Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Ligand controlled switchable selectivity in ruthenium catalyzed aerobic oxidation of primary amines

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EXPERIMENTAL SECTION

1. General considerations. Unless otherwise stated, all reactions were carried out under oxygen atmosphere in screw cap reaction tubes. All solids were weighed in air. All solvents were purchased from Merck, India and were used as received without using any drying agents. All primary amines were procured from Sigma Aldrich. Ruthenium complexes, $RuH(CO)Cl(PPh_3)_3$, $[Ru(isoQ)(PPh_3)_2(CO)(H)]ClO_4$ and $[Ru(bpy)(PPh_3)_2(CO)(H)]ClO_4$ as well as the BIAN ligands were synthesized according to the literature procedure.[1-5] TEMPO was obtained from Spectrochem Pvt. Ltd., India. For column chromatography, silica gel (100-200 mesh) from SRL Co. was used. A gradient elution using pet ether and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel 60F254) and visualized by UV (254 nm) lamp.

2. Analytical methods. The electrical conductivities of the complexes, [**1a**]ClO_4-[**1e**]ClO_4 and [**2**]ClO_4 in CH_3CN were checked by using Systronic 305 conductivity bridge. ^1H and ^{31}P NMR spectra were recorded using Bruker 400 MHz and 500 MHz instruments and unless otherwise stated all ^{31}P NMR spectra were obtained with ^1H decoupling. FT-IR spectra were recorded on a Nicolet spectrophotometer with samples prepared as KBr pellets. Cyclic voltammetry measurements were performed on a PAR model 273A electrochemistry system. Glassy carbon working electrode, platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used in a standard three-electrode configuration cell. A platinum wire-gauze working electrode was used for the constant potential coulometry experiment. The supporting electrolyte was Et_4NClO_4. All electrochemical experiments were carried out under dinitrogen atmosphere at 298 K. The half-wave potential E^0 was set equal to 0.5 (E_{pa} + E_{pc}), where E_{pa} and E_{pc} are anodic and cathodic cyclic voltammetry peak potentials, respectively. Electronic spectra were recorded on a Perkin Elmer λ-1050 spectrophotometer. The EPR measurements were carried out on a JEOL model FA200 ESR spectrometer. UV-vis studies were performed on BAS SEC2000 spectrometer system. The elemental analyses were carried out on a Thermoquest (EA 1112) microanalyzer. Electrospray mass spectra (ESI-MS) were recorded on a Bruker's Maxis Impact spectrometer (282001.00081).

Isolated compounds (nitriles and imines) were characterized by ^1H and ^{13}C NMR spectroscopy, as well as by gas chromatography mass spectrometry (GC-MS). Nuclear magnetic resonance spectra were recorded on Bruker 400 and 500 MHz instruments. Unless otherwise stated, all ^{13}C NMR spectra were obtained with ^1H decoupling. All GC analyses were performed on an Agilent 7890A GC system with an FID detector using a J & W DB-1 column (10 m, 0.1 mm I.D.) and using 1,3,5-Trimethoxybenzene as the internal standard. All GC-MS analyses were done using an Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD (with triple axis detector).

3. Crystallography. Single crystals of [**1a**]ClO_4, [**1b**]ClO_4 and [**1e**]ClO_4 were grown by slow evaporation of their 2:1 dichloromethane-hexane solution mixture. X-ray diffraction data were collected on a Rigaku Saturn-724+ CCD single crystal diffractometer. Data collection was evaluated by using the CrystalClear-SM Expert software. The data were collected by the standard ω scan technique. The structure was solved by direct method using SHELXS-97 and refined by full matrix least-squares with SHELXL-2014, refining on F^2.[6] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 U_{eq} of their parent atoms. Hydrogen atoms were included in the refinement process as per the riding model. Supplementary crystallographic data for the compounds in this paper have been provided by the Cambridge Crystallographic Data Centre (CCDC, www.ccdc.cam.ac.uk/data_request/cis): CCDC No. 1515770 ([**1a**]ClO_4), CCDC NO. 1515771 ([**1b**]ClO_4), CCDC No. 1515772 ([**1e**]ClO_4).

4. Computational details. Full geometry optimizations were carried out by using the density functional theory method at the (R)B3LYP level for **1b**$^+$, **1b**$^-$, **1e**$^+$, **1e**$^-$ and (U)B3LYP level for **1b**, **1e**, **1e**$^{2-}$.[7] Except ruthenium, all other elements were assigned with the 6-31G(d) basis set. The LANL2DZ basis set with effective core potential was employed for the ruthenium atom.[8] All calculations were performed with Gaussian09 program package.[9] Vertical electronic excitations based on (U)B3LYP optimized geometries were computed using the time-dependent density functional theory (TD-DFT) formalism[10] in acetonitrile using the conductor-like polarizable continuum model (CPCM).[11] *Chemissian 1.7*[12] was used to calculate the fractional contributions of various groups to each molecular orbital. All calculated structures were visualized with *ChemCraft*.[13]

5. Preparation of complexes. The complexes [**1a**]ClO_4-[**1e**]ClO_4 were prepared by following a general procedure. The method for the representative [**1a**]ClO_4 is given below.

*Synthesis of [Ru^{II}(OMe-BIAN)(PPh$_3$)$_2$(CO)(H)](ClO$_4$), [**1a**]ClO$_4$.* The precursor complex [Ru^{II}(H)(CO)(Cl)(PPh$_3$)$_3$] (100 mg, 0.105 mmol) and the ligand OMe-BIAN (34.86 mg, 0.105mmol) were taken in 30 mL of methanol and the mixture was heated to reflux for 3 h under aerobic condition. The initial greenish solution gradually changed to red. The reaction mixture was evaporated to dryness under reduced pressure. The resulting solid mass was dissolved in a minimum volume of acetonitrile, followed by addition of a saturated aqueous solution of sodium perchlorate to yield a dark red precipitate, which was filtered and washed thoroughly by ice water and dried in vacuo. The product was purified by column chromatography on a neutral alumina column. The reddish complex [**1a**]ClO_4 was eluted by a solvent mixture of CH_2Cl_2-CH_3CN (1:1). Evaporation of solvent under reduced pressure yielded the pure complex [**1a**]ClO_4.

[1a]ClO_4: Yield 85% (93.39 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11- 8.08 (m, 2H), 7.58-7.54 (t, *J*= 7.47 Hz, 1H), 7.47-7.43, 7.43 (m, 2H), 7.29-7.10 (m, 30H), 7.08-7.06 (d, *J*= 7.27 Hz, 1H) , 6.79-6.70 (dd, *J*= 28.62 Hz, 8.77 Hz, 4H), 6.46-6.44 (d, *J*= 9.18 Hz, 2H), 6.28- 6.24 (d, *J*= 9.18 Hz, 2H), 3.95 (s, 3H), 3.83 (s, 3H), −11.10-(−11.20) (t, *J*= 19.41 Hz, 1H); ^{31}P NMR (400 MHz, $CDCl_3$) δ 39.90. MS (ESI+/CH_3CN): *m/z* {**1a**}$^+$ calcd: 1047.26; found: 1047.23. Anal. Calcd (%) for $C_{63}H_{52}ClN_2O_7P_2Ru$: C, 65.94; H, 4.57; N, 2.44; found: C, 65.56; H, 4.14; N, 2.39. IR(KBr) ν(ClO_4,cm^{-1}) 1089, 619; (Ru–H + Ru–CO, cm^{-1}) 1947. Molar conductivity (CH_3CN): $\Lambda_M = 91\ \Omega^{-1}cm^2\ M^{-1}$.

[1b]ClO_4: Yield 78% (83.13 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.12 (dd, *J*= 8.18 Hz, 2.53 Hz, 2H), 7.57-7.54 (t, *J*= 7.043 Hz, 1H), 7.47-7.43 (t, *J*= 7.043 Hz, 1H), 7.39-7.37(d, *J*= 7.88 Hz, 1H), 7.29-7.09 (m, 31H), 7.02-7.01 (d, *J*= 7.88 Hz, 2H), 6.76-6.74 (d, *J*= 7.88 Hz, 2H), 6.67-6.65 (d, *J*= 7.88 Hz, 2H), 6.18-6.16 (d, *J*= 7.88 Hz, 2H), 2.50 (s, 3H), 2.35 (s, 3H), –11.08-(–11.18) (t, *J*= 19.82 Hz, 1H); ^{31}P NMR (400 MHz, $CDCl_3$) δ 39.59. MS (ESI+/CH_3CN): *m/z* {**1b**}$^+$ calcd: 1015.26; found: 1015.26. Anal. Calcd (%) for $C_{63}H_{52}ClN_2O_5P_2Ru$: C, 67.83; H, 4.70; N, 2.51; found: C, 67.99; H, 4.44; N, 2.84. IR(KBr) ν(ClO_4, cm^{-1}) 1089, 620; (Ru–H + Ru–CO, cm^{-1}) 1947. Molar conductivity (CH_3CN): $\Lambda_M = 93\ \Omega^{-1}\ cm^2\ M^{-1}$.

[1c]ClO_4: Yield 63% (65.75 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.15 (d, *J*= 7.96 Hz, 2H), 7.57-7.54 (t, *J*= 7.3 Hz, 1H), 7.49-7.43 (q, *J*= 6.3 Hz, 2H), 7.33-7.10 (m, 34H), 6.99- 6.92 (m, 3H), 6.75-6.73 (d, *J*= 7.96 Hz, 2H), 6.26-6.24 (d, *J*= 8.3 Hz, 2H), –11.05-(–11.14) (t, *J*= 19.124 Hz, 1H); ^{31}P NMR (400 MHz, $CDCl_3$) δ 39.31. MS (ESI+/CH_3CN): *m/z* {**1c**}$^+$ calcd: 987.22; found: 987.22. Anal. Calcd (%) for $C_{61}H_{48}ClN_2O_5P_2Ru$: C, 67.37; H, 4.45; N, 2.58; found: C, 67.78; H, 4.65; N, 2.36. IR(KBr) ν(ClO_4,cm^{-1}) 1086, 617; (Ru–H + Ru–CO, cm^{-1}) 1947. Molar conductivity (CH_3CN): $\Lambda_M = 86\ \Omega^{-1}\ cm^2\ M^{-1}$.

[1d]ClO_4: Yield 71% (79.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30-8.28 (d, *J*= 7.96 Hz, 2H), 7.64-7.61 (t, *J*= 7.7 Hz, 1H), 7.54-7.51 (t, *J*= 7.7 Hz, 1H), 7.33-7.13 (m, 33H) 6.97-6.96 (d, *J*= 7.58 Hz,1H), 6.91-6.89 (d, *J*= 8.78 Hz, 2H), 6.57-6.55 (d, *J*= 8.79 Hz, 2H), 6.20-6.18 (d, *J*= 8.54 Hz, 2H), –11.11-(–11.18) (t, *J*= 20.023 Hz, 1H); ^{31}P NMR (400 MHz, $CDCl_3$) δ 38.74. MS (ESI+/CH_3CN): *m/z* {**1d**}$^+$ calcd: 1055.14; found: 1055.15. Anal. Calcd (%) for: $C_{61}H_{46}Cl_3N_2O_5P_2Ru$: C, 63.36; H, 4.01; N, 2.42; found: C, 63.81; H, 3.81; N, 2.69. IR(KBr) ν(ClO_4,cm^{-1}) 1089, 620; (Ru–H + Ru–CO, cm^{-1}) 1950. Molar conductivity (CH_3CN): Λ_M = 92 Ω^{-1} cm^2 M^{-1}.

[1e]ClO_4: Yield 64% (72.37 mg) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.25 (d, *J*= 8.3 Hz, 2H), 8.04-8.02 (d, *J*= 8.8 Hz, 2H), 7.77-7.75 (d, *J*= 8.9 Hz, 3H), 7.69-7.15 (m, 33H), 6.91-6.89 (d, *J*= 7.42 Hz, 1H), 6.68-6.66 (d, *J*= 8.8 Hz, 1H), 6.48-6.46 (d, *J*= 8.9 Hz, 2H), –11.03-(–11.13) (t, *J*= 19.05 Hz, 1H); ^{31}P NMR (400 MHz, $CDCl_3$) δ 38.74. MS(ESI+/CH_3CN): *m/z* {**1e**}$^+$ calcd:

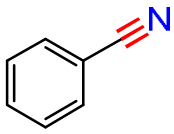
1077.19; found: 1077.19. Anal. Calcd (%) for $C_{61}H_{46}ClN_4O_9P_2Ru$: C, 62.22; H, 3.94; N, 4.76; found: C, 61.99; H, 3.78; N, 4.60. IR(KBr) $\nu(ClO_4,cm^{-1})$ 1089, 622; (Ru–H + Ru–CO, cm^{-1}) 1947. Molar conductivity (CH_3CN): $\Lambda_M = 89\ \Omega^{-1}\ cm^2\ M^{-1}$.

6. General procedure (A) for the oxidation of primary amines to nitriles. To an oven-dried screw cap reaction tube charged with a magnetic stir-bar, [**1a**]ClO_4 (2 mol%, 0.015 mmol) and TEMPO (20 mol%, 0.15 mmol) were added. Primary amine (0.75mmol) was then added in presence of toluene (3 mL) and the reaction tube was closed with screw cap followed by vigorous stirring in a preheated oil bath at 90 ^oC for 20 h under oxygen balloon pressure. Concentration of the reaction mixture was maintained at 0.25 mM. After completion, the reaction mixture was cooled to room temperature, diluted with water and extracted with (3x10 mL) of ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography using a mixture of pet ether:ethyl acetate as the eluent.

7. General procedure (B) for the oxidation of primary amines to imines. To an oven-dried screw cap reaction tube charged with a magnetic stir-bar, [**2**]ClO_4 (2 mol%, 0.015 mmol) and TEMPO (30 mol%, 0.225 mmol) were added. Primary amine (0.75mmol) was then added in presence of toluene (3 mL) and the reaction tube was closed with screw cap followed by vigorous stirring in a preheated oil bath at 110 ^oC for 24 h under oxygen balloon pressure. Concentration of the reaction mixture was maintained at 0.25 M. After completion, the reaction mixture was cooled to room temperature, diluted with water and extracted with (3x10 mL) of ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography using a mixture of pet ether:ethyl acetate as the eluent.

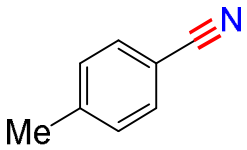
8. Details of products characterization

Nitriles



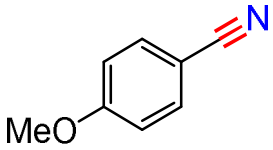
Benzonitrile (4a)[14,17]

Reaction was done by following the general procedure A with Benzylamine (0.75 mmol, 80 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 76%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66-7.645 (m, 2H), 7.63-7.59 (m, 1H), 7.47 (t, *J*= 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.78, 132.16, 129.13, 118.86, 112.46.



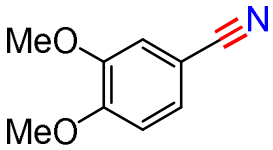
4-Methylbenzonitrile (4b)[15,17-19]

Reaction was done by following the general procedure A with 4-Methylbenzylamine (0.75 mmol, 91 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J*= 8.2, 2H), 7.26 (d, *J*= 8.5, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.72, 132.03, 129.85, 119.16, 109.30, 21.82.



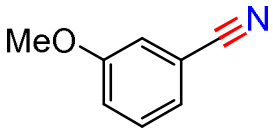
4-Methoxybenzonitrile (4c)[14,15,17-19]

Reaction was done by following the general procedure A with 4-Methoxybenzylamine (0.75 mmol, 102 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J*= 9.0 Hz, 2H), 6.97 (d, *J*= 9.0 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.87, 133.98, 119.20, 114.77, 104.02, 55.54.



3,4-Dimethoxybenzonitrile (4d)[16,18]

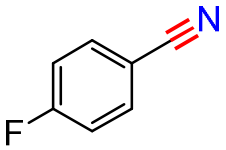
Reaction was done by following the general procedure A with 3,4-Dimethoxybenzylamine (0.75 mmol, 125 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 81%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J*= 8.3, 1.7 Hz, 1H), 7.09 (d, *J*= 1.8 Hz, 1H), 6.91 (d, *J*= 8.4 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.27, 149.10, 126.51, 119.42, 119.33, 114.10, 111.50, 104.00, 56.52.



3-Methoxybenzonitrile (4e)[14,18]

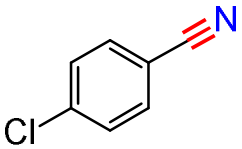
Reaction was done by following the general procedure A with 3-Methoxybenzylamine (0.75 mmol, 102 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO

(0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 1H), 7.26-7.23 (m, 1H), 7.14-7.12 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.82, 130.51, 124.69, 119.52, 118.94, 117.00, 113.39, 55.71.



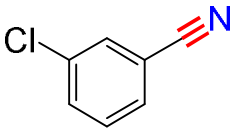
4-Fluorobenzonitrile (4f)[17,18]

Reaction was done by following the general procedure A with 4-Fluorobenzylamine (0.75 mmol, 94 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.66 (dd, *J*= 9.0, 5.1 Hz, 2H), 7.17 (t, *J*= 8.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.51, 163.96, 134.88 (d, *J*(C,F)= 9.2 Hz), 118.2, 117.06 (d, *J*(C,F)= 22.5 Hz), 108.75 (d, *J*(C,F)= 3.7 Hz). ^{19}F NMR ($CDCl_3$) δ -102.43.



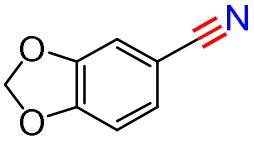
4-Chlorobenzonitrile (4g)[14,16,18,19]

Reaction was done by following the general procedure A with 4-Chlorobenzylamine (0.75 mmol, 106 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 44%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J*= 8.6, 2H), 7.47 (d, *J*= 8.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.59, 133.39, 131.00, 129.95, 118.25, 111.39.



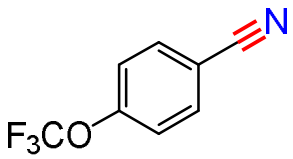
3-Chlorobenzonitrile (4h)[14]

Reaction was done by following the general procedure A with 3-Chlorobenzylamine (0.75 mmol, 107 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). GC Yield was 50%.



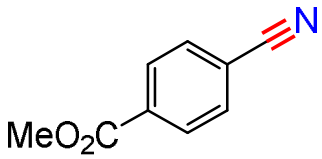
Benzo[d][1,3]dioxole-5-carbonitrile (4i)[17,18]

Reaction was done by following the general procedure A with Piperonylamine (0.75 mmol, 113 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.22 (dd, *J*= 8.1, 1.5 Hz, 1H), 7.06 (d, *J*= 1.5 Hz, 1H), 6.89 (d, *J*= 8.1 Hz, 1H), 6.09 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 148.2, 128.4, 119.1, 111.6, 109.3, 105.2, 102.4.



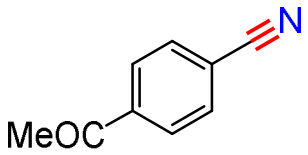
4-(Trifluoromethoxy)benzonitrile (4j)[18]

Reaction was done by following the general procedure A with 4-Trifluoromethoxybenzylamine (0.75 mmol, 143 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). GC yield was 51%.



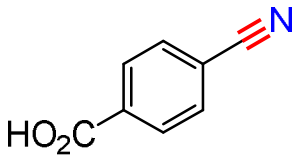
Methyl 4-cyanobenzoate (4k)

Reaction was done by following the general procedure A with Methyl 4-(aminomethyl)benzoate (0.75 mmol, 124 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 30 mol% TEMPO (0.3 mmol, 46 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 42%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.09 (d, *J*= 8.7 Hz, 2H), 7.73-7.71 (d, *J*= 8.7 Hz, 2H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.56, 134.04, 132.35, 130.20, 118.07, 116.47, 52.84.



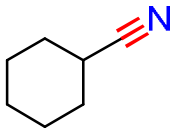
4-Acetylbenzonitrile (4l)

Reaction was done by following the general procedure A with methyl 4-Acetylbenzylamine (0.75 mmol, 112 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 30 mol% TEMPO (0.3 mmol, 46 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 51%. %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.01 (d, *J*= 8.3 Hz, 2H), 7.76-7.74 (d, *J*= 8.2 Hz, 2H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.49, 139.92, 132.65, 128.83, 117.91, 116.38, 26.65.



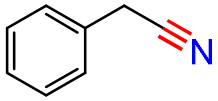
4-Cyanobenzoic acid (4m)

Reaction was done by following the general procedure A with methyl 4-aminomethylbenzoic acid (0.75 mmol, 113 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 30 mol% TEMPO (0.3 mmol, 46 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 44%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09-8.07 (d, *J*= 8.4 Hz, 2H), 7.98-7.96 (d, *J*= 8.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.07, 134.78, 132.58, 129.85, 118.17, 118.01, 115.10.



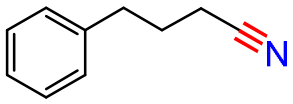
Cyclohexanecarbonitrile (4n)[17,19]

Reaction was done by following the general procedure A with Cyclohexylmethanamine (0.75 mmol, 85 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). GC yield was 75%.



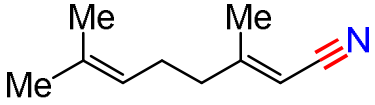
2-Phenylacetonitrile (4o)

Reaction was done by following the general procedure A with 2-Phenethylamine (0.75 mmol, 90 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). GC yield was 89%.



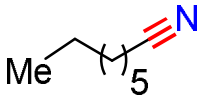
4-Phenylbutanenitrile (4p)[19]

Reaction was done by following the general procedure A with 4-Phenylbutanamine (0.75 mmol, 112 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.36 (m, 2H), 7.31-7.28 (m, 1H), 7.25 (d, *J*= 7.3 Hz, 2H), 2.84 (t, *J*= 7.4 Hz, 2H), 2.38 (t, *J*= 7.1 Hz, 2H), 2.08-2.02 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.30, 128.29, 128.07, 126.13, 119.11, 33.98, 26.53, 16.05.



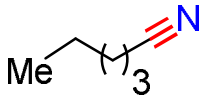
Geranylnitrile (4q)

Reaction was done by following the general procedure A with Geranylamine (0.75 mmol, 115 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.2-5.09 (m, 1H), 5.04-4.99 (m, 1H), 2.22-2.14 (m, 4H), 2.04 (d, *J*= 1.0 Hz, 3H), 1.68 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.07, 133.32, 122.26, 117.46, 95.50, 38.32, 25.47, 21.28, 18.34.



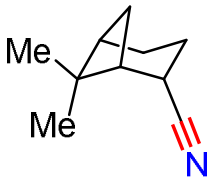
Octanenitrile (4r)[17]

Reaction was done by following the general procedure A with Octylamine (0.75 mmol, 98 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 83%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (t, *J*= 7.2 Hz, 2H), 1.66-1.62 (m, 2H), 1.46-1.40 (m, 2H), 1.33-1.25 (m, 6H), 0.88 (t, *J*= 6.90 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 120.03, 31.63, 28.77, 28.57, 25.52, 22.66, 17.27, 14.16.



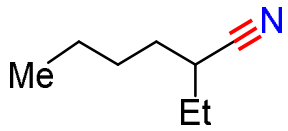
Hexanenitrile (4s)[20]

Reaction was done by following the general procedure A with Hexylamine (0.75 mmol, 76 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (t, *J*= 7.2 Hz, 2H), 1.69-1.63 (m, 2H), 1.46-1.33 (m, 4H), 0.92 (t, *J*= 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 120.06, 30.94, 25.24, 22.71, 22.05, 17.28, 13.92.



Myrtanylnitrile (4t)

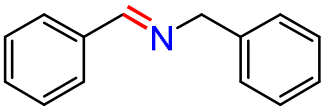
Reaction was done by following the general procedure A with Myrtanylamine (0.75 mmol, 115 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.18-3.14 (m, 1H), 2.23-1.42 (m, 8H), 1.249 (s, 3H), 1.176 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 124.38, 43.40, 40.09, 38.65, 34.86, 31.78, 29.37, 28.58, 27.11, 26.87, 25.47, 24.74, 22.85, 22.20, 18.11.



2-Ethylhexanenitrile (4u)[17]

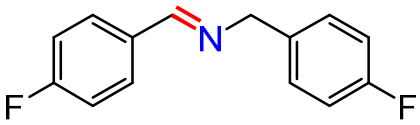
Reaction was done by following the general procedure A with 2-Ethylhexylamine (0.75 mmol, 97 mg) in presence of 2 mol% [**1a**]ClO_4 (0.015 mmol, 17 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 85%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.47-2.42 (m, 1H), 1.63-1.33 (m, 8H), 1.06 (t, *J*= 7.4 Hz, 3H), 0.91 (t, *J*= 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 122.49, 33.47, 31.76, 29.46, 28.32, 25.70, 22.92, 22.40, 22.01, 13.98, 11.75.

Imines



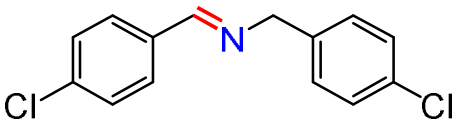
***N*-benzyl-1-phenylmethanimine (5a)**[21-23]

Reaction was done by following the general procedure B with Benzylamine (0.75 mmol, 80 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 30 mol% TEMPO (0.15 mmol, 35 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.82-7.80 (m, 2H), 7.45-7.43 (m, 3H), 7.37-7.36 (m, 4H), 7.31-7.26 (m, 1H), 4.85 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.16, 139.45, 136.31, 130.92, 128.76, 128.65, 128.44, 128.14, 127.14, 65.2.



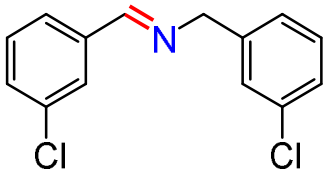
***N*-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (5b)**[21-23]

Reaction was done by following the general procedure B with 4-Fluorobenzylamine (0.75 mmol, 94 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 30 mol% TEMPO (0.15 mmol, 34 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 71%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.82-7.79 (m, 2H), 7.34-7.32 (m, 2H), 7.13 (t, *J*= 8.7 Hz, 2H), 7.07 (t, *J*= 8.7 Hz, 2H), 4.79 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.50, 163.51, 163.06, 161.11, 160.69, 135.05 (d, *J*(C,F)= 3.1 Hz), 132.43 (d, *J*(C,F)= 2.8 Hz), 130.29 (d, *J*(C,F)= 8.7 Hz), 129.59 (d, *J*(C,F)= 8.1 Hz), 115.84 (d, *J*(C,F)= 21.8 Hz), 115.41 (d, *J*(C,F)= 21.6 Hz), 64.23.



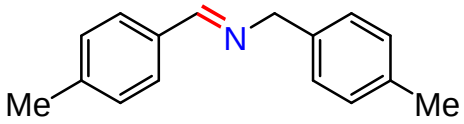
***N*-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (5c)**[21-23]

Reaction was done by following the general procedure B with 4-Chlorobenzylamine (0.75 mmol, 106 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 30 mol% TEMPO (0.15 mmol, 35 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.71 (d, *J*= 8.5 Hz, 2H), 7.40 (d, *J*= 8.5 Hz, 2H), 7.33-7.27 (m, 4H), 4.77 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.00, 137.73, 137.01, 134.56, 132.95, 129.60, 129.40, 129.07, 128.77, 64.30.



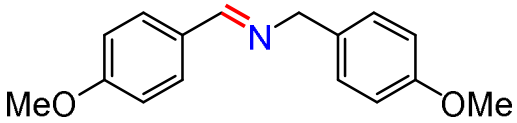
***N*-(3-chlorobenzyl)-1-(3-chlorophenyl)methanimine (5d)**[22]

Reaction was done by following the general procedure B with 3-Chlorobenzylamine (0.75 mmol, 106 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 30 mol% TEMPO (0.15 mmol, 34 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). GC yield was 65%.



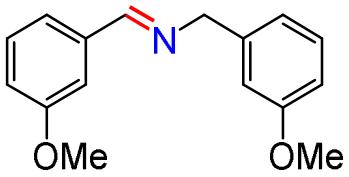
***N*-(4-methylbenzyl)-1-(*p*-tolyl)methanimine (5e)**[21-23]

Reaction was done by following the general procedure B with 4-Methylbenzylamine (0.75 mmol, 90 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 30 mol% TEMPO (0.15 mmol, 35 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.72 (d, *J*= 8.1 Hz, 2H), 7.28-7.18 (m, 6H), 4.81 (s, 2H), 2.42 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.80, 141.06, 136.60, 136.47, 133.74, 129.41, 129.27, 128.36, 128.07, 64.89, 21.60, 21.21.



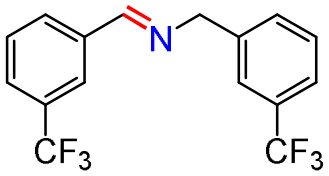
***N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (5f)**[21-23]

Reaction was done by following the general procedure B with 4-Methoxybenzylamine (0.75 mmol, 102 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 20 mol% TEMPO (0.15 mmol, 24 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.77 (d, *J*= 8.6 Hz, 2H), 7.30 (d, *J*= 8.4 Hz, 2H), 6.93 (t, *J*= 8.2 Hz, 4H), 4.74 (s, 2H), 3.75 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.35, 160.56, 158.32, 131.39, 129.53, 128.84, 113.64, 113.54, 64.00, 54.82, 54.73.



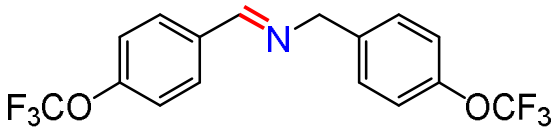
***N*-(3-methoxybenzyl)-1-(3-methoxyphenyl)methanimine (5g)**[21]

Reaction was done by following the general procedure B with 3-Methoxybenzylamine (0.75 mmol, 103 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 30 mol% TEMPO (0.15 mmol, 35 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 50%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.46 (s, 1H), 7.36-7.30 (m, 3H), 7.04-6.98 (m, 3H), 6.87-6.86 (m, 1H), 4.83 (s, 2H), 3.85 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.97, 159.82, 159.71, 140.77, 137.48, 129.96, 129.51, 129.44, 121.55, 120.25, 117.42, 113.60, 112.33, 111.68, 64.75, 55.19, 55.04.



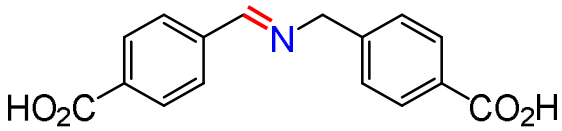
***N*-(3-(trifluoromethyl)benzyl)-1-(3-(trifluoromethyl)phenyl)methanimine (5h)**[22]

Reaction was done by following the general procedure B with 3-Trifluoromethylbenzylamine (0.75 mmol, 143 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 30 mol% TEMPO (0.15 mmol, 34 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.10 (s, 1H), 7.99 (d, *J*= 7.8 Hz, 1H), 7.71-7.47 (m, 6H), 4.89 (s, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 161.10, 140.19, 136.81, 131.56 (d, *J*(C,F)= 15.2 Hz), 131.21 (d, *J*(C,F)= 3.9 Hz), 129.36, 129.17, 127.56 (q, *J*(C,F)= 3.6 Hz), 125.13 (q, *J*(C,F)= 3.3 Hz), 124.79 (q, *J*(C,F)= 3.7 Hz), 124.13 (q, *J*(C,F)= 3.7 Hz), 64.53.



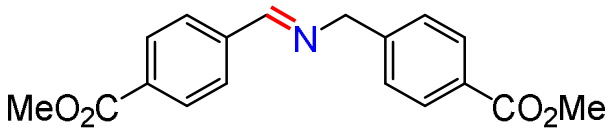
***N*-(4-(trifluoromethoxy)benzyl)-1-(4-(trifluoromethoxy)phenyl)methanimine (5i)**[24]

Reaction was done by following the general procedure B with 4-Trifluoromethoxybenzylamine (0.75 mmol, 143 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 30 mol% TEMPO (0.15 mmol, 34 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.83 (d, *J*= 8.7 Hz, 2H), 7.37 (d, *J*= 8.6 Hz, 2H), 7.27 (d, *J*= 7.2 Hz, 2H), 7.20 (d, *J*= 8.1 Hz, 2H), 4.82 (s, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 160.62, 151.06, 148.30, 137.86, 134.47, 131.57, 129.78, 129.20, 121.10, 120.92, 64.09.



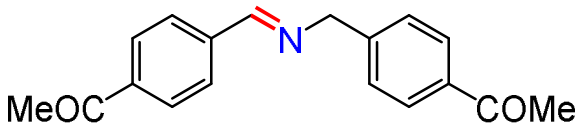
***N*-4-(((4-carboxybenzyl)imino)methyl)benzoic acid (5j)**

Reaction was done by following the general procedure B with 4-aminomethylbenzoic acid (0.75 mmol, 113 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 30 mol% TEMPO (0.15 mmol, 34 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). GC yield was 84%.



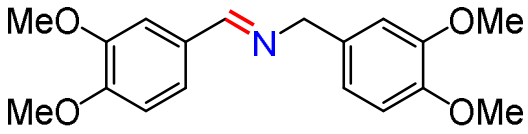
Methyl (*N*)-4-(((4-(methoxycarbonyl)benzyl)imino)methyl)benzoate (5k)

Reaction was done by following the general procedure B with 4-(aminomethyl)benzoate (0.75 mmol, 124 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 30 mol% TEMPO (0.15 mmol, 34 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). GC yield was 77%.



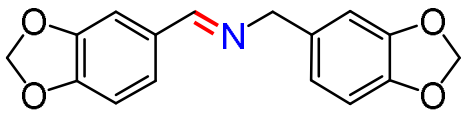
***N*-1-(4-(((4-acetylbenzyl)imino)methyl)phenyl)ethan-1-one (5l)**

Reaction was done by following the general procedure B with 4-acetylbenzylamine (0.75 mmol, 124 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 30 mol% TEMPO (0.15 mmol, 34 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). GC yield was 82%.



***N*-(3,4-dimethoxybenzyl)-1-(3,4-dimethoxyphenyl)methanimine (5m)**[23]

Reaction was done by following the general procedure B with 3,4-Dimethoxybenzylamine (0.75 mmol, 125.3 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 30 mol% TEMPO (0.15 mmol, 34 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). Yield was 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.49 (s, 1H), 7.2-7.17 (m, 1H), 6.89-6.83 (m, 4H), 4.74 (s, 2H), 3.93-3.87 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.28, 151.48, 149.38, 149.04, 148.15, 132.05, 129.47, 123.27, 120.23, 111.53, 111.31, 110.45, 108.93, 64.66, 56.18, 55.98, 55.95, 55.88.



1-(benzo[d][1,3]dioxol-5-yl)-*N*-(benzo[d][1,3]dioxol-5-ylmethyl)methanimine (5n)[23]
Reaction was done following general procedure B with Piperonylamine (0.75 mmol, 114 mg) in presence of 2 mol% [**2**]ClO_4 (0.015 mmol, 13 mg) and 30 mol% TEMPO (0.15 mmol, 34 mg) in toluene under O_2 atmosphere (O_2 = 1 atm). GC yield was 70%.

9. Mechanistic investigations.

a) Determination of the order for [1a]ClO_4 catalyzed nitrile formation with respect to amine.

Kinetic study was performed by taking the standard reaction of benzylamine. All the reactions were done by following the standard reaction protocol (*general procedure A*). Amount of product and reactant in each reaction was measured by gas chromatography using 1,3,5-Trimethoxybenzene as an internal standard.

Rate = k.[amine]^x[oxidant]^y
[x = order with respect to amine; y = order with respect to the oxidant; k = rate constant]

Run	Benzylamine (mmol)	[1a]ClO_4	TEMPO	T (^{o}C)	Toluene (mL)
1	0.25	2 mol%	20 mol%	90	3
2	0.5	2 mol%	20 mol%	90	3

From the different set of experiments (**Run 1** and **Run 2**) the following product formation plots were observed:

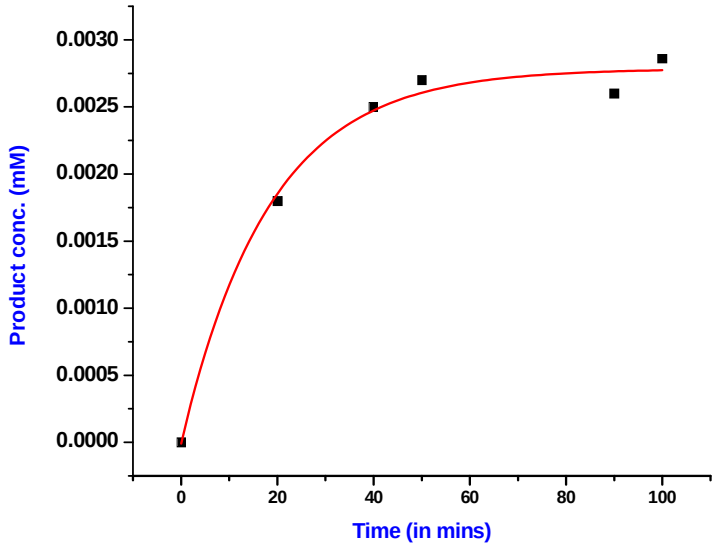


Figure S1a. Product formation plot in **Run 1** (amine = 0.25 mmol) (R^2 = 0.99).

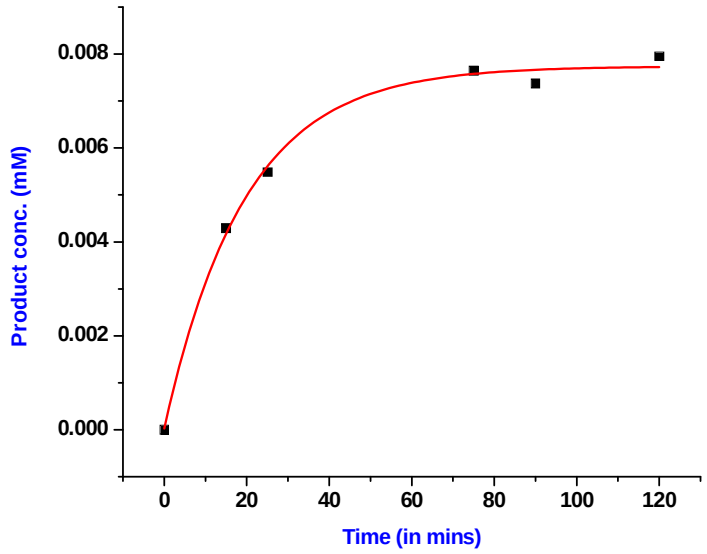


Figure S1b. Product formation plot in **Run 2** (amine = 0. 5 mmol) (R^2 = 0.97).

From the product formation plots (Figures S1 and S2), the order of the reaction with respect to amine (x) was found to be **1.28**.

b) Determination of the order for [2]ClO_4 catalyzed imine formation with respect to amine.

Kinetic study was performed by taking the standard reaction of benzylamine. All the reactions were done by following the standard reaction protocol (*general procedure B*). Amount of product and reactant in each reaction was measured by gas chromatography using 1,3,5-Trimethoxybenzene as an internal standard.

Rate = k.[amine]^x[oxidant]^y
[x = order with respect to amine; y = order with respect to the oxidant; k = rate constant]

Run	Benzylamine (mmol)	[2]ClO_4	TEMPO	T (^{o}C)	Toluene (mL)
1	0.25	2 mol%	20 mol%	90	1.5
2	0.5	2 mol%	20 mol%	90	1.5

From the different set of experiments (**Run 1** and **Run 2**) the following product formation plots were observed:

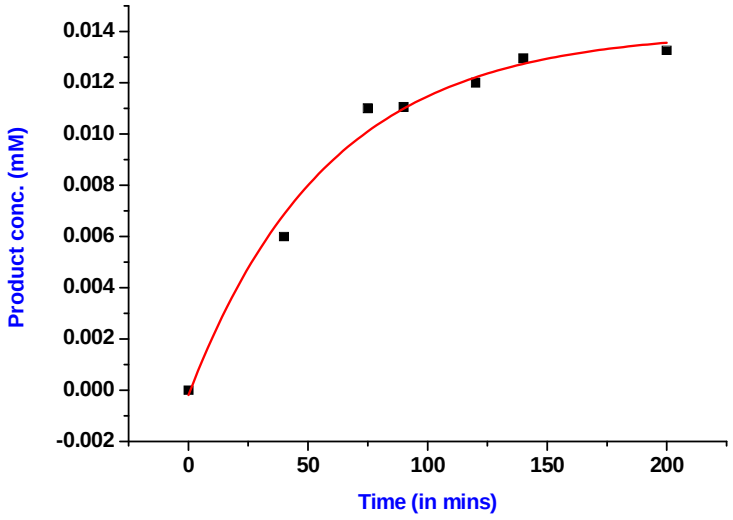


Figure S2a. Product formation plot in **Run 1** (amine = 0. 25 mmol) (R^2 = 0.98).

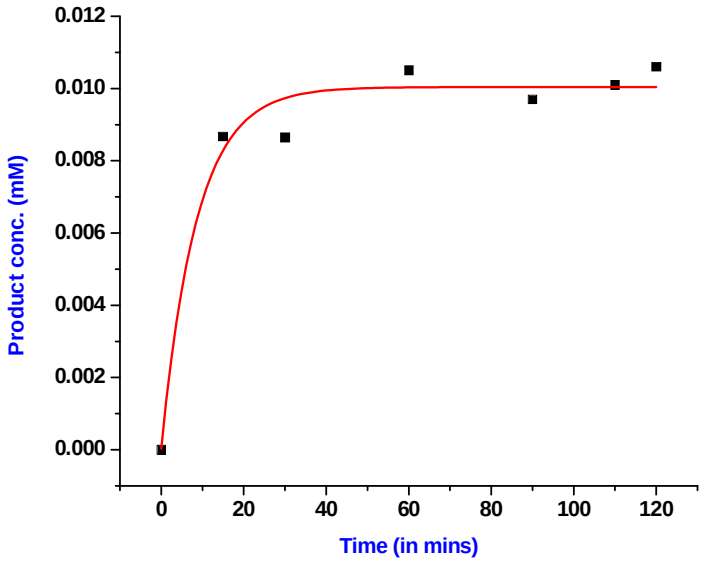


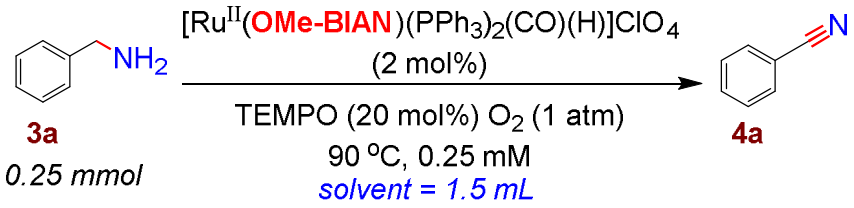
Figure S2b. Product formation plot in **Run 2** (amine = 0. 5 mmol) (R^2 = 0.97).

From the product formation plots (Figures S3 and S4), the order of the reaction with respect to amine (x) was found to be **1**.

c) Determination of k_H/k_D for [1a]ClO_4 catalyzed nitrile formation.

Kinetic study was performed by monitoring the reaction of benzylamine ($PhCH_2NH_2$) and deuterated benzylamine ($PhCD_2NH_2$). All the reactions were done by following the standard reaction protocol for [**1a**]ClO_4 catalyzed nitrile formation (*general procedure A*). Amount of product and reactant in each reaction was measured by gas chromatography using 1,3,5-Trimethoxybenzene as an internal standard.

Set 1:



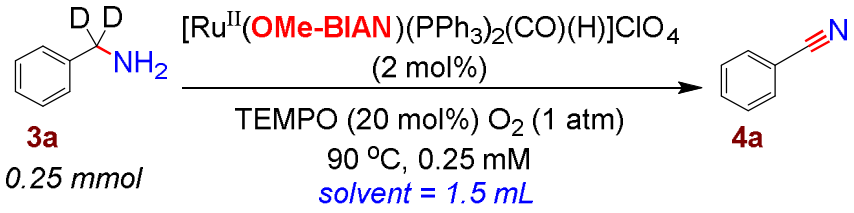
Rate (R_H) = $k_H.[PhC\mathbf{H_2}NH_2]^x$……..(1)

(x = order with respect to amine, k_H = rate constant for reaction of $PhC\mathbf{H_2}NH_2$)

From the product formation plot (as shown in Figure 1a in the MS),

6.9×10^{-5} (R_H) = $k_H.[0.25]^x$……(2)

Set 2:



Rate (R_D) = $k_D.[PhCD_2NH_2]^x$……..(3)

(x = order with respect to amine, k_D = rate constant for reaction of $PhCD_2NH_2$[25])

From the product formation plot (as shown in Figure 1a in the MS),

4.04×10^{-5} (R_H) = $k_D.[0.25]^x$……(4)

Hence, from equations (2) and (4) we get, [6.9/4.04] = (k_H/k_D)
So, (k_H/k_D) = 1.7 .

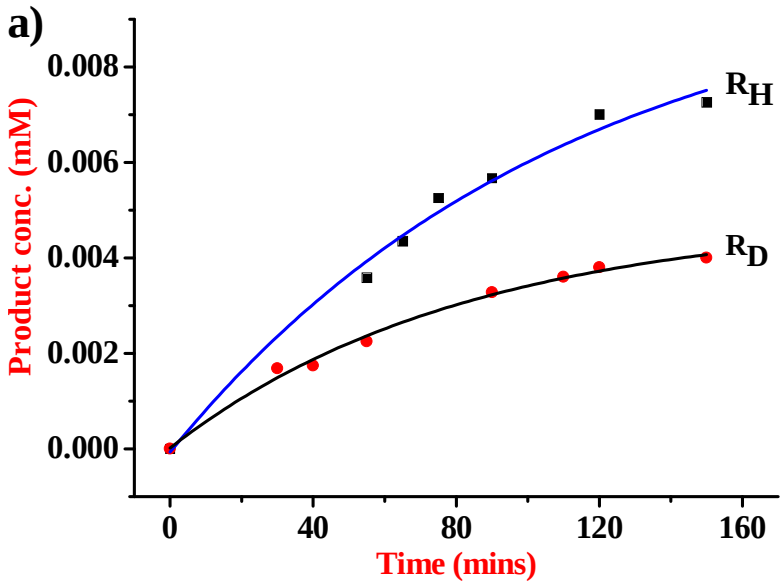
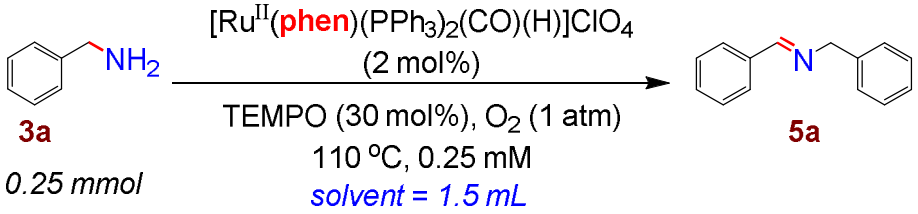


Figure S3. Kinetic isotope effect data for [**1a**]ClO_4 catalyzed oxidation of $PhCH_2NH_2$ and isotopically labeled $PhCD_2NH_2$ to nitrile

d) Determination of k_H/k_D for [2]ClO_4 catalyzed imine formation.

Kinetic study was performed by monitoring the reaction of benzylamine ($PhCH_2NH_2$) and deuterated benzylamine ($PhCD_2NH_2$). All the reactions were done by following the standard reaction protocol for [**2**]ClO_4 catalyzed imine formation (see *general procedure B*). Amount of product and reactant in each reaction was measured by gas chromatography using 1,3,5-Trimethoxybenzene as an internal standard.

Set 3:



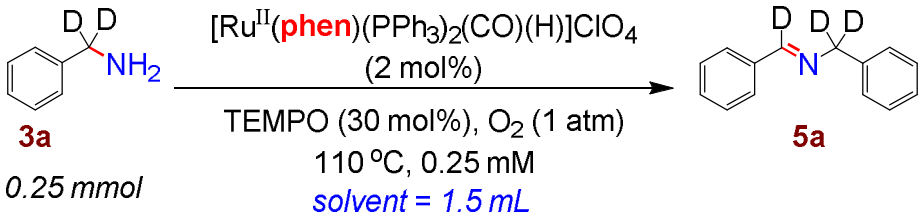
Rate (R_H) = k_H.[Ph**CH_2**NH_2]^x……..(5)

(x = order with respect to amine, k_H = rate constant for reaction of Ph**CH_2**NH_2)

From the product formation plot (as shown in Figure 1b in the MS),

1.64 x 10^{-4} (R_H) = k_H.[0.25]^x……(6)

Set 4:



Rate (R_D) = k_D.[Ph**CD_2**NH_2]^x……..(7)

(x = order with respect to amine, k_D = rate constant for reaction of Ph**CD_2**NH_2[25])

From the product formation plot (as shown in Figure 1b in the MS),

6.8 x 10^{-4} (R_H) = k_D.[0.25]^x……(8)

Hence, from equations (6) and (8) we get, [1.64/6.8] = (k_H/k_D)
So, (k_H/k_D) = 0.24.

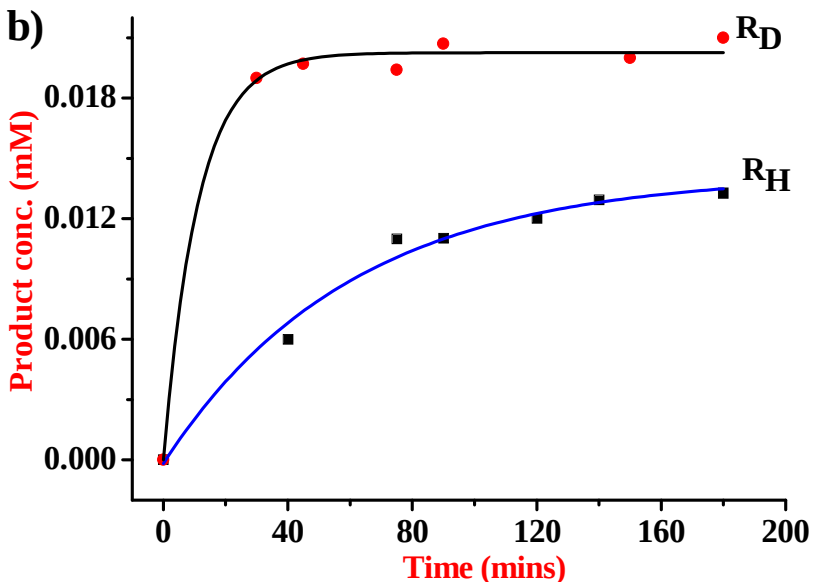


Figure S4. Kinetic isotope effect data for [**2**]ClO_4 catalyzed oxidation of $PhCH_2NH_2$ and isotopically labeled $PhCD_2NH_2$ to imine.

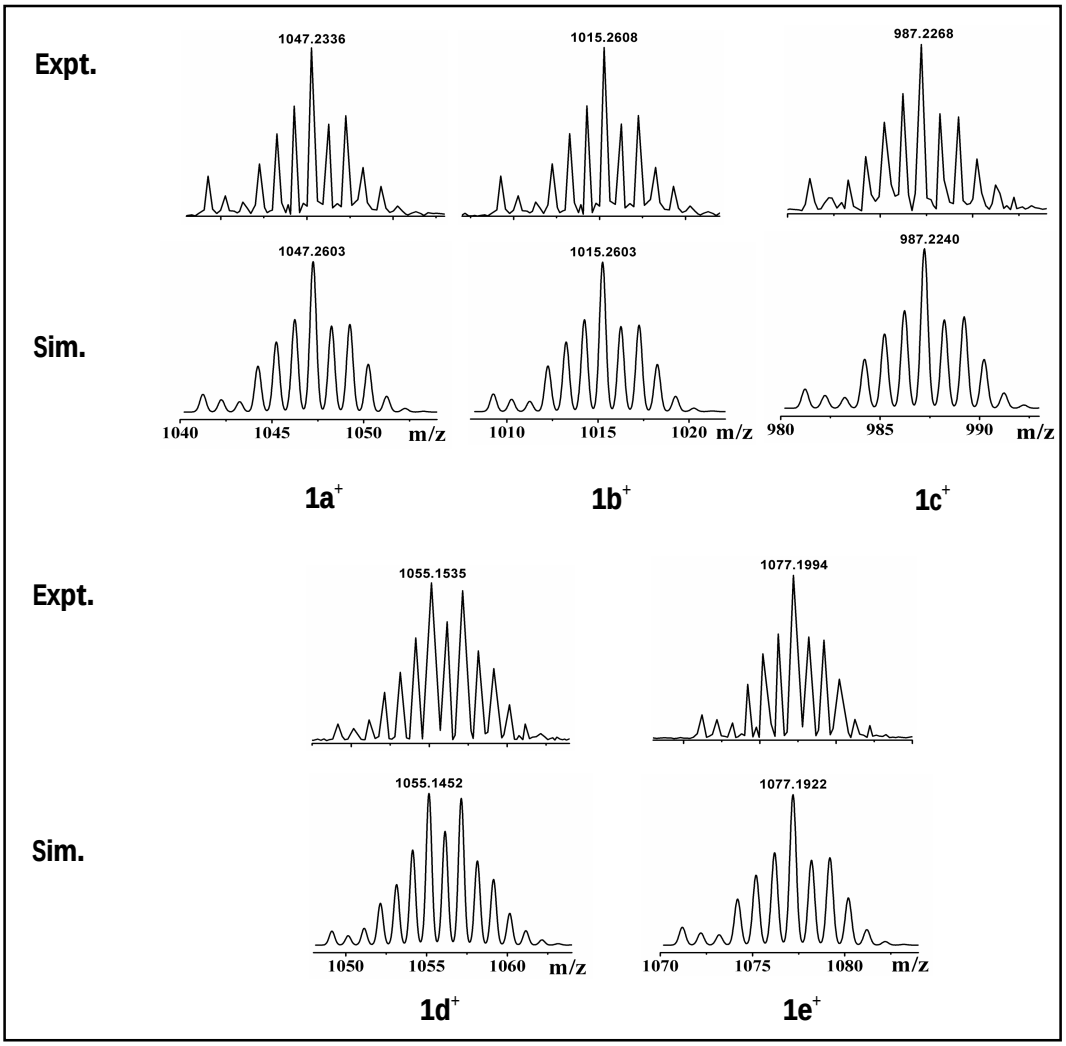


Figure S5. Mass spectra in CH_3CN.

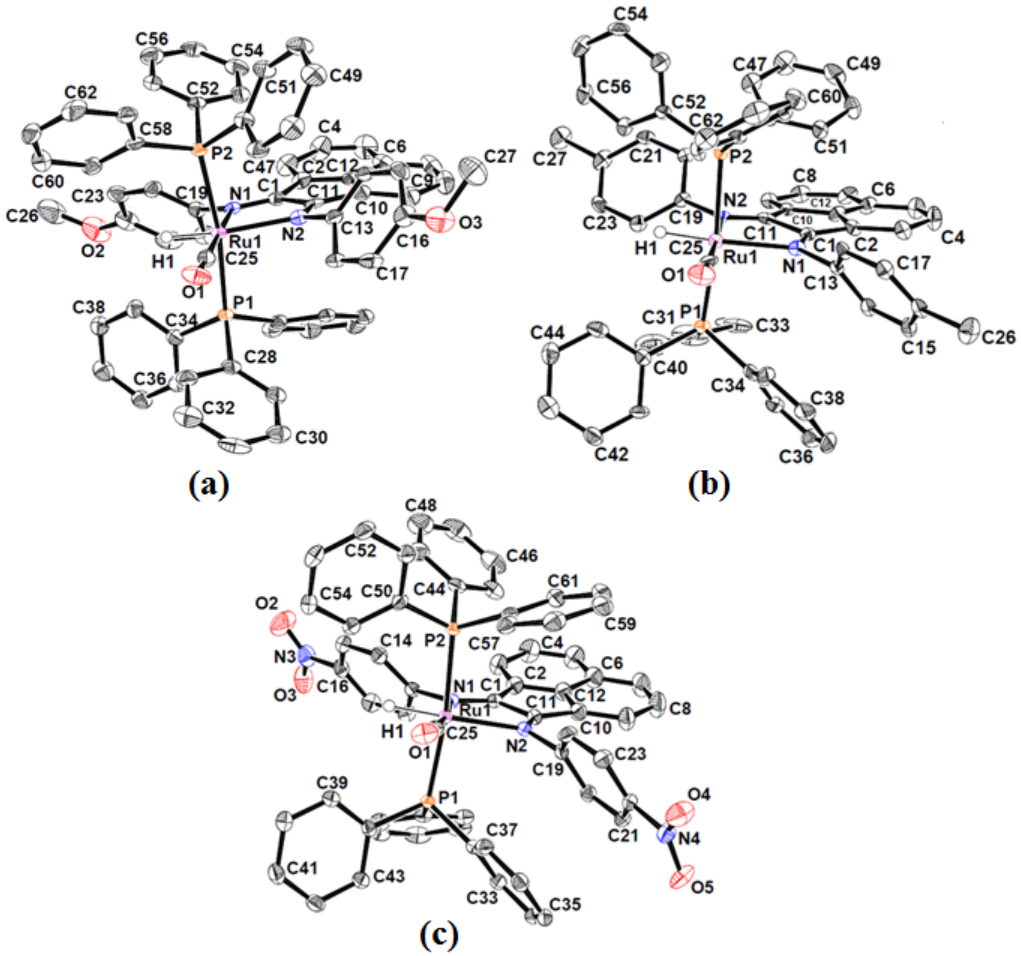


Figure S6. ORTEP diagrams of a) [**1a**]ClO_4, b) [**1b**]ClO_4 and c) [**1e**]ClO_4. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms (except Ru–H) and ClO_4 anions are omitted for clarity.

Table S1. Selected crystallographic parameters for [1a]$ClO_4.CH_2Cl_2$, [1b]$ClO_4.2CH_2Cl_2$ and [1e]$ClO_4.CH_2Cl_2$

complex	[**1a**]$ClO_4.CH_2Cl_2$	[**1b**]$ClO_4.2CH_2Cl_2$	[**1e**]$ClO_4.CH_2Cl_2$
empirical formula	$C_{64}H_{53}Cl_3N_2O_7P_2Ru$	$C_{65}H_{55}Cl_5N_2O_5P_2Ru$	$C_{62}H_{47}Cl_3N_4O_9P_2Ru$
formula weight	1231.45	1284.37	1261.39
crystal system	monoclinic	triclinic	triclinic
space group	*P*21/*c*	*P*ī	*P*ī
a (Å)	11.387(3)	11.8945(19)	11.897(2)
b (Å)	23.226(6)	14.063(2)	13.638(3)
c (Å)	20.986(6)	18.356(3)	20.788(4)
α (deg)	90	98.289(2)	100.4470(10)
β (deg)	95.277(5)	105.598(3)	100.464(2)
γ (deg)	90	90.117(3)	113.912(2)
V (Å³)	5527(3)	2923.8(8)	2907.6(10)
Z	4	2	2
μ (mm^{-1})	0.545	0.604	0.523
T (K)	150(2)	150(2)	150(2)
D_{calcd}(g cm^{-3})	1.480	1.459	1.441
F(000)	2528	1316	1288
θ range(deg)	3.05 to 25.00	3.05 to 25.00	3.04 to 25.00
data/restraints/ parameters	9711 / 0 / 712	10176 / 30 / 727	10198 / 0 / 734
R_1, wR_2 [$I>2\sigma(I)$]	0.0897, 0.2060	0.0738, 0.1681	0.0453, 0.1146
R_1, wR_2(all data)	0.0988, 0.2127	0.1091, 0.1946	0.0488, 0.1180
GOF	1.157	0.951	0.956
largest diff. peak/hole, (e $Å^{-3}$)	1.88/–1.39	1.65/–1.12	1.62 /–1.43

Table S2. Selected bond lengths (Å) for [1a]$ClO_4.CH_2Cl_2$, [1b]$ClO_4.2CH_2Cl_2$ and [1e]$ClO_4.CH_2Cl_2$

bond lengths (Å)	[**1a**]ClO_4**.**CH_2Cl_2	[**1b**]ClO_4**.**$2CH_2Cl_2$	[**1e**]ClO_4**.**CH_2Cl_2
Ru1–N1	2.167(5)	2.172(5)	2.139(3)
Ru1–N2	2.161(6)	2.150(5)	2.201(3)
Ru1–P1	2.3951(17)	2.3798(17)	2.3643(9)
Ru1–P2	2.3852(18)	2.3829(16)	2.4022(9)
Ru1–C25	1.835(7)	1.838(8)	1.846(3)
Ru1–H1	1.43(7)	1.55(5)	1.55(3)
N1–C1	1.298(8)	1.308(8)	1.302(4)
N2–C11	1.298(8)	1.320(8)	1.294(4)
C1–C11	1.505(9)	1.487(8)	1.492(4)
C1–C2	1.477(9)	1.475(9)	1.464(4)
C2–C12	1.419(10)	1.431(8)	1.415(5)
C10–C11	1.470(9)	1.474(9)	1.470(5)
C10–C12	1.409(10)	1.415(8)	1.420(5)
O1–C25	1.155(8)	1.165(8)	1.157(4)

Table S3. Selected bond angles (deg) for [1a]ClO_4.CH_2Cl_2, [1b]ClO_4.2CH_2Cl_2 and [1e]ClO_4.CH_2Cl_2

bond angles (deg)	[**1a**]ClO_4.CH_2Cl_2	[**1b**]ClO_4.2CH_2Cl_2	[**1e**]ClO_4.CH_2Cl_2
C(25)–Ru(1)–N(1)	177.3(2)	104.5(2)	175.15(12)
C(25)–Ru(1)–N(2)	104.5(2)	178.4(2)	108.39(12)
N(1)–Ru(1)–N(2)	76.18(19)	76.87(19)	75.90(10)
C(25)–Ru(1)–P(1)	90.9(2)	87.34(19)	88.72(10)
N(1)–Ru(1)–P(1)	86.46(14)	91.22(13)	93.50(7)
N(2)–Ru(1)–P(1)	95.39(14)	93.45(13)	91.00(7)
C(25)–Ru(1)–P(2)	87.0(2)	90.77(19)	85.04(10)
N(1)–Ru(1)–P(2)	95.58(14)	94.60(13)	92.28(7)
N(2)–Ru(1)–P(2)	92.72(14)	88.32(13)	96.73(7)
P(1)–Ru(1)–P(2)	171.89(6)	174.16(6)	171.29(3)
C(25)–Ru(1)–H(1)	86(3)	78(2)	86.8(12)
N(1)–Ru(1)–H(1)	93(3)	178(2)	89.0(12)
N(2)–Ru(1)–H(1)	169(3)	101(2)	164.8(12)
P(1)–Ru(1)–H(1)	88(3)	89.4(17)	88.4(12)
P(2)–Ru(1)–H(1)	84(3)	84.8(17)	85.2(12)

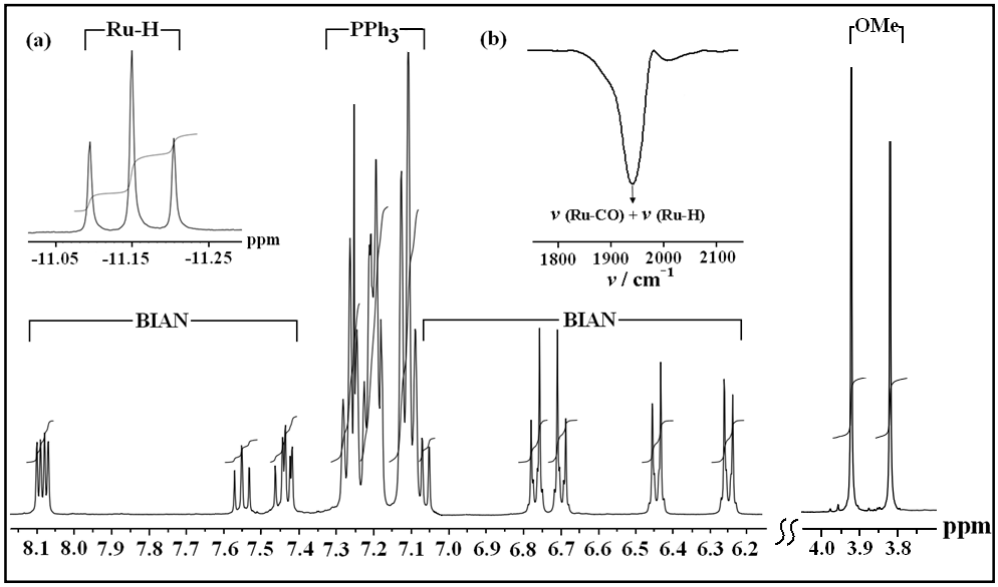


Figure S7. ^{1}H-NMR spectrum of [**1a**]ClO_4 in $CDCl_3$. Inset shows (a) triplet due to the hydridic (Ru–H) proton resonance and (b) overlapping Ru–CO/Ru–H vibrations in the IR spectrum of [**1a**]ClO_4 (as KBr disk).

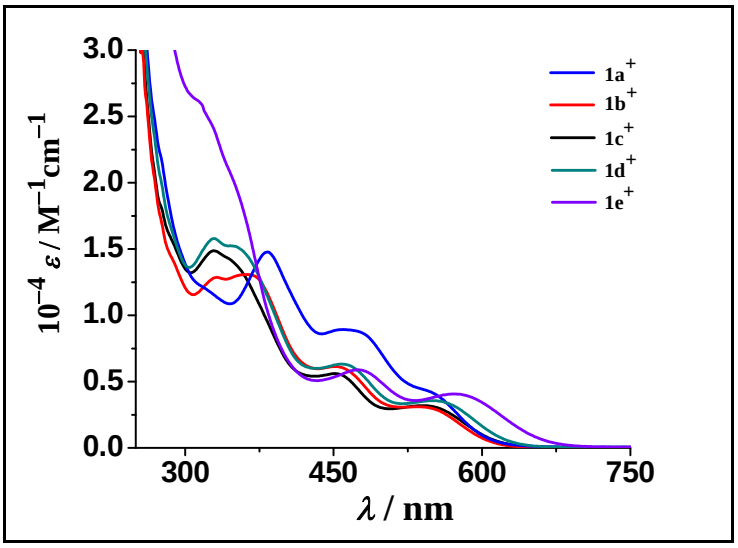


Figure S8. UV-vis spectra of **1a**$^{+}$ (blue), **1b**$^{+}$ (red), **1c**$^{+}$ (black), **1d**$^{+}$ (green), **1e**$^{+}$ (violet) in CH_3CN.

Table S4. UV-vis spectral data of complexes in CH_3CN

complex	λ/nm (ε/$M^{-1}cm^{-1}$)
1a^{+}	555 (3870), 470 (8840), 383 (14790)
1b^{+}	548 (2980), 454 (6090), 364 (13030)
1c^{+}	545 (3210), 454 (5540), 345 (14220)
1d^{+}	557 (3460), 462 (6200), 354 (15110)
1e^{+}	578 (4040), 474 (5970), 315 (25980)

Table S5. TD-DFT calculated electronic transitions for $1b^n$ and $1e^n$

λ / nm expt. (DFT)	ε / $M^{-1}cm^{-1}$ (*f*)	transitions	character
		$1b^+$ (S = 0)	
549 (523)	2930 (0.082)	HOMO→LUMO(0.69)	BIAN(π)/Ru(dπ)/PPh_3(π)→BIAN(π*)
461 (474) 461 (439)	5640 (0.114) 5640 (0.054)	HOMO-1→LUMO(0.66) HOMO-2→LUMO(0.63)	PPh_3(π)/BIAN(π)/Ru(dπ)→BIAN(π*) BIAN(π)/Ru(dπ)/PPh_3(π)→BIAN(π*)
368 (384) 368 (372)	14880 (0.092) 14880 (0.072)	HOMO-8→LUMO(0.38) HOMO-6→LUMO(0.42)	PPh_3(π)/BIAN(π)→BIAN(π*) PPh_3(π)/BIAN(π)→BIAN(π*)
		1b (S = 1/2)	
– (1135)	– (0.03)	HOMO→LUMO(α)(0.99)	BIAN(π)→BIAN(π*)
652 (658)	1380 (0.006)	HOMO→LUMO+1(α)(0.98)	BIAN(π)→PPh_3(π*)/Ru(dπ)
652 (553)	1380 (0.06)	HOMO→LUMO(β)(0.86)	BIAN(π)/Ru(dπ)→BIAN(π*)
544 (546)	2460 (0.02)	HOMO→LUMO+2(α)(0.75) HOMO→LUMO(β)(0.40)	BIAN(π)→PPh_3(π*) BIAN(π)/Ru(dπ)→BIAN(π*)
455 (436)	4960 (0.05)	HOMO-1→LUMO(β)(0.84)	BIAN(π)/Ru(dπ)/PPh_3(π)→BIAN(π*)
371 (388)	12040 (0.11)	HOMO→LUMO+17(α)(0.75) HOMO-1→LUMO(α)(0.39)	BIAN(π)→BIAN(π*)/PPh_3(π*) BIAN(π)/Ru(dπ)→BIAN(π*)
338 (354)	10260 (0.05)	HOMO-1→LUMO+1(β)(0.59) HOMO-2→LUMO(α)(0.40)	BIAN(π)/Ru(dπ)/PPh_3(π)→BIAN(π*) Ru(dπ)/BIAN(π)/PPh_3(π)→BIAN(π*)
		$1b^-$ (S = 0)	
–(1148)	–(0.06)	HOMO→LUMO(0.71)	BIAN(π)→Ru(dπ)/PPh_3(π*)
625 (627)	4480 (0.004)	HOMO→LUMO(0.67)	BIAN(π)→Ru(dπ)/PPh_3(π*)
375 (391)	14920 (0.11)	HOMO→LUMO+19(0.67)	BIAN(π)→PPh_3(π*)/Ru(dπ)/CO(π*)
364	14730	HOMO→LUMO+20(0.67)	BIAN(π)→BIAN(π*)/PPh_3(π*)/CO(π*)

(368)	(0.16)		
1e^{+} (S = 0)			
578 (573)	4080 (0.08)	HOMO→LUMO(0.68)	PPh_3(π)/Ru(dπ)/BIAN(π)→BIAN(π*)
478 (502)	6000 (0.08)	HOMO-1→LUMO(0.68)	PPh_3(π)/BIAN(π)/Ru(dπ)→BIAN(π*)
318 (299)	24325 (0.14)	HOMO-14→LUMO(0.37)	PPh_3(π)→BIAN(π*)
1e (S = 1/2)			
965 (1083)	3480 (0.19)	HOMO→LUMO(α)(0.95)	BIAN(π)→BIAN(π*)
716 (786)	5090 (0.06)	HOMO→LUMO+2(α)(0.93)	BIAN(π)→BIAN(π*)
591 (623)	6050 (0.13)	HOMO→LUMO(β)(0.95)	BIAN(π)/Ru(dπ)→BIAN(π*)
433 (439)	10080 (0.03)	HOMO-1→LUMO(α)(0.60) HOMO→LUMO+1(β)(0.38)	Ru(dπ)/BIAN(π)→BIAN(π*) BIAN(π)/Ru(dπ)→BIAN(π*)
1e^{-} (S = 0)			
962 (895)	6360 (0.43)	HOMO→LUMO(0.65)	BIAN(π)→BIAN(π*)
494 (457)	13760 (0.09)	HOMO-1→LUMO(0.66)	BIAN(π)/Ru(dπ)→BIAN(π*)
424 (388)	18800 (0.15)	HOMO-1→LUMO+1(0.66)	BIAN(π)/Ru(dπ)→BIAN(π*)/PPh_3(π*)
1e^{2-} (S = 1/2)			
–(1708)	–(0.15)	HOMO→LUMO(α)(0.88)	BIAN(π)→PPh_3(π*)
–(1483)	–(0.05)	HOMO→LUMO+1(α)(0.88)	BIAN(π)→PPh_3(π*)/Ru(dπ)
–(1106)	–(0.20)	HOMO→LUMO(β)(0.79)	BIAN(π)→PPh_3(π*)
937 (892)	11830 (0.008)	HOMO- 1→LUMO+1(α)(0.88)	BIAN(π)→PPh_3(π*)/Ru(dπ)
864 (892)	11250 (0.008)	HOMO- 1→LUMO+1(α)(0.88)	BIAN(π)→PPh_3(π*)/Ru(dπ)
495 (580)	15120 (0.05)	HOMO→LUMO+3(β)(0.65) HOMO→LUMO+12(α)(0.48)	BIAN(π)→PPh_3(π*) BIAN(π)→PPh_3(π*)
426 (436)	19300 (0.06)	HOMO→LUMO+18(α)(0.54) HOMO-1→LUMO(β)(0.52)	BIAN(π)→PPh_3(π*)/Ru(dπ)/BIAN(π*) BIAN(π)→PPh_3(π*)

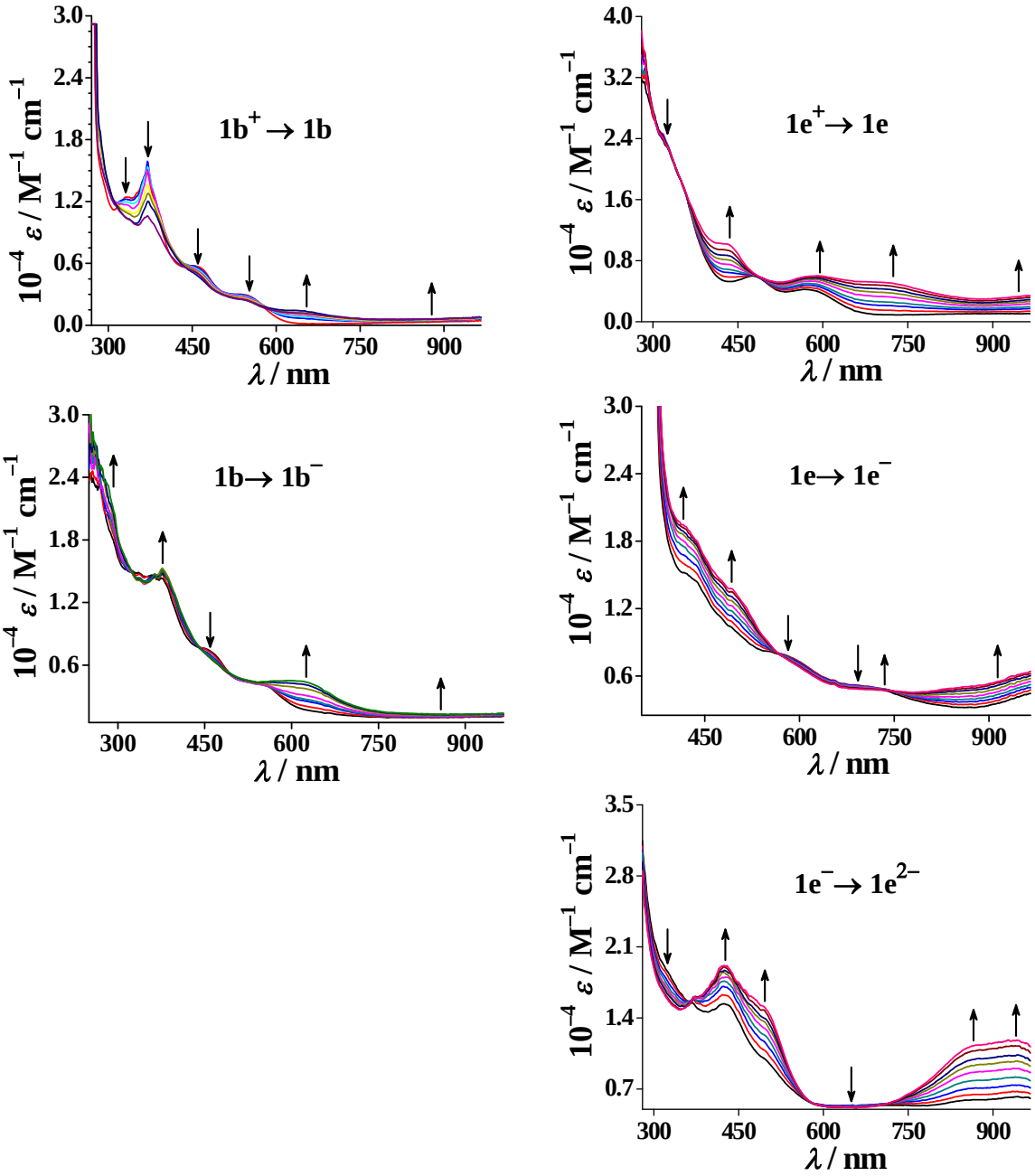


Figure S9. UV−vis spectroelectrochemical plots in CH_3CN/0.1 M NEt_4ClO_4.

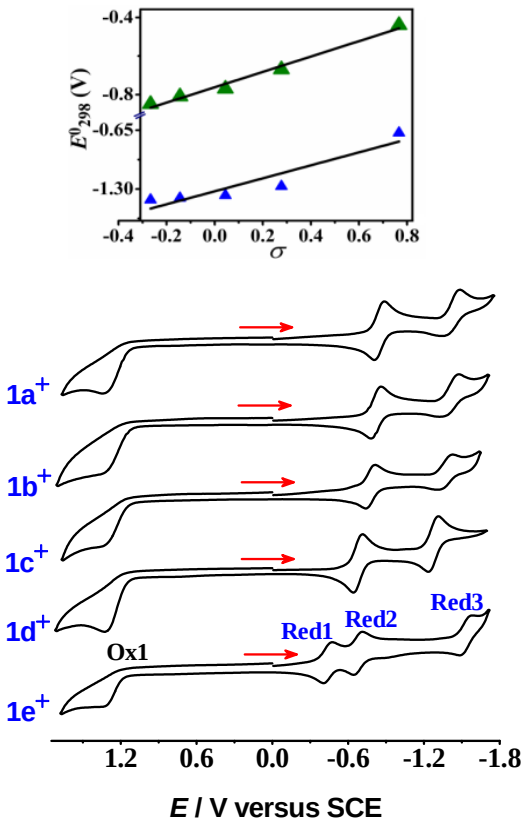


Figure S10. Cyclic voltammograms of $\mathbf{1a^+}$–$\mathbf{1e^+}$ in CH_3CN. Scan rate: 50 mV s^{-1}. Inset shows least-square plots of E^0_{298} versus σ of $\mathbf{1a^+}$–$\mathbf{1e^+}$ for Red1 (green) and Red2 (blue).

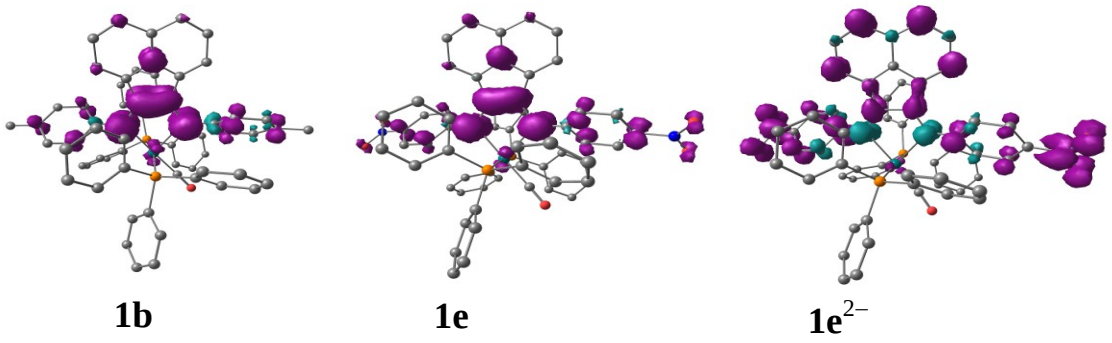
Table S6. Electrochemical data[a] of complexes

	E^o_{298}[V](ΔE[mV])[b]				K_c[c]	
	Ox1[d]	**Red1**	**Red2**	**Red3**	K_{c1}[c]	K_{c2}[c]
$\mathbf{1a^+}$	1.35	–0.85 (80)	–1.42(140)	-	4.6×10^9	-
$\mathbf{1b^+}$	1.33	–0.81 (80)	–1.40(140)	-	1.0×10^{10}	-
$\mathbf{1c^+}$	1.37	–0.77 (80)	–1.37(120)	-	1.5×10^{10}	-
$\mathbf{1d^+}$	1.33	–0.67 (60)	–1.27(80)	-	1.5×10^{10}	-
$\mathbf{1e^+}$	1.35	–0.44 (60)	–0.68(80)	–1.5 (100)	1.2×10^4	2.5×10^{14}

[a]From cyclic voltammetry in CH_3CN/0.1 M Et_4NClO_4 at 50 mV s^{-1}. [b]Potential in V versus SCE; peak potential differences ΔE_p/mV (in parentheses). [c]Comproportionation constant from $RT\ln K_c = nF(\Delta E)$. K_{c1} between Red1 and Red2; K_{c2} between Red2 and Red3. [d]Irreversible.

Table S7. DFT calculated selected MO compositions for $1b^n$ and $1e^n$

complex	MO	Ru/BIAN/PPh_3/CO/H (% contribution)	complex	MO	Ru/BIAN/PPh_3/ CO/H (% contribution)
$\mathbf{1b}^+$ (*S*=0)	LUMO	6/85/9/1/0	$\mathbf{1e}^+$ (*S*=0)	LUMO	6/85/9/1/0
1b (*S*=1/2)	SOMO *β*-LUMO	5/86/8/1/0 5/82/11/1/0	**1e** (*S*=1/2)	SOMO *β*-LUMO	5/86/8/1/0 3/90/5/1/0
$\mathbf{1b}^-$ (*S*=0)	HOMO	5/83/11/1/0	$\mathbf{1e}^-$ (*S*=0)	HOMO LUMO	4/88/8/1/0 2/95/3/0/0
			$\mathbf{1e}^{2-}$ (*S*=1/2)	SOMO	3/87/9/1/0



1b **1e** $\mathbf{1e}^{2-}$

Figure S11. Mulliken spin density plots for **1b**, **1e** and $\mathbf{1e}^{2-}$.

Table S8. DFT calculated Mulliken spin density values for $1b^n$ and $1e^n$

complex	Ru	BIAN	PPh_3	CO	H^-
1b (*S*=1/2)	0.010	0.971	0.017	0.005	–0.004
1e (*S*=1/2)	0.013	0.967	0.018	0.003	–0.004
$\mathbf{1e}^{2-}$(*S*=1/2)	0.021	0.949	0.026	0.001	0.001

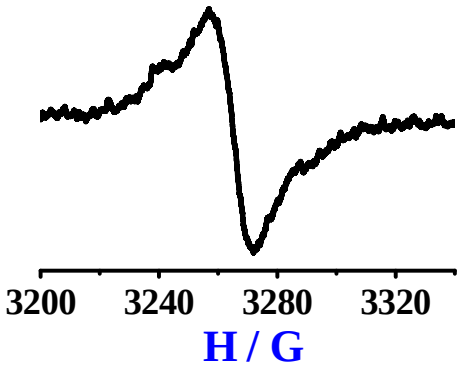
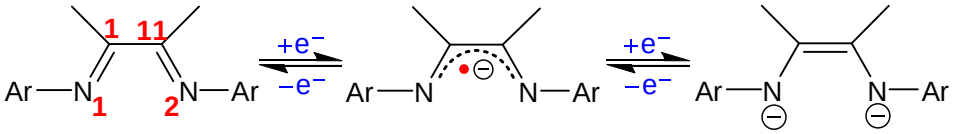
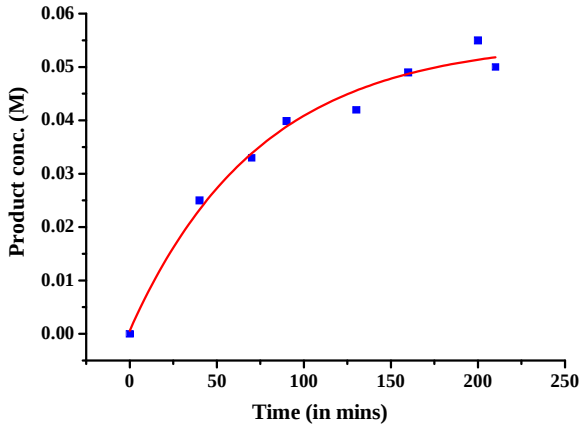


Figure S12. EPR spectrum of electrogenerated **1e** in CH_3CN at 77 K.

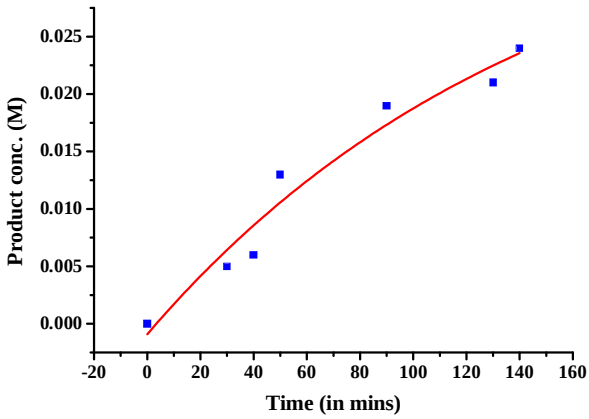
Table S9. Change in DFT calculated bond lengths of the *α*-diimine unit of BIAN on successive reductions in 1b^n and 1e^n



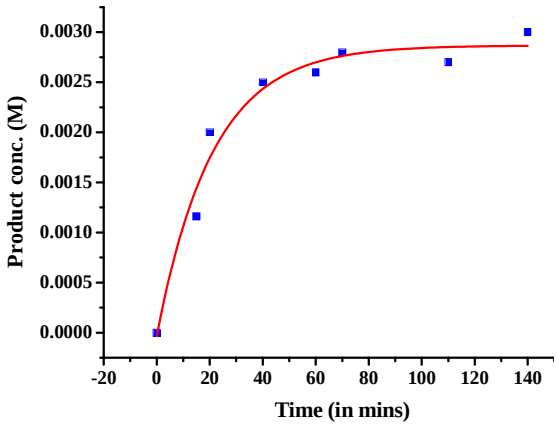
bond lengths (´)	**1b$^+$** *S*=0	**1b** *S*=1/2	**1b$^-$** *S*=0	**1e$^+$** *S*=0	**1e** *S*=1/2	**1e$^-$** *S*=0	**1e^{2-}** *S*=1/2
C1–C11	1.49	1.44	1.40	1.49	1.44	1.40	1.42
C1–N1	1.30	1.34	1.38	1.30	1.34	1.37	1.37
C11–N2	1.30	1.34	1.38	1.30	1.33	1.37	1.38



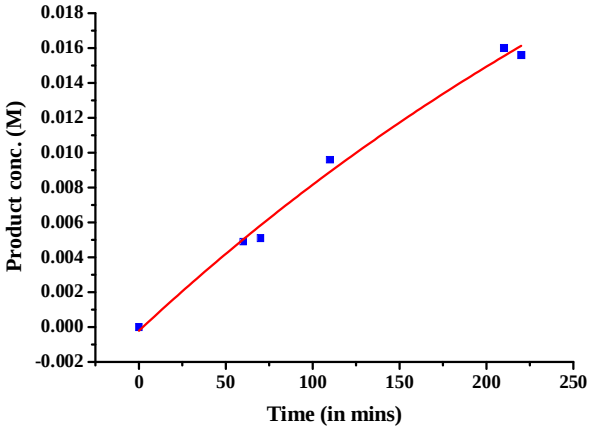
Product formation plot for 4-OMe-PhC**H**$_2$NH$_2$ = 0.25 mmol (R^2 = *0.98*)



Product formation plot for 4-Me-PhC**H**$_2$NH$_2$ = 0.25 mmol (R^2 = *0.94*)

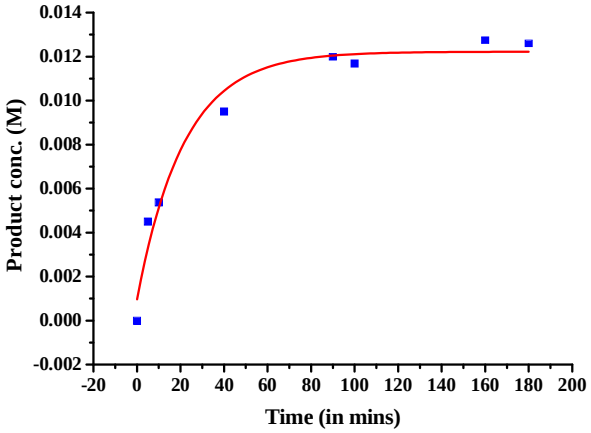


Product formation plot for 4-F-PhC**H**$_2$NH$_2$ = 0.25 mmol (R^2 = *0.96*)

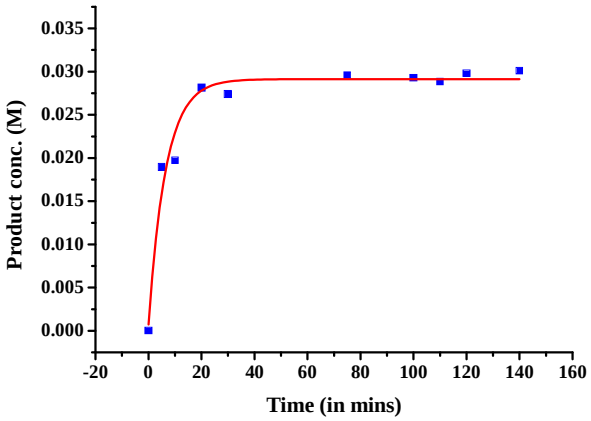


Product formation plot for 4-OCF$_3$ PhC**H**$_2$NH$_2$ = 0.25 mmol (R^2 = *0.99*)

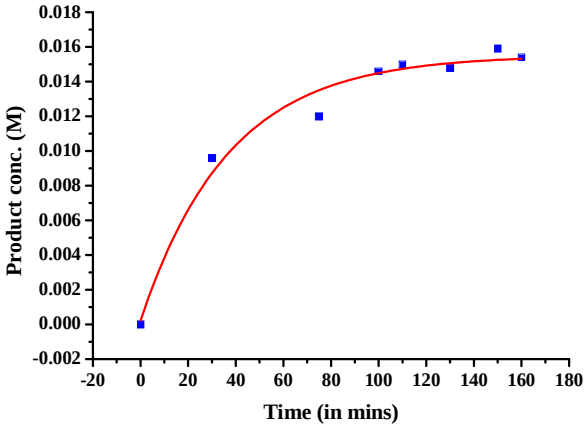
Figure S13. Product formation plots for various *p*-substituted benzylamines in [**1a**]ClO$_4$ catalyzed nitrile formation.



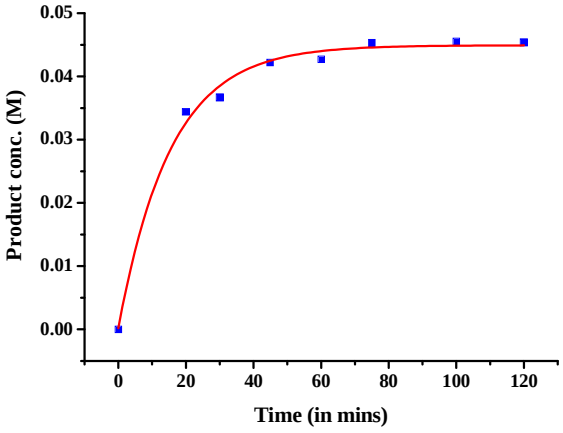
Product formation plot for 4-Me-PhC**H**$_2$NH$_2$ = 0.25 mmol (R^2 = *0.96*)



Product formation plot for 4-OMe-PhC**H**$_2$NH$_2$ = 0.25 mmol (R^2 = *0.96*)



Product formation plot for 4-F-PhC**H**$_2$NH$_2$ = 0.25 mmol (R^2 = *0.97*)



Product formation plot for 4-OCF$_3$ PhC**H**$_2$NH$_2$ = 0.25 mmol (R^2 = *0.99*)

Figure S14. Product formation plots for various *p*-substituted benzylamines in [**2**]ClO$_4$ catalyzed bimolecular imine formation.

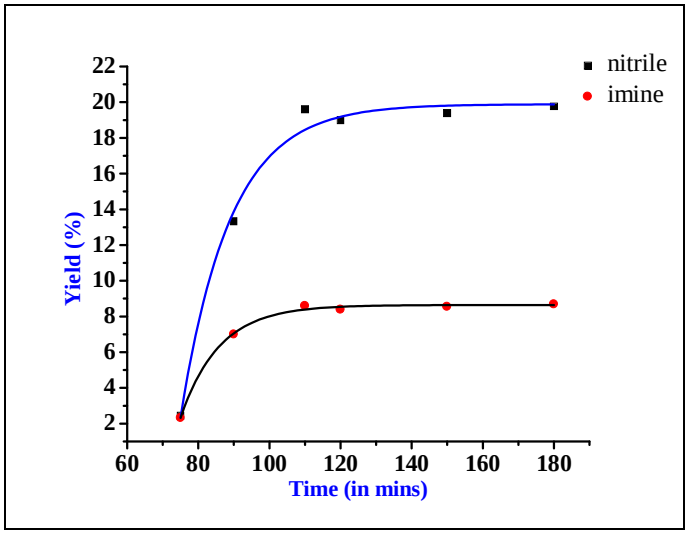
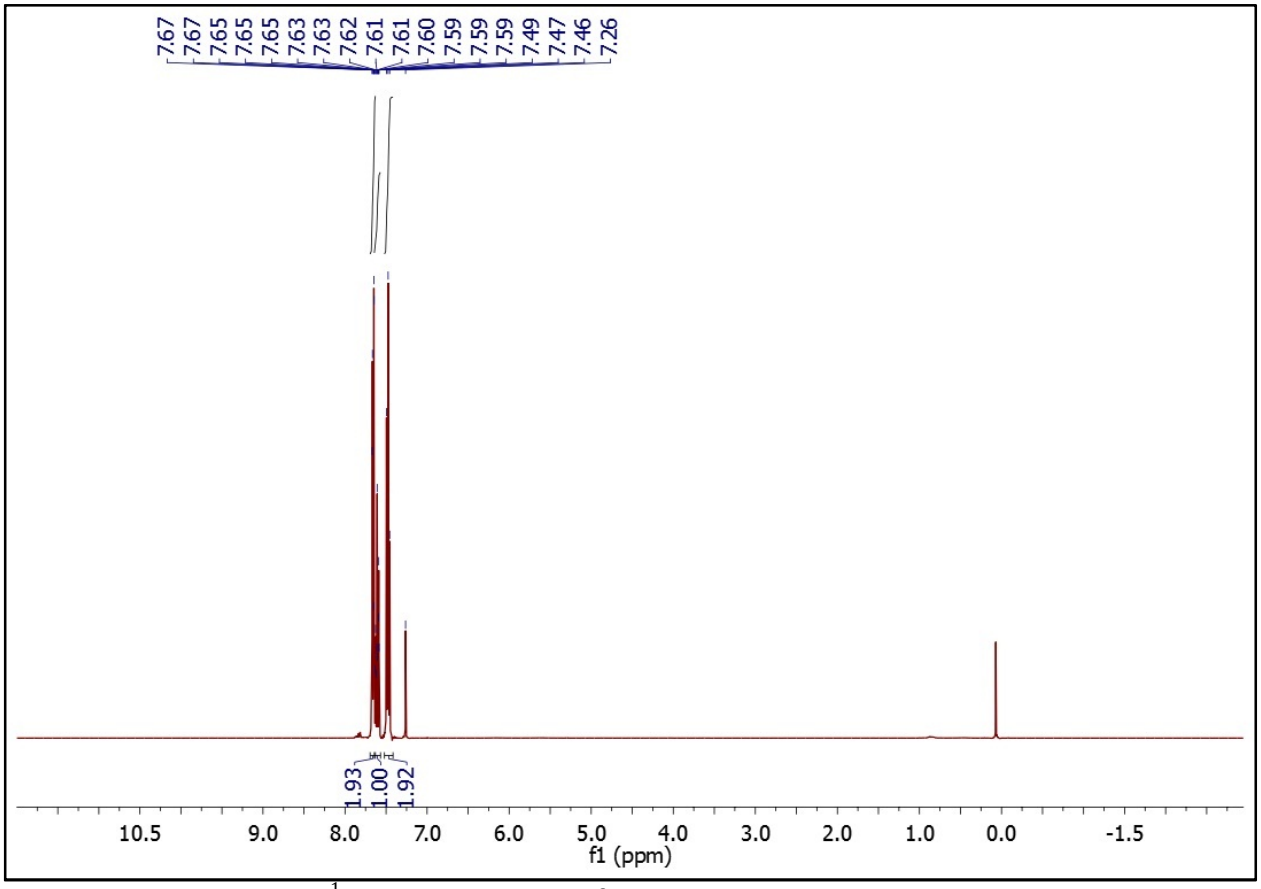
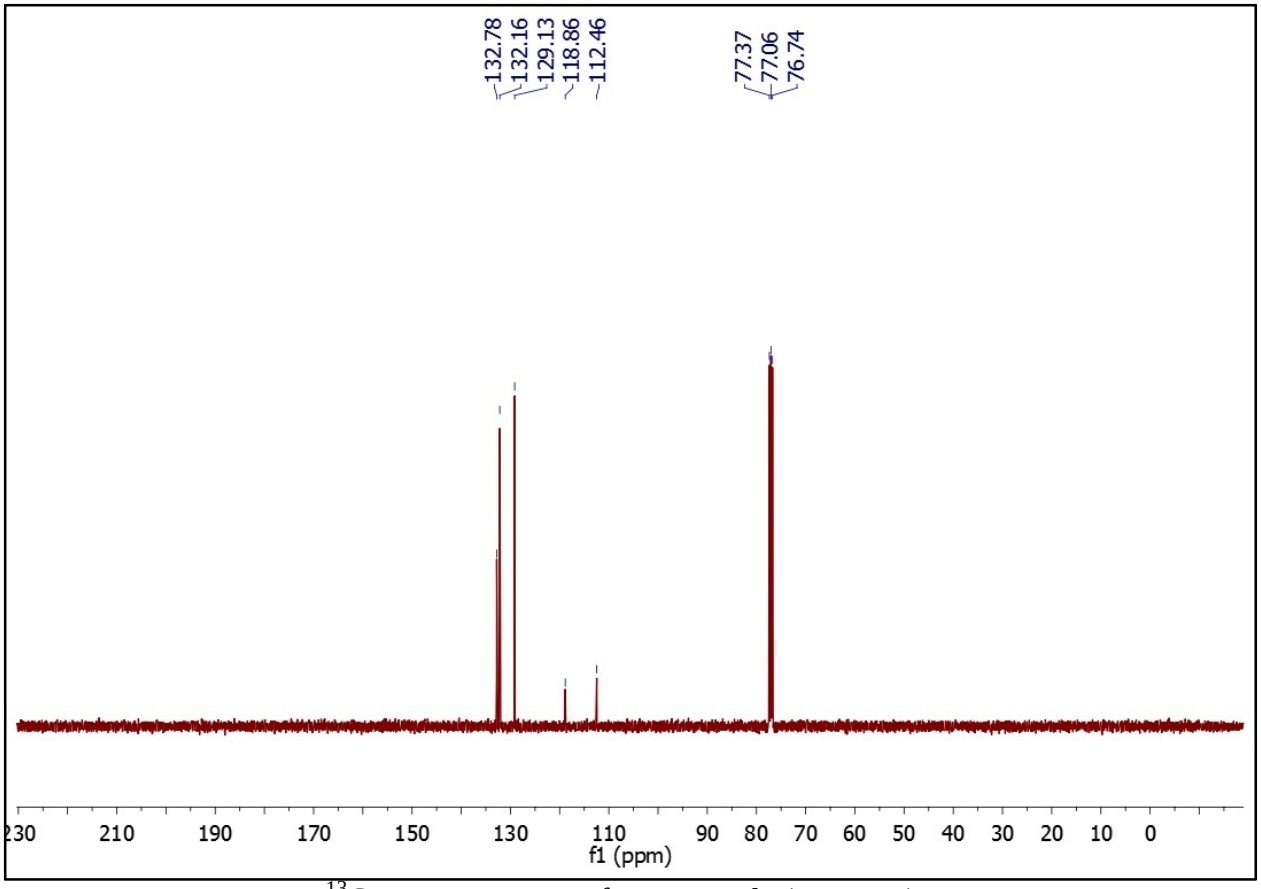


Figure S15. Product formation plot showing difference in the rate of nitrile and imine formation in [**1a**]ClO_4 catalyzed amine oxidation.

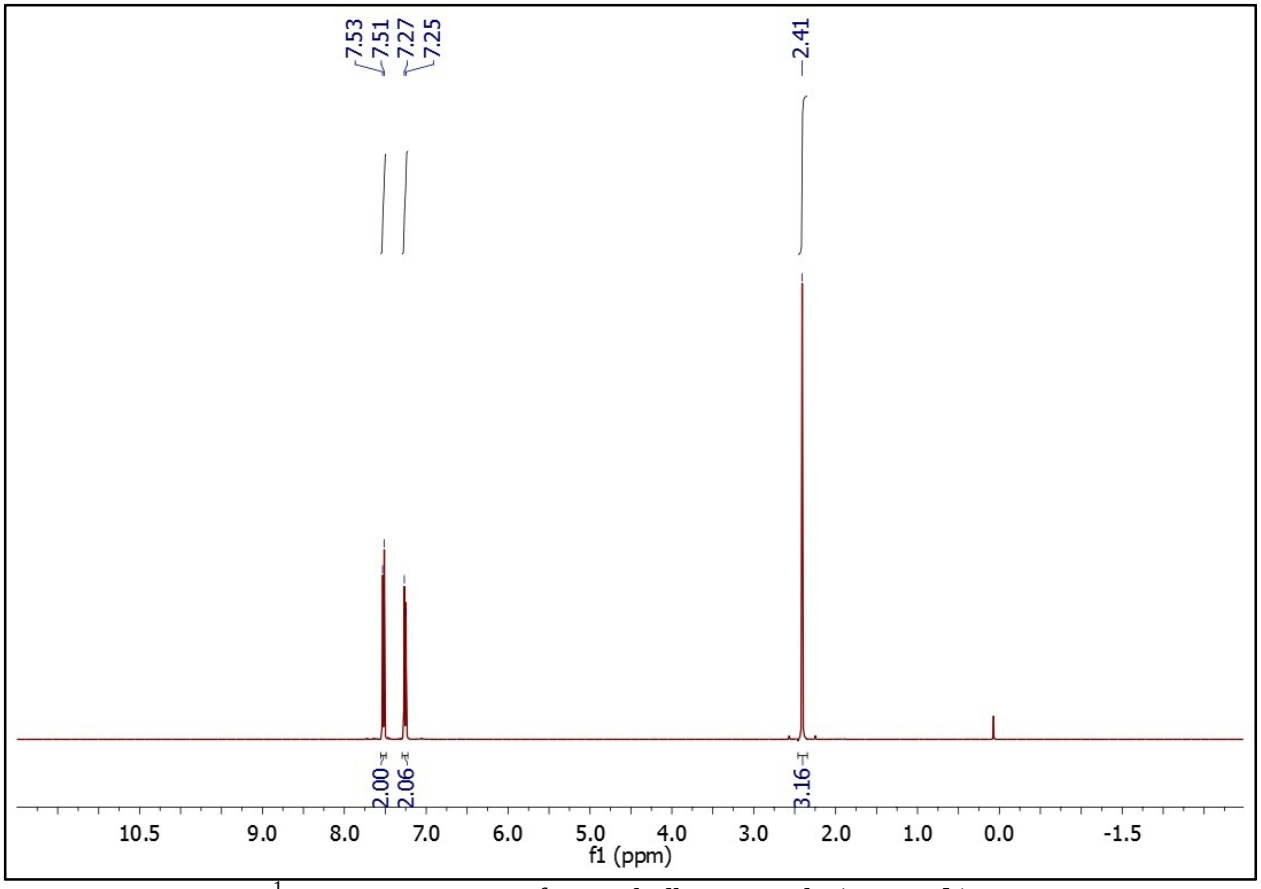
^{1}H and ^{13}C NMR spectral data of the isolated nitriles



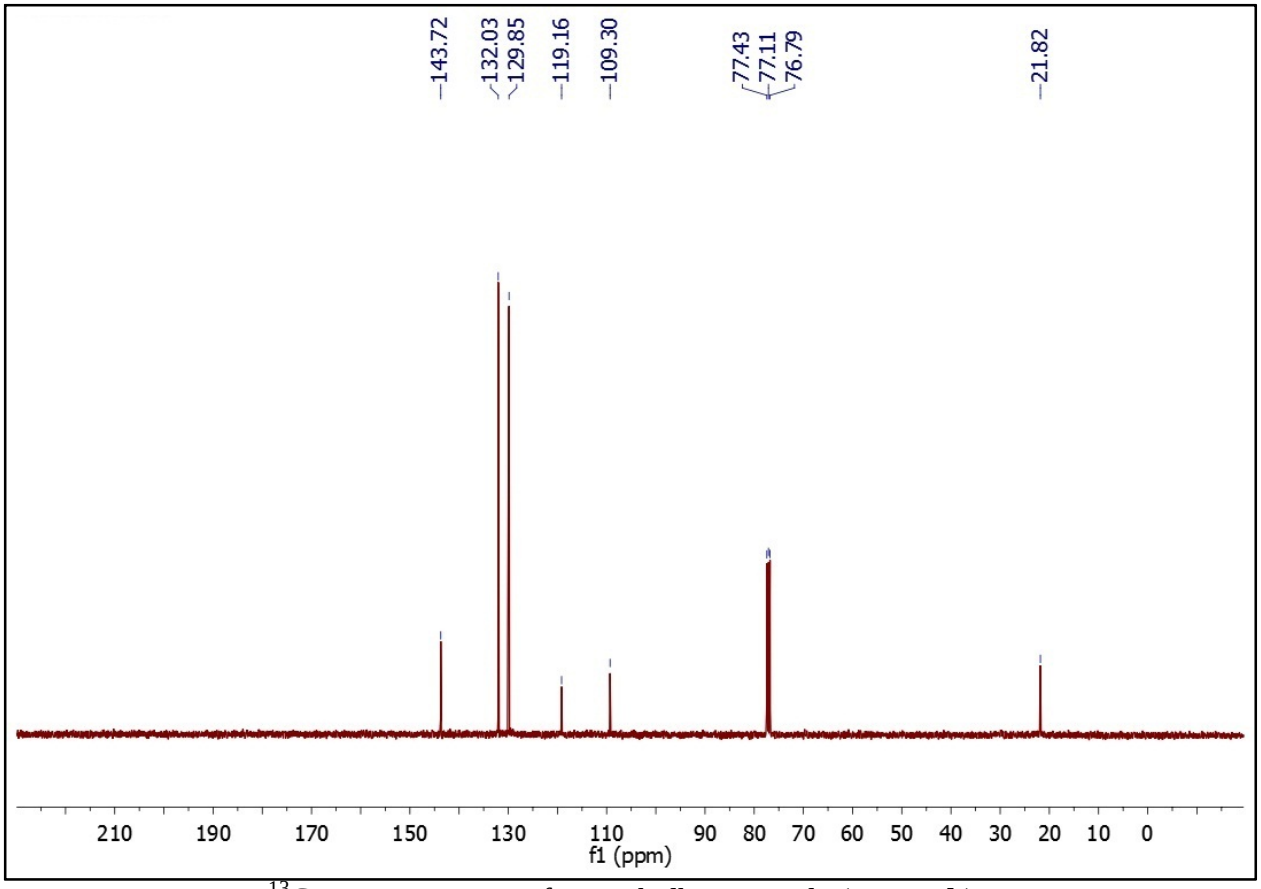
^{1}H NMR spectrum of Benzonitrile **(entry 4a)**.



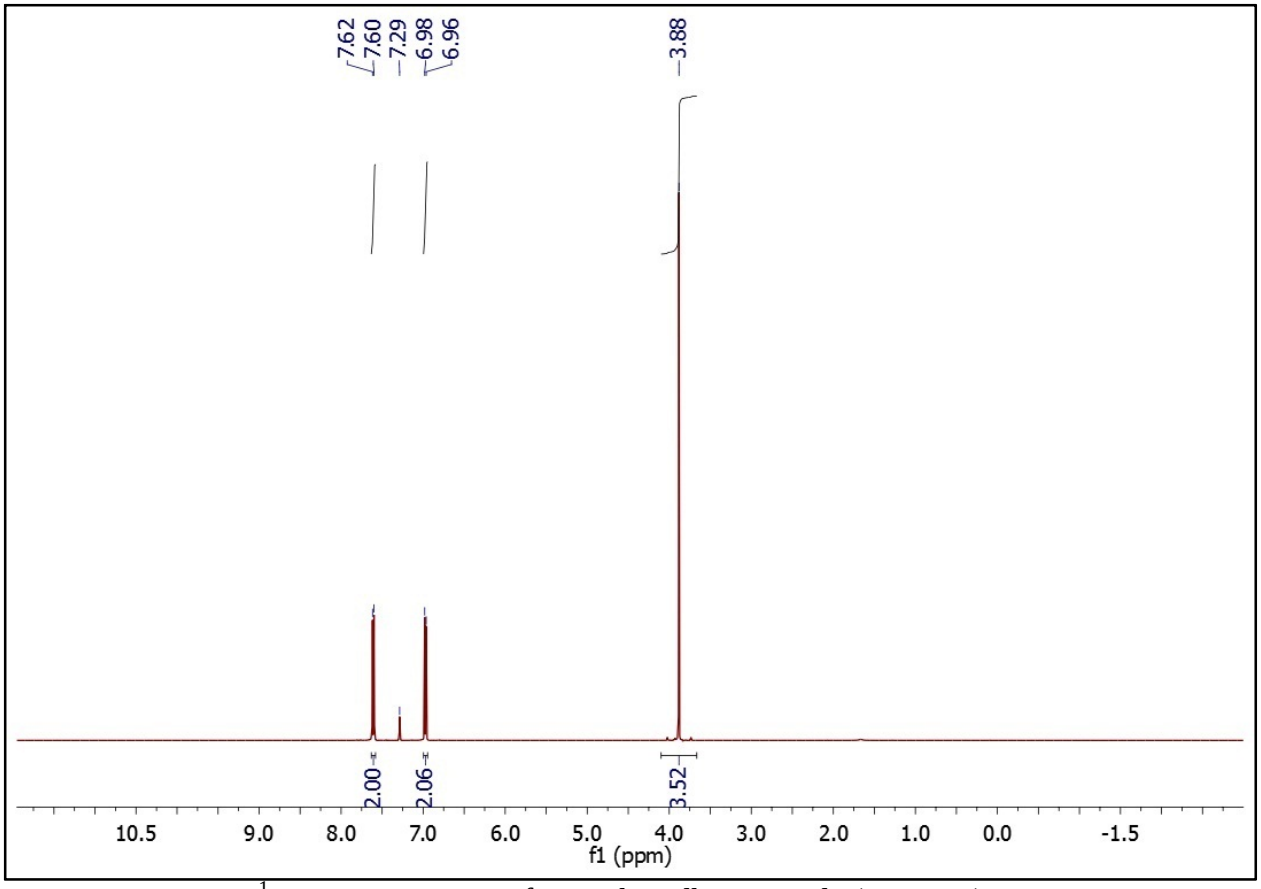
^{13}C NMR spectrum of Benzonitrile **(entry 4a)**.



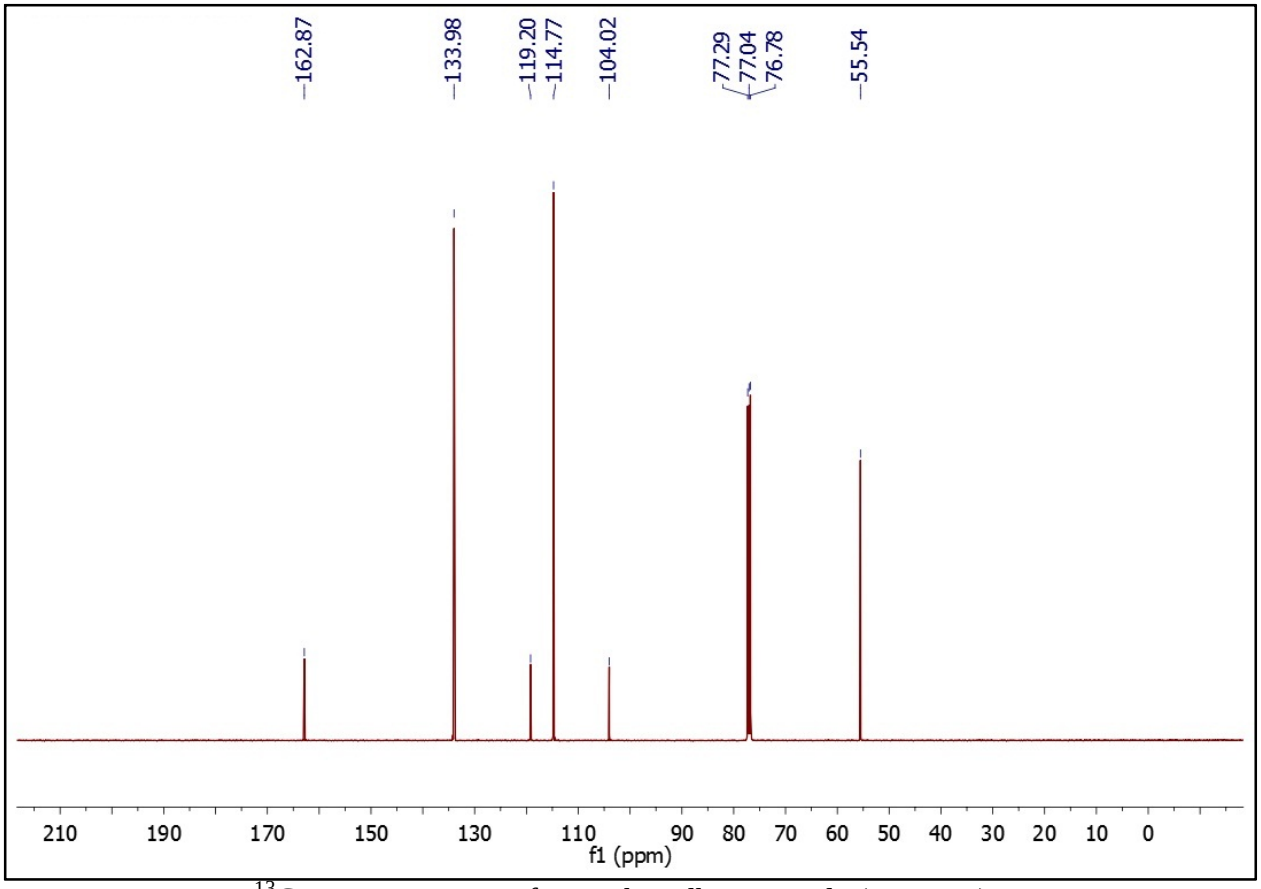
^{1}H NMR spectrum of 4-Methylbenzonitrile **(entry 4b)**.



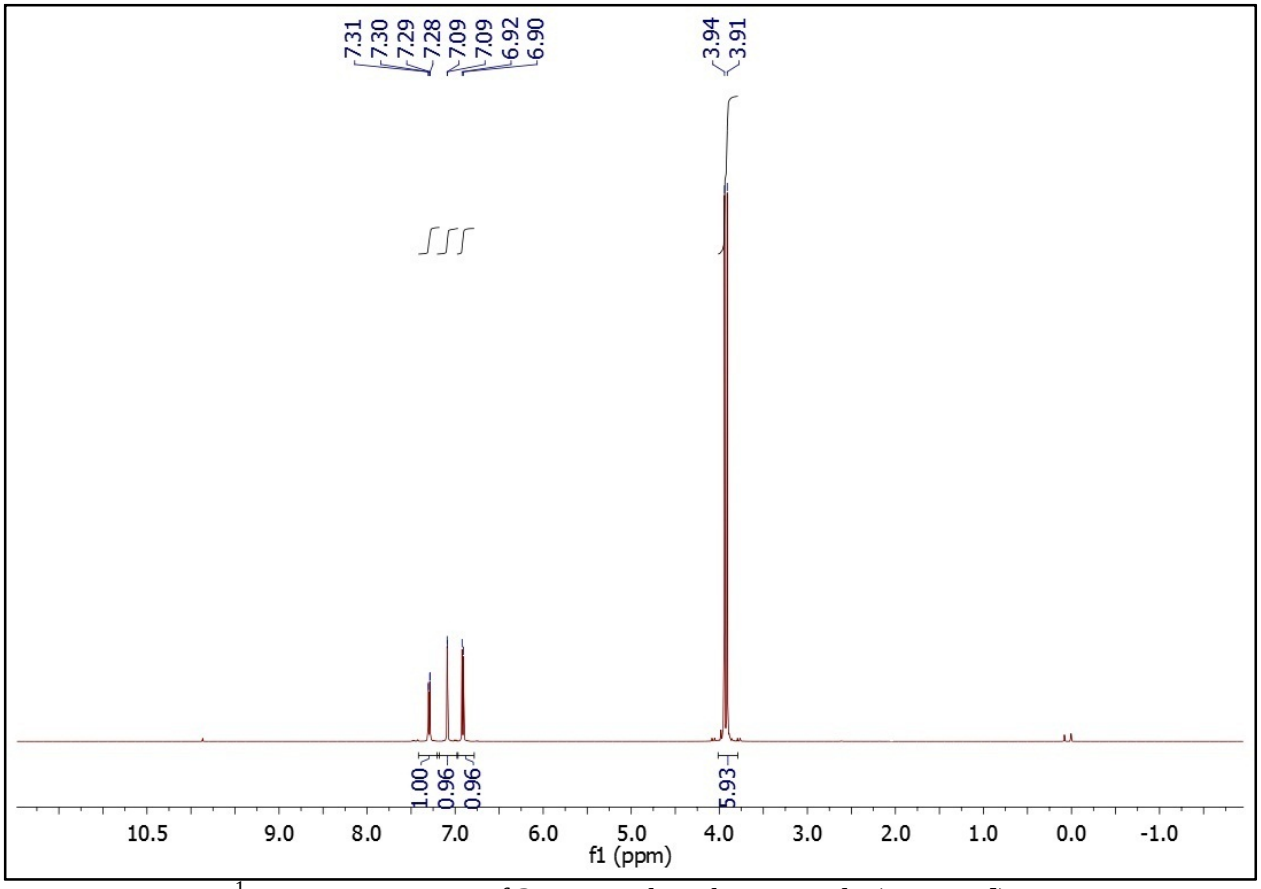
^{13}C NMR spectrum of 4-Methylbenzonitrile **(entry 4b)**.



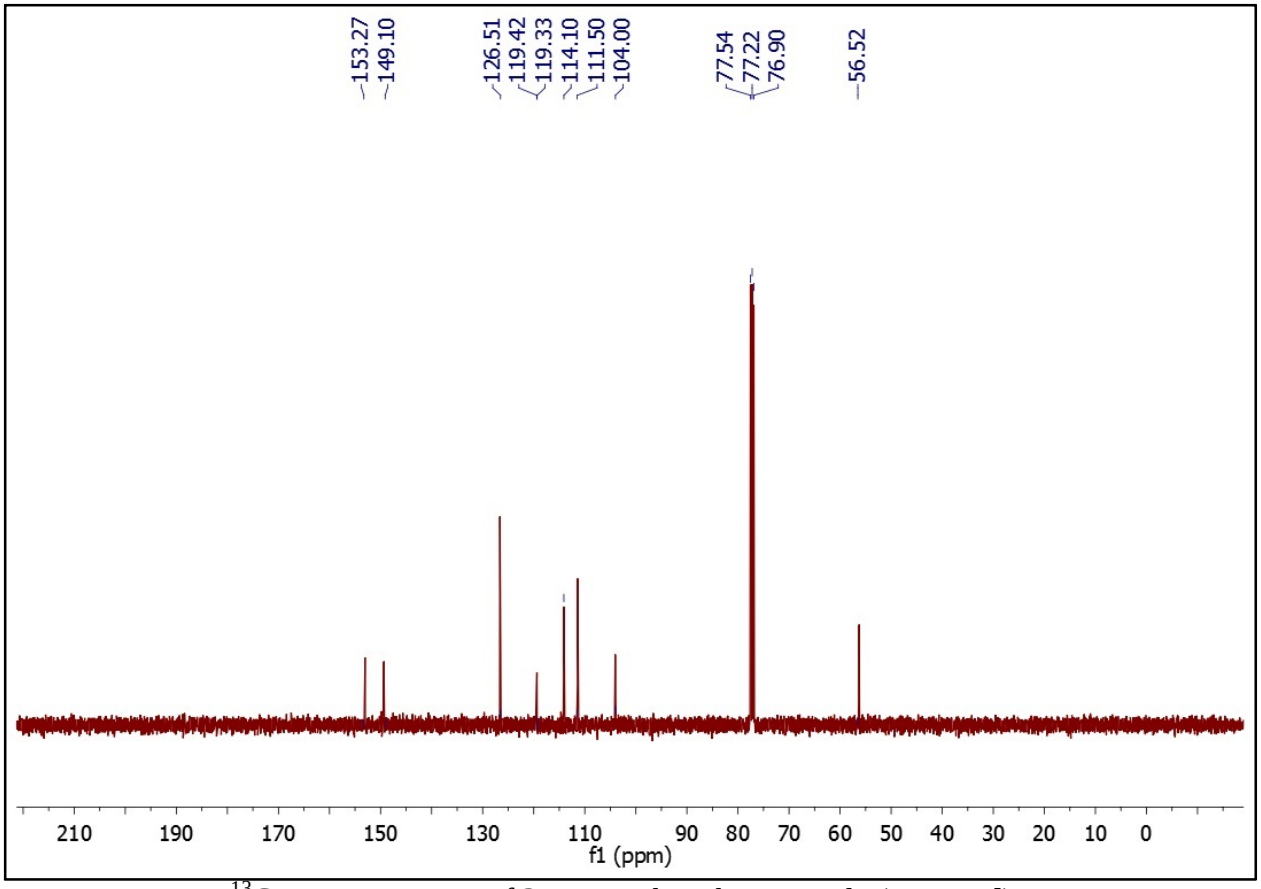
^{1}H NMR spectrum of 4-Methoxylbenzonitrile **(entry 4c)**.



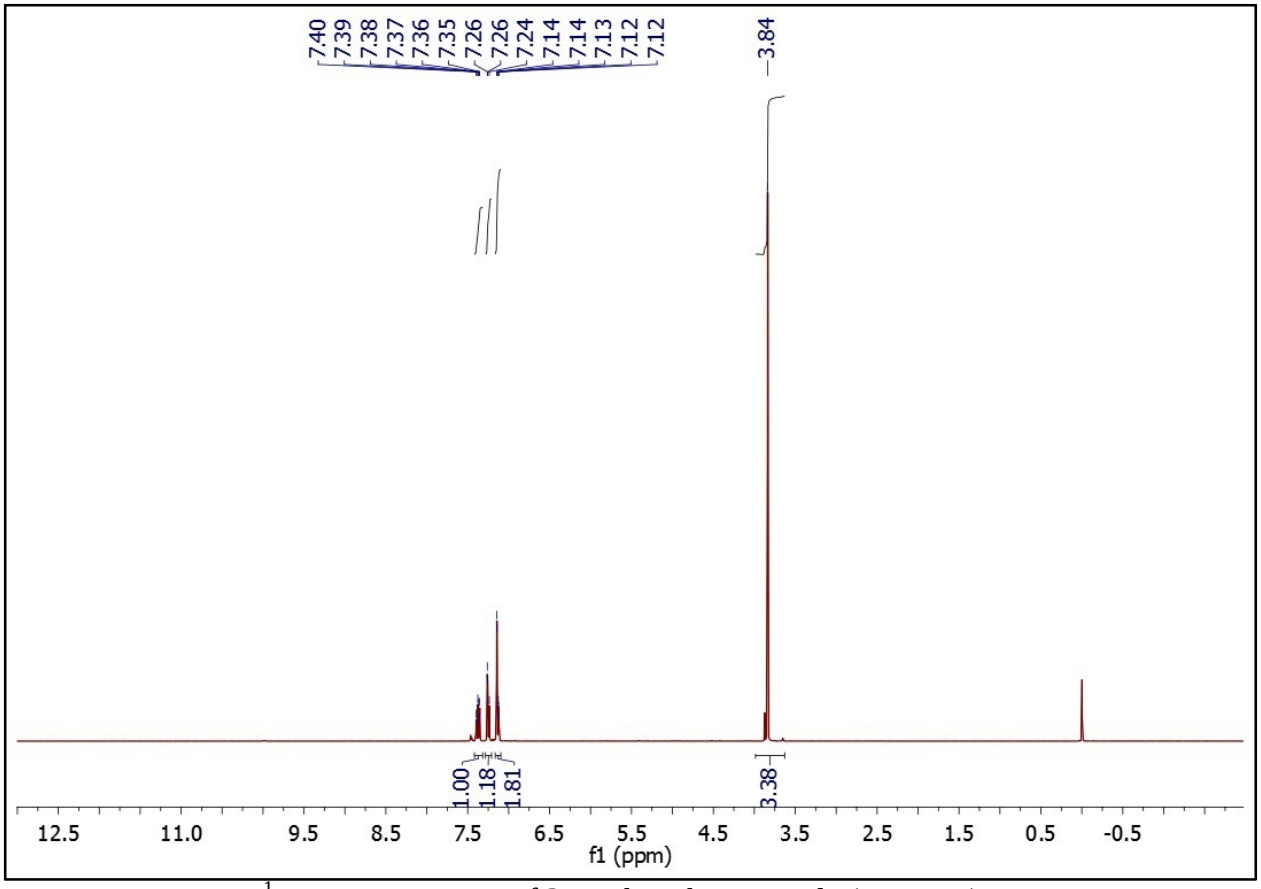
^{13}C NMR spectrum of 4-Methoxylbenzonitrile **(entry 4c)**.



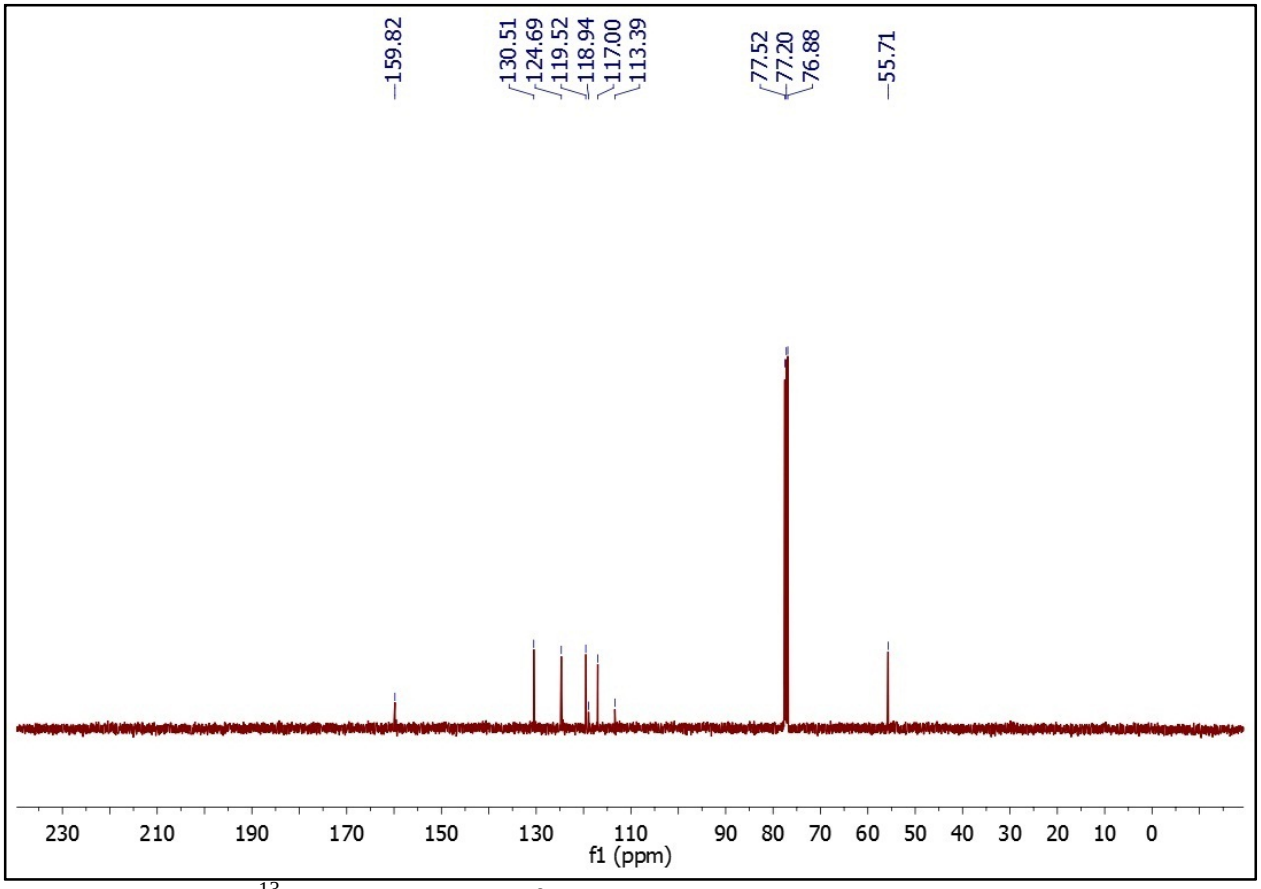
^{1}H NMR spectrum of 3,4-Dimethoxybenzonitrile **(entry 4d)**.



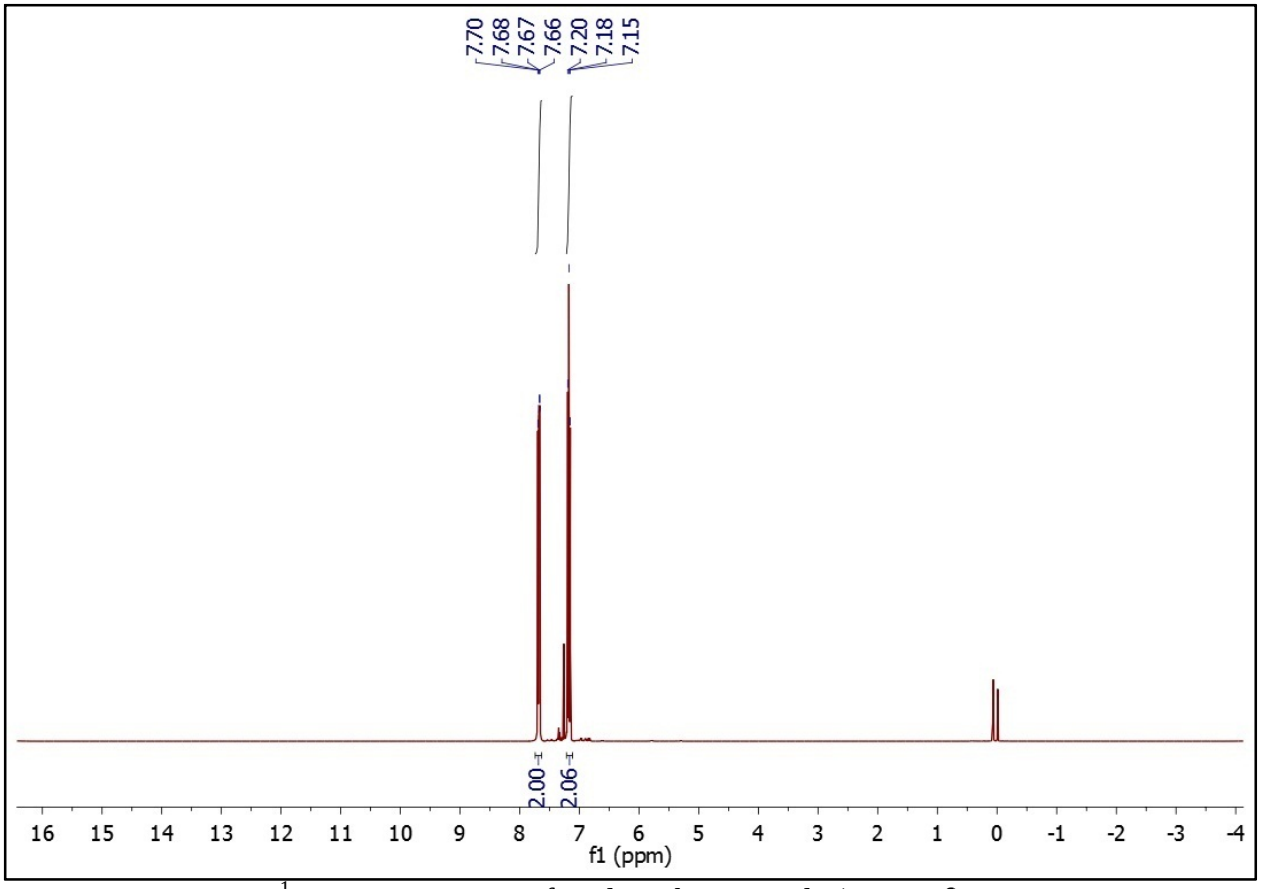
^{13}C NMR spectrum of 3,4-Dimethoxybenzonitrile **(entry 4d)**.



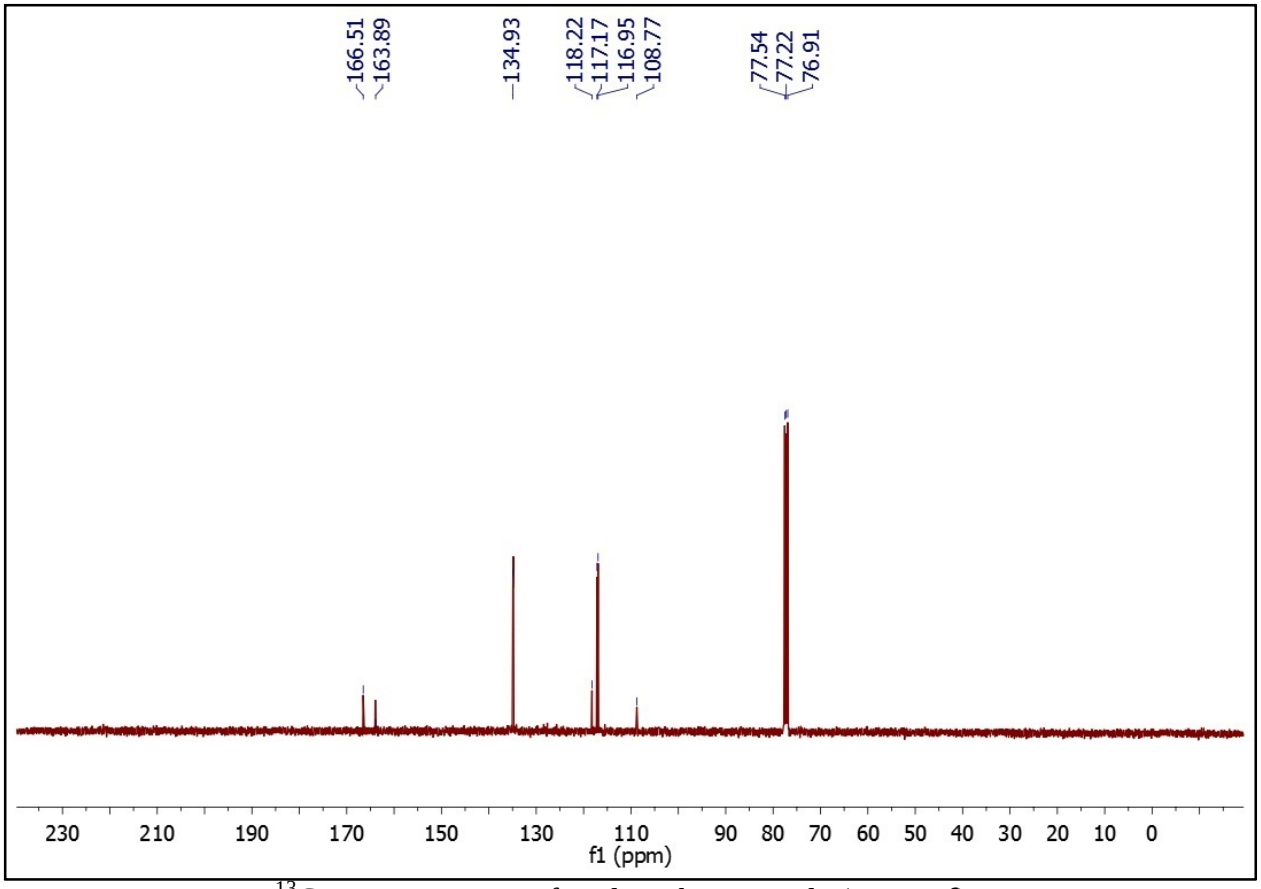
^{1}H NMR spectrum of 3-Methoxybenzonitrile **(entry 4e)**.



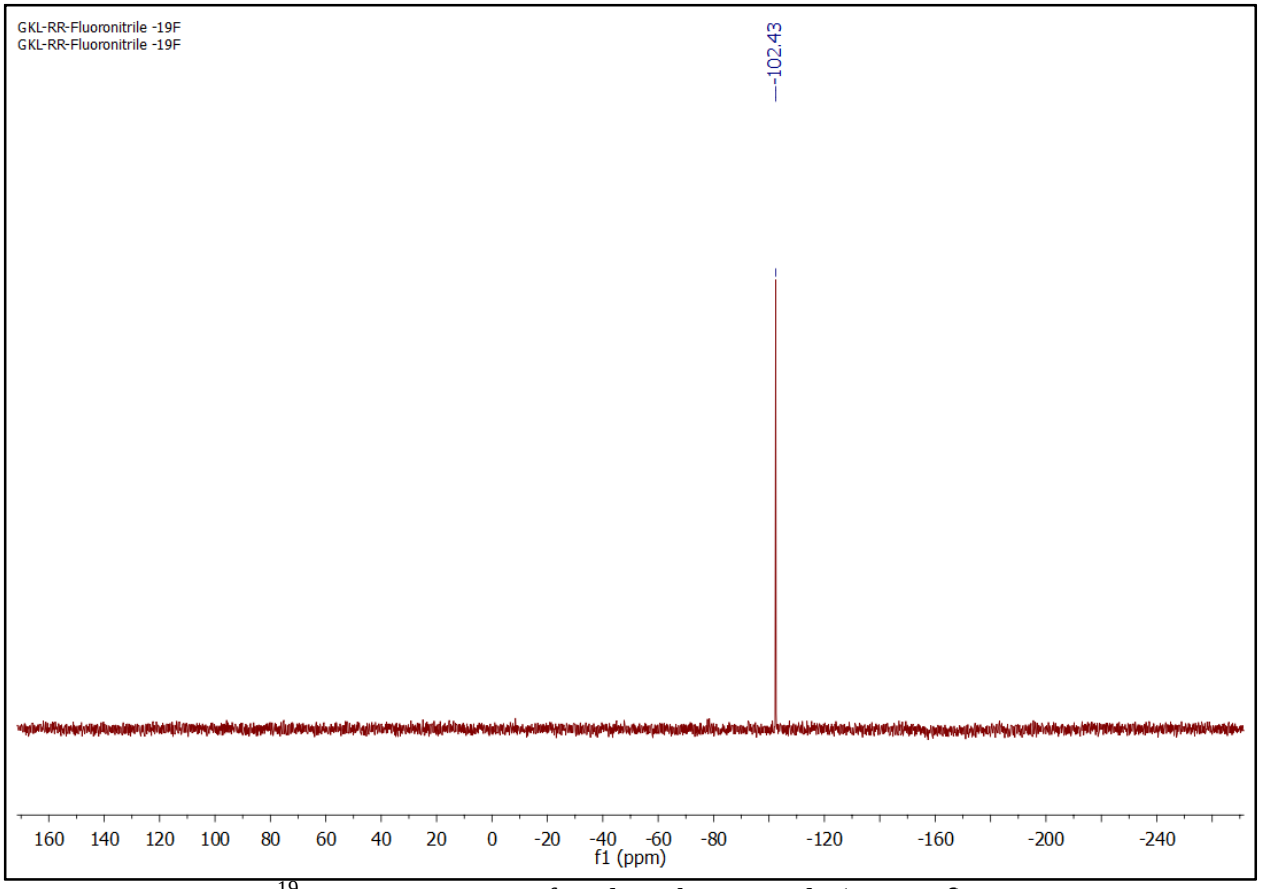
^{13}C NMR spectrum of 3-Methoxybenzonitrile **(entry 4e)**.



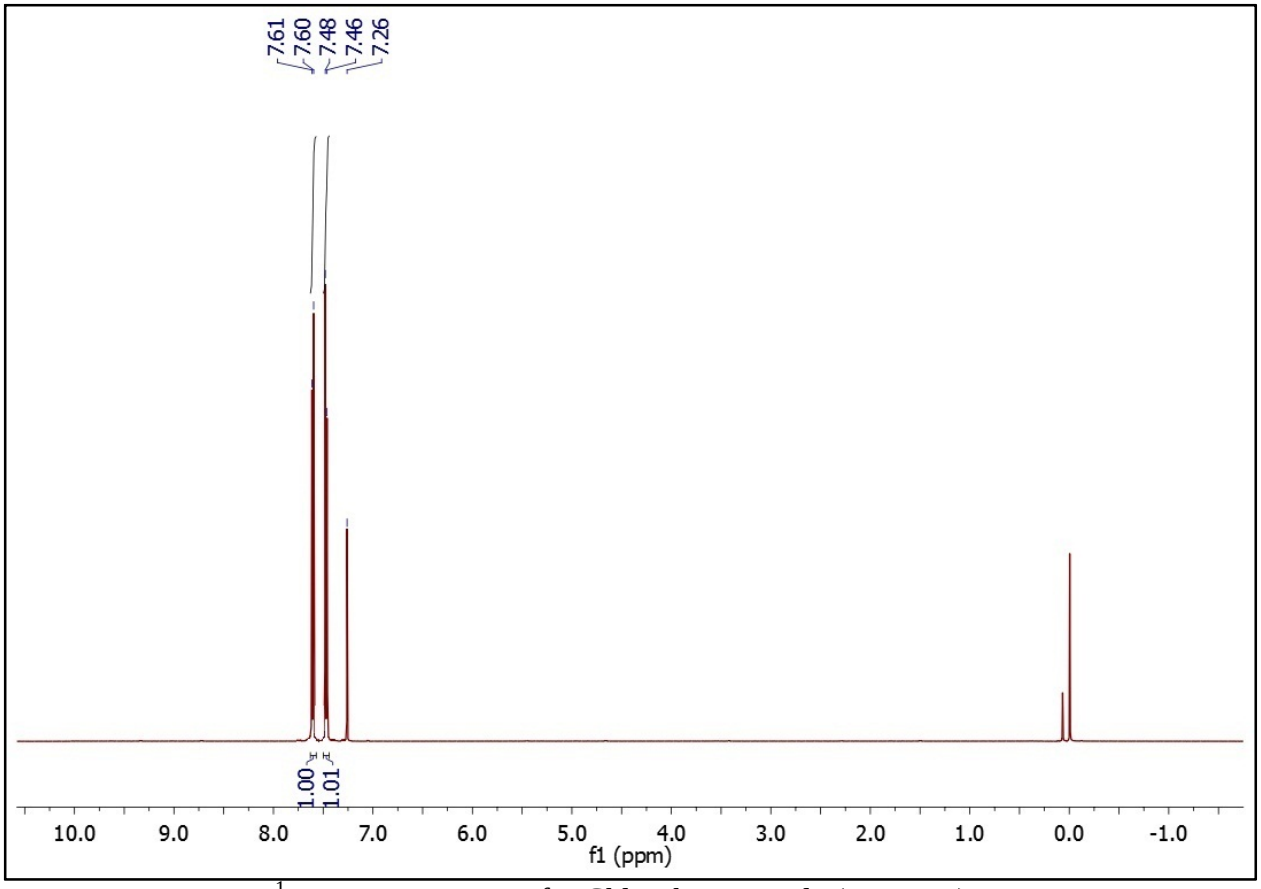
^{1}H NMR spectrum of 4-Fluorobenzonitrile **(entry 4f)**.



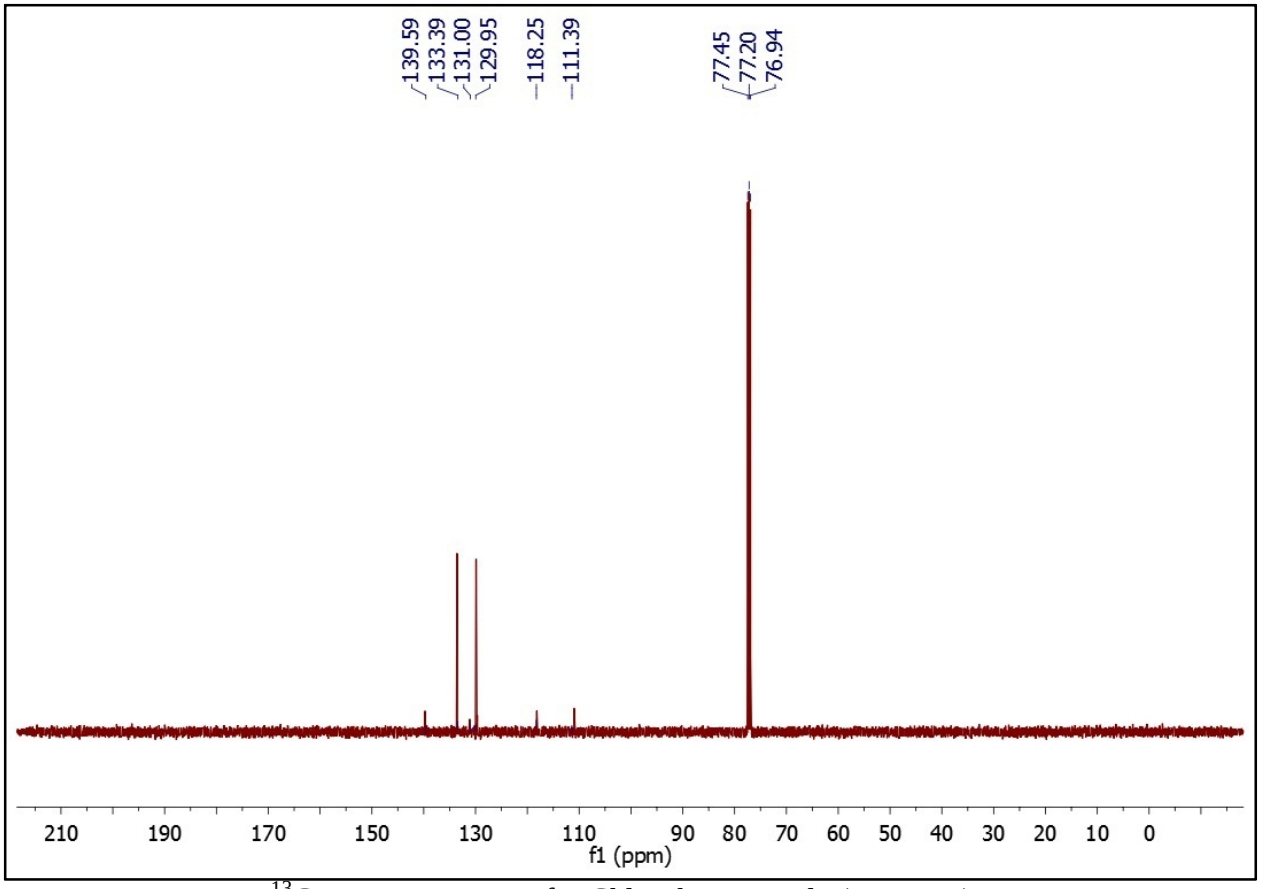
^{13}C NMR spectrum of 4-Fluorobenzonitrile **(entry 4f)**.



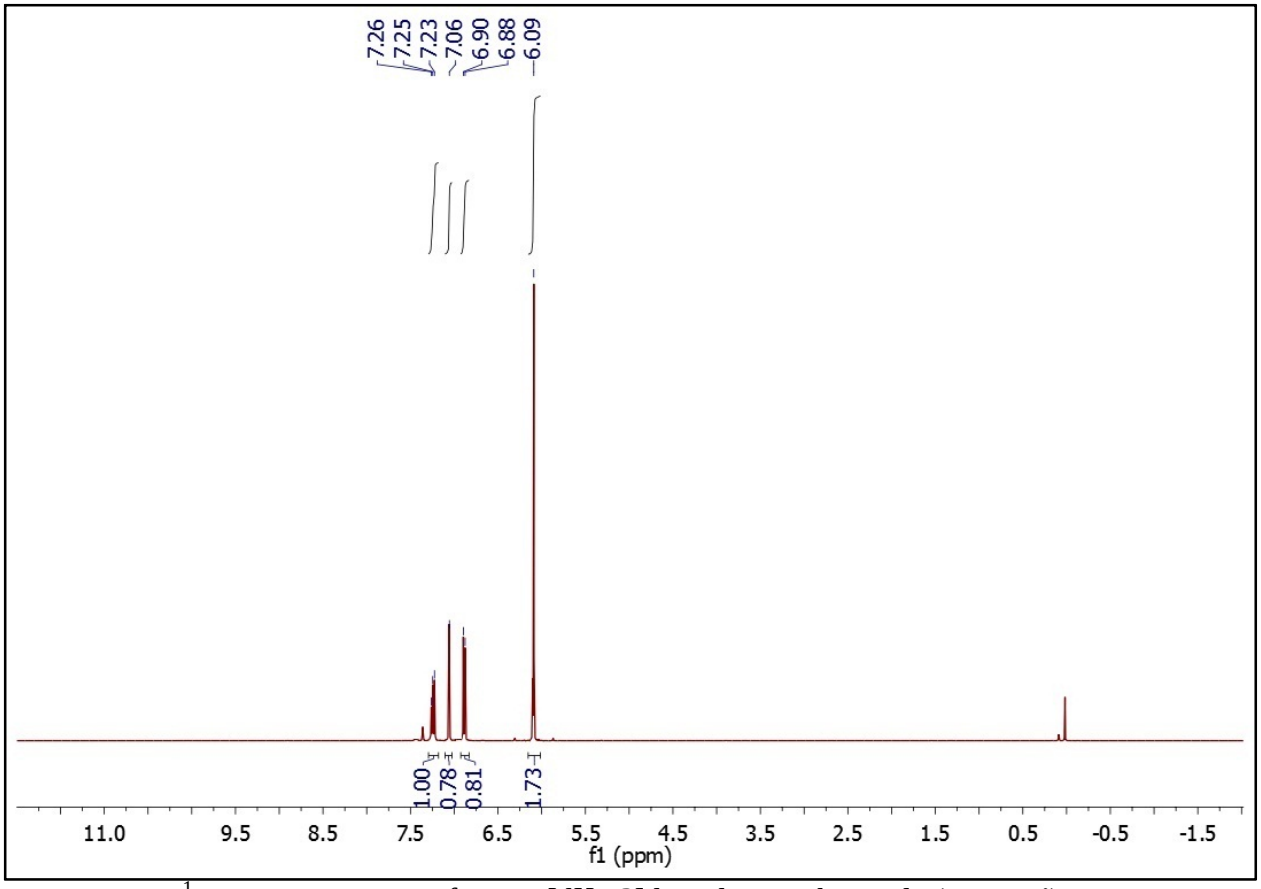
^{19}F NMR spectrum of 4-Fluorobenzonitrile **(entry 4f)**.



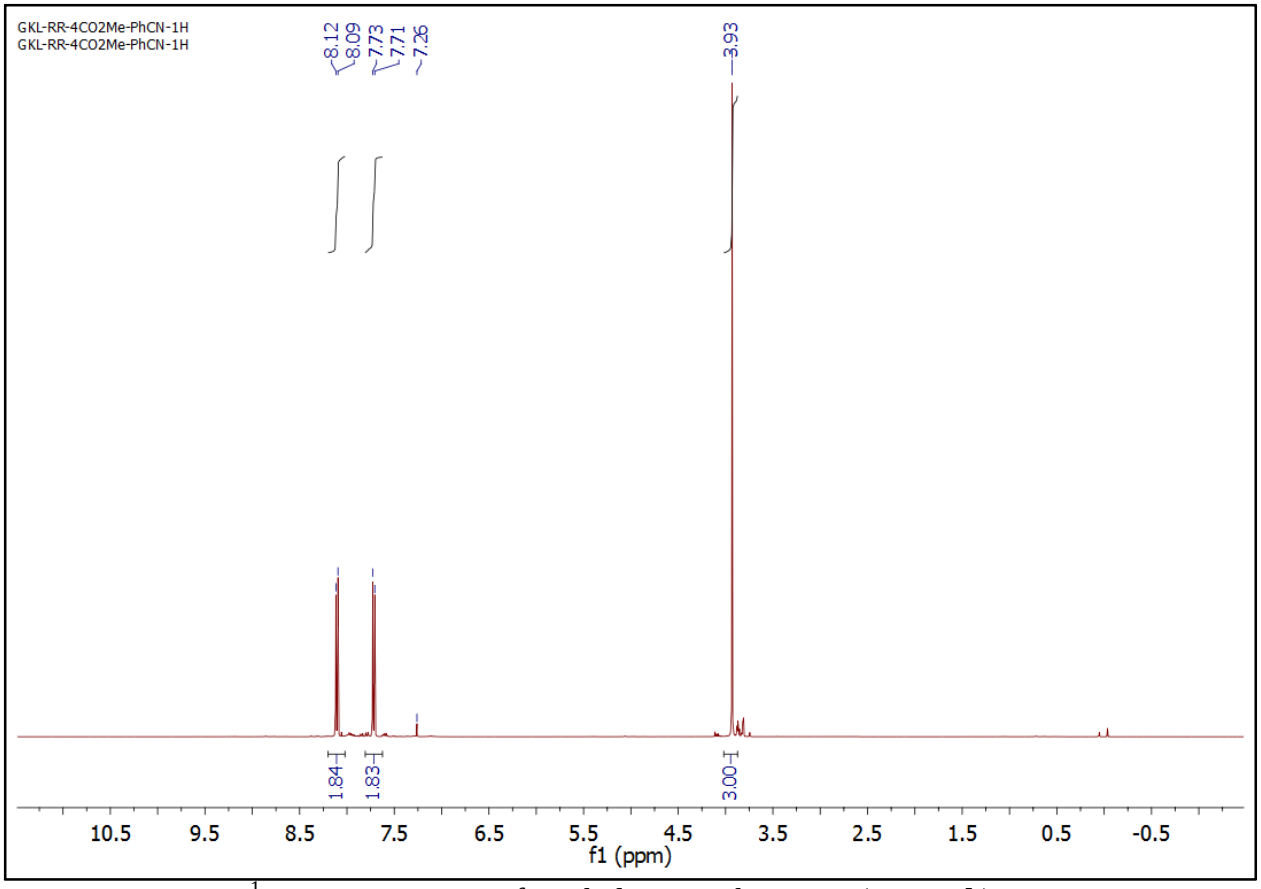
^{1}H NMR spectrum of 4-Chlorobenzonitrile **(entry 4g)**.



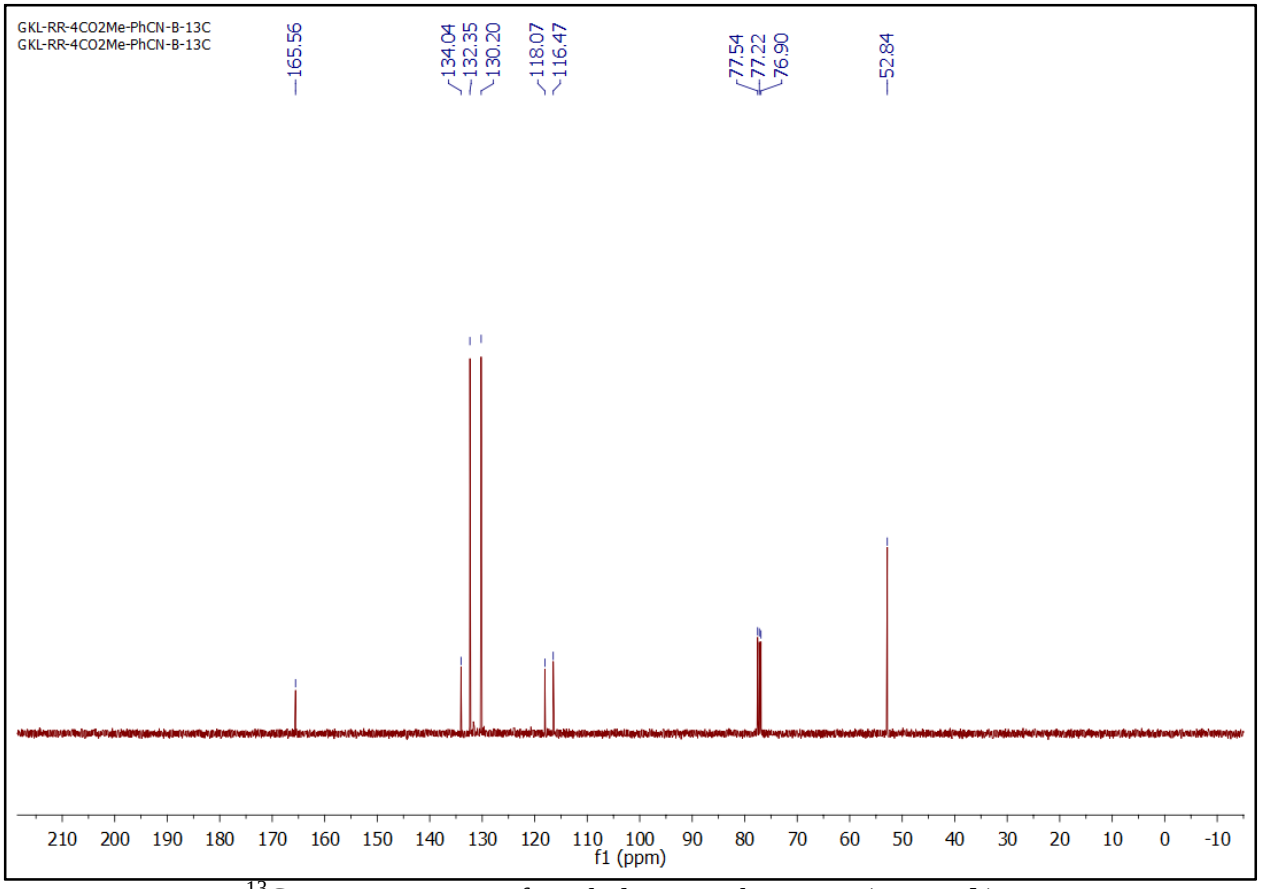
^{13}C NMR spectrum of 4-Chlorobenzonitrile **(entry 4g)**.



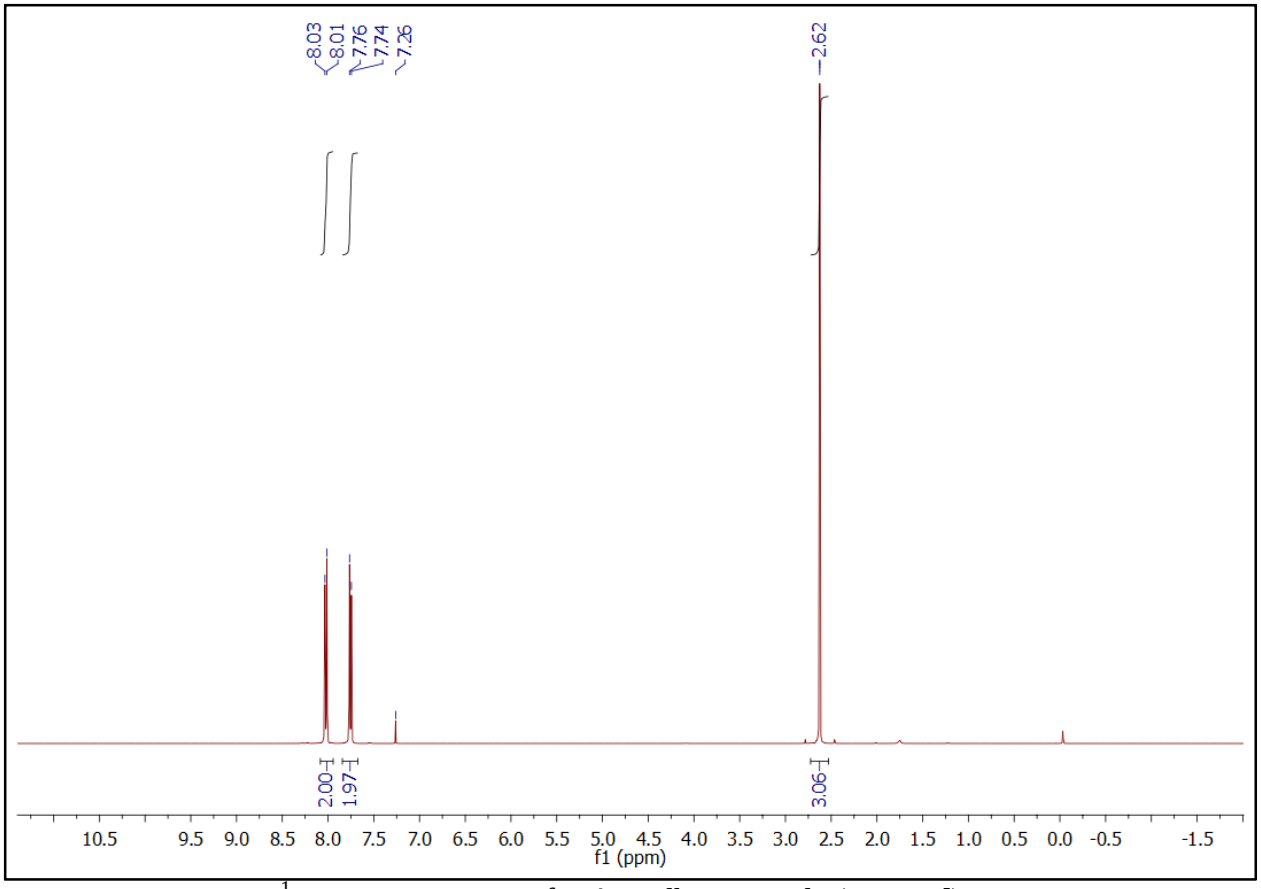
^{1}H NMR spectrum of Benzo[d][1,3]dioxole-5-carbonitrile **(entry 4i)**.



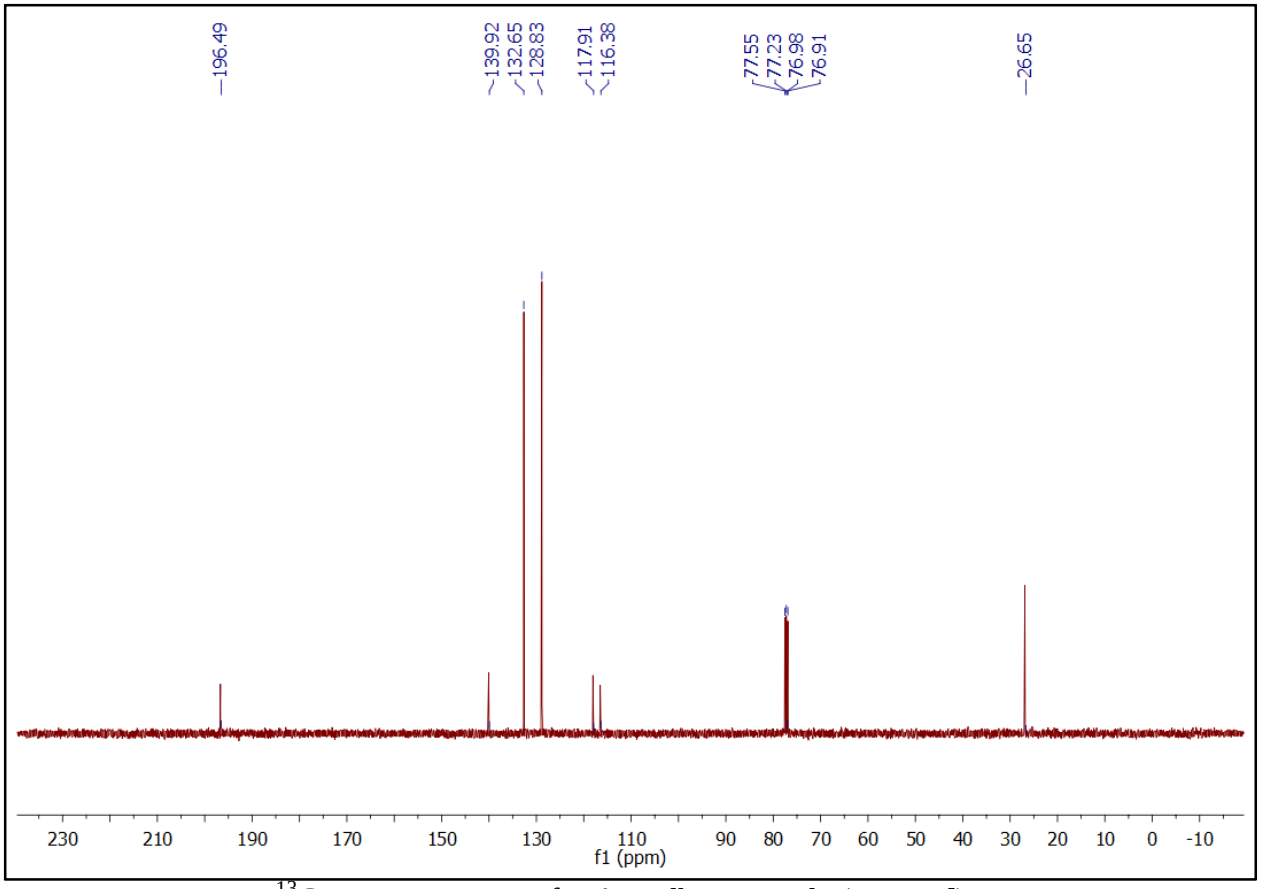
^{1}H NMR spectrum of Methyl 4-cyanobenzoate **(entry 4k)**.



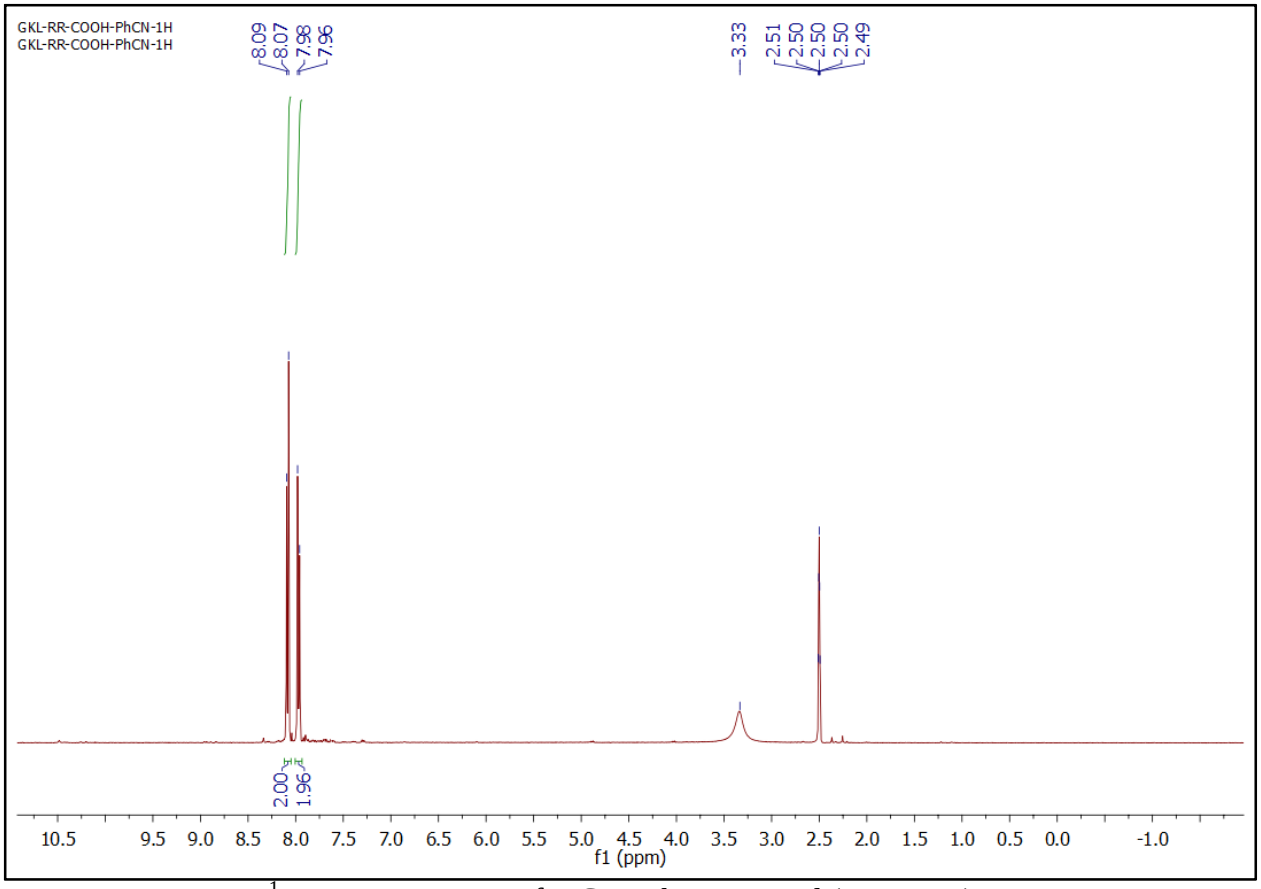
^{13}C NMR spectrum of Methyl 4-cyanobenzoate **(entry 4k)**.



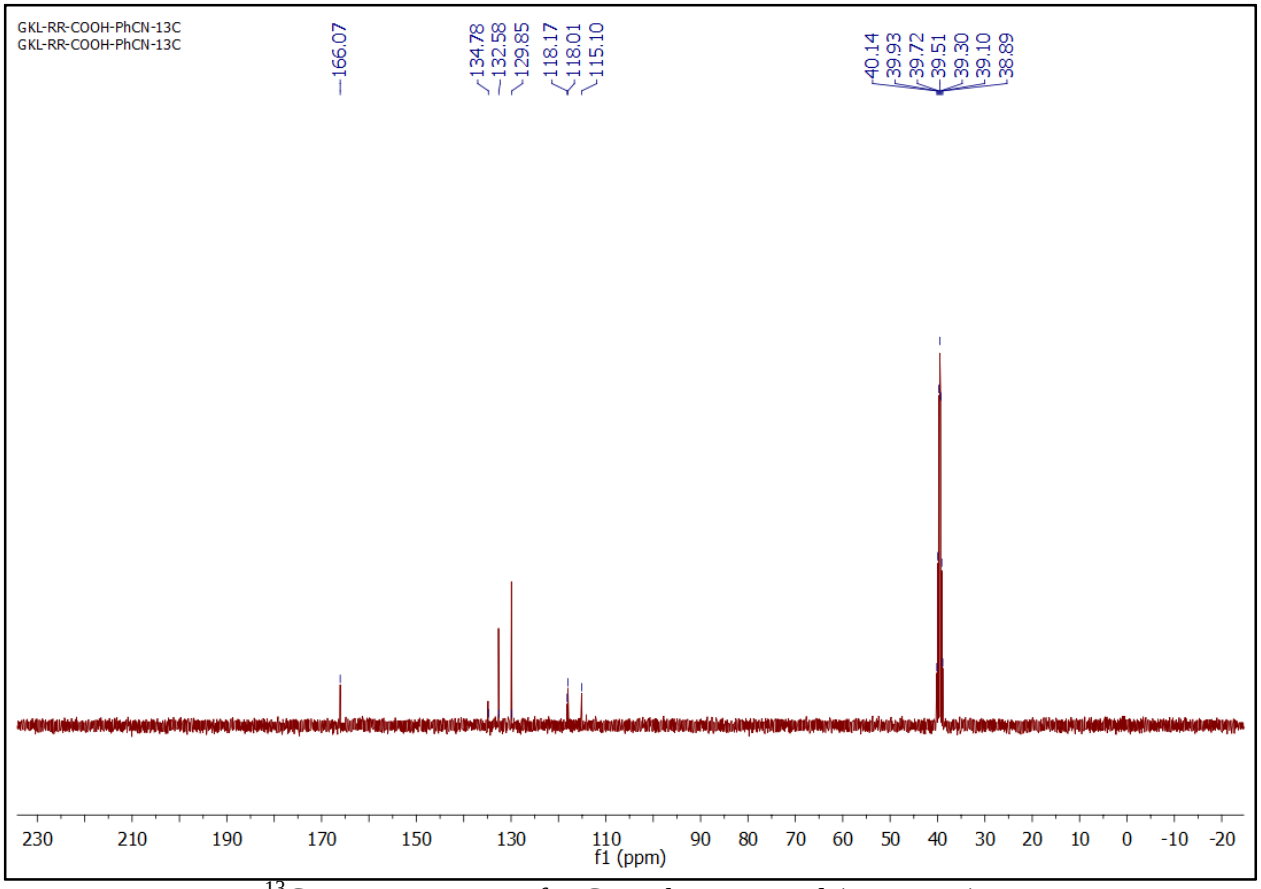
^{1}H NMR spectrum of 4-Acetylbenzonitrile **(entry 4l)**.



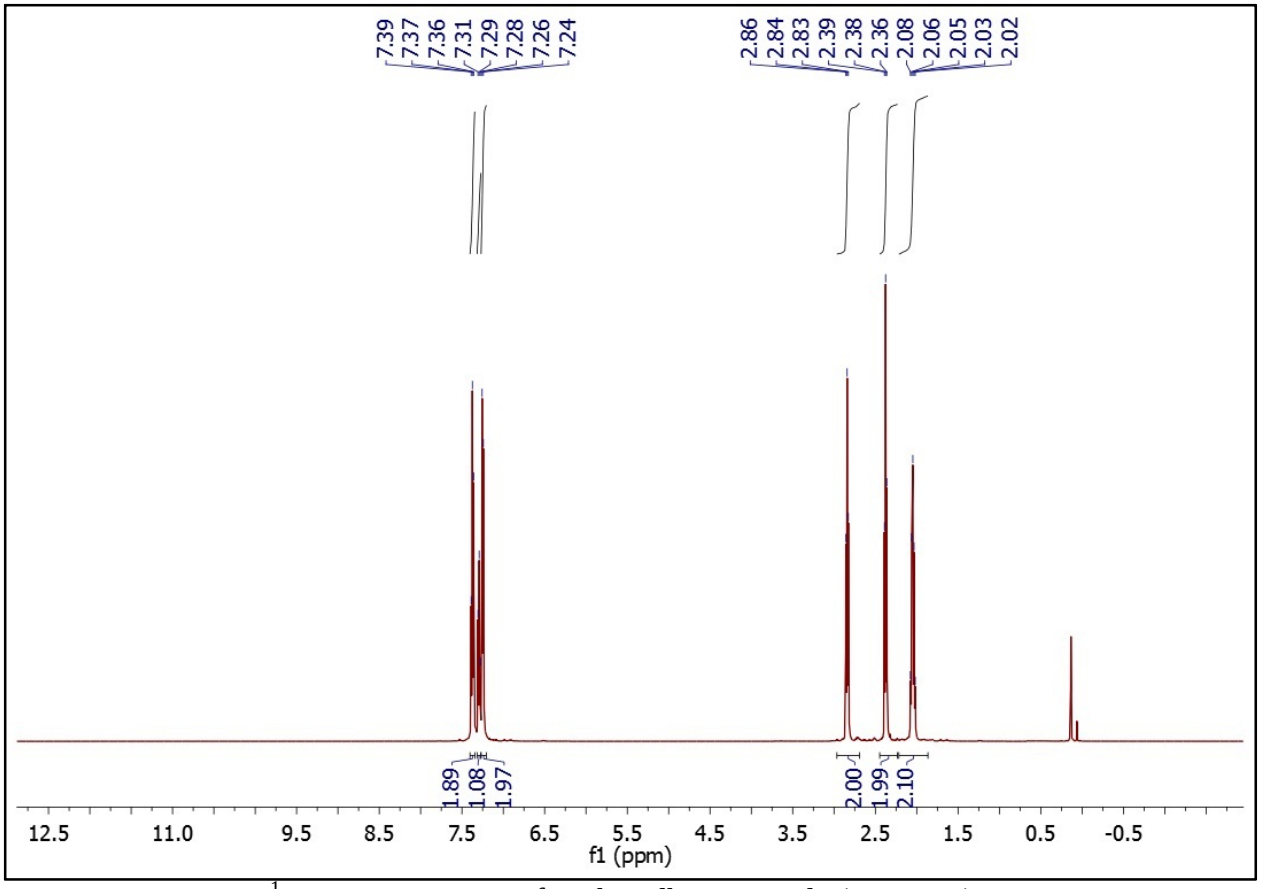
^{13}C NMR spectrum of 4-Acetylbenzonitrile **(entry 4l)**.



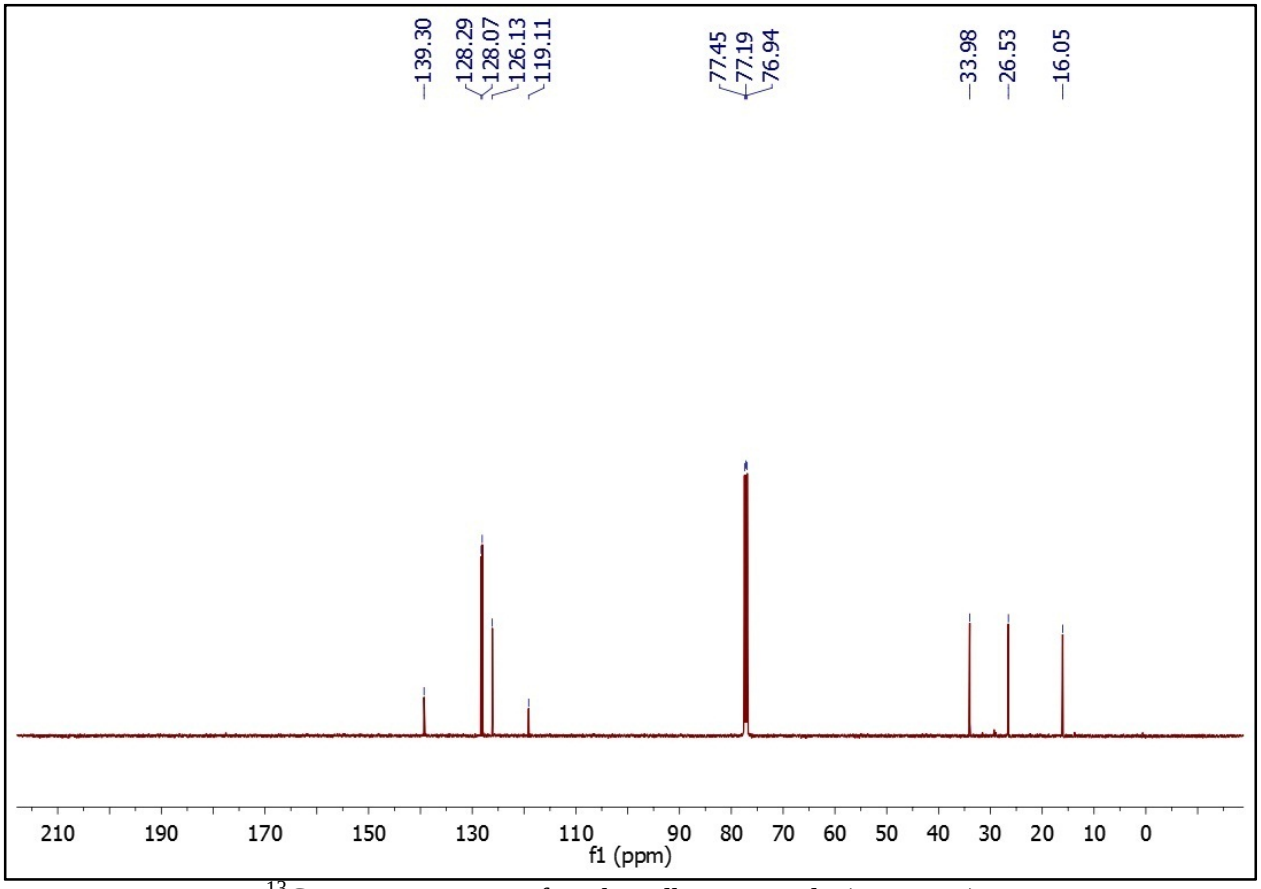
^{1}H NMR spectrum of 4-Cyanobenzoic acid **(entry 4m)**.



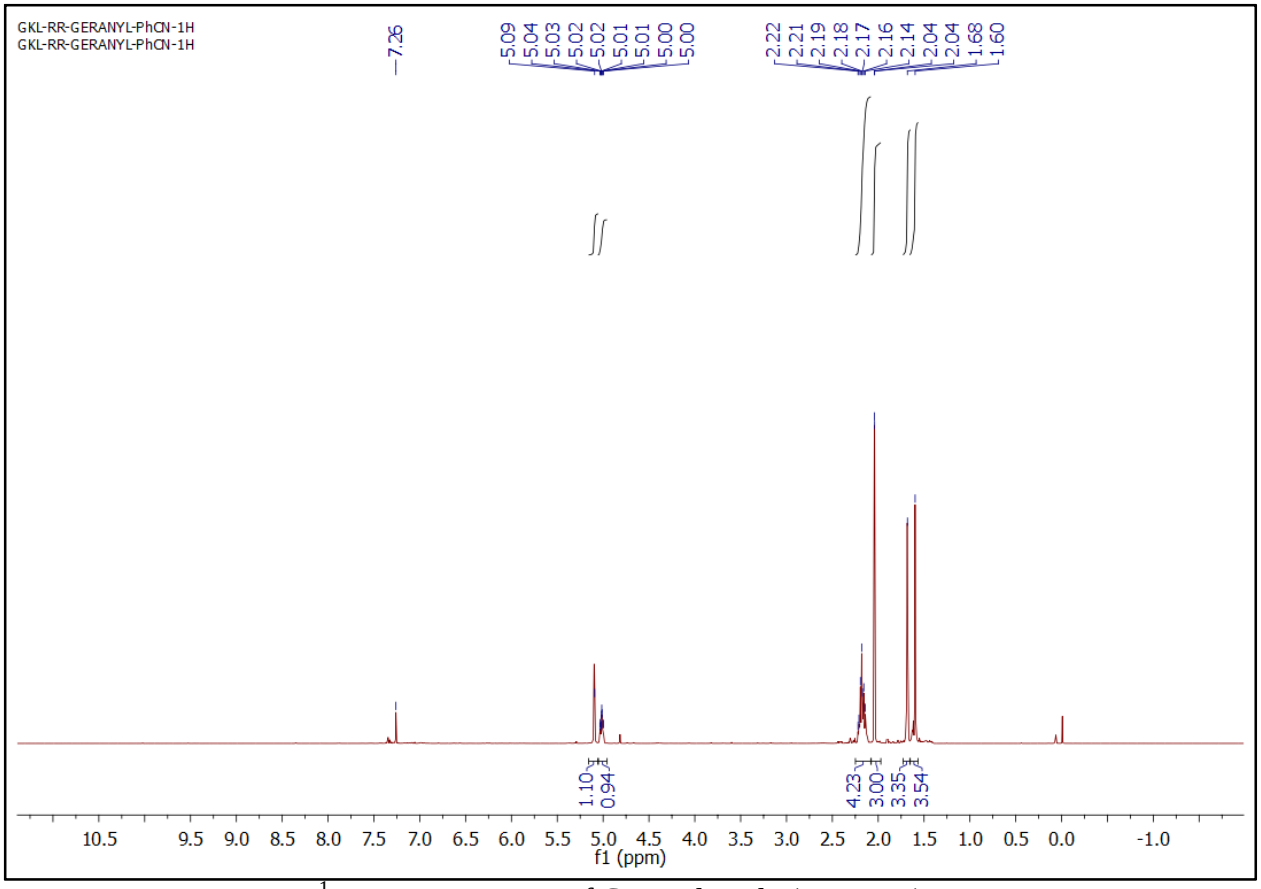
^{13}C NMR spectrum of 4-Cyanobenzoic acid **(entry 4m)**.



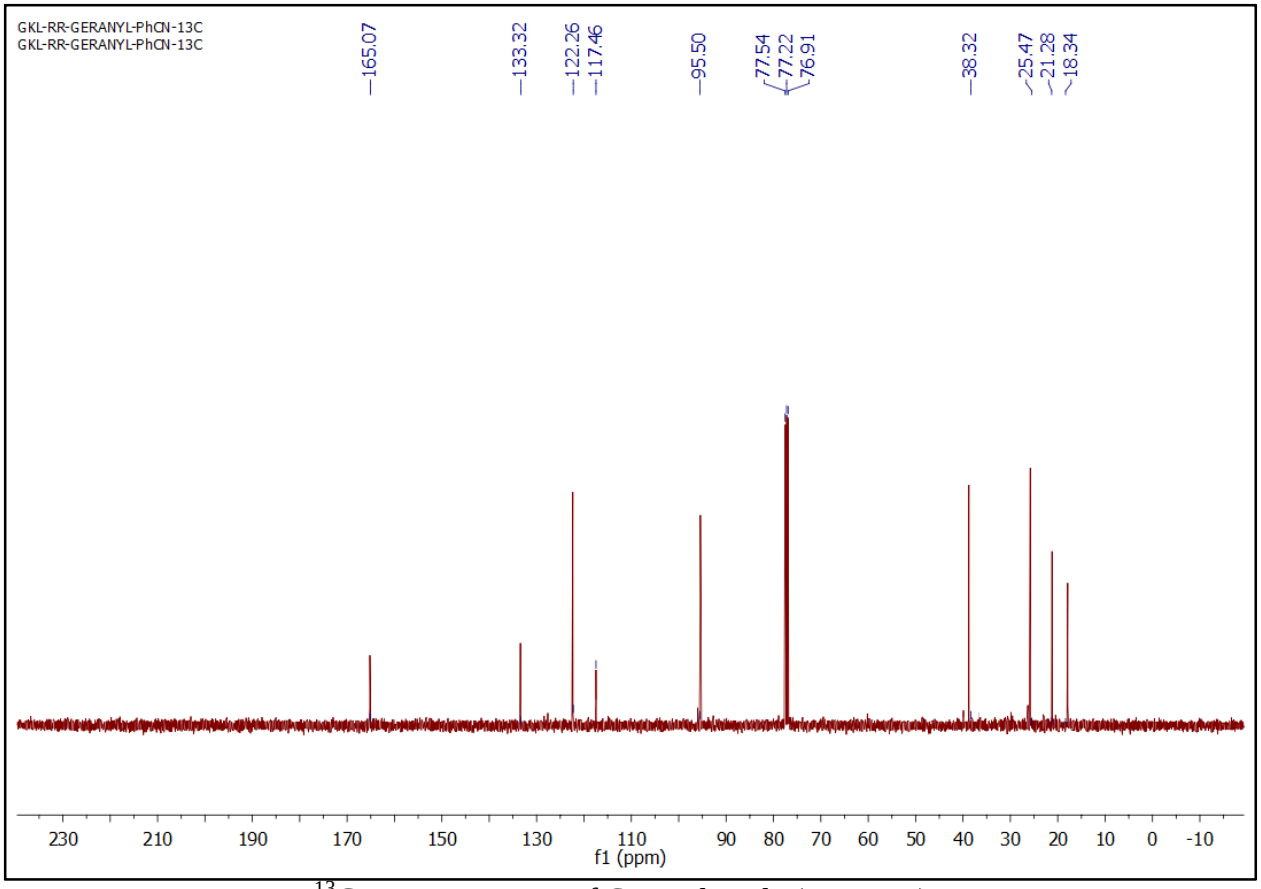
^{1}H NMR spectrum of 4-Phenylbutanenitrile **(entry 4p)**.



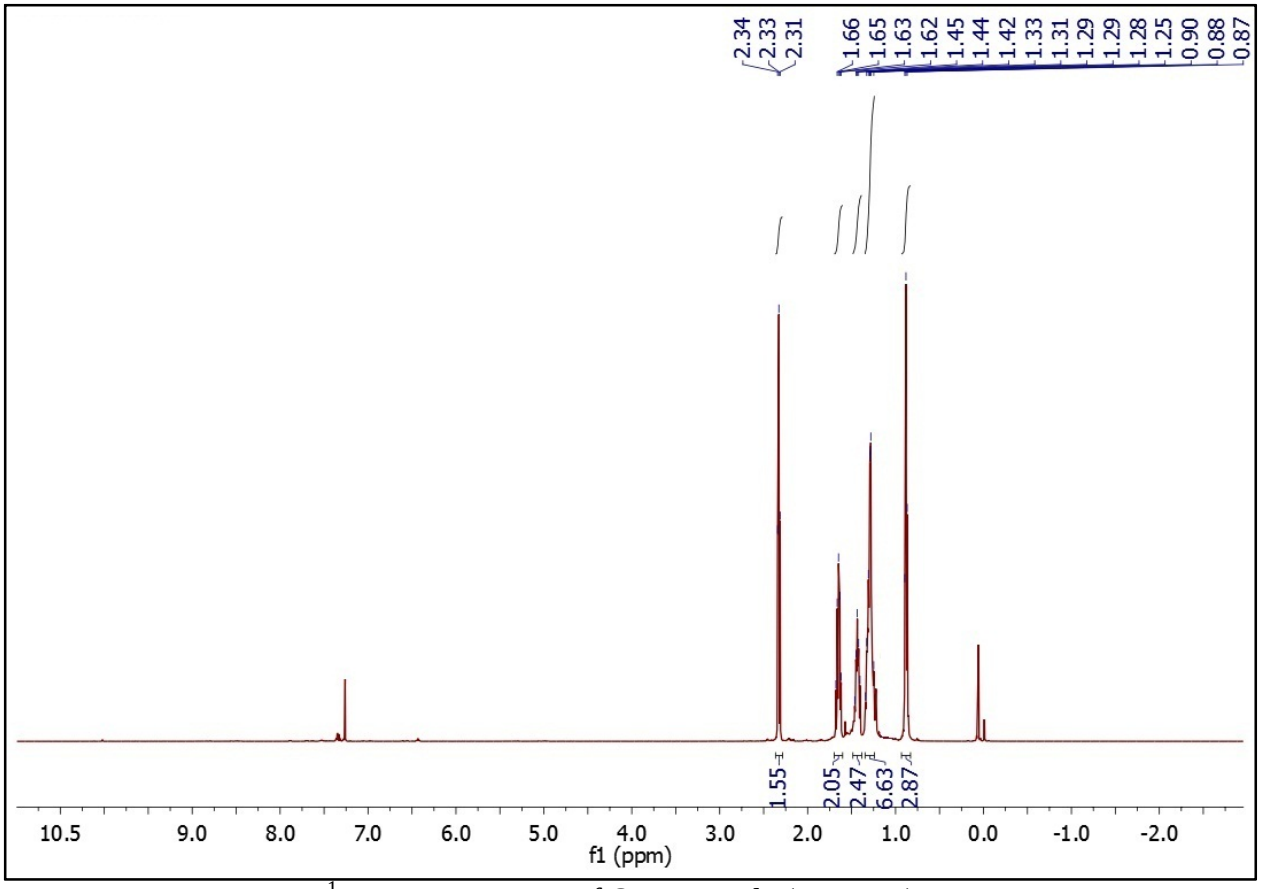
^{13}C NMR spectrum of 4-Phenylbutanenitrile **(entry 4p)**.



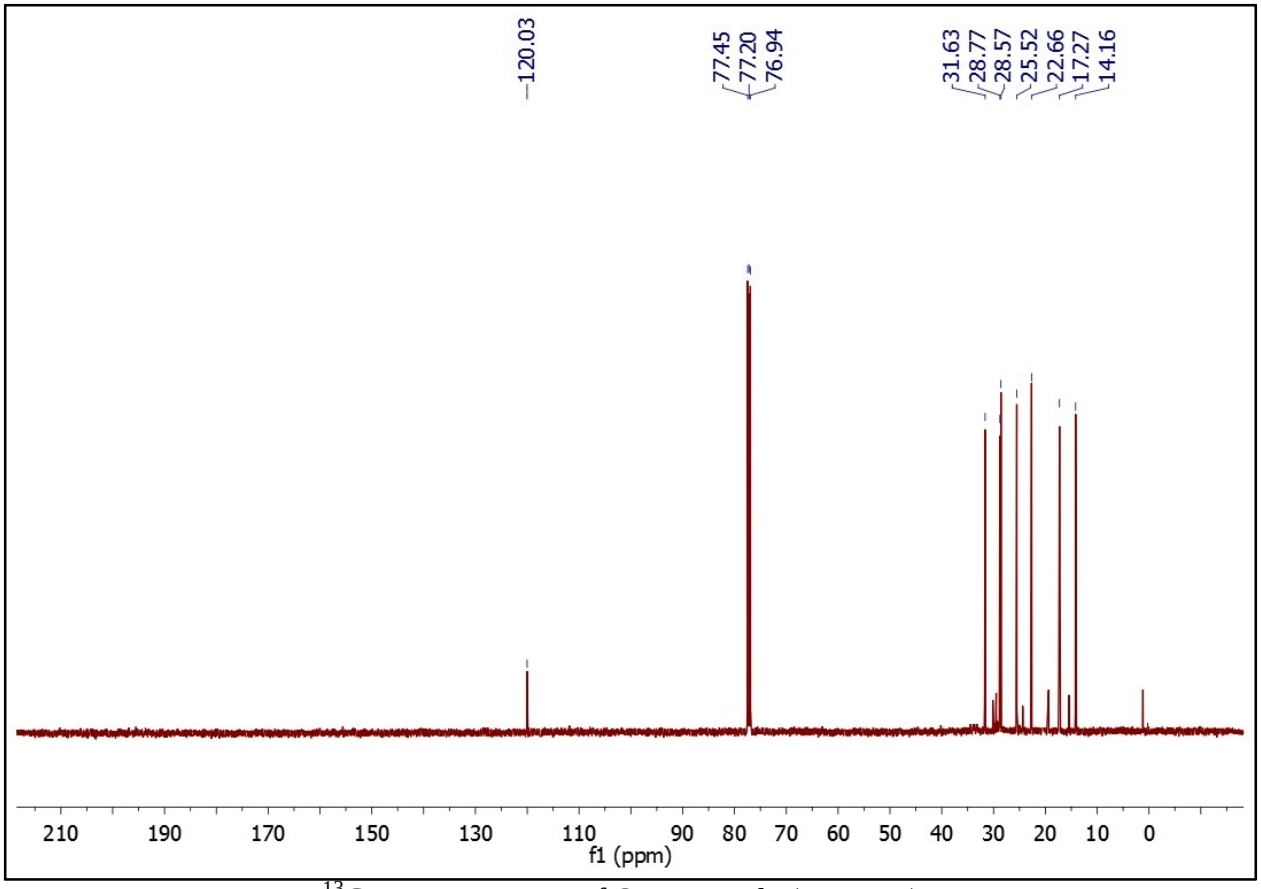
^{1}H NMR spectrum of Geranylnitrile **(entry 4q)**.



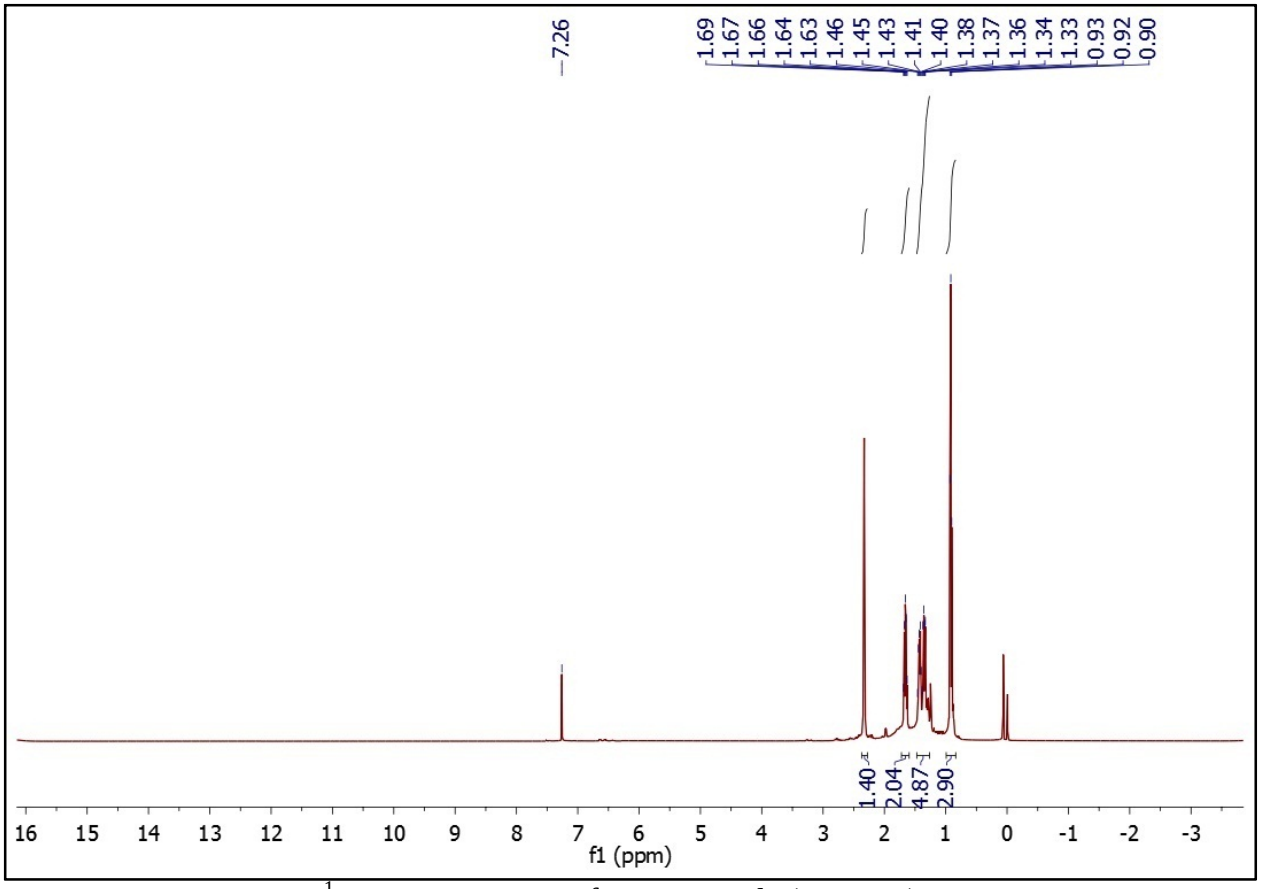
^{13}C NMR spectrum of Geranylnitrile **(entry 4q)**.



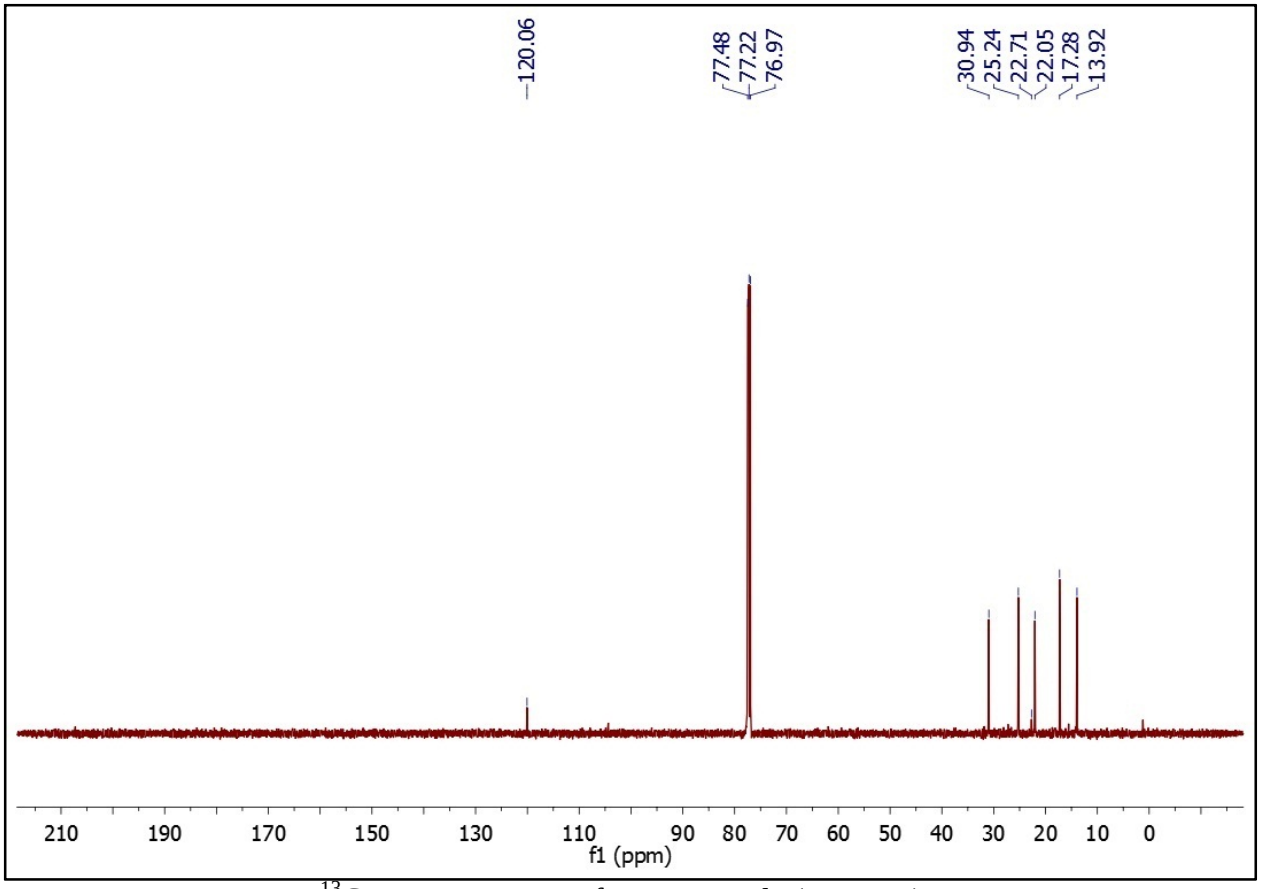
^{1}H NMR spectrum of Octanenitrile **(entry 4r)**.



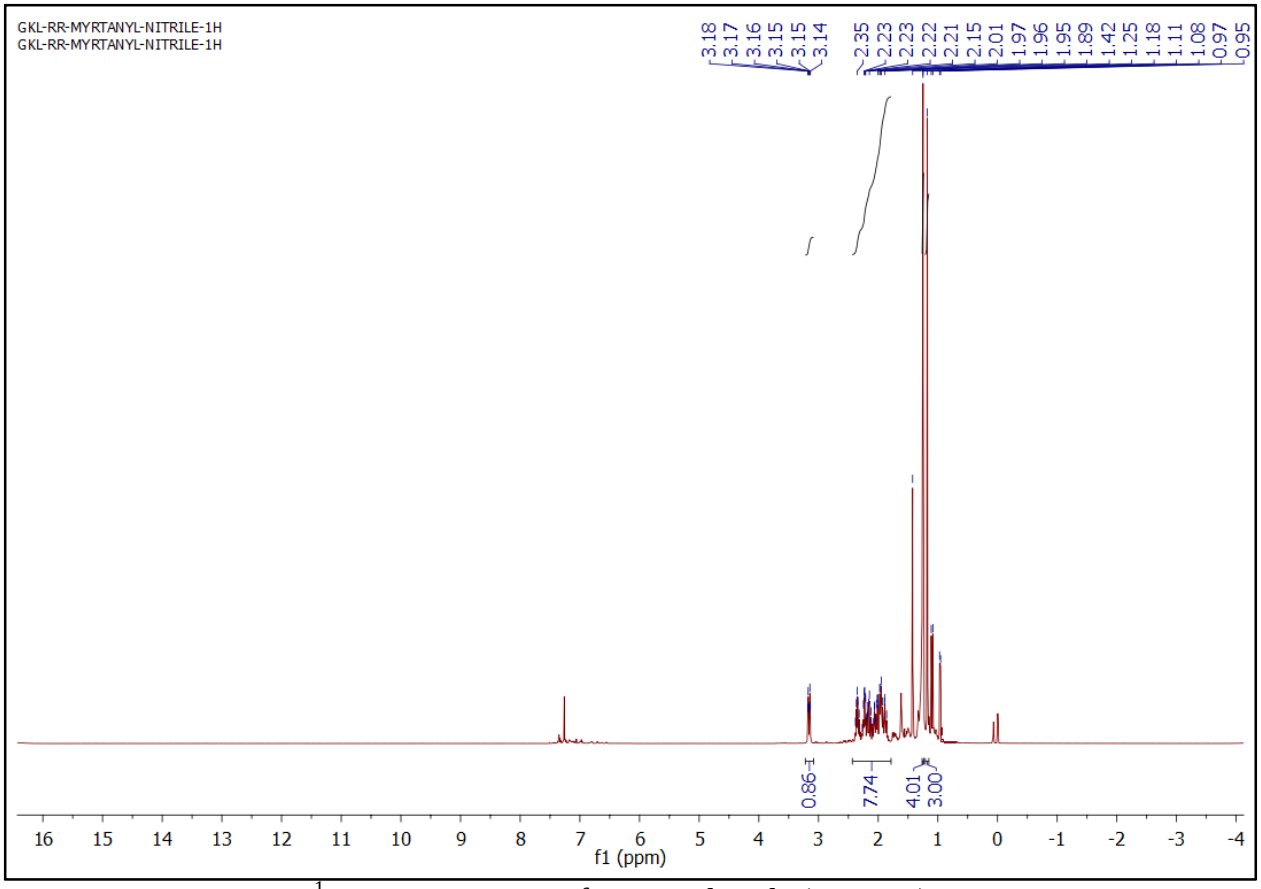
^{13}C NMR spectrum of Octanenitrile **(entry 4r)**.



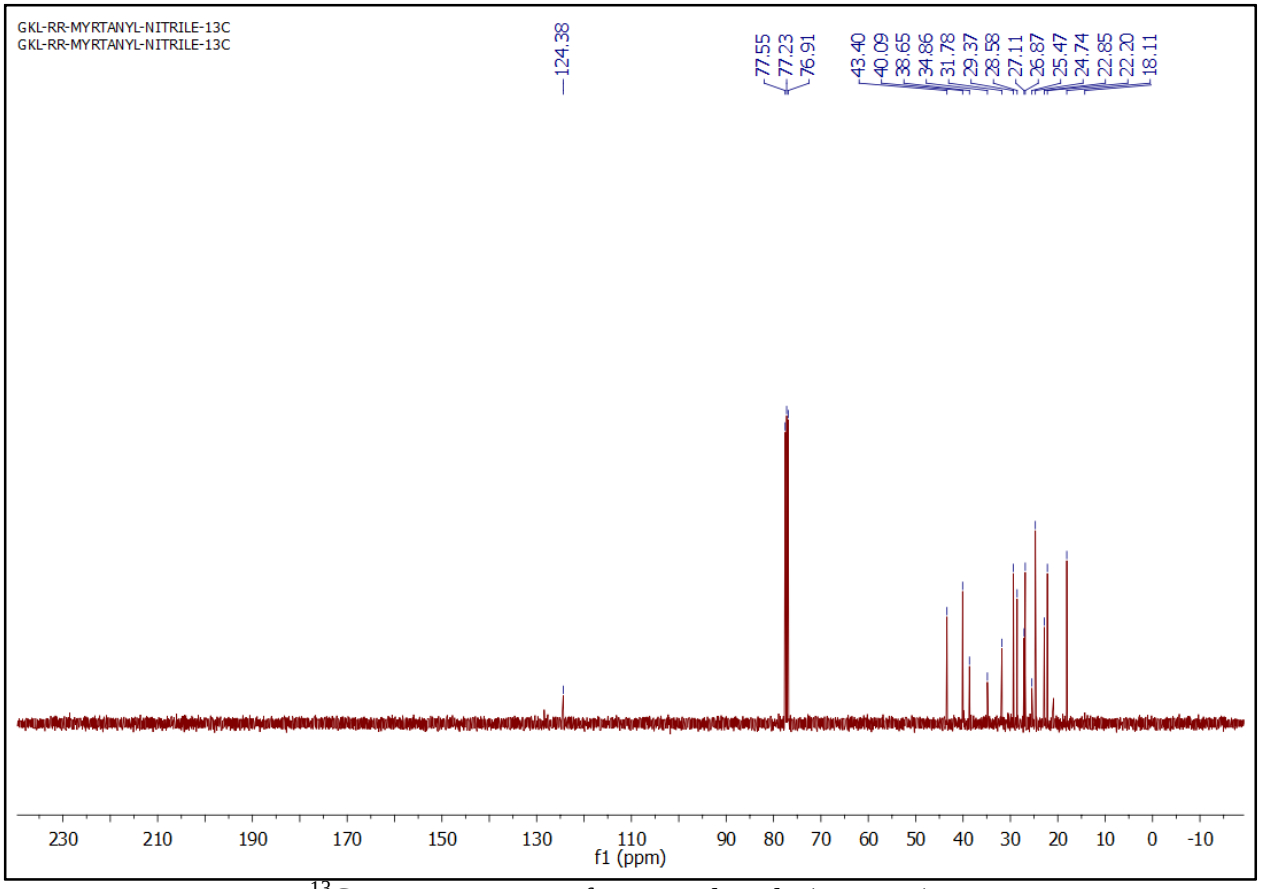
^{1}H NMR spectrum of Hexanenitrile **(entry 4s)**.



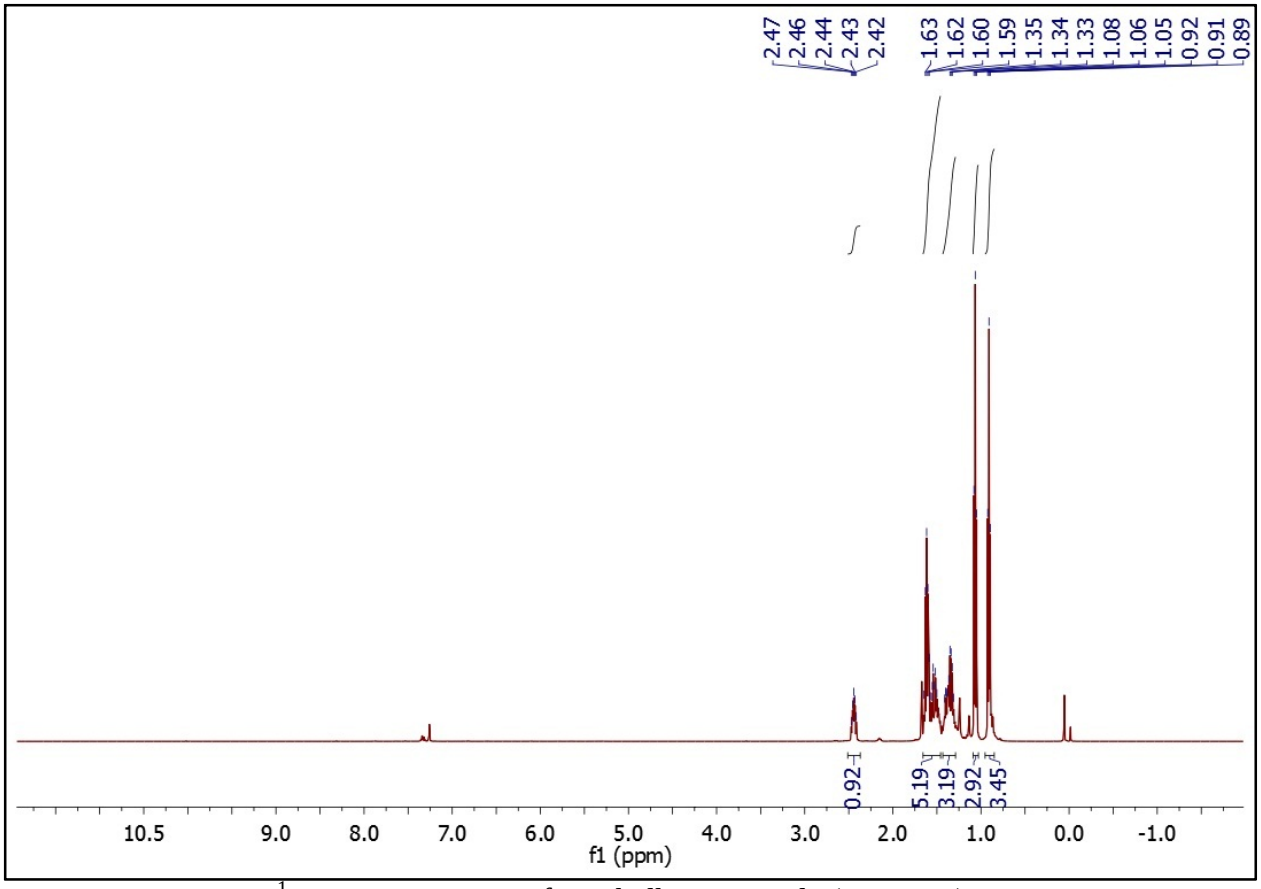
^{13}C NMR spectrum of Hexanenitrile **(entry 4s)**.



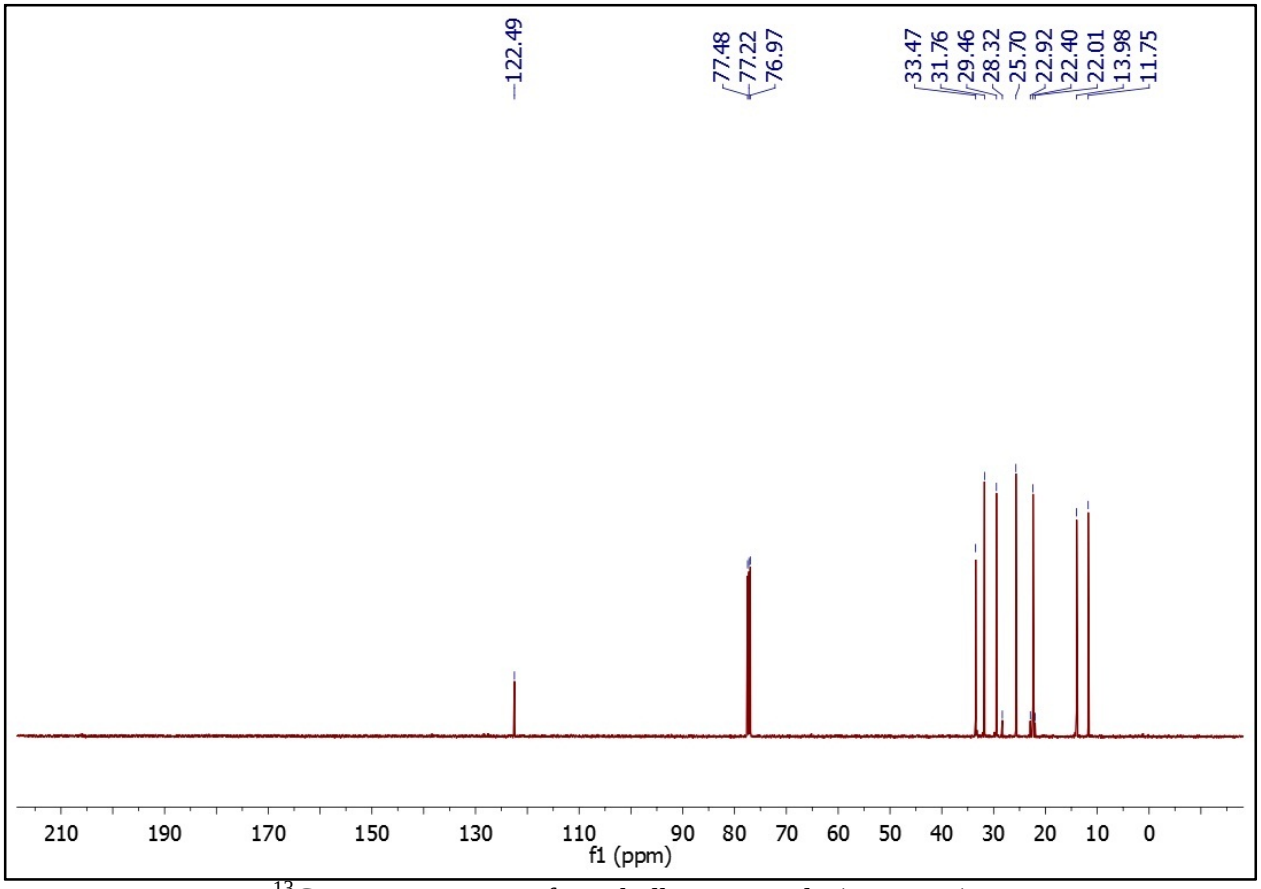
^{1}H NMR spectrum of Myrtanylnitrile **(entry 4t)**.



^{13}C NMR spectrum of Myrtanylnitrile **(entry 4t)**.

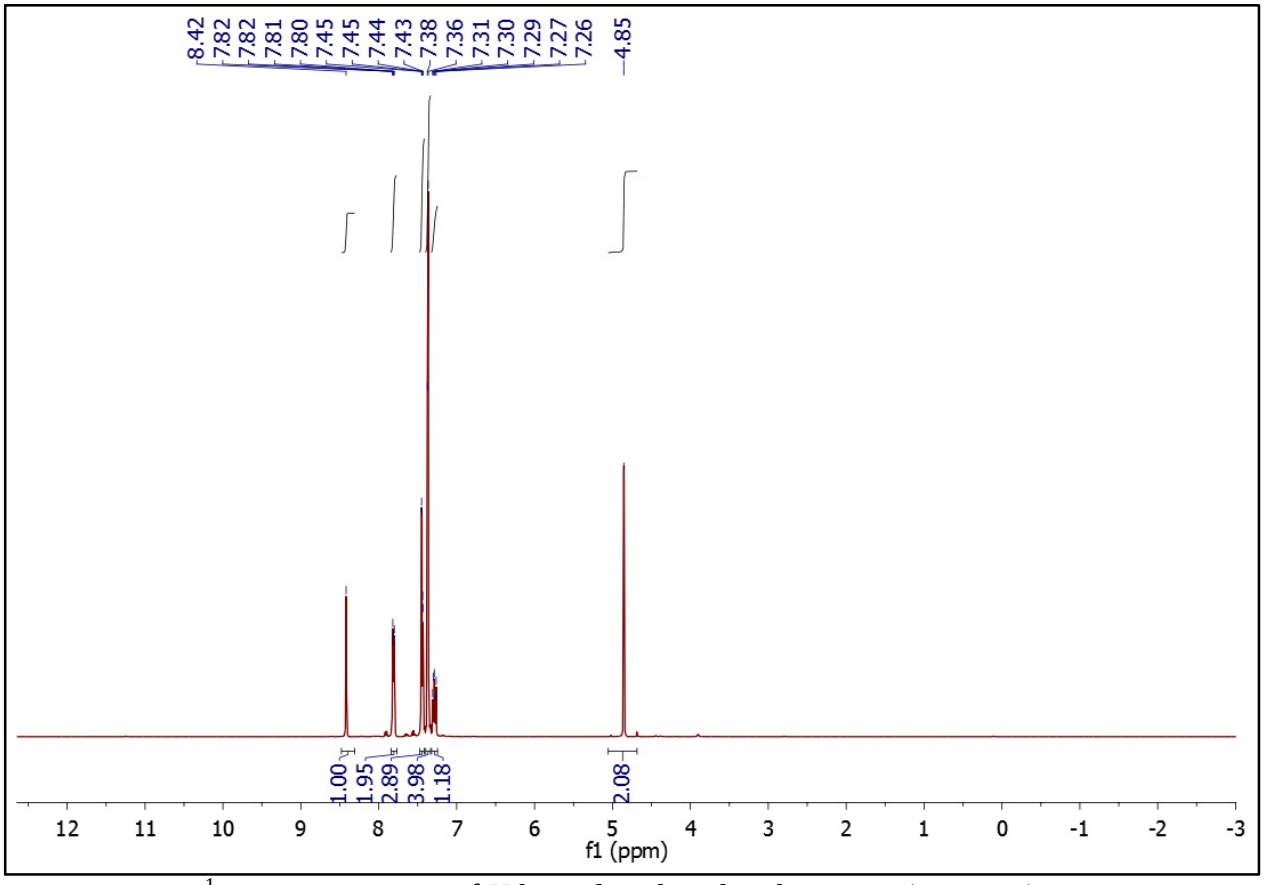


^{1}H NMR spectrum of 2-Ethylhexanenitrile **(entry 4u)**.

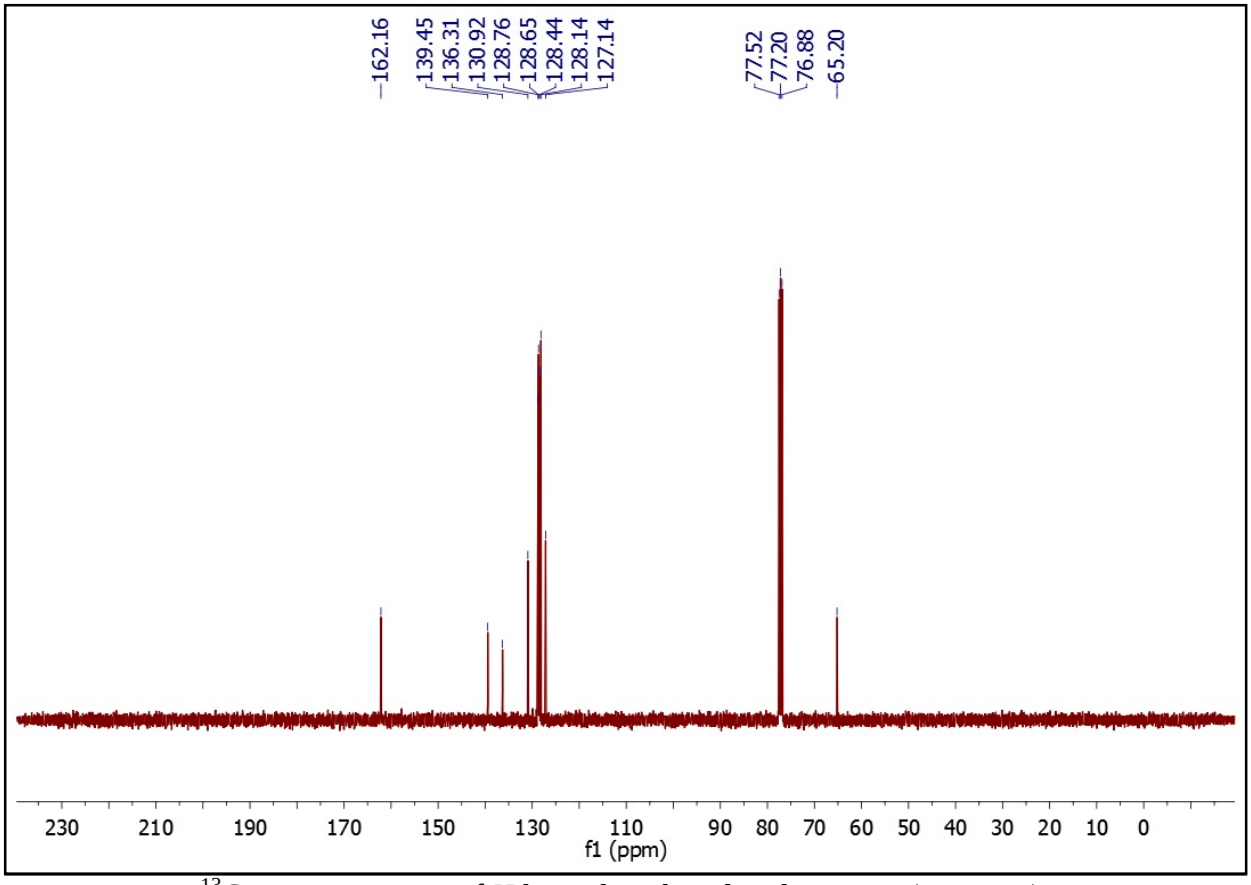


^{13}C NMR spectrum of 2-Ethylhexanenitrile **(entry 4u)**.

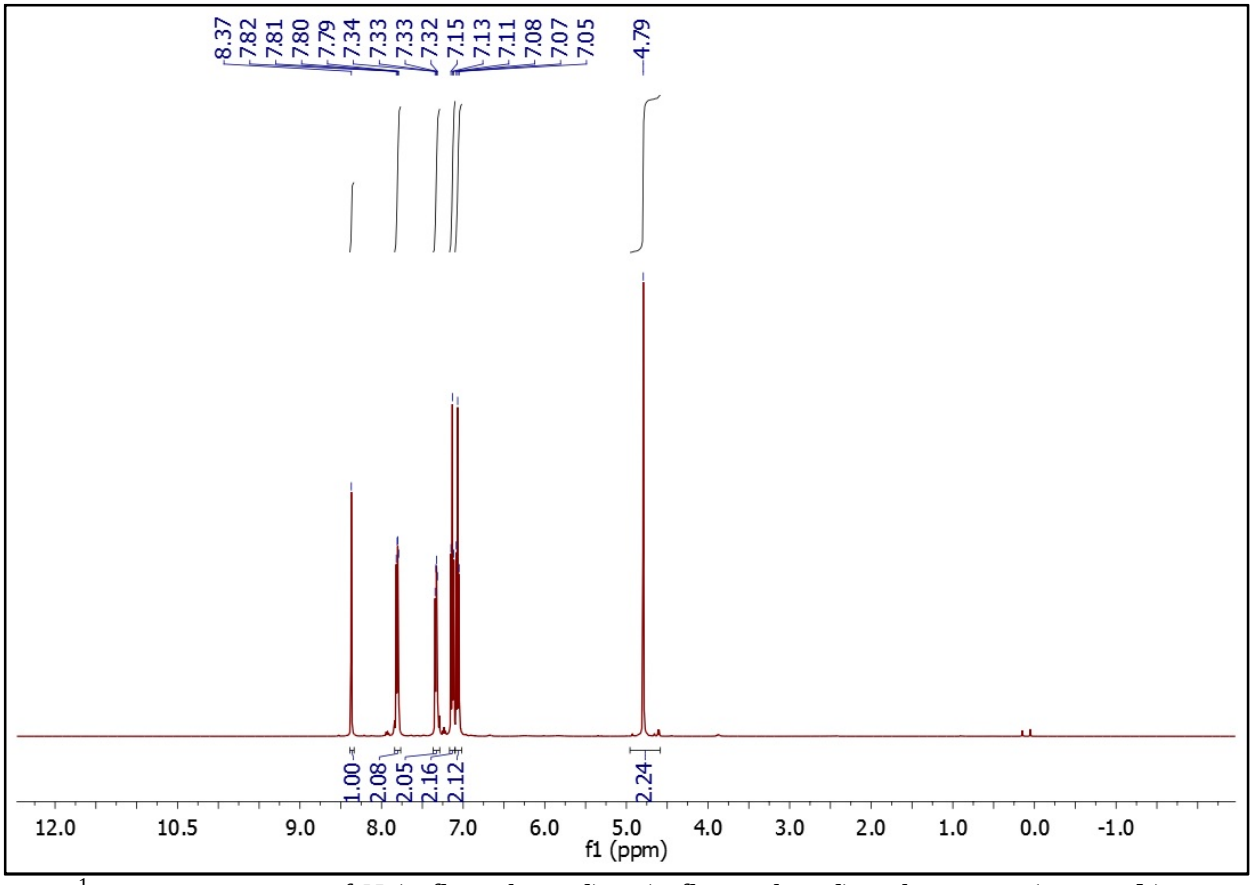
^{1}H and ^{13}C NMR spectral data of the isolated imines



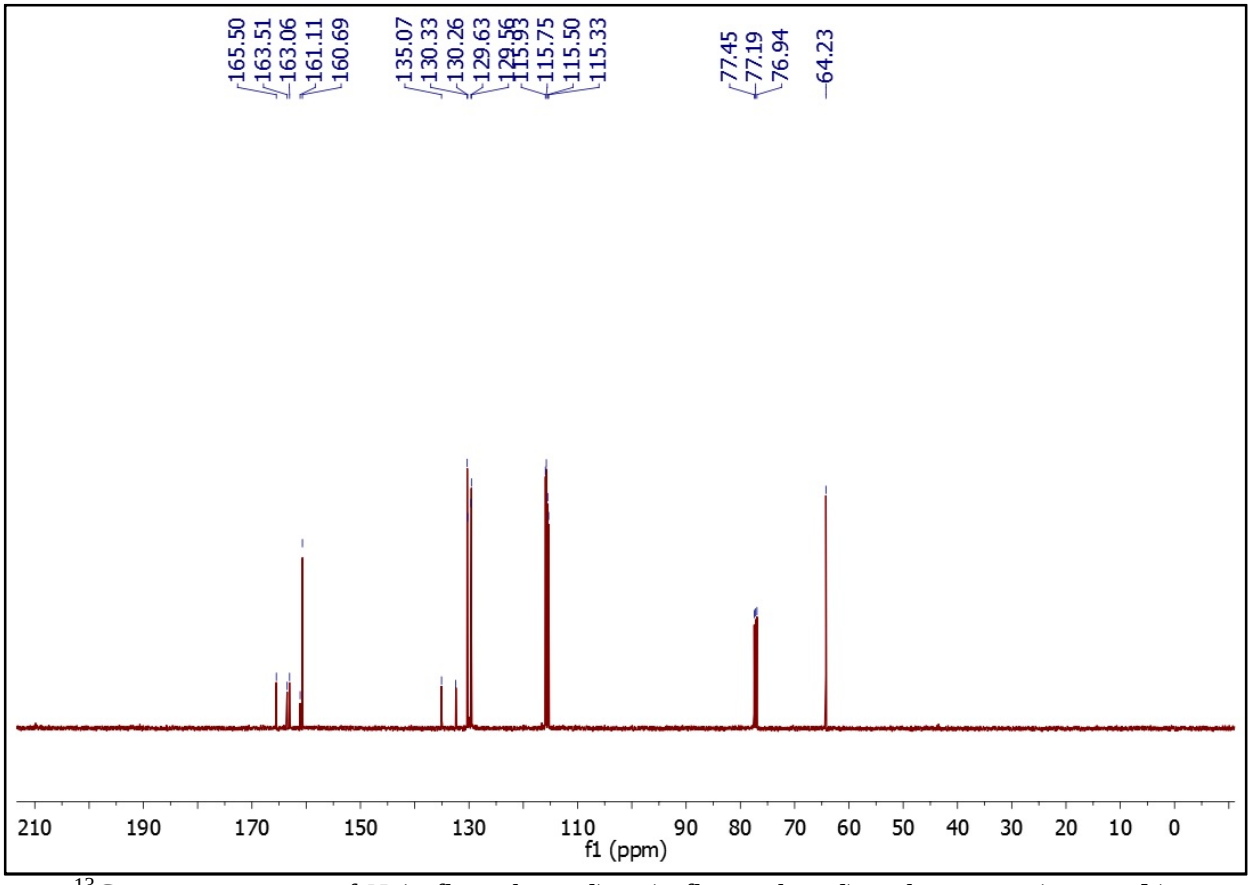
^{1}H NMR spectrum of *N*-benzyl-1-phenylmethanimine **(entry 5a)**.



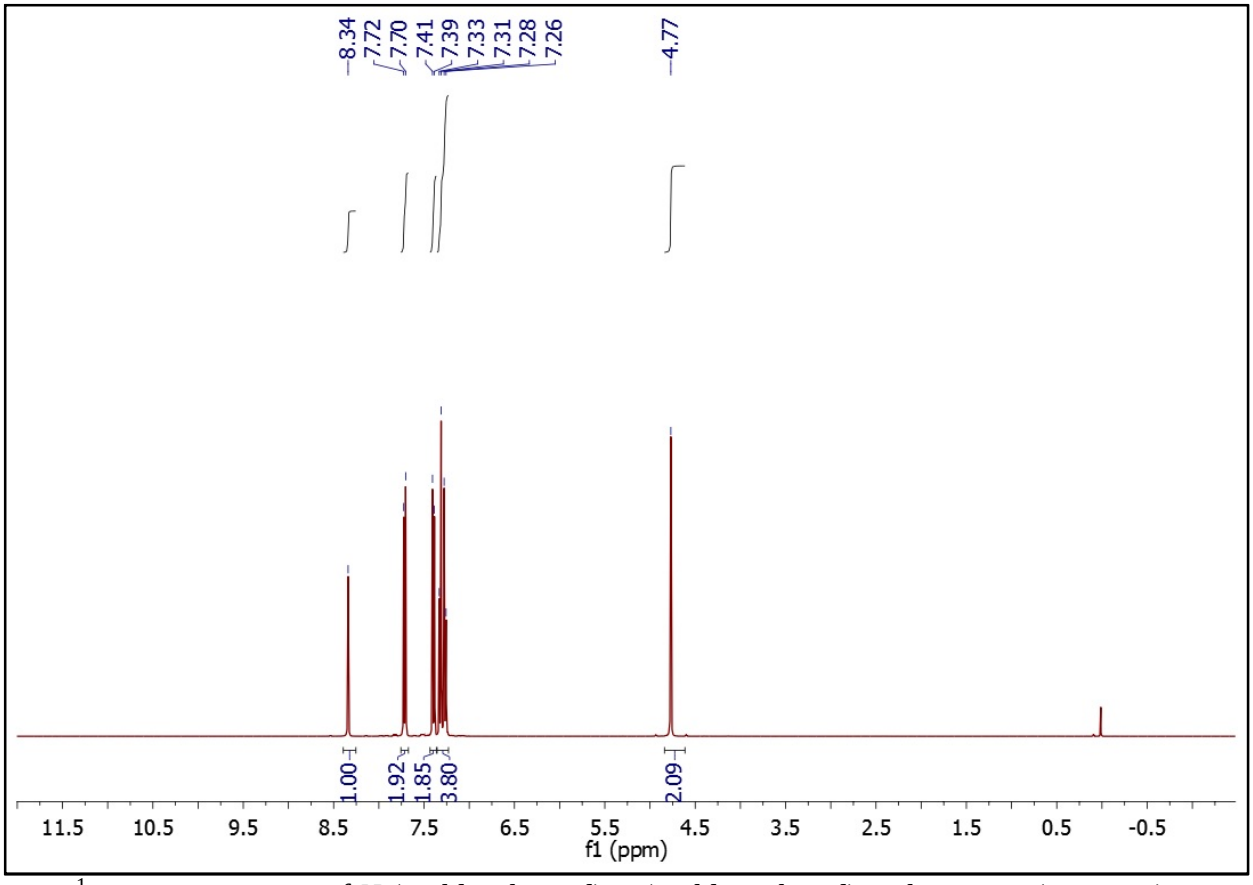
^{13}C NMR spectrum of *N*-benzyl-1-phenylmethanimine **(entry 5a)**.



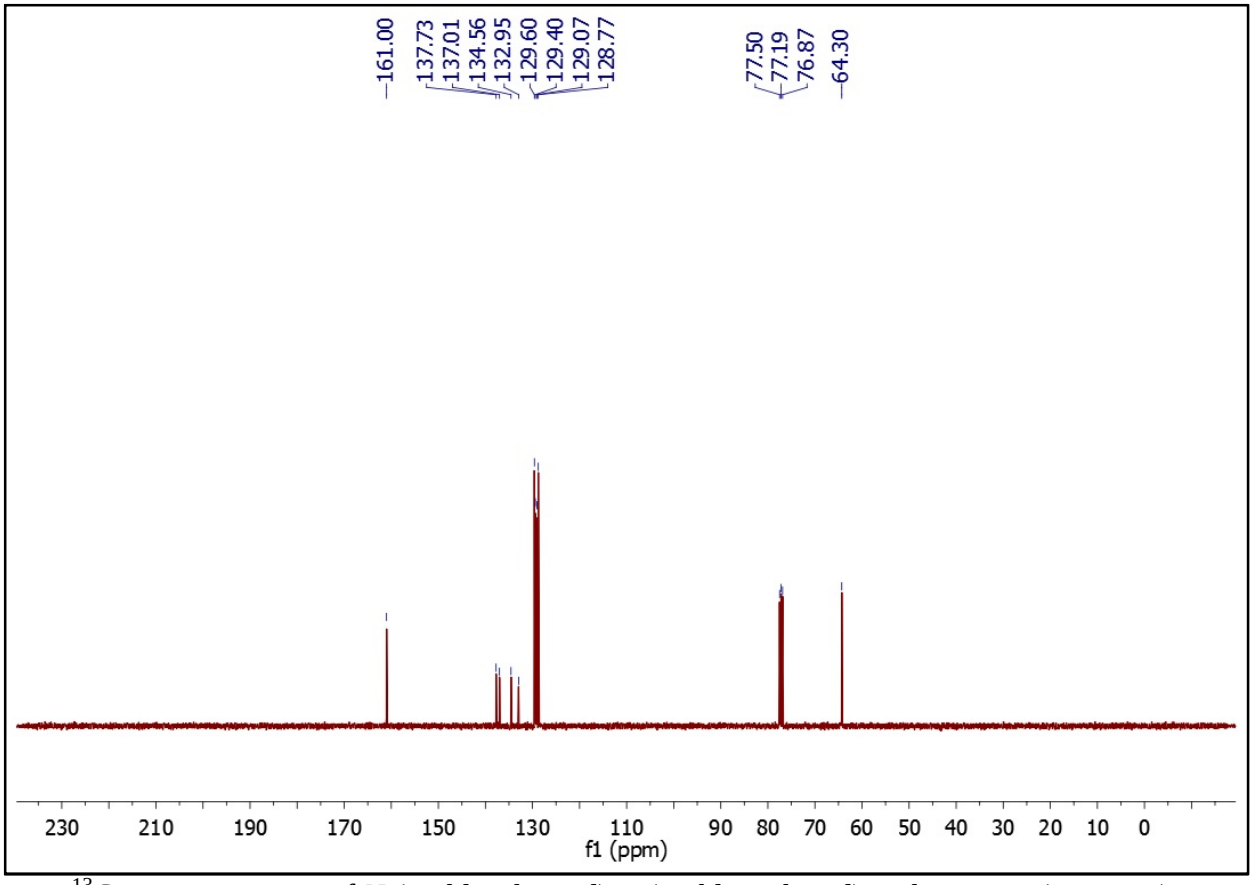
^{1}H NMR spectrum of *N*-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine **(entry 5b)**.



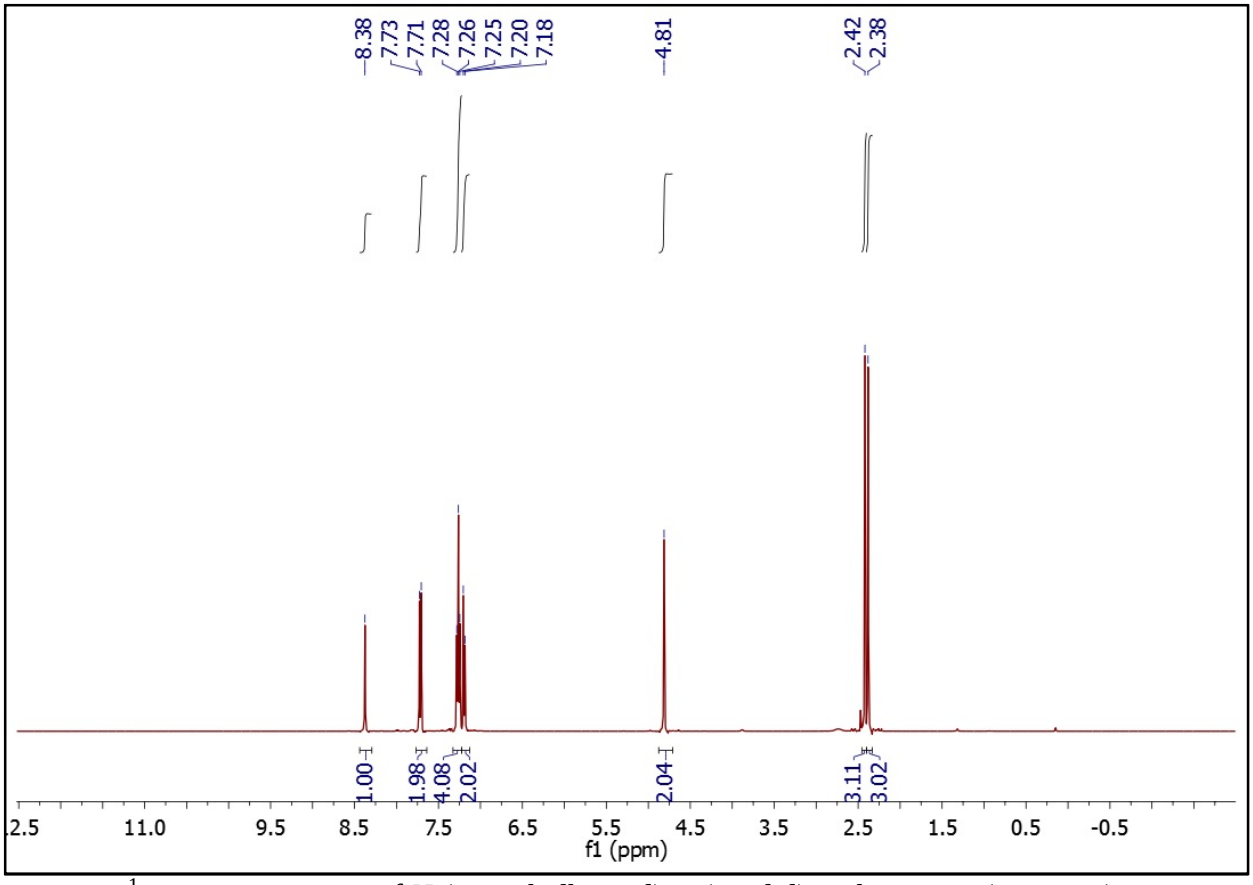
^{13}C NMR spectrum of *N*-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine **(entry 5b)**.



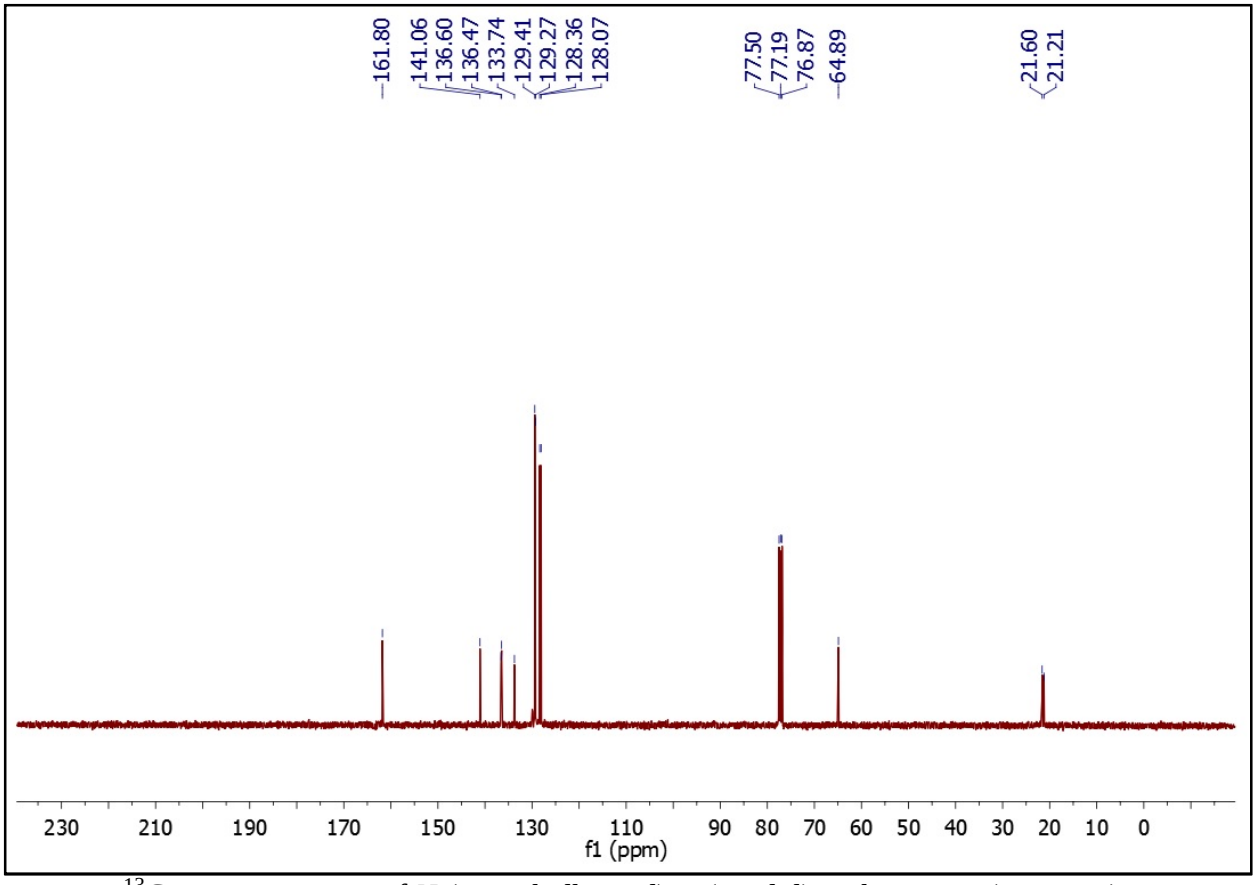
^{1}H NMR spectrum of *N*-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine **(entry 5c)**.



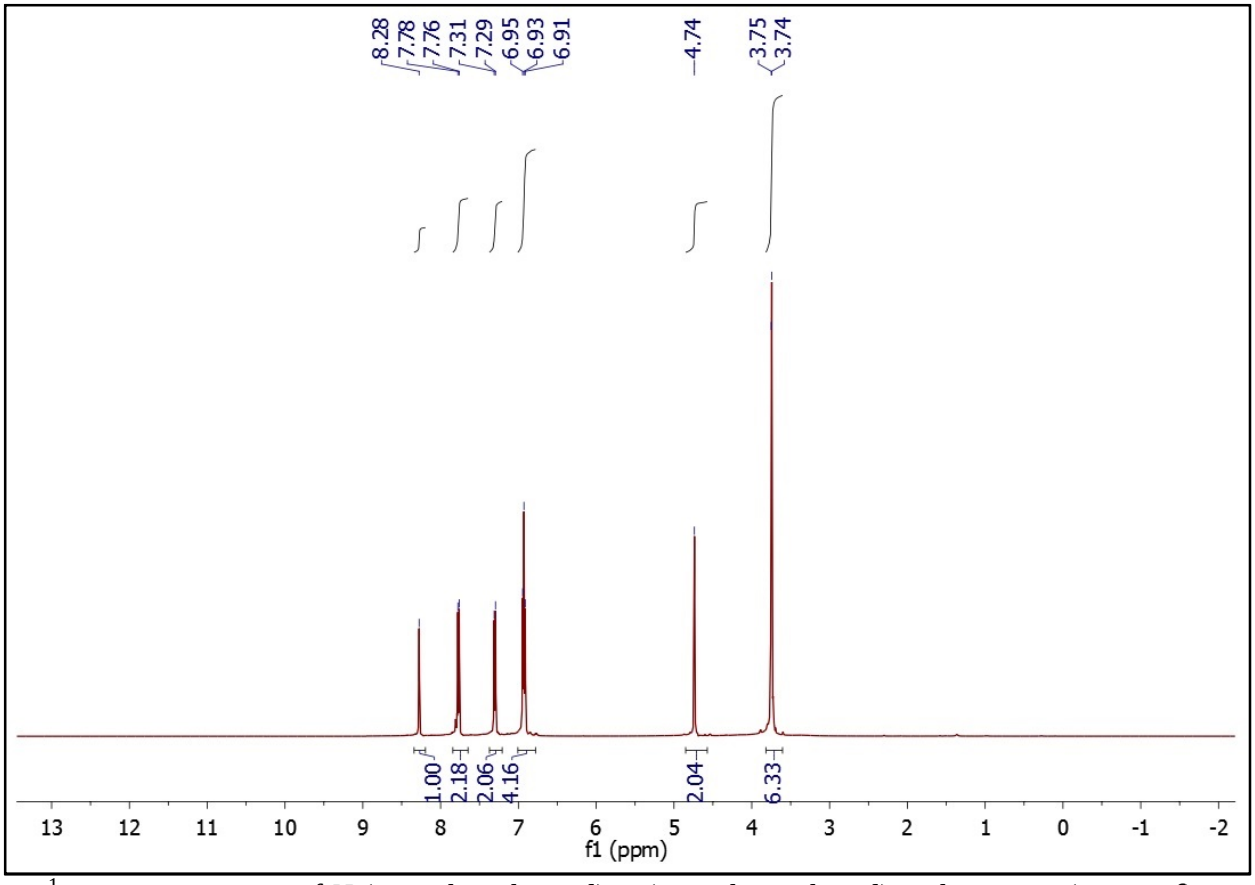
^{13}C NMR spectrum of *N*-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine **(entry 5c)**.



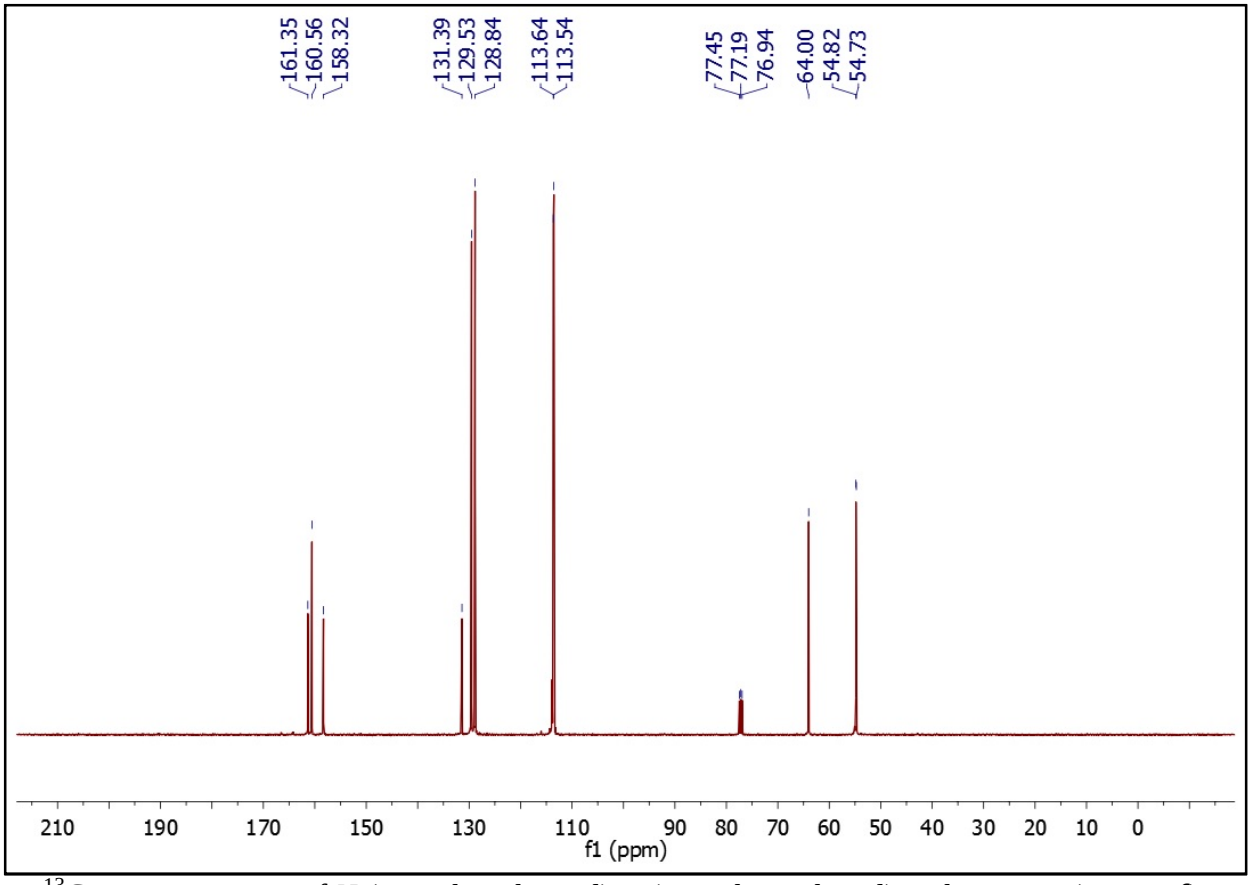
^{1}H NMR spectrum of *N*-(4-methylbenzyl)-1-(*p*-tolyl)methanimine **(entry 5e)**.



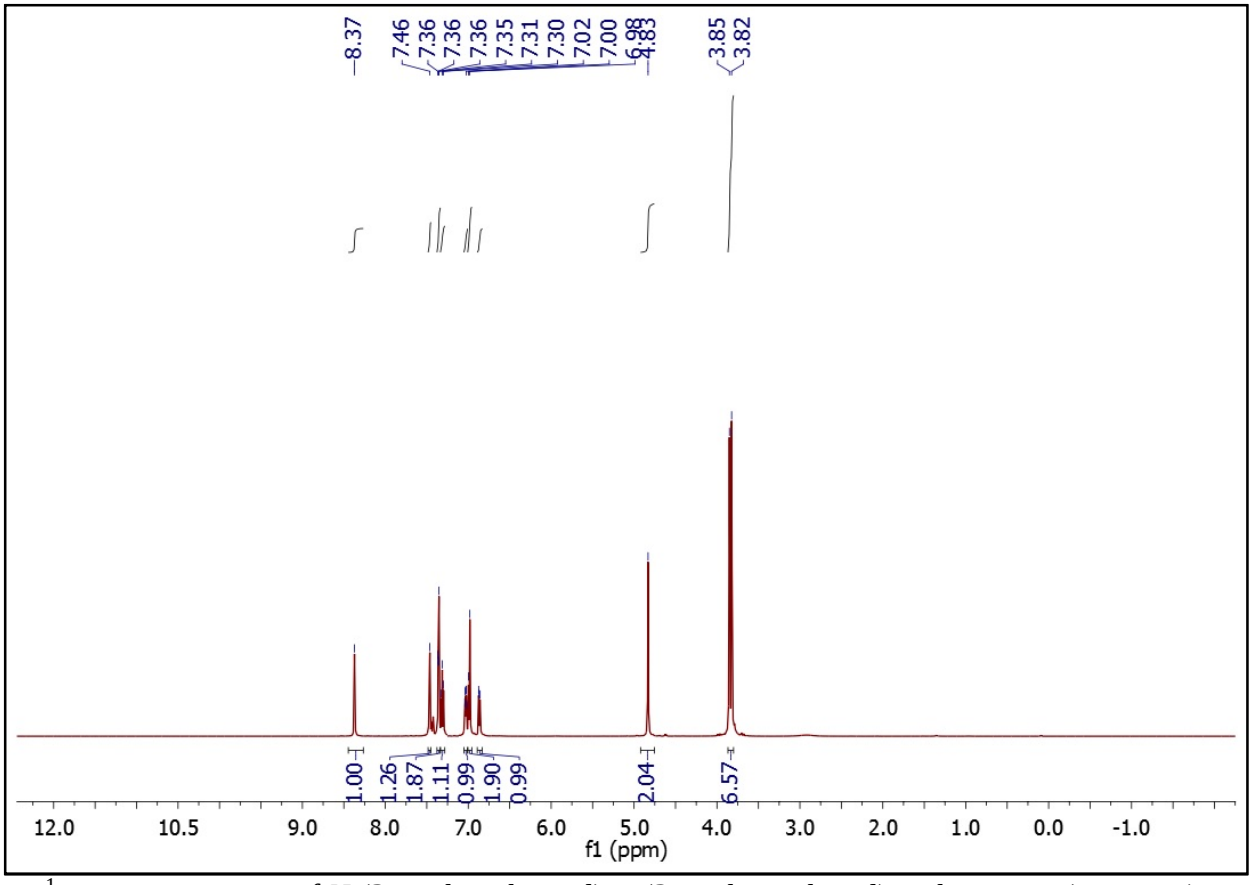
^{13}C NMR spectrum of *N*-(4-methylbenzyl)-1-(*p*-tolyl)methanimine **(entry 5e)**.



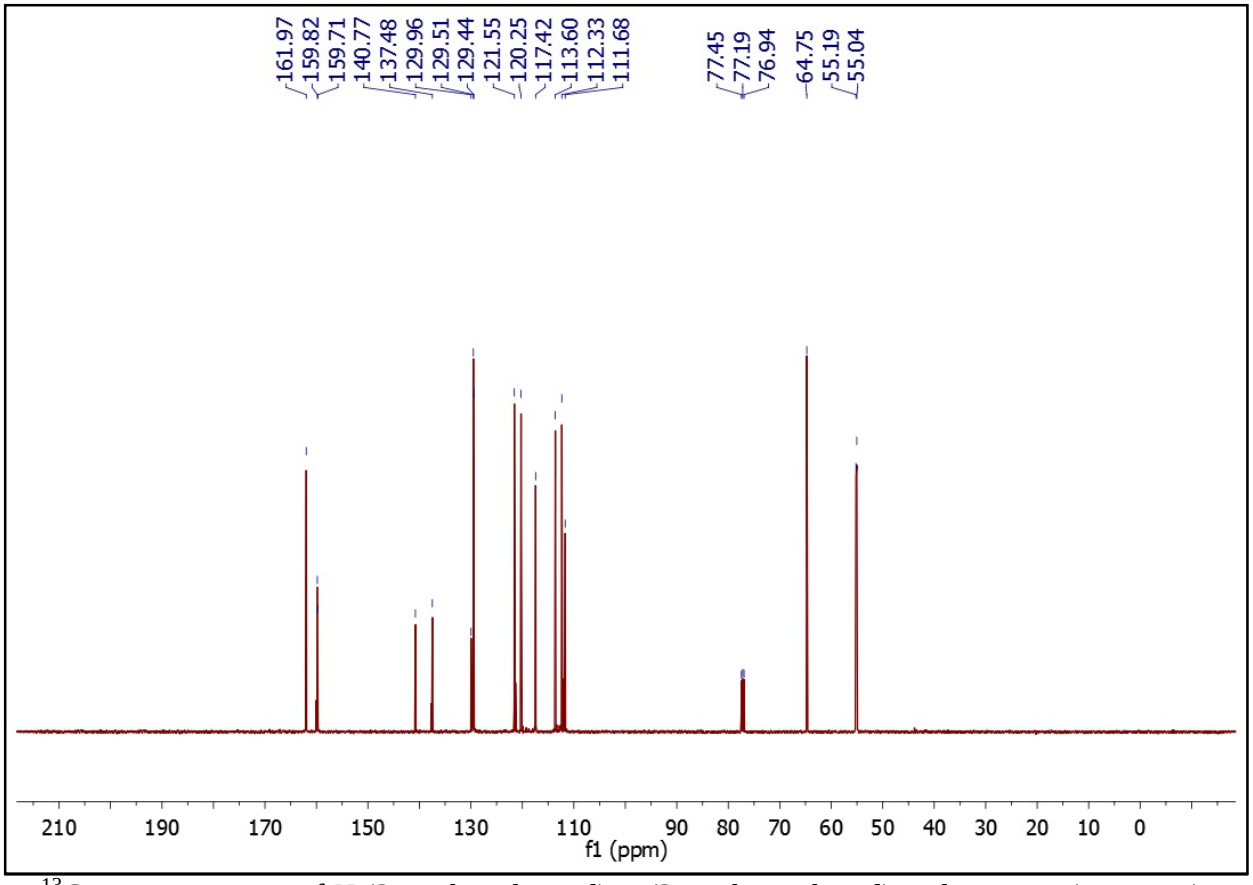
^{1}H NMR spectrum of *N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine **(entry 5f)**.



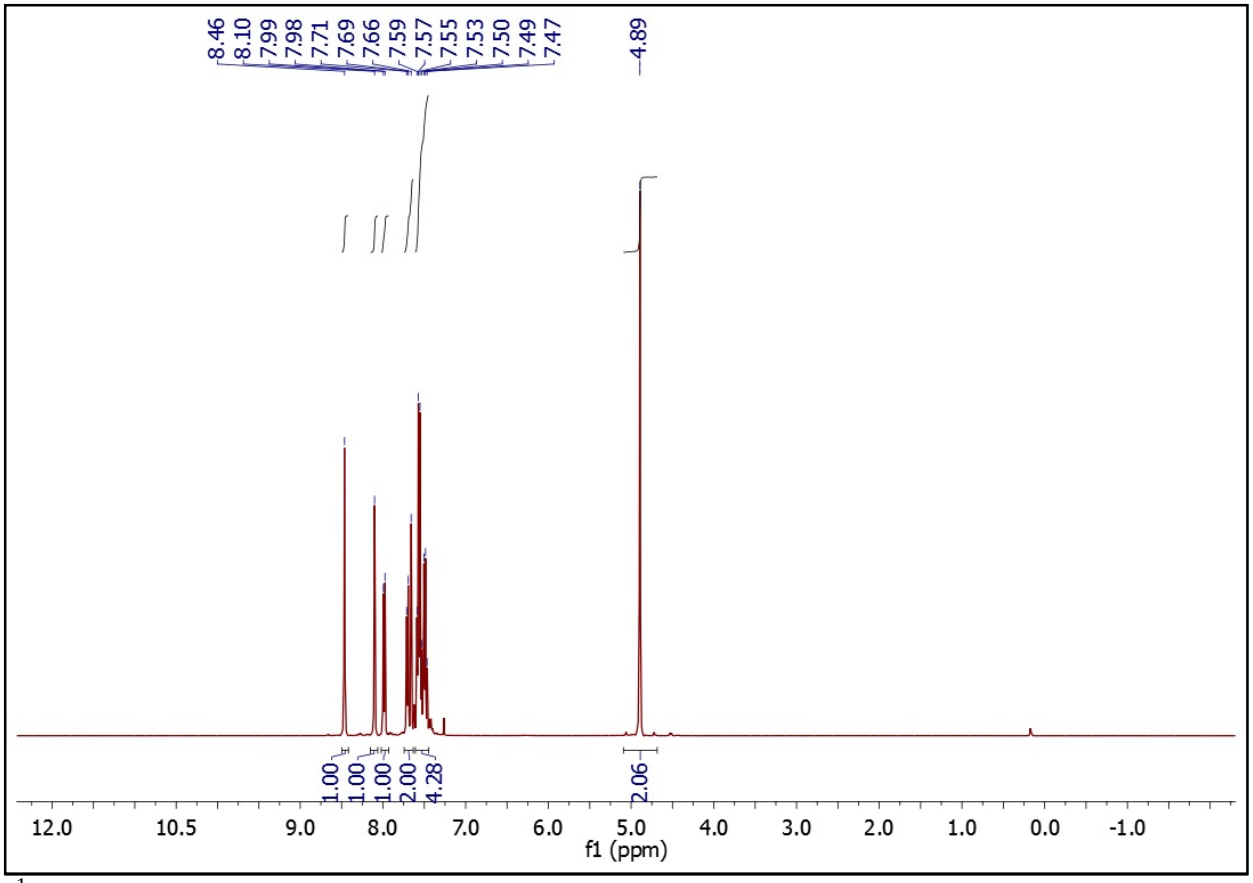
^{13}C NMR spectrum of *N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine **(entry 5f)**.



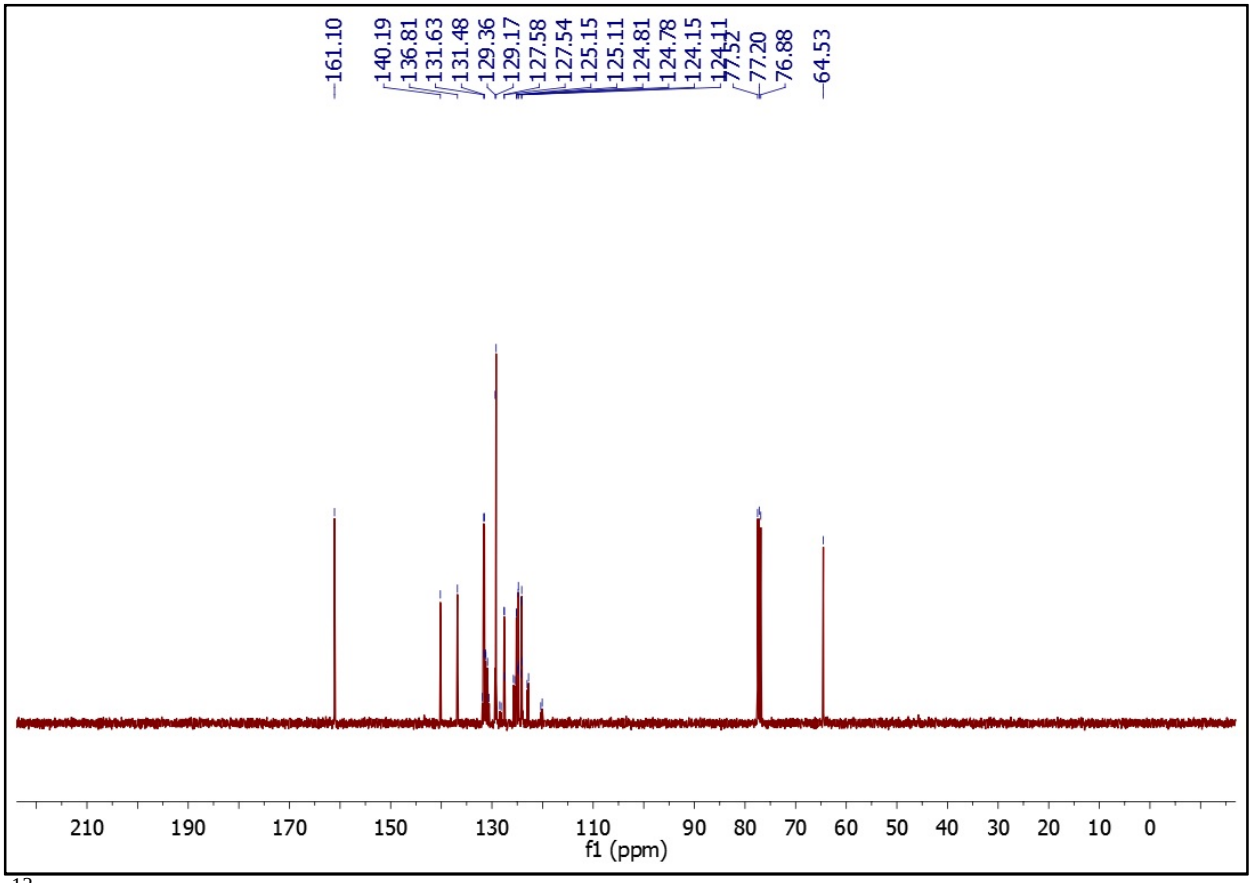
^{1}H NMR spectrum of *N*-(3-methoxybenzyl)-1-(3-methoxyphenyl)methanimine **(entry 5g)**.



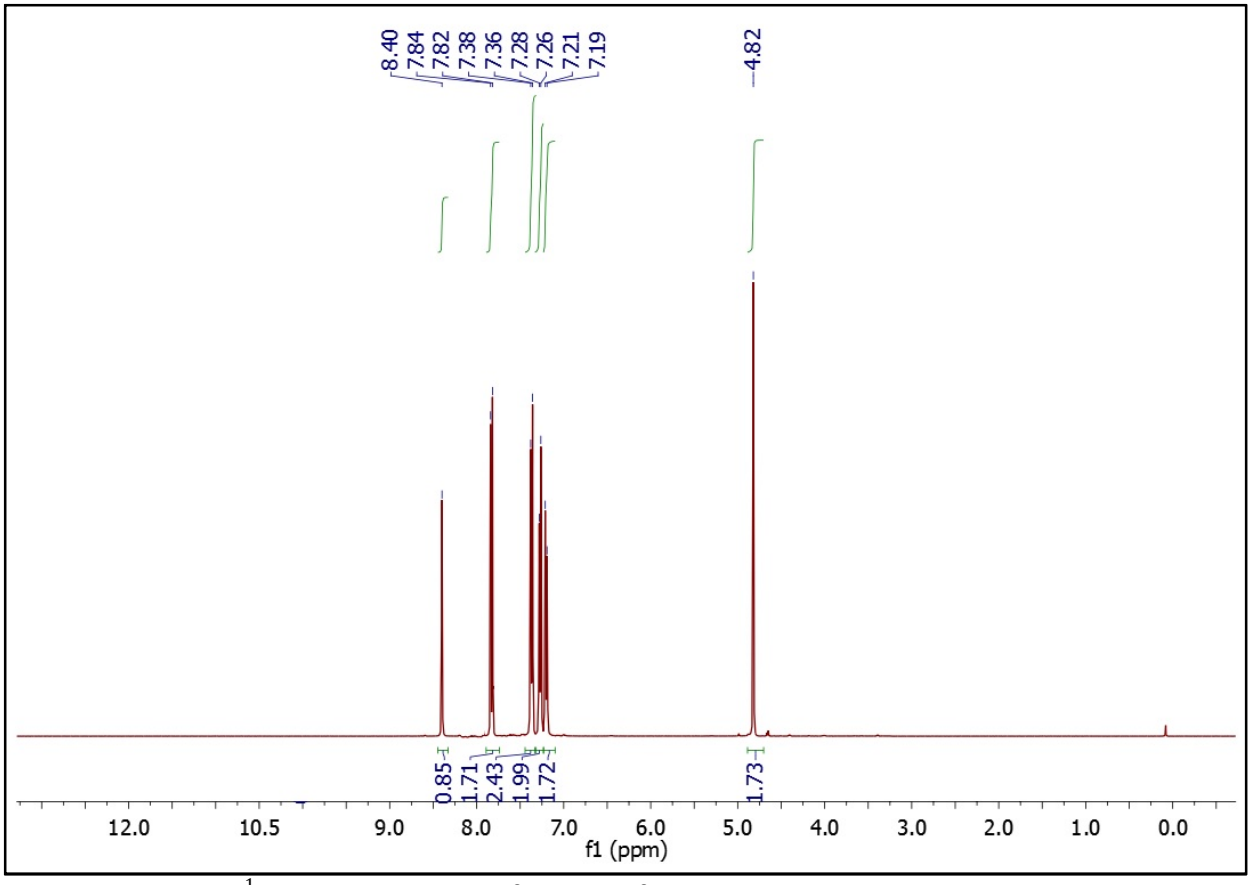
^{13}C NMR spectrum of *N*-(3-methoxybenzyl)-1-(3-methoxyphenyl)methanimine **(entry 5g)**.



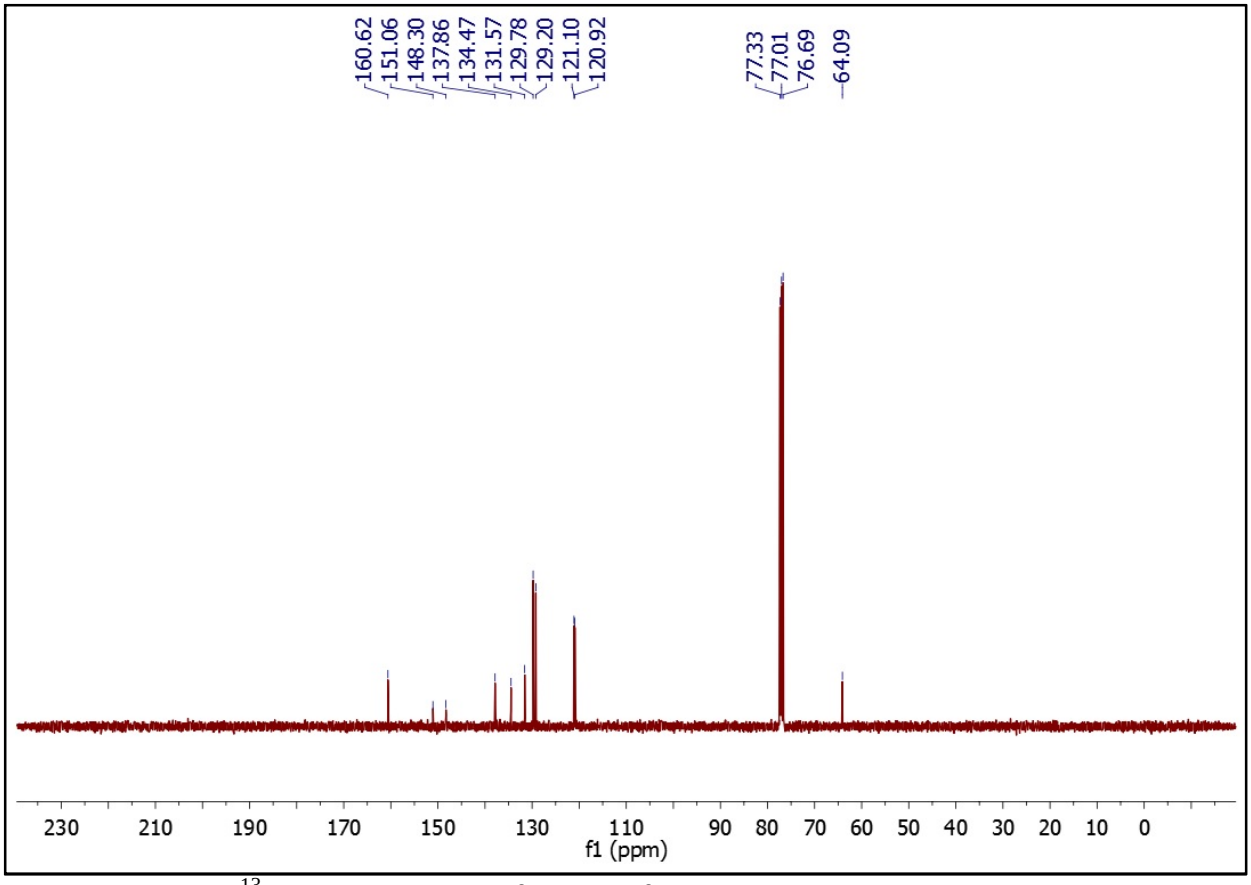
^{1}H NMR spectrum of *N*-(3-(trifluoromethyl)benzyl)-1-(3-(trifluoromethyl)phenyl)methanimine **(entry 5h)**.



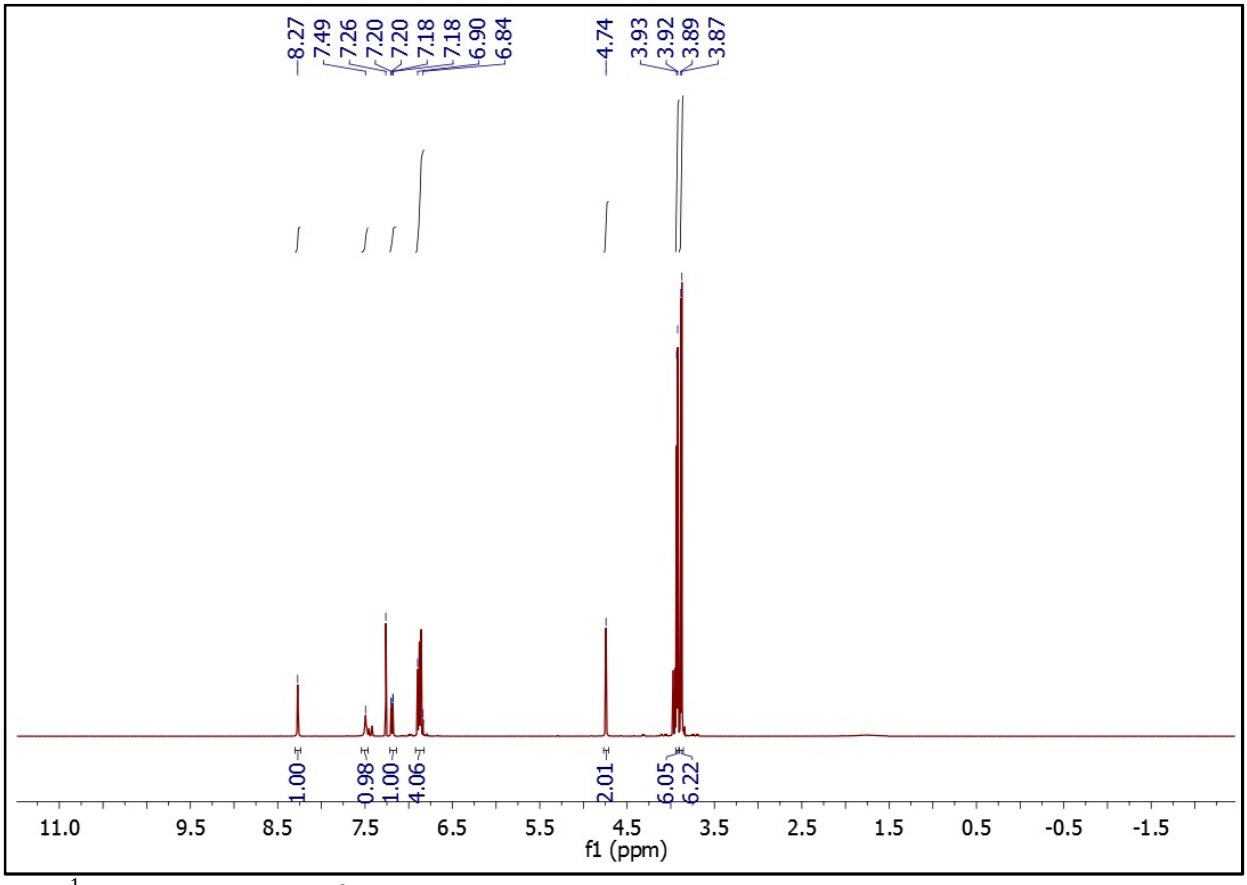
^{13}C NMR spectrum of *N*-(3-(trifluoromethyl)benzyl)-1-(3-(trifluoromethyl)phenyl)methanimine **(entry 5h)**.



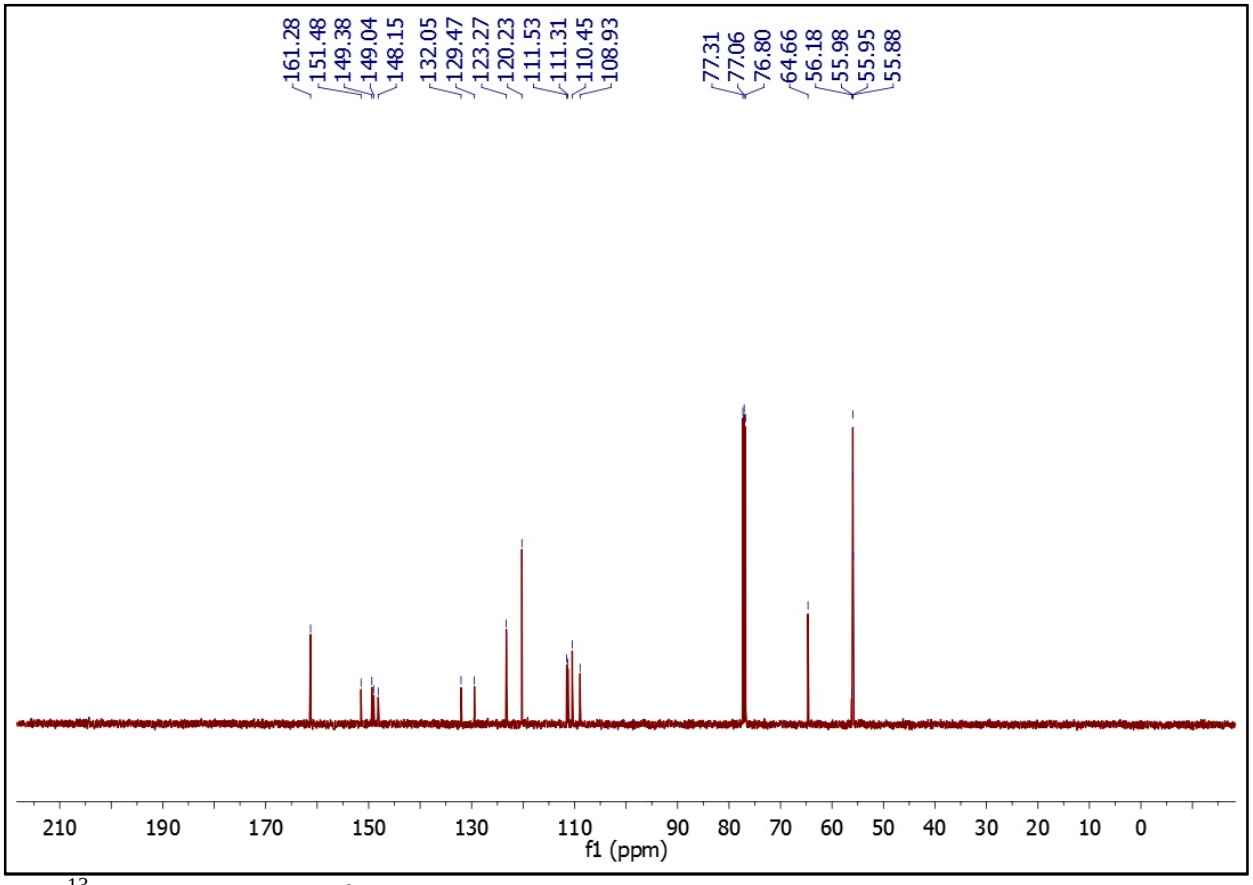
^{1}H NMR spectrum of *N*-(4-(trifluoromethoxy)benzyl)-1-(4-(trifluoromethoxy)phenyl)methanimine **(entry 5i)**.



^{13}C NMR spectrum of *N*-(4-(trifluoromethoxy)benzyl)-1-(4-(trifluoromethoxy)phenyl)methanimine (**entry 5i**).



^{1}H NMR spectrum of *N*-(3,4-dimethoxybenzyl)-1-(3,4-dimethoxyphenyl)methanimine (**entry 5m**).



^{13}C NMR spectrum of *N*-(3,4-dimethoxybenzyl)-1-(3,4-dimethoxyphenyl)methanimine (**entry 5m**).

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25 Preparation of D_2-Benzylamine: In a suspension of $LiAlD_4$ (0.208 g) in THF (3 mL) under N_2 atmosphere, a solution of benzamide (0.200 g) in THF (1 mL) was added drop wise at 0˚C temperature and the reaction mixture was refluxed for 2 h. Thereafter, the mixture was cooled to 0˚C temperature and 0.1 mL H_2O was added to it. Then 0.1 mL of 15% NaOH solution and 3ml another portion of H_2O were added to the same. After stirring the reaction mixture for 2 min at room temperature, it was filtered and the residue was washed with 10 ml of THF. The total organic mixture was dried over anhydrous Na_2SO_4 and concentrated in vacuum.