Aegle marmelos in heterocyclization: greener, highly efficient, one-pot three-component protocol for synthesis of highly functionalized 4*H*-benzochromenes and 4*H*-chromenes

Sachin Shinde[a], Shashikant Damte [a], Smita Morbale[a], Megha Patil[a], and Suresh S. Patil [a*]

Synthetic Research Laboratory, PG Department of Chemistry, P.D.V.P. College, Tasgaon,

Dist. Sangli,- 416312, Affiliated to Shivaji University, Kolhapur-416004-India.

*Email: sanyujapatil@yahoo.com

Supporting Information

INDEX

Preparation of catalyst

For the preparation of BFE, rind dry *Aeglemarmelos* (Bael) fruits were obtained from the local area and species were authenticated by the Department of Botany. The dry rinds (100 g) were broken into small pieces manually and thermally treated at 900^{o}C to obtain fine soft ash (5.3 g). This ash was then suspended in distilled water (25 mL) in conical flask and carefully stirred for 1 hr at room temperature. The mixture was then filtered to get clear extract which was denominated as BFE. The pH of extracts was measured using pH-meter (*ProLab 3000* laboratory pH meter) and it was found to be strongly alkaline with pH 12.6.

Typical procedure for the preparation of 2-amino-4-(4-chlorophenyl)-4*H*-[*h*]chromene (4d) (Table2, entry 4):

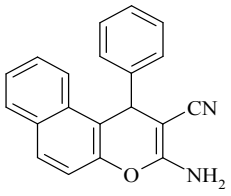
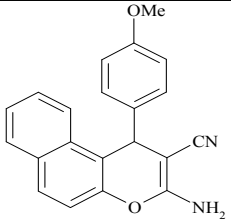
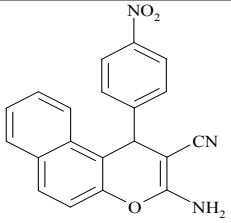
In a typical procedure, 25ml round-bottom flask was charged with a mixture of 4-chlorobenzaldehyde (0.140g,1 mmol), malononitrile (0.066g, 1 mmol), β-naphthol (0.144g, 1 mmol) and ethanol (5 mL) and was stirred thoroughly in the presence of BFE (3 mL) at ambient temperature till the completion of reaction as indicated by TLC (ethylacetate:hexane 2:8). After completion of the reaction, the reaction mixture was filtered, and the crude product was further purified by recrystalization from 96 % ethanol. The filtrate was extracted with ethyl acetate and then applied for next run for to check the recyclability of catalyst under the same reaction conditions. The

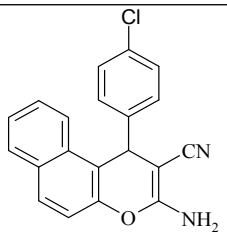
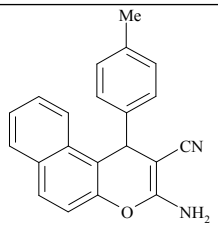
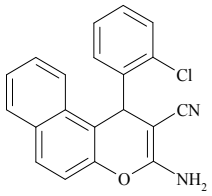
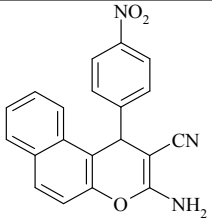
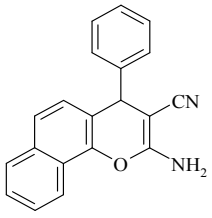
identity of the compound was ascertained on the basis of ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy.

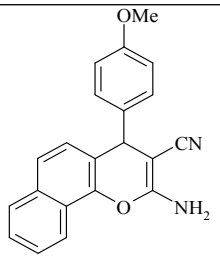
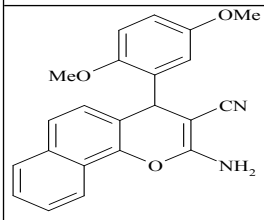
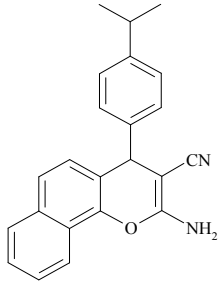
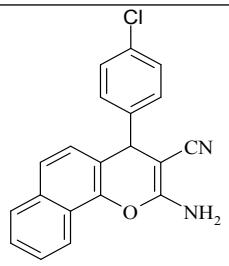
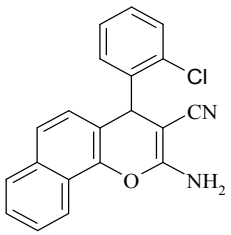
4.3 Typical procedure for the preparation of (2-amino-3-cyano-4*H*-benzochromen-4-yl) propane dinitrile (7d) (Table 3, entry 4):

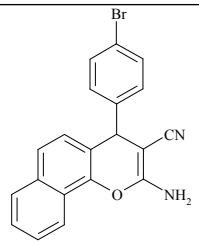
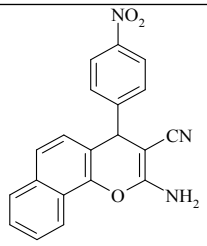
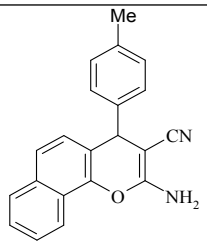
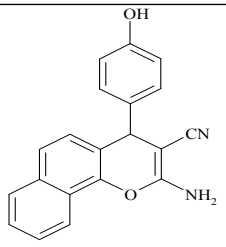
In a typical procedure, 25 ml round-bottom flask was charged with a mixture of 5-chlorosalialdehyde (0.156g,1 mmol), malononitrile (0.132g, 2 mmol) and ethanol (5 mL) and was stirred thoroughly in the presence of BFE (3 mL) at room temperature till the completion of reaction as indicated by TLC (ethylacetate:hexane 2:8). After completion of the reaction, the reaction mixture was filtered, and the crude product was further purified by recrystallization from 96 % ethanol. The identity of the compound was ascertained based on ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy.

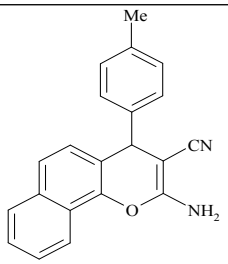
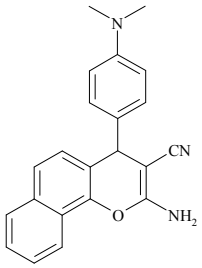
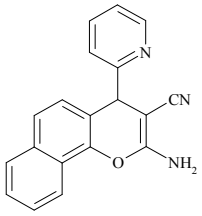
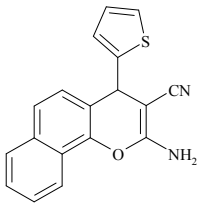
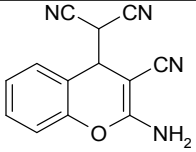
-**S2-S34**-

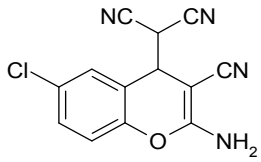
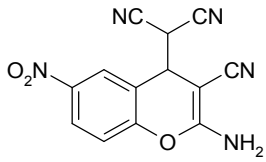
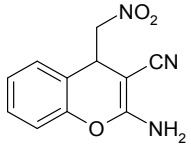
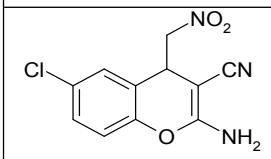
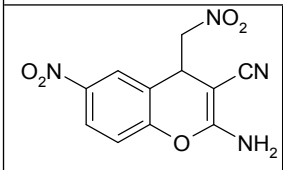
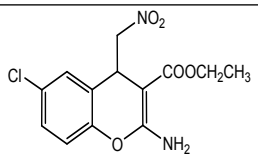
2-Amino-4-(phenyl)-4H-benzo[h]chromene-3-carbonitrile (4a)	
 -S2-	IR (KBr) ν_{max}/cm^{-1}:3431 and 3338 (NH_2), 2182 (CN),1661, 1576, 1423 (Ar-C=C) cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$/TMS):δ = 2.67 (s, 2H, NH_2), 4.72 (s, 1H, CH), 6.83 (d, 1H, ArH), 7.17-7.22 (m, 5H, ArH), 7.60-7.64 (m, 3H, ArH), 7.44 (d, 1H, *J* = 8.4, ArH), 7.67 (d, 1H, *J* = 8.4, ArH) ; ^{13}C NMR(75 MHz,$CDCl_3$):δ = 29.8, 60.3, 118.5, 119.4, 120.6, 122.3, 122.5, 122.6, 123.2, 123.5, 124.2, 124.4, 126.5, 137.5, 140.4, 162.6, 178.6 ppm.
2-Amino-4-(4-methoxyphenyl)-4H-benzo[h]chromene-3-carbonitrile (4b)	
 -S3-	IR (KBr) ν_{max}/cm^{-1}: 3417 and 3312 (NH2), 2245 (CN), 1680, 1580, 1410 cm^{-1}; ^{1}H NMR(300 MHz,$CDCl_3$/TMS): δ = 2.16 (s, 2H, NH_2),3.85 (s, 3, CH_3) 4.67 (s, 1H, CH), 6.89 (d, 1H, ArH), 7.66 (d, 2H, ArH), 7.30 (d, 2H, ArH), 7.51-7.45 (m, 3H, ArH), 7.89 (d, 1H, ArH), 7.98 (d, 1H, ArH) ;^{13}C NMR(75 MHz,$CDCl_3$): δ = 39.8, 53.2, 64.3, 115.4, 118.5, 120.6, 121.4,123.2, 124.5, 124.8, 128.2, 129.6, 129.8, 133.4, 136.5, 141.2, 158.4, 179.6 ppm.
2-Amino-4-4-(nitrophenyl)-4H-benzo[h]chromene-3-carbonitrile (4c)	
 -S4-	IR (KBr) ν_{max}/cm^{-1}:3450 and 3355 (NH_2), 2189 (CN), 1680, 1564 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$/TMS):δ 4.26 (s, 2H, NH_2), 5.84 (s, 1H, CH), 7.12 (d, 1H, ArH), 7.10-7.18 (m, 2H, ArH), 7.46-7.53 (m, 2H, ArH),7.53-7.79 (m, 3H, ArH),7.79 (d, 1H, ArH), 8.28 (d, 1H, ArH) ;^{13}C NMR(75 MHz,$CDCl_3$): 29.8, 59.3, 117.5, 120.6, 120.4, 121.1, 124.6,125.5, 125.6, 126.4, 126.5, 127.4, 127.5, 120.4, 143.5, 143.6, 145.5, 178.4 ppm.
2-Amino-4-(4-chlorophenyl)-4H-benzo[h]chromene-3-carbonitrile (4d)	

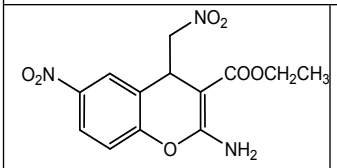
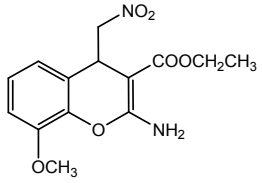
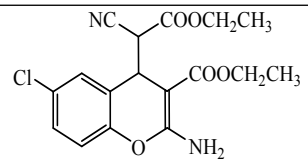
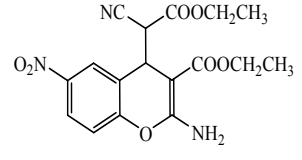
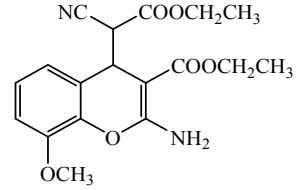
 -S5-	IR (KBr) ν_{max}/cm^{-1}:3454 and 3345 (NH_2) , 2181 (CN), 1665, 1574 cm^{-1} ; ^{1}H NMR (300 MHz,$CDCl_3$/TMS):δ 5.04 (s, 1H, CH), 7.16 (s, 2H, NH2), 7.31-7.33 (m, 1H, ArH), 7.42-7.45 (m, 1H, ArH), 7.54 (d, 2H, ArH), 7.65-7.79 (m, 4H, ArH), 7.85 (d, 2H, ArH) ;^{13}C NMR(75 MHz,$CDCl_3$): 40.7, 60.4,118.3, 119.5, 121.4,123.4, 124.6, 125.5, 126.3, 127.9, 128.6, 129.6, 131.5, 130.4, 134.6, 142.2,145.6, 210.4 ppm.
2-Amino-4-(4-methylphenyl)-4H-benzo[h]chromene-3-carbonitrile (4e)	
 -S6-	IR (KBr) ν_{max}/cm^{-1}:3478 and 3365 (NH_2), 2192 (CN), 1635, 1574 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$/TMS):δ 2.34 (s, 3H, CH_3),δ 4.04 (s, 1H, CH), 7.16 (s, 2H, NH2), 7.31-7.33 (m, 1H, ArH), 7.42-7.45 (m, 1H, ArH), 7.54 (d, 2H, ArH), 7.65-7.79 (m, 4H, ArH), 7.85 (d, 2H, ArH) ;^{13}C NMR(75 MHz,$CDCl_3$): 17.7,24.5, 59.4, 127.3, 127.5, 128.6, 129.2, 129.5, 129.4, 131.4, 132.4, 134.6,143.2,145.5, 145.6,152.6, 175.9, 189.3 ppm.
2-Amino-4-(2-chlorophenyl)-4H-benzo[h]chromene-3-carbonitrile (4f)	
 -S7-	IR (KBr) ν_{max}/cm^{-1}:3268 and 3345 (NH_2), 2198 (CN), 1633, 1544 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$/TMS):δ 6.59 (2H, s, NH_2), 4.02 (s, 1H, CH), 7.48-7.59 (3H, m, ArH), 7.11 (4H,s, ArH), 7.01-7.04 (1H, d, ArH), 7.76-7.79 (1H, d, ArH), 7.15-7.18 (1H, d, ArH); ^{13}C NMR(75 MHz,$CDCl_3$):17.7, 59.4,145.5, 132.4, 128.6, 127.5, 127.3, 175.9, 152.6, 118.3, 119.6, 128.3,128.3, 126.3, 129.3, 133.4,145.8, 179.5 ppm.
2-Amino-4-(4-nitrophenyl)-4H-benzo-[h] chromene-3-carbonitrile (4c)	
 -S8-	IR (KBr) ν_{max}/cm^{-1}:3568 and 3456 (NH_2), 2235 (CN), 1656, 1535cm^{-1}; ^{1}H NMR(300 MHz,$CDCl_3$):δ 4.76 (s, 2H, NH_2), 4.34 (s, 1H, CH), 7.22 (d, 1H, Ar-H), 7.34-7.39 (m, 2H, Ar-H), 7.56-7.67 (m, 2H, Ar-H),7.63-7.69 (m, 3H, Ar-H),7.89 (d, 1H, Ar-H), 8.38 (d, 1H, Ar-H) ;^{13}C NMR(75 MHz,$CDCl_3$): 34.8, 67.3, 119.5, 122.4, 124.6, 125.1, 125.6, 126.5, 126.6, 127.4, 127.5, 128.4, 128.5, 129.4, 146.5, 155.5, 167.4.189.4 ppm.
2-Amino-4-(phenyl)-4H-benzo[f]chromene-3-carbonitrile (5a)	
 -S9-	IR (KBr) ν_{max}/cm^{-1}:3449 and 3315(NH_2), 2203 (CN),1652, 1452, 1404 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$):δ= 4.74 (s, 2H, NH_2), 4.82 (s, 1H, CH), 6.03 (d, 1H, Ar-H), 7.36-7.42 (m, 5H, ArH), 7.65-7.69 (m, 3H, ArH), 8.94 (d, 1H, *J* = 8.4, ArH), 8.53 (d, 1H, *J* = 8.4, ArH) ; ^{13}C NMR(75 MHz,$CDCl_3$): 30.8, 62.3, 119.5, 123.4, 122.6, 123.1, 134.6, 135.5, 123.5, 126.6, 127.4, 128.2, 129.4,129.5, 130.5, 144.5, 149.4, 180.4 ppm.
2-Amino-4-(4-methoxyphenyl)-4H-benzo[f]chromene-3-carbonitrile (5b)	

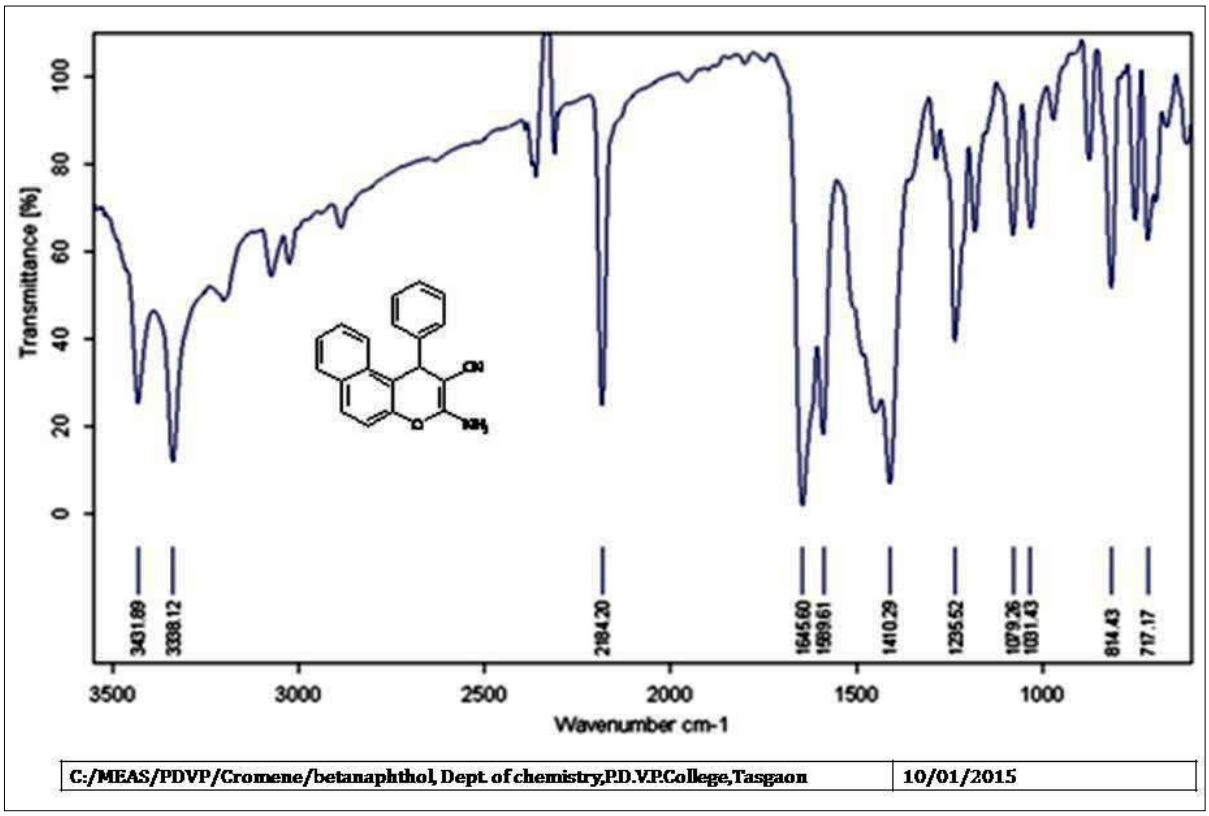
 -S10-	IR (KBr) ν_{max}/cm^{-1}:3478 and 3367 (NH_2), 2192 (CN), 1653, 1594 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$/TMS):δ 3.75 (s, 3H, CH_3O), 4.85(s, 2H, NH_2), 5.02 (s,1H,CH), 6.83 (d, 1H, ArH), 7.33 (d, *J*=8.7 Hz, 2H, ArH), 7.42 (d, *J*=8.7 Hz, 2H, ArH), 7.50-7.58 (m, 3H, ArH), 7.80 (d, 1H, ArH), 8.20 (d, 1H, ArH); ^{13}C NMR(75 MHz,$CDCl_3$): 29.8, 59.3, 113.7, 117.5, 120.4, 120.6, 121.1, 124.6, 125.5, 125.6, 126.4, 126.5, 127.4, 127.9, 128.4, 130.3, 143.5, 153.6, 178.4 ppm.
2-Amino-4-(2,5-dimethoxyphenyl)-4H-benzo[f]chromene-3-carbonitrile (5c)	
 -S11-	IR (KBr) ν_{max}/cm^{-1}: 3438 (NH2) and 3320 (CN), 2180, 1484 cm^{-1}; ^{1}HNMR(300 MHz,$CDCl_3$/TMS): δ = 5.80 (s, 2H, NH_2), 1.87 (s, 1H, CH), 6.66 (d, 1H, ArH), 6.77 (d, 2H, ArH), 6.90 (d, 2H, ArH), 7.11-7.33 (m, 3H, ArH), 7.81 (d, 1H, ArH), 8.18 (d, 1H, ArH) ; ^{13}C NMR(75 MHz,$CDCl_3$): δ = 28.8, 56.3, 116.5,123.4, 123.6, 125.1, 126.5, 126.6, 128.5, 128.6, 129.4, 129.7,129.9, 130.5, 139.1, 139.2, 139.5, 145.5, 177.4 ppm.
2-Amino-4-(4-isopropylphenyl)-4H-benzo[f]chromene-3-carbonitrile (5d)	
 -S12-	IR (KBr) ν_{max}/cm^{-1}: 3488 (NH_2), 2960 (CN), 1661, 1550 cm$^{-1;}$ ^{1}H NMR(300 MHz,$CDCl_3$/TMS): δ = 1.6 (d, 6H, CH_3) 4.86 (s, 2H, NH_2), 4.97 (s, 1H, CH), 7.00 (d, 1H, ArH), 7.16 (d, 2H, ArH), 7.50 (d, 2H, ArH), 7.87 (d, 1H, ArH), 8.23 (d, 1H, ArH); ^{13}C NMR(75 MHz,$CDCl_3$): δ, 24.8, 55.6, 113.5, 176.4, 113.5, 118.6, 123.5, 124.4, 125.5, 126.4, 124.6, 123.6, 122.4, 120.1, 127.4, 137.5,145.6,178,9 ppm.
2-Amino-4-(4-chlorophenyl)-4H-benzo[f]chromene-3-carbonitrile (5e)	
 -S13-	IR (KBr) ν_{max}/cm^{-1}:3488 and 3334 (NH_2) , 2960 (CN), 1681cm^{-1}; ^{1}H NMR(300 MHz,$CDCl_3$/TMS): δ =4.6 (s, 1H, CH), 5.01 (s, 2H, NH2), 7.32-7.35 (m, 1H, ArH), 7.43-7.46 (m, 1H, ArH), 7.55 (d, 2H, ArH), 7.66-7.74 (m, 4H, ArH), 8.20 (d, 2H, ArH) ;^{13}C NMR(75 MHz,$CDCl_3$): δ = 40.0, 60.9,119.5, 121.4, 124.6, 125.3, 126.5, 127.9, 128.6, 131.4, 130.5, 134.6, 142.2 , 143, 210 ppm.
2-Amino-4-(2-chlorophenyl)-4H-benzo[f]chromene-3-carbonitrile (5f)	
	IR (KBr) ν_{max}/cm^{-1}:3477 and 3324 (NH_2), 2978 (CN), 1712 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$/TMS): δ = 4.05 (s, 1H, CH), δ 4.75 (s, 2H, NH_2), 7.05(d, 2H, ArH), 7.34 (d, 2H, ArH), 7.14-7.18 (m, 4H, ArH), 2.73 (d, 1H, ArH), 3.66 (d, 1H, ArH); ^{13}C NMR(75 MHz,$CDCl_3$): δ = 41.0, 62.9,120.8,121.4,122.5,122.8, 123.4,124.5,124.7, 125.6, 126.3, 127.5, 128.9, 129.6, 132.4, 133.5, 135.6, 143.2 , 144, 213 ppm.

-S14-	
2-Amino-4-(4-bromophenyl)-4H-benzo[f]chromene-3-carbonitrile (5h)	
 -S15-	IR (KBr) ν_{max}/cm^{-1}: 3471 and 3354 (NH_2) , 2184 (CN), 1680, 1408 cm^{-1}; ^{1}H NMR(300 MHz,$CDCl_3$/TMS): δ =4.9 (s, 1H, CH), 4.07 (s, 2H, NH2), 7.01-7.03 (d, 1H, ArH), 7.02 (s, 2H, ArH), 7.40 (d, 1H, ArH), 7.05-7.10 (m, 2H, ArH), 7.89 (d, 3H, ArH), 8.1 (d,1H,ArH) ;^{13}C NMR(75 MHz,$CDCl_3$): δ = 30.0, 59.9,117.5,118.9,119.6,120.7, 121.4, 122.5,123.6, 124.3, 124.5, 125.9, 126.6, 128.4, 128.5, 140.6, 143.2 ,189.6 ppm.
2-Amino-4-(4-nitrophenyl)-4H-benzo[f]chromene-3-carbonitrile (5i)	
 -S16-	IR (KBr) ν_{max}/cm^{-1}:3355 (NH_2), 2185 (CN), 1668cm^{-1}; ^{1}H NMR(300 MHz,$CDCl_3$/TMS): δ = 4.84 (s, 2H, NH_2), 4.54 (s, 1H, CH), 7.32 (d, 1H, ArH), 7.15-7.20 (m, 2H, ArH), 7.54-7.56 (m, 2H, ArH),7.56-7.79 (m, 3H, ArH),7.83 (d, 1H, ArH), 8.67 (d, 1H, ArH) ;^{13}C NMR(75 MHz,$CDCl_3$): δ = 24.8, 67.3, 118.5, 124.6, 125.4, 123.1, 126.6, 126.5, 125.6, 127.4, 128.5, 129.4, 129.5, 145.5,146.6 , 146.5, 179.4 ppm.
2-Amino-4-(4-methylphenyl)-4H-benzo[f]chromene-3-carbonitrile (5k)	
 -S17-	IR (KBr) ν_{max}/cm^{-1}:3568 (NH_2), 2352 (CN), 1723, 1754 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$/TMS): δ = 4.14 (3H, s, CH_3), 5.88 (2H, s, NH_2), 5.90 (s, 1H, CH), 7.78-7.89 (3H, m, ArH), 7.21 (4H,s, ArH), 7.21-7.34 (1H, d, ArH), 7.86-7.89 (1H, d, ArH), 8.25-8.25 (1H, d, ArH); ^{13}C NMR(75 MHz,$CDCl_3$): δ = 32.8, 35.9, 65.0, 117.9, 123.1, 126.6, 127.4, 128.5, 128.6,129.6, 129.5, 131.4, 132.4, 133.5, 135.5, 145.5, 179.4,189.9 ppm.
2-Amino-4-(4-hydroxyphenyl)-4H-benzo[f]chromene-3-carbonitrile (5j)	
 -S18-	IR (KBr) ν_{max}/cm^{-1}: 3447 (NH_2) , 3317 (CN), 2185, 1665 cm^{-1}; ^{1}H NMR(300 MHz,$CDCl_3$/TMS): δ =2.3 (s,1H, OH), 3.3 (s, 1H, CH), 4.80 (s, 2H, NH2), 6.01 (d, 2H, ArH),7.0 (m, 2H, ArH), 7.4 (m, 3H, ArH), 7.9 (d, 1H, ArH), 8.20 (d, 1H, ArH), 9.30 (d, 1H, ArH) ;^{13}C NMR(75 MHz,$CDCl_3$): δ = 34.0, 62.9,119.5, 122.4, 124.6, 125.3, 126.5, 127.9, 129.6, 129.9, 130.5, 136.6, 145.6, 155.5, 155.7, 179.4,189.9 ppm.
2-Amino-4-(4-methylphenyl)-4H-benzo[f]chromene-3-carbonitrile (5k)	

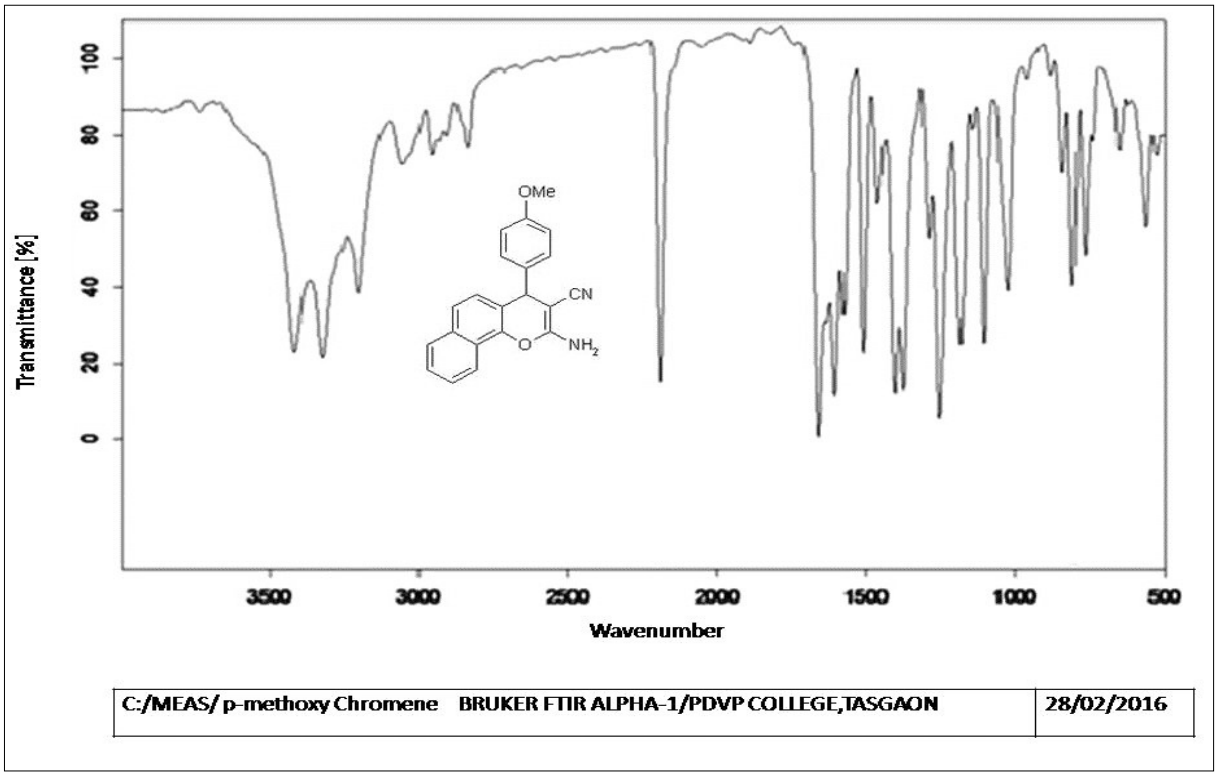
 -S19-	IR (KBr) ν_{max}/cm^{-1}:3468 (NH_2), 2252 (CN), 1623, 1554 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$/TMS):δ 3.20 (3H, s, CH_3), 4.99 (2H, s, NH_2), 5.02 (s, 1H, CH), 7.48-7.59 (3H, m, ArH), 7.11 (4H,s, ArH), 7.01-7.04 (1H, d, ArH), 7.76-7.79 (1H, d, ArH), 8.15-8.18 (1H, d, ArH); ^{13}C NMR(75 MHz,$CDCl_3$):29.8, 59.3, 117.5, 120.6, 125.5, 120.4, 121.1, 124.6, 125.6, 126.4, 126.5, 127.4, 128.4, 132.5,134.5, 143.5, 178.4 ppm.
2-Amino-4-(4-N,N-dimethylphenyl)-4H-benzo[f]chromene-3carbonitrile (5l)	
 -S20-	IR (KBr) ν_{max}/cm^{-1}:3477 and 3356 (NH_2) , 2198 (CN), 1662, 1408 cm^{-1}; ^{1}H NMR(300 MHz,$CDCl_3$/TMS): δ =3.2 (s, 6H, CH_3), 4.2 (s, 1H, CH), 6.09 (s, 2H, NH2), 6.60 (d, 2H, ArH), 7.23 (s, 2H, ArH), 7.42 (s, 1H, ArH), 7.45 (s, 1H, ArH), 7.80 (d, 2H, ArH),8.45 (s, 1H, ArH), 8.80 (d, 1H, ArH) ;^{13}C NMR(75 MHz,$CDCl_3$): δ = 32.0, 63.9,119.5, 124.5, 125.6, 125.7, 126.7, 127.9, 128.4, 128.6, 128.9, 129.5, 132.5,134.5, 141.6, 144.2 , 143.5, 178.9 ppm.
2-Amino-4-(pyridine-2-yl)-4H-benzo[f]chromene-3-carbonitrile (5p)	
 -S21-	IR (KBr) ν_{max}/cm^{-1}: 3489 and 3345 (NH_2) , 2234 (CN), 1656, 1478 cm^{-1}; ^{1}H NMR(300 MHz,$CDCl_3$/TMS): δ = 4.9 (s, 1H, CH), 7.01 (s, 1H, NH2), 7.23 (d, 2H, ArH), 7.45 (m, 4H, ArH), 7.09 (d, 1H, ArH), 7.2 (d, 1H, ArH), 8.30 (d, 1H, ArH), 8.50 (d, 1H, ArH) ;^{13}C NMR(75 MHz,$CDCl_3$): δ = 30.0, 59.9,117.5, 121.4, 123.6, 124.3, 124.5, 125.9, 126.6, 128.4, 128.5, 131.6, 134.5, 140.6, 143.2,145.2 , 146.8, 177.9 ppm.
2-Amino-4-(thiophine-2-yl)-4H-benzo[f]chromene-3-carbonitrile (5q)	
 -S22-	IR (KBr) ν_{max}/cm^{-1}: 3577 and 3346 (NH_2), 2134 (CN), 1652, 1468 cm^{-1}; ^{1}H NMR(300 MHz,$CDCl_3$/TMS): δ = 5.3 (s, 1H, CH), 6.01 (s, 2H, NH2), 7.33 (m, 3H, ArH), 7.7. (m, 3H, ArH), 7.9 (d, 1H, ArH), 8.20 (d, 1H, ArH),8.54 (d, 1H, ArH) ;^{13}C NMR(75 MHz,$CDCl_3$): δ = 33.0, 56.9,123.5, 125.4, 125.6, 125.7, 126.6, 127.3, 127.5, 128.9, 129.6, 130.4, 131.5, 137.6,138.9,143.6, 145.2,178.9 ppm.
2-Amino-3-cyano-4H-chromen-4-yl)propanedinitrile (7a)	
 -S23-	IR (KBr) ν_{max}/cm^{-1}: 3346 and 3341(NH_2), 2820, 2349, 1645c cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$/TMS): δ 4.48(d, 1H, -CH), 4.89 (d,1H, -CH), 6.24 (bs, 2H, NH_2), 7.06-7.53 (m, 4H, ArH) ppm; ^{13}C NMR (75 MHz,$CDCl_3$) : δ 175.9, 163.2, 130.4, 131.2, 131.6, 132.4, 137.6, 137.4, 138.8, 139.7, 64.2, 20.4, 19.4 ppm.
2-Amino-6-chloro-3-cyano-4H-chromen-4-yl)propanedinitrile (7d)	

 -S24-	IR (KBr) ν_{max}/cm^{-1}: 3431 and 3357(NH_2), 2196, 1665, 1582, 1239, 747 cm^{-1}; ^1H NMR (300 MHz,$CDCl_3$+DMSO-d_6/TMS): δ 4.32-4.36 (d, 1H, -CH), 4.52-4.70 (d, 1H, -CH), 6.14-6.42 (bs, 2H, NH_2), 7.12-7.16 (d, 1H, ArH), 7.20-7.25 (d, 1H, ArH), 7.30-7.34 (s, 1H, ArH) ppm; ^{13}C NMR (75 MHz,$CDCl_3$+DMSO-d_6): δ 31.5, 37.8, 49.5, 111.0,111.3,117.8,118.0,118.3,127.7,129.5,129.7,148.0,162.7 ppm.
2-amino-3-cyano-6-nitro-4H-chromen-4-yl)propanedinitrile (7e)	
 -S25-	IR (KBr) ν_{max}/cm^{-1}:3432 and 3301(NH_2), 1662, 1524, 1324, 1249, 1127, 895 cm^{-1}; ^1H NMR (300 MHz,$CDCl_3$/TMS): δ 4.42-4.46 (d, 1H, -CH), 4.72-4.77 (d, 1H, -CH),6.52 (bs, 2H, NH_2), 7.14 (d, 1H, ArH),7.7 (s, 1H, AH), 7.8 (d, 1H,ArH), ppm; ^{13}C NMR (75 MHz,$CDCl_3$): δ = 20.2,25.4, 66.1, 119.2, 119.6, 119.9, 120.4, 133.2, 134.1, 145.1, 178.6, 159.4,168.9.
2-Amino-4-(nitromethyl)-4H-chromene-3-carbonitrile(8a)	
 -S26-	IR (KBr) ν_{max}/cm^{-1}: 3353 and 3305(NH_2), 1786, 1793, 1566, 1340, 1257, 769 cm^{-1}; ^1H NMR (300 MHz,$CDCl_3$+DMSO-d_6/TMS) : δ 4.67 (d, 2H, -CH_2NO_2), 3.52 (t,1H, -CH),6.68 (bs, 2H, NH_2), 7.46-7.55 (m, 4H, ArH), ppm; ^{13}C NMR (75 MHz,$CDCl_3$): δ, 3.2, 56.6,71.2,86.1,86.9,136.8,143.2,147.3,158.4,169.7,162.4,169.2,169.8 ppm.
2-Amino-6-chloro-4-(nitromethyl)-4H-chromene-3-carbonitrile (8d)	
 -S27-	IR (KBr) ν_{max}/cm^{-1}: 3345 and 3228(NH_2), 2297, 1544, 1472, 1165, 1129, 1099, 1569, 830 cm^{-1}; ^1H NMR (300 MHz,$CDCl_3$+DMSO-d_6/TMS) :4.5 (t,1H,-HC),(dd,2H, -CH_2NO_2), 6.02-6.07 (bs,2H, -NH_2), 6.9-7.2 (d,1H, -ArH), 6.72-6.85 (dd, 2H, ArH).ppm; ^{13}C NMR (75 MHz,$CDCl_3$+DMSO-d_6): δ 167.8, 159.9, 154.6, 154.3, 136.7, 136.7, 130.6, 120.1, 117.9, 117.2, 117.8,179.2,179.8 ppm.
2-amino-6-nitro-4-(nitromethyl)-4H-chromene-3-carbonitrile (8c)	
 -S28-	IR (KBr) ν_{max}/cm^{-1}: 3432 and 3331(NH_2), 1661, 1523, 1294, 1020, 902, 827 cm^{-1}; ^1H NMR (300 MHz,$CDCl_3$/TMS): δ = 4.62 (t, 1H -CH), 4. 67(dd,2H, -CH_2NO_2) 6.1 (s, 2H, -NH_2), 6.6 (dd, 2H, ArH), 7.6 (dd, 1H, ArH), ppm; ^{13}C NMR (75 MHz,$CDCl_3$): δ =23.2,64.2, 82.1, 116.5, 119.2, 121.4, 124.2, 130.2, 143.2, 157.9, 176.5ppm.
Ethyl-2-amino-6-chloro-4-(nitromethyl)-4H-chromene-3-carboxylate(8f)	
 -S29-	IR (KBr) ν_{max}/cm^{-1}: 3244 and 3567(NH_2), 1578, 1659, 1362, 1564, 1251, 1188, 843 cm^{-1}, ^1H NMR (300 MHz,$CDCl_3$/TMS) : δ 1.35 (t, 3H, -CH_3),4.44 (m, 2H, -CH_2), 4.45-4.47 (dd,1H, -$CHNO_2$), 4.54-4.56 (dd,1H, -$CHNO_2$), 4.65-4.66 (dd,1H, -CH), 6.26-6.76 (bs, 2H, -NH_2), 6.98-7.30 (m, 3H, ArH) ppm; ^{13}C NMR (75 MHz,$CDCl_3$):δ13.4,36.1,66.0,75.5,89.7,118.6,124.5,128.0,128.9,130.9,149.5,163.7,178 .0 ppm.

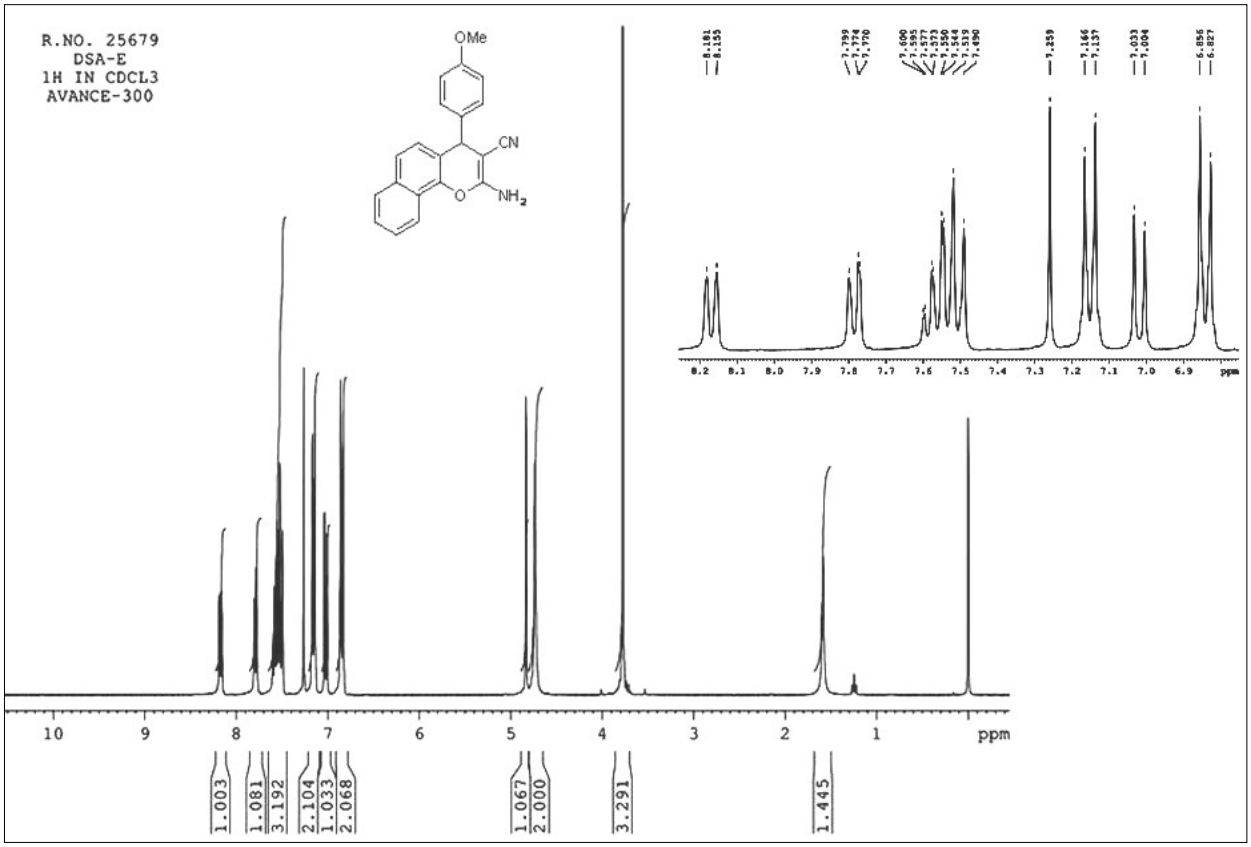
Ethyl-2-amino-6-nitro-4-(nitromethyl)-4H-chromene-3-carboxylate(8g)	
 -S30-	IR (KBr) ν_{max}/cm^{-1}: 3459 and 3334(NH_2), 1646, 1667, 1546, 1449, 1348, 1251, 1073, 746 cm^{-1},^{1}H NMR (300 MHz,$CDCl_3$/TMS): δ 1.38 (t, 3H, -CH_3), 4.20 (q, 2H, -CH_2), 4.34 (dd,1H, -$CHNO_2$), 4.64 (dd,1H, -$CHNO_2$), 4.68-4.76 (dd,1H, -CH), 6.25-6.75 (bs, 2H, -NH_2), 6.98-7.30 (m, 3H, ArH) ppm; ^{13}C NMR (75 MHz,$CDCl_3$): δ 15.4,34.1, 60.2, 71.4, 81.4, 120.9, 128.1, 129.6, 130.7, 150.2, 160.8, 168.1, 170.9ppm.
Ethyl-2-amino-8-methoxy-4-(nitromethyl)-4H-chromene-3-carboxylate(8h)	
 -S31-	IR (KBr): 3561 and 3467(NH_2),1678, 1385, 1593, 1693, 1477, 1454, 1645, 1576, 695 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$/TMS): δ 1.35 (t, 3H, -CH_3), 3.34 (s, 3H, -OCH_3), 4.07 (q, 2H, -CH_2), 4.43 (d,1H, -CH_2NO_2), 4.6 (t,1H,-$CHCH_2NO_2$), 6.44 (bs, 2H, -NH_2), 7.21 -7.36 (m, 3H, ArH) ppm; ^{13}C NMR (75 MHz,$CDCl_3$): δ 16.5, 23.7, 58.1, 63.6, 83.2, 89.2, 114.2, 124.5, 124.5, 132.2, 143.5,155.9, 162.2, 169.2 ppm.
Ethyl-2-amino-6-chloro-4-(1-cyano-2-ethoxy-2-oxoethyl)-4H-chromene-3-carboxylate(7g)	
 -S32-	IR (KBr) ν_{max}/cm^{-1}: 3469 and 3762(NH_2), 2984, 2985, 2450, 1878, 1680, 1582, 129, 1052, 821 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$/TMS) : δ 1.39 (t, 3H, -CH_3), 1.45 (t, 3H, -CH_3), 4.81 (d, 1H, -CH), 4.16 (q, 2H, -CH_2), 4.17 (q, 2H, -CH_2), 7.07-7.72 (bs, 2H, -NH_2), 6.44-6.48 (d, 1H, ArH), 6.79-6.84 (d, 1H, ArH), 7.35 (s, 1H, ArH); ^{13}C NMR (75 MHz,$CDCl_3$) : δ 16.1, 16.9, 19.9, 39.2, 60.2, 66.5, 88.1, 117.7, 120.2, 133.6, 134.2, 135.1, 136.4, 141.1, 145.4, 154.1, 175.1ppm.
Ethyl-6-nitro-2-amino-4-(1-cyano-2-ethoxy-2-oxoethyl)-6-nitro-4H-chromene-3-carboxylate(7h)	
 -S33-	IR (KBr) ν_{max}/cm^{-1}: 3566 and 3344(NH_2), 2344, 2642, 2262, 1742, 1678, 1542, 1365, 1558, 1239, 765 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$/TMS): δ 1.36 (t, 3H, -CH_3), 1.39(t, 3H, -CH_3), 3.72 (d, 1H, -CH), 4.15 (q, 2H, -CH_2), 4.22 (q, 2H, -CH_2), 6.26 (bs, 2H, NH_2), 6.86 (d, 1H, ArH), 7.74 (d, 1H, ArH), 7.92 (s, 1H, ArH) ppm; ^{13}C NMR (75 MHz,$CDCl_3$) : δ13.9, 14.1, 18.4, 36.2, 61.2, 62.1, 87.5, 117.1, 118.2, 119.5, 122.9, 131.2, 141.9, 158.1, 161.2, 168.1, 163.2 ppm.
Ethyl-2-amino-8-methoxy-4-(1-cyano-2-ethoxy-2-oxoethyl)-8-methoxy-4H-chromene-3-carboxylate(7i)	
 -S34-	IR (KBr) ν_{max}/cm^{-1}: 3396 and 3311(NH_2), 2979, 2914, 2242, 1734, 1589, 1319, 1225, 798 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$/TMS) : δ 1.26(t, 3H, -CH_3), 1.37 (t, 3H, -CH_3), 3.32 (s, 3H, -OCH_3), 3.79 (d, 1H, -CH), 4.15 (q, 2H, -CH_2), 4.18 (q, 2H, -CH_2), 4.28 (d, 1H, -CH), 6.25 (bs, 2H, NH_2), 6.94-7.20 (m, 3H, ArH) ppm; ^{13}C NMR (75 MHz,$CDCl_3$) : δ 14.9 , 14.7,19.4, 34.3, 56.5, 61.4, 62.6, 86.5, 112.4, 116.3, 121.5, 124.3, 131.5, 140.4, 154.6, 159.4, 164.6 165.8 ppm



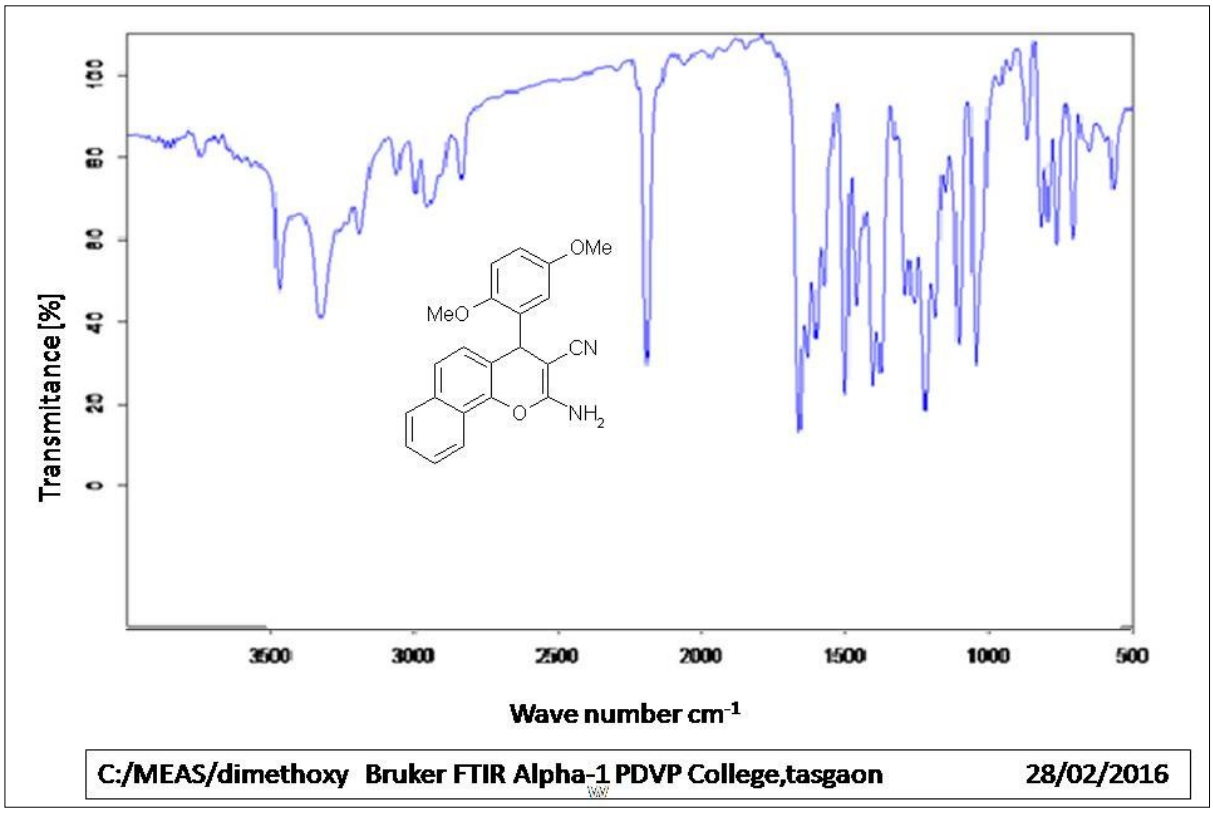
IR spectrum of compound 4a



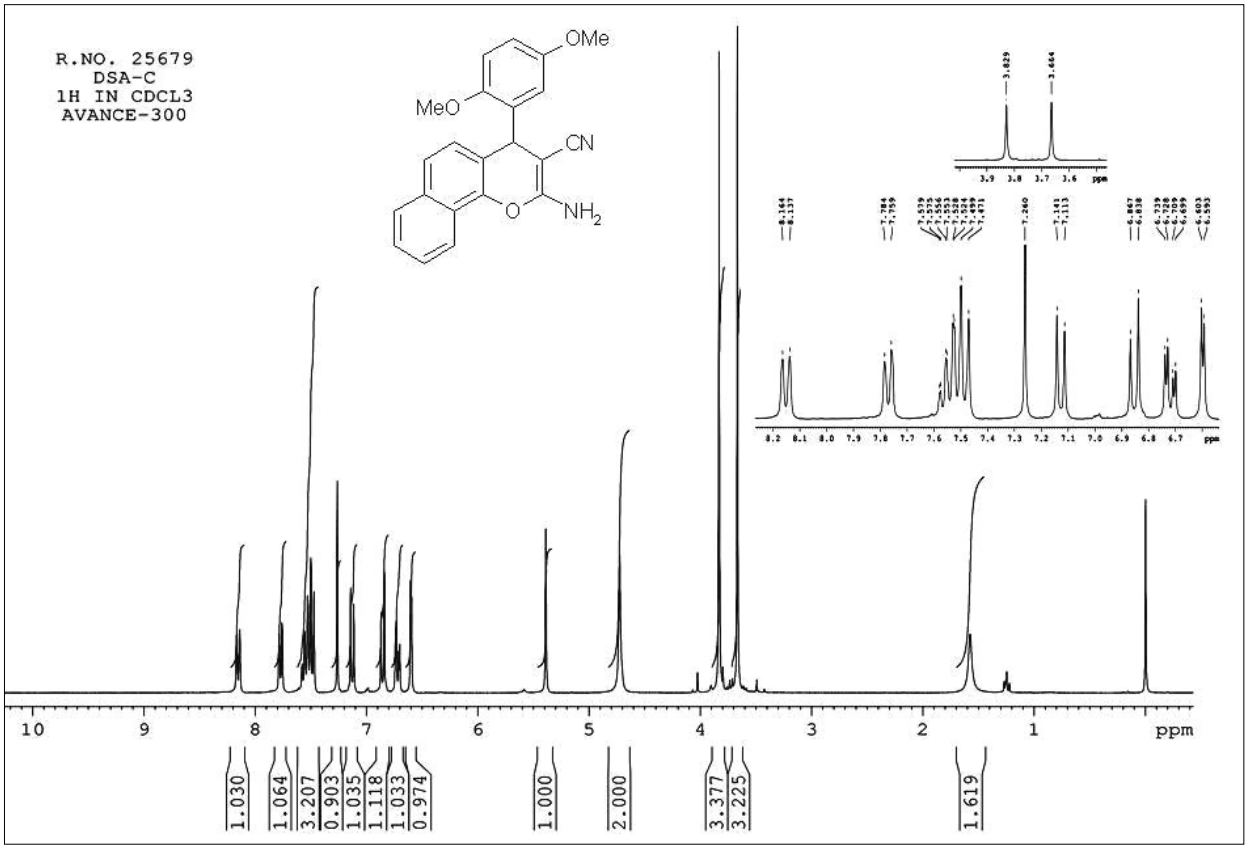
IR spectrum of compound 5b



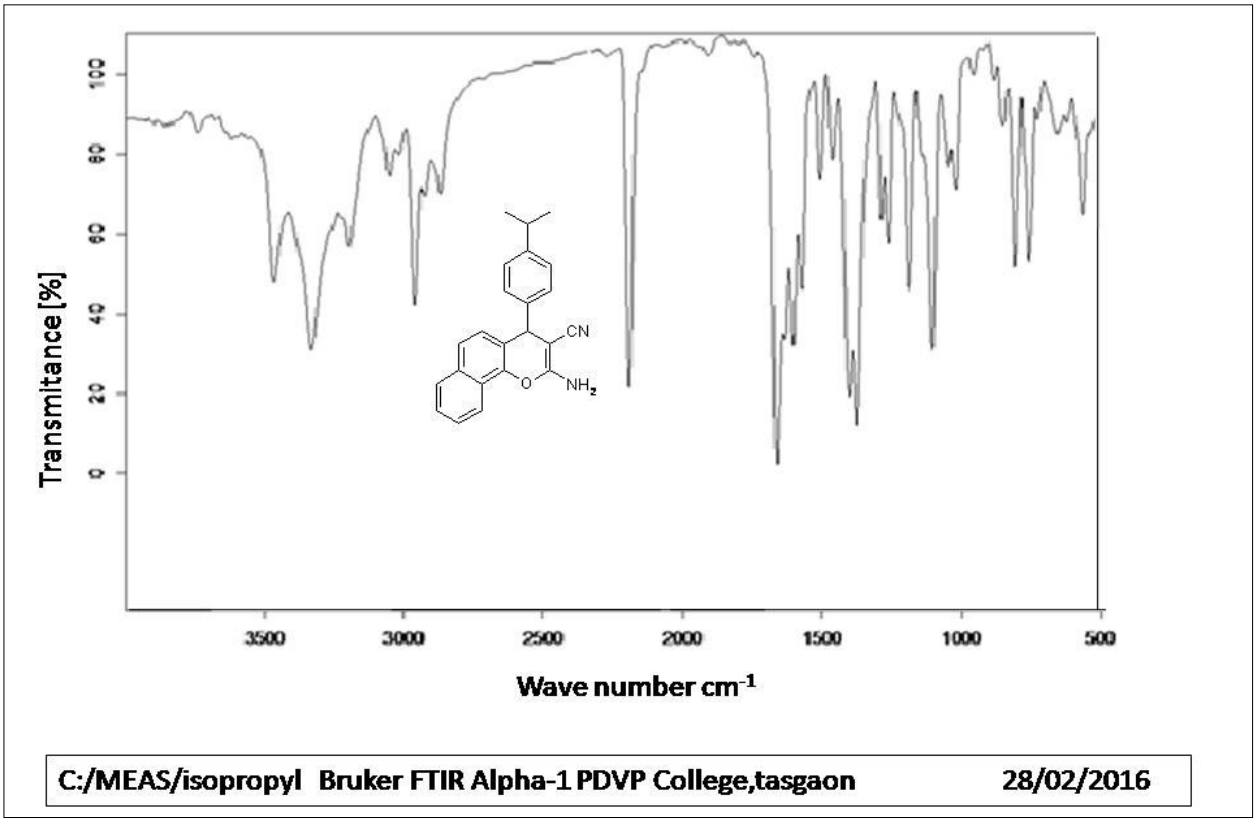
^{1}HNMR spectrum of compound 5b



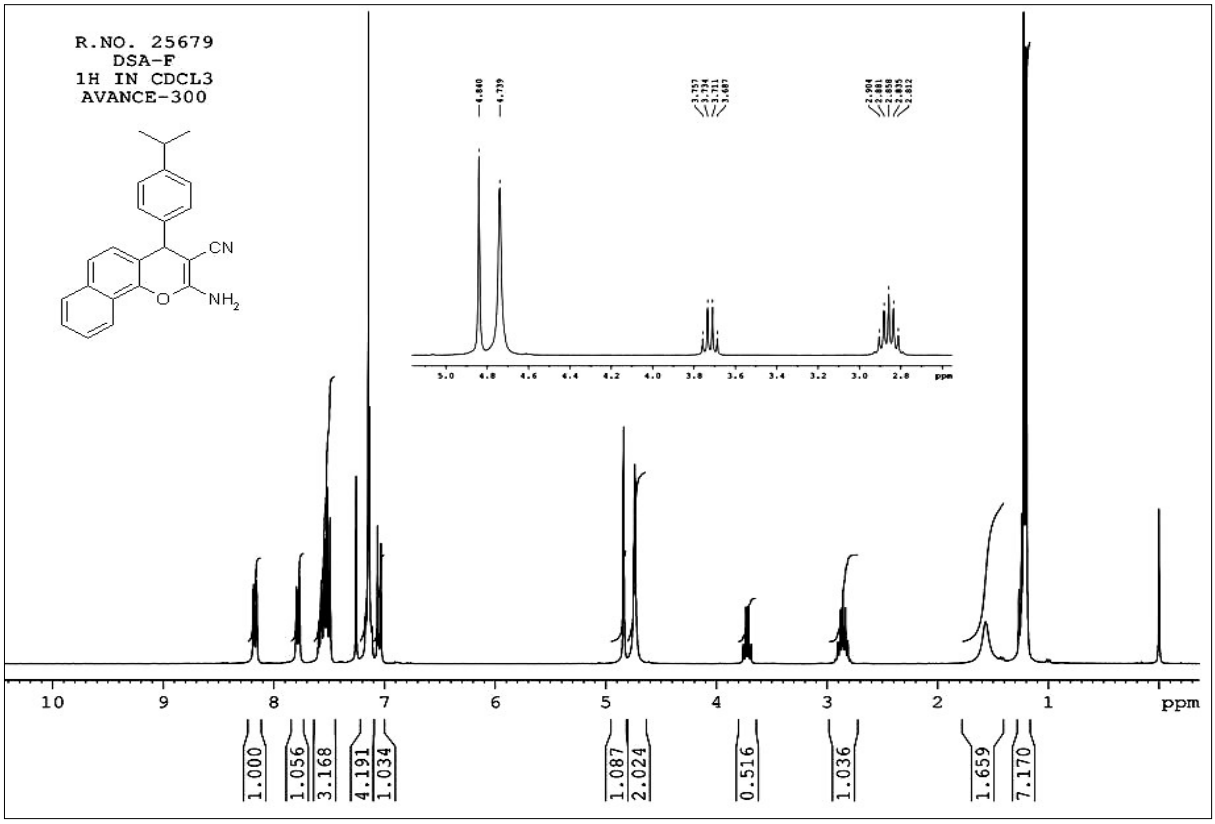
IR spectrum of compound 5c



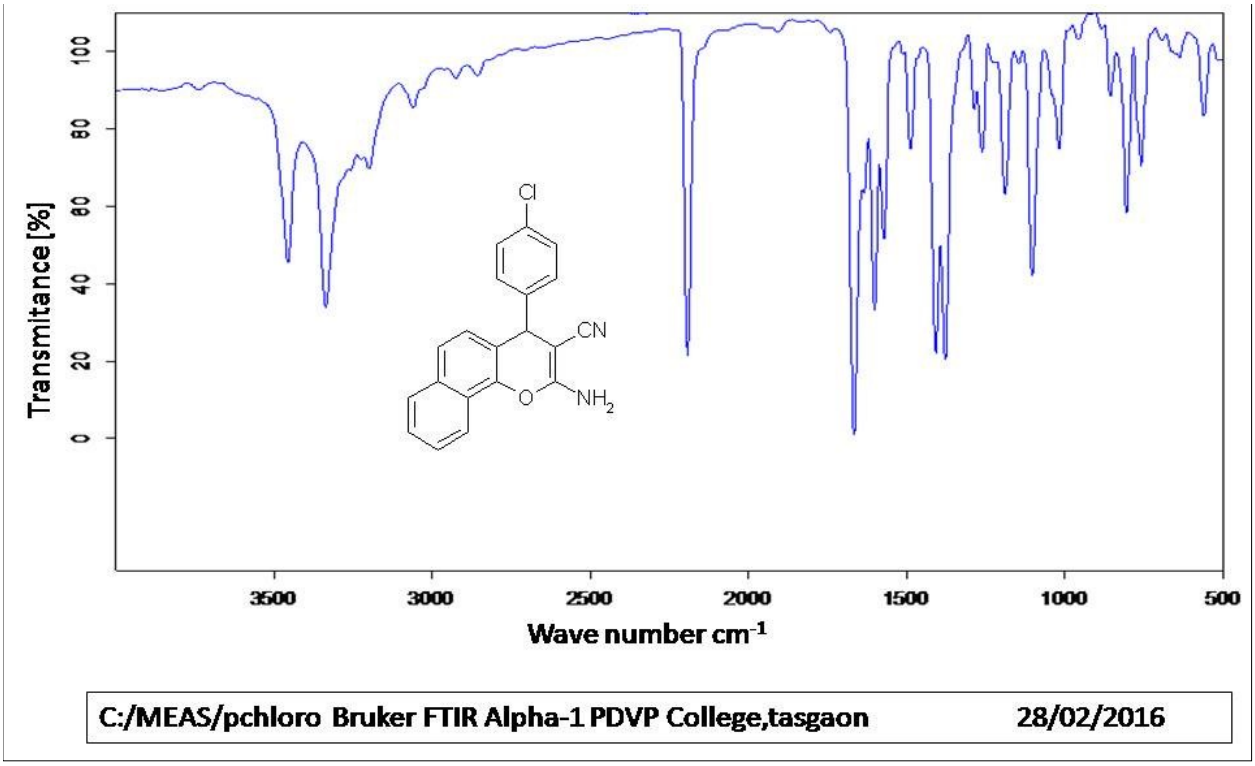
[1]HNMR spectrum of compound 5c



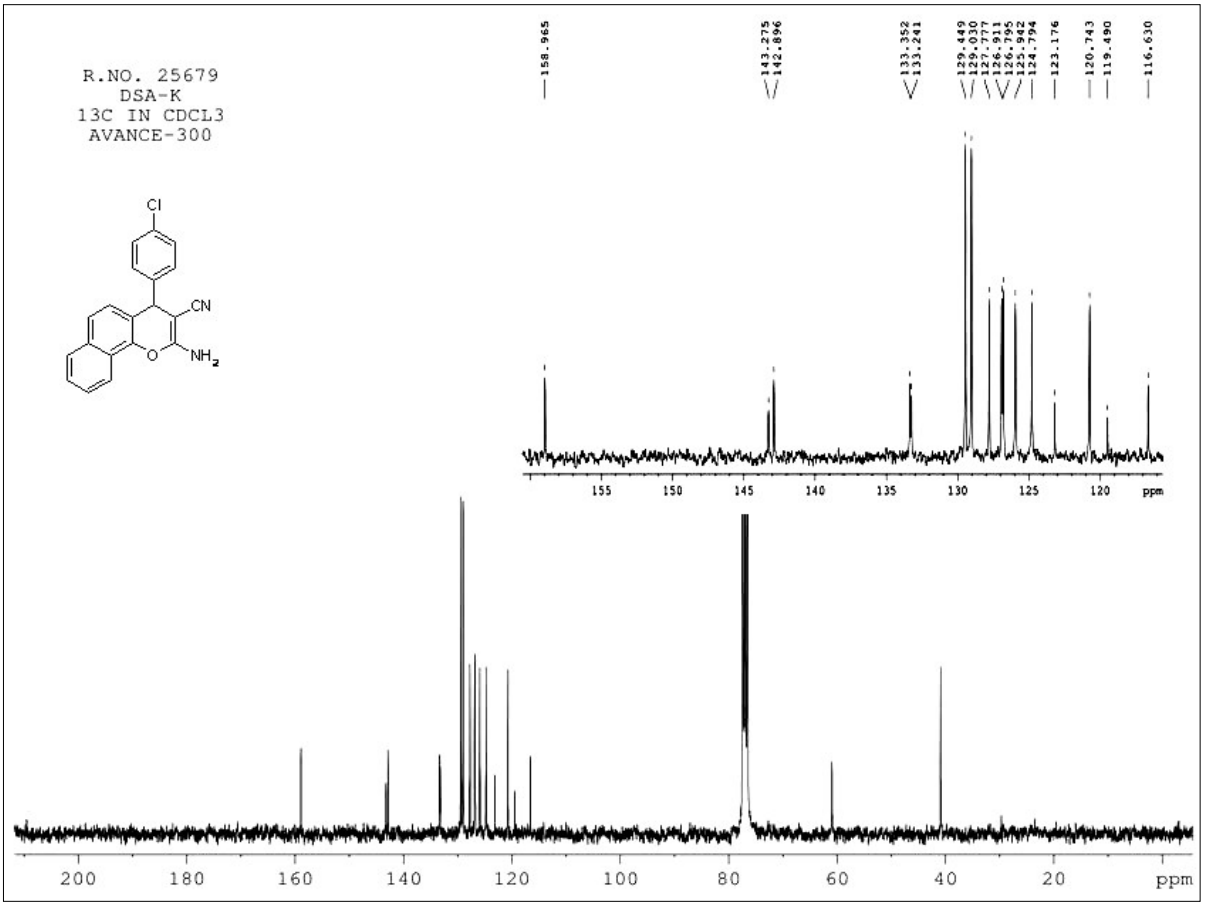
IR spectrum of compound 5d



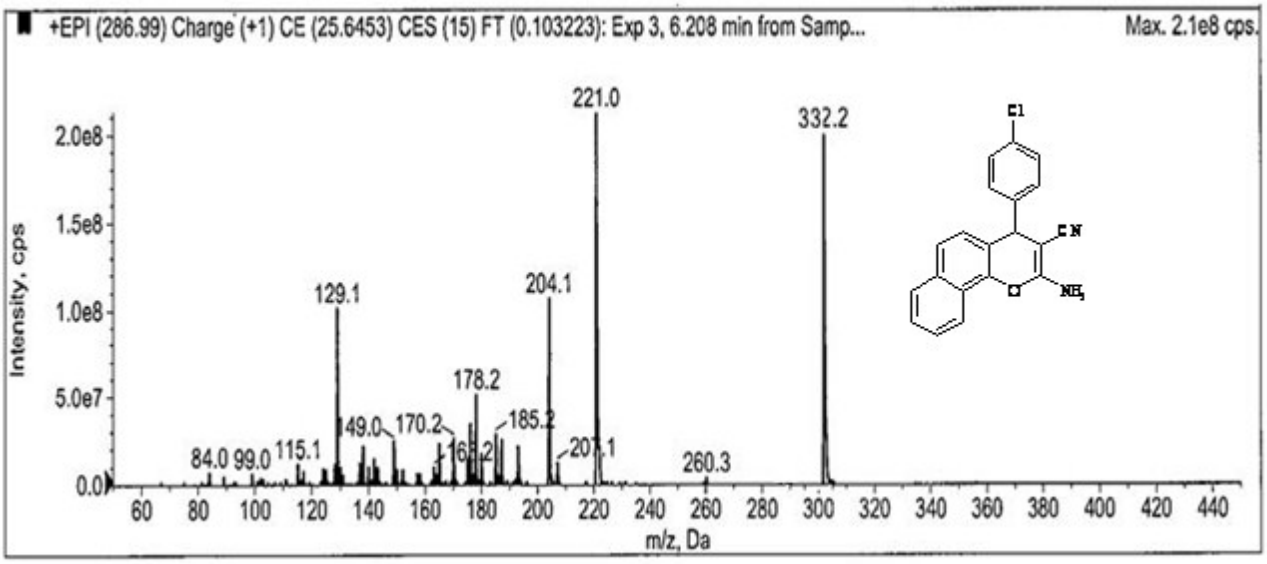
^{1}H NMR spectrum of compound 5d



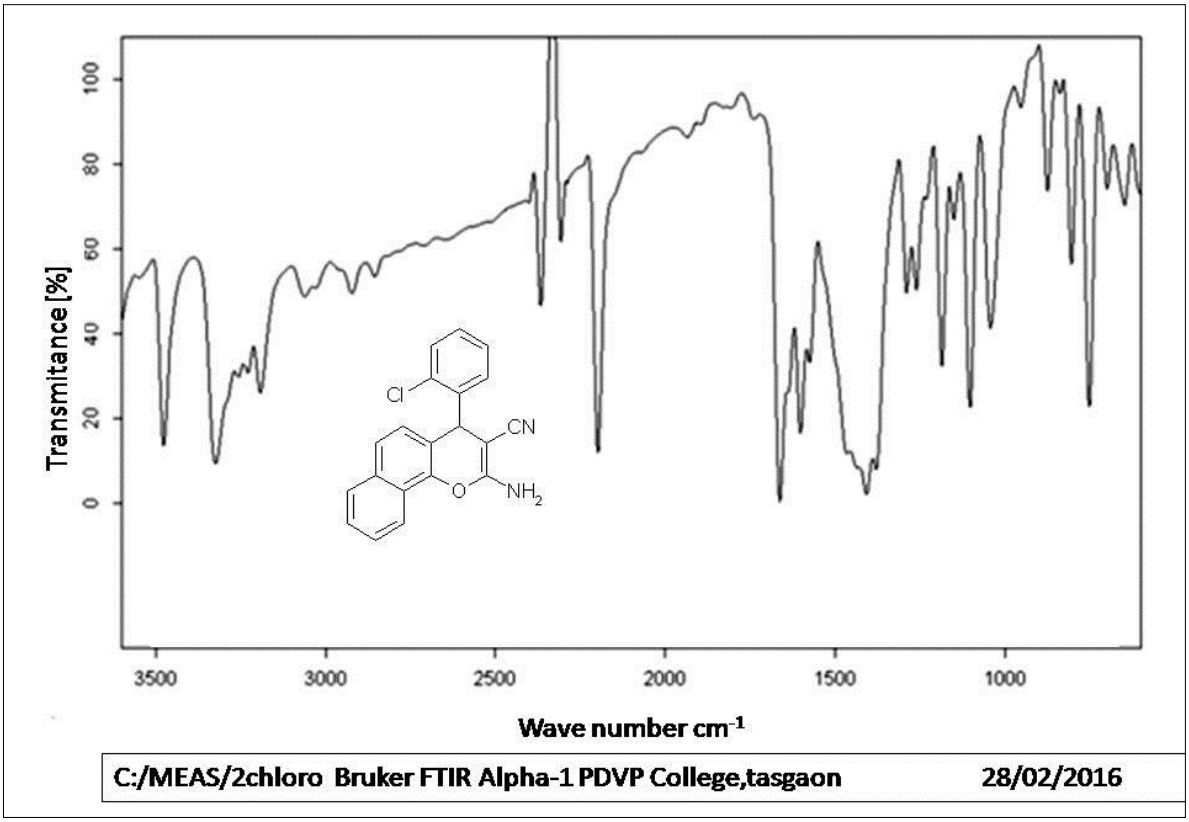
IR spectrum of compound 5e



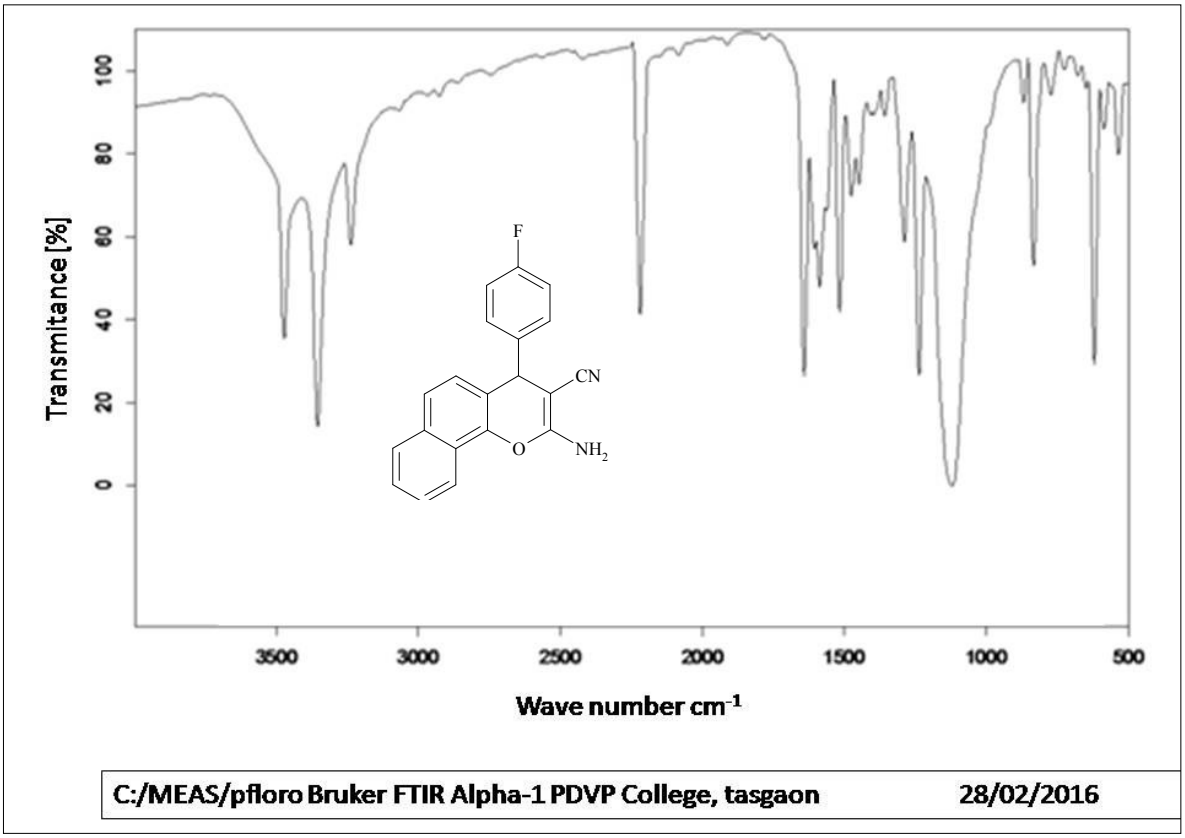
^{13}C NMR spectrum of compound 5e



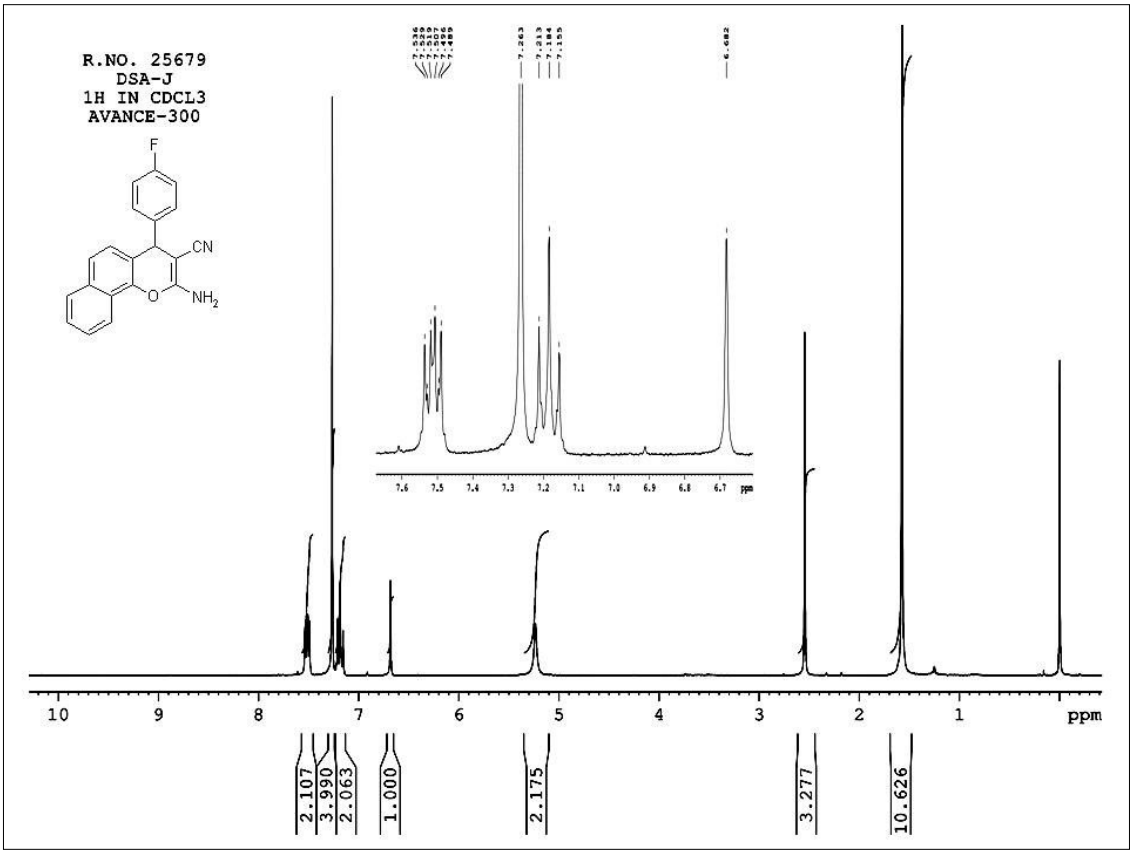
Mass spectrum of compound 5e



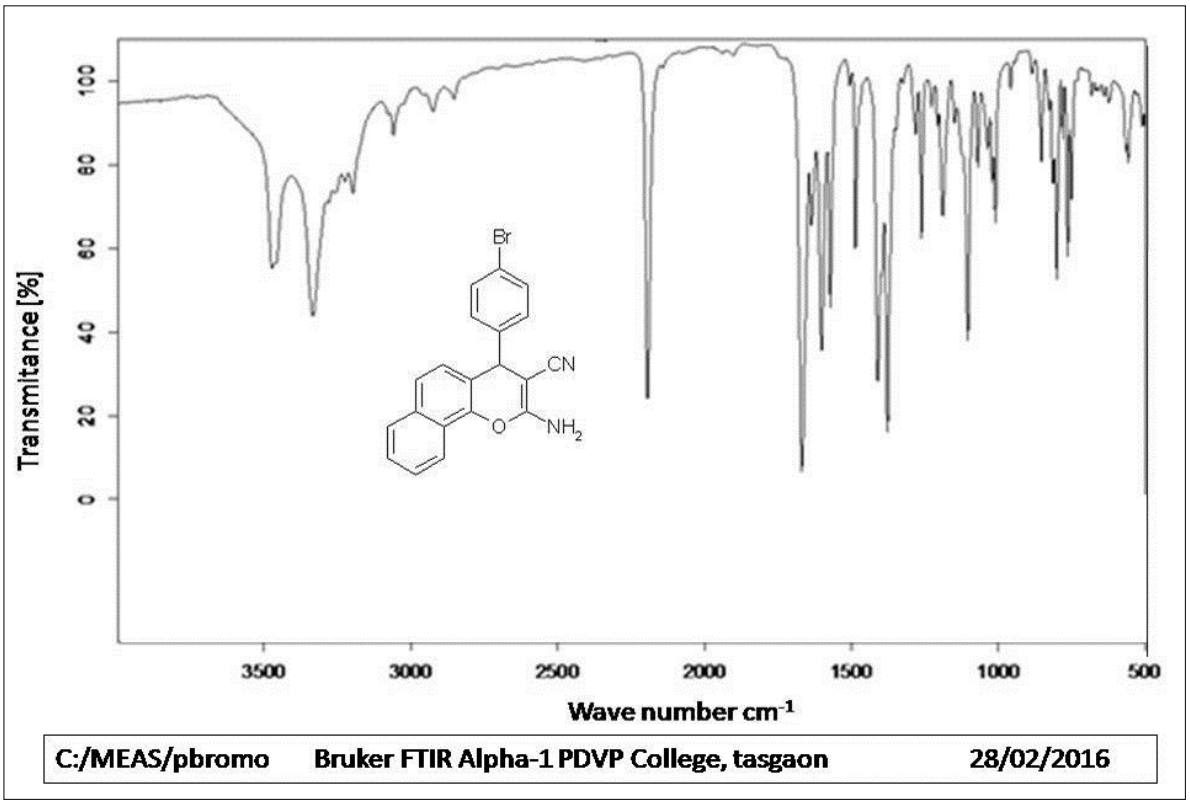
IR spectrum of compound 5f



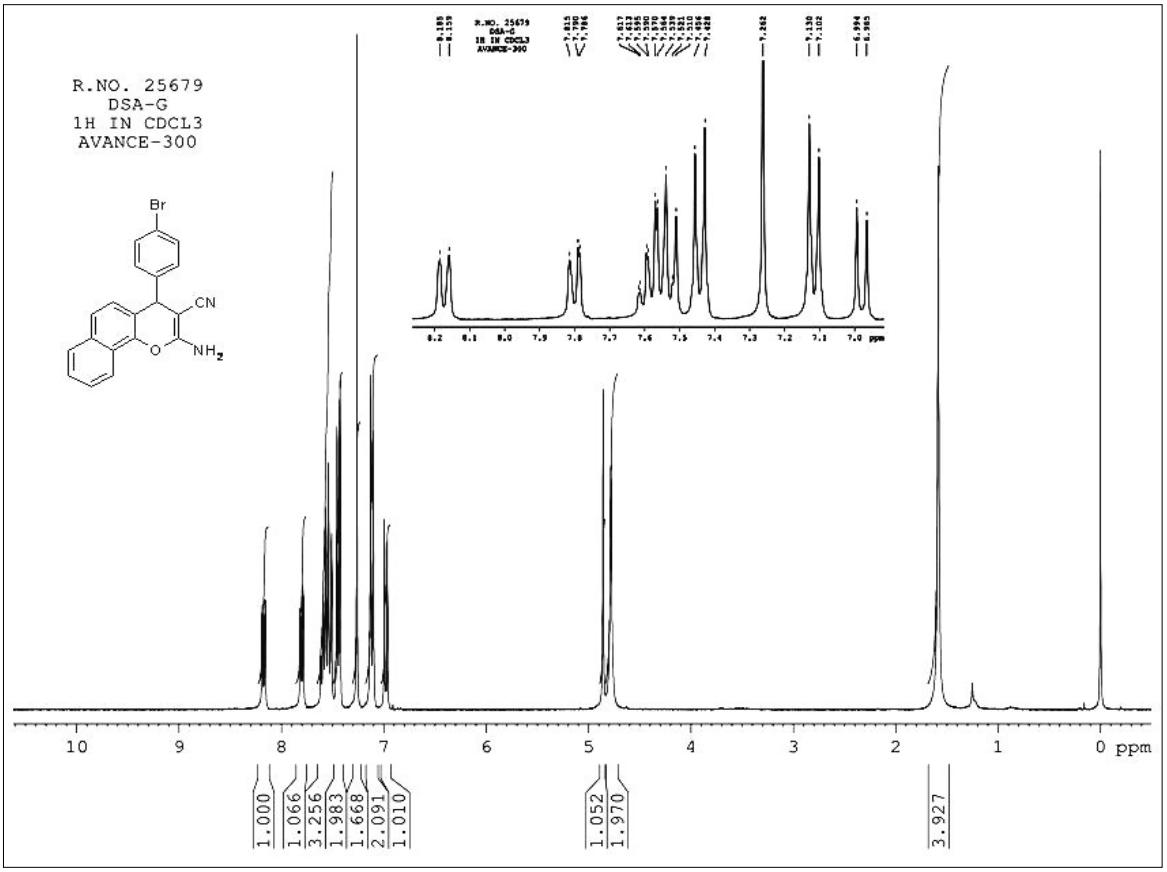
IR spectrum of compound 5g



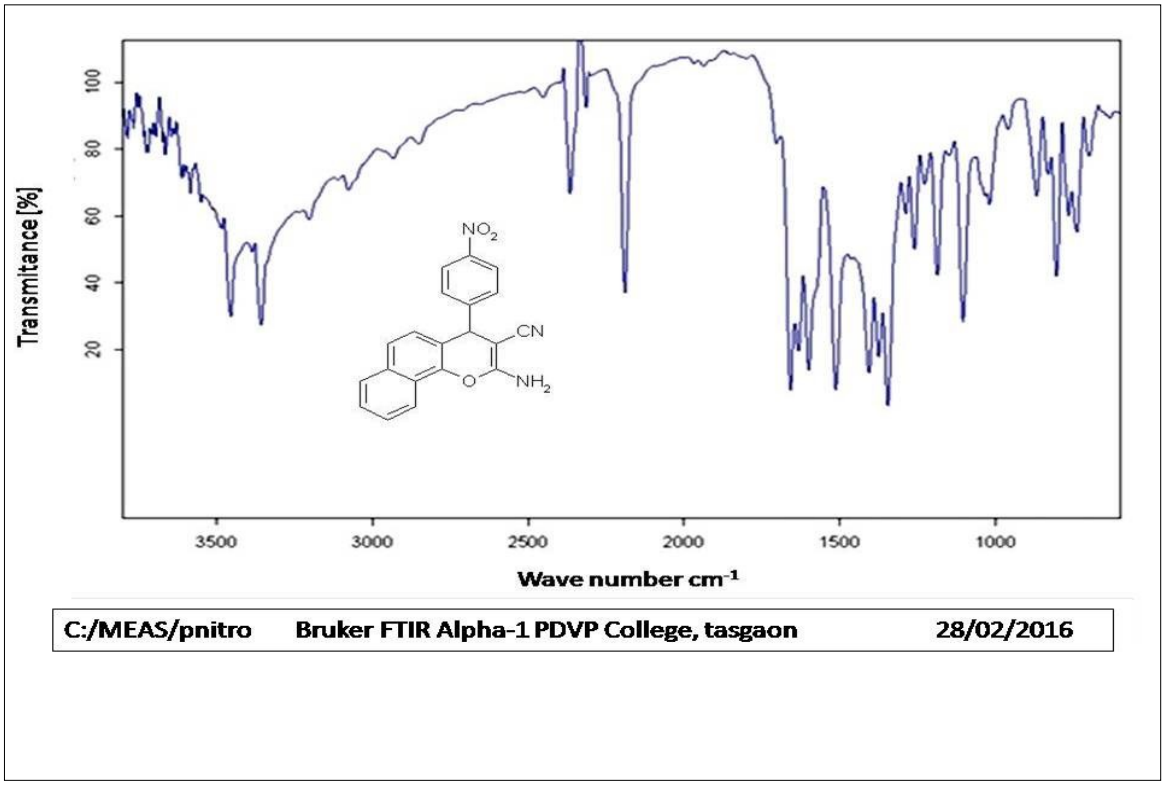
[1]HNMR spectrum of compound 5g



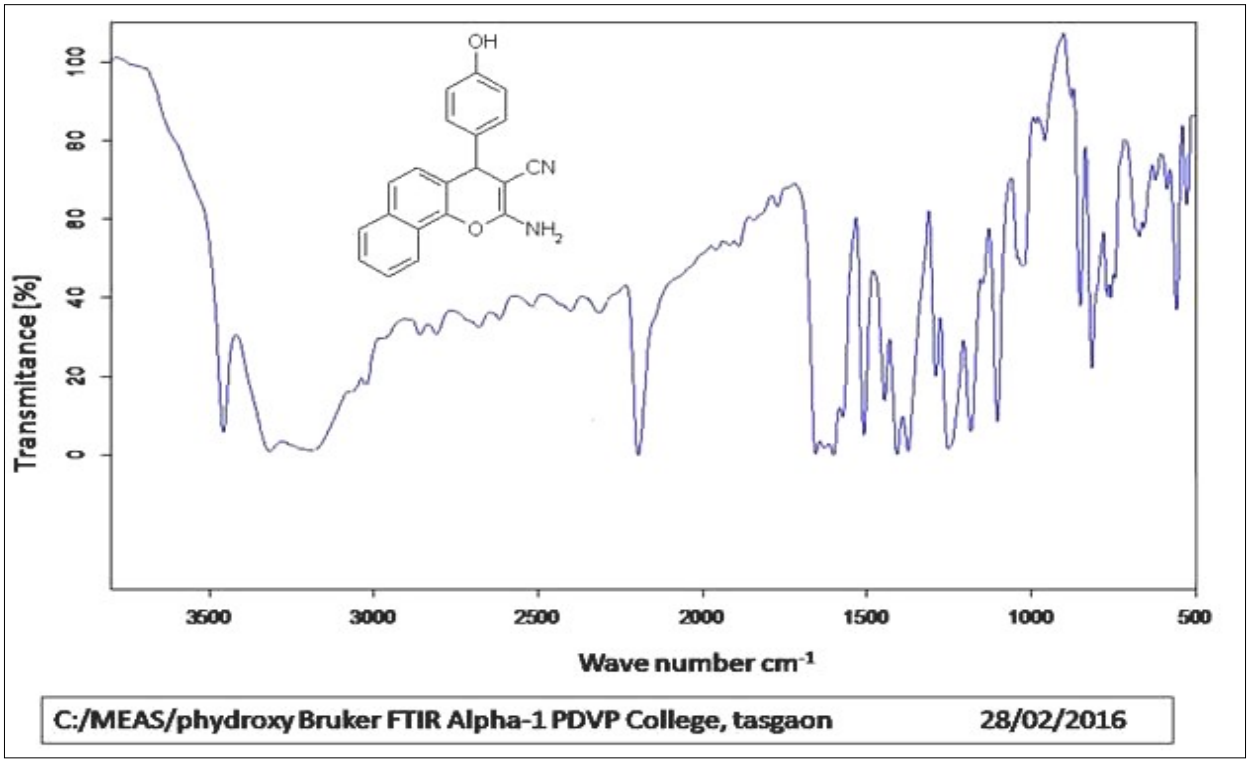
IR spectrum of compound 5h



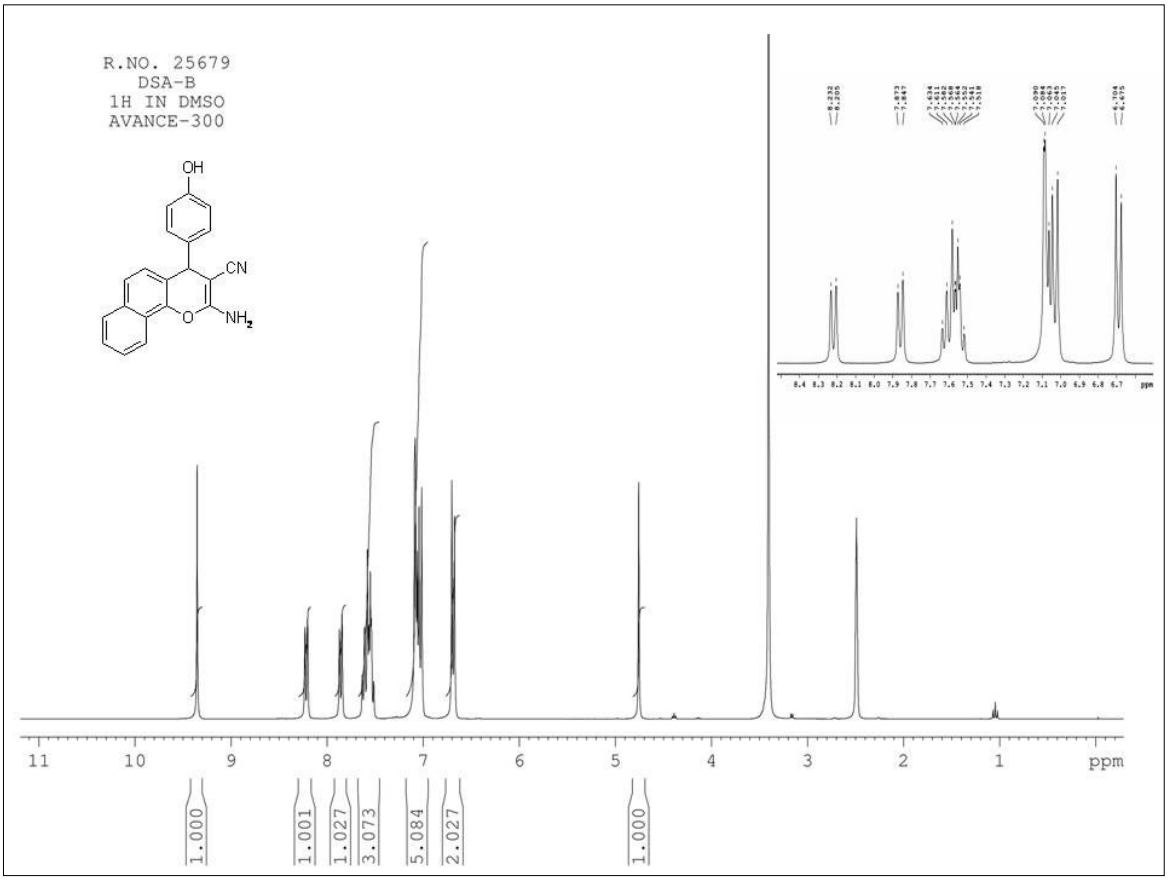
[1]HNMR spectrum of compound 5h



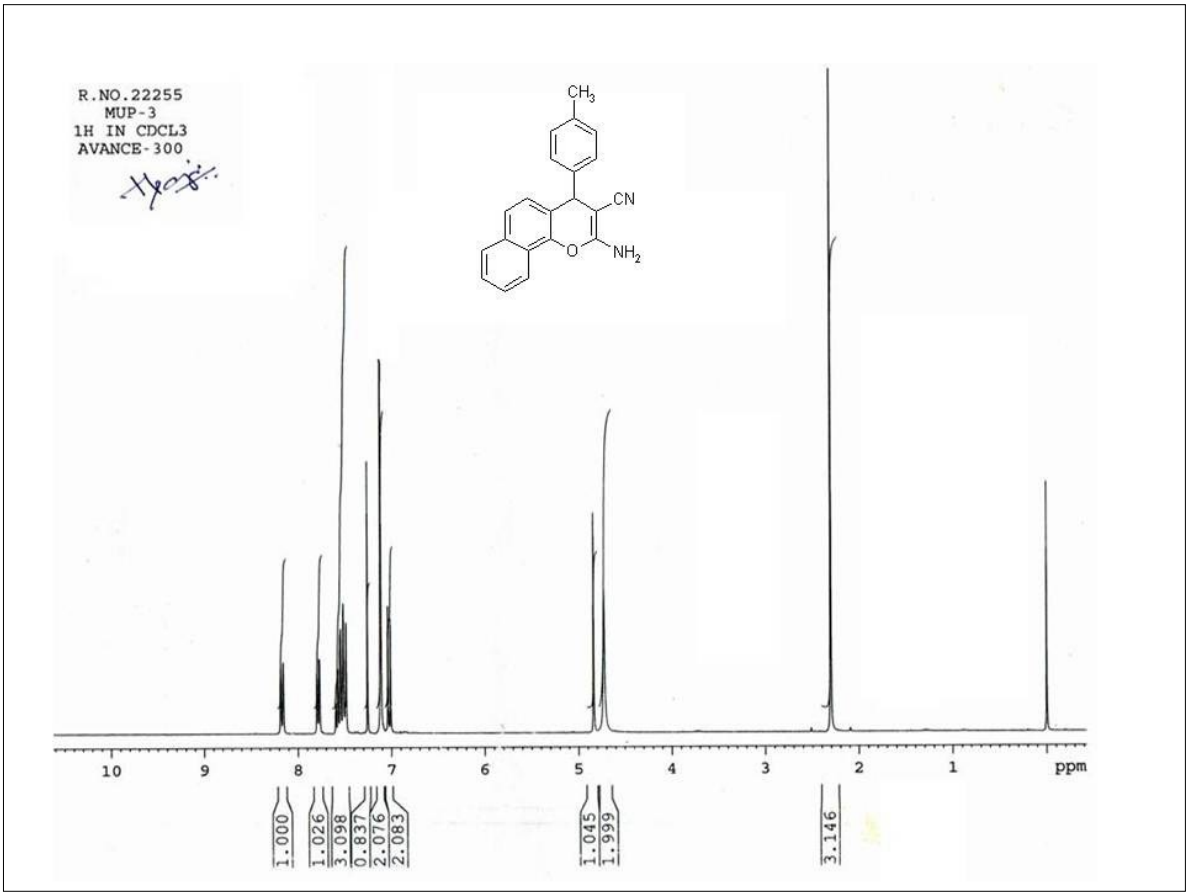
IR spectrum of compound 5i



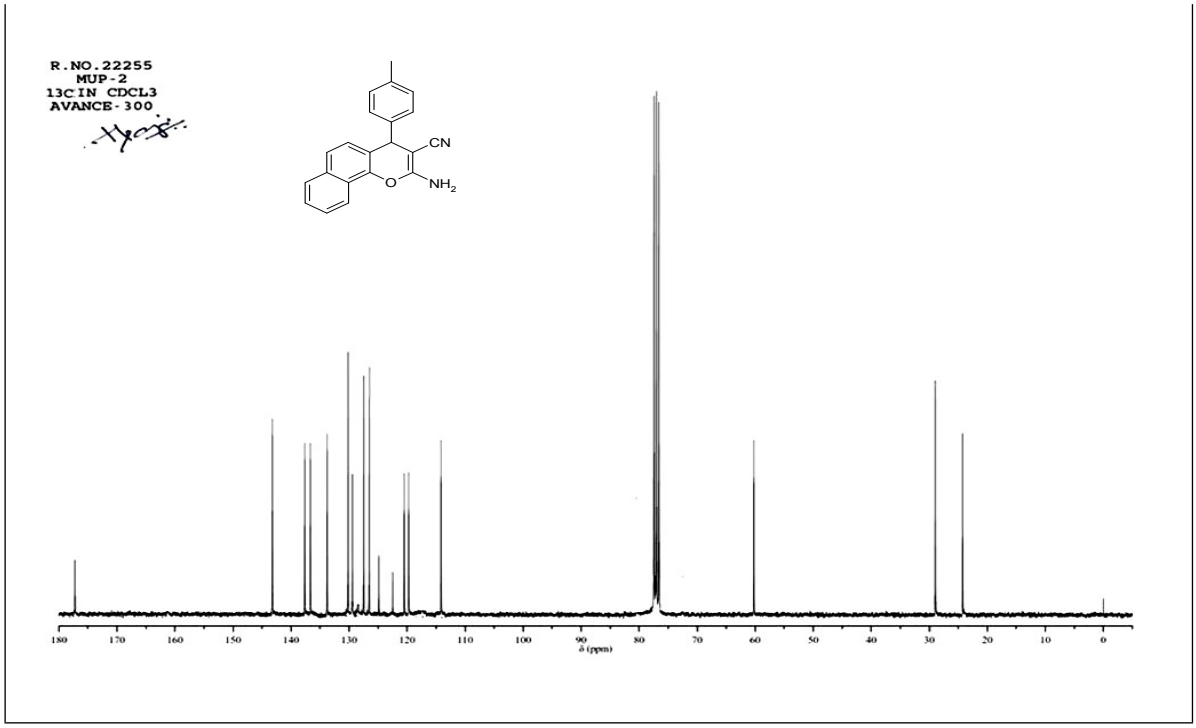
IR spectrum of compound 5j



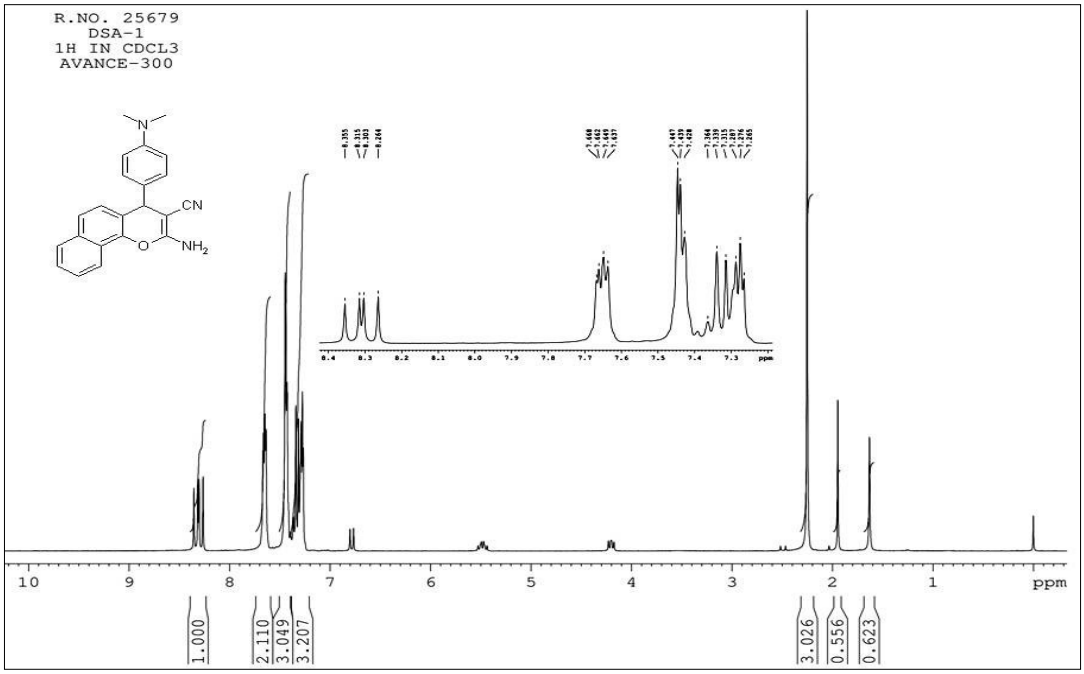
^{1}HNMR spectrum of compound 5j



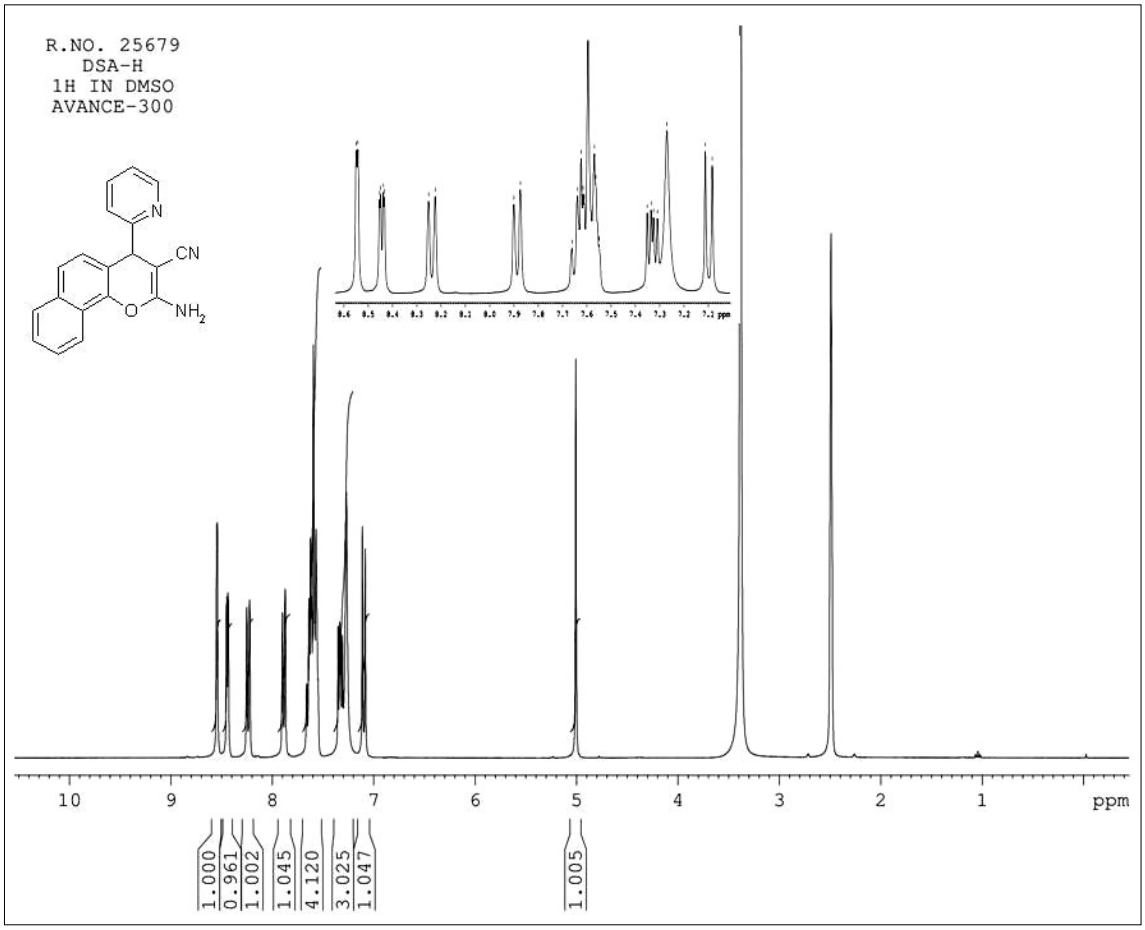
[1]HNMR spectrum of compound 5k



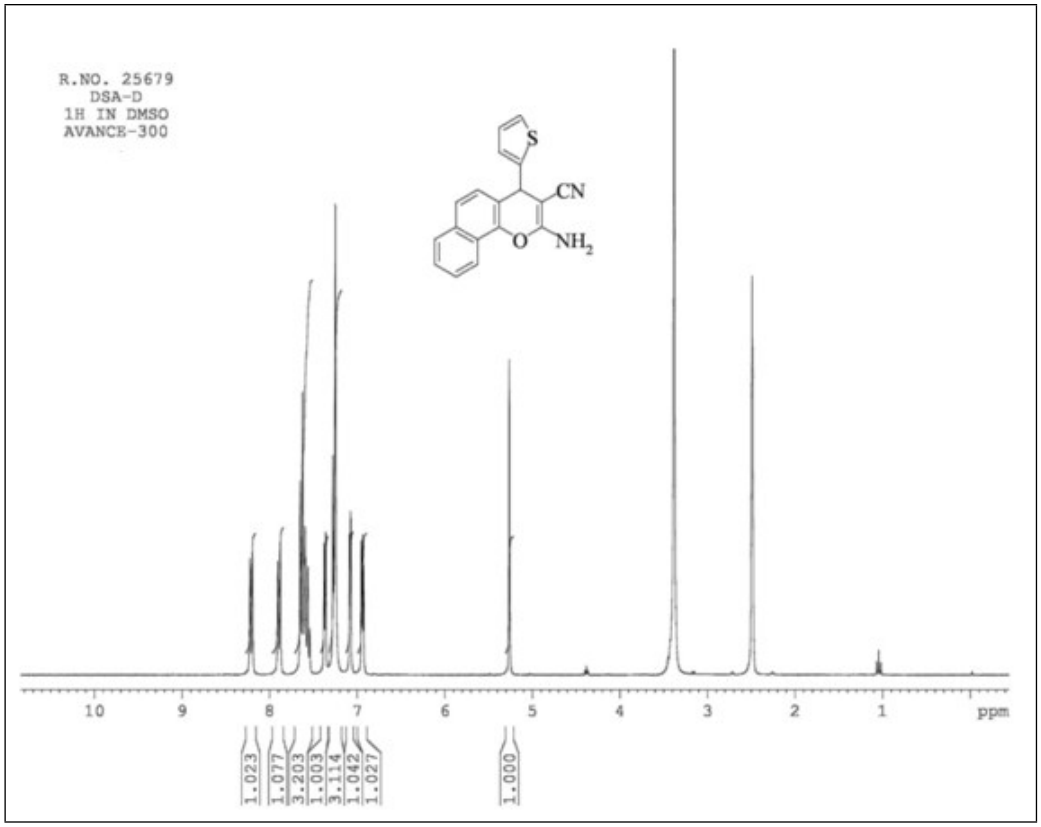
[13]C NMR spectrum of compound 5k



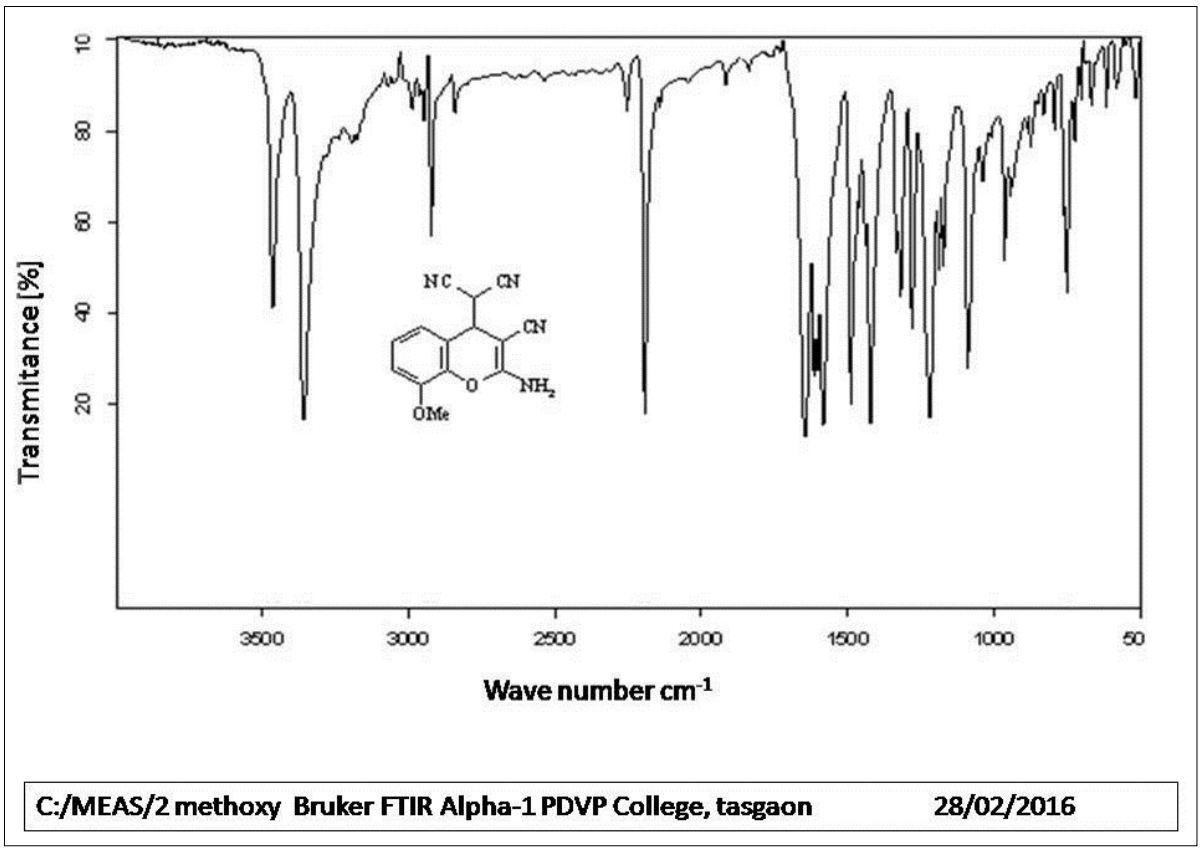
[1]HNMR spectrum of compound 5l



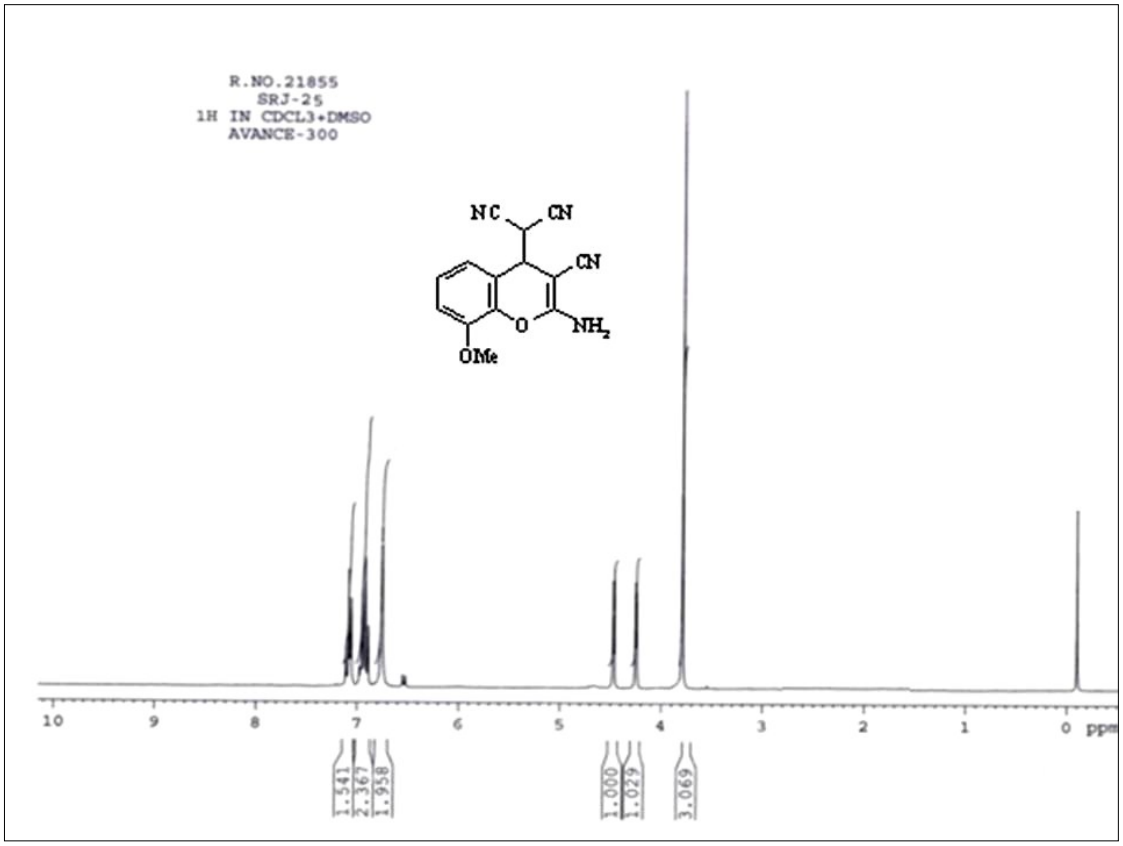
[1]HNMR spectrum of compound 5p



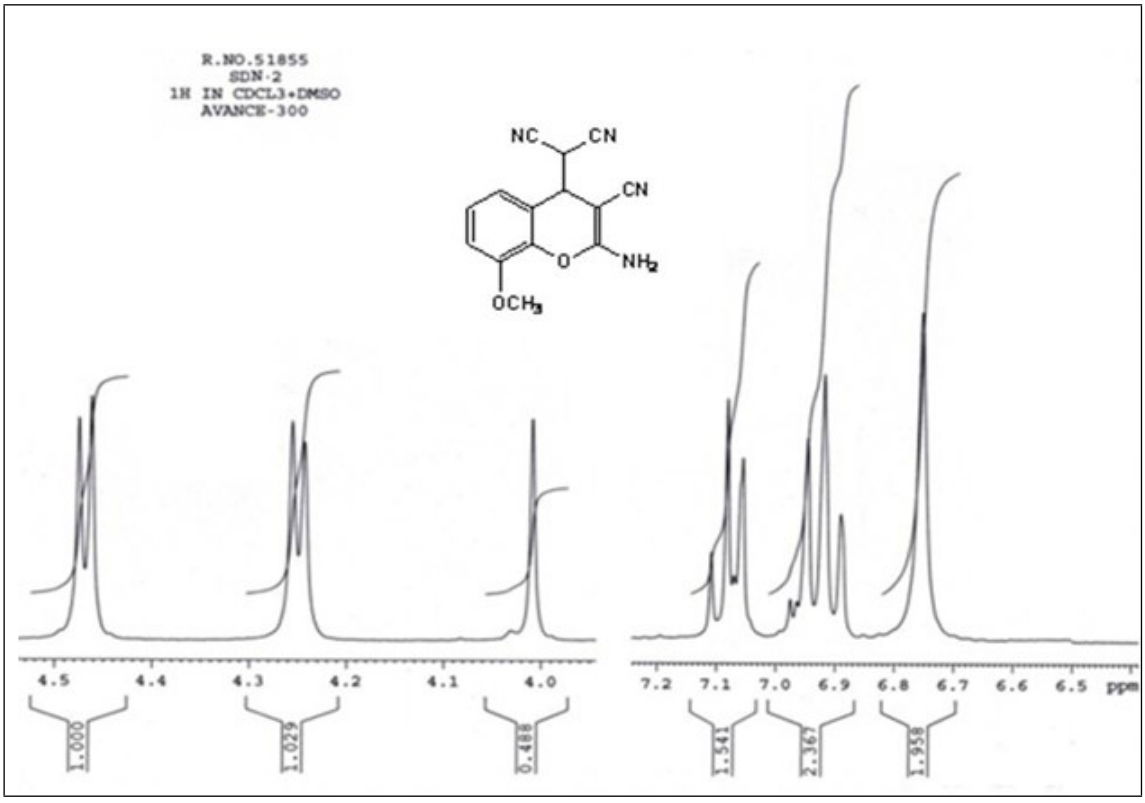
^{1}HNMR spectrum of compound 5q



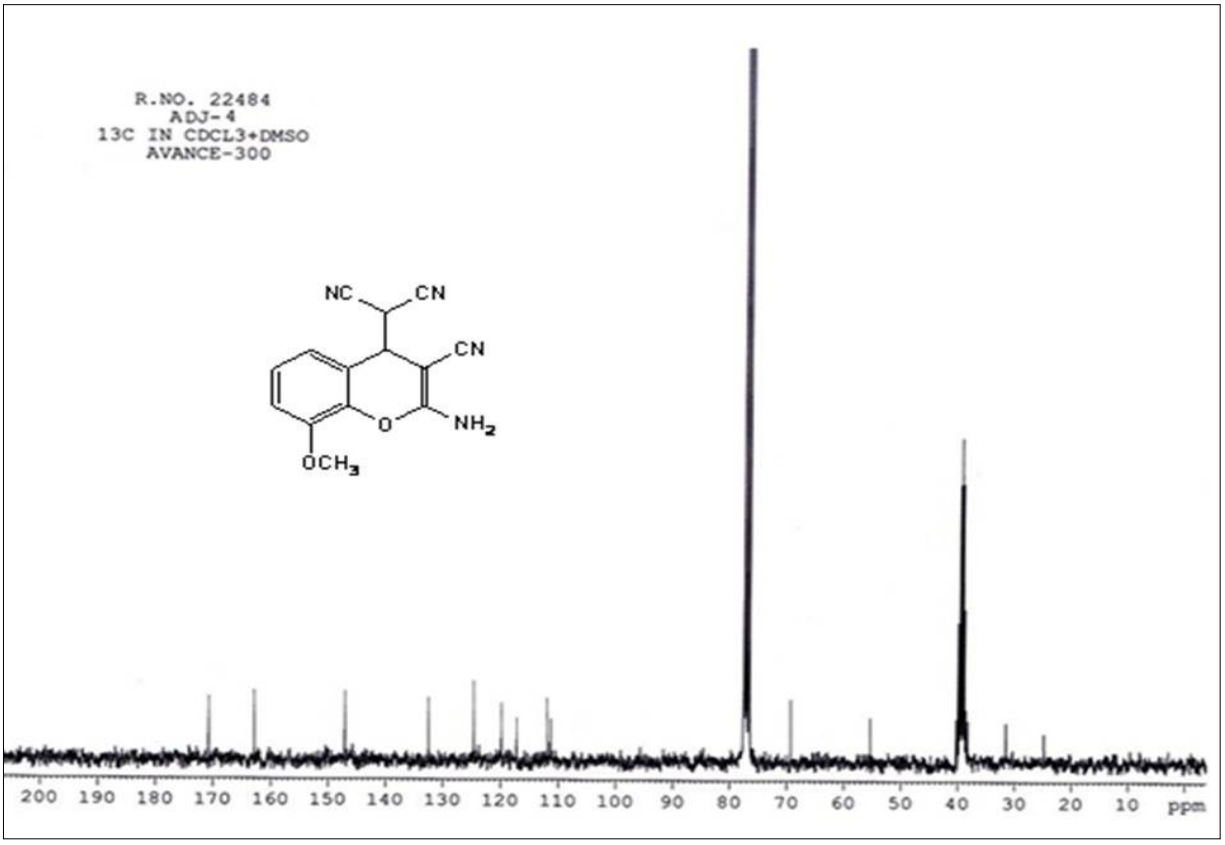
IR spectrum of compound 7c



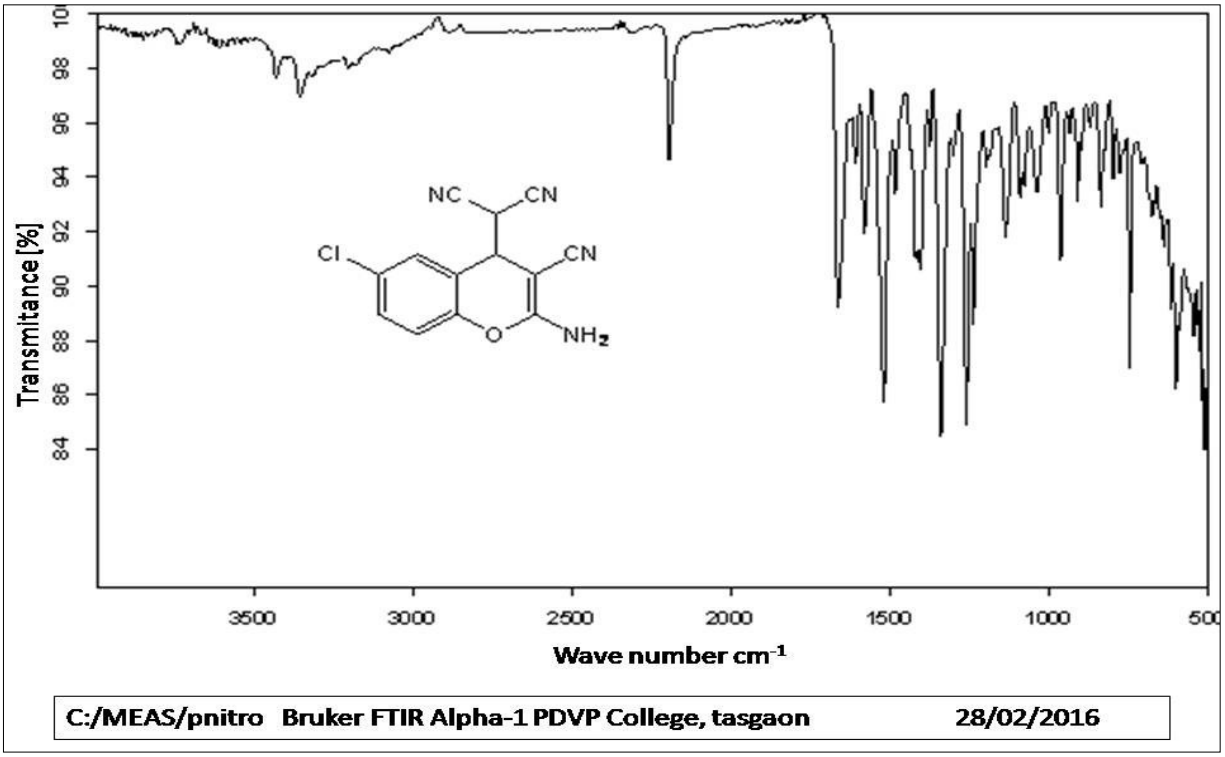
[1]HNMR spectrum of compound 7c



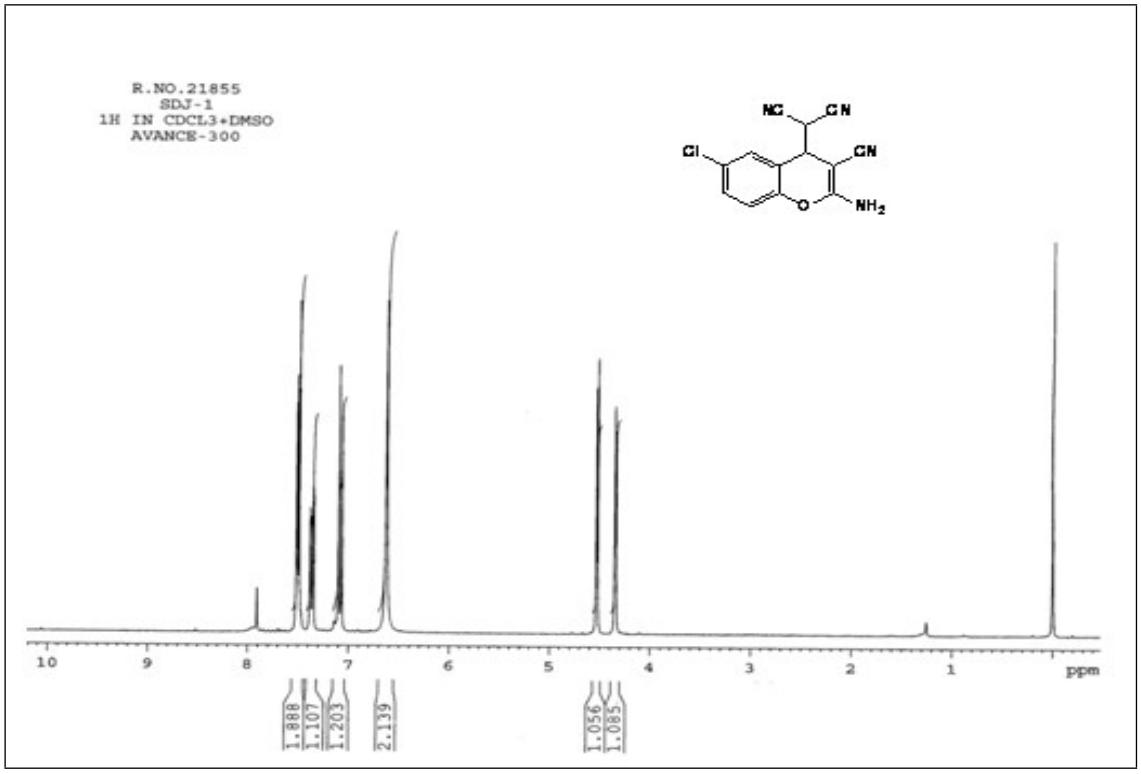
[1]HNMR spectrum of compound 7c



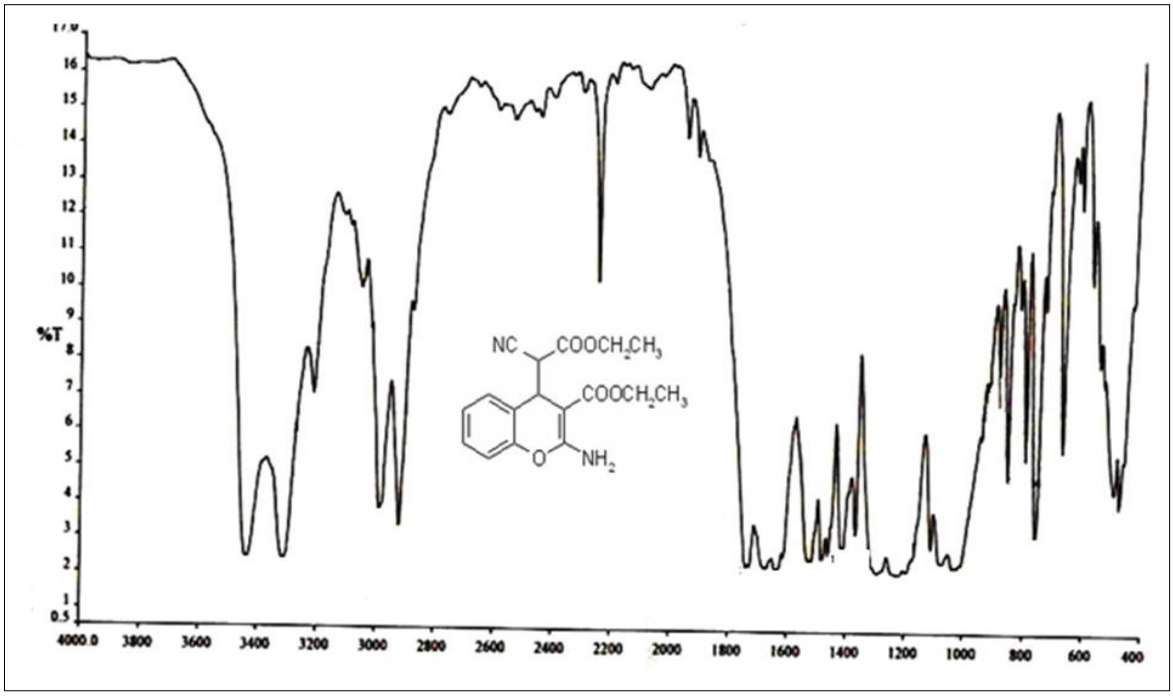
^{13}C NMR spectrum of compound 7c



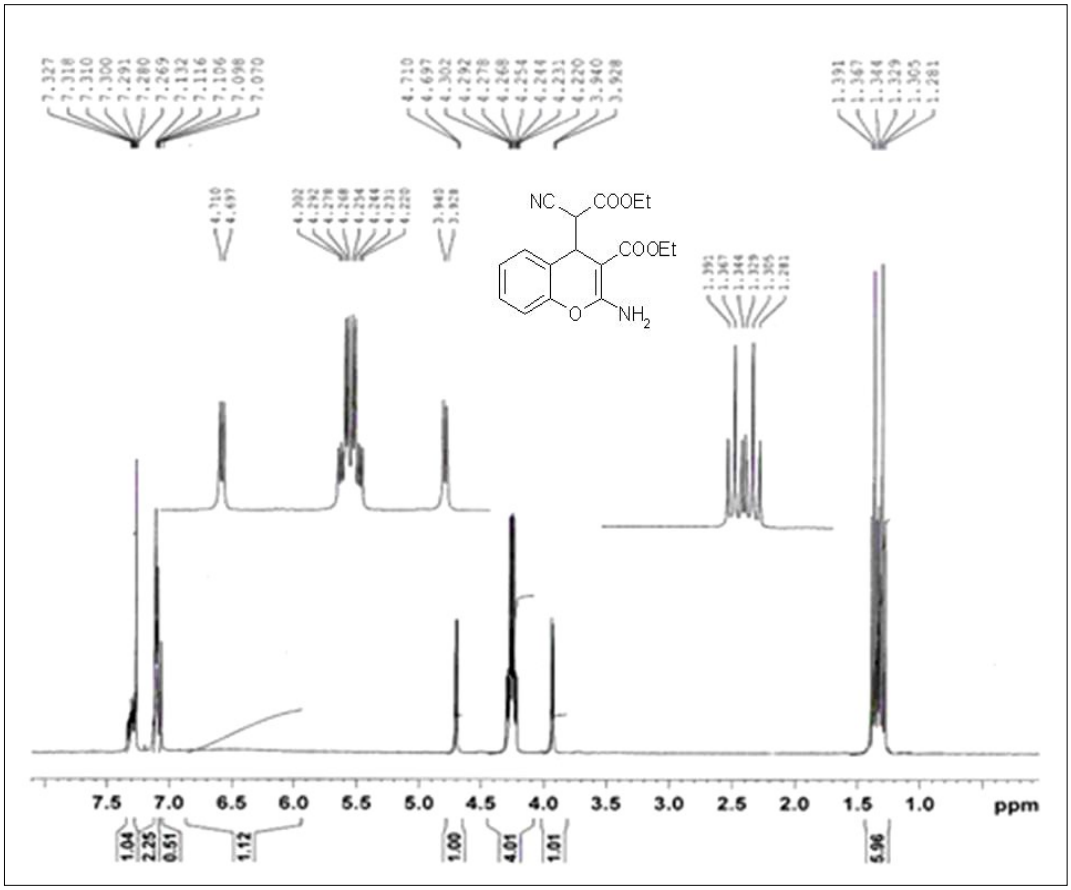
IR spectrum of compound 7d



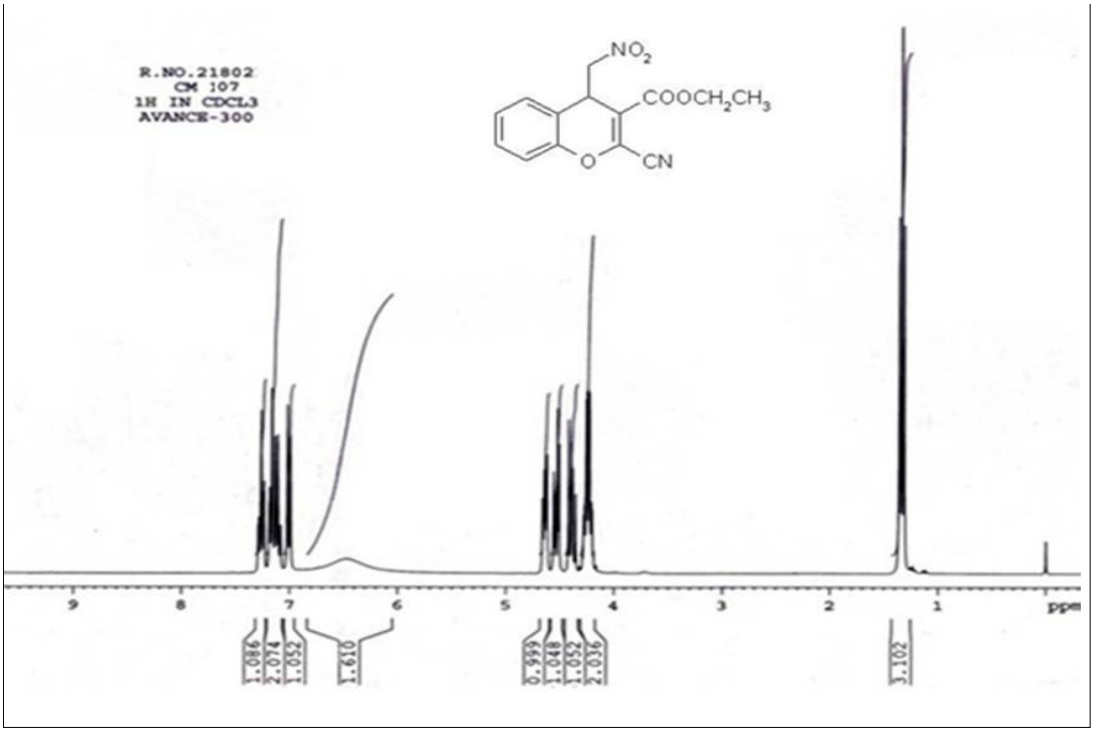
[1]HNMR spectrum of compound 7d



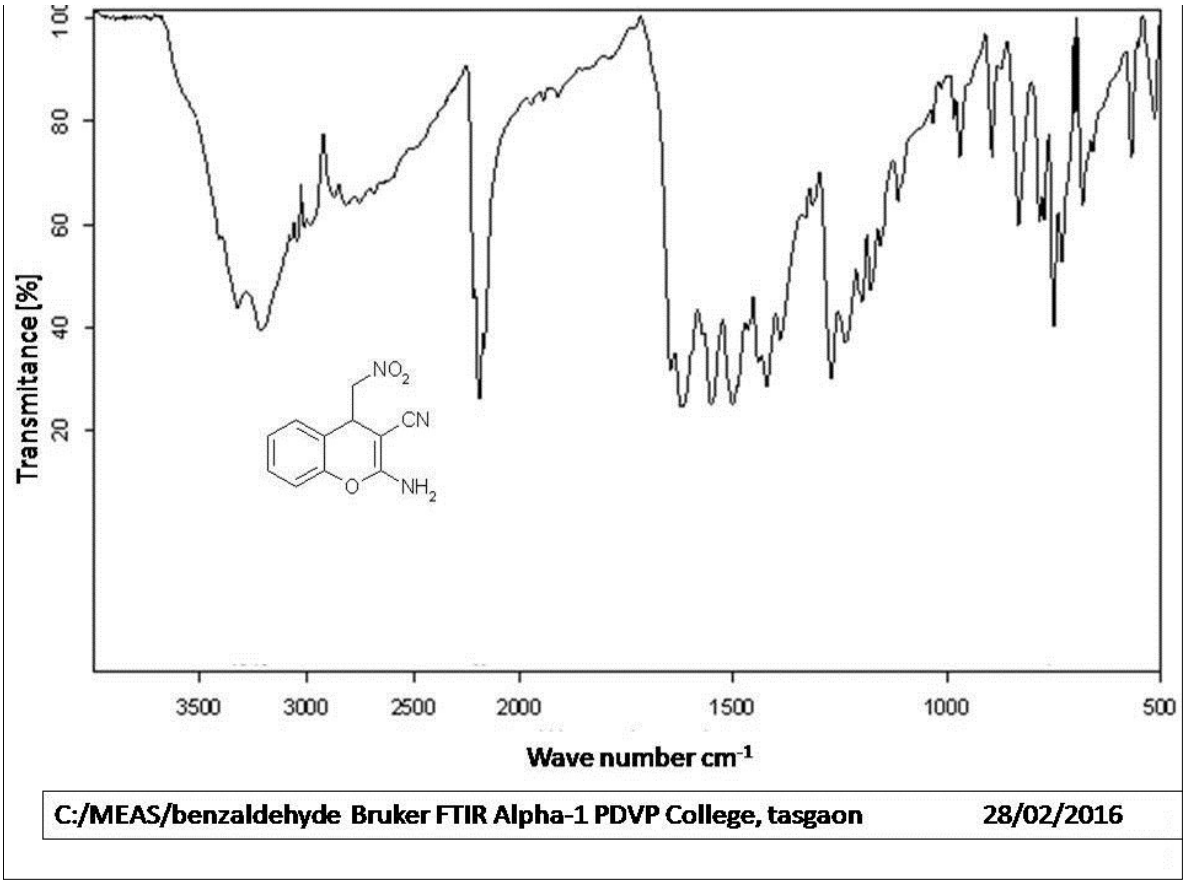
IR spectrum of compound 7f



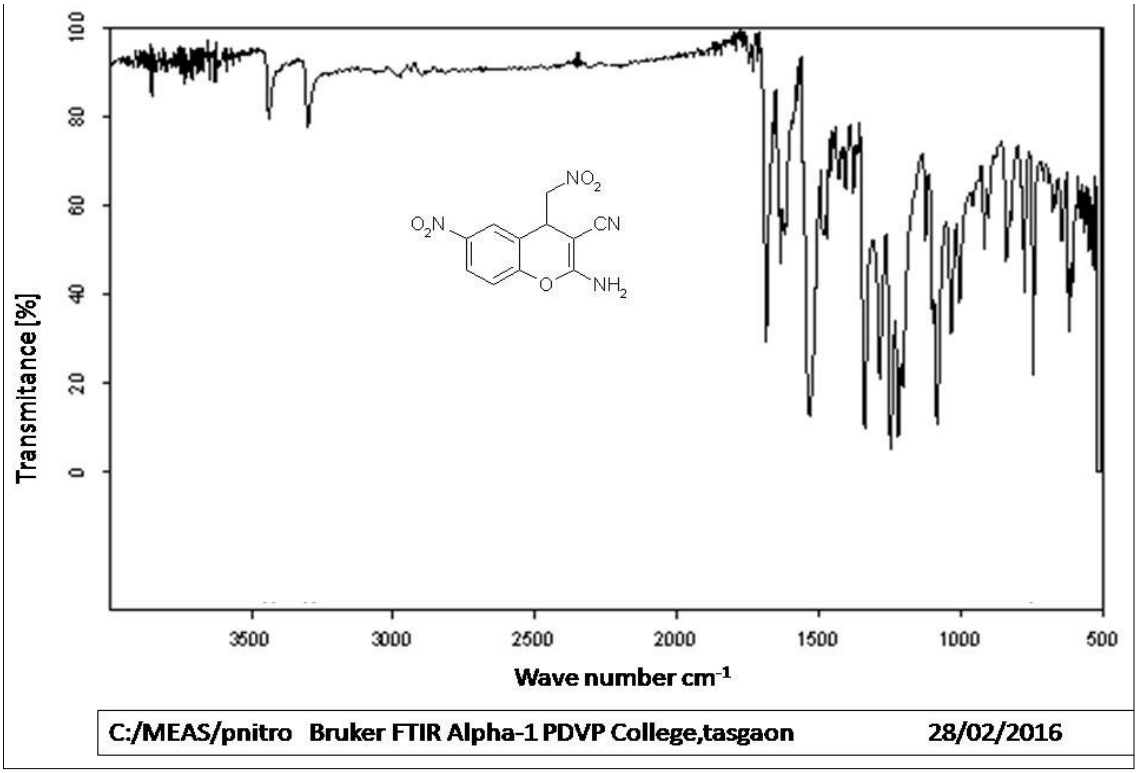
[1]HNMR spectrum of compound 7f



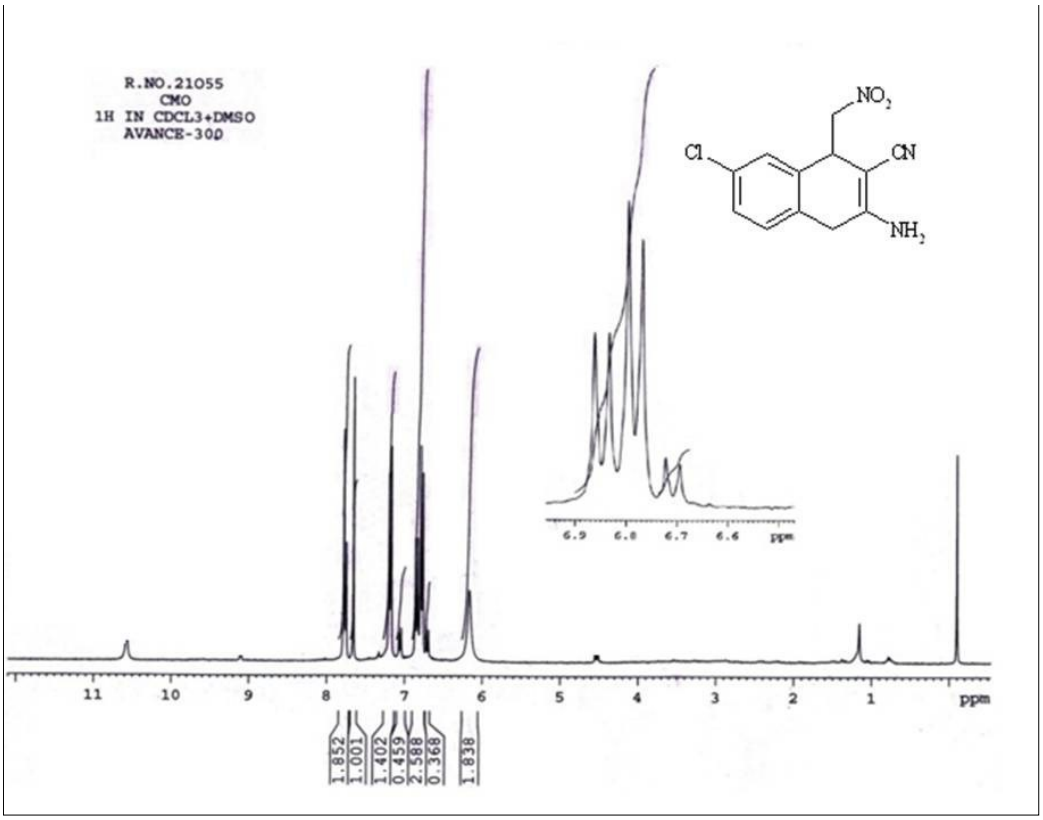
[1]HNMR spectrum of compound 8a



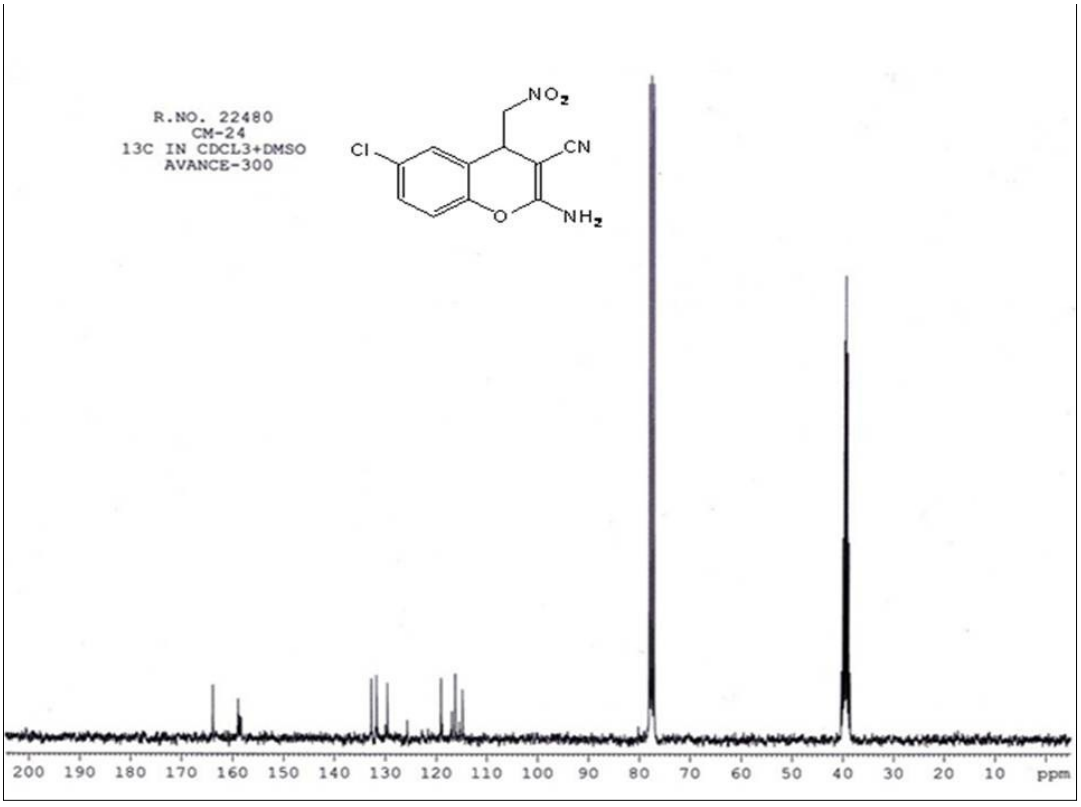
IR spectrum of compound 8a



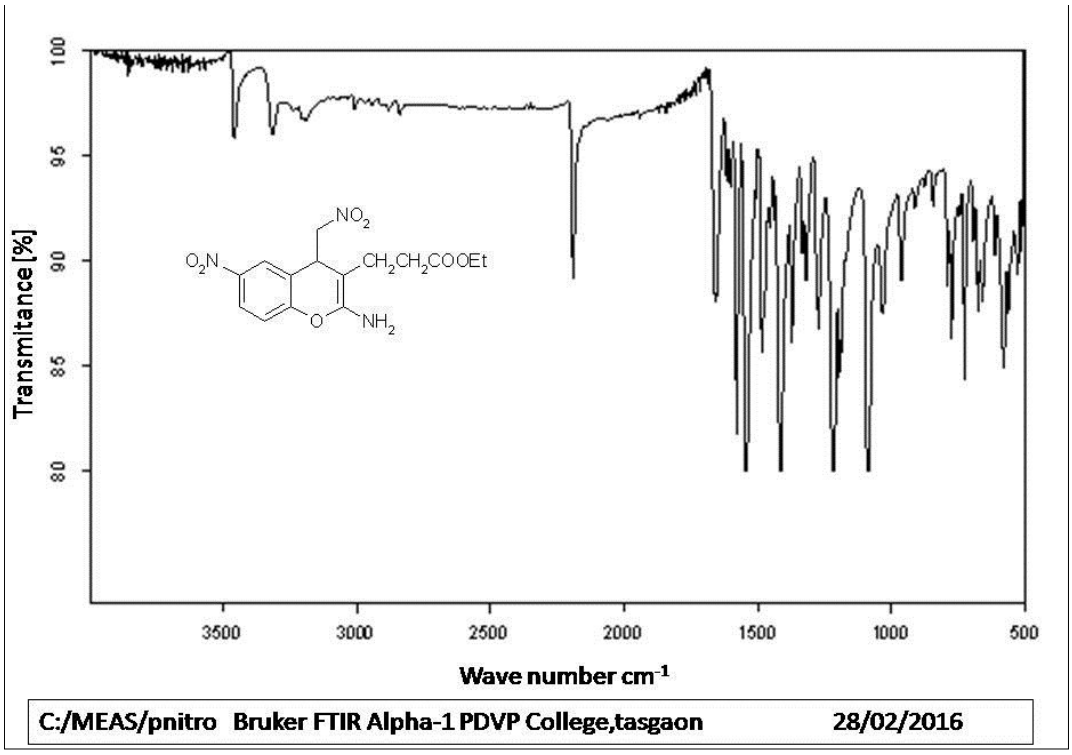
IR spectrum of compound 8c



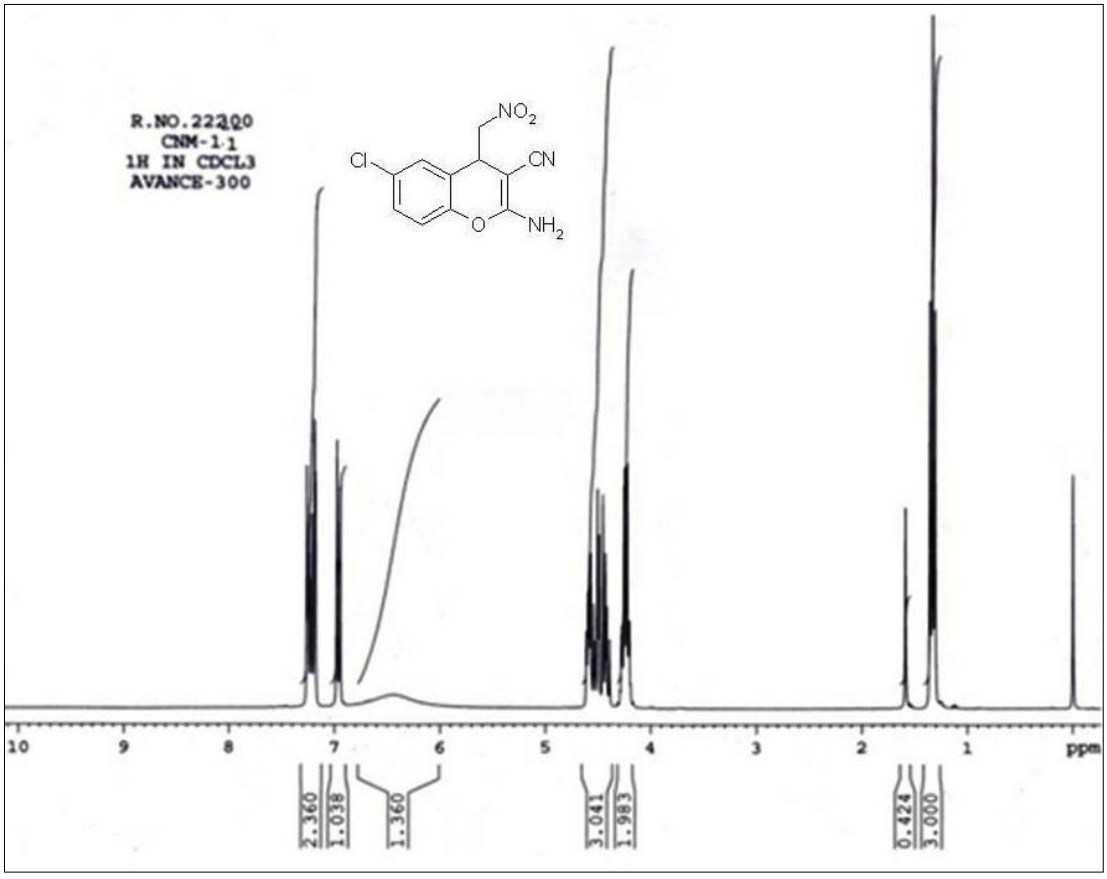
[1]HNMR spectrum of compound 8d



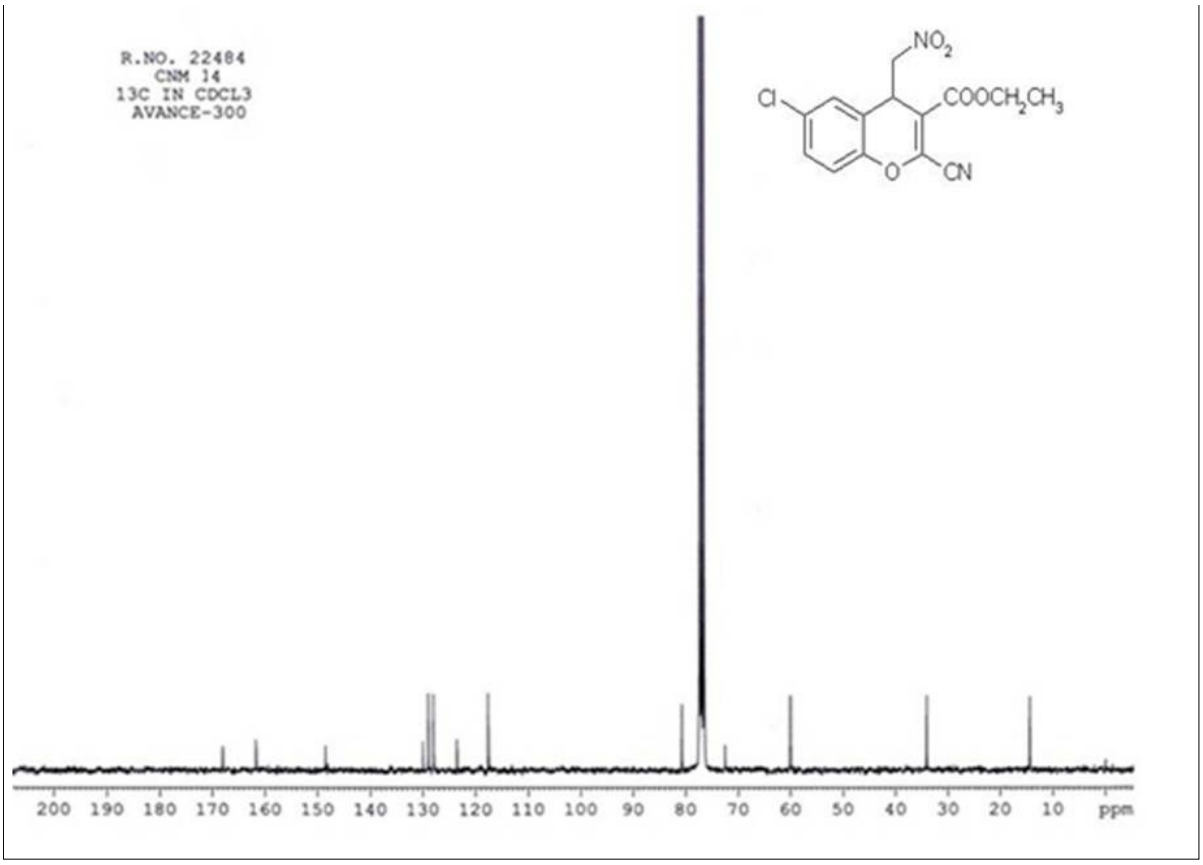
[13]C NMR spectrum of compound 8d



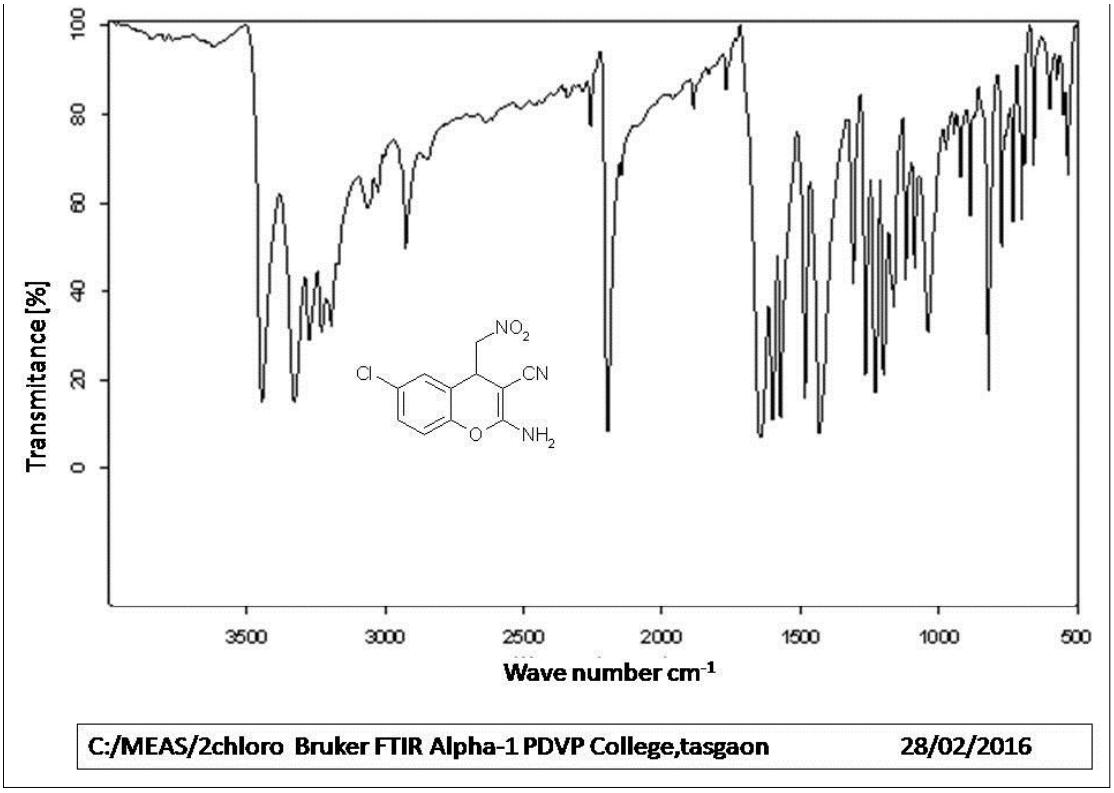
IR spectrum of compound 8g



[1]HNMR spectrum of compound 8d



^{13}C NMR spectrum of compound 8f



IR spectrum of compound 8d