SUPPLEMENTARY MATERIALS

Synthesis of 2,3-dihydroperimidines in different conditions in the presence of nano-γ-Al_2O_3/BF_3 and nano-γ-$Al_2O_3/BF_3/Fe_3O_4$as catalysts

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Catalyst 1: nano-γ-Al_2O_3/BF_3

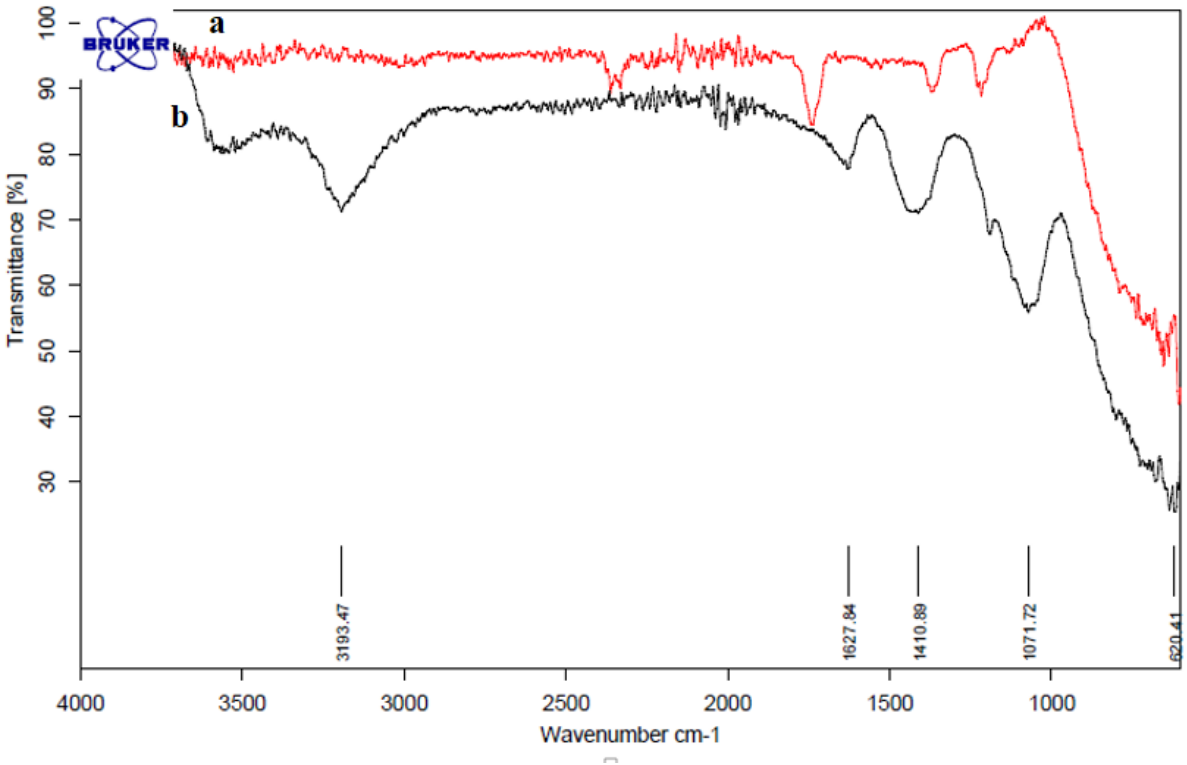


Fig 1. FT-IR spectra of: (a) nano-γ-Al_2O_3, (b) nano-γ-Al_2O_3 /BF_3

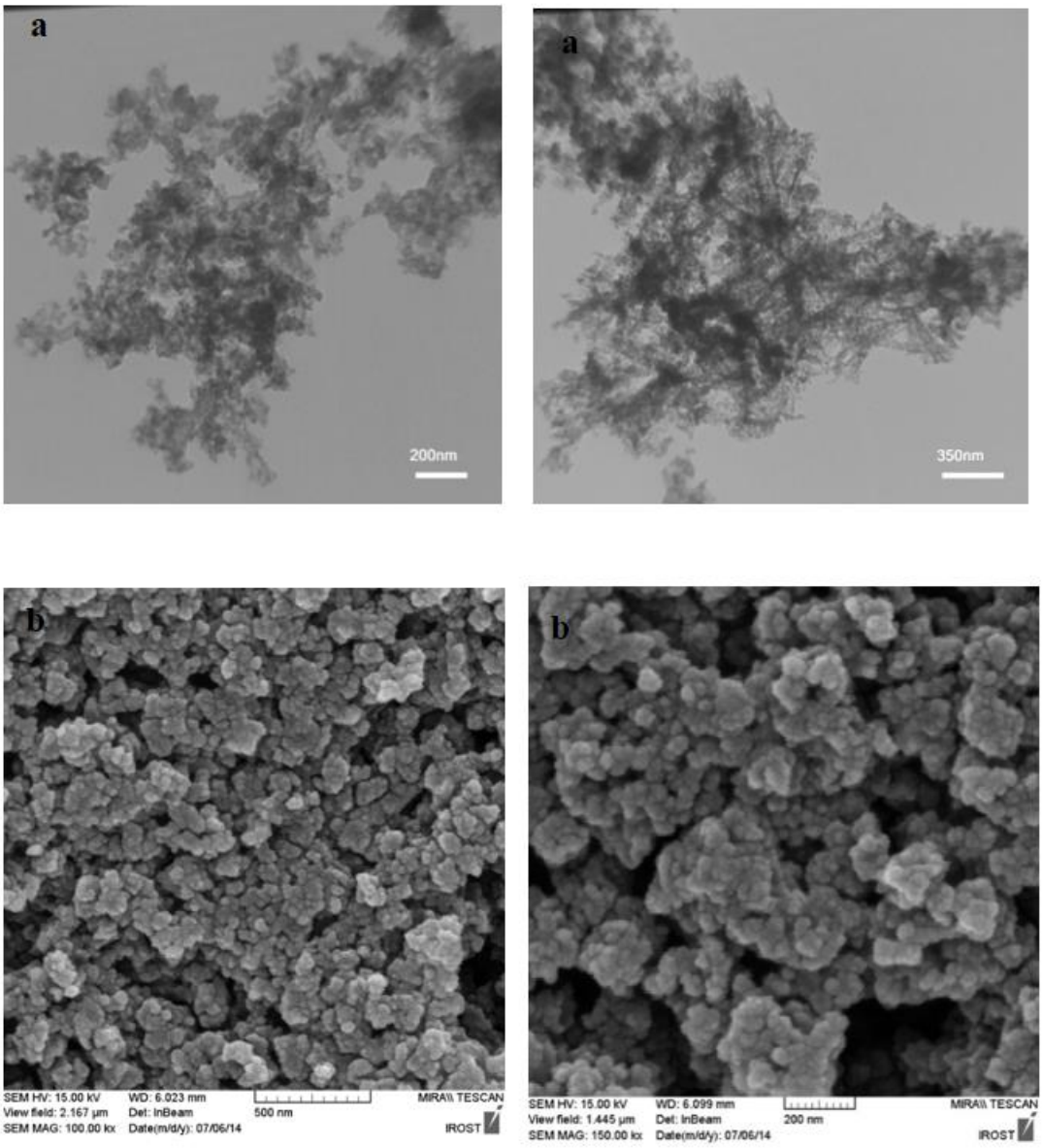


Fig2. TEM (a) and FESEM (b) images of nano-γ-Al_2O_3/BF_3

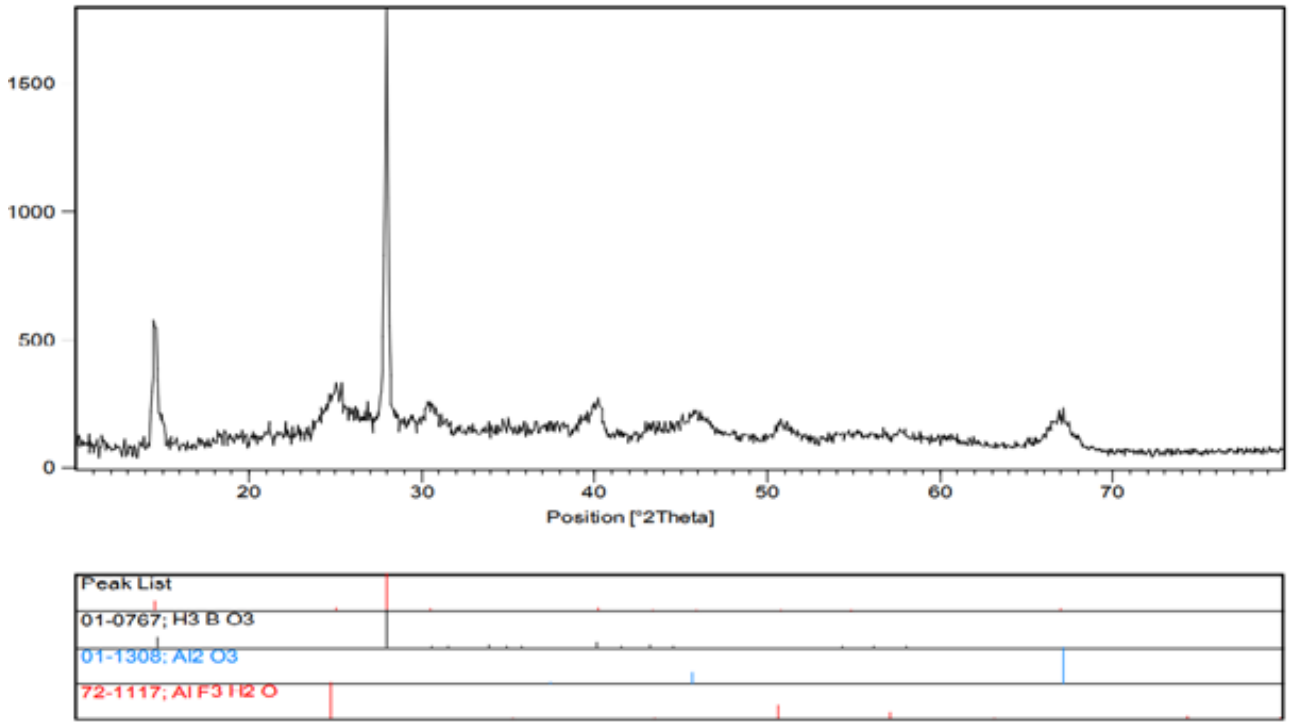


Fig 3. XRD patterns of nano-γ-Al_2O_3/BF3.

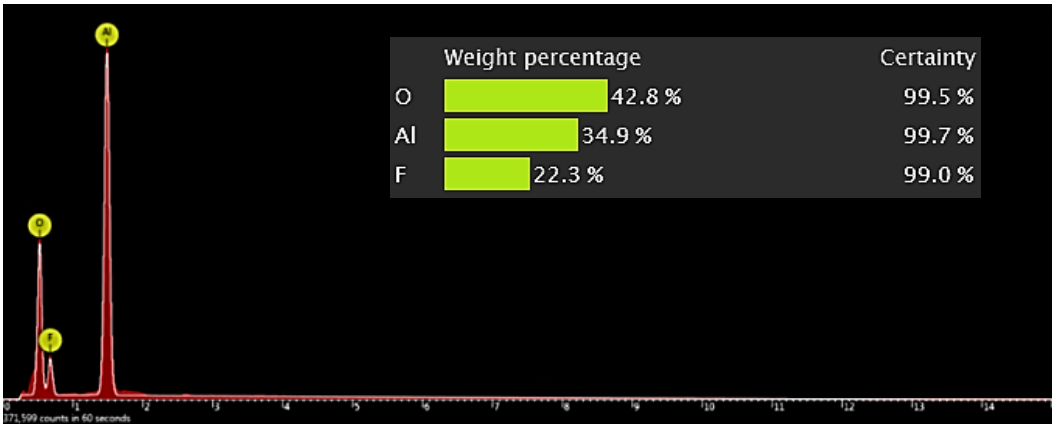


Fig 4. EDS analysis diagram of BF3/nano-γ-Al2O3

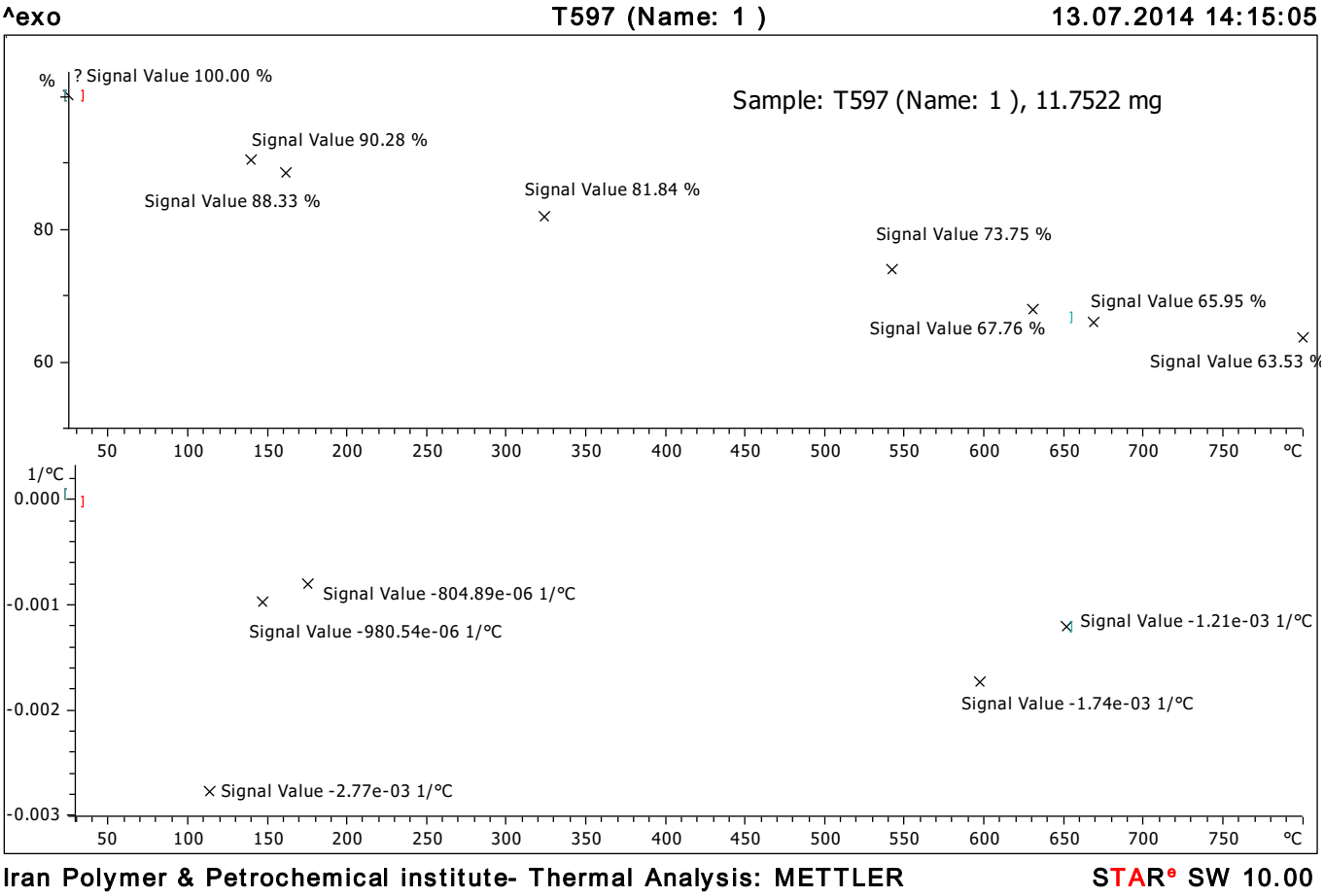


Fig 5. Thermal gravimetric analysis (TG-DTA) pattern of nano-γAl_2O_3/BF_3.

Catalyst 2: nano-γ-Al_2O_3/BF_3/Fe_3O_4

(این داده ها در دو سه مورد نیاز به چک کردن و تایید دارد)

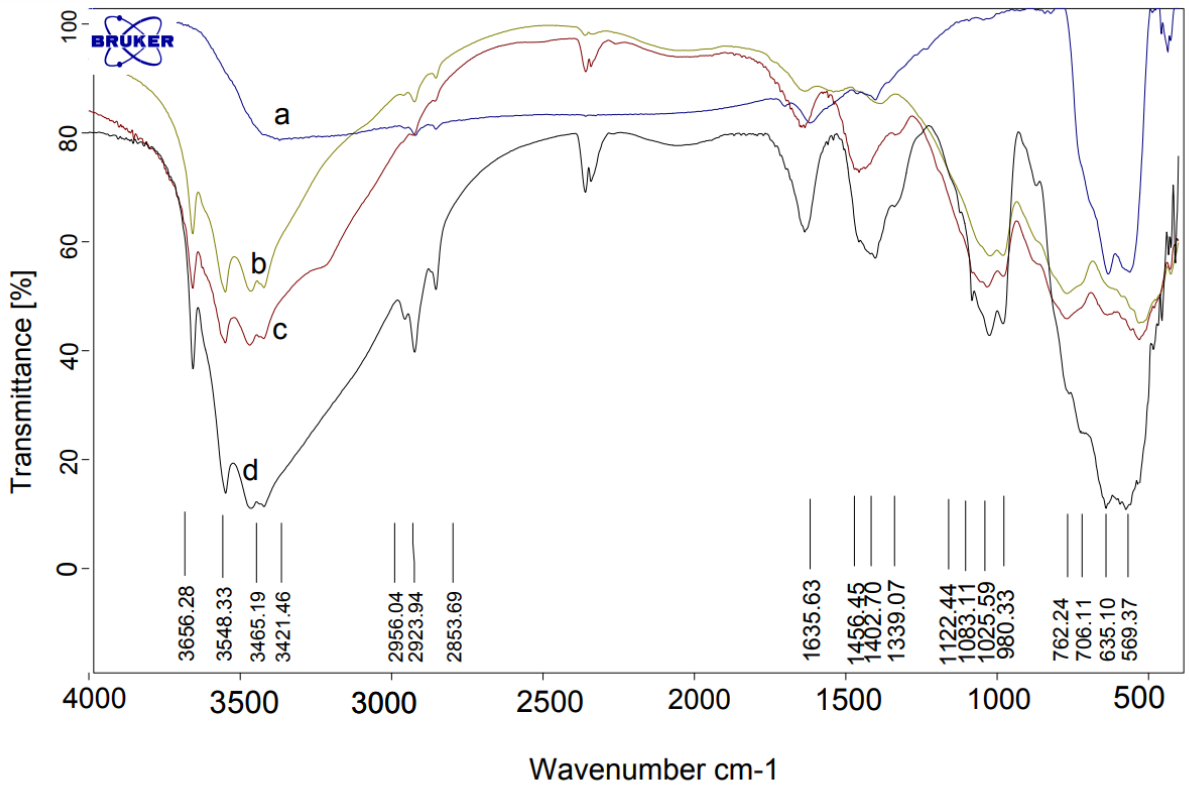


Fig ٦. FT-IR spectra of: (a) Fe_3O_4 b) nano-γ-Al_2O_3, (c) BF_3/nano-γ-Al_2O_3 (d) BF_3/nano-γ-Al_2O_3/Fe3O4

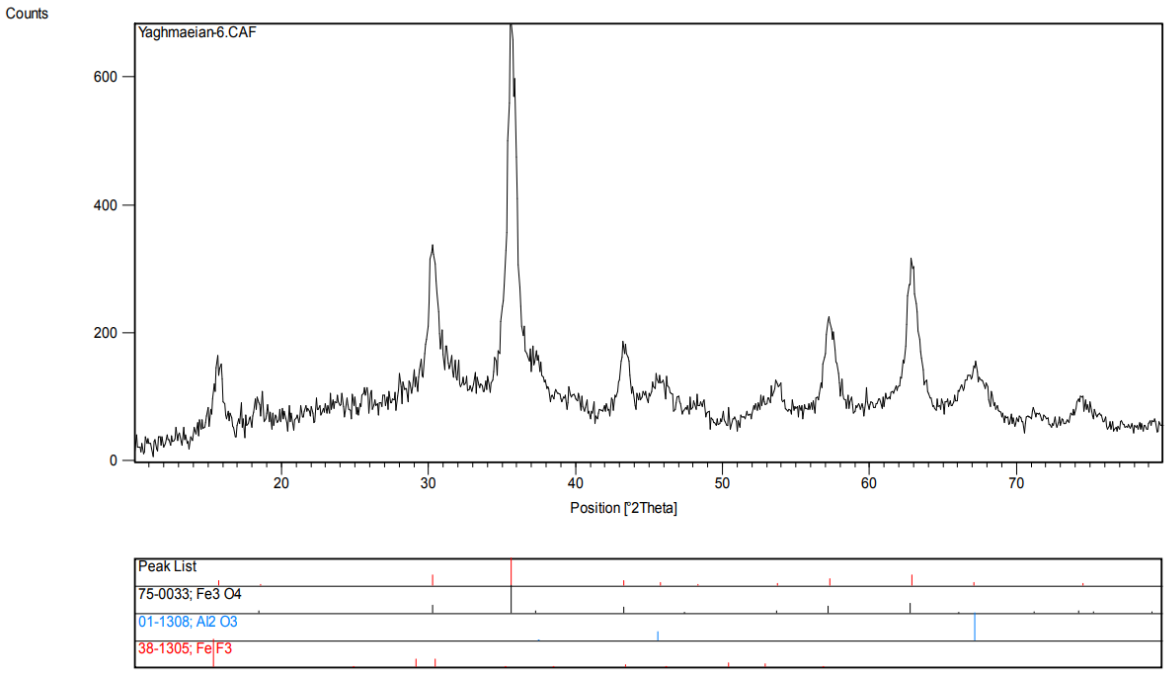


Fig ۷. X-ray diffraction (XRD) pattern of nano-γ-Al2O3/BF3/Fe3O4

روی طیف باید مشخص شود؟ یا به همین شکل کافی است؟

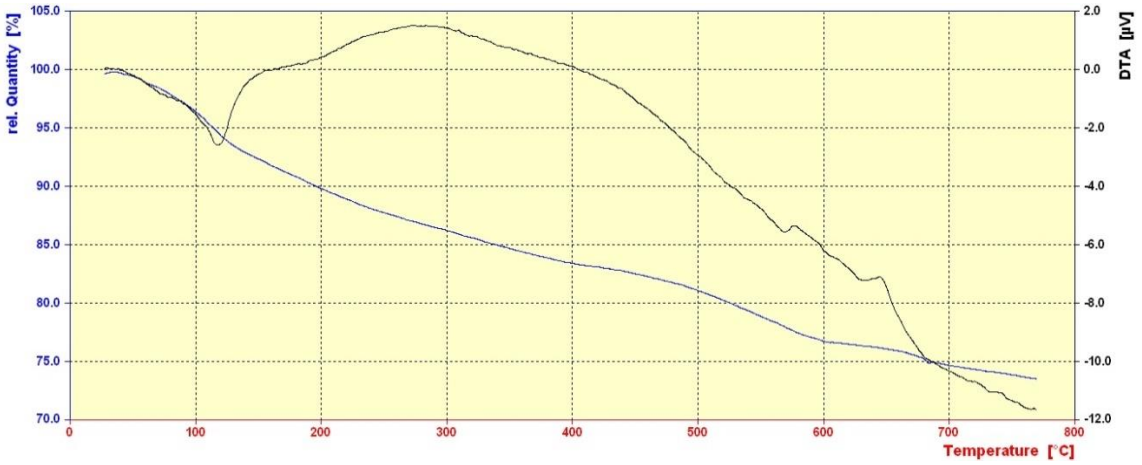


Fig ۸. Thermal gravimetric analysis (TG-DTA) pattern of nano-γ-Al_2O_3/BF_3/Fe3O4.

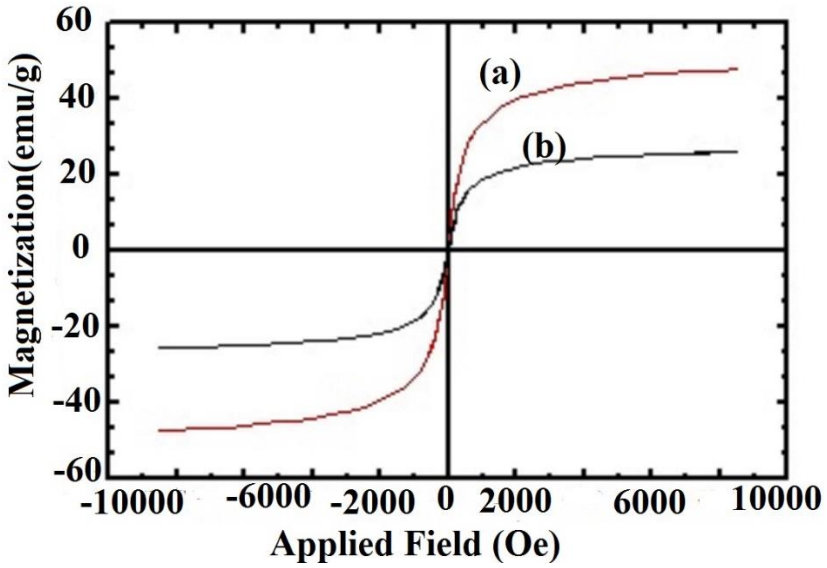


Fig ٩. VSM images of (a) Fe_3O_4 and (b) $Al_2O_3/BF_3/ Fe_3O_4$

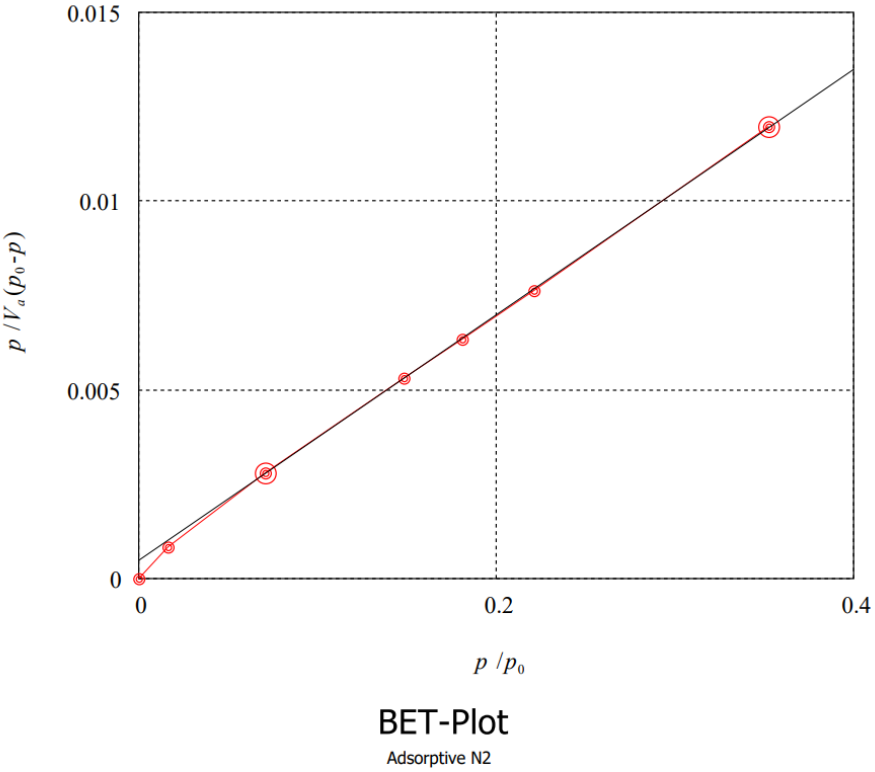


Fig ۱۰. Nitrogen adsorption of nano-γ-Al_2O_3/ BFn/Fe_3O_4

(ظاهرا یک نمودار دیگر هم باید داشته باشد؟)

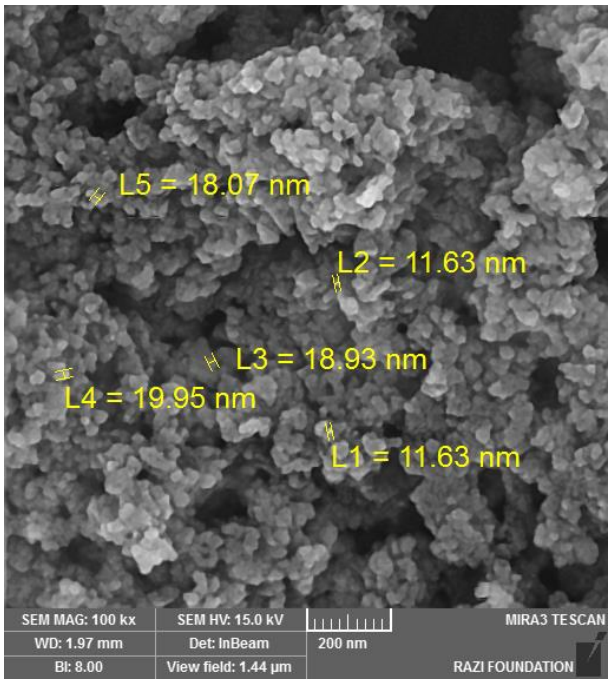


Figure ١١. FESEM image of nano-γ-$Al_2O_3/BF_3/Fe_3O_4$.

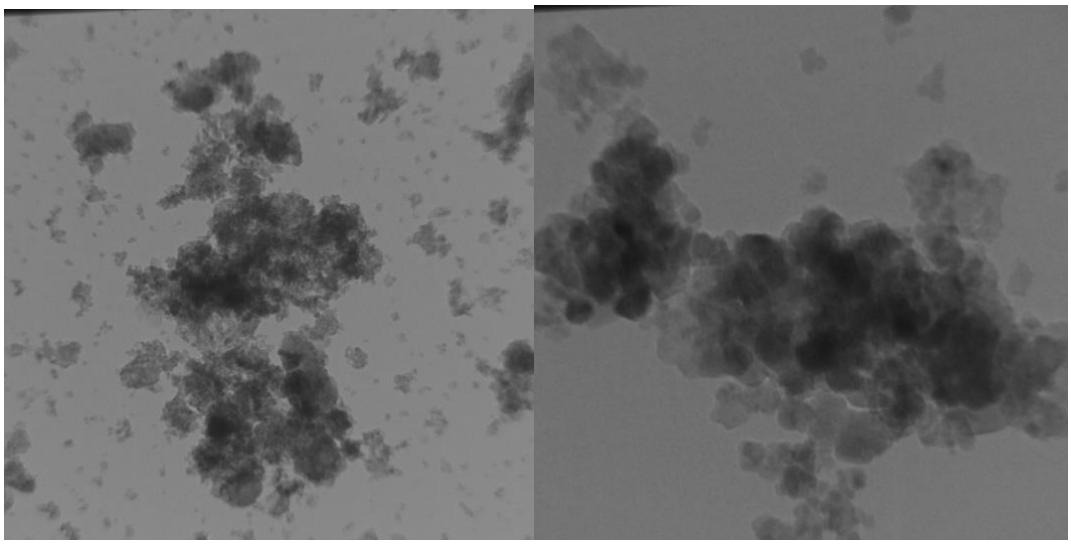


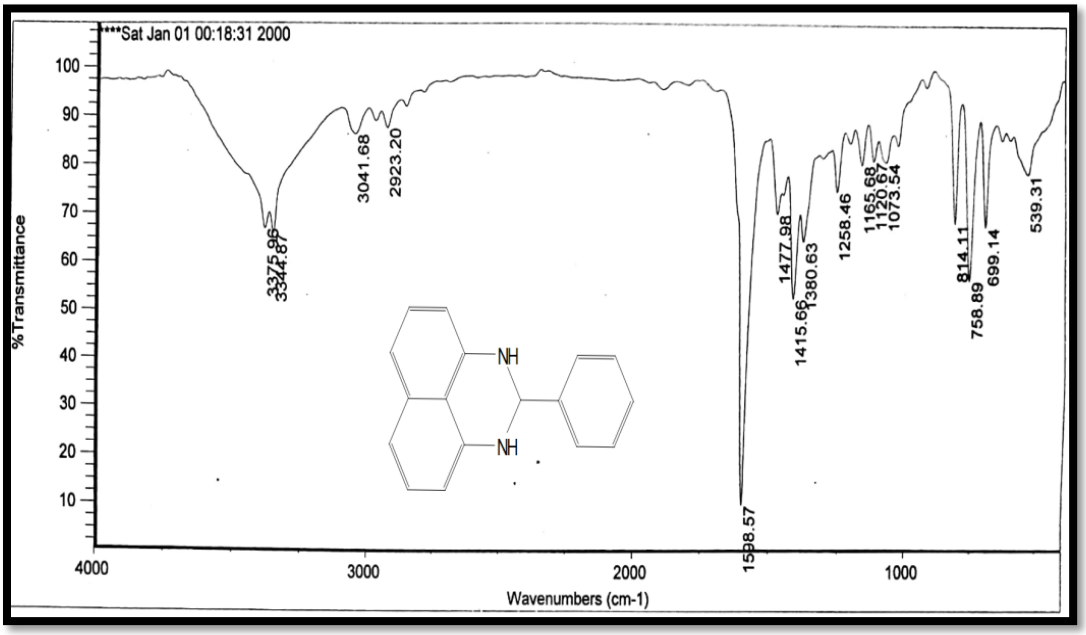
Figure ١٢. TEM images of nano-γ-$Al_2O_3/BF_3/Fe_3O_4$.

این عکسها درست است؟ با عکس موجود در مقاله های این کاتالیست متفاوت است

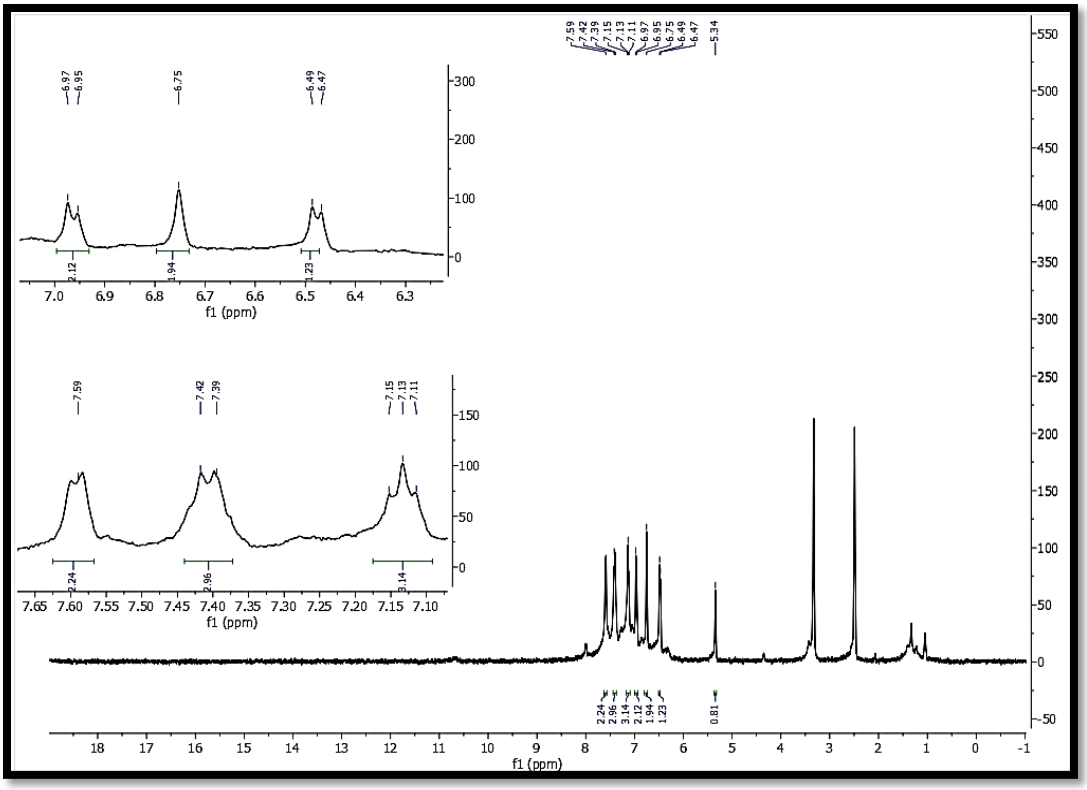
Products: 2,3-dihydroperimidine derivatives

Physical and spectral data

2-(phenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 1, 3a). Cream solid, M. F= $C_{17}H_{14}N_2$, M.W= 246.19, M.P $_{obs.}$ (°C)= 100-103, M.P $_{rep.}$ (°C) = 102-103, **FT-IR [ῡ (cm^{-1}) (KBr)]:** 3344-3375 (NH), 3041 (=C-H), 2923 (C-H aliphatic), 1598 (C=C aromatic).**^{1}H NMR (DMSO-d$_6$, 400 MHz)** δ (ppm): 5.31(1H, s, CH), 6.46 (1H, d, *J*=8 Hz, CH), 6.75 (2H, s, CH), 6.96 (2H, d, *J*=8 Hz, CH), 7.12 (3H, t, *J*= 8 Hz, CH), 7.40 (3H, d, *J=12* Hz, CH), 7.60 (2H, s, CH).

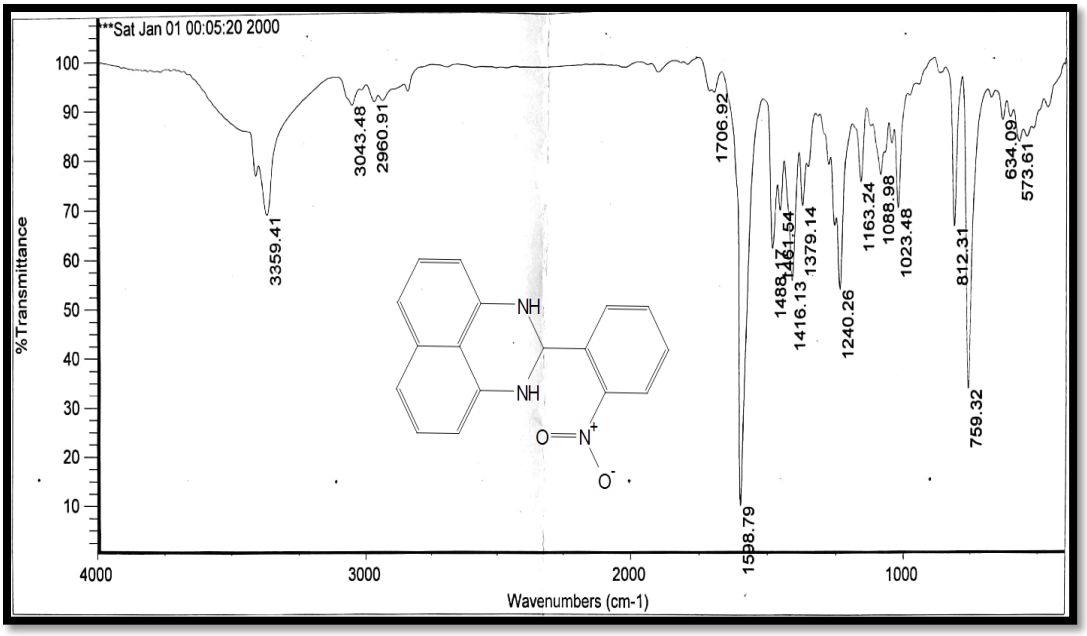


FT–IR spectrum of compound 3a

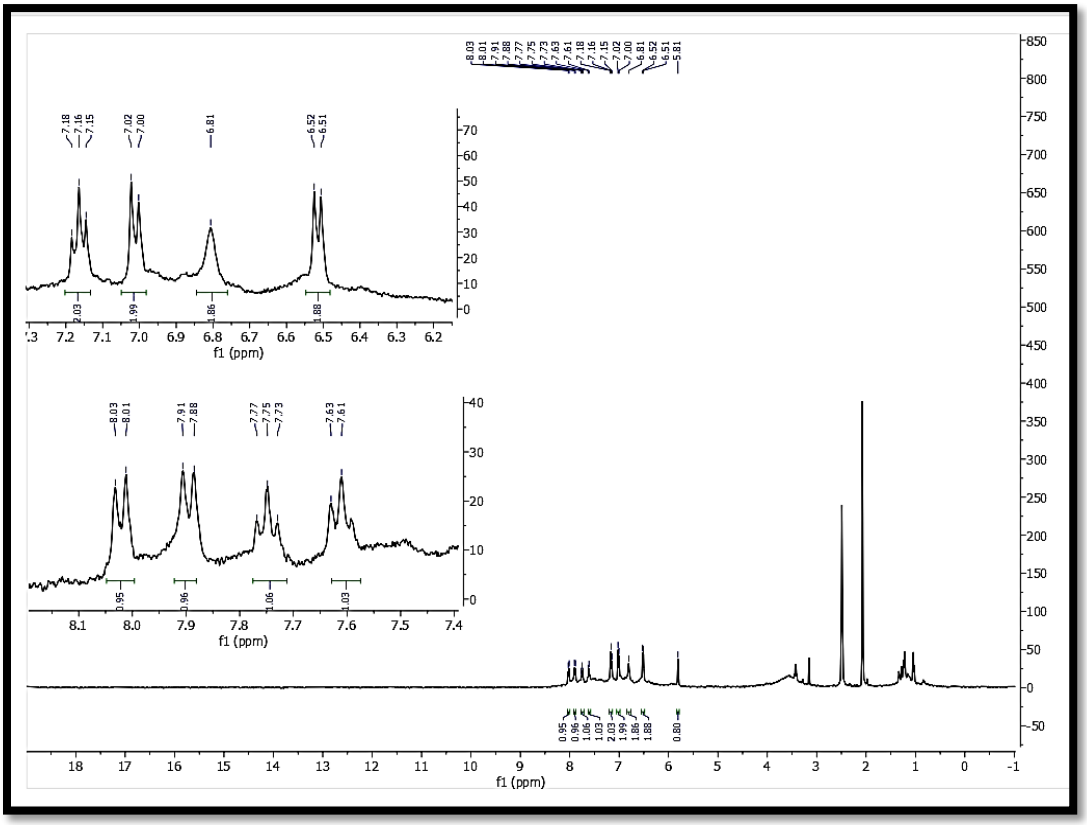


^{1}H NMR spectrum of compound 3a

2-(2-Nitrophenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 2, 3b). Orange solid, M. F= $C_{17}H_{13}N_3O_2$, M. W= 291.23, M.P $_{obs.}$ (°C) =190-193, M.P $_{rep.}$ (°C) = 192-194. **FT-IR [ῡ (cm^{-1}) (KBr)]:** 3359 (NH), 3043 (=C-H), 2960 (C-H aliphatic), 1898 (C=C aromatic), 1240 (N=O), 1163 (C-N).**^{1}H NMR (DMSO-d$_6$, 400 MHz)** δ (ppm): 5.79 (1H, s, CH), 6.51 (2H, d, *J* =4 Hz, CH), 6.80 (1H, s, NH), 7.01 (2H, d, *J* =*8* Hz, CH), 7.16 (2H, t, *J* =4 Hz, CH), 7.61 (1H, d, *J*=8 Hz, CH), 7.75 (1H, t, *J* = 8 Hz, CH), 7.90 (1H, d, *J* = *12* Hz, CH), 8.02 (1H, d, *J*=8 Hz).

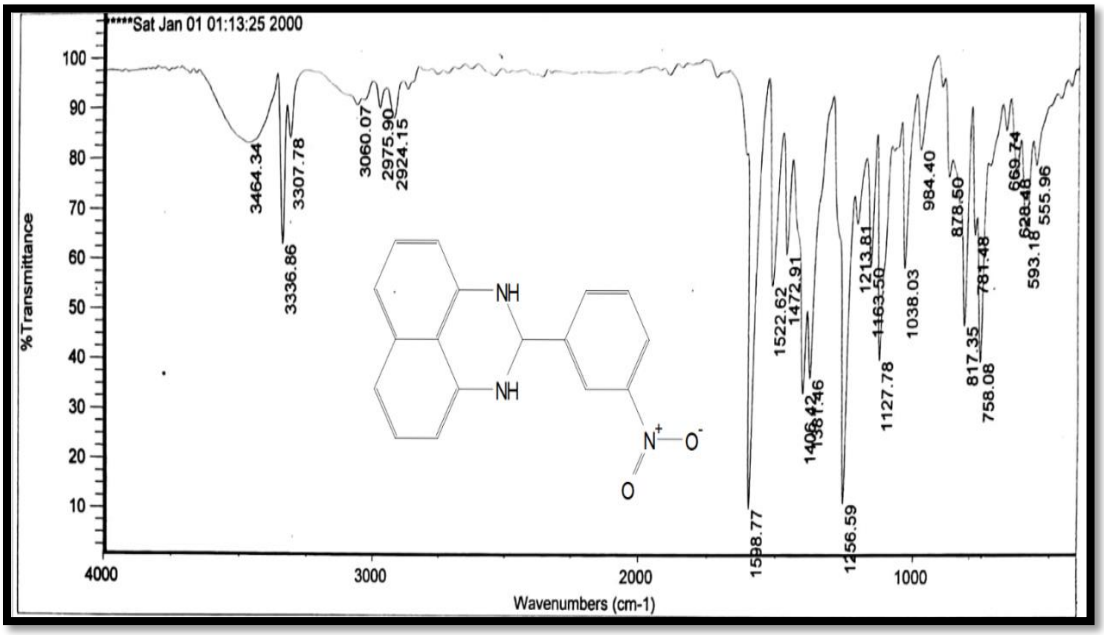


FT–IR spectrum of compound 3b

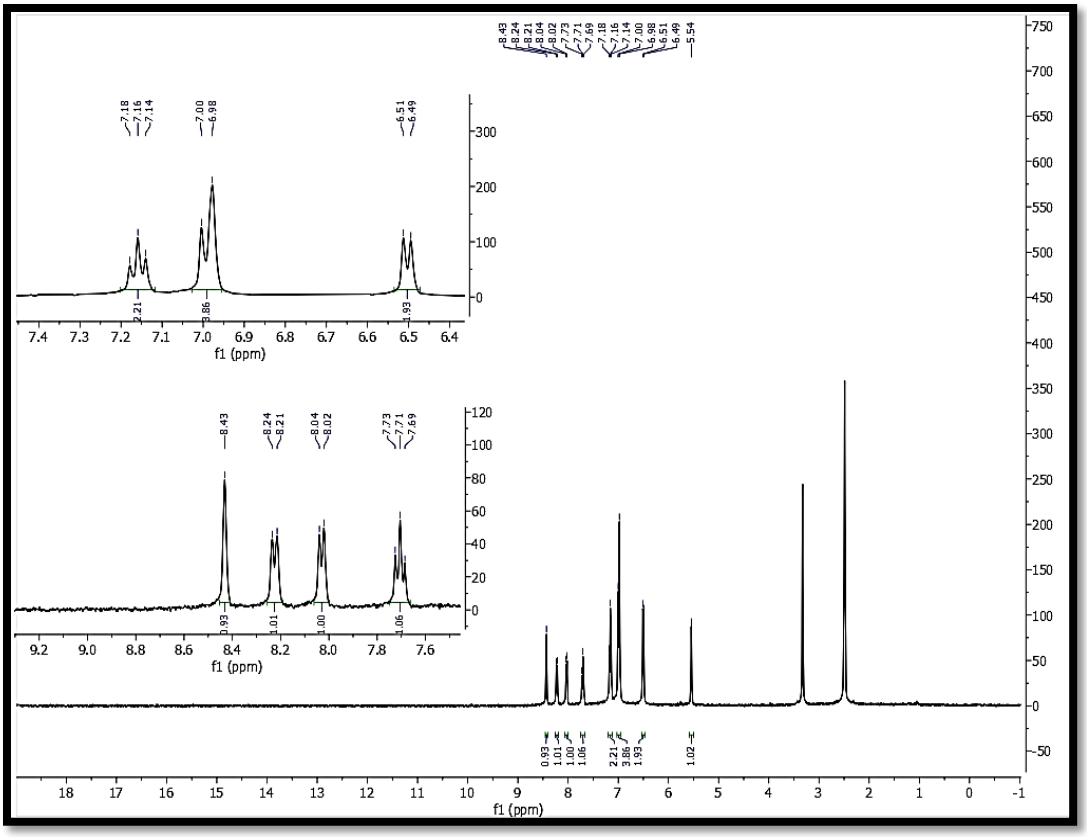


^{1}H NMR spectrum of compound 3b

2-(3-Nitrophenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 3, 3c): Orange solid, M. F= $C_{17}H_{13}N_3O_2$, M. W= 291.23, M.P $_{obs.}$ (°C)= 170-173, M.P $_{rep.}$ (°C) = 173. **FT-IR [$\bar{\upsilon}$ (cm^{-1}) (KBr)]:** 3343-3422 (NH), 3226 (=C-H), 2924 (C-H aliphatic), 1526-1601 (C=C aromatic), 1261 (C-N), 1349 (N=O). **^{1}H NMR (DMSO-d_6, 400 MHz)** δ(ppm): 5.5 (1H, s, CH), 6.50 (2H, d, *J* =8 Hz, CH), 7.00 (4H, d, *J*=8 Hz, CH, NH), 7.15 (2H, t, *J*=8 Hz, CH), 7.70 (1H, t, *J*=8 Hz, CH), 8.02 (1H, d, *J*=8 Hz, CH), 8.22 (1H, d, *J*=12 Hz, CH), 8.42 (1H, s, CH).

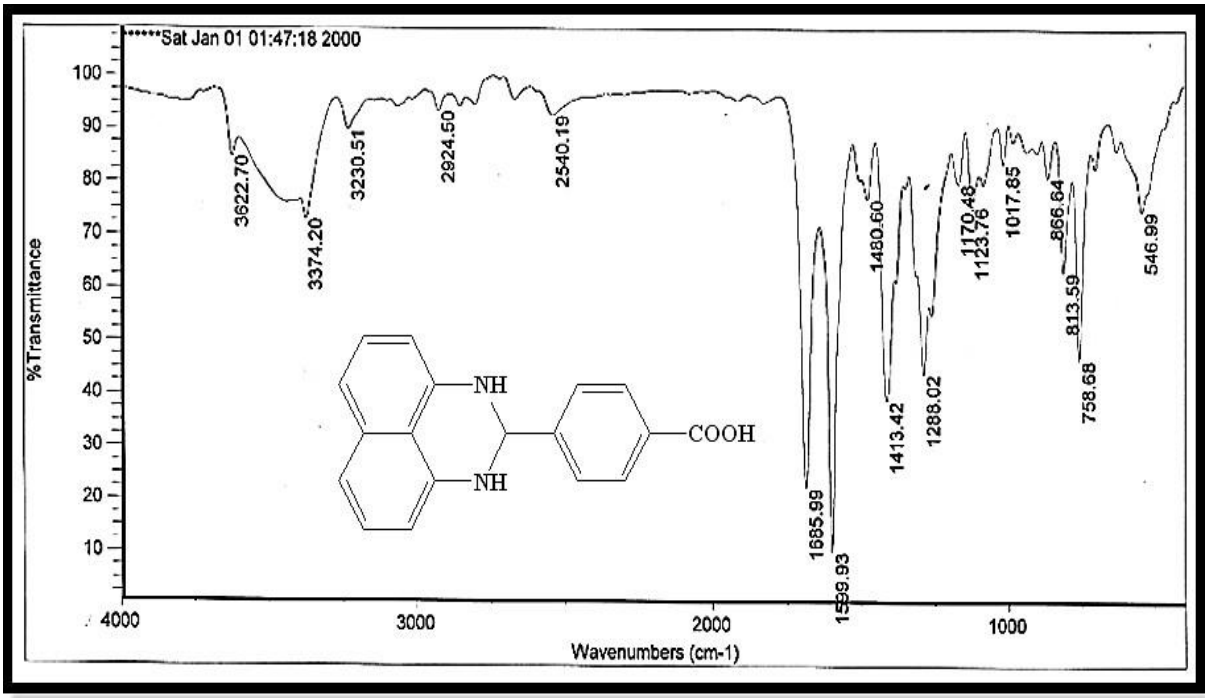


FT–IR spectrum of compound 3c

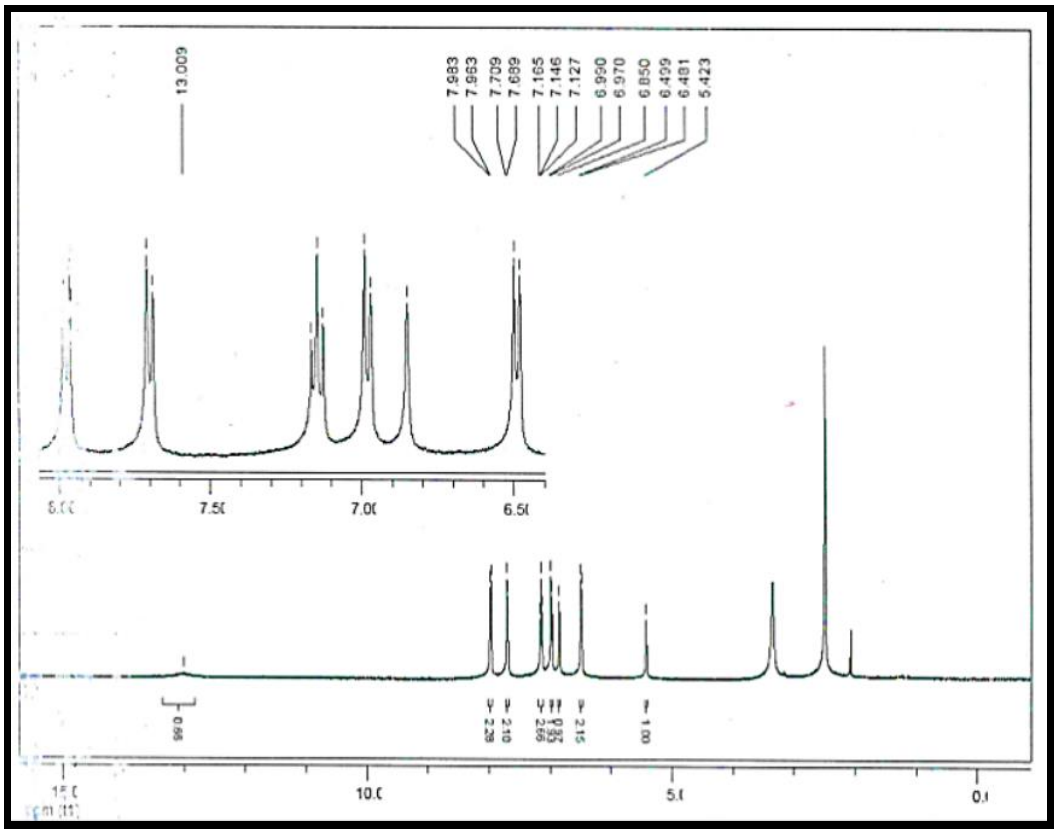


^{1}H NMR spectrum of compound 3c

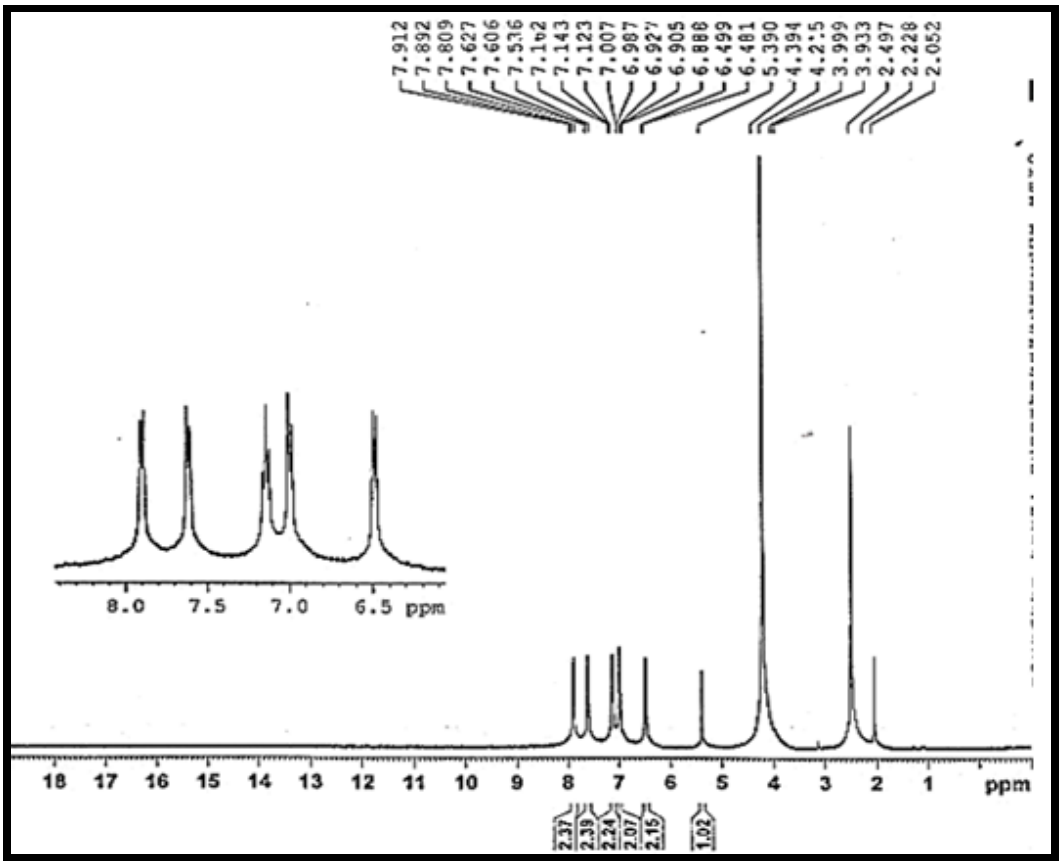
2-(4-Carboxyphenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 4, 3d). Pink Solid, M. F= $C_{18}H_{14}N_2O_2$, M. W= 290.16, M.P $_{obs.}$ (℃) = 247-249, M.P $_{rep.}$ (℃) = 248. **FT-IR [ῡ (cm-1) (KBr)]:** 1288 (C-N), 1599- 1480 (C=C aromatic), 1685 (C=O), 2924 (C-H aliphatic), 3230 (=C-H), 3374 (NH), 3622 (OH). **^{1}H NMR (DMSO-d6, 400 MHz)** δ (ppm): 5.42 (1H, s, CH), 6.49 (2H, d, *J=8* Hz, CH), 6.85 (2H, s, NH exchange with D2O), 7.00 (2H, d, *J* =8.0 Hz, CH), 7.14 (2H, t, *J* =8 Hz, CH), 7.70 (2H, d, *J* = 4 Hz, CH), 7.97 (2H, d, *J* = 8 Hz, CH), 13.01 (1H, s).**^{13}C NMR (DMSO-d6 75 MHz)** δ (ppm): 66.24, 104.93, 112.90, 115.90, 127.39, 128.54, 129.76, 131.30, 134.82, 143.14, 147.23, and 167.63.



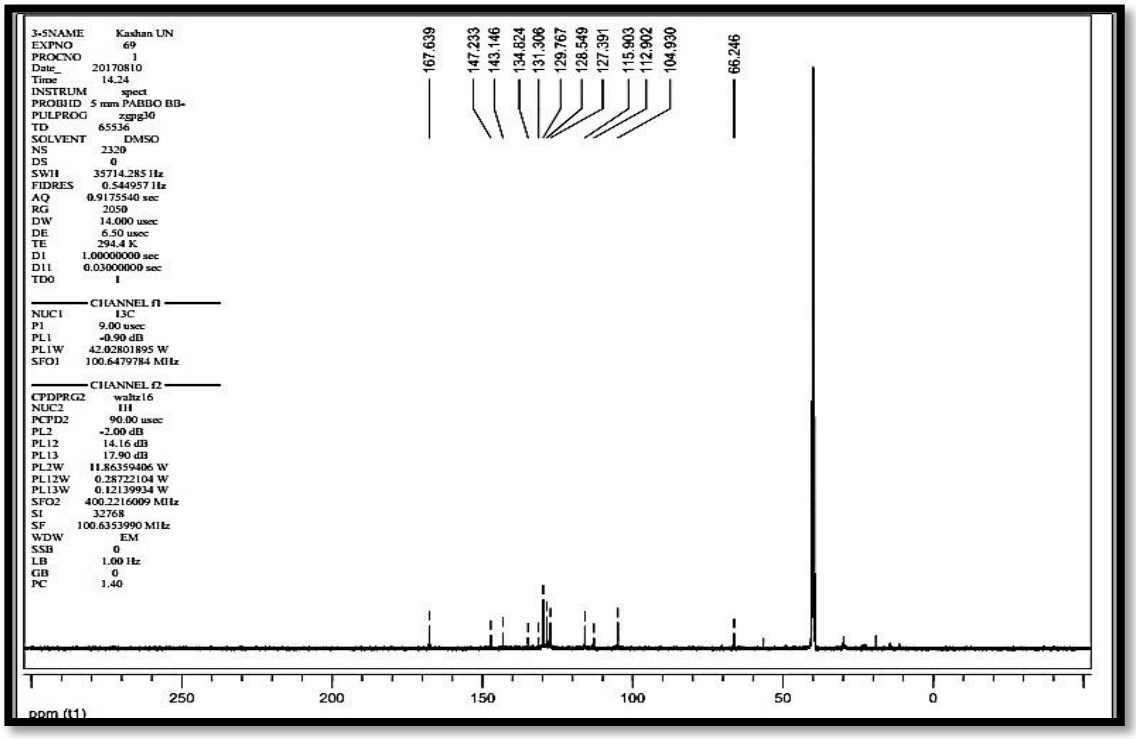
FT–IR spectrum of compound 3d



^{1}H NMR spectrum of compound 3d

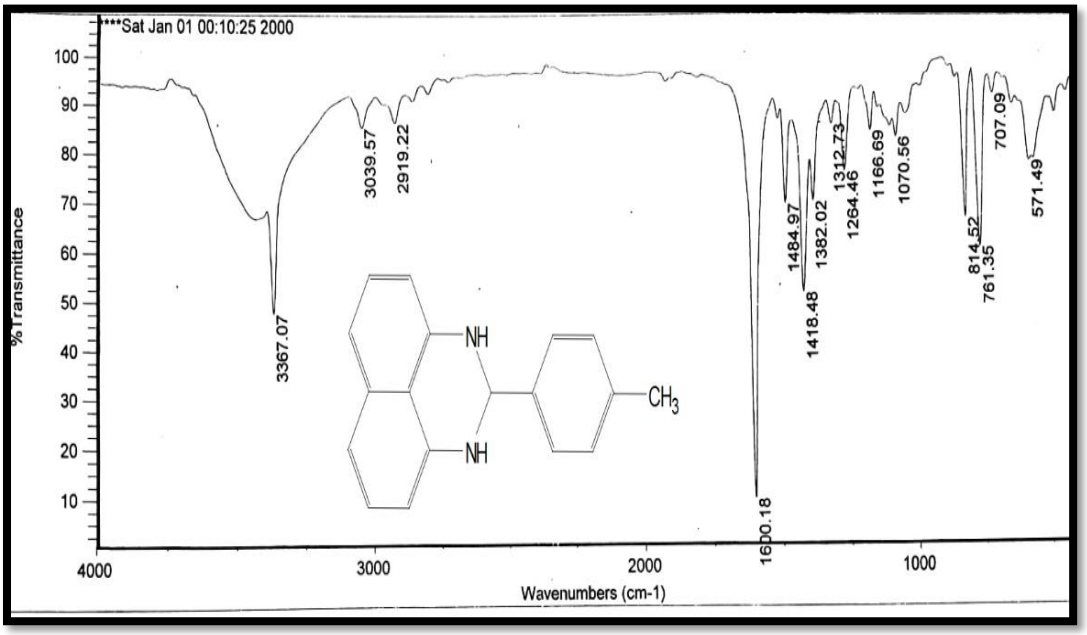


^{1}H NMR spectrum of compound 3d in the presence of D_2O

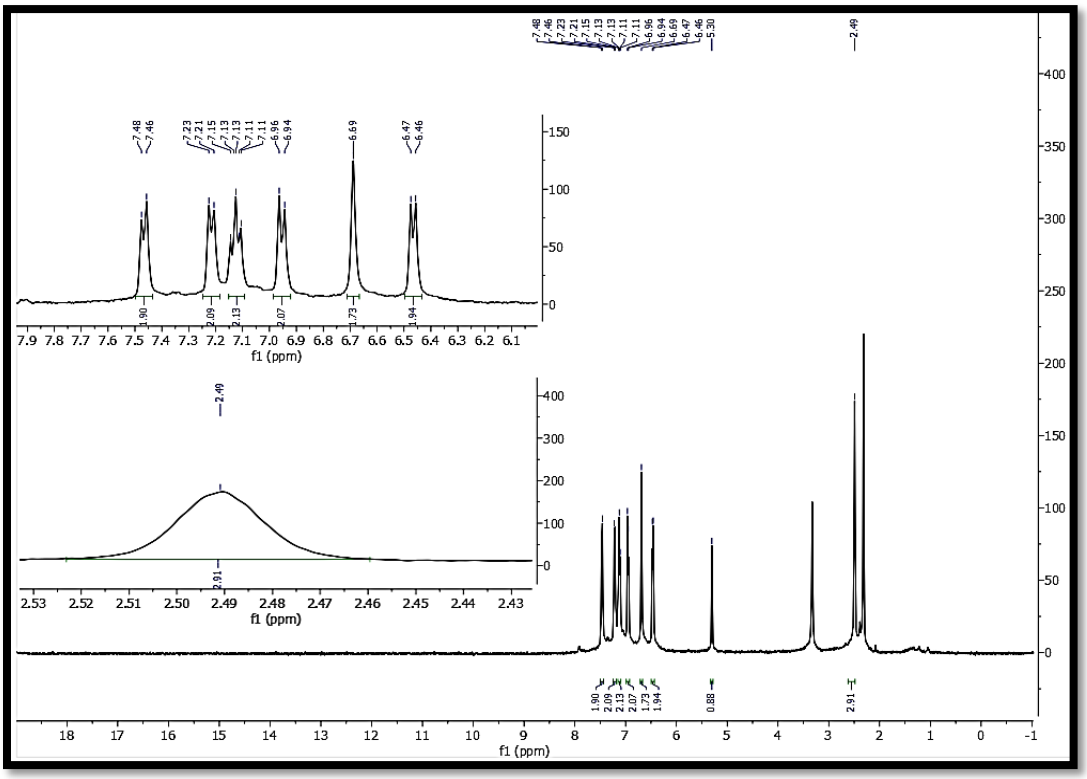


^{13}C- NMR spectrum of compound 3d

2-(4-Methylphenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 5, 3e)*:* Yellow solid, M. F= $C_{18}H_{16}N_2$, M.W=260.2, M.P $_{obs.}$ (°C)= 158-161, M.P $_{rep.}$ (°C) = 160-161. **FT-IR [ῡ (cm^{-1}) (KBr)]**: 3367 (NH), 3039 (=C-H), 2919 (C-H aliphatic), 1484-1600 (C=C aromatic), 761-814 (mono substoop). **^{1}H NMR (DMSO-d$_6$, 400 MHz)** δ(ppm): 2.50 (3H, s, CH_3), 5.3 (1H, s, CH), 6.47 (2H, d, *J*=4 Hz, CH), 6.7 (2H, s, NH), 6.96 (2H, d, CH, *J*= 8 Hz), 7.12 (2H, t, *J*= 8 Hz, CH), 7.22 (2H, d, *J*=8 Hz, CH), 7.46 (2H, d, *J*=8 Hz, CH).

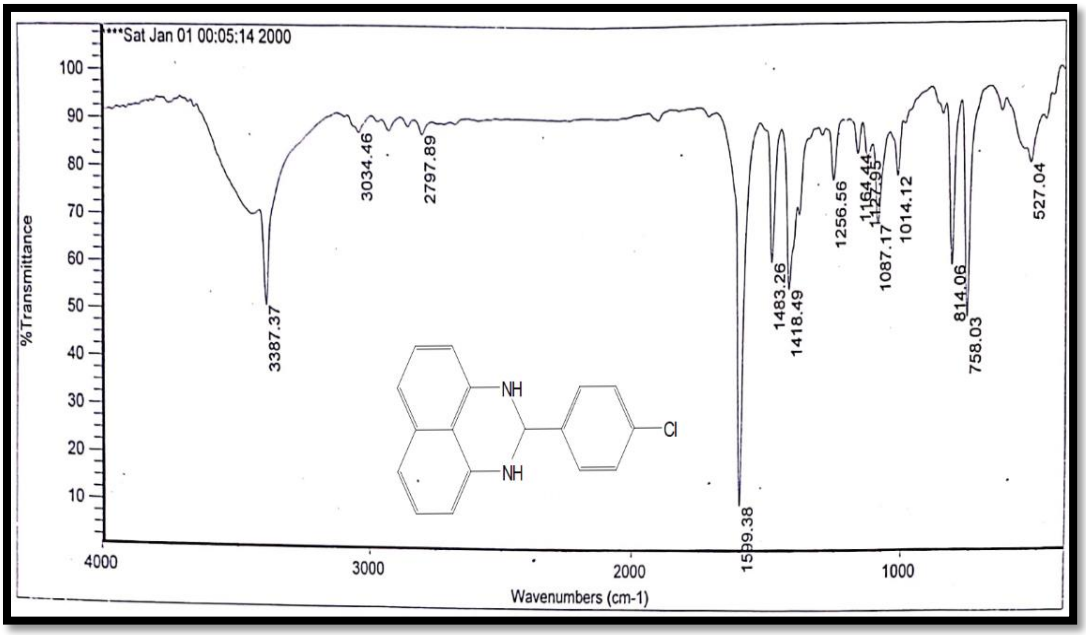


FT–IR spectrum of compound 3e

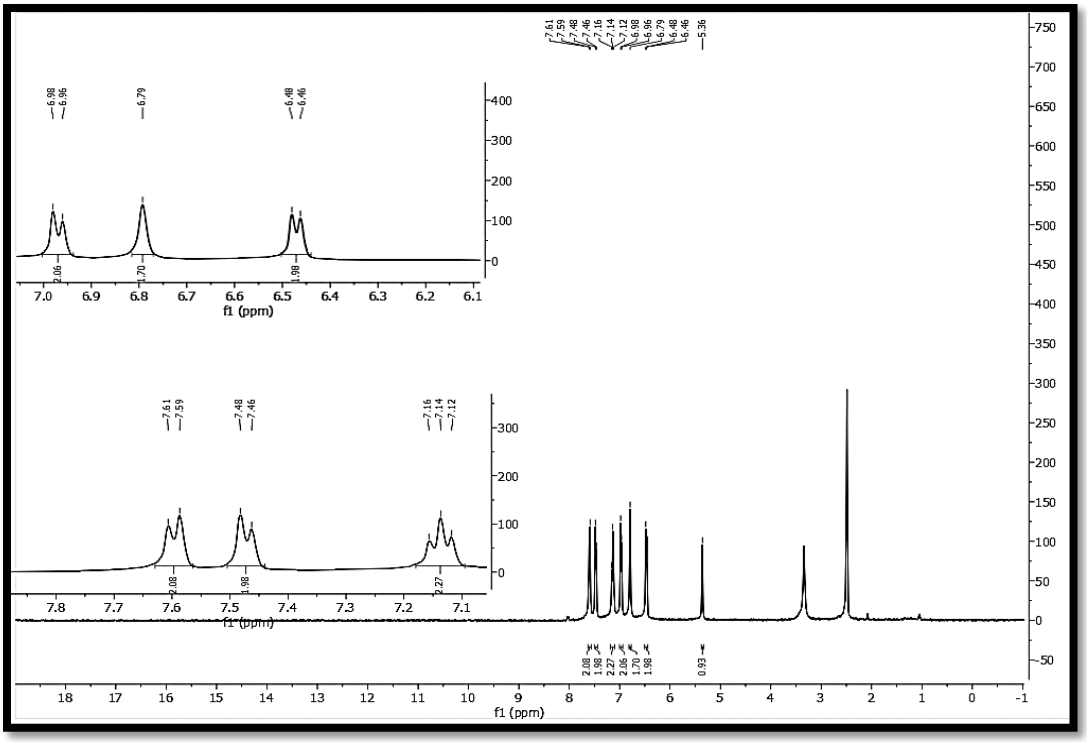


^{1}H NMR spectrum of compound 3e

2-(4-Cholorophenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 6, 3f)*:* Gray Solid, M. F= $C_{17}H_{13}N_2Cl$, M. W= 280.64, M.P $_{obs.}$ (°C)= 171-173, M.P $_{rep.}$ (°C) = 172-174. **FT-IR [ῡ (cm^{-1}) (KBr)]**: 3387 (NH), 3034 (=C-H), 2797 (C-H aliphatic), 1483-1599 (C=C aromatic), 1256 (C-N), 1087.17 (C-Cl), 758-814 (mono substoop). **^{1}H NMR (DMSO-d$_6$, 400 MHz)** δ (ppm): 5.36 (1H, s, CH), 6.46 (2H, d, *J*=8 Hz, CH), 6.8 (2H, s, NH), 6.97 (2H, d, *J*=8 Hz, CH), 7.14 (2H, t, *J*=8 Hz, CH), 7.46 (2H, d, *J*=8 Hz, CH), 7.60 (2H, d, *J*=8 Hz, CH).

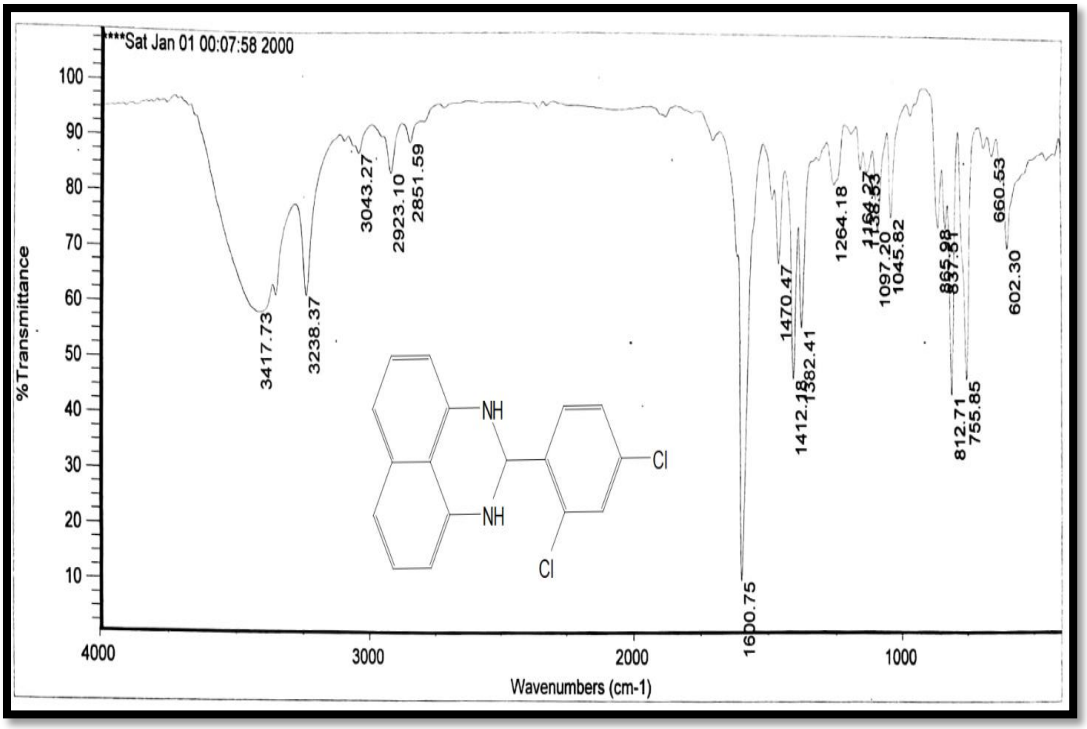


FT–IR spectrum of compound 3f

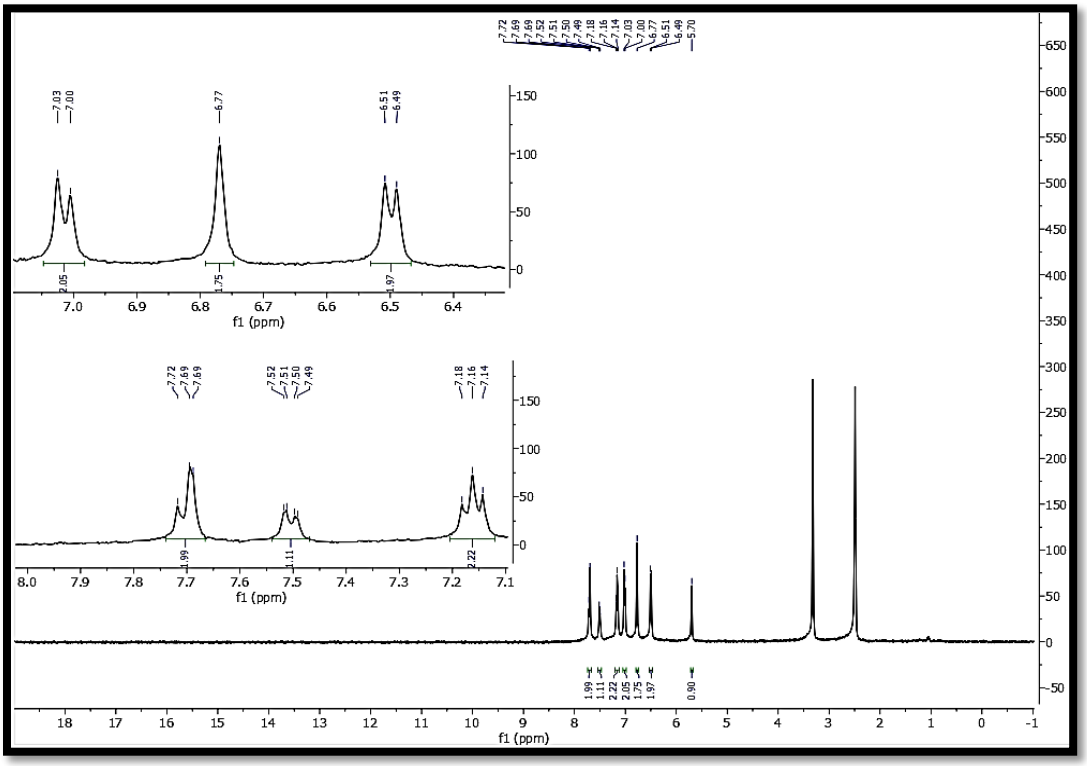


^{1}H-NMR spectrum of compound 3f

2-(2,4-Dichlorophenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 7, 3g): Cream solid, M. F= $C_{17}H_{12}N_2Cl_2$, M. W= 315.19, M.P $_{obs.}$ (℃) =159-161, M.P $_{rep.}$ (℃) =158-160. **FT-IR [ῡ (cm^{-1}) (KBr)]**: 3238-3417 (NH), 3043 (=C-H), 2851-2923 (C-H aliphatic), 1600 (C=C aromatic), 1264 (C-N), 1045 (C-Cl). **^{1}H NMR (DMSO-d$_6$, 400 MHz)** δ (ppm): 5.7 (1H, s, CH), 6.50 (2H, d, *J* =8 Hz, CH), 6.70 (2H, s, NH), 7.02 (2H, d, *J*= 12 Hz, CH), 7.16 (2H, t, *J*=8 Hz, CH), 7.50 (1H, d, *J*=4 Hz, CH), 7.69 (2H, t, *J*=12 Hz , CH).

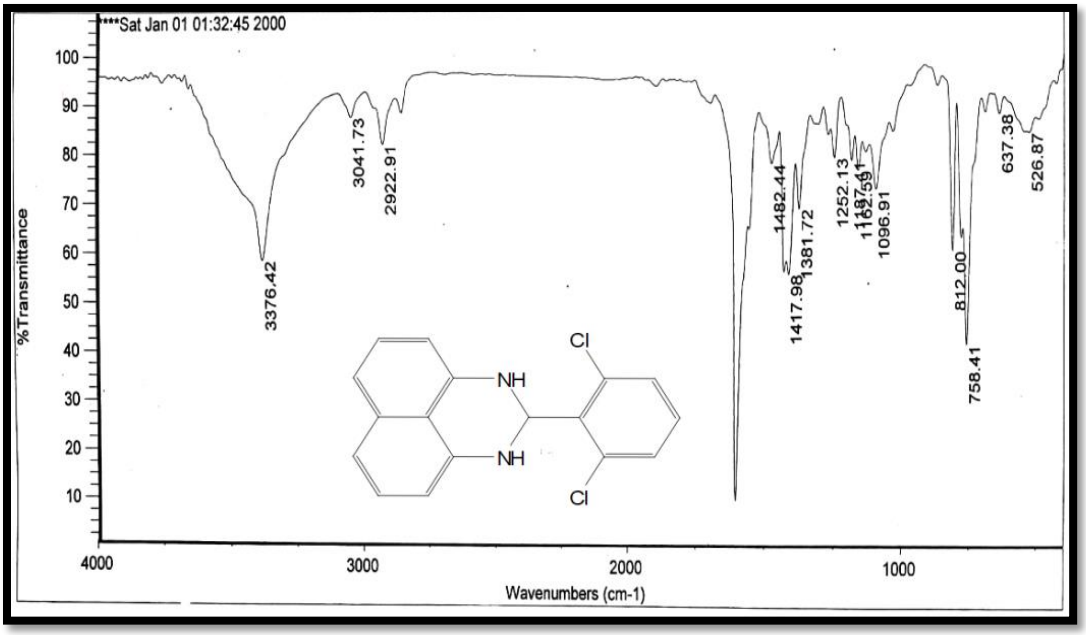


FT–IR spectrum of compound 3g

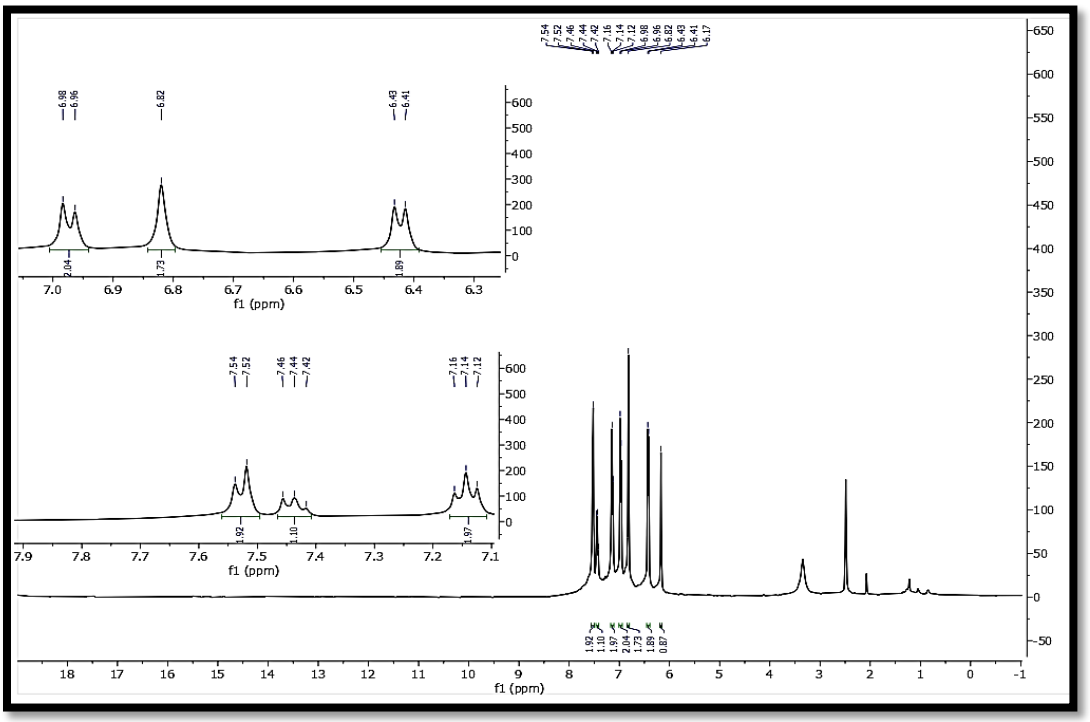


^{1}H-NMR spectrum of compound 3g

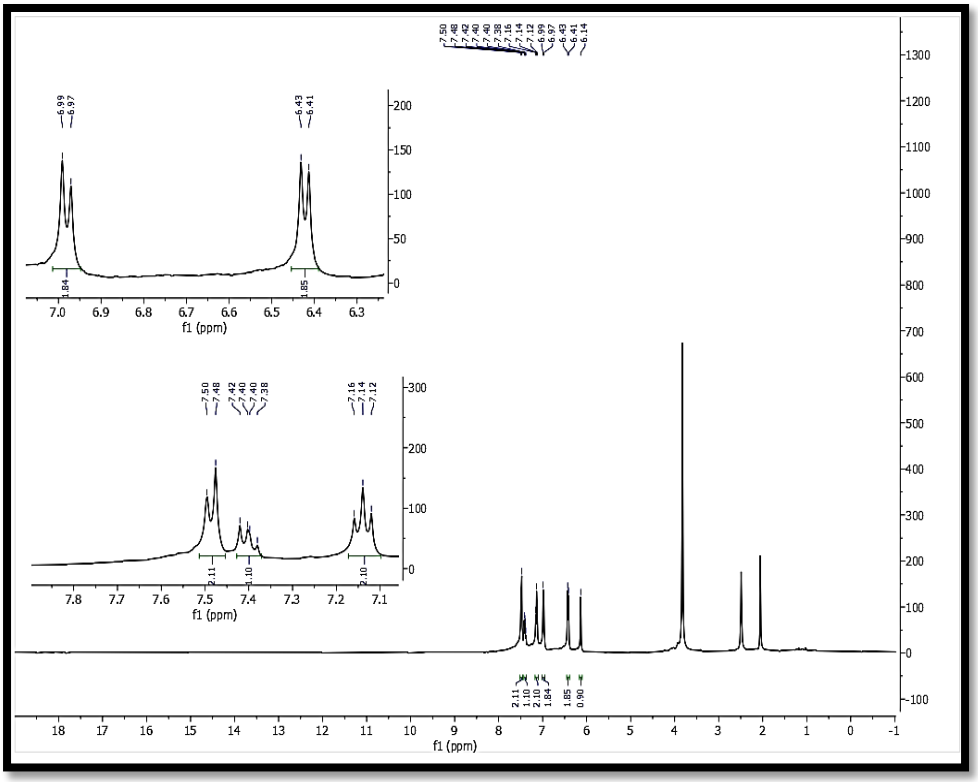
2-(2,6-Dichlorophenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 8, 3h). Cream solid, M.F= $C_{17}H_{12}N_2Cl_2$, M. W=315.19, M.P $_{obs.}$ (°C)= 205-207. **FT-IR [ῡ (cm^{-1}) (KBr)]:** 3376 (N-H), 3041 (=C-H), 2922 (C-H aliphatic), 1482-1603 (C=C aromatic), 1252 (C-N), 1096 (C-Cl). **^{1}H NMR (DMSO-d_6, 400 MHz)** δ (ppm): 6.15 (1H, s, CH), 6.42 (2H, d, *J*=8 Hz, CH), 6.7 (2H, s, NH exchange with D_2O), 6.97 (2H, d, *J*=8 Hz, CH), 7.14 (2H, t, *J*=8 Hz, CH), 7.44 (1H, t, *J*=8 Hz, CH), 7.53 (2H, d, *J*=8 Hz, CH).



FT-IR spectrum of compound 3h

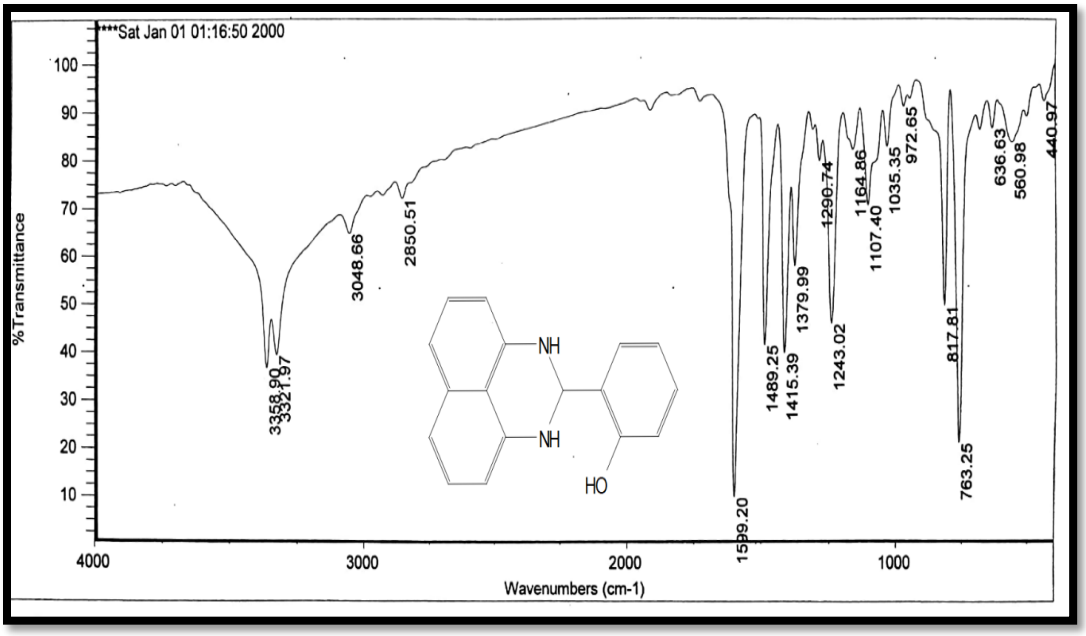


^{1}H-NMR spectrum of compound 3h

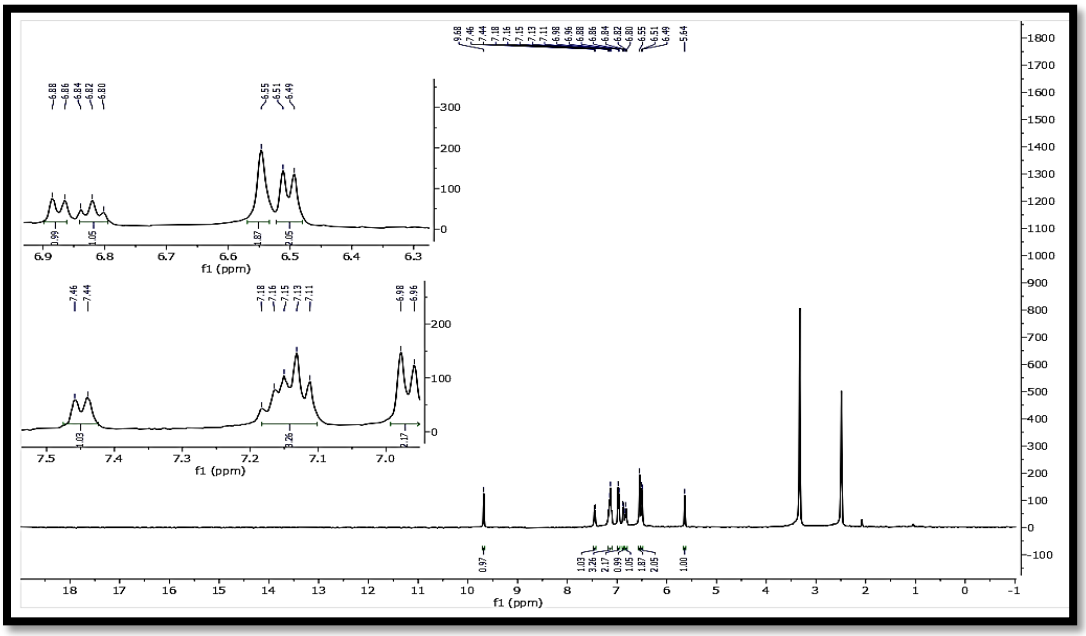


^{1}H-NMR spectrum of compound 3h in the presence of D_2O

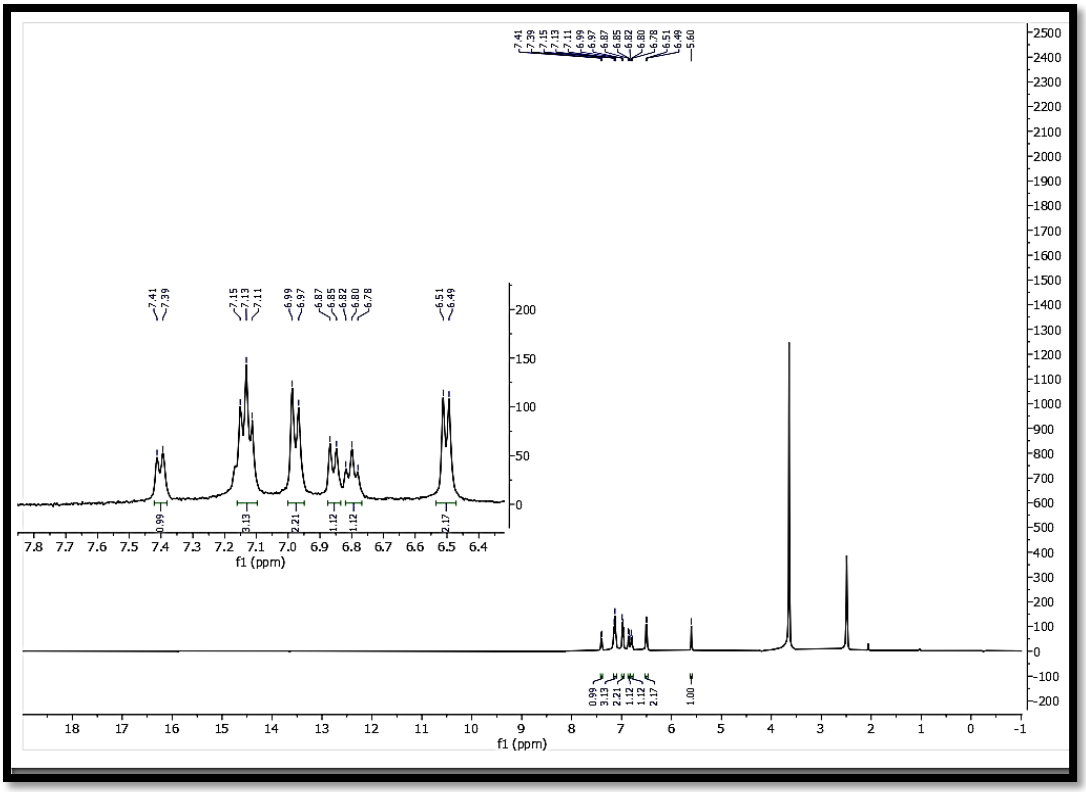
2-(2-Hydroxyphenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 9, 3i). White solid, M. F= $C_{17}H_{13}N_2O$, M.W=262.19, M.P $_{obs.}$ (℃)= 191-193, M.P $_{rep.}$ (℃) = 192-193. **FT-IR [$\bar{\upsilon}$ (cm^{-1}) (KBr)]:** 3358 (OH), 3321 (NH), 3048 (=C-H), 2850 (C-H aliphatic), 1489-1599 (C=C aromatic), 1243 (C-N), 1107 (C-O). **^{1}H NMR (DMSO-d_6, 400 MHz)** δ (ppm): 5.57(1H, s, CH), 5.2 (1H, s, CH), 6.50 (2H, d, *J*=8 Hz), 6.55(2H, s, NH exchange with D_2O), 6.82, (1H, t, *J*=8 Hz), 6.87 (1H,d, *J*=8 Hz), 6.97 (2H, d, *J*=8 Hz, CH), 7.13 (3H, m, CH), 9.52 (1H, s, OH, exchange with D_2O).



FT-IR spectrum of compound 3i

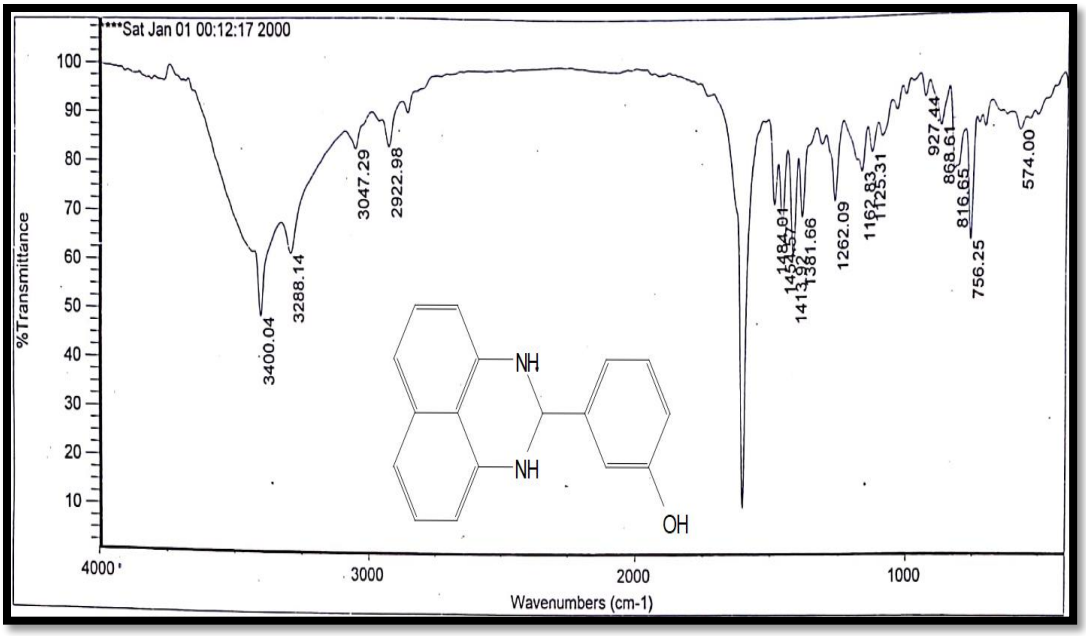


^{1}H-NMR spectrum of compound 3i

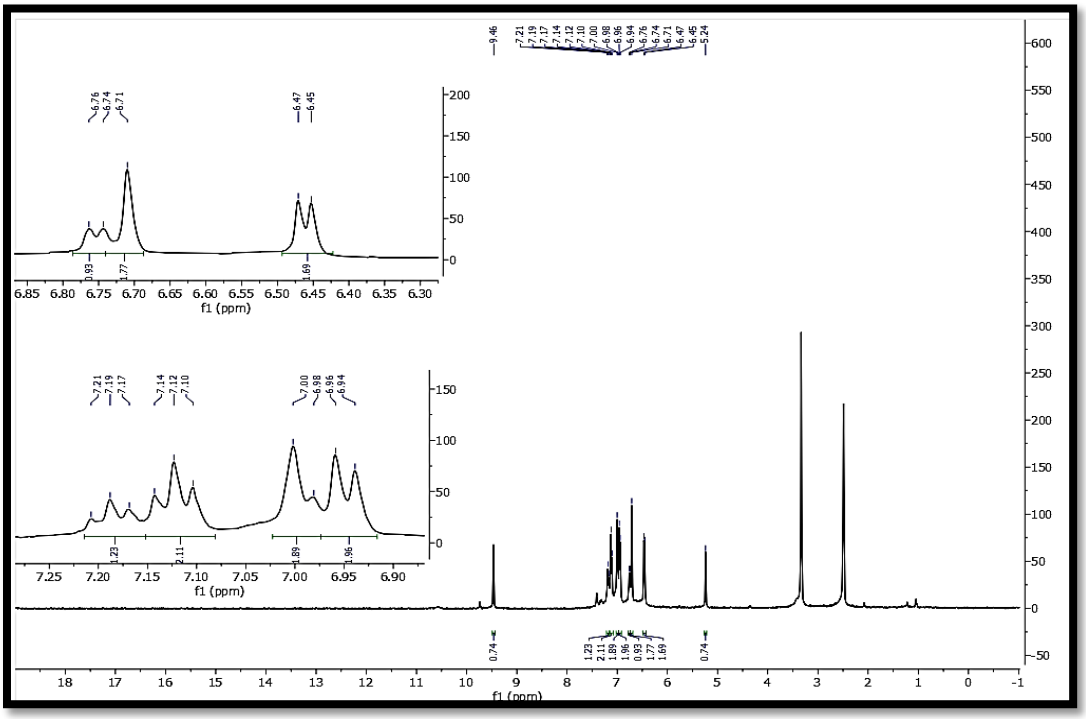


^{1}H-NMR spectrum of compound 3i in the presence of D_2O

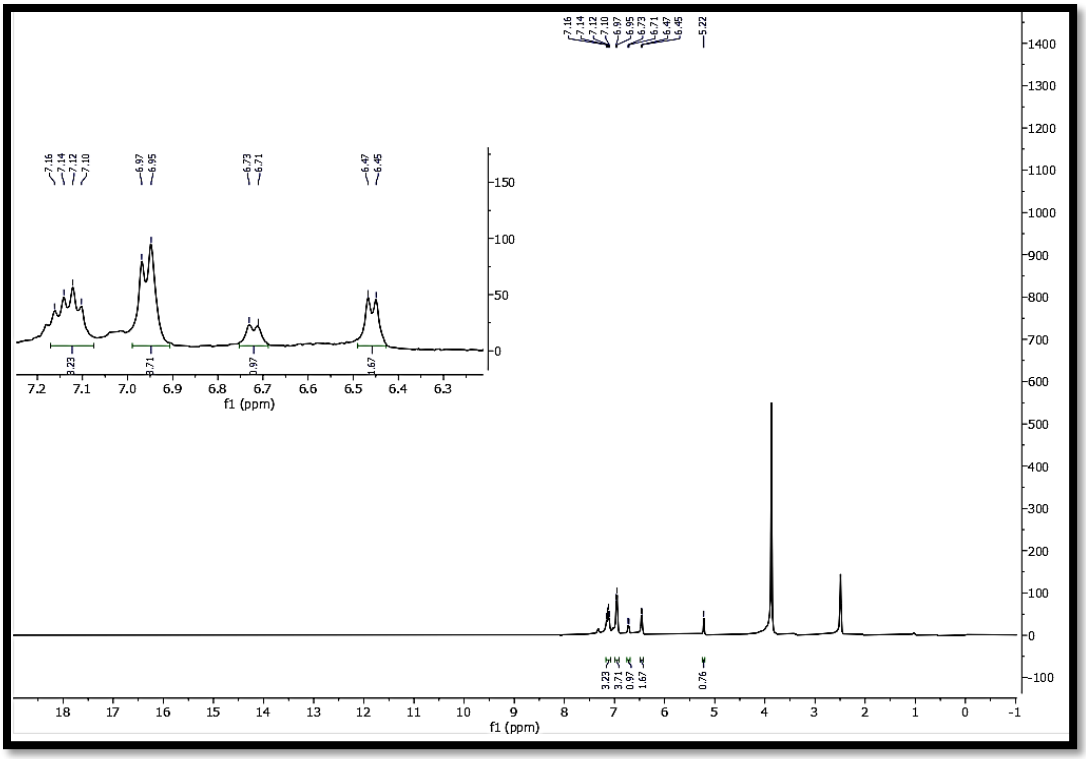
2-(3-Hydroxyphenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 10, 3j): White solid, M. F=$C_{17}H_{14}N_2O$, M. W=262.19, M.P $_{obs.}$ (°C)= 183-187, M.P $_{rep.}$ (°C) = 185-188. **FT-IR [$\bar{\upsilon}$ (cm^{-1}) (KBr)]**: 3427 (OH), 3233 (NH), 2923 (=C-H), 2852 (C-H aliphatic), 1602 (C=C aromatic), 1335 (C-N), 1123 (C-O). **^{1}H NMR (DMSO-d_6, 400 MHz)** δ (ppm): 5.2 (1H, s, CH), 6.46 (2H, d, *J*=8 Hz, CH), 6.7 (2H, s, NH exchange with D_2O), 6.75, (1H, d, *J*=8 Hz), 6.95 (2H, d, *J*=8 Hz), 6.99 (2H, d, *J*=8 Hz, CH), 7.12 (2H, t, *J*=8 Hz, CH), 7.19 (1H, t, *J*=8 Hz), 9.4 (1H, s, OH, exchange with D_2O).



FT-IR spectrum of compound 3j

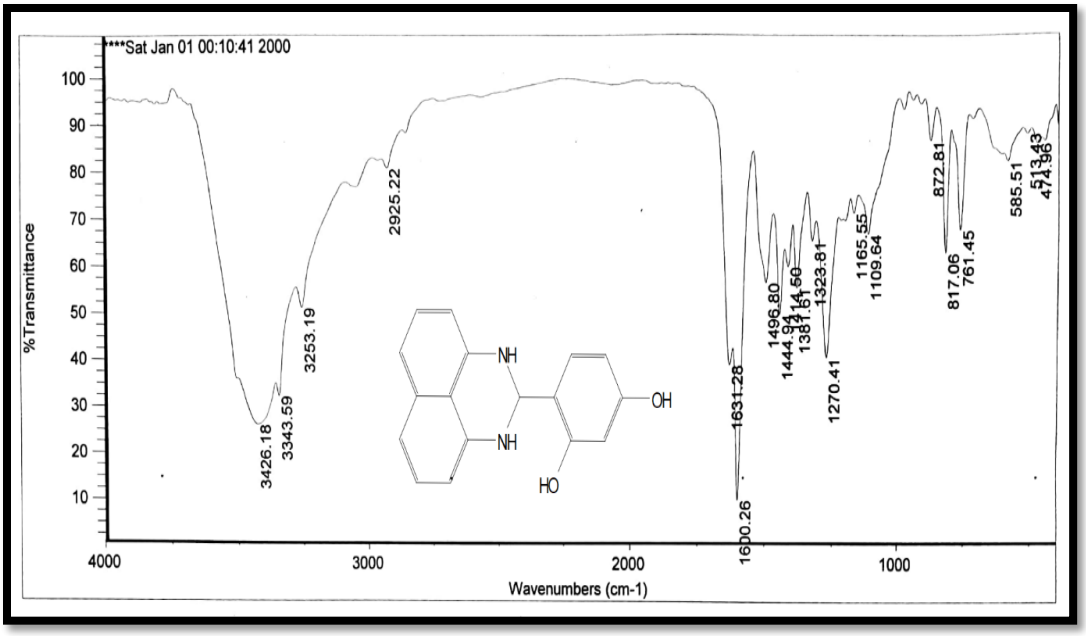


^{1}H-NMR spectrum of compound 3j

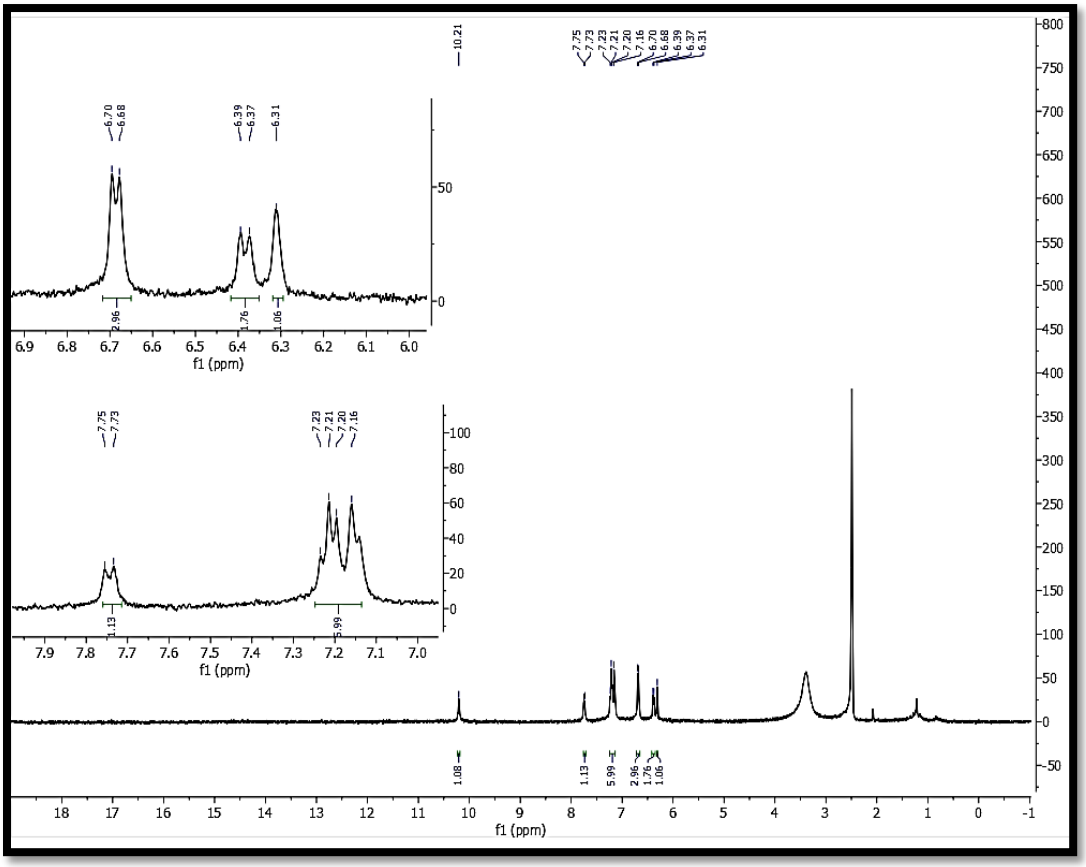


^{1}H-NMR spectrum of compound 3j in the presence of D_2O

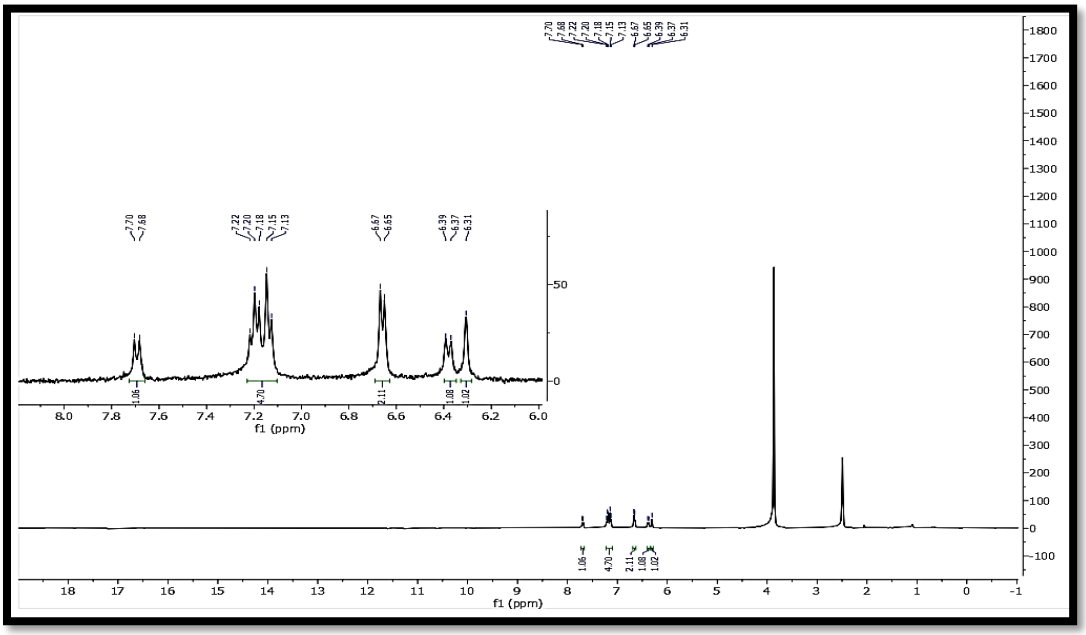
2-(2,4-Dihydroxyphenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 11, 3k). White solid, M.F=$C_{17}H_{14}N_2O_2$, M. W=278.19, M.P $_{obs.}$ (℃) =187-190. **FT-IR [ῡ (cm^{-1}) (KBr)]**: 3426 (OH), 3343 (NH), 3253 (=C-H), 2925 (C-H aliphatic), 1600 (C=C aromatic), 1270 (C-N), 1109 (C-O). **^{1}H NMR (DMSO-d$_6$, 400 MHz)** δ (ppm): 6.3 (1H, s, CH), 6.39 (1H, S, *J*=6.38 Hz, CH), 6.40 (1H, S ,NH exchange with D_2O) , 6.69 (3H, d, *J*=8 Hz, NH exchange with D_2O), 7.20 (6H, m, CH, OH exchange with D_2O), 7.74 (1 H, d, *J*=8 Hz, CH) , 10.1(1H, s, OH, exchange with D_2O).



FT-IR spectrum of compound 3k

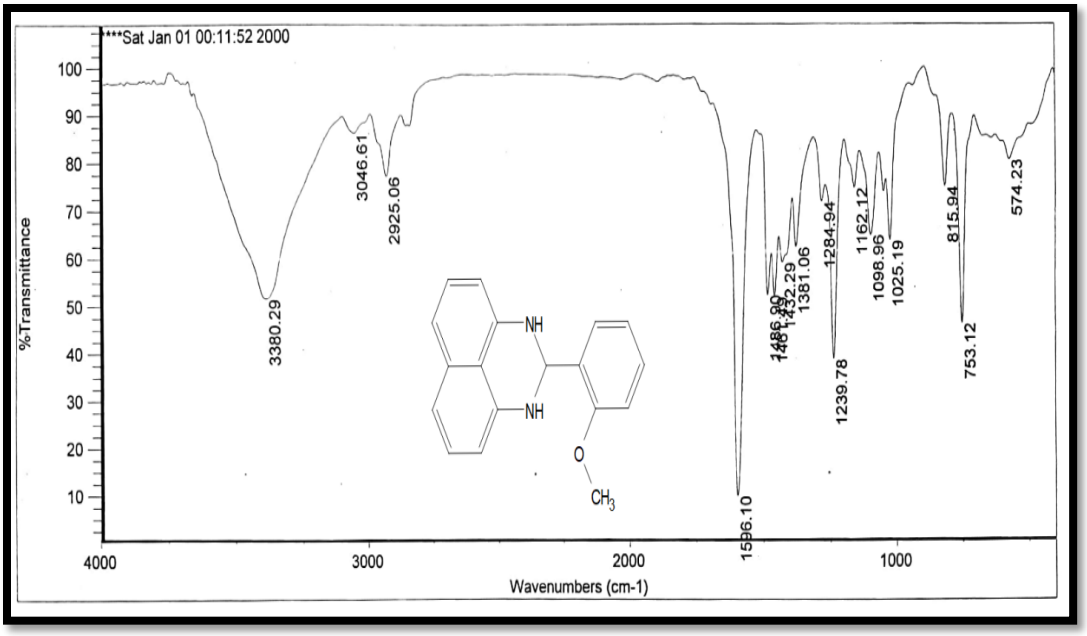


^{1}H-NMR spectrum of compound 3k

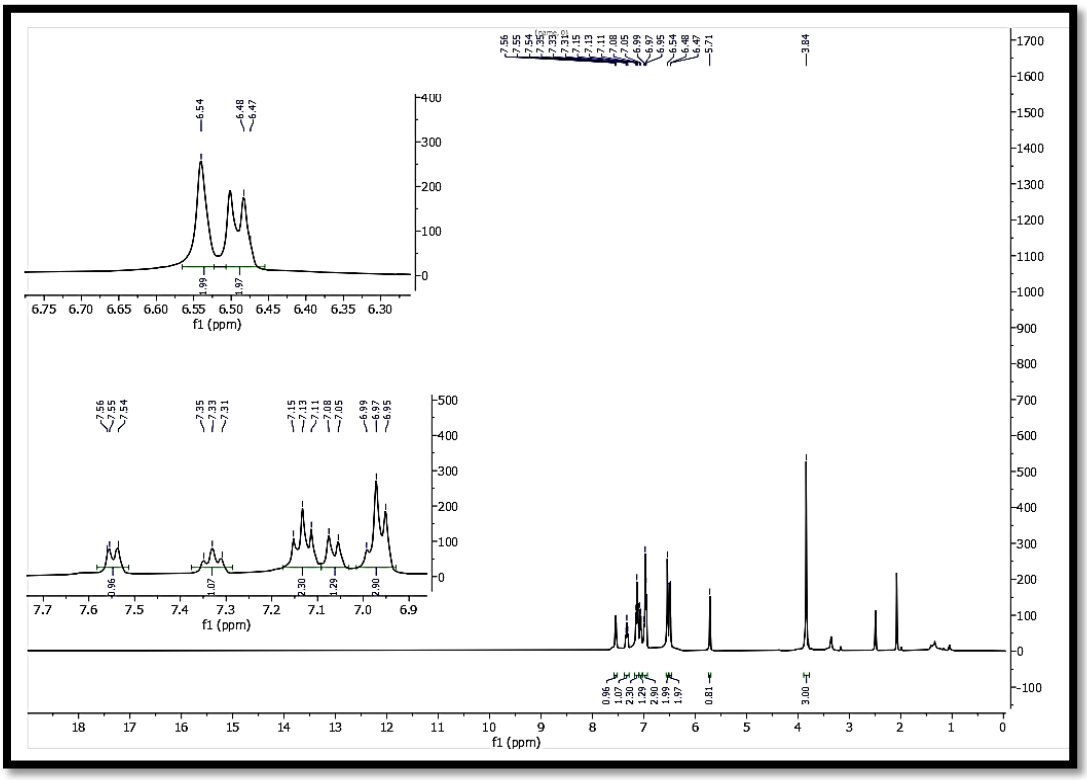


^{1}H-NMR spectrum of compound 3k in the presence of D_2O

2-(2-Methoxyphenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 12, 3l)*:* White solid, M. F=$C_{17}H_{16}N_2O$, M. W=264.19, M.P $_{obs.}$ (℃) = 122-126, M.P $_{rep.}$ (℃) = 124-127. **FT-IR [$\bar{\upsilon}$ (cm^{-1}) (KBr)]**: 3380 (NH), 3046 (=C-H), 2925 (C-H aliphatic), 1596 (C=C aromatic), 1239 (C-N), 1025 (C-O). **^{1}H NMR (DMSO-d_6, 400 MHz)** δ (ppm): 3.86 (3H, s, CH_3), 5.52 (1H, s, CH), 6.46 (2H, d, *J* =4 Hz, CH), 6.56 (2H, s, NH), 6.97 (3H, d, *J*=8 Hz, CH), 7.08 (1H, d, *J* =12 Hz), 7.12 (2H, t, *J* =8 Hz, CH), 7.33 (1H, t, *J*=8 Hz), 7.55 (1H, d, *J*=4 Hz).

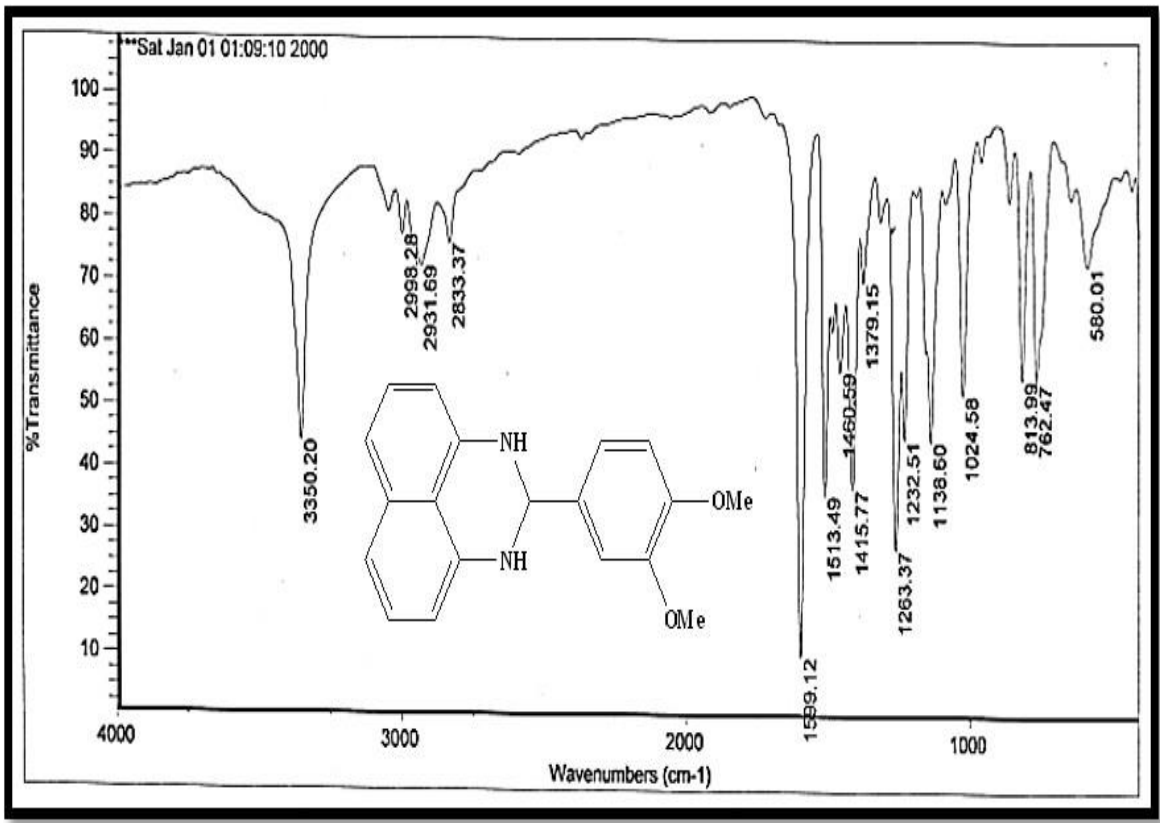


FT-IR spectrum of compound 3l

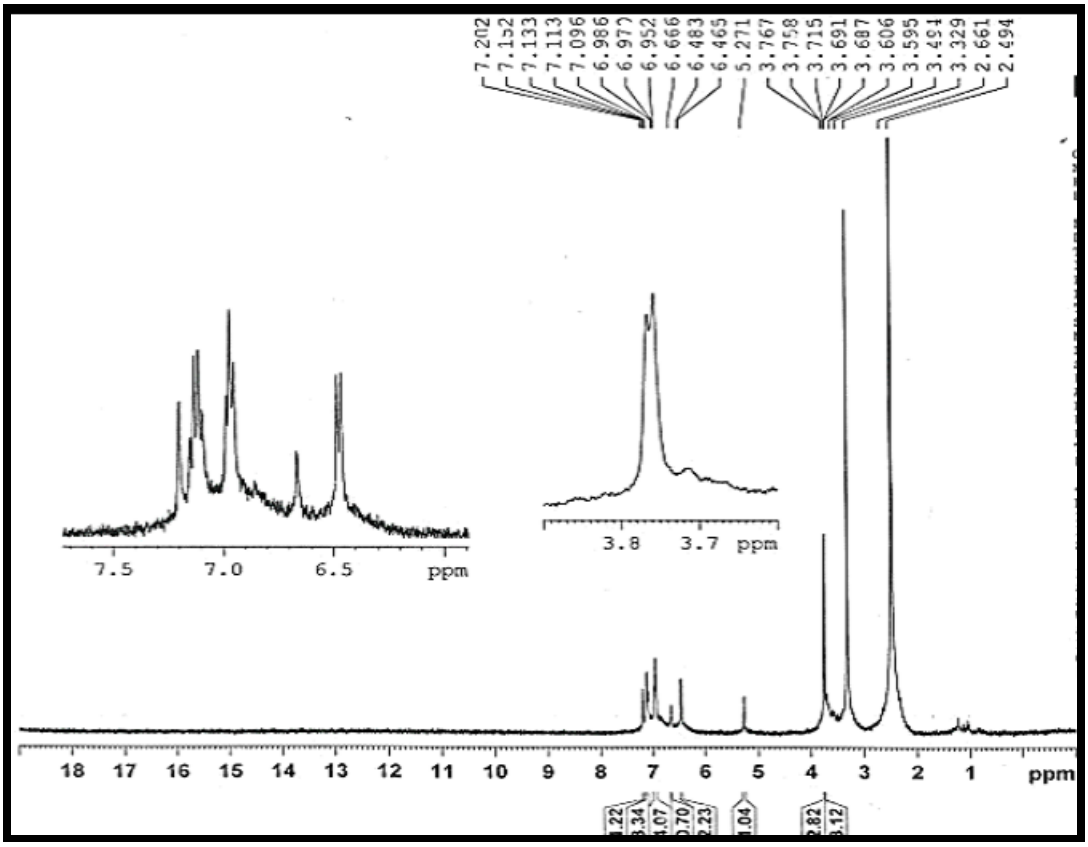


^{1}H-NMR spectrum of compound 3l

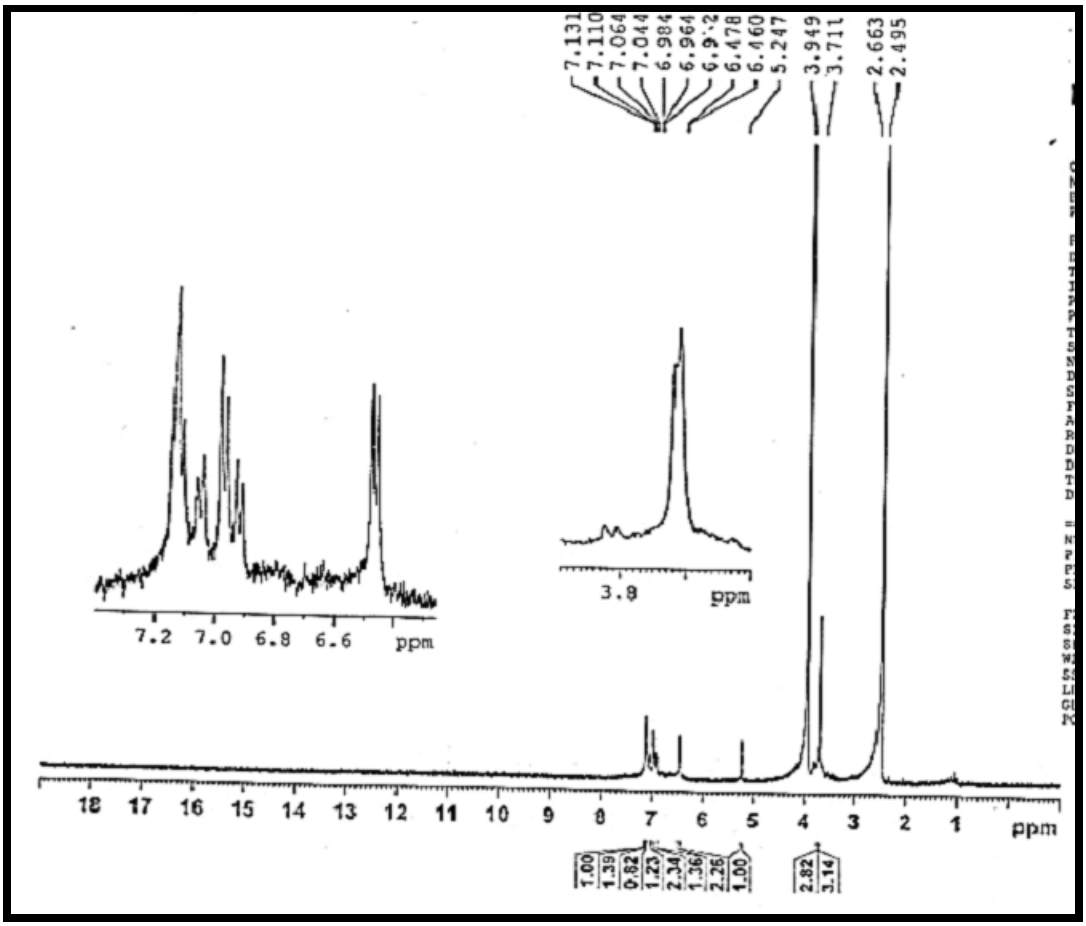
2-(3,4-Dimethoxyphenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 13, 3m): Yellow Solid, M. F= $C_{19}H_{18}N_2O_2$, M. W= 306.17, M.P $_{obs.}$ (°C) = 205-207, M.P $_{rep.}$ (°C) = 205-208. **FT-IR [ῡ (cm-1) (KBr)]:** 1024 (C-O), 1263 (C-N), 1379 (CH3 bend), 1599, 1460 (C=C aromatic), 2998 (C-H aliphatic), 3350 (NH). **^{1}H NMR (DMSO-d6, 400 MHz)** δ (ppm): 3,71 (3H, s, CH_3), 3.94 (3H, s, CH3), 5.27 (1H, s, CH), 6.47 (2H, d, *J* =7.2 Hz, CH), 6.66 (1H, s, NH exchange with D_2O), 6.97 (3H, d, *J* =8 Hz, CH), 7.12 (4H, d, *J* =8. Hz, CH), 7.20 (1H, s, NH exchange with D_2O).



FT-IR spectrum of compound 3m

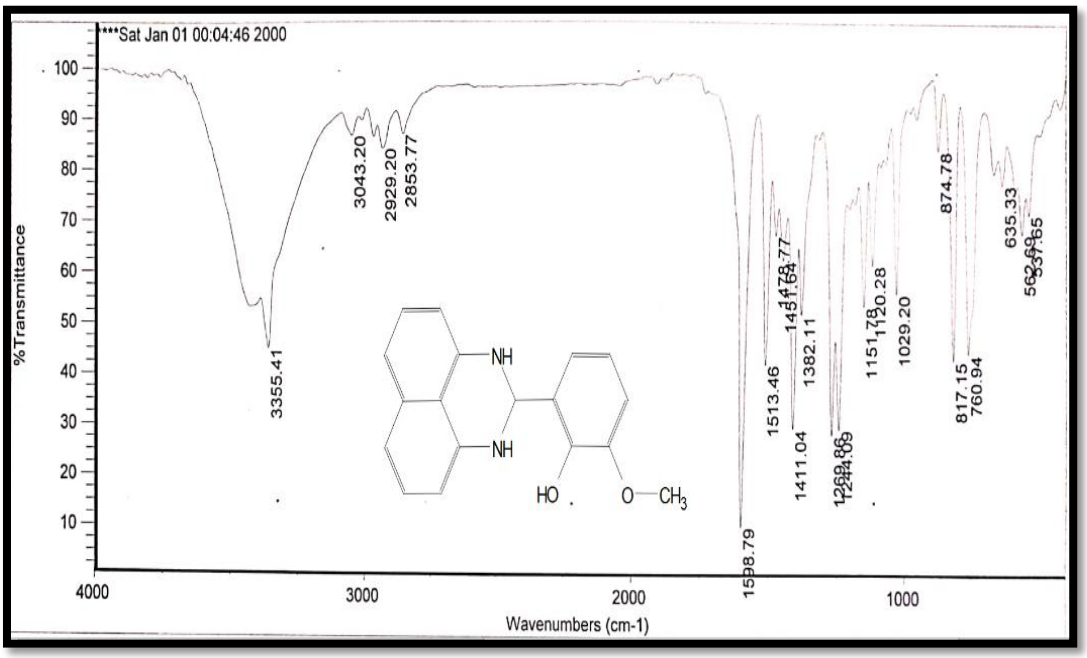


^{1}H-NMR spectrum of compound 3m

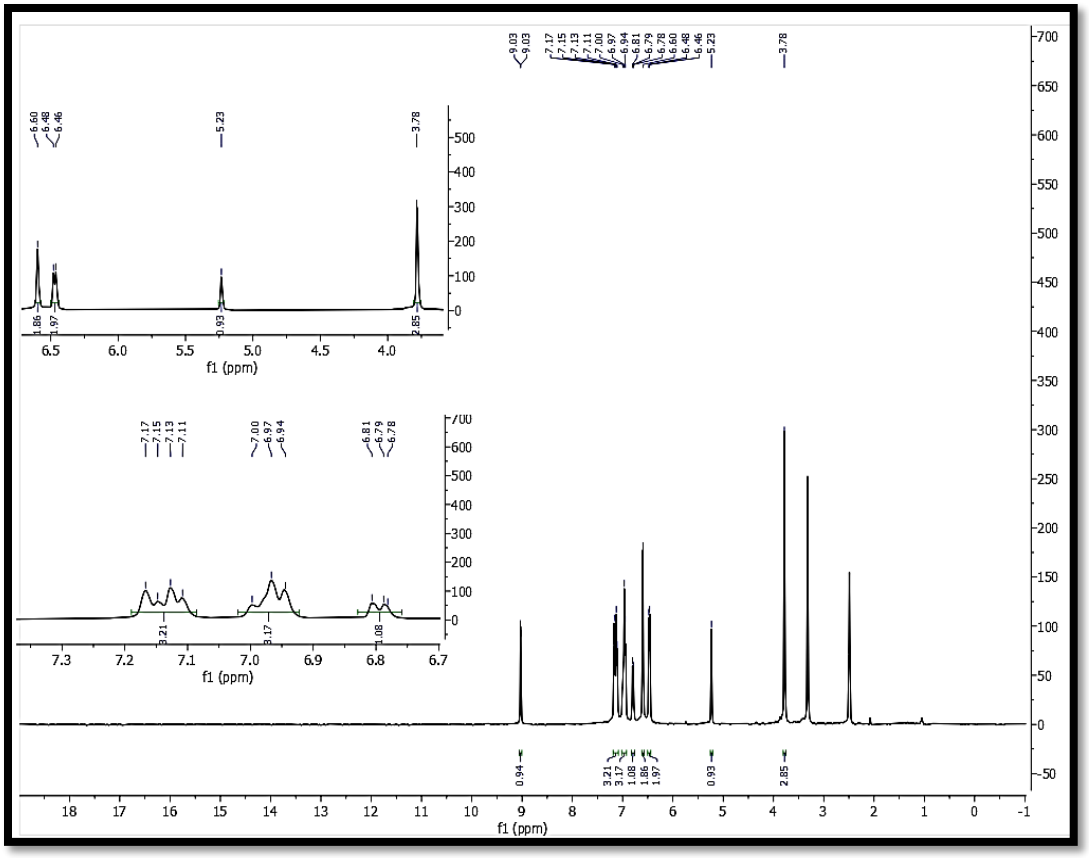


^{1}H-NMR spectrum of compound 3m in the presence of D_2O

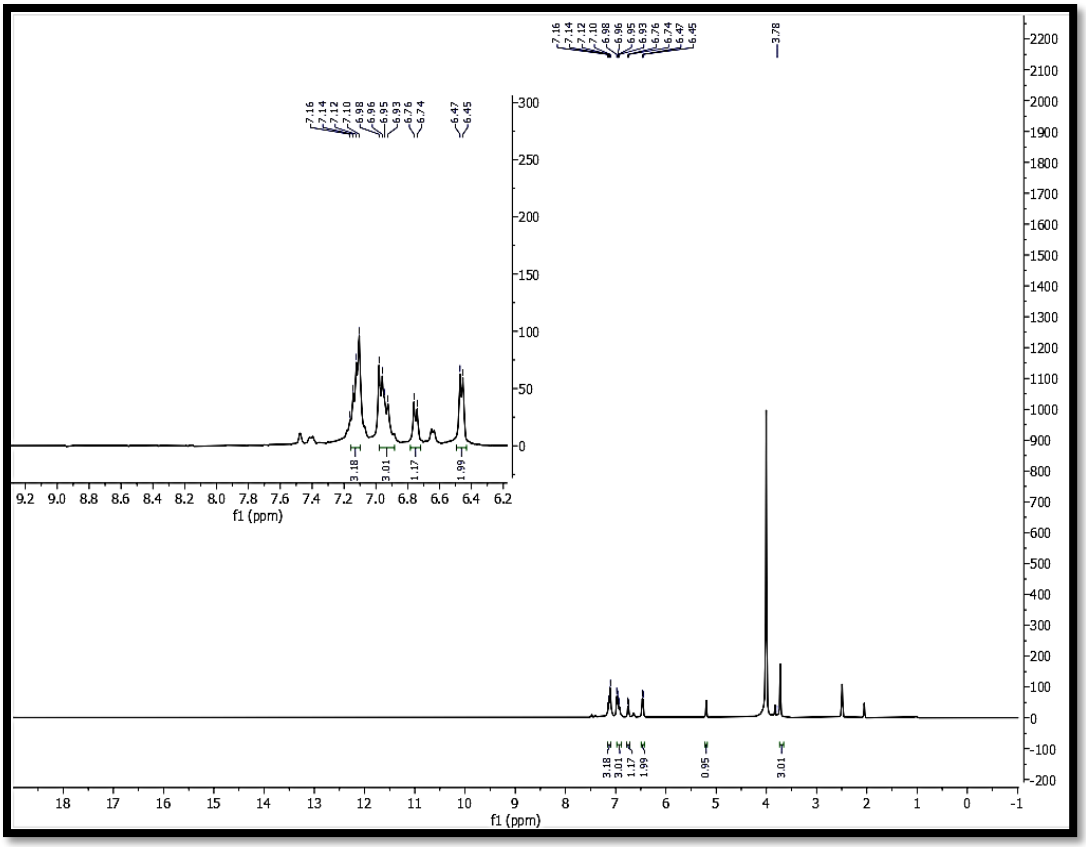
2-(2-Hydroxy, 3-Methoxyphenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 14, 3n). Cream solid, M. F= $C_{18}H_{15}N_2O_2$, M. W=291.2, M.P $_{obs.}$ (°C) = 187-189. **FT-IR [$\bar{\upsilon}$ (cm^{-1}) (KBr)]:** 3355 (NH, OH), 3043 (=C-H), 2853-2929 (C-H aliphatic), 1513-1598 (C=C aromatic), 1269 (C-N), 1151 (C-O). **^{1}H NMR (DMSO-d_6, 400 MHz)** δ (ppm): 3.8 (3H, s, CH_3), 5.2(1H, s, CH), 6.47 (2H, d, *J*=8 Hz), 6.60 (2H, s, NH exchange with D_2O), 6.78 (2H, d, *J*=4 Hz), 6.97 (3H, t, *J*=12 Hz), 7.18 (3H, m, CH), 9.1(1H, s, OH, exchange with D_2O).



FT-IR spectrum of compound 3n

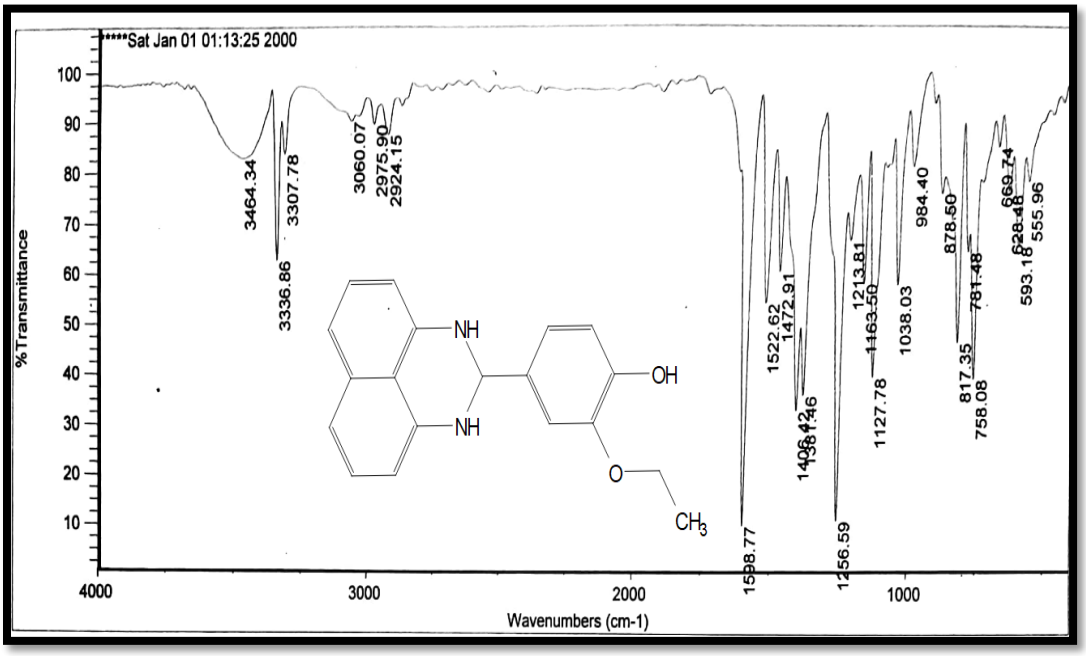


^{1}H-NMR spectrum of compound 3n

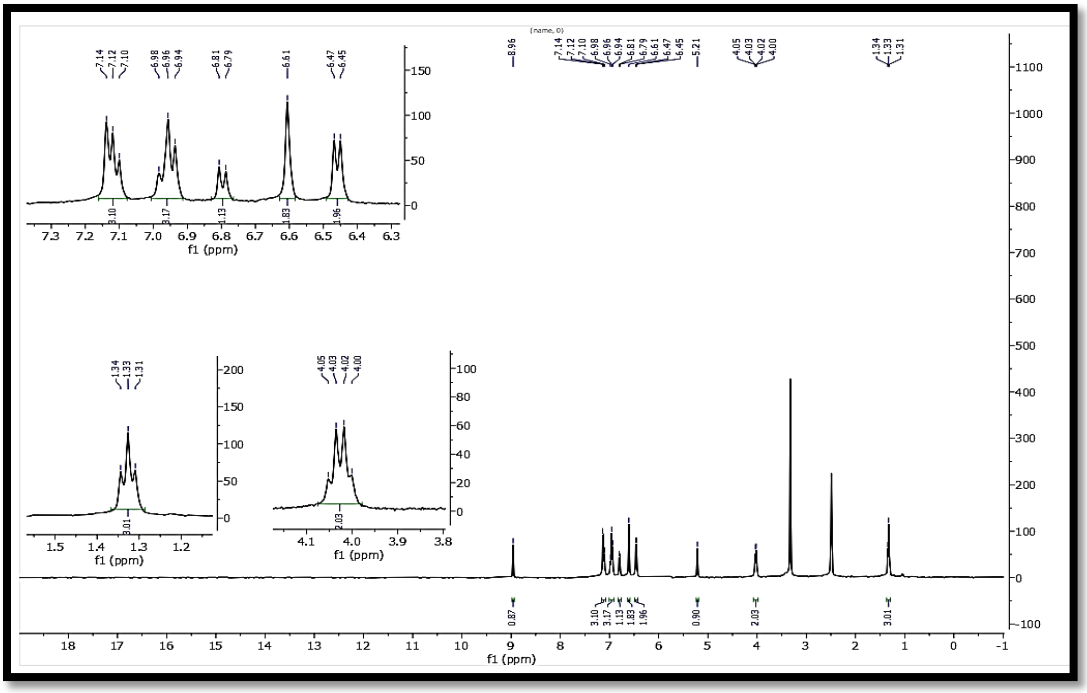


^{1}H-NMR spectrum of compound 3n in the presence of D_2O

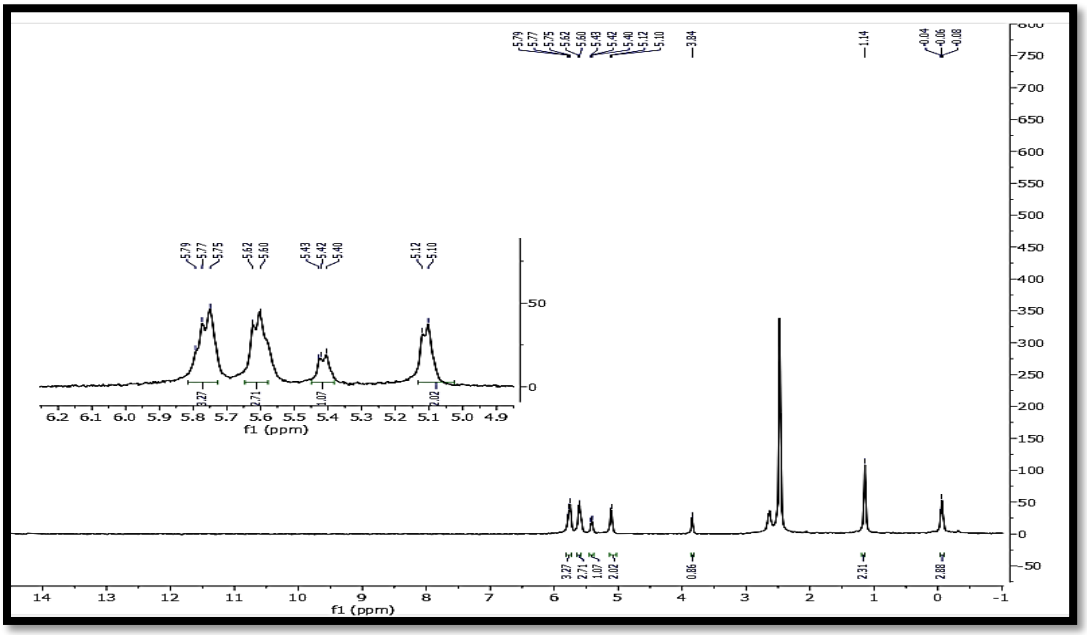
2-(3-Ethoxy, 4-hydroxyphenyl)-2,3-dihydro-1H-perimidine (Table 2, Entry 15, 3o): Pink solid, M. F=$C_{19}H_{18}N_2O_2$, M. W=306.21, M.P $_{obs.}$ (°C) = 190-191. **FT-IR [$\bar{\upsilon}$(cm^{-1}) (KBr)]**: 3464 (OH), 3307-3336 (NH), 3060 (=C-H), 2975 (C-H aliphatic), 1522-1598 (C=C aromatic), 1256 (C-N), 1038 (C-O) .**^{1}H NMR (DMSO-d$_6$, 400 MHz)** δ (ppm): 1.34 (3H, t, *J=8* Hz, CH_3), 4.02 (2H, q, *J=8* Hz, CH_2), 5.22 (1H, s, CH), 6.45 (2H, d , *J*=8 Hz, CH), 6.60 (2H, s, NH exchange with D_2O), 6.80 (1H, d, *J*=8 Hz, CH), 6.96 (3H, t, *J= 8* Hz, CH), 7.12 (3H, t, *J*=8 Hz, CH), 9.1(1H, s, OH, exchange with D_2O).



FT-IR spectrum of compound 3o



^{1}H-NMR spectrum of compound 3o



^{1}H-NMR spectrum of compound 3o in the presence of D_2O