Electronic Supplementary Information (ESI)

First Report of Application of Simple Molecular Complexes as Organo-Catalyst for Knoevenagel Condensation

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Electronic Supplementary Information

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1. General Information

All starting materials were purchased from Sigma-Aldrich and used as received without further purification. Fourier Transformed Infrared (FTIR) spectra were measured using KBr plate and wave numbers (ῡ) are reported in cm^{-1}. For recording, ^{1}H and ^{13}C NMR spectra of compounds, JEOL-300L spectrometers is used. Chemical shifts (δ) are given in parts per million (ppm) using the residue solvent peaks as reference relative to TMS. Silica gel 60 F254 precoatedplates are used for thin layer chromatographies (TLC). For crystallographic datacollection, an OXFORD DIFFRACTION X CALIBER EoSdiffractometerwith graphite monochromatized Mo Ka radiation at 298 K. is used. Drawings were made using ORTEP-III and Mercury.

2. Synthesis and characterization of catalyst

Synthesis of catalyst

N-methylpiperidine (1.01 mmol) was taken in 50 ml round bottom flask containing 5 ml $CHCl_3$ and 2, 4-dinitrophenol (1 mmole) was added. Immediate yellowish coloured liquid was obtained. Resulting yellowish solution was stirred for 1-3 h at room temperature and was kept in refrigerator. Finally yellow colour crystal was separated out from solvent. After detailed analysis, we found that 1:1 stoichiomeric molar complex for 2, 4-dinitrophenol was formed.

Analytical data for [MP(NP)$_2$]: $C_{18}H_{23}N_3O_6$ Complex: C, 58.25 % (58.20 %); H, 6.20 % (6.16 %); N, 10.65 % (10.63 %); M.P.:63.2 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$) :δ(ppm) 8.12 (d, *J* = 9 Hz, 4H), 6.80 (d, *J* = 9 Hz, 4H); 5.13 (broad, 1H), 2.81 (t, *J* = 8.1 Hz, 4H), 2.55 (s, 3H); 1.83-1.76 (m, 4H), 1.60-1.52 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$):δ (ppm) 165.8, 139.5, 126.5, 116.5, 55.6, 45.0, 23.8, 22.2.

Analytical data for [MP(DNP)]:$C_{12}H_{17}N_3O_5$ Complex: C, 50.88 % (58.80 %); H, 6.05 % (6.00 %); N, 14.83 % (14.80 %); M.P.:143.2˚C; ^{1}H-NMR (300 MHz, $CDCl_3$) :δ (ppm) 8.99 (s, 1H), 8.06 (d, *J* = 9.6 Hz, 1H), 6.69 (d, *J* = 9.3 Hz, 1H), 3.23 (broad, 1H), 3.17-3.02 (broad,

4H), 2.77 (broad, 3H), 1.93-1.87 (broad, 4H), 1.67-1.58 (broad, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$):δ (ppm) 170.3, 135.2, 132.1, 128.9, 126.7, 125.2, 55.6, 44.3, 22.9, 21.5.

Analytical data for [MP(TNP)]:$C_{12}H_{17}N_3O_5$ complex: C, 43.90 % (43.80 %); H, 4.91 % (5.00 %); N, 17.17 % (18.00 %); M.P.:226.6 ˚C; ^{1}H-NMR (300 MHz, $CDCl_3$) :δ (ppm) 8.88(s, 1H), 3.66 (broad, 1H), 2.86-2.02 (broad, 7H), 1.9 (broad, 4H), 1.93 (broad, 2H); ^{13}CNMR (75 MHz, $CDCl_3$): δ (ppm) 162.0, 141.63, 128.1, 126.5, 55.9, 44.5, 22.8, 21.4.

3. General procedure for synthesis of Knoevenagel products using MP(DNP) as catalyst

General procedure for Knoevenagel products using MP(DNP) as catalyst

A mixture of aldehyde (1.0 mmol), manolonitrile (1.01 mmol) and MP(DNP) (0.05 mmol) in round bottom flask containing ethanol was stirred at room temperature for appropriate time. After completion of the reaction, which was monitored by TLC, the solid product was collected by filtration, washed with water and aqueous ethanol. Pure product is obtained and recrystallization from ethanol (**3a-3x**).

General procedure for the preparation of 2-Amino-4*H*-chromenes

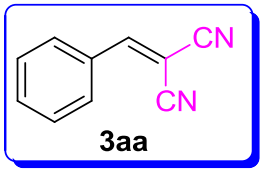
A mixture of salicylaldehyde (1 mmol), malononitrile (2.01 mmol) and MP(DNP) (0.05 mmol) in round bottom flask containing EtOH was stirred at room temperature for the appropriate time. After completion of the reaction, which was monitored by TLC, the solid product was collected by filtration, washed with water and aqueous ethanol. Pure product is obtained and recrystallized from ethanol.

General Procedure for Synthesis of hexahydroquinolines[1]

The mixture of the aldehydes (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol), ammonium acetate (2.5 mmol) and MP(DNP) containing (5 mol%) as catalyst were stirred at room temperature for the 15 minute time in ethanol solvent. After completion of the reaction (monitored by TLC), the ethanol is evaporated and 3 mL of water was added to the mixture. Solid product is obtained and washed several times with water (at least four times). For recycling the catalysts, after washing the solid products with water completely, the water containing the molecular complex (MP(DNP) was evaporated under reduced pressure and molecular complex (catalyst, MP(DNP)) was recovered and reused. The solid product was purified by recrystallization procedure in ethanol.

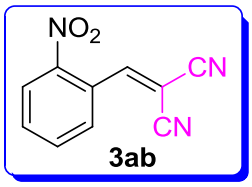
4. Characterization data of the isolated products

2-benzylidenemalononitrile (3aa)



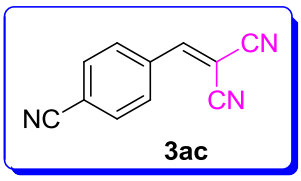
State: Solid; Colour: White; MP.: 83.5 °C (Lit.,[2] 82-83 °C); FTIR (KBr, cm^{-1}): 3097, 3075, 3032, 2934, 2223, 1551, 1568, 1490; ^{1}H-NMR (300MHz, $CDCl_3$): δ (ppm) 7.88 (d, J = 7.5 Hz, 2H), 7.76 (s, 1H), 7.61 (t, J = 5.0 Hz, 1H), (t, J = 5.0 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 159.9, 134.5, 130.9, 129.5, 113.6, 112.5, 82.8.

2-(2-nitrobenzylidene)malononitrile (3ab)



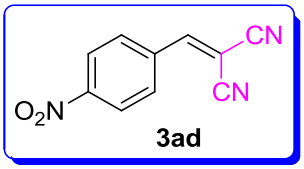
State: Solid; Colour: Gray; MP.: 140.2 °C (Lit.,[3] 136-138 °C); FTIR (KBr, cm^{-1}): 3118, 3066, 2996, 2953, 2229, 1723, 1623, 1603, 1569, 1523; ^{1}H-NMR (300MHz, $CDCl_3$): δ (ppm) 8.42 (s, 1H), 8.33 (d, J = 7.5 Hz, 1H), 7.88-7.76 (m, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 158.7, 134.8, 133.3, 130.4, 126.6, 125.7, 112.1, 110.9; 88.5.

2-(4-cyanobenzylidene)malononitrile (3ac)



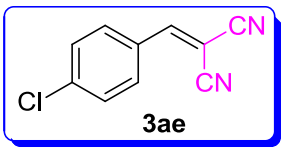
State: Solid; Colour: White; MP.: 155.2 °C (Lit.,[4] 154 °C); FTIR (KBr, cm^{-1}): 3110, 3100, 3080, 3043, 2229, 1588, 1550, 1501,1416; ^{1}H-NMR (300MHz, $CDCl_3$): δ (ppm) 7.99 (d, J = 8.4 Hz, 2H), 7.84 (s, 1H), 7.80 (d, J = 2.4 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 157.2, 134.2, 133.1, 130.6, 117.2, 112.6, 111.6, 86.9.

2-(4-nitrobenzylidene)malononitrile (3ad)



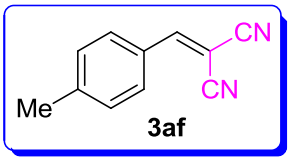
State: Solid; Colour: Light Yellow; MP.: 160.2 °C (Lit.,160-161 °C); FTIR (KBr, cm^{-1}): 3110, 3100, 3080, 3043, 2229, 1588, 1550, 1501,1416; ^{1}H-NMR (300MHz, $CDCl_3$): δ (ppm) 8.38 (d, J = 8.7 Hz, 2H), 8.71 (d, J = 8.8 Hz, 2H), 7.87 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 159.2, 137.2, 134.1, 133.6, 117.6, 112.6, 111.6, 87.9.

2-(4-chlorobenzylidene)malononitrile (3ae)



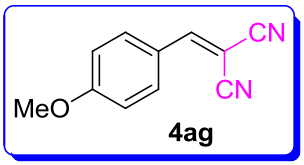
State: Solid; Colour: White; MP.: 163.0 °C (Lit.,[5]162 °C); FTIR (KBr, cm^{-1}): 3100, 3080, 3070, 3040, 2235, 1580, 1555, 1505, 1419; ^{1}H-NMR (300MHz, $CDCl_3$): δ (ppm) 7.83 (d, J = 8.4 Hz, 2H), 7.71 (s, 1H), 7.50 (d, J = 8.4 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 158.2, 141.1, 131.7, 130.0, 129.2, 117.2, 112.6, 111.6, 86.9.

2-(4-methylbenzylidene)malononitrile (3af)



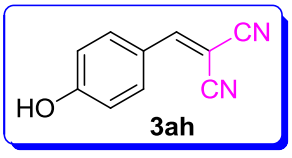
State: Solid; Colour: White; MP., 134.5 °C (lit.,[6] 134-135 °C); FTIR (KBr, cm^{-1}): 3034, 2962, 2925, 2223, 1590, 1554, 1509, 1453; ^{1}H-NMR (300MHz, $CDCl_3$): δ (ppm) 7.79 (d, J = 8.3 Hz, 2H), 7.69 (s, 1H), 7.32 (d, J = 8.3 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 159.7, 146.3, 130.8, 130.3, 128.3, 113.9, 112.8, 81.1.

2-(4-methoxybenzylidene)malononitrile (3ag)



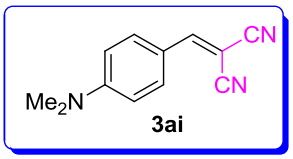
State: Solid; Colour: White; MP., 115 °C; (Lit.,[7] 114-115 °C)); FTIR (KBr, cm^{-1}): 3030, 2982, 2852, 2220, 1605, 1571, 1557, 1513; ^{1}H-NMR (300MHz, $CDCl_3$): δ (ppm) 7.91 (d, J = 10.5 Hz, 2H), 7.65 (s, 1H), 7.01 (d, J = 9.0 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 158.8, 133.4, 115.10, 114.1, 85.7, 55.7.

2-(4-hydroxybenzylidene)malononitrile (3ah)



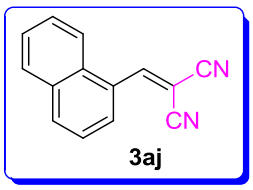
State: Solid; Colour: White; MP.: 190 °C (Lit.,[8] 188-189 °C); FTIR (KBr, cm^{-1}): 3350, 3330, 3090, 3070, 3035, 2937, 2228, 1555, 1565, 1495; ^{1}H-NMR(300 MHz, $CDCl_3$): δ (ppm) 10.38 (s, 1H), 7.82 (d, J = 8.7 Hz, 2H), 7.65 (s, 1H), 6.95 (d, J = 8.7 Hz, 2H); ^{13}C-NMR(75MHz, $CDCl_3$): δ (ppm) 163.2, 162.6, 154.6, 133.8, 132.0, 128.6, 122.8, 116.3, 115.8, 97.5, 62.0.

2-(4-(dimethylamino)benzylidene)malononitrile (3ai)



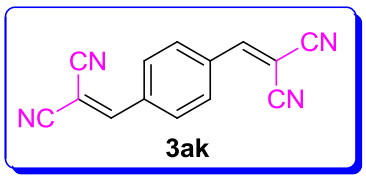
State: Solid; Colour: Brown; MP.: 180.2 °C (lit.,[9] 182-183°C); FTIR (KBr, cm^{-1}): 3050, 3030, 2939, 2225, 1545, 1555, 1499; ^{1}H-NMR(300MHz, $CDCl_3$): δ(ppm) 7.80 (d, J = 9.0 Hz, 2H), 7.45 (s, 1H), 6.69 (d, J = 8.4 Hz, 2H), 3.16 (s, 6H); ^{13}C-NMR(75MHz, $CDCl_3$): δ(ppm) 158, 133.7, 131.9, 111.5, 110.9, 40.0.

2-(naphthalen-1-ylmethylene)malononitrile (3aj)



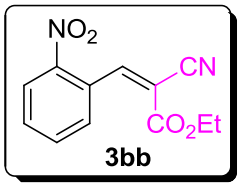
State: Solid; Colour: Yellow; MP., 175 °C; FTIR (KBr, cm^{-1}): 3010, 2987, 2952, 2225, 1604, 1575, 1555, 1514; ^{1}H-NMR (300 MHz, $CDCl_3$): δ(ppm) 8.65 (s, 1H), 8.27 (d, J = 7.2 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.71-7.58 (m, 3H); ^{13}C-NMR(75MHz, $CDCl_3$): δ (ppm) 157.6, 134.8, 133.4, 131.0, 129.3, 128.5, 127.4, 125.3, 122.2, 113.6, 112.4, 85.1.

2,2'-(1,4-phenylenebis(methan-1-yl-1-ylidene))dimalononitrile (3ak)



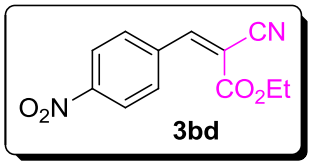
State: Solid; Colour: White; MP.: 205 °C (Lit.,[10] 206-208, dec); ^{1}H-NMR(300MHz, $CDCl_3$): δ (ppm) 8.04 (d, J = 7.0 Hz, 4H), 7.81 (s, 2H).

(E/Z)-ethyl-2-cyano-3-(2-nitrophenyl)acrylate (3bb)



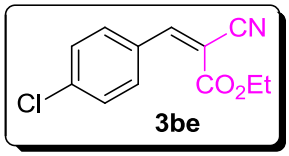
State: Solid; Colour: White; MP.: 105 °C (Lit.,[11] 101-103 °C); FTIR (KBr, cm-1): 3094, 3035, 2987, 2952, 2944, 2905, 2226, 1723, 1610, 1591, 1565, 1491; ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 8.69 (s, 1H), 8.25 (d, J = 8.1 Hz, 1H), 7.84-7.76 (dd, J_1 = 7.5 Hz, J_2 = 7.5 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 3.39 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C-NMR(75MHz, $CDCl_3$): δ (ppm) 178.4, 160.9, 153.1, 147.3, 134.4, 132.1, 130.5, 128.0, 125.4, 108.6, 72.2, 14.0.

(E/Z)-ethyl 2-cyano-3-(4-nitrophenyl)acrylate (3bd)



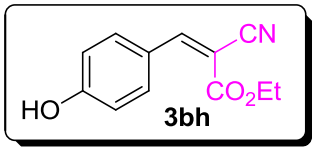
State: Solid; Colour: White; MP.: 172 °C (Lit.,[12] 170 °C); FTIR (KBr, cm-1): 3090, 3045, 2997, 2955, 2946, 2915, 2229, 1720, 1614, 1590, 1560, 1490; ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 8.34 (d, J = 9.0 Hz, 2H), 8.29 (s, 1H), 8.12 (d, J = 8.7 Hz, 2H), 4.43 (q, J = 3.6 Hz, 2H), 1.42 (t, J = 7.0 Hz, 3H); ^{13}C-NMR(75MHz, $CDCl_3$): δ (ppm) 161.3, 151.6, 149.6, 136.8, 131.4, 124.2, 114.4, 107.3, 63.2, 14.0.

(E or Z)-ethyl 3-(4-chlorophenyl)-2-cyanoacrylate (3be)



State: Solid; Colour: White; MP. 89 °C (Lit.,[13] 90 °C); FTIR (KBr, cm-1): 3095, 3040, 2997, 2954, 2943, 2910, 2223, 1722, 1610, 1595, 1560, 1491; ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 8.16 (s, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 4.35 (q, J = 7.0 Hz, 2H), 1.36 (t, J = 7.0 Hz, 3H); ^{13}C-NMR(75MHz, $CDCl_3$): δ (ppm) 162.1, 153.3, 139.5, 132.1, 129.8, 115.1, 103.4, 62.8, 14.1.

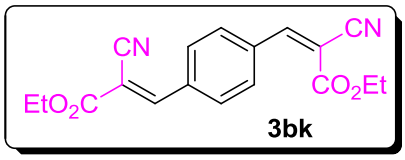
(E or Z)-ethyl 2-cyano-3-(4-hydroxyphenyl)acrylate (3bh)



State: Solid; Colour: White; MP.: 168 °C (lit.,[14] 170-171 °C); FTIR (KBr, cm-1): 3395, 3340, 3010, 2990, 2952, 2940, 2915, 2222, 1722, 1612, 1590, 1561, 1491; ^{1}H-NMR(300MHz, $CDCl_3$): δ (ppm) 8.17 (s, 1H), 7.95 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 5.96 (s, 1H)4.37 (q, J = 7.1Hz,

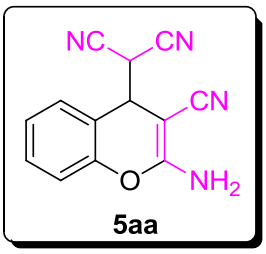
2H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (75MHz, $CDCl_3$): δ(ppm) 190.8, 163.2, 162.6, 154.6, 133.8, 132.0, 128.6, 122.8, 166.3, 115.8, 97.5, 62.0, 29.4, 14.0.

(2Z,2'E)-diethyl 3,3'-(1,4-phenylene)bis(2-cyanoacrylate) (3bk)



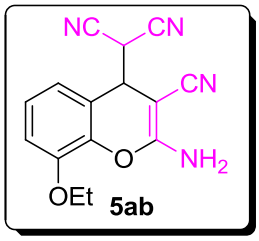
State: Solid; Colour: White; MP.: 200 °C; ^{1}H-NMR(300MHz, $CDCl_3$): δ (ppm) 8.25 (s, 2H), 8.09 (d, J = 7.0 Hz, 4H), 4.41 (q, J = 7.2 Hz, 4H), 1.41 (t, J = 7.0 Hz, 6H).

2-(2-amino-3-cyano-4*H*-chromen-4-yl)malononitrile(5aa)



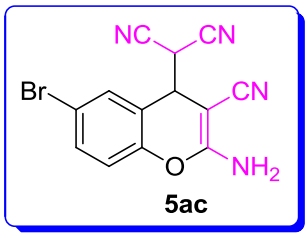
White solid; mp: 151.2 ˚C; FTIR (KBr, cm^{-1}): 3449, 3328, 2928, 2238, 2188, 1636, 1605, 1568, 1417, 1265, 1225, 1045; ^{1}H-NMR(300MHz, DMSO-d_6): δ(ppm) 7.50-7.38 (m, 4H),7.25 (t, J = 7.35Hz, 1H), 7.12 (d, J = 8.1, 1H) 5.05 (d, J = 3.6 Hz, 1H), 4.57 (d, J = 3.6Hz, 1H); ^{13}C-NMR(75MHz, DMSO-d_6): δ(ppm) 163.4, 149.7, 130.1, 128.8, 125.0, 119.4, 117.9, 116.3, 113.0, 112.9, 84.8, 37.1, 32.4; ESI-MS (m/z) = 235.2 (M-H).

2-(2-amino-3-cyano-8-ethoxy-4*H*-chromen-4-yl)malononitrile (5ab)



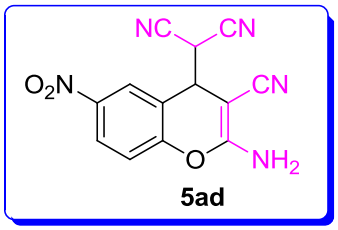
White solid; mp: 137.2 ˚C; FTIR (KBr, cm^{-1}): 3468, 3347, 2988, 2945, 2896, 2253, 2191, 1640, 1575, 1485, 1406, 1322, 1275, 1198, 1077; ^{1}H-NMR(300MHz, DMSO-d_6): δ(ppm) 7.18 (d, J = 7.8 Hz, 1H), 7.04-6.97 (m, 2H), 5.12 (s, 2H), 4.30 (d, J = 3.6 Hz, 1H), 4.11 (q, J = 6.9 Hz, 2H), 3.98 (d, J = 3.3 Hz, 1H), 1.46 (t, J = 6.9 Hz, 3H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ(ppm) 163.4, 146.4, 139.3, 124.9, 124.9, 119.7, 119.4, 118.9, 113.9, 113.1, 64.3, 48.8, 37.3, 32.4, 14.6; ESI-MS (m/z) = 281.2 $(M+H)^+$.

2-(2-amino-6-bromo-3-cyano-4*H*-chromen-4-yl)malononitrile (5ac)



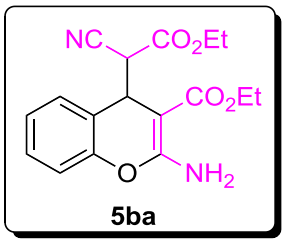
White solid; mp: 160 °C (lit. 160-161 °C); FTIR (KBr, cm^{-1}): 3404, 3313, 2907, 2254, 2198, 1652, 1592, 1520, 1429, 1342, 1250, 1089, 1036; ^{1}H-NMR (300 MHz, DMSO-d_6): δ(ppm) 7.70 (s, 1H), 7.60 (m, 3H), 7.12 (d, J = 8.7 Hz, 1H), 5.14 (d, J = 3.6 Hz, 1H), 4.61 (d, J = 3.6 Hz, 1H), ^{13}C-NMR (75 MHz, DMSO-d_6): δ(ppm) 163.1, 149.0, 132.9, 131.3, 120.3, 119.1, 118.6, 116.4, 112.8, 48.4, 36.7, 32.3, ESI-MS (m/z) = 314.9 $(M+H)^+$.

2-(2-amino-3-cyano-6-nitro-4*H*-chromen-4-yl)malononitrile (5ad)



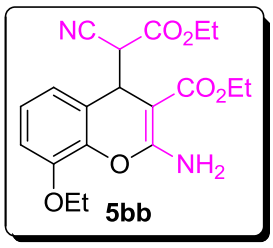
White solid; mp: 178.2 ˚C (lit. 180-181˚C); FTIR (KBr, cm^{-1}): 3405, 3312, 2908, 2255, 2198, 1654, 1590, 1525, 1427, 1345, 1250, 1088, 1034; ^{1}H-NMR(300MHz, DMSO-d_6): δ(ppm) 8.50 (s, 1H), 8.28 (d, 1H, J = 8.7 Hz), 7.78 (s, 2H); 7.39 (d, J = 9.0 Hz, 1H), 5.21 (d, J = 3.3 Hz, 1H); 4.79 (d, J = 3.6 Hz, 1H); ^{13}C-NMR(75 MHz, DMSO-d_6):δ (ppm) 162.7, 154.1, 143.8, 125.9, 125.3, 119.2, 118.8, 118.0, 112.8, 112.6, 48.5, 36.8, 32.5; MS (m/z) = 282.0 $(M+H)^+$.

Ethyl 2-amino-4-(1-cyano-2-ethoxy-2-oxoethyl)-4*H*-chromene-3-carboxylate (5ba)



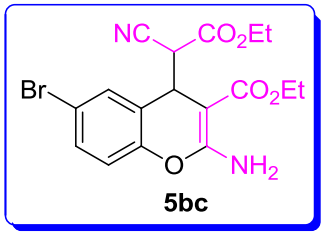
White solid; mp: 140.2 ˚C (lit. 141-143˚C); FTIR (KBr, cm^{-1}): 3400, 3310, 2912, 2250, 2188, 1650, 1588, 1520, 1429, 1345, 1252, 1085, 1035; ^{1}H-NMR(300MHz, DMSO-d_6): δ(ppm) 7.80 (s, 1H), 7.34 (d, J = 6.3 Hz, 1H), 7.17-7.06 (m, 3H), 4.52 (d, J = 7.5 Hz, 1H), 4.34 (d, J = 3.0 Hz, 1H), 4.19-3.99 (m, 4H), 1.26-1.08 (m, 6H); ^{13}C-NMR(75 MHz, DMSO-d_6):δ (ppm) 167.4, 165.1, 162.5, 150.0, 129.3, 128.6, 124.6, 121.4, 120.3, 116.5, 116.0, 71.2, 62.1, 59.1, 47.0, 46.3, 36.6, 36.6, 14.3, 14.2, 13.7, 13.5; MS (m/z) = 331.2 $(M+H)^+$

Ethyl 2-amino-4-(1-cyano-2-ethoxy-2-oxoethyl)-8-ethoxy-4H-chromene-3-carboxylate (5bb)



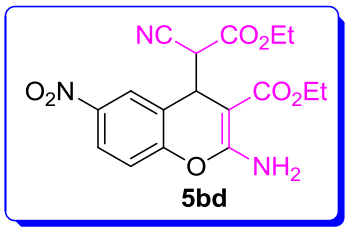
Light yellow solid; mp: 140.2 ˚C; FTIR (KBr, cm^{-1}): 3400, 3310, 2912, 2250, 2188, 1650, 1588, 1520, 1429, 1345, 1252, 1085, 1035; ^{1}H-NMR(300MHz, DMSO-d_6): δ(ppm) 7.81 (s, 1H), 7.03 (t, J = 2.5 Hz, 2H), 6.57 (d, J = 5.1 Hz, 1H),4.49 (d, J = 10.8 Hz, 1H), 4.31 (d, J = 1.8 Hz, 1H), 4.18-3.98 (m, 6H), 1.38-1.08 (m, 9H); ^{13}C-NMR(75 MHz, DMSO-d_6):δ (ppm) 167.5, 165.1, 162.4, 149.0, 146.4, 139.6, 124.4, 122.4, 121.2, 119.0, 118.5, 117.5, 116.2, 113.2, 100.3, 71.2, 64.2, 62.1, 59.1, 47.1, 36.5, 36.4, 14.6, 14.2, 14.0, 13.8, 13.5; MS (m/z) = 375.2 $(M+H)^+$

Ethyl 2-amino-6-bromo-4-(1-cyano-2-ethoxy-2-oxoethyl)-4*H*-chromene-3-carboxylate (5bc)



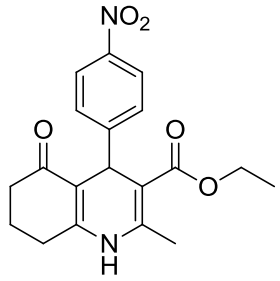
Gray solid; mp: 140.2 ˚C (lit. 141-143˚C); FTIR (KBr, cm^{-1}): 3402, 3315, 2912, 2251, 2185, 1652, 1581, 1522, 1425, 1344, 1250, 1080, 1039; ^{1}H-NMR (300MHz, DMSO-d_6): δ(ppm) 7.80 (s, 1H), 7.53 (d, 1H, J = 8.1 Hz), 7.21 (s, 1H), 7.09 (d, J = 8.7 Hz, 1H,), 4.55 (d, J = 3.3 Hz, 1H), 4.36 (d, J = 3.9 Hz, 1H), 4.21-4.00 (m, 4H), 1.23-1.10 (m, 6H); ^{13}C-NMR(75 MHz, DMSO-d_6): δ (ppm) 168.4, 165.9, 163.1, 150.0, 133.0, 131.8, 131.1, 124.3, 123.2, 119.3, 116.9, 71.7, 63.5, 63.2, 60.5, 47.7, 47.5, 37.0, 36.9, 15.0, 14.6, 14.3; MS (m/z) = 409.1 (M+H)+

Ethyl 2-amino-4-(1-cyano-2-ethoxy-2-oxoethyl)-6-nitro-4*H*-chromene-3-carboxylate (5bd)



Light yellow solid; Melting Point: 135.2 ˚C (lit. 134-135 ˚C); FTIR (KBr, cm-1): 3405, 3310, 2912, 2251, 2185, 1652, 1581, 1522, 1425, 1344, 1250, 1080, 1039; ^{1}H-NMR (300MHz, DMSO-d_6): δ (ppm) 8.65 (s, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.19 (d, J = 7.8 Hz, 2H), 6.92 (d, J = 8.1 Hz, 1H), 4.33-4.27 (m, 3H), 4.13-4.06 (m, 3H), 1.28-1.26 (m, 6H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ (ppm) 162.3, 149.0, 148.7, 147.2, 119.4, 119.0, 118.5, 117.5, 115.9, 100.3, 64.4, 62.2, 14.4, 14.0; MS (m/z) = 376.2 (M+H)+

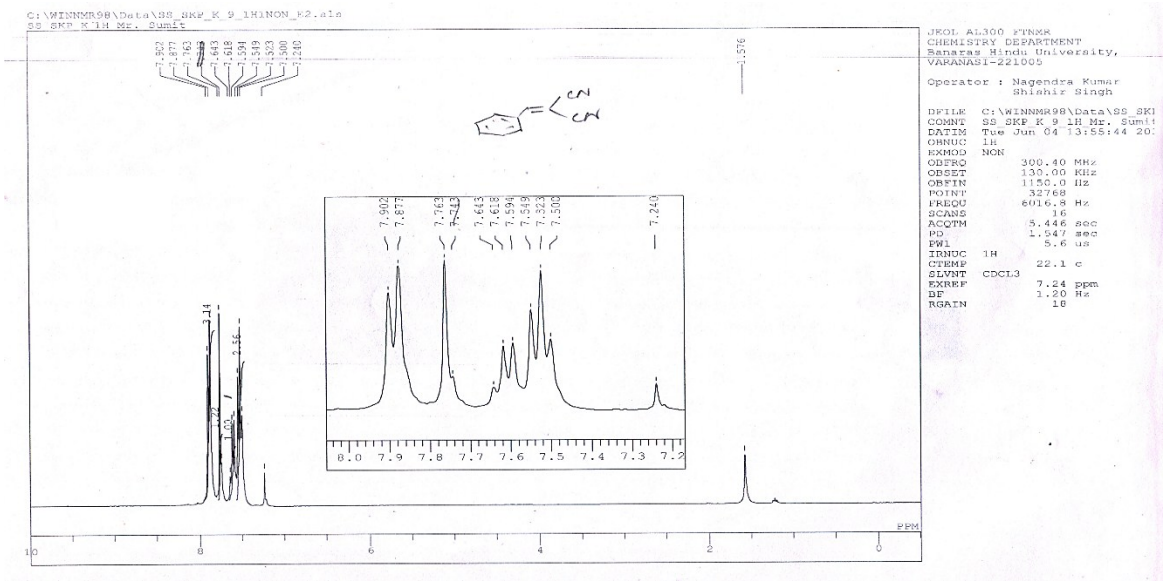
Ethyl 2-methyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate



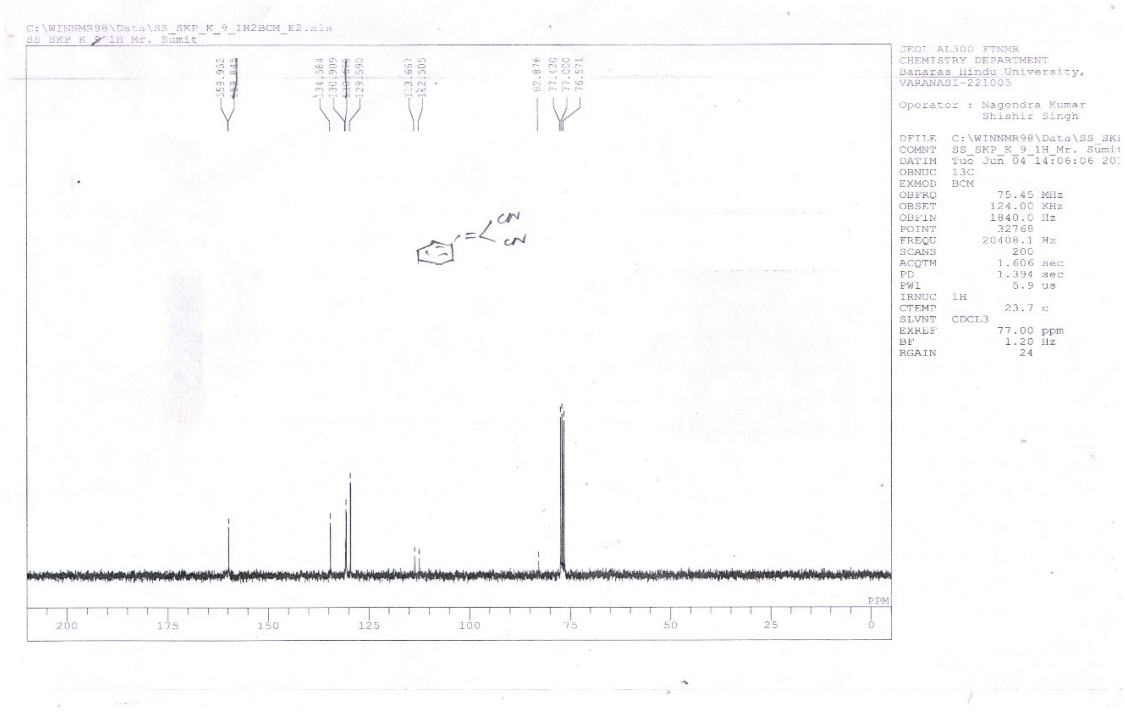
State: Solid; Colour: Yellow; Yield: 80 % (15 min); Melting Point; 133 °C; FTIR (KBr, cm^{-1}): 3289, 3207, 3075, 2947, 1698, 1642, 1604, 1516, 1485, 1226; ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 8.05 (d, J = 8.0 HZ, 2H), 7.46 (d, J = 12.0 Hz, 2H), 5.17 (s, 1H), 4.79 (s, 1H), 4.05 (q, J = 6.6 Hz, 2H), 2.45 (t, J = 12.0 Hz, 2H), 2.37 (s, 3H), 2.32 (t, 6.0 Hz, 2H), 2.02-1.97 (m, 2H), 1.17 (t, J = 6.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 196.0, 166.9, 154.6, 151.2, 146.0, 144.7, 128.8, 123.2, 111.8, 104.5, 60.0, 37.0, 36.8, 27.0, 20.8, 19.1, 14.1.

5. ^{1}H and ^{13}C NMR spectra of the selected synthesized derivatives

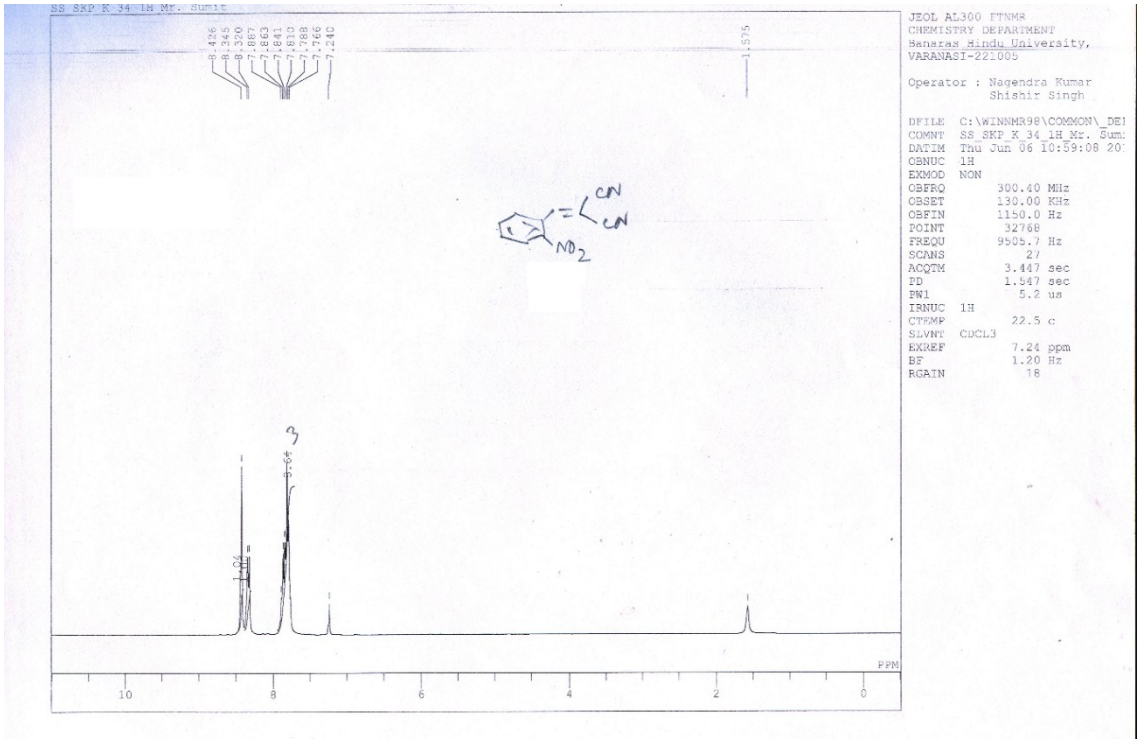
^{1}H-NMR of 2-benzylidenemalononitrile (3aa)



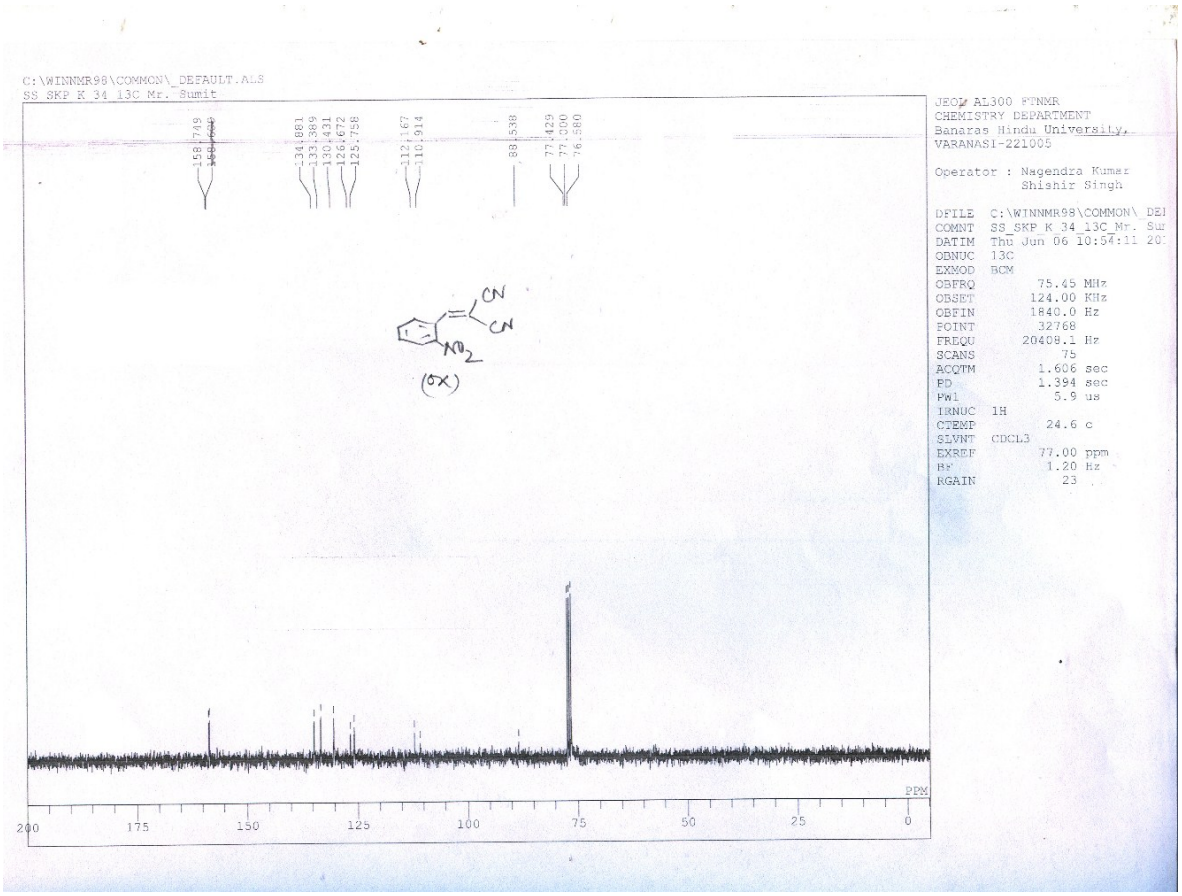
^{13}C-NMR of 2-benzylidenemalononitrile (3aa)



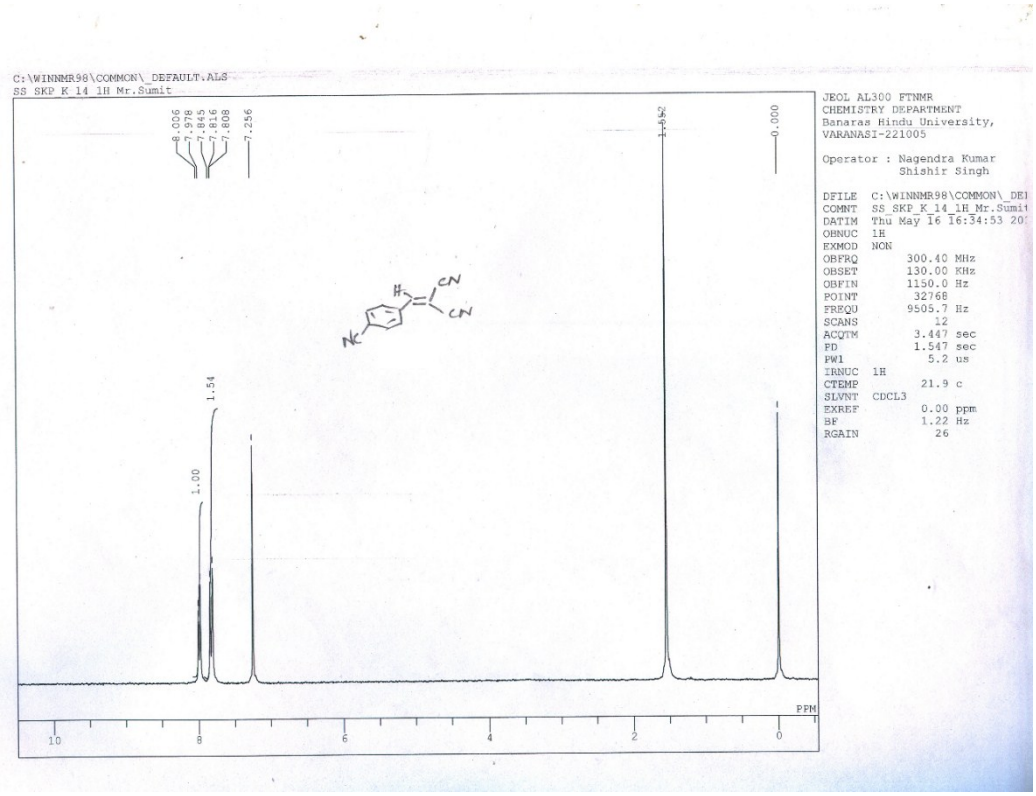
^{1}H-NMR of 2-(2-nitrobenzylidene)malononitrile (3ab)



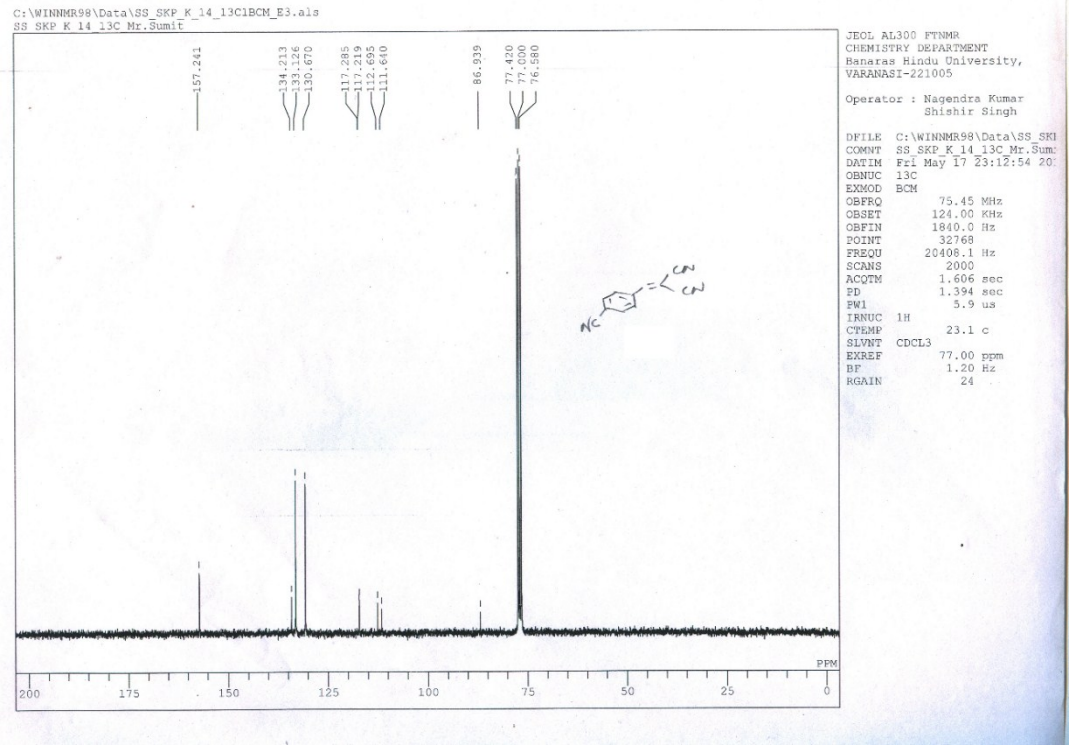
^{13}C-NMR of 2-(2-nitrobenzylidene)malononitrile (3ab)



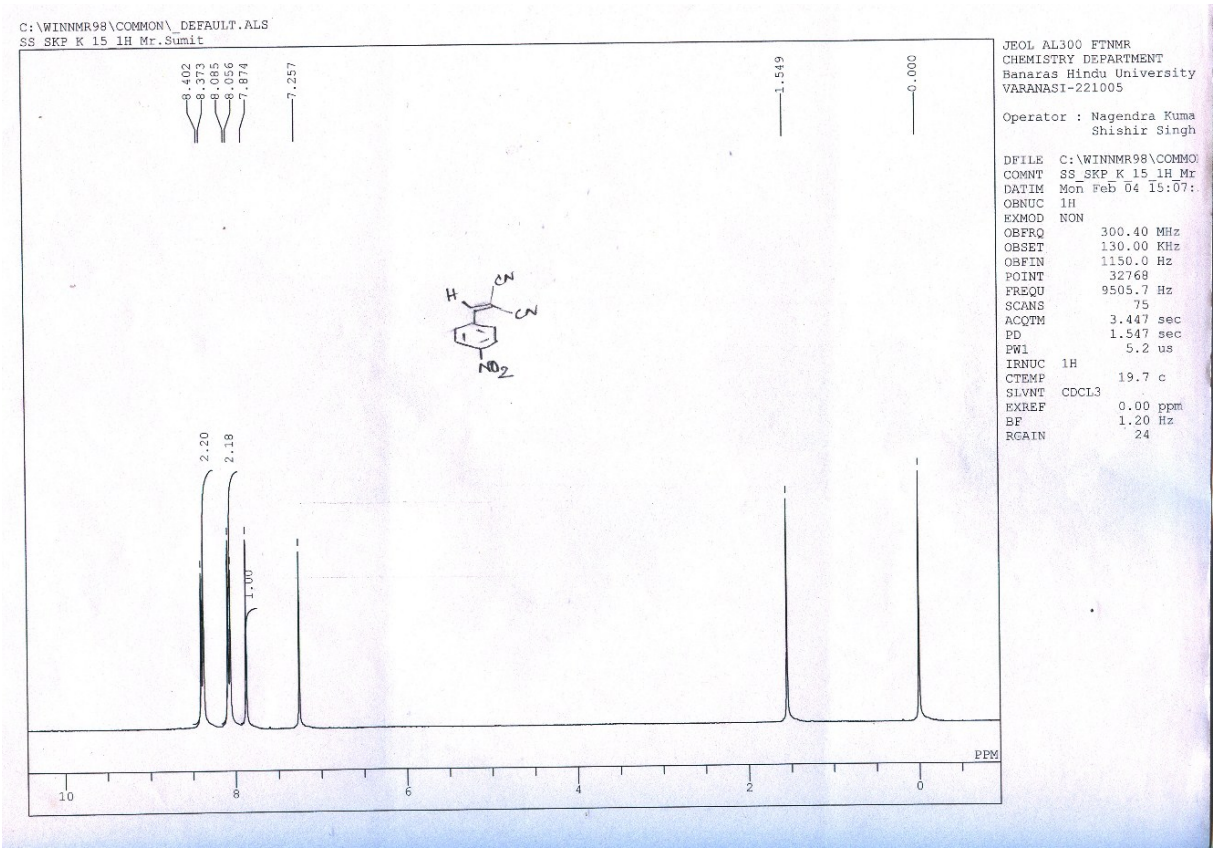
^{1}H-NMR of 2-(4-cyanobenzylidene)malononitrile (3ac)



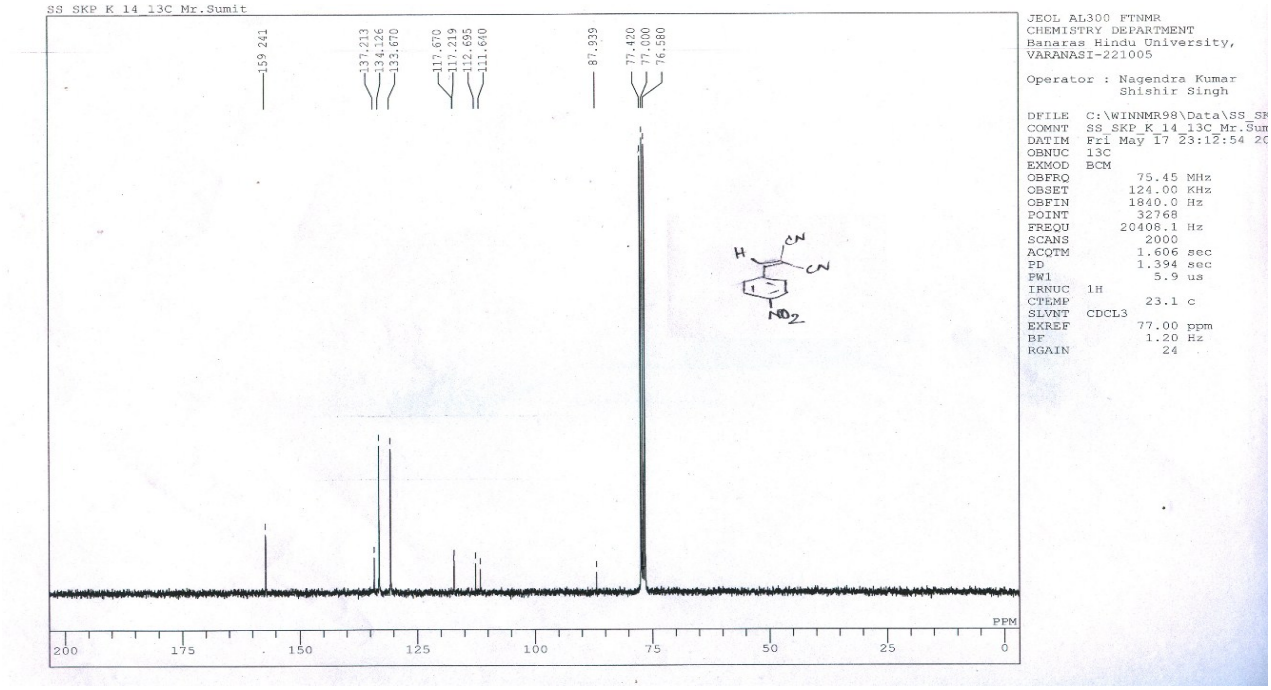
^{13}C-NMR of 2-(4-cyanobenzylidene)malononitrile (3ac)



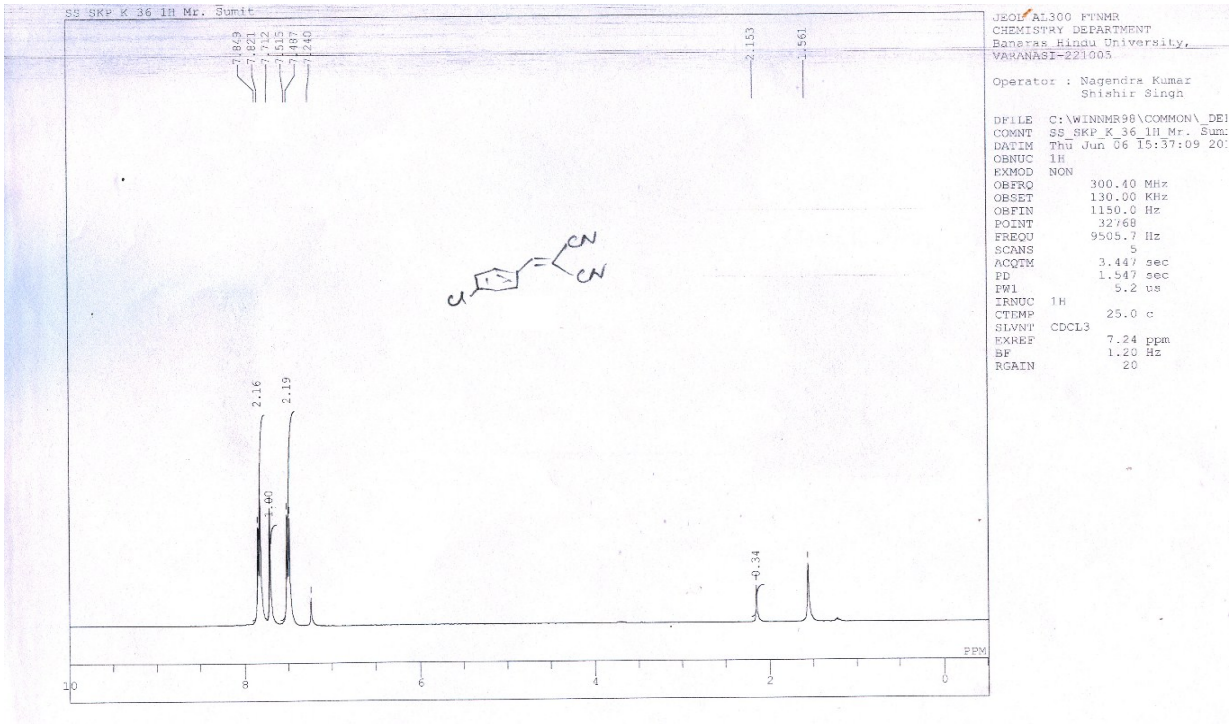
[1]H-NMR of 2-(4-nitrobenzylidene)malononitrile (3ad)



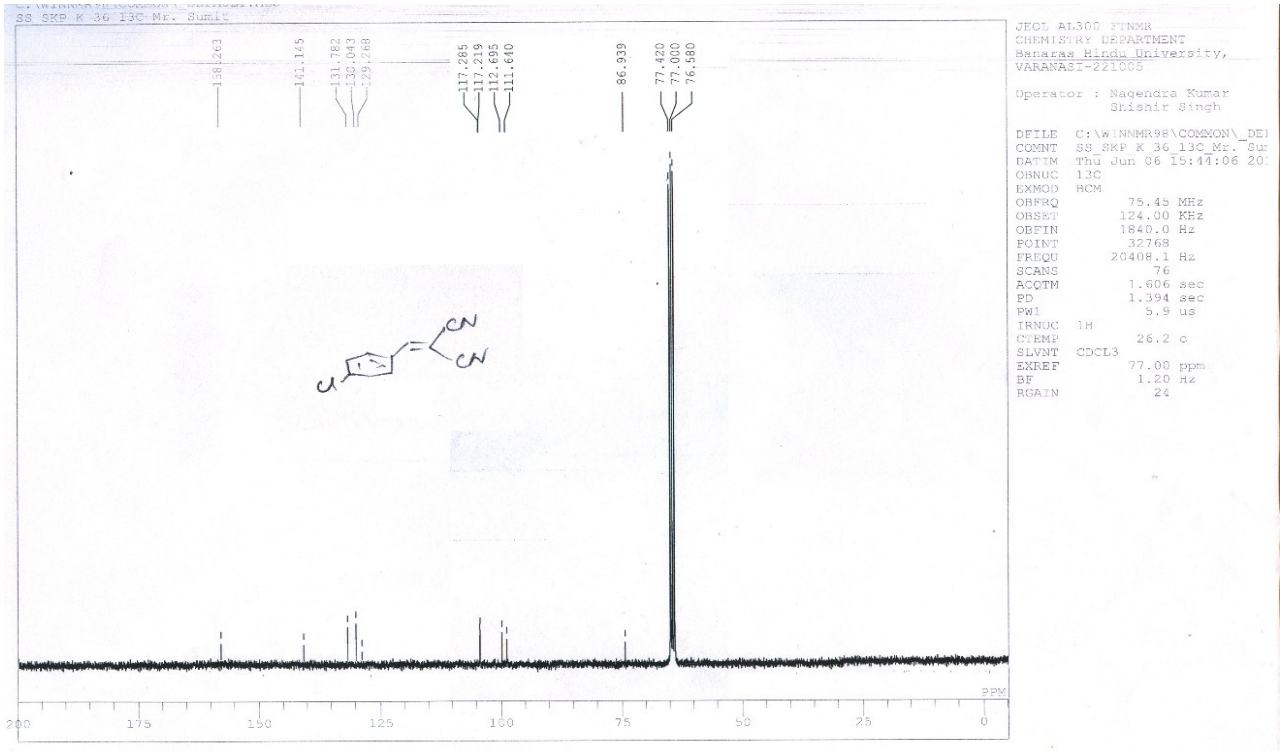
[13]C-NMR of 2-(4-nitrobenzylidene)malononitrile (3ad)



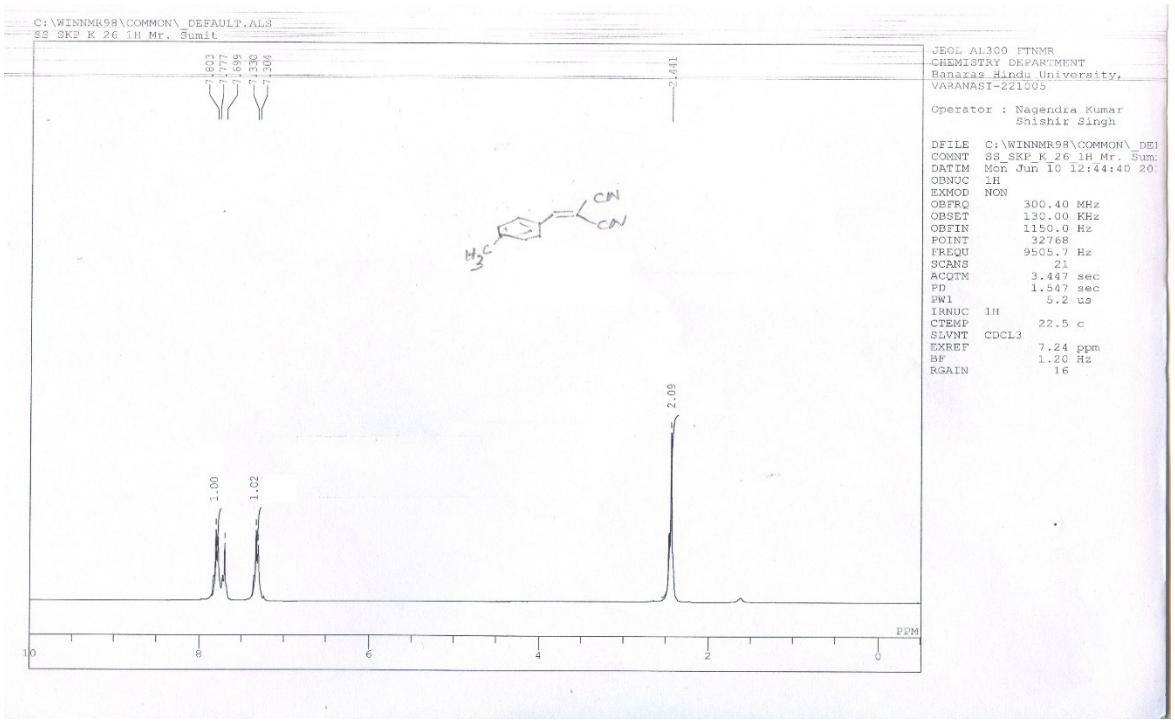
[1]H-NMR of 2-(4-chlorobenzylidene)malononitrile (3ae)



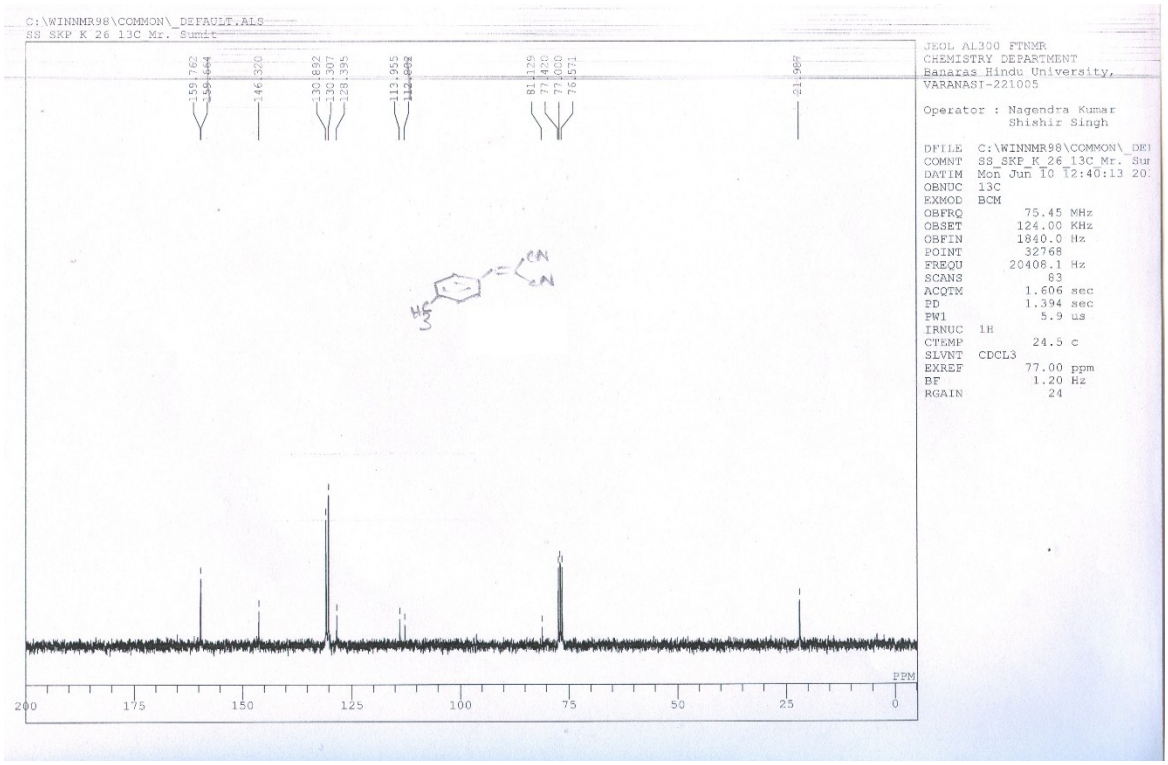
[13]C-NMR of 2-(4-chlorobenzylidene)malononitrile (3ae)



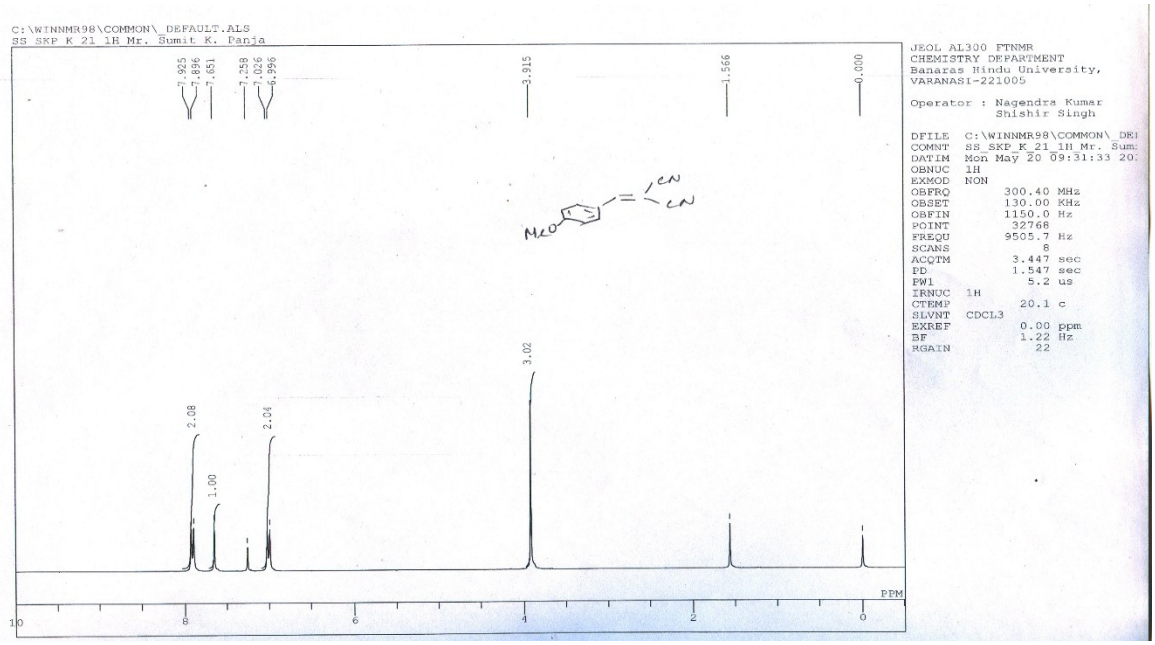
[1]H-NMR of 2-(4-methylbenzylidene)malononitrile (3af)



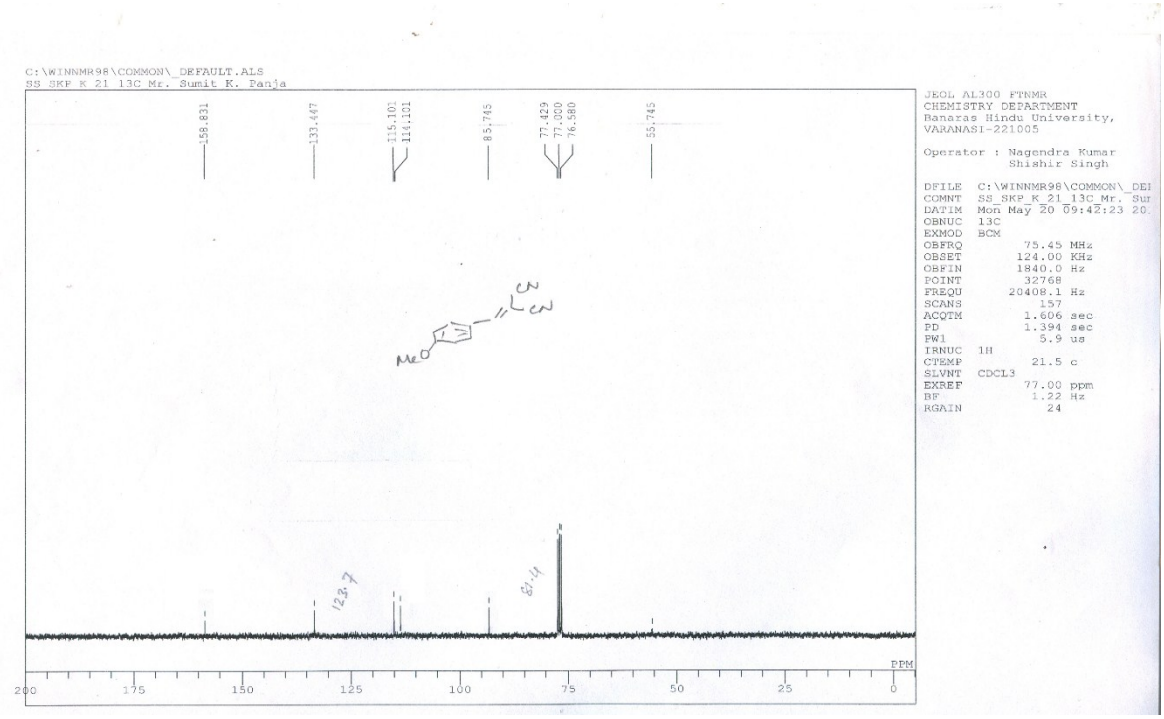
[13]C-NMR of 2-(4-methylbenzylidene)malononitrile (3af)



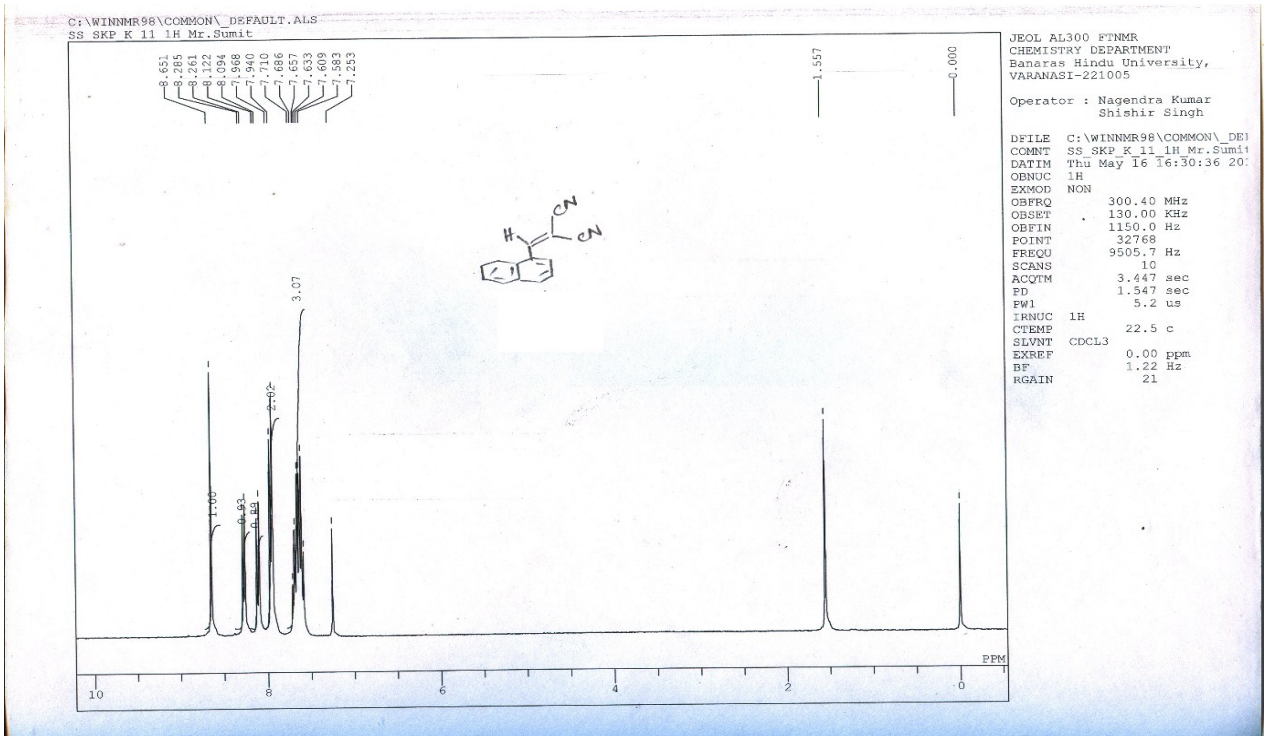
^{1}H-NMR of 2-(4-methoxybenzylidene)malononitrile (3ag)



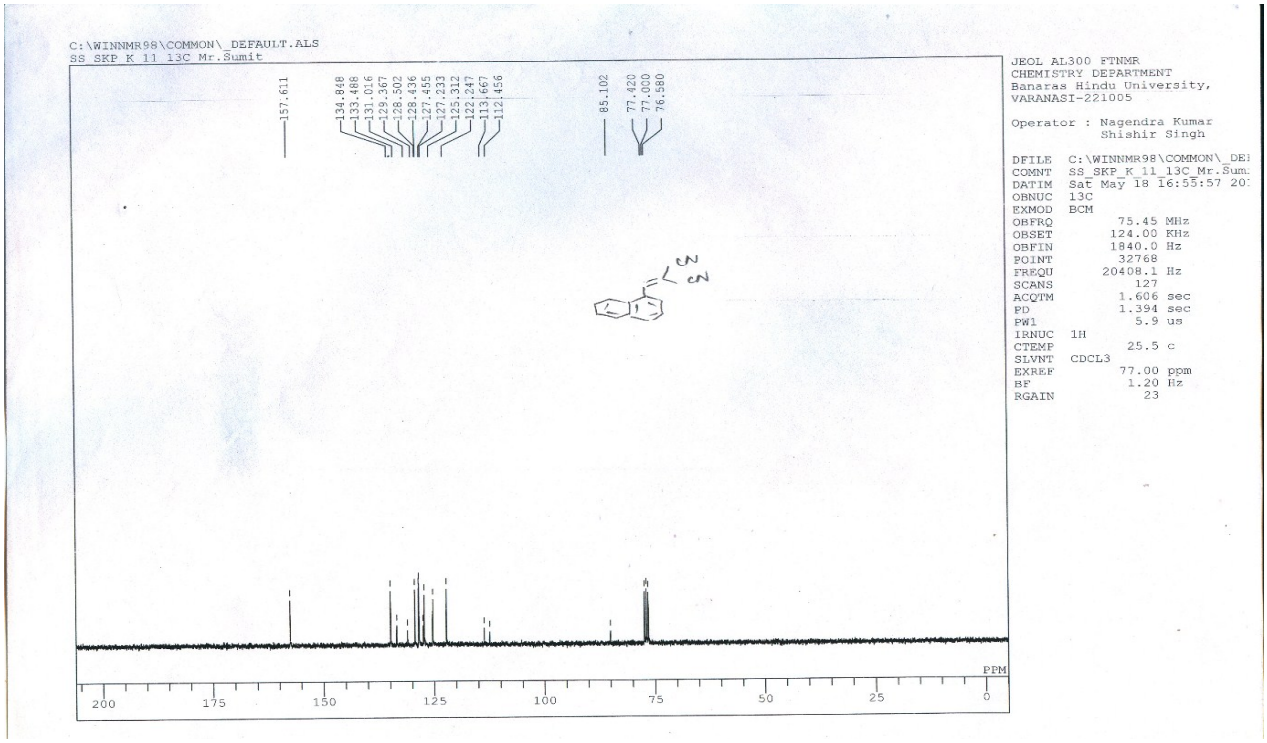
^{13}C-NMR of 2-(4-methoxybenzylidene)malononitrile (3ag)



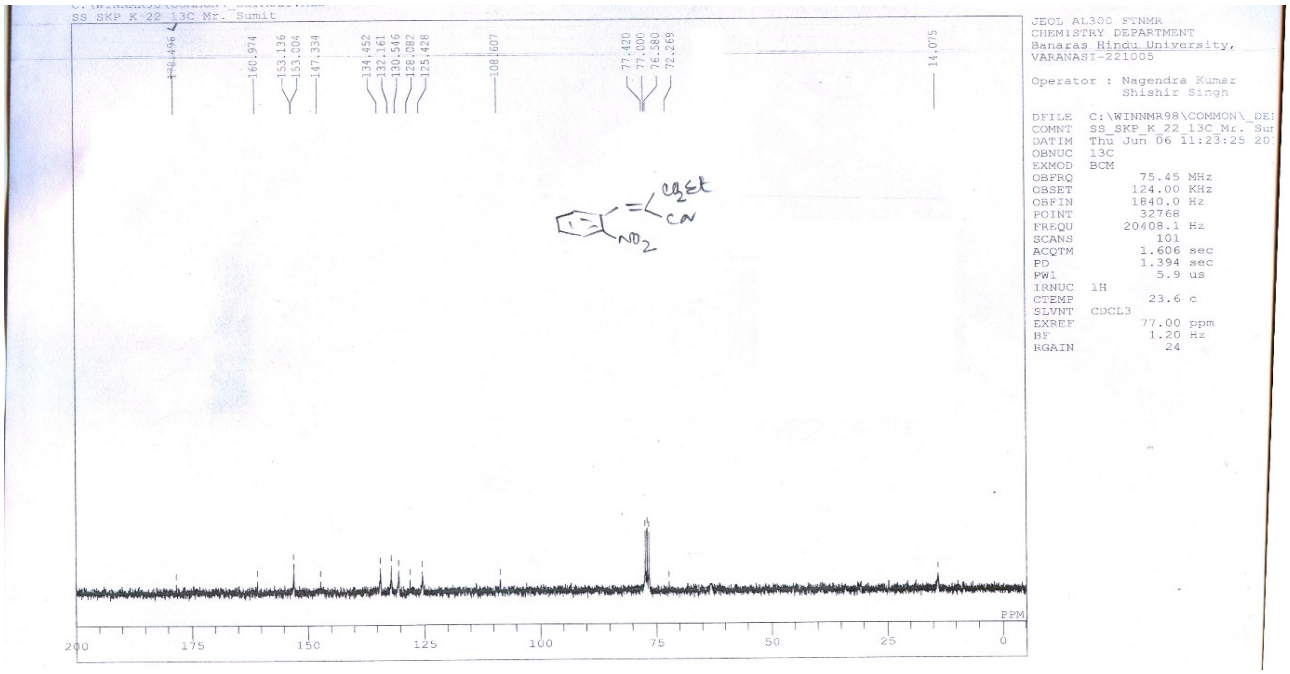
^{1}H-NMR of 2-(naphthalen-1-ylmethylene)malononitrile (3aj)



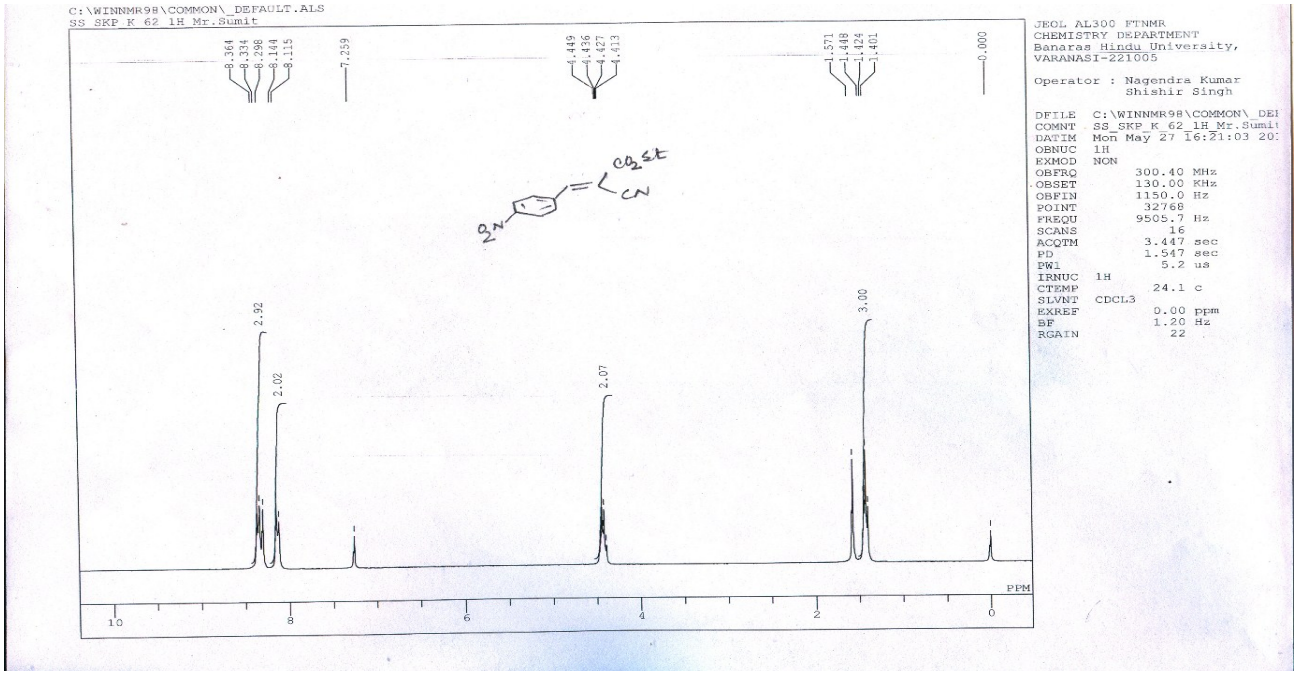
^{13}C-NMR of 2-(naphthalen-1-ylmethylene)malononitrile (3aj)



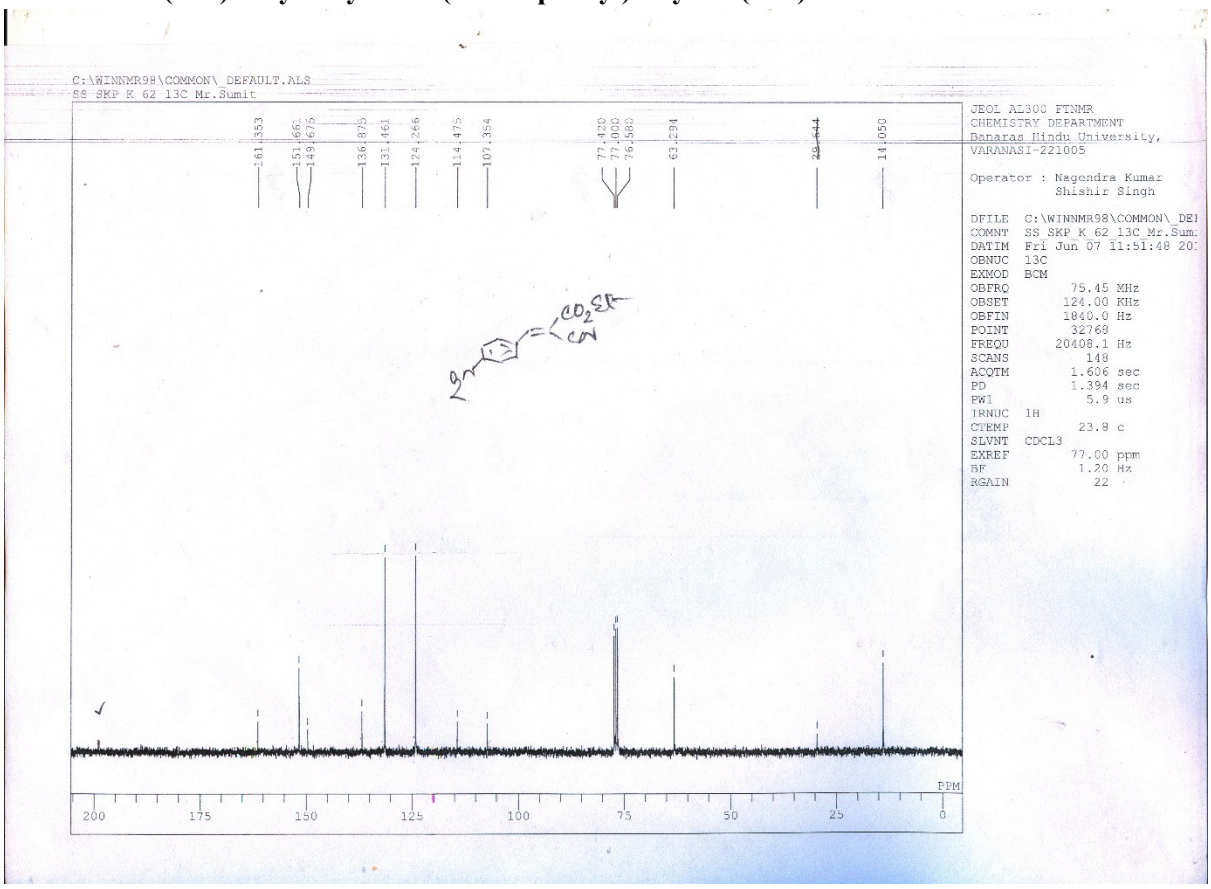
^{13}C-NMR of (E/Z)-ethyl-2-cyano-3-(2-nitrophenyl)acrylate (3bb)



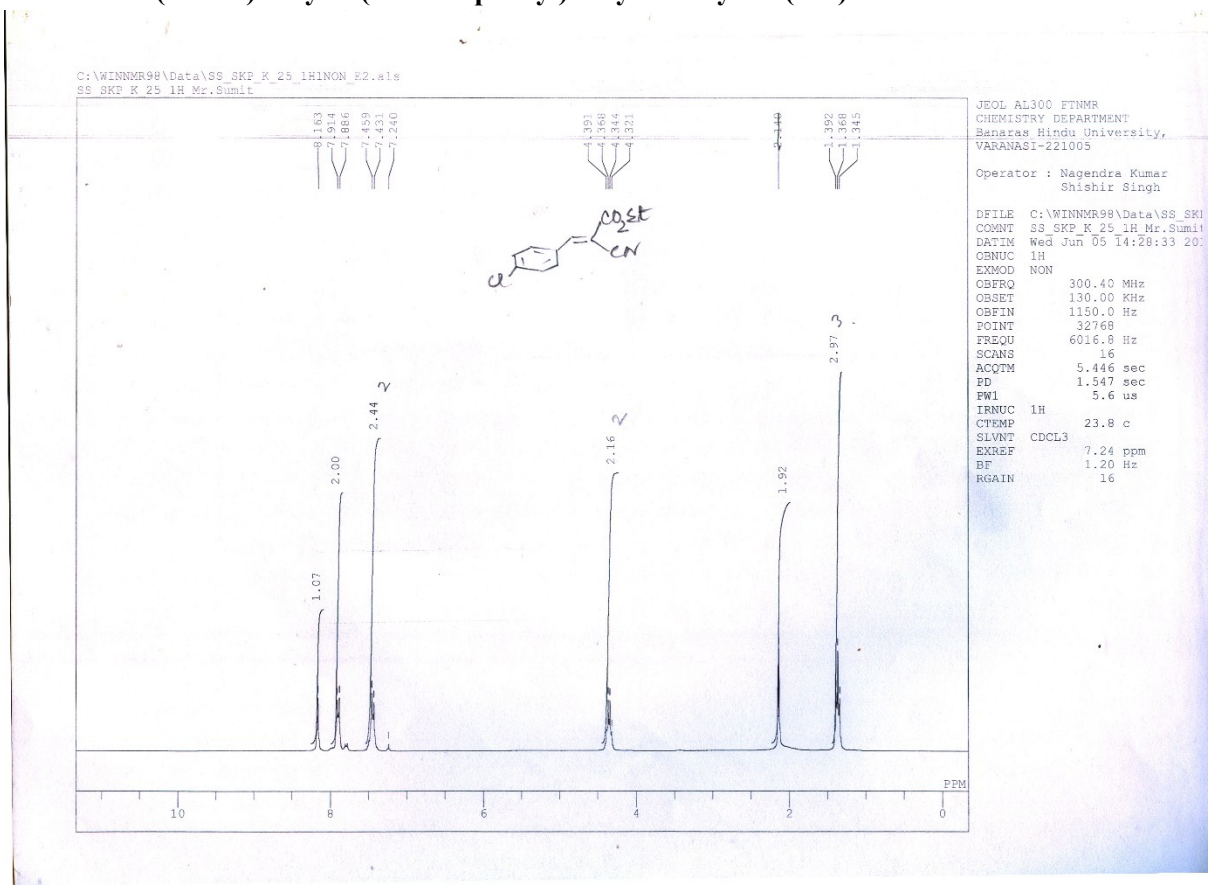
^{1}H-NMR of (E/Z)-ethyl 2-cyano-3-(4-nitrophenyl)acrylate (3bd)



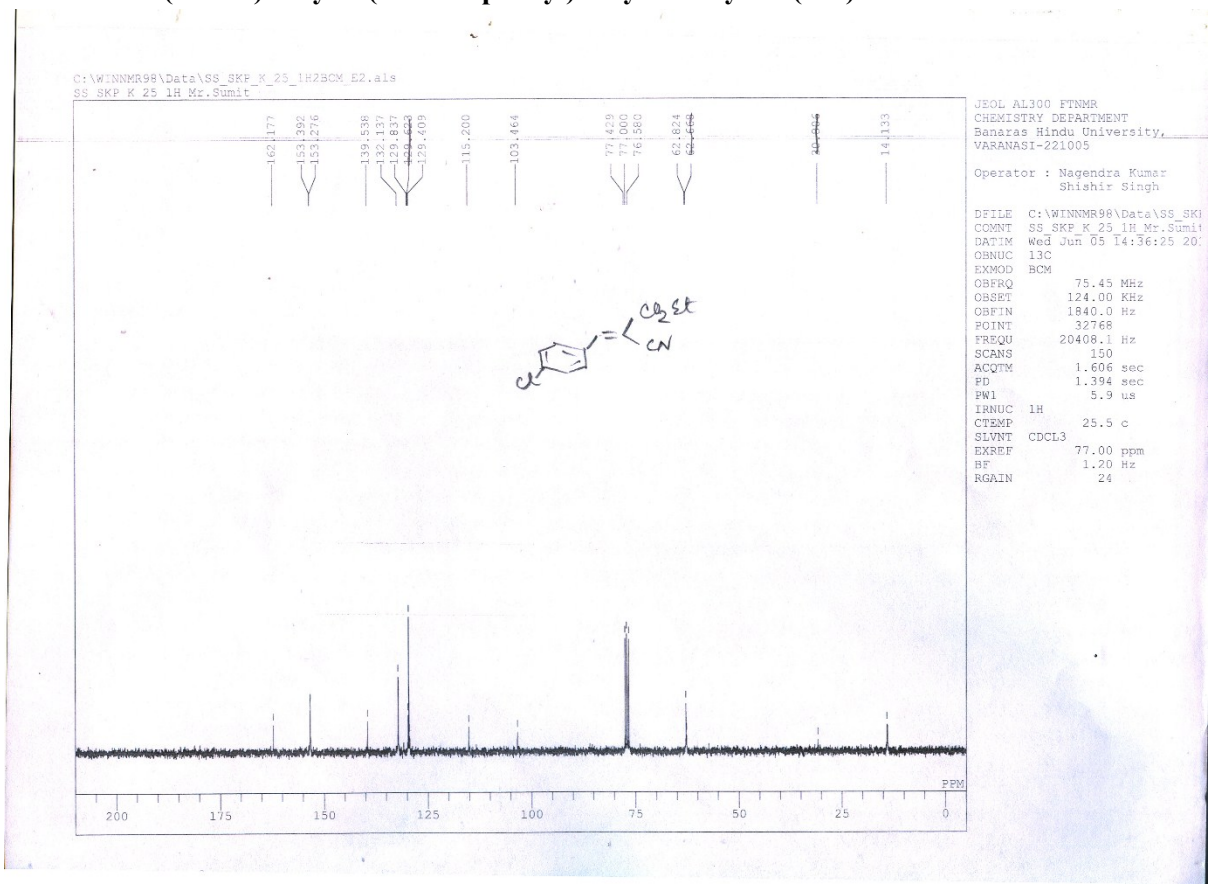
^{13}C-NMR of (E/Z)-ethyl 2-cyano-3-(4-nitrophenyl)acrylate (3bd)



^{1}H-NMR of (E or Z)-ethyl 3-(4-chlorophenyl)-2-cyanoacrylate (3be)

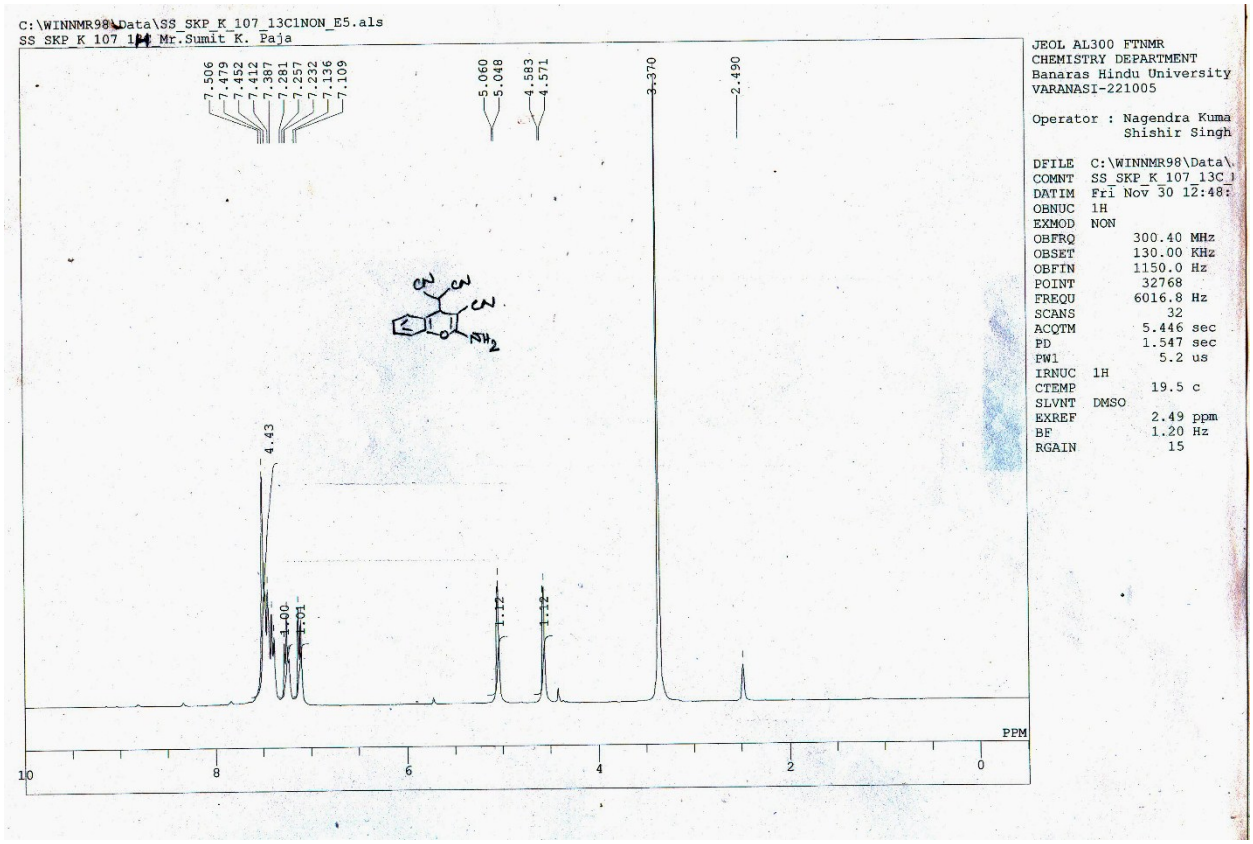


^{13}C-NMR of (E or Z)-ethyl 3-(4-chlorophenyl)-2-cyanoacrylate (3be)

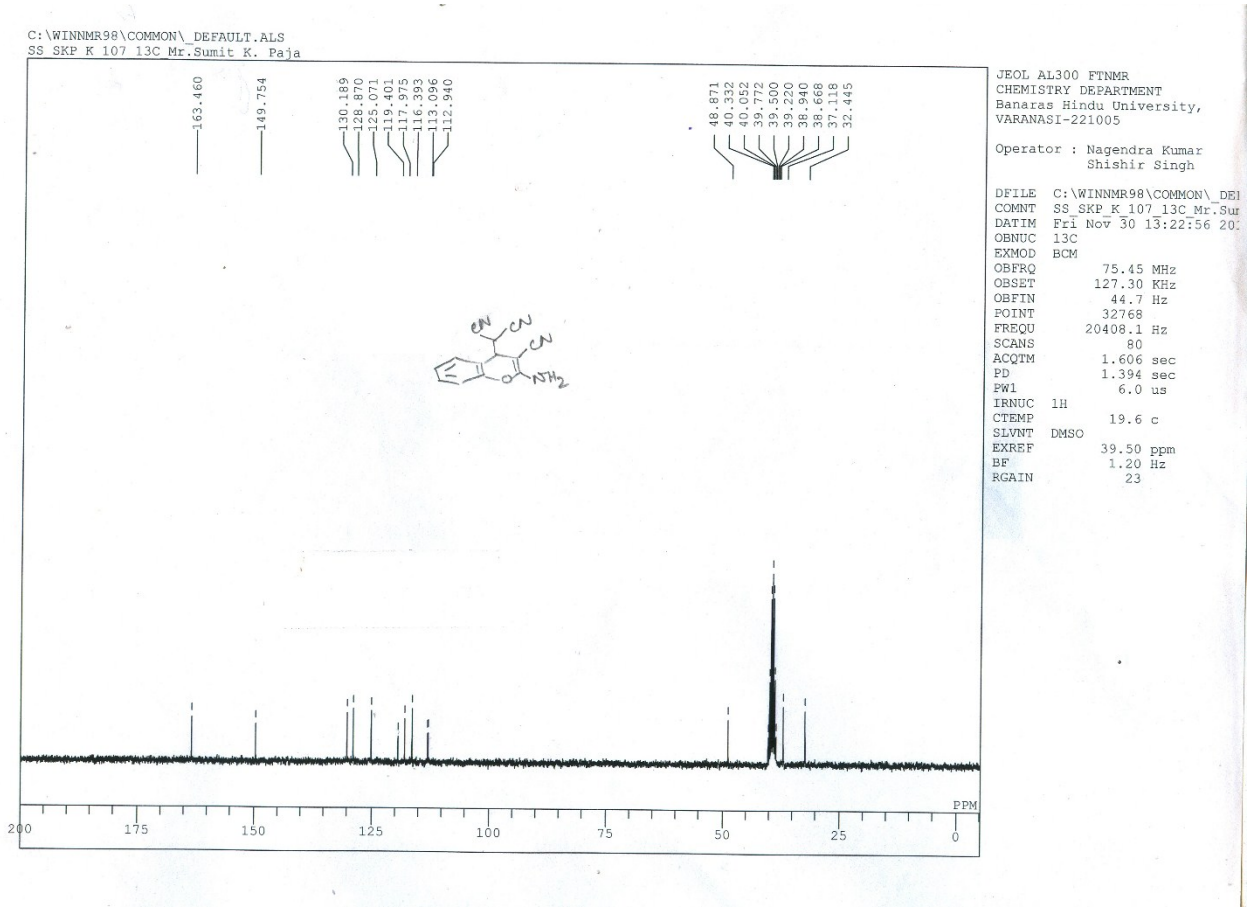


2-Amino-4*H*-Chromene Derivatives

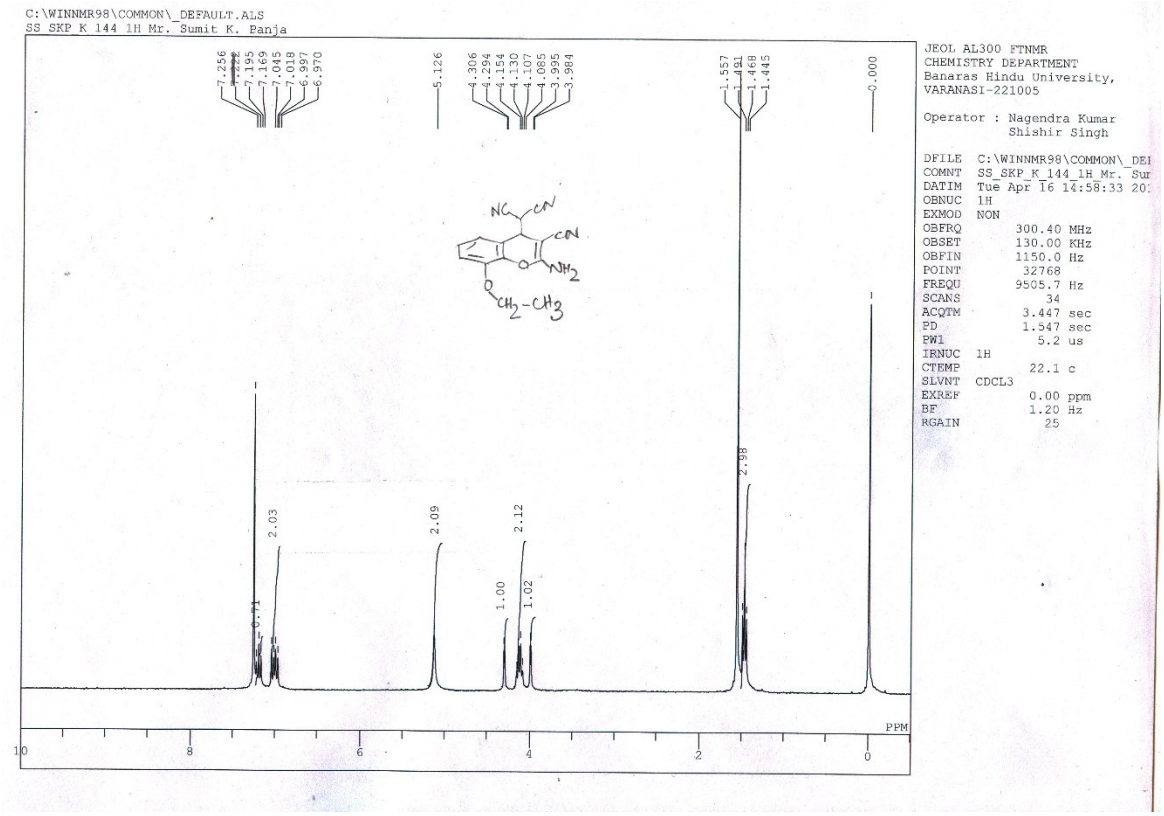
^{1}H-NMR of 2-(2-amino-3-cyano-4*H*-chromen-4-yl)malononitrile(5aa)



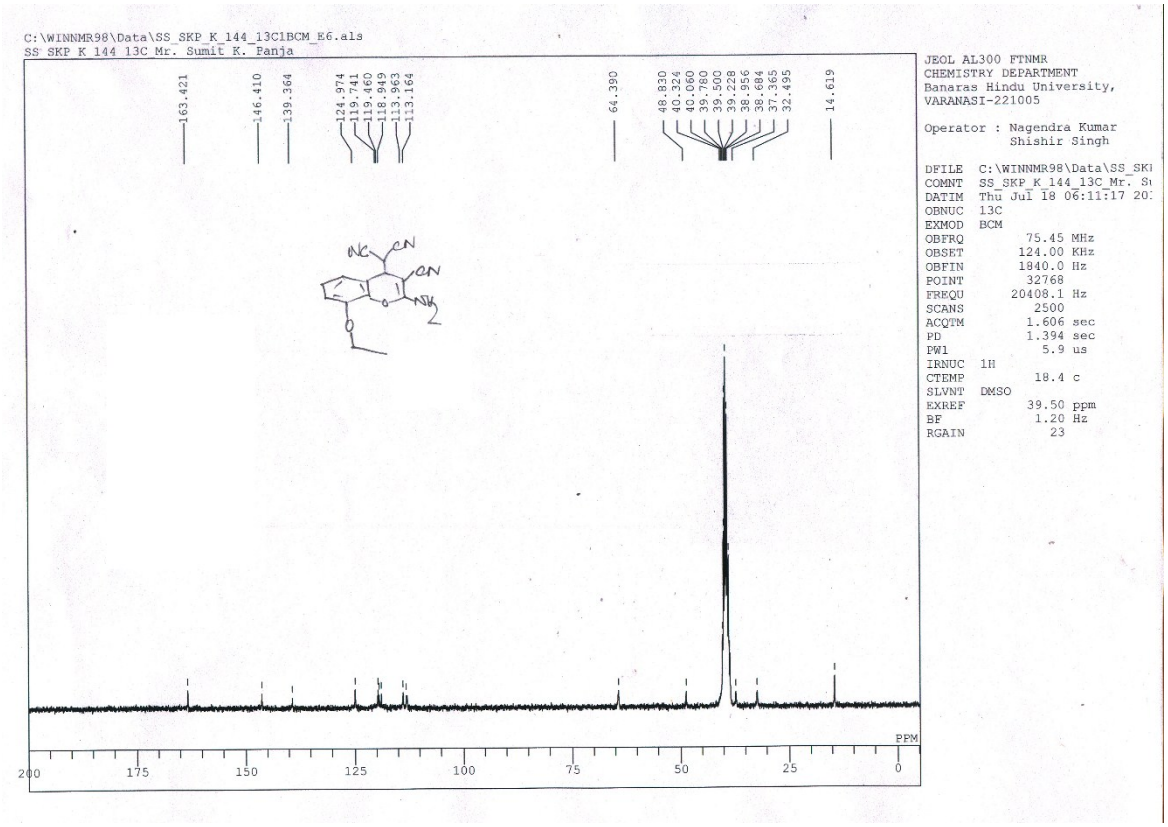
^{1}H-NMR of 2-(2-amino-3-cyano-4*H*-chromen-4-yl)malononitrile(5aa)



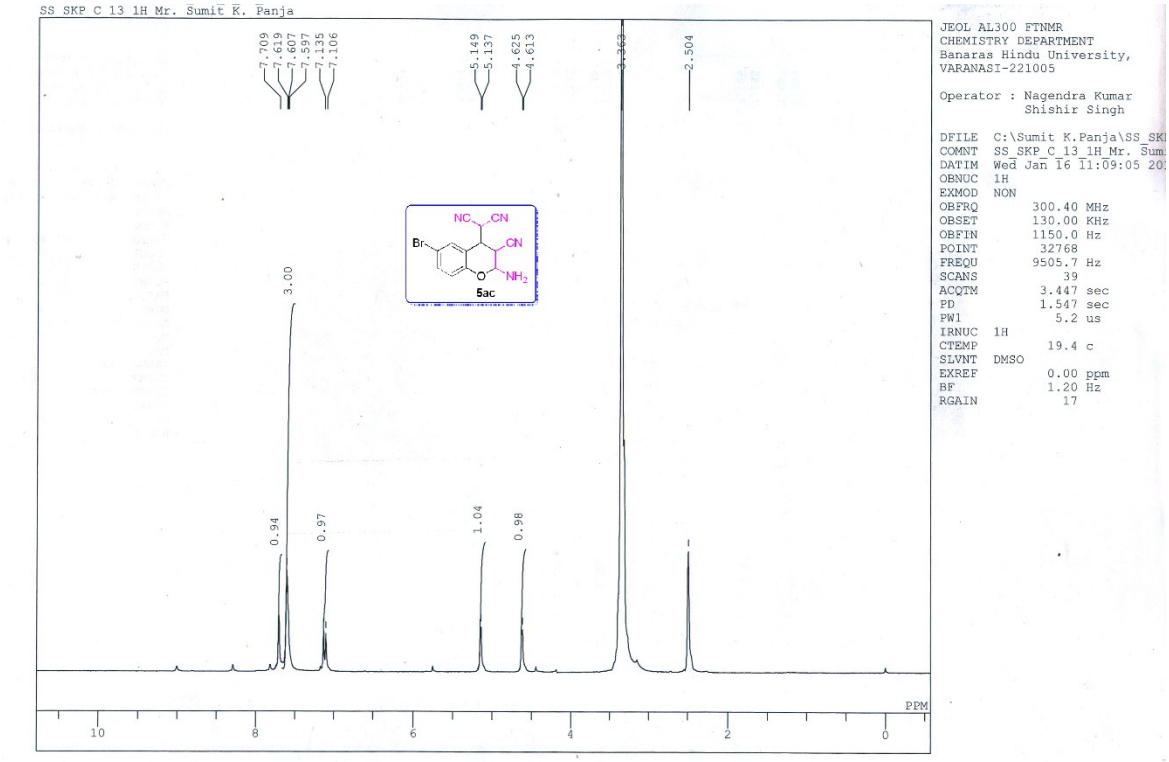
^{1}H-NMR of 2-(2-amino-3-cyano-8-ethoxy-4*H*-chromen-4-yl)malononitrile (5ab)



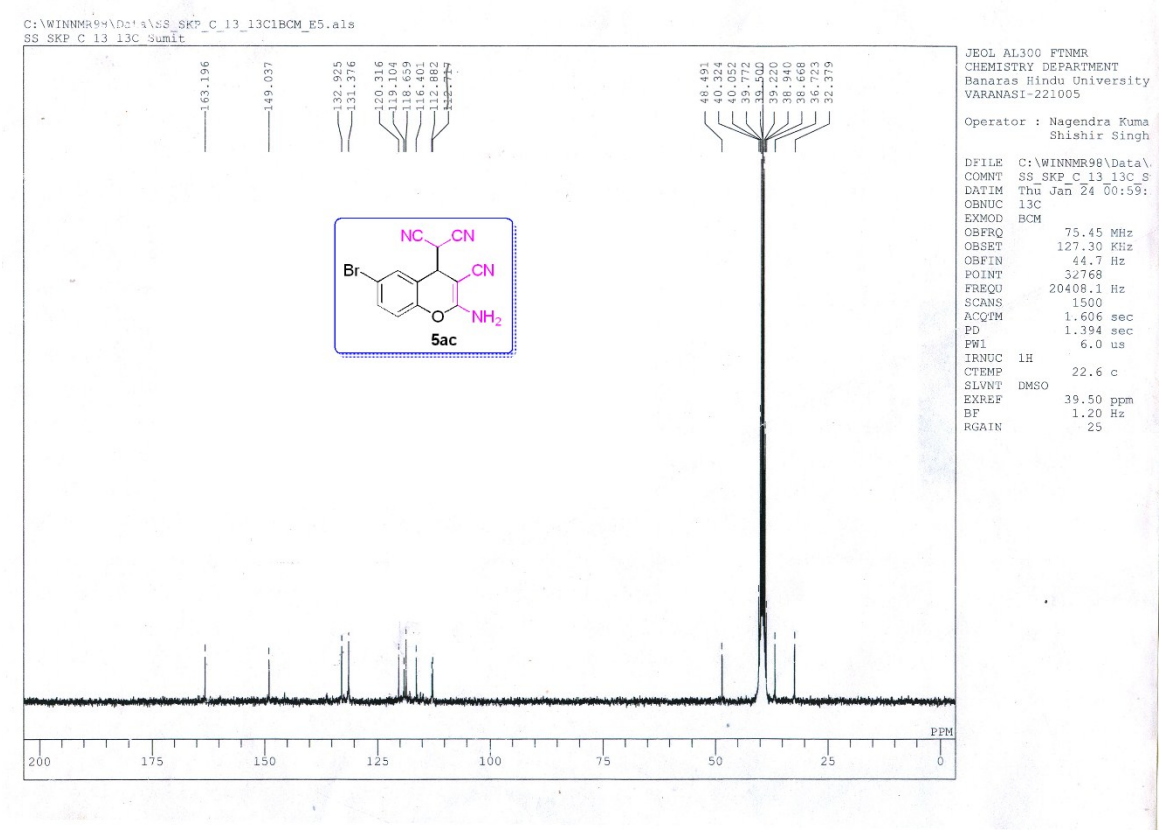
^{13}C-NMR of 2-(2-amino-3-cyano-8-ethoxy-4*H*-chromen-4-yl)malononitrile (5ab)



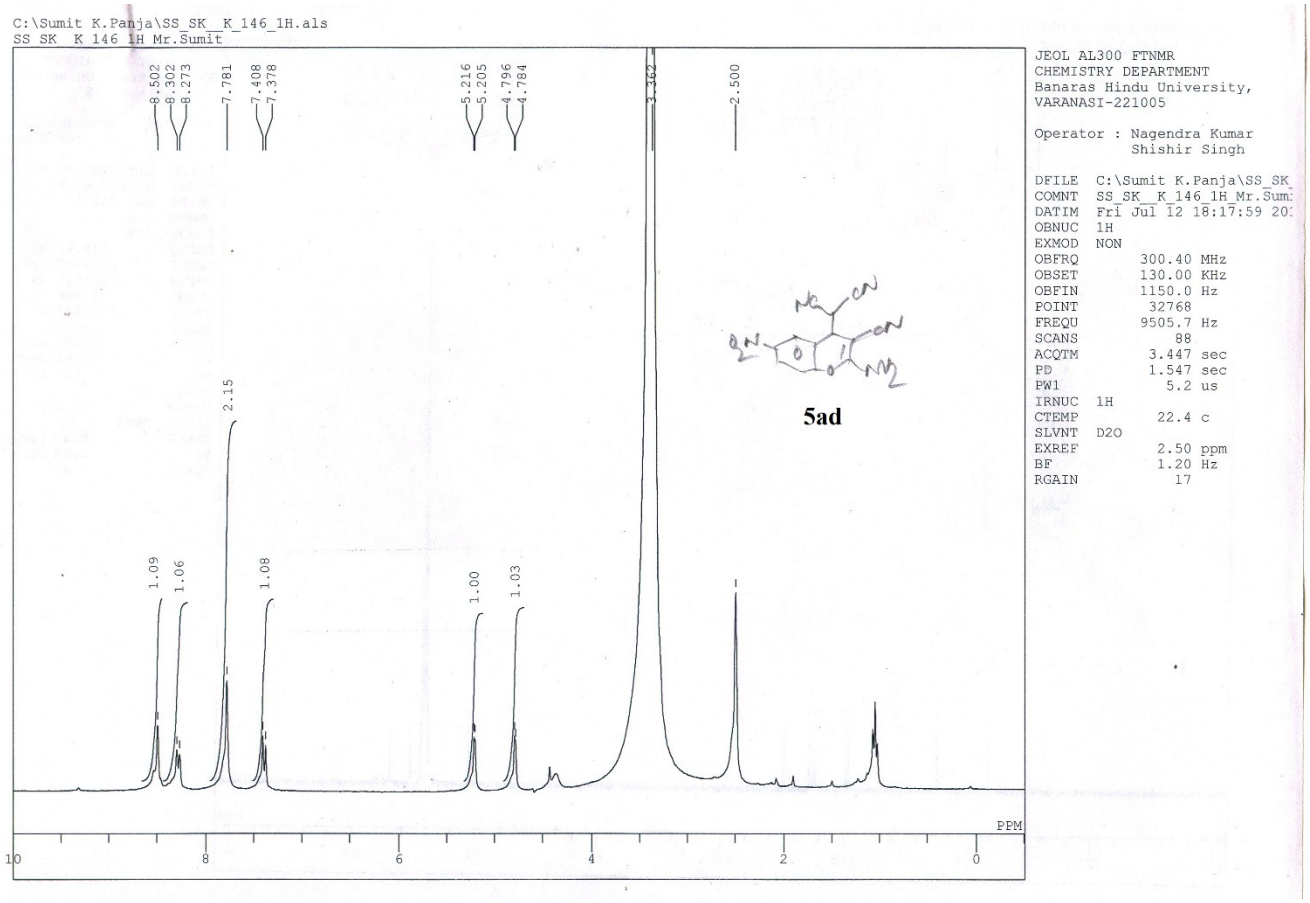
^{1}H-NMR of 2-(2-amino-6-bromo-3-cyano-4*H*-chromen-4-yl)malononitrile (5ac)



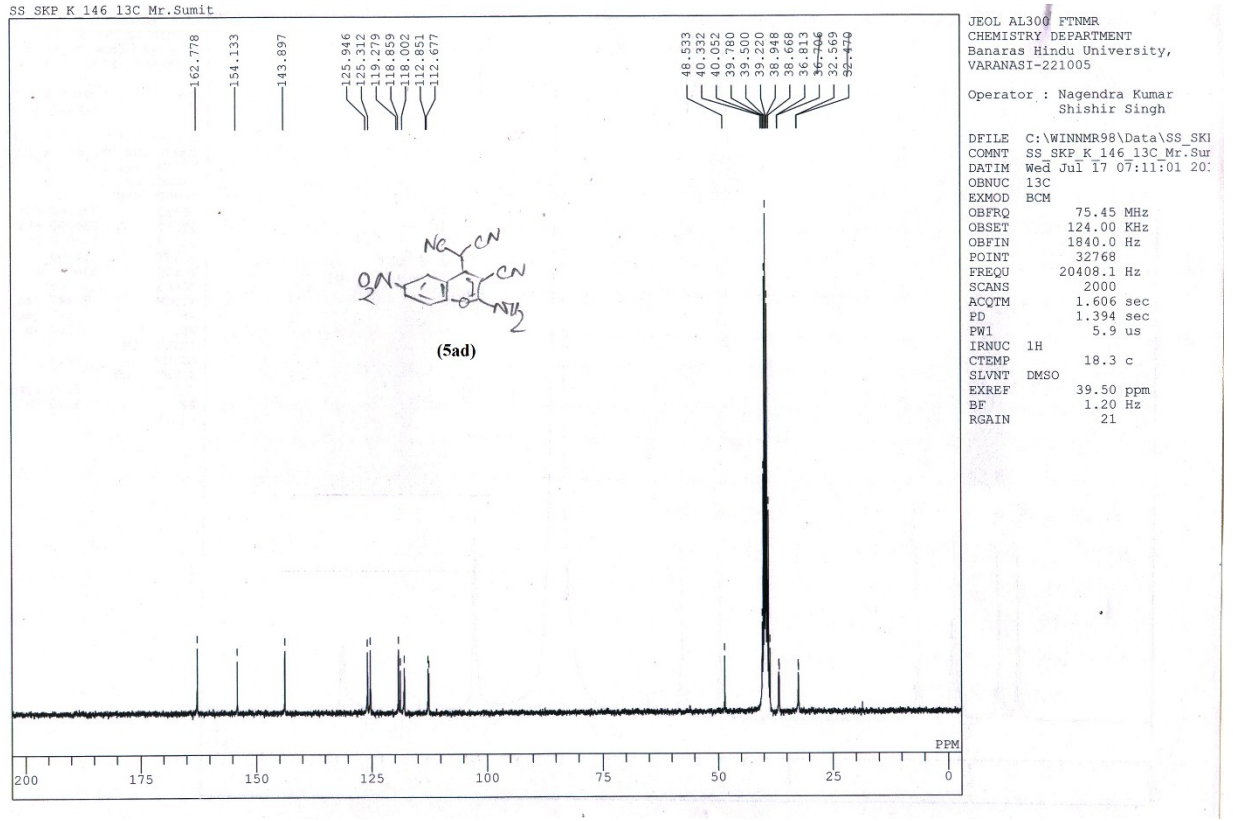
^{13}C-NMR of 2-(2-amino-6-bromo-3-cyano-4*H*-chromen-4-yl)malononitrile (5ac)



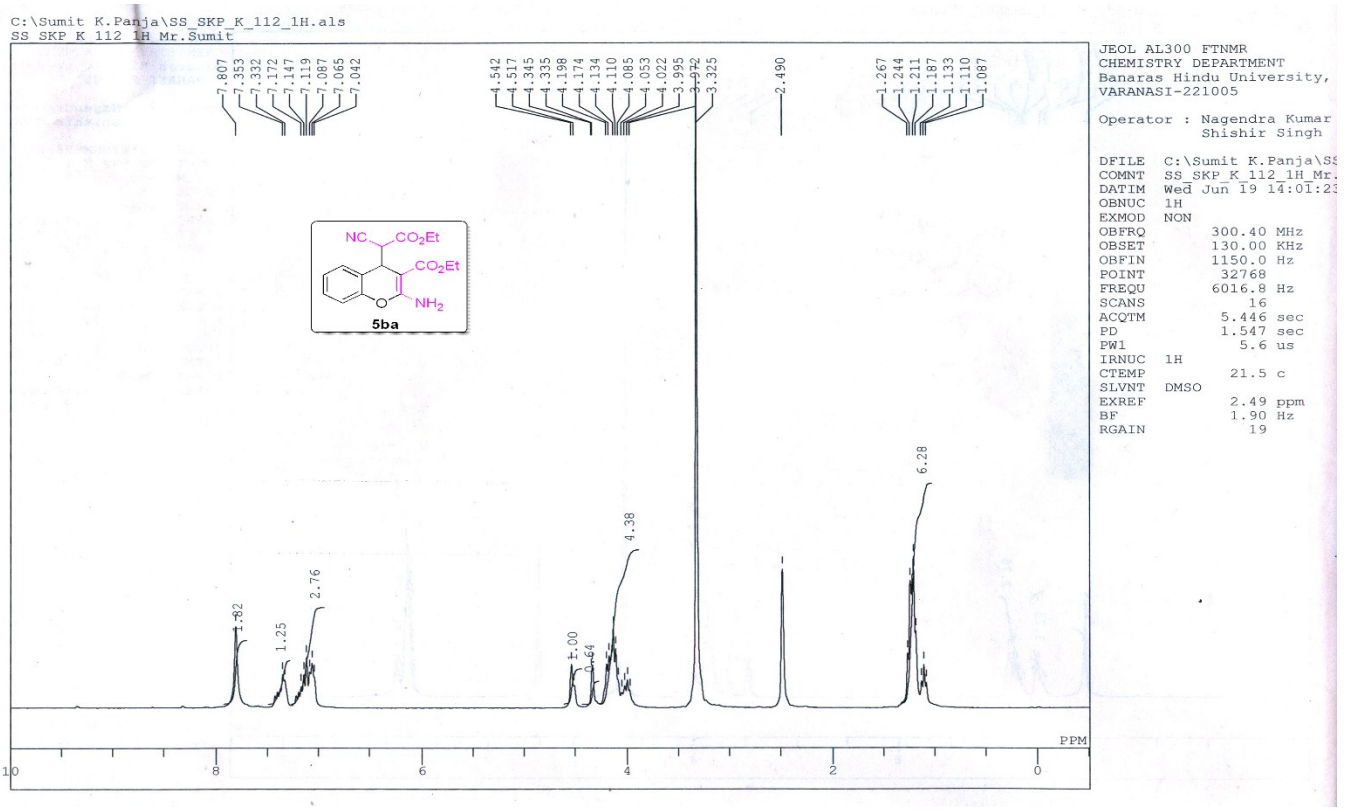
^{1}H-NMR of 2-(2-amino-3-cyano-6-nitro-4*H*-chromen-4-yl)malononitrile (5ad)



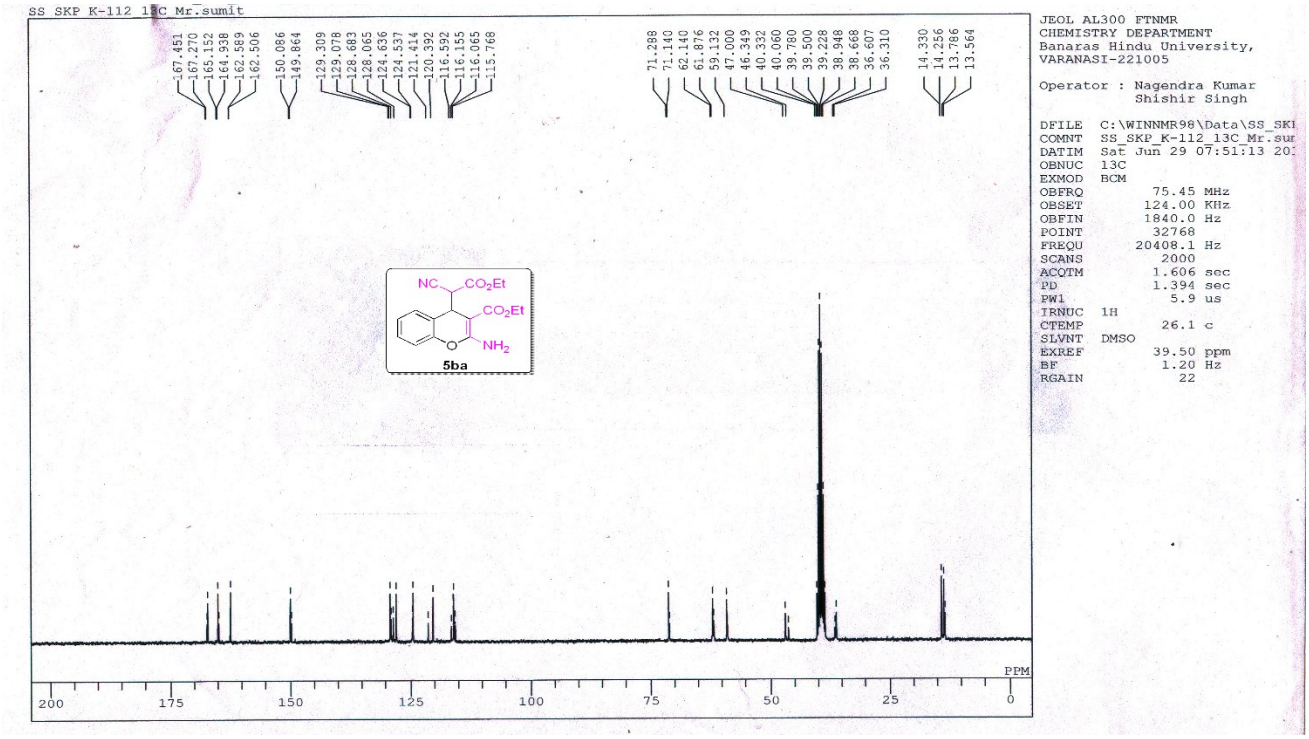
^{13}C-NMR of 2-(2-amino-3-cyano-6-nitro-4*H*-chromen-4-yl)malononitrile (5ad)



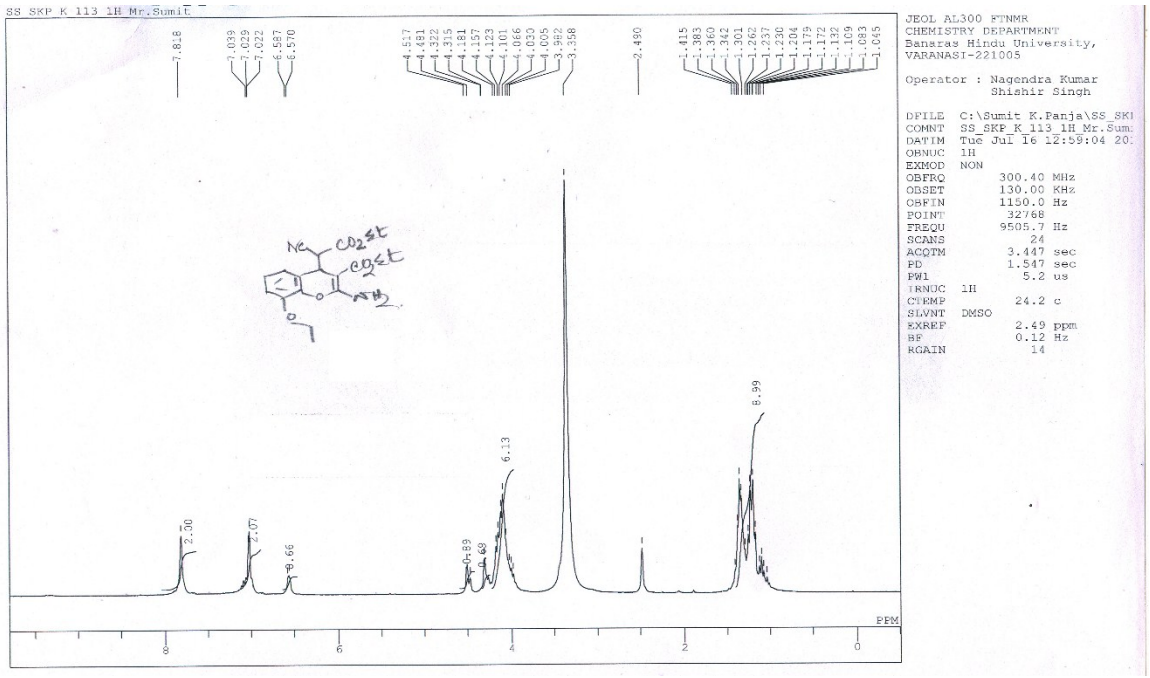
^{1}H-NMR of Ethyl 2-amino-4-(1-cyano-2-ethoxy-2-oxoethyl)-4*H*-chromene-3-carboxylate (5ba)



^{13}C-NMR of Ethyl 2-amino-4-(1-cyano-2-ethoxy-2-oxoethyl)-4*H*-chromene-3-carboxylate (5ba)



^{1}H-NMR of Ethyl 2-amino-4-(1-cyano-2-ethoxy-2-oxoethyl)-8-ethoxy-4H-chromene-3-carboxylate (5bb)



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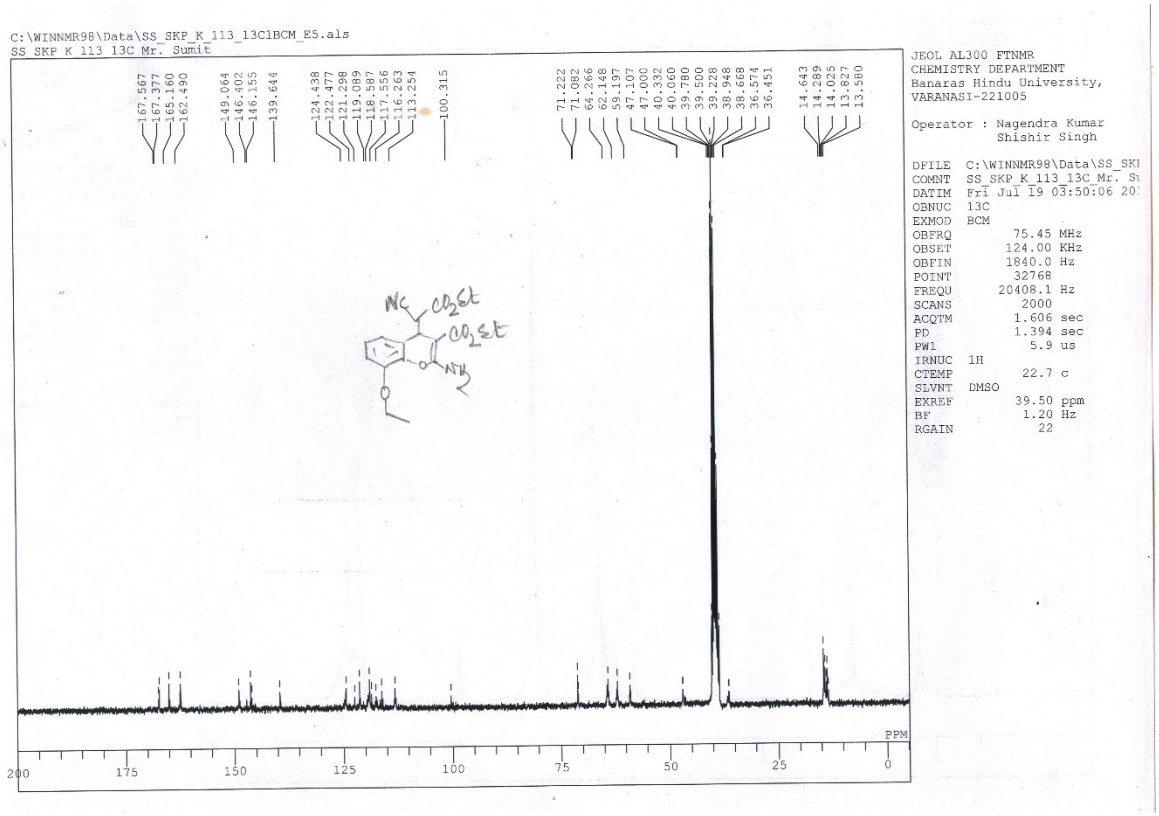
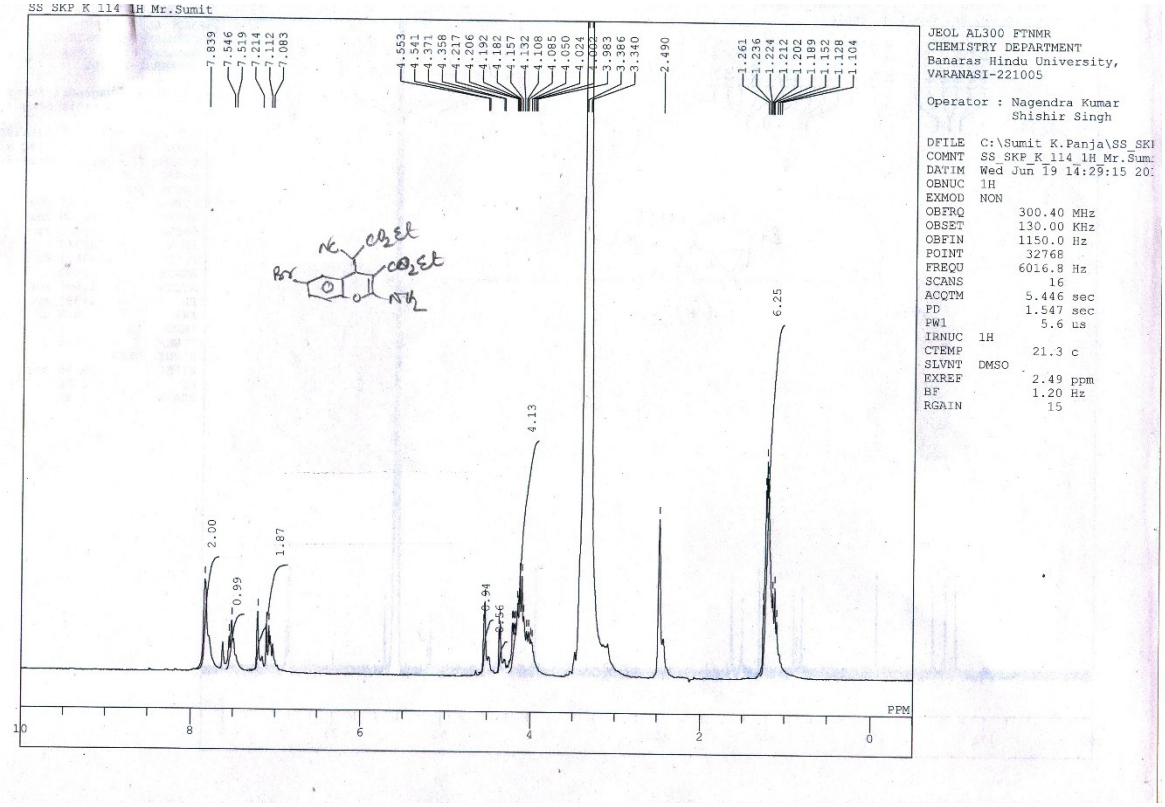


^{1}H-NMR of Ethyl 2-amino-6-bromo-4-(1-cyano-2-ethoxy-2-oxoethyl)-4*H*-chromene-3-carboxylate (5bc)



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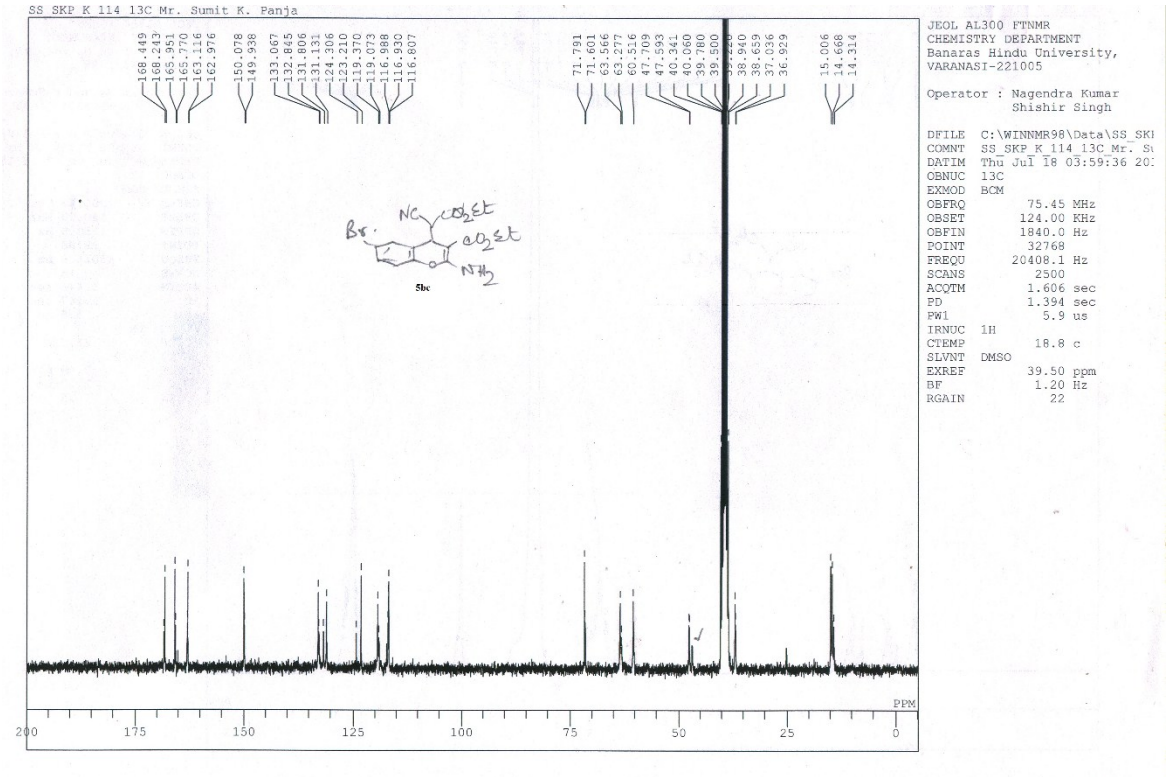
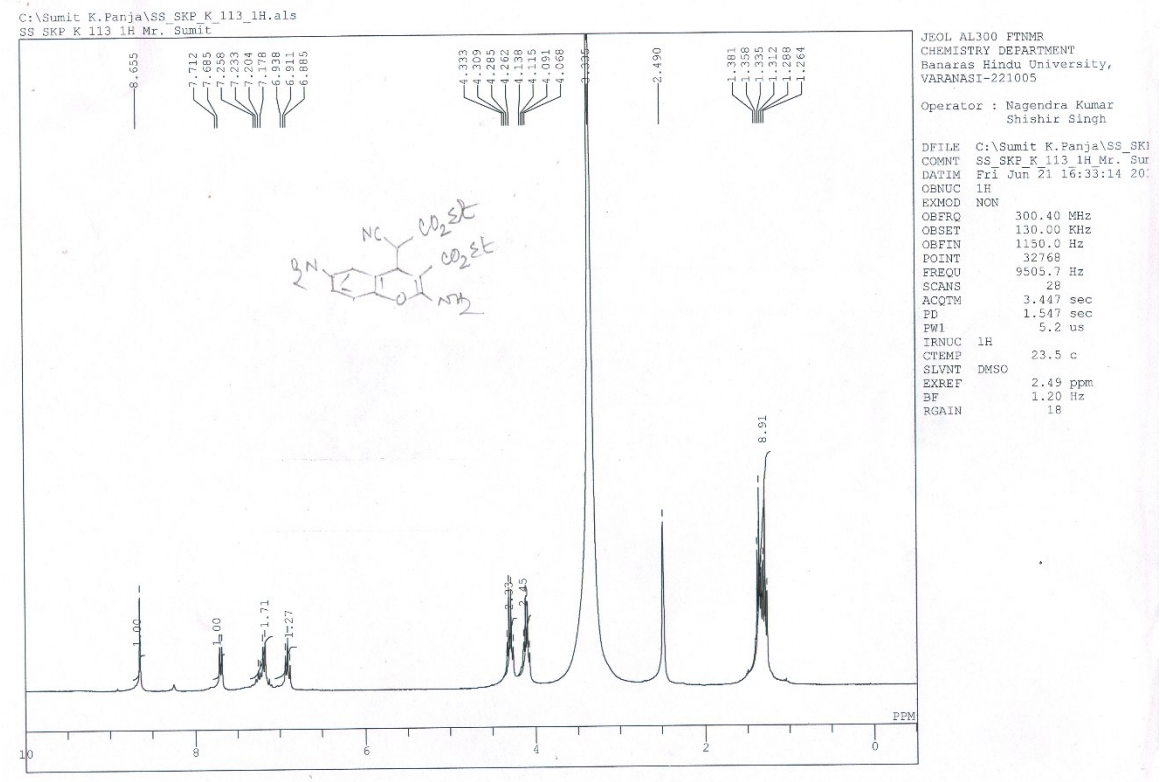
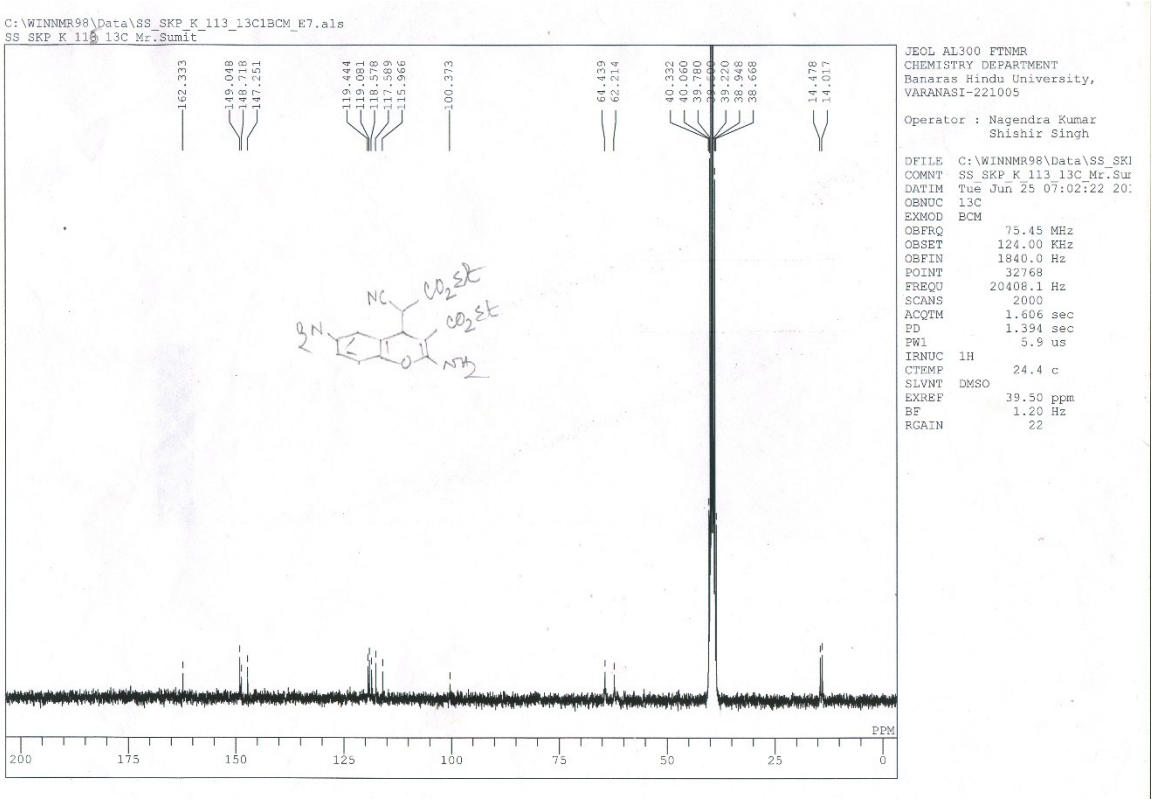


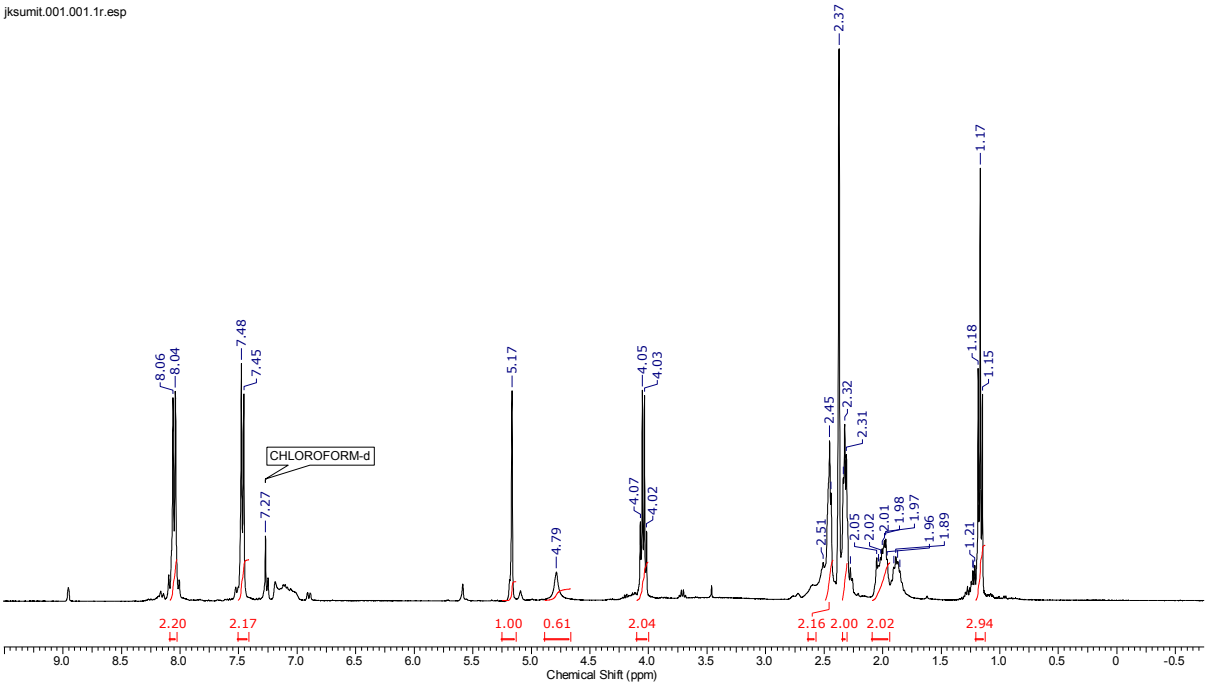
^{1}H-NMR of Ethyl 2-amino-4-(1-cyano-2-ethoxy-2-oxoethyl)-6-nitro-4*H*-chromene-3-carboxylate (5bd)



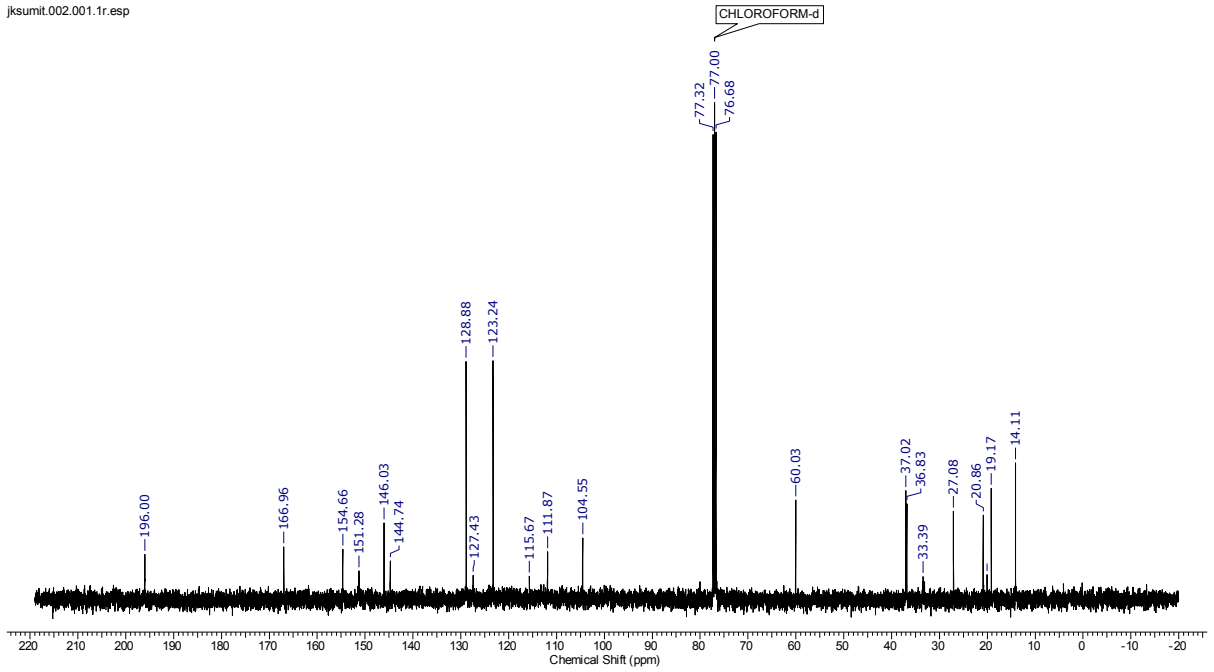
^{13}C-NMR of Ethyl 2-amino-4-(1-cyano-2-ethoxy-2-oxoethyl)-6-nitro-4*H*-chromene-3-carboxylate (5bd)



^{1}H-NMR of Ethyl 2-methyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate



^{13}C-NMR of Ethyl 2-methyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate



6. Single Crystal XRD measurement

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC No. 873550 for MP(DNP) (catalyst), 937875 for (2-(naphthalen-1-ylmethylene) malononitrile (3j),** Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk). Crystal data was collected on an OXFORD DIFFRACTION X CALIBER EoS diffractometer using graphite monochromatized Mo Ka radiation at 298 K. The structures were solved by direct methods and refined by full matrix least squares on F2 using SHELX-97.[8a] The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model. The refinement converged to a final R1 and wR2. Important crystal data were presented. Drawings were made using ORTEP-III and Mercury. Both the crystal structures have been deposited in CCDC and can be accessed freely. Single crystals of both compounds were recrystallised from acetonitrile, mounted in normal atomosphere of the diffractometer.

Table 1: Crystallographic Information of Catalyst (Molecular complexes)

Compound	$MP(NP)_2$	MP(DNP)	MP(TNP)
Formula	$C_{18}H_{23}N_3O_6$	$C_{12}H_{17}N_3O_5$	$C_{12}H_{16}N_4O_7$
Fw	377.39	283.29	328.29
a (Å)	6.5076(3)	7.5357(6)	7.123(5)
b (Å)	7.9798(6)	17.1542(11)	20.470(5)
c (Å)	18.3407(14)	10.8286(9)	10.498(5)
α (°)	90.054(6)	90	90

β (°)	92.065(5)	102.802(9)	93.020(5)
γ (°)	98.928(5)	90	90
V (Å^3)	940.25(11)	319.54(5)	1528.6(13)
Z	2	4	4
space group	P-1	P21/c	P21/n
D_{calcd} (g cm^{-3})	1.333	1.378	1.427
R (F_o^2)[a]	0.0523	0.0570	0.0583
$R_w(F_o^2)$[b]	0.1095	0.1282	0.1393
[a]$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ [b]$R_w = [\Sigma w(F_o^2 - F_c^2)^2/ \Sigma w(F_o^4)]^{1/2}$			

Table 1: Crystallographic Information of Synthesized compound

Compound	**Compound (3aj)**
Formula	
Fw	206.3
a (Å)	3.8280 (50)
b (Å)	15.7890 (50)
c (Å)	17.2300 (50)
α (°)	90 (5)
β (°)	91.29 (5)
γ (°)	90 (5)
V (Å3)	141.12 (14)
Z	4
space group	P 121/n1
D_{calcd} (g cm^{-3})	1.32
R (Fo2)[a]	0.0498
$R_w(F_o^2)$[b]	0.1204
[a]$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ [b]$R_w = [\Sigma w(F_o^2 - F_c^2)^2/ \Sigma w(F_o^4)]^{1/2}$	

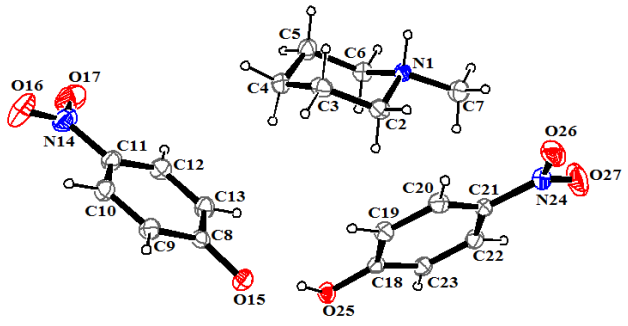


Figure 1: ORTEP diagram of Catalyst (MP(NP)$_2$)(**CCDC No.: 881652**)

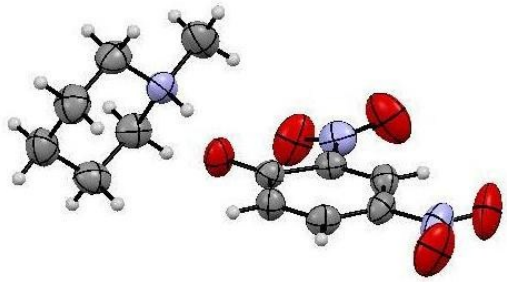


Figure 2: ORTEP diagram of Catalyst (MP(DNP)) (50 % ellipsoid probability) (CCDC No.: **873550**)

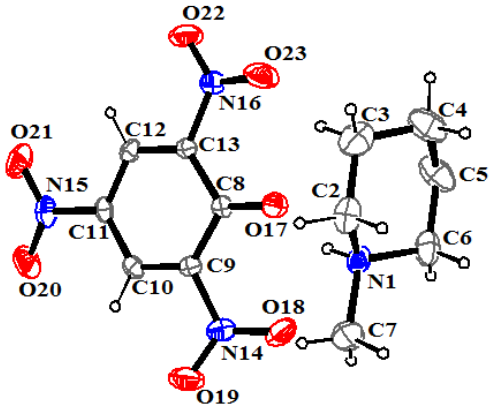


Figure 3: ORTEP diagram of MP(TNP) (CCDC No.: **917775**).

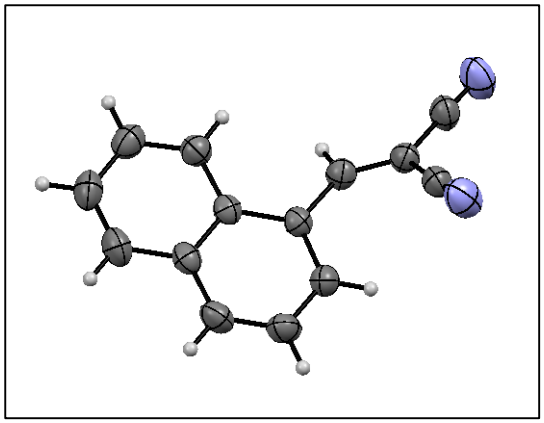


Figure 4: Single-crystal X-ray structure of (2-(naphthalen-1-ylmethylene)malononitrile (3aj) (CCDC No. **937875**)

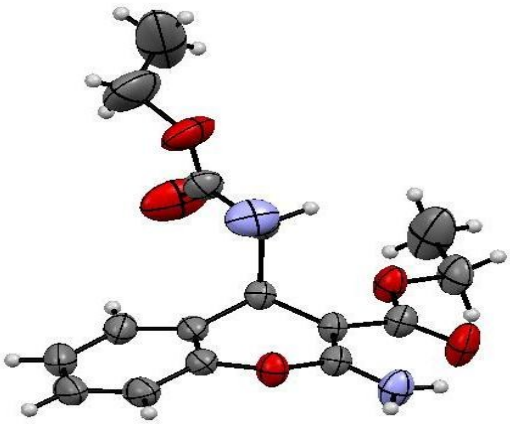


Figure 5: ORTEP diagram of ethyl 2-amino-4-(1-cyano-2-ethoxy-2-oxoethyl)-4*H*-chromene-3-carboxylate (5ba) (**CCDC No 946632**)

Thermal gravimetric Analysis of molecular Complex

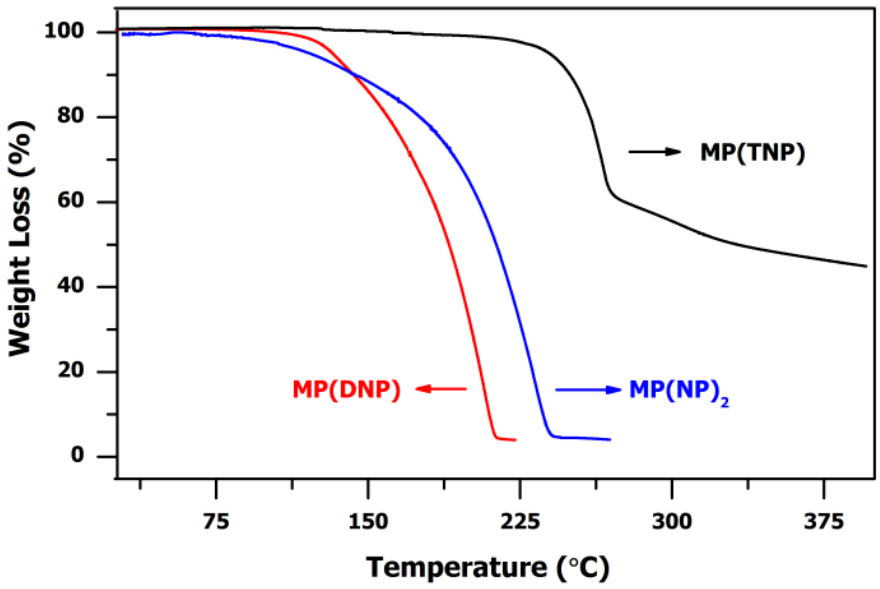


Figure 2: TGA Plots of Catalyst (Molecular Complexes)

References and notes

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