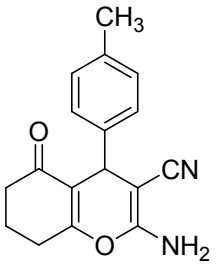
Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary data

A unique approach to magnetization of metal oxides: Nano-Fe_3O_4@TDI@TiO_2 as a highly efficient, magnetically separable and recyclable heterogeneous nanocatalyst

Elham Tabrizian and Ali Amoozadeh*

2-Amino-5-oxo-(4-Methylphenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 4, Entry 2)



Melting point= 232-234 °C; FT-IR (KBr, Cm^{-1}) ν_{max}: 3334, 3265, 2184, 1654, 1174. ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ: 1.96-2.07 (m, 2H), 2.26 (S, 3H, CH_3), 2.29-2.42 (m, 2H), 2.52-2.69 (m, 2H), 4.79 (S, H), 5.48 (S, 2H), 7.02- 7.05 (d, 2H, j=8), 7.19-7.21 (d, 2H, j=7.6). ^{13}C NMR (100 MHz, $CDCl_3$-*d*) δ: 20.31, 21.06, 27.15, 31.22, 36.98, 55.14, 113.52, 117.03, 128.25, 129.33, 135.86, 137.77, 141.53, 163.77, 196.52.

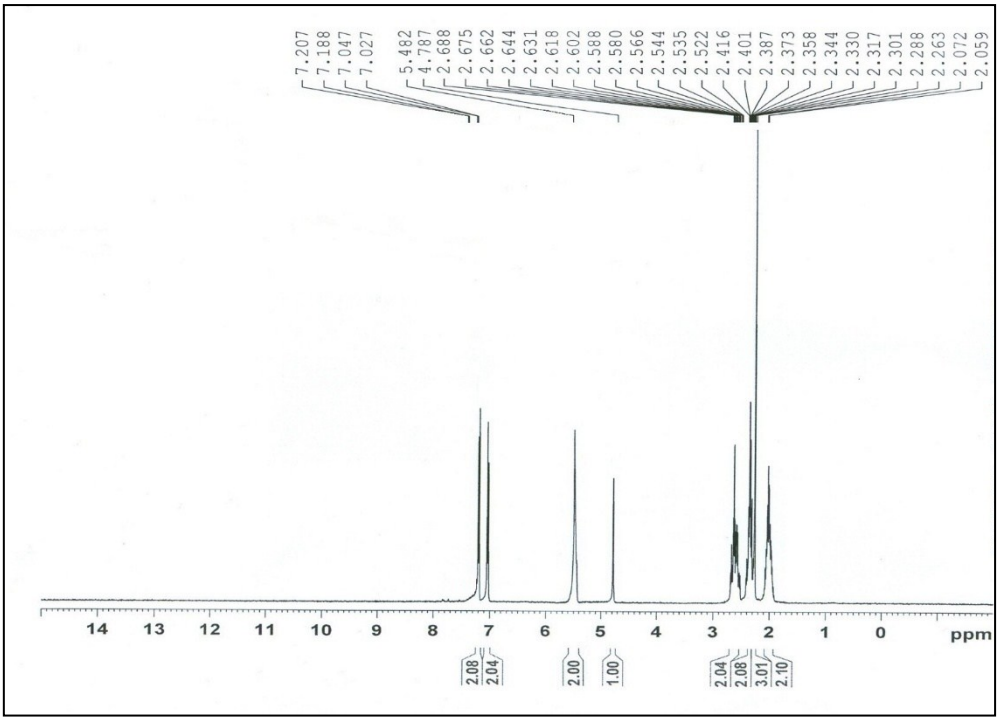


Fig. 1. ^{1}H NMR of 2-Amino-5-oxo-(4-Methylphenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile.

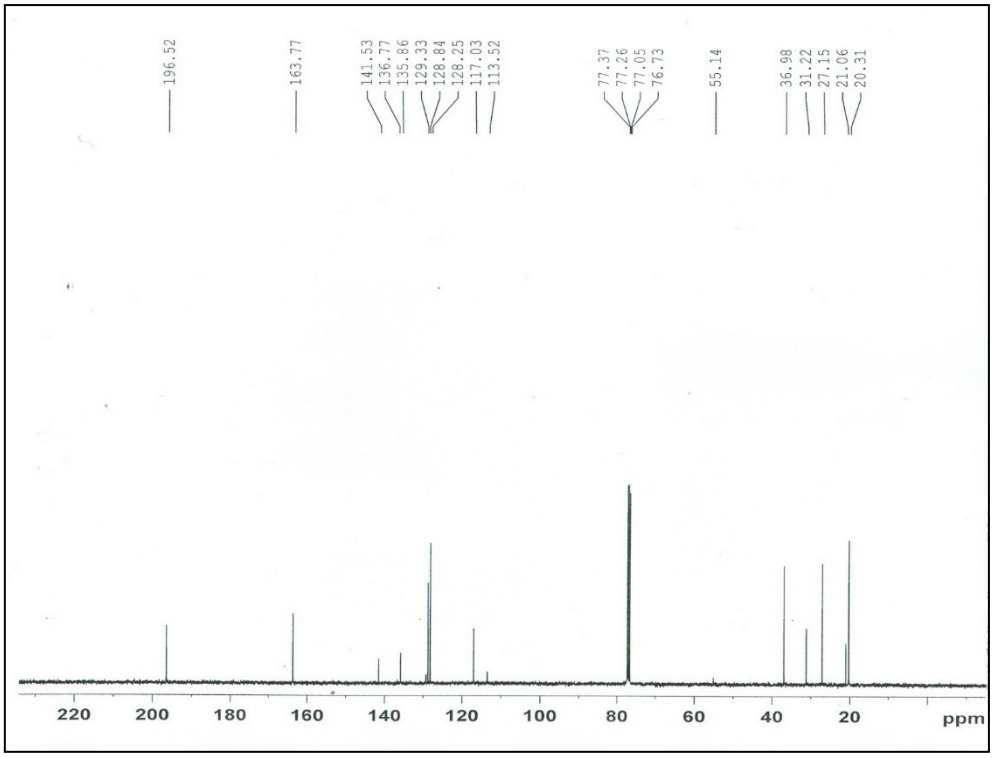
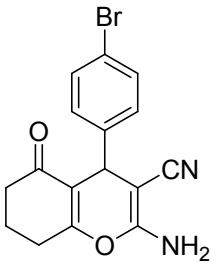


Fig. 2. ^{13}C NMR of 2-Amino-5-oxo-(4-Methylphenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile.

2-Amino-(4-bromophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 4, Entry 10)



Melting point= 229-232 °C; FT-IR (KBr, Cm^{-1}) ν_{max}= 3421, 3415, 2194, 1622, 1170, 1070. ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ: 1.92-2.08 (m, 2H), 2.12-2.40 (m, 2H), 2.53-2.65 (m, 2H), 4.76 (S, 1H), 6.14 (S, 2H), 7.13-7.12 (d, J= 8.4 Hz, 2H), 7.33-7.43 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*) δ: 20.10, 20.27, 27.13, 31.39, 36.76, 36.90, 116.41, 120.28, 129.43, 130.21, 131.17, 131.66, 131.83, 133.08, 143.47, 158.49, 164.12, 196.51, 133.08, 143.47, 158.49, 164.12, 196.51.

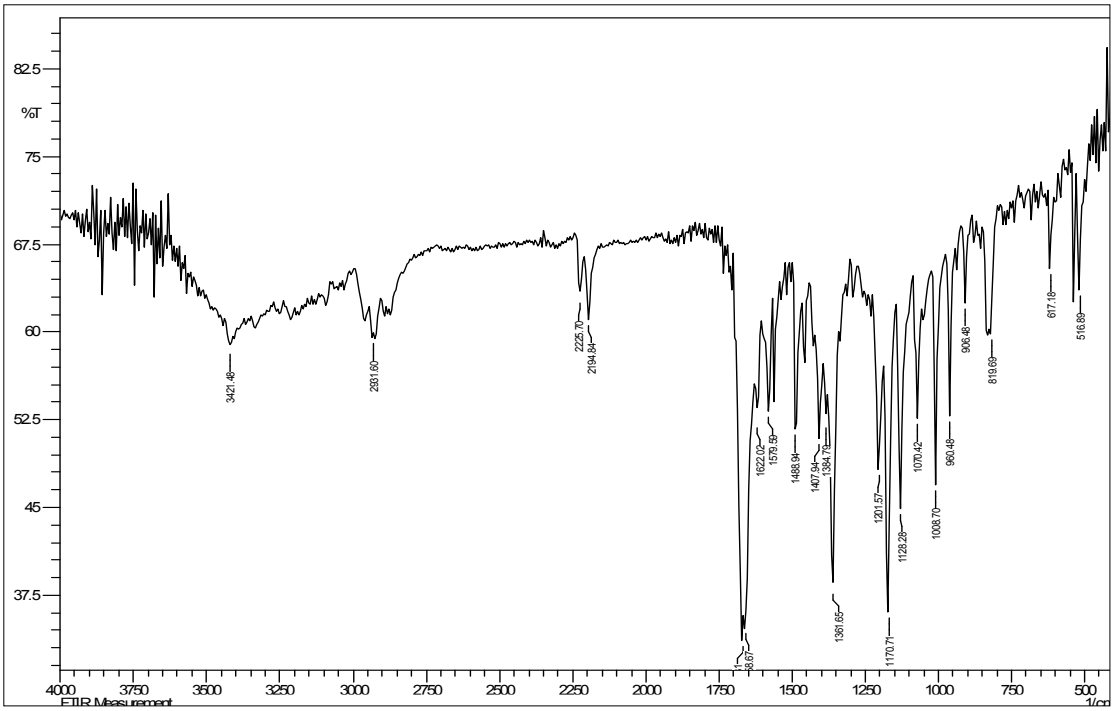


Fig. 3. FT-IR of 2-Amino-(4-bromophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile.

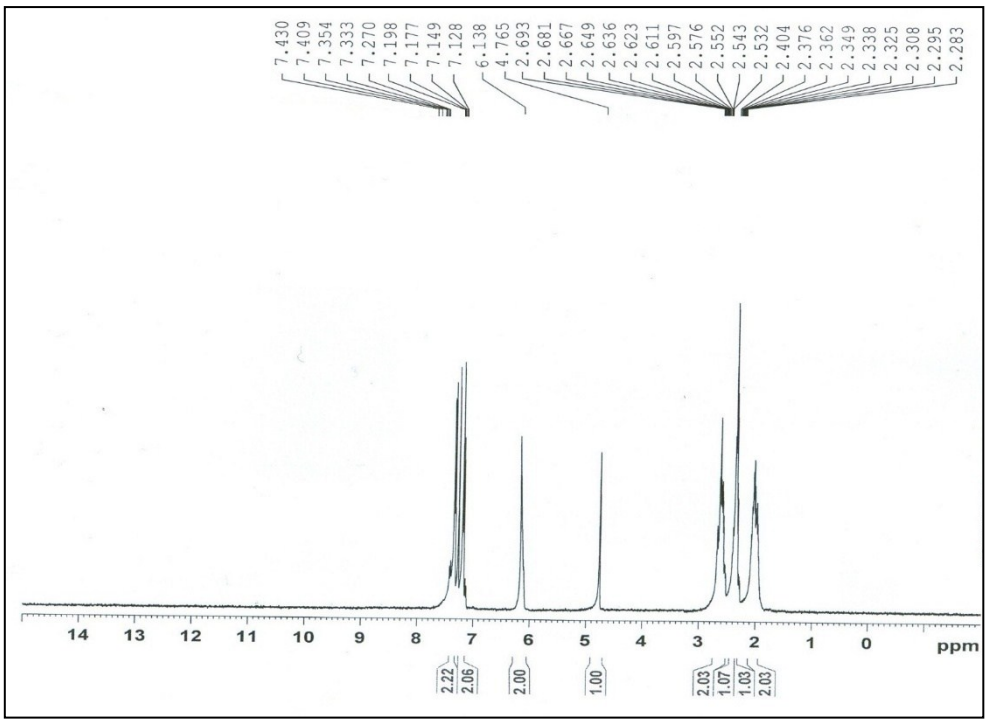


Fig. 4. [1]H NMR of 2-Amino-(4-bromophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile.

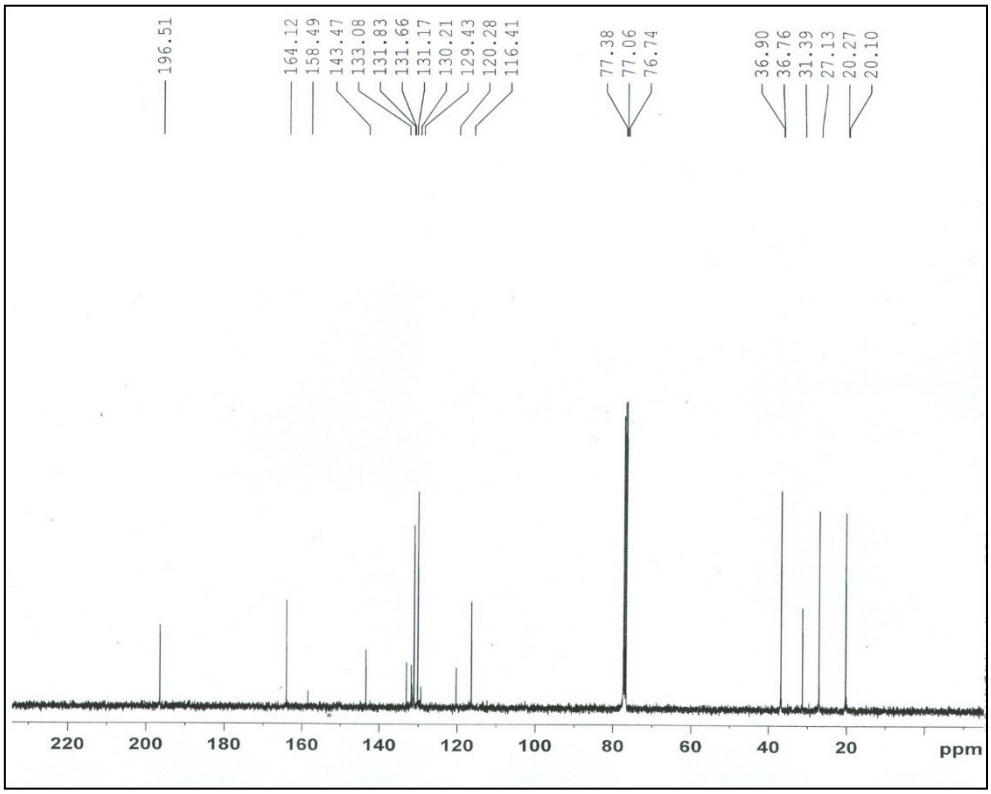
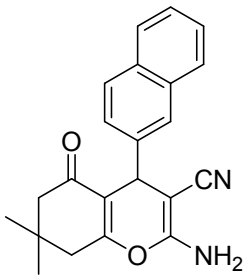


Fig. 5. [13]C NMR of 2-Amino-(4-bromophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile.

2-Amino-5-oxo-7,7-dimethyl-(2-naphthyle)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 4, Entry 26)



Melting point= 229-231 °C; FT-IR (KBr, Cm^{-1}) ν_{max}= 3352, 3319, 2189, 1625, 1163. ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ: 0.99 (S, 3H), 1.12 (S, 3H), 2.14-2.23 (q, 2H), 2.48-2.52 (S, 2H), 4.29 (S, 1H), 5.48 (S, 2H), 7.34-7.38 (m, 2H), 7.46-7.47 (d, J= 6.8 Hz, 2H), 7.73-7.79 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*) δ: 27.34, 29.28, 32.00, 32.21, 40.72, 40.92, 50.75, 125.30, 125.58, 126, 126.89, 127.14, 127.45, 127.66, 127.97, 128.48, 132.37, 133.40, 141.63, 162.29, 196.32.

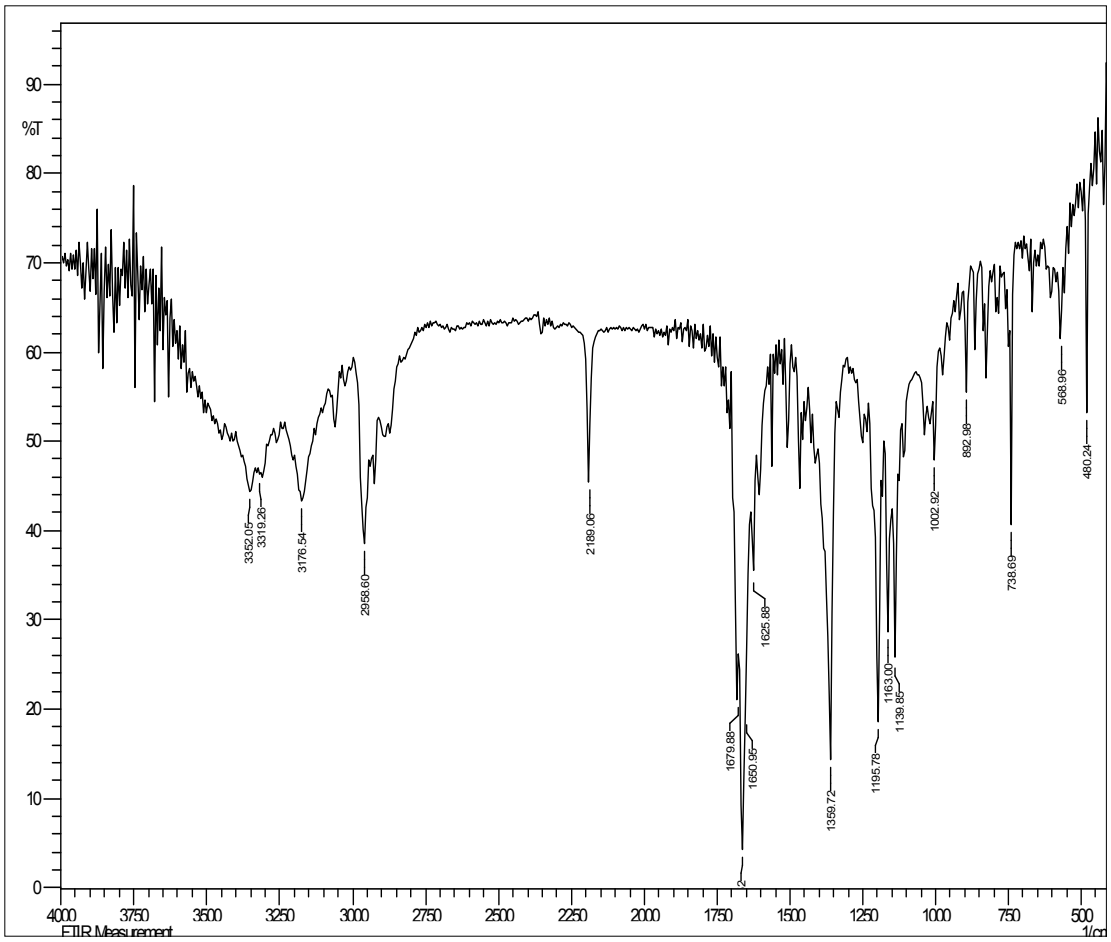


Fig. 6. FT-IR of 2-Amino-5-oxo-7,7-dimethyl-(2-naphthyle)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile.

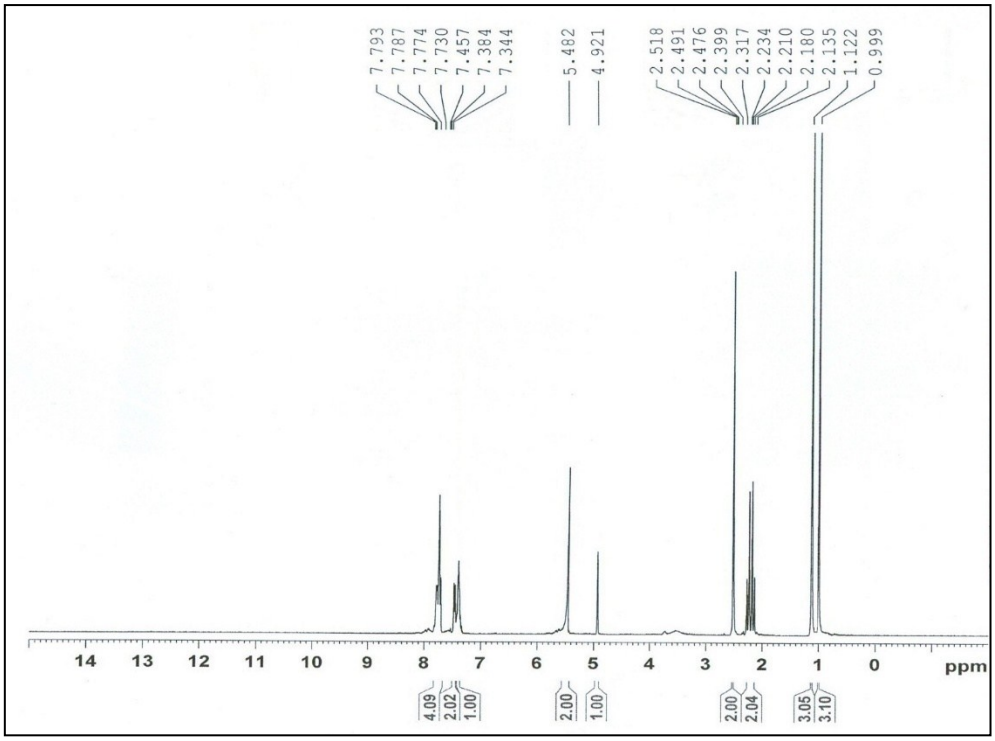


Fig. 7. [1]H NMR of 2-Amino-5-oxo-7,7-dimethyl-(2-naphthyle)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile.

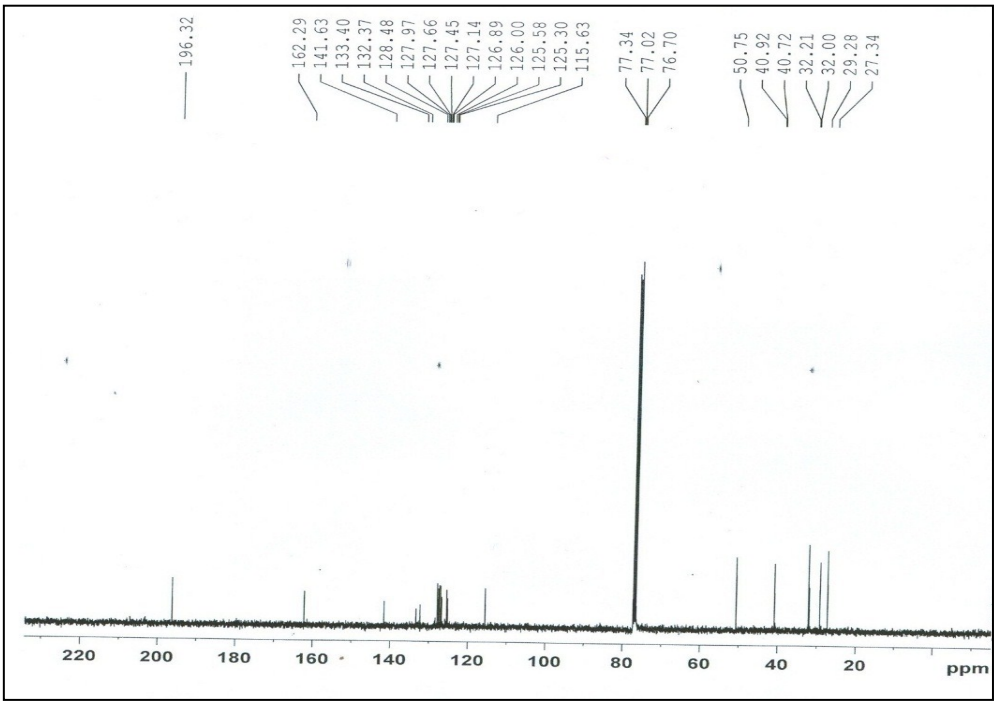
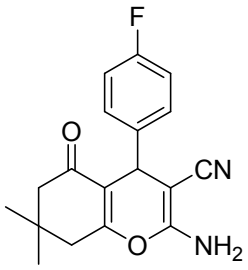


Fig. 8. [13]C NMR of 2-Amino-5-oxo-7,7-dimethyl-(2-naphthyle)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile.

2-Amino-5-oxo-7,7-dimethyl-(4-flourophenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (Table 4, Entry 24)



Melting point= 221-223 °C; FT-IR (KBr, Cm^{-1}) ν_{max}= 3350, 3309, 2198, 1654, 1174. ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ: 0.99 (S, 3H), 1.11 (S, 3H), 2.15-2.26 (q, J= 16 Hz, 2H), 2.46 (S, 2H), 4.73 (S, 1H), 5.581 (S, 2H), 6.87-6.29 (t, J= 8.8 Hz, 2H), 7.24-7.27 (d, j= 12.4, 2H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*) δ: 27.29, 29.26, 31.22, 32.20, 40.86, 50.73, 114.73, 114.94, 115.52, 129.80, 129.87, 139.97, 160.30, 162.30, 162.60, 196.36.

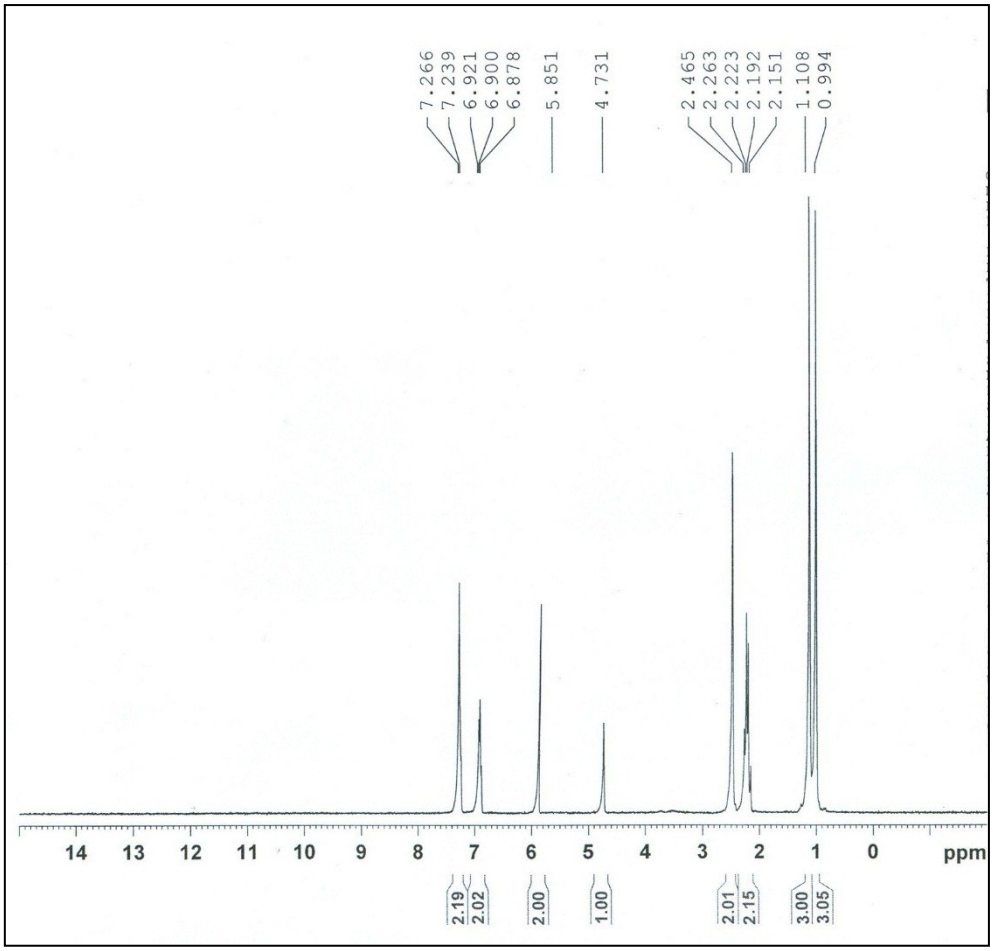


Fig. 9. ^{1}H NMR of 2-Amino-5-oxo-7,7-dimethyl-(4-flourophenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile.

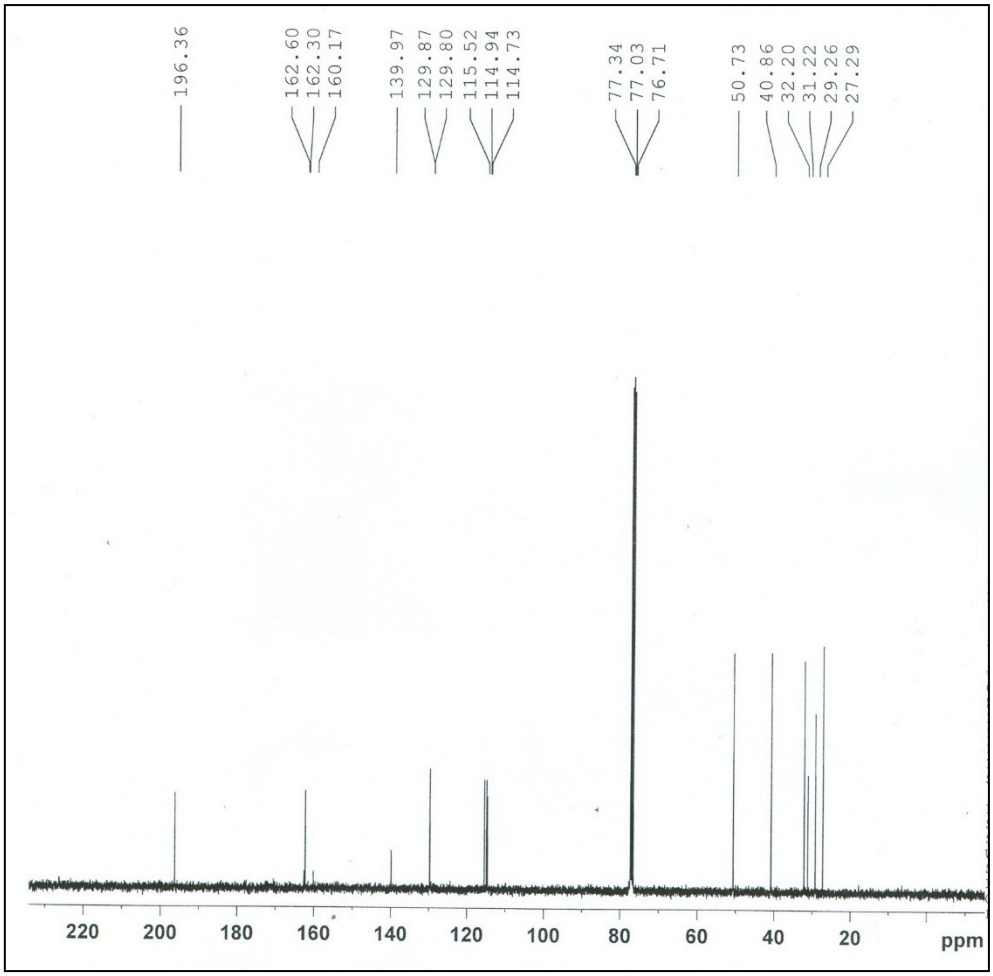
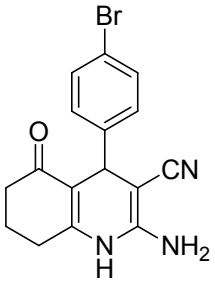


Fig. 10. ^{13}C NMR of 2-Amino-5-oxo-7,7-dimethyl-(4-flourophenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile.

2-amino-4-(4-bromophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (Table 5, Entry 9)



Melting point= 250-252 °C; IR (KBr, Cm^{-1}) ν_{max}: 3418, 3332, 3252, 2197, 1682, 1657, 1071. ^1H NMR (300 MHz, DMSO-d^6): δ 1.89 (m, 2H, CH_2), 2.26 (m, 2H, CH_2), 2.54 (m, 2H, CH_2), 3.34 (s, 1H, NH), 4.19 (s, 1H), 7.24 (m, 4H), 7.24 (s, 2H, NH). ^{13}C NMR (75 MHz, DMSO-d^6): δ 19.8, 26.5, 35.1, 36.3, 57.7, 113.4, 119.6, 120.1, 129.5, 130.7, 131.2, 132.3, 143.1, 149.5, 164.6, 195.9. Anal. Calc. for $C_{16}H_{14}BrN_3O$; C 55.83, H 4.10, N 12.21, O 4.65; Found: C 55.89, H 4.08, N 12.26, O 4.72.

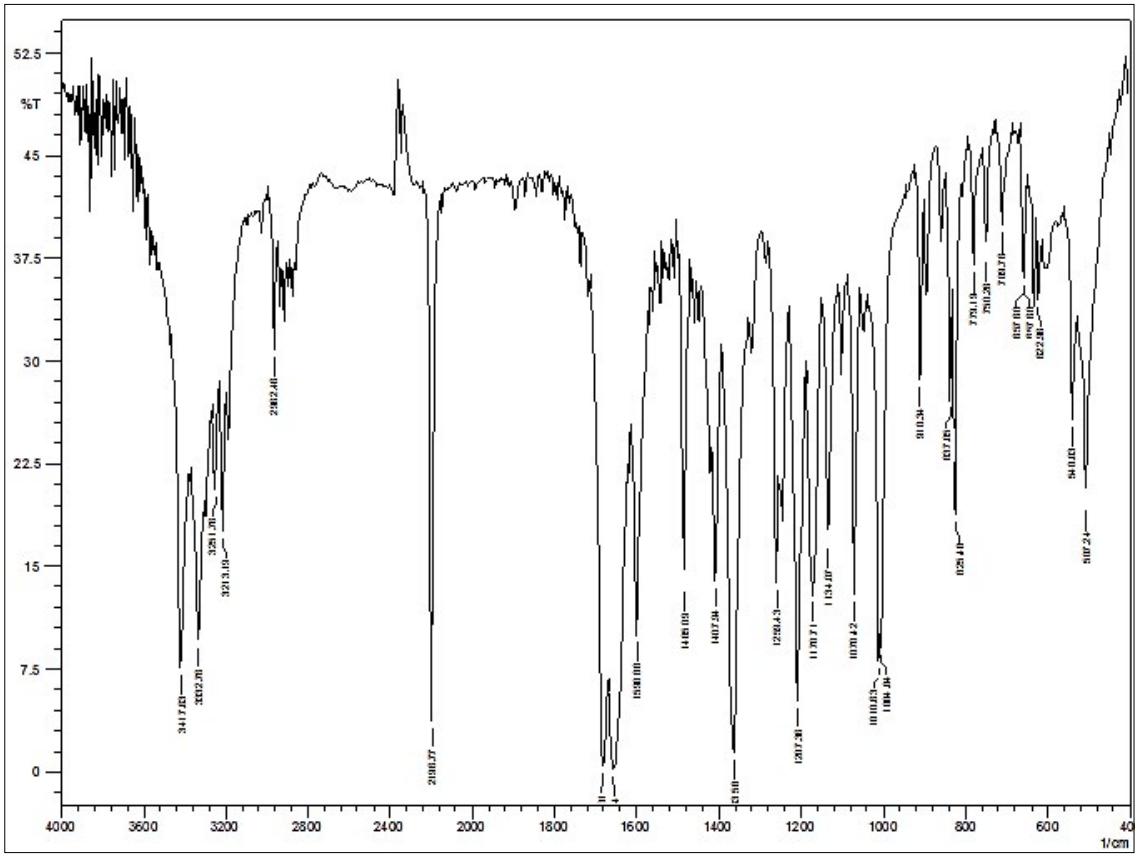


Fig. 11. FT-IR of 2-amino-4-(4-bromophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile.

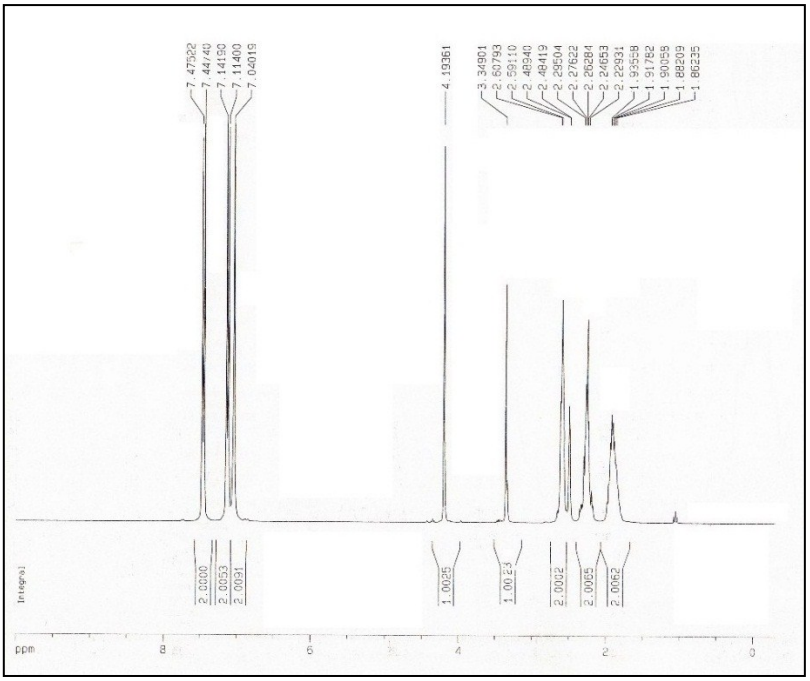


Fig. 12. [1]H NMR of 2-amino-4-(4-bromophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile.

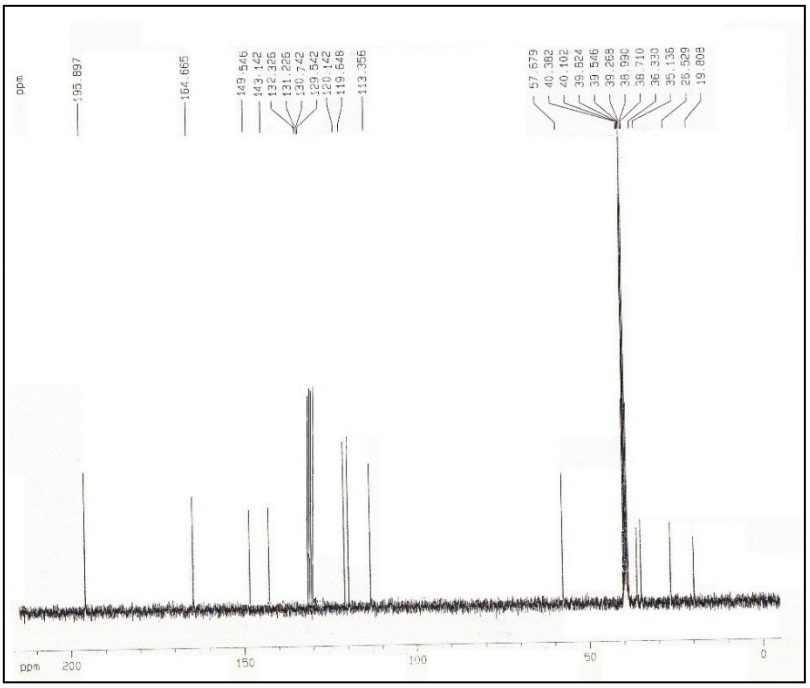
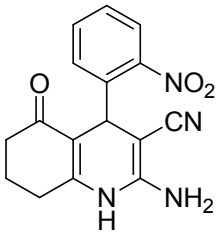


Fig. 13. [13]C NMR of 2-amino-4-(4-bromophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile.

2-amino-4-(2-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (Table 5, Entry 4)



Melting point= 228-230 °C; IR (KBr, Cm^{-1}) ν_{max}: 3337, 3462, 3236, 2197, 1684, 1661, 1529, 1365. ^{1}H NMR (300 MHz, DMSO-d^6): δ 1.03-1.07 (m, CH_2, 2H), 1.89-2.24 (m, CH_2, 2H), 2.48-2.59 (m, CH_2, 2H), 3.38 (s, NH, 1H), 4.94 (s, CH, 1H), 7.15 (s, NH_2, 2H), 7.35-7.80 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d^6): δ 19.7, 26.4, 30.1, 36.0, 56.4, 113.3, 119.1, 123.7, 127.8, 130.4, 133.4, 139.0, 149.0, 159.1, 164.7, 196.0. Anal. Calc. for $C_{16}H_{14}N_4O_3$; C 61.93, H 4.55, N 18.06, O 15.47; Found: C 61.99, H 4.48, N 18.13, O 15.54.

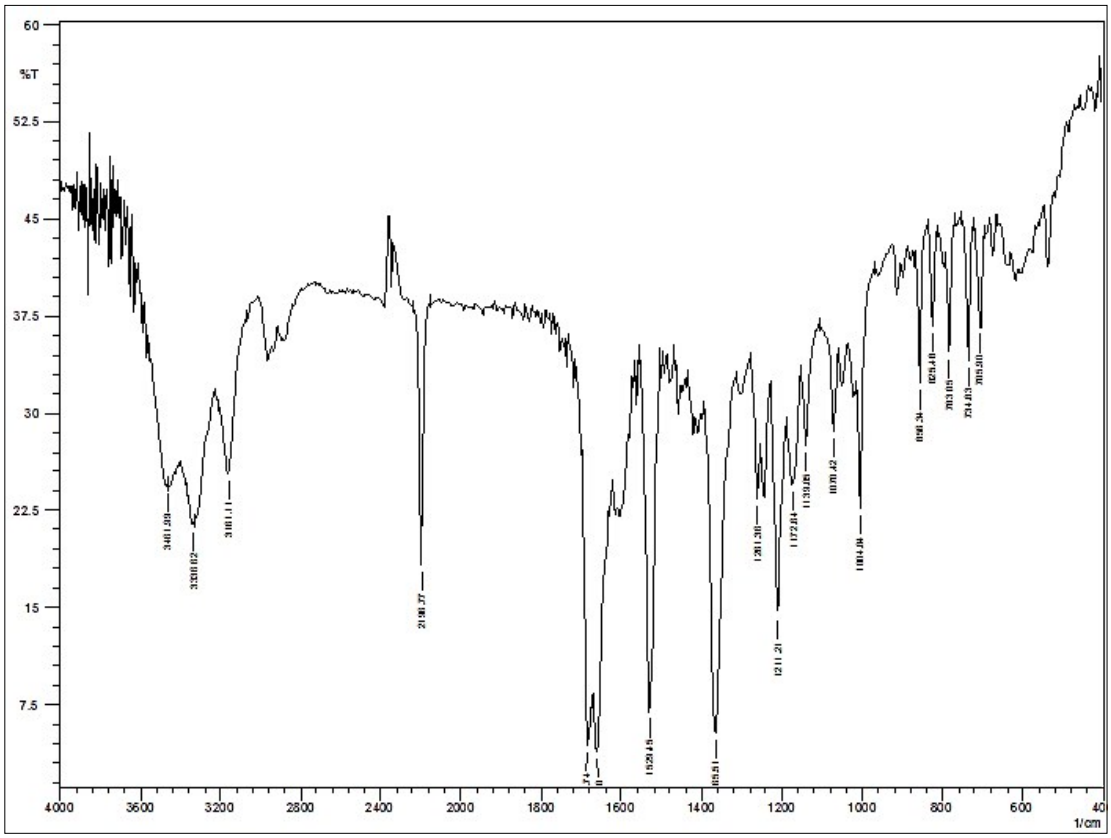


Fig. 14. FT-IR of 2-amino-4-(2-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile.

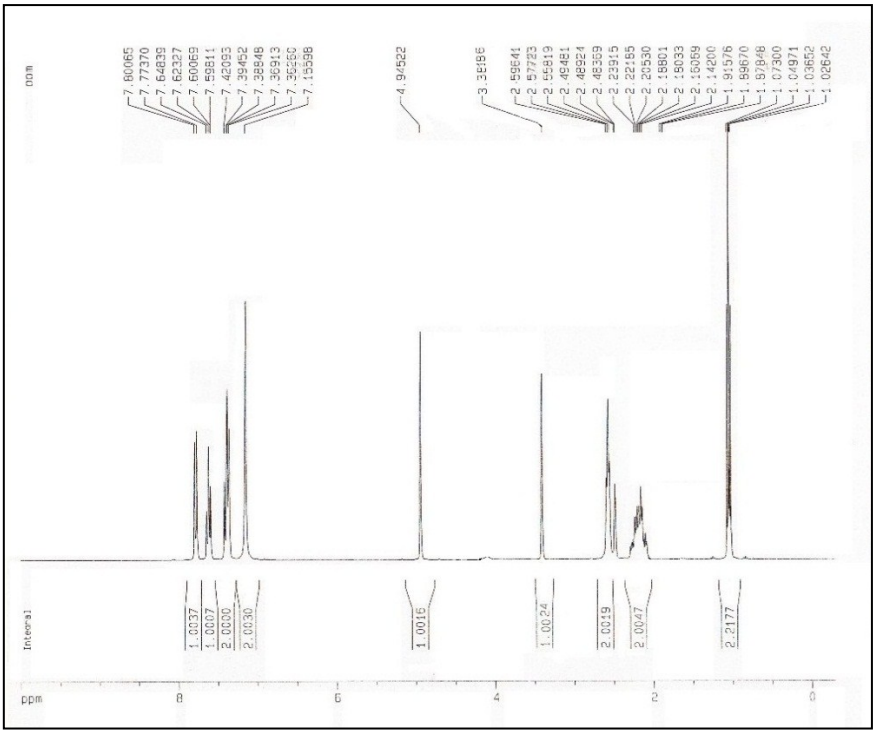


Fig. 15. [1]H NMR of 2-amino-4-(2-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile.

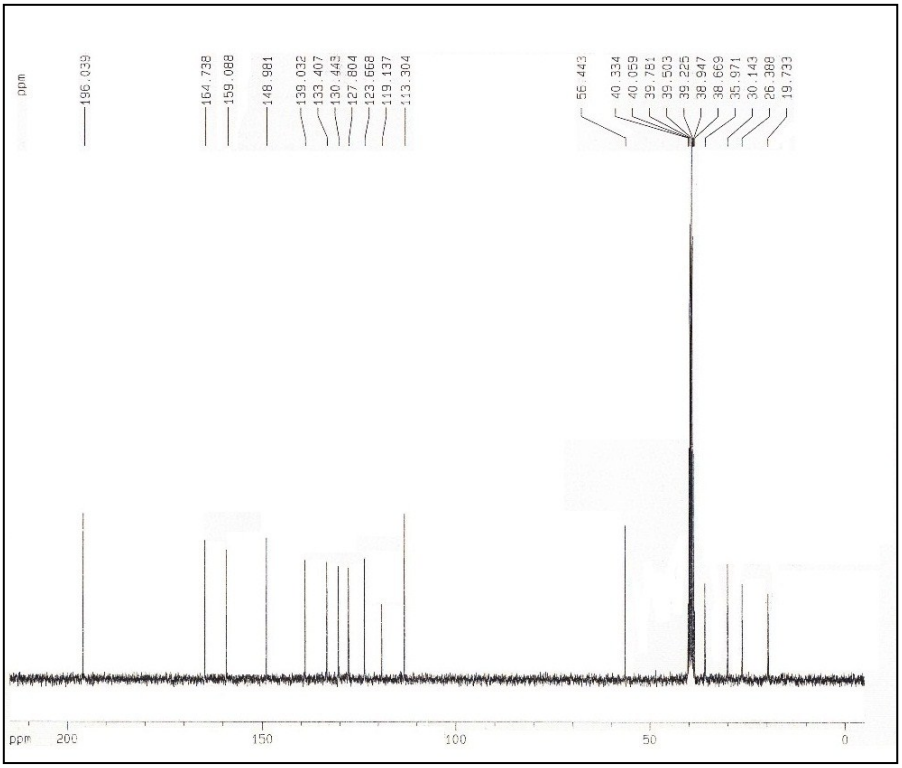
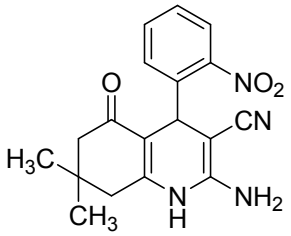


Fig. 16. [13]C NMR of 2-amino-4-(2-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile.

2-amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (Table 5, Entry 14)



Melting point= 231-234 °C; IR (KBr, Cm^{-1}) ν_{max}: 3472, 3330, 3302, 3000, 2195, 1661, 1650, 1529, 1450, 1365, 1352. ^{1}H NMR (300 MHz, DMSO-d^6): δ 0.88 (s, CH_3, 3H), 1.01 (s, CH_3, 3H), 1.99 (d, J= 15 Hz, CH, 1H), 2.17 (d, J= 15 Hz, CH, 1H), 2.43 (d, J= 18 Hz, CH, 1H), 2.51 (d, J= 18 Hz, CH, 1H), 3.34 (s, NH, 1H), 4.97 (s, CH, 1H), 7.10 (s, NH_2, 2H), 7.33-7.78 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d^6): δ 26.7, 28.3, 29.9, 31.8, 40.3, 49.6, 56.4, 112.4, 118.4, 123.6, 127.6, 130.2, 133.1, 139.0, 149.0, 149.5, 162.5, 195.6. Anal. Calc. for $C_{18}H_{18}N_4O_3$; C 63.89, H 5.36, N 16.56, O 14.19; Found: C 63.82, H 5.39, N 16.61, O 14.12.

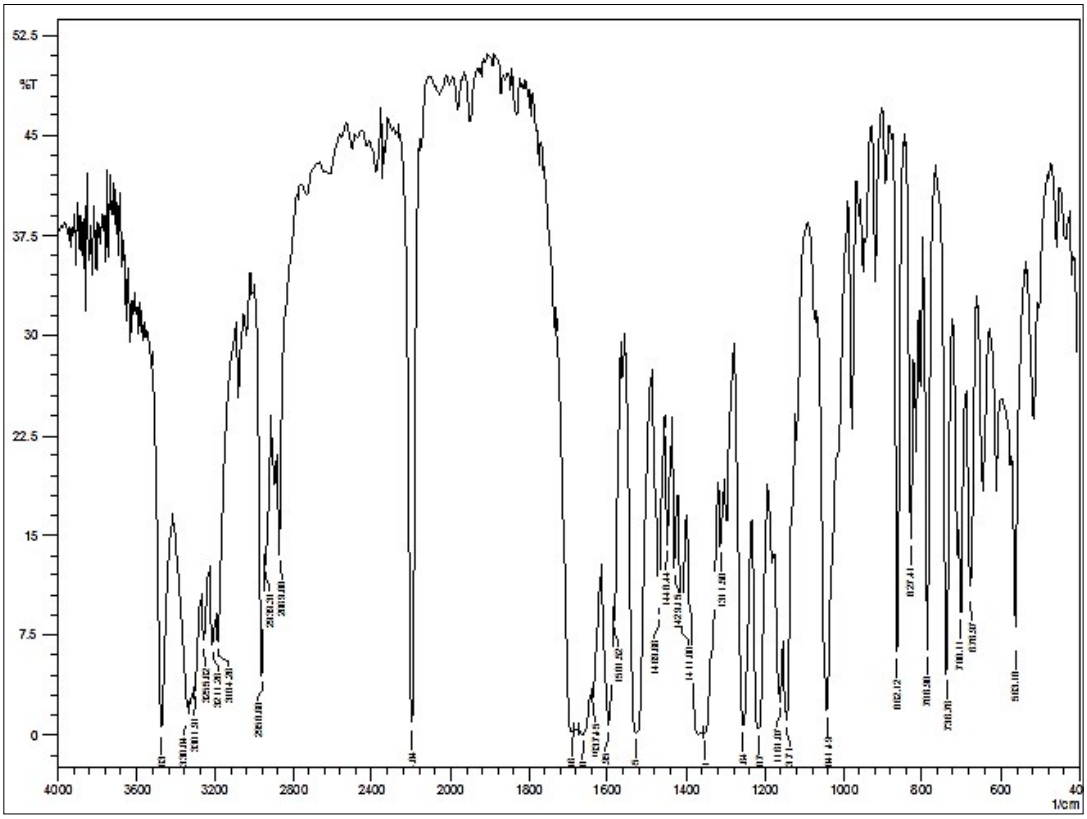


Fig. 17. FT-IR of 2-amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile.

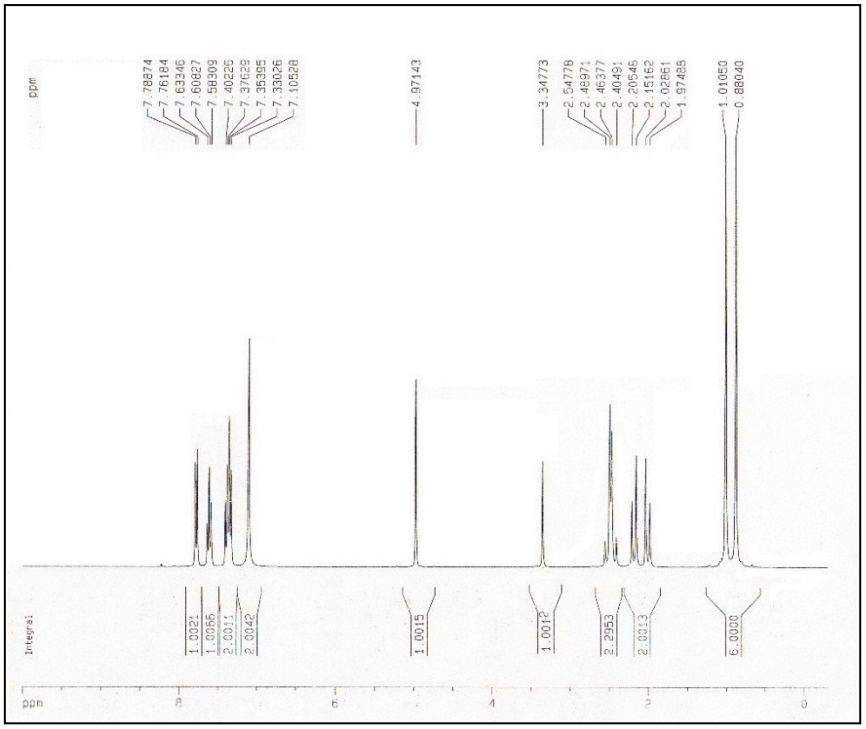


Fig. 18. [1]H NMR of 2-amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile.

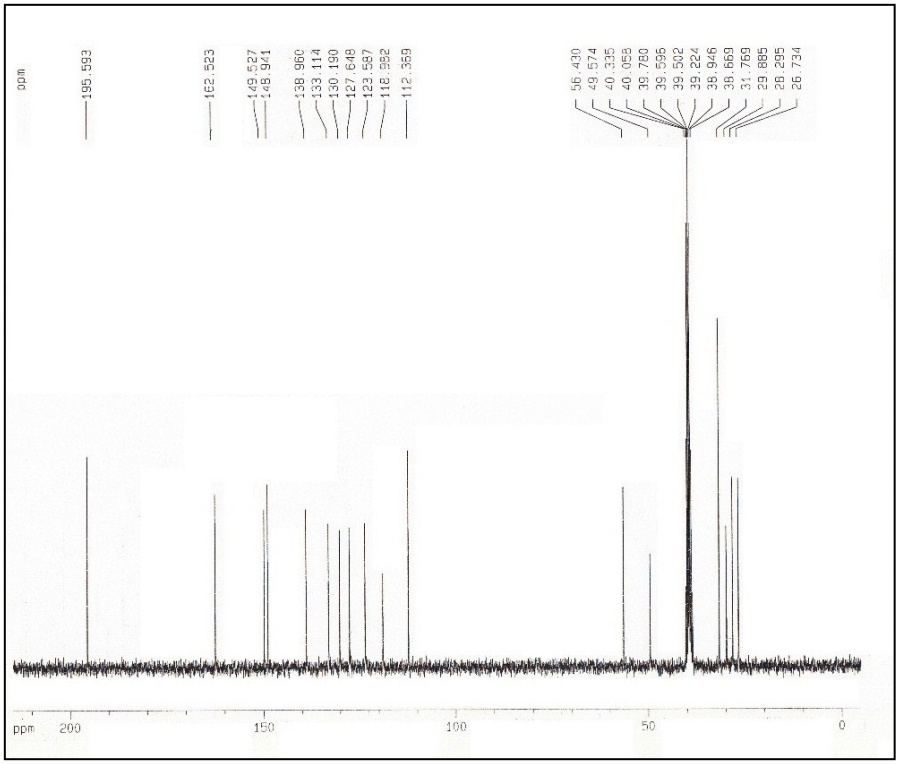
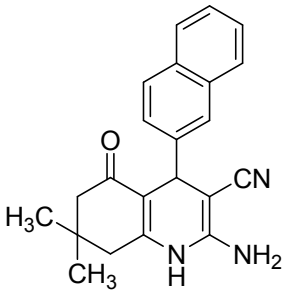


Fig. 19. [13]C NMR of 2-amino-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile.

2-amino-7,7-dimethyl-4-(naphthalen-2-yl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (Table 5, Entry 22)



Melting point= 260-263 °C; IR (KBr, Cm^{-1}) ν_{max}: 3346, 31.73, 3309, 3012, 2189, 1684, 1655, 1604, 1375. ^{1}H NMR (300 MHz, DMSO-d^6): δ 0.94 (s, CH_3, 3H), 1.02 (s, CH_3, 3H), 2.07 (d, J= 15 Hz, CH, 1H), 2.24 (d, J= 15 Hz, CH, 1H), 2.50 (m, CH_2, 2H), 3.38 (s, NH, 1H), 4.39 (s, CH, 1H), 7.09 (s, NH_2, 2H), 7.29-7.90 (m, Ar-H, 7H). ^{13}C NMR (75 MHz, DMSO-d^6): δ 26.7, 28.4, 31.8, 35.9, 50.0, 58.1, 112.6, 119.8, 125.6, 125.7, 126.2, 127.4, 127.7, 128.1, 132.0, 132.9, 135.0, 137.5, 148.5, 162.6, 195.7. Anal. Calc. for $C_{22}H_{21}N_3O$; C 76.94, H 6.16, N 12.24, O 4.66; Found: C 76.98, H 6.13, N 12.19, O 4.71.

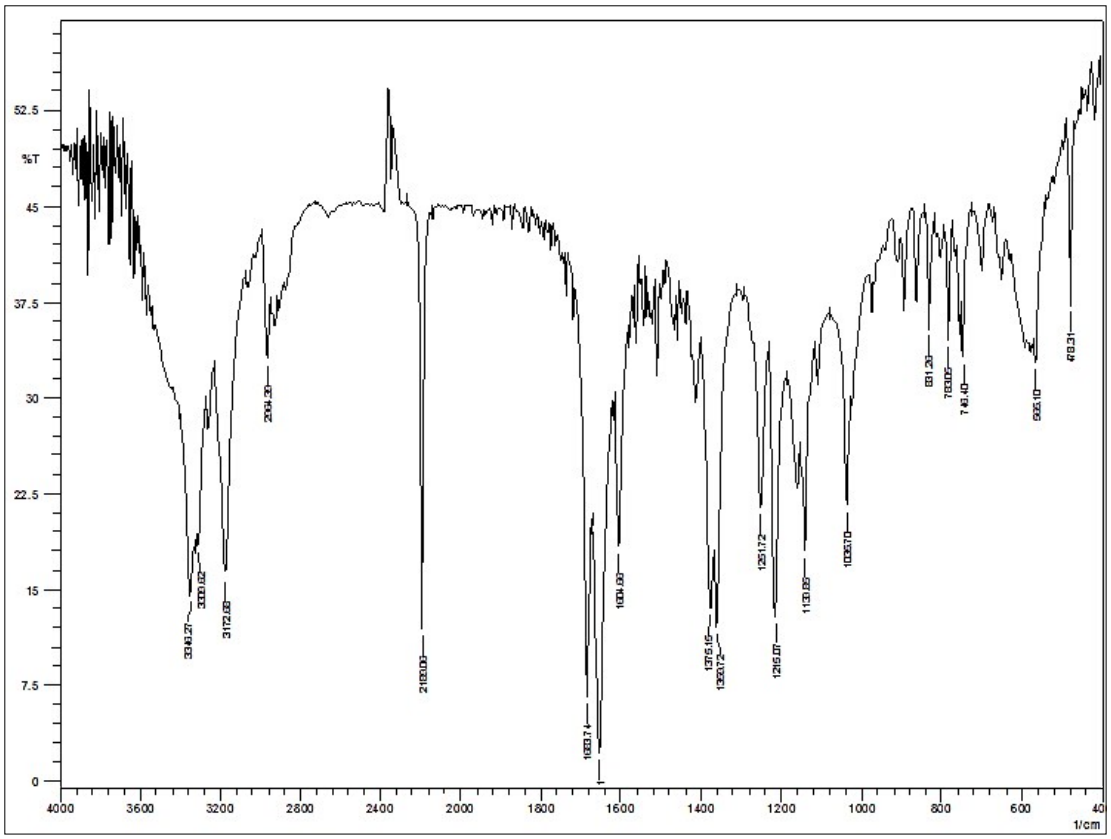


Fig. 20. FT-IR of 2-amino-7,7-dimethyl-4-(naphthalen-2-yl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile.

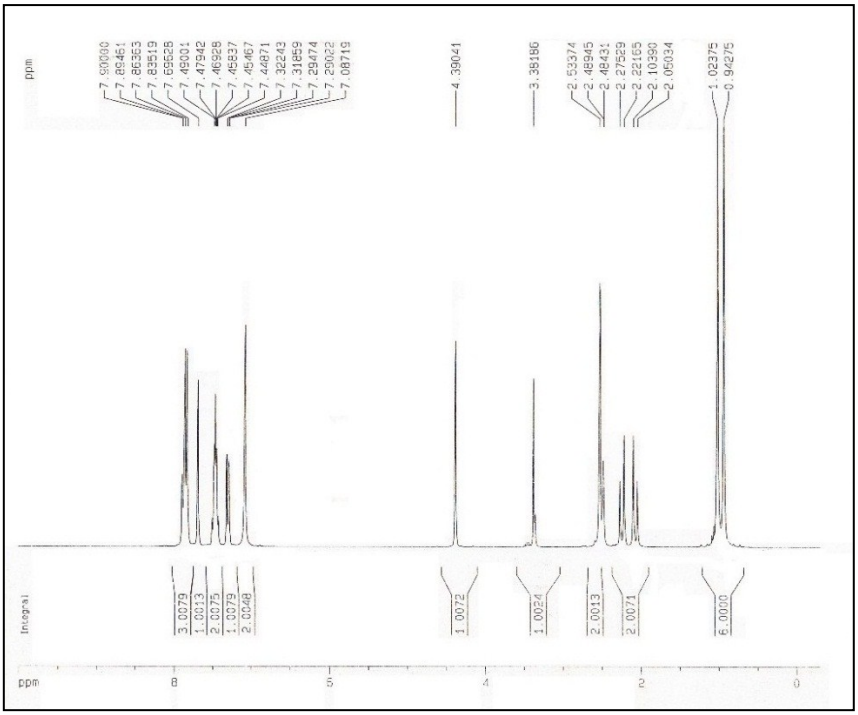


Fig. 21. [1]H NMR of 2-amino-7,7-dimethyl-4-(naphthalen-2-yl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile.

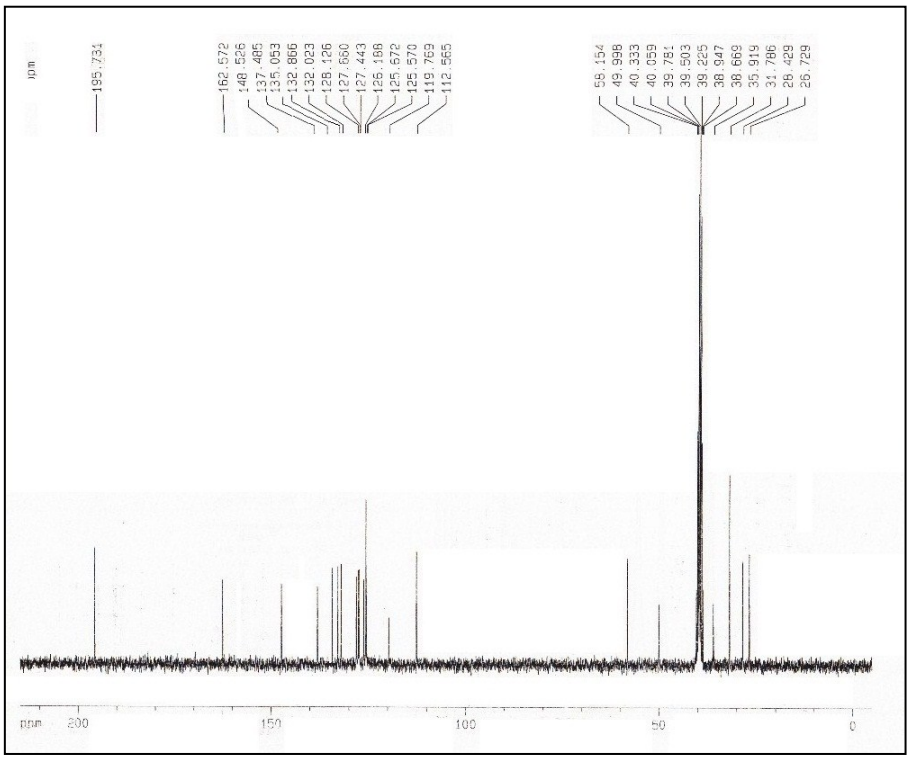


Fig. 22. [13]C NMR of 2-amino-7,7-dimethyl-4-(naphthalen-2-yl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile.