5 h. The mixture was filtrated and evaporated under reduced pressure. To the residue in Et_2O was centrifuged and decanted. The crude product was added to 1 M NaOH and stirred for 20 min. The mixture was purified with RP-HPLC (linear gradient from 40% to 75% MeCN) and lyophilized to afford protected callipeltin M (**19**) (17.6 mg, 12.2 μmol, 7%) as a white powder. **19**: ^{1}H NMR (500 MHz, CD_3OD) δ 8.13 (d, *J* = 6.0 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 5.25 (s, 2H), 5.21 (d, *J* = 9.0 Hz, 1H), 5.14 (q, *J* = 7.5 Hz, 1H), 4.87 (overlapped, 1H), 4.76 (m, 1H), 4.44-4.38 (m, 1H), 4.28 (m, 2H), 4.18 (m, 1H), 4.09 (m, 1H), 3.80-3.78 (m, 3H), 3.56-3.54 (m, 2H), 3.33 (s, 3H), 3.17-3.15 (m, 2H), 3.13 (s, 3H), 3.11 (s, 2H), 3.00 (s, 3H), 2.84 (s, 3H), 2.68-2.59 (m, 2H), 2.56 (s, 3H), 2.50 (s, 3H), 2.08 (s, 3H), 1.97-1.58 (m, 11H), 1.45 (s, 6H), 1.40 (d, *J* = 7.5 Hz, 3H), 1.30 (d, *J* = 6.0 Hz, 3H), 1.21 (s, 9H), 1.18-1.09 (m, 6H), 1.07-1.03 (m, 3H), 0.94 (d, *J* = 6.0 Hz, 3H), 0.91 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 175.3, 174.5, 174.4, 172.8, 172.4, 170.9, 159.0, 132.2, 130.4, 117.3, 94.7, 85.1, 75.9, 72.8, 68.8, 67.4, 63.8, 61.9, 60.3, 59.1, 57.3, 57.2, 54.3, 54.1, 43.9, 40.9, 40.2, 40.1, 32.5, 31.3, 28.7, 25.9, 25.1, 23.8, 21.7, 21.1, 19.6, 19.2, 18.4, 14.9, 14.7, 12.5, 10.5; HRMS (ESI) *m/z*: calcd. for $C_{68}H_{109}N_{12}O_{20}S$ $[M+H]^+$ 1445.7602, found 1445.7624; RP-HPLC: t_R = 20.3 min (linear gradient from 10% to 90% MeCN).

Protected callipeltin B (20)

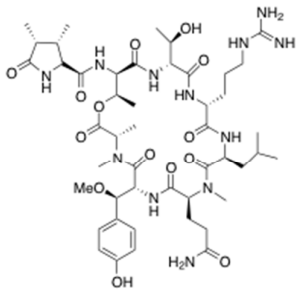


20

To the solution of protected callipeltin M (**19**) (0.9 mg, 622 nmol) in DMF (83 μL) was added the DIPCDI (0.5 μL, 3.11 μmol) and DMAP (1.5 mg, 12.4 μmol). After stirring for 18 h at 45 ^{o}C, reaction mixture was purified with RP-HPLC (linear gradient from 40% to 80% MeCN) and lyophilized to afford **20** (0.4 mg, 280 nmol, 44%) as a white powder. ^{1}H NMR (500 MHz, CD_3OD) δ 8.60 (d, *J* = 10.0 Hz, 1H), 8.38 (d, *J* = 10.0 Hz, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 7.72 (d, *J* = 7.0 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 5.42-5.33 (m, 2H), 5.27 (d, *J* = 7.0 Hz, 1H), 5.22 (d, *J* = 7.5 Hz, 1H), 4.99-4.92 (m, 2H), 4.73 (m, 1H), 4.54 (d, *J* = 10.0 Hz, 1H), 4.26 (m, 1H), 4.14 (m, 1H), 4.04 (m, 1H), 3.91 (d, *J* = 3.0 Hz, 1H), 3.80 (t, *J* = 5.0 Hz, 2H), 3.57 (t, *J* = 5.0 Hz, 2H), 3.17 (overlapped, 2H), 3.15 (s, 3H), 3.05 (s, 3H), 3.00 (s, 3H), 2.76 (m, 1H), 2.56 (s, 3H), 2.50 (s, 3H), 2.07 (s, 3H), 1.94-1.49 (m, 11H), 1.45 (s, 6H), 1.33-1.28 (m, 18H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.19 (d, *J* = 6.0 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 183.8, 176.8, 175.4, 174.7, 171.7, 171.4, 170.6, 158.9, 156.4, 131.9, 131.4, 130.8, 118.5, 116.9, 94.7, 87.7, 83.9, 76.3, 72.9, 68.8, 67.6, 63.3, 61.4, 59.1, 56.9, 56.6, 53.7, 52.3, 49.9, 44.1, 40.6, 40.3, 40.1, 36.5, 33.1, 32.8, 31.5, 30.8, 30.8, 30.6, 30.5, 30.3, 30.0, 28.7, 28.1, 26.9, 26.1, 25.9, 23.8, 23.7, 21.4, 20.3, 19.6, 18.4, 15.2, 14.5, 13.4, 12.5, 10.5; HRMS (ESI) *m/z*: calcd. for $C_{68}H_{107}N_{12}O_{19}S$ $[M+H]^+$ 1427.7496, found

1427.7498; RP-HPLC: t_R = 22.4 min (linear gradient from 10% to 90% MeCN).

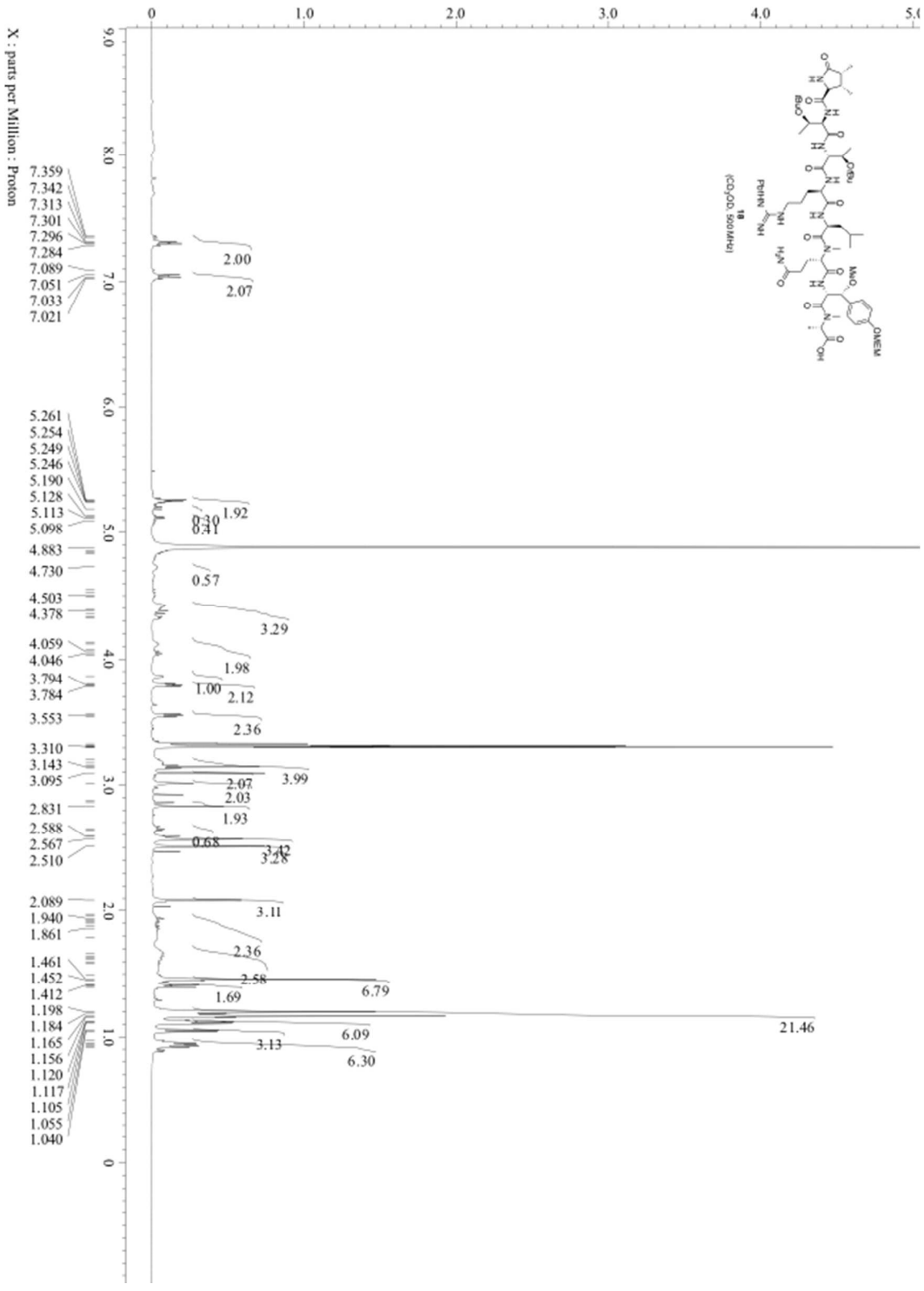
Callipeltin B (2)



2

20 (0.5 mg, 350 nmol) was dissolved in 10% TIPS/TFA (50 μL) and stirred for 1.5 h. To the mixture was added Et_2O and centrifuged to remove the supernatant. The crude product was purified with RP-HPLC (linear gradient from 20% to 60% MeCN) and lyophilized to afford callipeltin B (**2**) (0.3 mg, 290 nmol, 83%) as a white powder. ^{1}H NMR (800 MHz, CD_3OD) δ 8.61 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 8.8 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 2H), 6.75 (d, *J* = 7.2 Hz, 2H), 5.45 (m, 2H), 5.31 (q, *J* = 7.2 Hz, 1H), 4.92 (overlapped, 2H), 4.73 (m, 1H), 4.49 (d, *J* = 8.8 Hz, 1H), 4.15 (m, 1H), 4.09 (m, 1H), 4.07 (brs, 1H), 3.93 (brs, 1H), 3.17 (overlapped, 3H), 3.15 (s, 3H), 2.99 (s, 3H), 2.76 (m, 1H), 2.71 (s, 3H), 1.96-1.88 (m, 2H), 1.78-1.62 (m, 4H), 1.58-1.44 (m, 4H), 1.37 (m, 1H), 1.29 (d, *J* = 7.2 Hz, 3H), 1.26 (brs, 6H), 1.21 (d, *J* = 6.4 Hz, 3H), 1.18 (d, *J* = 7.2 Hz, 3H), 0.94 (d, *J* = 6.4 Hz, 3H), 0.92 (d, *J* = 5.6 Hz, 3H); ^{13}C NMR (200 MHz, CD_3OD) δ 183.9, 183.3, 177.2, 176.0, 174.9, 173.3, 172.0, 171.9, 171.8, 170.9, 158.6, 131.3, 129.5, 115.9, 84.2, 72.7, 67.2, 63.5, 62.0, 56.9, 56.5, 54.2, 54.1, 53.9, 53.8, 52.5, 49.9, 42.1, 40.8, 40.1, 32.5, 31.0, 30.1, 27.8, 26.4. 26.0, 25.7, 23.6, 21.6, 20.3, 15.2, 14.5, 13.6, 10.5; HRMS (ESI) *m/z*: calcd. for $C_{47}H_{75}N_{12}O_{14}$ $[M+H]^+$ 1031.5526, found 1031.5575; RP-HPLC: t_R = 13.0 min (linear gradient from

10% to 90% MeCN).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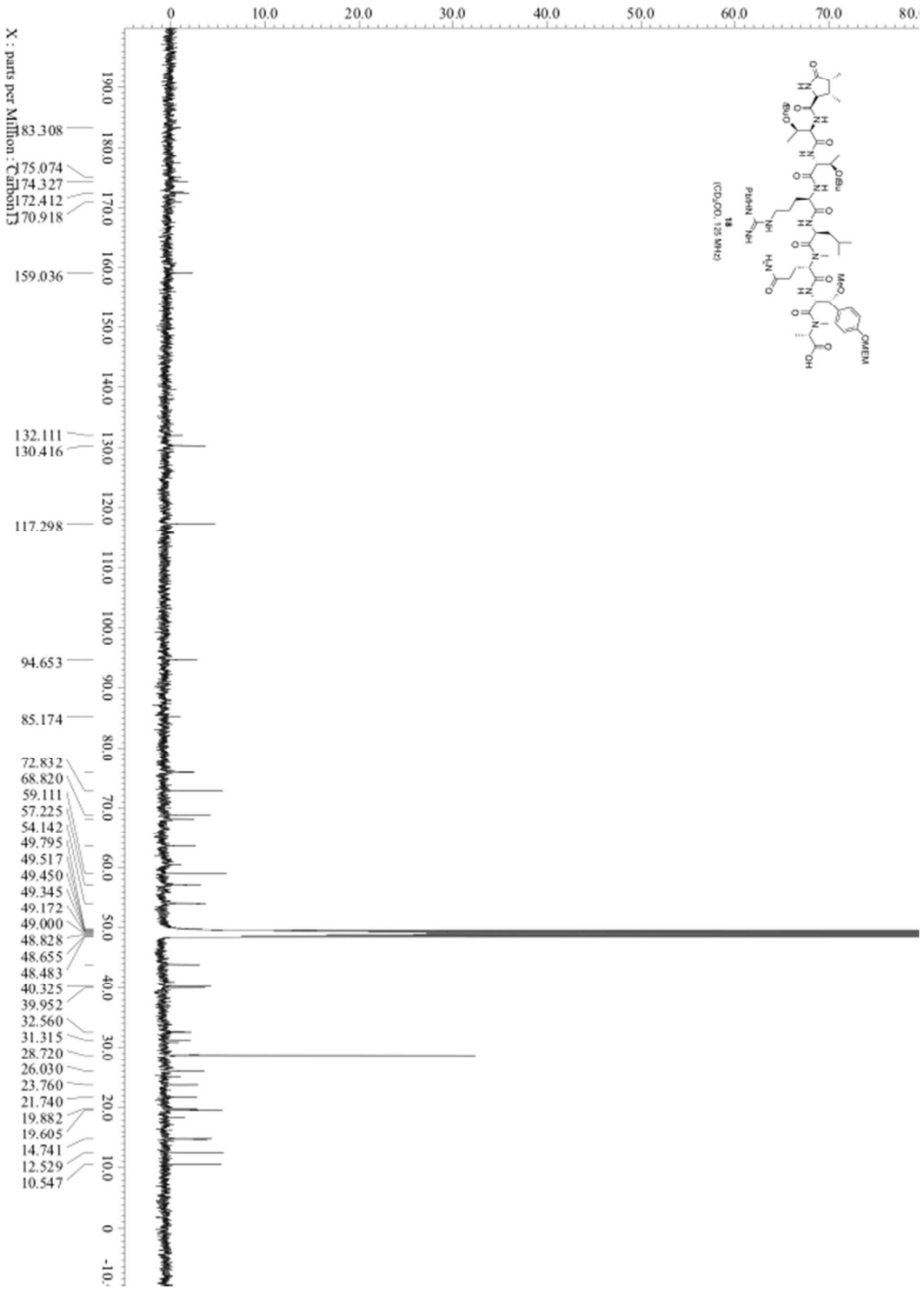
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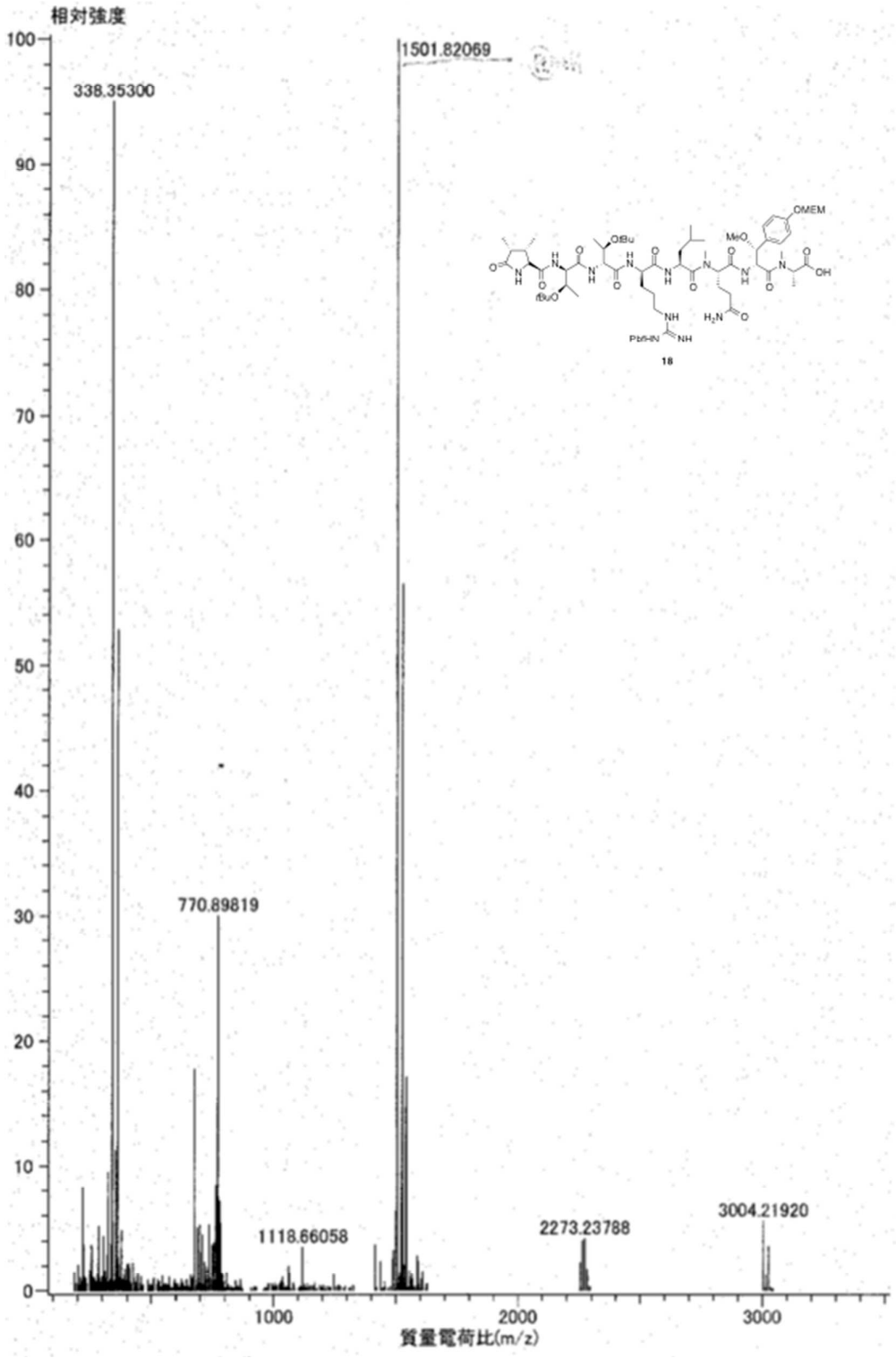
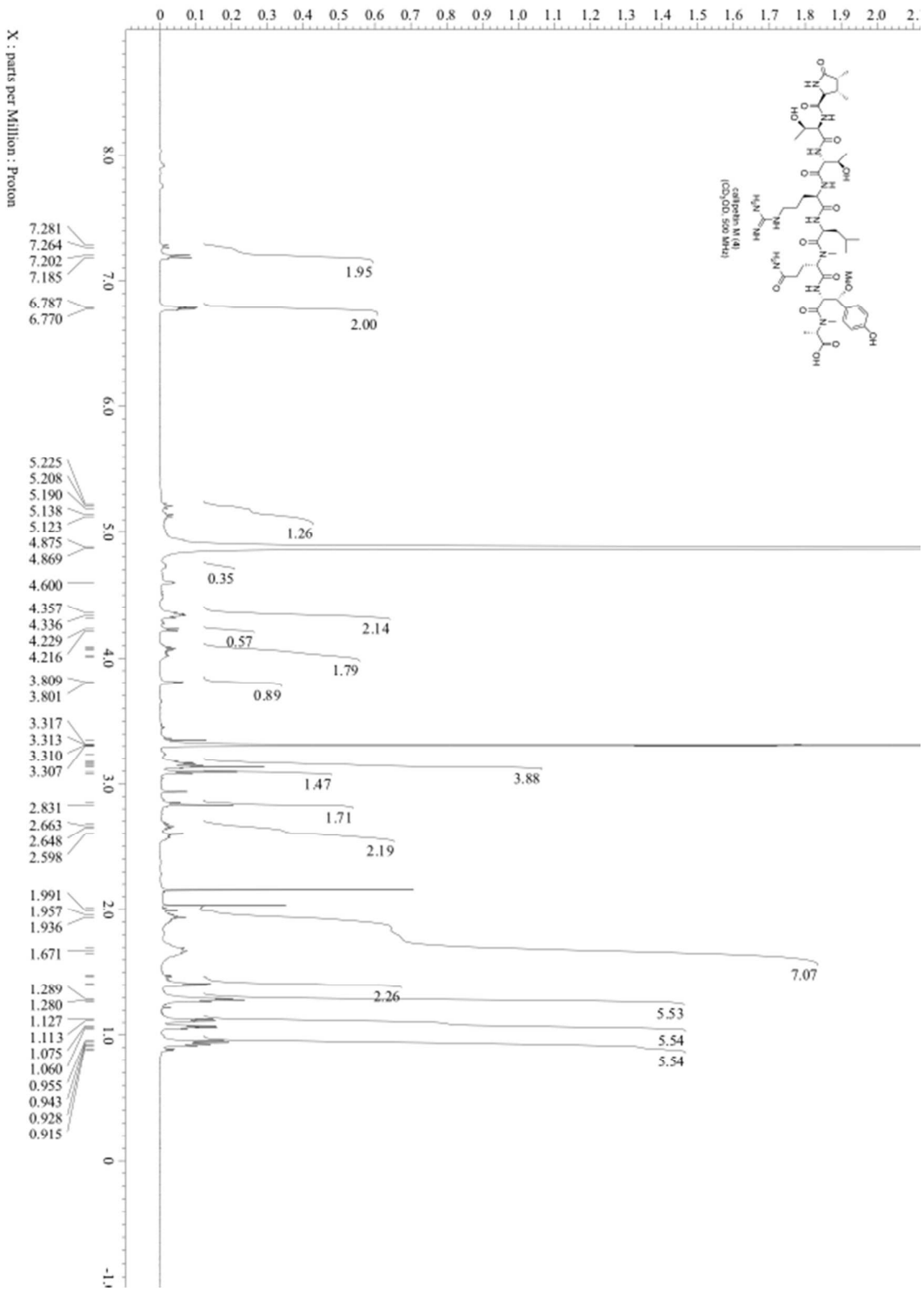
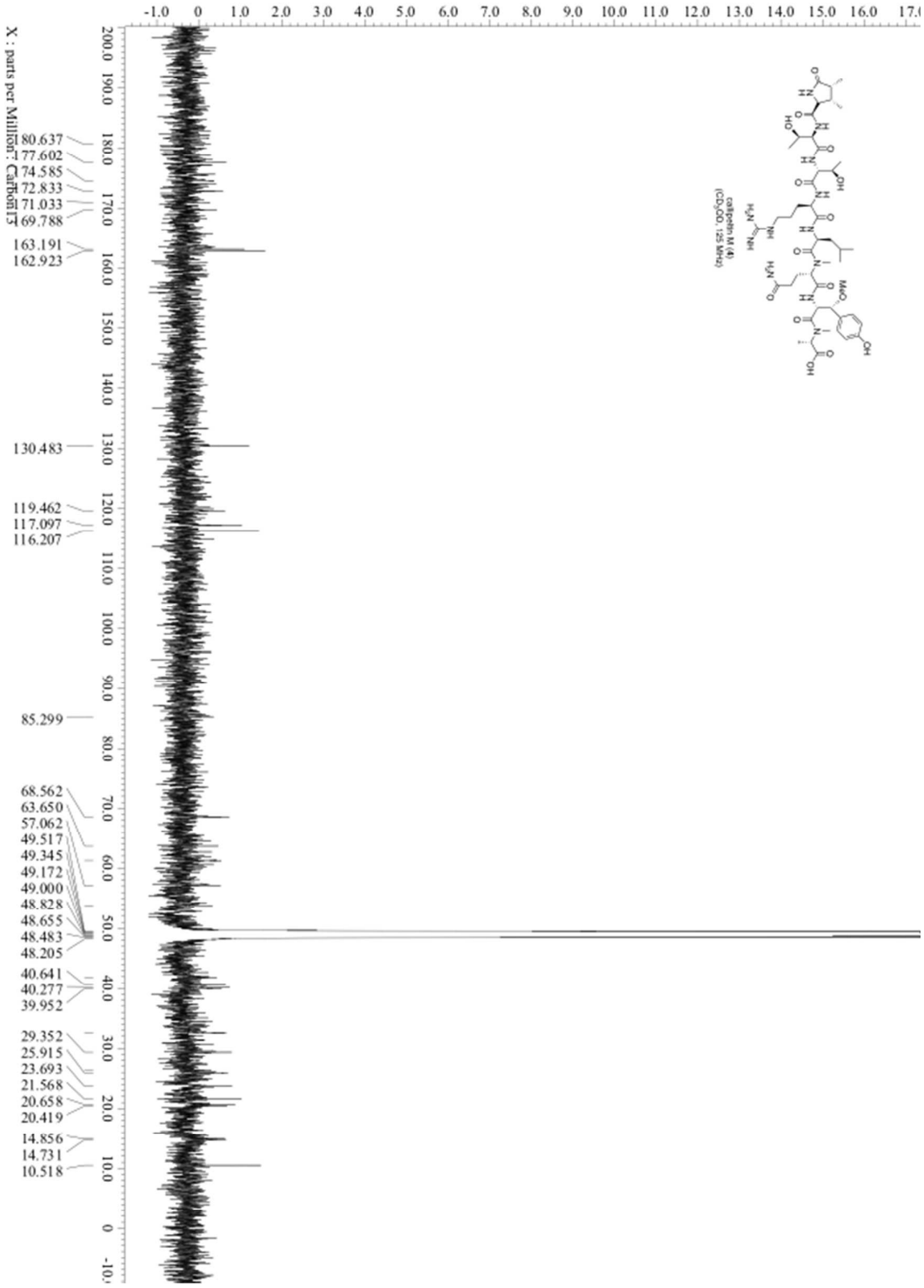
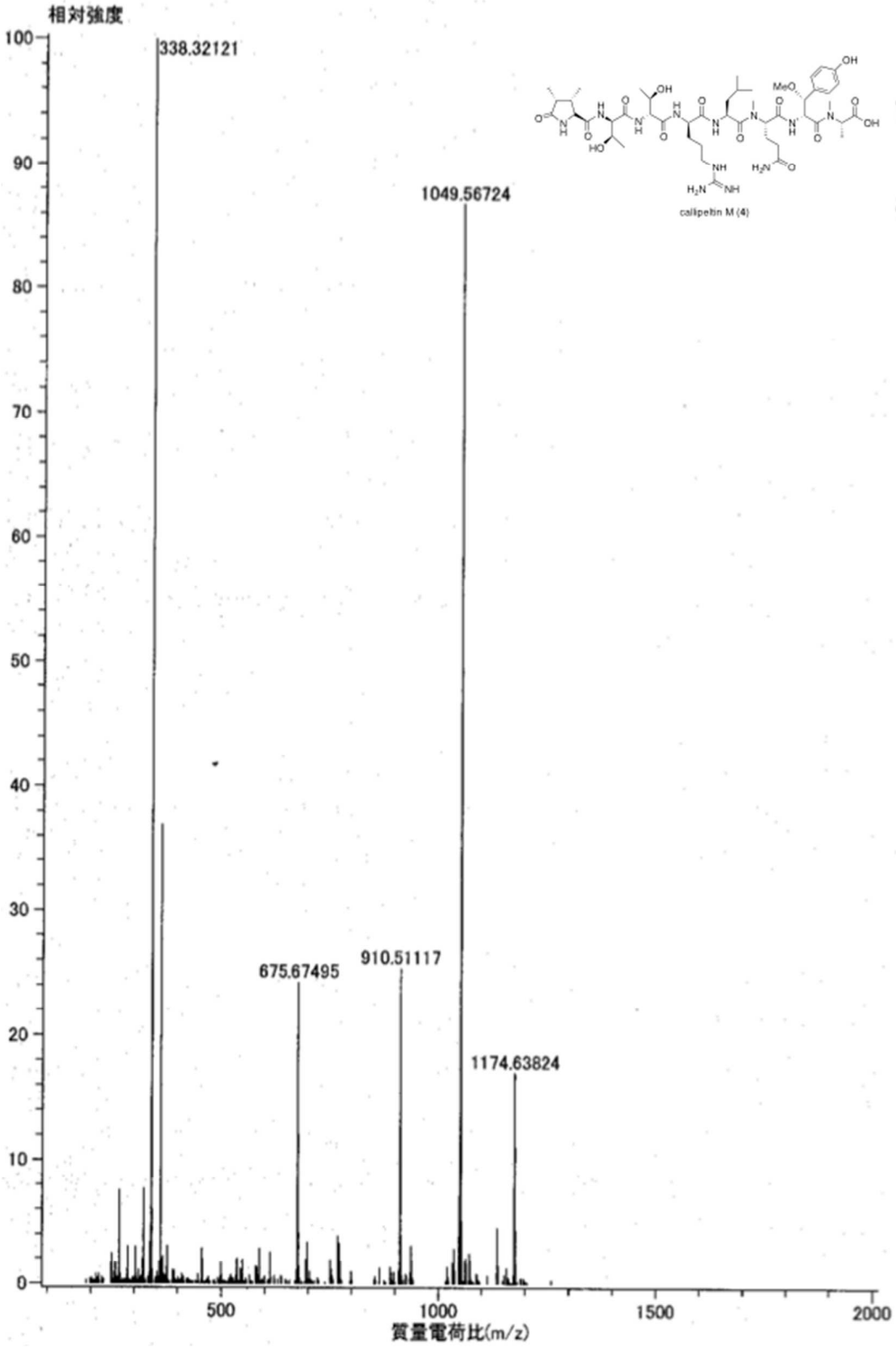
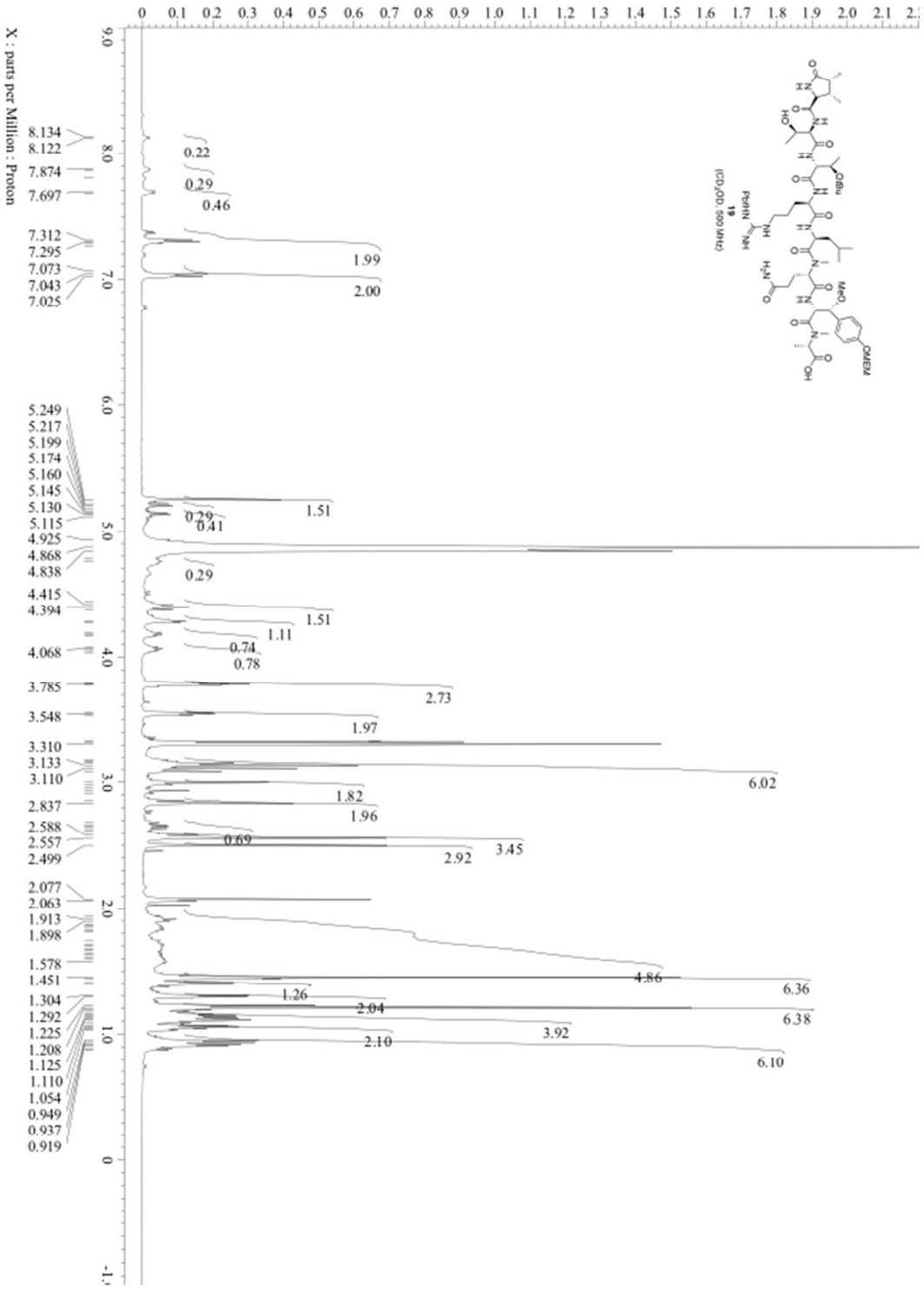
85.174
72.832
68.820
59.111
57.225
54.142
49.795
49.517
49.450
49.345
49.172
49.000
48.828
48.655
48.483
40.325
39.952
32.560
31.315
28.720
26.030
23.760
21.740
19.882
19.605
14.741
12.529
10.547
(CD3OD, 125 MHz)
OMEM

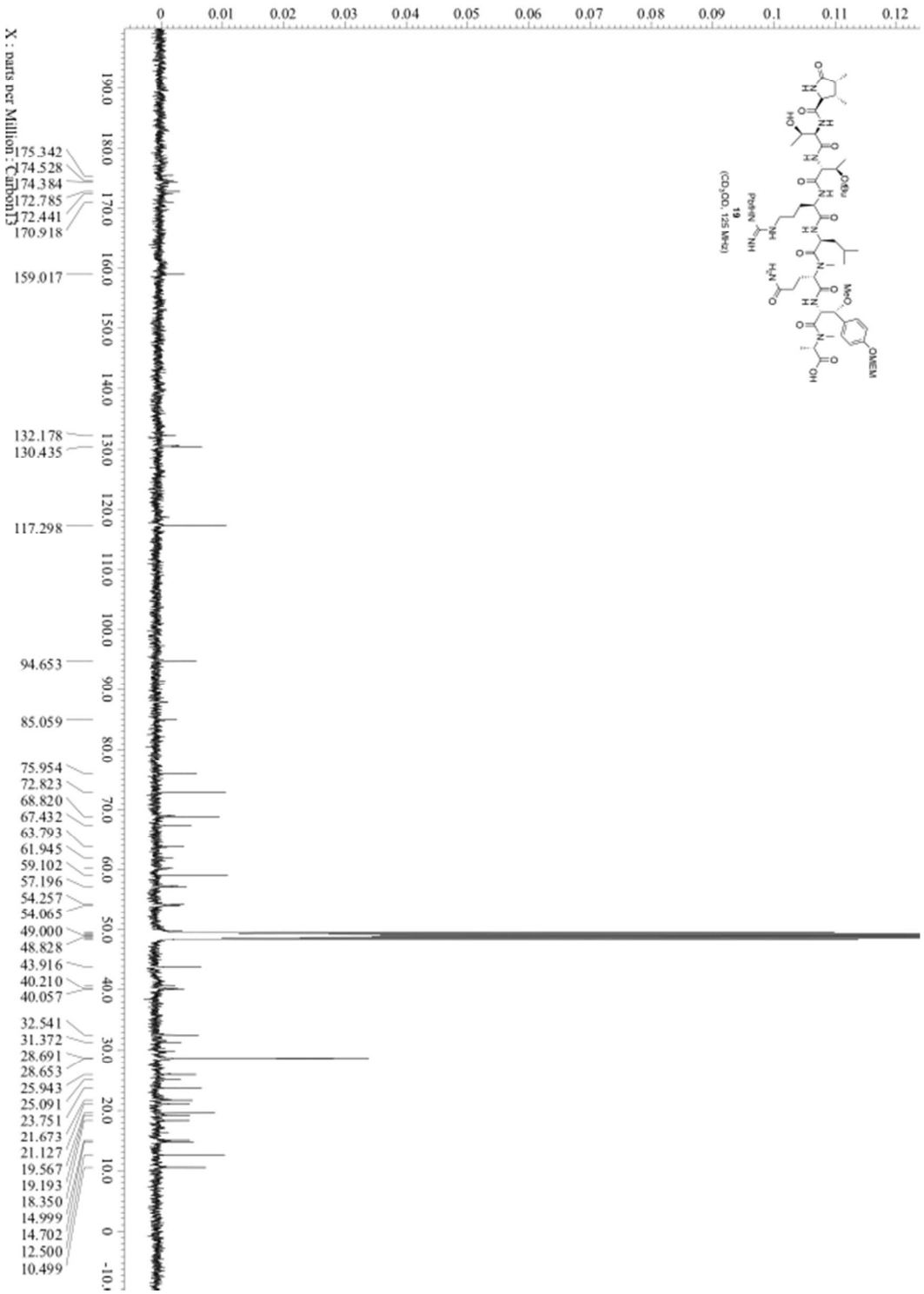

相対強度
100
90
80
70
60
50
40
30
20
10
0
338.35300
1501.82069
770.89819
1118.66058
2273.23788
3004.21920
1000
2000
3000
質量電荷比(m/z)
OMEM
MeO
OtBu
tBuO
OH
NH
PbfHN
NH
H2N
18

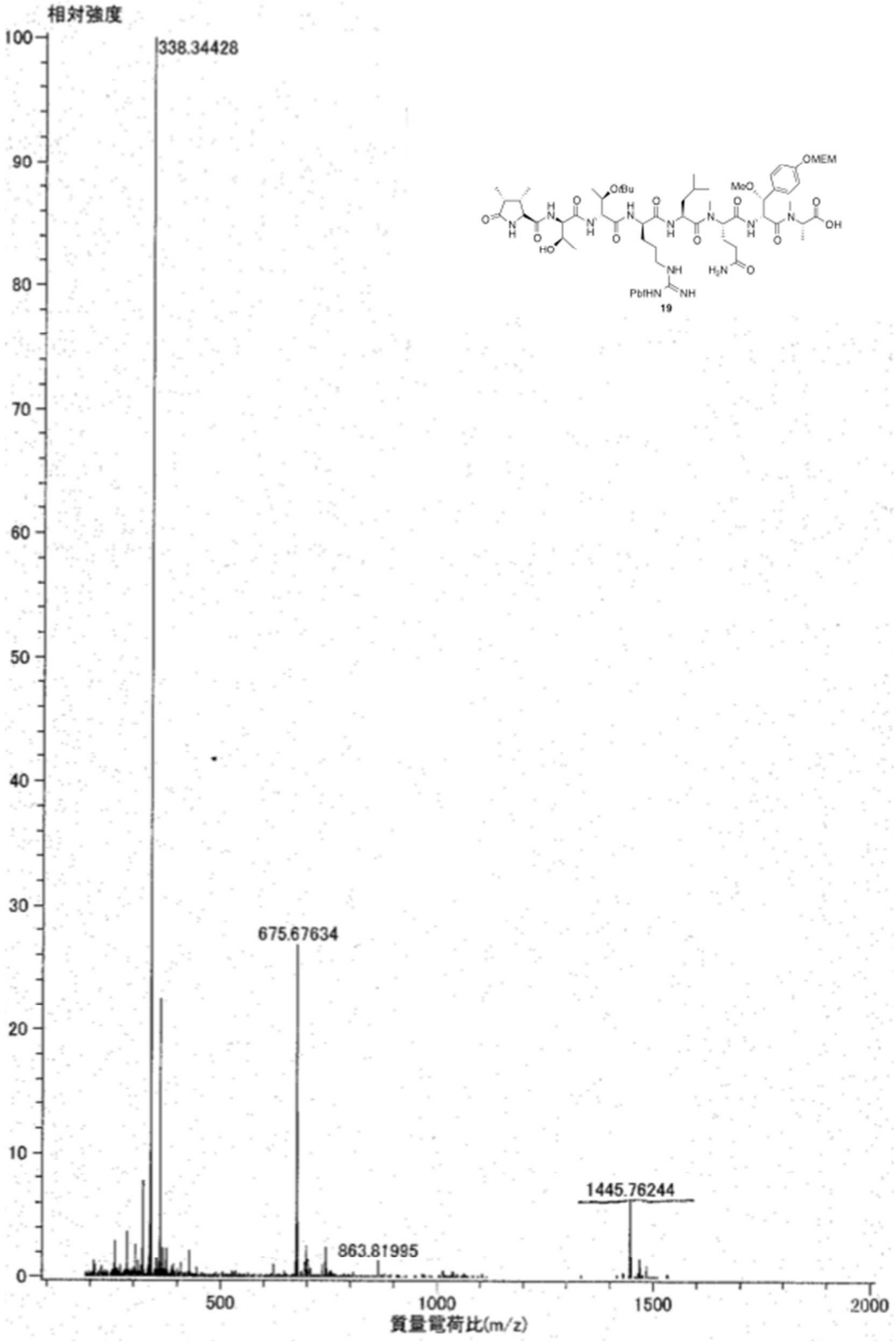

X : parts per Million : Proton
7.281
7.264
7.202
7.185
6.787
6.770
5.225
5.208
5.190
5.138
5.123
4.875
4.869
4.600
4.357
4.336
4.229
4.216
3.809
3.801
3.317
3.313
3.310
3.307
2.831
2.663
2.648
2.598
1.991
1.957
1.936
1.671
1.289
1.280
1.127
1.113
1.075
1.060
0.955
0.943
0.928
0.915
1.95
2.00
1.26
0.35
2.14
0.57
1.79
0.89
1.47
3.88
1.71
2.19
7.07
2.26
5.53
5.54
5.54

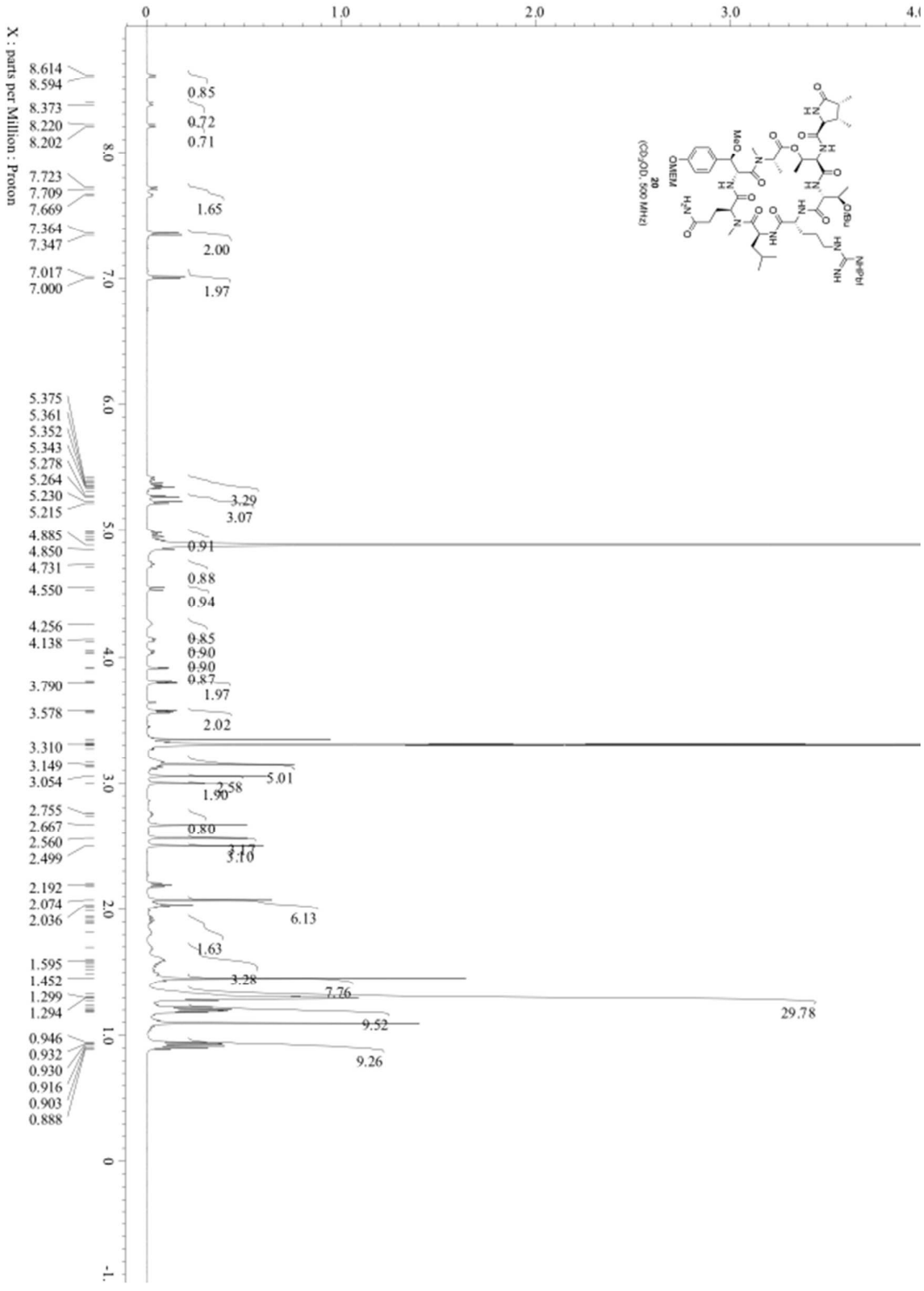

X : parts per Million? Carbon13
180.637
177.602
174.585
172.833
171.033
169.788
163.191
162.923
130.483
119.462
117.097
116.207
85.299
68.562
63.650
57.062
49.517
49.345
49.172
49.000
48.828
48.655
48.483
48.205
40.641
40.277
39.952
29.352
25.915
23.693
21.568
20.658
20.419
14.856
14.731
10.518

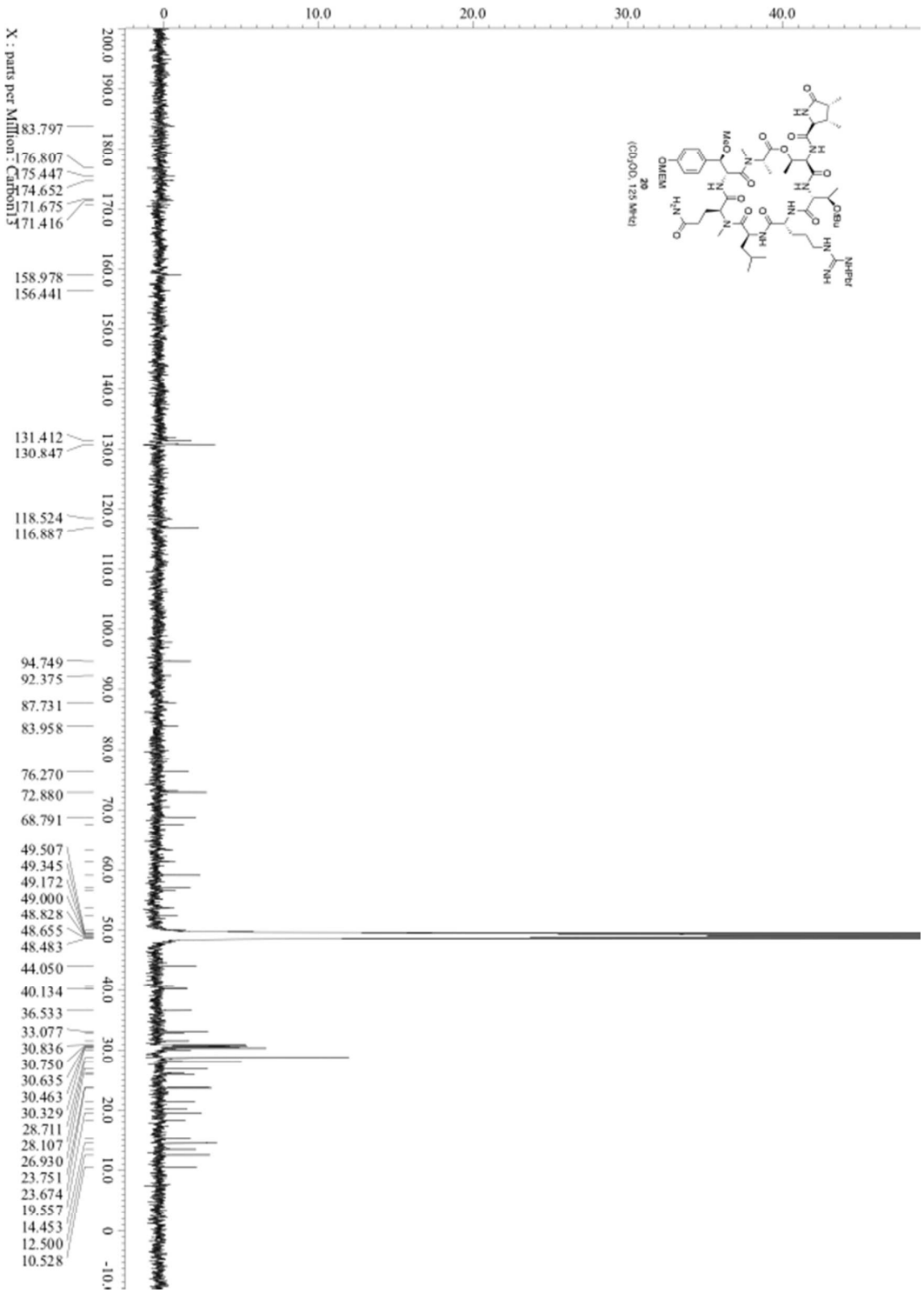

相対強度
100
90
80
70
60
50
40
30
20
10
0
338.32121
1049.56724
675.67495
910.51117
1174.63824
500
1000
1500
2000
質量電荷比(m/z)
callipeltin M (4)

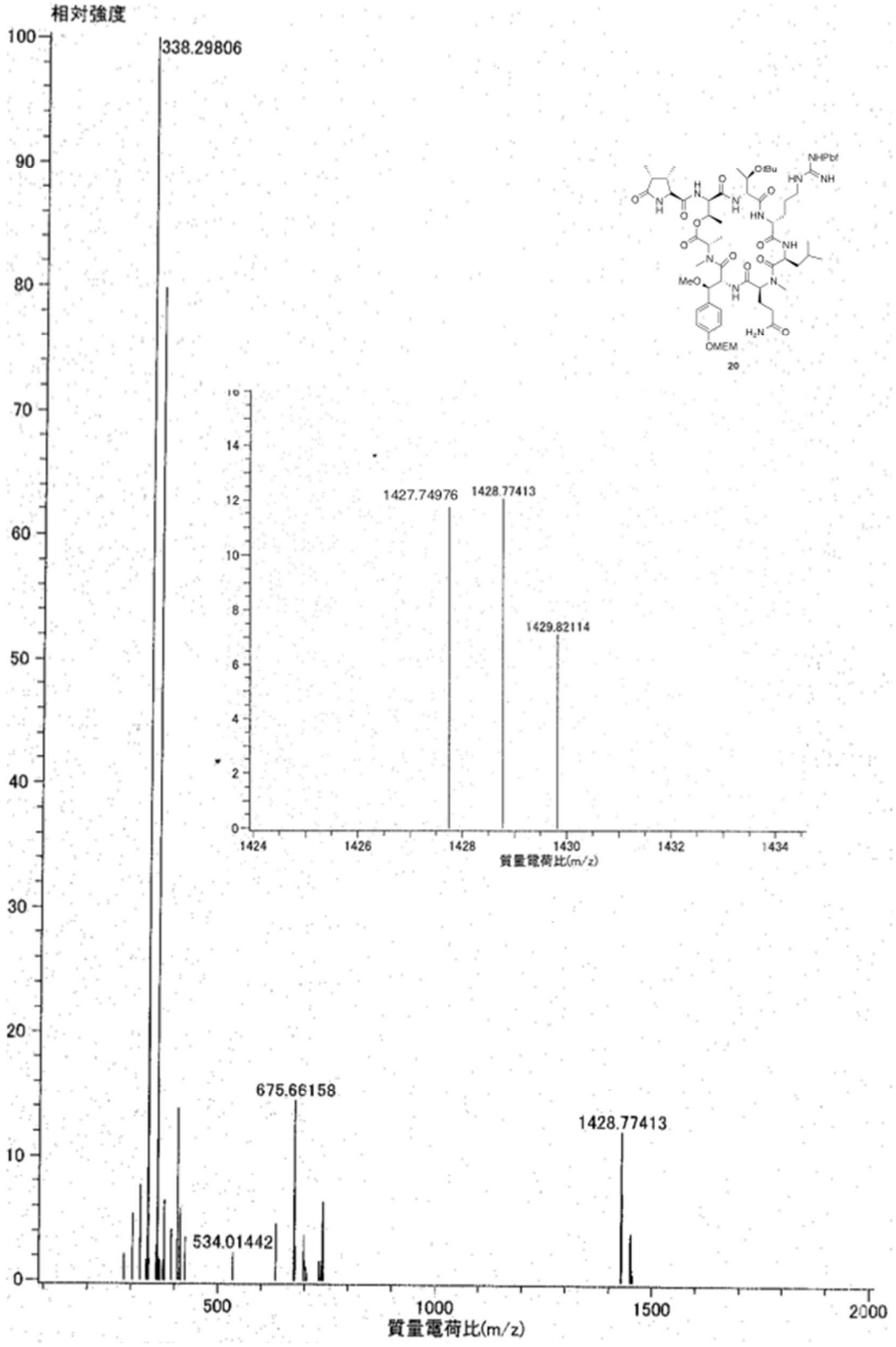

X : parts per Million : Proton
8.134
8.122
7.874
7.697
7.312
7.295
7.073
7.043
7.025
5.249
5.217
5.199
5.174
5.160
5.145
5.130
5.115
4.925
4.868
4.838
4.415
4.394
4.068
3.785
3.548
3.310
3.133
3.110
2.837
2.588
2.557
2.499
2.077
2.063
1.913
1.898
1.578
1.451
1.304
1.292
1.225
1.208
1.125
1.110
1.054
0.949
0.937
0.919
0.22
0.29
0.46
1.99
2.00
1.51
0.29
0.41
0.29
1.51
1.11
0.74
0.78
2.73
1.97
6.02
1.82
1.96
0.69
2.92
3.45
4.86
6.36
1.26
2.04
6.38
3.92
2.10
6.10
(CD3OD, 500 MHz)

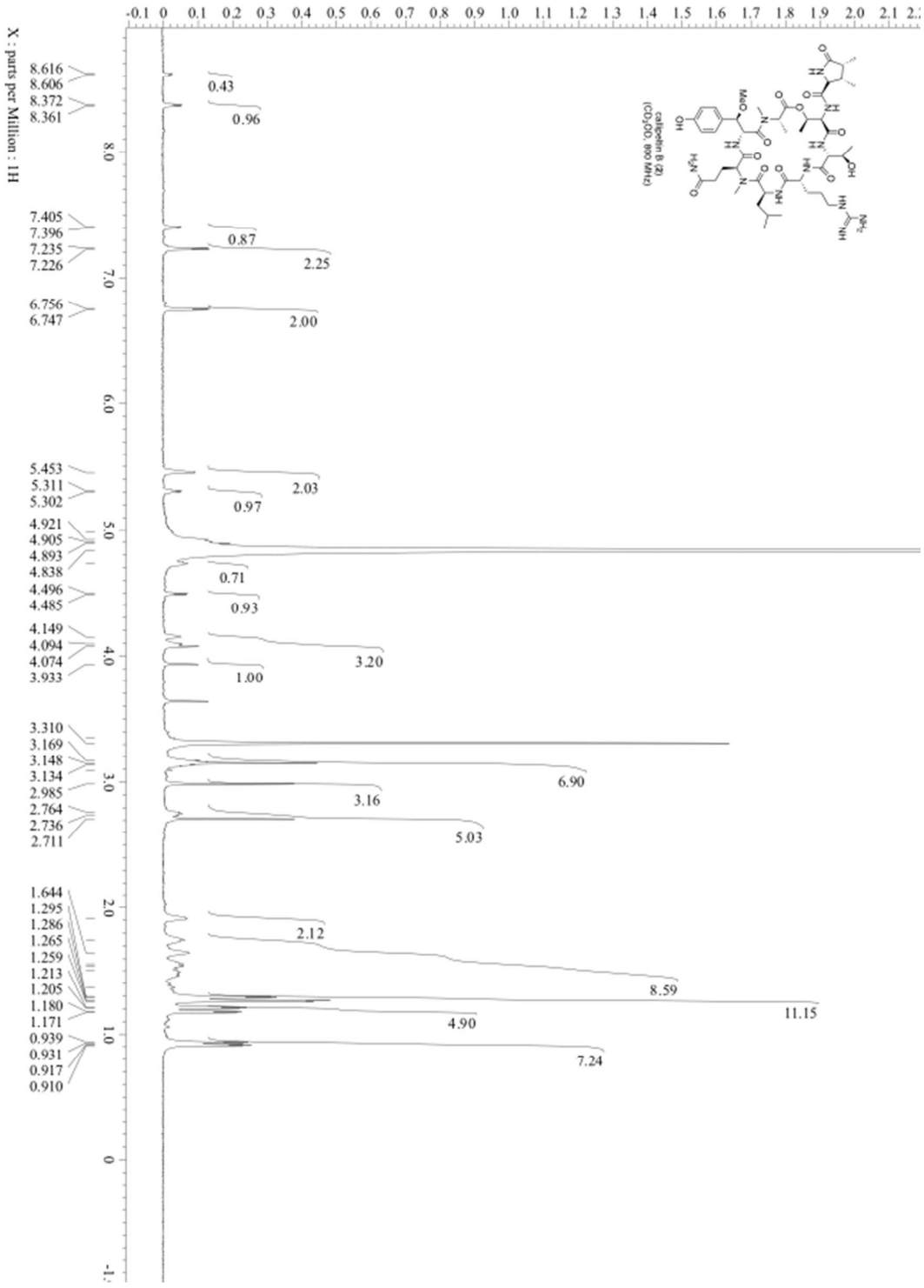

X : parts per Million : Carbon13
175.342
174.528
174.384
172.785
172.441
170.918
159.017
132.178
130.435
117.298
94.653
85.059
75.954
72.823
68.820
67.432
63.793
61.945
59.102
57.196
54.257
54.065
49.000
48.828
43.916
40.210
40.057
32.541
31.372
28.691
28.653
25.943
25.091
23.751
21.673
21.127
19.567
19.193
18.350
14.999
14.702
12.500
10.499

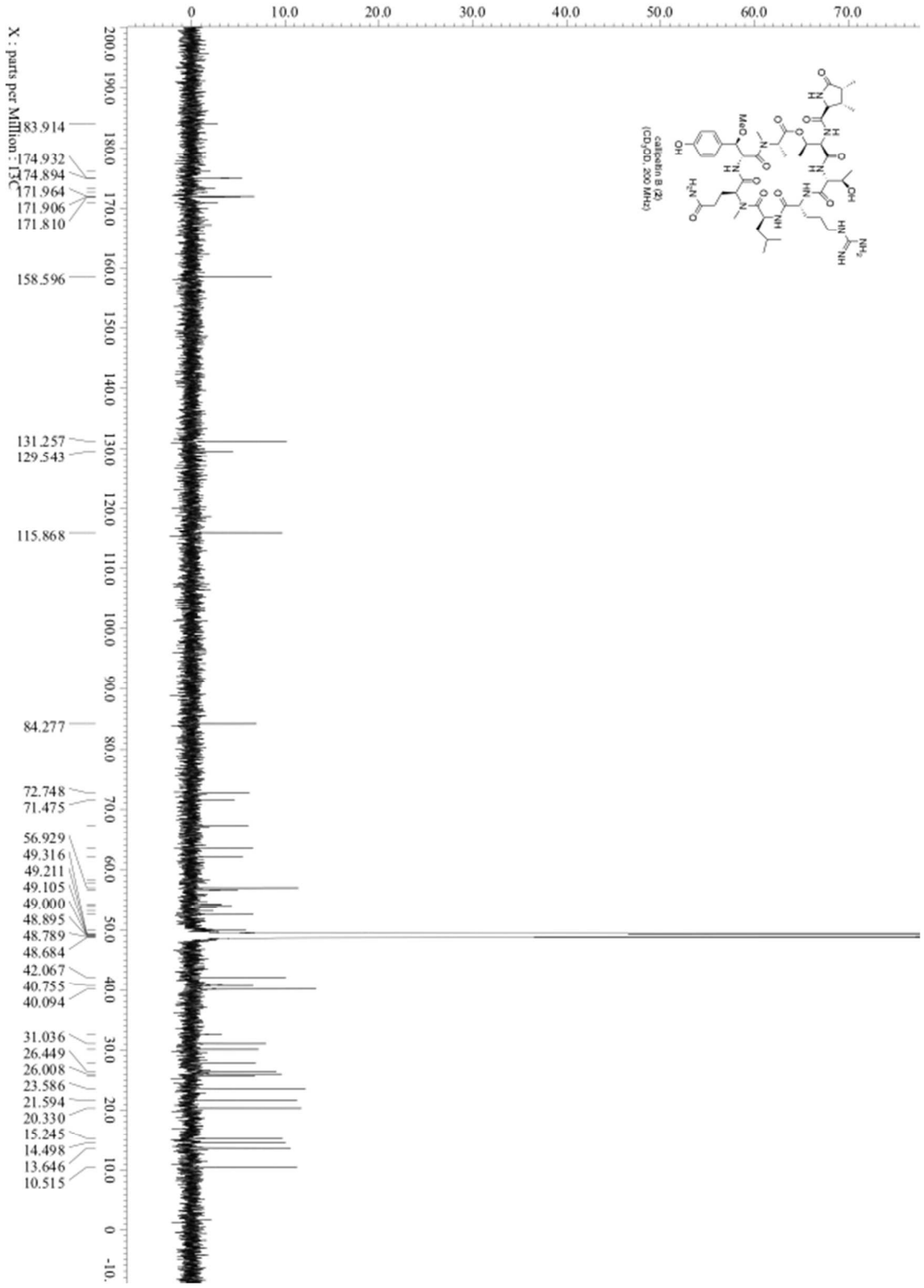

相対強度
100
90
80
70
60
50
40
30
20
10
0
338.34428
675.67634
863.81995
1445.76244
500
1000
1500
2000
質量電荷比(m/z)
OMEM
MeO
OtBu
OH
HO
PbfHN
NH
19


X : parts per Million : Proton
8.614
8.594
8.373
8.220
8.202
7.723
7.709
7.669
7.364
7.347
7.017
7.000
5.375
5.361
5.352
5.343
5.278
5.264
5.230
5.215
4.885
4.850
4.731
4.550
4.256
4.138
3.790
3.578
3.310
3.149
3.054
2.755
2.667
2.560
2.499
2.192
2.074
2.036
1.595
1.452
1.299
1.294
0.946
0.932
0.930
0.916
0.903
0.888
0.85
0.72
0.71
1.65
2.00
1.97
3.29
3.07
0.91
0.88
0.94
0.85
0.90
0.90
0.87
1.97
2.02
5.01
2.58
1.90
0.80
3.10
6.13
1.63
3.28
7.76
29.78
9.52
9.26
(CD3OD, 500 MHz)


X : parts per Million : Carbon13
183.797
176.807
175.447
174.652
171.675
171.416
158.978
156.441
131.412
130.847
118.524
116.887
94.749
92.375
87.731
83.958
76.270
72.880
68.791
49.507
49.345
49.172
49.000
48.828
48.655
48.483
44.050
40.134
36.533
33.077
30.836
30.750
30.635
30.463
30.329
28.711
28.107
26.930
23.751
23.674
19.557
14.453
12.500
10.528
0
10.0
20.0
30.0
40.0
MeO
OMEM
OtBu
NHPbf
(CD3OD, 125 MHz)


相対強度
338.29806
675.66158
534.01442
1428.77413
500
1000
1500
2000
質量電荷比(m/z)
1427.74976
1428.77413
1429.82114
1424
1426
1428
1430
1432
1434
質量電荷比(m/z)
20


X : parts per Million : 1H
8.616
8.606
8.372
8.361
0.43
0.96
7.405
7.396
7.235
7.226
0.87
2.25
6.756
6.747
2.00
5.453
5.311
5.302
2.03
0.97
4.921
4.905
4.893
4.838
0.71
4.496
4.485
0.93
4.149
4.094
4.074
3.933
3.20
1.00
3.310
3.169
3.148
3.134
2.985
2.764
2.736
2.711
6.90
3.16
5.03
1.644
1.295
1.286
1.265
1.259
1.213
1.205
1.180
1.171
0.939
0.931
0.917
0.910
2.12
8.59
11.15
4.90
7.24
catfishin B (2)
(CD3OD, 600 MHz)


X : parts per Million : 13C
183.914
174.932
174.894
171.964
171.906
171.810
158.596
131.257
129.543
115.868
84.277
72.748
71.475
56.929
49.316
49.211
49.105
49.000
48.895
48.789
48.684
42.067
40.755
40.094
31.036
26.449
26.008
23.586
21.594
20.330
15.245
14.498
13.646
10.515
caltrabin B (2)
(CD3OD, 200 MHz)

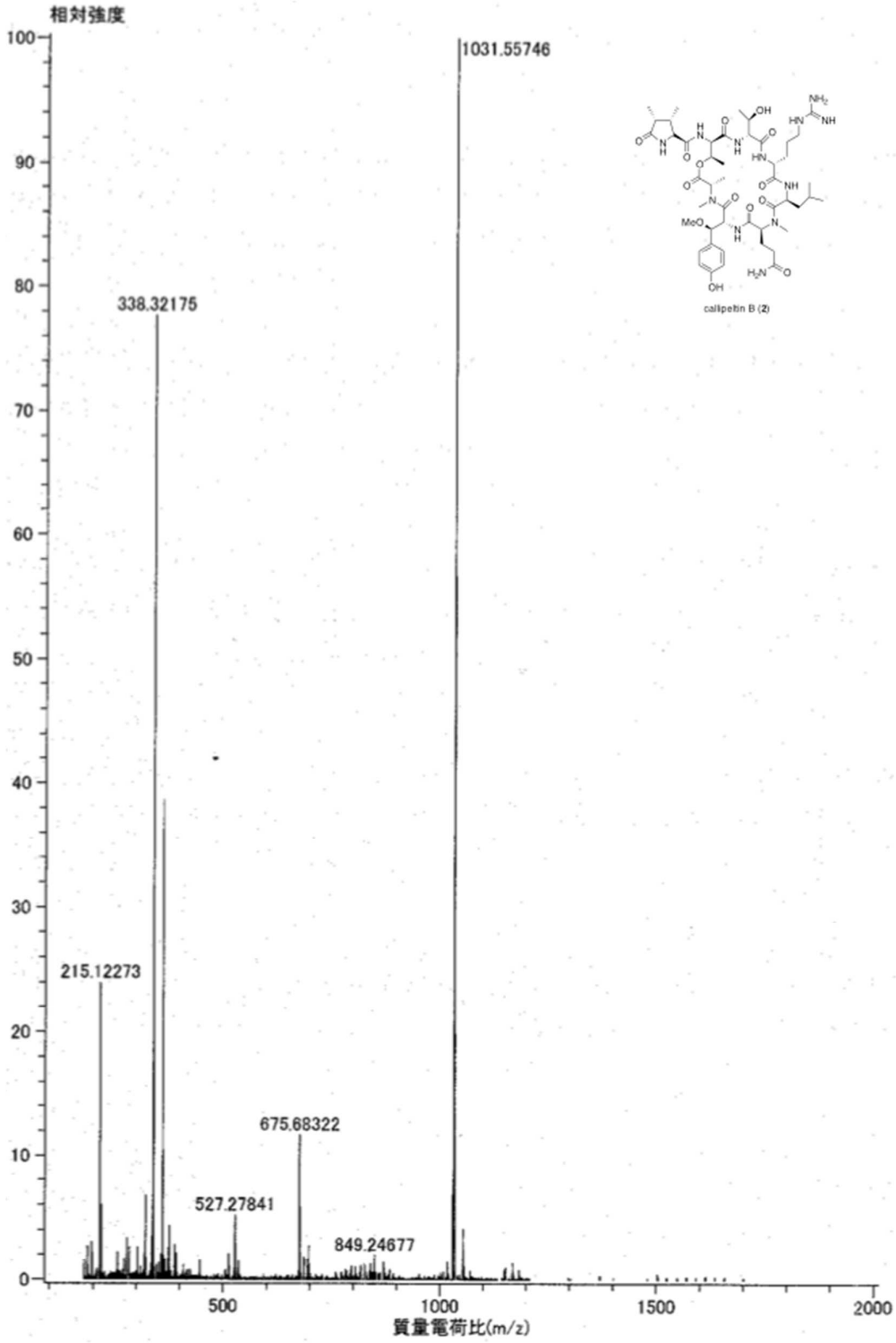

相対強度
100
90
80
70
60
50
40
30
20
10
0
1031.55746
338.32175
215.12273
675.68322
527.27841
849.24677
500
1000
1500
2000
質量電荷比(m/z)
callipeltin B (2)

Table S1. NMR spectroscopic data for 4

synthetic **4**		natural callipeltin M	
δ_H[a]	δ_C[b]	δ_H[a]	δ_C[b]
0.92 (d, J = 6.5 Hz, 3H)	10.5	0.94 (d, J = 7.4 Hz, 3H)	10.0
0.95 (d, J = 6.0 Hz, 3H)	14.7	0.94 (d, J = 7.4 Hz, 3H)	14.7
1.07 (d, J = 7.5 Hz, 3H)	14.9	1.07 (d, J = 7.3 Hz, 3H)	14.7
1.12 (d, J = 7.0 Hz, 3H)	20.4	1.12 (d, J = 7.2 Hz, 3H)	20.1
1.28 (m, 6H)	20.7	1.26 (d, overlapped, 3H)	20.1
	21.6	1.26 (d, overlapped, 3H)	21.6
1.40 (d, J = 7.5 Hz, 3H)	23.7	1.42 (d, J = 6.5 Hz, 3H)	23.9
1.47 (m, 1H)	24.9	1.40, 1.70 (m, 2H)	24.6
1.61-1.72 (m, 7H)	25.9	1.67 (m, 2H)	25.7
1.88-1.99 (m, 3H)	26.2	1.68, 1.93 (m, 2H)	26.2
	29.4	1.70 (m, 1H)	29.5
	30.7	1.70, 1.94 (m, 2H)	31.3
	32.5	1.94 (m, 2H)	32.4
2.57 (m, 1H)	32.6	2.59 (m, 1H)	32.6
2.66 (m, 1H)	39.9	2.68 (m, 1H)	39.7
2.83 (s, 3H)	40.3	2.80 (s, 3H)	39.7
3.10 (s, 3H)	40.6	3.10 (s, 3H)	40.6
3.13 (s, 3H)	41.8		42.2
3.16 (m, 2H)	48.2	3.18 (m, 2H)	48.9
3.81 (d, J = 4.0 Hz, 1H)	53.8	3.80 (d, J = 3.3 Hz, 1H)	53.9
4.01-4.09 (m, 2H)		4.02 (m, 1H)	53.9
	54.2	4.08 (m, 1H)	54.1
4.22 (d, J = 6.5 Hz, 1H)	57.1	4.22 (d, J = 7.0 Hz, 1H)	56.9
4.32-4.36 (m, 3H)	57.4	4.32 (d, J = 8.1 Hz, 1H)	
	61.2	4.33 (d, J = 6.7 Hz, 1H)	60.4
	61.3	4.35 (overlapped, 1H)	60.4
4.73 (m, 1H)	63.9	4.76 (m, 1H)	63.4
4.88 (overlapped, 1H)	68.5	4.90 (dd, J = 10.1, 4.7 Hz, 1H)	68.0
5.13 (q, J = 7.5 Hz, 1H)	68.6	5.14 (q, J = 6.5 Hz, 1H)	68.0
5.21 (t, J = 9.0 Hz, 1H)	85.3	5.23 (d, J = 8.1 Hz, 1H)	85.0
6.78 (d, J = 8.5 Hz, 2H)	116.2	6.79 (d, J = 8.1 Hz, 2H)	116.1
7.19 (d, J = 8.5 Hz, 2H)	130.5	7.21 (d, J = 8.1 Hz, 2H)	128.7
			129.6
	162.9		158.5
	163.2		
	169.8		169.7
	171.0		171.6
	172.8		172.1
	172.8		172.1
	173.6		173.3
	174.0		173.8
	174.6		174.5
	177.6		
	180.6		182.0

[a]Recorded in CD_3OD at 500 MHz. [b]Recorded in CD_3OD at 125 MHz.

Table S2. NMR spectroscopic data for 2

synthetic **2**		natural callipeltin B	
δ_H[a]	δ_C[b]	δ_H[a]	δ_C[b]
0.91 (d, *J* = 5.6 Hz, 3H)	10.5	0.92 (d, *J* = 7.2 Hz, 3H)	10.5
0.94 (d, *J* = 6.4 Hz, 3H)	13.6	0.94 (d, *J* = 6.4 Hz, 3H)	13.7
1.18 (d, *J* = 7.2 Hz, 3H)	14.5	1.18 (d, *J* = 8.0 Hz, 3H)	14.5
1.21 (d, *J* = 6.4 Hz, 3H)	15.2	1.21 (d, *J* = 7.2 Hz, 3H)	15.2
1.26 (brs, 6H)	20.3	1.26 (t, *J* = 5.6 Hz, 6H)	20.3
1.29 (d, *J* = 7.2 Hz, 3H)	21.6	1.30 (d, *J* = 7.0 Hz, 3H)	21.6
1.37 (m, 1H)	23.6	1.39 (m, 1H)	23.6
1.44-1.58 (m, 4H)	25.7	1.45-1.58 (m, 4H)	25.8
1.62-1.78 (m, 4H)	26.0	1.62-1.77 (m, 4H)	26.0
1.88-1.96 (m, 2H)	26.4	1.90-1.94 (m, 2H)	26.4
2.71 (s, 3H)	27.8	2.72 (s, 3H)	27.8
2.76 (m, 1H)	30.1	2.77 (m, 1H)	30.1
2.99 (s, 3H)	31.0	2.99 (s, 3H)	31.0
3.15 (s, 3H)	32.5	3.15 (s, 3H)	32.5
3.17 (overlapped, 3H)	40.1	3.17 (m, 3H)	40.1
3.93 (brs, 1H)		3.95 (d, *J* = 3.2 Hz, 1H)	40.1
4.07 (brs, 1H)	40.8	4.07 (d, *J* = 5.6 Hz, 1H)	40.7
4.09 (m, 1H)	42.1	4.10 (m, 1H)	42.1
4.15 (m, 1H)	49.9	4.16 (m, 1H)	49.9
4.49 (d, *J* = 8.8 Hz, 1H)	52.5	4.49 (d, *J* = 10.4, 1H)	52.5
4.73 (m, 1H)	53.8	4.73 (dd, *J* = 11.2, 3.2 Hz, 1H)	53.8
4.92 (overlapped, 2H)	53.9	4.91 (overlapped, 2H)	
5.31 (q, *J* = 7.2 Hz, 1H)	54.1	5.31 (q, *J* = 7.2 Hz, 1H)	54.1
5.45 (m, 2H)	54.2	5.46-5.49 (m, 2H)	
6.75 (d, *J* = 7.2 Hz, 2H)	56.5	6.76 (d, *J* = 8.0 Hz, 2H)	56.5
7.23 (d, *J* = 7.2 Hz, 2H)	56.9	7.23 (d, *J* = 8.0 Hz, 2H)	56.9
7.40 (d, *J* = 7.2 Hz, 1H)	62.0		62.1
8.37 (d, *J* = 8.8 Hz, 1H)	63.5		63.5
8.61 (d, *J* = 8.0 Hz, 1H)	67.2		67.2
	72.7		72.8
	84.2		84.2
	115.9		115.9
	129.5		129.5
	131.3		131.3
	158.6		158.6
	170.9		170.9
	171.8		171.8
	171.9		
	172.0		172.0
	173.3		173.4
	174.9		174.9
	176.0		175.9
	177.2		177.2
	183.3		183.3
	183.9		183.9

[a]Recorded in CD_3OD at 800 MHz. [b]Recorded in CD_3OD at 200 MHz.