

Core-shell Pd(0)@His-SiO₂/CoFe₂O₄ nano-composite as magnetically recoverable heterogeneous catalyst for deprotection of oximes and Heck coupling

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S1. General procedure for the oxidative deprotection of oximes

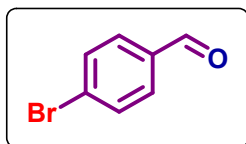
In a 50 mL round-bottom flask, oxime (1 mmole), TEMPO (0.30 mmole), Pd(0)@His-SiO₂/CoFe₂O₄ (1 mmole) and toluene (10 mL) was added and the reaction mixture was agitated at 90 °C. In order to monitor the progress of reaction, TLC was checked after repeated intervals. After the completion of reaction, the catalyst was taken out of the reaction mixture using an external magnet and was washed with acetone (3×5 mL), ethyl acetate (3×5 mL), and deionized water (3×5 mL). The catalyst was dried at room temperature for further use. Toluene was removed from the reaction mixture under a reduced pressure. The residue was diluted using ethyl acetate and washed with water (3×5 mL). The ethyl acetate layer was recovered and dried over anhydrous Na₂SO₄ and the obtained crude product was purified after the removal of solvent either by crystallization or by column chromatography using n-hexane and ethyl acetate as eluting solvents.

General procedure for the Heck coupling

In a 50 mL round-bottom flask, a combination of aryl halide (1 mmole), styrene (1 mmole), K₂CO₃ (1.5 mmole), Pd(0)@His-SiO₂/CoFe₂O₄ (1 mmole) as a catalyst and ethanol (10

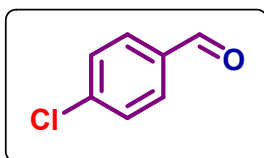
mL) were added. The reaction was stirred at 80 °C and the advancement of the reaction was monitored after repeated intervals using TLC. After the completion of the reaction, catalyst was separated from the reaction mixture with the help of an external magnet. Catalyst was washed with acetone (3×5 mL), ethyl acetate (3×5 mL), deionized water (3×5 mL) and dried at room temperature for its further use. The reaction mixture was then diluted with ethyl acetate, washed with water (3×5 mL) and the ethyl acetate layer was separated using a separating funnel. The obtained layer was dried over anhydrous Na₂SO₄ and crude product was then purified by column chromatography using n-hexane and ethyl acetate as eluting solvents.

S2. Spectral data of some compounds in Table 3



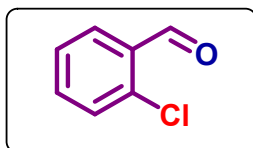
4-Bromobenzaldehyde (2a)

¹H NMR (400 MHz, CDCl₃): δ 10.00 (s, 1H, CHO), 7.78 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.71 (d, *J* = 7.8 Hz, 2H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ 191.45, 135.05, 132.44, 130.99, 129.79.



4-Chlorobenzaldehyde (2b)

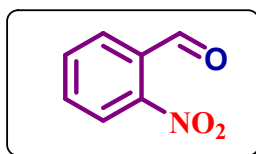
¹H NMR (400 MHz, CDCl₃): δ 10.00 (s, 1H, CHO), 7.84 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.53 (d, *J* = 8.2 Hz, 2H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ 191.06, 140.97, 134.70, 130.93, 129.47.



2-Chlorobenzaldehyde (2c)

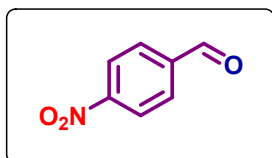
¹H NMR (400 MHz, CDCl₃): δ 10.34 (s, 1H, CHO), 7.79 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.44-7.27 (m, 3H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ 189.69, 137.78, 135.15,

132.28, 130.53, 129.26, 127.25.



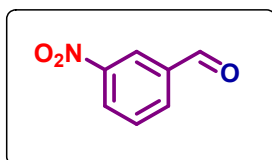
2-Nitrobenzaldehyde (2d)

¹H NMR (400 MHz, CDCl₃): δ 10.42 (s, 1H, CHO), 8.13 (d, *J* = 8 Hz, 1H, Ar-H), 7.96 (d, *J* = 8 Hz, 1H, Ar-H), 7.76-7.84 (m, 2H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ 188.24, 149.48, 133.92, 133.56, 131.22, 129.27, 124.32.



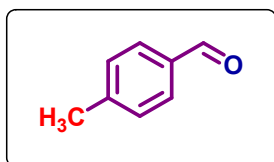
4-Nitrobenzaldehyde (2e)

¹H NMR (400 MHz, CDCl₃): δ 10.19 (s, 1H, CHO), 8.43 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.11 (d, *J* = 8.5 Hz, 2H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ 190.63, 151.87, 140.16, 130.63, 124.55.



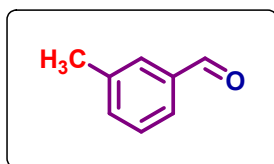
3-Nitrobenzaldehyde (2f)

¹H NMR (400 MHz, CDCl₃): δ 10.15 (s, 1H, CHO), 8.75 (s, 1H, Ar-H), 8.52 (d, *J* = 8.3 Hz, 1H, Ar-H), 8.26 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.80 (t, *J* = 7.2 Hz, 1H, Ar-H); ¹³C NMR (100 MHz, CDCl₃): δ 189.63, 148.67, 137.30, 134.42, 130.35, 128.49, 124.34.



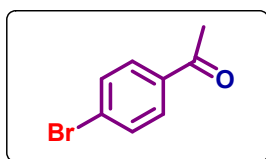
4-Methylbenzaldehyde (2g)

¹H NMR (400 MHz, CDCl₃): δ 9.97 (s, 1H, CHO), 7.78 (d, *J* = 7.7 Hz, 2H, ArH), 7.34 (d, *J* = 7.7 Hz, 2H, ArH), 2.44 (s, 3H, CH₃); ¹³C NMR (101 MHz, CDCl₃): δ 192.10, 145.52, 134.16, 129.74, 129.05, 21.91.



3-Methylbenzaldehyde (2h)

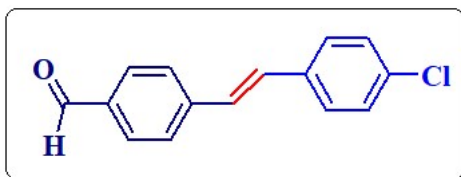
¹H NMR (400 MHz, CDCl₃): δ 10.01 (s, 1H, CHO), 7.71-7.69 (m, 2H, ArH), 7.48-7.42 (m, 2H, ArH), 2.46 (s, 3H, CH₃); ¹³C NMR (101 MHz, CDCl₃): δ 192.70, 138.94, 136.46, 135.34, 130.05, 128.90, 127.27, 20.94.



4-Bromoacetophenone (2i)

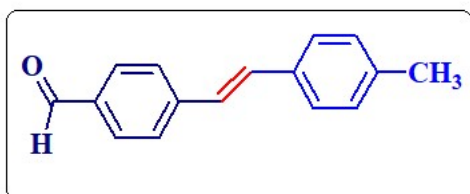
¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.63 (d, *J* = 8.5 Hz, 2H, Ar-H), 2.61 (s, 3H, COCH₃); ¹³C NMR (100 MHz, CDCl₃): δ 197.08, 135.73, 131.75, 129.87, 128.48, 26.46.

S3. Spectral data of some compounds in Table 4



4-(4-chlorostyryl)benzaldehyde (5b, 5e)

^1H NMR (400 MHz, CDCl_3): δ 9.69 (s, 1H, -CHO), δ 7.75-7.66 (m, 8H, Ar-H), 6.92 (d, J = 16.0 Hz, 1H, C=CH), 6.88 (d, J = 16.0 Hz, 1H, C=CH); ^{13}C NMR (100 MHz, CDCl_3): δ 193.27, 151.34, 132.93, 132.44, 132.26, 131.91, 131.68, 129.82, 129.71, 129.01, 125.67.



4-(4-methylstyryl)benzaldehyde (5c, 5f)

^1H NMR (400 MHz, CDCl_3): δ 9.74 (s, 1H, -CHO), δ 7.60 (d, J = 7.6 Hz, 4H, Ar-H), 7.46 (d, J = 7.5 Hz, 4H, Ar-H), δ 6.75 (d, J = 16 Hz, 1H, C=CH), δ 6.75 (d, J = 16 Hz, 1H, C=CH), δ 2.22 (s, 3H, -CH₃); ^{13}C NMR (100 MHz, CDCl_3): δ 191.07, 137.89, 137.26, 136.67, 133.12, 132.33, 130.68, 130.05, 128.70, 128.41, 123.35, 21.08.

S4. ¹H NMR and ¹³C NMR spectra of some compounds listed in Table 3

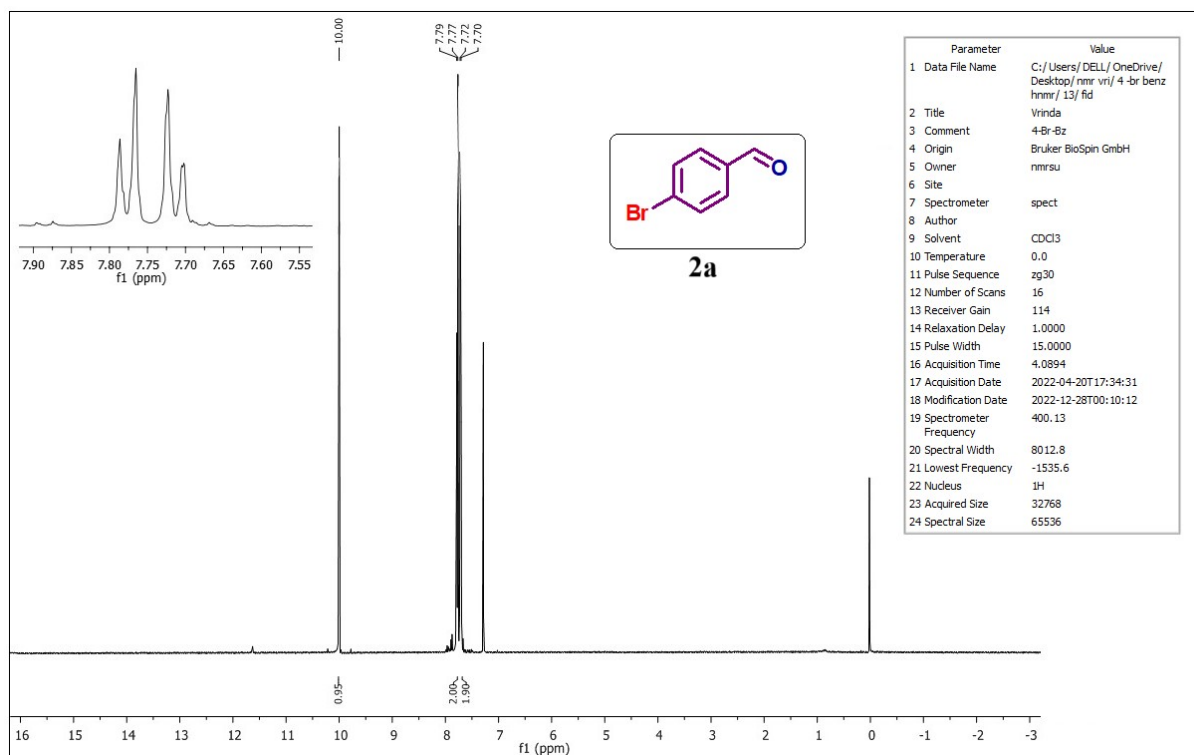


Figure 1. ¹H NMR spectra of 4-Bromobenzaldehyde.

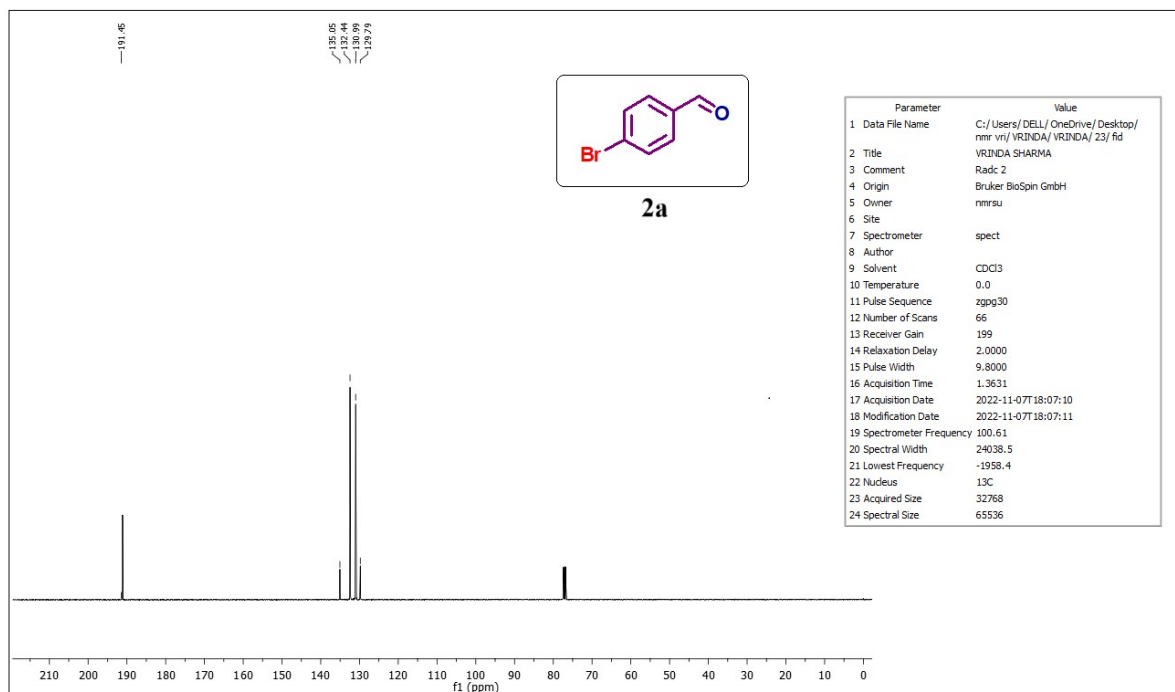


Figure 2. ¹³C NMR spectra of 4-Bromobenzaldehyde.

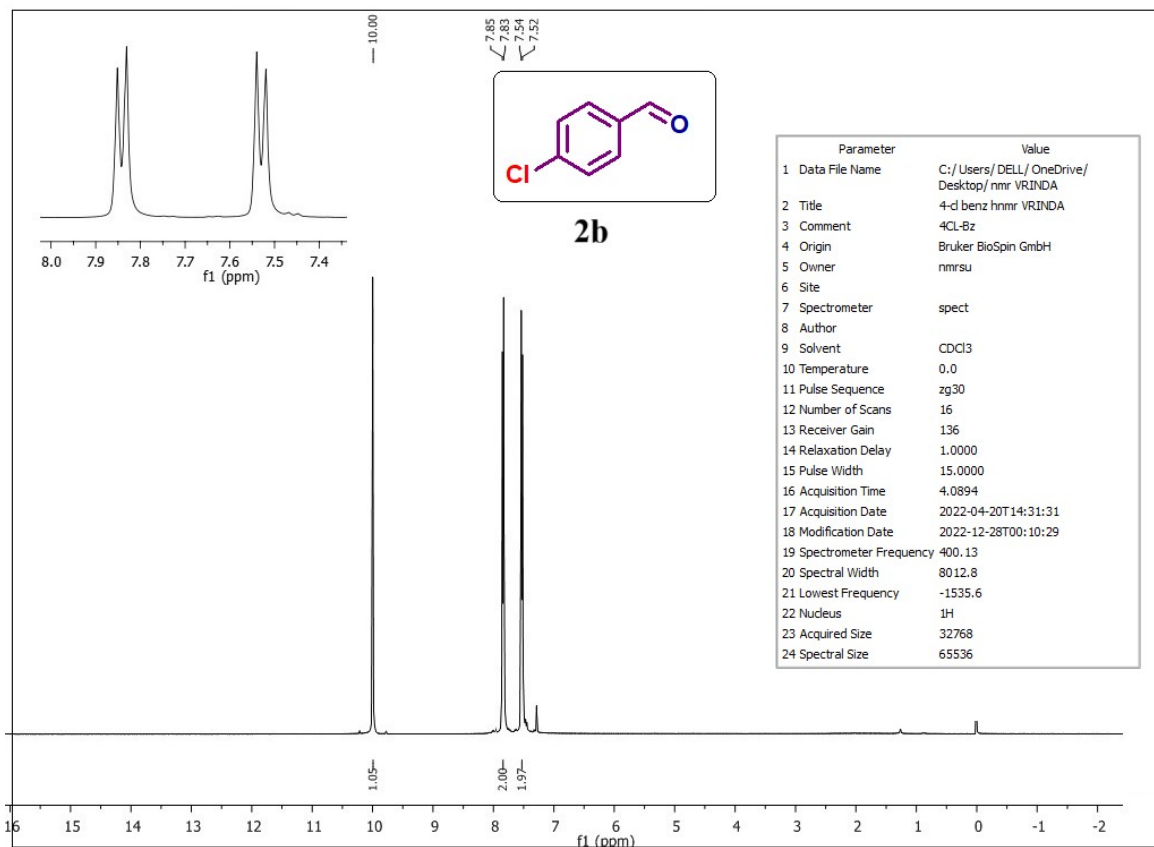


Figure 3. ¹H NMR spectra of 4-Chlorobenzaldehyde.

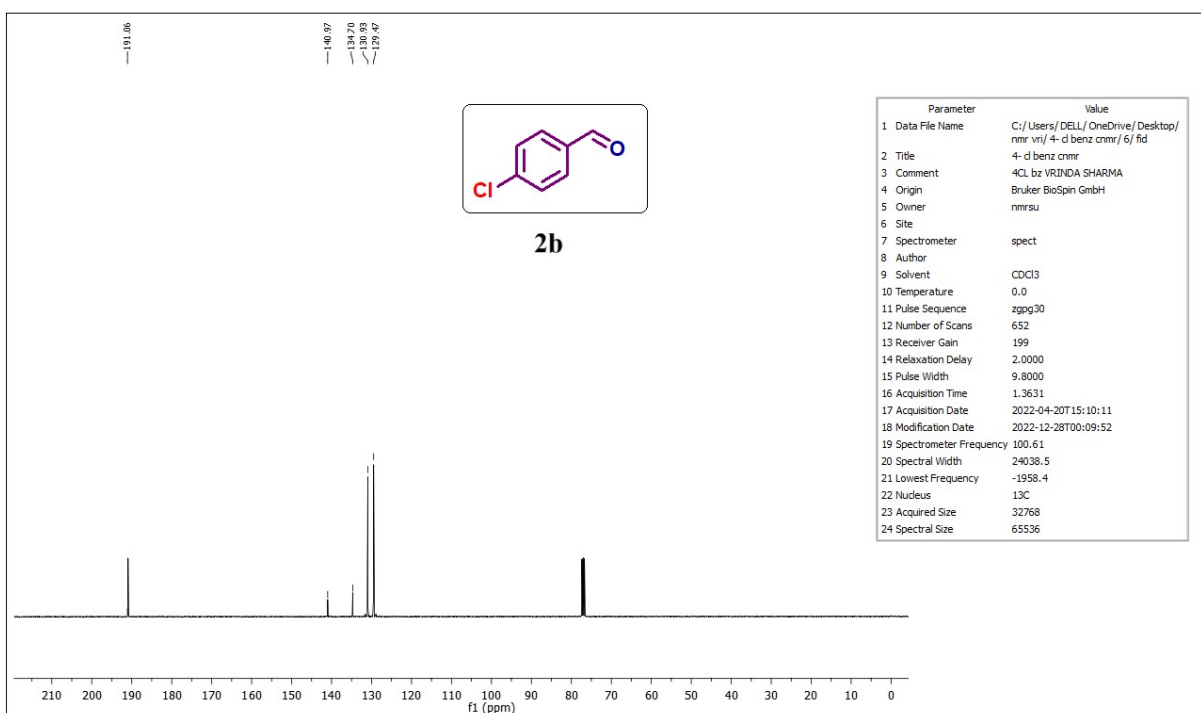


Figure 4. ¹³C NMR spectra of 4-Chlorobenzaldehyde.

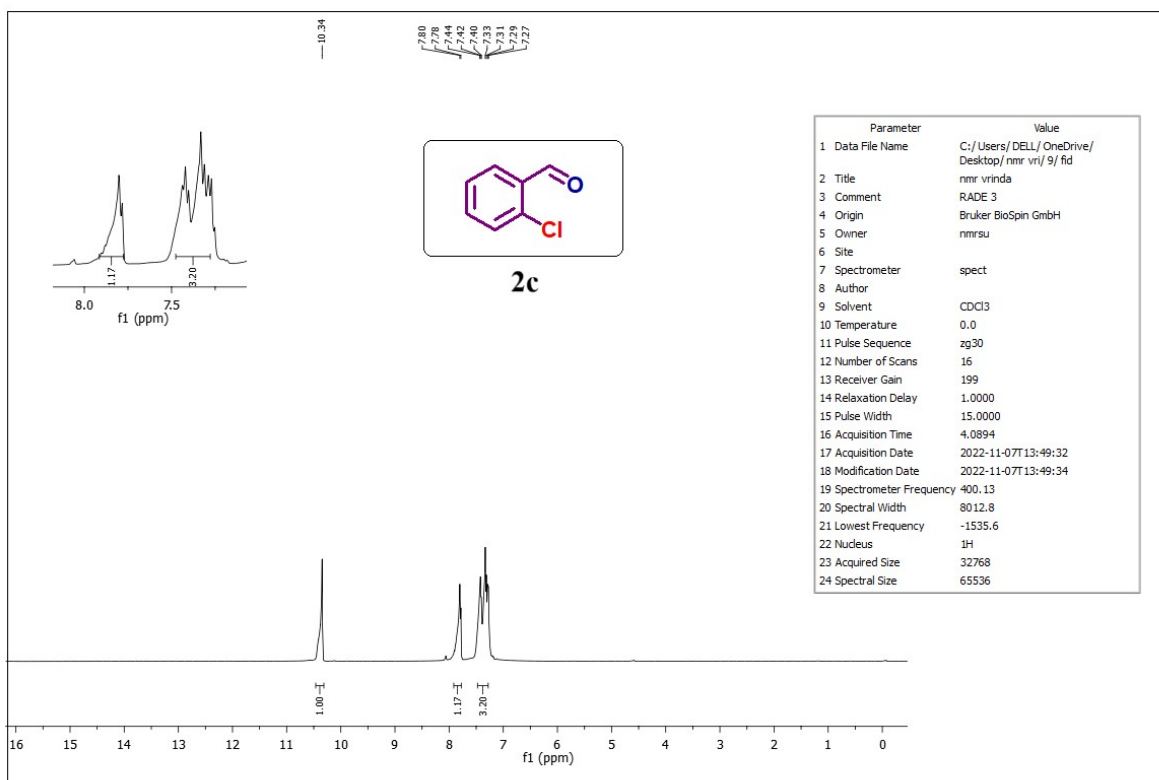


Figure 5. ¹H NMR spectra of 2-Chlorobenzaldehyde.

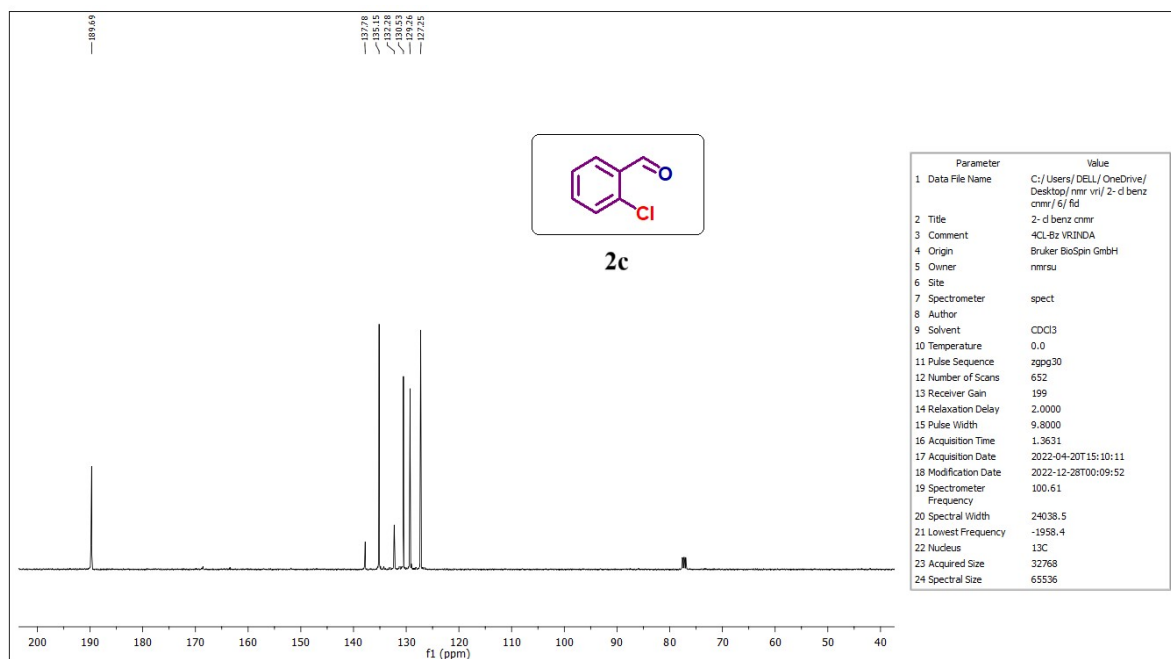


Figure 6. ¹³C NMR spectra of 2-Chlorobenzaldehyde.

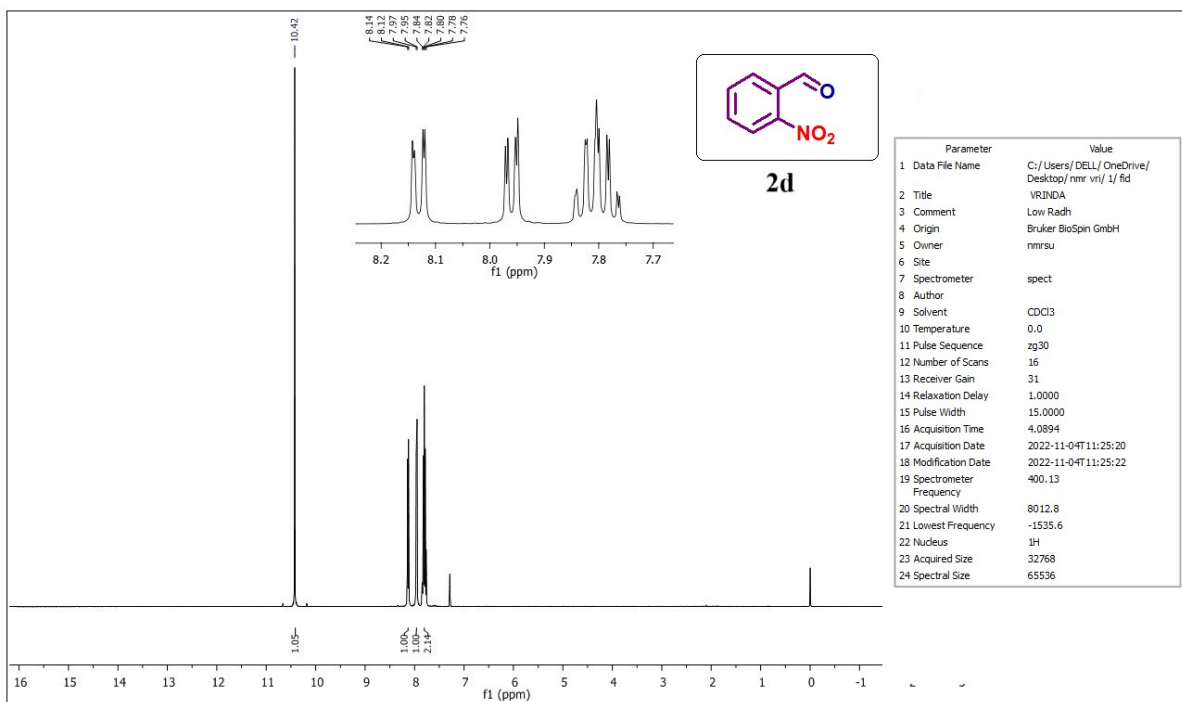


Figure 7. ^1H NMR spectra of 2-Nitrobenzaldehyde.

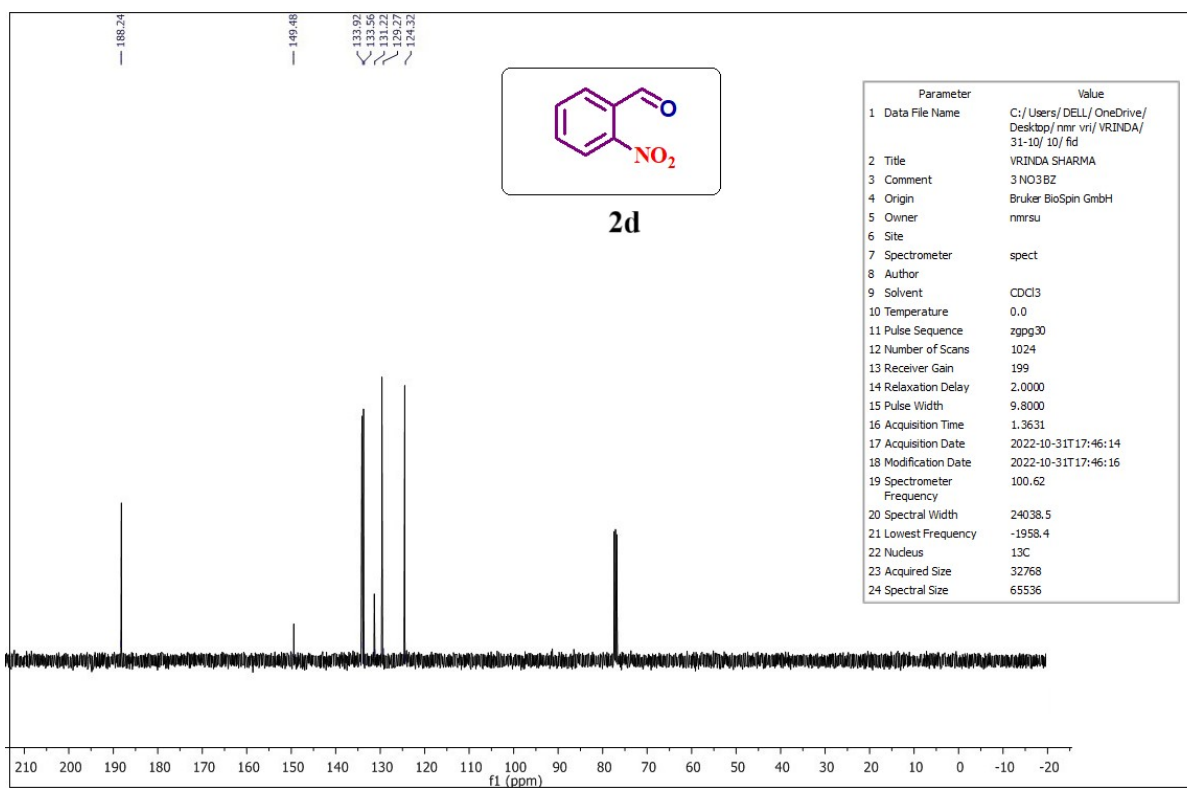


Figure 8. ^{13}C NMR spectra of 2-Nitrobenzaldehyde.

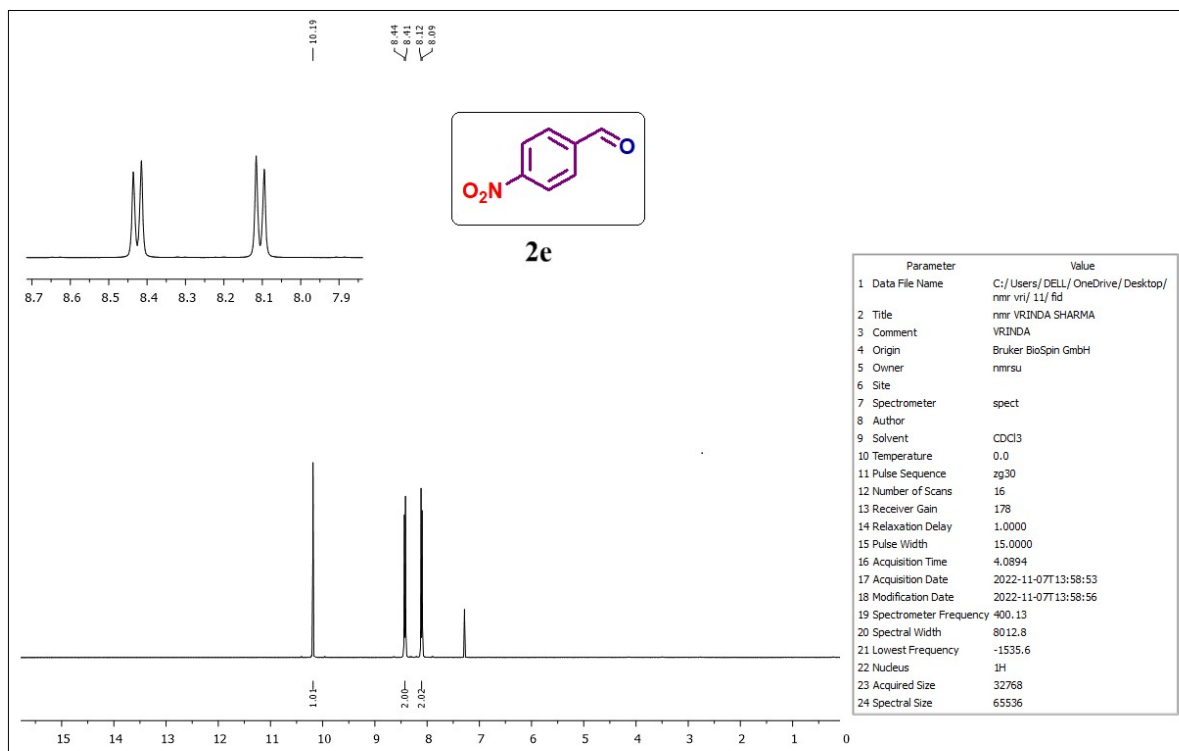


Figure 9. ¹H NMR spectra of 4-Nitrobenzaldehyde.

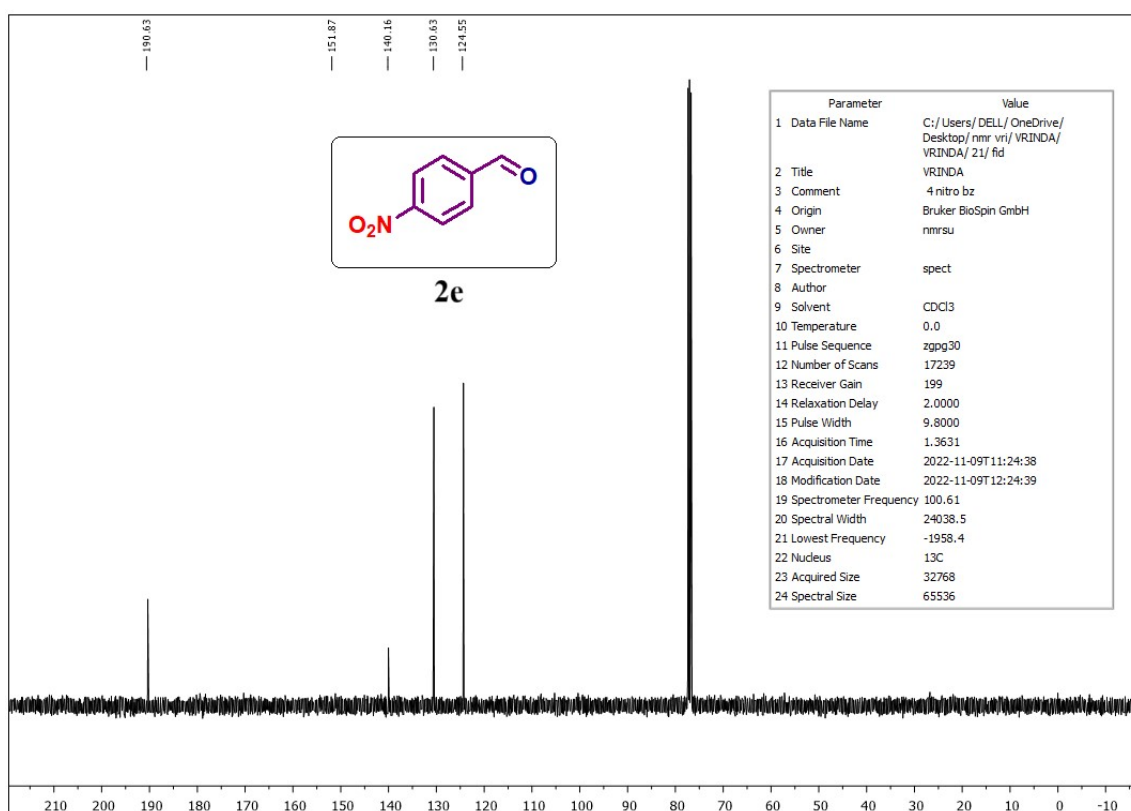


Figure 10. ¹³C NMR spectra of 4-Nitrobenzaldehyde.

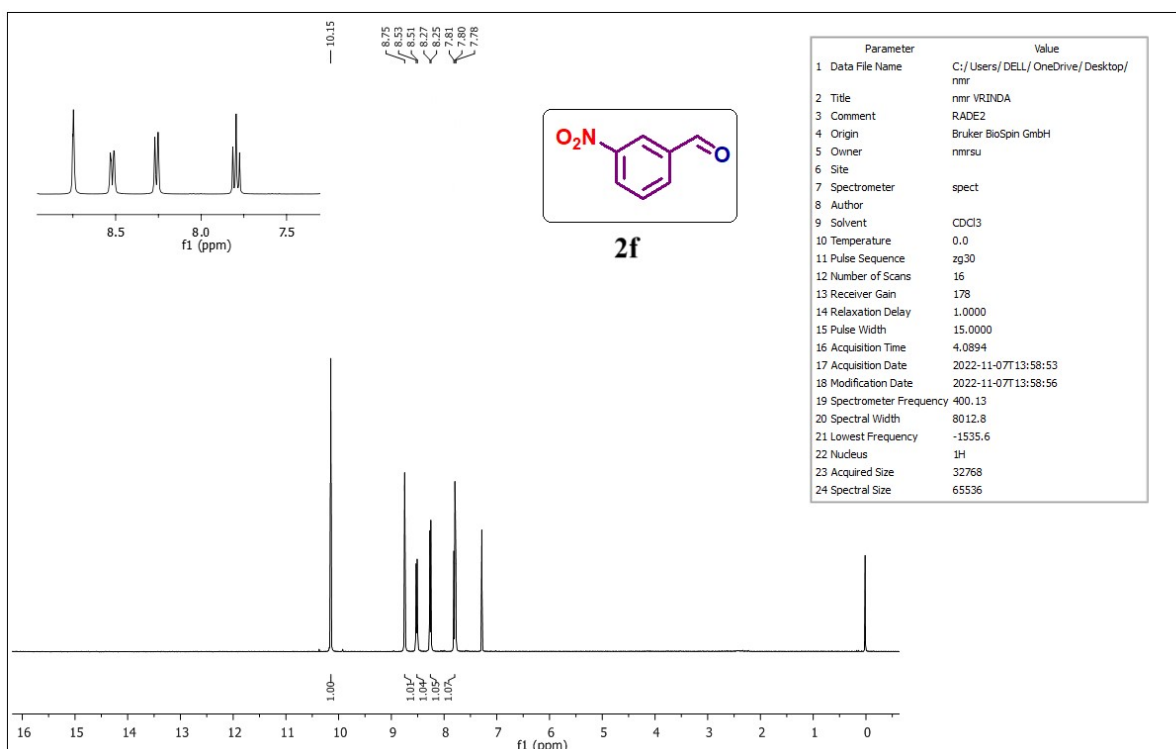


Figure 11. ^1H NMR spectra of 3-Nitrobenzaldehyde.

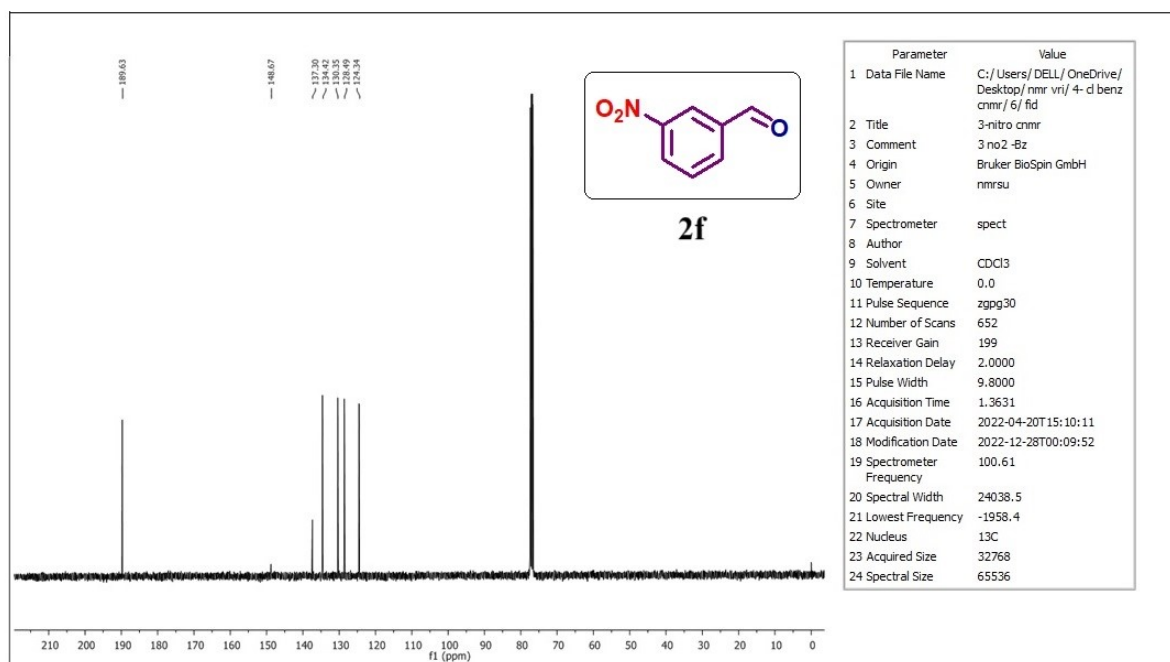


Figure 12. ^{13}C NMR spectra of 3-Nitrobenzaldehyde.

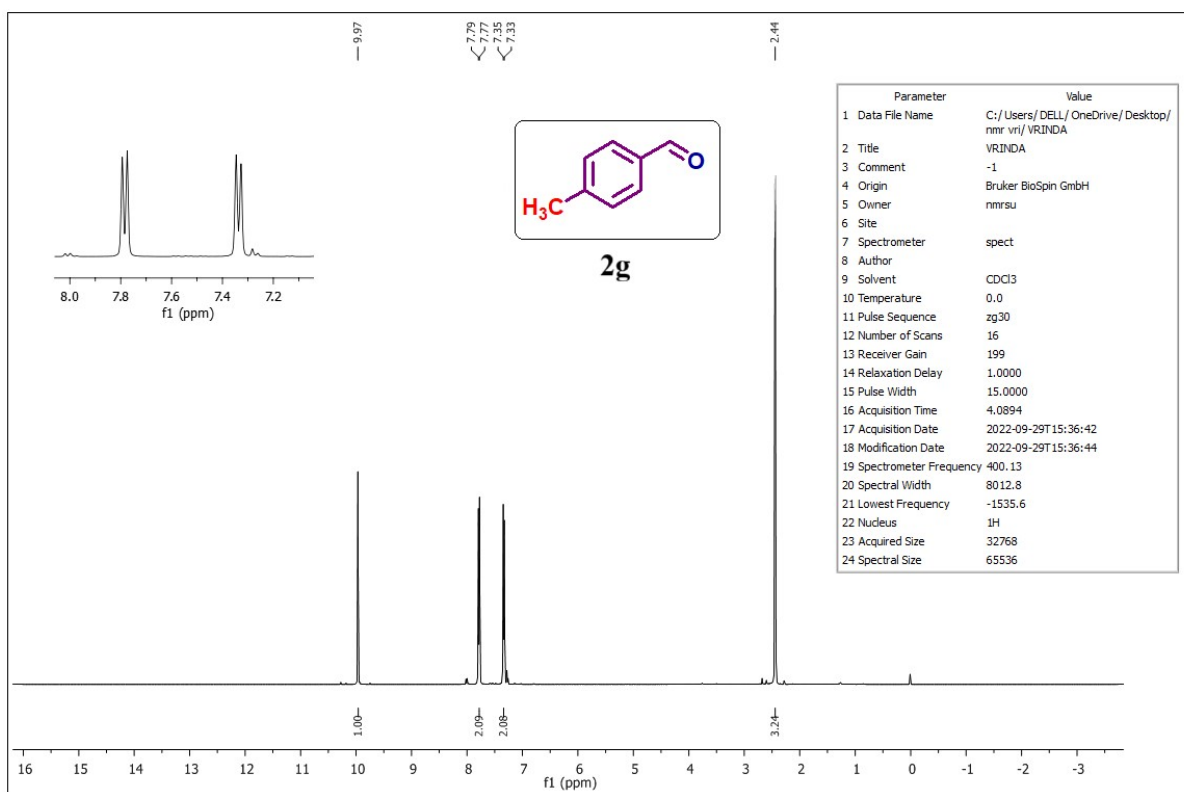


Figure 13. ¹H NMR spectra of 4-Methylbenzaldehyde.

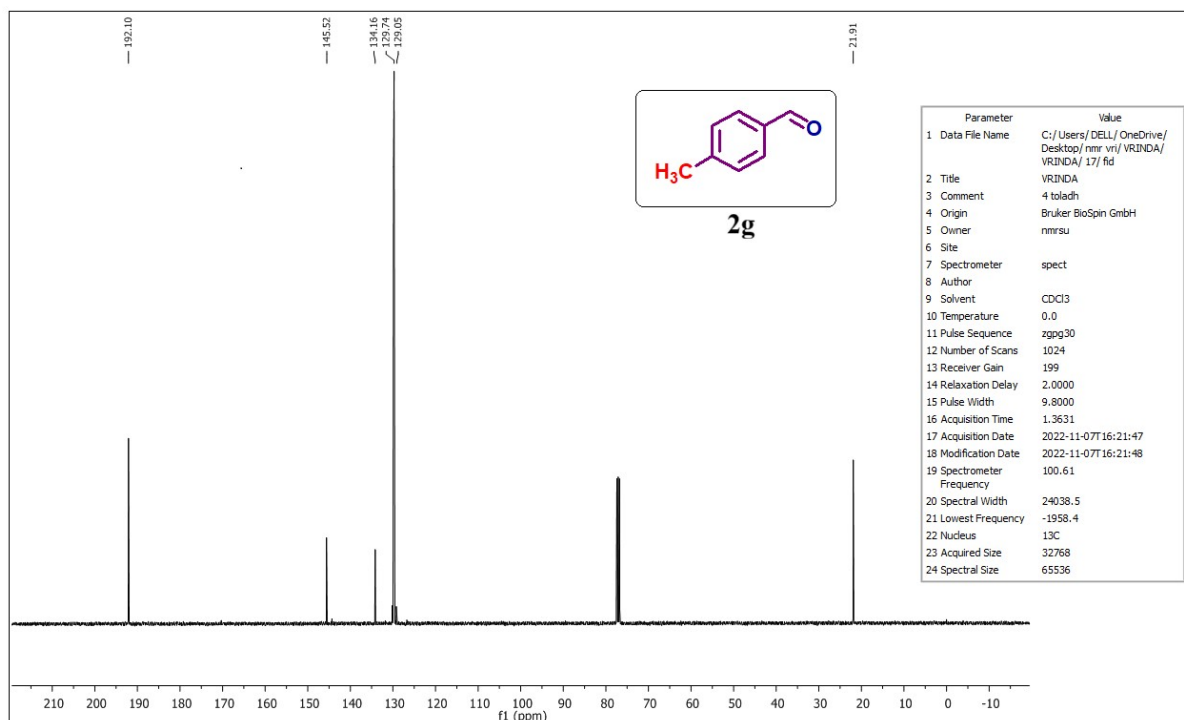


Figure 14. ¹³C NMR spectra of 4-Methylbenzaldehyde.

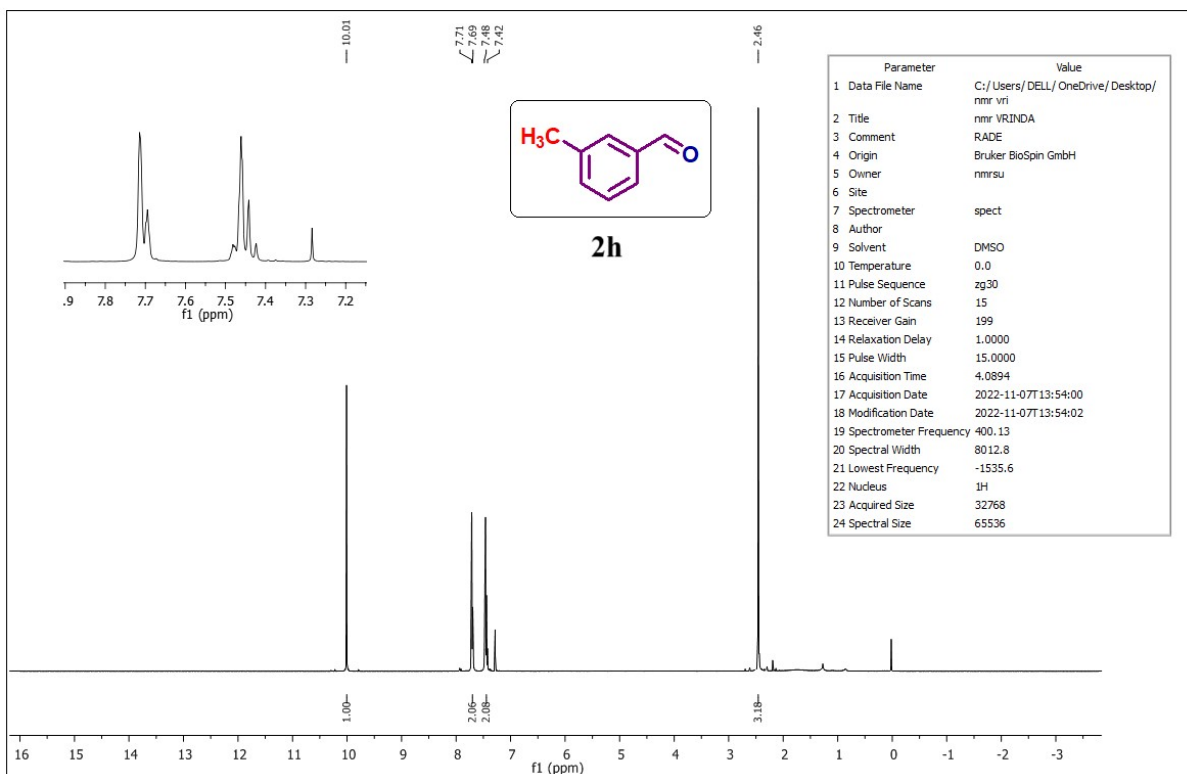


Figure 15. ¹H NMR spectra of 3-Methylbenzaldehyde.

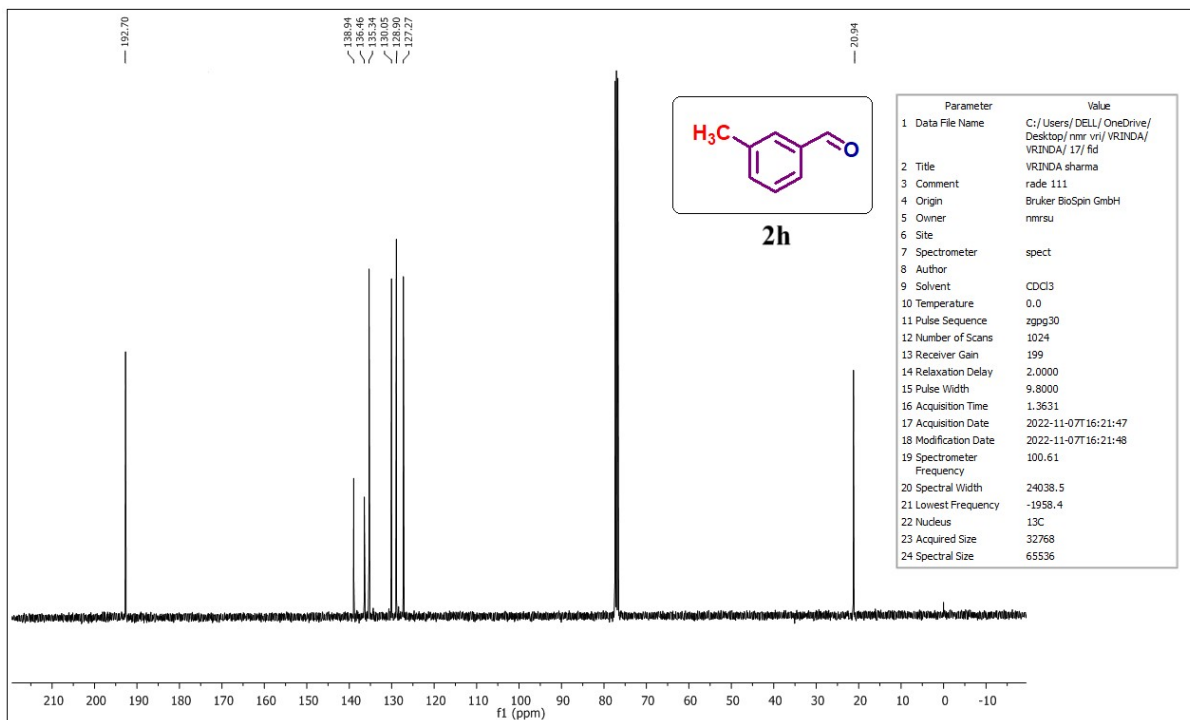


Figure 16. ¹³C NMR spectra of 4-Methylbenzaldehyde.

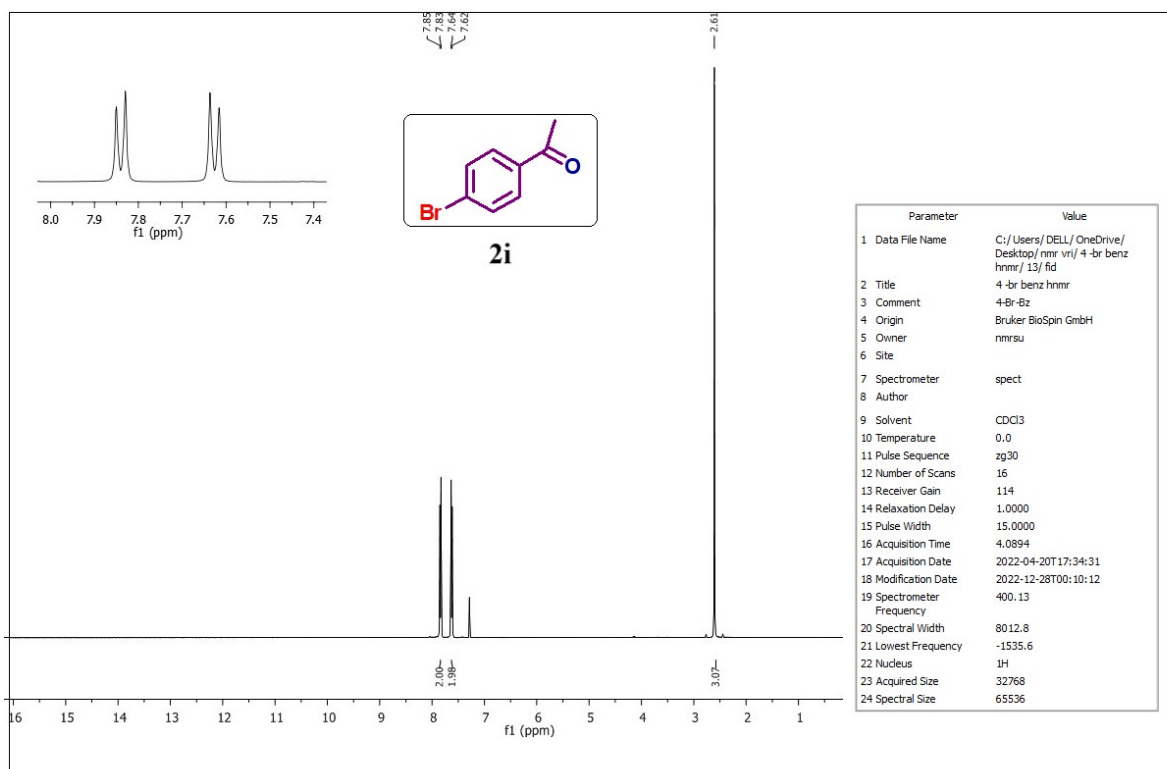


Figure 17. ¹H NMR spectra of 4-Bromoacetophenone.

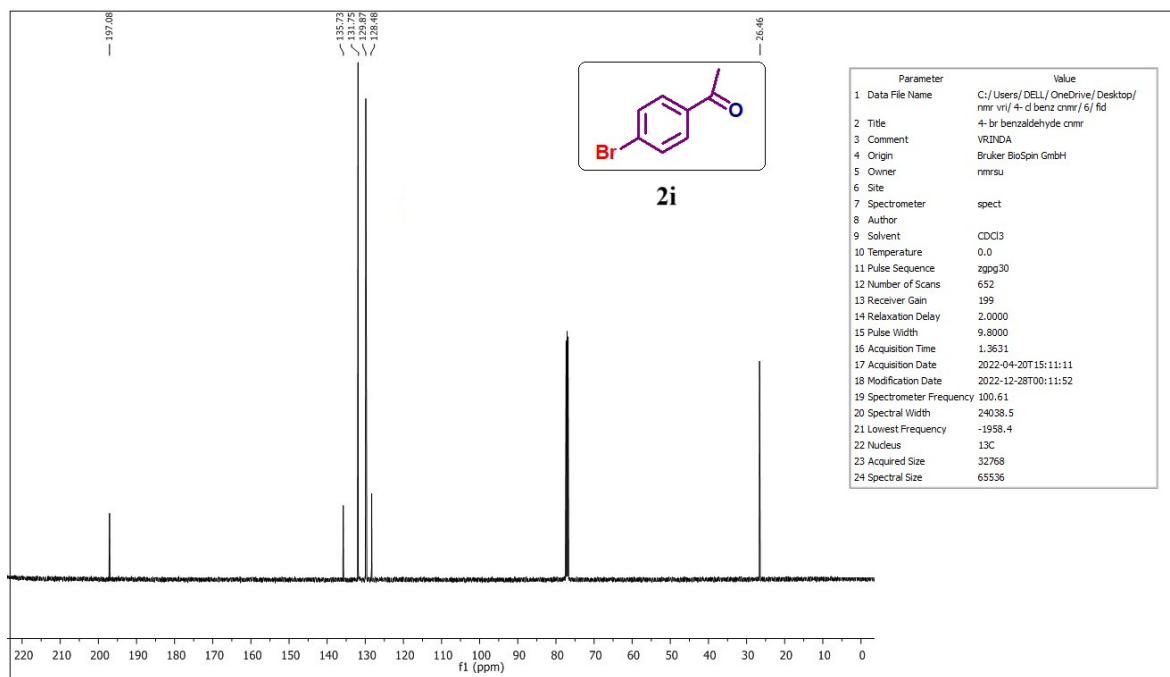


Figure 18. ¹³C NMR spectra of 4-Bromoacetophenone.

S5. ¹H NMR and ¹³C NMR spectra of some compounds listed in Table 4

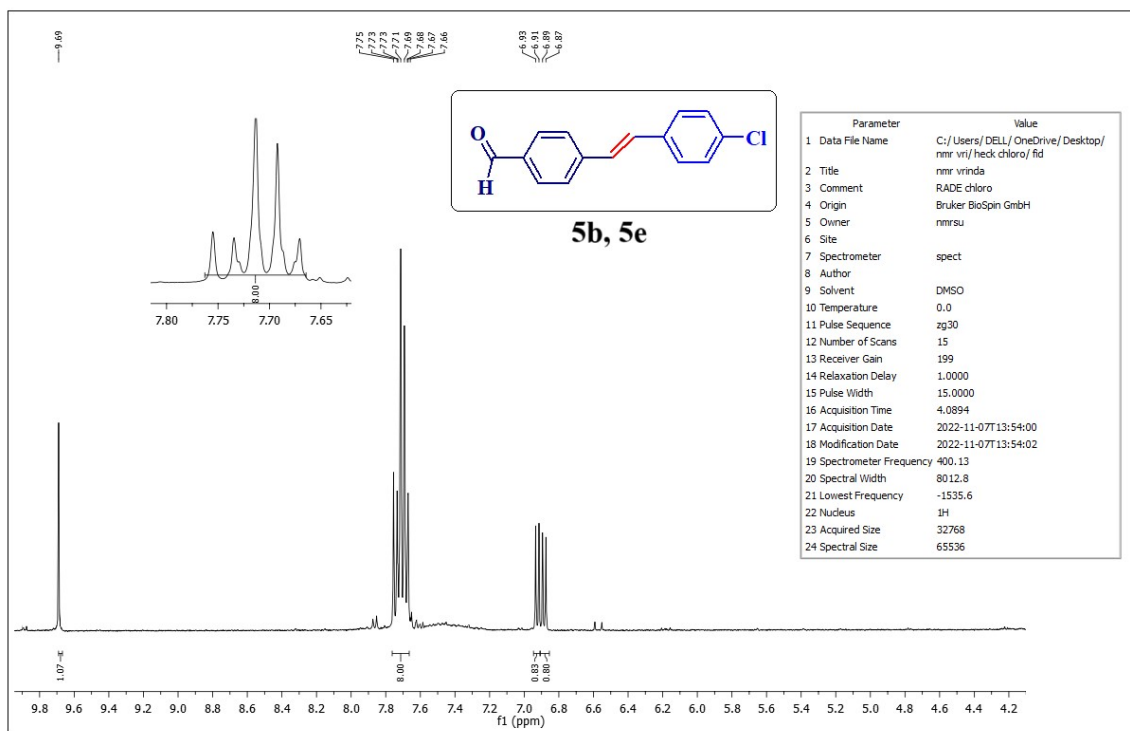


Figure 19. ¹H NMR spectra of 4-(4-chlorostyryl)benzaldehyde.

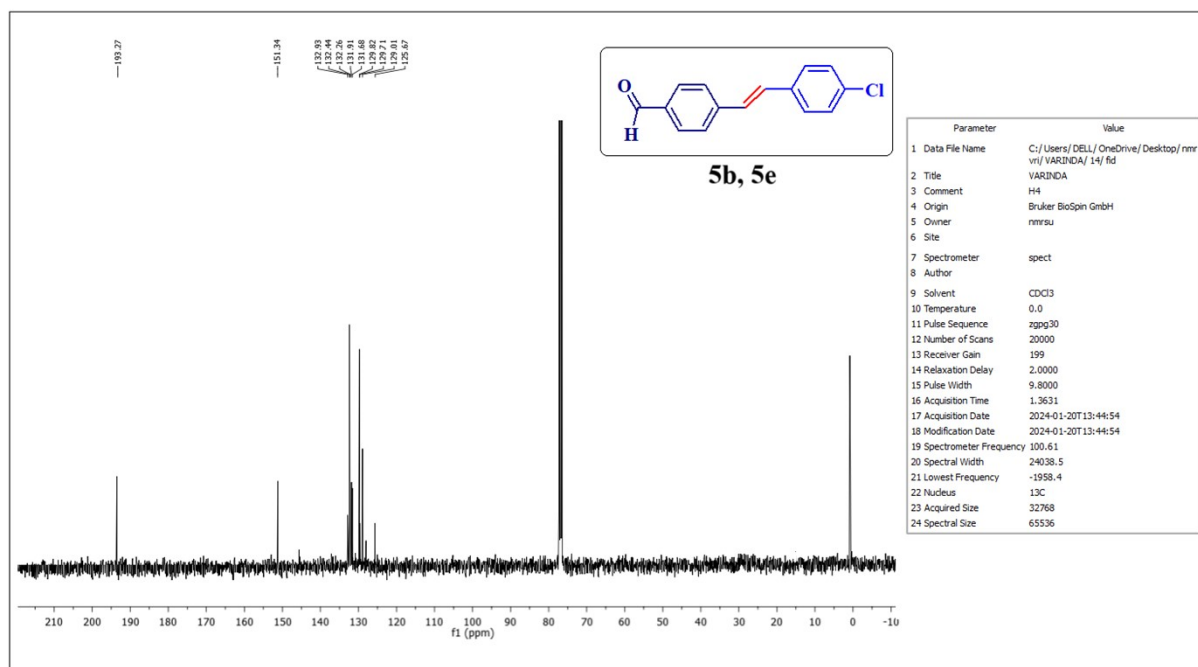


Figure 20. ¹³C NMR spectra of 4-(4-chlorostyryl)benzaldehyde.

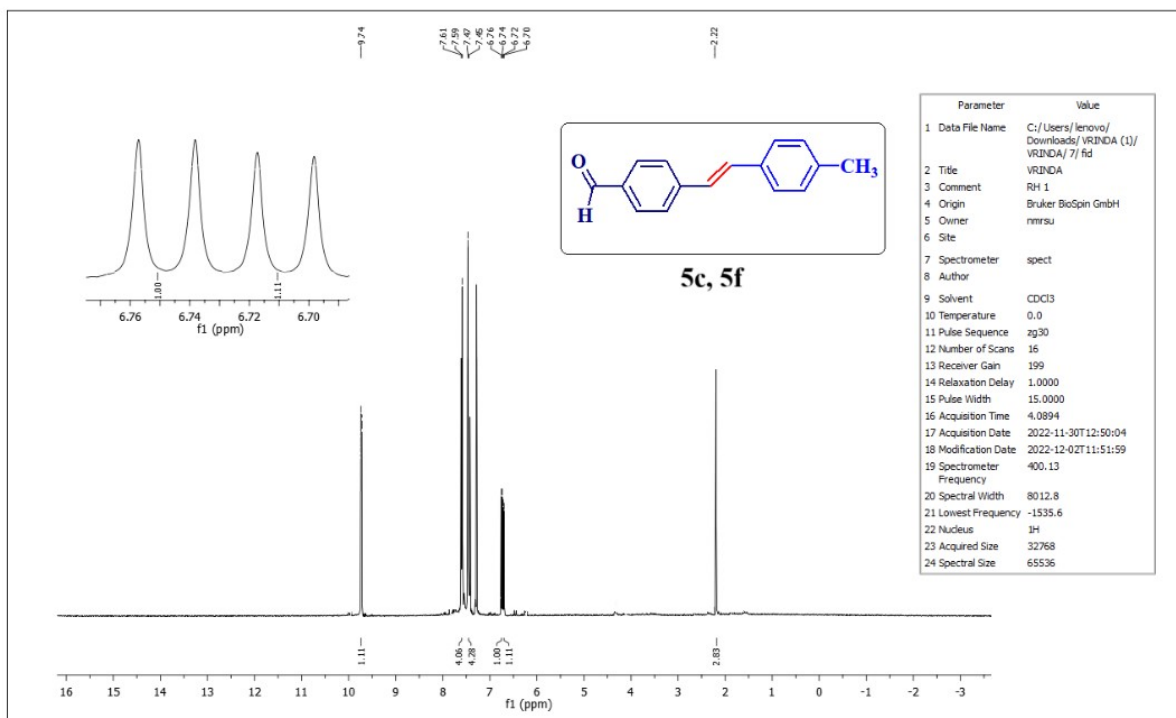


Figure 22. ¹H NMR spectra of 4-(4-methylstyryl)benzaldehyde.

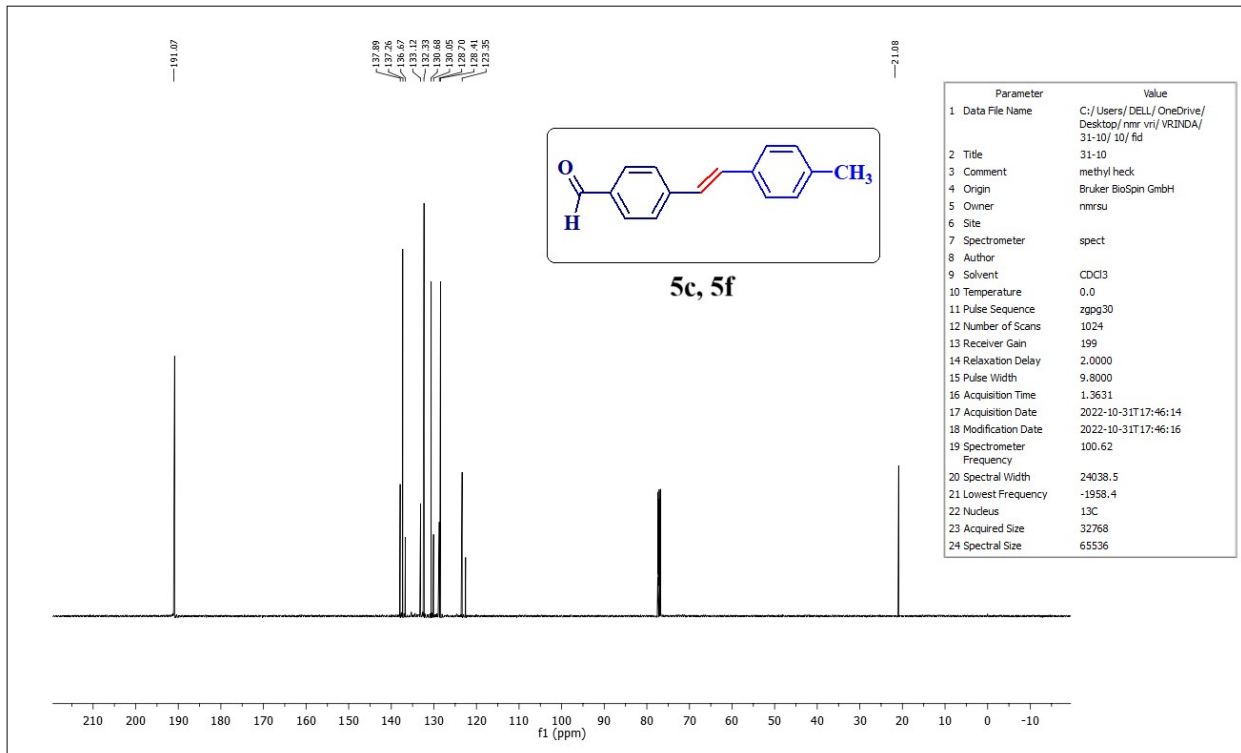


Figure 22. ¹³C NMR spectra of 4-(4-methylstyryl)benzaldehyde.