Electronic Supplementary Information

Condensation of malononitrile with salicylaldehydes and *o*-aminobenzaldehydes revisited: Solvent and catalyst free synthesis of 4*H*-chromenes and quinolines

Subrahmanya Ishwar Bhat,[a] Angshuman Roy Choudhury[b] and Darshak R. Trivedi[*a]

[a]Supramolecular Chemistry Laboratory, Department of Chemistry, National Institute of Technology Karnataka (NITK), Srinivasnagar, Surathkal, Mangalore 575025 Karnataka, India.

Phone No : +91-824-2474000 Ext. No:3205 ; Fax: +91-824-2474033 E-mail: darshak_rtrivedi@yahoo.co.in

[b]Indian Institute of Science Education and Research, Mohali, Sector 81, S. A. S. Nagar, Manauli PO, Punjab, India 140306

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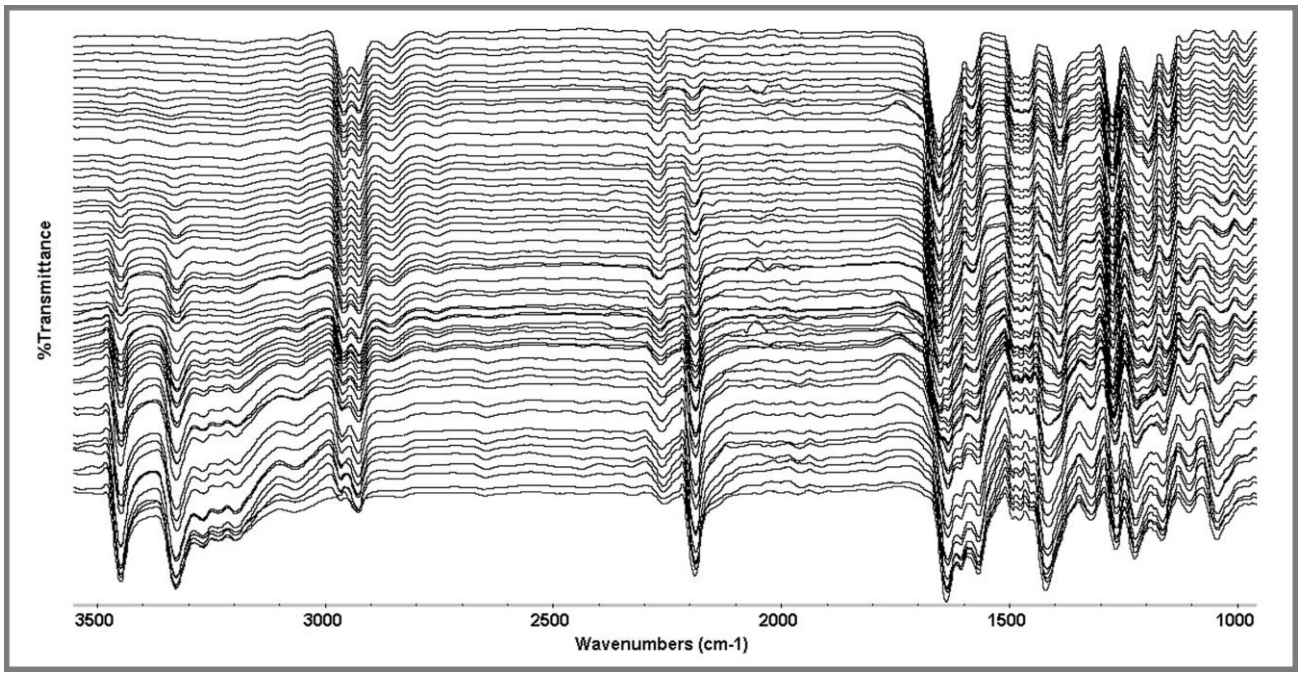
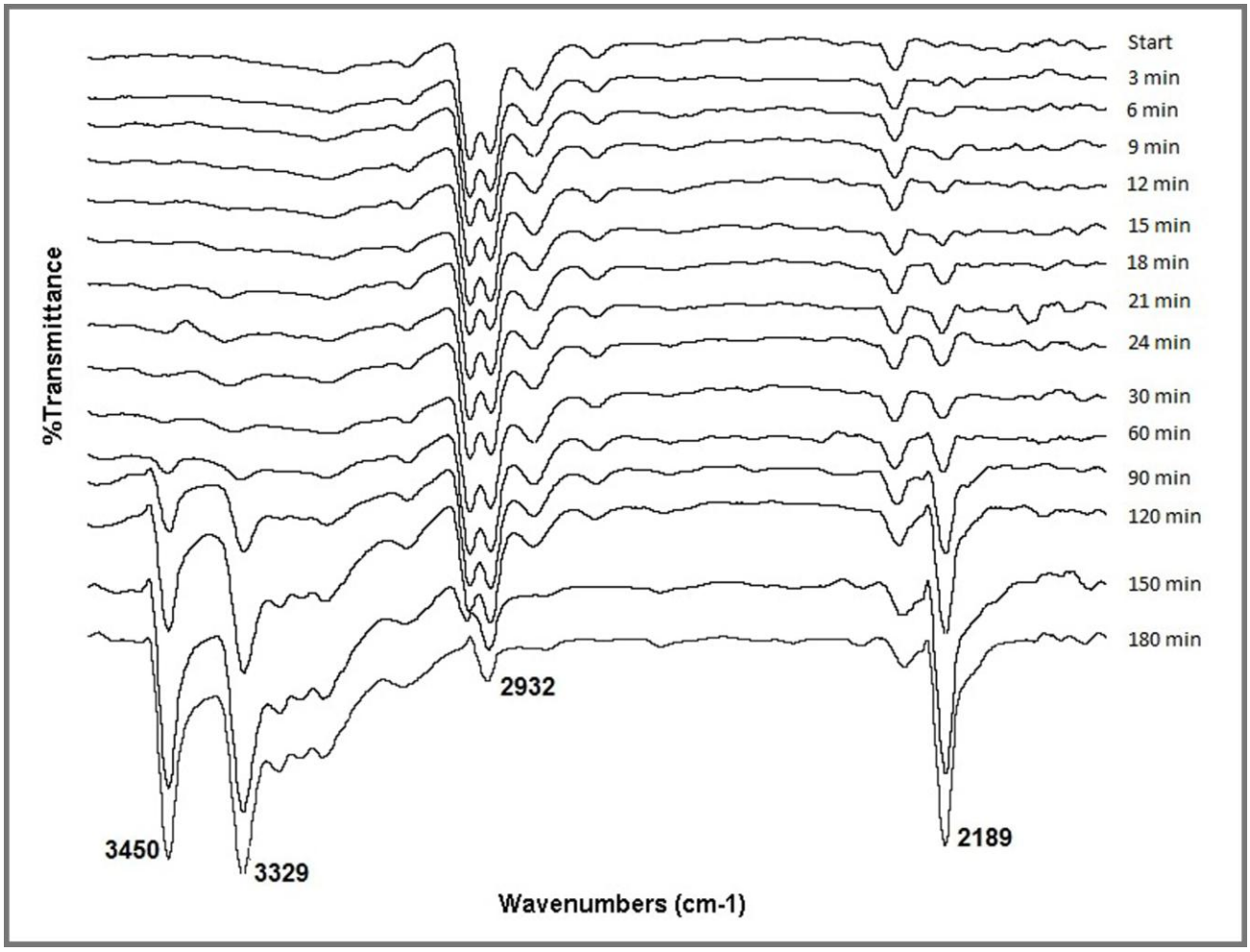
1. Fig. S1: IR spectra of reaction of salicylaldehyde with malononitrile under neat condition at room temperature (Complete)

The spectra were measured every 3 min for 3 h using neat samples

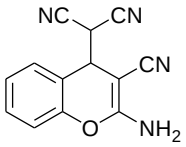


2. Fig. S2: IR spectra of reaction of salicylaldehyde with malononitrile (Expansion range: 2100-3500 range)



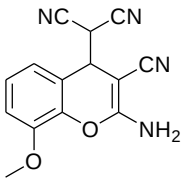
3. Characterization data

3a: **(2-amino-3-cyano-4*H*-chromen-4-yl)malononitrile**[1,2,3,4]



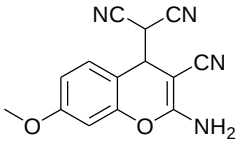
White solid; mp: 151~153 ˚C (lit. 150-153˚C)[5] ; IR (Neat, cm^{-1}): 3448, 3326, 2929, 2239, 2188, 1635, 1604, 1567, 1417, 1265, 1223, 1043; ^{1}HNMR(500MHz, DMSO-d_6) δ: 4.59(d, 1H, J = 4Hz), 5.07(d, 1H, J = 4Hz), 7.14(dd, 1H, J_1 = 8.5Hz, J_2 = 0.9Hz), 7.27(dt, 1H, J_1 = 7.5Hz, J_2 = 0.9Hz), 7.43-7.45(m, 1H), 7.47-7.49(m, 1H), 7.53(s, 2H); ESI MS (m/z) = 235.2 $(M-H)^-$.

3b: (2-amino-3-cyano-8-methoxy-4*H*-chromen-4-yl)malononitrile[1,2,3,4]



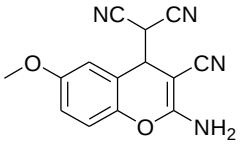
White solid; mp: 160~162 ˚C; IR (Neat, cm^{-1}): 3459, 3352, 2915, 2242, 2190, 1641, 1581, 1483, 1415, 1320, 1275, 1216, 1083; ^{1}HNMR(500MHz, DMSO-d_6) δ: 3.84(s, 3H), 4.57(d, 1H, J = 3Hz), 5.05(d, 1H, 3Hz), 7.00(d, 1H, J = 7.5Hz), 7.12(d, 1H, J = 8Hz), 7.19-7.22(m, 1H), 7.54(s, 2H).

3c: (2-amino-3-cyano-7-methoxy-4*H*-chromen-4-yl)malononitrile



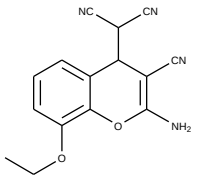
White solid; mp: 149~151 ˚C; IR (Neat, cm^{-1}): 3409, 3332, 2956, 2242, 2186, 1645, 1613, 1419, 1293, 1120, 1024; ^{1}HNMR(500MHz, DMSO-d_6) δ: 3.79(s, 3H), 4.50(d, 1H, J = 4Hz), 5.01(d, 1H, J = 4Hz), 6.65(d, 1H, J = 2.5Hz), 6.87(dd, 1H, J_1 = 8.5Hz, J_2 = 3Hz), 7.38(d, 1H, J = 8.5Hz), 7.49(s, 2H); ^{13}C NMR (125.75 MHz, DMSO-d_6) δ: 34.4, 38.7, 57.4, 103.2, 111.6, 113.5, 114.9, 115.1, 121.3, 131.5, 152.5, 162.2, 165.2; ESI MS (m/z) = 267.2$(M+H)^+$; Anal. Calcd for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04, Found: C, 63.26; H, 3.88; N, 21.22.

3d: (2-amino-3-cyano-6-methoxy-4*H*-chromen-4-yl)malononitrile[4]



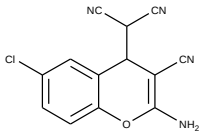
White solid; mp: 144~146 ˚C; IR (Neat, cm^{-1}): 3395, 3335, 2260, 2182, 1654, 1582, 1499, 1425, 1211, 1033; ^{1}HNMR(500MHz, DMSO-d_6) δ: 3.76(s, 3H), 4.54(d, 1H, J = 4Hz), 5.10(d, 1H, J = 3.5Hz), 6.98(dd, 1H, J_1 = 3Hz, J_2 = 9Hz), 7.06-7.08(m, 2H), 7.45(s, 2H).

3e: (2-amino-3-cyano-8-ethoxy-4*H*-chromen-4-yl)malononitrile



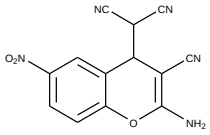
White solid; mp: 141~143 ˚C; IR (Neat, cm^{-1}): 3469, 3348, 2989, 2945, 2895, 2254, 2190, 1640, 1576, 1480, 1406, 1320, 1275, 1199, 1078; ^{1}HNMR(500MHz, DMSO-d_6) δ: 1.36(t, 3H, J = 7Hz), 4.09-4.16(m, 2H), 4.56(d, 1H, J = 4Hz), 5.04(d, 1H, 4Hz), 7.00(dd, 1H, J_1 = 8Hz, J_2 = 1Hz), 7.10-7.12(m, 1H), 7.18(t, 1H, J = 8Hz), 7.5(s, 2H); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 15.0, 32.8, 37.8, 49.4, 64.9, 113.4, 113.6, 114.5, 119.4, 119.8, 120.2, 125.4, 139.9, 146.8, 163.8; ESI MS (m/z) = 281.2 $(M+H)^+$; Anal. Calcd for $C_{15}H_{12}N_4O_2$: C, 64.28; H, 4.32; N, 19.99, Found: C, 64.37; H, 4.37; N, 20.06.

3f: (2-amino-6-chloro-3-cyano-4*H*-chromen-4-yl)malononitrile[4]



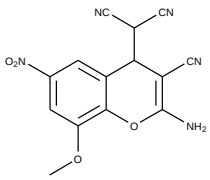
White solid; mp: 152~154 ˚C (lit. 151-154˚C)[4] ; IR (Neat, cm^{-1}): 3438, 3327, 2882, 2239, 2189, 1636, 1601, 1567, 1420, 1262, 1227, 1035; ^{1}HNMR(500MHz, DMSO-d_6) δ: 4.62(d, 1H, J = 3.5Hz), 5.15(d, 1H, J = 3.5Hz), 7.18(d, 1H, J = 8.5Hz), 7.48(dd, 1H, J_1 = 8.5Hz, J_2 = 2.5Hz), 7.58(d, 1H, 2.5Hz), 7.61(s, 2H).

3g: (2-amino-3-cyano-6-nitro-4*H*-chromen-4-yl)malononitrile[3,4]



White solid; mp: 179~181 ˚C (lit. 180-181˚C)[4] ; IR (Neat, cm^{-1}): 3403, 3316, 2901, 2256, 2195, 1654, 1596, 1521, 1428, 1344, 1251, 1089, 1036; ^{1}HNMR(500MHz, DMSO-d_6) δ: 4.81(d, 1H, J = 4Hz), 5.23(d, 1H, J = 4Hz), 7.40(d, 1H, J = 9Hz), 7.81(s, 2H), 8.30(dd, 1H, J_1 = 9Hz, J_2 = 2.5Hz), 8.53(d, 1H, J = 2.5Hz).

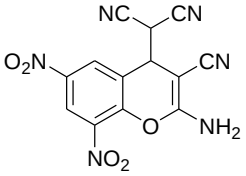
3h: (2-amino-3-cyano-8-methoxy-6-nitro-4*H*-chromen-4-yl)malononitrile



White solid; mp: 189~191 ˚C; IR (Neat, cm^{-1}): 3442, 3339, 2871, 2254, 2191, 1638, 1577, 1521, 1429, 1347, 1230, 1098; ^{1}HNMR(500MHz, DMSO-d_6) δ: 4.00(s, 3H), 4.77(d, 1H, J = 3.5Hz), 5.21(d, 1H, J = 3.5Hz), 7.82(s, 2H), 7.91(d, 1H, J = 2.5Hz), 8.10(d, 1H, J = 3Hz); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 32.8, 37.4, 49.1, 57.2, 108.1, 113.1, 113.2, 116.5, 119.2, 119.8, 144.1, 144.4,

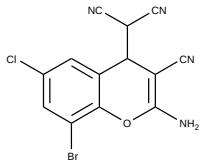
148.2, 163.1; ESI MS (m/z) = 312.2(M+H)$^+$; Anal. Calcd for $C_{14}H_9N_5O_4$: C, 54.02; H, 2.91; N, 22.50, Found: C, 53.96; H, 2.97; N, 22.63.

3i: (2-amino-3-cyano-6,8-dinitro-4*H*-chromen-4-yl)malononitrile



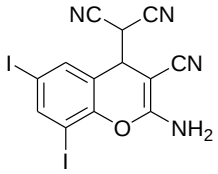
Light brown solid; mp: 188~190 ˚C; IR (Neat, cm^{-1}): 3406, 3321, 2900, 2257, 2199, 1645, 1528, 1419, 1339, 1260, 1216, 1092; ^{1}HNMR(500MHz, DMSO-d_6) δ: 4.92(d, 1H, *J* = 4Hz), 5.29(d, 1H, *J* = 4Hz), 8.02(s, 2H), 8.78(d, 1H, *J* = 3Hz), 8.89(d, 1H, *J* = 3Hz); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ:32.6, 37.2, 49.3, 112.8, 113.0, 118.6, 121.9, 122.5, 129.2, 138.4, 142.9, 146.9, 162.3; ESI MS (m/z) = 327(M+H)$^+$; Anal. Calcd for $C_{13}H_6N_6O_5$: C, 47.86; H, 1.85; N, 25.76, Found: C, 48.04; H, 1.89; N, 25.89.

3j: (2-amino-8-bromo-6-chloro-3-cyano-4*H*-chromene-4-yl)malononitrile



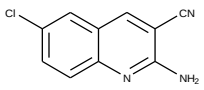
White solid; mp: 173~175 ˚C; IR (Neat, cm^{-1}): 3435, 3334, 2891, 2256, 2189, 1649, 1596, 1563, 1415, 1306, 1245, 1169, 1025; ^{1}HNMR(500MHz, DMSO-d_6) δ: 4.67(d, 1H, *J* = 4Hz), 5.17(d, 1H, *J* = 4.5Hz), 7.60(d, 1H, *J* = 2Hz), 7.75(s, 2H), 7.90(d, 1H, *J* = 2.5Hz); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 32.7, 37.7, 49.3, 111.1, 113.1, 113.2, 119.2, 121.8, 128.6, 129.4, 133.3, 146.3, 163.4; ESI MS (m/z) = 350.1 (M+H)$^+$; Anal. Calcd for $C_{13}H_6BrClN_4O$: C, 44.67; H, 1.73; N, 16.03, Found: C, 44.72; H, 1.79; N, 16.19.

3k: (2-amino-3-cyano-6,8-diiodo-4*H*-chromen-4-yl)malononitrile



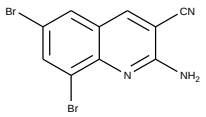
White solid; mp: 197~199 ˚C; IR (Neat, cm^{-1}): 3410, 3322, 2888, 2255, 2195, 1648, 1594, 1547, 1423, 1245, 1160, 1022; ^{1}HNMR(500MHz, DMSO-d_6) δ: 4.59(d, 1H, *J* = 4Hz), 5.13(d, 1H, *J* = 4Hz), 7.69(s, 2H), 7.82(s, 1H), 8.2(s, 1H); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 32.8, 37.4, 49.5, 87.3, 90.2, 113.1, 113.3, 119.2, 121.5, 137.8, 146.9, 149.9; ESI MS (m/z) = 489(M+H)$^+$; Anal. Calcd for $C_{13}H_6I_2N_4O$: C, 31.99; H, 1.24; N, 11.48, Found: C, 32.08; H, 1.32; N, 11.57.

4a: 2-amino-6-chloro-3-quinolinecarbonitrile



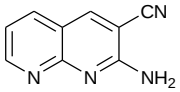
Pale yellow solid; mp: 311~313 ˚C; IR (Neat, cm^{-1}): 3432, 3364, 2221, 1653, 1605, 1550, 1476, 1254, 1195; ^{1}HNMR(500MHz, DMSO-d_6) δ: 6.71(s, 2H), 6.79(d, 1H, J = 9Hz), 7.32(dd, 1H, J_1 = 9Hz, J_2 = 2Hz), 7.77(d, 1H, J = 2.5Hz), 8.31(s, 1H,); ^{13}C NMR (125.75 MHz, DMSO-d_6) δ: 97.5, 118.1, 123.4, 128.4, 128.8, 129.4, 134.8, 146.5, 149.6, 157.9; ESI MS (m/z) = 204.1$(M+H)^+$; Anal. Calcd for $C_{10}H_6ClN_3$: C, 58.98; H, 2.97; N, 20.64, Found: C, 59.12; H, 3.08; N, 20.77.

4b: 2-amino-6,8-dibromo-3-quinolinecarbonitrile



Pale yellow solid; mp: 314~316 ˚C; IR (Neat, cm^{-1}): 3476, 3308, 2219, 1645, 1541, 1458, 1185; ^{1}HNMR(500MHz, DMSO-d_6) δ: 7.42(s, 2H), 8.03(d, 1H, J = 1.5Hz), 8.17(d, 1H, J = 2Hz), 8.69(s, 1H); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ: 114.1, 116.2, 121.7, 123.2, 130.7, 138.1, 145.4, 145.9, 156.8; ESI MS (m/z) = 328 $(M+H)^+$; Anal. Calcd for $C_{10}H_5Br_2N_3$: C, 36.73; H, 1.54; N, 12.85, Found: C, 36.77; H, 1.52; N, 12.92.

4c: 2-amino-1,8-naphthyridine-3-carbonitrile



Pale yellow solid; mp: 279~280 ˚C; IR (Neat, cm^{-1}): 3385, 3332, 2205, 1657, 1601, 1550, 1196; ^{1}HNMR(500MHz, DMSO-d_6) δ: 7.30(dd, 1H, J_1 = 8Hz, J_2 = 4Hz), 7.39(s, 2H), 8.18(dd, 1H, J_1 = 8Hz, J_2 = 2Hz), 8.76(s, 1H), 8.86(dd, 1H, J_1 = 4Hz, J_2 = 2Hz); ^{13}C NMR (125.75 MHz, DMSO-d_6) δ: 97.4, 117.2, 117.9, 120.7, 139.6, 148.7, 157.8, 158.8, 159.9; Anal. Calcd for $C_9H_6N_4$: C, 63.52; H, 3.55; N, 32.92, Found: C, 63.58; H, 3.63; N, 33.02.

(1) C. N. O'Callaghan, T. B. H. McMurry and J. E. O'Brien, *J. Chem. Soc. Perkin Trans. I*, 1995, 417-420.

(2) M. Costa, F. Areias, L. Abrunhosa, A. Venancio, and F. Proencüa *J. Org. Chem*, 2008, **73**, 1954-1962.

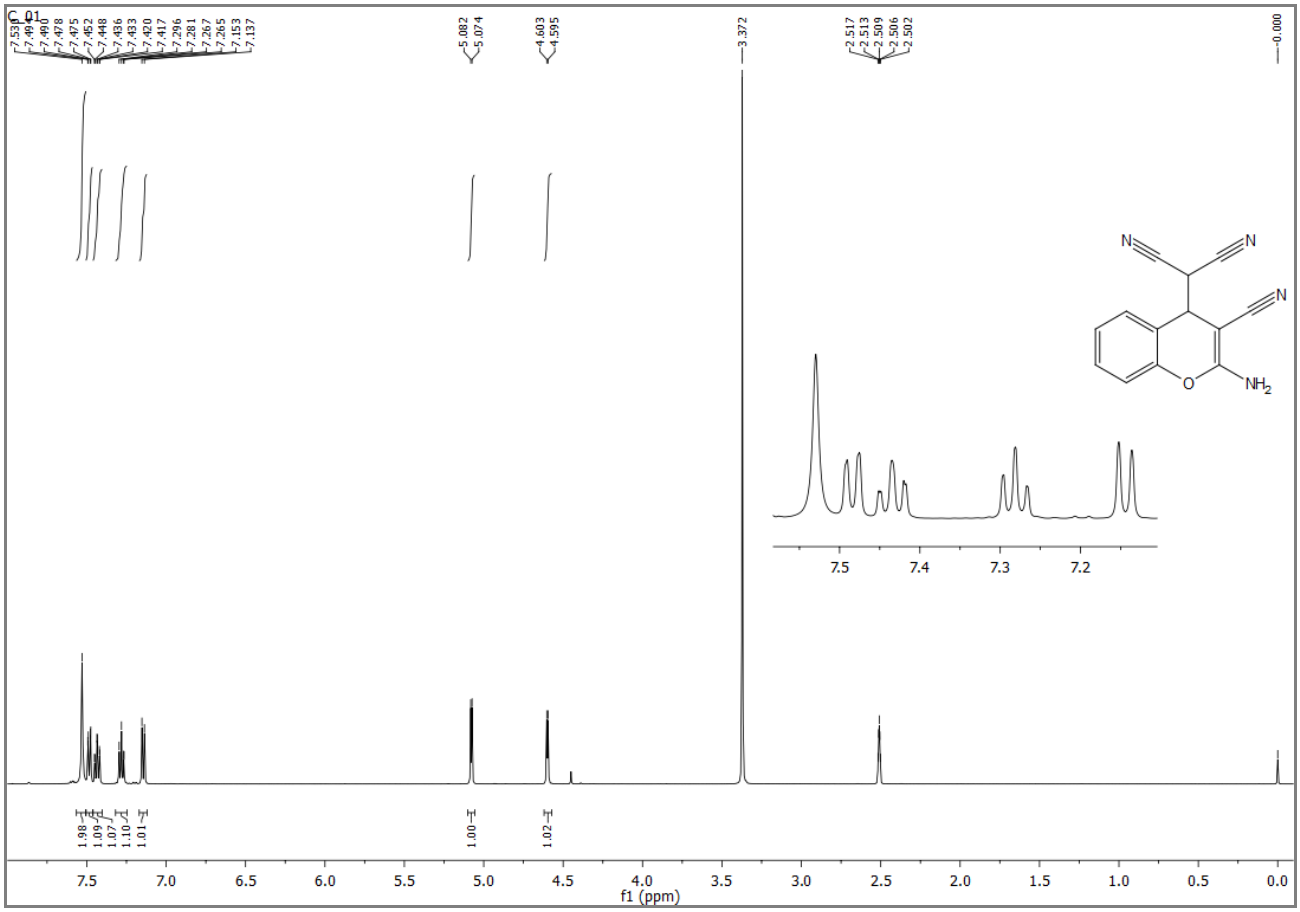
(3) J. S. Yadav, B. V. S. Reddy, M. K. Gupta, I. Prathap, and S.K. Pandey, *Catal. Commun.*, 2007, **8,** 2208–2211.

(4) R. G. Vaghei, Z. T. Semiromi and R. K. Nami, *J. Braz. Chem. Soc.*, 2011, **22,** 905-909.

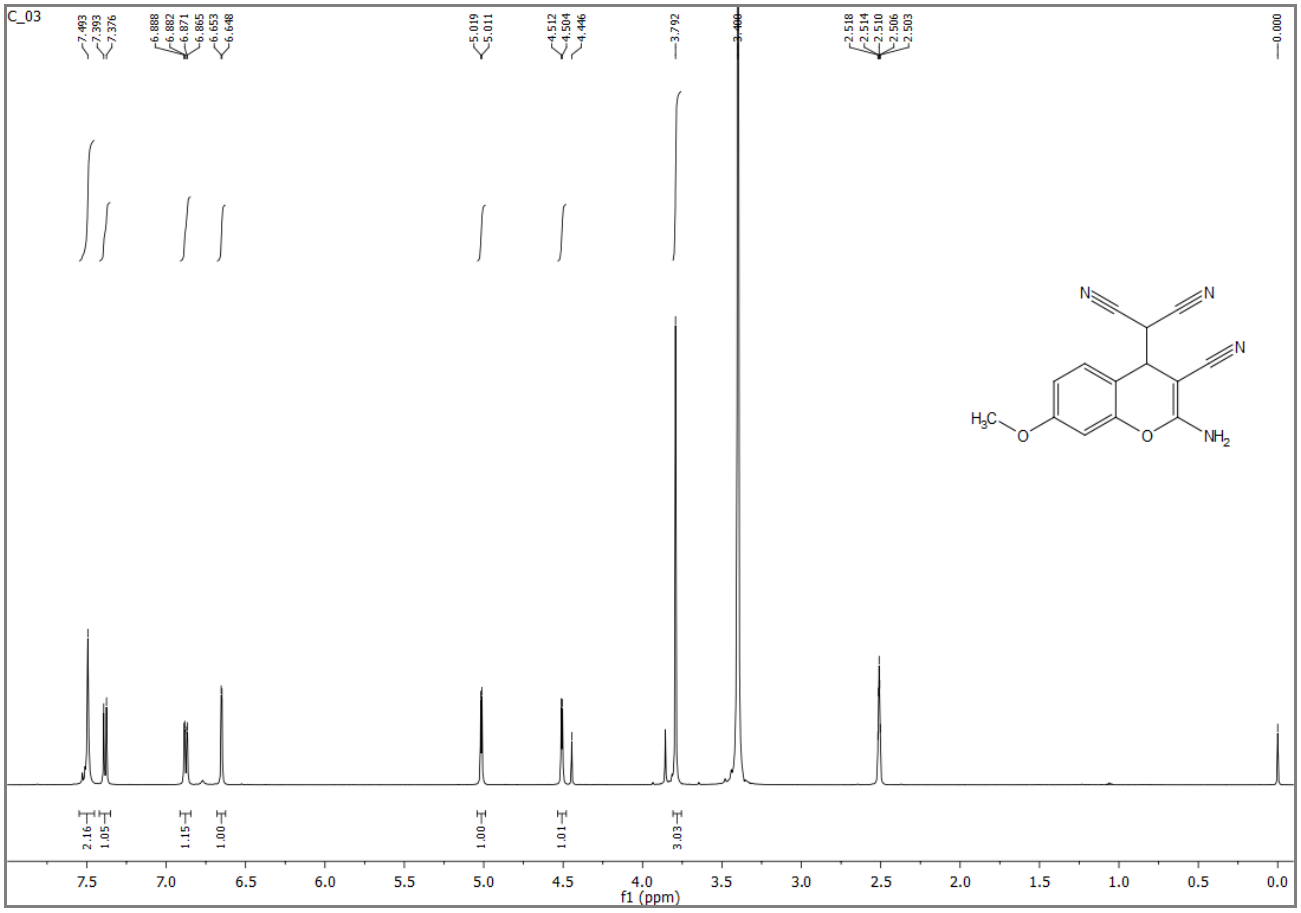
(5) J. F. Roudier and A. Foucaud, *Synthesis*, 1984, 159.

4. Copies of ^{1}H and ^{13}C NMR Spectra

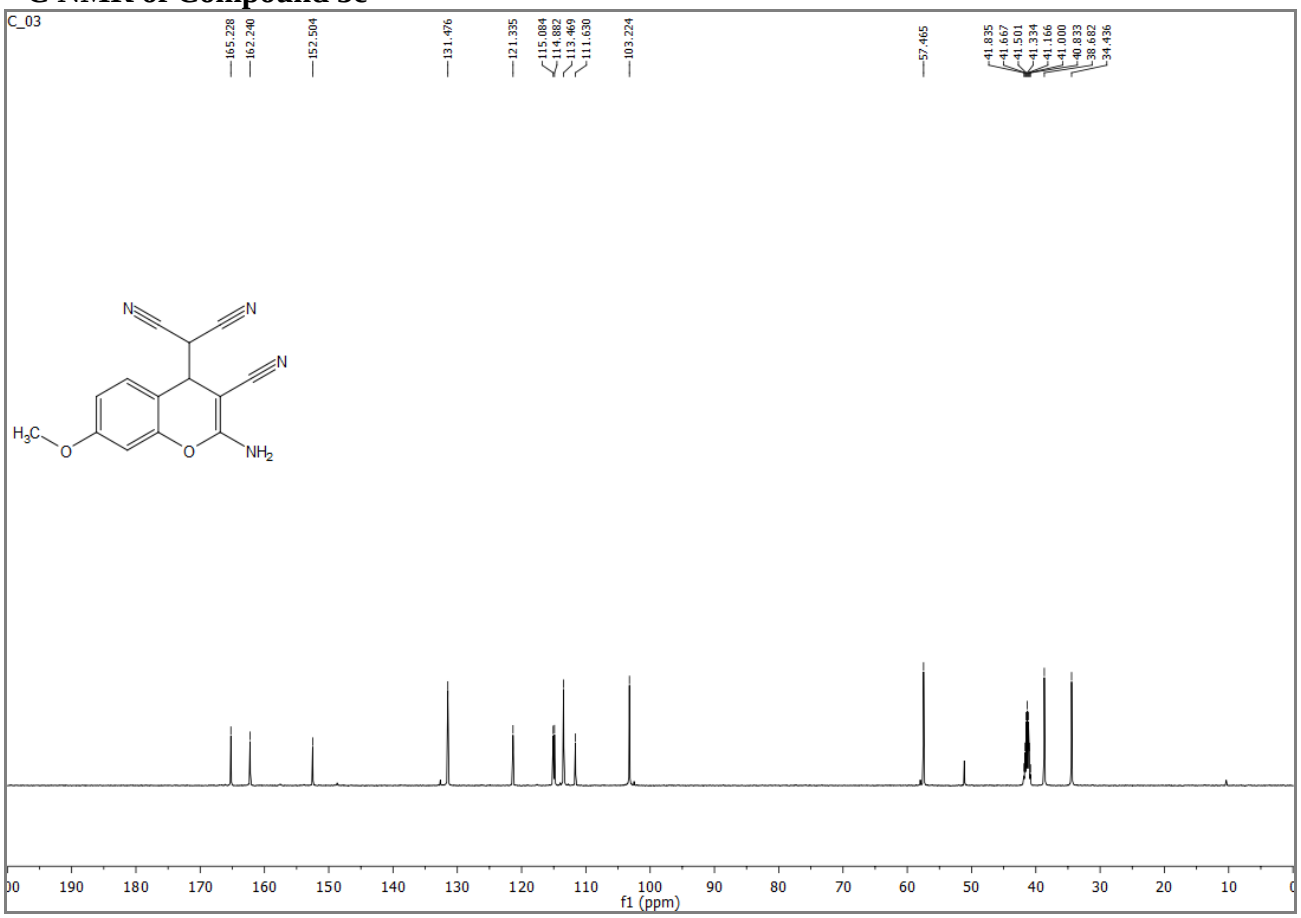
^{1}HNMR of Compound 3a



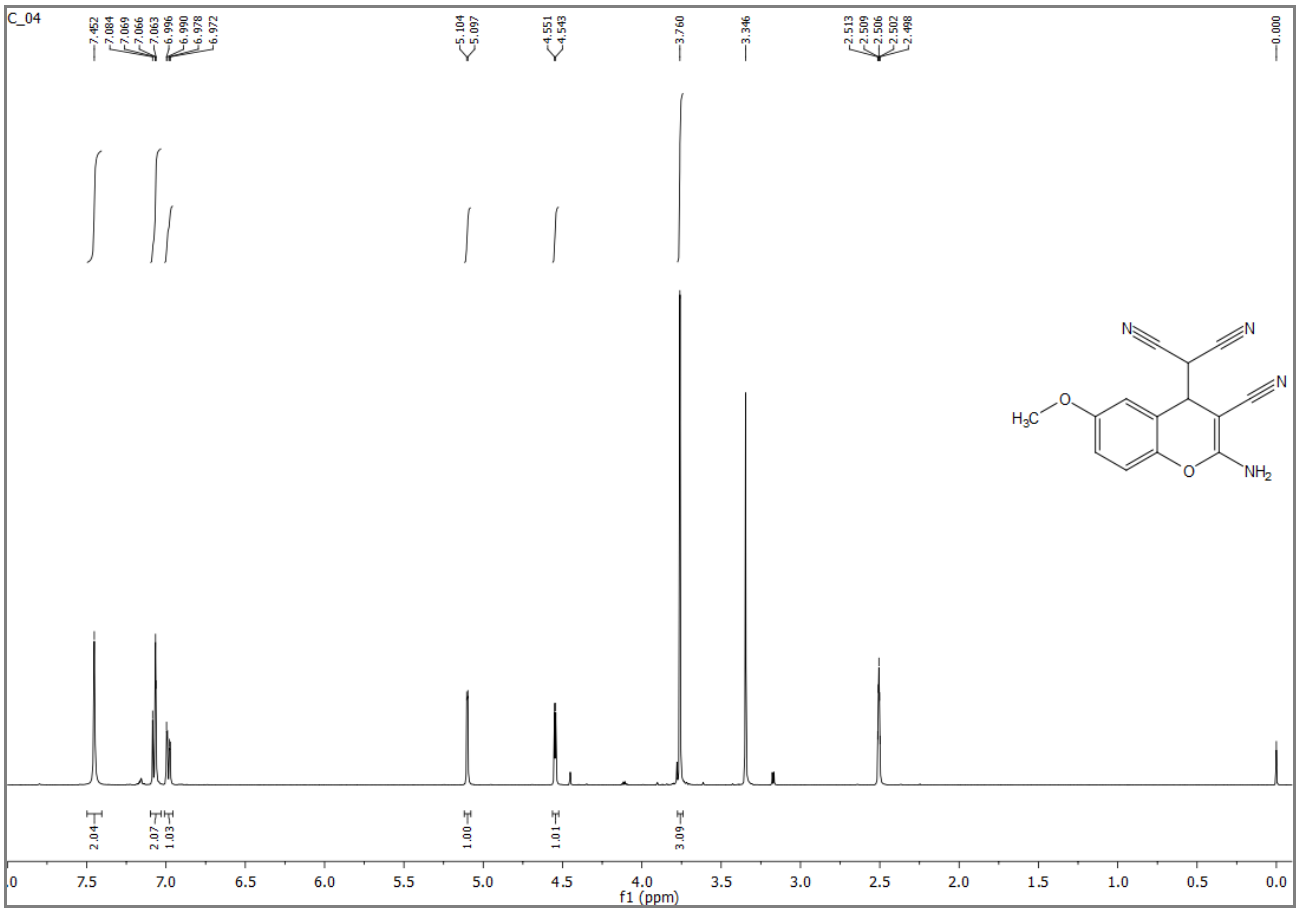
^{1}HNMR of Compound 3c



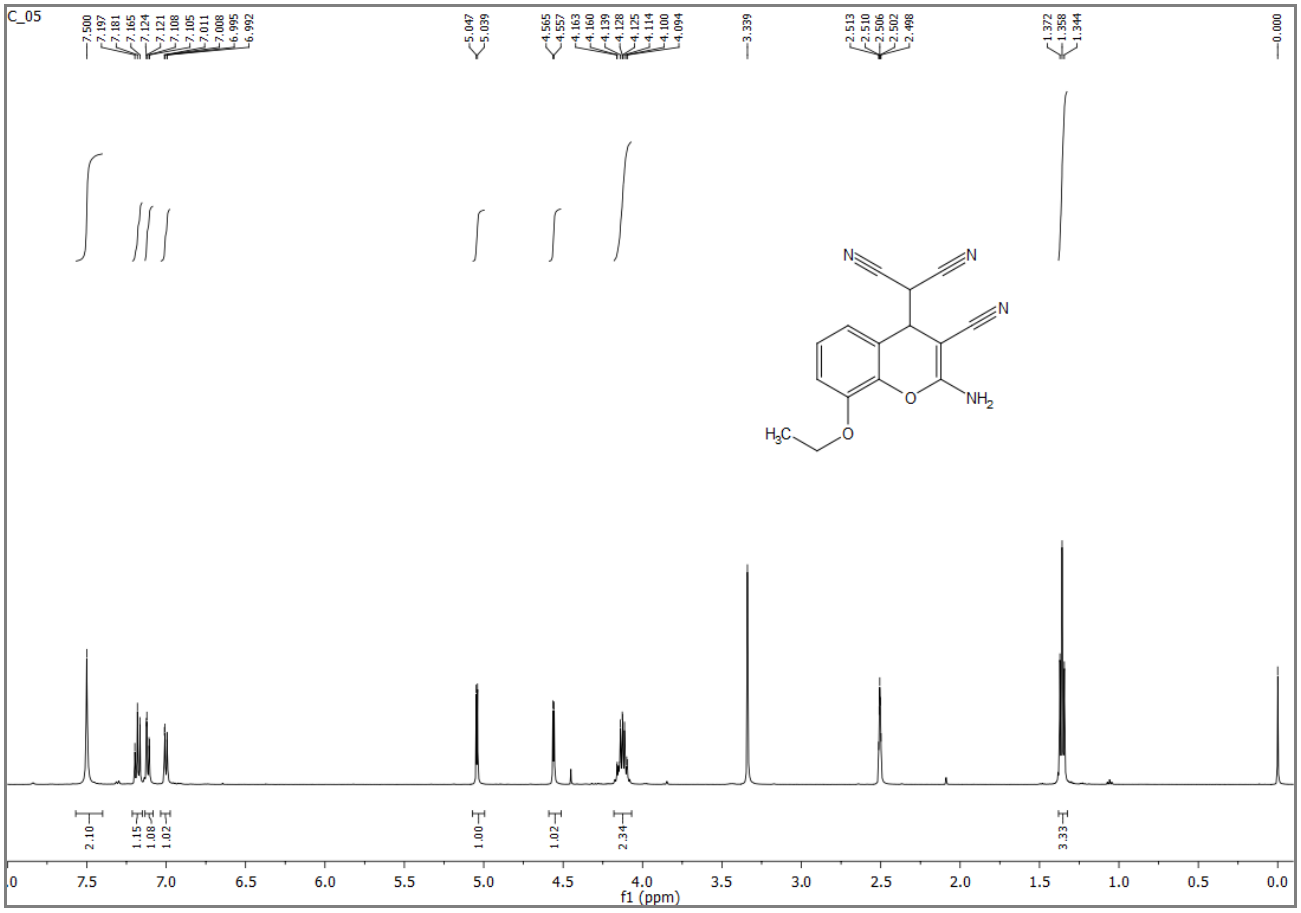
^{13}C NMR of Compound 3c



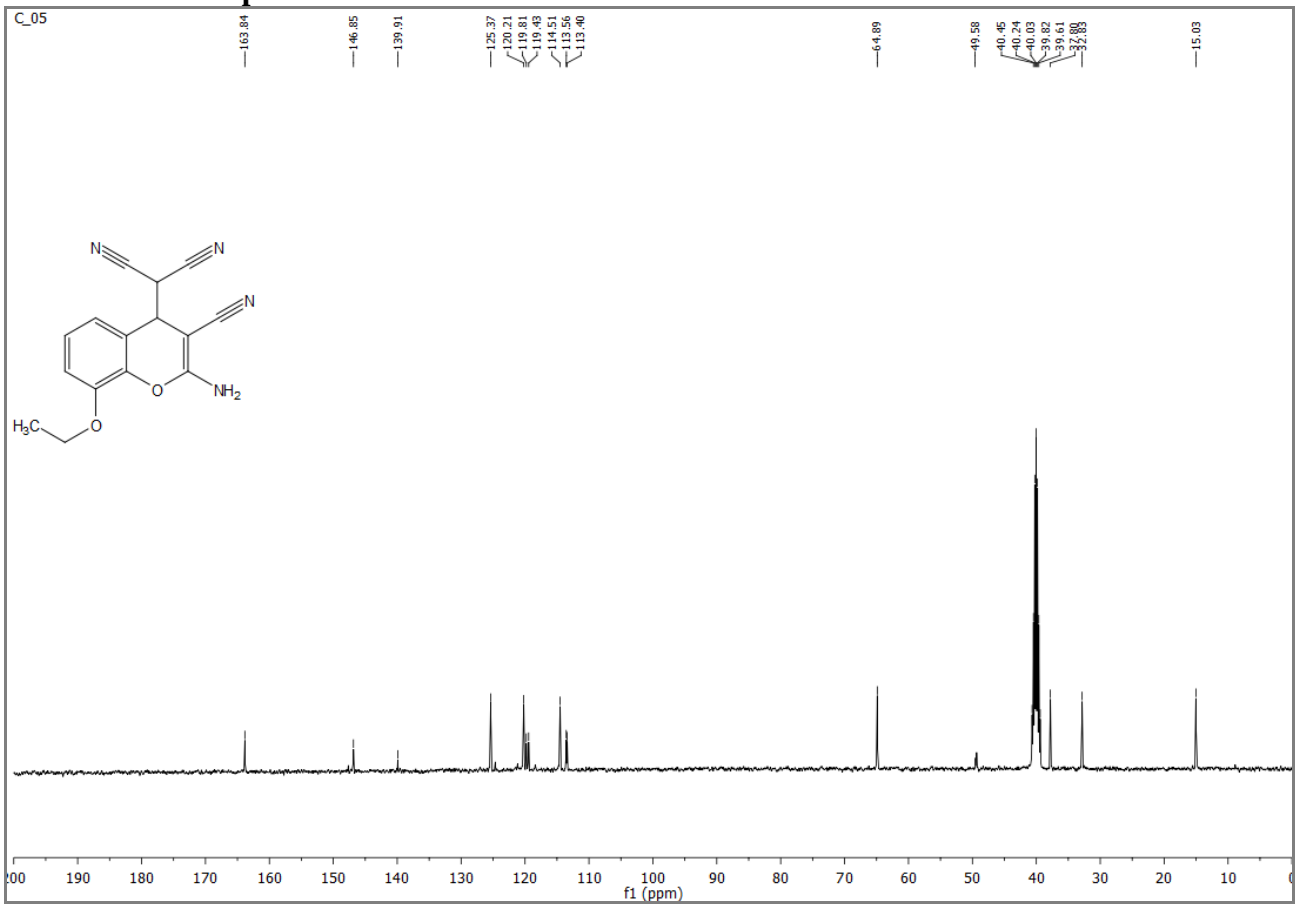
^{1}HNMR of Compound 3d



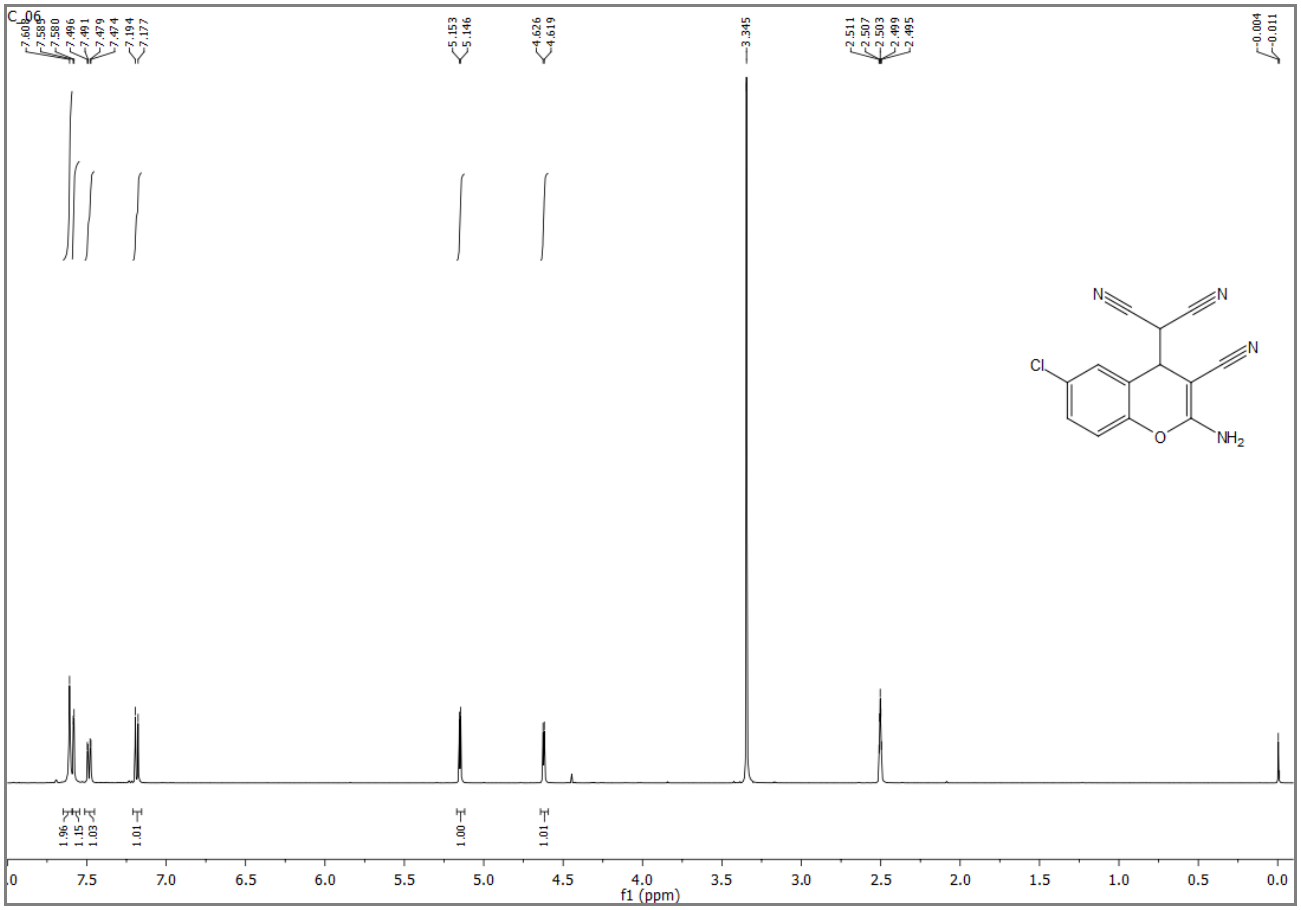
^{1}HNMR of Compound 3e



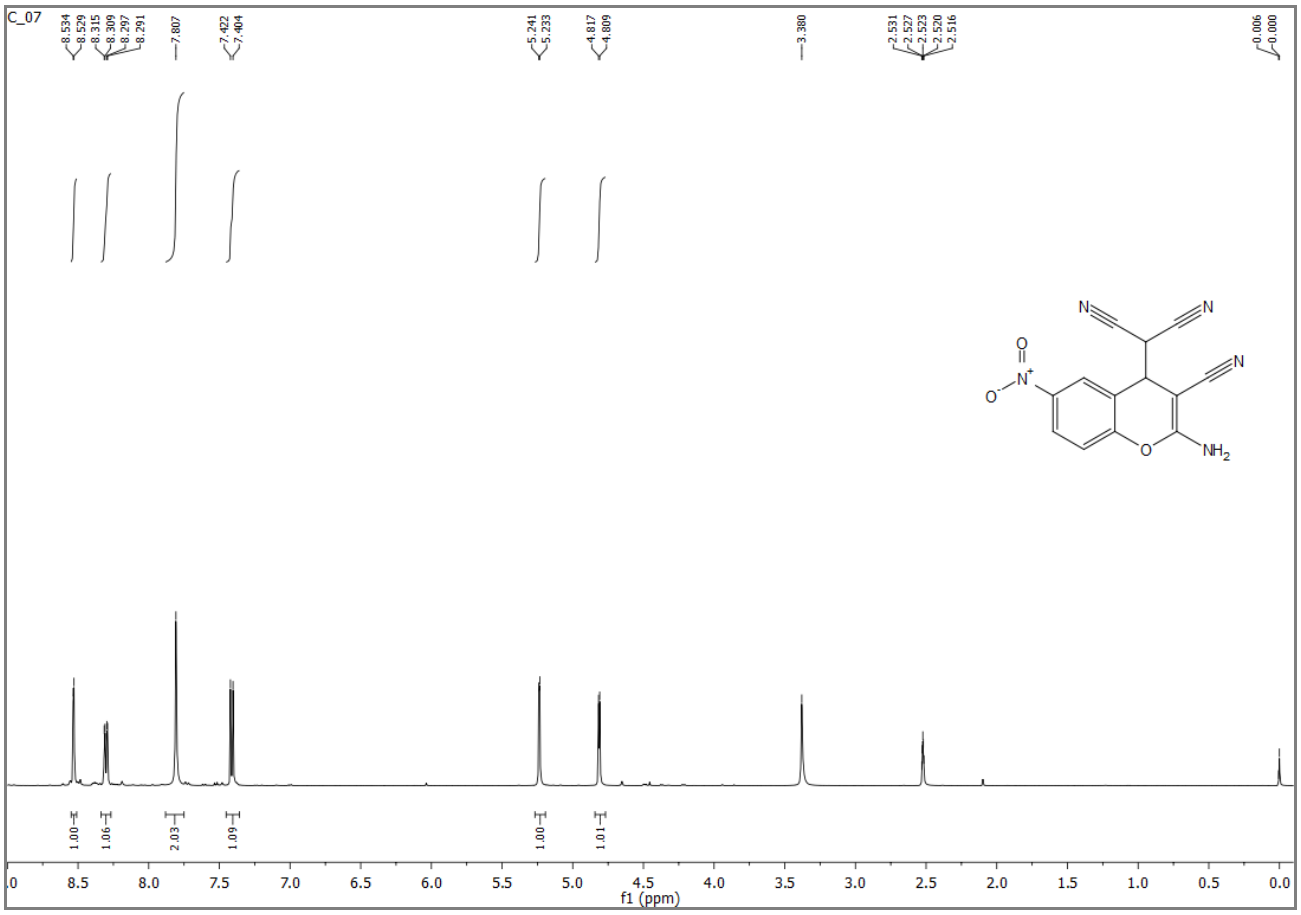
^{13}C NMR of Compound 3e



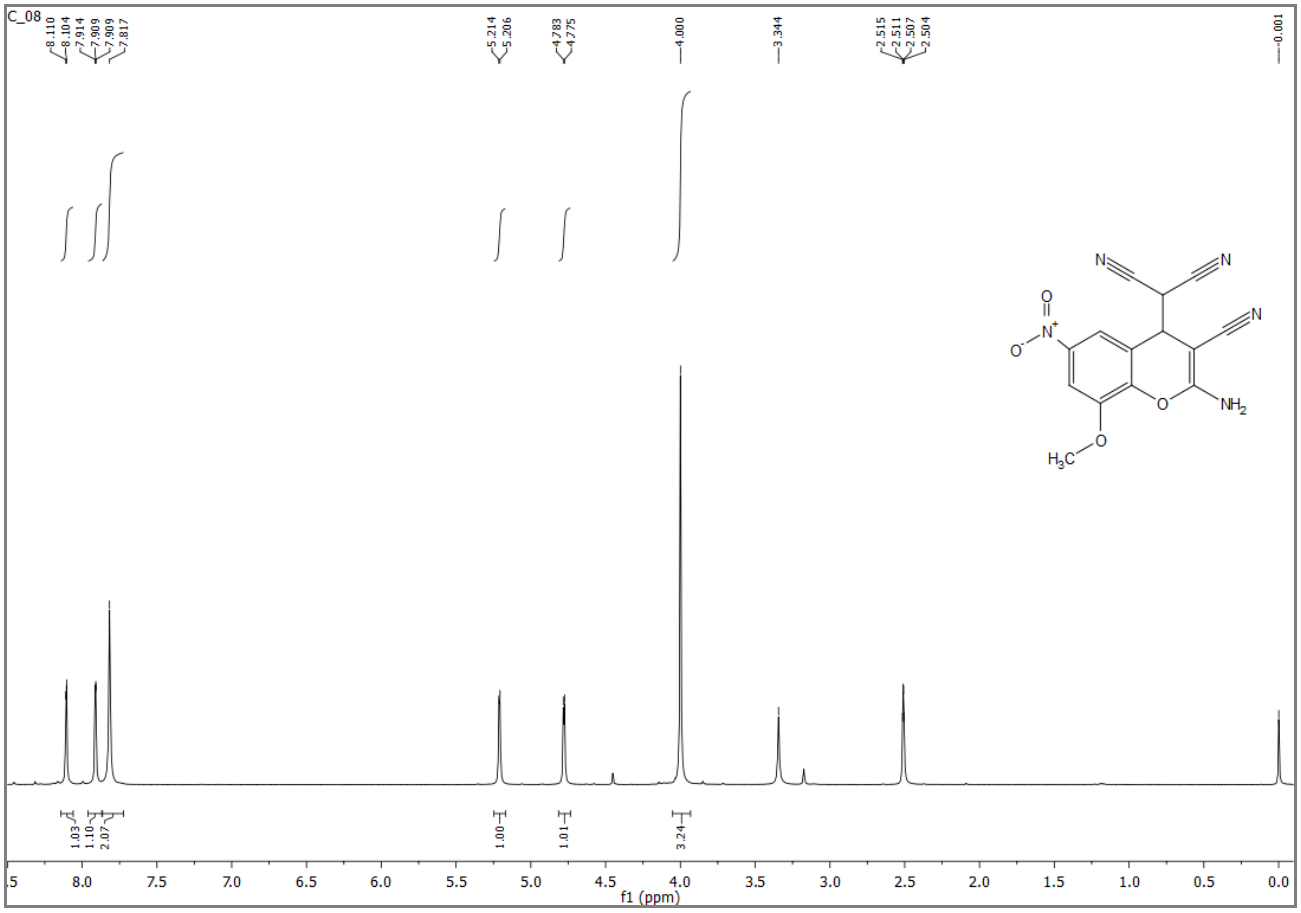
^{1}HNMR of Compound 3f



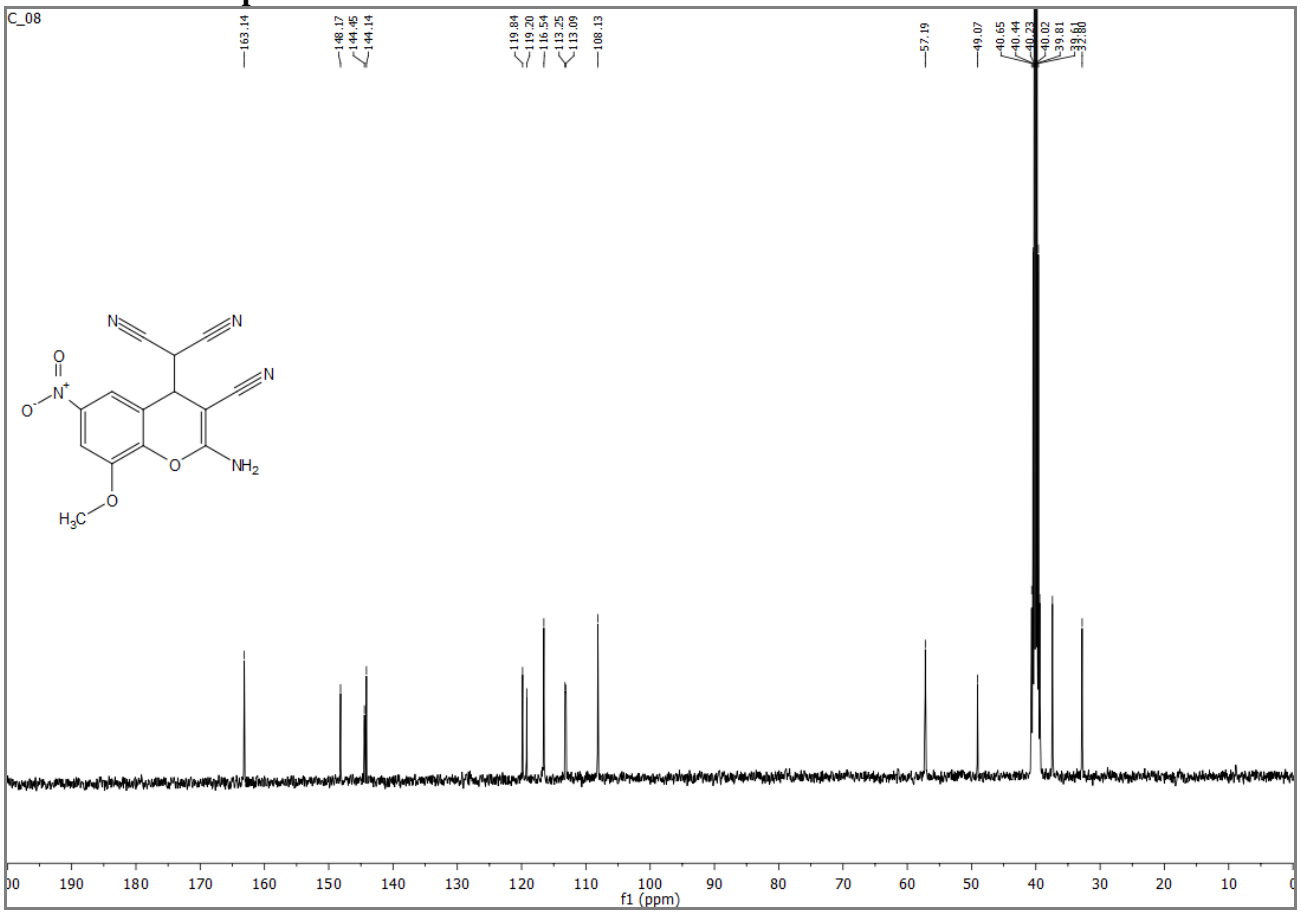
^{1}HNMR of Compound 3g



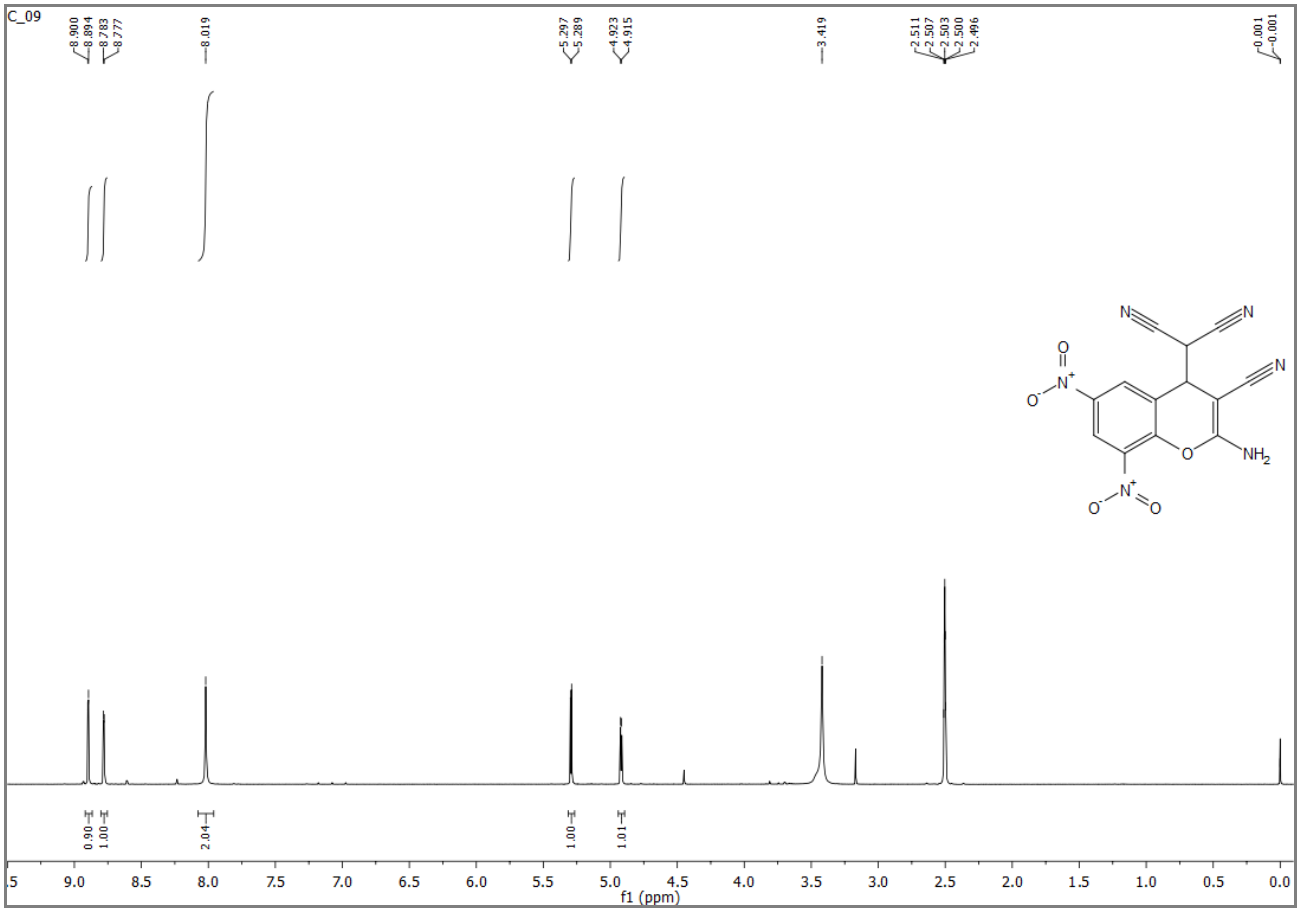
^{1}HNMR of Compound 3h



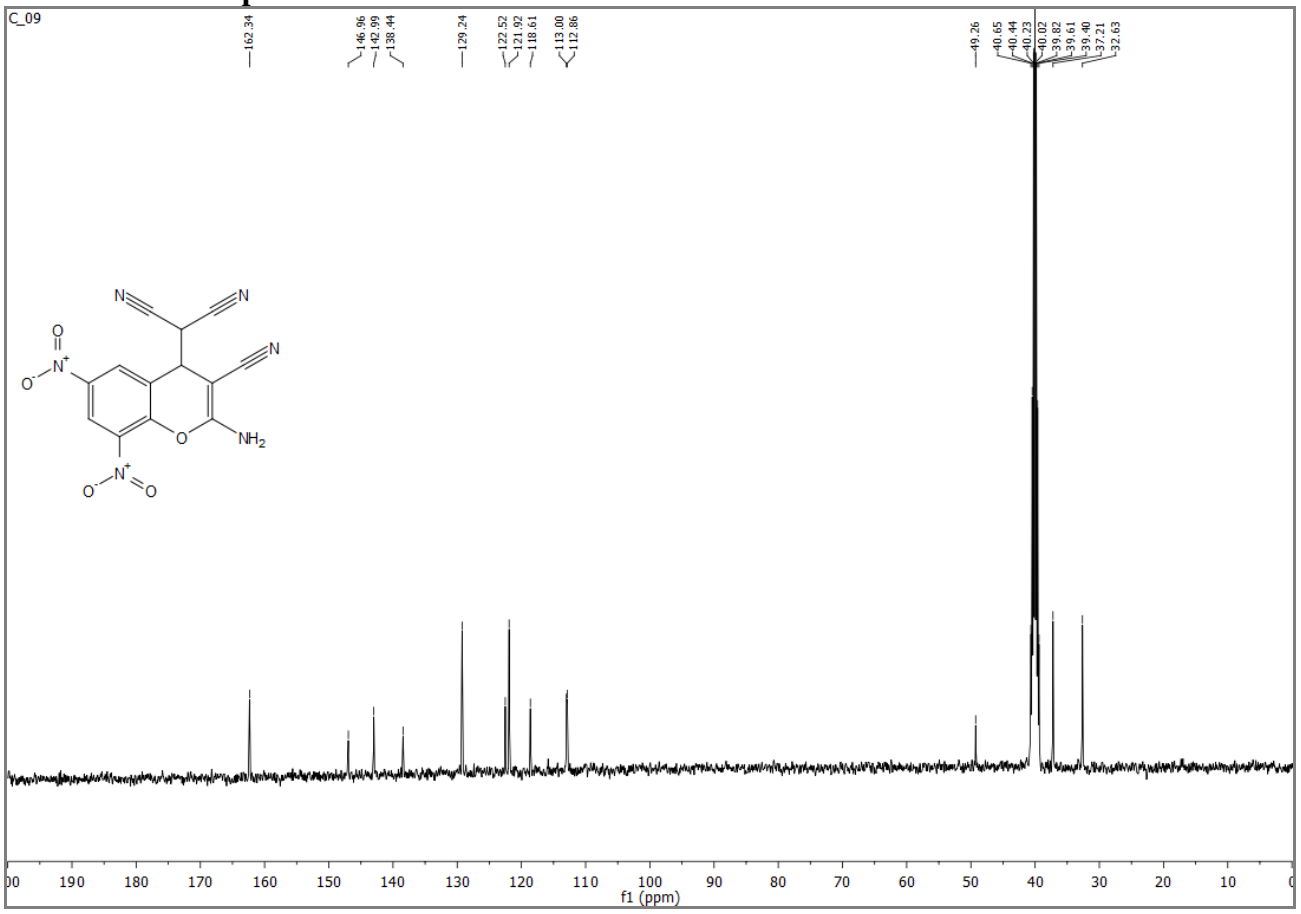
^{13}C NMR of Compound 3h



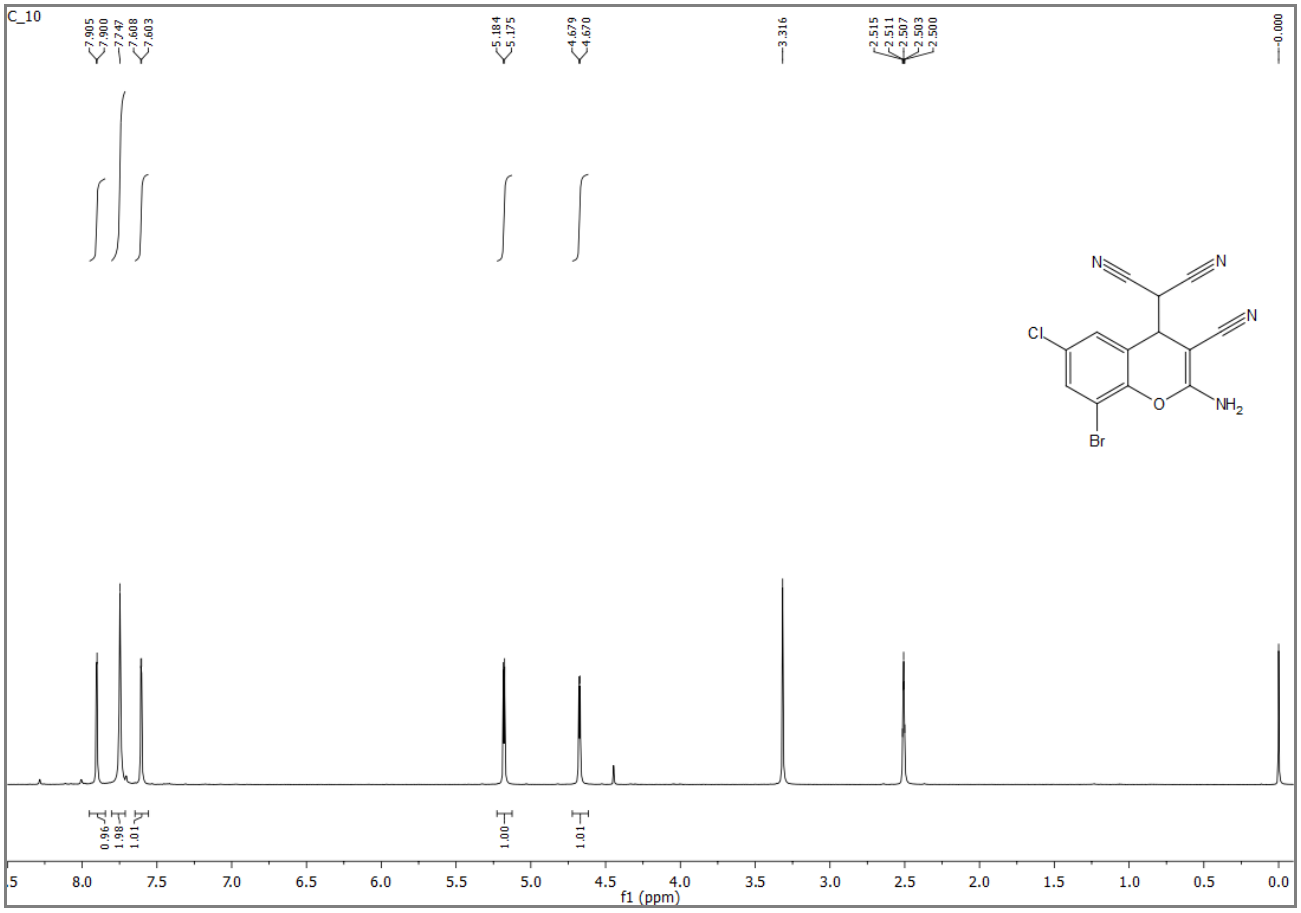
^{1}HNMR of Compound 3i



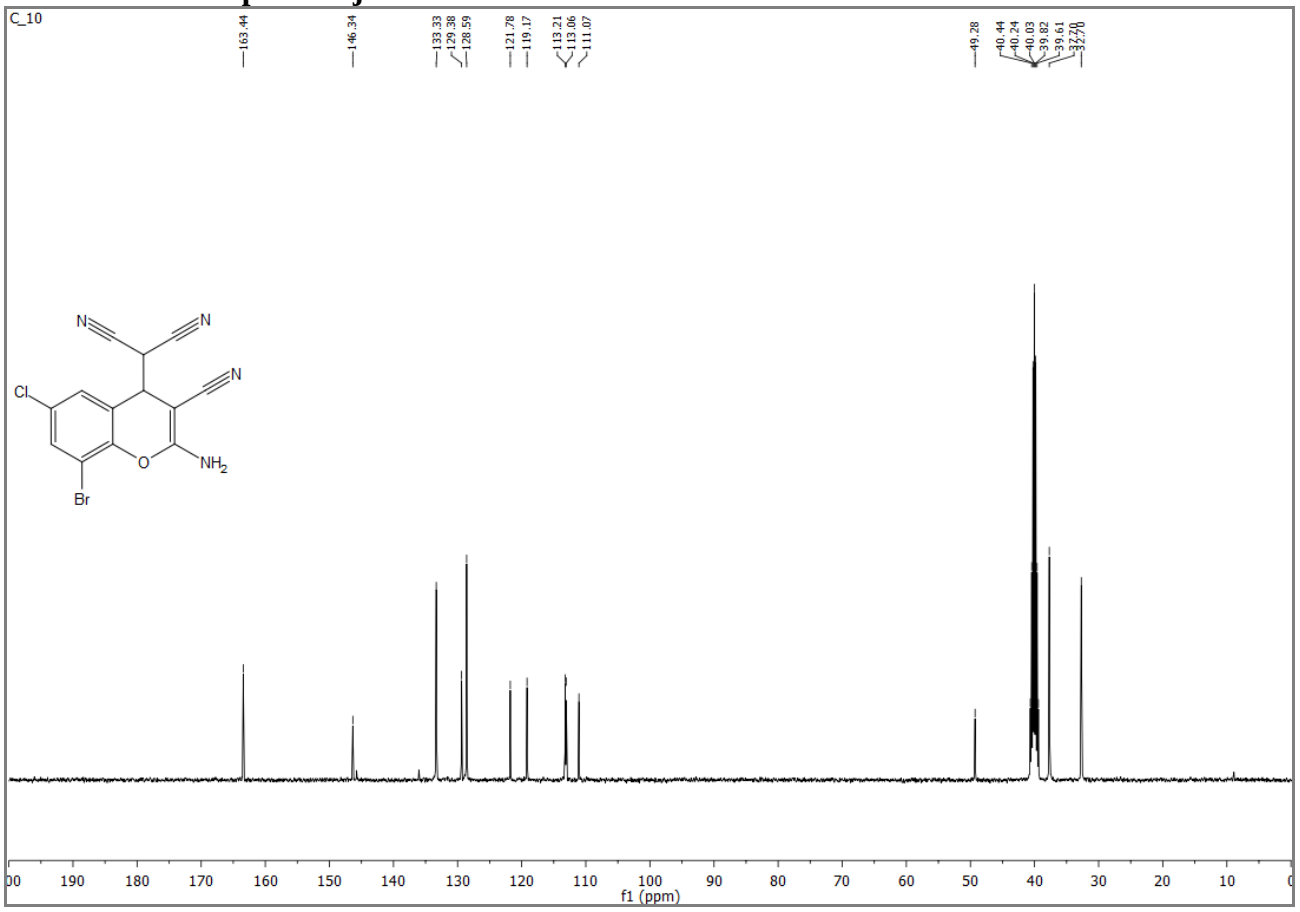
^{13}C NMR of Compound 3i



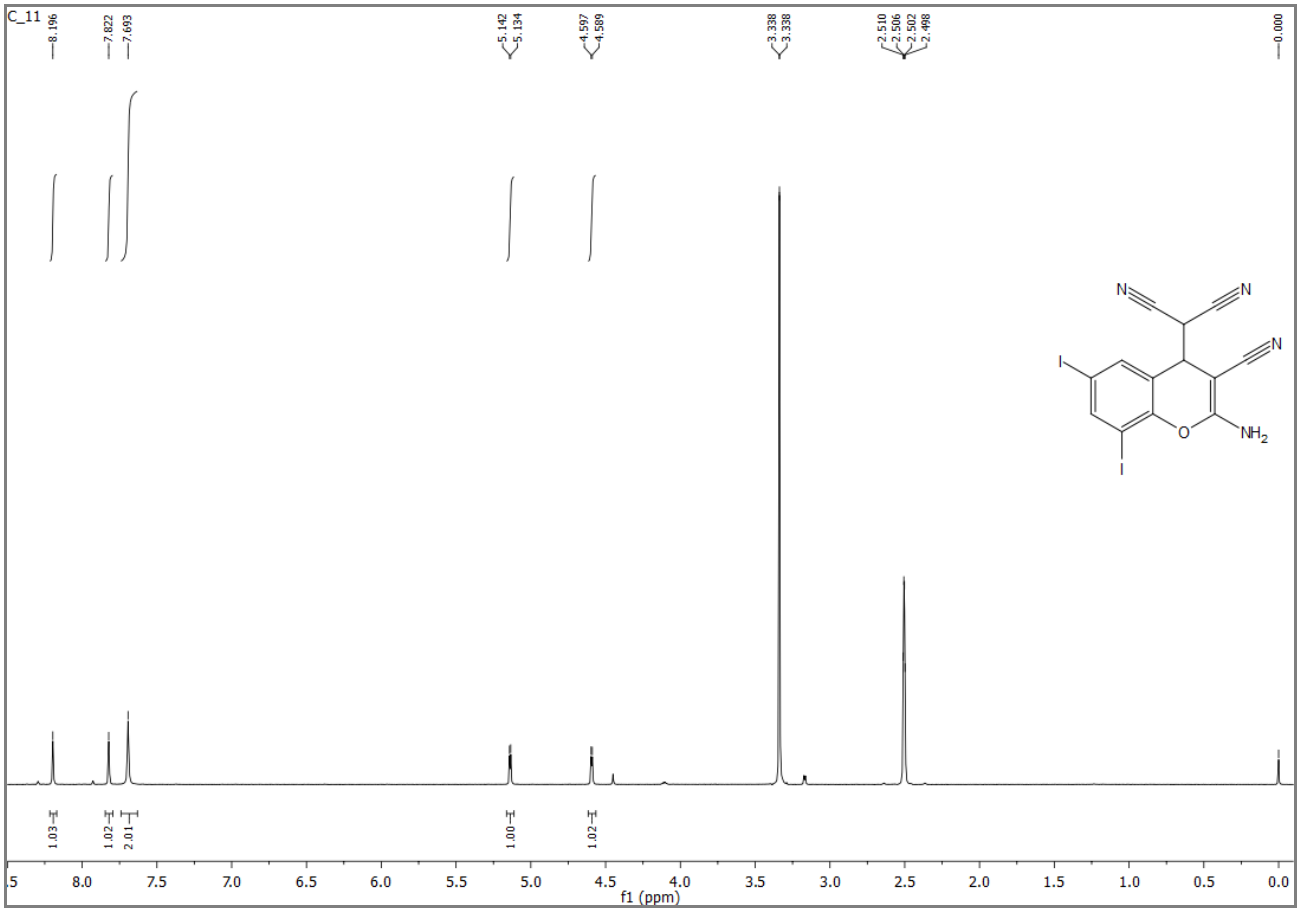
^{1}HNMR of Compound 3j



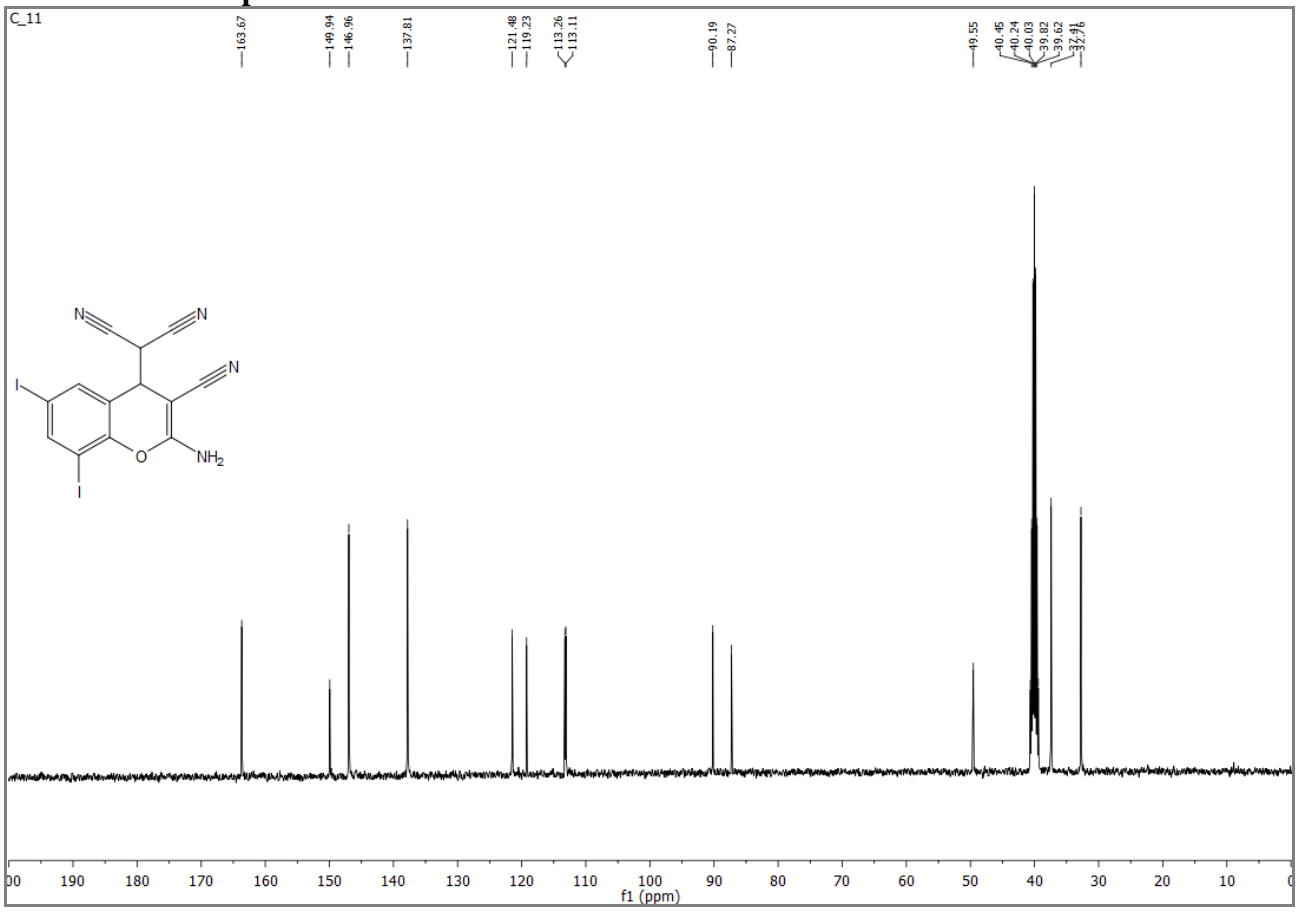
^{13}C NMR of Compound 3j



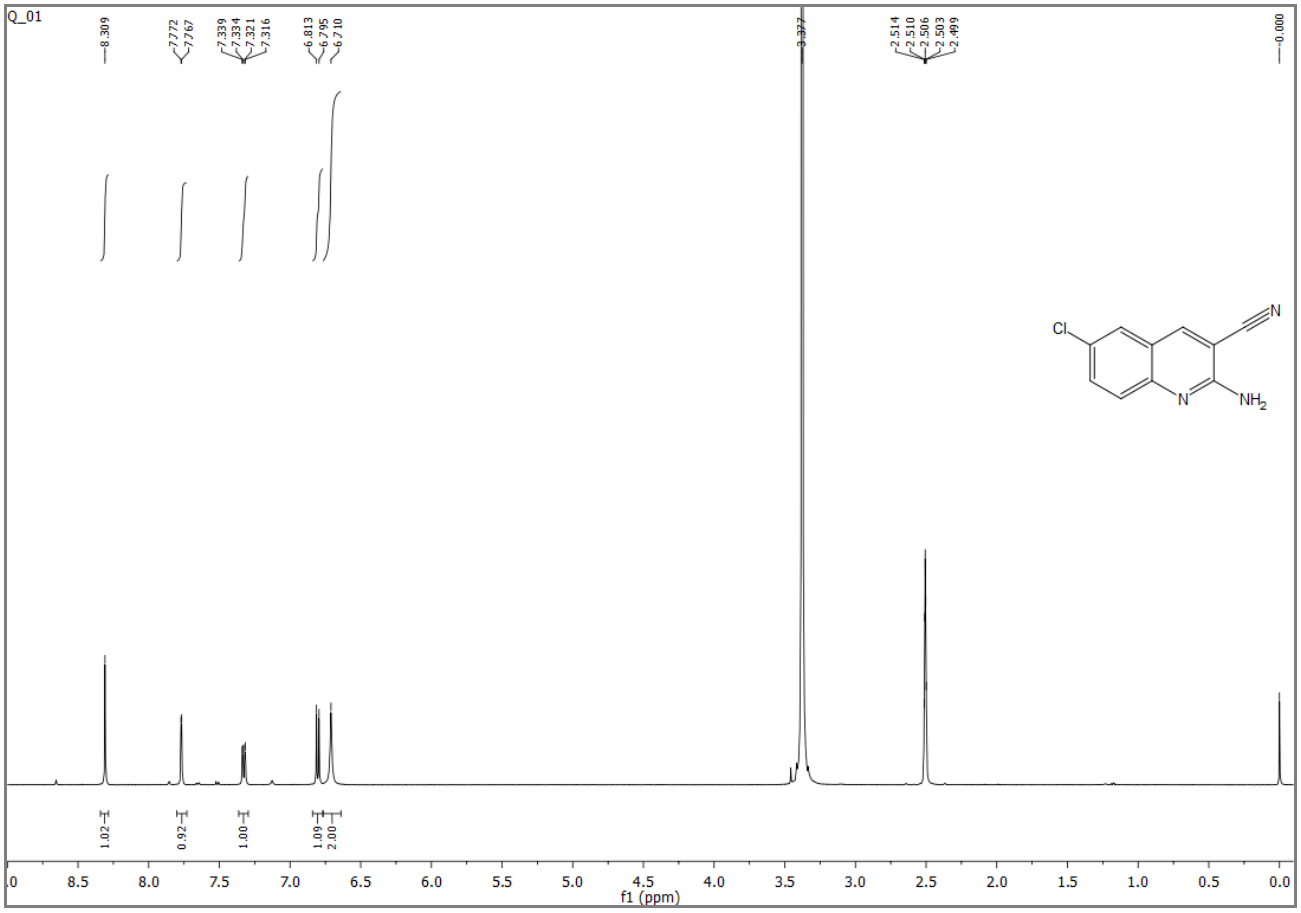
^{1}HNMR of Compound 3k



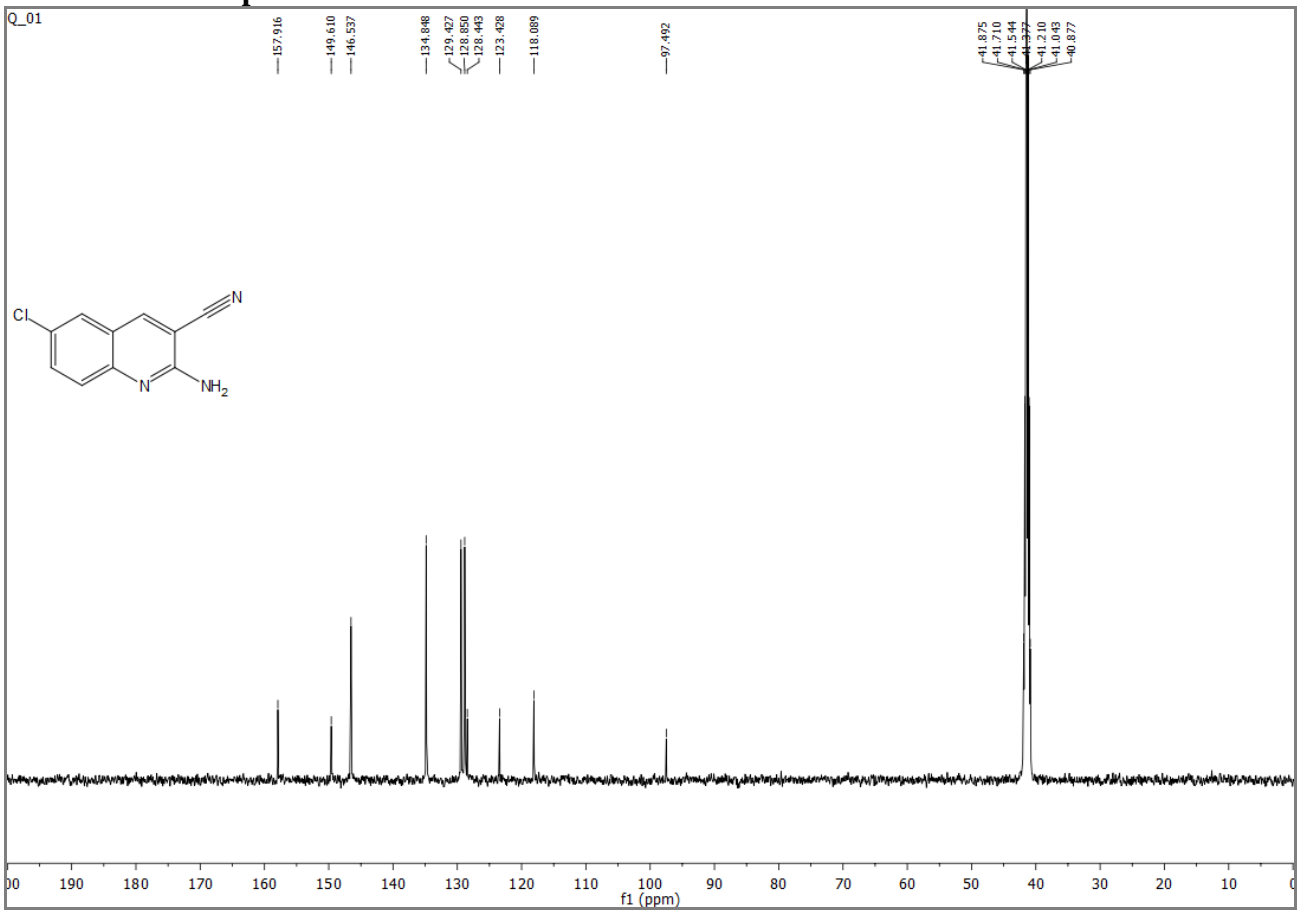
^{13}C NMR of Compound 3k



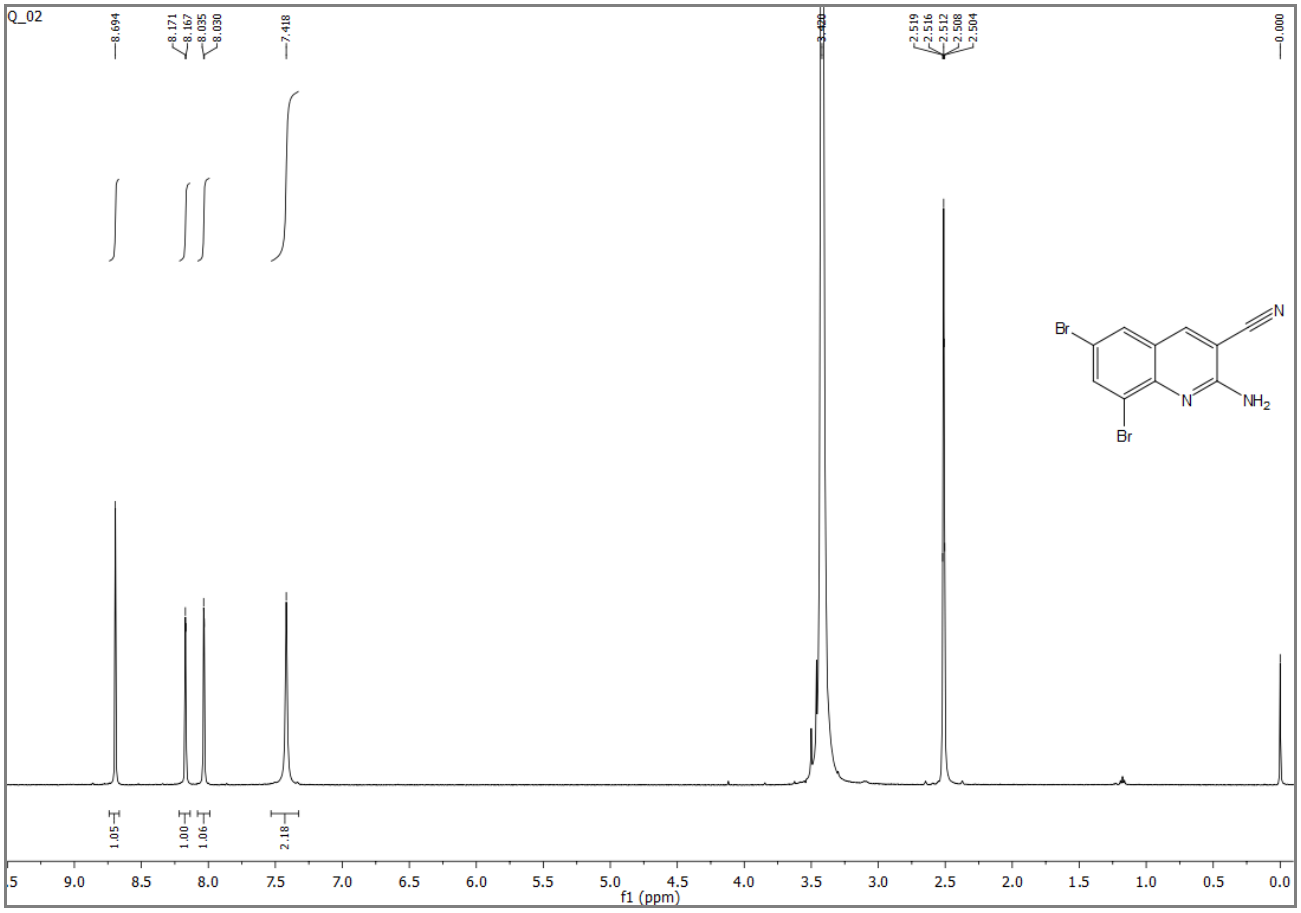
^{1}HNMR of Compound 4a



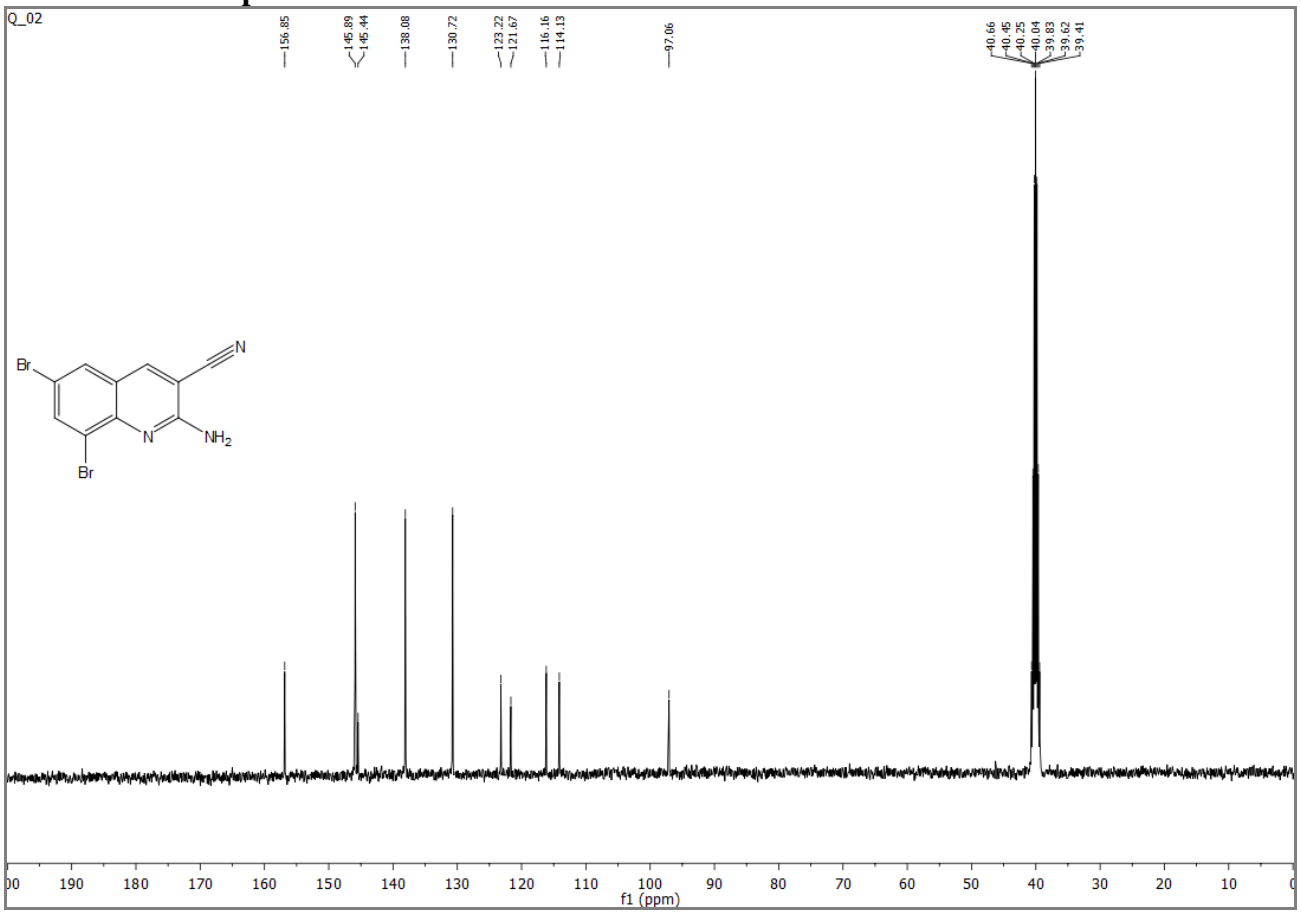
^{13}C NMR of Compound 4a



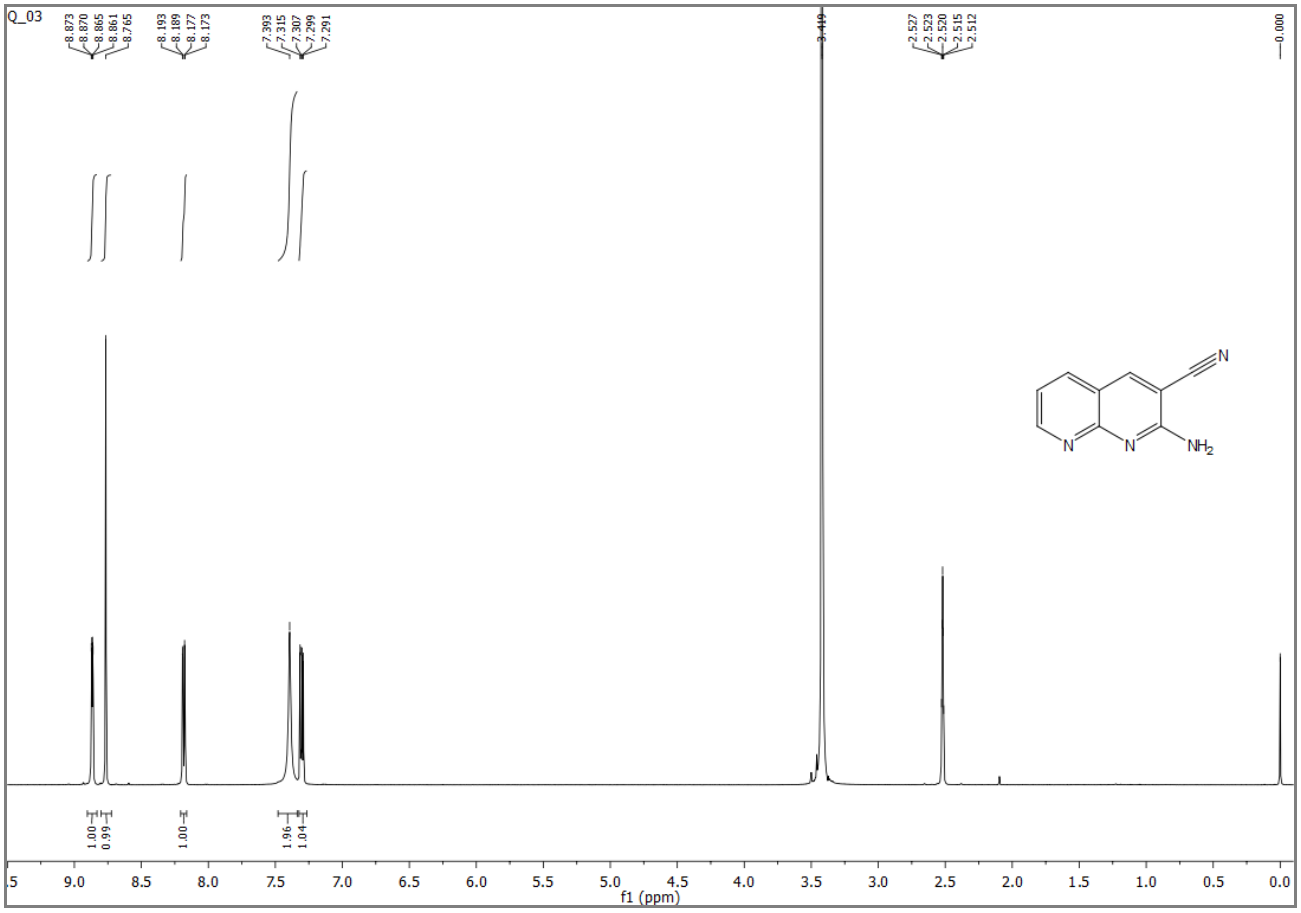
^{1}HNMR of Compound 4b



^{13}C NMR of Compound 4b



^{1}HNMR of Compound 4c



^{13}C NMR of Compound 4b