Supporting Information for: Thionium Ion-initiated Medium-sized Ring Formation: The Total Synthesis of Asteriscunolide D

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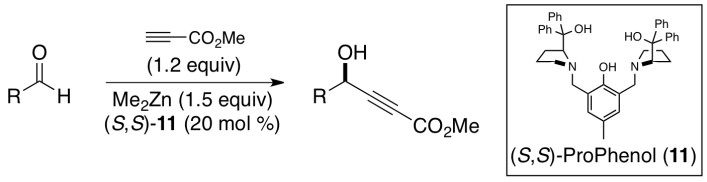
Table of Contents

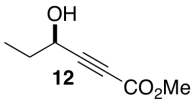
I. General Experimental: All reactions were performed under nitrogen atmosphere in oven-dried glassware unless otherwise stated. Solvents were purified on a Seca solvent purification system by Glass Contour. All commercially purchased reagents were used without further purification unless reported otherwise. Solvents and reagents were transferred via syringes, which had been dried in an oven and cooled in a desiccator. Analytical thin-layer chromatography was performed on pre-coated 250 μm layer thickness silica gel 60 F254 plates (EMD Chemicals Inc.). Visualization was performed by ultraviolet light and/or by staining with potassium permanganate or *para*-anisaldehyde. Flash column chromatography was performed using 40-63 μm silica gel (Silicycle silica gel) using compressed air. Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired using a Varian Inova 500 MHz, Varian Inova 300 MHz, or Varian Mercury 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and are calibrated to the residual solvent peak: proton ($CDCl_3$ 7.27 ppm). Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; br = broad; m = multiplet (range of multiplet is given). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded using a Varian Inova spectrometer at 125, 100, or 75 MHz. Chemical shifts are reported in parts per million (ppm) and are calibrated to the solvent peak: carbon ($CDCl_3$ 77.23 ppm). Infrared spectroscopic data was recorded on a Thermo Scientific Nicolet IR100 FT-IR spectrometer, using thin films of the sample on NaCl plates. The absorbance frequencies are recorded in wavenumbers (cm^{-1}). Chiral HPLC analysis was performed by comparison to racemic samples on Chiralpak® and Chiracel® columns, eluting with a heptane and isopropanol mixture, using a Thermo Separation Products Spectra SERIES P100 instrument, or using an Agilent Technologies 1200 Series HPLC equipped with a Daicel Chemical Chiralcel® IA column. Optical rotations were measured using a JASCO P2000 polarimeter using 5 cm glass cells with a sodium 589 nm filter and are reported as $[\alpha]_D$ (T), concentration (g/100 mL), and solvent. Melting points were determined on a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. High-resolution mass spectra were acquired by the Vincent Coates Foundation Mass Spectrometry Laboratory, Stanford University Mass Spectrometry (http://massspec.stanford.edu) on a Micromass Q-Tof API-US mass spectrometer (Waters Corporation, Milford, MA).

II. Experimental Procedures



Representative Procedure for the Zn-ProPhenol catalyzed Alkynylation of Aliphatic Aldehydes:

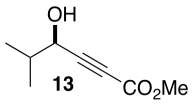
To a stirred solution of (*S*,*S*)-ProPhenol (**11**) (41.5 mg, 0.065 mmol, 20 mol %) and methyl propiolate (35.0 μL, 0.390 mmol, 1.2 equiv) in toluene (440 μL) was added dropwise dimethylzinc (407 μL, 1.2 M solution in toluene, 0.488 mmol, 1.5 equiv) at 0 °C. The reaction was warmed to room temperature and stirred for 30 min before addition of the aldehyde substrate (0.325 mmol, 1.0 equiv) at 0 °C. The reaction was stirred for 48 h at 4 °C prior to quenching with satd aq NH_4Cl (2 mL) and extraction with ether (3 x 5 mL). The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, and concentrated to provide the crude material, which was purified by flash chromatography.



Data for (*R*)-methyl 4-hydroxyhex-2-ynoate (12):

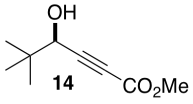
The reaction was performed with freshly distilled propionaldehyde (23 μL, 0.325 mmol). The crude product was purified by flash column chromatography (30% ether/ pet ether) to give **12** (29.6 mg, 64%). Colorless oil; R_f = 0.27 (30% ether/ pet ether); HPLC: 88% ee, Chiralcel OD-H column (n-heptane/2-propanol, 99:1, 0.8 mL/min, 220 nm); t_R: 15.0 min (minor), 16.3 min (major); $[\alpha]_D$ (23 °C): +5.5° (c = 0.77, $CHCl_3$); IR (film): 3415, 2971, 2939, 2881, 2237, 1719, 1437, 1252, 1117, 1062, 1035, 1012 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.43 (q, *J* = 6.2 Hz, 1H), 3.77 (s, 3H), 1.87 (s, 1H), 1.78 (quintet, *J* = 7.1 Hz, 2H), 1.03 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 88.3, 76.5, 63.5, 53.1, 30.3, 9.5. Characterization data are in agreement with values reported in the literature.[1]

[1] (a) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2005**, *127*, 17644. (b) For optical rotation values, see: Xu, T.; Liang, C.; Cai, Y.; Li, Jian; Li, Y.-M.; Hui, X.-P. *Tetrahedron: Asymmetry* **2009**, *20*, 2733.



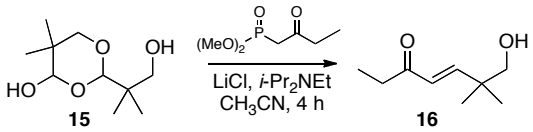
Data for (*R*)-methyl 4-hydroxy-5-methylhex-2-ynoate (13):

The reaction was performed with freshly distilled isobutyraldehde (30 μL, 0.325 mmol). The crude product was purified by flash column chromatography (25% ether/ pet ether) to give **13** (33.9 mg, 67%). Colorless oil; R_f = 0.28 (25% ether/ pet ether); HPLC: 92% ee, Chiralcel AS column (n-heptane/2-propanol, 98:2, 0.8 mL/min, 220 nm); t_R: 18.1 min (major), 20.6 min (minor); $[\alpha]_D$ (23 °C): +6.5° (c = 0.216, $CHCl_3$); IR (film): 3418, 2965, 2236, 1722, 1470, 1436, 1386, 1371, 1253, 1037 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.27 (t, *J* = 5.9 Hz, 1H), 3.77 (s, 3H), 1.99–1.91 (m, 1H), 1.87–1.85 (m, 1H), 1.02 (app t, *J* = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 87.5, 67.8, 53.1, 34.4, 18.2, 17.7. Characterization data are in agreement with values reported in the literature.[1]



Data for (*R*)-methyl 4-hydroxy-5,5-dimethylhex-2-ynoate (14):

The reaction was performed with freshly distilled pivaladehyde (35 μL, 0.325 mmol) and (*S*,*S*)-ProPhenol (**11**) (21 mg, 0.033 mmol, 10 mol %) . The crude product was purified by flash column chromatography (25% ether/ pet ether) to give **14** (53.9 mg, 97%). Colorless oil; R_f = 0.35 (25% ether/ pet ether); HPLC: 90% ee, Chiralcel AD-H column (n-heptane/2-propanol, 95:5, 0.8 mL/min, 220 nm); t_R: 12.8 min (minor), 14.5 min (major); $[\alpha]_D$ (23 °C): +2.27° (c = 0.89, $CHCl_3$); IR (film): 3444, 2960, 2908, 2872, 2236, 1715, 1480, 1483, 1436, 1395, 1367, 1258, 1083, 1043 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.16 (d, *J* = 6.1 Hz, 1H), 3.81 (s, 3H), 2.04 (d, J = 4.4 Hz, 1H), 1.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ154.0, 87.4, 76.9, 71.3, 53.1, 36.4, 25.5. Characterization data are in agreement with values reported in the literature.[1]

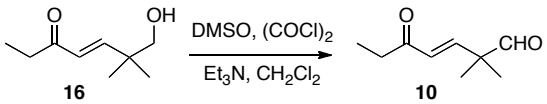


(*E*)-7-hydroxy-6,6-dimethylhept-4-en-3-one (16):

A stirred solution of 3-hydroxy-2,2-dimethylpropanal dimer (**15**)[2] (1.00 g, 4.90 mmol, 0.5 equiv) in acetonitrile (50 mL) was cracked at 65 °C for 3 h. The solution was cooled to room temperature and transferred via cannula to a stirred solution of dried (120 °C, 24 h) lithium

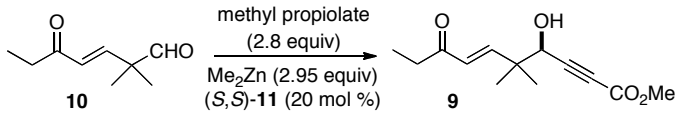
[2] Törmäkangas, O. P.; Saarenketo, P.; Koskinen, A. M. P. *Org. Process Res. Dev.* **2002**, *6*, 125.

chloride (746 mg, 17.6 mmol, 1.8 equiv), *N*,*N*-diisopropylethylamine (3.07 mL, 17.6 mmol, 1.8 equiv), and dimethyl 2-oxobutanephosphonate[3] (3.17 g, 17.6 mmol, 1.8 equiv) in acetonitrile (50 mL) at room temperature. The resultant solution was allowed to stir for 4 h prior to quenching with 1 M HCl (30 mL) and extraction with ether (3 x 100 mL). The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, and concentrated to provide the crude material, which was purified by flash chromatography (1:2 pet ether/ether) to afford **16** (1.4 g, 91%). Pale yellow oil; R_f = 0.35 (1:2 pet ether/ether); IR (film): 3439 (br), 2966, 2938, 1668, 1625, 1362 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.82 (d, *J* = 16.0 Hz, 1H), 6.12 (d, *J* = 16.5 Hz, 1H), 3.46 (s, 2H), 2.60 (q, *J* = 7.0 Hz, 2H), 1.10 (t, *J* = 7.5 Hz, 3H), 1.09 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.6, 152.7, 128.1, 71.2, 39.3, 33.9, 23.4, 8.3. HRMS (ESI+) calcd for $C_9H_{16}O_2Na^+$ ($M+Na^+$) 179.1043, found 179.1053.



(*E*)-2,2-dimethyl-5-oxohept-3-enal (10):

To a stirred solution of oxalyl chloride (2.16 mL, 25.2 mmol, 1.5 equiv) in CH_2Cl_2 (30 mL) at -78 °C was added dropwise a solution of dimethylsulfoxide (3.58 mL, 50.4 mmol, 3.0 equiv) in CH_2Cl_2 (30 mL). A solution of **16** (2.63 g, 16.8 mmol, 1.0 equiv) in CH_2Cl_2 (30 mL) was subsequently added dropwise followed by continued stirring for 1 h. Triethylamine (14.1 mL, 100.8 mmol, 6.0 equiv) was added dropwise and the temperature was maintained at –78 °C for an additional 75 min prior to quenching with satd aq NH_4Cl (30 mL) and allowing the mixture to warm to room temperature. The mixture was diluted with water (20 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, and concentrated to provide the crude material, which was purified by flash chromatography (1:1 pet ether/ether) affording **10** (2.6 g, 99%). Pale yellow oil; R_f = 0.65 (1:2 pet ether/ether); IR (film): 2976, 1729, 1701, 1626, 1123 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.46 (s, 1H), 6.82 (d, *J* = 16.5 Hz, 1H), 6.15 (d, *J* = 16.5 Hz, 1H), 2.61 (q, *J* = 7.0 Hz, 2H), 1.28 (s, 6H), 1.11 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 200.5, 146.3, 129.7, 49.2, 34.0, 21.4, 8.1.



(*R*,*E*)-methyl 4-hydroxy-5,5-dimethyl-8-oxodec-6-en-2-ynoate (9):

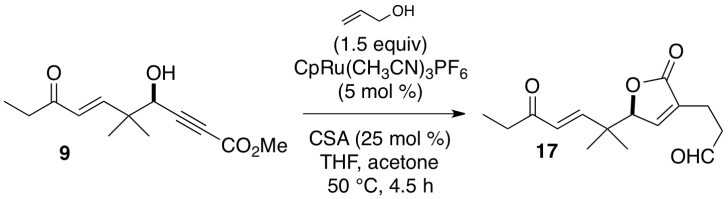
To a stirred solution of (*S*,*S*)-ProPhenol (2.16 g, 3.38 mmol, 0.2 equiv) in degassed (FPT) toluene (77 mL) was added at room temperature dimethyl zinc (1.2 M in toluene, 41.5 mL, 49.9 mmol, 2.95 equiv). The solution was allowed to stir at room temperature for 1 h prior to the dropwise addition of **10** (2.60 g, 16.9 mmol, 1.00 equiv) in degassed toluene (25 mL) at 0 °C.

[3] Coppola, G. M. *Synthesis* **1988**, 81.

The solution was allowed to stir at 4 °C for 36 h, and subsequently quenched upon the addition of satd aq NH_4Cl (50 mL) and warming to room temperature. The aqueous phase was extracted with ethyl acetate (3 x 50 mL) and the combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, and concentrated to provide the crude material. Purification by flash chromatography (2:1→1:2 pet ether/ether) afforded **9** (3.41 g, 83%). Yellow oil; R_f = 0.46 (1:2 pet ether/ether); HPLC: 84% ee, Chiralpak AD-H column (n-heptane/2-propanol, 90:10, 0.8 mL/min, 220 nm); t_R: 12.8 min (minor), 17.1 min (major); $[\alpha]_D$ (23 °C): +31.0° (c = 1.0, $CHCl_3$); IR (film): 3427 (br), 2975, 2236, 1716, 1672 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.90 (d, *J* = 16.0 Hz, 1H), 6.18 (d, *J* = 16.0 Hz, 1H), 4.32 (s, 1H), 3.78 (s, 3H), 2.62 (q, *J* = 7.5 Hz, 2H), 1.22 (s, 3H), 1.21 (s, 3H), 1.10 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.8, 153.8, 150.5, 129.0, 86.1, 77.8, 69.4, 53.0, 42.3, 33.7, 23.1, 22.3, 8.2. HRMS (ESI+) calcd for $C_{13}H_{18}O_4Na^+$ ($M+Na^+$) 261.1097, found 261.1102.

*Preparation of **9** using Me_2Zn (1.5 equiv) and methyl propiolate (1.2 equiv):*

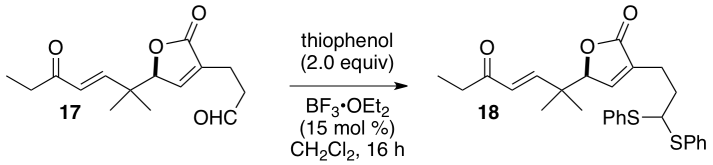
To a stirred solution of (*S*,*S*)-ProPhenol (**11**) (42 mg, 0.066 mmol, 20 mol %) and methyl propiolate (35.0 μL, 0.393 mmol, 1.2 equiv) in toluene (440 μL) was added dropwise dimethylzinc (406 μL, 1.2 M solution in toluene, 0.488 mmol, 1.5 equiv) at 0 °C. The reaction was warmed to room temperature and stirred for 30 min before addition of **10** (501 mg, 0.325 mmol, 1.0 equiv) at 0 °C. The reaction was stirred for 48 h at 4 °C prior to quenching with satd aq NH_4Cl (2 mL) and extraction with ether (3 x 5 mL). The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, and concentrated to provide the crude material, which was purified by flash chromatography (40% ether/ pet. ether) to give **9** (476 mg, 62%). HPLC: 78% ee, Chiralpak AD-H column (n-heptane/2-propanol, 90:10, 0.8 mL/min, 220 nm); t_R: 12.8 min (minor), 17.1 min (major).



(*S*,*E*)-3-(5-(2-methyl-5-oxohept-3-en-2-yl)-2-oxo-2,5-dihydrofuran-3-yl)propanal (17):

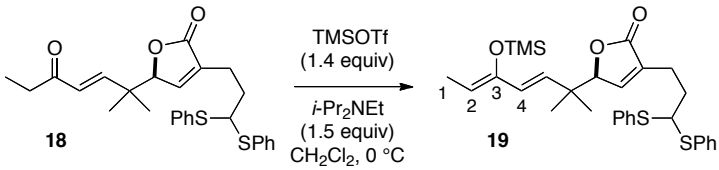
To a stirred solution of **9** (500 mg, 2.10 mmol, 1.00 equiv) in THF (4.6 mL, distilled from Na/benzophenone) and acetone (2.3 mL, distilled from anh $CaSO_4$) was added freshly distilled allyl alcohol (214 μL, 3.15 mmol, 1.50 equiv) followed by (1*S*)-(+)-camphorsulfonic acid (122 mg, 0.525 mmol, 0.250 equiv, dried by azeotropic removal of water with toluene and subsequently placed under high-vacuum for 6 hours) and $CpRu(CH_3CN)_3PF_6$ (45.6 mg, 0.105 mmol, 0.05 equiv). The flask was equipped with a reflux condenser and was heated at 50 °C (preheated oil bath) for 4.5 h. The mixture was cooled to room temperature and concentrated in vacuo to provide the crude material, which was purified by flash chromatography (1:5 pet ether/ether) affording **17** (304 mg, 55%). Yellow oil; R_f = 0.16 (1:5 pet ether/ether); IR (film): 2974, 2938, 1755, 1673, 1629, 1200 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 7.05 (s,

1H), 6.70 (d, *J* = 16.5 Hz, 1H), 6.13 (d, *J* = 16.0 Hz, 1H), 4.71 (s, 1H), 2.78 (t, *J* = 7.0 Hz, 2H), 2.63 (t, *J* = 6.5 Hz, 2H), 2.58 (q, *J* = 7.0 Hz, 2H), 1.15 (s, 3H), 1.13 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.8, 200.4, 173.0, 148.7, 146.8, 134.6, 128.9, 86.7, 41.3, 40.7, 34.2, 23.1, 22.4, 18.3, 8.1.



(*S*,*E*)-3-(3,3-bis(phenylthio)propyl)-5-(2-methyl-5-oxohept-3-en-2-yl)furan-2(5H)-one (18):

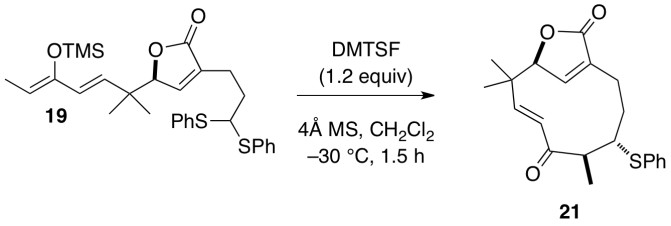
To a stirred solution of **17** (299 mg, 1.13 mmol, 1.0 equiv) in CH_2Cl_2 (87 mL) were added thiophenol (231 μL, 2.26 mmol, 2.0 equiv) and BF_3•OEt_2 (21.0 μL, 0.170 mmol, 0.15 equiv) at at 0 °C. The solution was allowed to warm to room temperature and stir for 16 h. The volatiles were removed in vacuo to provide the crude material, which was purified by flash chromatography (1:2 pet ether/ether) affording **18** (418 mg, 79%). Yellow oil; R_f = 0.47 (1:2 pet ether/ether); HPLC: 80% ee, Chiralpak AD-H column (n-heptane/2-propanol, 90:10, 0.8 mL/min, 220 nm); t_R: 21.1 min (minor), 23.0 min (major); $[\alpha]_D$ (23 °C): –21.3° (c = 1.0, $CHCl_3$); IR (film): 2972, 1758, 1699, 1673, 1629, 1439, 1085 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48–7.44 (m, 4H), 7.34–7.29 (m, 6H), 6.81 (app q, *J* = 1.5 Hz, 1H), 6.69 (d, *J* = 16.5 Hz, 1H), 6.10 (d, *J* = 16.0 Hz, 1H), 4.67 (app q, *J* = 1.5 Hz, 1H), 4.31 (t, *J* = 7.0 Hz, 1H), 2.65–2.62 (m, 2H), 2.57 (d, *J* = 7.5 Hz, 1H), 2.54 (d, *J* = 7.5 Hz, 1H), 2.10–2.05 (m, 2H), 1.10 (s, 3H), 1.09 (t, *J* = 7.0 Hz, 3H), 1.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.8, 173.0, 148.9, 145.6, 135.3, 133.8, 133.3 (2C), 133.2 (2C), 129.2 (2), 129.1 (2), 128.9 (2), 128.3, 128.2, 86.6, 58.2, 40.6, 34.1, 33.6, 23.2, 23.0, 22.3, 8.2; HRMS (ESI+) calcd for $C_{27}H_{30}O_3S_2Na^+$ ($M+Na^+$) 489.1529, found 489.1534.



(*S*)-3-(3,3-bis(phenylthio)propyl)-5-((3*E*,5*Z*)-2-methyl-5-((trimethylsilyl)oxy)hepta-3,5-dien-2-yl)furan-2(5*H*)-one (19):

To a stirred solution of **18** (455 mg, 0.975 mmol, 1.0 equiv) in CH_2Cl_2 (16.3 mL) at 0 °C were added diisopropylethylamine (254 μL, 1.46 mmol, 1.50 equiv) and TMSOTf (248 μL, 1.37 mmol, 1.4 equiv). The mixture was allowed to stir at 0 °C for 80 min, and subsequently quenched with satd aq $NaHCO_3$ (10 mL) and allowed to warm to room temperature. The aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, and concentrated to provide the crude material. Purification by flash chromatography (5:1 hexane/ethyl acetate) provided **19** (471 mg, 90%). Yellow oil; R_f = 0.67 (3:1 hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.44 (m, 4H), 7.34–7.28 (m, 6H), 6.82 (app q, *J* = 1.0 Hz, 1H), 5.86 (d, *J* = 15.5 Hz, 1H-4), 5.61 (d, *J*

= 15.5 Hz, 1H-5), 4.85 (q, *J* = 7.0 Hz, 1H-2), 4.59 (app q, *J* = 2.0 Hz, 1H), 4.32 (t, *J* = 7.0 Hz, 1H), 2.63–2.59 (m, 2H), 2.10–2.04 (m, 2H), 1.64 (d, *J* = 7.0 Hz, 3H-1), 1.12 (s, 3H), 0.95 (s, 3H), 0.19 (s, 9H); NOE: H-2/H-4 and H-2/CH_3-1; ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.6, 149.1, 146.7, 133.9, 133.8, 133.3, 133.2 (2C), 131.5 (2C), 129.2 (2C), 129.1 (2C), 128.5, 128.3, 128.2, 110.4, 87.8, 58.2, 39.9, 33.6, 29.9, 24.9, 23.3, 22.0, 12.0, 0.9.



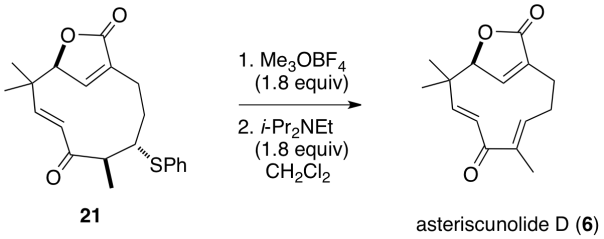
(4*S*,5*S*,10*S*,*E*)-5,9,9-trimethyl-4-(phenylthio)-11-oxabicyclo[8.2.1]trideca-1(13),7-diene-6,12-dione (21):

To a stirred solution of **19** (37 mg, 0.069 mmol, 1.0 equiv) and flame-dried 4Å MS (1.38 g, 20 mg/mL CH_2Cl_2) in CH_2Cl_2 (69 mL) at -30 °C was added dropwise a solution of freshly prepared DMTSF[4] (16.3 mg, 0.083 mmol, 1.2 equiv) in CH_3CN (830 μL). The mixture was allowed to stir for an additional 1.5 h at -30 °C prior to the addition of satd aq $NaHCO_3$ (10 mL). The stirred mixture was warmed to room temperature and filtered through celite to provide the biphasic mixture, free of molecular sieves. The aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL) and the combined organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated to provide the crude material, which was purified by flash chromatography (loaded column with minimal CH_2Cl_2) (3:1 hexane/ethyl acetate) affording **21** (10.2 mg, 41%). In an experiment using **19** (170 mg, 0.315 mmol), DMTSF (74 mg, 0.378 mmol, in 3.78 mL CH_3CN), and 4Å MS (6.3 g) in CH_2Cl_2 (315 mL) following the above procedure provided **21** (36 mg, 32%). White solid; mp 125–128 °C; R_f = 0.18 (3:1 hexane/ethyl acetate); HPLC: 82% ee, Chiralcel OD-H column (n-heptane/2-propanol, 90:10, 0.8 mL/min, 220 nm); t_R: 21.5 min (major), 24.4 min (minor); $[\alpha]_D$ (23 °C): –30.9° (c = 1.0, $CHCl_3$); IR (film): 2964, 2920, 1753, 1686, 1617, 1440, 1328, 1062 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58–7.56 (m, 2H), 7.34–7.28 (m, 3H), 6.96 (s, 1H), 6.16 (d, *J* = 17.0 Hz, 1H), 6.10 (d, *J* = 16.5 Hz, 1H), 4.78 (s, 1H), 3.02 (t, *J* = 10.5 Hz, 1H), 2.79 (t, *J* = 13.0 Hz, 1H), 2.51 (dddd, *J* = 14.0, 11.5, 11.5, 7.0 Hz, 1H), 2.37 (ddd, *J* = 14.0, 5.5, 2.5 Hz, 1H), 1.93 (dddd, *J* = 12.0, 9.5, 5.0, 2.5 Hz, 1H), 1.36 (s, 3H), 1.33 (s, 3H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 13.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.8, 175.1, 150.6, 149.1, 137.3, 133.9 (2C), 133.4, 129.0 (2C), 127.0, 127.8, 87.0, 54.3, 48.7, 41.9, 37.5, 26.3, 24.1, 21.4, 15.9. HRMS (ESI+) calcd for $C_{21}H_{24}O_3SNa^+$ ($M+Na^+$) 379.1338, found 379.1348.

Recrystallization of **21**: 18 mg was dissolved in 5 mL of pet ether/CH_2Cl_2 (5:1) in a 10 mL vial, which was sealed with Teflon tape. A small hole was made in the Teflon seal and the vial was placed inside a larger vial containing petroleum ether and the system was capped. After 4 d at room temperature, the solution was decanted and the crystals were washed with an additional 5 mL petroleum ether yielding 12 mg of enantiomerically enriched **21**. HPLC: 99% ee, Chiralcel

[4] Meerwein, H.; Zenner, K.-F.; Gipp, R. *Justus Liebigs Ann. Chem.* **1965**, *688*, 67.

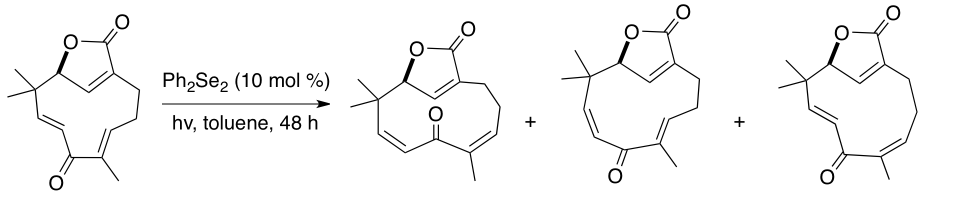
OD-H column (n-heptane/2-propanol, 90:10, 0.8 mL/min, 220 nm); t_R: 19.5 min (major), 21.0 min (minor); $[\alpha]_D$ (23 °C): –41.9° (c = 1.0, $CHCl_3$).



21 asteriscunolide D (**6**)

asteriscunolide D (6):

To a stirred solution of recrystallized **21** (25 mg, 0.070 mmol, 1.0 equiv) in CH_2Cl_2 (700 μL) at room temperature was added Me_3OBF_4 (18.6 mg, 0.126 mmol, 1.8 equiv) and the resultant suspension was allowed to stir at room temperature for 16 h under an atmosphere of argon. Diisopropylethylamine (21.9 μL, 0.126 mmol, 1.8 equiv) was added and the resultant solution was heated at 40 °C for 6 h in a sealed vial. The reaction mixture was cooled to room temperature, concentrated, and purified by flash chromatography (3:1 hexane/ethyl acetate) to provide **6** (14.1 mg, 82%). White solid; mp 136–137 °C; R_f = 0.38 (1:1 hexane/ethyl acetate); HPLC: 99% ee, Chiralcel IA column (n-heptane/ethyl acetate, 90:10, 0.8 mL/min, 254 nm); t_R: 55.3 min (minor), 68.8 min (major); $[\alpha]_D$ (23 °C): –155.3° (c = 1.16, $CHCl_3$); IR (film): 2925, 1756, 1659, 1263, 1087 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.03 (s, 1H), 6.10 (d, *J* = 16.5 Hz, 1H), 5.74 (d, *J* = 16.5 Hz, 1H), 5.53 (d, *J* = 10.0 Hz, 1H), 4.77 (s, 1H), 2.80–2.77 (m, 1H), 2.70–2.61 (m, 1H), 2.54–2.48 (m, 1H), 2.42–2.37 (m, 1H), 1.78 (s, 3H), 1.29 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.4, 172.8, 155.7, 150.5, 145.6, 139.8, 134.3, 130.1, 87.7, 41.4, 24.9, 24.8, 23.2, 21.7, 13.1; HRMS (ESI+) calcd for $C_{15}H_{18}O_3Na^+$ ($M+Na^+$) 269.1148, found 269.1151.



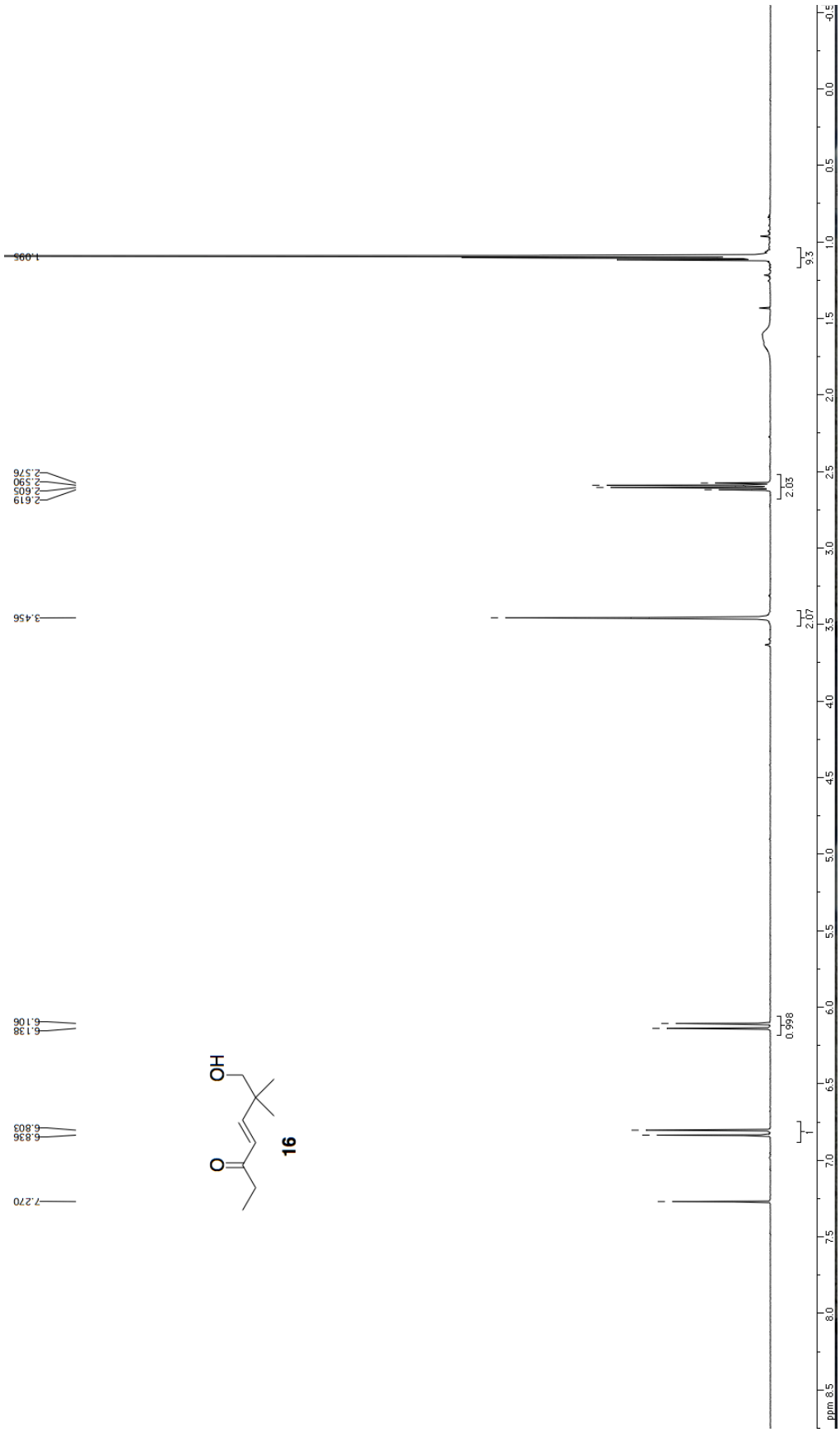
asteriscunolide D (**6**) asteriscunolide A (**3**) asteriscunolide B (**4**) asteriscunolide C (**5**)

Isomerization of asteriscunolide D (6):

A solution of **6** (5 mg, 0.020 mmol, 1.0 equiv) and diphenyl diselenide (0.6 mg, 0.002 mmol, 10 mol %) in toluene (200 μL) was degassed by three freeze-pump-thaw cycles in a sealed microwave vial. The resultant solution was irradiated (500 W halogen lamp) for 48 h and concentrated to provide the crude mixture, which was purified by flash chromatography (1:1 hexane/ethyl acetate) to provide **3** (1.6 mg), **4**/**5** (2.3 mg, 3:1 mixture), and recovered **6** (0.5 mg).

The ^{1}H NMR spectra are consistent with those reported.[5] Asteriscunolide A (**3**); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01 (t, *J* = 1.5 Hz, 1H), 6.17 (d, *J* = 14.0 Hz, 1H), 5.30 (d, *J* = 14.0 Hz, 1H), 4.70 (s, 1H), 2.71–2.64 (m, 2H), 2.38–2.31 (m, 1H), 2.20–2.14 (m, 1H), 1.96 (s, 3H), 1.42 (s, 3H), 1.21 (s, 3H). Asteriscunolide B (**4**); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.78 (s, 1H), 6.17 (d, *J* = 14.0 Hz, 1H), 6.16–6.13 (m, 1H), 5.49 (d, *J* = 14.0 Hz, 1H), 4.69 (s, 1H), 2.84–2.38 (m, 4H), 1.80 (s, 3H), 1.38 (s, 3H), 1.03 (s, 3H). Asteriscunolide C (**5**); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96 (s, 1H), 6.27 (d, *J* = 16.5 Hz, 1H), 5.91 (d, *J* = 16.5 Hz, 1H), 4.71 (s, 1H), 2.60–1.80 (m, 4H), 1.86 (s, 3H), 1.36 (s, 3H), 1.27 (s, 3H).

[5] For the isolation, and separation of **3**–**6**, see: (a) San Feliciano, A.; Barrero, A. F.; Medarde, M.; Miquel del Corral, J. M.; Aramburu Aizpiri, A.; S.-Ferrando, F. *Tetrahedron* **1984**, *40*, 873. For the structural reassignment of **3** and **4**, see: (c) San Feliciano, A.; Barrero, A. F.; Medarde, M.; Miguel del Corral, J. M.; Aramburu, A.; Perales, A.; Fayos, J.; S.-Ferrando, F. *Tetrahedron* **1985**, *41*, 5711.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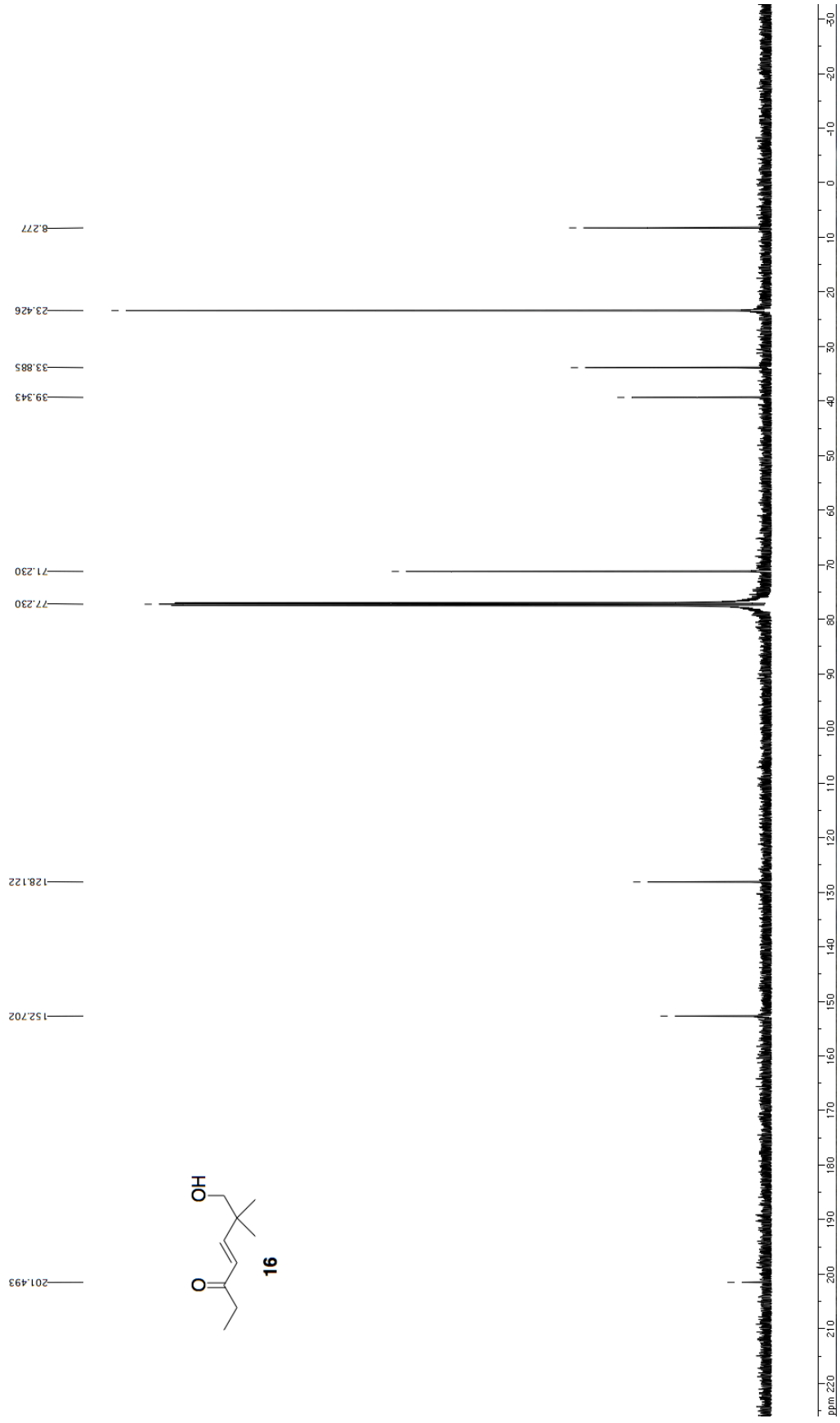
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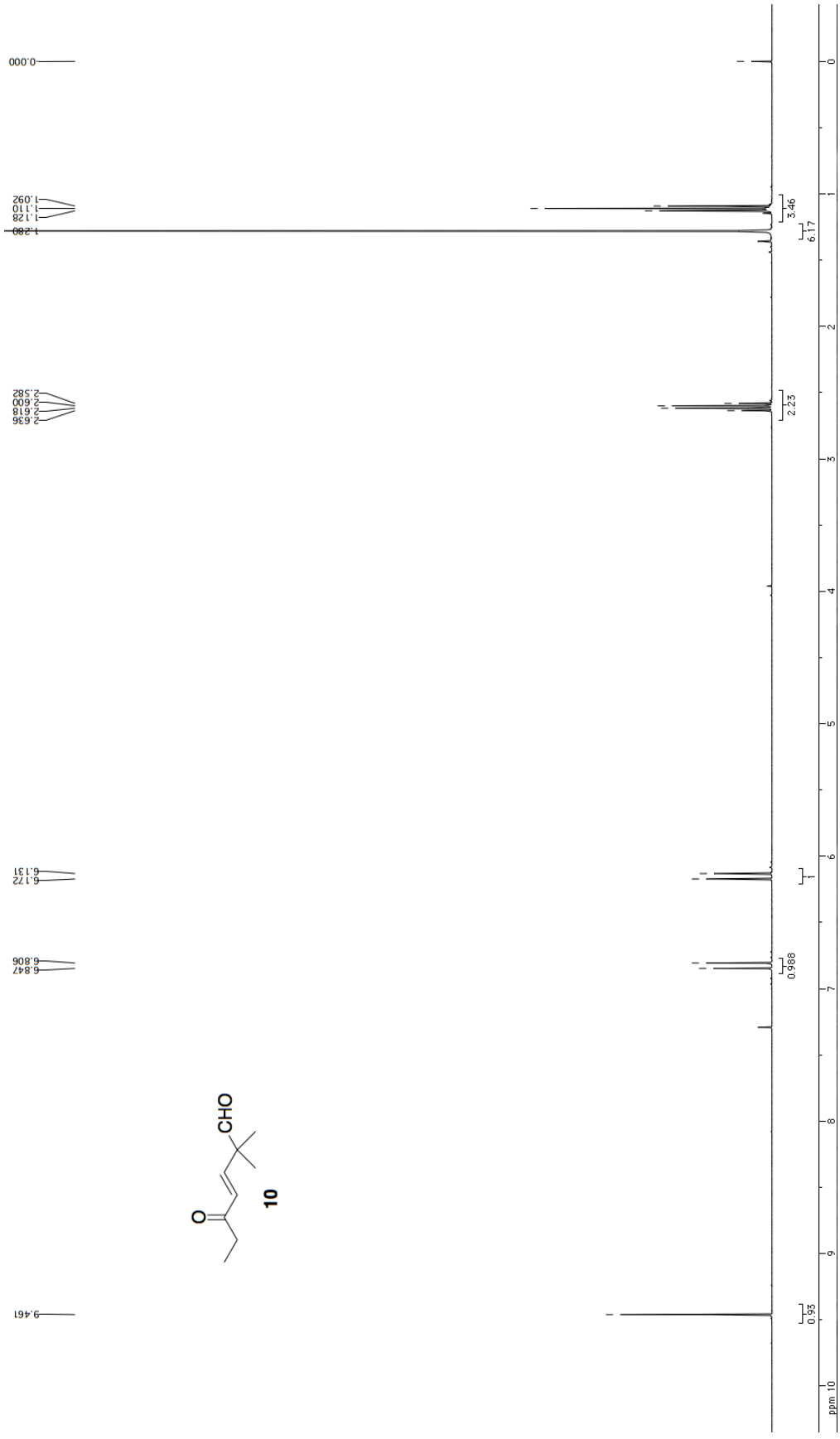
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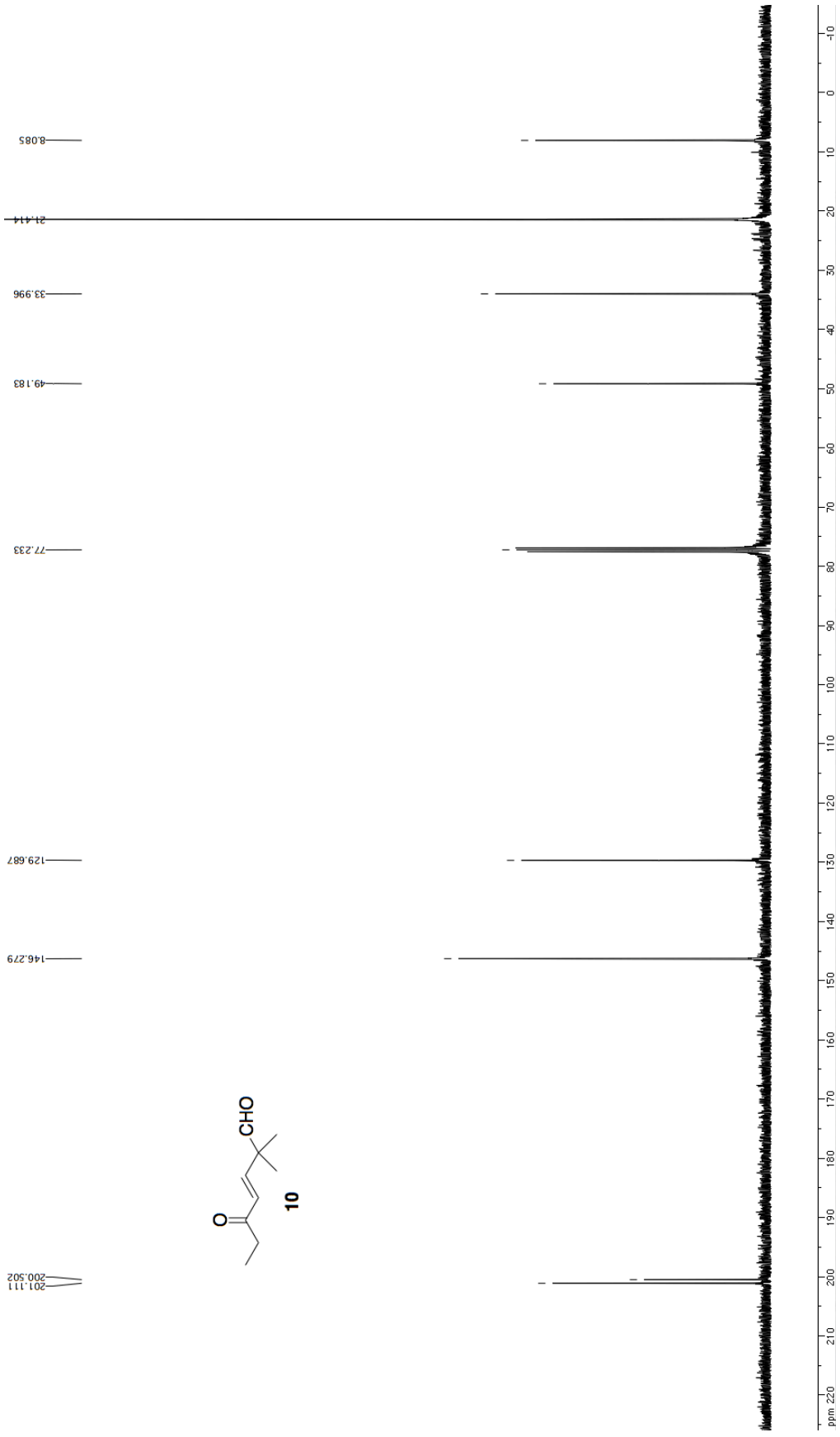
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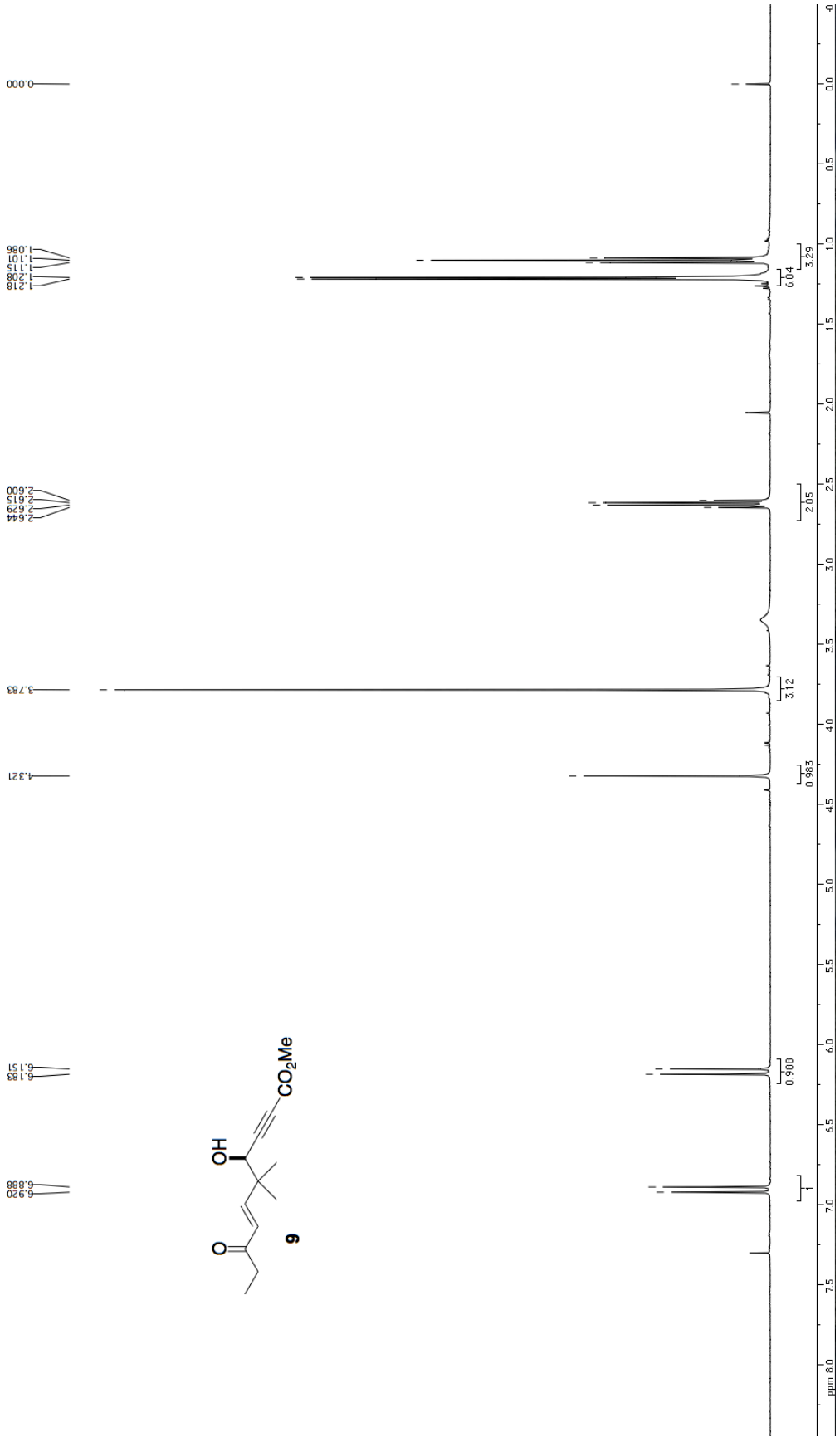
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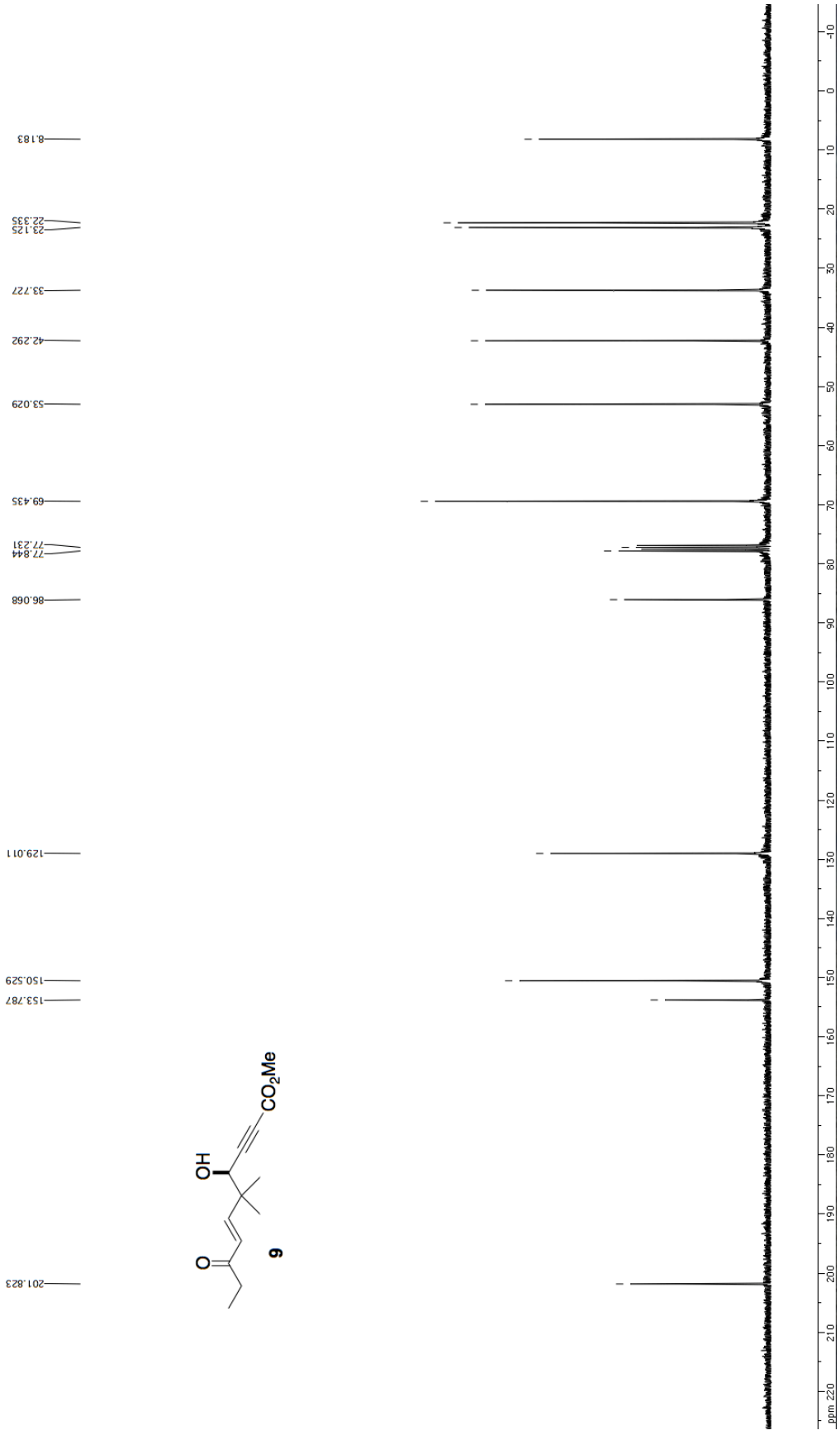
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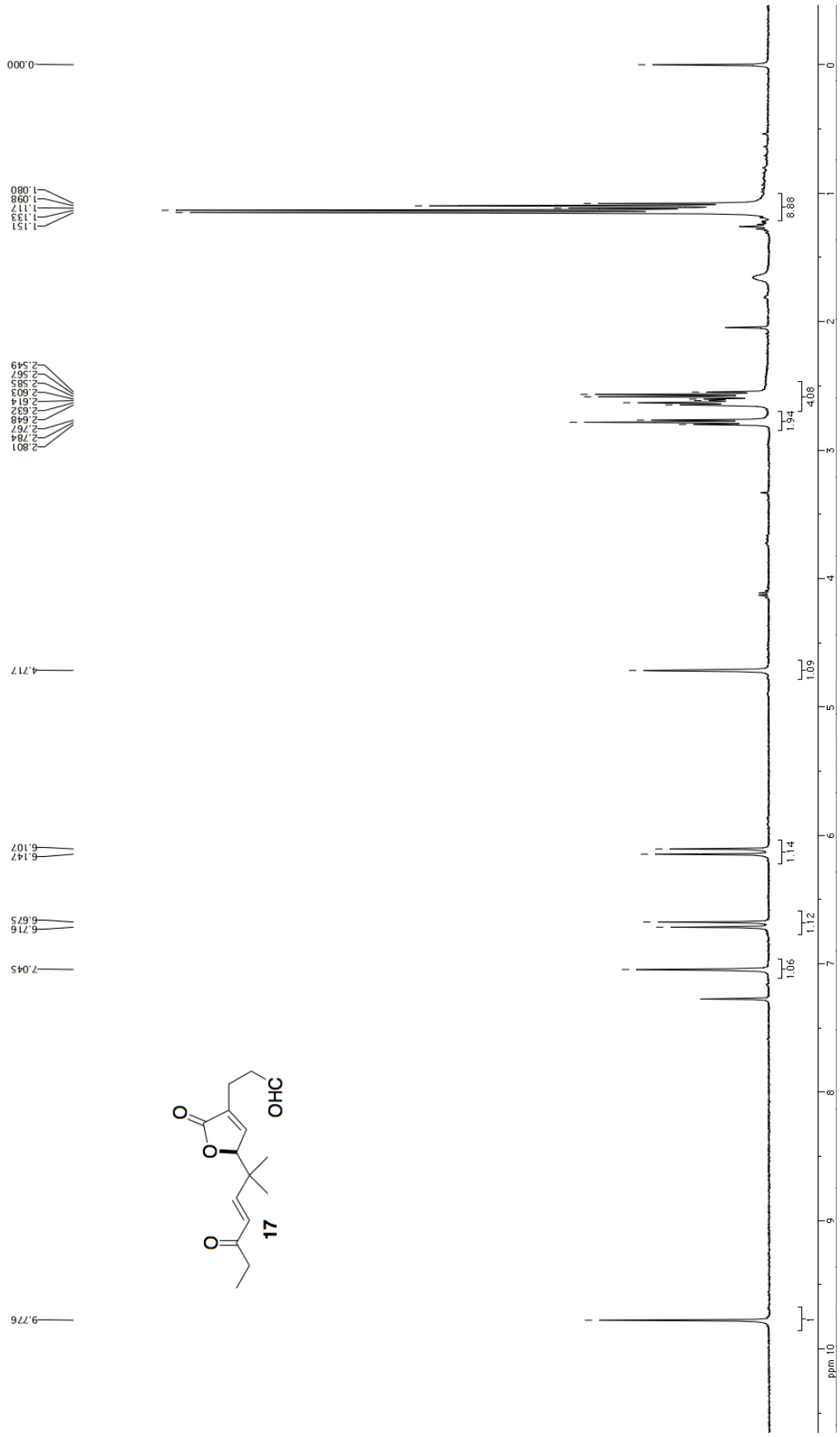
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O
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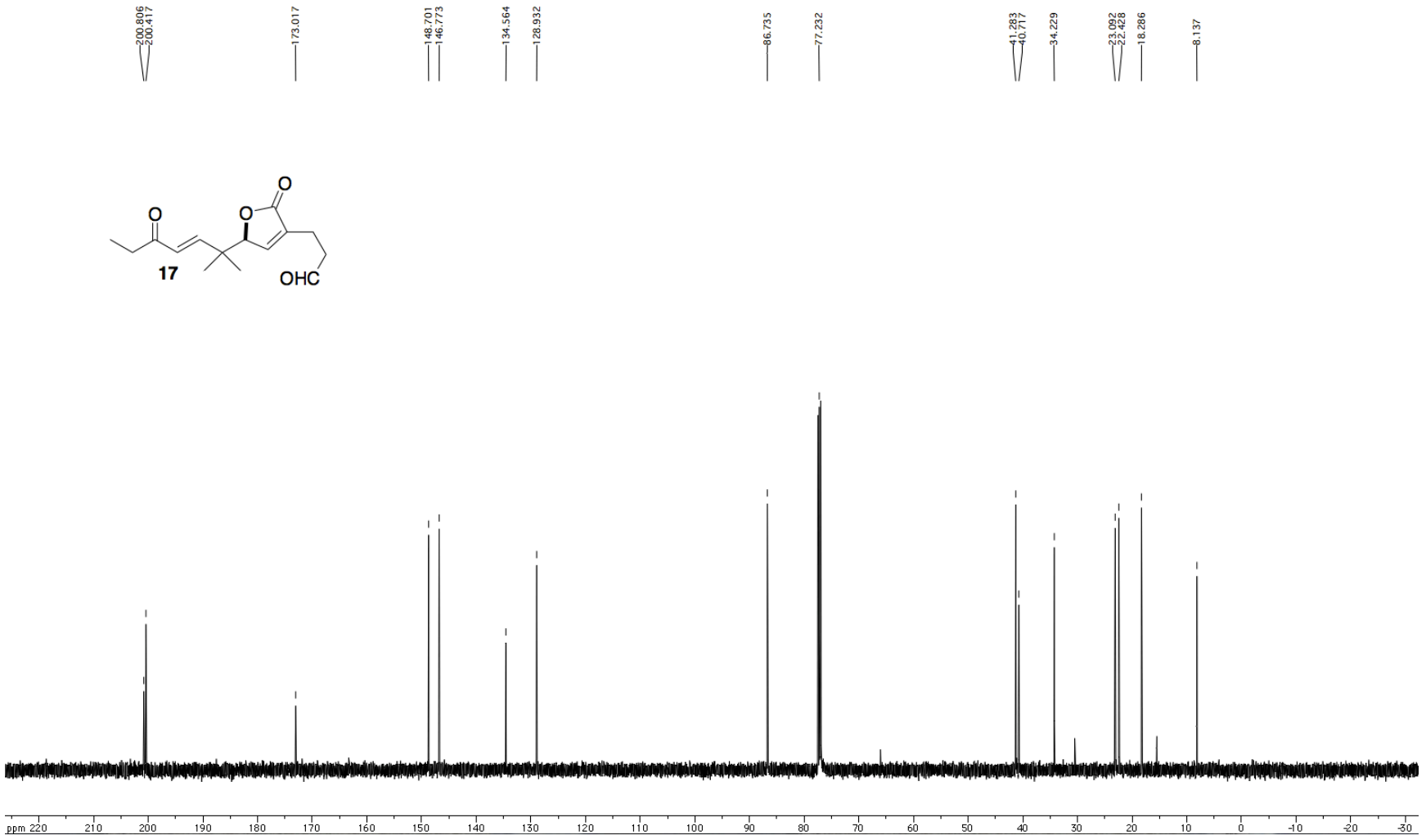
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OHC
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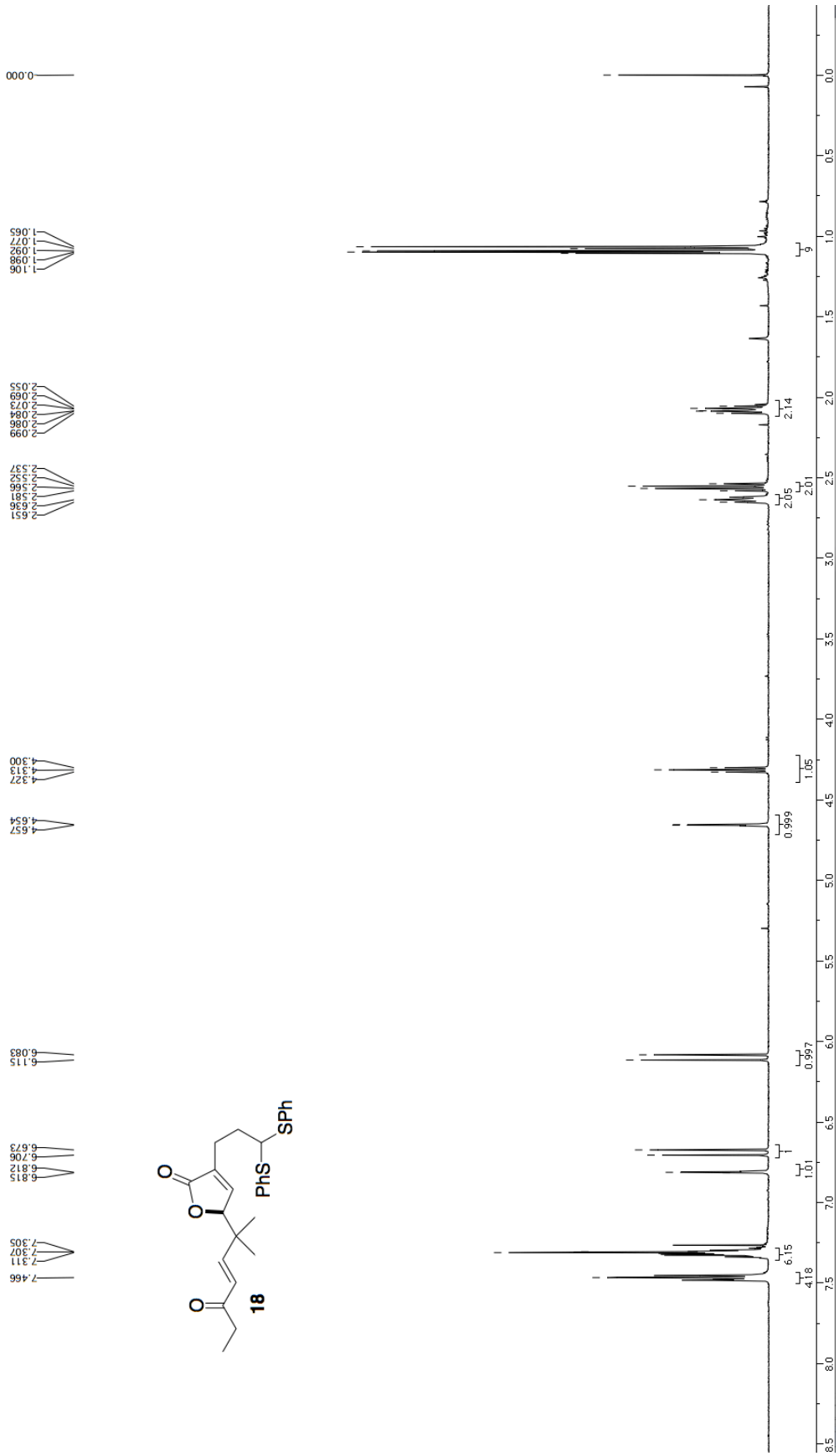
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SPh
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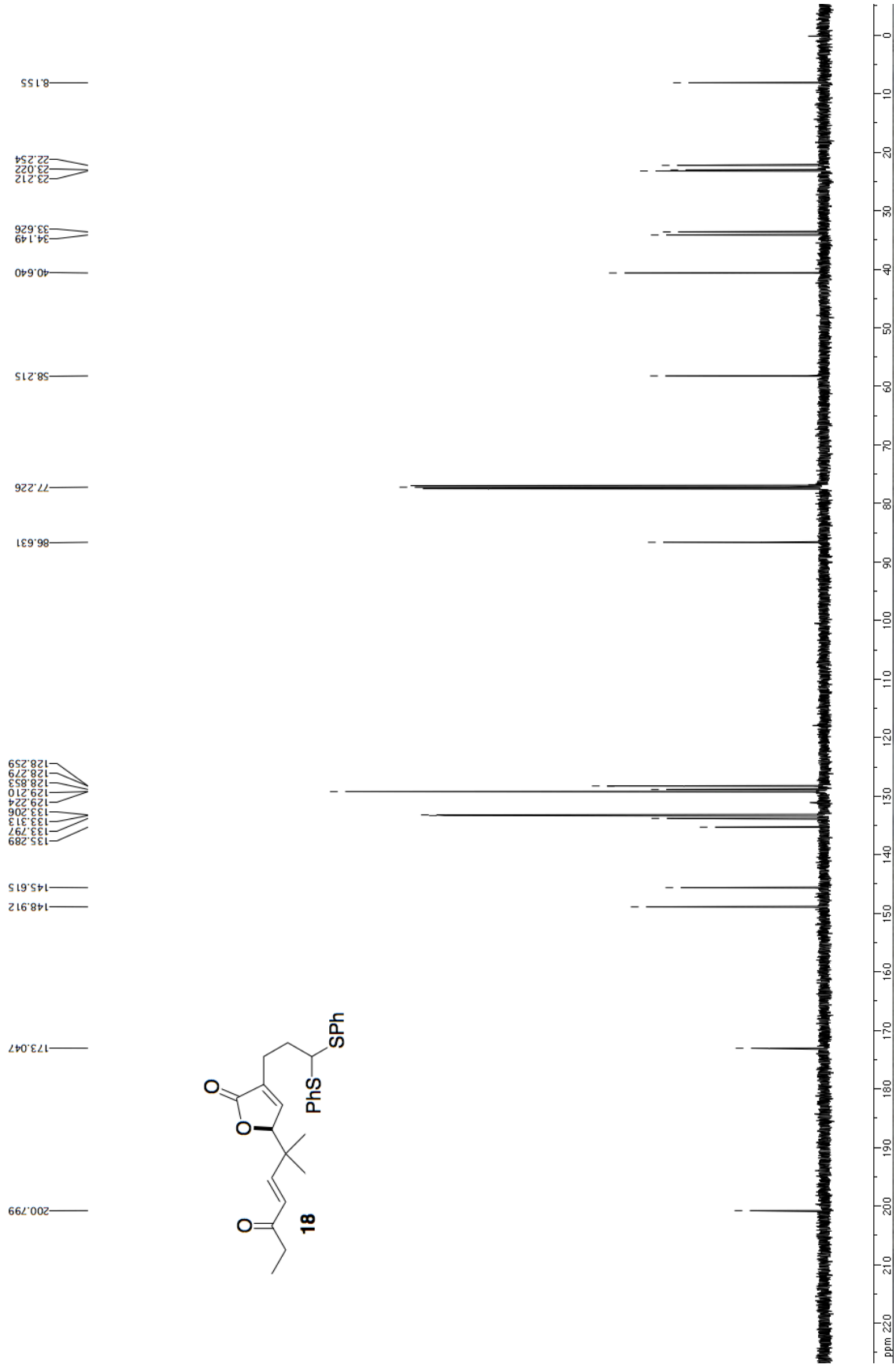
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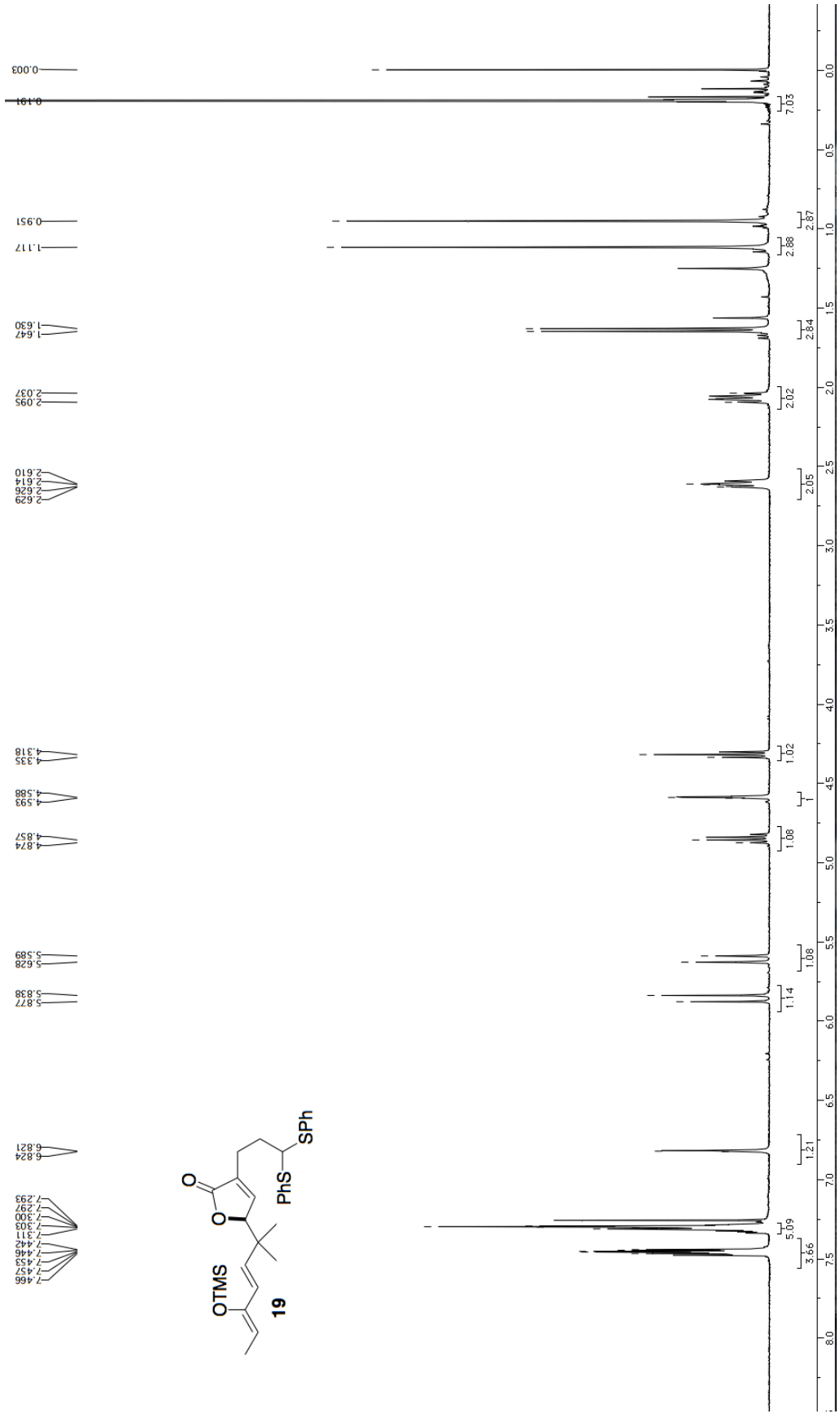
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5.838
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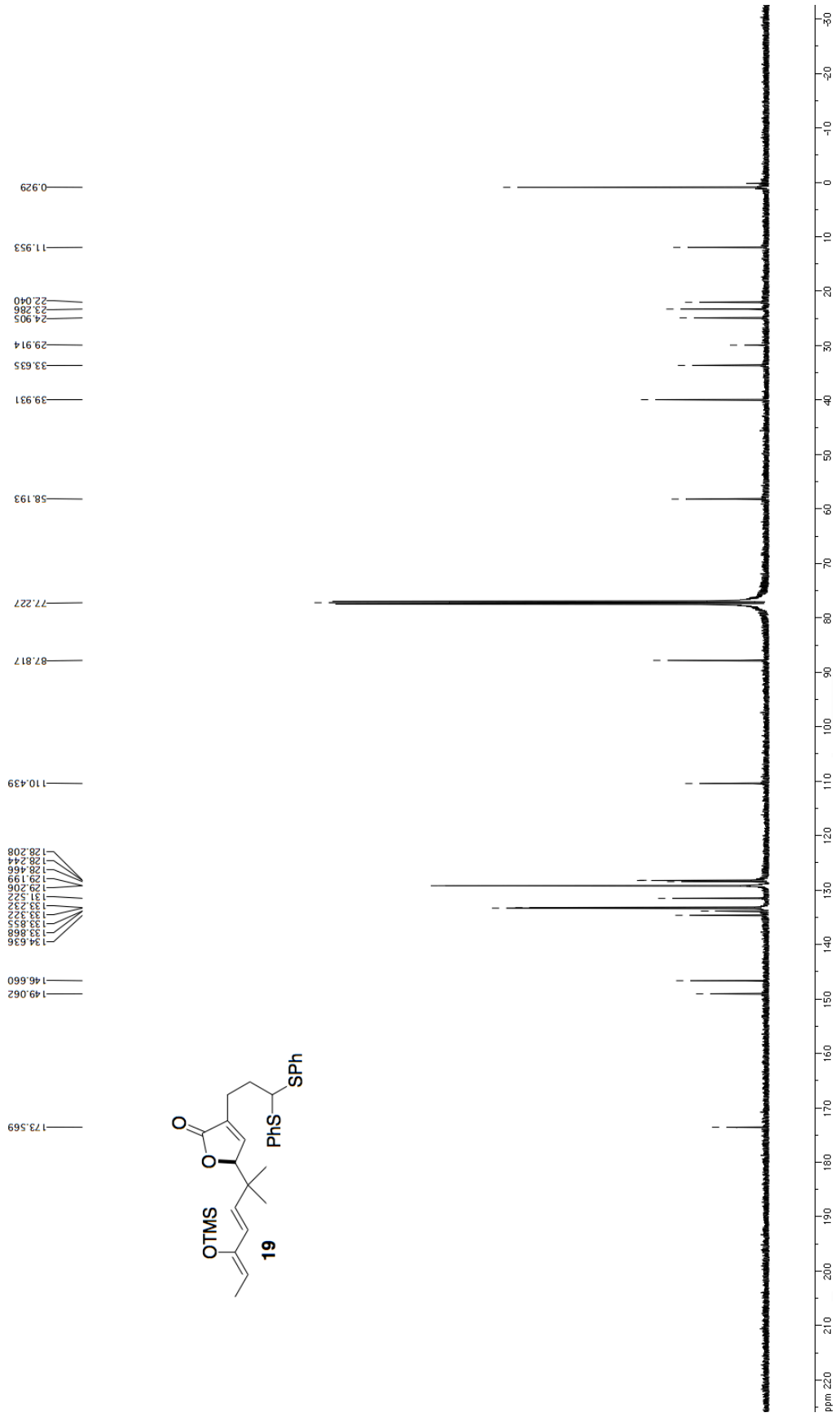
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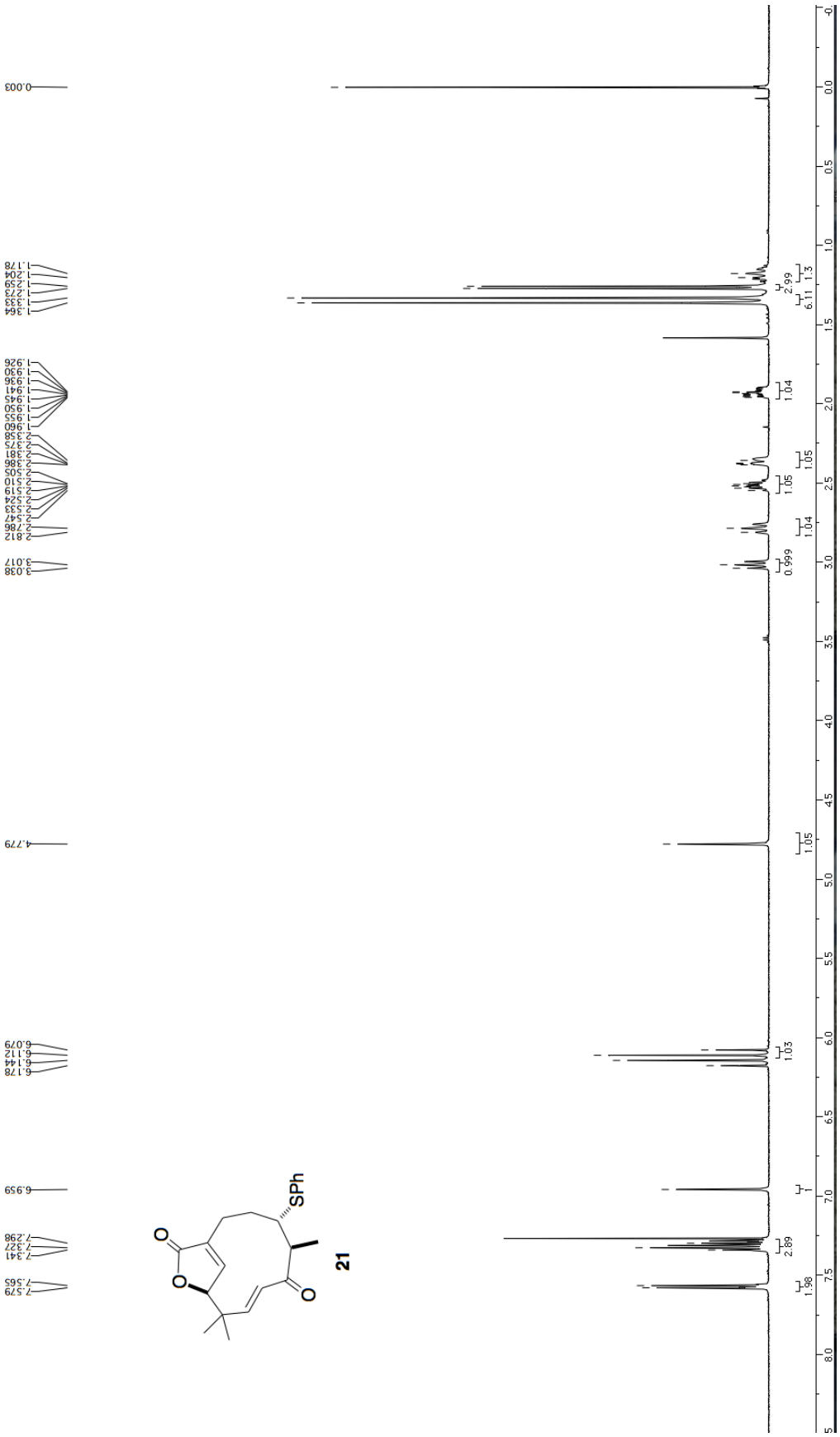
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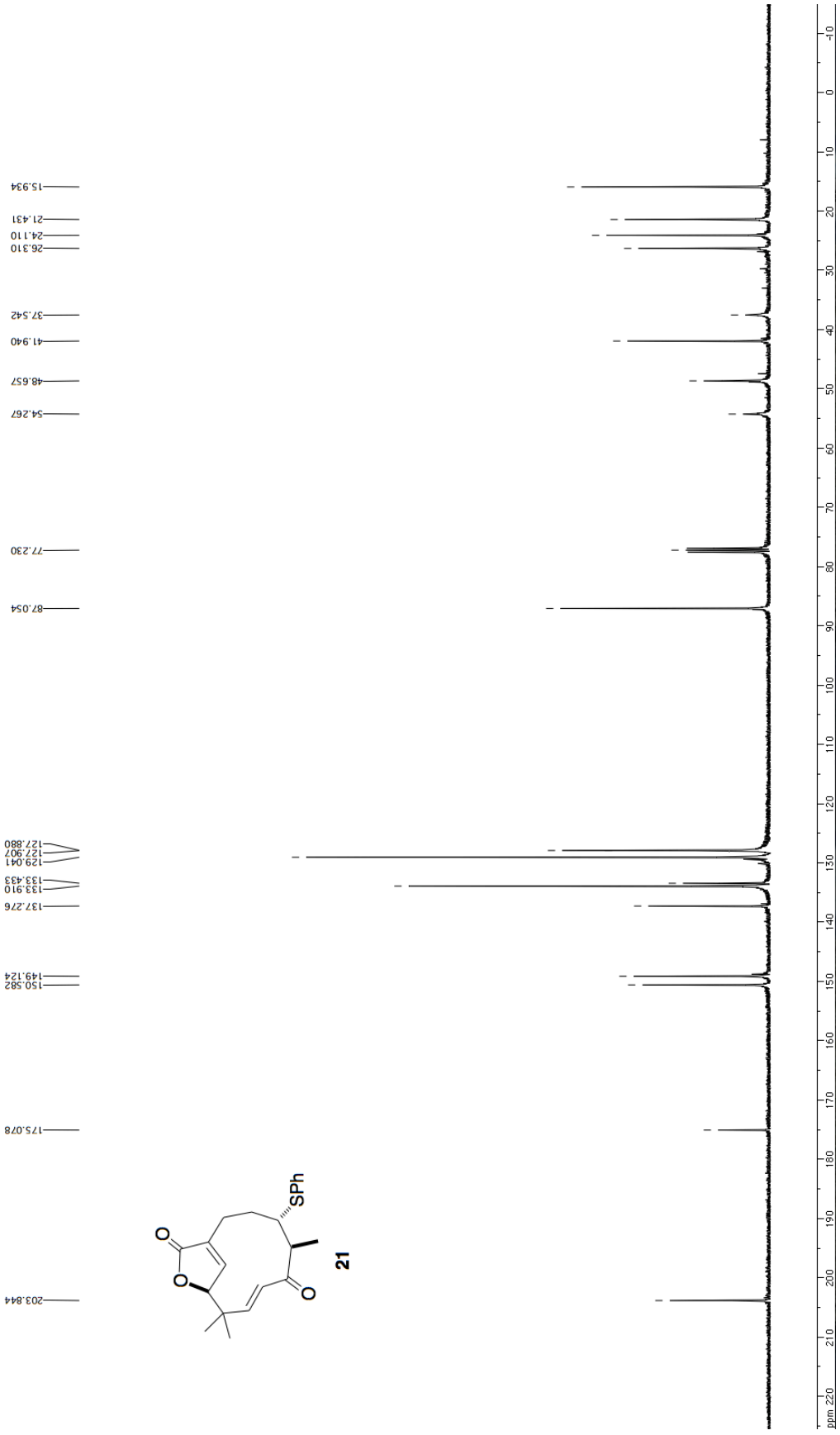
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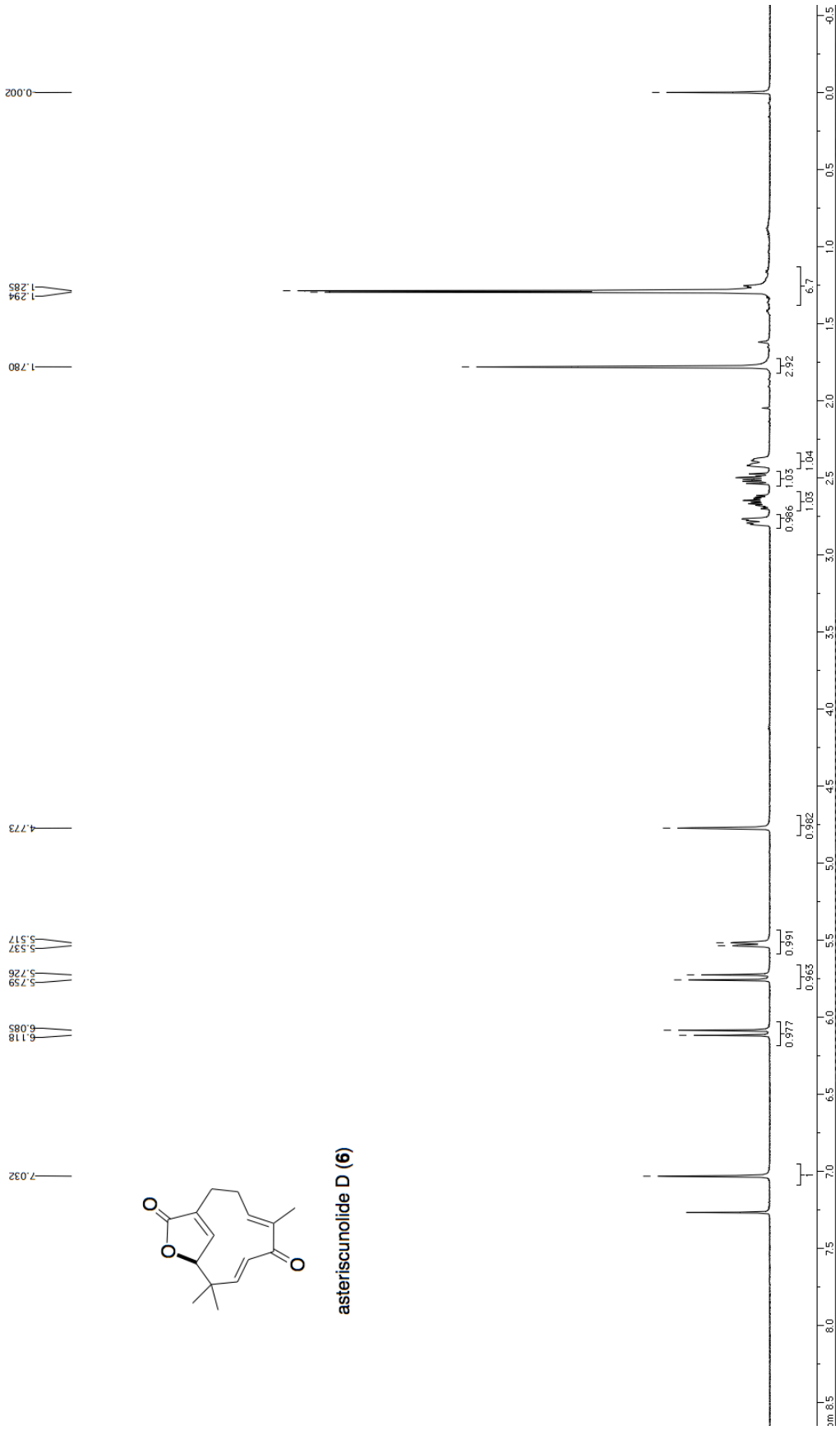
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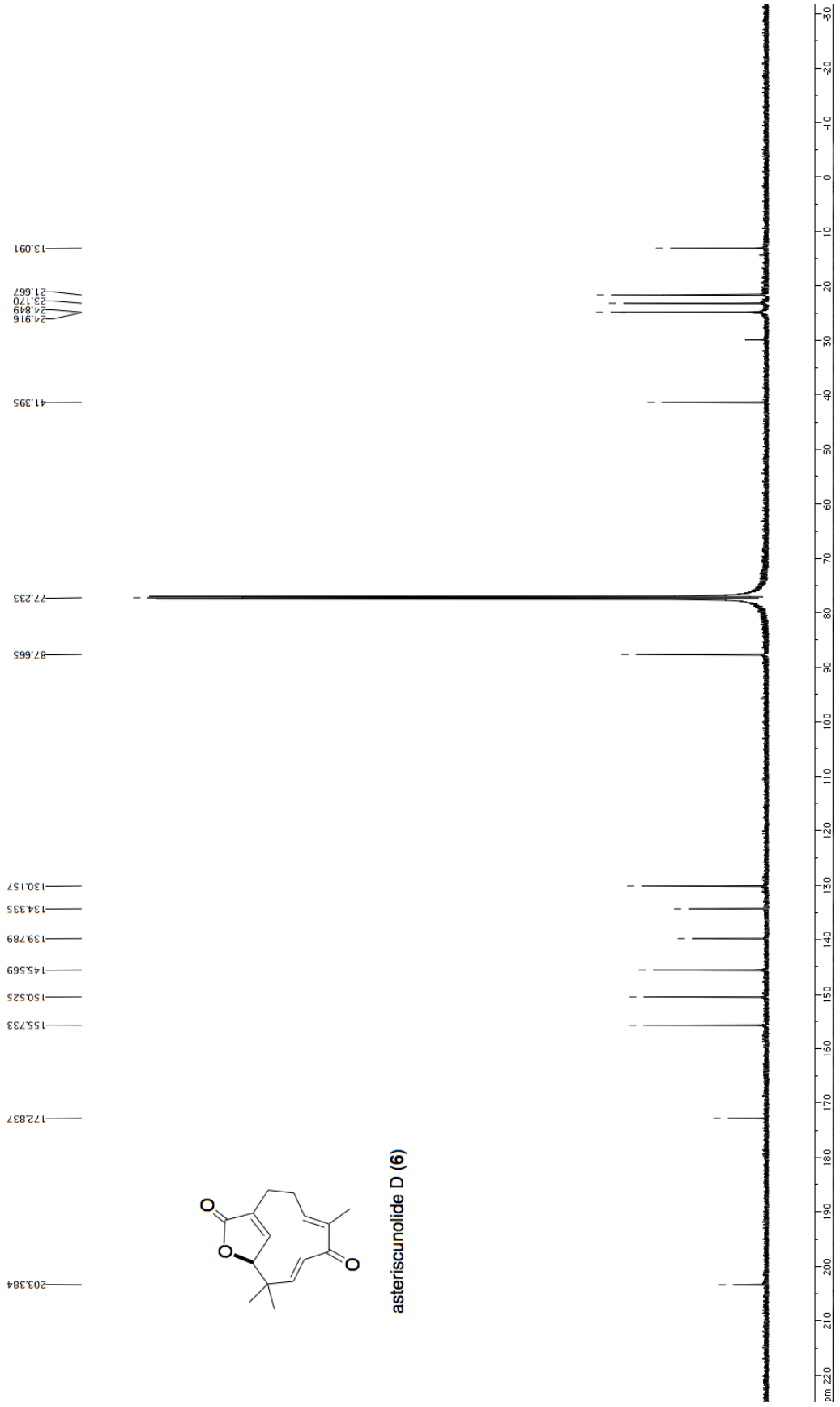
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asteriscunolide D (6)
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O
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180
170
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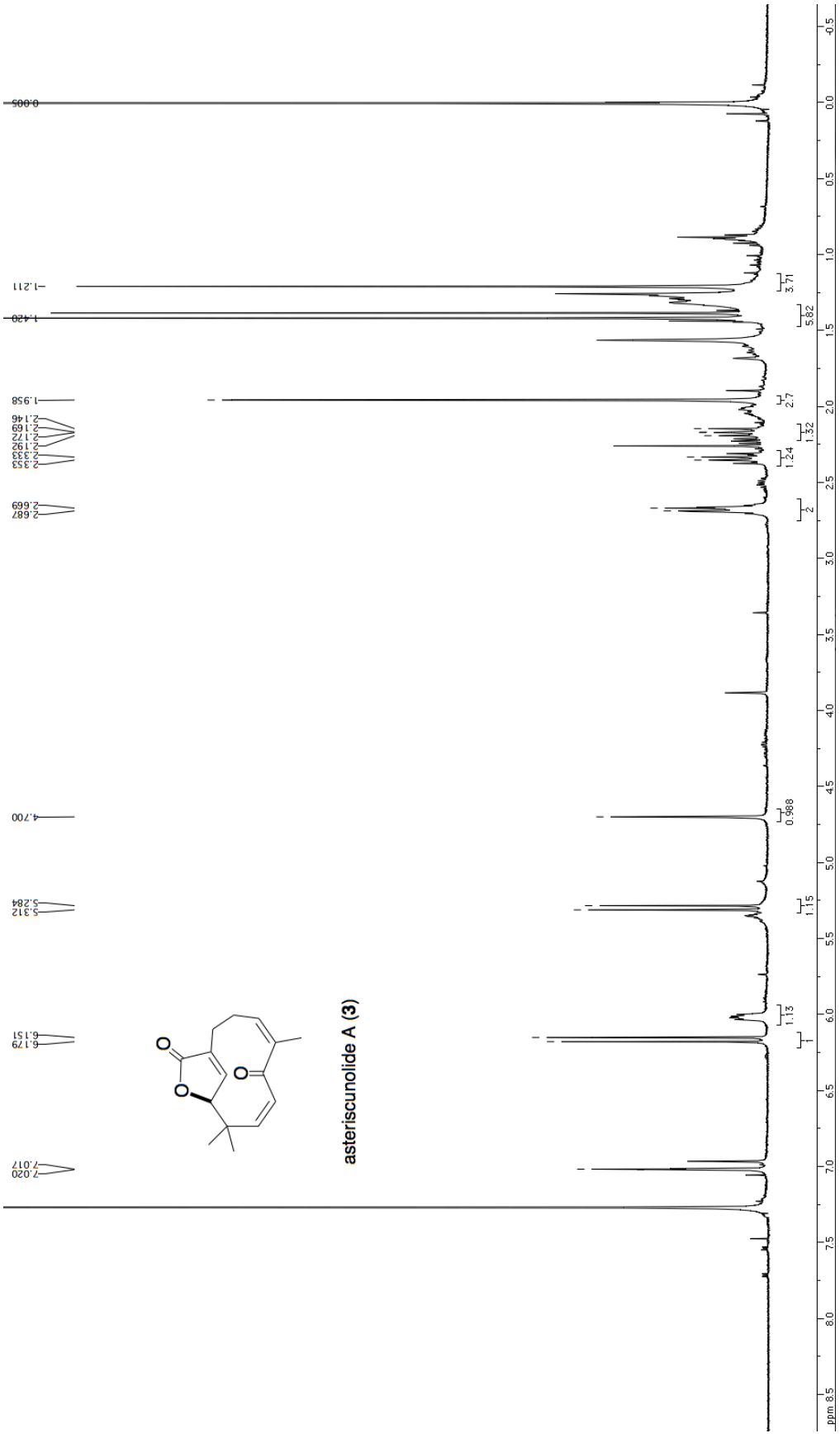
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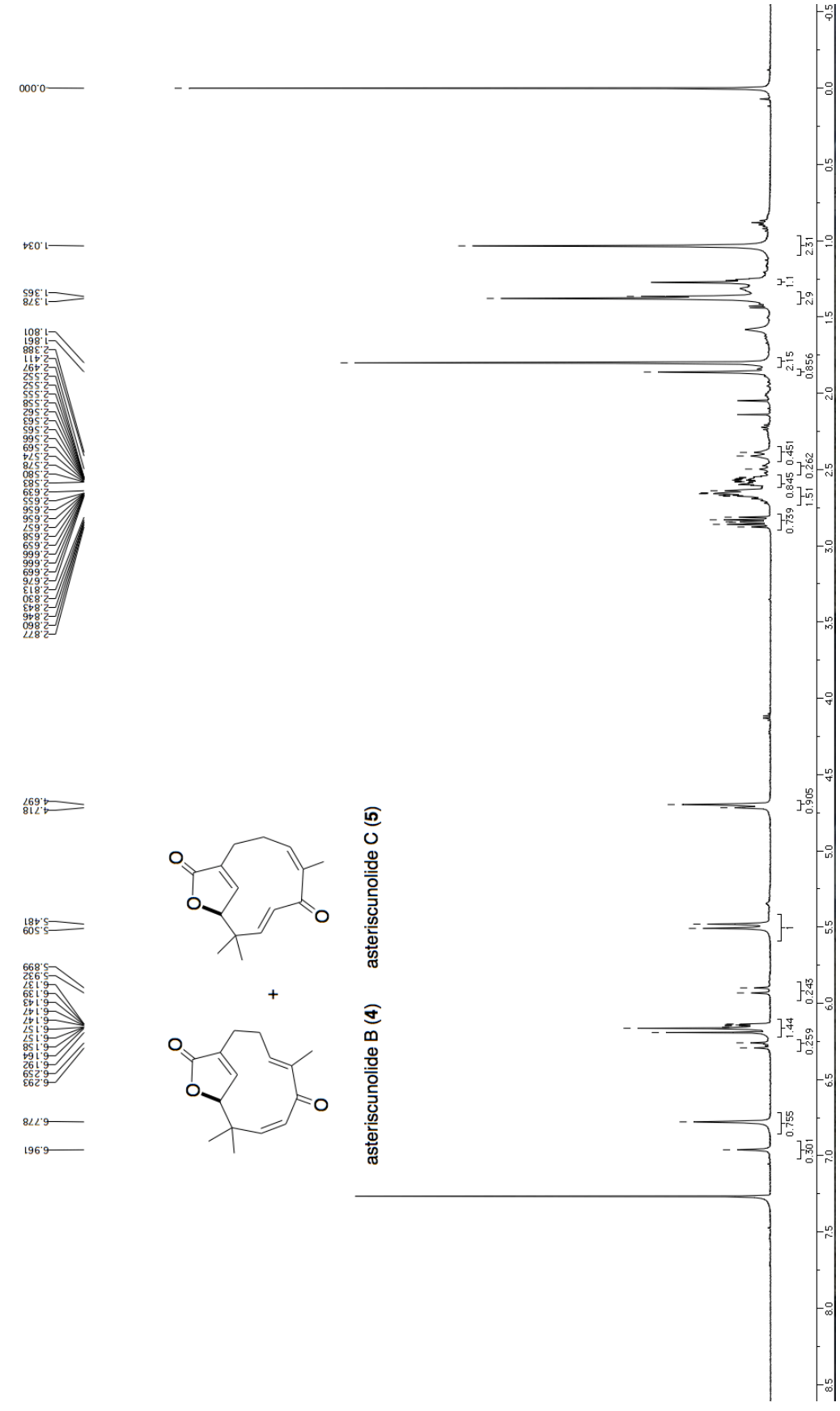
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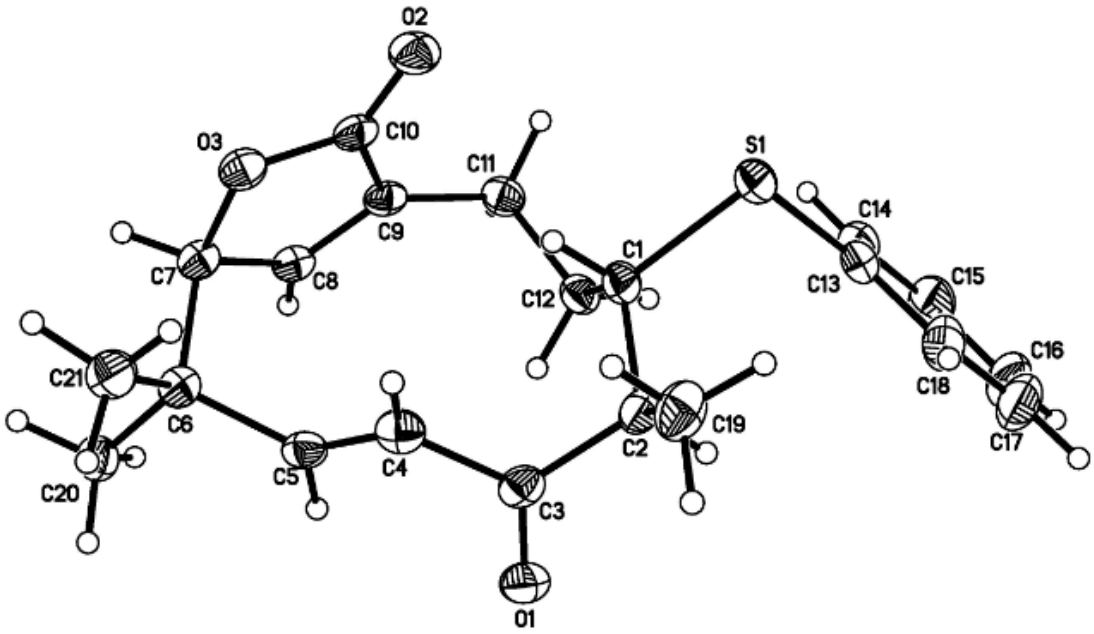
asteriscunolide C (5)
+

Sample: SU1126

X-ray Structure Report



DISCUSSION

The compound crystallizes as long, rod-like crystals from a dichloromethane / petroleum ether solution. There are two molecules of the compound in the unit cell of the acentric, primitive, monoclinic space group $P2_1$. The correct enantiomorph of the space group and handedness of the molecule were determined by comparison of intensities of Friedel pairs of reflections. The correct absolute configuration is depicted in the Figures. The Flack *x* parameter refined to 0.037(16); a value of zero (0) indicates the correct absolute configuration, a value of one (1) the inverted absolute configuration. A Bijvoet test was also appliled to the data yielding a Hooft *y* parameter of 0.058(9), again a value of zero indicates the correct absolute configuration. P2(true) and P3(true) values of 1.000 and 1.000 indicate the degree of enantiopurity (a value of one indicates an enantiopure sample).

The structure of the compound is as expected. The unsaturated bonds were located both by the presence of individual hydrogen atoms at those locations and by the bond distances (C4-C5 = 1.328(3) and C8-C9 = 1.333(3) Å).

The bond distances and angles within the molecule are otherwise as expected.

CRYSTAL SUMMARY

Crystal data for $C_{21}H_{24}O_3S$; M_r = 356.46; Monoclinic; space group $P2_1$; a = 5.8691(2) Å; b = 11.2351(4) Å; c = 14.3074(5) Å; α = 90°; β = 97.202(2)°; γ = 90°; V = 935.99(6) $Å^3$; Z = 2; T = 100(2) K; λ(Cu-Kα) = 1.54178 Å; μ(Cu-Kα) = 1.664 mm^{-1}; d_{calc} = 1.265g.cm^{-3}; 8446 reflections collected; 3122 unique (R_{int} = 0.0297); giving R_1 = 0.0347, wR_2 = 0.0870 for 3008 data with [I>2σ(I)] and R_1 = 0.0364, wR_2 = 0.0883 for all 3122 data. Residual electron density ($e^-.Å^{-3}$) max/min: 0.331/-0.131.

An arbitrary sphere of data were collected on a colorless rod-like crystal, having approximate dimensions of 0.76 × 0.13 × 0.07 mm, on a Bruker APEX diffractometer using a combination of ω- and φ-scans of 0.5°. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

Table 1. Crystal data and structure refinement for su1126.

Identification code	su1126
Empirical formula	$C_{21}H_{24}O_3S$
Formula weight	356.46
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P21
Unit cell dimensions	a = 5.8691(2) Å α = 90°
	b = 11.2351(4) Å β = 97.202(2)°
	c = 14.3074(5) Å γ = 90°
Volume	935.99(6) $Å^3$
Z	2
Density (calculated)	1.265 $g.cm^{-3}$
Absorption coefficient (μ)	1.664 mm^{-1}
F(000)	380
Crystal size	0.76 × 0.13 × 0.07 mm^3
θ range for data collection	3.11 to 69.60°
Index ranges	$-6 \le h \le 5$, $-13 \le k \le 13$, $-17 \le l \le 17$
Reflections collected	8446
Independent reflections	3122 [R_{int} = 0.0297]
Completeness to θ = 69.60°	93.2 %
Absorption correction	Numerical
Max. and min. transmission	0.9217 and 0.5473
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3122 / 1 / 229
Goodness-of-fit on F^2	1.055
Final R indices [I>2σ(I)]	R_1 = 0.0347, wR_2 = 0.0870
R indices (all data)	R_1 = 0.0364, wR_2 = 0.0883
Absolute structure parameter	0.037(16)
Largest diff. peak and hole	0.331 and -0.131 $e^-.Å^{-3}$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for su1126. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	1.04744(9)	0.58297(5)	0.41250(4)	0.031(1)
O(1)	0.4155(3)	0.76819(15)	0.18279(11)	0.030(1)
O(2)	1.2045(2)	0.44102(14)	0.17528(11)	0.028(1)
O(3)	1.0066(2)	0.46705(13)	0.03251(10)	0.023(1)
C(1)	0.8616(4)	0.60258(19)	0.30017(14)	0.023(1)
C(2)	0.7602(4)	0.7289(2)	0.28556(15)	0.024(1)
C(3)	0.6155(4)	0.73705(18)	0.18964(15)	0.023(1)
C(4)	0.7246(4)	0.69957(18)	0.10532(15)	0.024(1)
C(5)	0.5941(4)	0.64236(18)	0.03714(14)	0.022(1)
C(6)	0.6690(3)	0.5753(2)	-0.04609(14)	0.022(1)
C(7)	0.7706(3)	0.45281(18)	-0.01009(14)	0.020(1)
C(8)	0.6524(4)	0.40340(18)	0.06783(15)	0.020(1)
C(9)	0.7952(4)	0.40165(17)	0.14799(15)	0.020(1)
C(10)	1.0229(4)	0.43726(18)	0.12496(15)	0.021(1)
C(11)	0.7468(4)	0.38683(19)	0.24764(14)	0.023(1)
C(12)	0.6725(4)	0.50695(19)	0.28607(14)	0.023(1)
C(13)	0.8494(4)	0.6029(2)	0.49612(14)	0.030(1)
C(14)	0.7265(5)	0.5064(2)	0.52509(15)	0.035(1)
C(15)	0.5704(5)	0.5228(2)	0.58943(17)	0.041(1)
C(16)	0.5384(5)	0.6348(3)	0.62540(17)	0.042(1)
C(17)	0.6645(5)	0.7308(3)	0.59882(17)	0.042(1)
C(18)	0.8188(5)	0.7152(2)	0.53413(16)	0.034(1)
C(19)	0.9428(4)	0.8276(2)	0.29343(17)	0.033(1)
C(20)	0.4562(4)	0.5493(2)	-0.11758(15)	0.026(1)
C(21)	0.8456(4)	0.6441(2)	-0.09575(16)	0.028(1)
H(1A)	0.9612	0.5899	0.2492	0.027
H(2A)	0.6572	0.7433	0.3350	0.029
H(4A)	0.8816	0.7161	0.1007	0.029
H(5A)	0.4336	0.6435	0.0409	0.026
H(7A)	0.7625	0.3947	-0.0634	0.024
H(8A)	0.4974	0.3770	0.0612	0.024
H(11A)	0.8862	0.3577	0.2871	0.028
H(11B)	0.6233	0.3273	0.2502	0.028
H(12A)	0.5429	0.5386	0.2421	0.027
H(12B)	0.6151	0.4927	0.3473	0.027
H(14A)	0.7494	0.4293	0.5008	0.042
H(15A)	0.4859	0.4570	0.6086	0.049
H(16A)	0.4296	0.6461	0.6685	0.050
H(17A)	0.6449	0.8072	0.6250	0.050
H(18A)	0.9039	0.7812	0.5156	0.041
H(19A)	0.8674	0.9052	0.2834	0.049

H(19B)	1.0463	0.8151	0.2456	0.049
H(19C)	1.0311	0.8254	0.3562	0.049
H(20A)	0.3802	0.6243	-0.1377	0.040
H(20B)	0.3495	0.4986	-0.0881	0.040
H(20C)	0.5037	0.5083	-0.1725	0.040
H(21A)	0.7736	0.7157	-0.1254	0.042
H(21B)	0.9002	0.5934	-0.1441	0.042
H(21C)	0.9757	0.6670	-0.0495	0.042

Table 3. Anisotropic displacement parameters ($Å^2$) for su1126.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	0.0239(3)	0.0414(3)	0.0256(3)	-0.0083(2)	-0.0052(2)	0.0060(2)
O(1)	0.0284(10)	0.0305(8)	0.0317(8)	0.0017(7)	0.0049(6)	0.0089(7)
O(2)	0.0181(8)	0.0313(8)	0.0340(8)	-0.0049(7)	-0.0012(6)	0.0009(6)
O(3)	0.0179(8)	0.0238(8)	0.0283(8)	-0.0007(6)	0.0056(6)	-0.0006(6)
C(1)	0.0202(11)	0.0268(12)	0.0199(9)	-0.0033(8)	-0.0009(7)	-0.0001(8)
C(2)	0.0230(12)	0.0247(11)	0.0246(10)	-0.0064(9)	0.0045(8)	0.0003(8)
C(3)	0.0278(13)	0.0149(10)	0.0272(11)	0.0009(8)	0.0059(8)	-0.0001(8)
C(4)	0.0245(12)	0.0208(11)	0.0285(11)	0.0042(9)	0.0047(8)	-0.0010(8)
C(5)	0.0219(12)	0.0185(10)	0.0251(10)	0.0038(8)	0.0045(8)	0.0031(8)
C(6)	0.0215(11)	0.0213(10)	0.0230(10)	-0.0014(9)	0.0034(7)	0.0004(9)
C(7)	0.0153(11)	0.0198(10)	0.0247(10)	-0.0026(8)	0.0035(7)	-0.0023(7)
C(8)	0.0170(11)	0.0174(10)	0.0265(11)	-0.0022(8)	0.0027(7)	0.0000(7)
C(9)	0.0200(11)	0.0135(10)	0.0271(11)	-0.0019(8)	0.0017(8)	0.0013(7)
C(10)	0.0208(11)	0.0156(10)	0.0273(11)	-0.0027(8)	0.0033(8)	0.0033(7)
C(11)	0.0233(12)	0.0227(11)	0.0244(11)	0.0044(9)	0.0022(8)	0.0002(8)
C(12)	0.0196(11)	0.0264(11)	0.0207(10)	0.0004(8)	-0.0007(8)	0.0003(8)
C(13)	0.0309(13)	0.0385(14)	0.0184(9)	-0.0026(10)	-0.0038(8)	0.0098(10)
C(14)	0.0516(17)	0.0293(12)	0.0225(11)	0.0023(9)	-0.0016(10)	0.0115(11)
C(15)	0.0649(19)	0.0325(13)	0.0250(12)	0.0090(10)	0.0089(11)	0.0042(12)
C(16)	0.0643(19)	0.0392(15)	0.0249(12)	0.0009(11)	0.0145(11)	0.0081(13)
C(17)	0.0620(19)	0.0325(13)	0.0319(13)	-0.0078(11)	0.0087(12)	0.0071(12)
C(18)	0.0425(15)	0.0353(13)	0.0251(11)	-0.0056(10)	0.0025(9)	0.0001(11)
C(19)	0.0330(13)	0.0302(12)	0.0356(13)	-0.0099(10)	0.0050(10)	-0.0066(10)
C(20)	0.0247(13)	0.0309(12)	0.0238(11)	0.0007(8)	0.0041(8)	0.0006(8)
C(21)	0.0302(13)	0.0247(11)	0.0299(11)	0.0037(9)	0.0086(9)	0.0011(9)

Table 4. Bond lengths [Å] for su1126.

atom-atom	distance	atom-atom	distance
S(1)-C(13)	1.784(2)	S(1)-C(1)	1.839(2)
O(1)-C(3)	1.217(3)	O(2)-C(10)	1.210(2)
O(3)-C(10)	1.356(3)	O(3)-C(7)	1.450(2)
C(1)-C(12)	1.540(3)	C(1)-C(2)	1.543(3)
C(2)-C(3)	1.523(3)	C(2)-C(19)	1.536(3)
C(3)-C(4)	1.496(3)	C(4)-C(5)	1.328(3)
C(5)-C(6)	1.520(3)	C(6)-C(21)	1.537(3)
C(6)-C(20)	1.539(3)	C(6)-C(7)	1.561(3)
C(7)-C(8)	1.492(3)	C(8)-C(9)	1.333(3)
C(9)-C(10)	1.471(3)	C(9)-C(11)	1.498(3)
C(11)-C(12)	1.541(3)	C(13)-C(14)	1.393(4)
C(13)-C(18)	1.395(3)	C(14)-C(15)	1.390(4)
C(15)-C(16)	1.381(4)	C(16)-C(17)	1.388(4)
C(17)-C(18)	1.385(4)	C(1)-H(1A)	1.0000
C(2)-H(2A)	1.0000	C(4)-H(4A)	0.9500
C(5)-H(5A)	0.9500	C(7)-H(7A)	1.0000
C(8)-H(8A)	0.9500	C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900	C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900	C(14)-H(14A)	0.9500
C(15)-H(15A)	0.9500	C(16)-H(16A)	0.9500
C(17)-H(17A)	0.9500	C(18)-H(18A)	0.9500
C(19)-H(19A)	0.9800	C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800	C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800	C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800	C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800		

Symmetry transformations used to generate equivalent atoms:

Table 5. Bond angles [°] for su1126.

atom-atom-atom	angle	atom-atom-atom	angle
C(13)-S(1)-C(1)	101.90(9)	C(10)-O(3)-C(7)	109.23(15)
C(12)-C(1)-C(2)	111.40(17)	C(12)-C(1)-S(1)	111.70(14)
C(2)-C(1)-S(1)	113.89(14)	C(3)-C(2)-C(19)	109.13(19)
C(3)-C(2)-C(1)	109.83(17)	C(19)-C(2)-C(1)	113.61(18)
O(1)-C(3)-C(4)	121.5(2)	O(1)-C(3)-C(2)	120.88(19)
C(4)-C(3)-C(2)	117.57(19)	C(5)-C(4)-C(3)	117.6(2)
C(4)-C(5)-C(6)	128.2(2)	C(5)-C(6)-C(21)	113.01(18)
C(5)-C(6)-C(20)	108.95(17)	C(21)-C(6)-C(20)	109.04(17)
C(5)-C(6)-C(7)	108.34(16)	C(21)-C(6)-C(7)	110.09(17)
C(20)-C(6)-C(7)	107.25(17)	O(3)-C(7)-C(8)	103.66(16)
O(3)-C(7)-C(6)	110.29(16)	C(8)-C(7)-C(6)	112.33(17)
C(9)-C(8)-C(7)	110.30(19)	C(8)-C(9)-C(10)	107.11(19)
C(8)-C(9)-C(11)	130.3(2)	C(10)-C(9)-C(11)	121.98(18)
O(2)-C(10)-O(3)	121.38(18)	O(2)-C(10)-C(9)	129.3(2)
O(3)-C(10)-C(9)	109.31(17)	C(9)-C(11)-C(12)	109.77(16)
C(1)-C(12)-C(11)	115.25(18)	C(14)-C(13)-C(18)	119.4(2)
C(14)-C(13)-S(1)	120.48(18)	C(18)-C(13)-S(1)	120.1(2)
C(15)-C(14)-C(13)	120.2(2)	C(16)-C(15)-C(14)	120.0(3)
C(15)-C(16)-C(17)	120.2(2)	C(18)-C(17)-C(16)	120.1(3)
C(17)-C(18)-C(13)	120.1(3)	C(12)-C(1)-H(1A)	106.4
C(2)-C(1)-H(1A)	106.4	S(1)-C(1)-H(1A)	106.4
C(3)-C(2)-H(2A)	108.0	C(19)-C(2)-H(2A)	108.0
C(1)-C(2)-H(2A)	108.0	C(5)-C(4)-H(4A)	121.2
C(3)-C(4)-H(4A)	121.2	C(4)-C(5)-H(5A)	115.9
C(6)-C(5)-H(5A)	115.9	O(3)-C(7)-H(7A)	110.1
C(8)-C(7)-H(7A)	110.1	C(6)-C(7)-H(7A)	110.1
C(9)-C(8)-H(8A)	124.8	C(7)-C(8)-H(8A)	124.8
C(9)-C(11)-H(11A)	109.7	C(12)-C(11)-H(11A)	109.7
C(9)-C(11)-H(11B)	109.7	C(12)-C(11)-H(11B)	109.7
H(11A)-C(11)-H(11B)	108.2	C(1)-C(12)-H(12A)	108.5
C(11)-C(12)-H(12A)	108.5	C(1)-C(12)-H(12B)	108.5
C(11)-C(12)-H(12B)	108.5	H(12A)-C(12)-H(12B)	107.5
C(15)-C(14)-H(14A)	119.9	C(13)-C(14)-H(14A)	119.9
C(16)-C(15)-H(15A)	120.0	C(14)-C(15)-H(15A)	120.0
C(15)-C(16)-H(16A)	119.9	C(17)-C(16)-H(16A)	119.9
C(18)-C(17)-H(17A)	120.0	C(16)-C(17)-H(17A)	120.0
C(17)-C(18)-H(18A)	119.9	C(13)-C(18)-H(18A)	119.9
C(2)-C(19)-H(19A)	109.5	C(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5	C(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5	H(19B)-C(19)-H(19C)	109.5
C(6)-C(20)-H(20A)	109.5	C(6)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5	C(6)-C(20)-H(20C)	109.5

H(20A)-C(20)-H(20C)	109.5	H(20B)-C(20)-H(20C)	109.5
C(6)-C(21)-H(21A)	109.5	C(6)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5	C(6)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5	H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 6. Torsion angles [°] for su1126.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(13)-S(1)-C(1)-C(12)	-62.46(17)	C(13)-S(1)-C(1)-C(2)	64.82(17)
C(12)-C(1)-C(2)-C(3)	-54.3(2)	S(1)-C(1)-C(2)-C(3)	178.28(15)
C(12)-C(1)-C(2)-C(19)	-176.82(18)	S(1)-C(1)-C(2)-C(19)	55.7(2)
C(19)-C(2)-C(3)-O(1)	-110.7(2)	C(1)-C(2)-C(3)-O(1)	124.1(2)
C(19)-C(2)-C(3)-C(4)	72.3(2)	C(1)-C(2)-C(3)-C(4)	-52.9(2)
O(1)-C(3)-C(4)-C(5)	-34.5(3)	C(2)-C(3)-C(4)-C(5)	142.5(2)
C(3)-C(4)-C(5)-C(6)	-167.65(19)	C(4)-C(5)-C(6)-C(21)	-45.6(3)
C(4)-C(5)-C(6)-C(20)	-167.0(2)	C(4)-C(5)-C(6)-C(7)	76.7(3)
C(10)-O(3)-C(7)-C(8)	-3.4(2)	C(10)-O(3)-C(7)-C(6)	117.01(17)
C(5)-C(6)-C(7)-O(3)	-81.0(2)	C(21)-C(6)-C(7)-O(3)	43.0(2)
C(20)-C(6)-C(7)-O(3)	161.49(15)	C(5)-C(6)-C(7)-C(8)	34.0(2)
C(21)-C(6)-C(7)-C(8)	158.08(17)	C(20)-C(6)-C(7)-C(8)	-83.4(2)
O(3)-C(7)-C(8)-C(9)	6.1(2)	C(6)-C(7)-C(8)-C(9)	-112.93(19)
C(7)-C(8)-C(9)-C(10)	-6.2(2)	C(7)-C(8)-C(9)-C(11)	164.6(2)
C(7)-O(3)-C(10)-O(2)	179.31(19)	C(7)-O(3)-C(10)-C(9)	-0.1(2)
C(8)-C(9)-C(10)-O(2)	-175.3(2)	C(11)-C(9)-C(10)-O(2)	12.9(3)
C(8)-C(9)-C(10)-O(3)	4.0(2)	C(11)-C(9)-C(10)-O(3)	-167.75(17)
C(8)-C(9)-C(11)-C(12)	-82.0(3)	C(10)-C(9)-C(11)-C(12)	87.7(2)
C(2)-C(1)-C(12)-C(11)	149.19(18)	S(1)-C(1)-C(12)-C(11)	-82.20(19)
C(9)-C(11)-C(12)-C(1)	-68.1(2)	C(1)-S(1)-C(13)-C(14)	88.37(19)
C(1)-S(1)-C(13)-C(18)	-92.55(19)	C(18)-C(13)-C(14)-C(15)	1.7(3)
S(1)-C(13)-C(14)-C(15)	-179.24(18)	C(13)-C(14)-C(15)-C(16)	-0.5(4)
C(14)-C(15)-C(16)-C(17)	-1.1(4)	C(15)-C(16)-C(17)-C(18)	1.7(4)
C(16)-C(17)-C(18)-C(13)	-0.6(4)	C(14)-C(13)-C(18)-C(17)	-1.1(3)
S(1)-C(13)-C(18)-C(17)	179.80(19)		

Symmetry transformations used to generate equivalent atoms: