Alan Yu
Unknown J Analysis
Organic Lab 310
November 14, 2019

IR:

This IR was recorded on a ThermoFisher Nicolet iS10 FT-IR spectrometer using the salt plate method.

From the IR, starting from the right to left, a band is shown at the $3349.55cm^{-1}$ which can resemble a secondary amine group in the structure. On the right of this band also shows something of an alcohol stretch but that can be due to water from something like a wet salt plate.

$$C-\overset{\overset{H}{|}}{\underset{|}{N}}-C$$
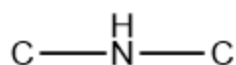
The next band of interest can be a band that is at $3064.35cm^{-1}$. This band can be said to be an sp^2 carbon to hydrogen bond.

$$R_2-CH$$
$$\underset{R_1}{|}$$
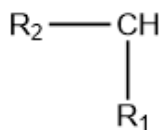
Right along with that band, the next band of interest is the band at $2971.79cm^{-1}$. This can be an sp^3 carbon to hydrogen bond.

$$R_3$$
$$|$$
$$R_2-CH$$
$$|$$
$$R_1$$
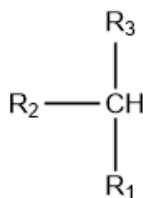
After this band, the next band of interest would be the three bands at the $1961.08cm^{-1}$, $1896.04cm^{-1}$, and $1818.49cm^{-1}$ which can be said to be the "fingers" of a benzene ring. This implies that there is a benzene ring in the structure.
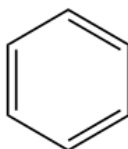
Right along with the benzene fingers, there is a band at $1683.39cm^{-1}$ which can be either an amide, ketone, aldehyde or ester that has shifted a little to the right. It wouldn't be an acid since there was no corresponding alcohol stretch that stood out.
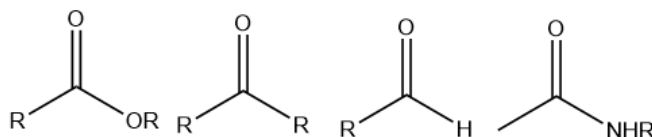
Along with the carbonyl, to the right from 1465.74cm^{-1} to 1443.22cm^{-1} has aromatic carbon to carbon stretches which can be backed up by the aromatic ring that is suggested to be a part of the compound.

Both NMR were recorded on a Varian 300MHz NMR machine using CDCl$_3$ as the solvent.

C^{13} NMR:

From the whole plot, it can be said that there are either six or seven different kinds of carbon environments. If the peaks around 128ppm are counted as one, then there are six different environments. Again from right to left, the first peak that is found in the carbon NMR is 204.327ppm which can be a part of the ketone or an aldehyde. This disbands the suggestion of having either an ester or an amide in the structure due to the range this peak appears in.
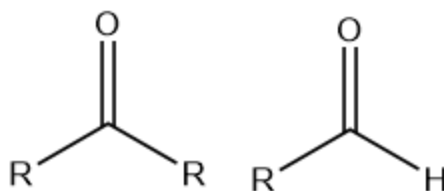
Following down the NMR, there are either three or four peaks that are distinct in the area, but since the two peaks around the 128.575ppm and 128.267ppm are so close in shift, there can be noise that shifted one of the peaks. With this assumption, this can be said as the region of the aromatic ring that was concluded in the IR part. Now with three different carbon signals, the best explanation for the amount of signals would be a benzene derivative that can retain the ketone and attach an amine.
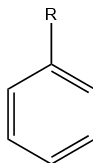
Following down the plot, there are three peaks around the 77ppm area which can be said to be the solvent CDCl$_3$ based on the "triplet" looking like group of peaks. The peak after the solvent peak is at 35.267ppm which can be an amine group that has been pointed out from the IR.

$$RCH_2NHR$$

For the last peak that is available, it is labeled as 19.110ppm which can be part of carbons in a chain.

$$R_2CH_2$$

H¹ NMR:

   Using the integrations, rounding numbers would have to be used. The peak at about 8ppm has an integration of 5.83 which can be rounded to 6. The following peak at 7.5ppm has an integration of 23.23 which can be rounded to 24 to yield 4 hydrogens in this area. At the 3.5ppm peak, it has an integration of 8.22 which can be roughly rounded up to 12, which is extremely inaccurate but yields 2 hydrogens in the peak. The final integration around 1.2ppm area has an integration of 52.72 which rounded yields roughly 54 to have 9 hydrogens in this area.

   From the H-NMR, there were only four peaks in the plot, but each one were split. Again, like the other plots from right to left, the first peak is right about the 8ppm area which can indicate either an amide hydrogen or a benzene hydrogen. Since the peaks are multiplets, it can be deduced that the peaks here are for benzene rather than for amides, but amides can still be a consideration of the final structure. This integration yields one hydrogen under this condition so this can be a benzene hydrogen that is far from where a substituent is.


OR
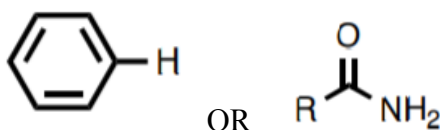
   The next peak down the line is around the 7.5ppm area which seems to be a combination of two multiplets which makes a better explanation for the benzene hydrogens. Since the peak that is more left has a doublet or a triplet and the peak right next to it has a triplet, it can be shown that these peaks fit the benzene hydrogens better than the peak from the 8ppm area. The integration for this is 4 which can yield the 4 other hydrogen spots left with a substituent that contains both the carbonyl, supposedly a ketone, and the amine, specifically a secondary amine, in the structure.

Carbonyl and Amine
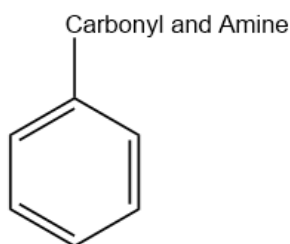
   The second to last peak is around the 3.5ppm region which has an integration that yields about 2 hydrogens which could either mean there is a primary amine which the IR did not display, or the integration should have been 1, which is the same as the 8ppm integration which can also yield a secondary amine in the structure.
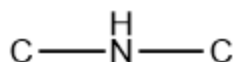
The final peak on the H-NMR is around 1.2ppm which also has an integration that yields 9 hydrogens. This chemical shift value can yield two possible structures which can be a tert-butyl group in the structure a little away from something electron donating or an alkyl (methylene) group in the structure.


OR
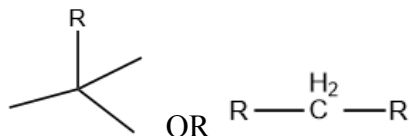
A suggestion from the carbon nmr suggest that there could be an aldehyde, but since the H-NMR does not display a peak around the 10ppm region, the subject of an aldehyde can be excluded from any structure consideration. Since an acid was excluded earlier, another way that the acid can be excluded from considerations is because there is no peak around the 10-11ppm area that corresponds to the acid.

Theoretical Crafting:
Since all three spectra deduce that there is a benzene ring, the base structure is a benzene ring that only one hydrogen is replaced with a substituent.
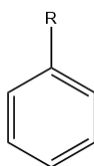

After the hydrogen is replaced with a substituent, in order to keep the carbonyl in check with an extra methyl group has to be added that keeps the carbonyl away from the conjugation from the benzene ring. Since the carbonyl is also deduced to be a ketone, there has to be another methyl group after the carbonyl to make it a ketone.
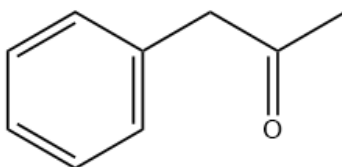

Now this structure is an example of what the unknown structure can be, but this structure is missing an amine group right now. Adding the secondary amine group requires that the structure keeps the ketone in check within the 204ppm range and without creating extra peaks in both NMR.
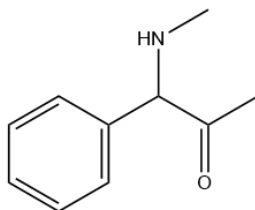
This amine is just added so that it can be seen as how the structure has an amine within the structure. The final addition would be the addition of a tert-butyl group so that the the 1.2ppm peak in the H-NMR can be satisfied. This would also require a distance away from the electronegative groups and also there can't be any more peaks that are added on randomly.
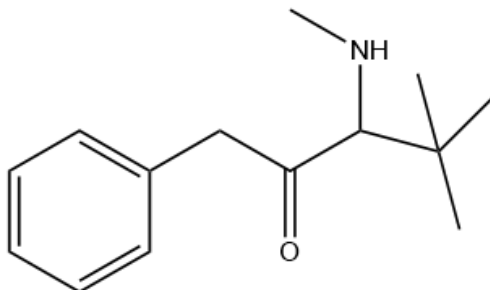

This structure is an incorrect structure, but highlights all the important features that the analyzed spectrum has given. Now assuming anything from the IR that shows an amine possible, we can omit that, by considering it was impurities, to deduce another structure. Without worrying about the amine, we go back a step with the ketone and benzene attachments. In this case the ketone can be attached directly onto the carbon but with another carbon with methyl substituents to preserve the ketone at 204ppm, by introducing electron density around to try to negate the effects of the benzene ring conjugation that will being the chemical shift down from 204ppm.
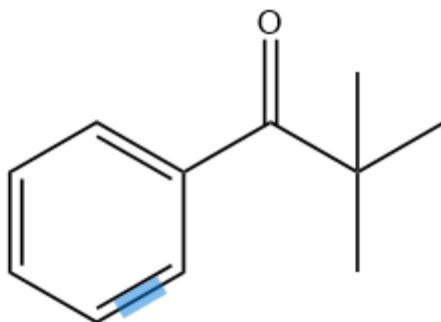
This is a sample structure of how the ketone would be in the unknown. This would show four different carbon peaks, but with two really close to each other on the plot. Using this, keeping the four carbon signals in benzene, we can keep deducing structures off this base structure. This structure here yields no hydrogen splitting around the 3.6ppm area, so this structure would not be the unknown structure. Removing a methyl group would provide the signals, but requires a new set of integrations to be used. The integrations are under multiples of 9 rather than 6 now. The new values, from ~8ppm to 1.2ppm is given to be 1, 3, 1, 6. This is still off but matches with the isopropyl group that is required off the ketone.
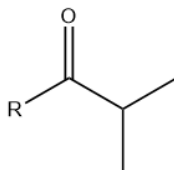
Predicted Structures with amines:
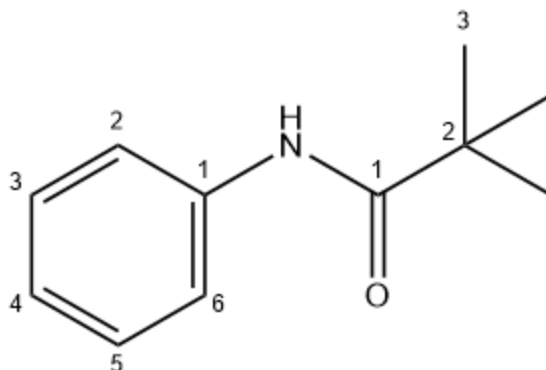
N-phenylpivalamide

The first predicted structure is pictured above due to the carbonyl that is introduced with a secondary amine and a carbonyl right next to the amine. This also contains a benzene which lines up as an aromatic substance. Although the carbonyl will have a shift from 204ppm to ~180ppm, this structure is a close consideration to what the unknown is.
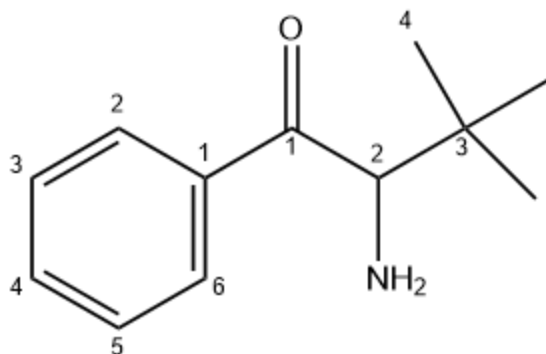

2-amino-3,3-dimethyl-1-phenylbutan-1-one

A second structure, pictured above, can be predicted as the structure due to the benzene ring that is present, carbonyl, and an amine in the structure. Although the carbonyl is right next to the benzene, it will be conjugated which will shift from 204ppm to something lower. Another issue to this structure is also the primary amine which contradicts the secondary amine the IR shows. This structure will also produce an extra carbon signal that is the carbon that is connecting the amine in the structure.
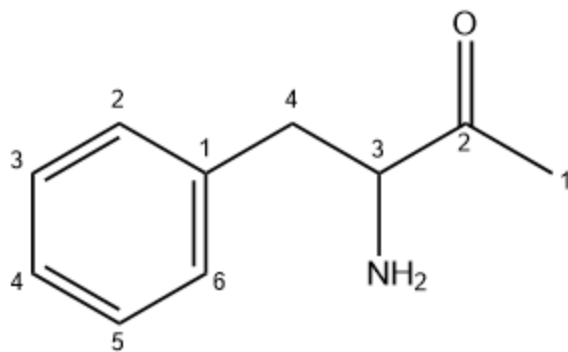
3-Amino-4-phenyl-butan-2-one

A third structure is assumed based on the amine, carbonyl, and benzene ring. This again, shows a primary amine where the IR shows a secondary amine. The carbonyl here has retained about the 204ppm region, but since there are two new carbons introduced in the C-NMR this assumed structure can be close to the unknown structure.

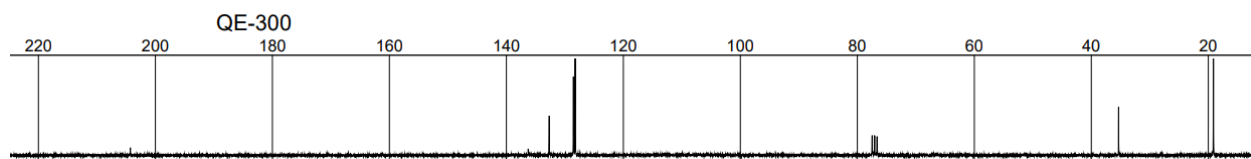**Predicted Structures without amines:**
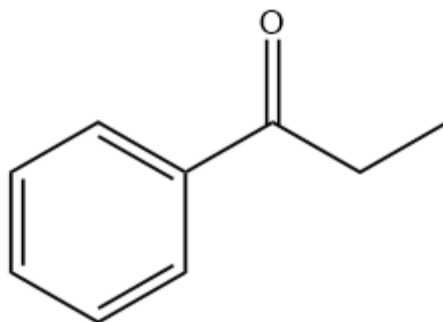
propiophenone

This structure is proposed, but since there is only one methyl group, the H-NMR that has 6 protons in the integrations do not match up. This also yields two protons adjacent to it which means that the integration of the protons around 3.5ppm require an integration of 2, which is now not the case based on the second set of assumptions that are assumed under the new set of integrations without amines. This structure is close to the possibility, but a methyl group would need to be added somewhere potentially the adjacent carbon to bring the proton down to one yielding the next structure predicted below.
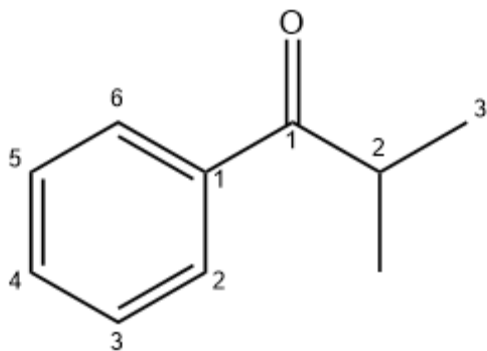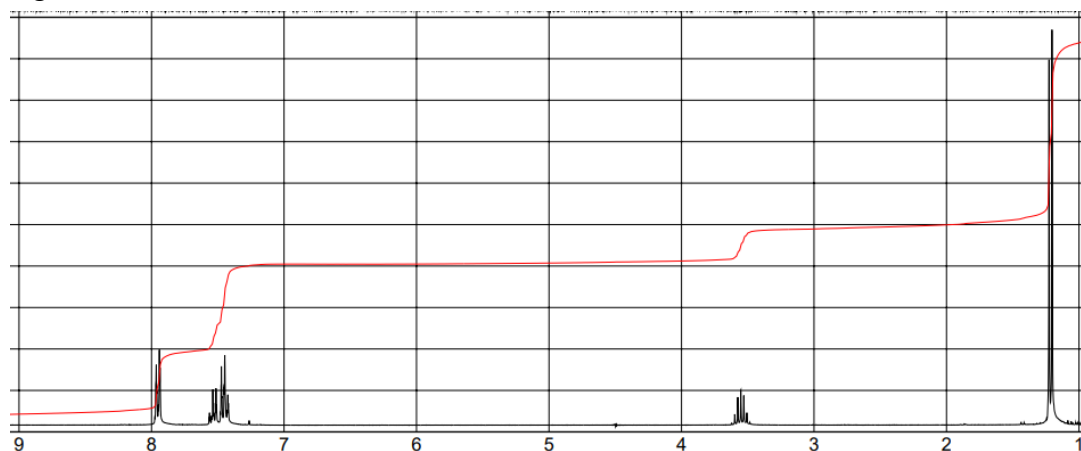
2-methyl-1-phenylpropan-1-one

   This structure has one less methyl substituent which goes against a thought of having a tert-butyl, but based on the NMR and IR on both Sigma-Aldrich and the Japanese Spectral database, everything matches up with the exception of a potential contaminant peak in the alcohol or amine region. **This structure pictured above will be considered as what Unknown J is.** This gives the ketone the 204ppm required, has the aromatic ring, benzene, and other carbons that yield the correct ppm. The structure fits the four benzene peaks, the proton splittings, majority of the IR. Although this structure goes against some analysis before, everything experimental can be taken with a grain of salt include that variant in the NH/OH band region.
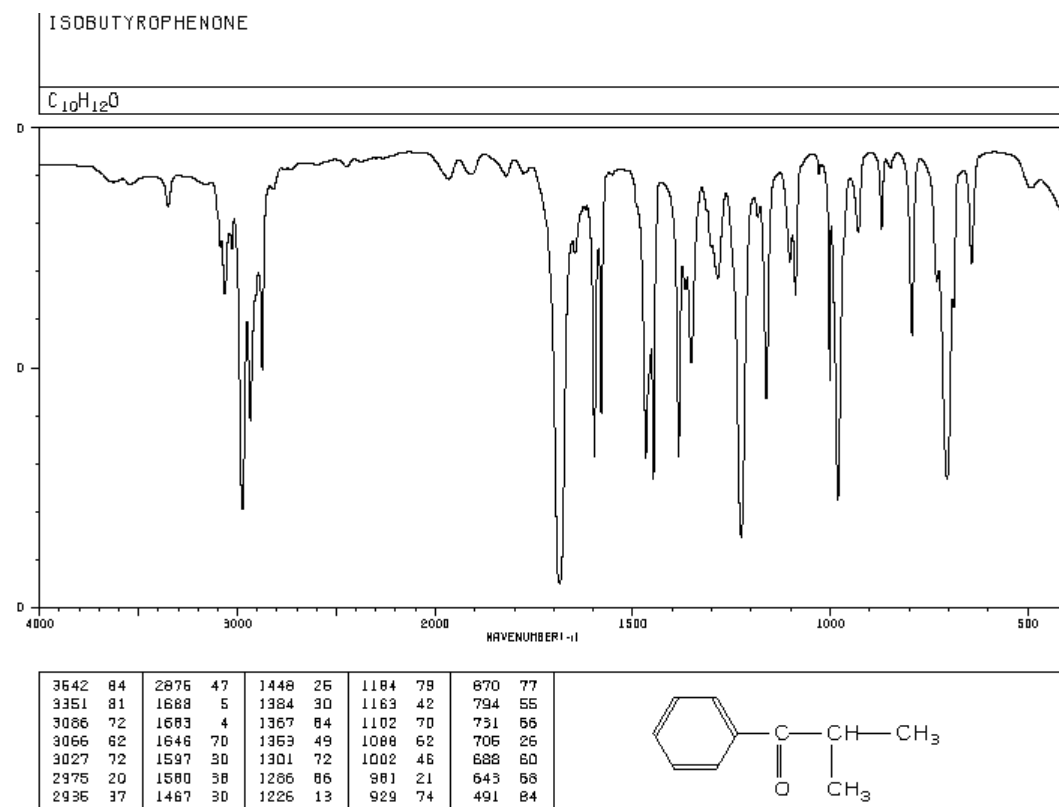
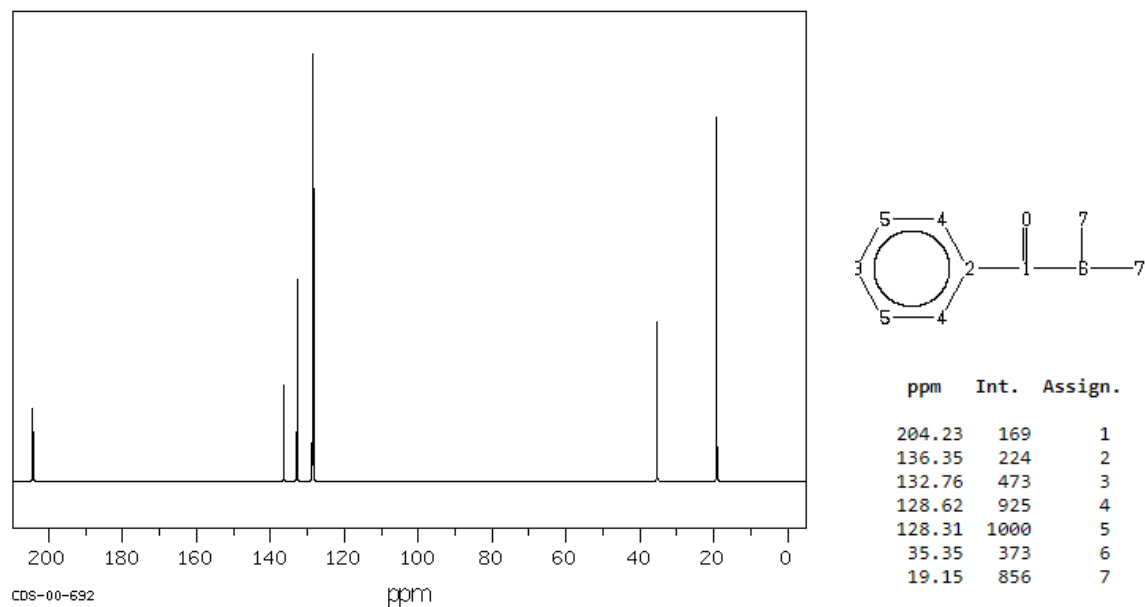Sigma-Aldrich C-NMR:

Sigma-Aldrich H-NMR:
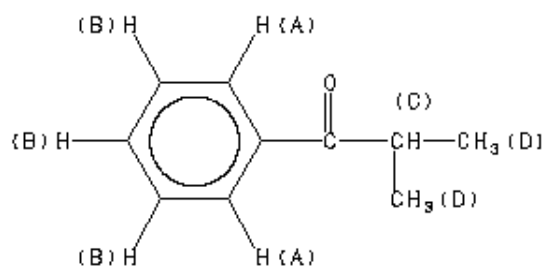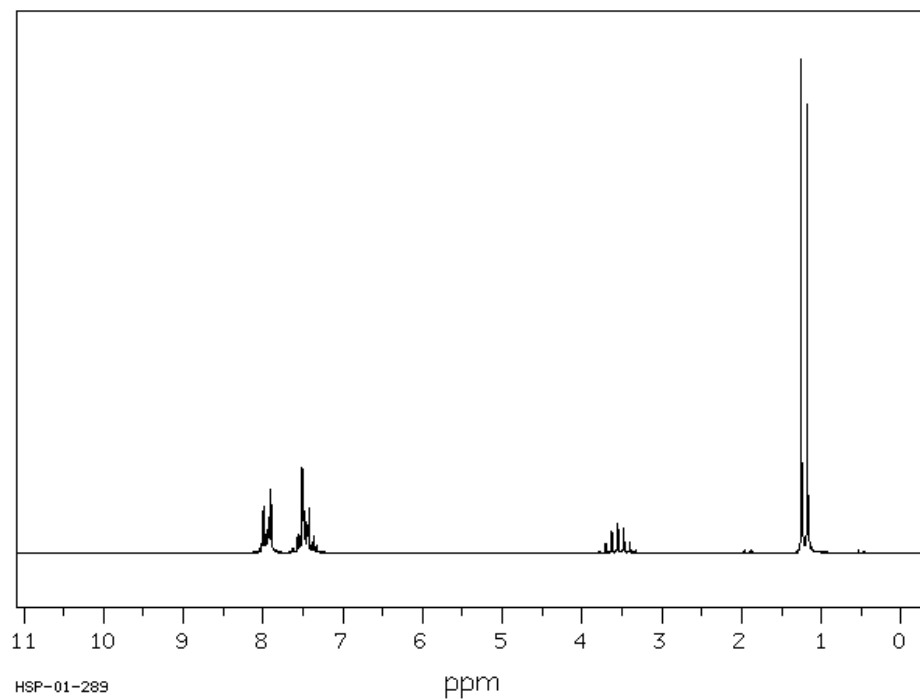
Japanese Spectral Database:

IR:

ISOBUTYROPHENONE

$C_{10}H_{12}O$

HAVENUMBER(-1)

3642	84	2876	47	1448	26	1184	79	870	77
3351	81	1688	5	1384	30	1163	42	794	55
3086	72	1683	4	1367	84	1102	70	731	56
3066	62	1646	70	1353	49	1088	62	706	26
3027	72	1597	30	1301	72	1002	46	688	60
2975	20	1580	38	1286	86	981	21	643	58
2935	37	1467	30	1226	13	929	74	491	84

C-NMR:

isobutyrophenone

CDS-00-692   ppm

ppm	Int.	Assign.
204.23	169	1
136.35	224	2
132.76	473	3
128.62	925	4
128.31	1000	5
35.35	373	6
19.15	856	7

-9-

H-NMR:

HSP-01-289

ppm

Assign.	Shift(ppm)
A	7.95
B	7.67 to 7.31
C	3.543
D	1.216

References:
Sigma-Aldrich
Japanese Spectral Database for Organic Compounds