

Microwave-assisted synthesis of 2-substituted benzoxazoles in the presence of potassium cyanide as catalyst

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Supplementary Information:

Experimental section

All the materials were of commercial reagent grade. The aromatic aldehydes and *o*-aminophenol were purified by standard procedures and purity determined by thin layer chromatography (TLC).

IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 spectrophotometer or an Impact 400 Nicolet FTIR spectrophotometer. ¹H NMR and ¹³C NMR were recorded in CDCl₃ solvent on a Bruker DRX-400 spectrometer with tetramethylsilane as internal reference. Melting points obtained with a Yanagimoto micro melting point apparatus are uncorrected. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company). Microwave irradiations were carried out in microwave oven specially designed for the organic synthesis (Milestone LAVIS 1000 Basic Microwave).

Typical procedure for the Synthesis of benzoxazoles from aryl aldehydes

A mixture of 2-aminophenol (0.13 gr, 1.1 mmol), substituted benzaldehydes (2.2 mmol) and potassium cyanide (1.1 mmol) in 4 ml *N,N*-dimethylformamide was irradiated in a microwave oven at 450 W. The progress of the reaction was monitored using thin-layer chromatography (petroleum ether/ethyl acetate, 6/2). After completion of the reaction, the mixture was cooled and extracted with ethyl acetate (3 × 10 mL) and the organic layer was

concentrated under reduced pressure. Then, recrystallization of crude product was carried out in a boiling mixture of ethanol/water (1:1) to give pure product.

2-Phenyl-1,3-benzoxazole (2a). Light brown solid; m.p= 98-100 °C (m.p = 102-103 °C)³⁸; IR (KBr)/ ν (cm⁻¹) 1615 (C=N), 1551, 1448 (C=C, Ar), 1242 (C-O-C); ¹H NMR (CDCl₃, 400 MHz)/ δ (ppm): 8.29-8.26 (2H, m, Ar), 7.80-7.78 (1H, m, Ar), 7.62-7.59 (1H, m, Ar), 7.56-7.54 (3H, m, Ar), 7.38-7.36 (2H, m, Ar).

2-(2-Hydroxyphenyl)-1,3-benzoxazole (2b). White solid; m.p= 123-124 °C (m.p = 125-126 °C)³⁹; IR (KBr)/ ν (cm⁻¹) 3143 (OH), 1630 (C=N), 1544, 1485 (C=C, Ar), 1248 (C-O-C); ¹H NMR (CDCl₃, 400 MHz)/ δ (ppm): 11.50 (1H, s, OH), 8.05-8.03 (1H, d, J= 7.6 Hz, Ar), 7.75 (1H, m, Ar), 7.63 (1H, m, Ar), 7.47-7.40 (3H, m, Ar), 7.14-7.12 (1H, d, J= 8 Hz, Ar), 7.04-7.00 (1H, m, Ar); ¹³C NMR (CDCl₃, 100 MHz)/ δ (ppm) 162.90, 158.70, 149.13, 140.00, 133.56, 127.10, 125.30, 125.00, 119.56, 119.25, 117.40, 110.66.

2-(3-Hydroxy-phenyl)-1,3-benzoxazole (2c). White solid; m.p=172-174 °C; IR (KBr)/ ν (cm⁻¹) 3428 (OH), 1600 (C=N), 1550, 1452 (C=C, Ar), 1241 (C-O-C); ¹H NMR (CDCl₃, 400 MHz)/ δ (ppm): 8.91 (1H, s, OH), 7.75-7.73 (3H, m, Ar), 7.70 (1H, m, Ar), 7.42-7.41 (3H, m, Ar), 7.00 (1H, m, Ar).

2-(2-Chlorophenyl)-1,3-benzoxazole (2d). Light yellow solid; m.p= 63-65 °C (m.p = 61-64 °C)¹⁸; IR (KBr)/ ν (cm⁻¹) 1606 (C=N), 1537, 1452 (C=C, Ar), 1244 (C-O-C); ¹H NMR (CDCl₃, 400 MHz)/ δ (ppm): 8.18-8.15 (1H, dd, J= 7.20, 1.6 Hz, Ar), 7.88-7.86 (1H, m, Ar), 7.65-7.63 (1H, m, Ar), 7.60-7.58 (1H, m, Ar), 7.49-7.38 (4H, m, Ar).

2-(4-Chlorophenyl)-1,3-benzoxazole (2e). Light brown solid; m.p= 149-151 °C (m.p = 153-154 °C)³⁸; IR (KBr)/ ν (cm⁻¹) 1614 (C=N), 1482, 1550 (C=C, Ar), 1243 (C-O-C); ¹H NMR

(CDCl₃, 400 MHz)/ δ (ppm): 8.20-8.19 (2H, m, Ar), 7.79-7.77 (1H, m, Ar), 7.61-7.58 (1H, m, Ar), 7.53-7.51 (2H, m, Ar), 7.39-7.37 (2H, m, Ar).

2-(2,4-Dichlorophenyl)-1,3-benzoxazole (2f). Light brown solid; m.p= 120-123 °C (m.p = 118-119 °C)⁴⁰; IR (KBr)/ ν (cm⁻¹) 1662 (C=N), 1588, 1466 (C=C, Ar), 1241 (C-O-C); ¹H NMR (CDCl₃, 400 MHz)/ δ (ppm): 8.14-8.12 (1H, d, J= 8.40 Hz, Ar), 7.86-7.84 (1H, m, Ar), 7.64-7.60 (2H, m, Ar), 7.43-7.40 (3H, m, Ar); ¹³C NMR (CDCl₃, 100 MHz)/ δ (ppm): 160.07, 150.51, 141.58, 137.54, 134.24, 132.51, 131.30, 127.43, 125.81, 124.82, 124.71, 120.56, 110.77.

2-(3-Methoxyphenyl)-1,3-benzoxazole (2g). Light yellow solid; m.p= 72-74 °C (m.p = 71.3-73.8 °C)⁴¹; IR (KBr)/ ν (cm⁻¹) 1642 (C=N), 1541, 1453 (C=C, Ar), 1278 (C-O-C); ¹H NMR (CDCl₃, 400 MHz)/ δ (ppm): 8.11 (1H, m, Ar), 7.47 (1H, m, Ar), 7.44-7.42 (2H, m, Ar), 7.26 (1H, m, Ar), 7.18-7.14 (1H, m, Ar), 7.09-7.07 (1H, m, Ar), 6.95-6.91 (1H, m, Ar), 3.89 (3H, s, Me).

2-(4-Methoxyphenyl)-1,3-benzoxazole (2h). Light yellow solid; m.p= 100-101 °C (m.p = 103-105 °C)³⁸; IR (KBr)/ ν (cm⁻¹) 1613 (C=N), 1501, 1452 (C=C, Ar), 1249 (C-O-C); ¹H NMR (CDCl₃, 400 MHz)/ δ (ppm): 8.22-8.20 (2H, d, J= 8.40 Hz, Ar), 7.75-7.74 (1H, m, Ar), 7.58-7.56 (1H, m, Ar), 7.35-7.32 (2H, m, Ar), 7.05-7.03 (2H, d, J= 8 Hz, Ar), 3.90 (3H, s, Me); ¹³C NMR (CDCl₃, 100 MHz)/ δ (ppm): 163.18, 162.32, 150.68, 142.30, 129.39, 124.60, 124.42, 119.70, 119.62, 114.36, 110.39, 55.45.

2-(3-Methylphenyl)-1,3-benzoxazole (2i). Light yellow solid; m.p= 80-81 °C (m.p = 79-80 °C)⁴¹; IR (KBr)/ ν (cm⁻¹) 1598 (C=N), 1550, 1451 (C=C, Ar), 1244 (C-O-C); ¹H NMR (CDCl₃, 400 MHz)/ δ (ppm): 8.08 (1H, s, Ar), 8.07-8.05 (1H, d, J= 7.60 Hz, Ar), 7.79-7.77 (1H, m, Ar), 7.60-7.58 (1H, m, Ar), 7.45-7.41 (1H, t, J= 7.80 Hz, Ar), 7.37-7.35 (3H, m, Ar), 2.47 (3H, s, Me).

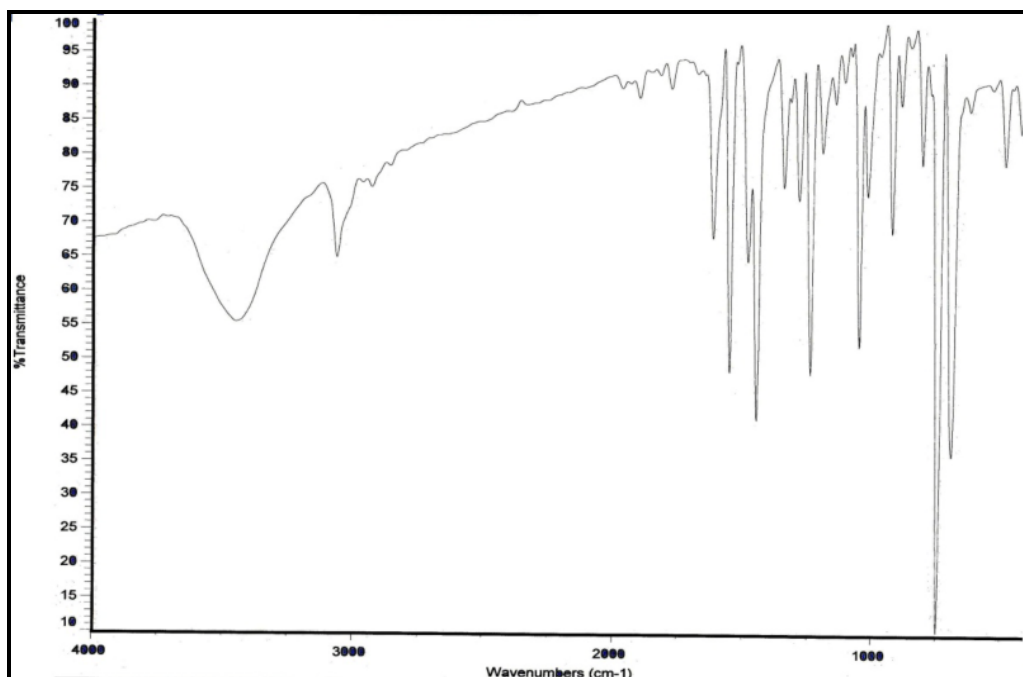
2-(4-Methylphenyl)-1,3-benzoxazole (2j). Light brown solid; m.p= 114-115 °C (m.p = 115-116 °C)³⁸; IR (KBr)/ ν (cm^{-1}) 1619 (C=N), 1500, 1451 (C=C, Ar), 1241 (C-O-C); ¹H NMR (CDCl_3 , 400 MHz)/ δ (ppm): 8.16-8.14 (2H, d, J= 8 Hz, Ar), 7.78-7.75 (1 H, m, Ar), 7.59-7.54 (1H, m, Ar), 7.36-7.34 (4H, m, Ar), 2.45 (3H, s, Me).

2-(4-Isopropyl-phenyl)-1,3-benzoxazole (2k). Light brown solid; m.p= 80-82 °C (m.p = 76-78 °C)⁴²; IR (KBr)/ ν (cm^{-1}) 1613 (C=N), 1553, 1451 (C=C, Ar), 1240 (C-O-C); ¹H NMR (CDCl_3 , 400 MHz)/ δ (ppm): 8.20-8.18 (2H, d, J= 8 Hz, Ar), 7.78-7.76 (1H, m, Ar), 7.60-7.58 (1H, m, Ar), 7.41-7.39 (2H, d, J= 8 Hz, Ar), 7.36-7.34 (2H, m, Ar), 3.00-2.99 (1H, m, CH), 1.32-1.30 (6H, d, J= 6.80 Hz, Me).

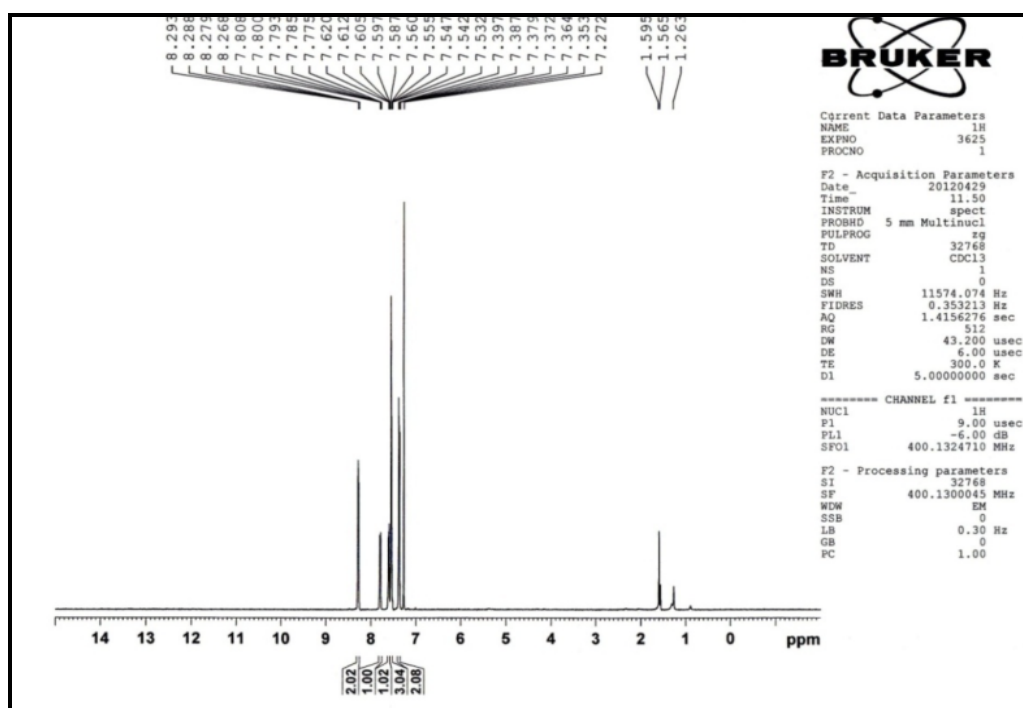
2-(2-Thiophen-2-yl)-1,3-benzoxazole (2l). Brown solid; m.p= 82-84 °C (m.p = 82-83 °C)³⁸; IR (KBr)/ ν (cm^{-1}) 1659 (C=N), 1576, 1481 (C=C, Ar), 1310 (C-O-C); ¹H NMR (CDCl_3 , 400 MHz)/ δ (ppm): 7.93-7.92 (1H, d, J= 4 Hz, Ar), 7.76-7.74 (1H, m, Ar), 7.58-7.54 (2H, m, Ar), 7.36-7.34 (2H, m, Ar), 7.22-7.19 (1H, m, Ar).

2-(2-Furan-2-yl)-1,3-benzoxazole (2m). Red brown solid; m.p= 80-82 °C (m.p = 85-86 °C)³⁸; IR (KBr)/ ν (cm^{-1}) 1640 (C=N), 1553, 1451 (C=C, Ar), 1246 (C-O-C); ¹H NMR (CDCl_3 , 400 MHz)/ δ (ppm): 7.77-7.76 (1H, m, Ar), 7.68 (1H, s, Ar), 7.57-7.56 (1H, m, Ar), 7.38-7.36 (2H, m, Ar), 7.29 (1H, m, Ar), 6.63 (1H, m, Ar).

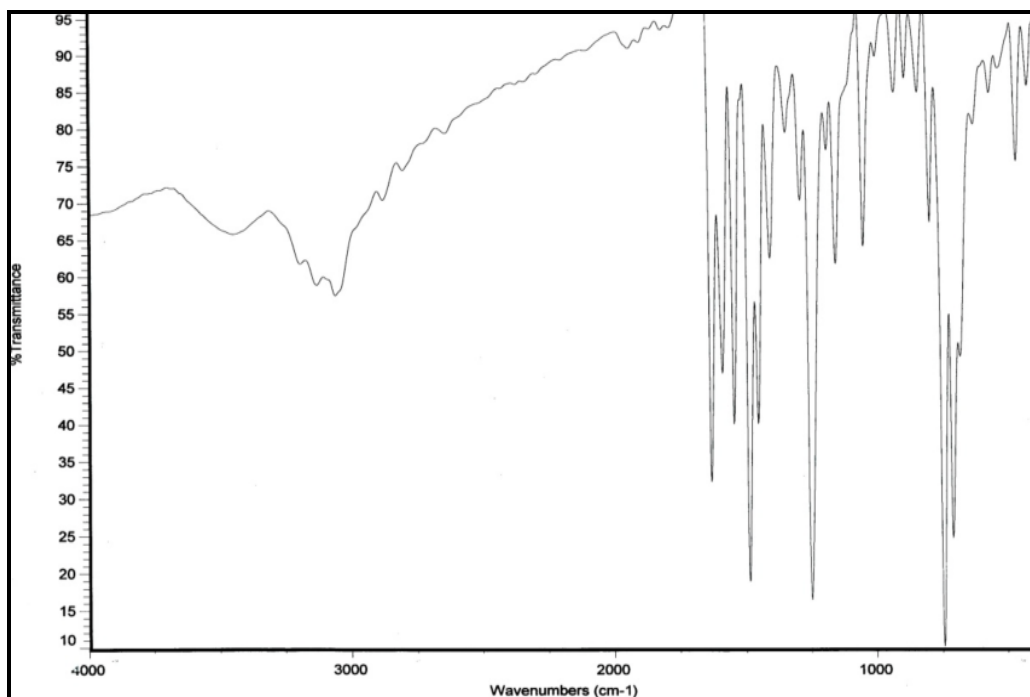
2-(4-N,N-Dimethylaminophenyl)-1,3-benzoxazole (2n). Light Brown solid; m.p=185-187 °C; IR (KBr)/ ν (cm^{-1}) 1613 (C=N), 1510, 1447 (C=C, Ar), 1239 (C-O-C); ¹H NMR (CDCl_3 , 400 MHz)/ δ (ppm): 8.13-8.11 (2H, d, J= 8 Hz, Ar), 7.71-7.69 (1H, d, J= 7.20 Hz, Ar), 7.54-7.52 (1H, d, J= 7.20 Hz, Ar), 7.31-7.27 (2H, m, Ar), 6.79-6.77 (2H, d, J= 8 Hz, Ar), 3.08 (6H, s, Me).



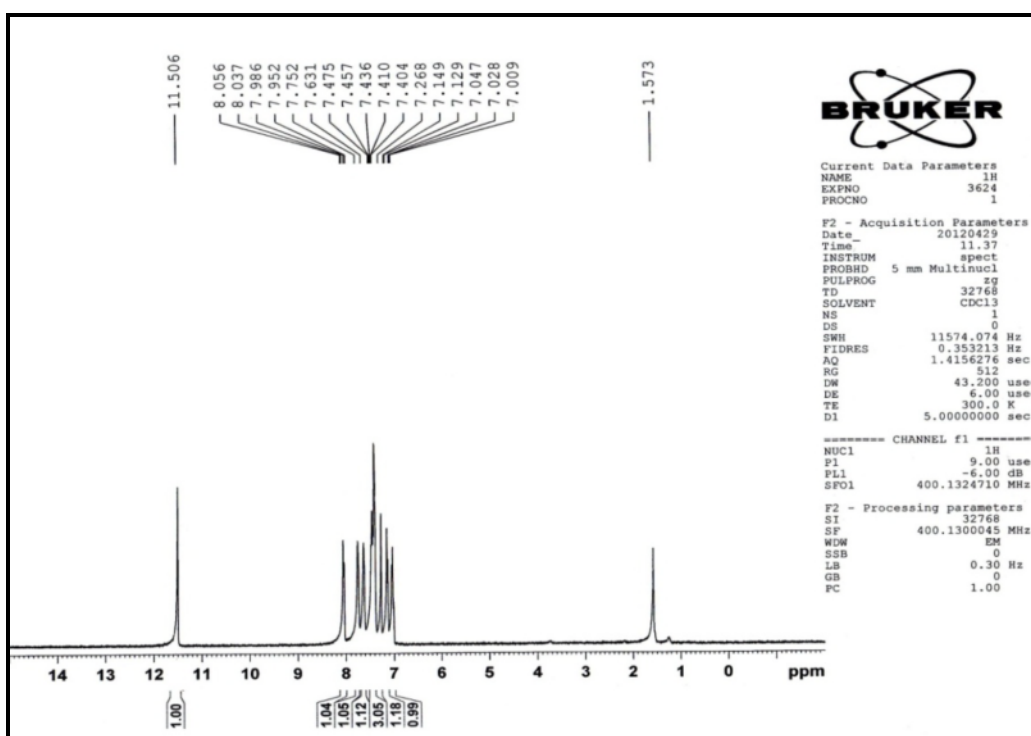
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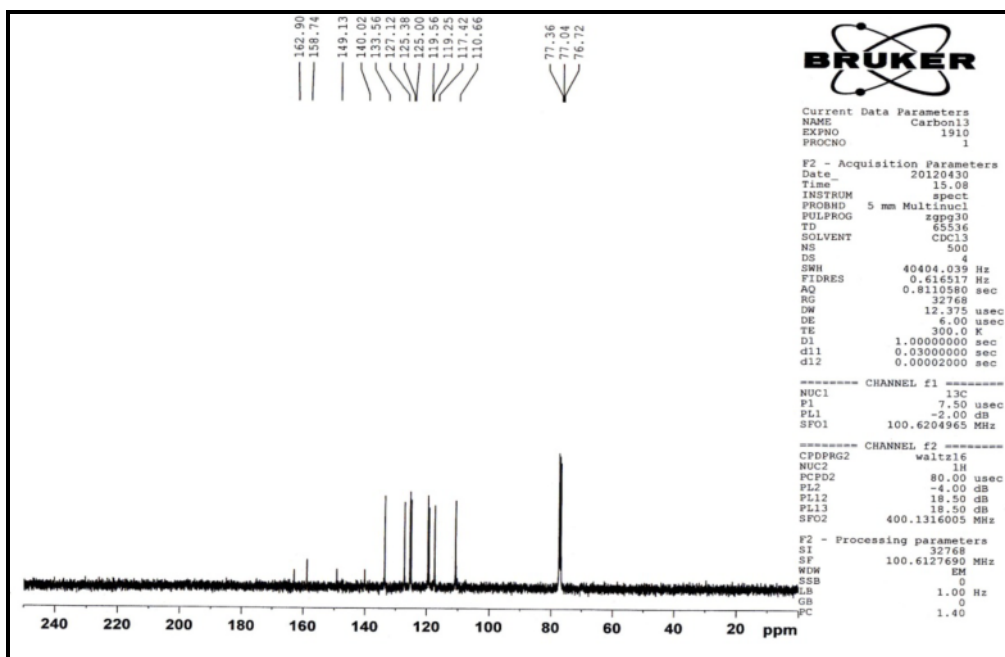
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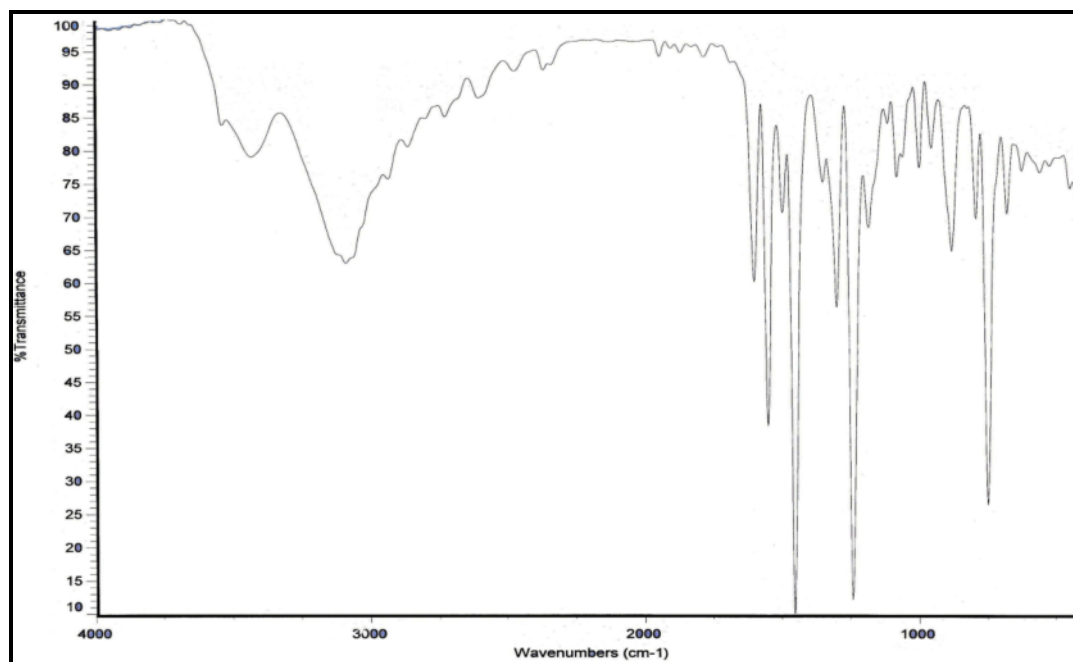
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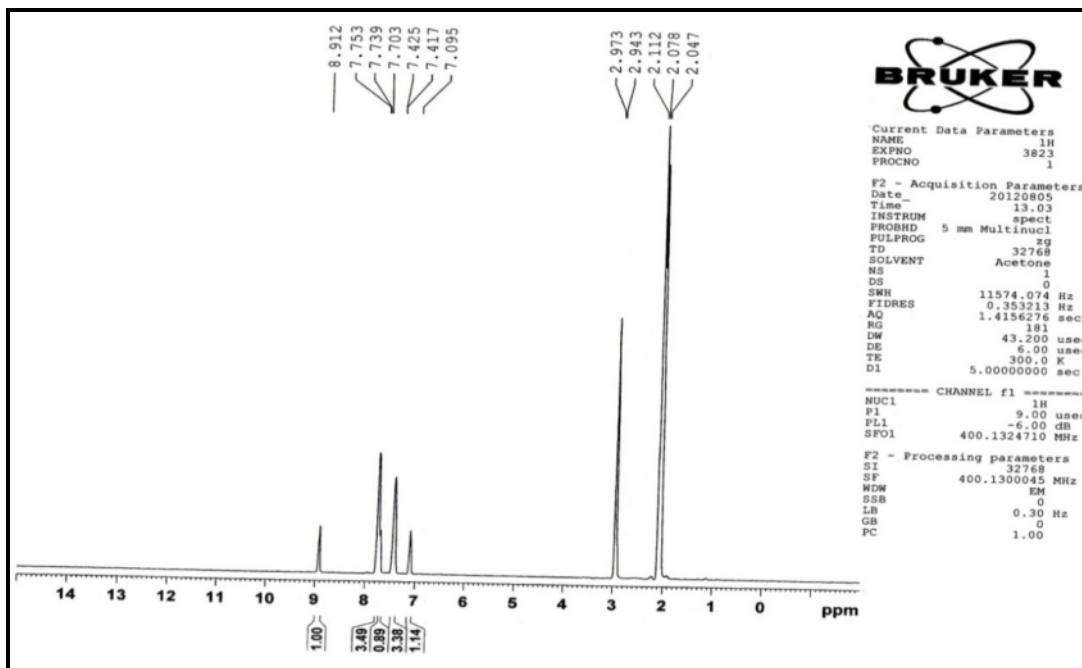
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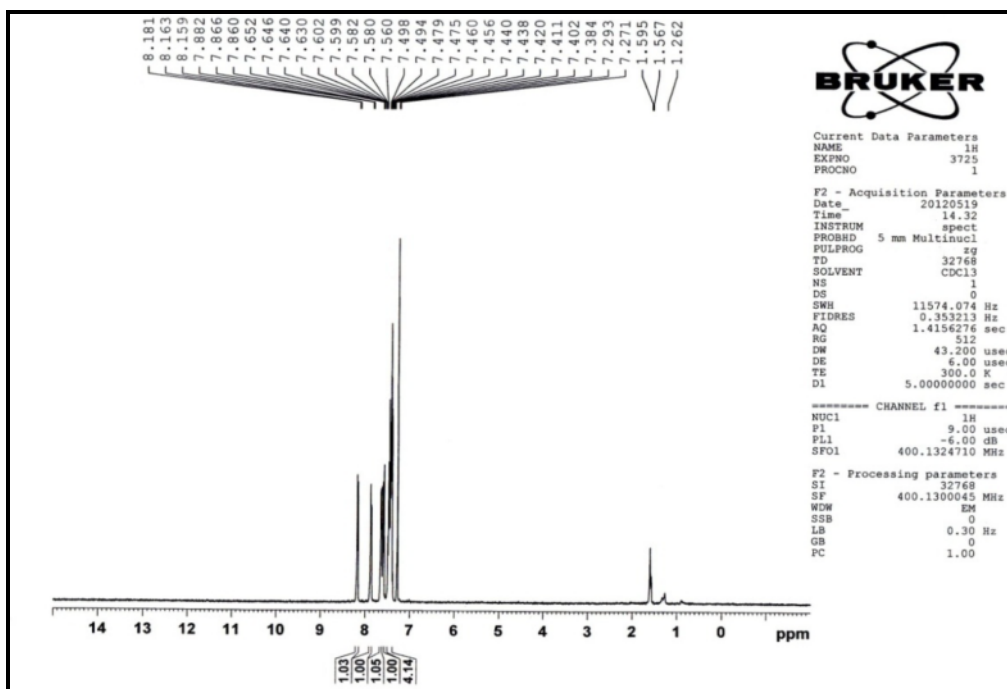
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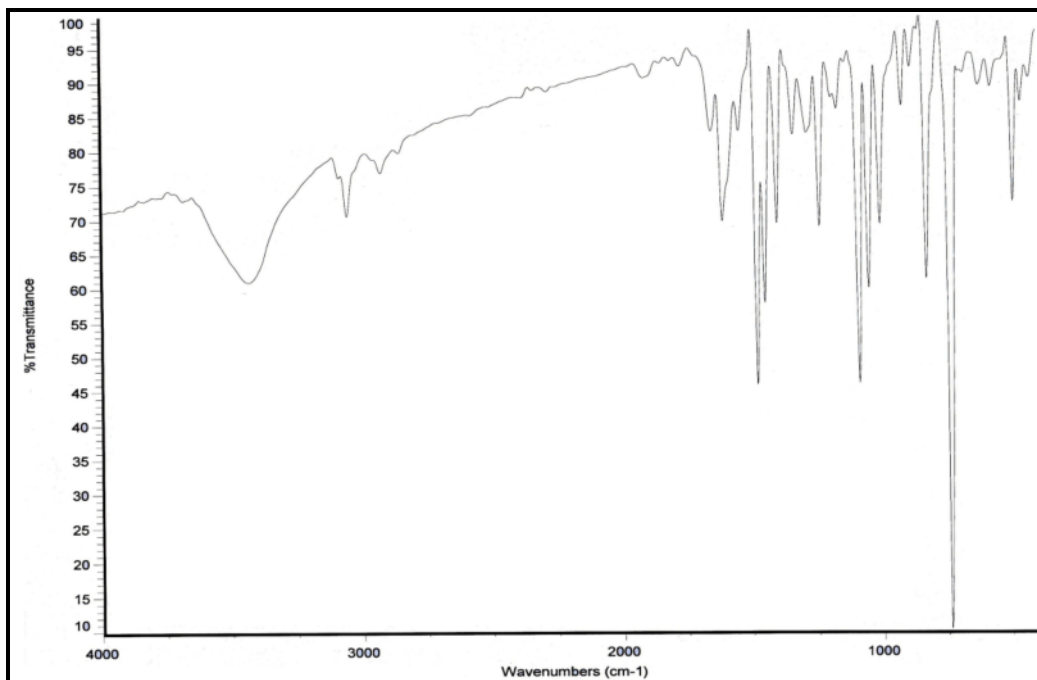
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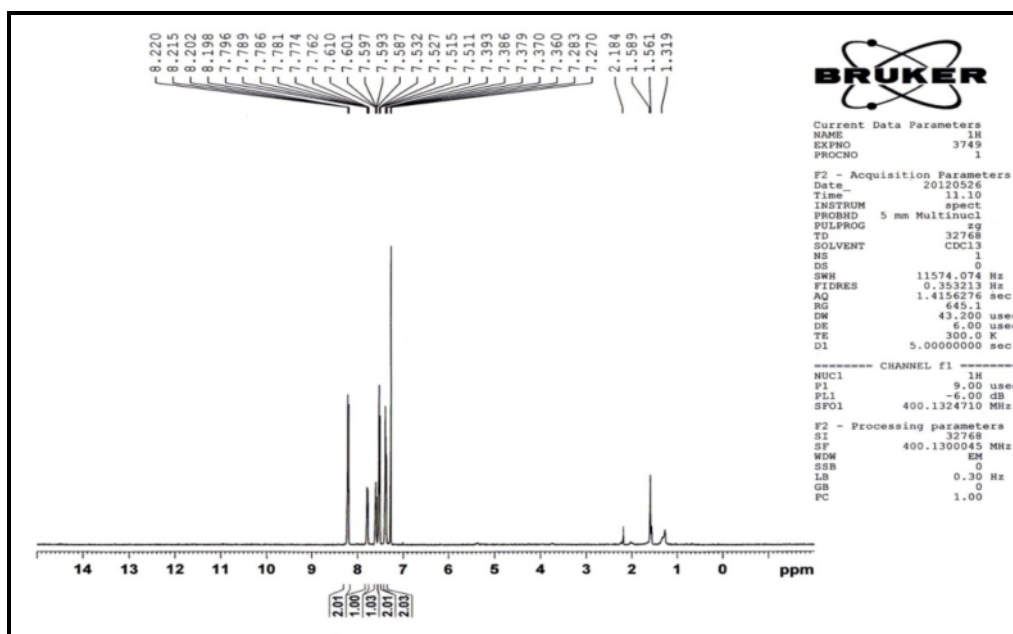
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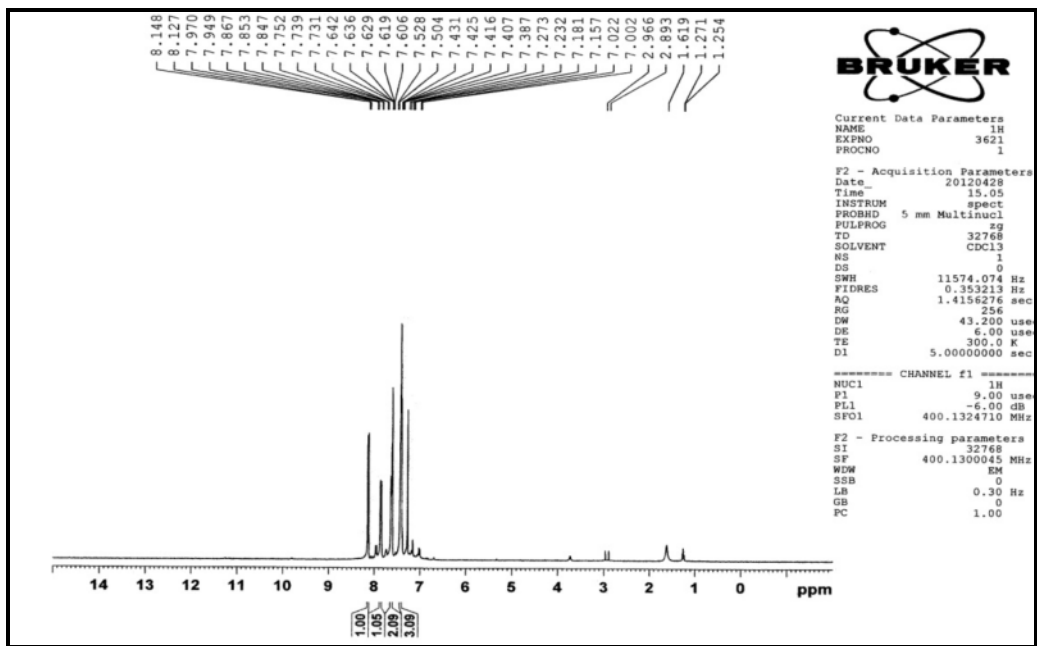
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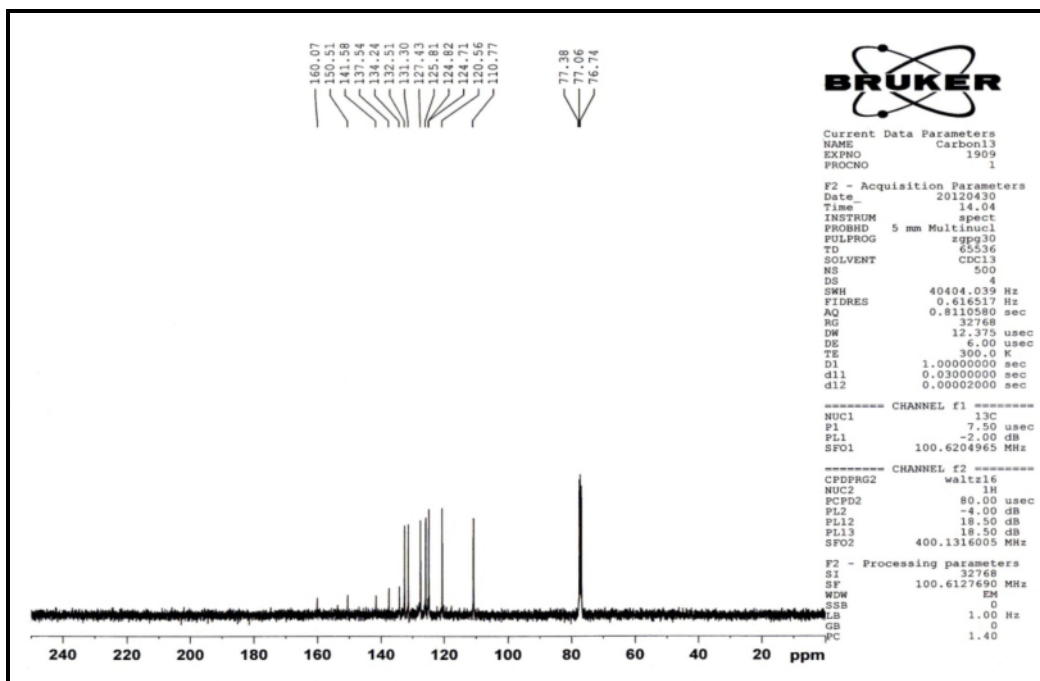
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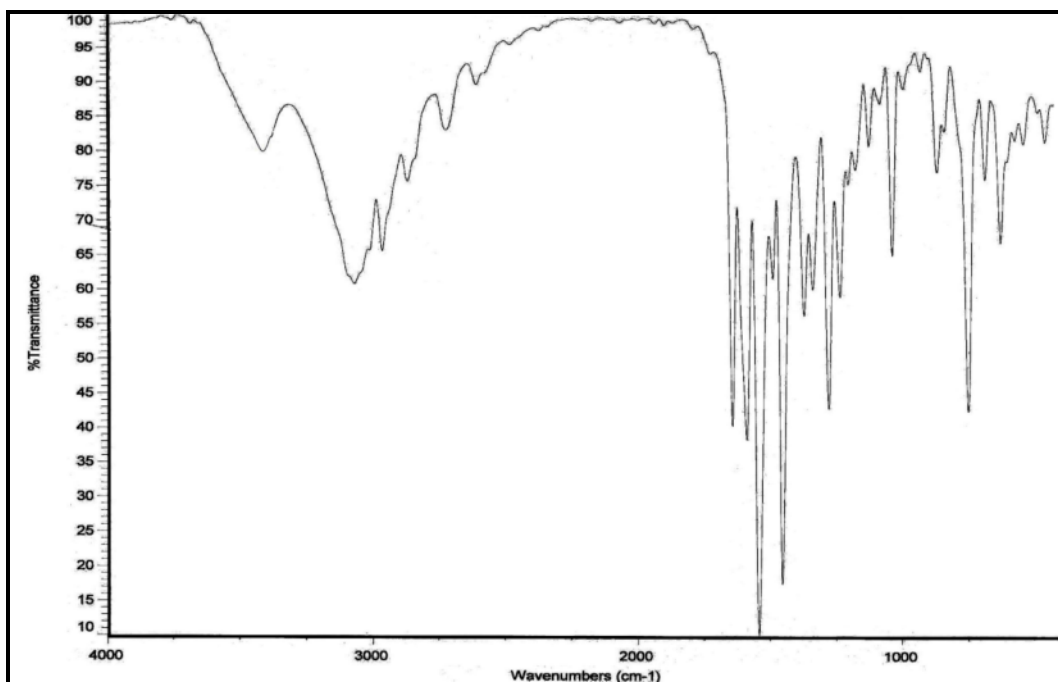
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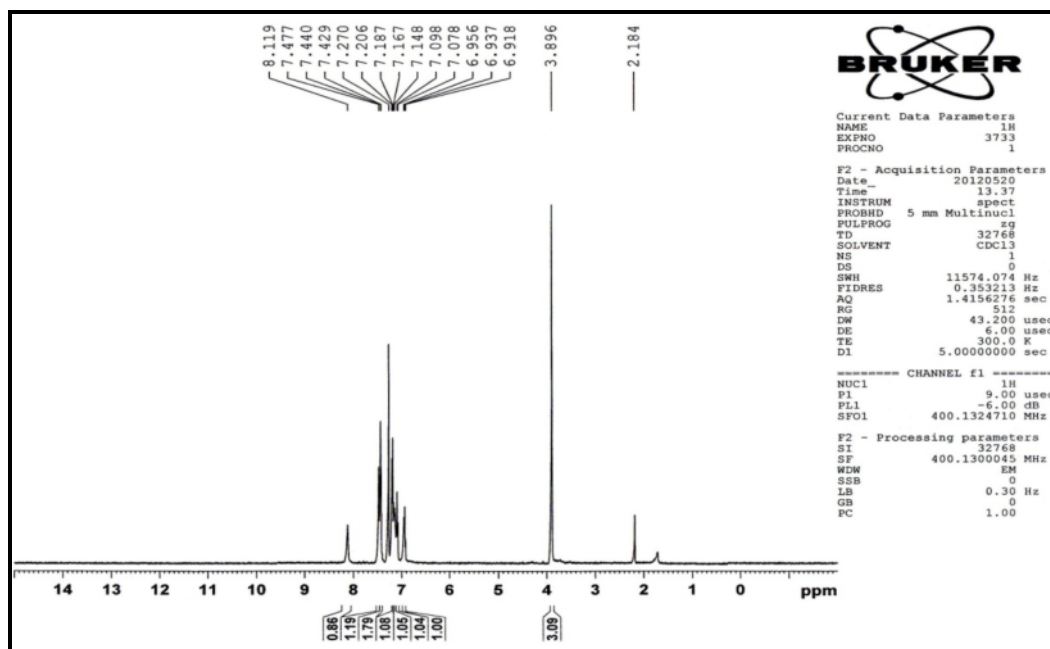
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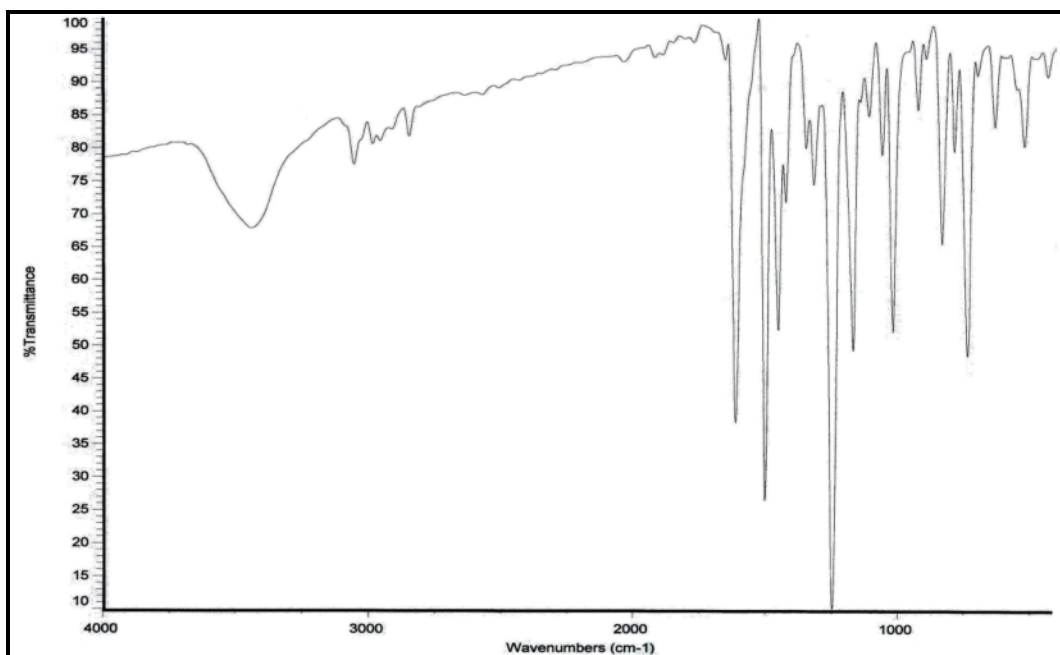
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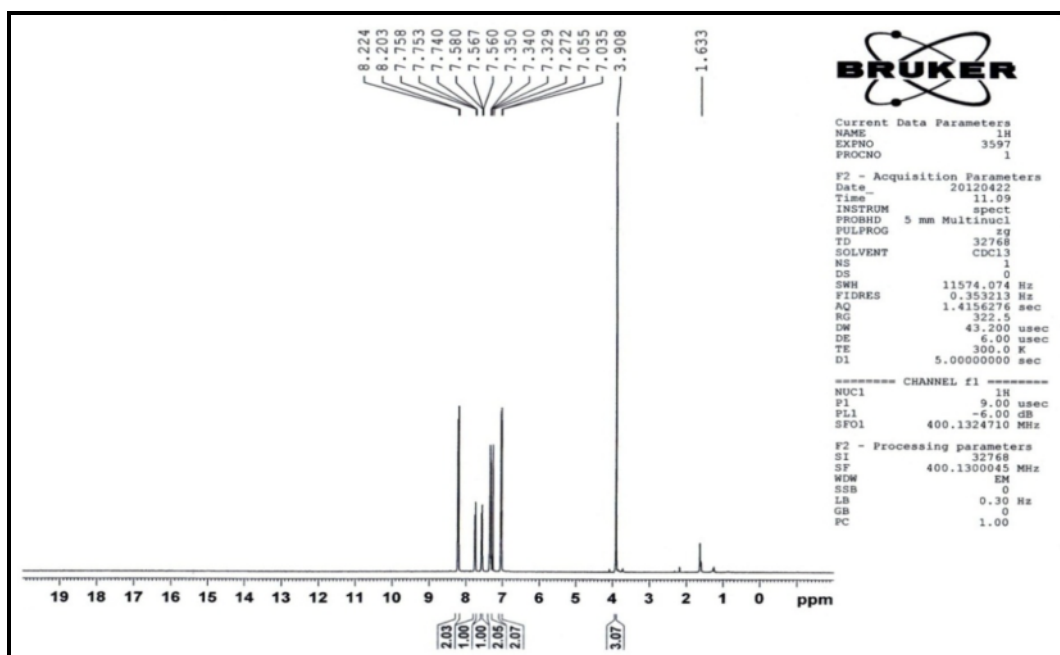
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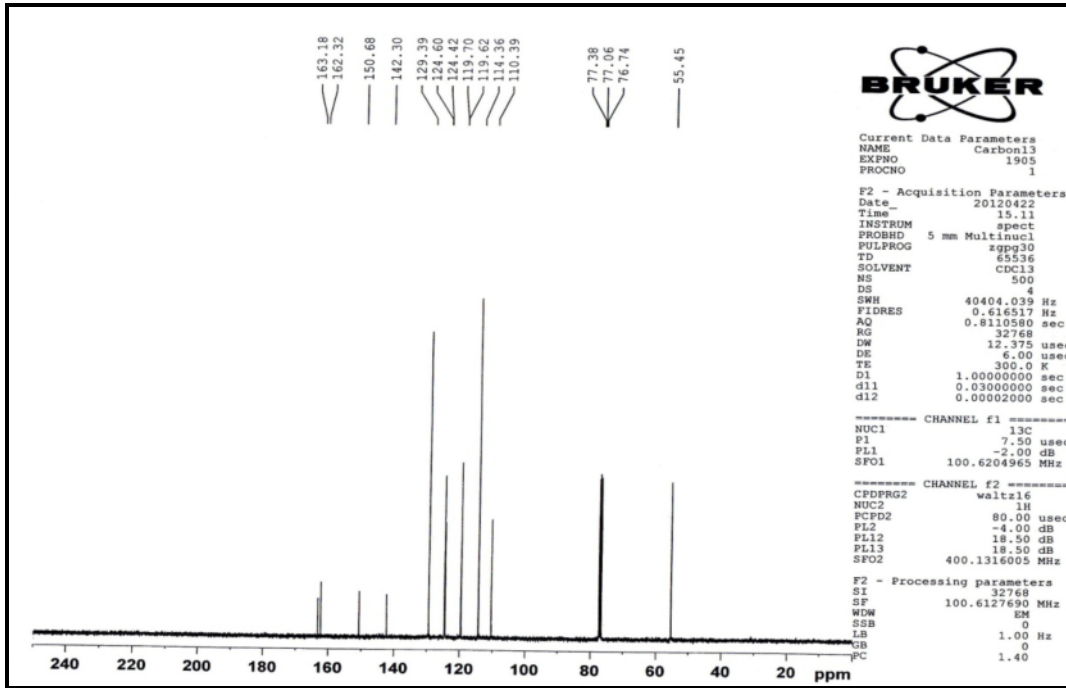
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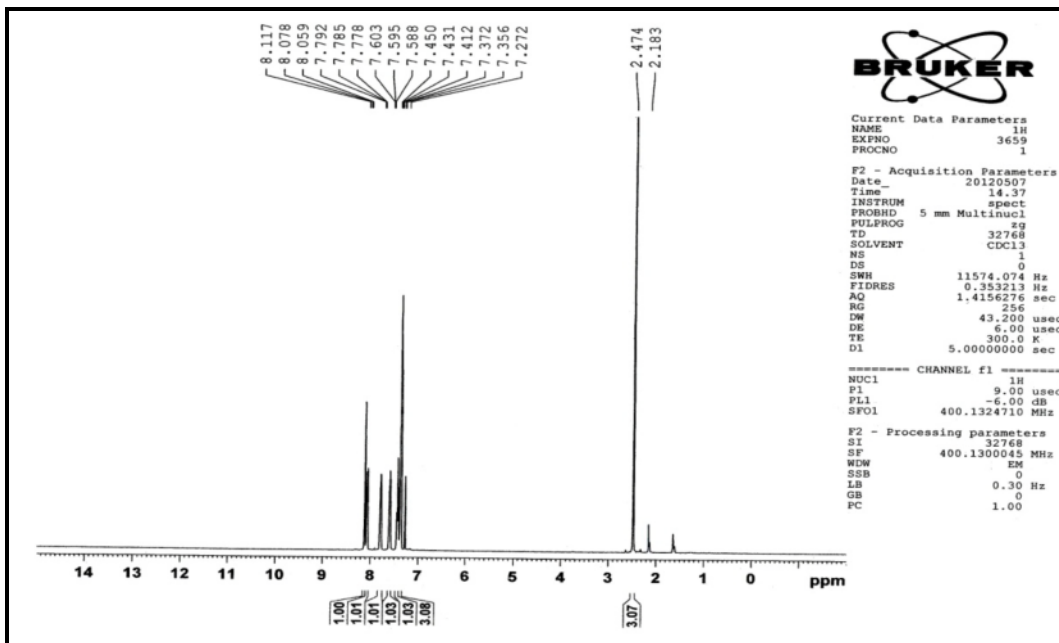
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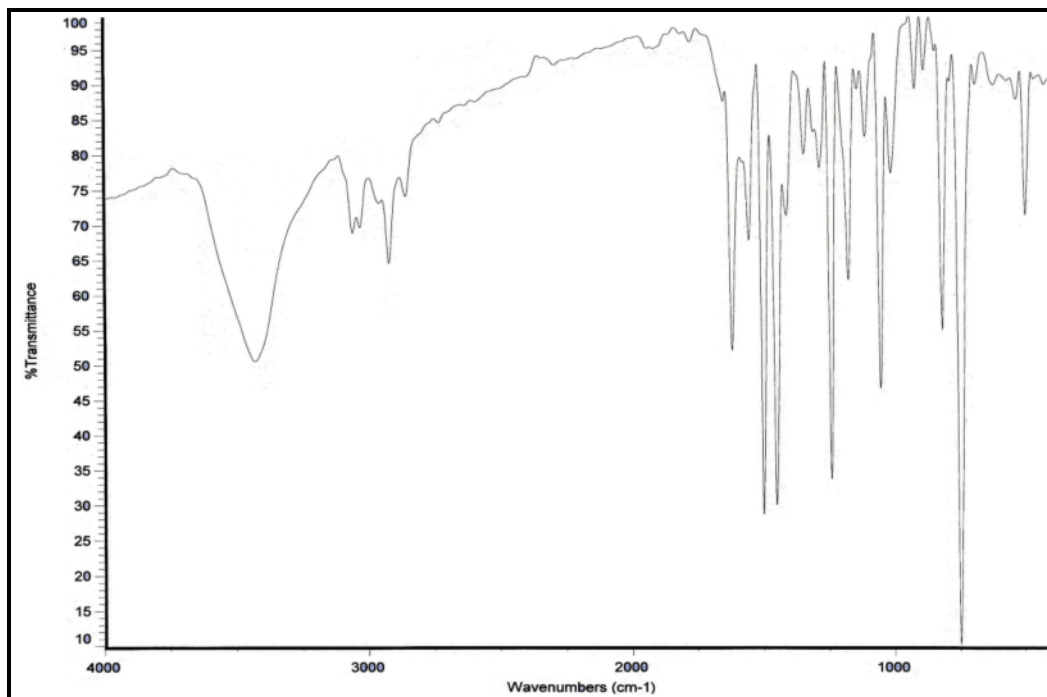
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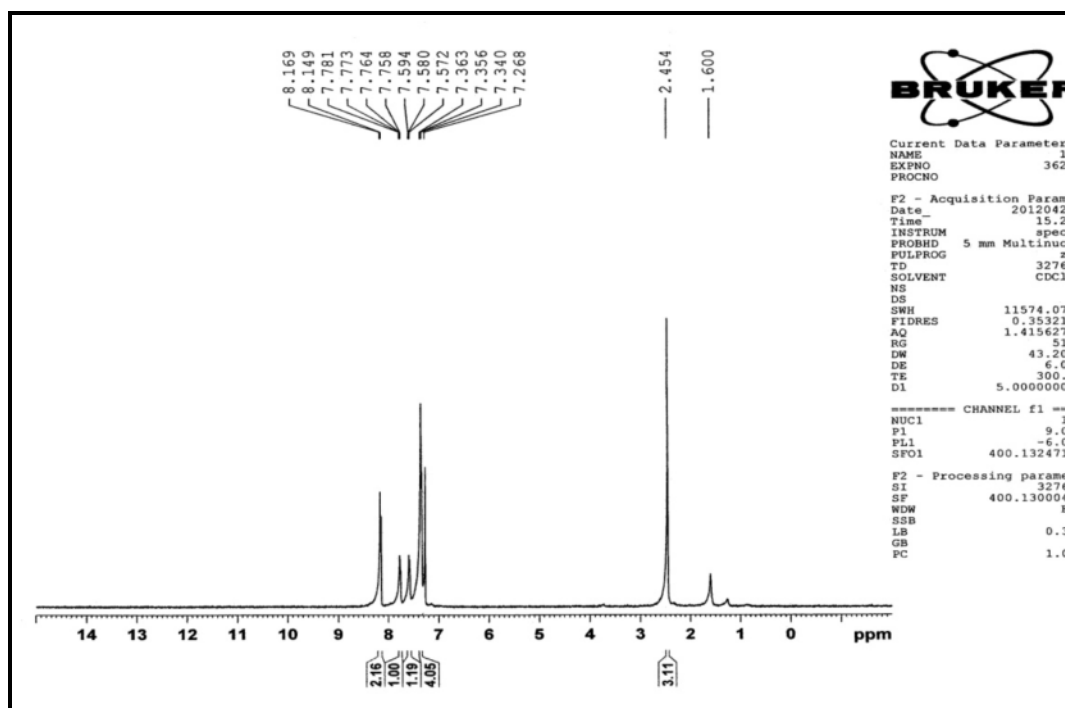
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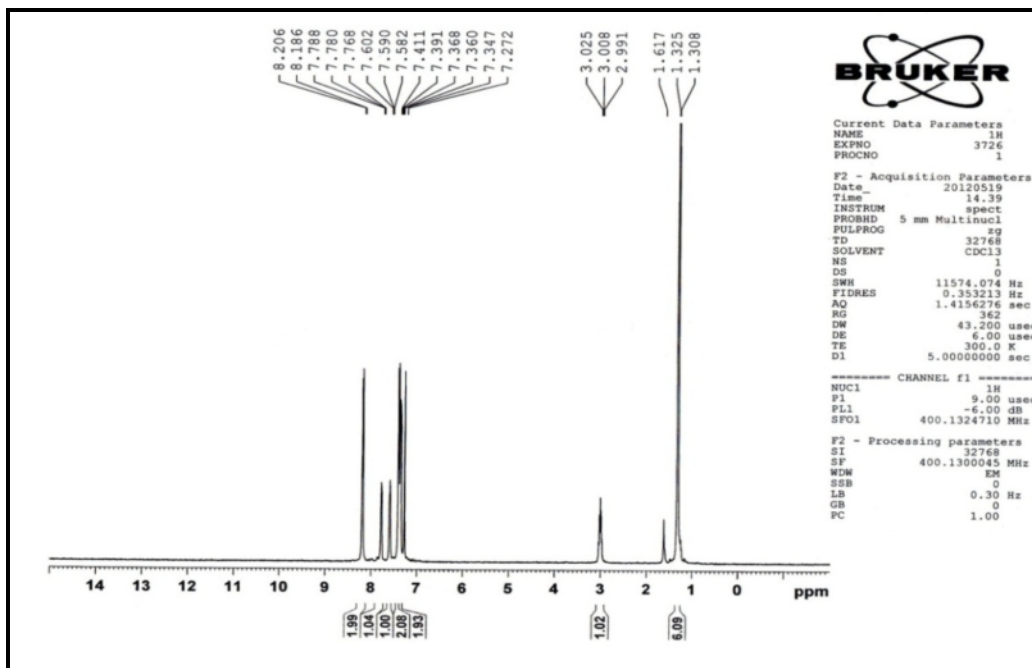
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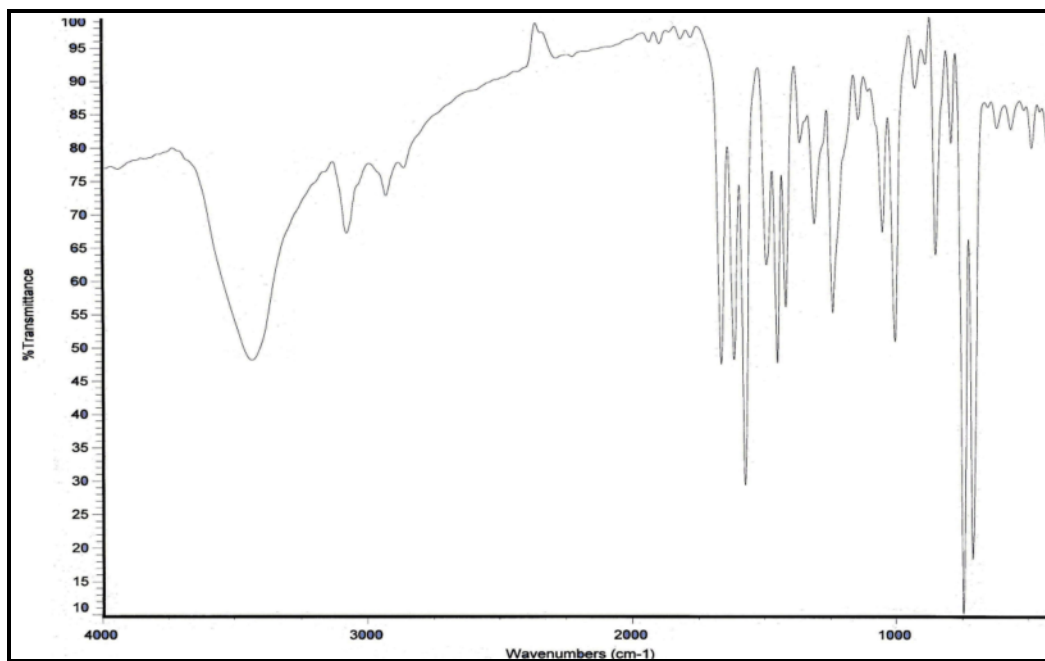
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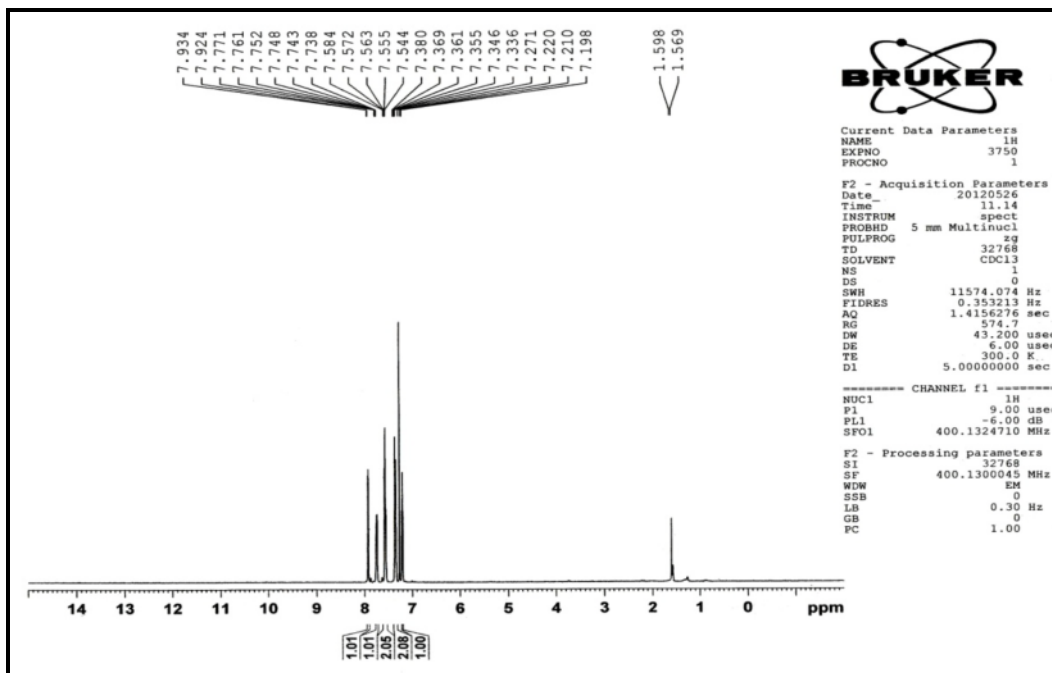
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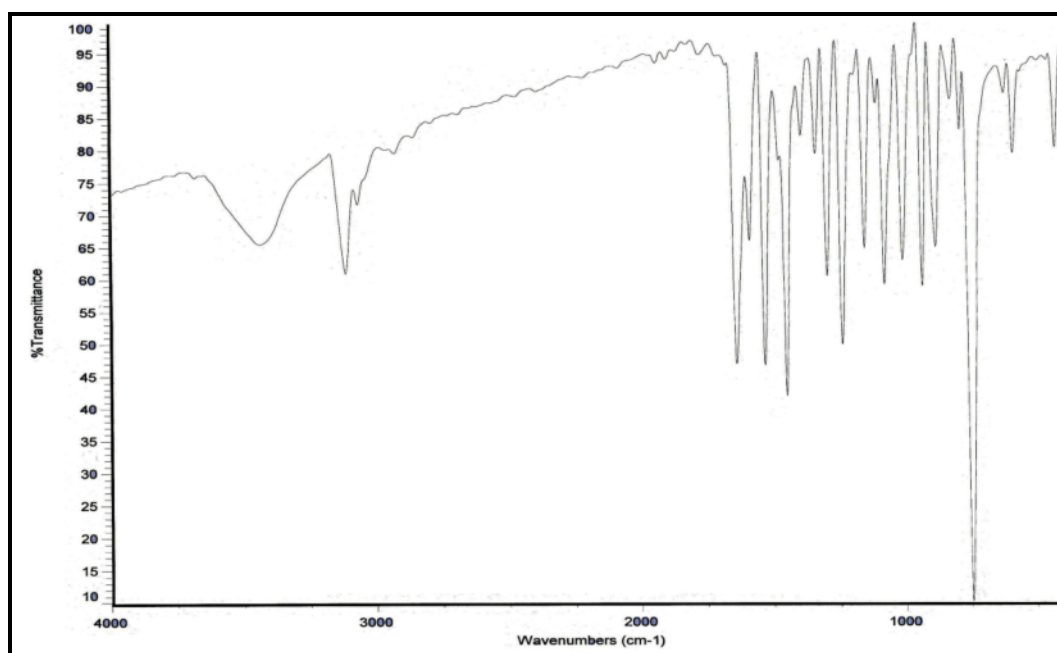
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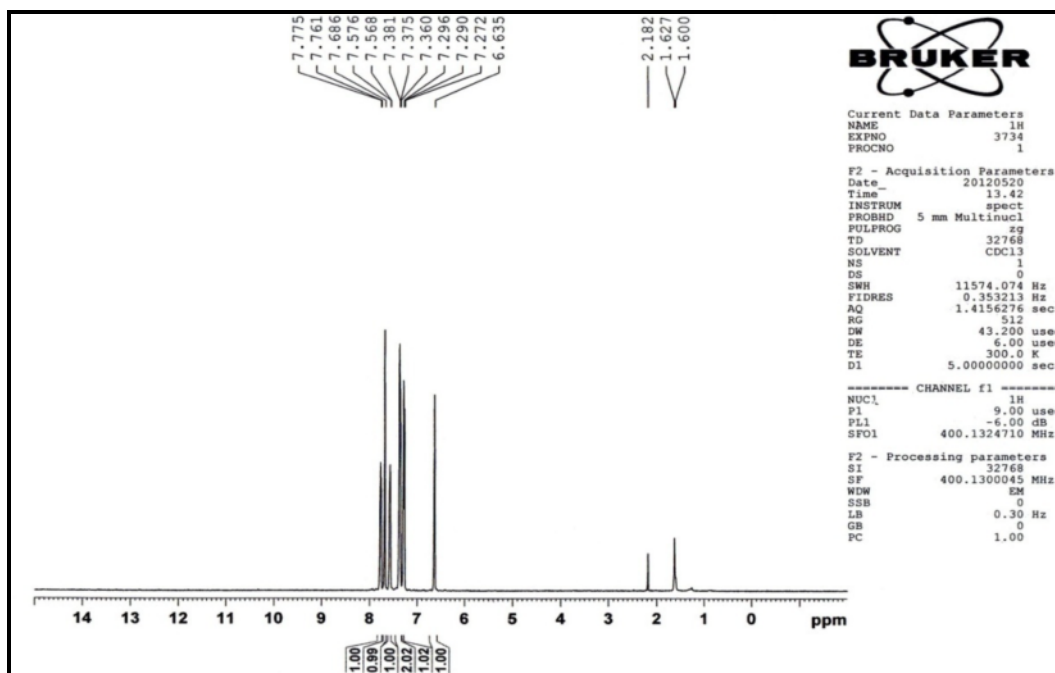
IR of 2-(2-Thiophen-2-yl)-1,3-benzoxazole



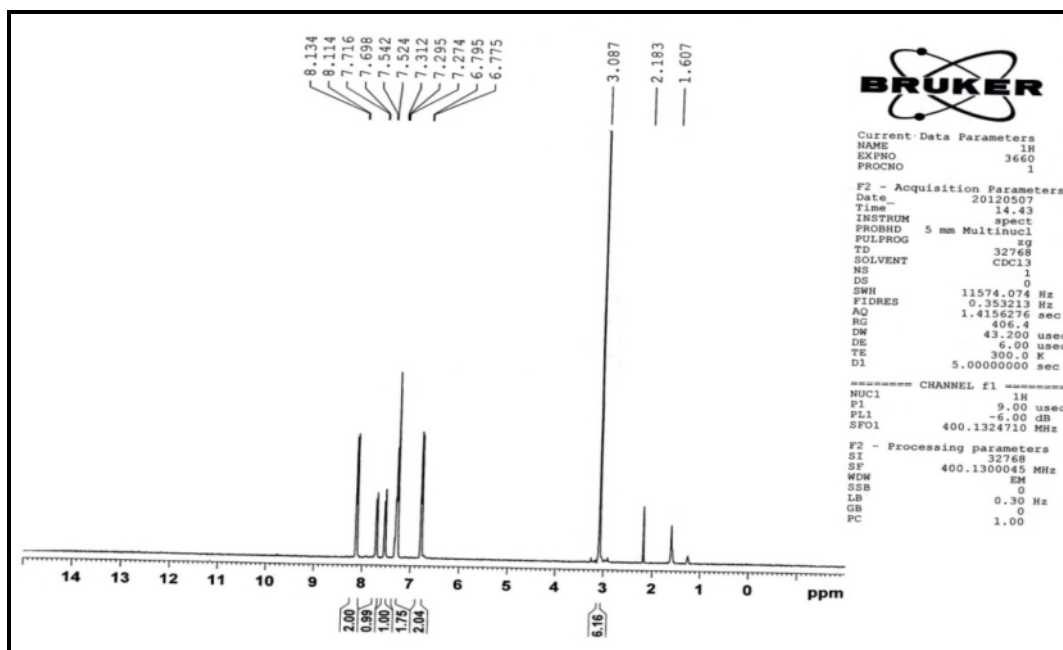
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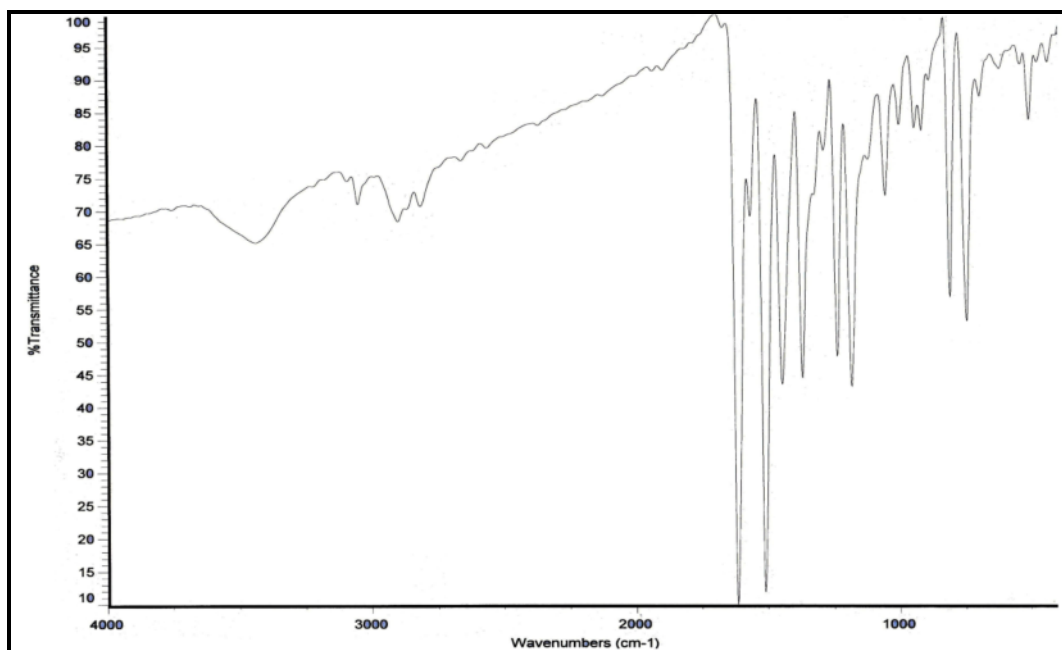
IR of 2-(2-Furan-2-yl)-1,3-benzoxazole



^1H NMR of 2-(2-Furan-2-yl)-1,3-benzoxazole



^1H NMR of 2-(4-N,N-Dimethylaminophenyl)-1,3-benzoxazole



IR of 2-(4-N,N-Dimethylaminophenyl)-1,3-benzoxazole