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Direct oxidative lactonization of alkenoic acids mediated solely by $NaIO_4$: beyond oxidant

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Contents

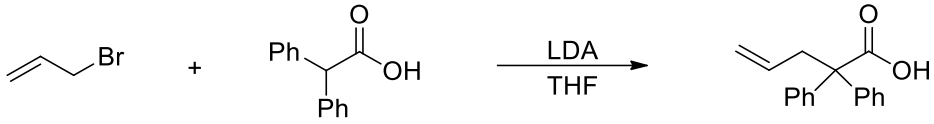
1. General information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer. Chemical shifts are reported in δ units relative to $CHCl_3$ [^{1}H δ = 7.26, ^{13}C δ = 77.36]. ICP-AES were recorded on a PerkinElmer Optima 7300 DV. Mass spectra were recorded by the mass spectrometry service at the University of Science and Technology of China. Glycial acid (ACS reagent 99.7%), allylacetic acid, triflic acid, and $NaIO_4$ were purchased from commercially sources. TfOH solution (1 M in AcOH-Ac_2O) was pre-prepared by dilution of TfOH into the mixture of AcOH and Ac_2O (2:1). Acetic anhydride was purified by distillation over P_2O_5 under an argon atmosphere.

2. General procedures

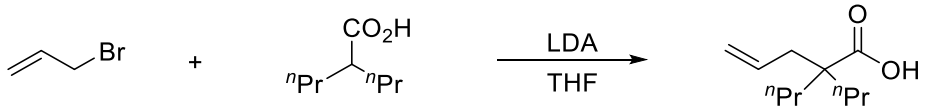
2.1. Procedure for the synthesis of acids

2, 2-diphenylpent-4-enoic acid (1b)



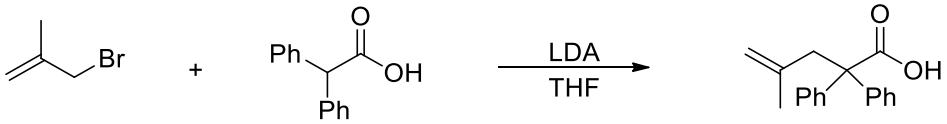
Prepared by literature procedure.[1] A solution containing 10 mmol of 2,2-diphenylacetic acid in 5 mL of dry THF was added to 25 mmol of lithium diisopropylamide (LDA, 2.0 mol/L in THF) in 25 mL of THF at 0 ℃. The suspension was stirred for 1 h at 25 ℃ and 0.5 h at 60 ℃. After the mixture was cooled to 0 ℃, 25 mmol of 3-bromoprop-1-ene was added and the reaction stirred for 2 h at 60 ℃. The mixture was poured into ice-cold water (50 mL) and washed with ether (50 mL × 3). The aqueous phase was acidification with 2 M HCl solution and extracted with ether (50 mL × 3). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluent to give the titled compound as a white solid (1.80 g, 71%).

2,2-dipropylpent-4-enoic acid (1c)



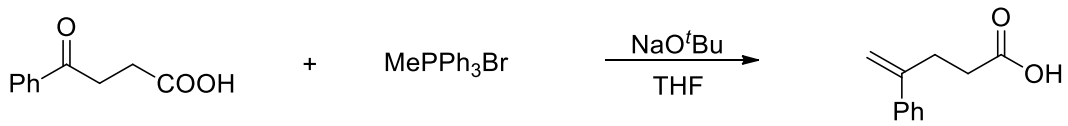
Above procedure for 2,2-diphenylpent-4-enoic acid (**1b**) was used and the titled compound was obtained as colorless oil (1.12 g, 61%).

4-methyl-2, 2-diphenylpent-4-enoic acid (1d)



Above procedure for 2,2-diphenylpent-4-enoic acid (**1b**) was used and the titled compound was obtained as a pale yellow solid (0.99 g, 74%).

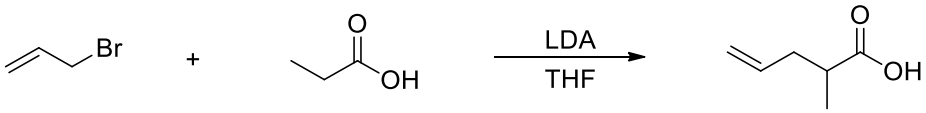
4-phenylpent-4-enoic acid (1e)



Prepared by literature procedure.[2] To a suspension of methyltriphenylphosphonium bromide (4.64

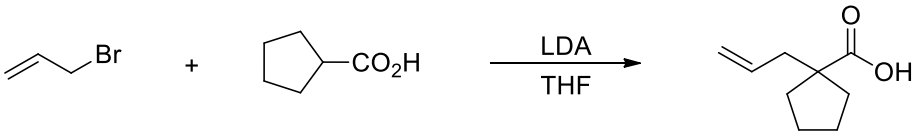
g, 13 mmol) in THF (20 mL) was added sodium *tert*-butoxide (2.92 g, 26 mmol) at 0 ℃. The mixture was then stirred for 30 min. 3-benzoylpropionic acid (1.71 g, 10 mmol) was then added to the reaction mixture at 0 ℃. The mixture was allowed to warm to room temperature, and was then stirred for 16 h. After evaporation of THF, dichloromethane and 1 M NaOH solution were added. The aqueous layer was washed with dichloromethane. 2 M HCl solution was then added until the pH of the aqueous layer was to 2, then extracted with dichloromethane twice and dried over $NaSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using petroleum etherand ethyl acetate as eluent to give the title compound as white solid (1.80 g, 67%).

2-methylpent-4-enoic acid (1f)



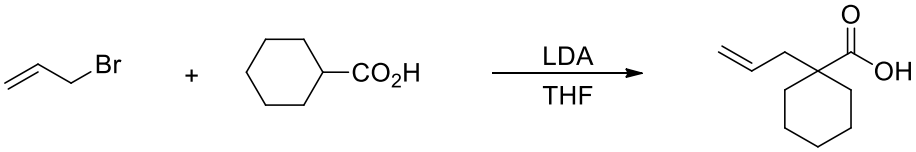
Above procedure for 2,2-diphenylpent-4-enoic acid (**1b**) was used and the titled compound was obtained as colorless oil (1.62 g, 95%).

1-allylcyclopentanecarboxylic acid (1g)



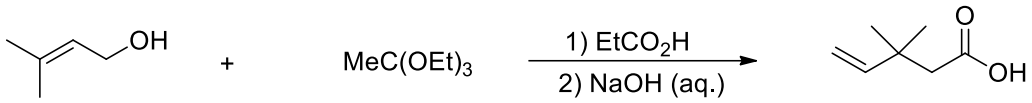
Above procedure for 2,2-diphenylpent-4-enoic acid (**1b**) was used and the titled compound was obtained as colorless oil (1.15 g, 75%).

1-allylcyclohexanecarboxylic acid (1h)



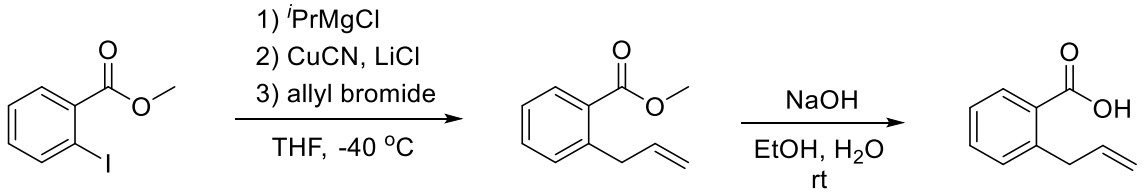
Above procedure for 2,2-diphenylpent-4-enoic acid (**1b**) was used and the titled compound was obtained as colorless oil (1.36 g, 75%).

3, 3-dimethylpent-4-enoic acid (1i)



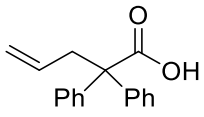
Prepared by literature procedure.[4] 3-Methyl-2-buten-1-ol (1.72 g, 20 mmol) and propionic acid (50 mg, 0.7 mmol) were added in 25 mL of triethyl orthoacetate, the solution was heated at 120-130 ℃ for 11 h. Then the reaction mixture was cooled to room temperature and poured into a mixture of 50 mL of ice cold 5% H_2SO_4. After being stirred overnight, the mixture was extracted with Et_2O, washed with saturated $NaHCO_3$, saturated NaCl and dried over Na_2SO_4. The solvent was removed by distillation at reduced pressure to give the crude product. The residue was added over 1 h to a solution of 50% NaOH (aq.) in 50 mL of EtOH-H_2O (l:l, v/v) at 5 ℃. After the addition was complete, the reaction mixture was warmed to room temperature, stirred for 4 h, partitioned between Et_2O and H_2O. The organic phase was washed with 5% KOH, and the combined aqueous phases were cooled in ice bath, acidified with concentrated HCl, and extracted with three portions of CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4, and the solvent was removed by distillation at reduced pressure. The crude product was purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluent to give the title compound as colorless oil (0.65 g, 51%).

2-allylbenzoic acid (1k)



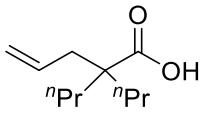
Prepared by literature procedure.[5] ^{i}PrMgCl (2.0 M in THF) (5.25 mL, 10.5 mmol) was added dropwise to a solution of methyl 2-iodobenzoate (1.83 g, 7.00 mmol) in THF (74 mL) at −40 ℃. The resulting mixture was stirred at −40 ℃ for 1.5 h. Then was added to a freshly prepared solution of CuCN (0.63 g, 7.00 mmol) and LiCl (0.59 g, 14.0 mmol) in THF (20 mL), followed dropwise addition of allyl bromide (2.43 mL, 28.0 mmol). After being stirred at −40 ℃, the mixture was allowed to warm to room temperature, diluted with EtOAc (50 mL) and filtered over Celite. The organic solution was washed with a 25% ammonia aqueous solution (100 mL). The aqueous layer was extracted with EtOAc (100 mL × 2). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$,

filtered and concentrated *in vacuo*. The crude product was filtered through a short pad of chromatography column (SiO_2, PE/EA = 50/1) and then dissolved in EtOH (50 mL). 2 M NaOH solution (50 mL) was added and the resulting mixture was stirred at room temperature for 4 h. EtOH was then removed under reduced pressure and the aqueous layer was extracted with Et_2O (75 mL × 2). The solution was acidified to pH 3 with 2 M HCl solution and extracted with Et_2O (75 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford 2-allyl benzoic acid (0.76 g, 67% over two steps) as a white solid without further purification.



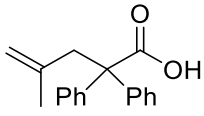
2,2-diphenylpent-4-enoic acid (1b)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34-7.25 (m, 10 H), 5.65-5.55 (m, 1 H), 4.97-4.91 (m, 2 H), 3.18 (d, *J* = 6.8 Hz, 2 H).[1]



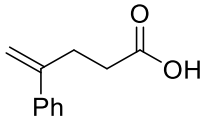
2,2-dipropylpent-4-enoic acid (1c)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.77-5.66 (m, 1 H), 5.10-5.06 (m, 2 H), 2.35 (d, *J* = 7.6 Hz, 2 H), 1.58-1.47 (m, 4 H), 1.33-1.18 (m, 4 H), 0.90 (t, *J* = 7.2 Hz, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.0, 134.1, 118.3, 49.5, 38.4, 37.5, 17.6, 14.9; **HRMS (ESI)** calcd for $C_{11}H_{19}O_2$ $[M-H]^-$ 183.1380, found: 183.1386; **IR** (neat): 3078, 2961, 2936, 2874, 1700, 1641, 1466, 1236, 916 cm^{-1}.



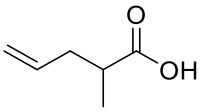
4-methyl-2,2-diphenylpent-4-enoic acid (1d)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.25 (m, 10 H), 4.73 (d, *J* = 1.2 Hz, 1 H), 4.58 (d, *J* = 1.2 Hz, 1 H), 3.21 (s, 2 H), 1.36 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.9, 143.0, 142.2, 129.4, 128.2, 127.3, 115.9, 60.5, 46.0, 24.7; **HRMS (ESI)** calcd for $C_{18}H_{17}O_2$ $[M-H]^-$ 265.1223, found: 265.1223; **IR** (neat): 3057, 2938, 1698, 1642, 1494, 1445, 1225, 898, 729, 699 cm^{-1}.



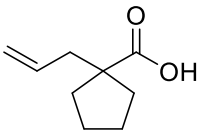
4-phenylpent-4-enoic acid (1e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.27 (m, 5 H), 5.33 (s, 1 H), 5.12 (d, *J* = 0.8 Hz, 1 H), 2.86 (t, *J* = 7.8 Hz, 2 H), 2.54 (t, *J* = 7.8 Hz, 2 H).[2]



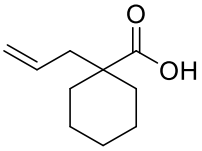
2-methylpent-4-enoic acid (1f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (br s, 1 H), 5.82-5.72 (m, 1 H), 5.11-5.04 (m, 2 H), 2.60-2.51 (m, 1 H), 2.48-2.41 (m, 1 H), 2.24-2.17 (m, 1 H), 1.19 (d, *J* = 7.2 Hz, 3 H).[3]



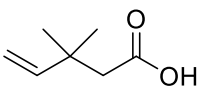
1-allylcyclopentanecarboxylic acid (1g)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.87 (br s, 1 H), 5.83-5.72 (m, 1 H), 5.10-5.04 (m, 2 H), 2.39 (d, *J* = 7.2 Hz, 2 H), 2.14-2.08 (m, 2 H), 1.73-1.63 (m, 4 H), 1.61-1.55 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.8, 135.0, 118.0, 53.7, 43.0, 35.9, 25.5; **HRMS (ESI)** calcd for $C_9H_{13}O_2$ $[M-H]^-$ 153.0910, found: 153.0918; **IR** (neat): 3078, 2957, 2874, 1698, 1641, 1453, 1406, 1279, 1234, 1196, 917 cm^{-1}.



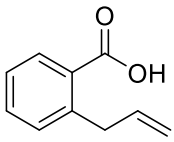
1-allylcyclohexanecarboxylic acid (1h)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 11.78 (br s, 1 H), 5.81-5.71 (m, 1 H), 5.08-5.03 (m, 2 H), 2.29 (d, *J* = 7.6 Hz, 2 H), 2.04 (d, *J* = 13.2 Hz, 2 H), 1.63-1.58 (m, 3 H), 1.46-1.36 (m, 2 H), 1.30-1.21 (m, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.2, 133.7, 118.3, 47.5, 44.7, 33.8, 26.1, 23.4; **HRMS (ESI)** calcd for $C_{10}H_{15}O_2$ $[M-H]^-$ 167.1067, found: 167.1074; **IR** (neat): 3078, 2934, 2858, 1698, 1641, 1454, 1416, 1283, 1245, 1139, 917 cm^{-1}.



3,3-dimethylpent-4-enoic acid (1i)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.92 (dd, *J* = 17.4, 10.6 Hz, 1 H), 5.03-4.96 (m, 2 H), 2.35 (s, 2 H), 1.17 (s, 6 H).[4]

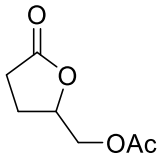


2-allylbenzoic acid (1k)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 (d, *J* = 8.0 Hz, 1 H), 7.53-7.49 (m, 1 H), 7.34-7.31 (m, 2 H), 6.11-6.00 (m, 1 H), 5.07-5.03 (m, 2 H), 3.84 (d, *J* = 6.4 Hz, 2 H).[5]

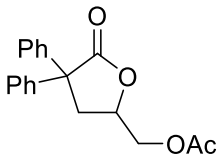
2.2. General reaction conditions.

$NaIO_4$ (1.25 mmol, 267 mg) was added to 2 mL solvent of AcOH-Ac_2O (2:1, v/v), followed by the addition of allylacetic acid (1 mmol, 100 mg) and TfOH (0.05 mmol). The resulting reaction mixture was stirred at corresponding temperature for desired time. After cooled down to room temperature, H_2O (20 mL) was added and resulting mixture was extracted with ethyl ether (20 mL × 3). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography.



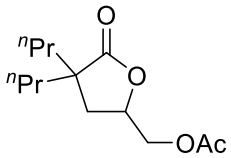
(5-oxotetrahydrofuran-2-yl) methyl acetate (2a)

Colorless oil, 112.3 mg, 71% yield ($NaIO_4$: 1.25 mmol, 0.267 g, 70 ℃, 14 h). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.75-4.70 (m, 1 H), 4.30 (dd, *J* = 12.4, 3.2 Hz, 1 H), 4.13 (dd, *J* = 12.4, 5.6 Hz, 1 H), 2.64-2.50 (m, 2 H), 2.39-2.30 (m, 1 H), 2.11-1.98 (m, 1 H), 2.09 (s, 3 H).[6]



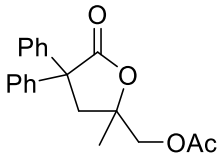
(5-oxo-4,4-diphenyltetrahydrofuran-2-yl) methyl acetate (2b)

Colorless oil, 257.6 mg, 83% yield ($NaIO_4$: 1.25 mmol, 0.267 g, 80 ℃, 24 h). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.25 (m, 10 H), 4.62-4.55 (m, 1 H), 4.41 (dd, *J* = 12.4, 3.2 Hz, 1 H), 4.19 (dd, *J* = 12.4, 6.0 Hz, 1 H), 3.02 (dd, *J* = 12.8, 5.2 Hz, 1 H), 2.78 (dd, *J* = 13.0, 10.6 Hz, 1 H), 2.09 (s, 3 H).[7]



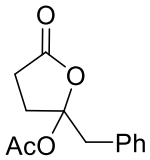
(5-oxo-4, 4-dipropyltetrahydrofuran-2-yl) methyl acetate (2c)

Colorless oil, 171.2 mg, 71% yield ($NaIO_4$: 1.25 mmol, 0.267 g, TfOH: 5 mol %, 60 ℃, 68 h). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.62-4.55 (m, 1 H), 4.27 (dd, *J* = 12.2, 3.0 Hz, 1 H), 4.04 (dd, *J* = 12.2, 6.2 Hz, 1 H), 2.08 (dd, *J* = 11.6, 6.4 Hz, 1 H), 2.06 (s, 3 H), 1.92 (dd, *J* = 12.6, 9.0 Hz, 1 H), 1.61-1.44 (m, 4 H), 1.39-1.14 (m, 4 H), 0.92-0.87 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.6, 170.9, 74.4, 65.7, 47.9, 39.8, 38.8, 34.2, 21.0, 17.9, 14.6 (two peaks); **HRMS (ESI)** calcd for $C_{13}H_{23}O_4$ $[M+H]^+$ 243.1591, found: 243.1587; **IR** (neat): 2961, 2936, 2875, 1770, 1747, 1459, 1371, 1236, 1192, 1130, 1045, 975, 934 cm^{-1}.



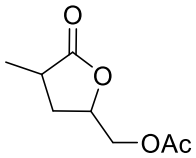
(2-methyl-5-oxo-4, 4-diphenyltetrahydrofuran-2-yl) methyl acetate (2d)

White solid, 204.4 mg, 63% yield ($NaIO_4$: 1.25 mmol, 0.267 g, TfOH: 10 mol %, 80 ℃, 96 h). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.25 (m, 10 H), 4.11 (d, *J* = 11.6 Hz, 1 H), 4.05 (d, *J* = 12.0 Hz, 1 H), 3.17(d, *J* = 14.0 Hz, 1 H), 2.96 (d, *J* = 14.0 Hz, 2 H), 1.99 (s, 3 H), 1.35 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.0, 170.8, 142.9, 142.6, 129.2, 129.0, 127.8 (three peaks), 127.7, 81.3, 68.7, 58.8, 45.4, 24.3, 20.9; **HRMS (ESI)** calcd for $C_{20}H_{21}O_4$ $[M+H]^+$ 325.1434, found: 325.1435; **IR** (neat): 3055, 2974, 2929, 1754, 1732, 1496, 1449, 1385, 1297, 1248, 1234, 1176, 1140, 1091, 1061, 982, 766, 709, 648 cm^{-1}.



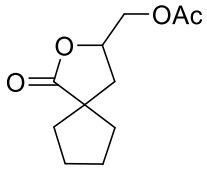
(5-oxo-2-phenyltetrahydrofuran-2-yl) methyl acetate (2e)

Colorless oil, 175.4 mg, 75% yield ($NaIO_4$: 1.25 mmol, 0.267 g, 70 ℃, 39 h). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 5 H), 3.35 (d, *J* = 14.0 Hz, 1 H), 3.25 (d, *J* = 14.4 Hz, 1 H), 2.82-2.73 (m, 1 H), 2.54-2.46 (m, 1H), 2.43-2.35 (m, 1 H), 2.25-2.16 (m, 1 H), 2.07 (s, 3 H).[6]



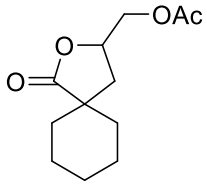
(4-methyl-5-oxotetrahydrofuran-2-yl) methyl acetate (2f)

Colorless oil, 131.9 mg, 77% yield ($NaIO_4$: 1.25 mmol, 0.267 g, 70 ℃, 24 h). For the mixture of *cis* and *trans* isomers: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.68-4.63 (m, 0.54 H), 4.56-4.49 (m, 1 H), 4.25 (dd, *J* = 12.4, 3.2 Hz, 1 H), 4.19 (dd, *J* = 12.2, 3.4 Hz, 0.56 H), 4.07 (dd, *J* = 12.0, 5.2 Hz, 0.54 H), 4.04 (dd, *J* = 12.4, 6.2 Hz, 1 H), 2.72-2.61 (m, 1.58 H), 2.47-2.40 (m, 1 H), 2.26-2.20 (m, 0.62 H), 2.04-1.97 (m, 0.55 H), 2.02 (s, 3 H), 2.02 (s, 1.57 H), 1.63-1.54 (m, 1 H), 1.23 (s, 3 H), 1.21 (s, 1.71 H).



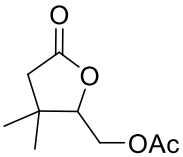
(1-oxo-2-oxaspiro [4.4] nonan-3-yl) methyl acetate (2g)

Colorless oil, 161.8 mg, 76% yield ($NaIO_4$: 1.25 mmol, 0.267 g, TfOH: 5 mol %, 70 ℃, 24 h). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.62-4.56 (m, 1 H), 4.28 (dd, *J* = 12.4, 3.2 Hz, 1 H), 4.09 (dd, *J* = 12.4, 6.4 Hz, 1 H), 2.20-2.11 (m, 2 H), 2.07 (s, 3 H), 1.93-1.79 (m, 4 H), 1.76-1.58 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.0, 170.9, 74.8, 65.4, 49.9, 39.0, 38.0, 37.2, 25.7, 25.6, 21.0; **HRMS (ESI)** calcd for $C_{11}H_{17}O_4$ $[M+H]^+$ 213.1121, found: 213.1121; **IR** (neat): 2956, 2872, 1770, 1746, 1448, 1371, 1234, 1188, 1155, 1043, 975, 933 cm^{-1}.



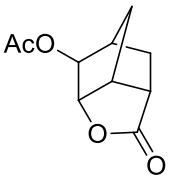
(1-oxo-2-oxaspiro [4.5] decan-3-yl) methyl acetate (2h)

Colorless oil, 172.0 mg, 76% yield ($NaIO_4$: 1.25 mmol, 0.267 g, TfOH: 5 mol %, 70 ℃, 24 h). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.66-4.60 (m, 1 H), 4.31 (dd, *J* = 12.4, 3.2 Hz, 1 H), 4.09 (dd, *J* = 12.4, 6.4 Hz, 1 H), 2.33 (dd, *J* = 12.8, 6.8 Hz, 1 H), 2.09 (s, 3 H), 1.86-1.72 (m, 4 H), 1.67-1.49 (m, 4 H), 1.42-1.21 (m, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.1, 171.0, 74.5, 65.7, 44.7, 35.5, 34.4, 32.3, 25.5, 22.4 (two peaks), 21.1; **HRMS (ESI)** calcd for $C_{12}H_{19}O_4$ $[M+H]^+$ 227.1278, found: 227.1276; **IR** (neat): 2935, 2859, 1766, 1743, 1450, 1372, 1236, 1194, 1167, 1032, 963, 942 cm^{-1}.



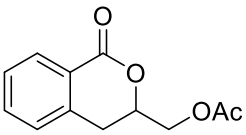
(3,3-dimethyl-5-oxotetrahydrofuran-2-yl) methyl acetate (2i)

Colorless oil, 80.1 mg, 43% yield ($NaIO_4$: 1.25 mmol, 0.267 g, 70 ℃, 24 h). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.30-4.24 (m, 2 H), 4.11 (dd, *J* = 11.2, 6.0 Hz, 1 H), 2.37 (s, 2 H), 2.06 (s, 3 H), 1.22 (s, 3 H), 1.08 (s, 3 H).[8]



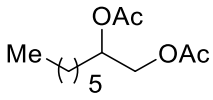
5-*exo*-Acetoxy-6-*endo*-hydroxybicyclo[2.2.l]heptane-2-*endo*-carboxylicacid lactone (2j)

White solid, 131.5 mg, 67% yield ($NaIO_4$: 1.25 mmol, 0.267 g, TfOH: 5 mol %, 60 ℃, 36 h). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.99 (s, 1 H), 4.86 (d, *J* = 7.2 Hz, 1 H), 2.76 (s, 1 H), 2.68 (d, *J* = 5.2 Hz, 1 H), 2.61 (d, *J* = 6.4 Hz, 1 H), 2.05 (dd, *J* = 15.4, 7.0 Hz, 1 H), 2.04 (s, 3 H), 1.76 (dd, *J* = 13.6, 6.4 Hz, 1 H), 1.69 (dd, *J* = 15.4, 5.8 Hz, 1 H), 1.47 (dd, *J* = 13.6, 5.2 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.4, 170.4, 84.3, 76.1, 46.2, 43.7, 42.7, 29.8, 25.4, 21.4; **HRMS (ESI)** calcd for $C_{10}H_{13}O_4$ $[M+H]^+$ 197.0808, found: 197.0808; **IR** (neat): 2988, 1784, 1728, 1378, 1249, 1197, 1113, 1024, 1005, 961, 930, 834 cm^{-1}.



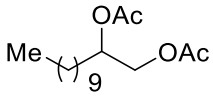
(1-oxoisochroman-3-yl) methyl acetate (2k)

Colorless oil, 200.9 mg, 91% yield ($NaIO_4$: 1.25 mmol, 0.267 g, TfOH: 5 mol %, 70 ℃, 48 h). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.40 (t, *J* = 7.6 Hz, 1 H), 7.26 (d, *J* = 7.6 Hz, 1 H), 4.79-4.75 (m, 1 H), 4.36 (d, *J* = 4.4 Hz, 2 H), 3.12 (dd, *J* = 16.4, 11.6 Hz, 1 H), 2.94 (dd, *J* = 16.4, 3.2 Hz, 1 H), 2.09 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 164.9, 138.4, 134.3, 130.7, 128.2, 127.8, 125.1, 76.1, 65.3, 30.0, 21.0; **HRMS (ESI)** calcd for $C_{12}H_{12}O_4Na$ $[M+Na]^+$ 243.0633, found: 243.0635; **IR** (neat): 2954, 1728, 1608, 1460, 1368, 1227, 1085, 1031 963, 942, 747, 695, 605 cm^{-1}.



octane-1,2-diyl diacetate (2l)

Colorless oil, 126.8 mg, 55% yield ($NaIO_4$: 0.5 mmol, 0.107 g, 80 ℃, 36 h). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.07-5.02 (m, 1 H), 4.20 (dd, *J* = 12.0, 3.2 Hz, 1 H), 4.00 (dd, *J* = 12.0, 6.8 Hz, 1 H), 2.04 (s, 3 H, two peaks), 1.58-1.50 (m, 2 H), 1.27-1.25 (m, 8 H), 0.85 (t, *J* = 6.6 Hz, 3 H).[9]



dodecane-1,2-diyl diacetate (2m)

Colorless oil, 54% yield ($NaIO_4$: 0.50 mmol, 0.107 g, 80 ℃, 46 h). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.07-5.01 (m, 1 H), 4.20 (dd, *J* = 11.6, 3.2 Hz, 1 H), 4.00 (dd, *J* = 11.8, 6.6 Hz, 1 H), 2.04 (s, 3 H), 2.03 (s, 3 H), 1.57-1.52 (m, 2 H), 1.27-1.23 (m, 16 H), 0.86 (t, *J* = 6.4 Hz, 3 H).[9]

3. Control reactions

Equation 1, Scheme 4. $NaIO_4$ (0-1.25 mmol, 0-267.4 mg) was added to 2 mL premixed solvent of AcOH-Ac_2O (2:1, v/v), followed by the addition of 5-(iodomethyl)-dihydrofuran-2(3*H*)-one (1 mmol, 226 mg) and TfOH (0.05 mmol). The resulting reaction mixture was stirred at 70 ℃ for 14 h. The conversions were collected on GC using ethyl 3-phenylpropionate as internal standard.

Equation 2, Scheme 4. $NaIO_4$ (0.25-1.25 equiv, 53.5-267.4 mg) was added to 2 mL premixed solvent of AcOH-Ac_2O (2:1, v/v), followed by the addition of allylacetic acid (1 mmol, 100 mg) and TfOH (0.05 mmol). The resulting reaction mixture was stirred at 70 ℃ for 14 h. The conversions were collected on GC using ethyl 3-phenylpropionate as internal standard.

Equation 3, Scheme 4. $NaIO_3$ (1.25 equiv, 247 mg) was added to 2 mL premixed solvent of AcOH-Ac_2O (2:1, v/v), followed by the addition of allylacetic acid (1 mmol, 100 mg) and TfOH (0.05 mmol). The resulting reaction mixture was stirred at 70 ℃ for 14 h. The conversions were collected on GC using ethyl 3-phenylpropionate as internal standard.

4. NMR monitoring experiments

All data were collected by ^{1}H NMR using ethyl 3-phenylpropionate as internal standard.

General procedure: Ethyl 3-phenyl-propionate (0.5 mmol, 89 mg) and $NaIO_4$ (6.25 mmol, 1.34 g) were added to 10 mL solvent of AcOH-Ac_2O (2:1, v/v), followed by the addition of allylacetic acid (5 mmol, 501 mg) and TfOH (0.25 mmol, 38 mg). The resulting reaction mixture was stirred at 70 ℃ and sampled 30 μL of reaction mixture for ^1H NMR tests. Allylacetic acid **[1a]**, (3-oxocyclopentyl)methyl acetate **[2a]** and 3-(iodomethyl)cyclopentan-1-one **[3a]** were determined using ethyl 3-phenylpropionate as internal standard by ^1H NMR. The results were demonstrated in Table S1 and Figure S1.

Table S1. [1a], [2a] and [3a] *v.s.* Time.

Time (min)	**1a** (%)	**2a** (%)	**3a** (%)
0	100	0	0
30	94	4	3
60	89	6	5
120	84	10	7
180	76	16	10
240	67	22	12
360	45	34	18
480	17	45	27
600	0	60	30
720		66	20
840		71	9
960		73	6

Conditions: $NaIO_4$ (6.25 mmol, 1.34 g), allylacetic acid (5 mmol, 501 mg), TfOH (0.25 mmol, 38 mg), solvent (10 mL), 70 ℃, ethyl 3-phenylpropionate (0.5 mmol, 89 mg) as internal standard.

5. ICP-AES experiments

The trace metals in the reaction mixture were measured by ICP-AES at Instruments Center for Physical Science of the University of Science and Technology of China.

中国科学技术大学理化科学实验中心

检　测　报　告

样品名称：　　报告日期：2014.9.19

送样单位：　　报告编号：

样品名称	测定元素含量(μg/mL)			
	Fe	Cu	Ru	Ir
	Not detected	Not detected	Not detected	Not detected
	Pb	Pt	Pd	Ag
	Not detected	Not detected	Not detected	Not detected
	Au			
	Not detected			
		俞华明	2014.9.19	

6. References

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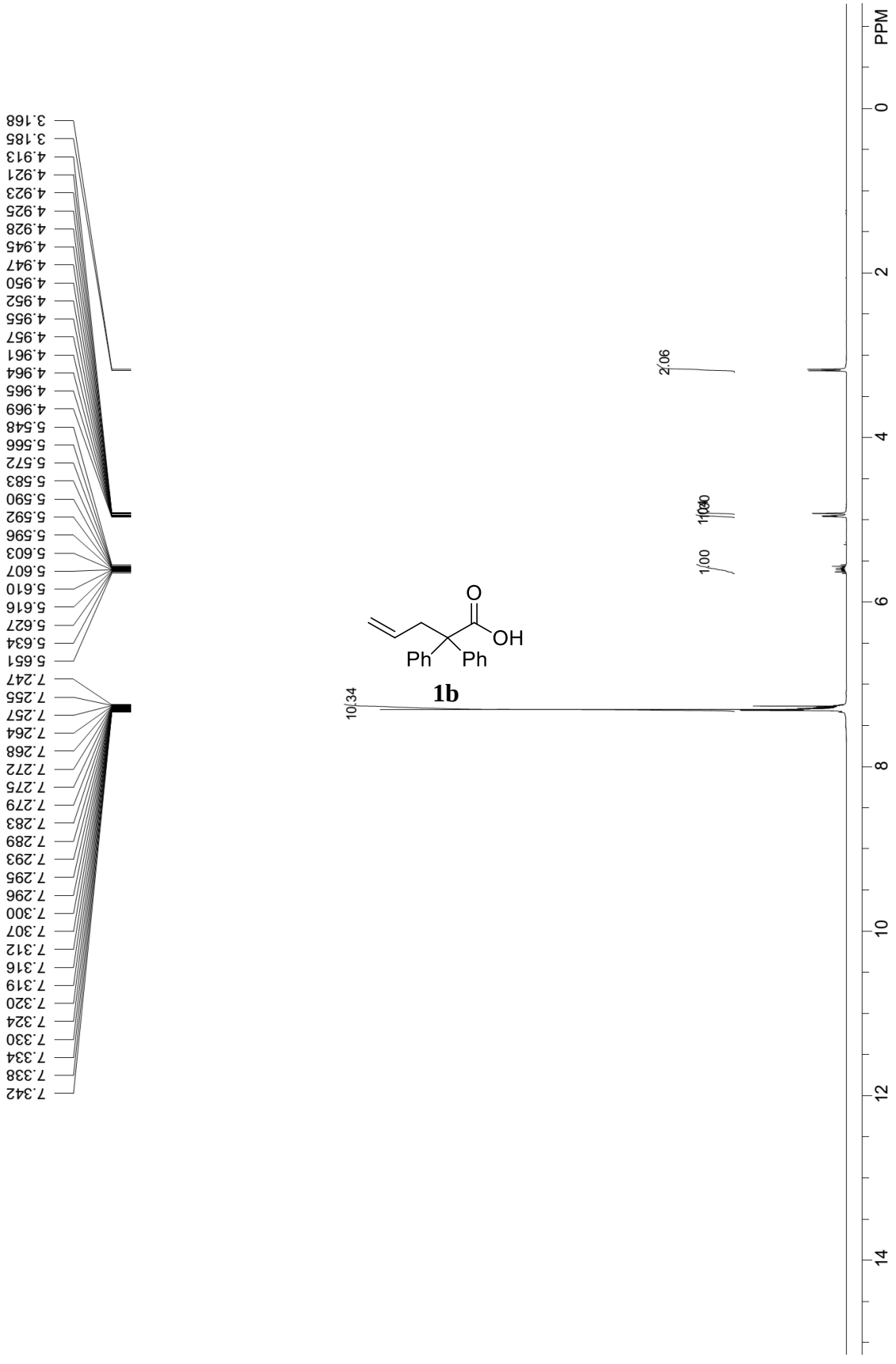
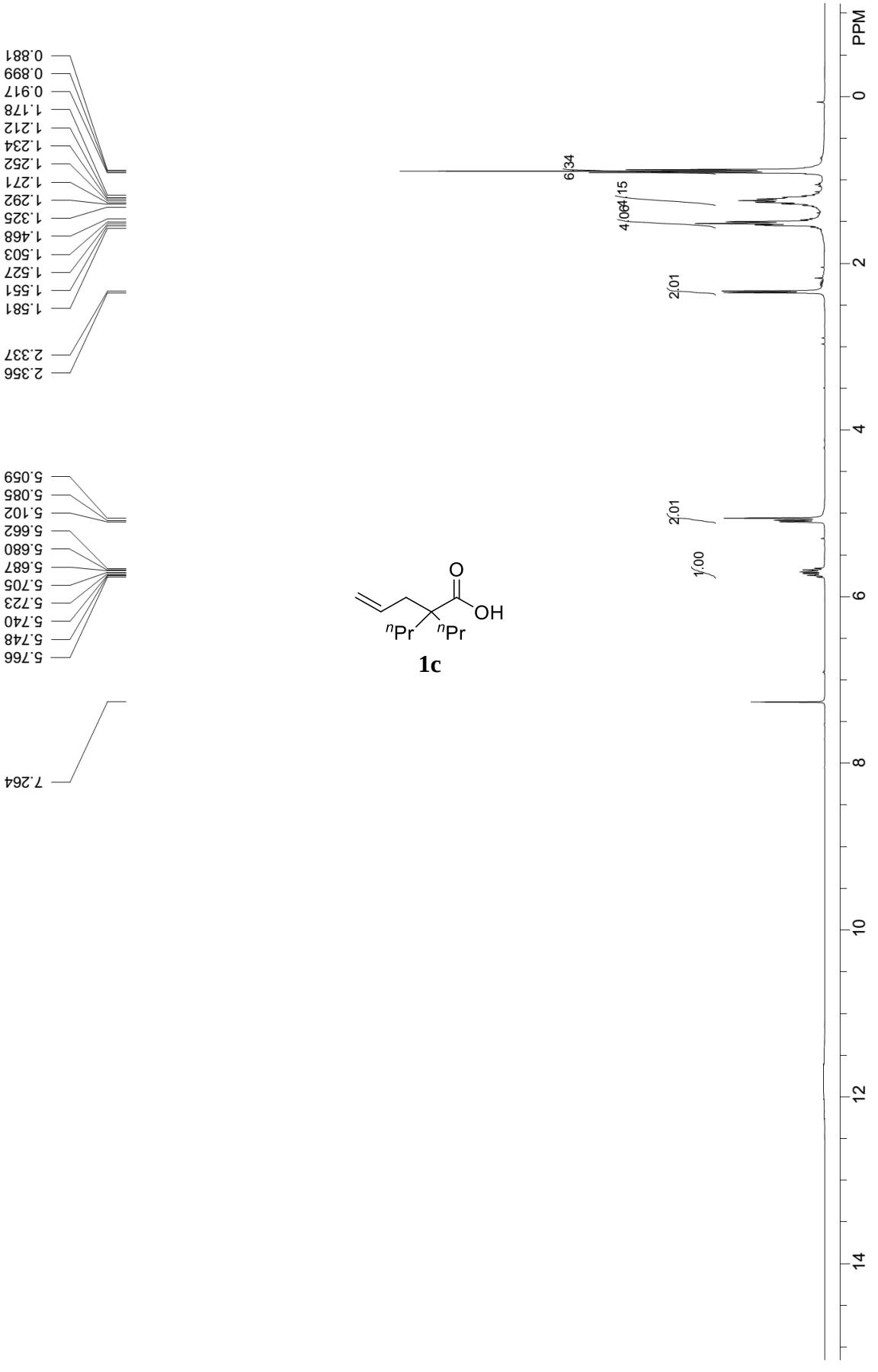
7 NMR spectra

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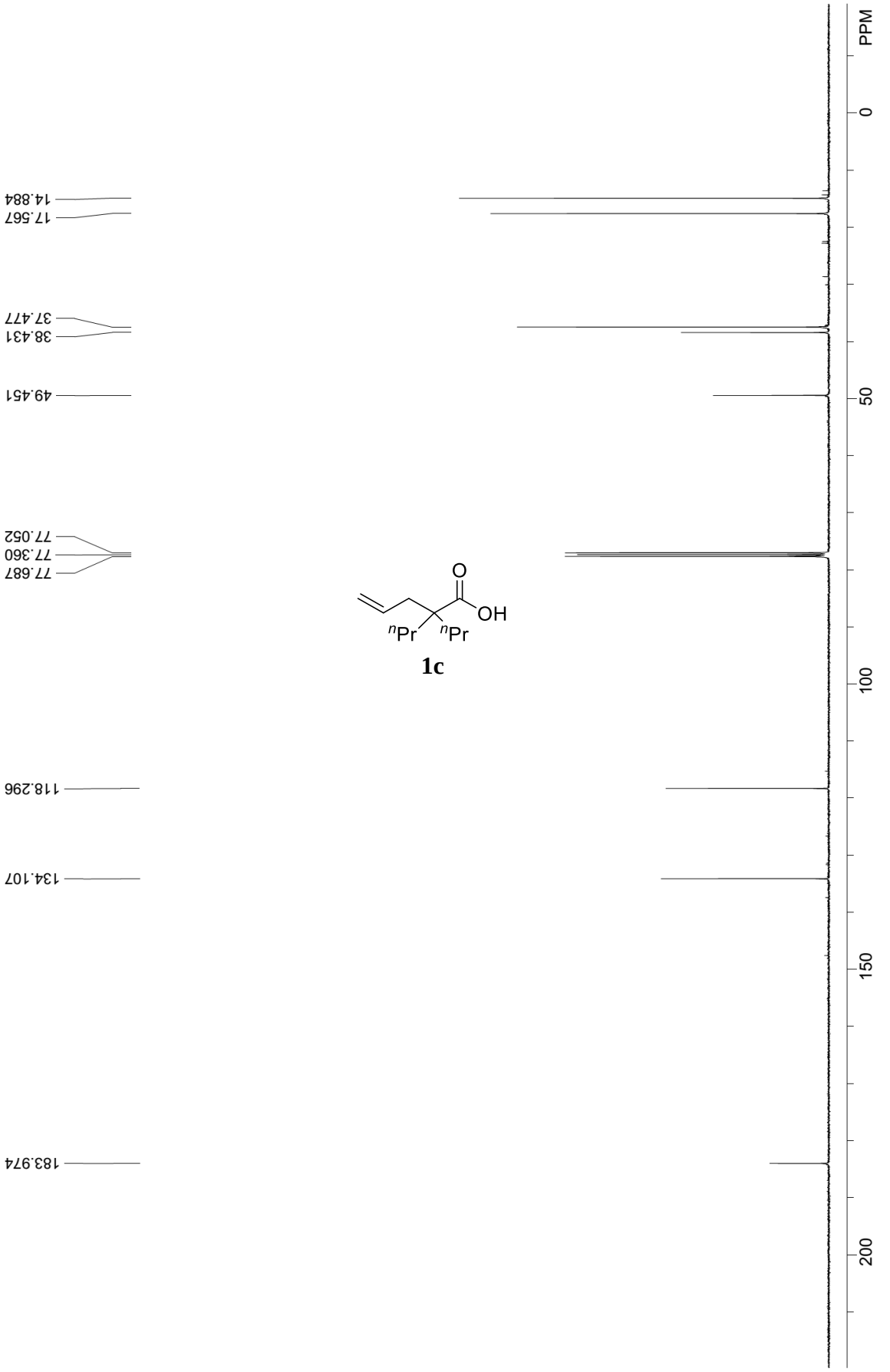
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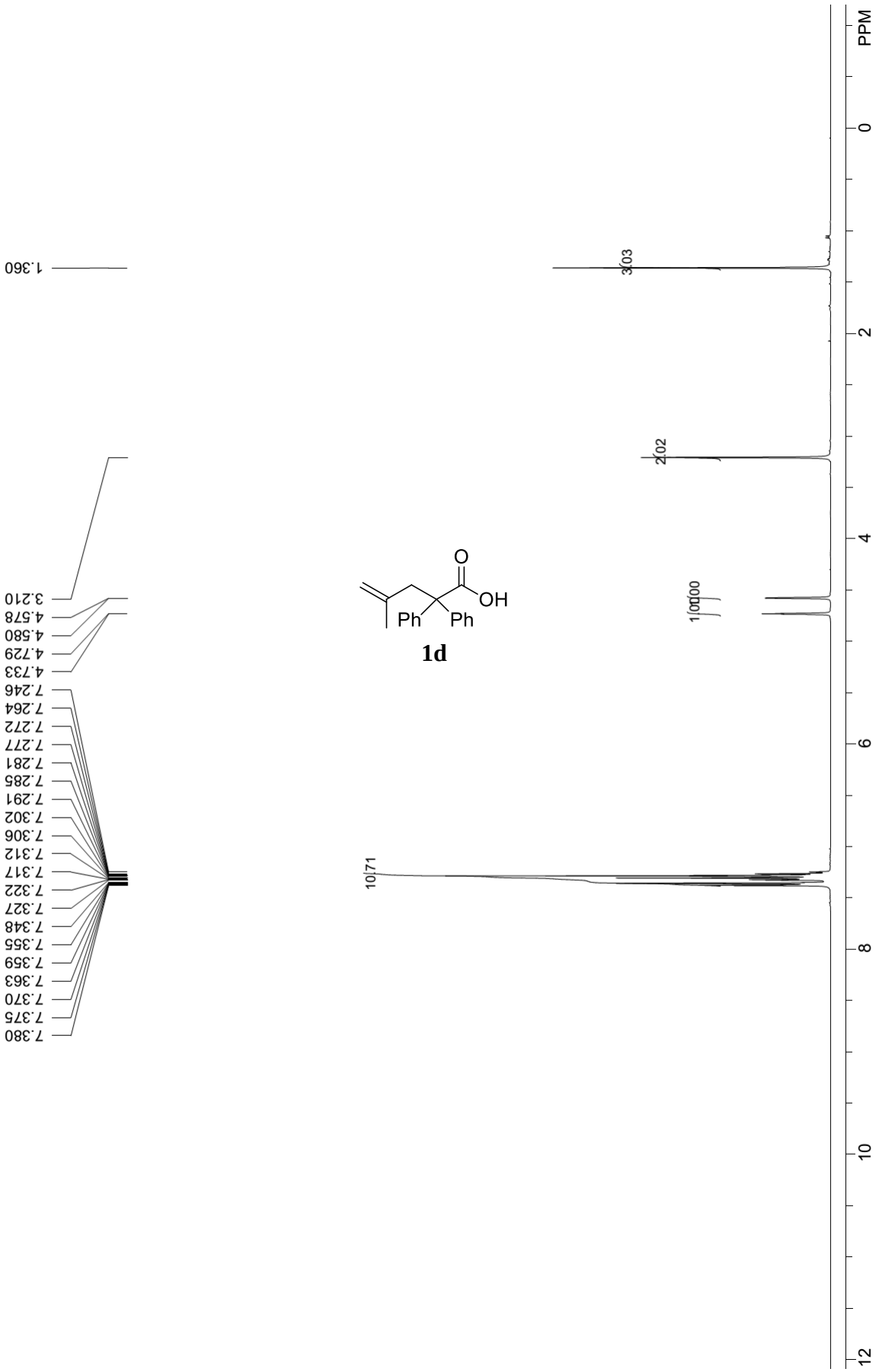
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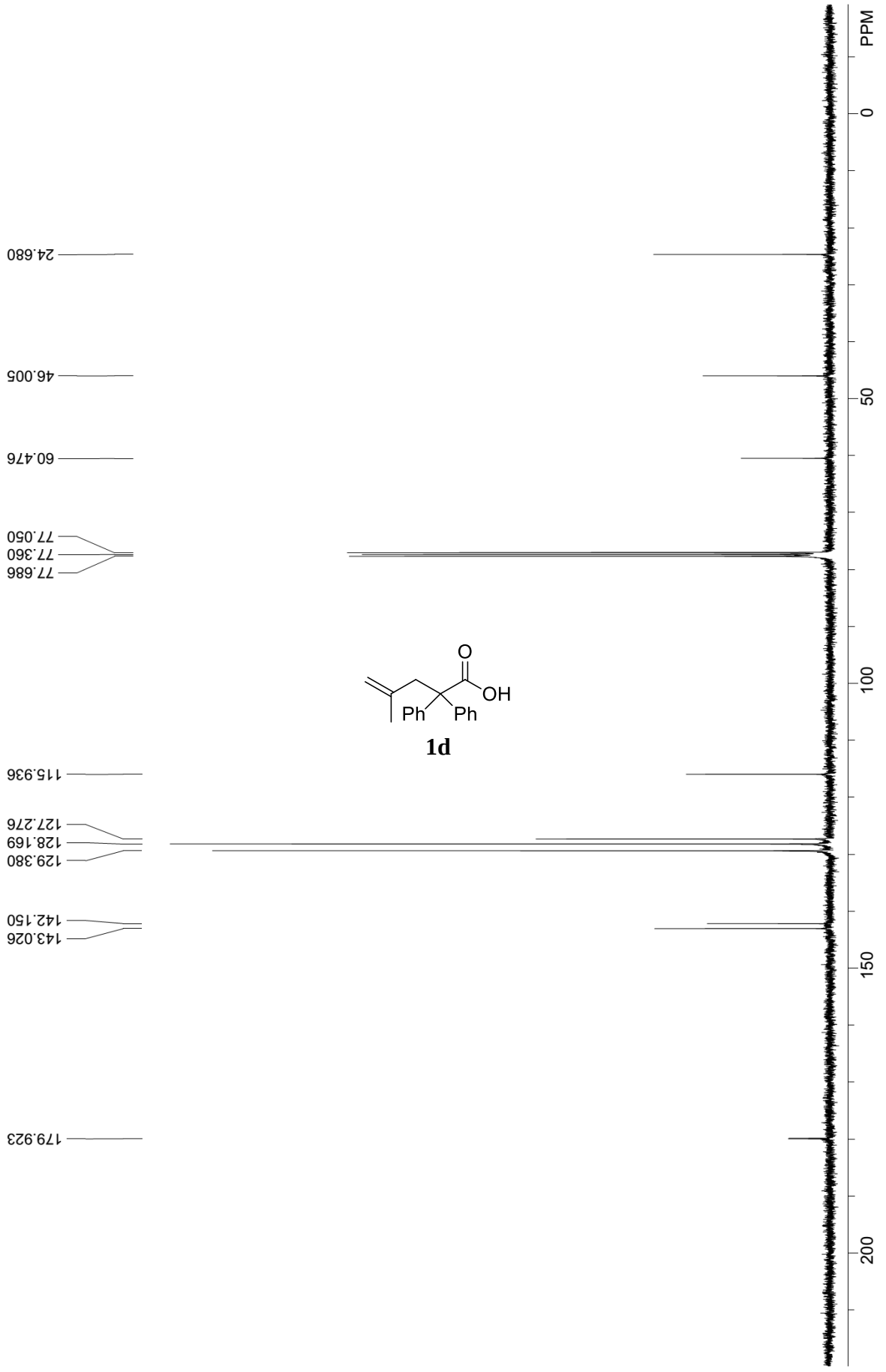
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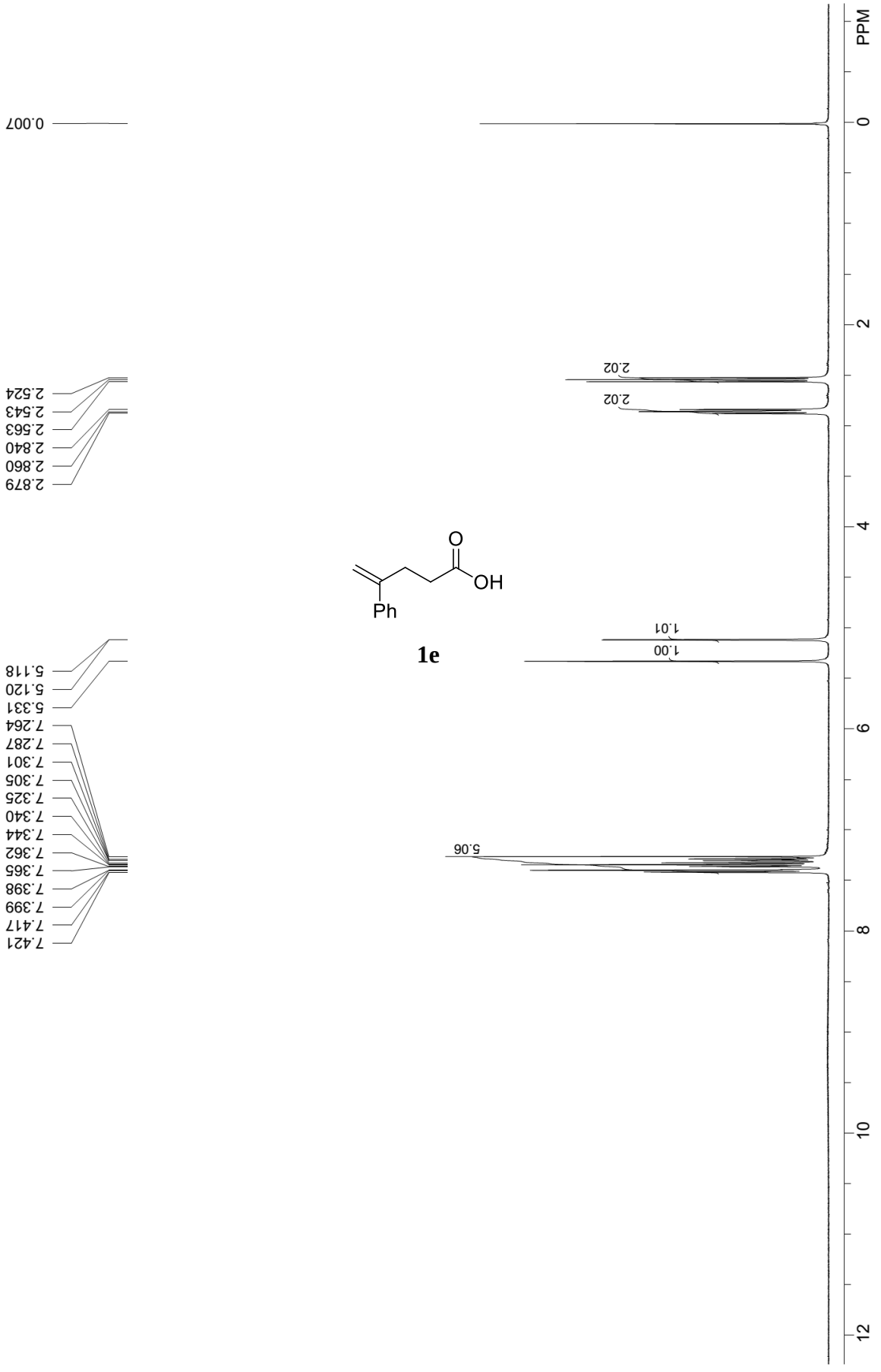
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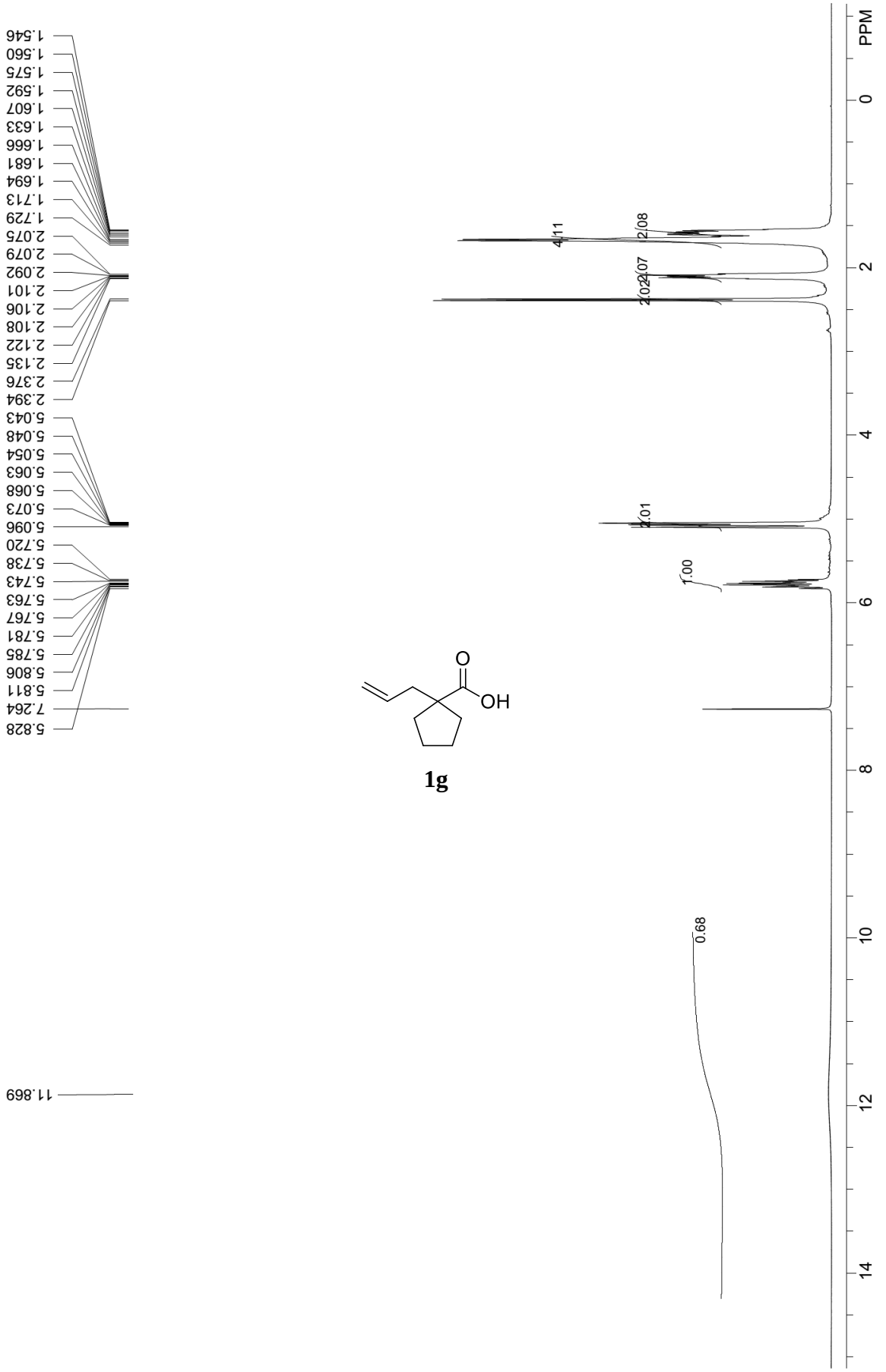
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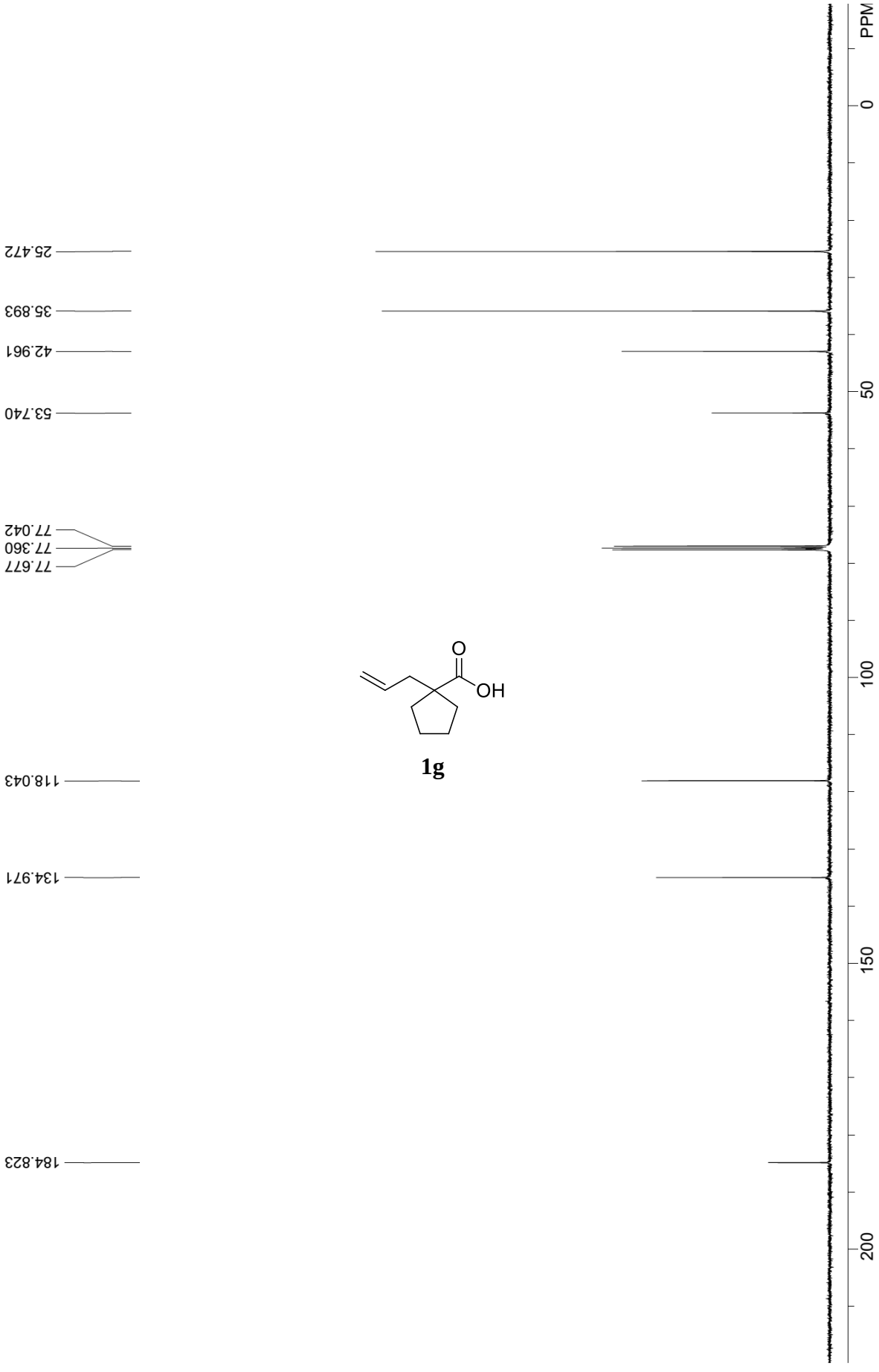
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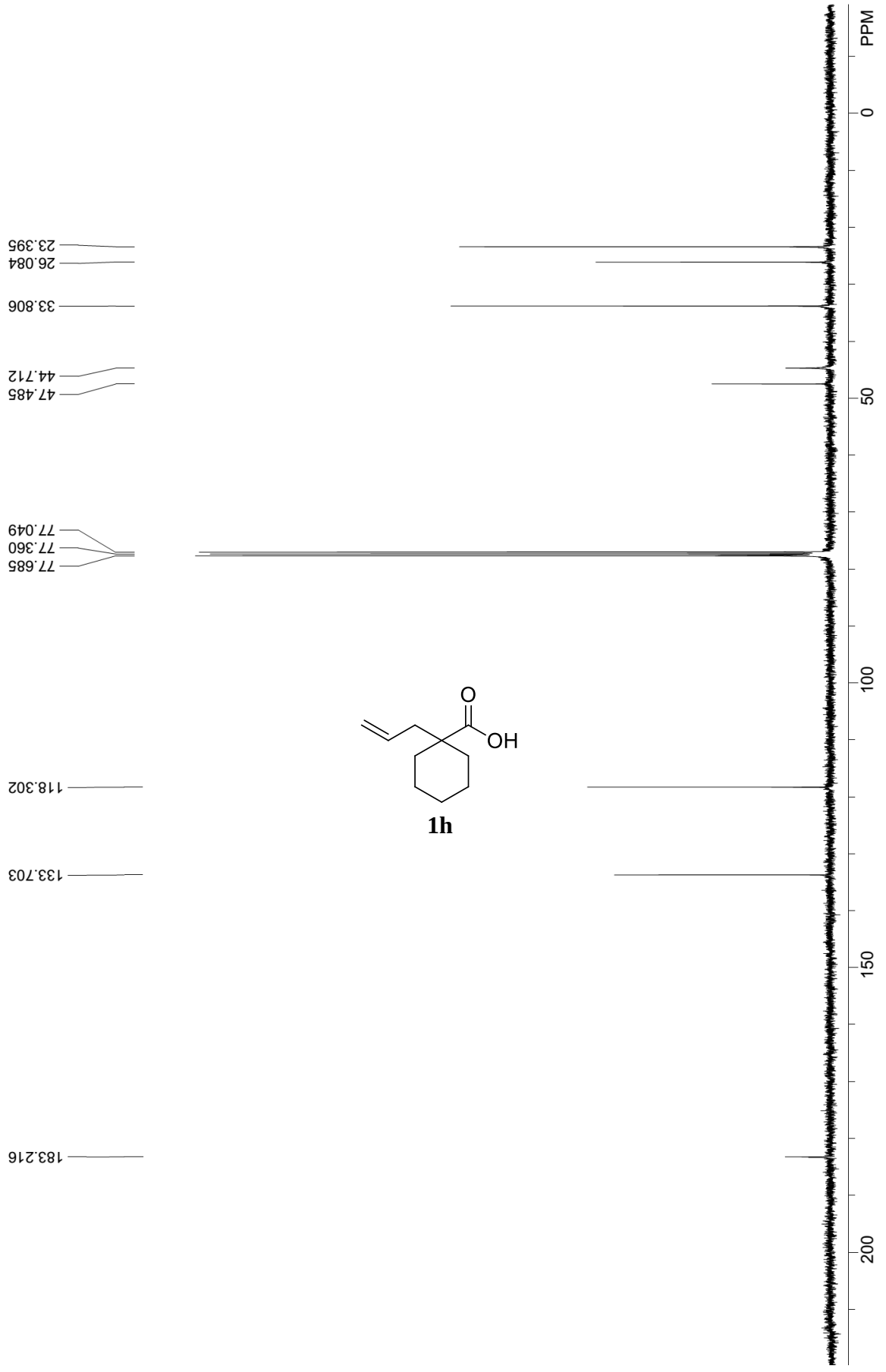
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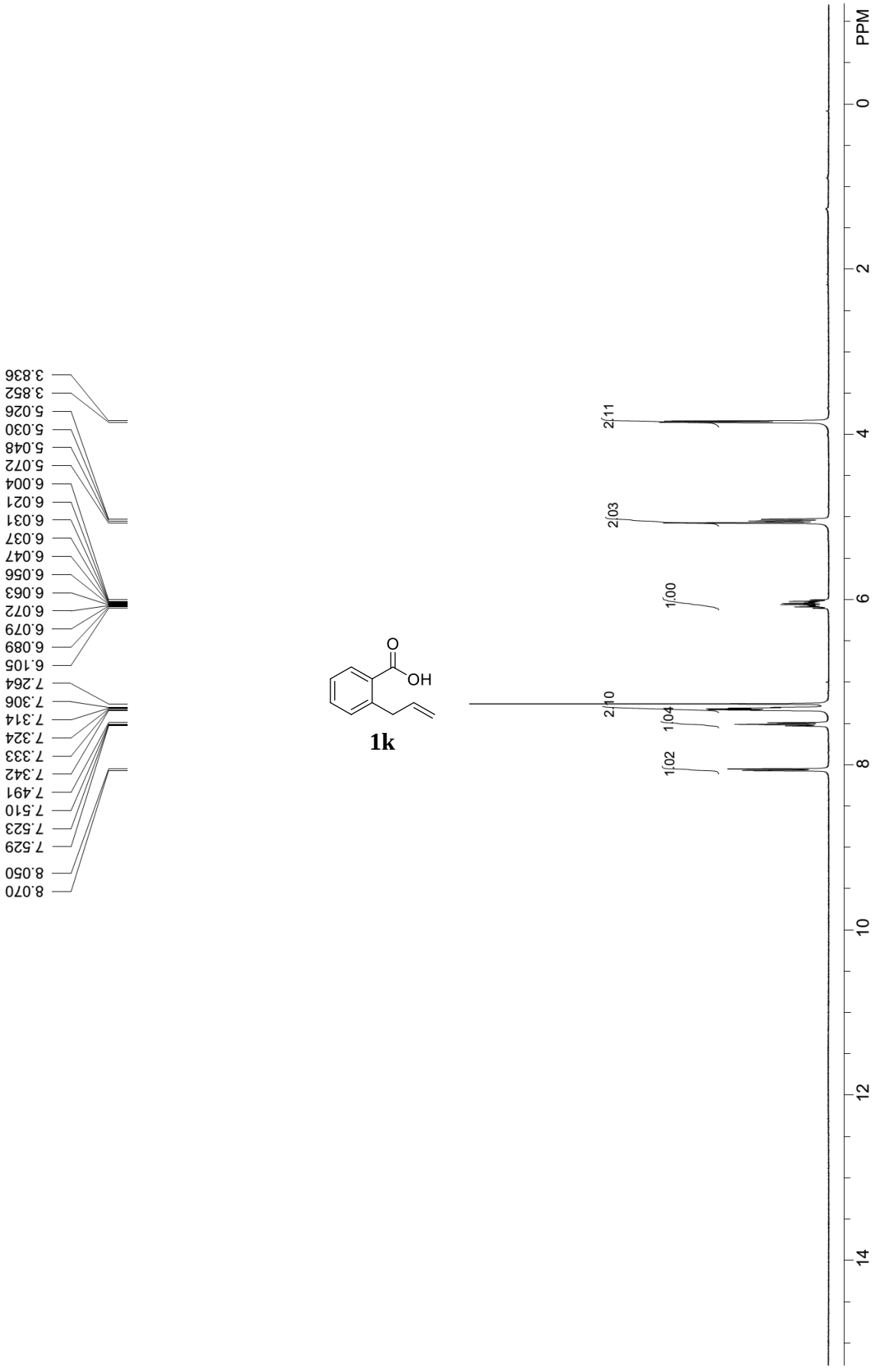
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6.056
6.063
6.072
6.079
6.089
6.105
7.264
7.306
7.314
7.324
7.333
7.342
7.491
7.510
7.523
7.529
8.050
8.070
O
OH
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1.04
1.02
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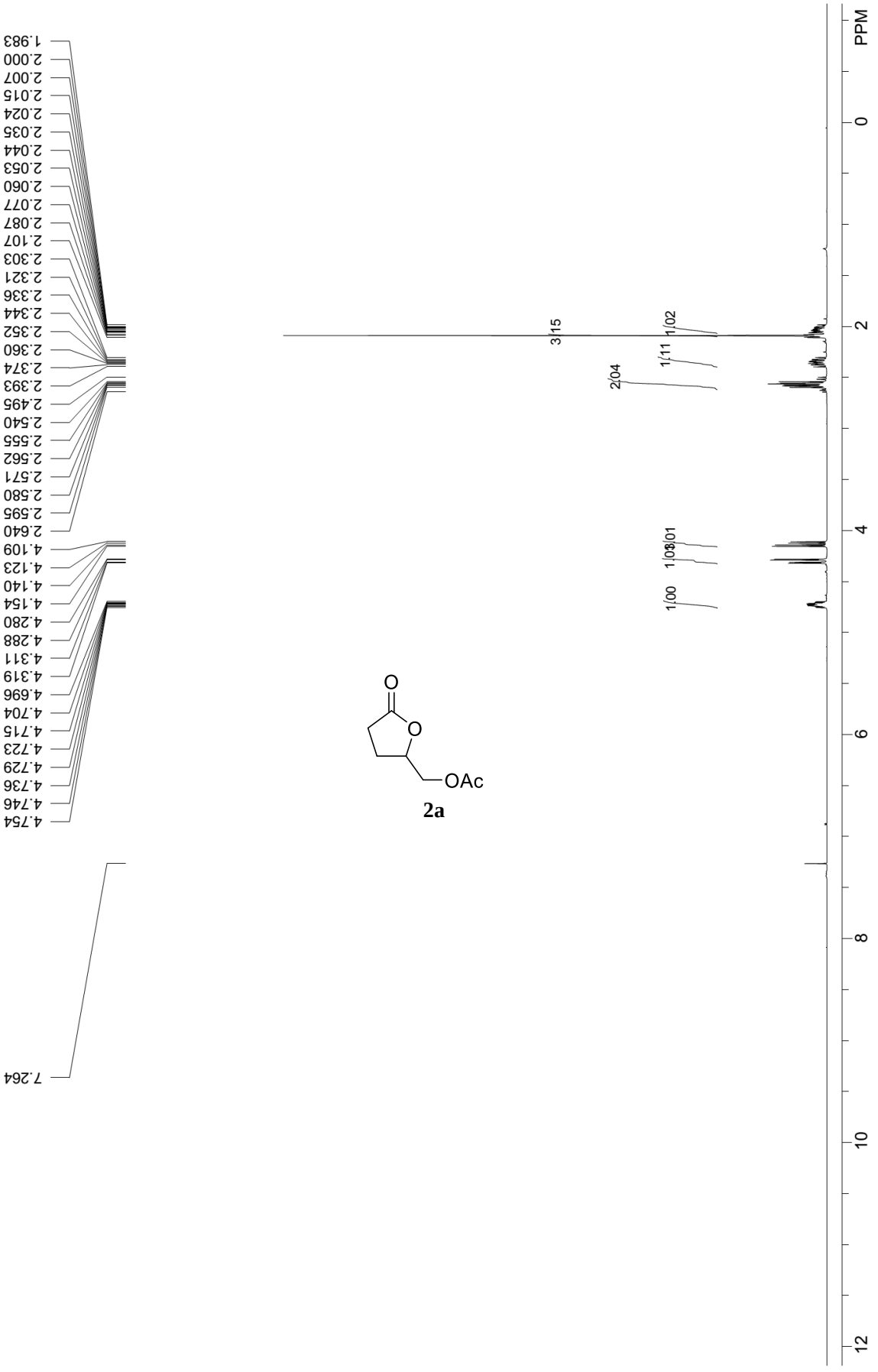
14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2.303
2.321
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2.344
2.352
2.360
2.374
2.393
2.495
2.540
2.555
2.562
2.571
2.580
2.595
2.640
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4.123
4.140
4.154
4.280
4.288
4.311
4.319
4.696
4.704
4.715
4.723
4.729
4.736
4.746
4.754
7.264
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1.11
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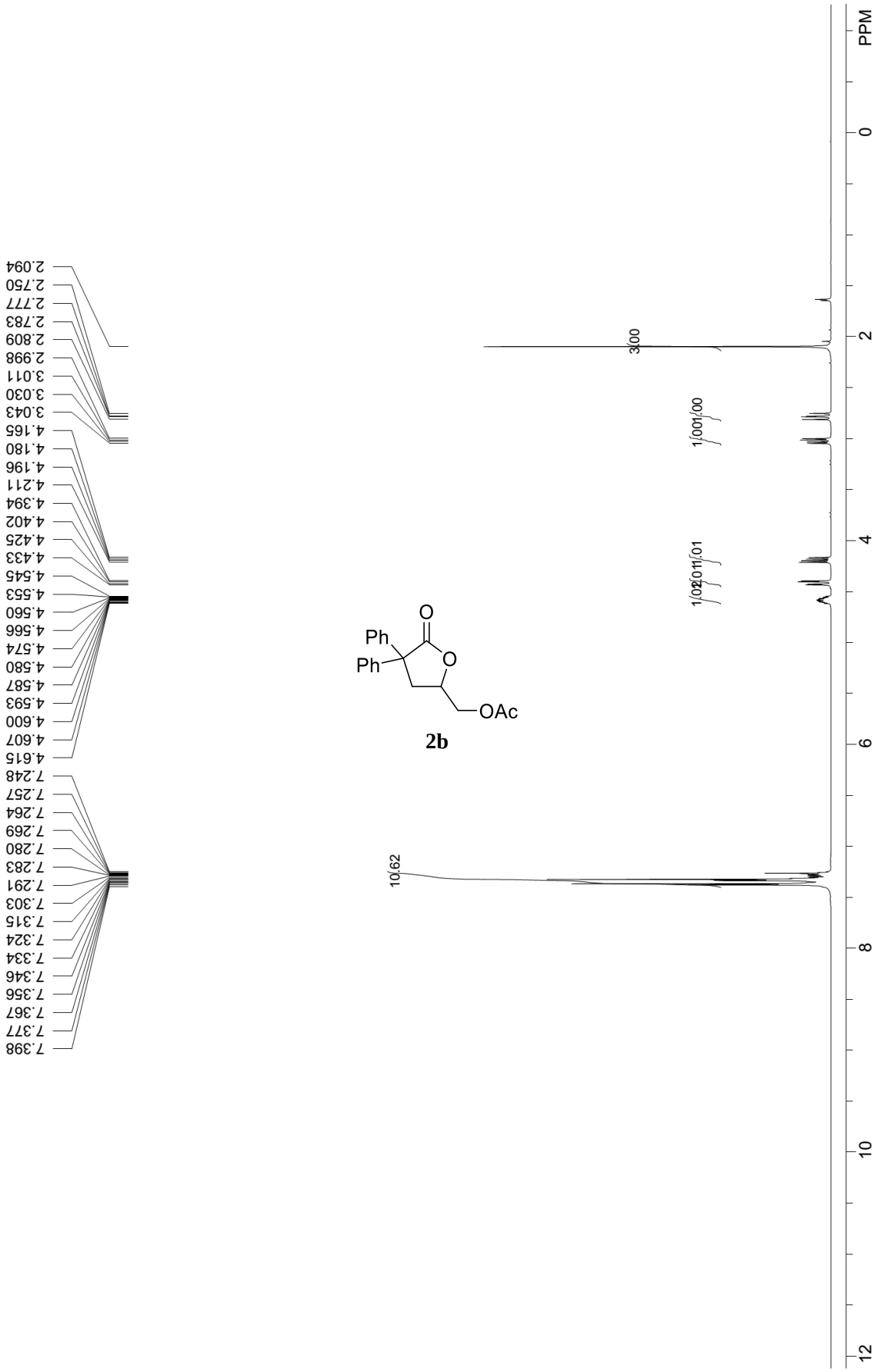
O
OAc

2a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4.180
4.196
4.211
4.394
4.402
4.425
4.433
4.545
4.553
4.560
4.566
4.574
4.580
4.587
4.593
4.600
4.607
4.615
7.248
7.257
7.264
7.269
7.280
7.283
7.291
7.303
7.315
7.324
7.334
7.346
7.356
7.367
7.377
7.398
3.00
1.00
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Ph
Ph
O
OAc
PPM
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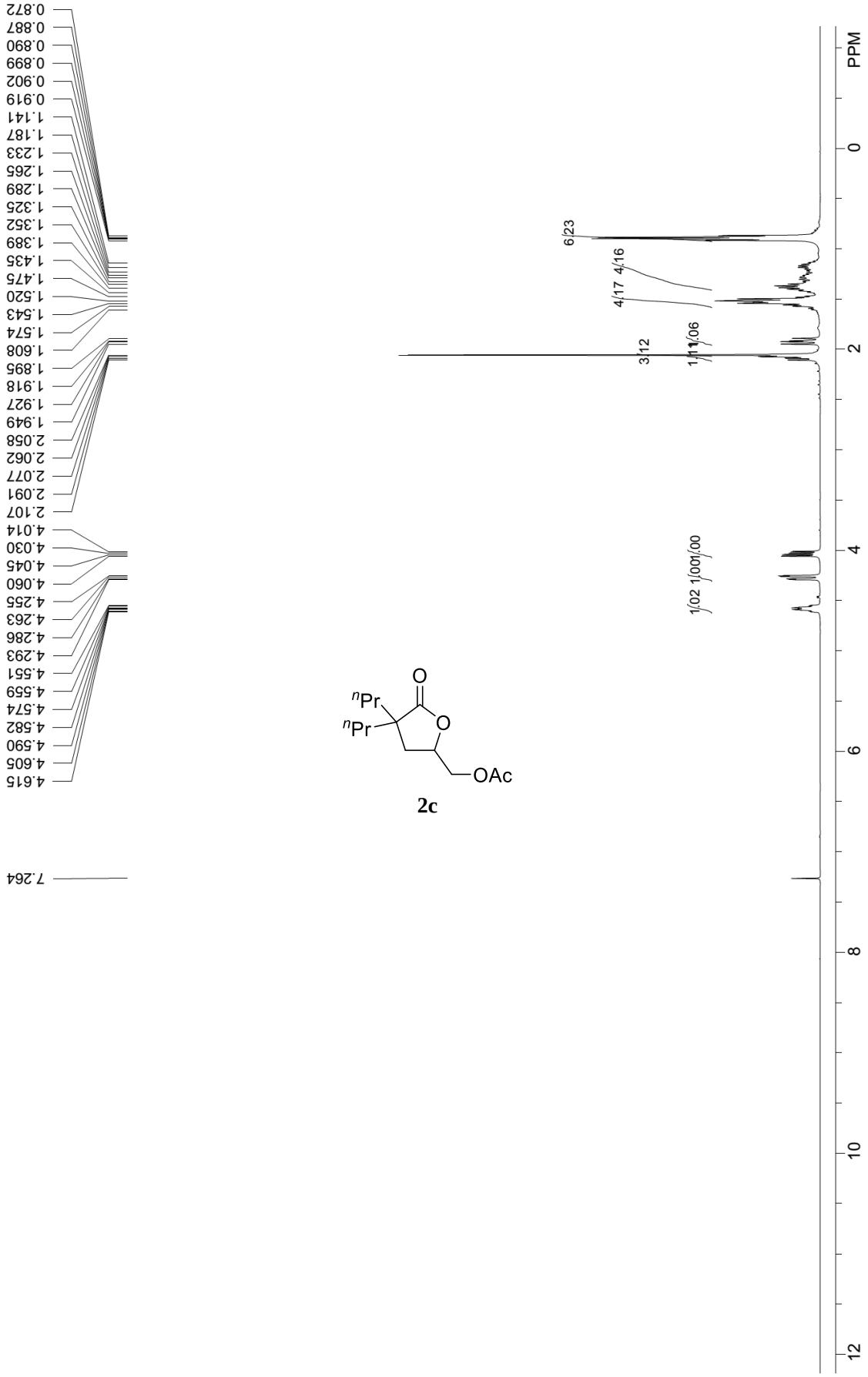
6
8
10
12

2b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1.233
1.265
1.289
1.325
1.352
1.389
1.435
1.475
1.520
1.543
1.574
1.608
1.895
1.918
1.927
1.949
2.058
2.062
2.077
2.091
2.107
4.014
4.030
4.045
4.060
4.255
4.263
4.286
4.293
4.551
4.559
4.574
4.582
4.590
4.605
4.615
7.264
6.23
4.17
4.16
3.12
1.11
1.06
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PPM
0
2
4
6
8
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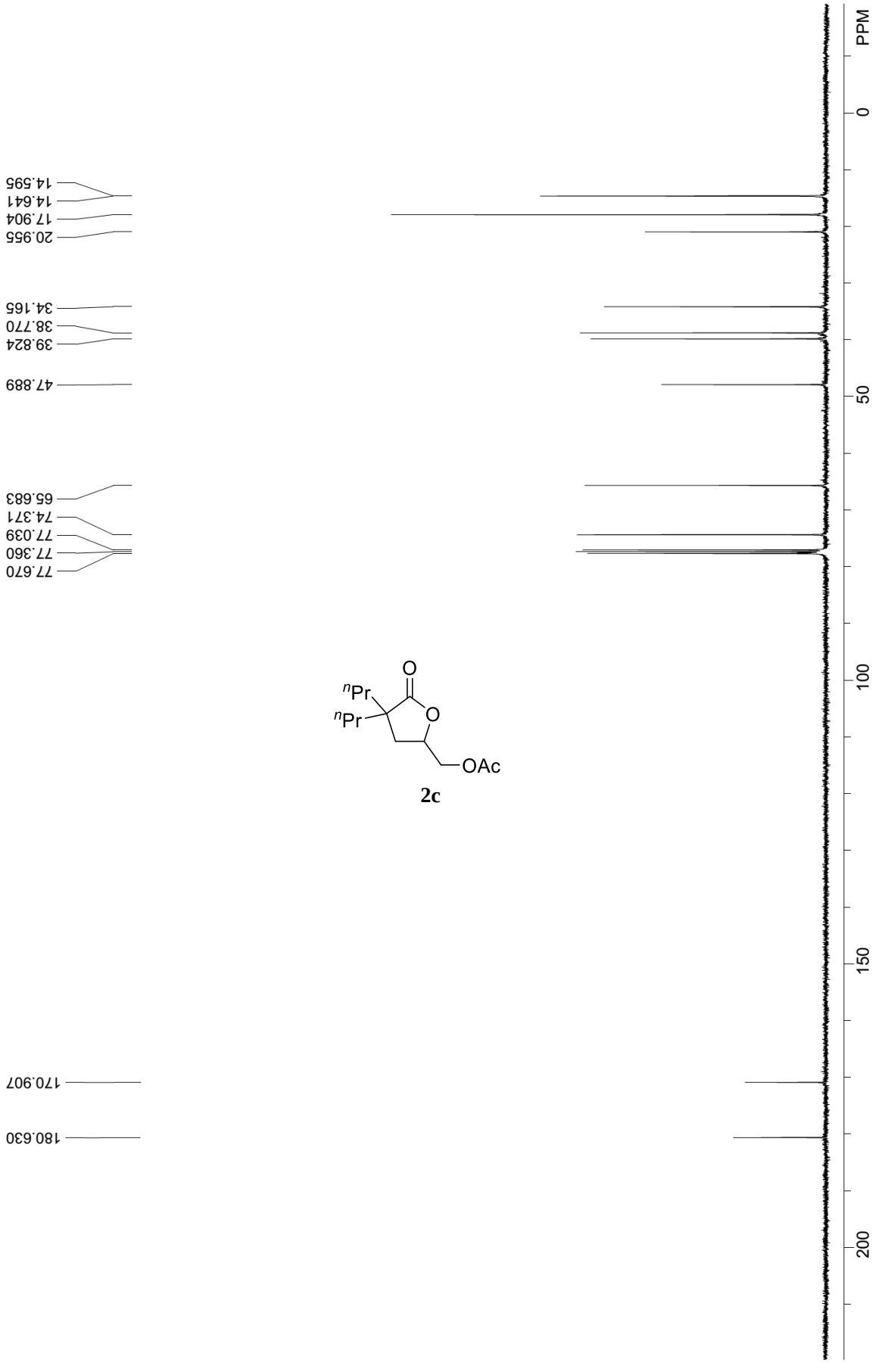
12
O
nPr
nPr
O
OAc

2c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17.904
20.955
34.165
38.770
39.824
47.889
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74.371
77.039
77.360
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180.630
PPM
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100
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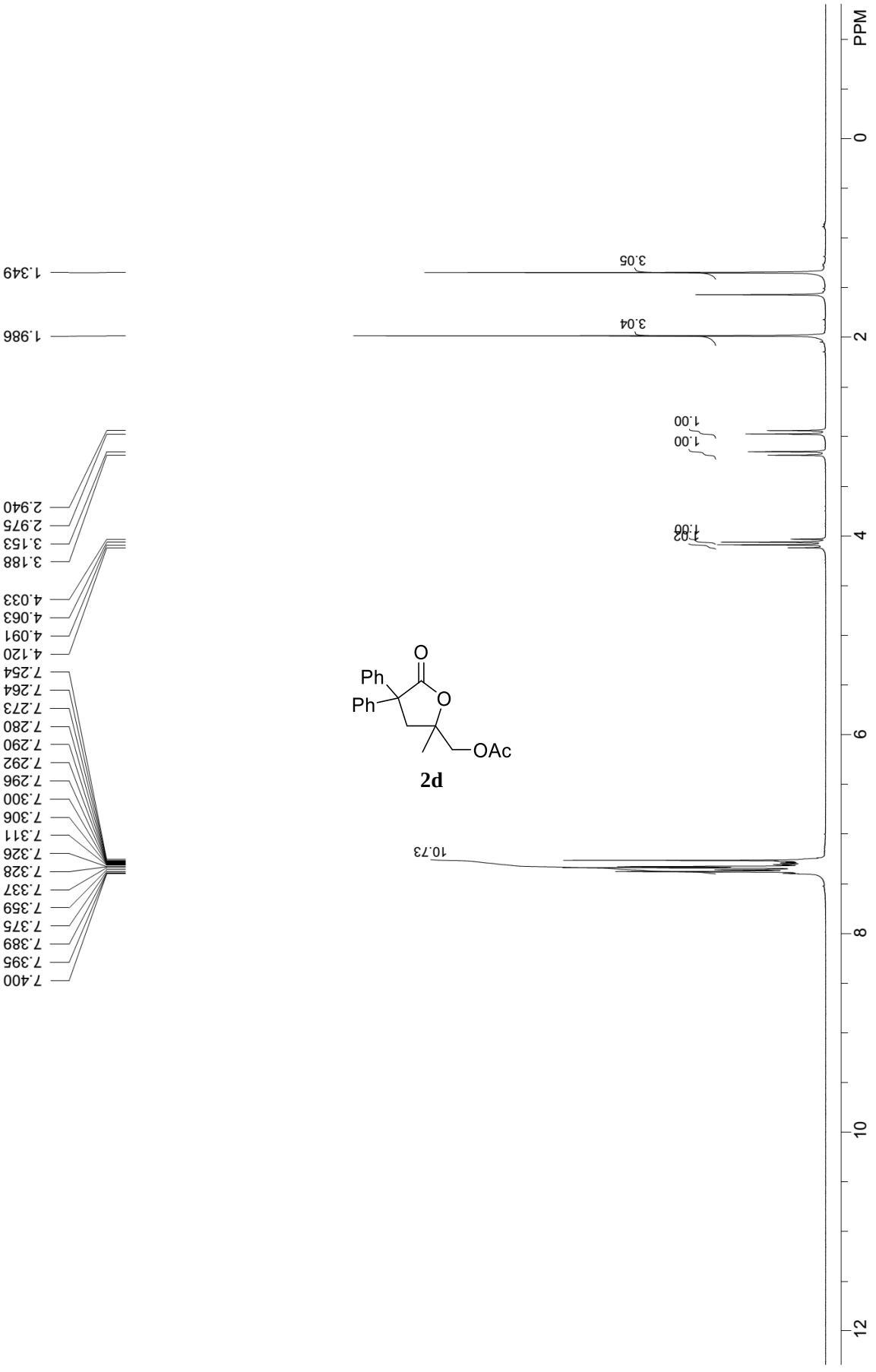
200
O
nPr
nPr
O
OAc

2c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4.063
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4.120
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7.264
7.273
7.280
7.290
7.292
7.296
7.300
7.306
7.311
7.326
7.328
7.337
7.359
7.375
7.389
7.395
7.400
3.05
3.04
1.00
1.00
3.02
1.00
10.73
O
Ph
Ph
O
OAc
PPM
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2
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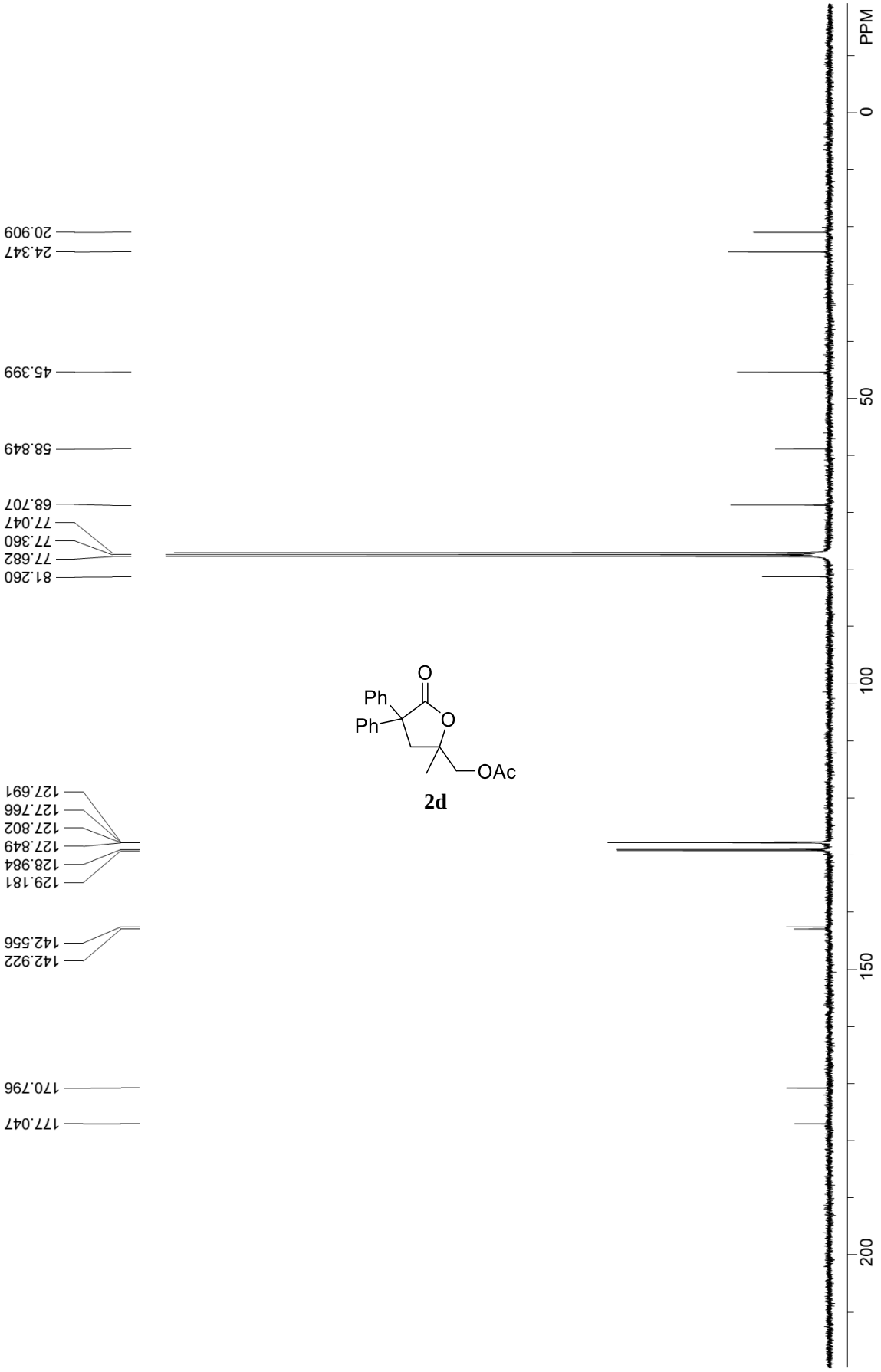
6
8
10
12

2d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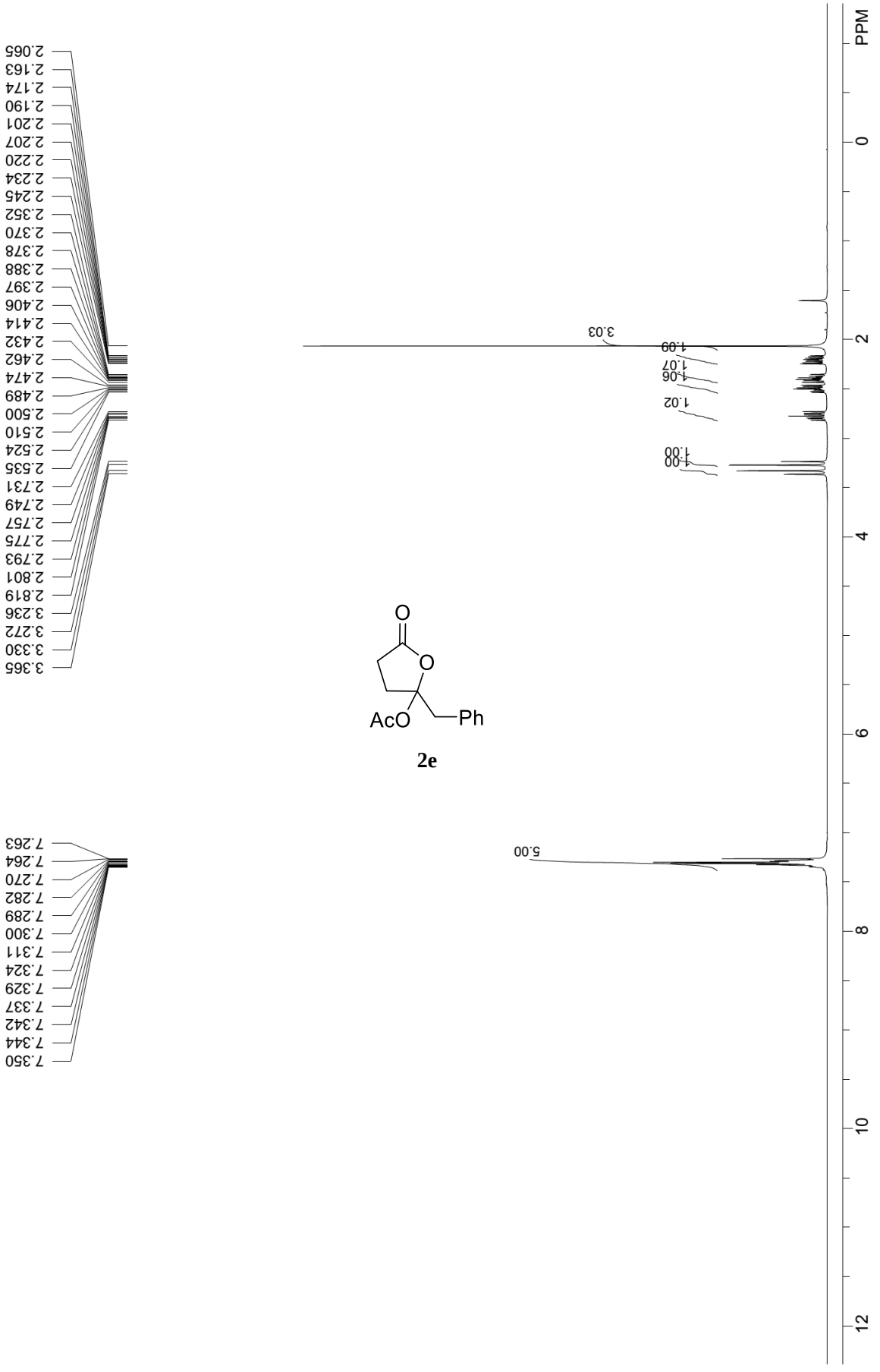
77.360
77.682
81.260
127.691
127.766
127.802
127.849
128.984
129.181
142.556
142.922
170.796
177.047
O
Ph
Ph
O
OAc

2d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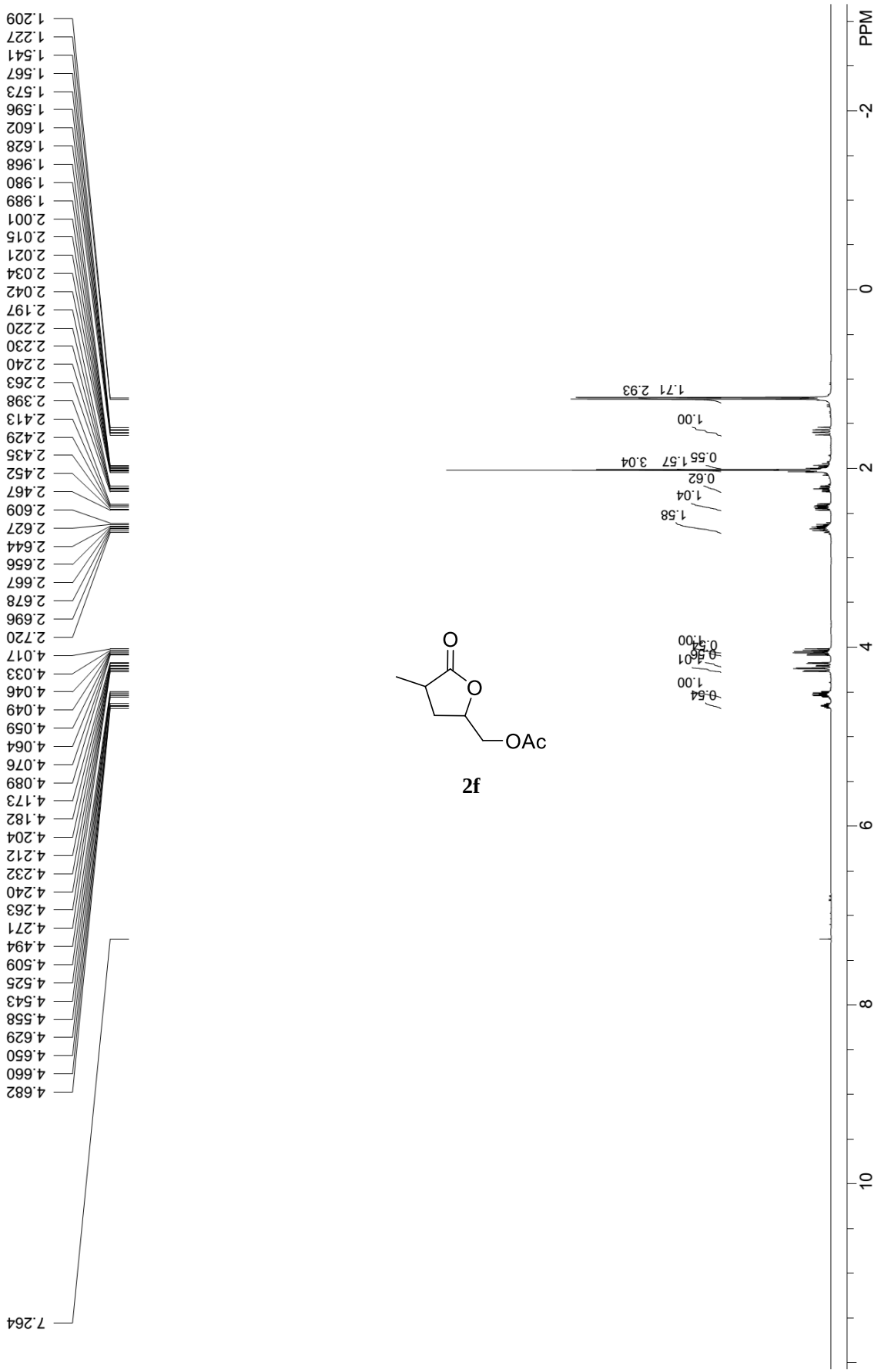
2.174
2.190
2.201
2.207
2.220
2.234
2.245
2.352
2.370
2.378
2.388
2.397
2.406
2.414
2.432
2.462
2.474
2.489
2.500
2.510
2.524
2.535
2.731
2.749
2.757
2.775
2.793
2.801
2.819
3.236
3.272
3.330
3.365
7.263
7.264
7.270
7.282
7.289
7.300
7.311
7.324
7.329
7.337
7.342
7.344
7.350
3.03
1.09
1.07
1.06
1.02
1.00
1.00
5.00
O
O
AcO
Ph
PPM
0
2
4
6
8
10
12

2e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1.567
1.573
1.596
1.602
1.628
1.968
1.980
1.989
2.001
2.015
2.021
2.034
2.042
2.197
2.220
2.230
2.240
2.263
2.398
2.413
2.429
2.435
2.452
2.467
2.609
2.627
2.644
2.656
2.667
2.678
2.696
2.720
4.017
4.033
4.046
4.049
4.059
4.064
4.076
4.089
4.173
4.182
4.204
4.212
4.232
4.240
4.263
4.271
4.494
4.509
4.525
4.543
4.558
4.629
4.650
4.660
4.682
7.264
1.71 2.93
1.00
0.55 1.57 3.04
0.62
1.04
1.58
1.00
1.00
0.64
O
O
OAc
PPM
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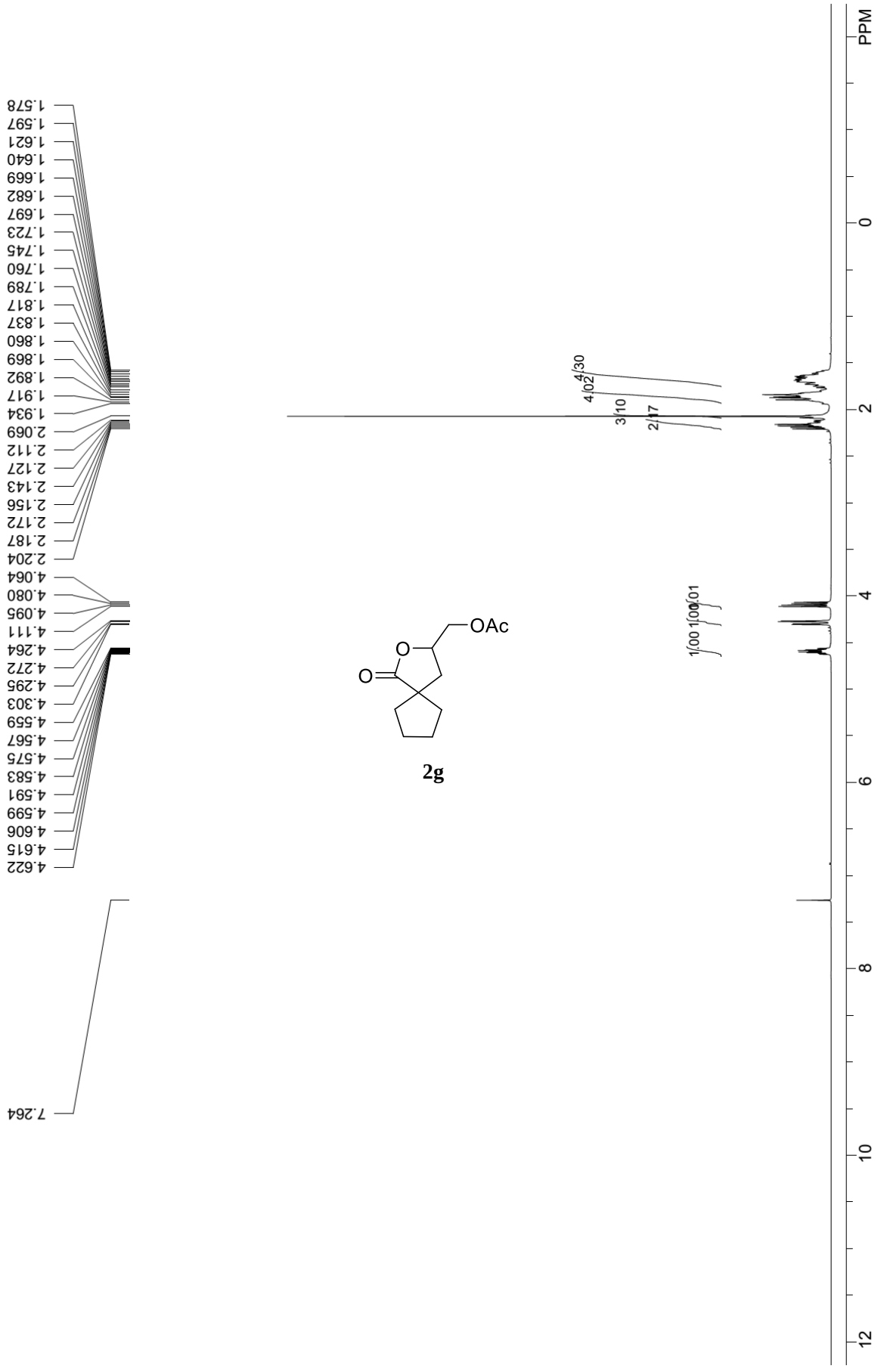
8
6
4
2
0
-2

2f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1.669
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1.723
1.745
1.760
1.789
1.817
1.837
1.860
1.869
1.892
1.917
1.934
2.069
2.112
2.127
2.143
2.156
2.172
2.187
2.204
4.064
4.080
4.095
4.111
4.264
4.272
4.295
4.303
4.559
4.567
4.575
4.583
4.591
4.599
4.606
4.615
4.622
7.264
4.30
4.02
3.10
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1.00
1.01
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O
O
2g
PPM
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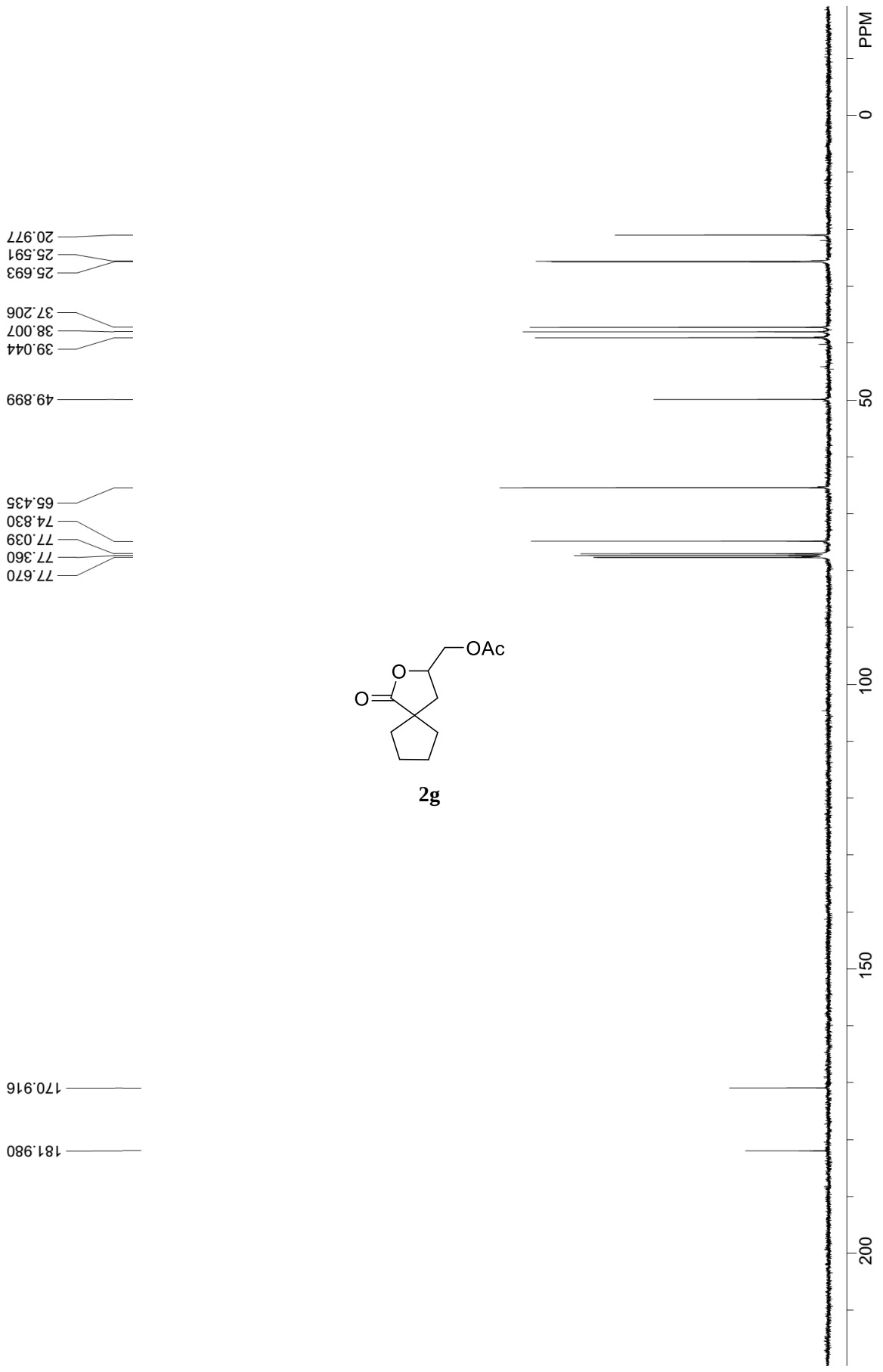
6
8
10
12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25.693
37.206
38.007
39.044
49.899
65.435
74.830
77.039
77.360
77.670
170.916
181.980
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O
O
PPM
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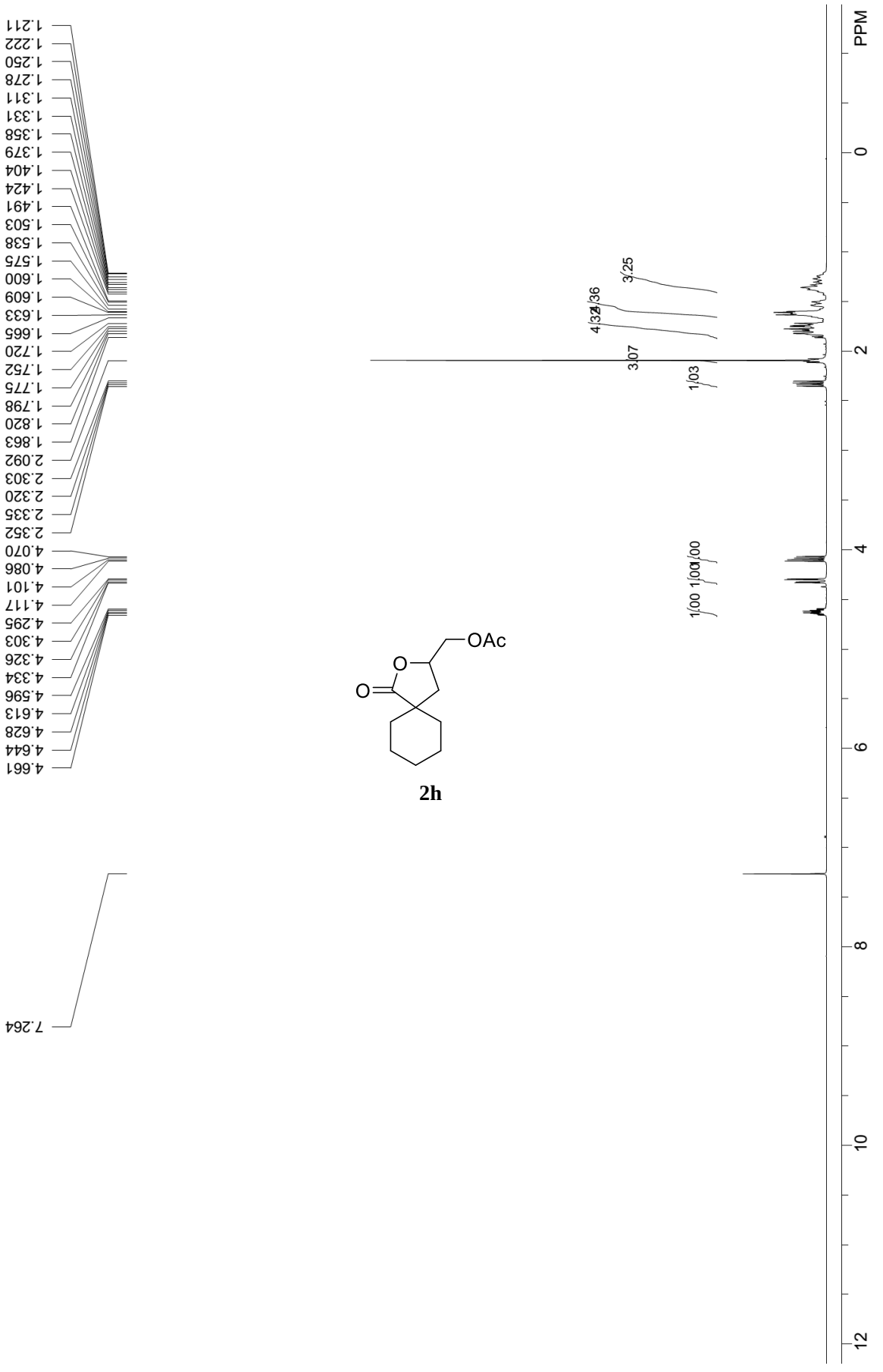
100
150
200

2g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1.250
1.278
1.311
1.331
1.358
1.379
1.404
1.424
1.491
1.503
1.538
1.575
1.600
1.609
1.633
1.665
1.720
1.752
1.775
1.798
1.820
1.863
2.092
2.303
2.320
2.335
2.352
4.070
4.086
4.101
4.117
4.295
4.303
4.326
4.334
4.596
4.613
4.628
4.644
4.661
7.264
4.32
4.36
3.25
3.07
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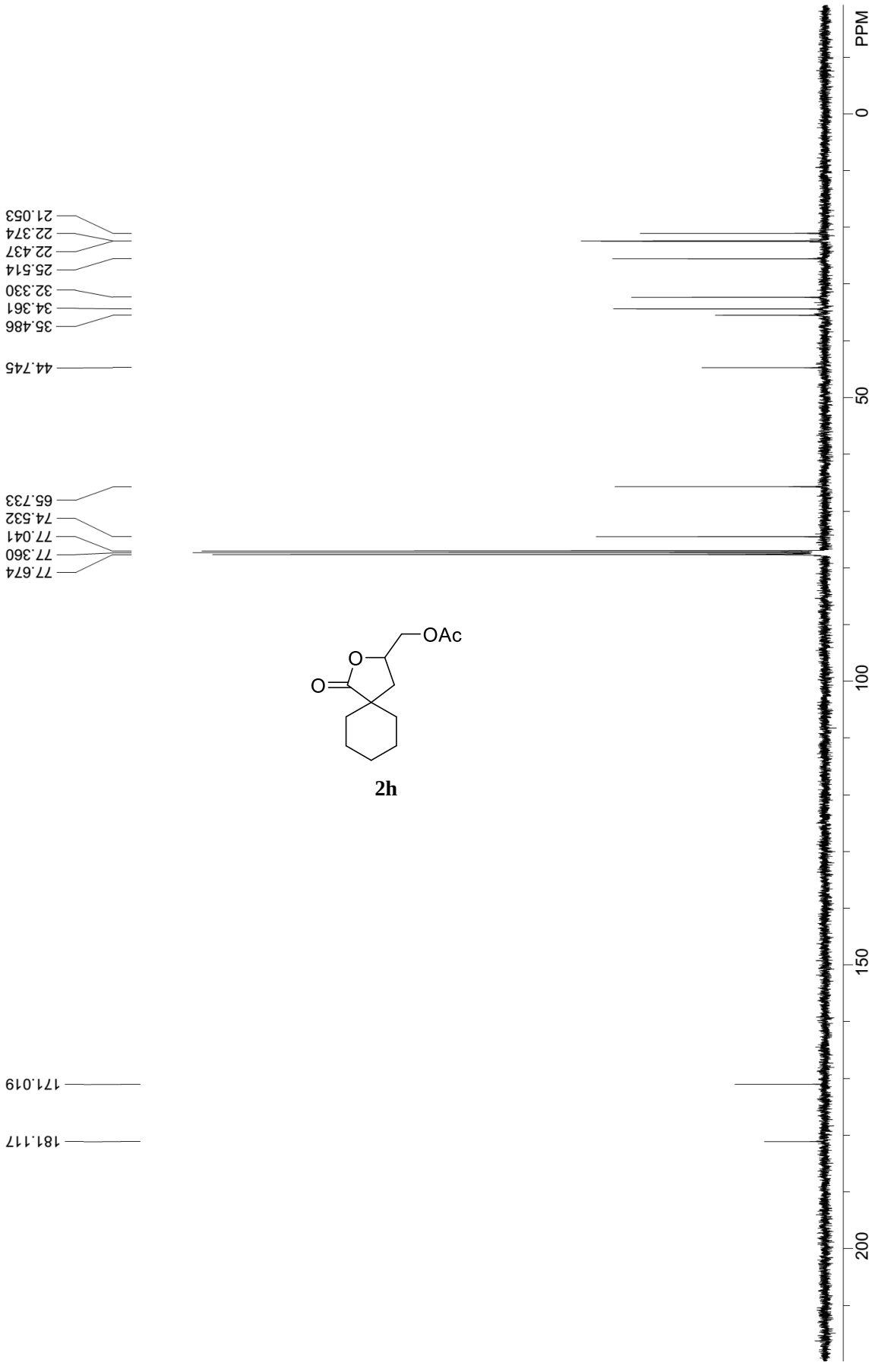
1.00
1.00
PPM
0
2
4
6
8
10
12
OAc
O
O

2h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44.745
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77.674
171.019
181.117
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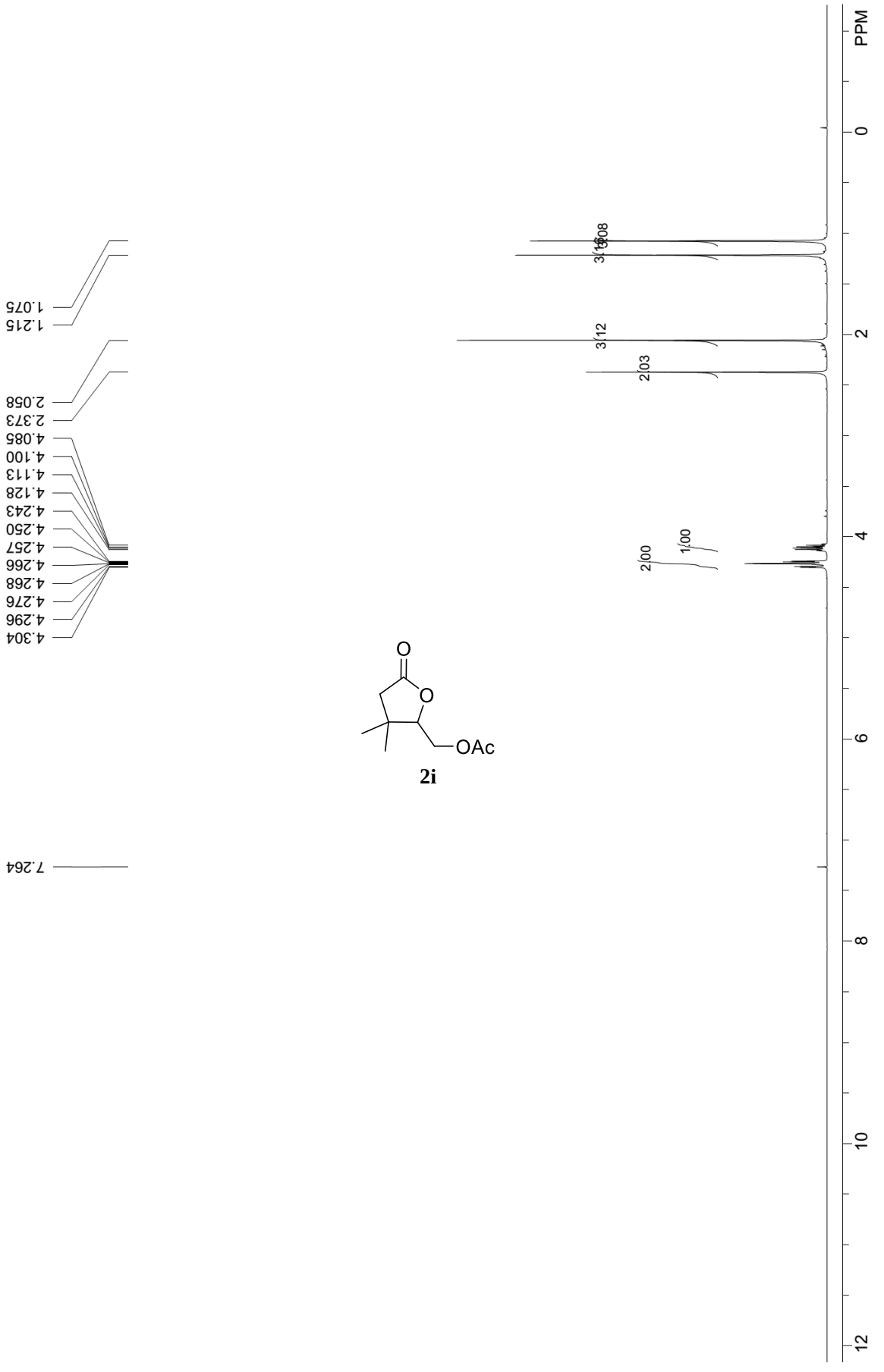
100
150
200
OAc
O
O

2h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4.266
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4.250
4.243
4.128
4.113
4.100
4.085
2.373
2.058
1.215
1.075
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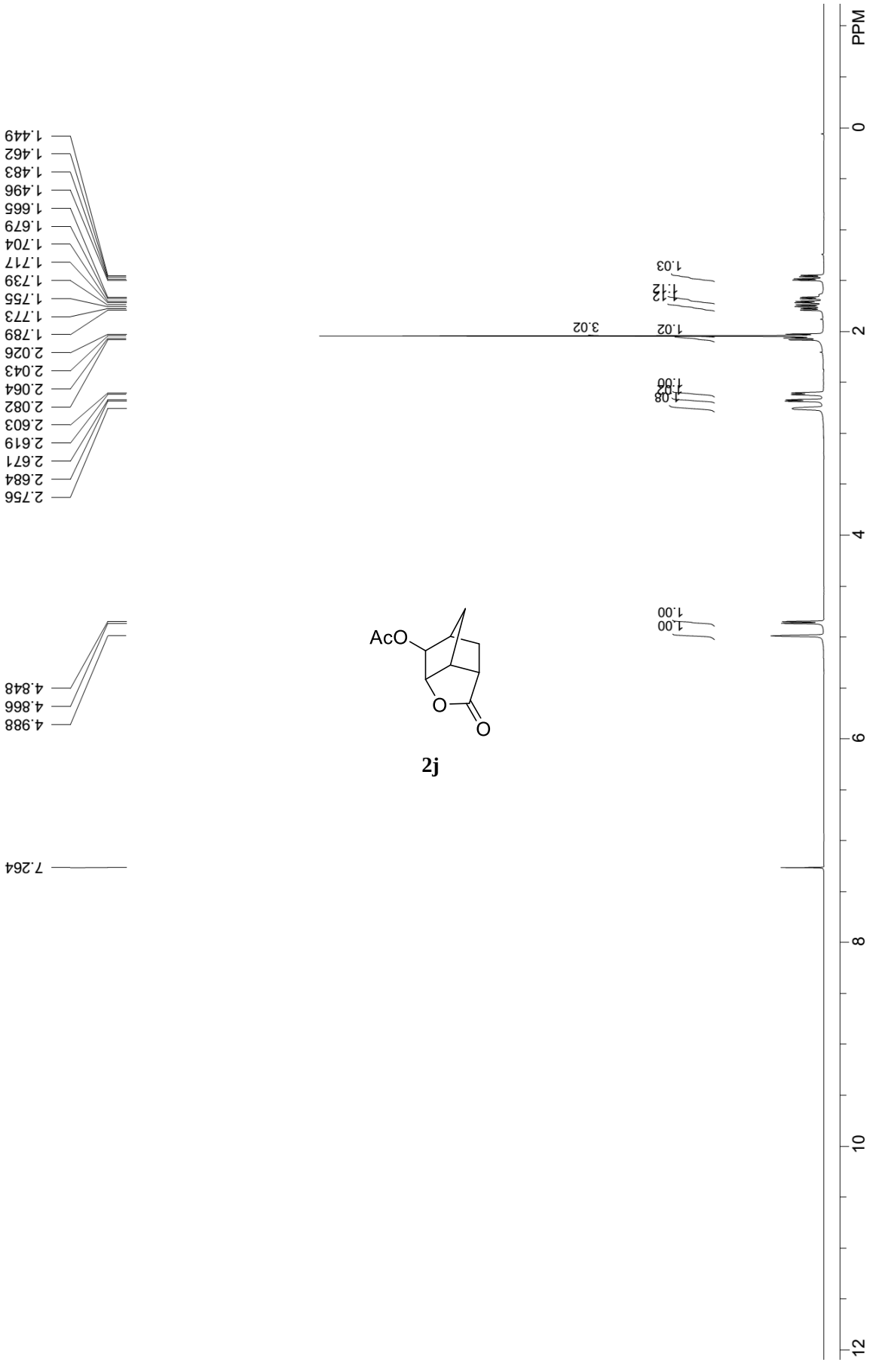
O
OAc
3.12
2.03
2.00
1.00
PPM
0
2
4
6
8
10
12

2i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6
8
10
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1.717
1.739
1.755
1.773
1.789
2.026
2.043
2.064
2.082
2.603
2.619
2.671
2.684
2.756
4.848
4.866
4.988
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1.00
1.08
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3.02
1.02
1.12
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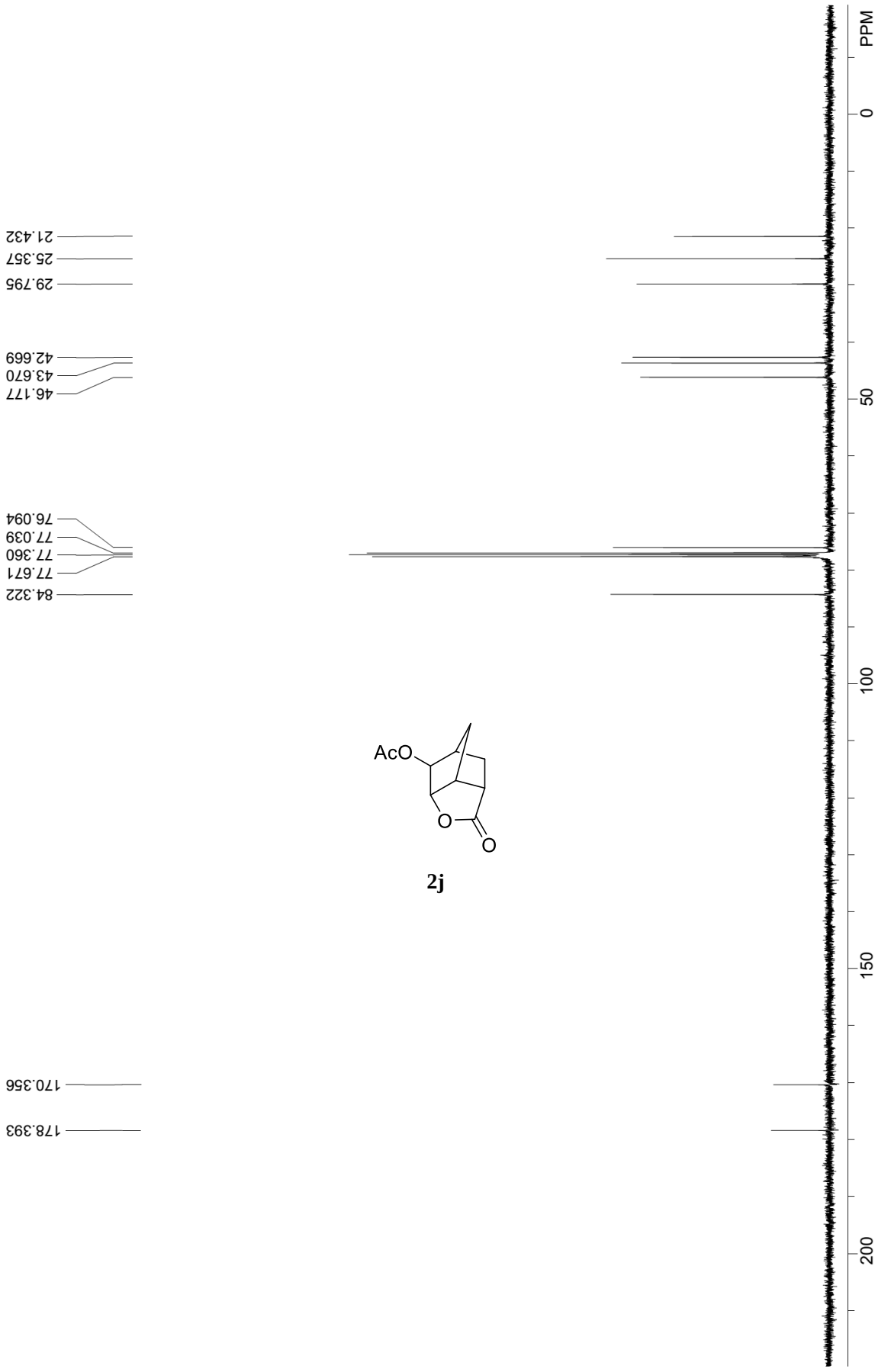
AcO
O
O

2j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77.671
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170.356
178.393
PPM
0
50
100
150
200
AcO
O
O

2j

2.094
2.920
2.928
2.961
2.969
3.085
3.114
3.126
3.155
4.353
4.364
4.749
4.758
4.767
4.778
4.787
7.255
7.264
7.274
7.382
7.401
7.420
7.532
7.551
7.570
8.074
8.094
3.13
1.03
1.08
2.01
1.01
1.00
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1.03
1.27
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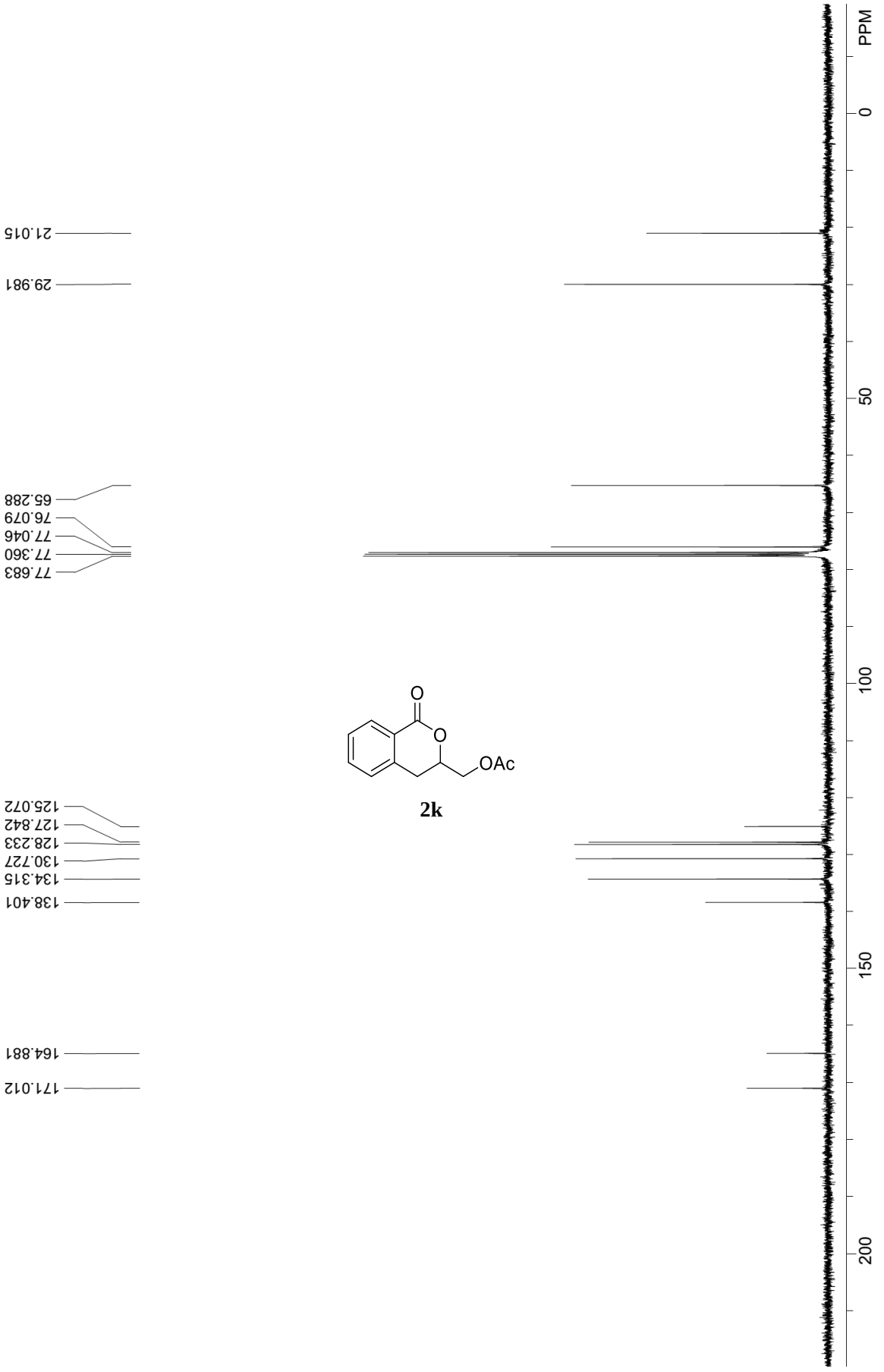
4
6
8
10
O
O
OAc

2k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125.072
127.842
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138.401
164.881
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O
O
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PPM
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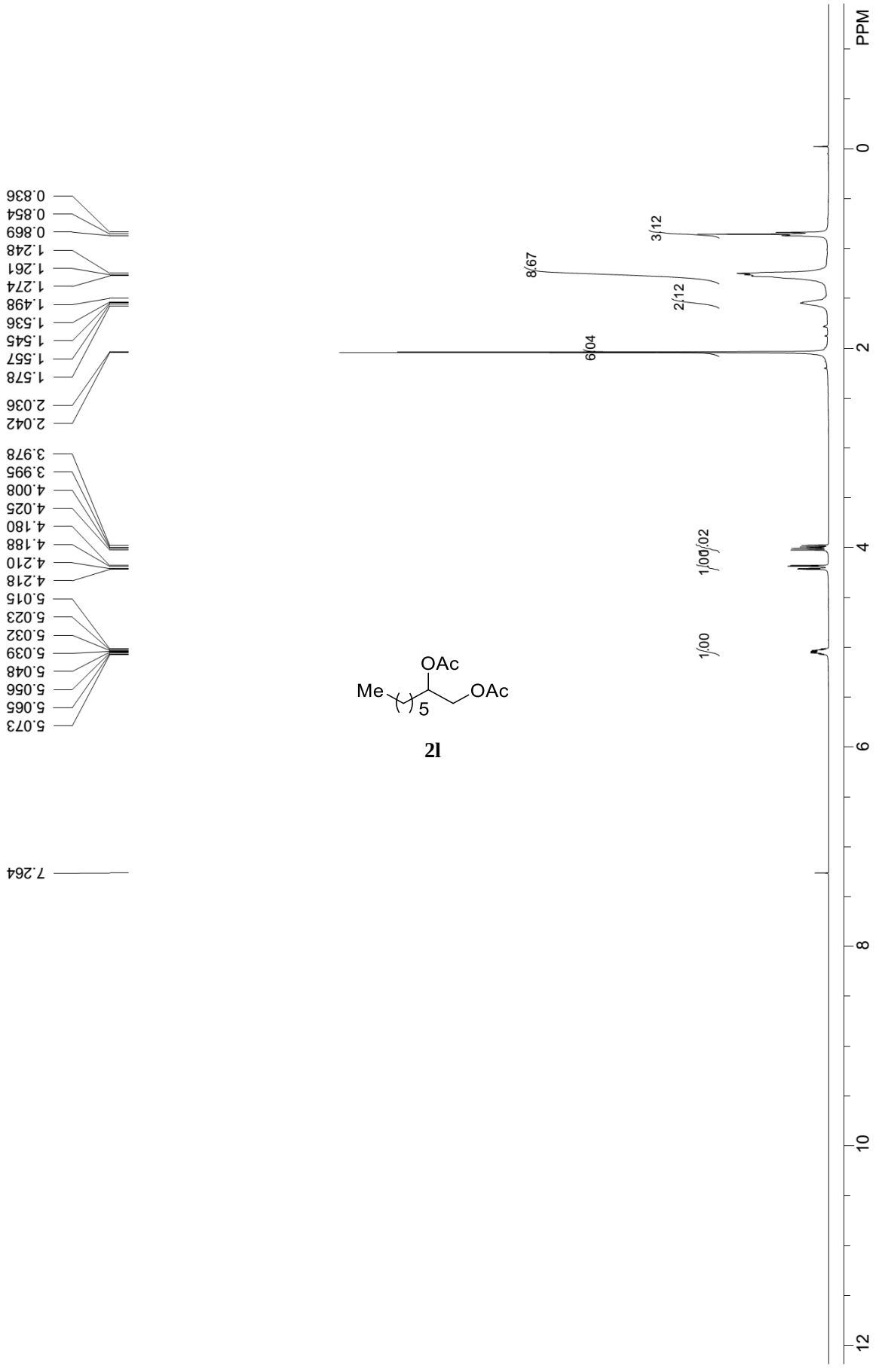
100
150
200

2k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1.557
1.578
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2.042
3.978
3.995
4.008
4.025
4.180
4.188
4.210
4.218
5.015
5.023
5.032
5.039
5.048
5.056
5.065
5.073
7.264
OAc
Me
5
OAc
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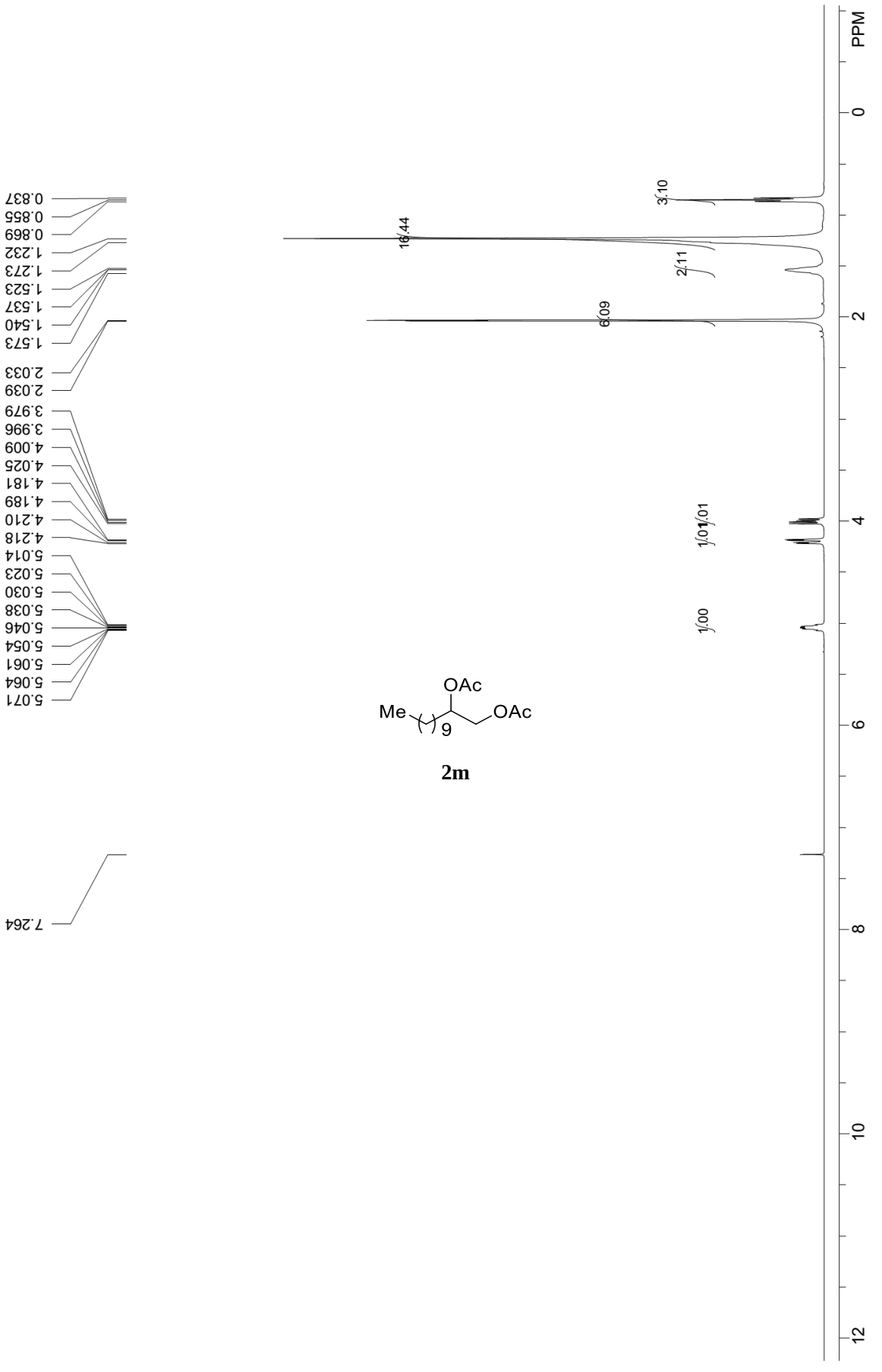
12

2l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2.11
6.09
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1.01
1.00
OAc
Me
9
OAc
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0.855
0.869
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1.273
1.523
1.537
1.540
1.573
2.033
2.039
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3.996
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4.181
4.189
4.210
4.218
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5.023
5.030
5.038
5.046
5.054
5.061
5.064
5.071
7.264

2m