

Supplementary

One-pot synthesis of chromenes in the presence of nano-cellulose/Ti^(IV)/Fe₃O₄ as natural based magnetic nano-catalysts under solvent free condition

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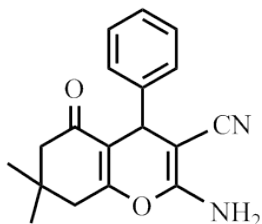
²Department of Chemistry, Faculty of Science, Yazd University, I.R.Iran

Physical and spectral data

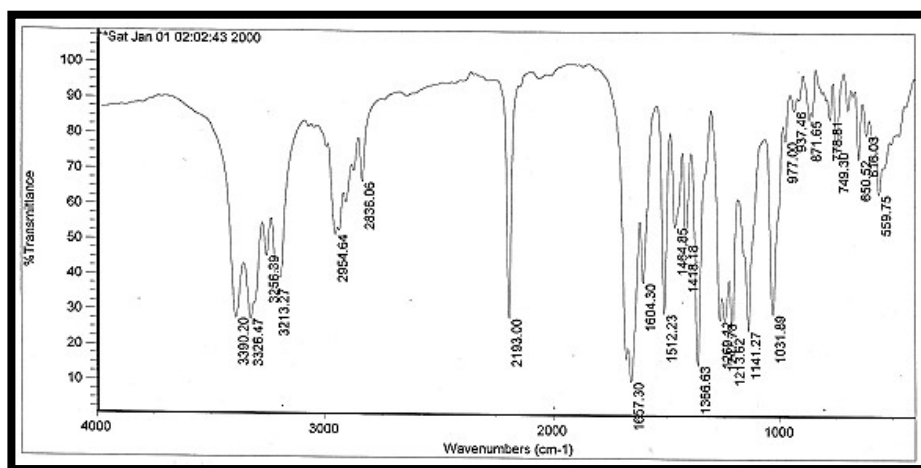
2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

FT-IR [KBr $\bar{\nu}$ (cm⁻¹)]: 3395, 3324 (NH₂), 3083, 3028 (C_{ArH}), 2198 (C≡N), 1661 (C=O), 1602 (C=C), 1035 (C-O).

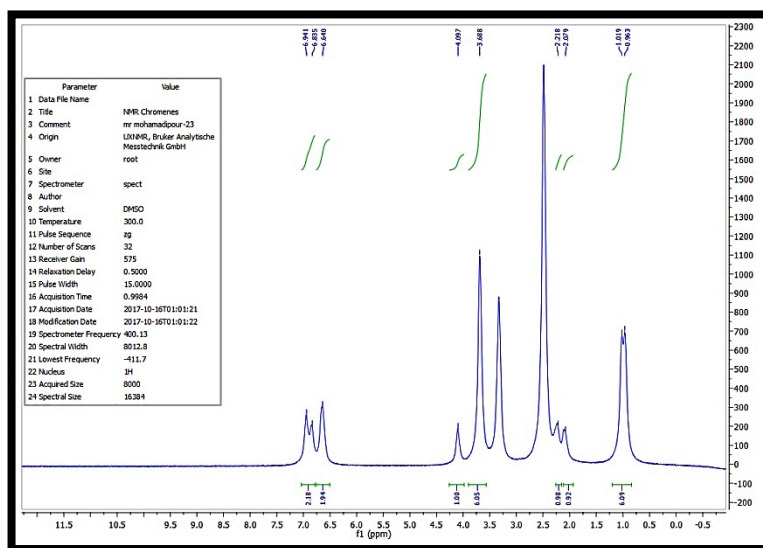
¹H NMR (400 MHz, DMSO-d₆) δ ppm: 0.94 (s, 3H, CH₃), 1.02 (s, 3H, CH₃), 2.08 (m, 2H, CH₂), 2.24 (m, 2H, CH₂), 4.15 (s, 1H, CH), 6.97 (s, 2H, NH₂), 7.14 (t, *J* = 7.12 Hz, 3H, Ar-H), 7.25-7.28 (m, 2H, Ar-H) .



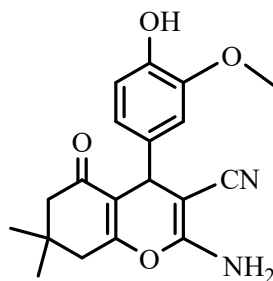
FT-IR



¹H NMR



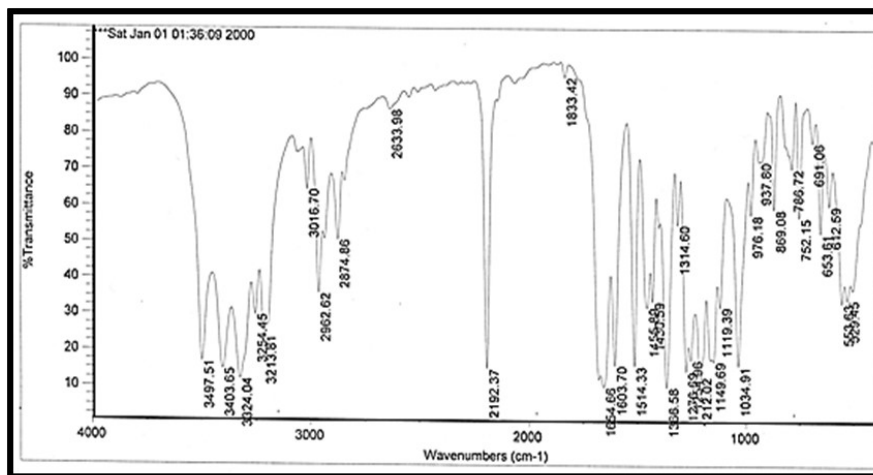
2-amino-4-(4-hydroxy-3-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile



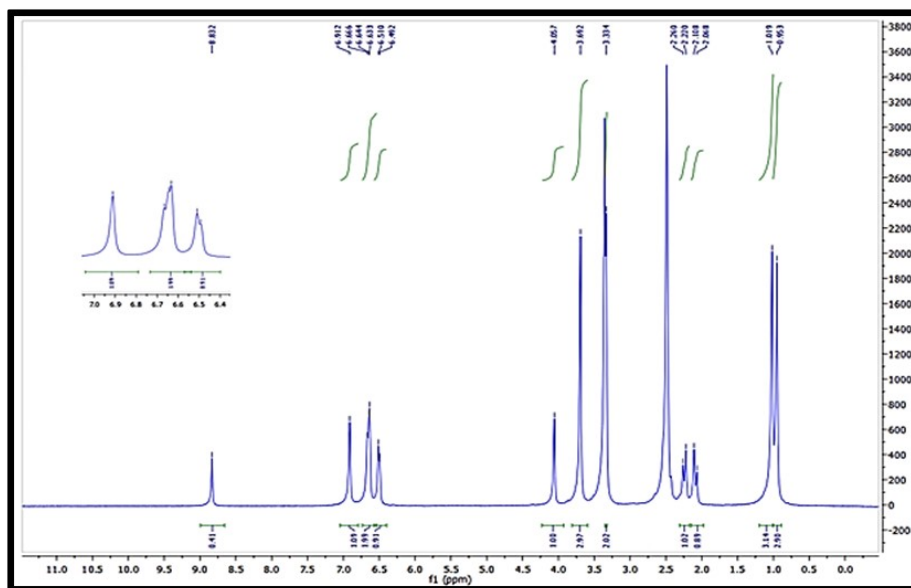
FT-IR [KBr $\bar{\nu}$ (cm⁻¹): 3497 (O-H), 3403, 3324 (NH₂), 3016 (Ar-H), 2192 (C≡N), 1654 (C=O), 1603 (C=C), 1034 (C-O).

¹H NMR (400 MHz, DMSO-d₆) δ ppm: 0.95 (s, 3H, CH₃), 1.02 (s, 3H, CH₃), 2.08 (m, 2H, CH₂), 2.23 (m, 2H, CH₂), 3.69 (s, 3H, OCH₃), 4.05 (s, 1H, CH), 6.48-6.51 (m, 1H), 6.62-6.66 (m, 2H), 6.89 (s, 2H, NH₂), 8.80 (s, 1H, OH).

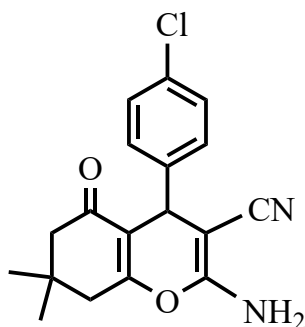
FT-IR



¹H NMR



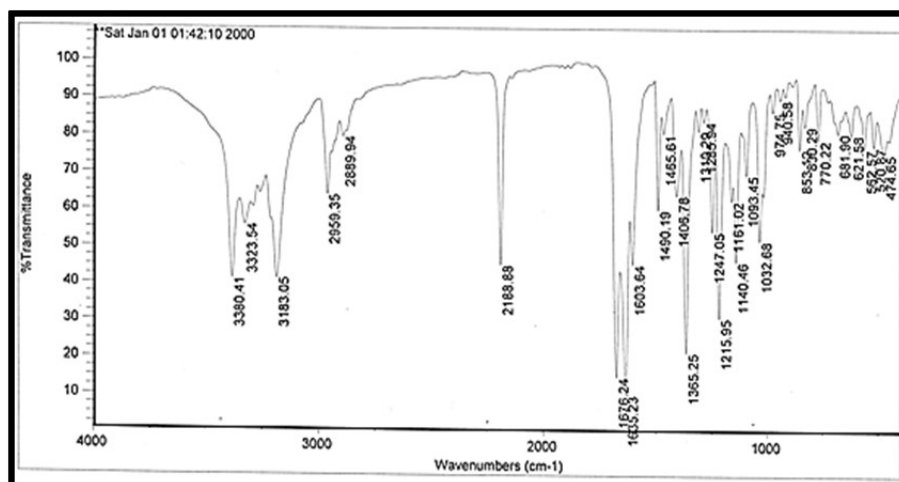
**2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H
chromene-3-carbonitrile**



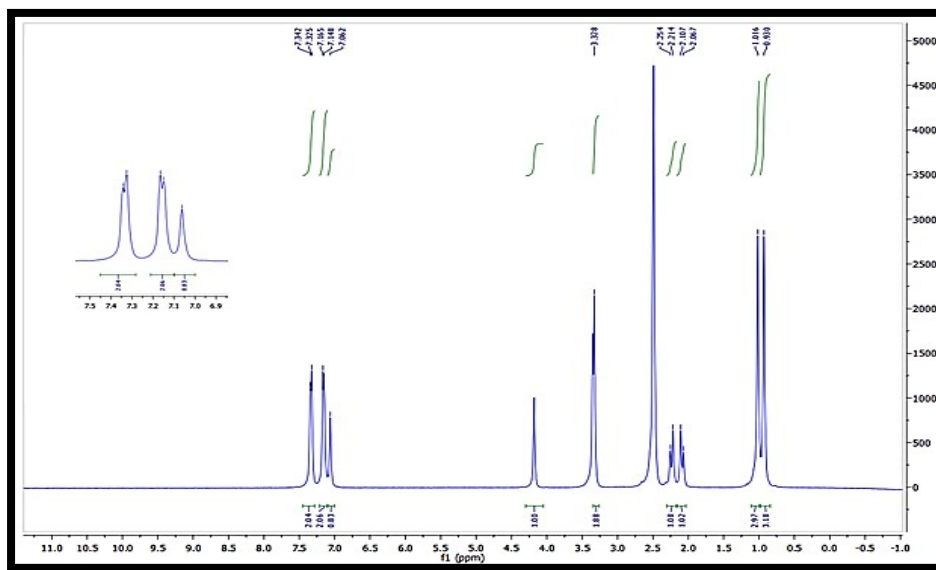
FT-IR [KBr $\bar{\nu}$ (cm⁻¹): 3380, 3323 (NH₂), 3183, 2959 (Ar-H), 2188 (C≡N), 1676 (C=O), 1603 (C=C), 1032 (C-O).

¹H NMR (400 MHz, DMSO-d₆) δ ppm: 0.92 (s, 3H, CH₃), 1.01 (s, 3H, CH₃), 2.08 (m, 2H, CH₂), 2.22 (m, 2H, CH₂), 4.17 (s, 1H, CH), 7.03 (s, 2H, NH₂), 7.15 (d, *J* = 8.44 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 1H).

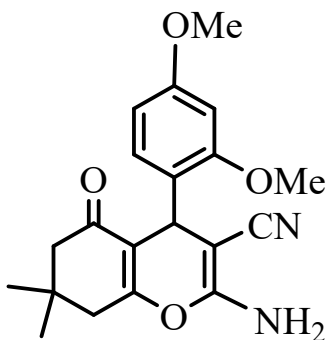
FT-IR



^1H NMR



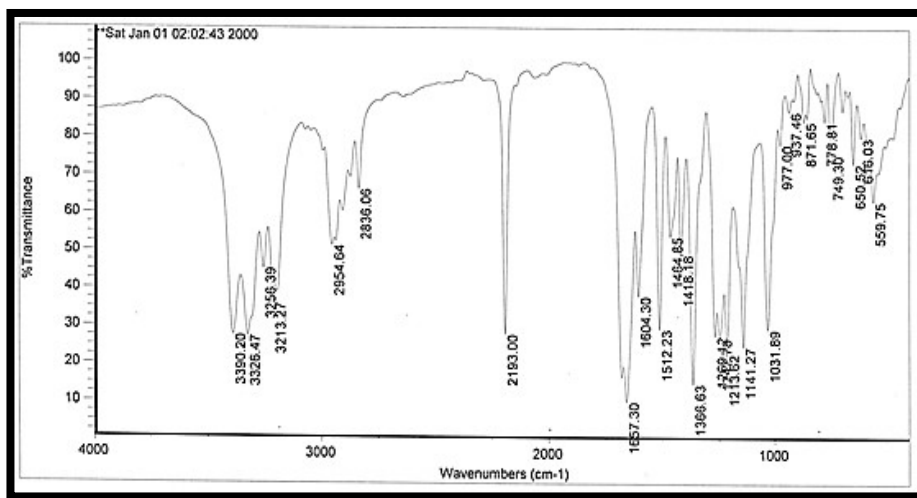
2-amino-4-(2,4-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile



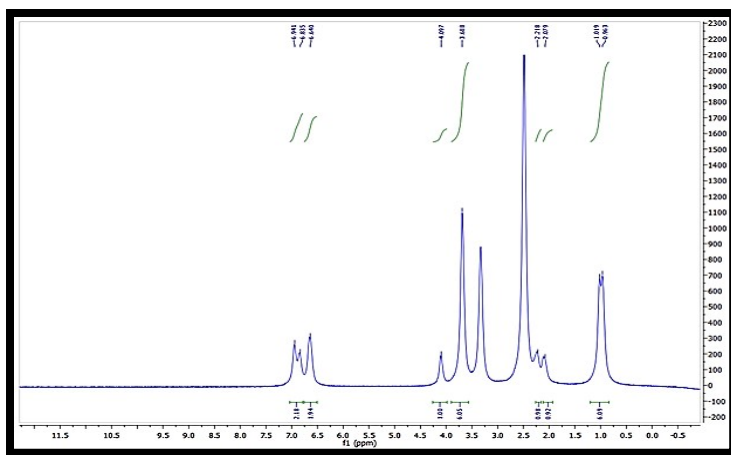
FT-IR [KBr $\bar{\nu}$ (cm^{-1})]: 3390, 3326 (NH_2), 3256, 3213, 2954 (Ar-H), 2193 ($\text{C}\equiv\text{N}$), 1657 ($\text{C}=\text{O}$), 1604 ($\text{C}=\text{C}$), 1031 ($\text{C}-\text{O}$).

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ ppm: 0.96 (3H, s, CH_3), 1.01 (3H, s, CH_3), 2.07 (m, 2H, CH_2), 2.21 (m, 2H, CH_2), 3.68 (6H, s, OCH_3), 4.09 (1H, s, CH), 6.83 (4H, br s, H-Ar, NH_2).

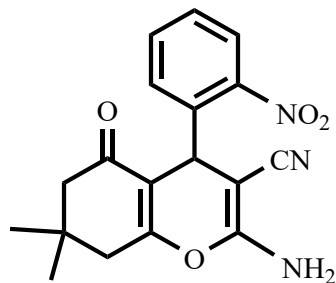
FT-IR



¹H NMR



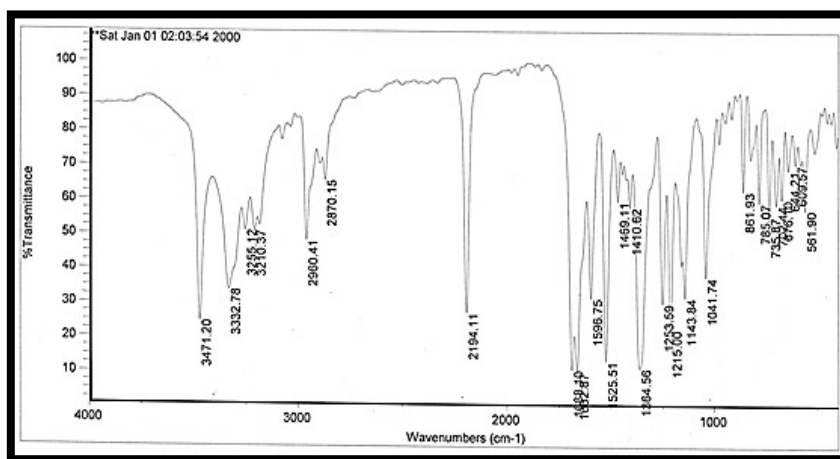
2-amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile



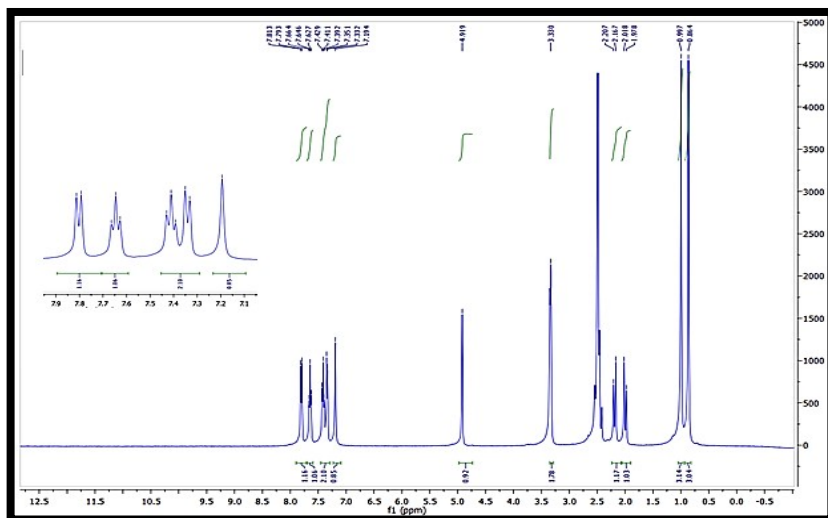
FT-IR [KBr $\bar{\nu}$ (cm⁻¹): 3471, 3332 (NH₂), 3255, 3210, 2960 (Ar-H), 2194 (C≡N), 1688 (C=O), 1602 (C=C), 1525, 1596 (NO₂), 1041 (C-O).

¹H NMR (400 MHz, DMSO-d₆) δ ppm: 0.81 (s, 3H, CH₃), 0.94 (s, 3H, CH₃), 1.94 (m, 2H, CH₂), 2.13 (m, 2H, CH₂), 4.86 (s, 1H), 7.11 (s, 2H, NH₂), 7.28 (dd, *J* = 6.78, 1.00 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.57-7.75 (m, 2H).

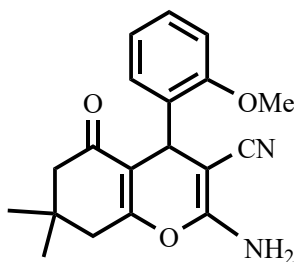
FT-IR



^1H NMR



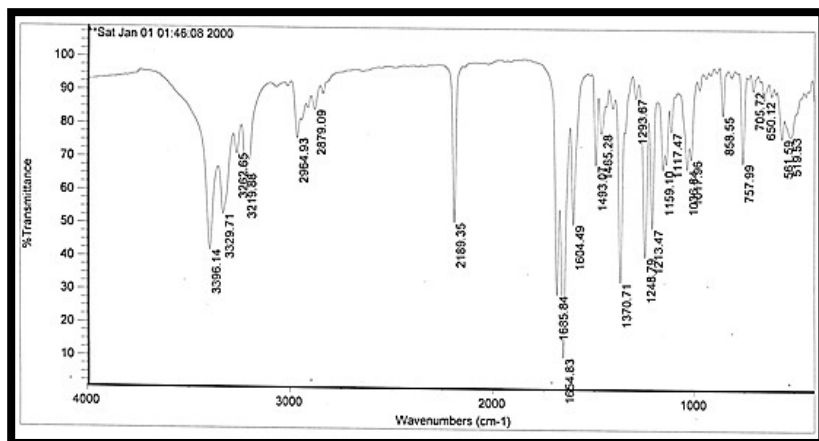
2-amino-4-(2-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile



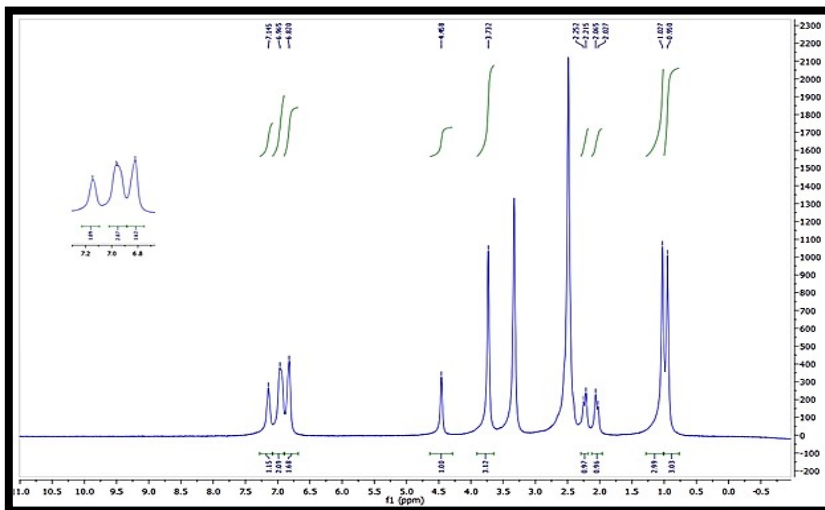
FT-IR [KBr $\bar{\nu}$ (cm^{-1})]: 3396, 3329 (NH_2), 3262, 3219, 2964 (Ar-H), 2189 ($\text{C}\equiv\text{N}$), 1685 ($\text{C}=\text{O}$), 1654 ($\text{C}=\text{C}$), 1036 ($\text{C}-\text{O}$).

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ ppm: 0.95 (3H, s, CH_3), 1.02 (3H, s, CH_3), 2.14 (m, 2H, CH_2), 3.73 (3H, s, OCH_3), 4.45 (1H, s, CH), 6.82 (2H, br s, NH_2), 6.96 (2H, br s, H-Ar), 7.14 (1H, br s, H-Ar).

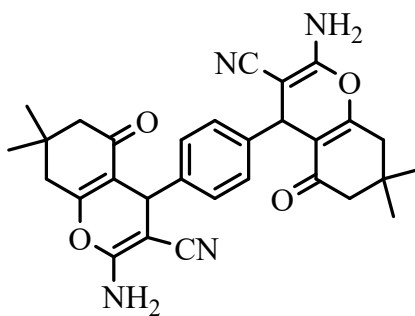
FT-IR



¹H NMR



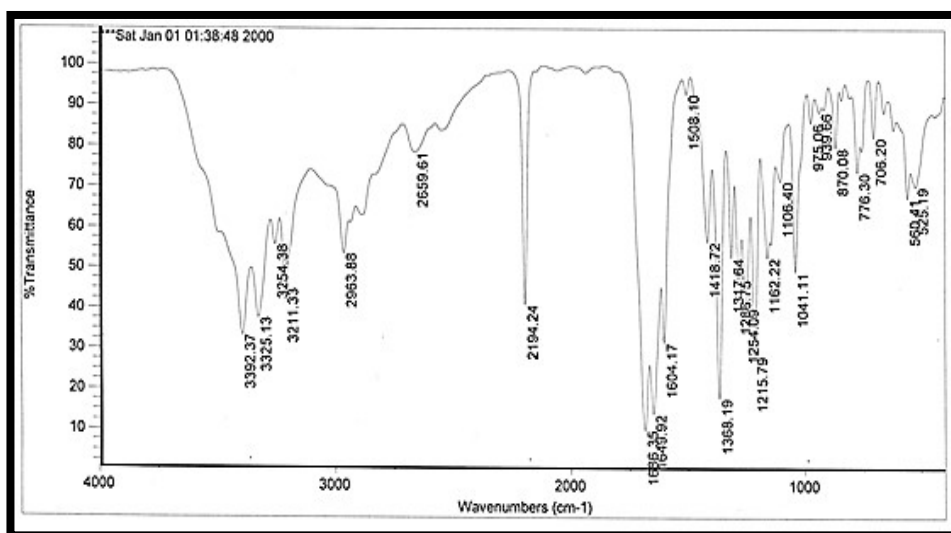
4,4'-(1,4-phenylene)bis(2-amino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3 carbonitrile)



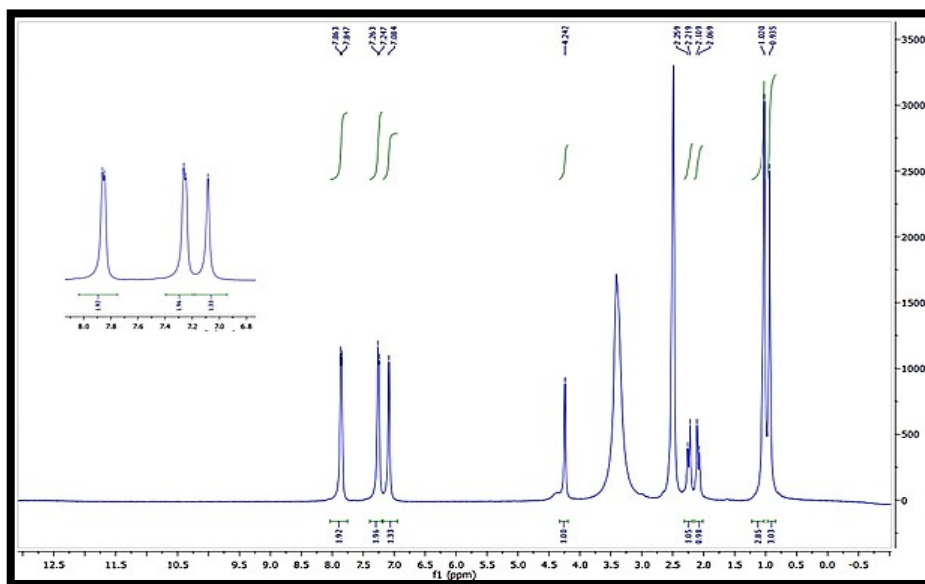
FT-IR [KBr $\bar{\nu}$ (cm⁻¹)]: 3392, 3325 (NH₂), 3254, 3211, 2963 (Ar-H), 2194 (C≡N), 1686 (C=O), 1649 (C=C), 1041 (C-O).

¹H NMR (400 MHz, DMSO-d₆) δ ppm: 0.93 (3H, s, CH₃), 1.02 (3H, s, CH₃), 2.15 (m, 2H, CH₂), 4.24 (1H, s, CH), 7.08 (2H, br s, NH₂), 7.25 (2H, d, *J* = 8, H-Ar), 7.85 (2H, d, *J* = 8, H-Ar).

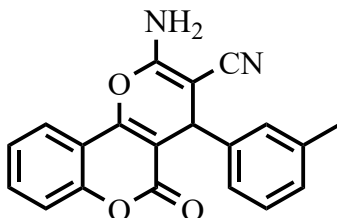
FT-IR



¹H NMR



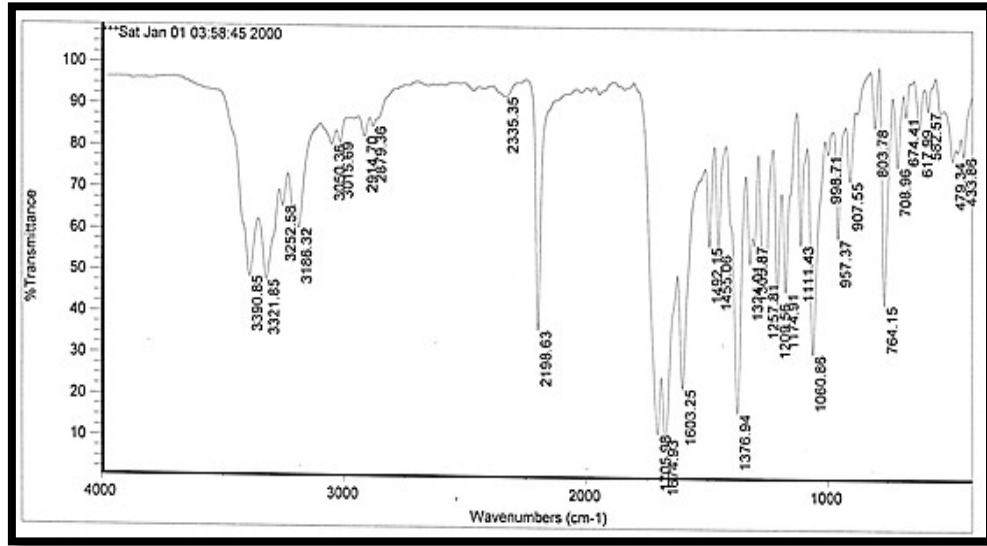
2-amino-5-oxo-4-(m-tolyl)-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile



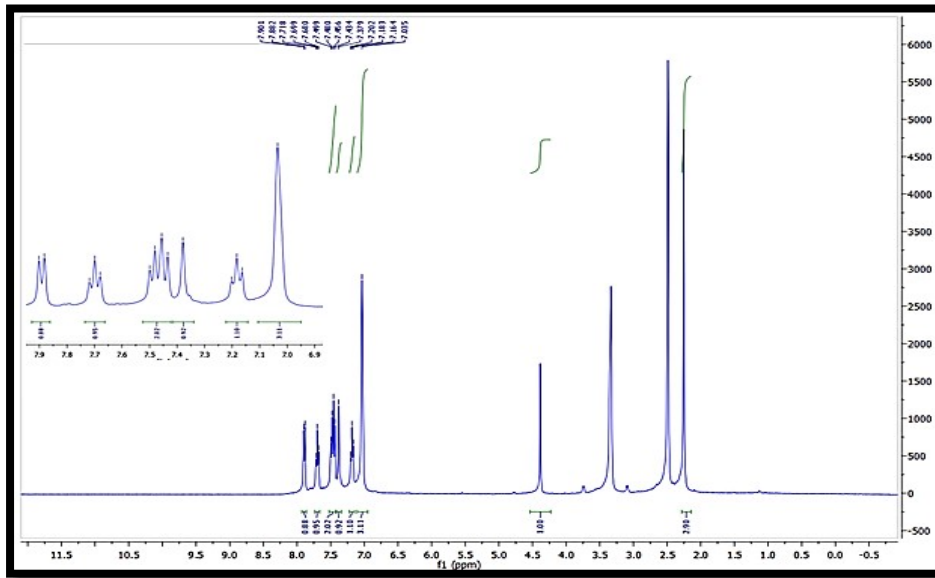
FT-IR [KBr $\bar{\nu}$ (cm^{-1})]: 3390, 3321 (NH_2), 3050, 3015 (Ar-H), 2198 ($\text{C}\equiv\text{N}$), 1705, 1674 ($\text{C}=\text{O}$), 1603 ($\text{C}=\text{C}$), 1060 ($\text{C}-\text{O}$).

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ ppm: 2.24 (3H, s, CH_3), 4.42 (1H, s, CH), 7.03 (3H, br s, NH_2), 7.183 (1H, t, $J = 8$, H-Ar), 7.379 (1H, s, H-Ar), 7.445 (1H, d, $J = 11$, H-Ar), 7.49 (1H, d, $J = 9.5$, H-Ar), 7.69 (1H, t, $J = 9.5$, H-Ar), 7.89 (1H, d, $J = 9.5$, H-Ar).

FT-IR

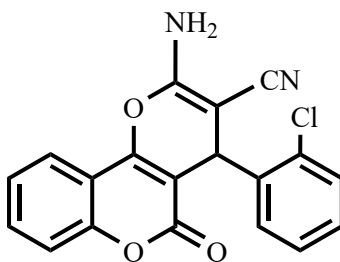


¹H NMR



**2-amino-5-oxo-4-(2-chlorophenyl)-4,5-dihydropyrano[3,2-c]
carbonitrile**

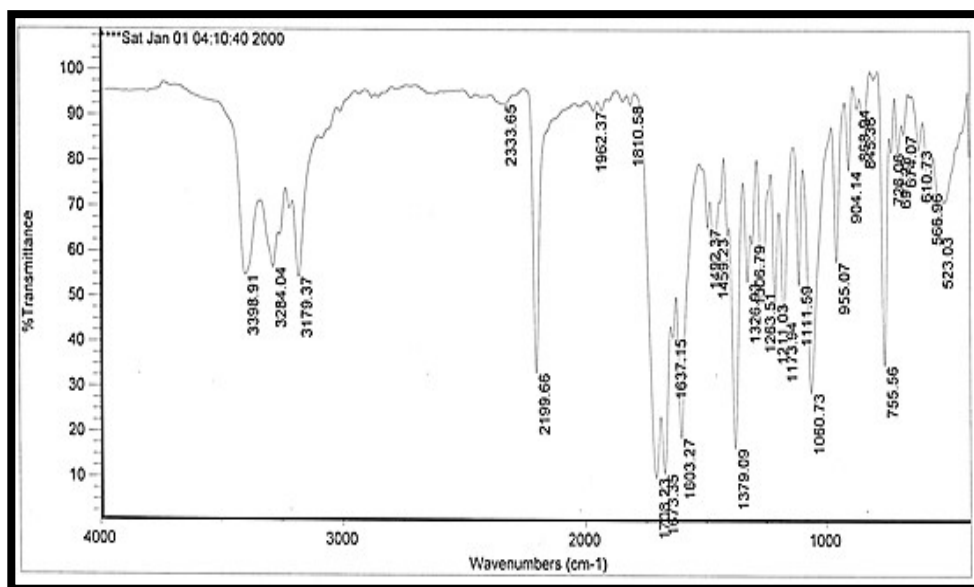
chromene-3



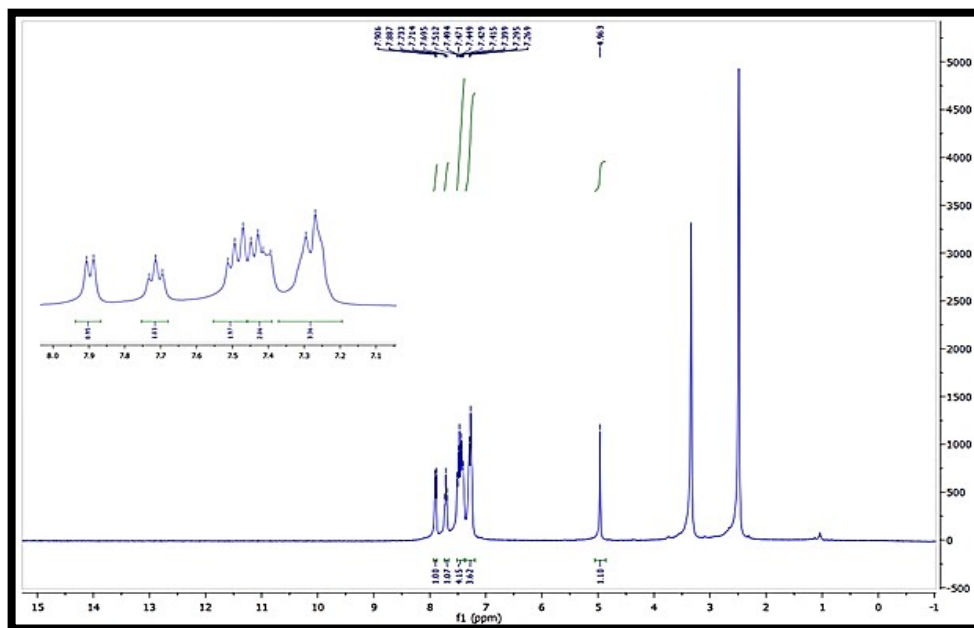
FT-IR [KBr $\bar{\nu}$ (cm⁻¹)]: 3398, 3284 (NH₂), 3179 (Ar-H), 2199 (C≡N), 1708, 1673 (C=O), 1603 (C=C), 1060 (C-O).

¹H NMR (400 MHz, DMSO-d₆) δ ppm: 4.96 (1H, s, CH), 7.28 (3H, m, NH₂, H-Ar), 7.47 (4H, m, H-Ar), 7.71 (1H, t, *J*= 9.5, H-Ar), 7.89 (1H, d, *J*= 9.5, H-Ar).

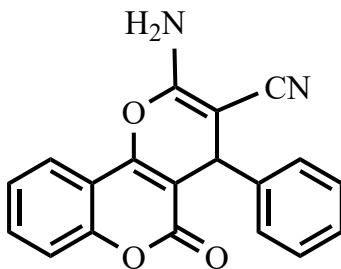
FT-IR



¹H NMR



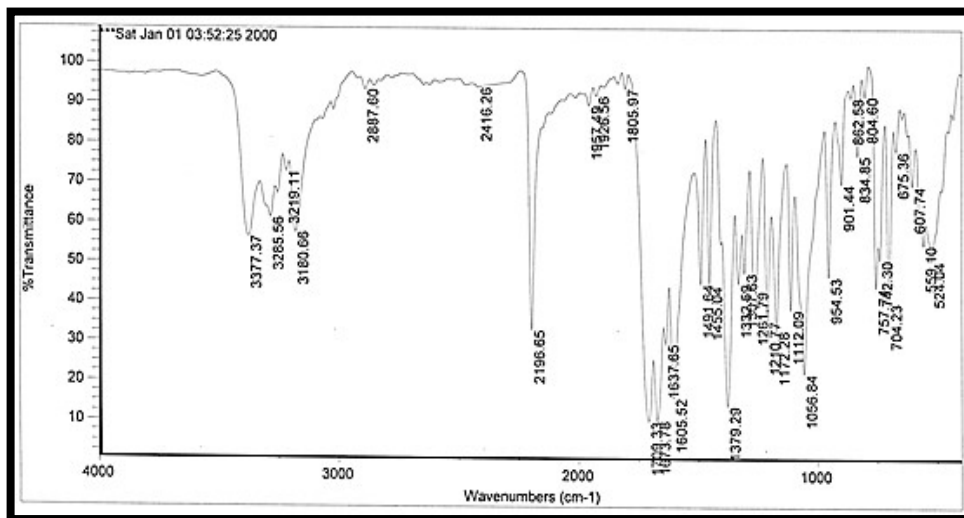
2-amino-5-oxo-4-phenyl-4,5-dihydroprano[3,2-c]chromene-3-carbonitrile



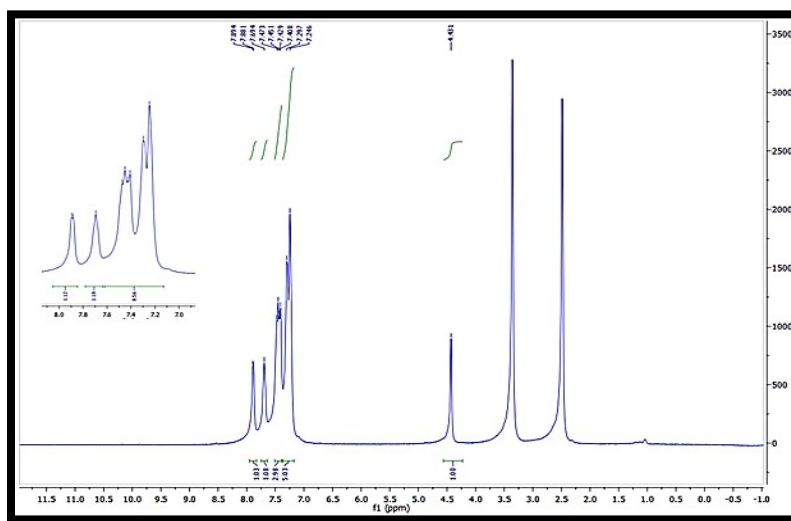
FT-IR [KBr $\bar{\nu}$ (cm⁻¹): 3377, 3285 (NH₂), 3180, 2887 (Ar-H), 2196 (C≡N), 1709, 1673 (C=O), 1605 (C=C), 1056 (C-O).

¹H NMR (400 MHz, DMSO-d₆) δ ppm: 4.43 (1H, s, CH), 7.24-7.47 (9H, m, NH₂, H-Ar), 7.69 (1H, br s, H-Ar), 7.88 (1H, d, J = 6.5, H-Ar).

FT-IR



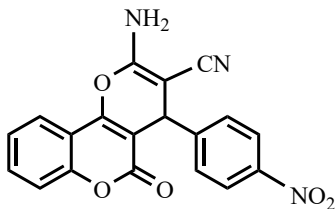
¹H NMR



2-amino-5-oxo-4-(4-nitrophenyl)-4,5-dihydropyrano[3,2-*c*]

chromene-3-

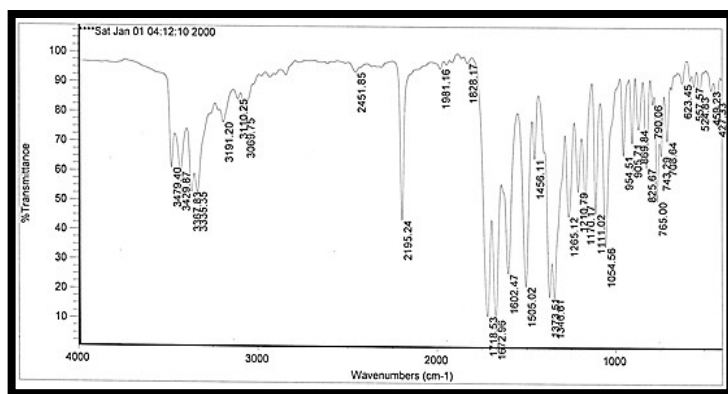
carbonitrile



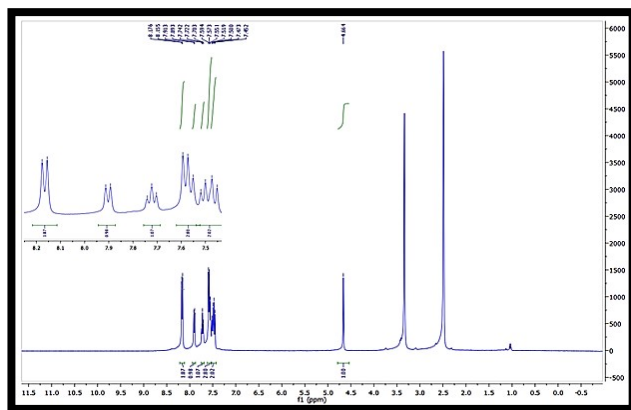
FT-IR [KBr $\bar{\nu}$ (cm⁻¹)]: 3335-3479 (NH₂), 3191, 3069 (Ar-H), 2195 (C≡N), 1718, 1672 (C=O), 1602 (C=C), 1505, 1456 (NO₂), 1054 (C-O).

¹H NMR (400 MHz, DMSO-d₆) δ ppm: 4.66 (1H, s, CH), 7.45-7.59 (4H, m, NH₂, H-Ar), 7.72 (1H, t, *J*= 10, H-Ar), 7.90 (1H, d, *J*= 10, H-Ar), 8.16 (1H, d, *J*= 10.5, H-Ar).

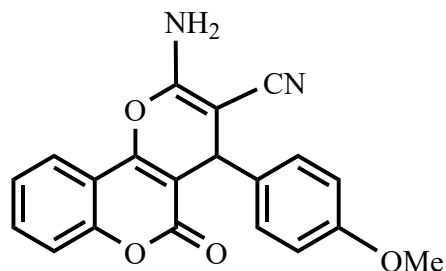
FT-IR



¹H NMR



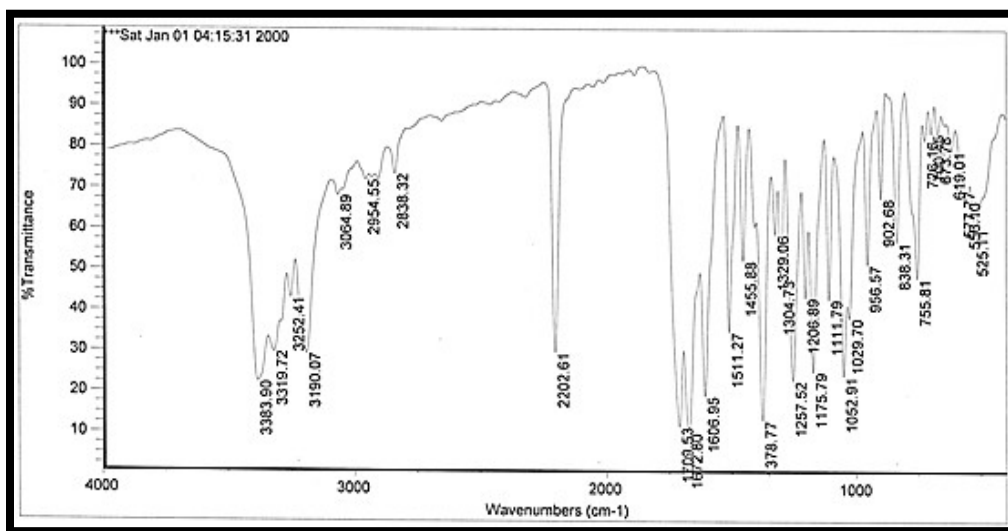
2-amino-4-(4-methoxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c] chromene-3-carbonitrile



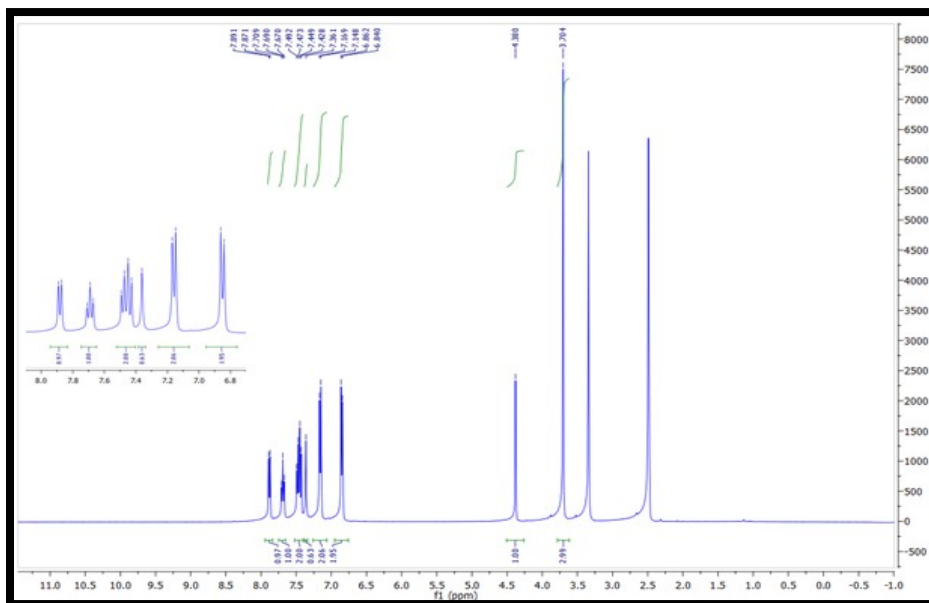
FT-IR [KBr $\bar{\nu}$ (cm⁻¹): 3383, 3319 (NH₂), 3252, 3190, 3064, 2954 (Ar-H), 2202 (C≡N), 1709, 1672 (C=O), 1606 (C=C), 1052 (C-O).

¹H NMR (400 MHz, DMSO-d₆) δ ppm: 3.70 (3H, s, OCH₃), 4.38 (1H, s, CH), 6.85 (2H, d, *J* = 11, H-Ar), 7.15 (2H, d, *J* = 11, H-Ar), 7.36 (2H, br s, NH₂), 7.43 (1H, d, *J* = 10.5, H-Ar), 7.48 (1H, d, *J* = 9.5, H-Ar), 7.69 (1H, t, *J* = 9.5, H-Ar), 7.88 (1H, d, *J* = 10, H-Ar).

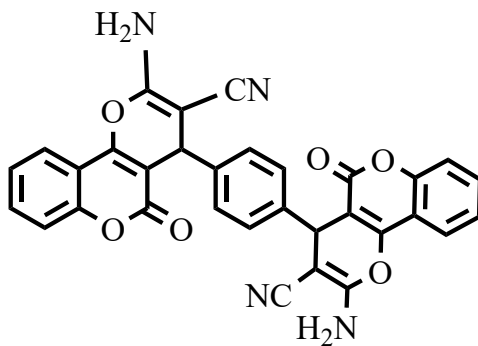
FT-IR



^1H NMR



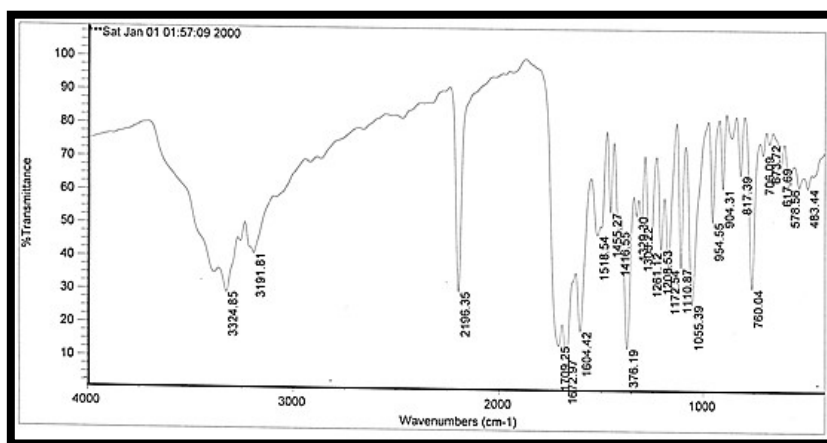
4,4'-(1,4-phenylene)bis(2-amino-5-oxo-4,5-dihydropyrano[3,2-c] chromene-3-carbonitrile)



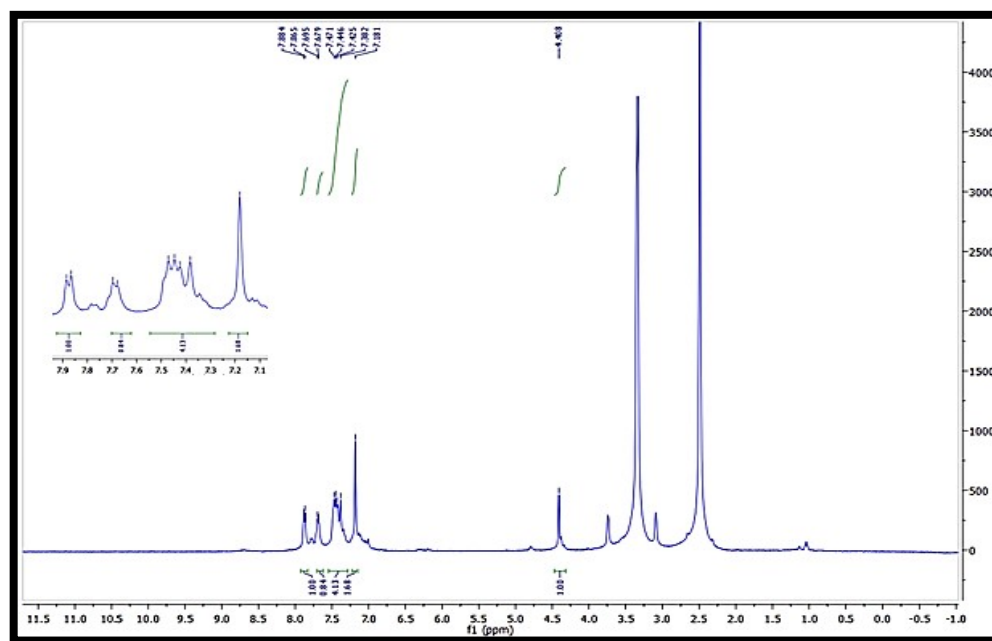
FT-IR [KBr $\bar{\nu}$ (cm⁻¹): 3324 (NH₂), 3191 (Ar-H), 2196 (C≡N), 1709, 1672 (C=O), 1604 (C=C), 1055 (C-O).

^1H NMR (400 MHz, DMSO-*d*₆) δ ppm: 4.40 (1H, s, CH), 7.26 (4H, br s, NH₂), 7.31 (3H, d, *J* = 6.0 Hz, H-Ar), 7.42 (3H, br s, H-Ar), 7.47 (2H, d, *J* = 10.8 Hz, H-Ar), 7.90 (2H, d, *J* = 6.8 Hz, H-Ar), 7.70 (2H, br s, H-Ar).

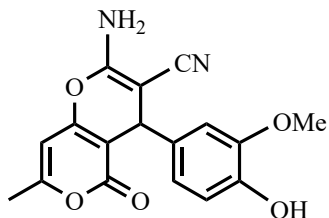
FT-IR



¹H NMR



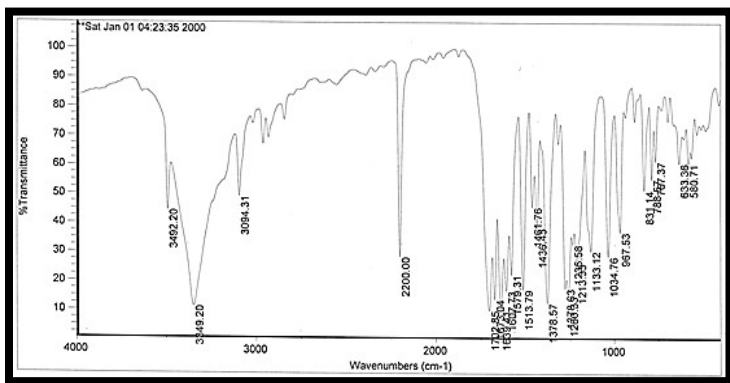
2-amino-4-(4-hydroxy-3-methoxyphenyl)-7-methyl-5-oxo-4,5 dihydropyrano[4,3-*b*]pyran-3-carbonitrile



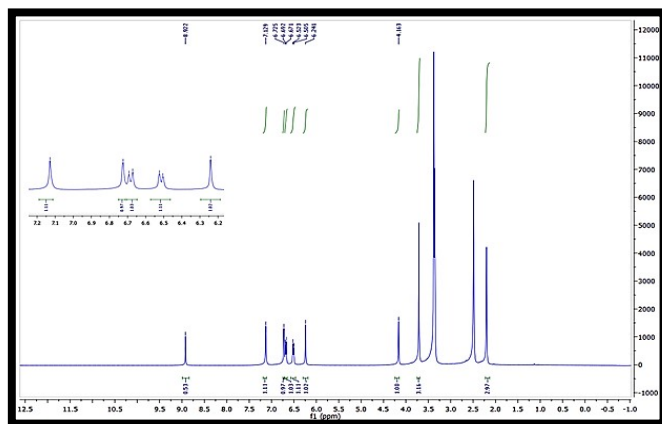
FT-IR [KBr $\bar{\nu}$ (cm⁻¹): 3492 (OH), 3349, 3094 (NH₂), 3094 (Ar-H), 2200 (C≡N), 1702, 1673 (C=O), 1639, 1607 (C=C), 1034 (C-O).

¹H NMR (400 MHz, DMSO-d₆) δ ppm: 2.22 (3H, s, CH₃), 3.74 (3H, s, OCH₃), 4.16 (1H, s, CH), 6.24 (1H, s, H-pyran), 6.51 (1H, d, *J* = 9, H-Ar), 6.68 (1H, d, *J* = 10.5, H-Ar), 6.72 (1H, s, H-Ar), 7.12 (2H, br s, NH₂), 8.92 (1H, br s, OH).

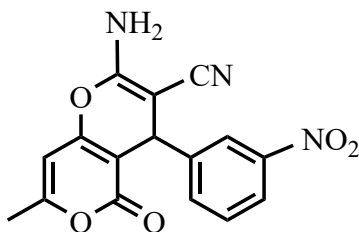
FT-IR



¹H NMR



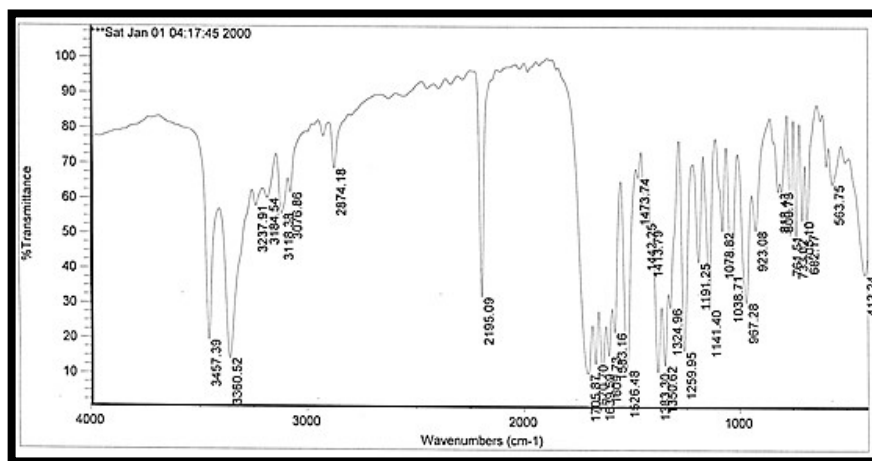
2-amino-7-methyl-4-(3-nitrophenyl)-5-oxo-4,5-dihydropyrano[4,3-b]pyran-3-carbonitrile



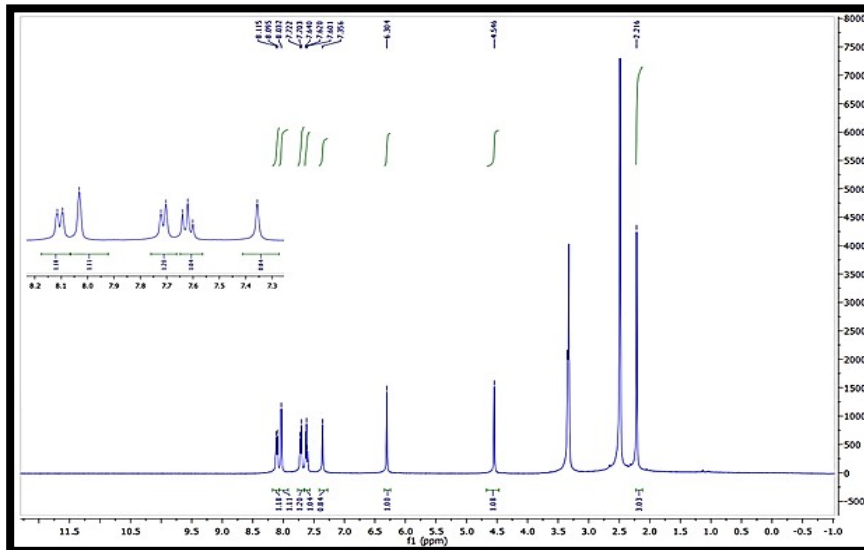
FT-IR [KBr $\bar{\nu}$ (cm⁻¹): 3457, 3360 (NH₂), 3237, 3184, 3118, 3076 (Ar-H), 2874, 2195 (C≡N), 1705, 1670 (C=O), 1639, 1609 (C=C), 1473, 1526 (NO₂), 1038 (C-O).

¹H NMR (400 MHz, DMSO-d₆) δ ppm: 2.21 (3H, s, CH₃), 4.54 (1H, s, CH), 6.30 (1H, s, H-pyran), 7.35 (1H, s, H-Ar), 8.03 (2H, s, NH₂), 8.11 (1H, d, $J=10$, H-Ar).

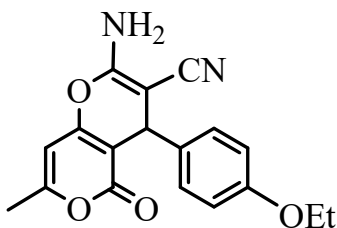
FT-IR



¹H NMR



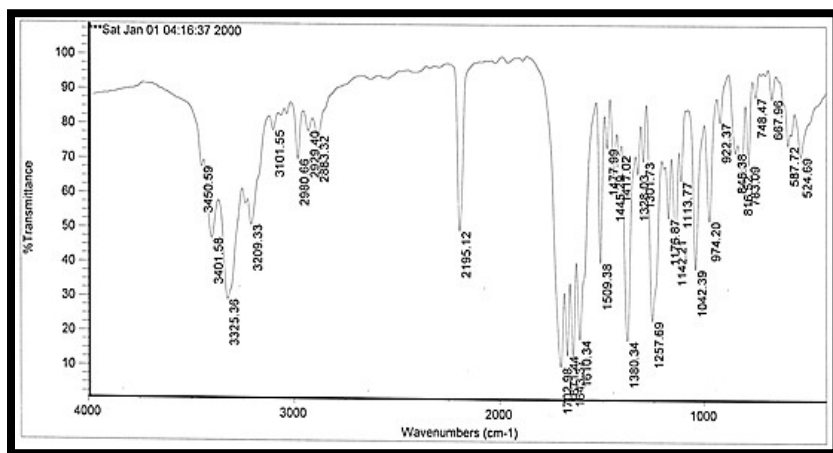
2-amino-4-(4-ethoxyphenyl)-7-methyl-5-oxo-4,5-dihydropyrano[4,3-*b*]pyran-3-carbonitrile



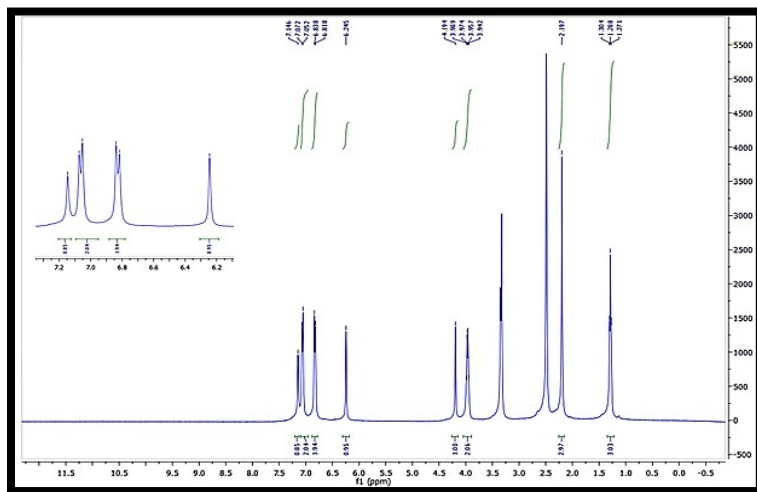
FT-IR [KBr $\bar{\nu}$ (cm⁻¹): 3450, 3401 (NH₂), 3209 (C-H), 3101, 2980 (Ar-H), 2929, 2883, 2195 (C≡N), 1702, 1671 (C=O), 1643, 1610 (C=C), 1042 (C-O).

¹H NMR (400 MHz, DMSO-d₆) δ ppm: 1.28 (3H, t, $J = 8$, CH₃), 2.19 (3H, s, CH₃), 3.96 (2H, q, $J = 7.5$, CH₂), 4.19 (1H, s, CH), 6.24 (1H, s, H-pyran), 6.82 (2H, d, $J = 10$, H-Ar), 7.06 (2H, d, $J = 10$, H-Ar), 7.14 (2H, br s, NH₂).

FT-IR

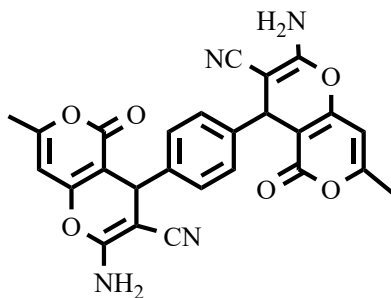


¹H NMR



4,4'-(1,4-phenylene)bis(2-amino-7-methyl-5-oxo-4,5-dihydropyranob)pyran-3-carbonitrile

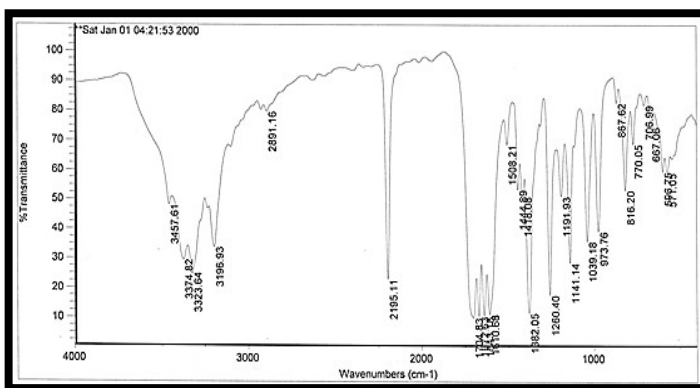
[4,3-



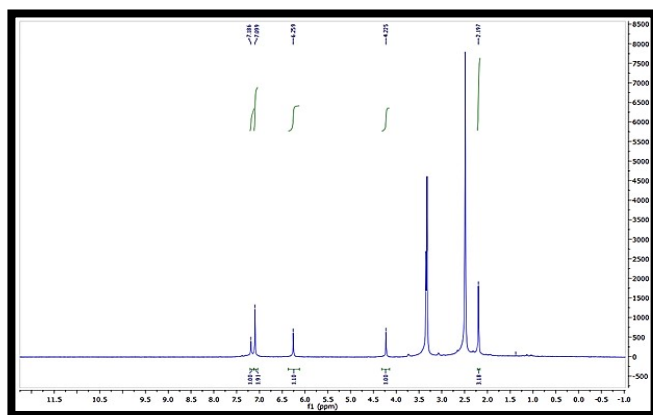
FT-IR [KBr $\bar{\nu}$ (cm^{-1})]: 3457, 3323 (NH_2), 3196 (Ar-H), 2891 (aliphatic C-H), 2195 ($\text{C}\equiv\text{N}$), 1704, 1677 ($\text{C}=\text{O}$), 1643, 1610 ($\text{C}=\text{C}$), 1039 ($\text{C}-\text{O}$).

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ ppm: 2.19 (3H, s, CH_3), 4.22 (1H, s, CH), 6.25 (1H, s, H-pyran), 7.09 (2H, s, NH_2), 7.18 (4H, s, H-Ar).

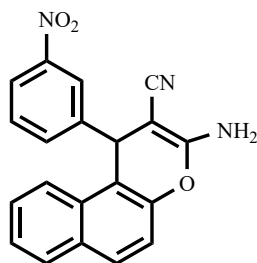
FT-IR



^1H NMR



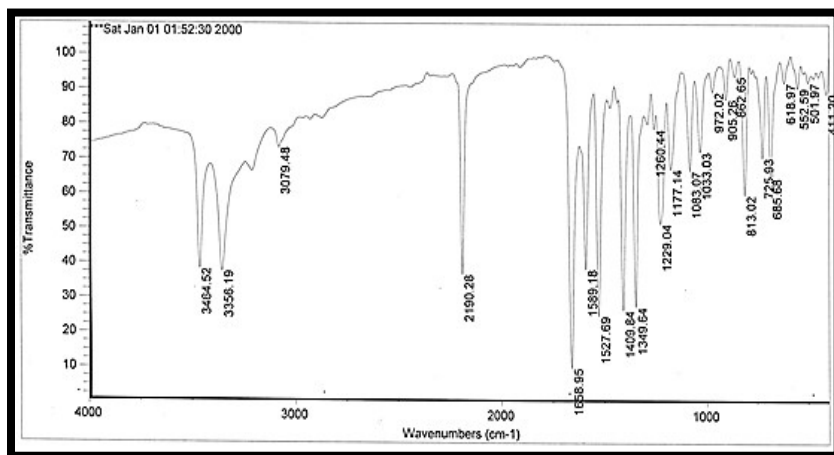
3-amino-1-(3-nitrophenyl)-1H-benzo[f]chromene-2-carbonitrile



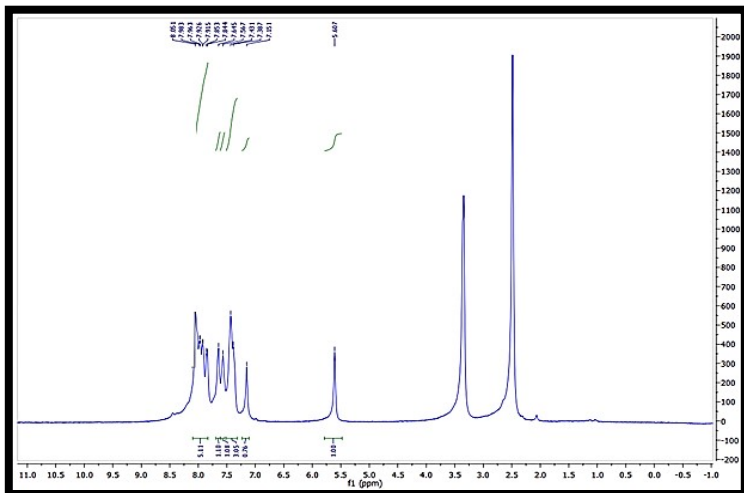
FT-IR [KBr $\bar{\nu}$ (cm⁻¹): 3404, 3356 (NH₂), 3196, 2891 (Ar-H), 2190 (C≡N), 1658 (C=O), 1643, 1610 (C=C), 1527, 1349 (NO₂), 1083 (C-O).

¹H NMR (400 MHz, DMSO-d₆) δ ppm: 5.40 (1H, s, CH), 7.20 (2H, s, NH₂), 7.42 (2H, d, *J* = 9.01 Hz, Ar-H), 7.51–7.57 (2H, m, Ar-H), 7.63 (1H, d, *J* = 7.74 Hz, Ar-H), 7.78 (1H, d, *J* = 9.11 Hz, Ar-H), 7.93 (1H, d, *J* = 9.06 Hz, Ar-H), 8.01 (1H, d, *J* = 8.01 Hz, Ar-H), 8.06 (1H, s, Ar-H), 8.05 (1H, d, *J* = 1.75 Hz, Ar-H).

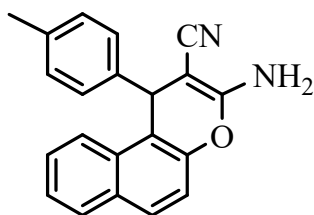
FT-IR



¹H NMR



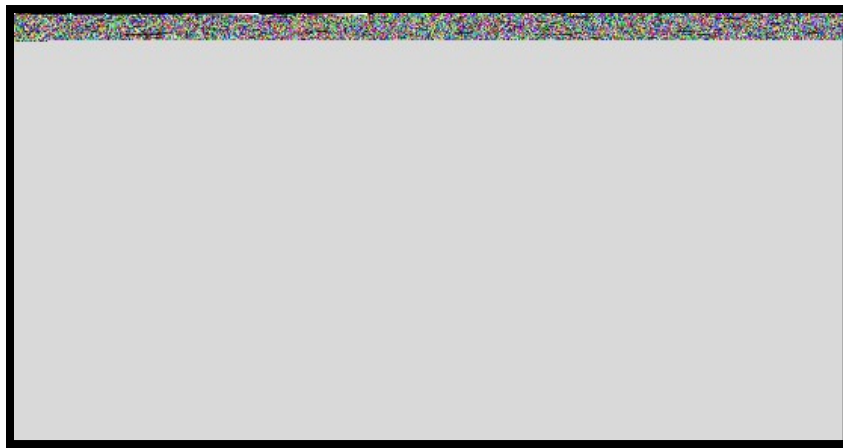
3-amino-1-(p-tolyl)-1*H*-benzo[*f*]chromene-2-carbonitrile



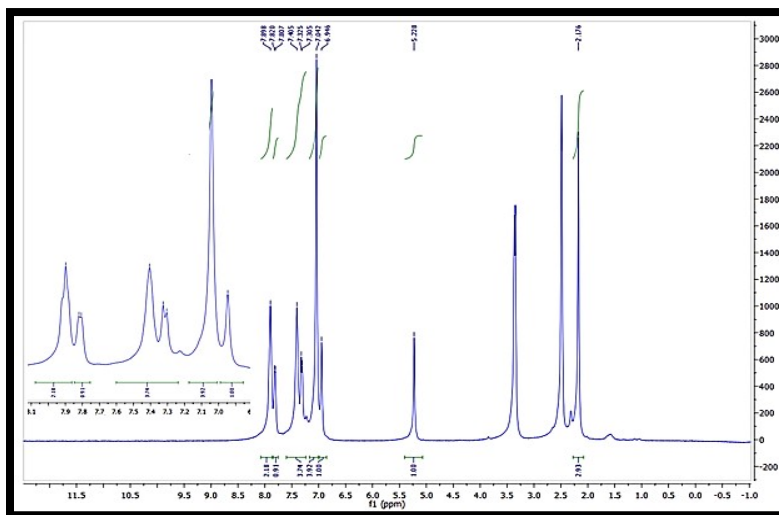
FT-IR [KBr $\bar{\nu}$ (cm⁻¹): 3404, 3356 (NH₂), 3079 (Ar-H), 2190 (C≡N), 1658, 1615 (C=C), 1035 (C-O).

¹H NMR (400 MHz, DMSO-d₆) δ ppm: 2.17 (3H, s, CH₃), 5.22 (1H, s, CH), 6.25 (1H, s, CH), 6.94 (1H, br s, H-Ar), 7.04 (4H, br s, H-Ar), 7.30-7.40 (8H, m, H-Ar, NH₂), 7.80-7.89 (3H, m, H-Ar).

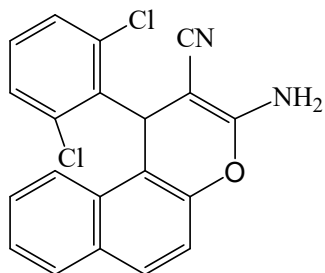
FT-IR



¹H NMR



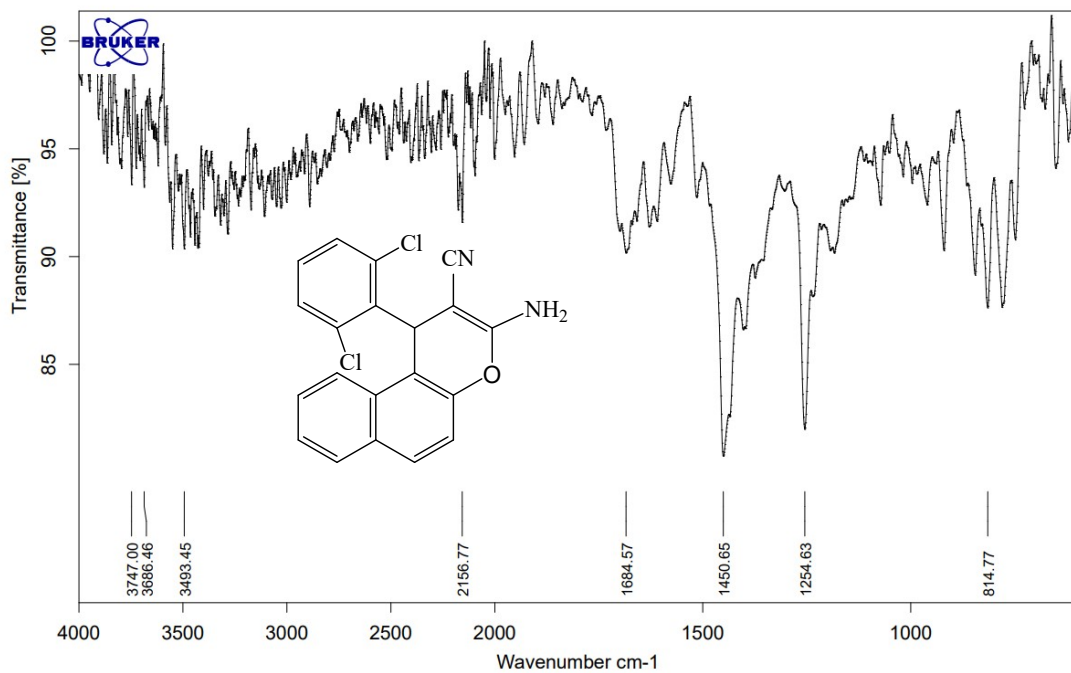
3-amino-1-(2,4-dichlorophenyl)-1H-benzo[f]chromene-2-carbonitrile



FT-IR [KBr $\bar{\nu}$ (cm^{-1})]: 34093, 3356 (NH_2), 2156 ($\text{C}\equiv\text{N}$), 1684, 1450 ($\text{C}=\text{C}$), 1254($\text{C}-\text{O}$).

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ ppm: 5.20 (1H, s, CH), 7.00-8.00 (11H, m, H-Ar, NH_2).

FT-IR



^1H NMR

