

Supplementary Information

Application of diacetoxyiodobenzene in the desulfurization of arylthioureas

Sushma Singh^{a,b}, Poonam Devi^a, Rashmi Pundeer^{a,c,*} & Vishwas Chaudhri^{d,*}

^aDepartment of Chemistry, Kurukshetra University, Thanesar, Kurukshetra-1361 19, Haryana, India

^bGovt. College, Hisar- 125 001, Haryana, India

^cIndira Gandhi University, Meerpur, Rewari- 122 502, Haryana, India

^dJ C Bose University of Science & Technology YMCA, Faridabad- 121 006, Haryana, India

*E-mail: vishwas_khurana@yahoo.co.in (VC)/ dr.rashmip@gmail.com (RP)

Received 31 December 2021; accepted (revised) 2 June 2022

Contents

1. Experimental
2. Spectroscopic data, Yield, m.p.
3. IR, NMR spectra
4. References

1. Experimental

Melting points were taken in open capillaries and are uncorrected. IR spectra were recorded on Perkin-Elmer IR spectrophotometer. The ¹H NMR spectra were recorded on Bruker 300 MHz instrument. Elemental analyses were carried out in Perkin-Elmer 2400 instrument. Most of the common chemicals were obtained from commercial suppliers. DIB used in present study was prepared according to literature procedure.^{1,2}

Typical procedure: Aqueous ammonia (25%, 2 mL) was added to a stirred solution of phenylthiourea **1** (1eq.) in acetonitrile (5 mL). DIB (1eq.) was added portion-wise over a period of 15 min. A lightyellow precipitate of sulfur started to separate out during this period. After the complete addition of DIB, it was kept stirring for 15 min and conversion to the corresponding 1-phenylcyanamide was confirmed by TLC. The conversion of the 1-phenylthiourea to phenylcyanamide (**1a**) was observed within 10 min of the complete addition of DIB. The reaction mixture was allowed to stand, and the precipitated sulfur was filtered. The organic layer was concentrated and admixed with ethyl acetate (15 mL). The ethyl acetate layer was washed with water (25 mL). The organic layer was dried over anhydrous Na₂SO₄, concentrated under reduced pressure. The oily liquid so obtained was characterized as cyanamide by spectral data.

2. Spectroscopic data, Yield, m.p.

Spectroscopic data of phenyl cyanamides **1a-1j**

Phenylcyanamide³(**1a**): 80% yield; oily liquid; IR (KBr): 3171, 2222, 1597, 1497, 1250, 748, 687cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 7.02-7.58 (m, 5H), 6.88 (br, s, 1H)

2-Methylphenylcyanamide⁴(**1b**): 84% yield; m.p. 77-78 °C; IR (KBr): 3052, 2270, 1549, 1498, 1198, 832, 752 cm⁻¹; ¹H NMR (400MHz, CDCl₃): 2.19 (s, 1H, CH₃), 6.89-7.04 (m, 4H).

4-Methylphenylcyanamide^{3,5} (**1c**): 86% yield; IR(KBr): 3063, 2214, 1597, 1512, 1466, 1250, 810, 756 cm⁻¹; ¹H NMR (400MHz, CDCl₃): 2.26 (s, 3H, CH₃), 6.90-7.14 (m, 4H)

2, 6-Dimethylphenyl cyanamide⁴ (**1d**): 54% yield; m.p. 143-146°C; IR(KBr): 3080, 2225, 1601, 1503, 1250, 1042, 876 cm⁻¹; ¹H NMR (400MHz, CDCl₃): 2.12 (s, 6H, CH₃), 6.93-7.11 (m, 3H), 6.73 (br, s, 1H, NH)

4-Methoxyphenyl cyanamide⁴ (**1e**): 74% yield; m.p. 87-88°C; IR(KBr): 2924, 2854, 2222, 1605, 1504, 1458, 1296, 1234, 1173, 1026, 825 cm⁻¹; ¹H NMR (400MHz, CDCl₃): 3.85 (s, 3H, OCH₃), 6.85-7.20 (m, 4H).

4-Chlorophenyl cyanamide³ (**1f**): 97%yield;m.p. 95-96°C; IR (KBr): 3152, 2222, 1620, 1511, 1461, 1302, 1065 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, δ): 6.58 (br, s, 1H), 6.95-7.32 (m, 4H)

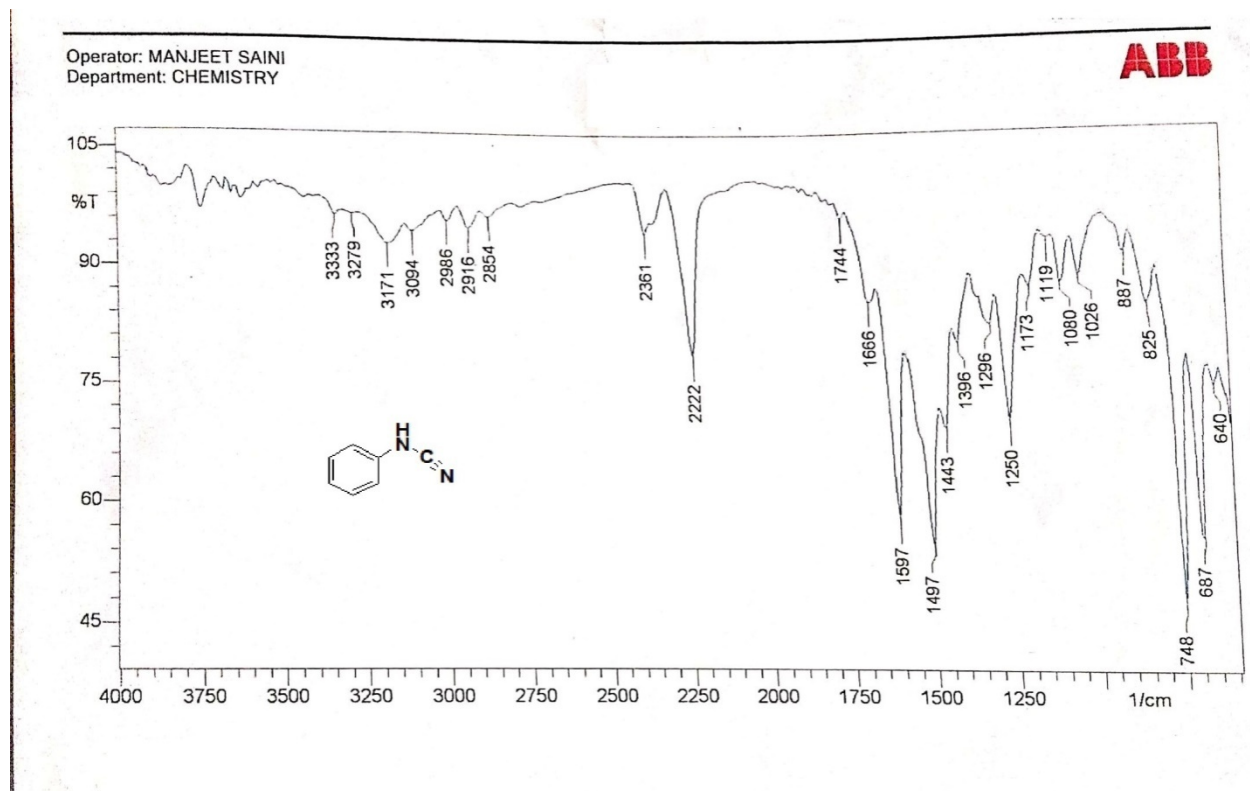
4-Bromophenylcyanamide⁴ (**1g**):93% yield; m.p. 111-113°C; IR(KBr): 3148, 3063,2924, 2854, 2230, 1597, 1481,1250, 1072, 1011, 810 cm⁻¹; ¹H NMR (400MHz, CDCl₃): δ 6.83 - 6.86 (d, J= 9 Hz, 2H), 7.42-7.45 (d, J= 9 Hz, 2H), 5.14 (br, s, 1H, NH)

3-Nitrophenyl cyanamid^{3,6} (**1h**): 74% Yield: m.p. 133-135°C; IR (KBr): 3145, 2928, 2238, 1624, 1365, 1266, 1082 cm⁻¹; ¹H NMR (400 MHz, CDCl₃+ DMSO): δ 7.41-7.85 (m, 4H)

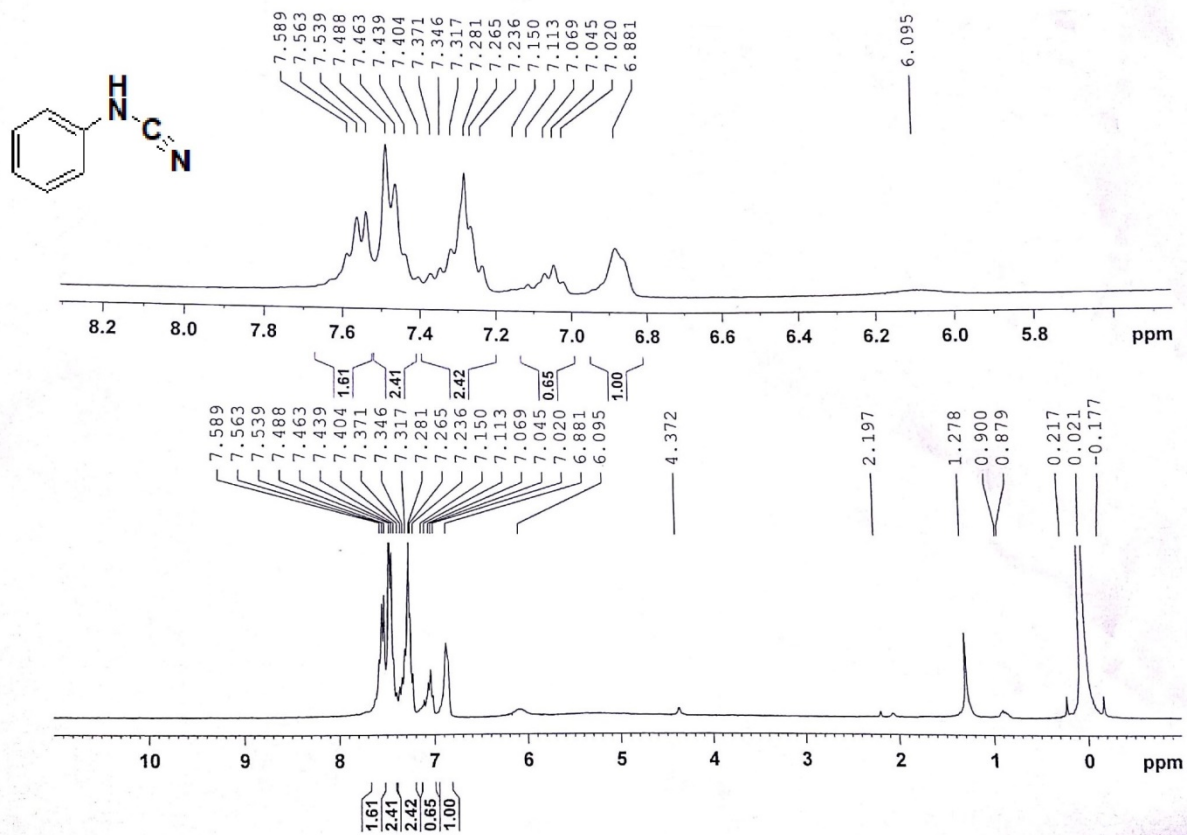
4-Nitrophenyl cyanamide^{4,6} (**1i**) 70%yield;m.p. 186-187°C; IR (KBr): 3217, 2152, 1589,1474, 1296, 1111, 841, 748, 625 cm⁻¹; ¹H NMR (400 MHz, CDCl₃+ DMSO): δ7.52 - 7.87 (m, 4H)

4-carboxyethylphenylcyanamide⁴ (**1j**): 15%yield; m.p. 150-152°C; IR (KBr): 3156, 2901, 1729, 1578, 1378, 898cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ1.34 (t, 3H), 4.32 (q, 2H), 7.65 – 6.8.7 (m, 4H), 12.11 (br, s, 1H, COOH)

3. IR, NMR spectra

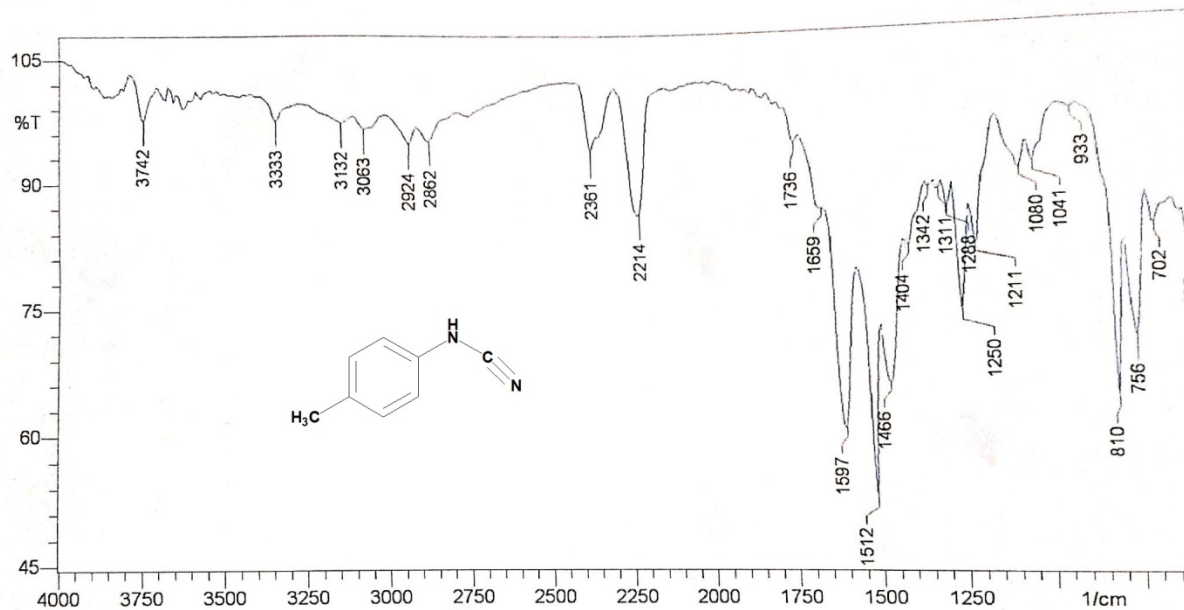


FigureS1: FTIR of 1a



FigureS2: ¹H NMR of 1a

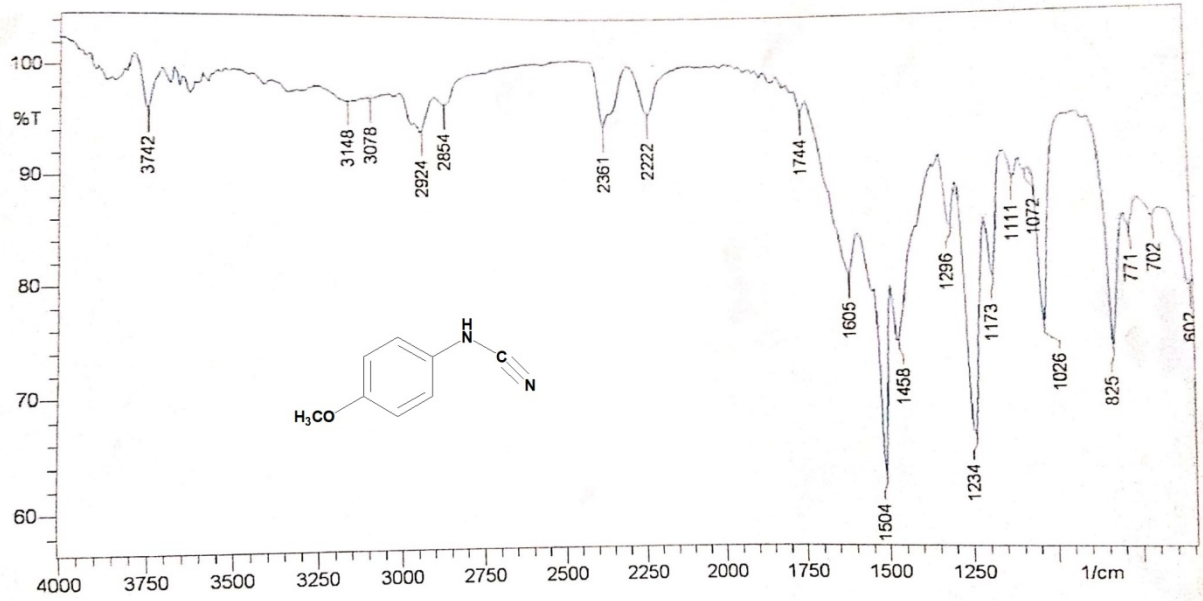
Operator: MANJEET SAINI
Department: CHEMISTRY



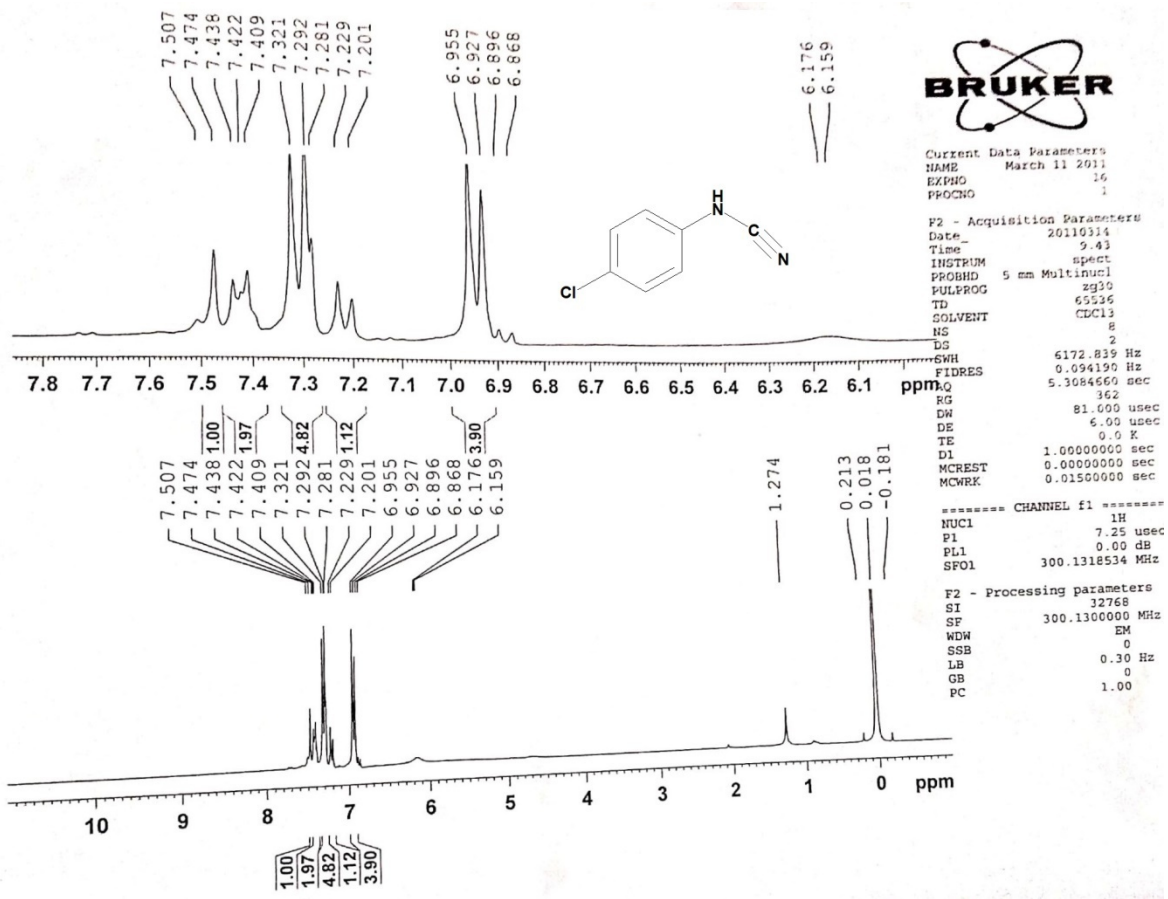
FigureS3: FTIR of 1c

Operator: MANJEET SAINI
Department: CHEMISTRY

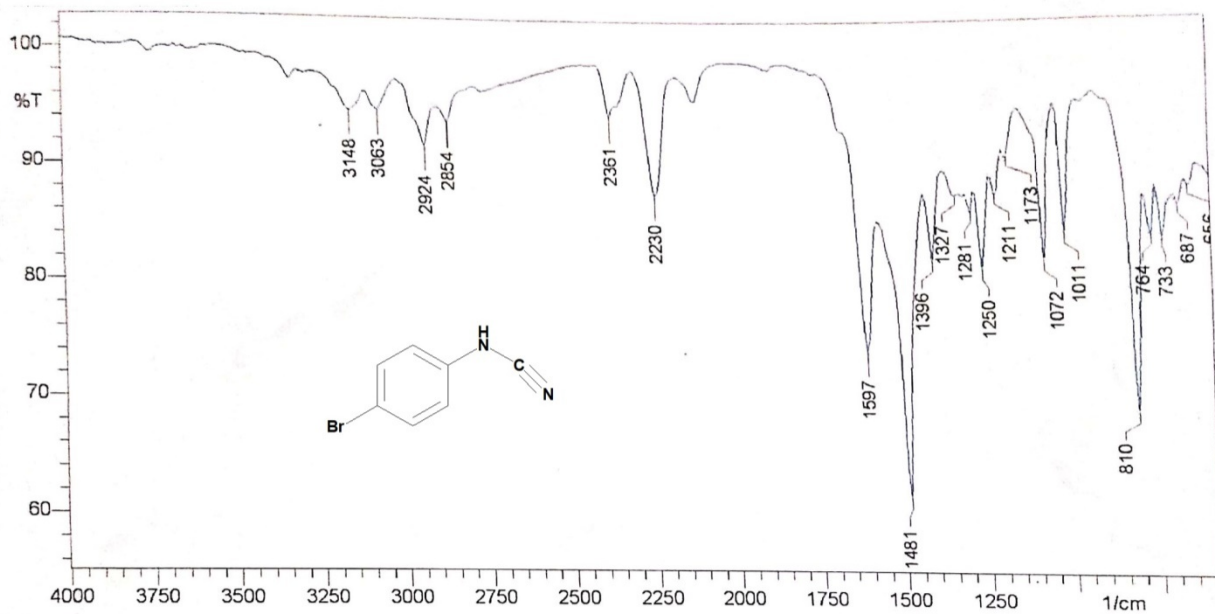
ABB



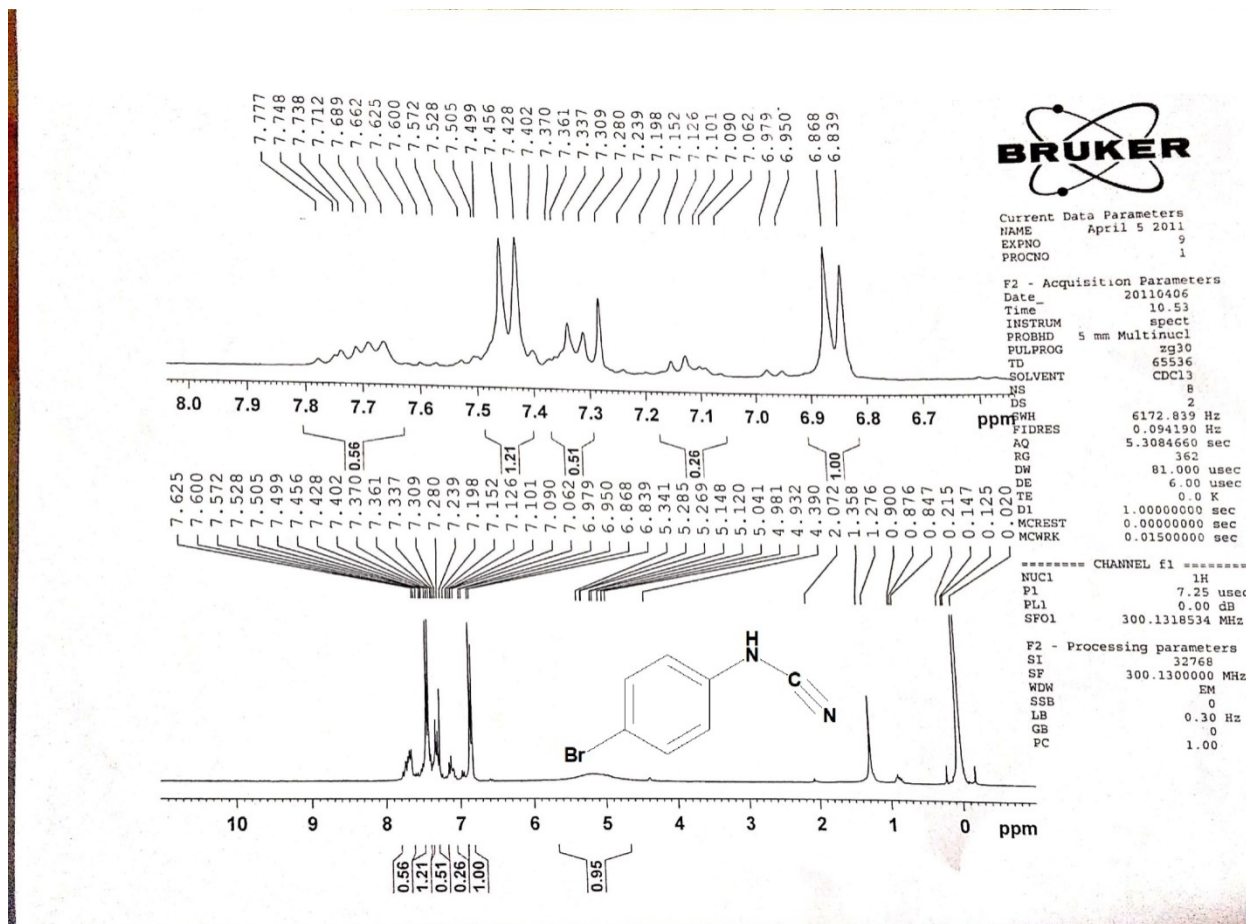
FigureS4: FTIR of 1e



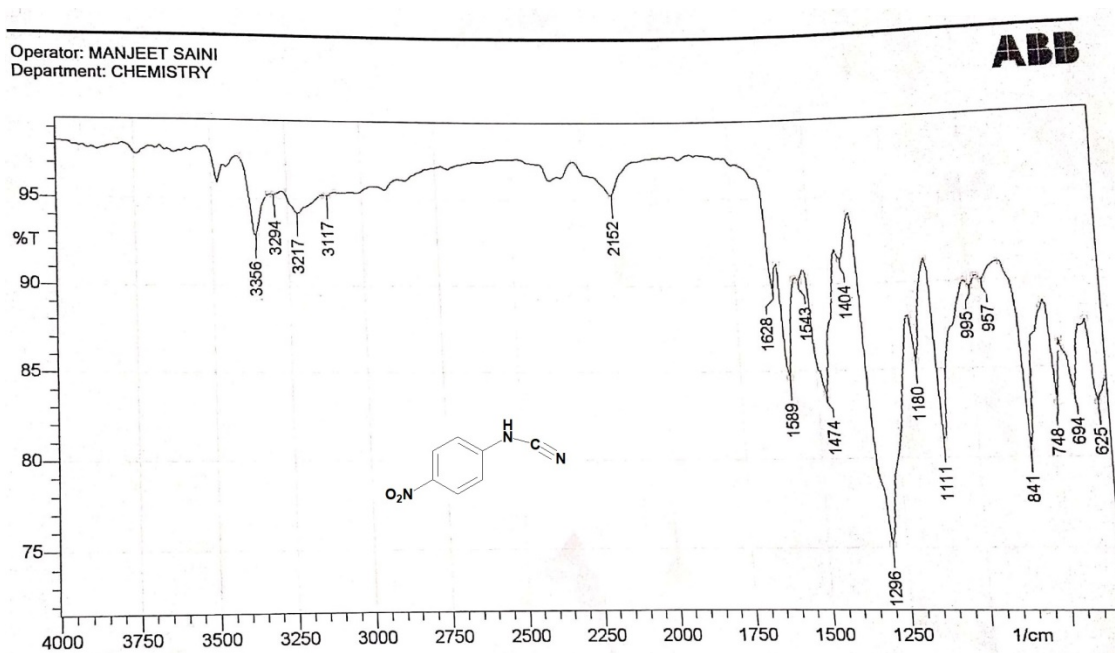
FigureS5: ¹H NMR of 1f



FigureS6: FTIR of 1g



FigureS7: ¹H NMR of 1g



FigureS8: FTIR of 1i

4. References

- 1H. J. Lucas and E. R. Kennedy, *Org. Synth. Coll. Vol. II*, 1943, 351.
- 2B. S. Furniss, A. J. Hannaford, V. Robergs, P. W. G. Smith and A. R. Tatchell. Vogel's Text Book of Practical Organic Chemistry. 1991, 5th edition.
- 3H. Ghosh, R. Yella, A. R. Ali, S. K. Sahoo and B. K. Patel. An efficient synthesis of cyanamide from amine promoted by a hypervalent iodine(III) reagent. *Tetrahedron Letters*, 2009, **50**, 2407-2410.
- 4K. Škoch, I. Cíarová and P. Štěpnicka. Selective gold-catalysed synthesis of cyanamides and 1-substituted 1H-tetrazol-5-amines from isocyanides. *Chem.-Eur. J.*, 2018, **24**, 13788.
- 5V. Kumar, M. P. Kaushik and A. Mazumdar. An efficient approach for the synthesis of N-1 substituted hydantoins. *Eur. J. Org. Chem.*, 2008, 1910-1916.
- 6F. F. Wong, C.-Y. Chen and M.-Y. Yeh. Sodium bis(trimethylsilyl)amide in the 'one-flask' transformation of isocyanates to cyanamides. *Synlett*, 2006, 559-562.