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2-Fluoroanthraquinone-catalyzed photooxidation of benzylic alcohols and aliphatic diols in supercritical carbon dioxide

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I. General information

Instruments

The reactions were carried out in a 22.4 cm^3 steel autoclave equipped with sapphire windows, magnetic stirrer, and pressure/temperature sensors. The ^1H, ^{13}C NMR spectra were recorded with a Bruker AM 300 spectrometer at 300.13, 75.47 MHz correspondingly. Silica gels 0.060-0.200 and 0.035-0.070 nm (Acros) were used for column chromatography. Solvents were purified by standard methods.

Materials

Carbon dioxide (Grade 4.5) and oxygen (Grade 3.5) were obtained from «Linde Gas Rus». Unless otherwise mentioned, all substrates were purchased from Tokyo Chemical Chemistry Co. 4-(Hydroxymethyl)acetophenone purchased was from Apollo Scientific, xanthydrol and 2,2-dimethyl-1,3-propanediol were purchased from Sigma Aldrich Co.

Light absorption spectra of catalyst (2-FAQ)

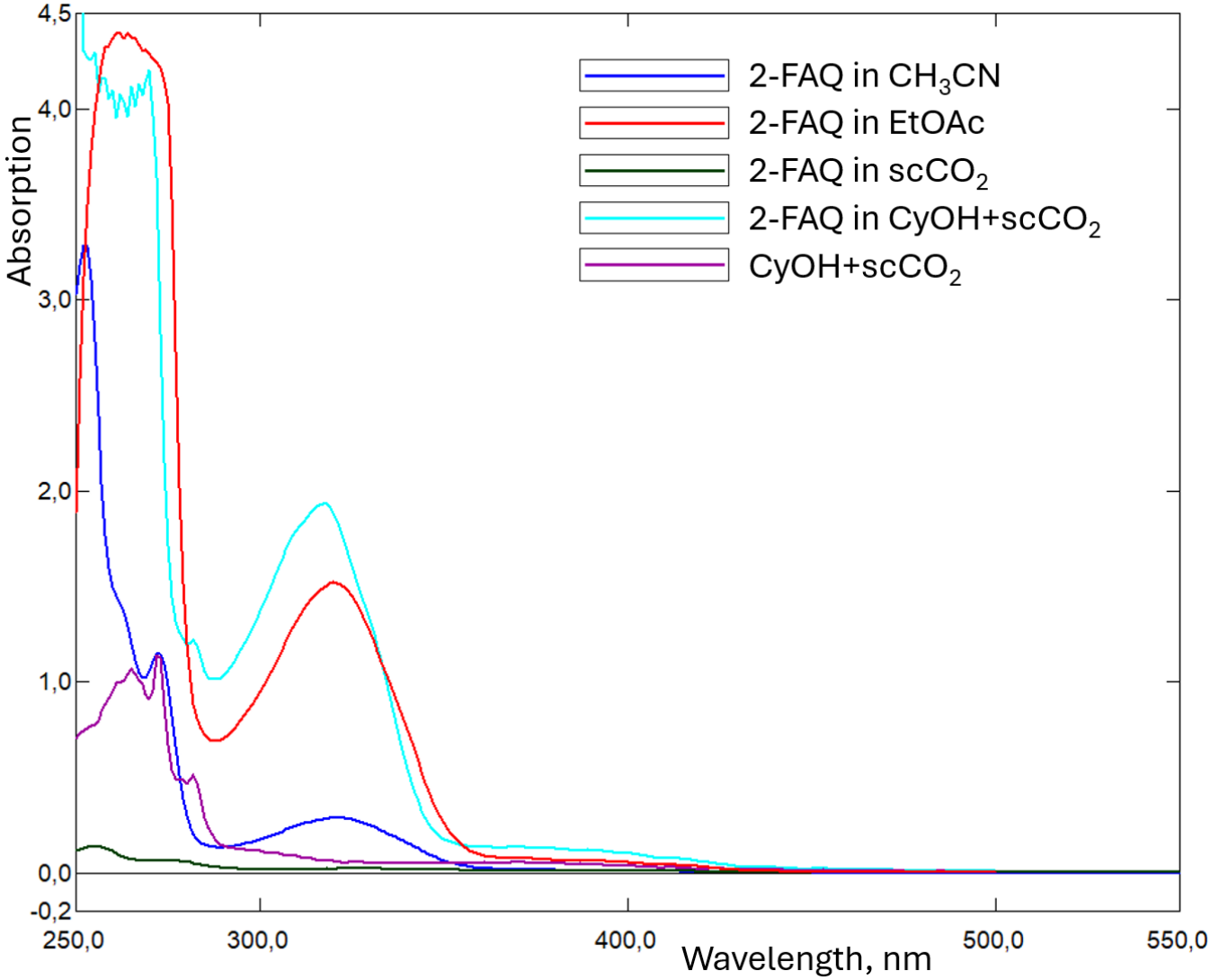


Figure S1.1. Absorption spectra of 2-FAQ in acetonitrile, ethyl acetate, $scCO_2$, and in a mixture of cyclohexanol+$scCO_2$ and the spectrum of pure cyclohexanol+$scCO_2$ mixture.

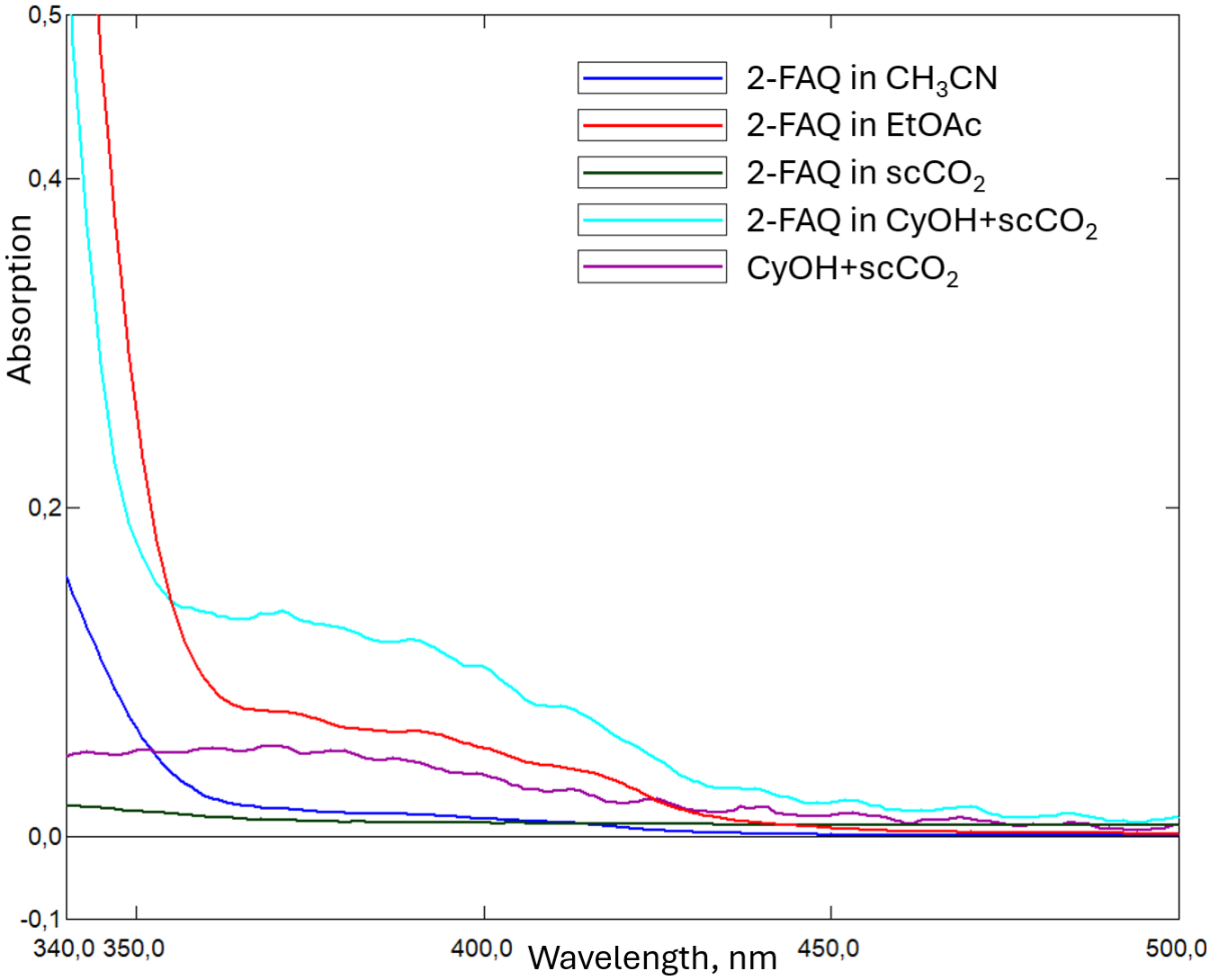


Figure S1.2. Detailed image of the absorption spectra of 2-FAQ in acetonitrile, ethyl acetate, $scCO_2$, and in a mixture of cyclohexanol+$scCO_2$ and the spectrum of pure cyclohexanol+$scCO_2$ mixture in the vicinity of 405 nm.

We have shown experimentally that 2-FAQ was insoluble in $scCO_2$. To verify that the catalyst absorbs light with a wavelength of 405 nm, which was used in the work, the absorption spectra of 2-FAQ were recorded in acetonitrile, ethyl acetate, and in a mixture of cyclohexanol+$scCO_2$ (Figure S1.2). The spectrum of a pure mixture of cyclohexanol+sc-CO_2 is included for comparison. The more detailed spectra are shown in Figure 1.2, from which it is clearly seen that in solutions 2-FAQ absorbs light with a wavelength of up to 425 nm, which legitimizes the use of the 405 nm light with to activate the catalyst in the photocatalytic oxidation reactions.

II. Set-up and General Procedure for oxidation

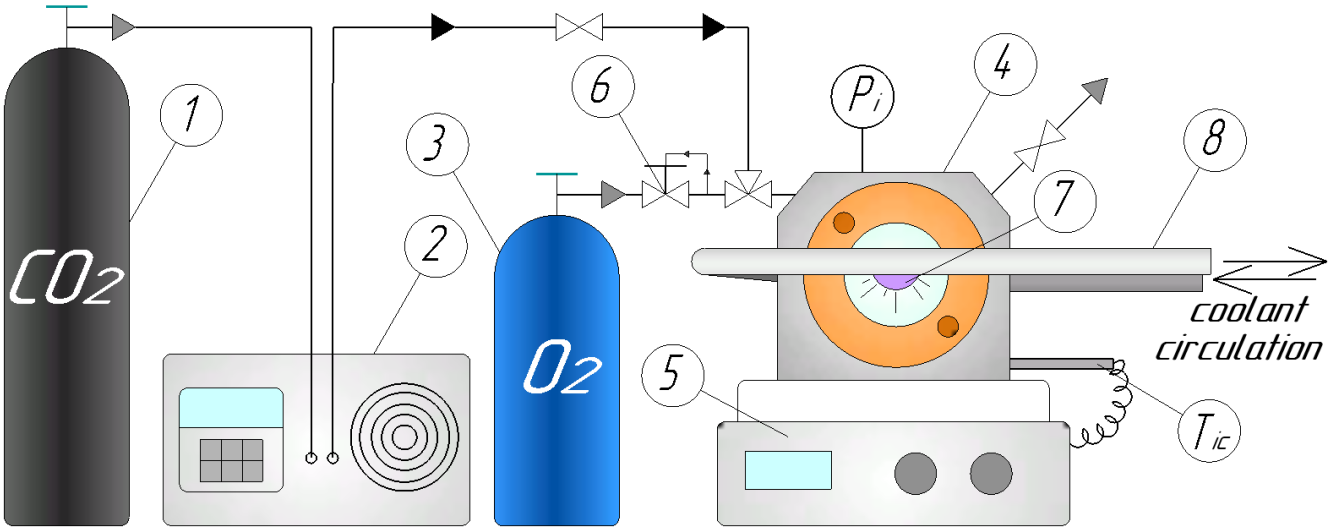


Figure S2. Experimental setup for photocatalytic oxidation in the $scCO_2$ medium. *1* – CO_2 tank; *2* – high-pressure pump with internal cooling *3* – O_2 tank; *4* – reactor-autoclave; *5* – magnetic stirrer/heater; *6* – pressure regulator; *7* – LED assembly; *8* – metal circuit with coolant.

The 22 cm^3 stainless steel autoclave (*4*) with a magnetic stirrer and sapphire windows (Figure S3) was loaded with alcohol **1** or diol **4** (1 mmol) and **2-FAQ** (2.3 mg, 1 mol%) thermostated at 25°C on magnetic stirrer/heater (*5*). Pure oxygen was fed into the autoclave from oxygen tank (*3*) *via* pressure regulator with manometer (*6*). The amount of oxygen was taken on the assumption that 1 mmol corresponded to 0.11 MPa. The reactor was heated to 45°C and filled with CO_2 from CO_2 tank (*1*) using pump (*2*) to reach total pressure of 8.6 MPa (~0.3 g cm^{-3} density). Two sets of 12W LEDs (*7*) emitting at 405 nm placed against the reactor windows were turned on and reaction mixture was stirred at 45°C and 8.6 MPa over reaction period. The generated heat was removed from the LEDs with metal circuit with circulating coolant (*8*). Upon the process ending, the LEDs were turned off, the autoclave was cooled, depressurized using valve, and opened. The conversion and selectivity values were determined based on comparison of substrate/product ^1H NMR picks integral intensities. Crude products were purified by column chromatography on silica gel (gradient from *n*-hexane to *n*-hexane/EtOAc = 10 : 1) to afford corresponding oxidation products.

Each of the two LED assemblies is of 12W power consumption and emits light in narrow region (405 ± 5 nm). Their effective light powers measured experimentally with power/energy meter Nova II, Ophir Optronics Solutions in a direct proximity and right behind the 16 mm sapphire glass were ~1600 mW and ~800 mW, respectively. Moreover, the sapphire glass exerts a collimating effect improving the efficiency of the light irradiation.

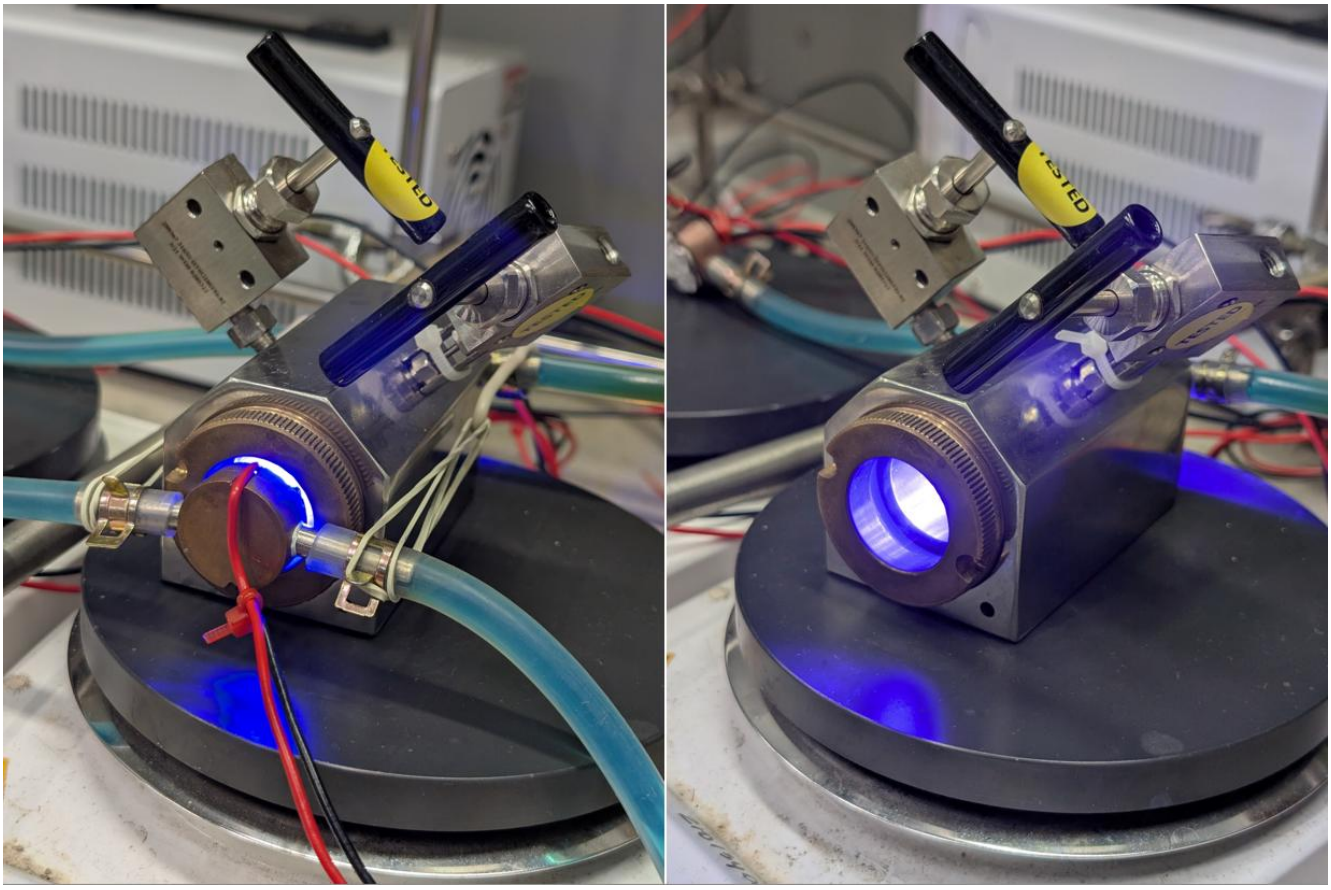


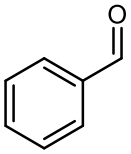
Figure S3. Real images of the reactor and the setup during the process.

General procedure for oxidation.

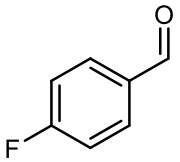
An alcohol **1** or diol **4** (1 mmol) and **2-FAQ** (2.3 mg, 1 mol%) were placed in 22 cm^3 stainless steel reactor-autoclave. The reactor was thermostated at 25°C and pure oxygen was fed into the autoclave from the oxygen tank *via* pressure regulator with manometer. The amount of oxygen was taken on the assumption that 1 mmol corresponds to 0.11 MPa. The reactor was heated to 45°C and filled with CO_2 from CO_2 tank using a pump to reach total pressure 8.6 MPa (~0.3 g cm^{-3} density). Two sets of 12W LEDs emitting at 405 nm placed against the reactor windows were turned on and reaction mixture was stirred at 45°C and 8.6 MPa over reaction period. Then, the LEDs were turned off, the autoclave was cooled, depressurized using valve, and opened. The conversion and selectivity values were determined based on comparison of substrate/product ^{1}H NMR picks integral intensities. Crude products were purified by column chromatography on silica gel (gradient from *n*-hexane to *n*-hexane/EtOAc = 10 : 1) to afford corresponding oxidation products.

The experiments in *n*-hexane and acetonitrile were performed in similar manner, only the organic solvents were pumped into reactor-autoclave instead of CO_2.

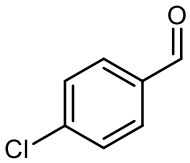
III. Characterization data



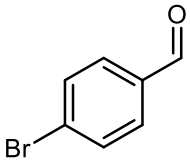
Benzaldehyde (2a). Colorless liquid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 2H).



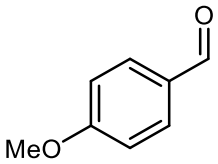
4-Fluorobenzaldehyde (2b). Colorless liquid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 7.88 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.18 (t, *J* = 8.5 Hz, 2H).



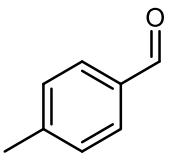
4-Chlorobenzaldehyde (2c). Pale yellow solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.95 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H).



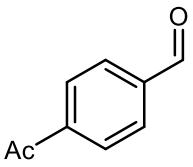
4-Bromobenzaldehyde (2d). Yellow solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.96 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H).



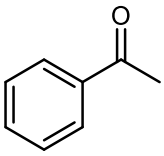
4-Methoxybenzaldehyde (2e). Colorless liquid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.85 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H).



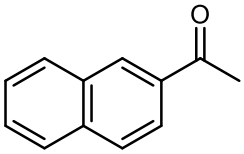
4-Methylbenzaldehyde (2f). Pale yellow solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.96 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H).



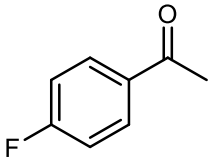
4-Acetylbenzaldehyde (2g). White solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 10.10 (s, 1H), 8.09 (d, *J* = 8.3 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 2.65 (s, 3H).



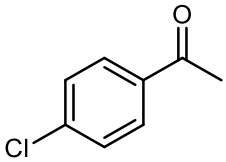
Acetophenone (2h). Colorless liquid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 2.59 (s, 3H).



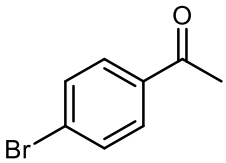
1-(Naphthalen-2-yl)ethan-1-one (2i). Pale yellow solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 8.03 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.87 (dd, *J* = 8.3, 3.5 Hz, 2H), 7.67 – 7.47 (m, 2H), 2.71 (s, 3H).



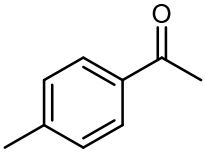
1-(4-Fluorophenyl)ethan-1-one (2j). Pale yellow solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.98 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.13 (dd, *J* = 8.9, 8.4 Hz, 2H), 2.59 (s, 3H).



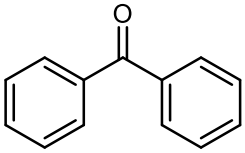
1-(4-Chlorophenyl)ethan-1-one (2k). Pale yellow solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 2.57 (s, 3H).



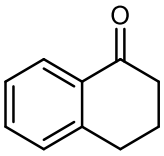
1-(4-Bromophenyl)ethan-1-one (2l). Pale yellow solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 2.58 (s, 3H).



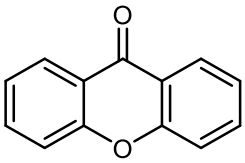
1-(p-Tolyl)ethan-1-one (2m). Colorless liquid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.57 (s, 3H), 2.40 (s, 3H).



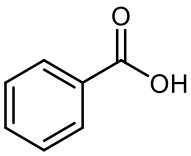
Benzophenone (2n). White solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.6 Hz, 4H), 7.41 (d, *J* = 8.6 Hz, 2H), 2.57 (s, 4H).



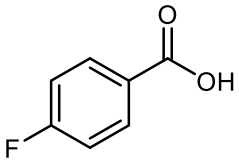
Tetralone-1 (2o). Pale yellow liquid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.48 (td, *J* = 7.5, 1.5 Hz, 1H), 7.37 – 7.18 (m, 2H), 2.98 (t, *J* = 6.1 Hz, 2H), 2.67 (t, *J* = 6.1 Hz, 2H), 2.15 (m, 2H).



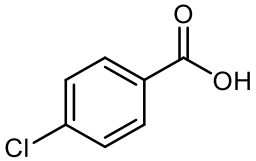
Xanthen-9-one (2p). White solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H).



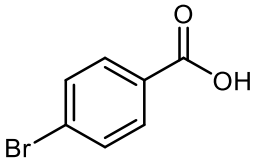
Benzoic acid (3a). White solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H).



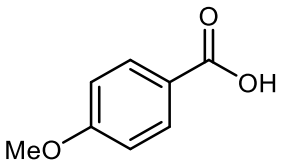
4-Fluorobenzoic acid (3b). White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.00 (dd, *J* = 8.6, 5.7 Hz, 2H), 7.31 (t, *J* = 8.8 Hz, 2H).



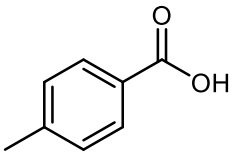
4-Chlorobenzoic acid (3c). White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H).



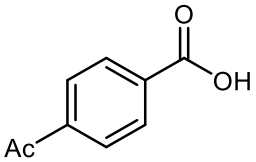
4-Bromobenzoic acid (3d). Pale yellow solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H).



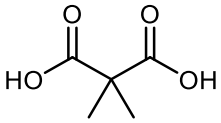
4-Methoxybenzoic acid (3e). Pale yellow solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.88 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 3.76 (s, 3H).



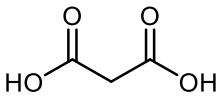
4-Methylbenzoic acid (3f). White solid. ^{1}H NMR (300 MHz, Chloroform-d) δ 8.06 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 2.48 (s, 3H).



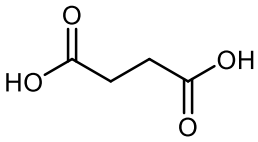
4-Acetylbenzoic acid (3g). White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.05 (s, 4H), 2.63 (s, 3H).



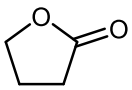
2,2-Dimethylmalonic acid (5a). White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.27 (s, 6H).



Malonic acid (5b). White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.23 (s, 2H).



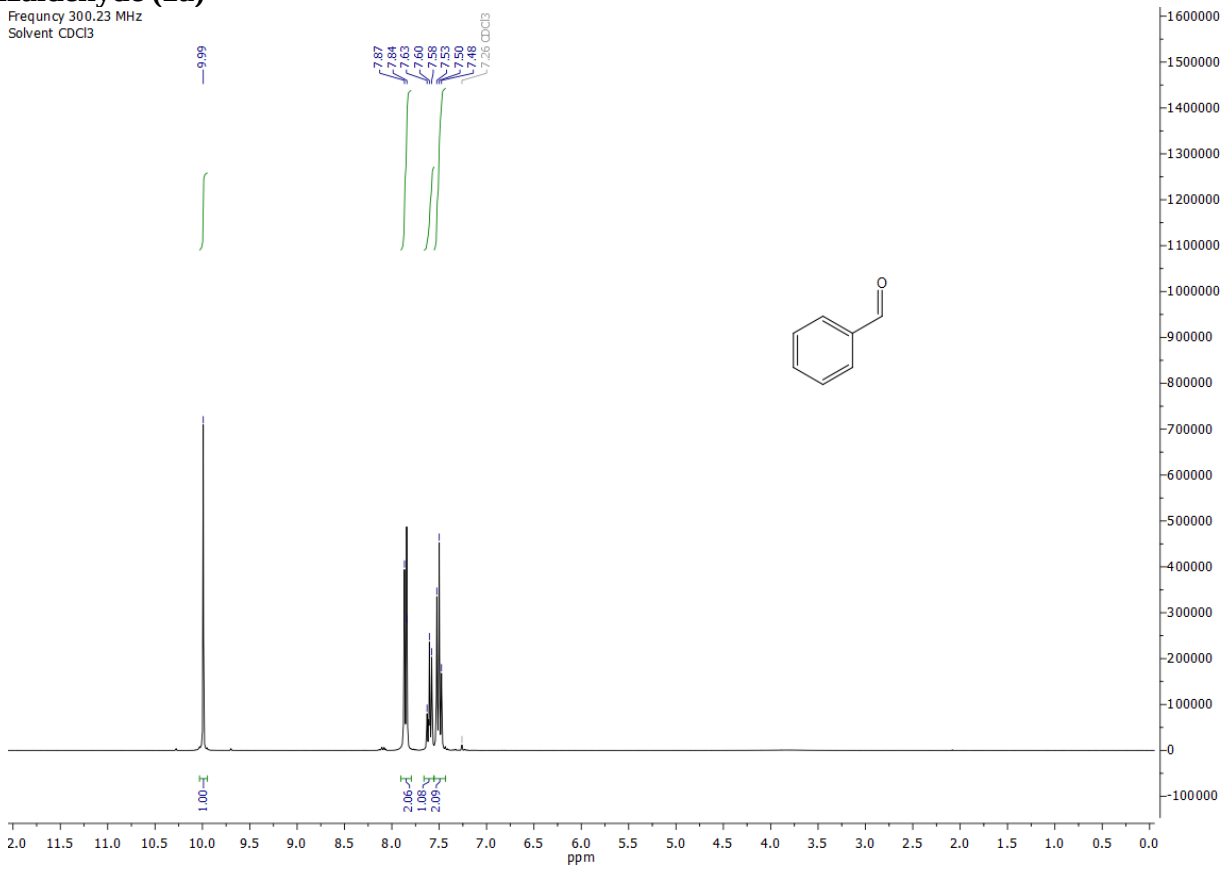
Succinic acid (5c). White solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 2.41 (s, J = 8.2 Hz, 4H).



γ-Butyrolactone (6). Colorless liquid. ^{1}H NMR (300 MHz, Chloroform-d) δ 4.28 (t, J = 7.0 Hz, 2H), 2.42 (t, J = 8.2 Hz, 2H), 2.20 (m, 2H).

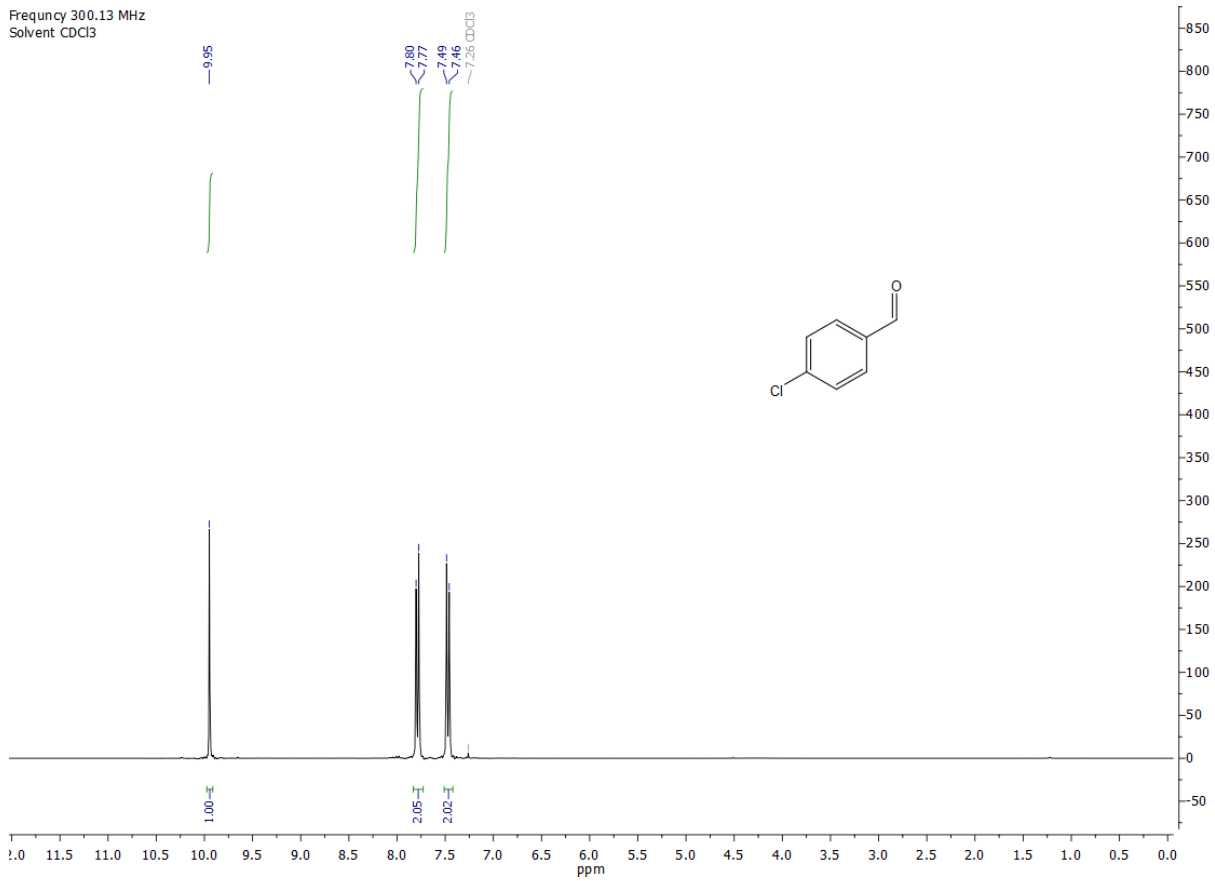
IV. NMR spectra of products

Benzaldehyde (2a)

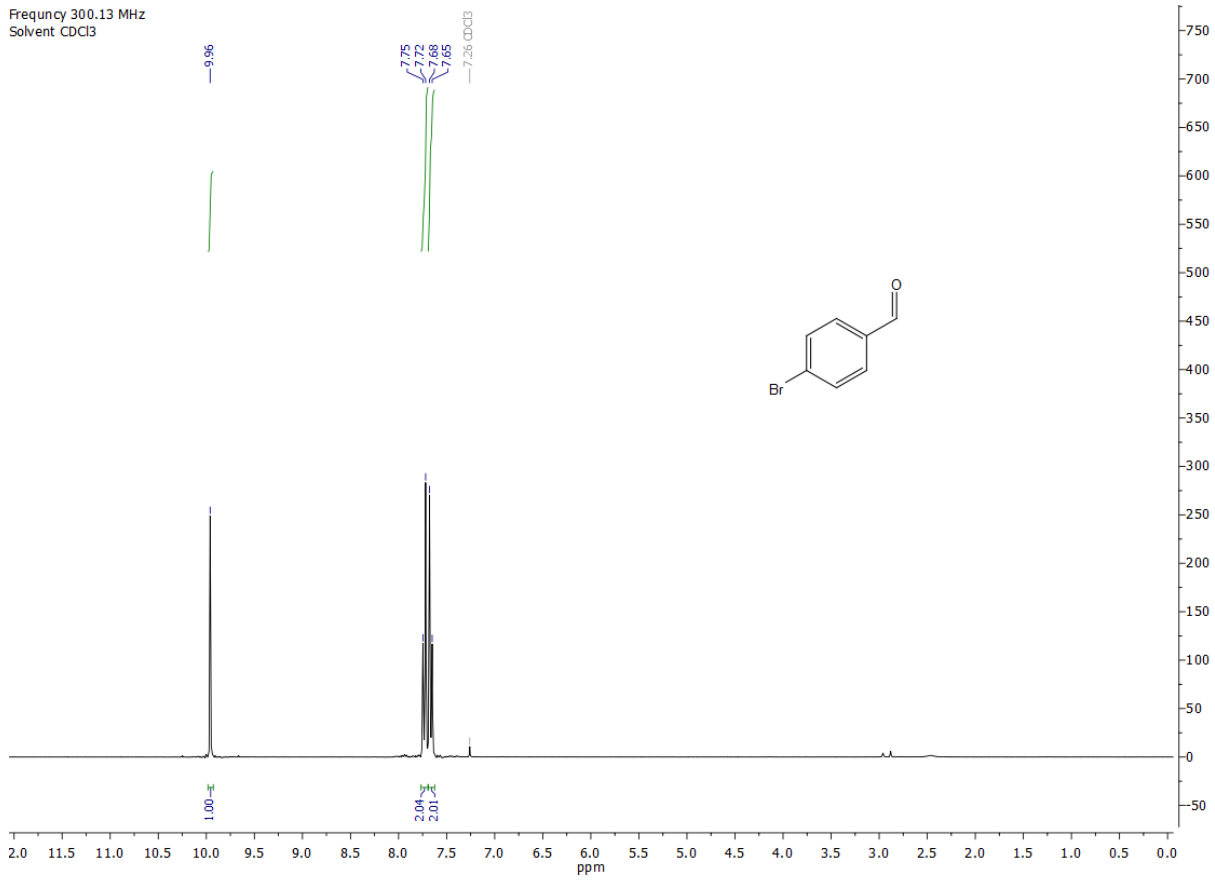


4-Fluorobenzaldehyde (2b)

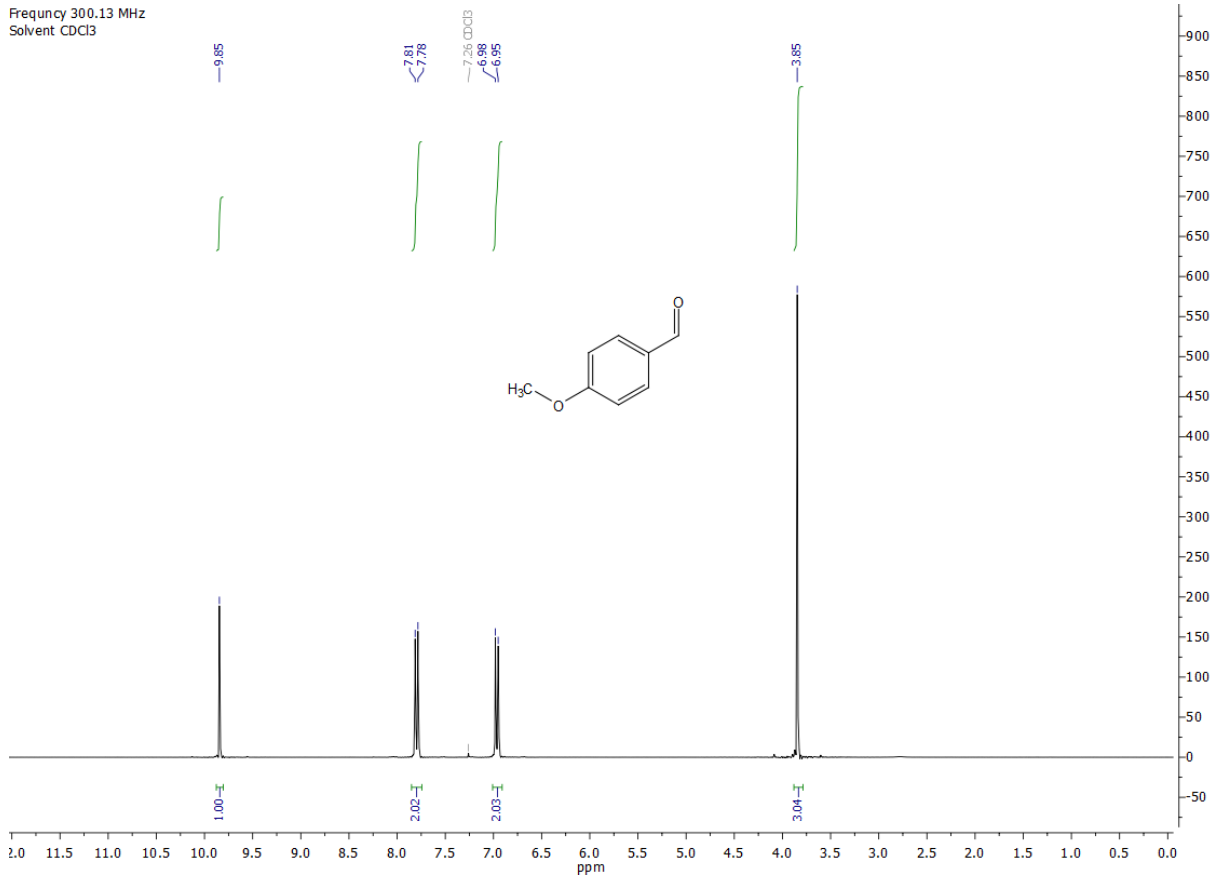
4-Chlorobenzaldehyde (2c)



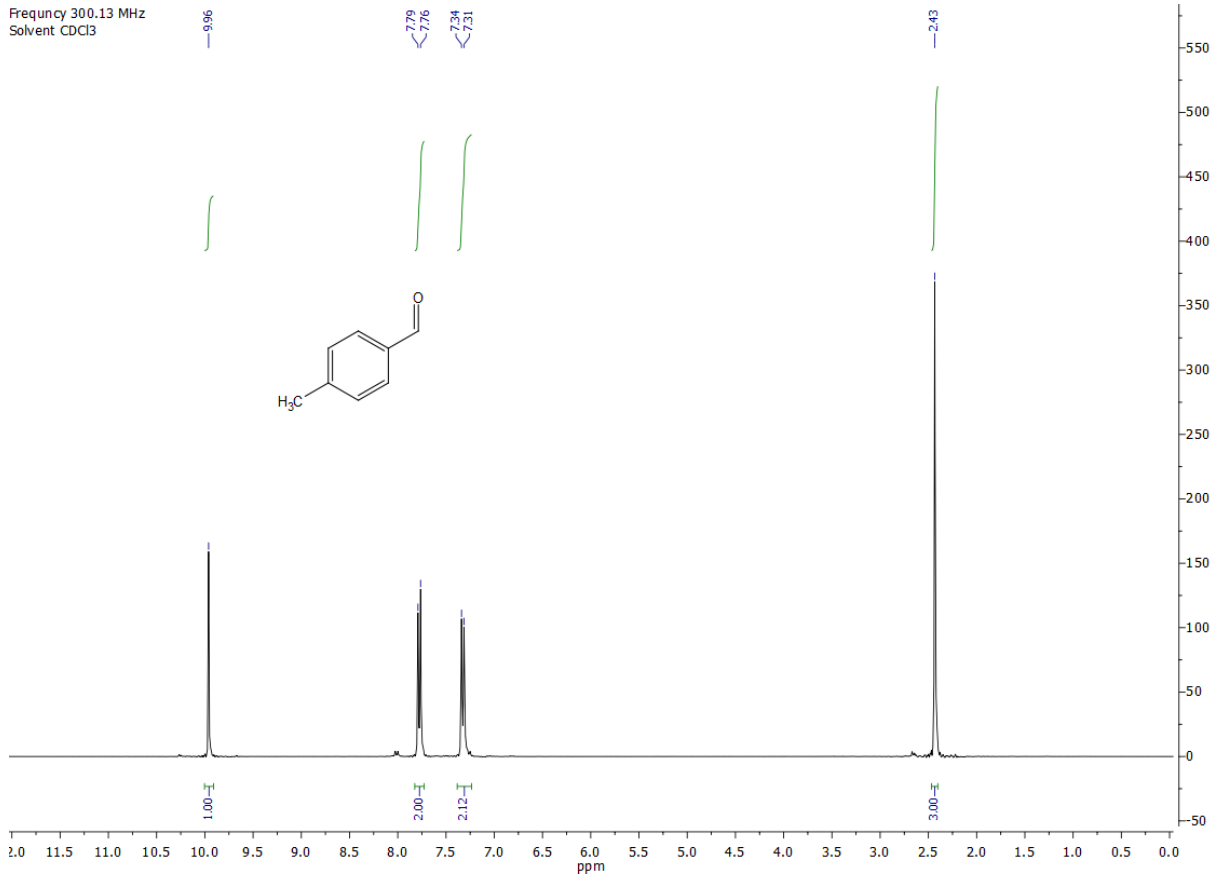
4-Bromobenzaldehyde (2d)



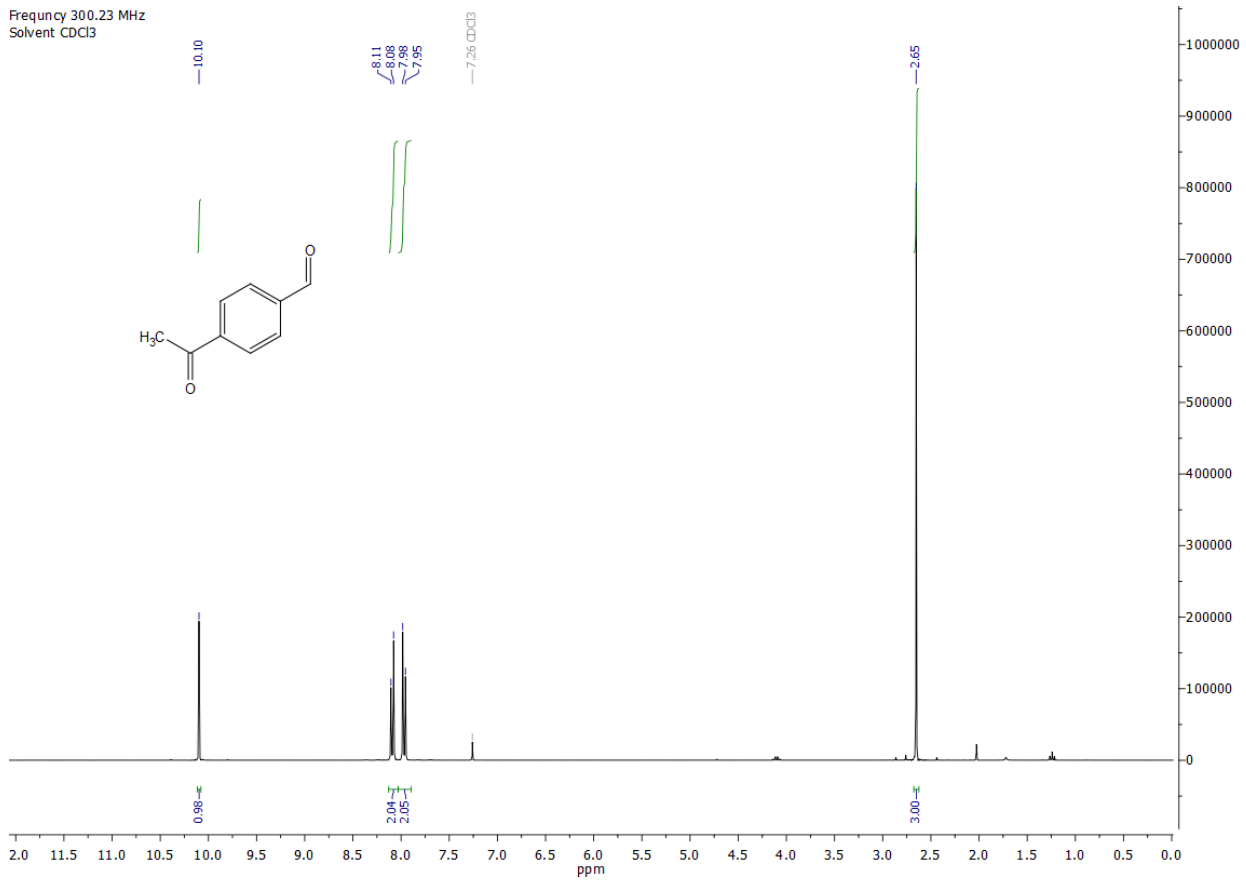
4-Methoxybenzaldehyde (2e)



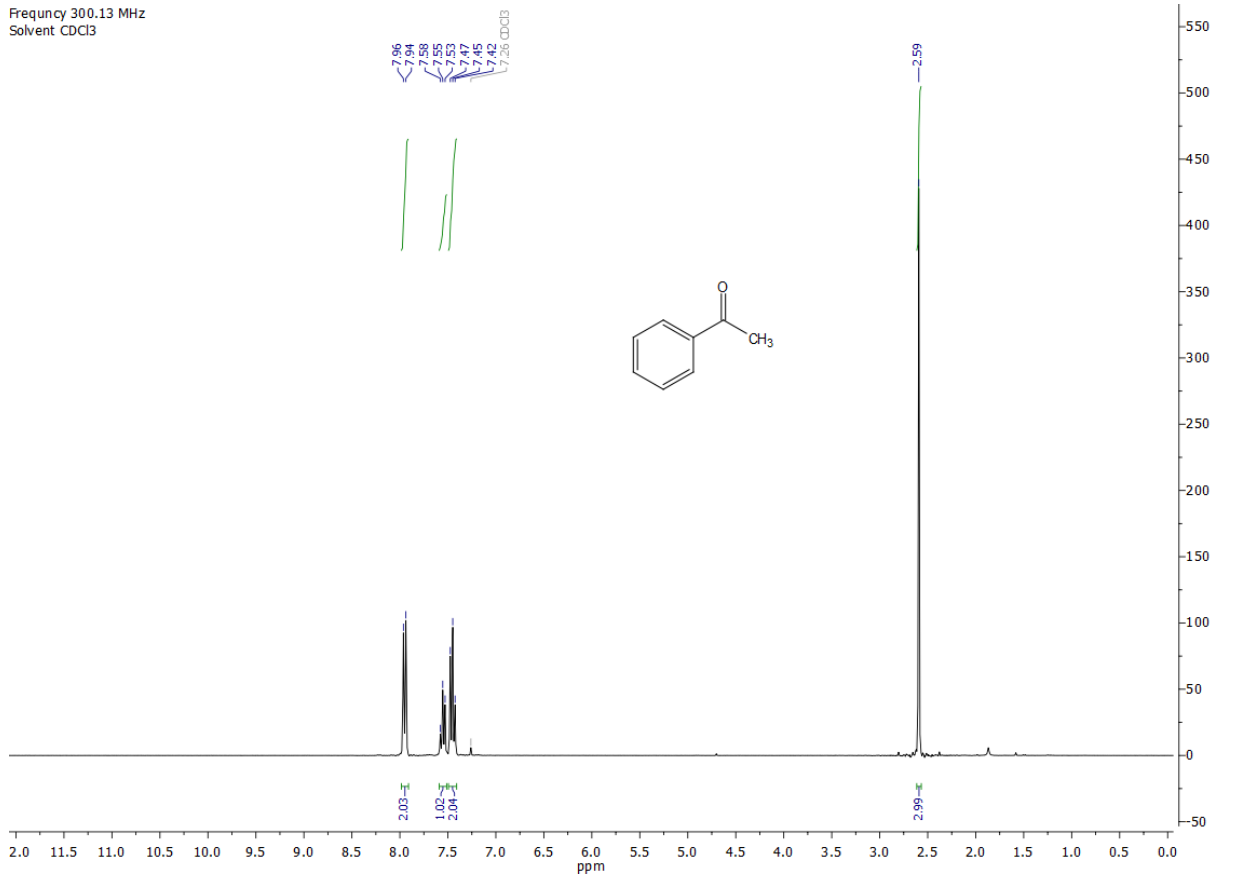
4-Methylbenzaldehyde (2f)



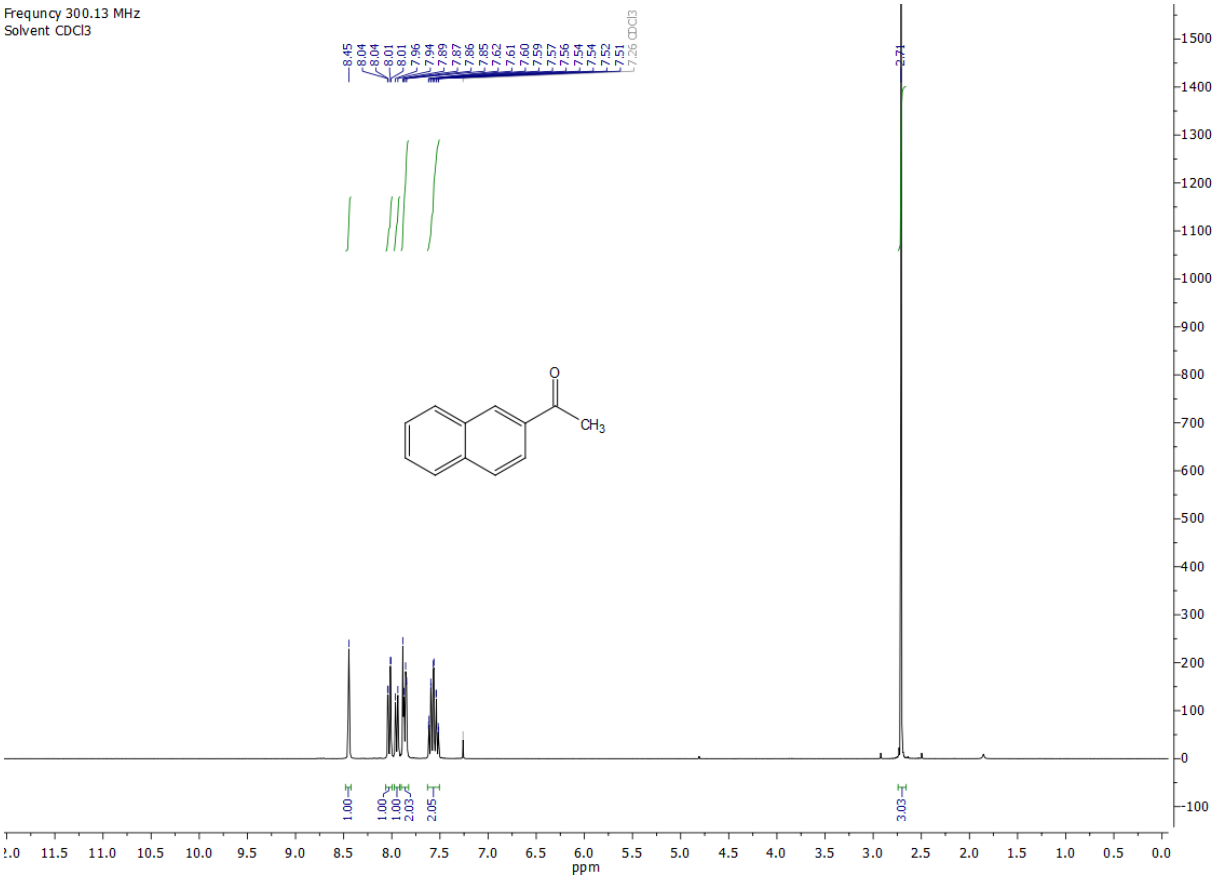
4-Acetylbenzaldehyde (2g)



Acetophenone (2h)

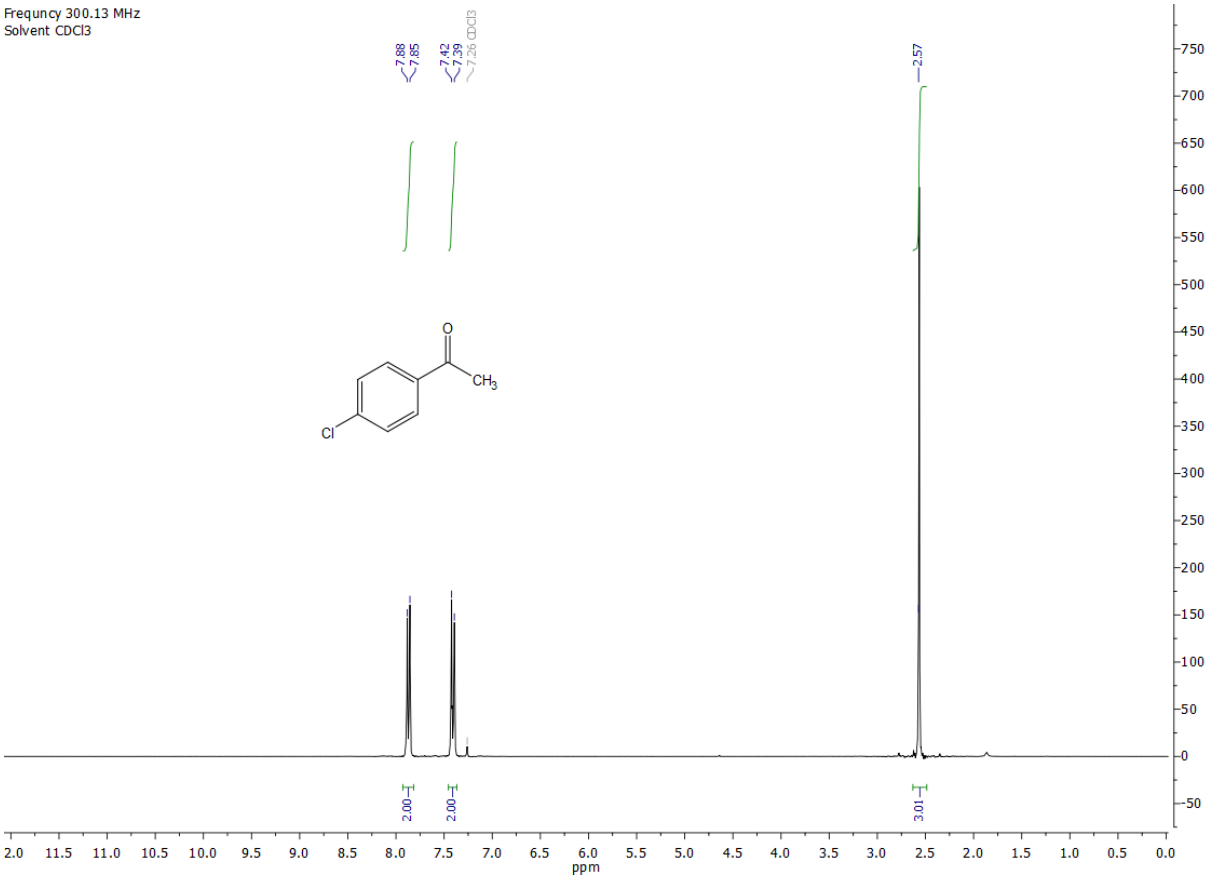


1-(Naphthalen-2-yl)ethan-1-one (2i)

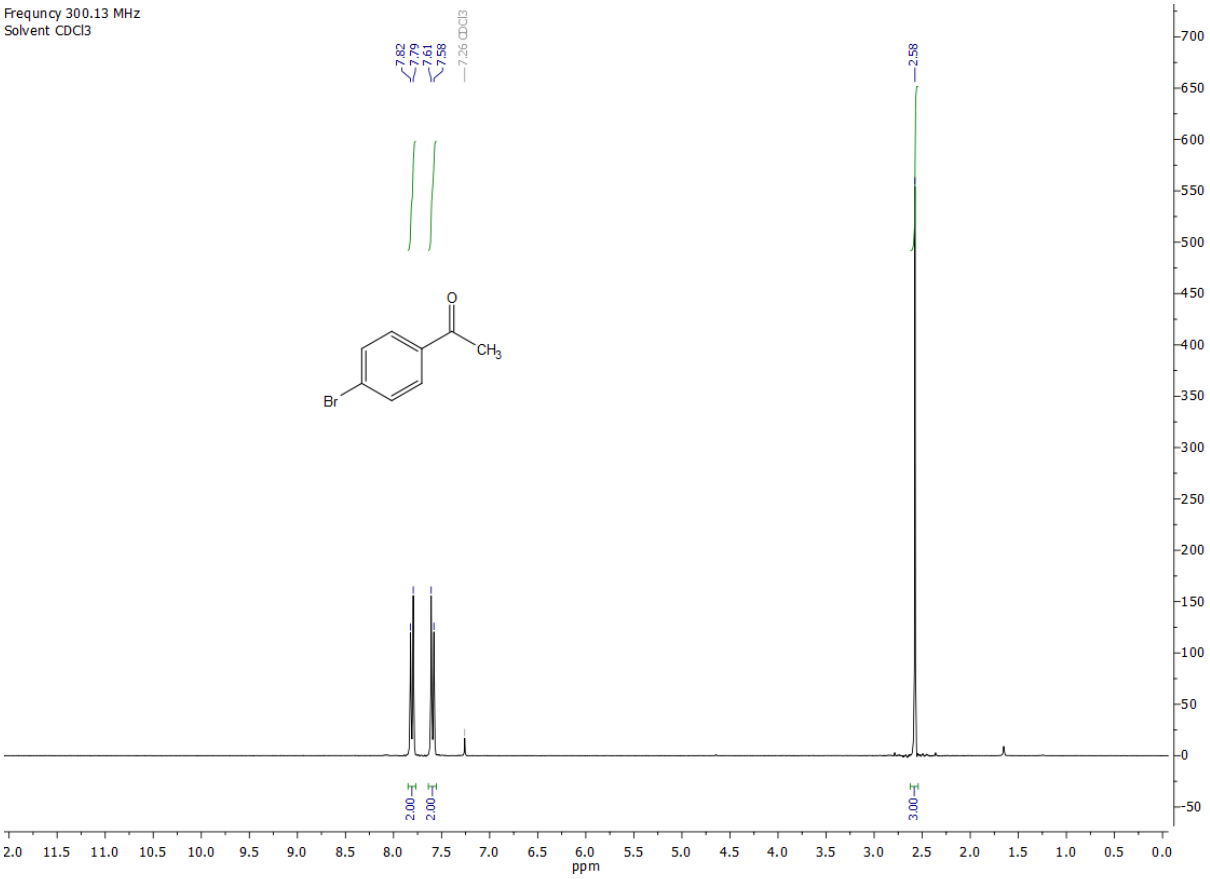


1-(4-Fluorophenyl)ethan-1-one (2j)

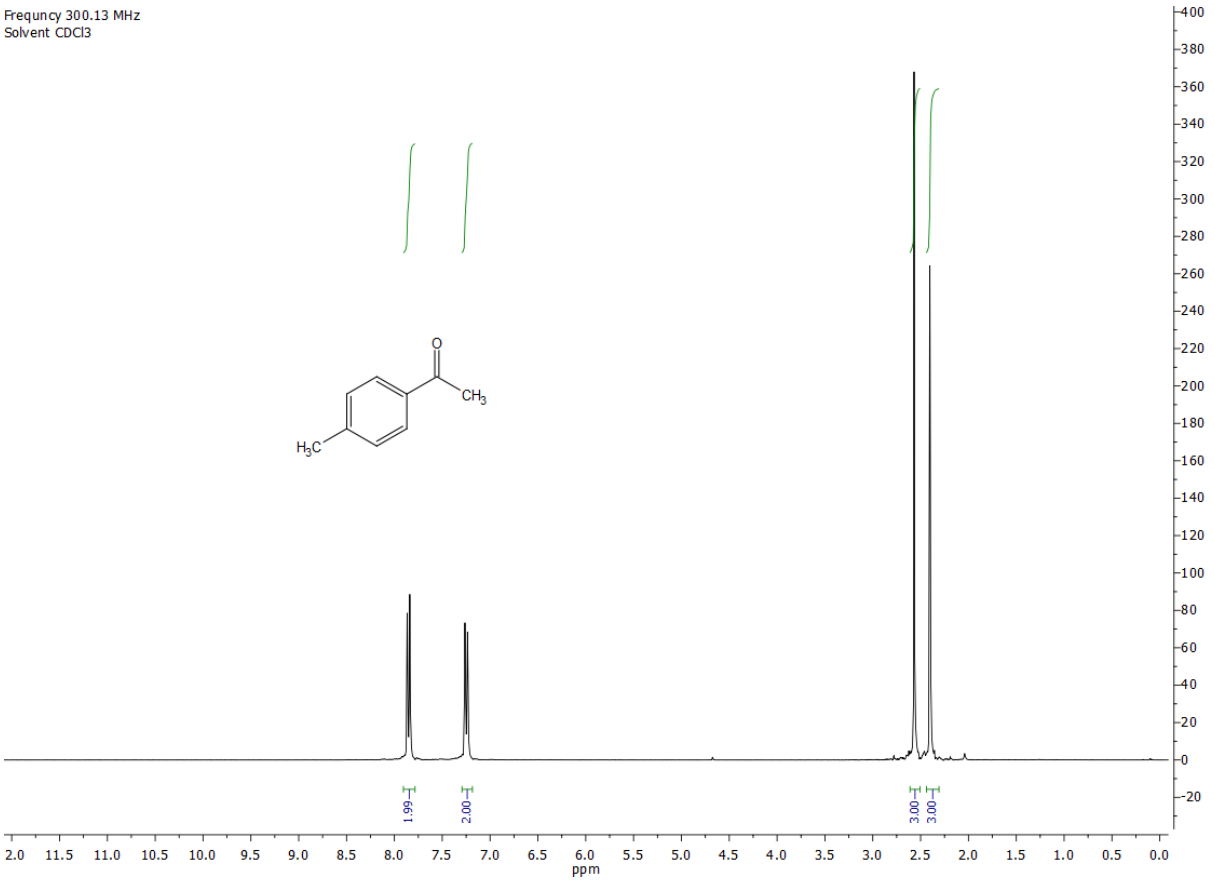
1-(4-Chlorophenyl)ethan-1-one (2k)



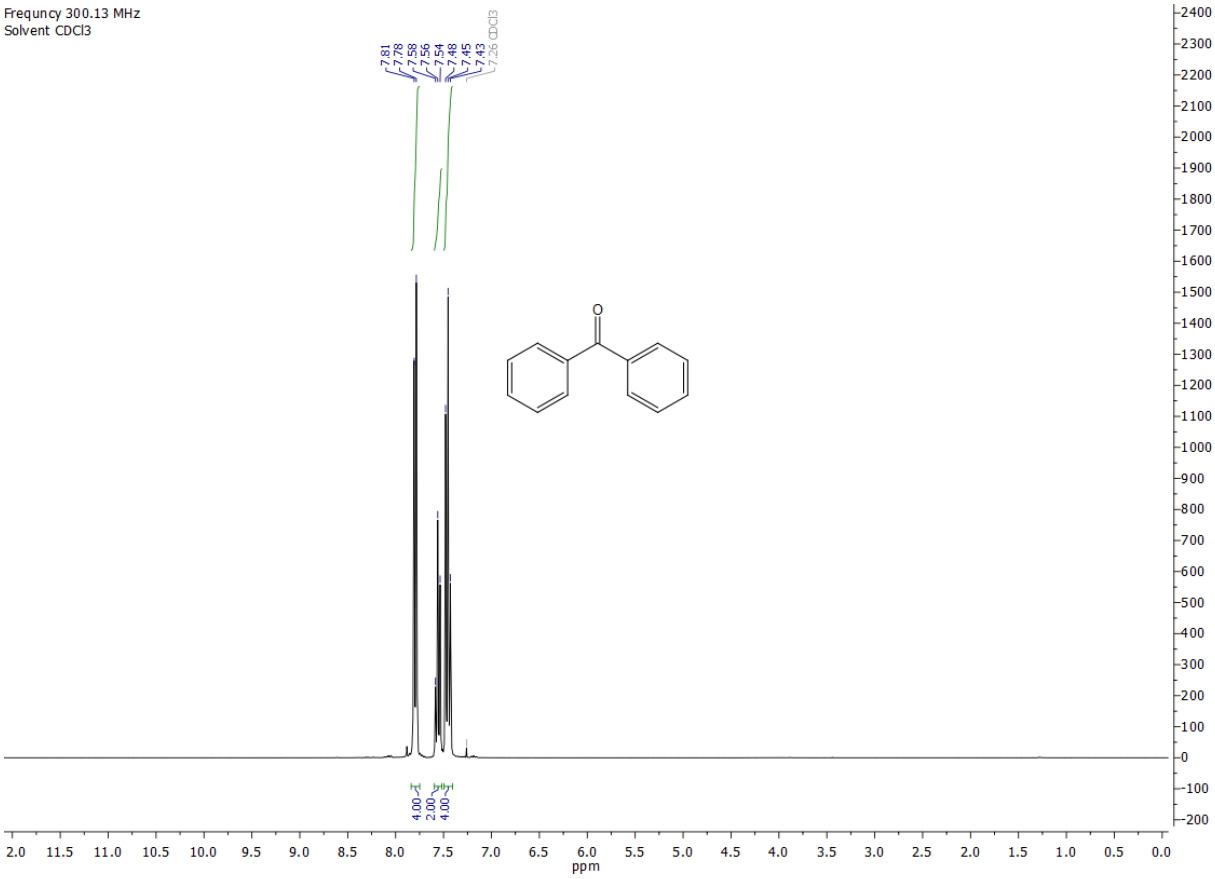
1-(4-Bromophenyl)ethan-1-one (2l)



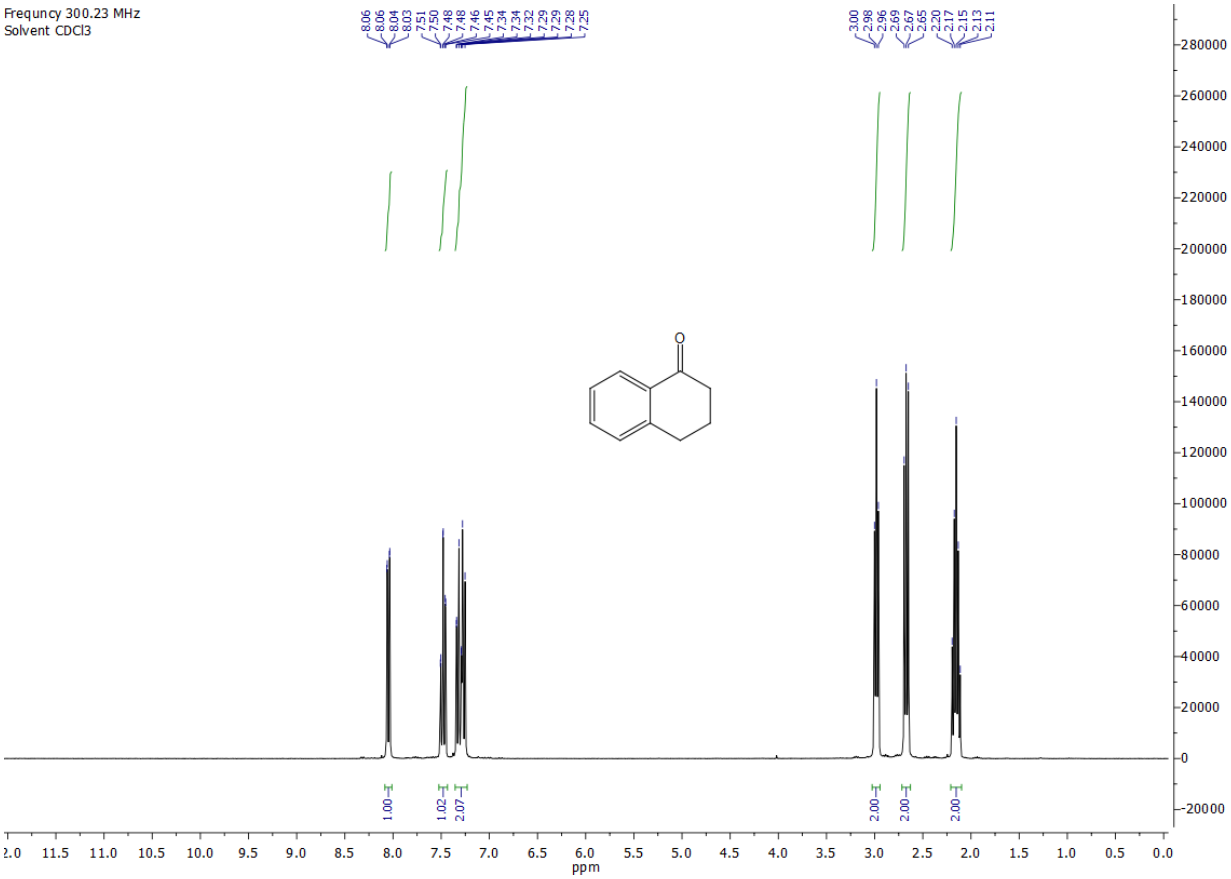
1-(*p*-Tolyl)ethan-1-one (2m)



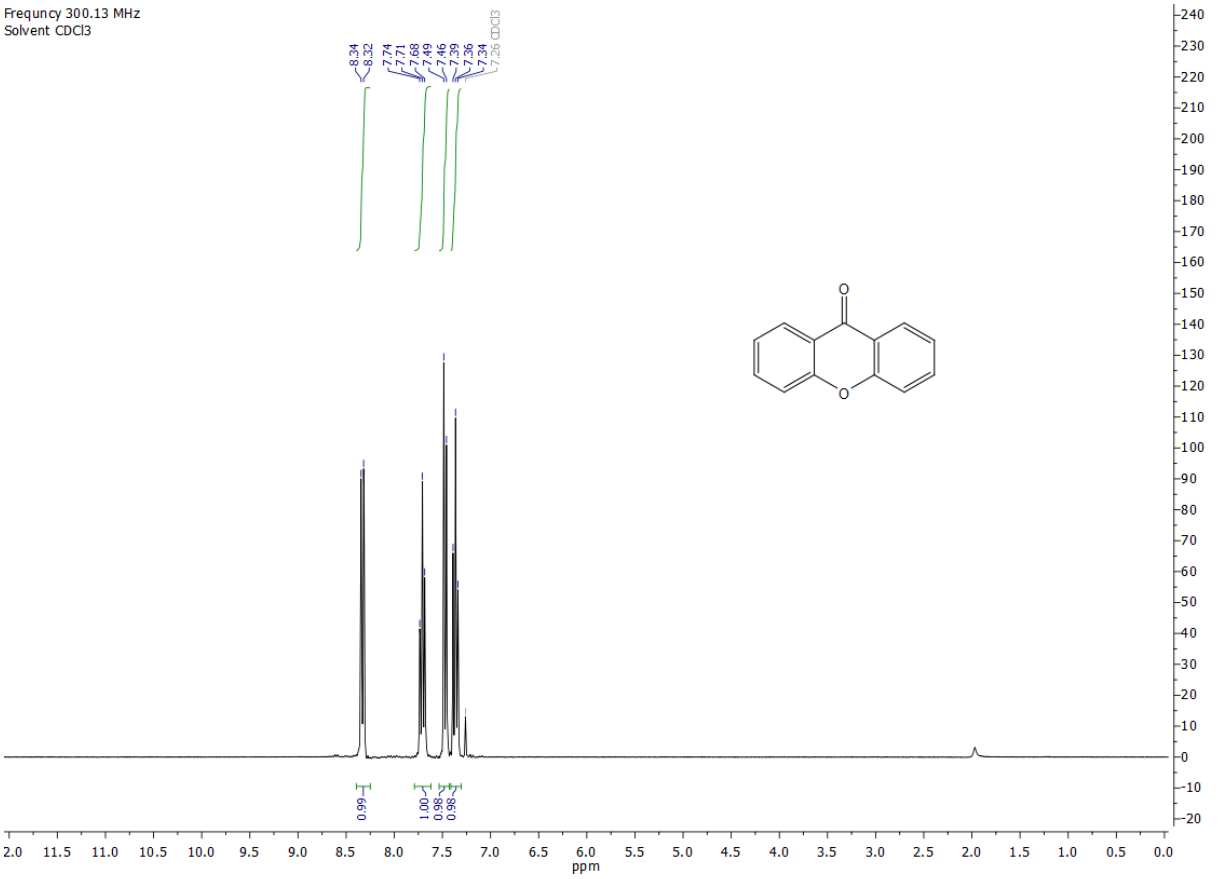
Benzophenone (2n)



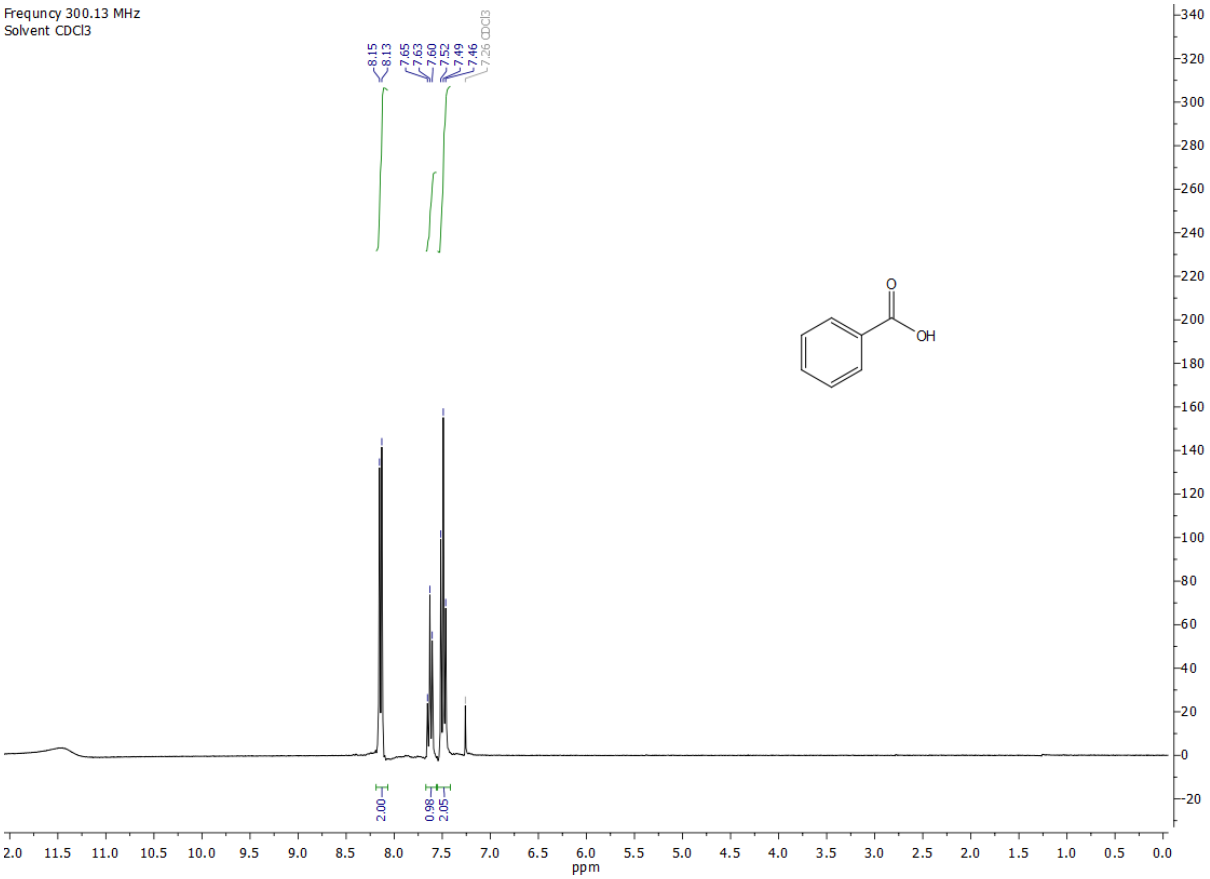
Tetralone-1 (2o)



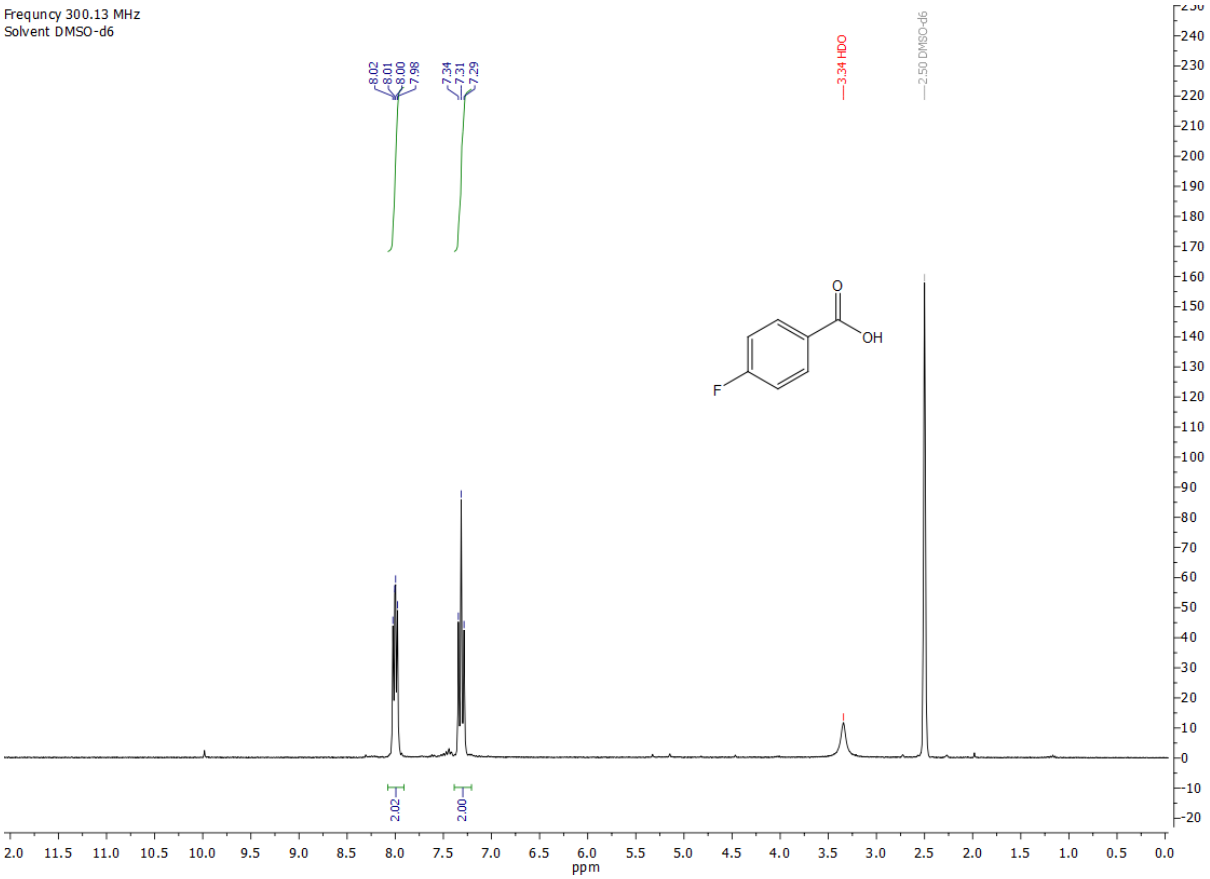
Xanthen-9-one (2p)



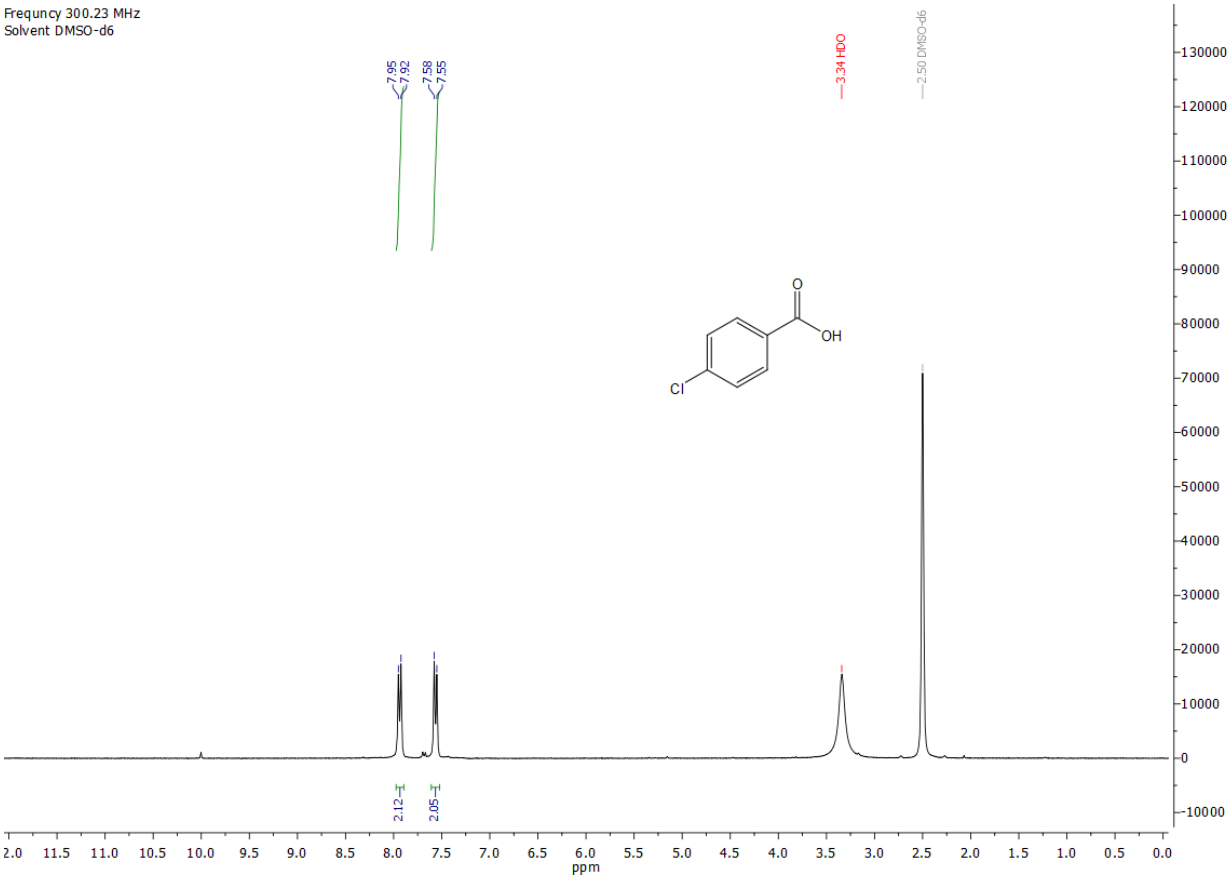
Benzoic acid (3a)



4-Fluorobenzoic acid (3b)



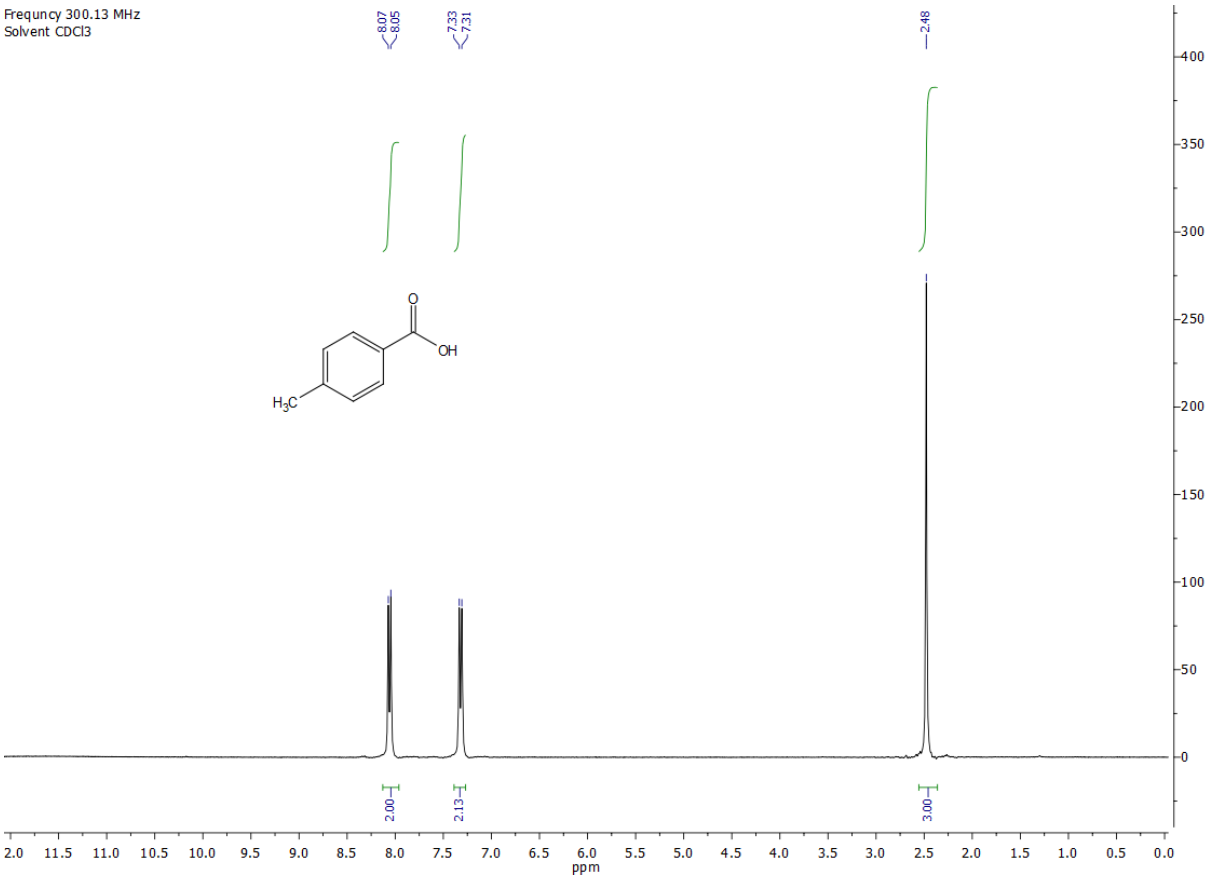
4-Chlorobenzoic acid (3c)



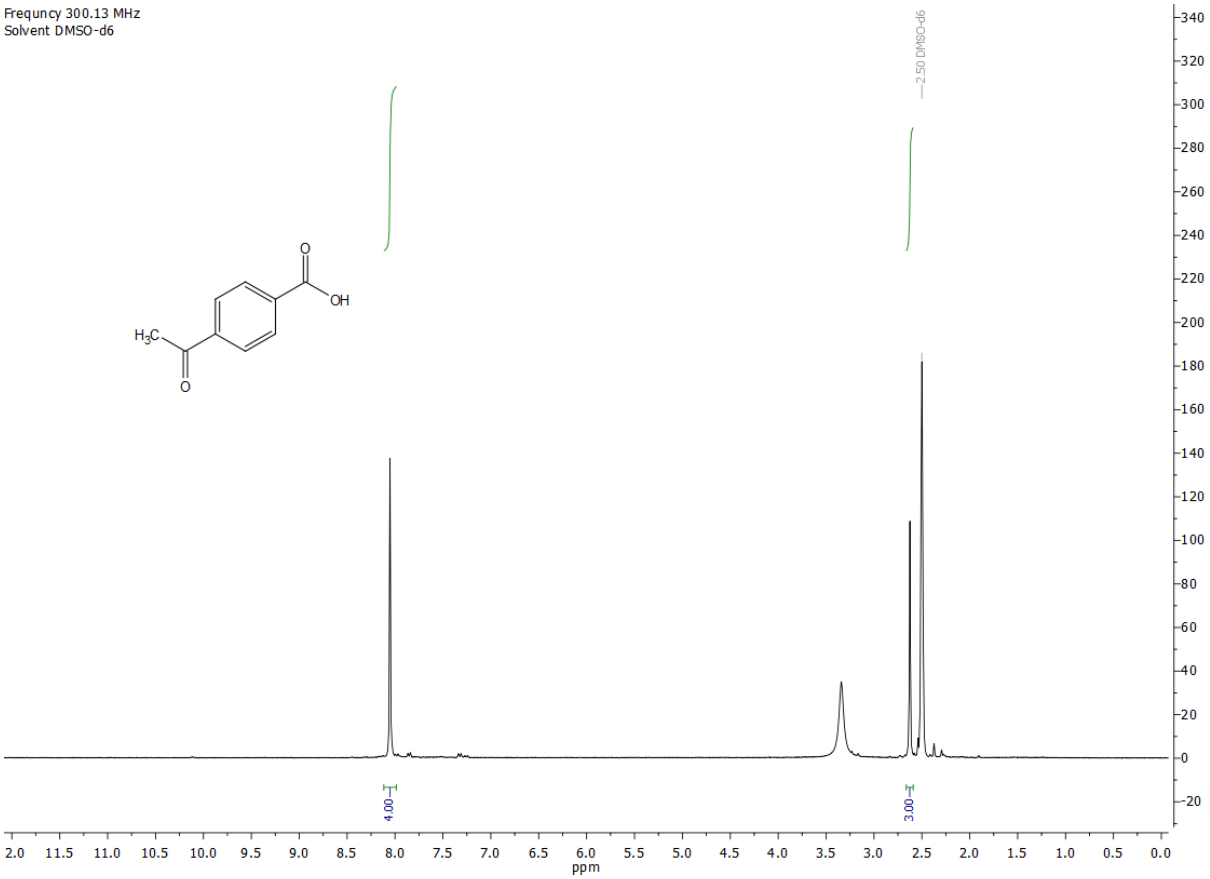
4-Bromobenzoic acid (3d)

4-Methoxybenzoic acid (3e)

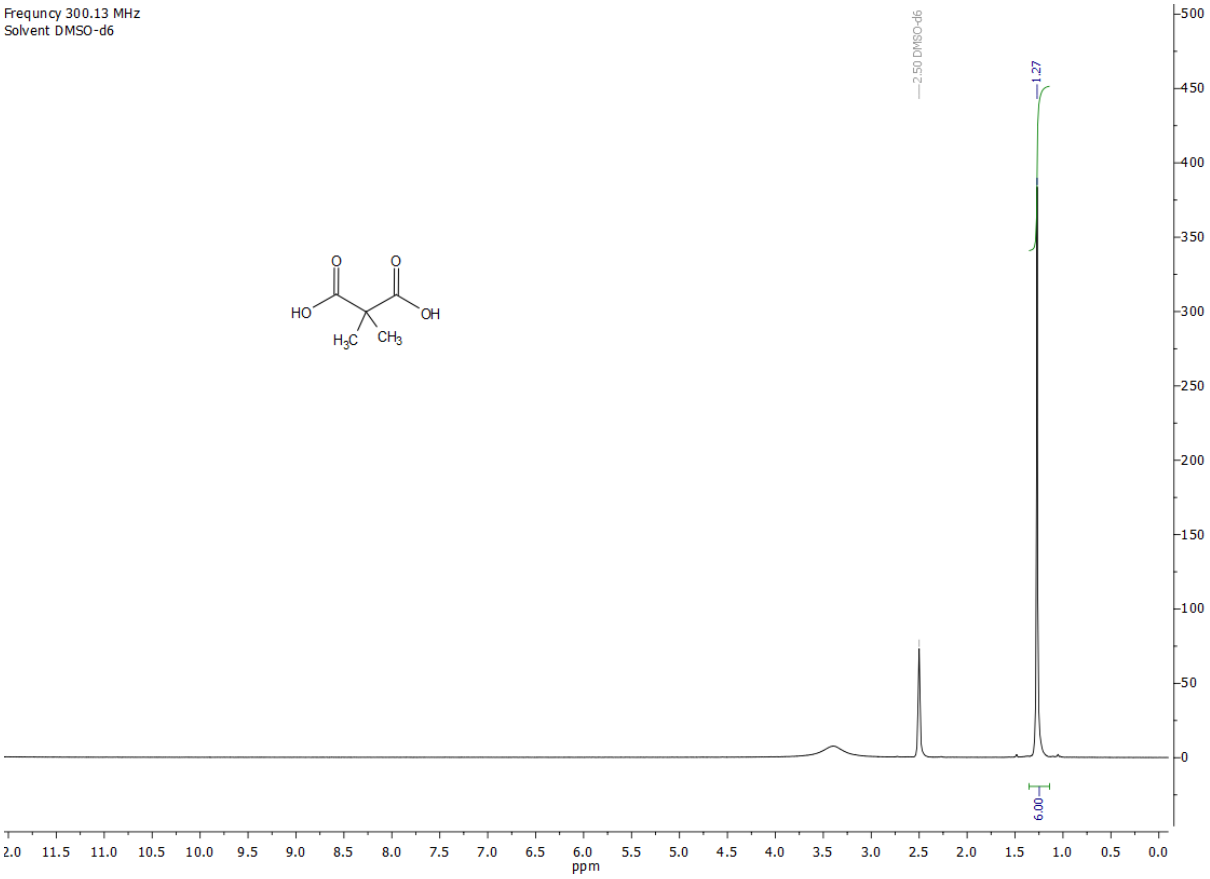
4-Methylbenzoic acid (3f)



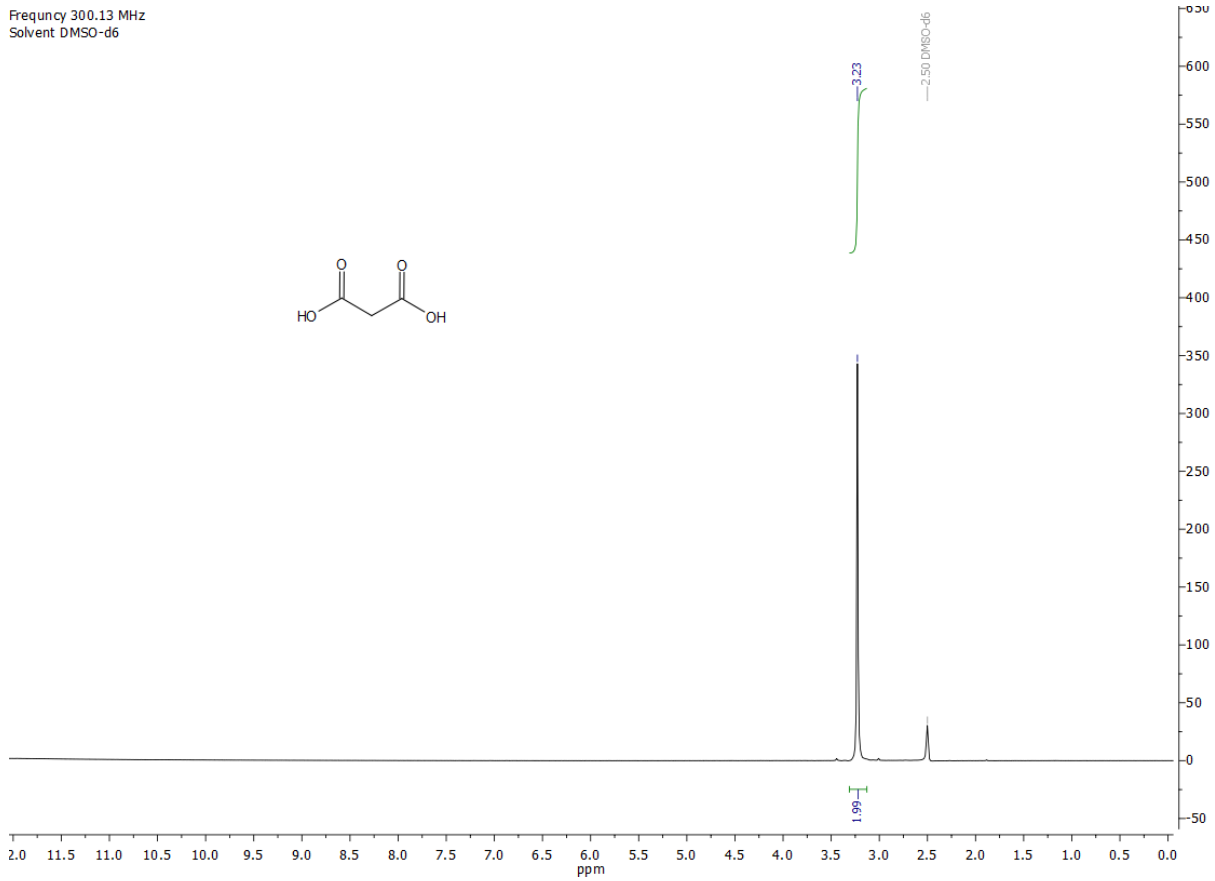
4-Acetylbenzoic acid (3g)



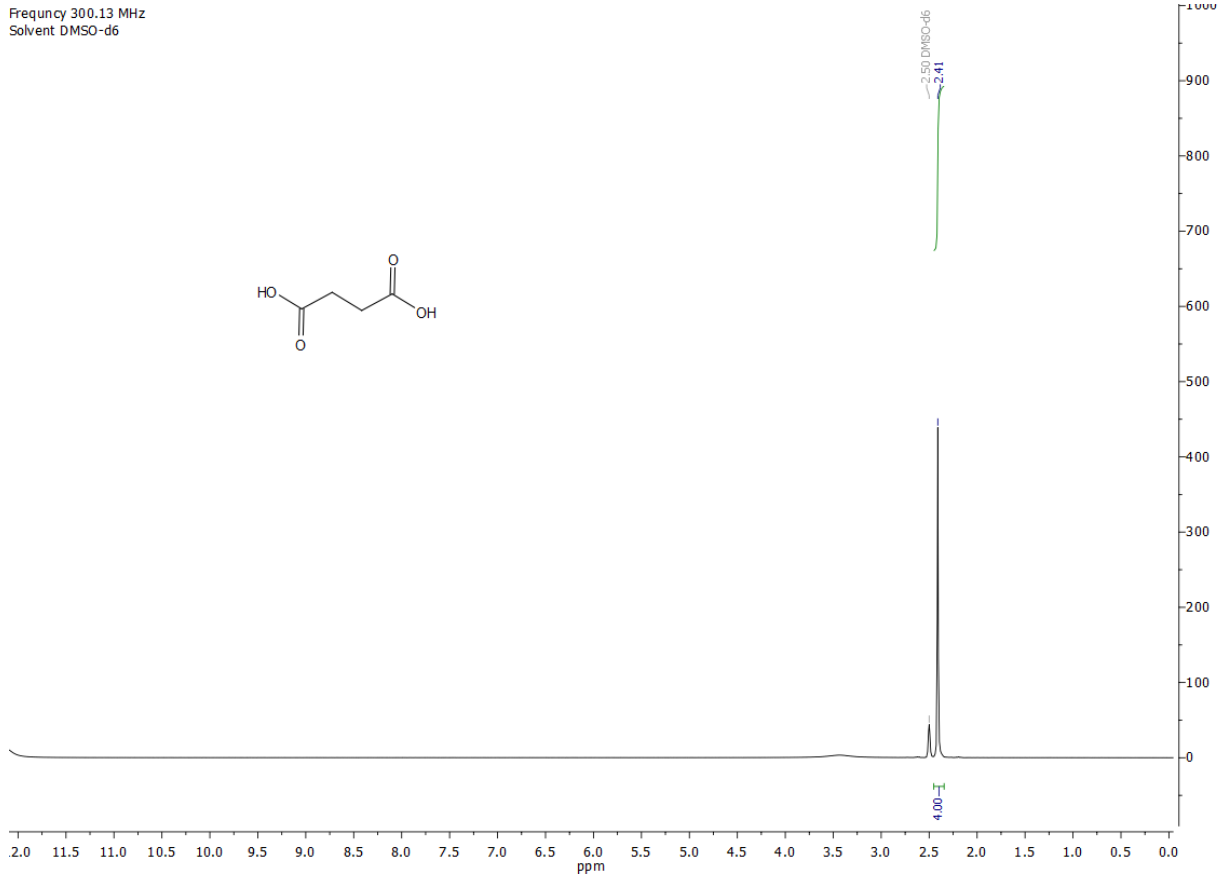
2,2-Dimethylmalonic acid (5a)



Malonic acid (5b)



Succinic acid (5c)



γ-Butyrolactone (6)