Supporting Information

Cu(II)-Catalyzed Acylation by Thiol Esters Under Neutral Conditions: Tandem Acylation-Wittig Reaction Leading to One-Pot Synthesis of Butenolides

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Experimental Section

General

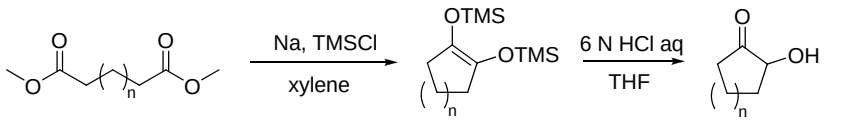
^{1}H-NMR, ^{13}C-NMR were measured in $CDCl_3$ solution using JEOL JNM AL-400, (^{1}H-NMR at 400 MHz, ^{13}C-NMR at 100 MHz, ^{31}P-NMR at 160 MHz) and JNM ECA-600 spectrometer (^{1}H NMR at 600 MHz, ^{13}C NMR at 150 MHz, ^{31}P NMR at 243 MHz) as the referenced standard (^{1}H NMR at 0.00 ppm (TMS), ^{13}CNMR at 77.03 ppm ($CDCl_3$), ^{31}P NMR at 0.00ppm (85% H_3PO_4)) otherwise noted. Chemical shifts are reported in ppm. Peak multiplicities are used the following abbreviation: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. IR spectra were recorded on Shimazu FT/IR-8300 spectrometers. Mass spectra and high resolution mass spectra were obtained on a JEOL JMS-700. Elemental analyses were performed with YANACO 026 CHN analyzer. Melting points were measured with a SRS Opti Melt MPA 100 apparatus are uncorrected. Analytical TLC was performed on precoated plates (0.25 mm, silica gel Merck 60 F_{254}). Column chromatography was performed on a silica gel (Kanto Chemical Co., Inc.). Preparative HPLC was performed on Kanto Mightysil Si60, and performed on a system utilizing a JAS.CO PU-2087 *plus* Intelligent Pump with Dynamic Mixer MX-2080.32, UV-2075 *plus* Intelligent UV/VIS Detector and RI-2031 *plus* Intelligent RI Detector. All reactions were performed under an air atmosphere unless otherwise noted, and dichloromethane (CH_2Cl_2), diethyl ether (Et_2O) and tetrahydrofuran (THF) were purchased from Kanto Chemical Co., Inc., and other solvent was distilled. Unless otherwise noted, reagents were obtained from chemical sources and without further purification.

The known compounds (2-hydroxycyclopentanone (**1b**), 2-hydroxycyclohexanone (**1c**), 2-hydroxycycloheptaone (**1d**), 2-hydroxycyclooctanone (**1e**), 2-hydroxycyclododecanone (**1f**), 2-hydroxyindan-1-one (**1i**), 2-hydroxy-2-methyl 1-indanone (**1j**), 4-Methyl-5-vinyl-8-oxabicyclo [3,2,1]octane-1,2-diol (**1k**), *cis*-2-hydroxy-6-methoxy-4,7-dimethyltetral-1-one (**1l**)) of structure were confirmed by the literatures.

The known compounds (2-hydroxyacetophenone (**1a**), 2-hydroxy-γ-butyrolactone (**1h**)) are commercially available reagents.

Preparation of acyloins.

1) General procedure for synthesis of **1b** and **1c**[1]



1b: n = 1, **1c**: n = 2

Sodium (0.45 g, 19.6 mmol) in refluxing toluene (11 mL) was stirred vigorously until sodium sand was obtained. Chlorotrimethylsilane (2.6 mL, 20.1 mmol) and the dimethyl ester (4.9 mmol) were then added to the mixture at room temperature. After reflux for 1.5 h, the mixture was filtrated and evaporated. The residue was dissolved in THF (16 mL), and 6M HCl aq. (2 mL) was added. After stirred for 0.5 h at rt, the resulting mixture was extracted with Et_2O. The combined organic layer was washed with sat. $NaHCO_3$ aq and brine, then dried over $MgSO_4$, and evaporated. The crude product was purified with silicagel column chromatography (10-30% EtOAc-Hex) to give the acyloin.

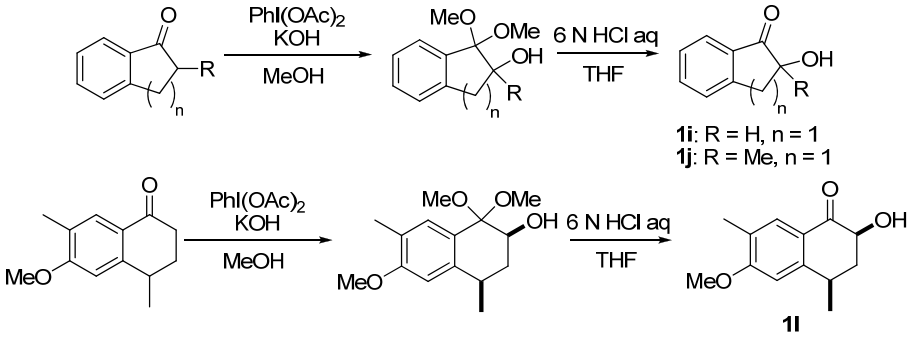
2-Hydroxycyclopentanone (1b)[2]**:**

Acyloin **1b** (25%) was obtained as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.62-1.73 (m, 1H), 1.76-1.89 (m, 1H), 2.01-2.09 (m, 1H), 2.15-2.25 (m, 1 H), 2.37-2.47 (m, 2 H), 2.69 (bs, 1H), 4.07 (t, *J* = 10.0 Hz, 1H).

2-Hydroxycyclohexanone (1c)[3]**:**

Acyloin **1c** (43%) was obtained as a colorless needle. Colorless needle (EtOH): mp 106.5-106.9 ºC; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.44-1.78 (m, 3H), 1.85-1.93 (m, 1H), 2.08-2.15 (m, 1H), 2.32-2.41 (m, 1 H), 2.43-2.50 (m, 1 H), 2.54-2.60 (m, 1H), 3.64 (d, *J* = 3.2 Hz, 1H), 4.10-4.15 (m, 1H).

2) General procedure for synthesis of **1i, 1j** and **1l**[4]



A solution of the ketone (10 mmol) and KOH (6.2 g, 111 mmol) in MeOH (50 mL) was stirred for 10 min at 0 °C, and $PhI(OAc)_2$ (3.9 g, 12 mmol) was added. The whole was stirred at the same

temperature for 1 h and at room temperature for 0.5 h. The reaction mixture was concentrated under reduced pressure to give a residue, which was dissolved in Et_2O, and the ethereal solution was washed with aqueous 3% $NaHCO_3$ aq. and H_2O, and evaporated. The residue was dissolved in THF (25 mL), and 6M HCl aq. (3 mL) was added. After stirred for 0.5 h at rt, the resulting mixture was extracted with Et_2O, and the combined organic layer was washed with sat. $NaHCO_3$ aq. and brine, then dried over $MgSO_4$. The crude product was purified with column chromatography (25% EtOAc-Hex) to give the acyloin.

2-Hydroxyindan-1-one (1i)[5]:

Acyloin **1i** (66%) was obtained as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.02 (dd, *J* = 16.8 Hz, 5.2 Hz, 1H), 3.1 (bs, 1H), 3.59 (dd, *J* = 16.8 Hz, 8.0 Hz, 1H), 4.55 (dd, *J* = 8.0 Hz, 5.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.64 (dt, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H).

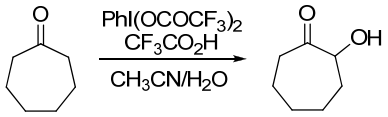
2-Hydroxy-2-methyl 1-indanone (1j)[6]:

Acyloin **1j** (66%) was obtained as a colorless prism. Colorless prism (Et_2O-Petroleum benzine): mp 56-57 ºC; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.45 (s, 3H), 2.59 (bs, 1H), 3.23 (d, *J* = 23.2 Hz, 1H), 3.28 (d, *J* = 23.2 Hz, 1H), 7.40-7.46 (m, 2H), 7.63-7.67 (m, 1H), 7.79 (d, *J* = 8.0 Hz, 1H).

***cis*-2-Hydroxy-6-methoxy-4,7-dimethyltetral-1-one (1l)[4]:**

Acyloin **1l** (71%) was obtained as a colorless prism. Colorless prisms (Et_2O-Hex): mp 105.5-106.5 ºC; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.46 (d, *J* = 7.2 Hz, 3H), 1.76 (ddd, *J* = 12.8 Hz, 12.8 Hz, 12.8 Hz, 1H), 2.22 (s, 3H), 2.49 (ddd, *J* = 12.8 Hz, 5.2 Hz, 5.2 Hz, 1H), 3.12-3.19 (m, 1H), 3.91 (s, 3H), 3.90-3.93 (m, 1H), 4.34 (ddd, *J* = 12.8 Hz, 5.2 Hz, 2.0 Hz, 1H), 6.78 (s, 1H), 7.84 (s, 1H).

3) **2-Hydroxycycloheptaone** (**1d**) [7, 8]

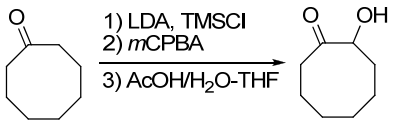


1d

To a solution of cycloheptanone (1.0 g, 8.9 mmol) in CF_3CO_2H (1.4 mL, 17.8 mmol), water (8.9 mL) and CH_3CN (45 mL) was added $PhI(OCOCF_3)_2$ (7.7 g, 17.8 mmol). The resulting mixture was stirred under reflux for 3 h. The reaction mixture was concentrated under reduced pressure to remove CH_3CN. The aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were then washed with a sat. $NaHCO_3$ aq., dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified with silica gel column chromatography (25% EtOAc-Hex) to give the acyloin **1d** (411 mg, 36%) as a colorless oil. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.32-1.38 (m, 1H), 1.57-1.72 (m, 3H), 1.78-1.84 (m, 1H), 1.86-1.91 (m, 1H), 2.03-2.08 (m, 1H), 2.47 (ddd, *J* = 17.4 Hz, 11.4 Hz, 3.6 Hz, 1H), 2.70 (dddd, *J* = 17.4 Hz, 6.6 Hz, 2.4 Hz, 0.6 Hz, 1H), 3.83 (bs, 1H),

4.30 (dd, *J* = 9.6 Hz, 3.6 Hz, 1H).

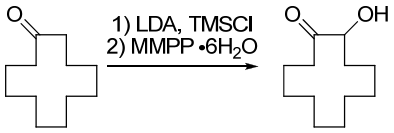
4) **2-Hydroxycyclooctanone** (**1e**)[9]



To a solution of diisopropilamine (2.73 mL, 19.5 mmol) in THF (30 mL), cooled to -78 ˚C under Ar, was added dropwise a solution of *n*-butyllithium (8.01 mL, 19.5 mmol, 2.42 M in hexane). The solution was stirred for 20 min at -78 ˚C and then chlorotrimethylsilane (freshly distilled from CaH, 3.8 mL, 30 mmol) and a solution of cyclooctanone (1.89 g, 15.0 mmol) in THF (7.5 mL) were added. After 1 h, to the resulting mixture was added triethylamine (6.3 mL, 45 mmol) and sat. $NaHCO_3$ aq., and the mixture was allowed to warm to room temperature. After separation of the two phases, the aqueous phase was extracted with hexane. The organic phase was washed with water, sat. $NaHCO_3$ aq. and brine. The combined organic phase was dried over Na_2SO_4, filtered and concentrated to afford a silyl enol ether as a pale yellow oil.

To a solution of the silyl enol ether in CH_2Cl_2 (40 mL) was added *m*CPBA (3.36 g, 18.0 mmol) at 0 ˚C. After a few hours, the resulting mixture was filtered and washed with sat. $NaHCO_3$ aq., brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was treated with AcOH in THF-H_2O (4:1, 45 mL) at room temperature for 1 h. The reaction mixture was quenched with sat. $NaHCO_3$ aq. and extracted with Et_2O. Organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated to give a residue, which was purified by silica gel column chromatography (20% EtOAc-Hex) to give the acyloin **1e** (0.68g, 32%) as a pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.87-0.97 (m, 1H), 1.33-1.44 (m, 2H), 1.63-1.86 (m, 4H), 1.94-2.07 (m, 2H), 2.31-2.42 (m, 2H), 2.71 (dt, *J* = 12.0 Hz, 4.0 Hz, 1H), 4.18 (dd, *J* = 6.4 Hz, 2.8 Hz, 1H).

5) **2-Hydroxycyclododecanone** (**1f**)[10]

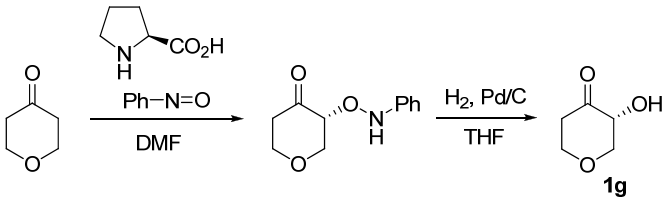


To a solution of diisopropylamine (1.82 mL, 13.0 mmol) in THF (20 mL) at -78 ˚C under Ar was added dropwise a solution of *n*-butyllithium (4.8 mL, 12.5 mmol, 2.6 M in hexane). The solution was stirred for 20 min at -78 ˚C and then chlorotrimethylsilane (freshly distilled from CaH, 3.81 mL, 30 mmol) and a solution of cyclododecanone (1.82g, 10.0 mmol) in THF (5 mL) was added. After 1 h, to the resulting mixture was added triethylamine (4.2 mL, 30 mmol) and sat. $NaHCO_3$ aq., and the mixture was allowed to warm to room temperature. The resulting mixture was filtered and separated. The water phase was extracted with hexane. The organic phase was washed with water, sat. $NaHCO_3$

aq. and brine. The combined organic phase was dried over Na_2SO_4, filtered and concentrated to afford a silyl enol ether as a pale yellow oil.

To a solution of the silyl enol ether in $CHCl_3$/50% $NaHCO_3$ aq. (1:1, 60 mL) was added MMPP-$6H_2O$ (2.97 g, 6.0 mmol) and TBAC (tetrabutylammonium chloride, 417 mg, 1.5 mmol), and then the reaction mixture was warmed to 50 ˚C. After 10 h, MMPP-$6H_2O$ (2.97g, 6.0 mmol) was added. After 4.5 h, the resulting mixture was separated, and the aqueous phase was washed with $CHCl_3$. The organic phase was washed with a sat. $NaHCO_3$ aq., and the combined organic phase was dried over $MgSO_4$, filtered and concentrated in vacuo to affored a yellow solid, which was purified by column chromatography (20% EtOAc-Hex) to give the acyloin **1e** as a colorless plate. Colorless plate (Hex): mp 77-78 ºC; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.82 (tq, *J* = 10.8 Hz, 3.6 Hz, 1H), 1.13-1.41 (m, 13H), 1.49-1.60 (m, 1H), 1.85-1.98 (m, 2H), 2.12 (dt, *J* = 17.6 Hz, 4.4 Hz, 1H), 2.21 (t, *J* = 12.4 Hz, 1H), 3.03 (ddd, *J* = 17.6 Hz, 12.0 Hz, 3.2 Hz, 1H), 3.54 (d, *J* = 5.2 Hz, 1H), 4.39 (dd, *J* = 8.0 Hz, 5.2 Hz, 1H).

6) **3-Hydroxydihydro-2*H*-pyran-4(3*H*)-one** (**1g**)[11]

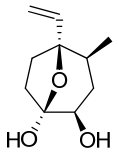


To a solution of tetrahydro-4*H*-pyran-4-one (0.45 mL, 5 mmol) and L-proline (34.5 mg, 0.3 mmol) in DMF (13 mL) was added a solution of nitrosobenzene (321 mg, 3 mmol) in DMF (4.5 mL) over 24 h at 0 ˚C by syringe pump, and the mixture was stirred for 30 min at that temperature. The reaction was quenched with phosphate buffer solution (pH 7.0), and the organic materials were extracted with ethyl acetate three times. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified with column chromatography (5-30% EtOAc/Hex) to give α-aminoxy ketone (0.30 g, 48%) as a yellow powder.

To a solution of the α-aminoxy ketone (350 mg, 1.68 mmol) in THF (17 mL) was added Pd/C (5%) (54 mg) at rt. The mixture was stirred for 1 h under hydrogen atmosphere. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The resister was purified by silica gel column chromatography (20-50% EtOAc-Hex) to give the acyloin **1g** (0.16 g, 81%) as a colorless oil. , ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.54-2.58 (m, 1H), 2.75-2.83 (m, 1H), 3.24 (t, *J* = 10.4 Hz, 1H), 3.51 (d, *J* = 4.0 Hz, 1H), 3.61 (dt, *J* = 12.0 Hz, 2.8 Hz, 1H), 4.27-4.34 (m, 2H), 4.44 (ddd, 10.8 Hz, 7.6 Hz, 1.6 Hz 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 8.4 (q), 28.5 (t), 67.8 (t), 72.9 (t), 75.8 (t), 120.4 (s), 158.8 (s), 174.2 (s); IR (neat): 2866, 1728, 1645 cm^{-1}. MS (EI)

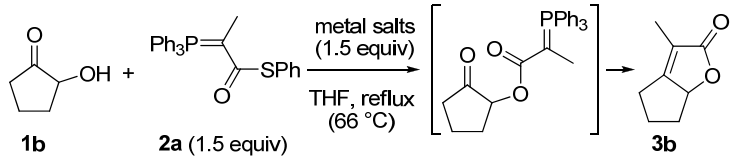
m/z: 116 (M^+), 73 (100%); HRMS (EI) calcd for $C_5H_8O_3$: 116.0473, found: 116.0469.

7) **4-Methyl-5-vinyl-8-oxabicyclo[3.2.1]octane-1,2-diol** (**1k**)[12]



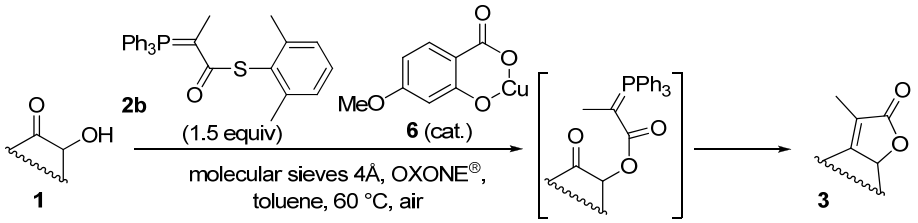
Colorless needle (EtOAc-Hex): mp 63-64 ºC; $[\alpha]_D^{25}$ –50.98 (c = 1.02, CHCl3); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.11 (d, *J* = 7.2 Hz, 3H), 1.56-1.63 (m, 1H), 1.74-1.79 (m, 1H), 1.84-2.01 (m, 4H), 2.09 (d, *J* = 9.6 Hz, 1H), 2.16 (ddd, *J* = 4.4 Hz, 6.8 Hz, 15.6 Hz, 1H), 3.60 (d, *J* = 1.6 Hz, 3.6 Hz, 9.6 Hz, 1H), 3.88 (bs, 1H), 5.08 (dd, *J* = 1.2 Hz, 11.2 Hz, 1H), 5.26 (dd, *J* = 1.2 Hz, 18.0 Hz, 1H), 5.90 (dd, *J* = 11.2 Hz, 18.0 Hz, 1H).

General procedure for one-pot synthesis of butenolides using stoichiometric amount of metal salts (Table 1).

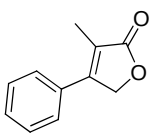


To solution of the 2-hydroxycyclopentanone **1b** (0.1 mmol) in toluene (1 mL), was added metal salt (150 mol %) and the Wittig reagent **2a** (0.15 mmol), and the mixture was refluxed under air. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (5-10-30% EtOAc-Hex) to give the butenolide **3b** as a colorless oil.

Procedure for one-pot synthesis of butenolides via a copper(II)-catalyzed acylation. (Table 3).



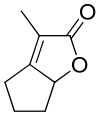
3-Methyl-4-phenylfuran-2(5*H*)-one (3a)[13]**:**



To a solution of the acyloine **1a** (27.2 mg, 0.2 mmol) in toluene (2 mL) was added Cu(II) catalyst

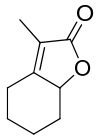
6 (2 mol %), Wittig reagent **2b** (136 mg, 0.3 mmol), molecular sieves 4 Å (100 mg, 500 mg/mmol) and OXONE® (184 mg, 0.6 mmol). The whole was stirred at 60 ˚C for 9 h. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (5-10% EtOAc-Hex) to give the butenolide **3a** (31.7 mg, 91%) as a colorless needle. Colorless needle (EtOAc-Hex): mp 121.8-122.3 ºC; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.14 (t, *J* = 2.0 Hz, 3H), 5.06 (q, *J* = 2.0 Hz, 2H), 7.45-7.52 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 10.4 (q), 70.5 (t), 123.1 (s), 127.3 (d), 129.2 (d), 130.2 (d), 131.5 (s), 154.9 (s), 175.5 (s); IR (KBr): 2960, 1735, 1651, 1454, 1344, 1091, 1045, 977 cm^{-1}; MS (EI) m/z: 174 (M^+), 174 (100%); HRMS (EI) calcd for $C_{11}H_{10}O_2$: 174.0681, found: 174.0680; Anal. calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.66; H, 5.83.

3-Methyl-4,5,6,6a-tetrahydro-2*H*-cyclopenta[*b*]furan-2-one (3b)[14]:



To a solution of the acyloine **1a** (20.0 mg, 0.2 mmol) in toluene (2 mL) was added Cu(II) catalyst **6** (2 mol %), Wittig reagent **2b** (136 mg, 0.3 mmol), molecular sieves 4 Å (100 mg, 500 mg/mmol) and OXONE® (184 mg, 0.6 mmol). The whole was stirred at 60 ˚C for 12 h. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (5-20% EtOAc-Hex) to give the butenolide **3b** (24.9 mg, 90%) as a colorless oil., ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.28 (dddd, *J* = 11.2 Hz, 11.2 Hz, 11.2 Hz, 8.8 Hz, 1H), 1.83 (d, *J* = 1.2 Hz, 3H), 2.06-2.29 (m, 3H), 2.48 (bt, *J* = 7.6 Hz, 2H), 4.91 (bt, *J* = 8.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 9.1 (q), 21.2 (t), 23.8 (t), 29.3 (t), 83.5 (d), 120.5 (s), 169.8 (s), 176.6 (s); IR (neat): 2974, 1751, 1699 cm^{-1}; MS (EI) m/z: 138 (M^+), 82 (100%); HRMS (EI) calcd for $C_8H_{10}O_2$: 138.0681, found: 138.0684.

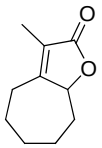
3-Methyl-5,6,7,7a-tetrahydrobenzofuran-2(4*H*)-one (3c)[15]:



To a solution of the acyloine **1c** (22.8 mg, 0.2 mmol) in toluene (2 ml) was added Cu(II) catalyst **6** (5 mol %), Wittig reagent **2b** (136 mg, 0.3 mmol), molecular sieves 4 Å (100 mg, 500 mg/mmol) and OXONE® (184 mg, 0.6 mmol). The whole was stirred at 60 ˚C for 8 h. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (5-20% EtOAc-Hex) to give the butenolide **3c** (28.3 mg, 93%) as a colorless oil., ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.15-1.33 (m, 2H), 1.46 (ddddd, *J* = 14.0 Hz,

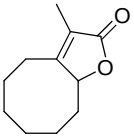
14.0 Hz, 14.0 Hz, 3.2 Hz, 3.2 Hz, 1H), 1.81 (d, *J* = 1.6 Hz, 3H), 1.89-2.02 (m, 2H), 2.11-2.15 (ddd, *J* = 14.0 Hz, 6.0 Hz, 6.0 Hz, 1H), 2.19-2.52 (m, 1H), 2.82 (ddd, *J* = 14.0 Hz, 2.4 Hz, 2.4 Hz, 1H), 4.58 (dd, *J* = 11.2 Hz, 6.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 8.1 (q), 22.7 (t), 26.2 (t x 2), 34.2 (t), 80.1 (d), 119.4 (s), 162.5 (s), 174.8 (s); IR (neat): 2945, 2864, 1747, 1681, 1637 cm^{-1}; MS (EI) m/z: 152 (M^+), 152 (100%); HRMS (EI) calcd for $C_9H_{12}O_2$: 152.0837, found: 152.0837.

3-Methyl-4,5,6,7,8,8a-hexahydro-2*H*-cyclohepta[*b*]furan-2-one (3d)[16]:



To a solution of the acyloine **1d** (25.7 mg, 0.2 mmol) in toluene (2 mL) was added Cu(II) catalyst **6** (5 mol %), Wittig reagent **2b** (136 mg, 0.3 mmol), molecular sieves 4 Å (100 mg, 500 mg/mmol) and OXONE® (184 mg, 0.6 mmol). The whole was stirred at 60 ˚C for 9 h. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (5-25% EtOAc-Hex) to give the butenolide **3d** (33.2 mg, >99%) as a colorless oil., ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.23-1.32 (m,1H), 1.38-1.56 (m,3H), 1.78 (d, *J* = 1.2 Hz, 3H), 1.83-1.94 (m, 3H), 2.31-2.35 (m, 1H), 2.48-2.56 (m, 1H), 2.63-2.68 (m, 1H), 4.85 (bd, *J* = 10.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 8.1 (q), 25.6 (t), 26.2 (t), 27.6 (t), 29.9 (t), 33.8 (t), 83.5 (d), 122.4 (s), 165.5 (s), 174.6 (s); IR (neat): 2929, 2858, 1747, 1668 cm^{-1}; MS (EI) m/z: 166 (M^+), 166 (100%); HRMS (EI) calcd for $C_{10}H_{14}O_2$: 166.0994, found: 166.0995.

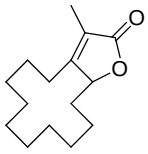
3-Methyl-5,6,7,8,9,9a-hexahydrocycloocta[*b*]furan-2(4*H*)-one (3e)[17]:



To a solution of the acyloine **1e** (28.4 mg, 0.2 mmol) in toluene (2 mL) was added Cu(II) catalyst **6** (8.5 mol %), Wittig reagent **2b** (136 mg, 0.3 mmol), molecular sieves 4 Å (100 mg, 500 mg/mmol) and OXONE® (184 mg, 0.6 mmol). The whole was stirred at 60 ˚C for 12 h. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (5-20% EtOAc-Hex) to give the butenolide **3e** (34.6 mg, 96%) as a colorless oil., ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.34-1.56 (m, 6H), 1.74-1.80 (m, 2H), 1.83 (d, *J* = 1.6 Hz, 3H), 1.99-2.05 (m, 1H), 2.10-2.18 (m, 1H), 2.28 (ddd, *J* = 14.4 Hz, 8.8 Hz, 6.0 Hz, 1H), 2.71 (ddd, *J* = 14.4 Hz, 6.0 Hz, 6.0 Hz, 1H), 4.88 (bs, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 8.5 (q), 20.7 (t), 25.0 (t), 25.9 (t), 26.7 (t), 27.0 (t), 28.6 (t), 82.7 (d), 124.3 (s), 164.1 (s), 174.7 (s); IR (neat): 2928, 2858, 1747, 1672, 1454, 1315, 1093, 1026 cm^{-1}; MS (EI) m/z: 180(M^+), 95 (100%);

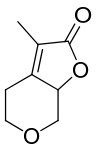
HRMS (EI) calcd for $C_{11}H_{16}O_2$: 180.1150, found: 180.1148.

3-Methyl-5,6,7,8,9,10,11,12,13,13a-decahydrocyclododeca[*b*]furan-2(4*H*)-one (3f):



To a solution of the acyloine **1f** (39.7 mg, 0.2 mmol) in toluene (2 mL) was added Cu(II) catalyst **6** (8.5 mol %), Wittig reagent **2b** (136 mg, 0.3 mmol), molecular sieves 4 Å (100 mg, 500 mg/mmol) and OXONE® (184 mg, 0.6 mmol). The whole was stirred at 60 ˚C for 7 h until disappearance of the starting material. After disappearance of the starting material, the whole was stirred at 110 ˚C for 1 h. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (5-20% EtOAc-Hex) to give the butenolide **3f** (40.2 mg, 85%) as a colorless needle. Colorless needle (EtOAc-Hex): mp 71-71.5 ºC; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.06-1.16 (m, 1H), 1.25-1.52 (m, 14H), 1.58-1.86 (m, 2H), 1.85 (d, *J* = 0.8 Hz, 3H), 2.06-2.15 (m, 1H), 2.40-2.44 (m, 2H), 4.90 (bs, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 9.0 (q), 19.3 (t), 22.2 (t), 22.8 (t), 23.3 (t), 24.16 (t), 24.19 (t), 24.3 (t), 25.1 (t), 25.2 (t), 29.9 (t), 82.6 (d), 124.9 (s), 162.1 (s), 174.9 (s); IR (KBr): 2937, 2747, 1737, 1668, 1469 cm^{-1}; MS (EI) m/z: 236 (M^+), 236 (100%); HRMS (EI) calcd for $C_{15}H_{24}O_2$: 236.1776, found: 234.1774; Anal. calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 75.96; H, 10.16.

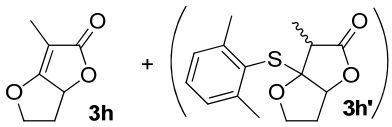
3-Methyl-4,5,7,7a-tetrahydro-2*H*-furo[2,3-*c*]pyran-2-one (3g):



To a solution of the acyloine **1g** (17.4 mg, 0.15 mmol) in toluene (1.5 mL) was added Cu(II) catalyst **6** (5 mol %), Wittig reagent **2b** (101.9 mg, 0.22 mmol), molecular sieves 4 Å (75 mg, 500 mg/mmol) and OXONE® (138.3 mg, 0.45 mmol). The whole was stirred at 60 ˚C for 4 h. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (5-30-50% EtOAc-Hex) to give the butenolide **3g** (19.4 mg, 84%) as a colorless prism. Colorless prism (Et_2O-Hex): mp 76-77 ºC; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.87 (t, *J* = 1.6 2.56-2.64 (m, 1H), 2.78 (dd, *J* = 14.0 Hz, 2.4 Hz, 1H), 2.99 (dd, *J* = 11.2 Hz, 11.2 Hz, 1H), 3.21 (ddd, *J* = 11.2Hz, 11.2 Hz, 2.4 Hz, 1H), 4.21 Hz, 3H), (dd, *J* = 10.4 Hz, 6.4 Hz, 1H), 4.53 (dd, *J* = 10.4 Hz, 6.4 Hz, 1H), 4.67-4.71 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 8.4 (q), 28.5 (t), 67.8 (t), 72.9 (t), 75.8 (d), 120.4 (s), 158.8 (s), 174.2 (s). IR (KBr):

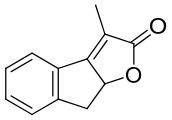
2970, 2926, 2858, 1741, 1687, 1097, 1085, 1037 cm^{-1}; MS (EI) m/z: 154 (M^+), 58 (100%); HRMS (EI) calcd for $C_8H_{10}O_3$: 154.0630, found: 154.0631.

3-Methyl-6,6a-dihydrofuro[3,2-*b*]furan-2(5*H*)-one (1h):



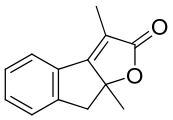
To a solution of the acyloine **1h** (20.4 mg, 0.2 mmol) in toluene (2 mL) was added Cu(II) catalyst **6** (2 mol %), Wittig reagent **2b** (136 mg, 0.3 mmol), molecular sieves 4 Å (100 mg, 500 mg/mmol) and OXONE® (184 mg, 0.6 mmol). The whole was stirred at 60 ˚C for 10 h until disappearance of the starting material. After disappearance of the starting material, the whole was stirred at 110 ˚C for 1 h. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (5-20-30-40% EtOAc-Hex) to give the butenolide **3h** (18.4 mg, 66%) and Michael adducts **3h'** (3.8 mg, 7%) as a colorless oil. The major product **3h**: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.75 (d, *J* = 1.6 Hz, 3H), 2.04 (dddd, *J* = 12.0 Hz, 12.0 Hz, 12.0 Hz, 8.8 Hz, 1H), 2.52 (ddd, *J* = 12.0 Hz, 6.8 Hz, 4.4 Hz, 1H), 4.64 (ddd, *J* = 12.0 Hz, 8.8 Hz, 4.4 Hz, 1H), 4.82 (dd, *J* = 8.8 Hz, 8.8 Hz, 1H), 4.96 (ddd, *J* = 12.0 Hz, 6.8 Hz, 1.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 6.6 (q), 30.7 (t), 76.2 (d), 77.0 (t), 94.7 (t), 176.5 (s), 179.1 (s); IR (0.1 mm NaCl, $CHCl_3$): 3030, 3003, 1764, 1701 cm^{-1}; MS (EI) m/z: 140 (M^+), 83 (100%); HRMS (EI) calcd for $C_7H_8O_3$: 140.0473, found: 140.0472.

3-Methyl-8,8a-dihydro-2*H*-indeno[2,1-*b*]furan-2-one (3i):



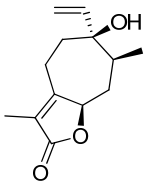
To a solution of the acyloine **1i** (29.6 mg, 0.2 mmol) in toluene (2 mL) was added Cu(II) catalyst **6** (1 mol %), Wittig reagent **2b** (136 mg, 0.3 mmol), molecular sieves 4 Å (100 mg, 500 mg/mmol) and OXONE® (184 mg, 0.6 mmol). The whole was stirred at 60 ˚C for 7 h. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (5-25% EtOAc-Hex) to give the butenolide **3i** (33.5 mg, 90%) as colorless needles (EtOAc-Hex): mp 133.8-134.8 ºC; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.07 (d, *J* = 2.0 Hz, 3H), 2.80 (dd, *J* = 14.8 Hz, 8.0 Hz, 1H), 3.41 (dd, *J* = 14.8 Hz, 7.2 Hz, 1H), 5.36-5.41 (m, 1H), 7.36-7.45 (m, 3H), 7.59-7.61 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 9.3 (q), 36.5 (t), 84.1 (d), 118.6 (t), 124.1 (d), 126.7 (d), 128.2 (d), 131.1 (d), 132.7 (s), 145.3 (s), 165.3 (s), 176.3 (s); IR (KBr): 1735, 1685 cm^{-1}; MS (EI) m/z: 186 (M^+), 158 (100%); HRMS (EI) calcd for $C_{12}H_{10}O_2$: 186.0681, found: 186.0683; Anal. calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.23; H, 5.36.

3,8a-Dimethyl-8,8a-dihydro-2*H*-indeno[2,1-*b*]furan-2-one (3j):



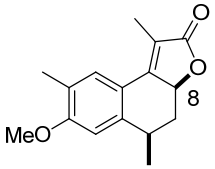
To a solution of the acyloine **1j** (32.4 mg, 0.2 mmol) in toluene (2 mL) was added Cu(II) catalyst **6** (1 mol %), Wittig reagent **2b** (136 mg, 0.3 mmol), molecular sieves 4 Å (100 mg, 500 mg/mmol) and OXONE® (184 mg, 0.6 mmol). The whole was stirred at 60 ˚C for 8 h. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (5-20% EtOAc-Hex) to give the butenolide **3j** (37.4 mg, 93%) as colorless needle. Colorless needle (EtOAc-Hex): mp 76.9-77.4 ºC; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.49 (s, 3H), 2.05 (s, 3H), 2.97 (d, *J* = 14.8 Hz, 1H), 3.11 (d, *J* = 14.8 Hz, 1H), 7.35-7.42 (m, 3H), 7.59-7.61 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 9.4 (q), 25.7 (q), 42.5 (t), 91.1 (s), 118.0 (s), 124.5 (d), 126.6 (d), 128.0 (d), 130.8 (d), 132.6 (s), 145.8 (s), 169.4 (s), 175.3 (s); IR (KBr): 1755, 1687 cm^{-1}; MS (EI) m/z: 200 (M^+), 129 (100%); HRMS (EI) calcd for $C_{13}H_{12}O_2$: 200.0837, found: 200.0840.

4,5,6,7,8,8a-Hexahydro-6-hydroxy-3,7-dimethyl-6-vinylcyclohepta[*b*]furan-2-one (3k):



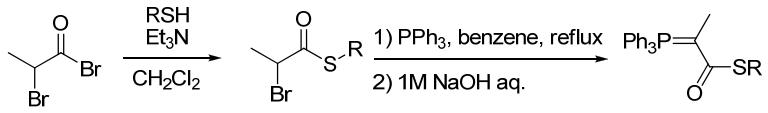
To a solution of the acyloine **1k** (36.8 mg, 0.2 mmol) in toluene (2 mL) was added Cu(II) catalyst **6** (10 mol %), Wittig reagent **2b** (136 mg, 0.3 mmol), molecular sieves 4 Å (100 mg, 500 mg/mmol) and OXONE® (184 mg, 0.6 mmol). The whole was stirred at 60 ˚C for 9 h until disappearance of the starting material. After disappearance of the starting material, the whole was stirred at 110 ˚C for 1 h. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (5-40% EtOAc-Hex) to give the butenolide **3k** (31.1 mg, 70%) as a colorless prism. Colorless prism (EtOAc-Hex): mp 151 ºC; $[\alpha]_D^{25}$ -140.27 (c 1.08, $CHCl_3$), ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.93 (d, *J* = 6.8 Hz, 3H), 1.34 (s, 1H), 1.56-1.65 (m, 1H), 1.74-1.81 (m, 1H), 1.78 (s, 3H), 1.84-1.88 (m, 2H), 2.12 (ddd, *J* = 13.6 Hz, 2.4 Hz, 2.4 Hz, 1H), 2.54 (bd, *J* = 20.0 Hz, 1H), 2.87-2.96 (m, 1H), 4.87 (bd, *J* = 12.0 Hz, 1H), 5.09 (d, *J* = 10.8 Hz, 1H), 5.20 (d, *J* = 17.6 Hz, 1H), 5.93 (dd, *J* = 10.8 Hz, 17.6 Hz, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ : 8.2 (q), 17.1 (q), 20.8 (t), 36.0 (t), 36.3 (t), 39.9 (d), 75.3 (s), 82.1 (d), 110.4 (t), 120.8 (d), 146.3 (d), 164.8 (s), 174.5 (s). IR (0.1 mm NaCl, $CHCl_3$): 3471, 1741, 1672 cm^{-1}; MS (EI) m/z: 222 (M^+), 204 (100%); Anal. calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.05; H, 8.12.

(±)-Heritonin (3l)[4,17]**:**



To a solution of the acyloine **1l** (44.0 mg, 0.2 mmol) in toluene (2 mL) was added Cu(II) catalyst **6** (5 mol %), Wittig reagent **2b** (136 mg, 0.3 mmol), molecular sieves 4 Å (100 mg, 500 mg/mmol) and OXONE® (184 mg, 0.6 mmol). The whole was stirred at 60 ˚C for 10 h until disappearance of the starting material. After disappearance of the starting material, the mixture was added xylene (3 ml), and then the whole was stirred at 138 ˚C for 1 h. The resulting mixture was filtered with pad on celite, and the solvent was evaporated under reduced pressure. The residue was purified with column chromatography (5-10% EtOAc-Hex) to give the butenolide **3l** (81%, 6:1 mixture of diastereomers) as a colorless prism and C8-isomer (14%) as a white solid. The major product **3l**: Colorless prisms (Et_2O-Hex): mp 107.5-109 ºC; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.45 (d, *J* = 7.2 Hz, 3H), 1.47 (ddd, *J* = 12.0 Hz, 12.0 Hz, 12.0 Hz, 1H), 2.13 (d, *J* = 1.8 Hz, 3H), 2.25 (s, 3H), 2.63 (ddd, *J* = 12.0 Hz, 4.8 Hz, 4.8 Hz 1H), 3.13 (ddq, *J* = 12.0 H, 4.8 Hz, 1.8 Hz, 1H), 3.89 (s, 3H), 4.89-4.92 (m, 1H), 6.86 (s, 1H), 7.42 (s, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 9.9 (q), 16.0 (q), 21.8 (q), 32.0 (d), 38.7 (t), 55.4 (q), 78.2 (d), 108.4 (d), 116.0 (s), 120.8 (s), 125.8 (s), 129.6 (d), 142.3 (s), 156.7 (s), 159.6 (s), 175.6 (s); IR (KBr): 1739, 1654, 1610, 1319, 1049 cm^{-1}; MS (EI) m/z: 258 (M^+), 258 (100%); HRMS (EI) calcd for $C_{13}H_{26}O_3$: 258.1256, found: 258.1254.

General procedure for synthesis of phosphorous ylides.



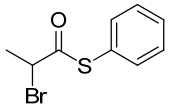
R = Ph, 2,6-dimethylphenyl

To a solution of 2-bromopropionyl bromide (3.0 g, 13.9 mmol) and thiol (14.6 mmol) in CH_2Cl_2 (14 ml) was added dropwise a Et_3N (2.9 mL, 20.9 mmol) at 0 ˚C. The resulting mixture was stirred for 0.5 h at rt. The mixture was quenched with 1M HCl aq, extracted with CH_2Cl_2, combined organic layer was washed with sat. $NaHCO_3$ aq. and brine, then dried over $MgSO_4$. The crude product was purified with silica gel column chromatography (10% EtOAc-Hex) to give the thiol ester as a colorless oil.

A solution of the thiol ester (13.1 mmol) and PPh_3 (5.1 g, 19.6 mmol) in benzene (4.4 mL) was refluxed for 3 h. The reaction mixture was concentrated under reduced pressure to remove benzene. The residue was dissolved in hot water, and then the aqueous phase was washed with EtOAc. The

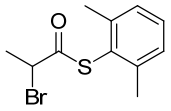
aqueous phase was added a solution of 10% NaOH aq., then extracted with $CHCl_3$. The organic layer was washed with water, dried over $MgSO_4$, concentrated to give a residue, which was recrystalized from EtOAc-Hex to give the phosphorous ylide.

S-phenyl 2-bromopropanethioate (11a):



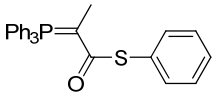
According to *the General procedure for synthesis of phosphorous ylides*, the thiol ester (>99%) was obtained as a colorless oil., ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.90 (d, J = 6.8 Hz, 3H), 4.61 (q, J = 6.8 Hz, 1H), 7.43 (s, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 22.1 (q), 47.6 (d), 126.9 (s), 129.4 (d), 129.8 (d), 134.6 (d), 194.7 (s); IR (neat): 1699, 1440, 935 cm^{-1}; MS (EI) m/z: 246 ($[M+H]^+$), 244 ($[M-1]^+$), 109 (100%); HRMS (EI) calcd for C_9H_9BrOS: 243.9557, found: 243.9561.

S-2,6-dimethylphenyl 2-bromopropanethioate (11b):



According to *the General procedure for synthesis of phosphorous ylides*, the thiol ester (>99%) was obtained as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.90 (d, J = 7.2 Hz, 3H), 2.37 (s, 6H), 4.65 (q, J = 7.2 Hz, 1H), 7.15-7.27 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 21.5 (q), 21.9 (t), 47.5 (d), 128.4 (d), 130.2 (d), 143.0 (s), 193.4 (s); IR (neat): 2976, 1695, 1464, 1440, 935 cm^{-1}; MS (EI) m/z: 274 ($[M+H]^+$), 272 ($[M-1]^+$), 137 (100%); HRMS (EI) calcd for $C_{11}H_{13}BrOS$: 271.9870, found: 271.9868.

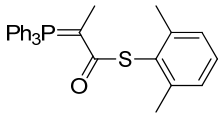
PPh_3=(Me)COSPh (propanethioic acid, 2-(triphenylphosphoranylidene)-, S-phenyl ester) 2a:



According to *the General procedure for synthesis of phosphorous ylides*, the phosphorous ylide **2a** (46%) was obtained as a colorless prism. Colorless prism (EtOAc-Hex): mp 153-174 ºC (decomp); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.76 (d, J = 15.0 Hz, 3H), 7.17-7.20 (m, 1H), 7.24-7.27 (m, 2H), 7.44-7.48 (m, 8H), 7.52-7.55 (m, 3H), 7.58-7.61 (m, 6H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ : 13.0 (d, J_{CP} = 12.9 Hz), 49.8 (d, J_{CP} = 106.2 Hz), 126.3 (d, J_{CP} = 89.0 Hz), 127.0 (s), 128.2 (s), 128.7 (d, J_{CP} = 11.6 Hz), 131.9 (d, J_{CP} = 2.9 Hz), 132.4 (s), 133.7 (d, J_{CP} = 8.9 Hz), 134.6 (s), 177.2 (d, J_{CP} = 10.1 Hz); ^{31}P-NMR (243 MHz, $CDCl_3$) δ : 21.3 (s); IR (KBr): 3057, 2854, 1581, 1568, 1481, 1437, 1311, 1276, 1168, 1101, 974 cm^{-1}; MS (FAB) m/z: 427 ($[M+H]^+$); HRMS (FAB) calcd for $C_{27}H_{24}OPS$ ($[M+H]^+$): 427.1285, found: 427.1285; Anal. calcd for $C_{27}H_{24}OPS$: C, 76.03; H, 5.44. Found: C,

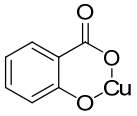
75.91; H, 5.43.

Propanethioic acid, 2-(triphenylphosphoranylidene)-, S-(2,6-dimethylphenyl) ester (2b):



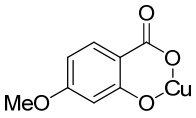
According to *the General procedure for synthesis of phosphorous ylides*, the the phosphorous ylide **2b** (16%) was obtained as a colorless prism. Colorless prisms (EtOAc-Hex): mp 166-186 ºC (decomp without melt); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.83 (d, J = 15.0 Hz, 3H), 2.43 (s, 6H), 7.03 (s, 3H), 7.41-7.44 (m, 6H), 7.51-7.59 (m, 9H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ : 13.19 (d, J_{CP} = 11.6 Hz), 22.3 (s), 49.9 (d, J_{CP} = 106.4 Hz), 126.7 (d, J_{CP} = 89.1 Hz), 127.5 (s), 128.1 (s), 128.6 (d, J_{CP} = 12.9 Hz), 133.1 (s), 131.7 (d, J_{CP} = 2.9 Hz), 133.7 (d, J_{CP} = 10.1 Hz), 143.5 (s), 177.8 (d, J_{CP} = 10.1 Hz); ^{31}P-NMR (160 MHz, $CDCl_3$) δ : 20.1 (s); IR (KBr): 3057, 2912, 2854, 1579, 1562, 1437, 1267, 1161, 1105, 972 cm^{-1}; MS (FAB) m/z: 455 ([M+H]$^{+}$); HRMS (FAB) calcd for $C_{29}H_{28}OPS$ ([M+H]$^{+}$): 454.1598, found: 454.1597; Anal. calcd for $C_{13}H_{18}O_3$: C, 76.63; H, 5.99. Found: C, 76.41; H, 5.99.

Cu (salicylate) 5[18]:



A mixture of $Cu(OH)_2$ (0.49 g, 5 mmol) and 4-methoxysalicylic acid (1.38 g, 10 mmol) in ethanol (25 mL) was refluxed for 4 h to give a brown suspension. On cooling to room temperature, the mixture was filtered off, washed with two portions of water and ethanol, and then air-dried to give the Cu complex **5** as brown powder (0.59 g, 59%). mp 349-394 ˚C (decomp.); Anal. Calc. for $C_7H_4CuO_3$: C, 42.11; H, 2.02. Found: C, 41.66; H, 2.05.; IR (KBr): 1602, 1568, 1529, 1456, 1410, 1232, 1149 cm^{-1}.

Cu(4-methoxysalicylate) 6[18]:



A mixture of $Cu(OH)_2$ (0.49 g, 5 mmol) and 4-methoxysalicylic acid (1.68 g, 10 mmol) in ethanol (25 mL) was refluxed for 4 h to give a yellow green suspension. On cooling to room temperature, the mixture was filtered off, washed with two portions of water and ethanol, and then air-dried to give the Cu complex **6** as a yellow green powder (1.11g, 97%). mp 210-258 ˚C (decomp.); Anal. Calc. for $C_8H_6CuO_4$: C, 41.84; H, 2.63. Found: C, 41.95; H, 2.71.; IR (KBr): 1604, 1579, 1533, 1502, 1450,

1390, 1242, 1203, 1172, 1099, 1030, 972 cm^{-1}.

The catalyst was recrystallized from DMSO to give green platelet crystal. The catalyst structure was determined by X-ray crystal structure analysis: CCDC773455 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge.

Crystallographic Data Centre.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula C10H12O5CuS

Formula Weight 307.81

Crystal Color, Habit green, platelet

Crystal Dimensions 0.10 X 0.06 X 0.02 mm

Crystal System monoclinic

Lattice Type Primitive

Indexing Images 6 images @ 64.0 seconds

Detector Position45.05 mm

Pixel Size 0.137 mm

Lattice Parameters a = 12.191(3) Å

b = 7.1808(17) Å

c = 13.680(3) Å

b = 103.631(4) o

V = 1163.8(5) Å3

Space Group P21/a (#14)

Z value 4

Dcalc 1.757 g/cm3

F000 628.00

m(MoKa) 20.611 cm-1

B. Intensity Measurements

Detector Rigaku Saturn

Goniometer Rigaku AFC10

Radiation MoKa (l = 0.71070 Å)

graphite monochromated

Detector Aperture 70 mm x 70 mm

Data Images 720 exposures

w oscillation Range (c=45.0, f=0.0) -110.0 - 70.0o

Exposure Rate 64.0 sec./o

Detector Swing Angle -20.04o

w oscillation Range (c=45.0, f=90.0) -110.0 - 70.0o

Exposure Rate 64.0 sec./o

Detector Swing Angle -20.04o

Detector Position 45.05 mm

Pixel Size 0.137 mm

2qmax 54.9o

No. of Reflections Measured Total: 8939

Unique: 2656 (Rint = 0.023)

Corrections Lorentz-polarization

Absorption

(trans. factors: 0.878 - 0.960)

C. Structure Solution and Refinement

Structure Solution Direct Methods (SIR97)

Refinement Full-matrix least-squares on F2

Function Minimized S w (Fo2 - Fc2)2

Least Squares Weights 1/[0.0005Fo2+1.0000s(Fo2)]/(4Fo2)

2qmax cutoff 54.9o

Anomalous Dispersion All non-hydrogen atoms

No. Observations (All reflections) 2656

No. Variables 166

Reflection/Parameter Ratio 16.00

Residuals: R1 (I>2.00s(I)) 0.0264

Residuals: R (All reflections) 0.0315

Residuals: wR2 (All reflections) 0.0723

Goodness of Fit Indicator 1.019

Max Shift/Error in Final Cycle 0.000

Maximum peak in Final Diff. Map 0.84 e-/Å3

Minimum peak in Final Diff. Map -0.39 e-/Å3

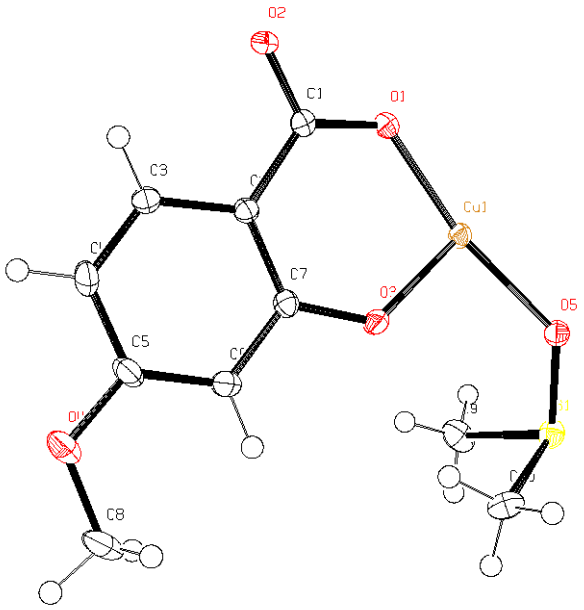


Figure. Crystal structure of **6**.

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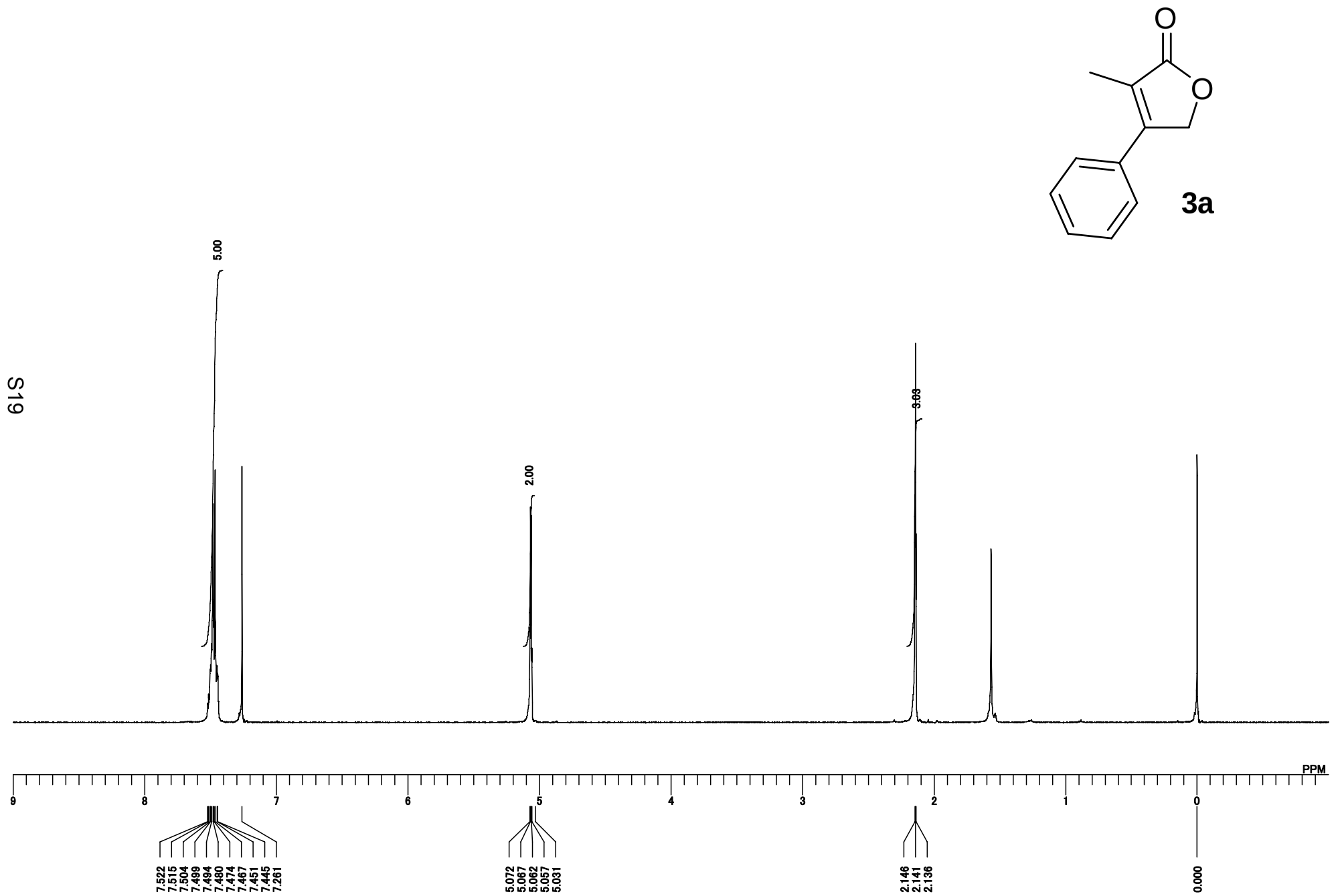
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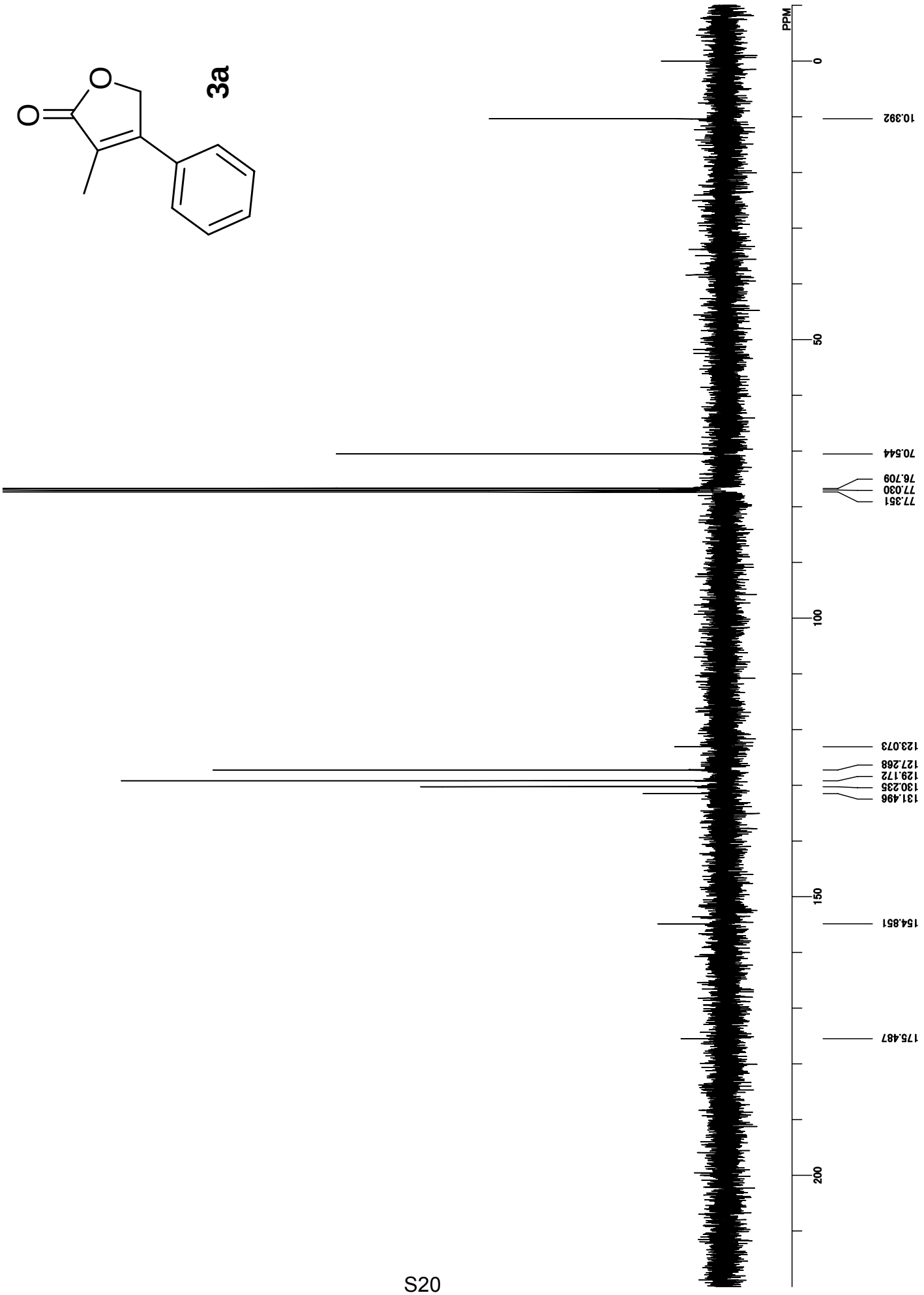
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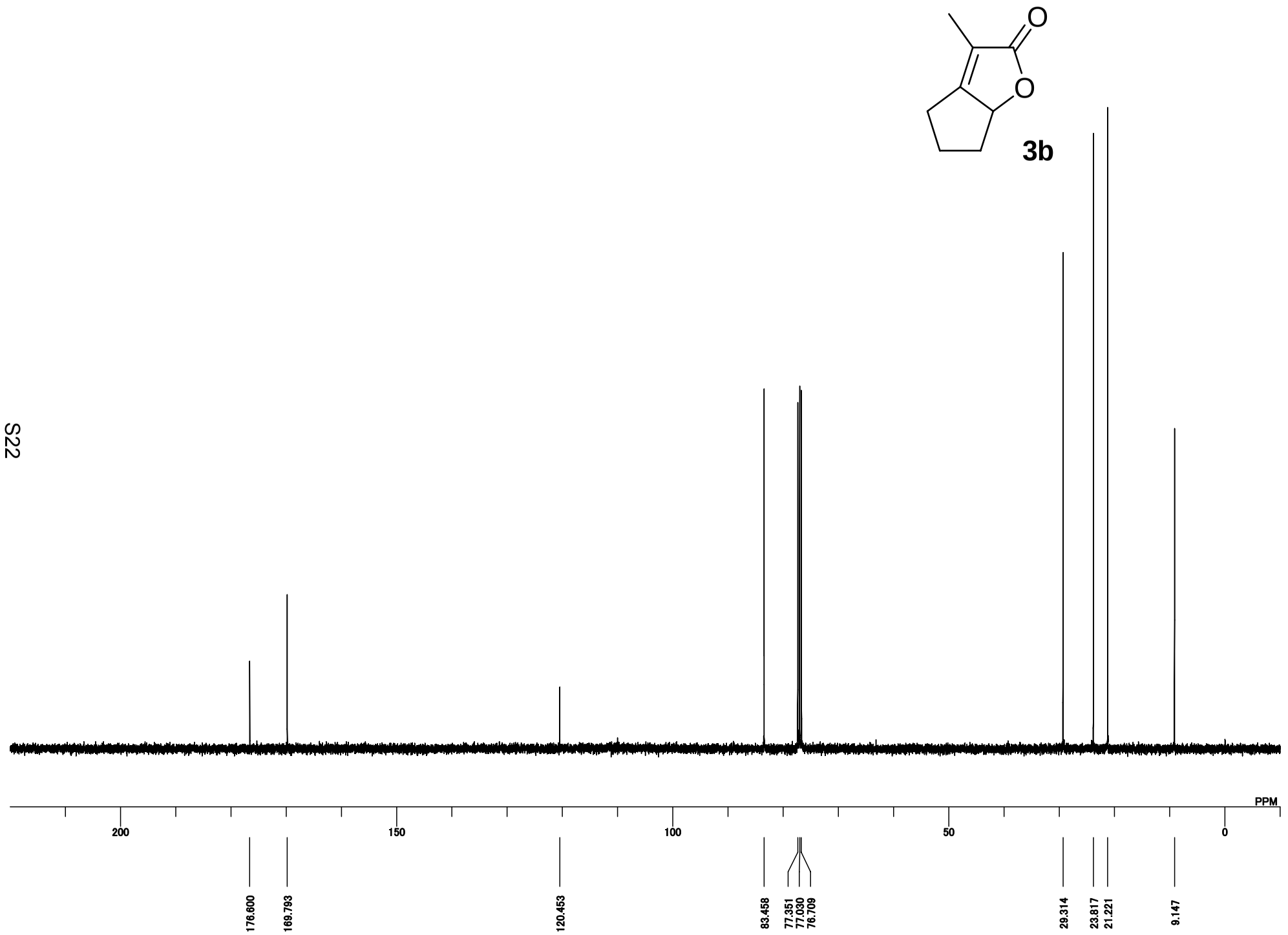
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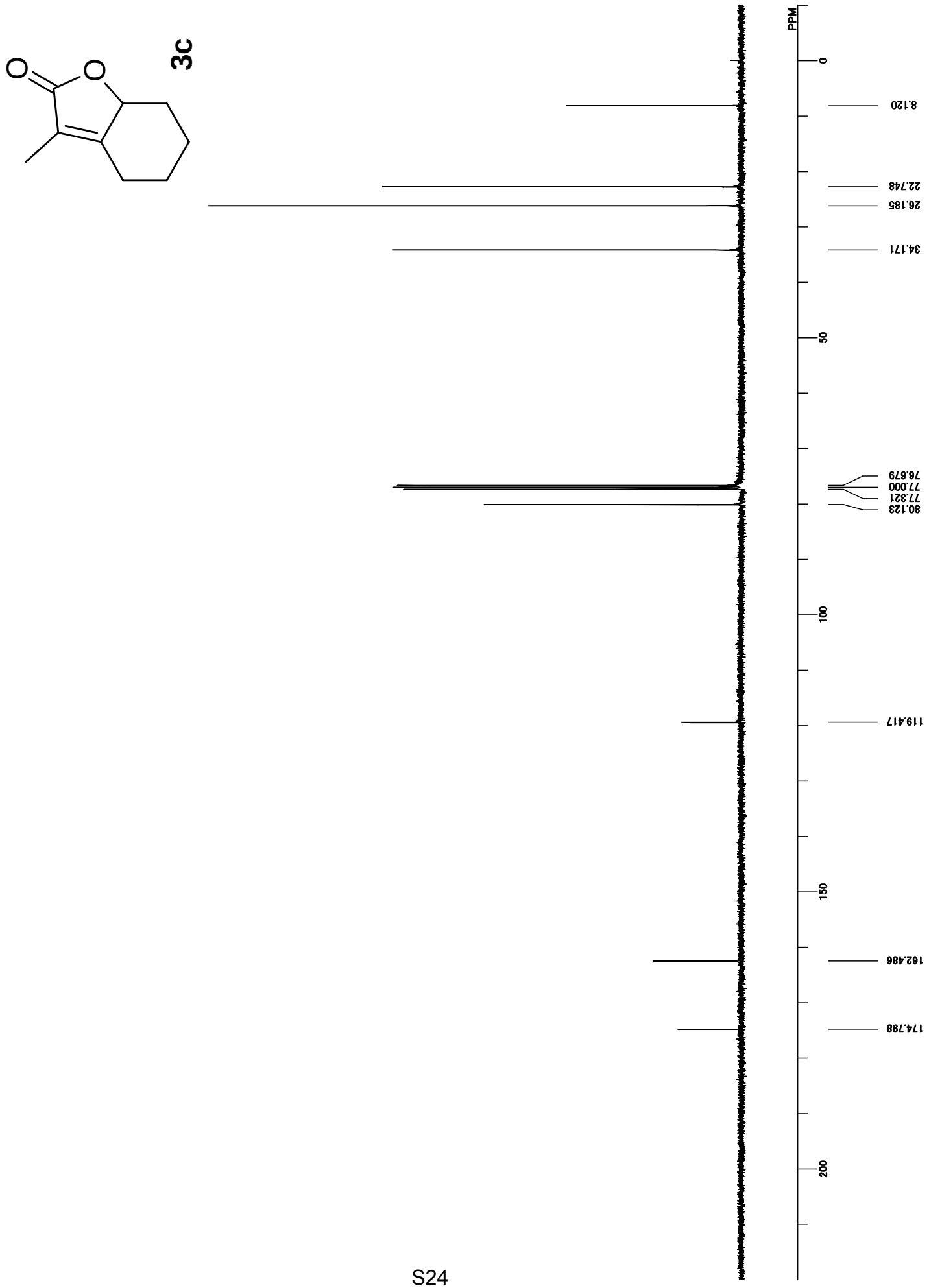
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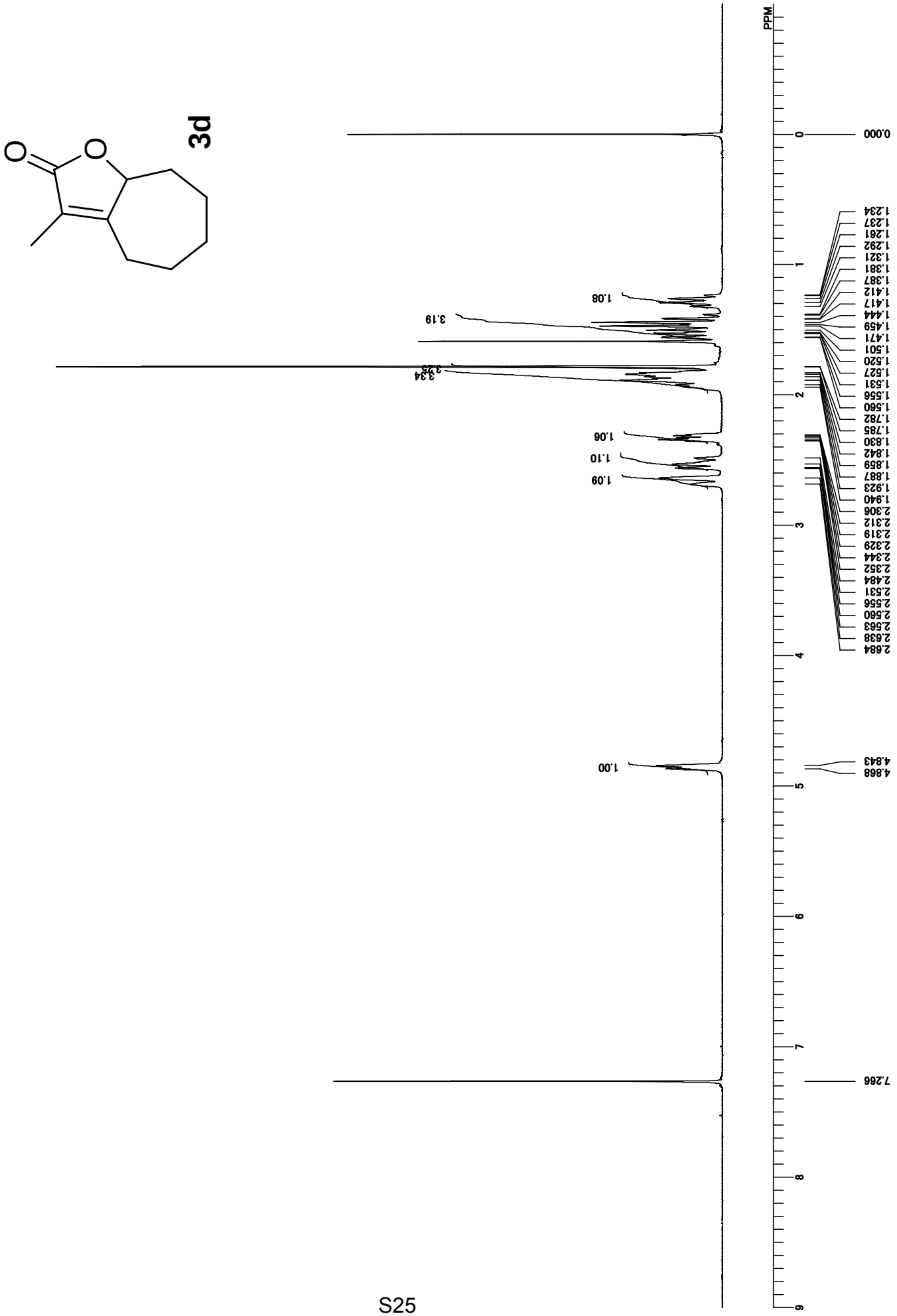
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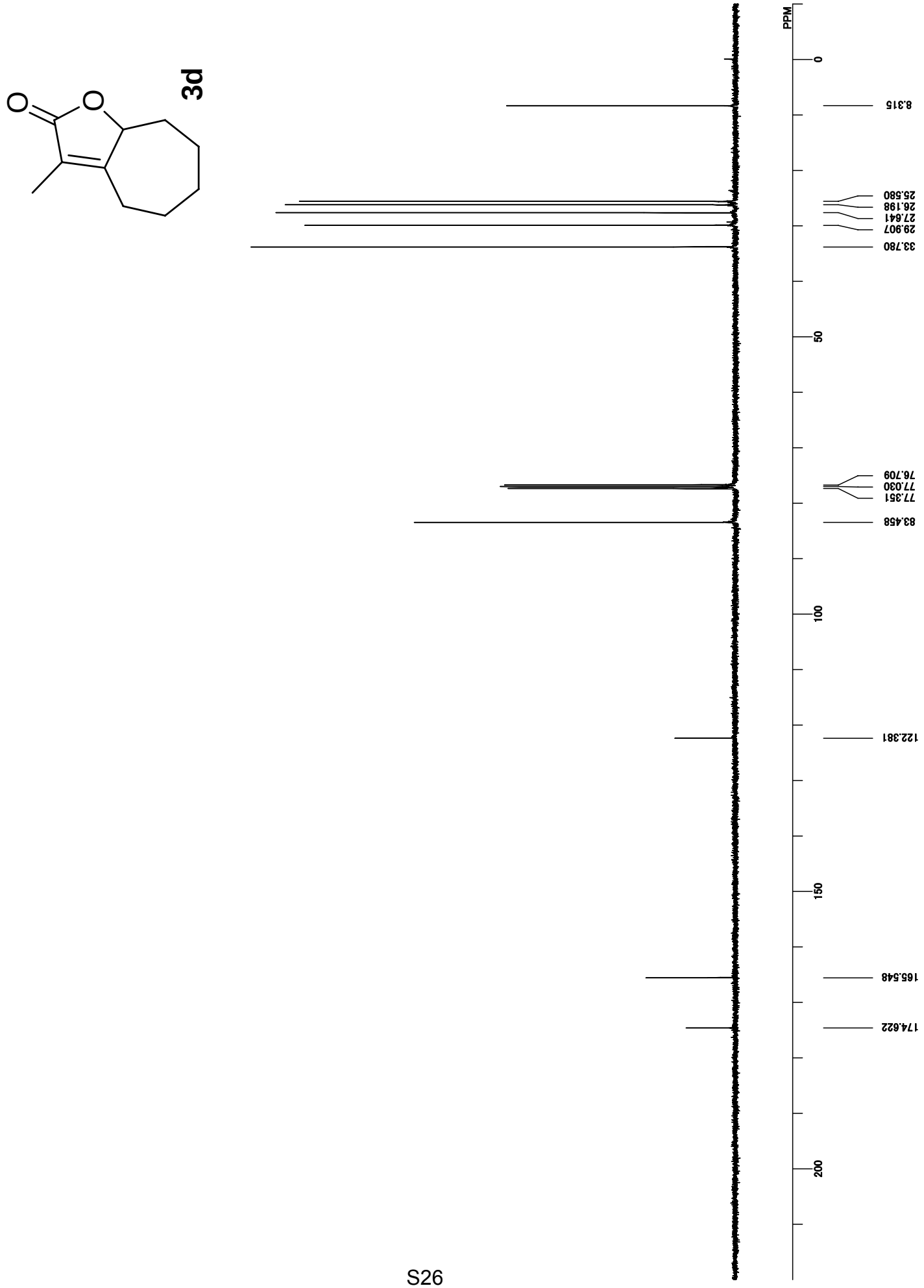
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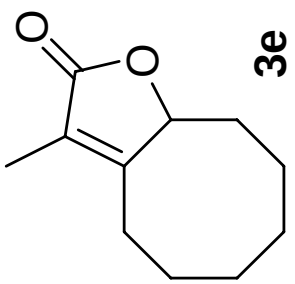
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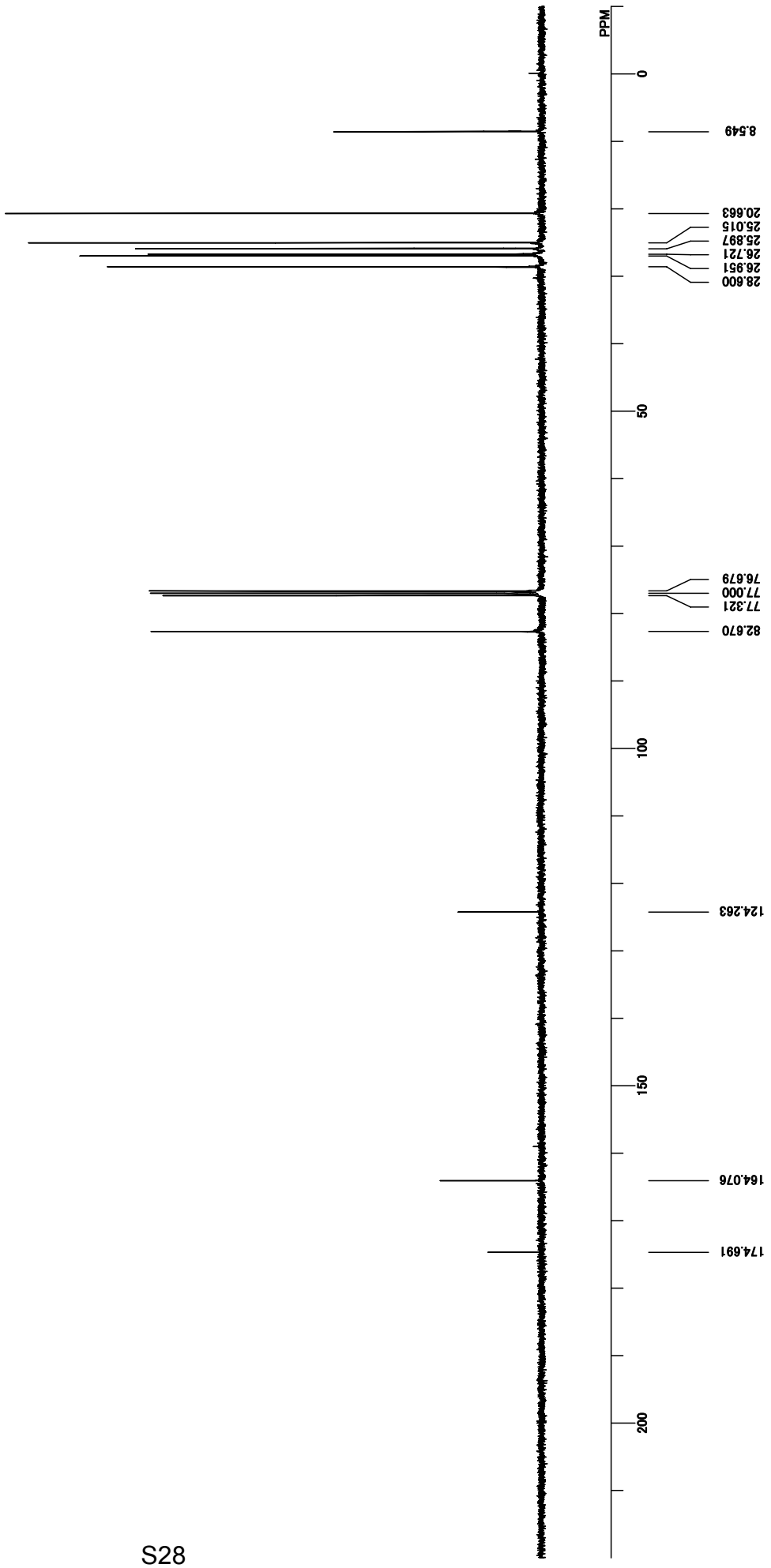
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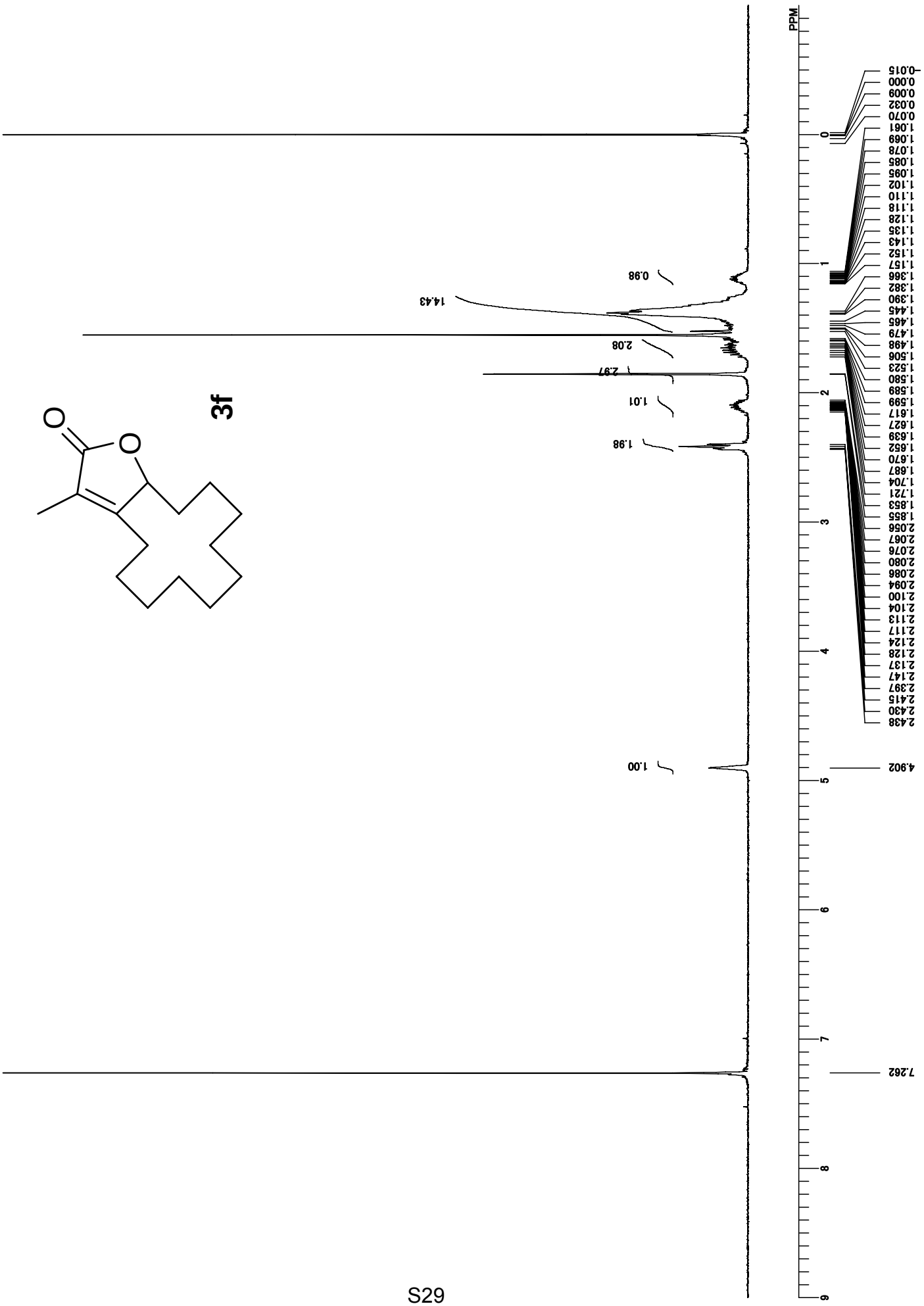
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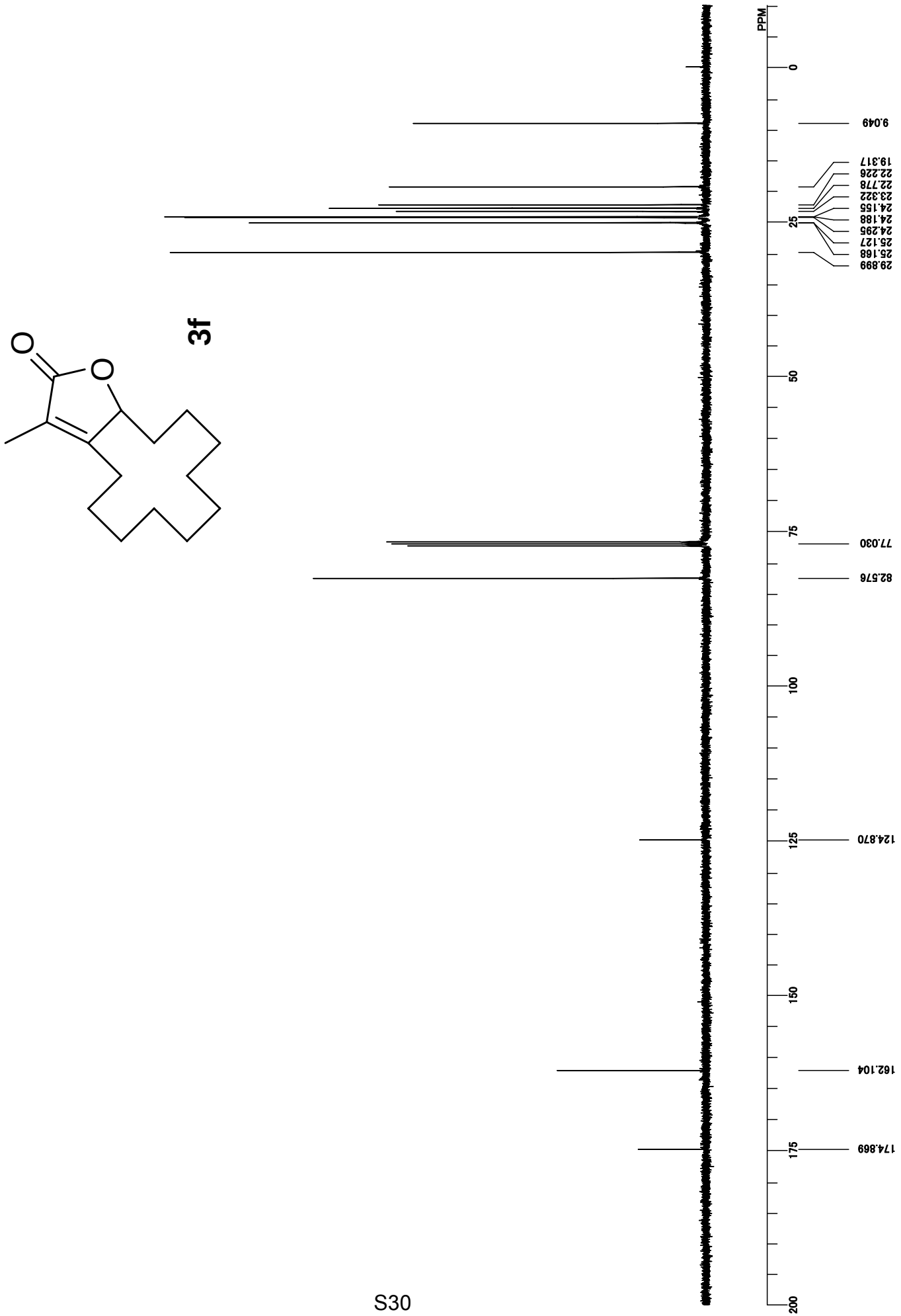
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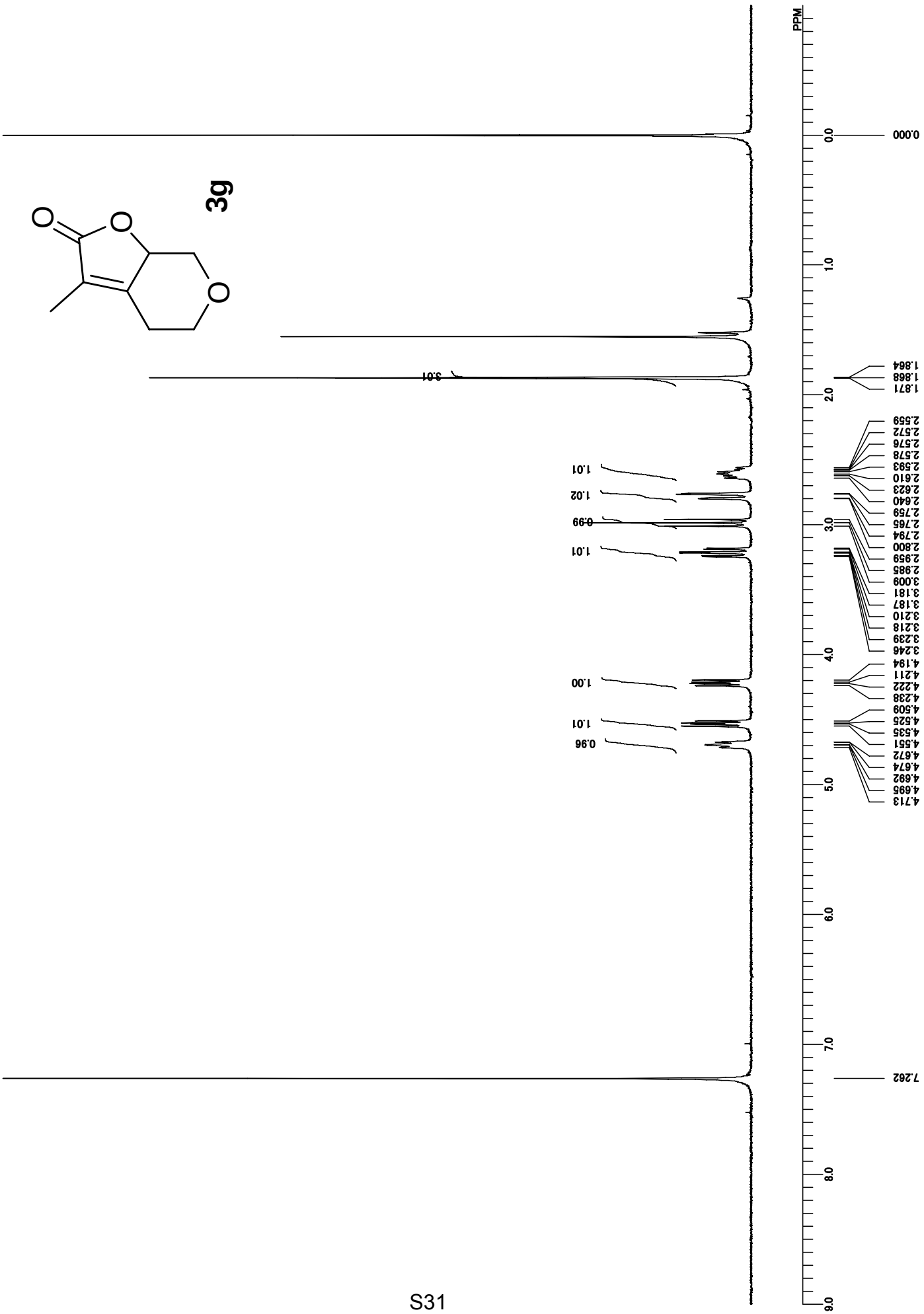
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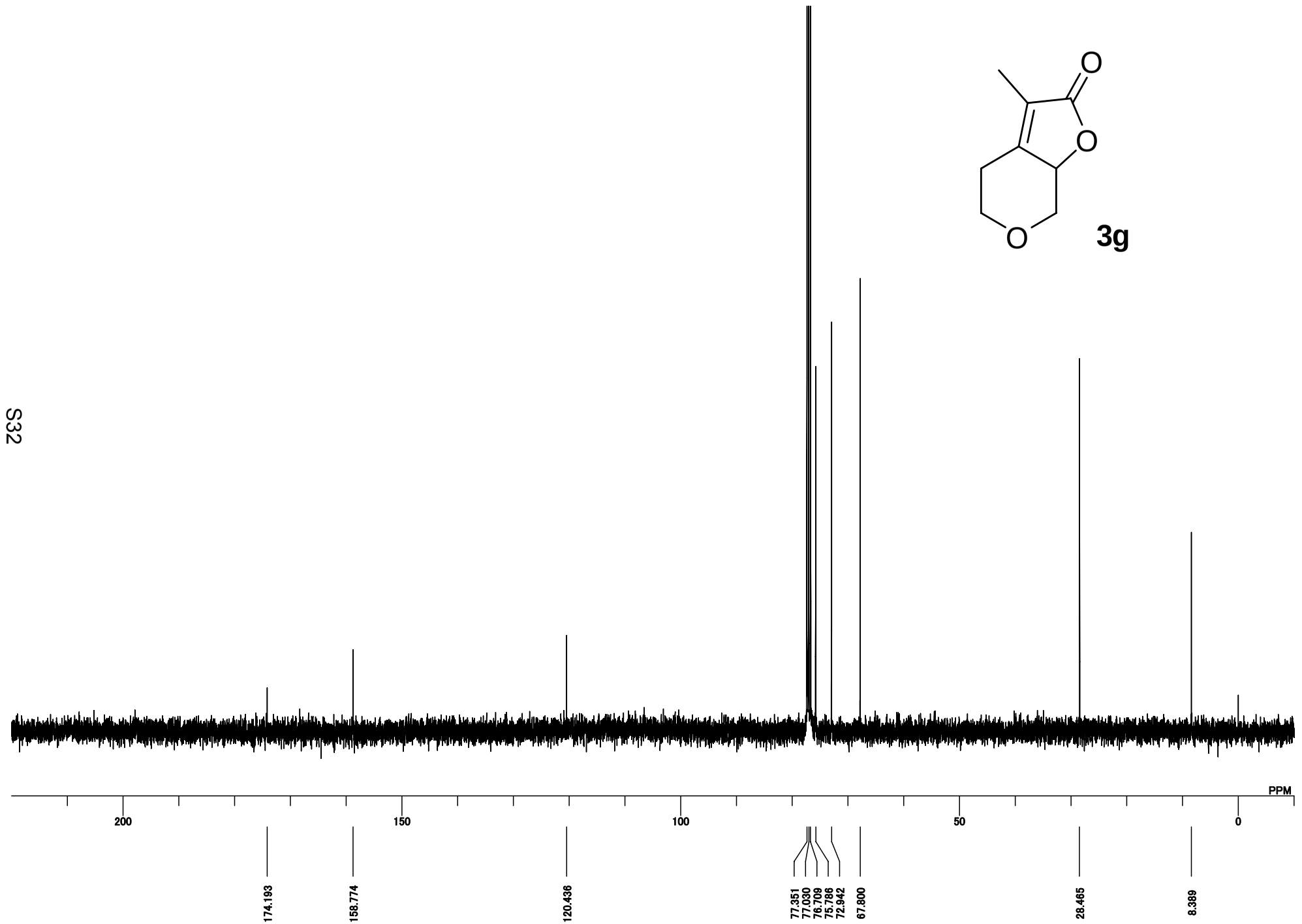
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2.537
2.548
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4.636
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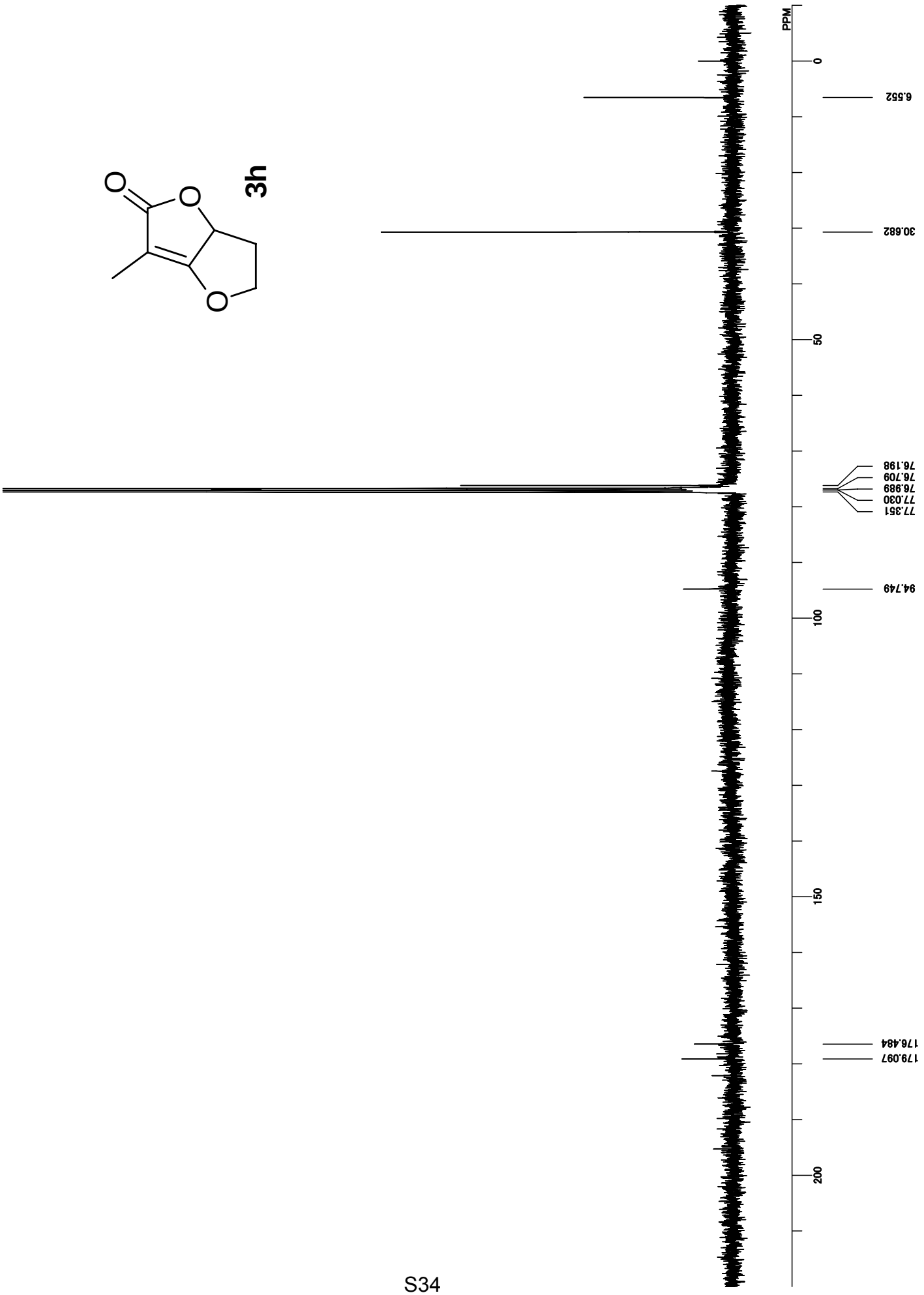
1.07
1.07
1.00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176.484
179.097

PPM
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2.0
3.0
4.0
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6.0
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5.378
5.370
5.365
5.360
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7.609
7.604
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7.408
7.404
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1.07
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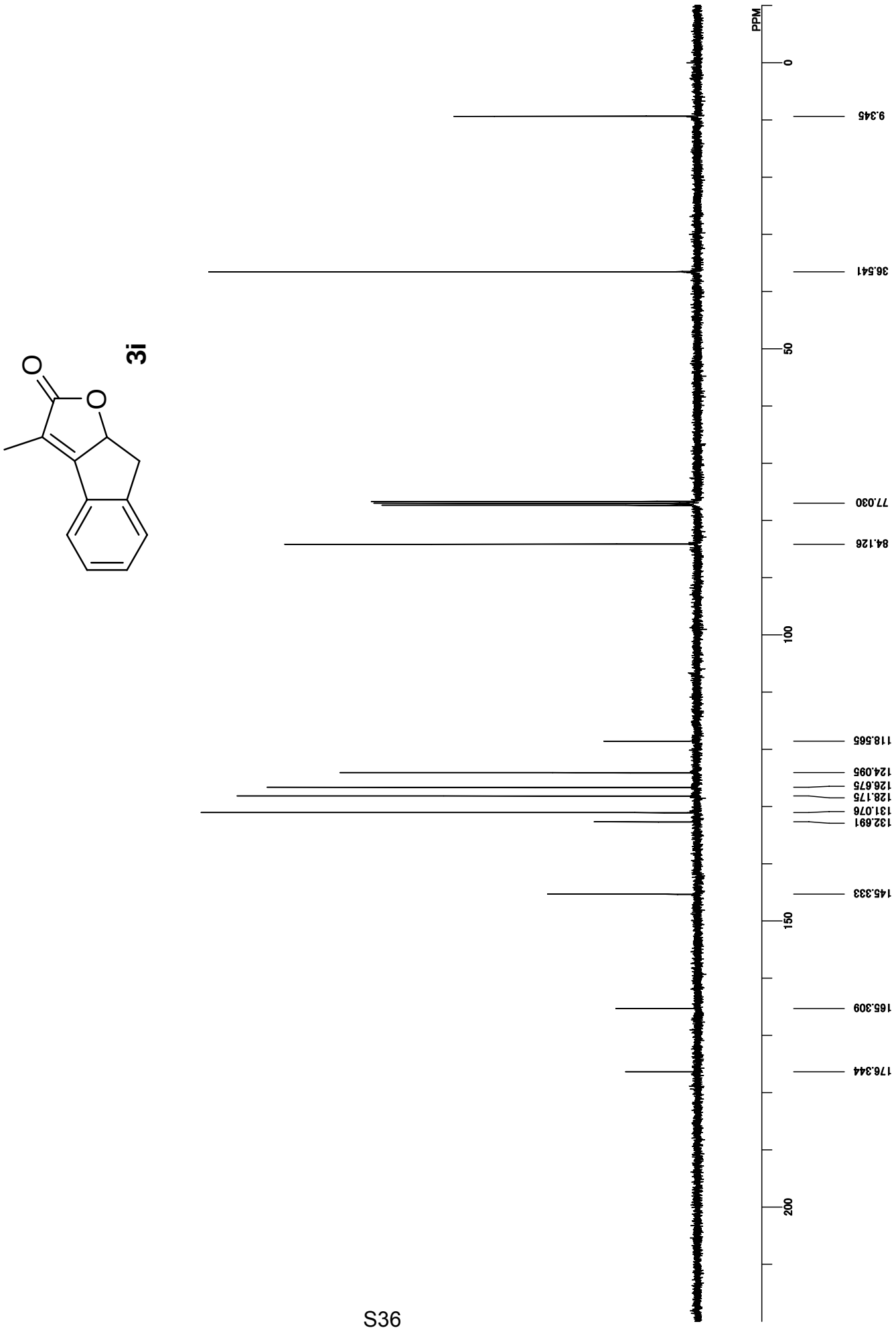
3i
O
O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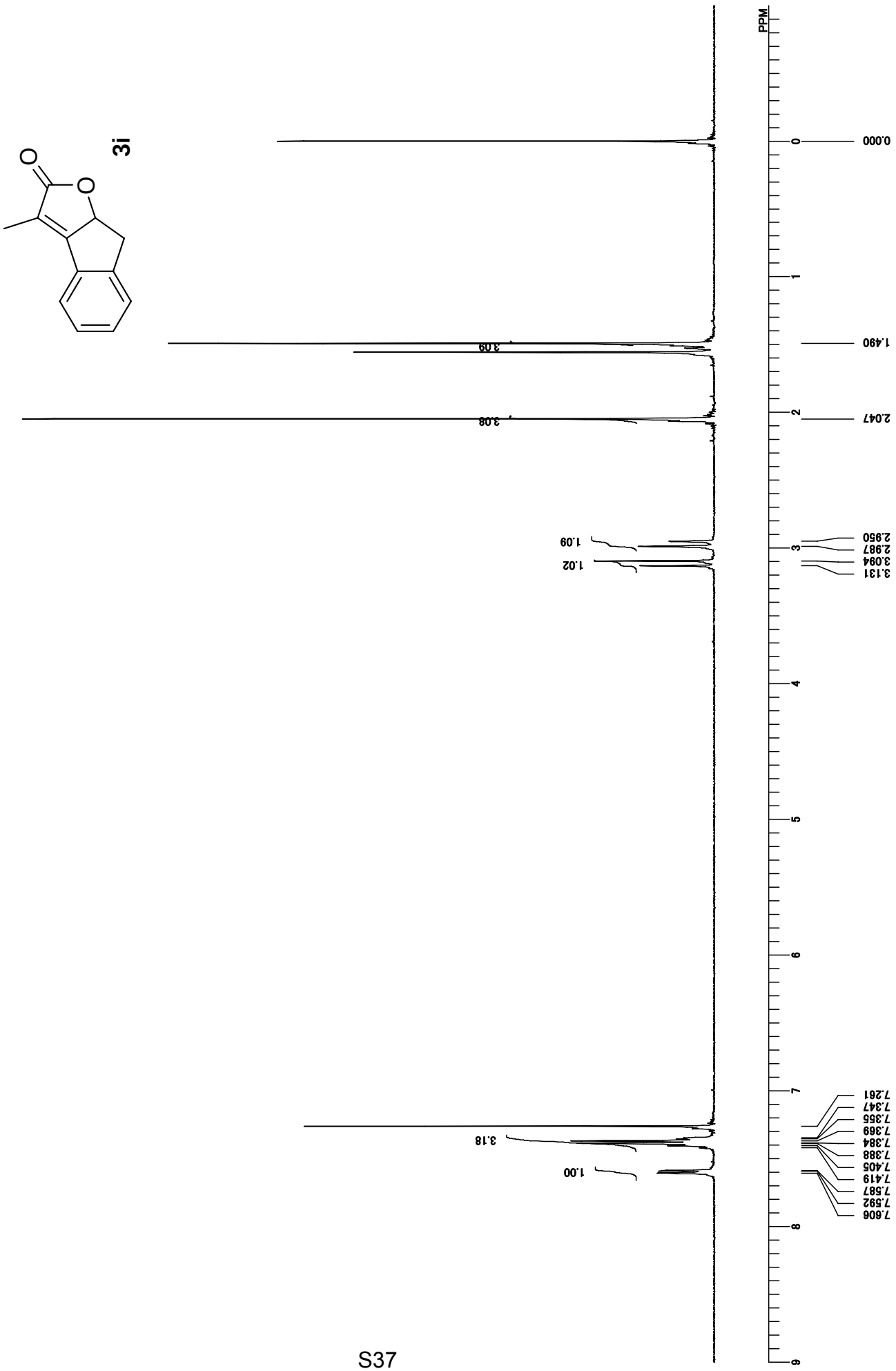
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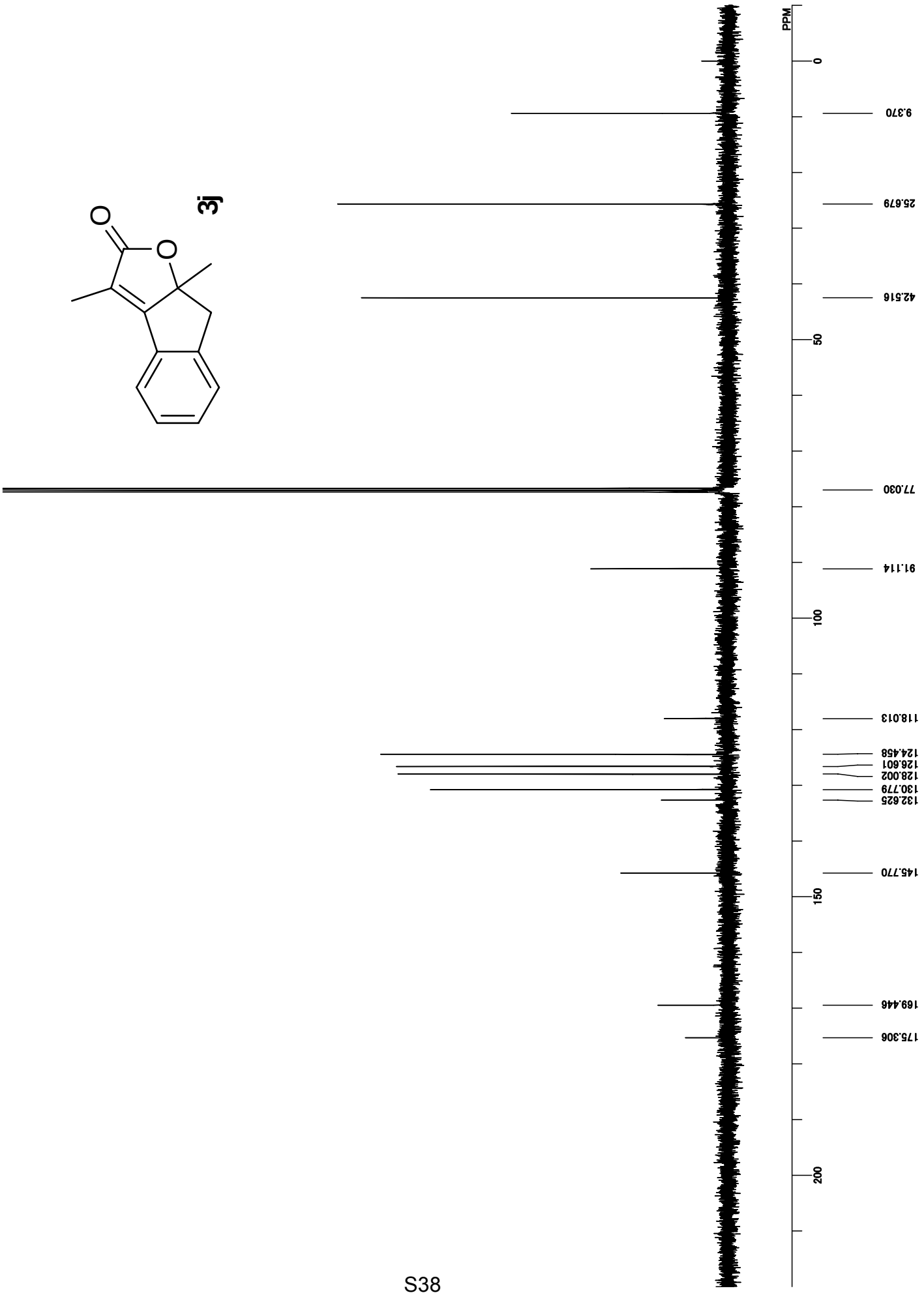
1.00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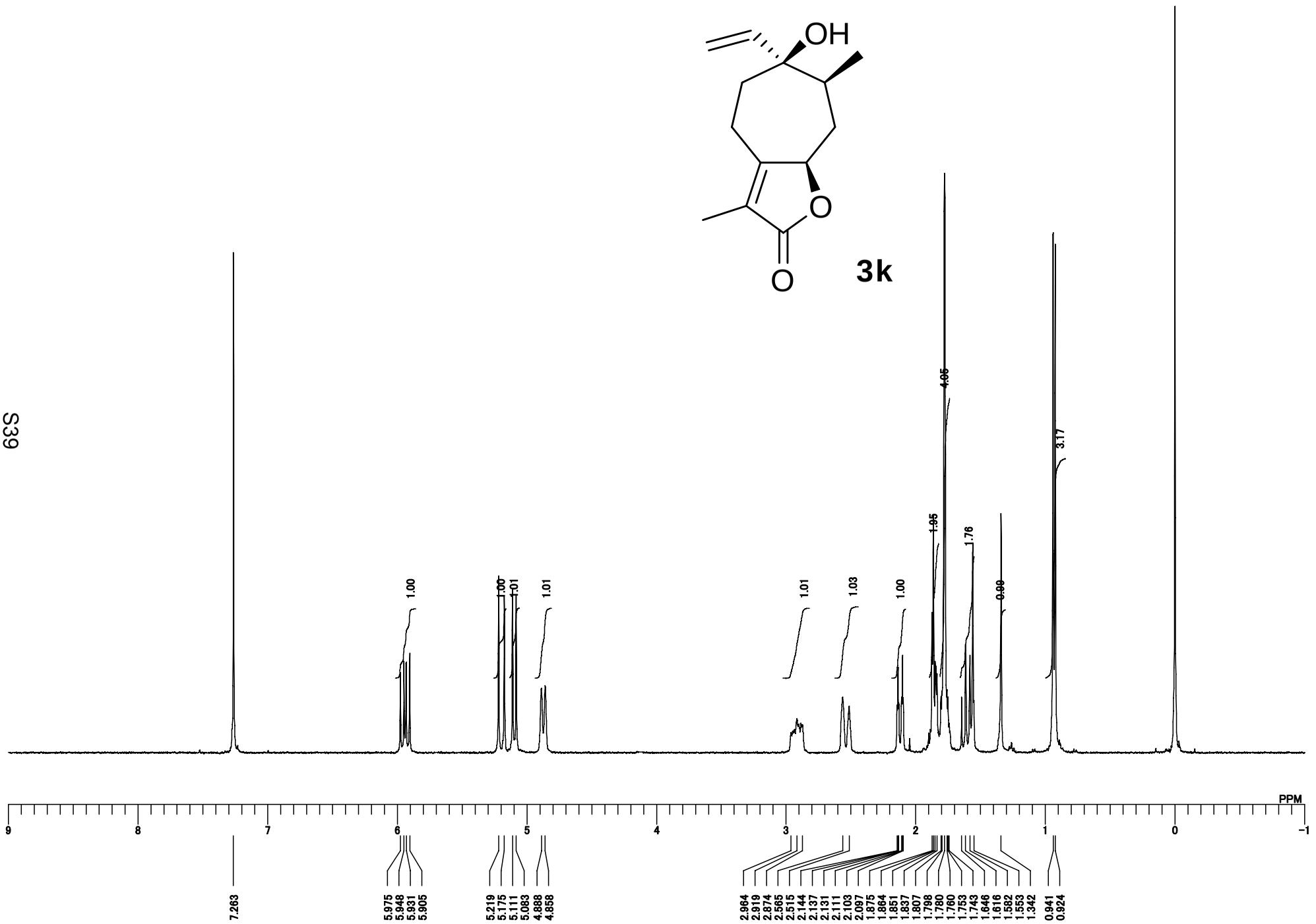
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O
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1.01
1.01
1.03
1.00
1.95
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1.76
0.90
3.17
PPM
9
8
7
6
5
4
3
2
1
0
−1
7.263
5.975
5.948
5.931
5.905
5.219
5.175
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5.083
4.888
4.858
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2.919
2.874
2.565
2.515
2.144
2.137
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2.103
2.097
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1.864
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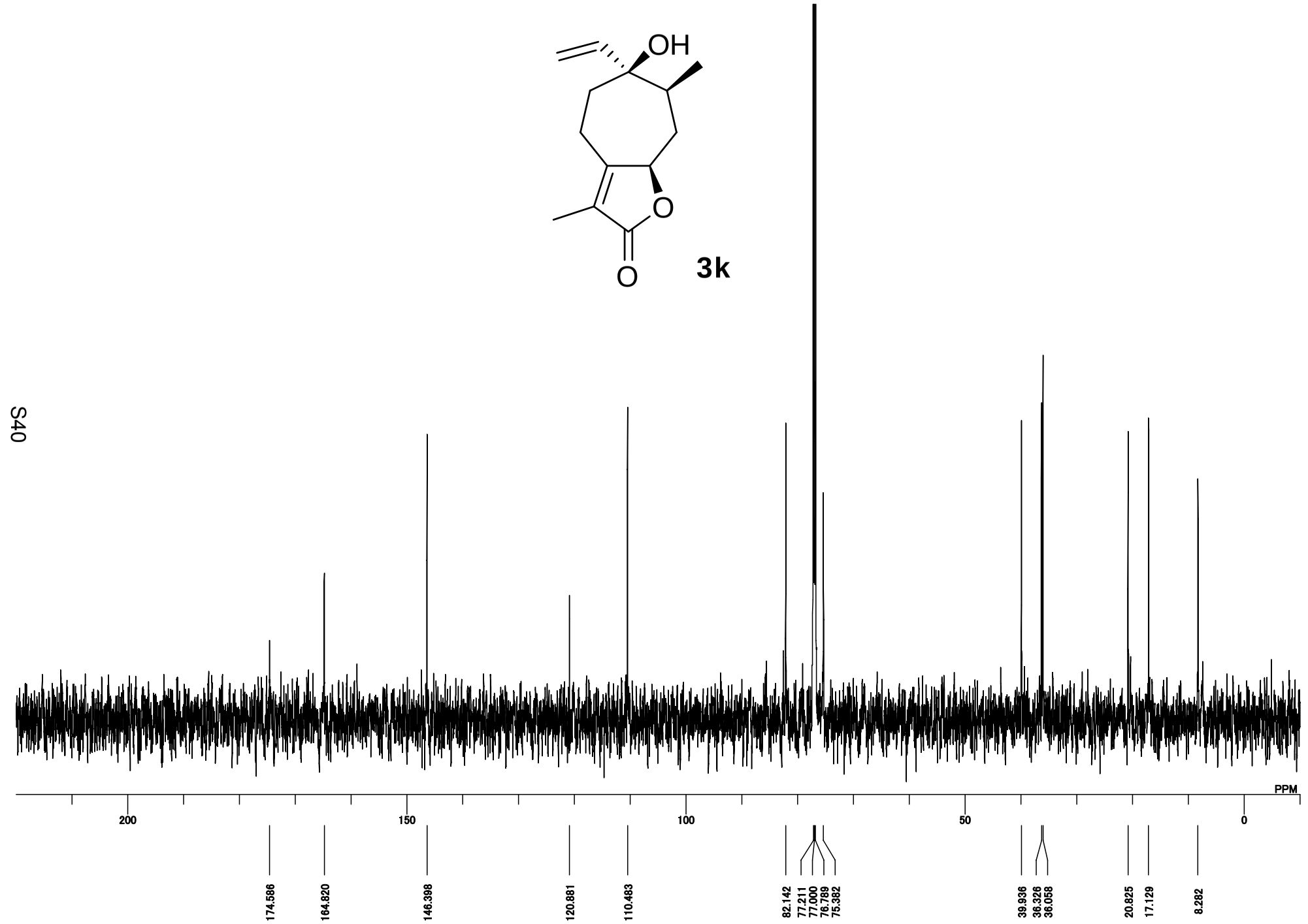
0.924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O
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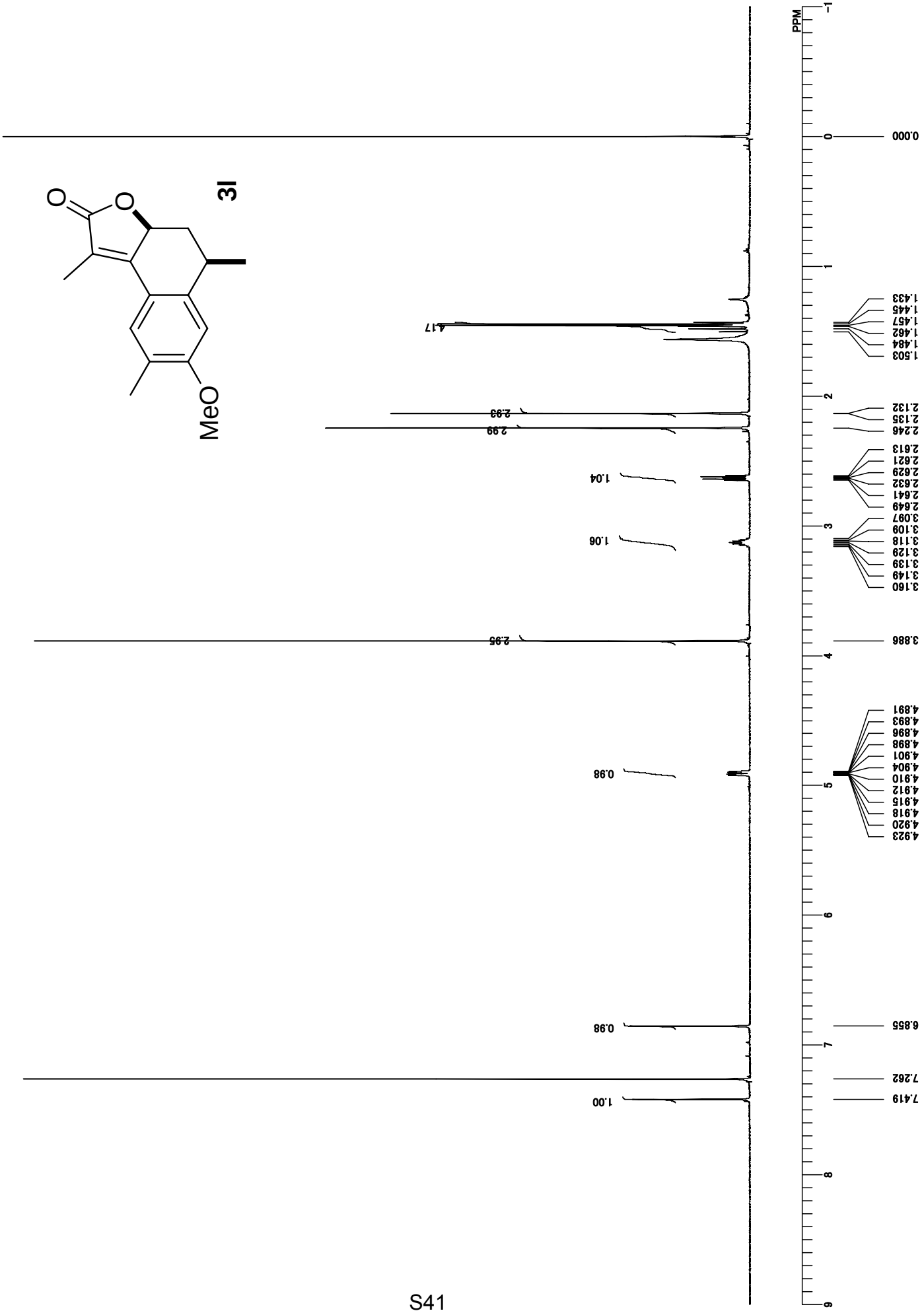
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O
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2.629
2.632
2.641
2.649
3.097
3.109
3.118
3.129
3.139
3.149
3.160
3.886
4.891
4.893
4.896
4.898
4.901
4.904
4.910
4.912
4.915
4.918
4.920
4.923
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1.06
1.04
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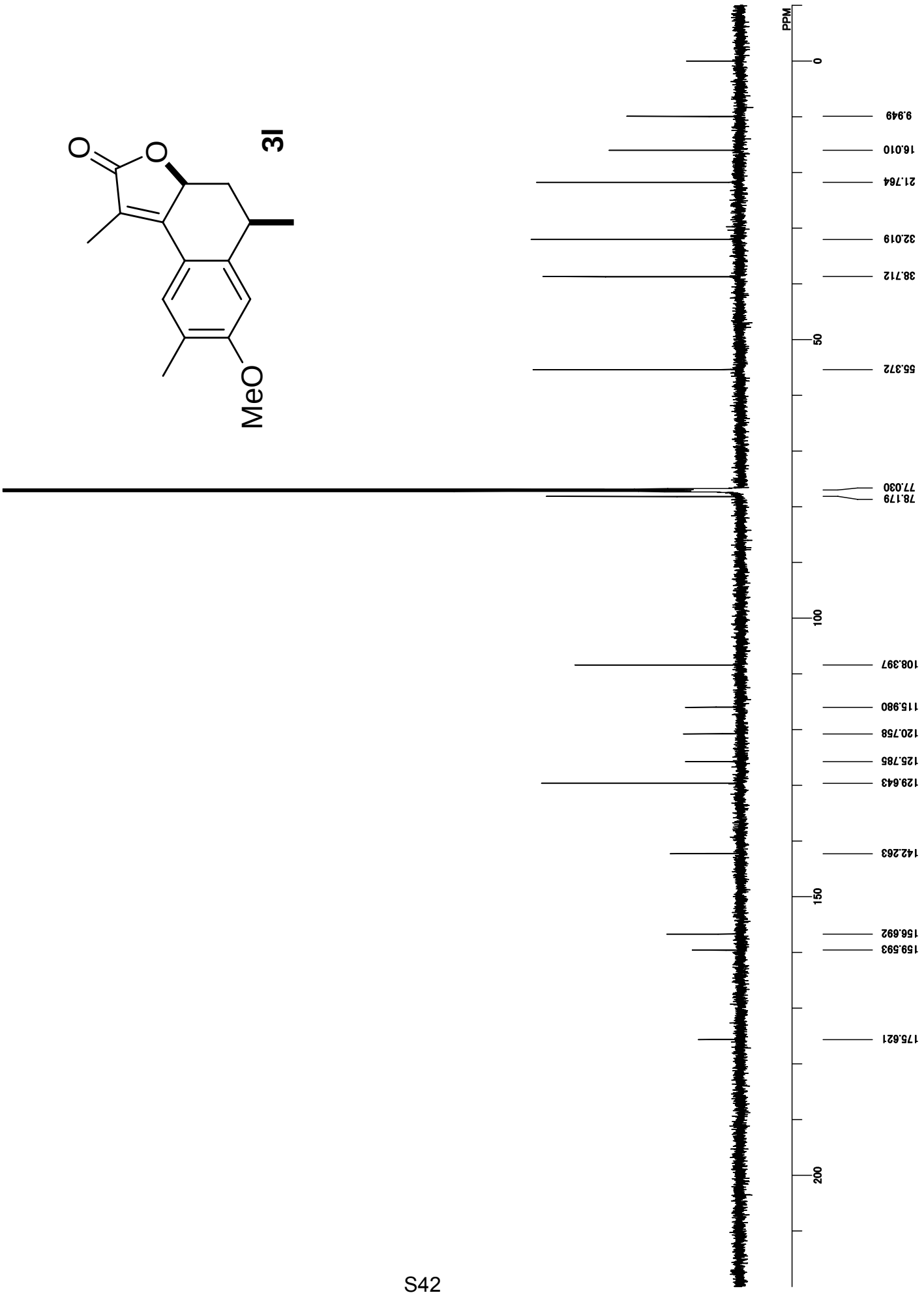
2.93
4.17
0.98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MeO
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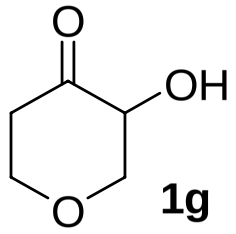
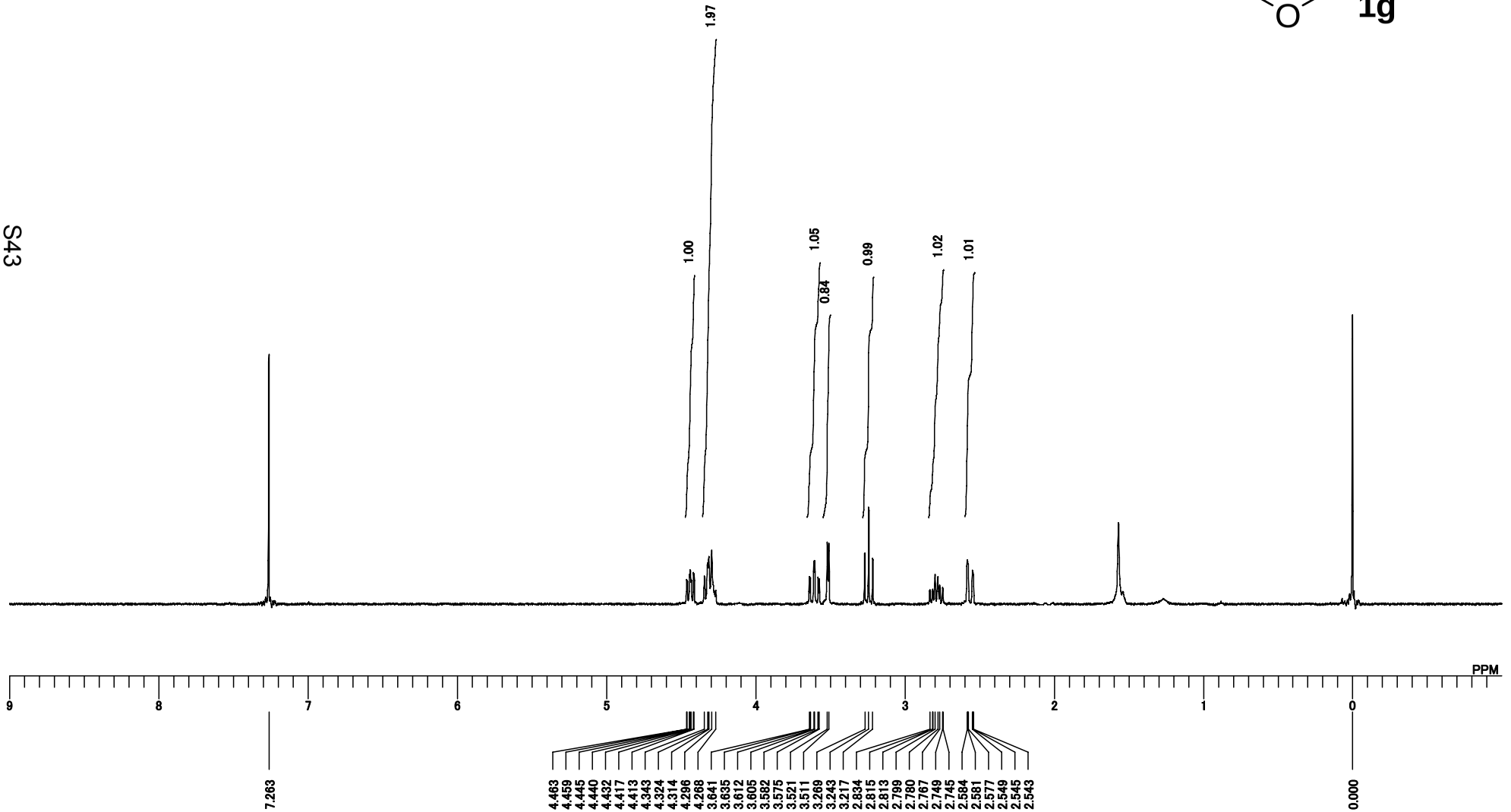
159.593
175.621


O
OH
O

1g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1.05
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0.99
1.02
1.01
PPM
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7
6
5
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2
1
0
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4.314
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3.612
3.605
3.582
3.575
3.521
3.511
3.289
3.243
3.217
2.834
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2.813
2.799
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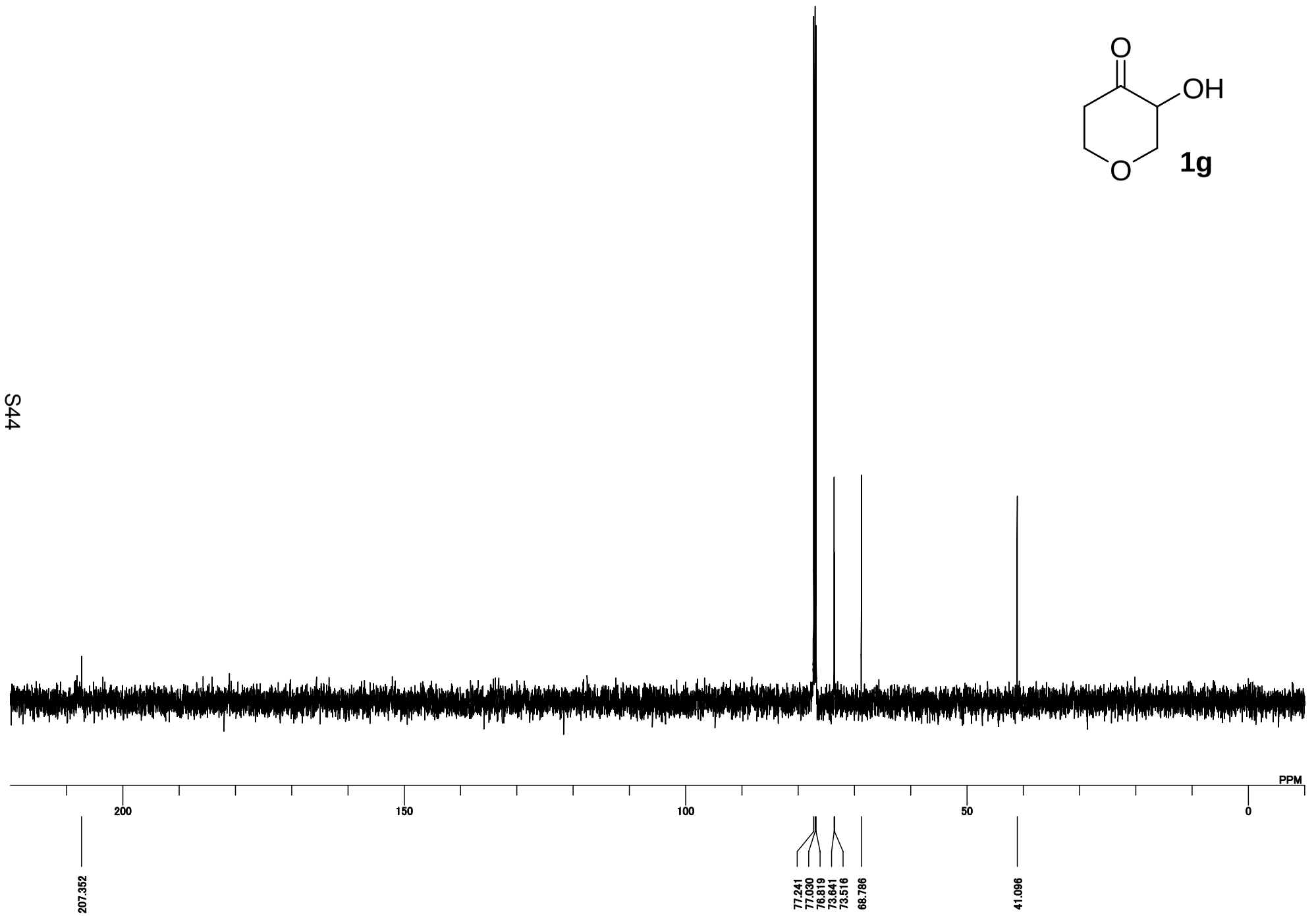
O
OH
O
1g
PPM
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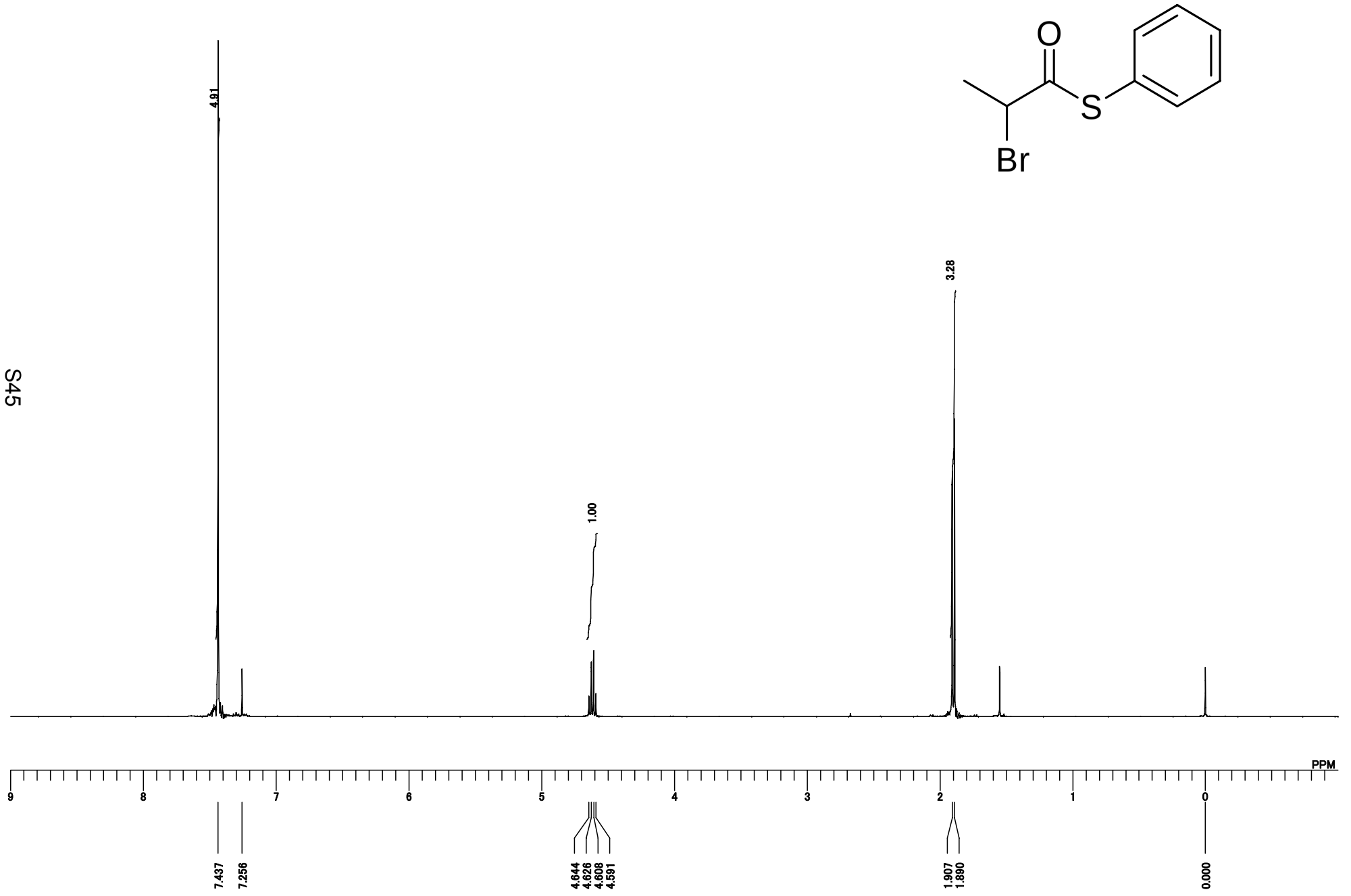
68.786
41.096


O
S
Br
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3.28
PPM
9
8
7
6
5
4
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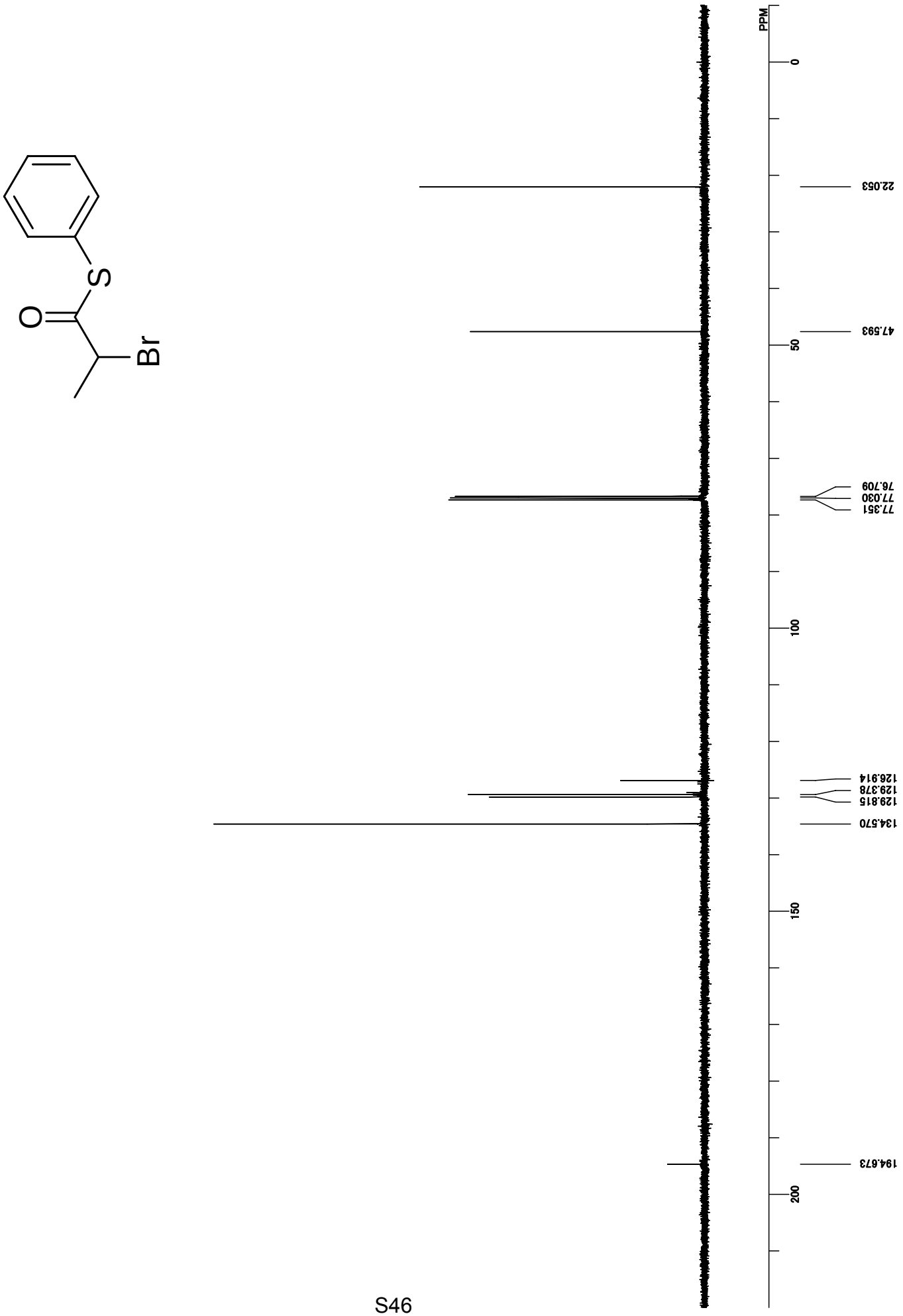
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Br
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100
150
200
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76.709
77.030
77.351
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129.378
129.815
134.570
194.673

PPM
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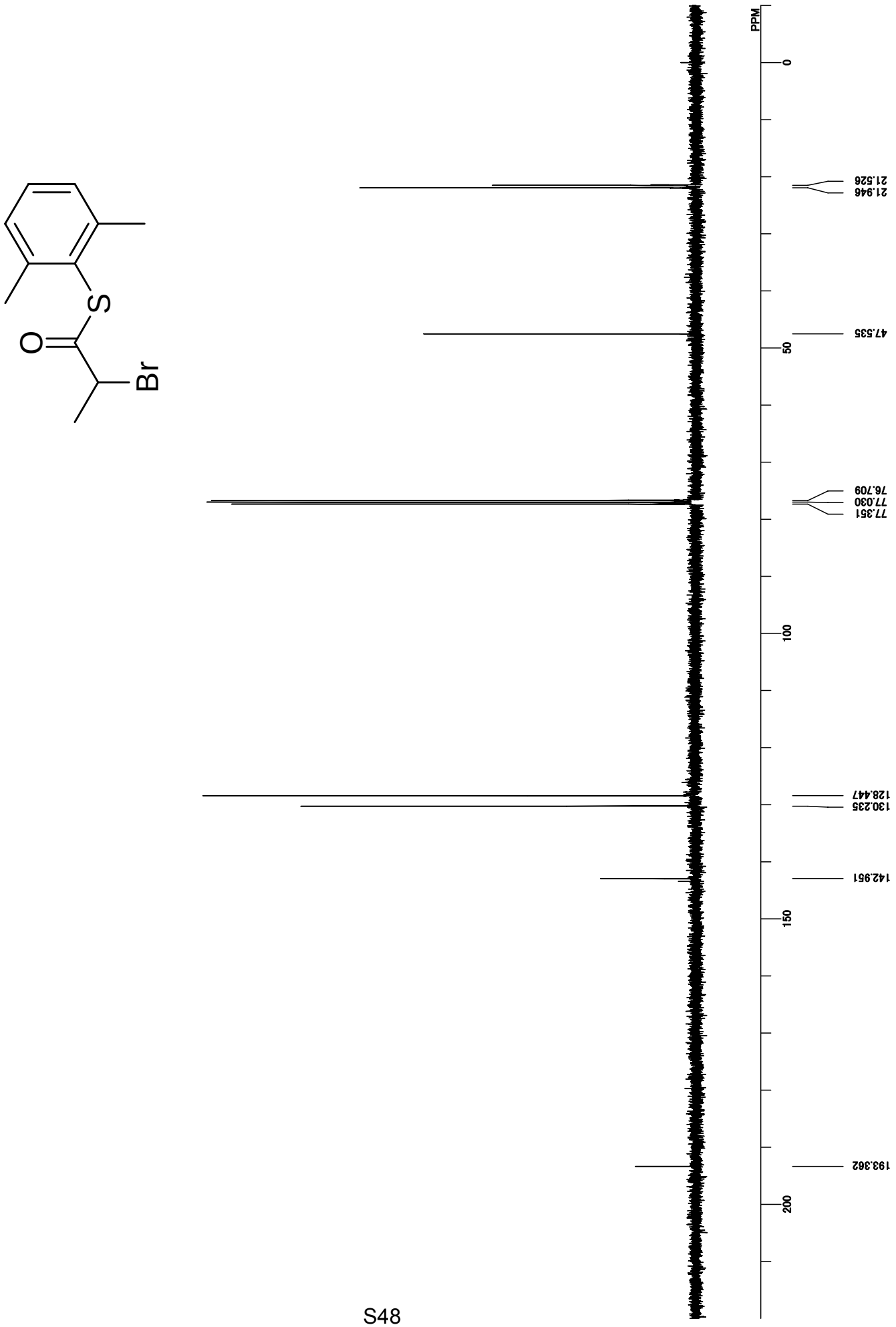
S
O
Br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Br
PPM
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150
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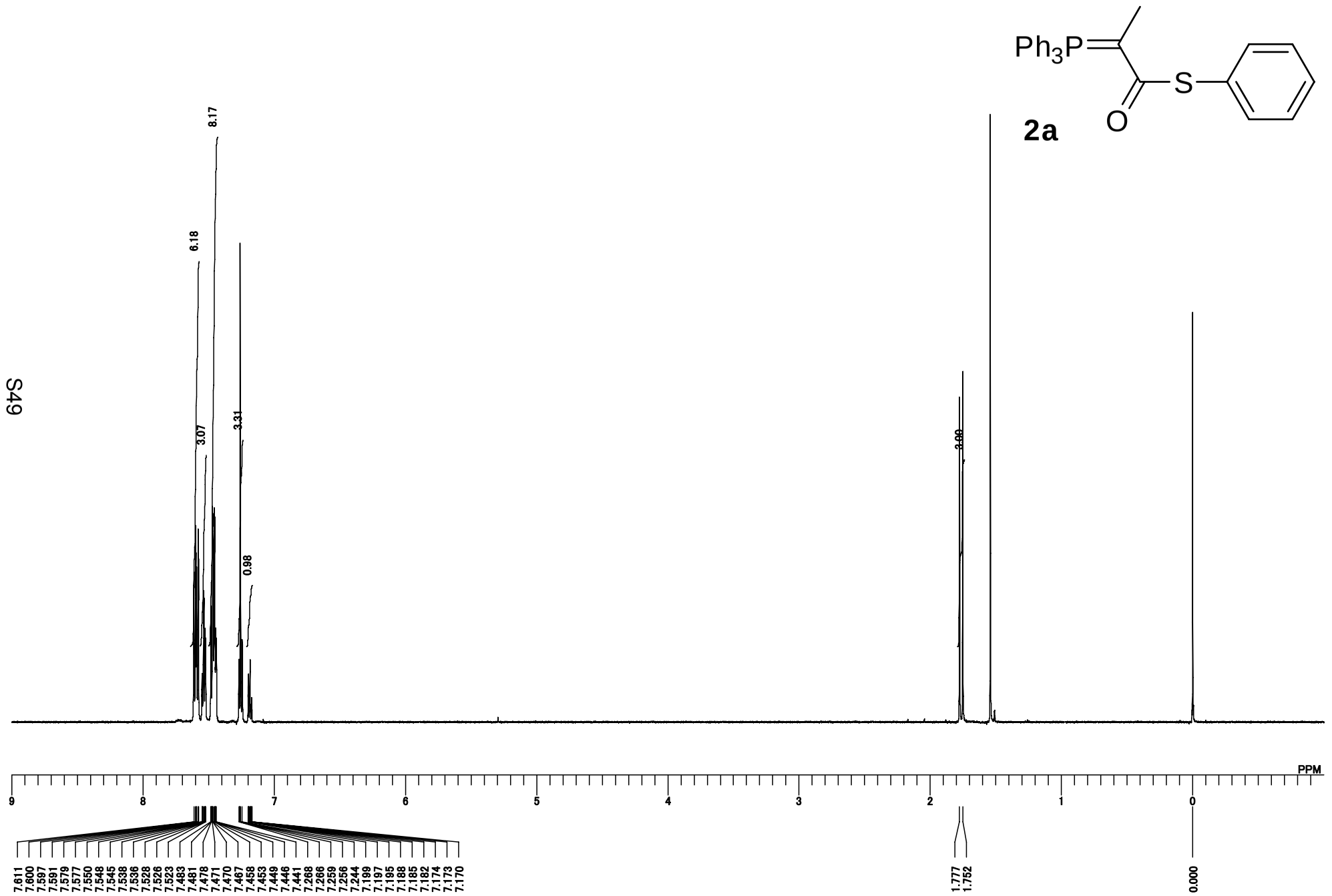
Ph3P
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0.98
3.00
PPM
9
8
7
6
5
4
3
2
1
0
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7.591
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7.467
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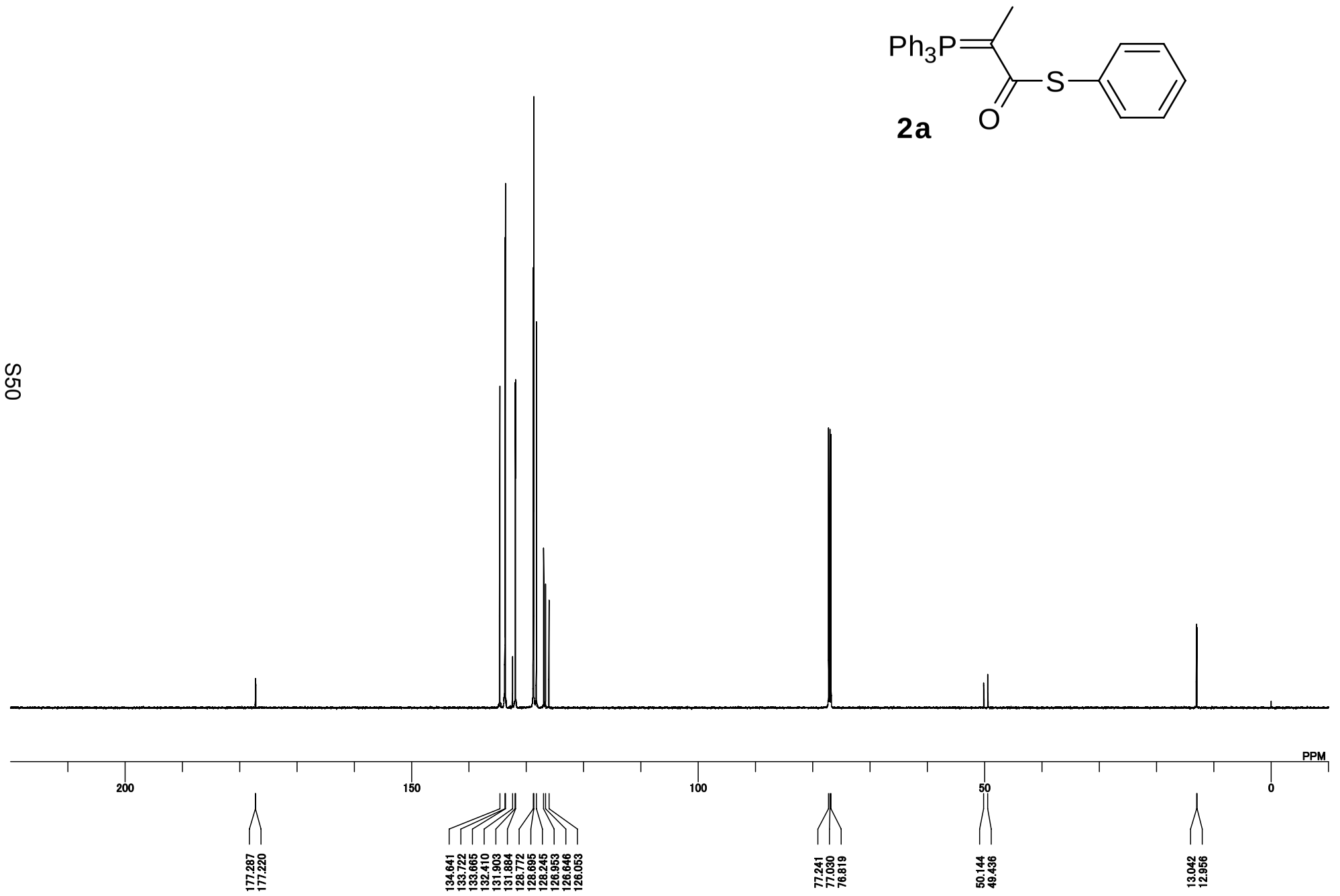
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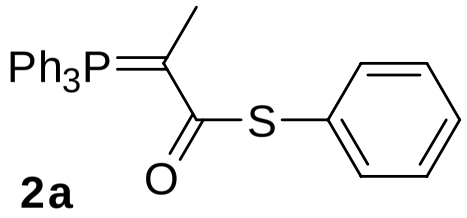

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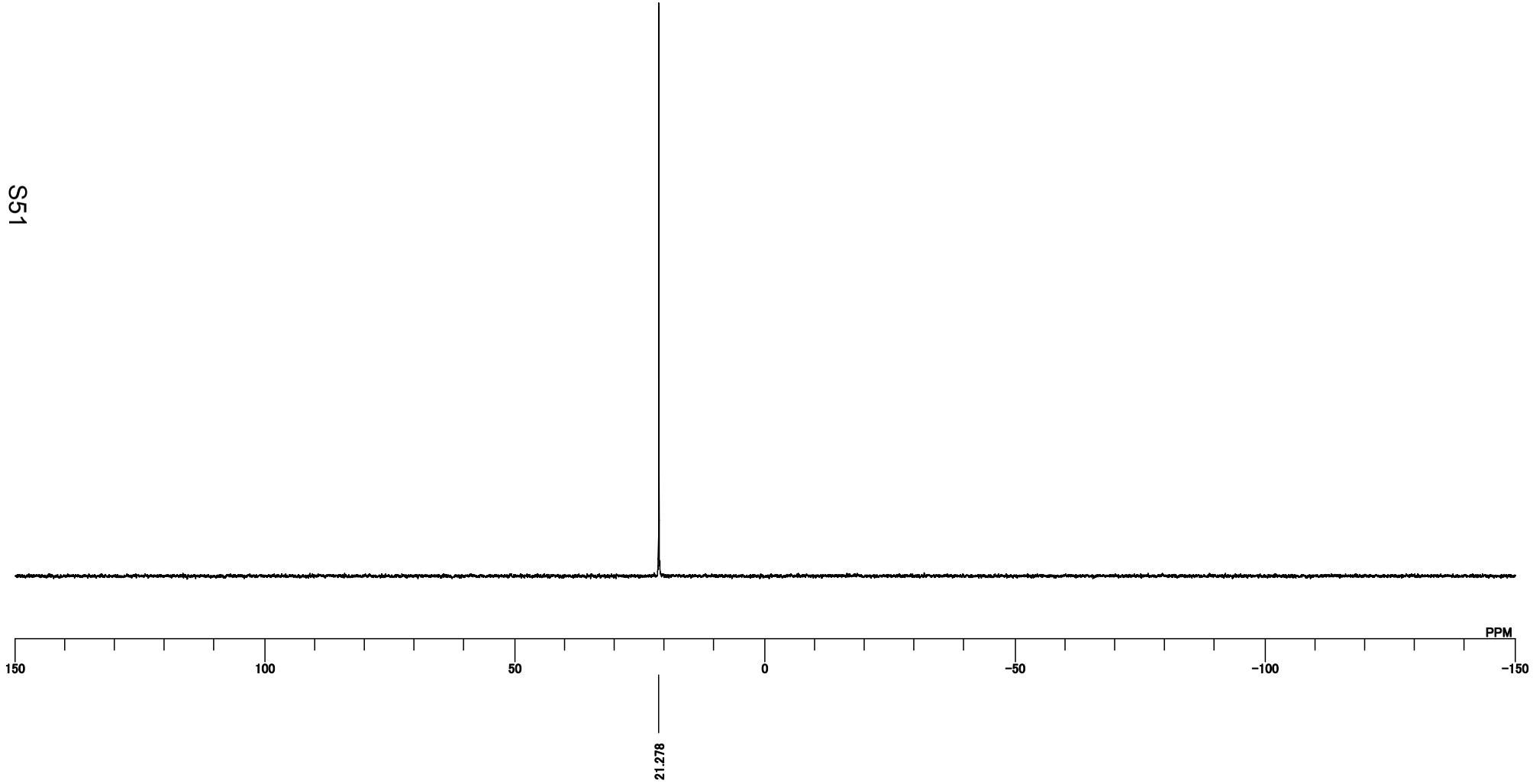

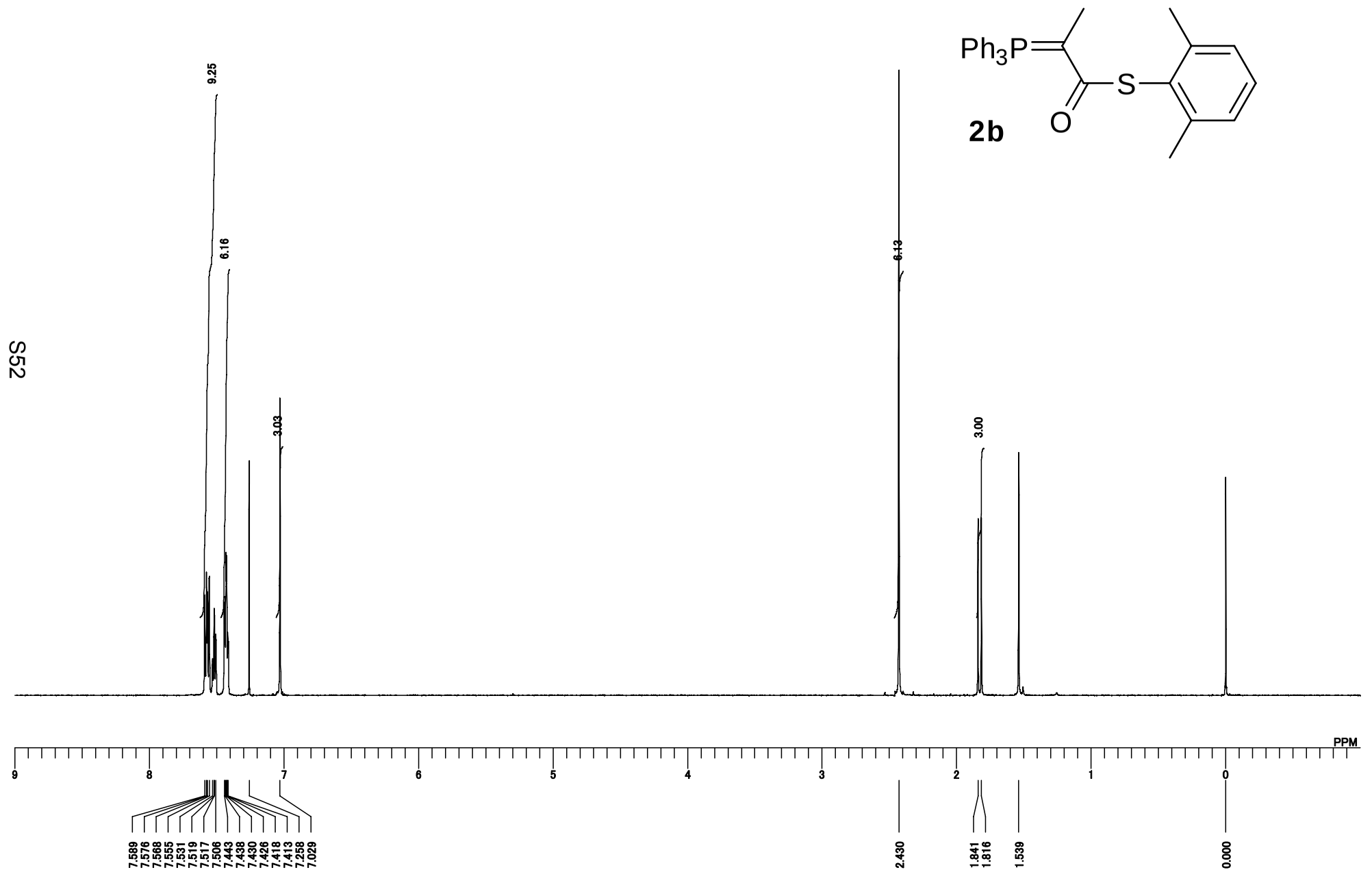
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8
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4
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Ph3P
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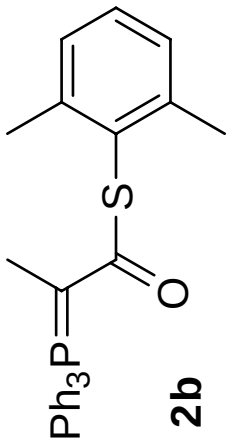
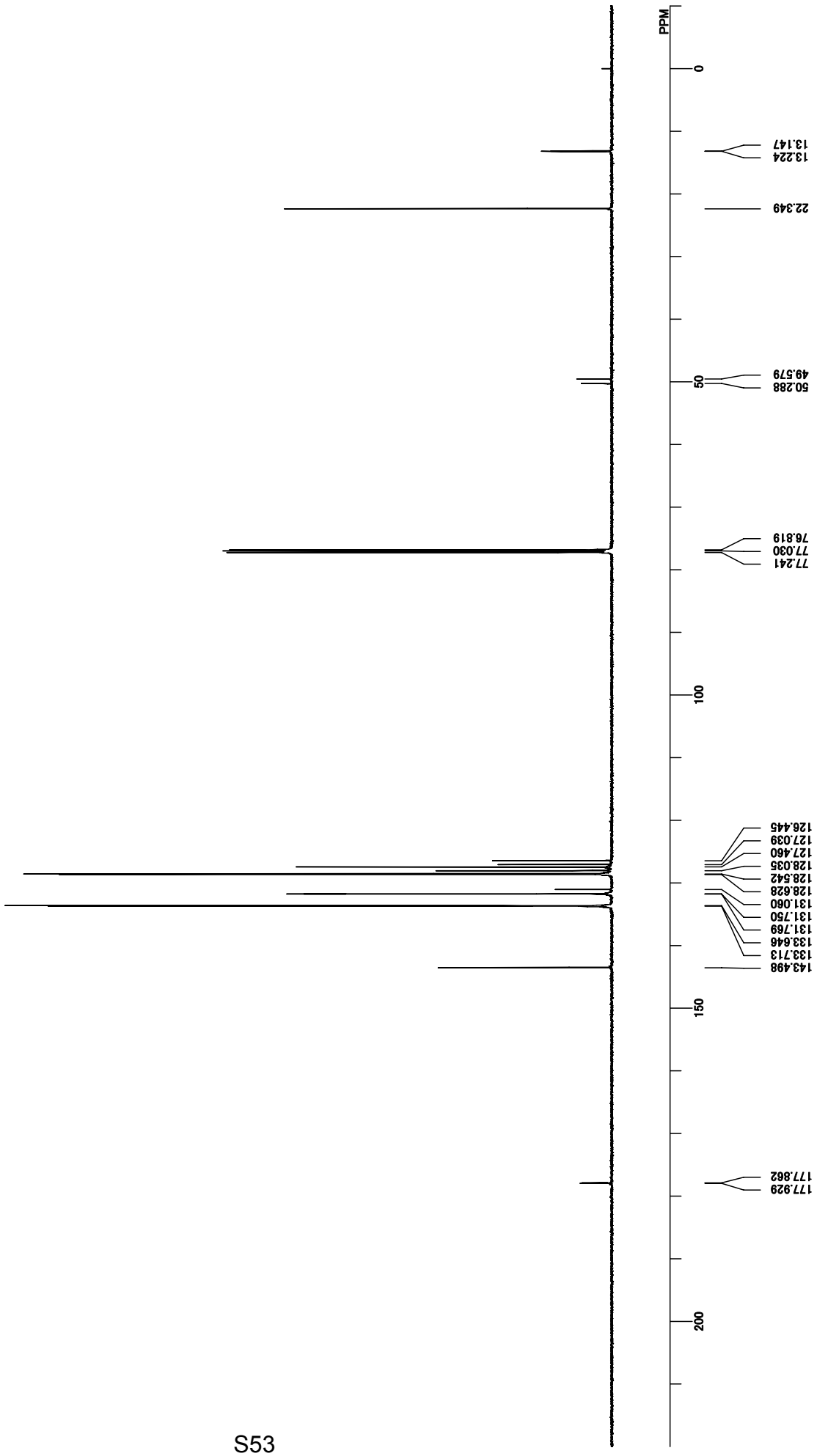
O

2b


S
O
Ph3P

2b


PPM
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150
200
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76.819
77.030
77.241
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127.039
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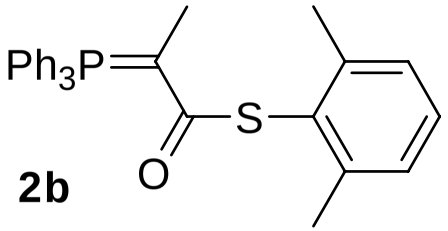

2b