[Supporting Information]

In-Situ Generation of Active Species "NO" for the Aerobic Oxidative deprotection of aldoximes Catalyzed by $FeCl_3$/TEMPO

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General Experimental

Reagents were purchased at commercial quality and used without further purification. Oximes were prepared using literature procedures.[1,2] Yields referred to isolated yields purified by column chromatography on silica gel (300-400 mesh) with hexane and ethyl acetate (10:1) to give the corresponding carbonyl compounds. ^{1}H 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 Oximes

A mixture of aldehyde (50.0 mmol), $NH_2OH \cdot HCl$ (74.0 mol, 5.13 g), CH_3COONa (125.0 mmol, 10.26 g), ethyl alcohol (10.0 mL) and water (40.0 mL) were placed in a 100 mL round-bottomed flask with a reflux condenser. Then the mixture was stirred under reflux, the progress was monitored by TLC. After the reaction, the contents were poured into a 250 mL beaker. After cooling, the precipitate was filtered with suction, thoroughly washed with water and dried under vacuum, then recrystallization with ethyl alcohol to obtain a pure solid.

4-Bromobenzaldehyde oxime (white solid, 93% yield)**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46(q, 2H), 7.54(q, 2H), 7.83(s, 1H), 8.11(s, 1H).

4-Nitrobenzaldehyde oxime (light yellow solid, 93% yield)**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76-7.78(q, 2H), 8.22(s, 1H), 8.25-8.28(q, 2H).

4-(Trifluoromethyl)benzaldehyde oxime (white solid, 91% yield)**:** ^{1}H NMR (500 MHz, DMSO-d^6): δ 7.77(d, J = 8.5 Hz, 2H), 7.82(d, J = 8.5 Hz, 2H), 8.26(s, 1H), 11.62(s, 1H).

4-Chlorobenzaldehyde oxime (white solid, 95% yield)**:** ^{1}H NMR (500 MHz, DMSO-d^6): δ 7.45-7.48(m, 2H), 7.60-7.63(q, 2H), 8.16(s, 1H), 11.38(s, 1H).

3-(Trifluoromethyl)benzaldehyde oxime (white solid, 91% yield)**:** ^{1}H NMR (500 MHz, DMSO-d^6): δ 7.58-7.62(q, 1H), 7.68(d, J = 7.5 Hz, 1H),

7.89(d, *J* = 8.0 Hz, 2H), 8.27(s, 1H), 11.55(s, 1H).

3-Nitrobenzaldehyde oxime (light yellow solid, 93% yield)**:** ^{1}H NMR (500 MHz, DMSO-d^6): δ 7.71(t, *J* = 8.2 Hz, 1H), 8.05-8.06(m, 1H), 8.21-8.24(m, 1H), 8.34 (s, 1H), 8.42(s, 1H), 11.66(s, 1H).

2-Chlorobenzaldehyde oxime (white solid, 90% yield)**:** ^{1}H NMR (500 MHz, DMSO-d^6): δ 7.42-7.44(q, 2H), 7.56-7.58(m, 1H), 7.63(s, 1H), 8.15(s, 1H), 11.44(s, 1H).

2-Nitrobenzaldehyde oxime (light yellow solid, 93% yield)**:** ^{1}H NMR (500 MHz, DMSO-d^6): δ 7.64-7.67(m, 1H), 7.75-7.79(m, 1H), 7.88-7.90(m, 1H), 8.03-8.05(m, 1H), 8.41(s, 1H), 11.78(s, 1H).

2-Bromobenzaldehyde oxime (white solid, 91% yield)**:** ^{1}H NMR (500 MHz, DMSO-d^6): δ 7.33-7.36(m, 1H), 7.42(t, *J* = 7.5 Hz, 1H), 7.68(d, *J* = 7.5 Hz, 1H), 7.79-7.81(q, 1H), 8.32(s, 1H), 11.70(s, 1H).

2,4-Dichlorobenzaldehyde oxime (white solid, 95% yield)**:** ^{1}H NMR (500 MHz, DMSO-d^6): δ 7.46-7.48(q, 1H), 7.70(s, 1H), 7.82(d, *J* = 8.5 Hz, 1H), 8.32(s, 1H), 11.81(s, 1H).

2-Chloro-6-fluoro-benzaldehyde oxime (white solid, 92% yield): ^{1}H NMR (500 MHz, DMSO-d^6): δ 7.31-7.34(m, 1H), 7.41(*J* = 8.0 Hz, 1H), 7.44-7.49(m, 1H), 8.24(s, 1H), 11.87(s, 1H).

4-*iso*-Propylbenzaldehyde oxime (white solid, 89% yield)**:** ^{1}H NMR (500 MHz, DMSO-d^6): δ 1.20-1.22(q, 6H), 2.87-2.92(m, 1H), 7.27(d, *J* = 8.2 Hz, 2H), 7.51(d, *J* = 8.2 Hz, 2H), 8.10(s, 1H), 11.11(s, 1H)

4-*tert*-Butylbenzaldehyde oxime (white solid, 92% yield)**:** ^{1}H NMR (500 MHz, DMSO-d^6): δ 1.29(s, 9H), 7.42-7.43(q, 2H), 7.51-7.53(q, 2H), 8.10(s, 1H), 11.12(s, 1H).

4-Methylbenzaldehyde oxime (white solid, 92% yield)**:** ^{1}H NMR (500 MHz, DMSO-d^6): δ 2.32(s, 3H), 7.21(d, *J* = 8.0 Hz, 1H), 7.48(d, *J* = 8.0 Hz, 1H), 8.09(s, 1H), 11.10(s, 1H).

3,4-Dimethylbenzaldehyde oxime (white solid, 93% yield)**:** ^{1}H NMR (500 MHz, DMSO-d^6): δ 2.23(s, 6H), 7.16(d, *J* =7.8 Hz, 1H), 7.30(t, *J* =4.6 Hz, 1H), 7.36(s, 1H), 8.05(s, 1H), 11.06(s, 1H).

4-Chloroacetophenone oxime (white solid, 93% yield)**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.29(s, 3H), 7.37(d, *J* = 10.0 Hz, 2H), 7.58(d, *J* = 10.0 Hz, 2H), 8.30 (s, 1H).

Acetophenone oxime (white solid, 94% yield)**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.33(s, 3H), 7.40-7.41(q, 3H), 7.64-7.66(q, 2H), 8.83 (s, 1H).

References

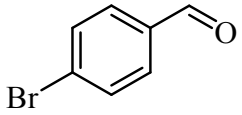
(1) A. Lachman, C. R. Noller, *Org. Synth.* **1943**, *2*, 70.

(2) J. S. Buck, W. S. Ide, J. R. Johnson, E. Amstutz, *Org. Synth.* **1943***, 2,* 622.

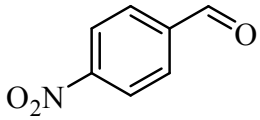
General Experimental Procedure for Deoximation to the Corresponding Carbonyl Compounds

Oxime (1.0 mmol), TEMPO (0.1 mmol, 0.0156 g), $FeCl_3$ (0.1 mmol, 0.0162 g) were introduced into a 50 ml round bottom flask equipped with a magnetic stirrer and the flask was purged several times with oxygen (balloon filled), and the system was immediately sealed. Then the solvent ($PhCH_3/H_2O$ 3/1, 4.0 mL) was injected into the flask and the reaction mixture was stirred at 60 ^oC for several hours. After the reaction, the mixture was cooled to room temperature and extracted with CH_2Cl_2. The combined organic phase was washed with aqueous $Na_2S_2O_3$ to remove the residual oxidants. The organic layer was dried over anhydrous Na_2SO_4 and then the solvent was removed under reduced pressure. The residue was further purified by column chromatography on silica gel (300-400 mesh) with hexane and ethyl acetate (10:1) to give the corresponding carbonyl compounds.

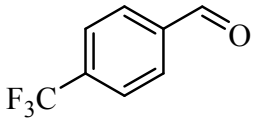
Characterization Data for Products



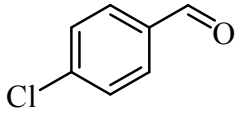
4-Bromobenzaldehyde (Table 2, entry 1): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70-7.71(q, 2H), 7.75-7.80(m, 2H), 10.00(s, 1H).



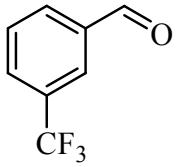
4-Nitrobenzaldehyde (Table 2, entry 2): ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08-8.10(q, 2H), 8.41(d, J = 8.5 Hz, 2H), 10.18(s, 1H).



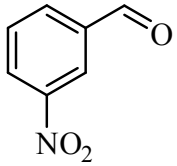
4-(Trifluoromethyl)benzaldehyde (Table 2, entry 3): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82(d, J = 8.0 Hz, 2H), 8.02(d, J = 7.5 Hz, 2H), 10.12(s, 1H).



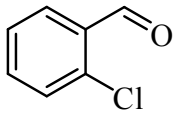
4-Chlorobenzaldehyde (Table 2, entry 4): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53-7.55(m, 2H), 7.83-7.86(m, 2H), 10.00(s, 1H).



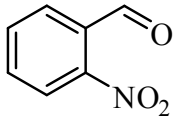
3-(Trifluoromethyl)benzaldehyde (Table 2, entry 5): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70(t, J = 8.0 Hz, 1H), 7.90(d, J = 8.0 Hz, 1H), 8.09(d, J = 8.0 Hz, 1H), 8.15(s, 1H), 10.90(s, 1H).



3-Nitrobenzaldehyde (Table 2, entry 6): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78(t, J = 7.8 Hz, 1H), 8.24-8.26(q, 1H), 8.50-8.53(m, 1H), 8.74(s, 1H), 10.15(s, 1H).

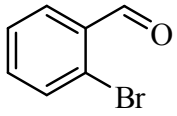


2-Chlorobenzaldehyde (Table 2, entry 7): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50(t, J = 8.0 Hz, 1H), 7.60-7.62(m, 1H), 7.77-7.79(m, 1H), 7.87(s, 1H), 10.00(s, 1H).

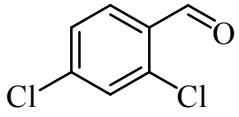


2-Nitrobenzaldehyde (Table 2, entry 8): ^{1}H NMR (500 MHz, $CDCl_3$): δ

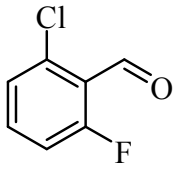
7.76-7.83(m, 2H), 7.97-7.99(q, 1H), 8.13-8.15(q, 1H), 10.46(s, 1H).



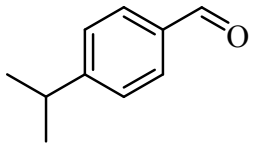
2-Bromobenzaldehyde (Table 2, entry 9): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.46(m, 2H), 7.65-7.67(m, 1H), 7.91-7.93(m, 1H), 10.37(s, 1H).



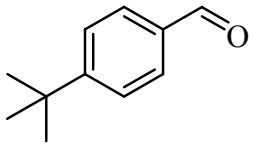
2,4-Dichlorobenzaldehyde (Table 2, entry 10): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.40(m, 1H), 7.50(s, 1H), 7.89(d, J = 8.5 Hz, 1H), 10.42(s, 1H).



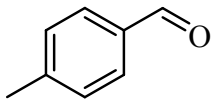
2-Chloro-6-fluoro-benzaldehyde (Table 2, entry 11): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10-7.14(t, J = 9.0 Hz, 1H), 7.30(d, J = 7.5 Hz, 1H), 7.48-7.52(m, 1H), 10.48(s, 1H).



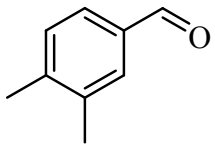
4-*iso*-Propylbenzaldehyde (Table 2, entry 12): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.30(d, J = 7.0 Hz, 6H), 2.98-3.03(m, 1H), 7.40(d, J = 8.5 Hz, 2H), 7.83(d, J = 8.5 Hz, 2H), 10.00(s, 1H).



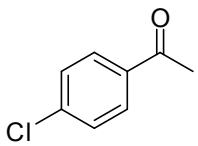
4-*tert*-Butylbenzaldehyde (Table 2, entry 13): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37(s, 9H), 7.57(d, J = 8.5 Hz, 2H), 7.84(d, J = 8.0 Hz, 2H), 10.00(s, 1H).



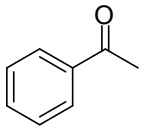
4-Methylbenzaldehyde (Table 2, entry 14): ^{1}H NMR (500 MHz, $CDCl_3$): δ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.45(s, 3H), 7.34(d, J = 8.0 Hz, 2H), 7.78(d, J = 8.0 Hz, 2H), 9.97(s, 1H).



3,4-Dimethylbenzaldehyde (Table 2, entry 15): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.35(s, 3H), 2.36(s, 3H), 7.30(d, J = 8.0 Hz, 1H), 7.63(d, J = 7.5 Hz, 1H), 7.66(s, 1H), 9.96(s, 1H).



4-Chloroacetophenone (Table 2, entry 16): liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.61(s, 3H), 7.45(d, J = 10.0 Hz, 2H), 7.91(d, J = 10.0 Hz, 2H).



Acetophenone (Table 2, entry 17): liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.62(s, 3H), 7.47(t, *J* = 7.5 Hz, 2H), 7.58(t, *J* = 7.5 Hz, 1H), 7.97(t, *J* = 5.0 Hz, 2H).

Figure 1. ^{1}HNMR spectra of **4-Bromobenzaldehyde** (Table 2, entry 1).

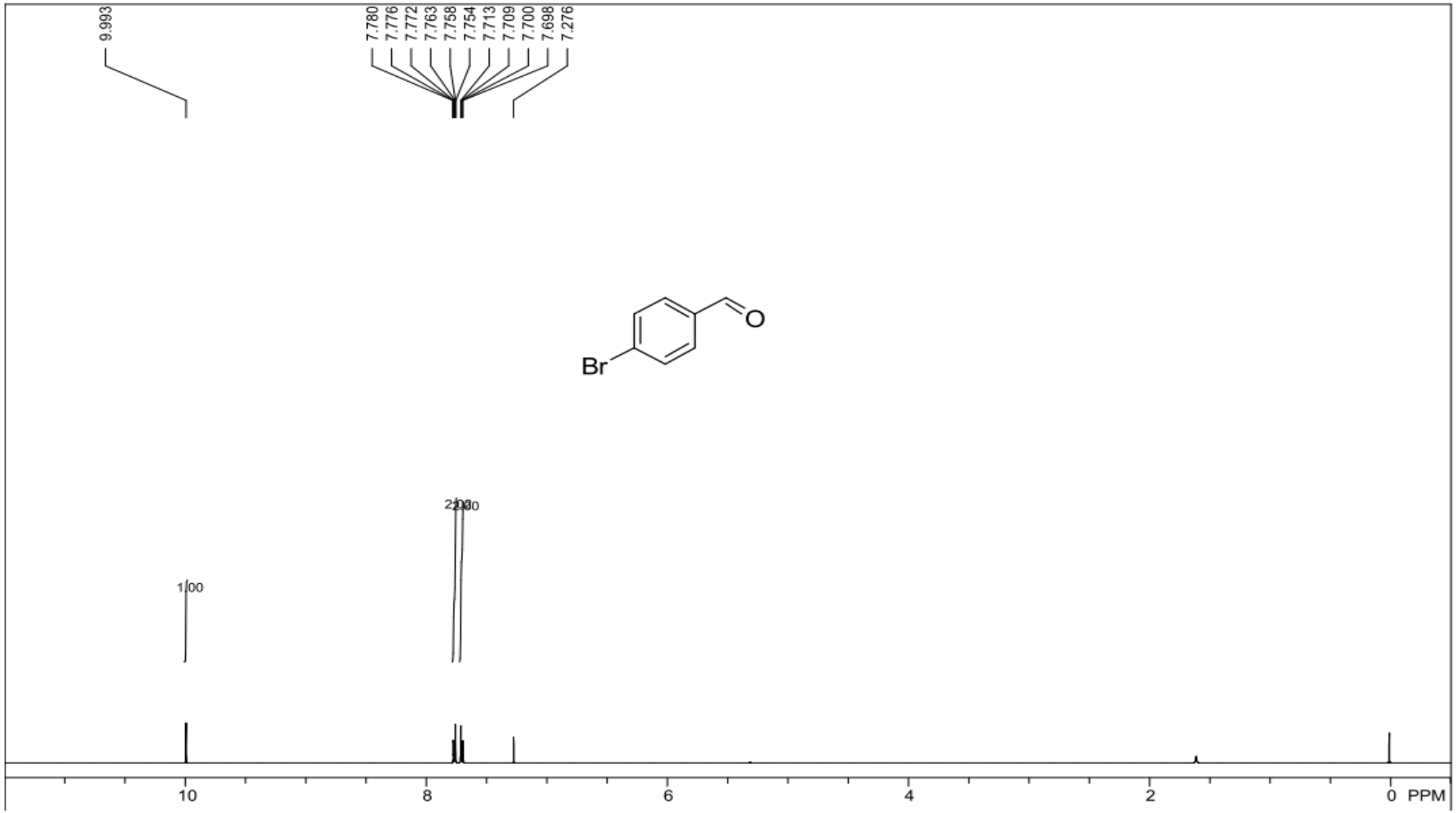


Figure 2. ^{1}HNMR spectra of **4-Nitrobenzaldehyde (**Table 2, entry 2).

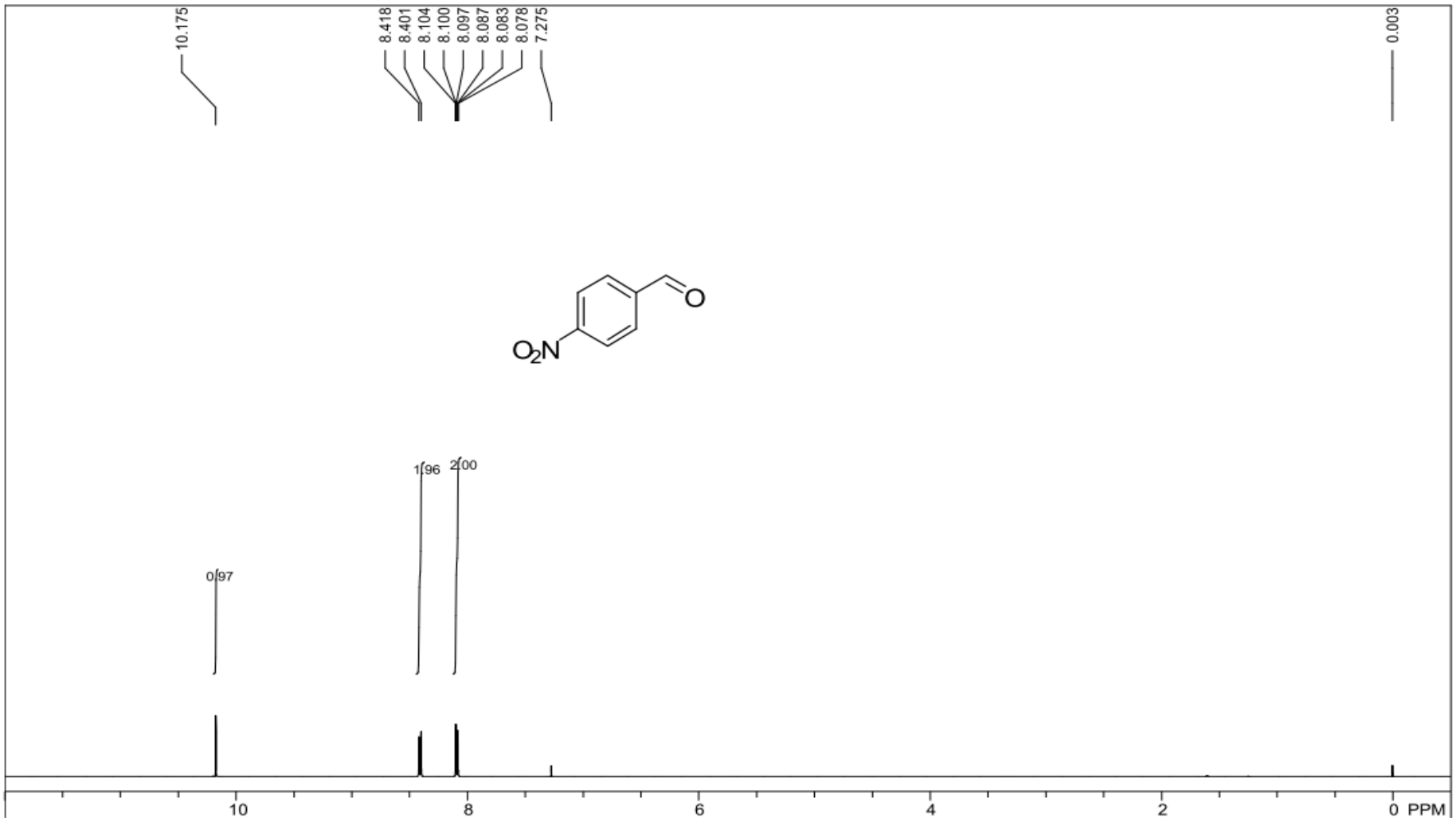


Figure 3. ^{1}HNMR spectra of **4-(Trifluoromethyl)benzaldehyde** (Table 2, entry 3).

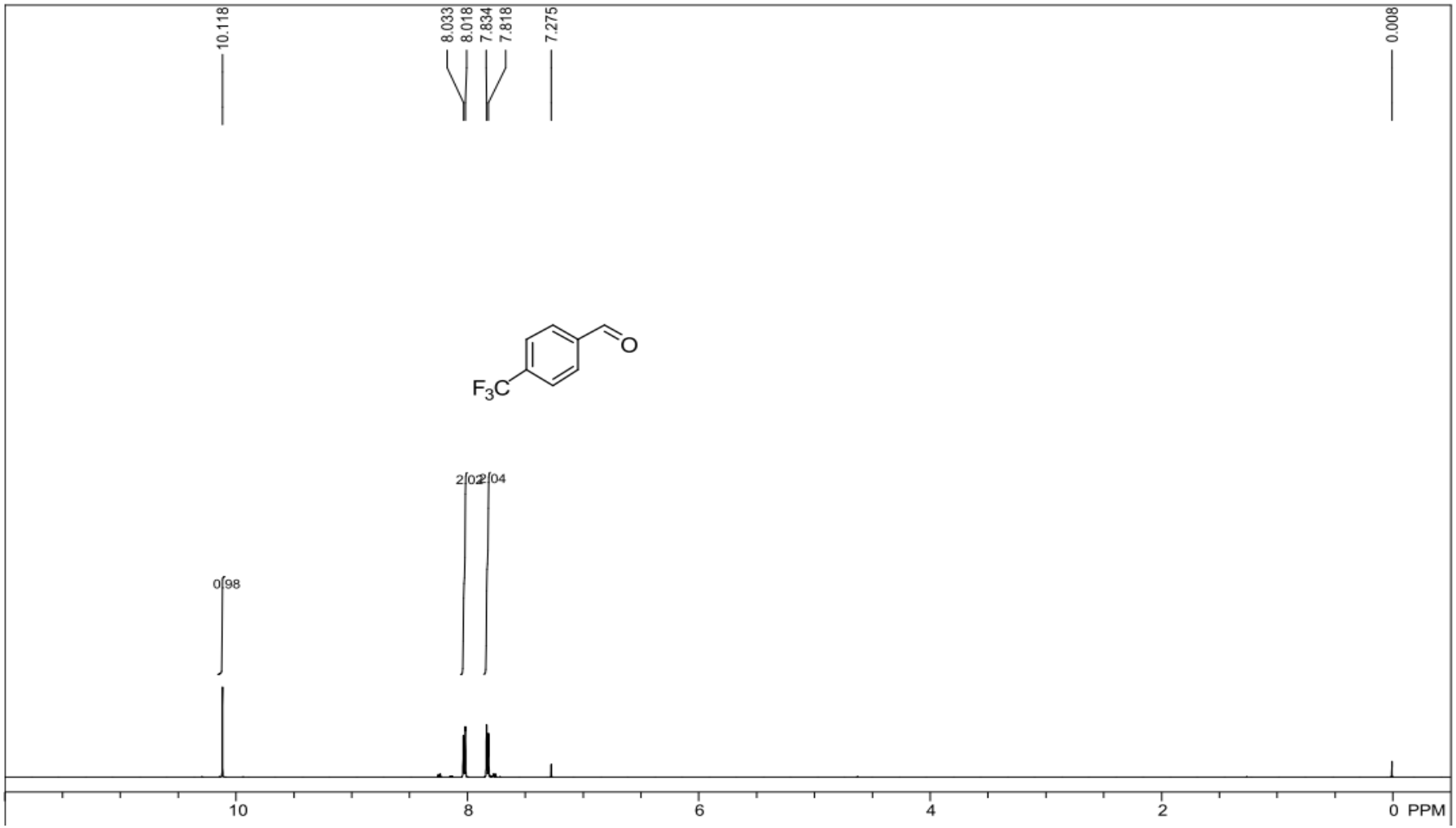


Figure 4. ^{1}HNMR of **4-Chlorobenzaldehyde** (Table 2, entry 4).

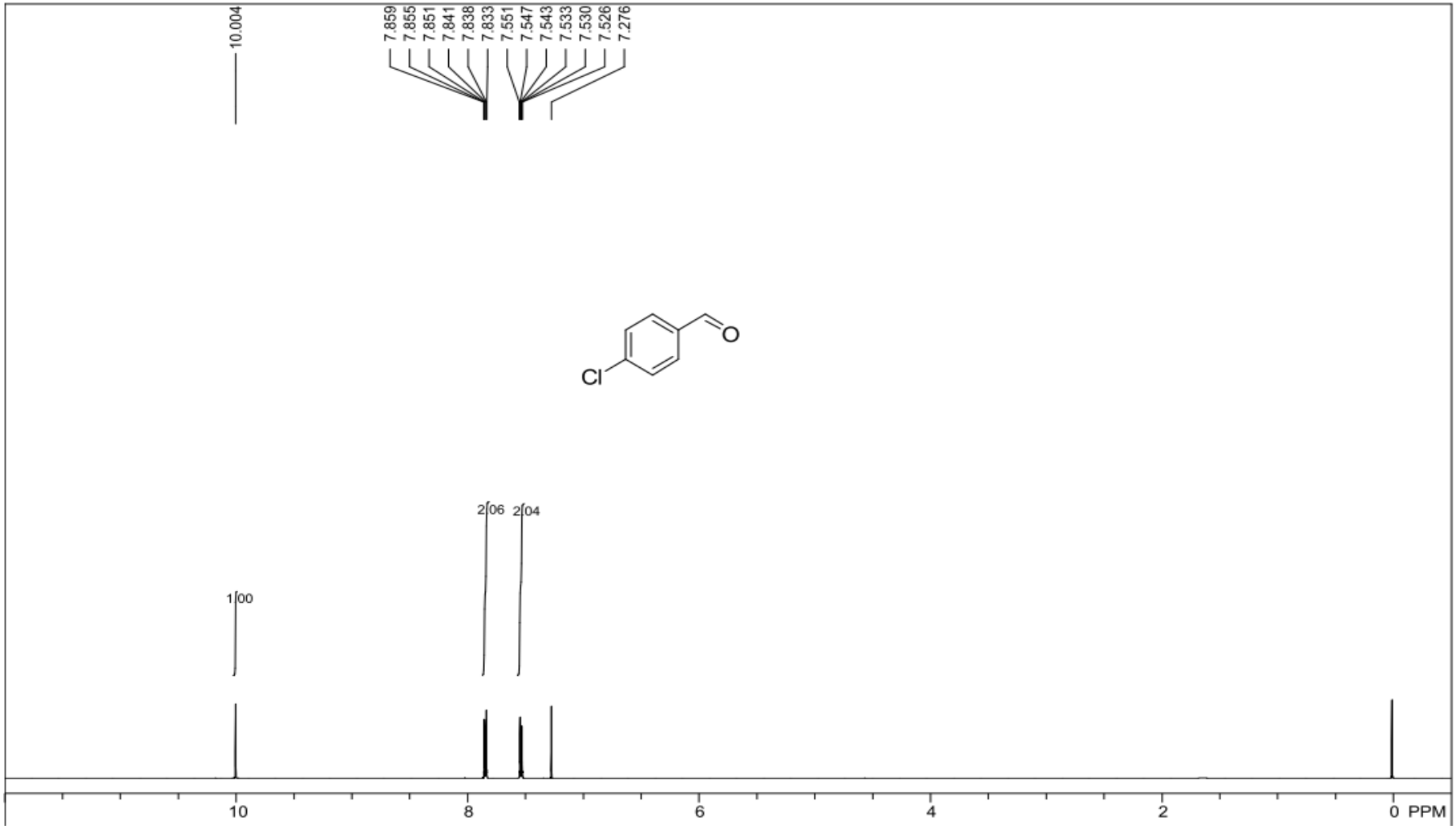


Figure 5. ^{1}HNMR spectra of **3-(Trifluoromethyl)benzaldehyde** (Table 2, entry 5).

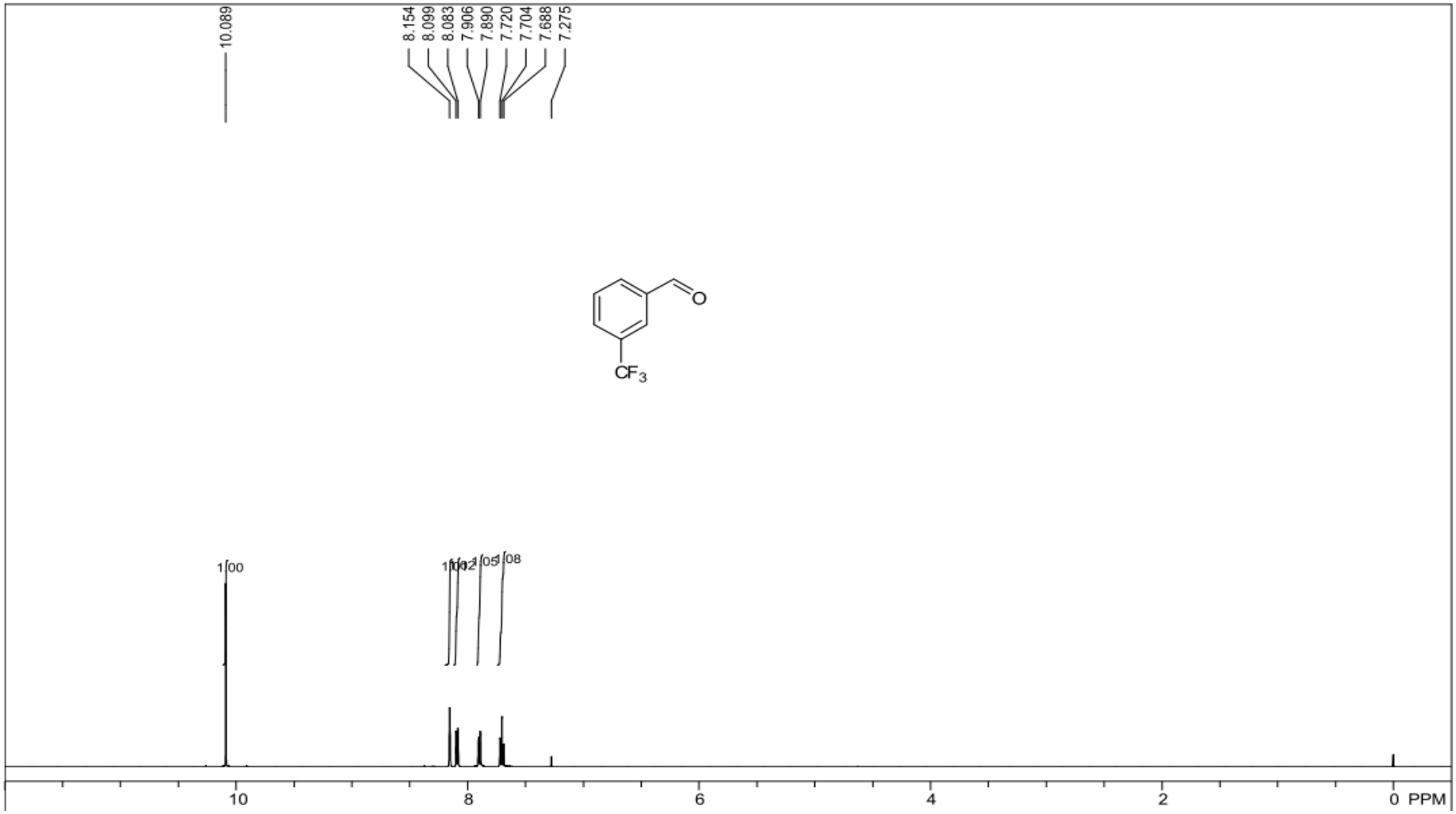


Figure 6. ^{1}HNMR spectra of **3-Nitrobenzaldehyde** (Table 2, entry 6).

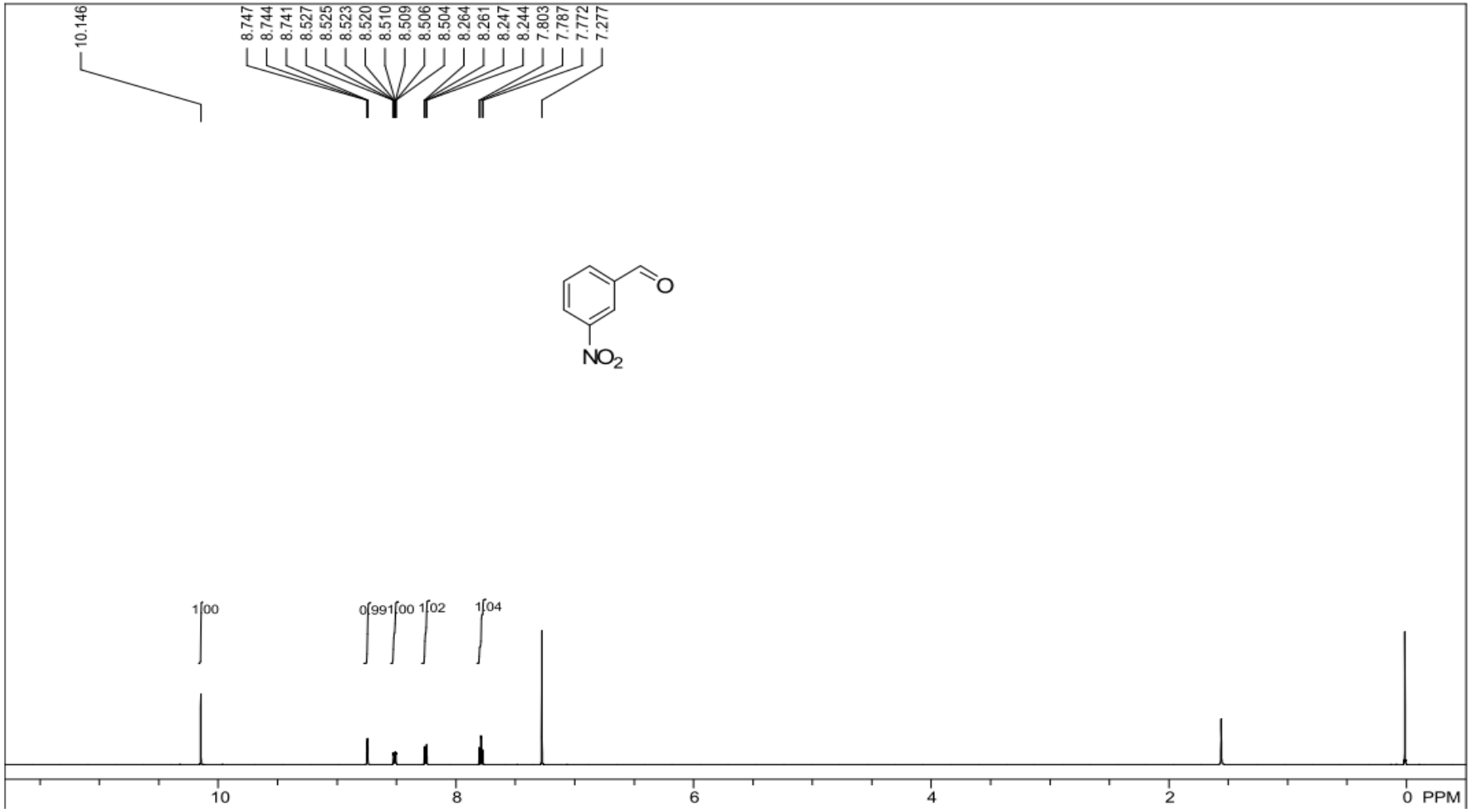


Figure 7. ^{1}HNMR spectra of **2-Chlorobenzaldehyde** (Table 2, entry 7).

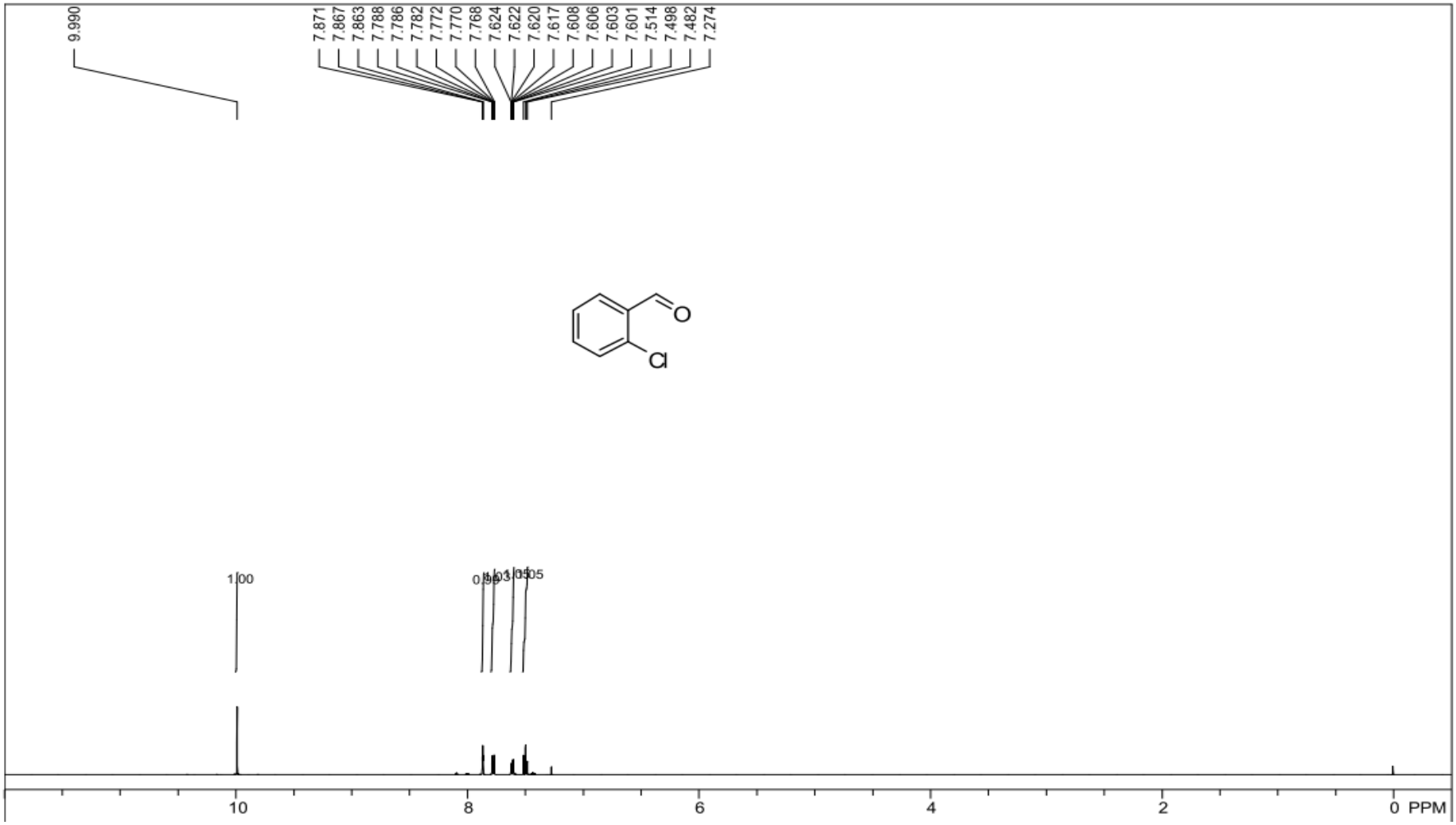


Figure 8. ^{1}HNMR of **2-Nitrobenzaldehyde** (Table 2, entry 8).

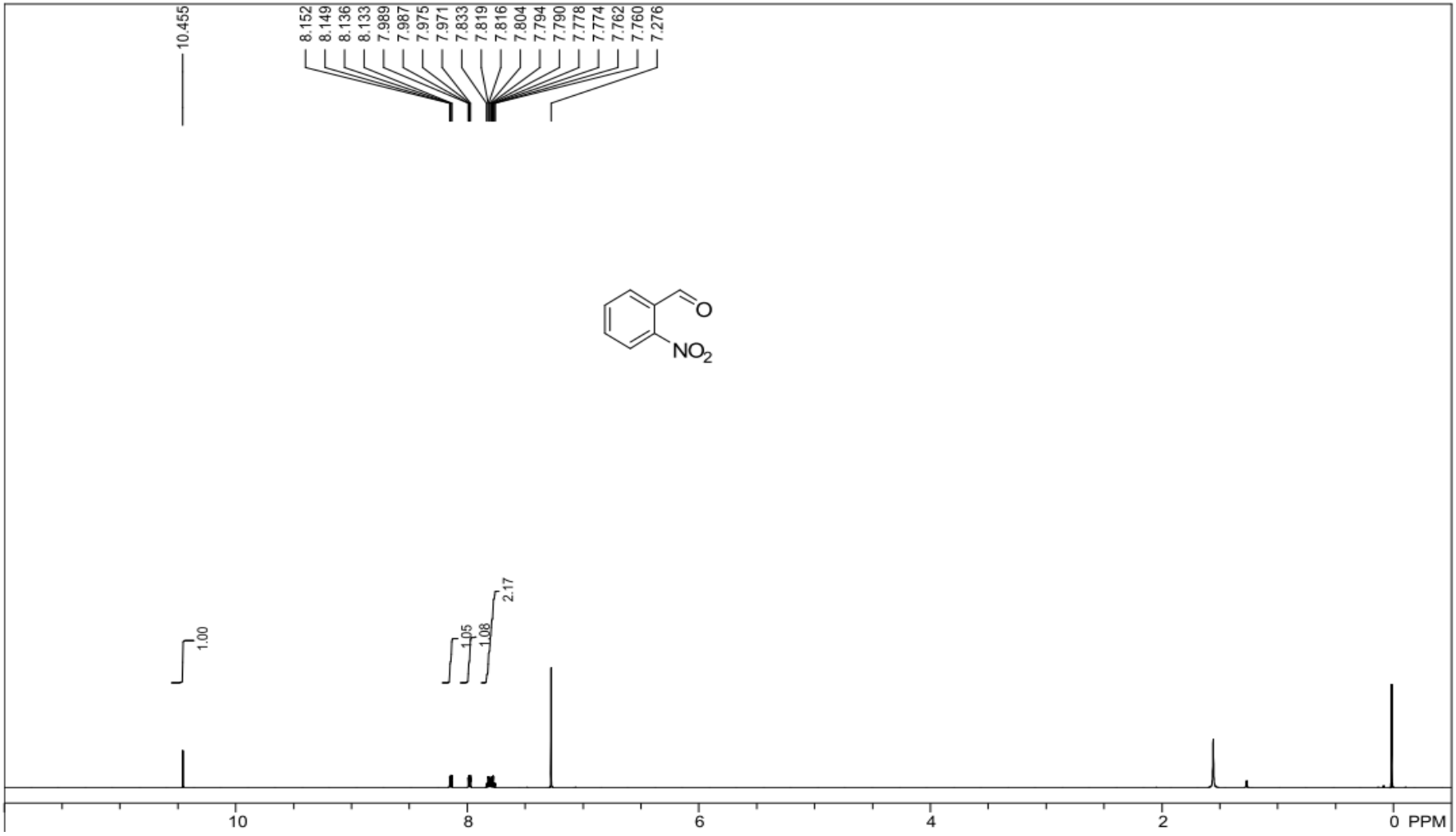


Figure 9. ^{1}HNMR spectra of **2-Bromobenzaldehyde** (Table 2, entry 9).

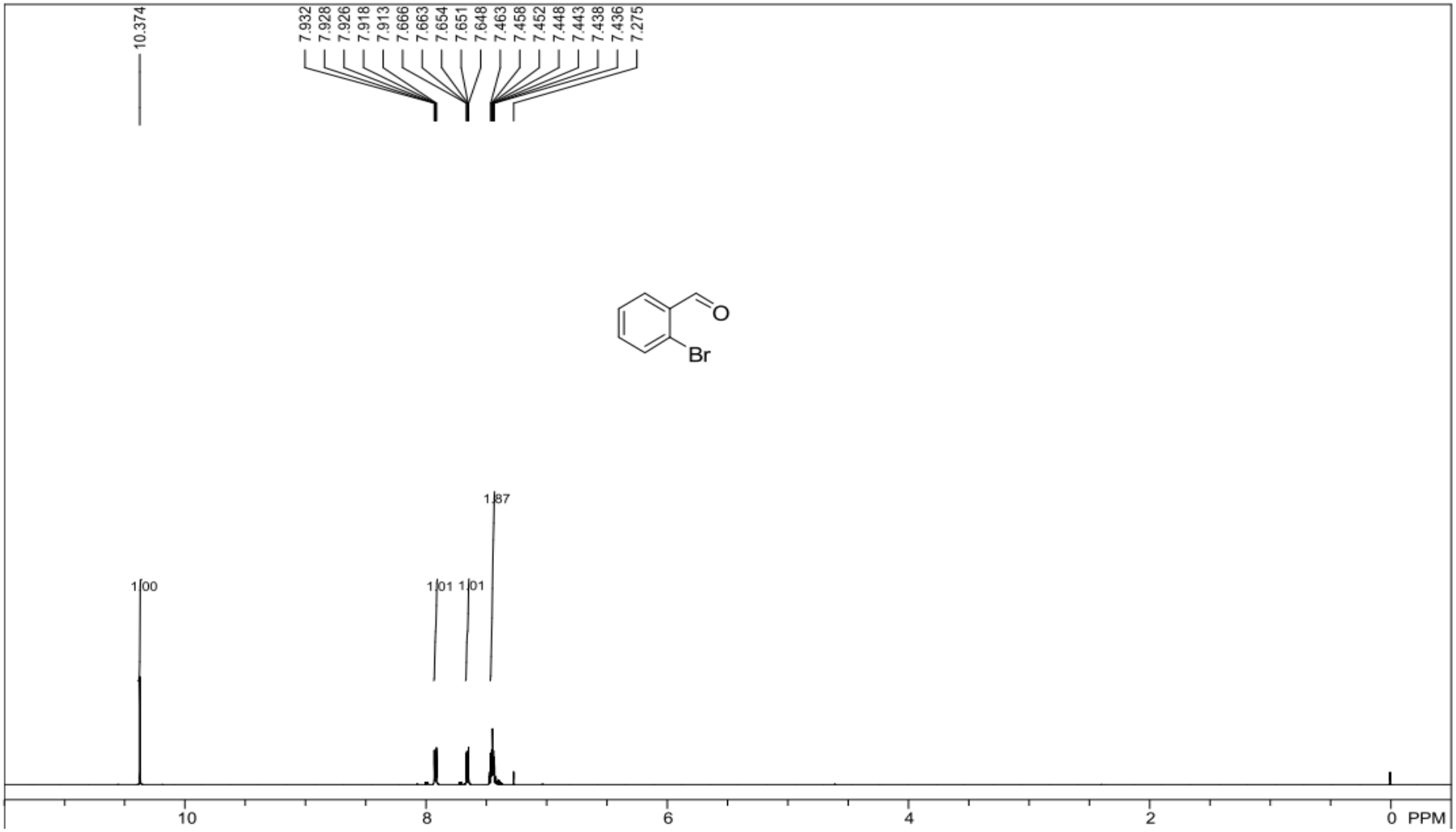


Figure 10. ^{1}HNMR spectra of **2,4-Dichlorobenzaldehyde** (Table 2, entry 10).

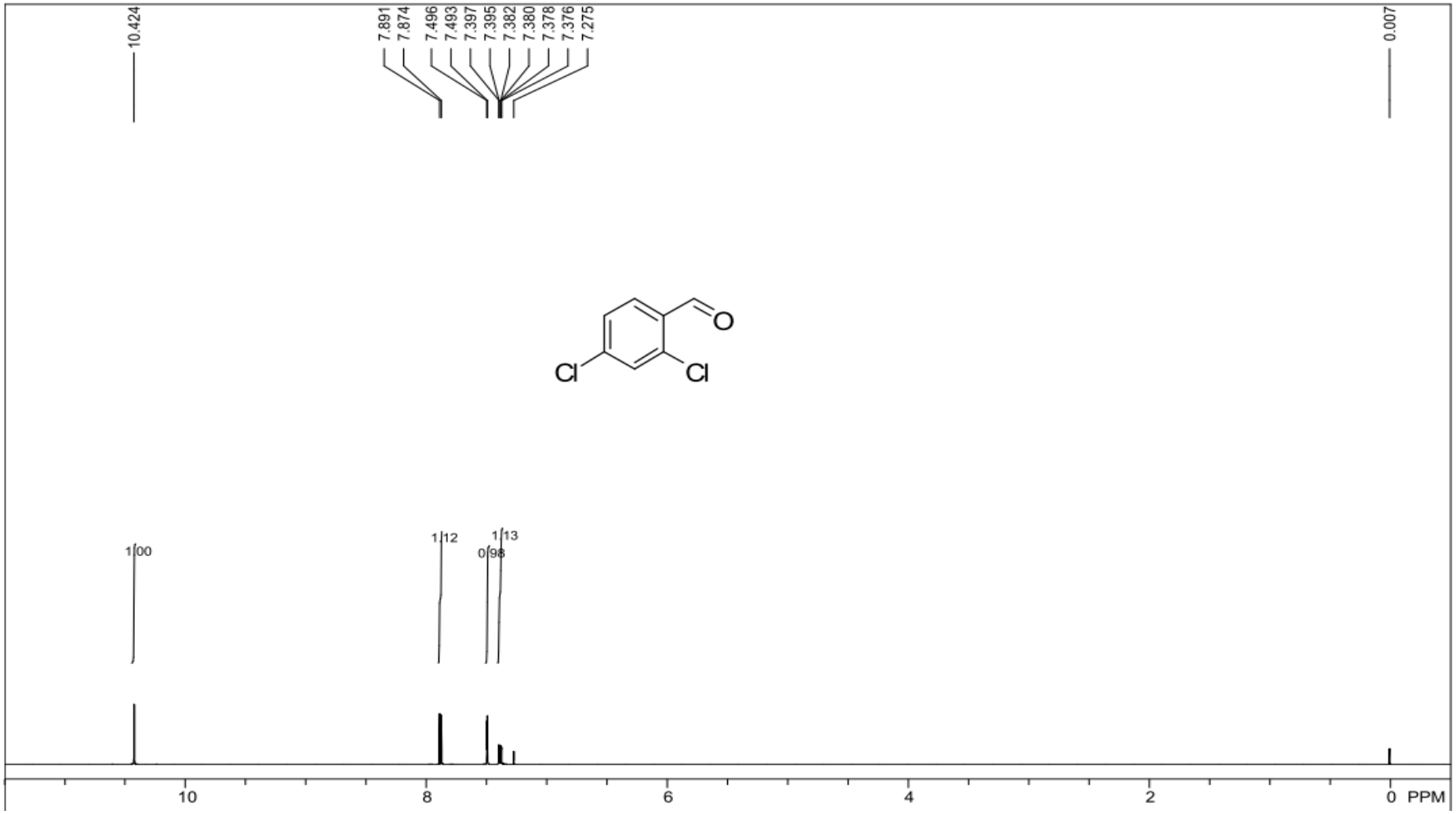


Figure 11. ^{1}HNMR spectra of **2-Chloro-6-fluoro-benzaldehyde** (Table 2, entry 11).

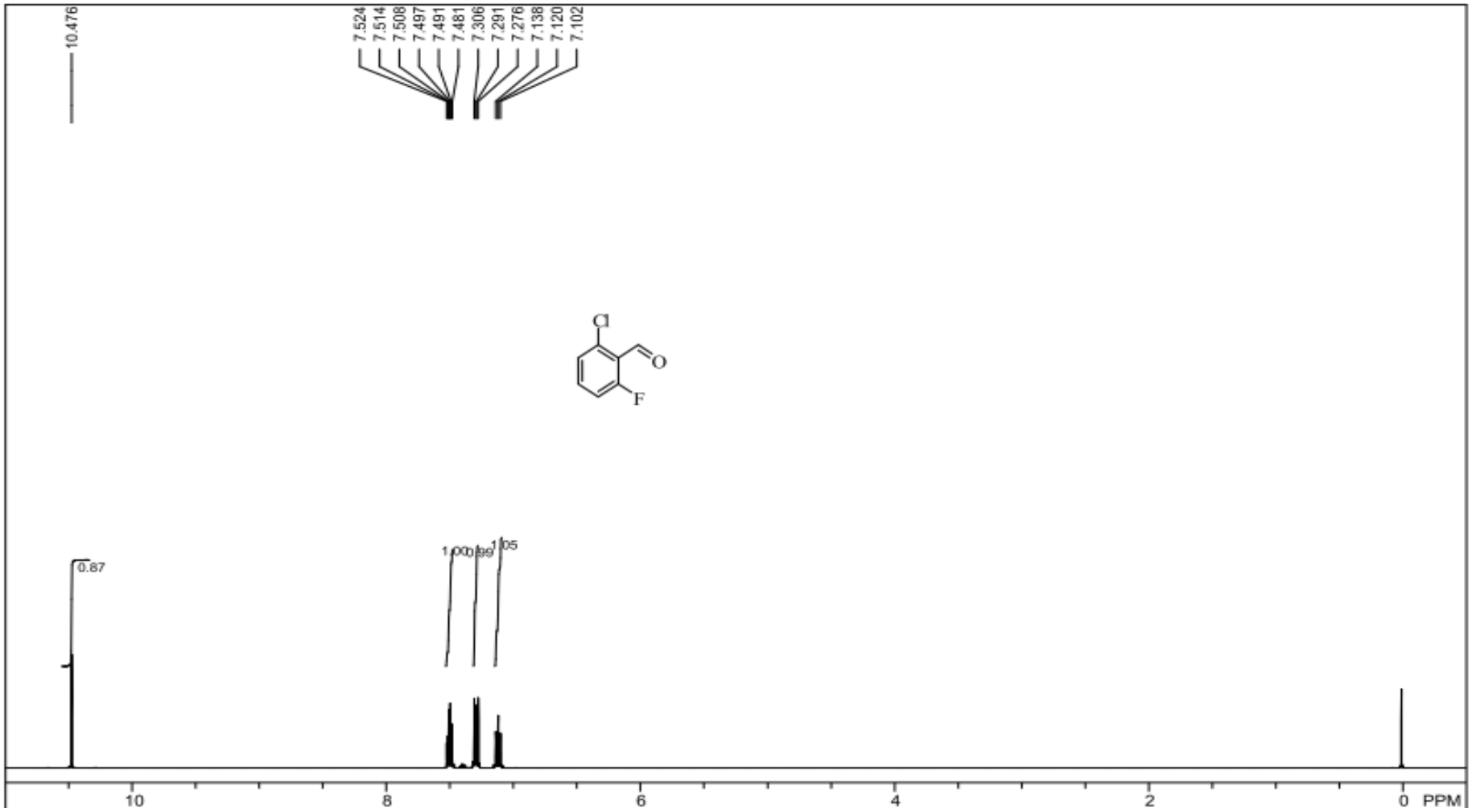


Figure 12. ^{1}HNMR spectra of **4-*iso*-Propylbenzaldehyde** (Table 2, entry 12).

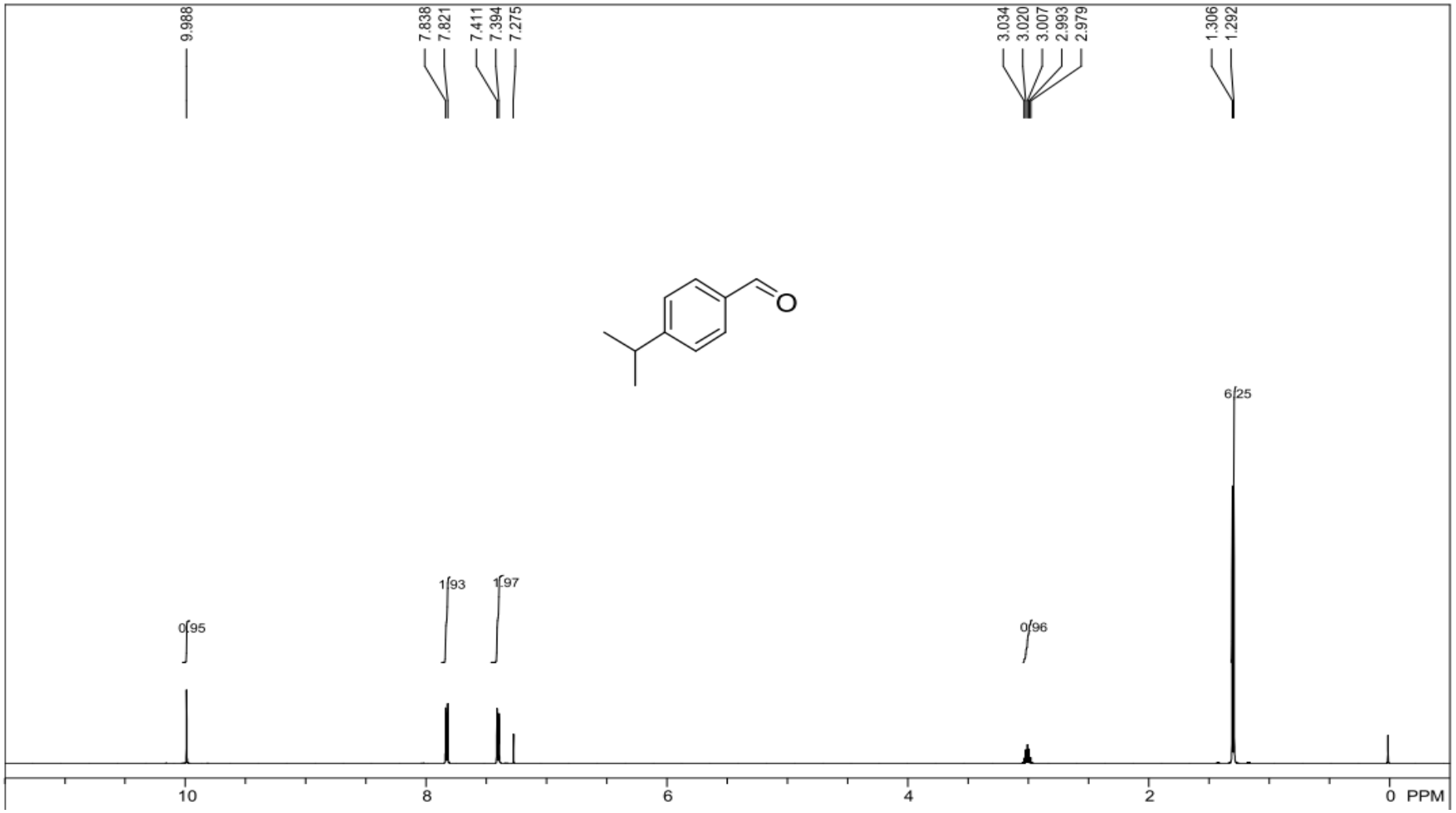


Figure 13. ^{1}HNMR spectra of **4-*tert*-Butylbenzaldehyde** (Table 2, entry 13).

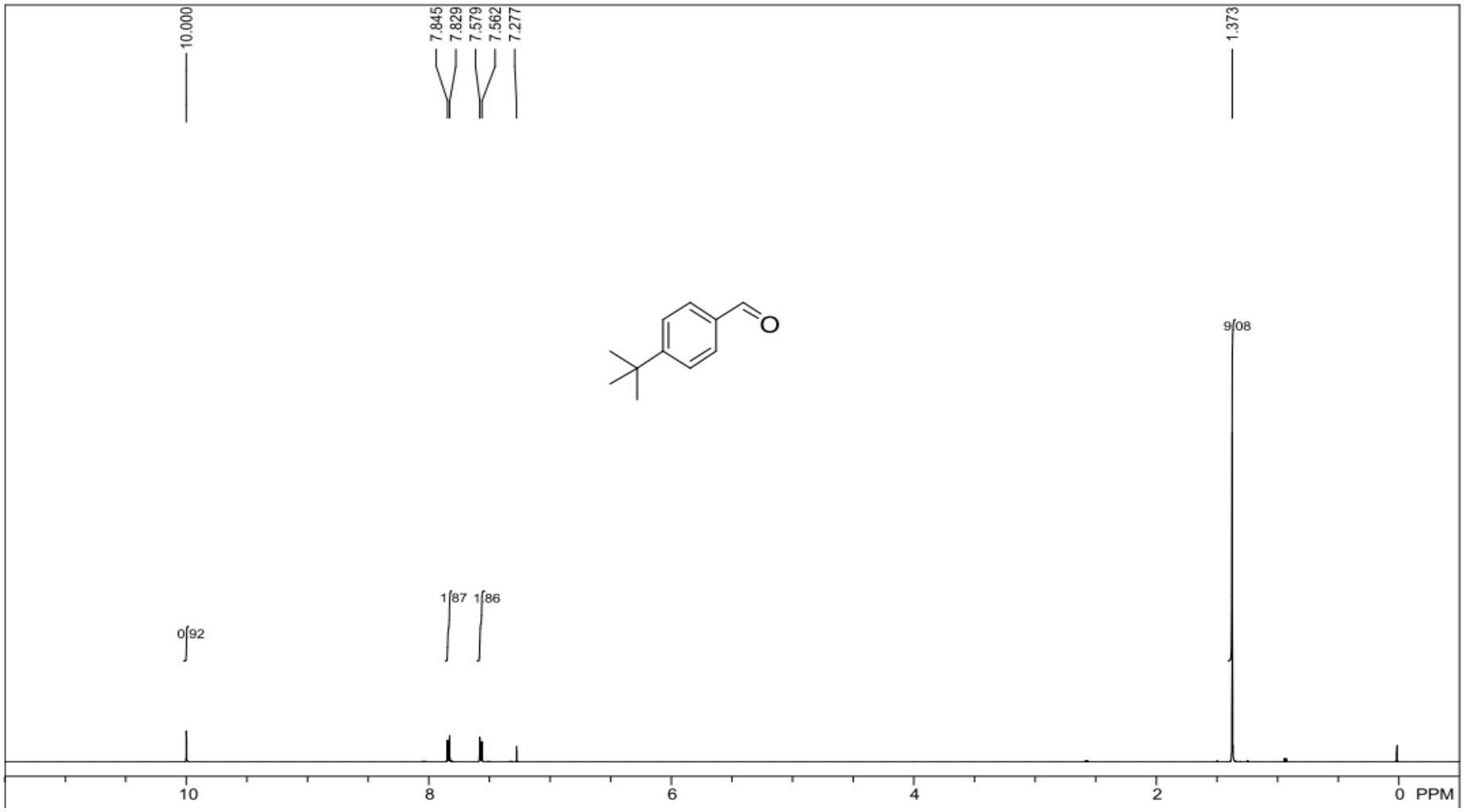


Figure 14. ^{1}HNMR spectra of **4-Methylbenzaldehyde** (Table 2, entry 14).

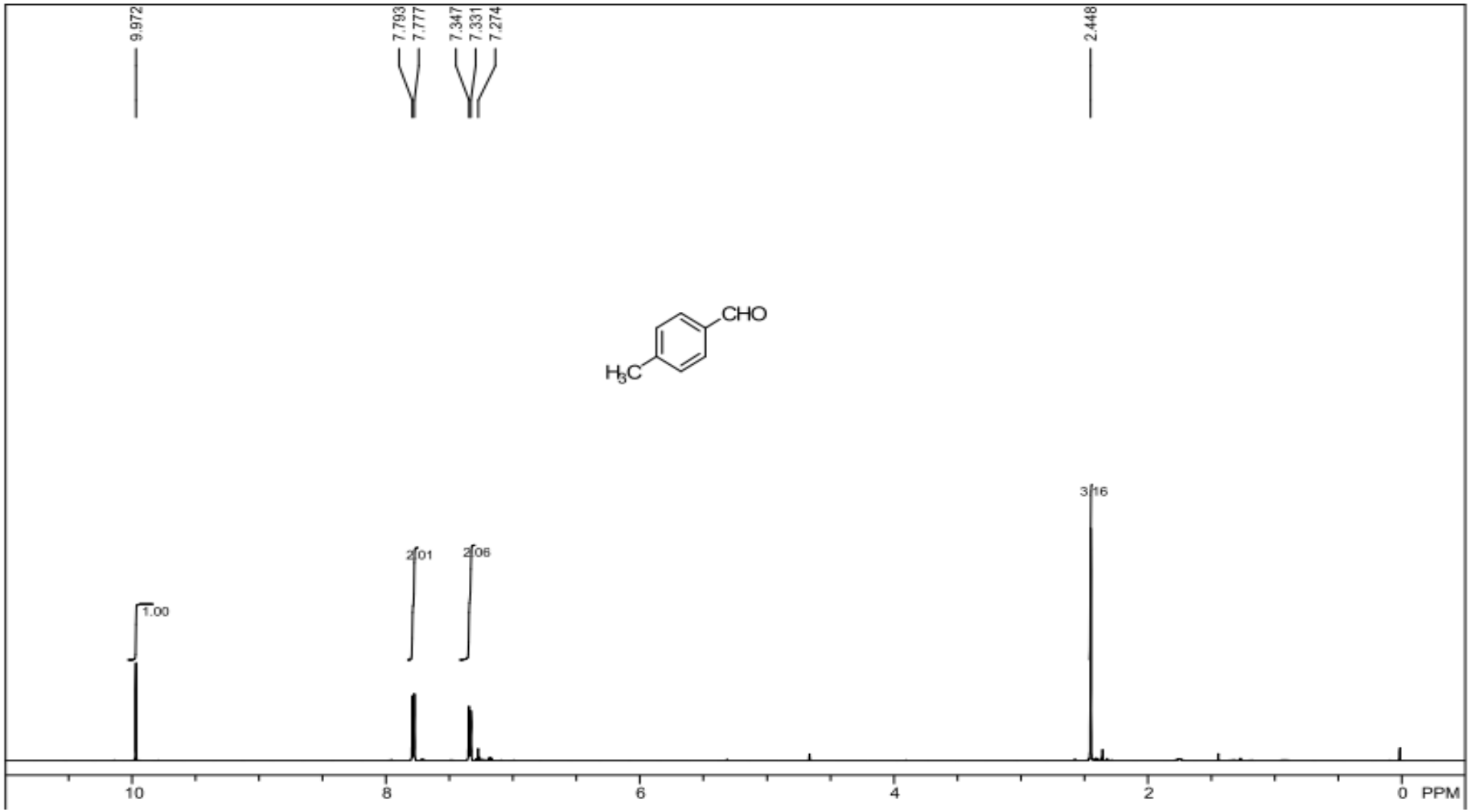


Figure 15. ^{1}HNMR spectra of **3,4-Dimethylbenzaldehyde** (Table 2, entry 15).

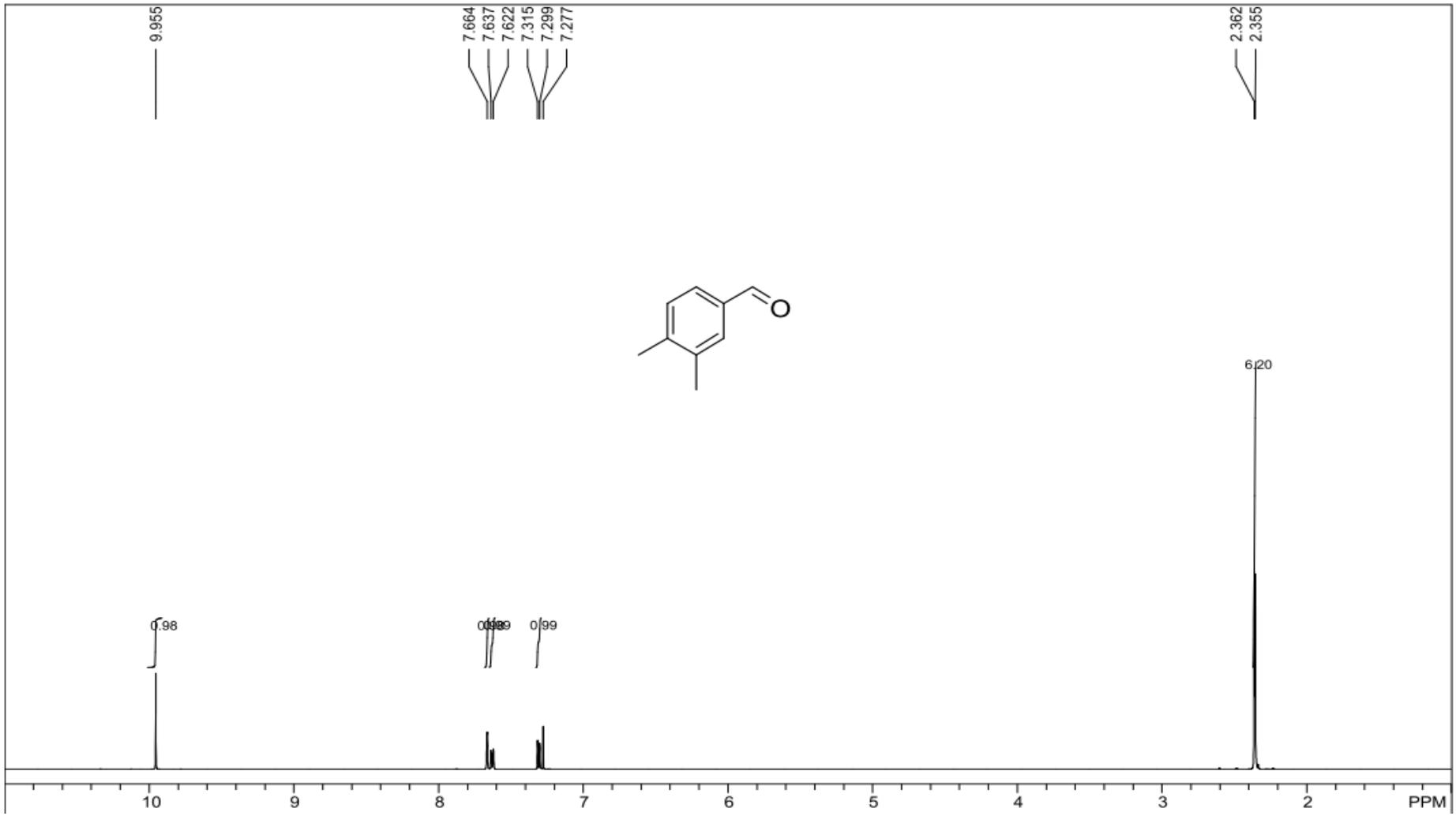


Figure 16. ^{1}HNMR spectra of **4-Chloroacetophenone** (Table 2, entry 16).

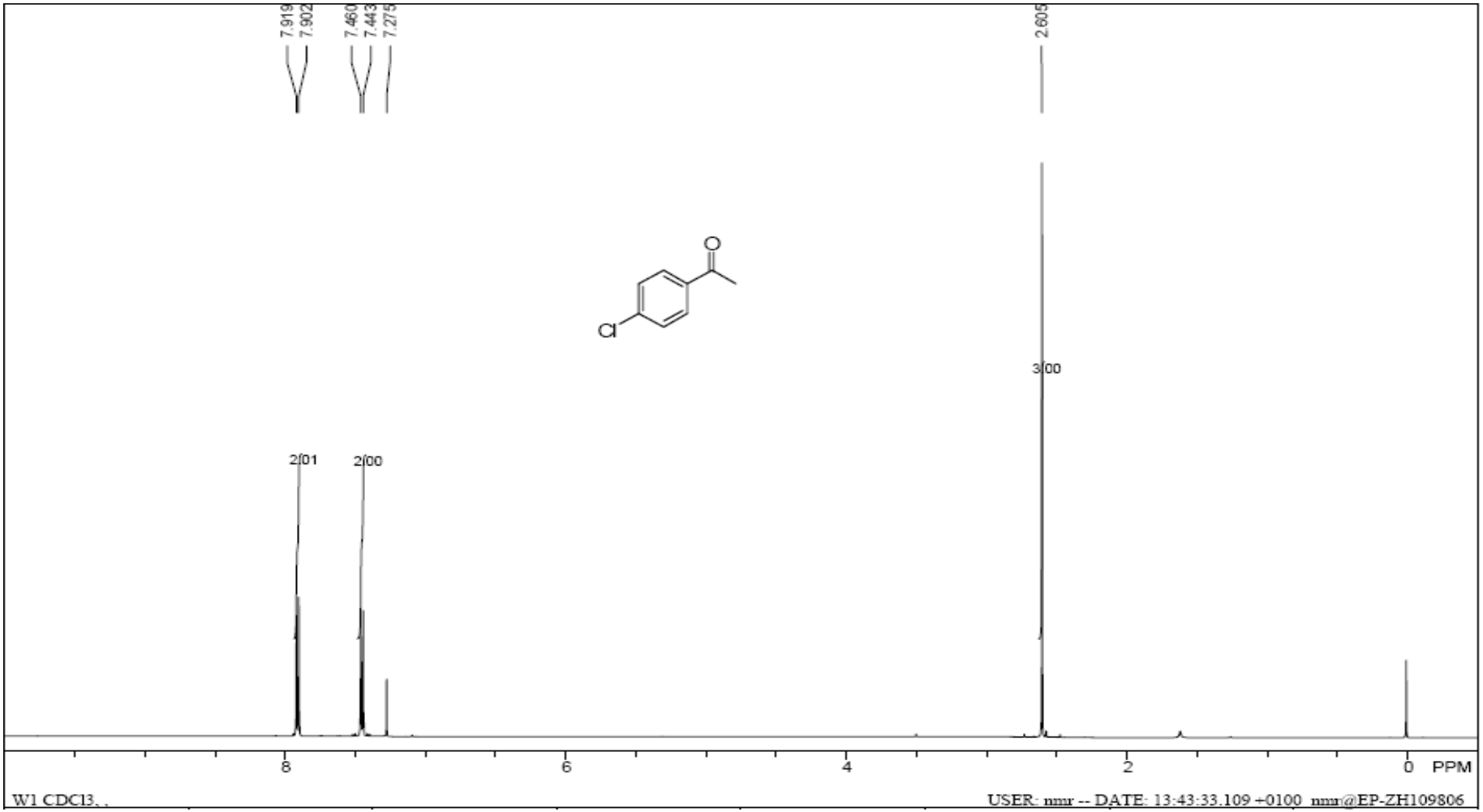


Figure 17. ^{1}HNMR spectra of **Acetophenone** (Table 2, entry 17).