

Total synthesis of jamaicamide B

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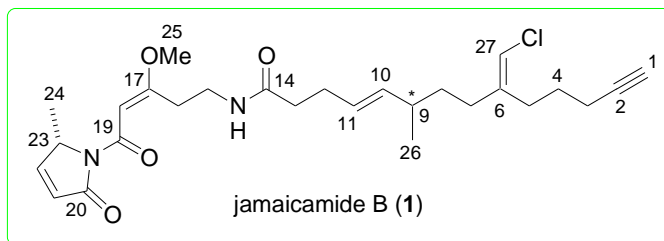
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General experimental section:

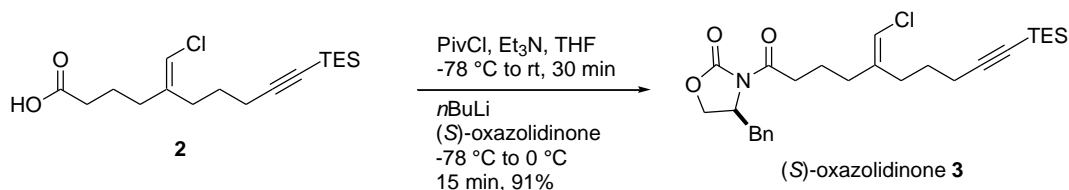
All non-aqueous reactions were conducted under an atmosphere of nitrogen with magnetic stirring unless otherwise indicated. *N,N*-Dimethylformamide (DMF) was purchased from commercial suppliers and was distilled under reduced pressure. Other solvents, such as acetone, dichloromethane (CH₂Cl₂), methanol (MeOH), acetonitrile (MeCN), diethyl ether (Et₂O), and tetrahydrofuran (THF) were purchased from commercial suppliers and stored over activated molecular sieves. All reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on Silica gel 60 F254 plates produced by Merck. Column chromatography was performed with acidic Silica gel 60 (spherical, 40-50 μm) or neutral Silica gel 60N (spherical, 40-50 μm) produced by Kanto Chemicals (Tokyo, Japan). Small amounts of solvent were removed using a BioChromato Smart Evaporator CEB8CL-AQ (Kanagawa, Japan).

Optical rotations were measured on a JASCO (Tokyo, Japan) P-2200 digital polarimeter at the sodium lamp ($\lambda = 589\text{nm}$) D line and are reported as follows: $[\alpha]_{\text{D}}^{\text{T}}$ (c g/100 mL, solvent). ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL (Tokyo, Japan) JNM-EXC 300 spectrometer (300 MHz) or on a JEOL JNM-ECA 500 spectrometer (500 MHz) or on a Bruker Avance III AD (400 MHz). ¹H NMR data are reported as follows: chemical shift (δ , ppm), integration, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constants (*J*) in Hz, assignments. ¹³C NMR data are reported in terms of chemical shift (δ , ppm). Electrospray ionization-mass spectrometer (ESI-MS) spectra were recorded on a JEOL JMS-T100LC instrument. Fast atom bombardment (FAB)-MS spectra were also observed on a JEOL JMS-700. MS data are reported in mass-to-charge ratio (*m/z*).

The carbon numbering on ^1H NMR of all compounds is corresponding with jamaicamide B (1).



(5'S)-Benzyl-1'-[(6E)-chloromethylene-1-triethylsilyl-dec-1-ynoyl]-oxazolidin-10-one, (5'S)-oxazolidinone 3:

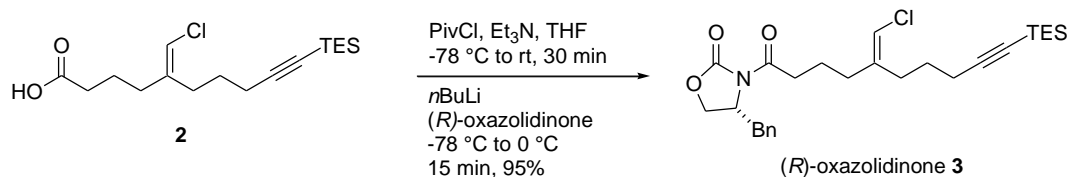


To a solution of **2** (508 mg, 1.54 mmol, 1.0 equiv) in THF (15 mL) cooled to $-78\text{ }^\circ\text{C}$ was added Et_3N (321 μL , 2.32 mmol, 1.5 equiv) and PivCl (228 μL , 1.85 mmol, 1.2 equiv). After stirring at $-78\text{ }^\circ\text{C}$ for 15 min, the reaction mixture was warmed to $0\text{ }^\circ\text{C}$, stirred for 20 min, and cooled to $-78\text{ }^\circ\text{C}$. To a solution of (*S*)-oxazolidinone (547 mg, 3.09 mmol, 2.0 equiv) in THF (8.6 mL) cooled to $-78\text{ }^\circ\text{C}$ was added 2.6 M *n*BuLi in hexane (1.09 mL, 2.934 mmol, 1.9 equiv). After the reaction mixture was stirring at $-78\text{ }^\circ\text{C}$ for 30 min, the reaction mixture was warmed to $0\text{ }^\circ\text{C}$. After stirred at $0\text{ }^\circ\text{C}$ for 20 min, the reaction mixture was cooled to $-78\text{ }^\circ\text{C}$ and added the ester **2** solution and warmed to $0\text{ }^\circ\text{C}$. After stirred for 15 min, the reaction mixture was diluted with EtOAc, and quenched with diluted NH_4Cl solution. The aqueous layer was then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 10:1) afforded (*5'S*)-oxazolidinone **3** as a colorless oil (686 mg, 1.41 mmol, 91%); R_f 0.51 (hexane/EtOAc = 3:1); ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.20 (5H, m, Bn), 5.87 (1H, s, H₂₇), 4.68-4.65 (1H, m, CH), 4.22-4.16 (2H, m, CH₂), 3.31-3.27 (1H, m, CH₂), 2.95-2.90 (2H, m, H₉), 2.78-2.74 (1H, m, CH₂), 2.36-2.27 (4H, m, H_{3/5}), 2.19 (2H, t, $J = 7.5\text{ Hz}$, H₇), 1.86-1.82 (2H, m, H₈), 1.70-1.64 (2H, m, H₄), 0.98 (9H, t, $J = 7.9\text{ Hz}$, TES), 0.58 (6H, q, $J = 7.9\text{ Hz}$, TES); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 172.8, 153.6, 141.3, 135.4, 129.5, 129.1,

Electronic Supplementary Information

127.5, 113.6, 108.0, 82.2, 66.4, 55.3, 38.0, 34.9, 34.3, 29.3, 26.5, 22.3, 20.0, 7.6, 4.6; ESI-
HRMS (m/z) calcd for $C_{27}H_{38}ClNO_3SiNa$ $[M+Na]^+$ 510.22072, found 510.22114.

(5'R)-Benzyl-1'-[(6E)-chloromethylene-1-triethylsilyl-dec-1-ynoyl]-oxazolidin-10-one, (5'R)-oxazolidinone 3:

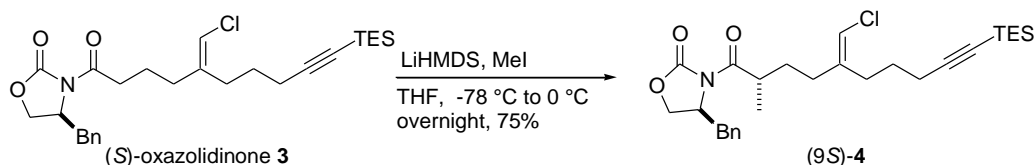


To a solution of **2** (556 mg, 1.69 mmol, 1.0 equiv) in THF (17 mL) cooled to -78 °C was added Et₃N (352 μL, 2.54 mmol, 1.5 equiv) and PivCl (250 μL, 2.03 mmol, 1.2 equiv). After stirring at -78 °C for 15 min, the reaction mixture was warmed to 0 °C, stirred for 20 min, and cooled to -78 °C. To a solution of (R)-oxazolidinone (600 mg, 3.38 mmol, 2.0 equiv) in THF (9.4 mL) cooled to -78 °C was added 2.6 M *n*BuLi in hexane (1.19 mL, 3.21 mmol, 1.9 equiv). After the reaction mixture was stirring at -78 °C for 30 min, the reaction mixture was warmed to 0 °C. After stirred at 0 °C for 20 min, the reaction mixture was cooled to -78 °C and added the ester **2** solution and warmed to 0 °C. After stirred for 15 min, the reaction mixture was diluted with EtOAc, and quenched with diluted NH₄Cl solution. The aqueous layer was then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 10:1) afforded (5'R)-oxazolidinone **3** as a colorless oil (787 mg, 1.61 mmol, 95%); *R*_f 0.51 (hexane/EtOAc = 3:1); ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.20 (5H, m, Bn), 5.88 (1H, s, H₂₇), 4.69-4.65 (1H, m, CH), 4.23-4.16 (2H, m, CH₂), 3.31-3.28 (1H, m, CH₂), 2.98-2.89 (2H, m, H₉), 2.80-2.74 (1H, m, CH₂), 2.37-2.27 (4H, m, H_{3/5}), 2.18 (2H, t, *J* = 7.5 Hz, H₇), 1.87-1.81 (2H, m, H₈), 1.70-1.62 (2H, m, H₄), 0.99 (9H, t, *J* = 7.9 Hz, TES), 0.58 (6H, q, *J* = 7.9 Hz, TES); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 172.7, 153.3, 141.3, 135.2, 129.5, 129.0,

Electronic Supplementary Information

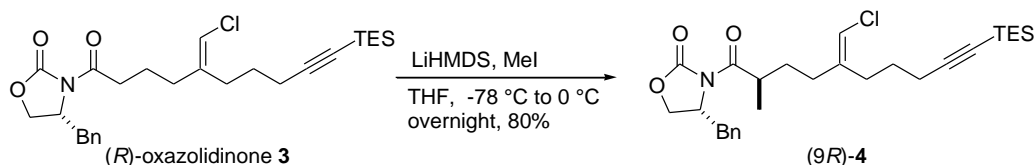
127.4, 113.5, 108.0, 82.2, 77.4, 77.2, 76.9, 66.3, 55.2, 38.0, 34.9, 34.3, 29.3, 26.4, 22.2, 20.0, 14.2, 7.60, 4.63; ESI-HRMS (m/z) calcd for $C_{27}H_{38}ClNO_3SiNa [M+Na]^+$ 510.22072, found 510.22210.

(5'S)-Benzyl-1'-[(6E)-chloromethylene-1-triethylsilyl-(9S)-methyl-dec-1-ynoyl]-oxazolidin-10-one, (9S)-4:

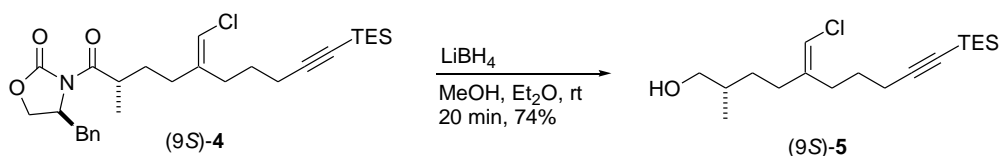


To a solution of (*S*)-oxazolidinone **3** (355 mg, 0.727 mmol, 1.0 equiv) in THF (3.63 mL) cooled to -78 °C was added 1.3 M LiHMDS (0.727 mL, 0.945 mmol, 1.3 equiv) and stirred at -78 °C for 35 min, warmed to 0 °C. After stirred for 10 min, to the reaction mixture was added MeI (226 μ L, 3.63 mmol, 5.0 equiv) at -78 °C. After stirring for overnight at 0 °C, the reaction mixture was diluted with EtOAc and quenched with saturated NH₄Cl solution. The aqueous layer was then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 10:1) afforded (*9S*)-**4** as a colorless oil (273 mg, 0.544 mmol, 75%); *R*_f 0.60 (hexane/EtOAc = 3:1); ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.20 (5H, m, Bn), 5.81 (1H, s, H₂₇), 4.67 (1H, m, CH), 4.24-4.16 (2H, m, CH₂), 3.68-3.67 (1H, m, H₉), 3.25-3.22 (1H, m, CH₂), 2.79-2.75 (1H, m, CH₂), 2.34-2.26 (4H, m, H_{3/5}), 2.10-2.07 (2H, m, H₇), 1.98-1.62 (4H, m, H_{8/4}), 1.24 (3H, d, *J* = 6.6 Hz, H₂₆), 0.99 (9H, t, *J* = 7.9 Hz, TES), 0.58 (6H, q, *J* = 7.9 Hz, TES); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 176.7, 153.2, 141.8, 135.3, 129.6, 129.1, 127.5, 113.2, 108.0, 82.2, 66.2, 55.4, 38.0, 37.7, 33.0, 31.3, 29.2, 26.5, 20.0, 18.1, 7.6, 4.6; ESI-HRMS (*m/z*) calcd for C₂₈H₄₀ClNO₃SiNa [M+Na]⁺ 524.23637, found 510.23683.

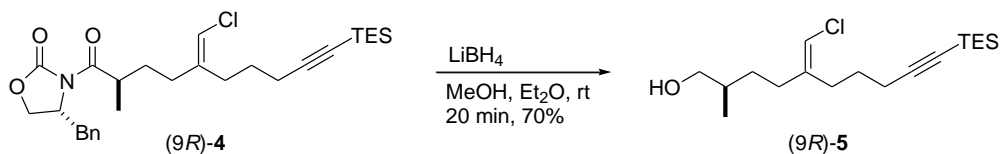
(5'R)-Benzyl-1'-[(6E)-chloromethylene-1-triethylsilyl-(9R)-methyl-dec-1-ynoyl]-oxazolidin-10-one, (9R)-4:



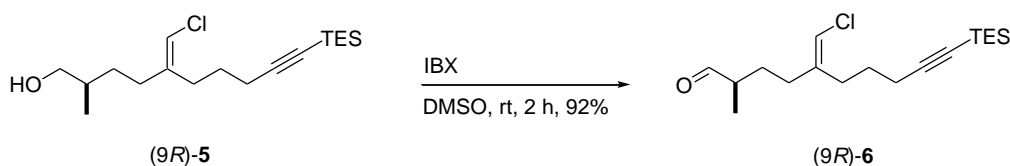
To a solution of (*R*)-oxazolidinone **3** (392 mg, 0.804 mmol, 1.0 equiv) in THF (4.0 mL) cooled to -78 °C was added 1.3 M LiHMDS (0.809 mL, 1.05 mmol, 1.3 equiv) and stirred at -78 °C for 35 min, warmed to 0 °C. After stirred for 10 min, to the reaction mixture was added MeI (275 μ L, 4.42 mmol, 5.5 equiv) at -78 °C. After stirring for overnight at 0 °C, the reaction mixture was diluted with EtOAc and quenched with saturated NH₄Cl solution. The aqueous layer was then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 10:1) afforded (*9R*)-**4** as a colorless oil (322 mg, 0.642 mmol, 80%); *R*_f 0.60 (hexane/EtOAc = 3:1); ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.20 (5H, m, Bn), 5.82 (1H, s, H₂₇), 4.70-4.65 (1H, m, CH), 4.25-4.16 (2H, m, CH₂), 3.70-3.66 (1H, m, H₉), 3.26-3.22 (1H, m, CH₂), 2.80-2.75 (1H, m, CH₂), 2.36-2.25 (4H, m, H_{3/5}), 2.14-2.01 (2H, m, H₇), 1.99-1.62 (4H, m, H_{8/4}), 1.23 (3H, d, *J* = 6.6 Hz, H₂₆), 0.99 (9H, t, *J* = 7.9 Hz, TES), 0.58 (6H, q, *J* = 7.9 Hz, TES); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 176.6, 153.2, 141.8, 135.3, 129.6, 129.1, 127.5, 113.3, 108.0, 82.2, 66.2, 55.4, 38.0, 37.7, 33.1, 31.3, 29.3, 26.5, 20.0, 18.1, 14.3, 7.66, 4.69; ESI-HRMS (*m/z*) calcd for C₂₈H₄₀ClNO₃SiNa [M+Na]⁺ 524.23637, found 524.23778.

(6E)-Chloromethylene-1-triethylsilyl-(9S)-methyl-dec-1-yn-10-ol, (9S)-5:

To a solution of (9S)-4 (267 mg, 0.531 mmol, 1.0 equiv) in Et₂O (4.2 mL) cooled to 0 °C was added MeOH (71 μL, 1.751 mmol, 3.3 equiv) and 4.0 M LiBH₄ (0.398 ml, 1.593 mmol, 4.0 equiv). After stirring at room temperature for 20 min, the reaction mixture was diluted with Et₂O at 0 °C and quenched with saturated NH₄Cl solution. The aqueous layer was then extracted with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 8:1) afforded (9S)-5 as a colorless oil (130 mg, 0.394 mmol, 74%); ¹H NMR (500 MHz, CDCl₃) δ 5.83 (1H, s, H27), 3.52-3.43 (2H, m, H10), 2.35-2.26 (4H, m, H3/5), 2.15-2.06 (2H, m, H7), 1.68-1.54 (4H, m, H8/4), 1.25-1.20 (1H, m H9), 1.00-0.92 (12H, m, TES/26), 0.59 (6H, q, *J* = 7.9 Hz, TES); ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 142.2, 112.9, 108.1, 82.2, 68.1, 35.4, 32.5, 31.2, 29.5, 26.5, 20.0, 16.5, 7.6, 4.7; ESI-HRMS (*m/z*) calcd for C₁₈H₃₃ClNaOSi [M+Na]⁺ 351.18869, found 351.18902.

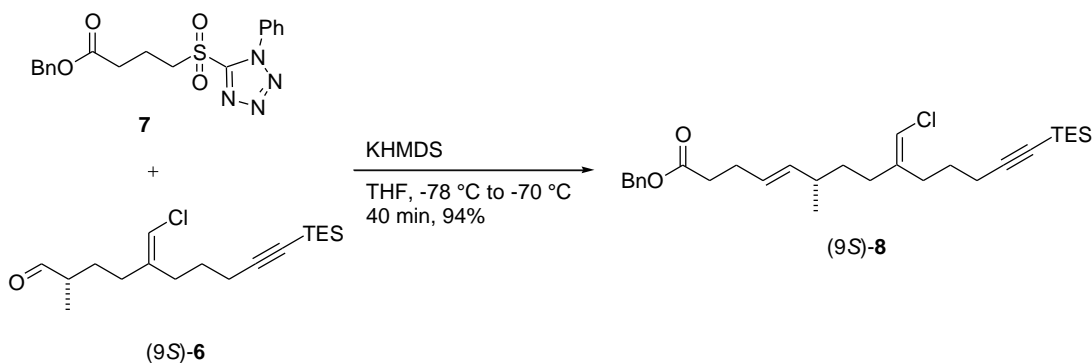
(6E)-Chloromethylene-1-triethylsilyl-(9R)-methyl-dec-1-yn-10-ol, (9R)-5:

To a solution of (9R)-4 (624.3 mg, 1.243 mmol, 1.0 equiv) in Et₂O (9.8 mL) cooled to 0 °C was added MeOH (76 μL, 1.865 mmol, 1.5 equiv) and 4.0 M LiBH₄ (0.373 ml, 1.492 mmol, 1.5 equiv). After stirring at room temperature for 20 min, the reaction mixture was diluted with Et₂O at 0 °C and quenched with saturated NH₄Cl solution. The aqueous layer was then extracted with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 8:1) afforded (9R)-5 as a colorless oil (287 mg, 0.871 mmol, 70%); ¹H NMR (500 MHz, CDCl₃) δ 5.83 (1H, s, H27), 3.50-3.46 (2H, m, H10), 2.37-2.27 (4H, m, H3/5), 2.20-2.05 (2H, m, H7), 1.69-1.54 (4H, m, H8/4), 1.24-1.21 (1H, m, H9), 1.01-0.93 (12H, m, TES/26), 0.59 (6H, q, *J* = 7.9 Hz, TES); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 142.2, 112.9, 1108.1, 82.2, 68.2, 35.5, 32.6, 31.3, 29.5, 26.5, 20.0, 16.6, 7.66, 4.70; ESI-HRMS (*m/z*) calcd for C₁₈H₃₃ClNaOSi [M+Na]⁺ 351.18869, found 351.18879.

(6E)-Chloromethylene-1-triethylsilyl-(9R)-methyl-dec-1-yn-10-al, (9R)-6:

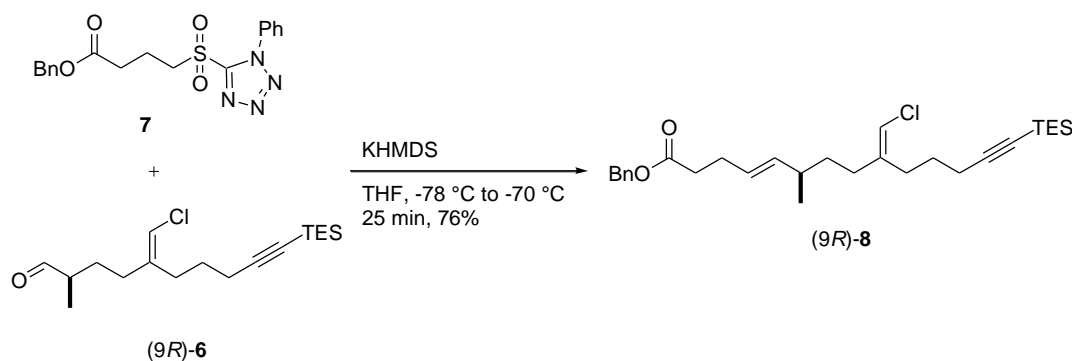
To a solution of (9R)-5 (287 mg, 0.870 mmol, 1.0 equiv) in DMSO (8.7 mL) was added IBX (610 mg, 2.18 mmol, 2.5 equiv). After stirring at room temperature for 2 h, the reaction mixture was quenched with H₂O and filtered. The aqueous layer was then extracted with hexane/EtOAc = 4:1. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 20:1) afforded (9R)-6 as a yellow oil (262 mg, 0.80 mmol, 92%); *R*_f 0.57 (hexane/EtOAc = 10:1); ¹H NMR (500 MHz, CDCl₃) δ 9.61 (1H, m, H10), 5.85 (1H, s, H27), 2.35-2.27 (4H, m, H3/5), 2.14-2.11 (2H, m, H7), 1.90-1.83 (1H, m, H9), 1.68-1.43 (4H, m, H8/4), 1.13 (3H, d, *J* = 6.9 Hz, H26), 0.99 (9H, t, *J* = 7.9 Hz, TES), 0.57 (6H, q, *J* = 7.9 Hz, TES); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 204.4, 141.2, 113.8, 107.9, 82.4, 45.8, 32.3, 29.3, 28.6, 26.4, 20.0, 13.5, 7.7, 4.7; ESI-HRMS (*m/z*) calcd for C₁₈H₃₁ClOSiNa [M+Na]⁺ 349.17304, found 349.17269.

(6E)-Chloromethylene-1-triethylsilyl-(9S)-methyl-tetradec-(10E)-ene-1-ynoic acid benzyl ester, (9S)-8:



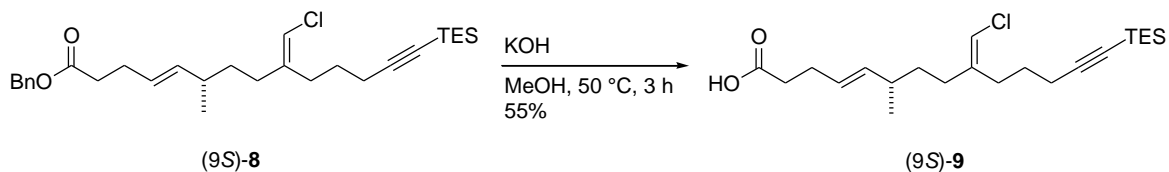
To a solution of the sulfone 7 (138 mg, 0.356 mmol, 3.0 equiv) in THF (3.56 mL) cooled to -78 °C was added 0.5 M KHMDS in toluene (0.688 mL, 0.344 mmol, 2.9 equiv). After the reaction mixture was stirred at -78 °C for 0.5 h, to the reaction mixture was added a solution of the aldehyde (9S)-6 (38.8 mg, 0.119 mmol, 1.0 equiv) in THF (0.659 mL) at -78 °C. After stirring at -70 °C for 40 min, the reaction mixture was quenched with saturated NH₄Cl solution. The aqueous layer was then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 20:1) afforded (9S)-8 as a yellow oil (54.2 mg, 0.111 mmol, 94%); *R*_f 0.49 (hexane/EtOAc = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.34 (5H, m, Bn), 5.78 (1H, s, H27), 5.40-5.24 (2H, m, H10/11), 5.11 (2H, s, Bn), 2.45-2.25 (8H, m, H3/5/12/13), 2.05-1.97 (3H, m, H7/9), 1.66-1.59 (2H, m, H4), 1.33-1.26 (2H, m, H8), 1.04-0.85 (12H, m, H26/TES), 0.57 (6H, q, *J* = 7.8 Hz, TES); ESI-HRMS (*m/z*) calcd for C₂₉H₄₃ClNaO₂Si [M+Na]⁺ 509.26185, found 509.26201.

(6E)-Chloromethylene-1-triethylsilyl-(9R)-methyl-tetradec-(10E)-ene-1-ynoic acid benzyl ester, (9R)-8:



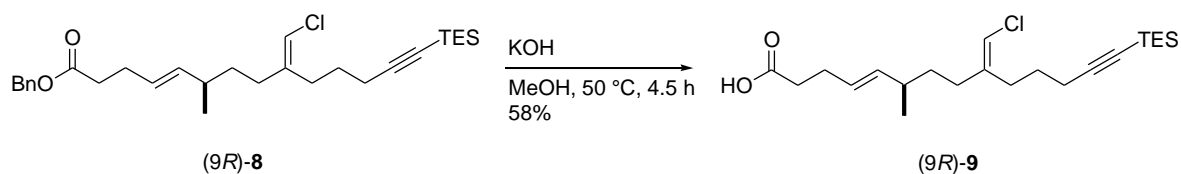
To a solution of the sulfone **7** (262 mg, 2.40 mmol, 3.0 equiv) in THF (24 mL) cooled to -78 °C was added 0.5 M KHMDS in toluene (4.64 mL, 2.32 mmol, 2.9 equiv). After the reaction mixture was stirred at -78 °C for 0.5 h, to the reaction mixture was added a solution of the aldehyde (9R)-**6** (262 mg, 0.800 mmol, 1.0 equiv) in THF (4.4 mL) at -78 °C. After stirring at -70 °C for 25 min, the reaction mixture was quenched with saturated NH₄Cl solution. The aqueous layer was then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 20:1) afforded (9R)-**8** as a yellow oil (267 mg, 0.548 mmol, 76%); *R*_f 0.49 (hexane/EtOAc = 10:1); ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.32 (5H, m, Bn), 5.78 (1H, s, H₂₇), 5.39-5.24 (2H, m, H_{10/11}), 5.11 (2H, s, Bn), 2.45-2.26 (8H, m, H_{3/5/12/13}), 2.05-1.98 (3H, m, H_{7/9}), 1.66-1.60 (2H, m, H₄), 1.40-1.27 (2H, m, H₈), 1.00-0.93 (12H, m, H_{26/28}), 0.57 (6H, q, *J* = 7.8 Hz, TES); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 172.8, 141.9, 136.9, 135.9, 128.4, 128.1, 126.8, 112.4, 107.9, 81.9, 66.0, 36.2, 34.6, 34.3, 32.6, 30.2, 29.2, 27.8, 26.2, 20.7, 19.8, 7.4, 4.5; ESI-HRMS (*m/z*) calcd for C₂₉H₄₃ClNaO₂Si [M+Na]⁺ 509.26185, found 509.26503.

(6E)-Chloromethylene-1-triethylsilyl-(9S)-methyl-tetradec-(10E)-ene-1-ynoic acid, (9S)-9:

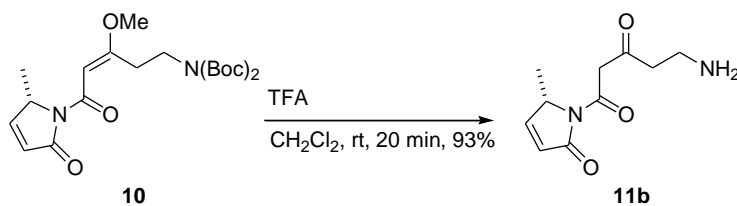


To a solution of (9S)-8 (9.8 mg, 20.1 μmol , 1.0 equiv) in MeOH (0.02 mL) was added 85% KOH (3.98 mg, 60.3 μmol , 3.0 equiv) in H₂O (0.1 mL). After stirring at 50 $^\circ\text{C}$ for 3 h, the reaction mixture was quenched with 2M HCl (30.2 μL). The aqueous layer was then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 5/1) afforded (9S)-9 as a yellow oil (4.4 mg, 11.1 μmol , 55%); R_f 0.47 (hexane/EtOAc = 3:1); ¹H NMR (500 MHz, CDCl₃) δ 5.79 (1H, s, H27), 5.40-5.28 (2H, m, H10/11), 2.43-2.26 (8H, m, H3/5/12/13), 2.05-1.99 (3H, m, H7/9), 1.67-1.61 (2H, m, H4), 1.43-1.30 (2H, m, H8), 1.00-0.96 (12H, m, H26/TES), 0.57 (6H, q, $J = 7.8$ Hz, TES); ESI-HRMS (m/z) calcd for C₂₂H₃₆ClO₂Si [M-H]⁻ 395.21731, found 395.21557.

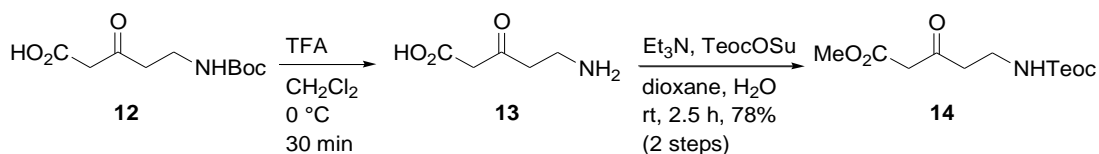
(6E)-Chloromethylene-1-triethylsilyl-(9R)-methyl-tetradec-(10E)-ene-1-ynoic acid, (9R)-9:



To a solution of (9R)-8 (278 mg, 0.57 mmol, 1.0 equiv) in MeOH (5.7 mL) was added 85% KOH (112.9 mg, 1.71 mmol, 3.0 equiv) in H₂O (2.82 mL). After stirring at 50 °C for 4.5 h, the reaction mixture was quenched with 1M HCl (3.4 mL). The aqueous layer was then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 5/1) afforded (9R)-9 as a yellow oil (131 mg, 0.331 mmol, 58%); *R*_f 0.47 (hexane/EtOAc = 3:1); ¹H NMR (500 MHz, CDCl₃) δ 5.79 (1H, s, H27), 5.41-5.28 (2H, m, H10/11), 2.44-2.26 (8H, m, H3/5/12/13), 2.07-1.99 (3H, m, H7/9), 1.67-1.61 (2H, m, H4), 1.43-1.32 (2H, m, H8), 1.01-0.96 (12H, m, H26/TES), 0.57 (6H, q, *J* = 7.8 Hz, TES); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 178.8, 142.2, 137.3, 126.8, 112.7, 108.2, 82.2, 36.6, 34.9, 34.2, 32.9, 26.5, 27.7, 26.5, 20.9, 20.1, 7.7, 6.7, 5.9, 4.9, 4.7; ESI-HRMS (*m/z*) calcd for C₂₂H₃₇ClNaO₂Si [M+Na]⁺ 419.21490, found 419.21432.

[21,22-Dihydro-(23*S*)-methyl-20-oxo-pyrrolinyl]-17,19-dioxo-pent-15-amine, 11b:

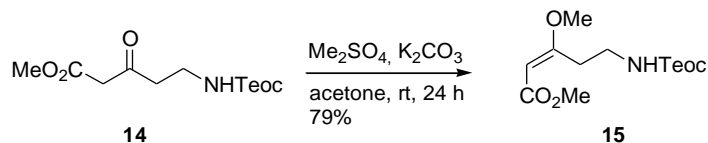
To a solution of **10** (5.9 mg, 0.013 mmol, 1.0 equiv) in CH₂Cl₂ (0.22 mL) was added TFA (0.073 mL). After stirring at rt for 20 min, the reaction mixture was concentrated *in vacuo* and afforded **11b** as a yellow oil (2.7 mg, 0.013 mmol, 93%); *R_f* 0.13 (hexane/EtOAc = 3:1); ¹H NMR (500 MHz, CDCl₃) δ 7.78 (2H, br, NH), 7.31 (1H, q, *J* = 5.1 Hz, H22), 6.05 (1H, d, *J* = 5.0 Hz, H21), 4.81 (1H, q, *J* = 5.1 Hz, H23), 4.00 (2H, q, *J* = 7.2 Hz, H15), 3.37 (2H, s, H18), 3.07 (2H, t, *J* = 3.7 Hz, H16), 1.47 (3H, m, H24); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 175.6, 172.6, 171.2, 152.4, 91.5, 82.3, 55.9, 44.1, 43.1, 31.7; ESI-HRMS (*m/z*) calcd for C₂₂H₃₆ClO₂ [M+H]⁺ 395.21731, found 395.21557.

2'-(Trimethylsilyl)ethoxycarbonylamino-17-oxo-pentanoic acid methyl ester, 14:

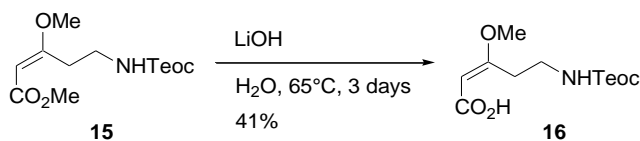
To a solution of **12** (0.500 g, 2.03 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added TFA (10 mL) at 0°C . After stirring at room temperature for 30 min, the reaction mixture was concentrated *in vacuo* to afford **13** as a pink oil, which was used for the second step without further purification.

Next, the residue **13** was dissolved in dioxane/ H_2O (20 mL) and the Et_3N (62 μL , 4.49 mmol, 2.2 equiv) and TeocOSu (63.5 mg, 2.45 mmol, 1.2 equiv) was added. After stirring at room temperature for 2.5 h, the reaction mixture was diluted with H_2O . The reaction mixture was extracted with ether, washed with brine, and dried over Na_2SO_4 . Concentration *in vacuo* and purification on silica gel column chromatography (hexane/ EtOAc = 2:1) afforded **14** as a colorless oil (0.453 g, 1.58 mmol, 78%); R_f 0.7 (hexane/ EtOAc = 1:1); ^1H NMR (500 MHz, CDCl_3) δ 5.08 (1H, s, H18), 4.12 (1H, t, J = 7.5 Hz, H16), 3.67 (3H, s, CO_2Me), 3.65 (3H, s, OMe), 3.41 (2H, m, Teoc), 2.94 (2H, t, J = 5.0 Hz, H15), 0.96 (2H, m, Teoc), 0.03 (9H, s, Teoc); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 202.34, 168.96, 167.51, 156.95, 63.28, 49.31, 43.21, 35.56, 17.76, -1.05, -1.25, -1.37; ESI-HRMS (m/z) calcd for $\text{C}_{12}\text{H}_{23}\text{NO}_5\text{SiNa}$ [$\text{M}+\text{Na}$] $^+$ 312.1243, found 312.1253.

2'-(Trimethylsilyl)ethoxycarbonylamino-17-methoxy-pent-(17E)-enoic acid methyl ester, **15:**

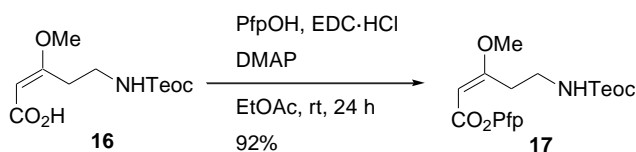


To a solution of **14** (0.092 g, 0.318 mmol, 1.0 equiv) and K_2CO_3 (0.051 g, 0.350 mmol, 1.1 equiv) in acetone (6 mL) was added Me_2SO_4 (0.036 μL , 0.350 mmol, 1.1 equiv). After stirring at room temperature for 24 h, the reaction mixture was concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 6:1) afforded **15** as a colorless oil (0.087 g, 0.251 mmol, 79%); R_f 0.79 (hexane/EtOAc = 1:1); ^1H NMR (500 MHz, CDCl_3) δ 5.08 (1H, s, H18), 5.07 (1H, br, NH) 3.68 (3H, s, CO_2Me), 3.64 (3H, s, H25), 3.42 (2H, m, Teoc), 2.95 (2H, t, $J = 6.6$ Hz, H15), 0.95 (2H, t, $J = 6.6$ Hz, Teoc), 0.03 (9H, s, Teoc); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 177.66, 156.92, 156.50, 101.61, 62.65, 54.76, 47.94, 40.04, 33.64, 17.46, -1.55, -1.75, -1.79; ESI-HRMS (m/z) calcd for $\text{C}_{13}\text{H}_{25}\text{NO}_5\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 326.1400, found 326.1415.

2'-(Trimethylsilyl)ethoxycarbonylamino-17-methoxy-pent-(17E)-enoic acid, 16:

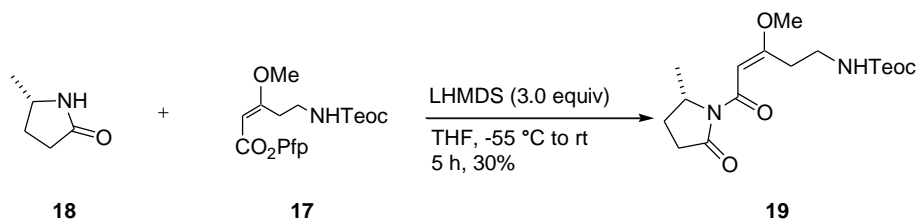
To a solution of **15** (67 mg, 0.22 mmol, 1.0 equiv) in THF (0.5 mL) was added H₂O (0.5 mL) and LiOH (11.5 mg, 0.48 mmol, 3.0 equiv). After stirring at 65 °C for 3 days, the reaction mixture was diluted with EtOAc. The aqueous layer was then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 5/1) afforded **16** as a colorless solid (24 mg, 0.09 mmol, 41%); *R*_f 0.2 (hexane/EtOAc = 1:1); ¹H NMR (500 MHz, CDCl₃) δ 5.07 (1H, s, H18), 4.96 (1H, br, NH), 4.08 (2H, t, *J* = 10.0 Hz, H16), 3.64 (3H, s, H25), 3.39 (2H, m, Teoc), 2.93 (2H, t, *J* = 5.0 Hz, 15H) 0.93 (2H, m, Teoc), 0.00 (9H, s, Teoc); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 175.32, 172.76, 156.74, 91.74, 62.86, 55.85, 38.90, 32.25, 17.67, -1.31, -1.51, -1.72; ESI-HRMS (*m/z*) calcd for C₁₁H₁₉NO₅ [M-H]⁻ 288.12672 found 288.12784.

2'-(Trimethylsilyl)ethoxycarbonylamino-17-methoxy-pent-(17E)-enoic acid pentafluorophenol ester, 17:



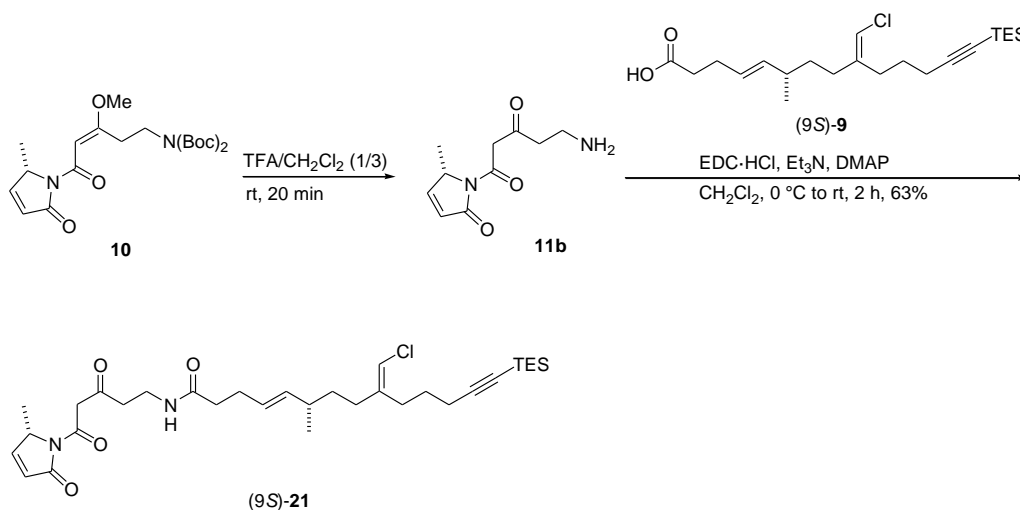
To a solution of **16** (50 mg, 0.19 mmol, 1.0 equiv), DMAP (25 mg, 0.173 mmol, 1.0 equiv), and PfpOH (95 mg, 0.519 mmol, 3.0 equiv) in EtOAc (5 mL) cooled to 0 °C was added EDC·HCl (40 mg, 0.208 mmol, 1.2 equiv). After stirring at room temperature for 24 h, the reaction mixture was diluted with EtOAc. The aqueous layer was then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 4:1) afforded **17** as a colorless solid (80.2 mg, 0.18 mmol, 92%); *R_f* 0.80 (hexane/EtOAc = 1:1); ¹H NMR (500 MHz, CDCl₃) δ 5.10 (1H, s, H18), 5.02 (1H, s, NH) 4.12 (2H, t, *J* = 10.0 Hz, H16), 3.67 (3H, s, H25), 3.42 (2H, m, Teoc), 2.96 (2H, t, *J* = 5.0 Hz, H15), 0.03 (9H, s, Teoc); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 178.72, 163.70, 156.94, 89.09, 63.24, 56.66, 38.93, 33.24, 17.92, -1.27, -1.47, -1.58; ESI-HRMS (*m/z*) calcd for C₁₈H₂₂F₅NNaO₅Si [M+Na]⁺ 478.10851, found 478.10818.

**{17-Methoxy-19-[(23*S*)-methyl-20-oxo-pyrrolidiny]-19-oxo-pent-(17*E*)-enyl}-2'-
(trimethylsilyl)ethoxycarbonyl-amine, (**19**):**



To a solution of **18** (0.18 g, 1.77 mmol, 3.0 equiv) in THF (4.0 mL) was added LiHMDS (1.56 mmol, 3.0 equiv) at $-55\text{ }^\circ\text{C}$. After stirring at $-55\text{ }^\circ\text{C}$ for 30 min, the reaction mixture was added a solution of **17** (0.27 g, 0.59 mmol, 1.0 equiv) in THF (3 mL). After stirring for 5 h at $-55\text{ }^\circ\text{C}$ to $0\text{ }^\circ\text{C}$, the reaction mixture was concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 10:1 to 5:1) afforded **19** as a colorless oil (0.066 g, 0.18 mmol, 30%); R_f 0.32 (hexane/EtOAc = 3:1); ^1H NMR (500 MHz, CDCl_3) δ 6.66 (1H, s, H18), 5.37 (1H, br, NH), 4.53 (1H, t, $J = 7.5$ Hz, H23), 4.12 (2H, m, Teoc), 3.71 (3H, s, H25), 3.42 (2H, m, H15), 2.92 (2H, t, $J = 7.5$ Hz, H16), 2.74 (1H, m, H21), 2.51 (1H, m, H21), 2.16 (1H, m, H22), 1.68 (1H, m, H22), 1.33 (3H, s, H24), 0.95 (2H, m, Teoc), 0.05 (9H, m, Teoc); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 175.39, 175.09, 166.42, 156.80, 94.99, 62.69, 55.96, 53.40, 39.21, 32.54, 24.86, 19.75, 17.70, -1.27, -1.47, -1.58; ESI-HRMS (m/z) calcd for $\text{C}_{17}\text{H}_{30}\text{N}_2\text{NaO}_5\text{Si}$ $[\text{M}+\text{Na}]^+$ 393.18217, found 393.18387.

***N*-{19-[21,22-Dihydro-(23*S*)-methyl-20-oxo-pyrrolyl]-17,19-dioxo-pentyl}-(6*E*)-chloromethylene-1-triethylsilyl-(9*S*)-methyl-tetradec-(10*E*)-ene-1-ynamide, (9*S*)-21:**



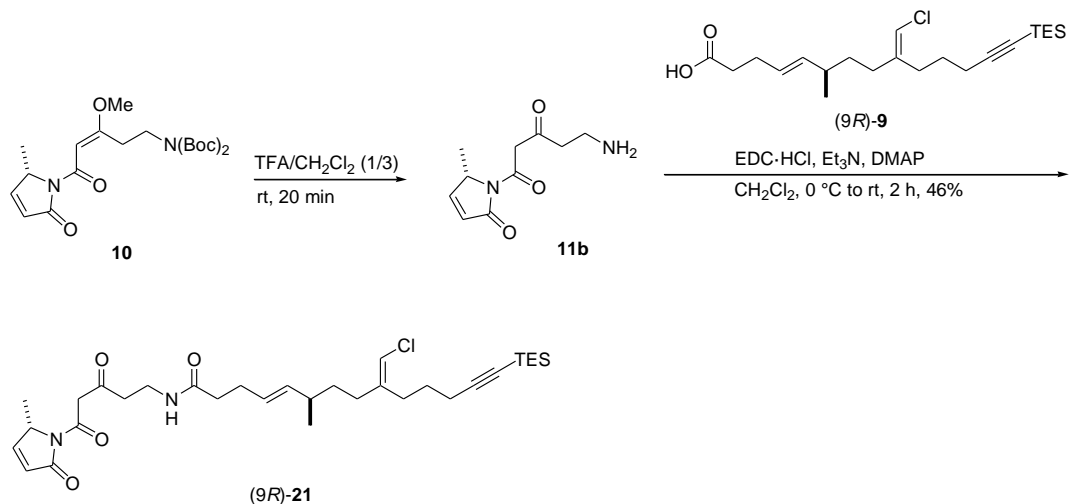
To a solution of **10** (43.6 mg, 0.10 mmol, 1.0 equiv) in CH₂Cl₂ (1.6 mL) was added TFA (0.516 mL). After stirring at rt for 20 min, the reaction mixture was concentrated *in vacuo* and afforded **11b**, which was used for next reaction without further purification.

Next, to a solution of **11b** in CH₂Cl₂ (0.5 mL) was added (9*S*)-**9** in CH₂Cl₂ (1.5 mL), DMAP (3.4 mg, 0.028 mmol, 0.3 equiv), Et₃N (38.6 μL, 0.279 mmol, 3.0 equiv) and EDC · HCl (26.7 mg, 0.139 mmol, 1.5 equiv) at 0 °C. After stirring at room temperature for 2 h, the reaction mixture was quenched with H₂O. The aqueous layer was then extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 1/3) afforded (9*S*)-**21** as a yellow oil (35 mg, 59.5 μmol, 63%); *R*_f 0.42 (hexane/EtOAc = 1:3); ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.28 (1H, dd, *J* = 10, 2.5 Hz, H₂₂), 6.04-6.02 (1H, s, H₂₁), 5.79 (1H, s, H₂₇), 5.39-5.24 (2H, m, H_{10/11}), 4.85-4.80 (1H, m, H₂₃), 3.99 (2H, s, H₁₈), 3.56-3.51 (2H, m, H₁₅), 2.81-2.78

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(2H, m, H16), 2.45-2.25 (8H, m, H3/5/12/13), 2.04-1.99 (3H, m, H7/9), 1.67-1.65 (2H, m, H4), 1.62-1.60 (3H, m, Me), 1.50-1.47 (2H, m, H24), 1.39-1.31 (2H, m, H8), 1.00-0.94 (9H, m, TES), 0.60-0.54 (6H, q, $J = 7.8$ Hz, TES); ESI-HRMS (m/z) calcd for $C_{32}H_{49}ClN_2O_4SiNa$ $[M+Na]^+$ 611.30478, found 611.30324.

***N*-{19-[21,22-Dihydro-(23*S*)-methyl-20-oxo-pyrrolyl]-17,19-dioxo-pentyl}-(6*E*)-chloromethylene-1-triethylsilyl-(9*R*)-methyl-tetradec-(10*E*)-ene-1-ynamide, (9*R*)-21:**

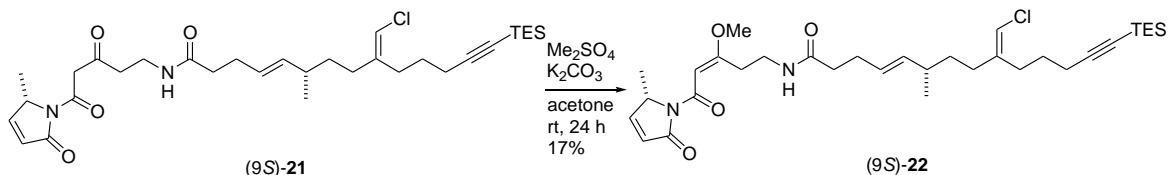


To a solution of **10** (44.0 mg, 0.10 mmol, 1.0 equiv) in CH₂Cl₂ (1.7 mL) was added TFA (0.521 mL). After stirring at rt for 20 min, the reaction mixture was concentrated *in vacuo* and afforded **11b**, which was used for next reaction without further purification.

Next, to a solution of **11b** in CH₂Cl₂ (0.5 mL) was added (9*R*)-**9** in CH₂Cl₂ (1.5 mL), DMAP (3.78 mg, 0.031 mmol, 0.3 equiv), Et₃N (28.6 μL, 0.206 mmol, 2.0 equiv) and EDC · HCl (29.8 mg, 0.155 mmol, 1.5 equiv) at 0 °C. After stirring at room temperature for 2 h, the reaction mixture was quenched with H₂O. The aqueous layer was then extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 1/3) afforded (9*R*)-**21** as a yellow oil (28 mg, 0.0476 mmol, 46%); *R_f* 0.42 (hexane/EtOAc = 1:3); ¹H NMR (500 MHz, CDCl₃) δ 7.30-7.28 (1H, m, H22), 7.23 (1H, brs, NH), 6.08 (1H, m, H21), 6.04-6.02 (1H, s, H18), 5.79 (1H,

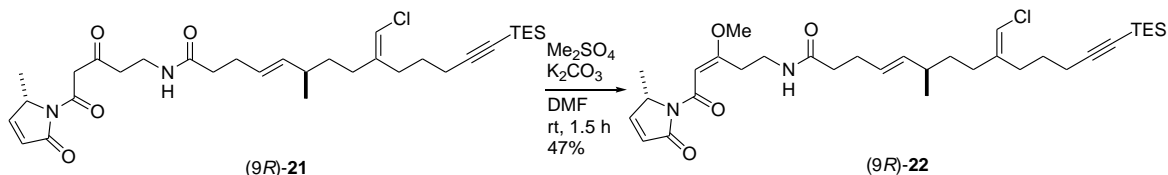
s, H27), 5.37-5.26 (2H, m, H10/11), 4.84-4.82 (1H, m, H23) , 3.56-3.53 (2H, m, H15), 2.82-2.79 (2H, m, H16), 2.32-2.16 (8H, m, H3/5/12/13), 2.04-1.99 (3H, m, H7/9), 1.67-1.65 (2H, m, H4), 1.62-1.60 (3H, m, Me), 1.50-1.47 (2H, m, H24), 1.39-1.31 (2H, m, H8), 1.00-0.94 (9H, m, TES), 0.60-0.54 (6H, q, $J = 7.8$ Hz, TES); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 203.3, 172.4, 170.1, 165.5, 154.4, 142.1, 136.8, 127.4, 125.1, 112.6, 108.0, 82.1, 58.1, 52.1, 42.4, 36.7, 36.3, 34.8, 34.0, 32.7, 29.4, 28.5, 26.4, 20.8, 19.9, 17.5, 7.49, 4.56; ESI-HRMS (m/z) calcd for $\text{C}_{32}\text{H}_{49}\text{ClN}_2\text{O}_4\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 611.30478, found 611.30412.

***N*-{19-[21,22-Dihydro-(23*S*)-methyl-5-oxo-pyrrolyl]-17-methoxy-19-oxo-pent-(17*E*)-enyl}-(6*E*)-chloromethylene-(10*E*)-ene-(9*S*)-methyl-1-triethylsilyl-tetradec-1-ynamide, (9*S*)-22:**



To a solution of (9*S*)-**21** (14.41 mg, 24.5 μmol , 1.0 equiv) and K_2CO_3 (3.7 mg, 26.9 μmol , 1.1 equiv) in acetone (175 μL) was added Me_2SO_4 . After stirring at rt for 24 h, the reaction mixture was concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 1/1) afforded (9*S*)-**22** as a yellow oil (2.5 mg, 4.2 μmol , 17%); R_f 0.58 (hexane/EtOAc = 1:3); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.30-7.28 (1H, m, H22), 6.73 (1H, s, H18), 6.70 (1H, brs, NH), 6.08 (1H, dd, $J = 5.8, 1.9$ Hz, H21), 5.79 (1H, s, H27), 5.39-5.24 (2H, m, H10/11), 4.85-4.80 (1H, m, H23), 3.75 (3H, s, Me), 3.49 (2H, m, H15), 3.03-2.80 (2H, m, H16), 2.45-2.25 (8H, m, H3/5/12/13), 2.04-1.99 (3H, m, H7/9), 1.66-1.60 (2H, m, H4), 1.50-1.47 (2H, d, H24), 1.39-1.31 (2H, m, H8), 1.00-0.94 (12H, m, H26/TES), 0.60-0.54 (6H, q, $J = 7.8$ Hz, TES); FAB-MS (m/z) calcd for $\text{C}_{33}\text{H}_{51}\text{ClN}_2\text{O}_4\text{Si}$ $[\text{M}+\text{H}]^+$ 603.3379, found 603.2319.

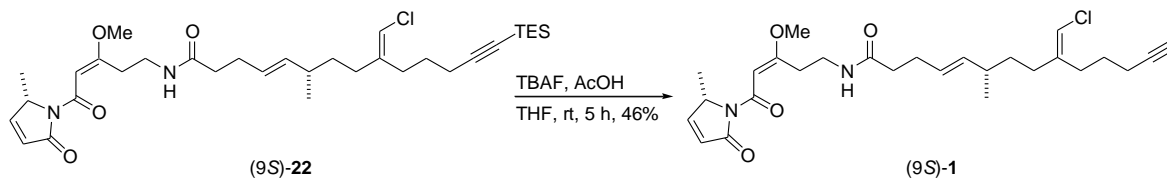
***N*-{19-[21,22-Dihydro-(23*S*)-methyl-5-oxo-pyrrolyl]-17-methoxy-19-oxo-pent-(17*E*)-enyl}-(6*E*)-chloromethylene-(10*E*)-ene-(9*R*)-methyl-1-triethylsilyl-tetradec-1-ynamide, (9*R*)-22:**



To a solution of (9*R*)-21 (17.64 mg, 30.0 μmol , 1.0 equiv) and K_2CO_3 (4.56 mg, 33.0 μmol , 1.1 equiv) in DMF (220 μL) was added Me_2SO_4 . After stirring at rt for 1.5 h, the reaction mixture was quenched with saturated NH_4Cl solution. The aqueous layer was then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 1/1) afforded (9*R*)-22 as a yellow oil (8.5 mg, 14.1 μmol , 47%); R_f 0.58 (hexane/EtOAc = 1:3); ^1H NMR (500 MHz, CDCl_3) δ 7.30-7.28 (1H, m, H22), 6.73 (1H, s, H18), 6.70 (1H, brs, NH), 6.08 (1H, dd, $J = 5.8, 2.0$ Hz, H21), 5.79 (1H, s, H27), 5.39-5.24 (2H, m, H10/11), 4.85-4.80 (1H, m, H23), 3.75 (3H, s, Me), 3.49 (2H, m, H15), 3.03-2.80 (2H, m, H16), 2.45-2.25 (8H, m, H3/5/12/13), 2.04-1.99 (3H, m, H7/9), 1.66-1.60 (2H, m, H4), 1.50-1.47 (2H, m, H24), 1.39-1.31 (2H, m, H8), 1.00-0.94 (12H, m, H26/TES), 0.60-0.54 (6H, q, $J = 7.8$ Hz, TES); ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 175.3, 172.4, 170.0, 166.0, 153.1, 142.1, 136.6, 127.5, 125.8, 112.6, 107.9, 95.0, 61.9, 58.1, 56.1, 38.2, 36.7, 36.3, 34.8, 32.7, 32.4, 29.3, 28.6, 26.3, 20.8, 19.9, 17.9, 7.49, 4.55.

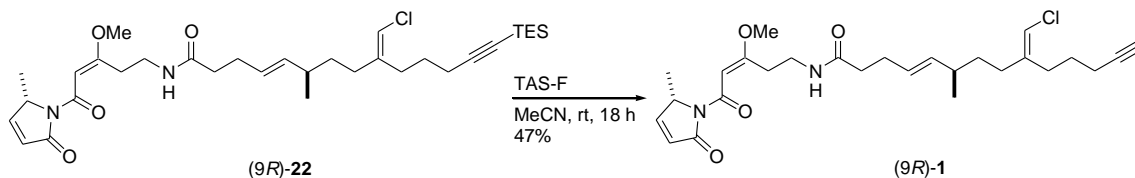
***N*-{19-[21,22-Dihydro-(23*S*)-methyl-20-oxo-pyrrolyl]-17-methoxy-19-oxo-pent-(17*E*)-enyl}-(6*E*)-chloromethylene-(10*E*)-ene-(9*S*)-methyl-tetradec-1-ynamide, (9*S*)-**

1:



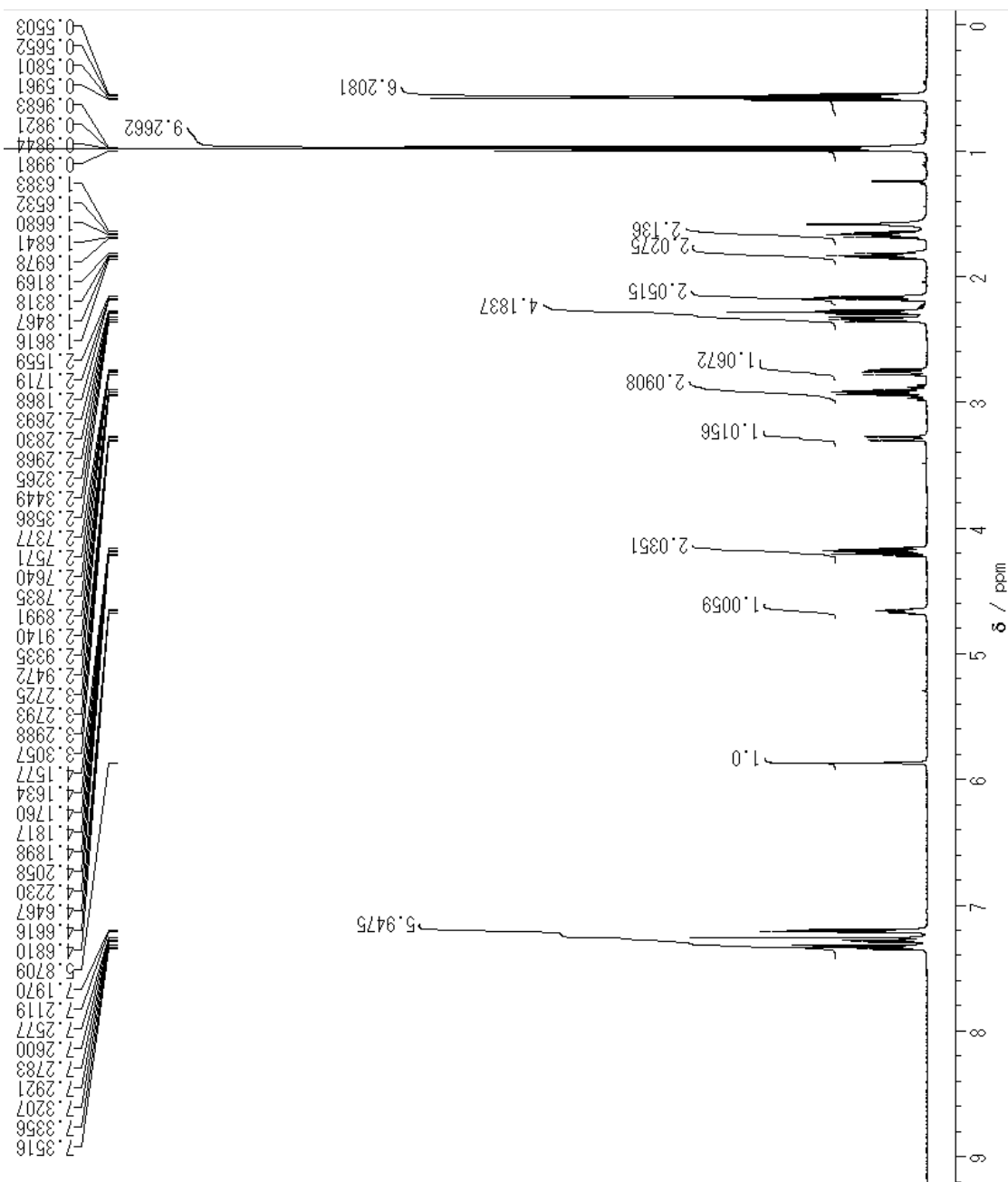
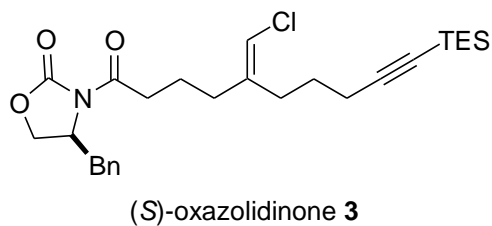
To a solution of (9*S*)-22 (3.5 mg, 5.8 μmol , 1.0 equiv) in THF (232 μL) was added AcOH (0.58 μL , 10.2 μmol , 1.75 equiv) in THF (5.8 μL) and 1.0 M TBAF (10.2 μL , 10.2 μmol , 1.75 equiv). After stirring at rt for 5 h, the reaction mixture was concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 1/1) afforded (9*S*)-1 as a yellow oil (1.6 mg, 2.7 μmol , 46%); R_f 0.52 (hexane/EtOAc = 1:3); $[\alpha]_D^{25} +1.5$ (c 1.6, MeOH); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.23-7.22 (1H, dd, $J = 6.0, 2.2$ Hz, H22), 6.73 (1H, s, H18), 6.72 (1H, brs, NH), 6.09 (1H, dd, $J = 6.0, 2.2$ Hz, H21), 5.79 (1H, s, H27), 5.39-5.33 (1H, dt, $J = 9.2, 7.1$ Hz, H11), 5.28-5.27 (1H, dd, $J = 9.2, 7.2$ Hz, H10), 4.87-4.85 (1H, m, H23), 3.75 (3H, s, Me), 3.52-3.49 (2H, m, H15), 3.00-2.84 (2H, m, H16), 2.31-2.26 (4H, m, H5/12), 2.22-2.16 (4H, m, H3/13), 2.04-1.99 (3H, m, H7/9), 1.66-1.60 (2H, m, H4), 1.50-1.47 (2H, d, $J = 7.2$ Hz, H24), 1.39-1.31 (2H, m, H8), 1.00-0.94 (3H, m, H26); ESI-HRMS (m/z) calcd for $\text{C}_{27}\text{H}_{37}\text{ClN}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 511.23395, found 511.23433.

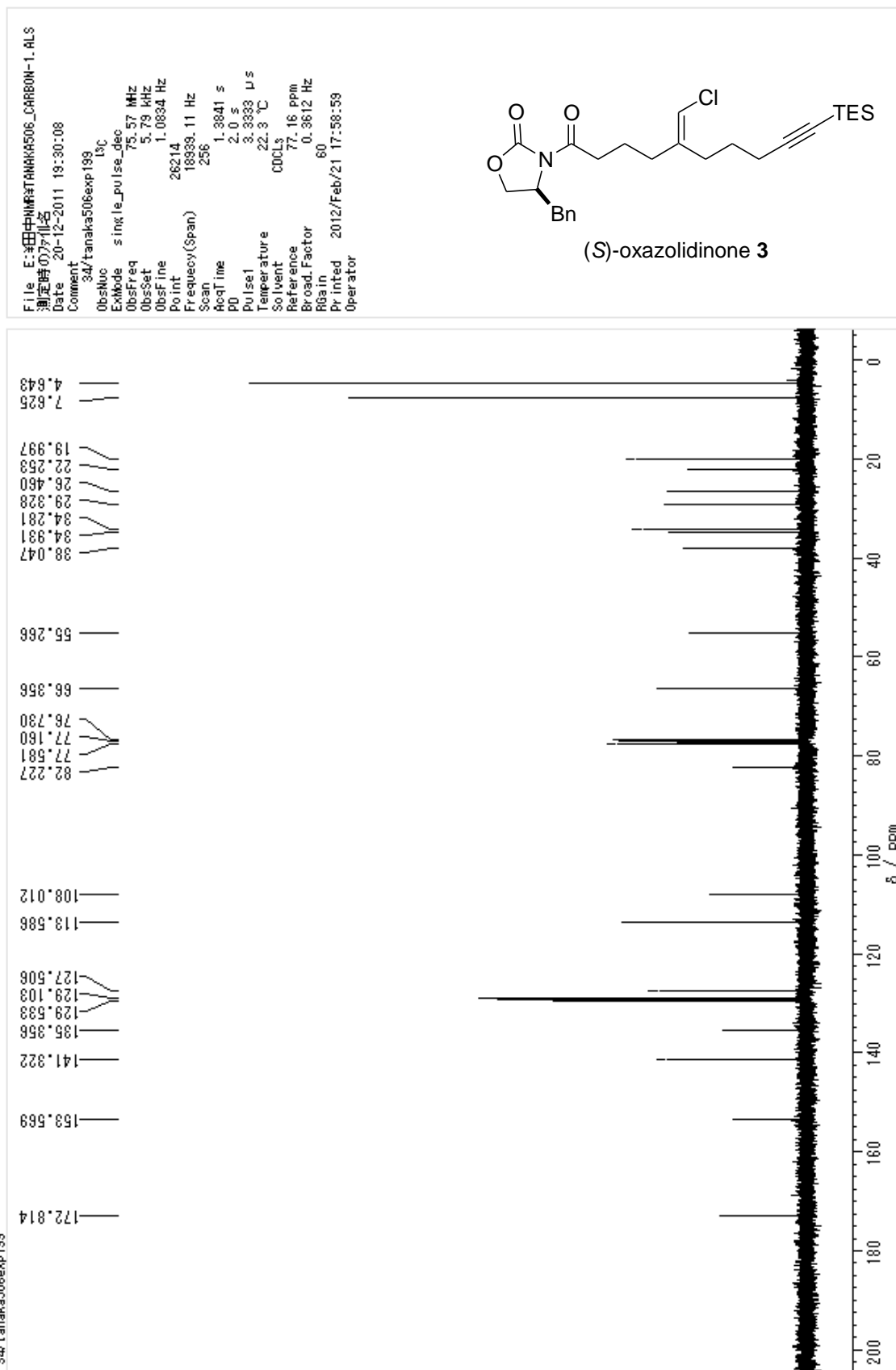
***N*-{19-[21,22-Dihydro-(23*S*)-methyl-20-oxo-pyrrolyl]-17-methoxy-19-oxo-pent-(17*E*)-enyl}-(6*E*)-chloromethylene-(10*E*)-ene-(9*R*)-methyl-tetradec-1-ynamide, (9*R*)-1:**



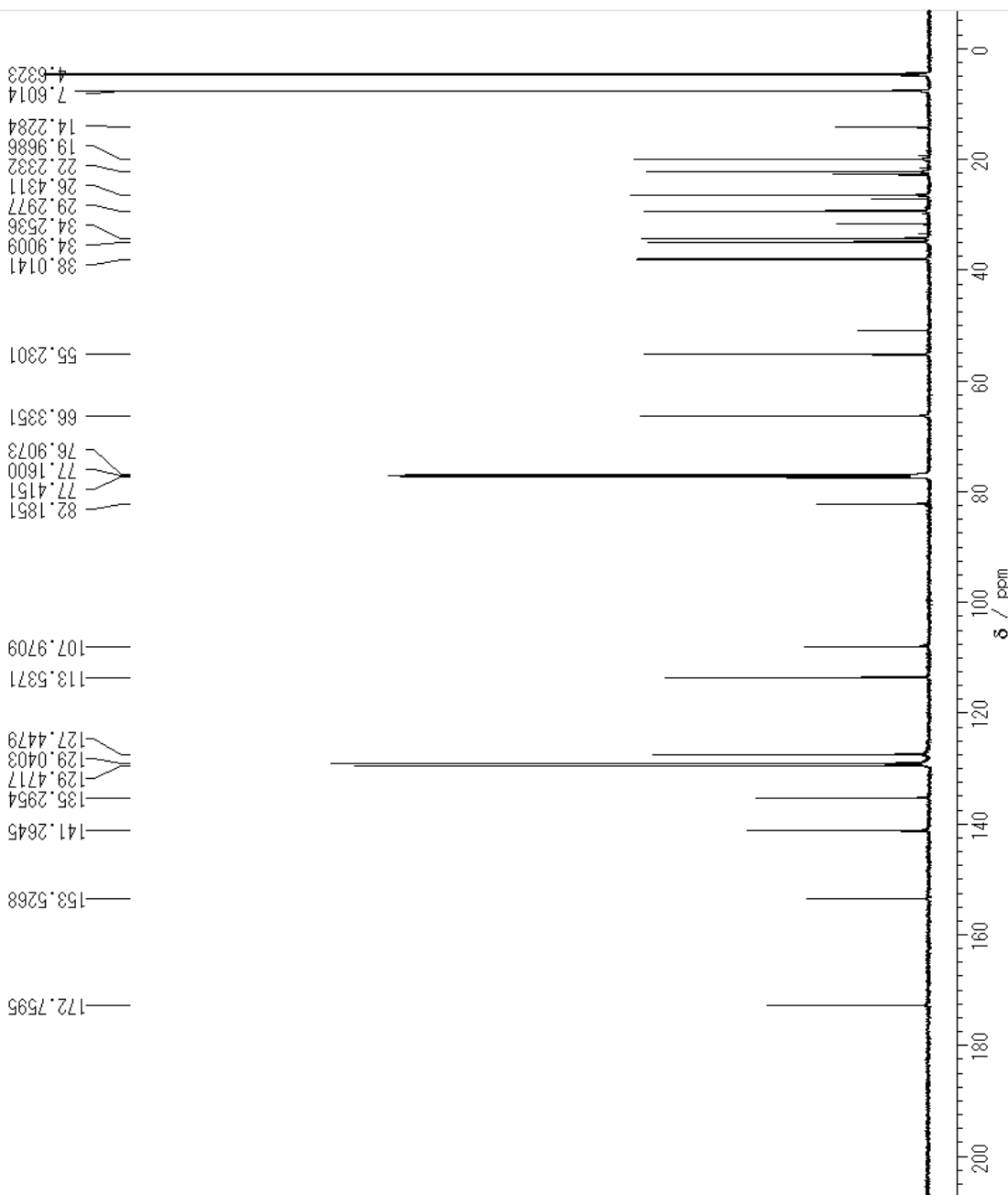
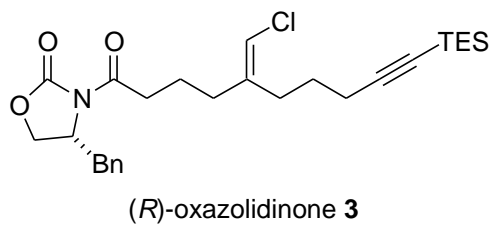
To a solution of (9*R*)-22 (1.01 mg, 1.65 μmol , 1.0 equiv) in MeCN (56 μL) was added TAS-F (0.68 mg, 2.48 μmol , 1.5 equiv) in MeCN (78 μL). After stirring at rt for 18 h, the reaction mixture was quenched with saturated NH_4Cl solution. The aqueous layer was then extracted with CH_2Cl_2 . The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo*. Purification on silica gel column chromatography (hexane/EtOAc = 1/1) afforded (9*R*)-1 as a yellow oil (0.38 mg, 7.8 μmol , 47%); R_f 0.52 (hexane/EtOAc = 1:3); $[\alpha]_D^{25} +43$ (c 0.13, MeOH); ^1H NMR (500 MHz, CDCl_3) δ 7.23-7.22 (1H, dd, J = 6.2, 1.9 Hz, H22), 6.73(1H, s, H18), 6.72 (1H, brs, NH), 6.09 (1H, dd, J = 5.9, 2.0 Hz, H21), 5.79 (1H, s, H27), 5.39-5.33 (1H, dt, J = 9.0, 6.9 Hz, H11), 5.28-5.27 (1H, dd, J = 9.0, 6.8 Hz, H10), 4.87-4.85 (1H, m, H23), 3.75 (3H, s, Me), 3.52-3.49 (2H, m, H15), 3.00-2.84 (2H, m, H16), 2.31-2.26 (4H, m, H5/12), 2.22-2.16 (4H, m, H3/13), 2.04-1.99 (3H, m, H7/9), 1.66-1.60 (2H, m, H4), 1.50-1.47 (2H, d, J = 7.6 Hz, H24), 1.39-1.31 (2H, m, H8), 1.00-0.94 (3H, d, J = 7.5 Hz, H26); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ 175.3, 172.4, 170.0, 166.0, 153.0, 141.8, 136.5, 127.5, 125.8, 112.7, 94.9, 84.0, 68.5, 58.0, 56.0, 38.1, 36.7, 36.2, 34.7, 32.5, 32.3, 29.3, 28.5, 26.0, 20.7, 18.3, 17.8; ESI-HRMS (m/z) calcd for $\text{C}_{27}\text{H}_{37}\text{ClN}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 511.23395, found 511.23185.

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 Broad.Factor 0.2864 Hz
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 Printed 2022/Jan/26 19:38:44
 Operator

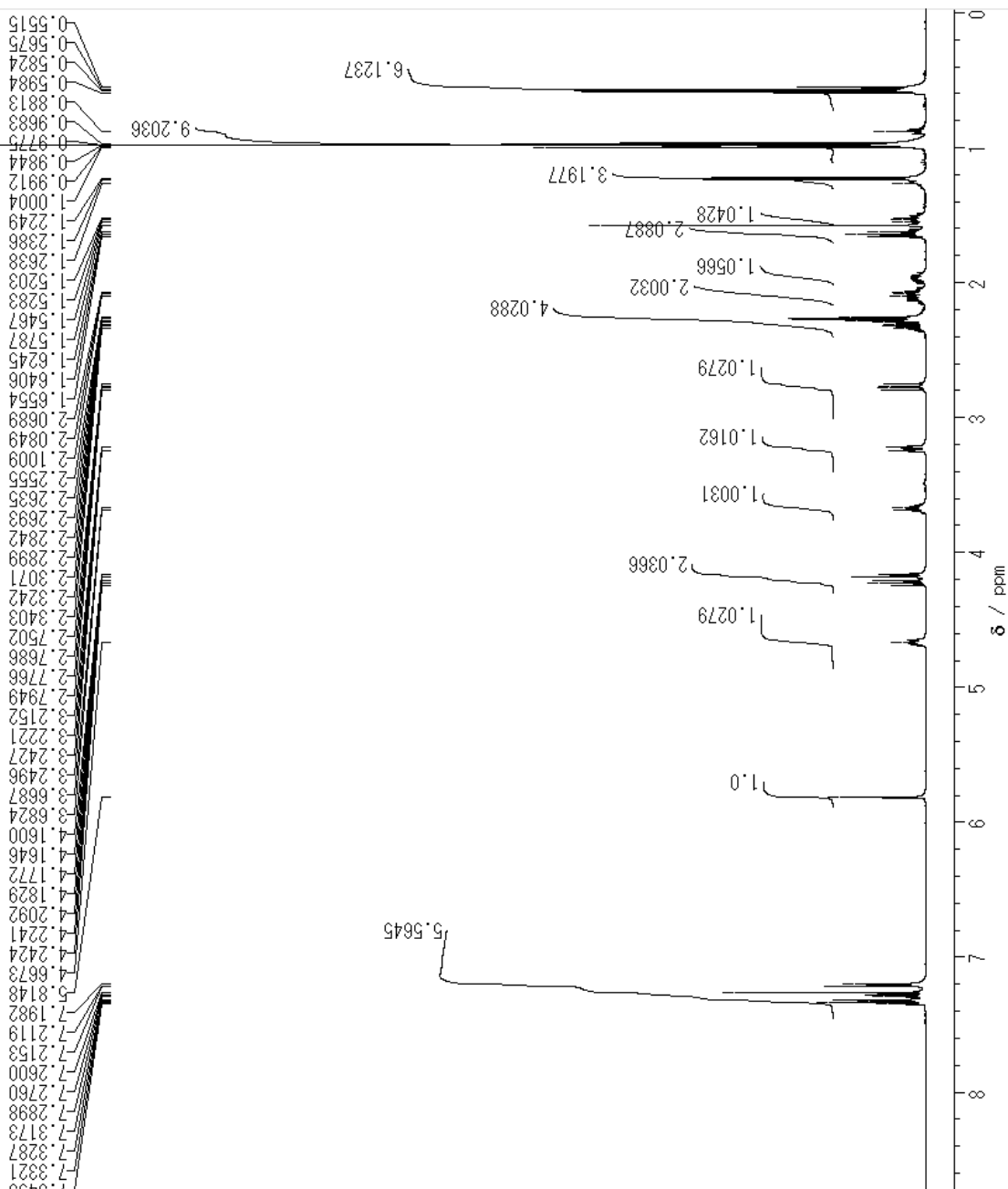
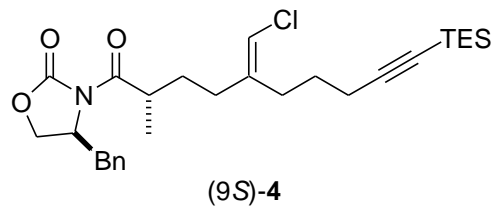


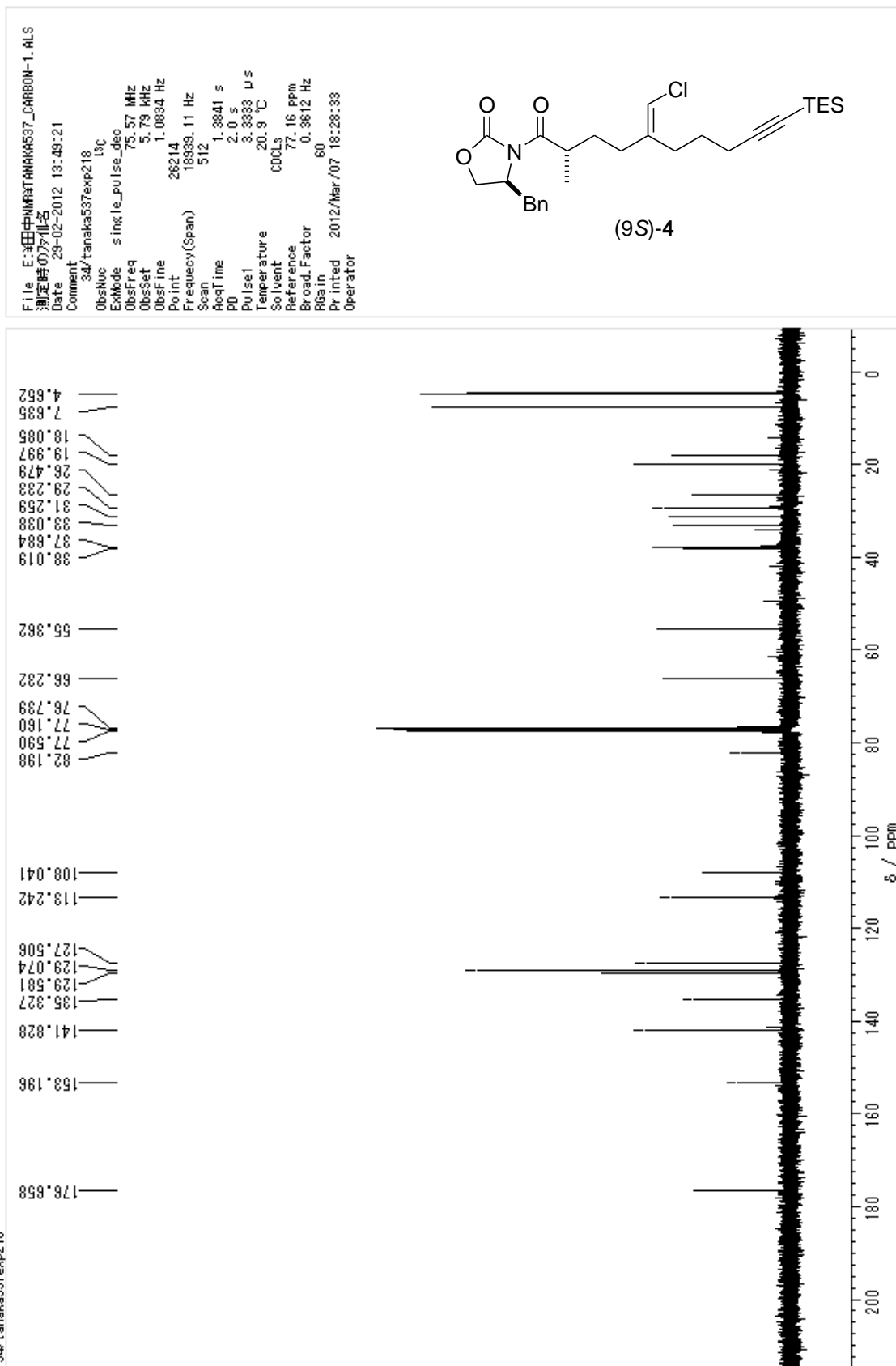


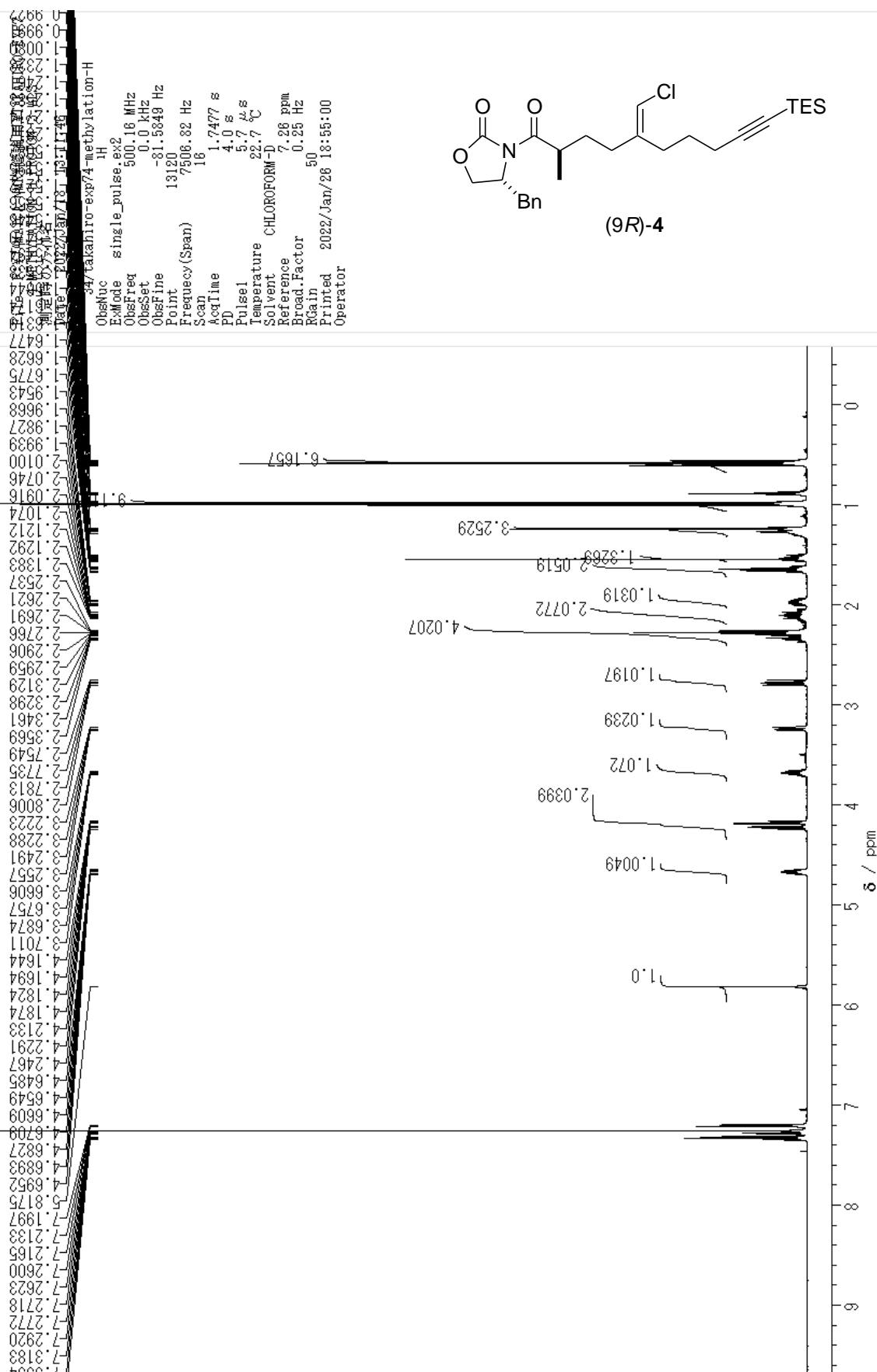
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 ObsFine 320.6217 Hz
 Point 2824
 Frequency(Span) 31444.86 Hz
 Sca1 1024
 AcqTime 0.834 s
 PD 2.0 s
 Pulse1 4.1917 μ s
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 Broad.Factor 0.25 Hz
 RGain 48
 Printed 2022/Jan/28 12:42:06
 Operator



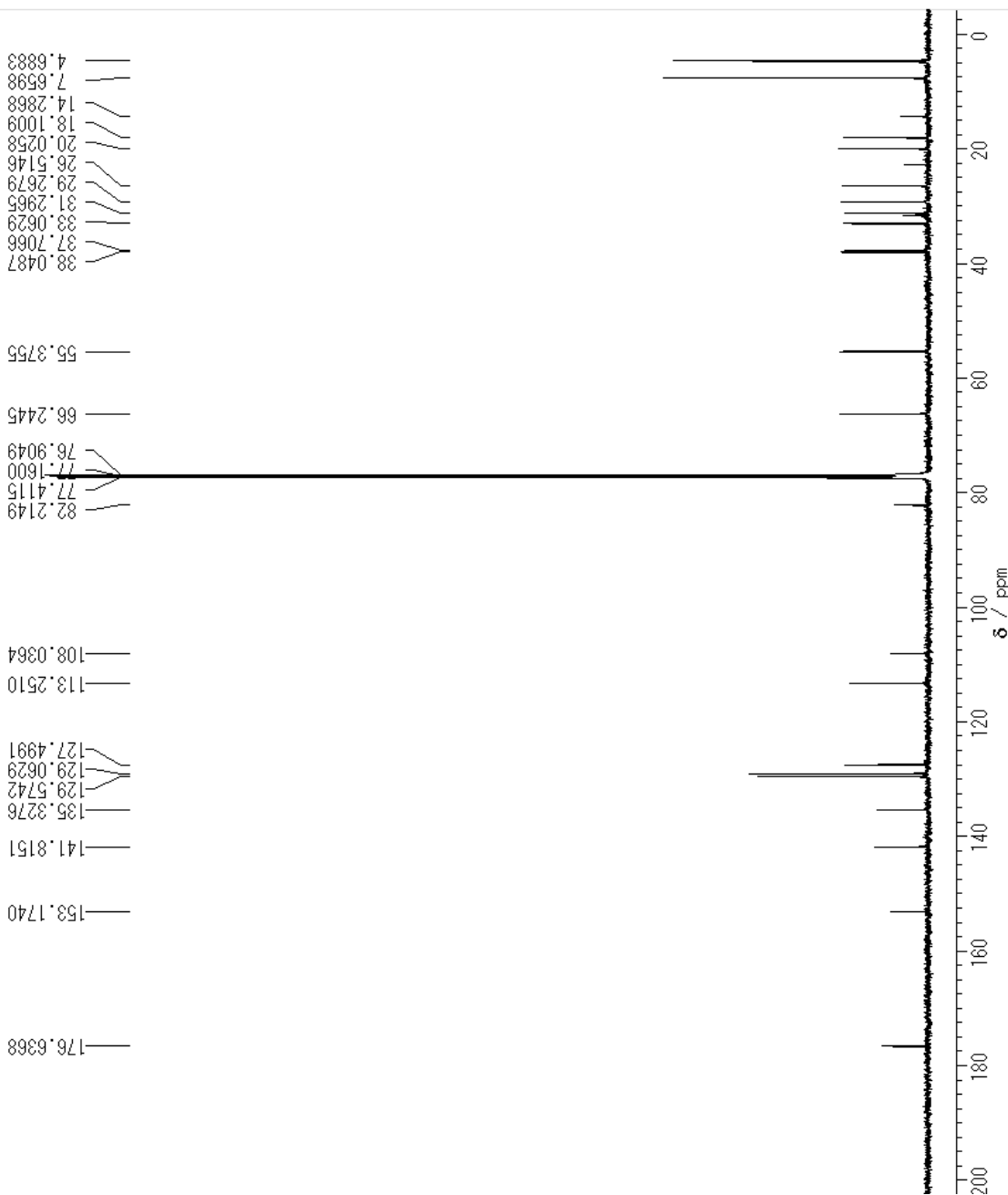
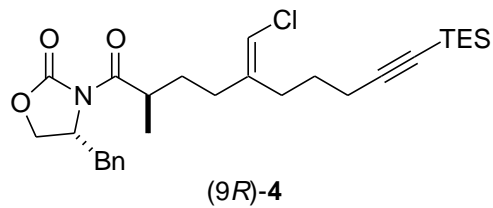
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 ObsFine 6.0082 Hz
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 Broad.Factor 0.2864 Hz
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 Printed 2022/Jan/26 18:47:42
 Operator



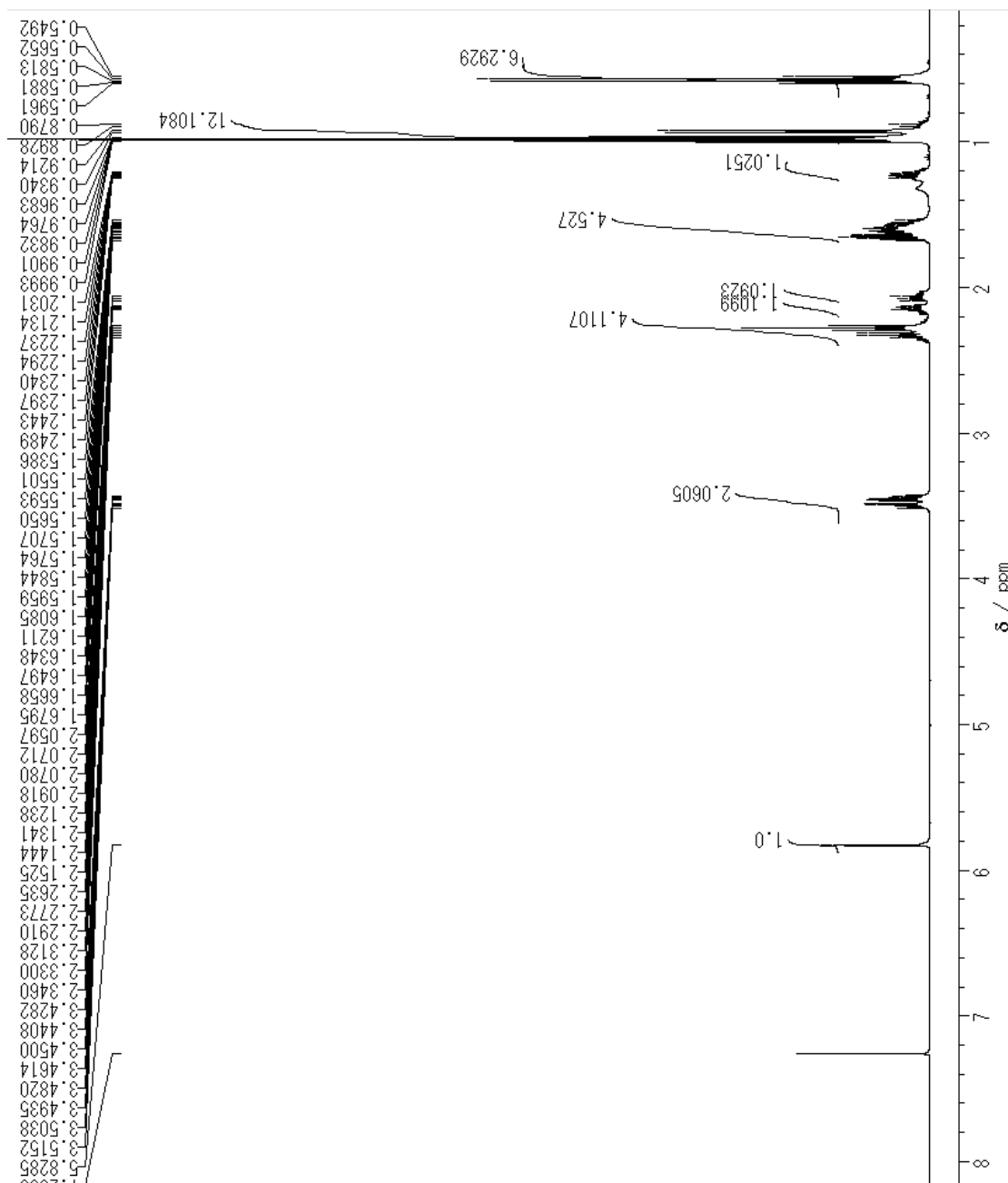
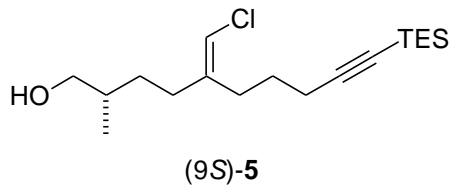


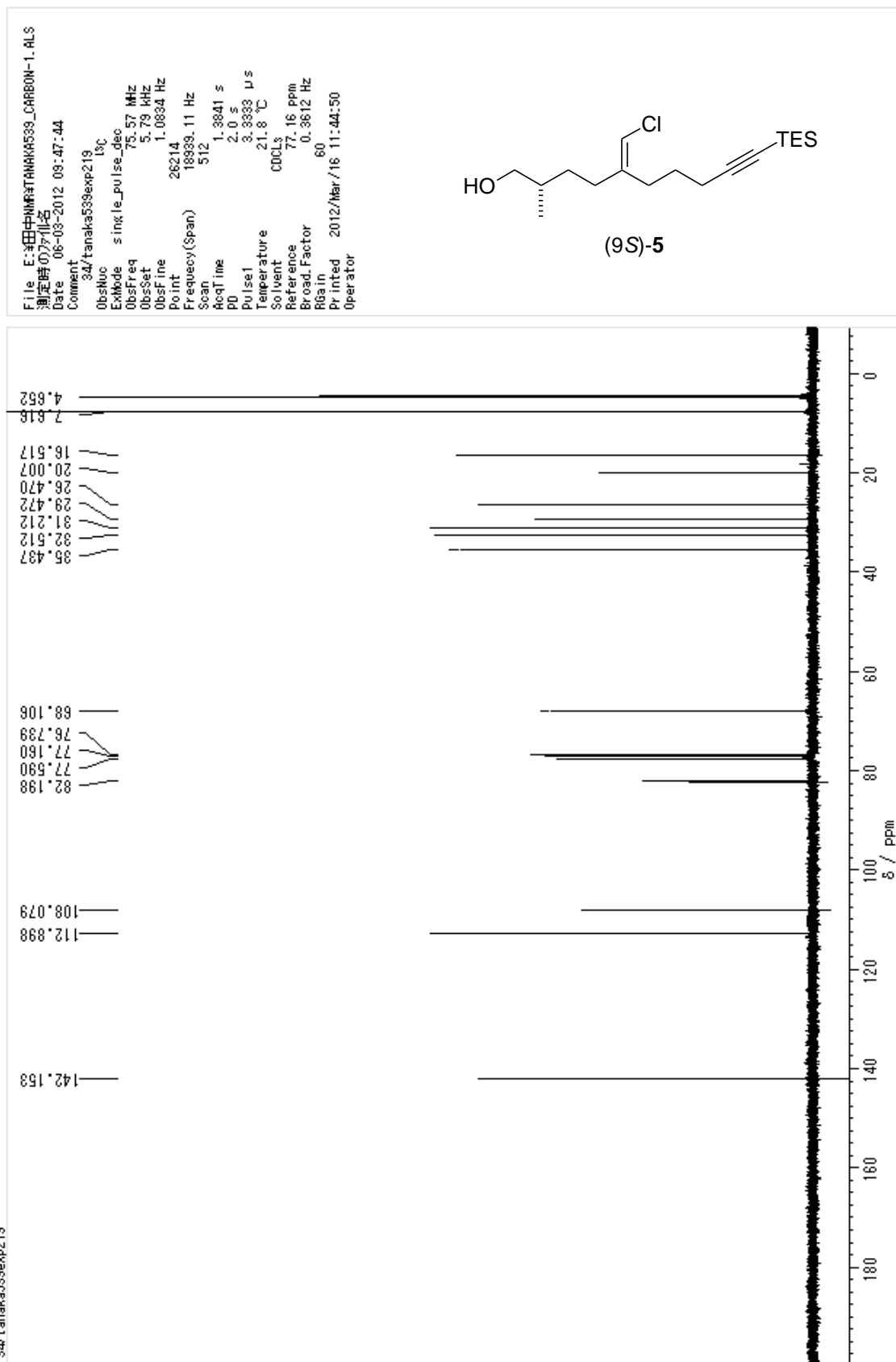


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 ObsFine 314.6243 Hz
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 Frequency(Span) 31444.86 Hz
 Scan 1024
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 PD 2.0 s
 Pulse 4.1817 μs
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 Solvent CHLOROFORM-D
 Reference 77.16 ppm
 Broad.Factor 0.25 Hz
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 Printed 2022/Jan/28 12:45:40
 Operator

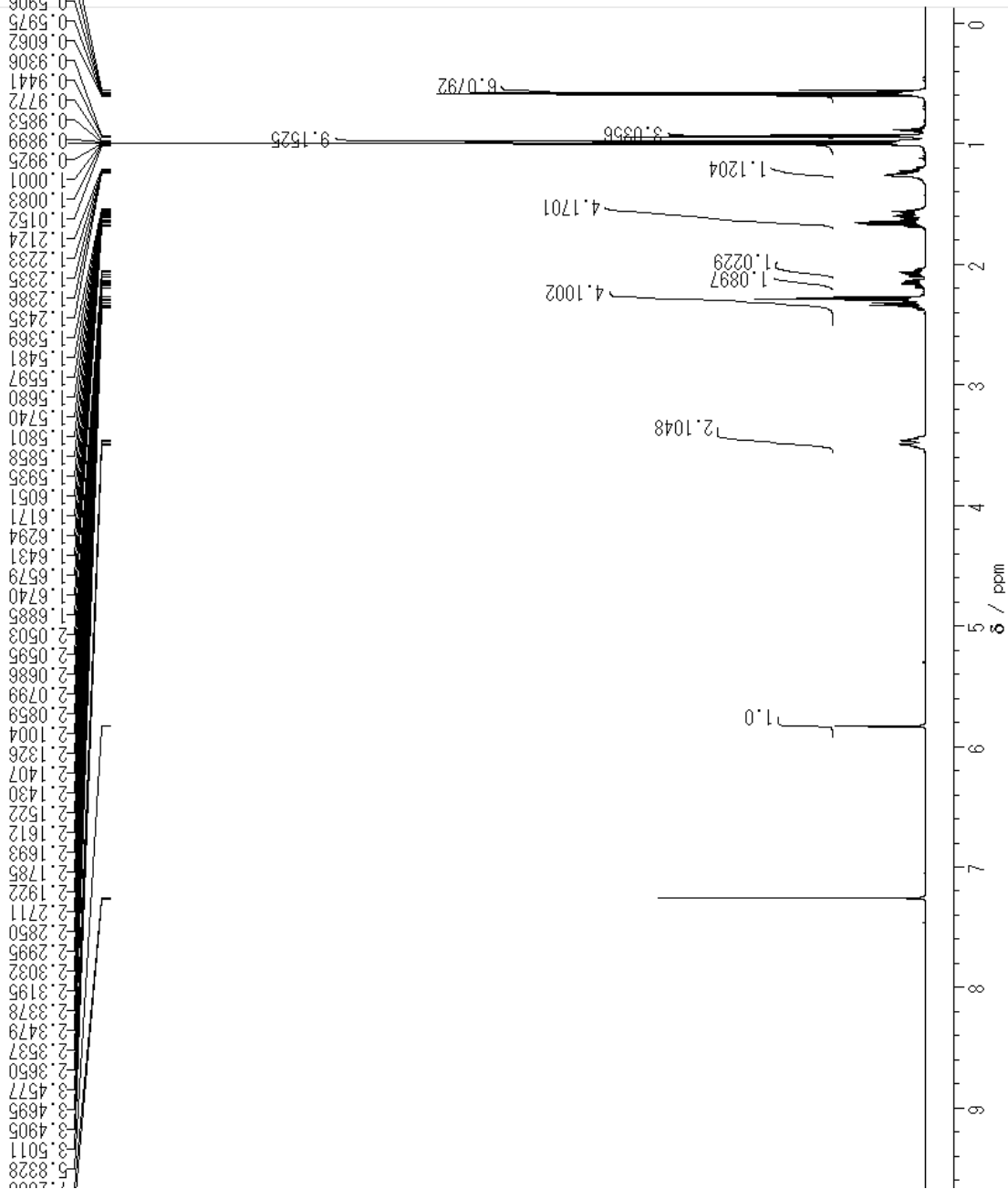
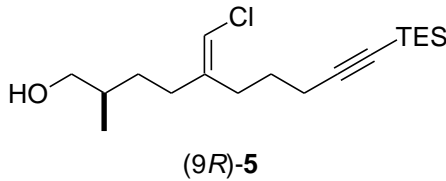


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 AcqTime 1.7459 s
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 Pulse1 6.02 μs
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 Printed 2022/Jan/26 19:02:19
 Operator

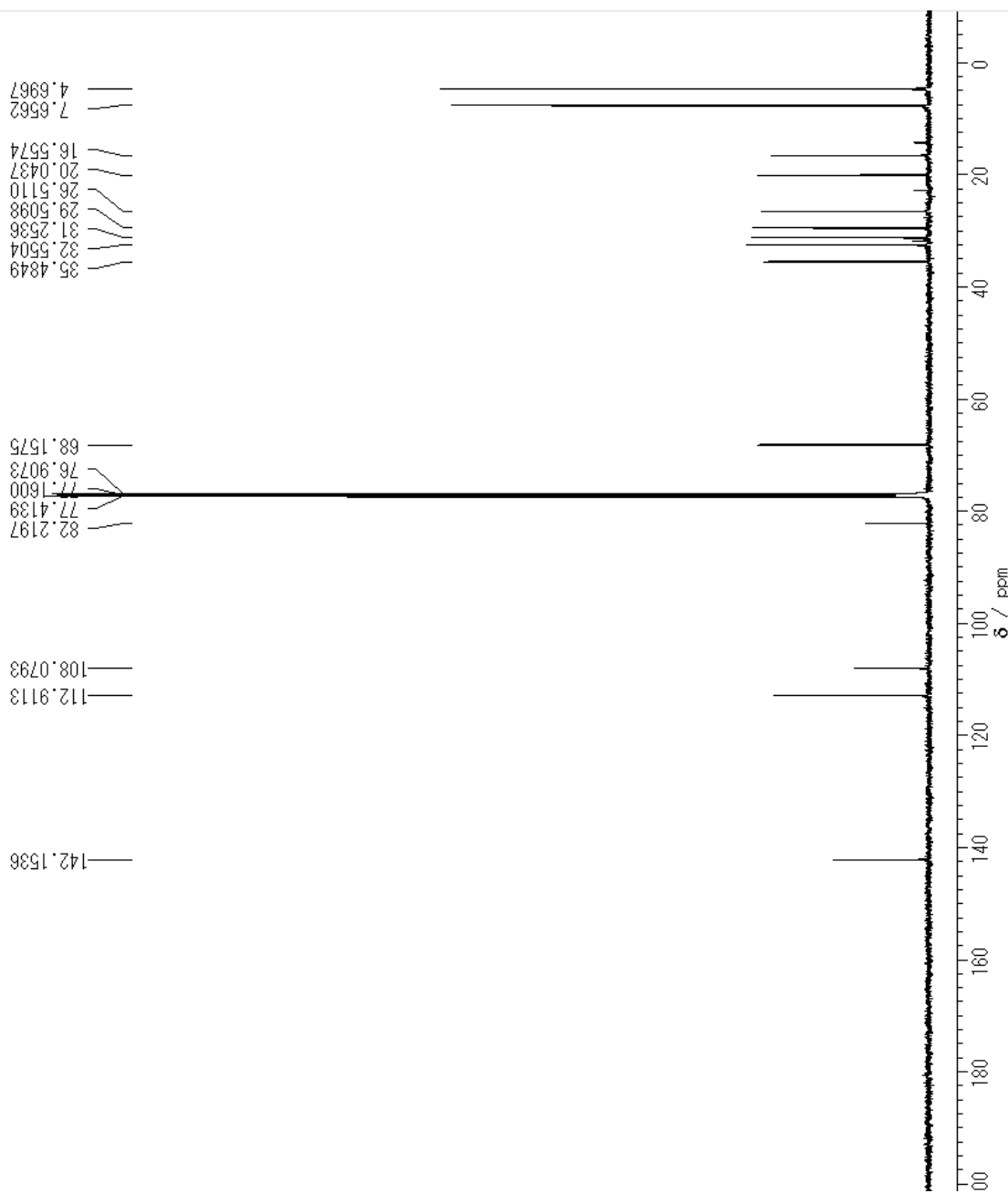
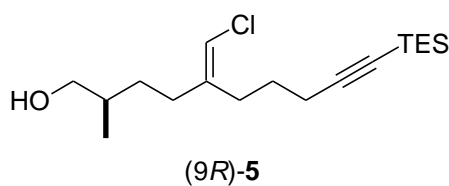




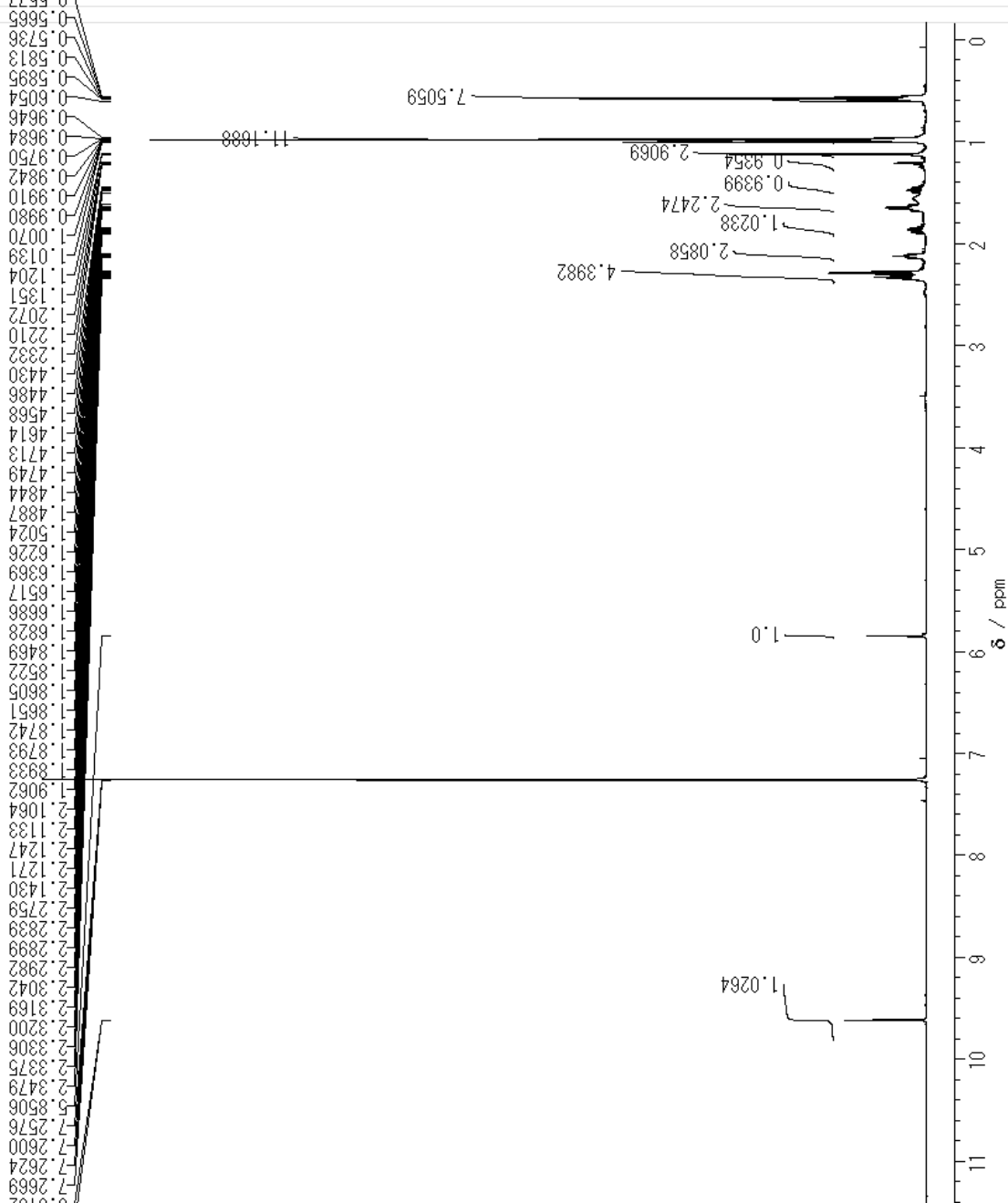
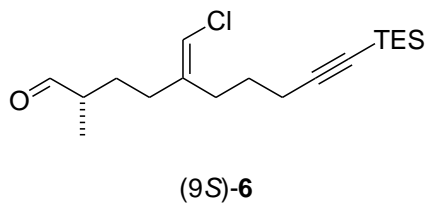
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 8-LIBH4-H PROTON-3-ALS
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 ObsSet 0.0 kHz
 ObsFine -81.5849 Hz
 Point 13180
 Frequency(Span) 7506.82 Hz
 Scap 16
 AcqTime 1.7477 s
 PD 4.0 s
 Pulse 5.7 μs
 Temperature 22.5 °C
 Solvent CHLOROFORM-D
 Reference 7.26 ppm
 Broad.Factor 0.25 Hz
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 Printed 2022/Jan/26 18:08:08
 Operator

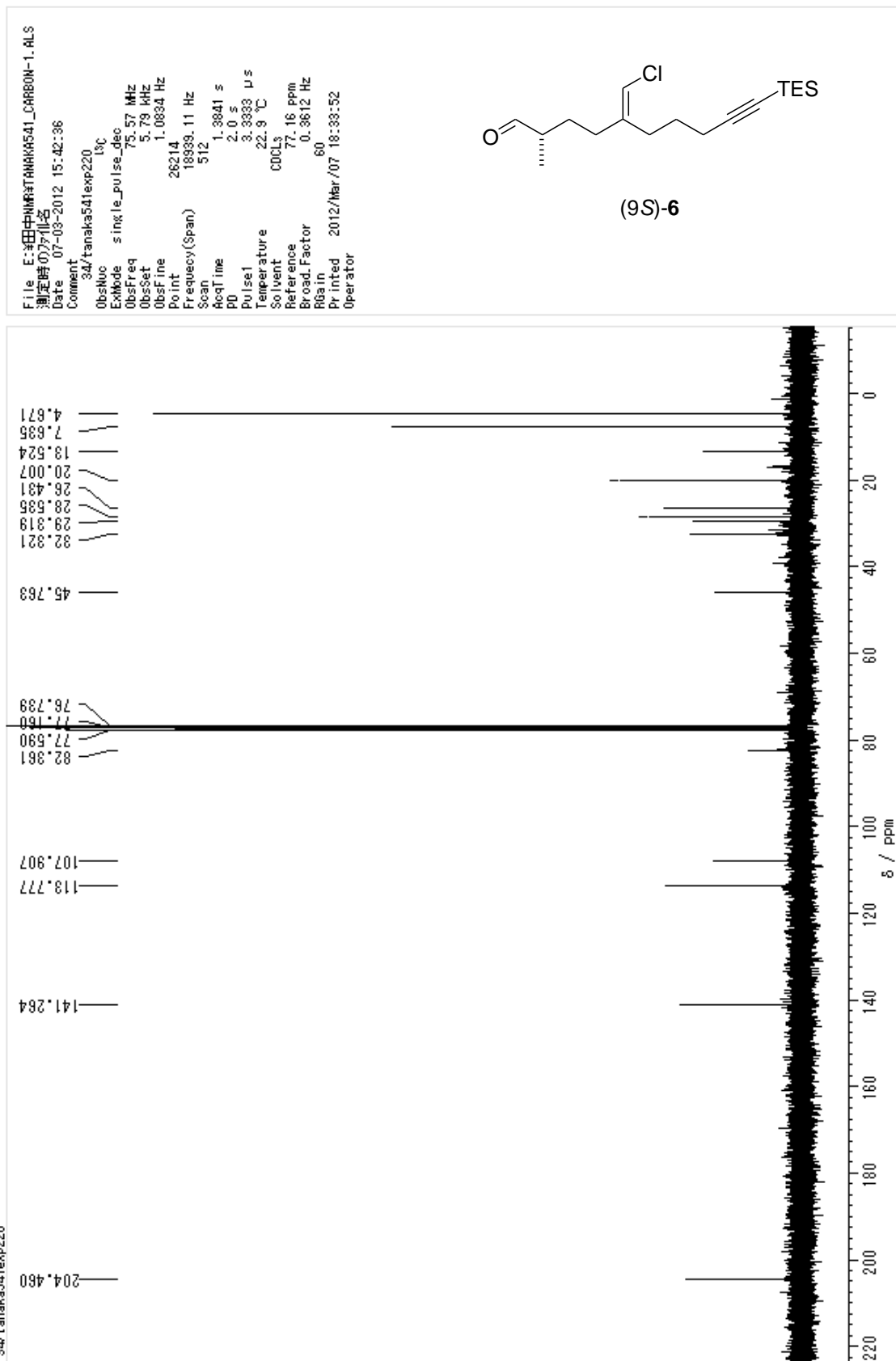


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 ObsSet: -5.0 kHz
 ObsFine: 313.4247 Hz
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 Frequency(Span): 31444.86 Hz
 Scan: 1024
 AcqTime: 0.834 s
 PD: 2.0 g
 Pulse1: 4.1817 μ s
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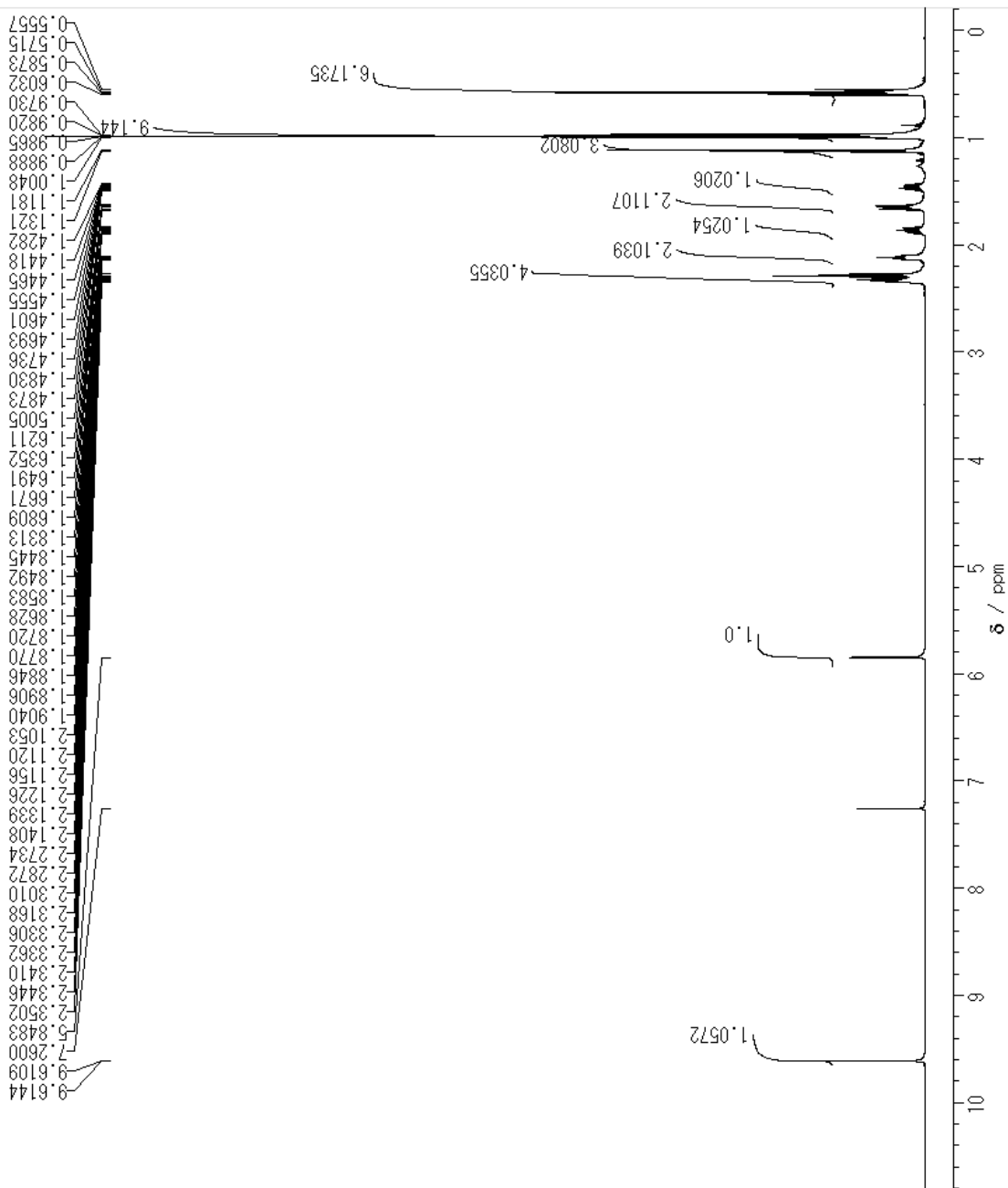
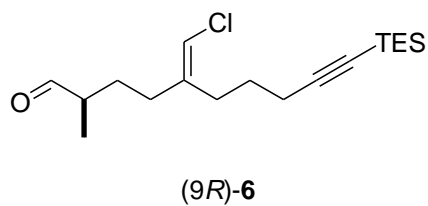


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 ObsSet 0.0 kHz
 ObsFine -81.5849 Hz
 Point 13120
 Frequency(Span) 7506.82 Hz
 Scan 16
 AcqTime 1.7477 s
 PD 4.0 s
 Pulse1 5.7 μ s
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 Solvent CHLOROFORM
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 Printed 2022/Jan/26 19:15:36
 Operator

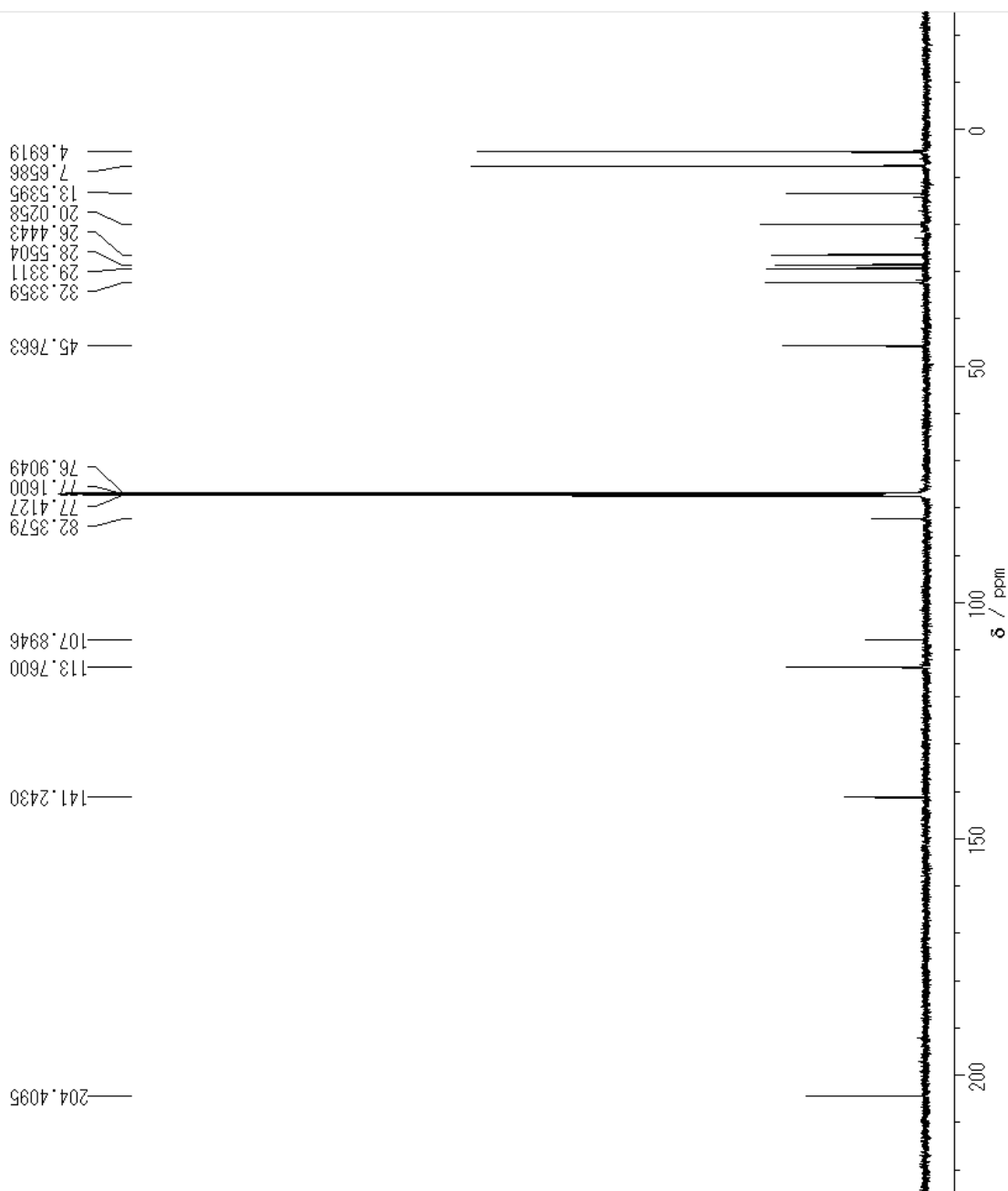
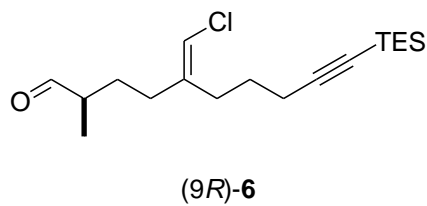


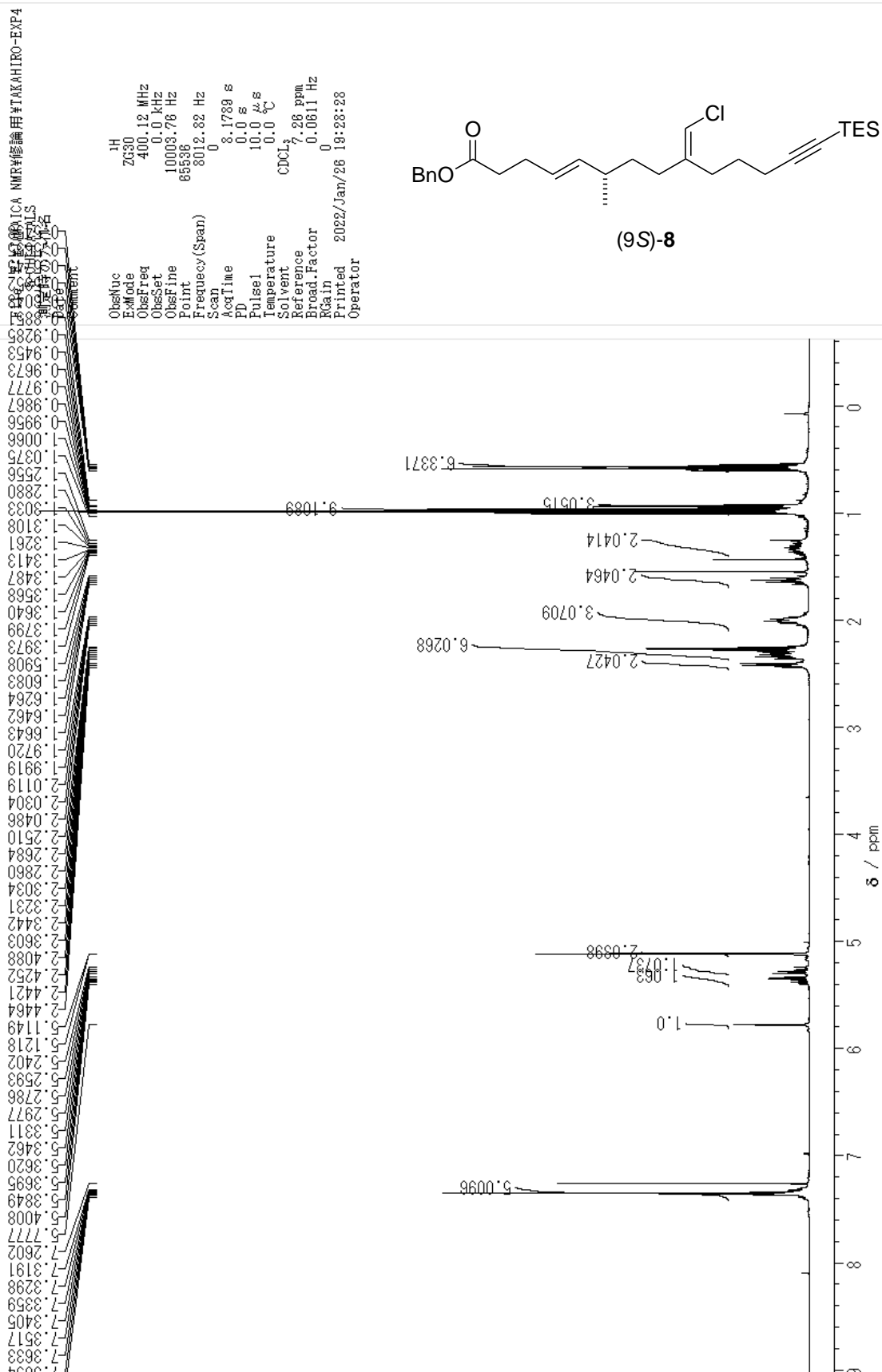


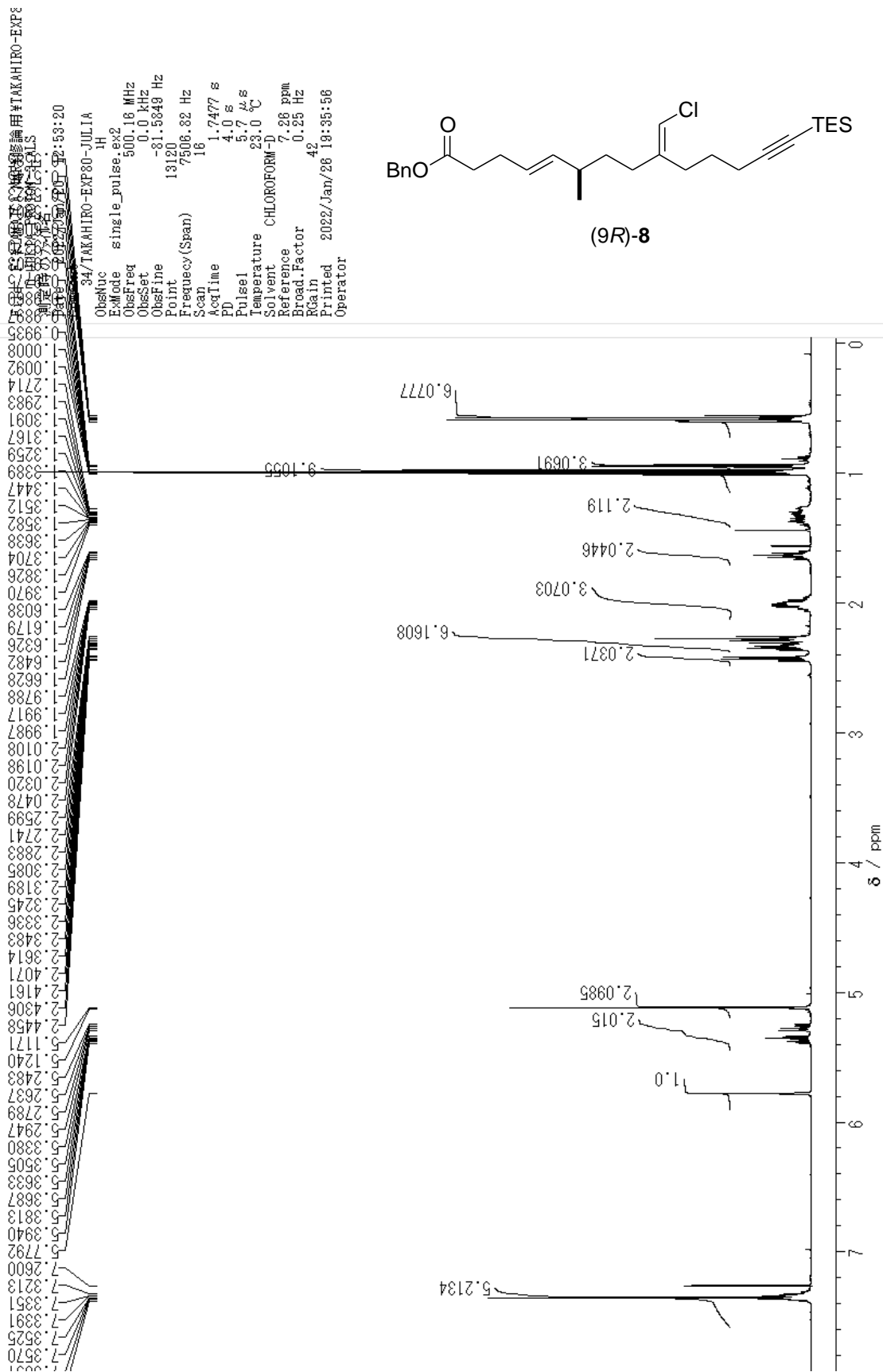
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 Operator



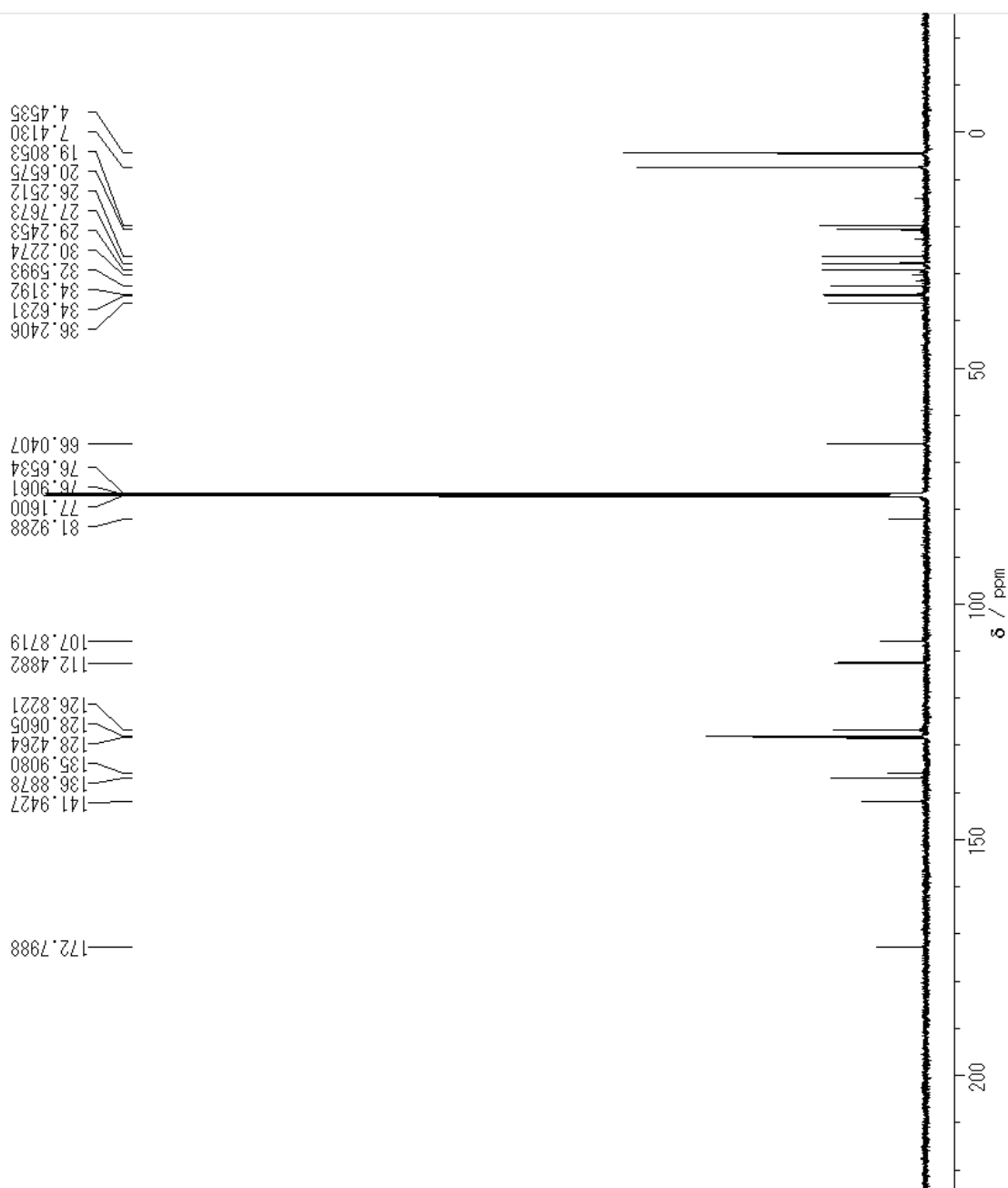
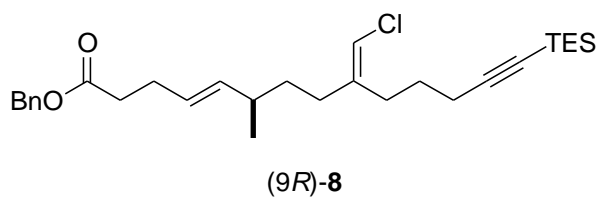
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 Frequency(Span) 31444.86 Hz
 Scan 1024
 AcqTime 0.834 s
 PD 2.0 s
 Pulse 4.1817 μ s
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 Solvent CHLOROFORM-D
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 Broad.Factor 0.25 Hz
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 Printed 2022/Jan/28 12:58:29
 Operator



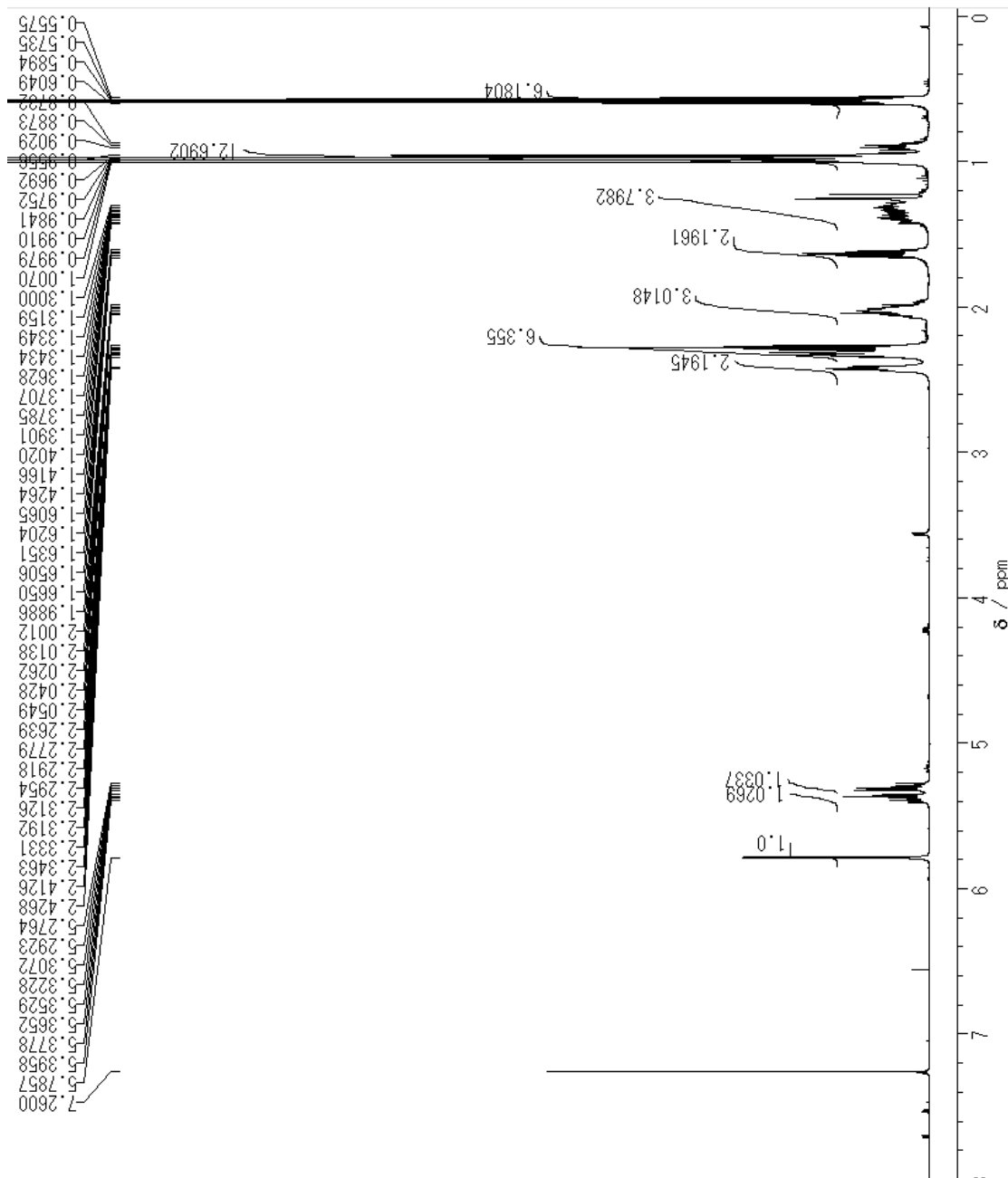
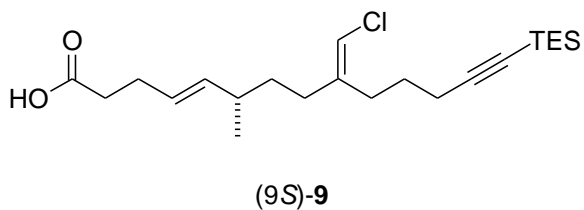




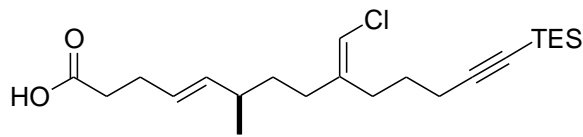
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 ObsSet -5.0 kHz
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 Scan 1024
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 PD 2.0 s
 Pulse 4.1917 μ s
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 Operator



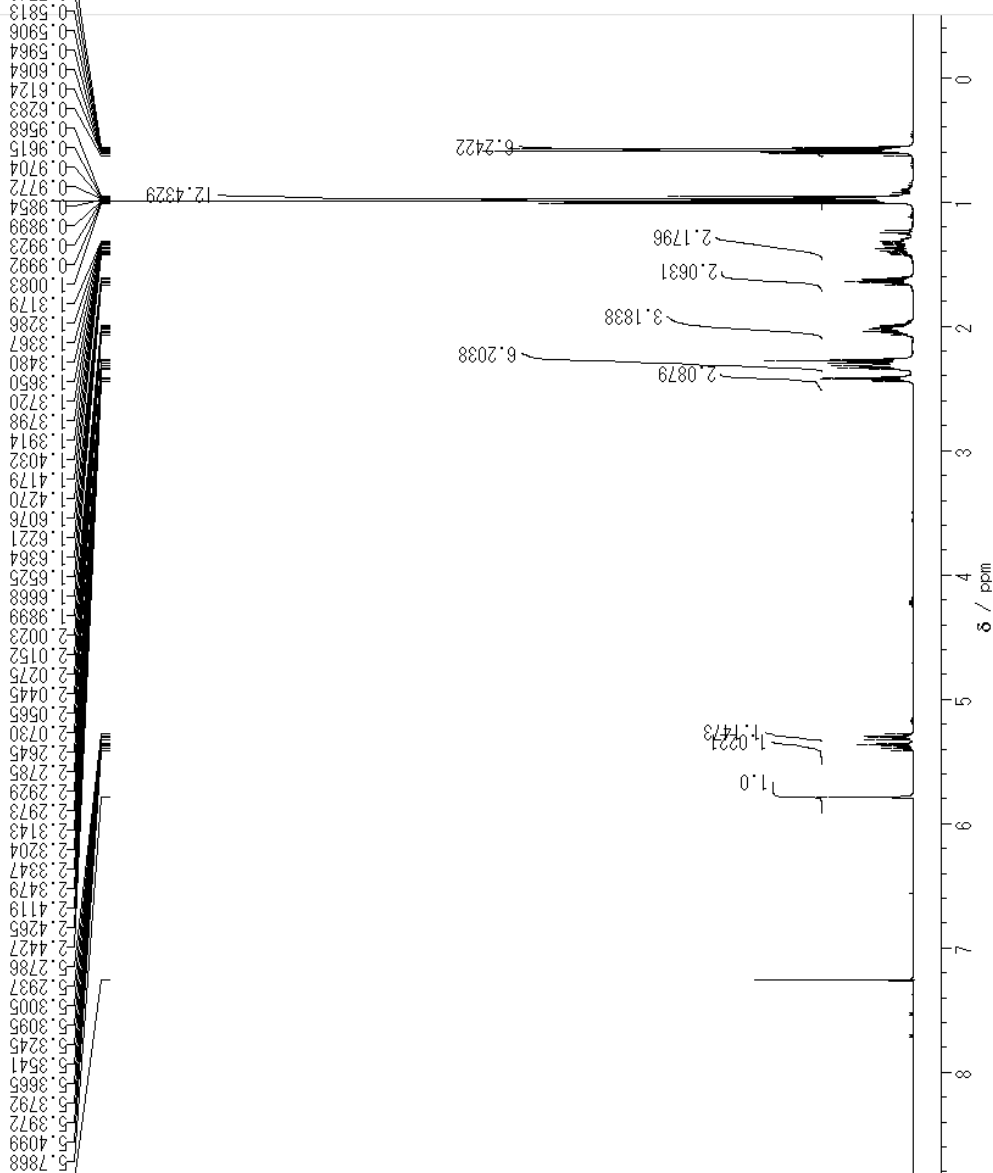
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 6-KOH-PROTON-3.MLS
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 Scan 16
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 Pulse 5.7 μs
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 RGain 38
 Printed 2022/Jan/26 19:42:20
 Operator



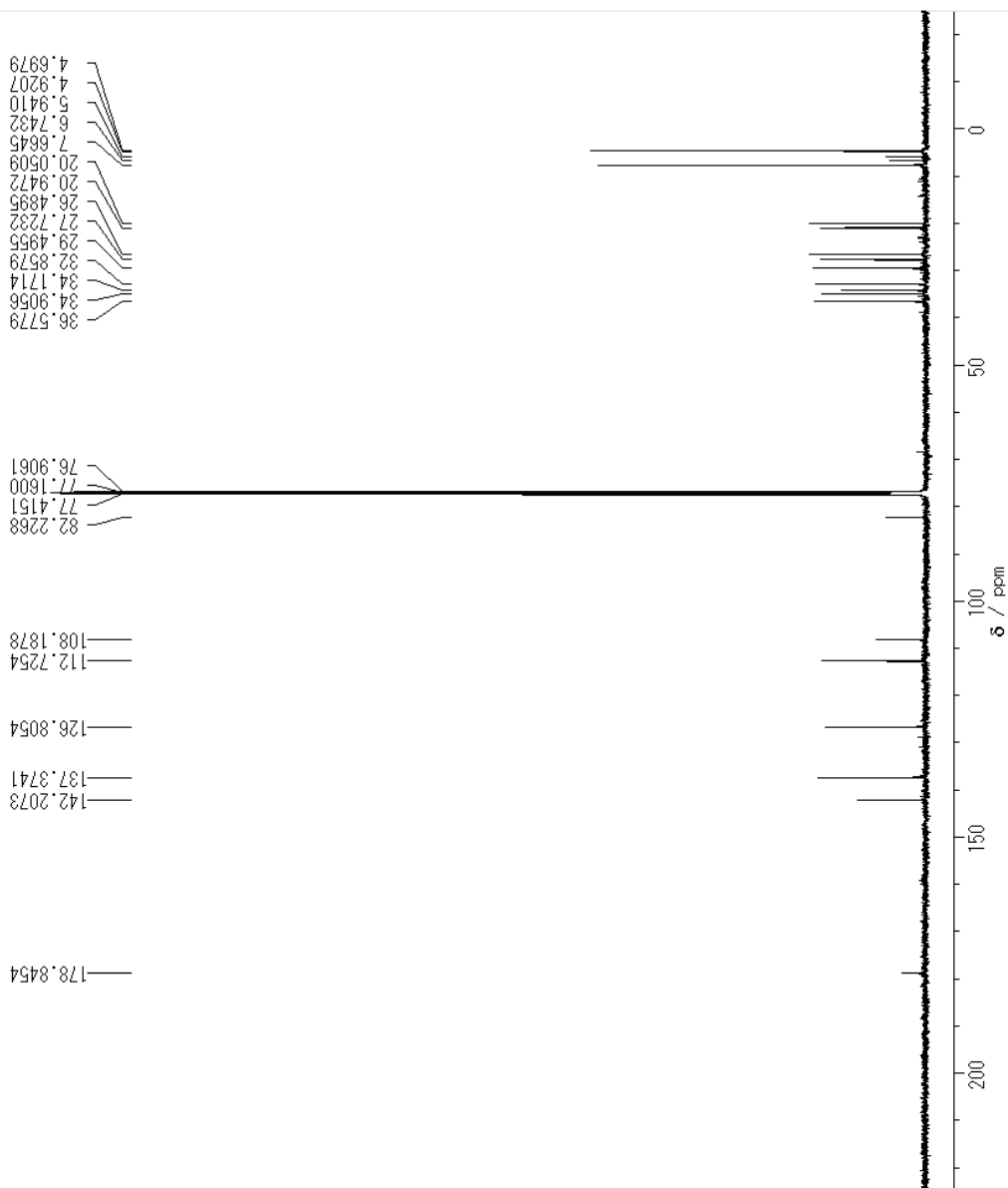
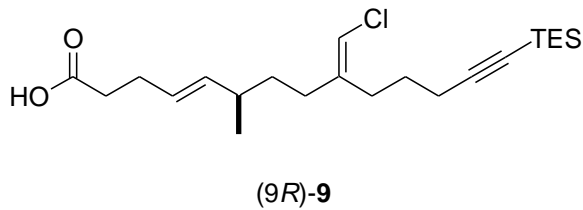
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 Operator



(9R)-9



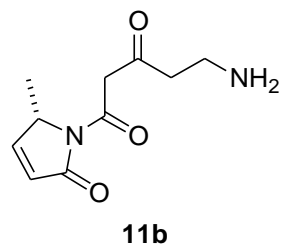
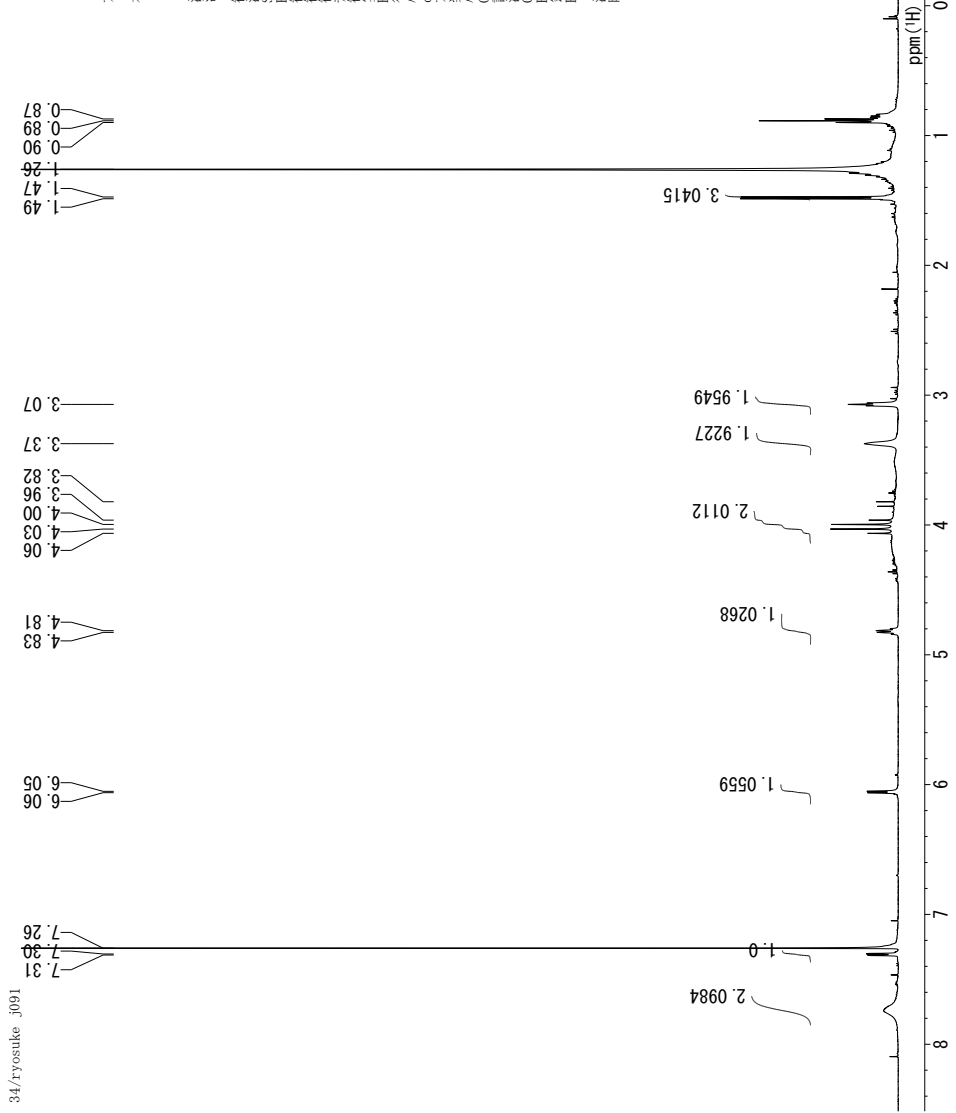
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 Operator



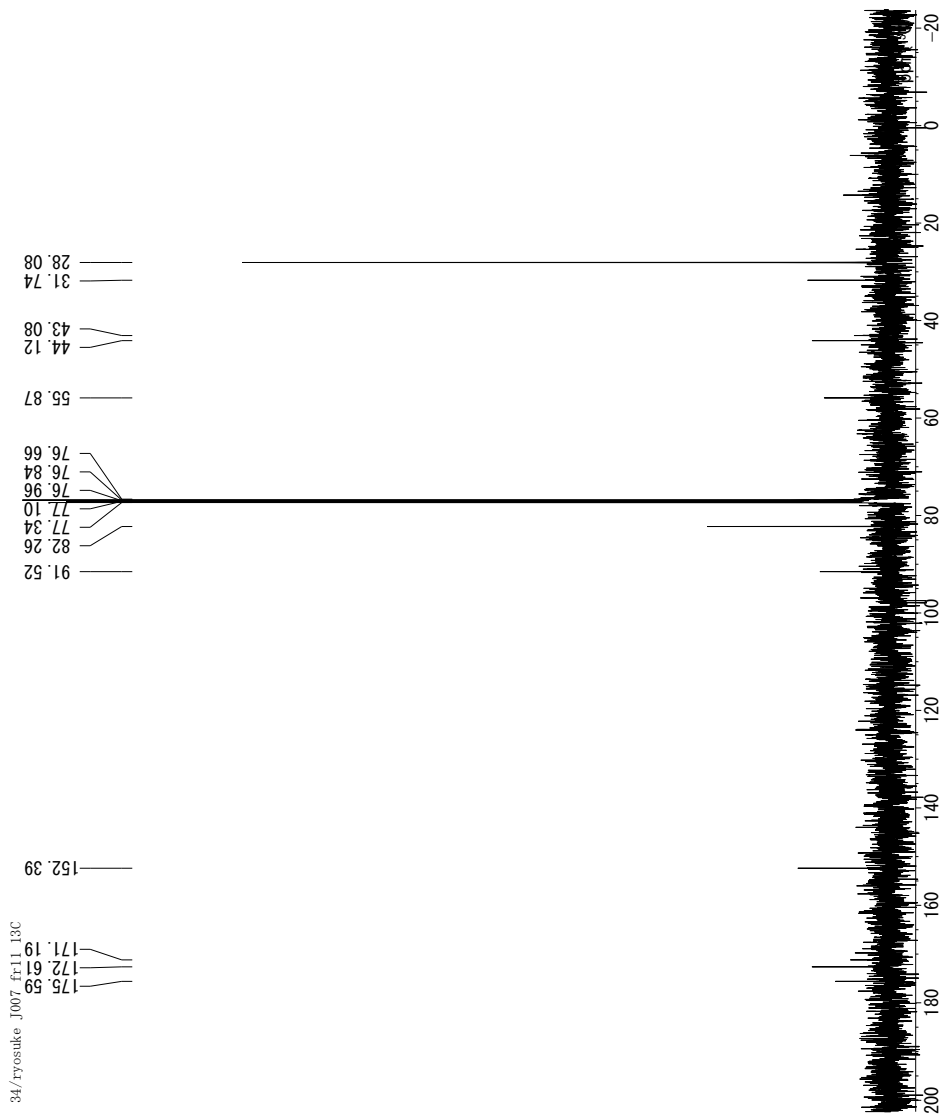
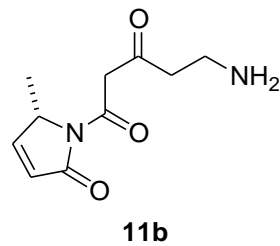
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 注釈

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 F2 (0 ppm) 500.152409813 MHz
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 観測周波数fine 6.0092 Hz
 フェーズ角 13120
 観測範囲 7507.393 Hz
 実観測回数 200
 FID取込時間 1.7459 s
 待ち時間 4.0 s
 入射幅 5.7 Hz
 decouple核種 ¹³C
 装置 ALICE
 入射波 577 MHz
 試料温度 38度
 測定溶媒 CDCl₃
 測定溶媒 25.4 °C
 Chemical shift参照値 7.26 ppm
 Broadening係数 0.2861 Hz
 窓関数 Exponential
 Receiver Gain 54

測定者
 印刷日時 2023/Dec/19 10:12:15



7144名 D:\USBNMR\NMR_以隣前~2022\J007_13
 C DIKETONE ROC DEPROTECTION_RMI
 初期714名 D:\USBNMR\NMR_以隣前~2022\RYO
 SUKE_J007_FR11_13C_CARBON-9_IDF
 測定日時 12/May/2022 18:17:52
 注釈
 34/ryosuke_J007_fr11_13C
 観測核種 single_pulse_dc
 SFO (ppm) 195.765311267 MHz
 Freq. (0 ppm) 125.752735994 MHz
 観測周波数(組) 125.77 MHz
 観測周波数offset -5.0 kHz
 観測周波数fine 314.6243 Hz
 テーポイント数 26224
 観測範囲 31456.86 Hz
 取得時間 14
 待機時間 0.8336 s
 待ち時間 2.6767 s
 観測核種 H
 decouple核種 H
 7144名
 装置 ECA 500
 観測核種 ^{13}C
 Gradient プログラム
 試料温度 23.0 °C
 測定溶媒 CHLOROFORM-D
 Chemical shift 参照値 100.0 ppm
 Decoupling モード 2.5 Hz
 観測数 Exponential
 Receiver gain 64
 測定者
 印刷日時 2023/Dec/19 10:16:20

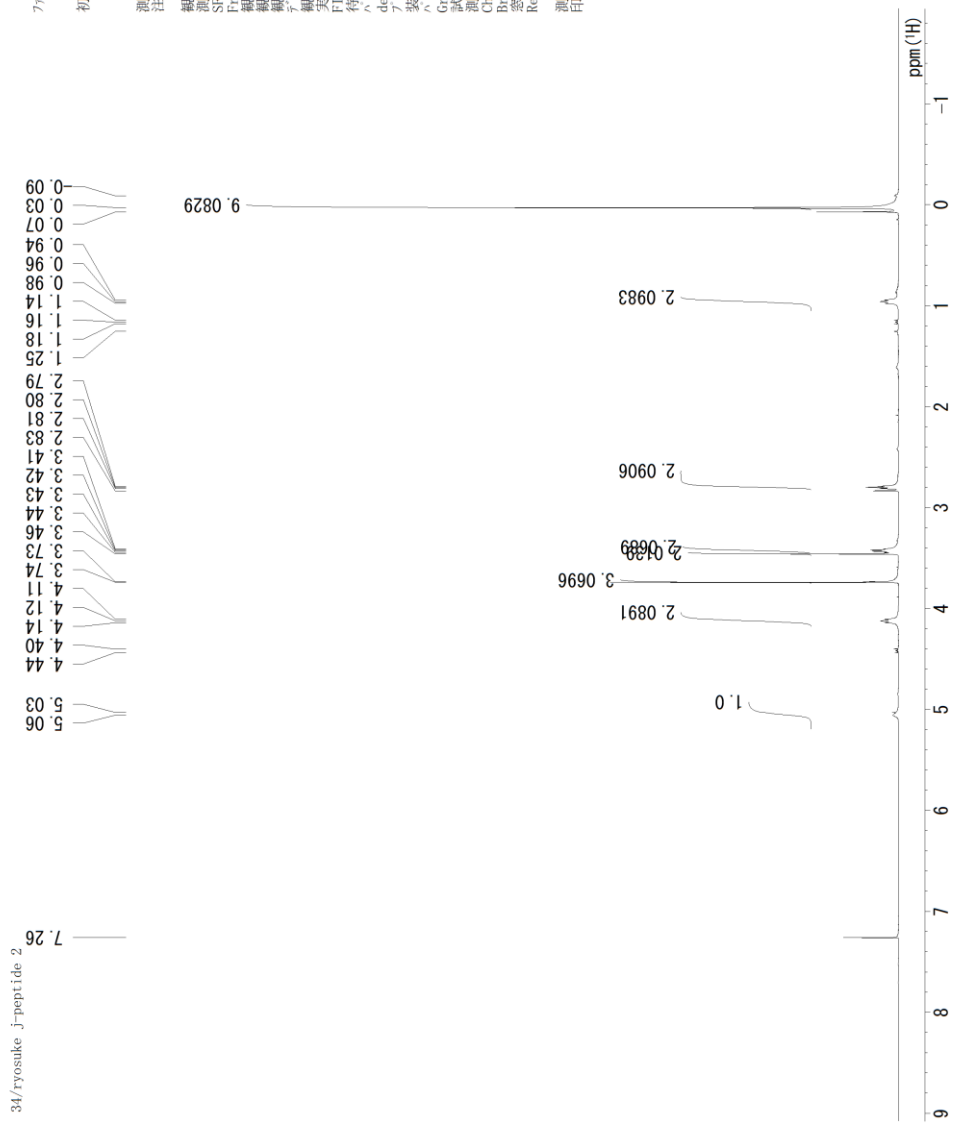
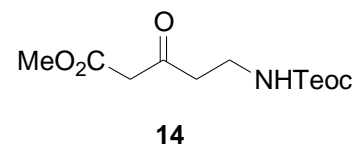


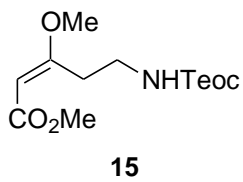
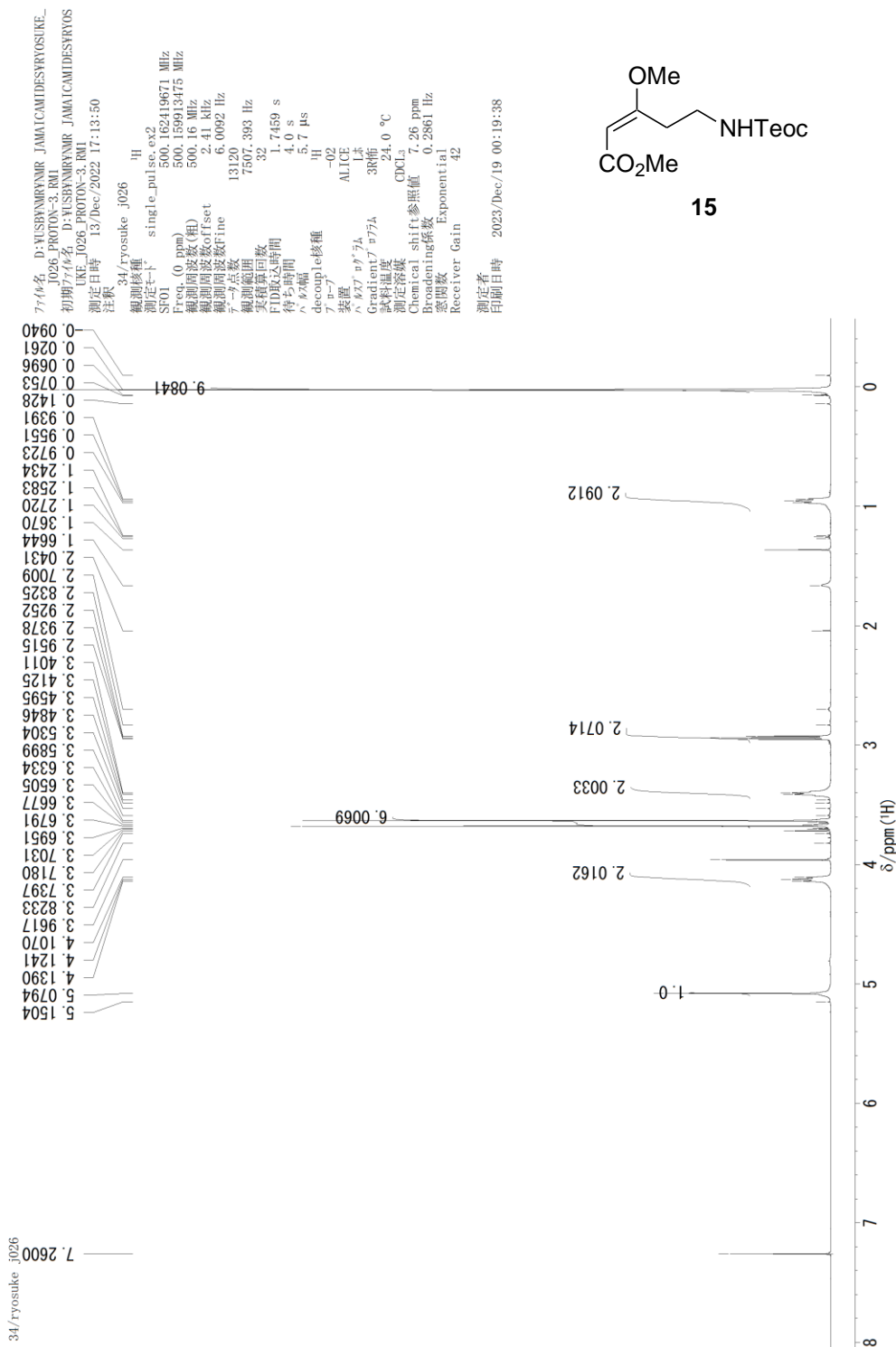
34/ryosuke_j-peptide 2

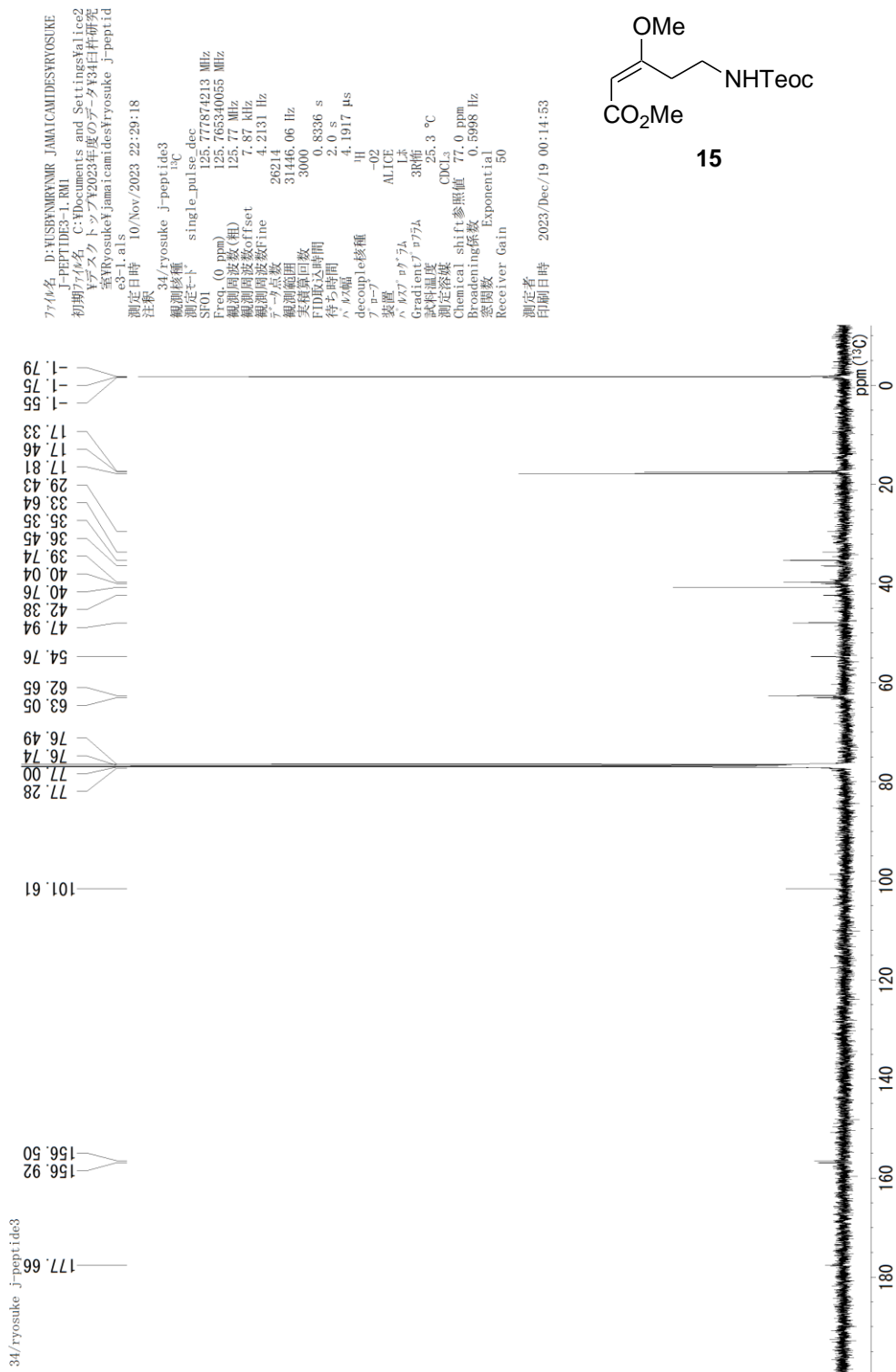
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 MI
 初期ファイル名 C:\Documents and Settings\alice2
 浅田亮介\デスクトップ\2023年度のアーカイブ\研究
 至\ryosuke\jama\camidesryosuke_j-peptide
 c\PROTON-3_6
 測定日時 10/Nov/2023 15:16:28
 注釈

34/ryosuke_j-peptide 2
 観測核種 ¹H
 測定モード single_pulse.ex2
 SF01 500.162416009 MHz
 Freq. (0 ppm) 500.15999813 MHz
 観測周波数(組) 500.16 MHz
 観測周波数offset 2.41 kHz
 観測周波数fine 6.0092 Hz
 テーパ点数 13120
 観測範囲 7507.383 Hz
 実掃戻回数 16
 FID貯込時間 1.7459 s
 待ち時間 4.0 s
 1/2幅 3.7 μs
 decouple核種 ¹³C
 プログラム ALICE
 核種 ¹³C
 1/2幅 17.7 μs
 観測核種 ¹³C
 観測周波数 386 MHz
 Gradient 7.774
 試料温度 25.0 °C
 測定溶媒 CDCl₃
 Chemical shift参照値 7.26 ppm
 Broadening係数 0.2861 Hz
 歪曲数 Exponential
 Receiver Gain 42

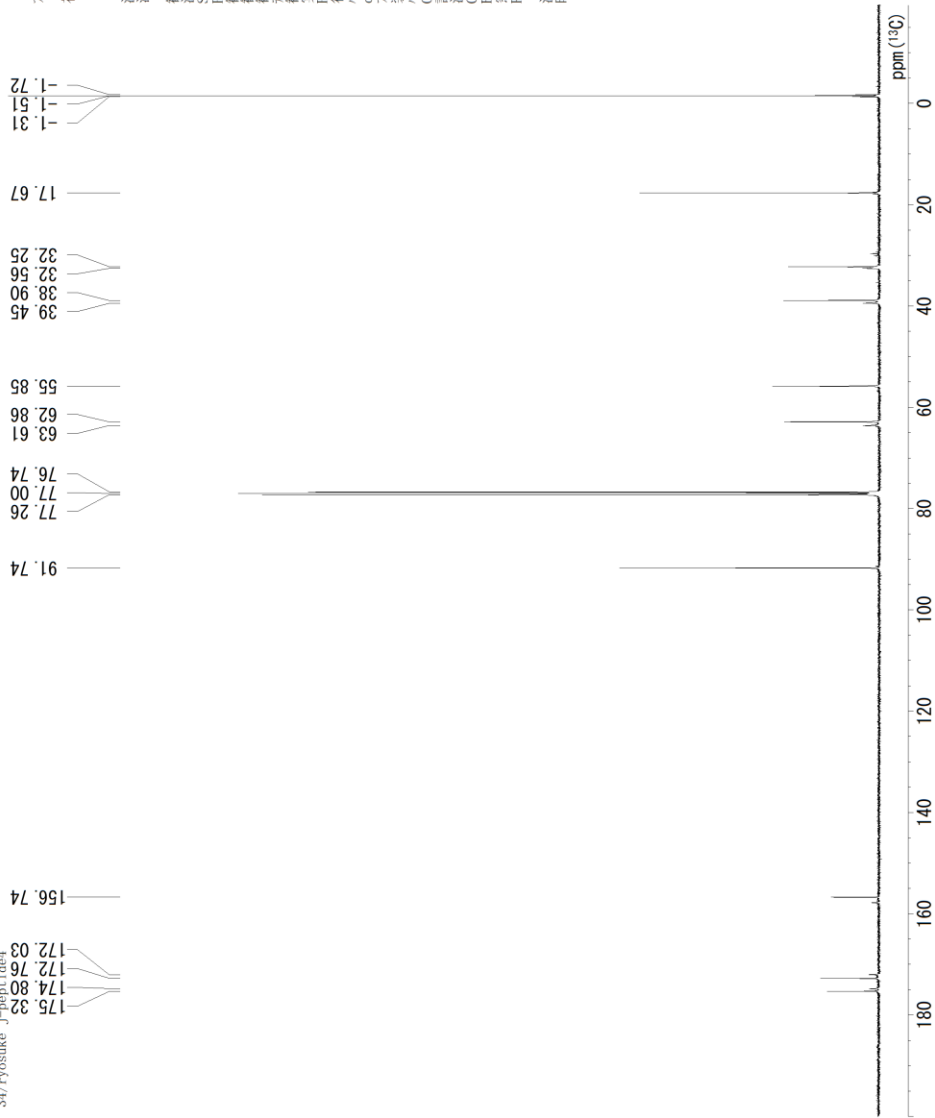
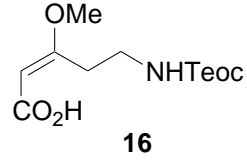
測定者
 印刷日時 2023/Dec/19 00:10:42







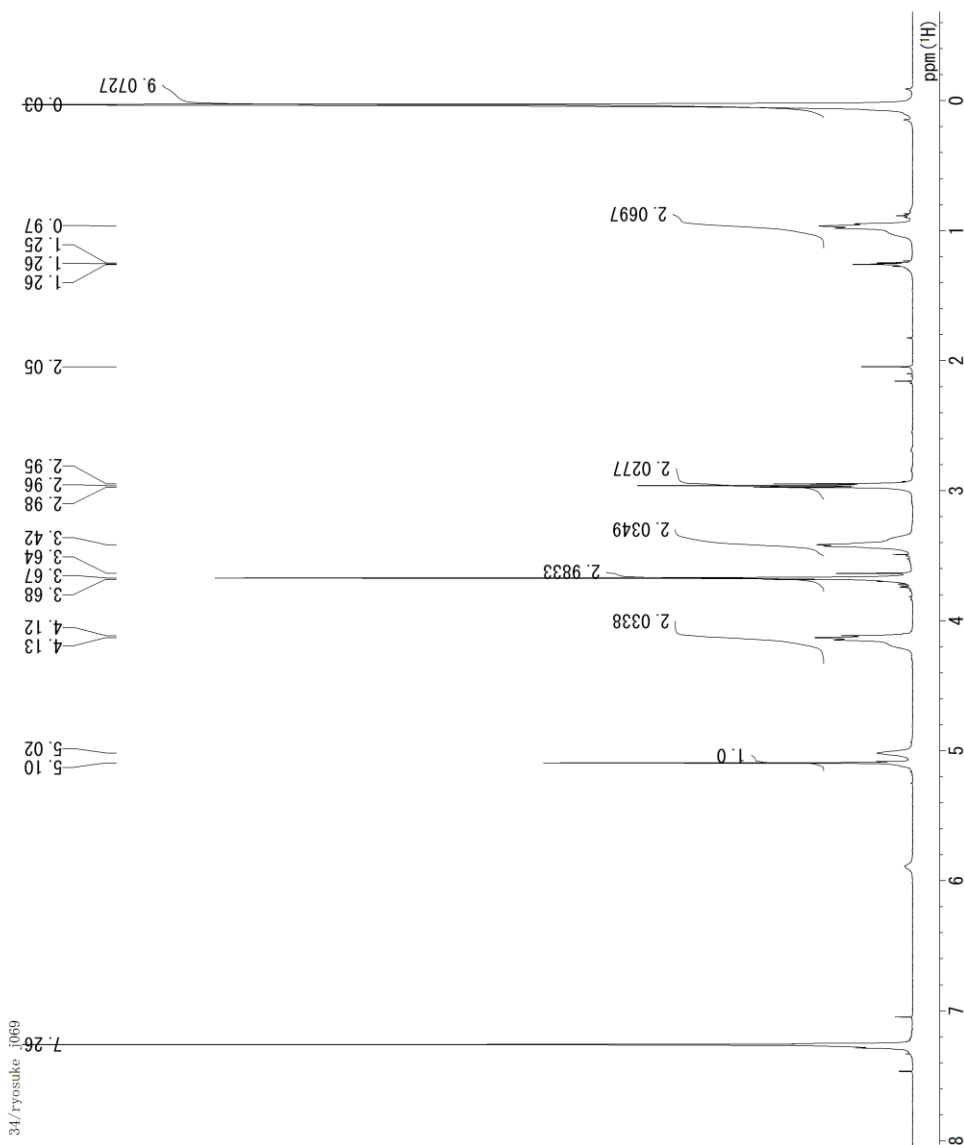
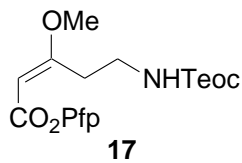
34/ryosuke_j-peptide1.ded
 34/ryosuke_j-peptide1.ded
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 J-PEPTIDE4-1.RM1
 初期ファイル名 C:\Documents and Settings\valice2
 ヴァルレストップ\2023年度のデータ\34日付研究
 室\RYOSUKE\jamaicamides\ryosuke_j-peptide
 e4-1.a1s
 測定日時 10/Dec/2023 00:56:59
 注釈 34/ryosuke_j-peptide1
 編測核種 ¹³C
 測定モード single_pulse_dec
 SFO1 125.777874213 MHz
 Freq. (0 ppm) 125.765310068 MHz
 編測周波数(相) 125.77 MHz
 編測周波数offset 7.87 kHz
 編測周波数Fine 4.2131 Hz
 テーパ点数 26214
 編測範囲 31446.06 Hz
 実積算回数 3000
 FID取込時間 0.8336 s
 待ち時間 2.0 s
 へルム 4.1917 μs
 decouple核種 H
 振数 402
 ALICE
 647.975A
 Gradient 38階
 試料温度 25.3 °C
 測定溶媒 CDCl₃
 Chemical shift 参照値 77.0 ppm
 Broadening係数 0.5998 Hz
 窓関数 Exponential
 Receiver Gain 54
 測定者 印刷日時 2023/Dec/19 00:21:58

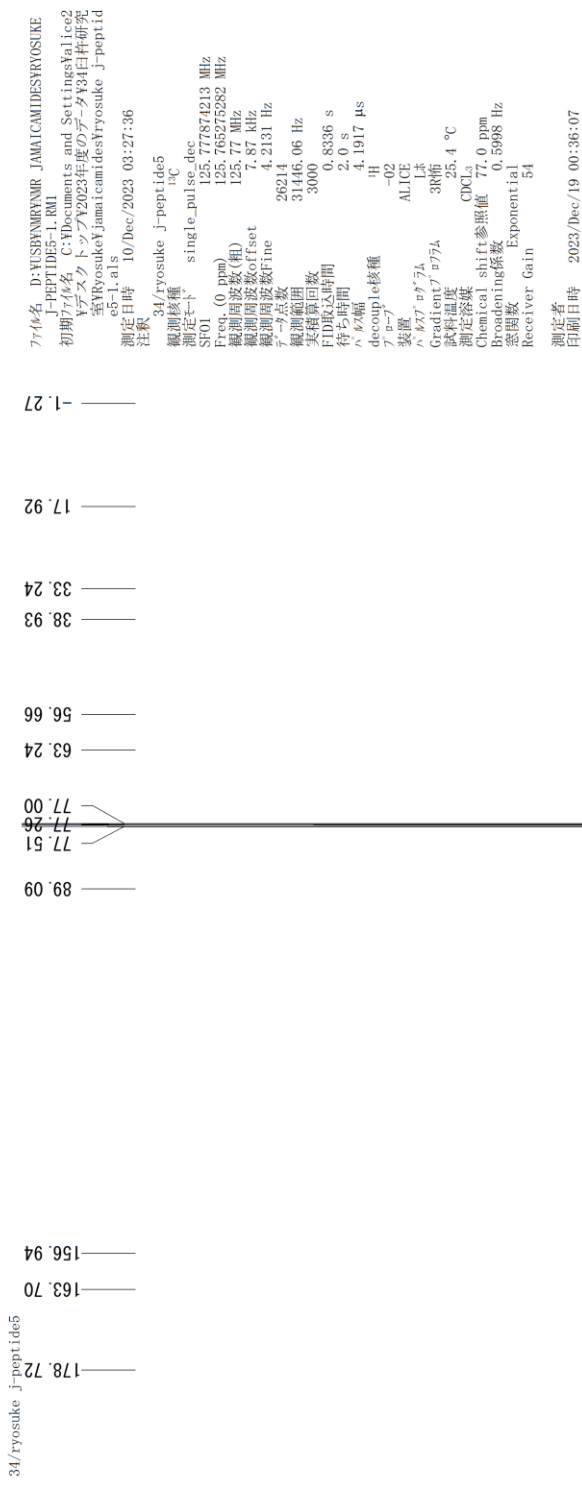


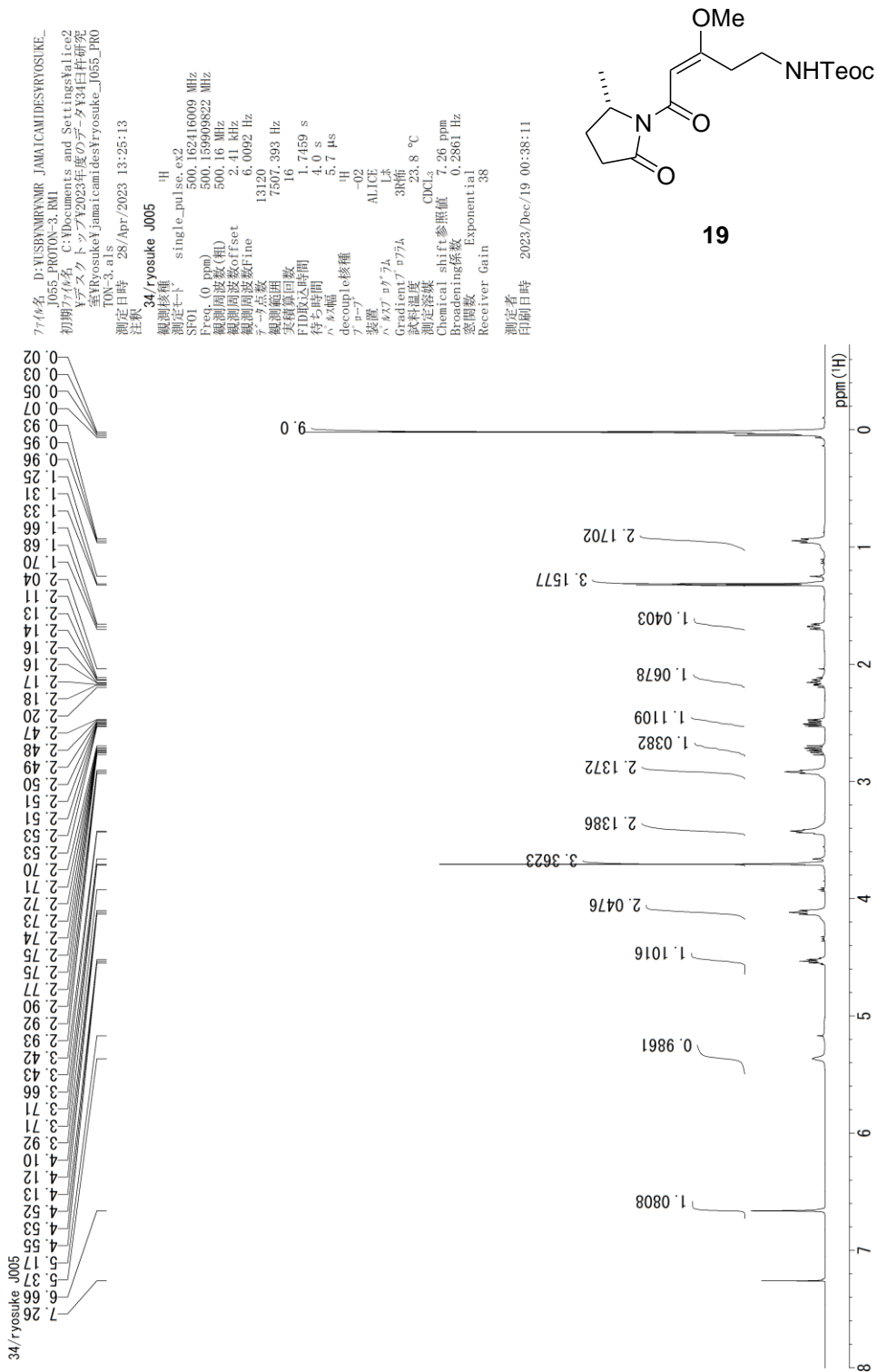
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 測定日時 06/Sep/2023 12:36:44
 注家 34/ryosuke_069

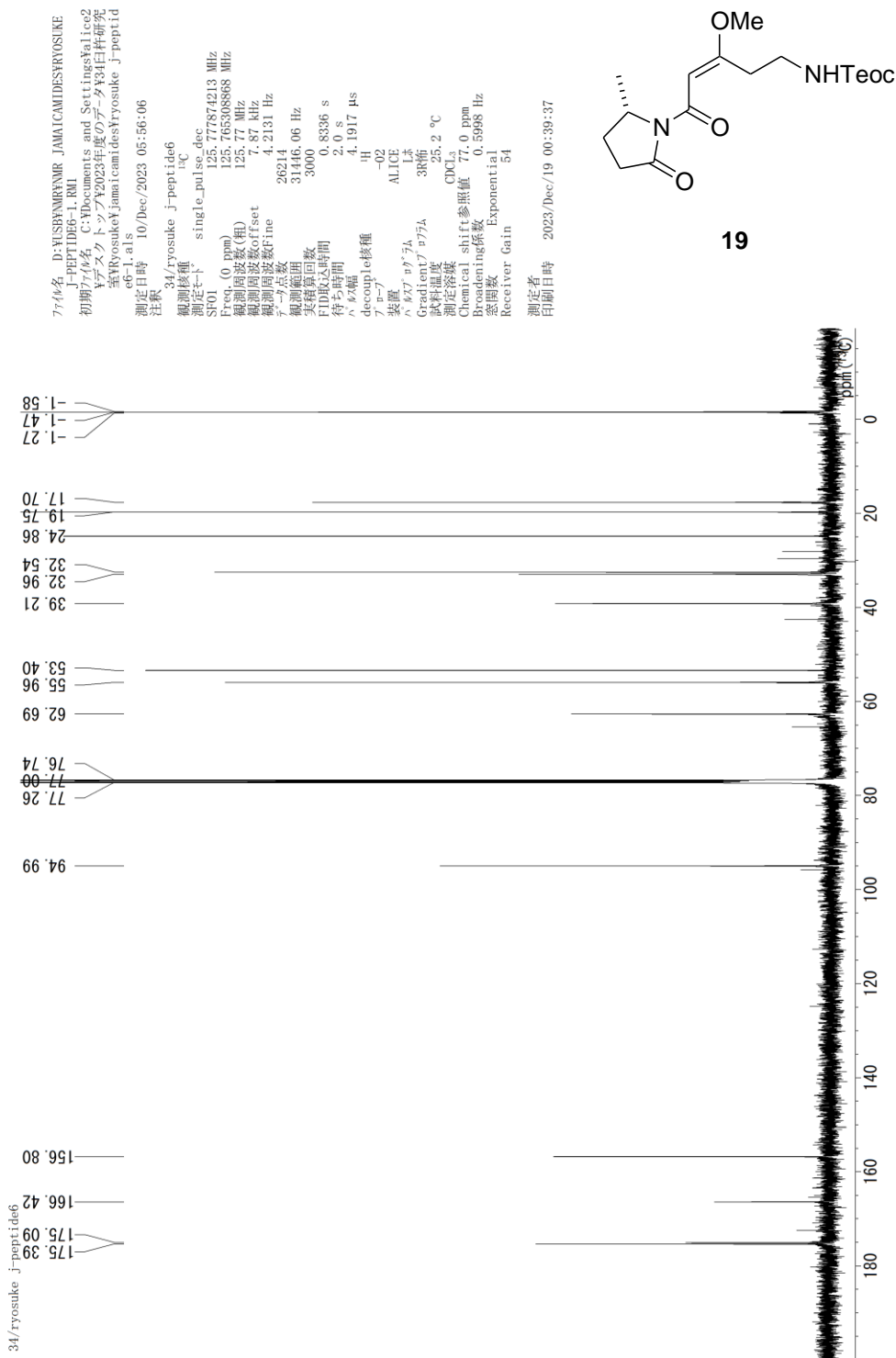
観測核種 1H
 測定モード single_pulse.et2
 P1 (s) 500.162416009 MHz
 P2 (s) 500.156909813 MHz
 観測周波数(観) 500.16 MHz
 観測周波数Offset 2.41 kHz
 観測周波数Offset 6.0082 Hz
 フェーズ数 13120
 観測周波数 7507.393 Hz
 実観測回数 16
 FID取り時間 1.7459 s
 待ち時間 4.0 s
 核種 1H
 decouple核種 13C
 プログラム ALICE
 装置 ALICE
 実験者 38
 Gradient プログラム 38
 Gradient プログラム 38
 試料温度 24.4 °C
 測定溶媒 CDCl3
 Chemical shift 参照値 7.26 ppm
 Broadening 係数 0.2861 Hz
 関数 Exponential
 Receiver Gain 44

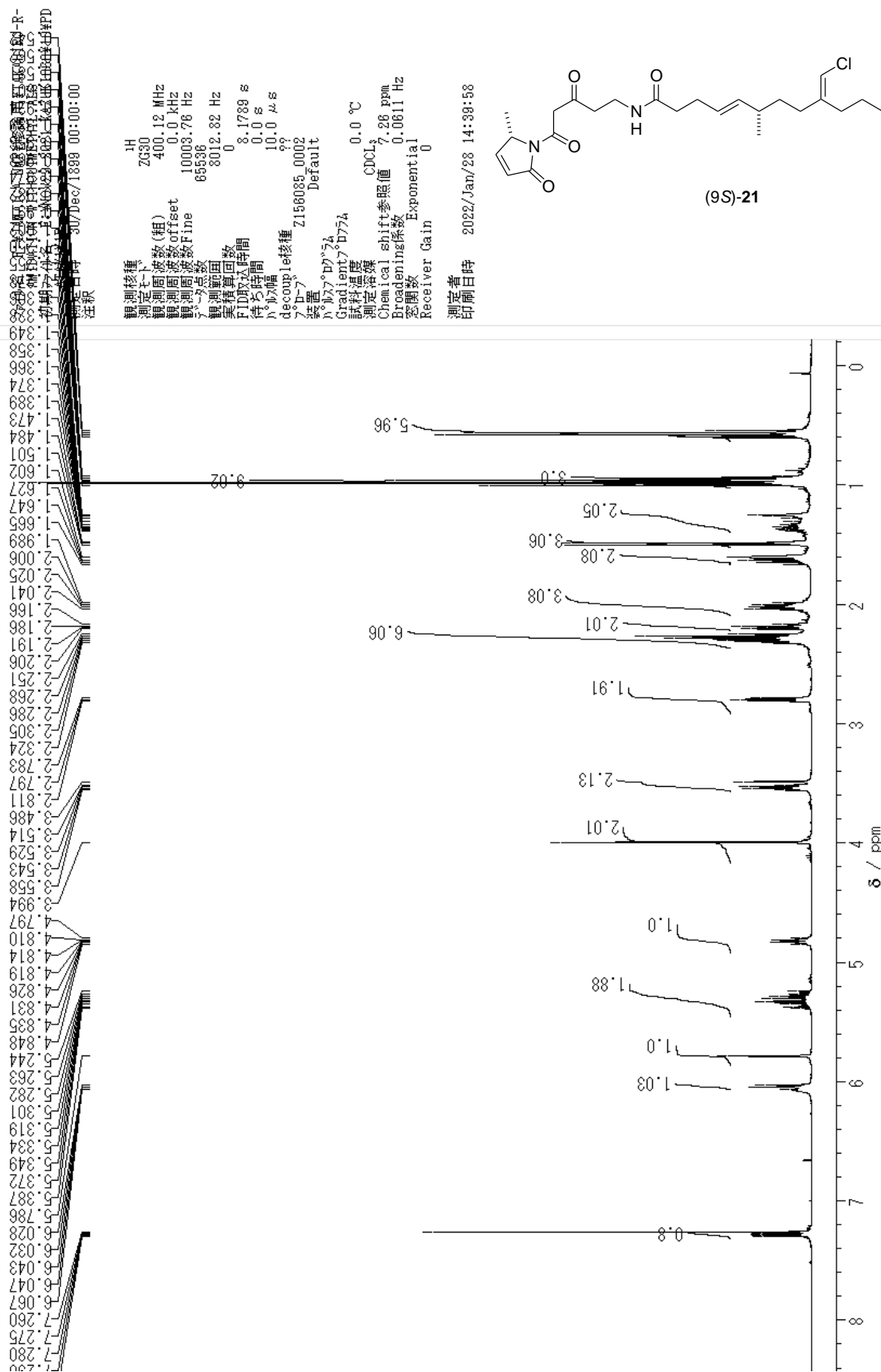
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 印刷日時





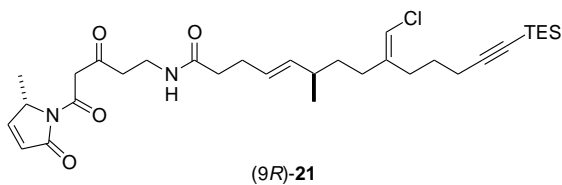




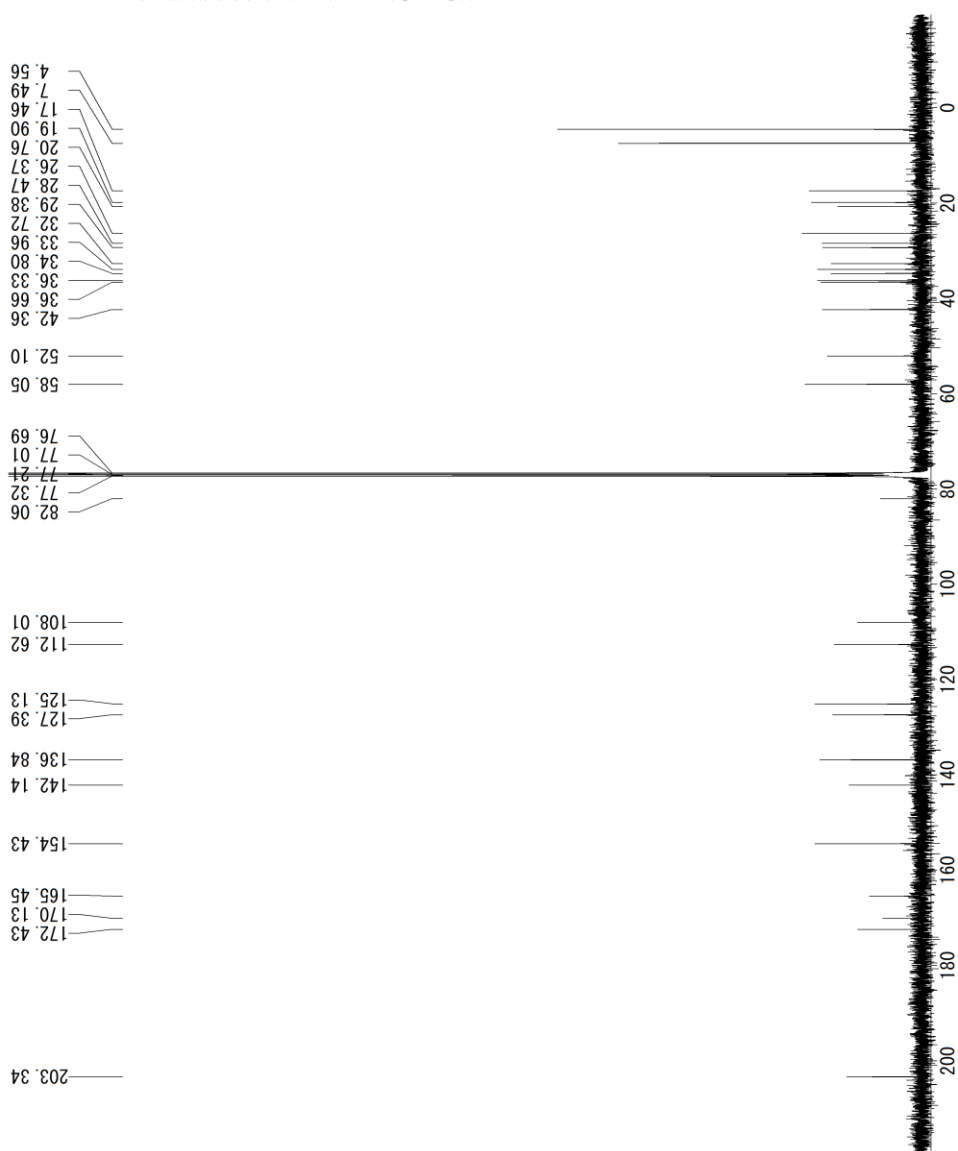


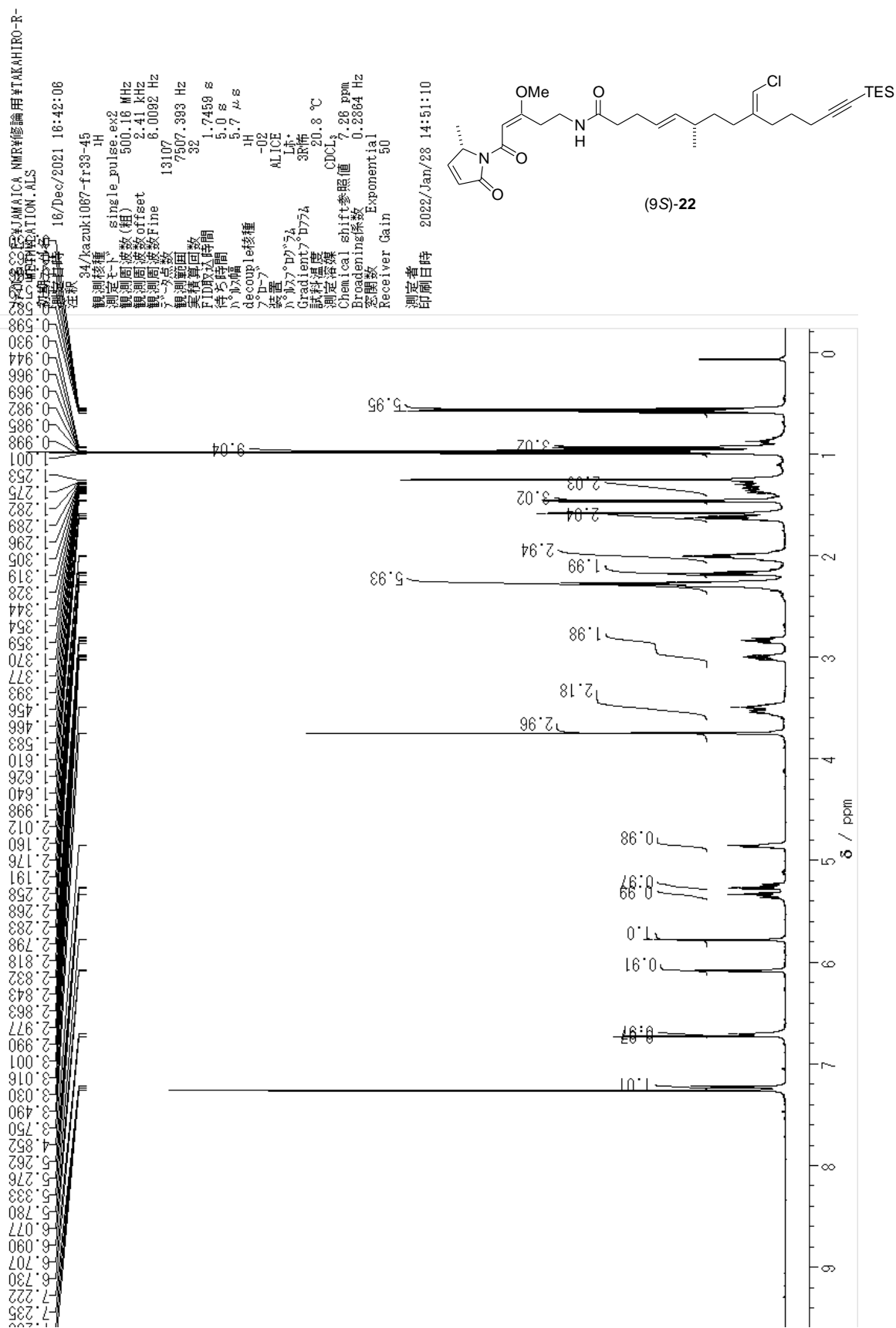
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 23-J082_13C\TOPDATA\Y111
 測定日時: 07/Aug/2023 13:57:39
 注釈:

観測核種 ¹³C
 測定モード ZFGC30
 SFO1 100.62929804 MHz
 100.612768526 MHz
 100.61 MHz
 観測周波数(相) 0.0 Hz
 観測周波数Offset 9998.688 Hz
 観測周波数Pine 24038.46 Hz
 観測周波数 1800
 観測温度 1.3631 S
 検出器 2.0 S
 FID積分時間 12.0 μs
 待ち時間
 観測モード decouple核種 OFF
 プログラム Z156085_0002 (PA BBO 400S1 BB-HK)
 装置 SPECT ZFGC30
 メーカー パナソニック
 Gradientプログラム 29.9994 °C
 試料温度 CDCl₃
 測定溶媒 Chemical shift参照値 219.4603 ppm
 Broadening係数 0.25 Hz
 窓関数 Exponential
 Receiver Gain 197

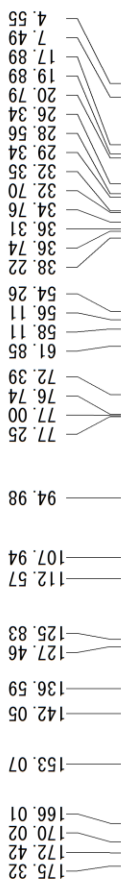


測定者 2023/Dec/19 00:41:50
 印刷日時





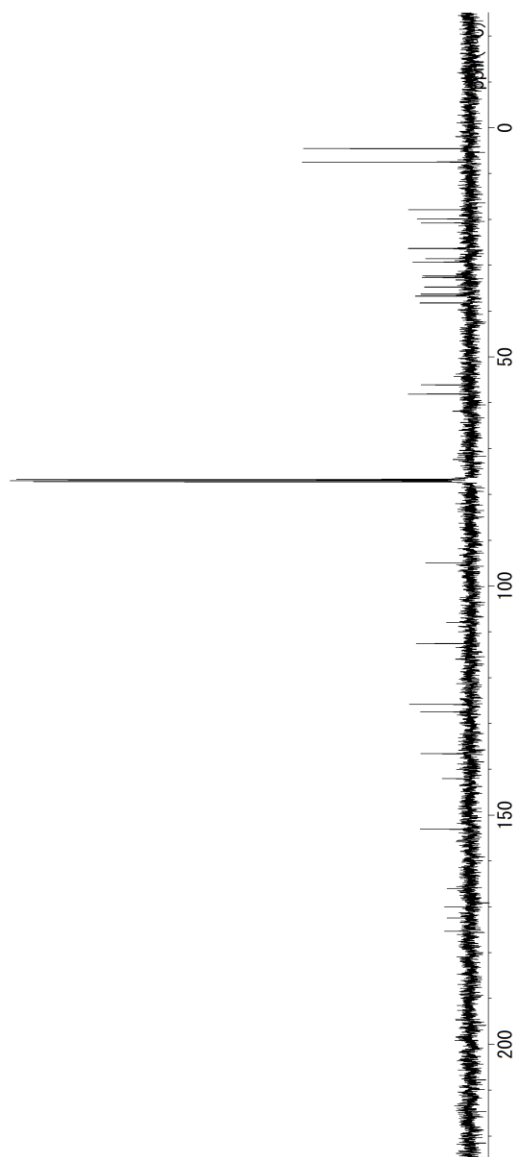
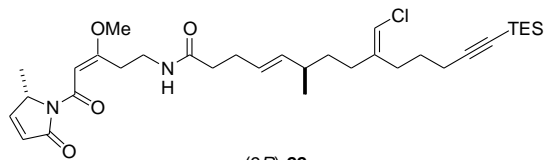
34/ryosuke_J083 C

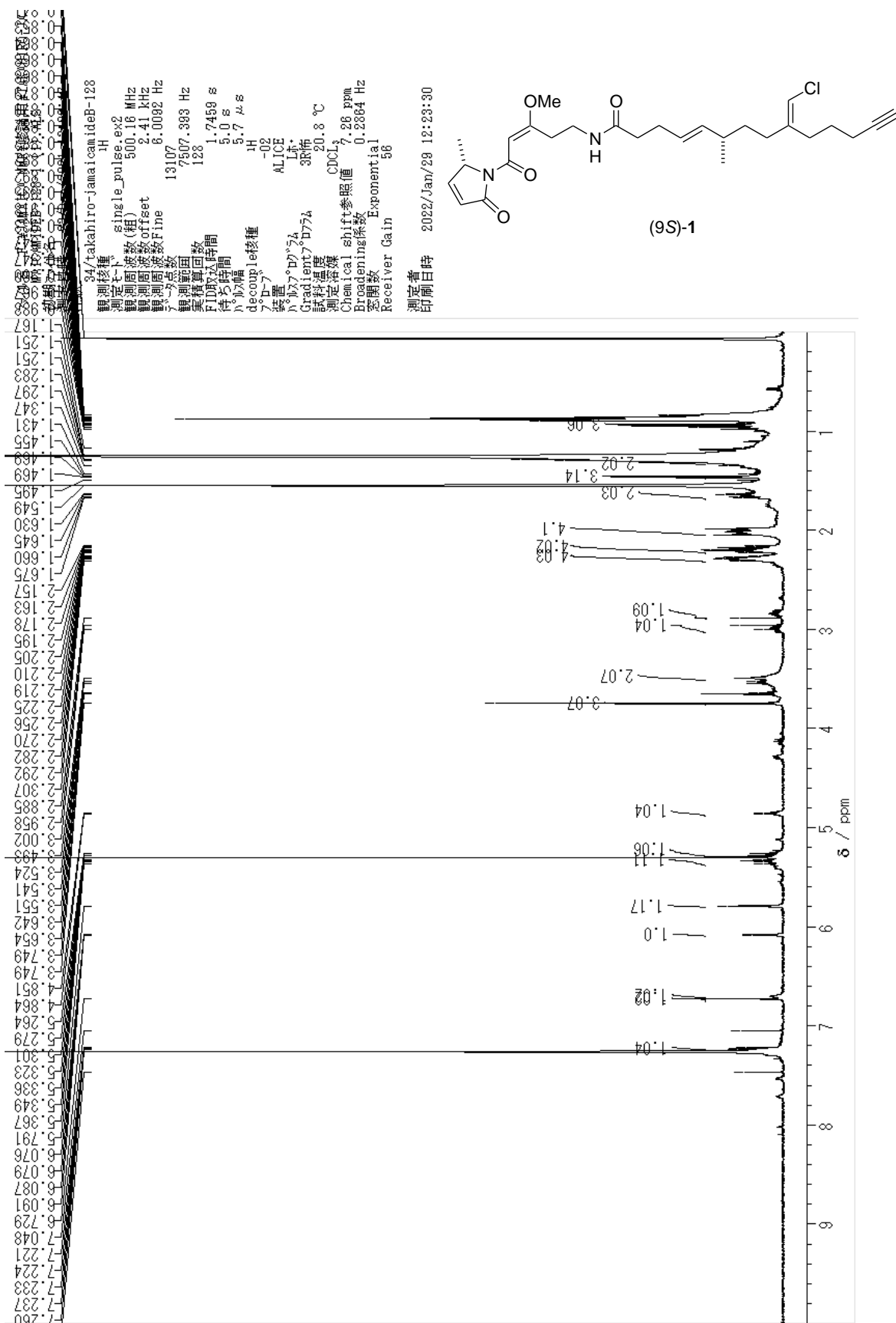


77.49
J083_C_CARBON-3_RMI
初測ファイル名 C:\Documents and Settings\valice2
Vデスクトップ\2023年度のデータ\34日付研究
室\ryosuke\jamaicami\des\ryosuke_J083_C_C
ARBON-3.sls
測定日時 22/Aug/2025 11:18:22
注釈

34/ryosuke_J083 C ¹³C
観測核種 ¹³C
測定モード single_pulse_dec
SP01 125.777874213 MHz
125.765309667 MHz
Frecd (0 ppm)
観測周波数(相) 125.77 MHz
観測周波数offset 7.87 kHz
観測周波数fine 4.2131 Hz
観測周波数 26224.06 Hz
31466.06 Hz
観測周波数 26
1.8336 s
FID取得時間 2.0 s
待ち時間 4.1917 Ms
decompile核種 H
7 p=7
-02
装置 ALICE
パルスプログラム 3RF
Gradientプログラム 3RF
試料温度 25.2 °C
測定溶媒 CDCl₃
Chemical shift参照値 77.0 ppm
Broadening係数 0.5996 Hz
窓関数 Exponential
Receiver Gain 54

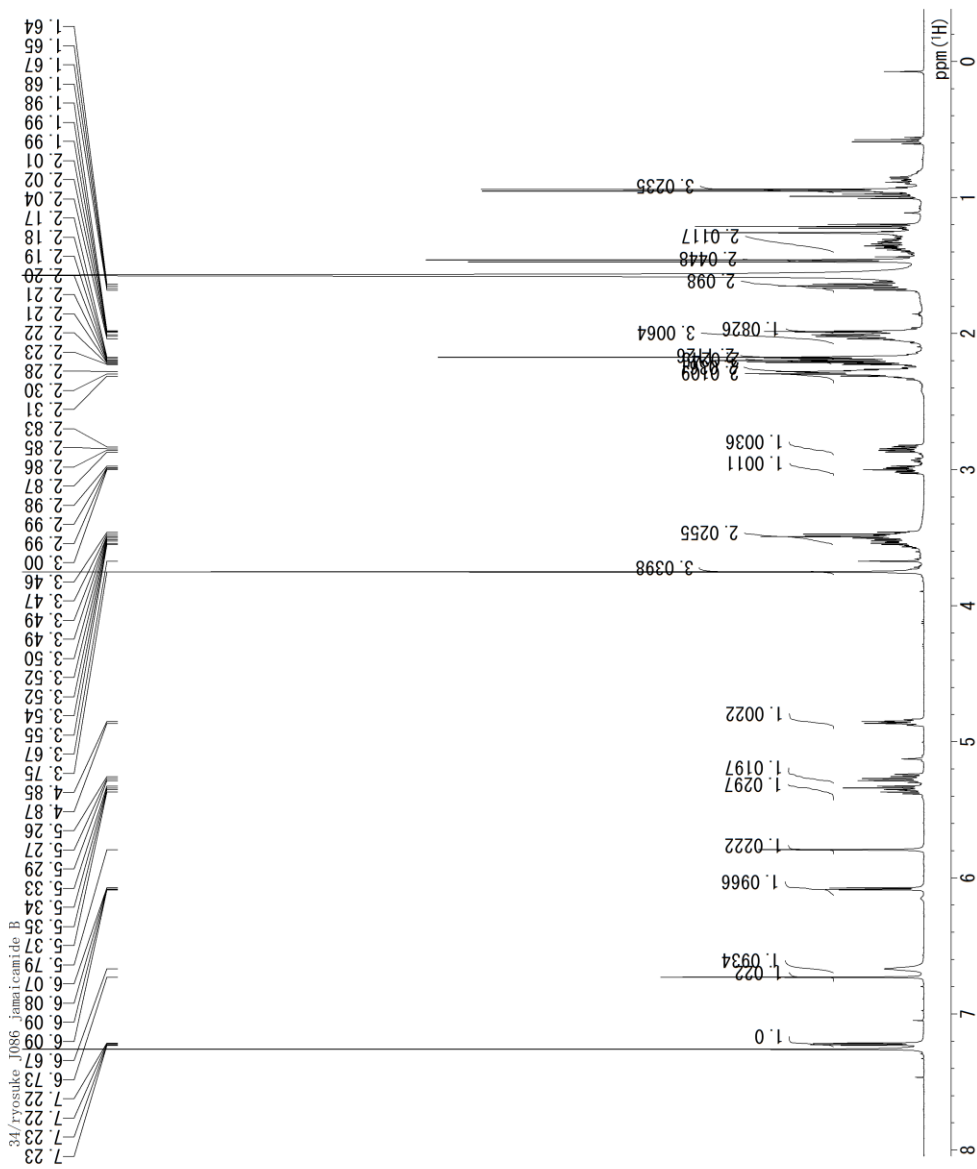
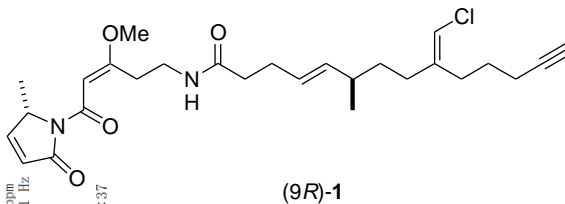
測定者
印刷日時 2023/Dec/19 00:44:11





ファイル名 D:\NMR\NMR JAMAICAMIDESRYOSUKE_1086_JAMAICAMIDE.B.PROTON-3.1MI
 初期ファイル名 C:\Documents and Settings\alice2
 ヴィスケクトップ2023年度のデータY34白粉研究
 至RYOSUKE\jamaicamidestryosuke_1086_jam
 aicamide.B.PROTON-3.als
 ai
 測定日時 31/Aug/2023 16:52:47
 注釈 34/ryosuke_1086_jamaicamide B

観測核種 H
 測定パルス single_pulse.ex2
 SF01 500.162416009 MHz
 Freq. (0 ppm) 500.159909813 MHz
 観測周波数(相) 500.16 MHz
 観測周波数offset 2.41 kHz
 観測周波数fine 6.0092 Hz
 テーパ点数 13120
 観測範囲 7507.393 Hz
 742
 実積算回数 1.7459 s
 FID取込時間 4.0 s
 待ち時間 5.7 μs
 ハルズ幅 H
 decouple核種 -02
 プローブ ALICE
 装置 ALICE
 ハルスプログラマ LR
 Gradientプログラマ 3R希
 試料温度 26.6 °C
 測定溶媒 CDCl₃
 Chemical shift参照値 7.26 ppm
 Broadening係数 0.2861 Hz
 歪周波 Exponential
 Receiver Gain 50
 測定者 2023/Dec/19 00:48:37
 印刷日時



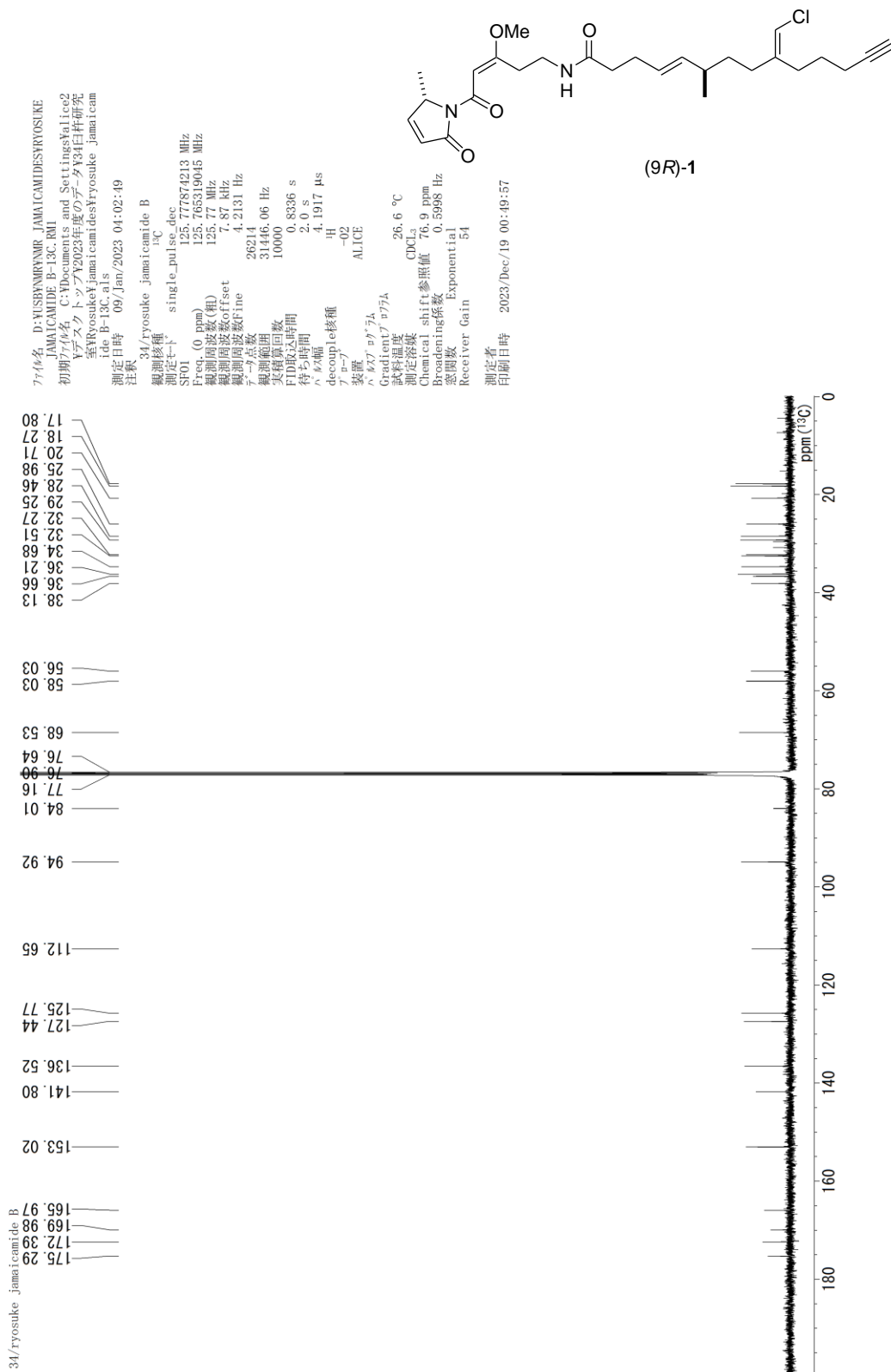


Table S1. Comparison of chemical shift of ¹H NMR of natural, (9*R*)-, and (9*S*)-jamaicamide B.

Position number	Natural (600 MHz)	(9 <i>R</i>)-jamaicamide B (500MHz)	(9 <i>S</i>)-jamaicamide B (500MHz)
1	1.97	1.98	2.00
2	-	-	-
3	2.19	2.21	2.22
4	1.64	1.65	1.65
5	2.26	2.28	2.28
6	-	-	-
7	1.99	2.00	2.01
8	1.33	1.35	1.35
9	2.01	2.02	2.02
10	5.26 (15.1, 7.8)	5.27 (9.0, 6.9)	5.27 (9.2, 7.2)
11	5.35 (15.1, 6.5)	5.35 (9.0, 6.8)	5.35 (9.2, 7.1)
12	2.28	2.31	2.30
13	2.17	2.18	2.18
14	-	-	-
15	3.5	3.5	3.5
16	2.98, 2.83	2.99, 2.86	2.99, 2.85
17	-	-	-
18	6.72	6.73	6.73
19	-	-	-
20	-	-	-
21	6.07, (6.2, 1.0)	6.09 (5.9, 2.0)	6.09 (6.0, 2.2)
22	7.21, (6.2, 1.9)	7.23 (6.1, 2.3)	7.23 (6.0, 2.2)
23	4.87	4.86	4.86
24	1.45 (6.6)	1.46 (7.6)	1.48 (7.2)
25	3.74	3.75	3.75
26	0.93 (6.7)	0.95 (7.5)	0.96 (-)
27	5.81	5.79	5.79
NH	6.68	6.67	6.72

Table S2. Comparison of chemical shift of ^{13}C NMR of natural and (9*R*)-jamaicamide B.

Position number	Natural (600 MHz)	(9 <i>R</i>)-jamaicamide B (500MHz)
1	68.6	68.7
2	84.1	84.2
3	18.3	18.5
4	26.1	26.2
5	29.3	29.5
6	141.9	142.0
7	32.6	32.5
8	34.7	34.9
9	36.3	36.4
10	136.6	136.7
11	127.5	127.7
12	28.5	28.7
13	36.7	36.9
14	172.4	172.6
15	38.2	38.3
16	32.2	32.7
17	175.4	175.5
18	94.9	95.1
19	166.0	166.2
20	170.1	170.2
21	125.9	126.0
22	153.1	153.2
23	58.1	58.3
24	17.9	18.0
25	56.1	56.3
26	20.8	20.9
27	112.7	112.9
NH	-	-