Supporting information

Highly *meta*-Selective Halogenation of 2-Phenylpyridine with Ruthenium (I) Catalysts

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1. General Experimental Information

General methods: Unless otherwise mentioned, materials obtained from commercial suppliers were used without further purification. Ru Catalyst was purchased from Sigma Aldrich, $PhI(OCOCF_3)_2$ was purchased from Alfa Aesar. Thin-layer chromatography plates were visualized by exposure to UV light/iodine and/or by immersion in an acidic staining solution of phosphomolybdic acid followed by heating on a hot plate. The ^1H NMR spectra were obtained on 300, 400 and 500 MHz, and $^{13}C\{^1H\}$-NMR spectra 75, 100 and 125 MHz, spectrometers with tetramethylsilane and chloroform-d_1 respectively, as the internal standard. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.26 for ^1H NMR and δ = 77.0 for $^{13}C\{^1H\}$-NMR). Data for ^1H NMR are reported as follows: chemical shift (multiplicity, coupling constant, number of hydrogens). Multiplicity is abbreviated as follows: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet).

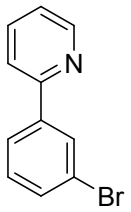
2. Experimental procedures

General Procedure for the Halogenation :

In an pressure tube, N-Halosuccinamide (0.75 mmol) was added to a stirred mixture of aryl compounds (2-phenylpyridine or 2-phenylpyrazole (0.5 mmol)], $[Ru(\pi\text{-}C_5H_5)(CO)_2]_2$ (10 mg, 2.5 mol%), $PhI(OCOCF_3)_2$ (86 mg, 20 mol%) in Toluene (2.0 mL). The reaction mixture was then stirred at 110 ºC for 5 h. The progress of the reaction was monitored by TLC. After the completion of reaction, it was quenched by brine solution and extracted with ethyl acetate. The combined organic extracts were dried over anhydrous sodium sulphate and solvent was evaporated under reduced pressure to give the product which was subjected to purification by silica gel (100-200 mesh) column chromatography using hexane/ethyl acetate as elutent to yield desired mono *meta*-halogenated products either as colorless solid or colorless oil.

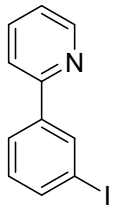
3. Characterization data of products

2-(3-bromophenyl)pyridine, 2a (Table 2)



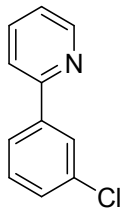
Colourless Oil, Yield, 98 mg, 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 4.5 Hz, 1H), 8.17 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.76-7.66 (m, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.25 (t, *J* = 5.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 149.6, 141.3, 136.8, 131.7, 130.1, 129.9, 125.3, 122.9, 122.5, 120.4; IR ($CHCl_3$) ν_{max} 677, 739, 765, 1065, 1152, 1561, 1583, 3008, 3060 cm^{-1}; EI-HRMS (TOF) calcd for $C_{11}H_8NBr$: 233.99120, Found 233.99129;

2-(3-iodophenyl)pyridine, 2b (Table 2)



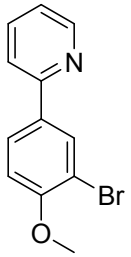
Colourless Oil, Yield, 106 mg, 76%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, *J* = 1.3 Hz, 1H), 8.30 (s, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.72-7.61 (m, 3H), 7.20(d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 149.6, 137.8, 136.9, 135.9, 130.3, 126.0, 122.6, 120.6, 94.7; IR ($CHCl_3$) ν_{max} 666, 765, 1074, 1077, 1457, 1557, 1715, 2853, 2921, 3446 cm^{-1}; ESI-MS: *m/z* 282 $(M+2)^+$;

2-(3-chlorophenyl)pyridine, 2c (Table 2)



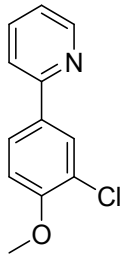
Colourless Oil, 68 mg, 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 4.4 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 2H), 7.78-7.71 (m, 2H), 7.50-7.39 (m, 2H), 7.25-7.22(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 149.8, 142.6, 137.0, 134.1, 128.7, 123.3, 123.1, 120.6; IR ($CHCl_3$) ν_{max} 693, 744, 1024, 1460, 1585, 1736, 2853, 2923 cm^{-1}; EI-HRMS (TOF) calcd for $C_{11}H_9NCl$:190.0409, Found 190.0418.

2-(3-bromo-4-methoxyphenyl)pyridine, 2d (Table 2)



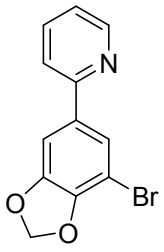
Colourless Solid, mp 68-70 ^{o}C, Yield, 120 mg, 92 % ; ^{1}H NMR (400 MHz,$CDCl_3$): δ 8.66 (d, *J* = 4.6 Hz, 1H), 8.23 (d, *J* = 2.2 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.5, 136.8, 131.7, 126.9, 121.8, 119.8, 112.0, 111.7, 56.2; IR (KBr) ν_{max} 630, 754, 892, 1051, 1305, 1443, 1601, 2937 cm^{-1}; EI-HRMS (TOF) calcd for $C_{12}H_{10}NOBr$: 264.0085, Found 264.0017.

2-(3-chloro-4-methoxyphenyl)pyridine, 2e (Table 2)



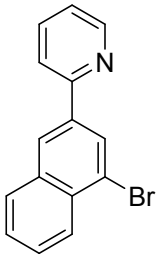
Colourless Oil, Yield, 91 mg, 84 % ; ^{1}HNMR (500 MHz,$CDCl_3$): δ 8.70 (d, *J* = 4.4 Hz, 1H), 7.73(dd, *J* = 7.7, 15.4 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.56 (s, 1H), 7.24 (dd, *J* = 2.5, 8.5 Hz, 1H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.92 (dd, *J* = 2.5 Hz, 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 156.5, 149.4, 149.3, 135.7, 132.2, 124.8, 121.9, 115.1, 114.0, 113.2, 55.5; IR ($CHCl_3$) ν_{max} 531, 756, 889, 1023, 1356, 1423, 1669, 2864, 2981, 3443; ESI-MS: *m/z* 220 $(M+H)^{+}$.

2-(7-bromobenzo[d][1,3]dioxol-5-yl)pyridine, 2f (Table 2)



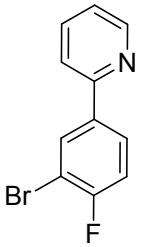
Colourless Oil, Yield, 113 mg, 82 % ; ^{1}H NMR (500 MHz,$CDCl_3$): δ 8.68 (d, *J* = 4.8 Hz, 1H), 7.74 (dd, *J* = 1.8 Hz, 7.7 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.28-7.25 (m, 1H), 7.11(s, 1H), 7.03 (s, 1H), 6.02 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 149.3, 145.8, 124.9, 122.2, 113.0, 111.0, 101.9; IR ($CHCl_3$) ν_{max} 550, 600, 747, 786, 866, 1035, 1229, 1465, 1588, 1724, 2923, 3417 cm^{-1}; EI-HRMS (TOF) calcd for $C_{12}H_8O_2NBr$: 277.9811, Found 277.9801.

2-(4-bromonapthalen-2-yl)pyridine, 2g (Table 2)



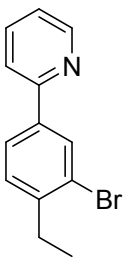
Colourless Solid, mp 75-77 ^{o}C, Yield, 126 mg, 90 % ; ^{1}H NMR (300 MHz,$CDCl_3$): δ 8.75 (d, *J* = 4.7 Hz, 1H), 8.50 (d, *J* = 1.5 Hz, 1H), 8.43 (s, 1H), 8.25 (d, *J* = 8.3 Hz, 1H) 7.94 (d, *J* = 7.7 Hz, 1H), 7.88-7.77 (m, 2H), 7.65-7.53 (m, 2H), 7.30-7.27 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.8, 136.9, 132.1, 129.1, 128.5, 127.9, 127.1, 127.0, 126.0, 123.5, 122.6, 120.7; IR (KBr) ν_{max} 601, 758, 1031, 1636, 3450. EI-HRMS (TOF) calcd for $C_{15}H_{10}NBr$: 284.0069, Found 284.0068.

2-(3-bromo-4-fluorophenyl)pyridine, 2h (Table 2)



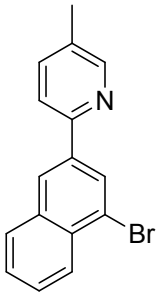
Colourless Solid, mp 85-87 ^{o}C, Yield, 85 mg, 68 % ; ^{1}H NMR (500 MHz,$CDCl_3$): δ 8.68 (d, *J* = 4.7 Hz, 1H), 8.24 (dd, *J* = 2.1 Hz, 6.7 Hz, 1H), 7.92-7.89 (m, 1H), 7.76 (dd, *J* = 1.8 Hz, 7.9 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.27-7.24 (m, 1H), 7.21 (t, *J* = 8.3 Hz, 1H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.0, 158.6, 154.9, 149.7, 136.9 ($J_{C\text{-}F}$ = 206.0 Hz), 132.1, 127.3 ($J_{C\text{-}F}$ = 7.2 Hz), 127.2, 122.5, 120.2, 116.6, 116.4, 109.6, 109.4; IR (KBr) ν_{max} 672, 778, 885, 990, 1262, 1434, 1464, 1590, 1722, 2853, 2924, 3062 cm^{-1}; EI-HRMS (TOF) calcd for $C_{11}H_7NBrF$: 251.9818, Found 251.9817.

2-(3-bromo-4-ethylphenyl)pyridine, 2i (Table 2)



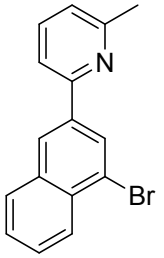
Colourless Oil, Yield, 110 mg, 85 % ; ^{1}H NMR (400 MHz,$CDCl_3$): δ 8.68 (d, *J* = 5.3 Hz, 1H), 8.19 (d, *J* = 1.8 Hz, 1H), 7.86 (dd, *J* = 1.8 Hz, 7.9 Hz, 1H), 7.77-7.72 (m, 1H), 7.68(d, *J* = 7.9 Hz. 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.25-7.21 (m, 1H), 2.82 (q, *J* = 7.6Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8, 149.6, 144.0, 138.6, 136.8, 131.0, 129.6, 125.8, 124.8, 122.3, 120.3, 29.1, 14.1; IR ($CHCl_3$) ν_{max} 740, 779, 827, 1032, 1382, 1431, 1461, 1588, 1727, 2854, 2925, 3055 cm^{-1}; EI-HRMS (TOF) calcd for $C_{13}H_{13}NBr$: 262.0224, Found 262.0225.

2-(4-bromonaphthalen-2-yl)-4-methylpyridine, 2j (Table 2)



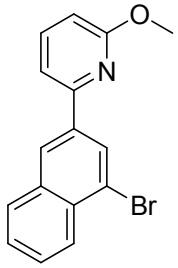
Colourless Oil, Yield, 133 mg, 90 % ; ^{1}H NMR (300 MHz,$CDCl_3$): δ 8.59 (d, *J* = 4.5 Hz, 1H), 8.47 (d, *J* = 1.5 Hz, 1H), 8.42 (s,1H), 8.25 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.68-7.52 (m, 3H), 7.10 (d, *J* = 4.5 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6, 149.5, 148.0, 137.2, 134.4, 131.9, 129.0, 128.5, 127.7, 127.0, 126.9, 125.9, 123.5, 121.6, 21.2; IR ($CHCl_3$) ν_{max} 521, 668, 841, 1026, 1215, 1636, 2925, 3021, 3449 cm^{-1}; EI-HRMS (TOF) calcd for $C_{16}H_{12}NBr$: 298.0223, Found 298.0225;

2-(4-bromonapthalen-2-yl)-6-methylpyridine, 2k (Table 2)



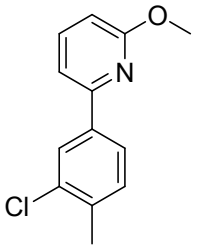
Colourless Oil, Yield, 130 mg, 88 % ; ^{1}H NMR (500 MHz,$CDCl_3$): δ 8.50 (d, *J* = 1.6 Hz, 1H), 8.41 (s, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.70-7.52 (m, 4H), 7.14 (d, *J* = 7.3 Hz, 1H), 2.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.6, 155.2, 137.5, 137.0, 134.4, 129.0, 128.7, 127.7, 126.9, 125.9, 122.1, 117.7, 29.6; IR ($CHCl_3$) νmax 628, 776, 843, 1022, 1267, 1651, 2863, 3347 cm^{-1}; EI-HRMS (TOF) calcd for $C_{16}H_{12}NBr$: 298.0225, Found 298.0222.

3-bromo-2-methoxy-6-(naphthalen-2-yl)pyridine, 2l (Table 2)



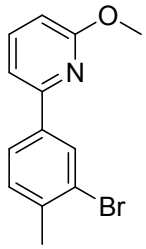
Colourless Solid, mp 92-94 ^{o}C , Yield, 143 mg, 92 % ; ^{1}H NMR (500 MHz,$CDCl_3$): δ 8.47 (s, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.94-7.89 (m, 2H), 7.86 (d, *J* = 7.9 Hz, 2H), 7.52-7.49 (m, 2H), 7.37 (d, *J* = 7.9 Hz, 1H), 4.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3, 153.3, 142.1, 135.3, 133.6, 133.3, 128.6, 128.3, 127.6, 126.5, 126.3, 125.9, 124.1, 114.2, 105.3, 54.3; IR (KBr) ν_{max} 514, 570, 691, 756, 814, 1004, 1067, 1126, 1252, 1383, 1568, 2856, 2953, 3057, 3449 cm^{-1}; EI-HRMS (TOF) calcd for $C_{16}H_{12}ONBr$: 314.0172, Found 314.0175.

2-(3-chloro-4-methylphenyl)-6-methoxypyridine, 2m (Table 2)



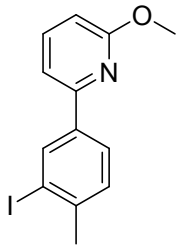
Colourless Solid, mp 61-63 ^{o}C, Yield, 99 mg, 85 % ; ^{1}H NMR (500 MHz,$CDCl_3$): δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.25 (s, 1H), 4.12 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.5, 152.7, 139.1, 138.6, 135.2, 129.3, 126.4, 116.0, 113.1, 54.0, 21.2; IR (KBr) ν_{max} 526, 579, 645, 750, 889, 1009, 1180, 1315, 1377, 1464, 1731, 2855, 2924, 3420 cm^{-1}; EI-HRMS (TOF) calcd for $C_{13}H_{12}ONBr$: 234.0679, Found 234.0680

2-(3-bromo-4-methylphenyl)-6-methoxypyridine, 2n (Table 2)



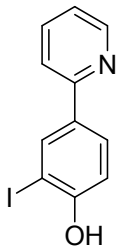
Colourless Solid, mp 73-75 ^{o}C, Yield, 121 mg, 88 % ; ^{1}H NMR (500 MHz,$CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.26-7.24 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 1H), 4.10 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 153.5, 142.0, 139.2, 135.2, 129.3, 128.1, 126.4, 1114.1, 113.5, 104.7, 54.2, 21.2; IR (KBr) ν_{max} 563, 697, 760, 804, 1102, 1149, 1245, 1463, 1559, 1672, 2856, 2923, 3422 cm^{-1}; EI-HRMS (TOF) calcd for $C_{13}H_{12}ONBr$: 278.0169, Found 278.0175.

2-(3-iodo-4-methylphenyl)-6-methoxypyridine, 2o (Table 2)



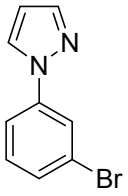
Colourless Oil, Yield, 116 mg, 72 % ; ^{1}H NMR (500 MHz,$CDCl_3$): δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 1H), 4.08 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.2, 154.5, 148.3, 139.2, 135.2, 129.3, 126.3, 114.0, 54.4, 21.2; IR ($CHCl_3$) ν_{max} 695, 801, 866, 1023, 1259, 1458, 1730, 2857, 2923, 3449; ESI-MS: *m/z* 325 $(M+2\text{-}OMe)^{+\cdot}$

2-iodo-4-(pyridin-2-yl)phenol, 2p (Table 2)



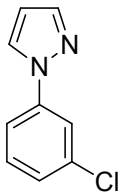
Colourless Oil, Yield, 122 mg, 83 % ; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (d, *J* = 4.4 Hz, 1H), 8.36 (d, *J* = 1.9 Hz, 1H), 7.86 (dd, *J* = 1.9 Hz, 8.2 Hz, 1H), 7.74 (dd, *J* = 1.6 Hz, 7.9 Hz, 1H), 7.25 (s, 1H), 7.24-7.20 (m, 1H), 7.06 (d, *J* = 8.5 Hz,1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7,155.4, 149.4, 136.97, 136.90, 128.7, 121.9, 119.9, 115; IR ($CHCl_3$) ν_{max} 801, 1020, 1086, 1260, 1374, 1460, 1732, 2854, 2923, 3448 cm^{-1}; EI-HRMS (TOF) calcd for $C_{11}H_8ONI$: 297.9724, Found 297.9723.

1-(3-bromophenyl)-1H-pyrazole, 2q (Table 2)



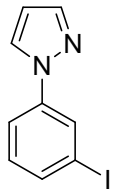
Colourless Solid, mp 82-84 ^{o}C, Yield, 110 mg, 96 % ; ^{1}H NMR (500 MHz,$CDCl_3$): δ 7.93 (s, 1H), 7.67 (s, 1H), 7.64 (dd, *J* = 1.2 Hz, 8.8 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.33-7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4,139.6, 129.5, 127.0, 126.9, 119.0, 95.6; IR (KBr) ν_{max} 647, 685, 751, 844, 948, 1340, 1498, 1597, 3049, 3117, 3448 cm^{-1}; EI-HRMS (TOF) calcd for $C_9H_7N_2Br$: 222.9863, Found 222.9865.

1-(3-chlorophenyl)-1H-pyrazole, 2r (Table 2)



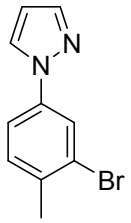
Colourless Solid, mp 73-75 ^{o}C, Yield 83 mg, 94 % ; ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.90 (d, *J* = 0.4 Hz, 1H), 7.63 (dd, *J* = 0.9Hz, 8.6 Hz, 3H), 7.47-7.44 (m, 2H), 7.33-7.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 139.3, 129.4, 126.9, 124.7, 118.8, 112.2; IR (KBr) ν_{max} 645, 683, 752, 948, 1033, 1330, 1378, 1495, 1595, 3114, 3449 cm^{-1}; EI-HRMS (TOF) calcd for $C_9H_7N_2Cl$: 179.0369, Found 179.0370.

1-(3-iodophenyl)-1H-pyrazole, 2s (Table 2)



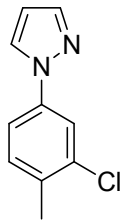
Colourless Solid, mp 79-81 ^{o}C , Yield, 121 mg, 90 % ; ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.94 (s, 1H), 7.71 (s, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.32–7.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 139.3, 131.1, 129.4, 126.9, 118.9; IR (KBr) ν_{max} 600, 643, 683, 751, 942, 1322, 1492, 1594, 1691, 2854, 3115, 3451 cm^{-1}; EI-HRMS (TOF) calcd for $C_9H_7N_2I$: 270.9723, Found 270.9726.

1-(3-bromo-4-methylphenyl)-1H-pyrazole, 2t (Table 2)



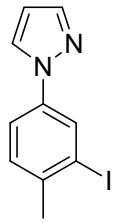
Colourless Solid, mp 90-92 ^{o}C, Yield, 110 mg, 94 % ; ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.87 (s, 1H), 7.64 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 137.3, 136.8, 129.9, 126.8, 118.9, 95.2, 20.8; IR (KBr) ν_{max} 605, 814, 851, 948, 1031, 1331, 1507, 1609, 2921, 3042, 3109, 3449 cm^{-1}; EI-HRMS (TOF) calcd for $C_{10}H_9N_2Br$: 237.0020, Found 237.0021.

1-(3-chloro-4-methylphenyl)-1H-pyrazole, 2u (Table 2)



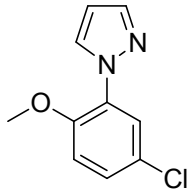
Colourless Solid, mp 93-95 ^{o}C, Yield, 90 mg, 94 % ; ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.85 (s, 1H), 7.61 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 136.8, 129.9, 124.7, 118.8, 111.9, 20.8; IR (KBr) ν_{max} 607, 648, 848, 813, 958, 1338, 1455, 1509, 2919, 3043, 3112, 3449 cm^{-1}; EI-HRMS (TOF) calcd for $C_9H_7N_2Br$: 193.0527, Found 193.0527.

1-(3-iodo-4-methylphenyl)-1H-pyrazole, 2v (Table 2)



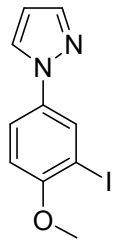
Colourless Solid, mp 70-72 ^{o}C , Yield, 124 mg, 88 % ; ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.90 (s, 1H), 7.69 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 2.38 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 137.2, 136.9, 131.2, 129.9, 119.0, 20.9; IR (KBr) ν_{max} 601, 808, 849, 933, 1452, 1521, 1604, 2854, 2917, 3113, 3448 cm^{-1}; EI-HRMS (TOF) calcd for $C_{10}H_9N_2I$: 284.9880, Found 284.9883.

1-(5-chloro-2-methoxyphenyl)-1H-pyrazole, 2w (Table 2)



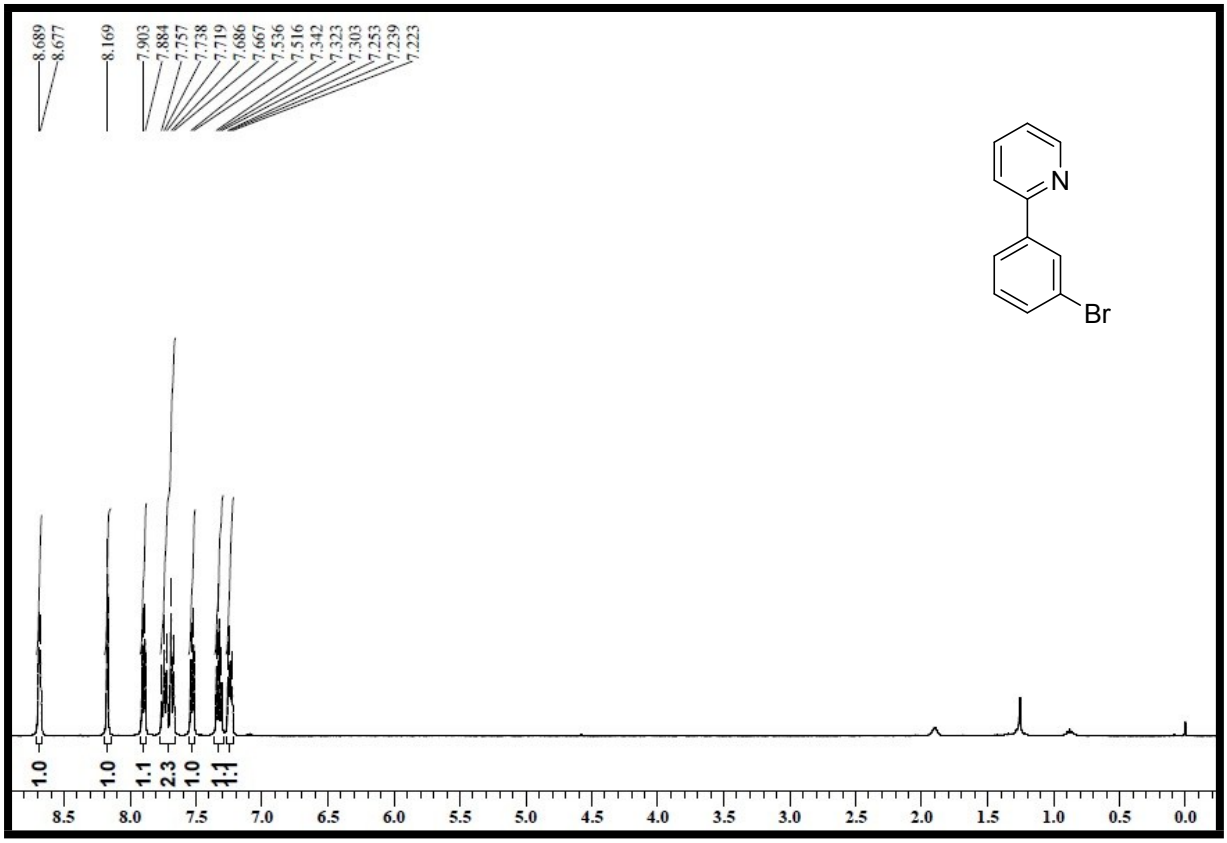
Colourless Oil, Yield, 79 mg, 76 % ; ^{1}H NMR (400 MHz,$CDCl_3$): δ 8.04 (d, *J* = 0.4 Hz, 1H), 7.69 (dd, *J* = 1.5 Hz, 7.8 Hz, 1H), 7.61, (s, 1H), 7.31(dd, *J* = 1.7 Hz, 7.5 Hz, 1H), 7.08-7.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 138.4, 129.4, 129.1, 128.3, 124.6, 121.1, 110.6, 55.8; IR ($CHCl_3$) ν_{max} 609, 674, 750, 799, 846, 1023, 1181, 1246, 1284, 1463, 1517, 1599, 2853, 2924 cm^{-1}; EI-HRMS (TOF) calcd for $C_{10}H_9ON_2Cl$: 209.0475, Found 209.0476.

1-(3-iodo-4-methoxyphenyl)-1H-pyrazole, 2w (Table 2)

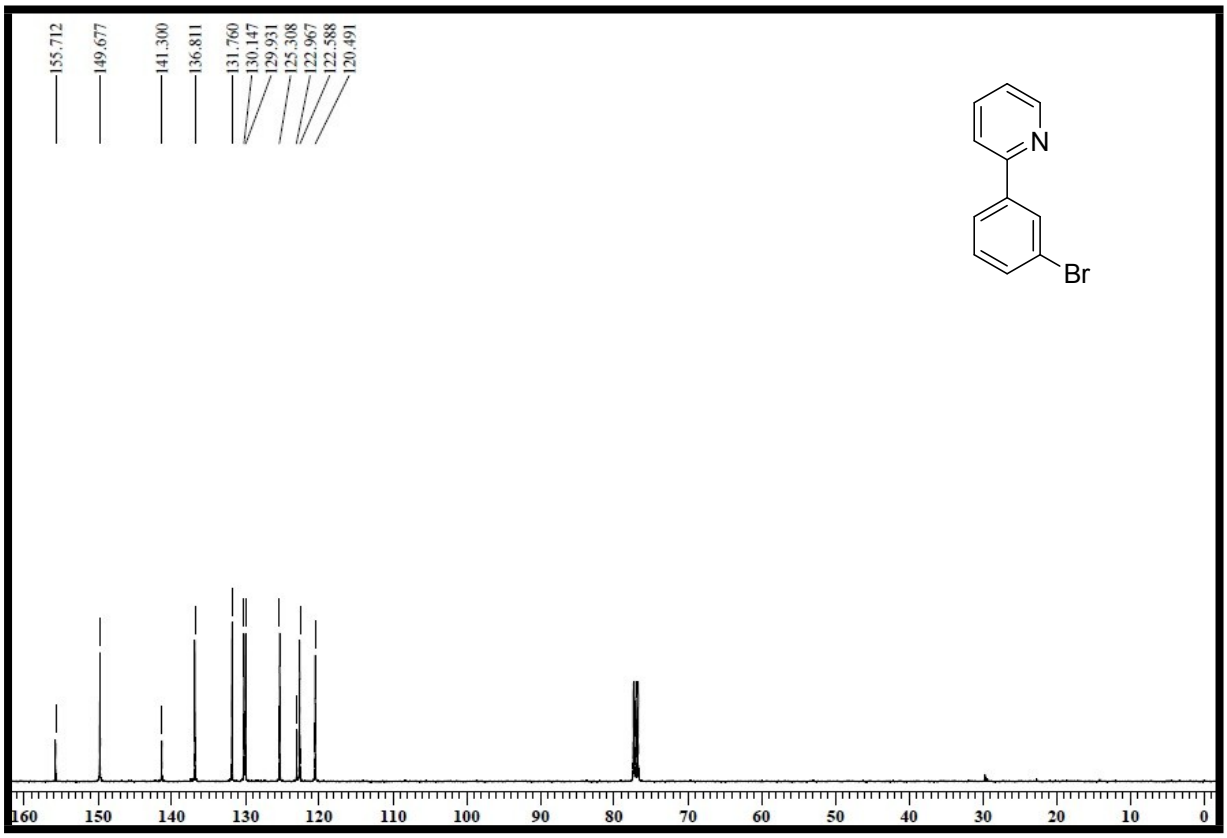


Colourless Solid, mp 75-77 ^{o}C, Yield, 134 mg, 90 % ; ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.85 (s, 1H), 7.68 (s, 1H), 7.54(d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 145.4, 133.2, 131.3, 120.8, 114.5, 55.5; IR (KBr) ν_{max} 562, 601, 643, 765, 827, 934, 1152, 1321, 1604, 1725, 2854, 2917, 3003 cm^{-1}. ESI-MS: *m/z* 300 $(M)^{+}$.

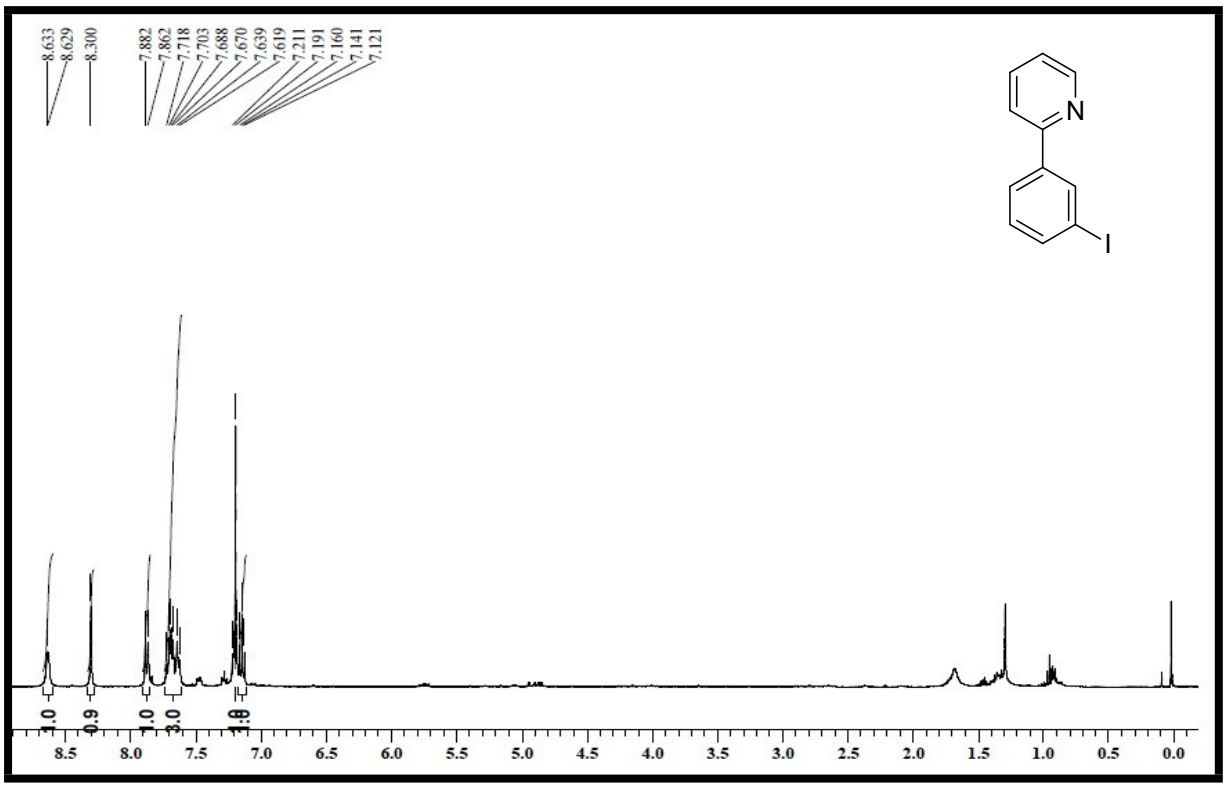
^{1}H NMR spectra of product 2a (Table 2)



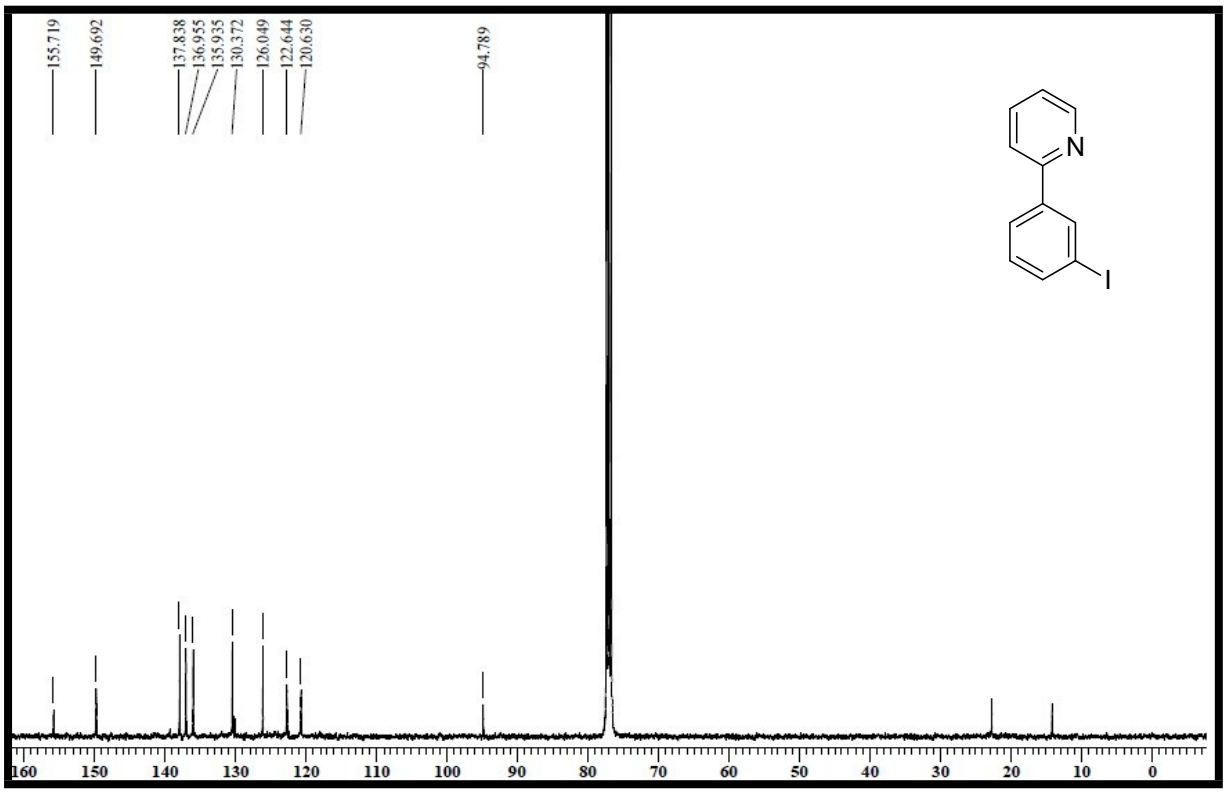
^{13}C NMR spectra of product 2a (Table 2)



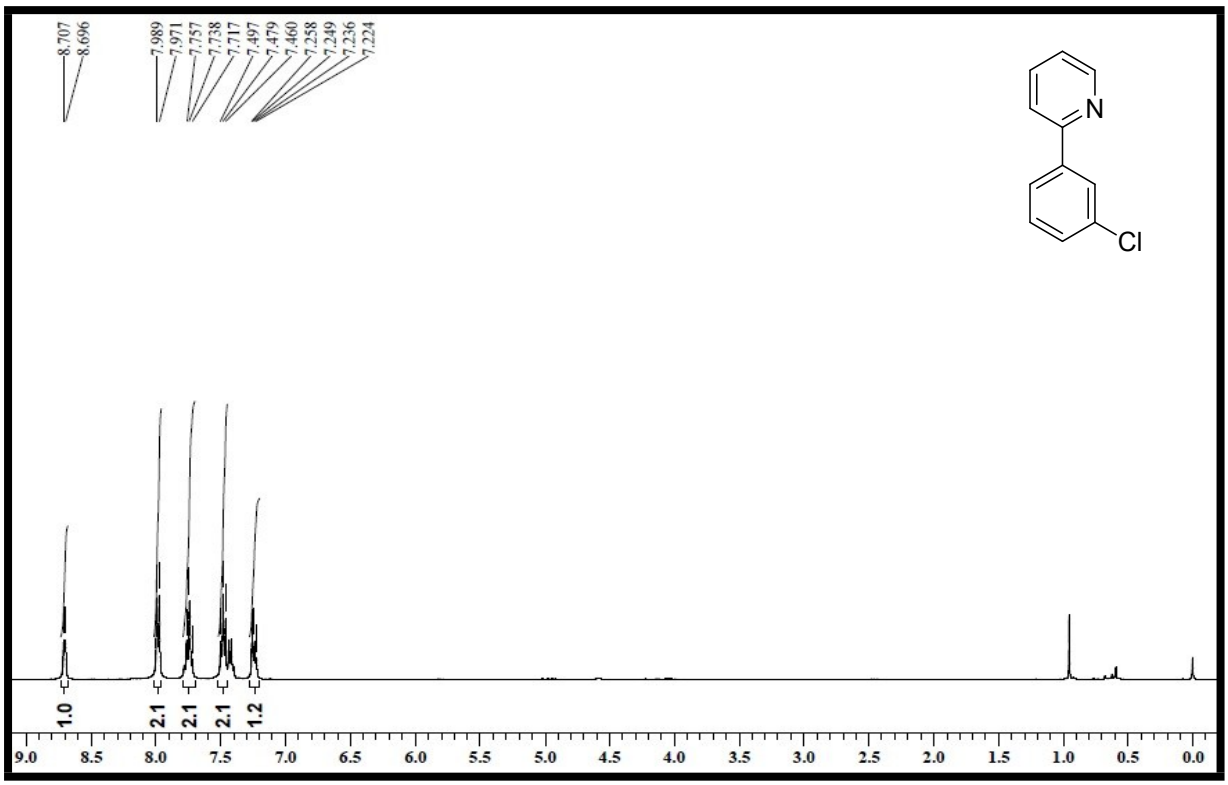
^{1}H NMR spectra of product 2b (Table 2)



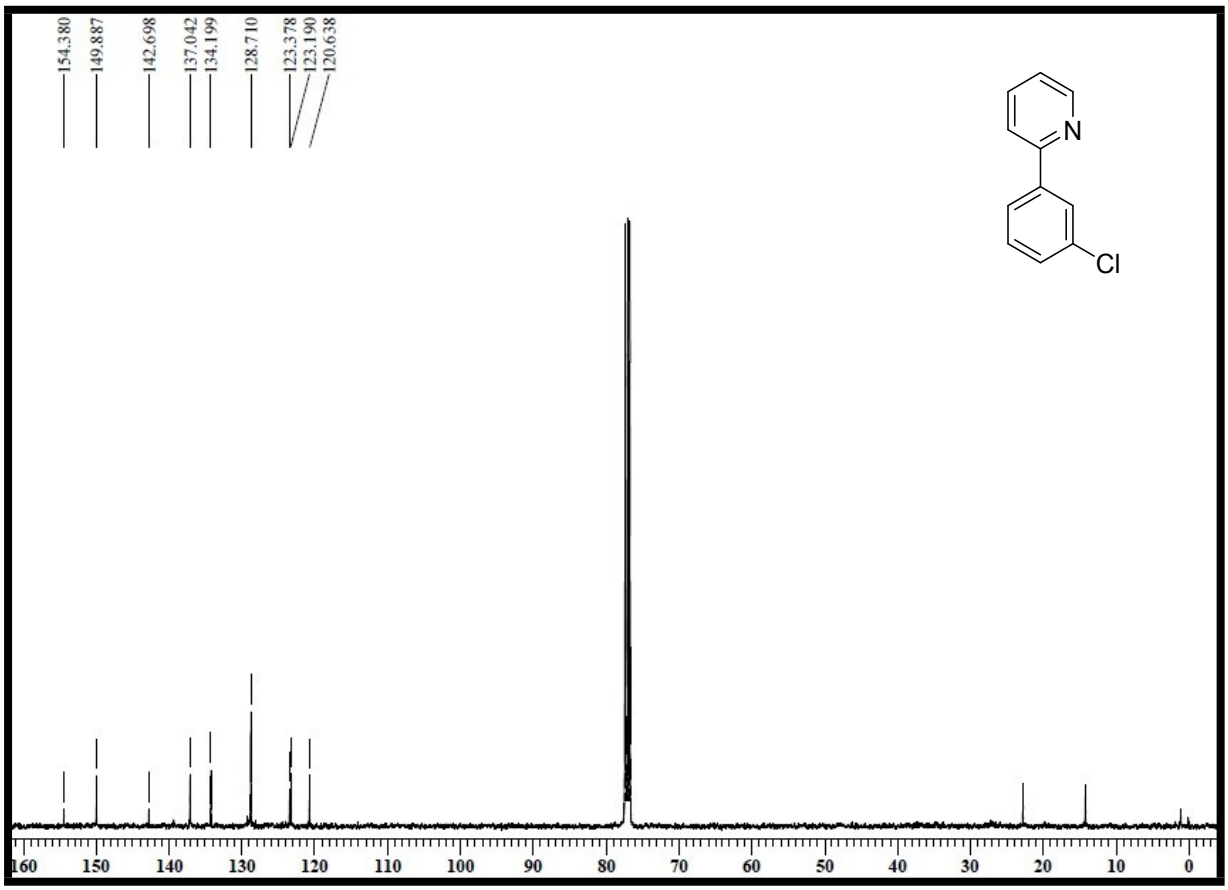
^{13}C NMR spectra of product 2b (Table 2)



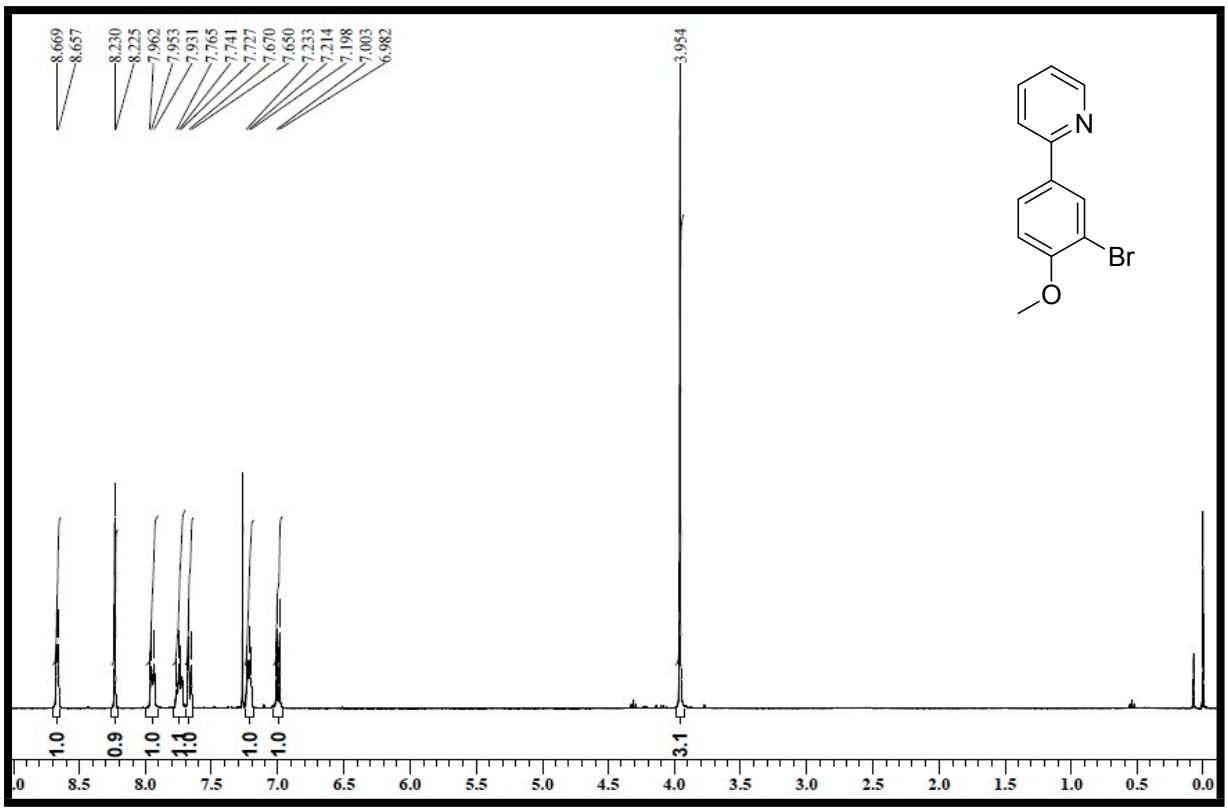
^{1}H NMR spectra of product 2c (Table 2)



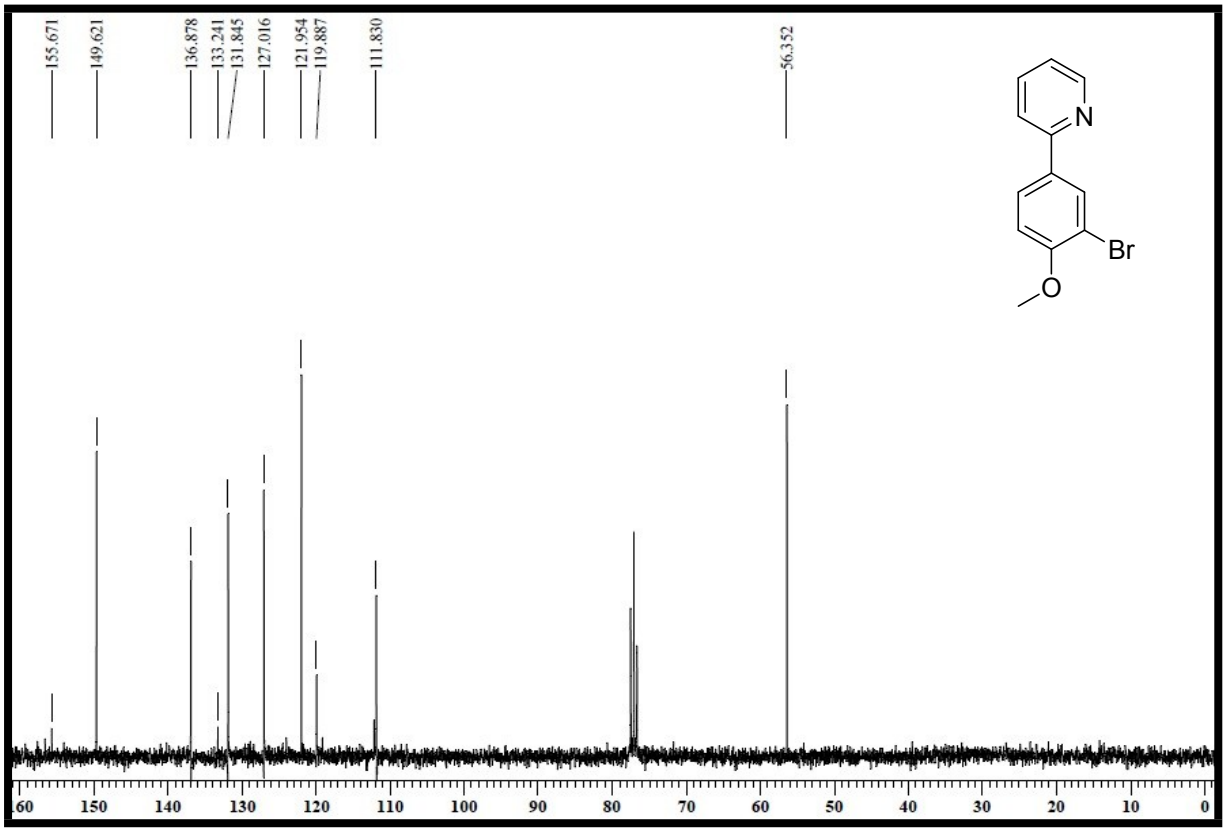
^{13}C NMR spectra of product 2c (Table 2)



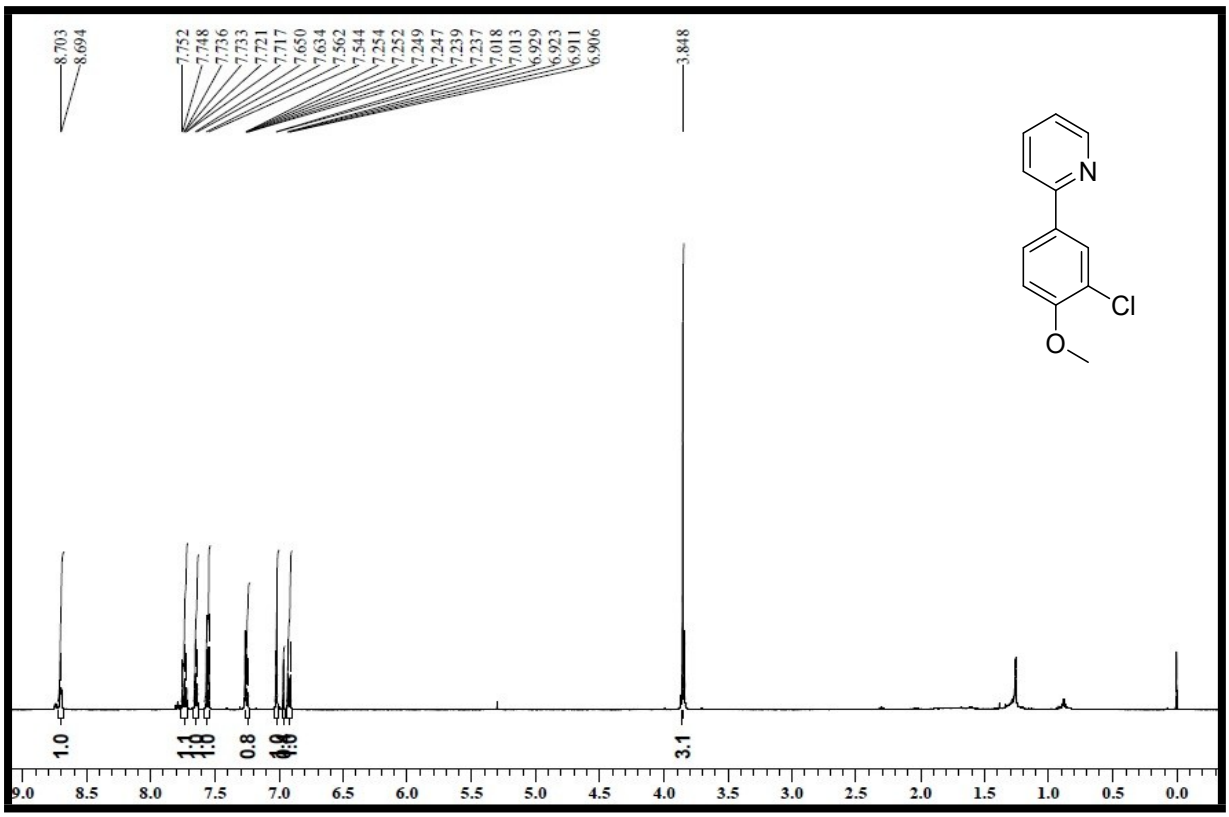
^{1}H NMR spectra of product 2d (Table 2)



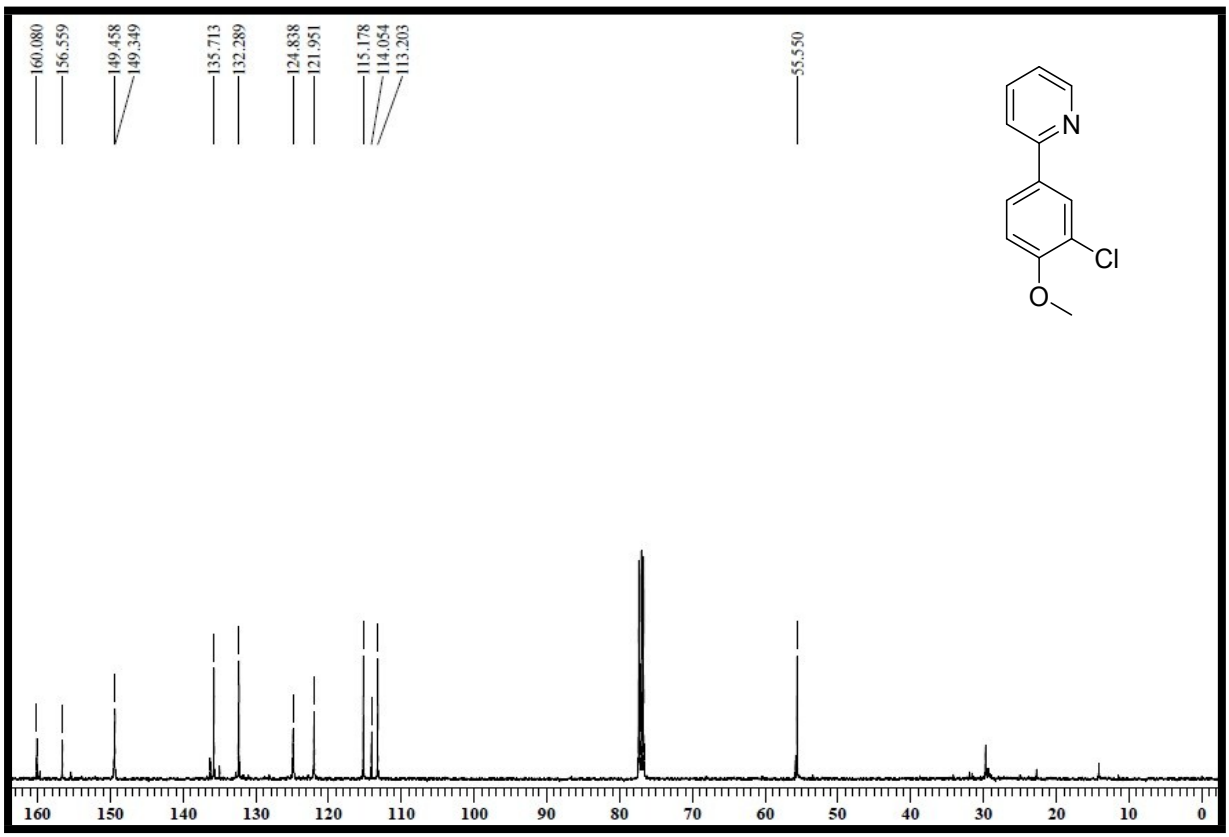
^{13}C NMR spectra of product 2d (Table 2)



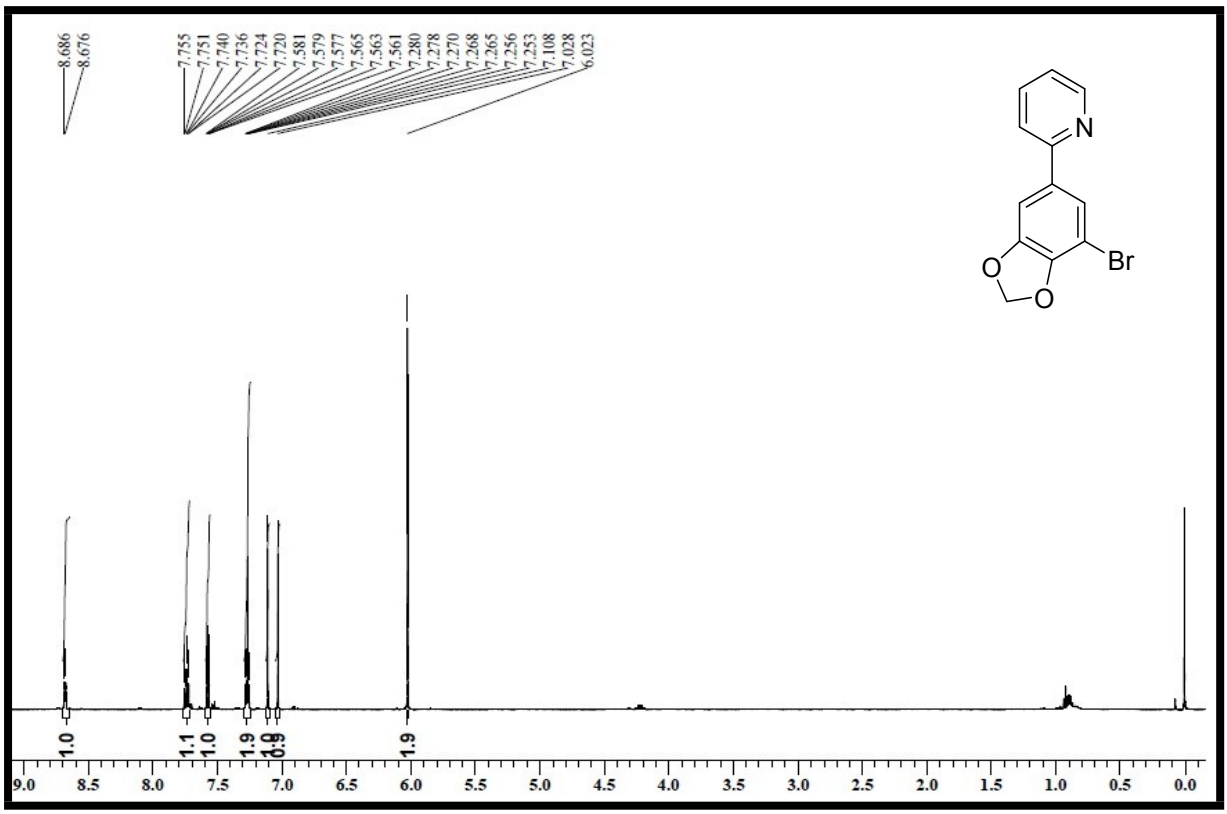
^{1}H NMR spectra of product 2e (Table 2)



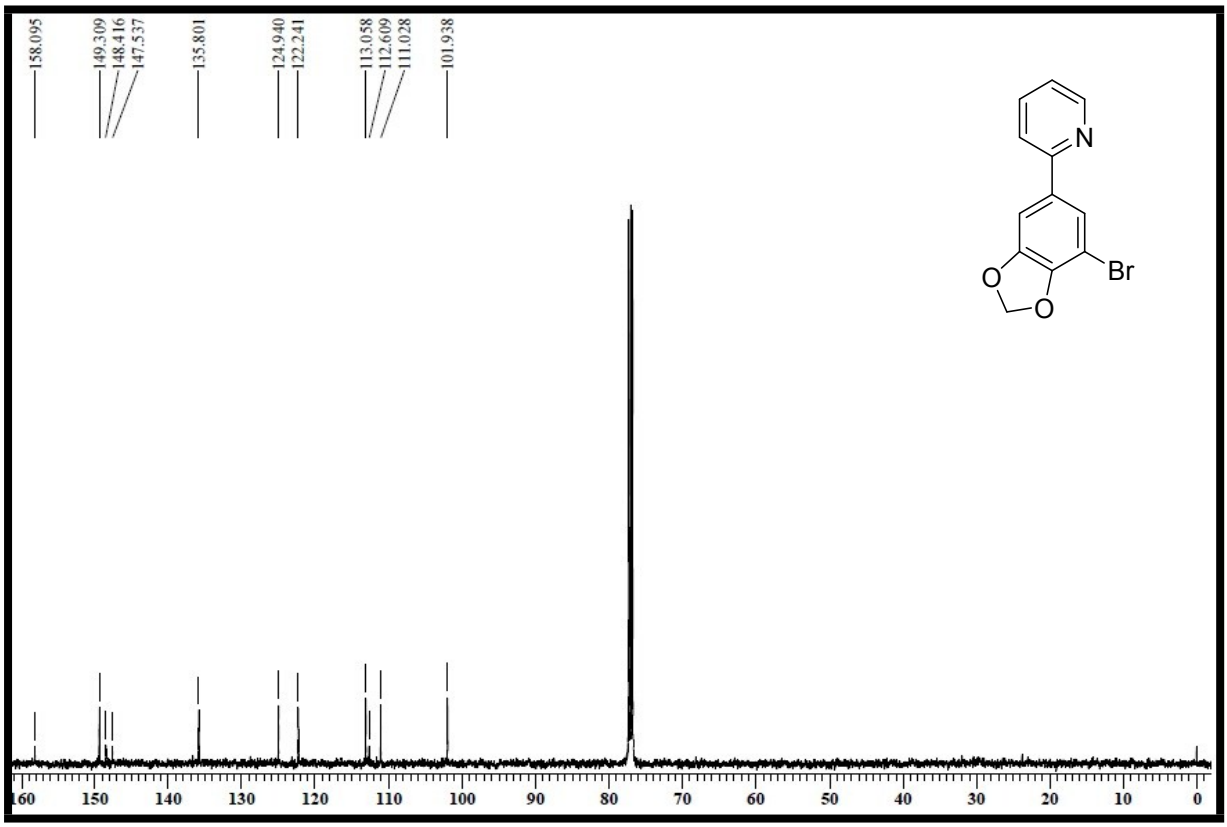
^{13}C NMR spectra of product 2e (Table 2)



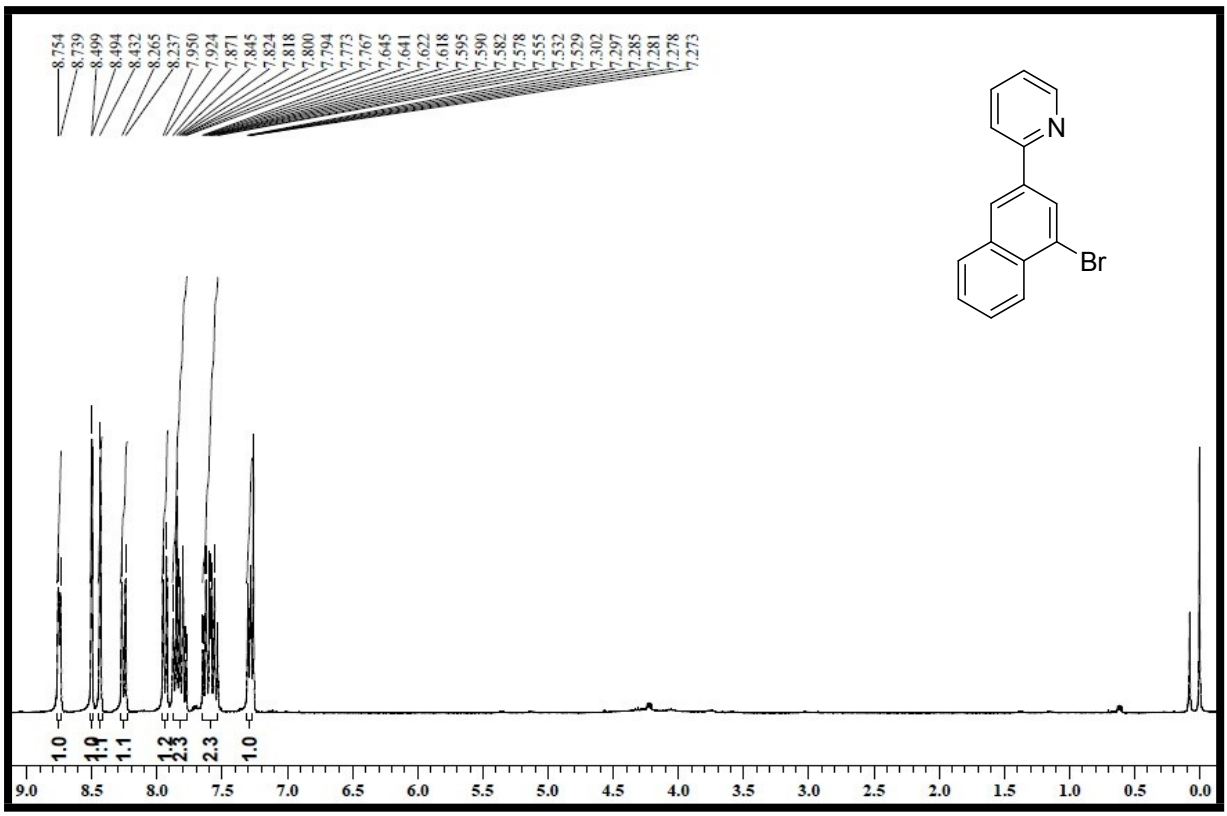
^{1}H NMR spectra of product 2f (Table 2)



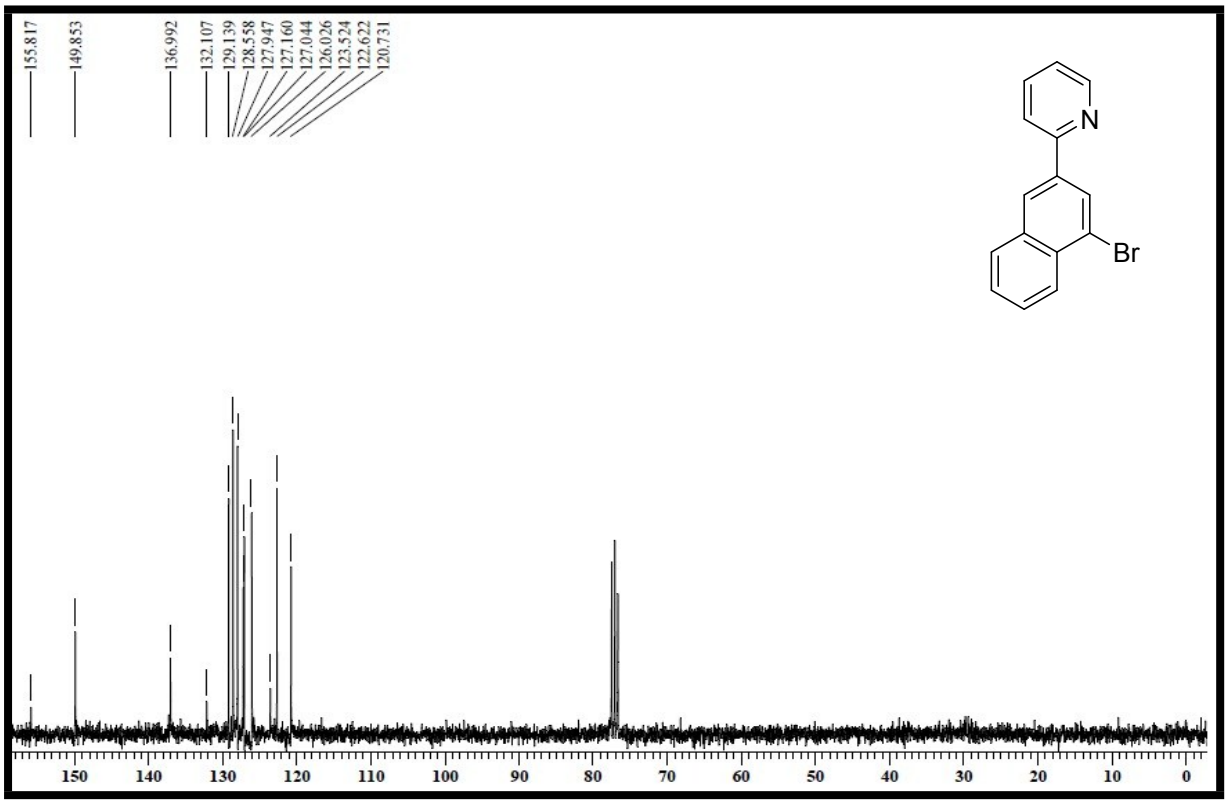
^{13}C NMR spectra of product 2f (Table 2)



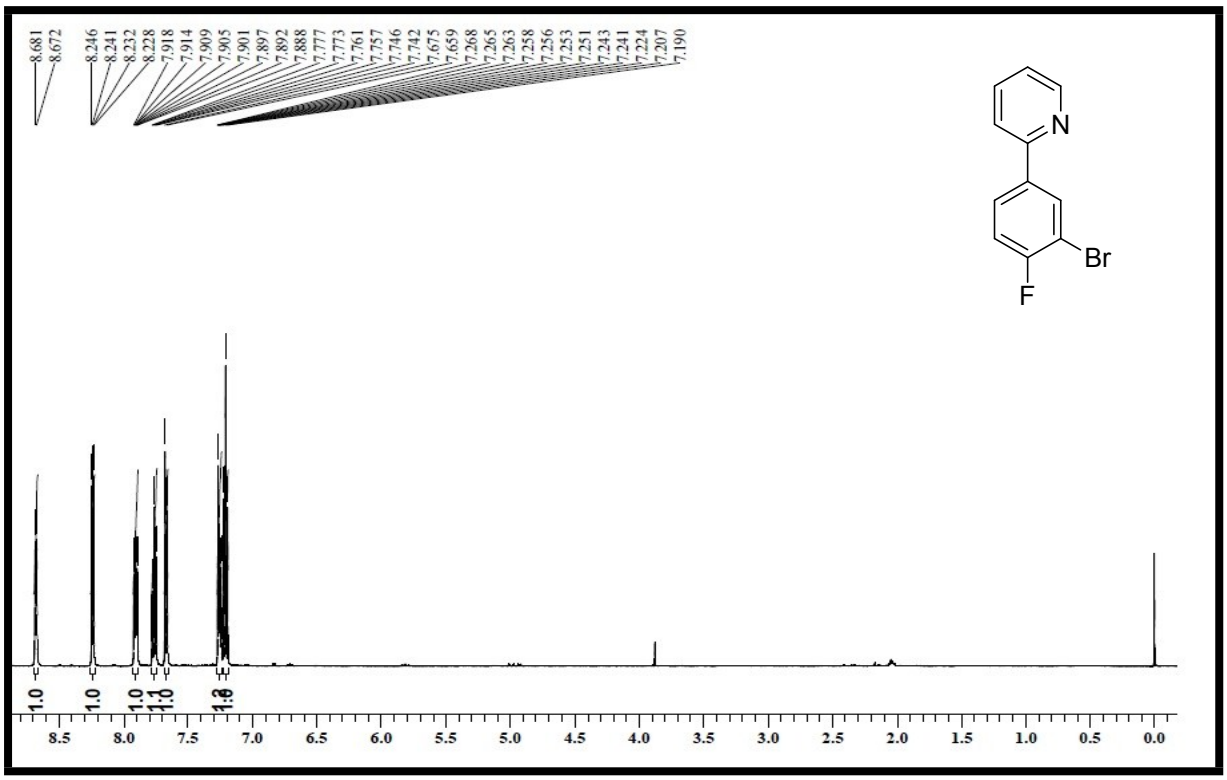
^{1}H NMR spectra of product 2g (Table 2)



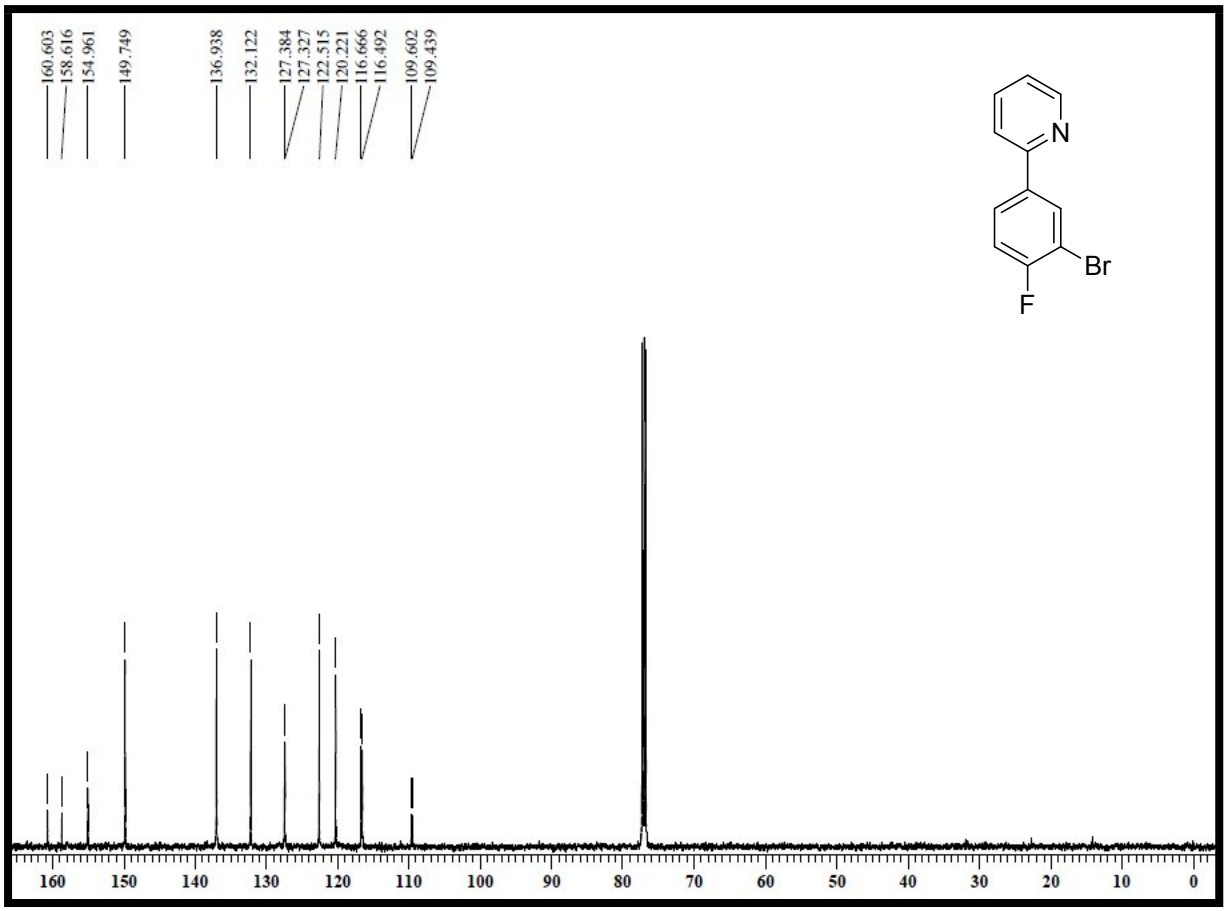
^{13}C NMR spectra of product 2g (Table 2)



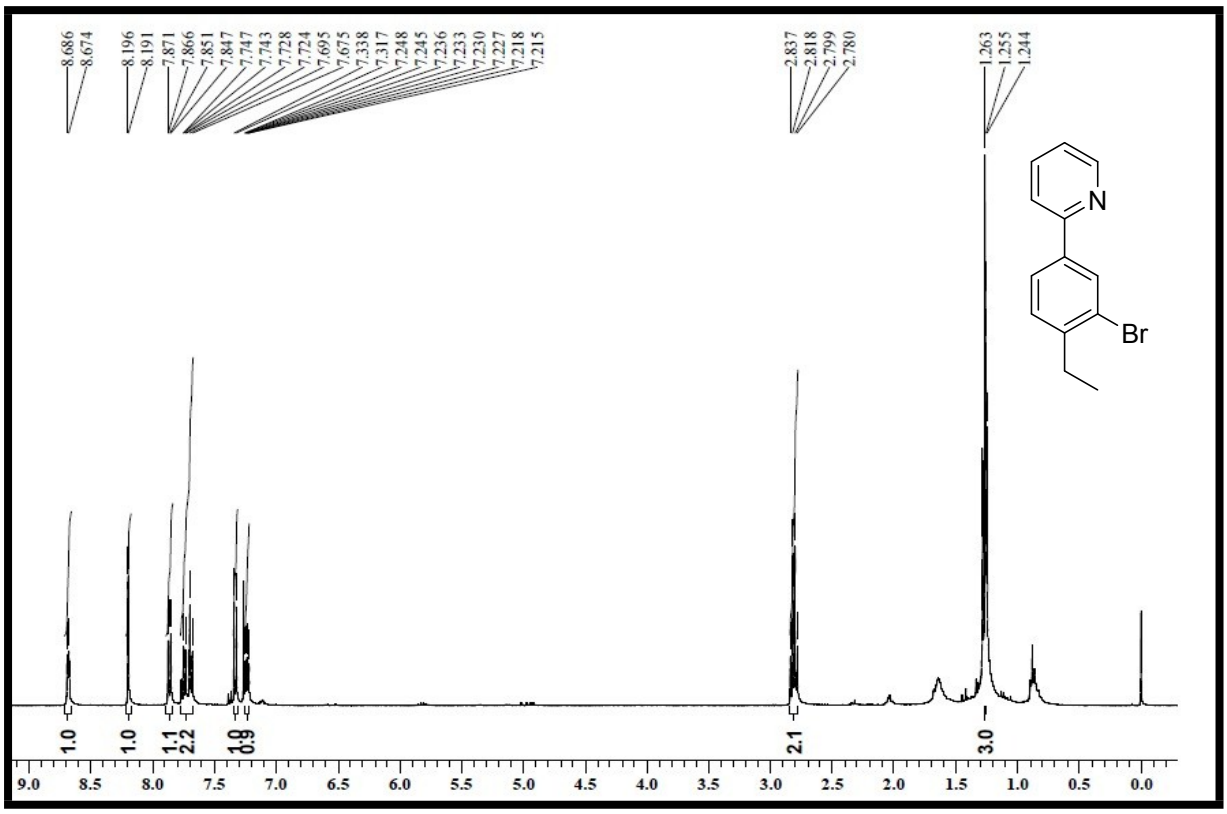
^{1}H NMR spectra of product 2h (Table 2)



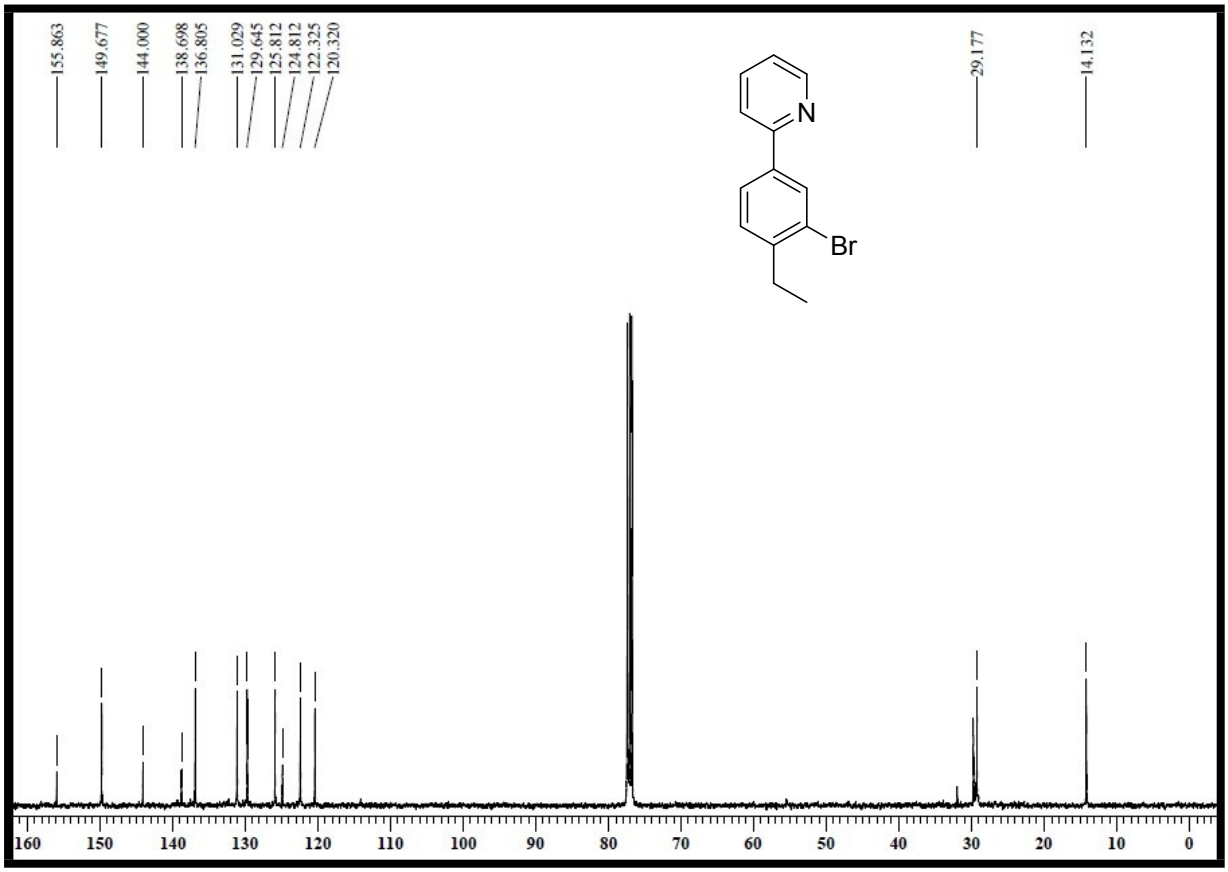
^{13}C NMR spectra of product 2h (Table 2)



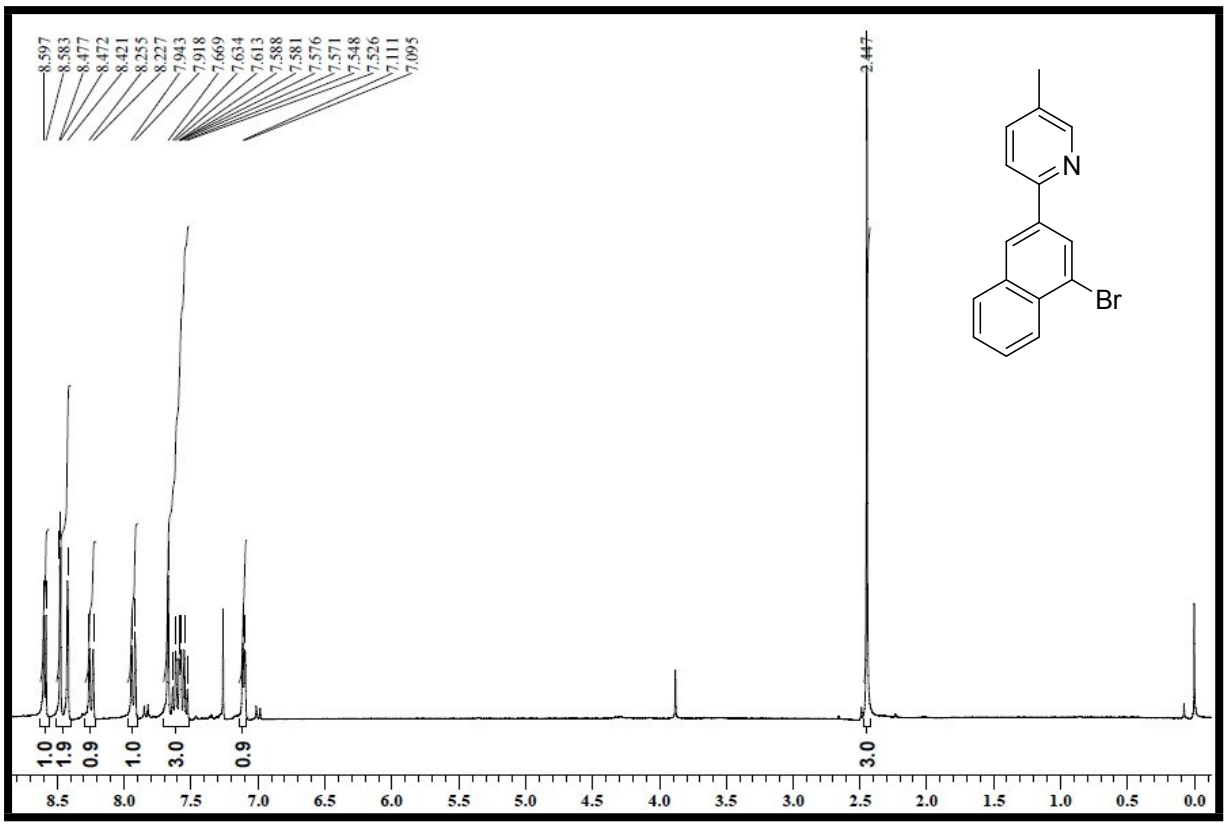
^{1}H NMR spectra of product 2i (Table 2)



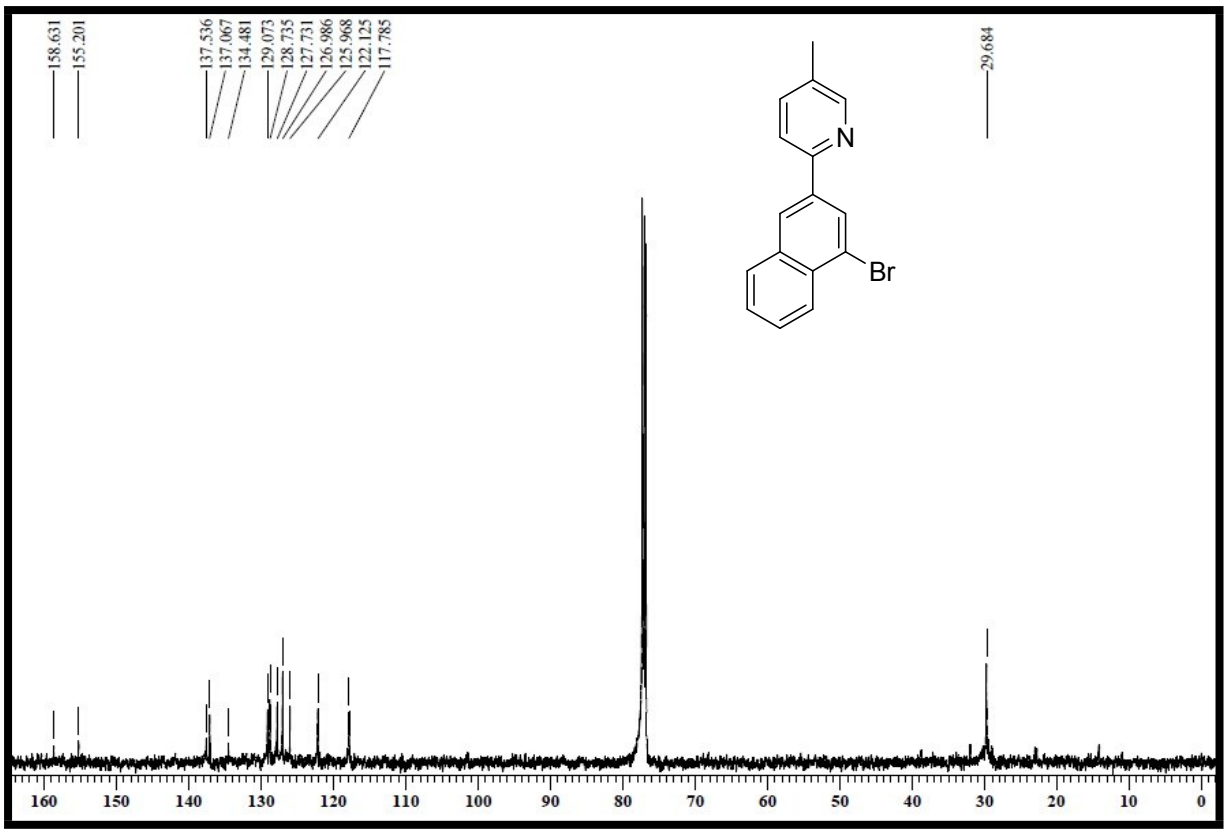
^{13}C NMR spectra of product 2i (Table 2)



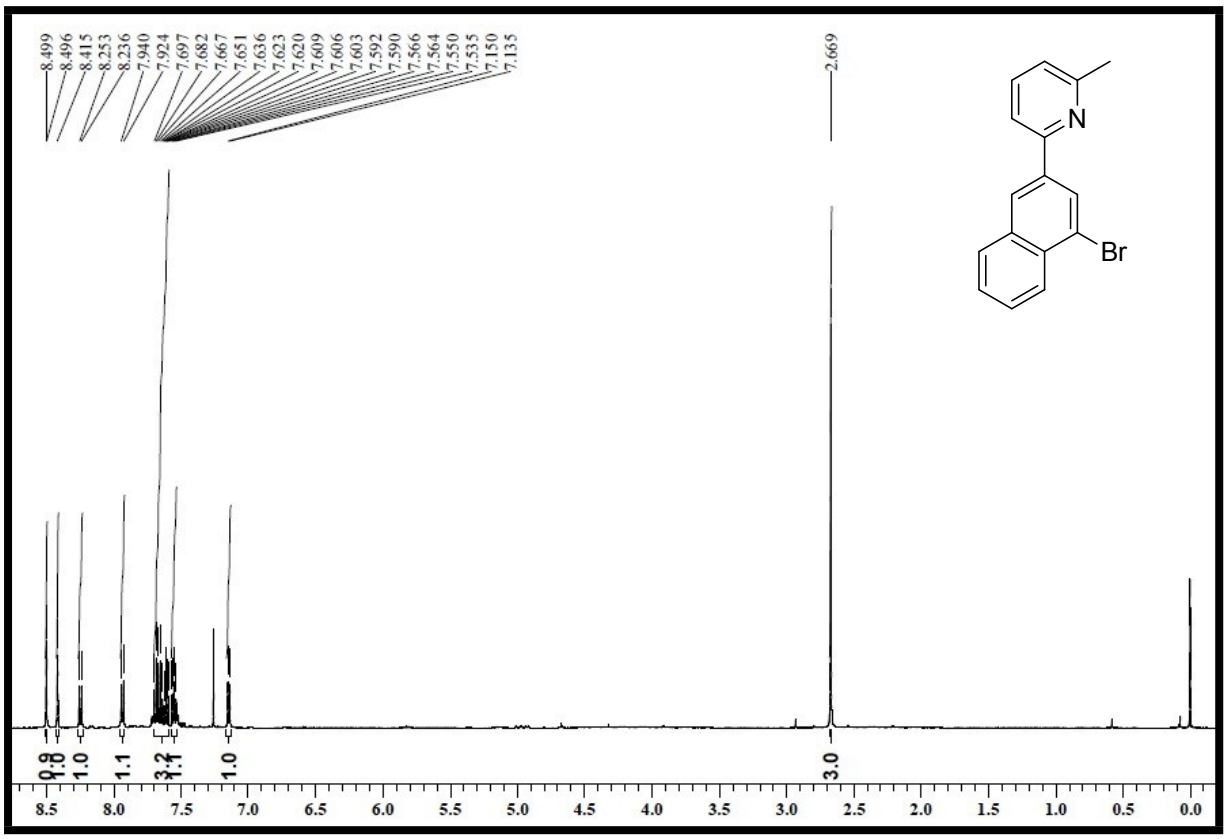
^{1}H NMR spectra of product 2j (Table 2)



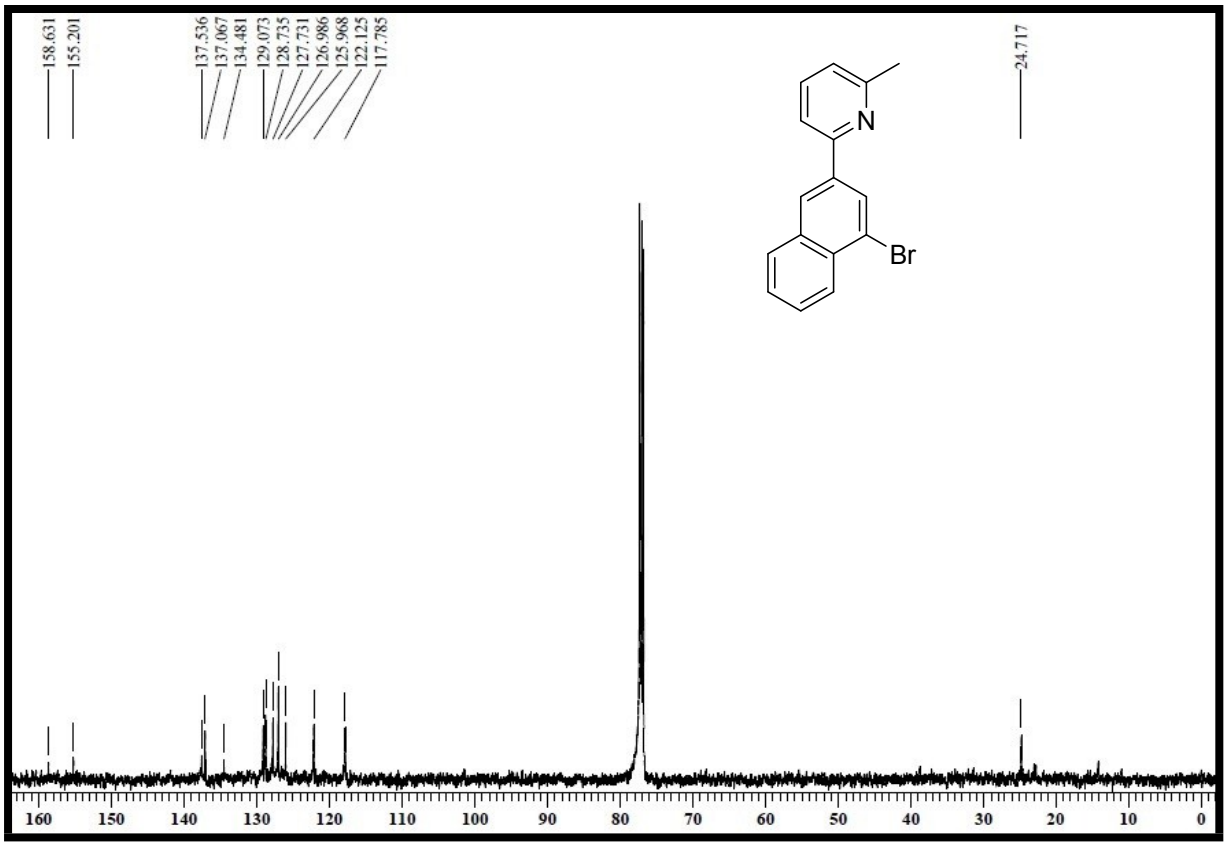
^{13}C NMR spectra of product 2j (Table 2)



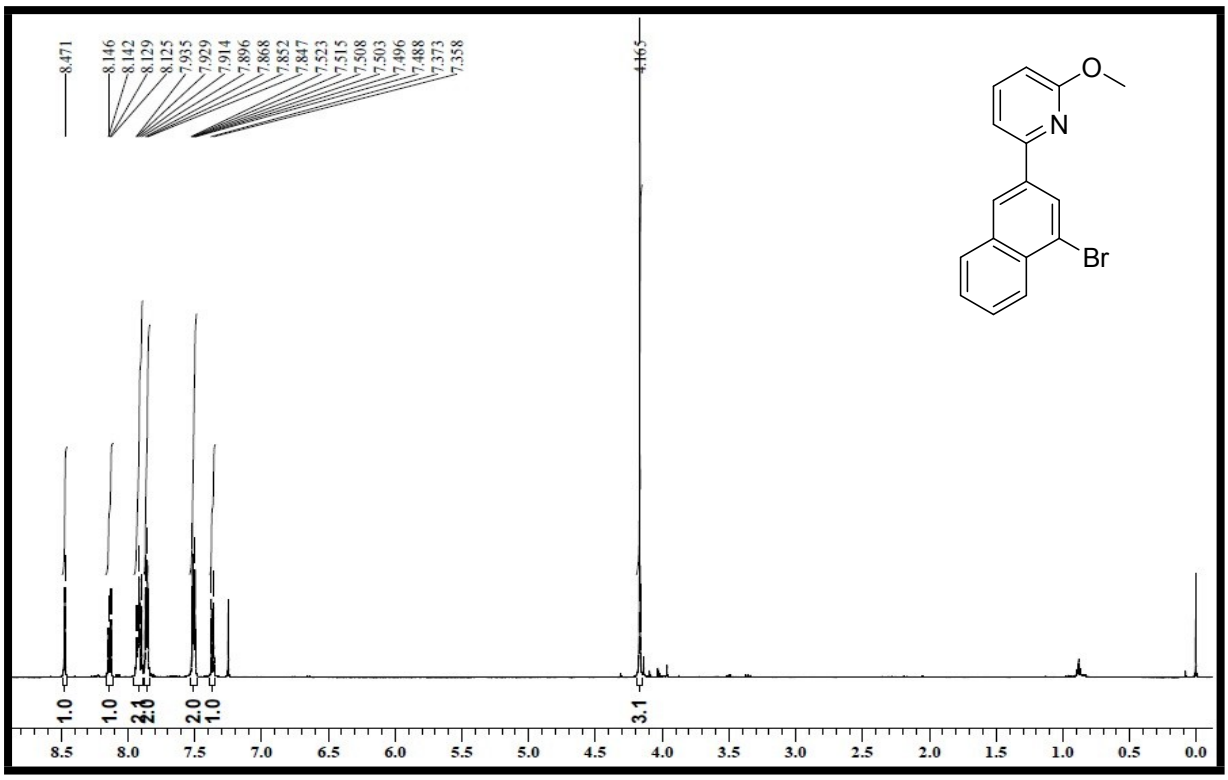
^{1}H NMR spectra of product 2k (Table 2)



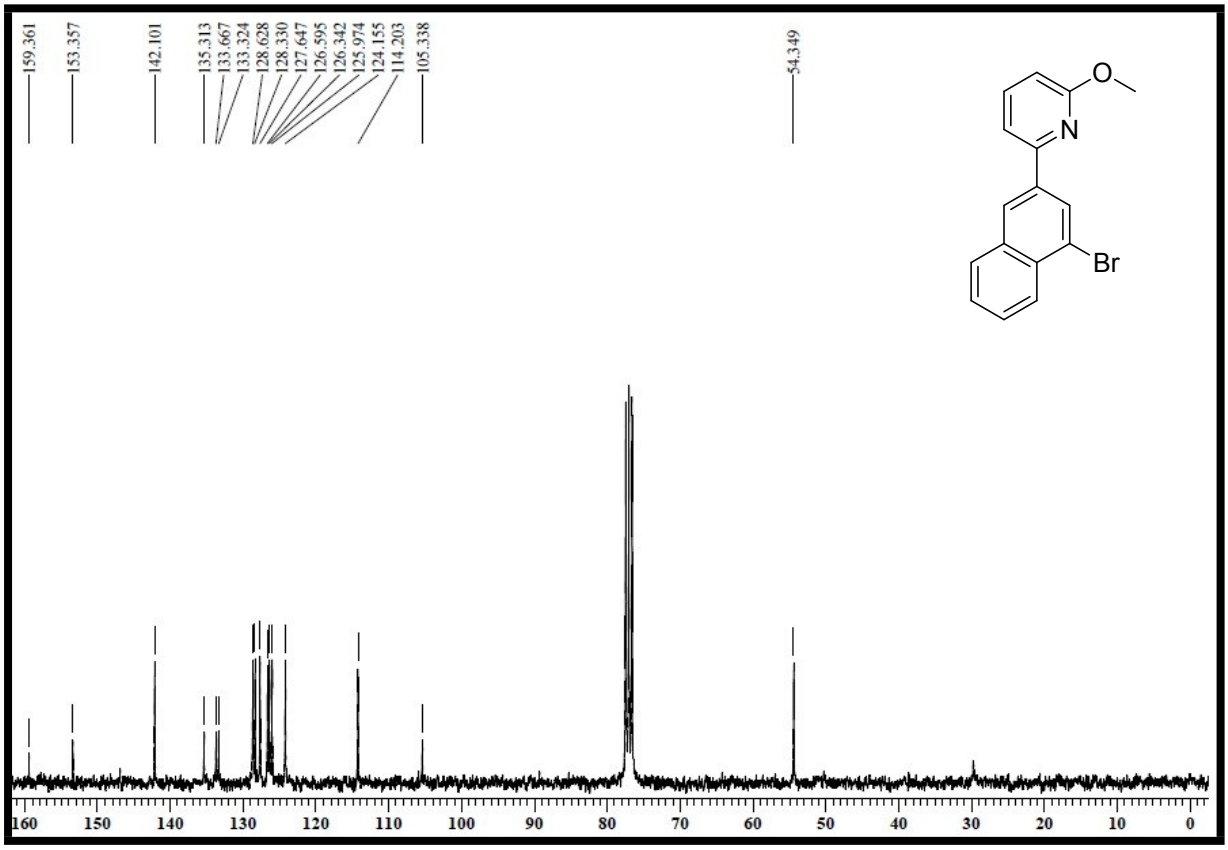
^{13}C NMR spectra of product 2k (Table 2)



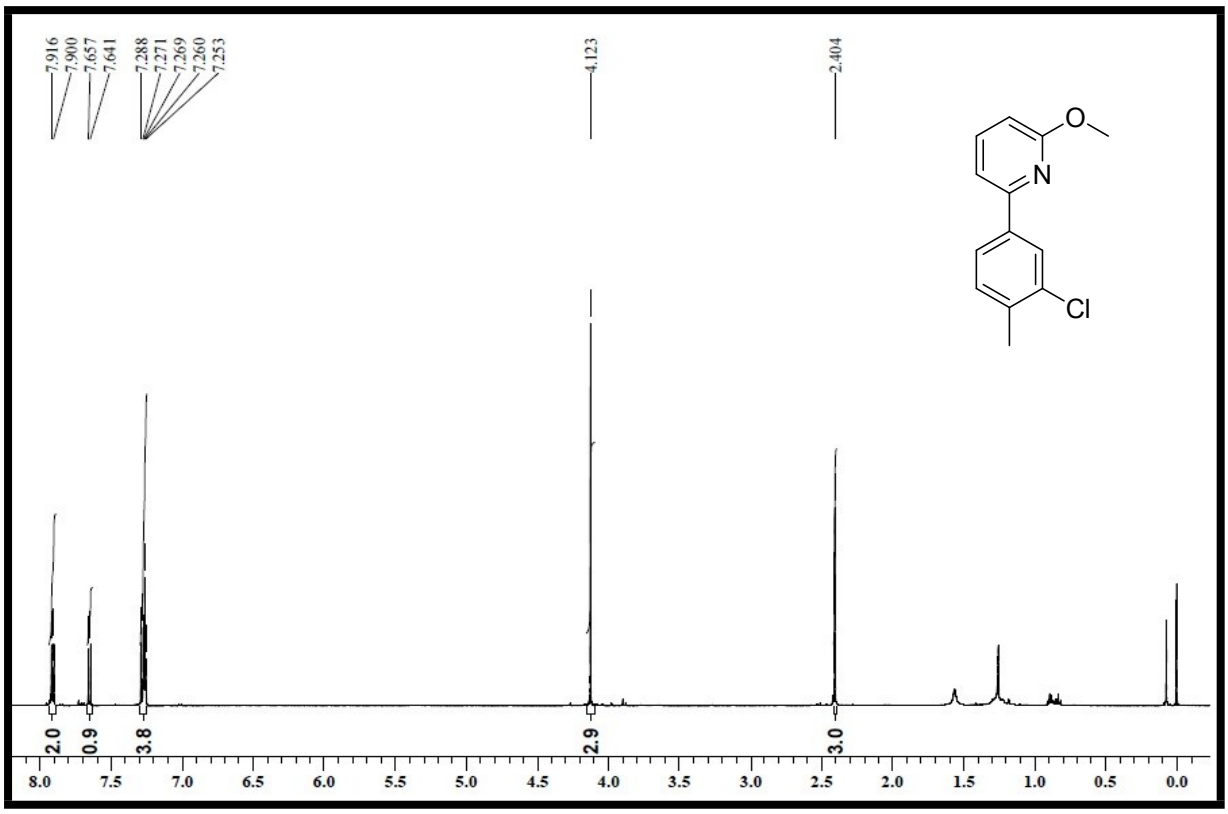
^{1}H NMR spectra of product 2l (Table 2)



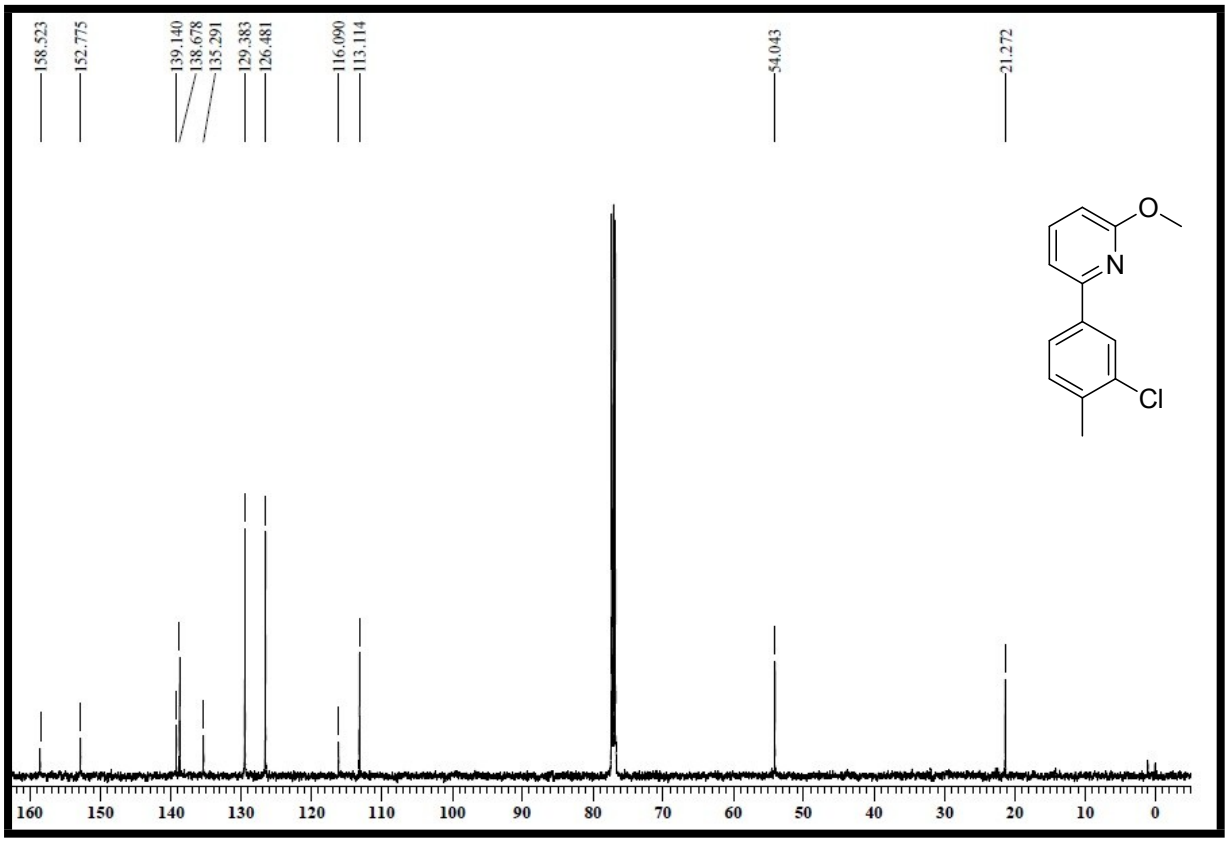
^{13}C NMR spectra of product 2l (Table 2)



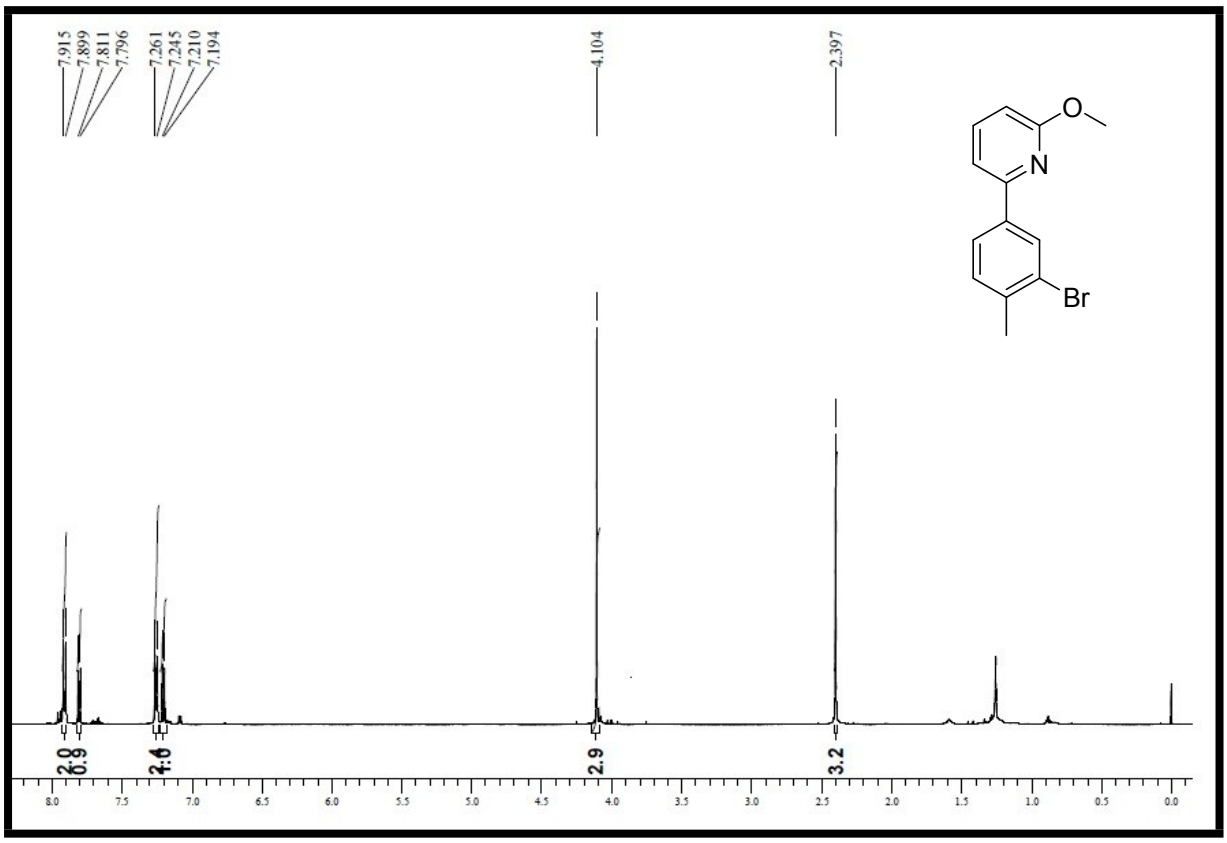
^{1}H NMR spectra of product 2m (Table 2)



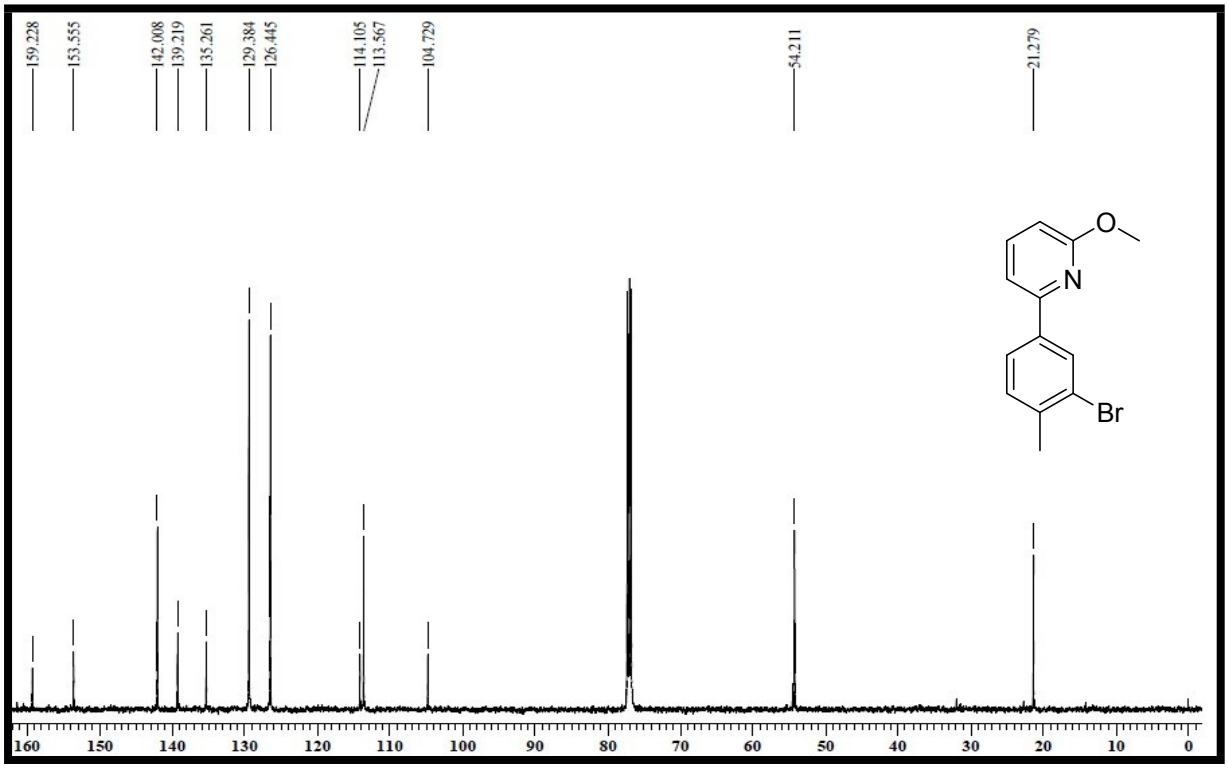
^{13}C NMR spectra of product 2m (Table 2)



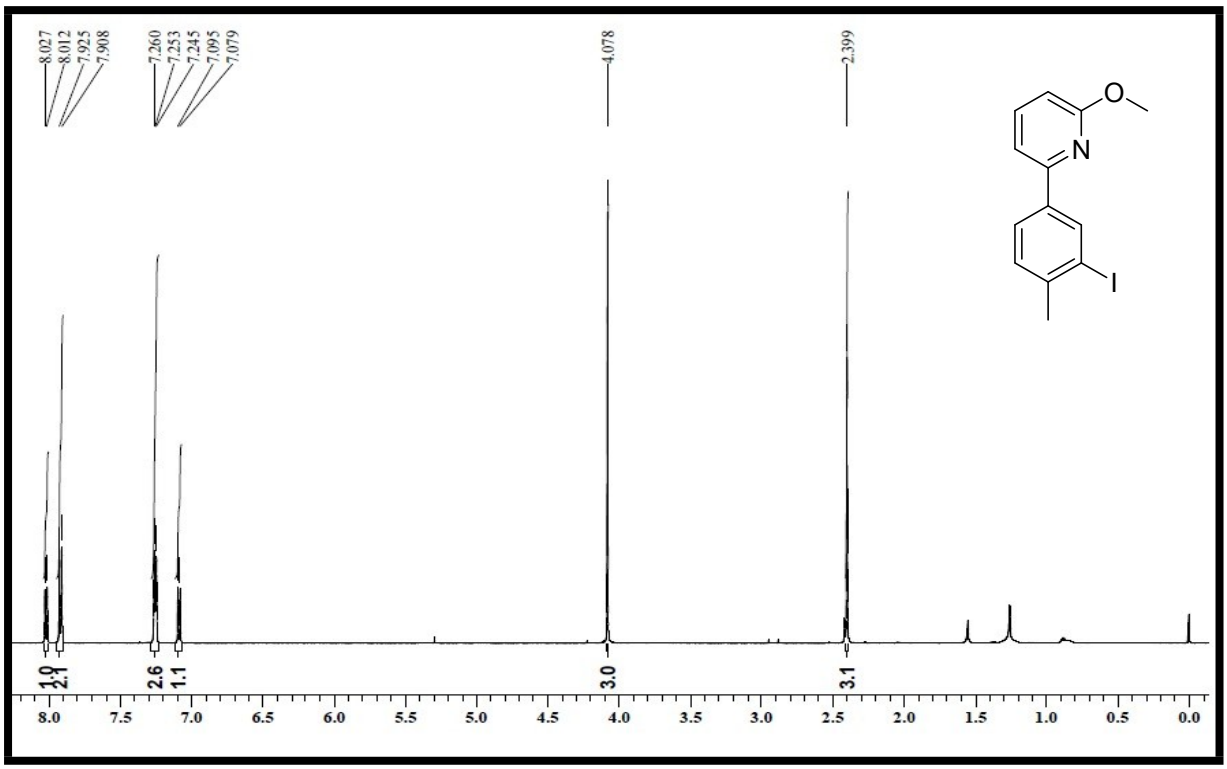
^{1}H NMR spectra of product 2n (Table 2)



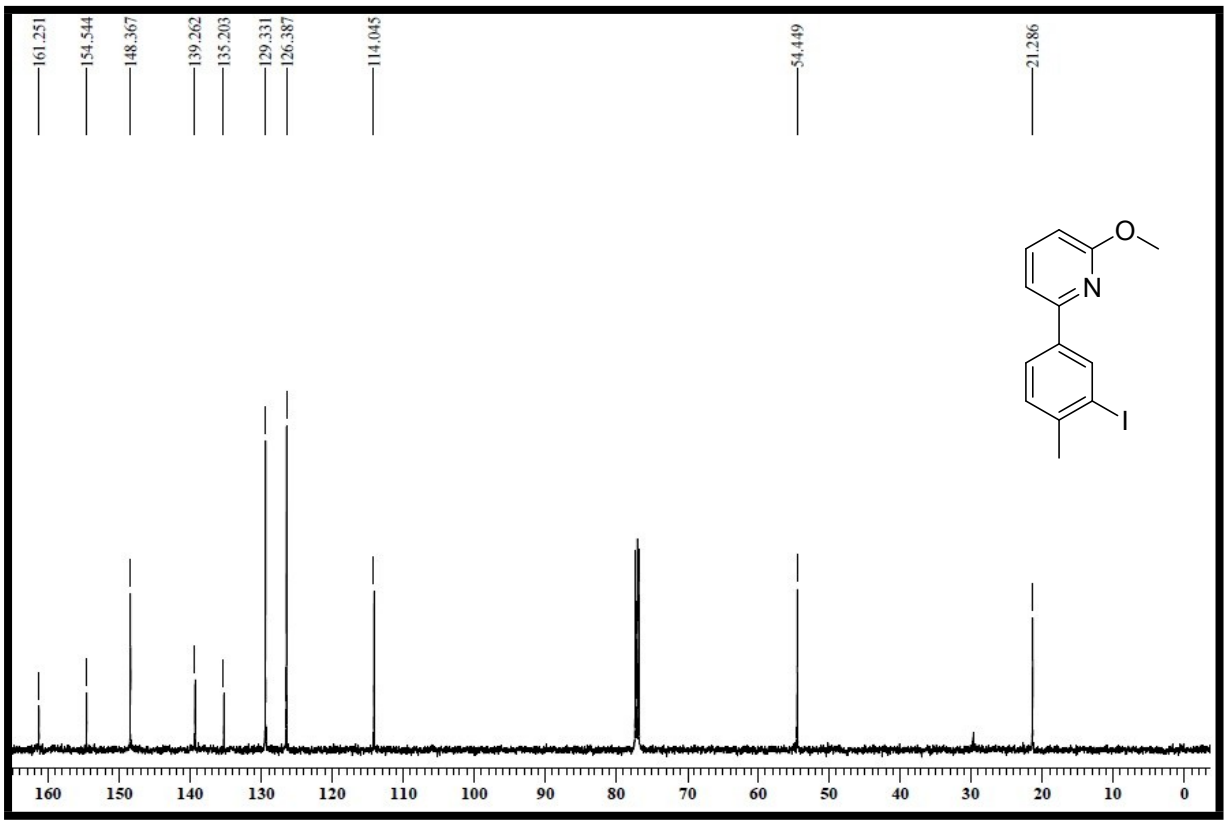
^{13}C NMR spectra of product 2n (Table 2)



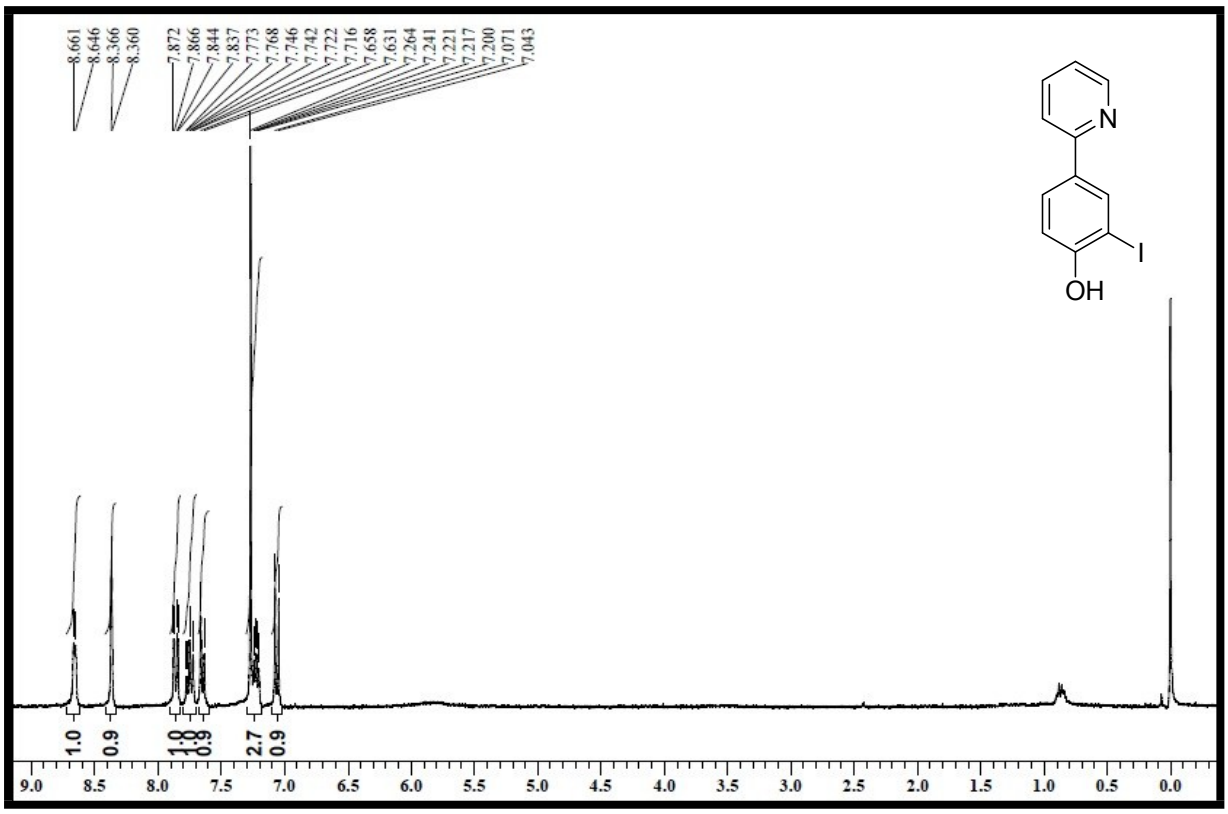
^{1}H NMR spectra of product 2o (Table 2)



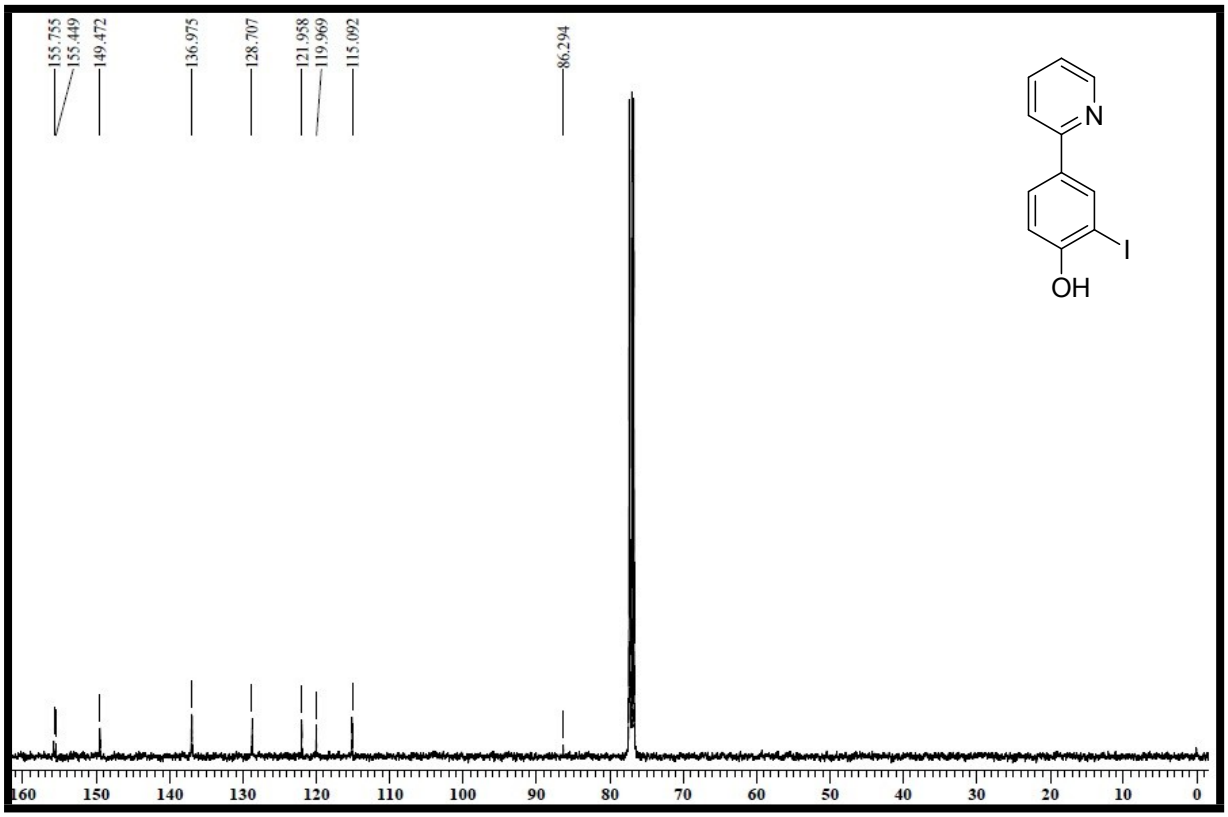
^{13}C NMR spectra of product 2o (Table 2)



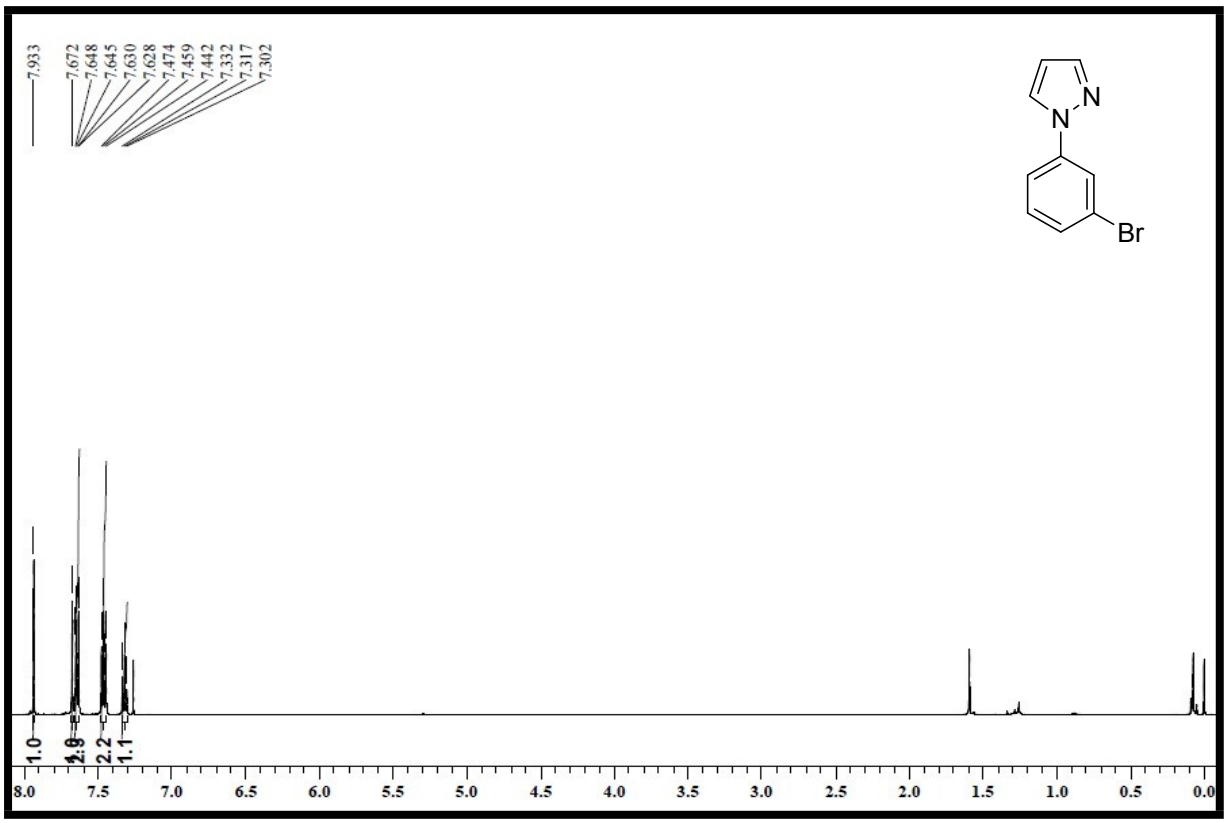
^{1}H NMR spectra of product 2p, (Table 2)



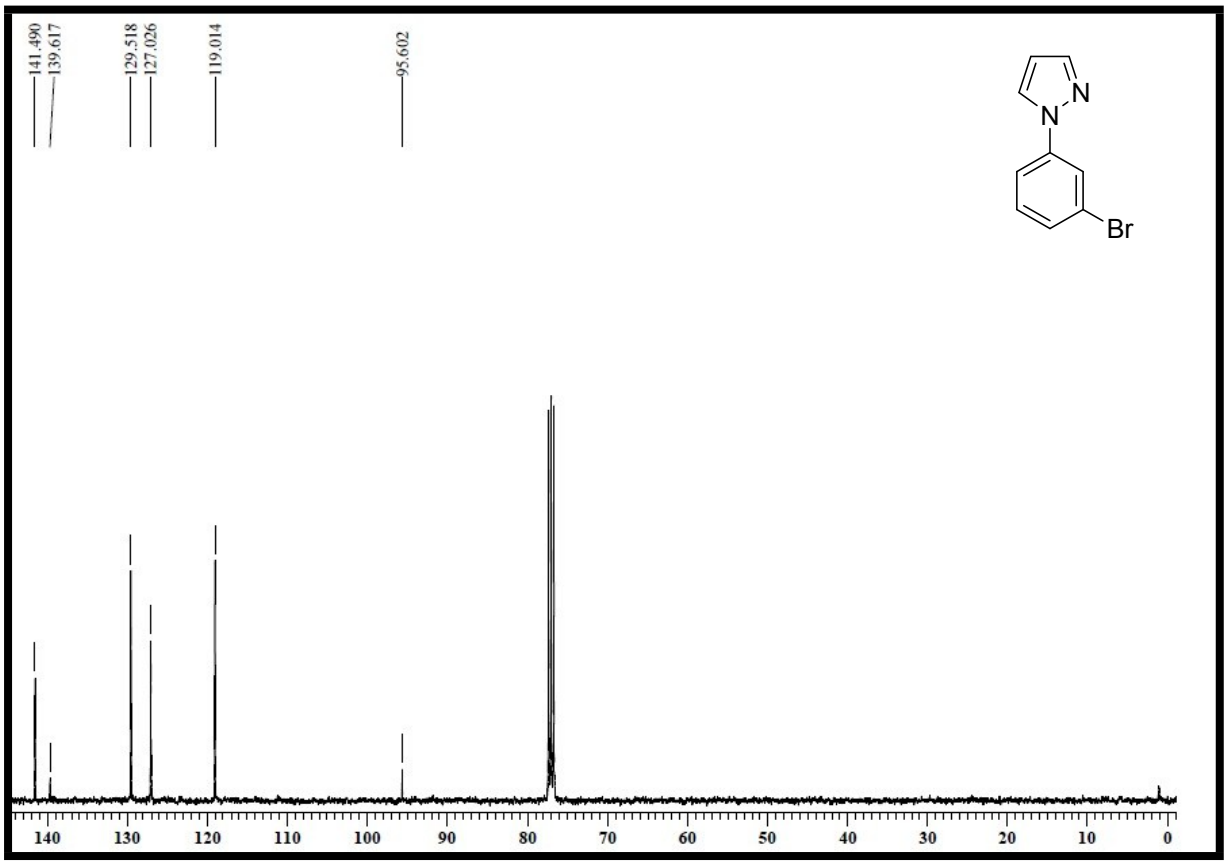
^{13}C NMR spectra of product 2p (Table 2)



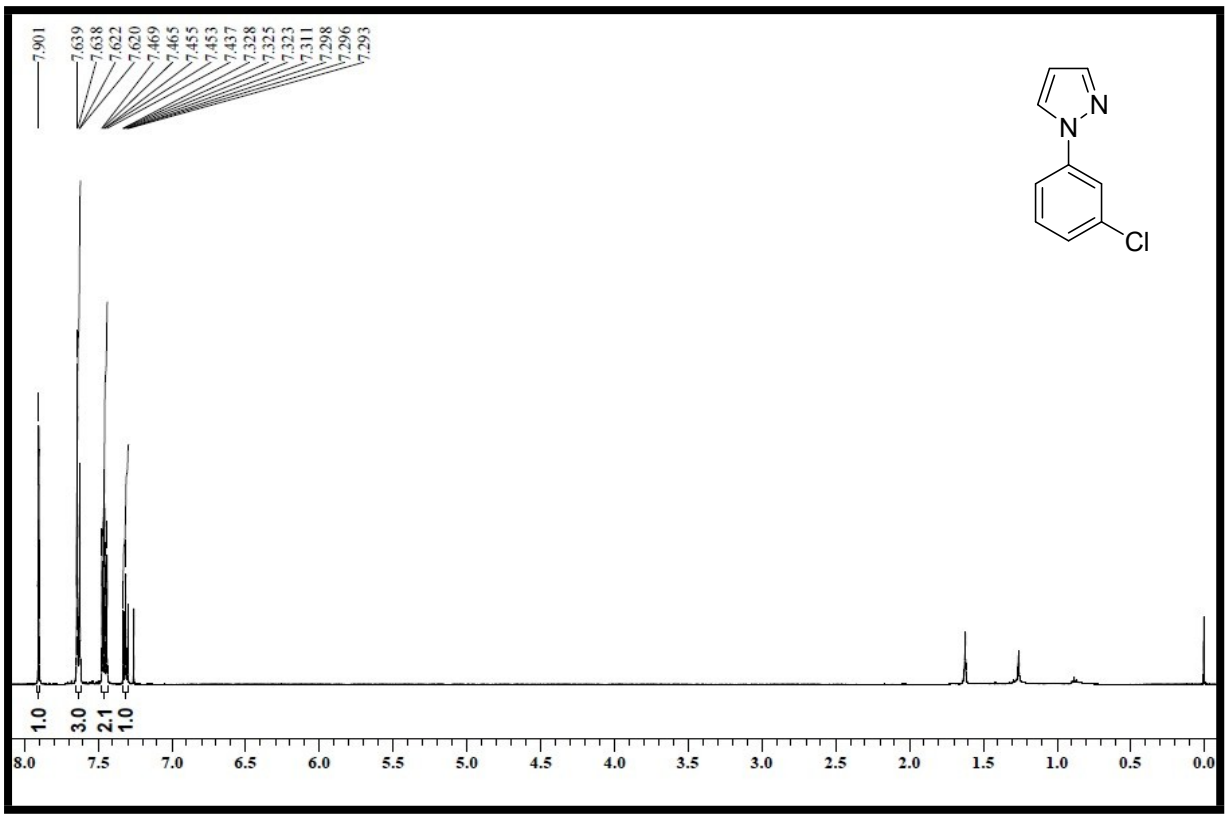
^{1}H NMR spectra of product 2q (Table 2)



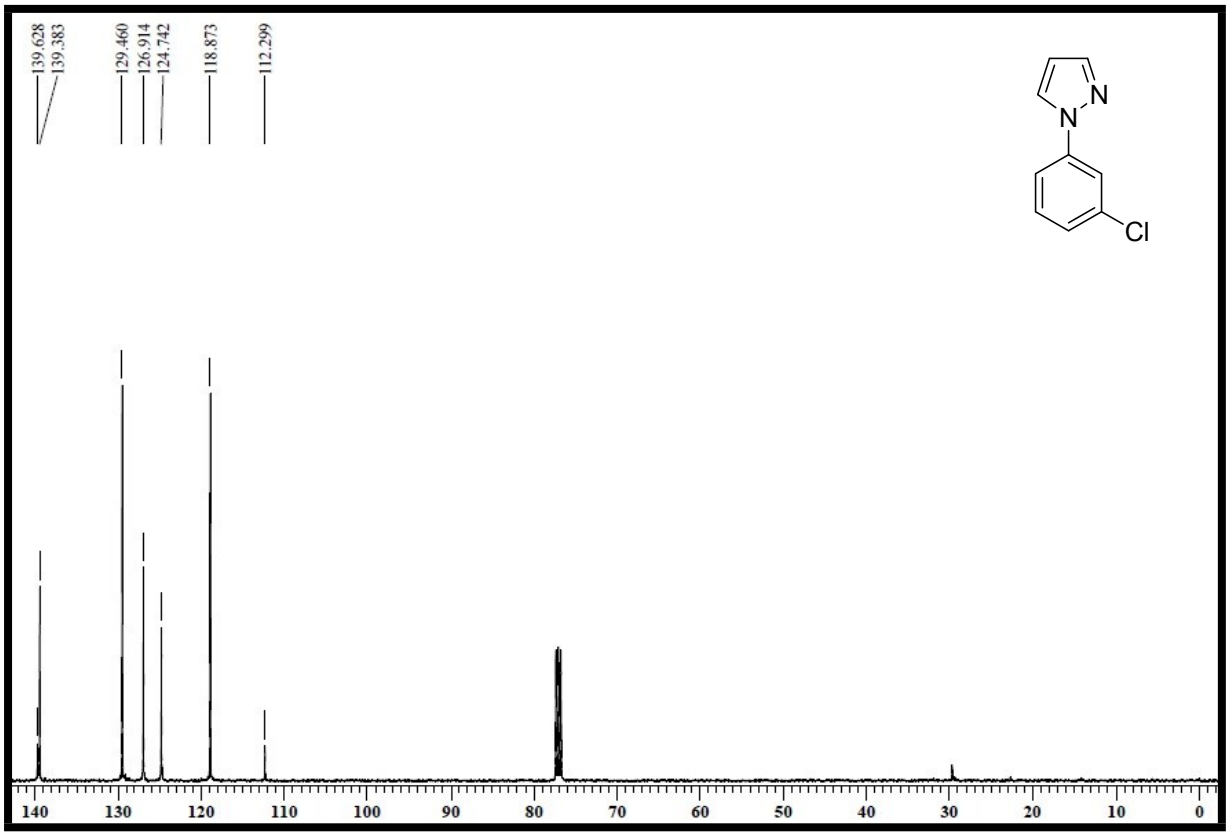
^{13}C NMR spectra of product 2q (Table 2)



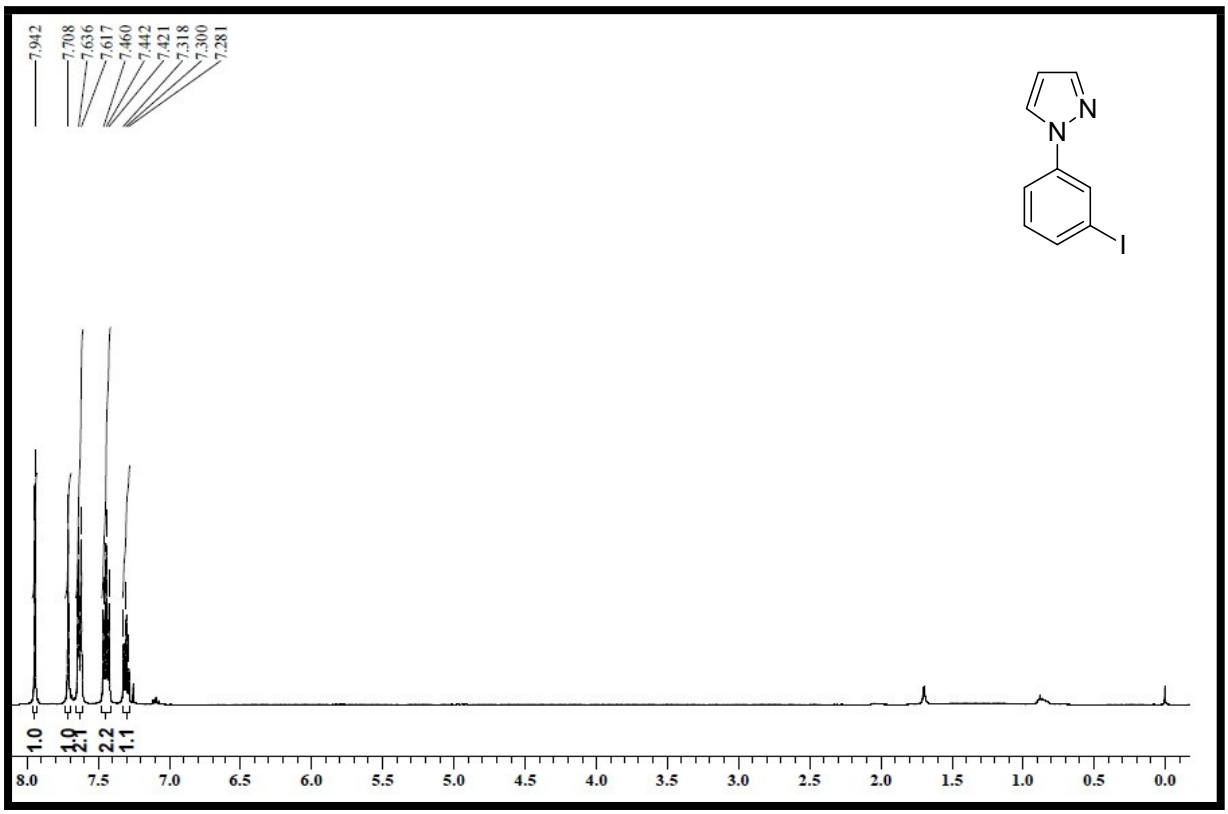
^{1}H NMR spectra of product 2r (Table 2)



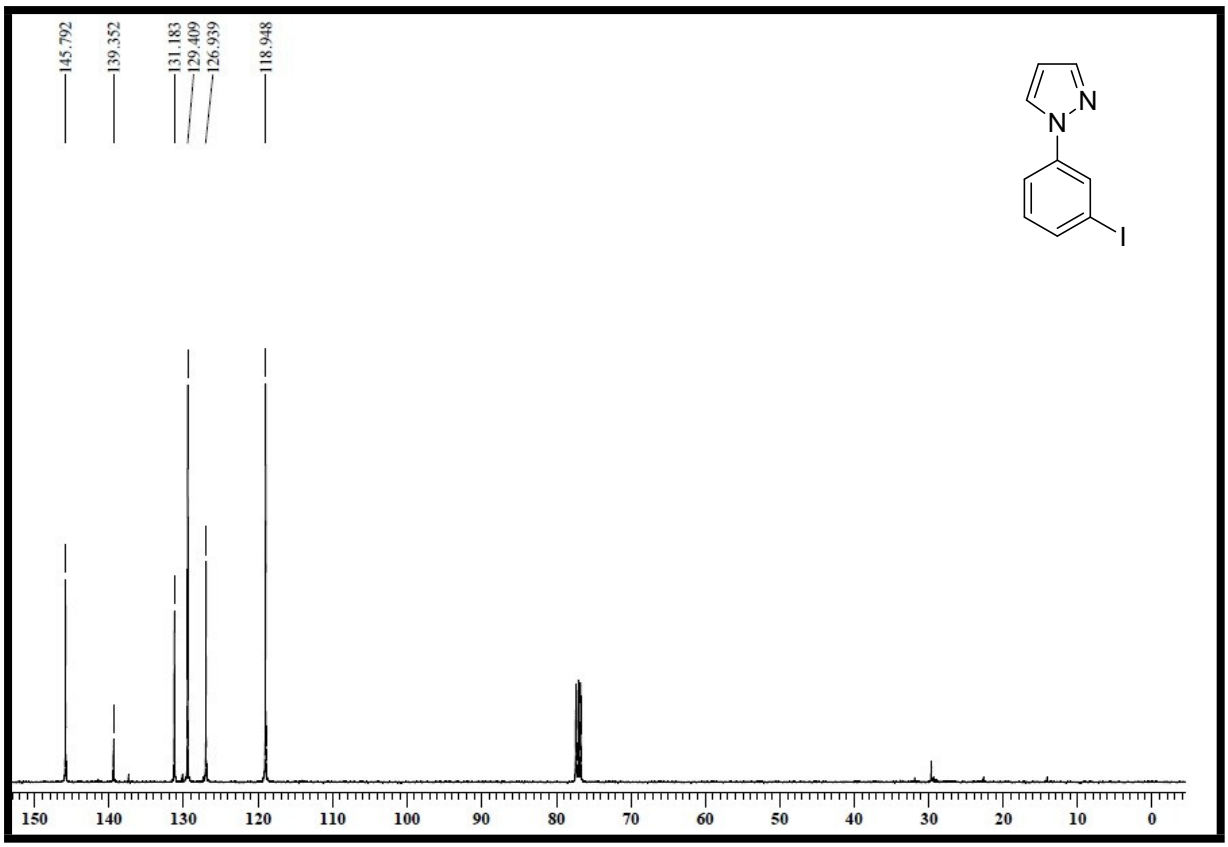
^{13}C NMR spectra of product 2r (Table 2)



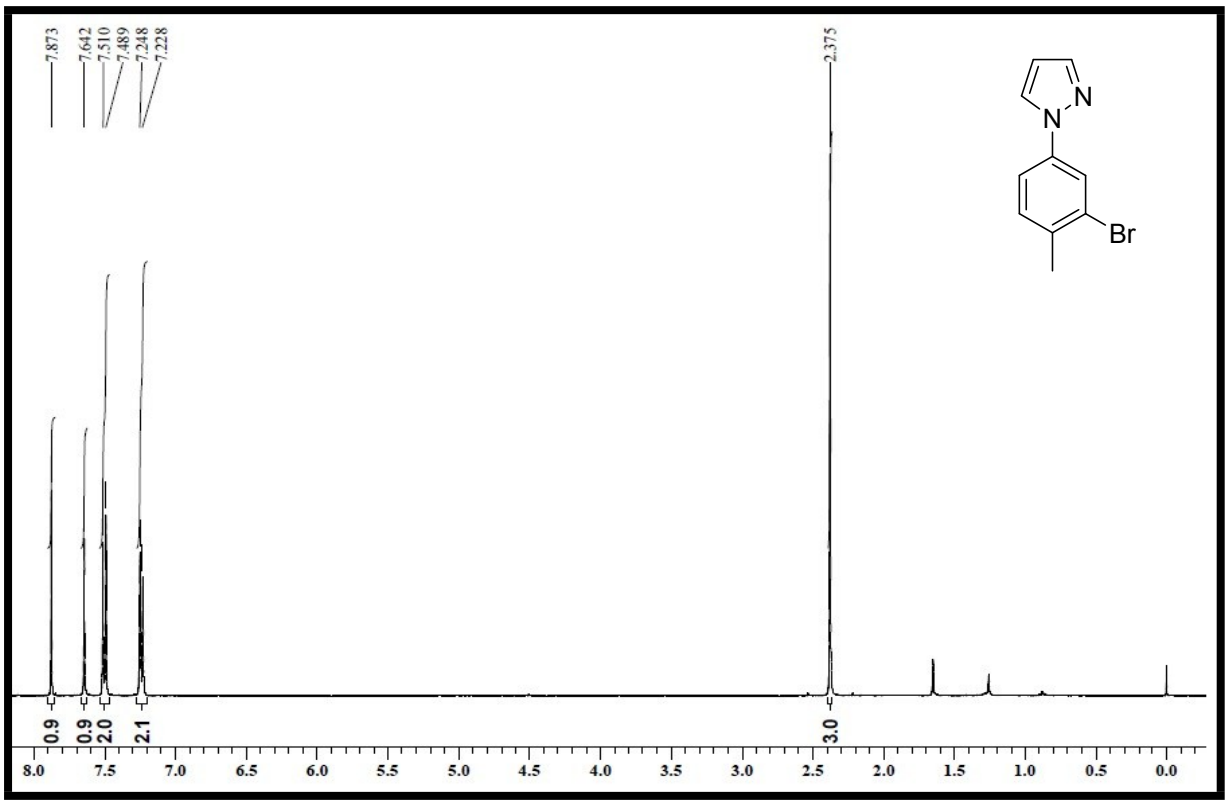
^{1}H NMR spectra of product 2s (Table 2)



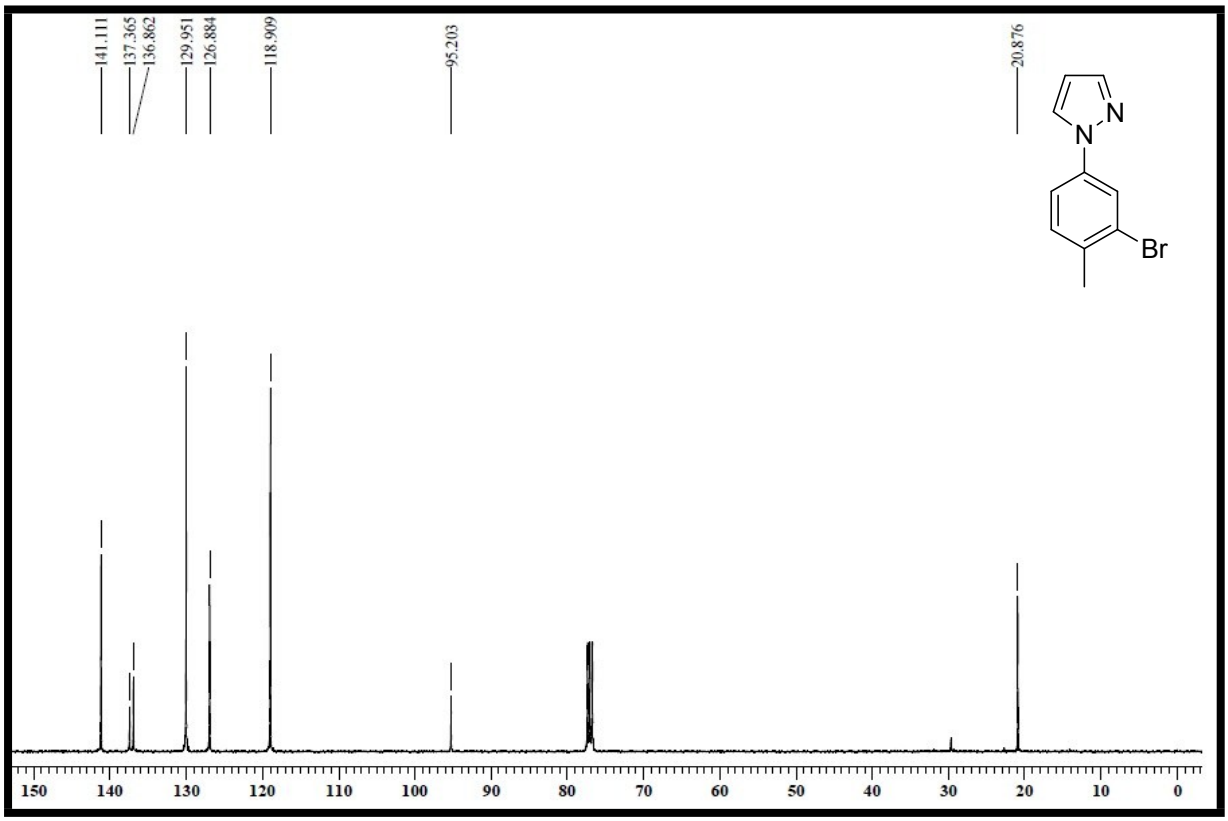
^{13}C NMR spectra of product 2s (Table 2)



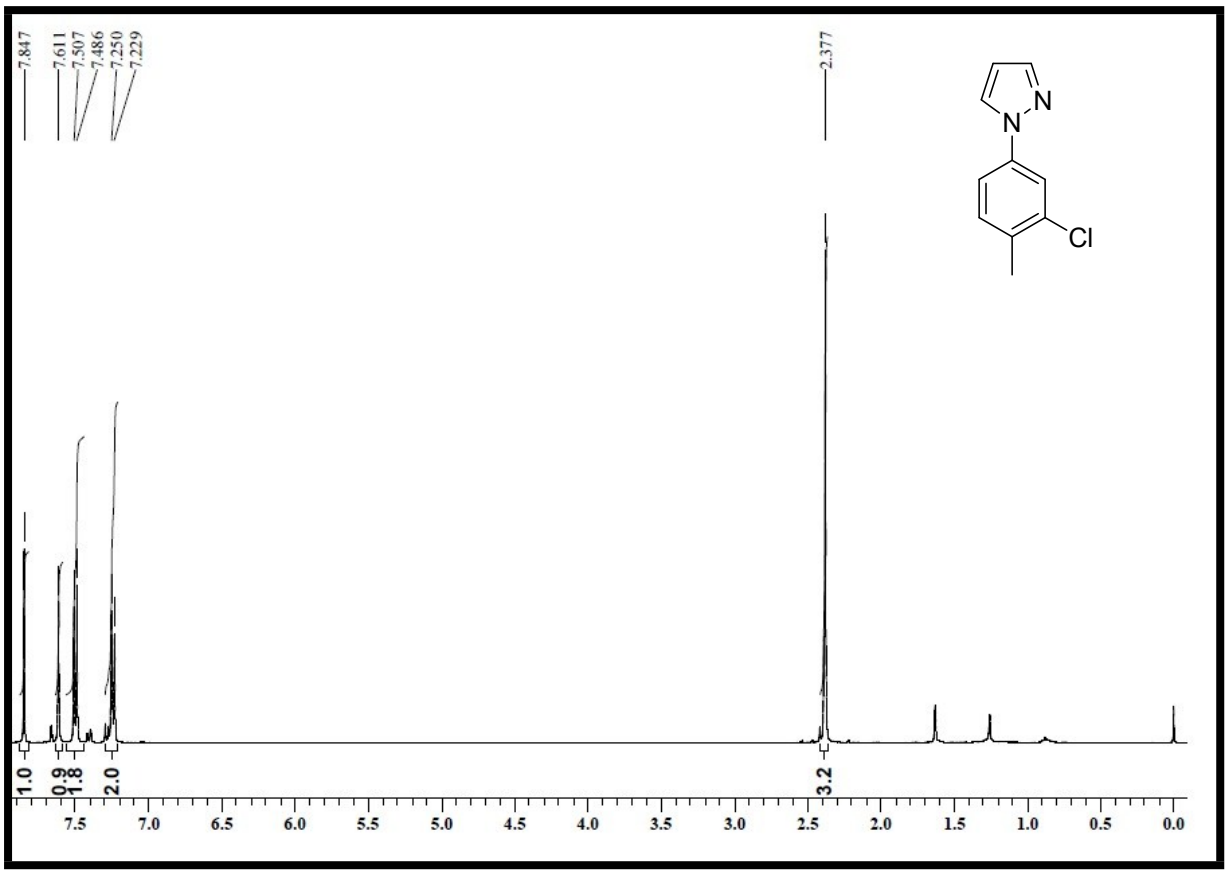
^{1}H NMR spectra of product 2t (Table 2)



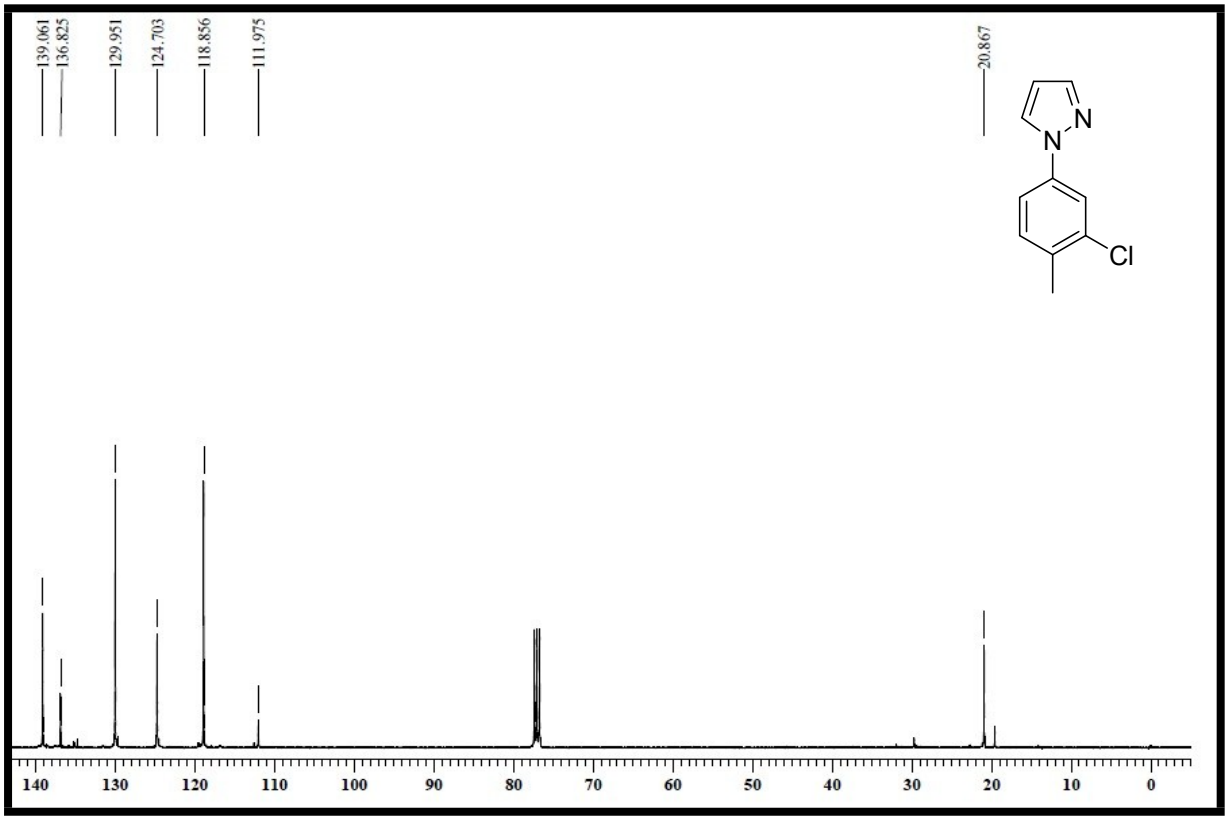
^{13}C NMR spectra of product 2t (Table 2)



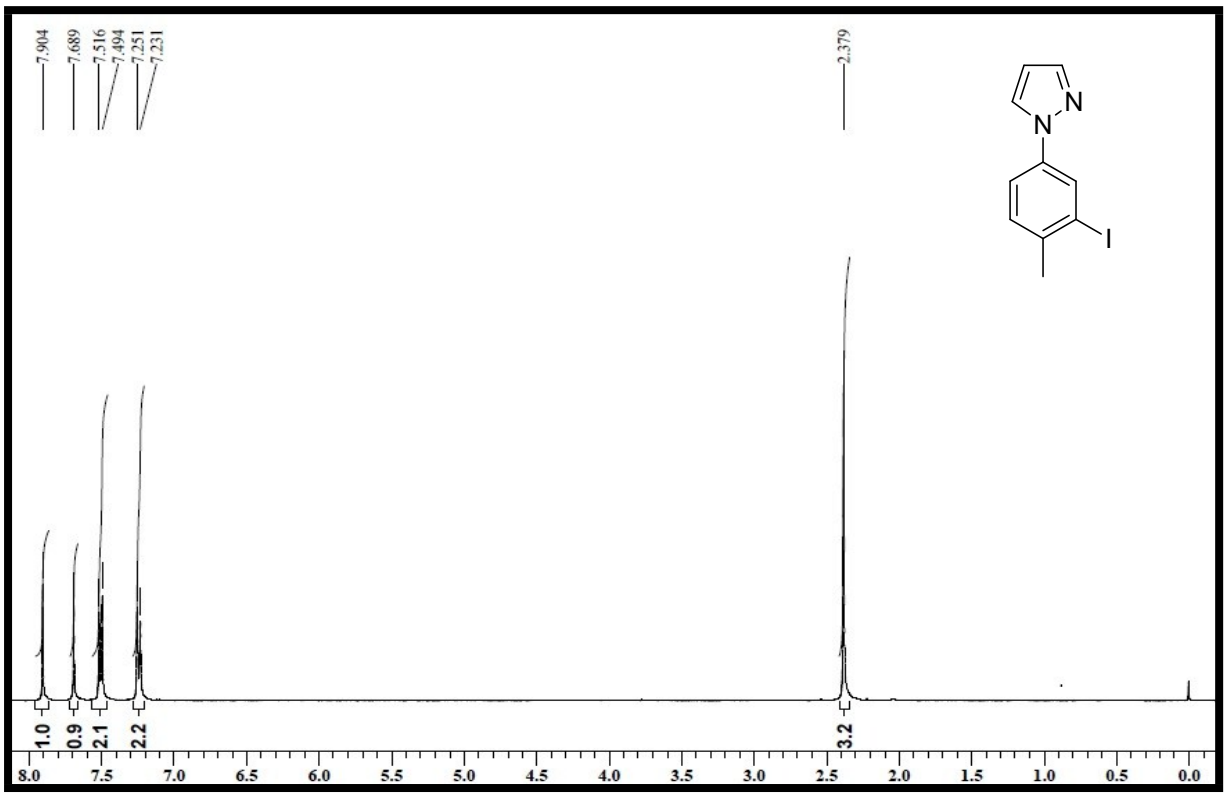
^{1}H NMR spectra of product 2u (Table 2)



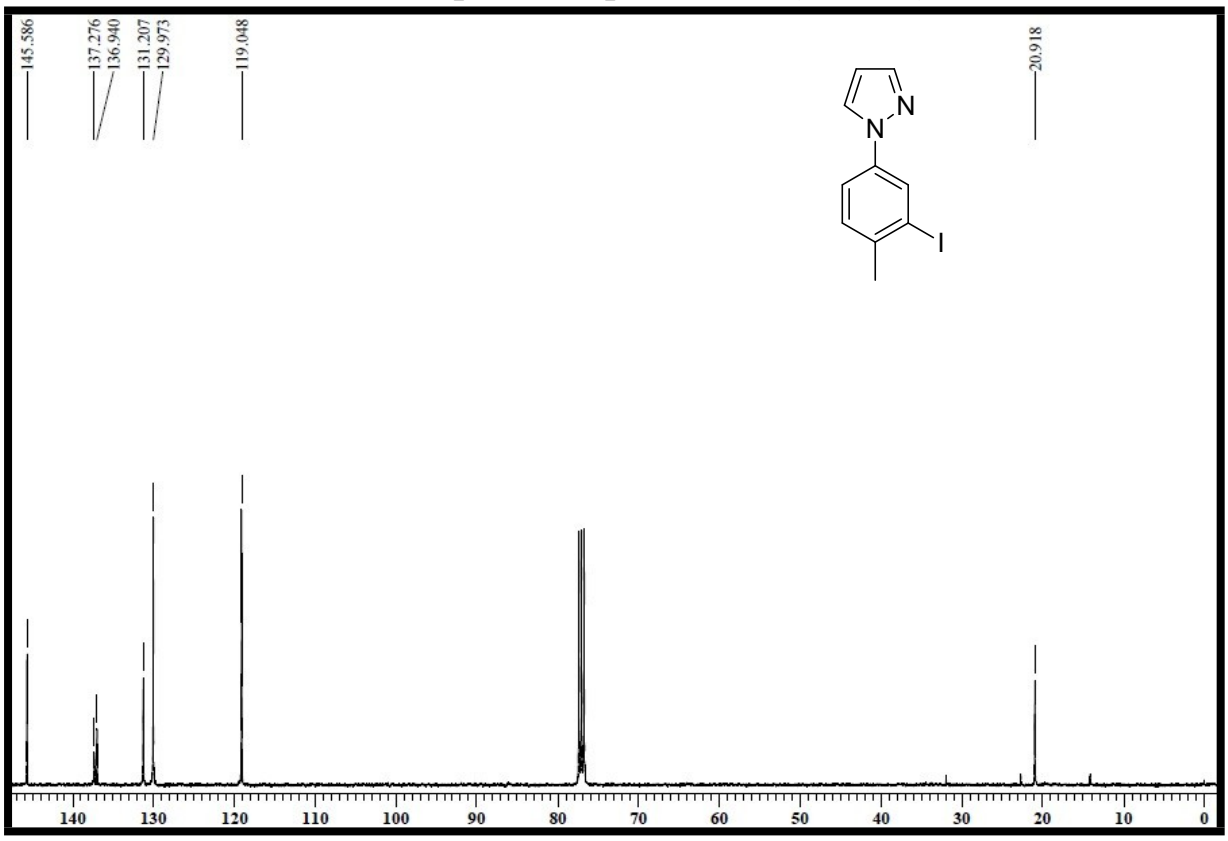
^{13}C NMR spectra of product 2u (Table 2)



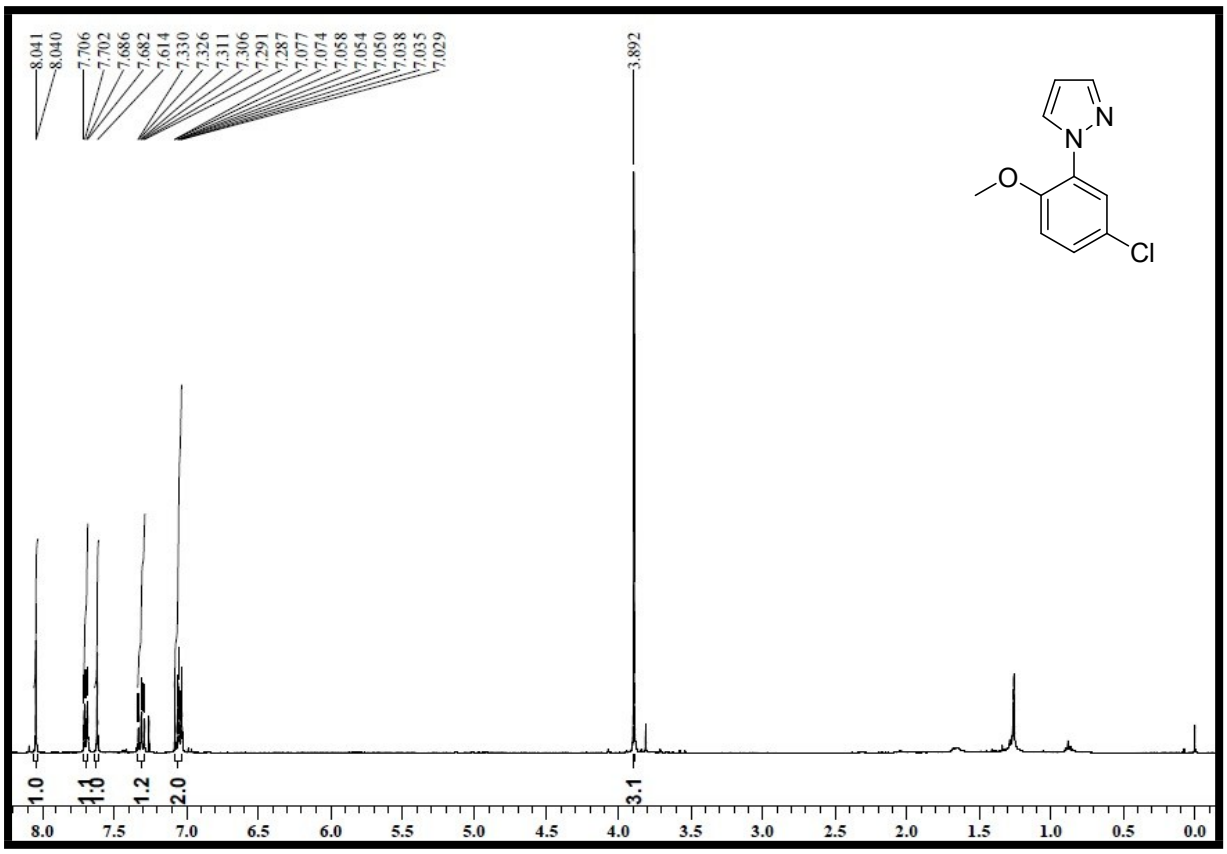
^{1}H NMR spectra of product 2v (Table 2)



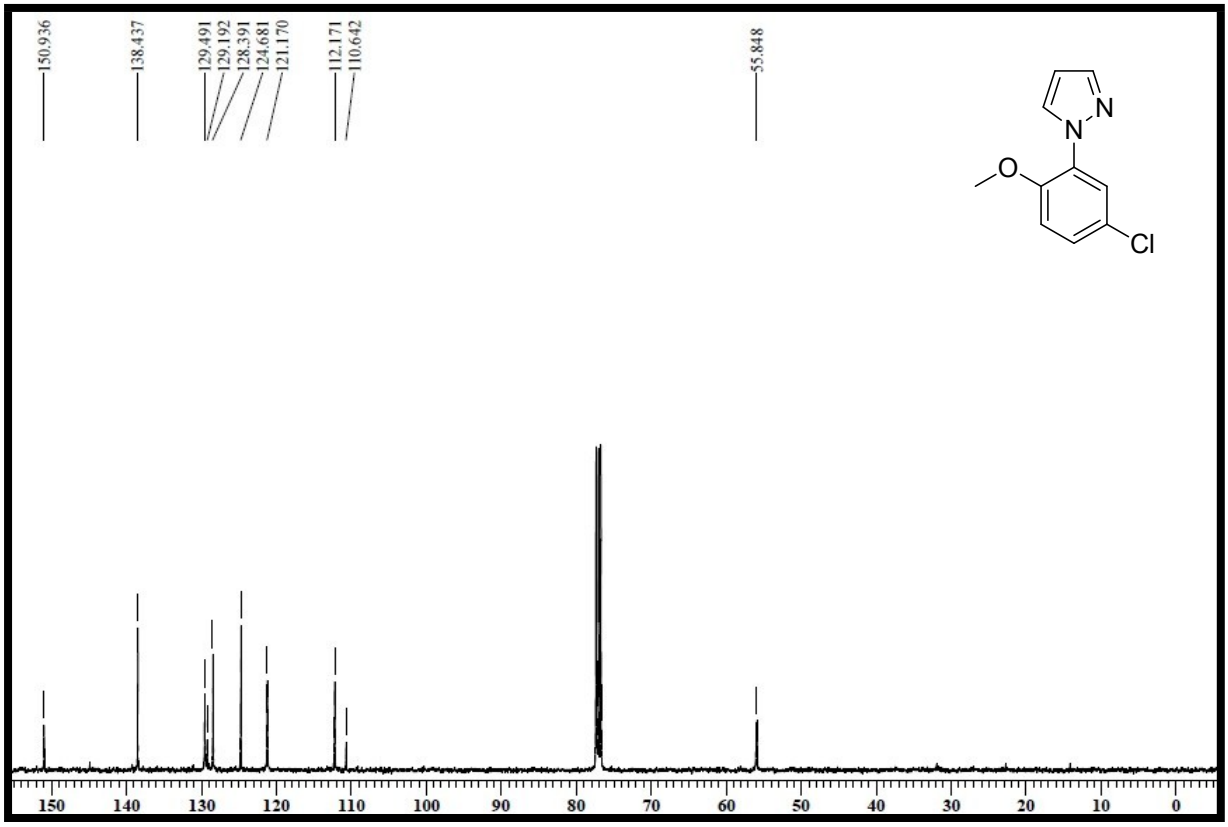
^{13}C NMR spectra of product 2v (Table 2)



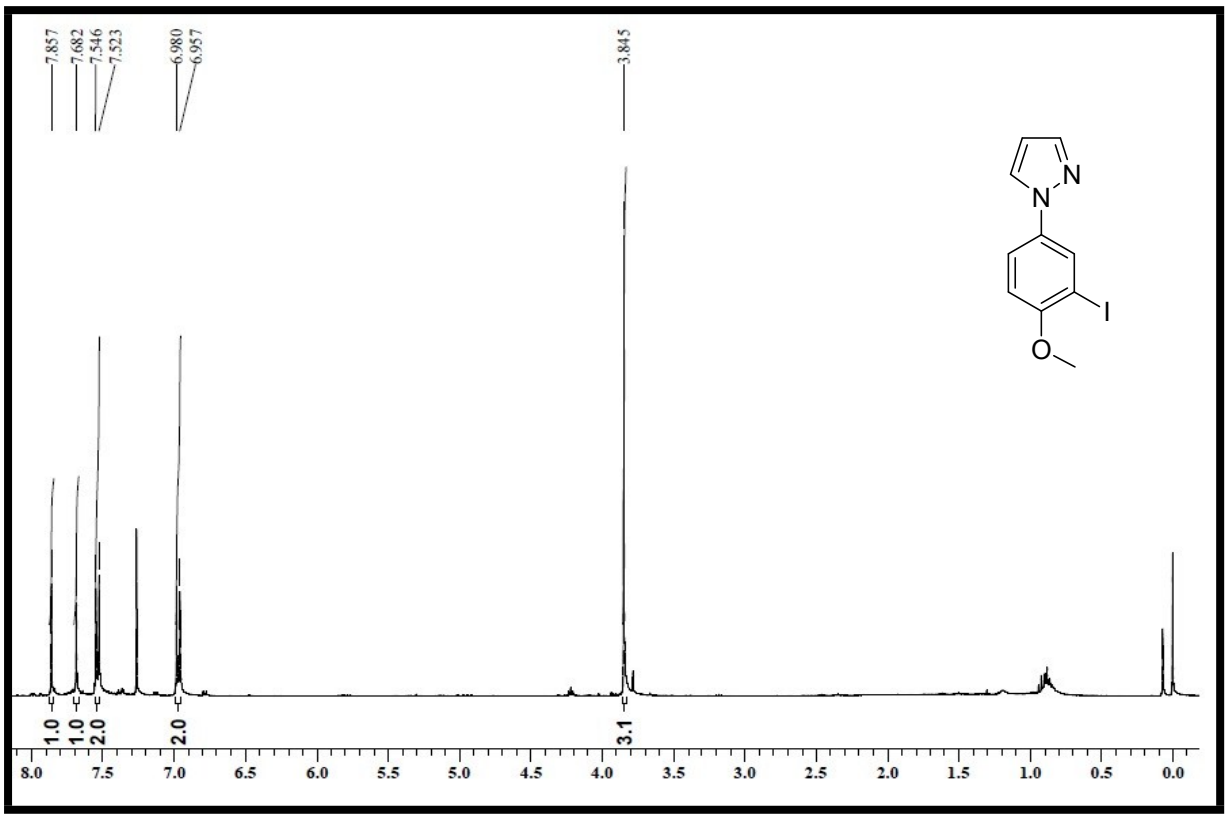
^{1}H NMR spectra of product 2w (Table 2)



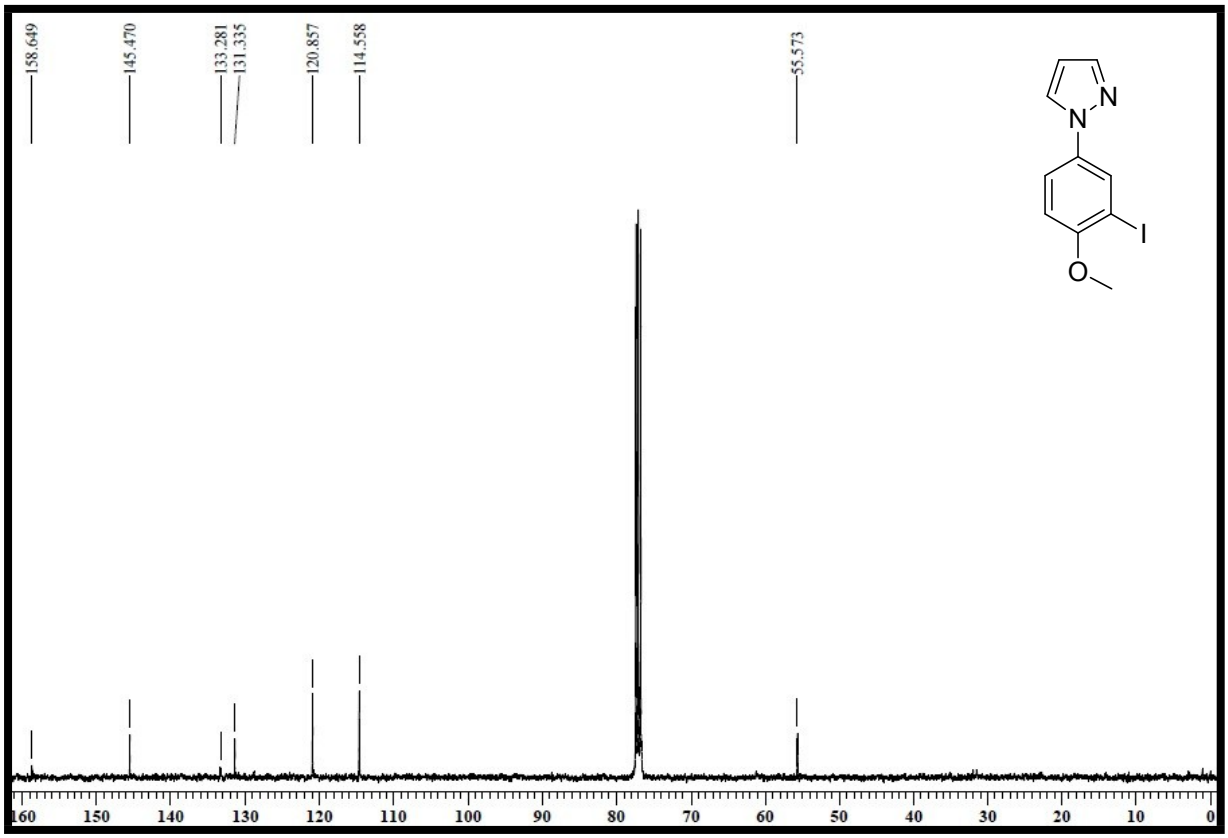
^{13}C NMR spectra of product 2w (Table 2)



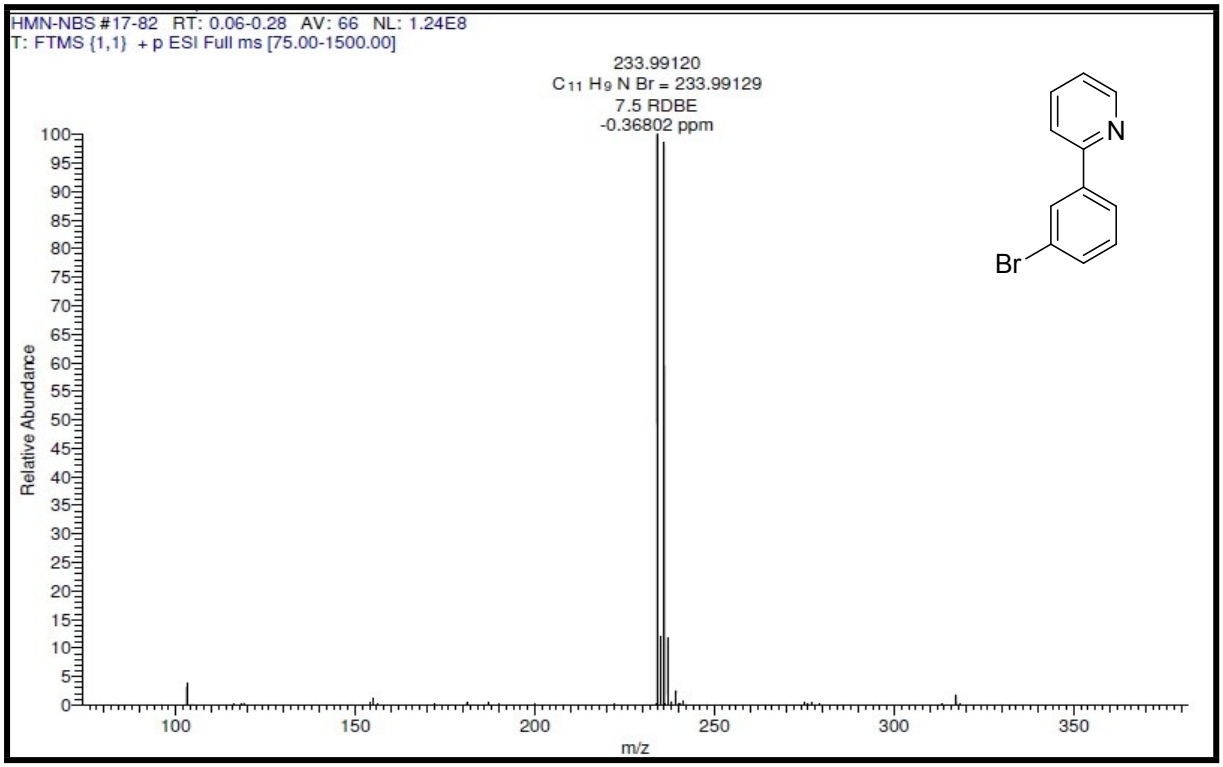
^{1}H NMR spectra of product 2x (Table 2)



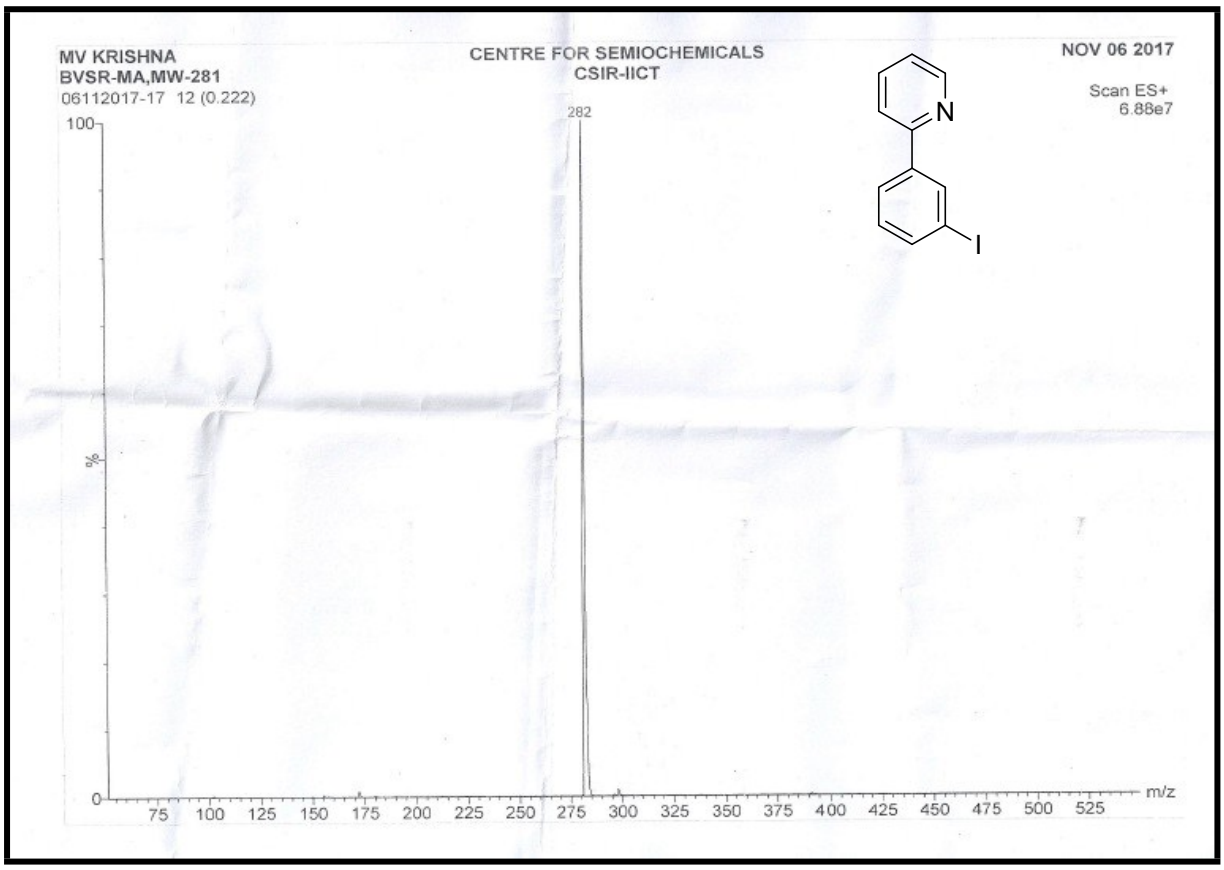
^{13}C NMR spectra of product 2x (Table 2)



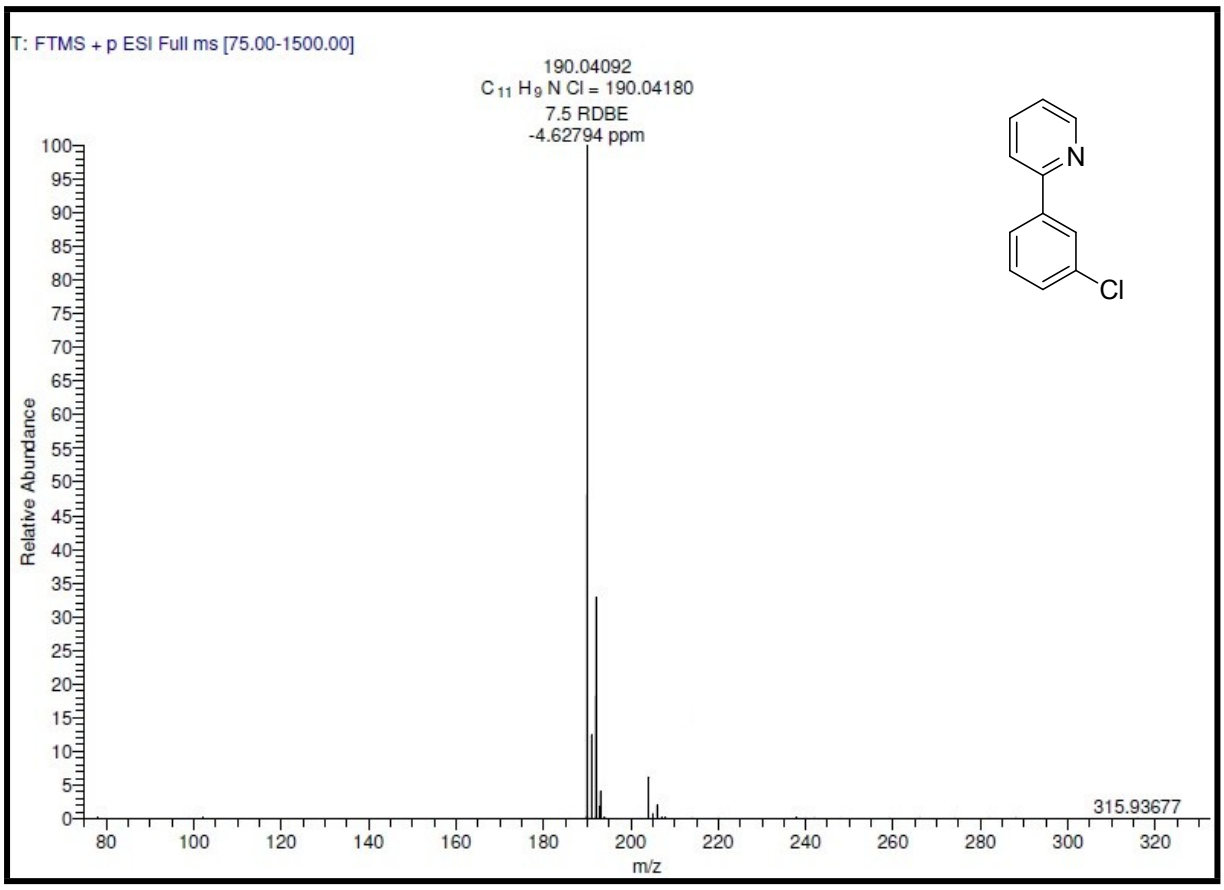
HRMS spectra of product 2a



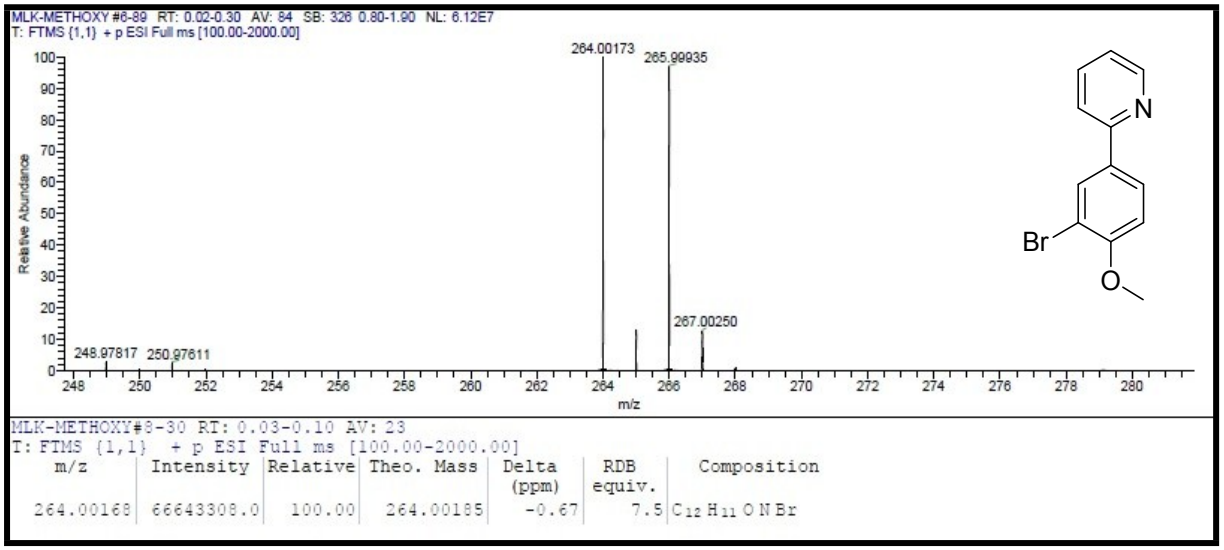
ESI mass spectra of product 2b



HRMS spectra of product 2c



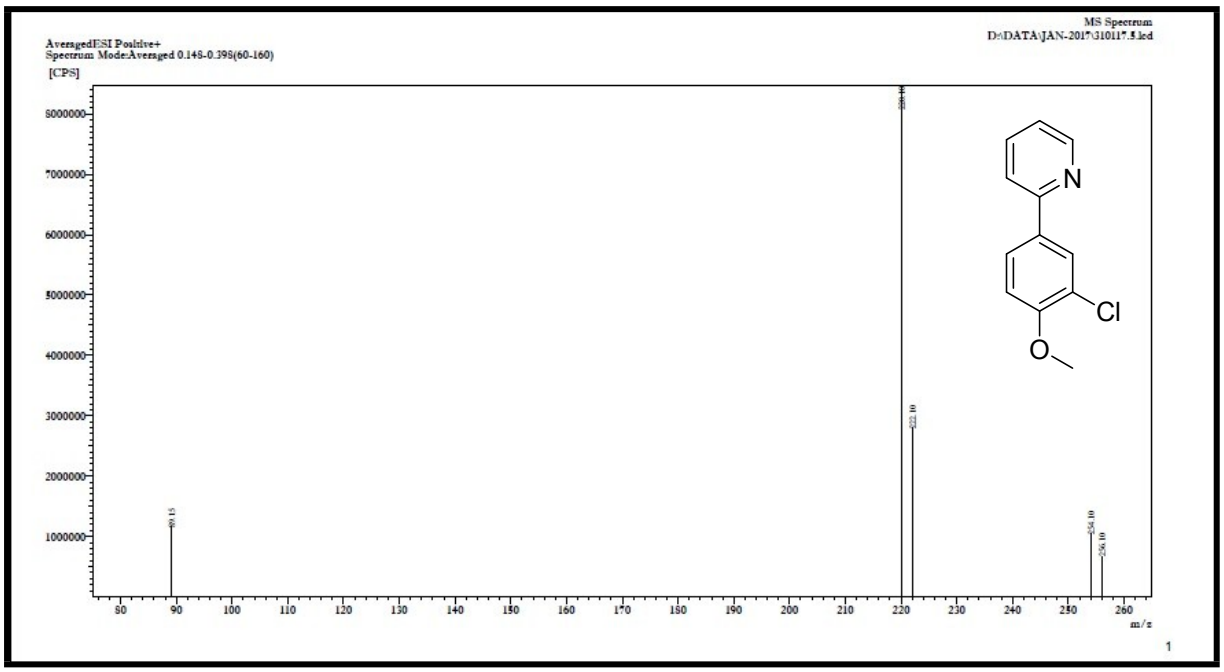
HRMS spectra of product 2d



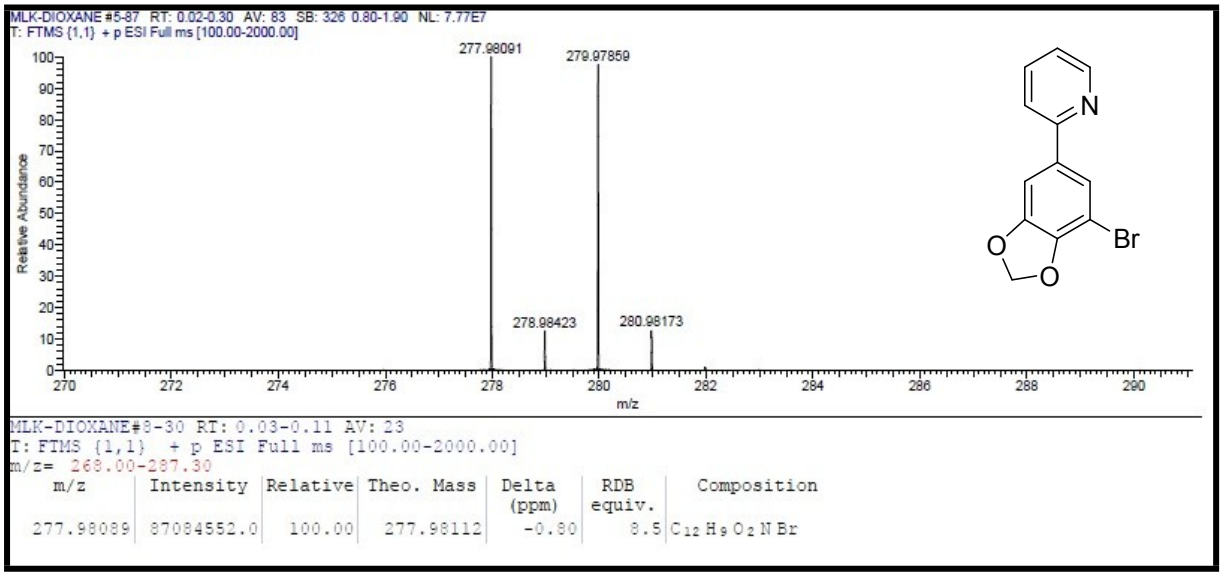
MLK-METHOXY#8-30 RT: 0.03-0.10 AV: 23
T: FTMS {1,1} + p ESI Full ms [100.00-2000.00]

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
264.00168	66643308.0	100.00	264.00185	-0.67	7.5	$C_{12}H_{11}ONBr$

ESI mass spectra of product 2e



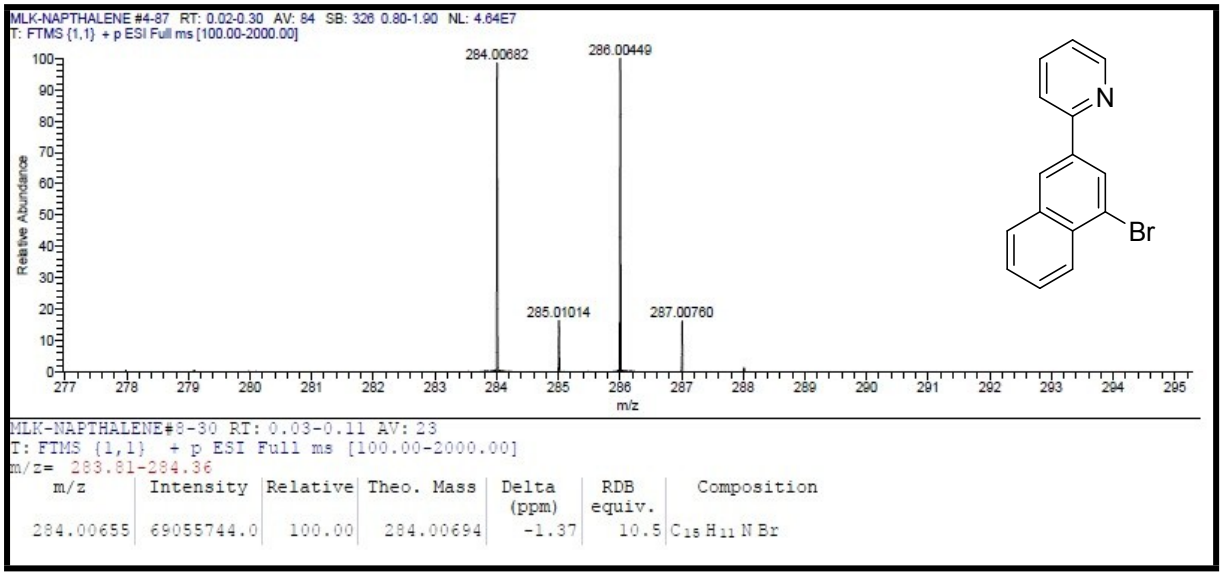
HRMS spectra of product 2f



MLK-DIOXANE#8-30 RT: 0.03-0.11 AV: 23
T: FTMS {1,1} + p ESI Full ms [100.00-2000.00]
m/z= 268.00-287.30

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
277.98089	87084552.0	100.00	277.98112	-0.80	8.5	$C_{12}H_9O_2NBr$

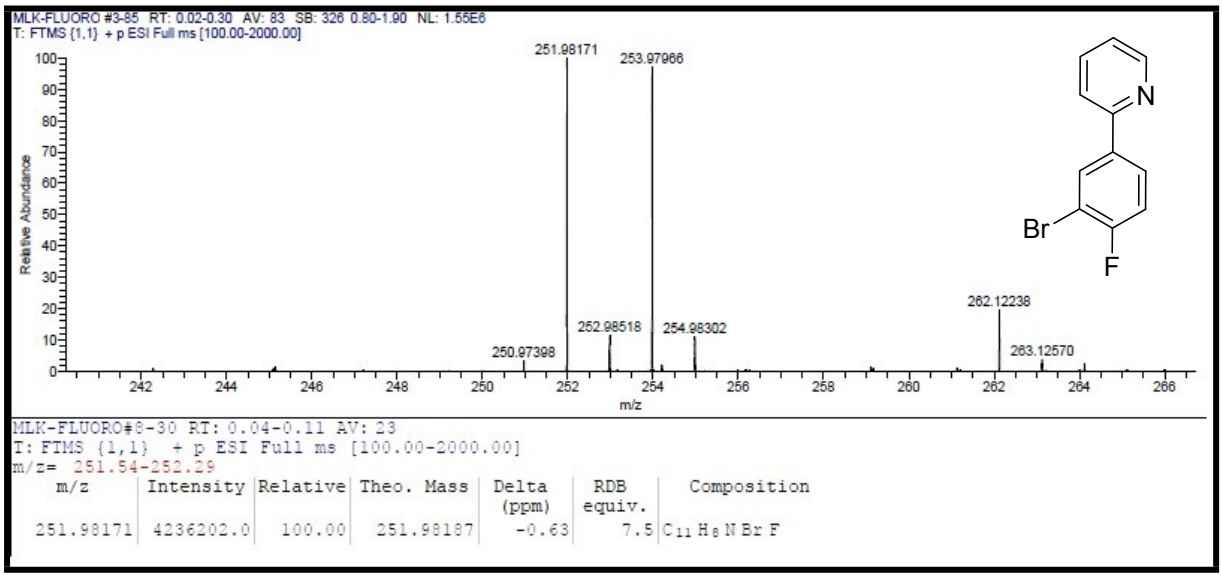
HRMS spectra of product 2g



MLK-NAPTHALENE#8-30 RT: 0.03-0.11 AV: 23
T: FTMS {1,1} + p ESI Full ms [100.00-2000.00]
m/z= 283.81-284.36

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
284.00655	69055744.0	100.00	284.00694	-1.37	10.5	$C_{15}H_{11}NBr$

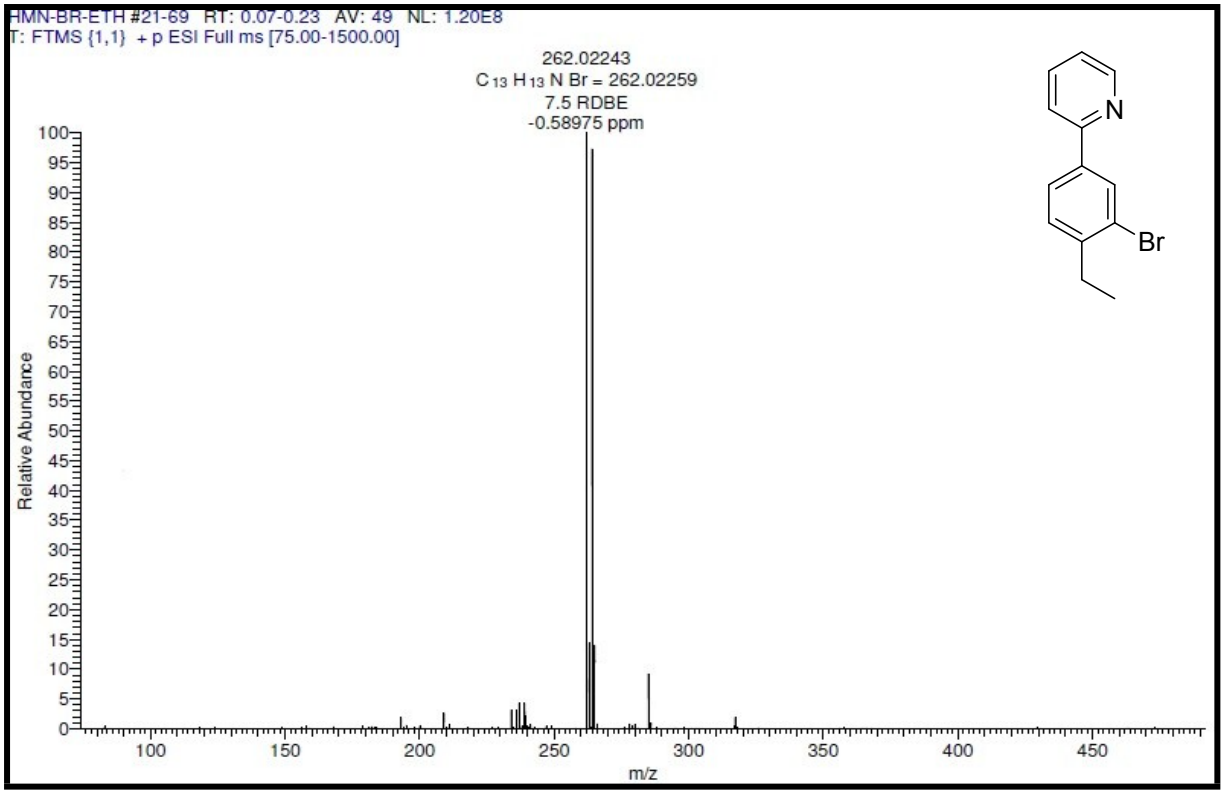
HRMS spectra of product 2h



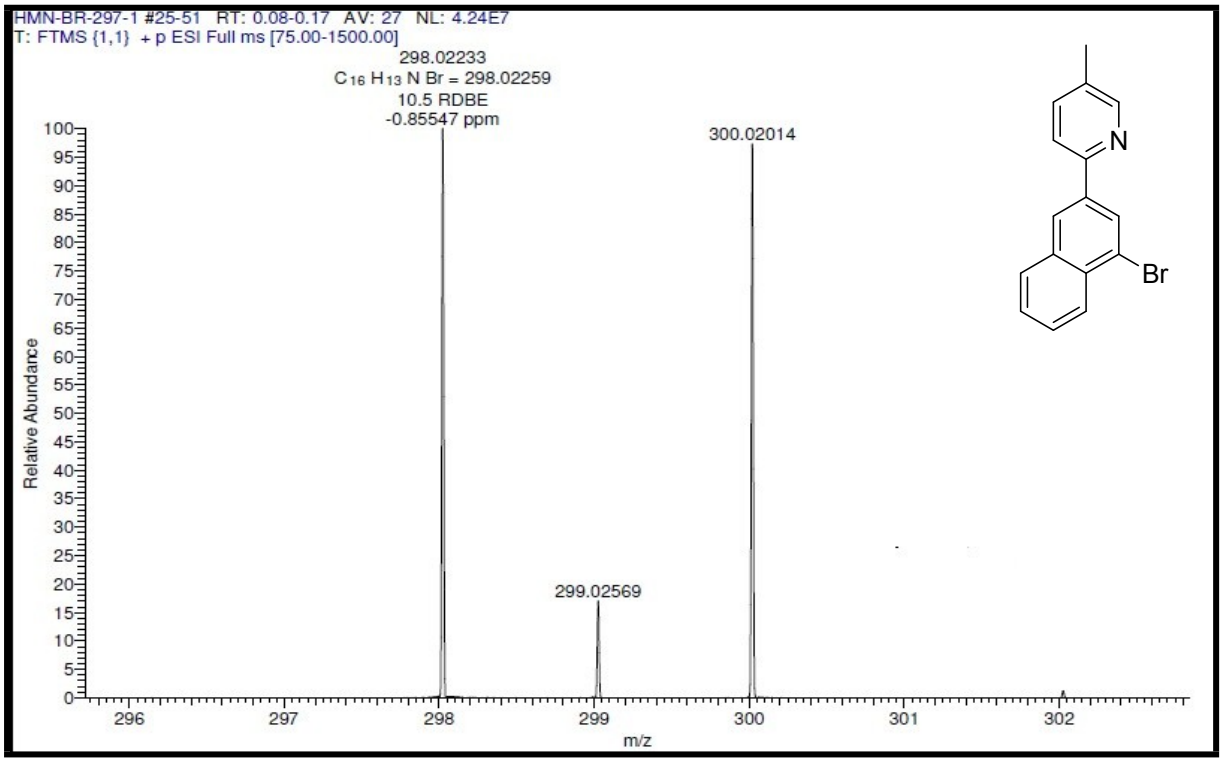
MLK-FLUORO#8-30 RT: 0.04-0.11 AV: 23
T: FTMS {1,1} + p ESI Full ms [100.00-2000.00]
m/z= 251.54-252.29

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
251.98171	4236202.0	100.00	251.98187	-0.63	7.5	$C_{11}H_{8}NBrF$

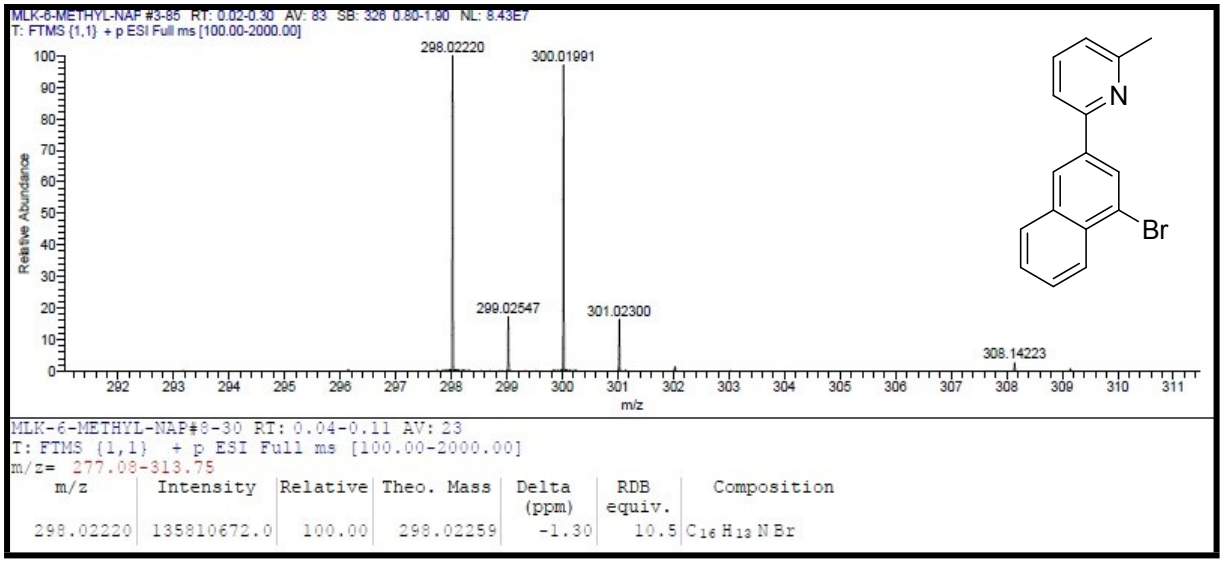
HRMS spectra of product 2i



HRMS spectra of product 2j

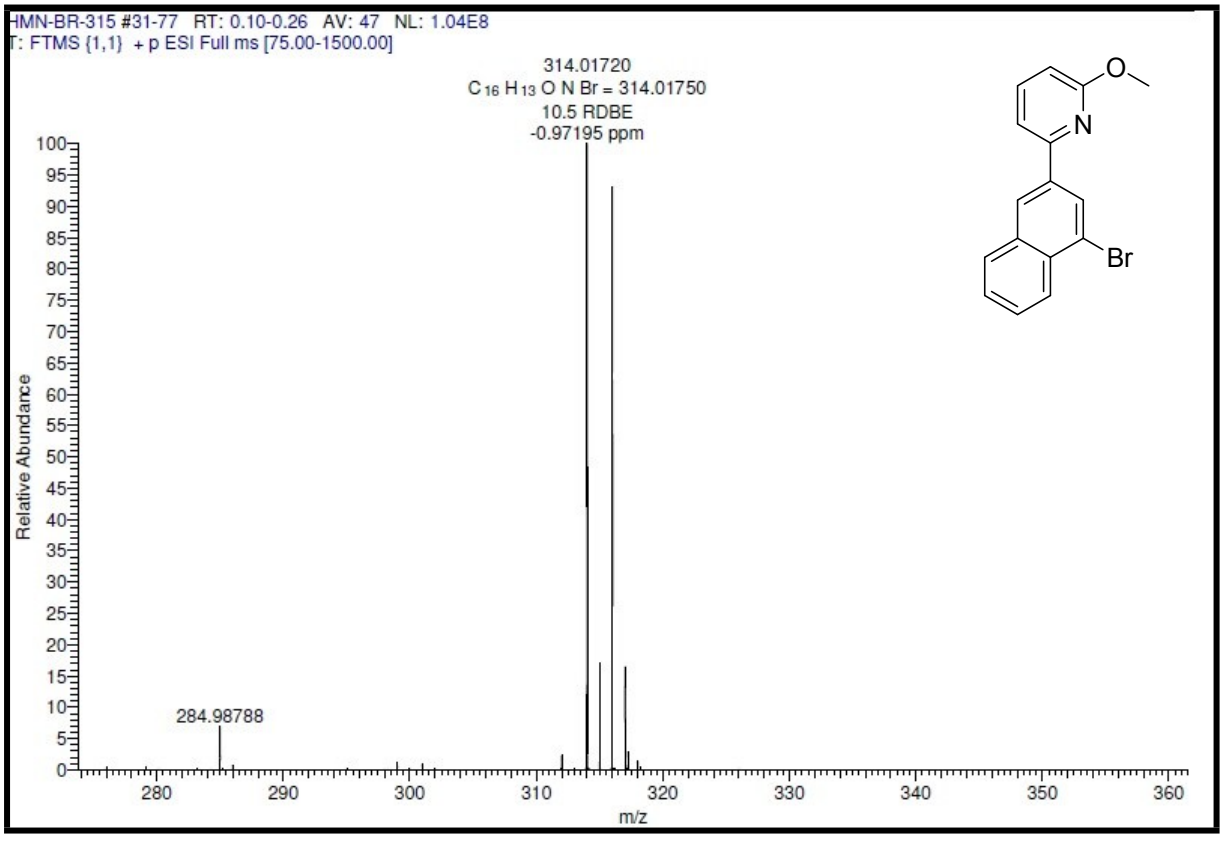


HRMS spectra of product 2k

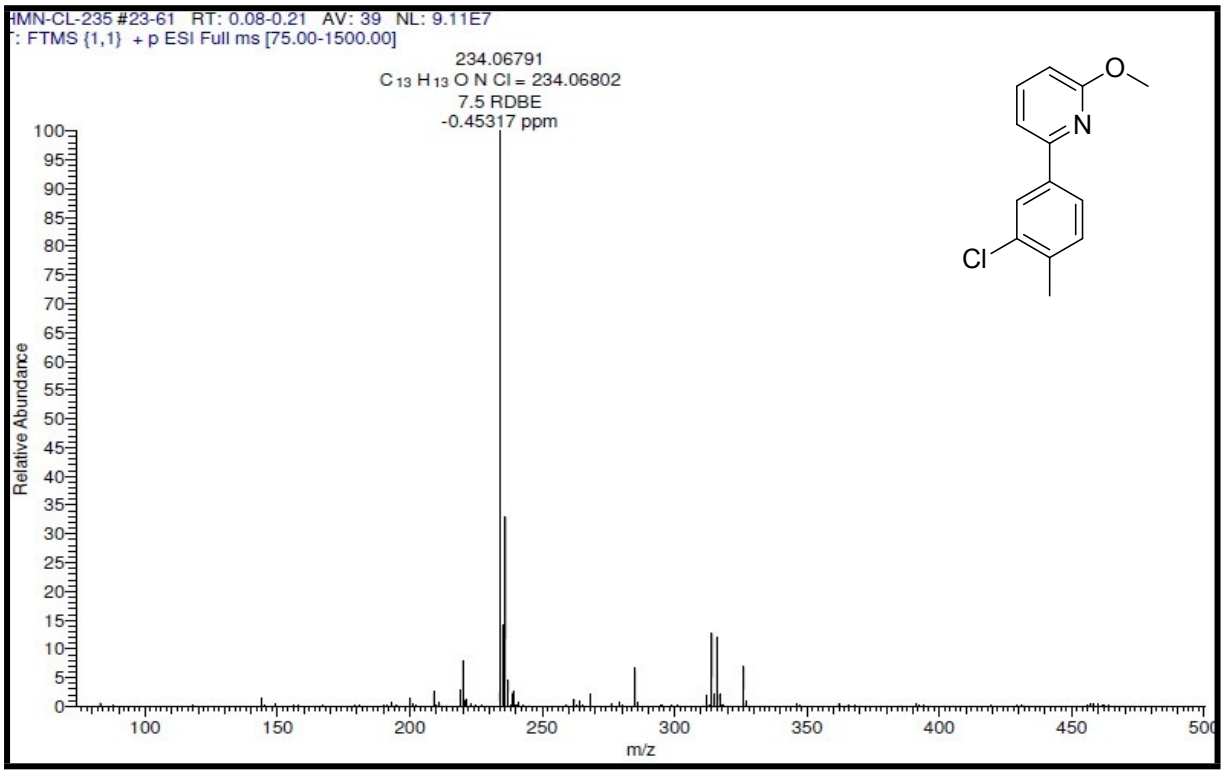


m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
298.02220	135810672.0	100.00	298.02259	-1.30	10.5	$C_{16}H_{13}NBr$

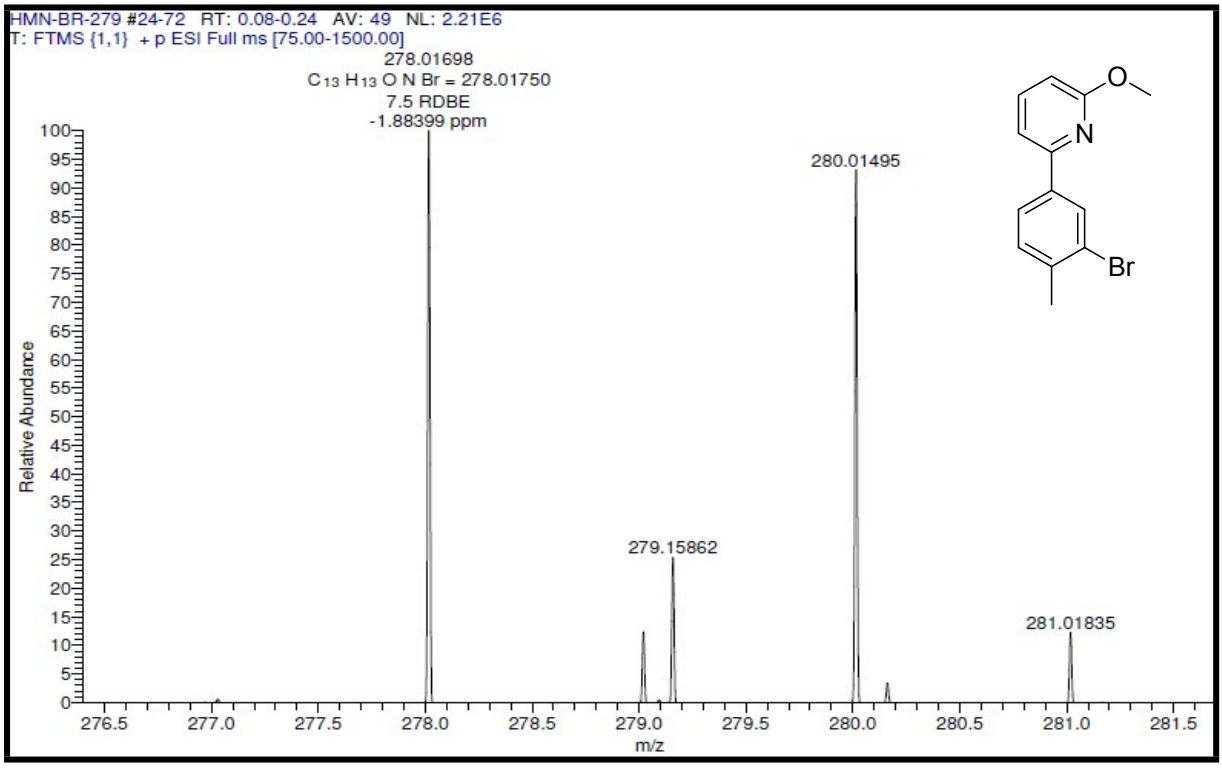
HRMS spectra of product 2l



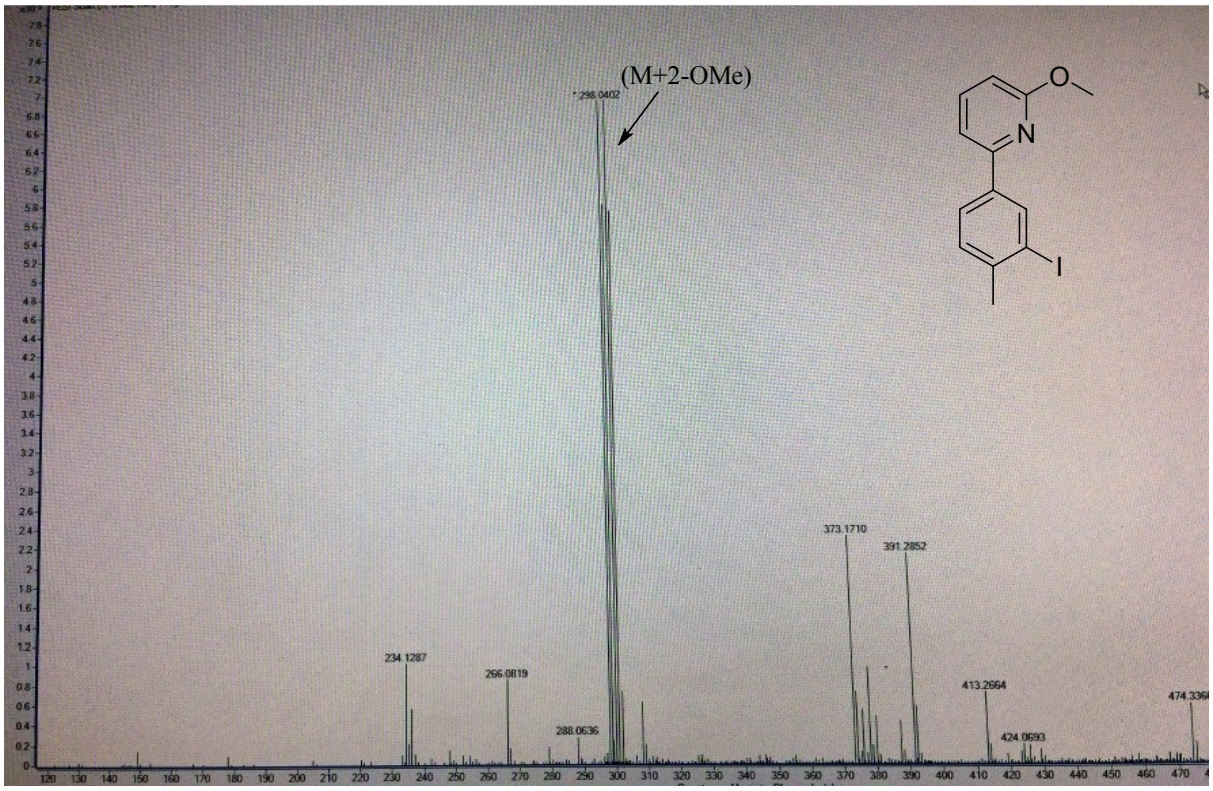
HRMS spectra of product 2m



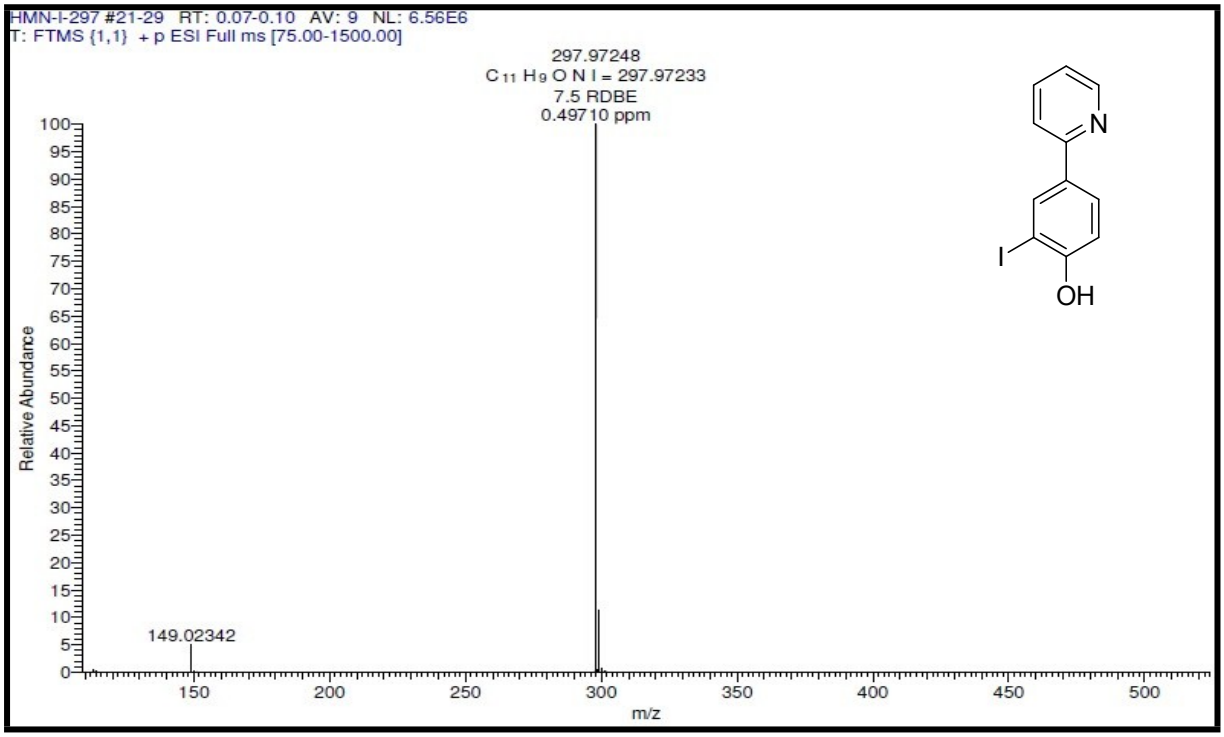
HRMS spectra of product 2n



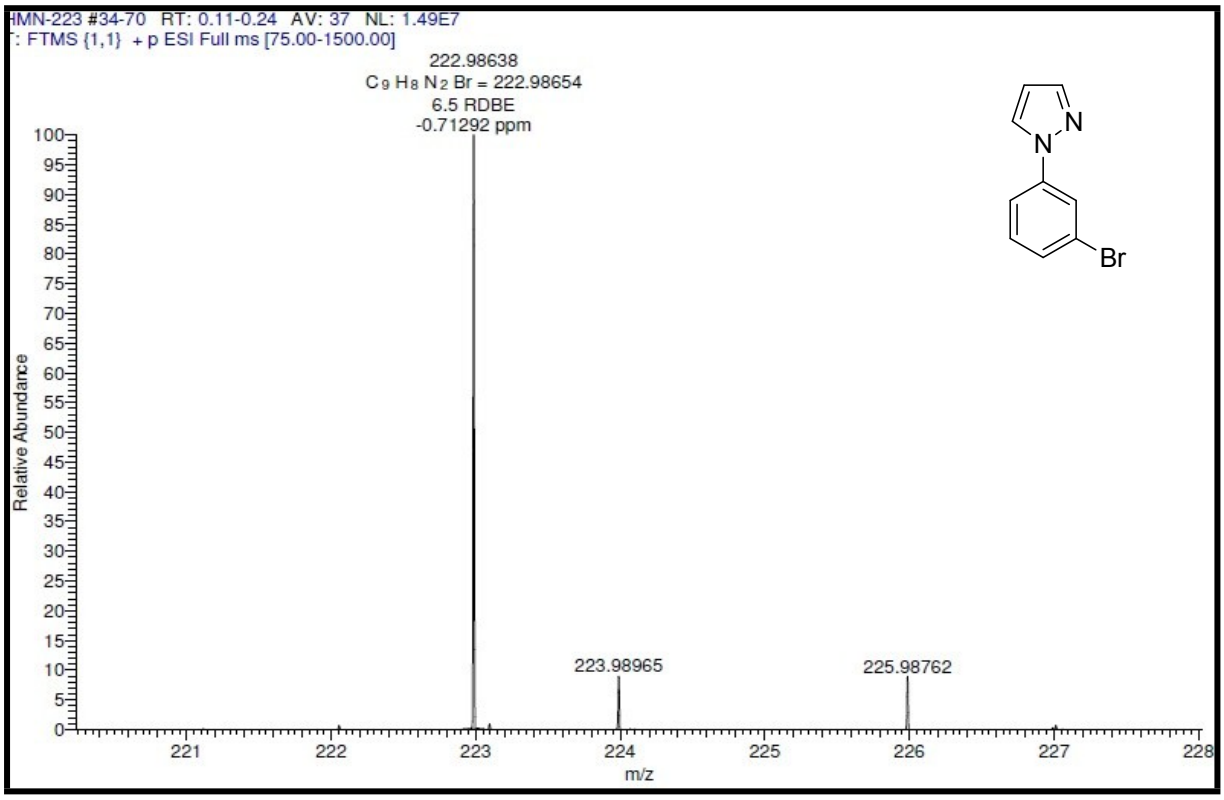
ESI mass spectra of product 2o



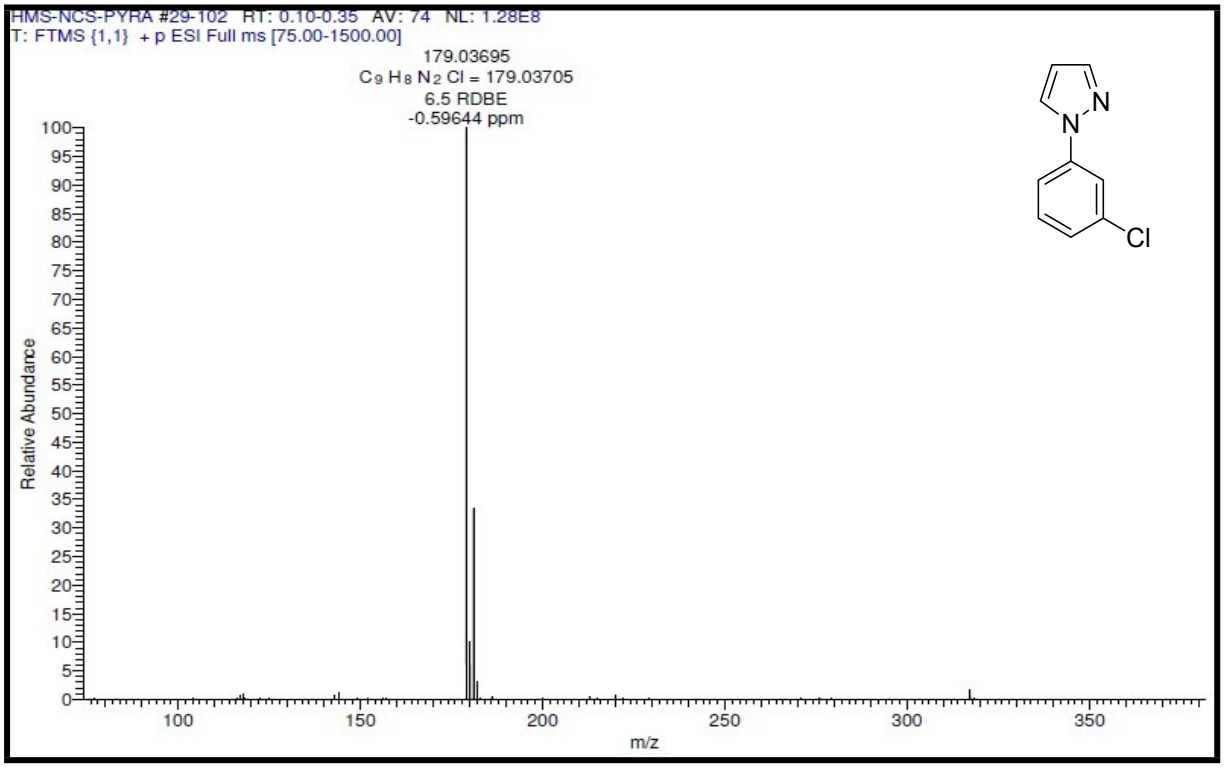
HRMS spectra of product 2p



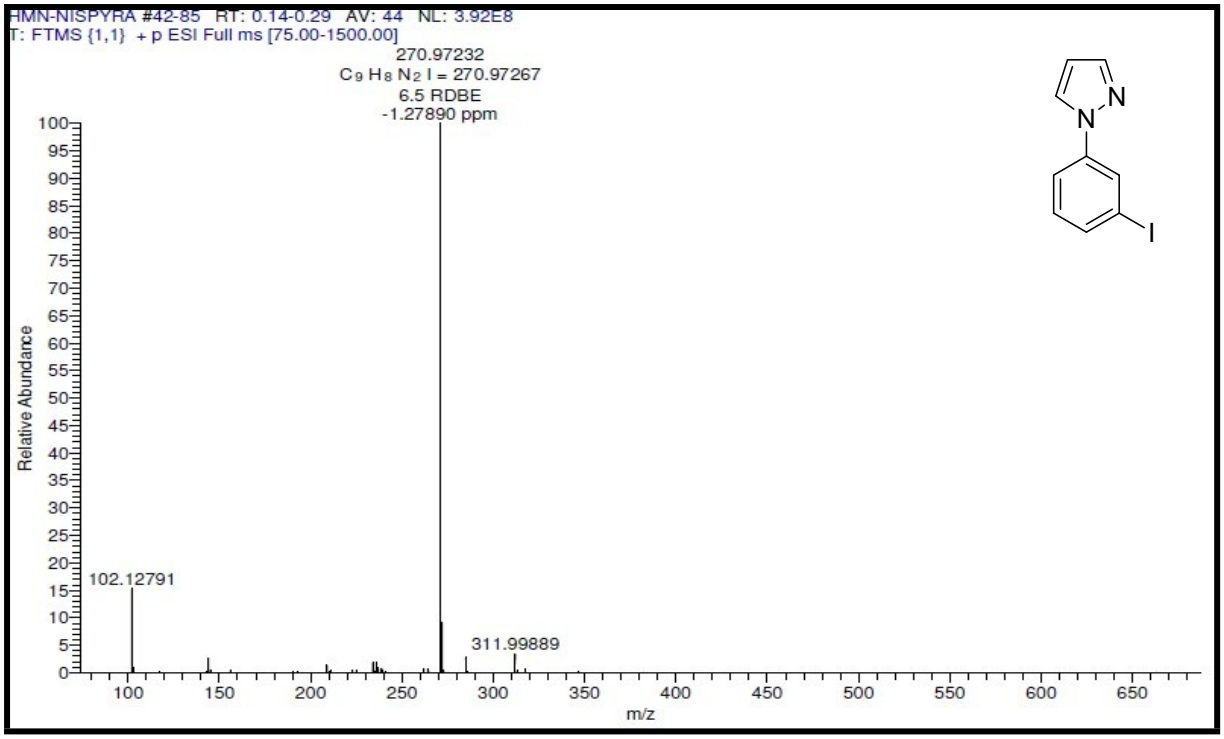
HRMS spectra of product 2q



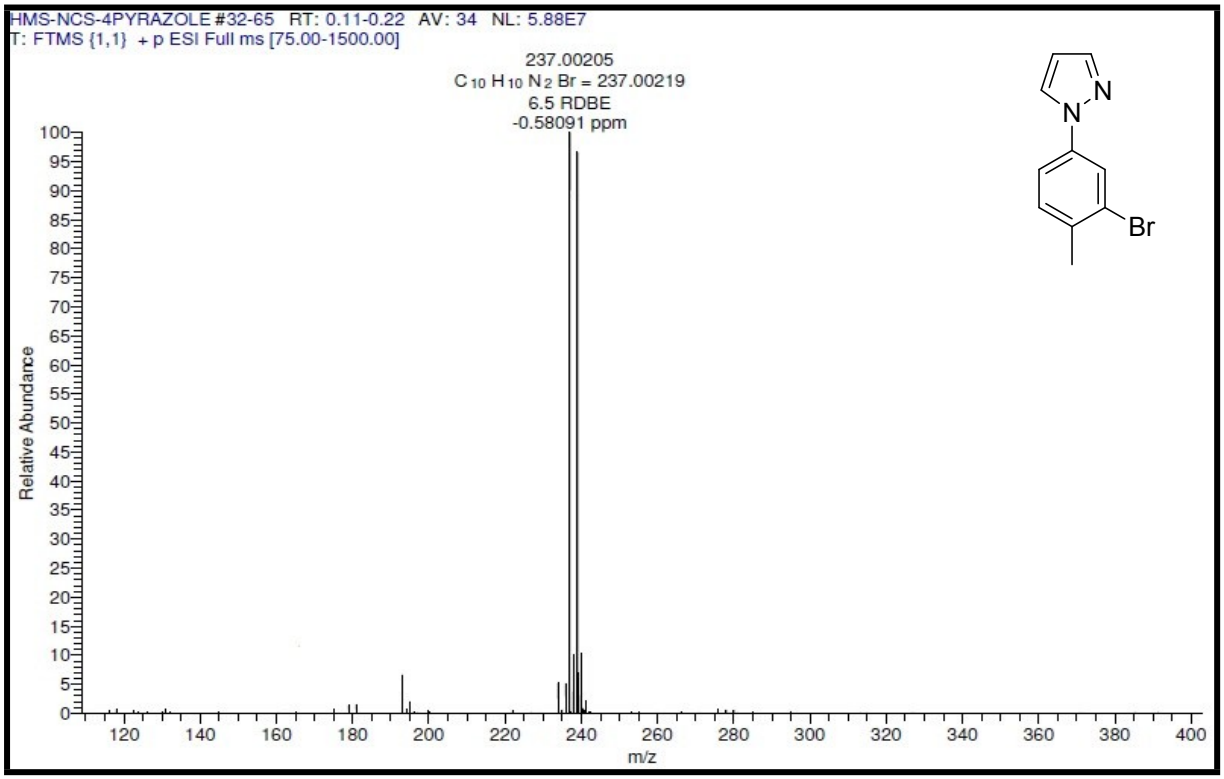
HRMS spectra of product 2r



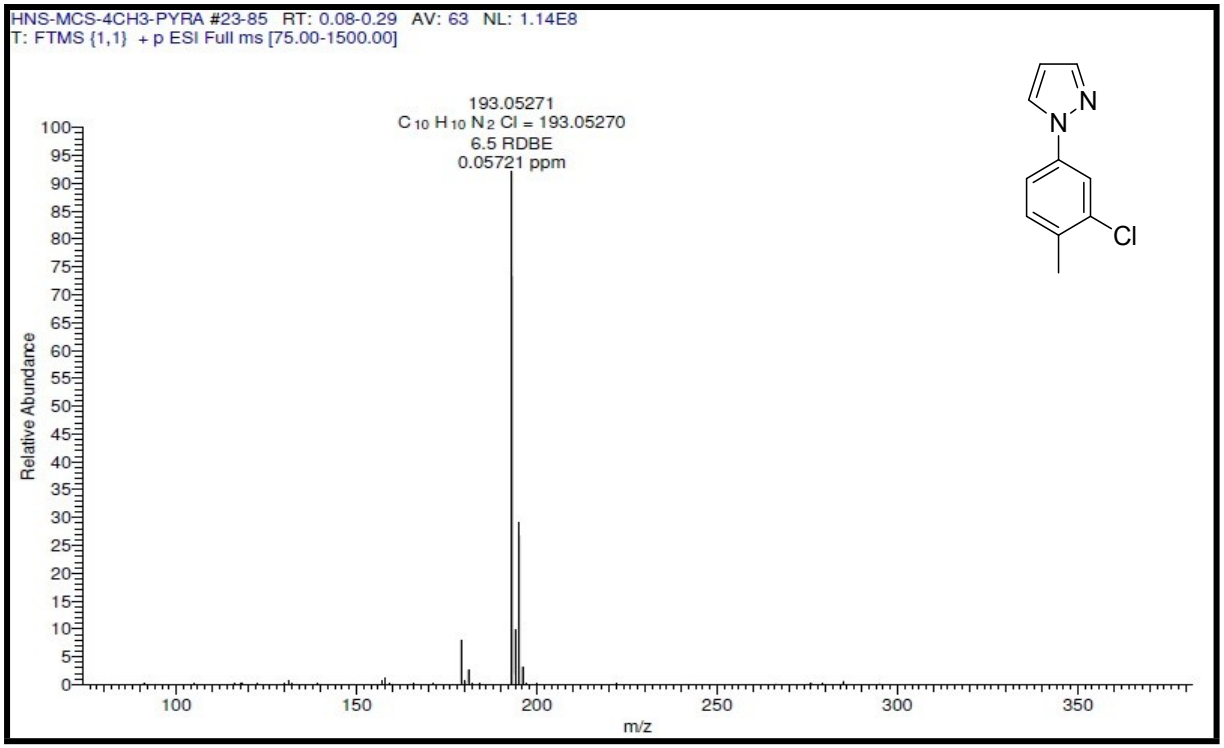
HRMS spectra of product 2s



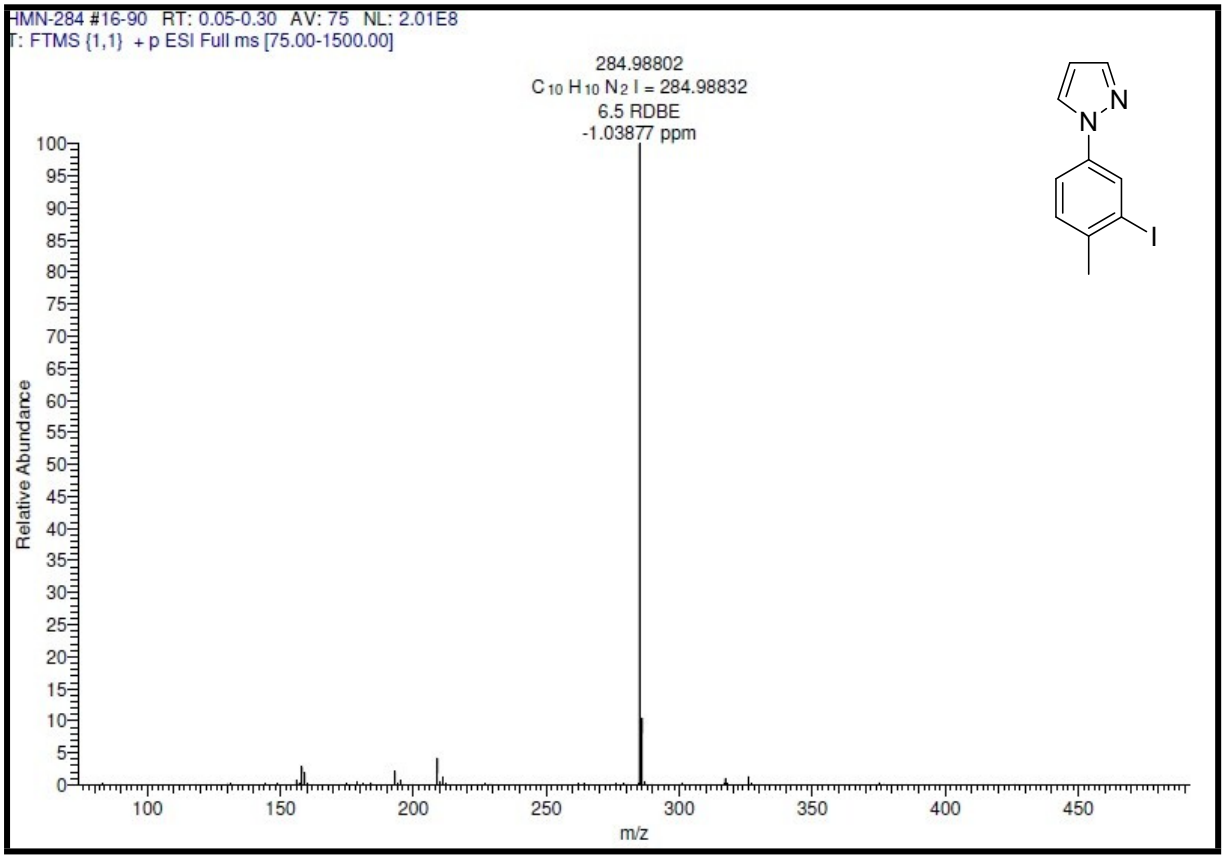
HRMS spectra of product 2t



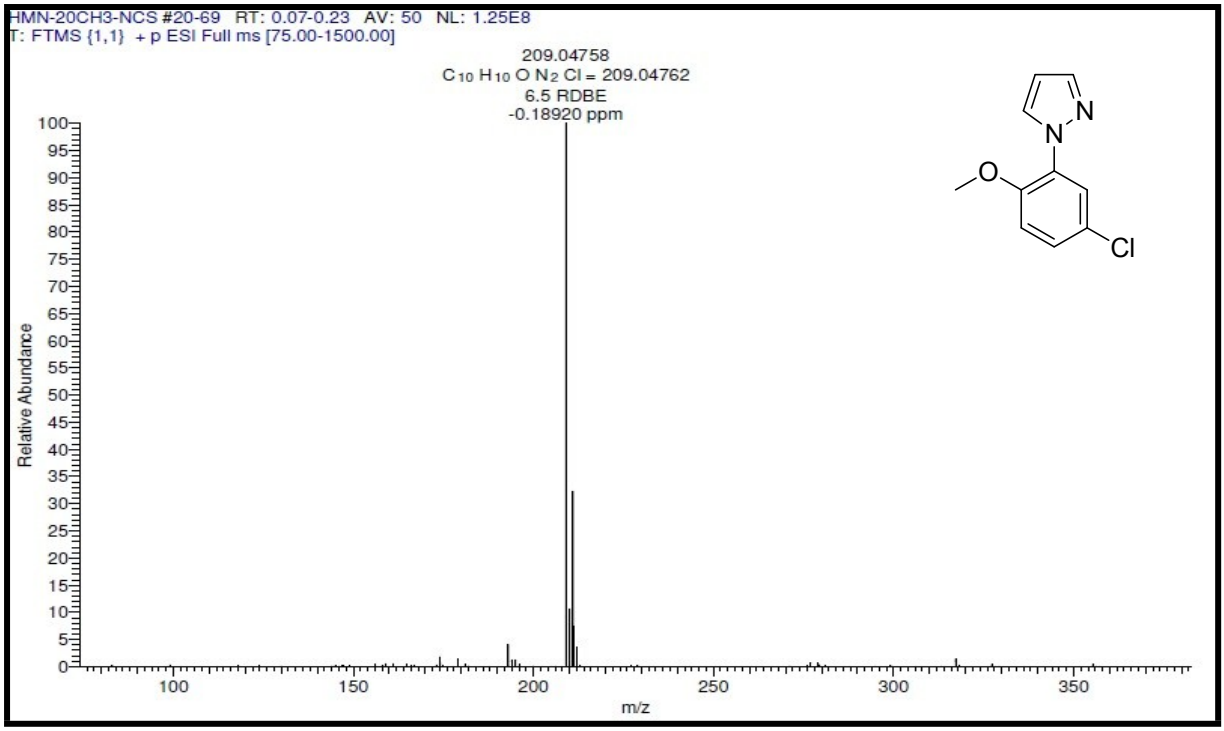
HRMS spectra of product 2u



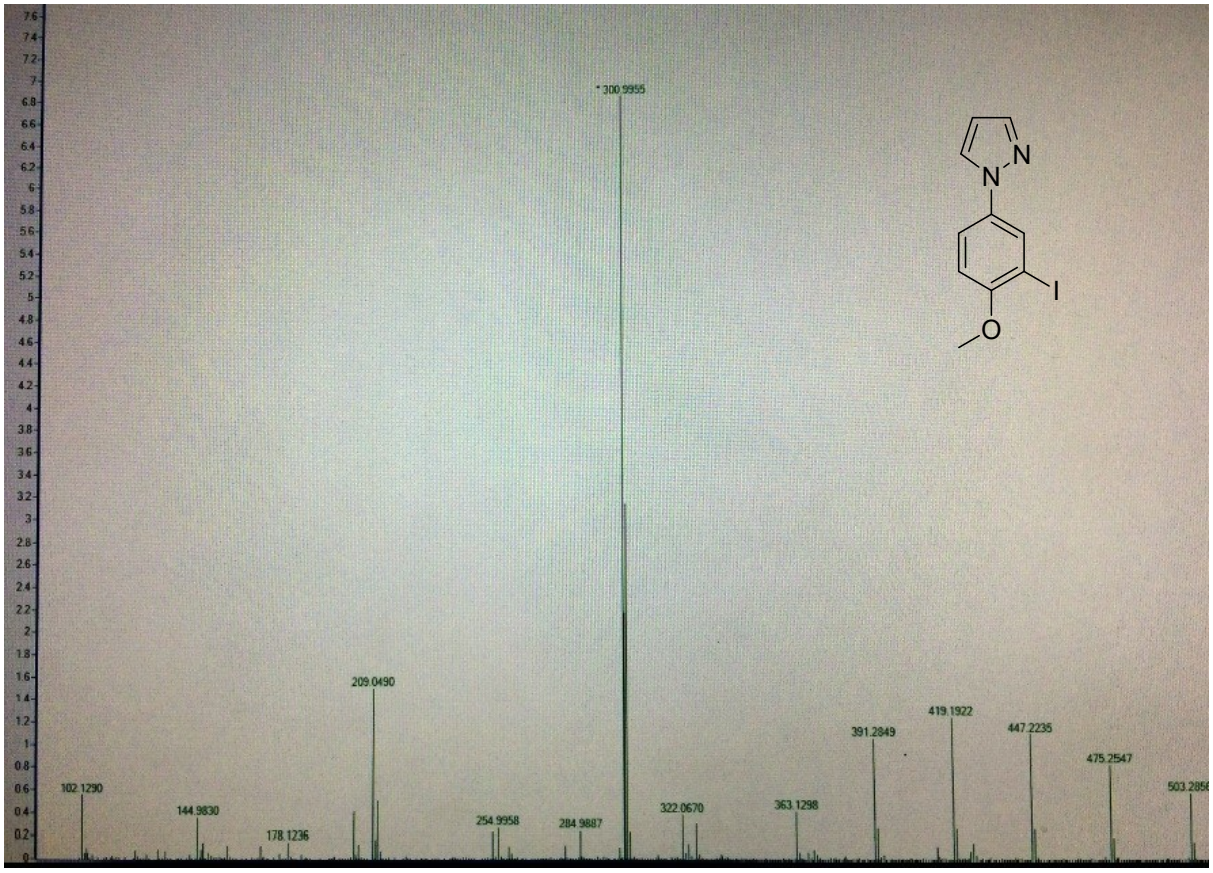
HRMS spectra of product 2v



HRMS spectra of product 2w



ESI mass spectra of product 2w



X-ray structural data for product **2d**.

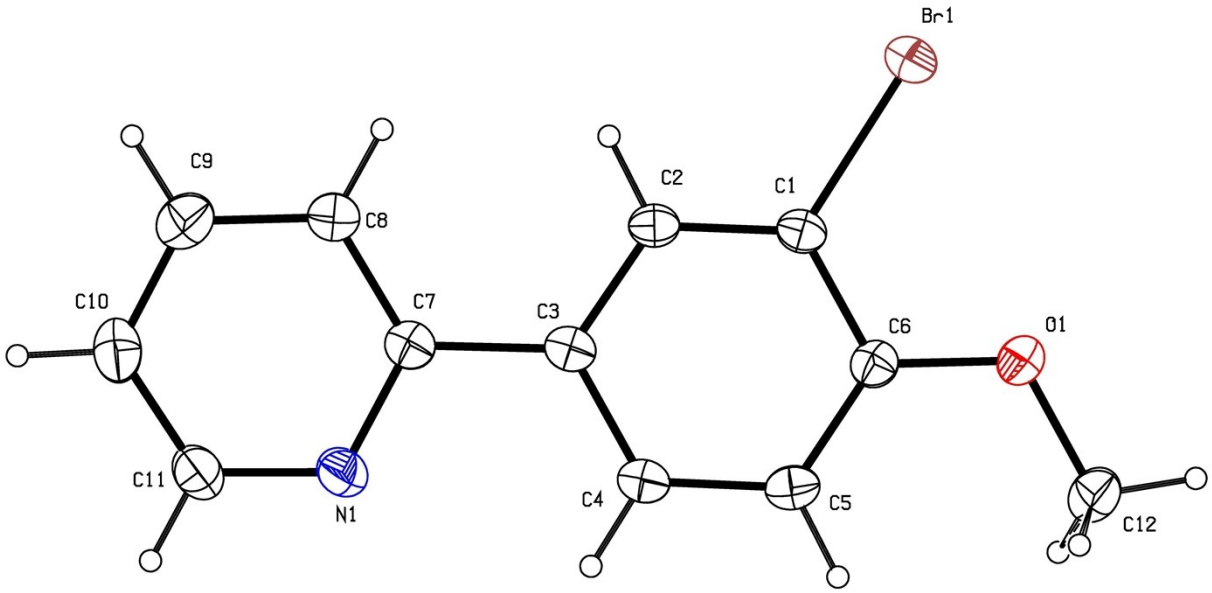
X-ray data were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method.[1] Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS[2] and refinement was carried out by full-matrix least-squares technique using SHELXL.[2] Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(c)$ for other H atoms]. The methyl groups were allowed to rotate but not to tip.

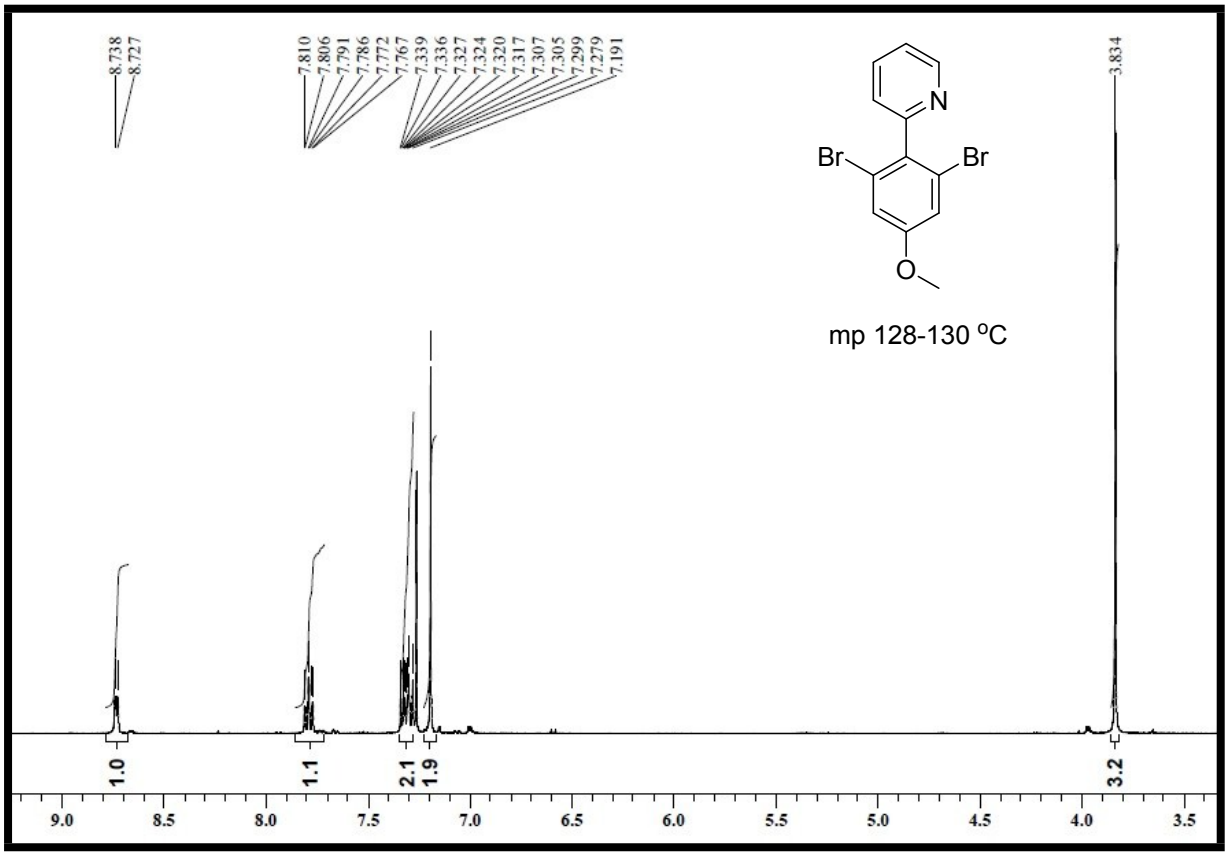
Crystal Data for AY21: $C_{12}H_{10}NBrO$ (M =264.12 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 12.062(3) Å, b = 4.0452(9) Å, c = 21.707(5) Å, β = 90.12(2)°, V = 1059.2(4) Å^3, Z = 4, T = 294.15 K, μ(MoKα) = 3.851 mm^{-1}, *Dcalc* = 1.656 g/cm^3, 8894 reflections measured (3.376° ≤ 2Θ ≤ 56.856°), 2177 unique (R_{int} = 0.0728, R_{sigma} = 0.1088) which were used in all calculations. The final R_1 was 0.0416 (I > 2σ(I)) and wR_2 was 0.0822 (all data). CCDC 1585913 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

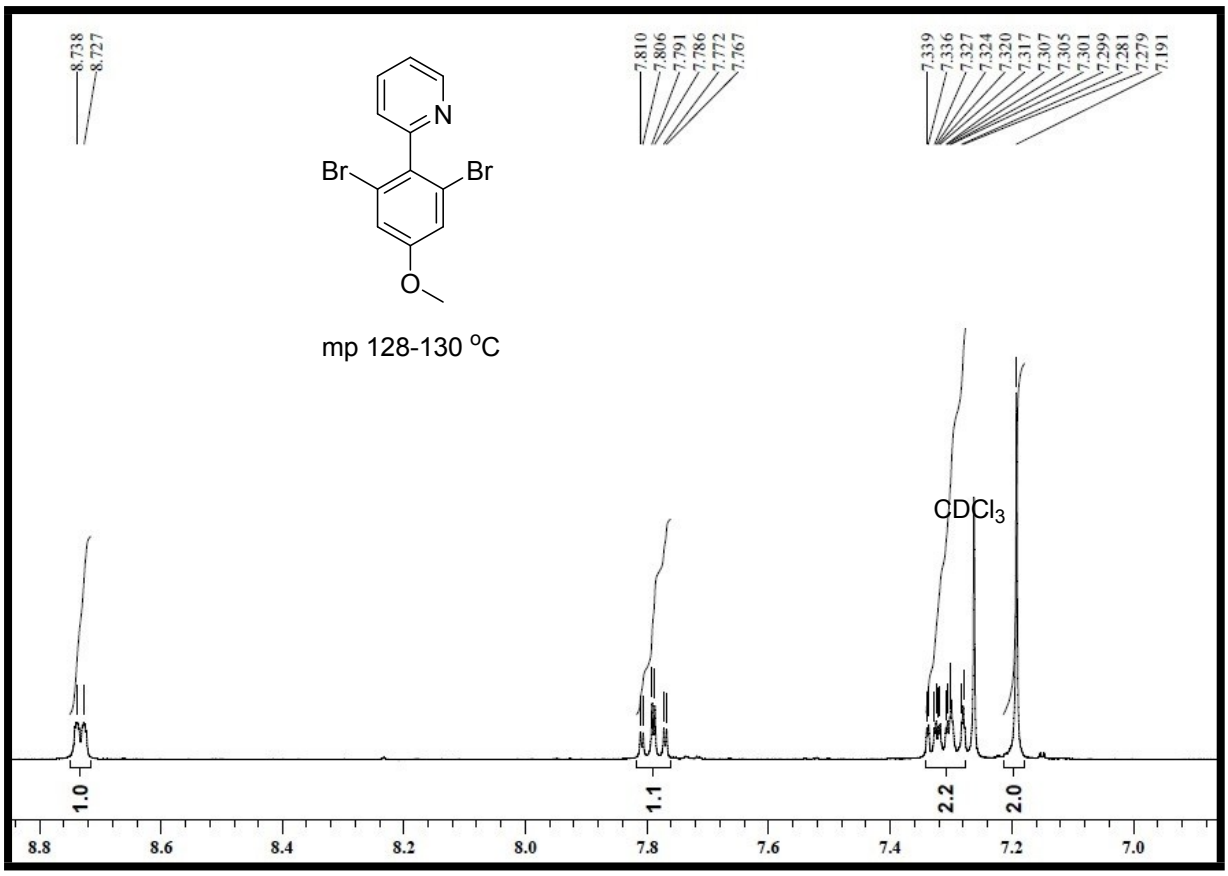
1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. Sheldrick, G. M. (2015). Acta Cryst. C71, 3–8.

Figure caption: The molecular structure of AY61, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.



Scheme 2: NMR and Mass spectral characterization of data for direct C-H bromination of substrate **2d** in the presence of D_2O giving rise to *ortho*-dibrominated product **2d'** .

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7.281
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1.1
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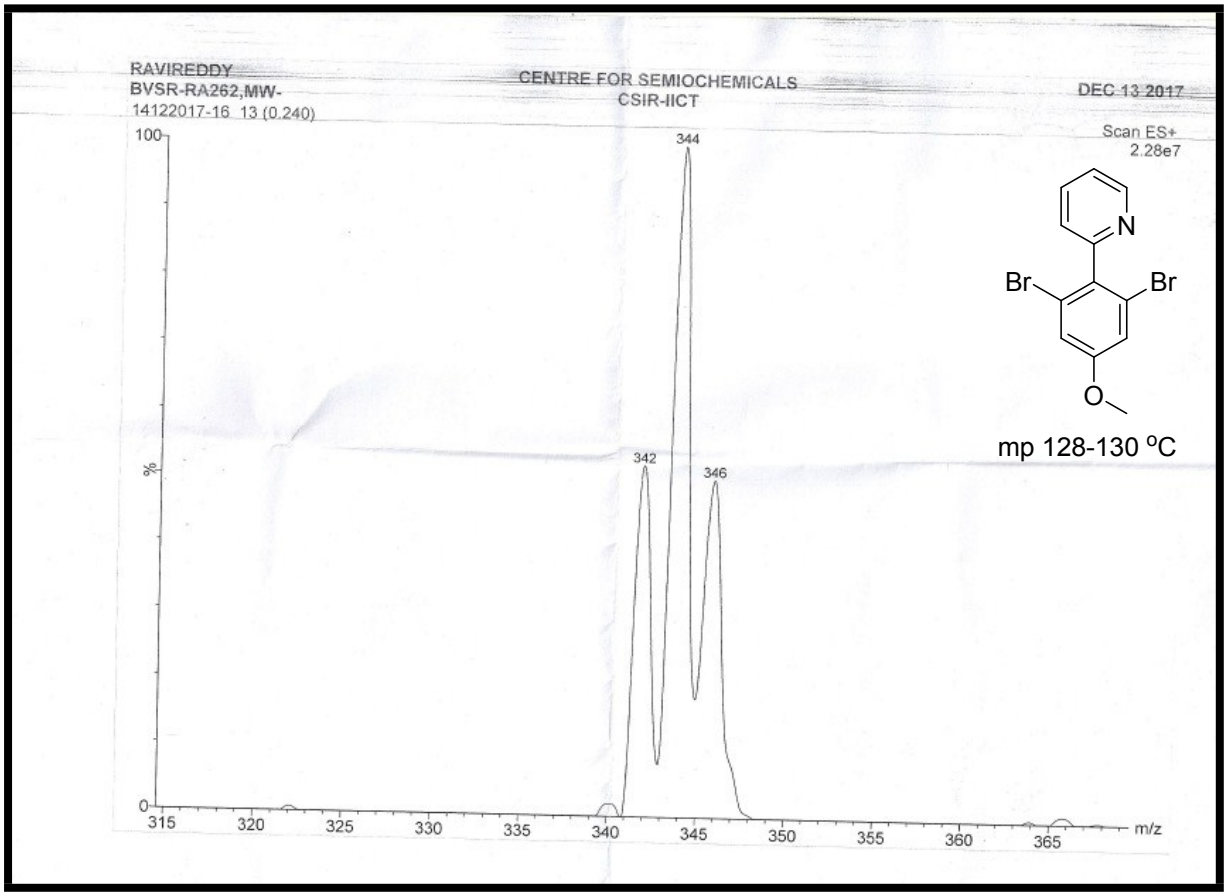
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