

EXPERIMENT 3: Oxidation of Alcohols – Solid-Supported Oxidation and Qualitative Tests

Relevant Sections in the text (Wade, 7th ed.)

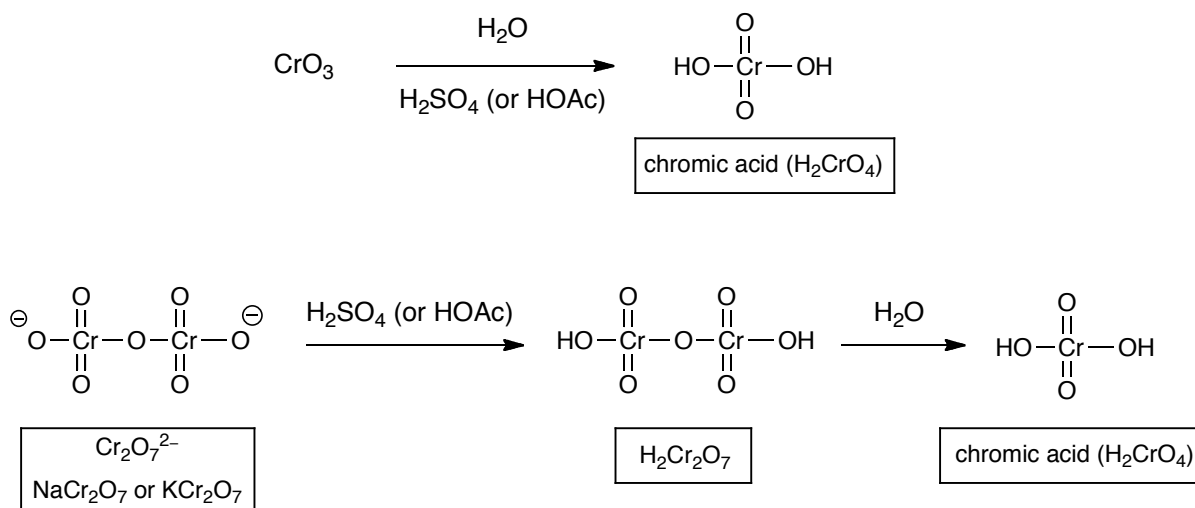
- 11.1 (p. 464) Oxidation states of alcohols and related functional groups
- 11.2 (p. 466-468) Oxidation of alcohols incl. chromium reagents

A portion of this experiment is based on a paper by Cainelli, G.; Cardillo, G.; Orena, M.; Sandri, S. J. *Am. Chem. Soc.* 1976, 98, 6737 and by an experiment reported by L. G. Wade and L. M. Stell in *J. Chem. Ed.* 1980, 57, 438.

General Concepts

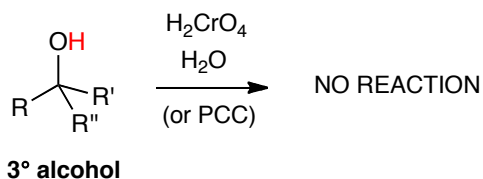
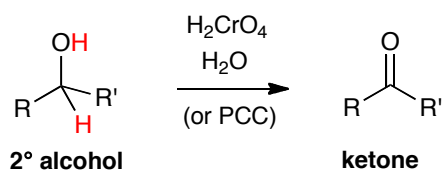
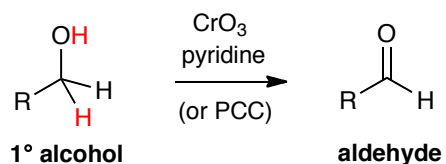
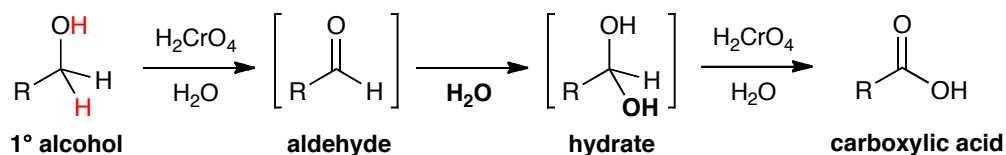
Efficient preparation of aldehydes and ketones is essential considering their importance in organic synthesis. Furthermore, the significance of reversible oxidation-reduction systems between alcohols and their related carbonyl compounds provide incentive to further understand their interrelationships.

Although there are several methods to synthesize carbonyl compounds, the most common process is the oxidation of alcohols using an oxidizing agent such as the chromate ion (Cr^{6+}). For example, chromic acid (H_2CrO_4) or pyridinium chlorochromate (PCC, $\text{C}_5\text{H}_5\text{NH}^+ \text{ClCrO}_3^-$), becomes reduced to Cr^{3+} . Since chromic acid is not stable, it is made by the addition of CrO_3 to water. Either sulfuric or acetic acid is also added to act as a catalyst since the rate of oxidation of alcohols by chromic acid is much greater in an acidic solution. Alternatively, an aqueous solution of Cr^{6+} can be prepared by adding potassium or sodium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$ or $\text{Na}_2\text{Cr}_2\text{O}_7$) to an aqueous acidic solution. The reactions in both methods are called chromate or chromic acid oxidation.

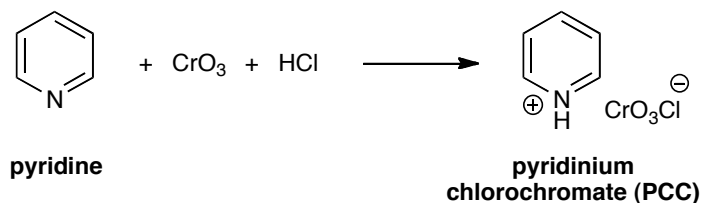


Primary and secondary alcohols are oxidized into their respective aldehydes and ketones. Tertiary alcohols however, do not react with chromate because they lack a hydrogen atom on the *carbinol* carbon. Aldehydes are difficult to prepare easily from primary alcohols since the reaction continues to the

corresponding carboxylic acid. However, if pyridine is added or pyridinium chlorochromate (PCC) is used as the oxidizing agent, the reaction ceases at the aldehyde.



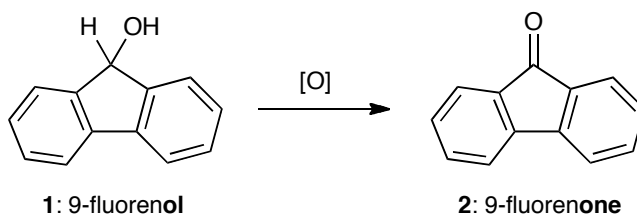
Pyridinium chlorochromate (PCC) is soluble in organic solvents (such as CH_2Cl_2), so it allows for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively, in non-aqueous conditions.



In this laboratory experiment we will use the known reactivity of the chromic acid oxidizing agent, but instead of using CrO_3 in a strong aqueous acid we will use it as a solid supported reagent. The solid-support consists of a polymer resin that contains the active form of CrO_3 . This Cr^{6+} modified resin effectively oxidizes appropriate substrates and has a few experimental advantages. First, it avoids the need to use strong acid aqueous solutions. Because the Cr is retained on the solid support it makes work-up of the reaction relatively simple, and it makes recovery of the heavy-metal Cr byproduct trivial. Because this resin can also be regenerated and reused, whereas the heavy metal products from the other simpler reactions are usually discarded, this experiment also is a “green” or more environmentally friendly

reaction. (The improper disposal of large quantities of so called “hexavalent chromium” (Cr^{6+}) was the topic of the movie “Erin Brockovich”).

As an example of an oxidation reaction using a solid support you will convert 9-fluorenol (**1**) (9-hydroxyfluorene) to 9-fluorenone (**2**). You will follow the progress of the reaction by TLC since the polarity of the product is very different than the starting material. You will then characterize your product by its melting point and IR and NMR spectroscopy compared to your starting material.



In contrast to the primary and secondary alcohols, tertiary alcohols are relatively stable to cold chromic acid but under more vigorous conditions (higher temperature; stronger acid) even tertiary alcohols (like ketones) suffer oxidative cleavage of carbon-carbon bonds. This relationship has led to the development of a convenient qualitative test for distinguishing primary and secondary alcohols (and aldehydes) from tertiary alcohols (and ketones). The qualitative test involves the addition of a solution of CrO_3 in sulfuric acid (Jones' Reagent) to a solution of the compound being tested in acetone. This reagent oxidizes primary and secondary alcohols and all aldehydes (via its hydrate) with a distinctive color change (orange to green or blue-green) and it gives **no** visible reaction with tertiary alcohols and ketones under the conditions of the test. Primary and secondary alcohols and *aliphatic* aldehydes give a positive test within a few seconds while aromatic aldehydes require 30 seconds to one minute. Tertiary alcohols and ketones produce no visible change in several minutes. [The reagent will slowly oxidize tert-butyl alcohol and phenol]. This test, in conjunction with those to be described in the next experiment, Tollens, Purpald, Fehling's, and the Iodoform tests, have proved to be invaluable tools for detecting the presence of ketones and aldehydes in unknown compounds.

PART A: OXIDATION OF 9-FLUORENOL (1)

***HAZARDS*:** Always work in the fumehood. Toluene, acetone, hexanes, ethanol, 1-propanol, and 2-propanol are volatile and flammable. Acidic Chromic Acid (Jones' Reagent) is corrosive. Both it and the solid-support contain chromium, a heavy metal, and is potentially environmentally damaging so handle and dispose of it as instructed. Some of the compounds are irritants.

***NOTE*:** The polymer-resin supported CrO_3 is prepared for you. It is made by mixing 15.0 g of CrO_3 in 100 mL of water with 35 g of an anion exchange resin that has quaternary ammonium groups – in our case Amberlite IRA 400. This mixture is stirred for 30 minutes, rinsed with water and acetone and then dried *in vacuo* at 50 °C for 5 hours. The loading level is about 3.8 mmol of CrO_3 per gram of resin.

- Transfer 1.0g of 9-fluorenone (**calculate the number of mmol before the experiment: _____**) and 5g of the dry polymer supported CrO_3 reagent to a 100 mL round-bottom flask with 35 mL of toluene (methylbenzene).
- Add a stir bar (obtain one from your TA) and clamp the flask in a sand bath. Attach a water-cooled reflux condenser and heat to reflux using a heating mantle for 1 hour. Follow the course of the reaction by TLC using fluorescent indicating silica plates and 30% acetone in hexanes as the eluent. Test a sample at 20, 40, and 60 minutes and run a TLC each time against a solution of 9-fluorenone (starting material) dissolved in toluene.
- Visualize your TLC using UV-light and draw representations of your TLC plates for your report. Discuss how the TLCs change over the course of the experiment. Determine the R_f of your starting material and the product.

***NOTE*:** While the reaction is at reflux, you should start on Part D. Multi-task!!

PART B: WORK-UP AND PURIFICATION

- Cool the reaction mixture to room temperature. Gravity filter the polymer resin into a **tared** 250 mL round bottom flask, rinsing with a small amount of toluene.
- Remove the toluene solvent using a rotary evaporator.
- Place the used polymer in the recycling bottle provided. **DO NOT THROW CHROMIUM IN THE REGULAR trash containers!** Ask your TA if you are unsure of chromium disposal. Make sure that you return your stir-bar (after cleaning) to your TA.
- After ensuring that the product is dry, measure the mass of your crude solid product.

- Recrystallize the crude product from ethanol. You will need between 5–10 mL of ethanol; be careful that you don't use too much solvent (review the recrystallization experiment from Chem 2273a).
- Record the mass of the recrystallized product.

PART C: CHARACTERIZATION

- Measure the melting point of the dry, recrystallized product and compare to that of pure fluorenone: 80-83 °C. Obtain an IR spectrum of your product as a thin film (read experiment 3 of Chem 2273a and/or ask your TA to tell you how to do this) and compare it to the IR of the starting 9-fluorenol provided.
- NMR data of both 9-fluorenol and 9-fluorenone is provided for you; assign the spectra, comment on features that let you know if the reaction proceeded (i.e. appearance/disappearance of peaks).

PART D: QUALITATIVE TESTS – CHROMIC ACID TEST

- Conduct the test on each of the following compounds:
 - 9-fluorenol
 - your product
 - cyclohexanol
 - benzaldehyde
 - 1-propanol
 - 2-propanol
 - *tert*-butyl alcohol
- Add 1 mL of reagent-grade acetone (other grades contain alcohol) into a clean, small test tube and dissolve ONE drop of the liquid or about 10 mg (a bit on the tip of a spatula) of a solid alcohol or carbonyl compound.
- Add ONE drop of the acidic chromic anhydride reagent (Jones Reagent) to the acetone solution, and tap the side of the test tube to mix the contents.
- A positive oxidation reaction is indicated by the disappearance of the dark orange color of the Jones reagent (Cr^{6+}) and the formation of a green/blue-green precipitate. Record your observations (colour changes, time) in a table format. Discuss the results of your qualitative tests in terms of the reaction equations.

FORMAL REPORT DISCUSSION

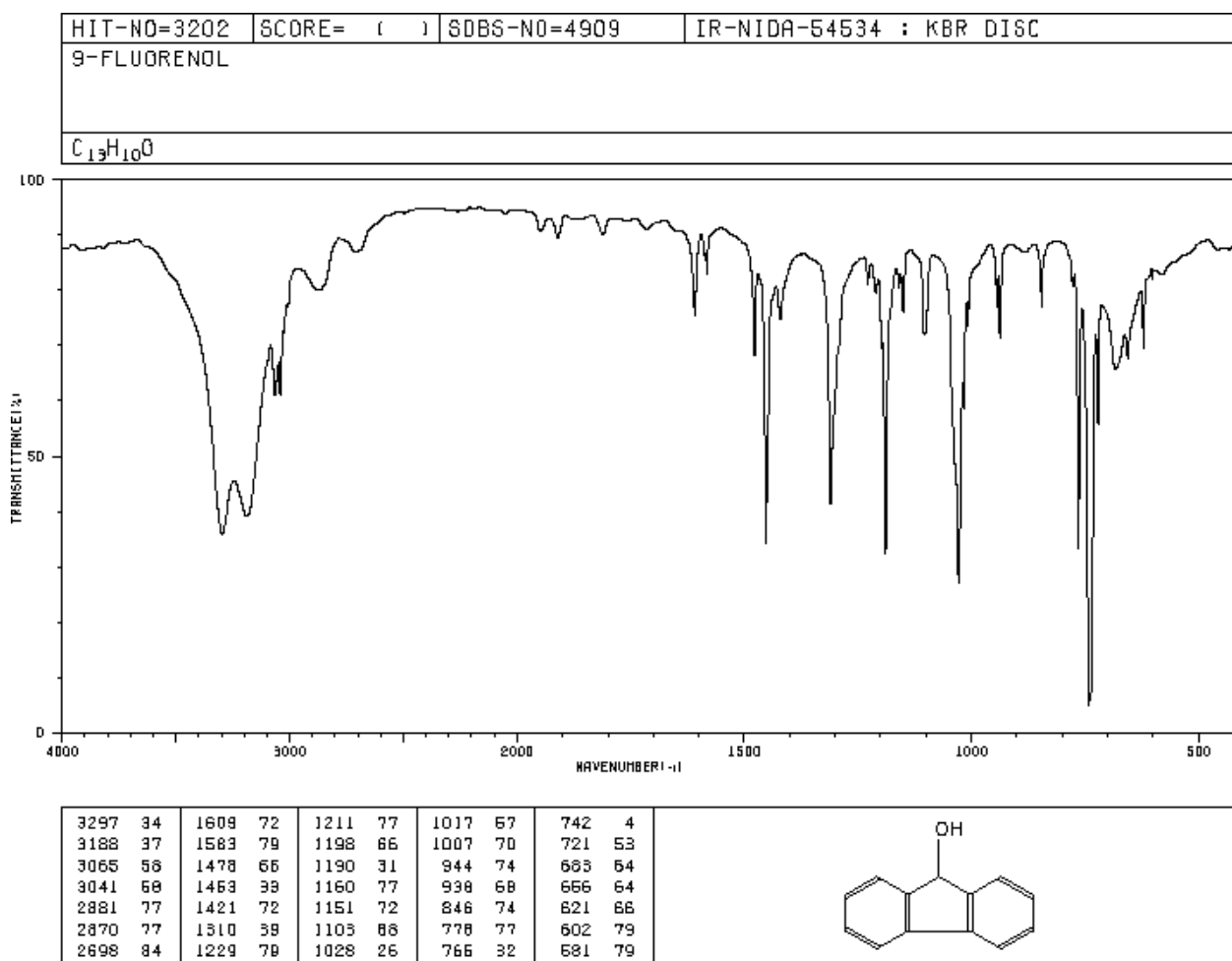
Write up a formal report as outlined in the lab report guidelines:

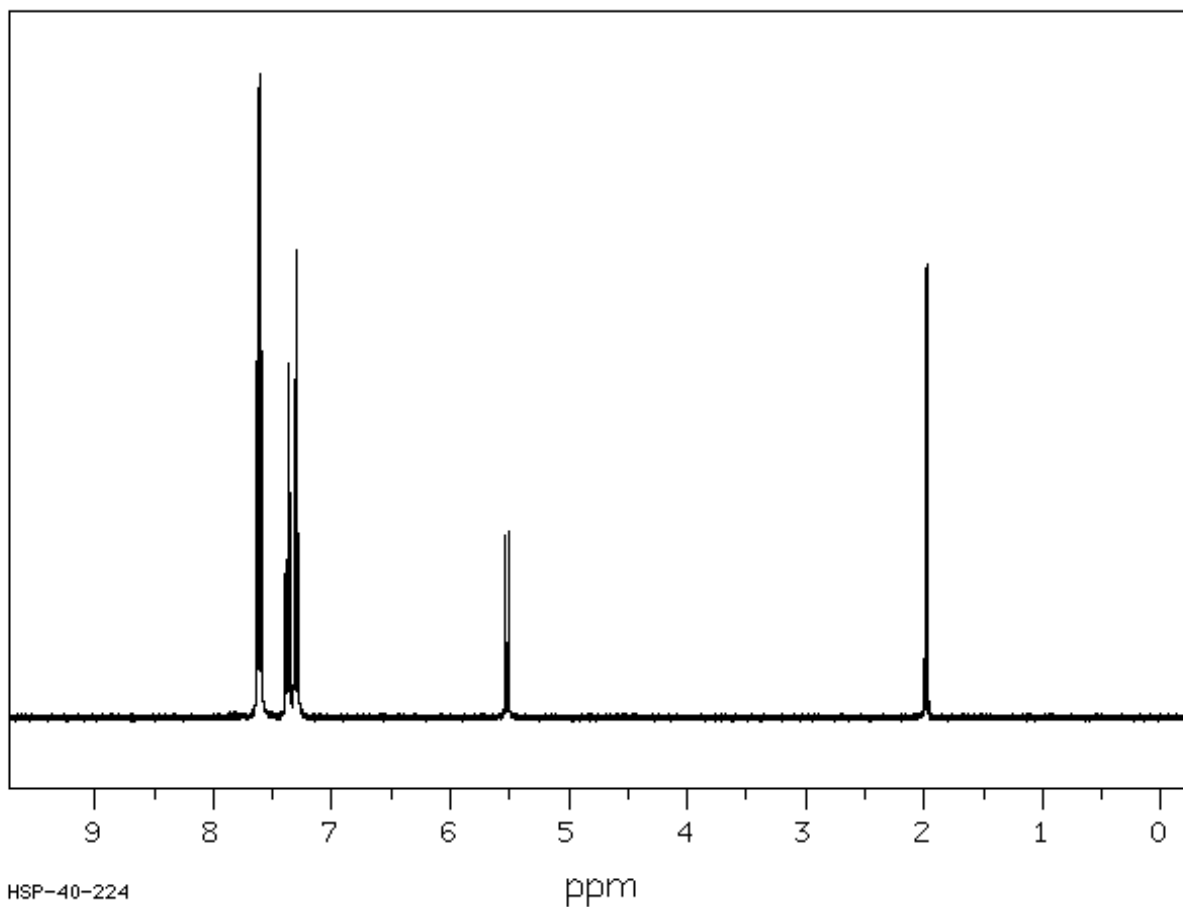
- Explain the reaction, along with a possible general mechanism.
- Comment briefly on the use of TLC to follow the course of the reaction
- Report mass and percent yield (crude & recrystallized. Explain possible reasons for your low (or too HIGH) yield.
- Melting point – explain the significance of the result
- Assign spectra (IR, NMR). Comment on what features best let you know the reaction proceeded.
- Discuss the qualitative tests briefly after presenting them (*neatly!*) in a table format.

SPECTRAL DATA COURTESY OF: National Institute of Advanced Industrial Science and Technology (AIST)

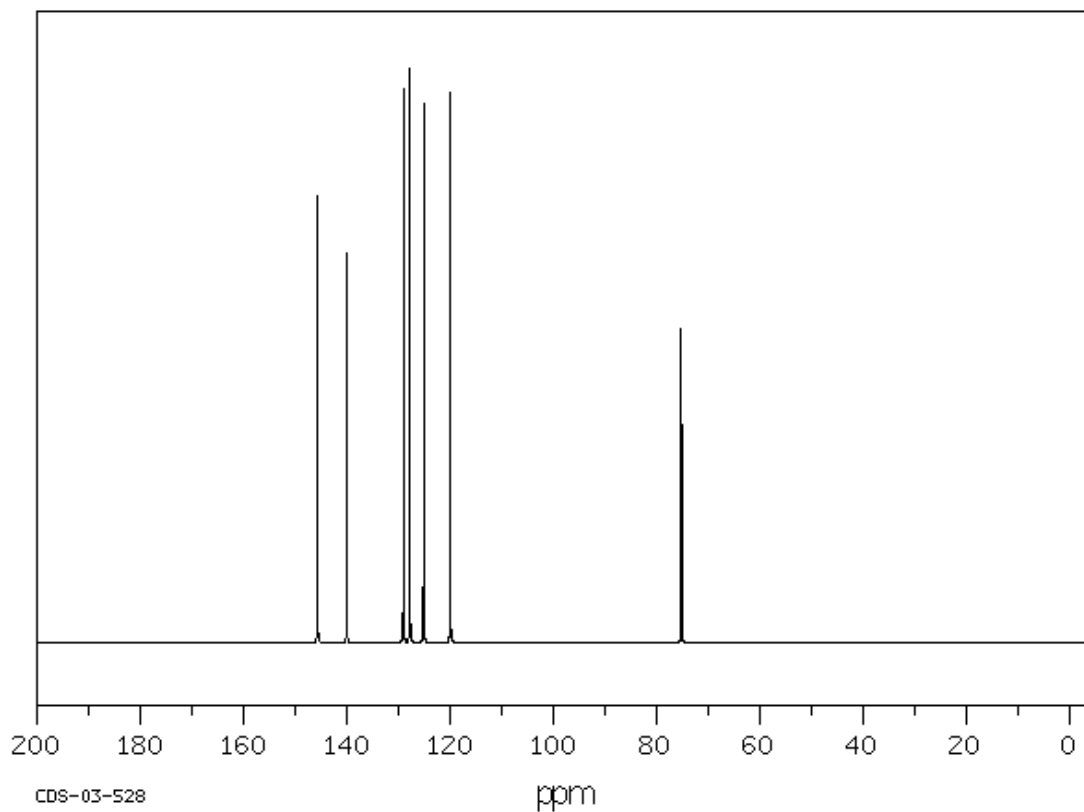
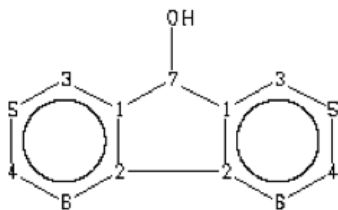
***NOTE*: You have to obtain the IR spectrum of 9-fluorenone (your product) yourself.**

IR Spectrum of 9-fluorenone



¹H NMR Spectrum of 9-Fluoreno1 (400 MHz in CDCl₃)**Peak Data:**

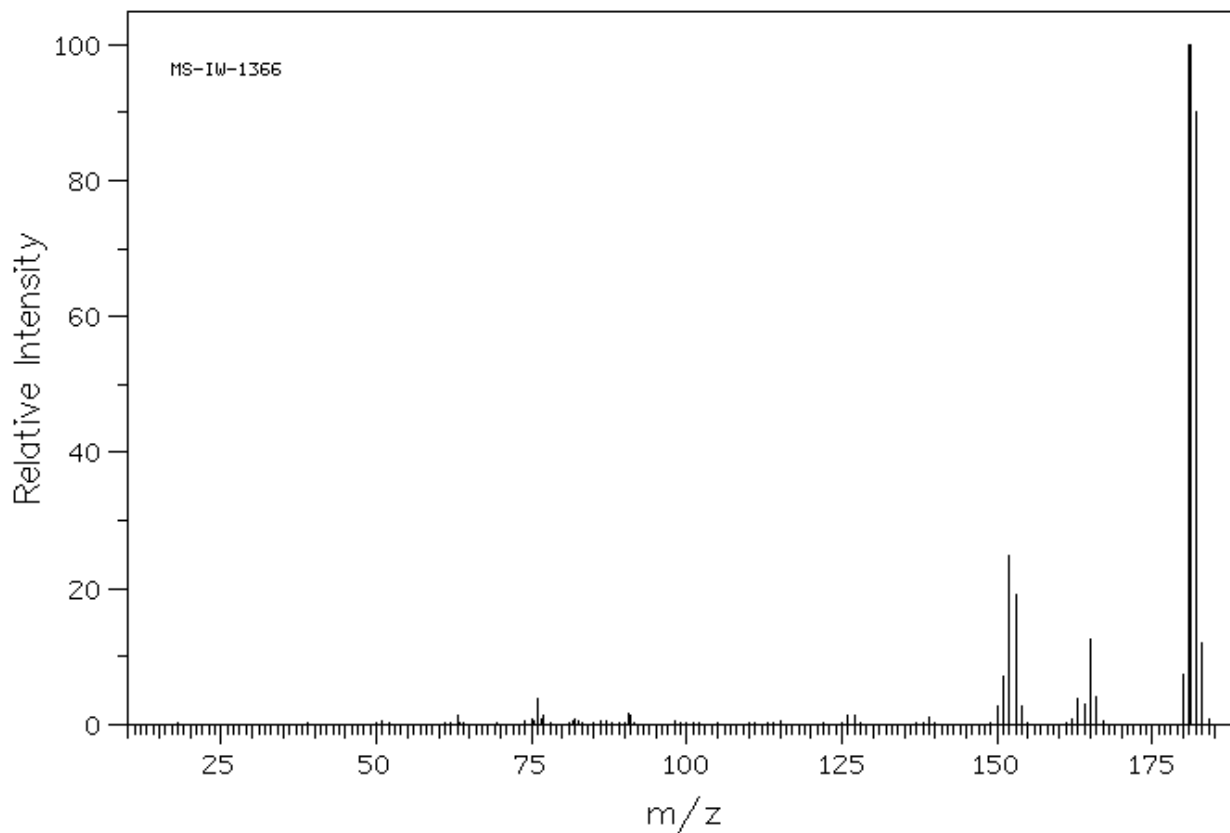
Hz	ppm	Int.
3050.42	7.633	555
3046.88	7.624	86
3046.26	7.623	81
3043.21	7.615	980
3042.48	7.613	1000
3035.03	7.595	569
3034.55	7.594	554
3033.94	7.592	525
3033.20	7.590	290
2954.10	7.392	223
2953.61	7.391	229
2952.88	7.389	247
2946.66	7.374	526
2946.17	7.372	538
2945.43	7.371	550
2939.21	7.355	350
2938.72	7.354	346
2937.99	7.352	335
2937.99	7.352	335
2925.42	7.320	516
2924.19	7.317	527
2921.88	7.312	63
2917.97	7.302	728
2916.87	7.299	679
2910.64	7.283	287
2909.42	7.280	273
2211.79	5.535	284
2201.66	5.509	290
796.51	1.994	698
786.50	1.968	704

^{13}C NMR Spectrum of 9-Fluorenone**Peak Data:****ppm Int. Assign.**

145.70	776	1
140.01	678	2
129.03	965	3
127.79	1000	4
125.12	937	5
119.95	958	6
75.20	545	7

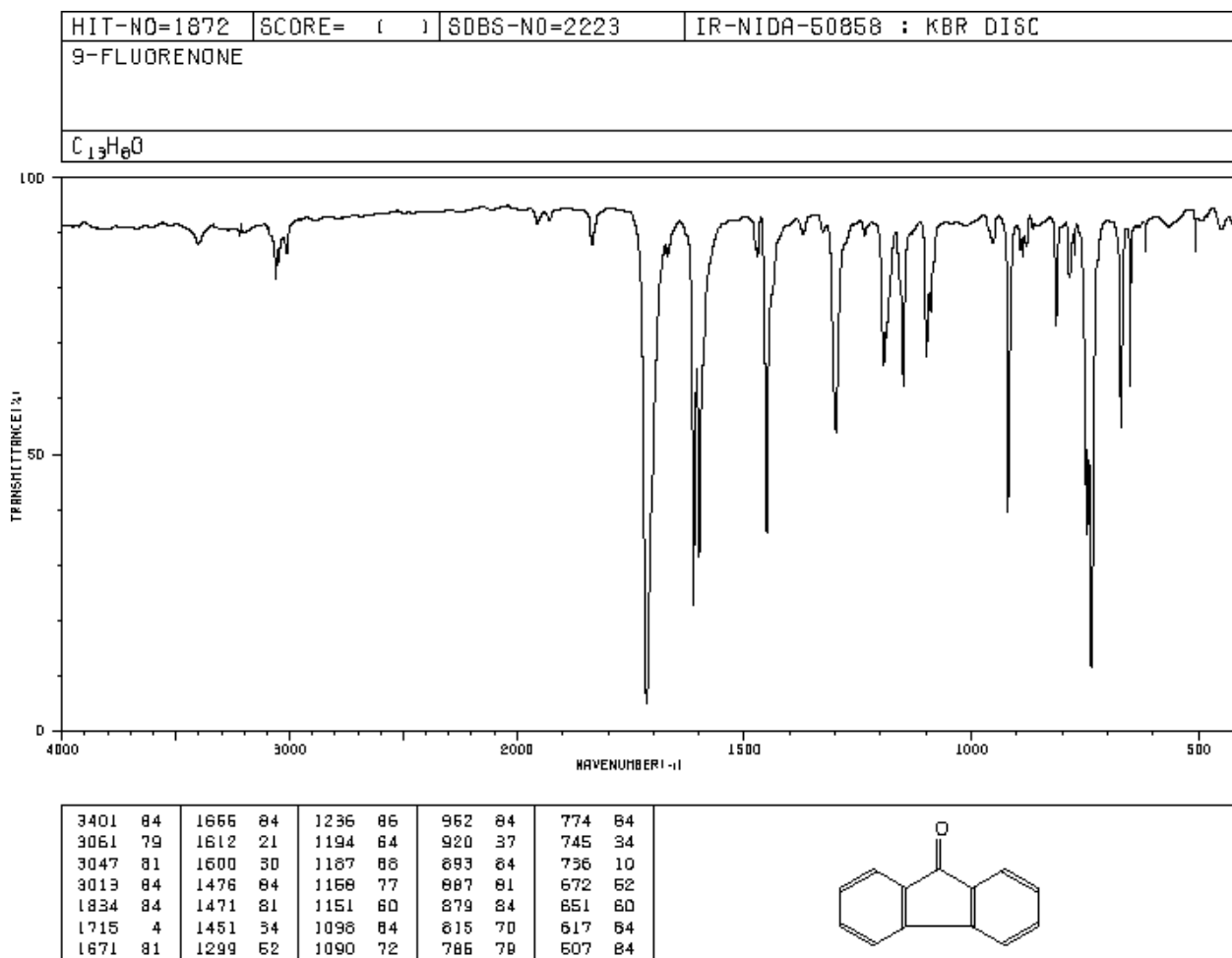
Mass Spectral Data of 9-Fluorenol

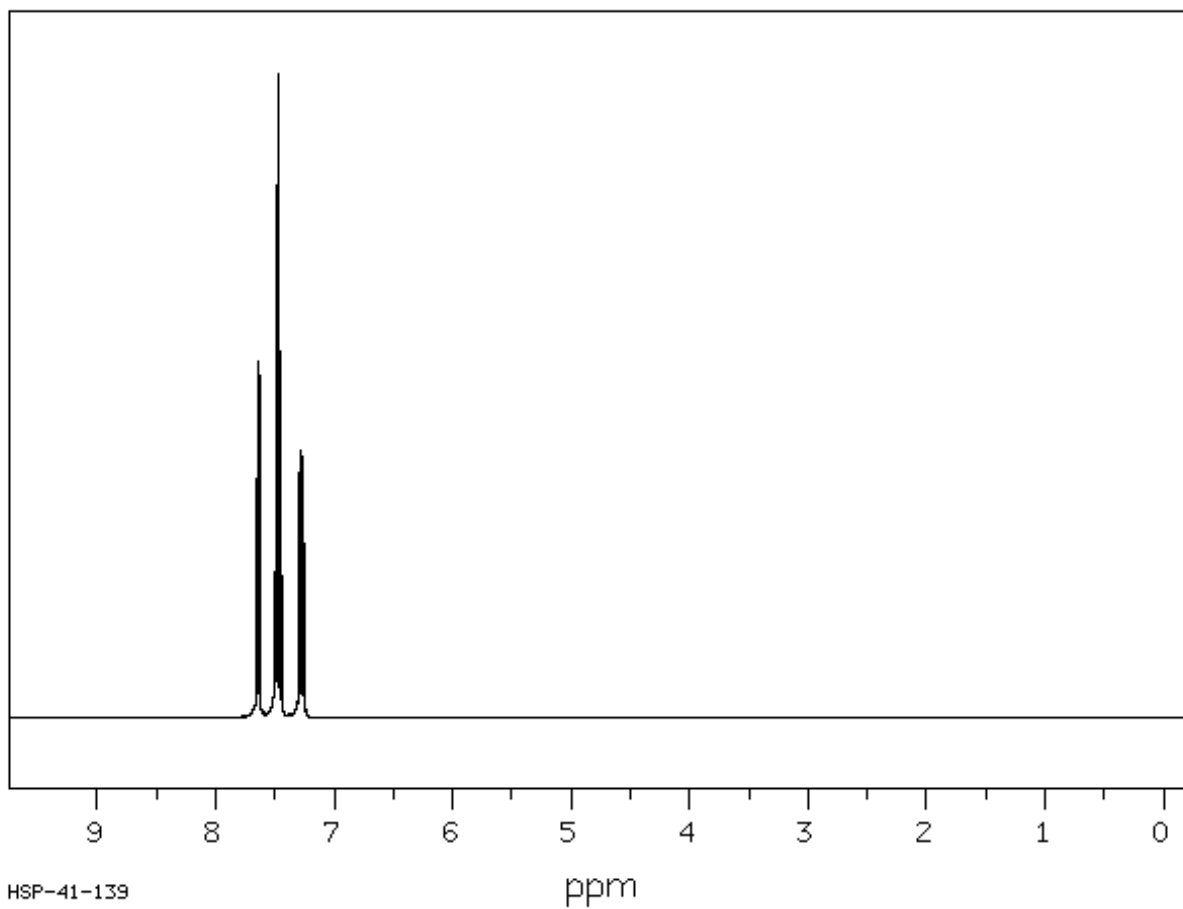
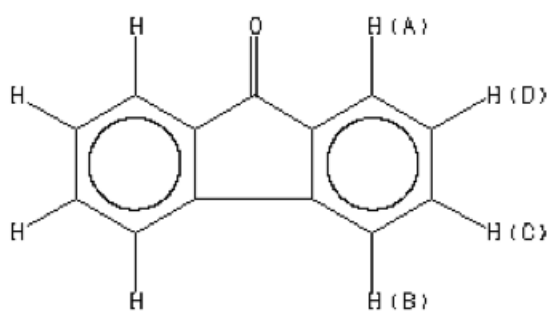
MS-IW-1366 SDBS NO. 4909
9-fluorenol
C₁₃H₁₀O (Mass of molecular ion: 182)

**Peak Data:**

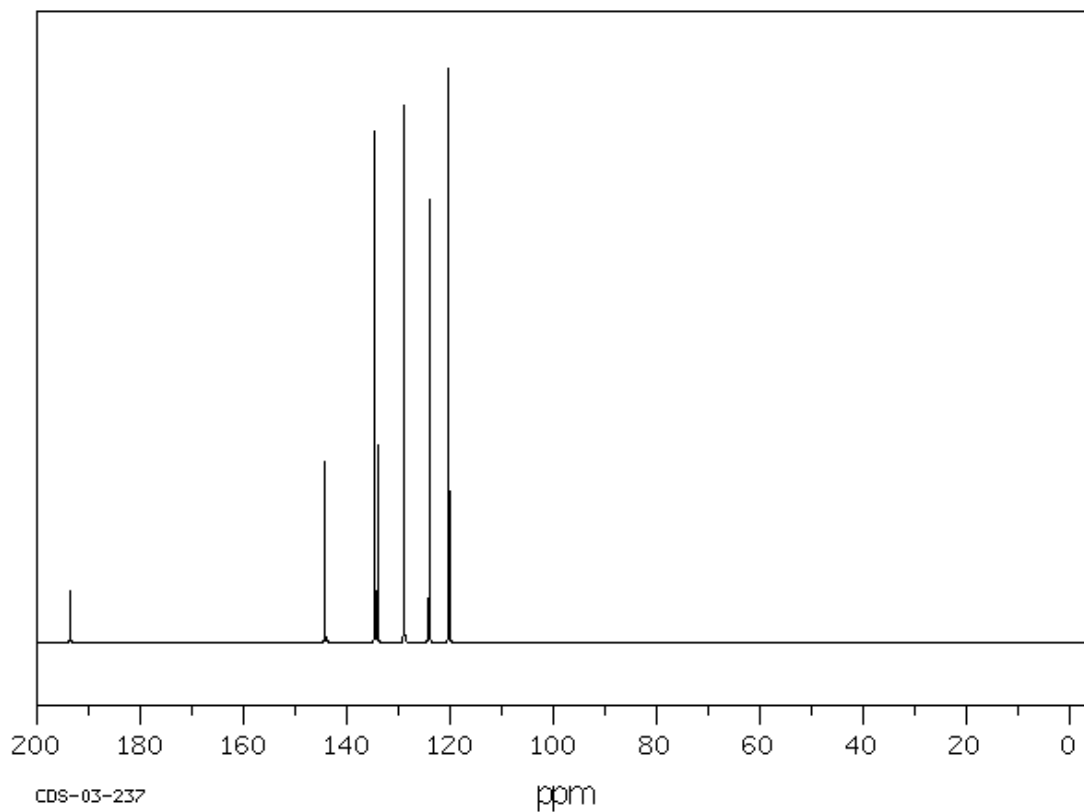
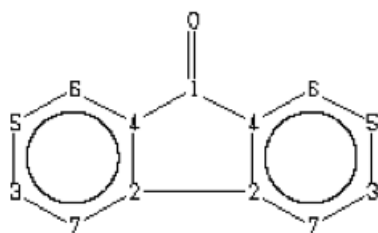
m/z	intensity
76.0	3.8
151.0	7.2
152.0	24.8
153.0	19.0
163.0	3.9
164.0	3.0
165.0	12.6
166.0	4.0
180.0	7.3
181.0	100.0
182.0	90.1
183.0	12.1

IR Spectrum of 9-fluorenone



¹H NMR Spectrum of 9-Fluorenone (400 MHz in CDCl₃)**Peak Data:****Assign. Shift(ppm)**

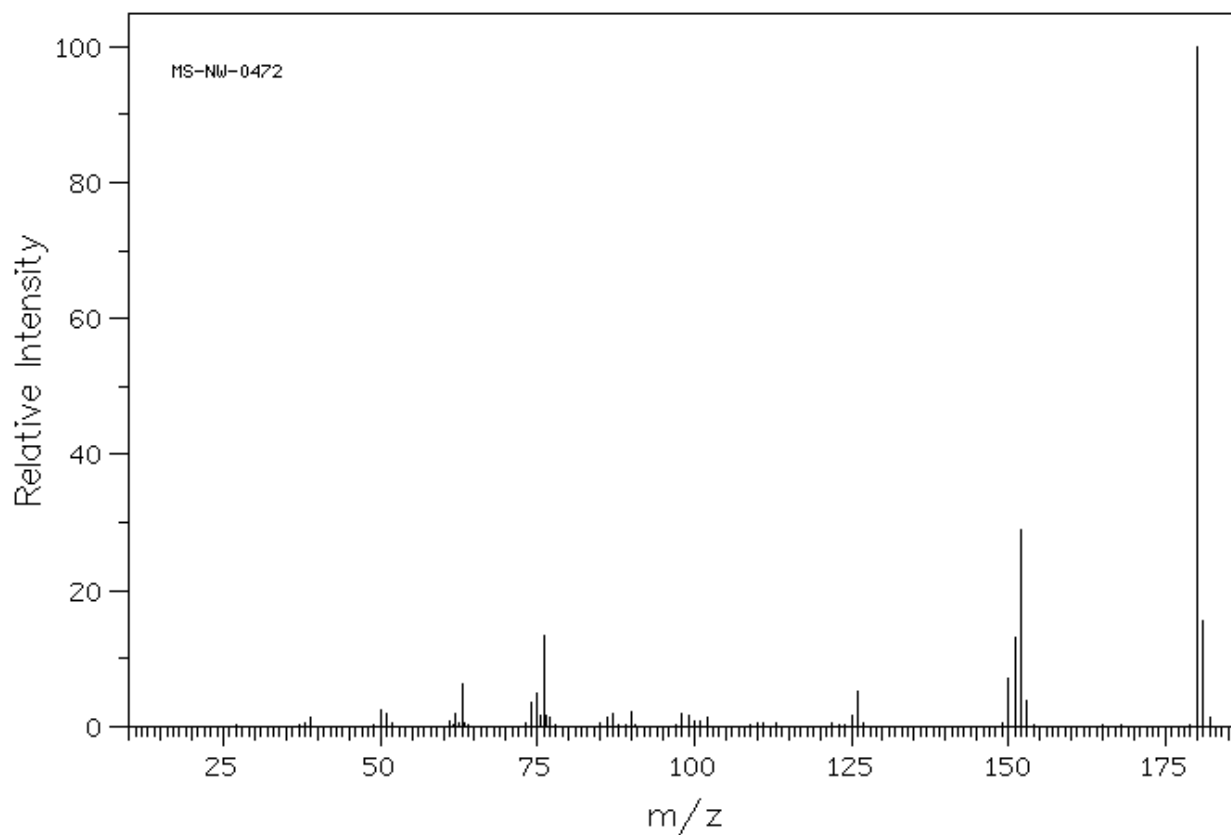
A	7.638
B	7.48
C	7.47
D	7.274

^{13}C NMR Spectrum of 9-Fluorenone**Peak Data:****ppm Int. Assign.**

193.62	90	1
144.25	313	2
134.53	891	3
133.99	343	4
128.91	935	5
124.05	771	6
120.22	1000	7

Mass Spectral Data of 9-Fluorenone

MS-NW-0472 SDBS NO. 2223
9-fluorenone
C₁₃H₈O (Mass of molecular ion: 180)

**Peak Data:**

m/z	intensity
63.0	6.2
74.0	3.5
75.0	5.0
76.0	13.4
126.0	5.1
150.0	7.2
151.0	13.0
152.0	28.9
153.0	3.8
180.0	100.0
181.0	15.4