# Supporting Information

# Borax Catalyzed Domino Reactions: Synthesis of Highly Functionalised Pyridines, Dienes, Anilines and Dihydropyrano[3,2-c] Chromenes

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**General**

All reagents were purchased either from Sigma or Merck. Solvents were dried and purified using standard techniques. Melting points were recorded on a SRS-EZ-Melt melting point apparatus and are uncorrected. IR spectra were recorded in KBr on a Shimadzu IR Afinity I. $^{1}H$ NMR spectra and $^{13}C$ NMR spectra were recorded on a Bruker 300 MHz, 500 MHz and Varian 400 MHz spectrometer in $CDCl_3$ or DMSO-$d^6$ using TMS as an internal reference and chemicals shifts are reported in parts per million (ppm). $^{1}H$ NMR Spectra are reported in the order: multiplicity as s (singlet), d (doublet), t (triplet), m (multiplet), brs (broad singlet) , coupling constant (*J* value) in hertz (Hz) and no of protons. Elemental analyses were carried out in a Perkin Elmer 2400 automatic CHN analyzer or Elementer Vario EL III.

**Synthesis of 2-Amino-4-(aryl)-6-(alkyl or aryl)-3,5-pyridinedicarbonitriles (1-19):** To a solution of aldehyde (1.0 mmol), malononitrile (2.1 mmol) and borax (0.1mmol) in 3 mL of ethanol was added thiols (1.0mmol) at room temperature in a round bottom flask equipped with condenser. The whole was stirred under reflux condition for the required time (Table 2) and then allowed to cool to room temperature. The progress of the reaction was monitored by TLC and after completion of the reaction the reaction mixture was gradually cooled to room temperature. The solid product was filtered off, washed with ethanol and dried to obtain the corresponding product.

**Synthesis of dienes and aniline derivatives (20-26):** To a solution of aldehyde (1.0 mmol), malononitrile (2.1 mmol) and borax (0.1mmol) in 3 mL of ethanol was added cyclic ketones (1.0mmol) at room temperature in a round bottom flask equipped with condenser. The whole

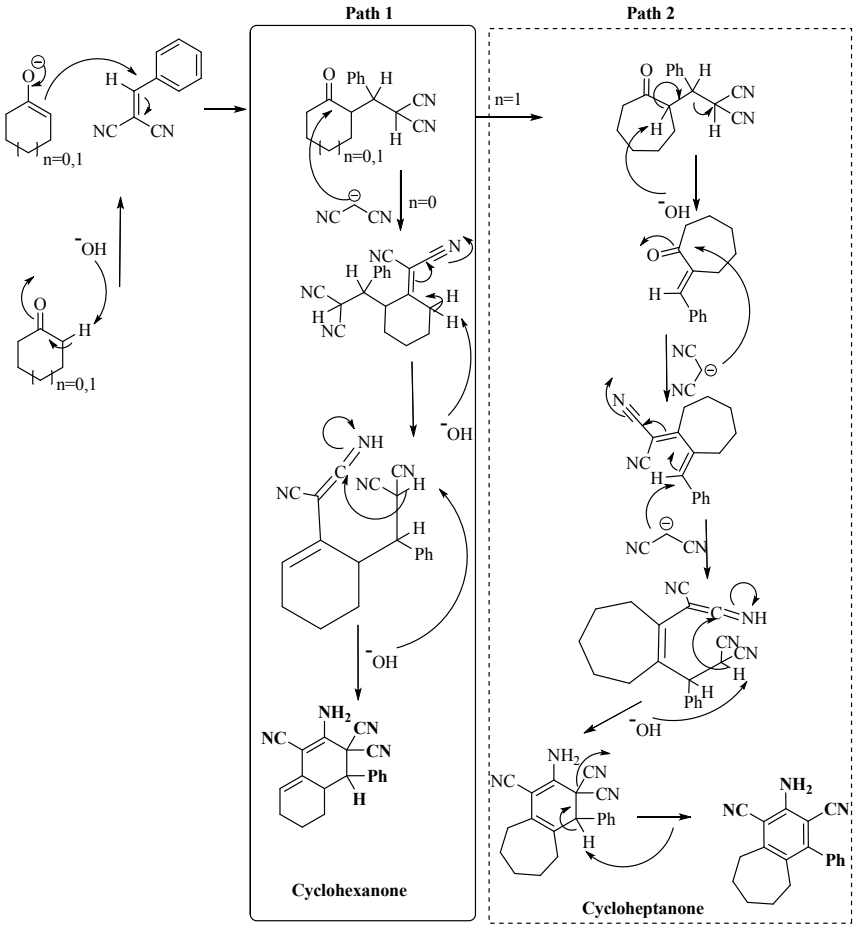
was stirred under reflux condition for the required time (Table 3) and then allowed to cool to room temperature. The progress of the reaction was monitored by TLC and after completion of the reaction the reaction mixture was gradually cooled to room temperature. The solid product was filtered off, washed with ethanol and dried to obtain the corresponding product.

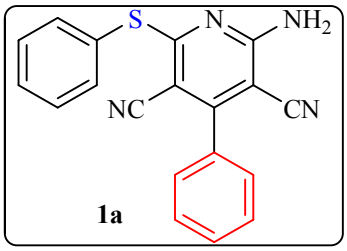
**Synthesis of dihydropyrano[3,2-c]chromene derivatives (27-32):** To a solution of 4-hydroxy derivatives (1.0 mmol), malononitrile (1.1 mmol) and borax (0.1mmol) in 3 mL of water was added dimethyl/ diethyl acetylenedicarboxylate (1.0mmol) at room temperature in a round bottom flask equipped with condenser. The whole was stirred under reflux condition for the required time (Table 4) and then allowed to cool to room temperature. The progress of the reaction was monitored by TLC and after completion of the reaction the reaction mixture was gradually cooled to room temperature. The solid product was filtered off, washed with ethanol and dried to obtain the corresponding product.

**Recyclability of catalyst:** The mother liquor containing borax, obtained after filtration of the reaction mixture, was reused with the addition of fresh substrate and subjected to the same reaction condition as mentioned above. The reuses of catalyst for five cycles are shown below.

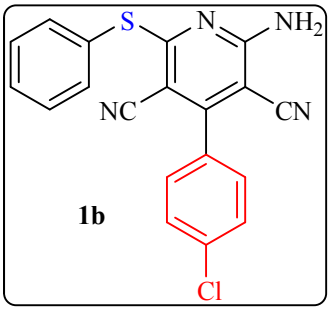
| Run | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| % Yield | 92 | 90 | 89 | 87 | 87 |

**Proposed reaction mechanism for the formation of diene and aniline (for Table 3).**

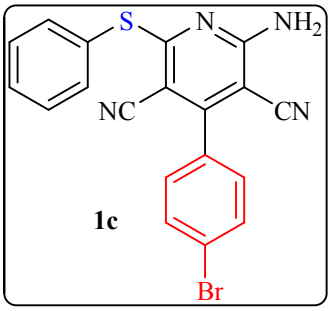


1. 

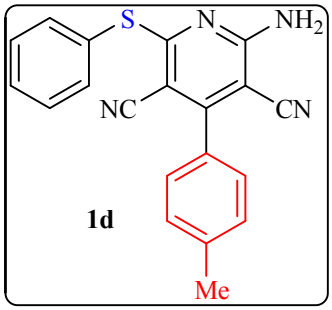
*2-amino-4-phenyl-6-(phenylthio)pyridine-3,5-dicarbonitrile (**1a**)* : Yield 88%. Solid, m.p. 230-232°C (227-228°C). IR $\nu_{max}$ (KBr): 3478, 3327, 3212, 2215, 1625, 1549, 1525, 1422, 1260, 1018 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.49 (brs, 2H), 7.35-7.56 (m, 10H) ppm.

2. 

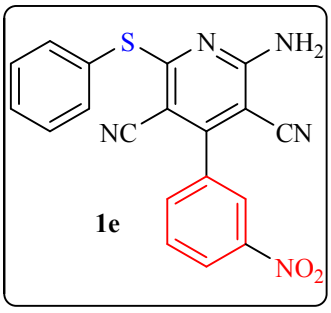
*2-amino-4-(4-chlorophenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (**1b**)* : Yield 92%. Solid, m.p. 220-222°C (222-224°C). IR $\nu_{max}$ (KBr): 3487, 3347, 3221, 2214, 1635, 1546, 1523, 1496, 1260, 1094 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.53 (brs, 2H), 7.38-7.61 (m, 9H) ppm.

3. 

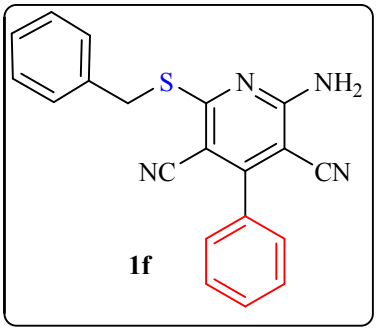
*2-amino-4-(4-bromophenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile (**1c**)* : Yield 90%. Solid, m.p. 248-250°C (255-257°C). IR $\nu_{max}$ (KBr): 3479, 3349, 3218, 2213, 1630, 1544, 1521, 1417, 1260, 1015 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.52 (brs, 2H), 7.41-7.42 (m, 2H), 7.44-7.53 (m, 5H), 7.69-7.71 (m, 2H) ppm.

4. 

*2-amino-6-(phenylthio)-4-p-tolylpyridine-3,5-dicarbonitrile **(1d)*** : Yield 88%. Solid, m.p. 208-210°C (208-211°C). IR $\nu_{max}$ (KBr): 3475, 3337, 3213, 2217, 1626, 1544, 1509, 1419, 1260, 1021 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.43 (s, 3H), 5.48 (brs, 2H), 7.36-7.47 (m, 7H), 7.50-7.53 (m, 2H) ppm.

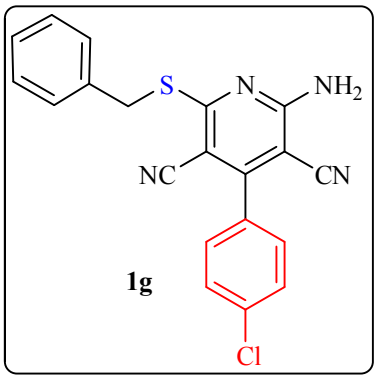
5. 

*2-amino-4-(3-nitrophenyl)-6-(phenylthio)pyridine-3,5-dicarbonitrile **(1e)*** : Yield 82%. Solid, m.p. 220-222°C (219-220°C). IR $\nu_{max}$ (KBr): 3485, 3401, 3321, 3230, 2212, 1647, 1624, 1581, 1532, 1353, 1252, 1239 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.61 (brs, 2H), 7.48-7.57 (m, 5H), 7.77-7.89 (m, 2H), 8.42-8.44 (m, 2H) ppm.

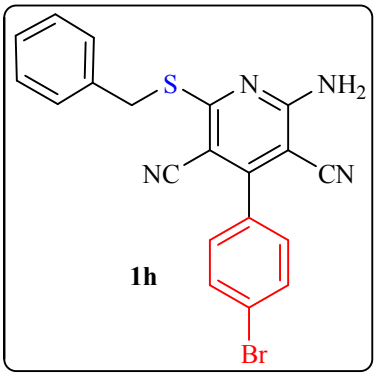
6. 

*2-amino-6-(benzylthio)-4-phenylpyridine-3,5-dicarbonitrile **(1f)*** : Yield 86%. Solid, m.p. 190-192 °C (193-195°C). IR $\nu_{max}$ (KBr): 3440, 3327, 3217, 2214, 2206, 1627, 1545, 1522, 1416, 1263, 1025 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d^6$): $\delta$ = 4.50 (s, 2H), 7.23-7.27 (m, 1H), 7.29-7.33 (m, 2H), 7.45-7.51 (m, 4H), 7.52-7.57 (m, 3H), 7.92 (s, 2H) ppm. $^{13}C$ NMR (100 MHz, DMSO-

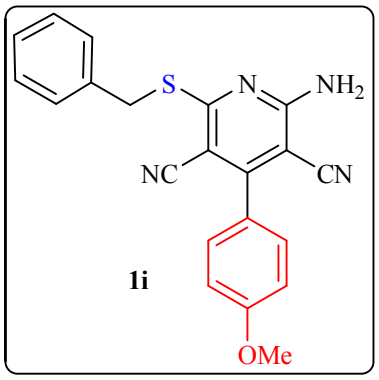
$d^6$+$CDCl_3$) : 33.6, 85.8, 93.5, 114.9, 115.1, 127.0, 128.1, 128.2, 128.4, 128.9, 130.0, 133.6, 136.8, 157.8, 159.5, 166.7.

7. 

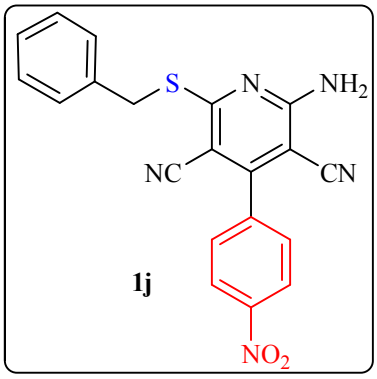
*2-amino-6-(benzylthio)-4-(4-chlorophenyl)pyridine-3,5-dicarbonitrile (**1g**)* : Yield 84%. Solid, m.p. 199-201°C (203-204°C). IR $\nu_{max}$ (KBr): 3439, 3331, 3218, 2211, 1628, 1545, 1494, 1319, 1262, 1028 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d^6$): $\delta$ = 4.49 (s, 2H), 7.18-7.26 (m, 1H), 7.28-7.36 (m, 2H), 7.45-7.49 (m, 4H), 7.52-7.56 (m, 2H), 7.97 (s, 2H) ppm. $^{13}C$ NMR (100 MHz, DMSO-$d^6$+$CDCl_3$) : 33.5, 85.7, 93.2, 114.8, 114.9, 127.1, 128.2, 128.6, 129.0, 129.9, 132.2, 135.7, 136.8, 156.6, 159.5, 166.7.

8. 

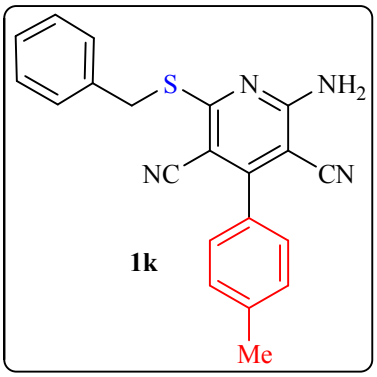
*2-amino-6-(benzylthio)-4-(4-bromophenyl)pyridine-3,5-dicarbonitrile(**1h**)* : Yield 83%. Solid, m.p. 202-204°C. IR $\nu_{max}$ (KBr): 3438, 3328, 3220, 2211, 1630, 1542, 1520, 1321, 1263, 1040 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d^6$): $\delta$ = 4.49 (s, 2H), 7.22-7.26 (m, 1H), 7.28-7.32 (m, 2H), 7.41-7.45 (m, 2H), 7.47-7.49 (m, 2H), 7.69-7.72 (m, 2H), 7.90 (brs, 2H) ppm. $^{13}C$ NMR (100 MHz, DMSO-$d^6$+$CDCl_3$) : 33.4, 85.6, 93.1, 114.8, 114.9, 124.1, 127.1, 128.2, 129.1, 130.2, 131.6, 132.8, 137.0, 156.7, 159.5, 166.6. Elemental Analysis for $C_{20}H_{13}BrN_4S$ calculated C, 57.02; H, 3.11; N, 13.30; obtained C, 56.95; H, 3.09; N, 13.34.

9. 

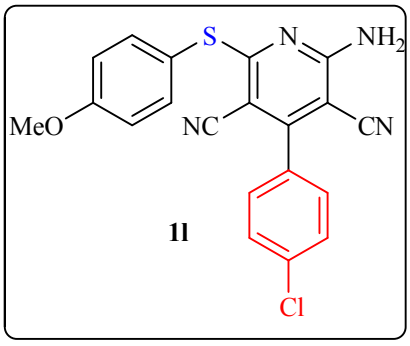
*2-amino-6-(benzylthio)-4-(4-methoxyphenyl)pyridine-3,5-dicarbonitrile (**1i**)* : Yield 84%. Solid, m.p. 225-227°C (228-230°C). IR $\nu_{max}$ (KBr): 3472, 3331, 3211, 2216, 1617, 1544, 1508, 1415, 1258, 1176, 1018 $cm^{-1}$. $^{1}H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 3.85 (s, 3H), 4.44 (s, 2H), 5.74 (brs, 2H), 7.02 (d, $J$ = 7.2, 2H), 7.25-7.33 (m, 3H), 7.38 (d, $J$ = 6.0, 2H), 7.47 (d, $J$ = 7.2, 2H) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$) : 34.9, 55.5, 86.7, 96.3, 114.5, 115.2, 115.8, 125.3, 127.7, 128.8, 129.2, 130.3, 136.3, 157.9, 159.4, 161.8, 168.7.

10. 

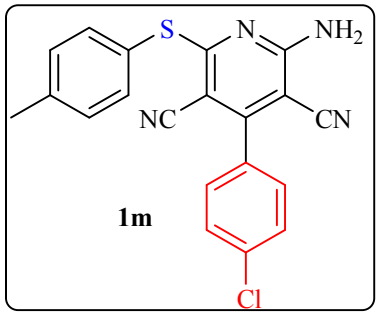
*2-amino-6-(benzylthio)-4-(4-nitrophenyl)pyridine-3,5-dicarbonitrile (**1j**)* : Yield 81%. Solid, m.p. 210-212°C. IR $\nu_{max}$ (KBr): 3435, 3329, 3219, 2215, 1630, 1548, 1349, 1263, 1105, 1041 $cm^{-1}$. $^{1}H$ NMR (500 MHz, $CDCl_3$ +DMSO-$d^6$): $\delta$ = 4.45 (s, 2H), 6.12 (brs, 2H), 7.25-7.34 (m, 5H), 7.37 (d, $J$ = 7.2, 2H), 7.65 (d, $J$ = 7.8, 2H) ppm. $^{13}C$ NMR (125 MHz, DMSO-$d^6$+$CDCl_3$) : 35.0, 86.3, 95.7, 114.3, 114.8, 124.4, 127.9, 128.8, 129.2, 129.9, 135.9, 139.5, 149.2, 155.8, 159.3, 169.1. Elemental Analysis for $C_{20}H_{13}N_5O_2S$ calculated C, 62.00; H, 3.38; N, 18.08; obtained C,61.88; H, 3.36; N, 18.11.

11. 

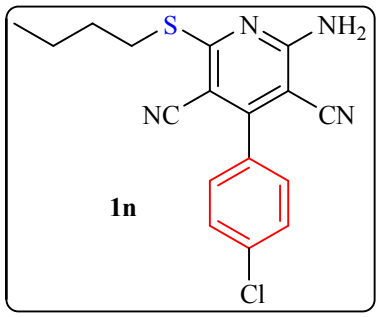
*2-amino-6-(benzylthio)-4-p-tolylpyridine-3,5-dicarbonitrile (**1k**)*: Yield 86%. Solid, m.p. 210-212°C. IR $\nu_{max}$ (KBr): 3472, 3330, 3211, 2218, 1617, 1545, 1507, 1321, 1235, 1108, 1040 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 2.38 (s, 3H), 4.42 (s, 2H), 5.96 (brs, 2H), 7.23-7.32 (m, 5H), 7.36-7.38 (m, 4H) ppm. $^{13}C$ NMR (125 MHz, DMSO-$d^6$+$CDCl_3$) : 21.6. 34.9, 86.7, 96.1, 115.1, 115.7, 127.7, 128.5, 128.8, 129.2, 129.8, 130.4, 136.4, 141.4, 158.4, 159.5, 168.5.

12. 

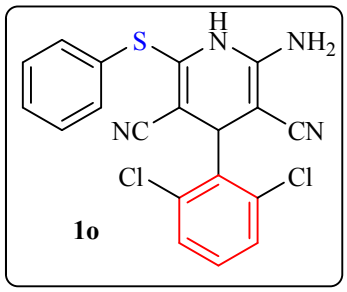
*2-amino-4-(4-chlorophenyl)-6-(4-methoxyphenylthio)pyridine-3,5-dicarbonitrile (**1l**)* : Yield 91%. Solid, m.p. 220-222°C. IR $\nu_{max}$ (KBr): 3467, 3345, 3222, 2212, 1633, 1546, 1525, 1494, 1253, 1179, 1024 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 3.85 (s, 3H), 5.56 (brs, 2H), 6.96 (d, *J*= 9.0, 2H), 7.43-7.53 (m, 6H) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): 55.5, 87.0, 95.4, 114.8, 115.1, 115.2, 117.4, 129.5, 129.9, 131.6, 137.5(2C), 157.1, 159.4, 161.2, 170.3. Elemental Analysis for $C_{20}H_{13}ClN_4OS$ calculated C, 61.14; H, 3.34; N, 14.26; obtained C, 61.09; H, 3.31; N, 14.30.

13. 

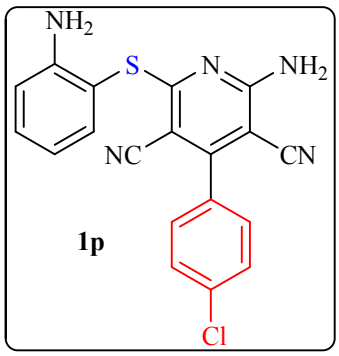
*2-amino-4-(4-chlorophenyl)-6-(p-tolylthio)pyridine-3,5-dicarbonitrile (**1m**)* : Yield 90%. Solid, m.p. 240-242°C (245-246°C). IR $\nu_{max}$ (KBr): 3477, 3345, 3221, 2213, 1635, 1573, 1545, 1495, 1258, 1180, 1016 $cm^{-1}$. $^{1}H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 2.43 (s, 3H), 5.66 (brs, 2H), 7.24-7.25 (m, 2H), 7.40 (d, *J*= 7.2, 2H), 7.45 (d, *J*= 7.2, 2H), 7.51 (d, *J*= 7.2, 2H) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): 21.5, 87.1, 95.5, 114.8, 115.2, 123.5, 129.5, 129.9, 130.3, 131.7, 135.8, 137.4, 140.5, 157.2, 159.4, 169.8.

14. 

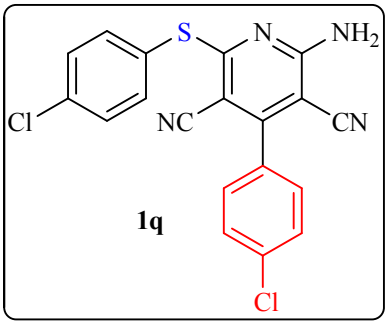
*2-amino-6-(butylthio)-4-(4-chlorophenyl)pyridine-3,5-dicarbonitrile (**1n**)* : Yield 80%. Solid, m.p. 108-110°C. IR $\nu_{max}$ (KBr): 3480, 3345, 3220, 2955, 2214, 1630, 1573, 1543, 1493, 1417, 1264, 1014 $cm^{-1}$. $^{1}H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 0.97 (t, *J*= 7.2, 3H), 1.43-1.51 (m, 2H), 1.69-1.74(m, 2H), 3.21 (t, *J*= 7.2, 2H), 5.67 (brs, 2H), 7.46 (d, *J*= 8.4, 2H), 7.51 (d, *J*= 8.4, 2H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): 13.6, 21.9, 30.4, 30.8, 86.1, 96.6, 114.8, 115.3, 129.4, 129.9, 131.6, 137.3, 156.7, 159.2, 169.9. Elemental Analysis for $C_{17}H_{15}ClN_4S$ calculated C, 59.56; H, 4.41; N, 16.34; obtained C, 59.52; H, 4.38; N, 16.37.

15. 

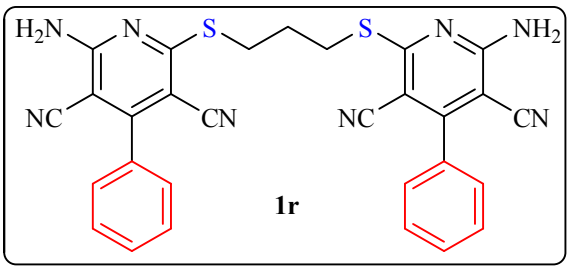
*2-amino-4-(2,6-dichlorophenyl)-6-(phenylthio)-1,4-dihydropyridine-3,5-dicarbonitrile* ***(1o)*** : Yield 78%. Solid, m.p. 300-302°C (319-320°C). IR $\nu_{max}$ (KBr): 3460, 3358, 3232, 2209, 2171, 1647, 1579, 1490, 1438, 1250, 1018 $cm^{-1}$. $^{1}H$ NMR (400 MHz, DMSO-$d^6$): $\delta$ = 5.64 (s, 1H), 5.87 (brs, 2H), 7.34-7.41 (m, 2H), 7.43-7.48 (m, 2H), 7.49-7.53 (m, 4H) ppm. $^{13}C$ NMR (100 MHz, DMSO-$d^6$): 39.4, 51.6, 86.1, 118.2, 120.5, 128.3, 128.6, 129.7, 130.0, 130.3, 130.6, 130.9, 135.6, 144.5, 152.7.

16. 

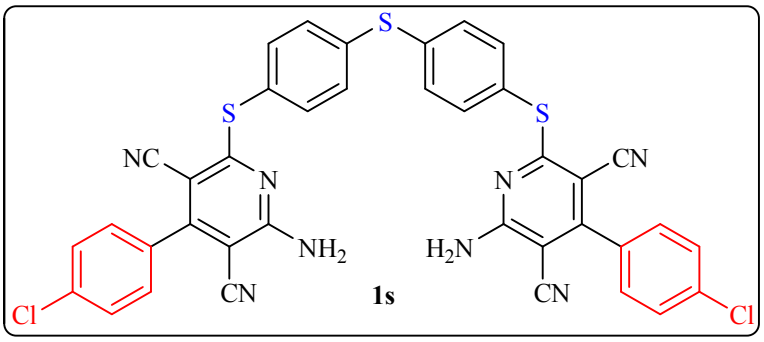
*2-amino-6-(2-aminophenylthio)-4-(4-chlorophenyl)pyridine-3,5-dicarbonitrile* ***(1p)*** : Yield 82%. Solid, m.p. 235-237°C (239-240°C). IR $\nu_{max}$ (KBr): 3396, 3329, 3222, 2212, 1639, 1544, 1524, 1493, 1262, 1094 $cm^{-1}$. $^{1}H$ NMR (400 MHz, DMSO-$d^6$): $\delta$ = 5.44 (brs, 2H), 6.57-6.61 (m, 1H), 6.81-6.83 (m, 1H), 7.18-7.28 (m, 2H), 7.57-7.64 (m, 2H), 7.66-7.72 (m, 2H), 7.77 (brs, 2H) ppm. $^{13}C$ NMR (100 MHz, DMSO-$d^6$): 86.3, 93.4, 107.3, 115.1, 115.3, 115.5, 116.3, 128.9, 130.4, 131.7, 132.9, 135.3, 137.2, 151.2, 157.2, 159.5, 166.8.

17. 

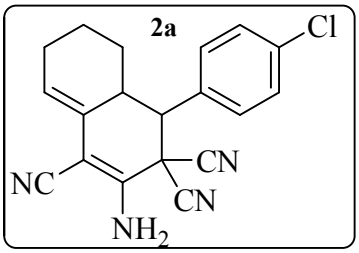
*2-amino-4-(4-chlorophenyl)-6-(4-chlorophenylthio)pyridine-3,5-dicarbonitrile (**1q**):* Yield 85%. Solid, m.p. 258-260°C (261-262°C). IR $\nu_{max}$ (KBr): 3480, 3349, 3219, 2214, 1632, 1573, 1544, 1525, 1494, 1259, 1235, 1093, 1014 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d^6$): $\delta$ = 7.44-7.54 (m, 2H), 7.55-7.63 (m, 4H), 7.65-7.68 (m, 2H), 7.90 (brs, 2H) ppm. $^{13}C$ NMR (100 MHz, DMSO-$d^6$): 87.2, 93.14, 114.9, 115.2, 125.9, 128.9, 129.5, 130.5, 132.7, 134.9, 135.4, 136.8, 157.6, 159.6, 165.8.

18. 

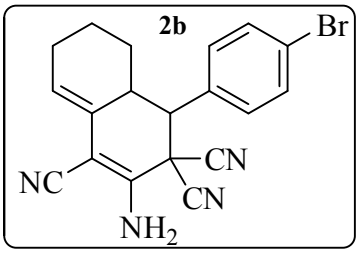
*6,6'-(propane-1,3-diylbis(sulfanediyl))bis(2-amino-4-phenylpyridine-3,5-dicarbonitrile) (**1r**)* : Yield 83%. Solid, m.p. 255-257°C. IR $\nu_{max}$ (KBr): 3463, 3329, 3214, 2212, 2186, 1618, 1548, 1524, 1441, 1266, 1042 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.99-2.02 (m, 3H), 3.22-3.26 (m, 6H), 6.54 (brs, 4H), 7.31-7.37 (m, 10H) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): 28.0, 28.9, 86.5, 95.5, 115.2, 115.3, 128.3, 128.8, 130.6, 133.6, 158.1, 159.7, 160.0 Elemental Analysis for $C_{29}H_{20}N_8S_2$ calculated C, 63.95; H, 3.70; N, 20.57; obtained C, 63.89; H, 3.68; N, 20.60.

19. 

*6,6'-(4,4'-thiobis(4,1-phenylene)bis(sulfanediyl))bis(2-amino-4-(4-chlorophenyl)pyridine-3,5-dicarbonitrile) (**1s**) :* Yield 75%. Solid, m.p. 188-190°C. IR $\nu_{max}$ (KBr): 3477, 3336, 3223, 2222, 1630, 1547, 1499, 1255, 1096, 1003 $cm^{-1}$. $^{1}H$ NMR (400 MHz, DMSO-$d^6$): $\delta$ = 7.26-7.50 (m, 8H), 7.51-7.69 (m, 8H), 7.94 (brs, 4H) ppm. $^{13}C$ NMR (100 MHz, DMSO-$d^6$): 87.2, 93.3, 114.9, 115.1, 126.4, 128.6, 128.9, 130.4, 131.3, 131.7, 132.7, 135.4, 135.8, 136.0, 157.5, 159.6. Elemental Analysis for $C_{38}H_{20}Cl_2N_8S_3$ calculated C, 60.39; H, 2.67; N, 14.83; obtained C, 60.35; H, 2.66; N, 14.85.

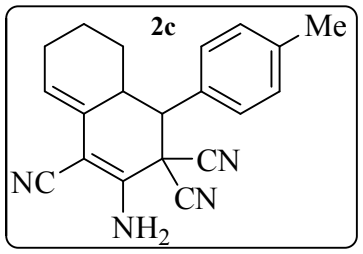
20. 

*2-amino-4-(4-chlorophenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(4H)-tricarbonitrile (**2a**)* : Yield 89%. Solid, m.p. 232-234°C. IR $\nu_{max}$ (KBr): 3421, 3344, 3252, 3227, 2944, 2908, 2864, 2832, 2212, 1646, 1603, 1567, 1494, 1447, 1413, 1392, 1278, 1093, 1015$cm^{-1}$. $^{1}H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 0.86-0.95 (m, 1H), 1.44-1.54 (m, 2H), 1.71-1.74 (m, 1H), 2.04-2.23 (m, 2H), 2.74-2.80 (m, 1H), 3.45-3.48 (m, 1H), 5.77-5.78 (m, 1H), 7.25 (brs, 2H), 7.44-7.61 (m, 4H) ppm.

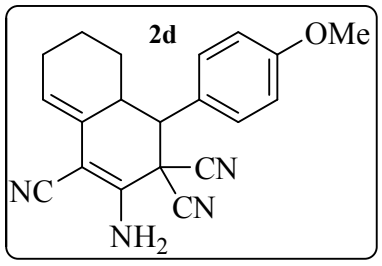
21. 

*2-amino-4-(4-bromophenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(4H)-tricarbonitrile (**2b**)* : Yield 88%. Solid, m.p. 240-

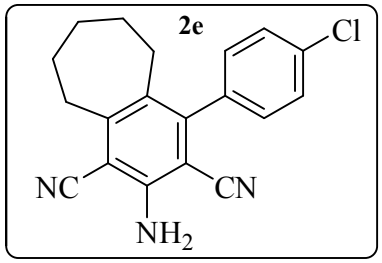
242°C. IR $\nu_{max}$ (KBr): 3455, 3344, 3220, 2939, 2862, 2208, 1729, 1641, 1598, 1567, 1447, 1431, 1393, 1275, 1250, 1042 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 0.83-0.96 (m, 1H), 1.07-1.28 (m, 1H), 1.49-2.56 (m, 5H), 3.09-3.11 (m, 1H), 5.79-5.81 (m, 1H), 6.97 (brs, 2H), 7.14-7.23 (m, 2H), 7.49-7.53 (m, 2H) ppm.

22. 

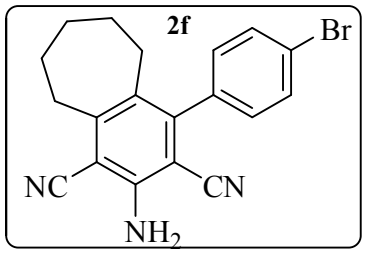
*2-amino-4-p-tolyl-4a,5,6,7-tetrahydronaphthalene-1,3,3(4H)-tricarbonitrile (**2c**)* : Yield 85%. Solid, m.p. 240-242°C. IR $\nu_{max}$ (KBr): 3419, 3341, 3247, 2944, 2874, 2217, 1647, 1595, 1516, 1387, 1119 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 0.84-0.94 (m, 1H), 1.24-1.59 (m, 2H), 1.71-1.83 (m, 1H), 2.05-2.32 (m, 2H), 2.37 (s, 3H), 2.73-2.79 (m, 1H), 3.23-3.28 (m, 1H), 5.76-5.78 (m, 1H), 7.14 (brs, 2H), 7.16-7.47 (m, 4H) ppm. $^{13}C$ NMR (100 MHz, DMSO-$d^6$+$CDCl_3$): 20.7, 24.9, 26.9, 34.1, 42.8, 51.0, 78.3, 82.0, 112.3, 115.9, 120.6, 126.5, 128.5, 128.9, 129.1, 131.1, 131.9, 138.2, 143.1 ppm.

23. 

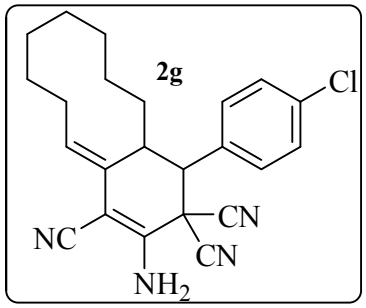
*2-amino-4-(4-methoxyphenyl)-4a,5,6,7-tetrahydronaphthalene-1,3,3(4H)-tricarbonitrile (**2d**)* : Yield 87%. Solid, m.p. 238-240°C. IR $\nu_{max}$ (KBr): 3420, 3341, 3252, 2947, 2833, 2212, 2175, 1650, 1599, 1557, 1515, 1442, 1430, 1256, 1181, 1028 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 0.84-0.93 (m, 1H), 1.42-1.74 (m, 3H), 2.04-2.23 (m, 2H), 2.71-2.77 (m, 1H), 3.26-3.29 (m, 1H), 3.82 (s, 3H), 5.76-5.77 (m, 1H), 6.89-7.04 (m, 2H), 7.12 (s, 2H), 7.29-7.49 (m, 2H) ppm.

24. 

*2-amino-4-(4-chlorophenyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-1,3-dicarbonitrile (**2e**)* : Yield 83%. Solid, m.p. 246-248°C. IR $\nu_{max}$ (KBr): 3466, 3342, 3322, 2945, 2850, 2202, 1650, 1606, 1570, 1490, 1406, 1178, 1010 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.15-1.48 (m, 4H), 1.67-1.82 (m, 2H), 2.01-2.21 (m, 2H), 2.51-2.58 (m, 1H), 2.87-2.89 (m, 1H), 6.91 (brs, 2H), 7.20-7.25 (m, 2H), 7.42-7.44 (m, 2H) ppm.

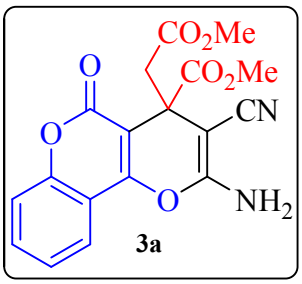
25. 

*2-amino-4-(4-bromophenyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-1,3-dicarbonitrile (**2f**)* : Yield 82%. Solid, m.p. 250-252°C. IR $\nu_{max}$ (KBr): 3467, 3341, 3320, 2935, 2857, 2200, 1646, 1603, 1569, 1491, 1405, 1223, 1076, 1006 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.16-1.48 (m, 4H), 1.67-1.81 (m, 2H), 2.12-2.18 (m, 2H), 2.50-2.57 (m, 1H), 2.93-2.95 (m, 1H), 7.09 (brs, 2H), 7.19-7.21 (m, 2H), 7.59-7.61 (m, 2H) ppm.

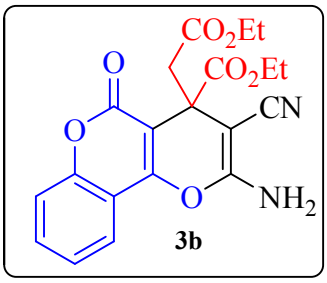
26. 

*(E)-2-amino-4-(4-chlorophenyl)-4a,5,6,7,8,9,10,11-octahydrobenzo[10]annulene-1,3,3(4H)-tricarbonitrile **(2g)*** : Yield 76%. Solid, m.p. 230-232°C. IR $_{\nu max}$ (KBr): 3350, 3229, 3099, 2926, 2857, 2200, 1672, 1586, 1421, 1093 $^{cm-1.}$ $^1H$ NMR (400 MHz, DMSO-$d^6$)*:* $\delta$ = 1.29-1.45 (m, 7H), 1.57-1.63 (m, 2H), 2.15-2.20 (m, 2H), 2.51-2.53 (m, 2H), 2.79-2.83 (m, 2H), 6.23-6.37 (m, 2H), 7.28-

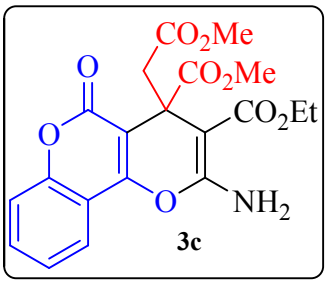
7.30 (m, 2H), 7.34-7.36 (m, 2H), 8.17 (brs, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-d$^6$+$CD_Cl_3$): 28.5, 28.6, 28.7, 28.8, 28.9 (2C), 32.4, 42.0, 76.9, 99.5, 112.7, 113.0, 127.2, 128.2, 131.2, 131.7, 136.2, 157.6, 163.4 ppm. Elemental Analysis for $C_{20}H_{13}N_5O_2S$ calculated C, 62.00; H, 3.38; N, 18.08; obtained C, 61.96; H, 3.36; N, 18.11.

27. 

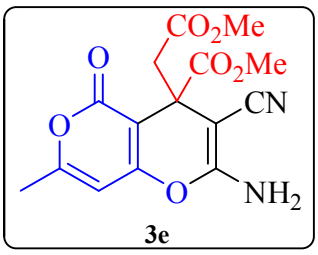
**3a** *methyl 3-amino-2-cyano-4-(2-methoxy-2-oxoethyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-4-carboxylate(**3a**)* : Yield 87%. Solid, m.p. 205-207°C (204.7-205.5°C). IR $\nu_{max}$ (KBr): 3448, 3327, 3214, 3184, 2992, 2196, 1731, 1670, 1623, 1596, 1460, 1364, 1264, 1179 cm$^{-1}$. $^1$H NMR (400 MHz, DMSO-d$^6$): $\delta$ = 3.05-3.09 (m, 1H), 3.23-3.27 (m, 1H), 3.51 (s, 3H), 3.68 (s, 3H), 7.46-7.50 (m, 2H), 7.63 (brs, 2H), 7.71-7.58 (m, 1H), 7.92-7.94 (m, 1H) ppm.

28. 

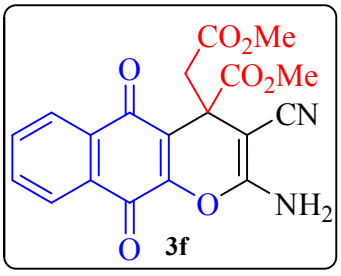
**3b** *ethyl 3-amino-2-cyano-4-(2-ethoxy-2-oxoethyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-4-carboxylate(**3b**)* : Yield 83%. Solid, m.p. 208-210°C (207.9-208.8°C). IR $\nu_{max}$ (KBr): 3394, 3321, 3207, 2988, 2193, 1715, 1666, 1601, 1446, 1357, 1228, 1098, 1024 cm$^{-1}$. $^1$H NMR (400 MHz, DMSO-d$^6$): $\delta$ = 1.00 (t, $J$ = 7.08, 3H), 1.17 (t, $J$ = 7.04, 3H), 3.00-3.04 (m, 1H), 3.18-3.22 (m, 1H), 3.90-3.95 (m, 2H), 4.11-4.20 (m, 2H), 7.48-7.51 (m, 2H), 7.66 (brs, 2H), 7.73-7.77 (m, 1H), 7.90-7.93 (m, 1H) ppm.

29. 

3c *2-ethyl 4-methyl 3-amino-4-(2-methoxy-2-oxoethyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-2,4-dicarboxylate(**3c**)* : Yield 85%. Solid, m.p. 208-210°C (209.4-210.7°C). IR $\nu_{max}$ (KBr): 3427, 3329, 3086, 2988, 1720, 1617, 1544, 1455, 1374, 1260, 1024 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d^6$): $\delta$ = 1.18 (t, $J$ = 7.04, 3H), 3.00-3.18 (m, 1H), 3.20-3.22 (m, 1H), 3.39 (s, 3H), 3.60 (s, 3H), 4.11-4.20 (m, 2H), 7.48-7.51 (m, 2H), 7.65 (brs, 2H), 7.73-7.77 (m, 1H), 7.90-7.92 (m, 1H) ppm.

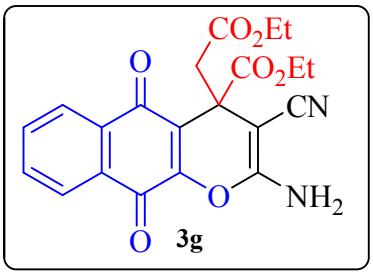
30. 

3e *methyl 3-amino-2-cyano-4-(2-methoxy-2-oxoethyl)-7-methyl-5-oxo-4,5-dihydropyrano[4,3-b]pyran-4-carboxylate(**3e**)* : Yield 86%. Solid, m.p. 154-156°C. IR $\nu_{max}$ (KBr): 3475, 3361, 3185, 2956, 2193, 1731, 1609, 1431, 1357, 1204, 985 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d^6$): $\delta$ = 2.05 (s, 3H), 2.67-2.71 (m, 1H), 2.87-2.91 (m, 1H), 3.44 (s, 3H), 3.59 (s, 3H), 6.08 (s, 1H), 7.31 (brs, 2H) ppm. $^{13}C$ NMR (100 MHz, DMSO-$d^6$): 19.4, 37.2, 42.8, 52.4, 53.0, 55.2, 88.1, 97.9, 98.7, 112.0, 117.1, 159.1, 161.2, 163.8, 166.5, 170.6 ppm. Elemental Analysis for $C_{15}H_{14}N_2O_7$ calculated C, 53.89; H, 4.22; N, 8.38 obtained C, 53.84; H, 4.20; N, 8.41.

31. 

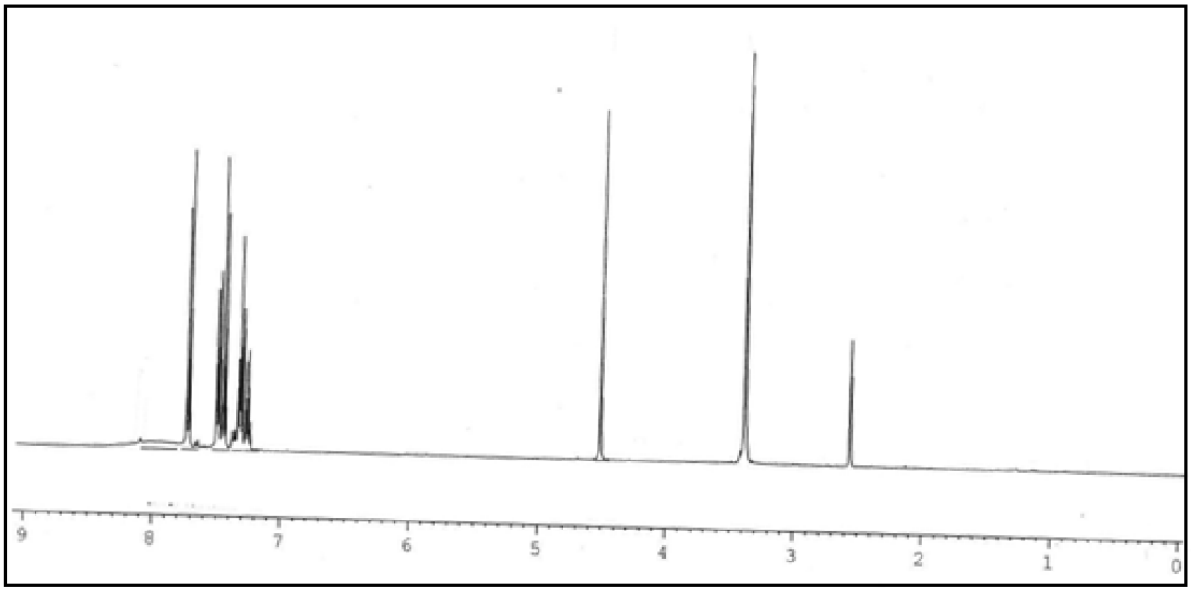
3f *methyl 3-amino-2-cyano-4-(2-methoxy-2-oxoethyl)-5,10-dioxo-5,10-dihydro-4H-benzo[g]chromene-4-carboxylate(**3f**)* : Yield 84%. Solid, m.p.

142-144°C. IR $\nu_{max}$ (KBr): 3337, 3200, 2956, 2210, 1731, 1633, 1431, 1357, 1058 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d^6$): $\delta$ = 3.51 (s, 3H), 3.68 (s, 3H), 3.85-3.86 (m, 1H), 3.91-3.92 (m, 1H), 7.53 (brs, 2H), 7.64-7.78 (m, 2H), 7.80-7.85 (m, 1H), 7.86-7.87 (m, 1H) ppm. $^{13}C$ NMR (100 MHz, DMSO-$d^6$+ $CDCl_3$): 36.9, 45.8, 51.9, 52.5, 53.0, 89.1, 106.6, 112.84, 117.7, 124.7, 124.9, 129.9, 131.6, 133.2, 135.8, 161.2, 163.8, 172.1, 180.1, 186.2 ppm. Elemental Analysis for $C_{19}H_{14}N_2O_7$ calculated C, 59.69; H, 3.69; N, 7.33 obtained C, 59.65; H, 3.67; N, 7.35.

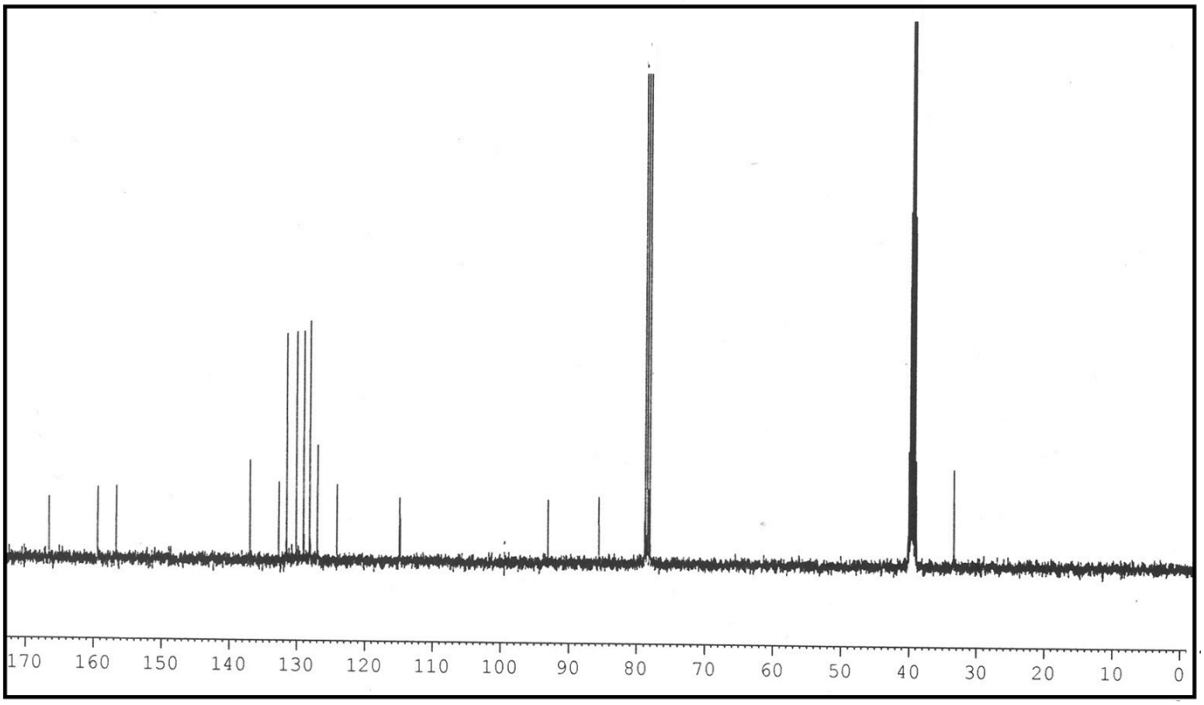
32. 

**3g** *ethyl 3-amino-2-cyano-4-(2-ethoxy-2-oxoethyl)-5,10-dioxo-5,10-dihydro-4H-benzo[g]chromene-4-carboxylate(**3g**)* : Yield 83%. Solid, m.p. 136-138°C. IR $\nu_{max}$ (KBr): 3321, 3200, 2980, 2201, 1722, 1633, 1446, 1366, 1195, 1017 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d^6$): $\delta$ = 1.04 (t, $J$ = 7.04, 3H), 1.17 (t, $J$ = 7.08, 3H), 3.00-3.04 (m, 1H), 3.18-3.22 (m, 1H), 3.90-3.95 (m, 2H), 4.12-4.19 (m, 2H), 7.62-7.85 (m, 4H), 7.87-7.88 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, DMSO-$d^6$+ $CDCl_3$): 14.3, 14.7, 44.7, 58.9, 60.5, 62.0, 76.5, 106.5, 112.8, 117.7, 124.9, 125.1, 129.9, 131.6, 133.2, 135.6, 170.4, 172.9, 174.1, 180.2, 186.3 ppm. Elemental Analysis for $C_{21}H_{18}N_2O_7$ calculated C, 61.46; H, 4.42; N, 6.83 obtained C, 61.42; H, 4.40; N, 6.86.

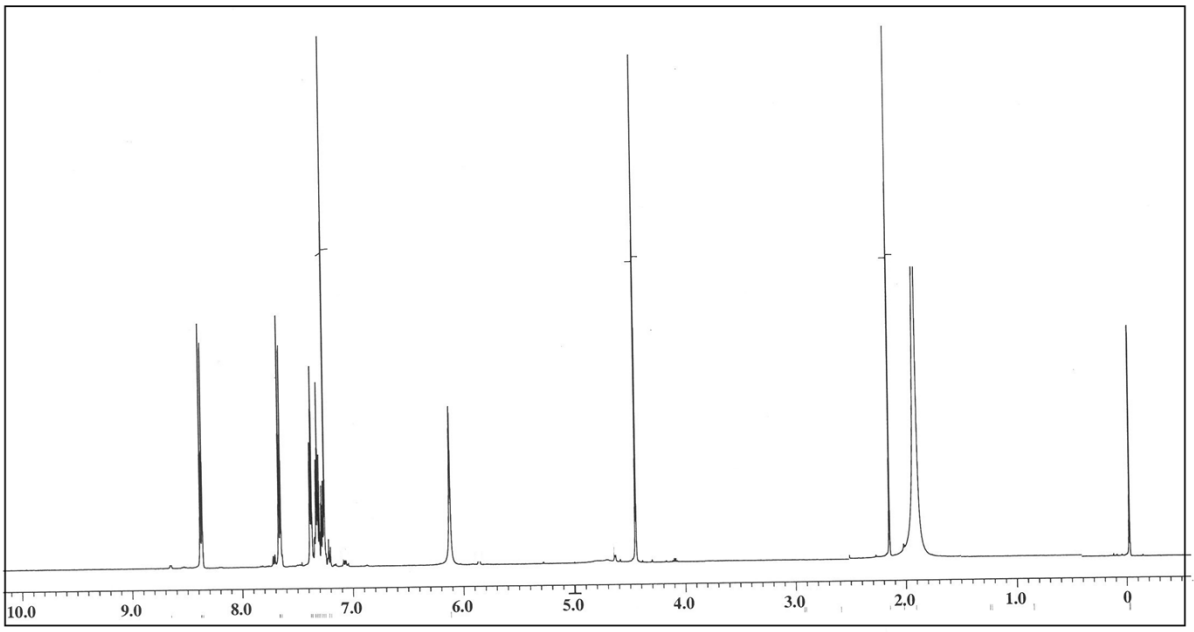
Copies $^{1}$H-NMR and $^{13}$C-NMR of unknown derivatives:



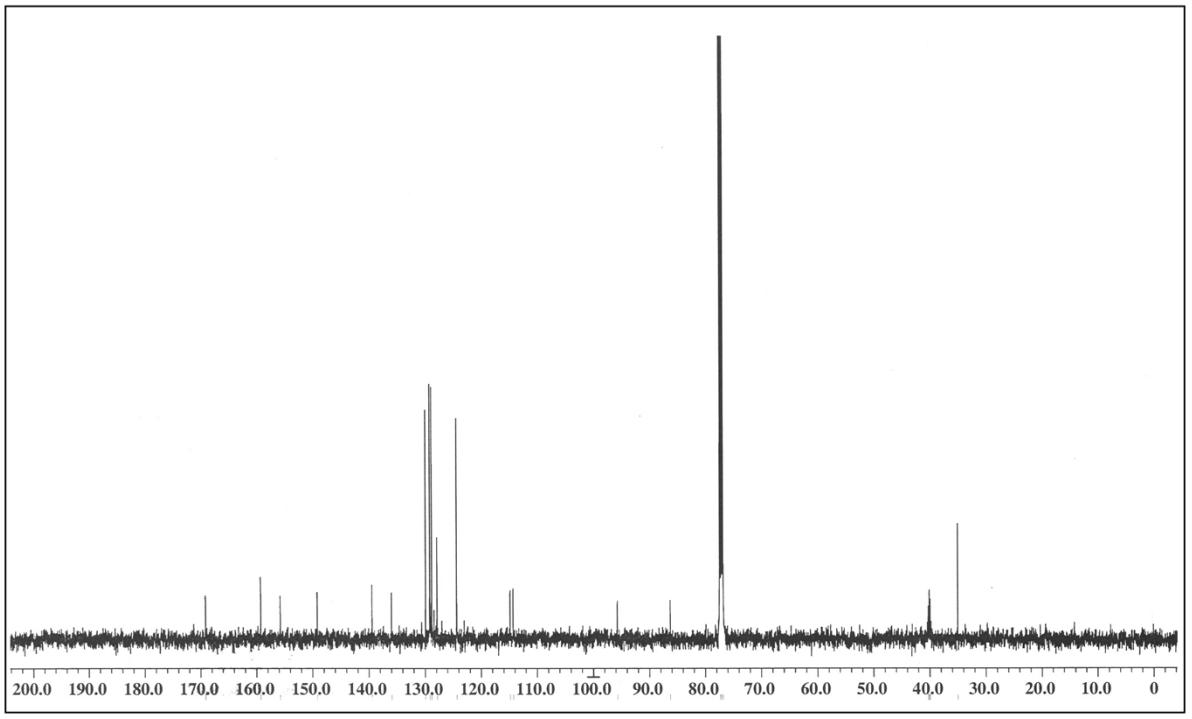

$^{1}$H-NMR of compound -**1h**



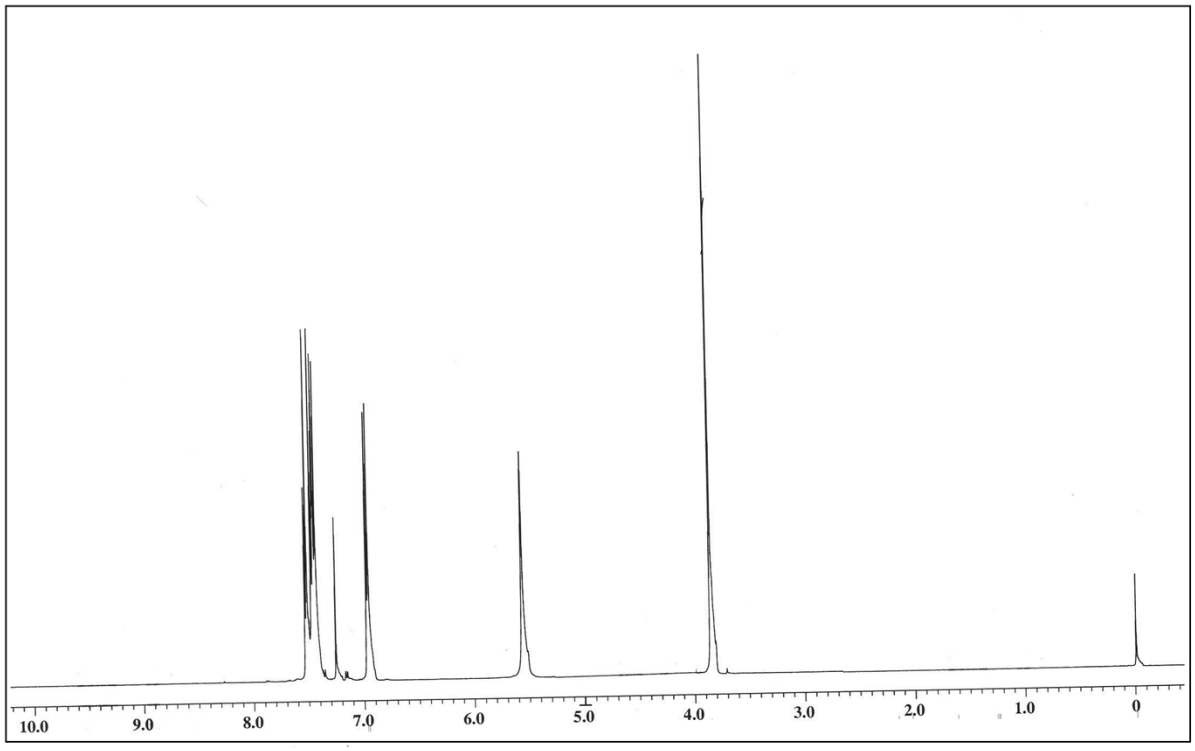

$^{13}$C-NMR of compound -**1h**



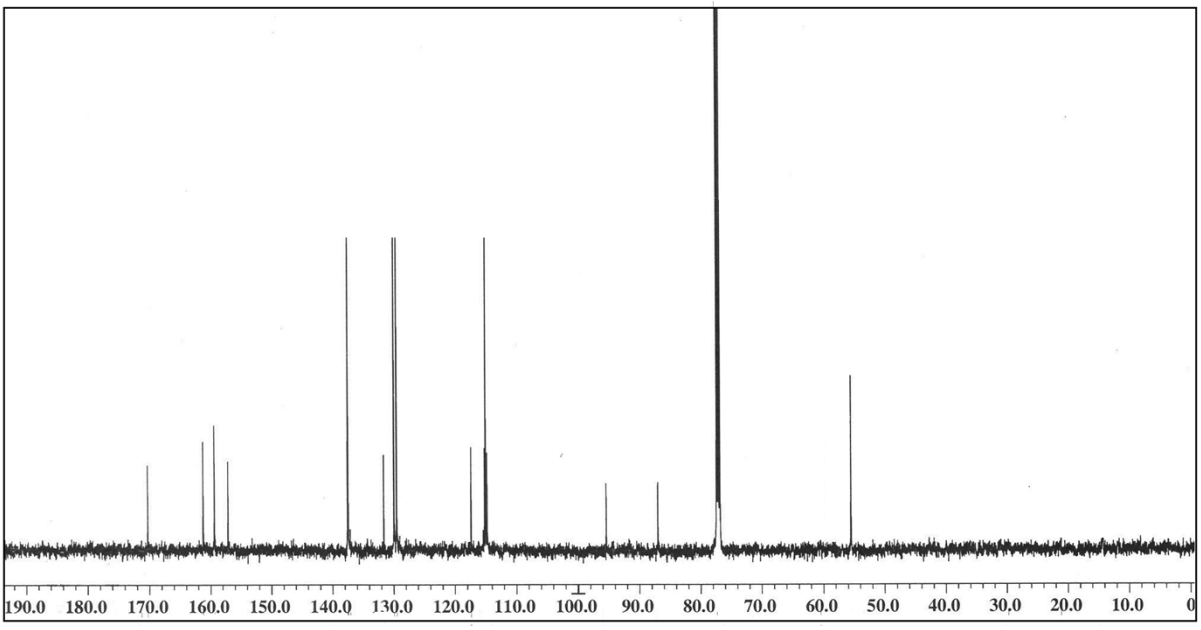

$^{1}$H-NMR of compound -**1j**



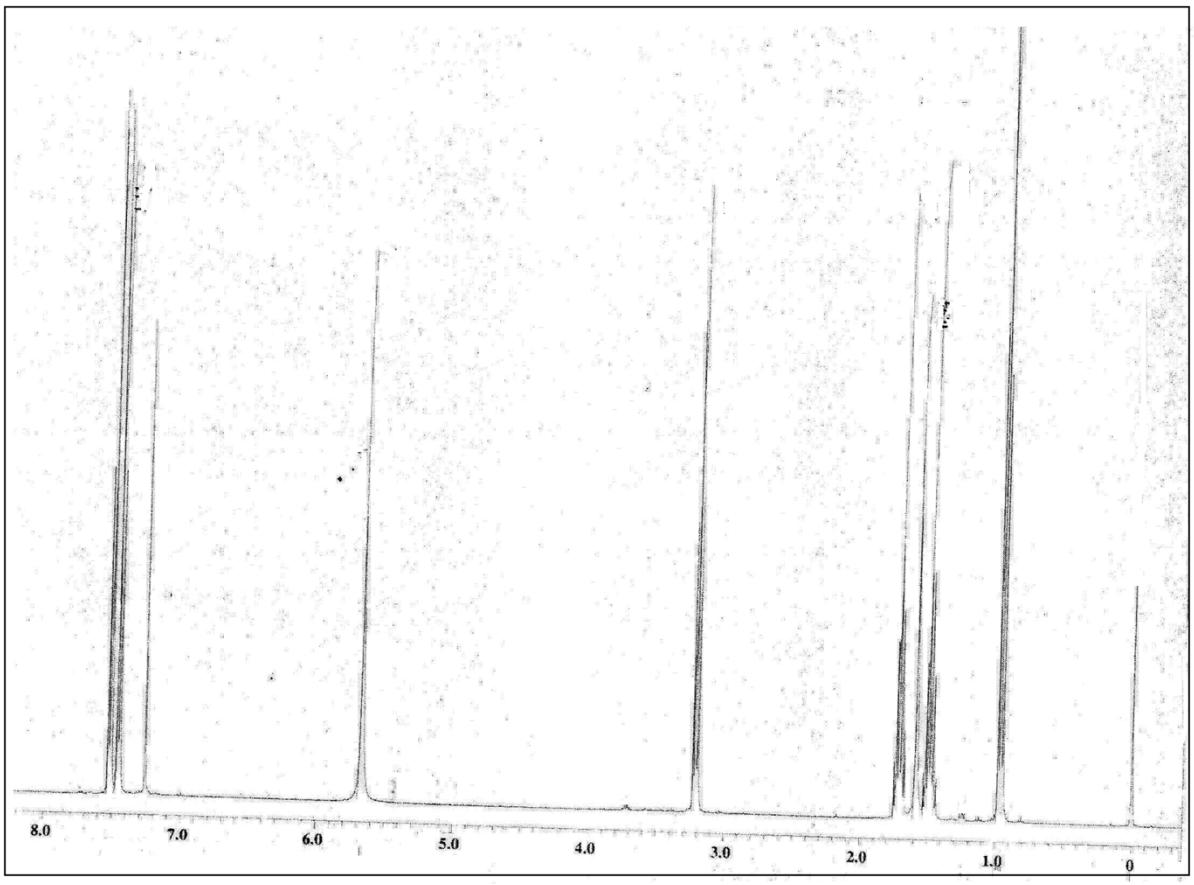

$^{13}$C-NMR of compound -**1j**



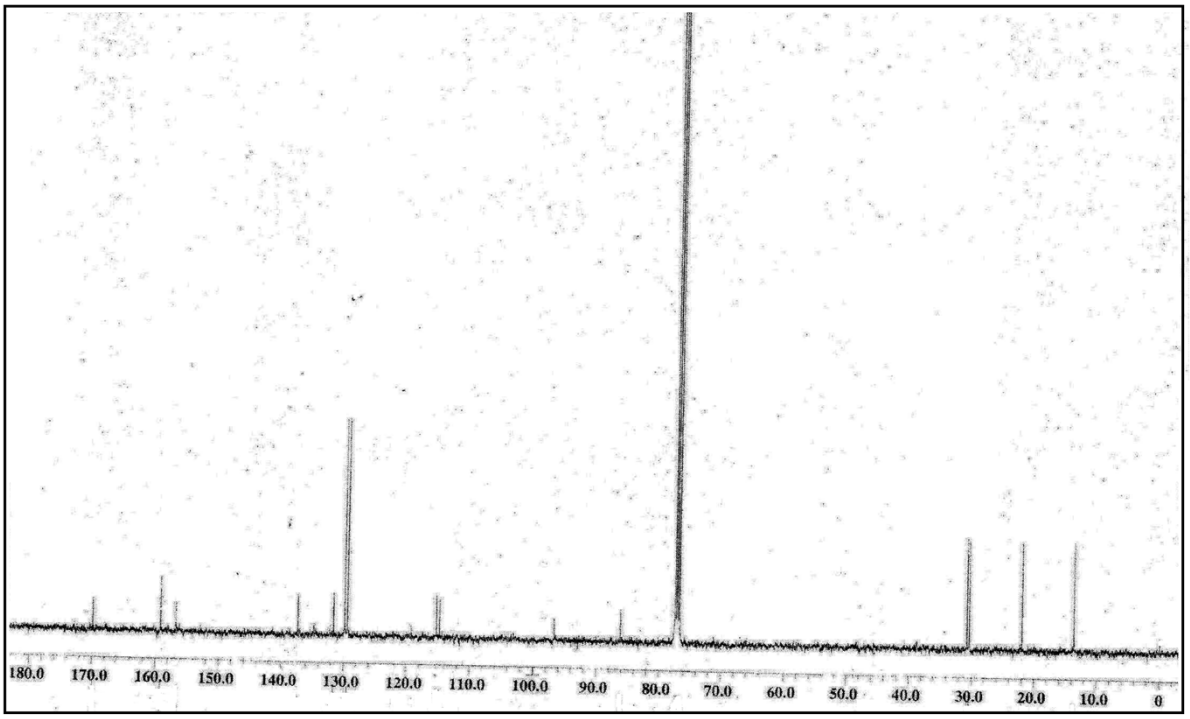

$^{1}$H-NMR of compound -**1l**



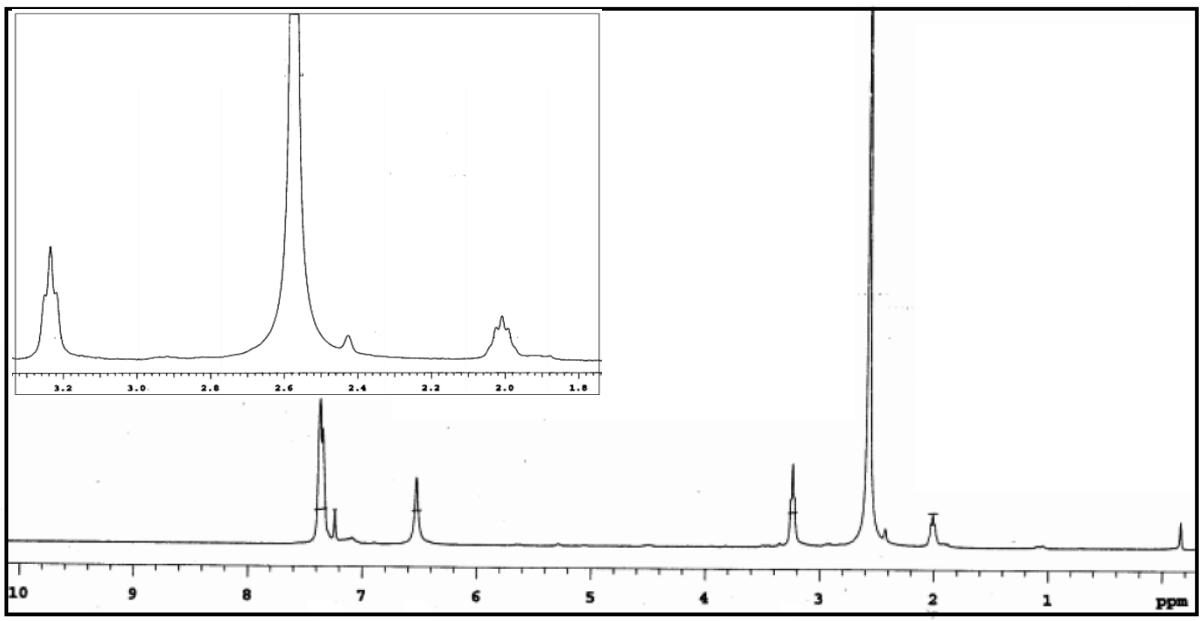

$^{13}$C-NMR of compound -**1l**



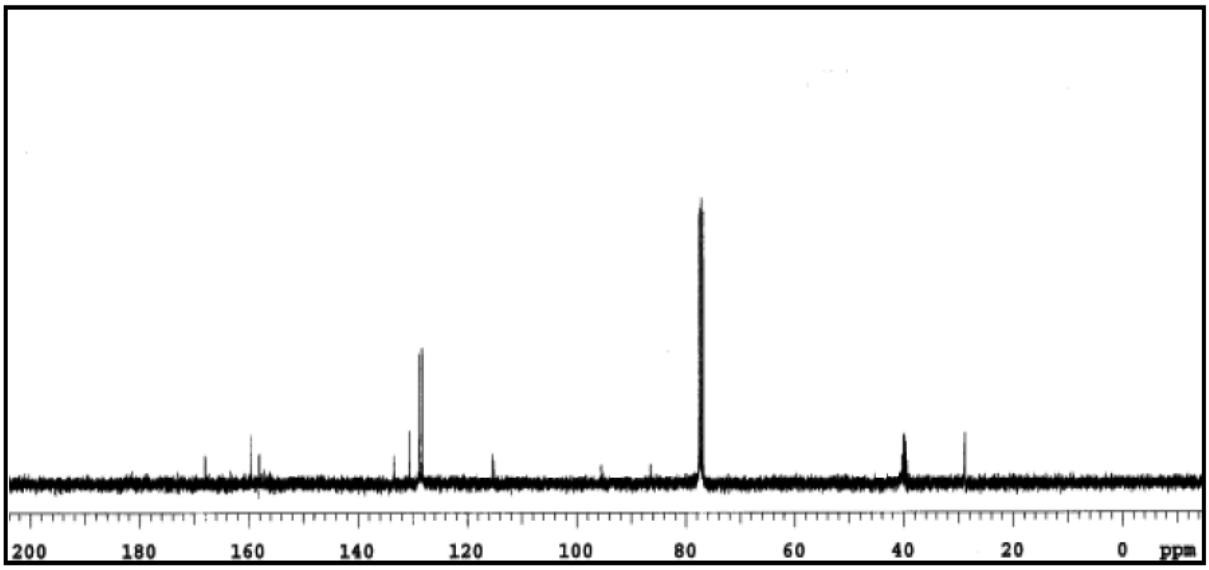

$^{1}$H-NMR of compound -**1n**



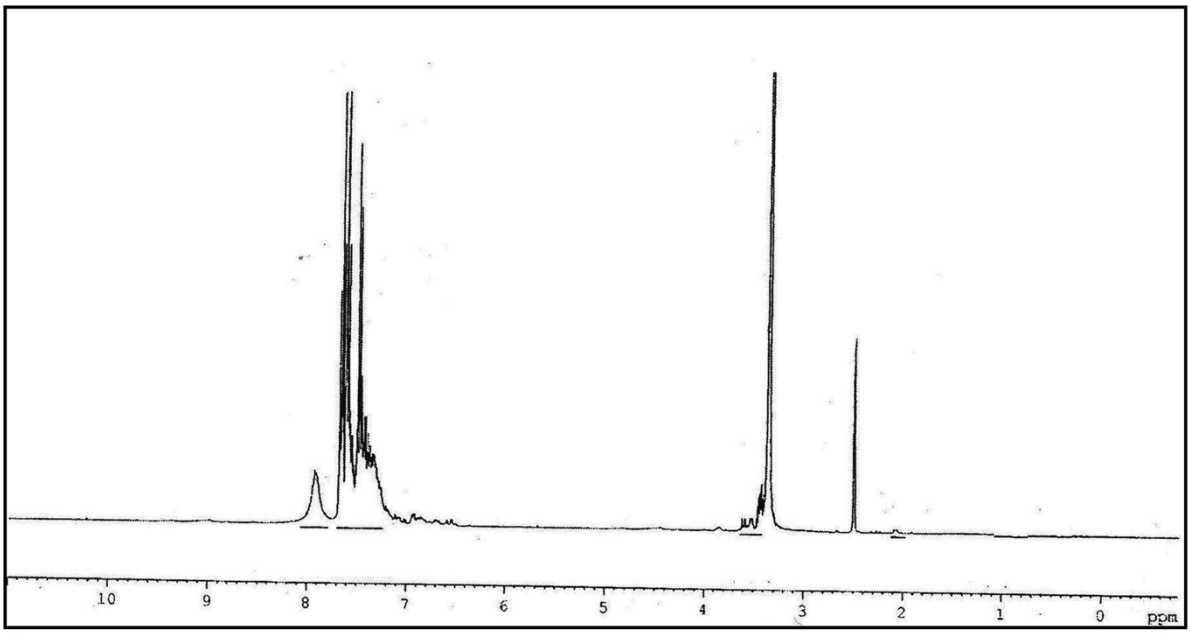

$^{13}$C-NMR of compound -**1n**



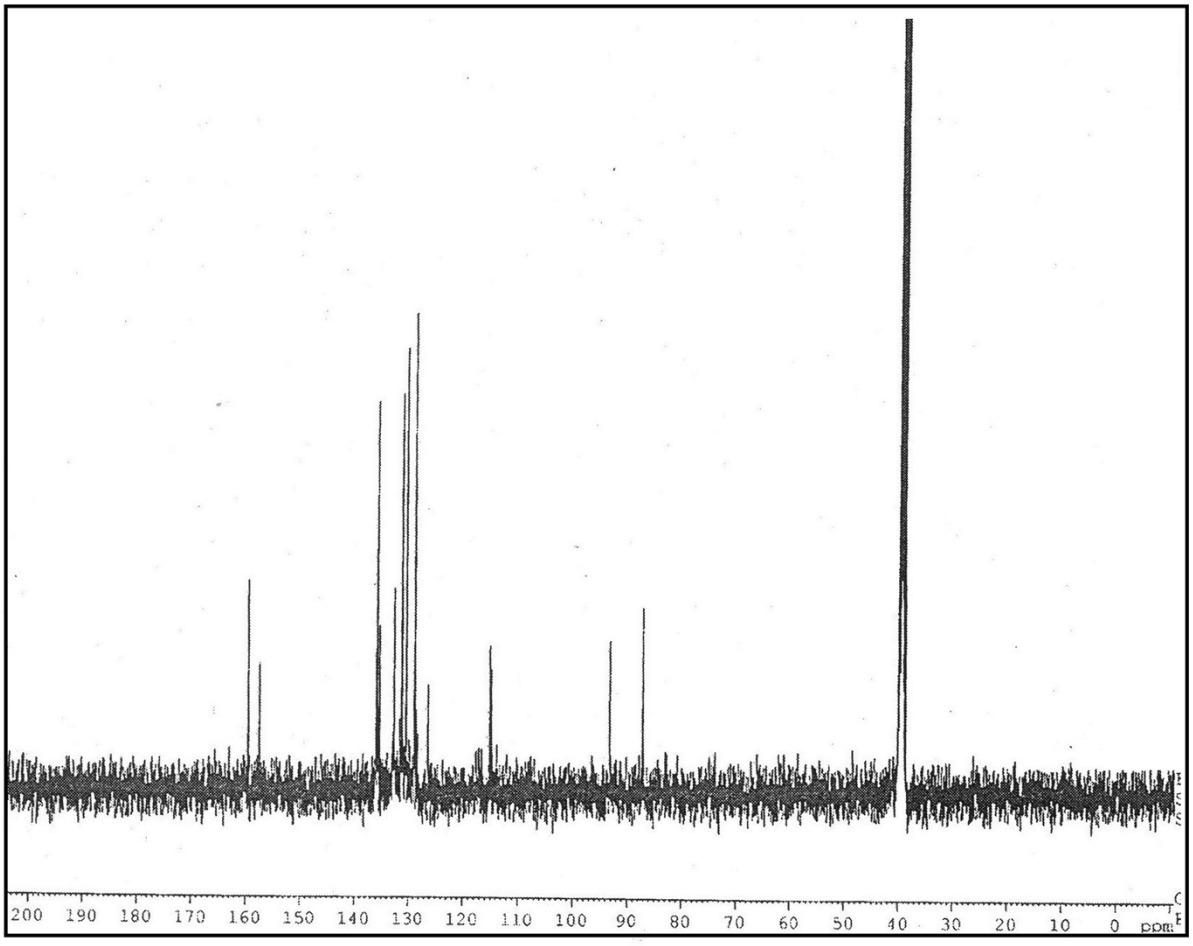

$^{1}$H-NMR of compound -**1r**



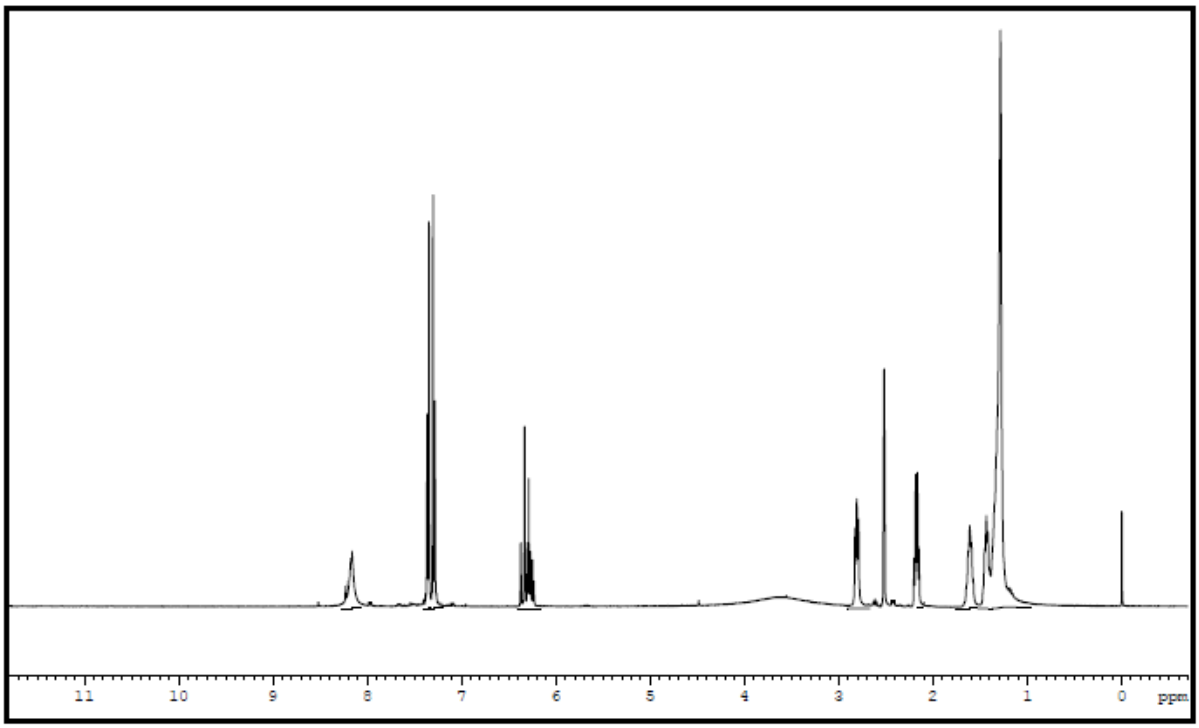

$^{13}$C-NMR of compound -**1r**



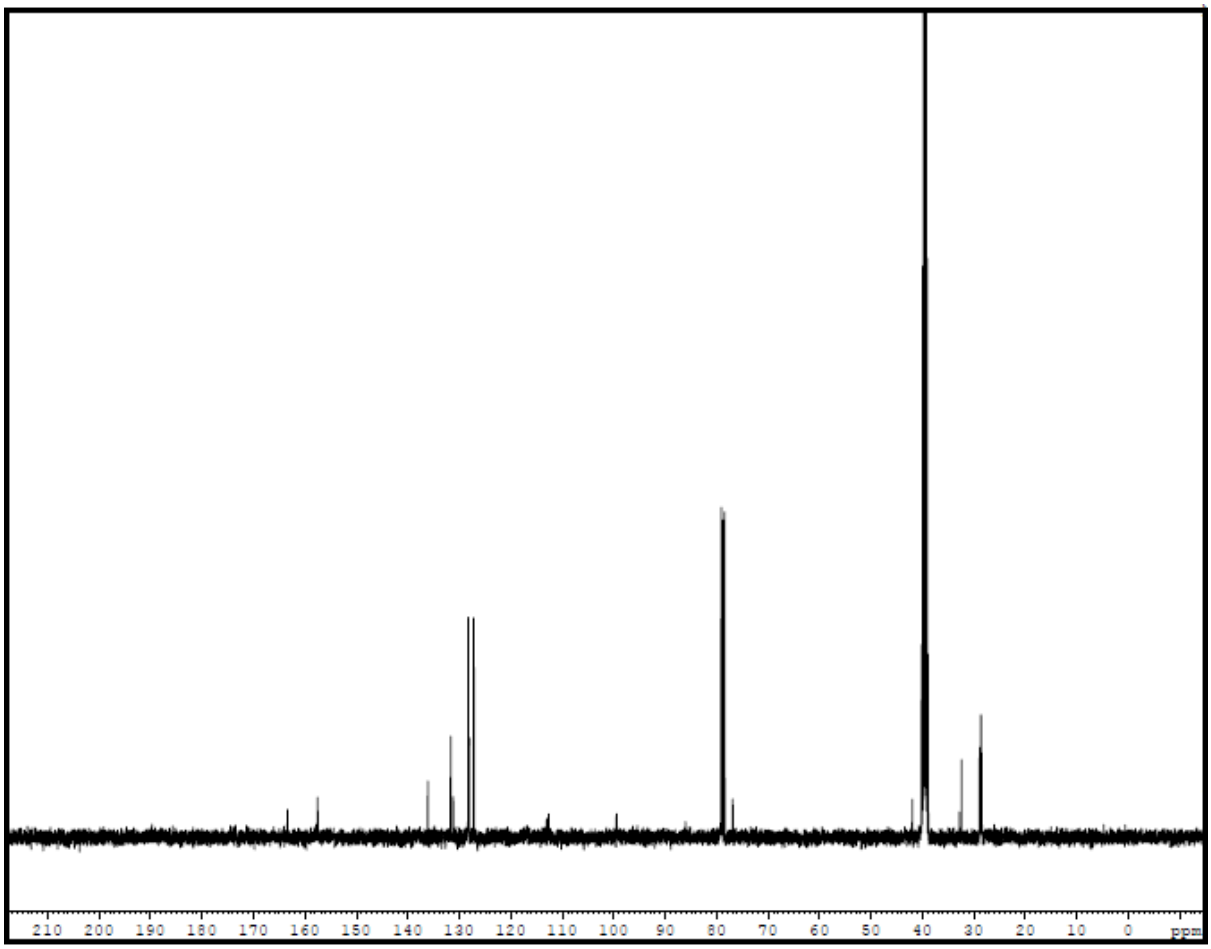

$^{1}$H-NMR of compound **-1s**



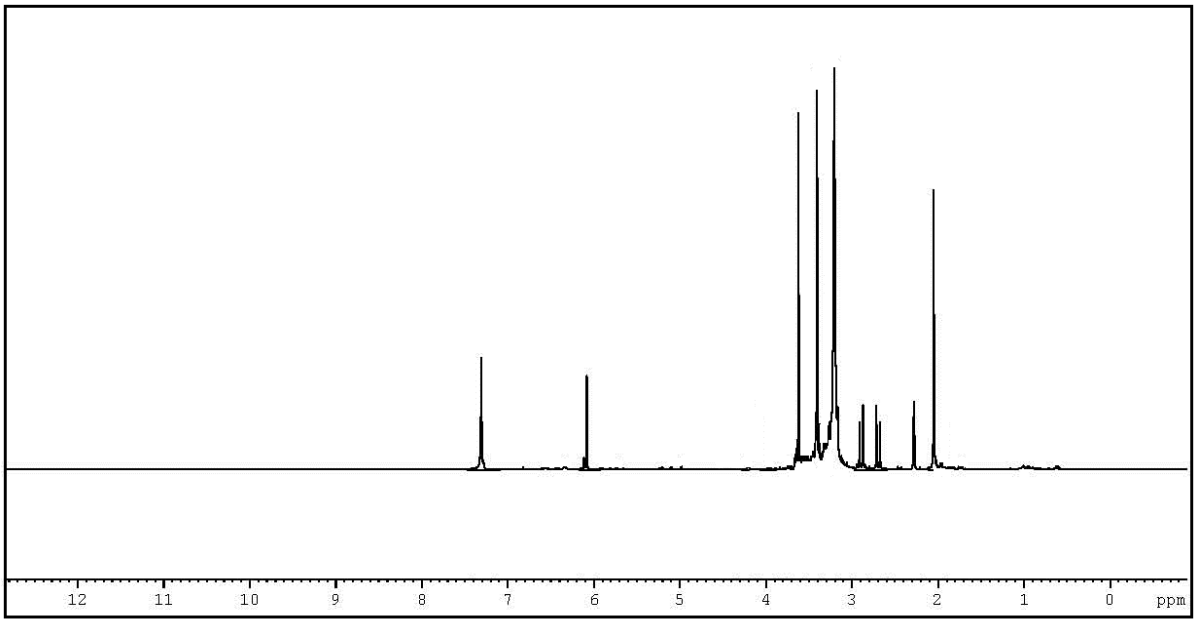

$^{13}$C-NMR of compound **-1s**



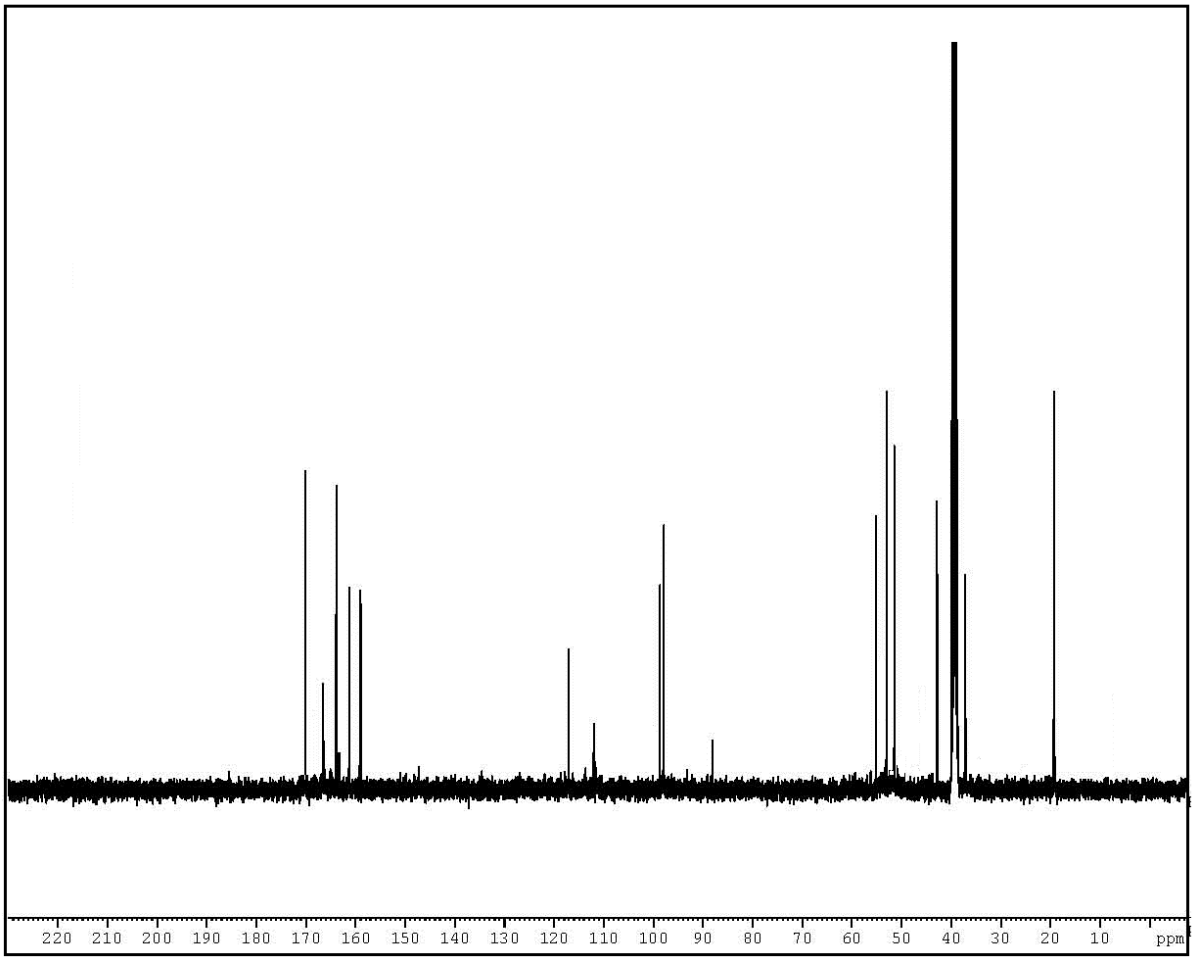

$^{1}$H-NMR of compound **-2g**



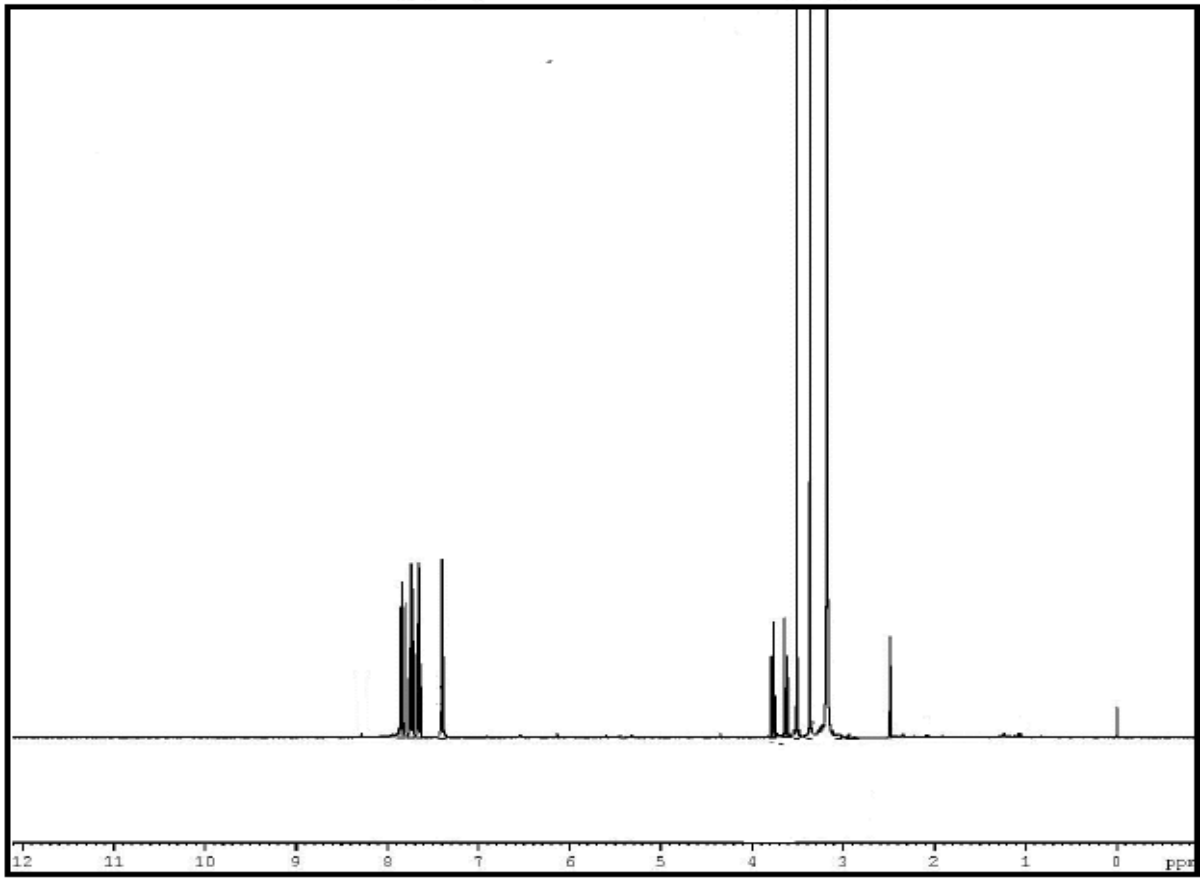

$^{13}$C-NMR of compound **-2g**



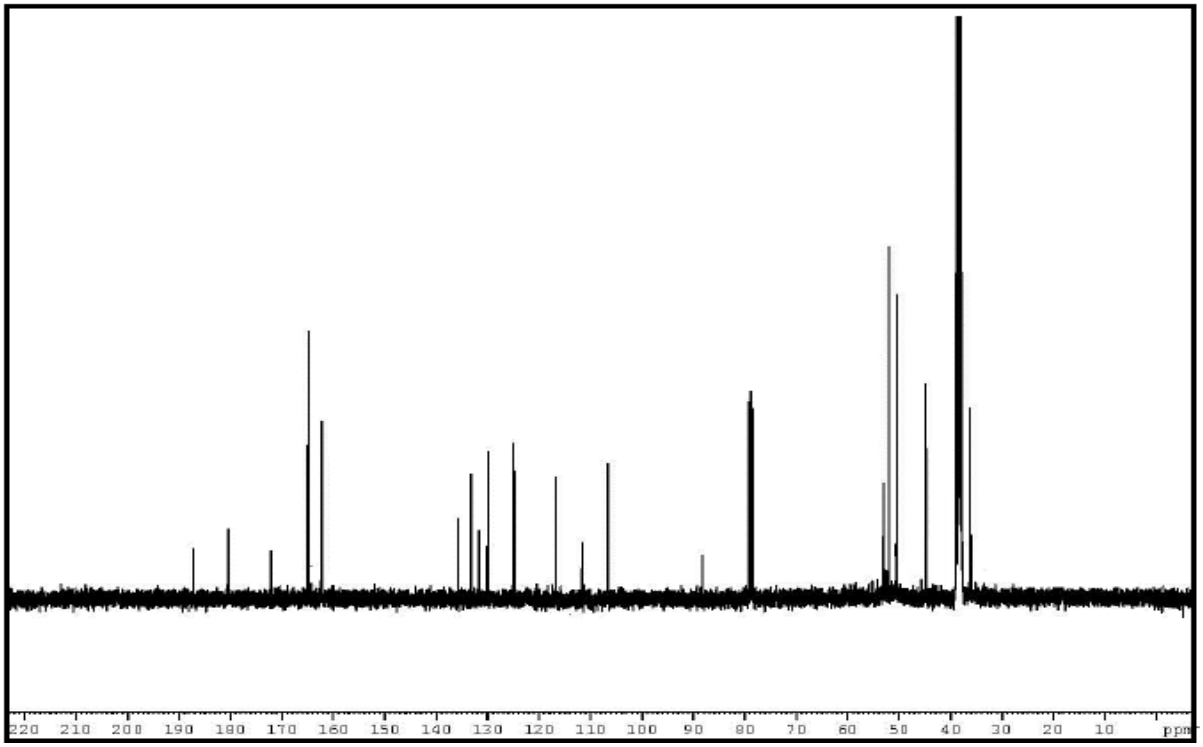

$^{1}$H-NMR of compound -**3d**



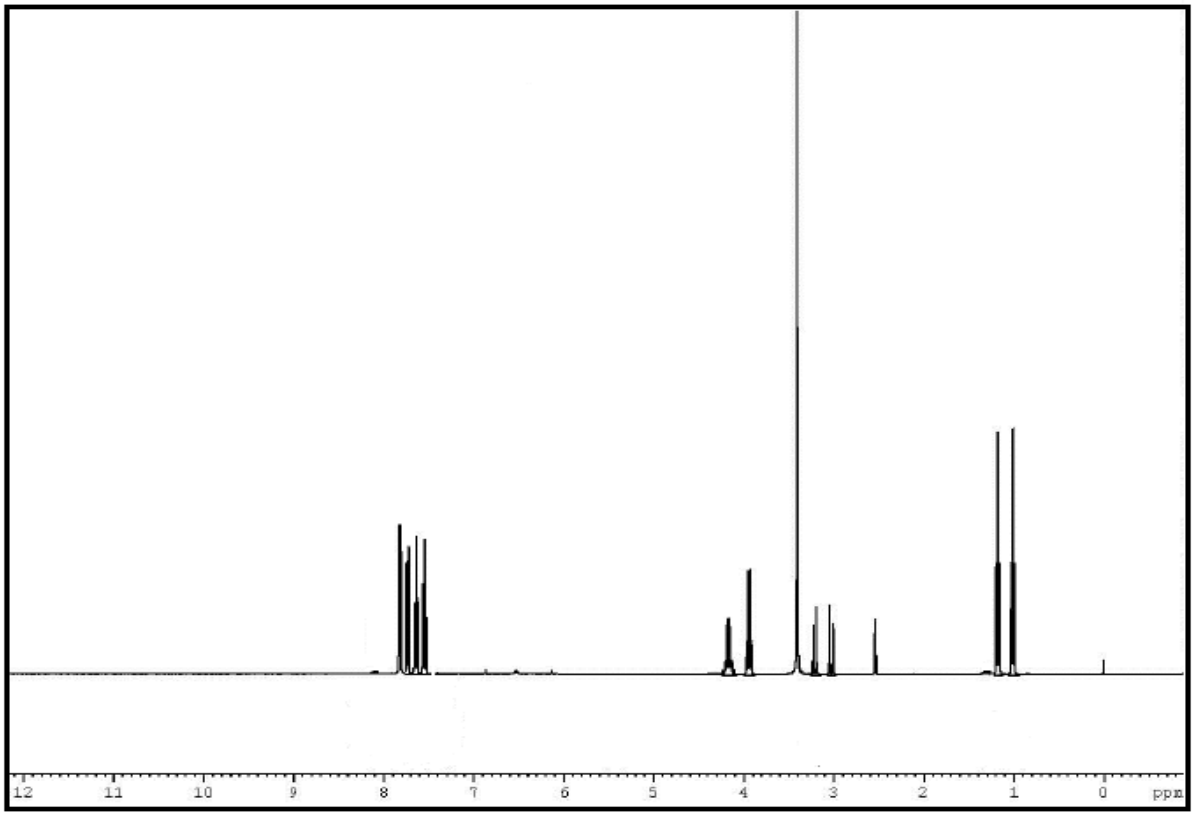

$^{13}$C-NMR of compound -**3d**



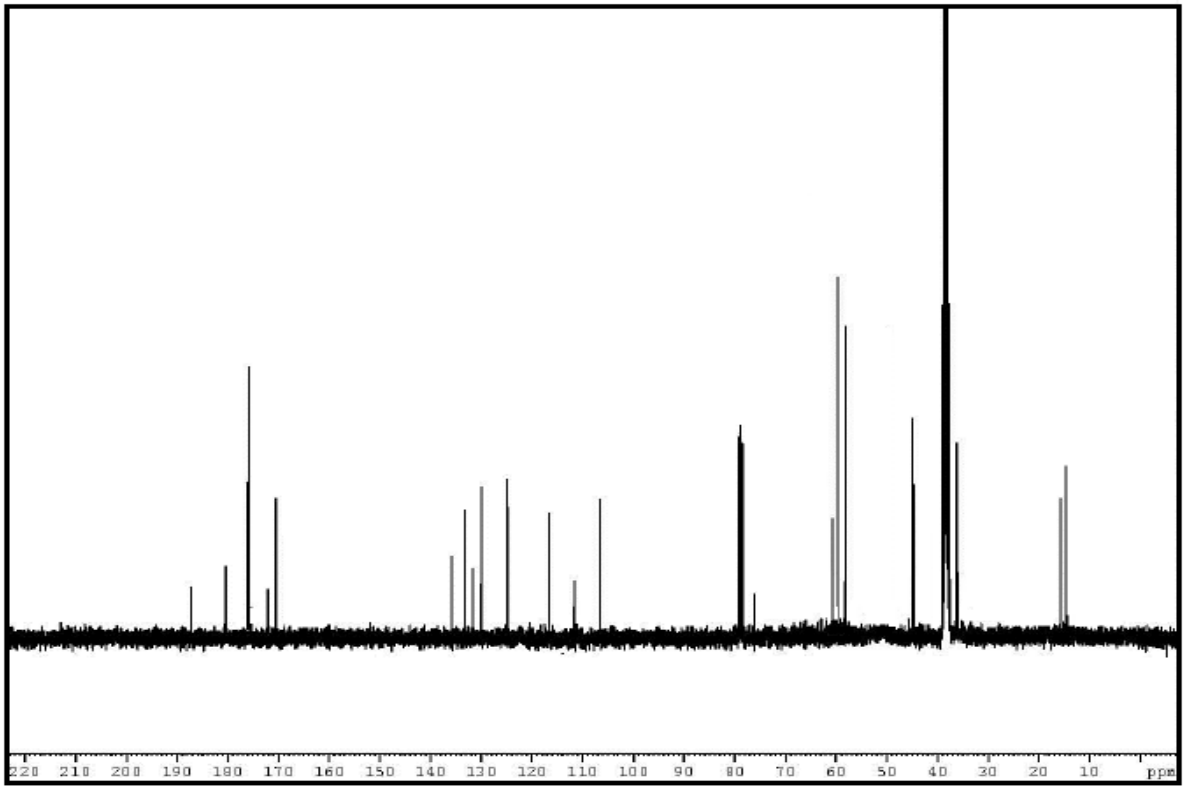

$^{1}$H-NMR of compound-**3e**




$^{13}$C-NMR of compound -**3e**




$^{1}$H-NMR of compound **-3f**




$^{13}$C-NMR of compound **-3f**