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Promising hydrogen peroxide stabilizers for large-scale application: unprecedented effect of aryl alkyl ketones

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Hydrogen peroxide of special purity grade

Name of indicator	Hydrogen peroxide of special purity grade
Mass fraction of organic carbon, %, no more	$1*10^{-3}$
Mass fraction of non-volatile residue, %, no more	$5*10^{-4}$
Mass fraction of free acids (in terms of sulfuric acid), %, no more	$2*10^{-5}$
Mass fraction of sulfates (SO_4^{2-}), %, no more	$2*10^{-5}$
Mass fraction of chlorides (Cl^-), %, no more	$4*10^{-5}$
Mass fraction of phosphates (PO_4^{3-}), %, no more	$2*10^{-6}$
Mass fraction of nitrates (NO^{3-}), %, no more	$1*10^{-6}$
Mass fraction of aluminum (Al), %, no more	$1*10^{-6}$
Mass fraction of boron (B), %, no more	$1*10^{-6}$
Mass fraction of manganese (Mn), %, no more	$1*10^{-6}$
Mass fraction of iron (Fe), %, no more	$1*10^{-6}$
Mass fraction of nickel (Ni), %, no more	$1*10^{-6}$
Mass fraction of copper (Cu), %, no more	$1*10^{-6}$
Mass fraction of barium (Ba), %, no more	$1*10^{-6}$
Mass fraction of lead (Pb), %, no more	$1*10^{-6}$
Mass fraction of bismuth (Bi), %, no more	$1*10^{-6}$
Mass fraction of gallium (Ga), %, no more	$1*10^{-6}$
Mass fraction of gold (Au), %, no more	$1*10^{-6}$
Mass fraction of cadmium (Cd), %, no more	$1*10^{-6}$
Mass fraction of potassium (K), %, no more	$1*10^{-6}$
Mass fraction of calcium (Ca), %, no more	$1*10^{-6}$

Mass fraction of cobalt (Co), %, no more	$1*10^{-6}$
Mass fraction of lithium (Li), %, no more	$1*10^{-6}$
Mass fraction of magnesium (Mg), %, no more	$1*10^{-6}$
Mass fraction of molybdenum (Mo), %, no more	$1*10^{-6}$
Mass fraction of arsenic (As), %, no more	$1*10^{-6}$
Mass fraction of sodium (Na), %, no more	$1*10^{-6}$
Mass fraction of tin (Sn), %, no more	$1*10^{-6}$
Mass fraction of silver (Ag), %, no more	$1*10^{-6}$
Mass fraction of strontium (Sr), %, no more	$1*10^{-6}$
Mass fraction of antimony (Sb), %, no more	$1*10^{-5}$
Mass fraction of titanium (Ti), %, no more	$1*10^{-6}$
Mass fraction of phosphorus (P), %, no more	$1*10^{-6}$
Mass fraction of chromium (Cr), %, no more	$1*10^{-6}$
Mass fraction of zirconium (Zr), %, no more	$1*10^{-6}$
Mass fraction of zinc (Zn), %, no more	$1*10^{-6}$
Mass fraction of beryllium (Be), %, no more	$1*10^{-6}$
Mass fraction of tantalum (Ta), %, no more	$1*10^{-6}$
Mass fraction of thallium (Tl), %, no more	$1*10^{-6}$
Mass fraction of niobium (Nb), %, no more	$1*10^{-6}$
Mass fraction of germanium (Ge), %, no more	$2*10^{-5}$
Mass fraction of vanadium (V), %, no more	$4*10^{-5}$

Experimental procedure

NMR spectra were recorded on a commercial instrument (300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C) in $CDCl_3$ and DMSO-d_6. Aryl alkyl ketones **1-15**, 3-bromobenzoic, 4-chlorobenzoic, and 4-methoxybenzoic acids are commercial products (Acros). Aqueous solution of hydrogen peroxide (Russian domestic production, special purity grade) was used. The concentration of H_2O_2 was determined by iodometric titration. The GLC analysis was performed on a chromatograph equipped with a flame-ionization detector (FID) and a CR-1 column (30m*0.32 mm*1.0 μm); helium as a carrier gas (at a flow rate of 41.1 cm/min). The injection volume was 1 μl, the injector temperature was 350 °C. The initial and final temperatures of the thermostat were 70 and 300 °C, respectively; the temperature was raised at a rate 10 °C/min. The temperature of the detector was 320 °C. Laboratory glassware: heat-resistant glass (borosilicate), SiO_2 – 80.64 %; B_2O_3 – 12.0 %; Al_2O_3 – 2.0 %; CaO – 0.36 %; Na_2O – 4.0 %; K_2O – 1.0 %; flasks were used for the experiments for the first time.

General procedure for experiments with aryl alkyl ketones 1-5 (Table 1).

In runs 1-12, aryl alkyl ketone **1-5** (0.001-0.104 g, 0.008-0.866 mmol, 0.013-1.385 mmol of **1-5** / 1 mol of H_2O_2) was added with stirring to a solution of H_2O_2 (18.379-21.249 g, 0.541-0.625 mol, 16.07-18.58 ml, 33.63-36.84 wt%). Then the mixture was stirred at 22-25 °C until homogeneity. The solutions were stored in the dark at 22-25 °C for 16-24 months. The concentration of hydrogen peroxide was determined by iodometric titration.

General procedure for experiments with acetophenones 6-15.

Acetophenone **6-15** (0.092-0.101 g, mmol 0.428-0.735, the ratio 0.760-1.272 mmol of acetophenone / 1 mol of H_2O_2) was added to a 36.80-36.84 % solution of H_2O_2 (18.384-19.844 g, 0.541-0.584 mol, 16.08-17.35 ml). Then the mixture was stirred at 22-25 °C until homogeneity. The solutions were stored in the dark at 22-25 °C for 16 months. The concentration of hydrogen peroxide was determined by iodometric titration.

Solutions containing 3-bromoacetophenone **13** (run 20), 4-chloroacetophenone **11** (run 18), or 4-methoxyacetophenone **6** (run 13) were analyzed by GLC; the presence of 3-bromobenzoic, 4-chlorobenzoic, and 4-methoxybenzoic acids was confirmed based on the retention times equal to those of the standard samples of these acids. The retention times of 3-bromobenzoic, 4-chlorobenzoic, and 4-methoxybenzoic acids were 13.5, 11.7, and 13.0 min, respectively.

Isolation of 3-bromobenzoic, 4-chlorobenzoic, and 4-methoxybenzoic acids.

Organic products were extracted with diethyl ether (10×20 ml) from a hydrogen peroxide solution stabilized by 3-bromoacetophenone **13**, 4-chloroacetophenone **11**, or 4-methoxyacetophenone **6**. The combined organic extracts were washed with water (10 ml), dried over $MgSO_4$, and filtered. The solvent was removed *in vacuo* using a water jet pump. Arenecarboxylic acids were isolated by column chromatography (light petroleum : ethyl acetate, 1:10, as the eluent).

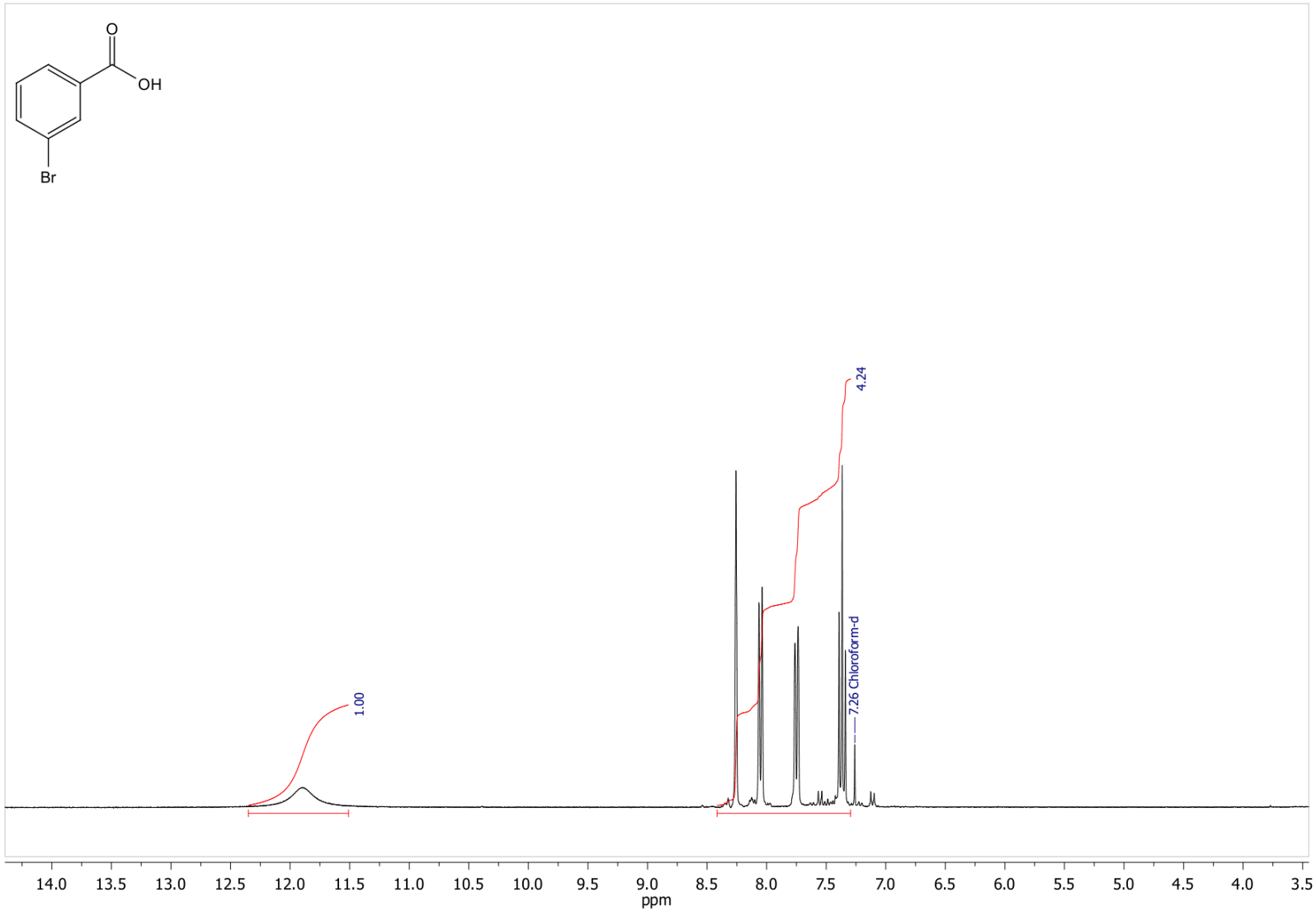
NMR spectra of arylcarboxylic acids.

3-Bromobenzoic acid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.37 (t, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 8.26 (s, 1H), 11.90 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.8, 128.9, 130.2, 131.3, 133.4, 137.0, 171.1.

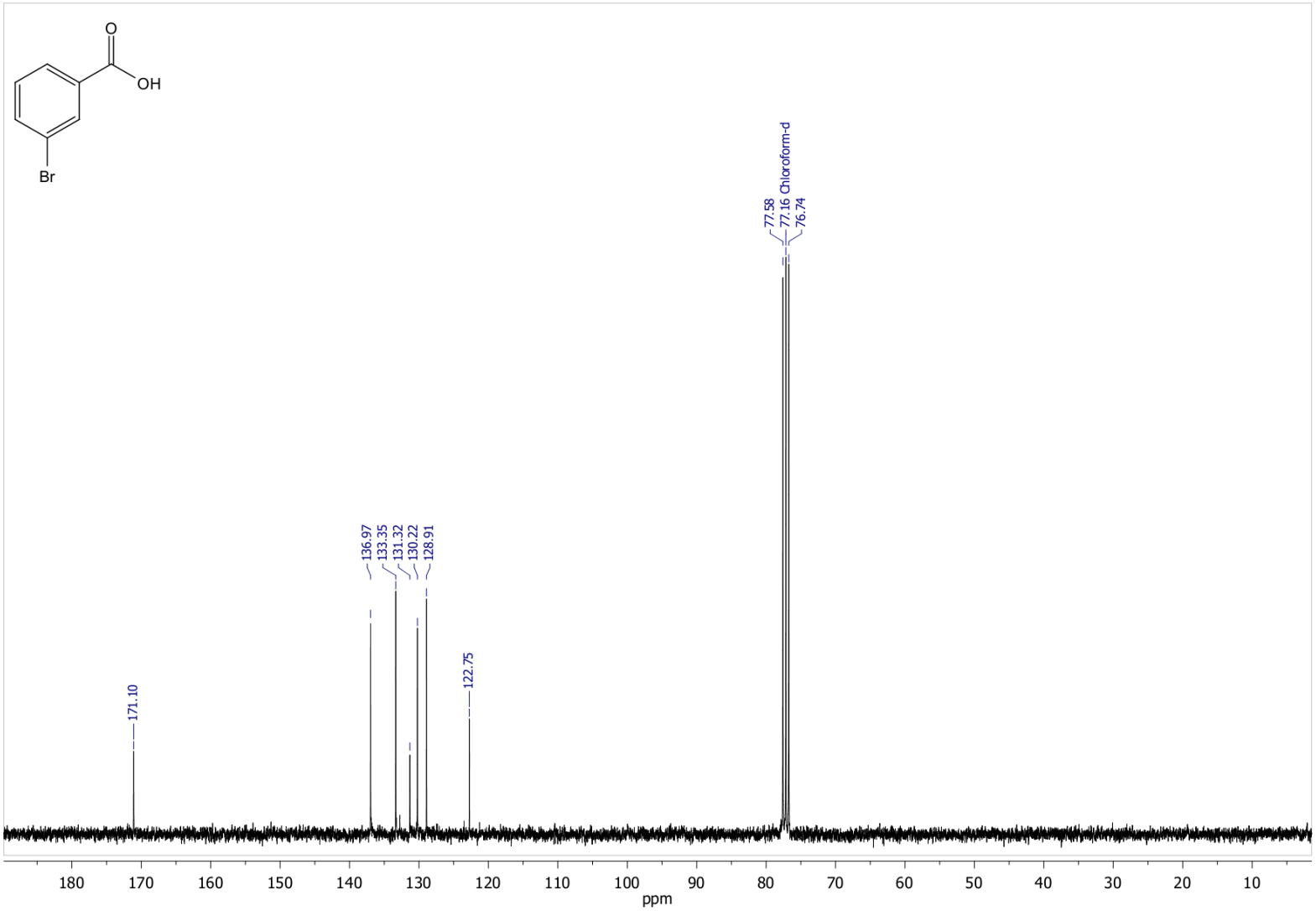
4-Chlorobenzoic acid. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 7.56 (d, 2H, *J* = 7.6 Hz), 7.94 (d, 2H, *J* = 7.6 Hz), 13.16 (br. s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 128.7, 129.7, 131.1, 137.8, 166.4.

4-Methoxybenzoic acid. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 3.81 (s, 3H), 7.01 (d, 2H, *J* = 8.1 Hz), 7.89 (d, 2H, *J* = 8.1 Hz), 12.59 (br. s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 55.4, 113.8, 123.0, 131.3, 162.8, 167.0.

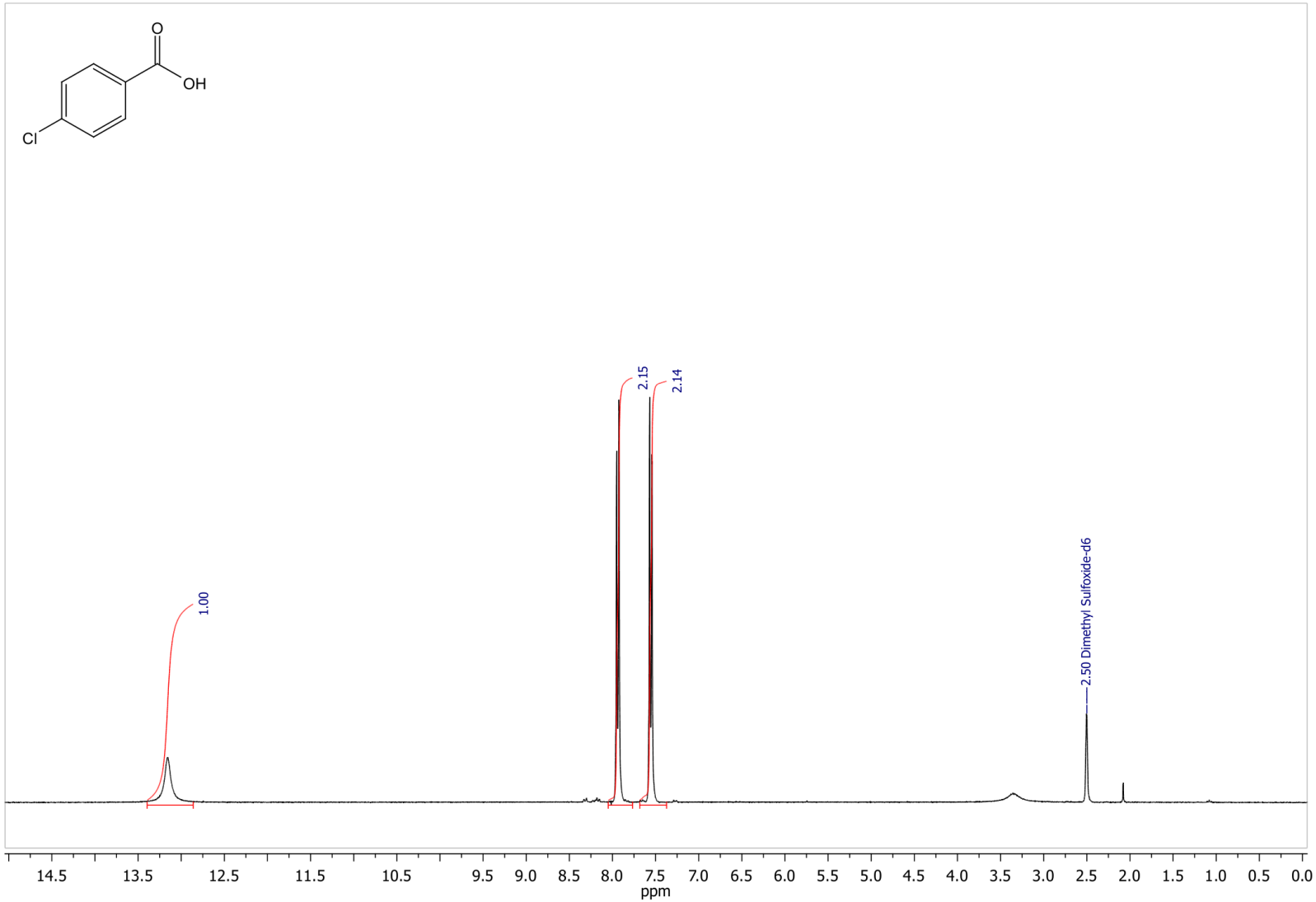
^{1}H NMR of 3-Bromobenzoic acid



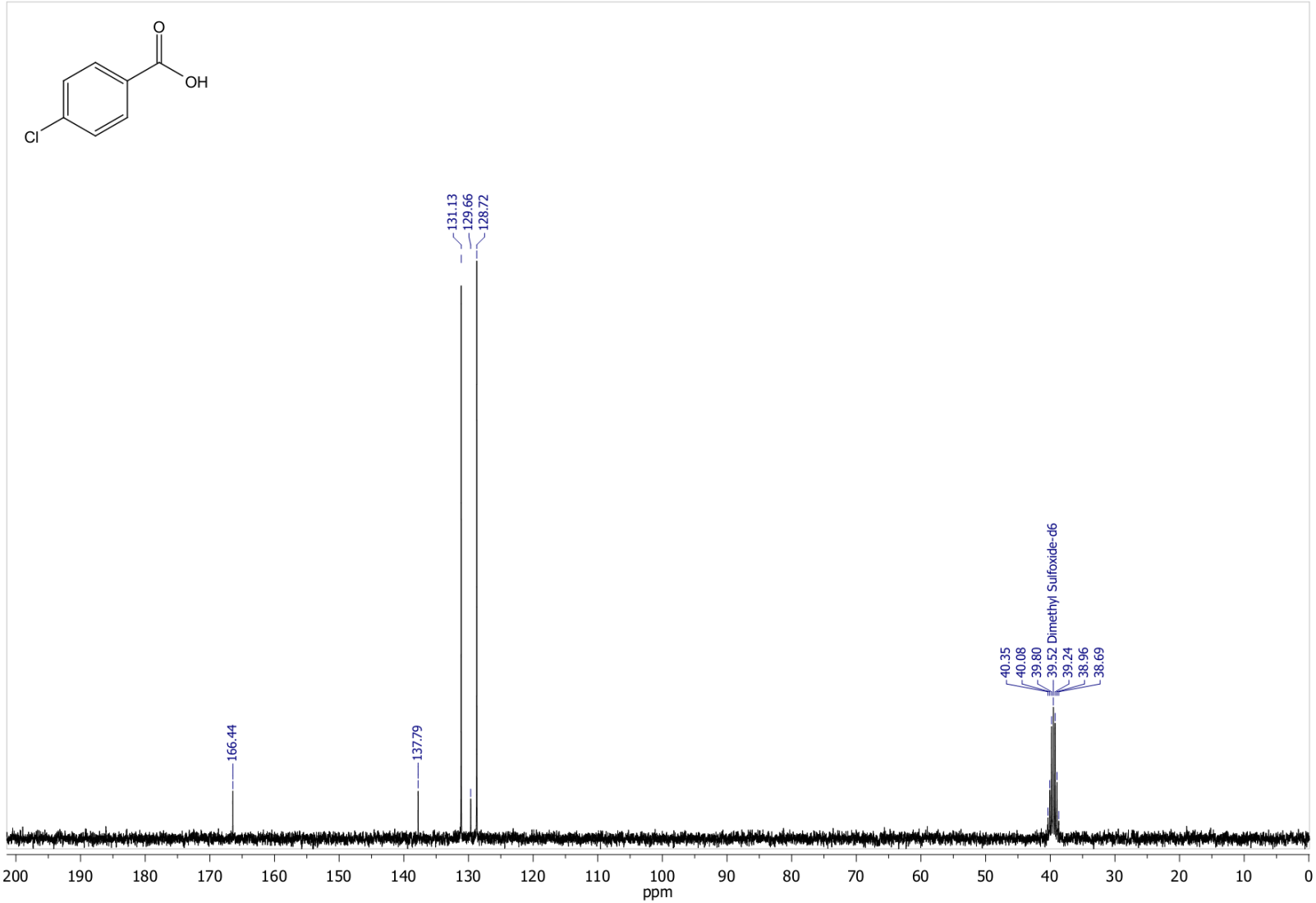
^{13}C NMR of 3-Bromobenzoic acid



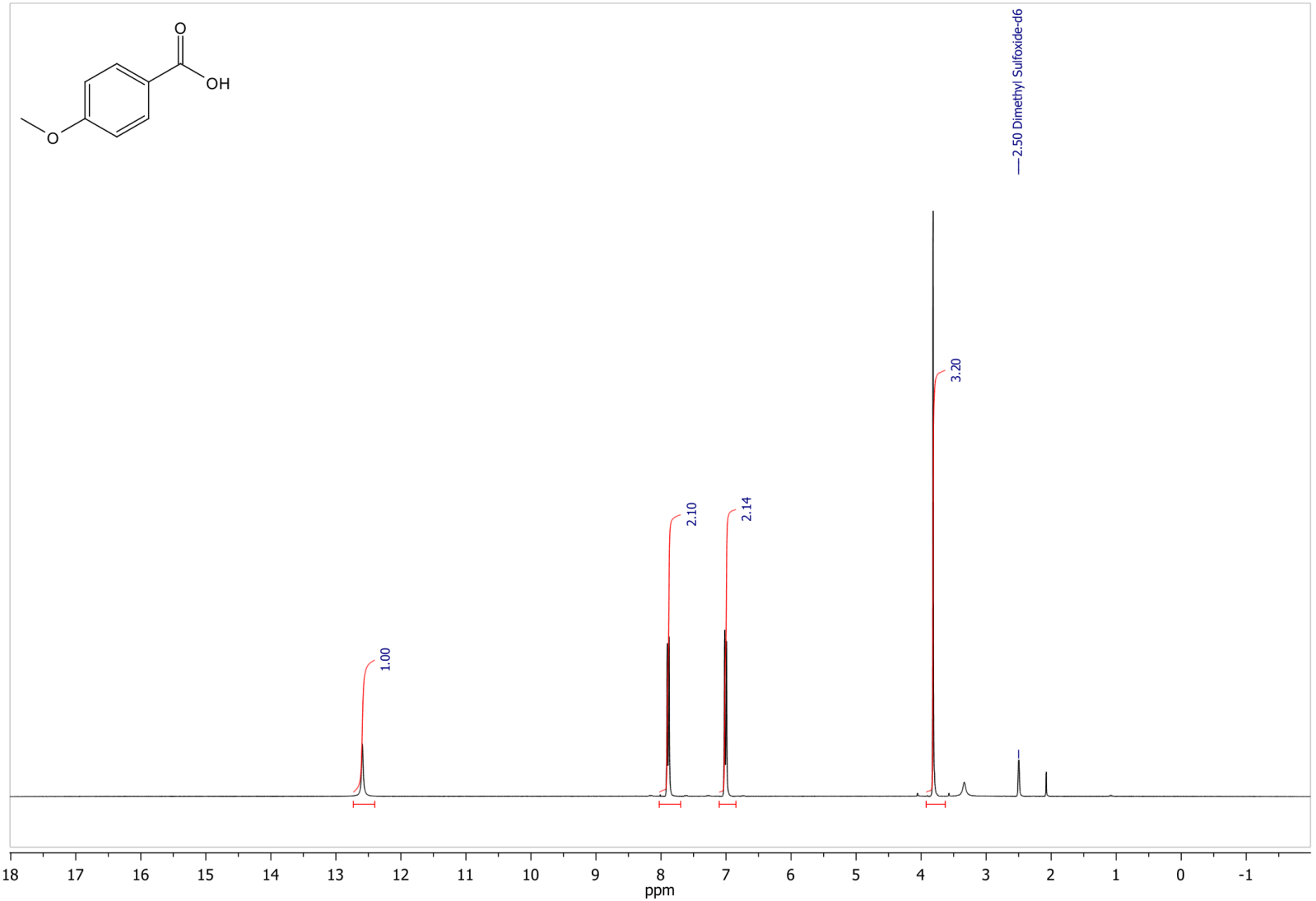
^{1}H NMR of 4-Chlorobenzoic acid



^{13}C NMR of 4-Chlorobenzoic acid



^{1}H NMR of 4-Methoxybenzoic acid



^{13}C NMR of 4-Methoxybenzoic acid