Supporting information

An Aerobic Oxidation of Alcohols into Carbonyl Synthons using Bipyridyl-Cinchona based Palladium catalyst

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1.1. Materials and methods

5,5 -dimethyl-2,2 -bipyridine, AIBN, (+)-Cinchonine, N-bromosuccinimide were purchased from sigma Aldrich. 2-Methyl Benzaldehyde, 4-Methyl Benzaldehyde, 2-Methoxy Benzaldehyde, 4-Methoxy Benzaldehyde, 3-Methoxy,4-Hydroxy Benzaldehyde, 2-Chloro Benzaldehyde, 4-Chloro Benzaldehyde,2,3- Dichloro Benzaldehyde, 3-Nitro Benzaldehyde, 4-tert-Butyl Benzaldehyde, Mesitaldehyde, 2,6-Dimethyl Benzaldehyde, 3,5-Dibromo-2,4,6-trimethylbenzaldehyde, Acetophenone, Propiophenone, Benzophenone, Cyclododecanone. All the solvents for reactions were obtained from laboratory grade. All the solvents for Analysis were purchased from analytical grade.

The melting points were measured in open capillary tubes and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker (Avance) 300 & 400 MHz NMR instrument using TMS as an internal standard, $CDCl_3$ and DMSO as a solvent. Standard Bruker software was used throughout. Chemical shifts are given in parts per million (δ-scale) and the coupling constants are given in Hertz. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of n-hexane and ethyl acetate as an eluent. Column chromatography was carried out in silica gel (60-120 mesh) using n-hexane, DCM, methanol and ethyl acetate as an eluent. Pressure reactions were carried out using PREMEX A-Linie Avalon Instrument. Distillation of the products were carried out using Glass oven – B585 Kugelrohr (Buchi make) instrument. Electrospray Ionization Mass Spectrometry (ESI-MS) analyses were recorded in LCQ Fleet, Thermo Fisher Instruments Limited, US. ESI-MS was performed in positive ion mode. The collision voltage and ionization voltage were −70 V and −4.5 kV, respectively, using nitrogen as atomization and desolvation gas. The desolvation temperature was set at 300°C. The relative amount of each component was determined from the LC-MS chromatogram, using the area normalization method. GC was recorded using Agilent GC 6890 N, split ratio: 1:100 250°C, FID: 300°C, Flow rate: Nitrogen 30 mL/min. Column: HP-5; 30m x d:0.32 mm x f: 0.25 mm, -60 to 325°C. GCMS was recorded using 5977B GC/MSD Single quadrupole analyser using Helium as carrier gas.

2.0: Experimental Section.

2.1: Preparation of cinchona based palladium catalyst (5)

2.1.1: Preparation of 5,5 -bis(bromomethyl)-2,2 -bipyridine (2)

NBS (1.93 g, 10.85 mmol) was added in solid lots slowly to a mixture of 1 (1 g, 5.42 mmol), AIBN (17 mg, 0.10 mmol) in CCl_4 (75 mL) and it was refluxed for 2h under nitrogen atmosphere. The precipitated succinimide was hot filtered and the solid was washed with CCl_4 (100 mL). The combined CCl_4 phases were evaporated. The remaining solid was dissolved in CH_2Cl_2 (100 mL) and extracted with 0.5 M $Na_2S_2O_3$ solution (2 × 150 mL). The combined $Na_2S_2O_3$ fractions were extracted with CH_2Cl_2 (50 mL) and the combined CH_2Cl_2 layers were dried (Na_2SO_4) and concentrated it. The crude product was purified by column chromatography (silica gel, EtOAc/hexane, 1:4) white powder. Yield is 63%, MP: 193–194°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (d, J = 3 Hz, 2H), 8.39 (d, J = 9 Hz, 2H), 7.87-7.84 (m, 2H), 4.53 (s,

4H).^{13}C NMR (75 MHz, CDCl3) δ_C 149.78, 143.67, 131.82, 128.19, 115.44, 23.74. ESI-MS (M+); 342.88.

2.1.2: Synthesis of cinchonine (contains free -OH) based CPTC (4)

A mixture of 5,5 -bis(bromomethyl)-2,2 -bipyridine 2 (1g, 2.9 mmol), cinchona (free OH) 3 (6.38 mmol) was dissolved in THF (50 mL) and heated to reflux for overnight. The resulting brown solid was filtered, washed with diethyl ether and dried it to yield 4 (yield 90%).^{1}H NMR (400 MHz, DMSO) δ 9.12 (s, 2H), 9.00 (d, J = 4 Hz, 2H), 8.64 (d, J = 8 Hz, 2H), 8.41 (t, J = 8 Hz, 4H), 8.12 (d, J = 8 Hz, 2H), 7.88-7.71 (m, 6H), 6.86 (t, J = 6 Hz, 2H), 6.55 (s, 2H), 6.09 – 5.98 (m, 2H), 5.33 – 5.22 (m, 6H), 5.11 (d, J = 16 Hz, 2H), 4.00 (t, J = 16 Hz, 4H), 3.58-3.50 (m, 2H), 3.11 (d, J = 8 Hz, 2H), 2.67 (d, J = 8 Hz, 2H), 2.33 (t, J = 12Hz, 2H), 1.91 (s, 2H), 1.79 (d, J = 8 Hz, 2H), 1.08 (t, J = 8 Hz, 2H), 0.87 (t, J = 8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO) δ_C 155.60, 153.60, 150.14, 147.99, 144.89, 142.76, 137.05, 129.42, 128.79, 127.29, 125.02, 124.33, 120.75, 120.08, 118.94, 117.03, 67.38, 64.68, 59.37, 55.92, 54.08, 36.69, 27.51, 26.34, 22.98. ESI-MS (M+) ; 931.28.

2.1.3: Synthesis of cinchona (contains free -OH) based CPTC –palladium catalyst (5)

A mixture of 4 (2.0 g, 1.73 m mol), palladium acetate (0.4g), DMF (10 mL) were stirred at 100°C for about 16h. The solvent was then removed under reduced pressure and the residual mass was diluted with diethyl ether (50 mL), filtered and washed thoroughly with diethyl ether (25 mL). It was then dried under vacuum for 12h until constant weight. The yield was (2.1 g, 88%).

3.1 General procedure for the oxidation of alcohols (7b to 23 b).

A mixture of alcohol (6.0 mmol), Toluene (5.0 mL), K_2CO_3 (5 mol %) and catalyst 5 (1 mol %) were pressurised in a mini-clave apparatus using oxygen gas (5 bar) at 80°C for about 8h. The reaction is monitored by GC for reaction completion. The mass is then removed from the reactor filtered over hyflo bed and diluted with water (20 mL). It is then extracted using diethyl ether (10 mL x 2). The combined organic layers were washed with water (5 mL x s), dried over sodium sulphate and concentrated to remove solvent. Then it was purified by column chromatography using silica gel 60-120 mesh size (Hexane: Ethyl acetate) as an eluent or by distillation using Kugelrohr instrument. The purified product is then analysed by NMR and mass to confirm the product.

4.0 Characterization of products

4.1: 2-Methylbenzaldehyde (7b)

Colourless Liquid. Yield: 84.0%. GC purity: 94.6%. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.26 (s, 1H), 7.79 (dd, J = 7.6, 1.5 Hz, 1H), 7.47 (td, J = 7.5, 1.6 Hz, 1H), 7.36 (td, J = 7.5, 1.2 Hz, 1H), 7.28 – 7.22 (m, 1H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 192.73, 140.53, 134.07, 133.58, 131.98, 131.70, 126.25, 19.52.

4.2: 4-Methylbenzaldehyde (8b)

Colourless Liquid. Yield :89.5%. GC purity: 93.7%. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.96 (s, 1H), 7.77 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 191.94, 145.49, 134.13, 129.71, 21.83.

4.3: 2-Methoxybenzaldehyde (9b)

Pale yellow Liquid. Yield: 80.5%. GC purity: 94.2% ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.45 (s, 1H), 7.80 (dd, J = 7.7, 1.8 Hz, 1H), 7.52 (ddd, J = 8.2, 7.4, 1.8 Hz, 1H), 7.08 – 6.90 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 189.62, 161.75, 135.83, 128.38, 124.80, 120.55, 111.58, 55.53.

4.4: 4-Methoxy benzaldehyde (10b)

Pale brown oil. Yield: 86.6%. GC purity: 99.10 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.88 (s, 1H), 7.88-7.86 (d, J = 8 Hz, 2H), 7.18-7.16 (d, J = 8 Hz, 2H), 3.83 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 55.8,114.8,129.2,132.3,166.4,191.0.

4.5: 3-Methoxy-4-hydroxy benzaldehyde (11b)

Off-white solid. Yield: 73.5%. GC purity: 99.62%, $^{1}HNMR$ (400 MHz, $CDCl_3$) δ_H 9.81 (s, 1H), 7.43-7.41 (d, J = 8Hz,1H), 7.05-7.03 (d, J = 8Hz, 1H), 6.75 (s, 1 H), 5.65 (s, 1H), 3.93 (s, 3H), 4.22 (s,1H), 3.83 (s,3H), ^{13}C NMR (100 MHz, CDCl3) δ_C 191.16, 151.93, 147.30, 129.73, 127.58, 114.55, 108.96, 56.08.

4.6: 2-Fluorobenzaldehyde (12b)

Yellow liquid, Yield :61.99%, GC Purity: 98.25%. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.37 (d, J = 0.8 Hz, 1H), 7.88 (td, J = 7.4, 1.9 Hz, 1H), 7.61 (dddd, J = 8.4, 7.3, 5.4, 1.9 Hz, 1H), 7.33 – 7.09 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.12, 166.34, 162.92, 136.29, 128.64, 124.58, 116.45.

4.7: 3-Fluorobenzaldehyde (13b)

Yellow liquid, Yield :61.99%, GC Purity: 98.25%. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.00 (d, J = 1.9 Hz, 1H), 7.69 (dt, J = 7.5, 1.3 Hz, 1H), 7.61 – 7.48 (m, 2H), 7.39 – 7.26 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 190.82, 164.69, 161.38, 138.36, 130.74, 126.00, 121.52, 115.27.

4.8: 4-Fluorobenzaldehyde (14b)

Yellow liquid, Yield :76.58%, GC Purity: 90.56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.98 (s, 1H), 7.92 (dd, J = 8.7, 5.4 Hz, 2H), 7.22 (t, J = 8.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 190.45, 168.16, 164.76, 132.91, 132.18, 116.30

4.9: 2-Chlorobenzaldehyde (15b)

Light Brown Liquid, Yield: 69.6 %. GLC purity: 92.11% ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.47 (d, J = 0.8 Hz, 1H), 7.91 (dd, J = 7.7, 1.8 Hz, 1H), 7.53 (ddd, J = 8.0, 7.1, 1.8 Hz, 1H), 7.48 – 7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 189.67, 137.81, 135.03, 132.32, 130.49, 129.24, 127.18.

4.10: 4-Chlorobenzaldehyde (16b)

Light brown solid. Yield: 78.5%. GLC purity: 97.7%. MP: 46-50°C (Litt: 47-51°C) ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.98 (s, 1H), 7.82 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 190.75, 140.81, 134.61, 130.80, 129.34.

4.11: 2,3- Dichloro benzaldehyde (17b)

Pale yellow solid, Yield: 82.6 %, GC purity: 90.15 % (decomposes upon storage), MP 62- 65°C (64-67°C, Litt). ^{1}HNMR (400 MHz, $CDCl_3$) δ_H 10.47 (s, 1H), 7.84-7.82 (d, J = 8Hz,1H), 7.71-7.69 (d, J = 8Hz, 1H),7.33-7.37 (t, J = 6Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 189.34, 136.02, 135.59, 134.33, 134.20, 127.42, 127.60.

4.12: 2-Nitrobenzaldehyde(18b)

Brown solid, Yield: 88%; GLC purity: 95.89%, mp 42-44°C (reported 42- 44^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.41 (s, 1H), 8.12-8.10 (m, 1H), 7.95-7.93 (m, 1H), 7.81-7.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 188.31, 149.69, 134.22, 133.84, 131.45, 129.75, 124.62.

4.13: 3-NitroBenzaldehyde (19b)

Pale yellow solid, Yield: 58.6 %, GC purity: 92.64 %, MP 57.5-58.5°C (Litt : 57-58.5). ^{1}HNMR (400 MHz, $CDCl_3$) δ_H 10.14 (s, 1H), 8.72 (s, 1H), 8.51-8.49 (d, J = 8Hz, 1H), 8.27-8.25 (d, J = 8Hz, 1H),7.82-7.78 (t, J = 6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 189.83, 148.76, 137.38, 134.74, 130.44, 128.59, 124.40.

4.14: 4-t-butyl benzaldehyde(20b)

Colourless Liquid, Yield: 85.5%. GC purity: 90.41%, ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.88 (s, 1H), 7.83-7.81 (d, J = 8 Hz, 2H), 7.48-7.46 (d, J = 8 Hz, 2H), 1.35 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 31.3,34.2,125.5,129.5,133.8,157.1,193.0

4.15: 2,6-Dimethylbenzaldehyde (21b)

Pale brown Liquid, Yield: 78.66%. GC purity: 96.36%. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.62 (s, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 2H), 2.61 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.39, 140.99, 132.85, 132.30, 129.58, 20.34.

4.16: Mesitaldehyde (22b)

Colourless Liquid, Yield: 80.14%. GC purity: 95.87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.53 (s, 1H), 6.87 (s, 2H), 2.56 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.76, 143.66, 141.31, 130.38, 129.82, 21.31, 20.33.

4.17: 3,5-Dibromo-2,4,6-trimethylbenzaldehyde (23b)

Colourless solid; yield 68.8%; GC Purity: 95.45%. MP 162-164 °C (lit.2 160 °C, decomposes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 10.47 (s, 1H), 2.74 (s, 3H), 2.57 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 194.0, 142.5, 137.6, 135.0, 127.7, 26.9, 20.4.

4.18: 1-phenylethan-1-one (24b)/ (Acetophenone)

Colourless oil. Yield: 87.55%. GC purity: 99.73 % ^{1}HNMR (400 MHz, $CDCl_3$) δ_H 7.94-7.57 (m,5H), 2.52 (s,3H). 13C NMR (100 MHz, CDCl3) δ_C 197.11, 133.14, 128.80, 128.64, 26.45.

4.19: Propiophenone (25b)

Colourless liquid, Yield: 82.33%. GLC purity: 98.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_C 7.94-7.91 (m, 2H), 7.53-7.48 (m, 1H), 7.43-7.39 (m, 2H), 2.95 (q, J1 = J2 = 7.2 Hz, 2H), 1.19 (t, J1 = J2 = 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 200.79, 136.90, 132.86, 128.54, 127.95, 31.75, 8.22.

4.20: Benzophenone (26b)

Colourless solid; yield 88.12%; GLC purity: 97.32%. MP 48-50°C, reported 47-51^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.81-7.79 (m, 2H), 7.60-7.56 (m, 1H), 7.50-7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 196.89, 137.72, 132.53, 130.17, 128.39.

4.21: Cyclohexanecarbaldehyde (27b)

Pale yellow Liquid; yield 83%; GLC Purity: 95.23% ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.59 (s, 1H), 2.24-2.19 (m, 1H), 1.90-1.20 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 205.17, 50.07, 26.08, 26.02, 25.12

4.22: Cyclohexanone (28b)

Colourless liquid; yield: 81%; 1H NMR (400 MHz, CDCl3): δ_H 4.49-4.39 (m, 1H), 3.33-2.90 (m, 1H), 2.41- 2.12 (m, 3H), 2.11-1.61 (m, 4H); 13C NMR (100 MHz, CDCl3): δ_C 211.52,42.00, 27.11, 25.07.

4.23: Cyclohexane-1,4-dione (29b)

Colourless solid; yield 97%; MP: 75-77^{o}C (reported 77-78.5 oC); 1H NMR (400 MHz, CDCl3): δ 2.67 (s, 4H); 13C NMR (100 MHz, CDCl3): δ 208.51, 36.73.

4.24: Cyclododecanone (30b)

Colourless solid, Yield: 70.6%. GC purity: 99.76%. MP 57-59°C (reported 58-60°C). ^{1}HNMR (400 MHz, $CDCl_3$) δ_H 2.48-2.45(m, 4H), 1.74-1.68 (m, 4H), 1.28-1.30 (m, 14 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 212.88, 40.25, 24.73, 24.58, 24.20, 24.20, 22.54, 22.31.

4.25 Piperonyl aldehyde (31b)

Light yellow waxy solid, Yield : 86.25%, GC purity : 96.78%, MP : 35-39°C (reported : 37-39°C) ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.30 (s, 1H), 7.16 (dd, J = 8.1, 1.7 Hz, 1H), 7.14

(d, J = 1.7 Hz, 1H), 6.62 (d, J = 8.1 Hz, 1H), 5.99 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 186.81, 152.20, 151.48, 146.02, 128.14, 107.47, 105.06, 103.89.

4.26: 4-Acetamidobenzaldehyde (32b)

Brown solid (slight decomposition observed in storage), Yield: 78.99%, GC purity: 98.25%, MP: 146-152°C (reported: 148-152°C)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.91 (s, 1H), 8.00 (s, 1H), 7.89 – 7.79 (m, 2H), 7.71 (d, J = 8.4 Hz, 2H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 191.14, 168.86, 143.62, 132.14, 131.14, 119.22, 24.76

4.27: 4-(Trifluoromethyl)benzaldehyde (33b)

Light brown Liquid, Yield: 74.52%, GC purity : 92.9%.^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.09 (s, 1H), 8.00 (dt, J = 7.9, 0.9 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 191.07, 138.63, 135.79, 135.36, 129.89, 126.11, 121.60, 117.99.

4.28: 2,4-Bis(trifluoromethyl)benzaldehyde (34b)

Yellow Liquid, Yield: 58.23%, GC purity: 87.25%, ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.04 (d, J = 0.5 Hz, 1H), 8.06 (d, J = 1.5 Hz, 1H), 7.90 (dd, J = 7.5, 0.5 Hz, 1H), 7.72 (dd, J = 7.5, 1.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 189.42, 134.81, 134.80, 134.74, 133.42, 133.17, 129.59, 129.57, 129.56, 129.54, 126.95, 126.92, 126.88, 126.85, 125.22, 125.19, 125.16, 125.13, 124.91, 123.66, 122.76.

4.29: 4-Biphenylcarboxaldehyde (35b)

Yellow solid, Yield: 86.54%, GC Purity: 98.66%, MP: 58-62°C (reported: 57-59°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.06 (s, 1H), 7.96 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.68 – 7.60 (m, 2H), 7.53 – 7.36 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 191.84, 147.13, 139.65, 135.15, 130.21, 128.96, 128.42, 127.63, 127.3.

4.30: 2-Pyridinecarboxaldehyde (36b)

Brown Liquid, Yield: 82.77%, GC purity: 96.35%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.81 (dt, J = 4.8, 1.3 Hz, 1H), 7.98 (dt, J = 7.8, 1.2 Hz, 1H), 7.91 (td, J = 7.6, 1.6 Hz, 1H), 7.57 (ddd, J = 7.4, 4.8, 1.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 193.20, 152.60, 150.02, 136.89, 127.70, 121.51.

4.31: 4-Pyridinecarboxaldehyde (37b)

Yellow Liquid, Yield : 76.25%, GC purity : 91.25%, ^{1}H NMR (400 MHz, $CDCl_3$) δ_C 9.98 (s, 1H), 8.77 (d, J = 6.0 Hz, 2H), 7.60 (d, J = 6.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_H 191.29, 150.97, 141.15, 121.85.

4.32: 3-Pyridinecarboxaldehyde(38b)

Light brown liquid (darkens upon storage), Yiled : 68.5%, GC purity : 89.23%. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.04 (s, 1H), 8.99 (d, J = 2.1 Hz, 1H), 8.75 (dd, J = 4.9, 1.8 Hz,

1H), 8.08 (dt, J = 7.9, 2.0 Hz, 1H), 7.41 (dd, J = 7.9, 4.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 190.60, 154.55, 151.85, 135.58, 131.19, 123.87

4.33: 5-Nitrofuran-2-carbaldehyde (39b)

Colourless solid; yield 68%; MP:38-40^{o}C (reported 37-39^{o}C); ^{1}H NMR (400 MHz, CDCl3): δ_H 9.82 (s, 1H), 7.41 (d, J = 4 Hz, 1H), 7.34 (d, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl3): δ_C 178.45, 151.09, 118.92, 111.86.

4.34 1-Napthaldehyde (40b)

Light brown Liquid, Yield: 86.23%, GC purity : 96.18%,^{1}H NMR (400 MHz, $CDCl_3$) δ_H 10.38 (s, 1H), 9.26 (dd, J = 8.6, 1.1 Hz, 1H), 8.08 (dt, J = 8.2, 1.0 Hz, 1H), 8.01 – 7.83 (m, 2H), 7.79 – 7.44 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 193.45, 136.60, 135.19, 133.60, 131.27, 130.41, 128.97, 128.38, 126.86, 124.77.

4.35 2-Naphthaldehyde (41b)

Pale yellow solid, Yield: 83.5%, GC purity: 94.68%, MP: 59-63°C (reported :59-61°C**)** ^{1}HNMR (400 MHz, $CDCl_3$) δ_H 10.16 (s, 1H), 8.34 (s, 1H), 8.05 – 7.84 (m, 4H), 7.62 (dddd, J = 17.6, 8.2, 6.9, 1.4 Hz, 2H); ^{13}C NMR (101 MHz, CDCl3) δ_C 192.23, 136.42, 134.5, 134.08, 132.61, 129.50, 129.08, 128.05, 127.07, 122.74.

NMR Spectra's

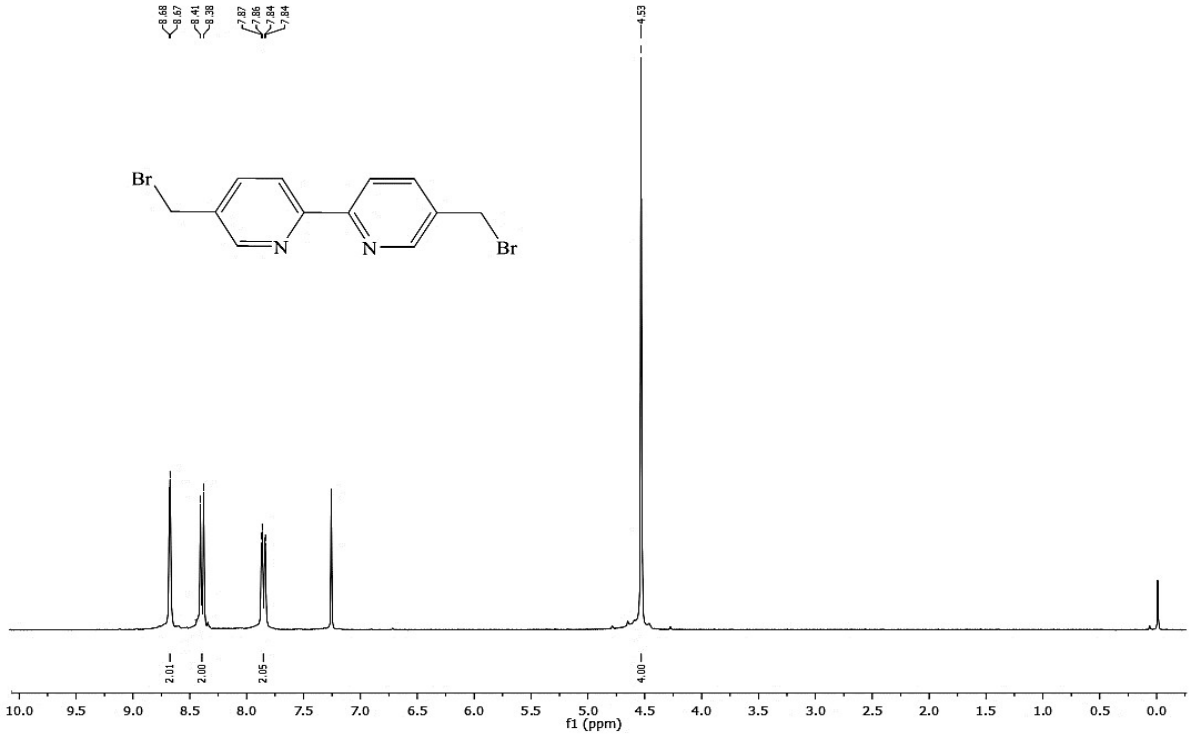

Figure 1 : ^{1}H NMR spectrum of 5,5′-bis(bromomethyl)-2,2′-bipyridine (2).

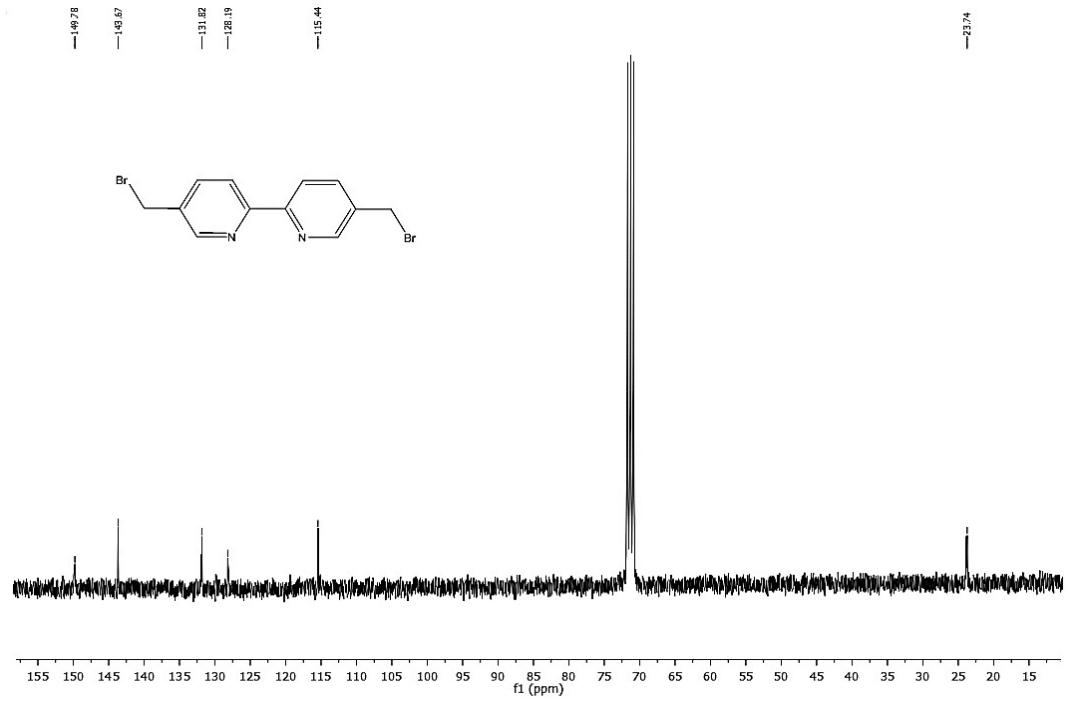

Figure 2 : ^{13}C NMR spectrum of 5,5′-bis(bromomethyl)-2,2′-bipyridine (2).

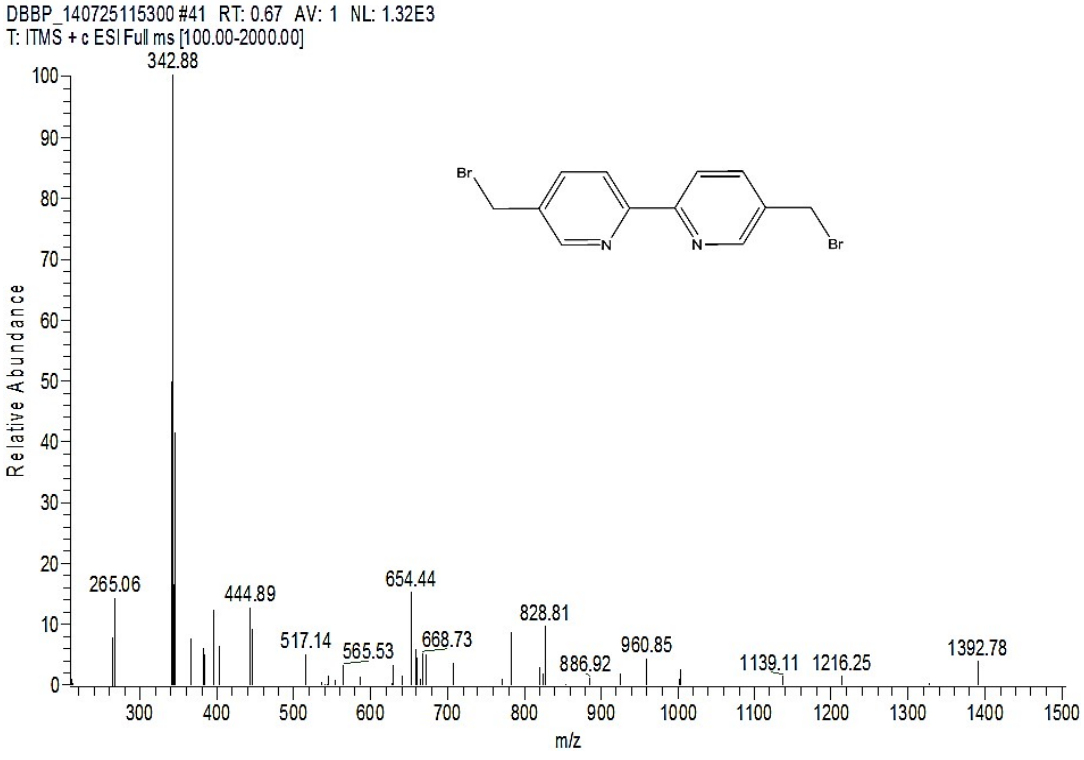

Figure 3.5: ESI - Mass spectrum of 5,5′-bis(bromomethyl)-2,2′-bipyridine (2).

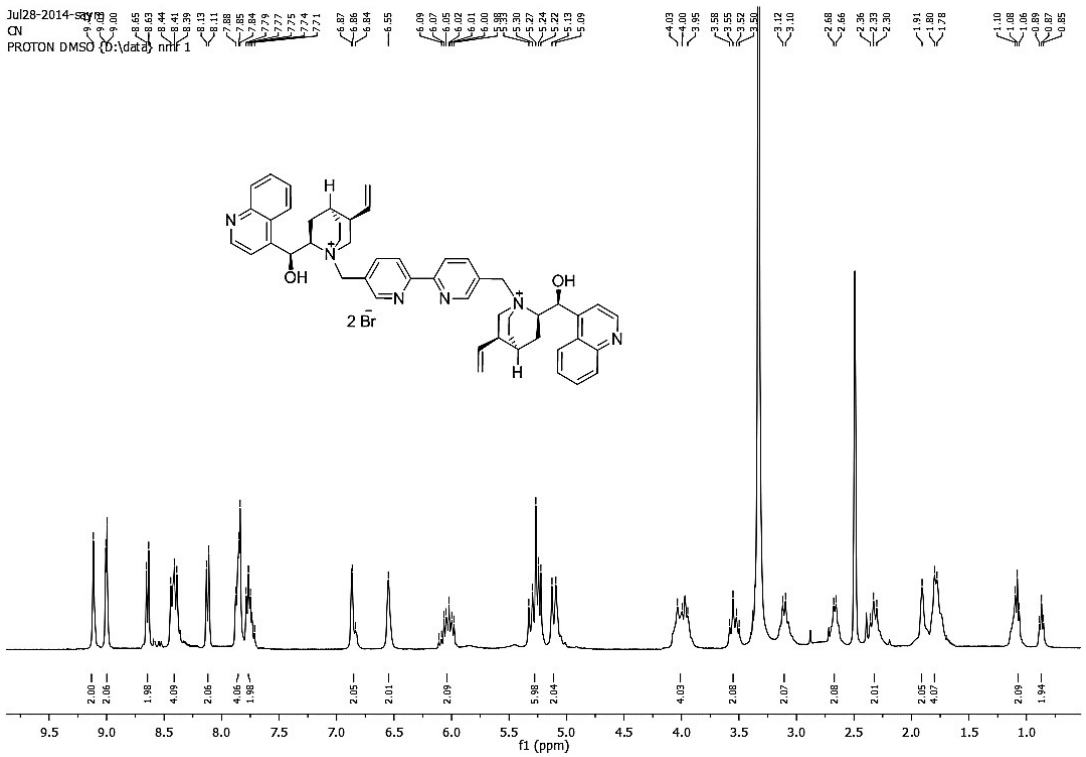

Figure 4: ^{1}H NMR spectrum of cinchonine (contains free -OH) based CPTC (4).

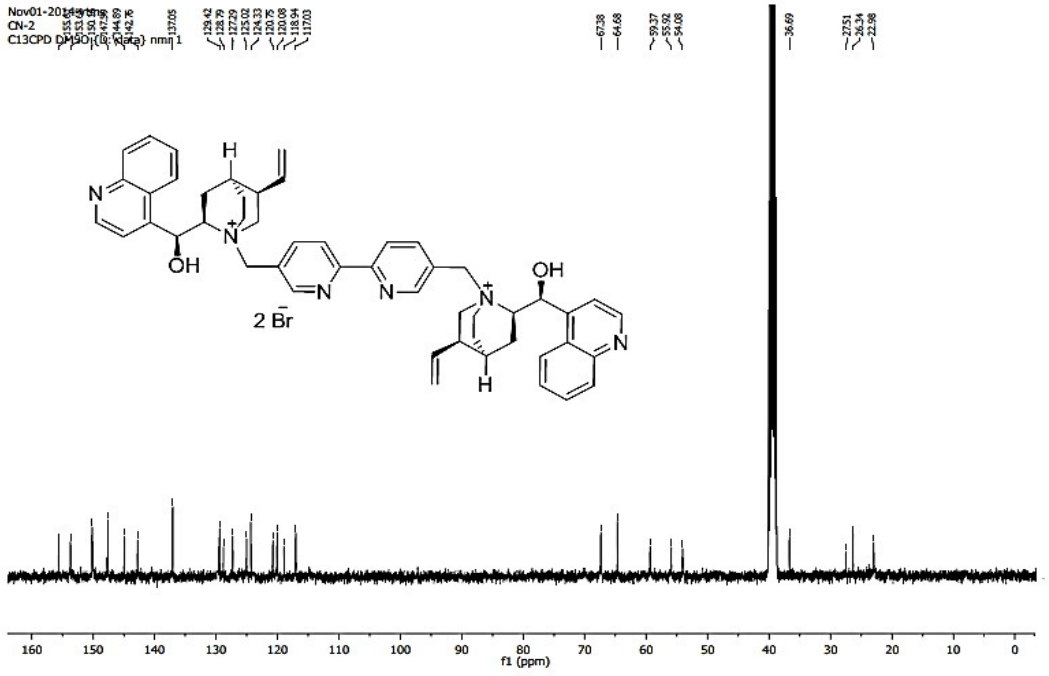

Figure 5 : ^{13}C NMR spectrum of cinchonine (contains free -OH) based CPTC (4).

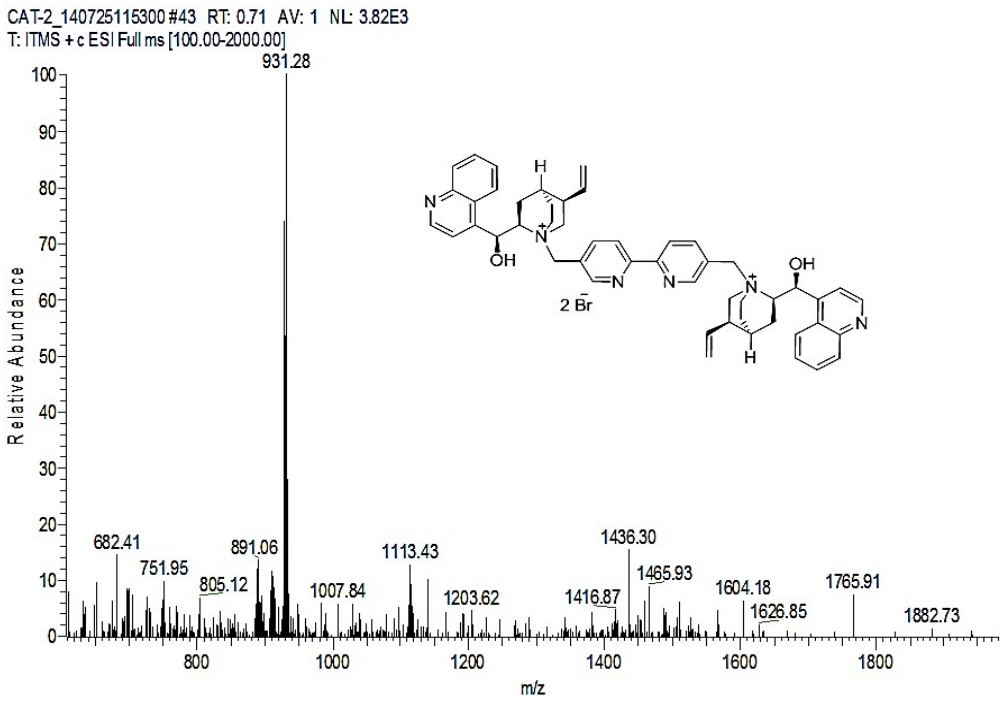

Figure 6 : ESI - Mass spectrum of cinchonine (contains free -OH) based CPTC (4).

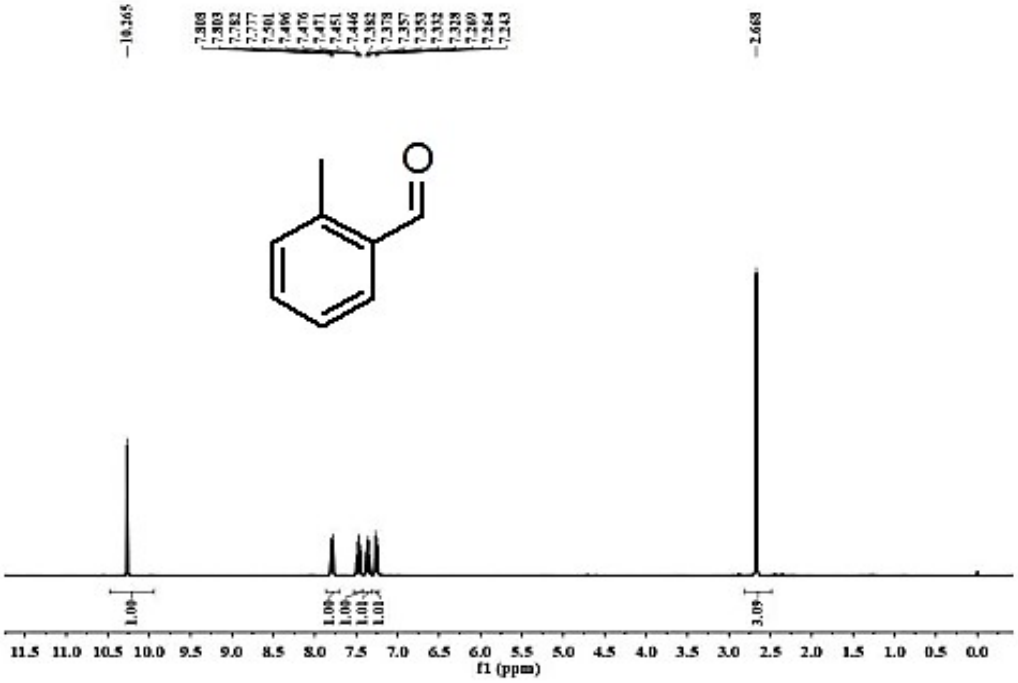

Figure 7: ^{1} H NMR spectrum of Entry 7b ($CDCl_3$,400 MHz).

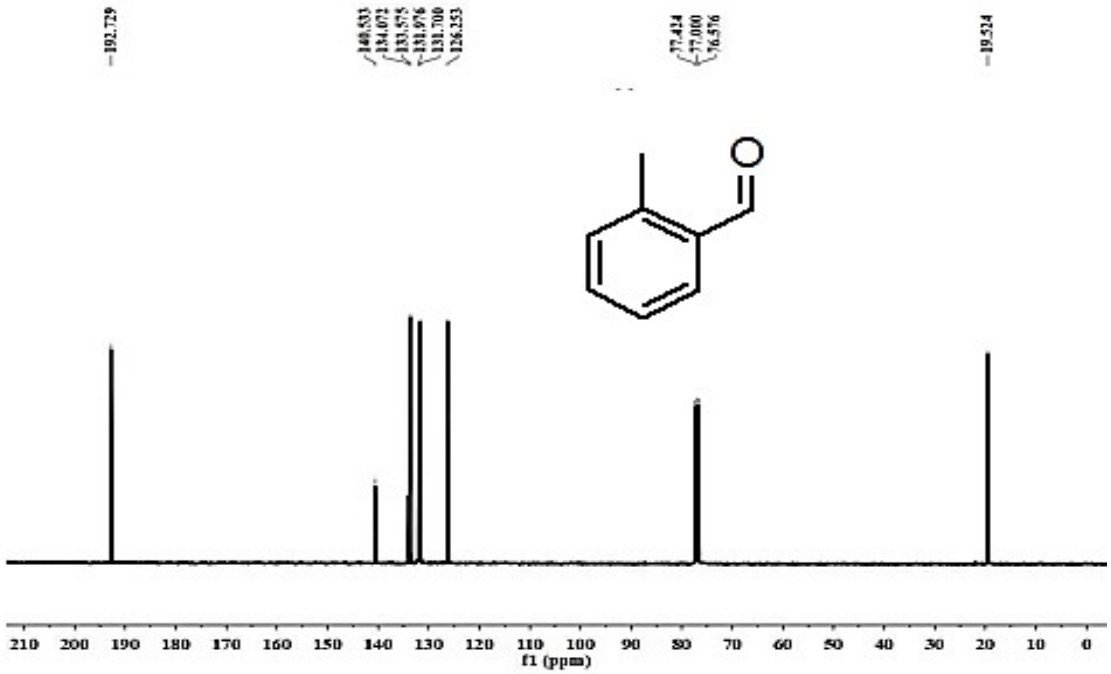

Figure 8 : ^{13} C NMR spectrum of Entry 7b ($CDCl_3$).

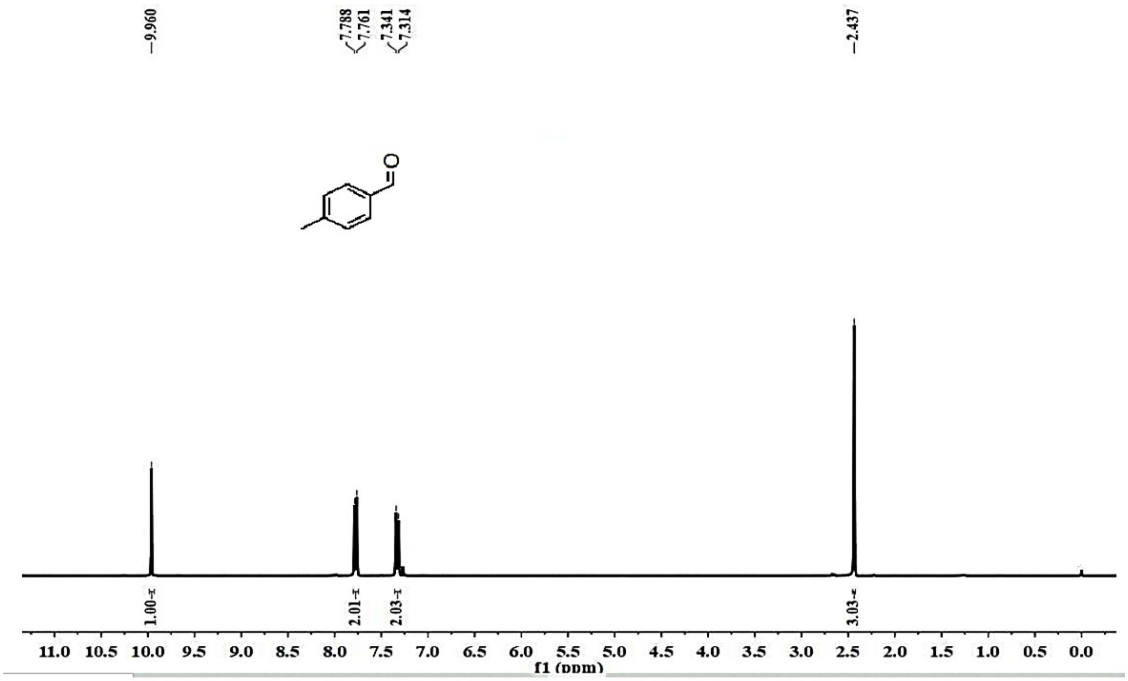

Figure 9: ^{1} H NMR spectrum of Entry 8b ($CDCl_3$,400 MHz).

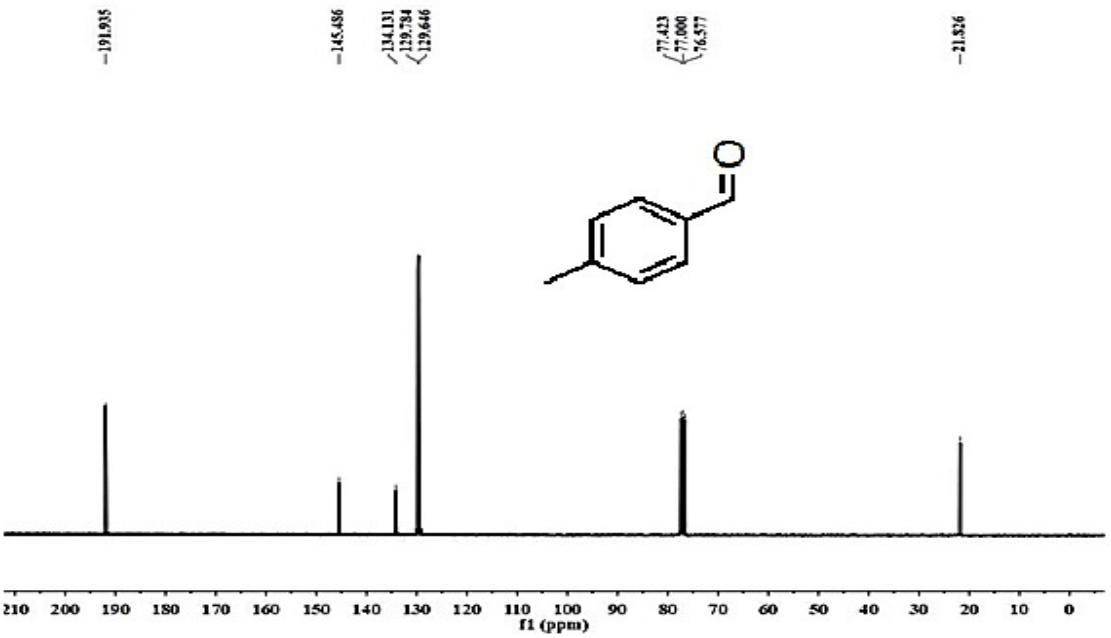

Figure 10 : ^{13} C NMR spectrum of Entry 8b ($CDCl_3$).

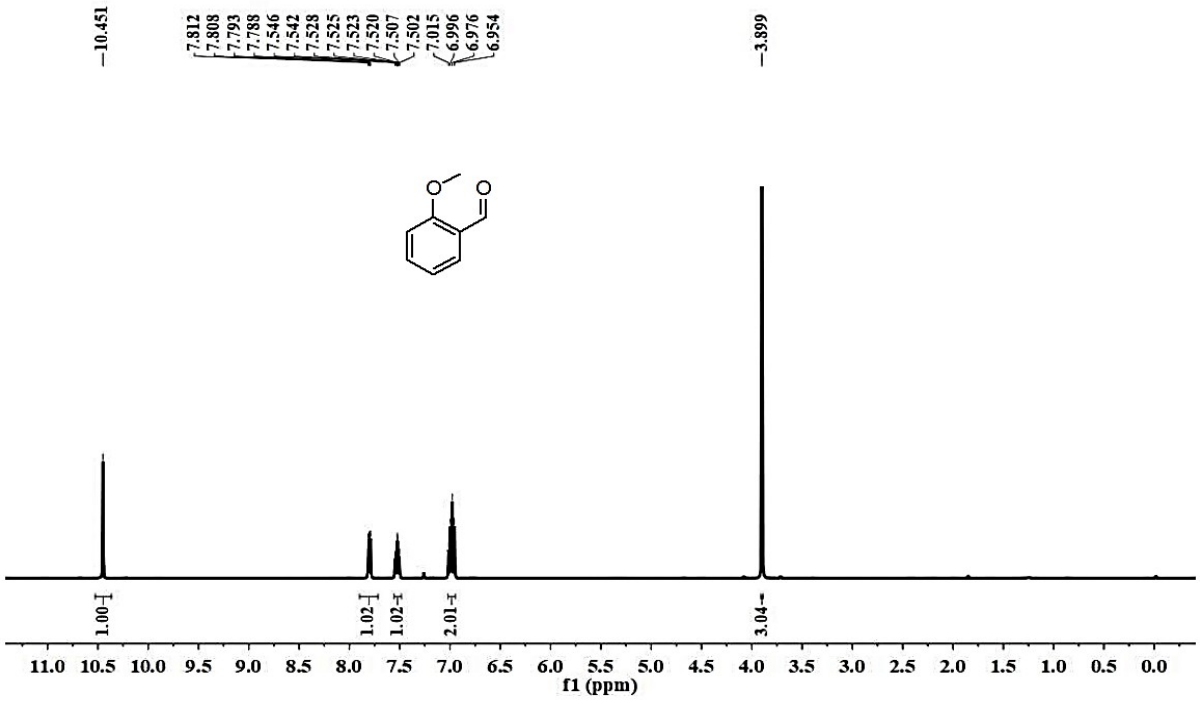

Figure 11: ^{1} H NMR spectrum of Entry 9b ($CDCl_3$,400 MHz).

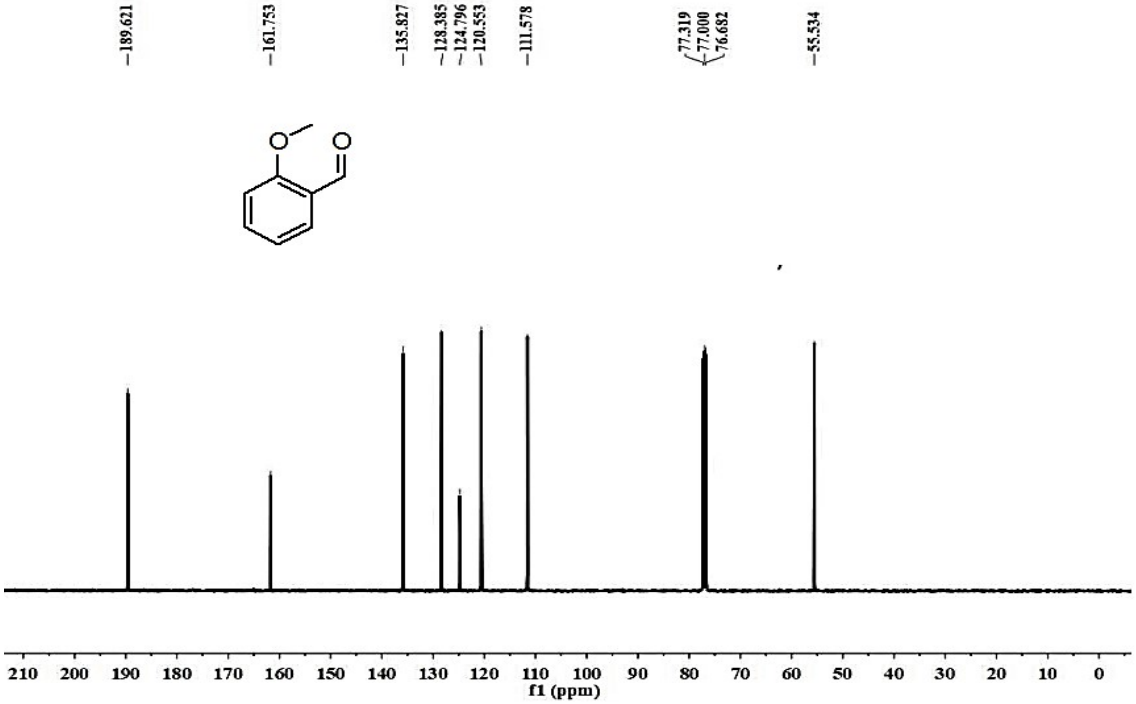

Figure 12 : ^{13} C NMR spectrum of Entry 9b ($CDCl_3$).

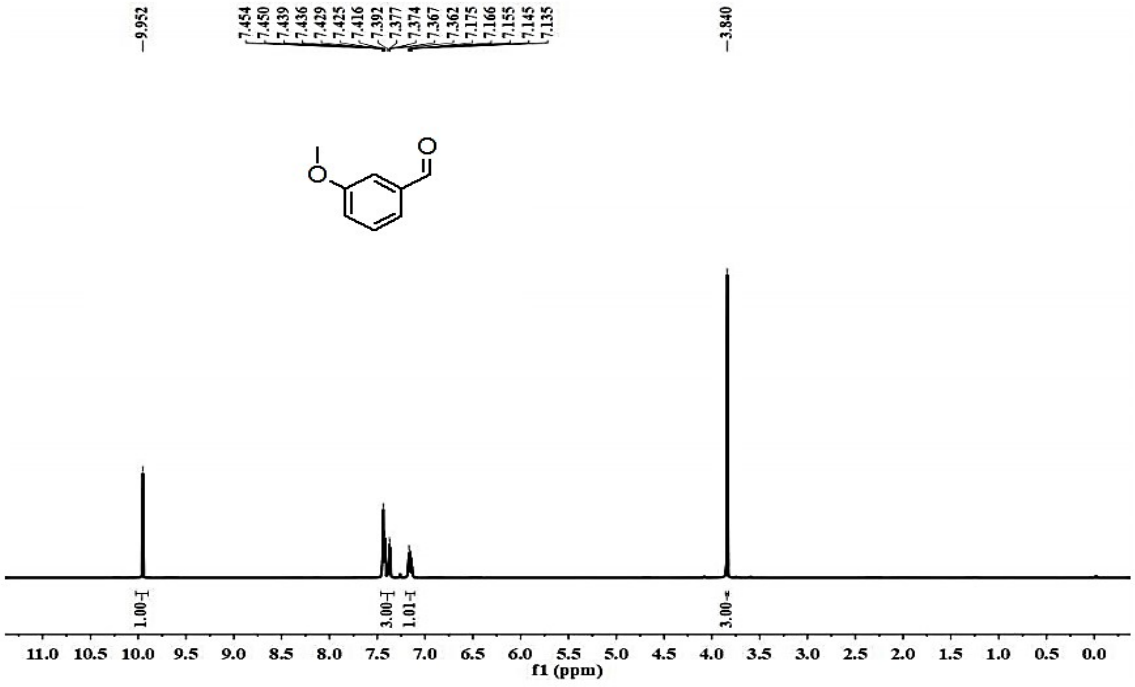

Figure 13: ^{1} H NMR spectrum of Entry 10b ($CDCl_3$,400 MHz).

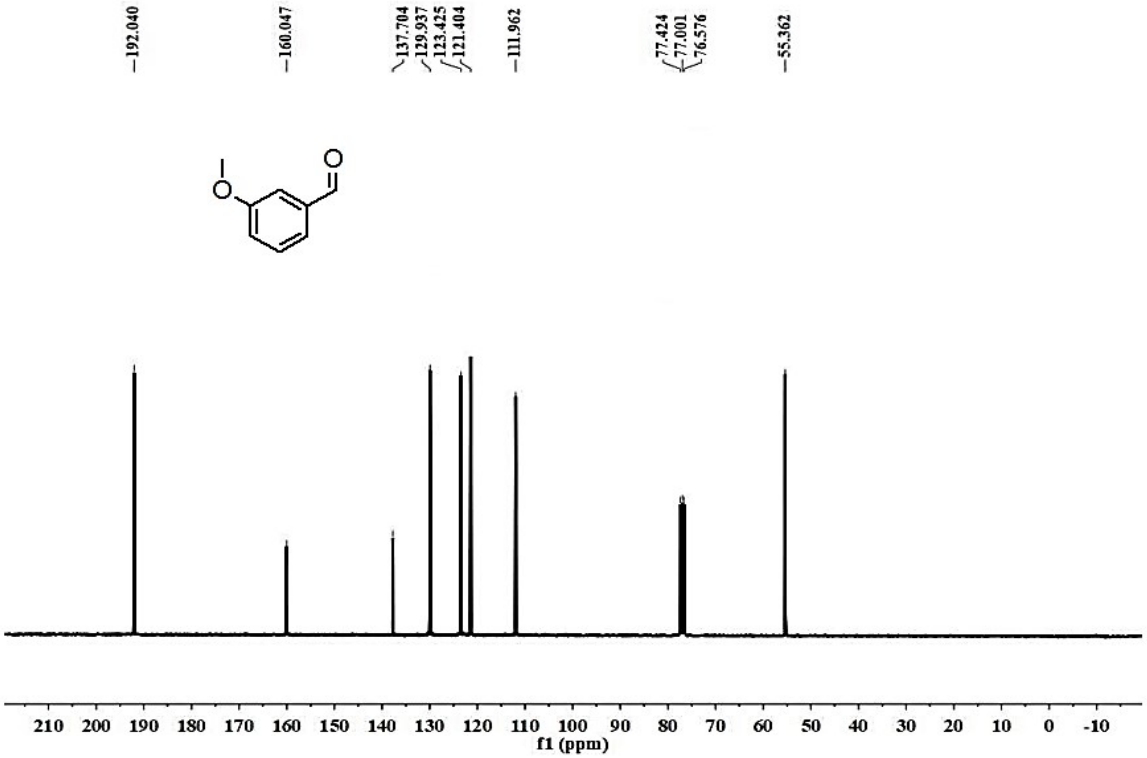

Figure 14 : ^{13} C NMR spectrum of Entry 10b ($CDCl_3$).

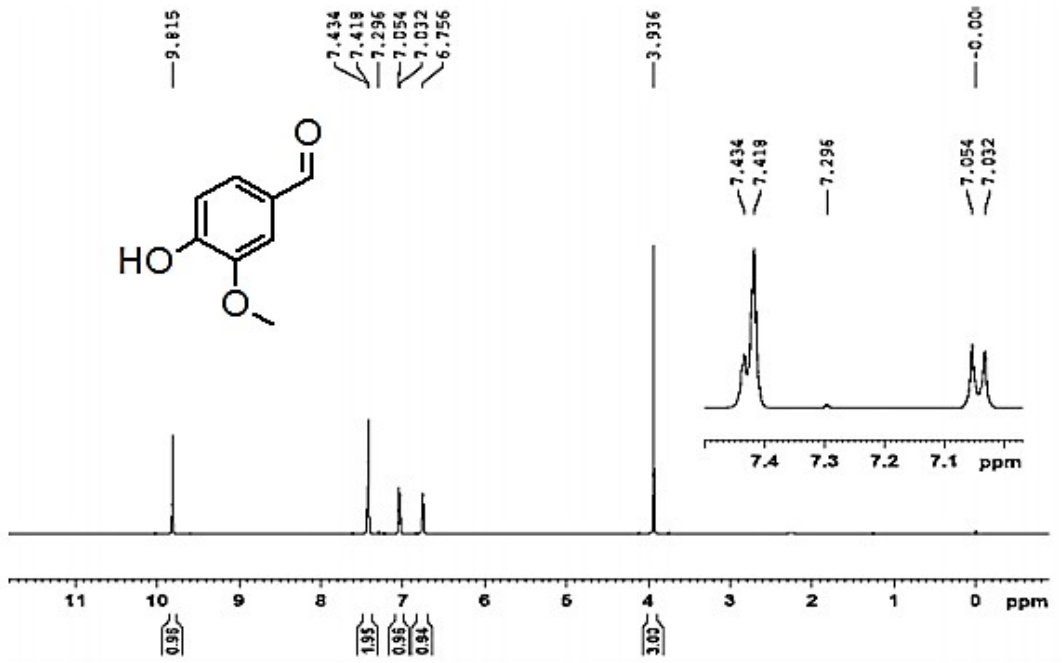

Figure 15: ^{1} H NMR spectrum of Entry 11b ($CDCl_3$,400 MHz).

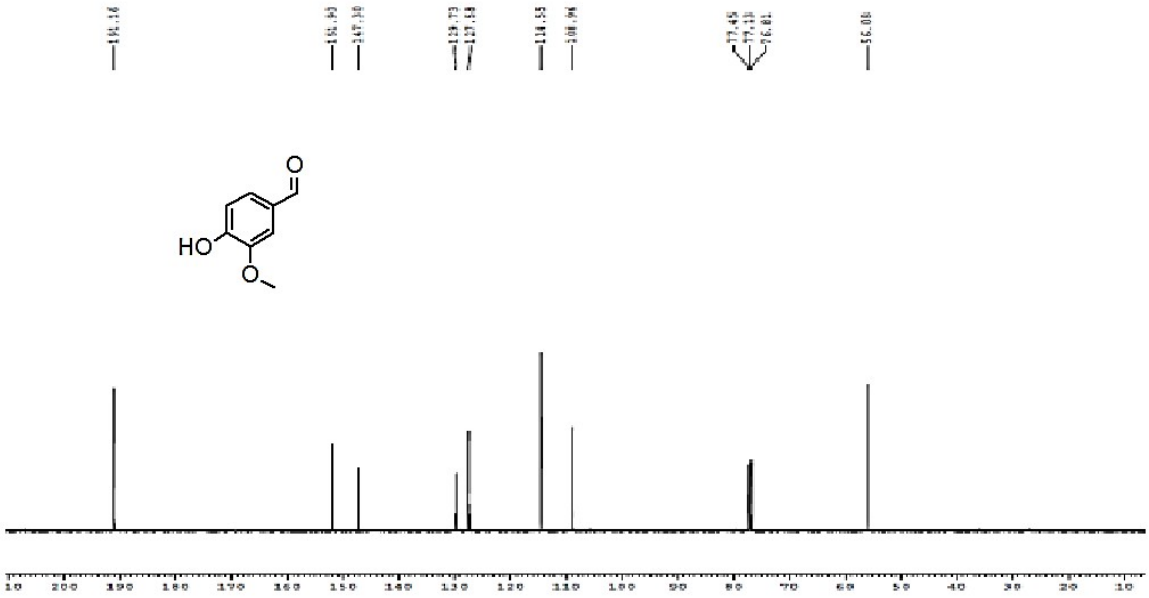

Figure 16 : ^{13} C NMR spectrum of Entry 11b ($CDCl_3$).

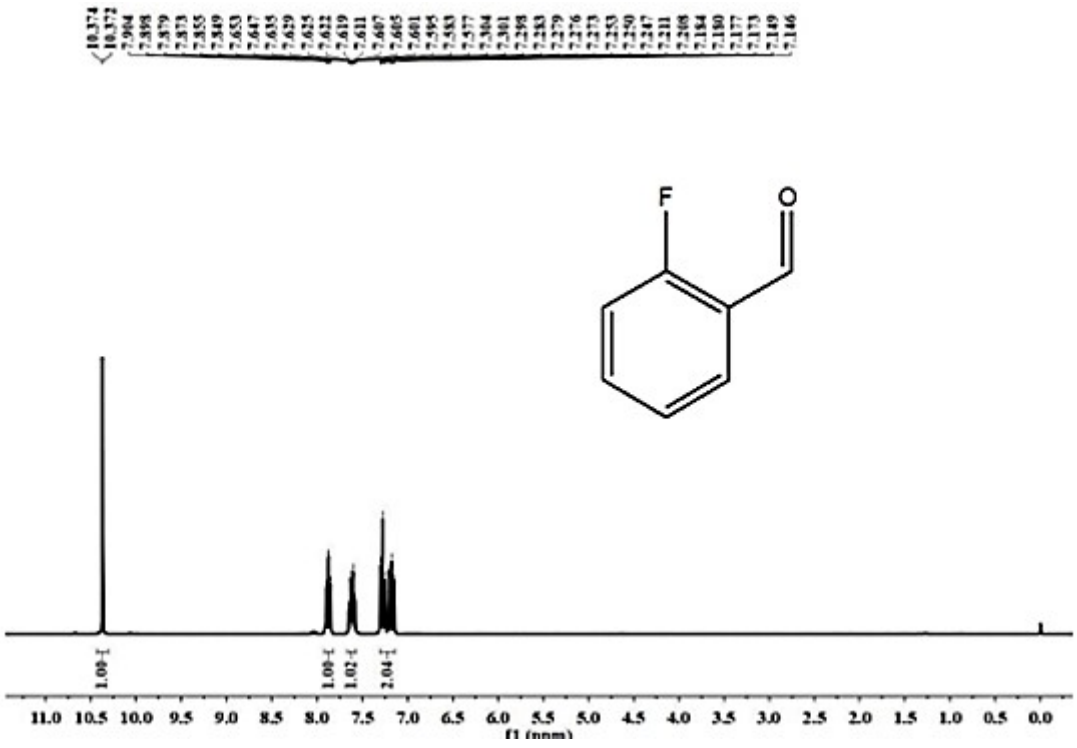

Figure 17: ^{1} H NMR spectrum of Entry 12b($CDCl_3$,400 MHz).

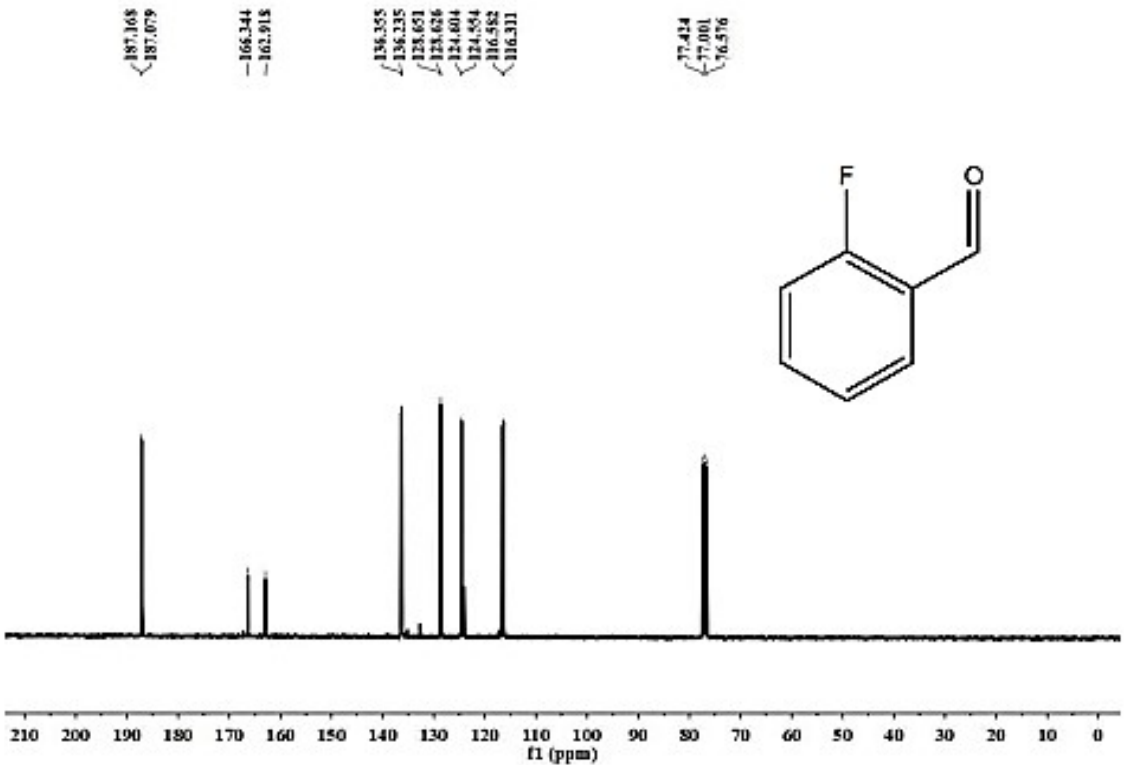

Figure 18 : ^{13} C NMR spectrum of Entry 12b ($CDCl_3$).

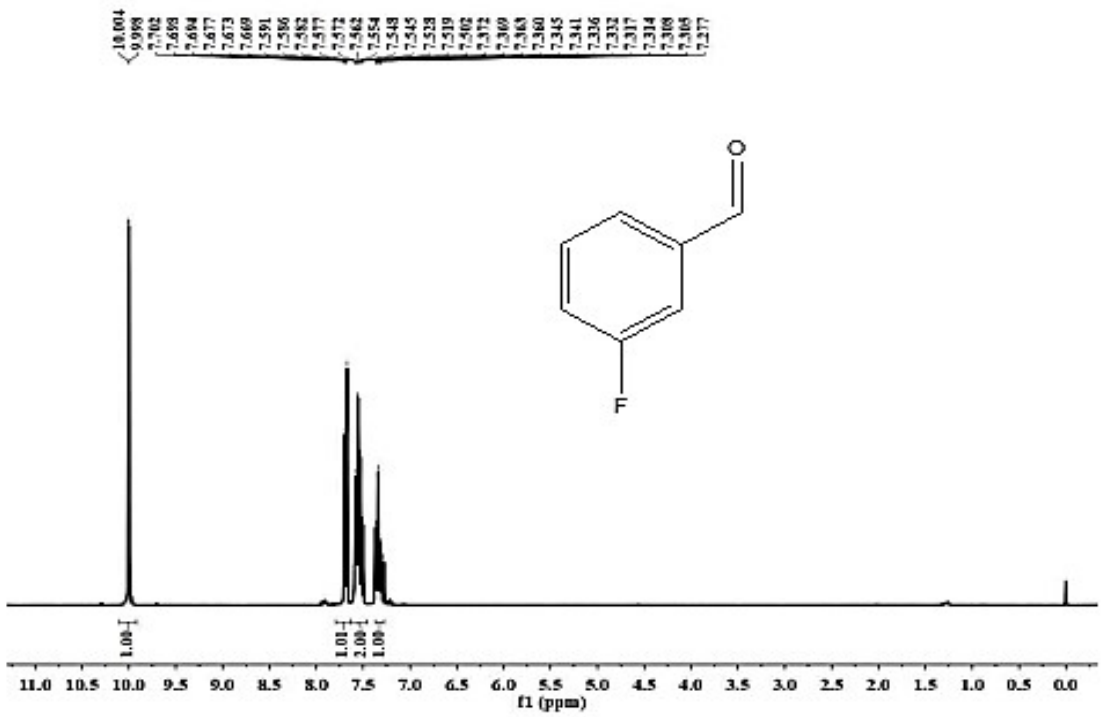

Figure 19: ^{1} H NMR spectrum of Entry 13b($CDCl_3$,400 MHz

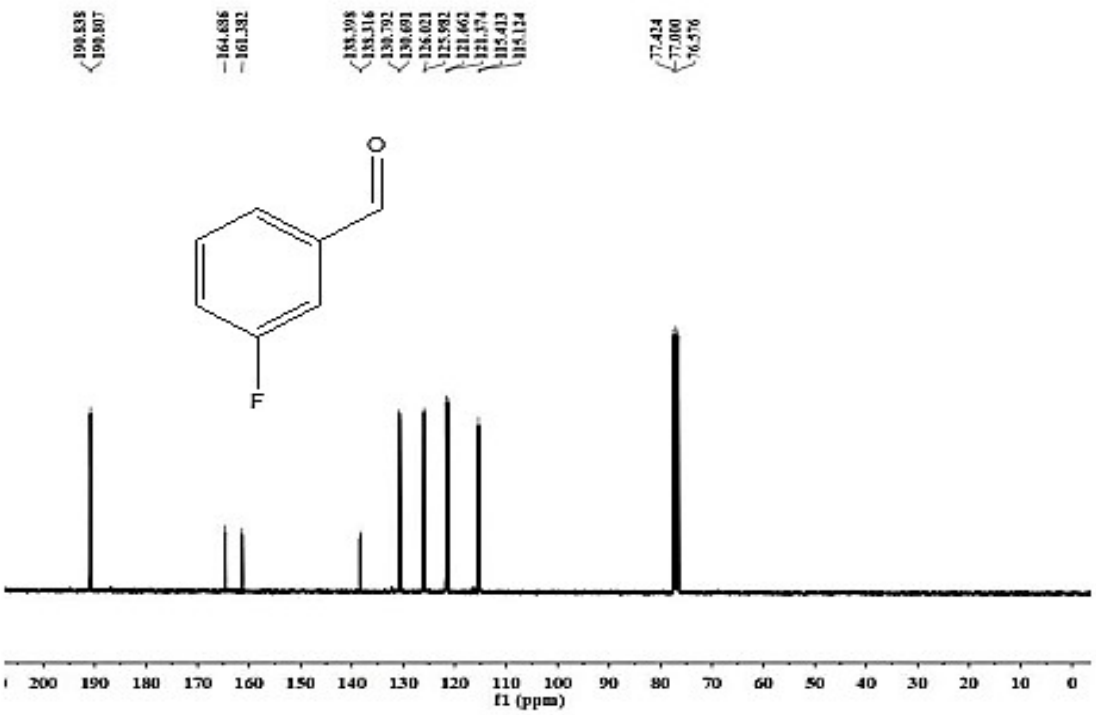

Figure 20 : ^{13} C NMR spectrum of Entry 13b ($CDCl_3$).

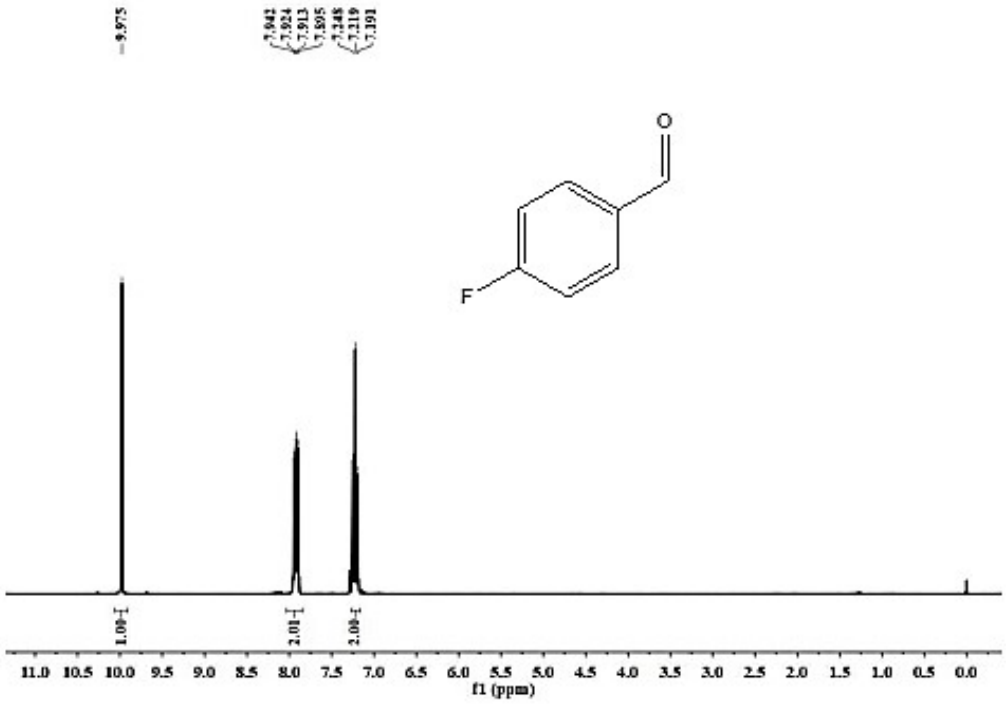

Figure 21: ^{1} H NMR spectrum of Entry 14b($CDCl_3$,400 MHz

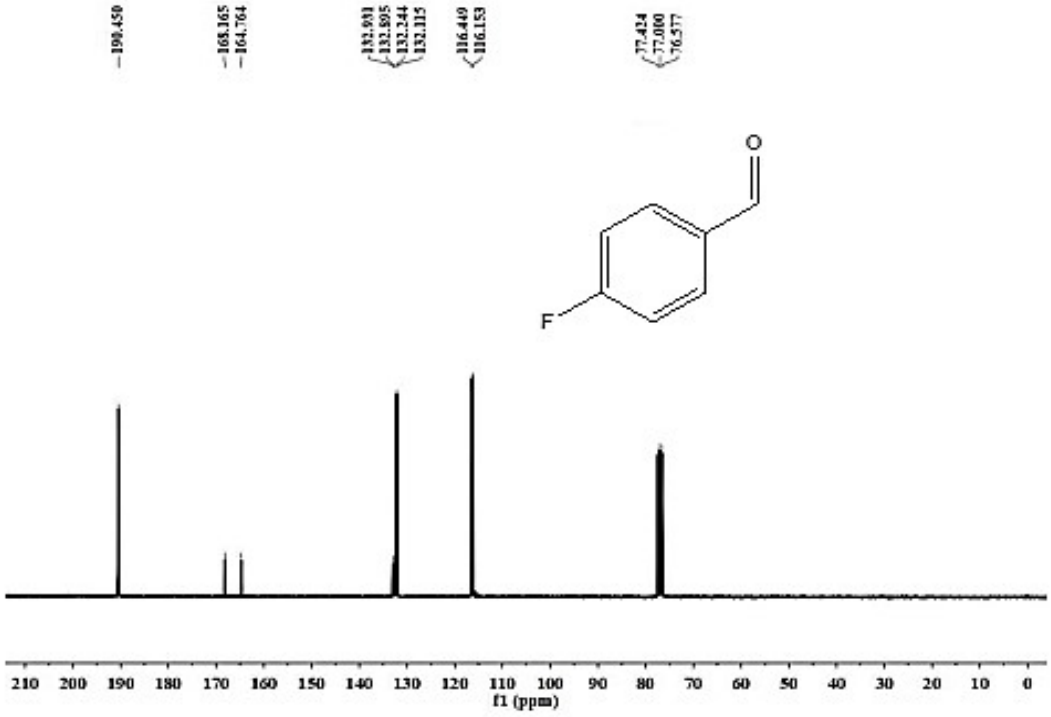

Figure 22 : ^{13} C NMR spectrum of Entry 14b ($CDCl_3$).

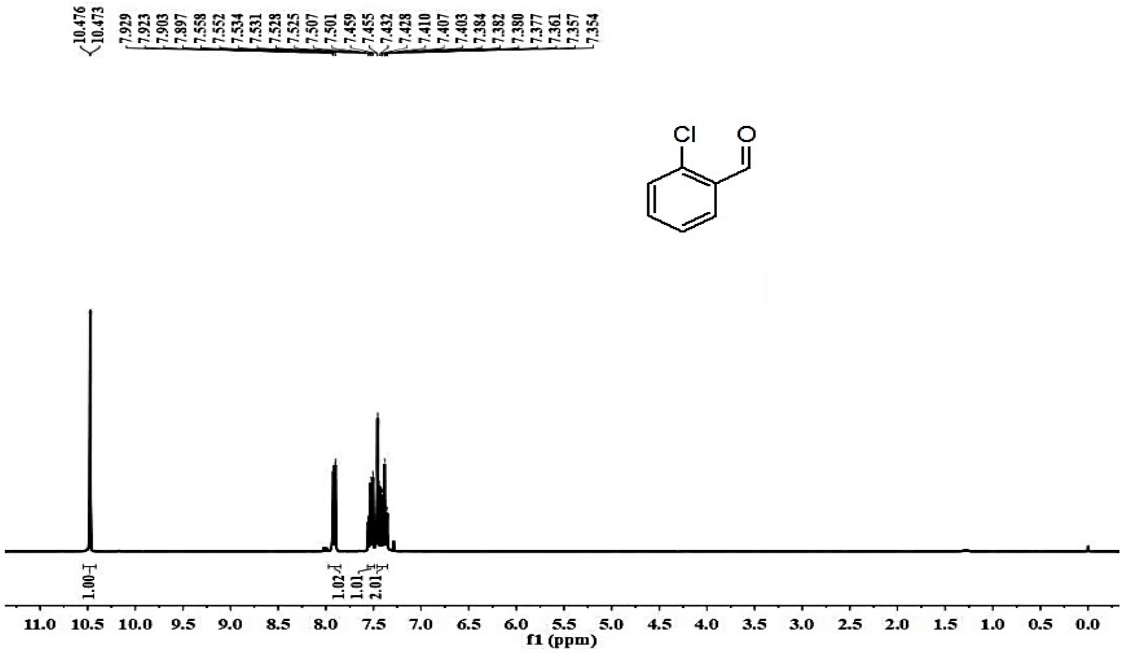

Figure 23: ^{1} H NMR spectrum of Entry 15b ($CDCl_3$,400 MHz).

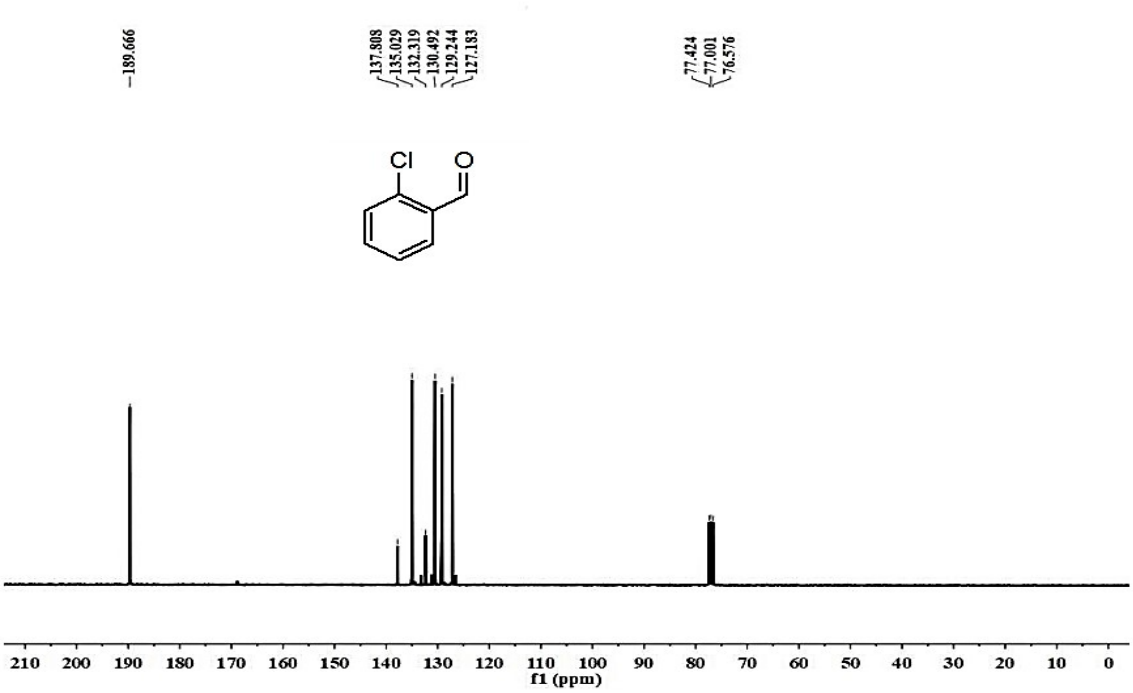

Figure 24 : ^{13} C NMR spectrum of Entry 15b ($CDCl_3$).

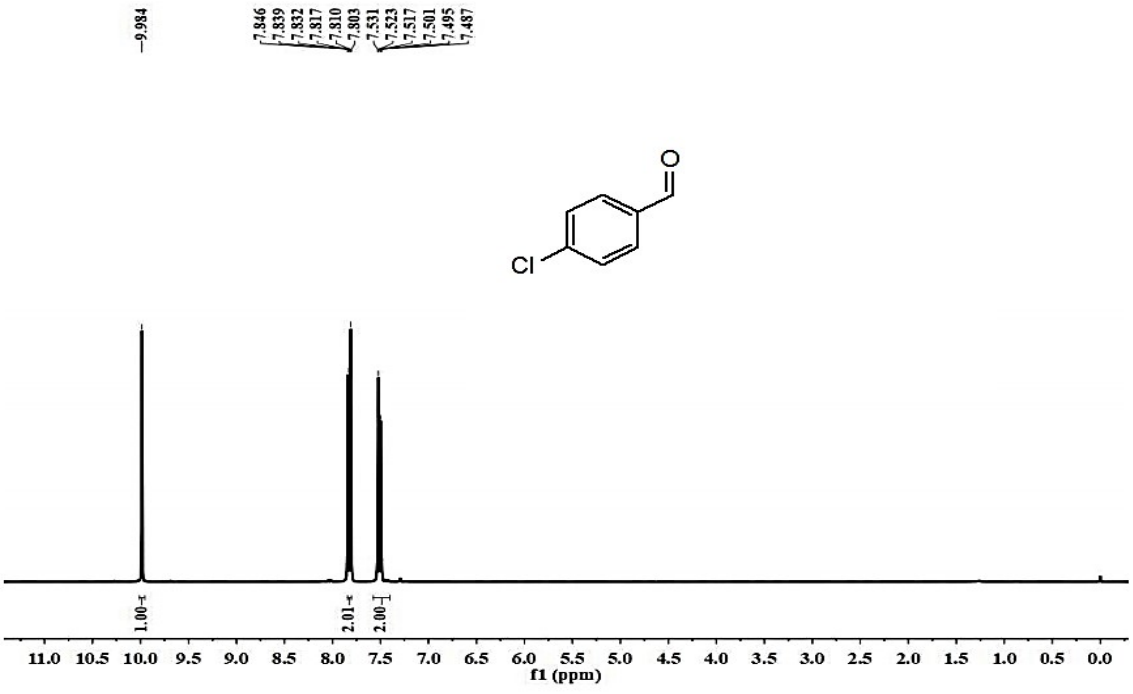

Figure 25: ^{1} H NMR spectrum of Entry 16b ($CDCl_3$,400 MHz).

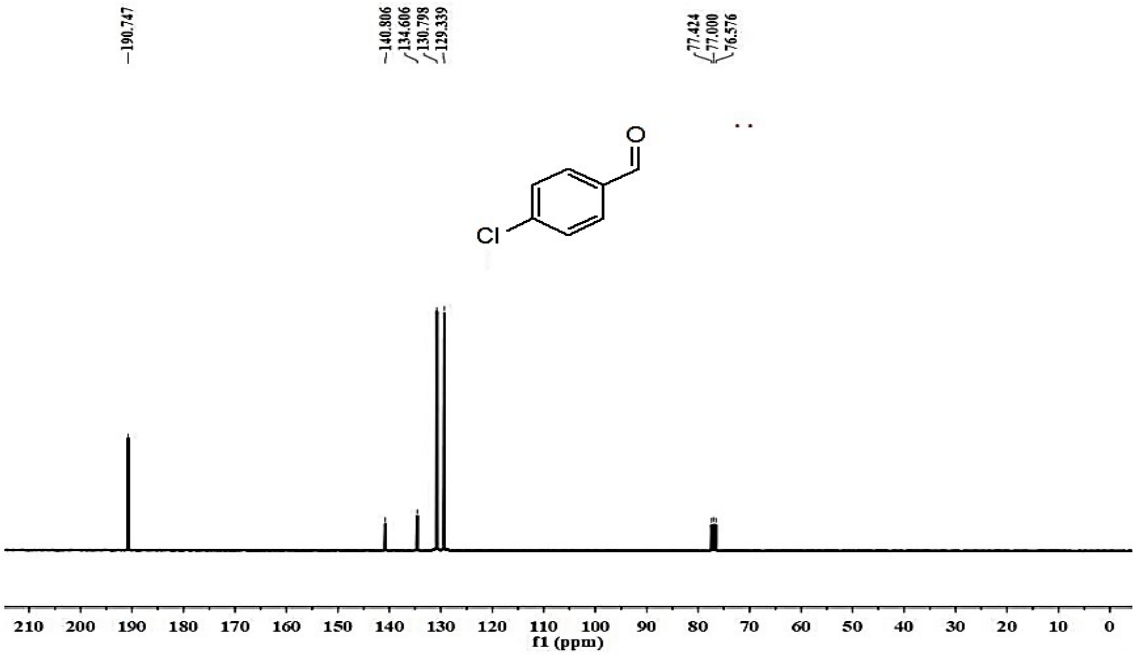

Figure 26 : ^{13} C NMR spectrum of Entry 16b ($CDCl_3$).

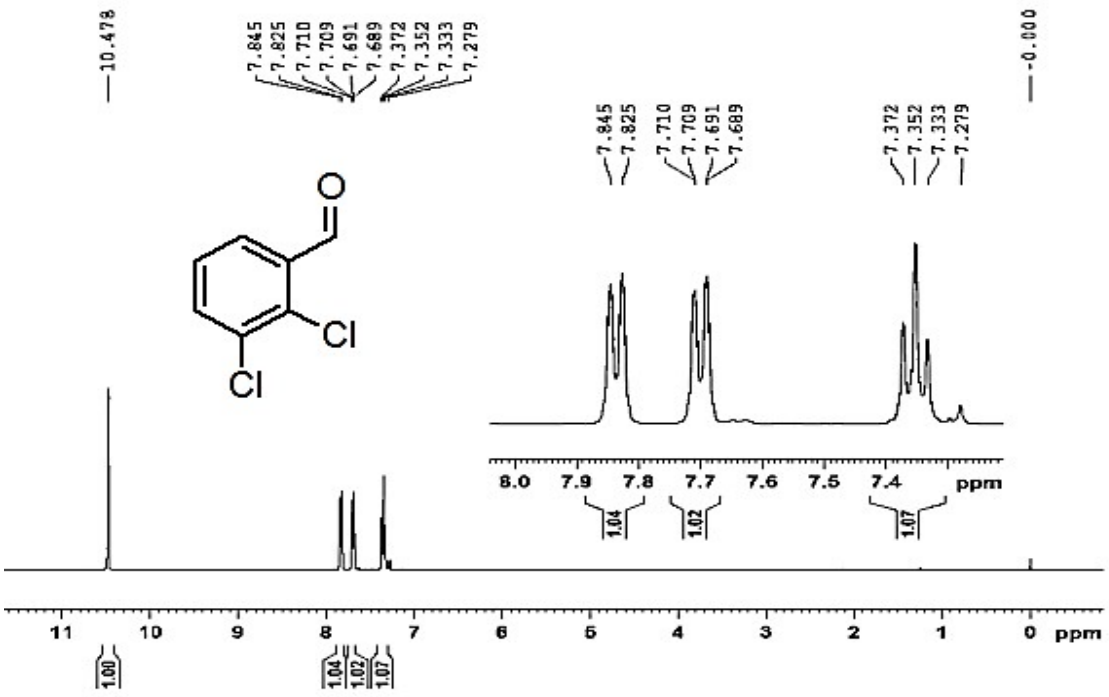

Figure 27: ^{1} H NMR spectrum of Entry 17b ($CDCl_3$,400 MHz).

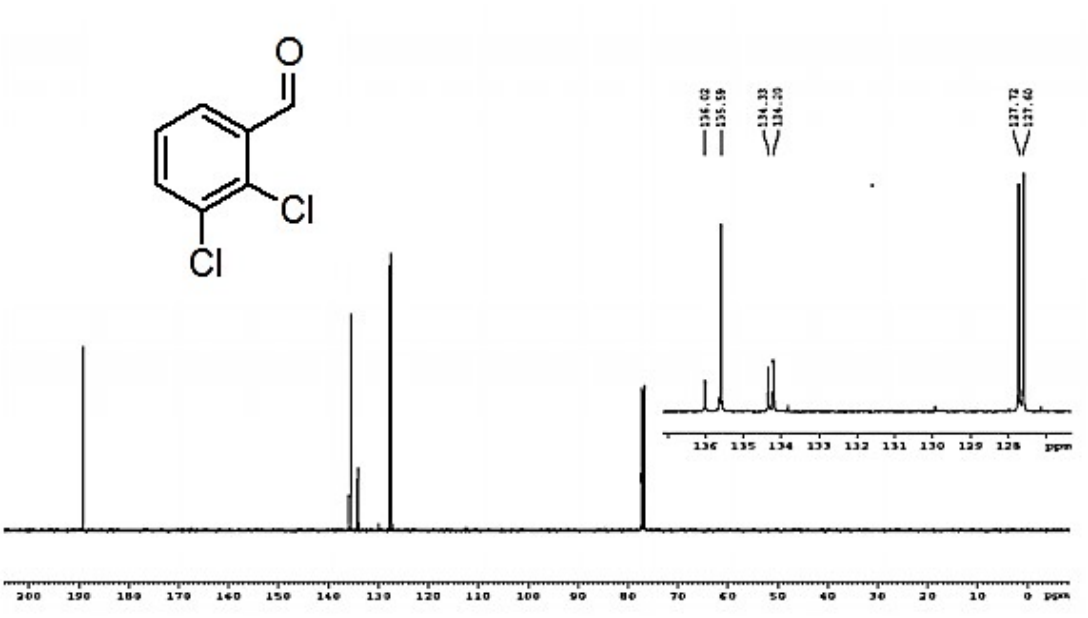

Figure 28 : ^{13} C NMR spectrum of Entry 17b ($CDCl_3$).

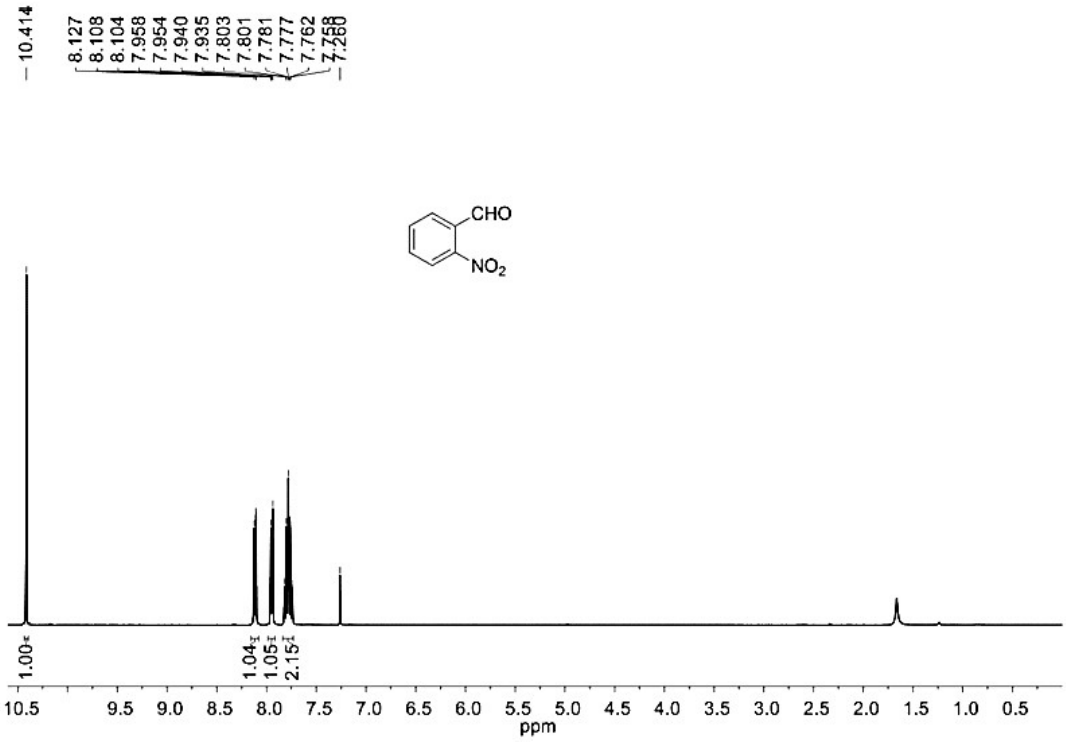

Figure 29: ^{1} H NMR spectrum of Entry 18b ($CDCl_3$,400 MHz).

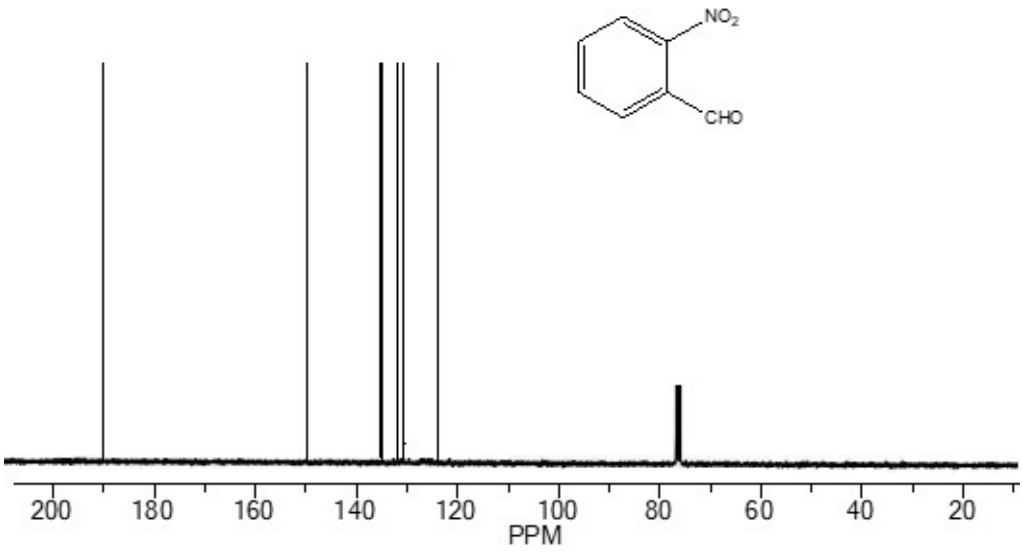

Figure 30 : ^{13} C NMR spectrum of Entry 18b ($CDCl_3$).

Figure 31: ^{1} H NMR spectrum of Entry 19b ($CDCl_3$,400 MHz)

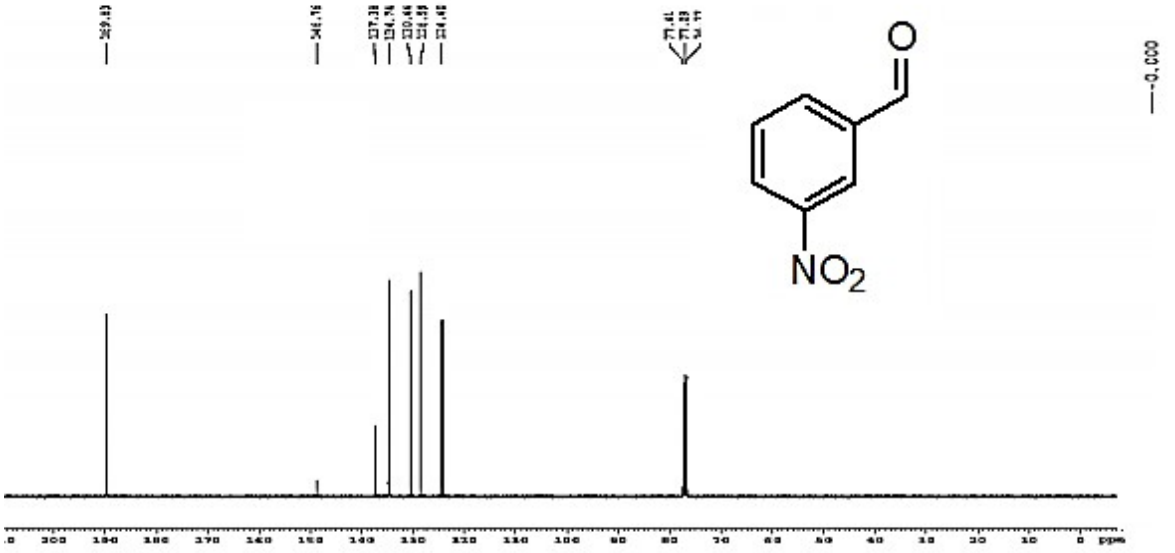

Figure 32 : ^{13} C NMR spectrum of Entry 19b ($CDCl_3$)

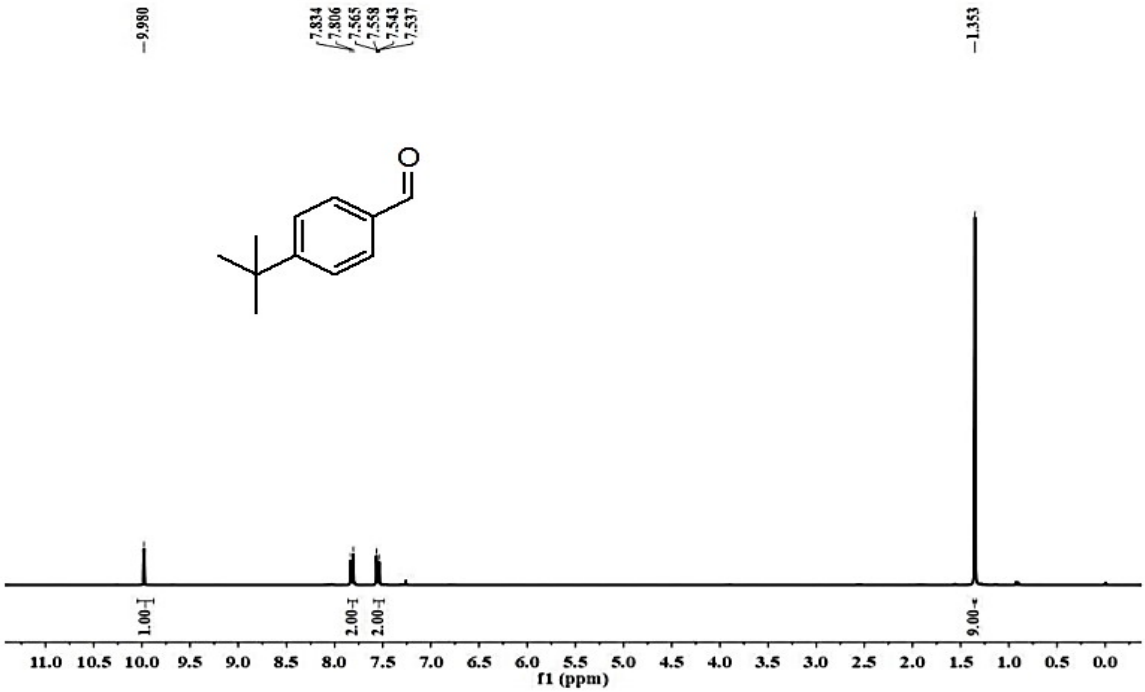

Figure 33: ^{1} H NMR spectrum of Entry 20b ($CDCl_3$,400 MHz)

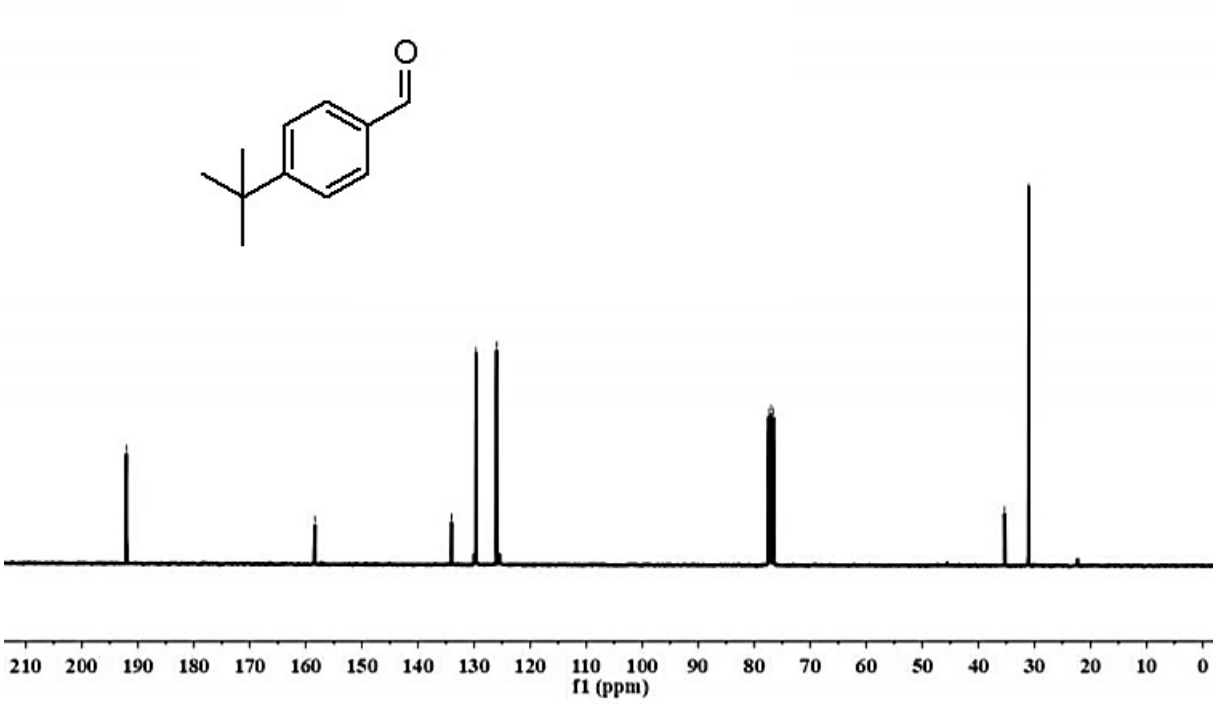

Figure 34 : ^{13} C NMR spectrum of Entry 20b ($CDCl_3$)

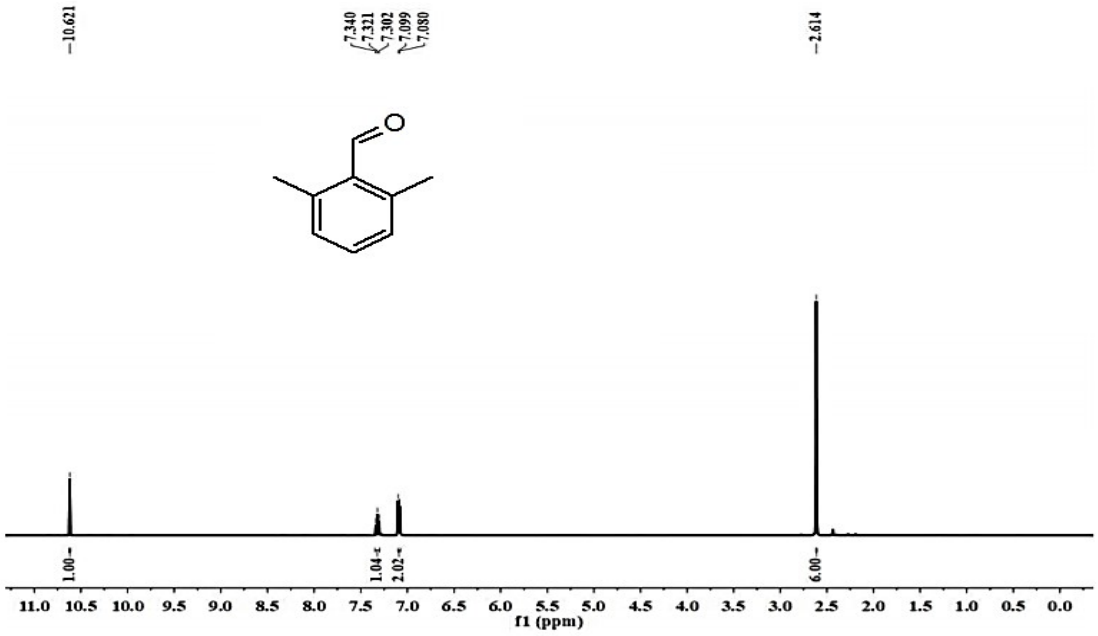

Figure 35: ^{1} H NMR spectrum of Entry 21b ($CDCl_3$,400 MHz)

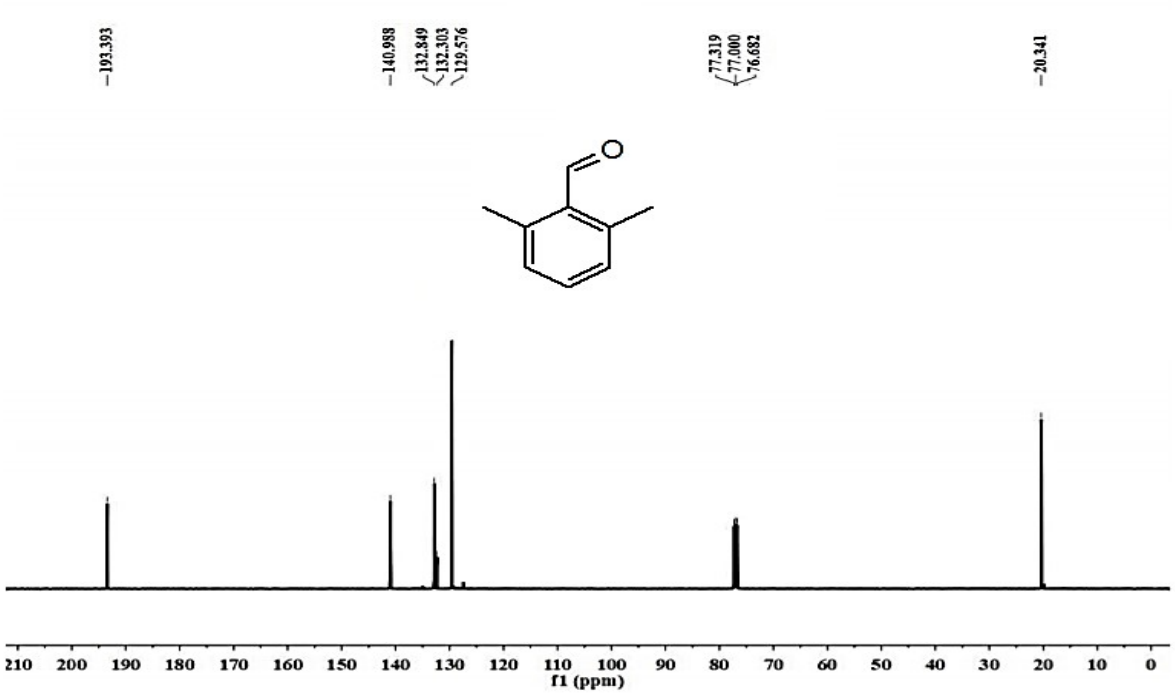

Figure 36 : ^{13} C NMR spectrum of Entry 21b ($CDCl_3$)

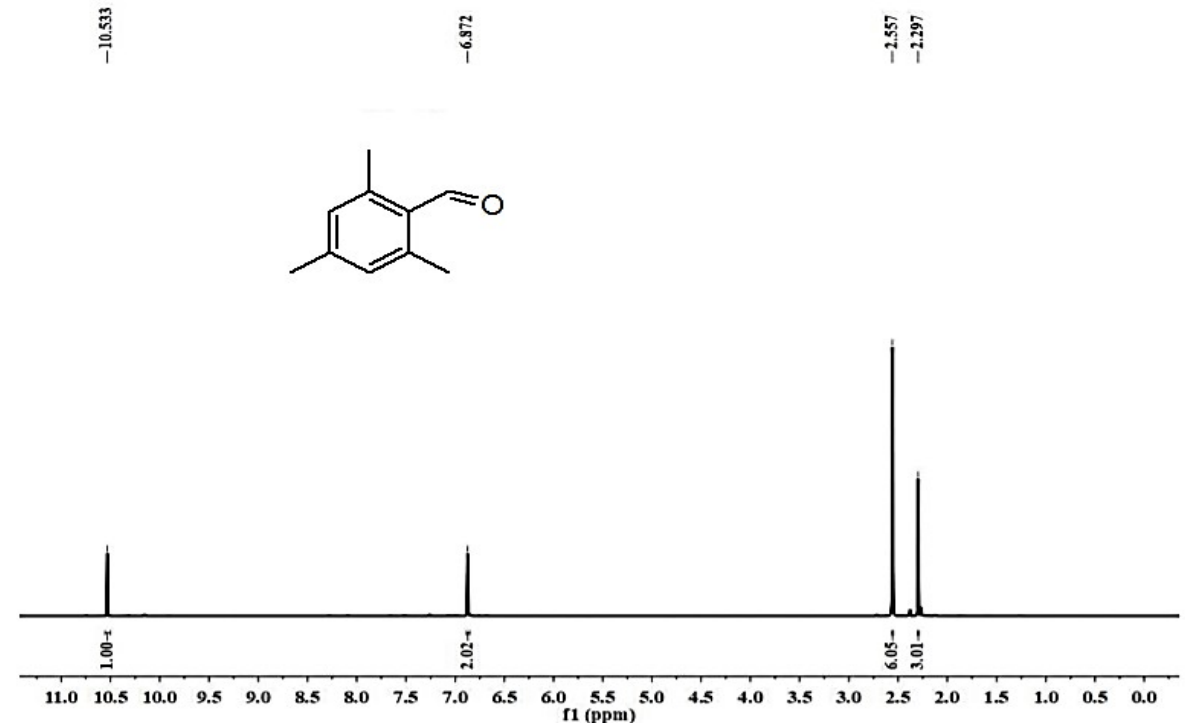

Figure 37: ^{1} H NMR spectrum of Entry 22b ($CDCl_3$,400 MHz)

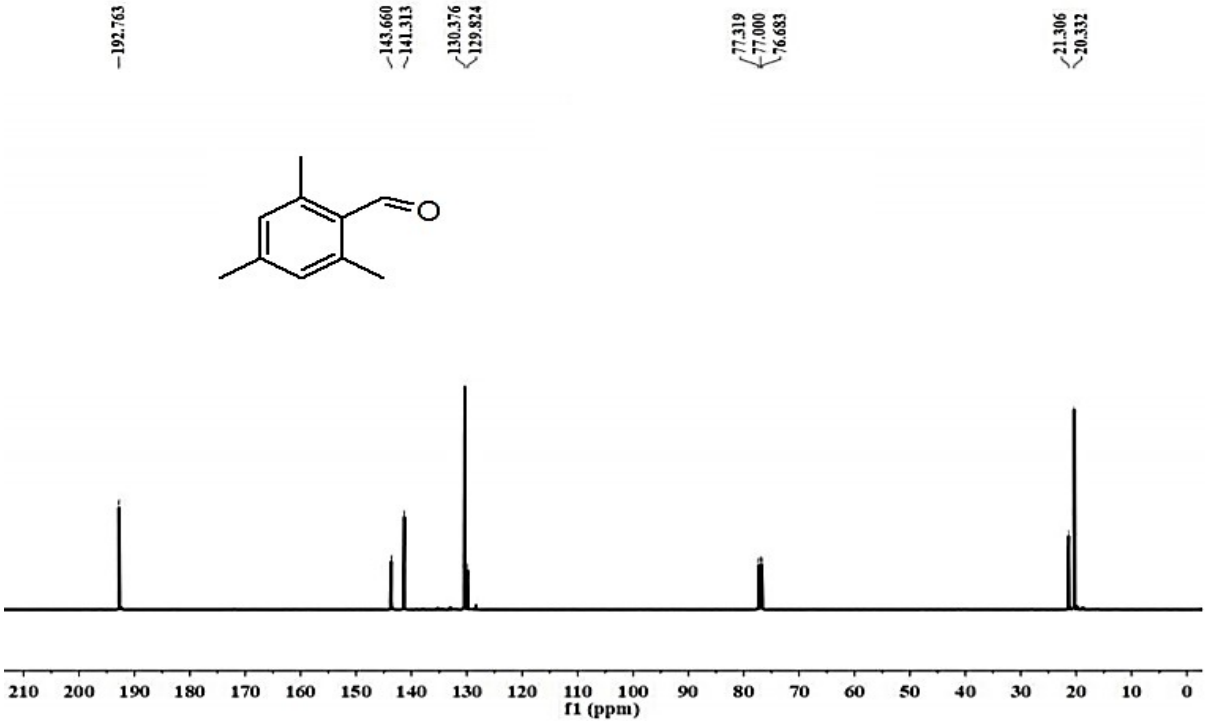

Figure 38 : ^{13} C NMR spectrum of Entry 22b ($CDCl_3$)

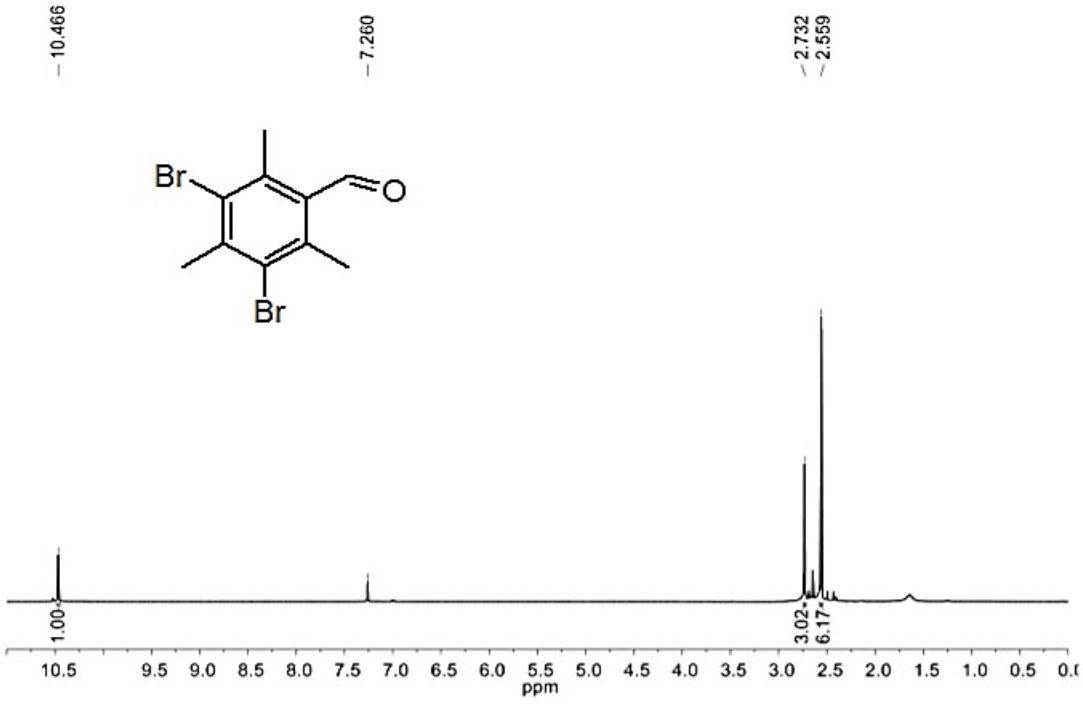

Figure 39: ^{1} H NMR spectrum of Entry 23b ($CDCl_3$,400 MHz)

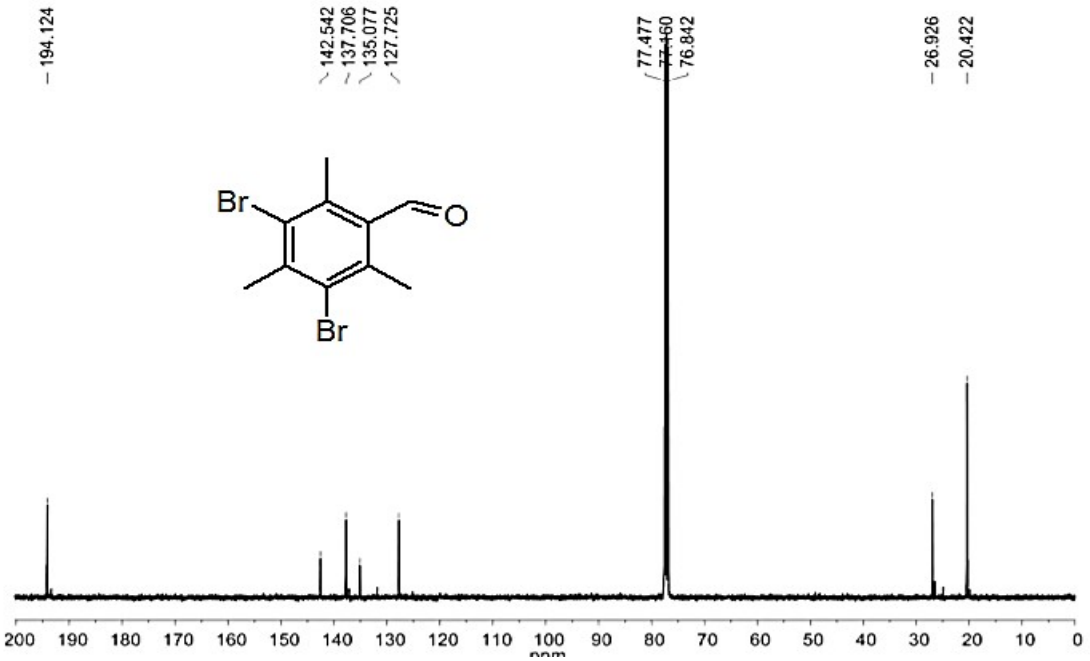

Figure 40 : ^{13} C NMR spectrum of Entry 23b ($CDCl_3$)

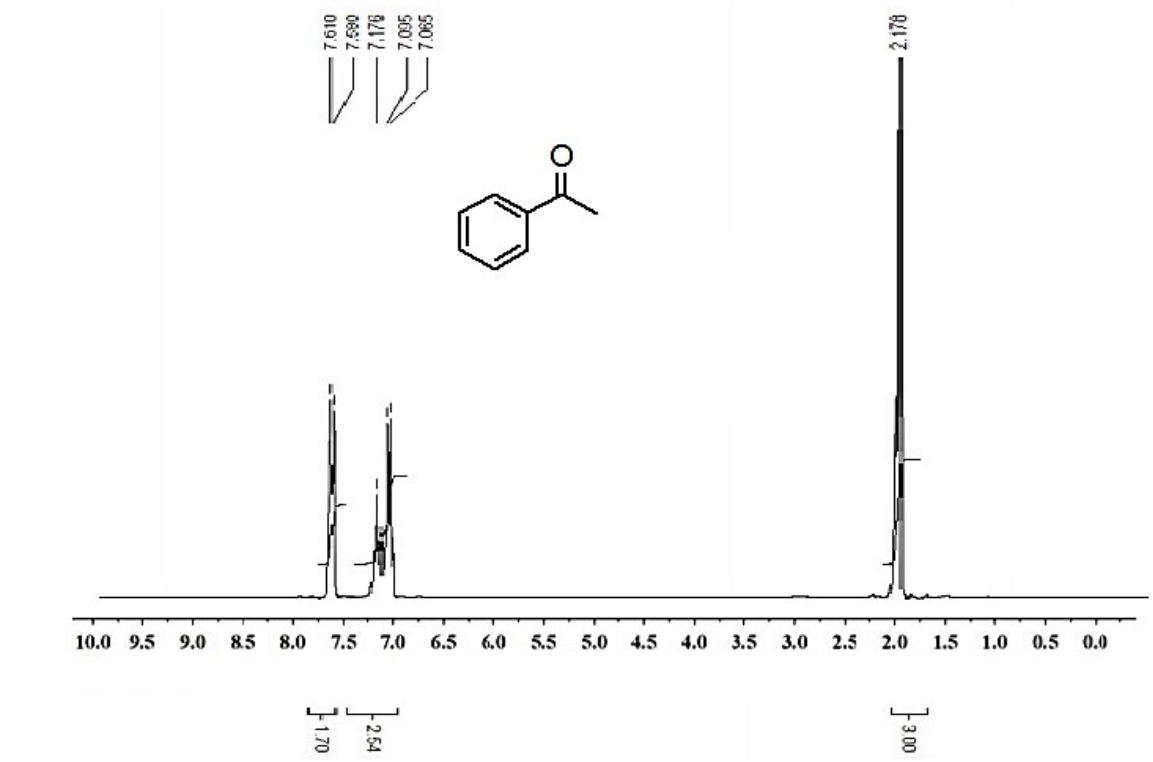

Figure 41: ^{1} H NMR spectrum of Entry 24b ($CDCl_3$,400 MHz)

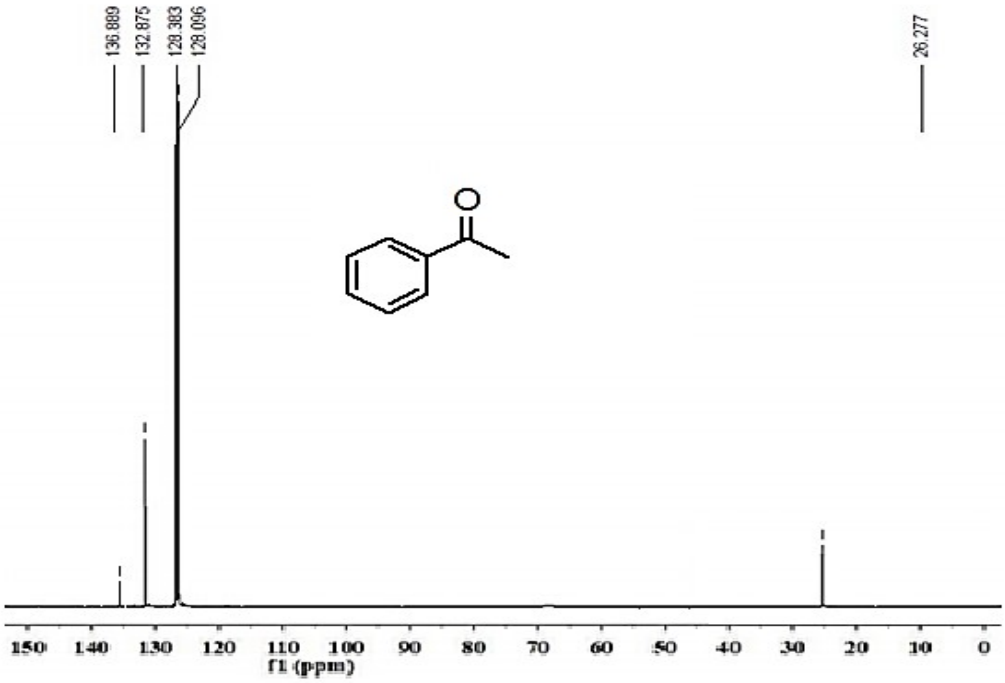

Figure 42 : ^{13} C NMR spectrum of Entry 24b ($CDCl_3$)

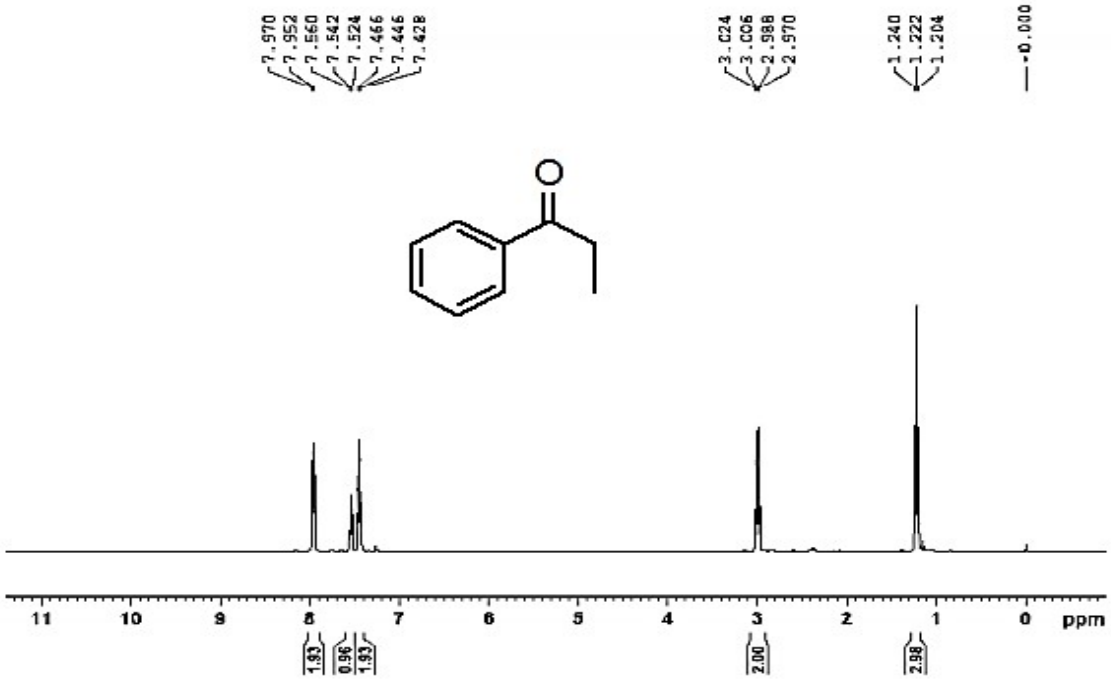

Figure 43: ^{1} H NMR spectrum of Entry 25b ($CDCl_3$,400 MHz)

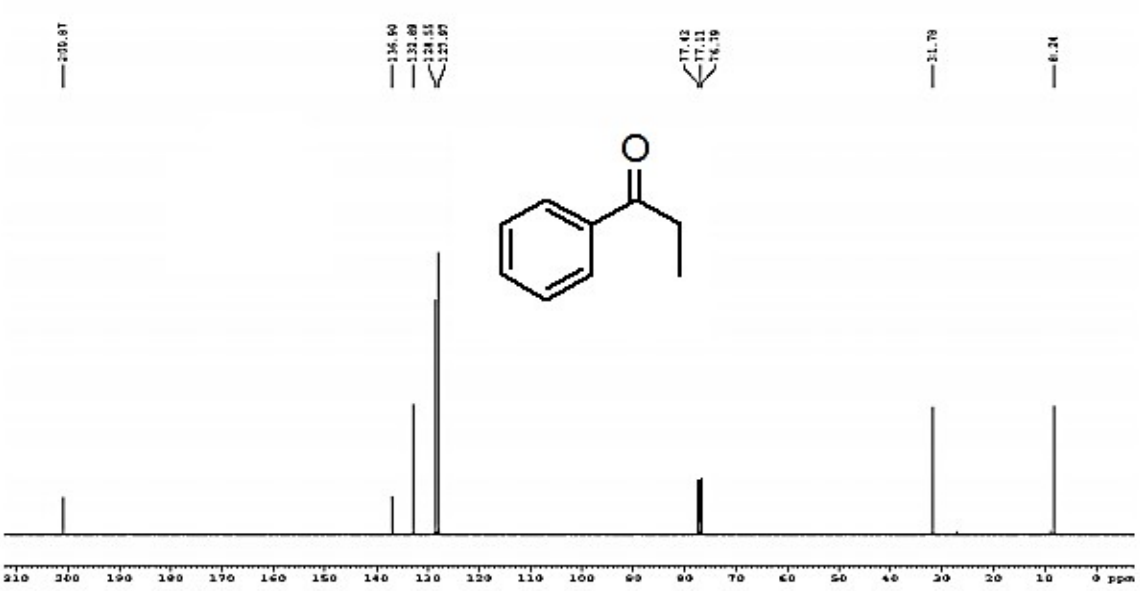

Figure 44 : ^{13} C NMR spectrum of Entry 25b ($CDCl_3$)

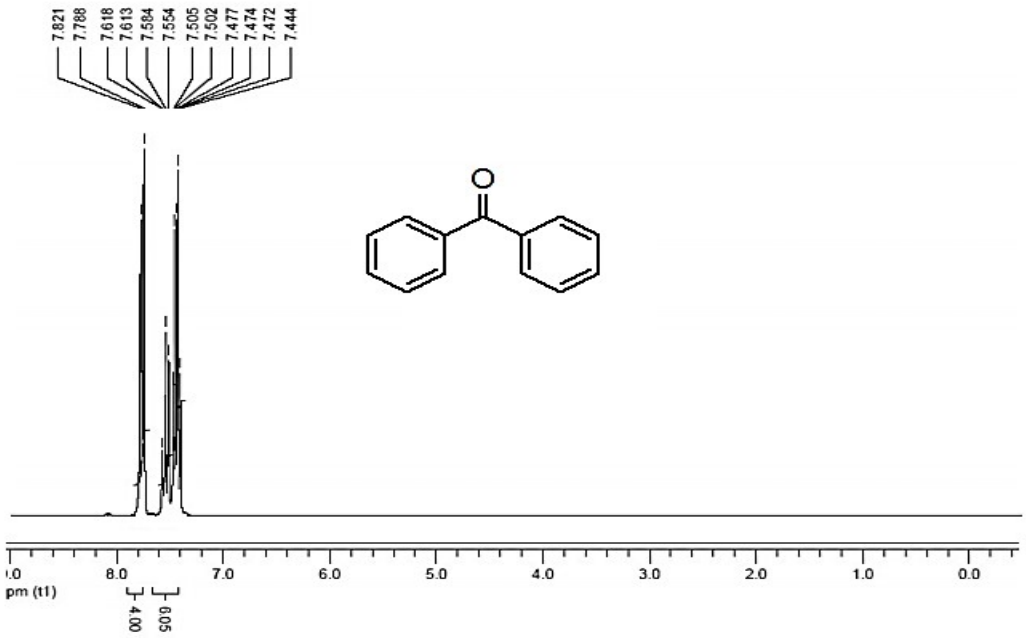

Figure 45: ^{1} H NMR spectrum of Entry 26b ($CDCl_3$,400 MHz)

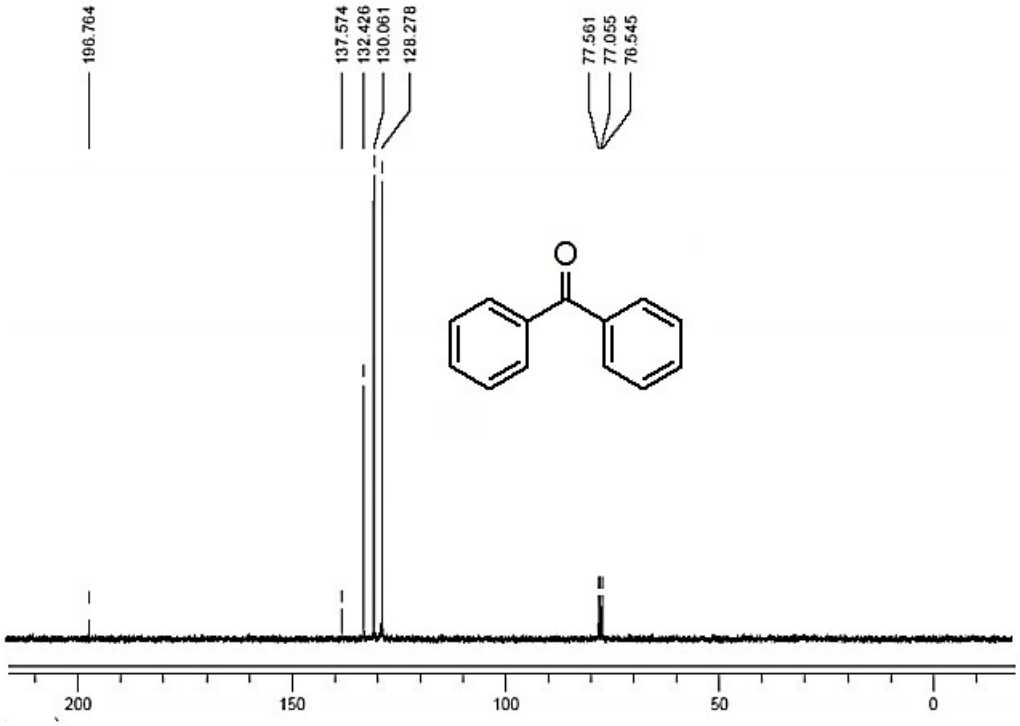

Figure 46 : ^{13} C NMR spectrum of Entry 26b ($CDCl_3$).

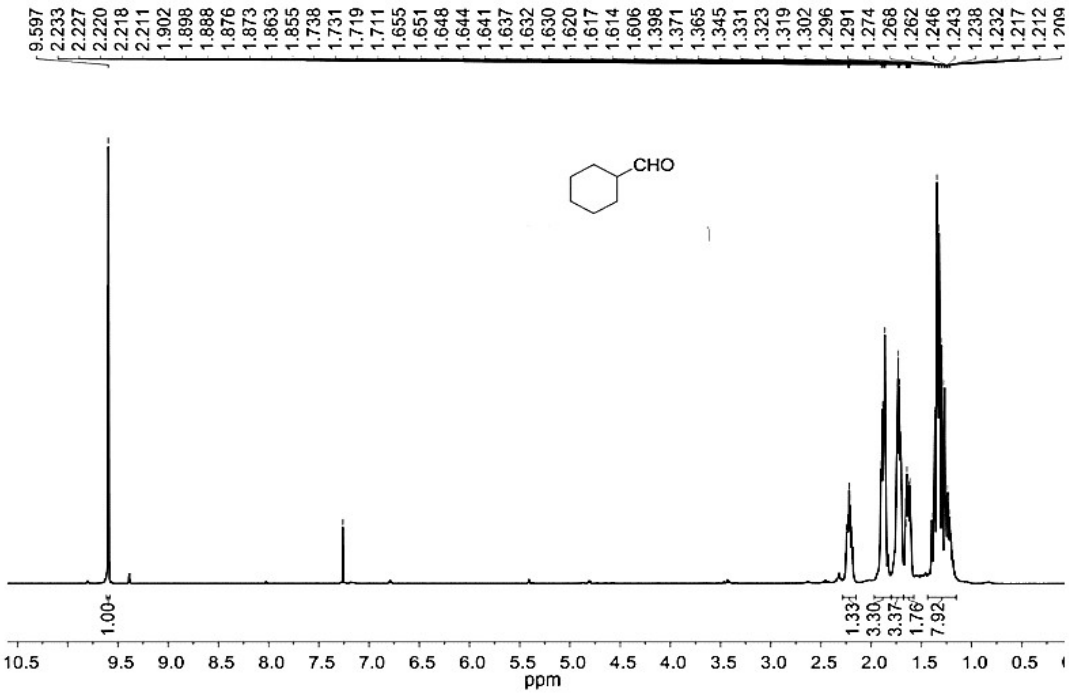

Figure 47: ^{1} H NMR spectrum of Entry 27b ($CDCl_3$,400 MHz)

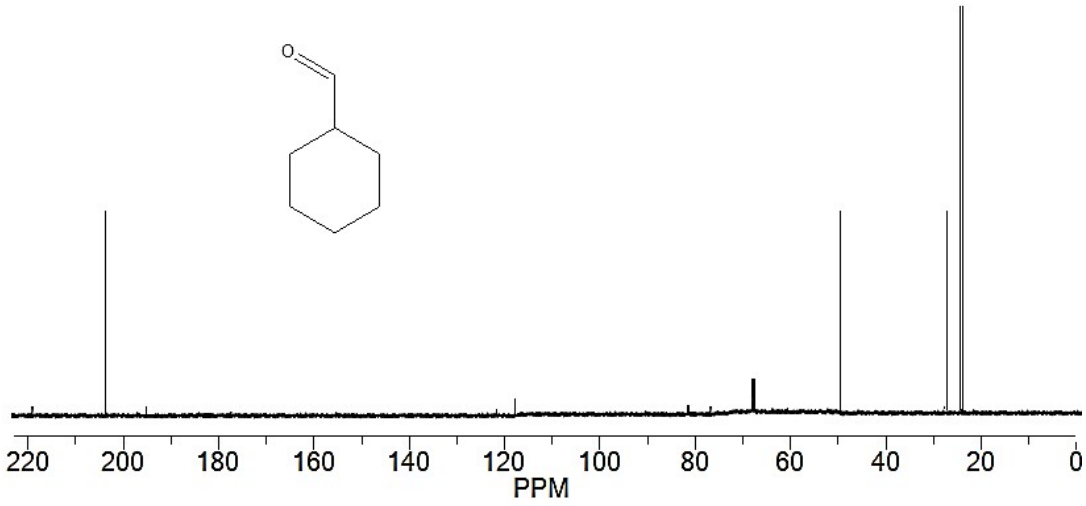

Figure 48 : ^{13} C NMR spectrum of Entry 27b ($CDCl_3$).

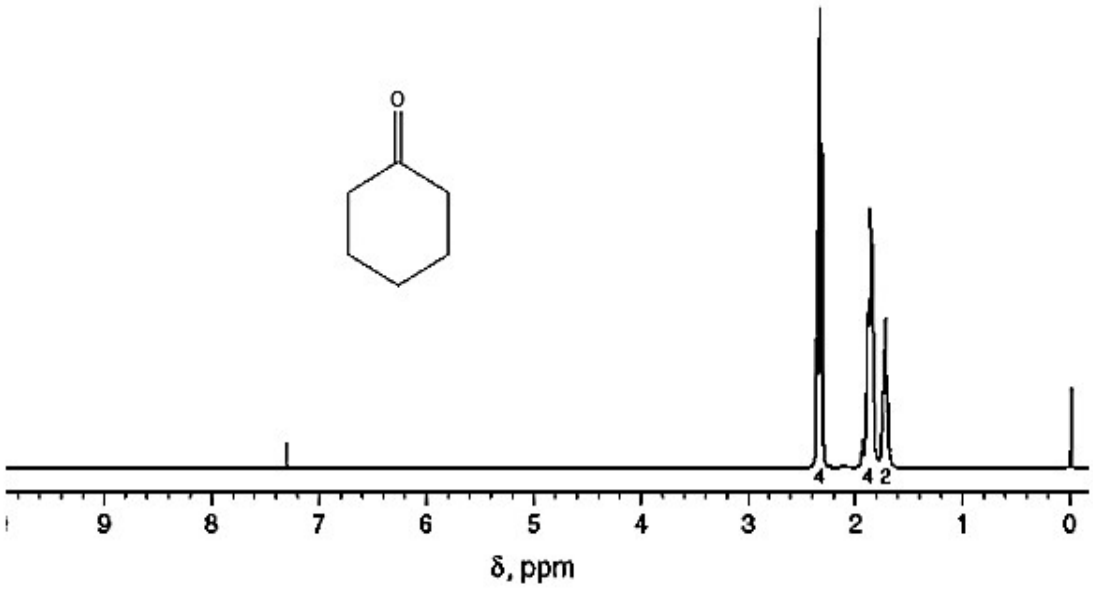

Figure 49: ^{1} H NMR spectrum of Entry 28b ($CDCl_3$,400 MHz)

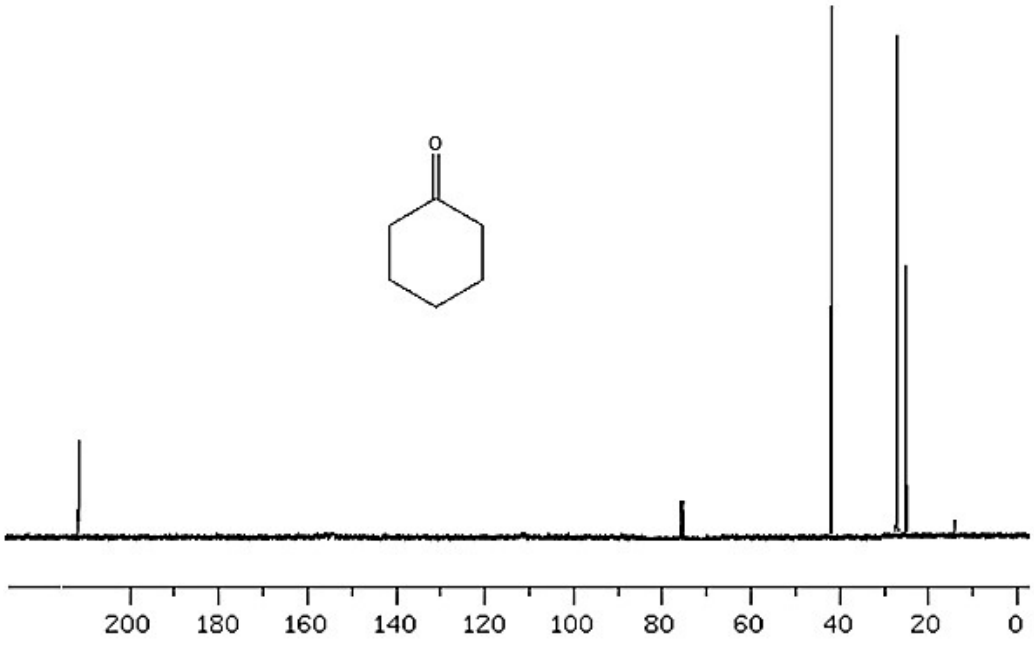

Figure 50 : ^{13} C NMR spectrum of Entry 28b ($CDCl_3$).

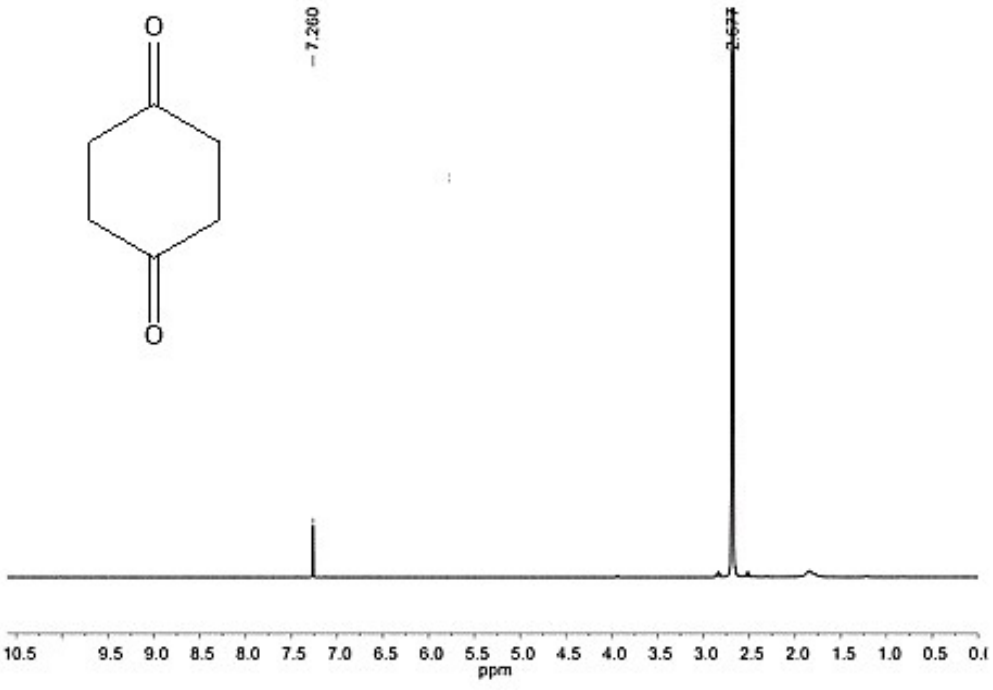

Figure 51: ^{1} H NMR spectrum of Entry 29b ($CDCl_3$,400 MHz)

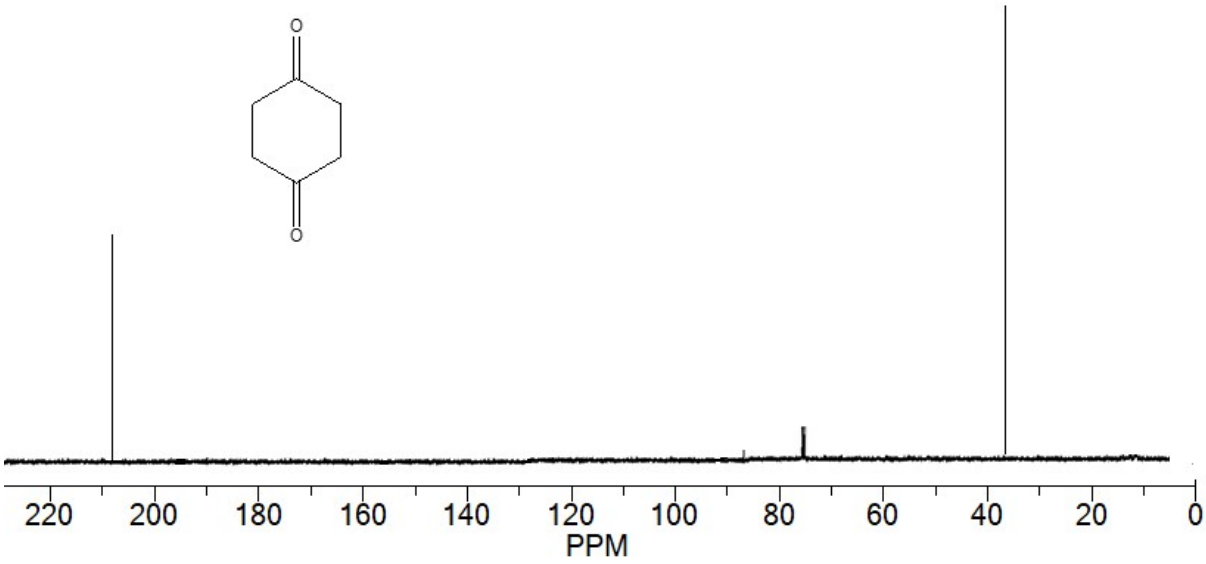

Figure 52 : ^{13} C NMR spectrum of Entry 29b ($CDCl_3$).

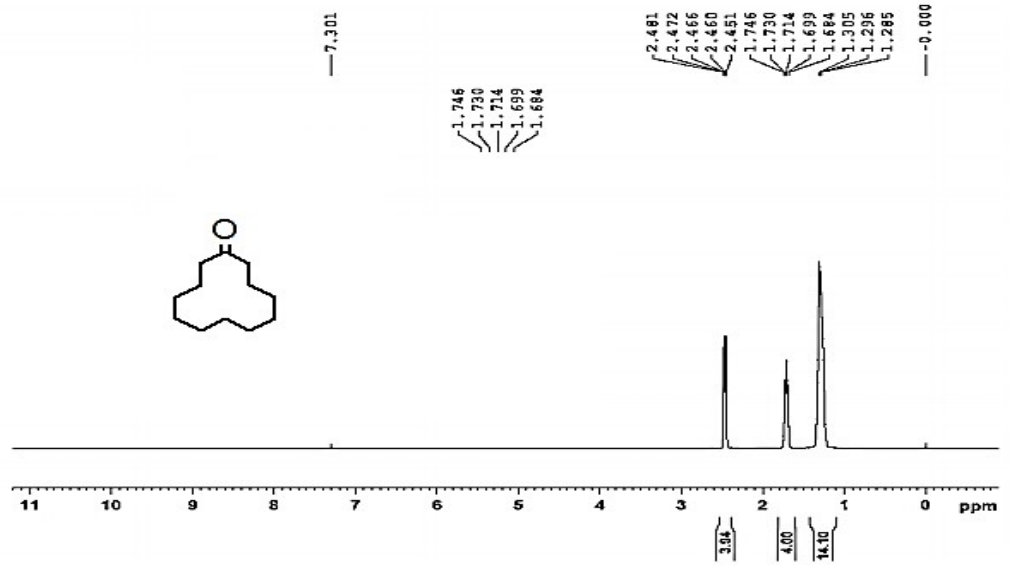

Figure539: ^{1} H NMR spectrum of Entry 30b ($CDCl_3$,400 MHz)

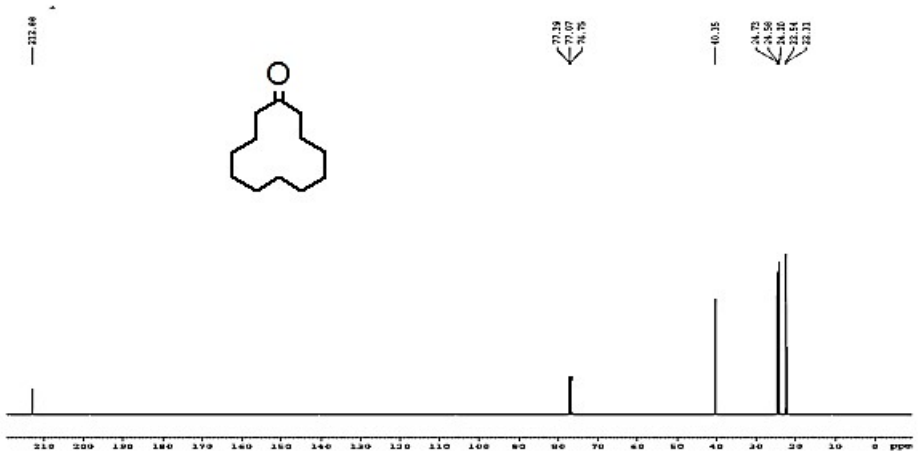

Figure 54 : ^{13} C NMR spectrum of Entry 30b ($CDCl_3$)

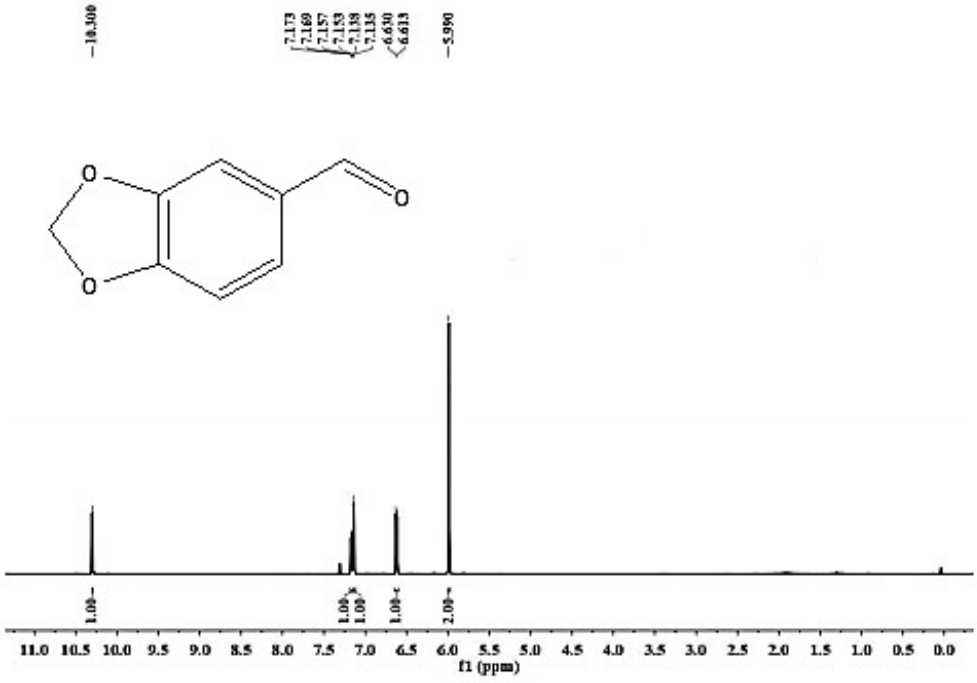

Figure 55: ^{1} H NMR spectrum of Entry 31b ($CDCl_3$,400 MHz)

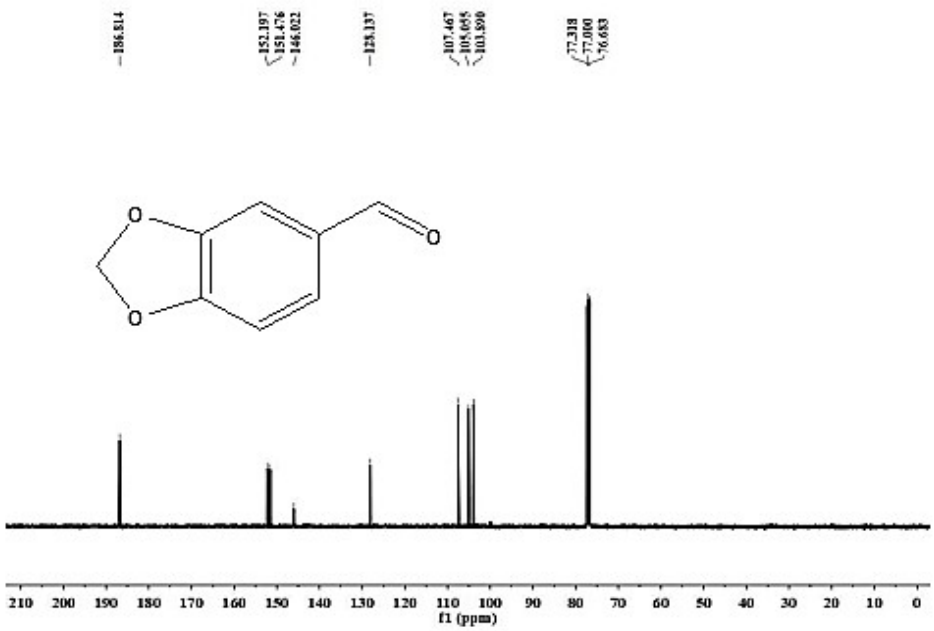

Figure 56 : ^{13} C NMR spectrum of Entry 31b ($CDCl_3$)

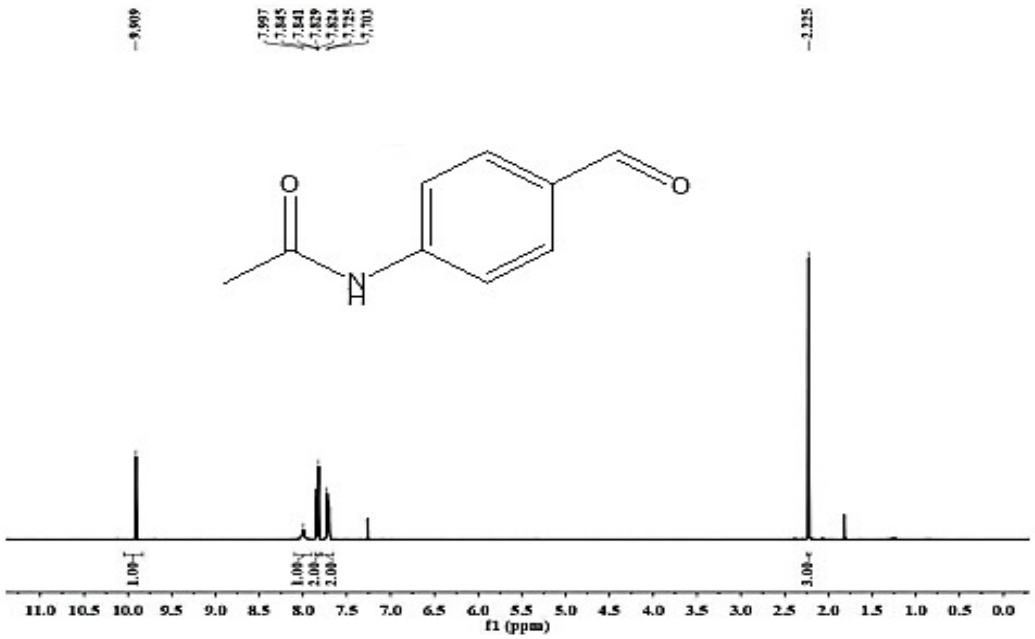

Figure 57: ^{1} H NMR spectrum of Entry 32b ($CDCl_3$,400 MHz)

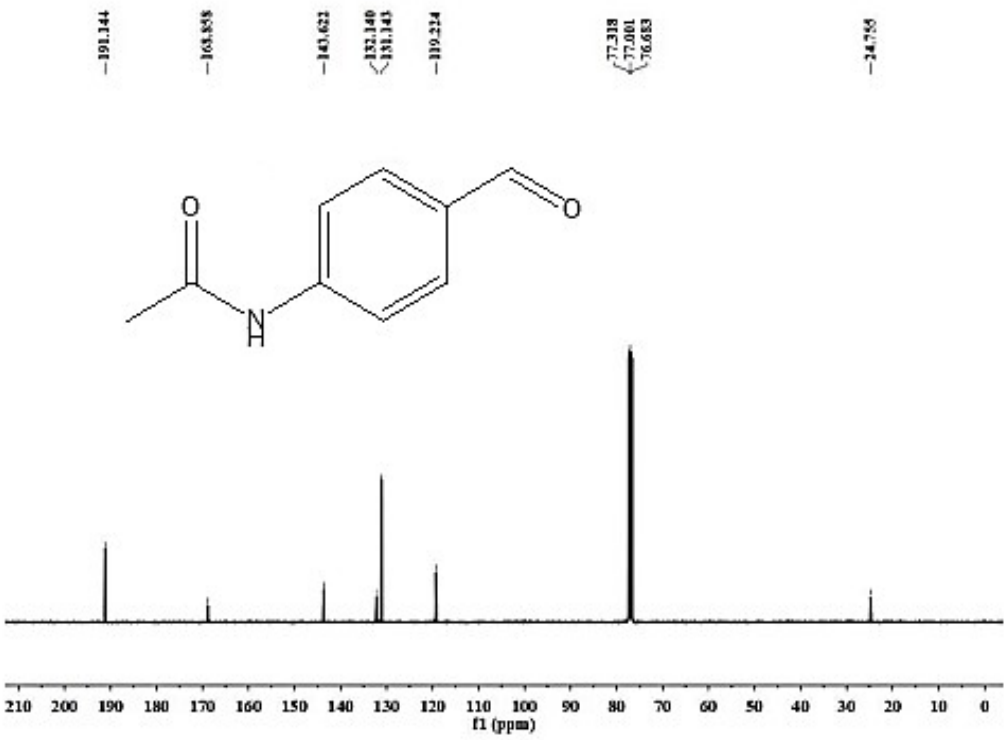

Figure 58 : ^{13} C NMR spectrum of Entry 32b ($CDCl_3$)

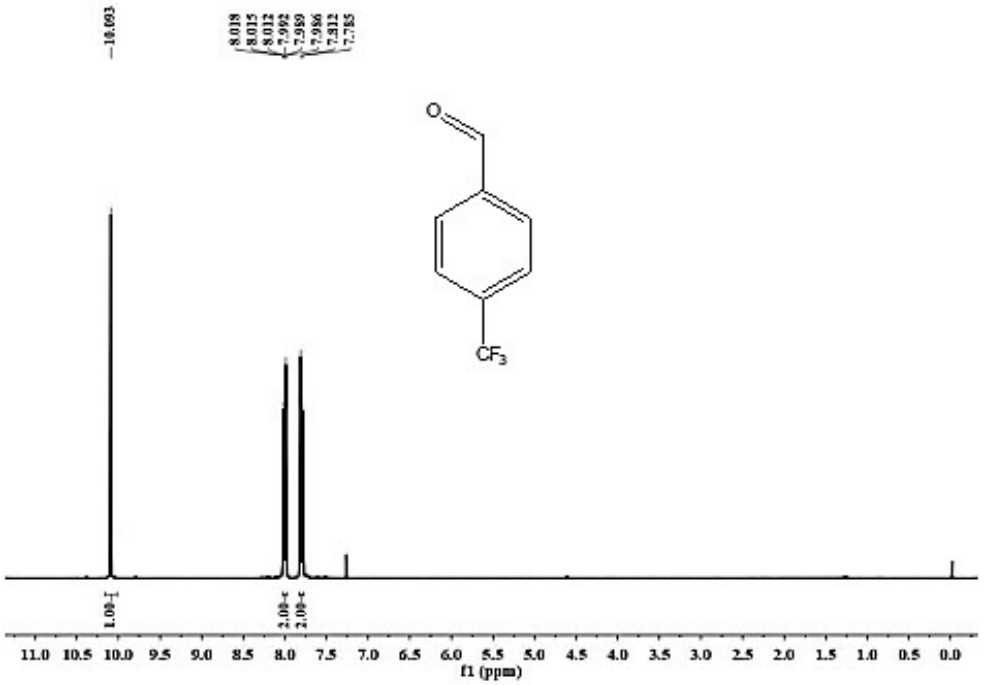

Figure 59: ^{1} H NMR spectrum of Entry 33b ($CDCl_3$,400 MHz)

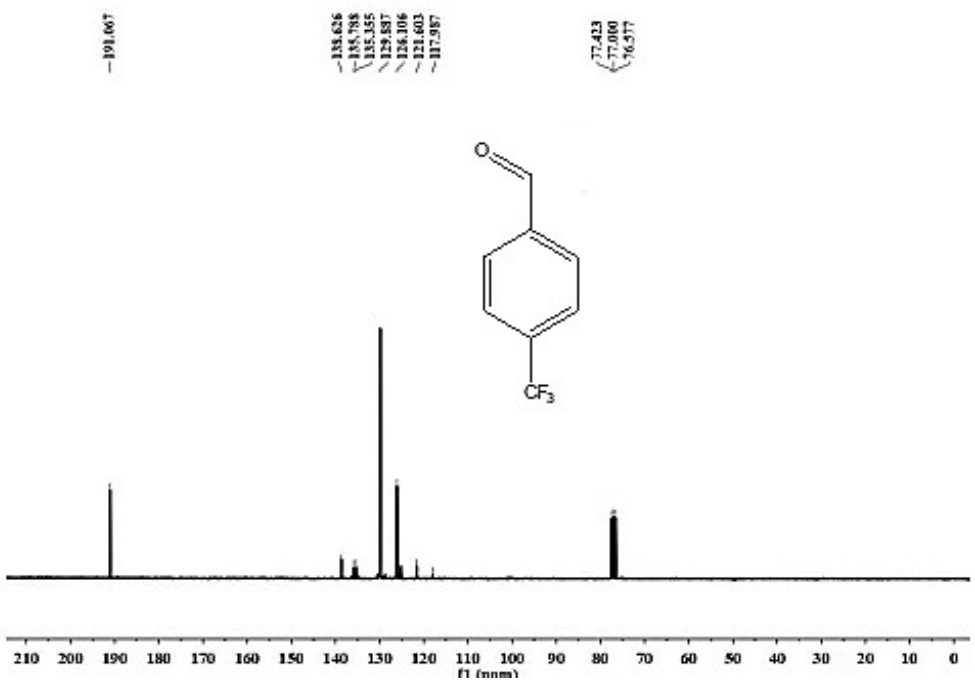

Figure 60 : ^{13} C NMR spectrum of Entry 33b ($CDCl_3$

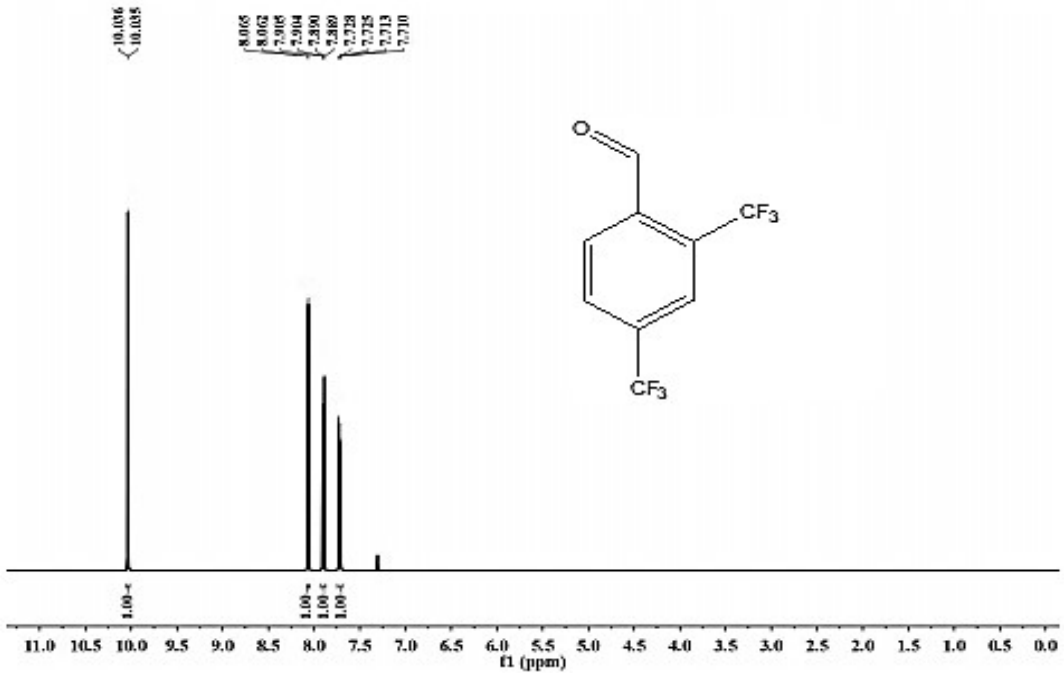

Figure 59: ^{1} H NMR spectrum of Entry 34b ($CDCl_3$,400 MHz)

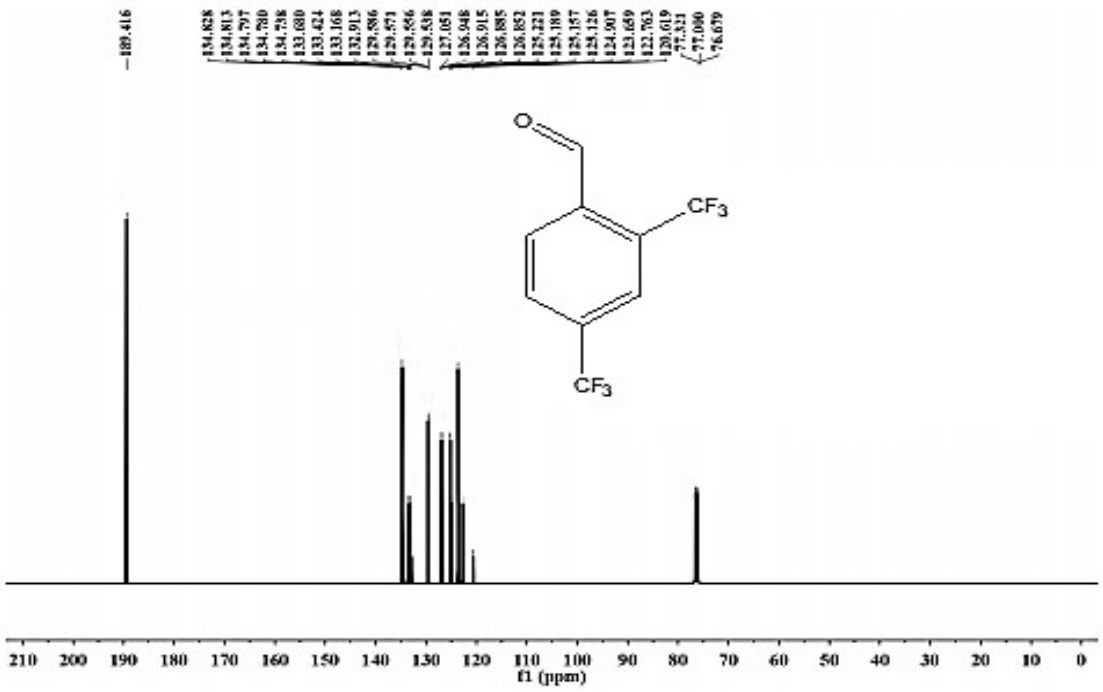

Figure 60 : ^{13} C NMR spectrum of Entry 34b ($CDCl_3$

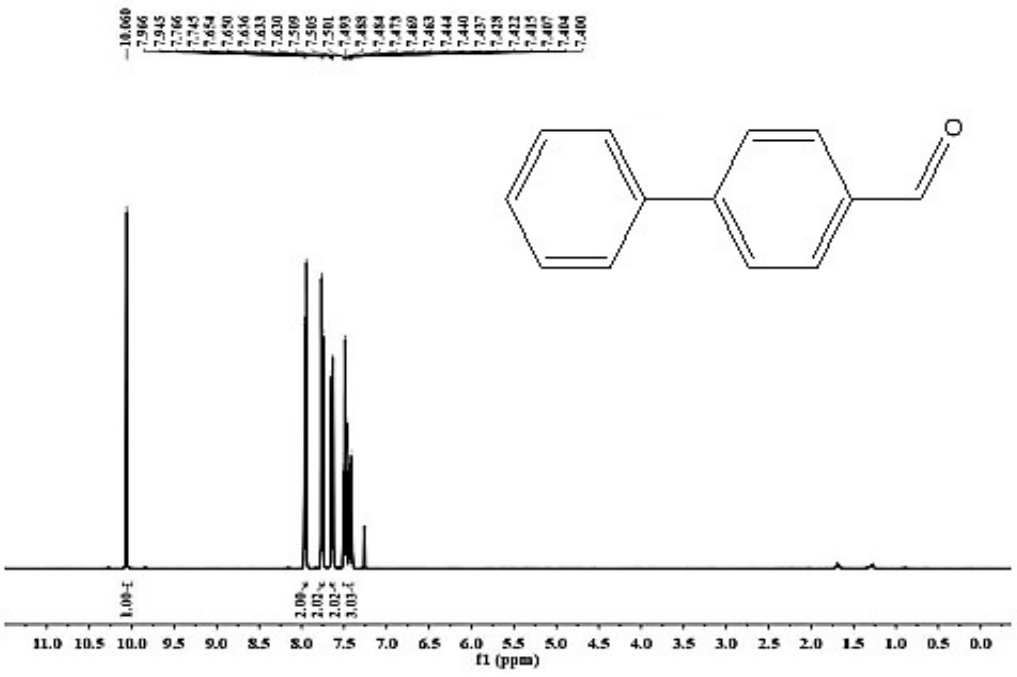

Figure 61: ^{1} H NMR spectrum of Entry 35b ($CDCl_3$,400 MHz)

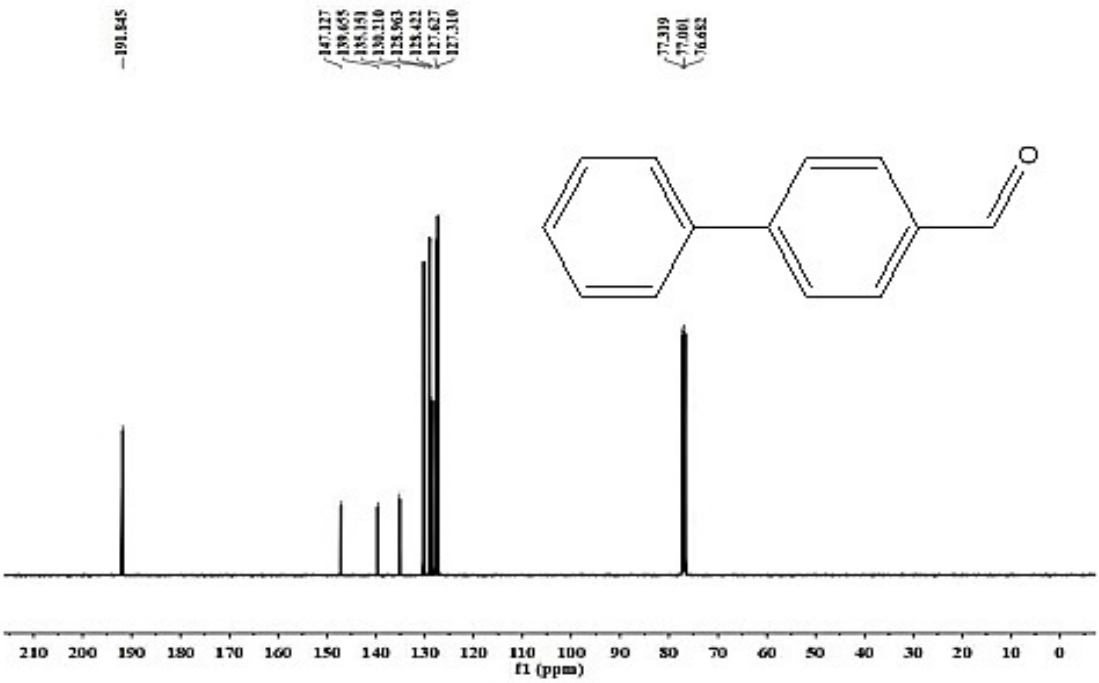

Figure 62 : ^{13} C NMR spectrum of Entry 35b ($CDCl_3$

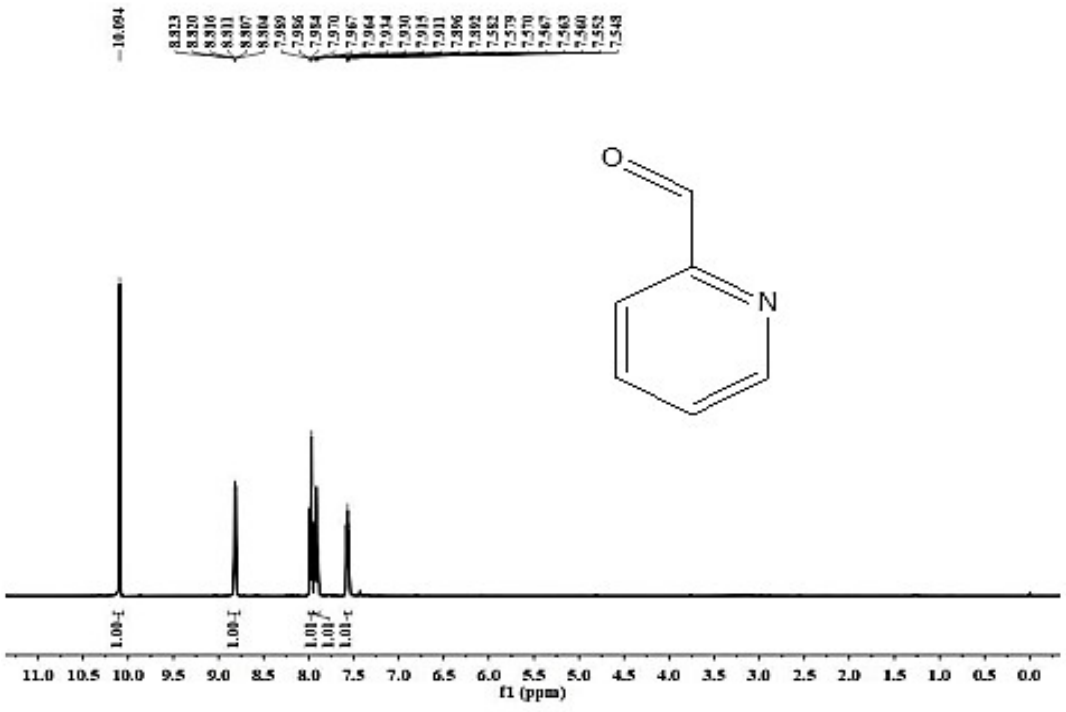

Figure 62: ^{1} H NMR spectrum of Entry 36b ($CDCl_3$,400 MHz)

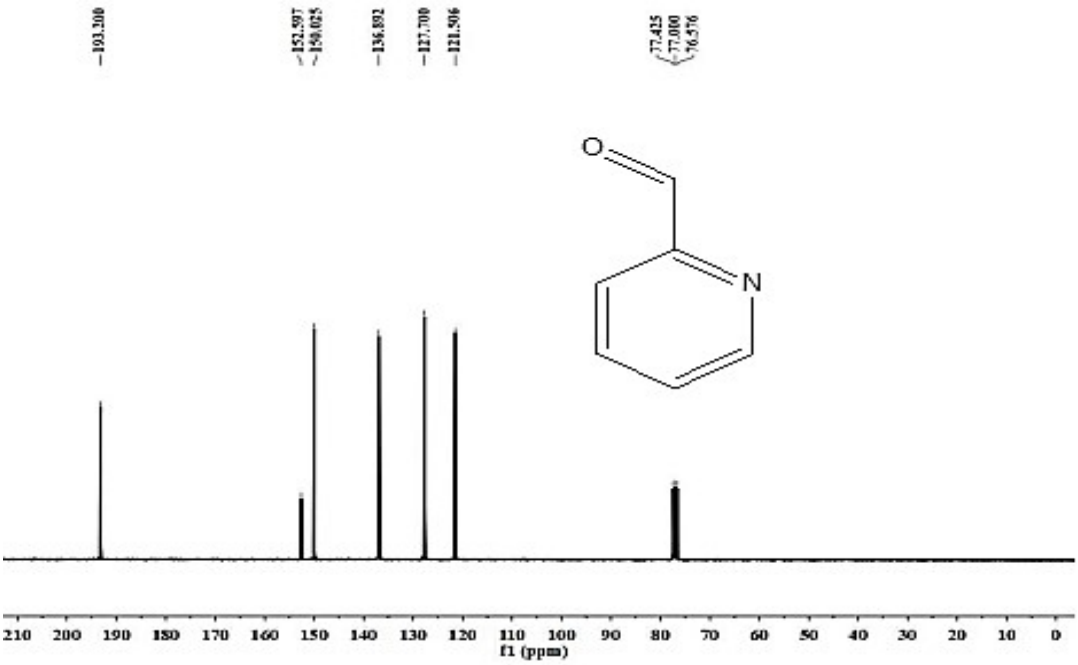

Figure 63 : ^{13} C NMR spectrum of Entry 36b ($CDCl_3$

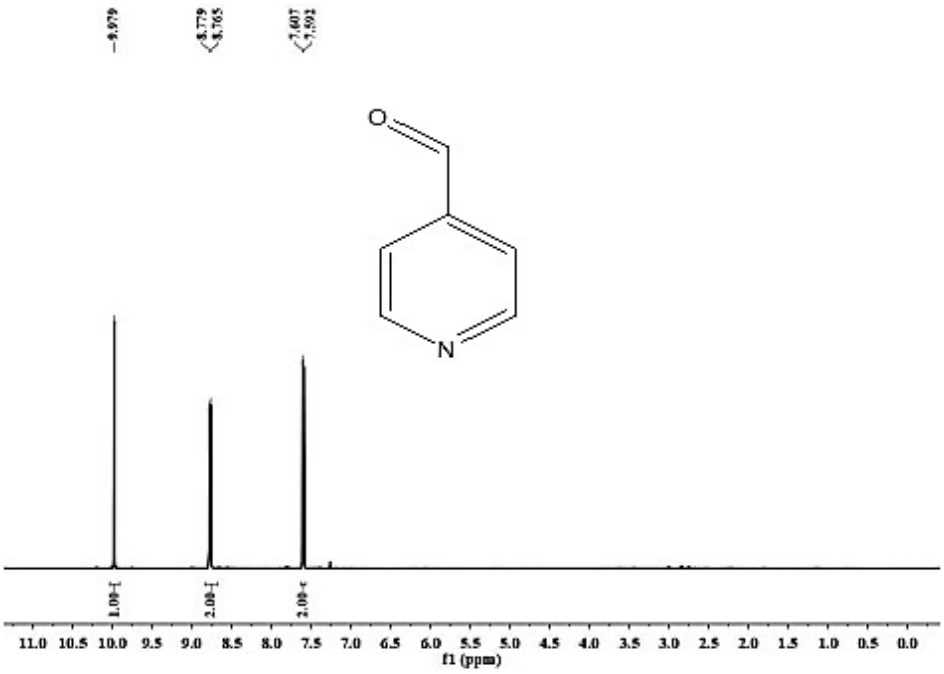

Figure 63: ^{1} H NMR spectrum of Entry 37b ($CDCl_3$,400 MHz)

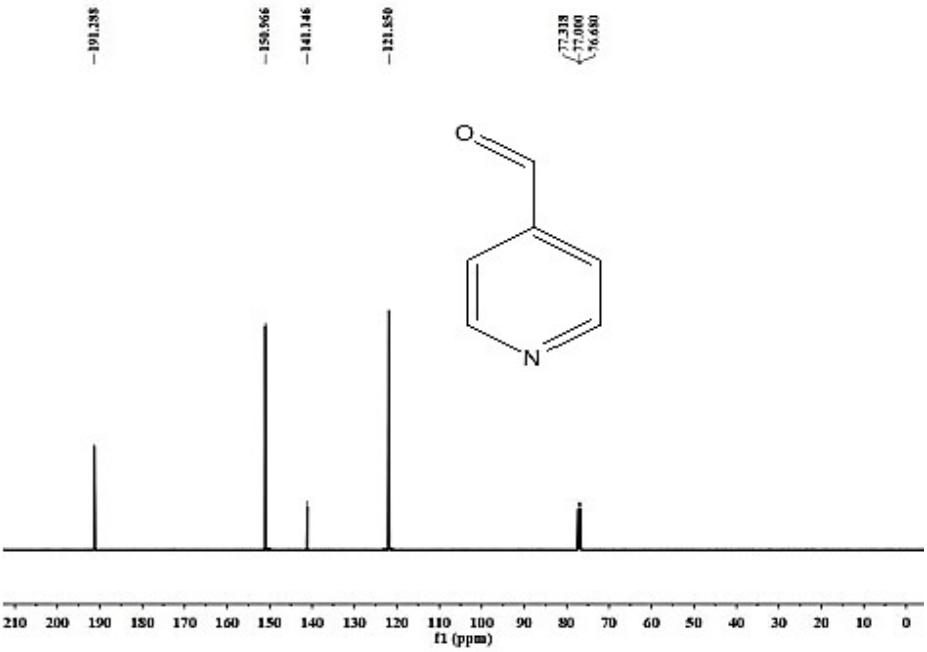

Figure 64 : ^{13} C NMR spectrum of Entry 37b ($CDCl_3$

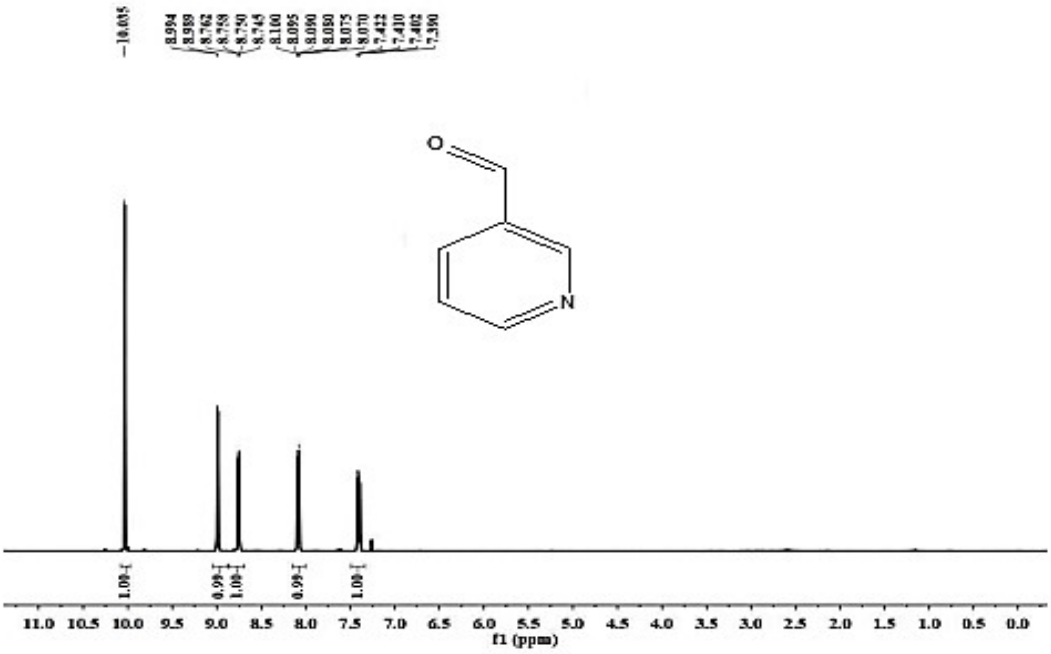

Figure 65: ^{1} H NMR spectrum of Entry 38b ($CDCl_3$,400 MHz)

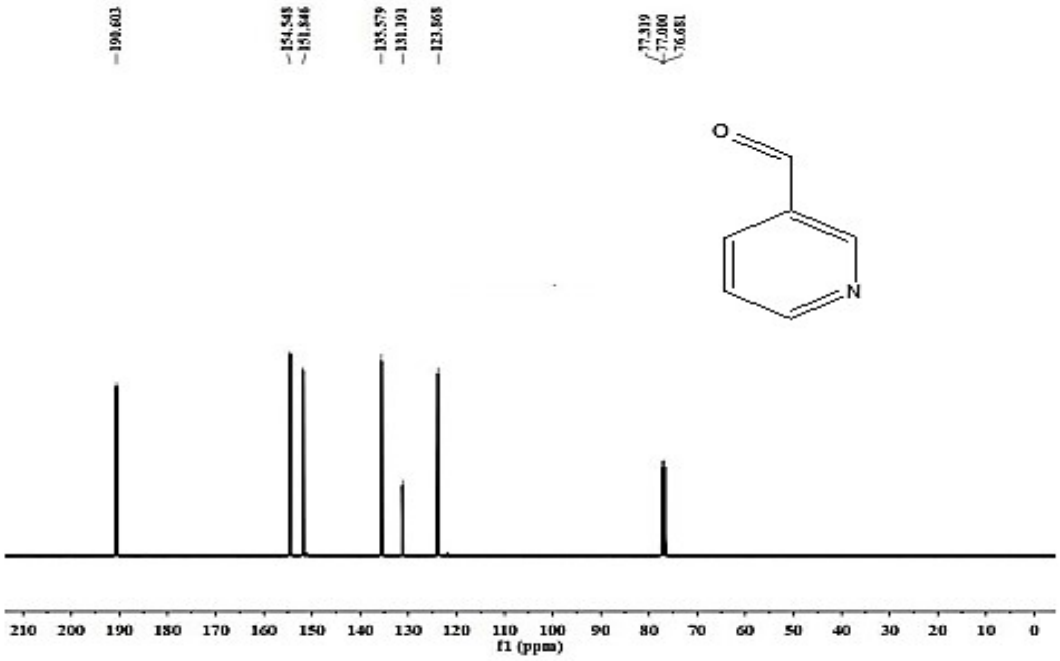

Figure 66 : ^{13} C NMR spectrum of Entry 38b ($CDCl_3$

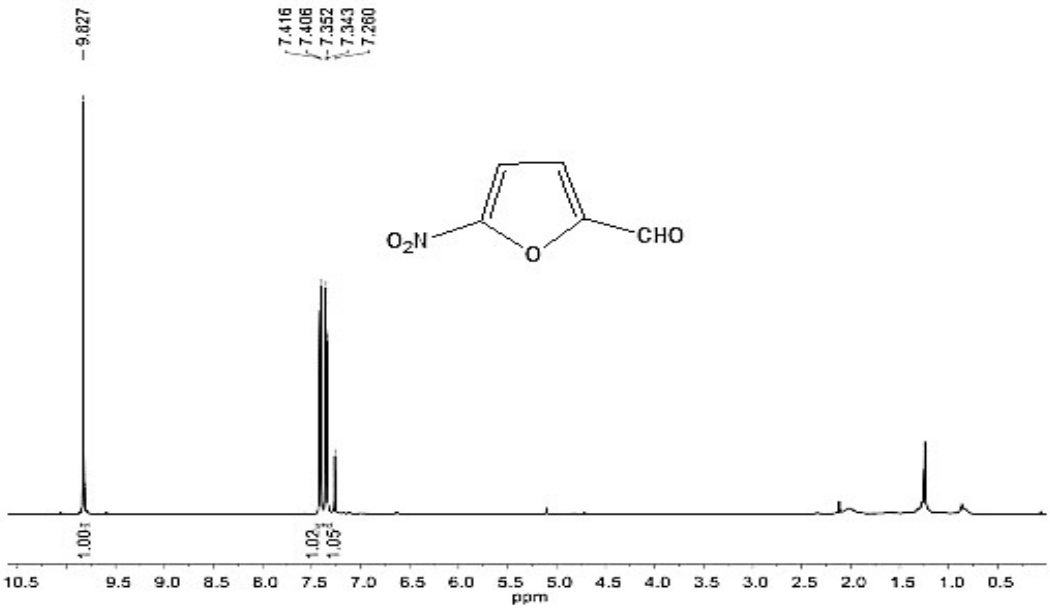

Figure 67: ^{1} H NMR spectrum of Entry 39b ($CDCl_3$,400 MHz)

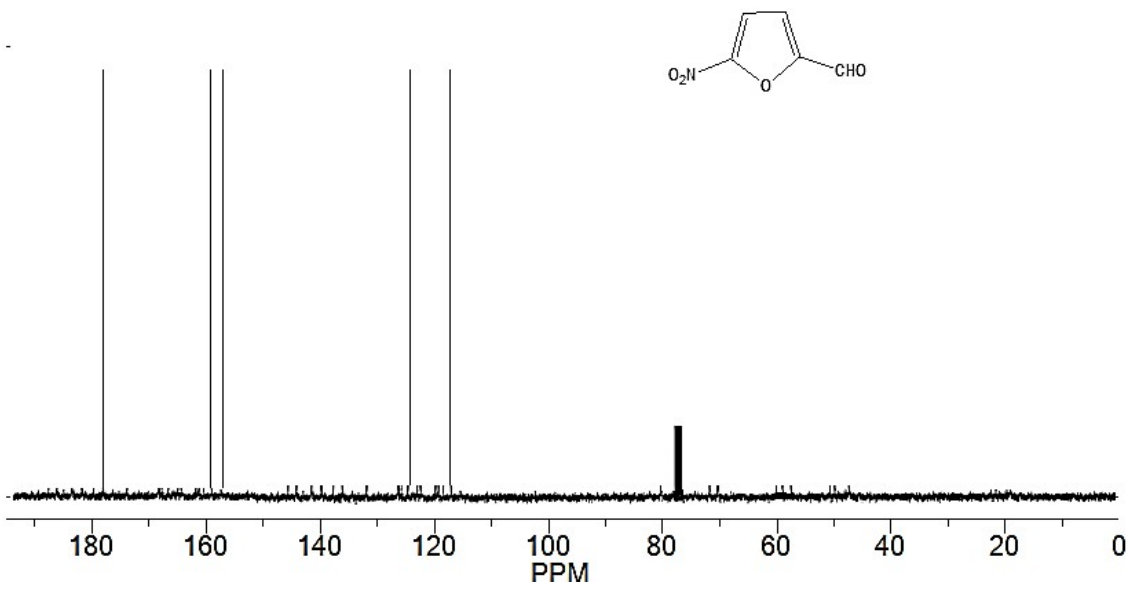

Figure 68 : ^{13} C NMR spectrum of Entry 39b ($CDCl_3$

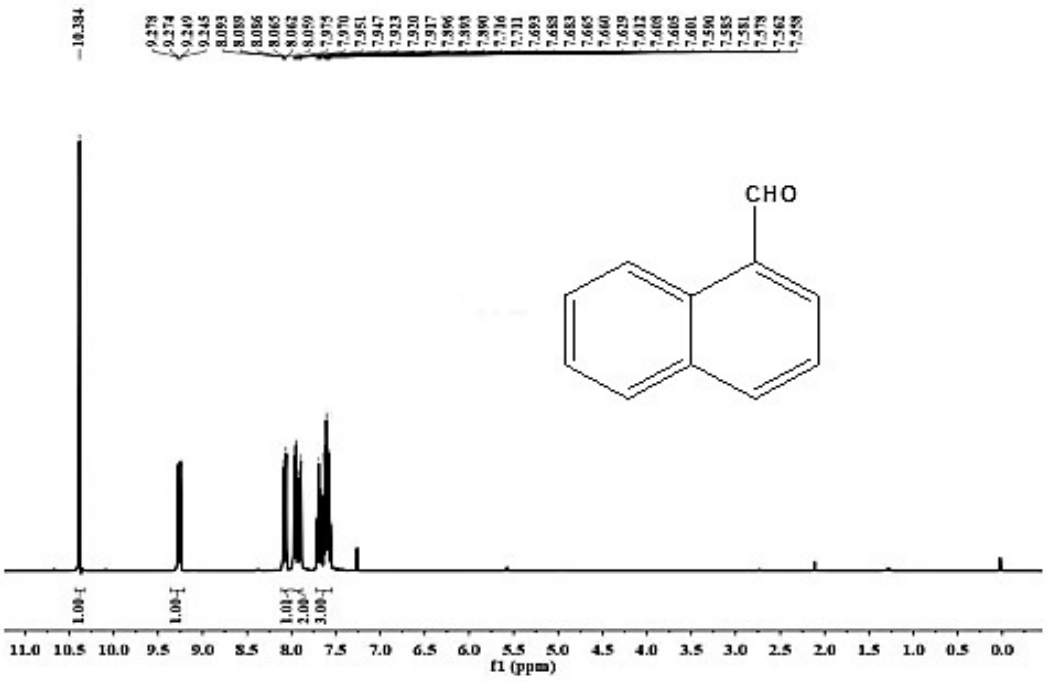

Figure 69: ^{1} H NMR spectrum of Entry 40b ($CDCl_3$,400 MHz)

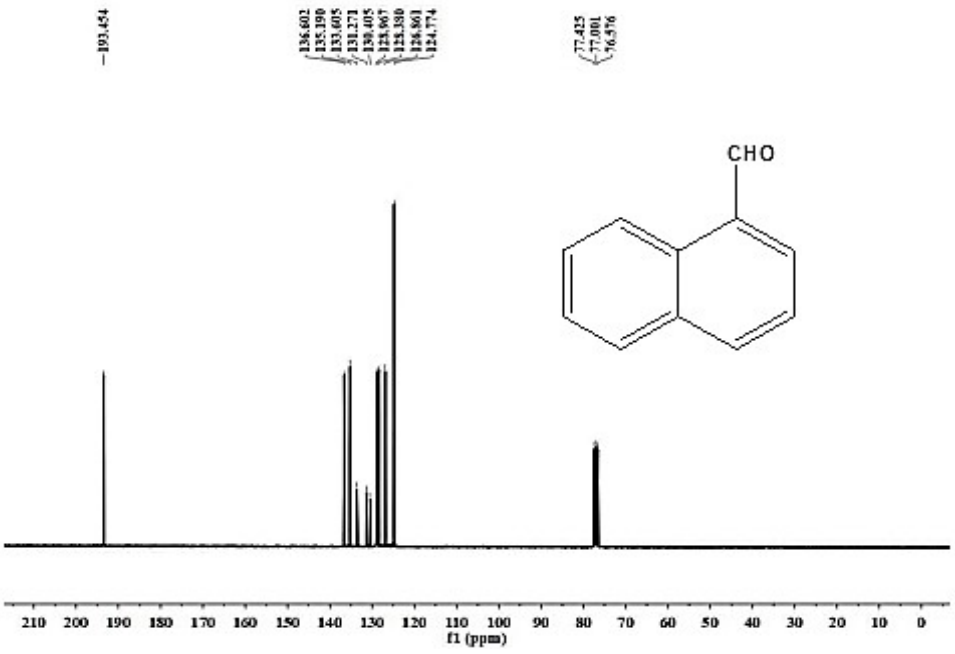

Figure 70 : ^{13} C NMR spectrum of Entry 40b ($CDCl_3$)

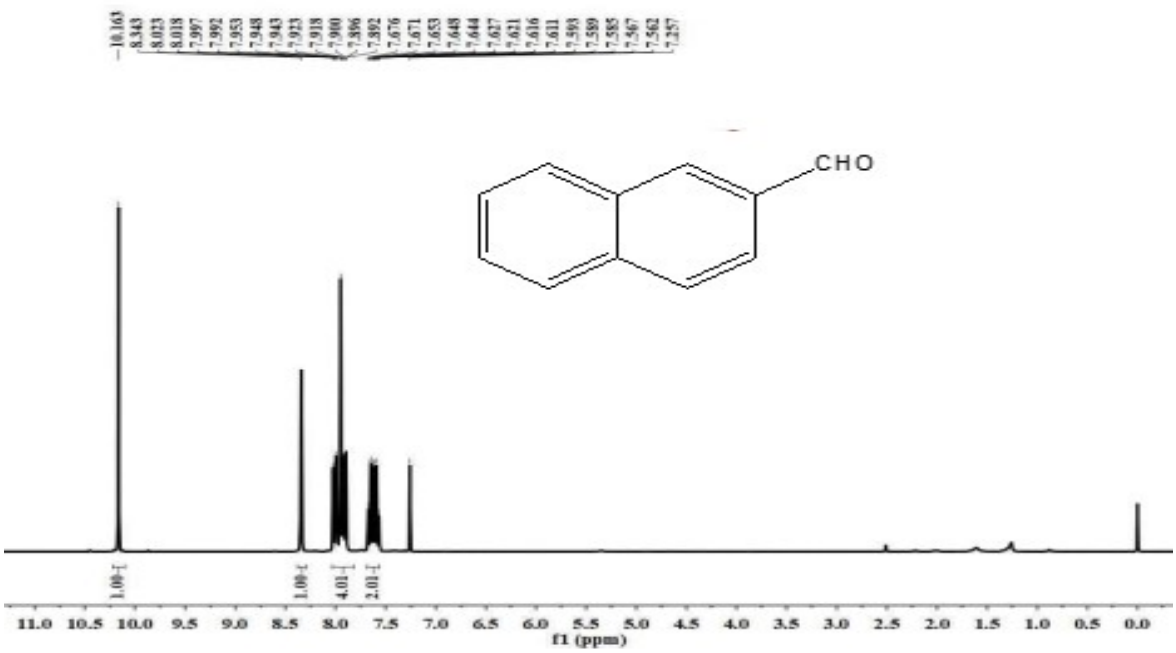

Figure 71: ^{1} H NMR spectrum of Entry 41b ($CDCl_3$,400 MHz)

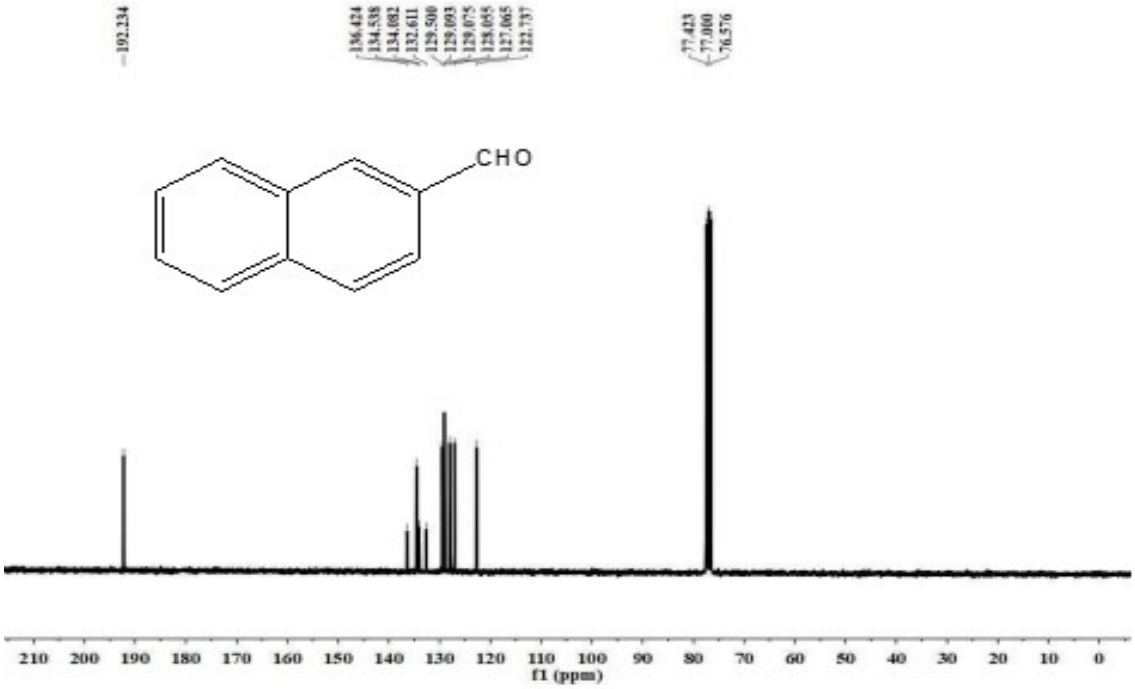

Figure 72 : ^{13} C NMR spectrum of Entry 41b ($CDCl_3$)

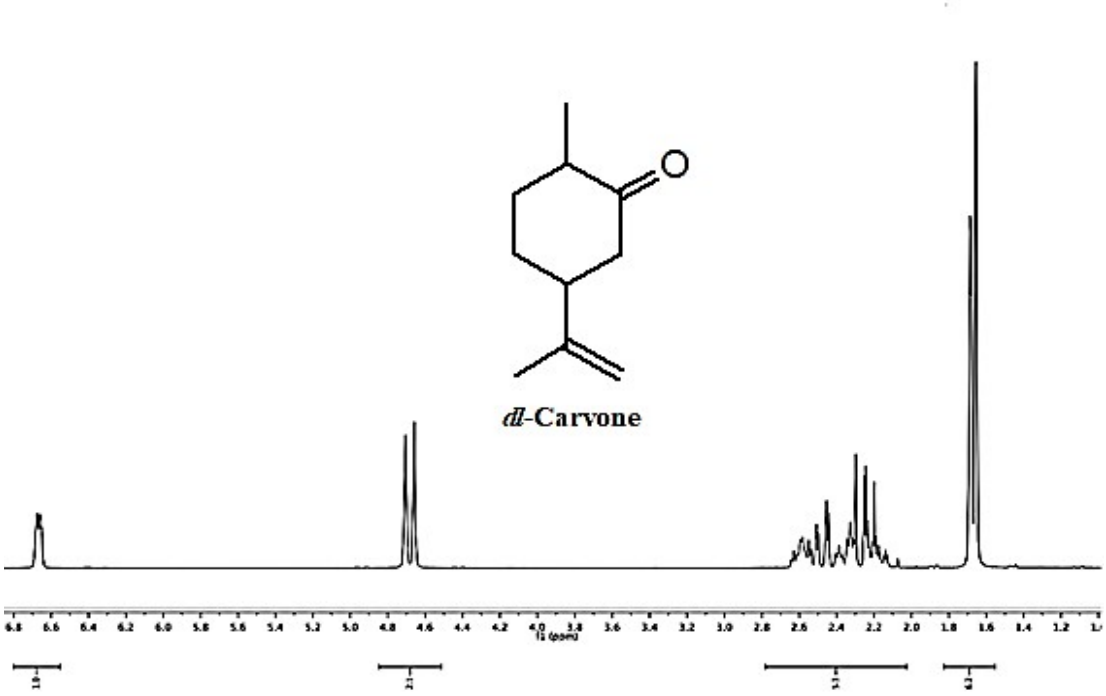

Figure 73: ^{1} H NMR spectrum of *dl*-Carvone ($CDCl_3$,400 MHz)

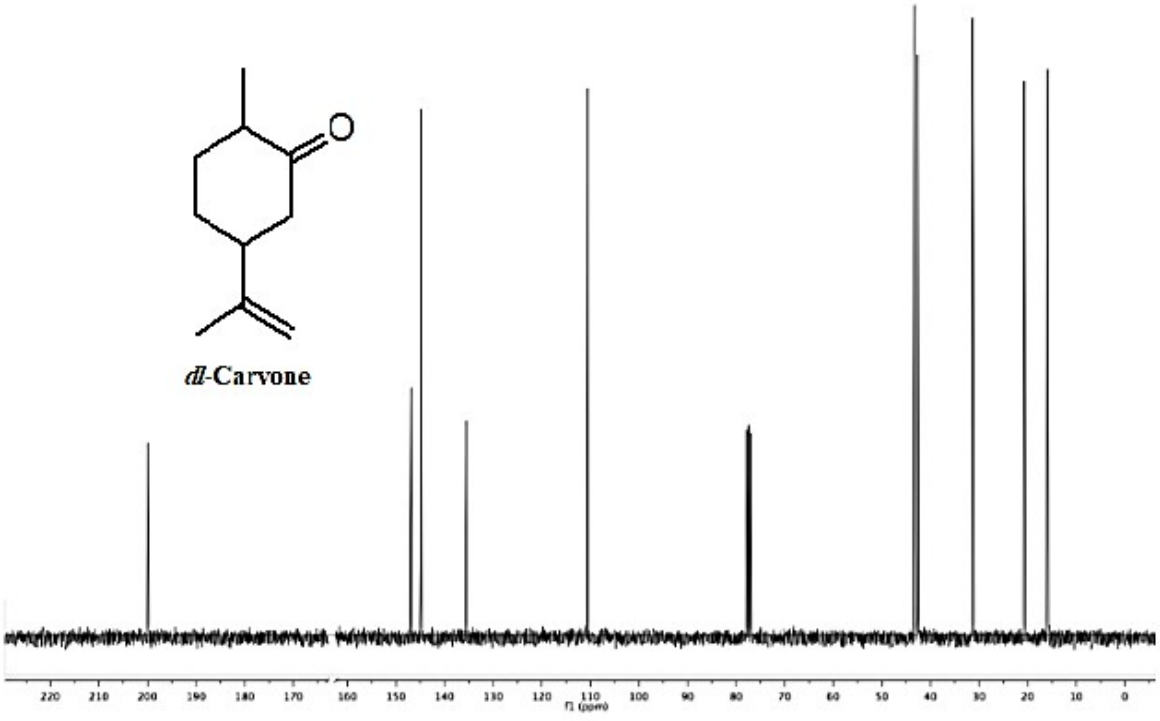

Figure 74 : ^{13} C NMR spectrum of *dl*-Carvone ($CDCl_3$)