

## [Supporting Information]

# Highly selective Wacker reaction of styrene derivatives: a green and efficient aerobic oxidative process promoted by benzoquinone/NaNO<sub>2</sub>/HClO<sub>4</sub> under mild conditions

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## General Experimental

All the olefins were commercially available except 4-isopropylstyrene, 3,4-dimethylstyrene, 2,4-dichlorostyrene and 3,4,5-trimethoxystyrene, which were prepared according to the literature procedures.<sup>1</sup> Column chromatography was performed with silica gel (300-400 mesh) produced by Qingdao Marine Chemical Factory, Qingdao (China). NMR spectra were recorded on Bruker AVANCE III 500MHz instrument with TMS as internal standard. Coupling constants were reported in Hertz (Hz).

## Experimental Sections

### General Procedure for Preparation of Olefins.

(1) Into a 150 mL round-bottomed flask,  $\text{Ph}_3\text{P}$  (20.0 mmol) dissolved in dry THF (30.0 mL) was added, and  $\text{CH}_3\text{I}$  (24.0 mmol) was added dropwisely into the stirred reaction mixture. Then the reaction mixture was stirred under reflux for 2 h. After that, the contents were poured into a 250 mL beaker. After it cooled down, the mixture was filtrated and thoroughly washed with xylene and dried under vacuum. The product ( $\text{Ph}_3\text{P}^+\text{CH}_3\text{I}^-$ ) was obtained as a white solid. Yield: 95%;

(2) Under nitrogen atmosphere,  $\text{Ph}_3\text{P}^+\text{CH}_3\text{I}^-$  (10.0 mmol), *t*-BuOK (15.0 mmol), THF (100.0 mL) were placed in a 250 mL round-bottomed flask, the reaction mixture was stirred at 0 °C for 1 h, then 3,4-dimethylbenzaldehyde (8.0 mmol) in dry THF (30.0 mL) solution was added dropwisely. The reaction mixture was stirred at room temperature and monitored by TLC. After the reaction, the mixture was filtrated and the filtrate was extracted with ethyl acetate. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and removed the solvent under reduced pressure. The residue was further purified by column chromatography on silica gel (300-400 mesh) with *n*-hexane and ethyl acetate (v/v 20:1), The product 3,4-dimethylstyrene was obtained as a colorless liquid. Yield: 55%.

**3,4-dimethylstyrene** (colorless liquid, 55% yield):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.34 (d,  $J = 5.5$  Hz, 6H), 5.26 (d,  $J = 11.0$  Hz, 1H), 5.80 (t,  $J = 8.8$  Hz, 1H), 6.73-6.78 (q, 1H), 7.17 (d,  $J = 8.0$  Hz, 1H), 7.25 (d,  $J = 7.5$  Hz, 2H).

**4-isopropylstyrene** (colorless liquid, 45% yield):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.29 (s,  $J$  = 6.5 Hz, 6H), 2.94 (s, 1H), 5.22 (d,  $J$  = 11.0 Hz, 1H), 5.74 (d,  $J$  = 18.0 Hz, 1H), 6.71-6.76 (q, 1H), 7.23 (d,  $J$  = 8.5 Hz, 2H), 7.38 (d,  $J$  = 7.5 Hz, 2H).

**2,4-dichlorostyrene** (light yellow liquid, 40% yield):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.42 (d,  $J$  = 11.0 Hz, 1H), 5.74 (d,  $J$  = 17.0 Hz, 1H), 7.02-7.08 (q, 1H), 7.22-7.24 (q, 1H), 7.39 (d,  $J$  = 2.0 Hz, 1H), 7.50 (d,  $J$  = 8.0 Hz, 1H).

**3,4,5-trimethoxystyrene** (colorless liquid, 57% yield):  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.80 (d,  $J$  = 3.5 Hz, 9H), 5.15 (d,  $J$  = 11.5 Hz, 1H), 5.61 (d,  $J$  = 17.0 Hz, 1H), 6.54-6.60 (q, 3H).

## References

- (1) X. Y. Liu, Z. Z. Li, Y. D. Wu, Z. Y. Zhang, S. Z. Liang, X. L. Jia and J. N. Xiang, *Acta Chim. Sinica* 2008, **66**, 1086.

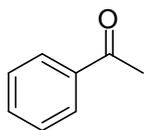
### **General Experimental Procedure for Oxidation of Olefins to the Corresponding Carbonyl Compounds.**

Palladium acetate (0.02 mmol), benzoquinone (0.1 mmol) and sodium nitrite (0.2 mmol) were introduced into a 25 mL Schlenk flask equipped with a magnetic stirrer and the flask was purged several times with oxygen (balloon filled). Then styrene (1.0 mmol), HClO<sub>4</sub> (0.4 mmol) and aqueous methanol (v/v 8:1, 5.0 mL) were added and the flask was immediately sealed. The mixture was fiercely stirred at oxygen atmosphere for 5 h. After that, the reaction solution was evaporated under vacuum and the crude product was purified by column chromatograph using silica gel with *n*-hexane/ethyl acetate (v/v 5:1) as eluent. The product acetophenone was obtained as a colorless liquid. Yield: 91%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.62 (s, 3H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.97 (t, *J* = 4.5 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 26.5, 128.2, 128.5, 133.0, 137.1, 198.1.

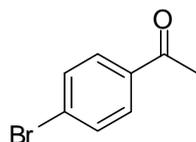
### **Gram-Scale Experimental Procedure for Oxidation of Styrene.**

Palladium acetate (1.0 mmol), benzoquinone (5.0 mmol) and sodium nitrite (10.0 mmol) were introduced into a 1000 mL three necks flask, equipped with a magnetic stirrer and the flask was purged several times with oxygen (balloon filled). Then styrene (50.0 mmol), HClO<sub>4</sub> (20.0 mmol) and aqueous methanol (v/v 8:1, 250 mL) were added and the flask was immediately sealed. The mixture was fiercely stirred at 25 °C for several hours. After the reaction, the solution was evaporated under vacuum and the crude product was purified by column chromatograph using silica gel with *n*-hexane/ethyl acetate (v/v 5:1) as eluent. The product acetophenone was obtained as a colorless liquid. Yield: 92%.

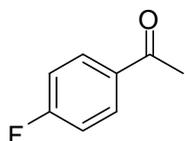
## Characterization Data for Products



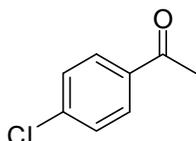
**Acetophenone (Table 2, entry 1):** liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.62 (s, 3H), 7.47 (t,  $J = 7.5$  Hz, 2H), 7.58 (t,  $J = 7.0$  Hz, 1H), 7.97 (t,  $J = 4.5$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.5, 128.2, 128.5, 133.0, 137.1, 198.1.



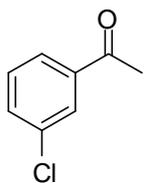
**4-Bromoacetophenone (Table 2, entry 2):** mp 50-51 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.60 (s, 3H), 7.61-7.63 (q, 2H), 7.83-7.84 (q, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.5, 128.4, 129.8, 131.9, 135.8, 197.1.



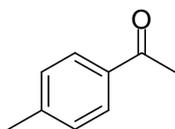
**4-Fluoroacetophenone (Table 2, entry 3):** liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.58 (s, 3H), 7.13 (t,  $J = 8.8$  Hz, 2H), 7.97-8.00 (q, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.5, 115.5, 115.7, 130.9, 131.0, 133.6, 184.7, 186.8, 196.4.



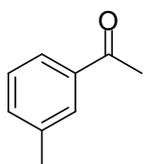
**4-Chloroacetophenone (Table 2, entry 4):** liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.61 (s, 3H), 7.45 (d,  $J = 8.5$  Hz, 2H), 7.91 (d,  $J = 8.5$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.5, 128.9, 129.7, 135.4, 139.6, 196.8.



**3-Chloroacetophenone (Table 2, entry 5):** liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.59 (s, 3H), 7.41 (t,  $J = 7.8$  Hz, 1H), 7.52-7.54 (m, 1H), 7.82-7.83 (m, 1H), 7.92 (t,  $J = 1.8$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.5, 126.4, 128.4, 129.9, 133.0, 134.9, 138.7, 196.6.

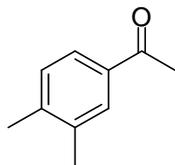


**4-Methylacetophenone (Table 2, entry 6):** liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.41 (s, 3H), 2.57 (s, 3H), 7.25 (d,  $J = 8.0$  Hz, 2H), 7.86 (d,  $J = 8.5$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.6, 26.5, 28.4, 129.2, 134.7, 143.9, 198.0.

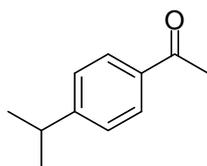


**3-Methylacetophenone (Table 2, entry 7):** liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):

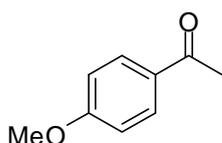
$\delta$  2.42 (s, 3H), 2.60 (s, 3H), 7.34-7.39 (m, 2H) 7.77 (t,  $J = 7.0$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.3, 26.6, 125.6, 128.4, 128.7, 133.8, 137.2, 138.3, 198.3.



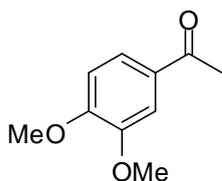
**3,4-Dimethylacetophenone (Table 2, entry 8):** liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.45 (s, 3H), 3.82 (d,  $J = 6.0$  Hz, 6H), 6.77 (d,  $J = 9.0$  Hz, 1H), 7.41 (d,  $J = 2.0$  Hz, 1H), 7.45 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.0, 55.8, 55.9, 109.9, 110.1, 123.2, 130.4, 148.9, 153.2, 196.6.



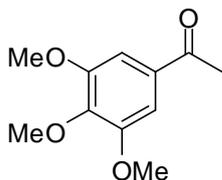
**4-Isopropylacetophenone (Table 2, entry 9):** liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.28 (d,  $J = 7.0$  Hz, 6H), 2.59 (s, 3H), 2.98 (s, 1H), 7.32 (d,  $J = 8.5$  Hz, 2H), 7.91 (d,  $J = 8.5$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  23.6, 26.5, 34.2, 126.6, 128.6, 135.1, 154.6, 197.8.



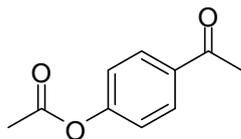
**4-Methoxyacetophenone (Table 2, entry 10):** mp 38-39 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.56 (s, 3H), 3.88 (s, 3H), 6.94 (d,  $J = 8.5$  Hz, 2H), 7.95 (d,  $J = 9.0$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.3, 26.6, 125.6, 128.4, 128.7, 133.8, 137.2, 138.3, 198.3.



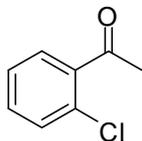
**3,4-Dimethoxyacetophenone (Table 2, entry 11):** mp 49-51 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.57 (s, 3H), 3.94 (d,  $J = 6.0$  Hz, 6H), 6.89 (d,  $J = 8.5$  Hz, 1H), 7.53 (d,  $J = 2.5$  Hz, 1H), 7.57-7.59 (q, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.1, 55.9, 56.0, 110.0, 110.1, 123.2, 130.5, 149.0, 153.3, 196.7.



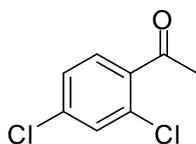
**3,4,5-Trimethoxyacetophenone (Table 2, entry 12):** mp 78-81 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.60 (s, 3H), 3.93 (d,  $J = 2.5$  Hz, 9H), 7.22 (s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.4, 56.3, 60.9, 105.9, 132.5, 143.1, 153.1, 196.9.



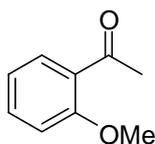
**4-Acetoxyacetophenone (Table 2, entry 13):** mp 53-55 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.34 (s, 3H), 2.61 (s, 3H), 7.20 (d,  $J = 9.0$  Hz, 2H), 8.01 (d,  $J = 8.5$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.1, 26.5, 121.8, 129.9, 134.7, 154.4, 168.8, 196.9.



**2-Chloroacetophenone (Table 2, entry 14):** liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.64 (s, 3H), 7.28-7.33 (m, 1H), 7.36-7.42 (m, 2H), 7.53-7.55 (q, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  30.7, 126.9, 129.4, 130.6, 131.3, 132.0, 139.1, 200.4.



**2,4-Dichloroacetophenone (Table 2, entry 15):** mp 33-34 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.64 (s, 3H), 7.30-7.33 (q, 1H), 7.45(d,  $J = 2.0$  Hz, 1H), 7.54 (d,  $J = 8.5$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  30.6, 127.4, 130.5, 130.7, 132.5, 137.2, 137.7, 198.8.



**2-Methoxyacetophenone (Table 2, entry 16):** mp 33-34 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.62 (s, 3H), 3.91 (s, 3H), 6.96-7.01 (q, 2H), 7.45-7.48 (m, 1H), 7.73-7.75 (q, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.8, 55.4, 111.6, 120.5, 128.3, 130.3, 133.6, 158.9, 199.8.

Figure 1.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of Acetophenone

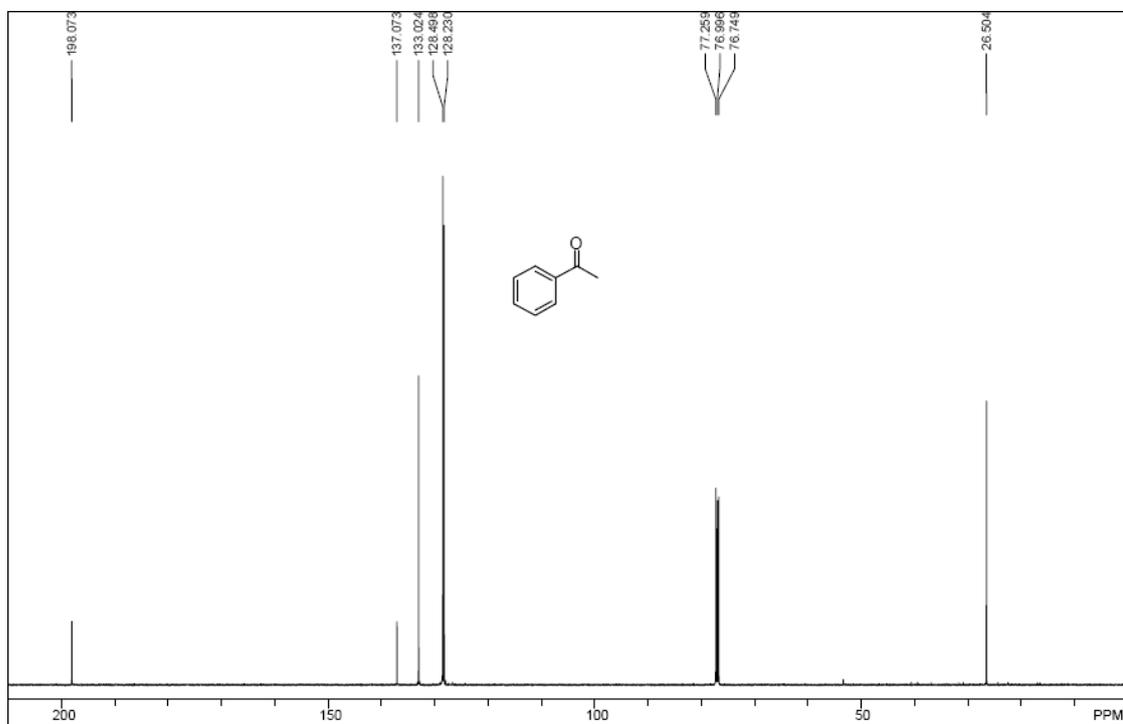
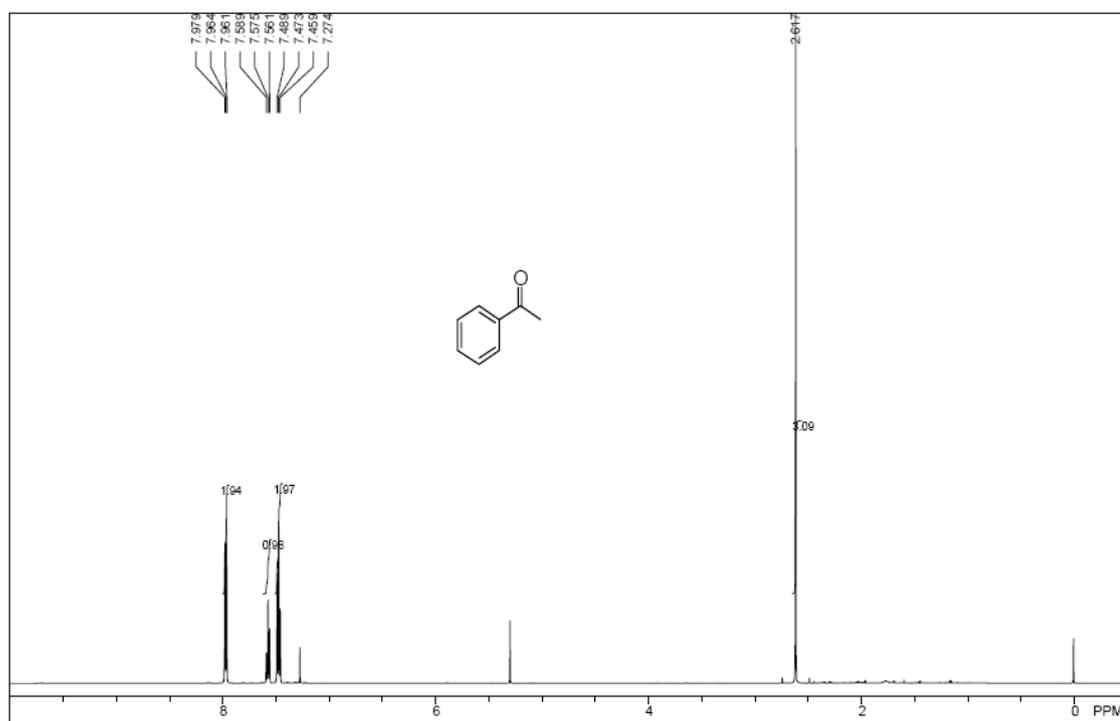


Figure 2.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 4-Bromoacetophenone

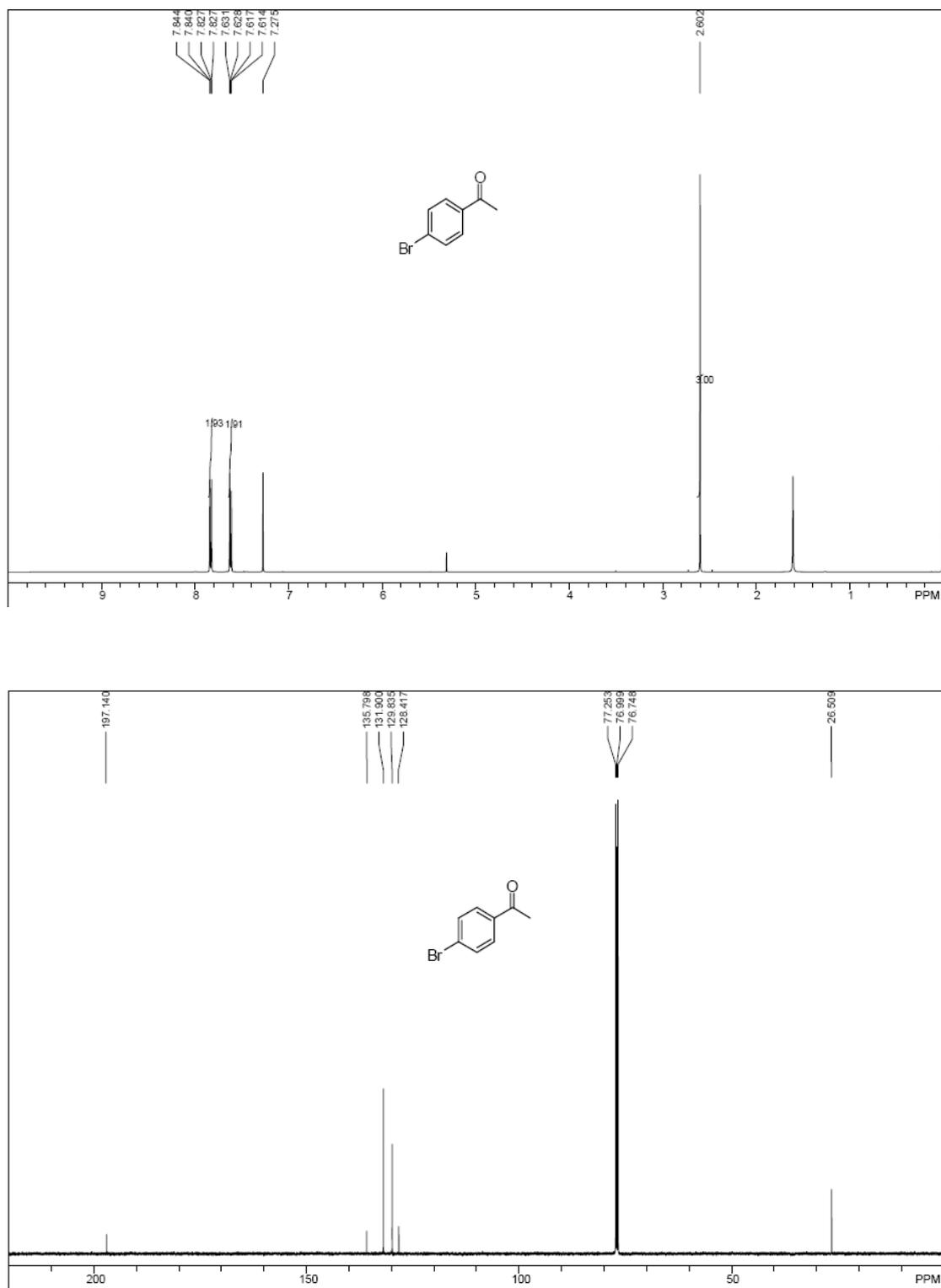
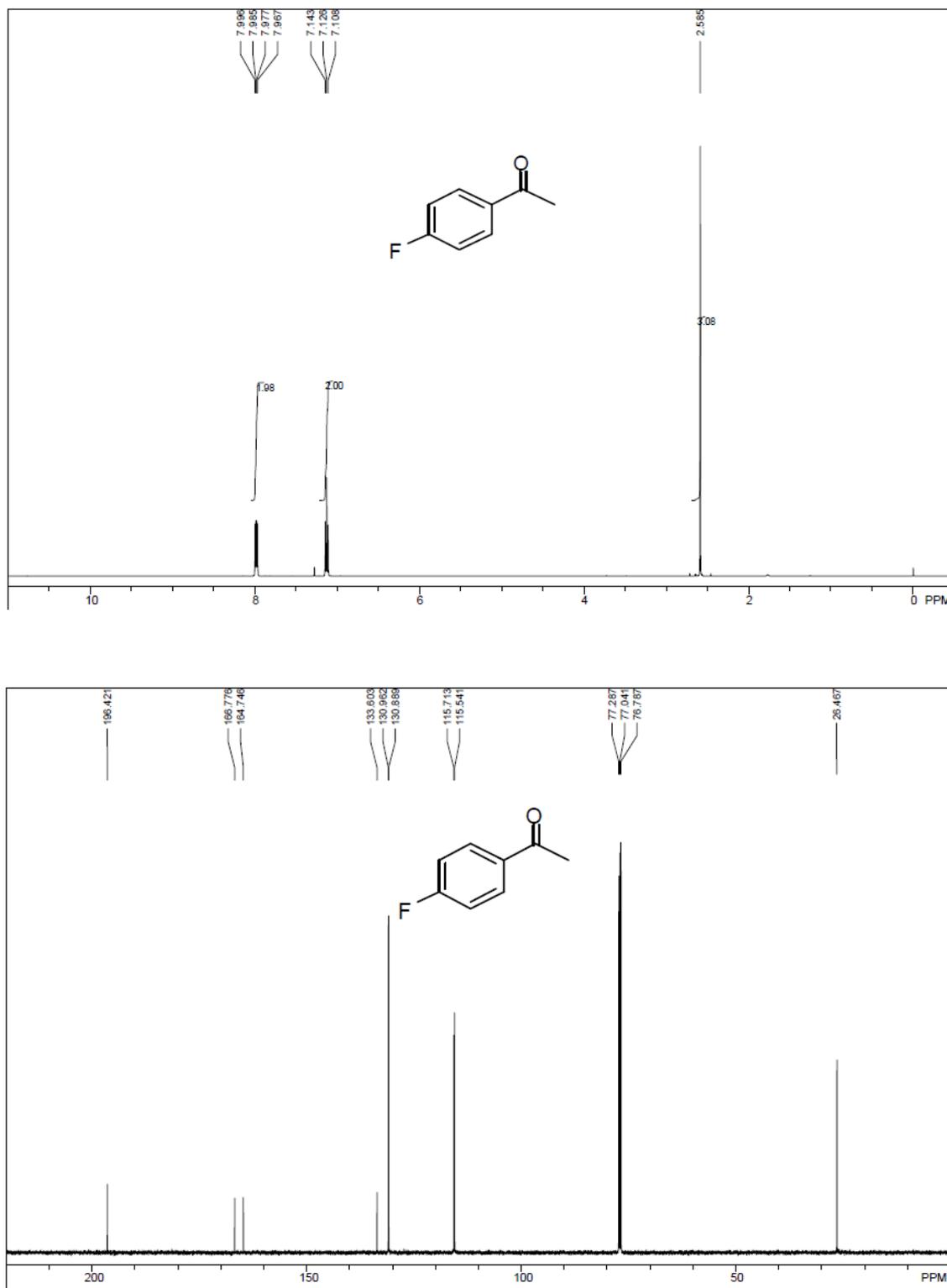


Figure 3.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 4-Fluoroacetophenone



**Figure 4.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 4-Chloroacetophenone

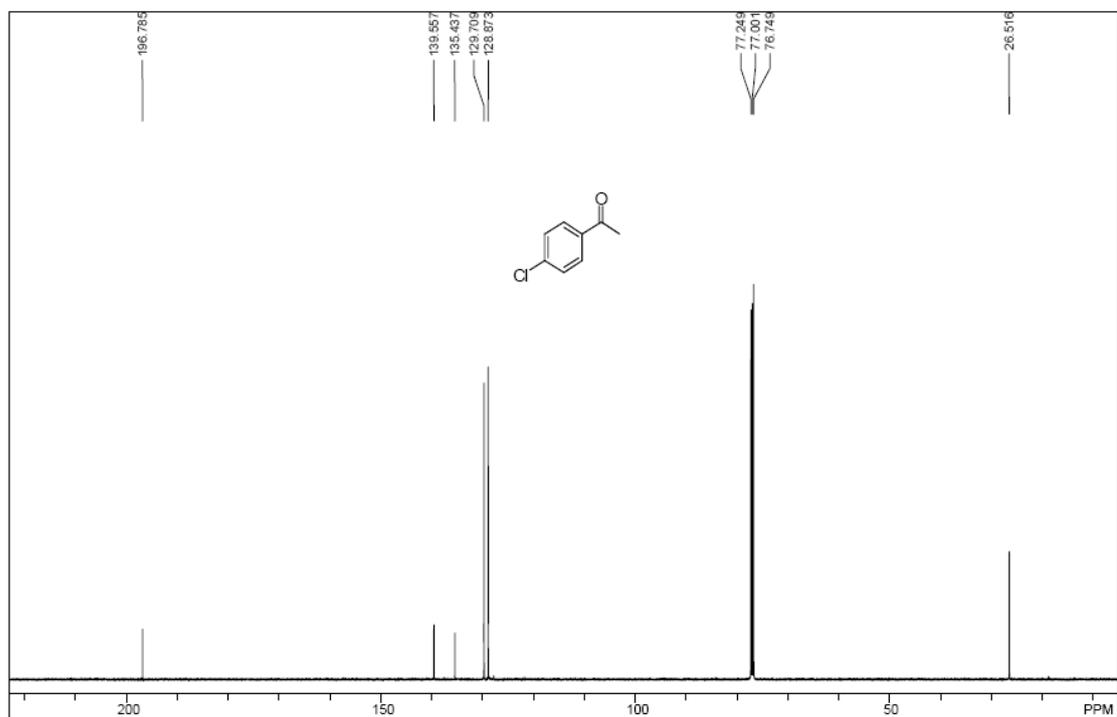
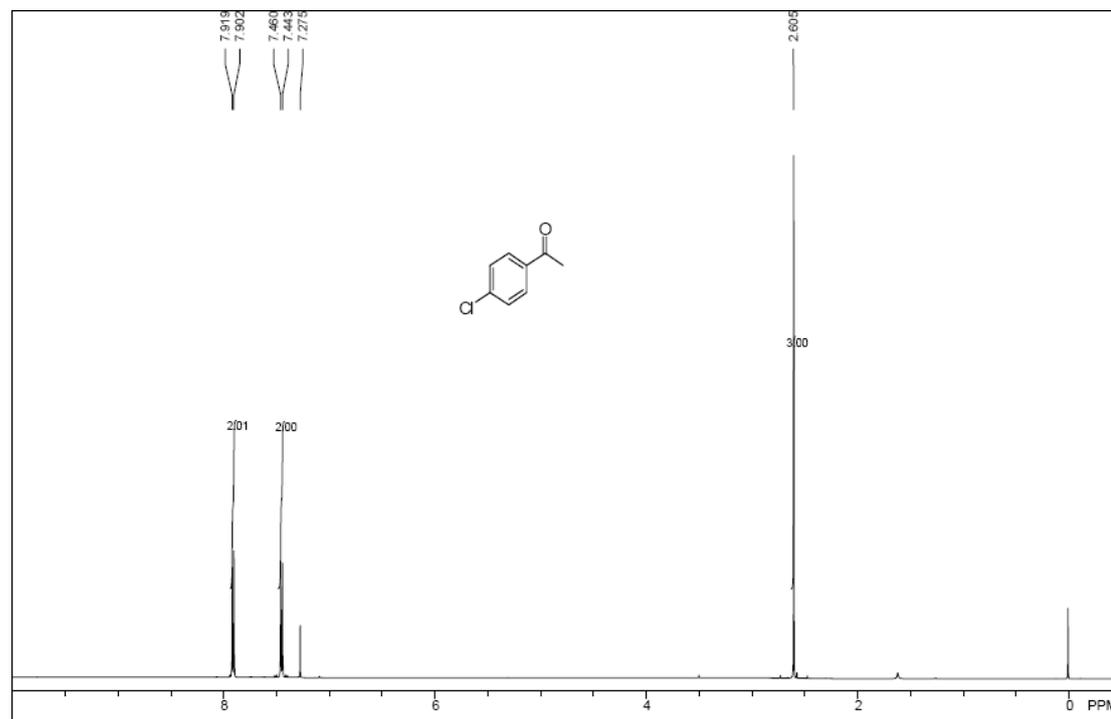


Figure 5.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 3-Chloroacetophenone



Figure 6.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 4-Methylacetophenone

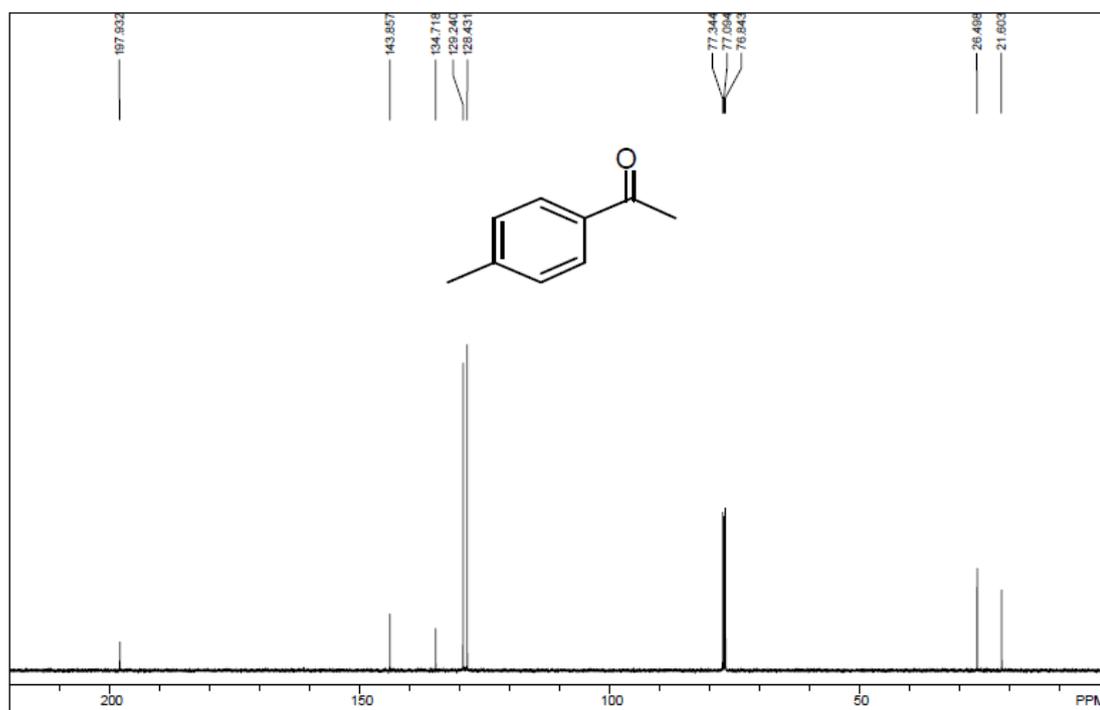
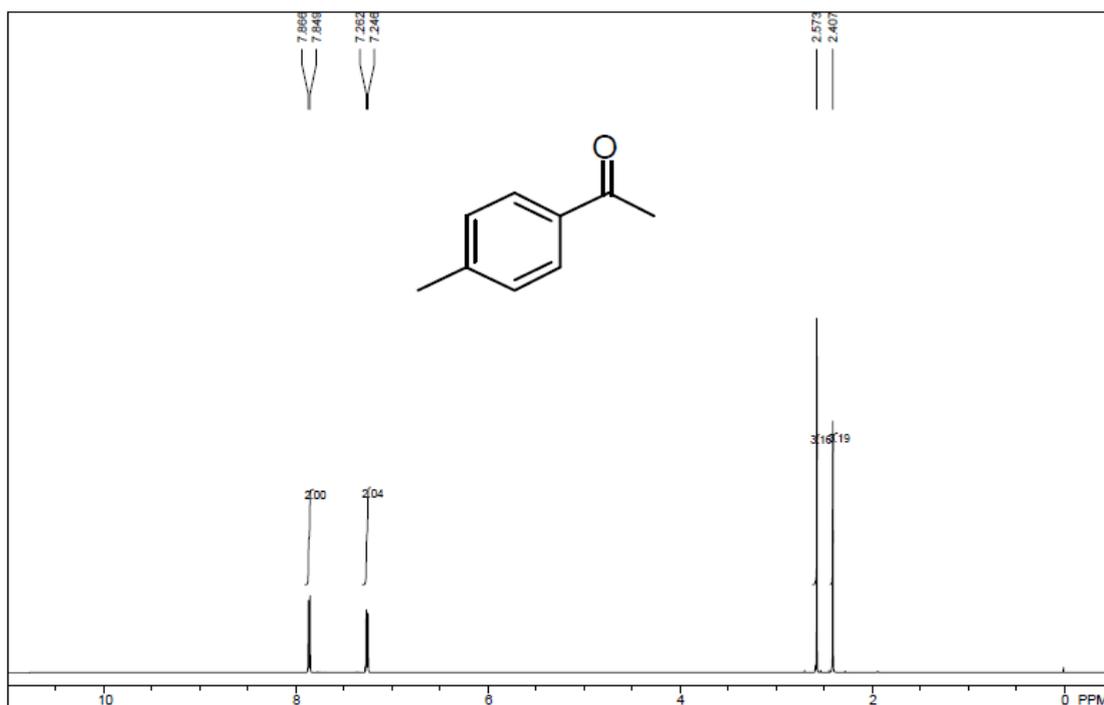


Figure 7.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 3-Methylacetophenone

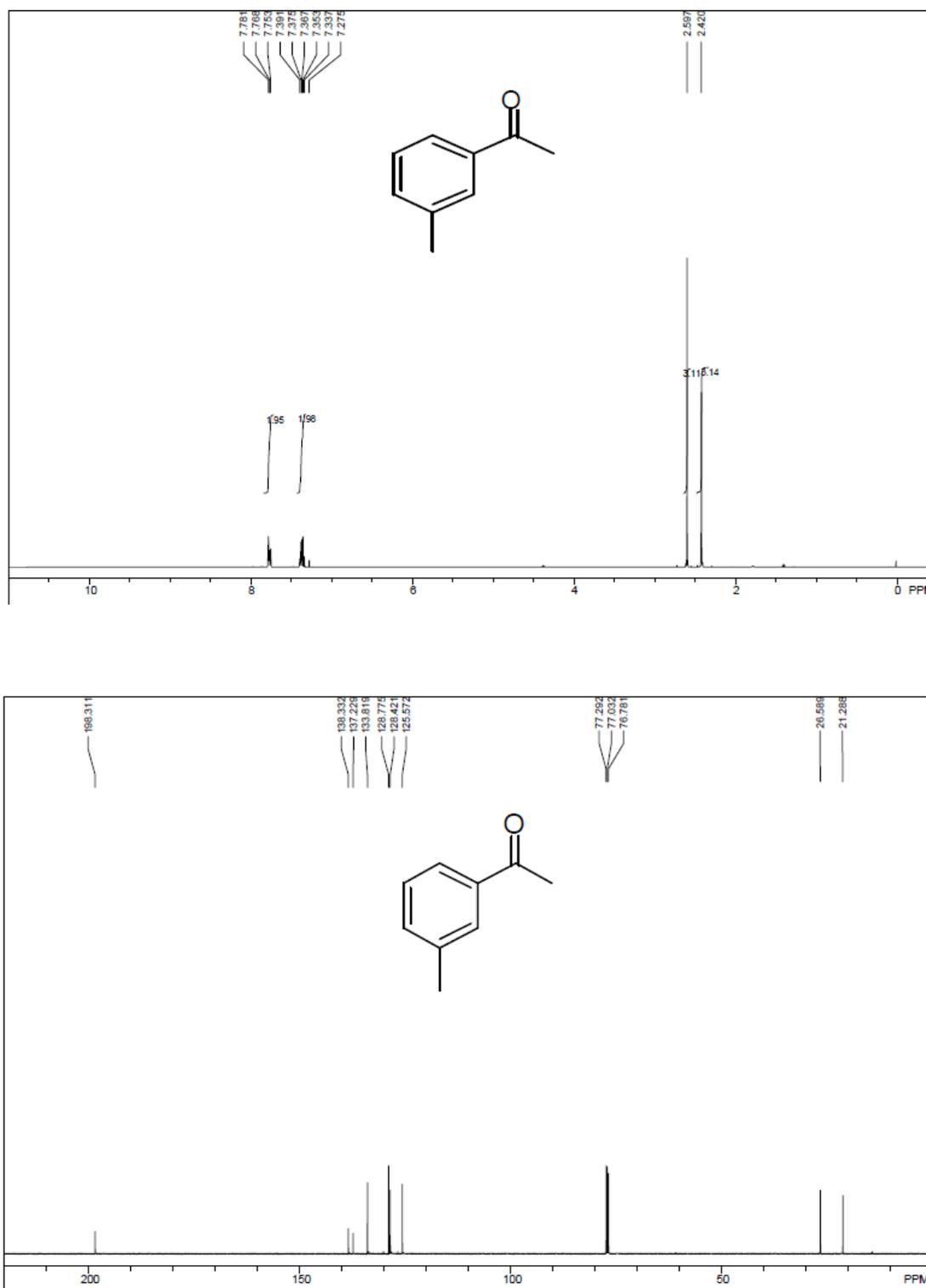


Figure 8.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 3,4-Dimethylacetophenone

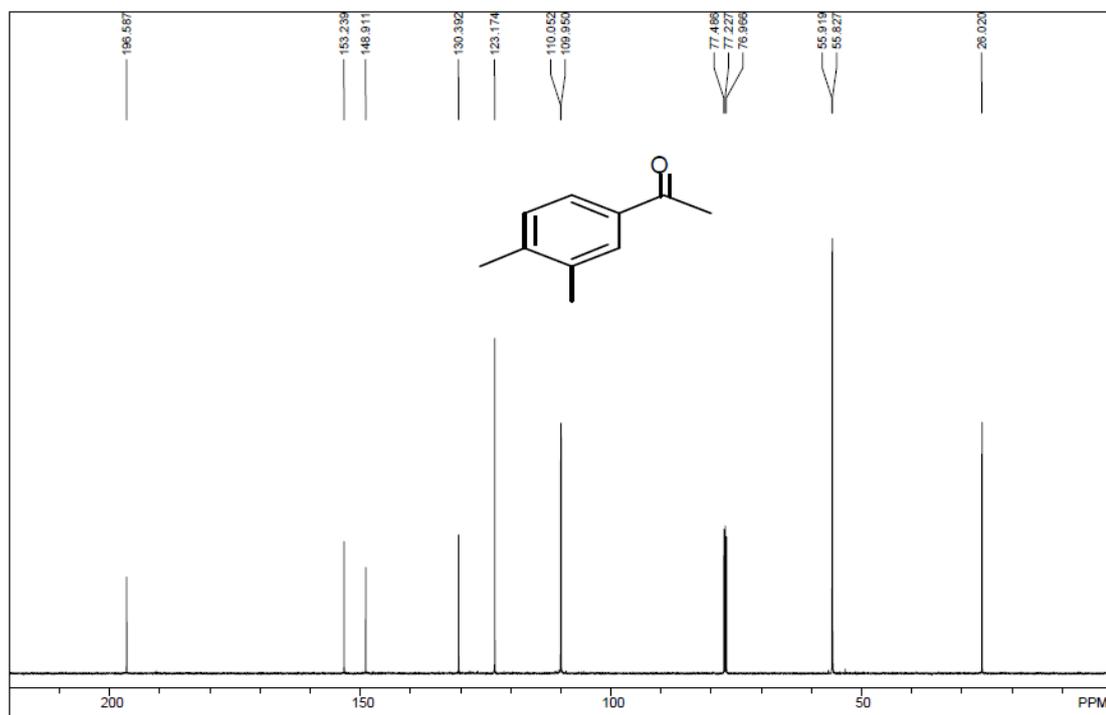
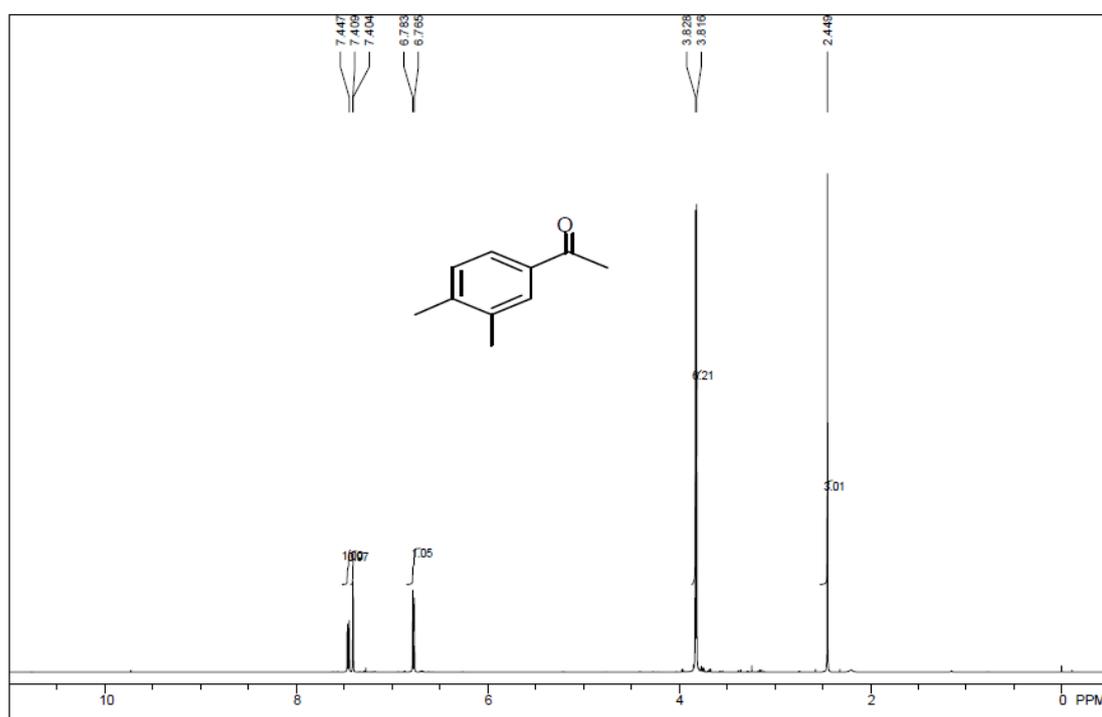


Figure 9.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 4-Isopropylacetophenone

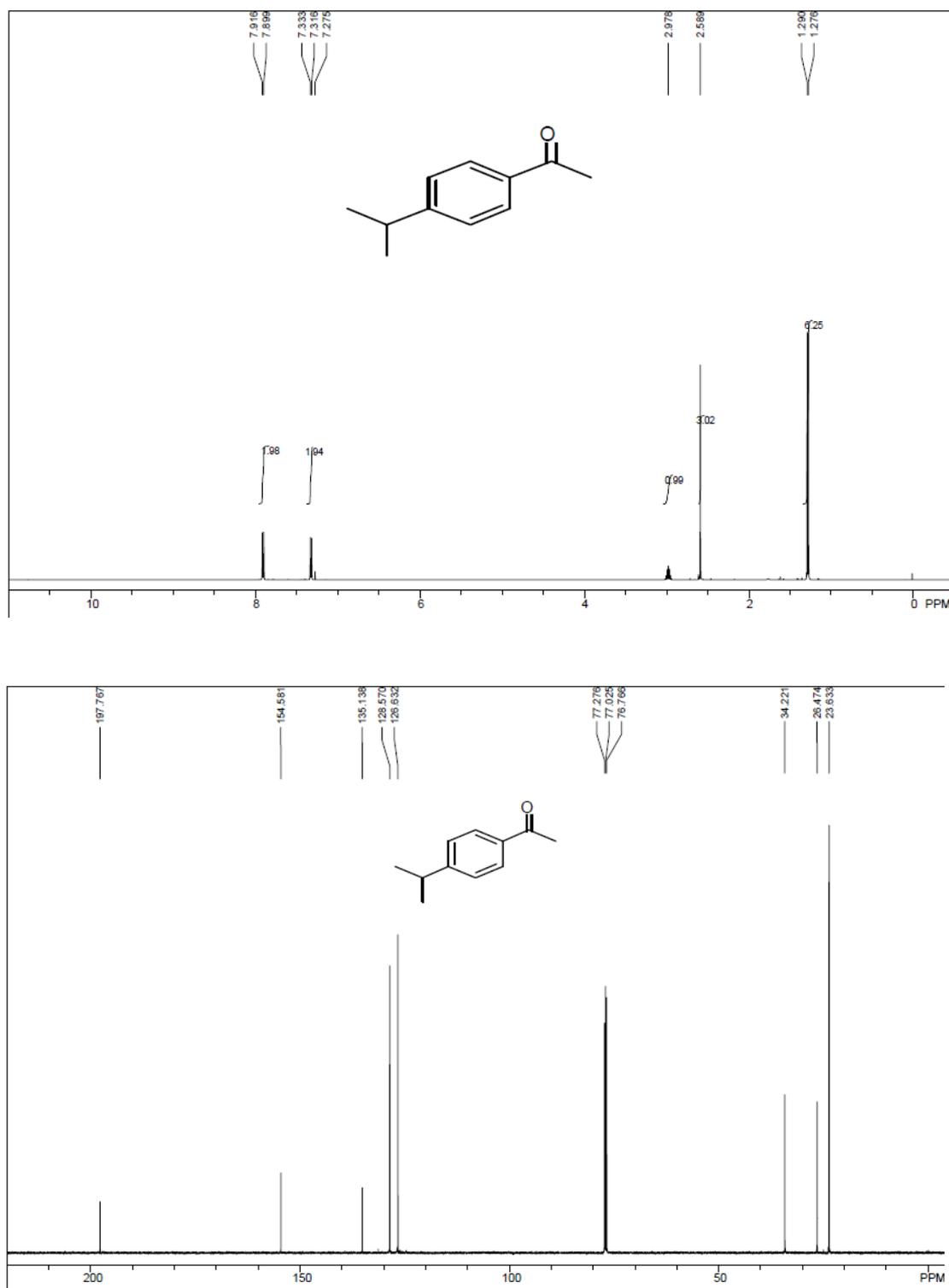


Figure 10.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 4-Methoxyacetophenone

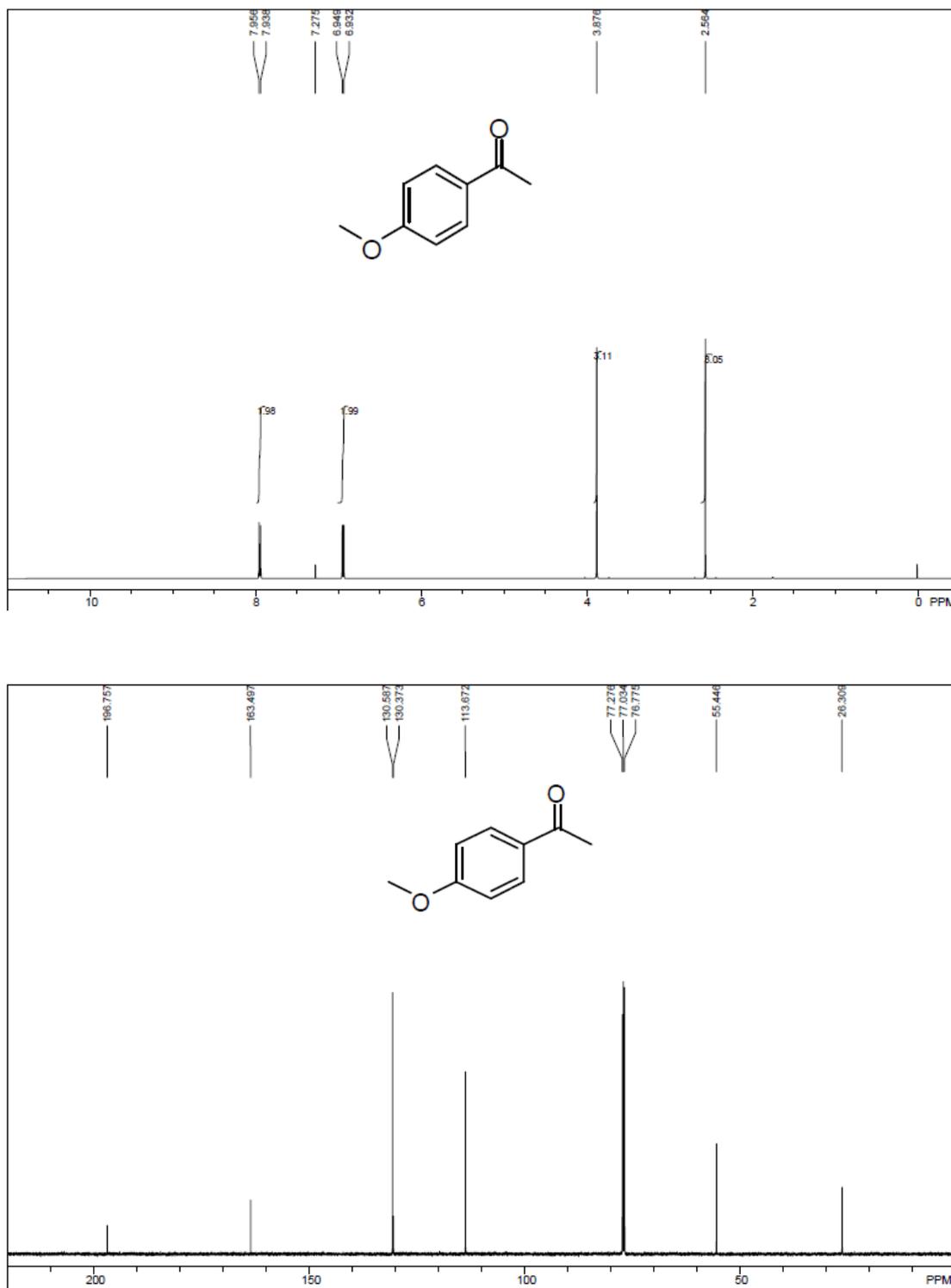


Figure 11.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 3,4-Dimethoxyacetophenone

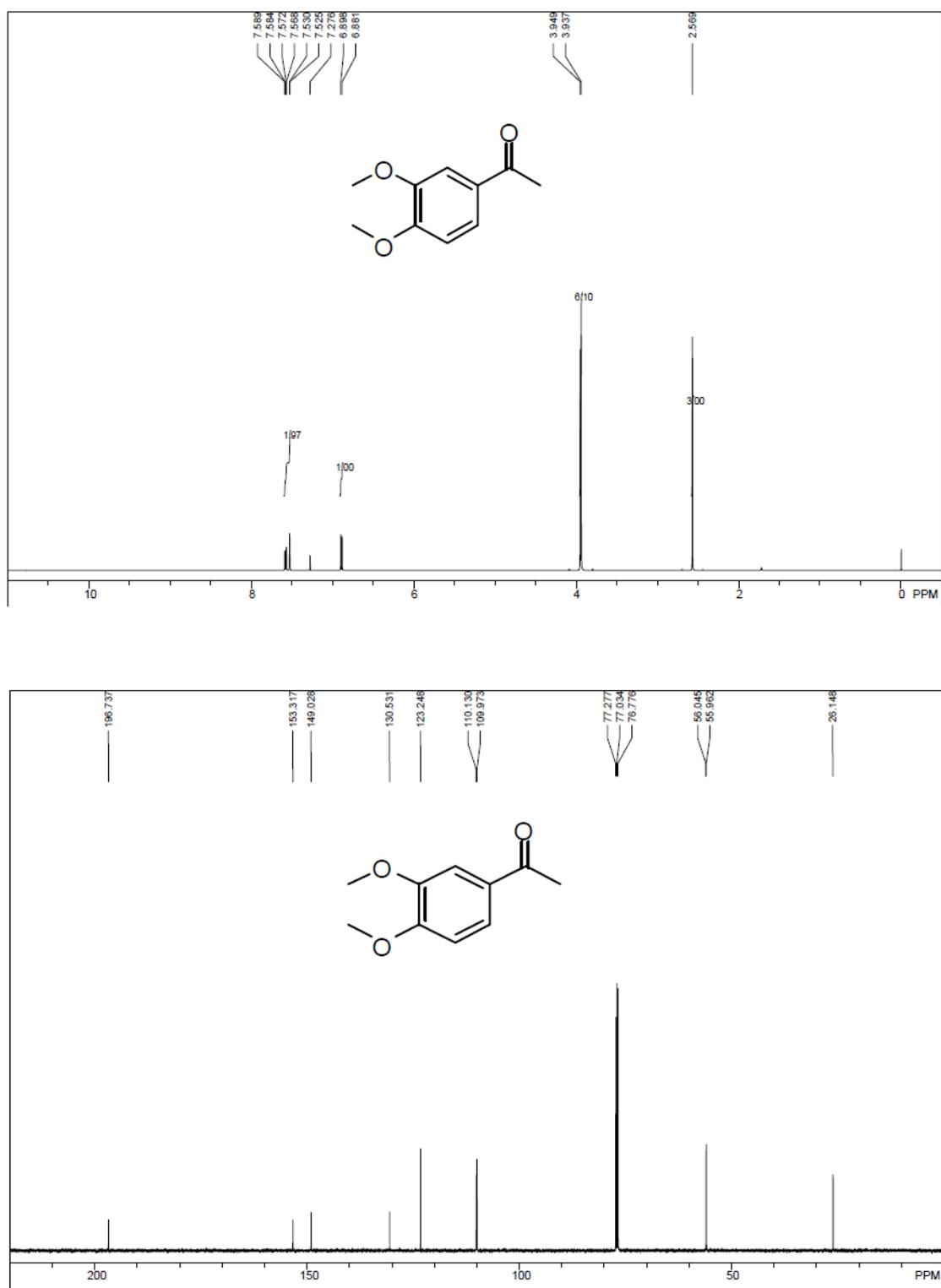


Figure 12.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 3,4,5-Trimethoxyacetophenone

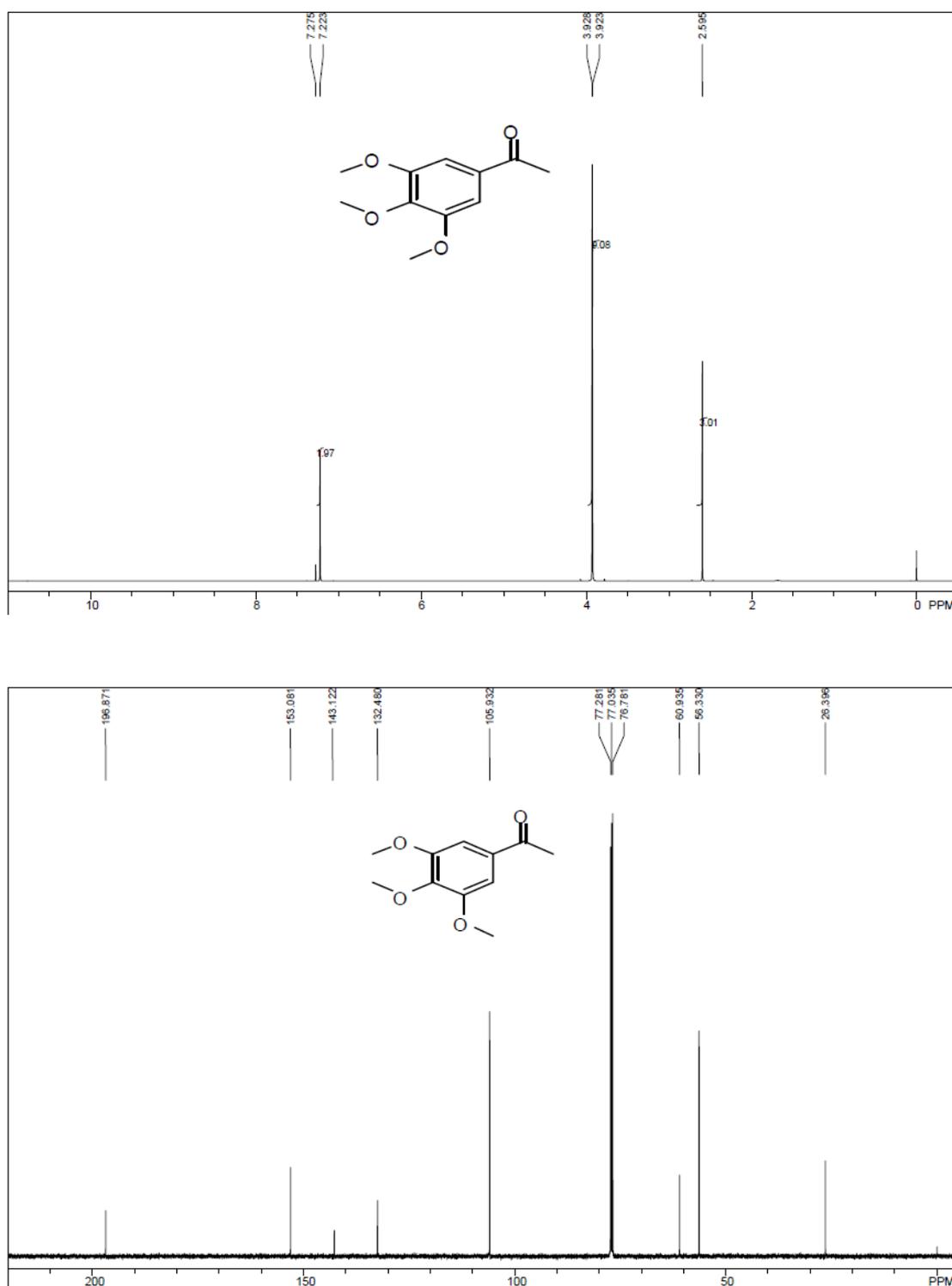


Figure 13.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 4-Acetoxyacetophenone

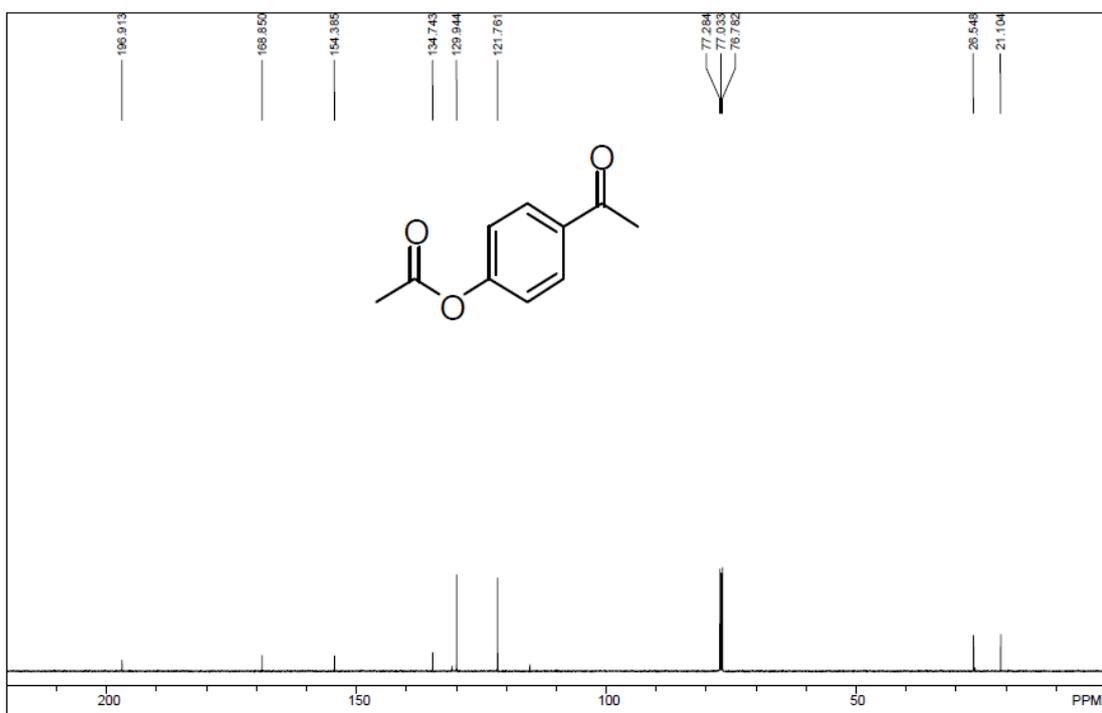
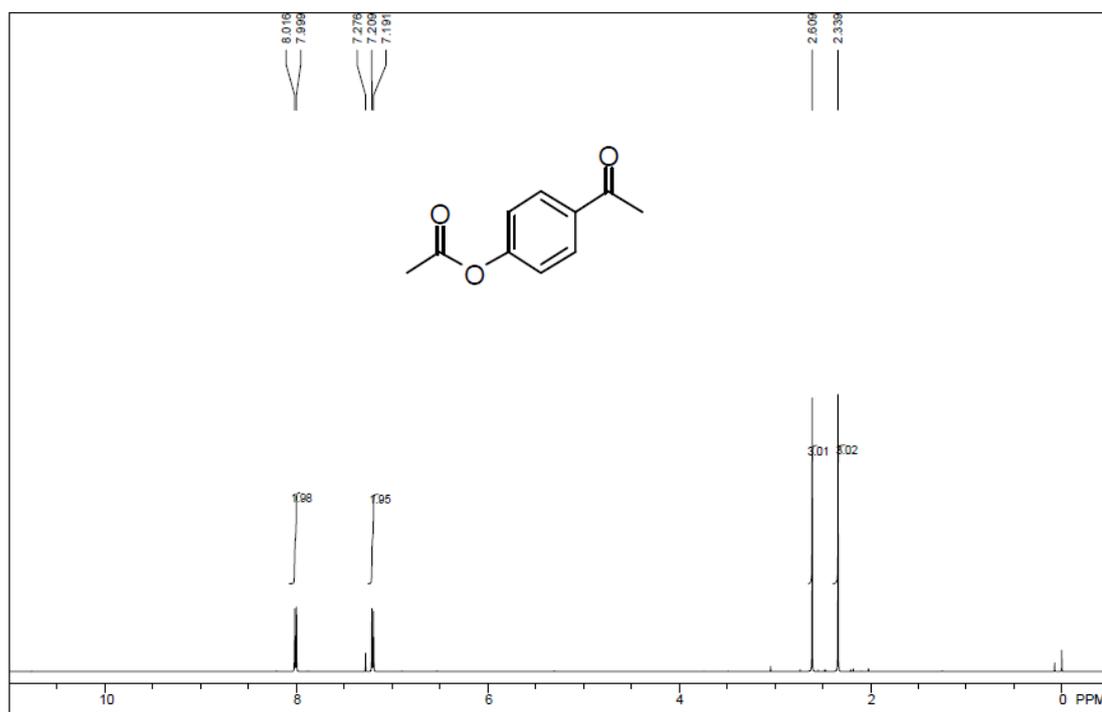


Figure 14.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 2-Chloroacetophenone

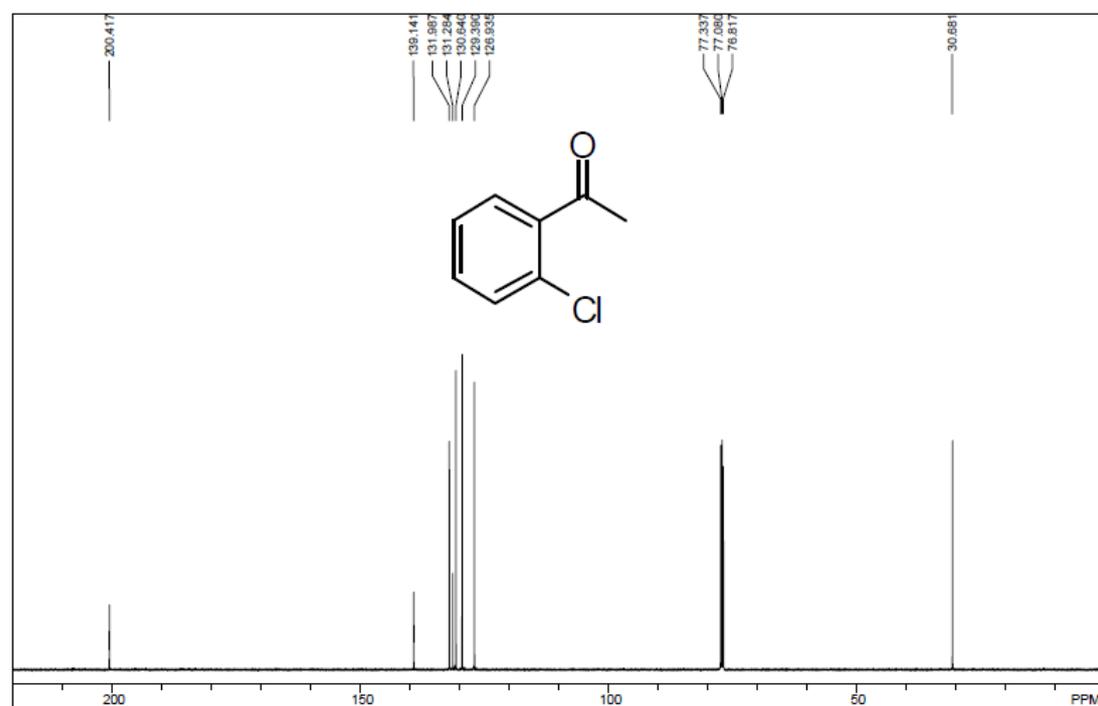
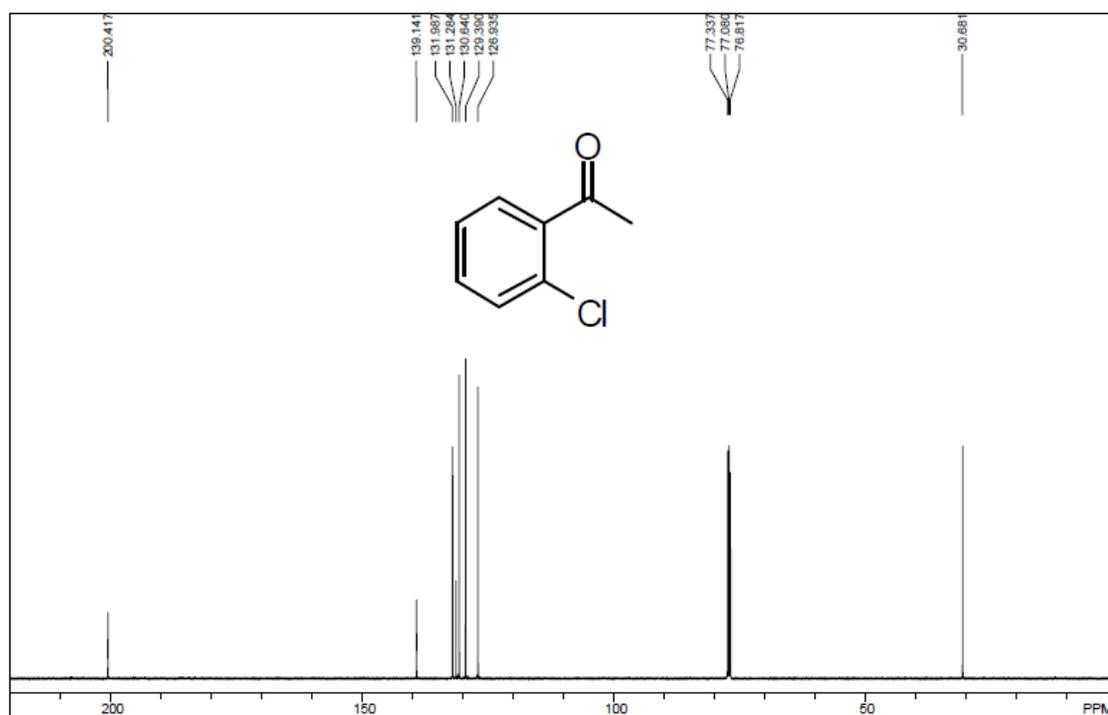


Figure 15.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 2,4-Dichloroacetophenone

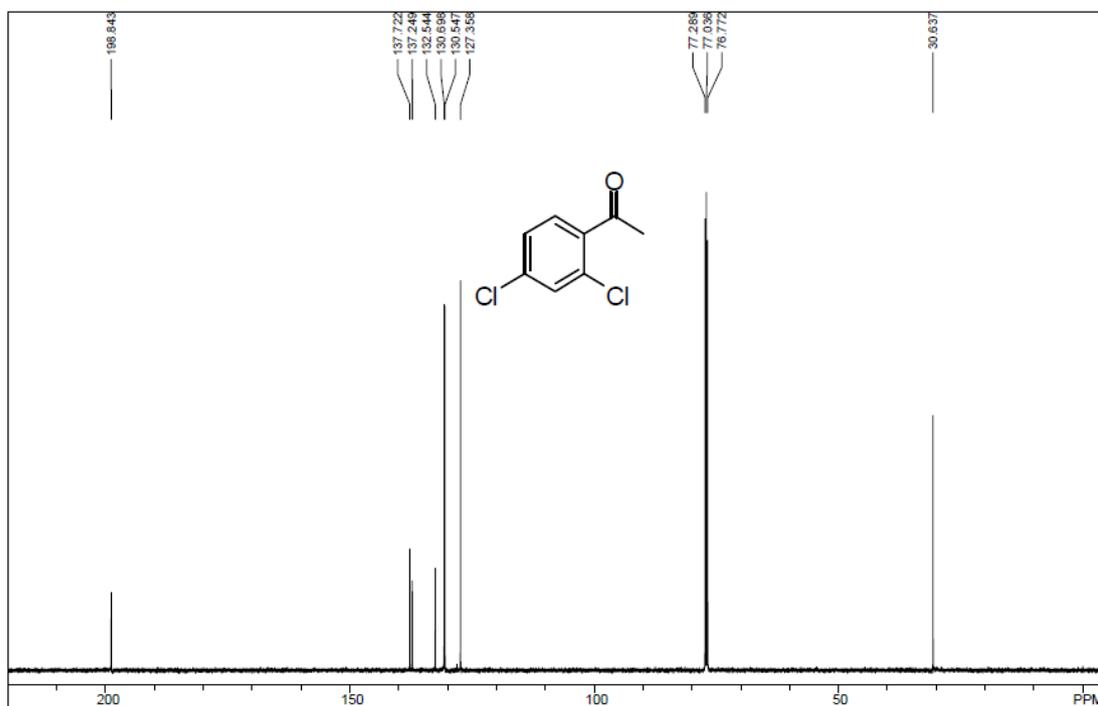
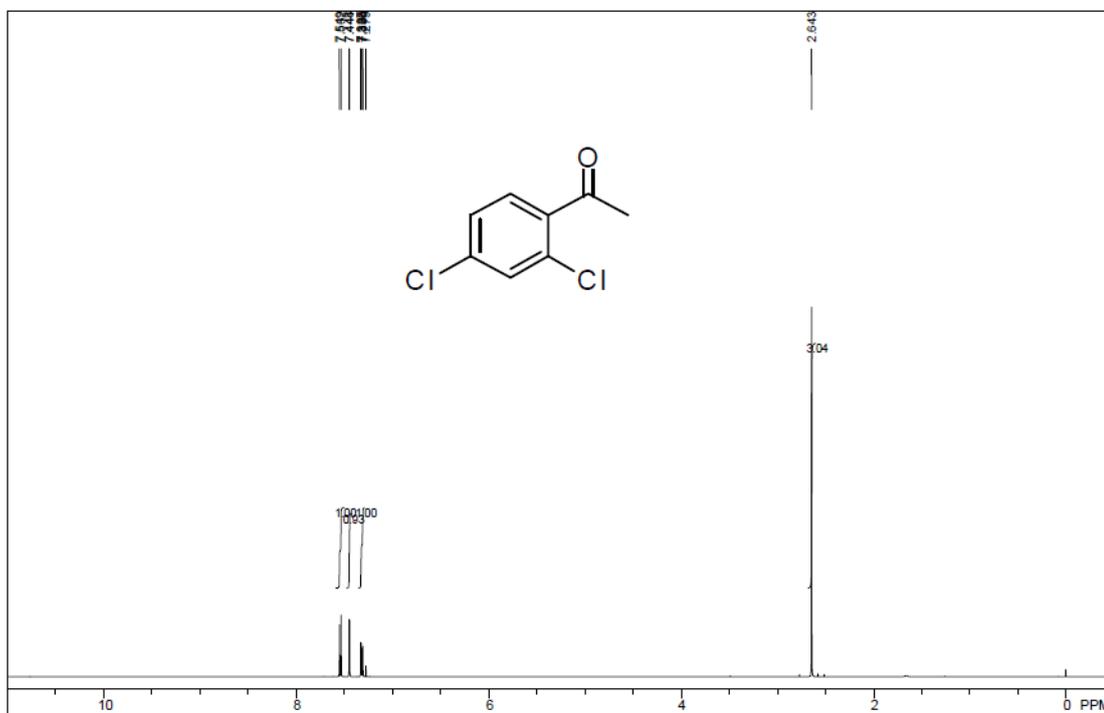


Figure 16.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of 2-Methoxyacetophenone

