Supplementary data

Tandem Knoevenagel-Michael-Cyclocondensation Reaction of Malononitrile, Various Aldehydes and Dimedone using Acetic Acid Functionalized Ionic Liquid

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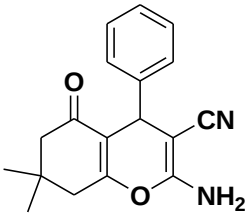
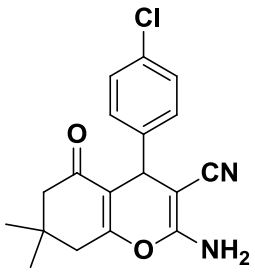
Data of compounds

2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(1)***



mp: 228-230^{o}C; IR (KBr, cm^{-1}): 3397, 3325, 3252, 2961, 2200, 1680, 1660, 1604, 1371, 1214, 695. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.94 (s, 3H), 1.02 (s, 3H), 2.08 (d, *J* = 16.04 Hz, 1H), 2.24 (d, *J* = 16.04 Hz, 1H), 2.48-2.53 (m, 2H), 4.15 (s, 1H), 6.97 (s, 2H), 7.14 (t, *J* = 7.12 Hz, 3H), 7.25-7.28 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 26.76, 28.35, 31.76, 35.53, 49.93, 58.27, 112.69, 119.68, 127.10, 128.29, 144.70, 158.44, 162.46, 195.62.

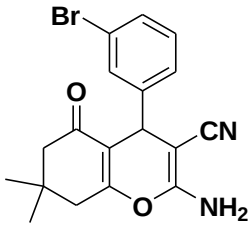
2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile ***(2)***



mp: 155-158 ^{o}C; IR (KBr, cm^{-1}): 3394,3325, 2964, 2193, 1685, 1658, 1370, 1214. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.92 (s, 3H), 1.01 (s, 3H), 2.08 (d, *J* = 16.04 Hz, 1H), 2.22 (d, *J* = 16.08 Hz, 1H), 2.47-2.53 (m, 2H), 4.17 (s, 1H), 7.03 (s, 2H), 7.15 (d, *J* = 8.44 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 20.71, 26.81, 28.26, 31.76, 35.07, 49.90, 57.73, 59.71, 112.29, 119.51, 128.24, 129.07, 131.07, 143.70, 158.46, 162.58, 170.30, 195.64.

2-amino-4-(3-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

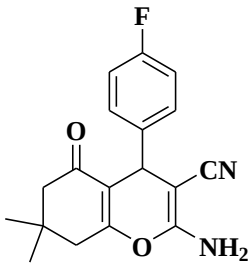
(3)



mp: 224-226 ^{o}C; IR (KBr, cm^{-1}): 3346, 3258, 3168, 2963, 2192, 1684, 1658, 1605, 1371, 1215, 695. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.92 (s, 3H), 0.99 (s, 3H), 2.08 (d, *J* = 16.04 Hz, 1H), 2.21 (d, *J* = 16.04 Hz, 1H), 2.48-2.52 (m, 2H), 4.17 (s, 1H), 7.05 (s, 2H), 7.12 (d, *J* = 7.72 Hz, 1H), 7.21-7.26 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 26.74, 28.27, 31.79, 35.29, 49.88, 57.61, 112.05, 119.45, 121.51, 126.32, 129.48, 129.89, 130.59, 147.43, 158.49, 162.81, 195.66.

2-amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

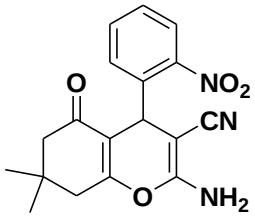
(4)



mp: 173-175^{o}C; IR (KBr, cm^{-1}): 3365, 3327, 2965, 2189, 1685, 1216, 850, 567. ^{1}HNMR (90 MHz, $CDCl_3$): δ (ppm) 0.99 (s, 3H), 1.10 (s, 3H), 2.09-2.26 (m, 2H), 2.39-2.58 (m, 2H), 4.72 (s, 1H), 6.79-6.98 (m, 2H), 7.18-7.33 (m, 4H).

2-amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

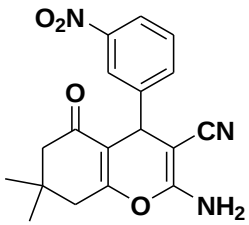
(5)



mp: 226-228 ^{o}C; IR (KBr, cm^{-1}): 3474, 3331, 3255, 2197, 1686, 1662, 1597,1525, 1364, 1214, 643. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.81 (s, 3H), 0.94 (s, 3H), 1.94 (d, *J* = 16.12 Hz, 1H), 2.13 (d, *J* = 16.16 Hz, 1H), 2.46 (Distorted AB System, 2H), 4.86 (s, 1H), 7.11 (s, 2H), 7.28 (dd, *J* = 6.78, 1.00 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.57-7.75 (m, 2H). ^{13}CNMR (100 MHz, DMSO-d_6):δ = 26.65, 28.24, 29.89, 31.80, 49.51, 56.30, 112.27, 123.68, 127.83, 130.23, 133.32, 138.91, 148.92, 159.14, 162.69, 195.9.

2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

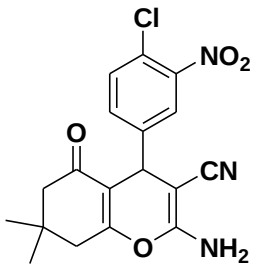
(6)



mp: 183-185 ^{o}C; IR (KBr, cm^{-1}): 3336, 2959, 2187, 1681, 1660, 1601, 1350, 1211. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.90 (s, 3H), 0.98 (s, 3H), 2.05 (d, *J* = 16.08Hz, 1H), 2.21 (d, *J* = 16.08 Hz, 1H), 2.44 (Distorted AB System, 2H), 4.35 (s, 1H), 7.13 (s, 2H), 7.62-7.54 (m, 2H), 7.91 (d, *J* = 1.88 Hz, 1H), 8.03-7.92 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 26.70,

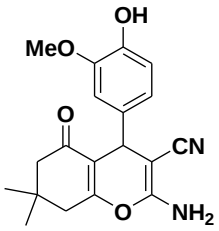
28.29, 31.80, 35.36, 49.82, 57.14, 111.73, 119.32, 121.61, 121.75, 129.99, 134.15, 146.96, 147.73, 158.59, 163.13, 195.74.

*2-amino-4-(4-chloro-3-nitrophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**7**)*



mp: 214-216 ^{o}C; IR (KBr, cm^{-1}): 3403, 3364, 3323, 3180, 2969, 2188, 1682, 1654, 1603, 1538, 1369, 1217, 1161, 1041. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.92 (s, 3H), 0.99 (s, 3H), 2.09 (d, *J* = 16.00 Hz, 1H), 2.21 (d, *J* = 16.00 Hz, 1H), 2.47 (m, 2H), 4.34 (s, 1H), 7.15 (s, 2H), 7.47-7.50 (m, 1H), 7.67 (d, *J* = 8.32 Hz, 1H), 7.82 (d, *J* = 1.72 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 27.01, 28.09, 31.78, 34.97, 49.83, 56.74, 111.27, 119.25, 122.87, 124.04, 131.48, 132.75, 145.94, 147.51, 158.54, 163.25, 195.79; MS: m/z = 373 (M^{+}).

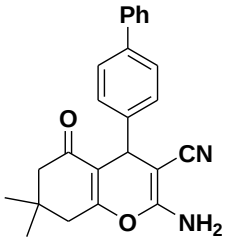
*2-amino-4-(4-hydroxy-3-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**8**)*



mp: 227-230^{o}C; IR (KBr, cm^{-1}): 3497, 3403, 3325, 3254, 2193, 1679, 1656, 1604, 1366, 1214, 554. ^{1}H NMR (400 MHz, DMSO-d_6):δ = 0.95 (s, 3H), 1.02 (s, 3H), 2.08 (d, *J* = 16.08 Hz, 1H),

2.23 (d, *J* = 16.08 Hz, 1H), 2.48-2.53 (m, 2H), 3.69 (s, 3H), 4.05 (s, 1H), 6.48-6.51 (m, 1H), 6.62-6.66 (m, 2H), 6.89 (s, 2H), 8.80 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 14.04, 26.58, 28.47, 31.71, 34.93, 49.99, 55.54, 58.69, 113.18, 115.29, 119.33, 135.77, 145.20, 147.20, 158.46, 162.12, 195.66.

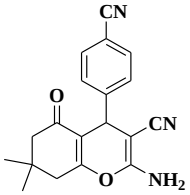
*2-amino-4-(4-benzophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**9**)*



mp: 246-248 ^{o}C; IR (KBr, cm^{-1}): 3386, 3320, 3211, 2193, 1682, 1654, 1606, 1366, 1214, 691. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.98 (s, 3H), 1.04 (s, 3H), 2.12 (d, *J* = 16.08 Hz, 1H), 2.26 (d, *J* = 16.04 Hz, 1H), 2.53 (Distorted AB System, 2H), 4.22 (s, 1H), 7.02 (s, 2H), 7.23 (d, *J* = 8.16 Hz, 2H), 7.34 (t, *J* = 7.32 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.57-7.64 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 26.88, 28.30, 31.81, 35.24, 49.97, 58.11, 112.58, 119.71, 126.56, 127.74, 128.85, 138.50, 139.86, 143.93, 158.49, 162.54, 195.71; MS: m/z = 370 (M^+).

2-amino-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

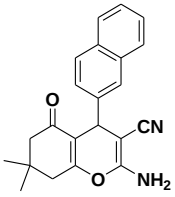
(10)



mp: 223-225 ^{o}C; IR (KBr, cm^{-1}): 3399, 3323, 3212, 2962, 2225, 1685, 1656, 1602, 1214, 858. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.91 (s, 3H), 1.00 (s, 3H), 2.07 (d, *J* = 16.03 Hz, 1H), 2.22 (d, *J* = 16.04Hz, 1H), 2.46 (Distorted AB System, 2H), 4.25 (s, 1H), 7.11 (s, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.72, 26.92, 31.78, 35.77, 49.83, 57.09, 59.71, 109.40, 111.70, 118.73, 119.32, 128.30, 132.37, 150.19, 158.53, 163.05, 170.30, 195.67.

2-amino-7,7-dimethyl-4-(naphthalen-2-yl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

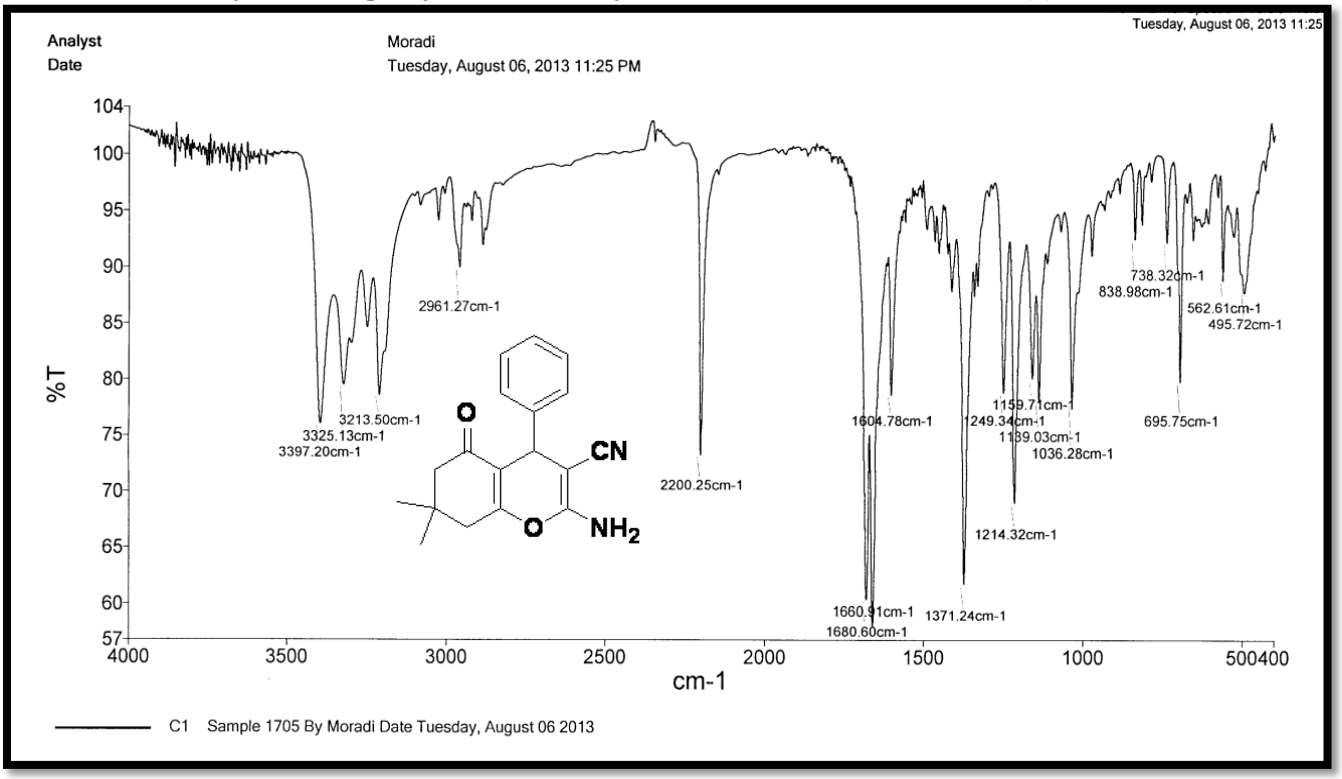
(11)

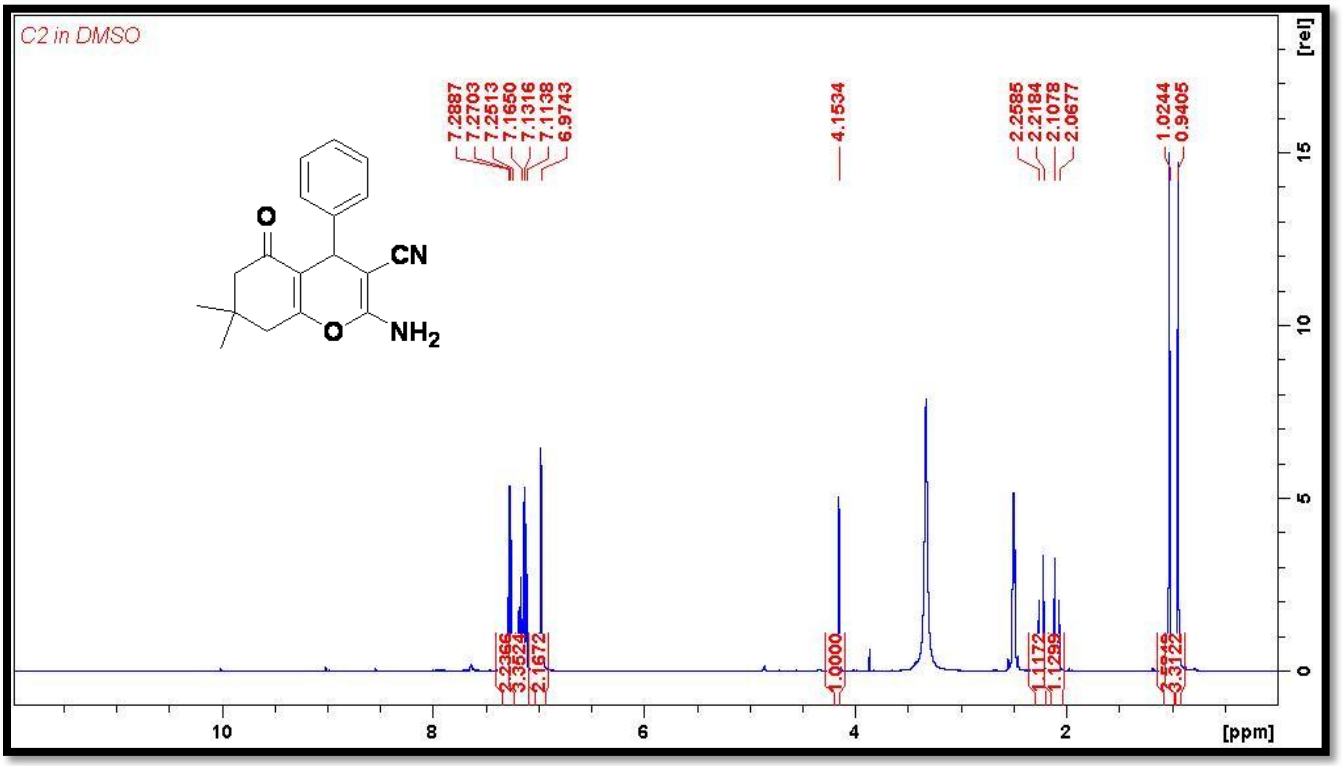


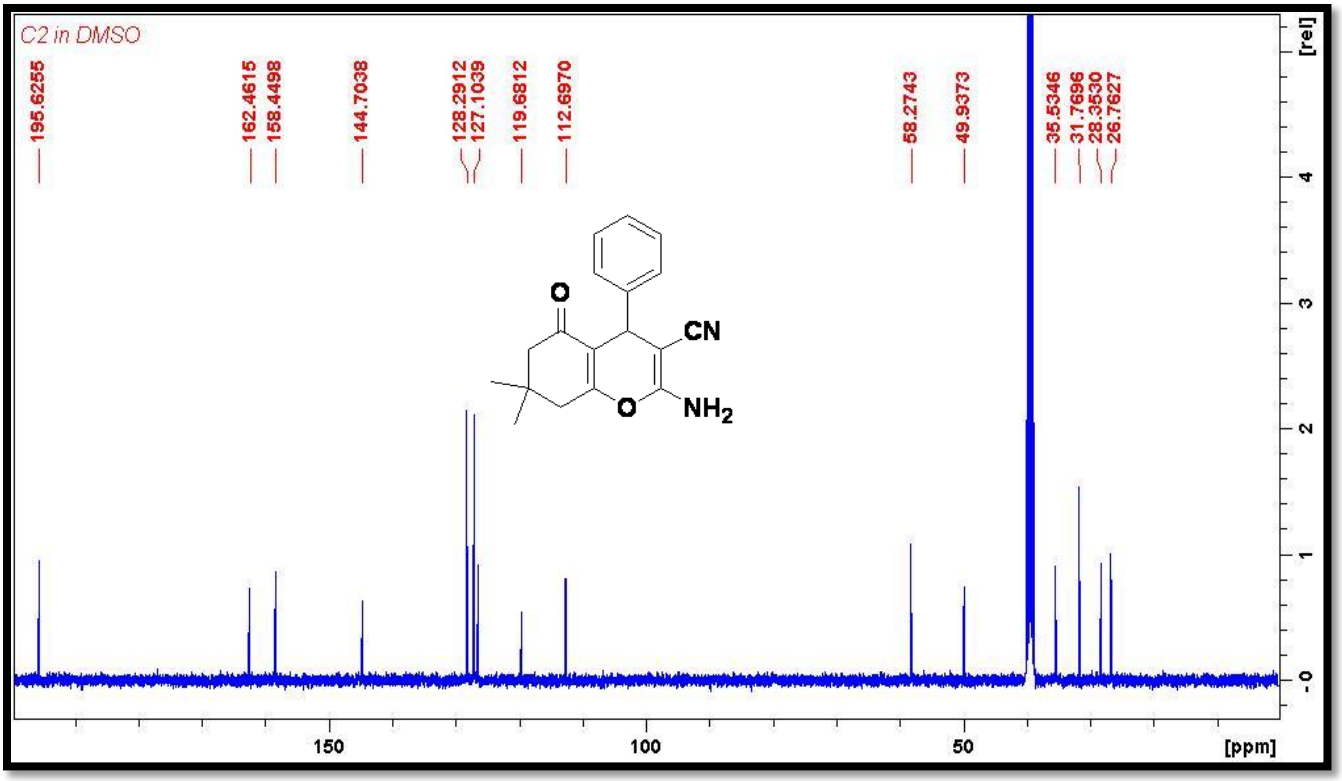
mp: 262-265^{o}C; IR (KBr, cm^{-1}): 3349, 3174, 2964, 2189, 1684, 1654, 1605, 1376, 1215, 1140, 1036. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.85 (s, 3H), 0.93 (s, 3H), 1.97 (d, *J* = 16.04 Hz, 1H), 2.15 (d, *J* = 16.04 Hz, 1H), 2.39 (Distorted AB System, 2H), 4.25 (s, 1H), 6.95 (s, 2H), 7.16-7.19 (m, 1H), 7.35-7.39 (m, 2H), 7.56 (s, 1H), 7.73-7.78 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 26.70, 28.37, 31.78, 35.85, 49.96, 58.08, 112.50, 119.69, 125.60, 126.15, 127.40, 127.61, 131.96, 132.80, 142.00, 158.46, 162.55, 195.72; MS: m/z = 344 (M^{+}).

NMR, IR and Mass spectra of compounds:

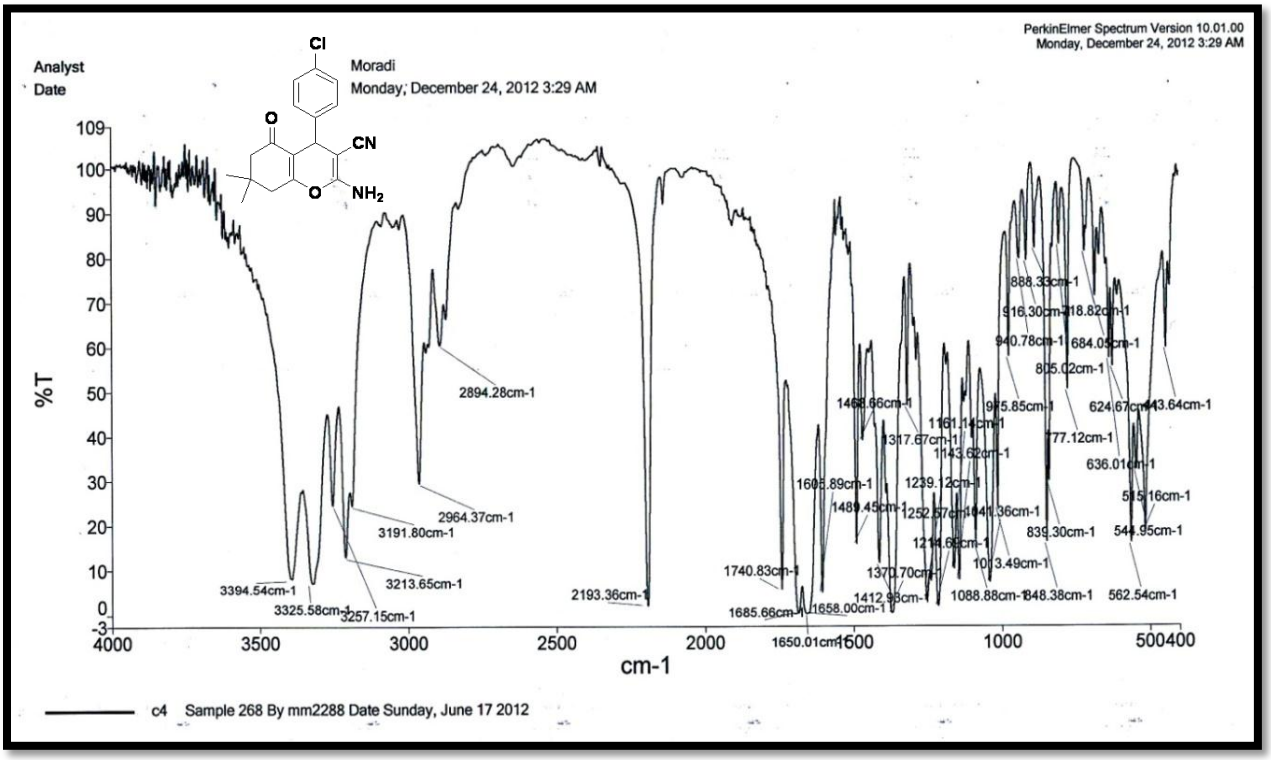
2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (1)

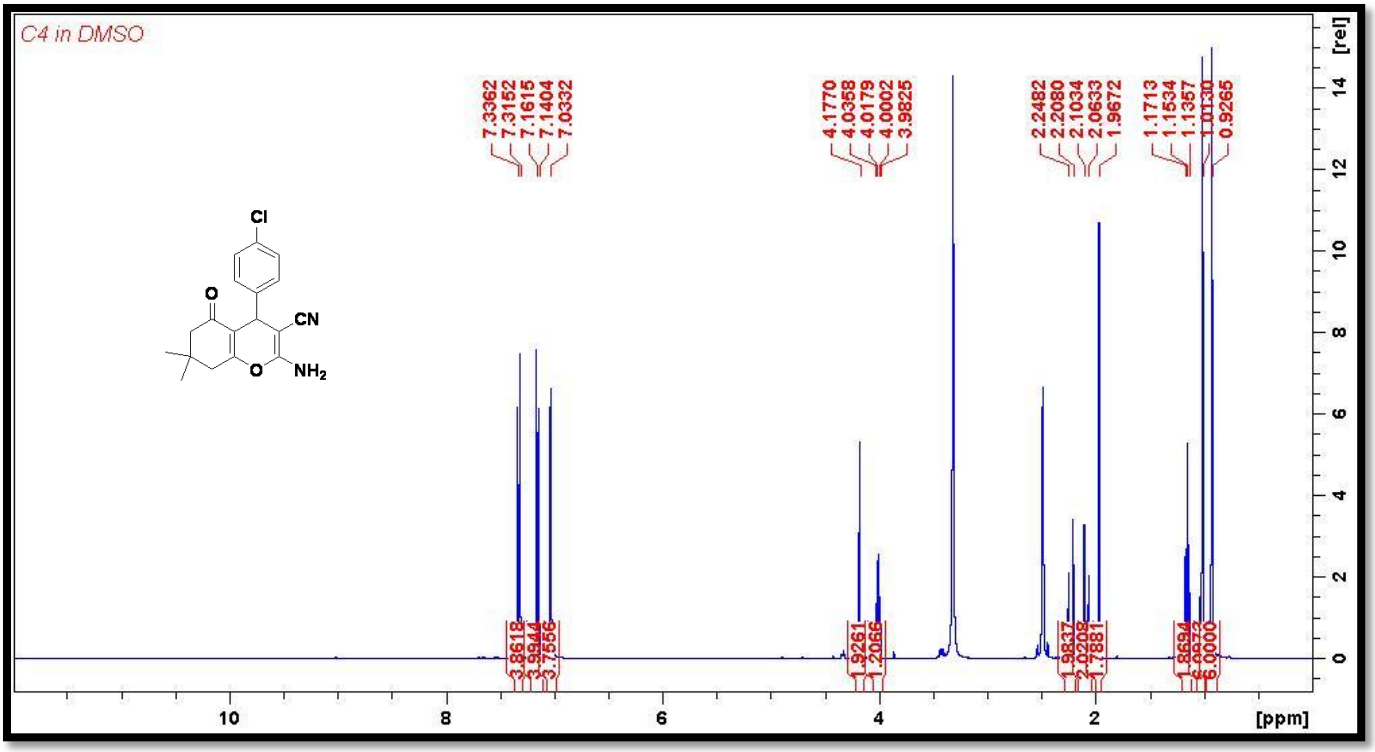


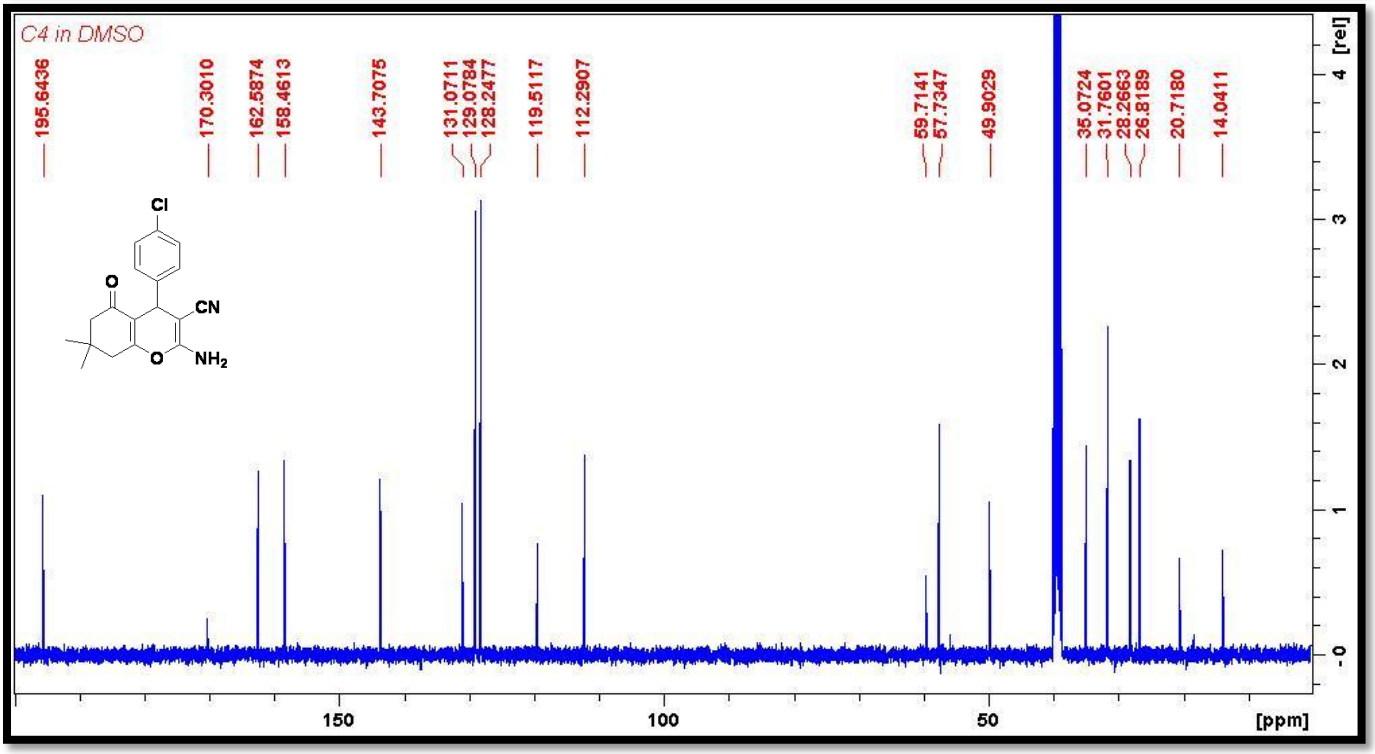




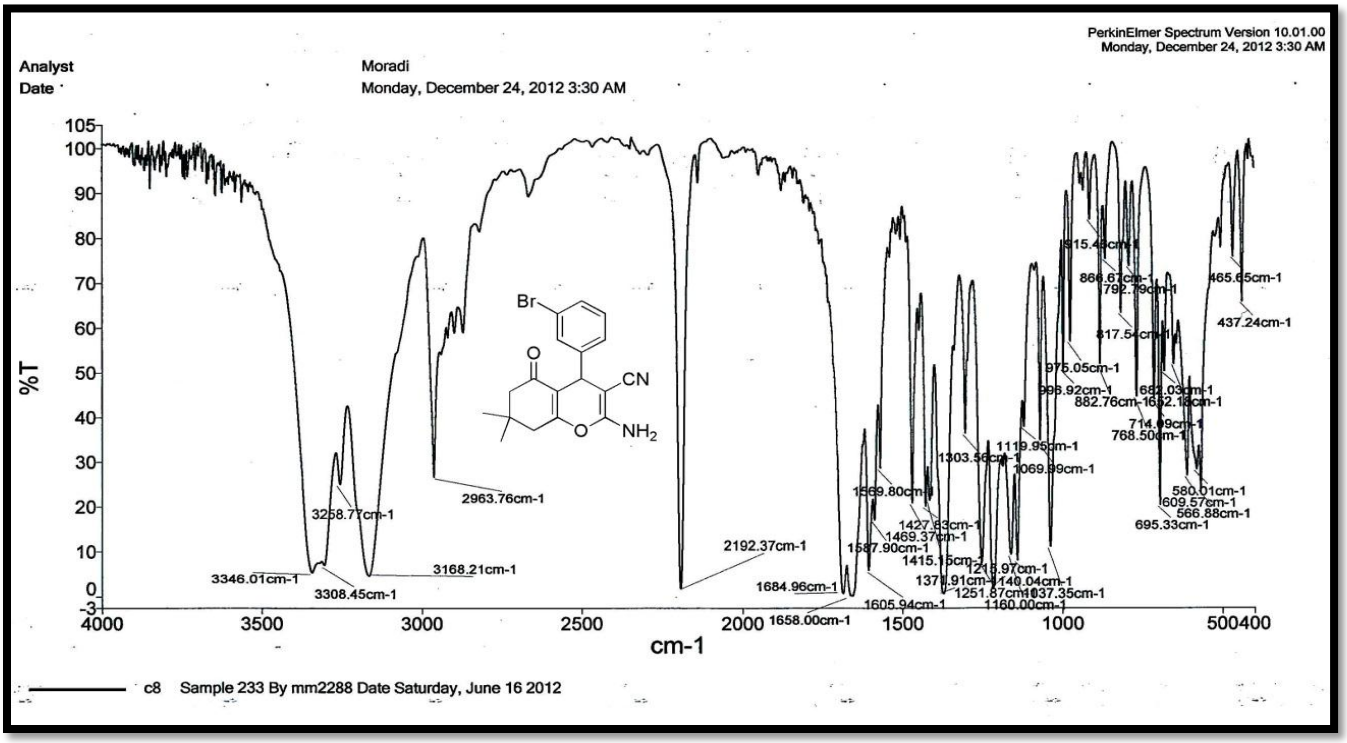
2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (2)

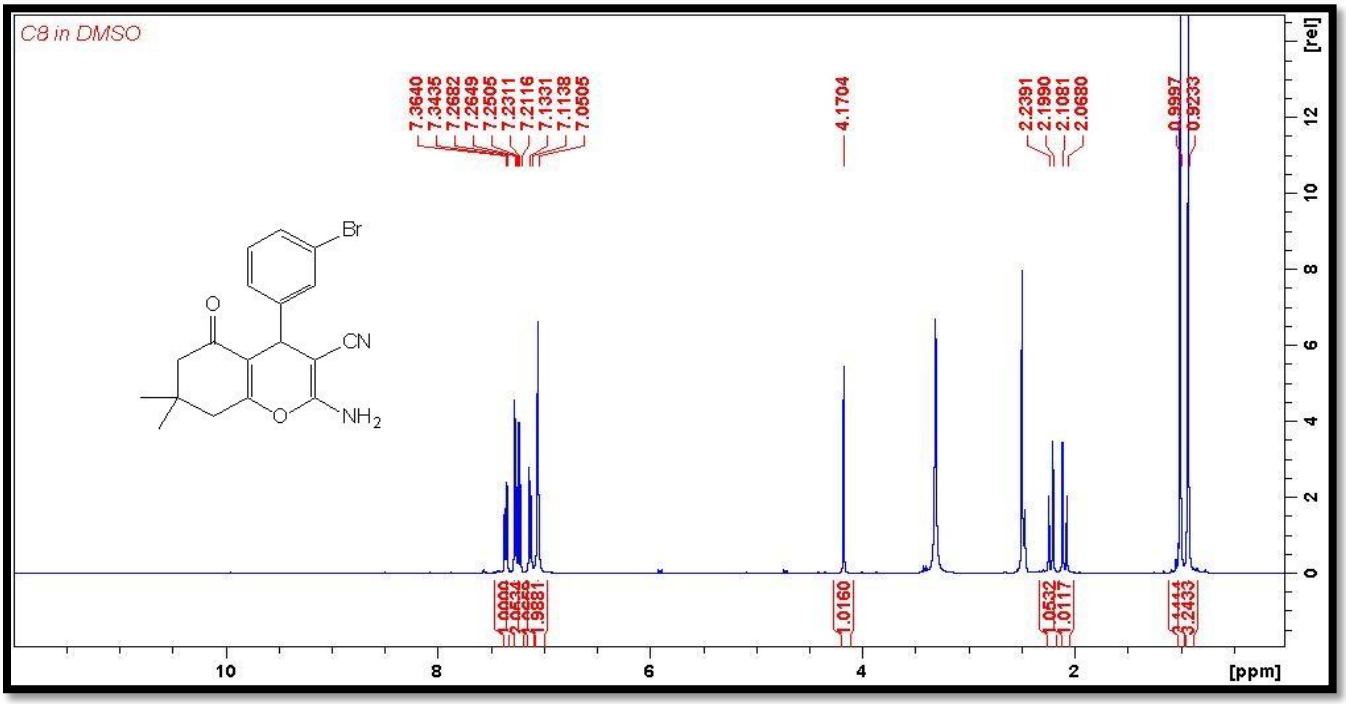


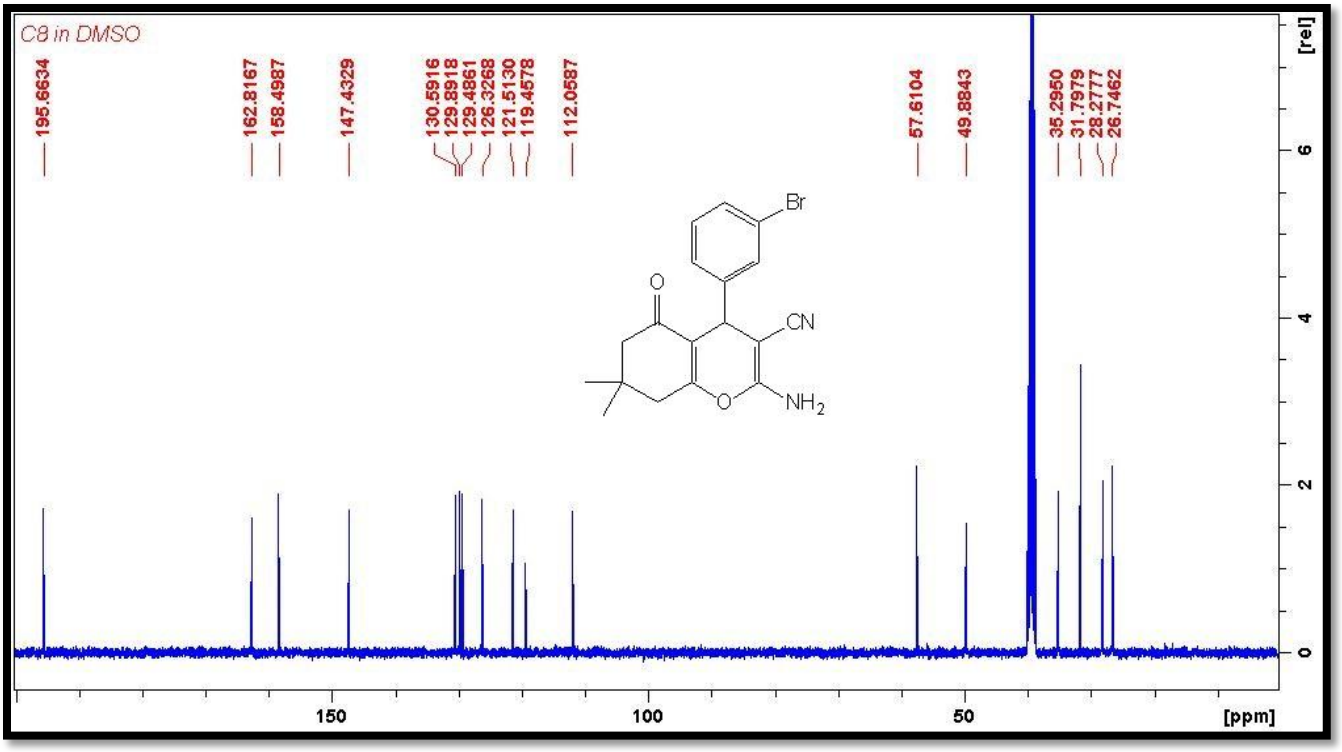




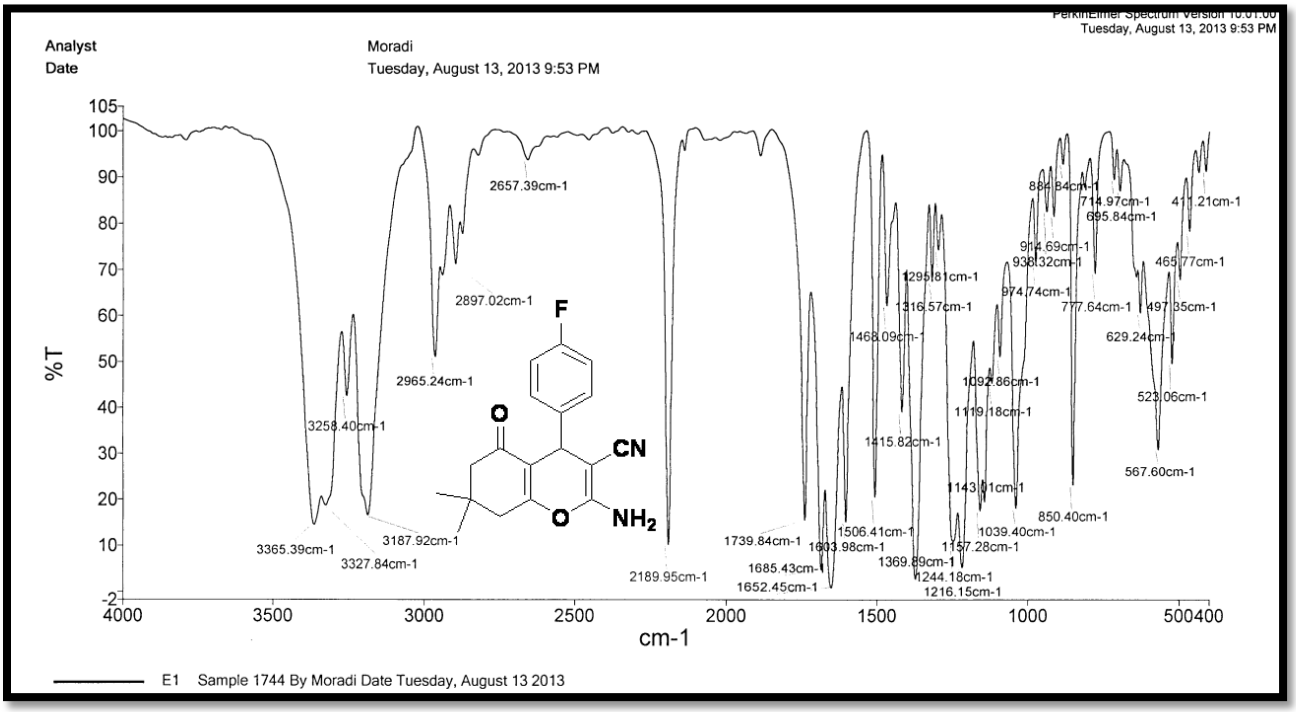
2-amino-4-(3-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (3)

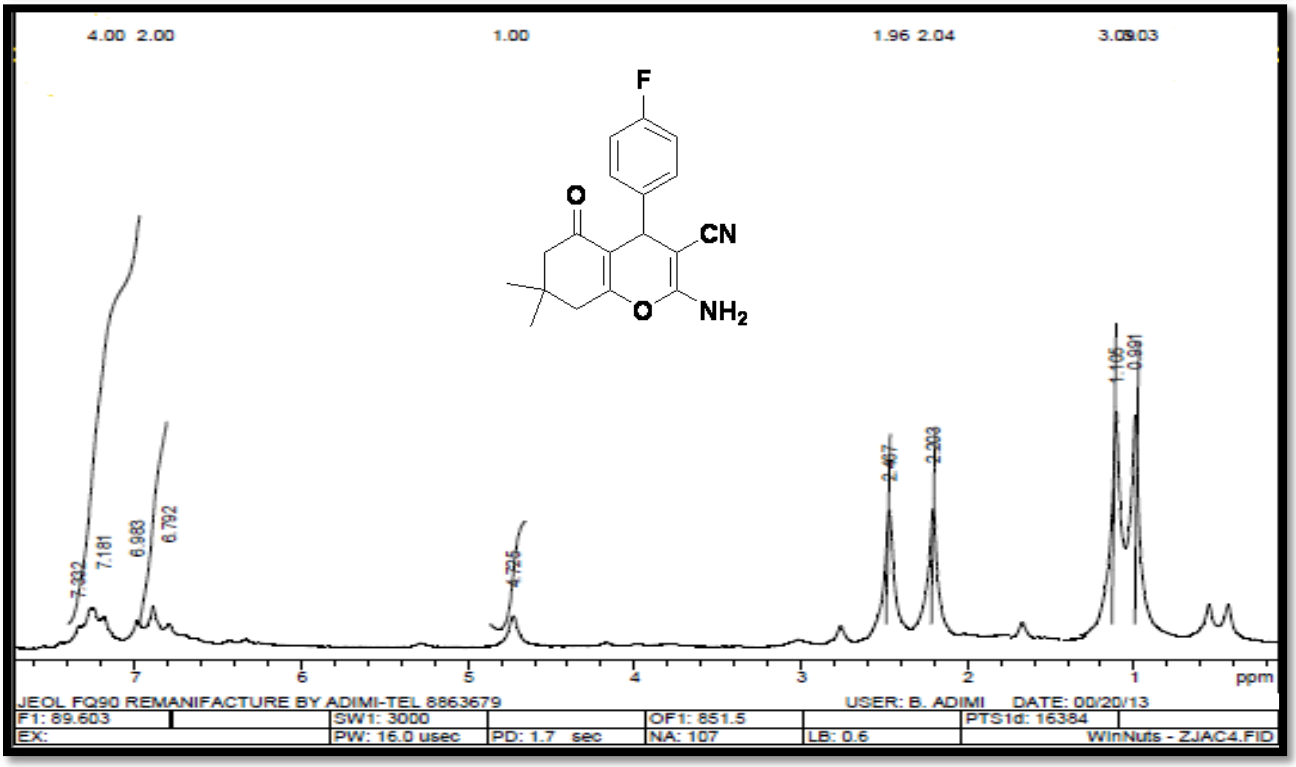




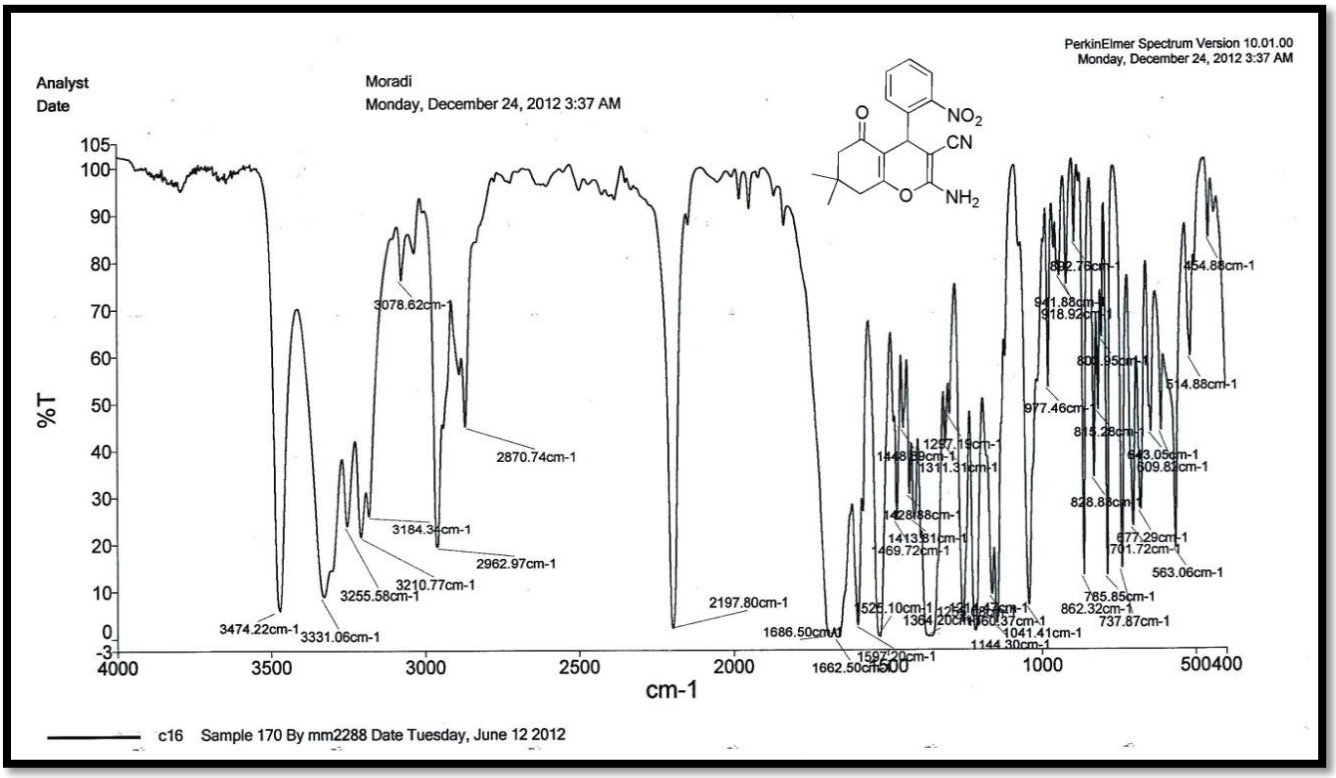


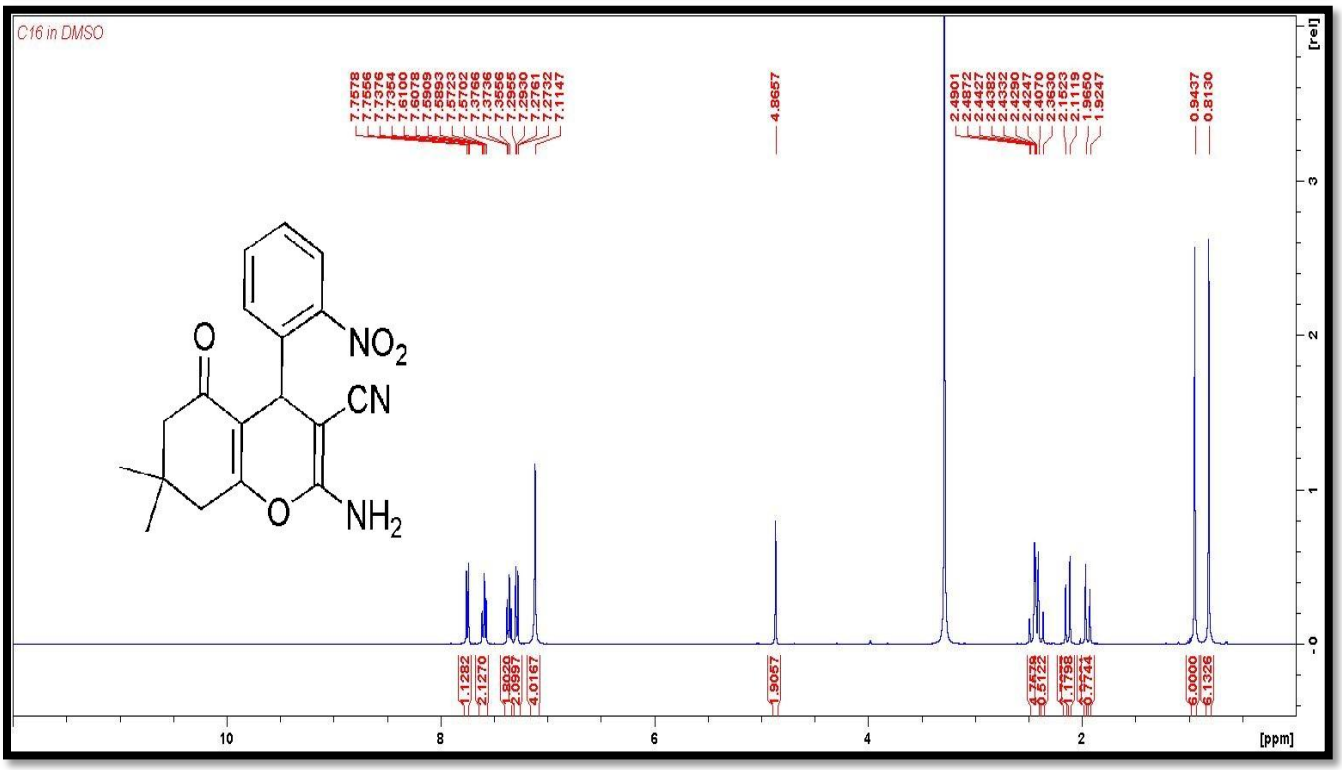
2-amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4)

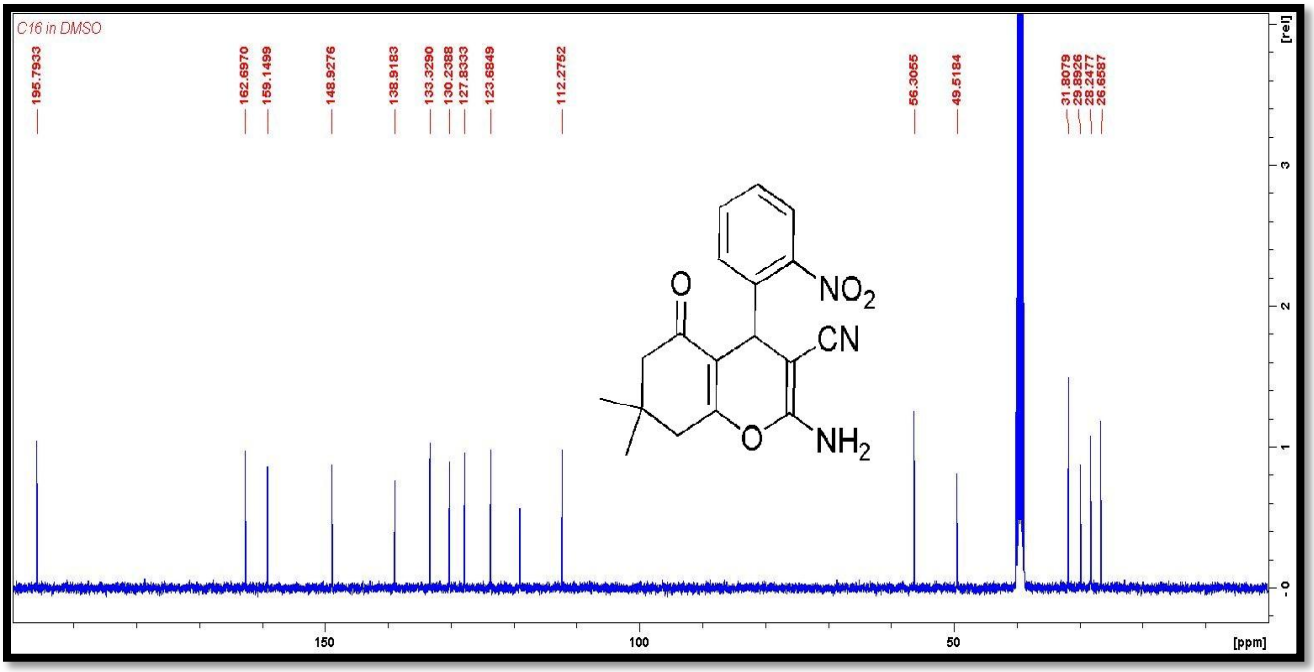




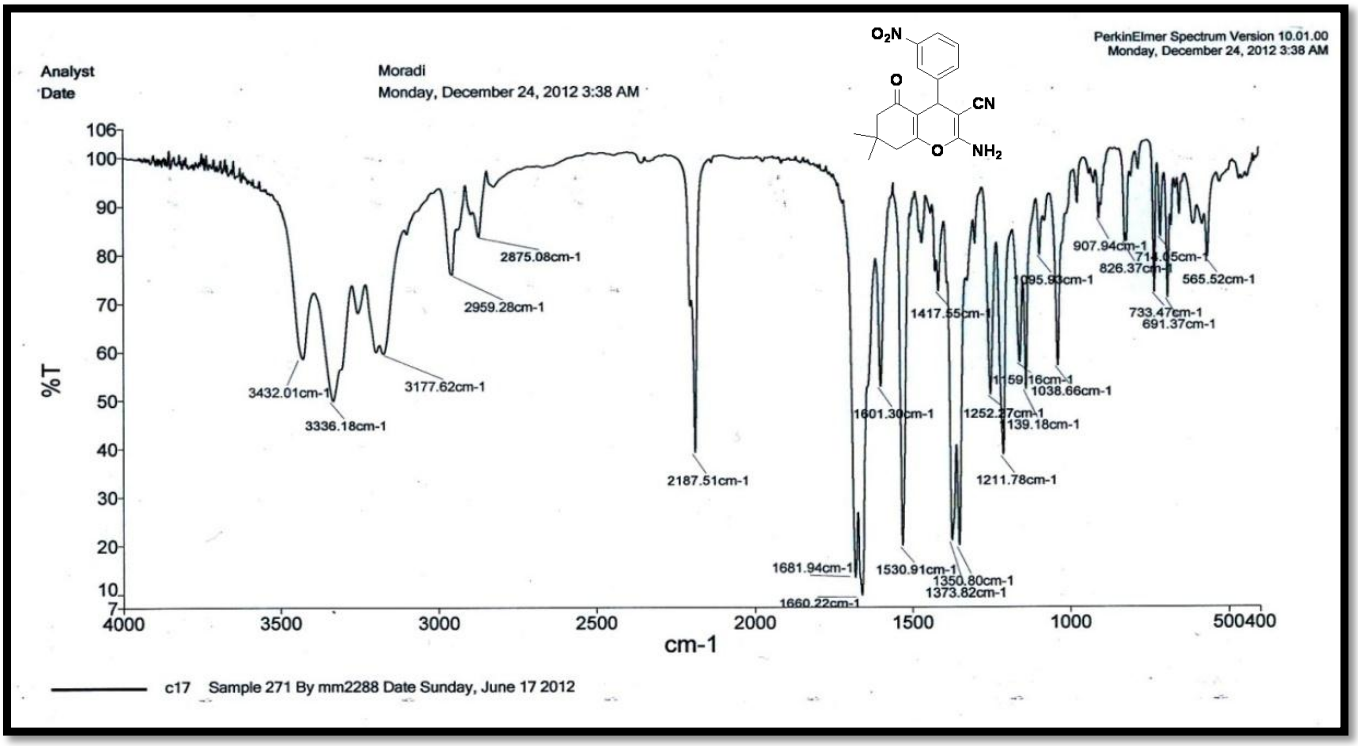
2-amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (5)

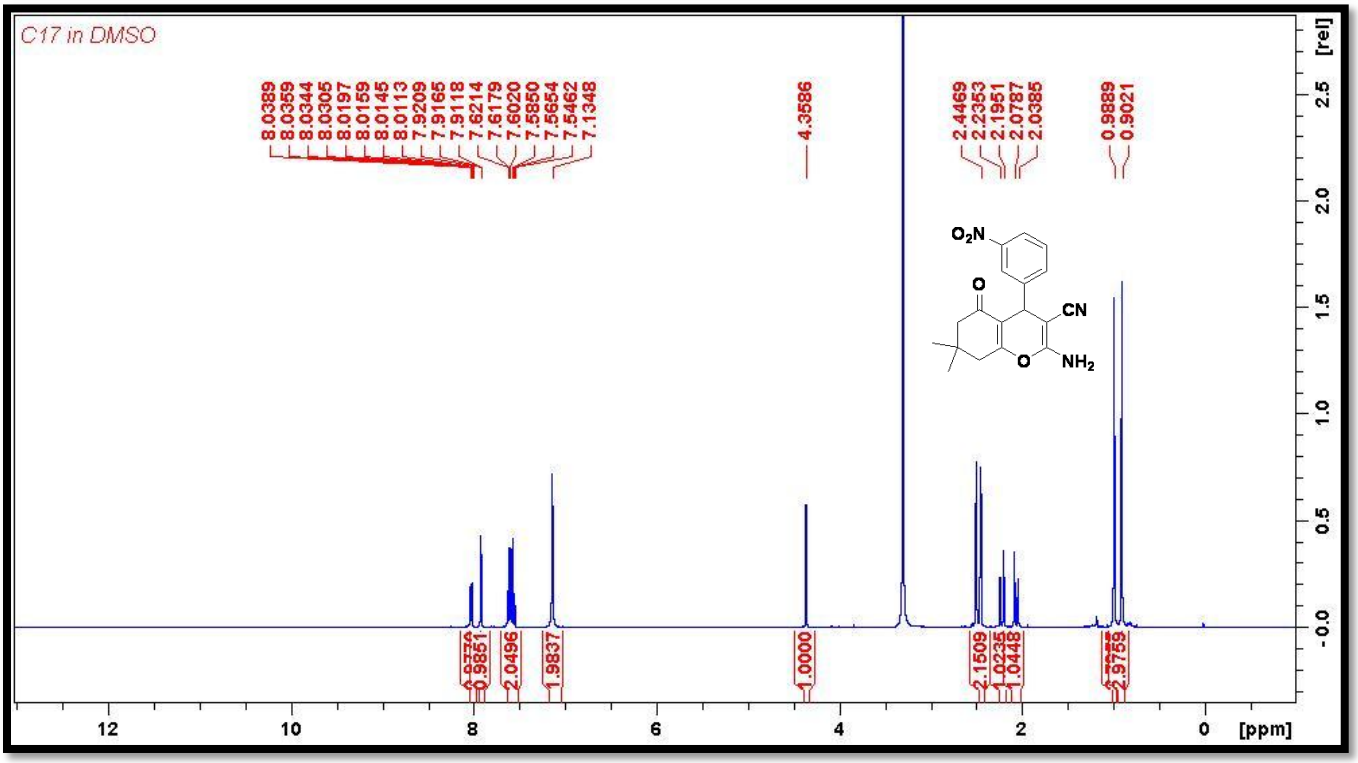


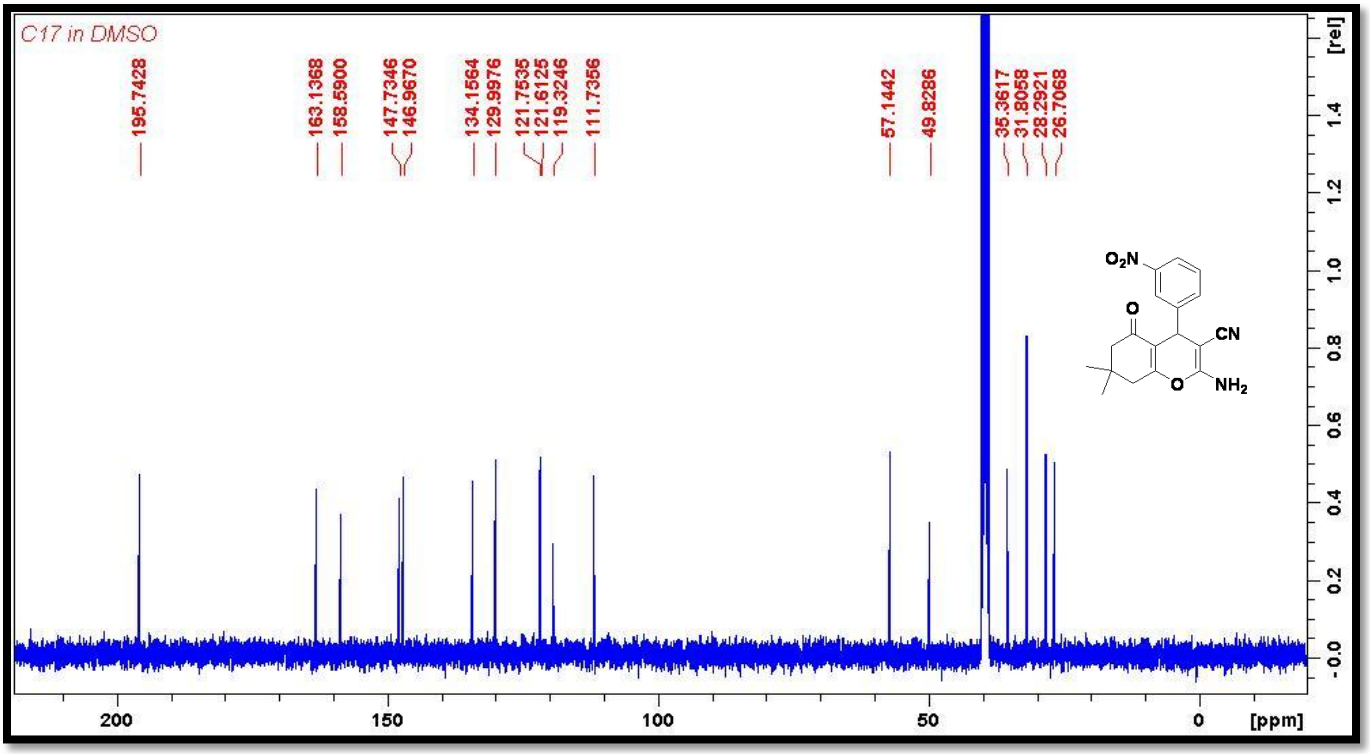




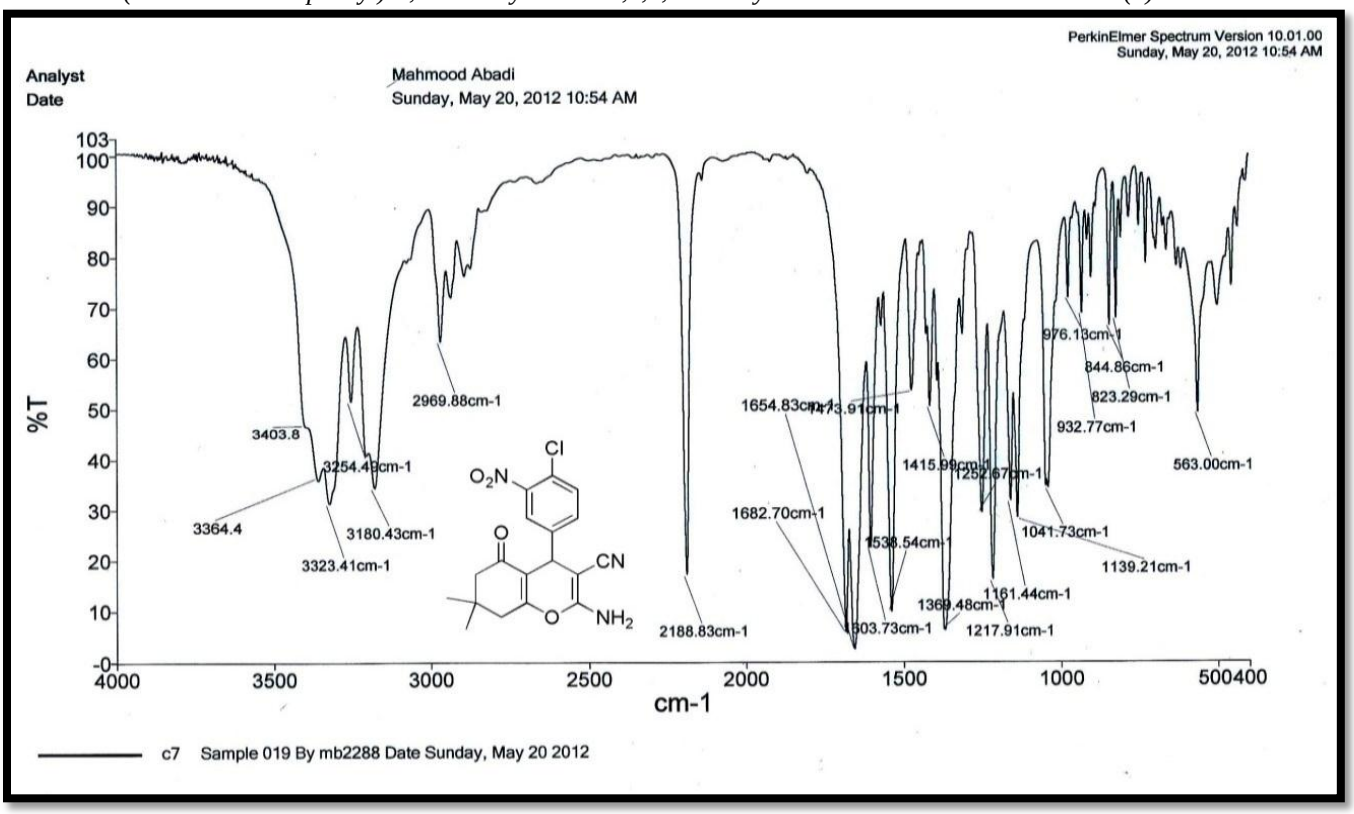
2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6)

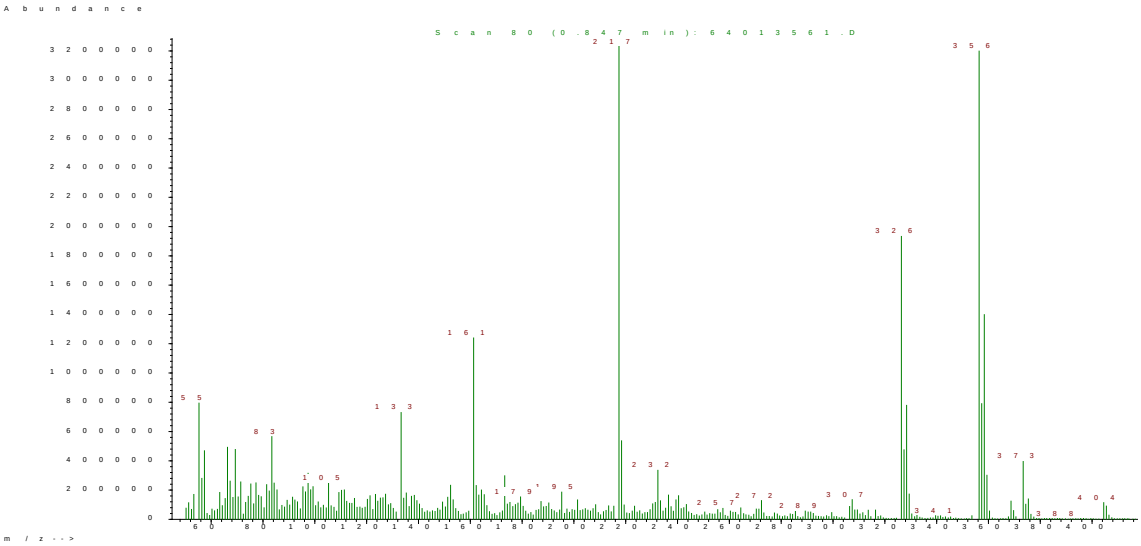


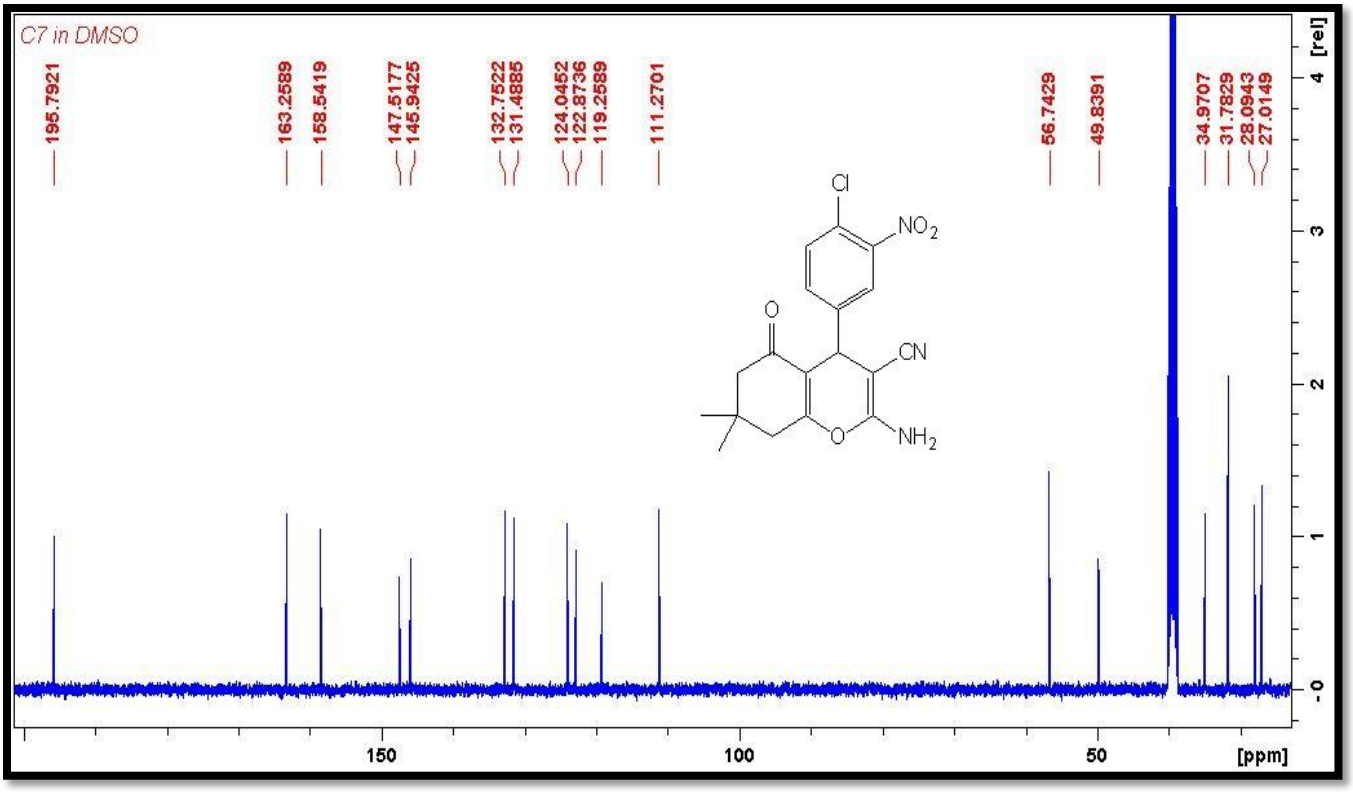




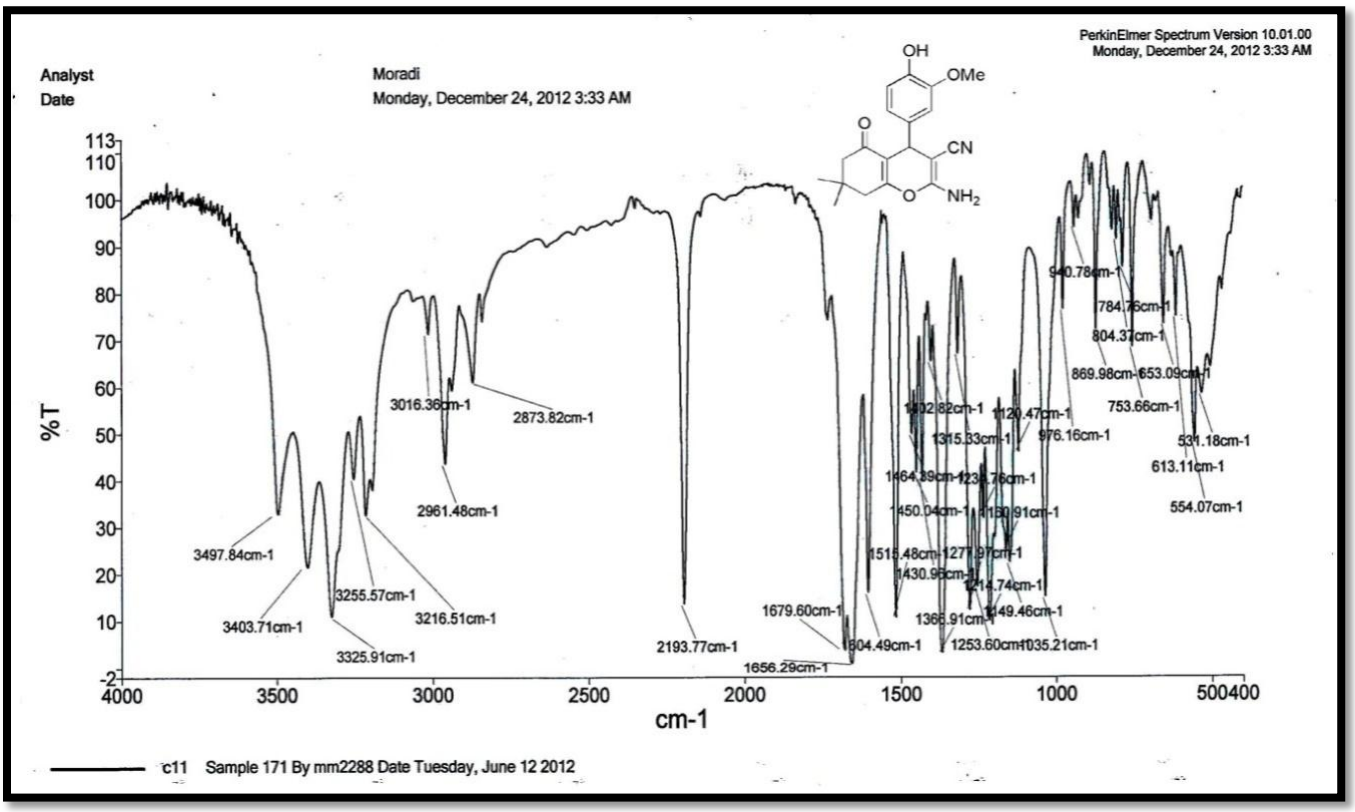
2-amino-4-(4-chloro-3-nitrophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7)

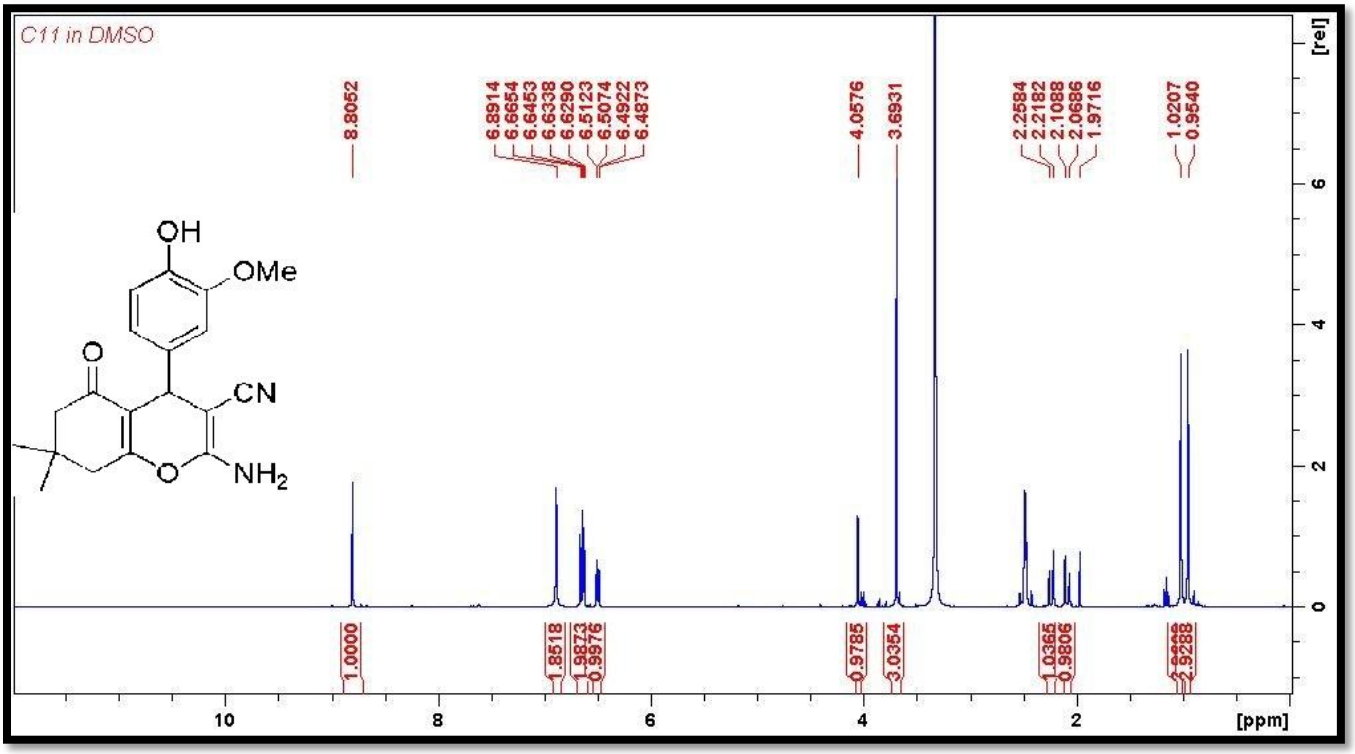


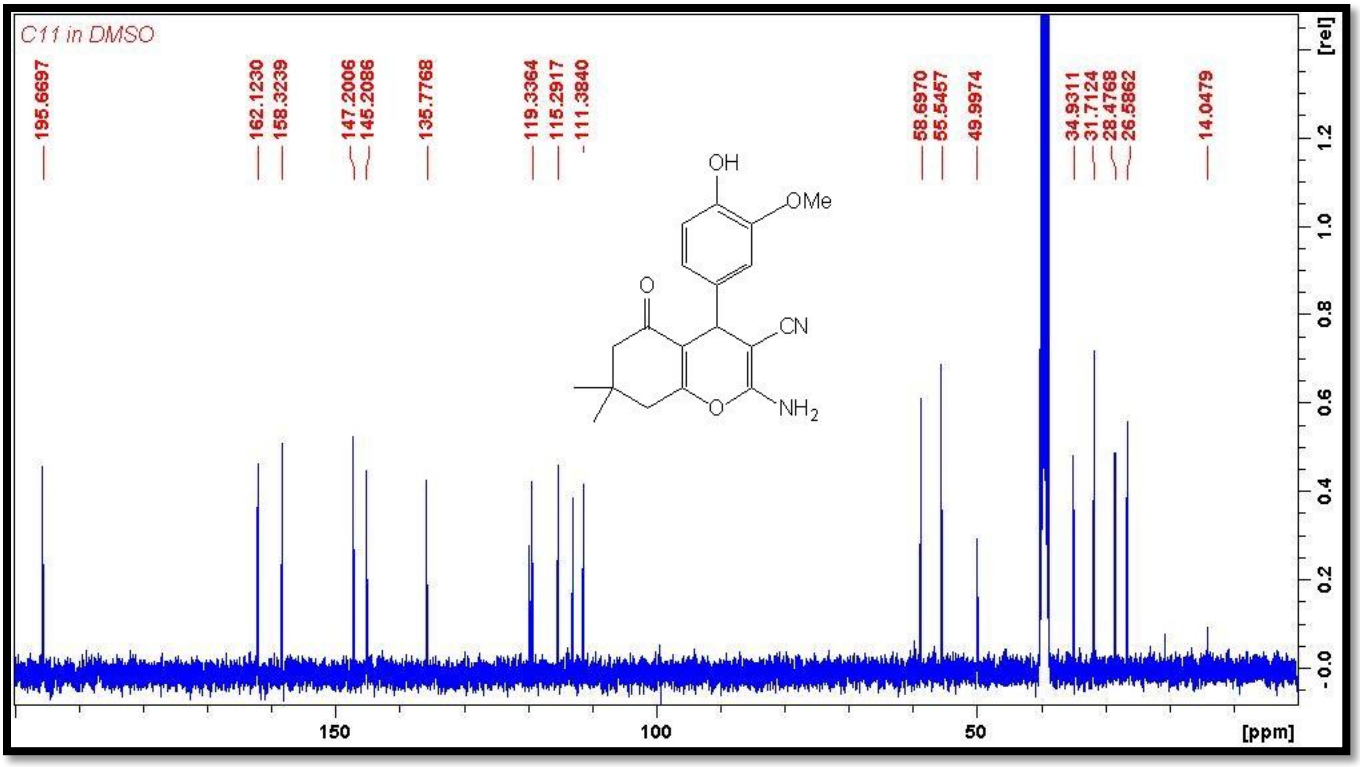




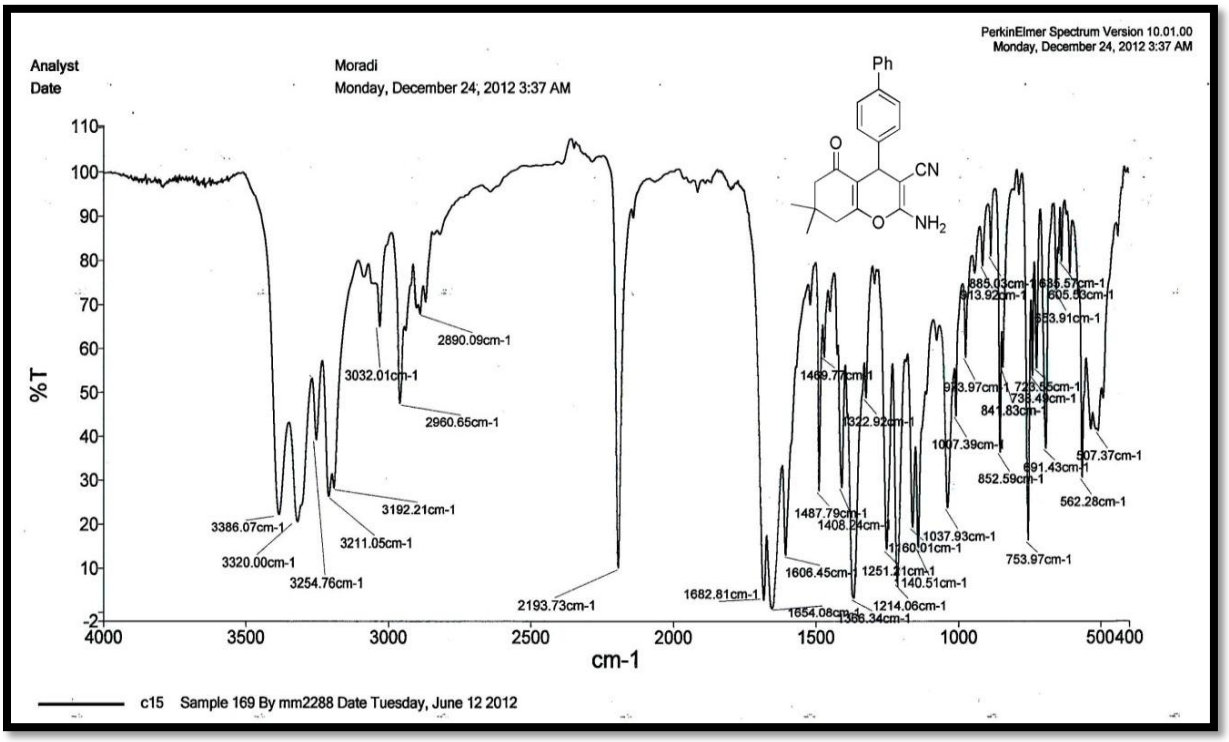
2-amino-4-(4-hydroxy-3-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (8)

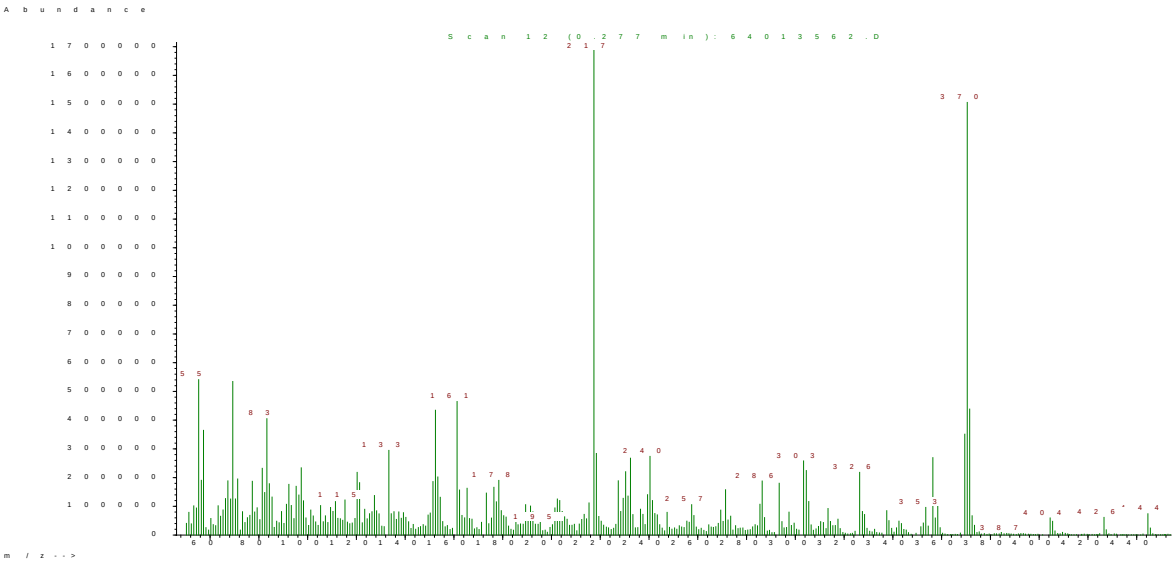


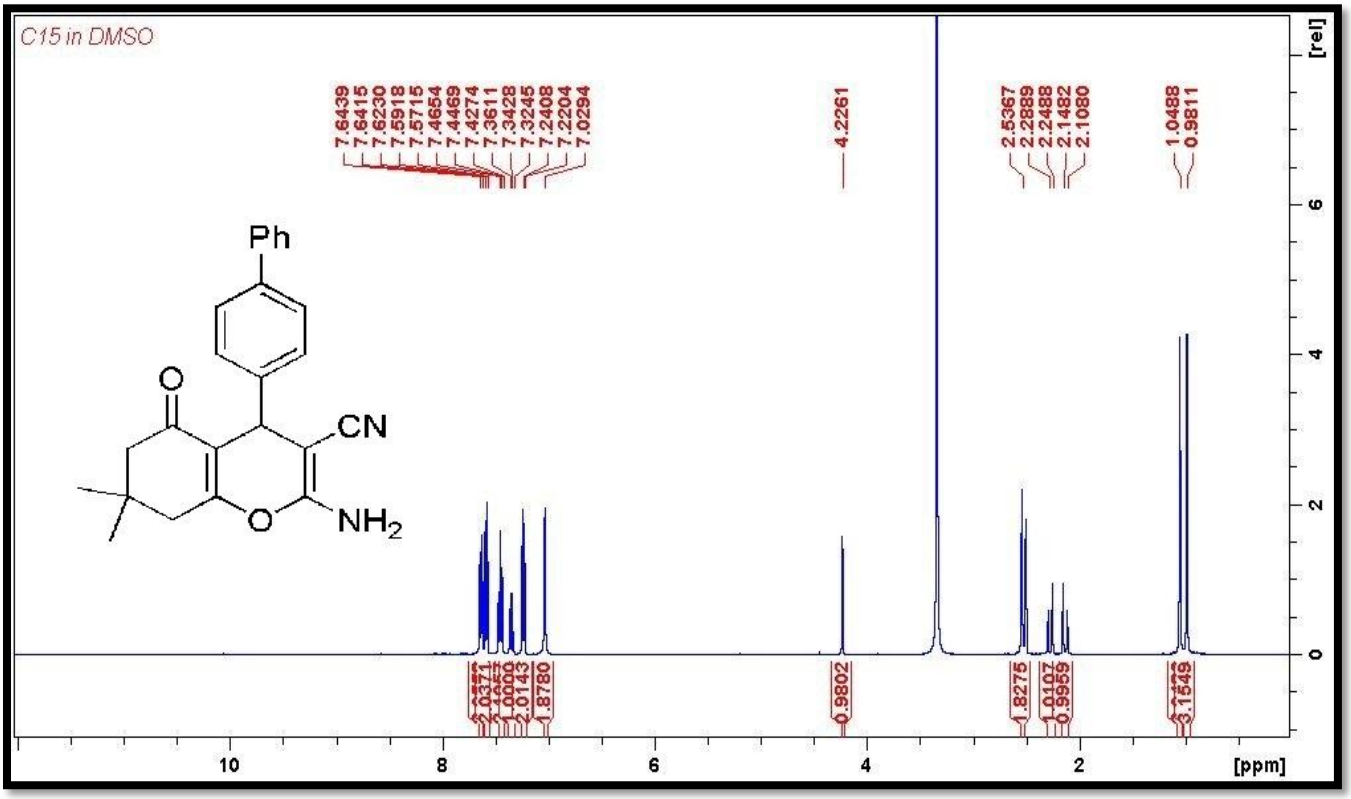


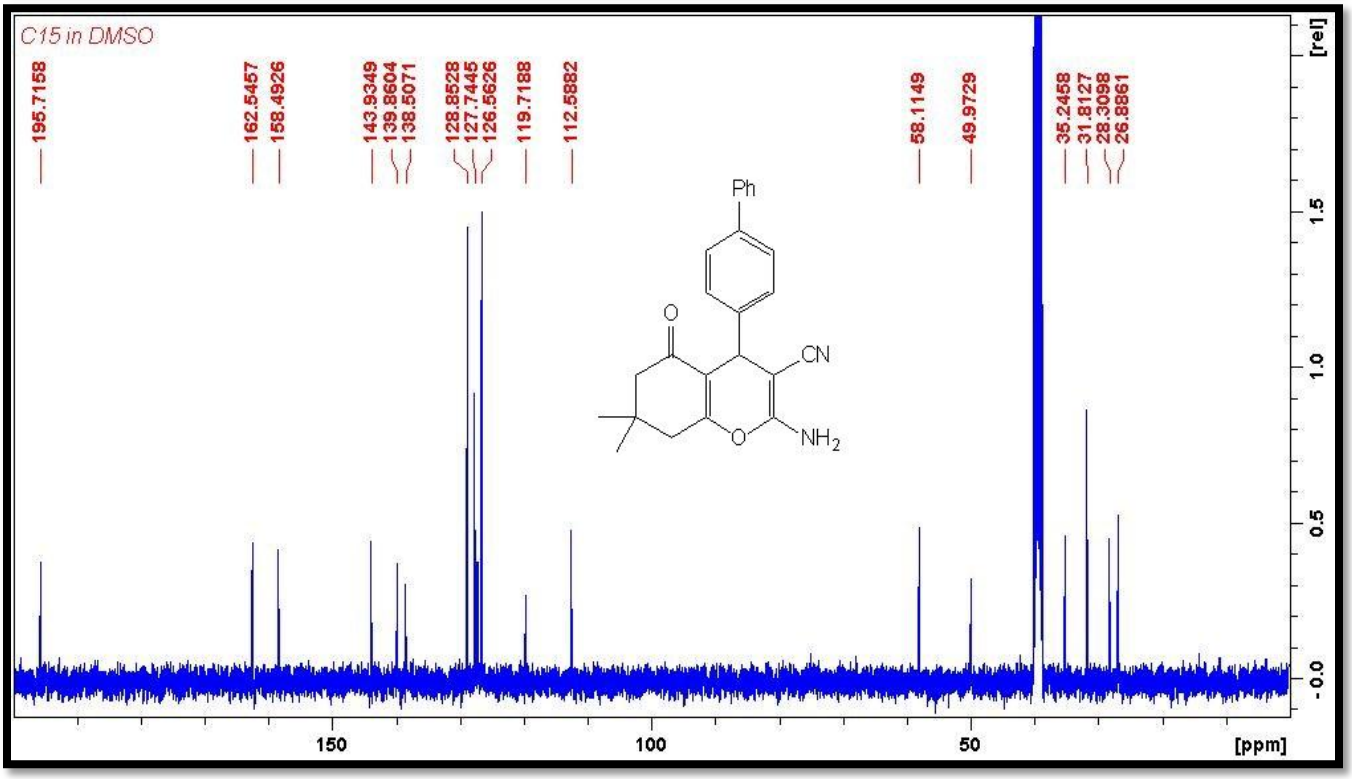


2-amino-4-(4-benzophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (9)

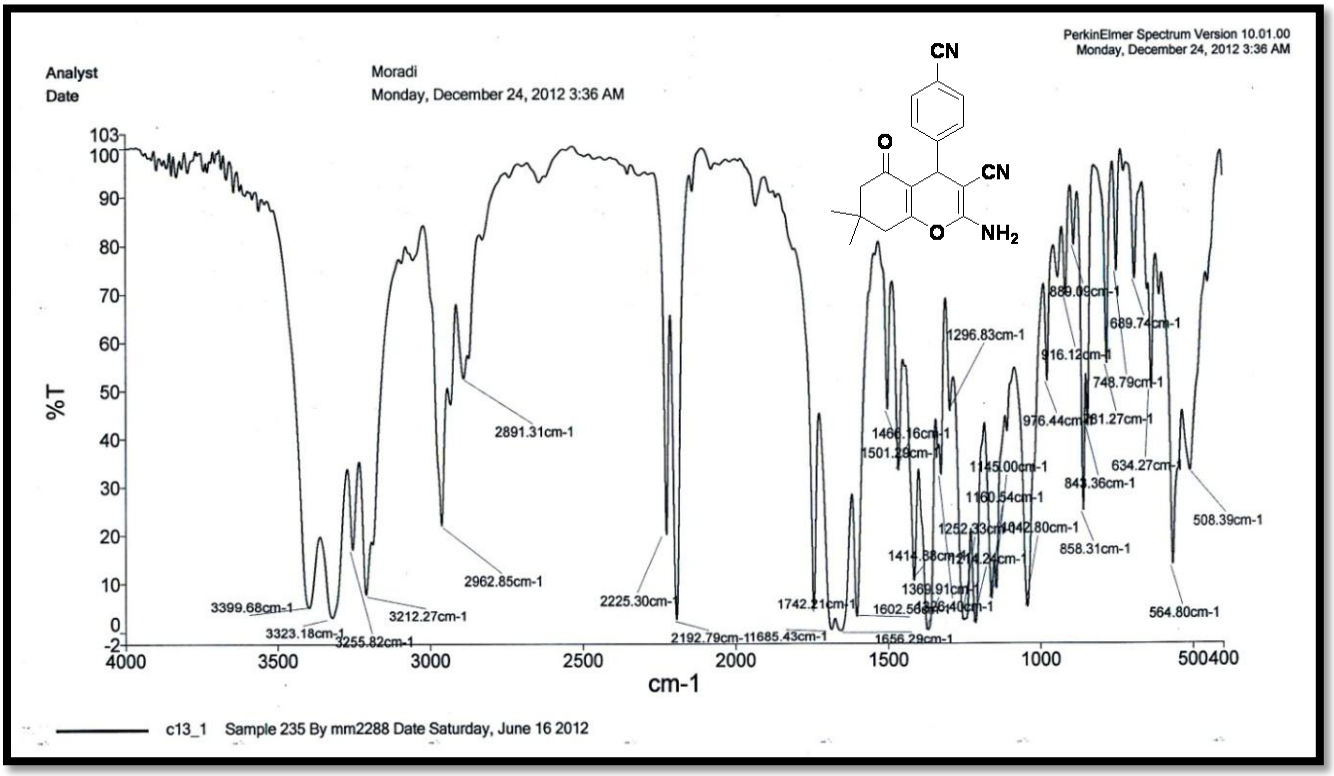


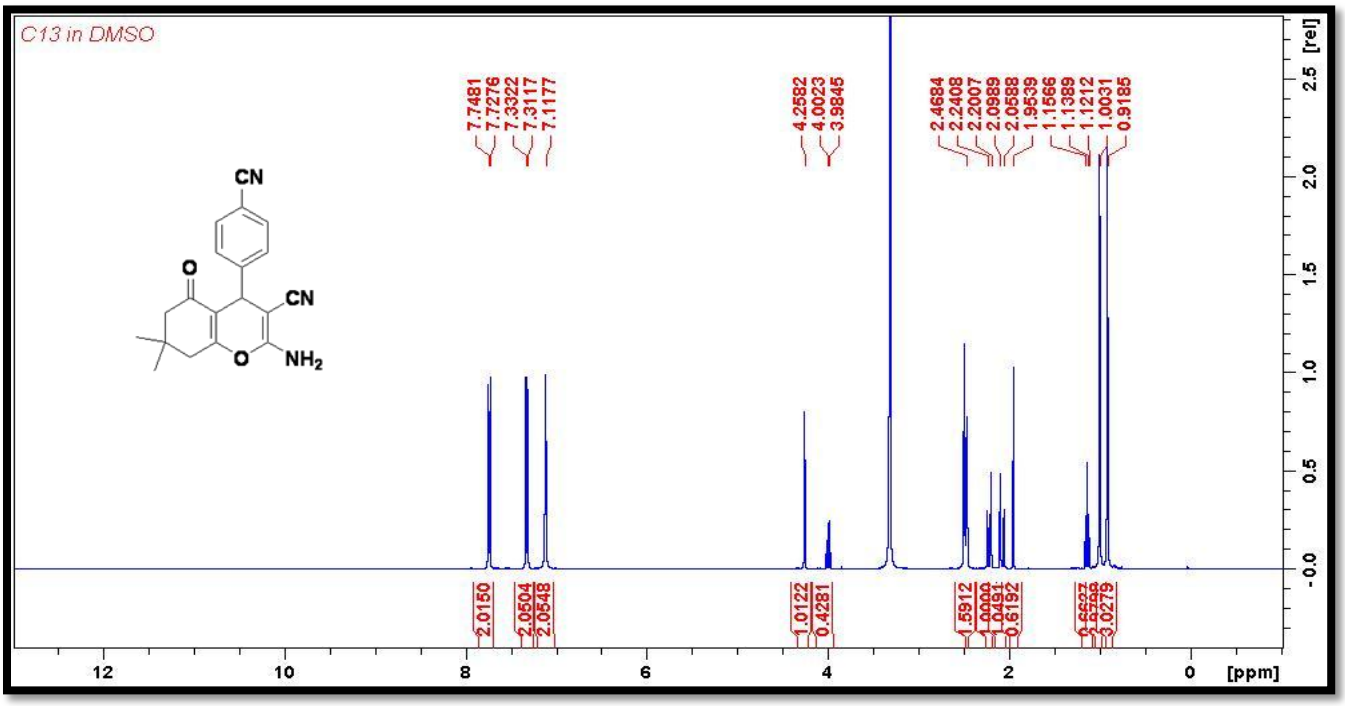


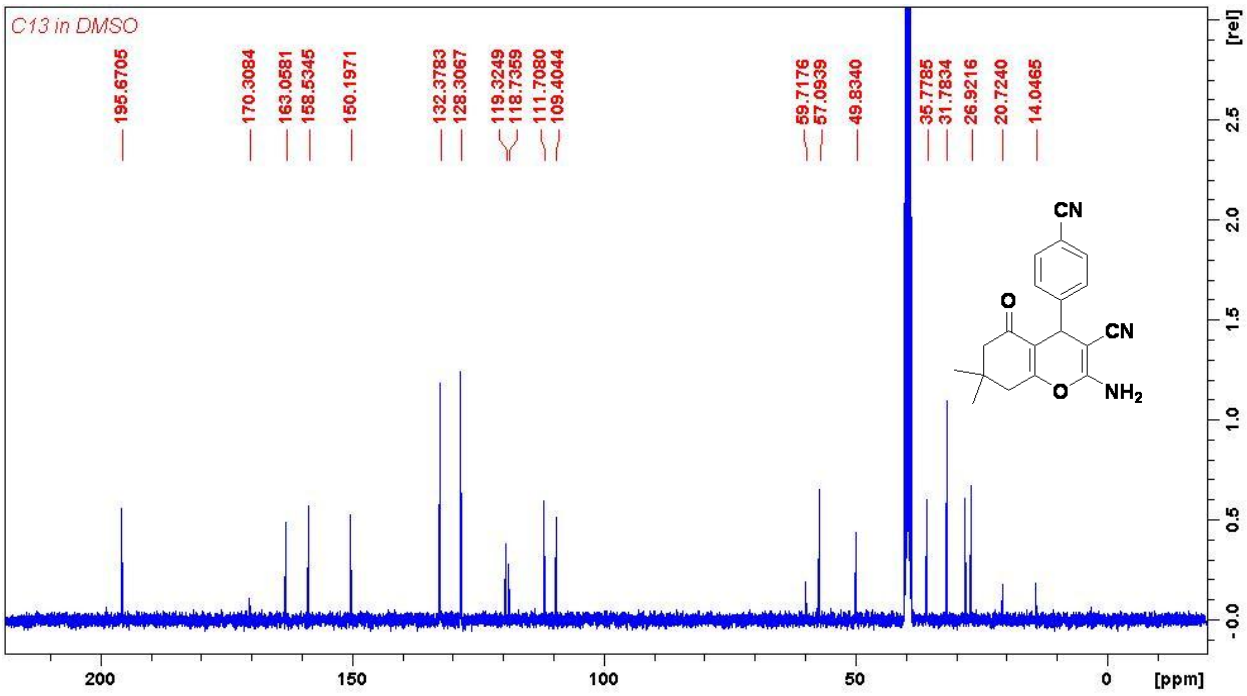




2-amino-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (10)







2-amino-7,7-dimethyl-4-(naphthalen-2-yl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (11)