Supplementary Material (ESI) for Green Chemistry

A one-pot preparation of cyanamide from dithiocarbamate using molecular iodine

Jayashree Nath,[a] Bhisma K. Patel,*[b] Latonglila Jamir,[c] Upasana Bora Sinha,[c] K.V.V. V. Satyanarayana[d]

[a] Centre for the Environment, Indian Institute of Technology Guwahati, Guwahati -781 039, Assam, India.
[b] Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati -781 039, Assam, India.
E-mail: patel@iitg.ernet.in .[c] Department of Chemistry ,Nagaland University, Lumami Campus798 601, Nagaland, India.[d] Department of Chemistry ,Gitam Institute of Science, Gitam University, Visakhapatanam, 530045, AP - India.

List of Contents

1. General procedure S2

2. Spectral data S2-S4

3. Spectra (^{1}H NMR, ^{13}C NMR, and IR) of compounds S5-S28

Dithiocarbamate salt of amines can be prepared following any one of the literature reports (Wang, R.; Dolman, S. J. *J. Org. Chem.* **2007**, *72*, 3969, Li, G.; Tajima, H.; Ohtani, T. *J. Org. Chem.* **1997**, *62*, 4539) or the following modified literature procedure.

General procedure for the preparation of dithiocarbamate salt (1):

To a mixture of carbon disulfide (1.9g, 25 mmol) and triethylamine (3.03g, 30 mmol) under an ice cooled condition, was added aniline (0.93g, 10 mmol) drop wise with constant stirring. After complete addition of aniline, the reaction was stirred at room temperature for 2 hrs during which precipitation of phenyl dithiocarbamic acid salt was observed. Progress of the reaction was monitored by TLC. After completion of the reaction the product was filtered, washed with hexane : ethylacetate (5 : 95) (4 x 5 mL) to get rid of unreacted aniline and excess triethylamine. The product (Yield : 2.48g, 92 %) was dried in vacuum dessicator and used as such for the next reaction.

Note : This reaction is sluggish (18-24 hrs) particularly with bulky substrates and substrate containing electron withdrawing groups. In these cases the reactions were allowed to continue at room temperature until precipitation of dithiocarbamate salt was observed (18-24 hrs).

Spectral data:

Phenyl cyanamide (1a). Gummy; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.02-7.07 (m, 3H), 7.28-7.33 (m, 2H), 7.64 (brs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 112.2, 115.5, 123.6, 129.8, 137.4; IR (KBr) 3175 (m), 2919 (m), 2227 (s), 1600 (s), 1501 (s), 1249 (m), 891 (w), 748 (s); elemental analysis for $C_7H_6N_2$ (118.13): calcd. C 71.17, H 5.12, N 23.71; found C 71.27, H 5.09, N 23.67.

2-Methoxy-phenyl cyanamide (2a). Oily Liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 3.87 (s, 3H, OCH_3), 6.88 (m, 1H), 6.95-7.05 (m, 2H), 7.18 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 55.9, 110.8, 111.0, 114.9, 121.5, 123.8, 126.8, 146.9; IR (KBr) 3219 (m), 2939 (m), 2839 (m), 2224 (s), 1603 (s), 1509 (s), 1454 (s), 1259 (s), 1026 (m), 746 (m); elemental analysis for $C_8H_8N_2O$ (148.16): calcd. C 64.85, H 5.44, N 18.90; found C 64.79, H 5.42, N 18.78.

2-Chloro-phenyl cyanamide (4a). White Solid; Mp: 101-103 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 6.56 (brs,1H), 7.05 (m, 1H), 7.31 (m, 2H), 7.35 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 110.0, 116.2, 120.4, 124.5, 128.6, 129.9, 134.3; IR (KBr) 3163 (s), 2921 (w), 2243 (s), 1598 (s), 1500 (s), 1426 (m), 1295 (m), 1049 (w), 746 (s); elemental analysis for $C_7H_5ClN_2$ (152.58): calcd. C 55.10, H 3.30, N 18.36; found C 55.11, H 3.32, N 18.29.

3-Nitro-phenyl cyanamide (6a). Yellow Solid; Mp: 133-135 ^{o}C; ^{1}H NMR ($CDCl_3$ + DMSO, 400 MHz,) δ (ppm) 7.38 (d, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 8.4 Hz, 1H), 7.85 (m, 2H); ^{13}C NMR ($CDCl_3$ + DMSO, 100 MHz,) δ (ppm) 109.6, 110.7, 116.8, 120.8, 130.1, 139.9, 148.4; IR (KBr) 3147 (m), 2919 (m), 2241 (s), 1621 (w), 1531 (s), 1354 (s), 1260 (m), 1071 (w), 937 (w), 871 (m), 733 (s); elemental analysis for $C_7H_5N_3O_2$ (163.14): calcd. C 51.54, H 3.09, N 25.76; found C 51.58, H 3.12, N 25.7

4-Acetyl-phenylcyanamide (8a). White Solid; Mp: 153-157 ^{o}C; ^{1}H NMR ($CDCl_3$ + DMSO, 400 MHz,) δ (ppm) 2.56 (s, 3H, CH_3), 7.08 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$ + DMSO, 100 MHz,) δ (ppm) 25.9, 110.9, 114.5, 129.8, 131.2, 142.9, 196.2; IR (KBr) 3188 (s), 2966 (m), 2228 (s), 1666 (s), 1599 (s), 1585 (s), 1411 (m), 1362 (m), 1278 (s), 1176 (m), 962 (w); elemental analysis for $C_9H_8N_2O$ (160.18): calcd. C 67.49, H 5.03, N 17.48; found C 67.53, H 5.08, N 17.44.

4-Chloro-phenyl cyanamide (9a). White Solid; Mp: 95 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 6.91 (d, *J* = 8.0 Hz, 2H,), 7.28 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 111.4, 116.9, 128.9, 129.9, 136.2; IR (KBr) 3166 (m), 2954 (w), 2234 (s), 1600 (m), 1494 (s), 1399 (w), 1251 (m), 1091 (m), 1011 (w), 820 (m); elemental analysis for $C_7H_5ClN_2$ (152.58): calcd. C 55.10, H 3.30, N 18.36; found C 55.09, H 3.33, N 18.32.

4-Hydroxy-phenyl cyanamide (10a). White solid; Mp: 259-261 ^{o}C; ^{1}H NMR ($CDCl_3$ + DMSO, 400 MHz,) δ (ppm) 5.67 (brs, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 8.98 (brs, 1H, OH); ^{13}C NMR ($CDCl_3$ + DMSO, 100 MHz,) δ (ppm) 112.8, 115.6, 115.8, 129.5, 152.2; IR (KBr) 3213 (s), 2992 (w), 2230 (s), 1613 (w), 1519 (s), 1444 (m),

1258 (m), 1224(s), 815 (m); elemental analysis for $C_7H_6N_2O$ (134.14): calcd. C 62.68, H 4.51, N 20.88; found C 62.72, H 4.55, N 20.83.

2-Iodo-4-methyl-phenyl cyanamide (13a). White solid; Mp: 144 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 2.29 (s, 3H), 6.17 (brs, 1H), 7.17 (m, 2H), 7.56 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 20.4, 84.2, 110.7, 115.4, 130.9, 135.4, 139.6; IR (KBr) 3229 (s), 2919 (w), 2217 (s), 1603 (w), 1502 (s), 1420 (m), 1383 (m), 1283 (w), 1032 (w), 866 (w), 805 (m); elemental analysis for $C_8H_7IN_2$ (258.06): calcd. C 37.23, H 2.73, N 10.86; found C 37.28, H 2.68, N 10.80.

2,4-Dimethyl-phenyl cyanamide (14a). White solid; Mp: 115-119 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 2.18 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 6.74 (brs, 1H, NH), 6.93 (s, 1H), 6.99 (d, J = 8.0 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 17.3, 20.7, 112.8, 115.7, 124.7, 127.9, 131.8, 133.2, 133.3; IR (KBr) 3186 (s), 2915 (w), 2233 (s), 1599 (w), 1512 (s), 1433 (m), 1271 (w), 1031 (w), 812 (m); elemental analysis for $C_9H_{10}N_2$ (146.19): calcd. C 73.94, H 6.89, N 19.16; found C 73.87, H 6.86, N 19.14.

Cyclohexyl-cyanamide (16a). Gummy; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.31 (m, 5H), 1.61 (m, 1H), 1.78 (m, 2H), 1.95 (m, 2H), 3.09 (m, 1H), 3.91 (brs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 24.3, 25.1, 32.6, 54.3, 115.9; IR (KBr) 3196 (m), 2933 (s), 2857 (m), 2217 (s), 1453 (m), 1367 (w), 1167 (w), 892 (w); elemental analysis for $C_7H_{12}N_2$ (124.19): calcd. C 67.70, H 9.74, N 22.56; found C 67.67, H 9.70, N 22.50.

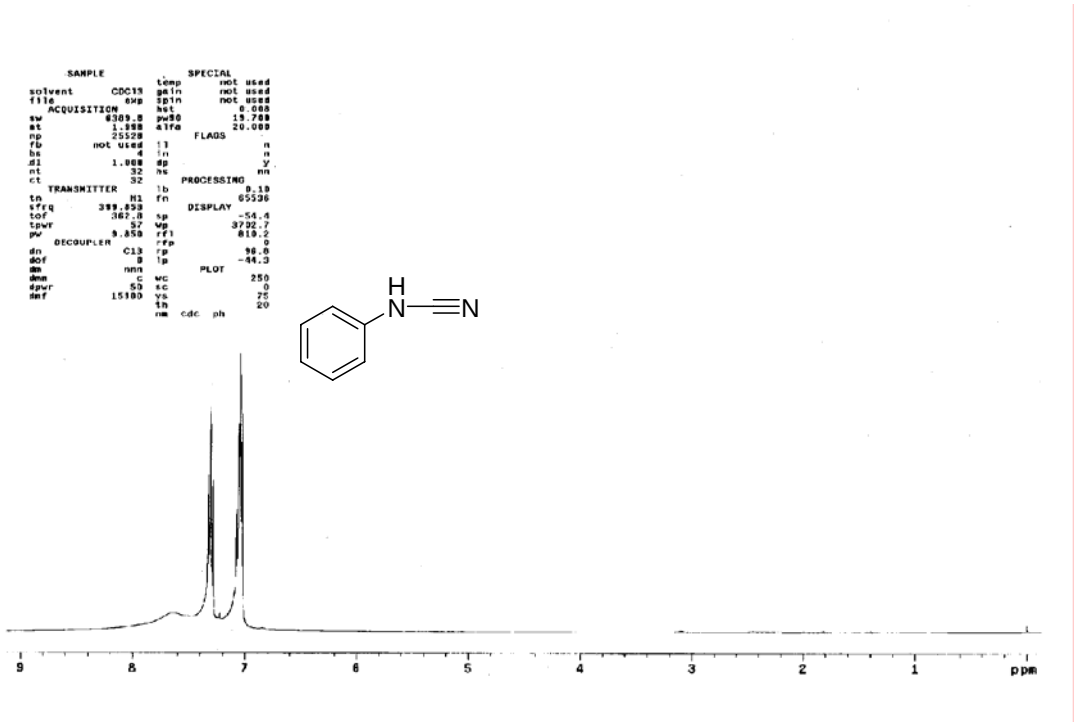
***n*-Butyl-cyanamide (17a).** Gummy; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 0.94 (t, J = 7.6 Hz, 3H, CH_3), 1.40 (m, 2H, CH_2), 1.58 (m, 2H, CH_2), 3.06 (m, 2H, CH_2), 4.61 (brs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 13.6, 19.5, 31.7, 45.7, 117.2; IR (KBr) 3207 (s), 2961 (s), 2875 (m), 2221 (s), 1614 (m), 1463 (m), 1373 (w), 1171 (w), 1015 (w); elemental analysis for $C_5H_{10}N_2$ (98.15): calcd. C 61.19, H 10.27, N 28.54; found C 61.22, H 10.23, N 28.48.

Benzyl cyanamide (18a). Gummy; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 4.11 (d, J = 5.2 Hz, 2H, CH_2), 4.66 (brs, 1H), 7.27-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 49.9, 116.7, 127.9, 128.4, 128.9, 136.4; IR (KBr) 3207 (m), 2925 (w), 2220 (s), 1455 (m),

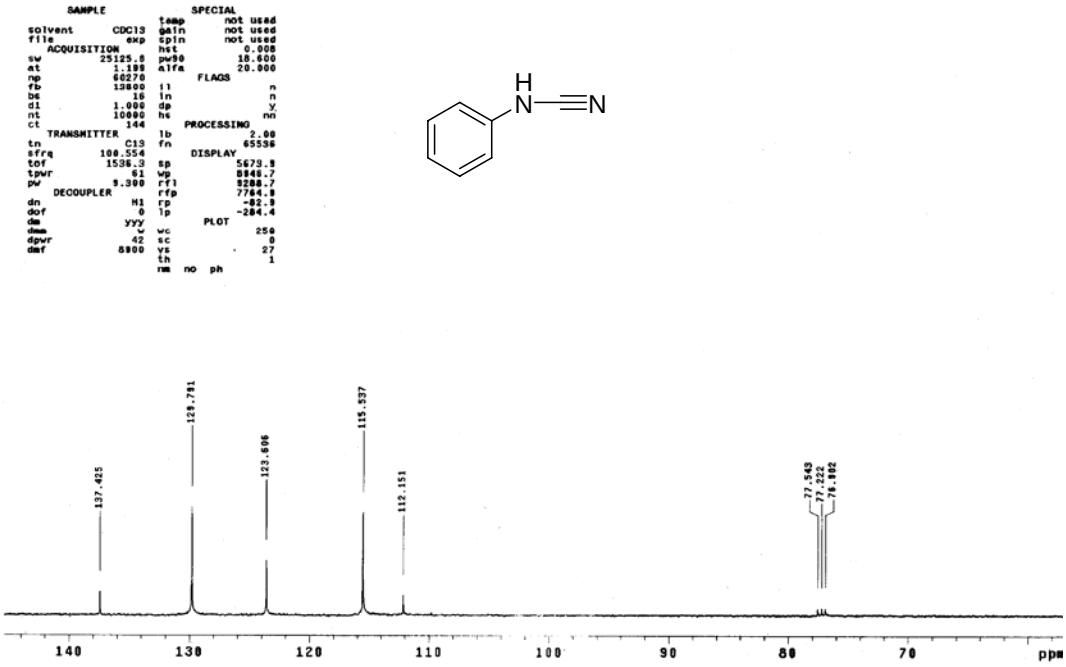
1359 (w), 1210 (w), 1155 (w), 1014 (w), 895 (w); elemental analysis for $C_8H_8N_2$ (132.17): calcd. C 72.70, H 6.10, N 21.19; found C 72.66, H 6.13, N 21.11.

Benzo[1,3]dioxol-5-ylmethyl-cyanamide (**19a).** White Solid; Mp: 82-84 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 4.05 (d, J = 5.2 Hz, 2H, CH_2), 4.57 (brs, 1H), 5.94 (s, 2H, OCH_2), 6.77 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 49.9, 101.4, 108.46, 108.54, 116.5, 121.7, 130.1, 147.8, 148.2; IR (KBr) 3233 (m), 2952 (w), 2897 (w), 2220 (s), 1850 (w), 1609 (w), 1500 (m), 1445 (m), 1370 (m), 1323 (m), 1252 (s), 1038 (m), 925 (m), 862 (w), 809 (m); elemental analysis for $C_9H_8N_2O_2$ (176.18): calcd. C 61.36, H 4.58, N 15.90; found C 61.41, H 4.61, N 15.85.

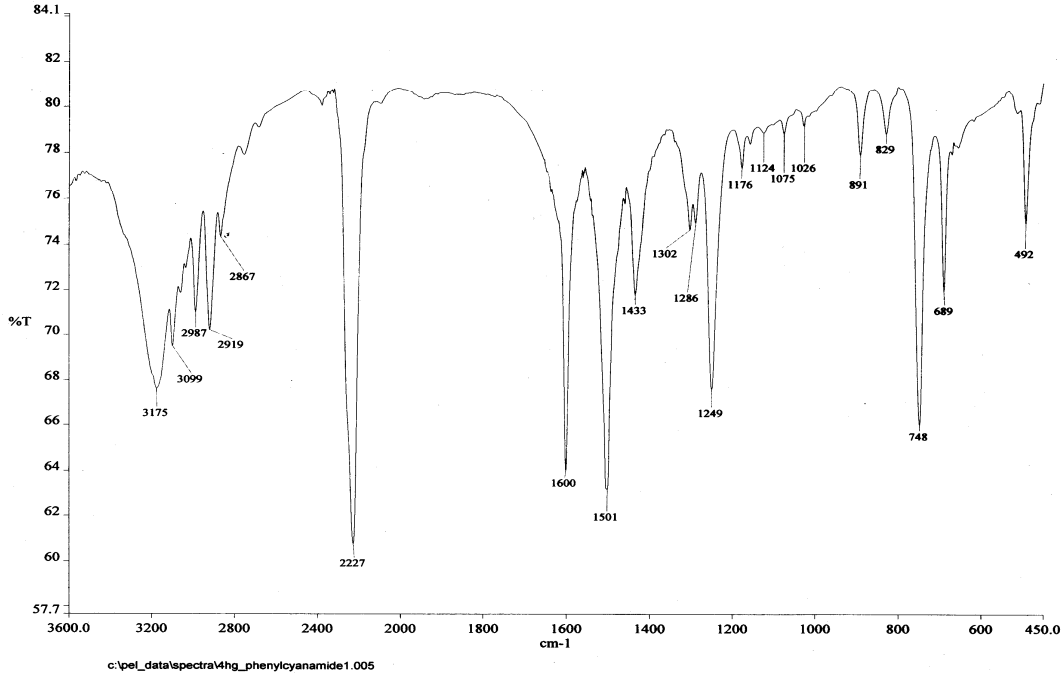
Phenyl cyanamide (1a): ^{1}H NMR ($CDCl_3$, 400 MHz):



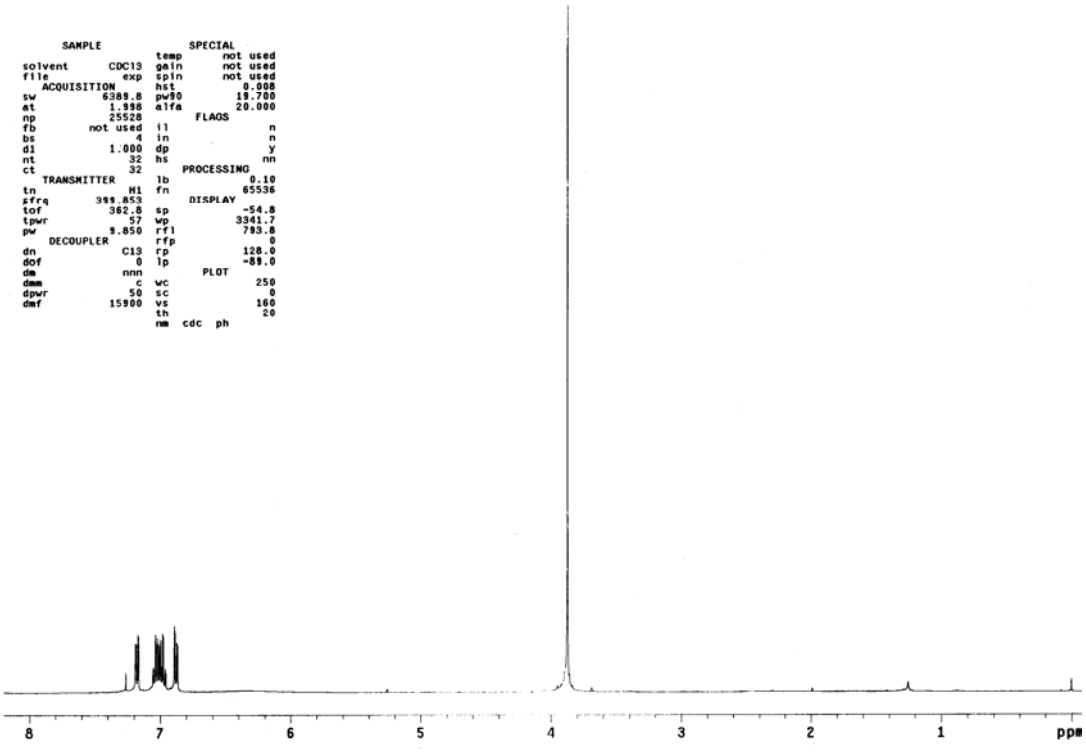
Phenyl cyanamide (1a): ^{13}C NMR ($CDCl_3$, 100 MHz):



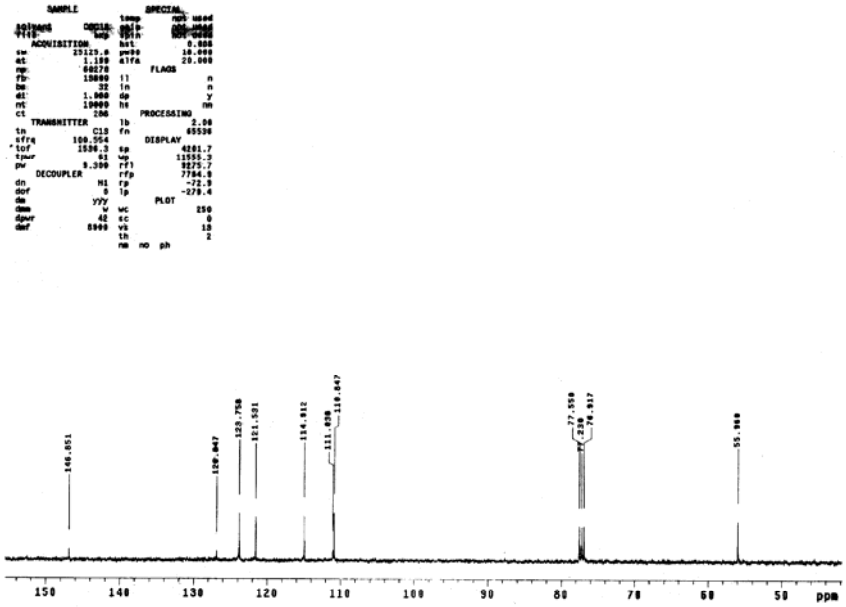
Phenyl cyanamide (1a): IR(KBr):



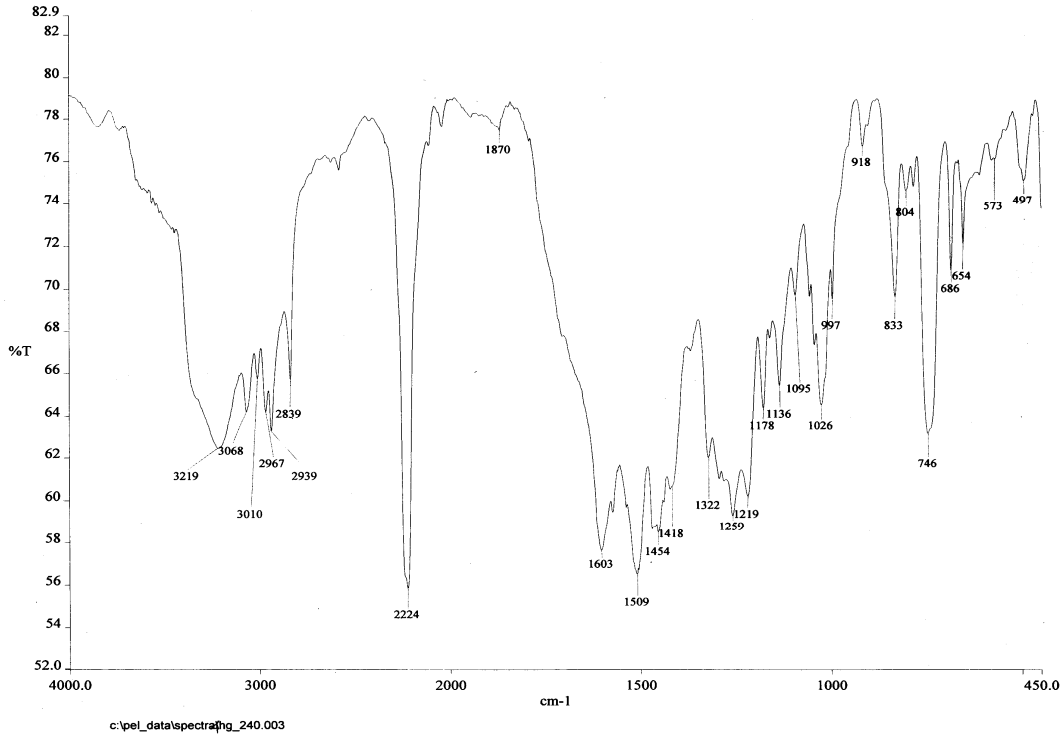
2-Methoxy-phenyl cyanamide (2a): ^{1}H NMR ($CDCl_3$, 400 MHz):



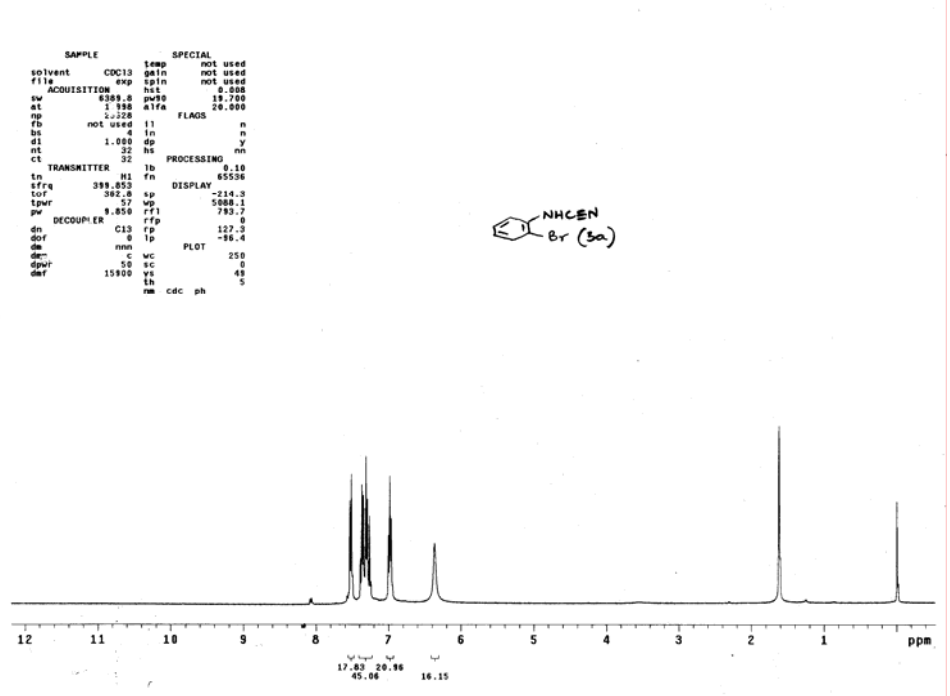
2-Methoxy-phenyl cyanamide (2a): ^{13}C NMR ($CDCl_3$, 100 MHz):



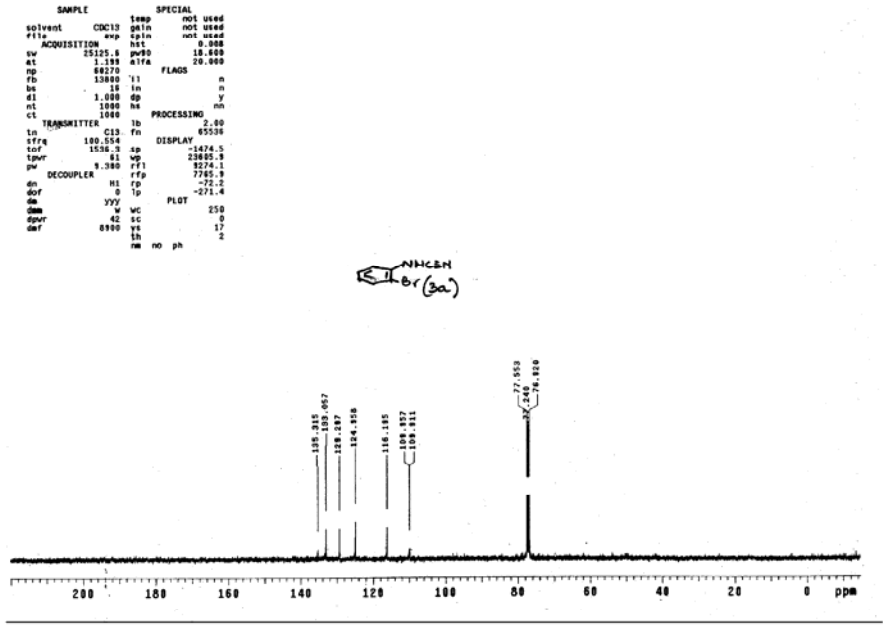
2-Methoxy-phenyl cyanamide (2a): IR(KBr):



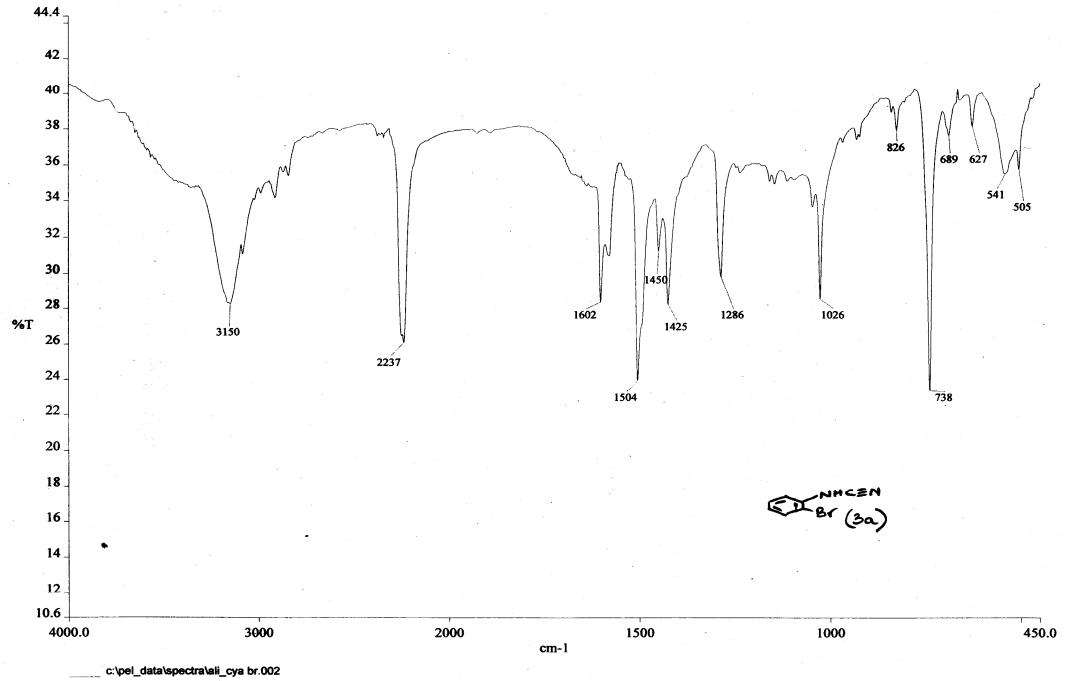
2-Bromo phenyl cyanamide (3a): ^{1}H NMR ($CDCl_3$, 400 MHz):



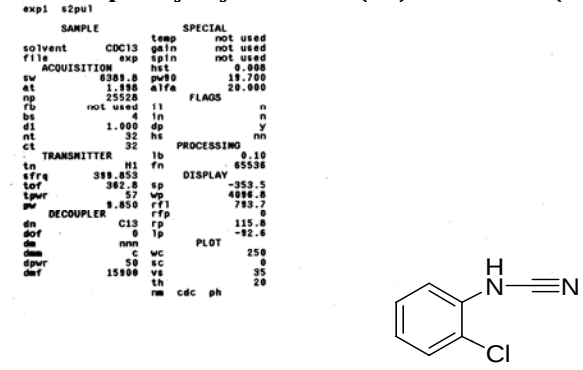
2-Bromo phenyl cyanamide (3a): ^{13}C NMR ($CDCl_3$, 100 MHz):

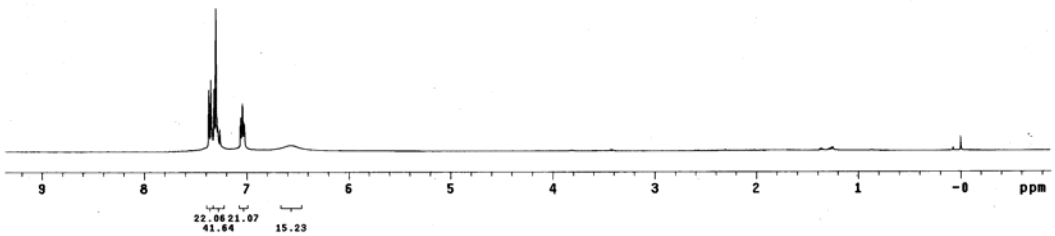


2-Bromo phenyl cyanamide (3a): IR (KBr):

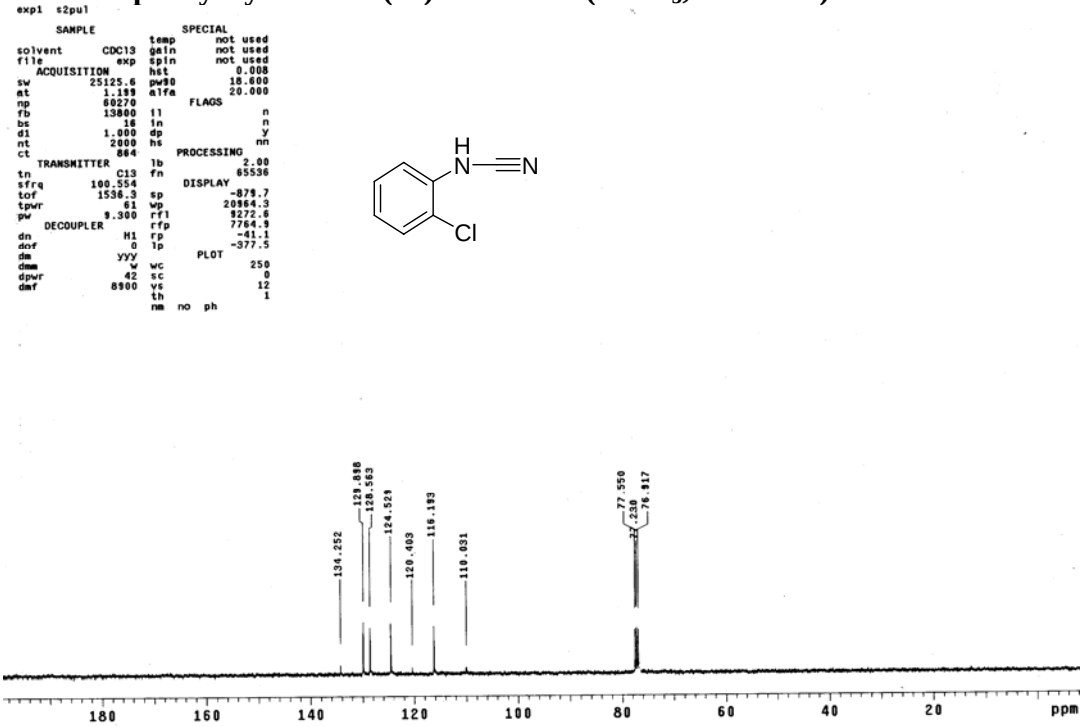


2-Chloro-phenyl cyanamide (4a): ^{1}H NMR ($CDCl_3$, 400 MHz):

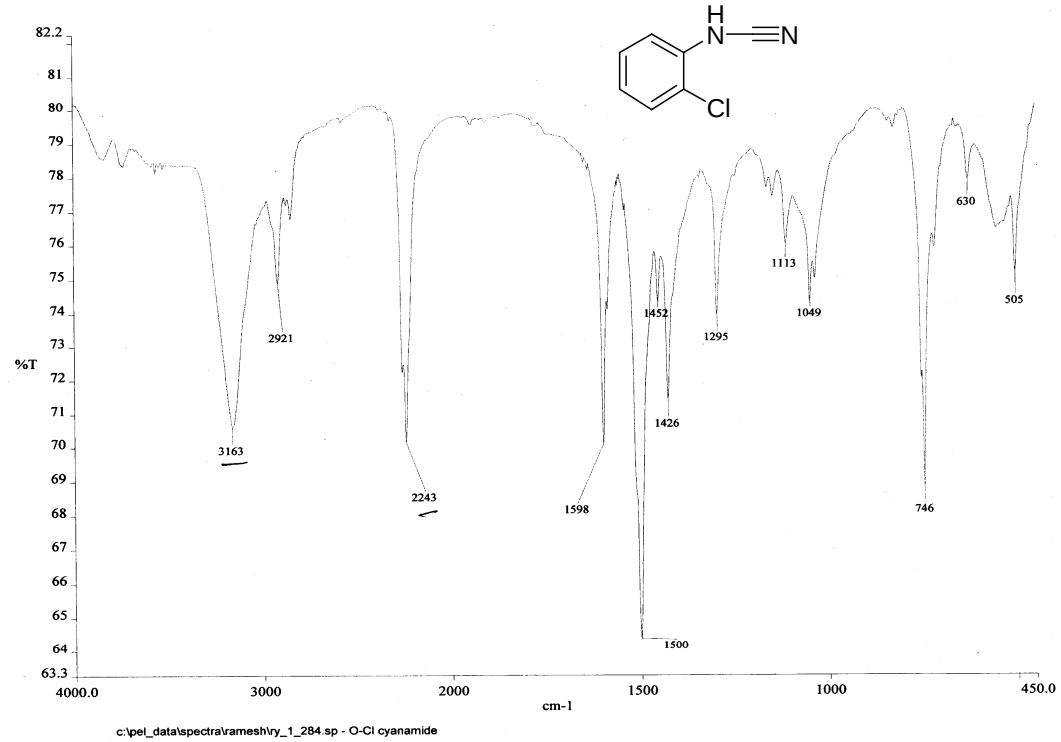




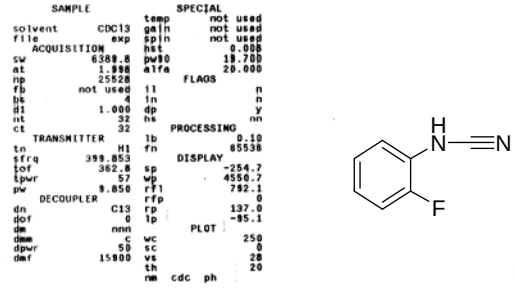
2-Chloro-phenyl cyanamide (4a): ^{13}C NMR ($CDCl_3$, 100 MHz):

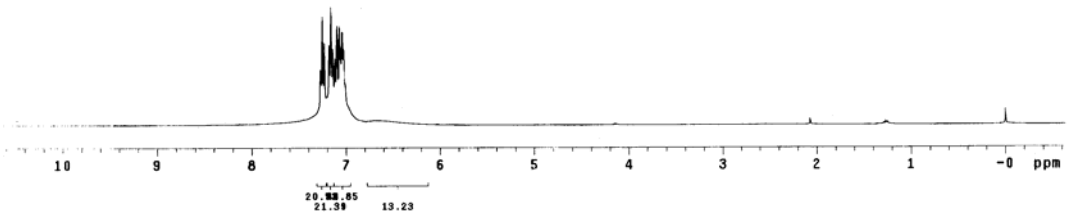


2-Chloro-phenyl cyanamide (4a): IR(KBr):

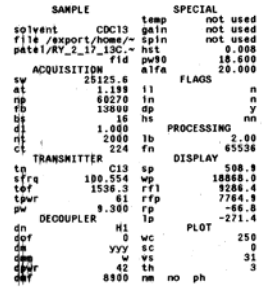


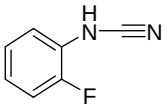
2-Fluoro-phenyl cyanamide (5a): ^{1}H NMR ($CDCl_3$, 400 MHz):

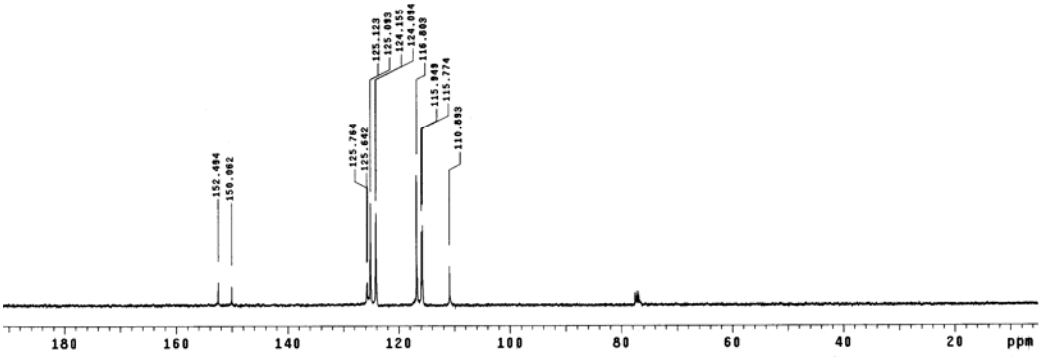




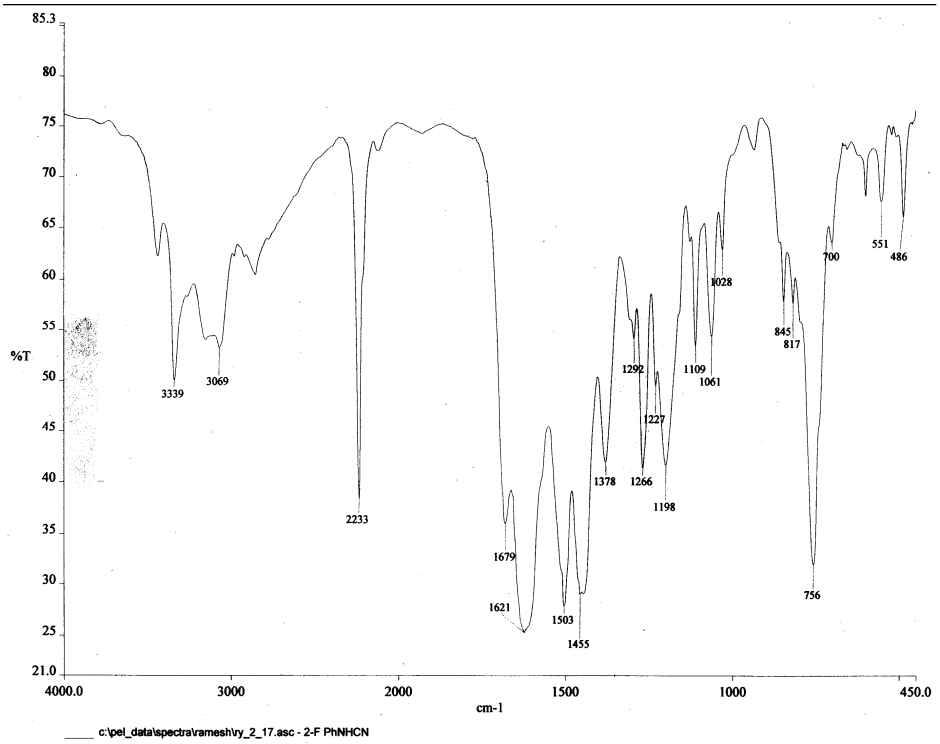
2-Fluoro-phenyl cyanamide (5a): ^{13}C NMR ($CDCl_3$, 100 MHz):



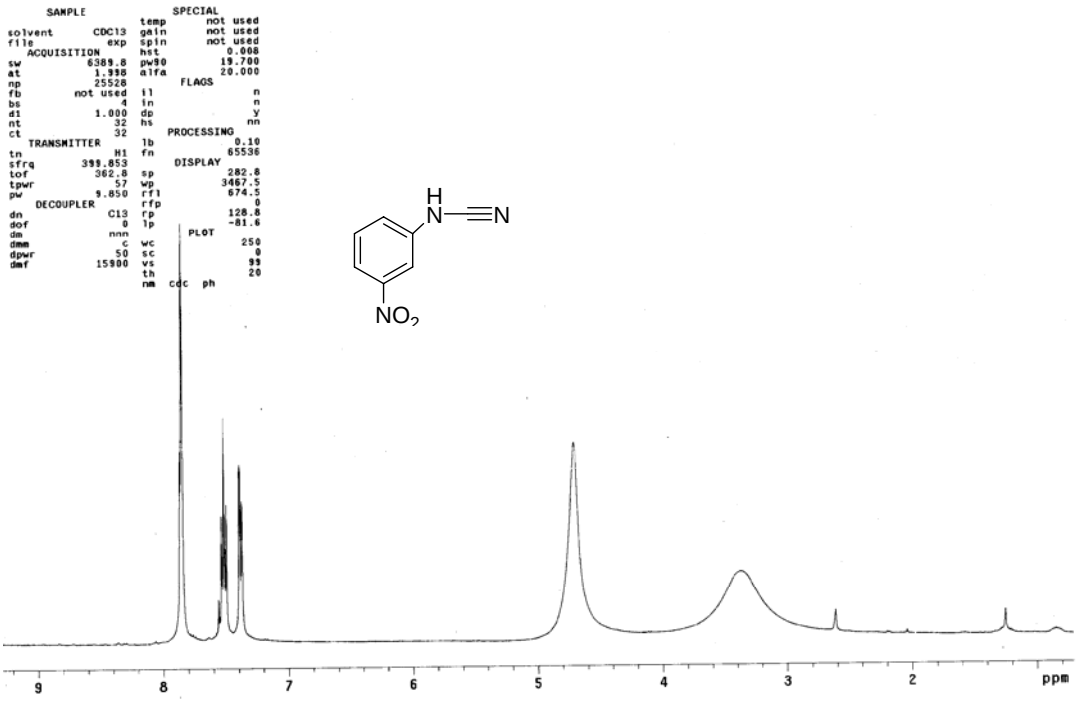




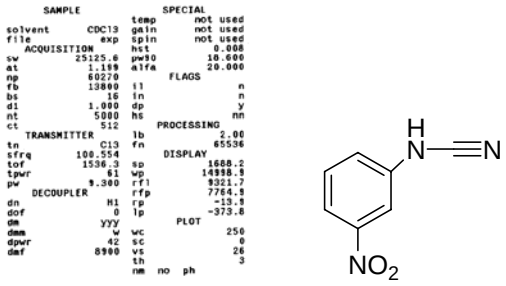
2-Fluoro-phenyl cyanamide (5a): IR (KBr):

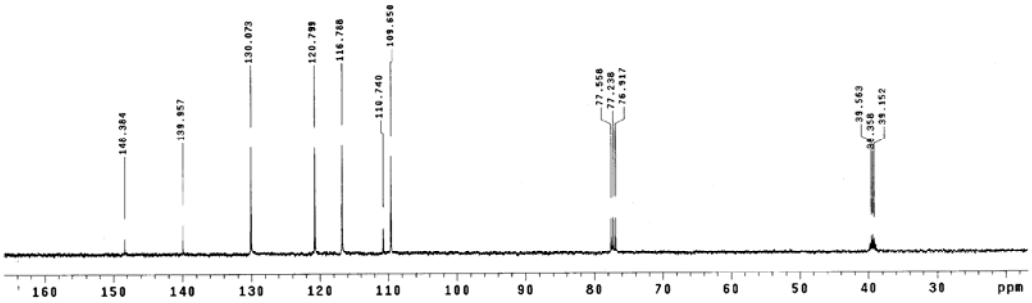


3- Nitrophenylcyanamide (6a): ^{1}HNMR ($CDCl_3$ + DMSO, 400MHz):

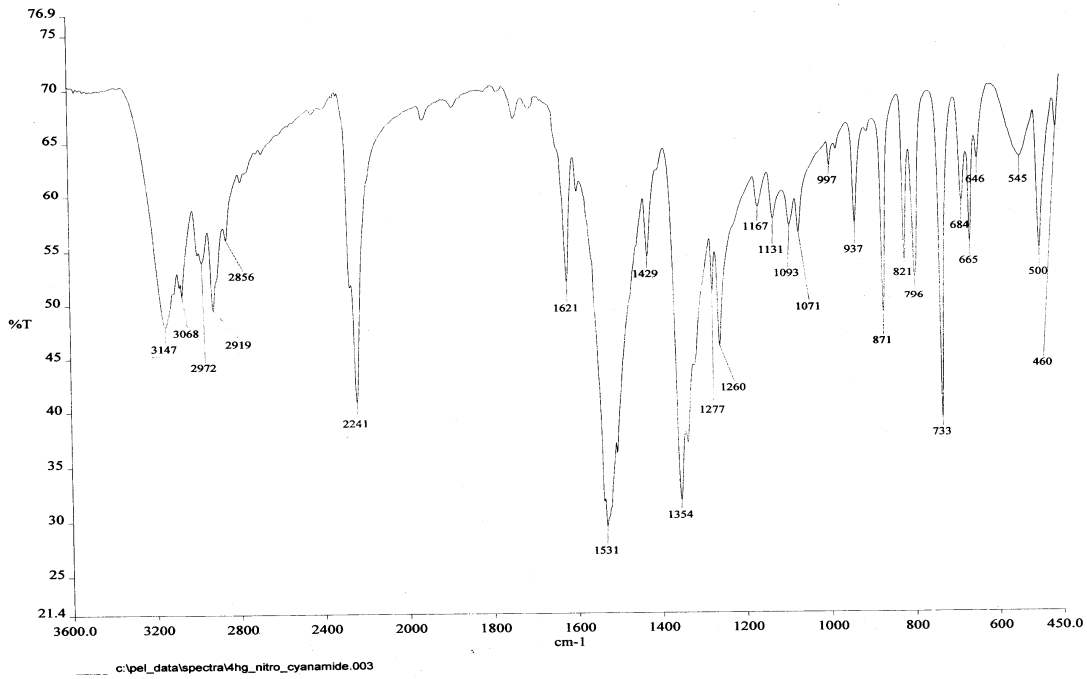


3-Nitro-phenyl cyanamide (6a): ^{13}C NMR ($CDCl_3$ + DMSO, 100 MHz):

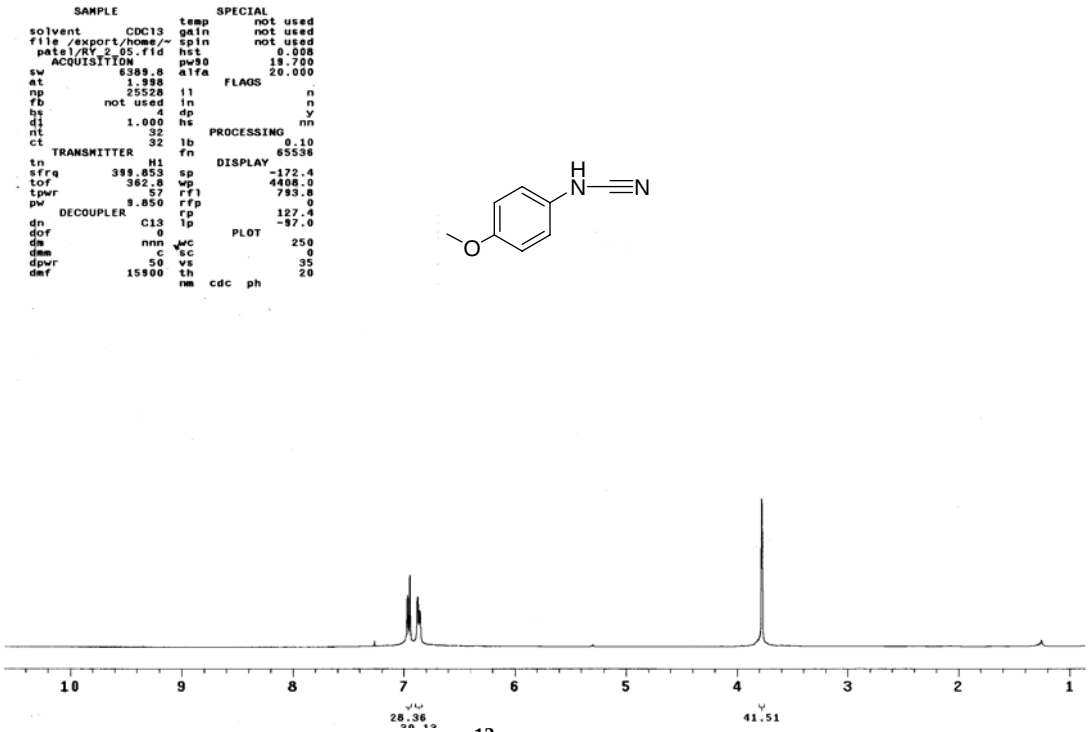




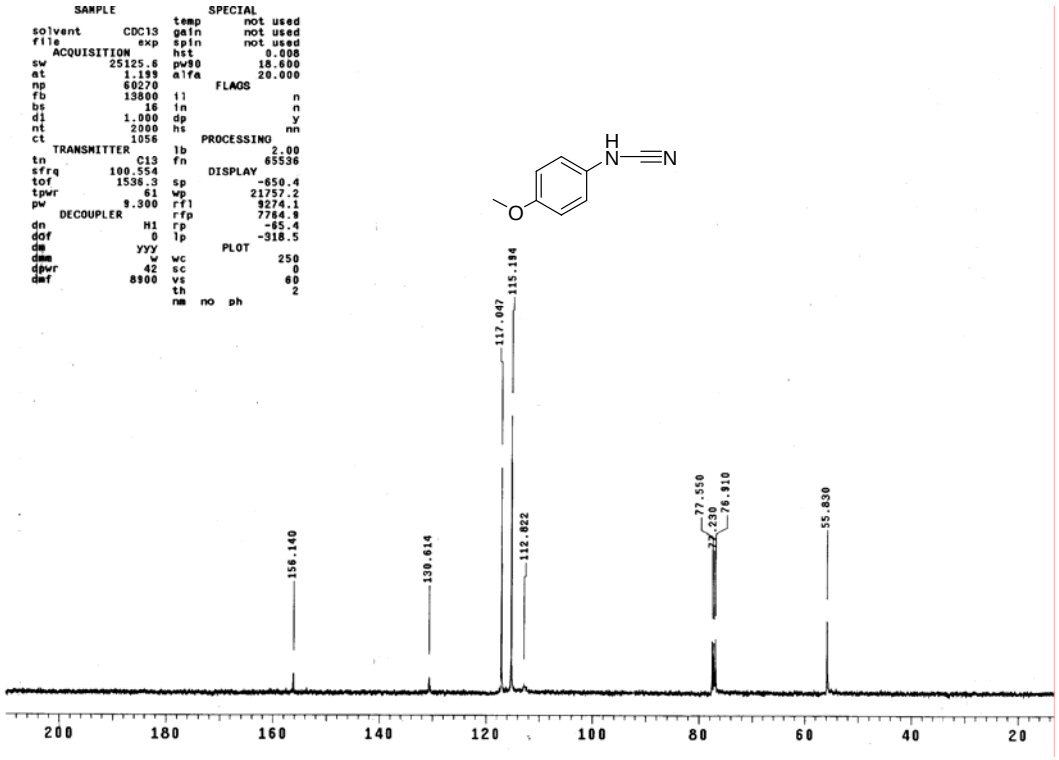
3-Nitro-phenyl cyanamide (6a): IR (KBr):



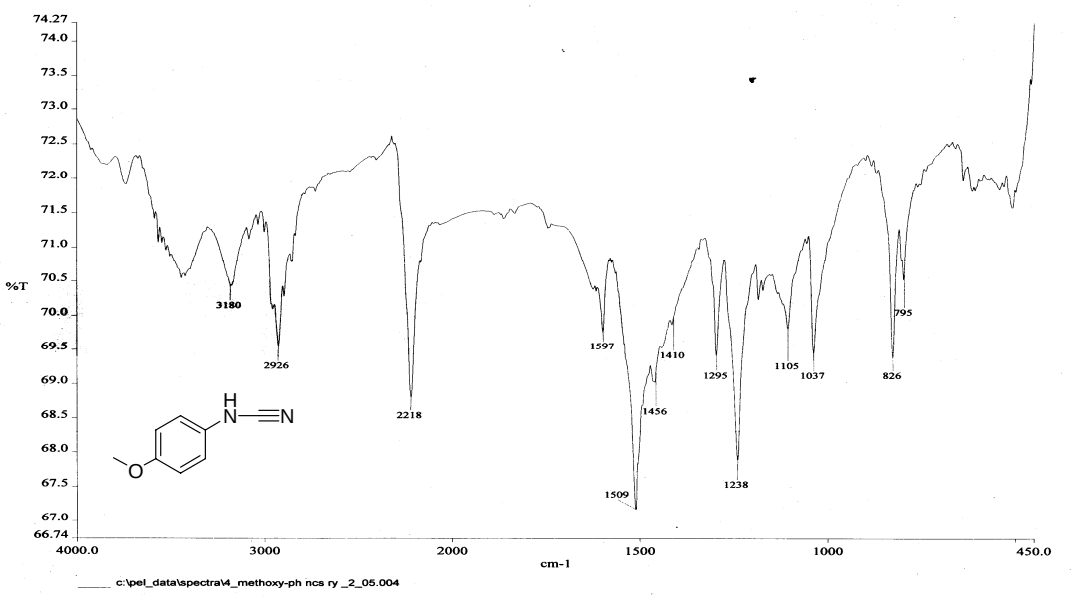
4-Methoxy-phenyl cyanamide (7a): ^{1}H NMR ($CDCl_3$, 400 MHz):



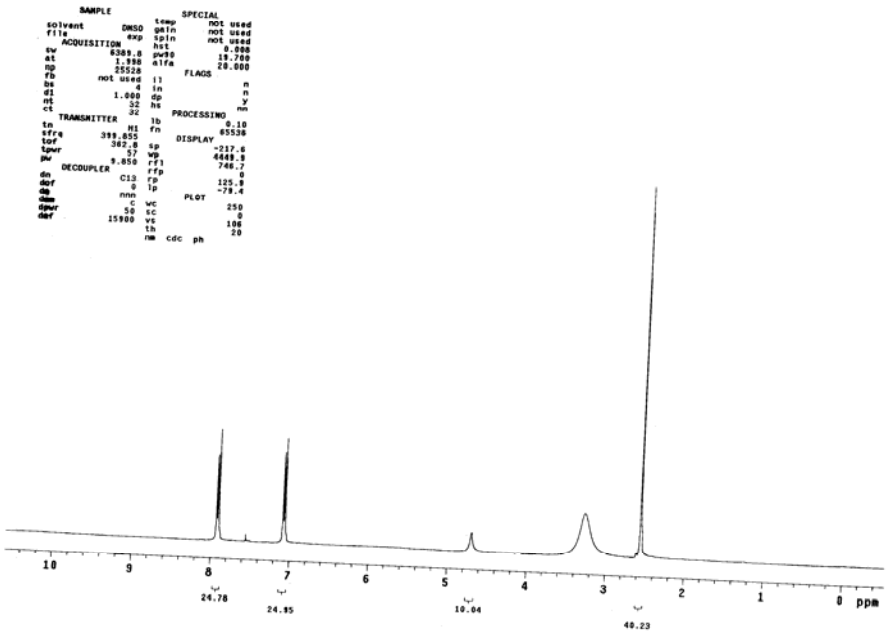
4-Methoxy-phenyl cyanamide (7a): ^{13}C NMR ($CDCl_3$, 100 MHz):



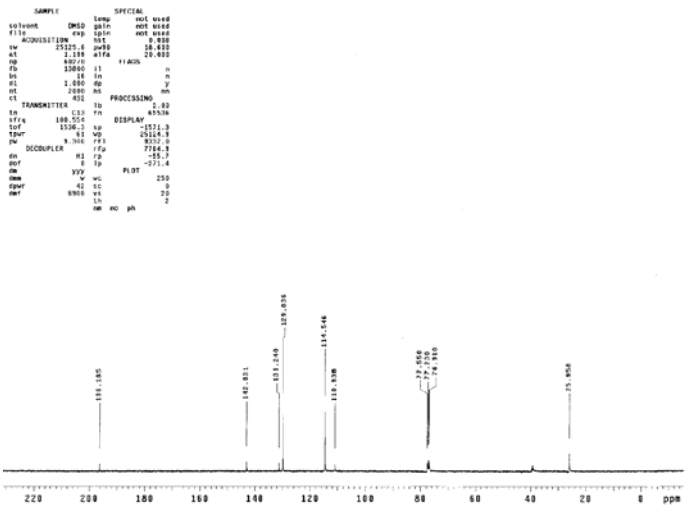
4-Methoxy-phenyl cyanamide (7a): IR (KBr):



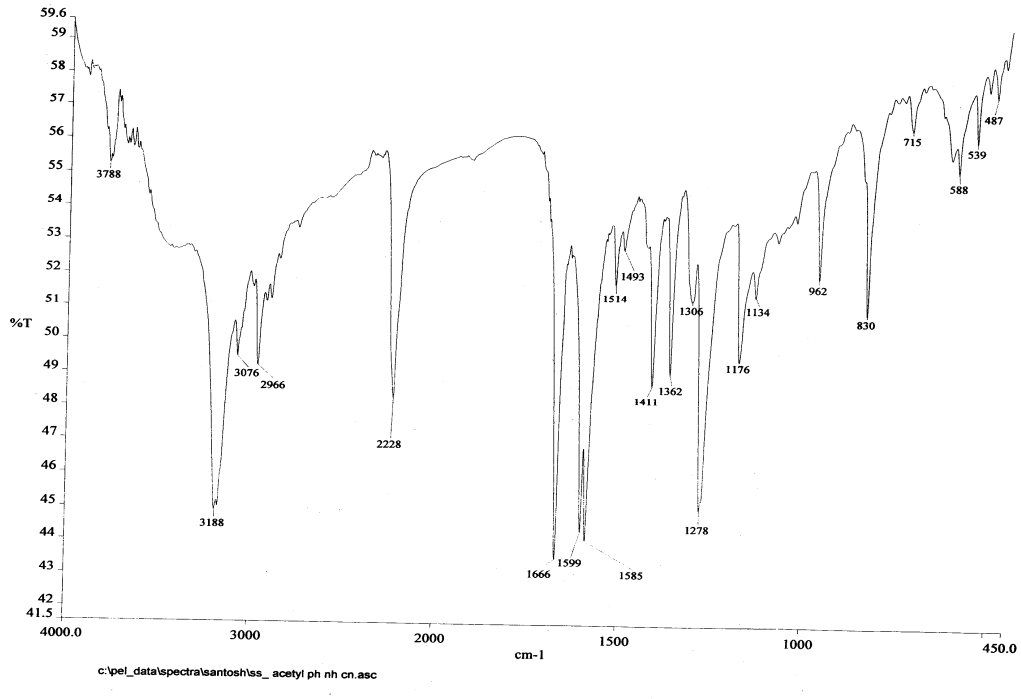
4-Acetyl-phenylcyanamide (8a): ^{1}H NMR ($CDCl_3$ + DMSO, 400 MHz):



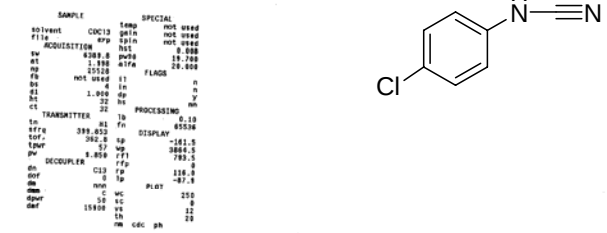
4-Acetyl-phenylcyanamide (8a): ^{13}C NMR ($CDCl_3$ + DMSO, 100 MHz):

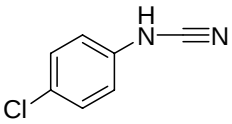


4-Acetyl-phenylcyanamide (8a): IR (KBr):

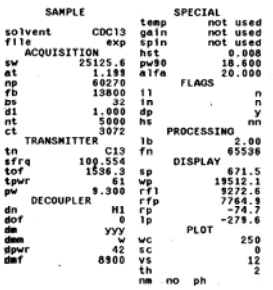


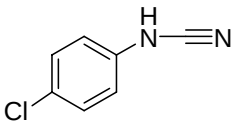
4-Chloro-phenyl cyanamide (9a): ^{1}H NMR ($CDCl_3$, 400 MHz):

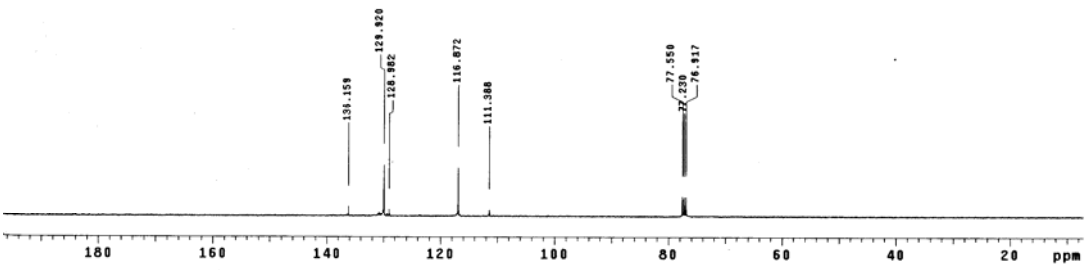




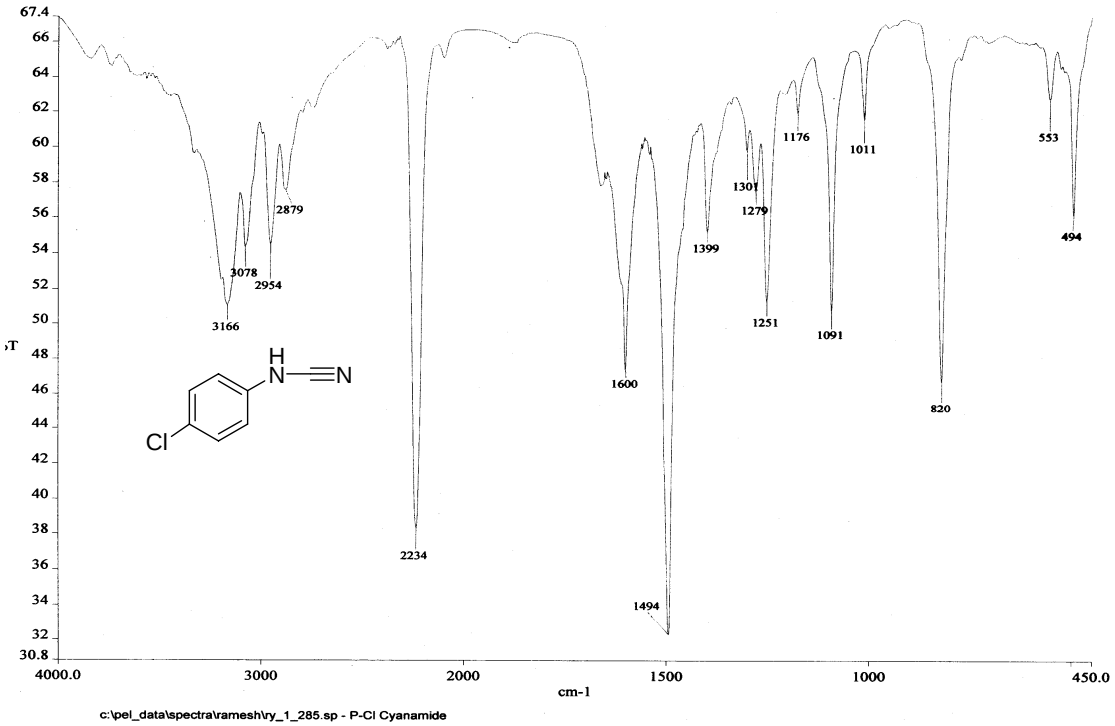
4-Chloro-phenyl cyanamide (9a): ^{13}C NMR ($CDCl_3$, 100 MHz):



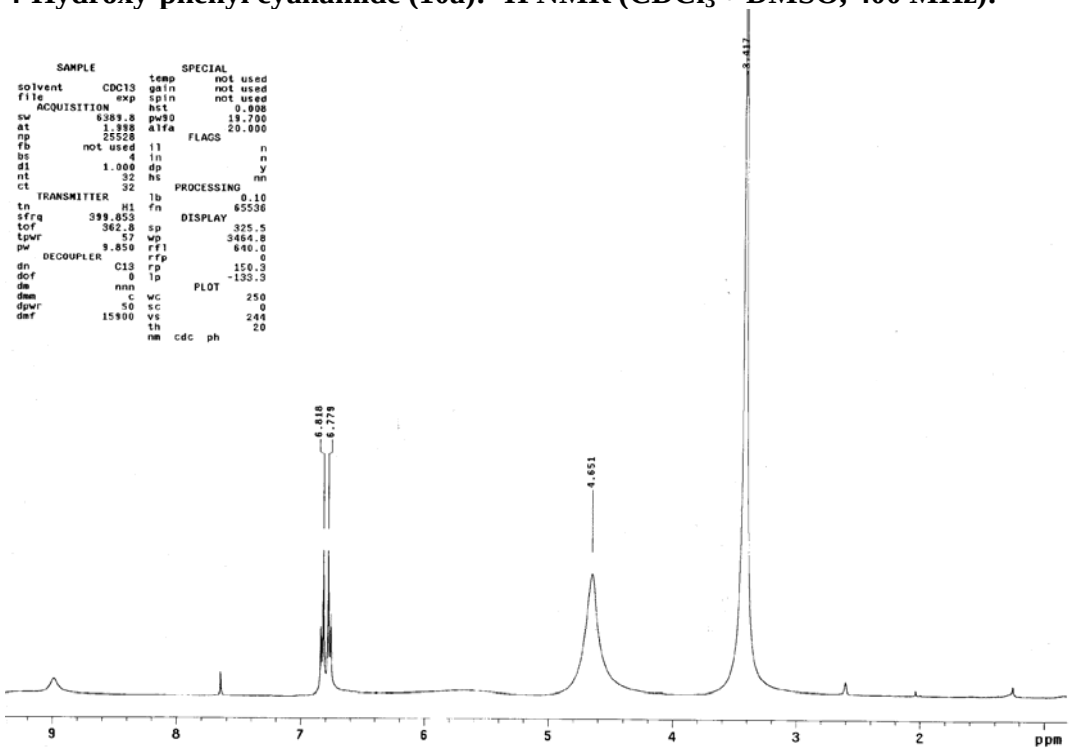




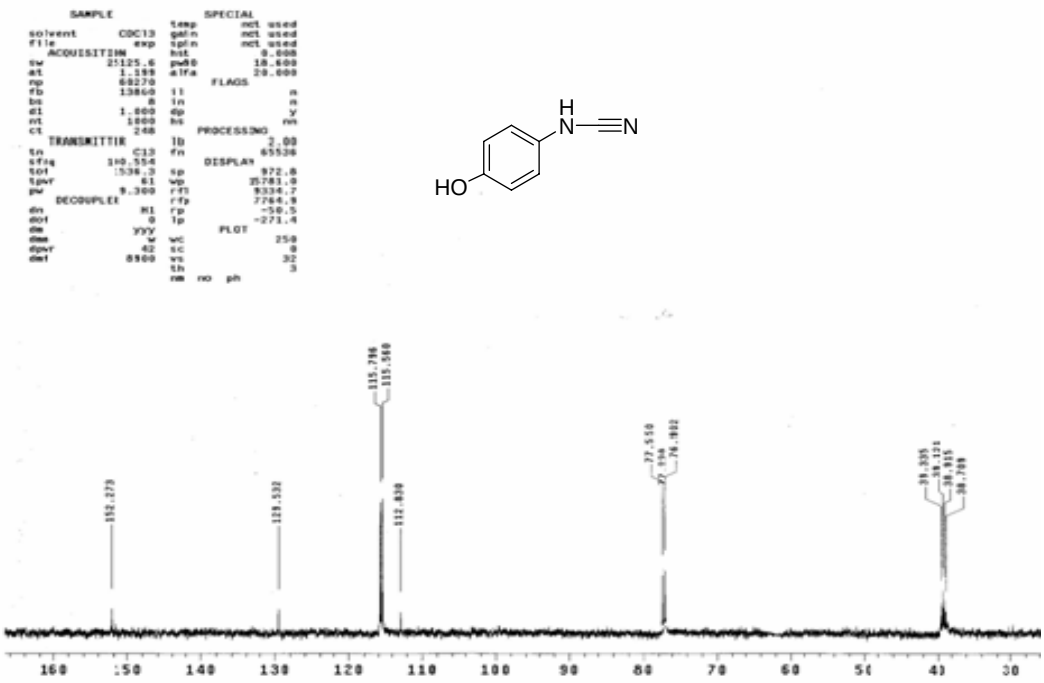
4-Chloro-phenyl cyanamide (9a): IR (KBr):



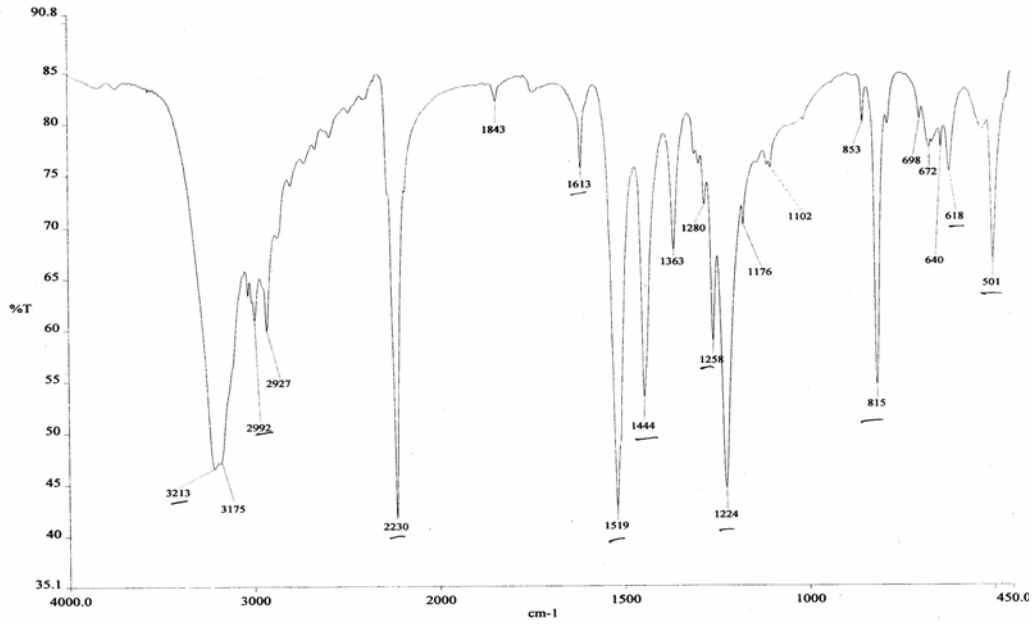
4-Hydroxy-phenyl cyanamide (10a): ^{1}H NMR ($CDCl_3$ + DMSO, 400 MHz):



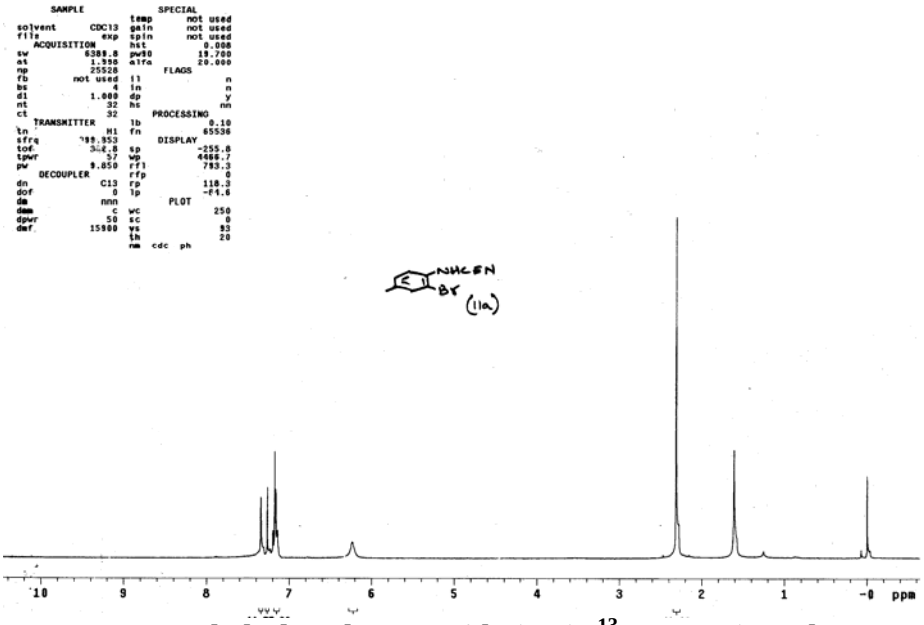
4-Hydroxy-phenyl cyanamide (10a): ^{13}C NMR ($CDCl_3$ + DMSO, 100 MHz):



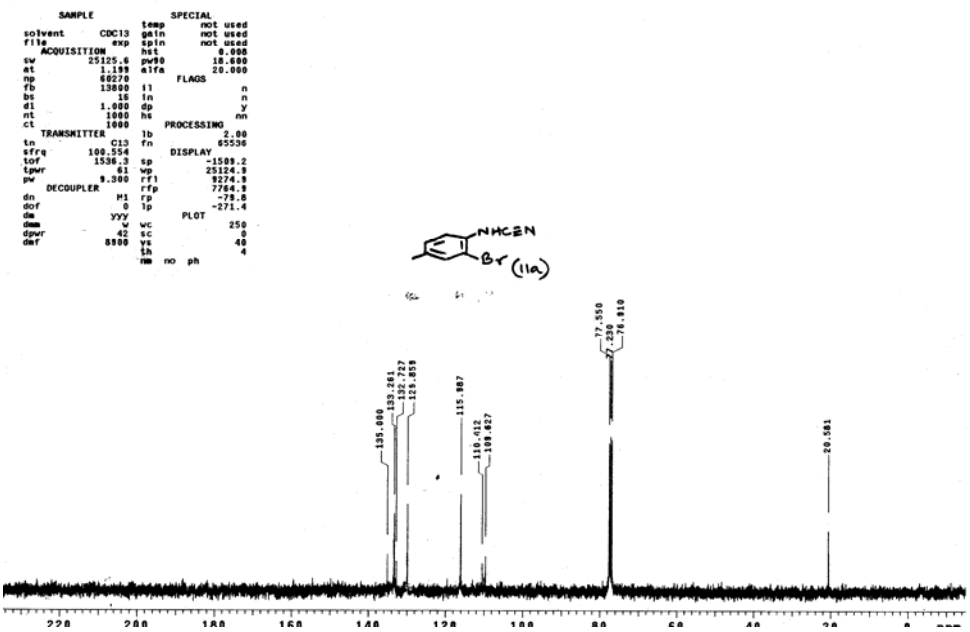
4-Hydroxy-phenyl cyanamide (10a): IR (KBr):



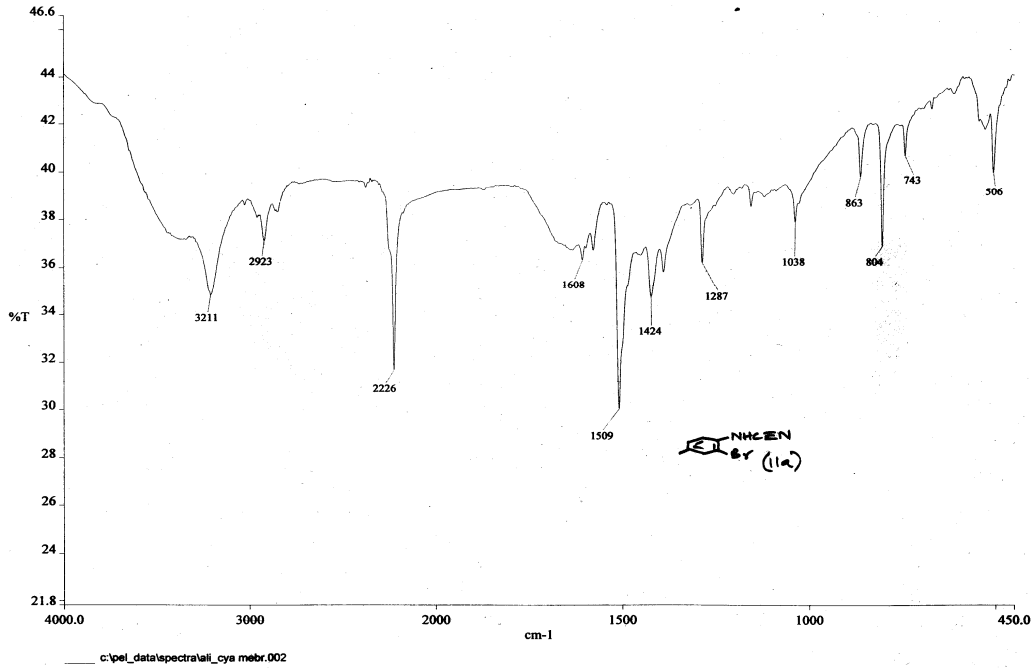
2-Bromo-4-Methyl-phenyl cyanamide (11a): ^{1}H NMR ($CDCl_3$, 400 MHz):



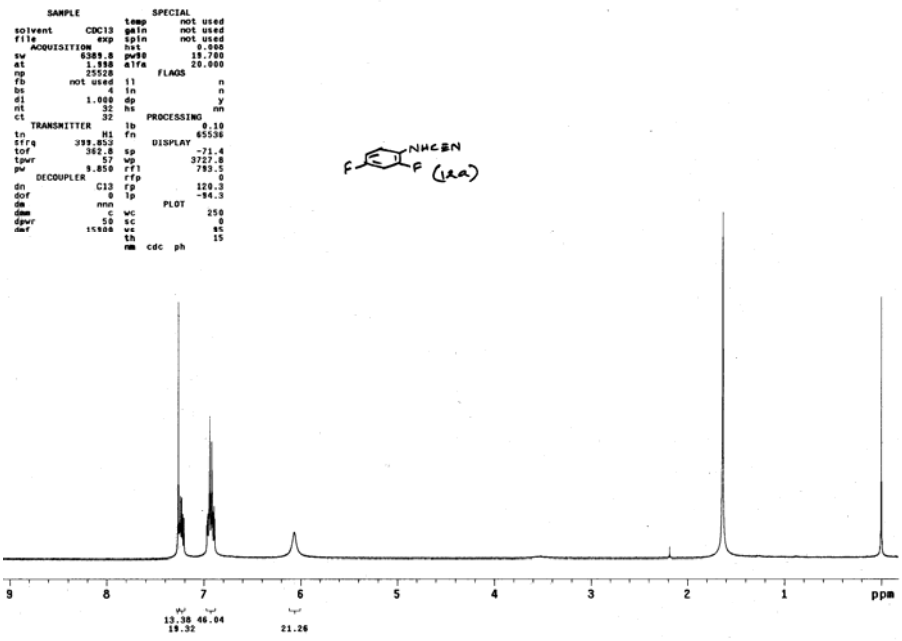
2-Bromo-4-Methyl-phenyl cyanamide (11a): ^{13}C NMR ($CDCl_3$, 100 MHz):



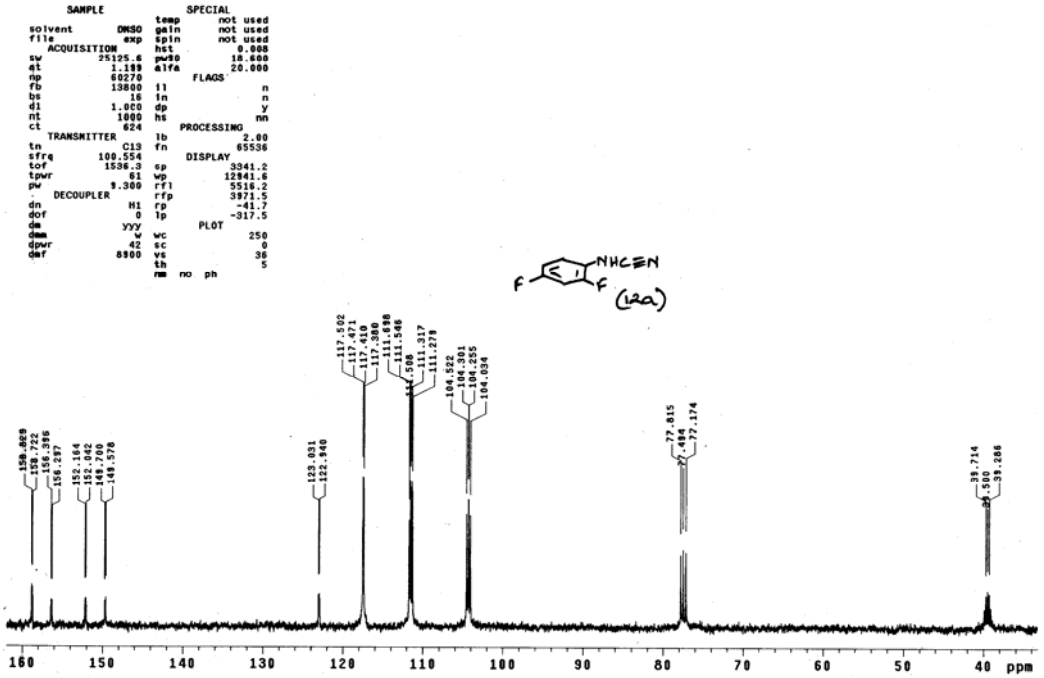
2-Bromo-4-Methyl-phenyl cyanamide (11a): IR (KBr):



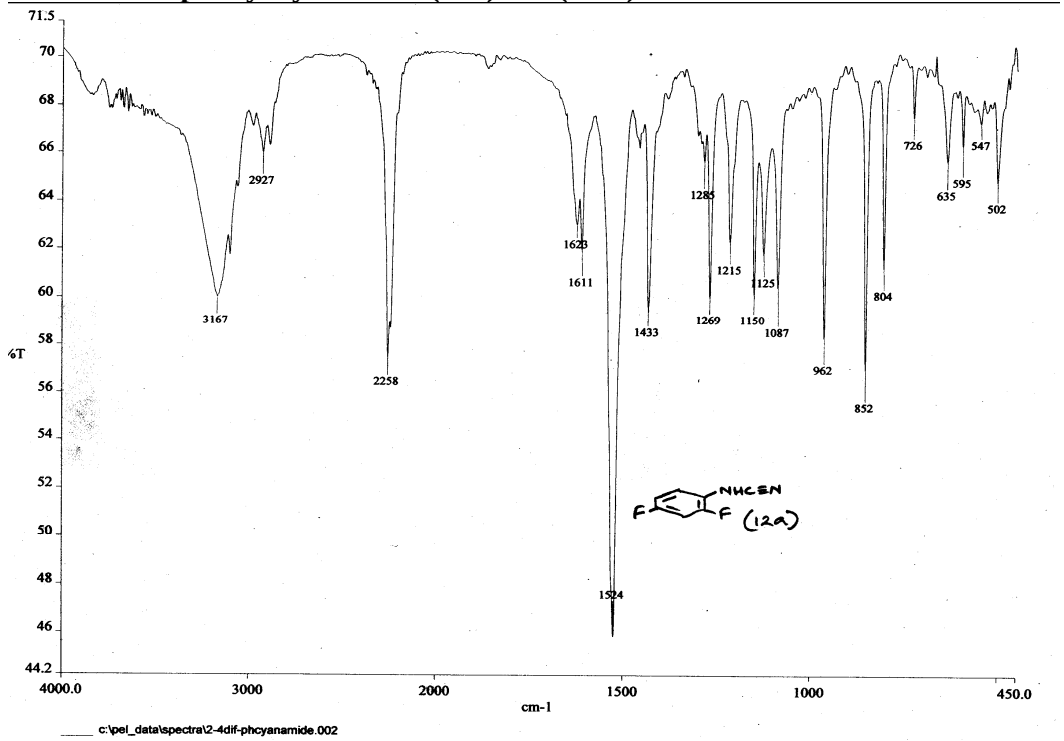
2-4-Difluoro phenyl cyanamide (12a): ^{1}H NMR ($CDCl_3$, 400 MHz):



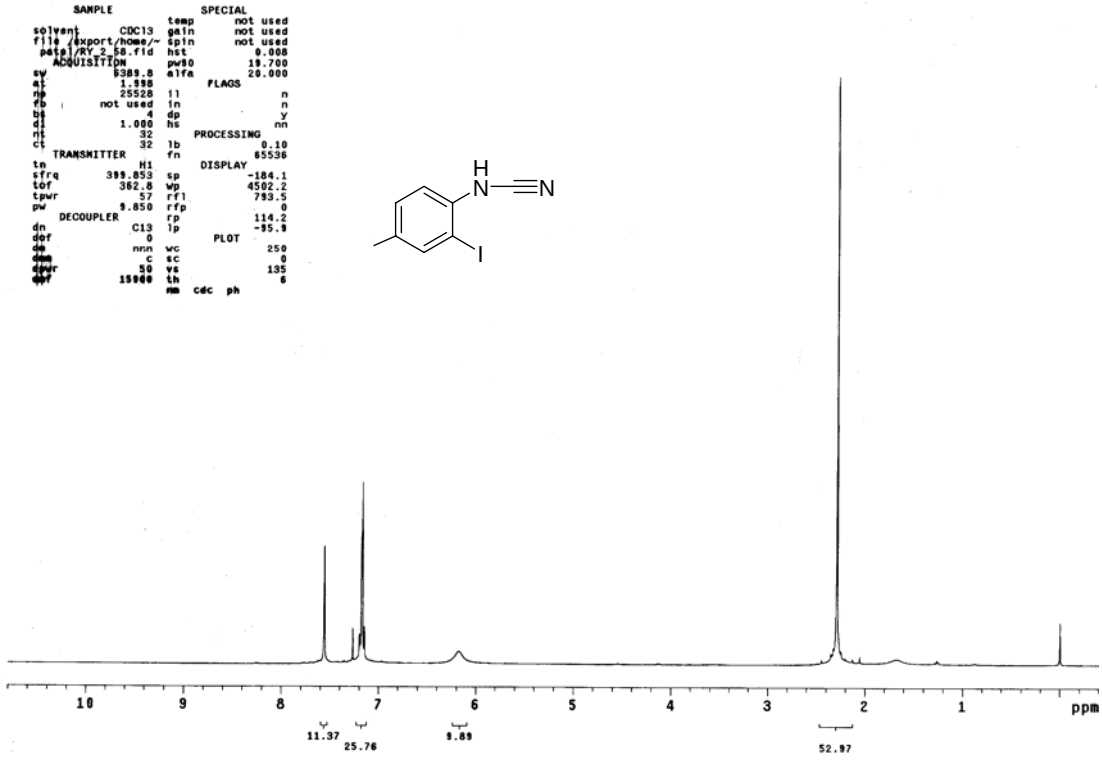
2-4-Difluoro phenyl cyanamide (12a): ^{13}C NMR ($CDCl_3$, 100 MHz):



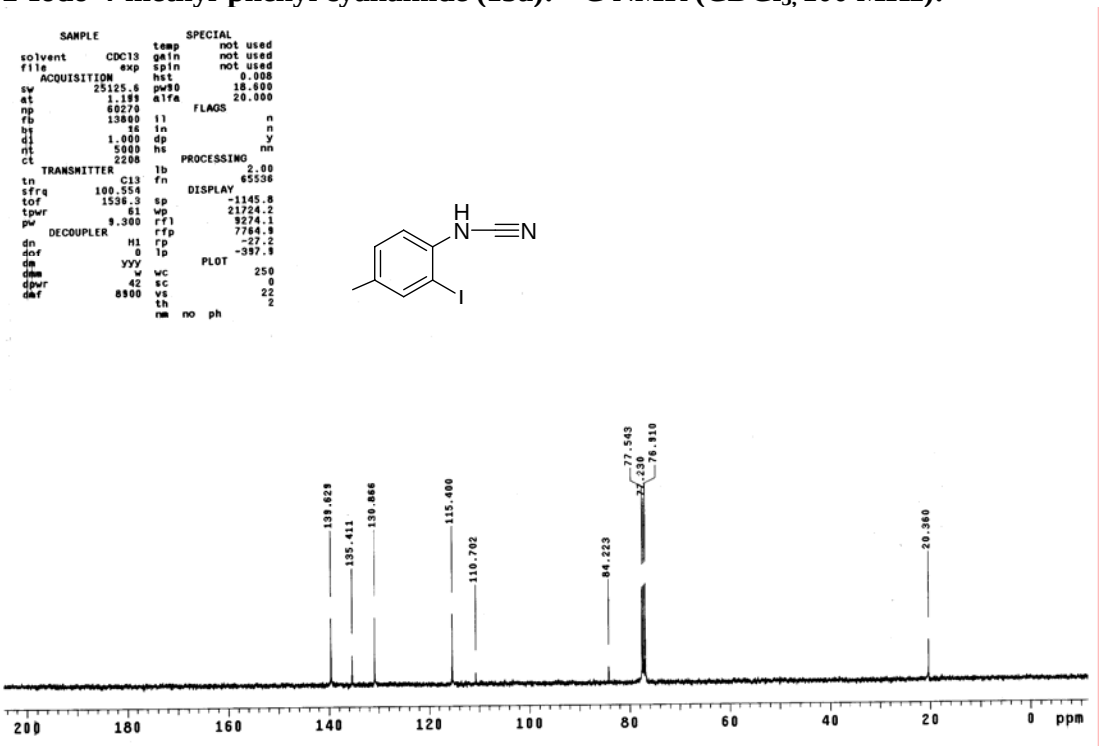
2-4-Difluoro phenyl cyanamide (12a): IR (KBr):



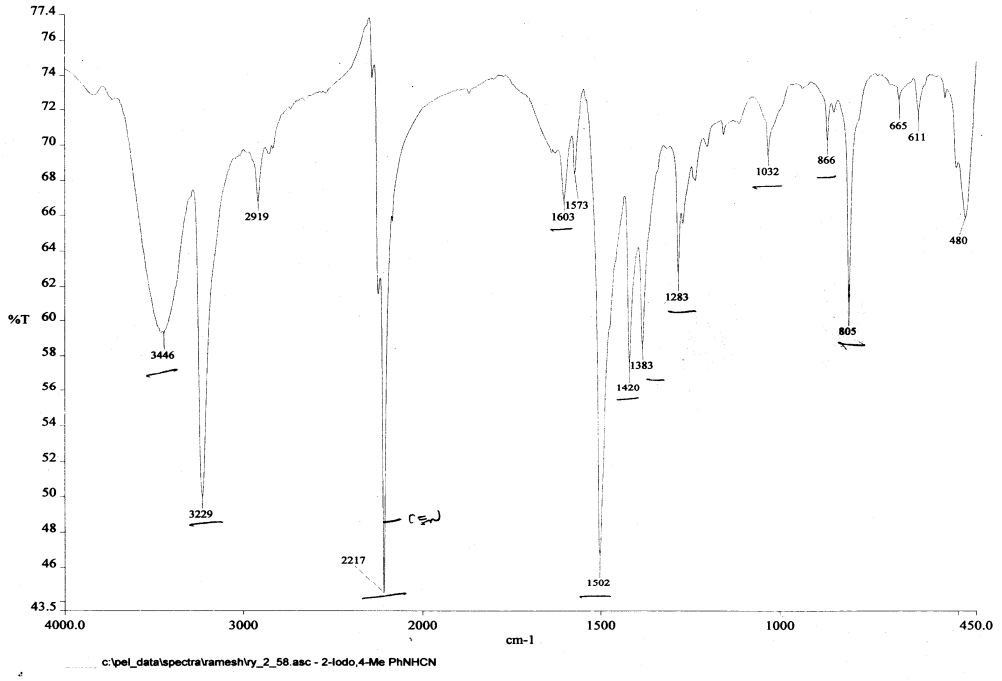
2-Iodo-4-methyl-phenyl cyanamide (13a): ^{1}H NMR ($CDCl_3$, 400 MHz):



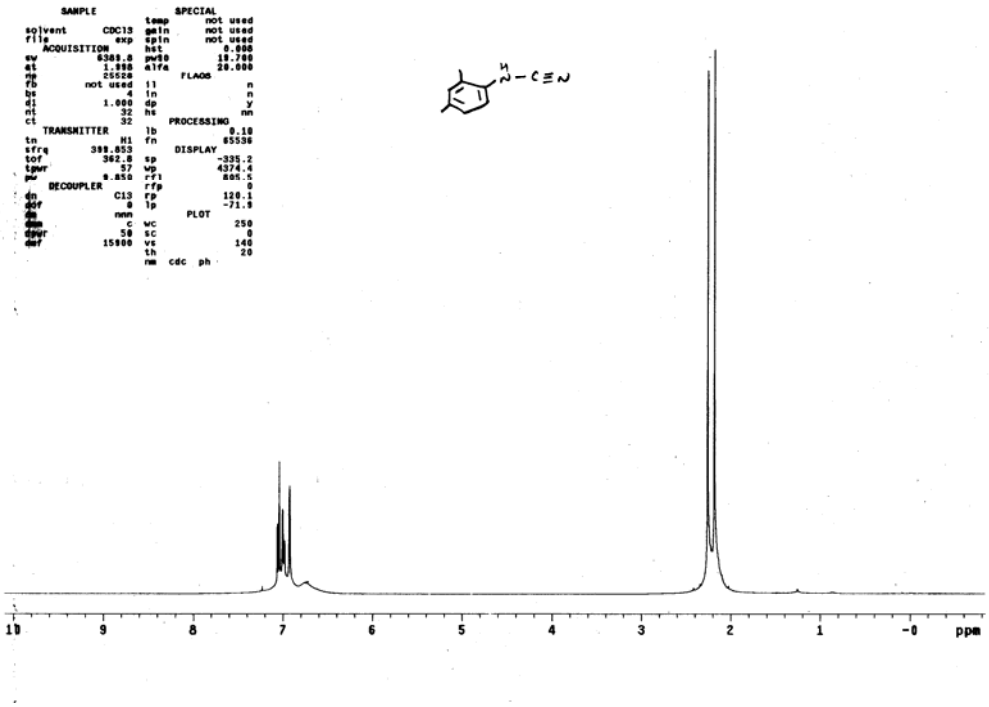
2-Iodo-4-methyl-phenyl cyanamide (13a): ^{13}C NMR ($CDCl_3$, 100 MHz):



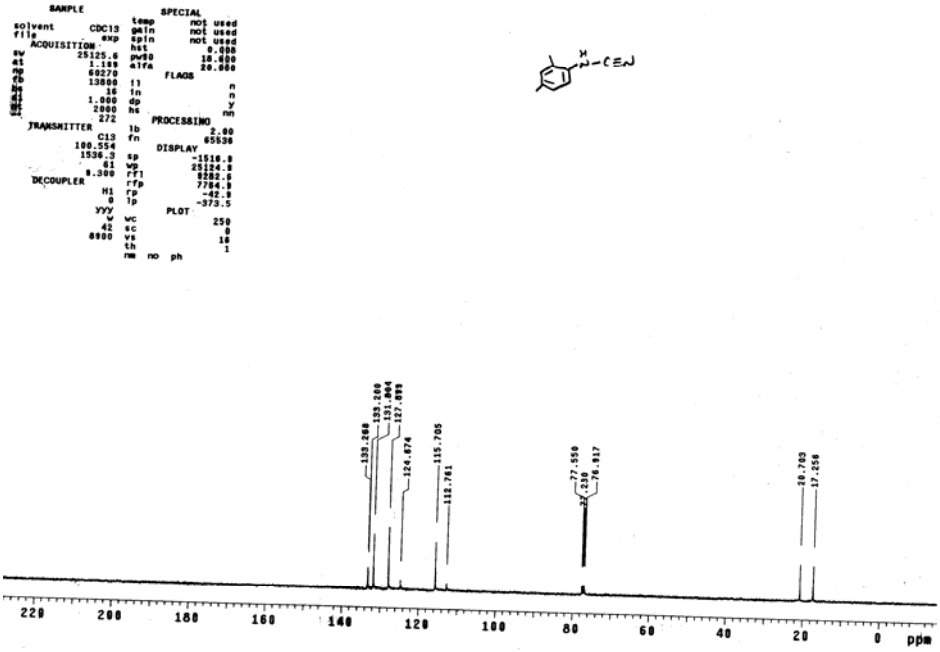
2-Iodo-4-methyl-phenyl cyanamide (13a): IR (KBr):



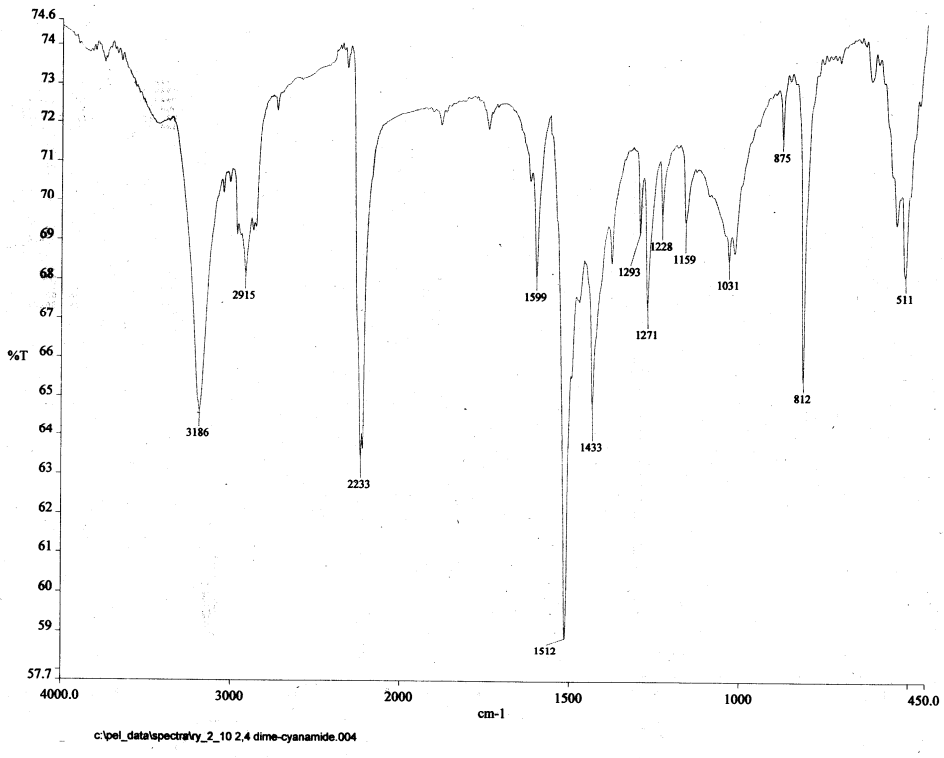
2,4-Dimethyl-phenyl cyanamide (14a):^{1}H NMR ($CDCl_3$, 400 MHz):



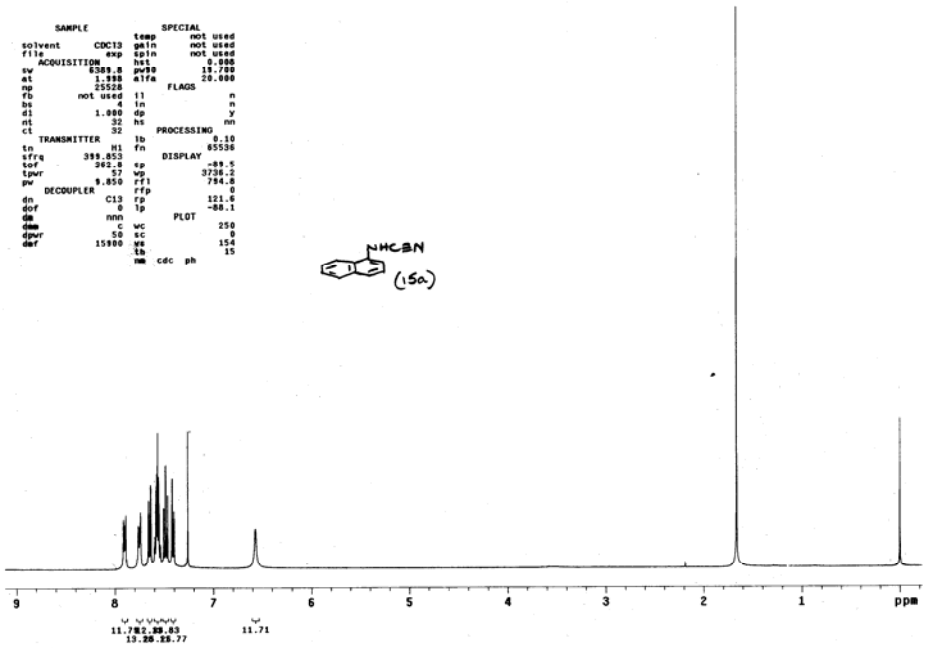
2,4-Dimethyl-phenyl cyanamide (14a):^{13}C NMR ($CDCl_3$, 100 MHz):



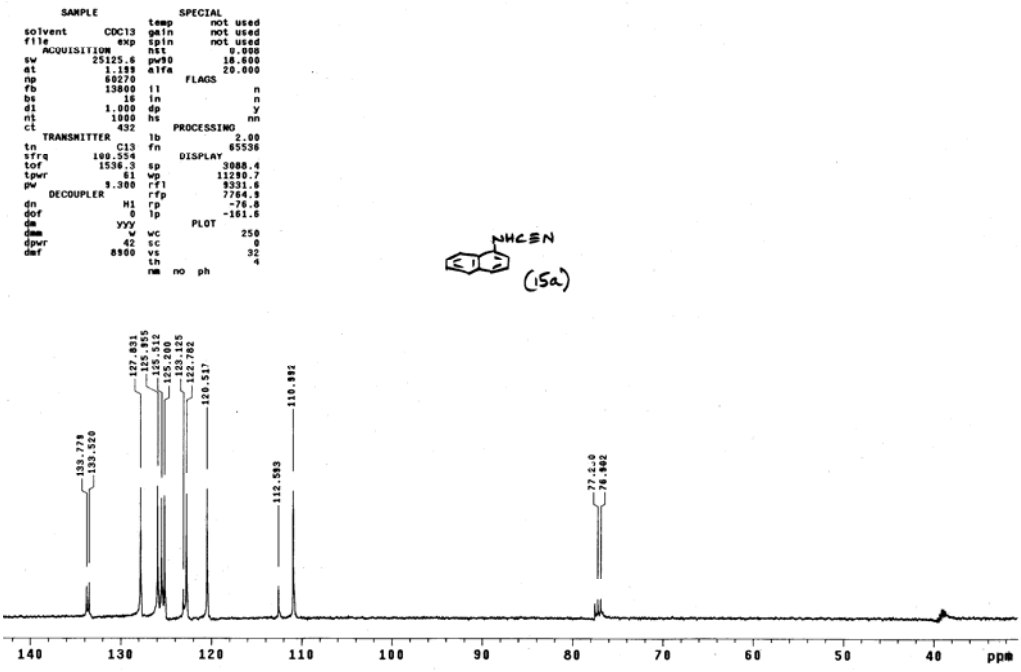
2,4-Dimethyl-phenyl cyanamide (14a): IR (KBr):



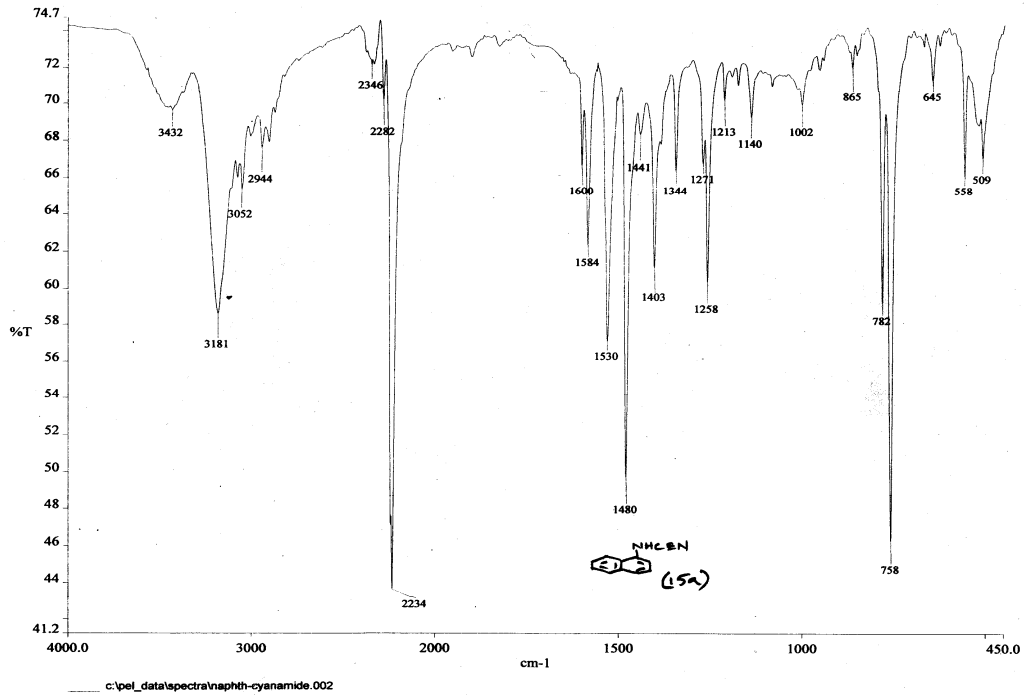
1-Naphthyl cyanamide (15a): ^{1}H NMR ($CDCl_3$, 400 MHz):



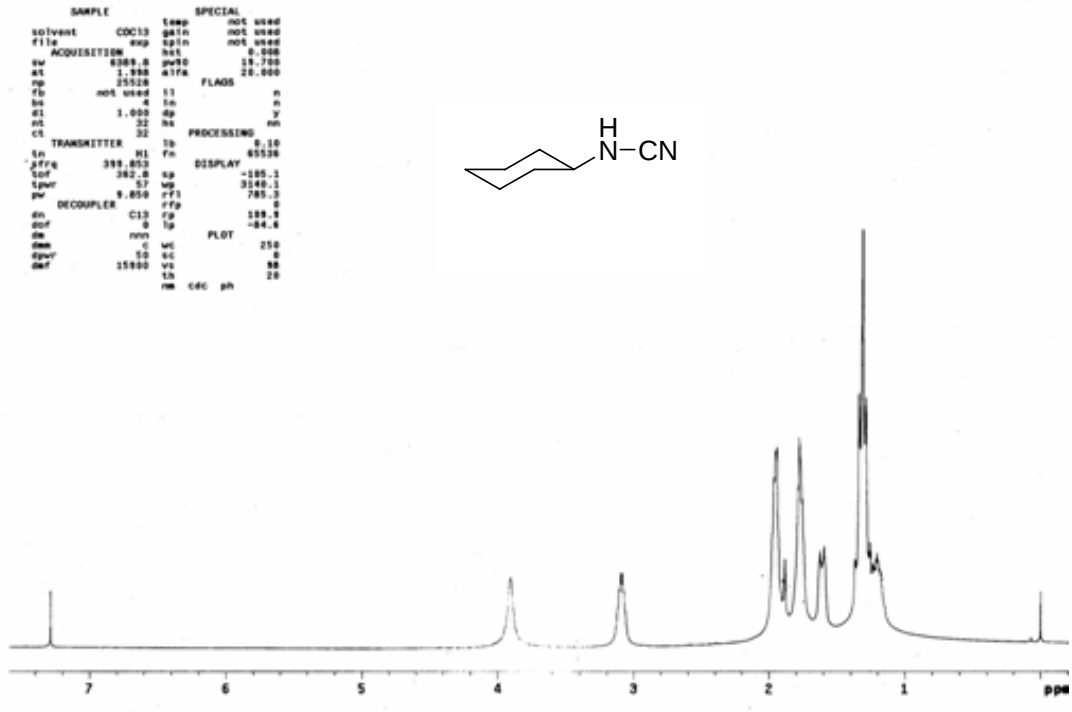
1-Naphthyl cyanamide (15a): ^{13}C NMR ($CDCl_3$, 100 MHz):



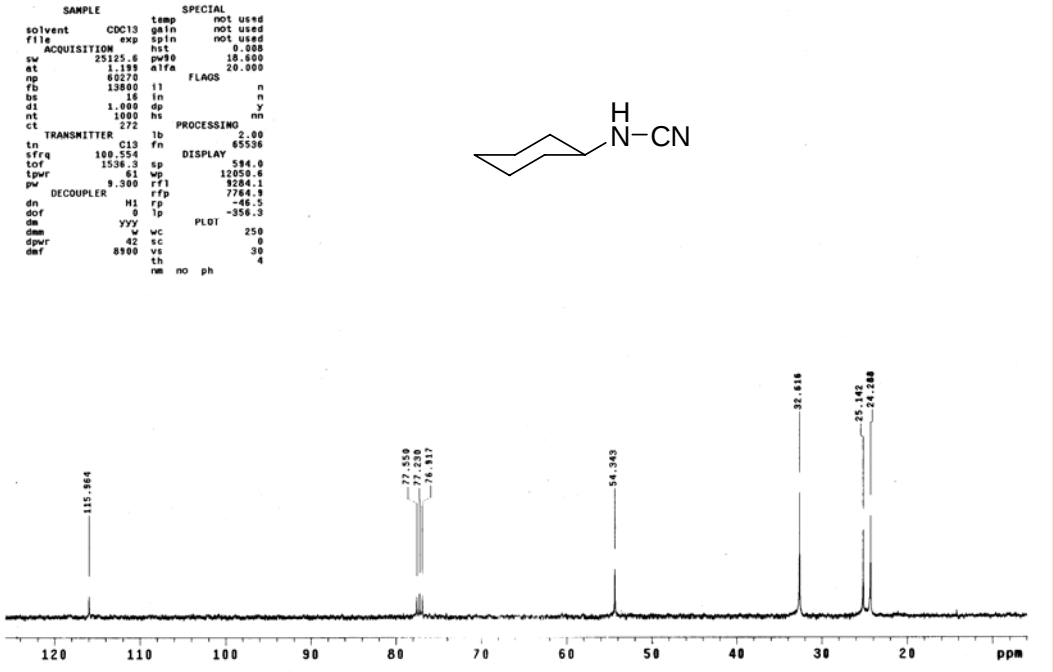
1-Naphthyl cyanamide (15a): IR (KBr):



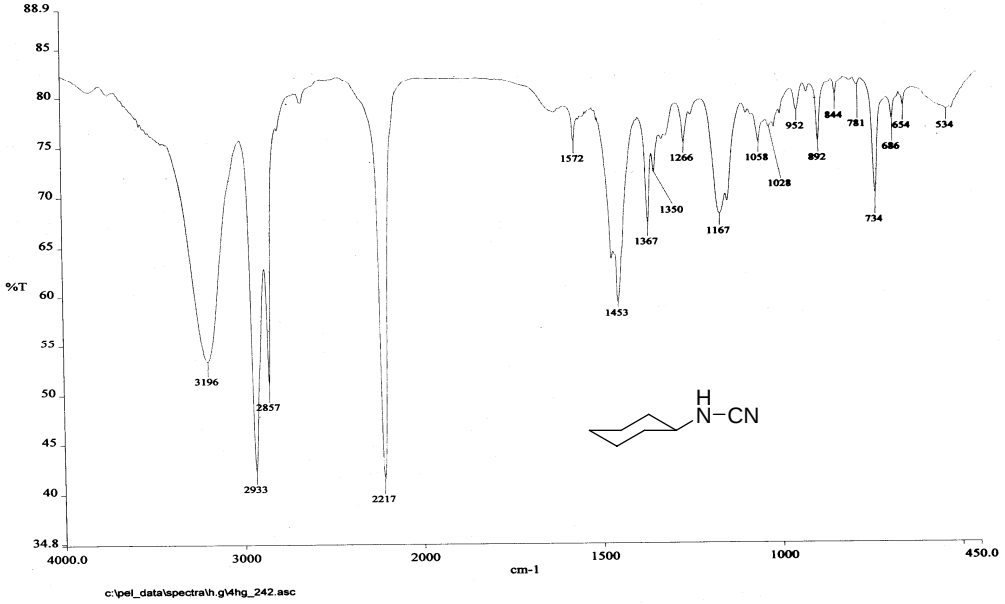
Cyclohexyl-cyanamide (16a): ^{1}H NMR ($CDCl_3$, 400 MHz):



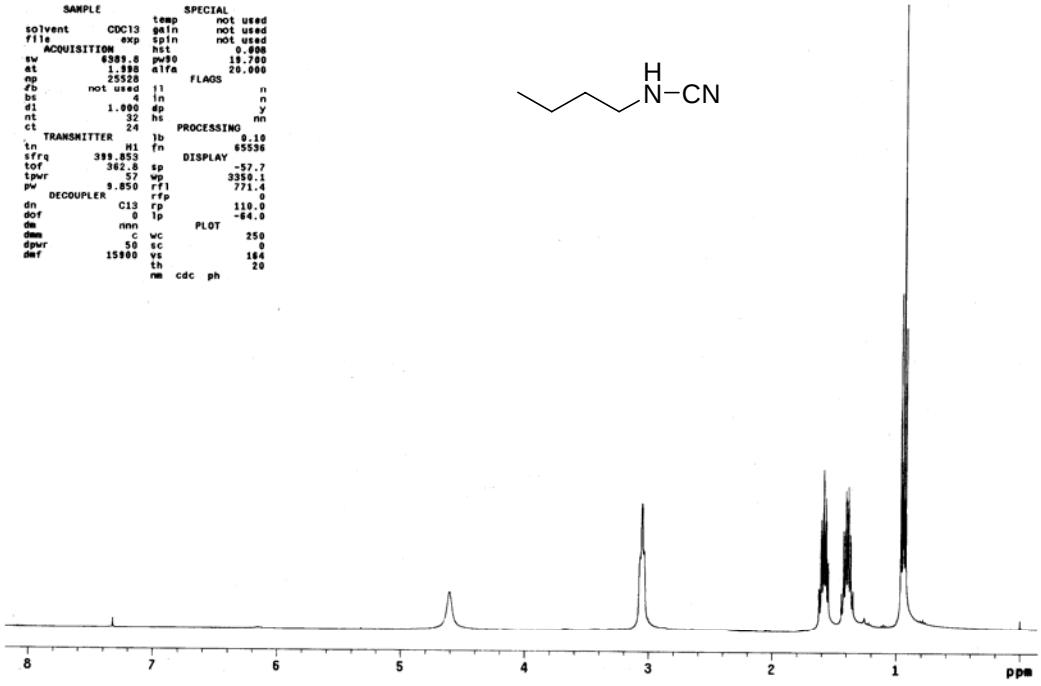
Cyclohexyl-cyanamide (16a): ^{13}C NMR ($CDCl_3$, 100 MHz):



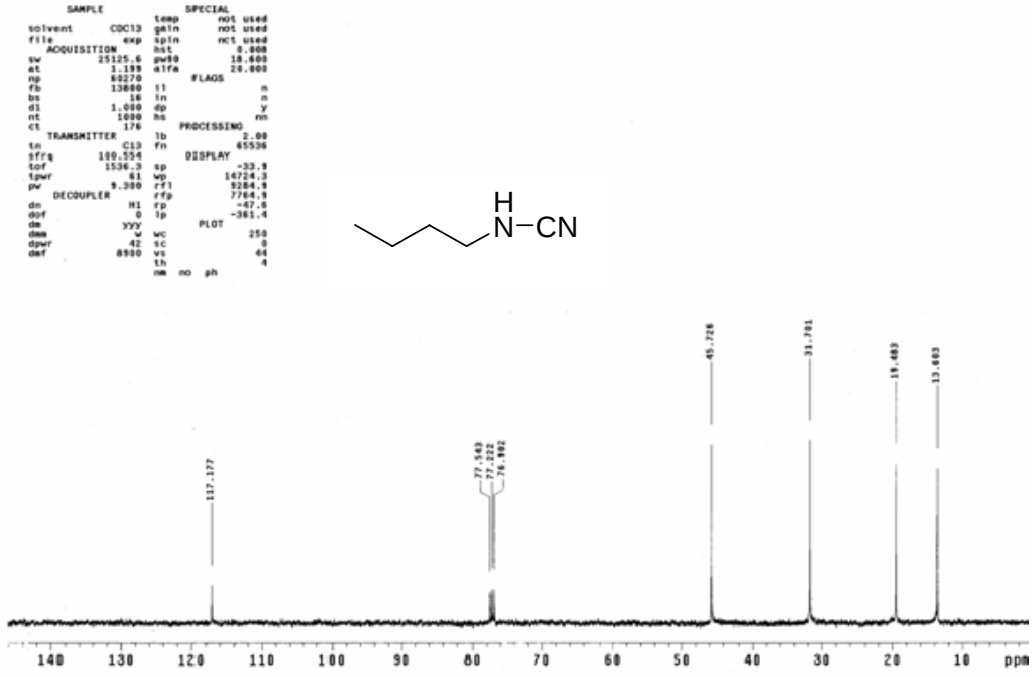
Cyclohexyl-cyanamide (16a): IR (KBr):



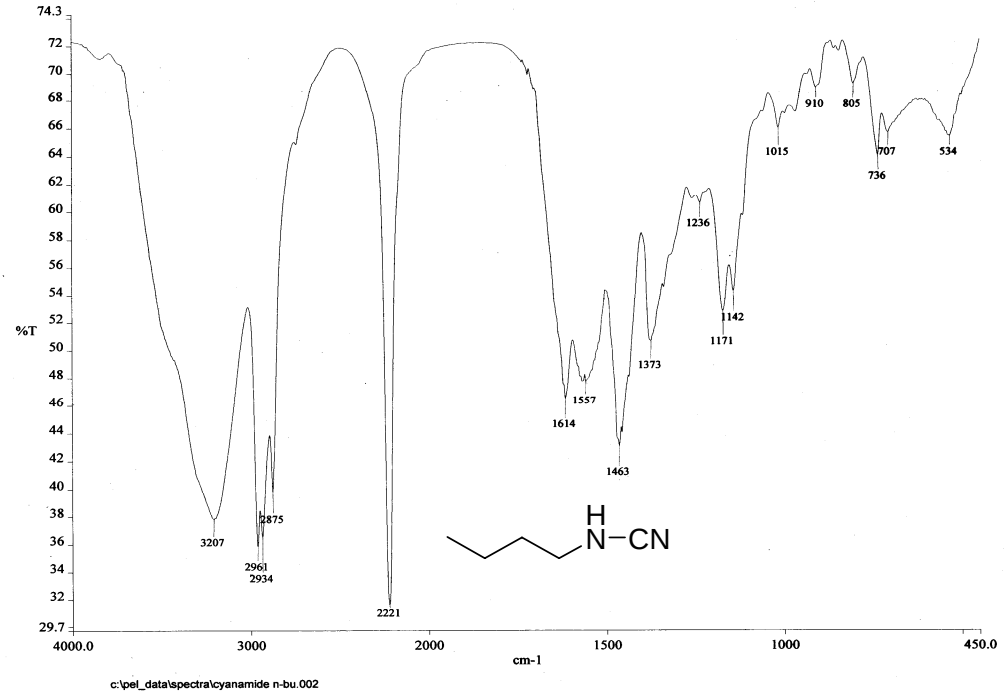
_n_-Butyl-cyanamide (17a): ^{1}H NMR ($CDCl_3$, 400 MHz):



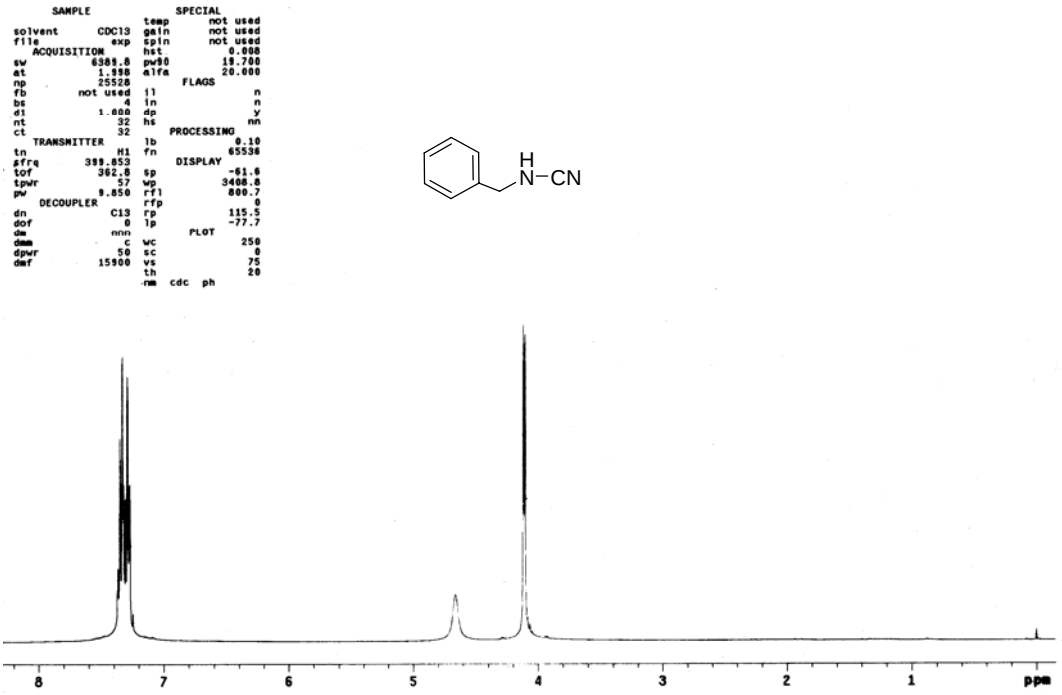
n-Butyl-cyanamide (17a): ^{13}C NMR ($CDCl_3$, 100 MHz):



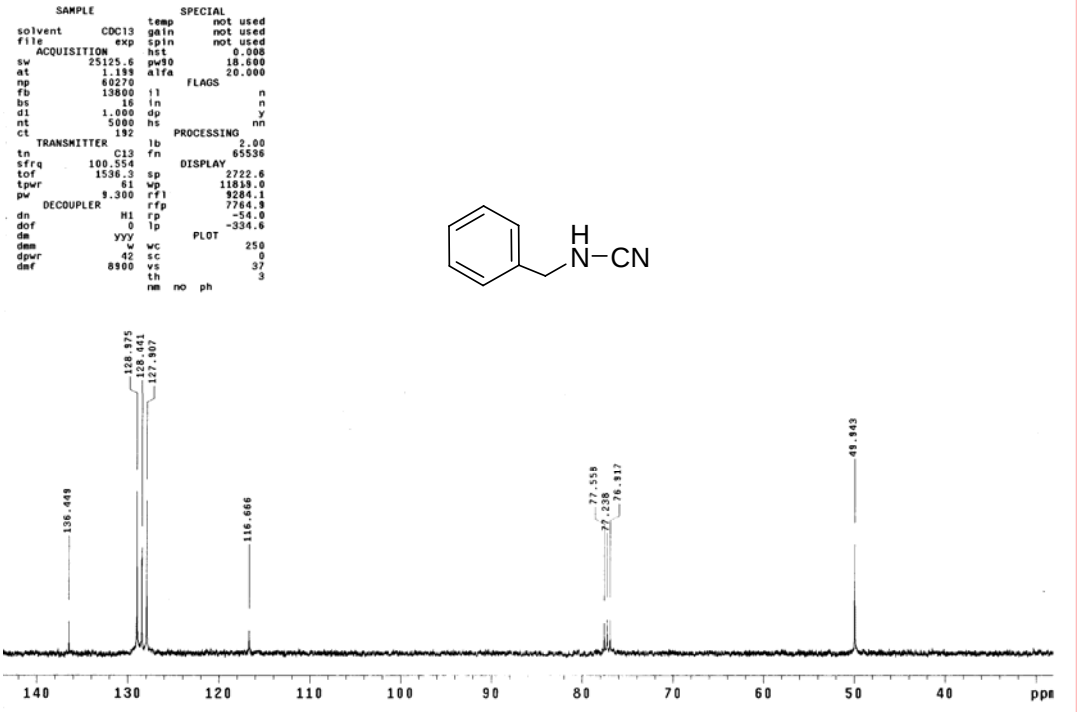
n-Butyl-cyanamide (17a): IR (KBr):



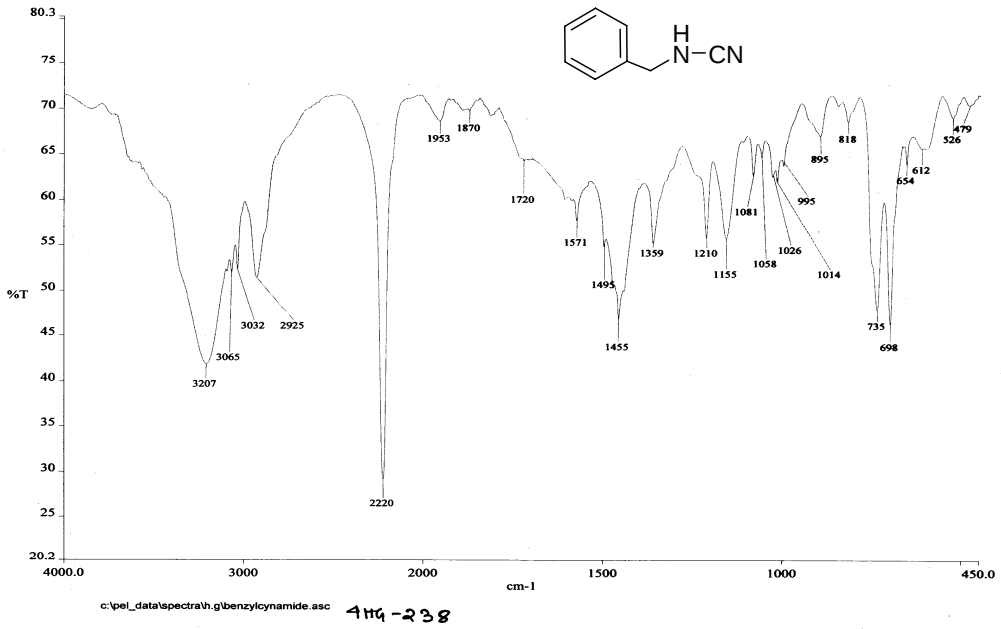
Benzyl cyanamide (18a): ^{1}H NMR ($CDCl_3$, 400 MHz):



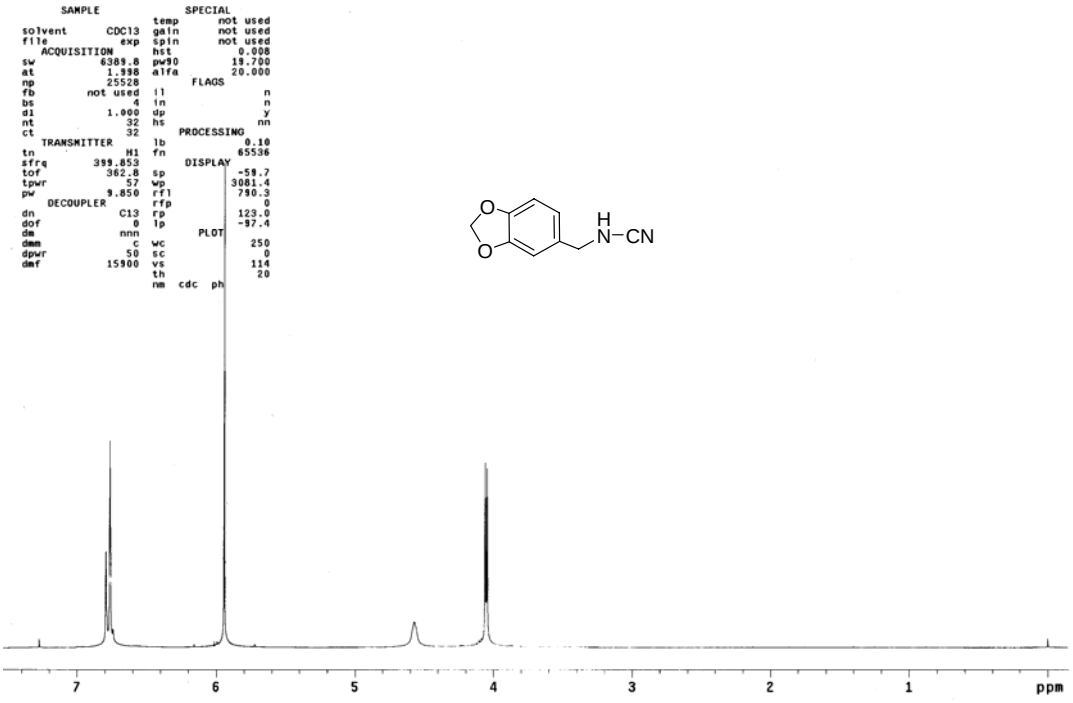
Benzyl cyanamide (18a): ^{13}C NMR ($CDCl_3$, 100 MHz):



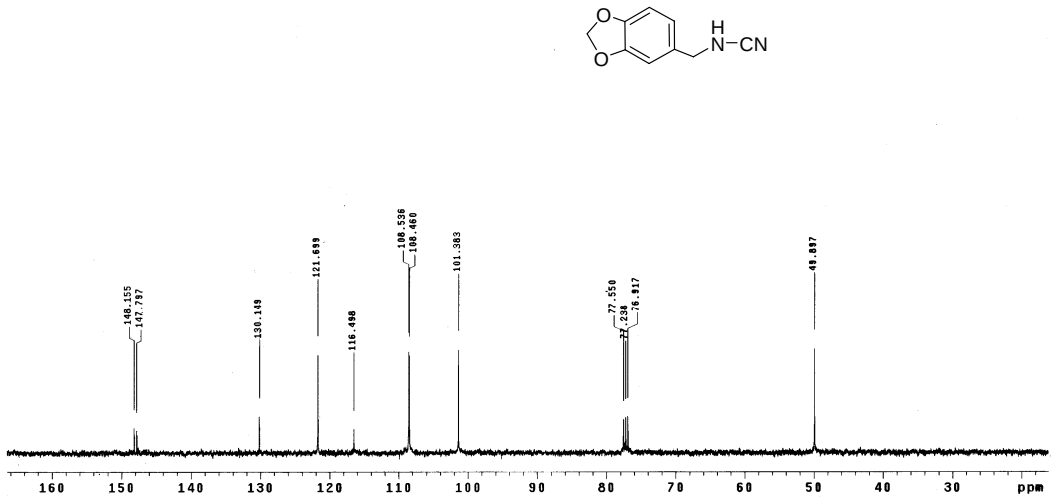
Benzyl cyanamide (18a): IR (KBr):



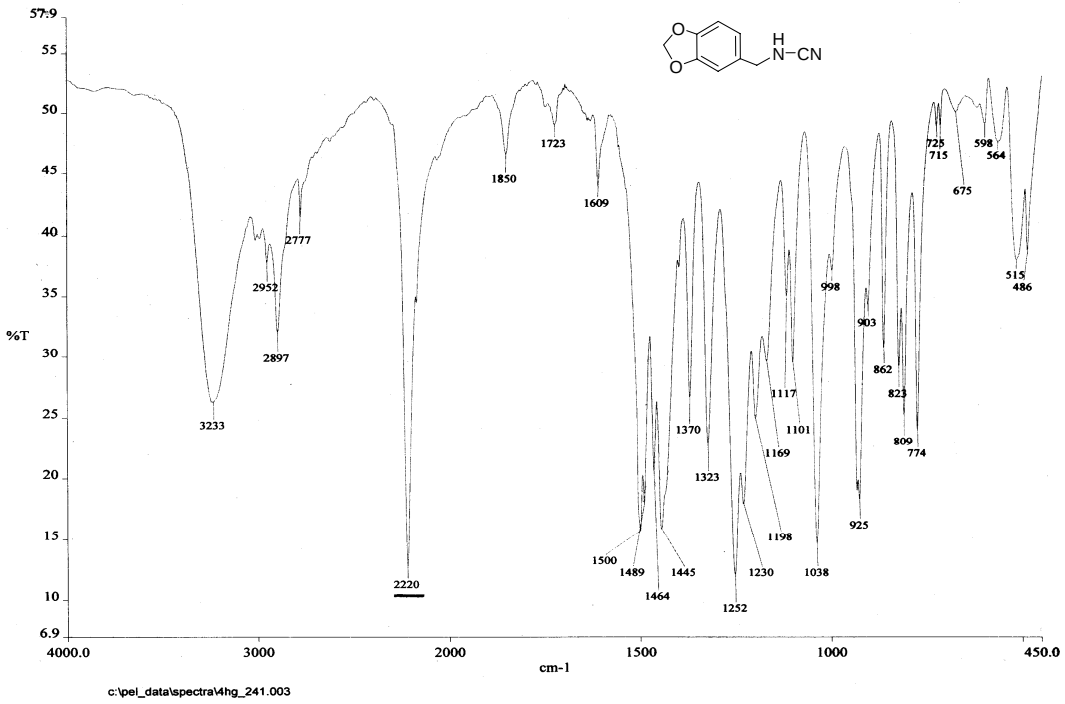
Benzo[1,3]dioxol-5-ylmethyl-cyanamide (19a): ^{1}H NMR ($CDCl_3$, 400 MHz):



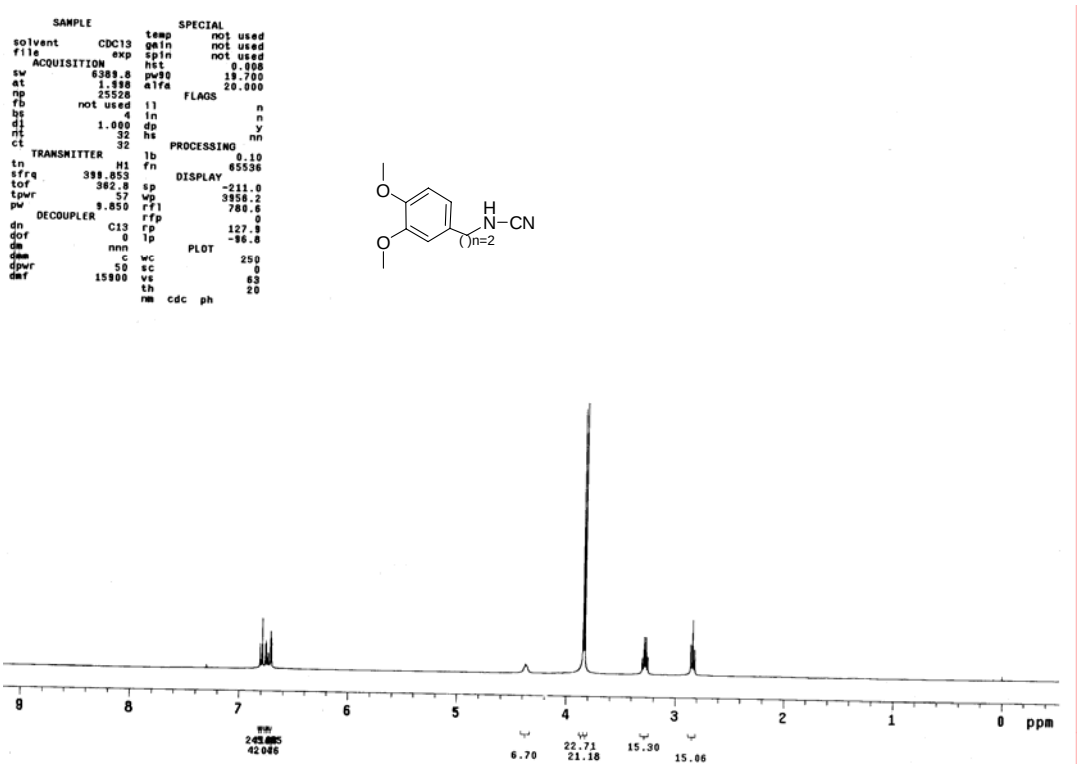
Benzo[1,3]dioxol-5-ylmethyl-cyanamide (19a): ^{13}C NMR ($CDCl_3$, 100 MHz):



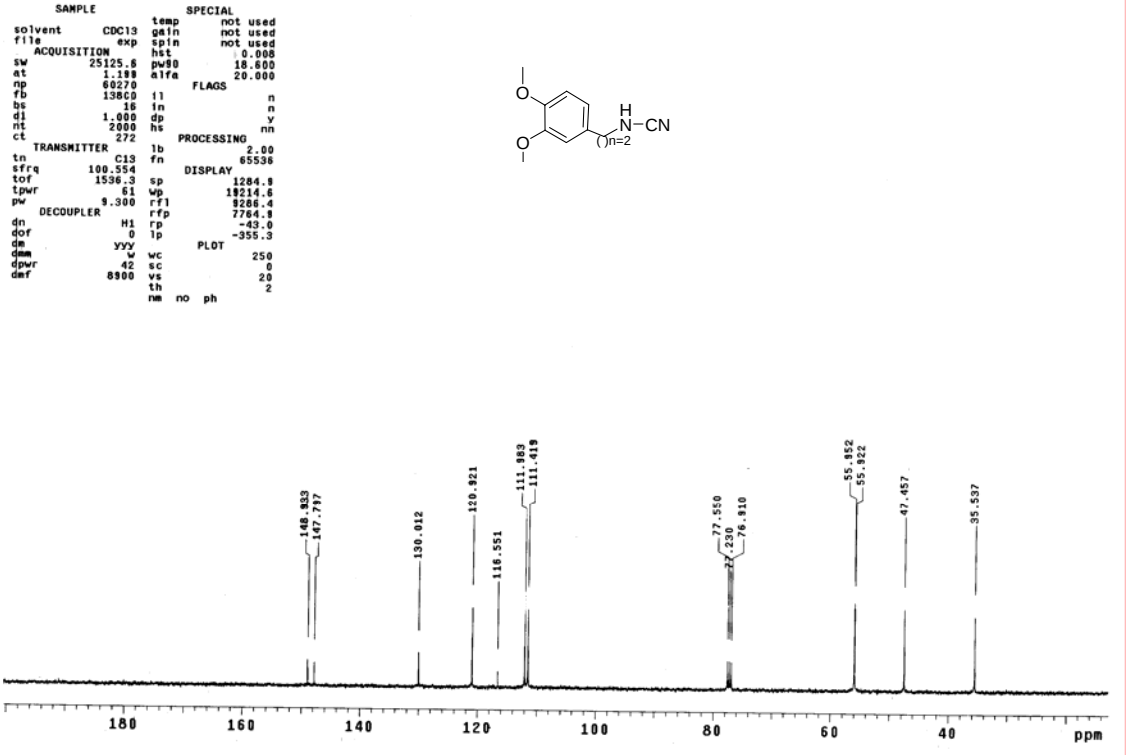
Benzo[1,3]dioxol-5-ylmethyl-cyanamide (19a): IR (KBr):



3,4-Dimethoxyphenylethylcyanamide (20a): ^{1}H NMR ($CDCl_3$, 400 MHz):



3,4-Dimethoxyphenylethylcyanamide (20a): ^{13}C NMR ($CDCl_3$, 100 MHz):



3,4-Dimethoxyphenylethylcyanamide (20a): IR (KBr):