L-Arg@ZY-Fe_3O_4 mesoporous nanomaterial: a novel magnetically recoverable bio-organocatalyst for three-component synthesis of 4*H*-Pyran and -chromene derivatives

Mehdi Kalhor*, Samira Zebardast

Department of Chemistry, Payame Noor University, Tehran, 19395-4697, Iran

E-mail addresses: mekalhor@pnu.ac.ir, mekalhor@gmail.com,

Supporting Information

Experimental

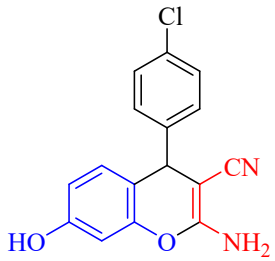
1.1. Chemicals and apparatus

Chemical substances were purchased from the Merck, Fluka and Aldrich Chemical Companies and used as received. Melting points (°C) were determined in an open-glass capillary using an electro-thermal digital melting point apparatus and are uncorrected. Progress of the catalytic process was monitored by thin layer chromatography (TLC) using silica gel plates in the solvent system (ethyl acetate/*n*-hexane, 2:1). FT-IR spectra were obtained with KBr disc on a galaxy series FT-IR 5000 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 and 100 MHz respectively. NMR spectra were obtained in DMSO-d_6 solvent and are reported as parts per million (ppm) downfield from Me_4Si as internal standard. Nitrogen adsorption and desorption isotherms (BET analysis) were measured at 196 °C by a USA Micromeritics (MicroActive for TriStar II Plus Version 2.03, Serial # 283) system after the samples were vacuum dried at 110°C overnight. Field emission scanning electron microscopy (FESEM) images were performed on a Carl Zeiss EVO LS 10 (Germany) FE-SEM that it equipped with energy dispersive X-ray spectrometer (EDX). Nanocomposites based zeolite-Y were characterized using a Holland Philips Xpert X-ray powder diffraction (XRD) diffractometer (CuK, radiation, λ= 0.154056 nm), at a scanning speed of 2°/min from 10° to 100°(2θ). The TGA/DTA measurements were carried out by using a TA-Q600 instrument (made in the USA). TGA/DTA runs were recorded at a scan rate of 10° min^{-1} up to 700 °C under pure argon atmosphere.

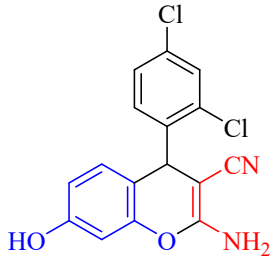
1.2. General procedure for the catalytic synthesis of 2-amino-chromenes

A mixture of aromatic aldehyde (1 mmol), malononitrile (1 mmol), phenols (resorcinol or 2-naphthol) or dimedone (1 mmol), and nano Arg@ZY-Fe_3O_4 (15 mg, 10% wt/wt) was stirred in aqueous medium at 90 °C for desired time (Table 1). After the satisfactory completion of the reaction, as indicated by TLC monitoring (*n*-hexane and ethyl acetate (2:1) as eluents), the reaction mixture was filtered and then the resulting solid was solved in EtOH. The nanocatalyst was separated from the solution using an external magnet. The filtrate was added to 10 ml of cold water and precipitate was filtered off and washed with cold ethanol-water mixture. The final product was obtained in most cases in pure form. However, if necessary, recrystallization could be performed in ethanol-water mixtures. All pure products are known and were identified by comparison of their melting point, FT-IR and ^{1}H NMR with those of authentic samples.

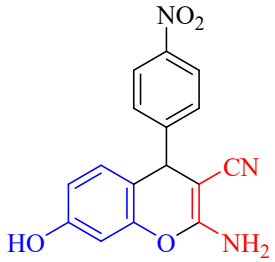
Spectroscopic data for selected compounds



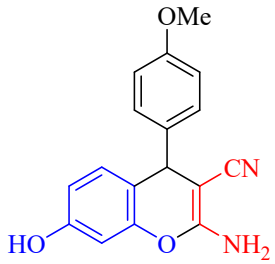
2-Amino-4-(4-chlorophenyl)-7-hydroxy-4*H*-chromene-3-carbonitrile (6b): FT-IR (KBr, υ_{max}): 3430 (NH_2), 2958 (C-H), 2352 (CN), 1601, 1588, 1509, 1366 (C=C), 1244, 1179 (C-O), 1032 (C-N), 829 (C-Cl) cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ_H 9.70 (s, 1H, OH), 7.33 (d, J = 6.40 Hz, 2H, H-Ar), 7.16-6.37 (m, 7H, H-Ar and NH_2), 4.62 (s, 1H, CH) ppm.



2-Amino-4-(2,4-dichlorophenyl)-7-hydroxy-4*H*-chromene-3-carbonitrile (6c): FT-IR (KBr, υ_{max}): 3477 (NH_2), 3044, 2937 (C-H), 2227 (CN), 1580, 1453, 1380 (C=C), 1290, 1217, 1144 (C-O), 1109, 1050 (C-N), 866, 821 (C-Cl), 620 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ_H 9.77 (br, 1H, OH), 7.57-7.37 (m 2H, H-Ar), 7.21 (d, J = 8.40 Hz, 1H, H-Ar), 6.98 (s, 2H, NH_2), 6.71 (d, J = 8.40 Hz, 1H, H-Ar), 6.48-6.39 (m, 2H, H-Ar), 5.11 (s, 1H, CH) ppm.

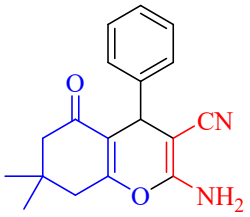


2-Amino-7-hydroxy-4-(4-nitrophenyl)-4*H*-chromene-3-carbonitrile (6f): FT-IR (KBr, υ_{max}): 3418, 3331 (NH_2), 2962 (C-H), 2187 (CN), 1662, 1602, 1529, 1382 (C=C and C=N), 1512, 1344 (NO_2), 1250, 1212, 1140 (C-O), 1037 (C-N), 819, 408 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ_H 9.77 (s, 1H, OH), 8.16 (d, J = 8.00 Hz, 2H, H-Ar), 7.42 (d, J = 8.00 Hz, 2H, H-Ar), 7.01 (s, 2H, NH_2), 6.77-6.40 (m, 3H, H-Ar), 4.82 (s, 1H, CH) ppm.

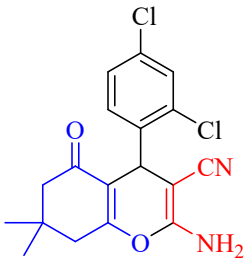


2-Amino-7-hydroxy-4-(4-methoxyphenyl)-4*H*-chromene-3-carbonitrile (6h): FT-IR (KBr, υ_{max}): 3391 (NH_2), 3046, 2921 (C-H), 2352 (CN), 1601, 1513, 1468, 1407 (C=C), 1278, 1172 (C-O), 1010 (C-N), 844, 813, 741. 480 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ_H 9.67 (s,

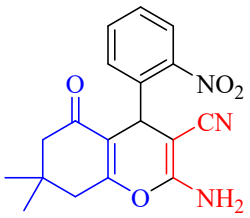
1H, OH), 7.09 (d, J = 7.20 Hz, 3H, H-Ar), 7.04 (s, 1H, H-Ar), 6.82 (s, 2H, NH_2), 6.77 (d, J = 8.40 Hz, 1H, H-Ar), 6.47 (d, J = 8.00 Hz, 1H, H-Ar), 6.39 (s, 1H, H-Ar), 4.55 (s, 1H, CH), 2.22 (s, 3H, OCH_3) ppm.



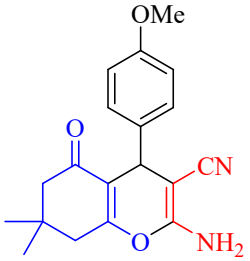
2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (7a): FT-IR (KBr, υ_{max}): 3395, 3323, 3212 (NH_2), 2960 (C-H), 2199 (CN), 1681 (C=O), 1660, 1597, 1371 (C=C), 1248, 1213 (C-O), 1036 (C-N), 695 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-*d6*): δ_H 7.28 (t, J = 7.20 Hz, 2H, H-Ph), 7.21-7.15 (m, 3H, H-Ph), 6.98 (s, 2H, NH_2), 4.20 (s, 1H, CH), 2.53 (s, 2H, CH_2), 2.27 (d, J = 16.05 Hz, 1H, CH_2), 2.12 (d, J = 16.05 Hz, 1H, CH_2), 1.06 (s, 3H, CH_3), 0.97 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, DMSO-*d6*): δ_C 195.6 (C=O), 158.5, 162.5, 144.7, 128.3, 127.1, 126.6, 119.7, 112.8, 58.4, 50.0, 35.6, 31.8, 28.4, 26.8 ppm.



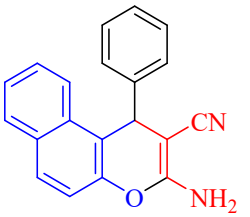
2-amino-4-(2,4-dichlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (7c): FT-IR (KBr, υ_{max}): 3353 (NH_2), 2959 (C-H), 2218 (CN), 1722 (C=O), 1612, 1468, 1380 (C=C), 1234 (C-O), 1070 (C-N), 861 (C-Cl), 584, 406 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 7.51-7.21 (m, 3H, H-Ar),7.07 (s, 2H, NH_2), 4.66 (s, 1H, CH), 3.43 (d br, 2H, CH_2), 2.21 (d br, 2H, CH_2), 1.03 (s, 3H, CH_3), 0.97 (s, 3H, CH_3) ppm.



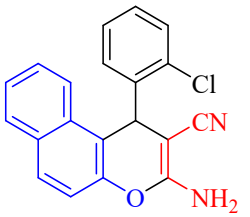
2-Amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (7d): FT-IR (KBr, υ_{max}): 3458, 3376 (NH_2), 2927 (C-H), 2196 (CN), 1614 (C=O), 1519, 1351 (NO_2), 1382 (C=C), 1213, 1142 (C-O), 1066 (C-N), 743, 407 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 7.80-7.35 (m, 4H, H-Ar), 7.18 (s, 2H, NH_2), 4.93 (s, 1H, CH), 2.17 (d br, 4H, $2CH_2$), 1.00 (s, 3H, CH_3), 0.87 (s, 3H, CH_3) ppm.



2-amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7f): ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 7.05-6.94 (d br, 4H, H-Ar), 6.84 (s, 2H, NH_2), 4.12 (s, 1H, CH), 3.71 (s, 3H, OCH_3), 3.32 (br, 2H, CH_2), 2.24-2.10 (d br, 2H, CH_2), 1.03 (s, 3H, CH_3), 0.95 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-*d6*): δ_C 196.1 (C=O), 158.5, 162.6, 158.9, 158.3, 137.3, 128.6, 120.2, 114.1, 113.4, 59.0, 55.2 , 50.4, 32.2, 28.9, 21.2 ppm.

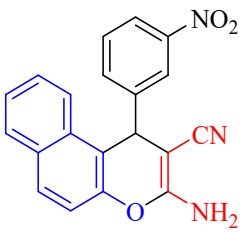


3-Amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile (8a): FT-IR (KBr, υ_{max}): 3393, 3230 (NH_2), 2916 (C-H), 2228 (CN), 1633, 1457 (C=C), 1171, 1118 (C-O), 1029 (C-N), 742, 480 cm^{-1}; ^{1}H NMR (400 MHz, Acetone-d_6): δ_H 8.30 (s, 1H, H-Ar), 7.89 (s, 1H, H-Ar), 7.61 (s br, 3H, H-Ar), 7.33-7.15 (t br, 6H, H-Ar), 6.44 (s, 2H, NH_2), 4.93 (d, 1H, CH) ppm.



3-Amino-1-(2-chlorophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (8b):

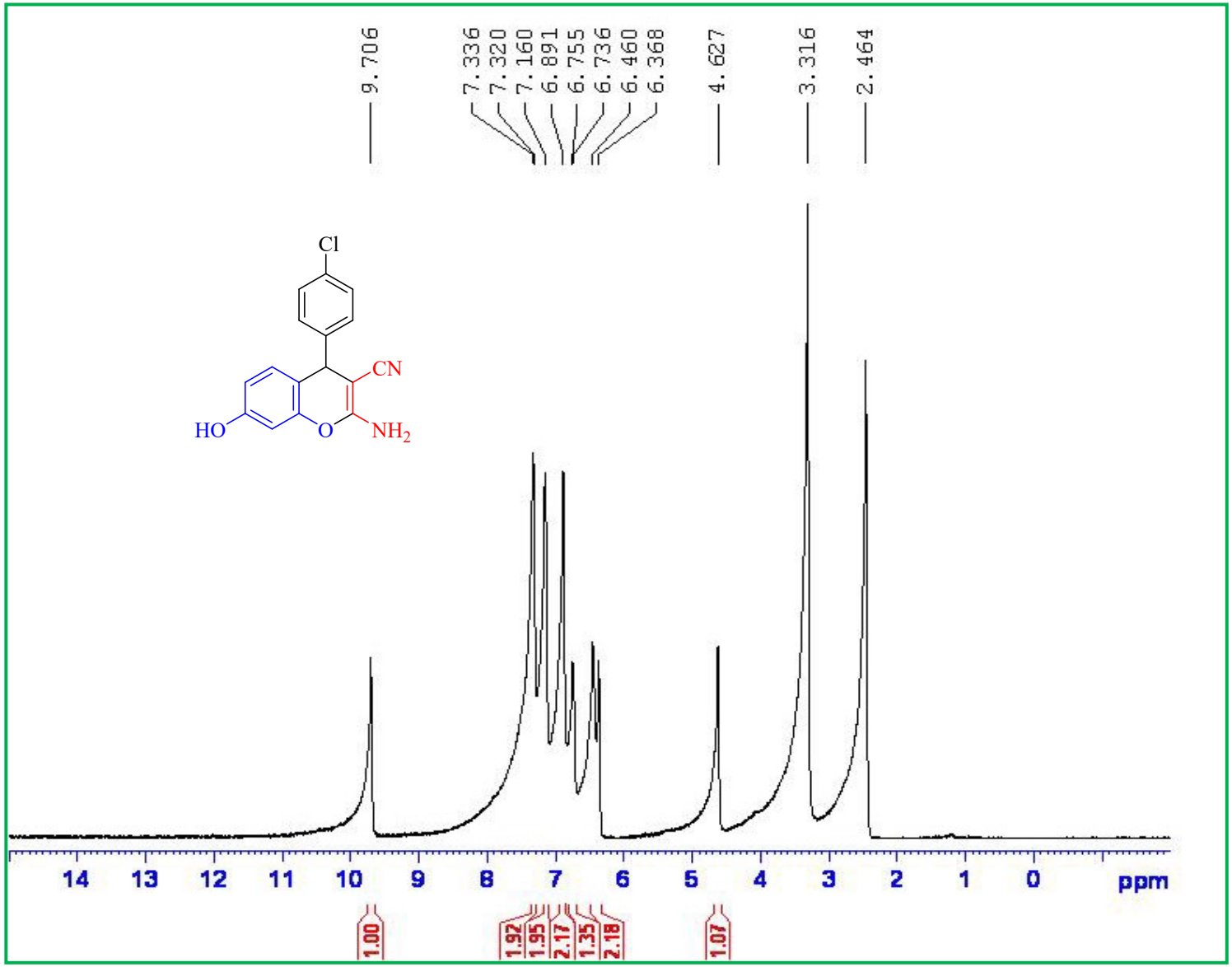
^{1}H NMR (DMSO-d_6, 500 MHz): δ_H 7.96-7.90 (m, 2H, H-Ar), 7.64 (d, J = 8.45 Hz, 1H, H-Ar), 7.46-7.40 (m, 3H, H-Ar), 7.34 (d, J = 8.85 Hz, 1H, H-Ar), 7.18 (t, J = 3.90 Hz, 1H, H-Ar), 7.04 (d br, 3H, H-Ar and NH_2), 5.71 (s, 1H, CH) ppm; ^{13}C NMR (125 MHz, DMSO-*d6*): δ_C 159.9, 151.5, 147.2, 142.6, 131.1, 130.8, 130.1, 128.7,128.5, 128.2, 119.9, 118.4, 116.8, 114.8 , 114.0, 112.5, 59.2, 35.1 ppm.



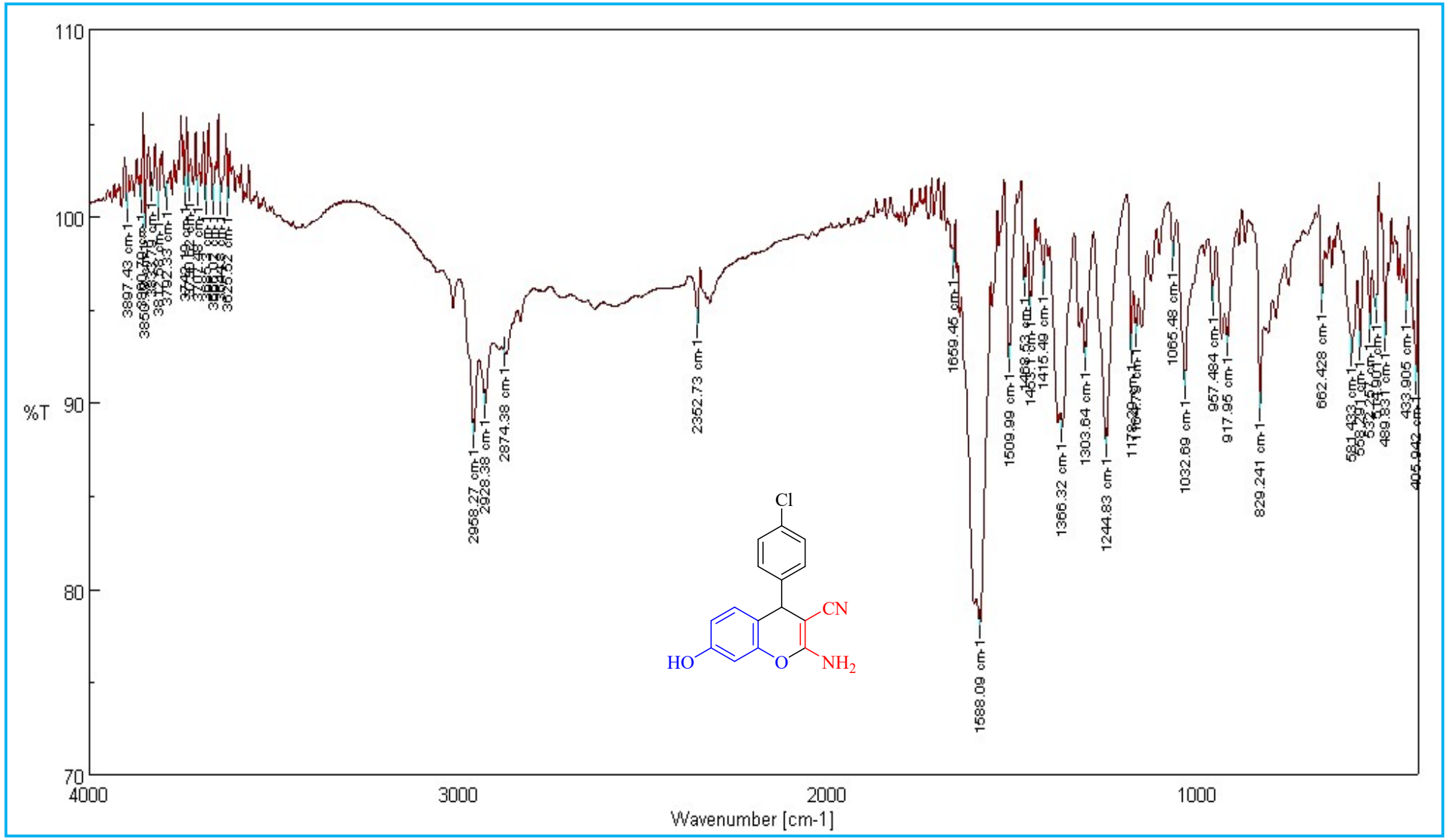
3-Amino-1-(3-nitrophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (8c): FT-IR (KBr, υ_{max}): 3452 (NH_2), 3084, 2921 (C-H), 2225 (CN), 1590 (C=C), 1529, 1354 (NO_2), 1215 (C-O), 952 (C-N), 817, 737, 673, 620 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 8.27 (d, J = 7.65 Hz, 1H, H-Ar) 8.13 (s, 1H, H-Ar), 7.92 (d, J = 7.65 Hz, 1H, H-Ar), 7.76-7.60 (m, 6H, H-Ar), 7.34 (s, 2H,

NH_2), 7.17 (d, J = 8.40 Hz, 1H, H-Ar), 5.21 (s, 1H, CH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ_H 160.9, 148.4, 148.3, 143.3, 135.0, 133.3, 130.9, 128.2, 127.5, 127.3, 126.4, 124.7, 123.2, 122.6, 122.5, 121.2, 120.7, 117.2, 55.8 ppm.

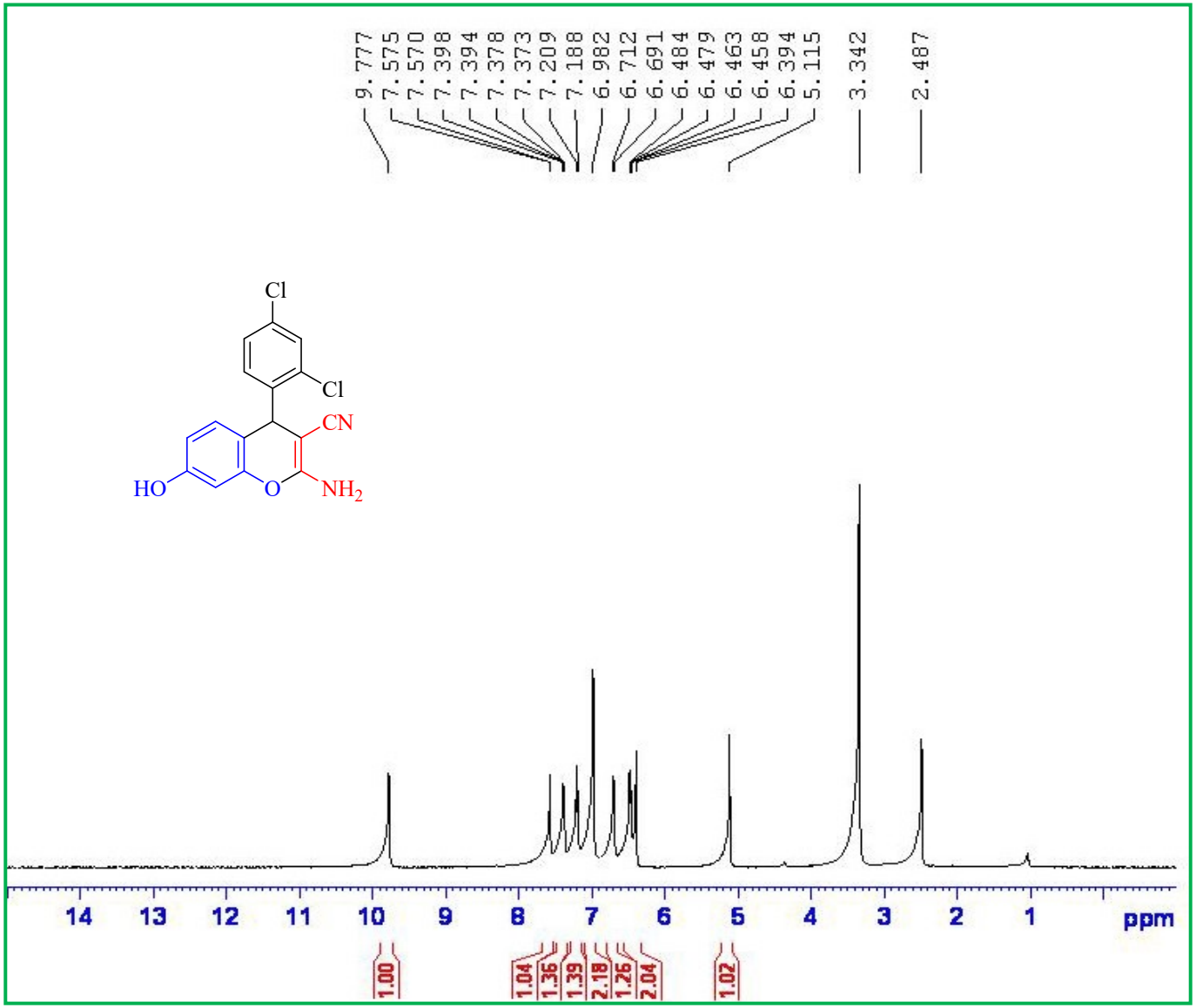
^{1}H NMR spectrum of 2-Amino-4-(4-chlorophenyl)-7-hydroxy-4*H*-chromene-3-carbonitrile (6b)



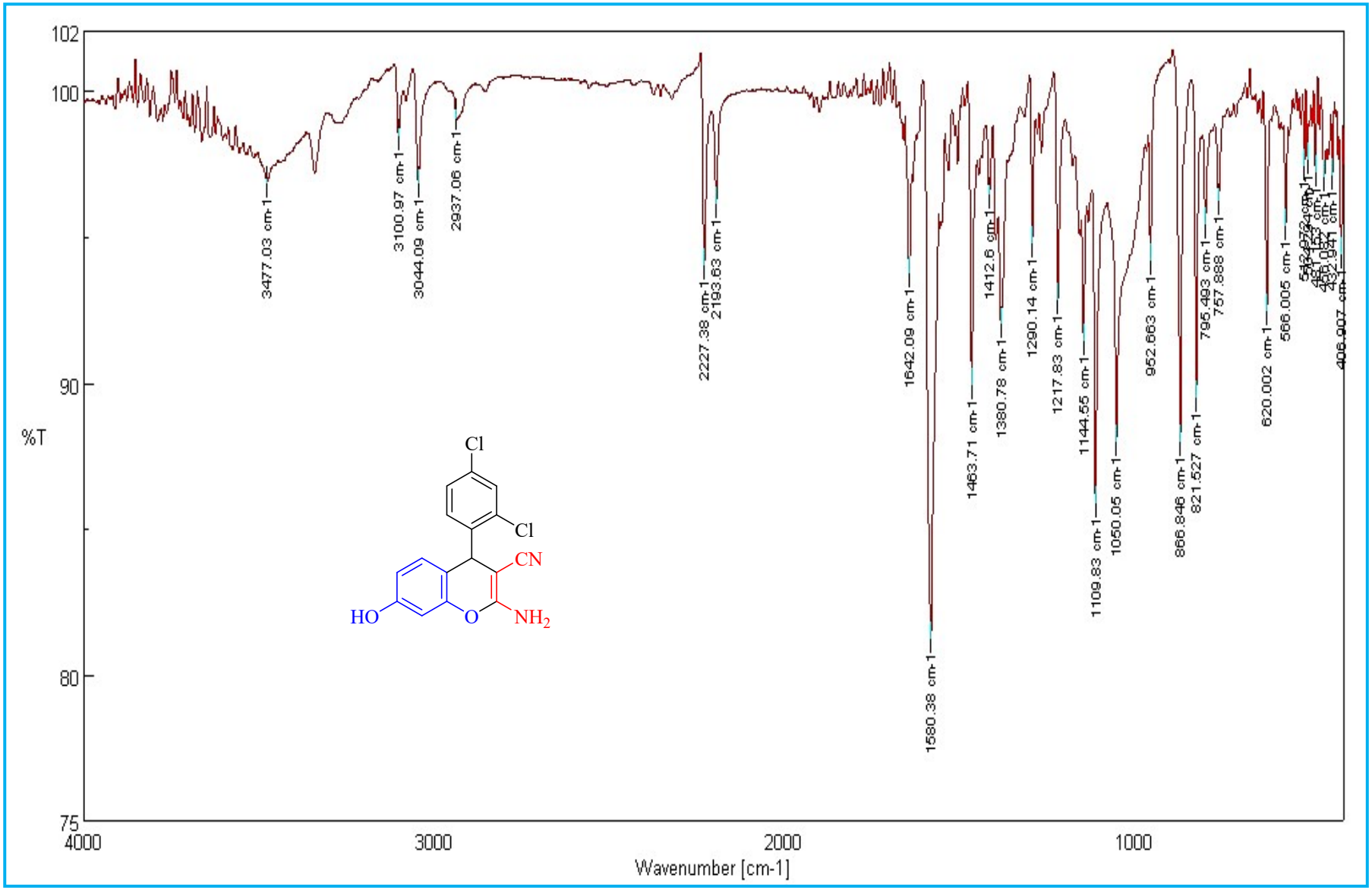
FT-IR spectrum of 2-Amino-4-(4-chlorophenyl)-7-hydroxy-4*H*-chromene-3-carbonitrile (6b)



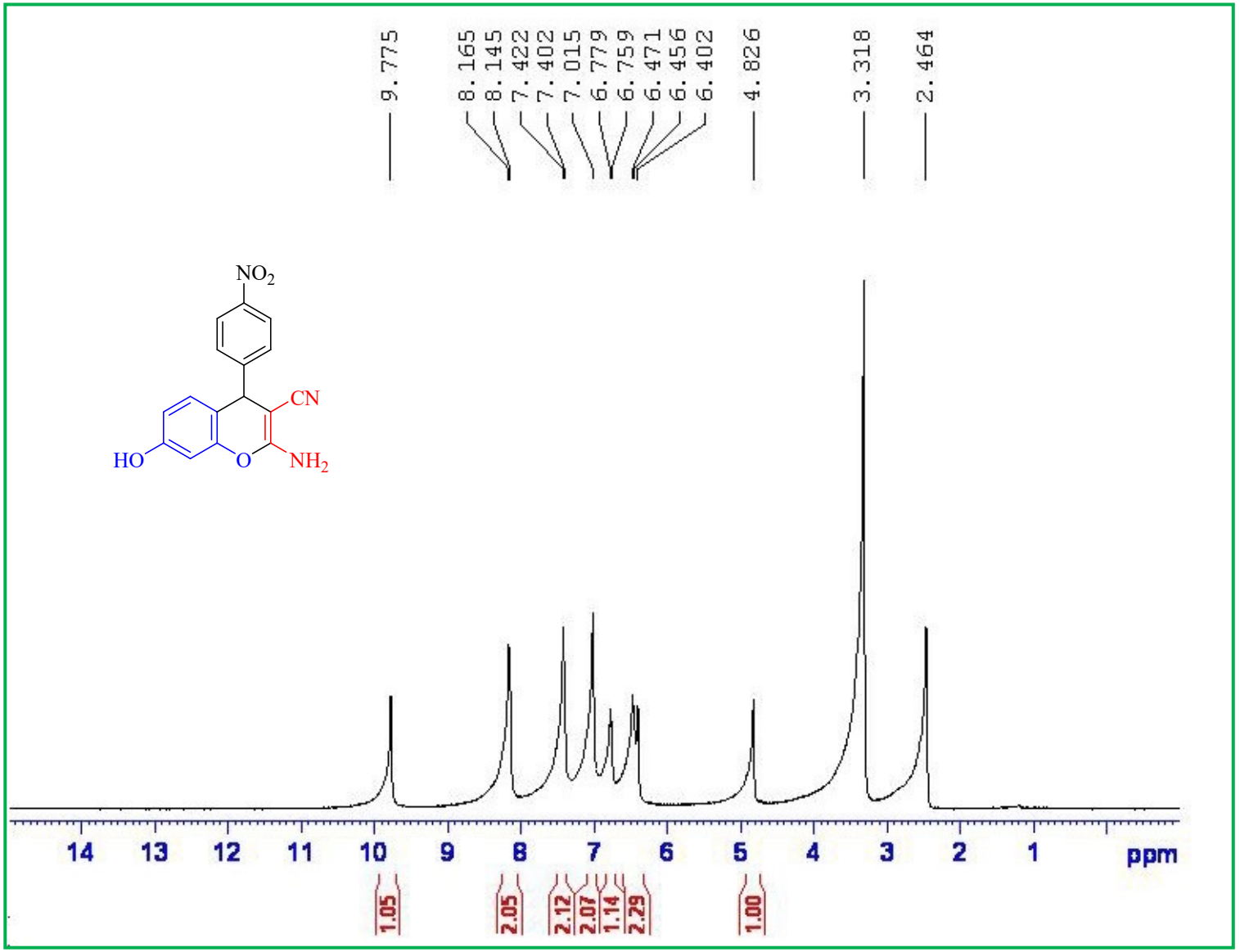
^{1}H NMR spectrum of 2-Amino-4-(2,4-dichlorophenyl)-7-hydroxy-4*H*-chromene-3-carbonitrile (6c)



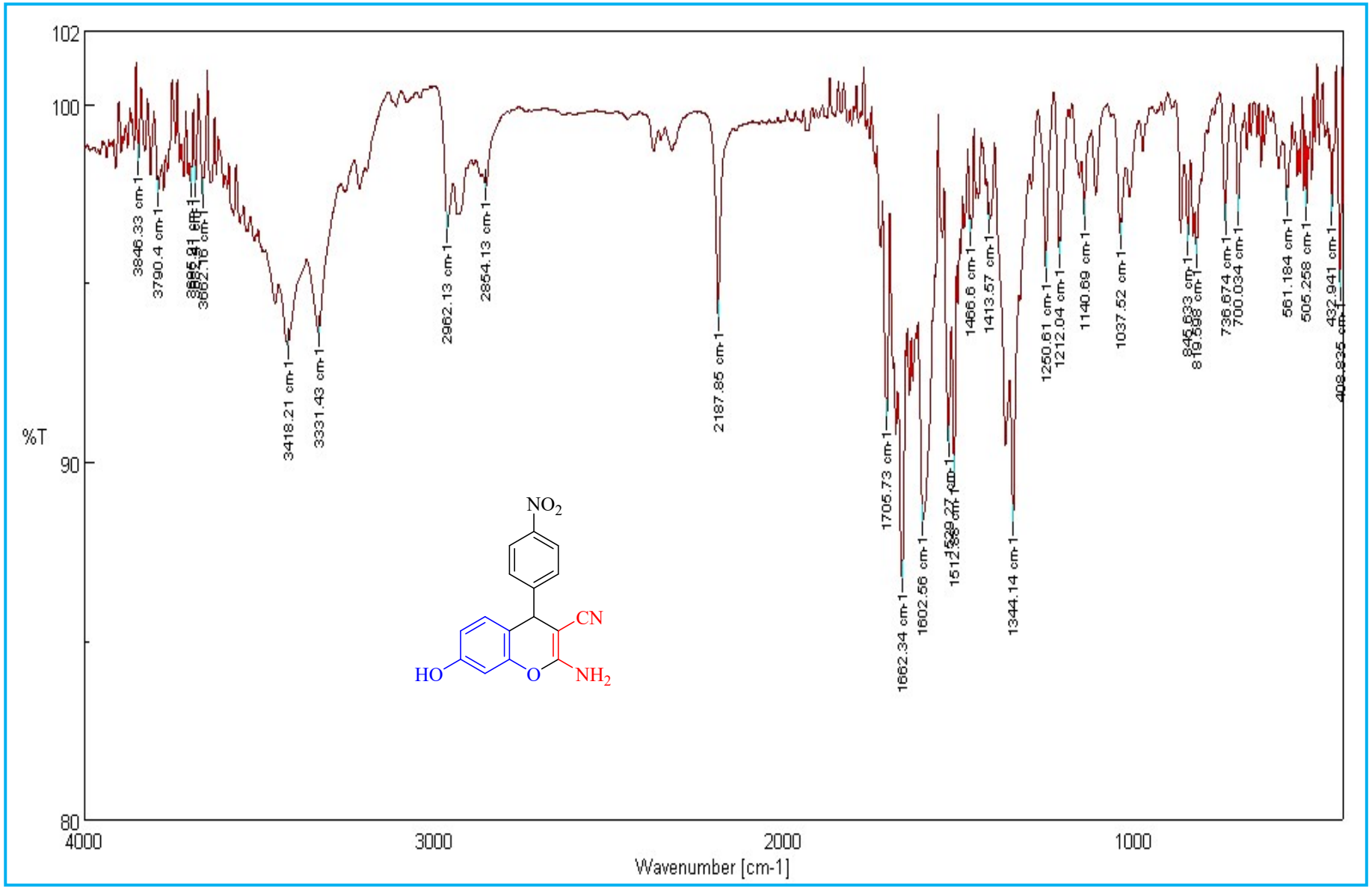
FT-IR spectrum of 2-Amino-4-(2,4-dichlorophenyl)-7-hydroxy-4*H*-chromene-3-carbonitrile (6c)



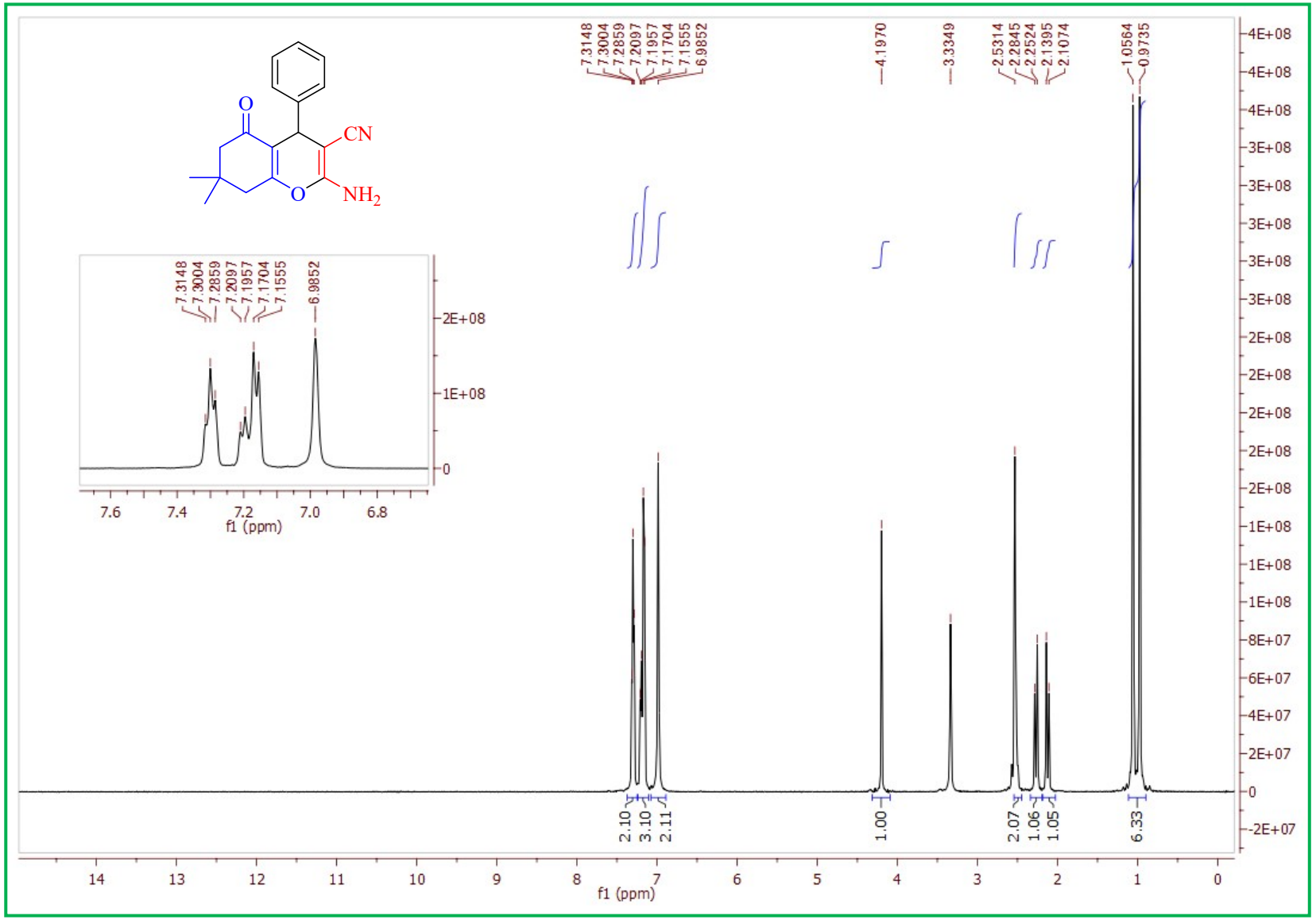
^{1}H NMR spectrum of 2-Amino-7-hydroxy-4-(4-nitrophenyl)-4*H*-chromene-3-carbonitrile (6f)



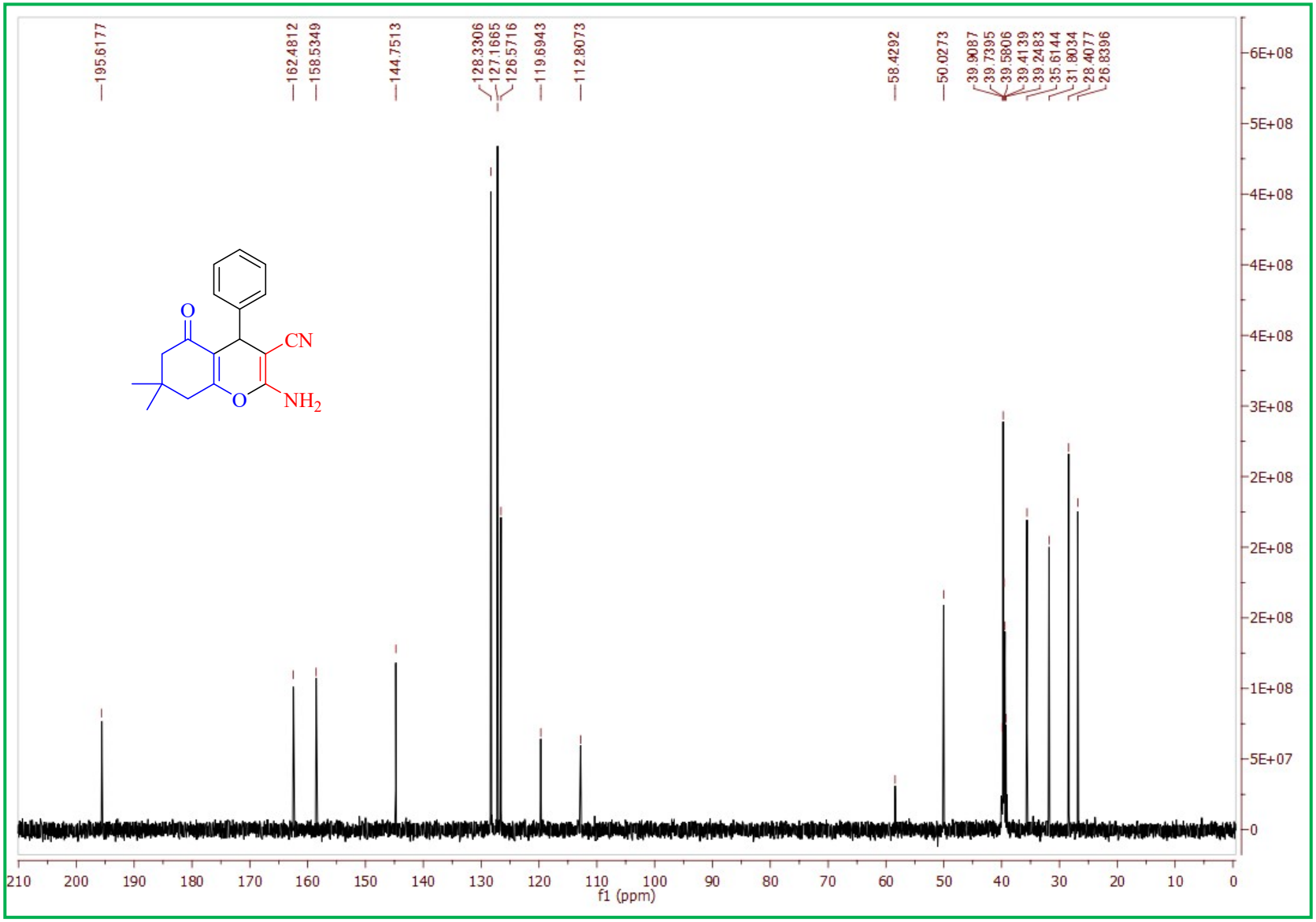
FT-IR spectrum of 2-Amino-7-hydroxy-4-(4-nitrophenyl)-4*H*-chromene-3-carbonitrile (6f)



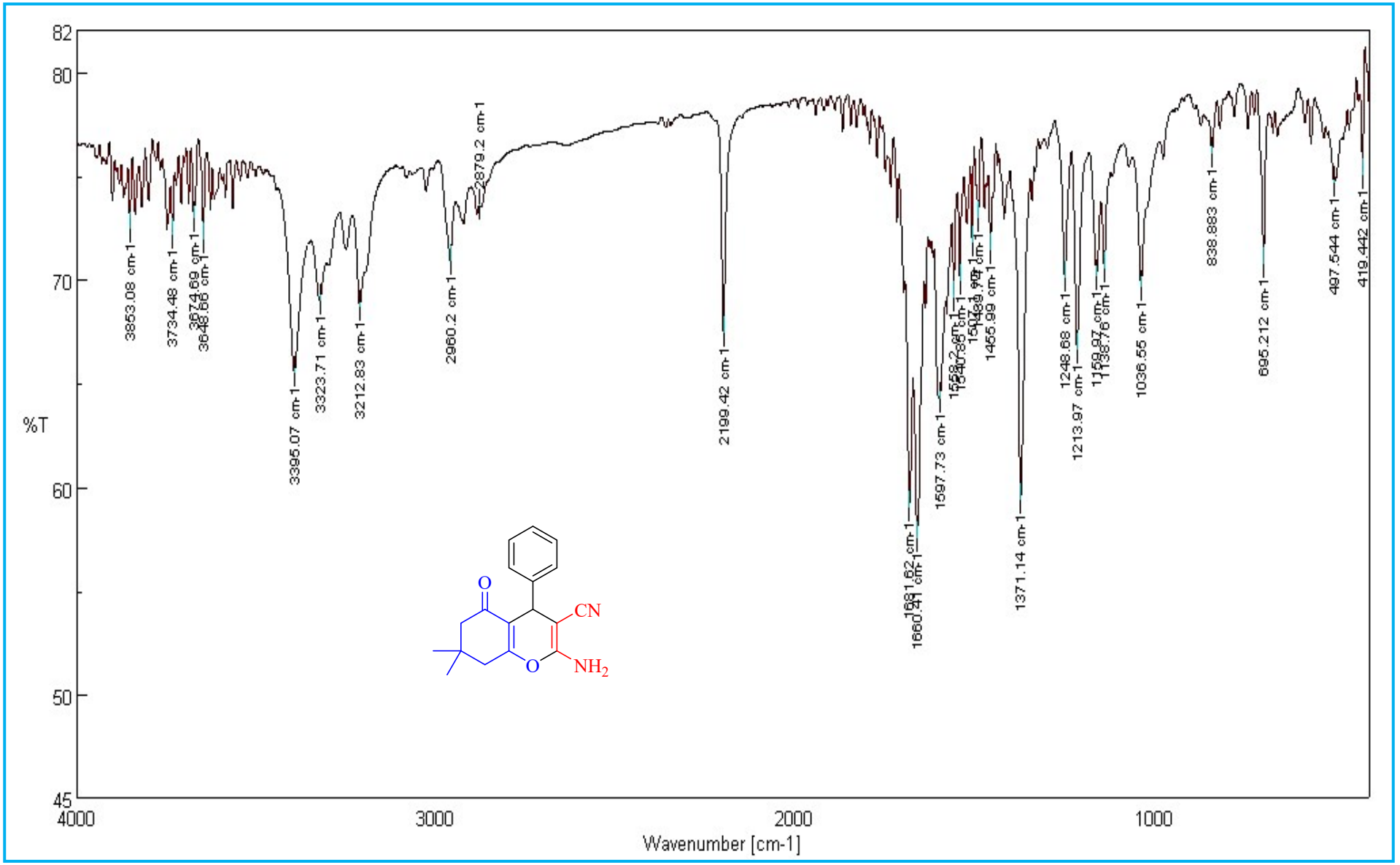
^{1}H NMR spectrum of 2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (7a)



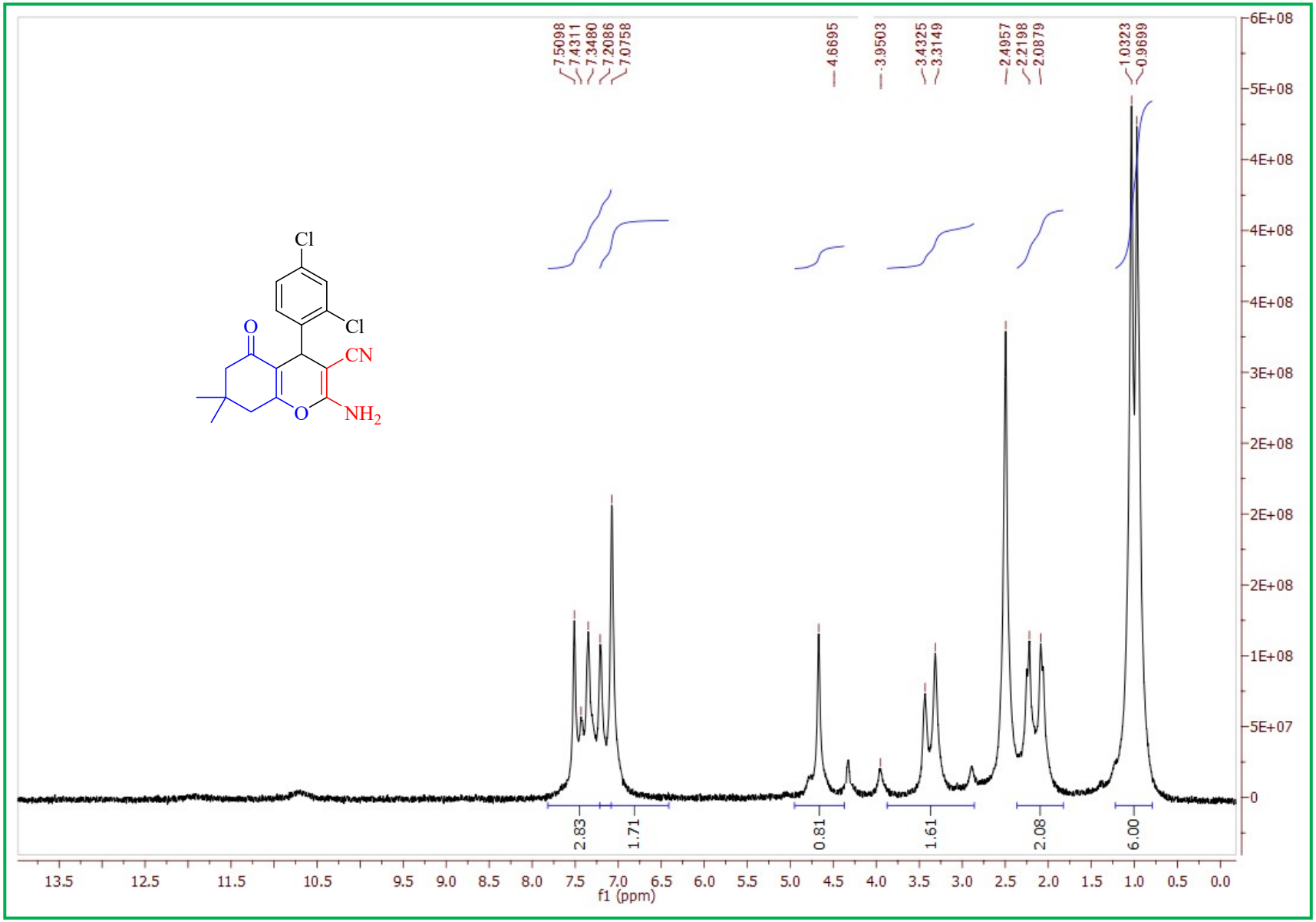
^{13}C NMR spectrum of 2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (7a)



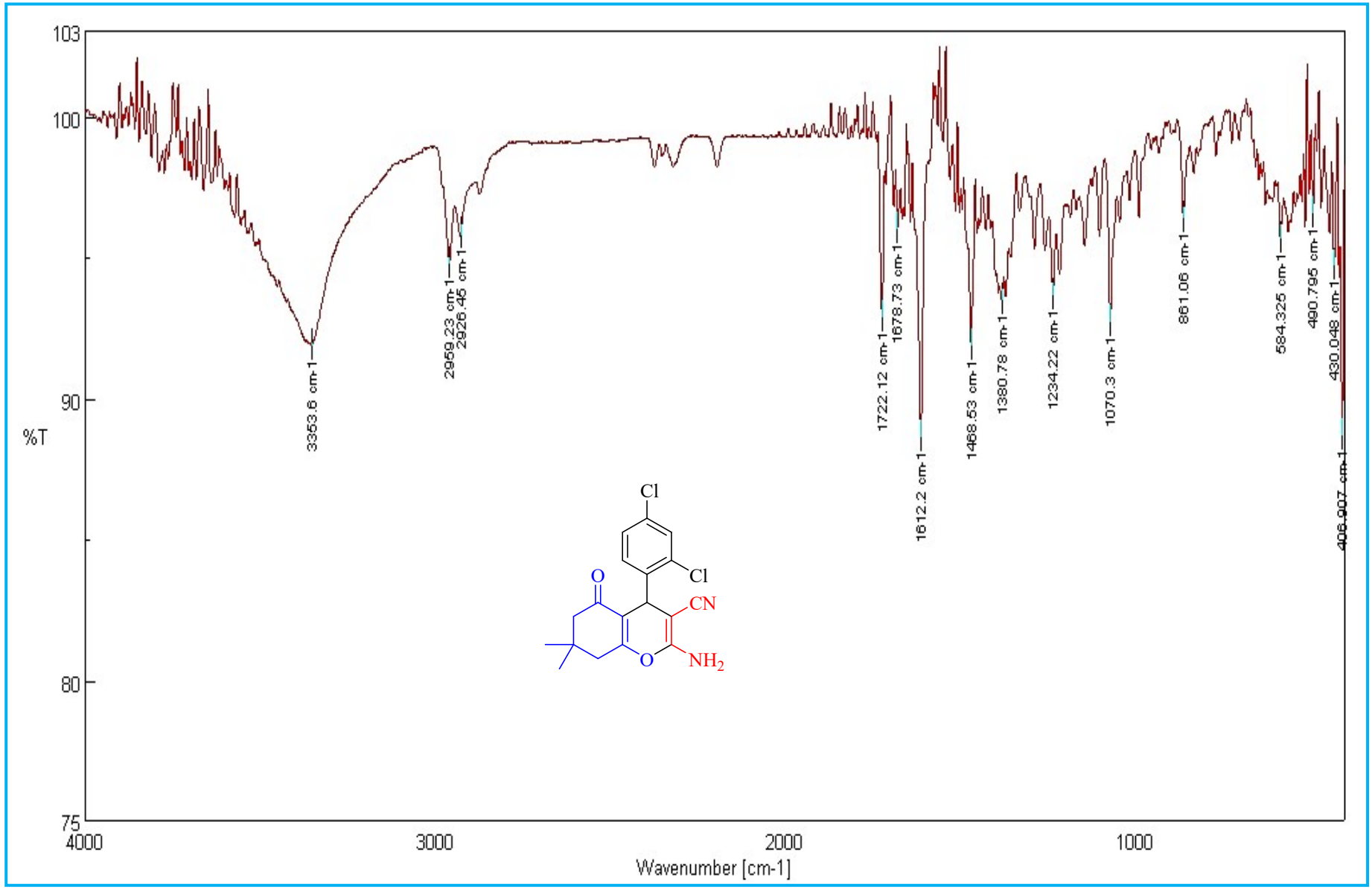
FT-IR spectrum of 2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (7a)



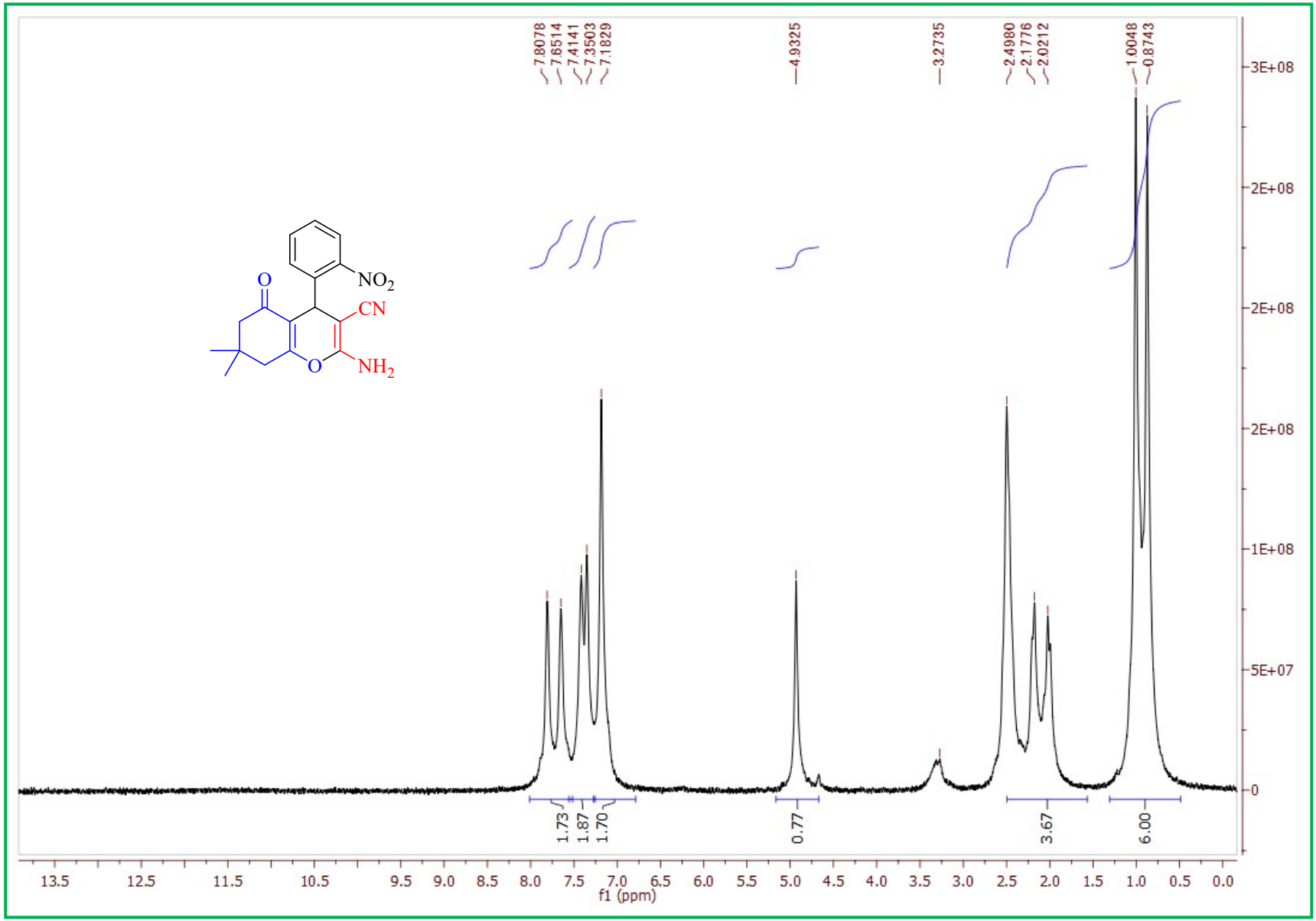
^{1}H NMR spectrum of 2-amino-4-(2,4-dichlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (7c)



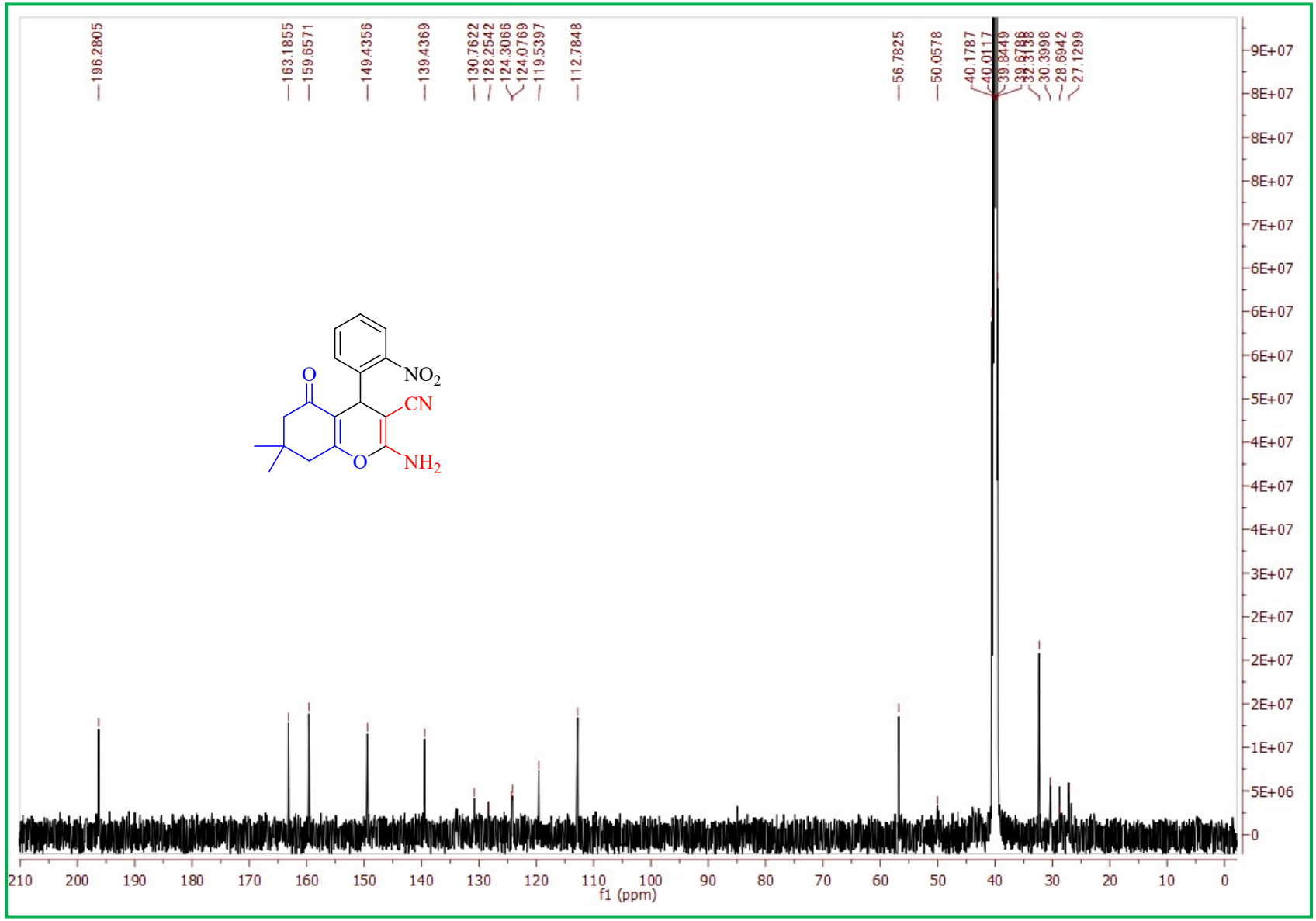
FT-IR spectrum of 2-amino-4-(2,4-dichlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (7c)



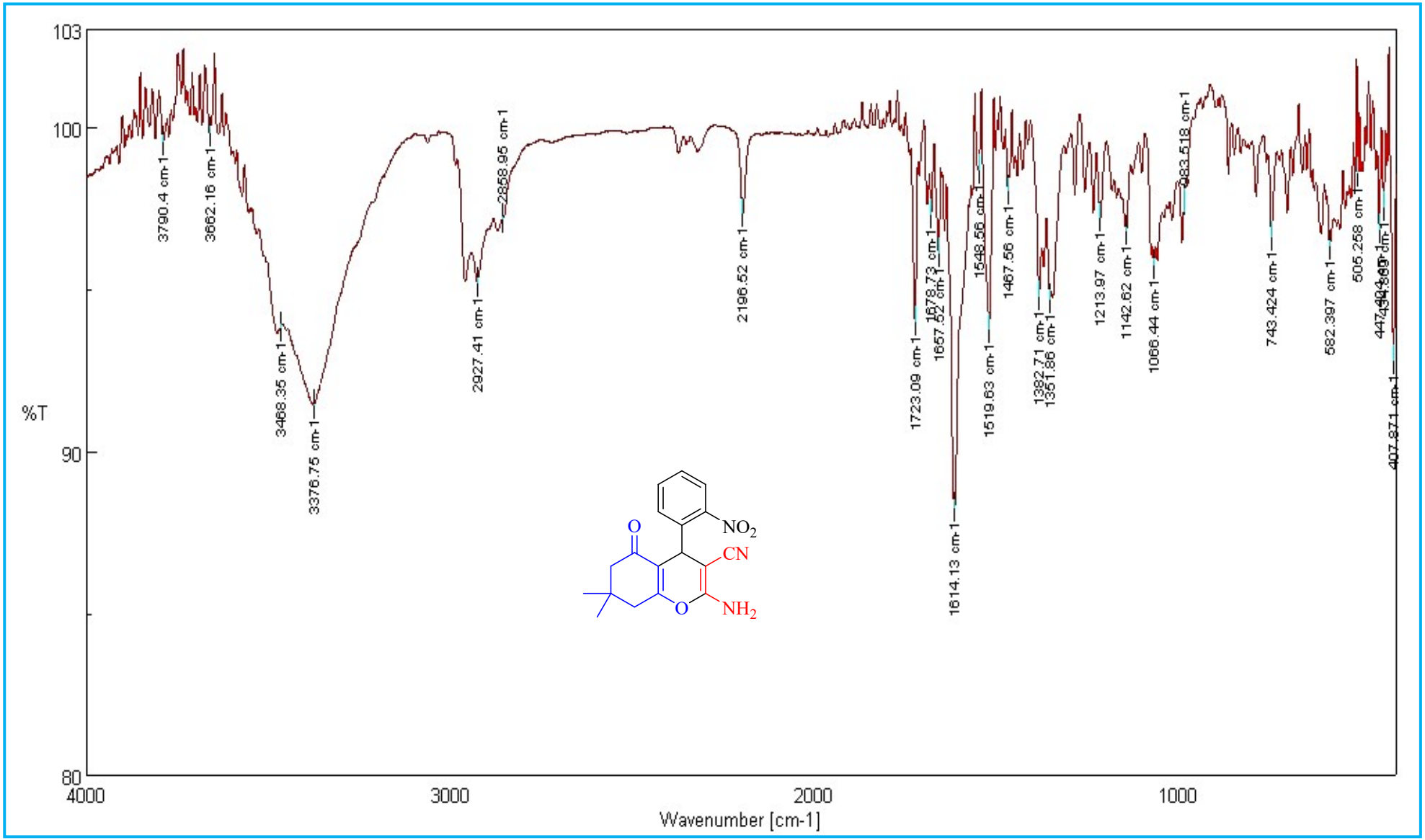
^{1}H NMR spectrum of 2-Amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (7d)



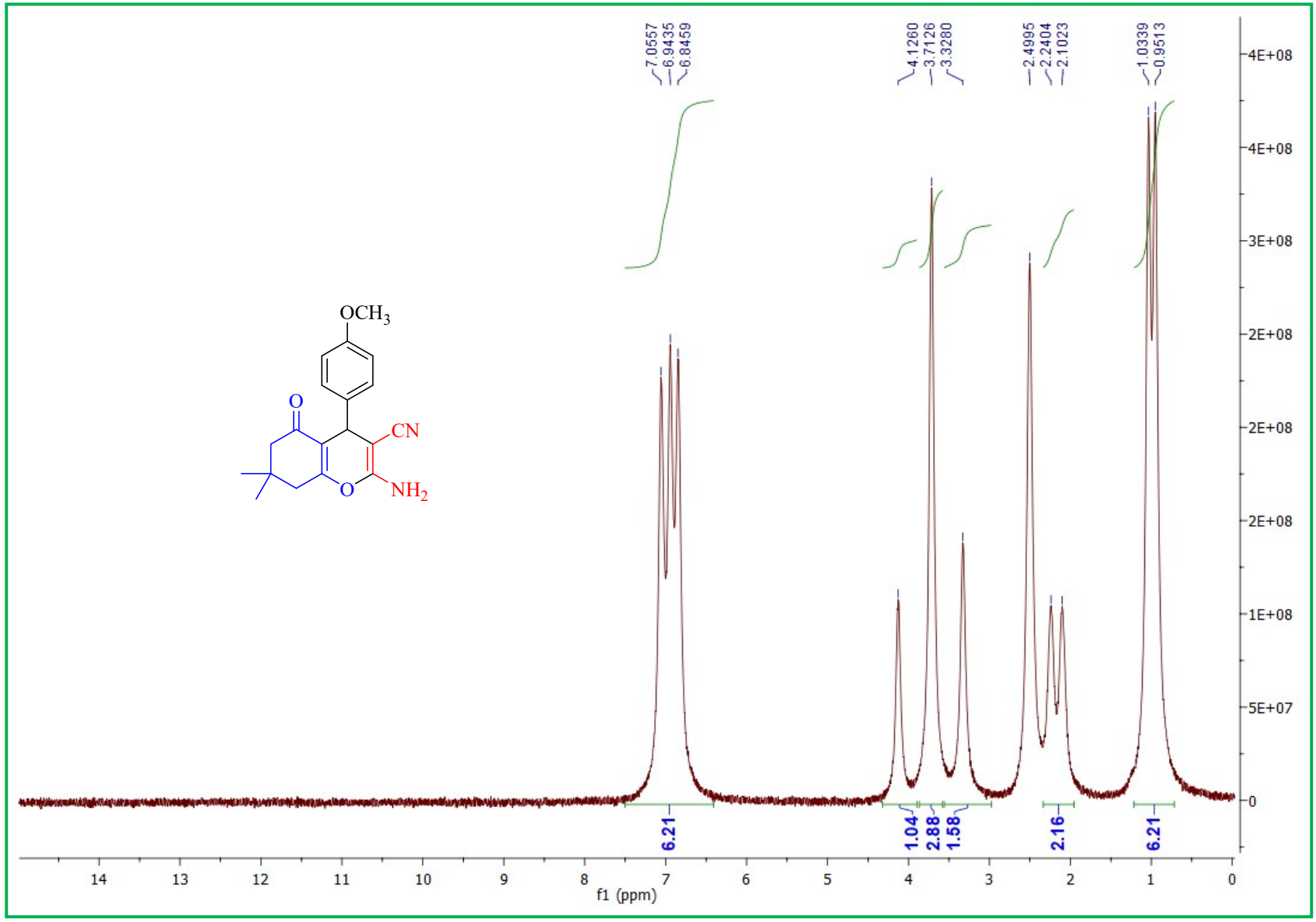
^{13}C NMR spectrum of 2-Amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (7d)



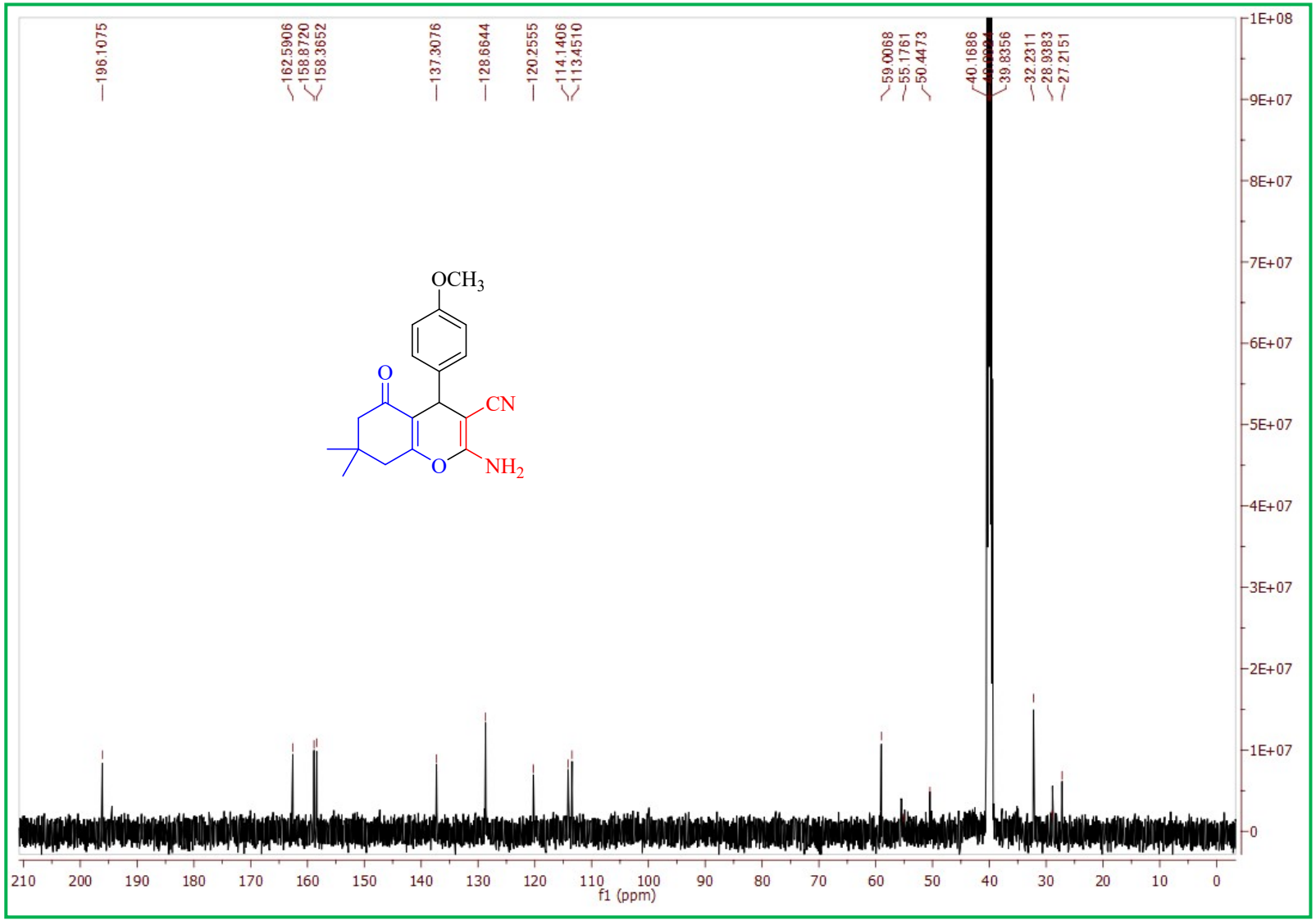
FT-IR spectrum of 2-Amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (7d)



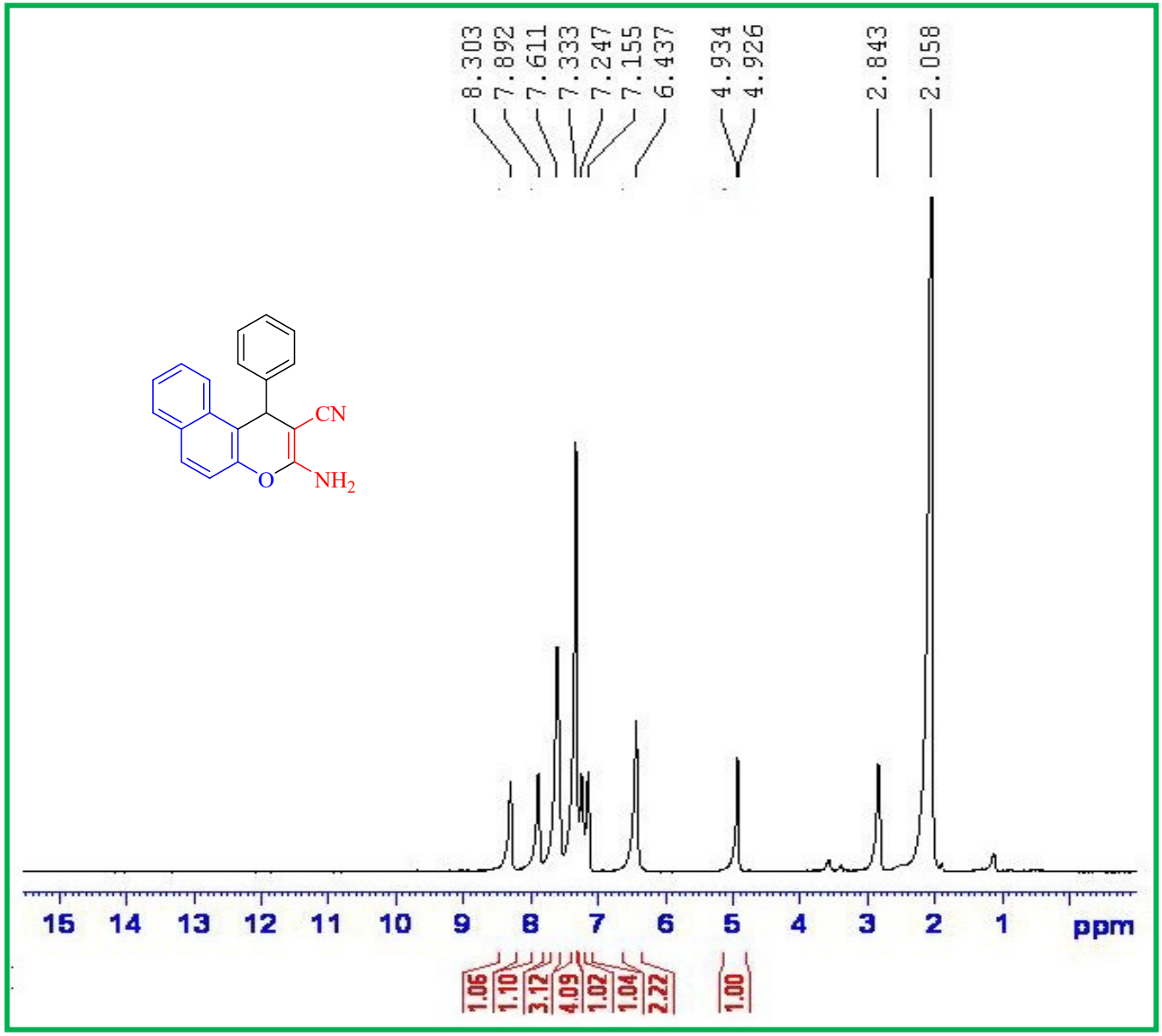
^{1}H NMR spectrum of 2-amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7f)



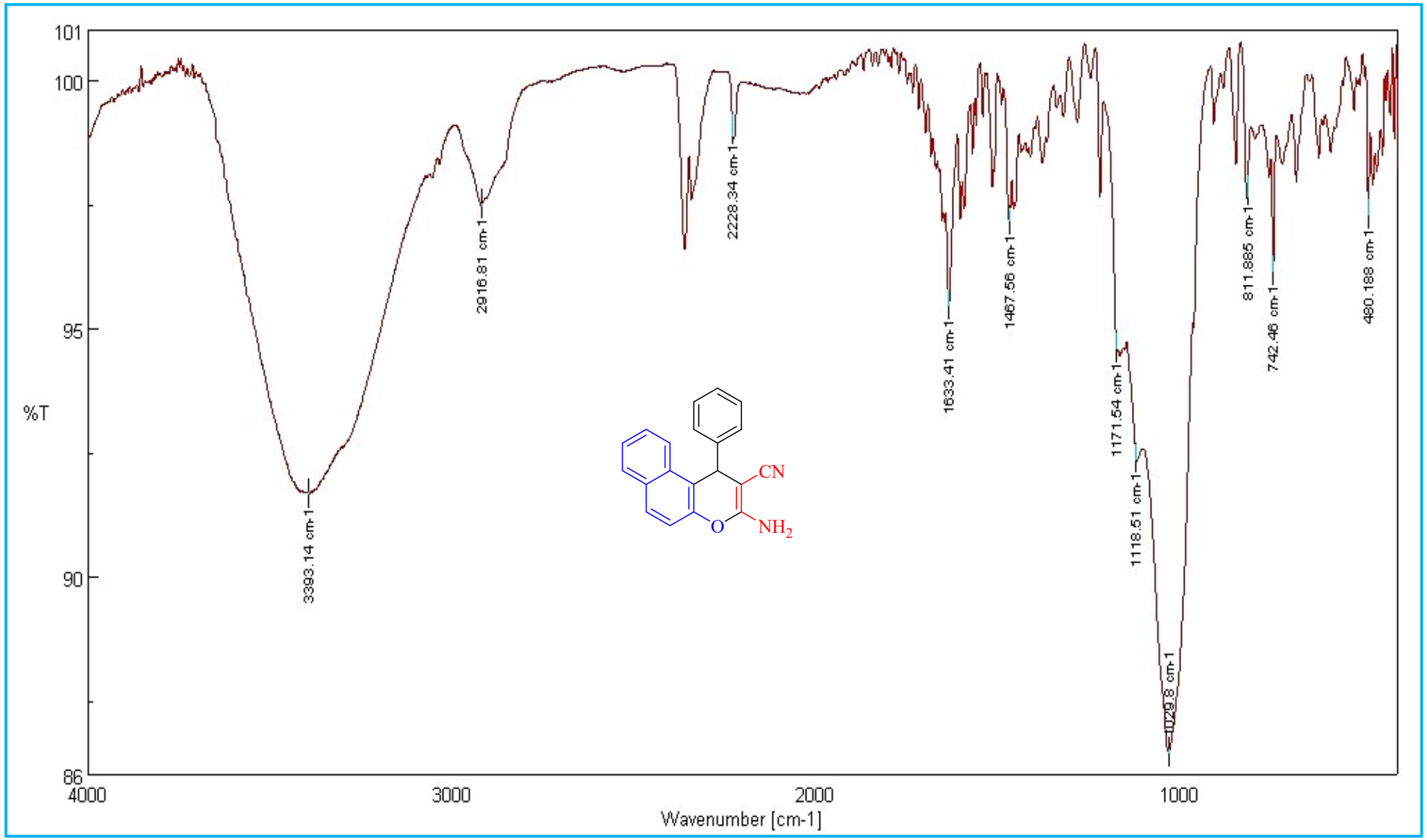
^{13}C NMR spectrum of 2-amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7f)



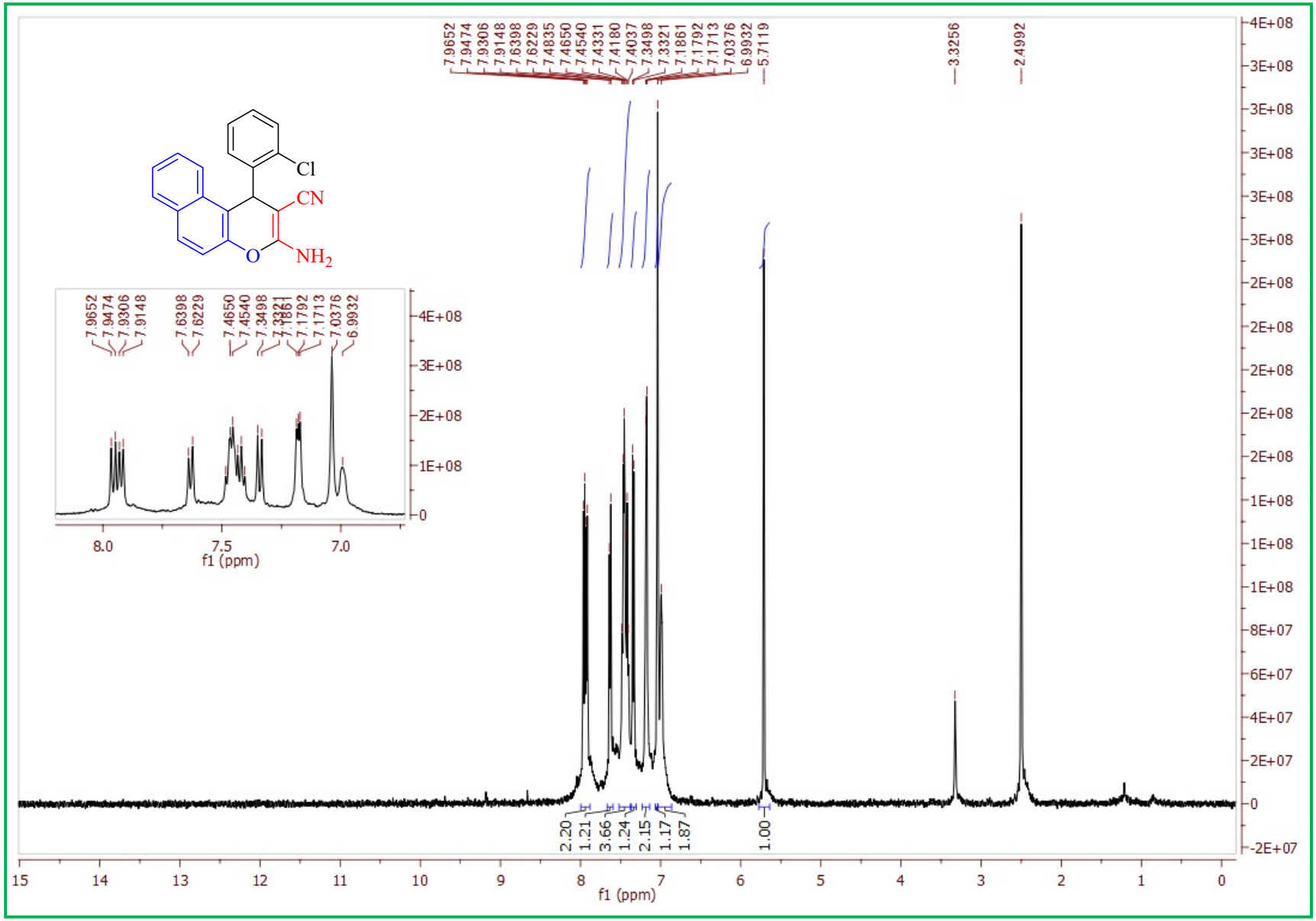
^{1}H NMR spectrum of 3-Amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile (8a)



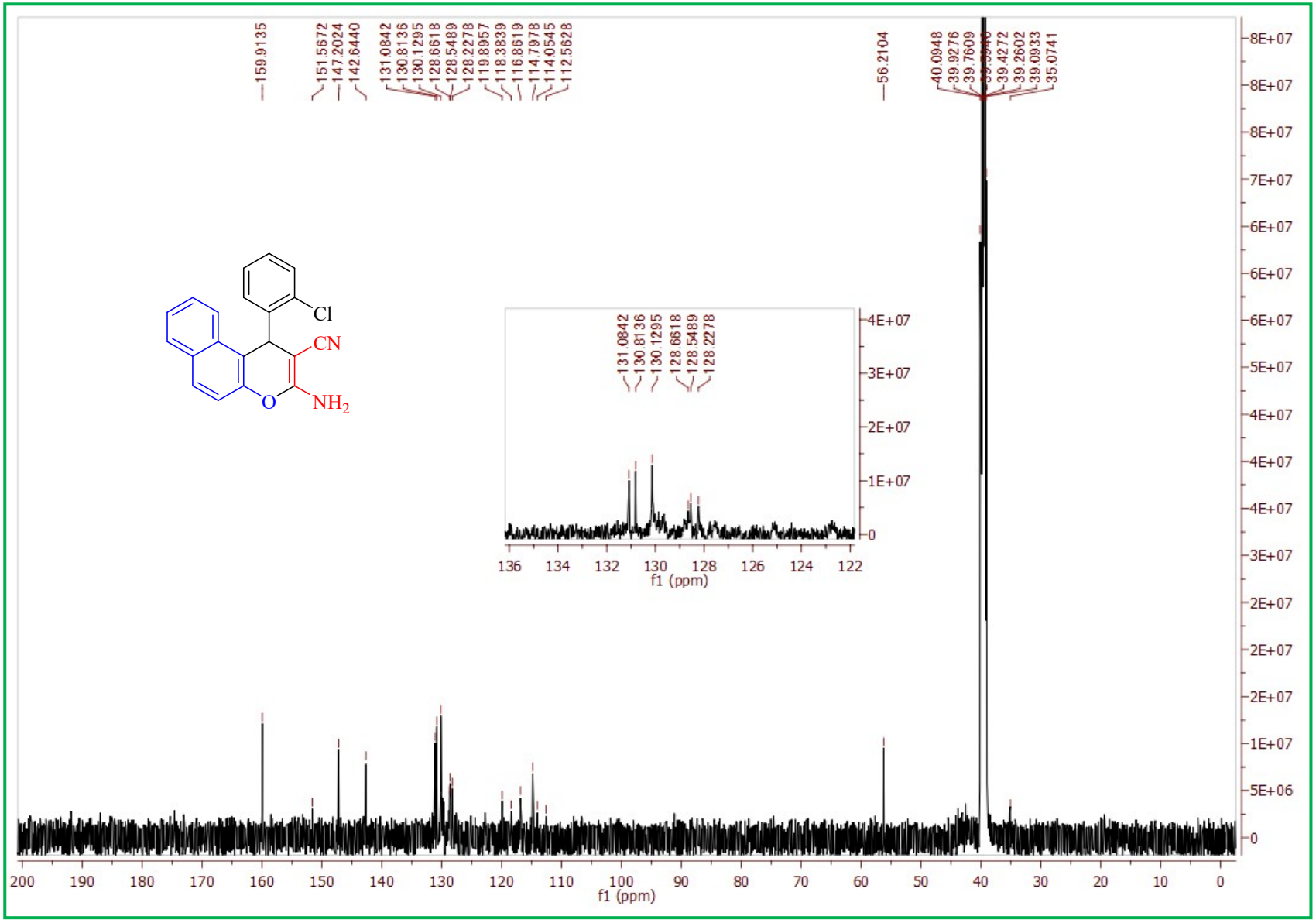
FT-IR spectrum of 3-Amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile (8a)



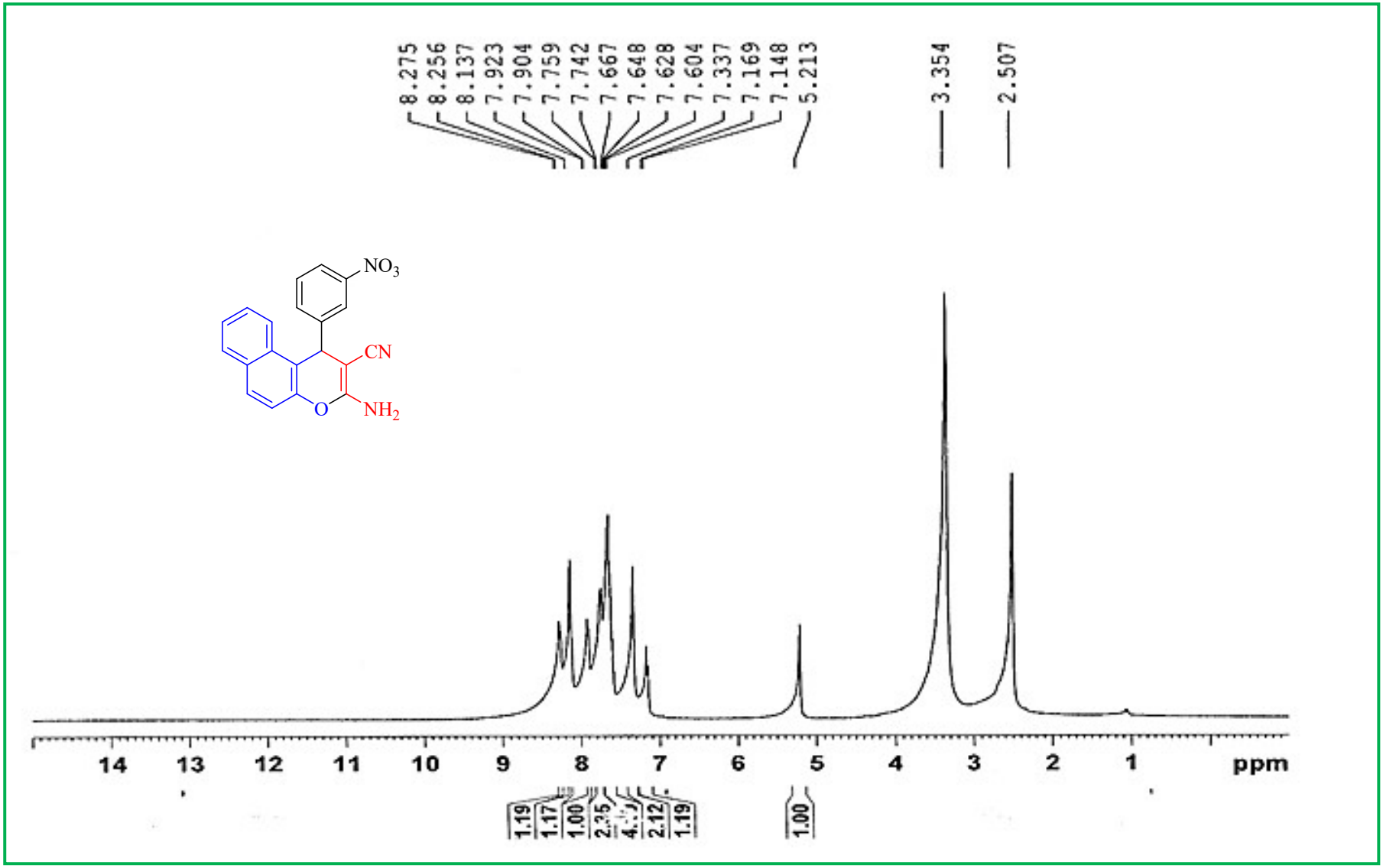
^{1}H NMR spectrum of 3-Amino-1-(2-chlorophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (8b)



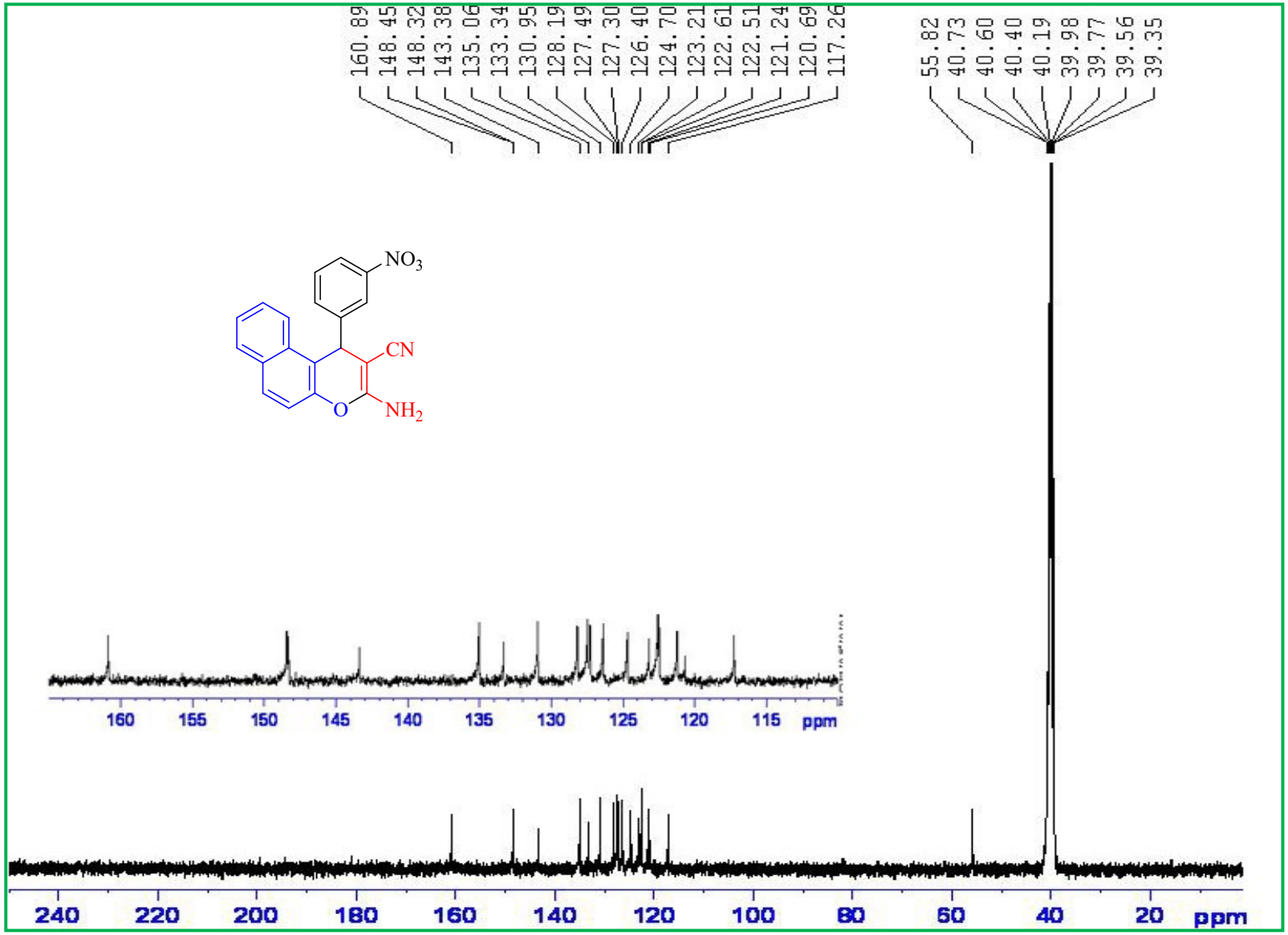
^{13}C NMR spectrum of 3-Amino-1-(2-chlorophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (8b)



^{1}H NMR spectrum of 3-Amino-1-(3-nitrophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (8c)



^{13}C NMR spectrum of 3-Amino-1-(3-nitrophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (8c)



FT-IR spectrum of 3-Amino-1-(3-nitrophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (8c)