

Supporting information

Environmentally benign synthesis of 4-amino-quinoline-2-ones using recyclable ionic liquid choline hydroxide

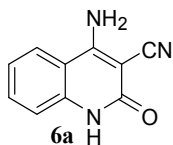
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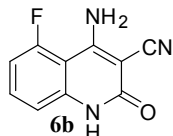
Spectroscopic data for 6a-6m

4-Amino-1,2-dihydro-2-oxo-3-quinolinecarbonitrile (6a)



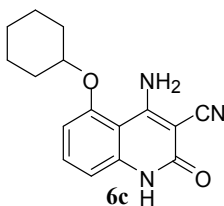
83%; mp 308-310 °C; IR (neat) ν = 3355, 3248, 2215, 1679, 1635, 1600, 1509, 1468, 1162 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ = 7.15 (td, 1H, C6-H, J = 8.0 & 1.4 Hz), 7.22 (dd, 1H, C5-H, J = 8.0 & 0.9 Hz), 7.56 (td, 1H, C7-H, J = 8.3 & 1.2 Hz), 8.11 (dd, 1H, C8-H, J = 8.0, 1.0 Hz); MS = 186.2 (M+H).

4-Amino-5-fluoro-2-oxo-1,2-dihydroquinoline-3-carbonitrile (6b)



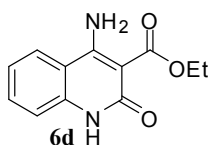
74%; mp above 330 °C; IR (neat) ν = 3515, 3348, 1653, 1621, 1588, 1499, 1478, 1416, 1241, 1054, 802 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ = 6.99 (dd, 1H, C6-H, J = 8.0 Hz), 7.06 (d, 1H, C8-H, J = 8.0 Hz), 7.53-7.59 (m, 1H, C7-H); MS = 204.2 (M+H).

4-amino-5-(cyclohexyloxy)-2-oxo-1,2-dihydroquinoline-3-carbonitrile (6c)



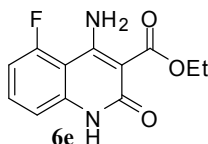
69%; decompose at 280 °C; IR (neat) ν = 3454, 3344, 2209, 1639, 1591, 1543, 1481, 1407, 1258, 1080, 886 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ = 1.33 (bs, 1H), 1.38-1.44, (m, 2H), 1.49-1.60 (m, 3H), 1.64 (bs, 2H), 1.98-2.01 (m, 2H), 4.68 (quintet, 1H), 6.80 (d, 1H, C6-H, J = 8.1 Hz), 6.85 (d, 1H, C8-H, J = 8.1 Hz), 7.45 (t, 1H, C7-H, J = 8.3 Hz), 7.56 (bs, 1H, NH), 8.10 (bs, 1H, NH), 11.18 (bs, 1H, NH); MS = 284.4 (M+H).

Ethyl-4-amino-2-oxo-1,2-dihydroquinoline-3-carboxylate (6d)



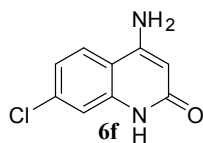
75%; mp 243-245 °C; IR (neat) ν = 3350, 2992, 1656, 1624, 1590, 1522, 1470, 1420, 1287, 1251, 1082, 1030, 812 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ = 1.25 (t, 3H, CH_3 , J = 8 Hz), 4.21 (q, 2H, CH_2 , J = 8 Hz), 7.11 (td, 1H, C6-H, J = 8.0 & 0.4 Hz), 7.18 (dd, 1H, C5-H, J = 0.4 & 8.0 Hz), 7.50 (td, 1H, C7-H, J = 8 & 0.4 Hz), 8.07 (dd, 1H, C8-H, J = 8 & 0.4 Hz), 8.28 (bs, 2H, NH_2), 10.81 (bs, 1H, NH); MS = 233.4 (M+H).

Ethyl-4-amino-5-fluoro-2-oxo-1,2-dihydroquinoline-3-carboxylate (6e)



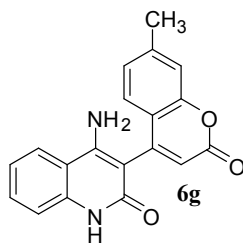
72%; mp 204 °C; IR (neat) ν = 3406, 2986, 1642, 1586, 1530, 1473, 1417, 1264, 1228, 1058 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ = 1.25 (t, 3H, CH_3 , J = 8 Hz), 4.21 (q, 2H, CH_2 , J = 8 Hz), 6.92 (dd, 1H, C6-H, J = 8.0 Hz), 7.03 (d, 1H, C8-H, J = 8.0 Hz), 7.48-7.53 (m, 1H, C7-H), 8.12 (bs, 1H, NH_2), 11.05 (bs, 1H, NH); MS = 251.2 (M+H).

4-Amino-7-chloroquinolin-2(1H)-one (6f)



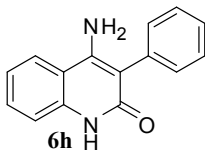
62%; mp 220 °C; IR (neat) ν = 3466, 3145, 2815, 1688, 1630, 1440, 1361, 1273, 1242, 1087, 1002 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ = 5.40 (s, 1H, C3-H), 6.62 (bs, 2H, NH_2), 7.12 (dd, 1H, C6-H, J = 8.7 & 2.1 Hz), 7.22 (d, 1H, C8-H, J = 2.1 Hz), 7.87 (d, 1H, C5-H, J = 8.7 Hz), 10.801 (bs, 1H, NH) MS = 195.6 (M+H), 196.4 (M+2).

4-Amino-3-(7-methyl-coumarin-4-yl)quinolin-2(1H)-one (6g)



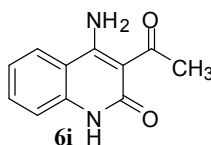
74%; mp above 330 °C; IR (neat) ν = 3378, 3206, 1684, 1651, 1620, 1584, 1504, 1408, 1268, 1203, 1147, 829 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ = 2.40 (s, 3H, CH_3), 6.27 (s, 1H, C3'-H), 6.51 (bs, 2H, NH_2), 7.04 (dd, 1H, C8'-H, J = 8.0 & 0.6 Hz), 7.14 (t, 1H, C6-H, J = 8.0 Hz), 7.16 (d, 1H, C5-H, J = 8.0 Hz), 7.26-7.28 (m, 2H, C5'-H & C6'-H), 7.51 (t, 1H, C7-H, J = 8 Hz), 7.53-7.56 (m, 3H, PhH), 8.02 (d, 1H, C8-H, J = 8.0 Hz), 11.13 (bs, 1H, NH); MS = 319.4 (M+H).

4-Amino-3-phenylquinolin-2(1H)-one (6h)



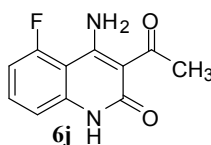
82%; decompose at 300 °C; IR (neat) ν = 3437, 3200, 1629, 1591, 1500, 1395, 1009 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ = 5.86 (bs, 2H, NH_2), 7.10 (t, 1H, C6-H, J = 8.0 Hz), 7.23 (d, 1H, C5-H, J = 8.0 Hz), 7.36 (t, 2H, PhH, J = 8 Hz), 7.45 (t, 1H, C7-H, J = 8. Hz), 7.53-7.56 (m, 3H, PhH), 8.16 (d, 1H, C8-H, J = 8.0 Hz), 8.38 (bs, 2H, NH_2), 10.87 (bs, 1H, NH); MS = 237.3 (M+H).

3-Acetyl-4-aminoquinolin-2(1*H*)-one (6i)



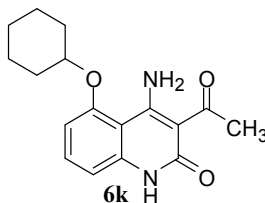
80%; mp 318 °C; IR (neat) ν = 3353, 3164, 2880, 1659, 1604, 1578, 1477, 1426, 1254, 1160, 970 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ = 2.56 (s, 3H, CH_3), 7.13 (td, 1H, C6-H, J = 8.2 & 1.1 Hz), 7.20 (dd, 1H, C5-H, J = 8.3 & 1.0 Hz), 7.53 (td, 1H, C7-H, J = 8.3 & 1.2 Hz), 8.12 (dd, 1H, C8-H, J = 8.2, 0.9 Hz); MS = 203.2 (M+H).

3-Acetyl-4-amino-5-fluoroquinolin-2(1*H*)-one (6j)



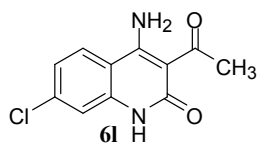
72%; mp 270 °C; IR (neat) ν = 3476, 1656, 1616, 1591, 1475, 1421, 1259, 1062, 896, 802 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ = 2.56 (s, 3H, CH_3), 6.90-6.96 (m, 1H, C6-H), 7.04 (d, 1H, C8-H, J = 8.0 Hz), 7.50-7.56 (m, 1H, C7-H), 7.97 (bs, 1H, NH), 11.08 (bs, 2H, NH_2); MS = 221.4 (M+H).

3-Acetyl-4-amino-5-(cyclohexyloxy)quinolin-2(1*H*)-one (6k)



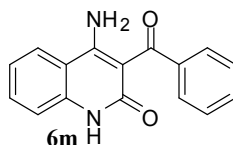
67%; mp 285 °C; IR (neat) ν = 3401, 3166, 2929, 1665, 1597, 1515, 1473, 1359, 1087, 947 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ = 1.27-1.32 (m, 1H), 1.38-1.45, (m, 2H), 1.52-1.62 (m, 3H), 1.67-1.70 (m, 2H), 1.98-2.01 (m, 2H), 2.54 (s, 3H, CH_3), 4.64 (quintet, 1H), 6.78 (t, 2H, C6-H & C8-H, J = 8.0 Hz), 7.41 (t, 1H, C7-H, J = 8.0 Hz), 8.78 (bs, 1H, NH), 10.77 (bs, 1H, NH), 11.23 (bs, 1H, NH); MS = 301.3 (M+H).

3-Acetyl-4-amino-7-chloroquinolin-2(1*H*)-one (6l)



74%; mp 269-270 °C; IR (neat) ν = 3402, 3169, 2847, 1666, 1597, 1576, 1514, 1476, 1358, 1088, 861, 770 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ = 2.54 (s, 3H, CH_3), 7.17-7.22 (m, 2H, C6-H & C8-H), 8.15 (d, 1H, C5-H, J = 8.0 Hz), 10.97 (bs, 1H, NH), MS = 221.4 (M+H).

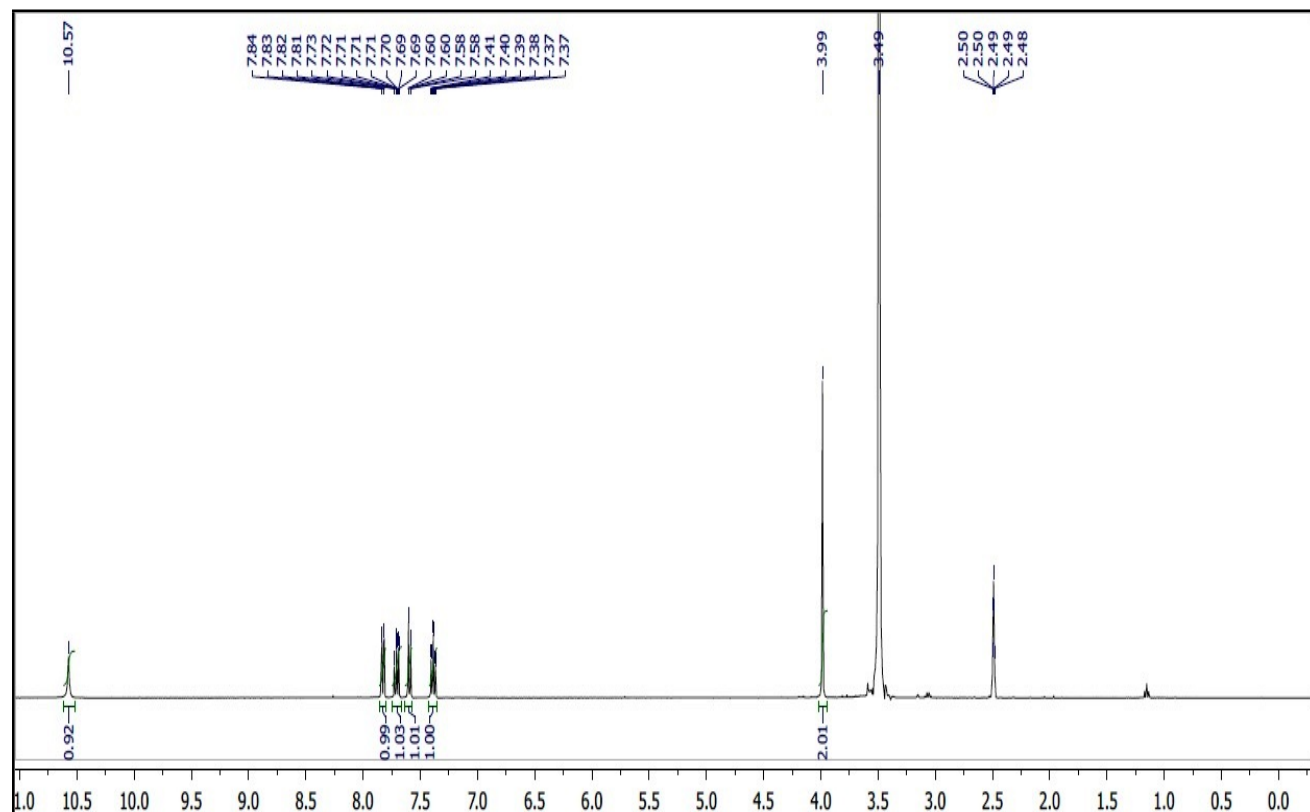
4-Amino-3-benzoylquinolin-2(1*H*)-one (6m)



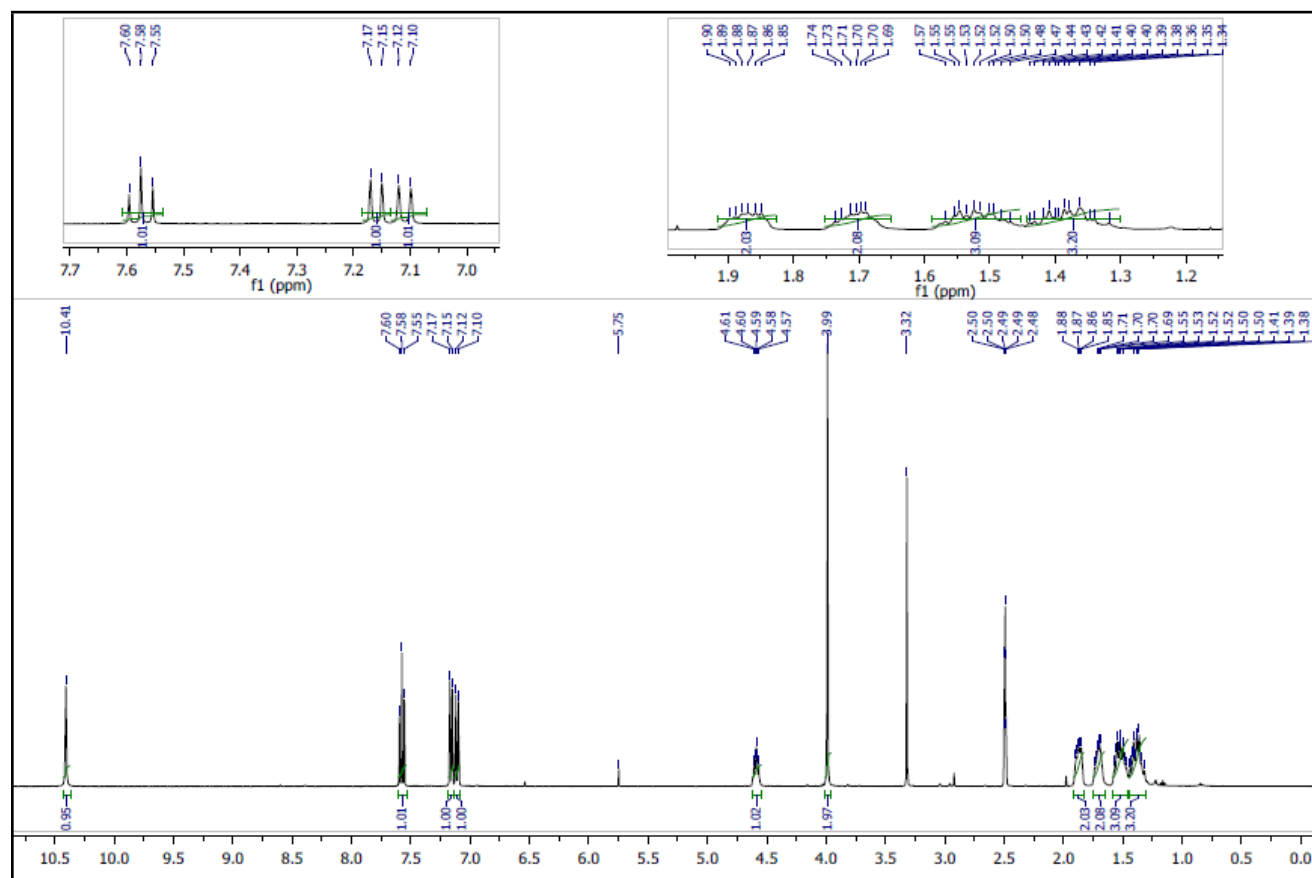
73%; mp 269-270 °C; IR (neat) ν = 3469, 2835, 1656, 1596, 1518, 1471, 1260, 950 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ = 7.16 (t, 1H, C6-H, J = 8.0 Hz), 7.23 (d, 1H, C5-H, J = 8.0 Hz), 7.36 (t, 2H, PhH, J = 8 Hz), 7.45 (t, 1H, C7-H, J = 8. Hz), 7.53-7.56 (m, 3H, PhH), 8.16 (d, 1H, C8-H, J = 8.0 Hz), 8.38 (bs, 2H, NH_2), 10.87 (bs, 1H, NH); MS = 265.3 (M+H).

¹H NMR Spectra

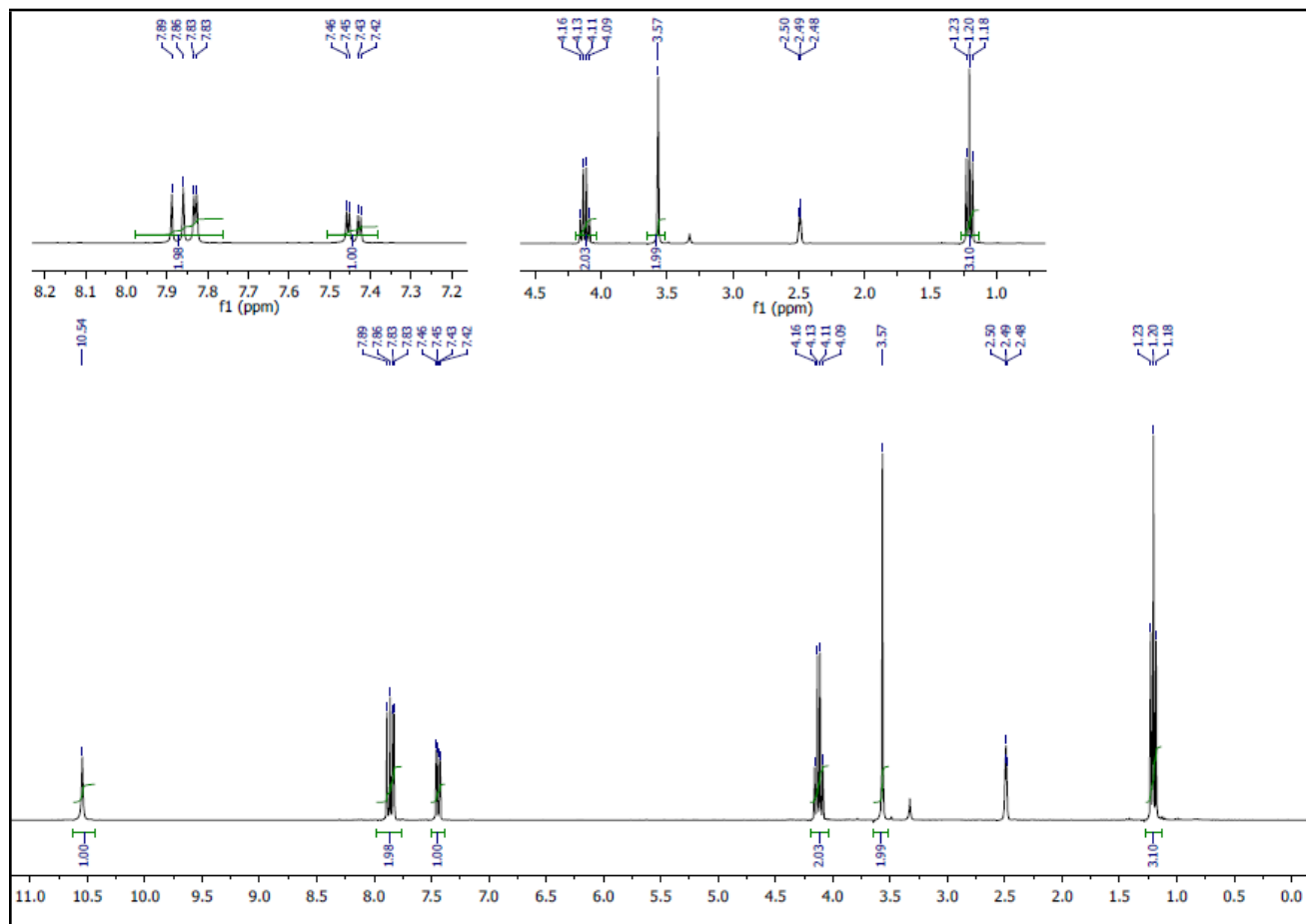
2-cyano-*N*-(2-cyanophenyl)acetamide (3a)



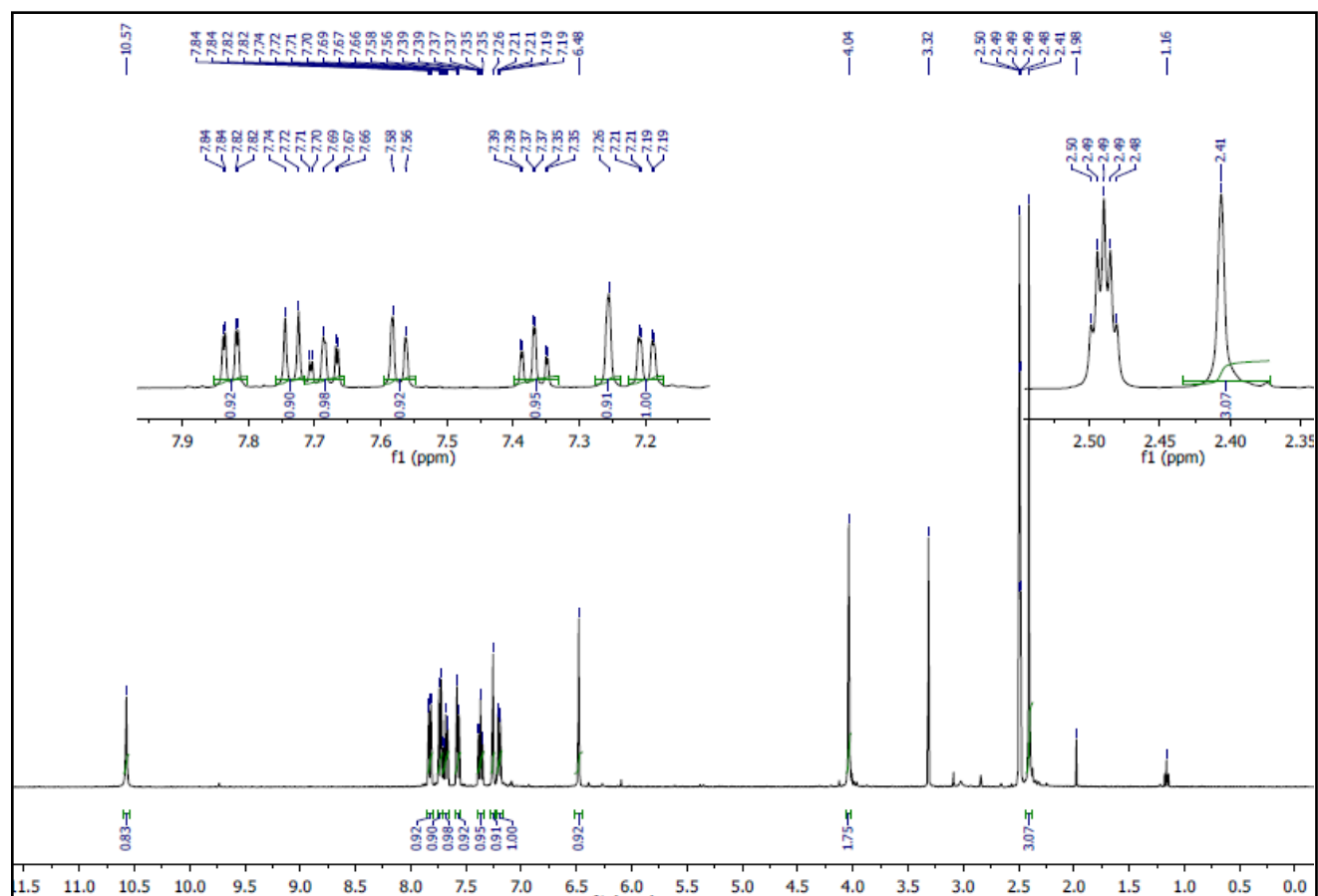
2-cyano-N-(2-cyano-3-(cyclohexyloxy)phenyl)acetamide (3c)



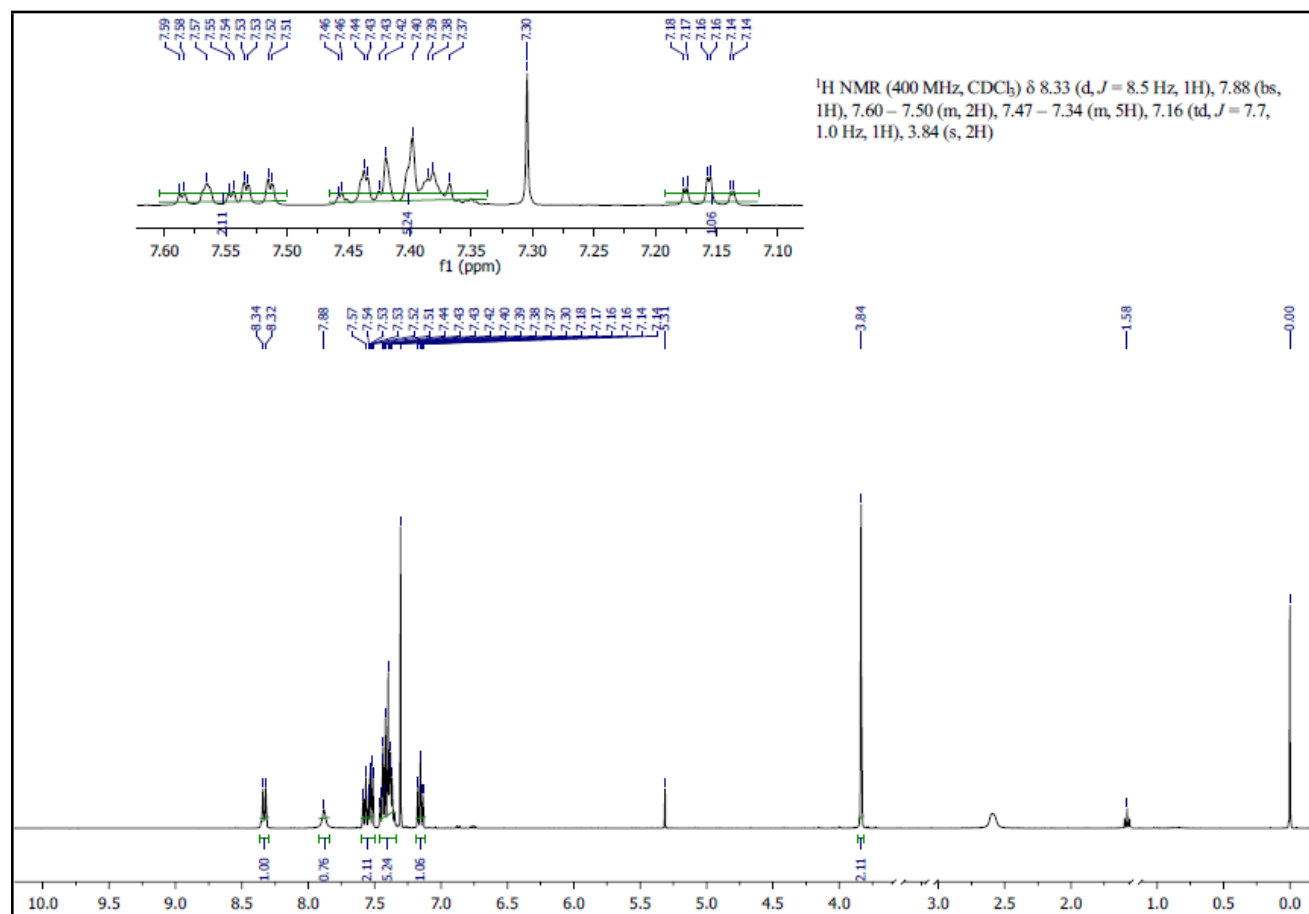
Ethyl 3-(5-chloro-2-cyanophenylamino)-3-oxopropanoate (3f)



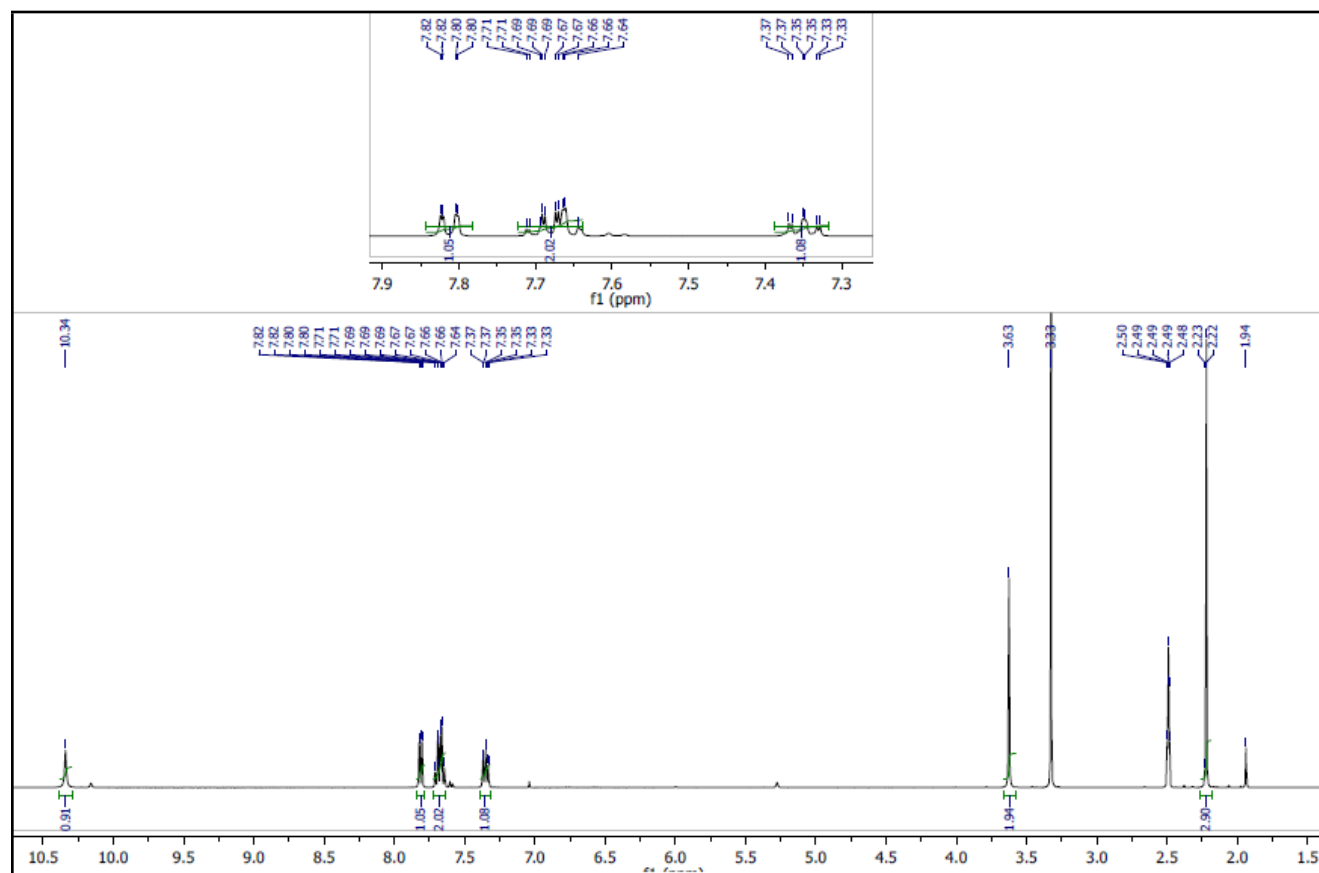
***N*-(2-cyanophenyl)-2-(7-methylcoumarin-4-yl)acetamide (3g)**



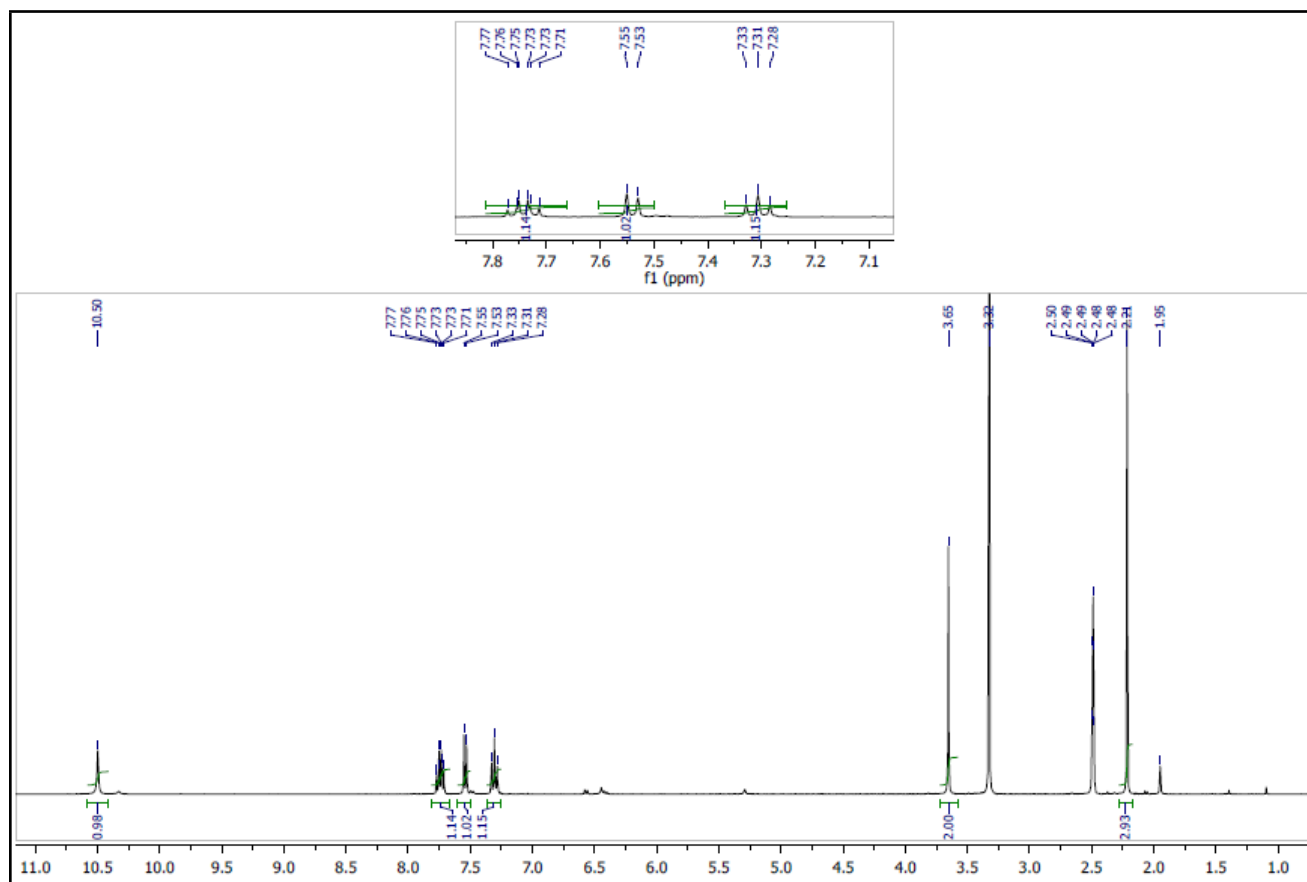
***N*-(2-cyanophenyl)-2-phenylacetamide (3h)**



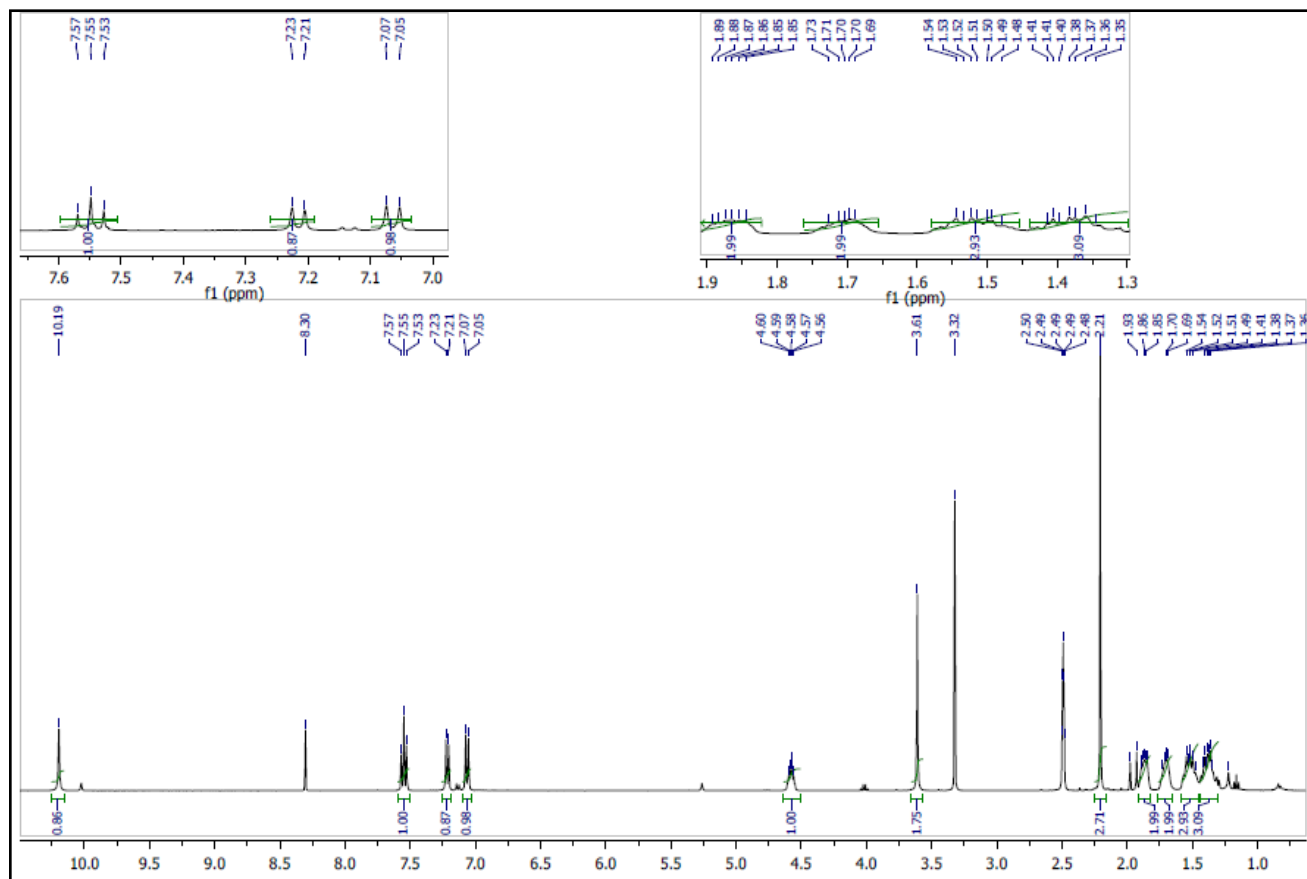
***N*-(2-cyanophenyl)-3-oxobutanamide (5a)**



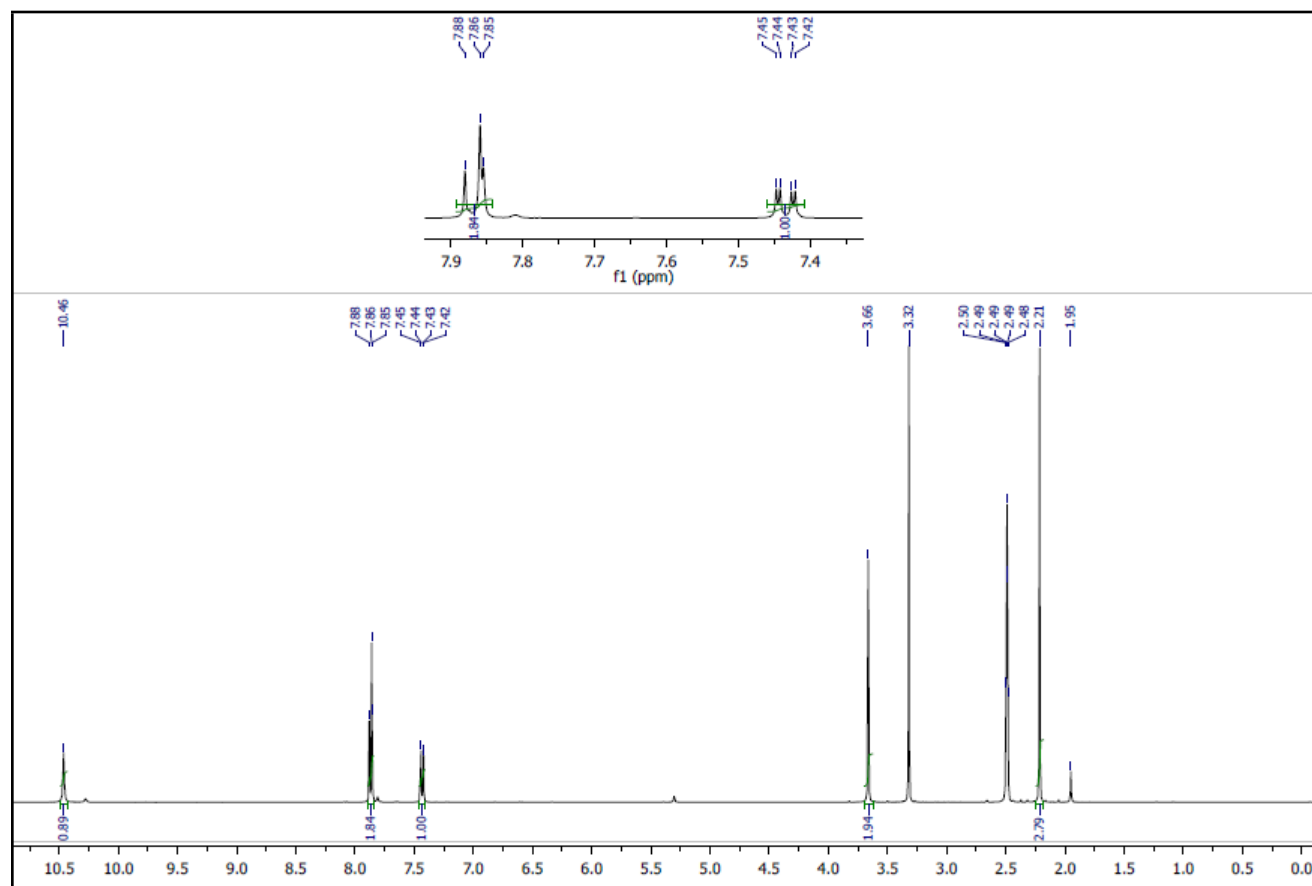
***N*-(2-cyano-3-fluorophenyl)-3-oxobutanamide (5b)**



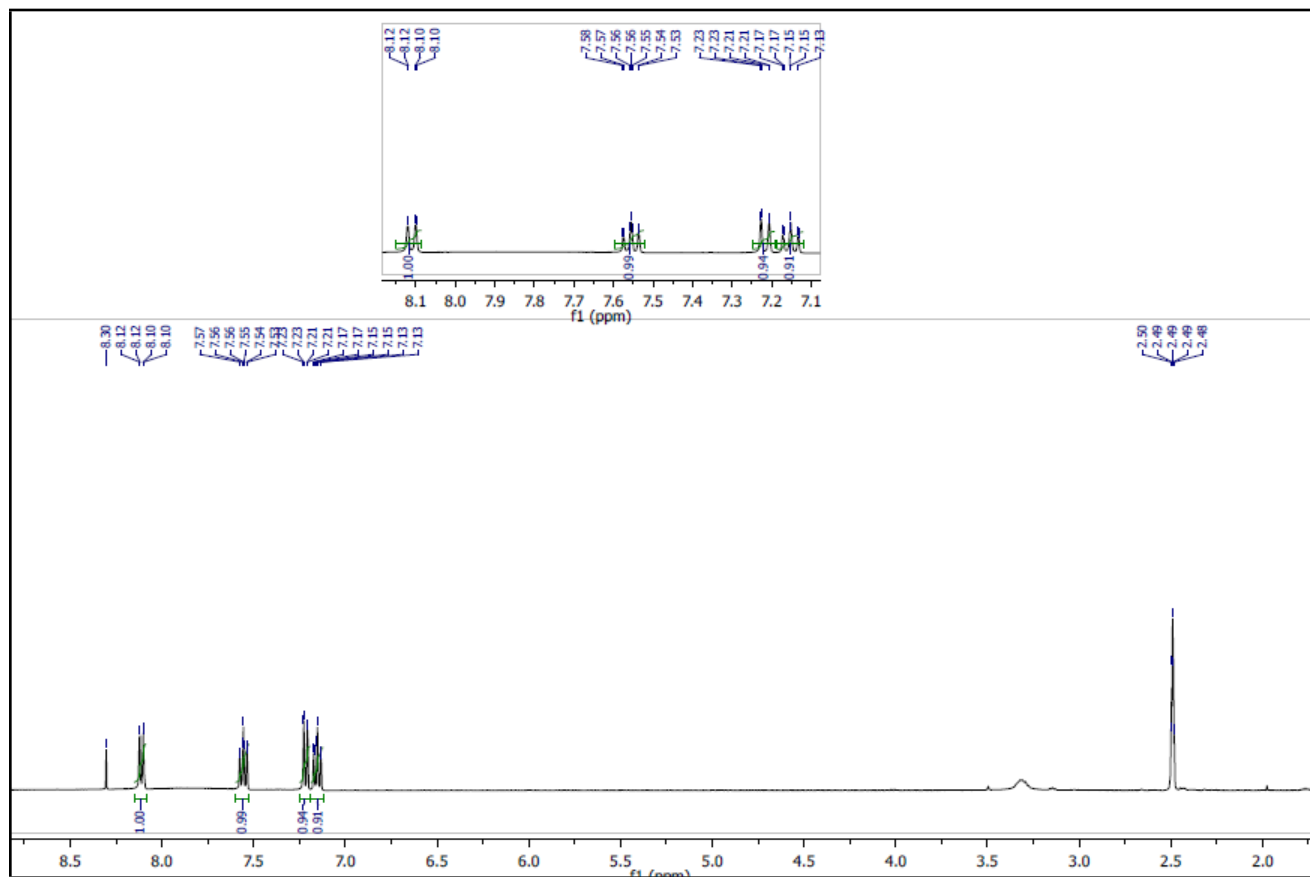
***N*-(2-cyano-3-(cyclohexyloxy)phenyl)-3-oxobutanamide (5c)**



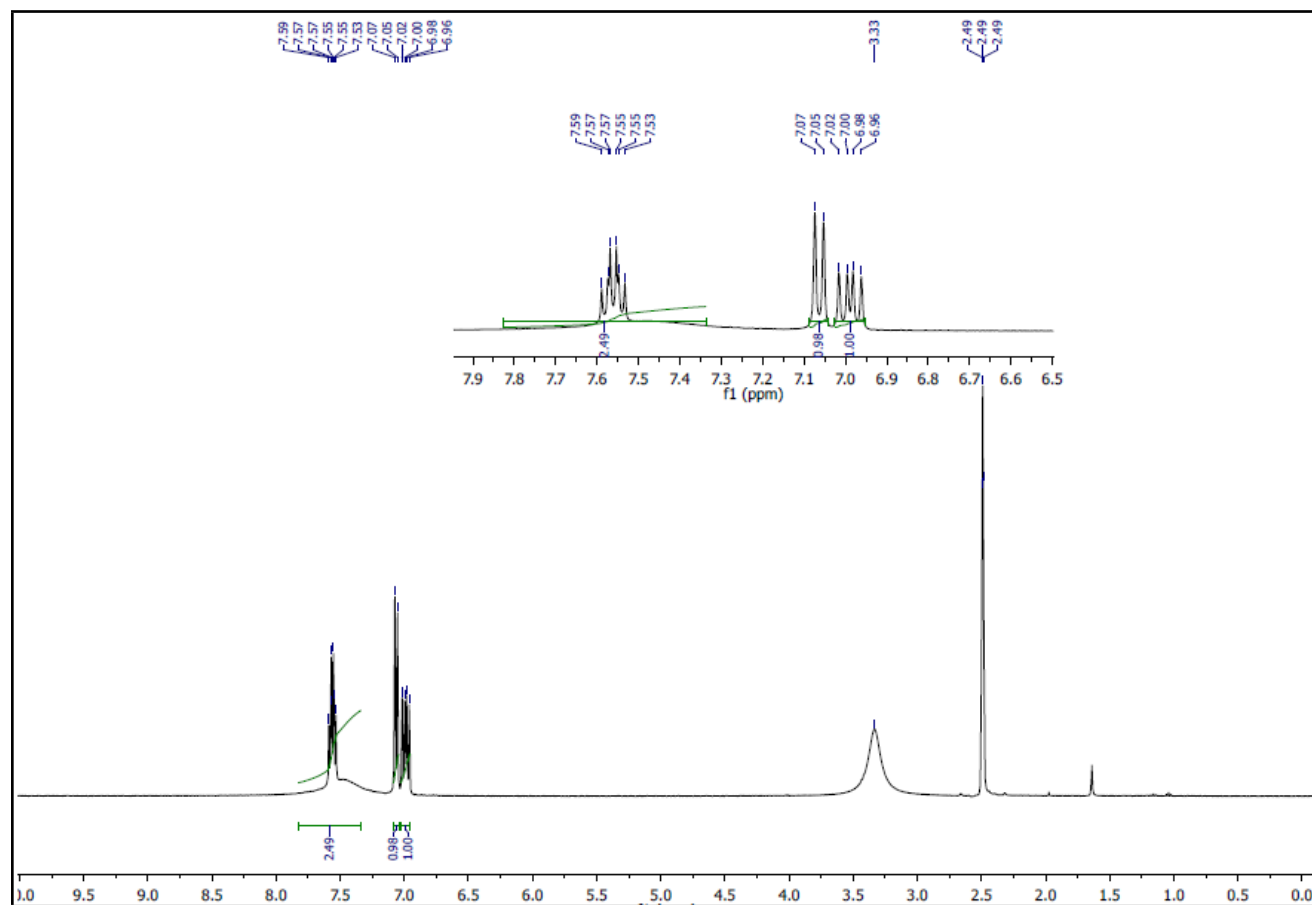
N-(5-chloro-2-cyanophenyl)-3-oxobutanamide (5d)



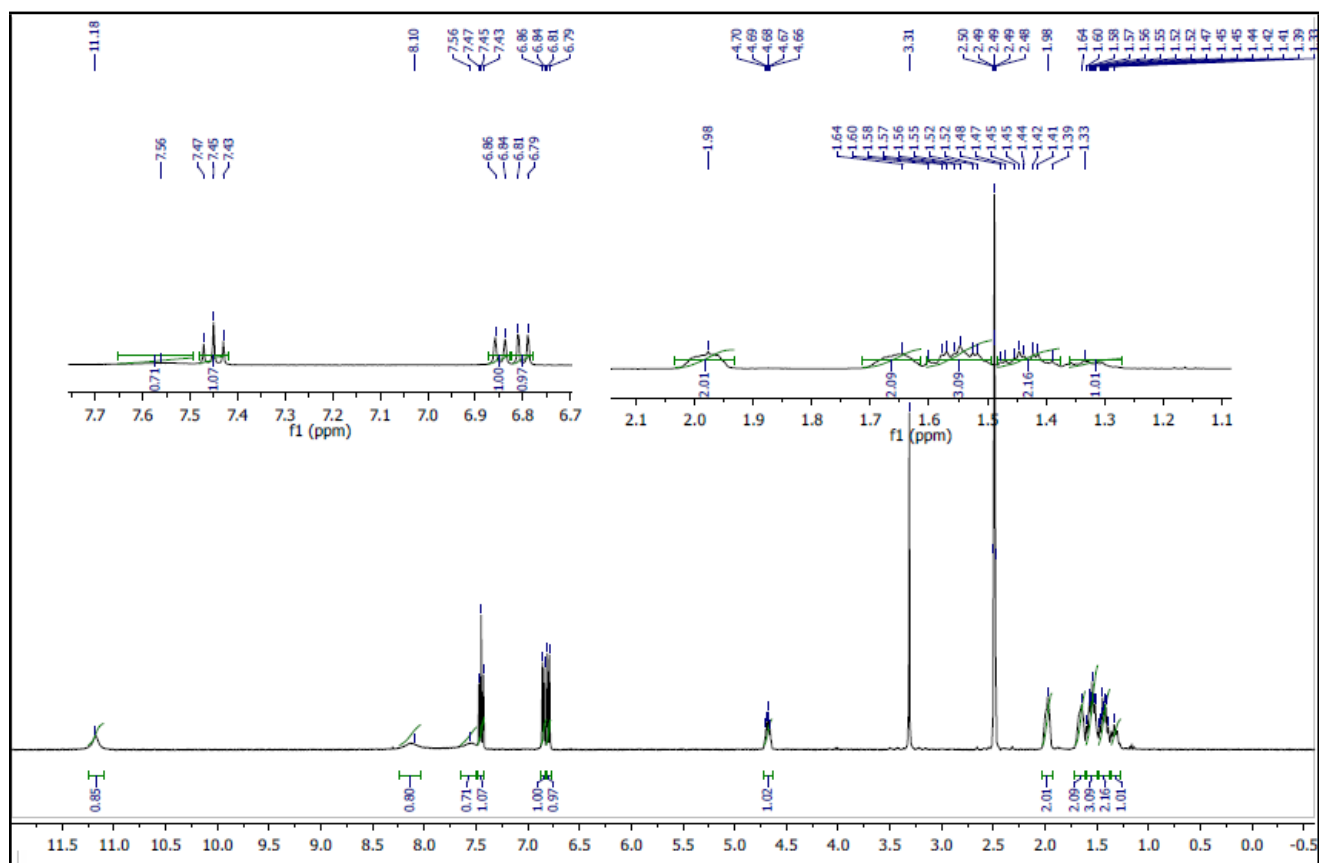
4-Amino-1,2-dihydro-2-oxo-3-quinolinecarbonitrile (6a)



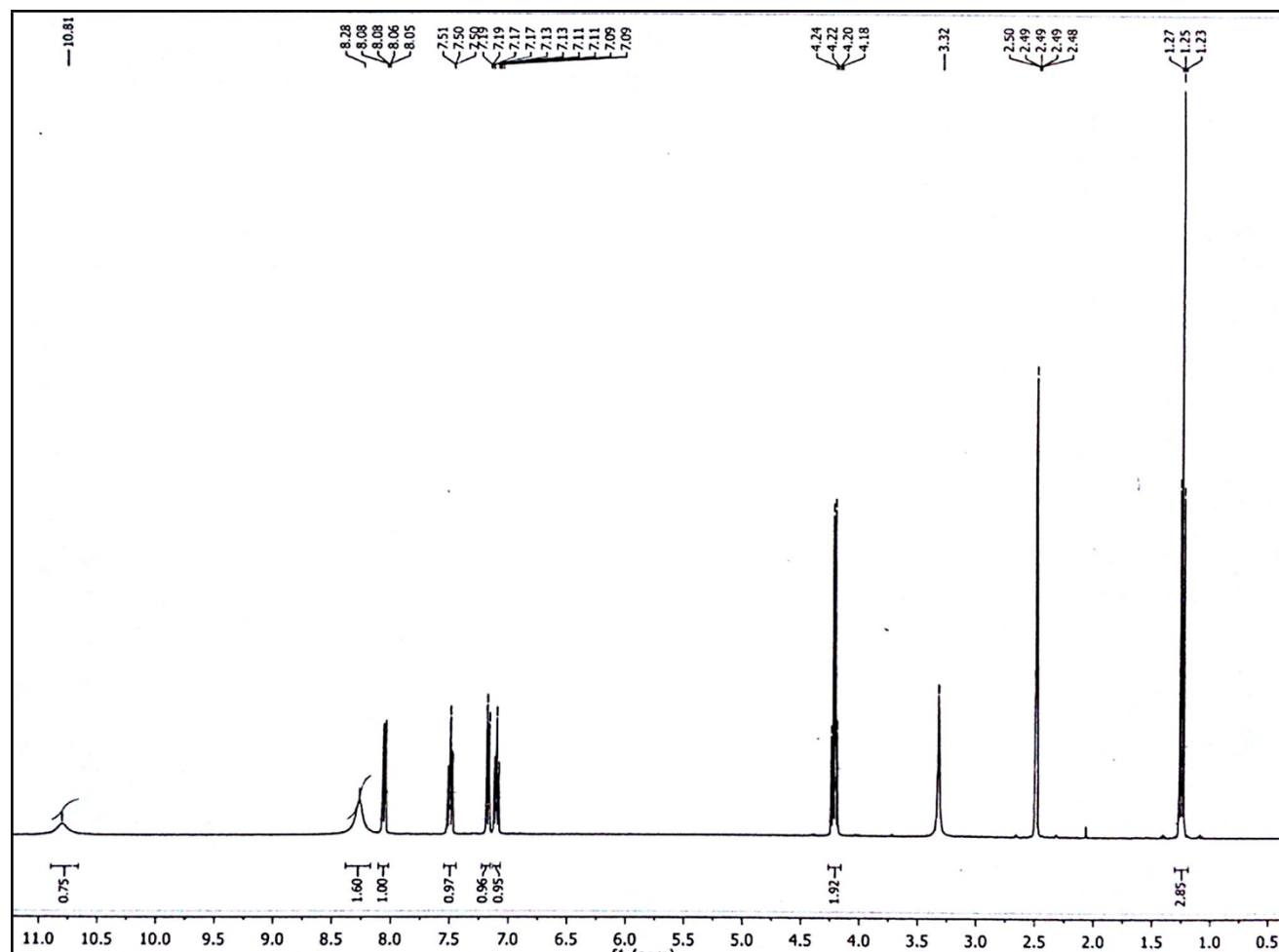
4-Amino-5-fluoro-2-oxo-1,2-dihydroquinoline-3-carbonitrile (6b)



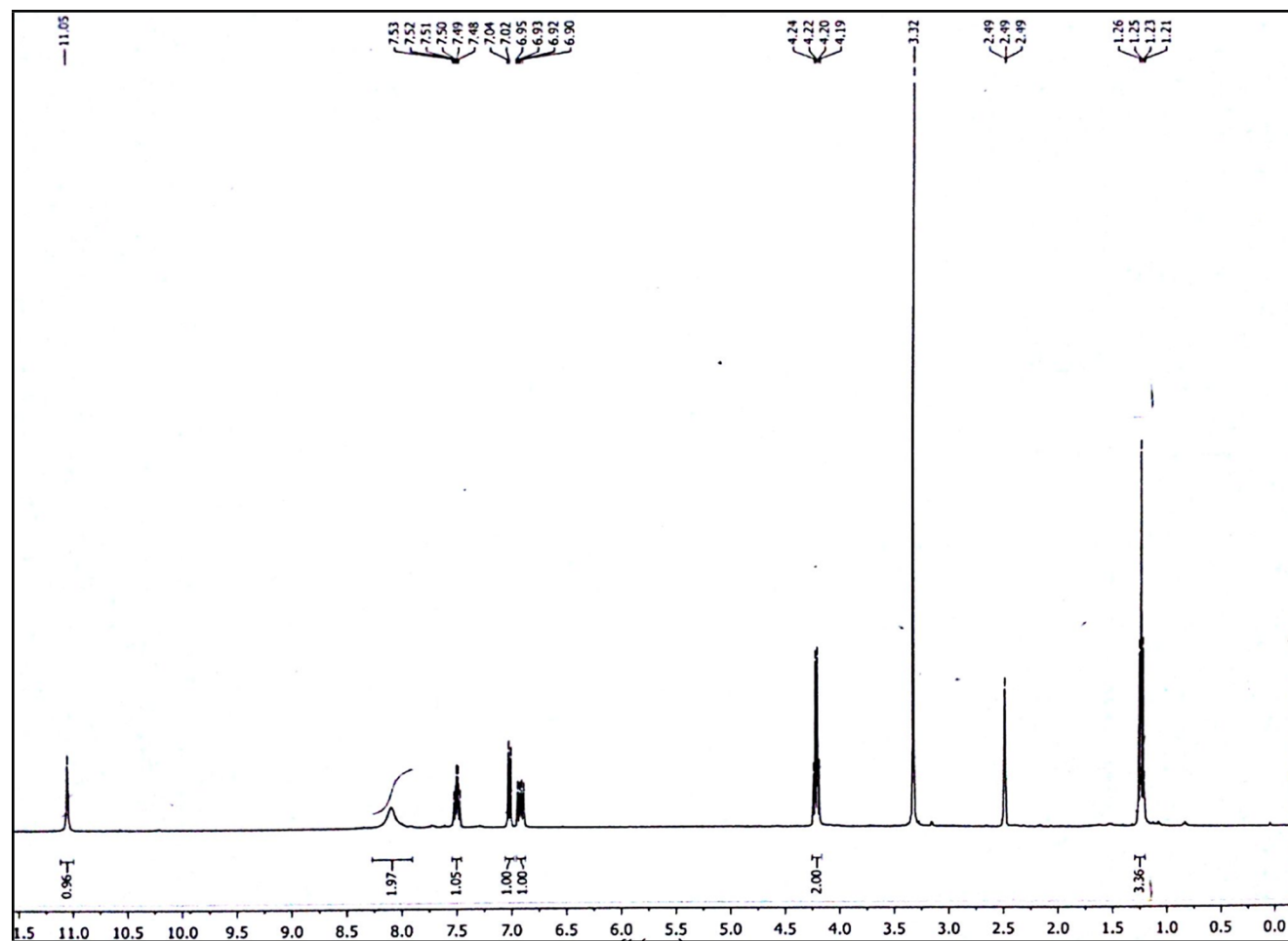
4-amino-5-(cyclohexyloxy)-2-oxo-1,2-dihydroquinoline-3-carbonitrile (6c)



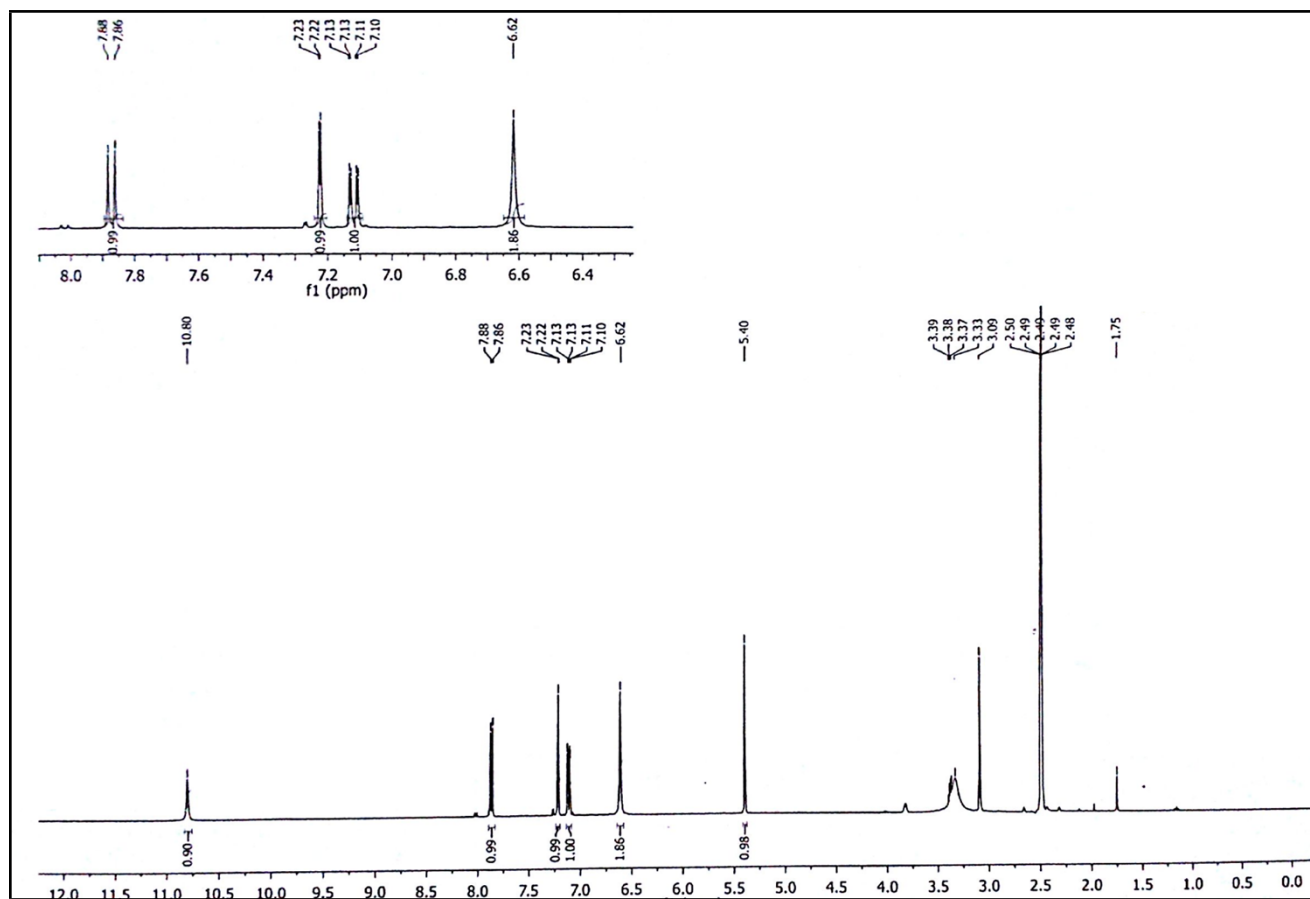
Ethyl-4-amino-2-oxo-1,2-dihydroquinoline-3-carboxylate (6d)



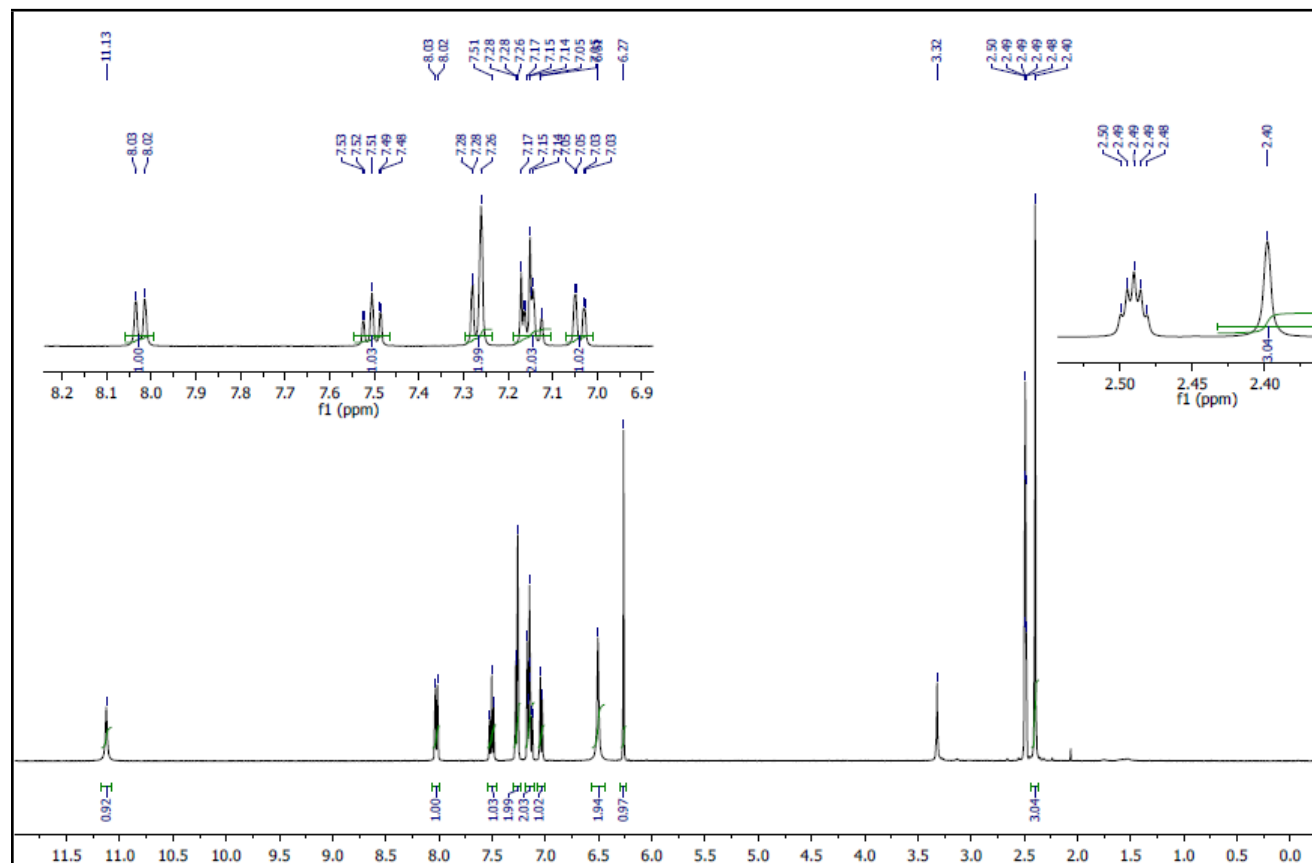
Ethyl-4-amino-5-fluoro-2-oxo-1,2-dihydroquinoline-3-carboxylate (6e)



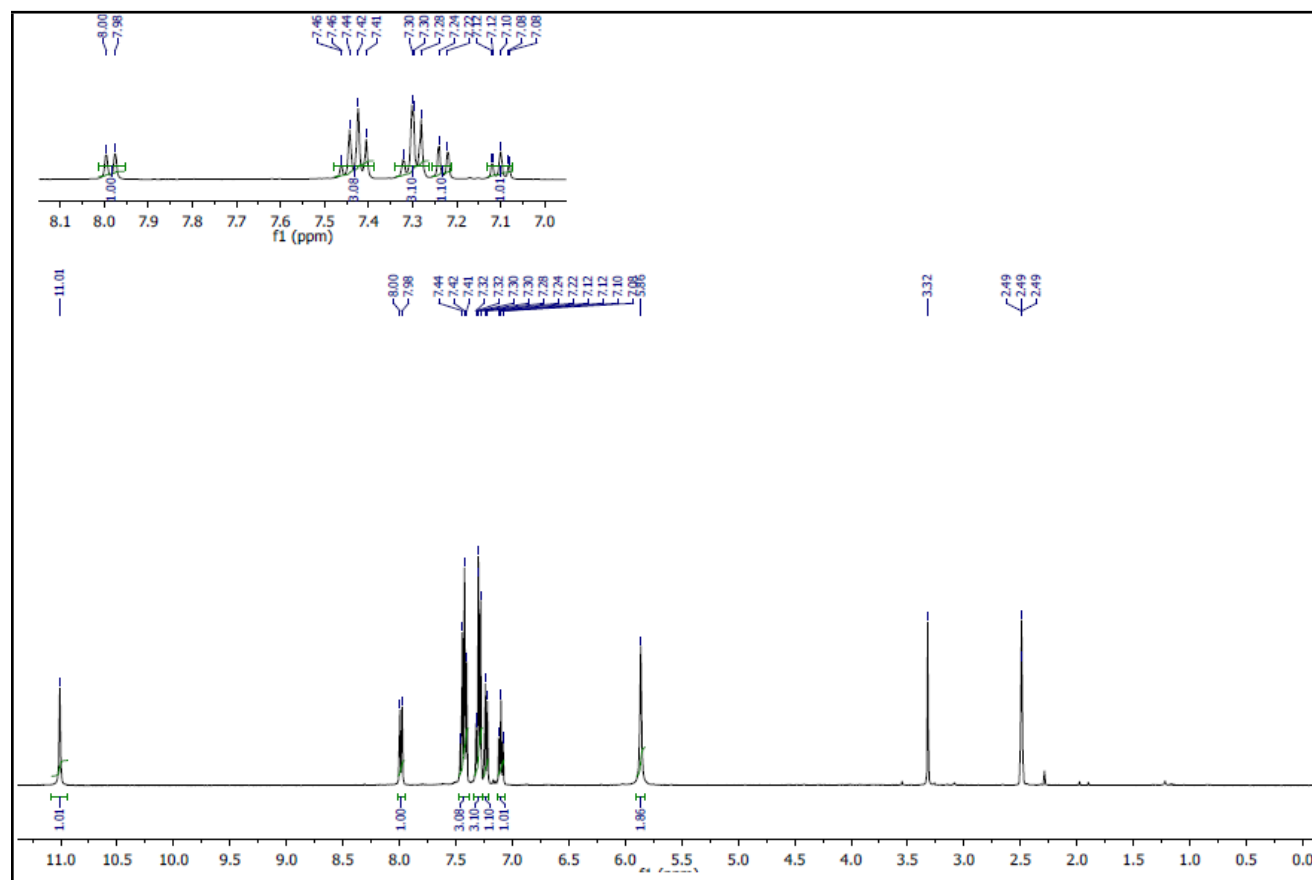
4-Amino-7-chloroquinolin-2(1*H*)-one (6f)



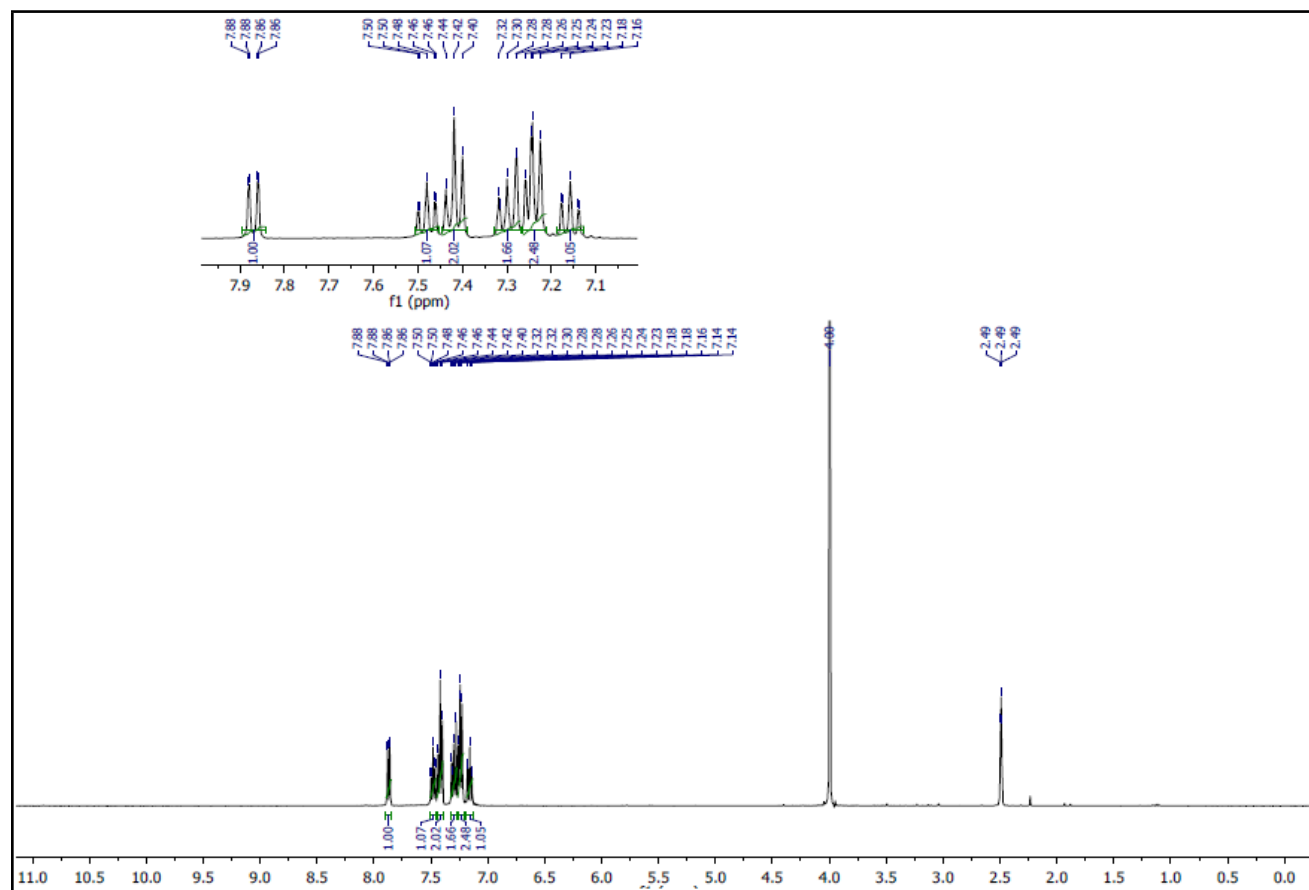
4-Amino-3-(7-methyl-coumarin-4-yl)quinolin-2(1*H*)-one (6g)



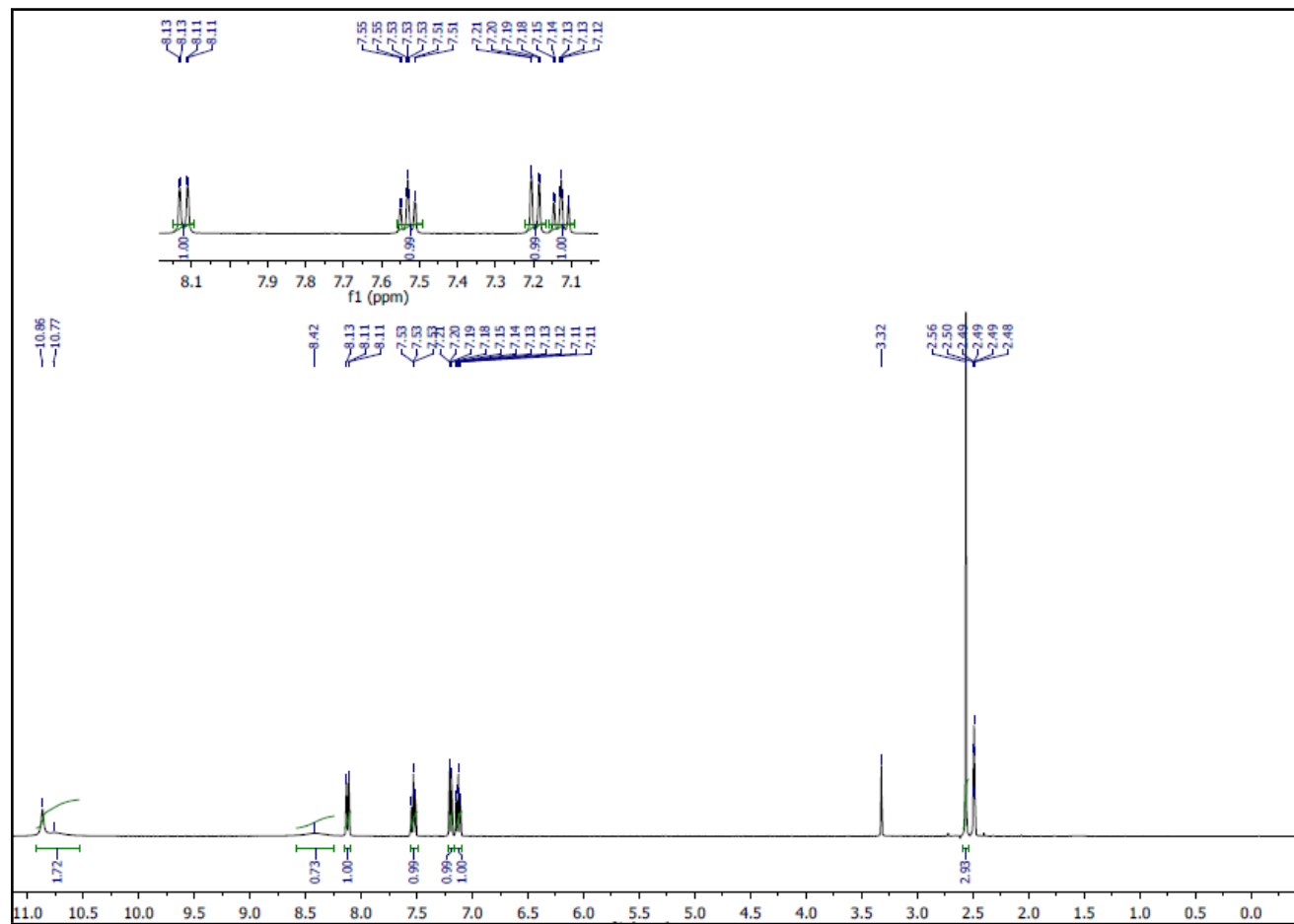
4-Amino-3-phenylquinolin-2(1*H*)-one (6h)



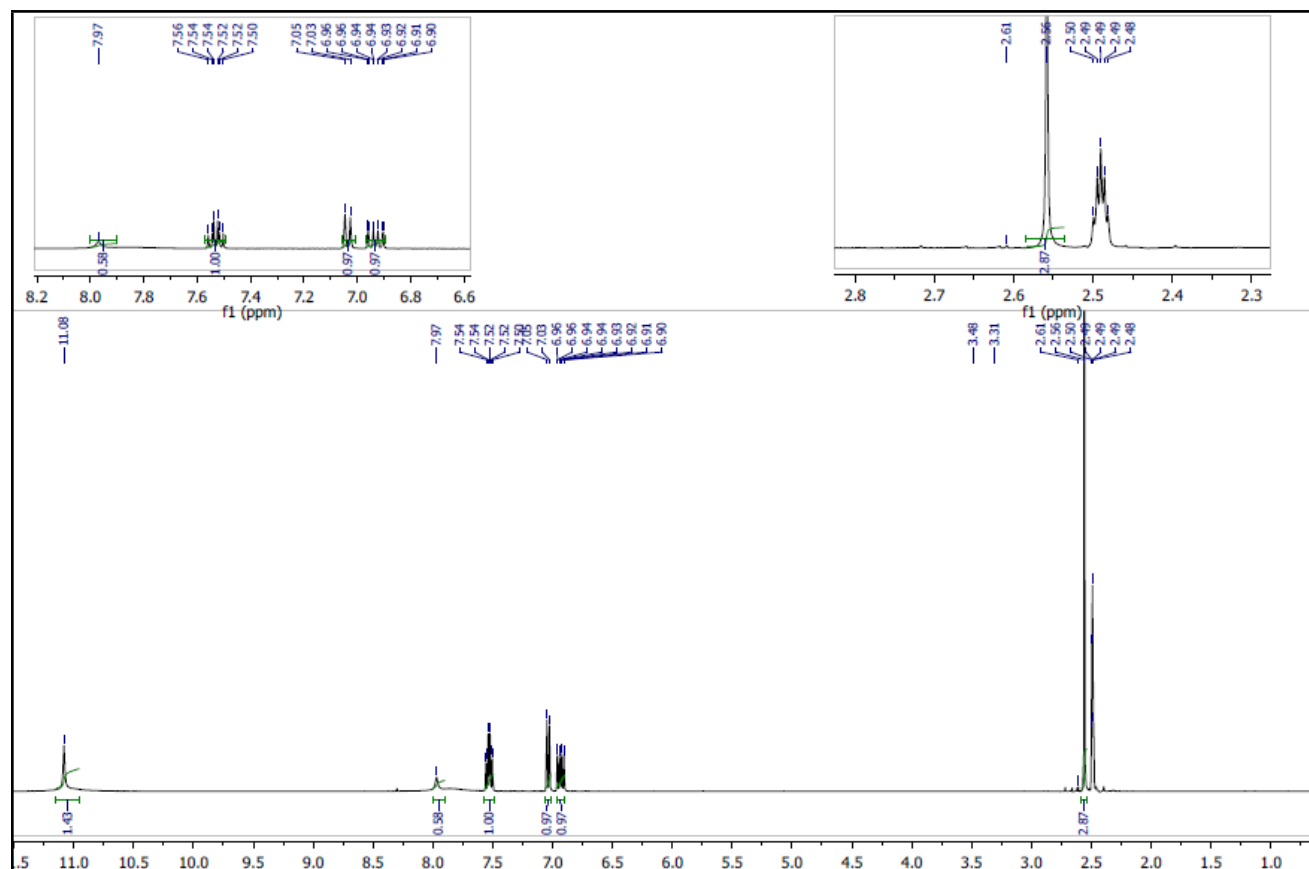
4-Amino-3-phenylquinolin-2(1*H*)-one (D₂O exchange) (6h)



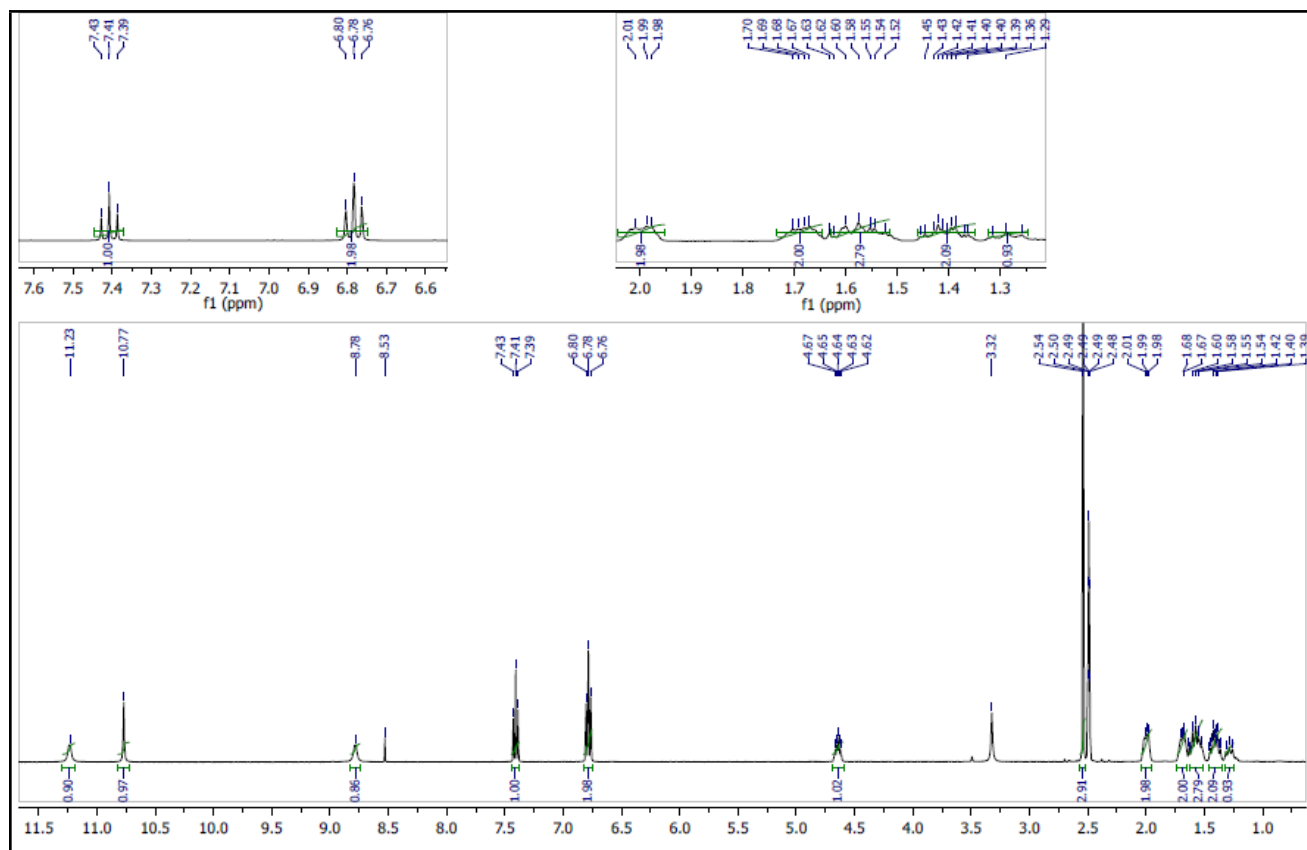
3-Acetyl-4-aminoquinolin-2(1*H*)-one (6i)



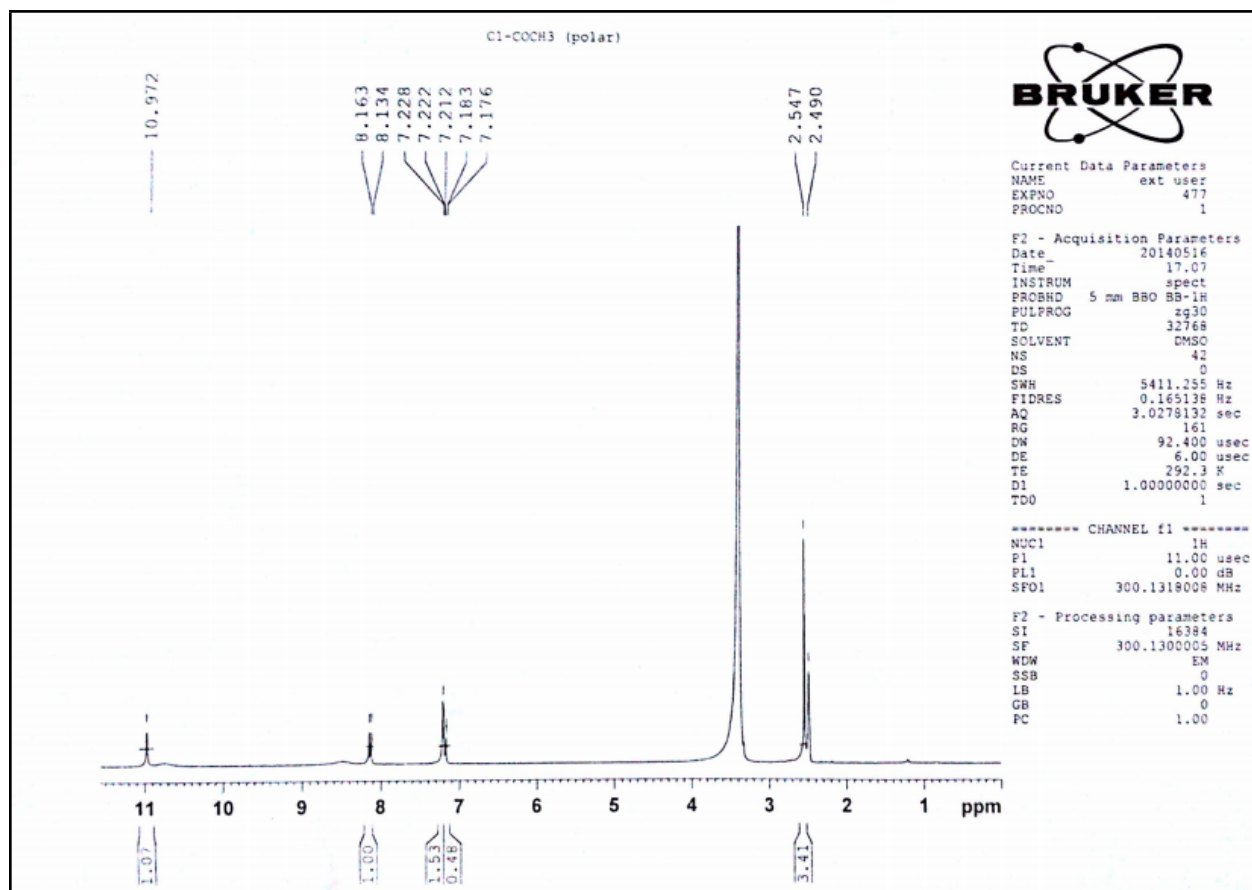
3-Acetyl-4-amino-5-fluoroquinolin-2(1*H*)-one (6j)



3-Acetyl-4-amino-5-(cyclohexyloxy)quinolin-2(1*H*)-one (6k)



3-Acetyl-4-amino-7-chloroquinolin-2(1H)-one (6l)



4-Amino-3-benzoylquinolin-2(1H)-one (6m)

