Gold/Copper catalyzed activation of aci-form of nitromethane in the synthesis of methylene bridged bis-1,3-dicarbonyl compounds

Rengarajan Balamurugan* and Seetharaman Manojveer

School of Chemistry, University of Hyderabad, Gachibowli, Hyderabad-500046, INDIA

rbsc@uohyd.ernet.in

Electronic Supplementary Information

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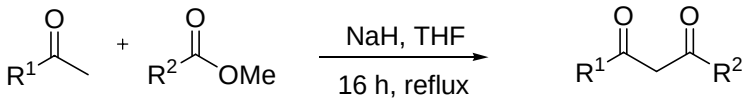
1. General information:

Chemicals and solvents were obtained from various commercial sources. All starting materials were prepared by following known literature procedures. Copper triflate and NaH (60% dispersed in mineral oil) were purchased from Aldrich Chemical Co. Nitromethane was obtained from SD-Fine chemicals. Diethyl and dimethyl carbonate were purchased from AVRA synthesis. THF was dried over sodium and freshly distilled before use. ^{1}H and ^{1}3C spectra were recorded on a Bruker Avance 400 MHz using solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. IR spectra were recorded on JASCO FT/IR-5300 spectrometer. Elemental (C, H, N) analysis were done using Thermo Finnigan Flash EA 1112 analyser. UV- Absorption was measured by CARY 100 BIO UV- Visible spectrometer. For TLC, silica gel plates 60 F254 were used and compounds were visualized by UV light and/or by treatment with Seebach solution (phosphomolibdic acid (2.5 g), $Ce(SO_4)_2$ (1 g), Conc. H_2SO_4 (6 mL), H_2O (94 mL)) followed by heating. Column chromatography was performed on silicagel (100-200 mesh) using ethyl acetate and hexanes mixture as eluent.

2. General procedure for the preparation of compounds 1a-1j[1]

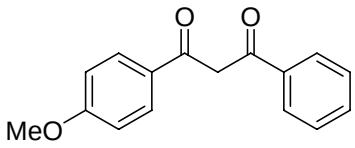


1a - 1j

To an oven dried RB flask were added NaH (60% in mineral oil, 2.5 mmol) and dry THF (3.5 mL). The mixture was cooled to 0 ºC then the corresponding ester (1.1 mmol) and ketone (1.0 mmol) were added. The suspension was heated to reflux for 16 h. After cooled down to room temperature the reaction mixture was quenched with ethyl acetate and 10% hydrochloric acid. The organic layer was separated and washed two times with brine solution and dried over sodium sulfate. The organic layer was concentrated under reduced pressure and purified by column chromatography (silica gel, hexanes/ EtOAc) to furnish desire product.

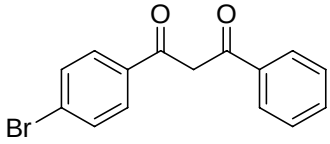
3. Analytical data of compounds (1b-1j)

1-(4-methoxyphenyl)-3-phenylpropane-1,3-dione (1b)[2]



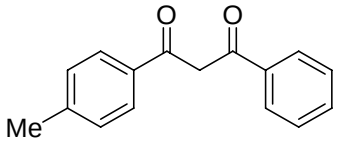
Yield = 94%. Enol form; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99- 7.96 (m, 4H), 7.54-7.46 (m, 3H), 6.98 (d, J = 8.8 Hz, 2H), 6.80 (s, 1 H), 3.88 (s, 3H).

1-(4-bromophenyl)-3-phenylpropane-1,3-dione (1c)[2]



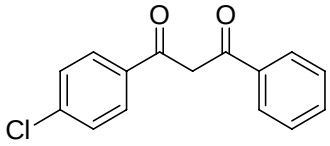
Yield = 81%. Enol form; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 7.2 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.58-7.55 (m, 1H), 7.51-7.47 (m, 2H), 6.81 (s, 1H).

1-Phenyl-3-p-tolylpropane-1,3-dione (1d)[1]



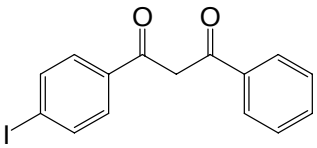
Yield = 94%. Enol form; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 7.2 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.54-7.44 (m, 3H), 7.26 (d, J = 8.0 Hz, 2H), 6.82 (s, 1H), 2.40 (s, 3H).

1-(4-Chlorophenyl)-3-phenylpropane-1,3-dione (1e)[1]



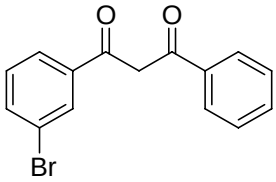
Yield = 89%. Enol form; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.2 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.57-7.55 (m, 1H), 7.50-7.44 (m, 4H), 6.80 (s, 1H).

1-(4-Iodophenyl)-3-phenylpropane-1,3-dione (1f)



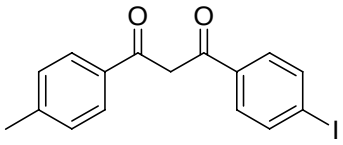
Yellow solid (82%); MP 104-106 °C; Enol form; R_f = 0.55 (in 20% EtOAc/Hexane); IR (KBr): 3045, 2916, 1583, 1302, 1064, 1005, 837, 760, 684, 463 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.6 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.56-7.52 (m, 1H), 7.48-7.44 (m, 2H), 6.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.9, 184.5, 137.8, 135.2, 134.8, 132.5, 128.6, 128.4, 127.1, 99.8, 92.8; Anal.Calc'd for $C_{15}H_{11}IO_2$: C, 51.45; H, 3.17; Found: C, 51.58; H, 3.12.

1-(3-Bromophenyl)-3-phenylpropane-1,3-dione (1g)[3]



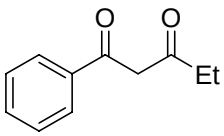
. Yield = 80%. Enol form; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.98 (d, J = 7.2 Hz, 2H), 7.88 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.52-7.47 (m, 2H), 7.35 (t, J = 8.0 Hz, 1H), 6.80 (s, 1H).

1-(4-Iodophenyl)-3-*p*-tolylpropane-1,3-dione (1h)



White solid (Yield = 65%); MP 174- 176 $^{\circ}$C; Enol form; R_f = 0.7 (in 20% EtOAc/Hexane); IR (KBr): 3034, 2926, 2845, 1738, 1604, 1581, 1510, 1298, 1269, 1182, 1003, 839, 779 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 8.4 Hz, 2H), 7.81(d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 6.77 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 183.9, 143.5, 137.8, 134.9, 132.5, 129.4, 128.4, 127.2, 99.6, 92.5, 21.6; Anal.Calc'd for $C_{16}H_{13}IO_2$: C, 52.77; H, 3.60; Found: C, 52.61; H, 3.68.

1-Phenylpentane-1,3-dione (1j)[4]



Yield = 82%. Keto-enol tautomer; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 0.2H), 7.95 (d, J = 8.0 Hz, 0.2H), 7.88 (d, J = 7.2 Hz, 2H), 7.61-7.57 (m, 0.2H), 7.53-7.50 (m, 1H),

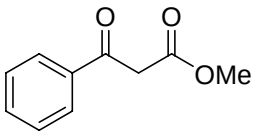
7.46-7.43 (m, 2H), 6.18 (s, 1H), 4.10 (s, 0.2H), 3.00 (q, J = 7.2 Hz, 0.1H), 2.62 (q, J = 7.2 Hz, 0.2H), 2.47 (q, , J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.2 Hz, 0.4H).

4. General procedure for the preparation of compounds 1l-1x[5]

An oven-dried RB flask was charged with acetophenone or substituted acetophenone (2.0 mmol) and NaH (4.0 mmol) under nitrogen atmosphere at room temperature. Then dimethyl carbonate/diethyl carbonate (2.0 mL) was added. The resulting mixture was refluxed for 4 h. After cooled down to room temperature, the reaction mixture was quenched with a mixture of ethyl acetate and 10% hydrochloric acid. The organic layer was separated and washed two times with brine solution and dried over sodium sulfate. Then the organic layer was concentrated under reduced pressure and purified by column chromatography (silica gel, hexanes/ EtOAc) to afford the desired product.

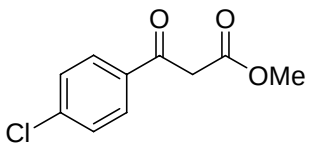
5. Analytical data of compounds (1l-1x)

Methyl 3-oxo-3-phenylpropanoate (1m)[5]



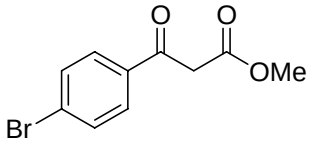
Yield = 96%. Keto-enol tautomer; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.51 (s, 0.1H), 7.94 (d, J = 7.6Hz, 2H), 7.77 (d, J = 7.6 Hz, 0.4H), 7.62-7.58 (m, 1H), 7.50-7.46 (m, 2.2H), 7.43-7.27 (m, 0.4H), 5.68 (s, 0.2H), 4.13 (s, 2H), 3.83 (s, 1H), 3.74 (s, 3H).

Methyl 3-(4-chlorophenyl)-3-oxopropanoate (1n)[5]



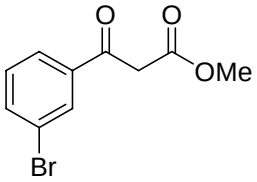
Yield = 75%. Keto-enol tautomer; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.50 (s, 0.3H), 7.88 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 0.6H), 7.46 (J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 0.6H), 5.65 (s, 0.3H), 3.98 (s, 2H), 3.81 (s, 1H), 3.75 (s, 3H).

Methyl 3-(4-bromophenyl)-3-oxopropanoate (1o)[5]



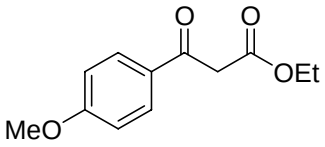
Yield = 93%. Keto-enol tautomer; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.48 (s, 0.3H), 7.81-7.79 (m, 2H), 7.63-7.61 (m, 2.7H), 7.54 (d, J = 8.4 Hz, 0.6H), 5.65 (s, 0.3H), 3.98 (s, 2H), 3.80 (s, 1H), 3.75 (s, 3H).

Methyl 3-(3-bromophenyl)-3-oxopropanoate (1p)[6]



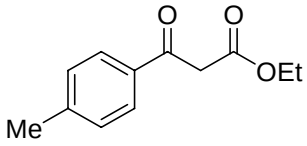
Yield = 95%. Keto-enol tautomer; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.46 (s, 0.3H), 8.07(s, 1H), 7.92-7.85 (m, 1.4H), 7.74-7.69 (m, 1. 4H), 7.60-7.58 (m, 0.3H), 7.40-7.30 (m, 1.3H), 5.66 (s, 0.3H), 3.98 (s, 2H), 3.81 (s, 1H), 3.76 (s, 3H).

Ethyl 3-(4-methoxyphenyl)-3-oxopropanoate (1q)[7]



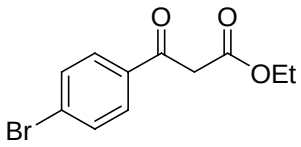
Yield = 86%. Keto-enol tautomer; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.65 (s, 0.1H), 7.99 (d, J = 8.8 Hz, 0.2H), 7.92 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 8.8 Hz, 0.2H), 6.94 (d, J = 8.8 Hz, 2H), 5.58 (s, 0.1H), 4.21 (q, J = 7.2 Hz, 2H), 3.94 (s, 2H), 3.87 (s, 3H), 1.33 (t, J = 7.2 Hz, 0.4H), 1.25 (t, J = 7.2 Hz, 3H).

Ethyl 3-oxo-3-p-tolylpropanoate (1r)[8]



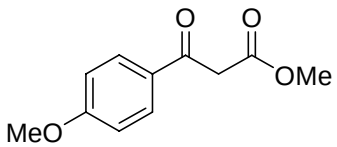
Yield = 83%. Keto-enol tautomer; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.59 (s, 0.1H), 7.84 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 0.2H), 7.27 (d, J = 8.0 Hz, 2H), 7.22 (J = 8.0 Hz, 0.2H), 5.63 (s, 0.1H), 4.28-4.18 (m, 2.3H), 3.96 (s, 2H), 2.41 (s, 3H), 1.33 (t, J = 7.2 Hz, 0.4H), 1.25 (t, J = 7.2 Hz, 3H).

Ethyl 3-(4-bromophenyl)-3-oxopropanoate (1s)[9]



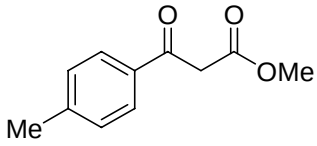
Yield = 80%. Keto-enol tautomer; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.57 (s, 0.3H), 7.81 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.4 Hz, 3H), 7.55 (J = 8.8 Hz, 1H), 5.64 (s, 0.3H), 4.27 (q, J = 7.2 Hz, 0.6H), 4.21 (q, J = 7.2 Hz, 2H)), 1.33 (t, J = 7.2 Hz, 1H), 1.26 (t, J = 7.2 Hz, 3H).

Methyl 3-(4-methoxyphenyl)-3-oxopropanoate (1t)[5]



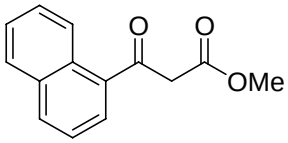
Yield = 92%. Keto-enol tautomer; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.53 (s, 0.1H), 7.87 (d, J = 9.2 Hz, 2H), 7.68 (d, J = 8.8 Hz, 0.2H), 6.90-6.86 (m, 2.2H), 5.54 (s, 0.1H), 3.92 (s, 2H), 3.82 (s, 3H), 3.69 (s, 3H).

Methyl 3-oxo-3-p-tolylpropanoate (1u)[5]



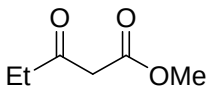
Yield = 96%. Keto-enol tautomer; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.52 (s, 0.2H), 7.84 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 0.3H), 7.27 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 0.3H), 5.64 (s, 0.2H), 3.98 (s, 2H), 3.78 (s, 0.5H), 3.74 (s, 3H), 2.41 (s, 3H), 2.38 (s, 0.6H).

Methyl 3-(naphthalen-1-yl)-3-oxopropanoate (1v)[5]



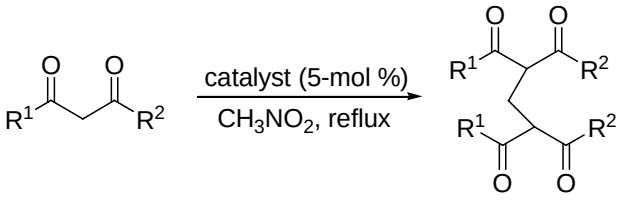
Yield = 92%. Keto-enol tautomer; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.65 (s, 0.3H), 8.77 (d, J = 8.4 Hz, 1H), 8.34 (d, J = 7.6 Hz, 0.3H), 8.02 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 7.6 Hz, 2H), 7.87 (d, J = 8.0 Hz, 0.7H), 7.64-7.60 (m, 1.5H), 7.56-7.48 (m, 1.5H), 5.51 (s, 0.3H), 4.13 (s, 2H), 3.83 (s, 1H), 3.75 (s, 3H).

Methyl 3-oxopentanoate (1x)[10]



Yield = 75%. Keto-enol tautomer; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.69 (s, 3H), 3.42 (s, 1.6H), 2.53 (q, J = 7.2Hz, 1.6H), 2.20 (s, 0.5H), 1.30 (d, J = 7.2 Hz 0.5H), 1.03 (t, J = 7.2 Hz, 2.4H).

6. General Procedure for the Synthesis of methylene-bridged bis-1,3-dicarbonyl compounds (2a-2y)

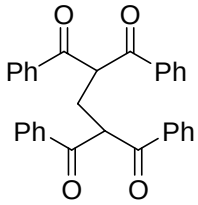


1a - 1y **2a - 2y**

Gold (III) chloride or Copper (II) triflate (5.0 mol %) was charged into a solution of 1, 3 dicarbonyl compound (1.0 mmol) in nitromethane (10 mL). The resulting mixture was heated to reflux. The reaction was monitored by TLC. After the completion of the reaction, nitromethane was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, hexanes/ EtOAc) to furnish the pure compound.

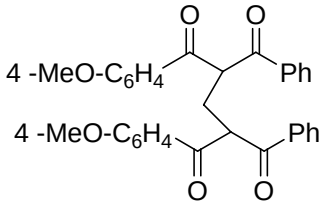
7. Analytical data of products 2a-2y

2,4-Dibenzoyl-1,5-diphenylpentane-1,5-dione (2a)[5]



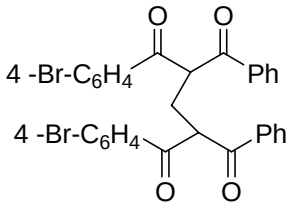
Light yellow powder; R_f = 0.4 (in 20% EtOAc/Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 7.2 Hz, 8H), 7.60-7.58 (m, 4H), 7.50-7.46 (m, 8H), 5.74 (t, J = 7.2 Hz, 2H), 2.75 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 135.4, 133.9, 129.0, 128.8, 53.9, 28.9.

2,4-Dibenzoyl-1,5-bis(4-methoxyphenyl)pentane-1,5-dione (2b)



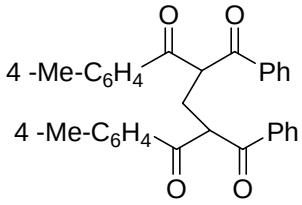
Light yellow powder; MP 66-68 °C; R_f = 0.3 (in 33% EtOAc/Hexane); IR (KBr): 3059, 3011, 2932, 2843, 1689, 1664, 1549, 1510, 1421, 1259, 1170, 1026, 949 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.8 Hz, 2H), 8.15-8.11 (m, 4H), 8.06 (d, J = 7.6 Hz, 2H), 7.56-7.52 (m, 2H), 7.48-7.41 (m, 4H), 6.98-6.92 (m, 4H), 5.68 (t, J = 6.8 Hz, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 2.74 (t, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 195.1, 195.0, 164.1, 164.0, 135.6, 135.5, 133.7, 133.6, 131.3, 131.1, 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 114.2, 114.1, 55.4, 53.7, 29.1; Anal.Calc'd for $C_{33}H_{28}O_6$: C, 76.14; H, 5.42; Found: C, 76.23; H, 5.38.

2,4-Dibenzoyl-1,5-bis(4-bromophenyl)pentane-1,5-dione (2c)



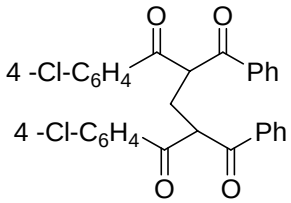
Light yellow powder; MP 70-72 °C; R_f = 0.4 (in 20% EtOAc/Hexane); IR (KBr): 3061, 2928, 2854, 1695, 1670, 1583, 1448, 1396, 1257, 1070, 1008, 947, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ. 8.12-8.07 (m, 4H), 8.03-7.97 (m, 4H), 7.64-7.57 (m, 6H), 7.51-7.45 (m, 4H), 5.64 (t, J = 6.8 Hz, 2H), 2.78-2.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 195.6, 135.2, 134.0, 132.4, 130.3, 130.2, 129.9, 129.3, 129.1, 128.8, 128.7, 53.9, 28.7; Anal.Calc'd for $C_{31}H_{22}Br_2O_4$: C, 60.22; H, 3.59; Found: C, 60.35; H, 3.51.

2,4-Dibenzoyl-1,5-di*p*-tolylpentane-1,5-dione (2d)



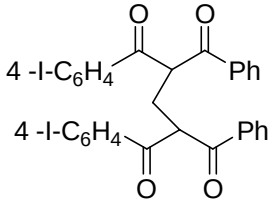
Light yellow powder; MP 62-64 °C; R_f = 0.35 (in 20% EtOAc/Hexane); IR (KBr): 3059, 3034, 2922, 1693, 1668, 1604, 1448. 1261, 1182, 949, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.14-8.11 (m, 4H), 8.06-8.03(m, 4H), 7.55-7.53 (m, 2H), 7.47-7.44 (m, 4H), 7.27-7.23 (m, 4H), 5.72 (t, J = 6.8 Hz, 2H), 2.74 (t, J = 6.8 Hz, 2H), 2.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 196.1, 144.8, 135.4, 133.7, 132.9, 132.9, 129.6, 128.9, 128.7, 53.8, 28.9, 21.6; Anal.Calc'd for $C_{33}H_{28}O_4$: C, 81.12; H, 5.78; Found: C, 81.35; H, 5.71.

2,4-Dibenzoyl-1,5-bis(4-chlorophenyl)pentane-1,5-dione (2e)



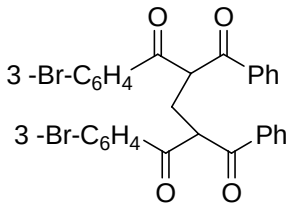
Light yellow powder; MP 62-64 °C; R_f = 0.4 (in 20% EtOAc/Hexane); IR (KBr): 3065, 2922, 1695, 1672, 1587, 1487, 1257, 1093, 946, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.13-8.06 (m, 8H), 7.61-7.56 (m, 2H), 7.50-7.44 (m, 8H), 5.66 (t, J = 6.8 Hz, 2H), 2.77-2.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 195.4, 140.5, 140.4, 135.2, 135.2, 134.0, 133.7, 130.2, 130.1, 129.3, 129.0, 128.7, 128.6, 128.3, 53.9, 28.7; Anal.Calc'd for $C_{31}H_{22}Cl_2O_4$: C, 70.33; H, 4.19; Found: C, 70.12; H, 4.23.

2, 4-Dibenzoyl-1,5-bis(4-iodophenyl)pentane-1,5-dione (2f)



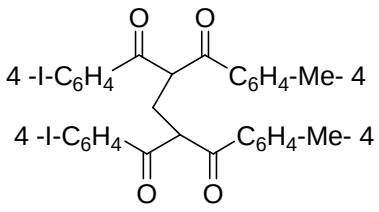
Light yellow powder; MP 64-66 °C; R_f = 0.4 (in 20% EtOAc/Hexane); IR (KBr): 3057, 2922, 2852, 1693, 1668, 1579, 1446, 1392, 1257, 1180, 1059, 1003, 947, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.12-8.07 (m, 4H), 7.86-7.84 (m, 8H), 7.60-7.59 (m, 2H), 7.51-7.46 (m, 4H), 5.62 (t, J = 6.8 Hz, 2H), 2.75-2.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 195.9, 138.4, 135.2, 134.6. 134.1, 130.1, 130.1, 129.1, 128.7, 102.3, 53.8, 28.7; Anal.Calc'd for $C_{31}H_{22}I_2O_4$: C, 52.27; H, 3.11; Found: C, 52.09; H, 3.18.

2,4-Dibenzoyl-1,5-bis(3-bromophenyl)pentane-1,5-dione (2g)



Light yellow powder; MP 52-54 °C; R R_f= 0.25 (in 20% EtOAc/Hexane); IR (KBr): 3065, 2928, 2856, 1693, 1670, 1595, 1564, 1446, 1419, 1251, 1188, 1068, 999, 949, 750, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 2H), 8.12 (t, J = 6.4 Hz, 3H), 8.06 (t, J = 7.6 Hz, 3H), 7.71 (d, J = 7.2 Hz, 2H), 7.60 (d, J = 7.2 Hz, 2H), 7.53-7.49 (m, 4H), 7.39-7.35 (m, 2H), 5.63 (t, J = 6.8 Hz, 2H), 2.75-2.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 195.2, 136.7, 135.1, 134.1. 131.7, 130.6, 129.1, 128.8, 127.3, 123.5, 53.9, 28.6; Anal.Calc'd for $C_{31}H_{22}Br_2O_4$: C, 60.22; H, 3.59; Found: C, 60.12; H, 3.51.

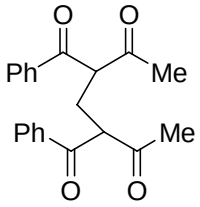
2,4-Bis(4-iodobenzoyl)-1,5-dip-tolylpentane-1,5-dione (2h)



Light yellow powder; MP 88-90 °C; R_f = 0.5 (in 20% EtOAc/Hexane); IR (KBr): 3032, 2922, 1693, 1668, 1604, 1579, 1392, 1259, 1180, 1005, 943 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 7.6 Hz, 4H), 7.83 (s, 8H), 7.27 (d, J = 7.6 Hz, 4H), 5.58 (t, J = 6.8 Hz, 2H), 2.72-2.62 (m,

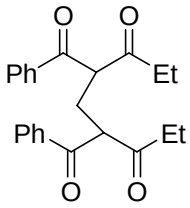
2H), 2.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 195.8, 145.1, 138.3, 134.7, 132.8, 130.0, 129.7, 128.9, 102.2, 53.8, 28.8, 21.7; Anal.Calc'd for $C_{33}H_{26}I_2O_4$: C, 58.53; H, 3.54; Found: C, 53.42; H, 3.61.

3,5-Dibenzoylheptane-2,6-dione (2i)[5]



Light yellow solid; R_f = 0.2 (in 20% EtOAc/Hexane); The ratio of two diastereomers is 1.3:1. **Two diastereomers;** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 7.2 Hz, 2H), 8.03 (d, J = 7.6 Hz, 2H), 7.65-7.58 (m, 2H), 7.54-7.47 (m, 4H), 4.72 (t, J = 6.8 Hz, 1H), 4.65 (t, J = 6.8 Hz, 1H), 2.65-2.45 (m, 2H), 2.19 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.9, 203.4, 196.6, 196.4, 135.9, 135.6, 134.0, 128.9, 128.8, 128.7, 59.3, 59.1, 29.4, 29.1, 27.3, 26.9.

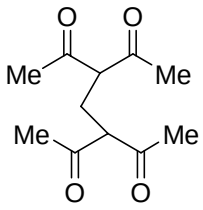
4,6-Dibenzoylnonane-3,7-dione (2j)



Yellow oil; R_f = 0.2 (in 20% EtOAc/Hexane); IR (neat): 2976, 2939, 1720, 1672, 1595, 1448, 1111, 1018 cm^{-1}; The ratio of two diastereomers is 1:1. **Two diastereomers**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15-8.10 (m, 1H), 8.06 (d, J = 7.6 Hz, 2H), 8.02 (d, J = 7.6 Hz, 2H) 7.63- 7.57 (m, 2H), 7.53-7.46 (m, 5H), 4.75 (t, J = 6.8 Hz, 1H), 4.67 (t, J = 6.8 Hz, 1H), 2.59-2.36 (m, 6H), 1.05 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.7, 206.5, 206.0, 196.7, 196.5, 196.2, 135.9, 135.6, 133.8, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 58.3,

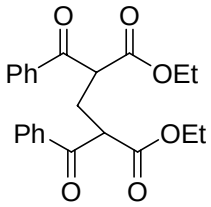
58.1, 53.6, 35.7, 35.5, 35.3, 29.5, 28.1, 27.5, 27.2, 7.6, 7.5; Anal.Calc'd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64; Found: C, 75.89; H, 6.59.

3,5-Diacetylheptane-2,6-dione (2k)[11]



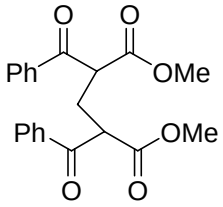
Light yellow oil; R_f = 0.25 (in 33% EtOAc/Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (t, J = 7.2 Hz 0.4H), 3.68 (t, J = 6.4 Hz 2H), 2.83 (d, J = 7.2 Hz, 1H), 2.28 (t, J = 6.4 Hz, 2H), 2.22 (s, 6H), 2.21 (s, 5H), 2.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.5, 203.1, 191.7, 106.7, 68.1, 64.6, 30.2, 29.4, 26.0, 24.7, 23.1.

Diethyl 2,4-dibenzoylpentanedioate (2l)[5]



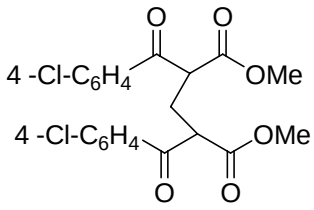
Light yellow oil; R_f = 0.4 (in 20% EtOAc/Hexane); The ratio of two diastereomers is 1.1:1. **Two diastereomers:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 7.2 Hz, 4H), 7.63-7.56 (m, 2H), 7.52-7.45 (m, 4H), 4.63 (t, J = 7.2 Hz, 1H), 4.55 (t, J = 7.2 Hz, 1H), 4.27-4.18 (m, 2H), 4.13-4.07 (m, 2H), 2.79-2.54 (m, 2H), 1.22 (t, J = 7.2 Hz, 3H), 1.11 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 194.7, 169.6, 169.2, 135.7, 135.3, 133.7, 128.8, 128.7, 128.0, 61.6,51.4, 51.2, 28.1, 27.5, 13.9, 13.8.

Dimethyl 2,4-dibenzoylpentanedioate (2m)[5]



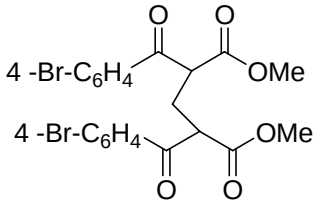
Colourless oil; R_f = 0.4 (in 20% EtOAc/Hexane); The ratio of two diastereomers is 1.3:1. **Two diastereomers**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 7.2 Hz, 4H), 7.62-7.59 (m, 2H), 7.57-7.46 (m, 4H), 4.67 (t, J = 7.2 Hz, 1H), 4.58 (t, J = 7.2 Hz, 1H), 3.75 (s, 3H), 3.64 (s, 3H), 2.78-2.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 194.6, 170.2, 169.7, 135.6, 135.2, 133.9, 128.9, 128.8, 52.6, 51.2, 50.9, 28.3, 27.7.

Dimethyl 2,4-bis(4-chlorobenzoyl)pentanedioate (2n)[5]



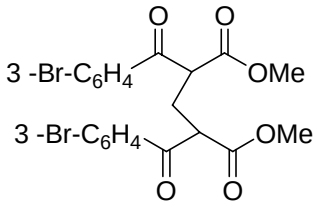
Light yellow oil; R_f = 0.5 (in 20% EtOAc/Hexane); The ratio of two diastereomers is 1.2:1. **Two diastereomers**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.98 (m, 4H), 7.49-7.45 (m, 4H), 4.61 (t, J = 7.2 Hz, 1H), 4.51 (t, J = 7.2 Hz, 1H), 3.75 (s, 3H), 3.64 (s, 3H), 2.74-2.50 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 193.8, 193.4, 169.9, 169.4, 140.6, 133.9, 133.5, 130.3, 130.2, 129.2, 52.7, 51.0, 50.8, 28.1, 27.4.

Dimethyl 2,4-bis(4-bromobenzoyl)pentanedioate (2o)[5]



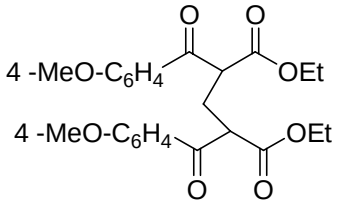
Yellow oil; R_f = 0.4 (in 20% EtOAc/Hexane); The ratio of two diastereomers is 1.4:1. **Two diastereomers:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.89 (m, 4H), 7.66-7.62 (m, 4H), 4.60 (t, J = 7.2 Hz, 1H), 4.50 (t, J = 7.2 Hz, 1H), 3.75 (s, 3H), 3.64 (s, 3H), 2.74-2.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.1, 193.6, 169.9, 169.4, 134.3, 133.9, 133.2, 130.4, 130.3, 129.4, 52.7, 51.0, 50.8, 28.1, 27.4.

Dimethyl 2,4-bis(3-bromobenzoyl)pentanedioate (2p)



Light yellow oil; R_f = 0.4 (in 20% EtOAc/Hexane); IR (neat): 3067, 2953, 1747, 1684, 1566, 1435, 1251, 1070, 974 cm^{-1}; The ratio of two diastereomers is 1.3:1. **Two diastereomers**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 10.4 Hz, 2H), 7.98 (t, J = 8.4 Hz, 2H), 7.73 (t, J = 8.4 Hz, 2H), 7.38 (q, J = 8.0 Hz, 2H), 4.59 (t, J = 7.2 Hz, 1H), 4.51 (t, J = 7.2 Hz, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 2.74-2.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 193.3, 169.6, 169.3, 137.3, 136.9, 136.7, 131.7, 131.6, 130.4, 127.4, 127.3, 123.1, 52.8, 51.0, 50.8, 27.9, 27.4. Anal.Calc'd for $C_{21}H_{18}Br_2O_6$: C, 47.97; H, 3.45; Found: C, 47.85; H, 3.41.

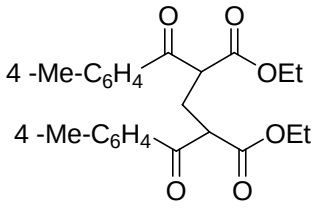
Diethyl 2, 4-bis (4-methoxybenzoyl) pentanedioate (2q)



Yellow oil; R_f = 0.35 (in 33% EtOAc/Hexane); IR (KBr): 2986, 2937, 1739, 1670, 1601, 1510, 1458, 1261, 1172, 1026, 956, 844 cm^{-1}; The ratio of two diastereomers is 1.3:1. **Two**

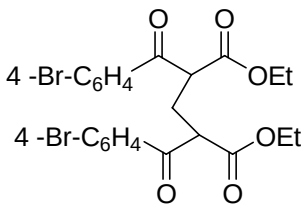
diastereomers: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.8 Hz, 4H), 6.98-6.92 (m, 4H), 4.57 (t, J = 7.2 Hz, 1H), 4.49 (t, J = 7.2 Hz, 1H), 4.27-4.18 (m, 2H), 4.14-4.06 (m, 2H), 3.88 (s, 3 H), 3.86 (s, 3H), 2.75-2.51 (m, 2H), 1.25 (t, J = 7.2 Hz, 3H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 193.2, 169.9, 169.5, 163.9, 131.3, 131.2, 128.7, 128.2, 113.9, 113.6, 61.4, 55.4, 51.2, 50.9, 28.5, 27.8, 14.1. 13.9, 13.8; Anal.Calc'd for $C_{25}H_{28}O_8$: C, 65.78; H, 6.18; Found: C, 65.85; H, 6.12.

Diethyl 2,4-bis(4-methylbenzoyl)pentanedioate (2r)



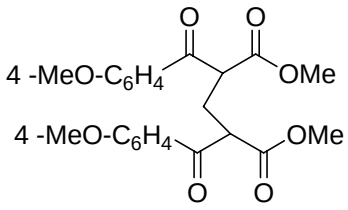
Yellow oil; R_f = 0.4 (in 20% EtOAc/Hexane); IR (neat): 3034, 2984, 2935, 1739, 1682, 1606, 1572, 1444, 1257, 1097, 1033, 962 cm^{-1}; The ratio of two diastereomers is 1.1:1. **Two diastereomers**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.92 (m, 4H), 7.30-7.24 (m, 4H), 4.58 (t, J = 7.2 Hz, 1H), 4.50 (t, J = 7.2 Hz, 1H), 4.25-4.17 (m, 2H), 4.12-4.07 (m, 2H), 2.75-2.52 (m, 2 H), 2.42 (s, 3H), 2.40 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H), 1.12 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.7, 194.4, 169.7, 169.4, 144.7, 133.4, 132.9, 129.4, 129.0, 128.9, 128.1, 61.5, 51.4, 51.2, 28.2, 27.7, 21.6, 13.9, 13.8; Anal.Calc'd for $C_{25}H_{28}O_6$: C, 70.74; H, 6.65; Found: C, 70.65; H, 6.59.

Diethyl 2,4-bis(4-bromobenzoyl)pentanedioate (2s)



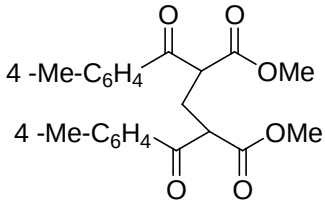
Light yellow oil; R_f = 0.5 (in 20% EtOAc/Hexane); IR (KBr): 3097, 29864, 1739, 1684, 1585, 1460, 1390, 1248, 1070, 839 cm^{-1}; The ratio of two diastereomers is 1.2:1. **Two diastereomers:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.4 Hz, 4H), 7.66-7.61 (m, 4H), 4.56 (t, J = 7.2 Hz, 1H), 4.47 (t, J = 7.2 Hz, 1H), 4.26-4.16 (m, 2H), 4.14-4.07 (m, 2H), 2.74-2.50 (m, 2H), 1.22 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.1, 193.7, 169.3, 168.9, 134.5, 134.0, 132.1, 130.3, 130.2, 129.2, 129.2, 61.8, 51.3, 51.1, 27.9, 27.3, 13.9, 13.8;. Anal.Calc'd for $C_{23}H_{22}Br_2O_4$: C, 49.84; H, 4.00; Found: C, 49.75; H, 4.08.

Dimethyl 2,4-bis(4-methoxybenzoyl)pentanedioate (2t)[5]



Colourless oil; R_f = 0.4 (in 20% EtOAc/Hexane); The ratio of two diastereomers is 1.3:1. **Two diastereomers;** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.0 Hz, 4H), 6.98-6.93 (m, 4H), 4.6 (t, J = 7.2 Hz, 1H), 4.53 (t, J = 7.2 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.75 (s, 3H), 3.64 (s, 3H), 2.75-2.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.6, 193.1, 170.4, 169.9, 164.1, 131.1, 131.2, 128.6, 128.1, 113.9, 55.4, 52.4, 50.9, 50.6, 28.6, 27.9.

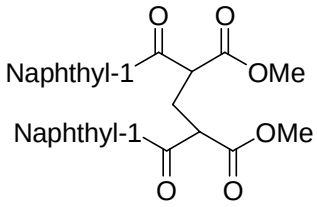
Dimethyl 2, 4-bis(4-methylbenzoyl)pentanedioate (2u)[5]



Colourless oil; R_f = 0.5 (in 20% EtOAc/Hexane); The ratio of two diastereomers is 1.3:1. **Two diastereomers**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.2 Hz, 4H), 7.31-7.25 (m, 4H), 4.63 (t, J = 7.2 Hz, 1H), 4.55 (t, J = 7.2 Hz, 1H), 3.74 (s, 3H), 3.63 (s, 3H), 2.76-2.52 (m, 2H), 2.42

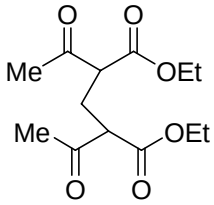
(s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.6, 194.2, 170.2, 169.8, 144.8, 133.2, 132.7, 129.4, 129.0, 128.9, 52.5, 51.1, 50.8. 28.3, 27.8, 21.6.

Dimethyl 2,4-di(1-naphthoyl)pentanedioate (2v)[5]



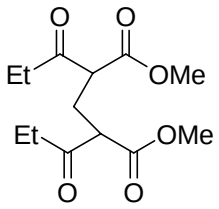
Yellow oil; R_f = 0.4 (in 20% EtOAc/Hexane); The ratio of two diastereomers is 1:1. **Two diastereomers**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.15 (s, 0.2H), 8.61-8.57 (m, 2H), 8.01-7.82 (m, 7H), 7.62-7.24 (m, 8H), 4.73 (q, J = 7.2 Hz, 2H), 3.80 (s, 0.7H), 3.67 (s, 2.5H), 3.58 (s, 2.1H), 2.91-2.7 3(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 197.8, 169.9, 169.8, 134.5, 133.9, 133.8, 133.6, 133.5, 132.9, 130.3, 130.1, 129.9, 128.7, 128.4, 128.3, 127.9, 127.7, 126.6, 126.5, 126.4, 126.2, 125.6, 125.5, 124.8, 124.2, 53.9, 53.8, 52.5, 52.0, 28.4, 27.8, 26.1.

Diethyl 2,4-diacetylpentanedioate (2w)[12]



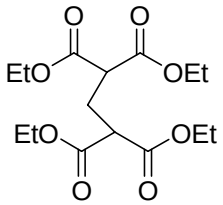
Yellow oil; R_f = 0.2 (in 20% EtOAc/Hexane); The ratio of two diastereomers is 1:1. **Two diastereomers**; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.26-4.16 (m, 4H), 3.55 and 3.54 (t, J = 7.2 Hz, 2H), 2.46-2.31 (m, 2H), 2.26 (s, 6H), 1.30-1.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.2, 168.9, 61.6, 56.6, 56.4, 29.4, 29.1, 25.4, 25.3, 13.9.

Dimethyl 2,4-dipropionylpentanedioate (2x)



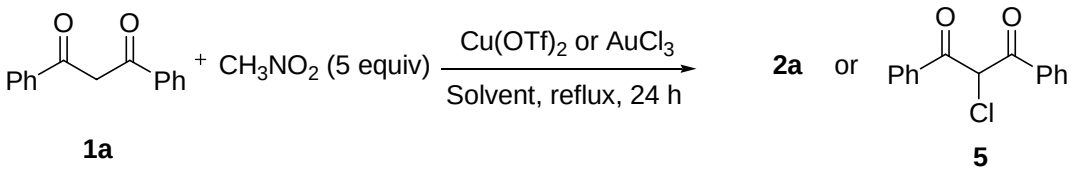
Light yellow oil; R_f = 0.32 (in 20% EtOAc/Hexane); IR (KBr): 2976, 2955, 1745, 1716, 1439, 1356, 1170, 1107 1020 cm^{-1}; The ratio of two diastereomers is 1:1. **Two diastereomers**; ^1H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 3H), 3.72 (s, 2H), 3.70 (s, 1H), 3.62-3.56 (m, 2H), 2.65-2.32 (m, 6H), 2.15 (d, J = 2.4 Hz, 1H), 1.36 (s, 1H), 1.06 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.0, 204.9, 172.6, 169.9, 169.5, 58.4, 55.3, 55.2, 54.4, 54.3, 52.5, 35.7, 35.5, 32.5, 32.3, 26.2, 26.1, 25.8, 25.7, 20.0, 19.8, 7.4; Anal.Calc'd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40; Found: C, 57.23; H, 7.55.

Tetraethyl propane-1,1,3,3-tetracarboxylate (2y)[13]



Light yellow oil; R_f = 0.32 (in 20% EtOAc/Hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 4.18 (q, J = 7.2 Hz, 8H), 3.45 (t, , J = 7.6 Hz, 2H), 2.45 (t, , J = 7.6 Hz, 2H), 1.25 (t, , J = 7.2 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 61.6, 49.3, 27.2, 13.9.

8. Reactions with Stoichimetric nitromethane



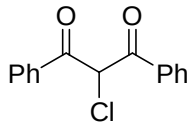
1a **5**

Entry	Solvent	$Cu(OTf)_2$ **2a** Yield[a,b]	$AuCl_3$ **5** Yield[a,b]
1	Dichloroethane	1 (91)	14 (84)
2	Toluene	3 (90)	13 (86)
3	Acetonitrile	10 (80)	15 (82)
4	Tetrahydrofuran	5 (91)	10 (88)

[a] Isolated yields.
[b] values in the parenthesis represent the percentage of recovered unreacted starting material.

9. Analytical data of product 5

2-Chloro-1,3-diphenylpropane-1,3-dione (5)[14]



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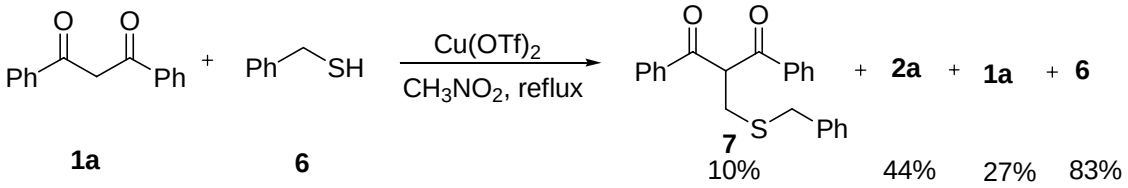
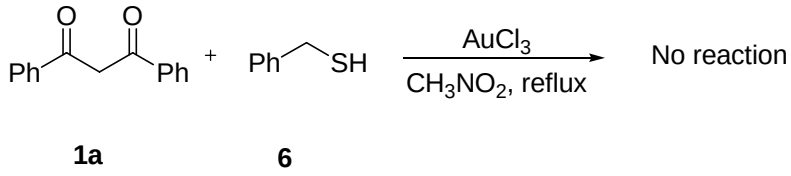
R_f = 0.45 (in 20% EtOAc/Hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 7.6 Hz, 4H), 7.61 (t, J = 7.6 Hz, 2H), 7.48 (t, J = 7.6 Hz, 4H), 6.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 134.3, 133.8, 129.3, 128.9, 128.0, 62.9.

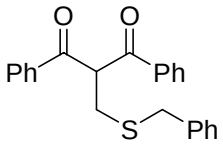
10. Experimental details of trapping studies with benzyl thiol

To the solution of $Cu(OTf)_2$ or $AuCl_3$ (5 mol%) and dibenzoyl methane (1.0 mmol) in nitromethane (10 ml), benzyl thiol (1.2 mmol) was added. The reaction mixture was heated to reflux for 24 h. Then solvent was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel, hexanes/EtOAc) to furnish desire products.



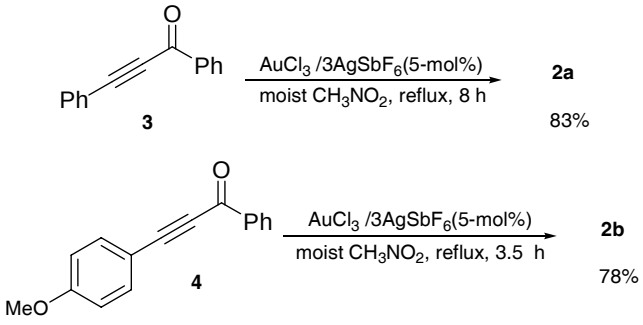


2-(Benzylthiomethyl)-1,3-diphenylpropane-1,3-dione (6)



Yellow oil; R_f = 0.33 (in 20% EtOAc/Hexane); IR (neat): 3061, 3028, 2924, 1956, 1903, 1695, 1670, 1597, 1581, 1493, 1448, 1408, 1323, 1286, 1259, 1074, 1028, 1001, 761, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 7.2 Hz, 4H), 7.55 (t, J = 7.2 Hz, 2H), 7.41 (t, J = 7.2 Hz, 4H), 7.34-7.28 (m, 5H), 5.32 (t, J = 6.8 Hz, 1H), 3.75 (s, 2H), 3.19 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5, 138.2, 135.7, 133.6, 129.5, 128.9, 128.6, 127.2, 57.6, 37.7, 30.7; Anal.Calc'd for $C_{23}H_{20}O_2S$: C, 75.64; H, 5.59; Found: C, 76.48; H, 5.65.

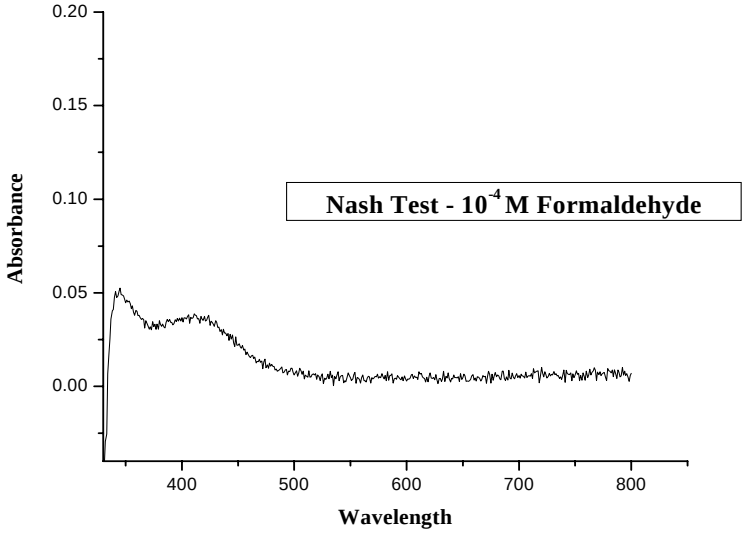
11. General procedure for the $AuCl_3$ catalyzed conversion of alkynones into methylene bridged bis-1,3-dicarbonyls

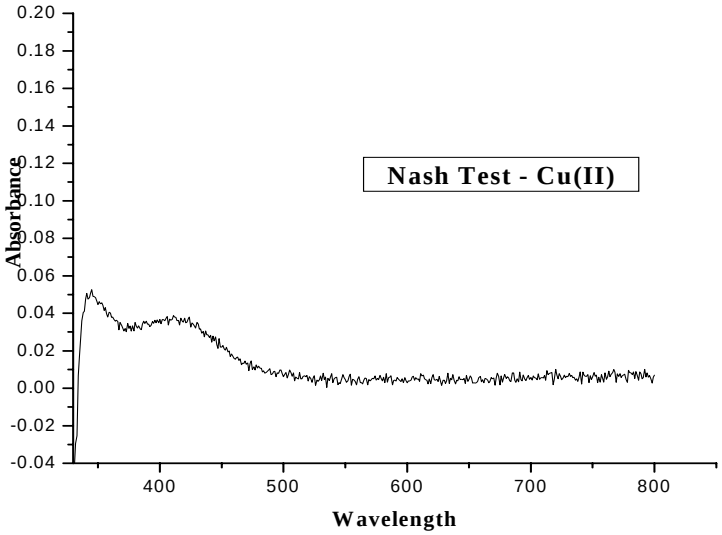


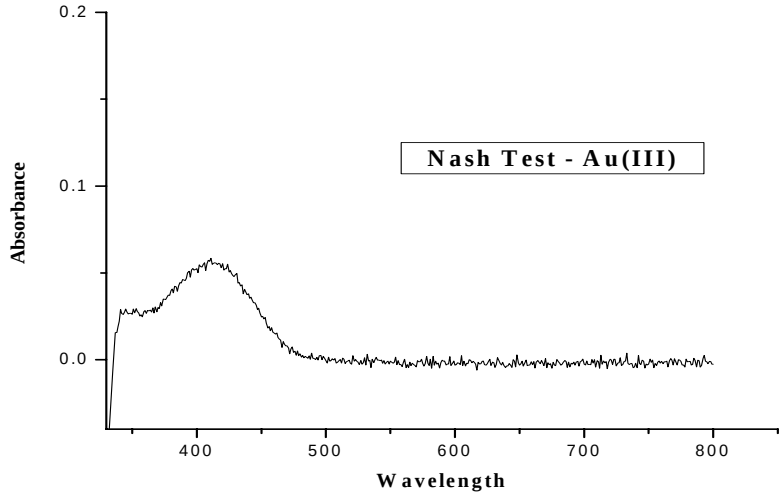
To a solution of alkynone **3**/**4** (1.0 mmol) in moist nitromethane (15 mL), $AuCl_3$ (15 mg, 0.05 mmol) and $AgSbF_6$ (51 mg, 0.15 equiv) were added. The reaction mixture was heated to reflux. After completion of the reaction as indicated by the TLC, the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel (100 – 200 mesh) and EtOAc/hexanes mixture to get **2a** and **2b** respectively.

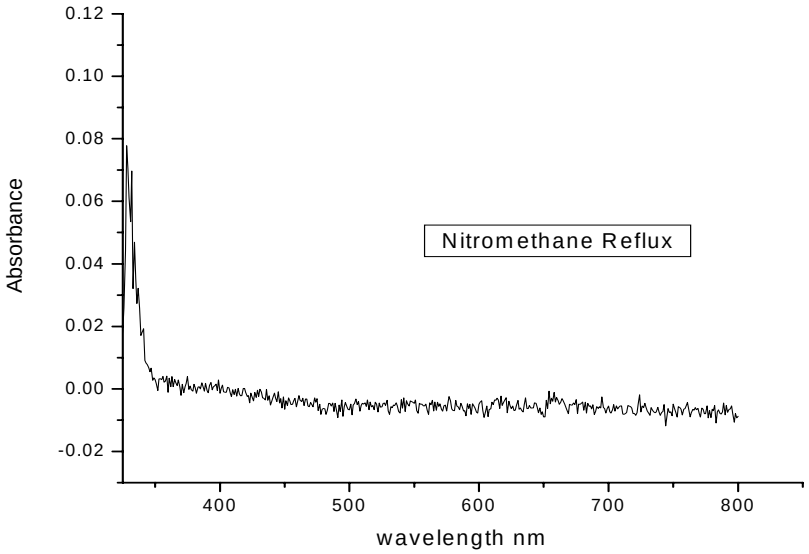
12. Experimental details for Nash test

The Nash reagent was prepared by dissolving NH_4OAc (15 g, 0.19 mol), 2, 4-pentanedione (0.2 ml, 2 mmol) and acetic acid (0.3 ml, 5 mmol) in 100 ml of water.[6] An oven dried RB flask was charged with 5 ml of nitromethane and catalyst (2.5 mol %). Resulting solution was refluxed for 3 hours then cooled down to room temperature. 10 ml of hexane was added into 0.5 ml of the reaction mixture and then stirred it well for 10 minutes at room temperature. 0.01 ml of the reaction mixture in hexane was added to 5 ml of Nash reagent and incubated at 60 ˚C for 5 minutes. The formaldehyde formation was determined by measuring the absorbance of solution at 412 nm.[15]

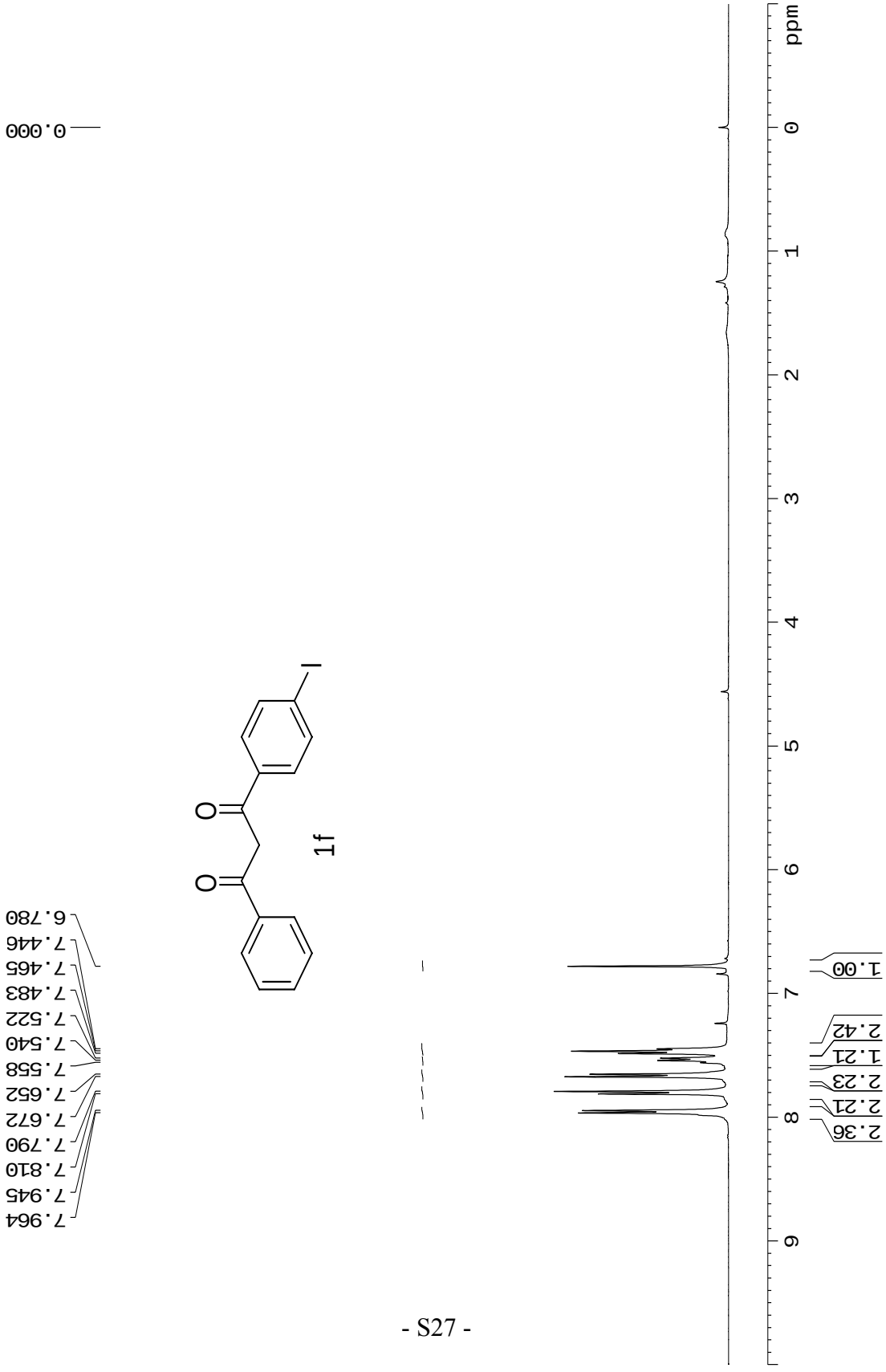


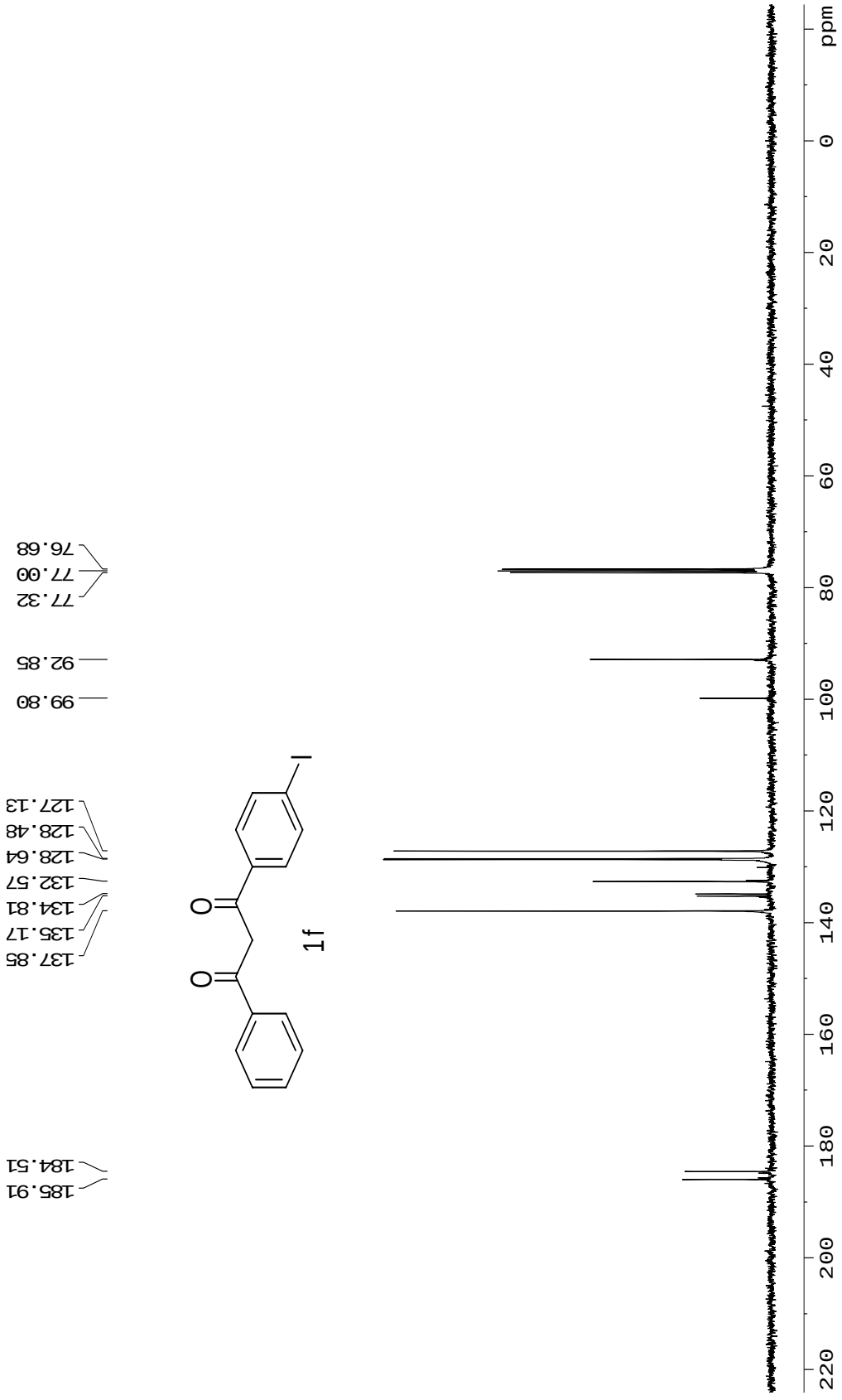



Nash Test - Au(III)
Absorbance
0.2
0.1
0.0
400
500
600
700
800
Wavelength


Nitromethane Reflux
Absorbance
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
400
500
600
700
800
wavelength nm

13. ^{1}H and ^{13}C spectra of compounds 1f and 1h

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40
60
80
100
120
140
160
180
200
220
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184.51
137.85
135.17
134.81
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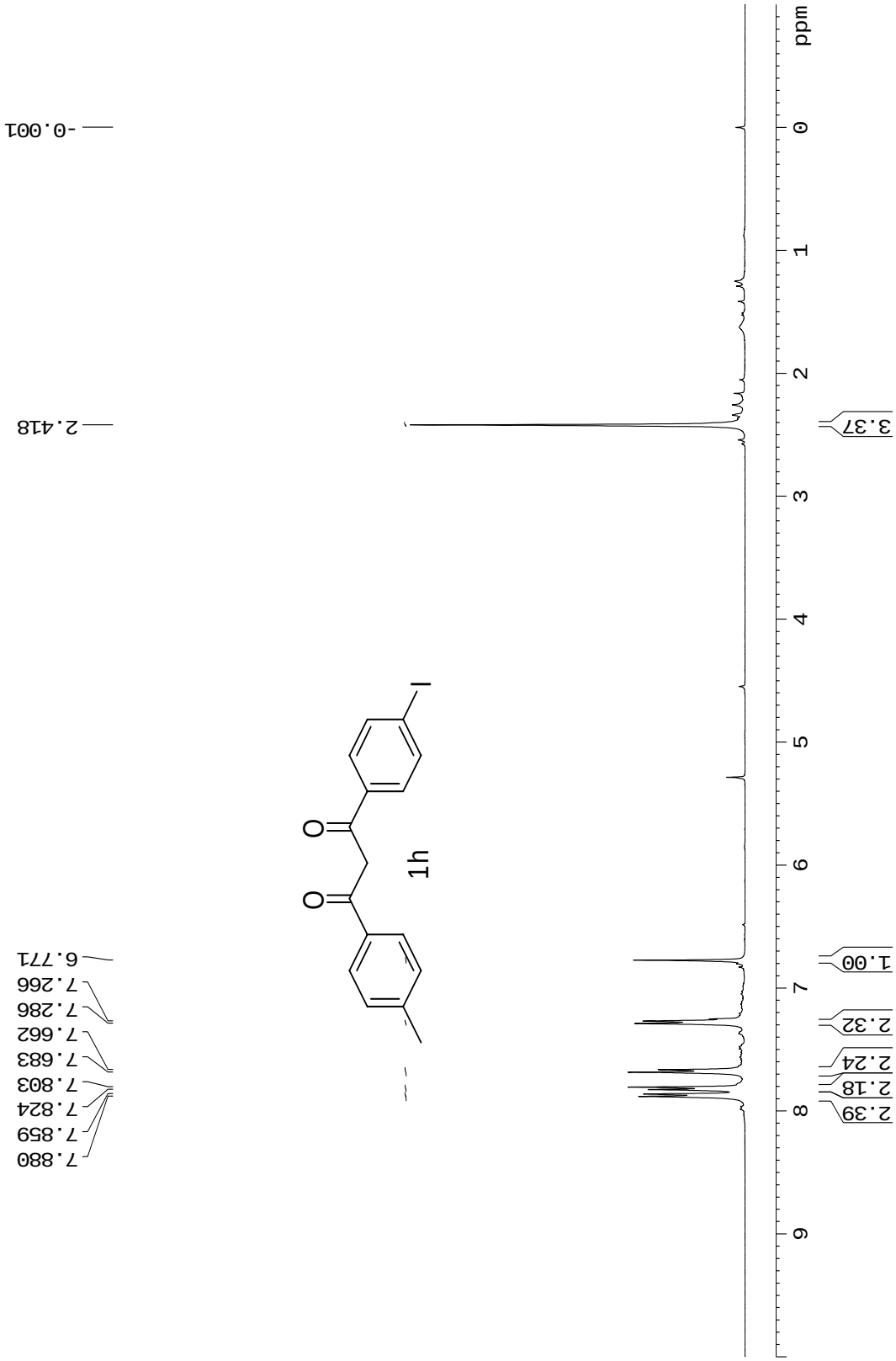
128.64
128.48
127.13
99.80
92.85
77.32
77.00
76.68
O
O
I
1f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7.803
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7.662
7.286
7.266
6.771
1h
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O
O
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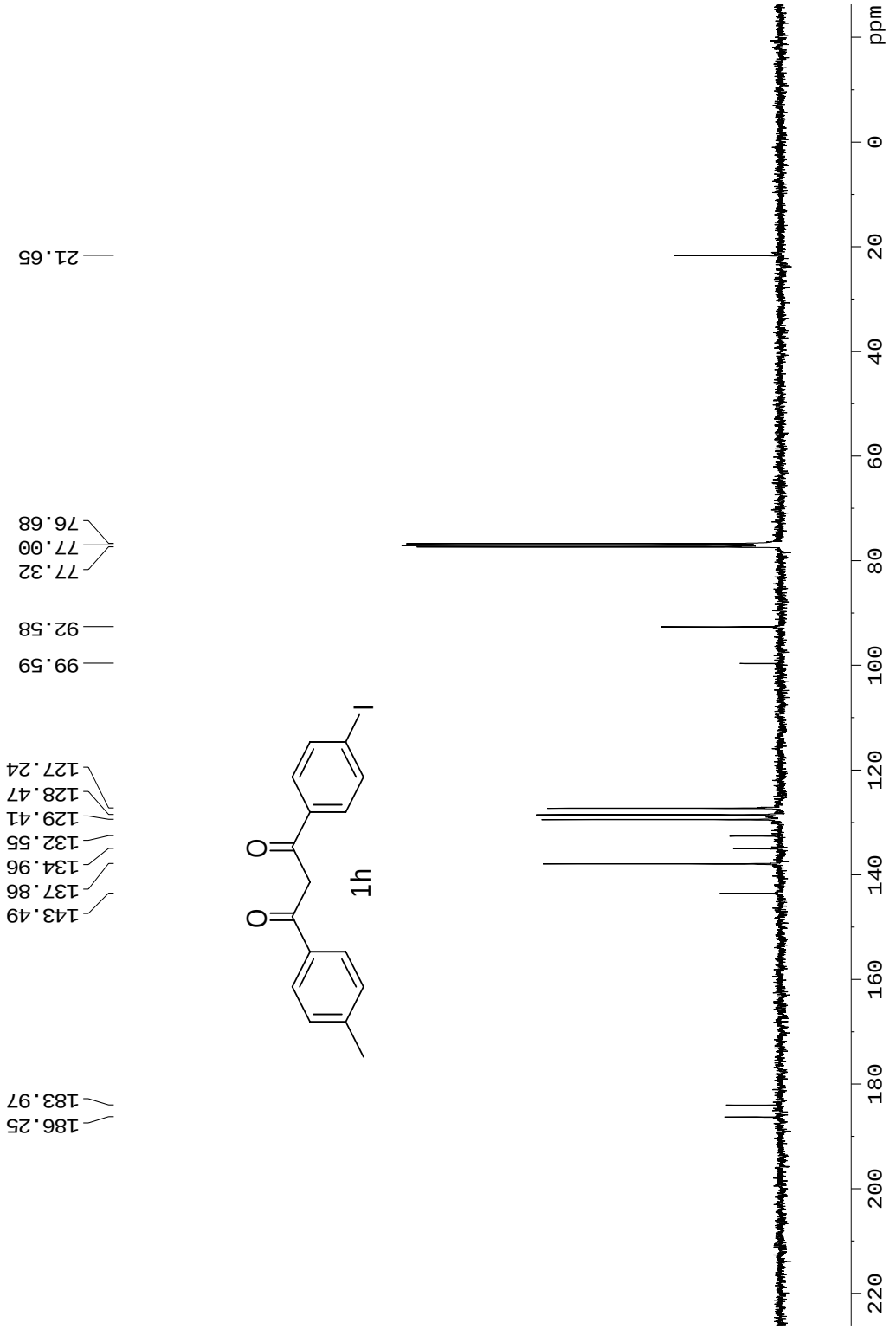
2.39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128.47
129.41
132.55
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143.49
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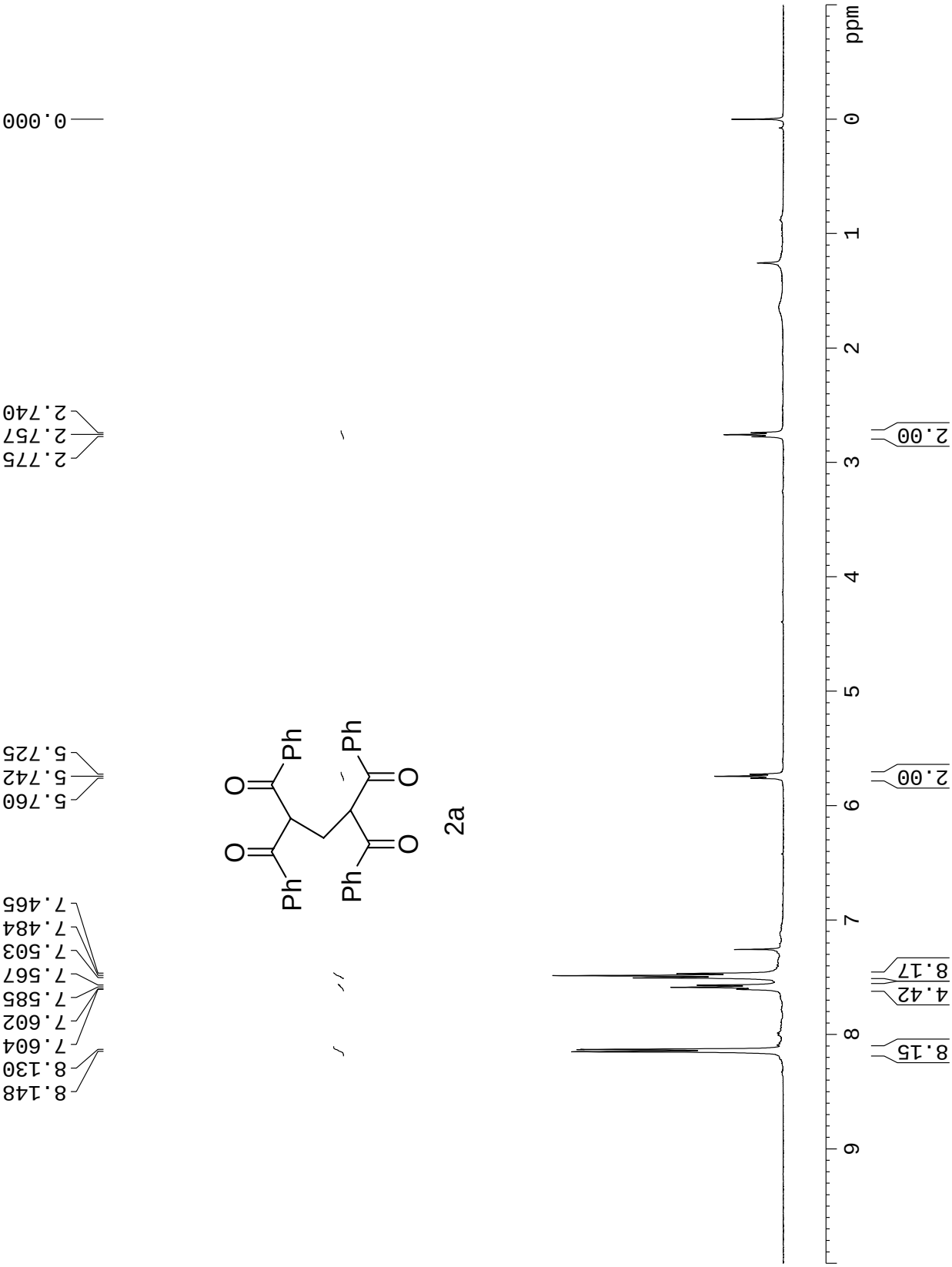
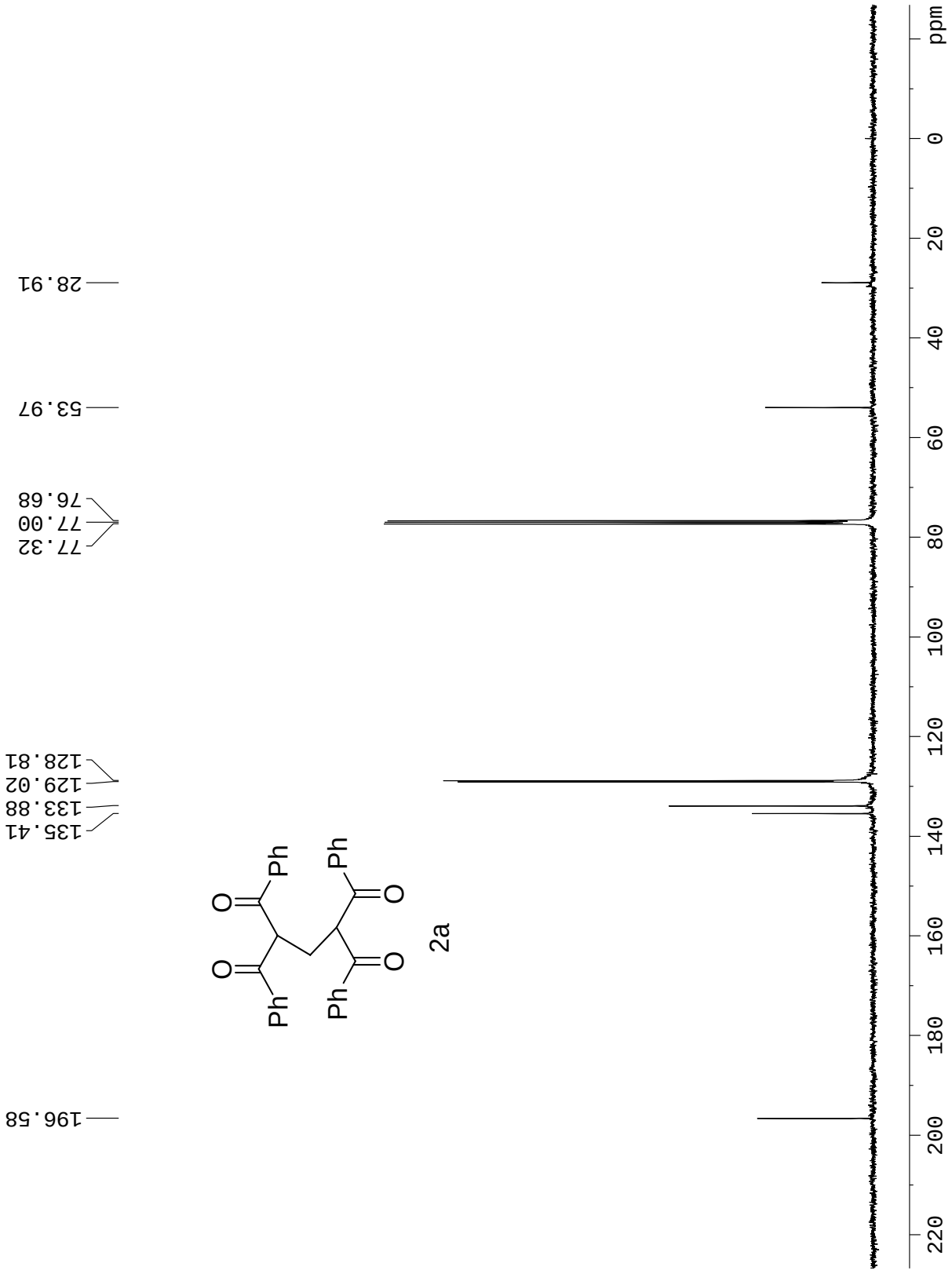
186.25
O
O
I
1h

14. ^{1}H and ^{13}C spectra of products 2a-2y

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77.32
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129.02
133.88
135.41
196.58
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O
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Ph
Ph
Ph
2a
ppm
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40
60
80
100
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140
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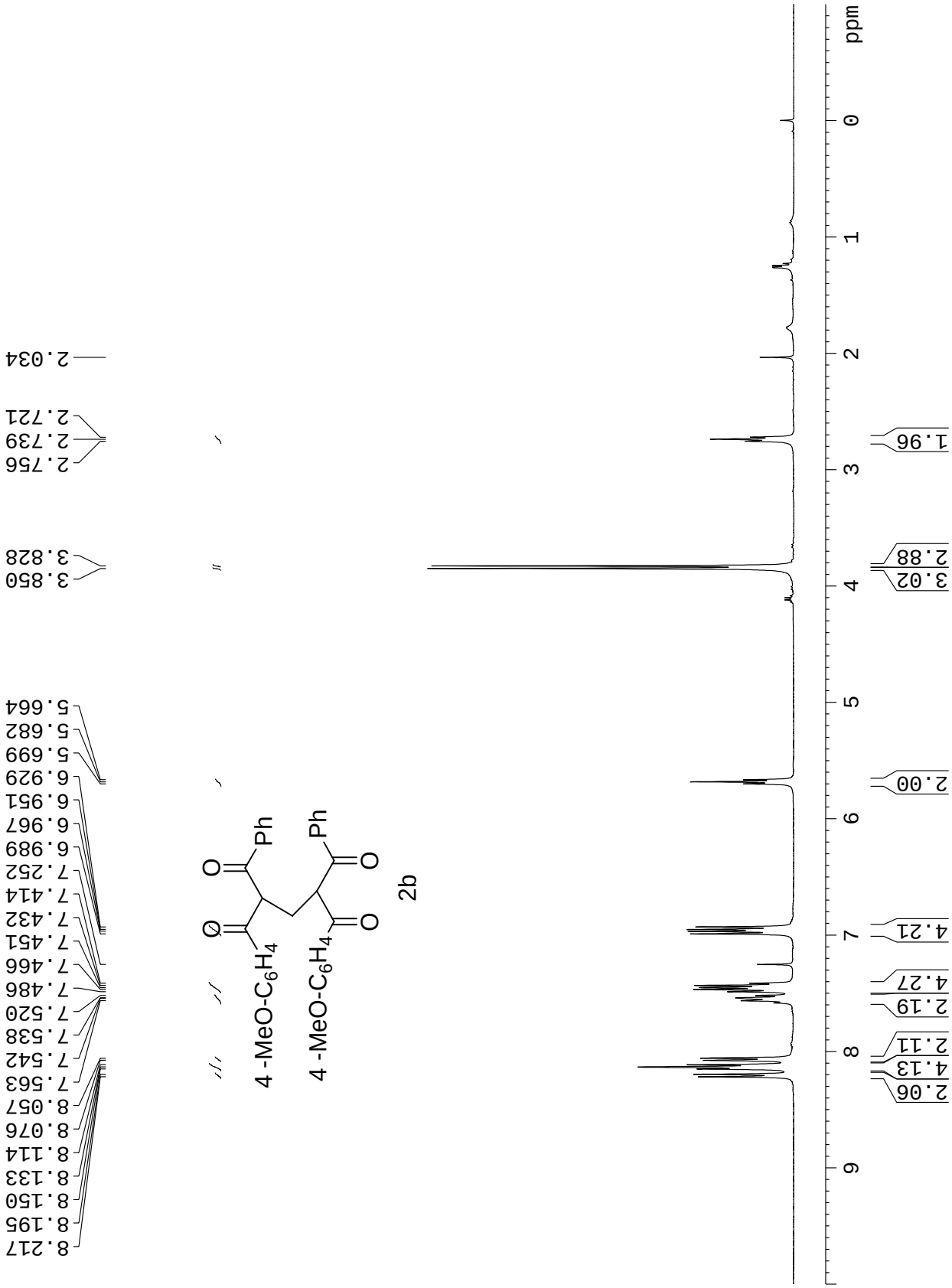
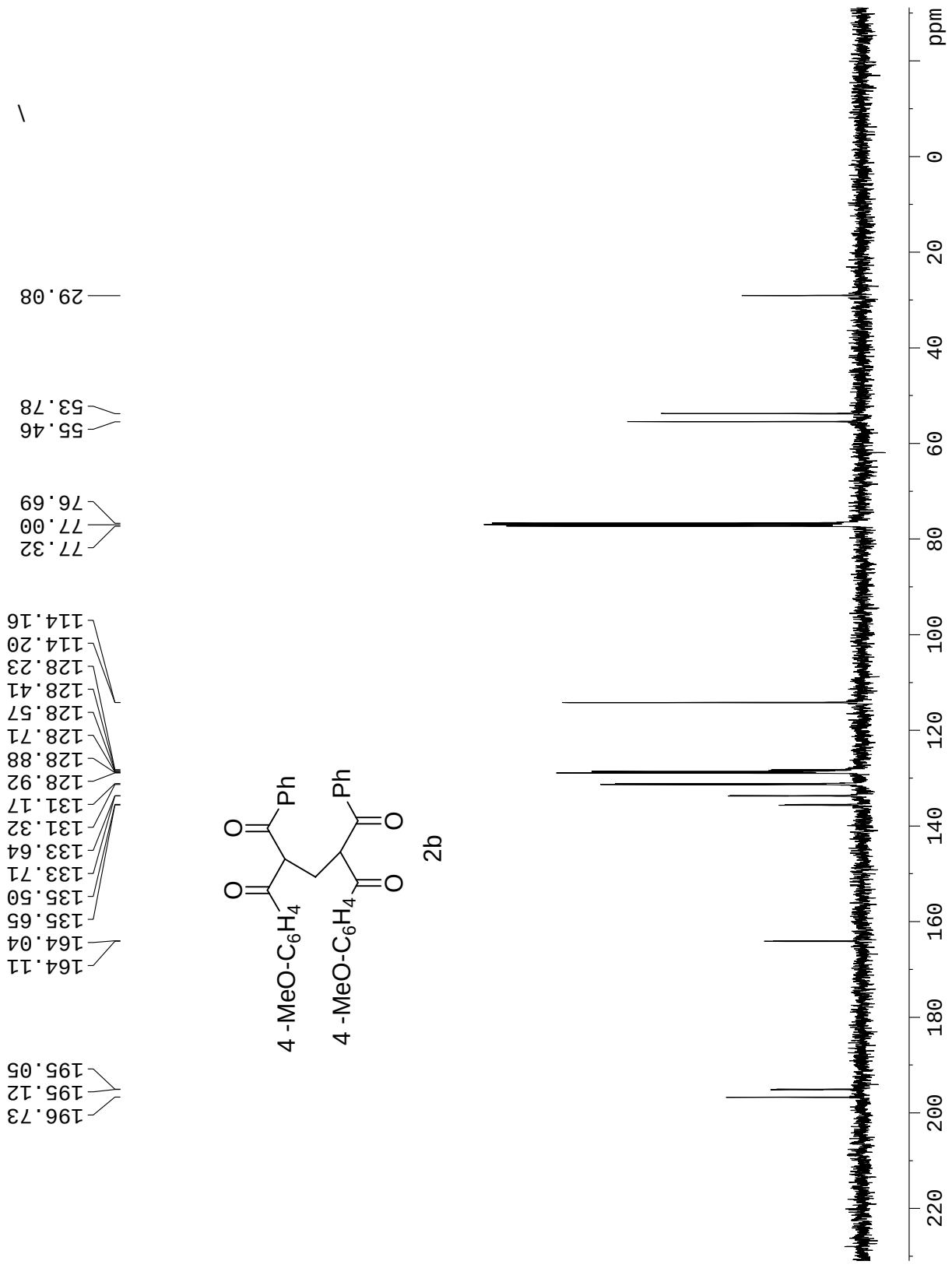
200
220

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77.00
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114.20
128.23
128.41
128.57
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128.88
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131.17
131.32
133.64
133.71
135.50
135.65
164.04
164.11
195.05
195.12
196.73
O
O
Ph
Ph
O
O
4 -MeO-C6H4
4 -MeO-C6H4
2b
ppm
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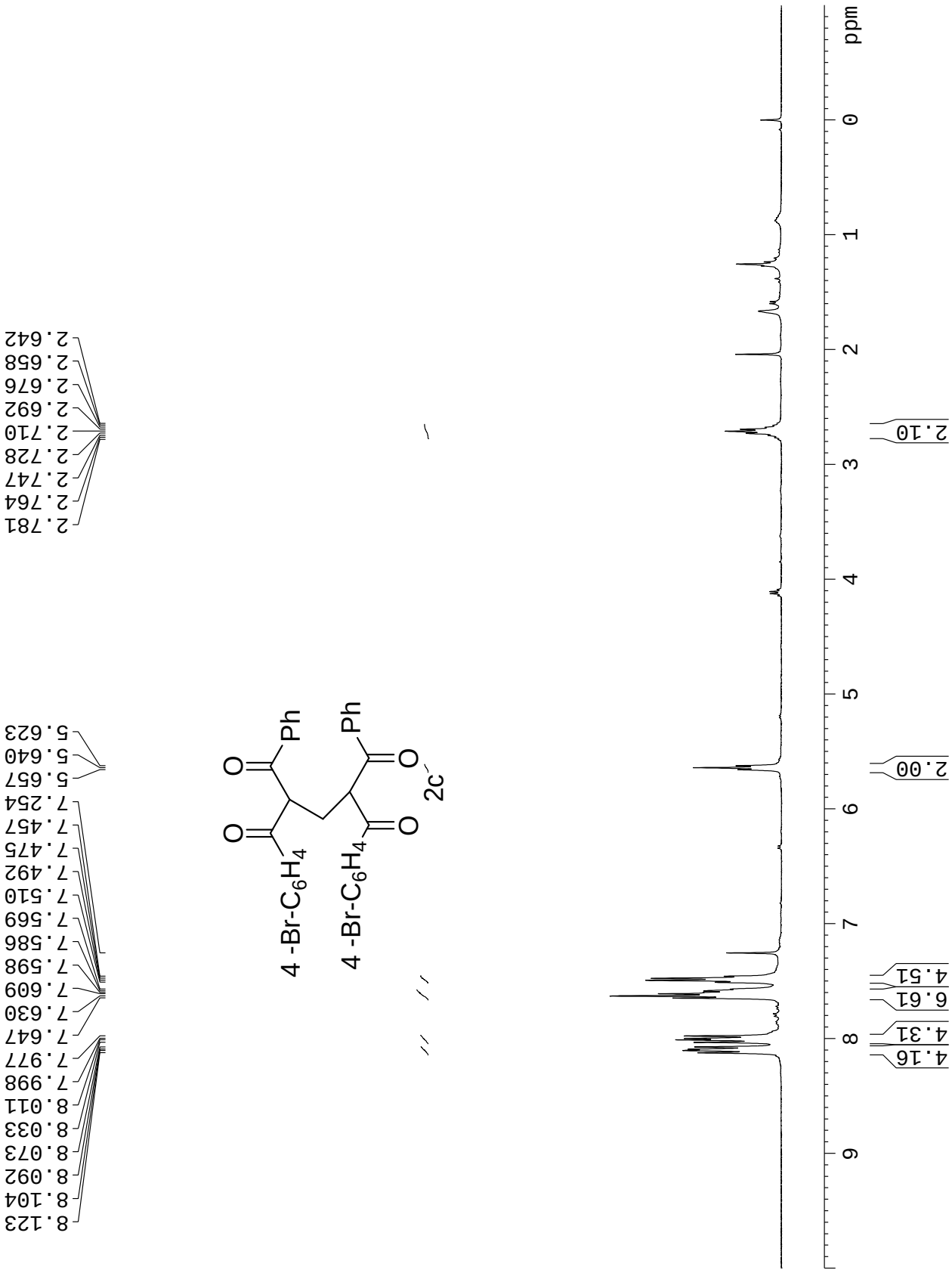
60
80
100
120
140
160
180
200
220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4.51
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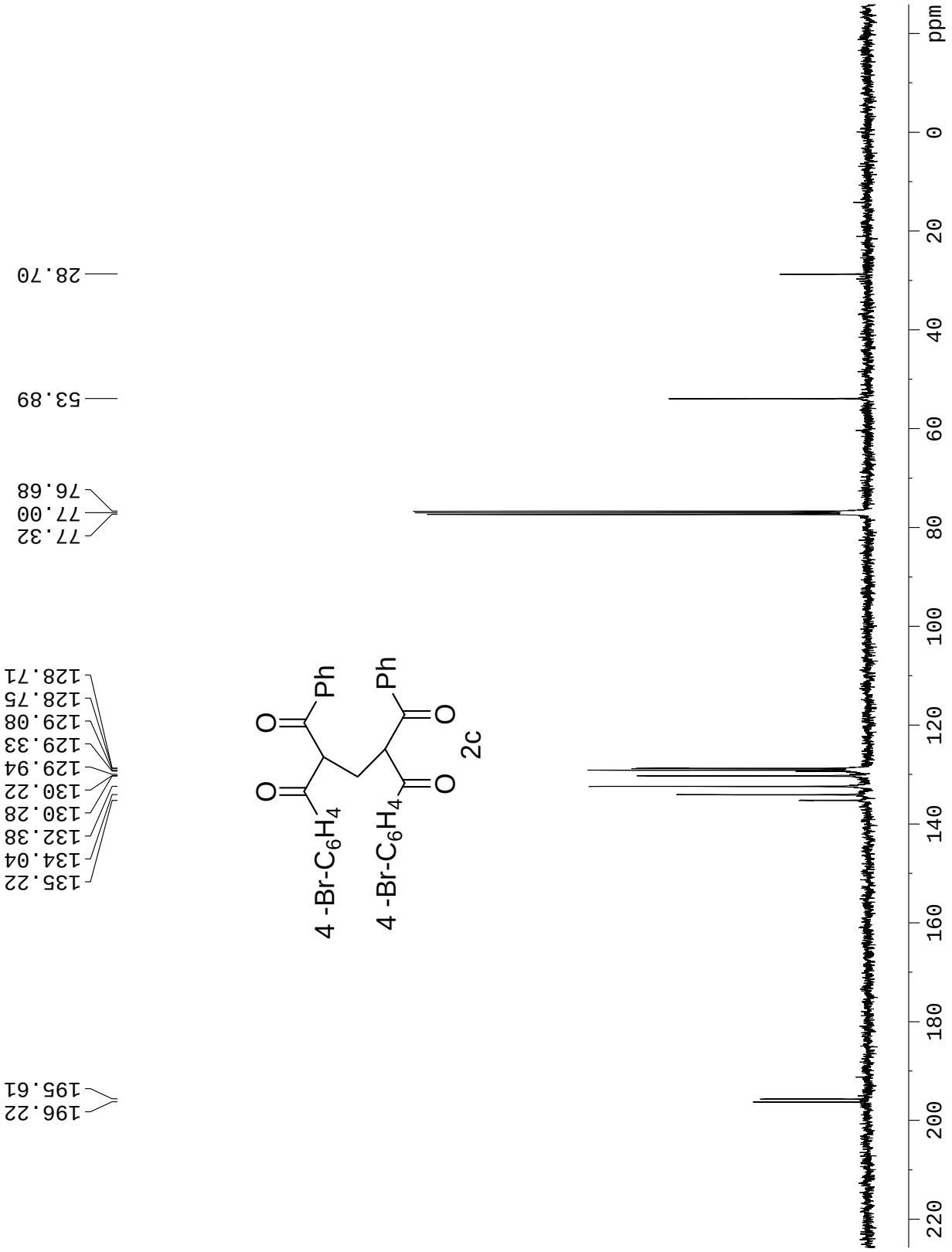
2.676
2.692
2.710
2.728
2.747
2.764
2.781
8.123
8.104
8.092
8.073
8.033
8.011
7.998
7.977
7.647
7.630
7.609
7.598
7.586
7.569
7.510
7.492
7.475
7.457
7.254
5.657
5.640
5.623
O
Ph
4 -Br-C6H4
2c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77.00
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129.08
129.33
129.94
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130.28
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134.04
135.22
196.22
195.61
O
Ph
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2c
ppm
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80
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140
160
180
200
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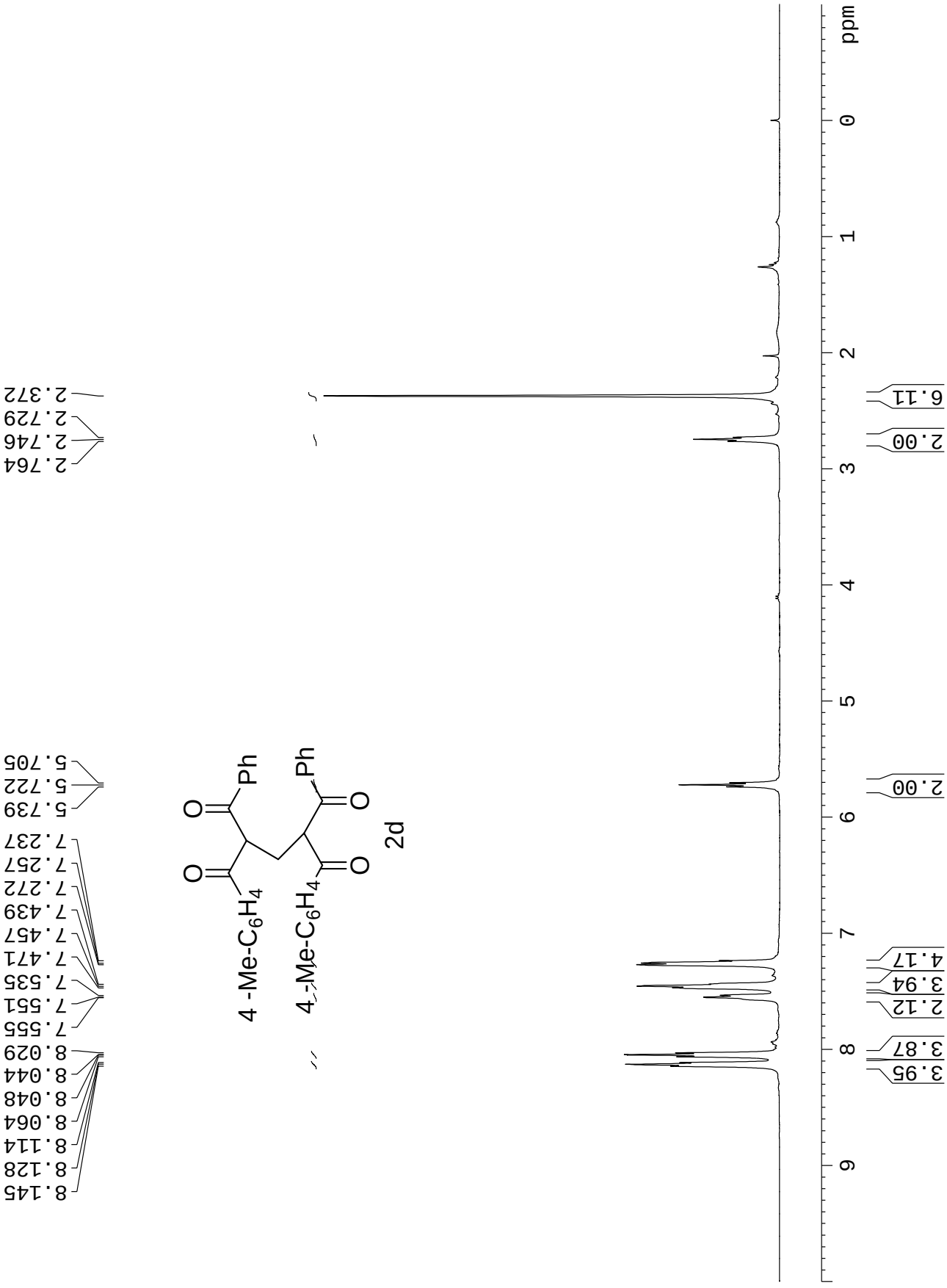
ppm
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3
4
5
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7
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8.048
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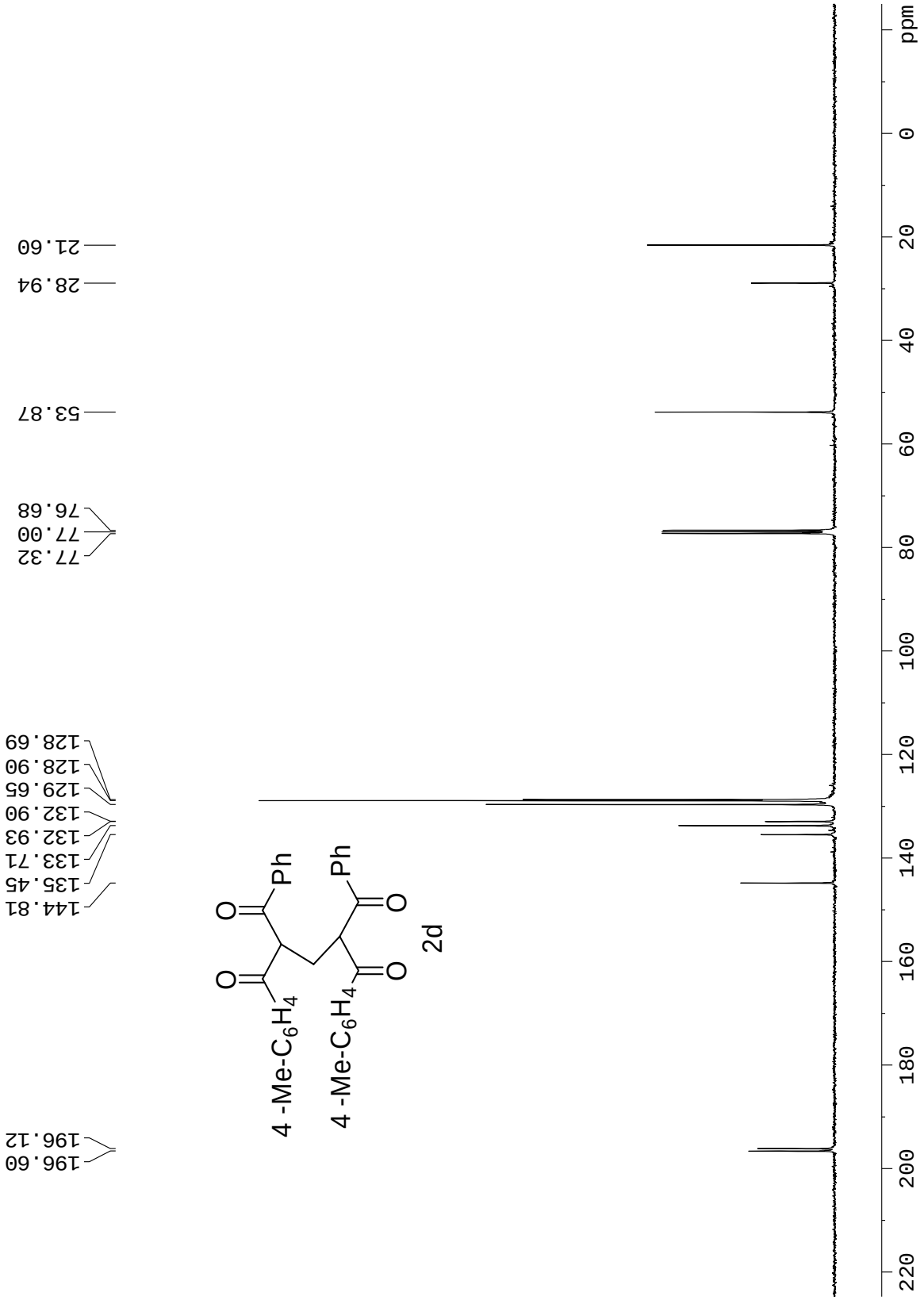
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196.12
196.60
4 -Me-C6H4
Ph
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O
4 -Me-C6H4
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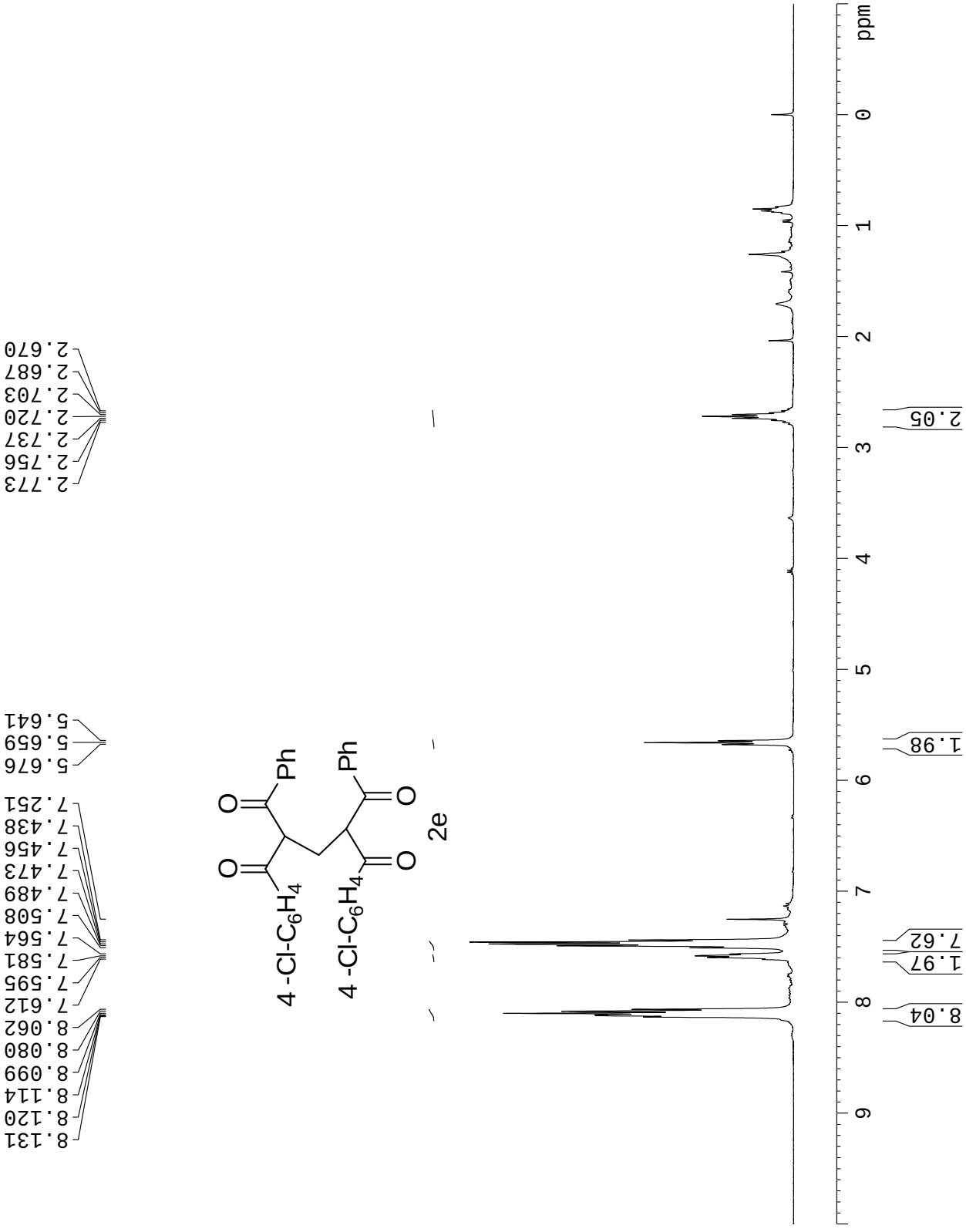
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7.612
7.595
7.581
7.564
7.508
7.489
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O
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Ph
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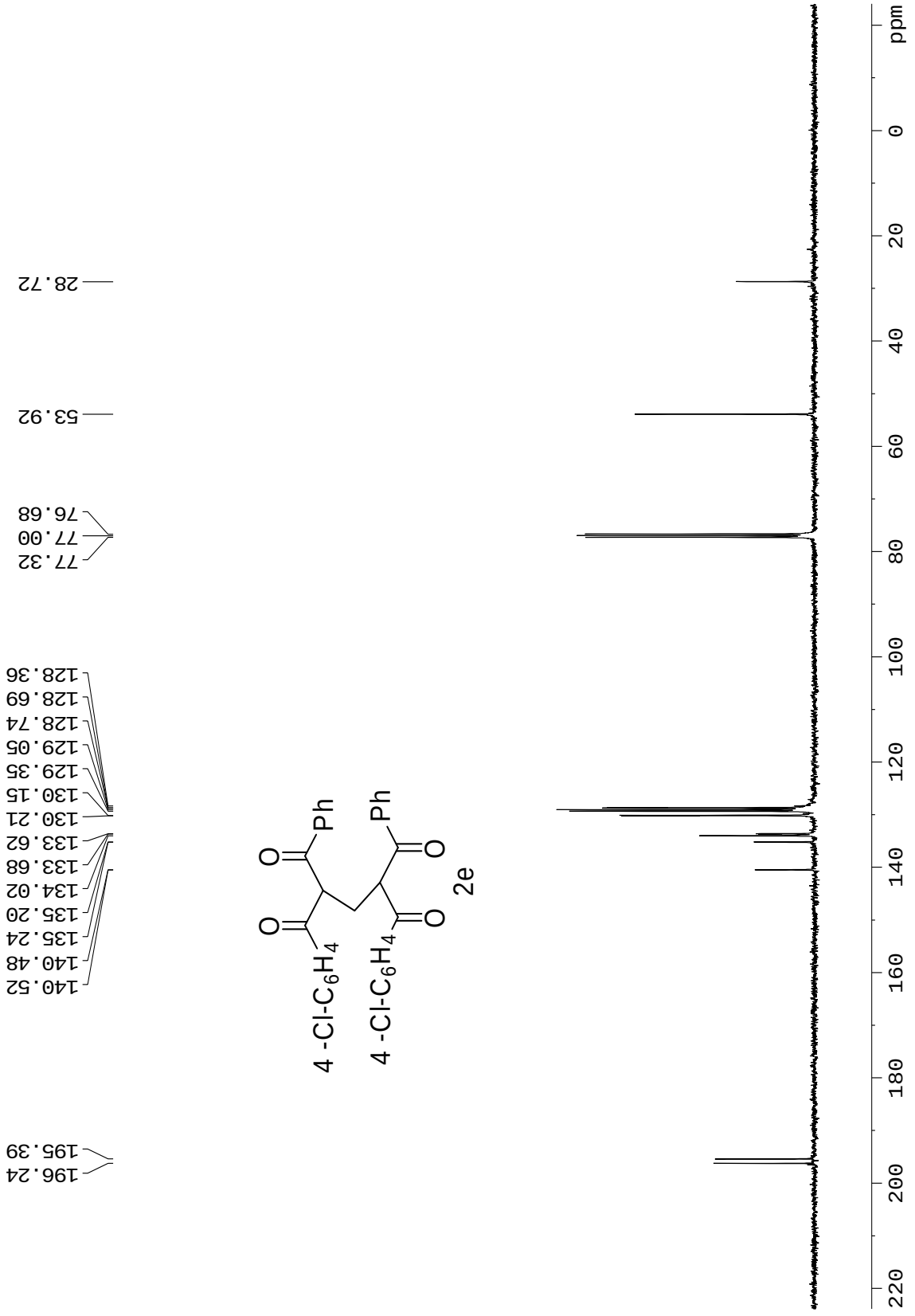
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135.24
140.48
140.52
195.39
196.24
O
Ph
O
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O
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2e
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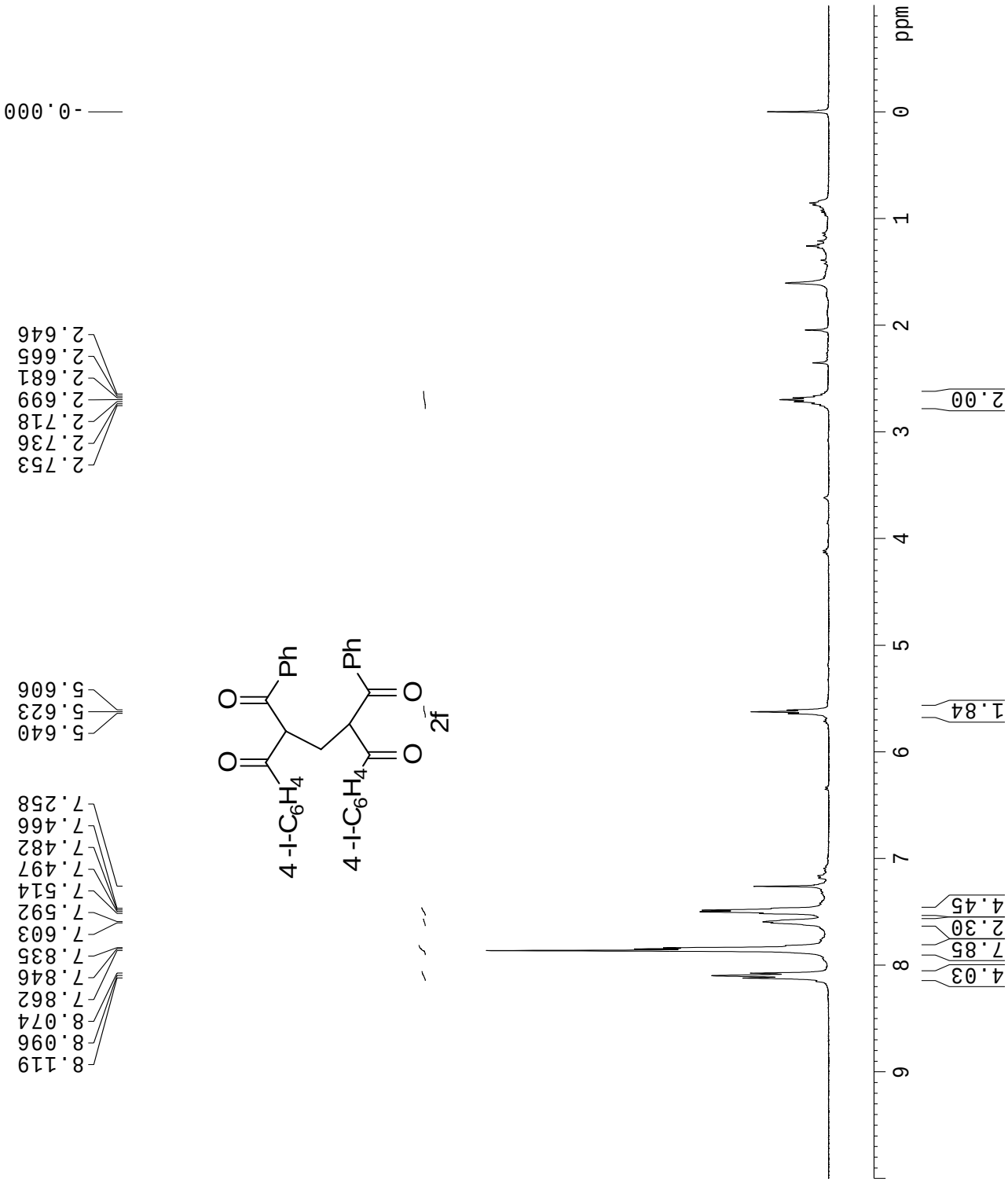
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8.074
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7.846
7.835
7.603
7.592
7.514
7.497
7.482
7.466
7.258
Ph
O
O
4 -I-C6H4
Ph
O
O
4 -I-C6H4
2f
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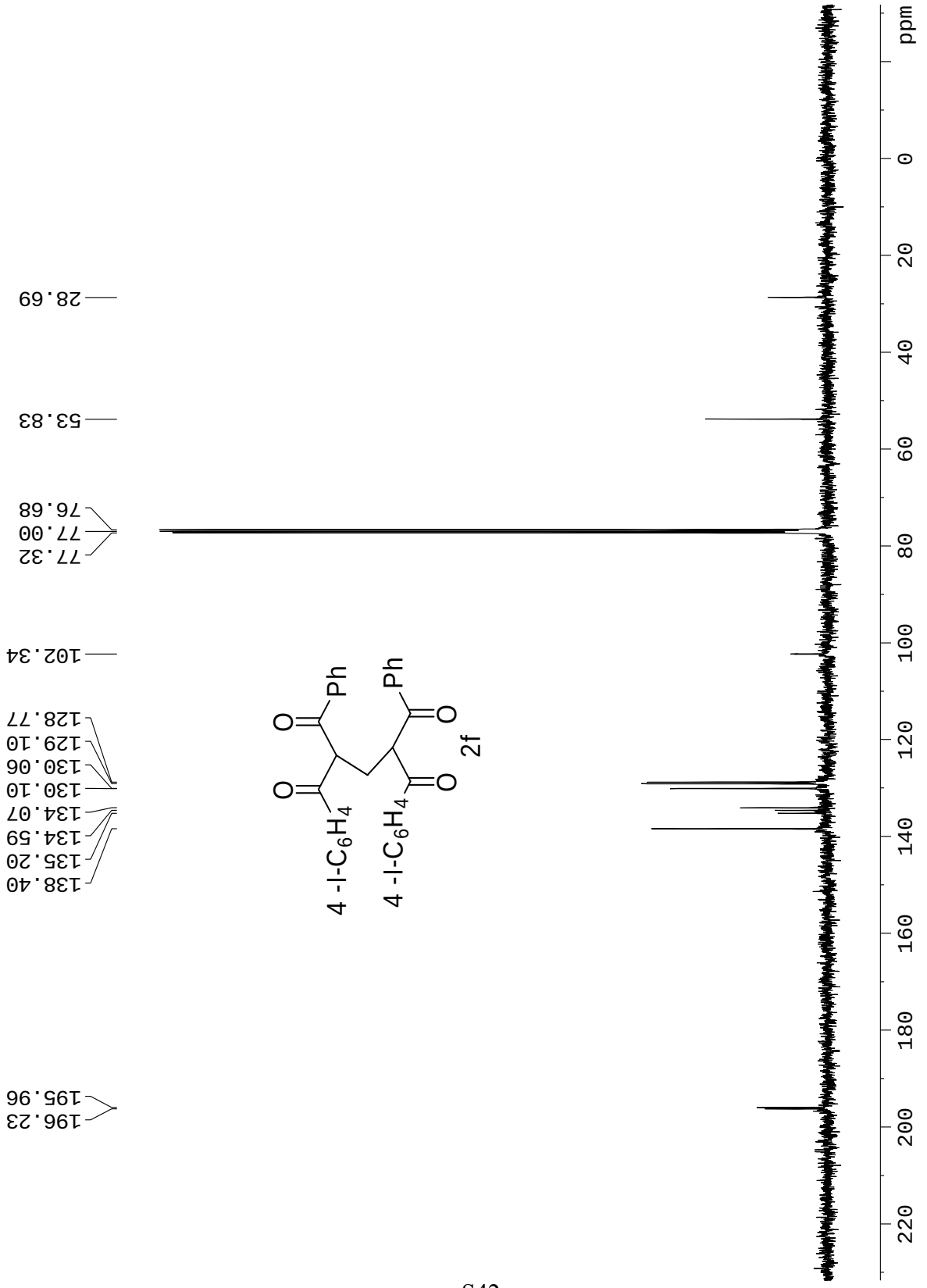
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195.96
196.23
ppm
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60
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200
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Ph
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O
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Ph
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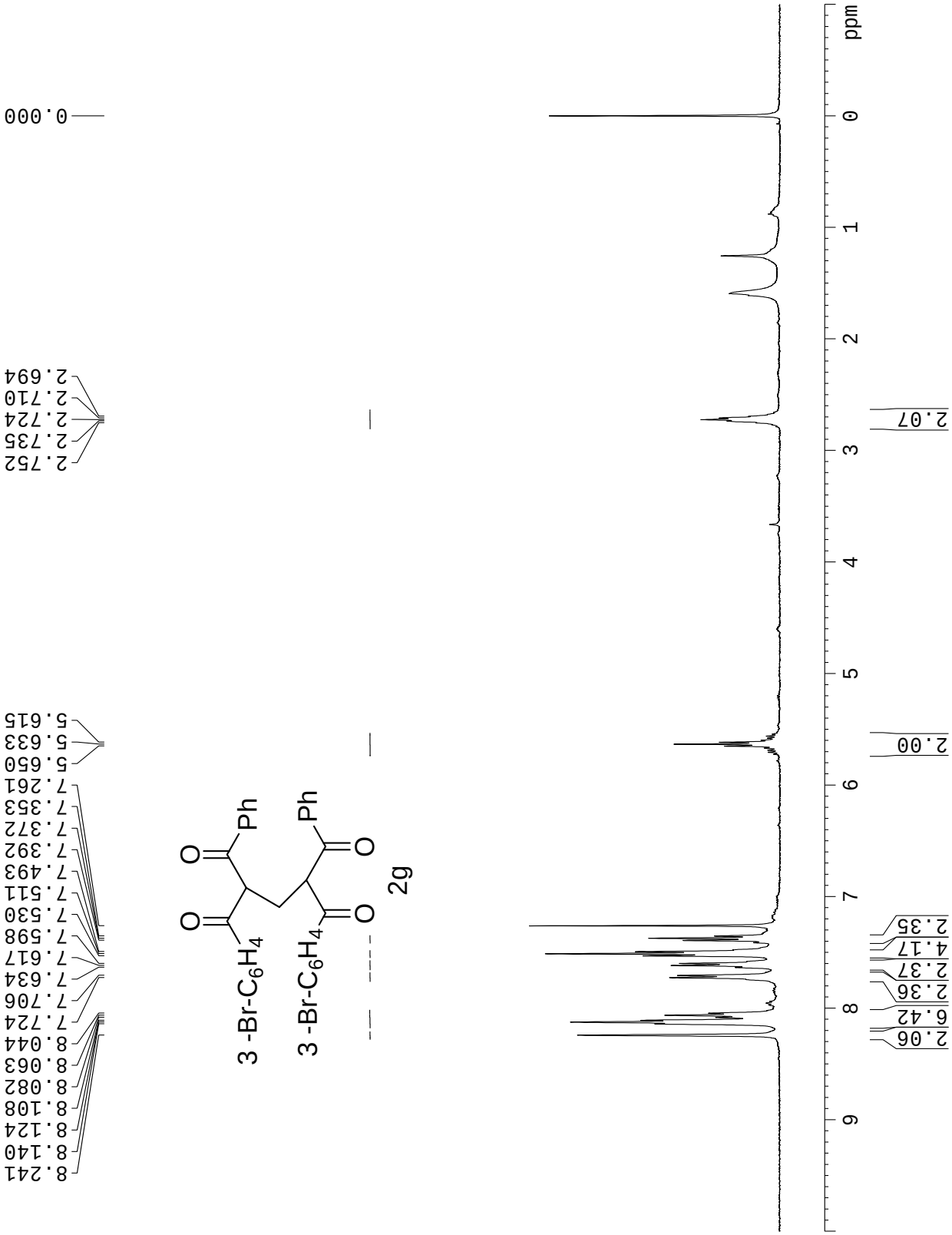
O
4 -I-C6H4
2f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7.598
7.617
7.634
7.706
7.724
8.044
8.063
8.082
8.108
8.124
8.140
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O
Ph
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O
O
Ph
3 -Br-C6H4
2g
ppm
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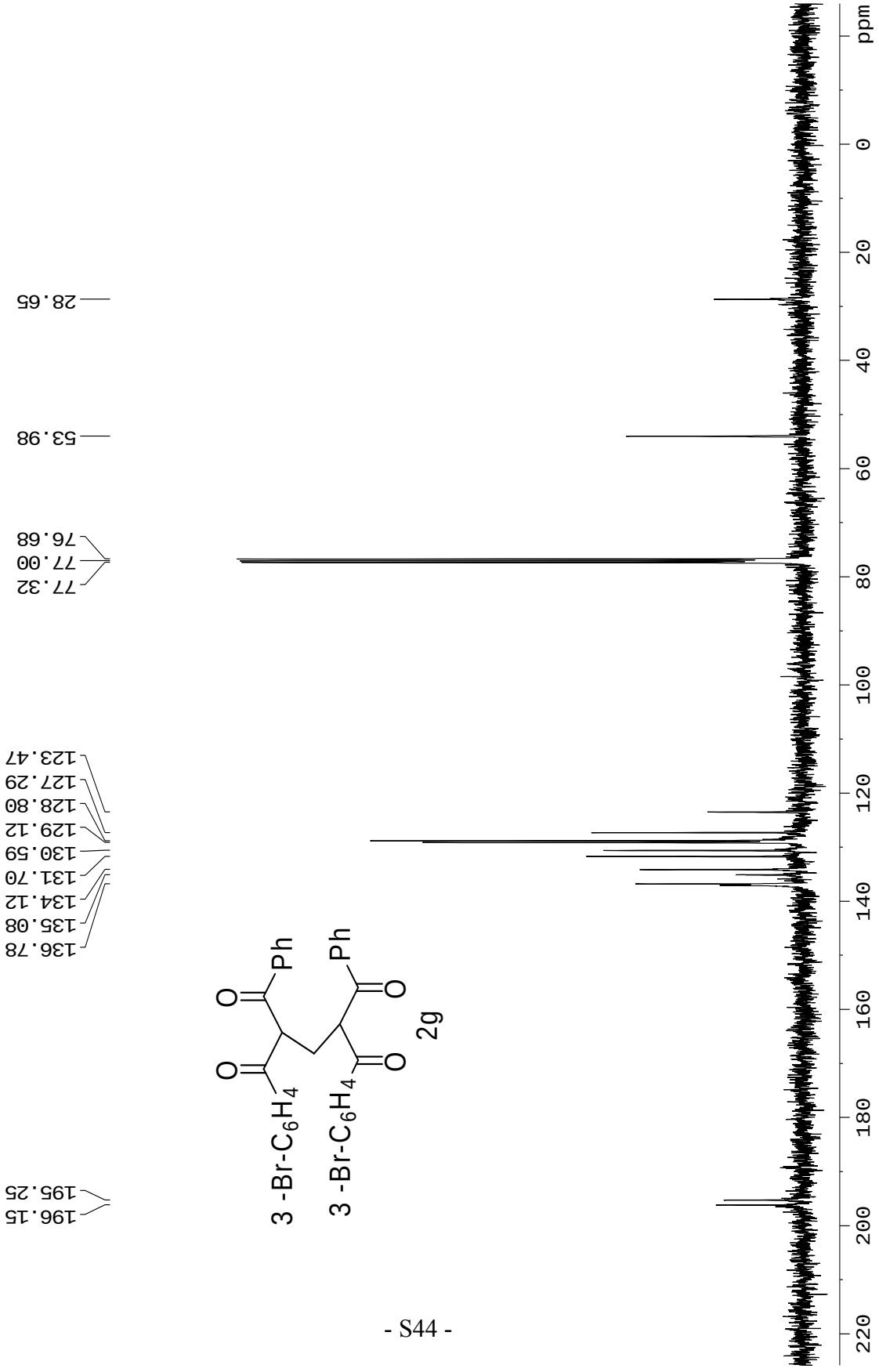
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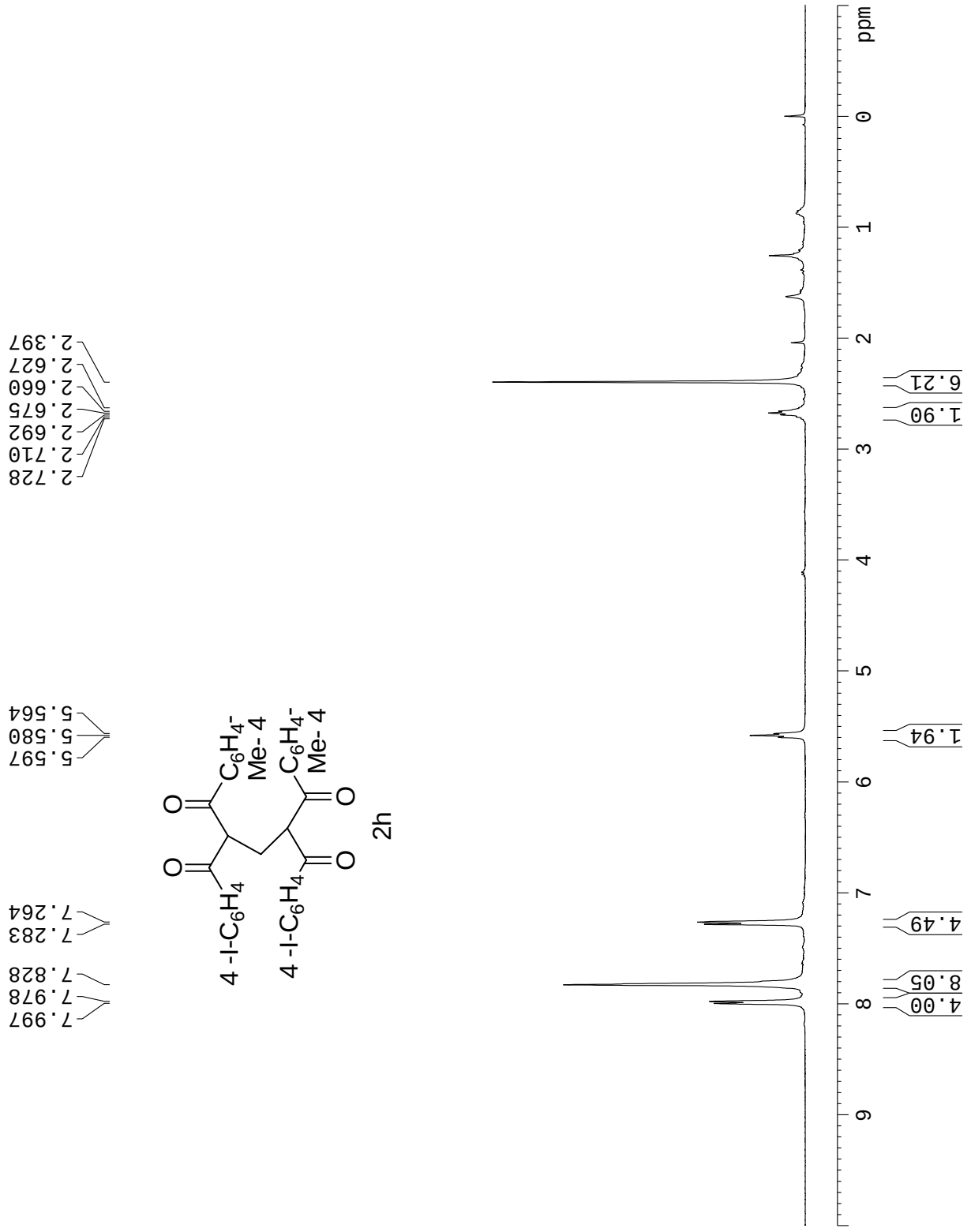
O
Ph
O
3 -Br-C6H4
2g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2.675
2.692
2.710
2.728
5.564
5.580
5.597
7.264
7.283
7.828
7.978
7.997
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4 -I-C6H4
C6H4-
Me- 4
C6H4-
Me- 4
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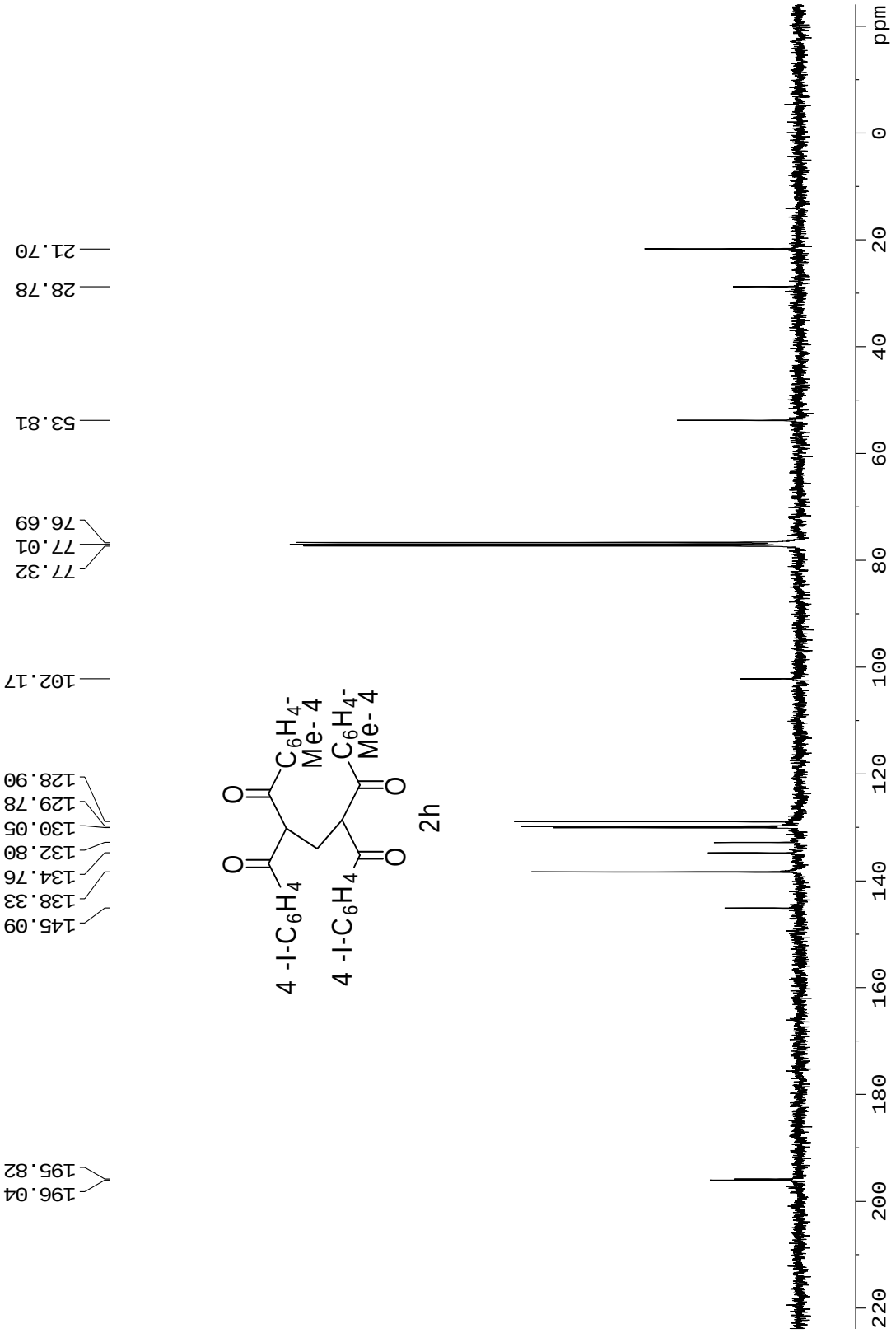
O
O
O
2h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102.17
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129.78
130.05
132.80
134.76
138.33
145.09
196.04
195.82
2h
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O
O
C6H4-
Me- 4
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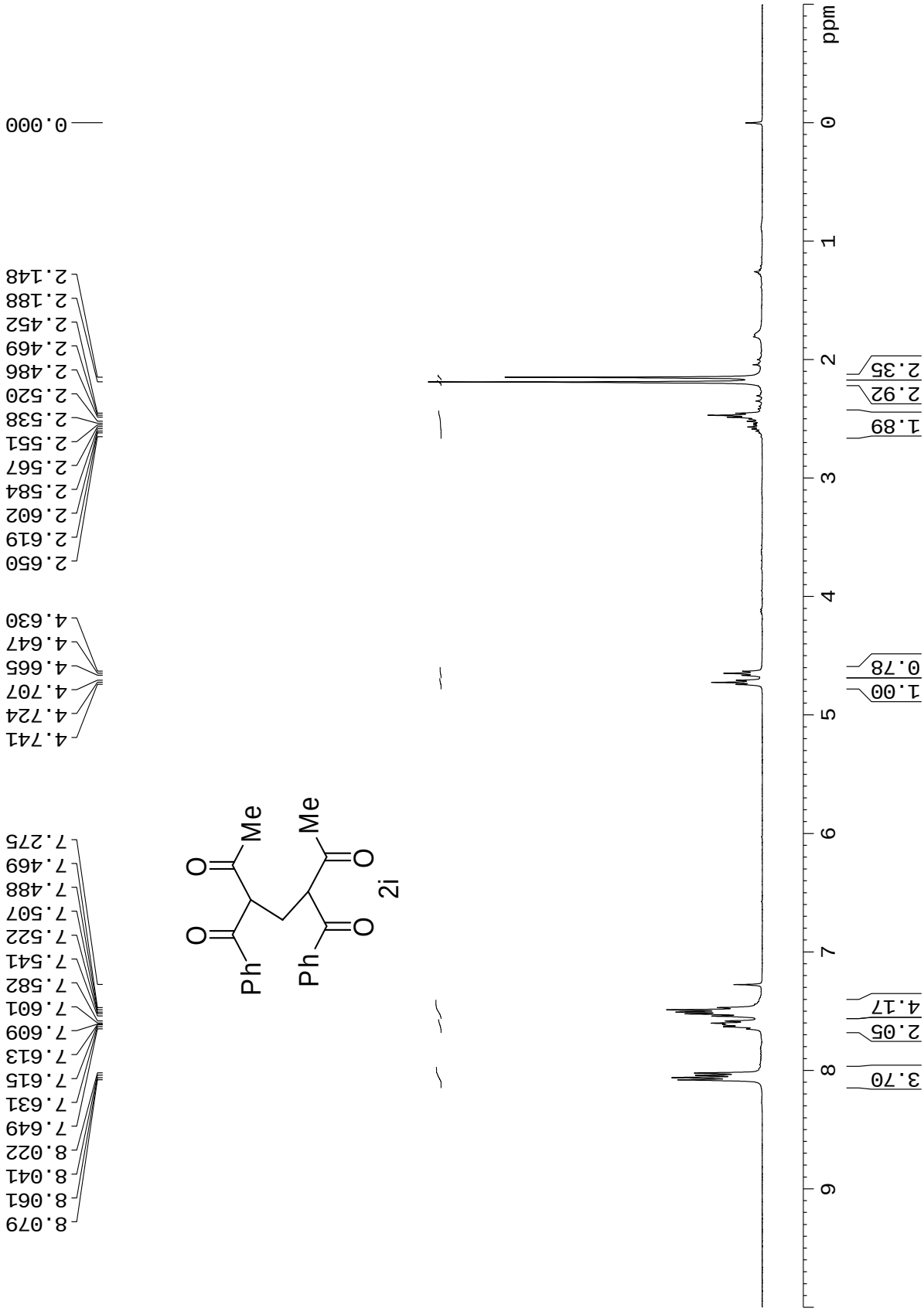
O
C6H4-
Me- 4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4.630
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7.541
7.582
7.601
7.609
7.613
7.615
7.631
7.649
8.022
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8.061
8.079
O
Me
Me
O
O
O
Ph
Ph
2i
ppm
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2
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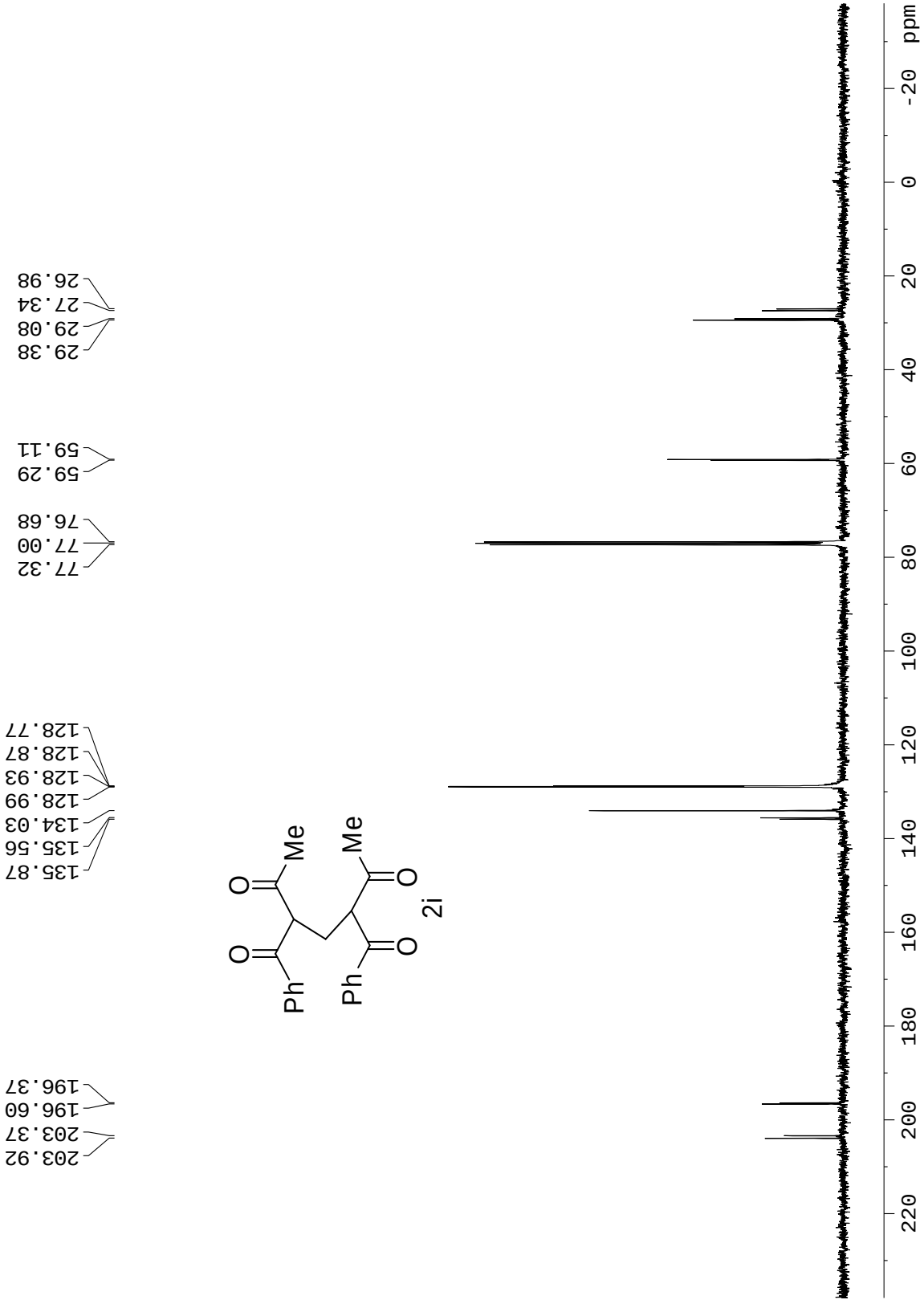
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135.87
196.37
196.60
203.37
203.92
Me
Me
O
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Ph
2i
ppm
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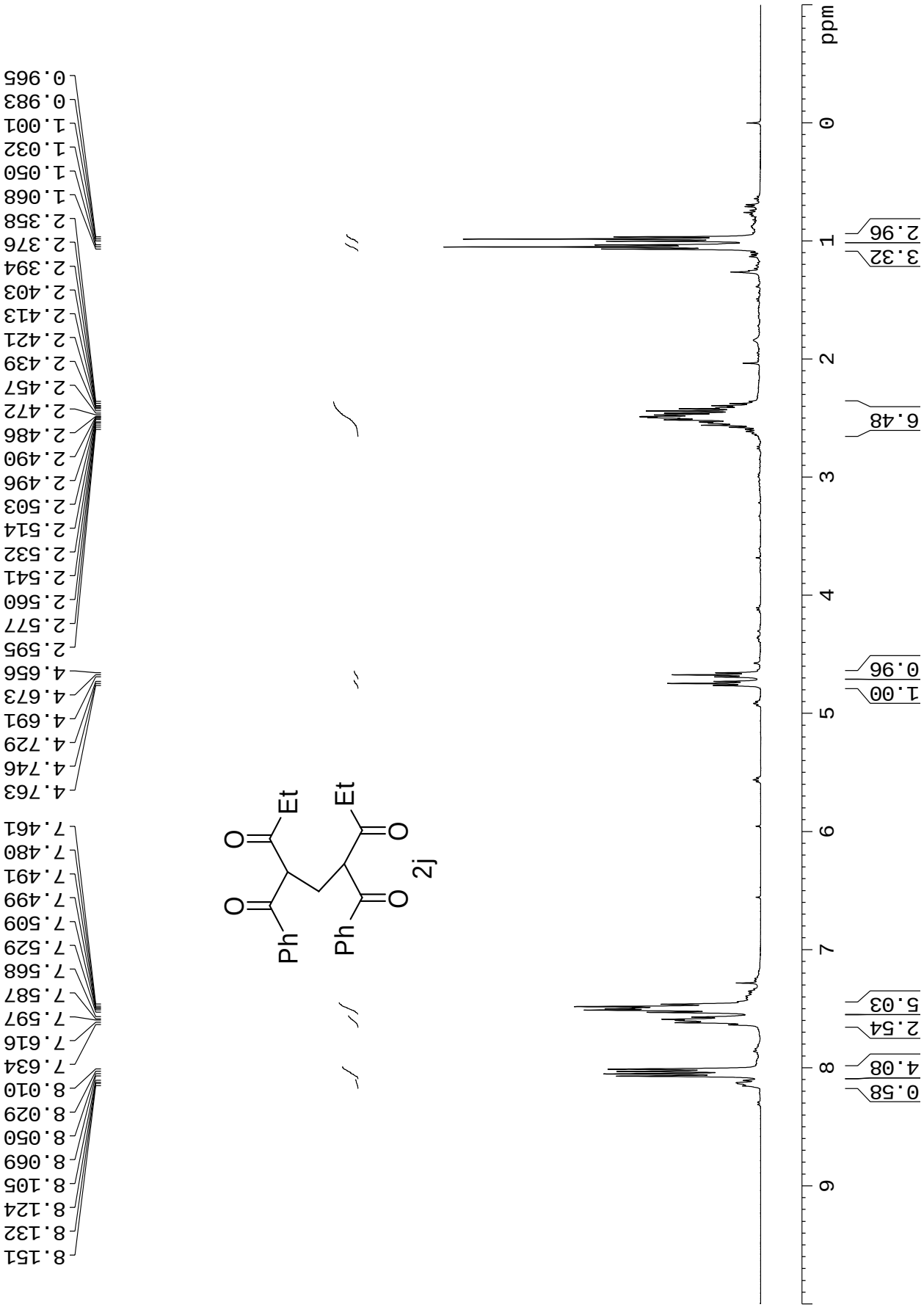

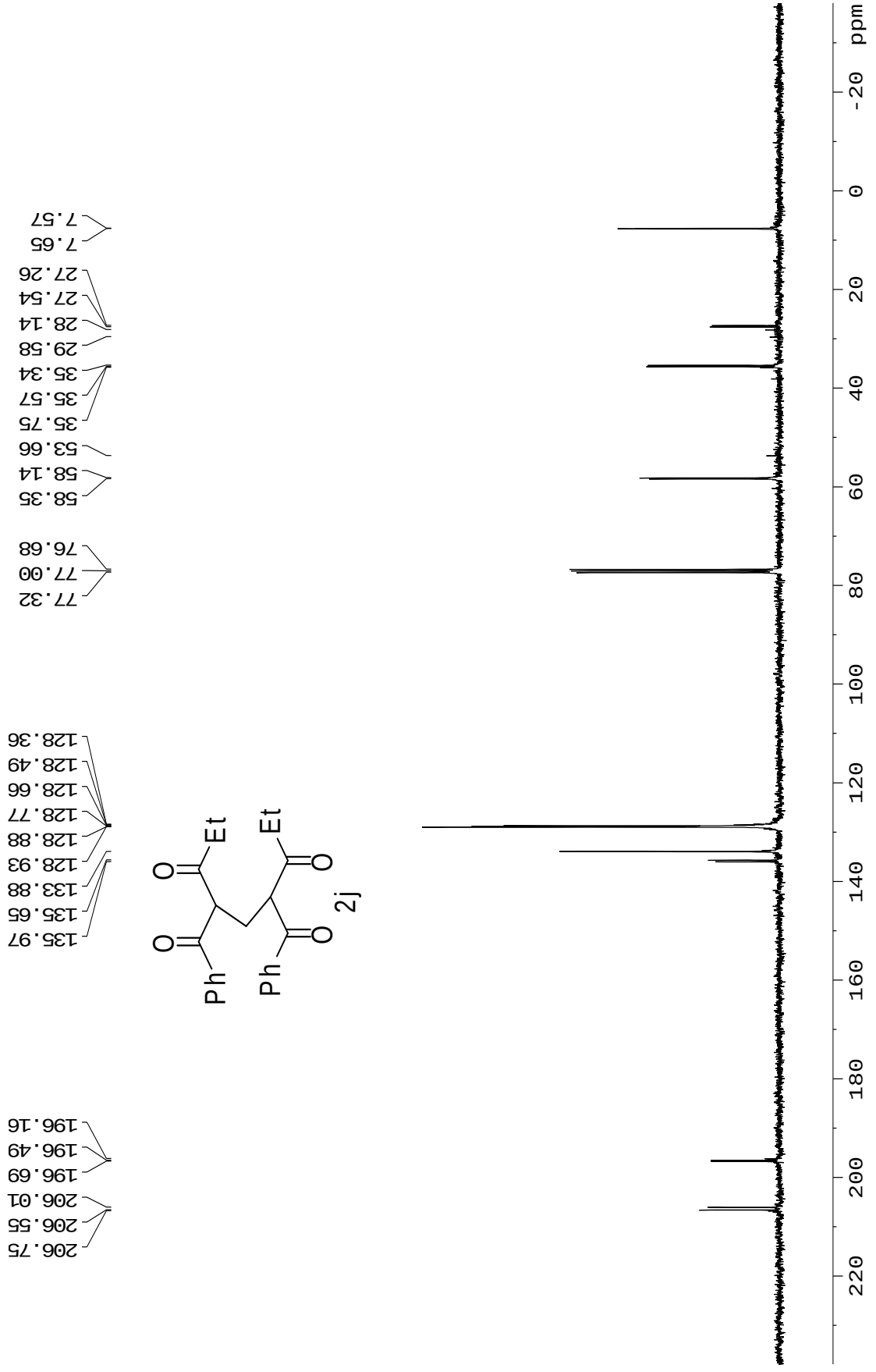

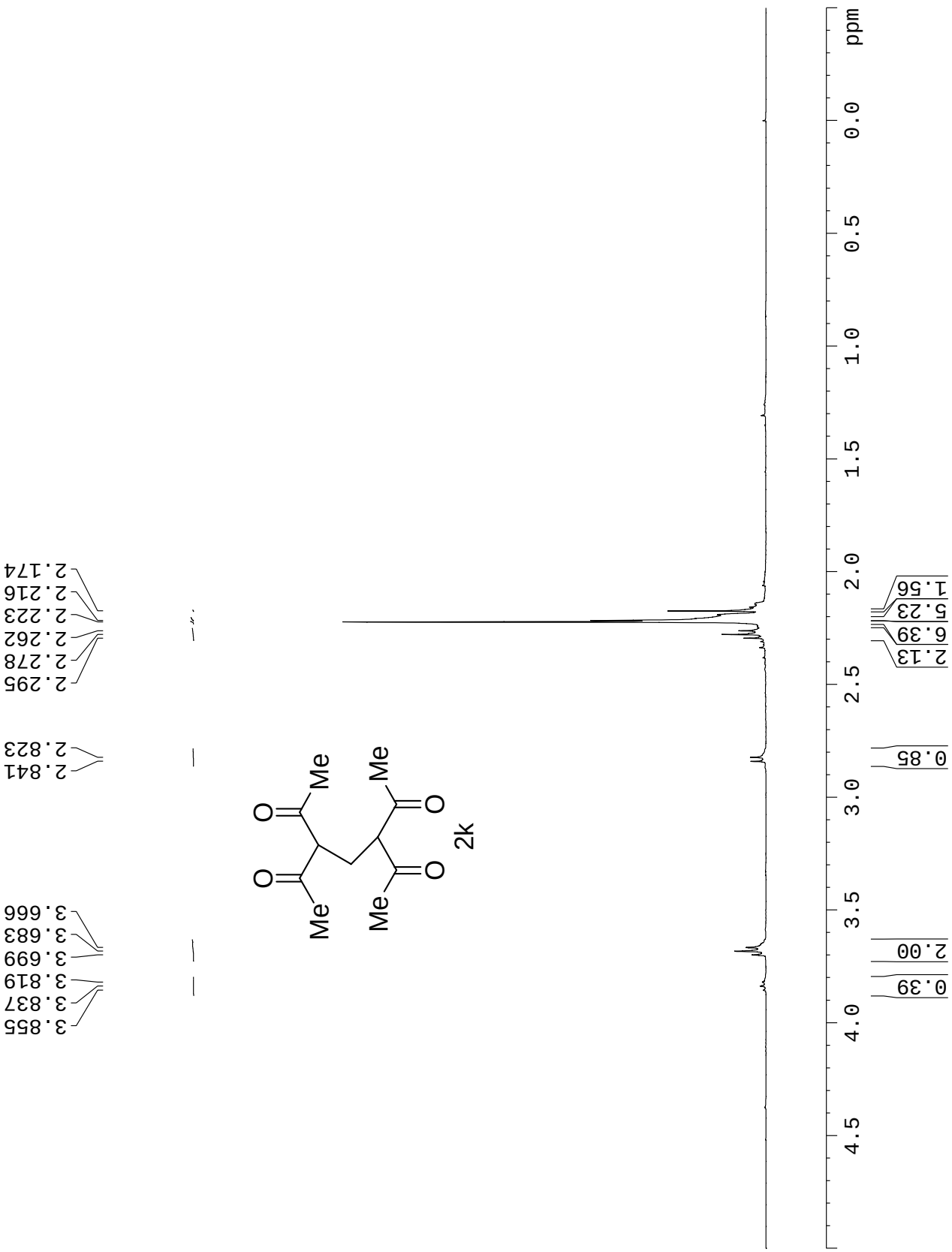
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2.223
2.262
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2.295
2.823
2.841
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Me
Me
Me
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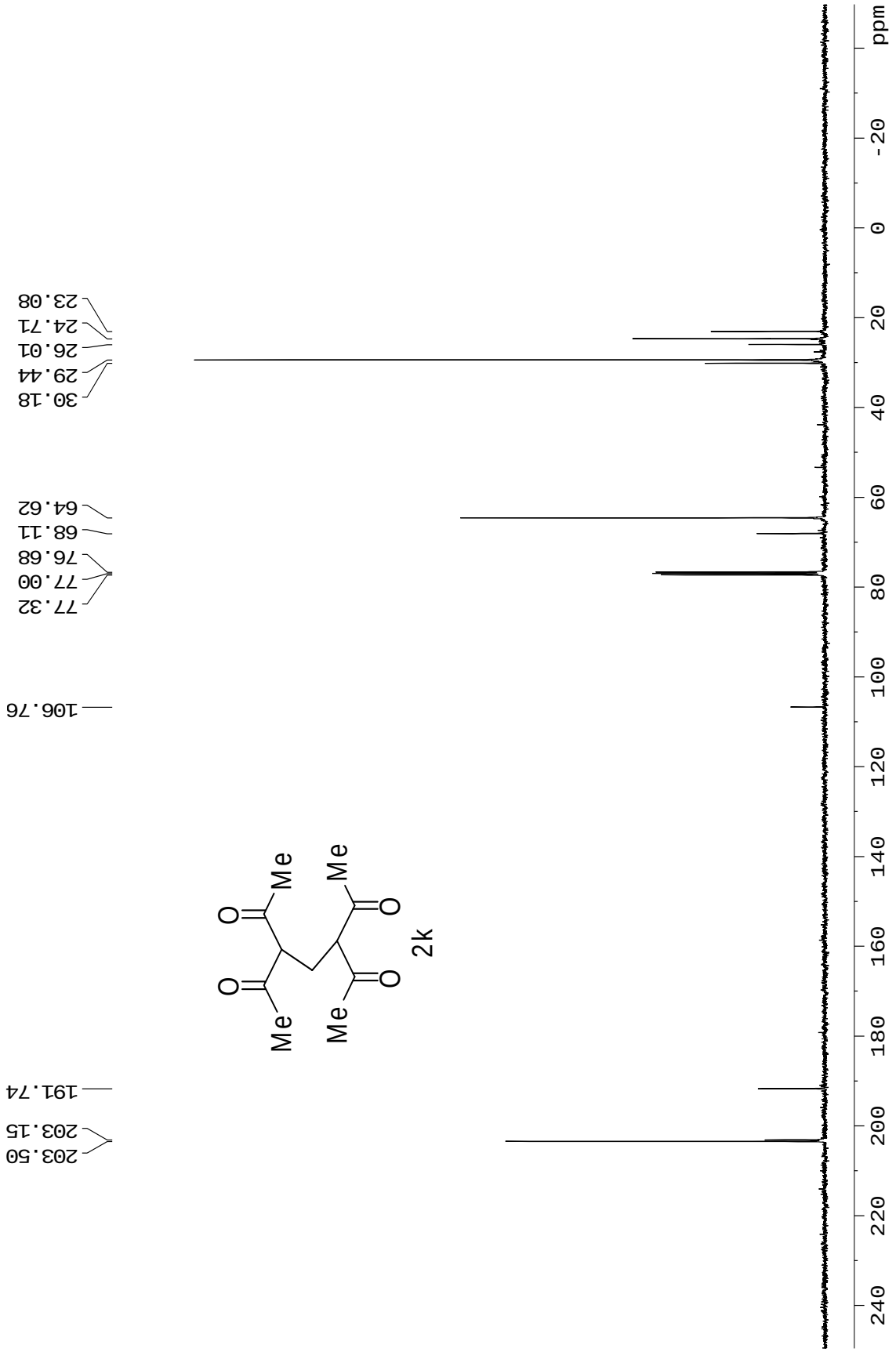
O
O
O
2k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Me
Me
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ppm
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0
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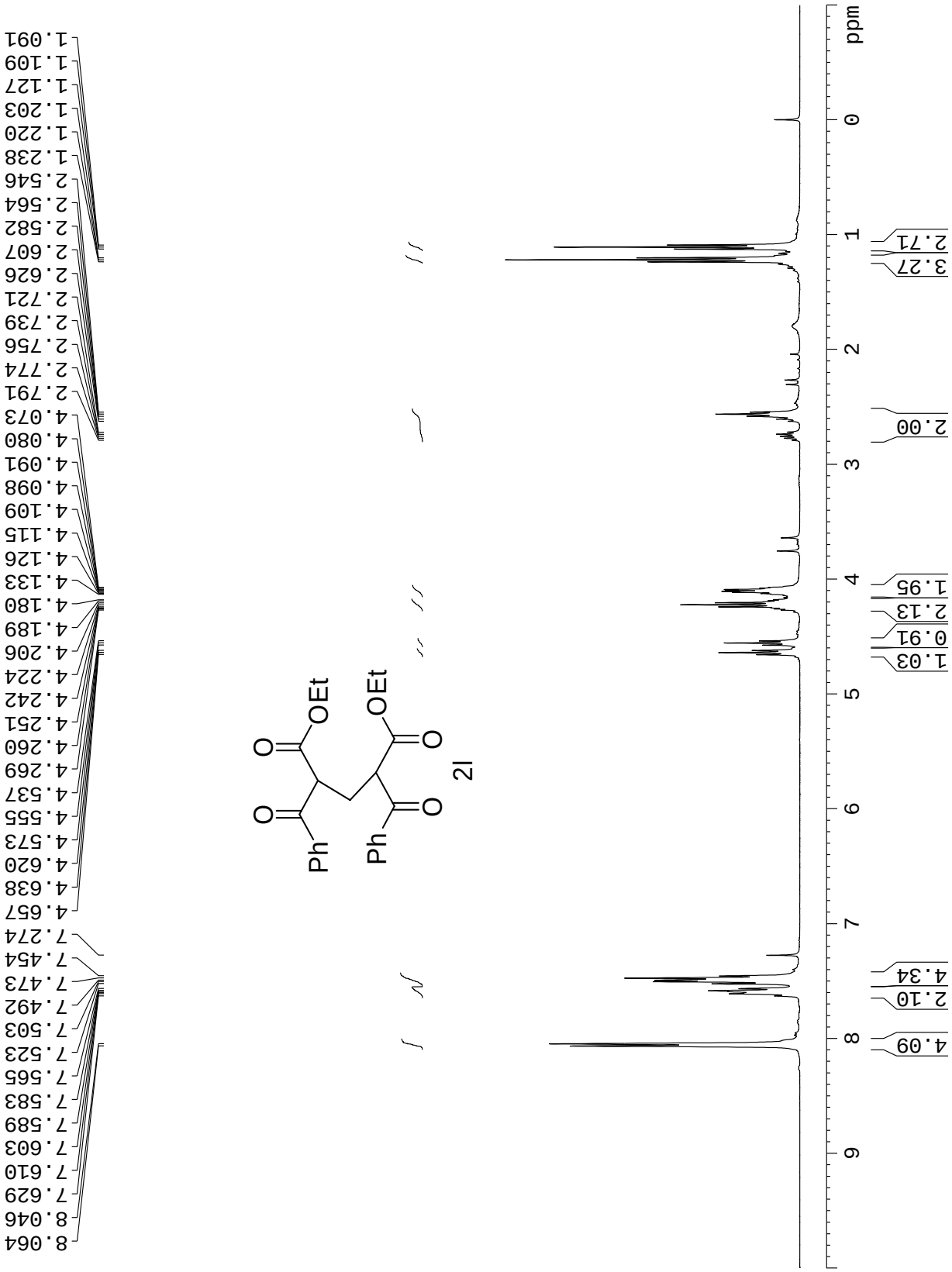
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2.739
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4.080
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4.115
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4.260
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4.537
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7.629
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OEt
OEt
O
O
O
O
Ph
Ph
2I
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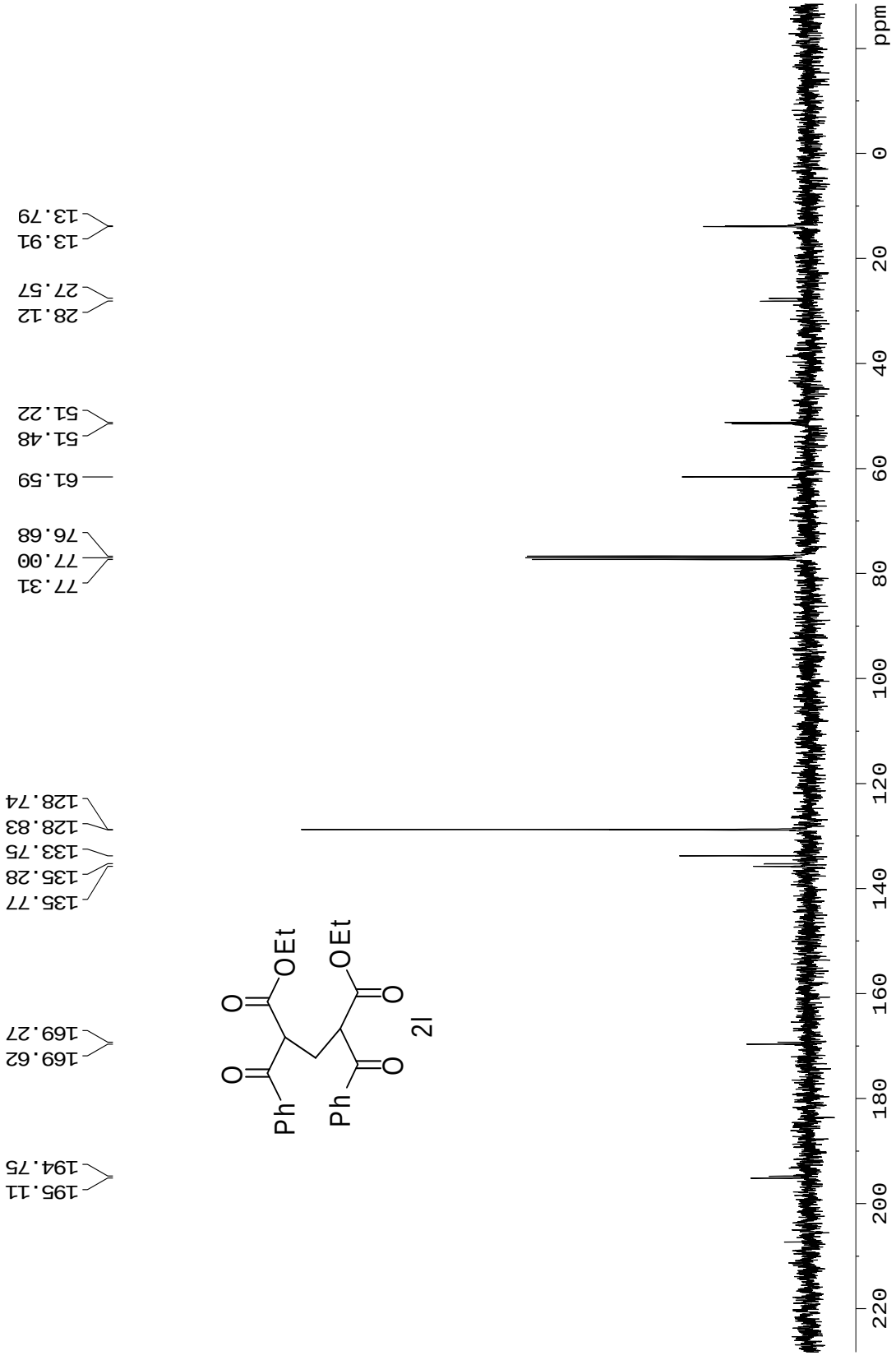
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169.62
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195.11
OEt
OEt
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Ph
Ph
2I
ppm
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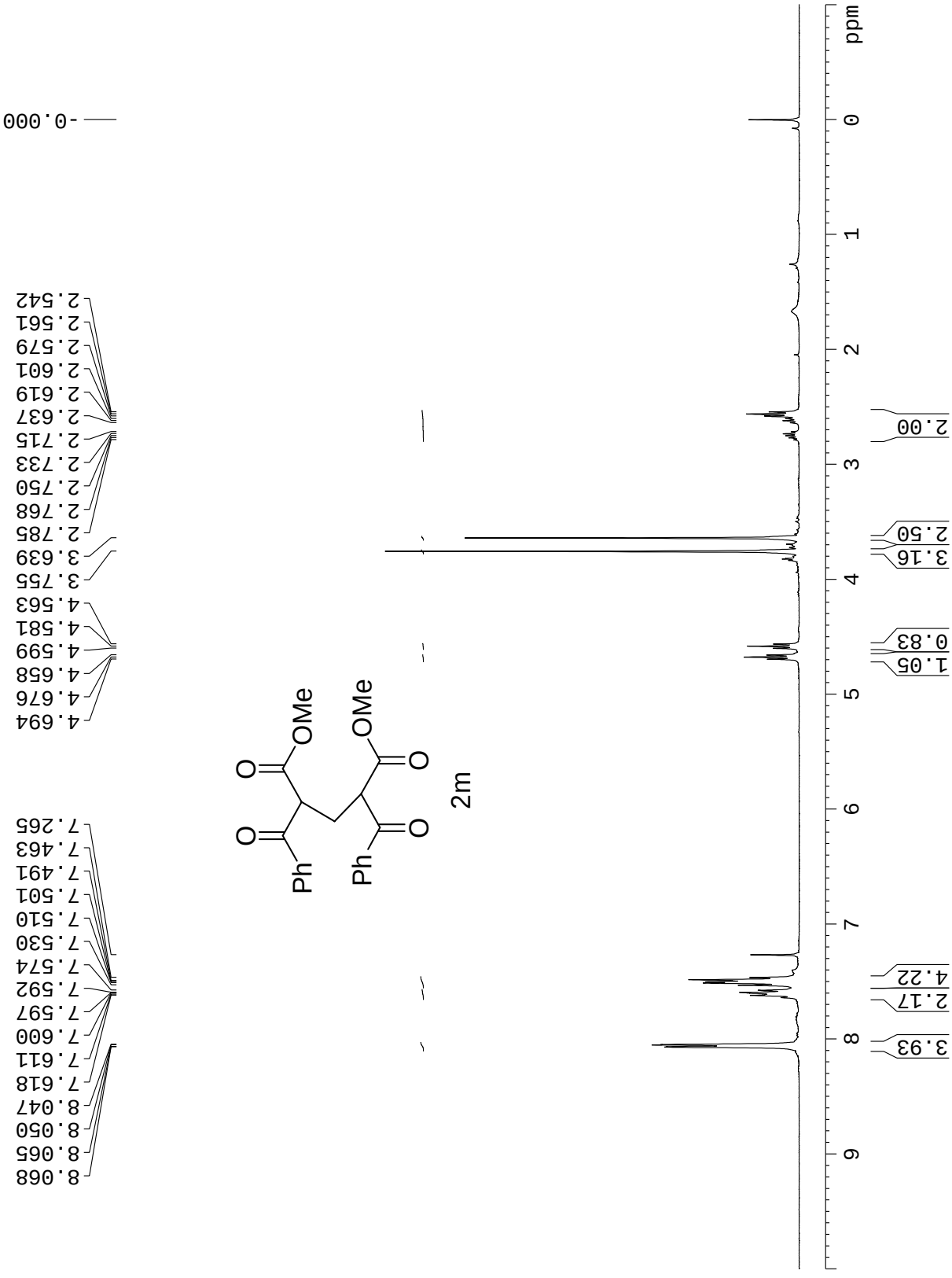
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8.068
OMe
OMe
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O
O
O
Ph
Ph
2m
ppm
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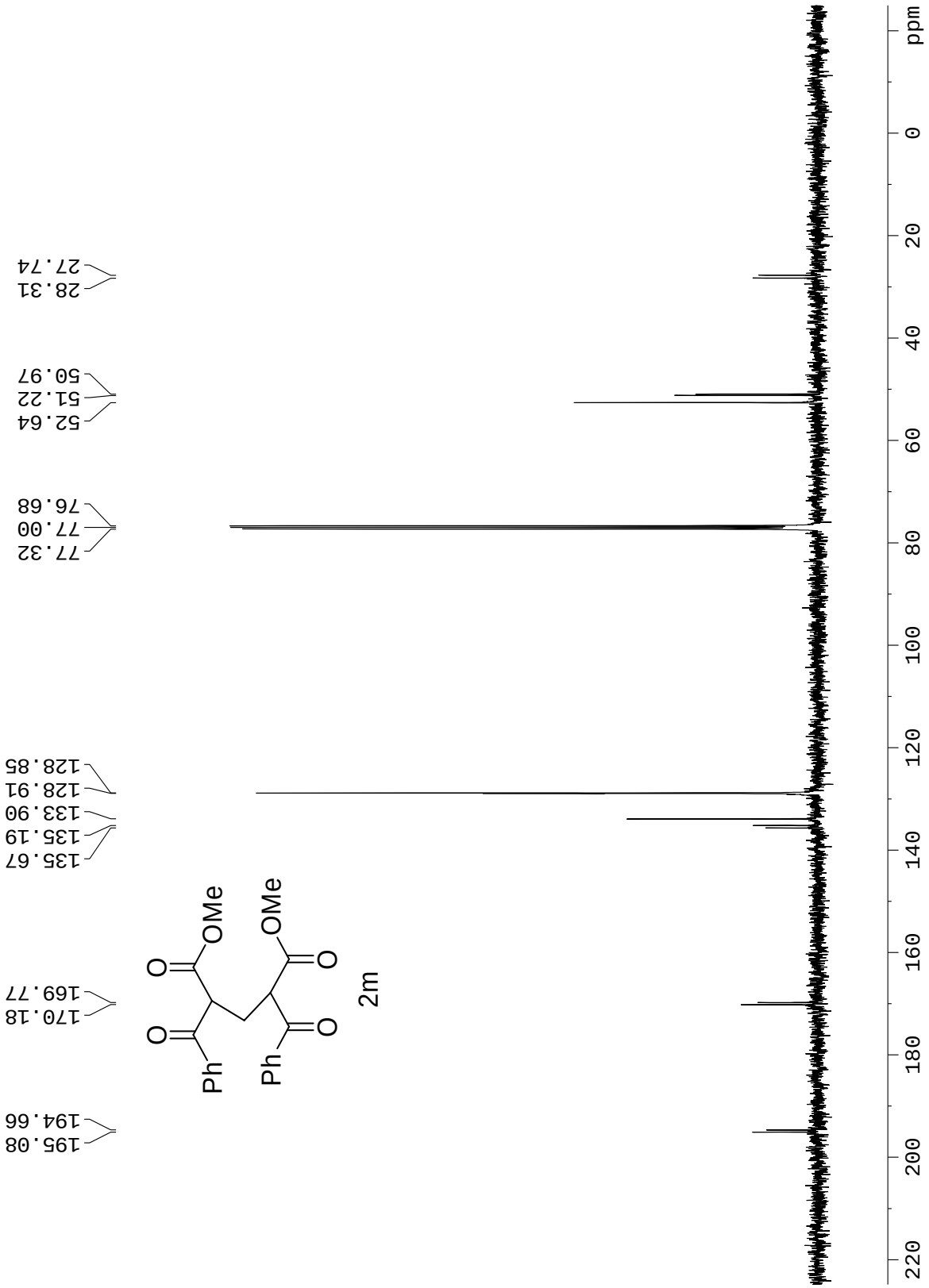

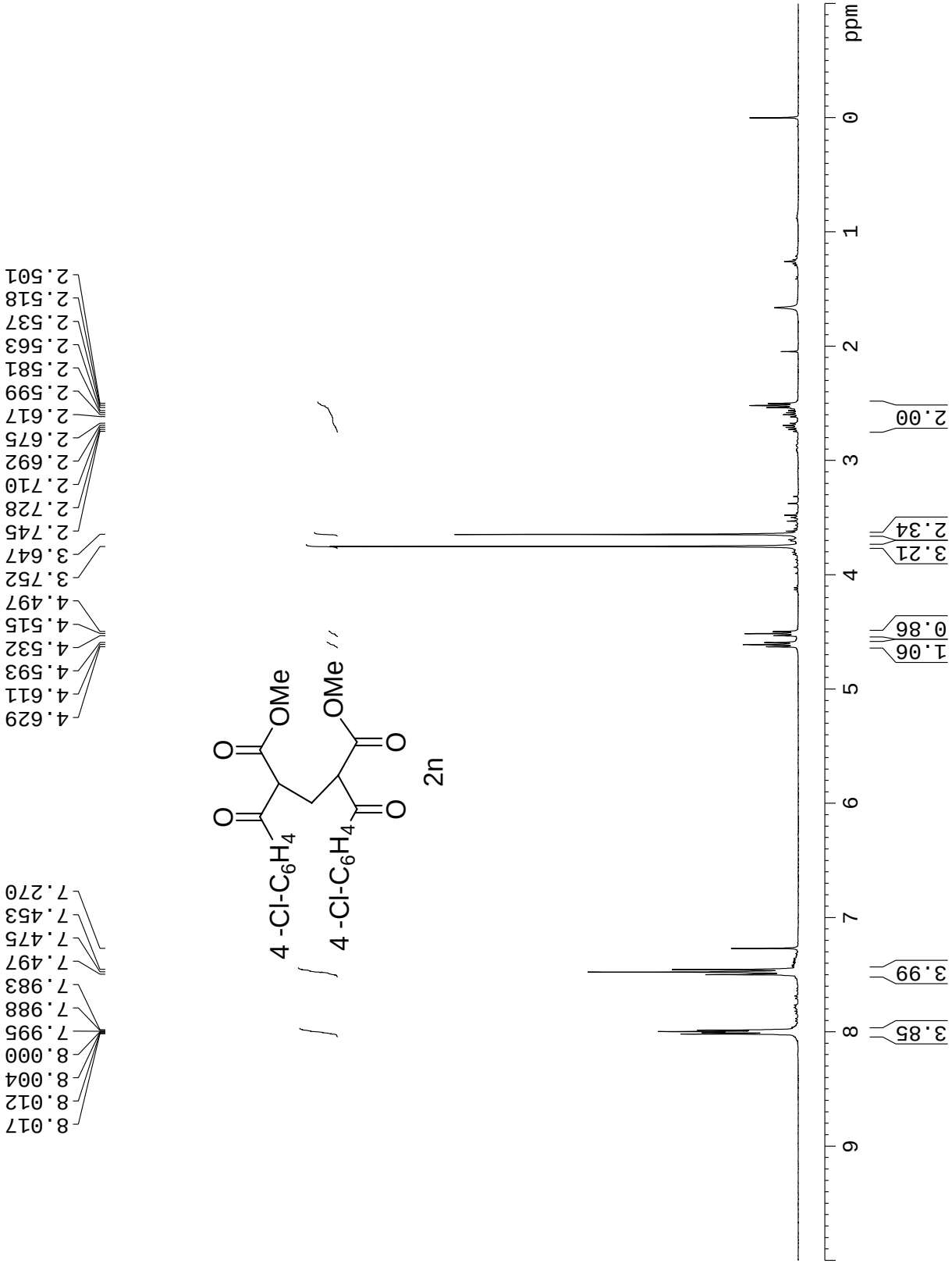
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2n
4 -Cl-C6H4
4 -Cl-C6H4
OMe
OMe
O
O
O
O
2.501
2.518
2.537
2.563
2.581
2.599
2.617
2.675
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2.710
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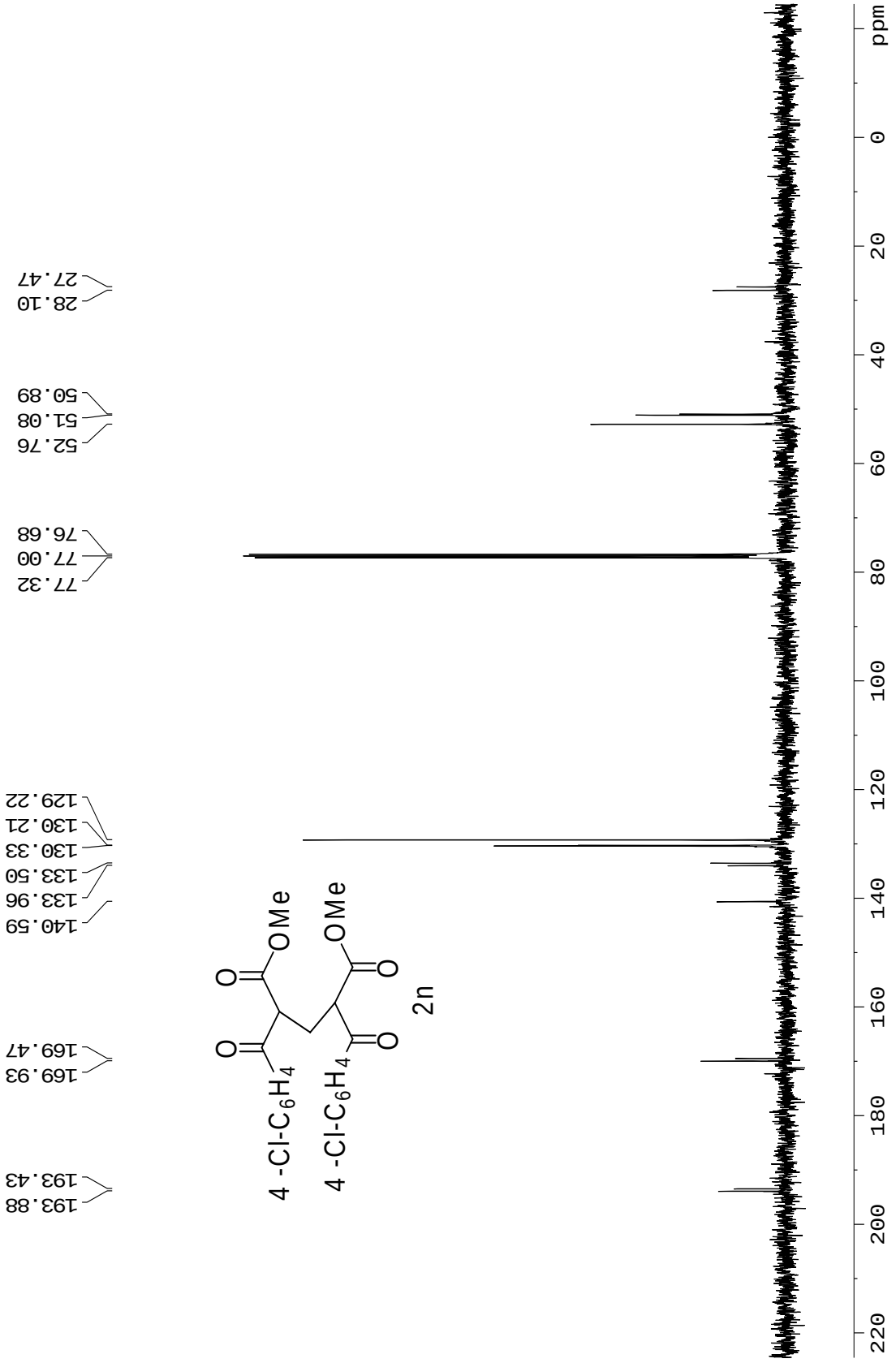
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52.76
51.08
50.89
28.10
27.47
4 -Cl-C6H4
OMe
O
O
4 -Cl-C6H4
OMe
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2n
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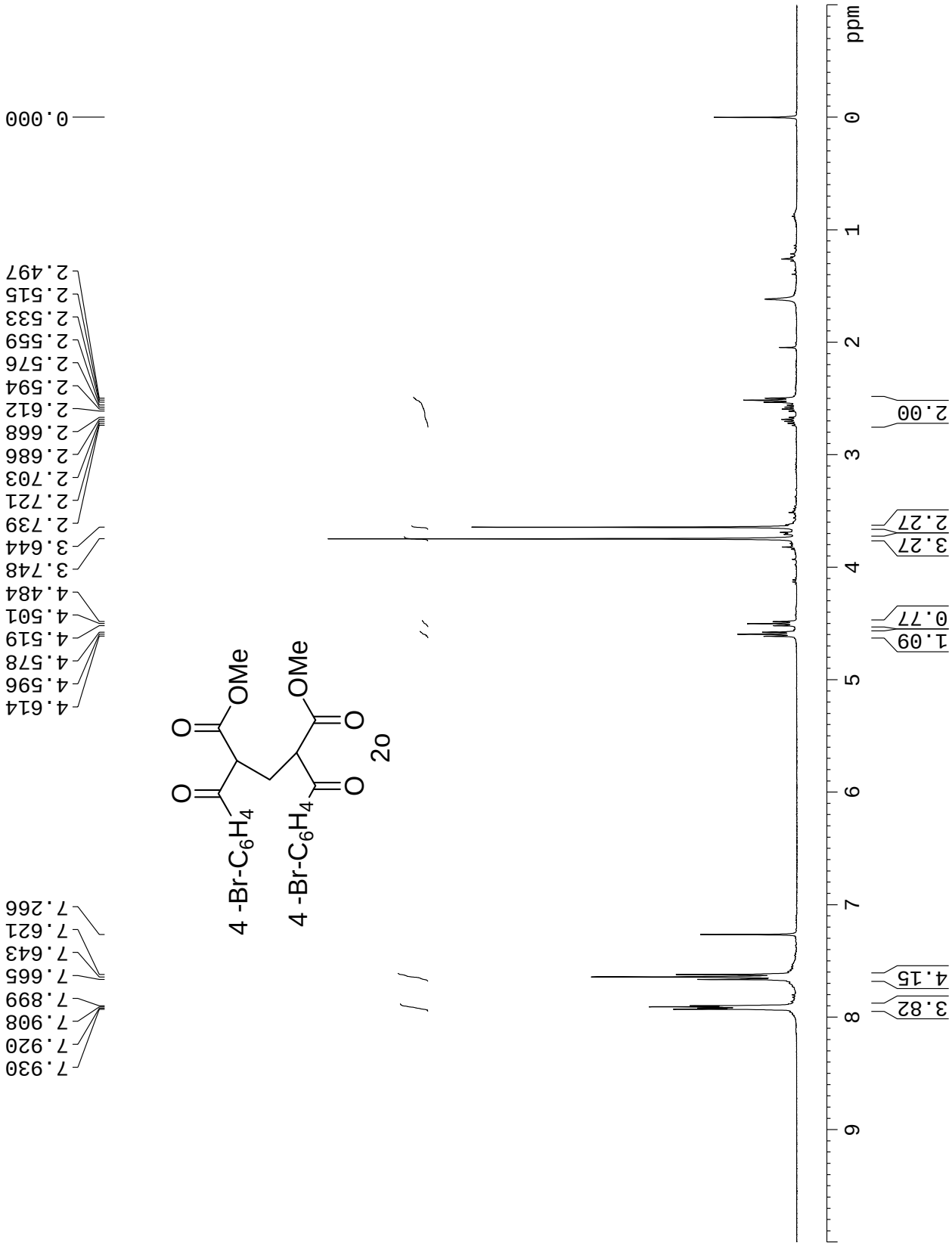
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4.578
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ppm
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6
7
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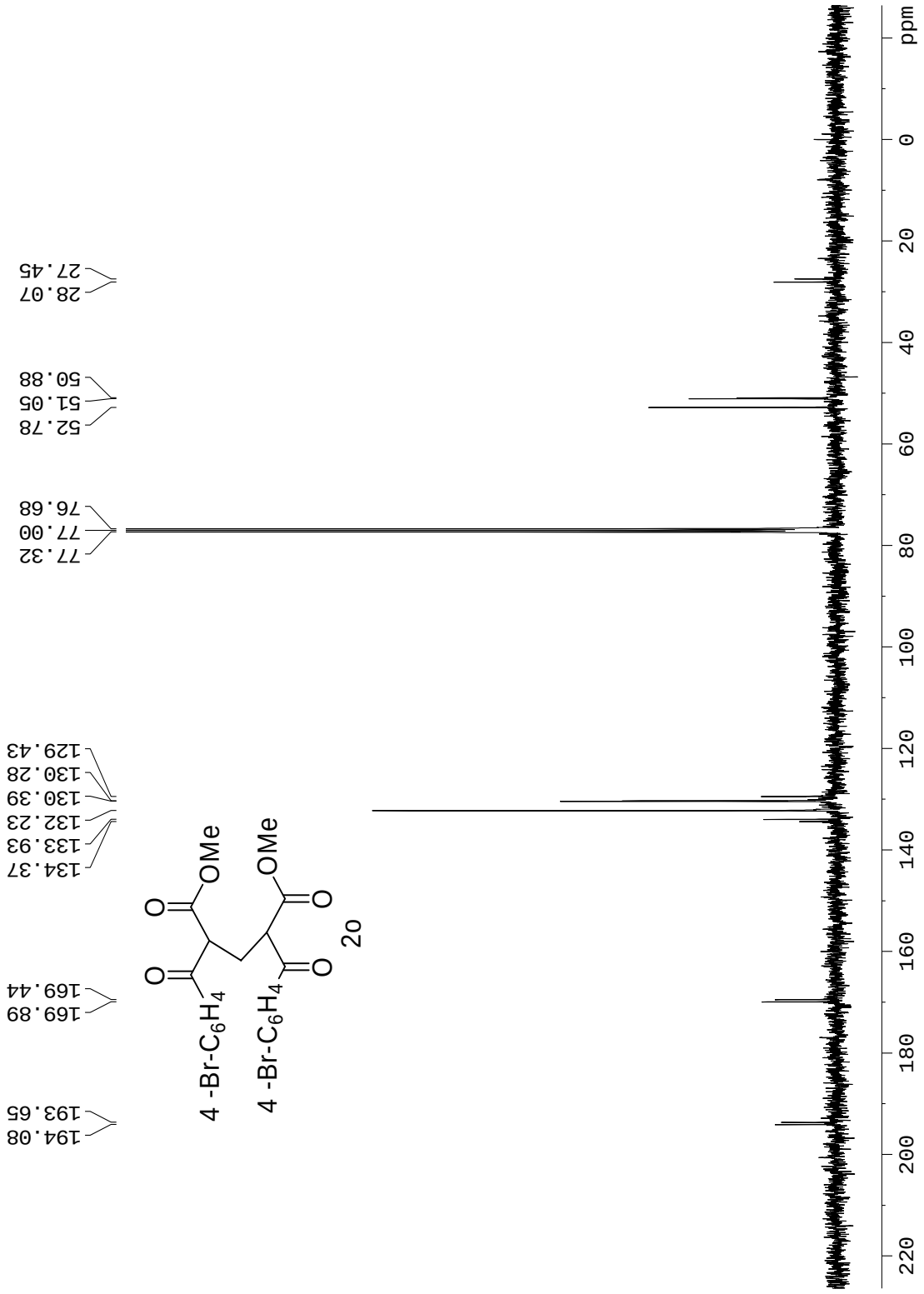
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50.88
28.07
27.45
OMe
OMe
O
O
O
O
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2o
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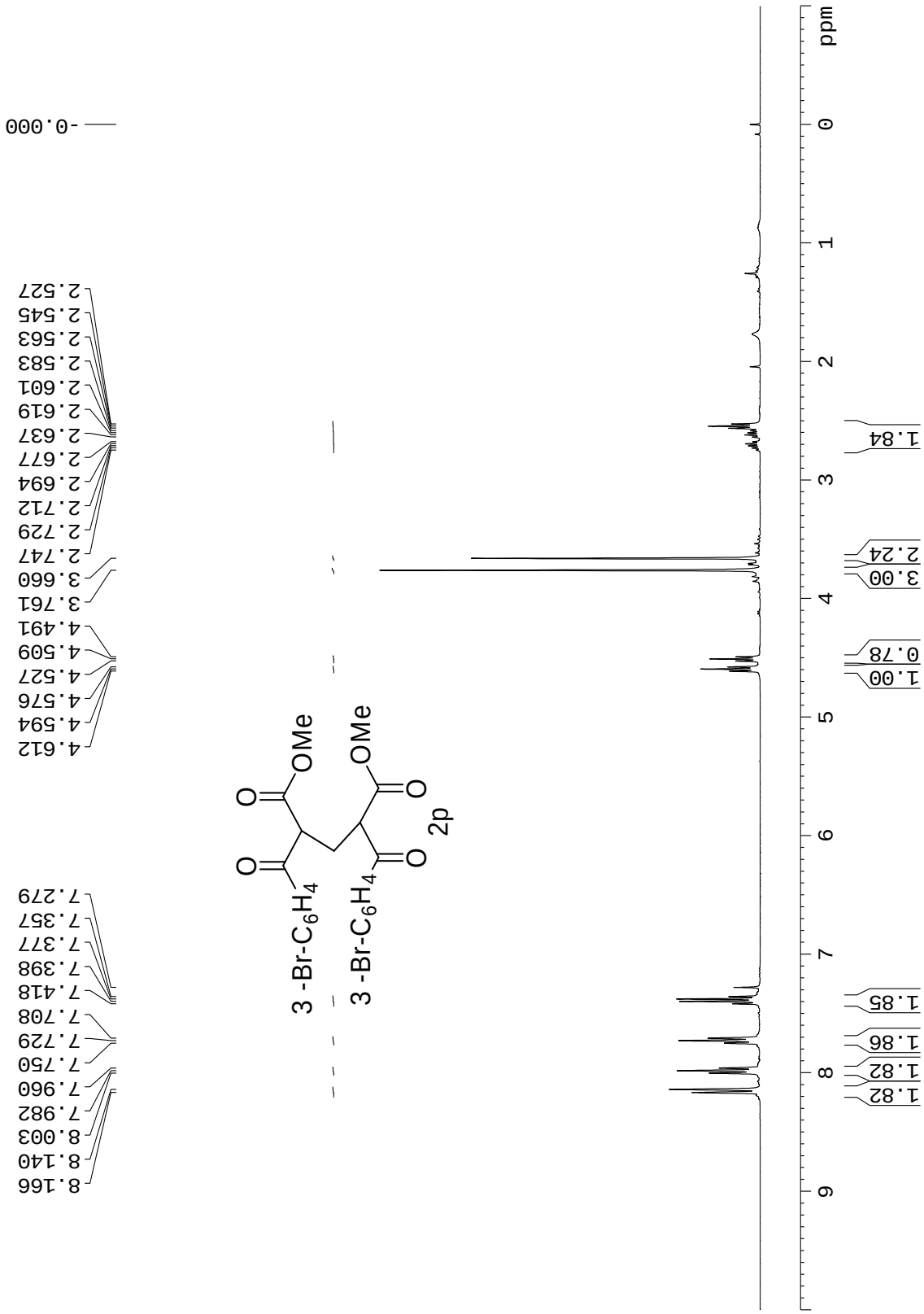
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1.85
1.86
1.82
1.82
ppm
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3
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OMe
OMe
O
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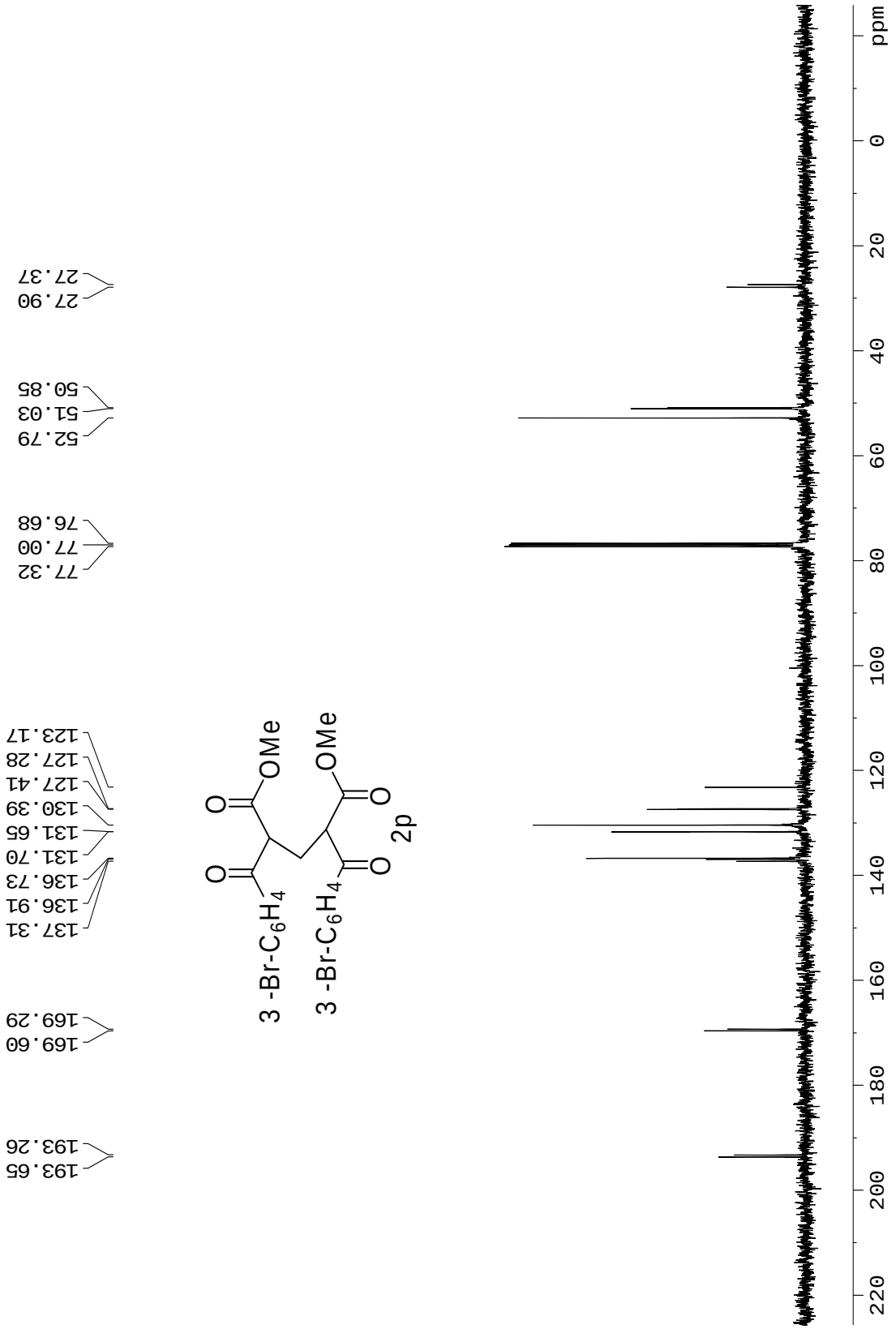
O
O
3 -Br-C6H4
3 -Br-C6H4
2p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51.03
50.85
27.90
27.37
OMe
OMe
O
O
O
O
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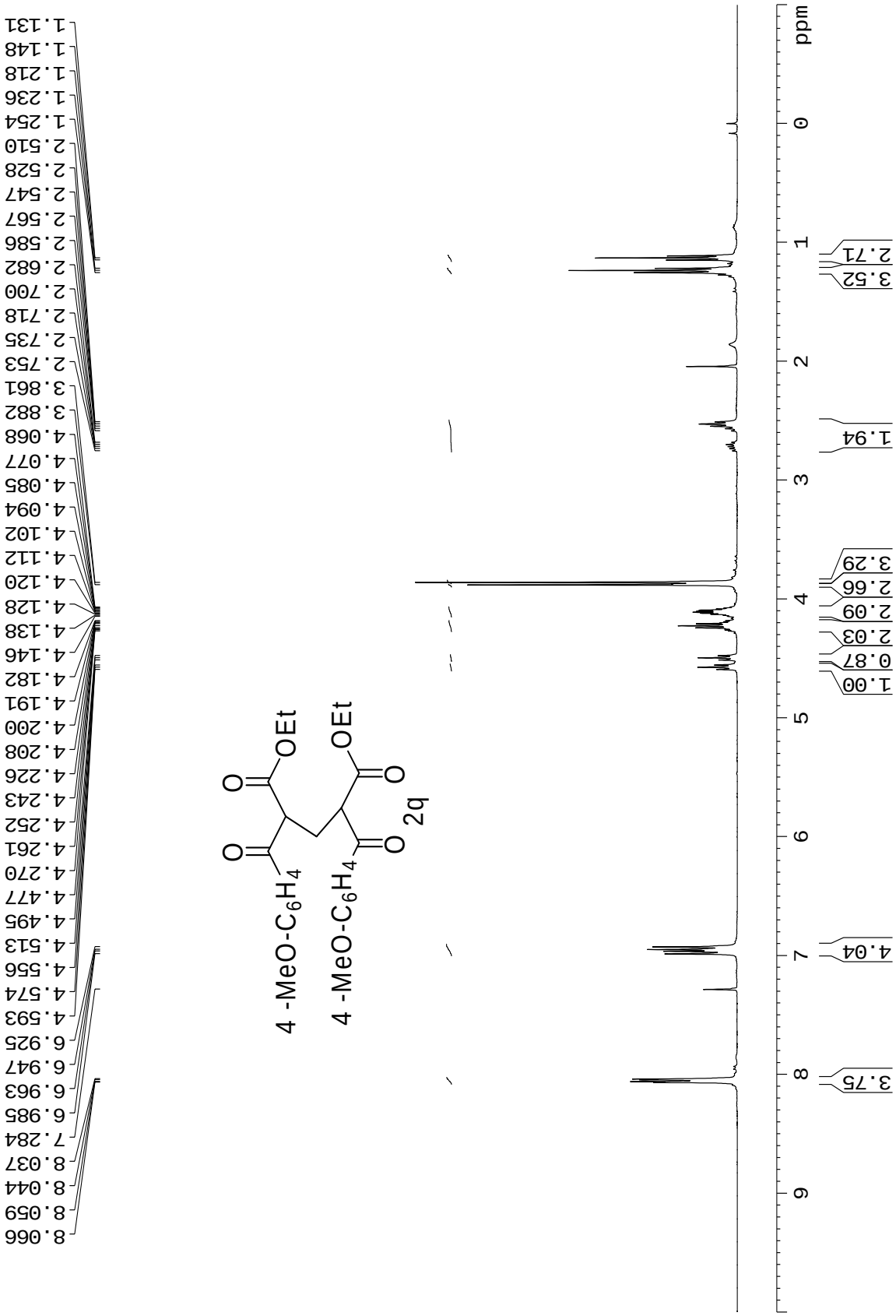
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3.29
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OEt
O
O
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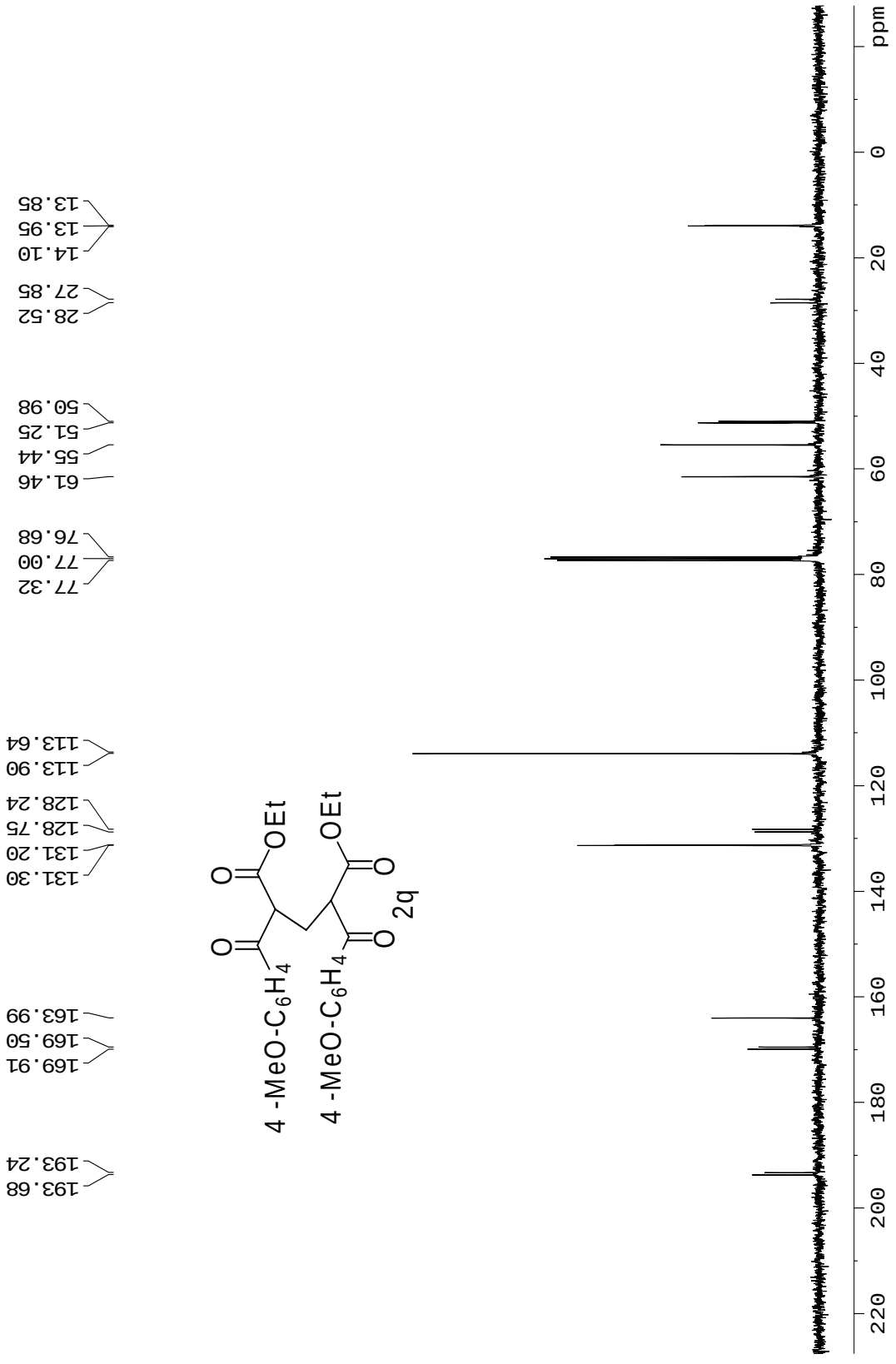
2q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169.50
169.91
193.24
193.68
4 -MeO-C6H4
4 -MeO-C6H4
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OEt
O
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O
O
2q
ppm
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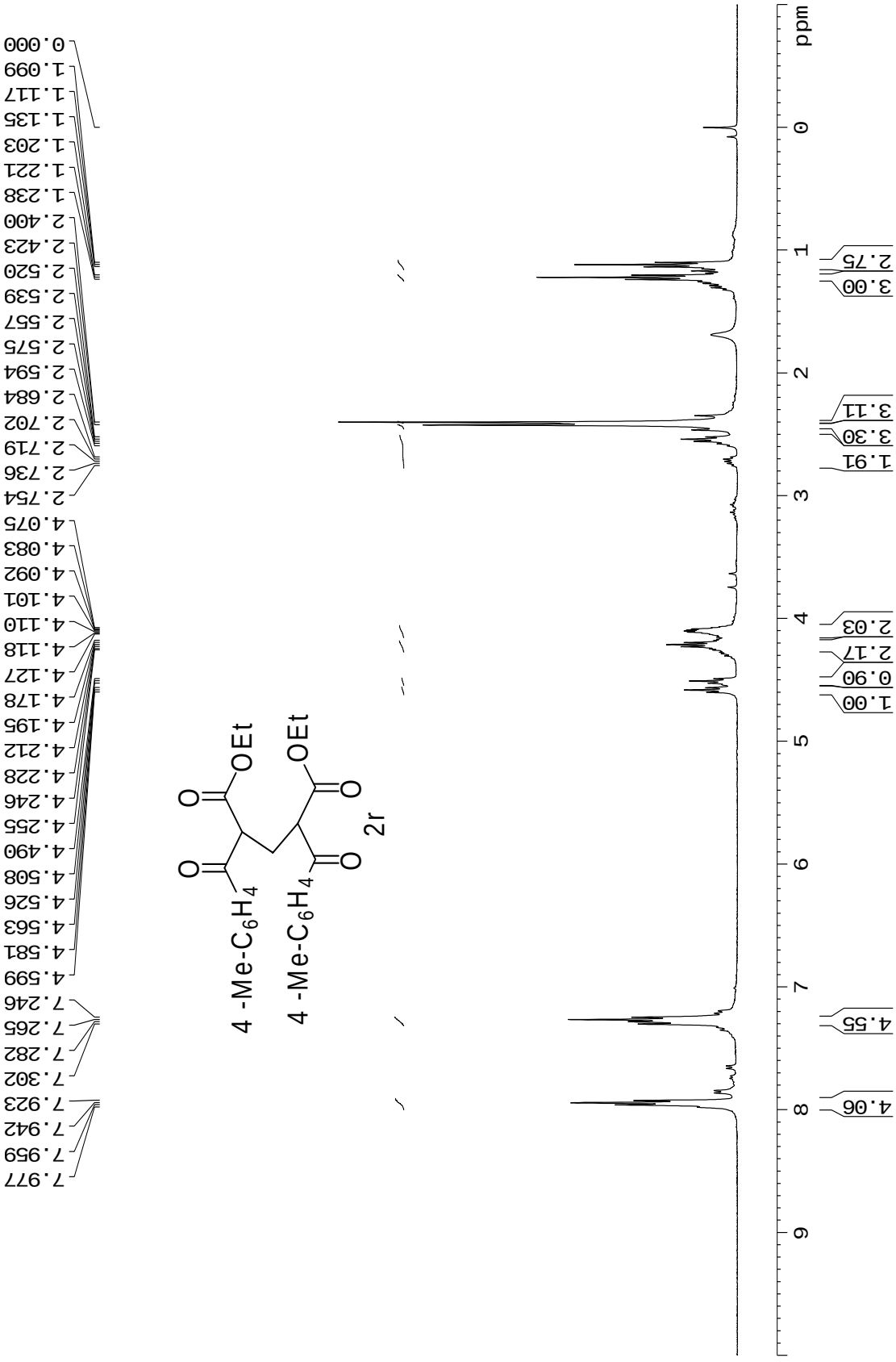
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4.599
7.246
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OEt
O
O
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OEt
O
O
2r
ppm
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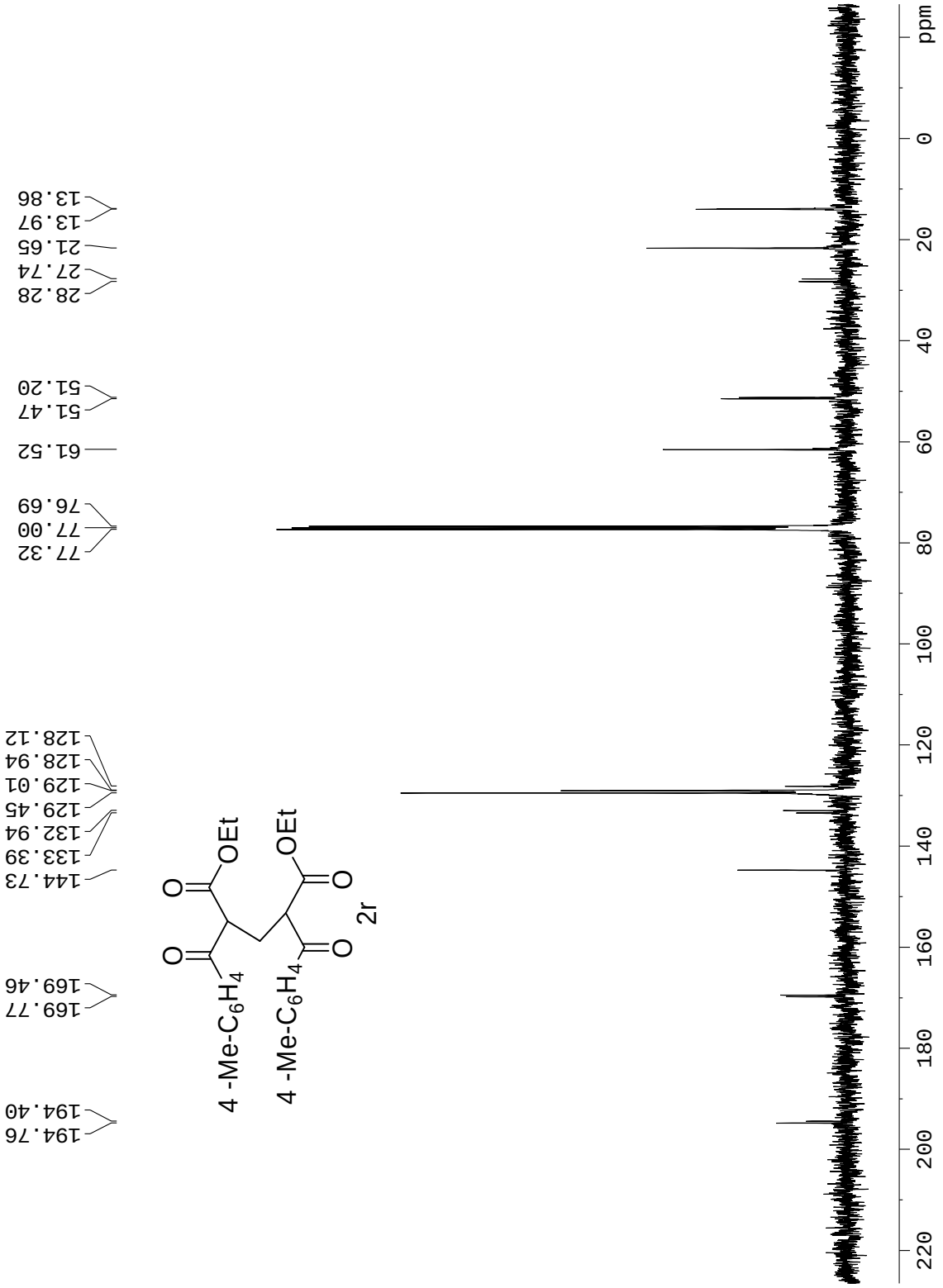
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4 -Me-C6H4
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OEt
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O
O
2r
ppm
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200
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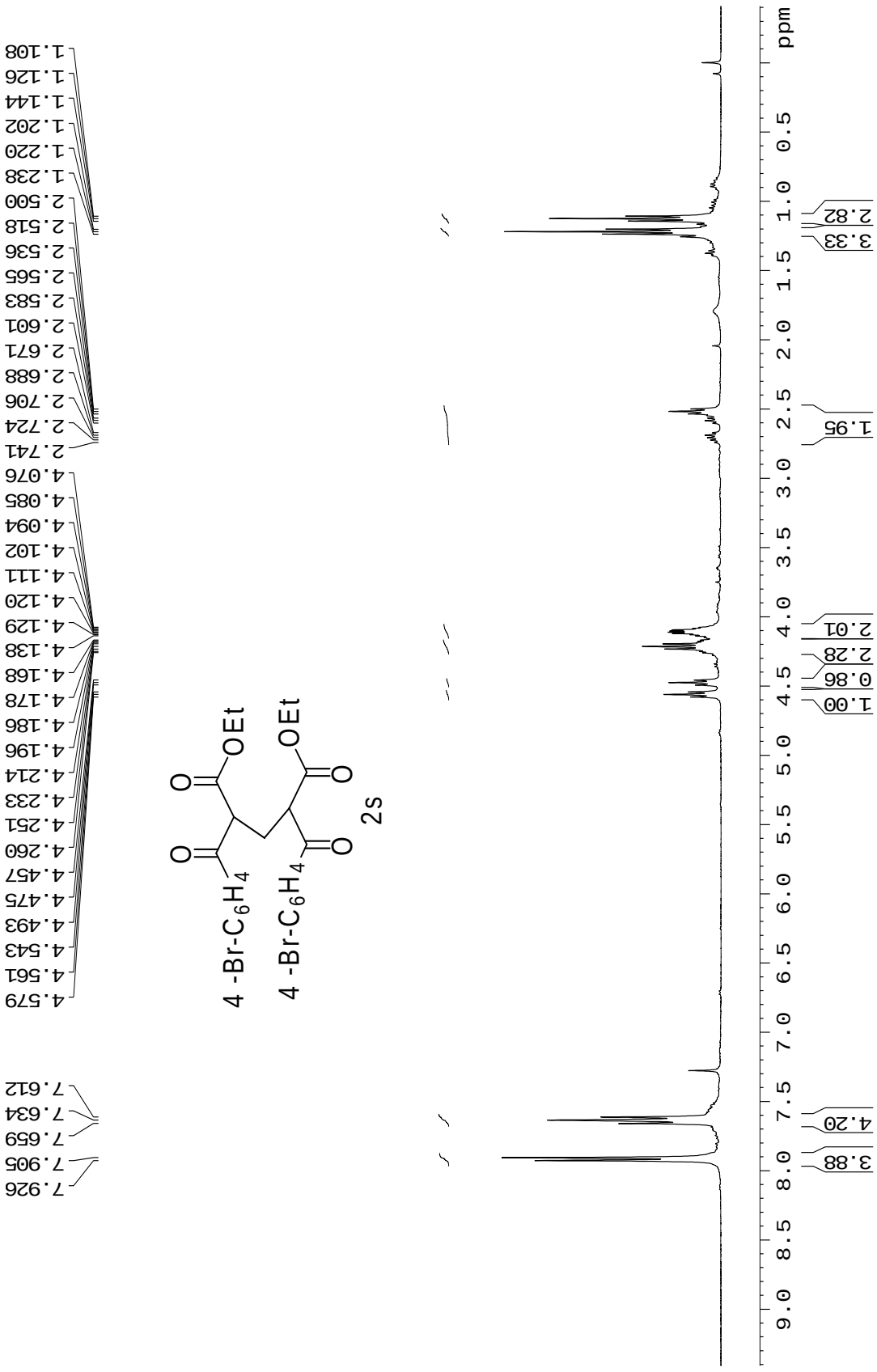
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OEt
O
O
O
O
2s
ppm
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5.5
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4.0
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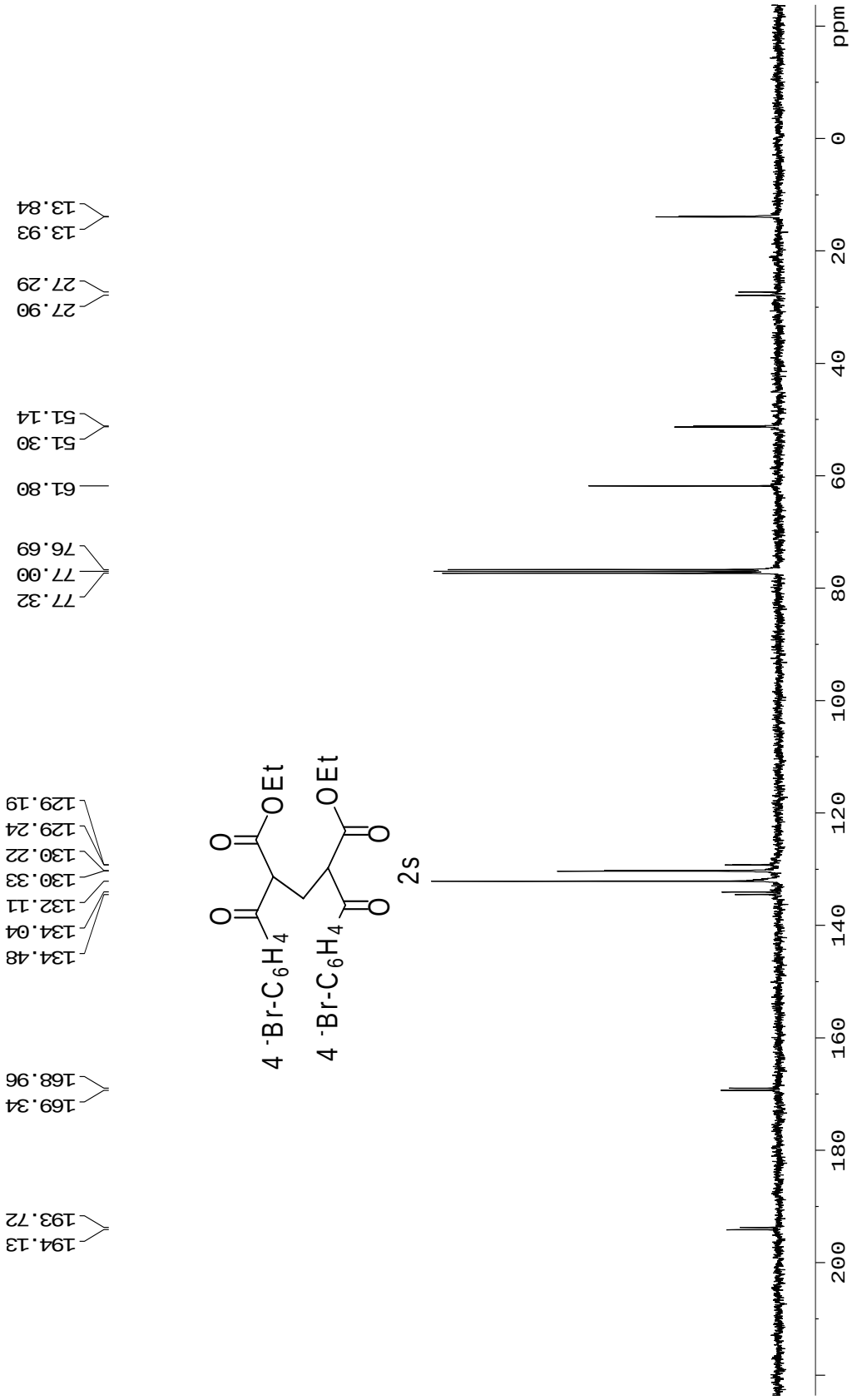
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130.22
130.33
132.11
134.04
134.48
168.96
169.34
193.72
194.13
4-Br-C6H4
4-Br-C6H4
OEt
OEt
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O
O
O
2s
ppm
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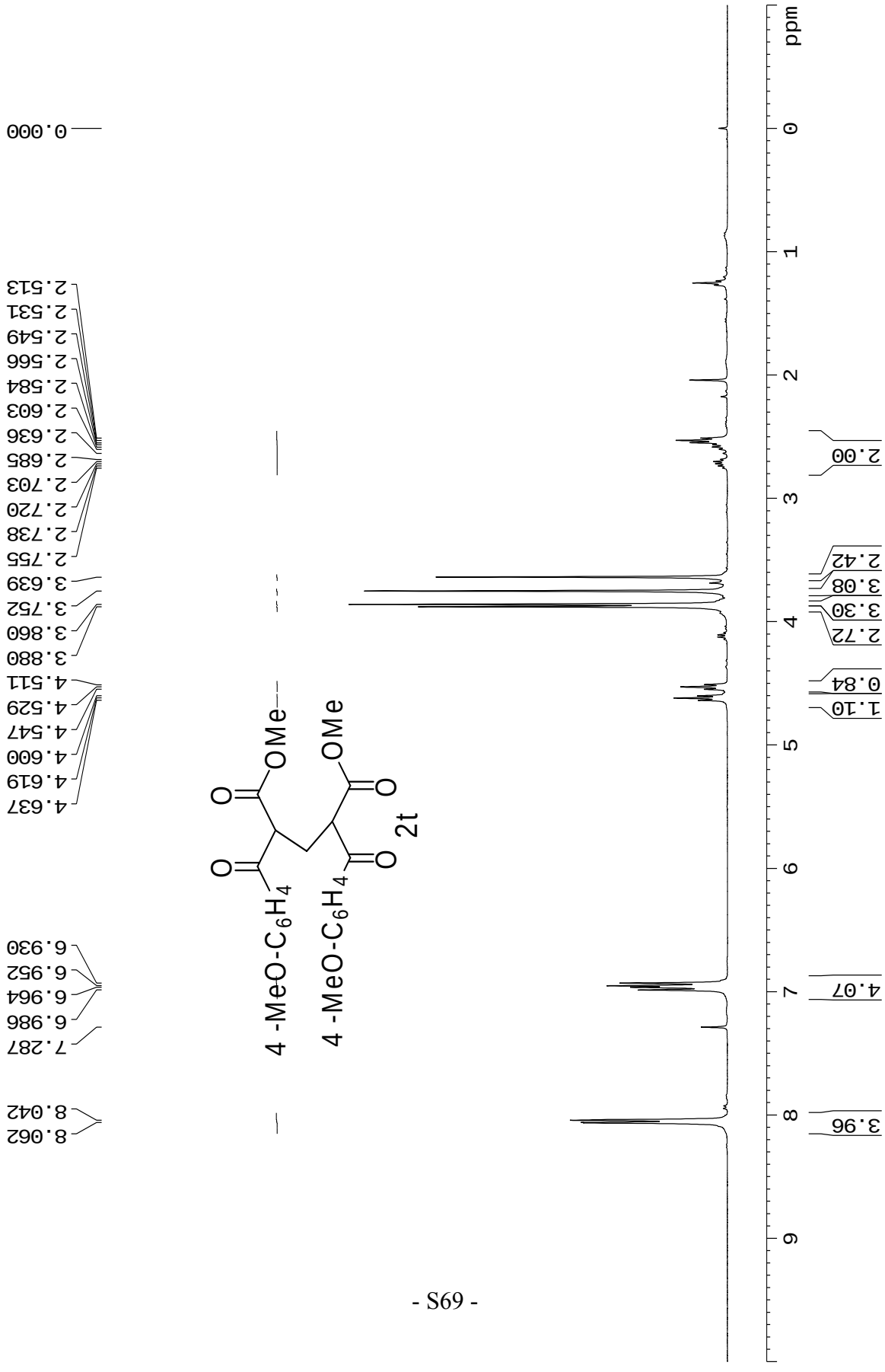

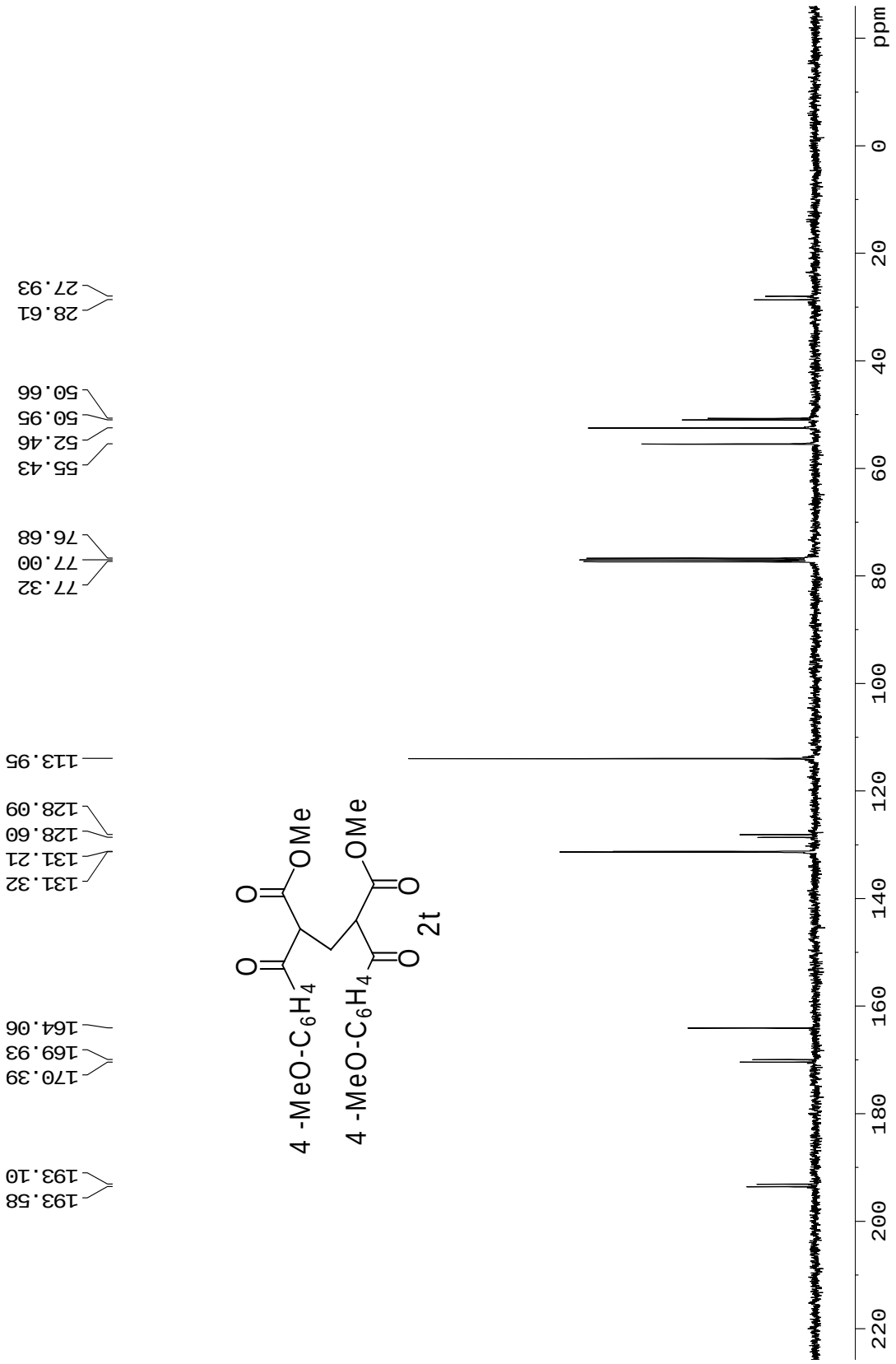
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77.00
77.32
113.95
128.09
128.60
131.21
131.32
164.06
169.93
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193.10
193.58
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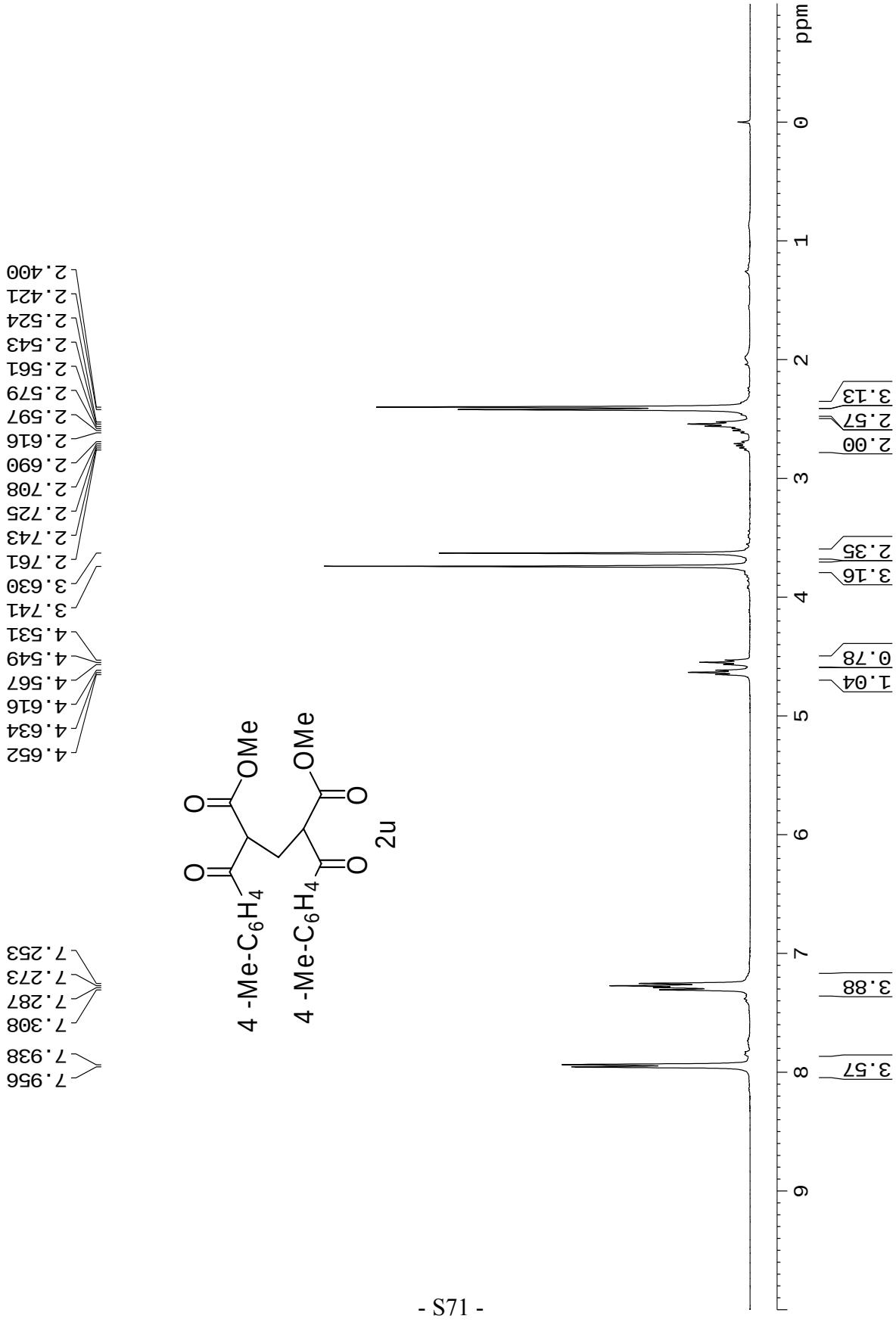
OMe
O
O
4 -MeO-C6H4
OMe
O
O
2t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2.579
2.561
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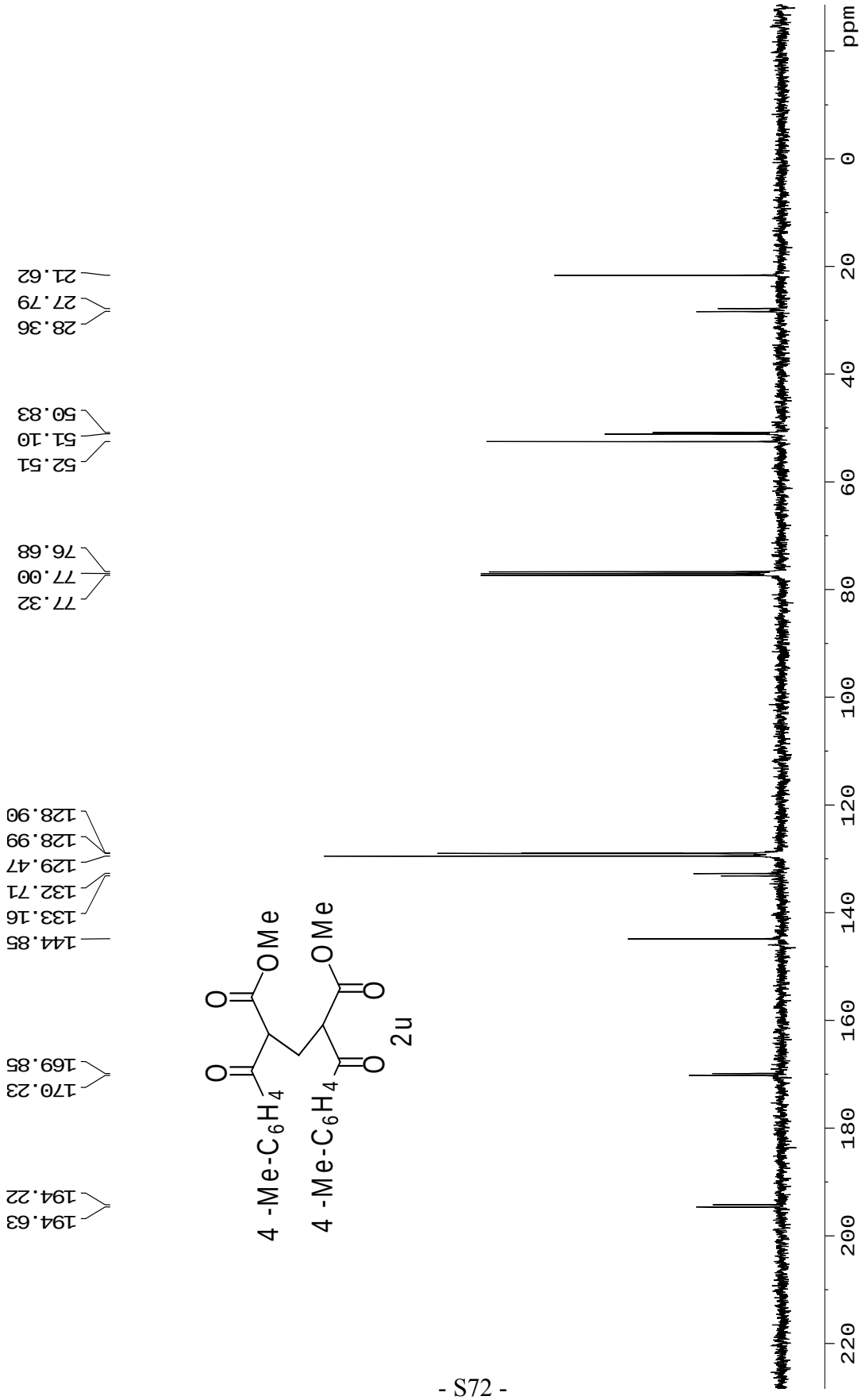
2u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76.68
77.00
77.32
128.90
128.99
129.47
132.71
133.16
144.85
169.85
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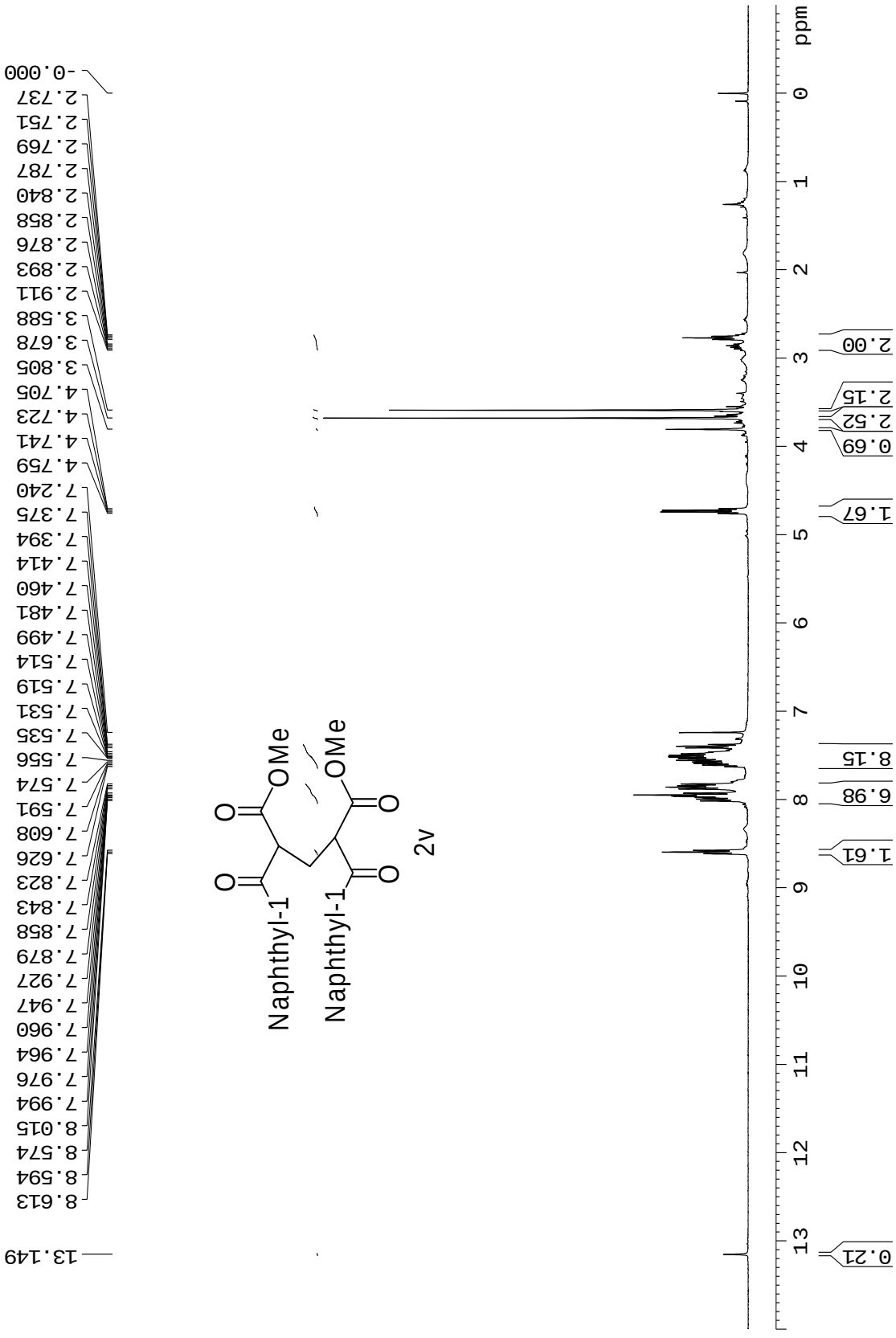
194.63
4 -Me-C6H4
OMe
O
O
4 -Me-C6H4
OMe
O
O
2u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0.21
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8.015
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OMe
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O
O
O
Naphthyl-1
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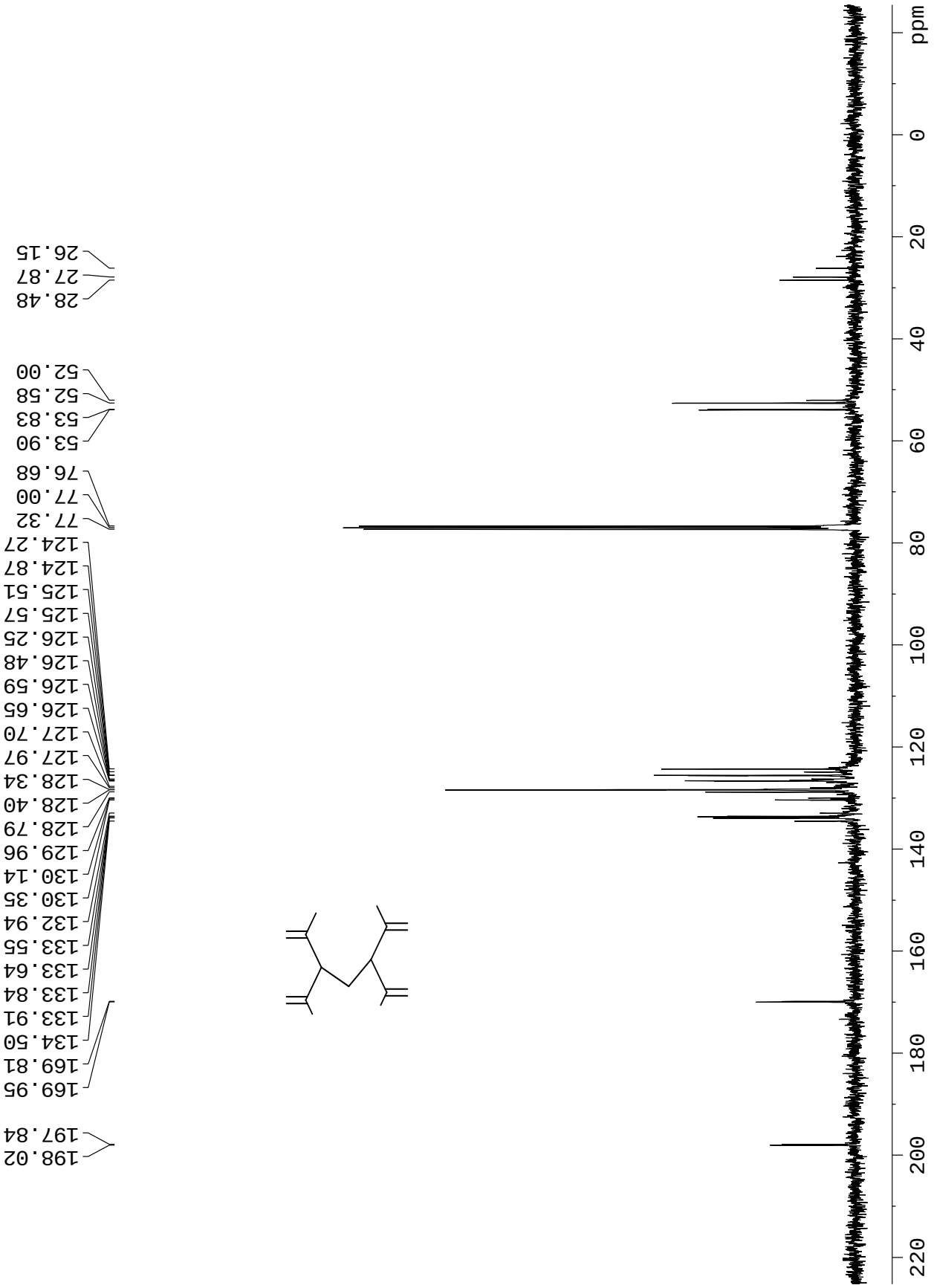
2v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125.57
126.25
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133.84
133.91
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200
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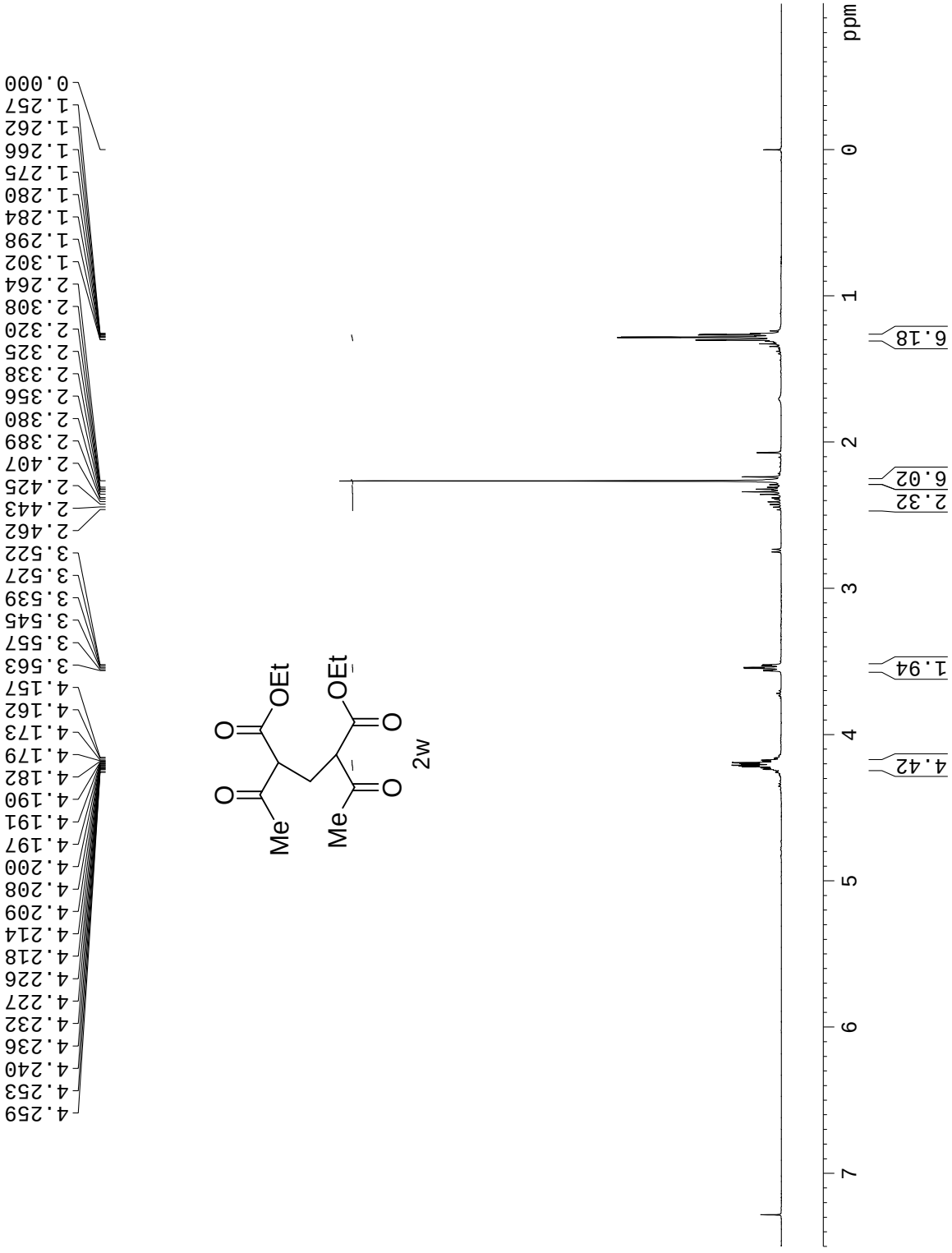
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2.356
2.380
2.389
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3.527
3.539
3.545
3.557
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4.182
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4.218
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4.259
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OEt
O
O
O
O
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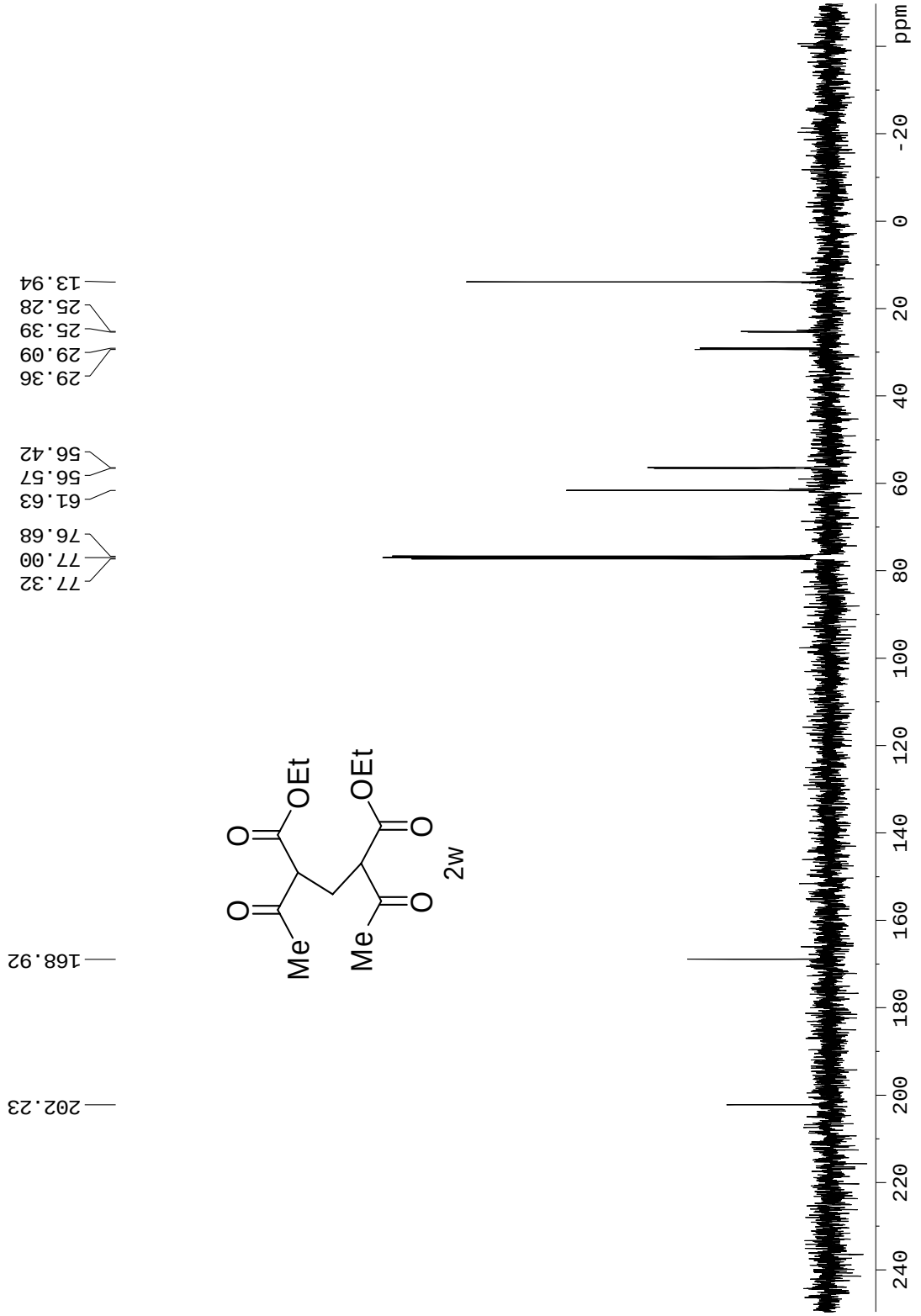
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61.63
56.57
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OEt
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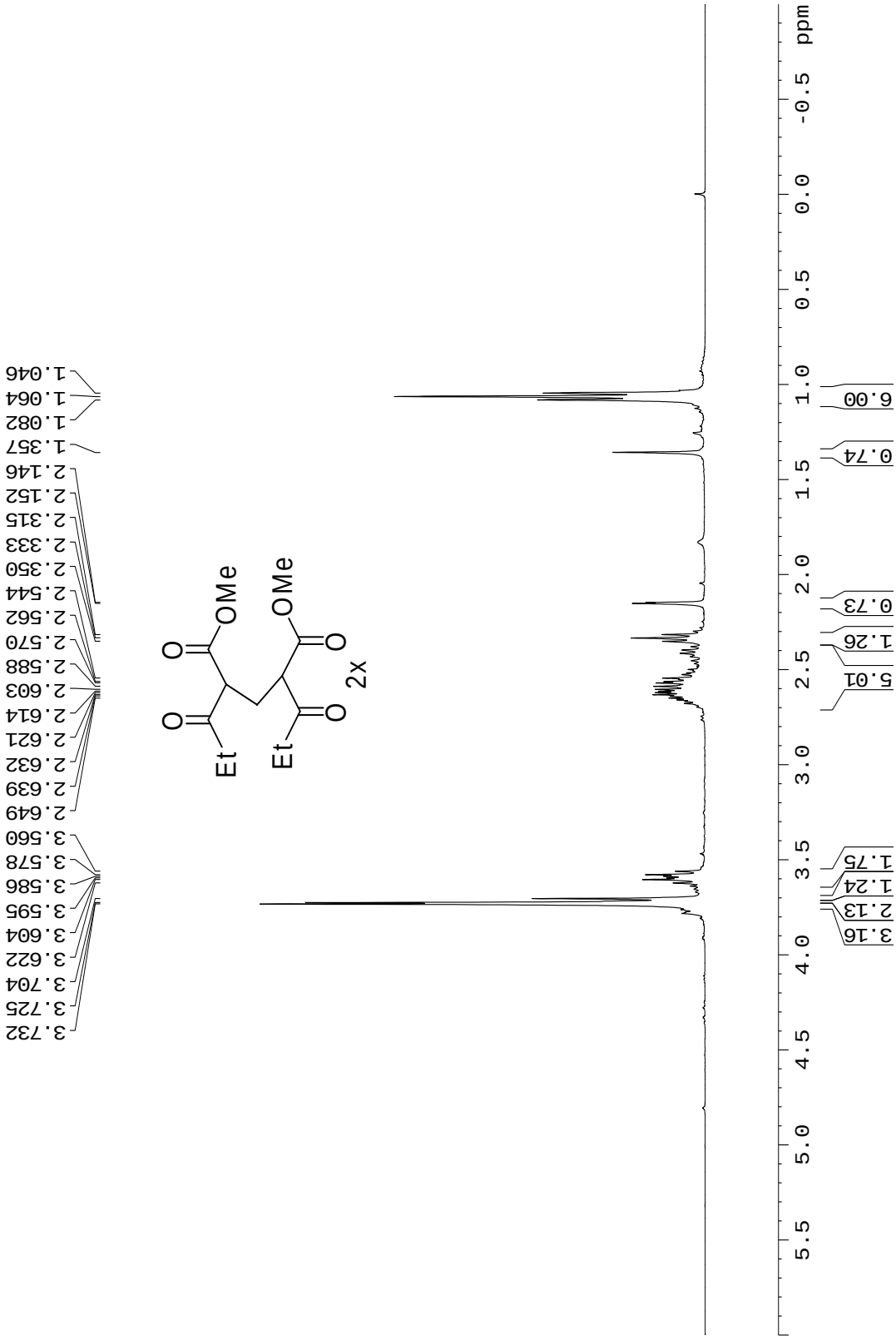
Me
2w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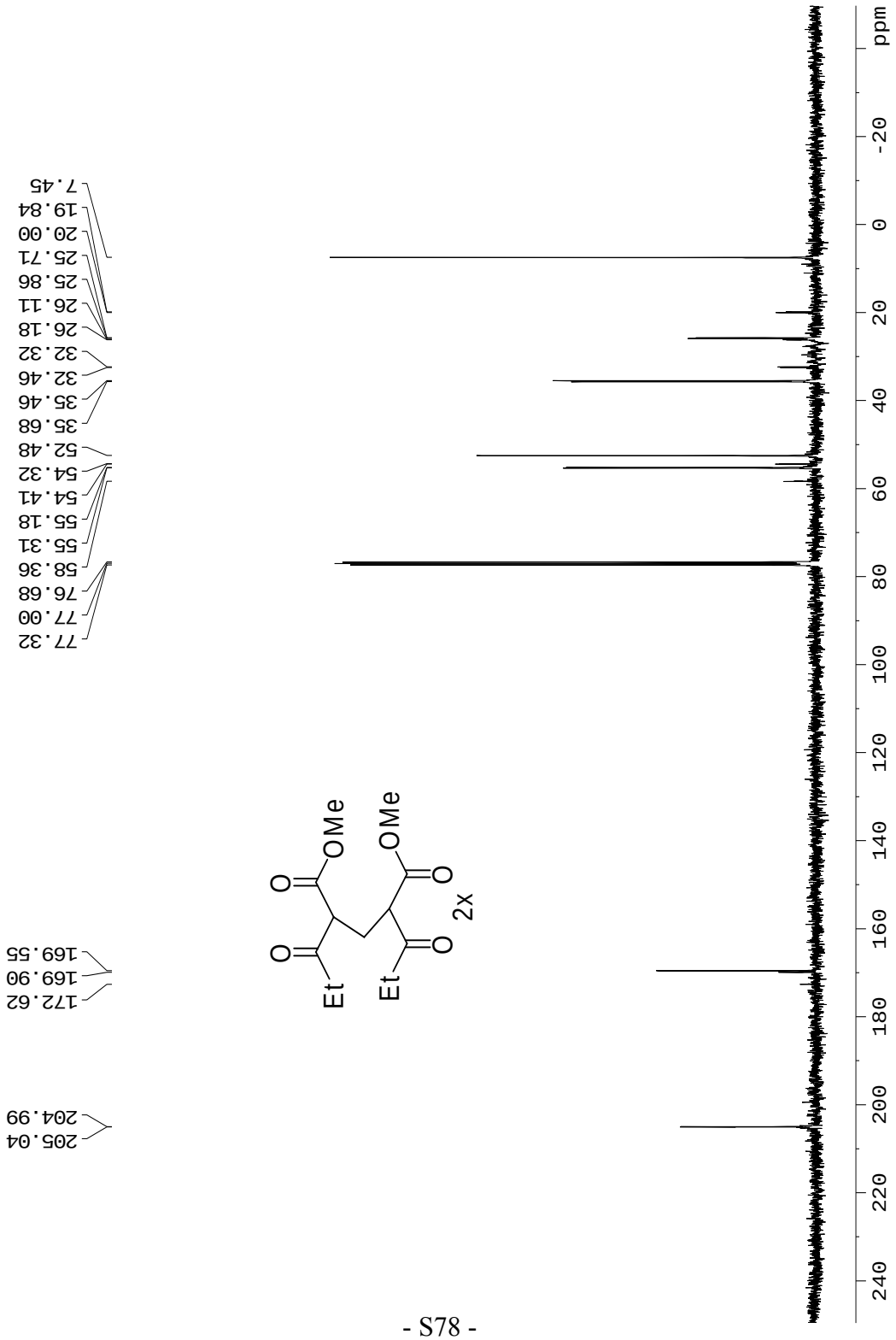
OMe
Et
Et
2x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52.48
35.68
35.46
32.46
32.32
26.18
26.11
25.86
25.71
20.00
19.84
7.45
O
OMe
Et
2x
ppm
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200
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120
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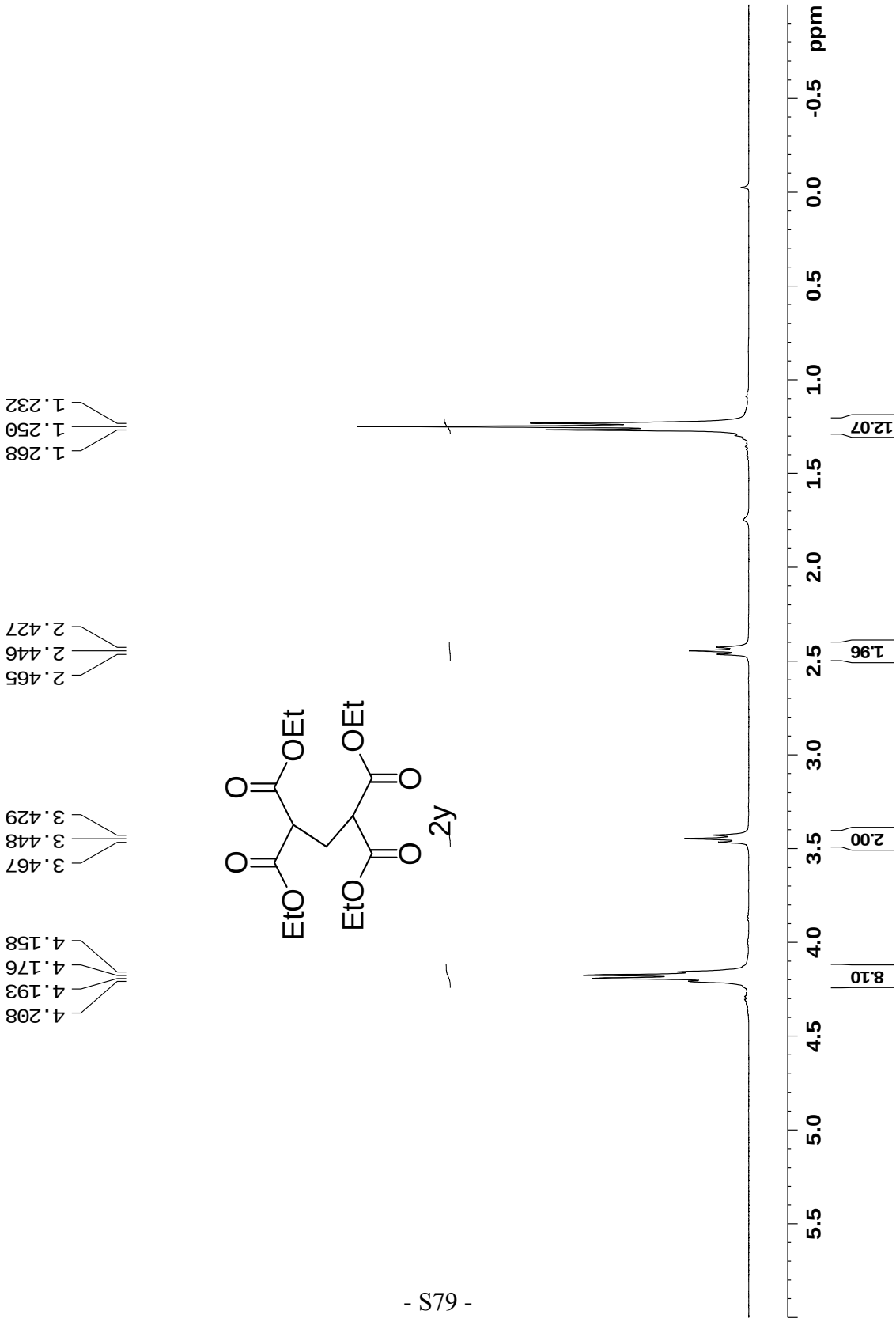
40
20
0
-20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1.250
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2.427
2.446
2.465
3.429
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4.208
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OEt
O
O
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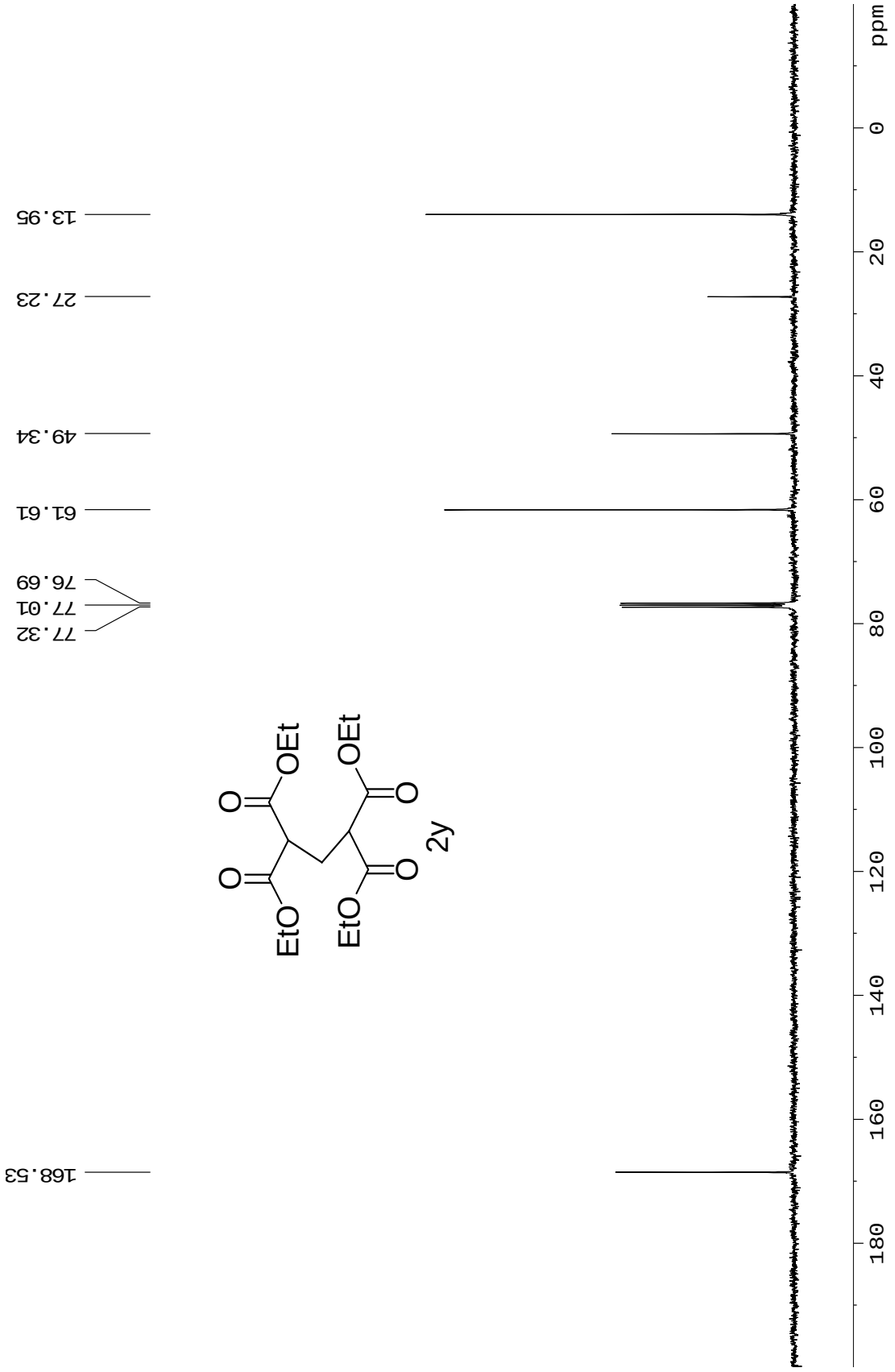
EtO
EtO
2y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EtO
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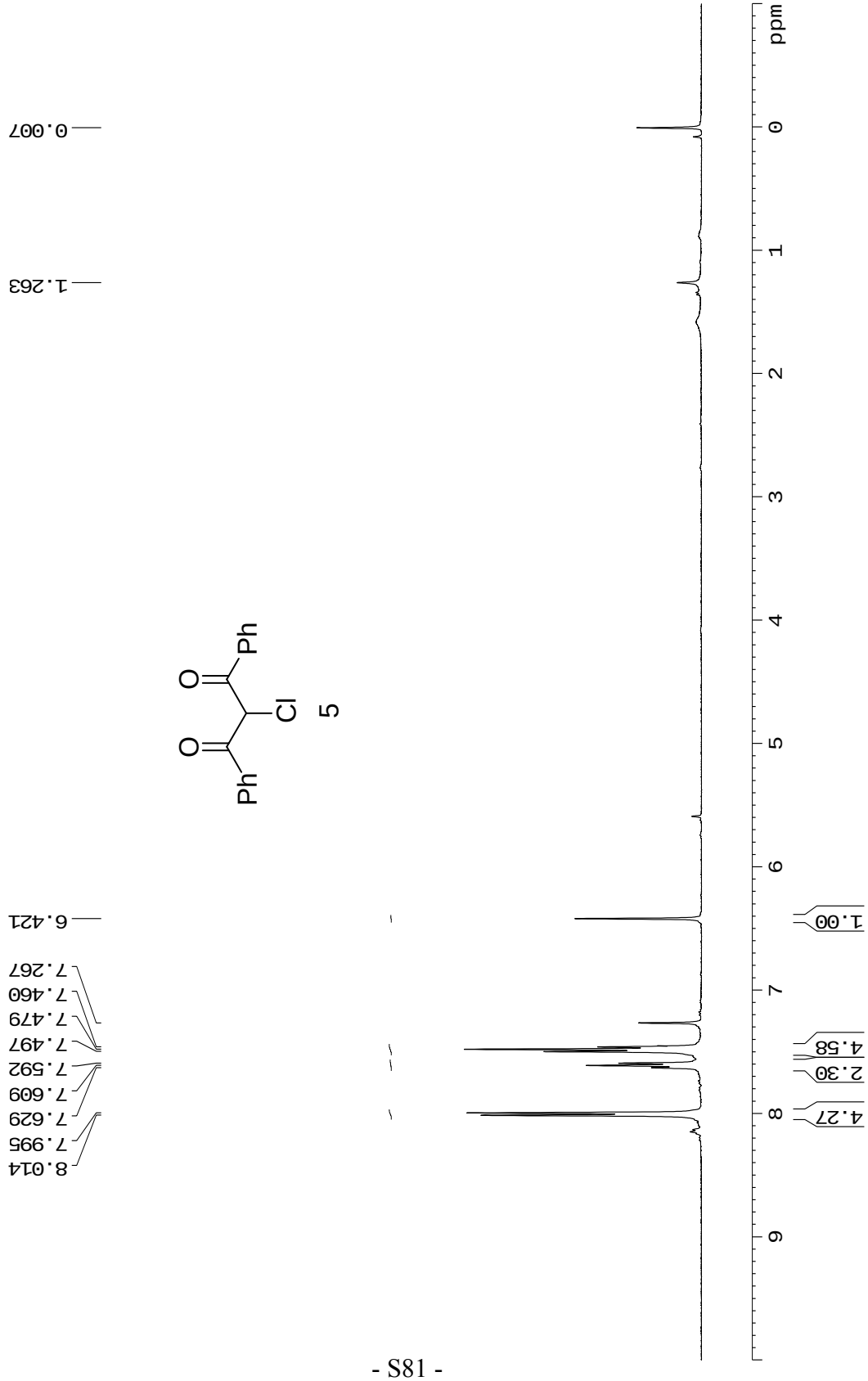
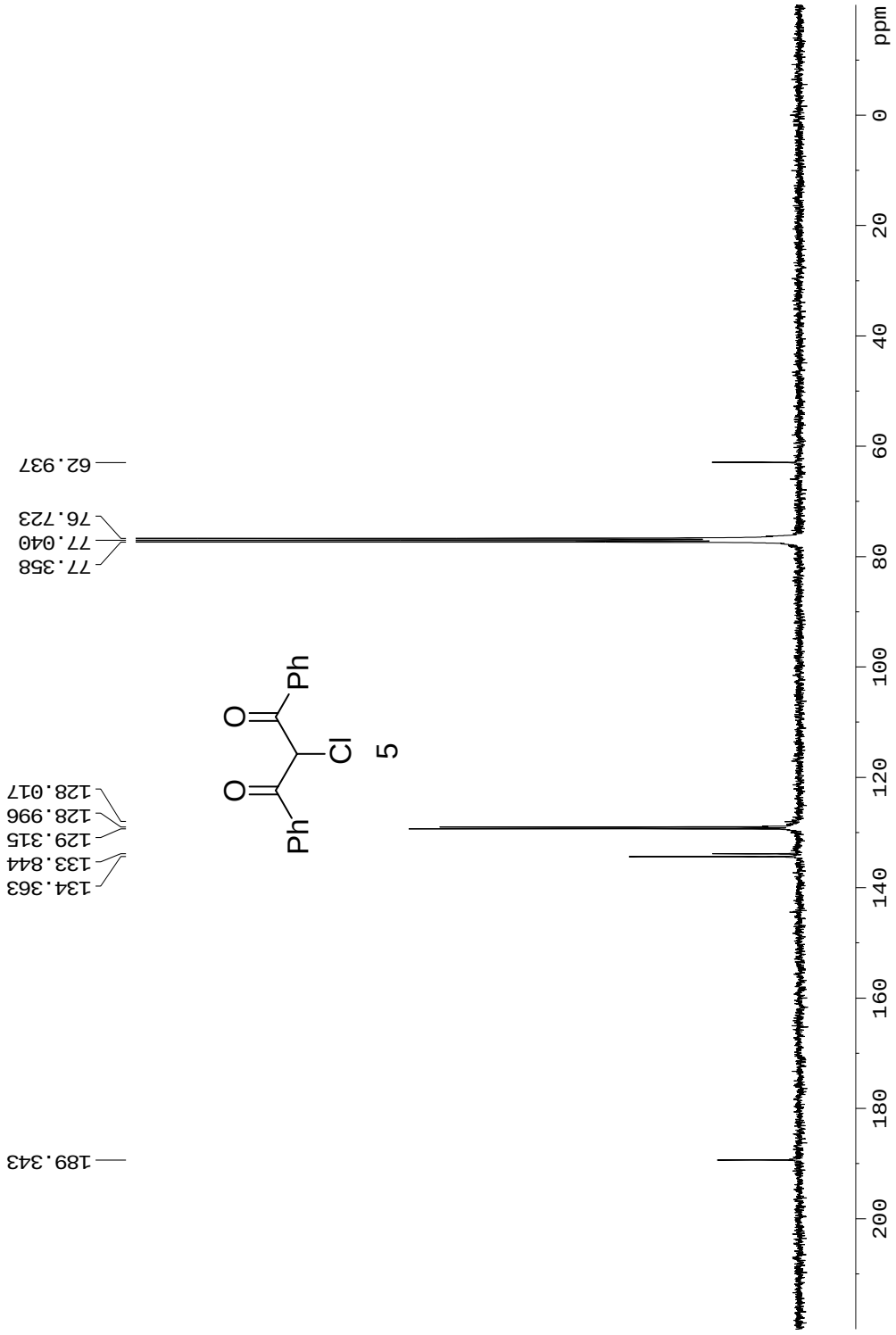
160
180

15. ^{1}H and ^{13}C spectra of products 5 and 7

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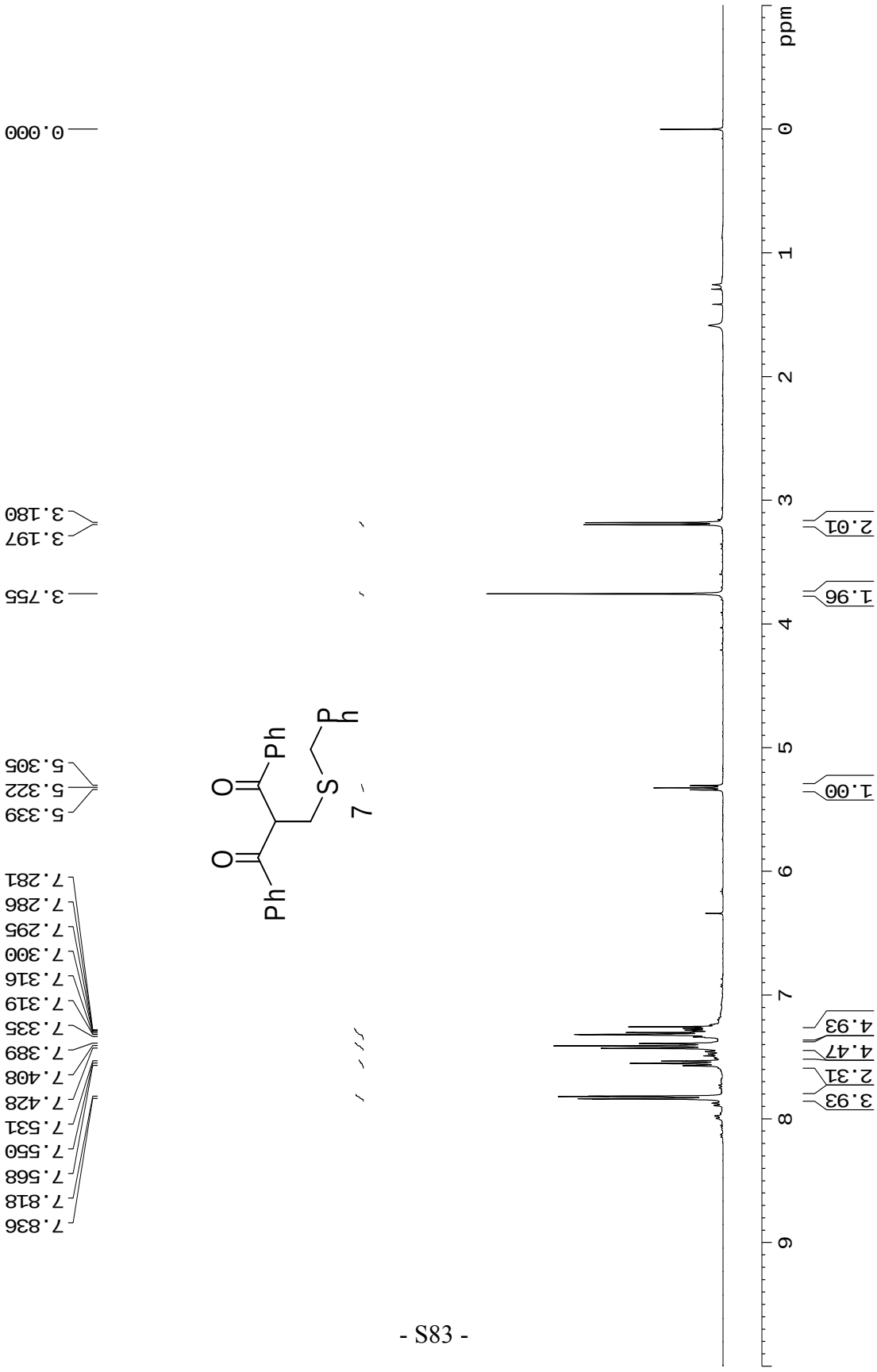
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7.295
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7.335
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3.93
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O
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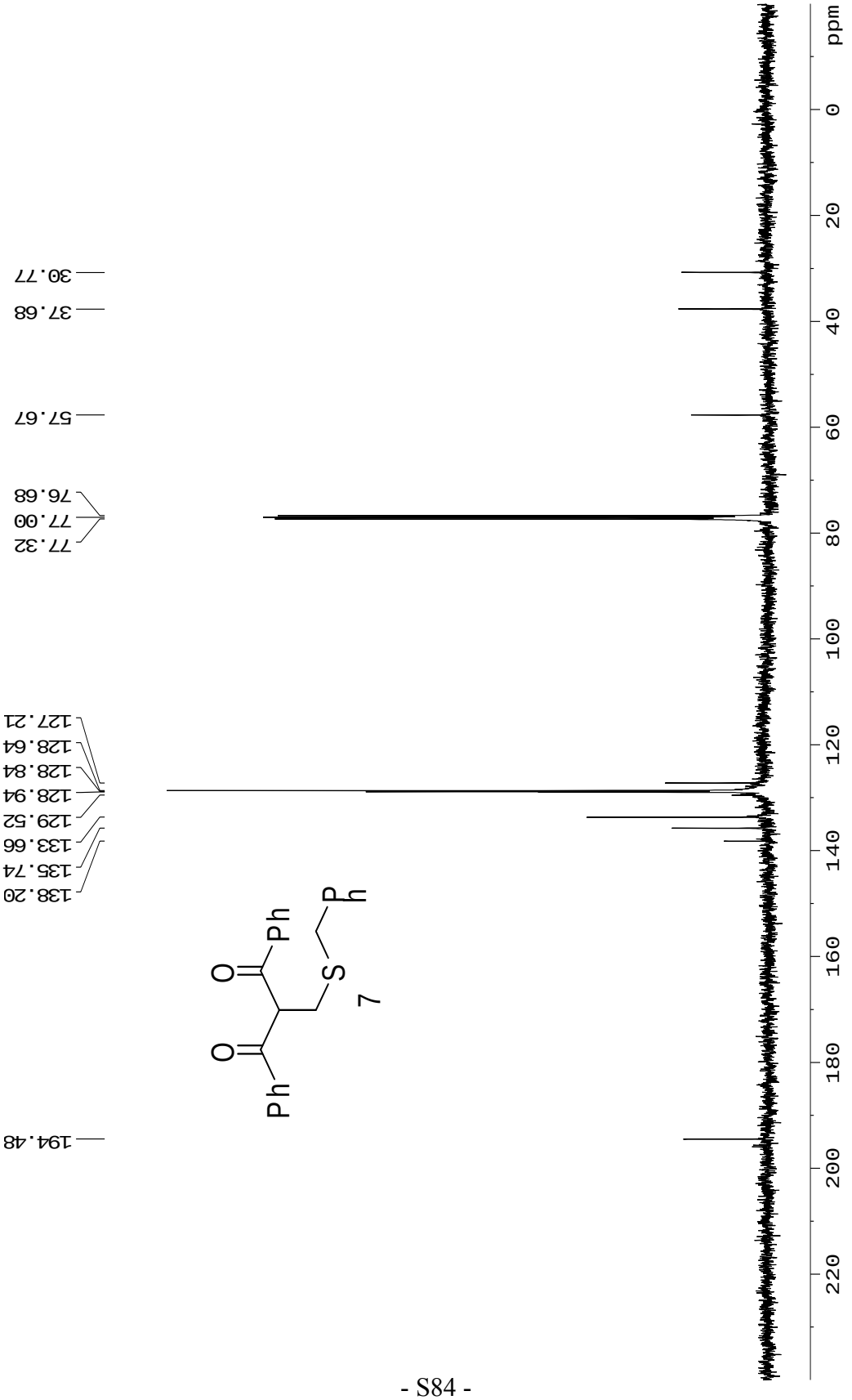
Ph
S
7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128.64
128.84
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133.66
135.74
138.20
194.48
O
Ph
S
Ph
O
7

16. References

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