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Supporting Information

Organocatalytic Mannich/cyclization/aromatization sequence: direct synthesis of substituted pyrrole-3-carboxaldehydes

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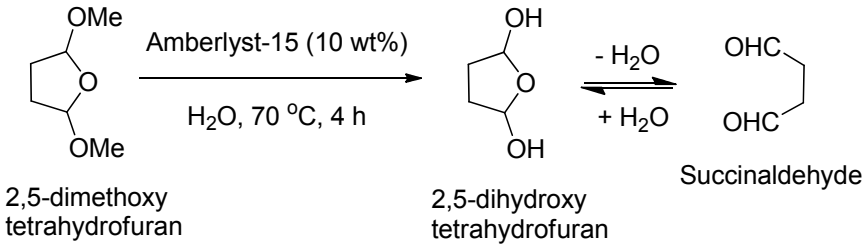
General Experimental Methods

All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on SiO_2 gel F254 plates. The column chromatography was performed on silica gel (100-200 meshes) using mixture of EtOAc and petroleum ether (60-80 ^oC). All other reagents were of analytical grade and used without further purification. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. High resolution mass spectra were recorded using quadrupole electrospray ionization (ESI) technique.

Preparation of succinaldehyde 3 (3M sol.):

To a stirred solution of 2,5-dimethoxy tetrahydrofuran (2.0 g, 15.15 mmol) in H_2O (5.0 mL) was added Amberlyst-15 (10 wt%) and further heated at 70 ^oC for 4 h in an open flask. The resulting solution was cooled to rt and used directly for the said reaction.



Typical procedure for the synthesis of pyrrole-3-carboxaldehydes (4): Succinaldehyde **3** (0.3 mL, 0.9 mmol, 3M solution) was added to a mixture of preformed *N*-PMP aldimine **2** (0.3 mmol) and L-proline (7.0 mg, 0.06 mmol) in DMSO (3.0 mL) at room temperature. The reaction mixture was stirred at room temperature until the aldimine was consumed as monitored by TLC.

The reaction was quenched with saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (6 mL) with three times. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude adduct was taken in Toluene (3 mL) and CH_3CO_2H (50 mol%, 9 μL) and then DDQ (75 mg, 0.33 mmol) was added. The reaction mixture was stirred and heated at 70 ^oC for 2 h and cooled to room temperature. The reaction was quenched with saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (5 mL) twice and combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification through silica gel column chromatography by eluting the mixture of EtOAc/ hexane, gave pyrrole 3-carbxaldehydes **4** with 58-82% yields. In almost all the cases, we also obtained about <10% initial starting aldehyde due to cleavage of corresponding imine under these conditions.

1-(4-methoxyphenyl)-2-(3-nitrophenyl)-1*H*-pyrrole-3-carbaldehyde (4a): (75 mg, 78%, semi-solid) ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.73 (s, 3H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 3.0 Hz, 1H), 6.87 (d, *J* = 3.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 7.41-7.49 (m, 2H), 8.01 (t, *J* = 1.4 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 9.65 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.51, 108.85, 114.65 (2C), 123.26, 124.97, 125.59, 125.82, 127.32 (2C), 129.29, 130.87, 131.15, 136.65, 138.27, 147.95, 159.33, 186.01; IR (KBr)/cm^{-1} 2920, 1746, 1680, 1244, 1172; HRMS (ESI): Calcd for $C_{18}H_{14}N_2O_4$ (MH^+) 323.1032; Found 323.1013.

1-(4-methoxyphenyl)-2-(4-nitrophenyl)-1*H*-pyrrole-3-carbaldehyde (4b): (79 mg, 82%, pale yellow pasty liquid); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 3.0 Hz, 1H), 6.94 (d, *J* = 3.0 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 2H), 9.73 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.48, 109.06, 114.63 (2C),

123.40 (2C), 125.17, 126.15, 127.13 (2C), 130.96, 131.60 (2C), 135.99, 138.24, 147.40, 159.30, 186.01; IR (KBr)/cm^{-1} 2933, 1724, 1660, 1249, 1174; HRMS (ESI): Calcd for $C_{18}H_{14}N_2O_4$ (MH^+) 323.1032; Found 323.1060.

2-(2-chlorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrole-3-carbaldehyde (4c): (64 mg, 69%, gummy liquid) ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.76 (s, 3H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 3.0 Hz, 1H), 6.92 (d, *J* = 3.0 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 7.28-7.32 (m, 2H), 7.35-7.37 (m, 2H), 9.51 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.42, 107.66, 114.17 (2C), 114.84, 122.81, 124.75, 125.12, 126.56 (2C), 129.80, 130.59, 131.56, 133.50, 135.42, 139.00, 158.88, 186.30; IR (KBr)/cm^{-1} 2918, 1726, 1680, 1246, 1172; HRMS (ESI): Calcd for $C_{18}H_{14}ClNO_2$ (MH^+) 312.0791; Found 312.0798.

2-(3-chlorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrole-3-carbaldehyde (4d): (69 mg, 74%, semi-solid), ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 3.0 Hz, 1H), 6.90 (d, *J* = 3.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 1.6 Hz, 1H), 7.23-7.28 (m, 2H), 8.32 (d, *J* = 8.0 Hz, 1H), 9.70 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.44, 107.91, 114.38 (2C), 124.67, 125.29, 127.04 (2C), 128.67, 129.03, 129.46, 130.81, 131.03, 131.27, 134.16, 140.30, 158.97, 186.58; IR (KBr)/cm^{-1} 2920, 1714, 1666, 1246, 1173; HRMS (ESI): Calcd for $C_{18}H_{14}ClNO_2$ (MH^+) 312.0791; Found 312.0792.

2-(4-chlorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrole-3-carbaldehyde (4e): (72 mg, 77%, gummy liquid), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 3.4 Hz, 1H), 6.87 (d, *J* = 3.4 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 9.67 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.47, 108.09, 114.44 (2C), 122.74, 123.09, 124.55, 125.26, 127.13 (2C), 128.24, 131.55 (2C), 132.37 (2C), 140.68, 159.01, 186.63; HRMS (ESI): Calcd for $C_{18}H_{14}ClNO_2$ (MH^+) 312.0791; Found 312.0789.

2-(2-fluorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrole-3-carbaldehyde (4f): (63 mg, 71%, gummy liquid), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 3.0 Hz, 1H), 6.93 (d, *J* = 3.0 Hz, 1H), 6.99-7.06 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 1.6 Hz, 1H), 7.24-7.27 (m, 1H), 7.34-7.36 (m, 1H), 9.61 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.43, 108.01, 114.23 (2C), 115.06, 115.90, 116.07, 124.05, 125.31, 126.57 (2C), 131.23, 131.79, 133.23, 135.79, 158.98, 161.23, 186.36; IR (KBr)/cm^{-1} 2908, 1730, 1680, 1247, 1174; HRMS (ESI): Calcd for $C_{18}H_{14}FNO_2$ (MH^+) 296.1087; Found 296.1094.

2-(4-fluorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrole-3-carbaldehyde (4g): (67 mg, 76%, gummy liquid), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 3.0 Hz, 1H), 6.86 (d, *J* = 3.0 Hz, 1H), 6.97-7.02 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.17 (dd, *J* = 8.8 Hz, 4.9 Hz, 2H), 9.65 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.43, 107.83, 114.35 (2C), 115.37, 115.55, 124.51, 124.96 (2C), 127.12 (2C), 131.50, 132.69 (2C), 141.07, 158.94, 163.74, 186.65; IR (KBr)/cm^{-1} 2912, 1726, 1672, 1249, 1170; HRMS (ESI): Calcd for $C_{18}H_{14}FNO_2$ (MH^+) 296.1087; Found 296.1070.

2-(3-bromo-4-fluorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrole-3-carbaldehyde (4h): (77 mg, 76%, slightly yellow semi-solid), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.83 (d, *J* = 3.0 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 3.0 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.03-7.09 (m, 1H), 7.45 (dd, *J* = 6.6 Hz, 2.0 Hz, 2H), 9.67 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.49, 108.15, 114.50 (2C), 116.26, 116.48, 124.74, 125.29, 127.16 (2C), 131.13, 131.52, 135.87, 199.08, 157.86, 159.14, 160.35, 186.26; IR (KBr)/cm^{-1} 2910, 1714, 1681, 1246, 1181; HRMS (ESI): Calcd for $C_{18}H_{13}BrFNO_2$ (MH^+) 374.0192; Found 374.0235.

2-(4-bromophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrole-3-carbaldehyde (4i): (78 mg, 73%, amorphous solid), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.84 (d,

J = 3.2 Hz, 1H), 6.87 (d, *J* = 3.2 Hz, 1H), 6.99 (, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 9.67 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.15, 107.78, 114.13 (2C), 122.43, 122.77, 124.24, 124.95, 126.81 (2C), 127.92, 131.23 (2C), 132.06 (2C), 140.36, 158.70, 186.31; IR (KBr)/cm^{-1} 2914, 1714, 1668, 1248, 1178; HRMS (ESI): Calcd for $C_{18}H_{14}BrNO_2$ (MH^+) 356.0286; Found 356.0295.

1-(4-methoxyphenyl)-2-phenyl-1*H*-pyrrole-3-carbaldehyde (4j): (54 mg, 65%, pasty liquid), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 3.2 Hz, 1H), 6.87 (d, *J* = 3.2 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.18-7.20 (m, 2H), 7.28-7.32 (m, 3H), 9.67 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.36, 107.60, 114.21 (2C), 124.37, 124.91, 127.01 (2C), 128.19 (2C), 128.46, 129.16, 130.91 (2C), 131.65, 142.42, 158.76, 187.06; IR (KBr)/cm^{-1} 2912, 1710, 1672, 1244, 1174; HRMS (ESI): Calcd for $C_{18}H_{15}NO_2$ (MH^+) 278.1181; Found 278.1200.

1-(4-methoxyphenyl)-2-(naphthalene-1-yl)-1*H*-pyrrole-3-carbaldehyde (4k): (60 mg, 61%, amorphous solid), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 6.60 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 3.2 Hz, 1H), 7.00 (d, *J* =3.2 Hz, 2H), 7.37-7.45 (m, 4H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.1Hz, 1H), 9.38 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.32, 107.51, 114.06 (2C), 124.83, 125.62, 125.97(2C), 126.25 (2C), 126.92, 127.11 (2C), 128.26, 129.63, 130.43, 131.88, 133.32, 133.44, 140.87, 158.63, 186.87; HRMS (ESI): Calcd for $C_{22}H_{17}NO_2$ (MH^+) 328.1337; Found 328.1335.

1-(4-methoxyphenyl)-2-(naphthalene-2-yl)-1*H*-pyrrole-3-carbaldehyde (4l): (62 mg, 63%, amorphous solid), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 3.2 Hz, 1H), 6.92 (d, *J* = 3.2 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.50-7.52 (m, 2H), 6.70 (d, *J* = 8.3 Hz, 1H), 7.79-7.83 (m, 3H), 9.74 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.27, 107.51, 114.03 (2C), 124.82, 125.58, 125.92, 126.22 (2C), 126.89, 127.07 (2C),

128.24, 129.62, 130.40, 131.85, 133.30, 133.42 (2C), 140.91, 158.62, 186.88; IR (KBr)/cm^{-1} 2922, 1715, 1668, 1248, 1172; HRMS (ESI): Calcd for $C_{22}H_{17}NO_2$ (MH^+) 328.1337; Found 328.1311.

1-(4-methoxyphenyl)-2-(pyridine-2-yl)-1*H*-pyrrole-3-carbaldehyde (4m): (60 mg, 72%, semi-solid), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.85-6.91 (m, 2H), 7.01-7.09 (m, 3H) 7.20 (m, 1H), 7.54-7.58 (m, 1H), 8.60 (d, *J* = 4.6 Hz, 1H), 9.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.44, 108.14, 114.35 (2C), 120.95, 122.63, 125.55, 125.79, 126.94 (2C), 131.97, 135.89, 139.76, 149.12, 149.68, 158.96, 187.65; HRMS (ESI): Calcd for $C_{17}H_{14}N_2O_2$ (MH^+) 279.1133; Found 279.1223.

1-(4-methoxyphenyl)-2-(pyridine-4-yl)-1*H*-pyrrole-3-carbaldehyde (4n): (62 mg, 74%, semi-solid), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 3.2 Hz, 1H), 6.94 (d, *J* = 3.2 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 4.6 Hz, 2H), 8.55 (d, *J* = 4.6 Hz, 2H), 9.75 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.51, 109.04, 114.65 (2C), 125.25, 125.38 (2C), 126.31, 127.12 (2C), 130.94, 137.53, 138.04, 149.06 (2C), 159.37, 186.04; HRMS (ESI): Calcd for $C_{17}H_{14}N_2O_2$ (MH^+) 279.1133; Found: 279.1140.

1-(4-methoxyphenyl)-2-(thiophen-2-yl)-1*H*-pyrrole-3-carbaldehyde (4o): (58 mg, 68%, gummy liquid), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 3.5 Hz, 1H), 6.96 (d, *J* = 3.5 Hz, 1H), 7.08 (m, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 5.0 Hz, 1H), 9.75 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.50, 107.90, 114.28 (2C), 125.46, 125.71, 127.05, 127.58 (2C), 128.42, 129.57, 130.55, 131.50, 131.48, 159.34, 186.76; HRMS (ESI): Calcd for $C_{16}H_{13}NO_2S$ (MH^+) 284.0755; Found 284.0749.

1-(4-methoxyphenyl)-2-(5-nitrofuran-2-yl)-1*H*-pyrrole-3-carbaldehyde (4p): (69 mg, 74%, semi-solid), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 6.21 (d, *J* = 3.8 Hz, 1H), 6.85 (d, *J* = 3.5

Hz, 1H), 6.90 (d, *J* = 3.5 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 3.8 Hz, 1H) 9.68 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.67, 110.04, 111.70, 112.65, 112.82, 114.83 (2C), 118.68, 127.70 (2C), 128.15, 134.17, 147.14, 151.00, 160.28, 186.22; HRMS (ESI): Calcd for $C_{16}H_{12}N_2O_5$ (MH^+) 313.0824; Found: 313.0833.

(*E*)-1-(4-methoxyphenyl)-2-styryl-1*H*-pyrrole-3-carbaldehyde (4q): (54 mg, 60%, pasty liquid), ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.75 (bs, 2H), 6.81-6.85 (m, 1H), 6.90-6.93 (m, 3H), 7.19-7.23 (m, 4H), 7.27-7.31 (m, 3H), 9.95 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.60, 109.81, 114.66 (2C), 115.73, 124.37, 125.04, 126.75 (2C), 127.39 (2C), 128.43, 128.76 (2C), 131.76, 135.52, 136.58, 138.93, 159.49, 186.00; HRMS (ESI): Calcd for $C_{20}H_{17}NO_2$ (MH^+) 304.1337; Found 304.1306.

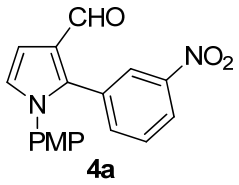
1-(4-methoxyphenyl)-1*H*-pyrrole-3-carbaldehyde (4r): (35 mg, 58%, liquid), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (s, 3H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 3.5 Hz, 1H), 6.86 (d, *J* = 3.5 Hz, 1H) 6.99 (d, *J* = 8.8 Hz, 2H), 7.6 (bs, 1H) 9.57 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.08, 107.86, 114.68 (2C), 122.92, 126.18, 127.88 (2C), 135.46, 142.82, 158.86, 185.68; HRMS (ESI): Calcd for $C_{12}H_{11}NO_2$ (MH^+) 202.0868; Found 202.0876.

(*E*)-Methyl 3-(1-(4-methoxyphenyl)-2-phenyl-1*H*-pyrrol-3-yl)acrylate (9): To a stirred solution of phosphonium bromide (330 mg, 0.79 mmol) in dry THF (3 mL) was added NaH (0.032 mg, 0.79 mmol, 60% in oil) in portions at rt and further stirred for 30 min at the same temperature. The solution of compound **4j** (200 mg, 0.71 mmol) in THF (2 mL) was added to this stirred mixture at 0 ^{o}C and further stirred at rt for overnight. After usual work-up, the crude material was passed through a small silica gel column gave compound **9** as pasty liquid (182 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.85 (s, 3H), 6.38 (d, *J* = 14.2 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 3.2 Hz, 1H), 6.87 (d, *J* = 3.2 Hz, 1H), 7.02 (d, *J* = 8.8 Hz,

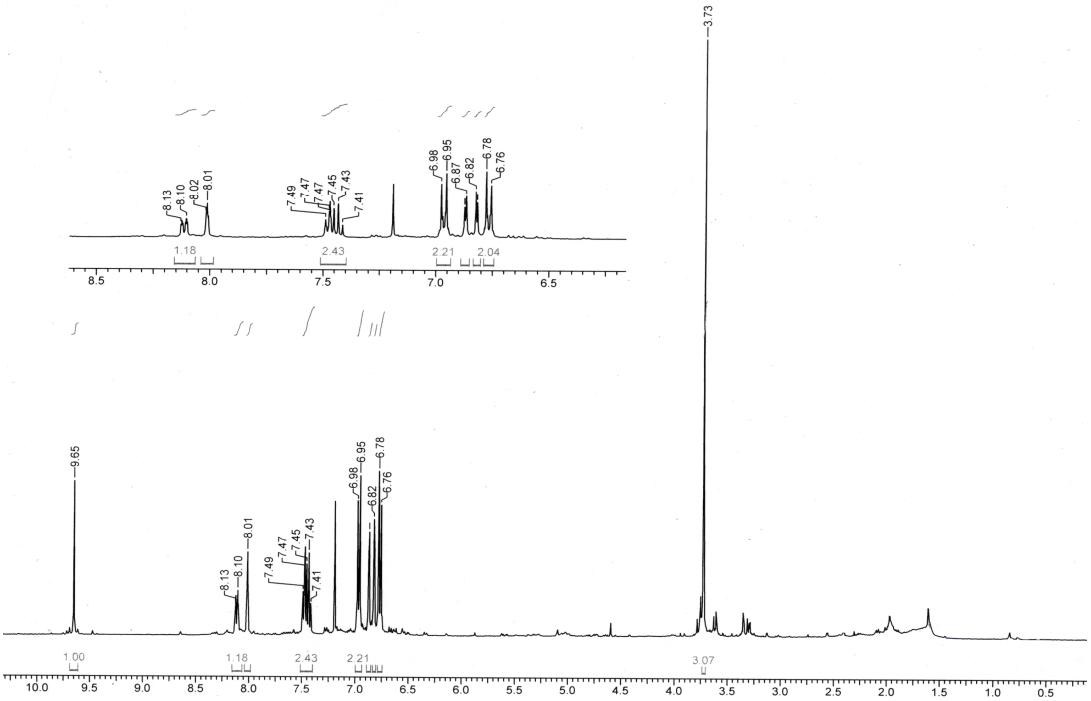
2H), 7.19-7.35 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.28, 55.31, 107.56, 113.21, 114.78 (2C), 124.28, 124.78, 124.85 (2C), 126.95 (2C), 128.06, 128.29, 129.11, 131.86, 132.55, 141.27, 146.34, 158.66, 168.56; HRMS (ESI): Calcd for $C_{21}H_{19}NO_3$ (MH^+) 334.1443; Found 334.1445.

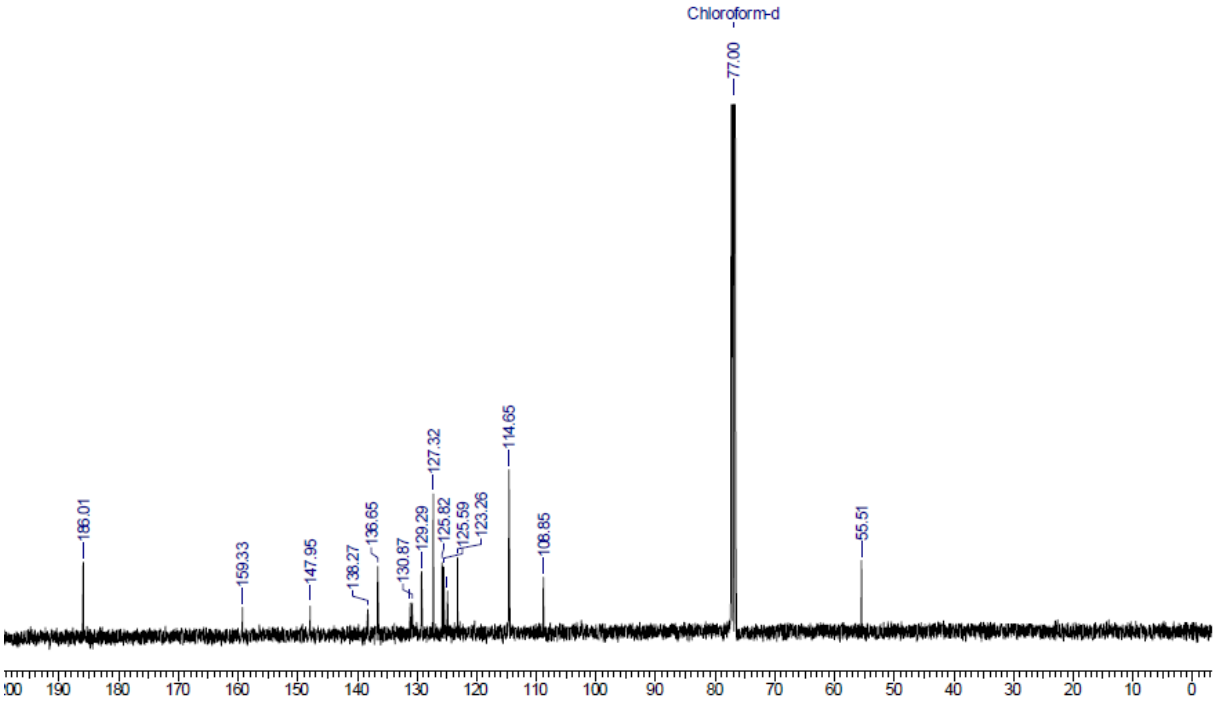
1-(4-methoxyphenyl)-2-phenyl-1*H*-pyrrole-3-carbonitrile (10): To a stirred solution of **4j** (250 mg, 0.9 mmol) in EtOH (5 mL) was added $NH_2OH.HCl$ (0.12 g, 1.8 mmol) and further reflux for 5 h. The reaction was cooled to rt and solvent was removed under reduced pressure. The resulting mixture was further extracted between EtOAc (10 mL) and H_2O (6 mL). The organic layer was separated, dried over Na_2SO_4 and concentrated under reduced pressure results crude oxime, which was used further without purification.

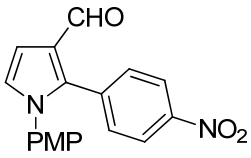
In a separate flask, 2,4,6-Trichloro-[1,3,5]triazine (TCT) (1.83 g, 10.0 mmol) was added to DMF (2 mL), and stirred at rt until a white solid forms. Then crude oxime solution in DMF (3 mL) was added, the mixture was stirred at room temperature, monitored (TLC) until completion (10 h). Water (2 mL) was added then extracted twice with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude material was purified the through a small silica gel column gave compound **10** as slight yellow liquid (207 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.76 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 3.2 Hz, 1H), 6.86 (d, J = 3.2 Hz, 1H), 7.06 (d, J = 8.8 Hz, 2H), 7.25-7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.38, 97.34, 108.20, 114.28 (2C), 124.32 124.86, 127.21 (2C), 128.03, 128.34 (2C), 129.08, 130.87 (2C), 131.08, 142.22, 158.73; HRMS (ESI): Calcd for $C_{18}H_{14}N_2O$ (MH^+) 275.1184; Found 275.1168.



4a



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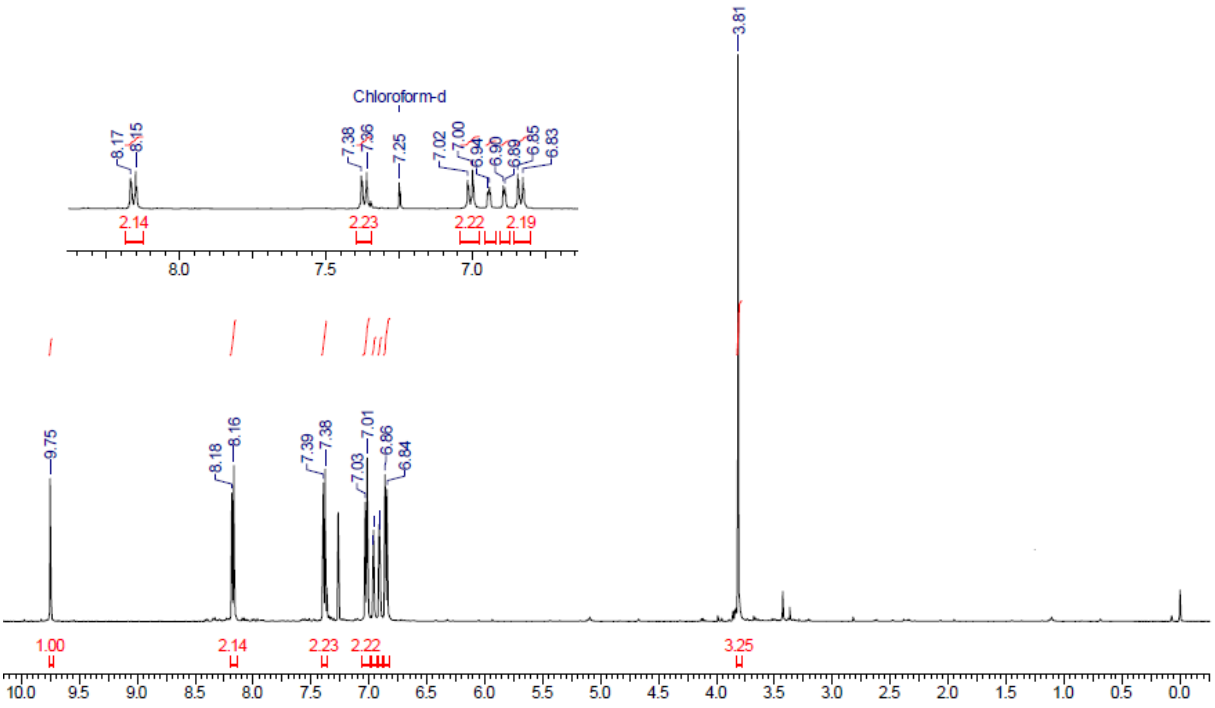
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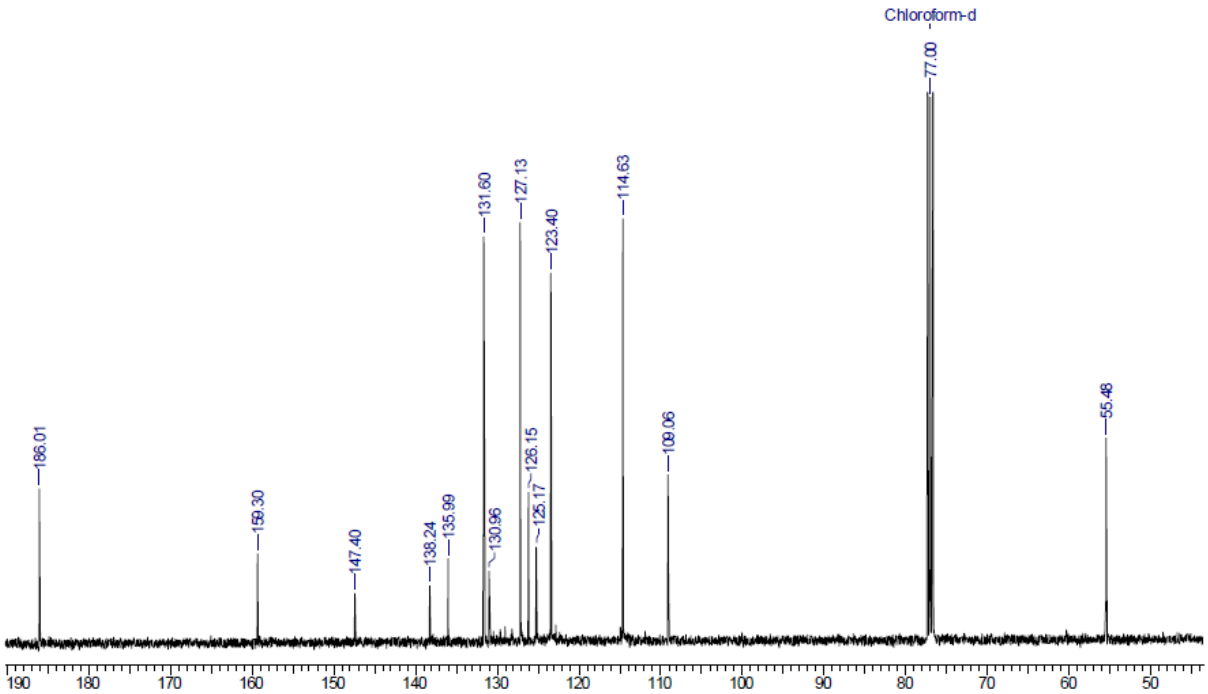
3.25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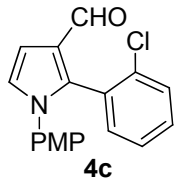

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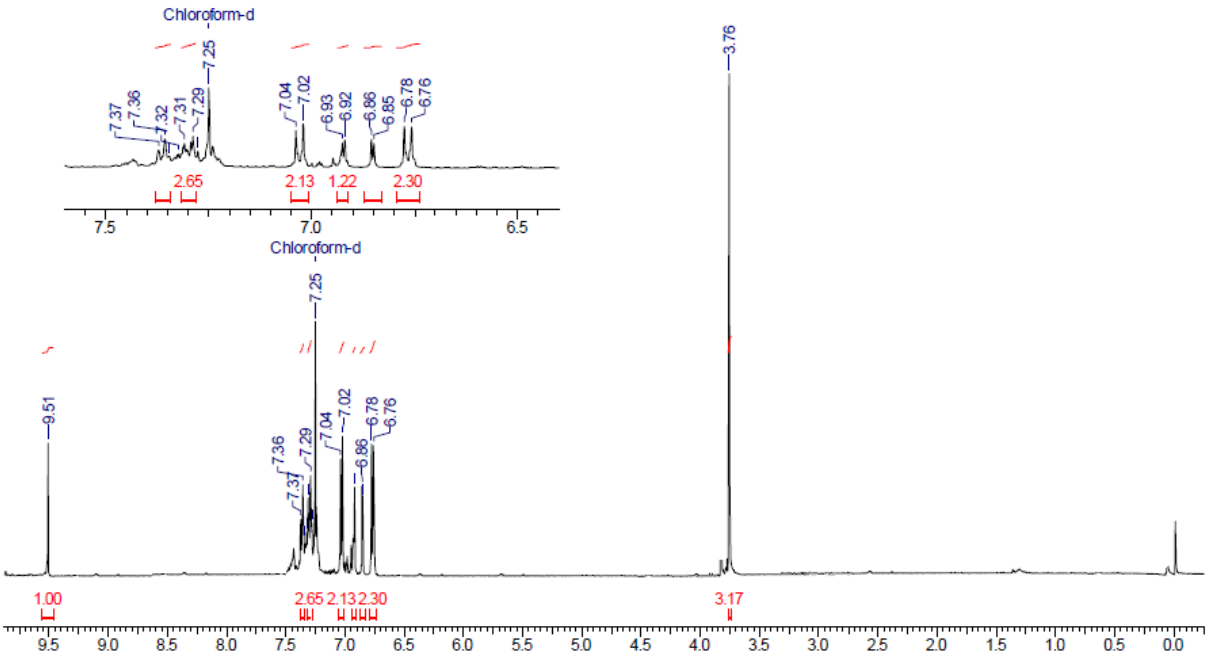

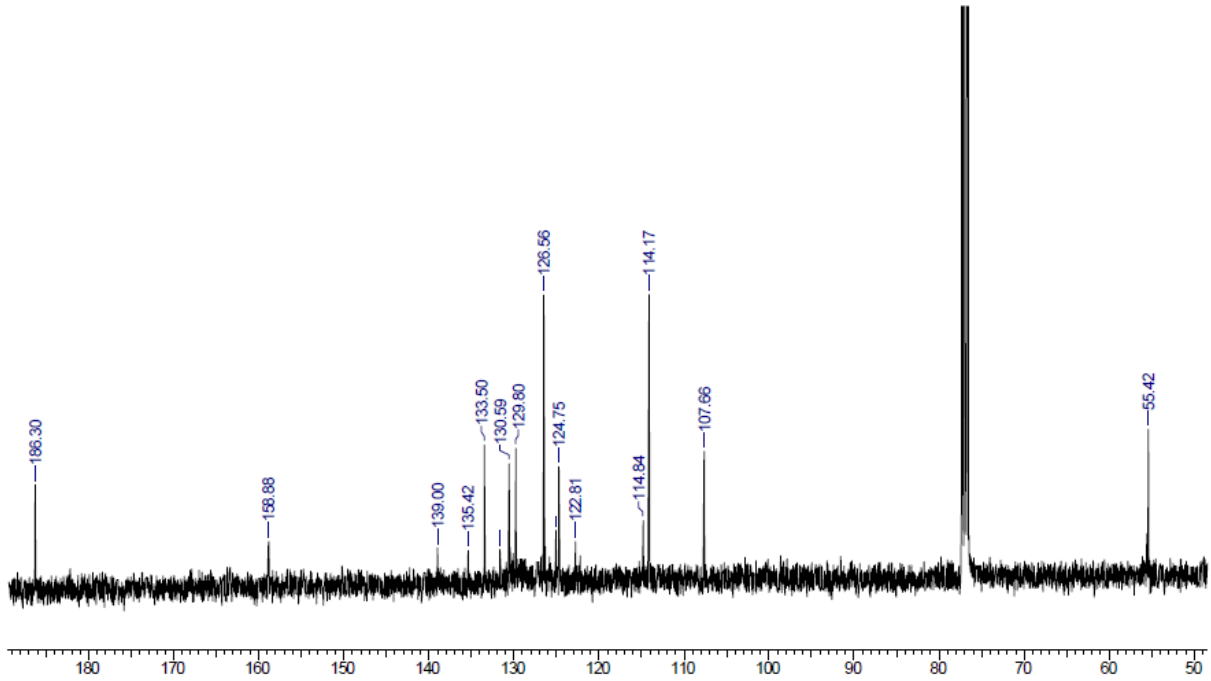

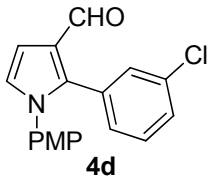

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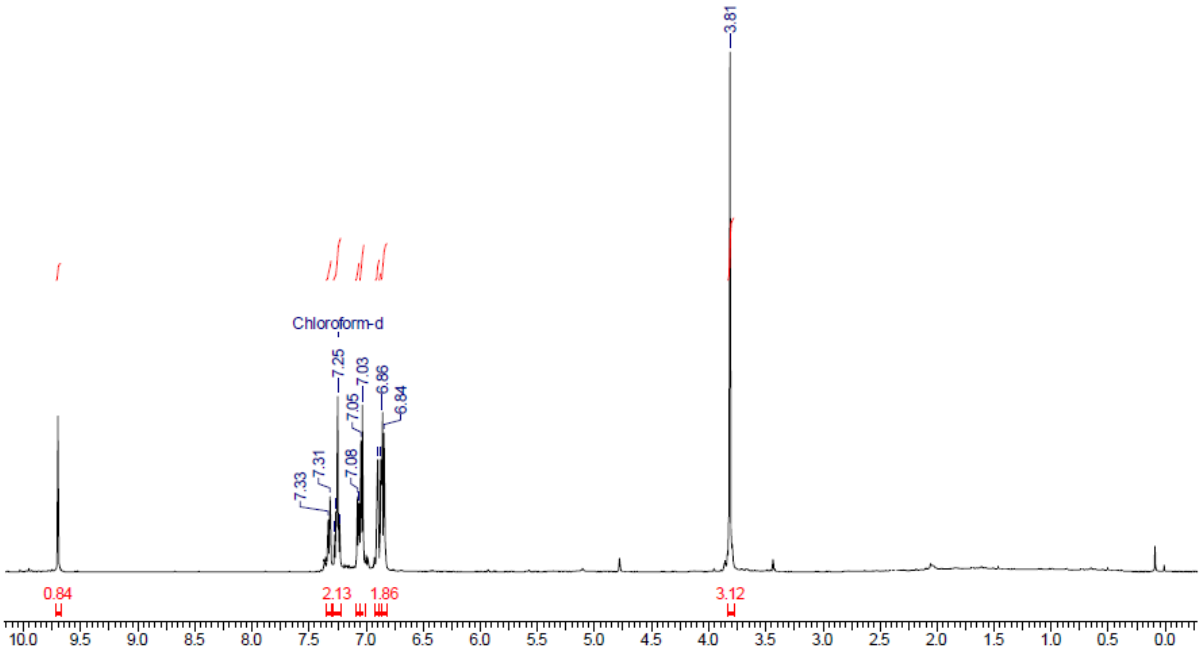

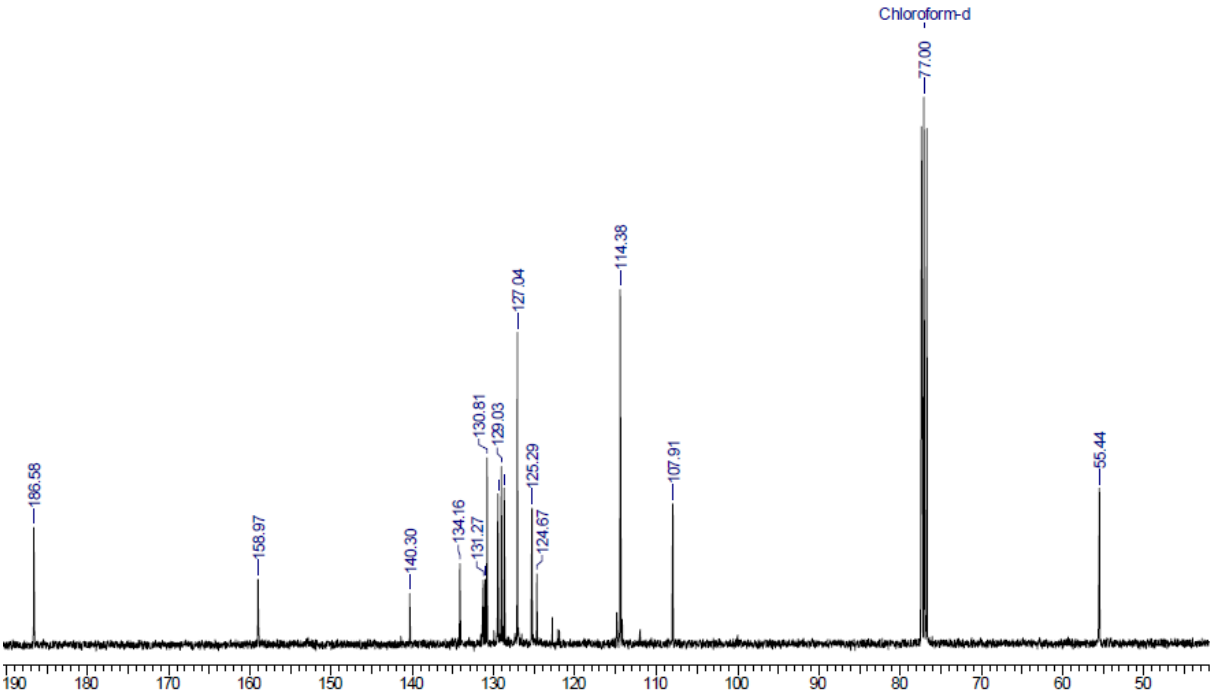

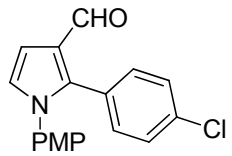
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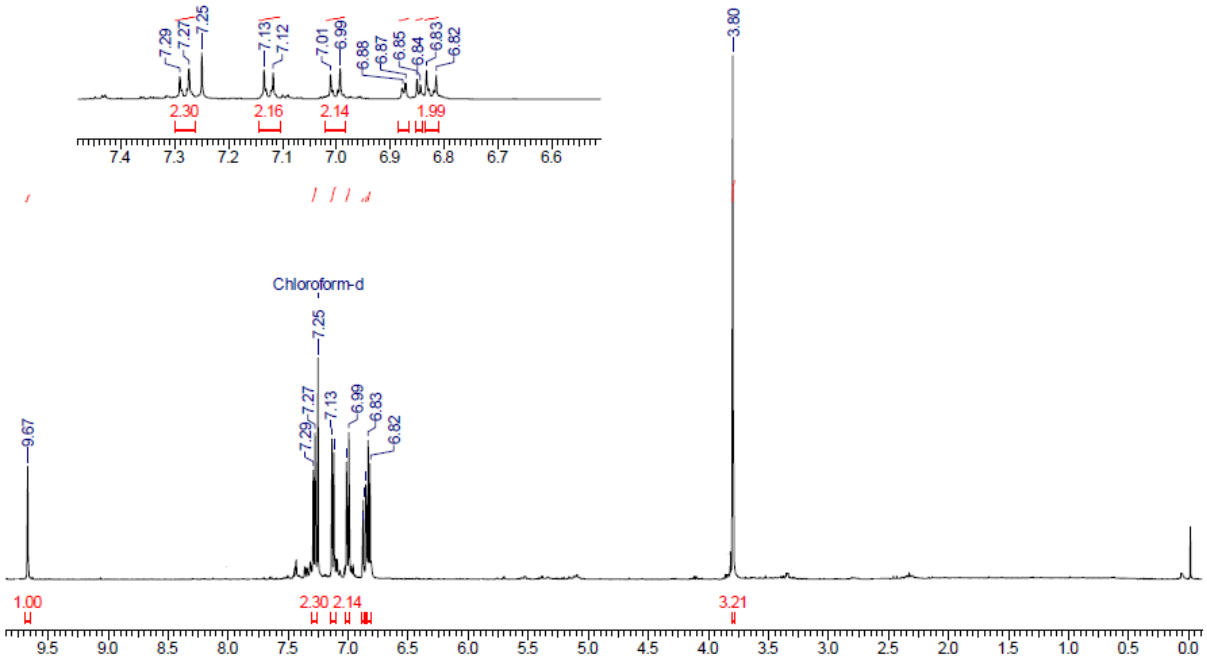
4e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2.16
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Chloroform-d
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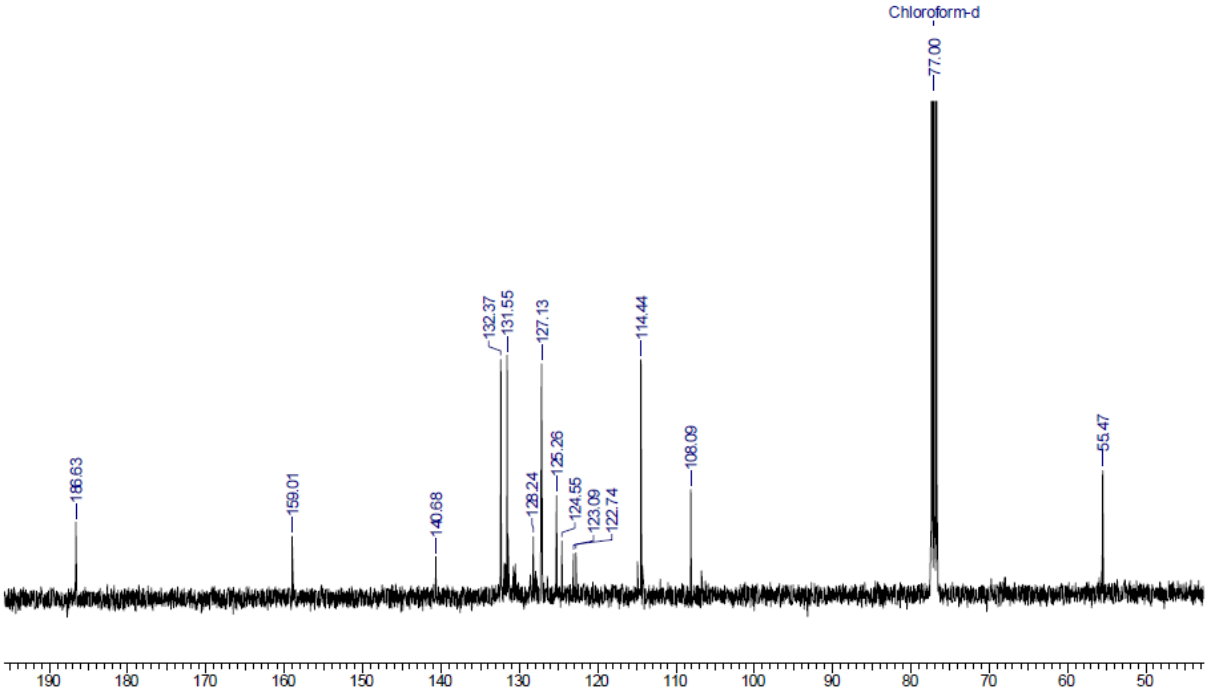
1.00
2.30 2.14
3.21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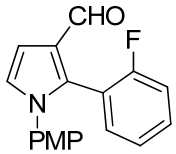

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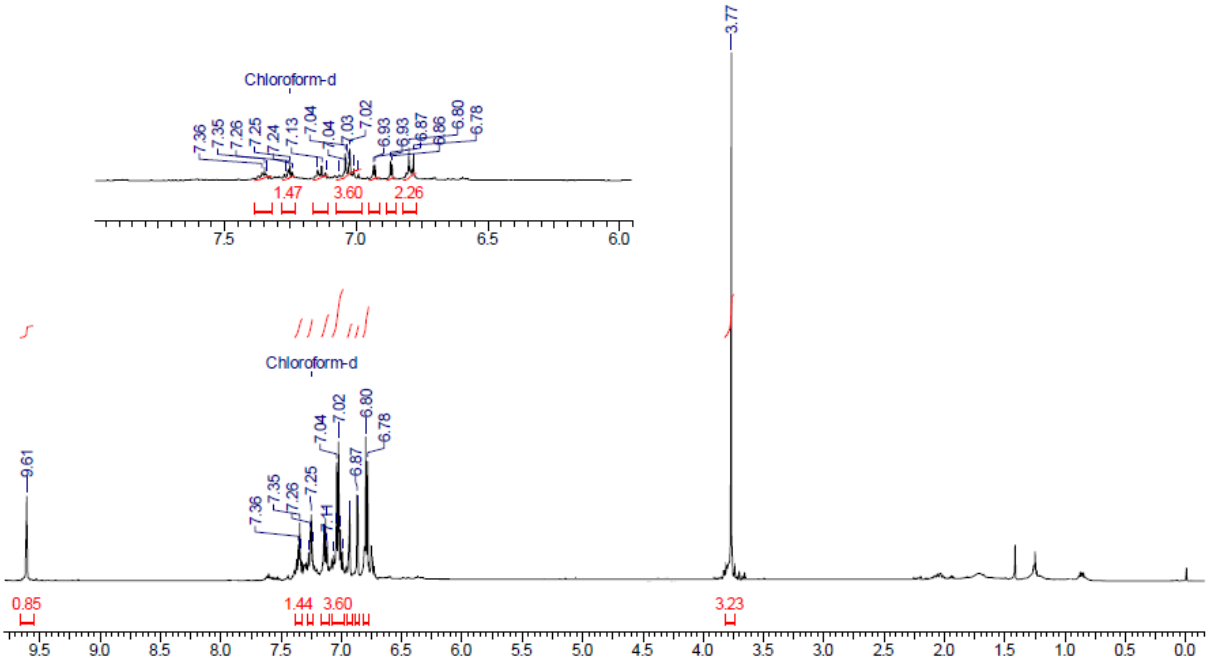

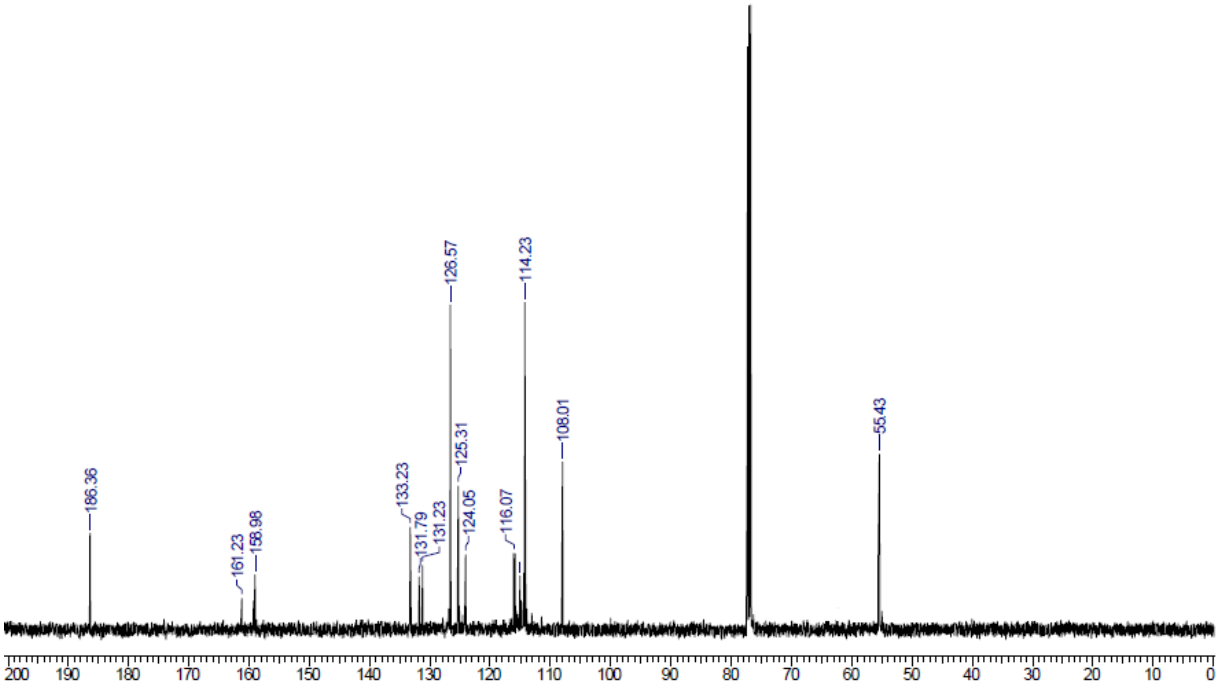

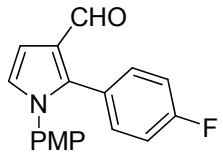
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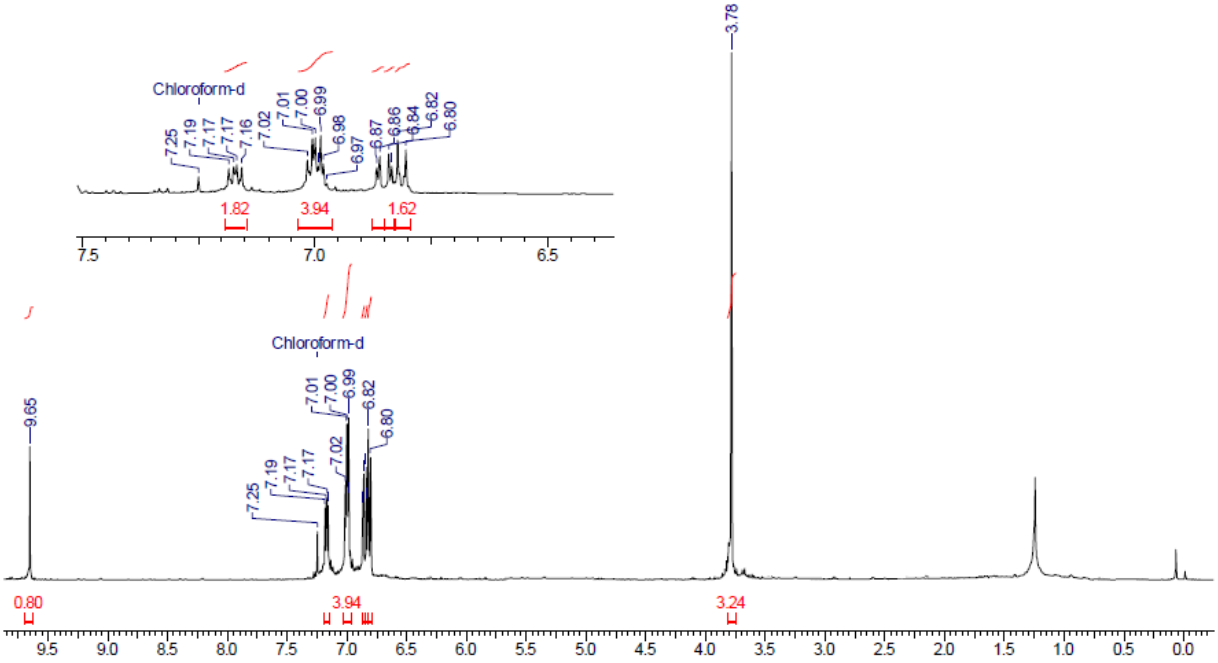
PMP
F

4g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6.84
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7.0
6.5
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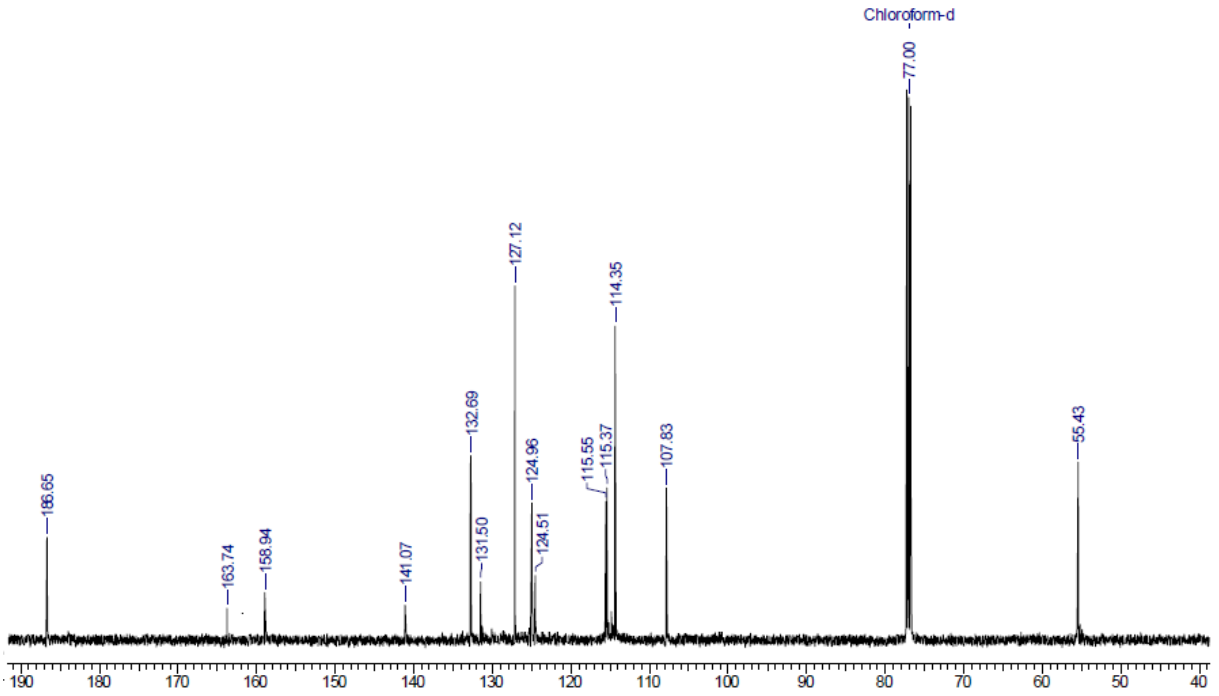
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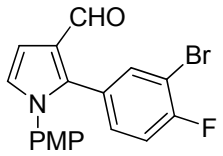

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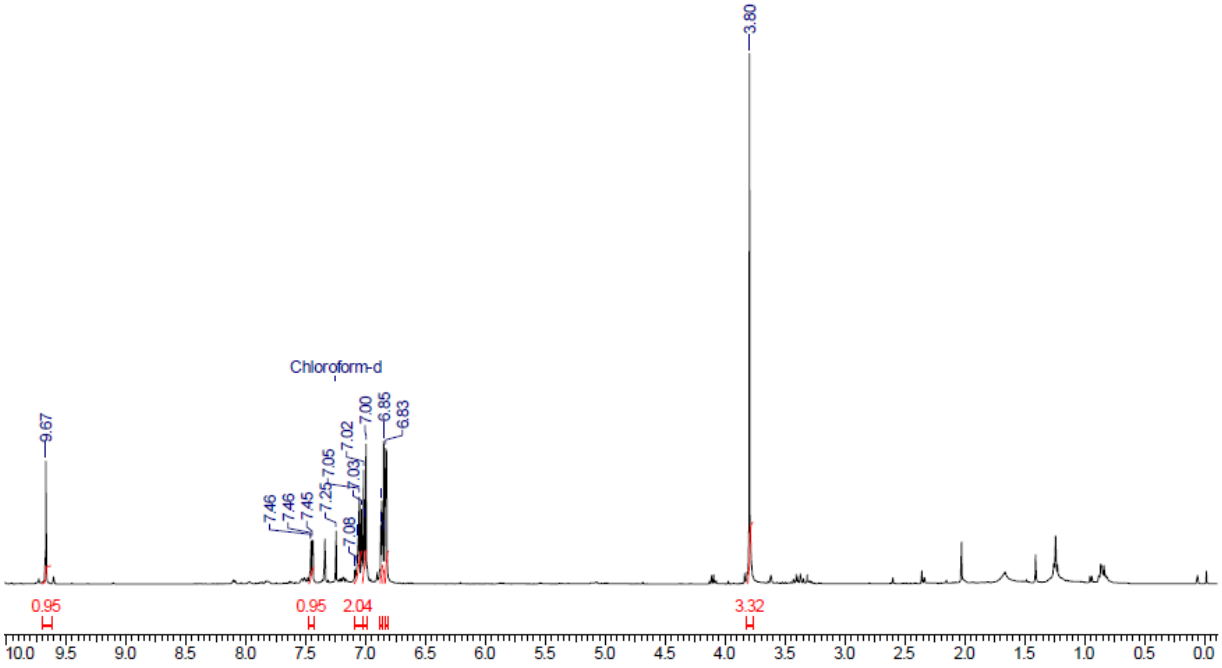

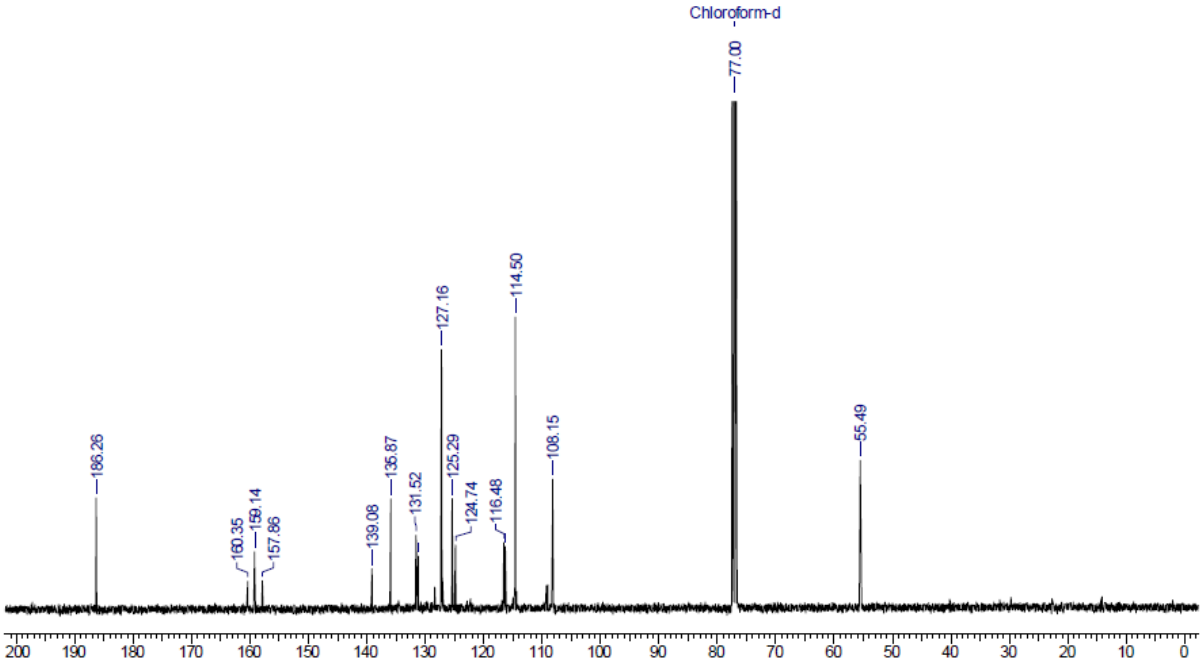

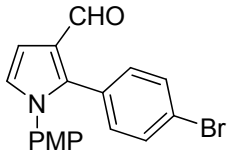

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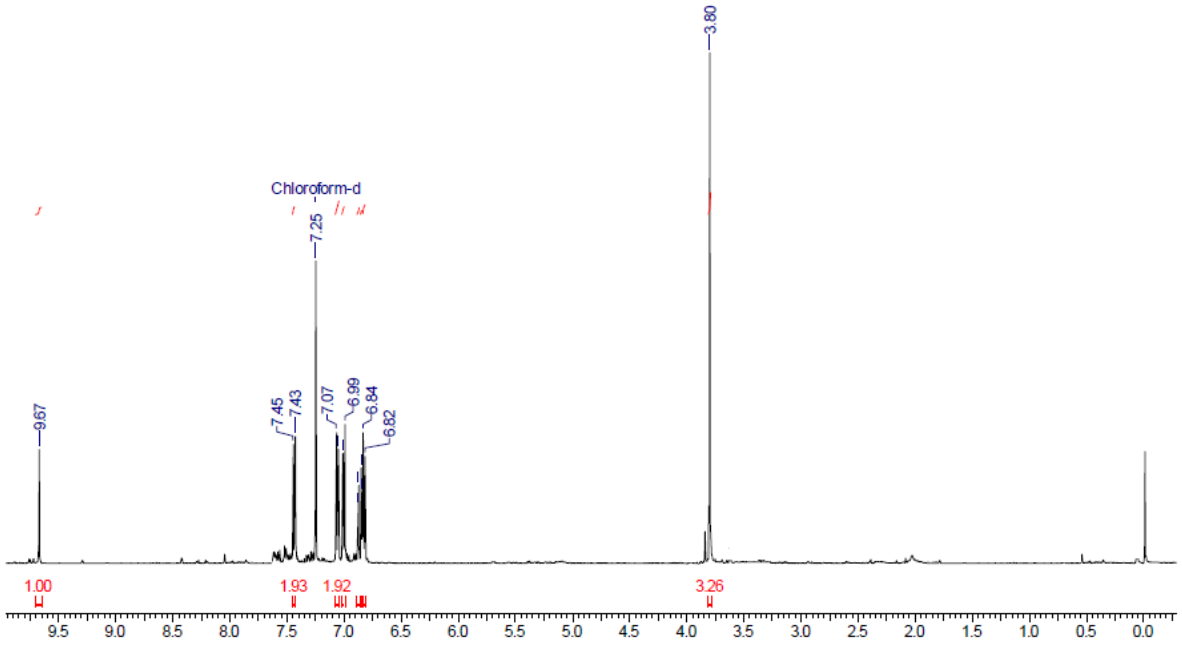

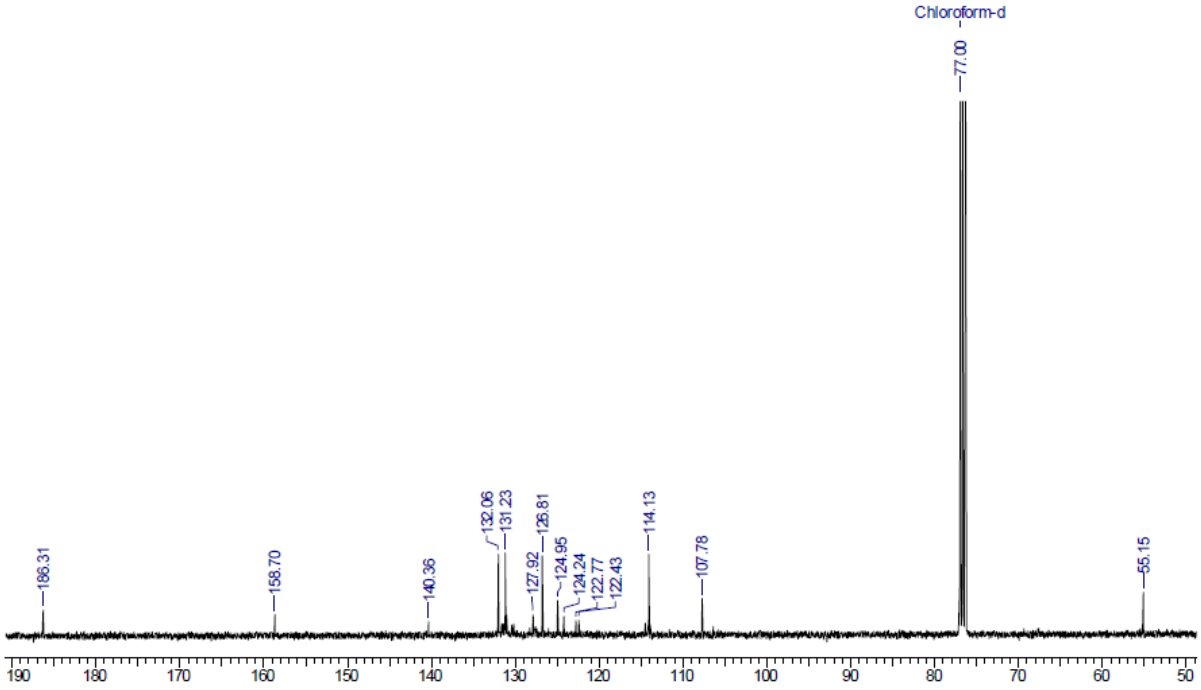

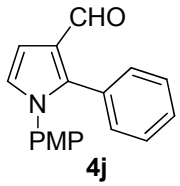

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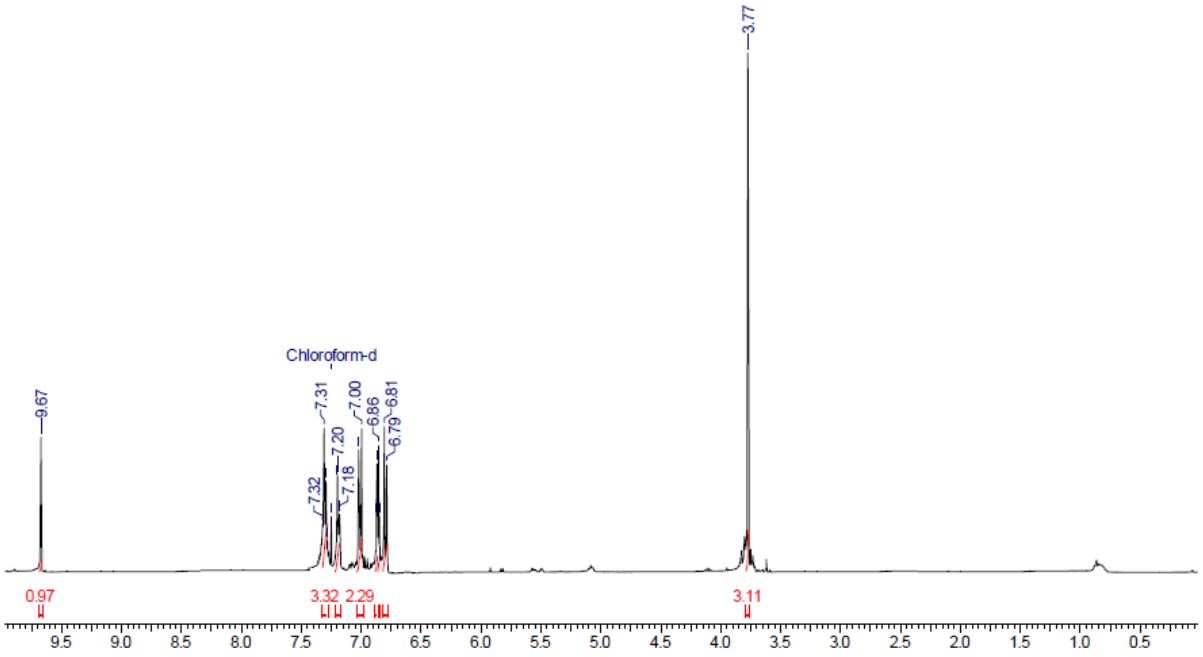

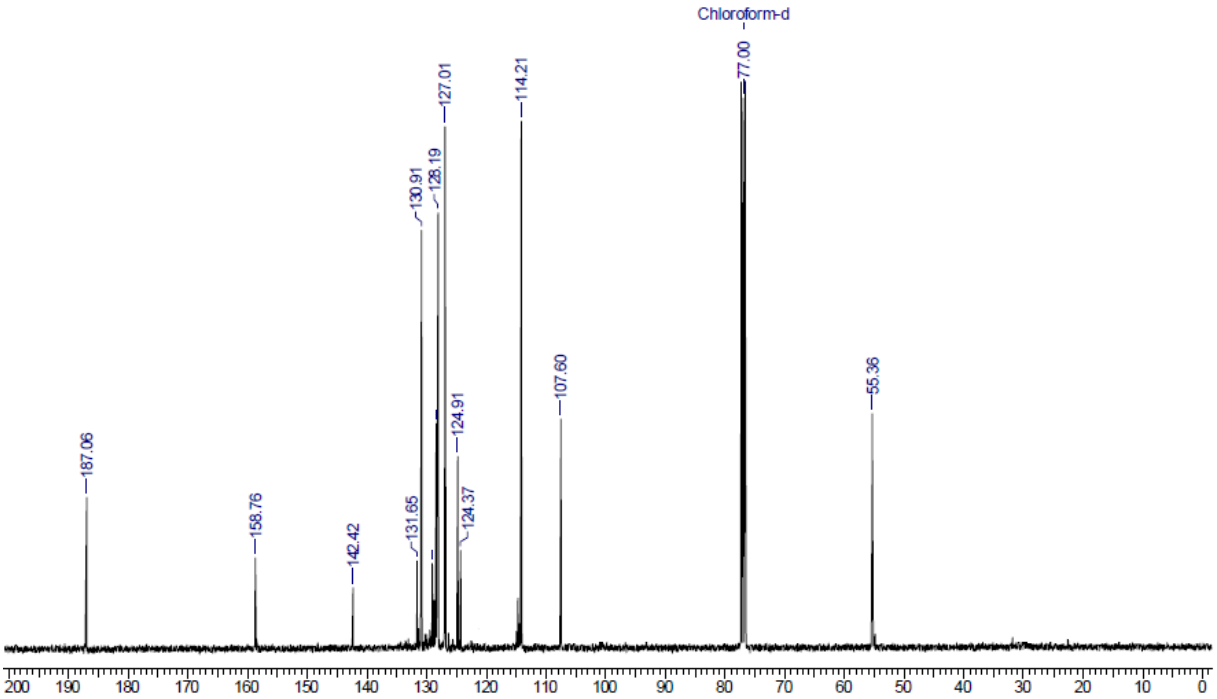

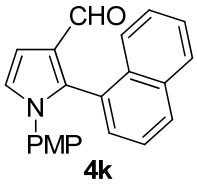

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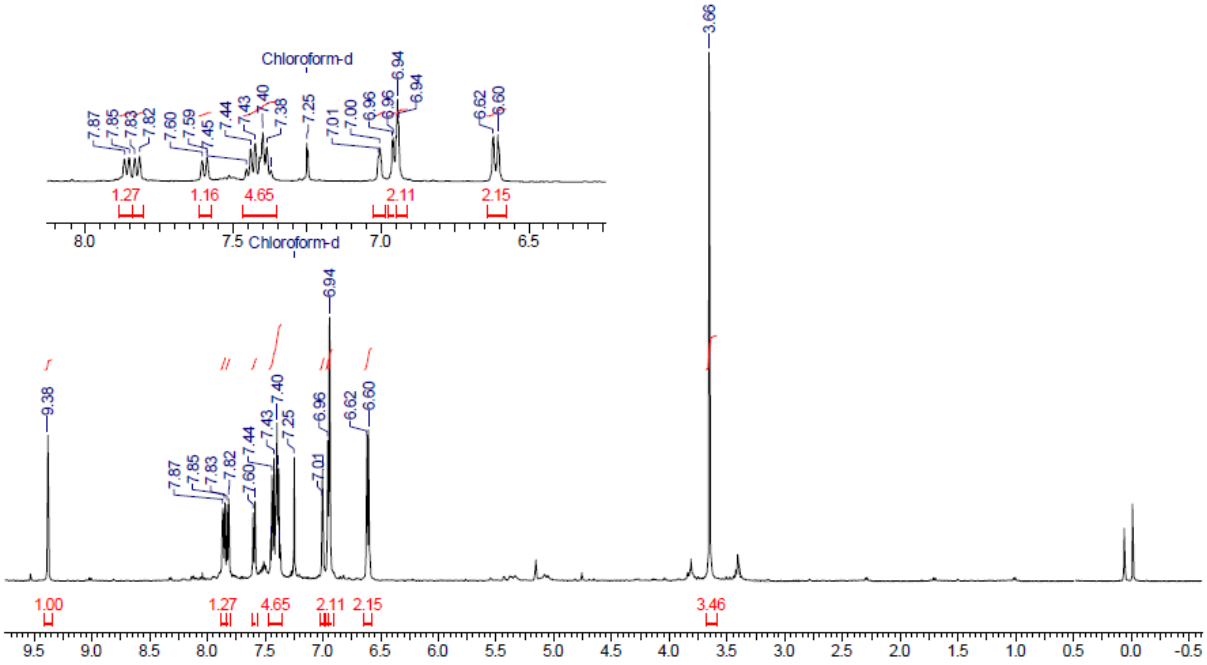

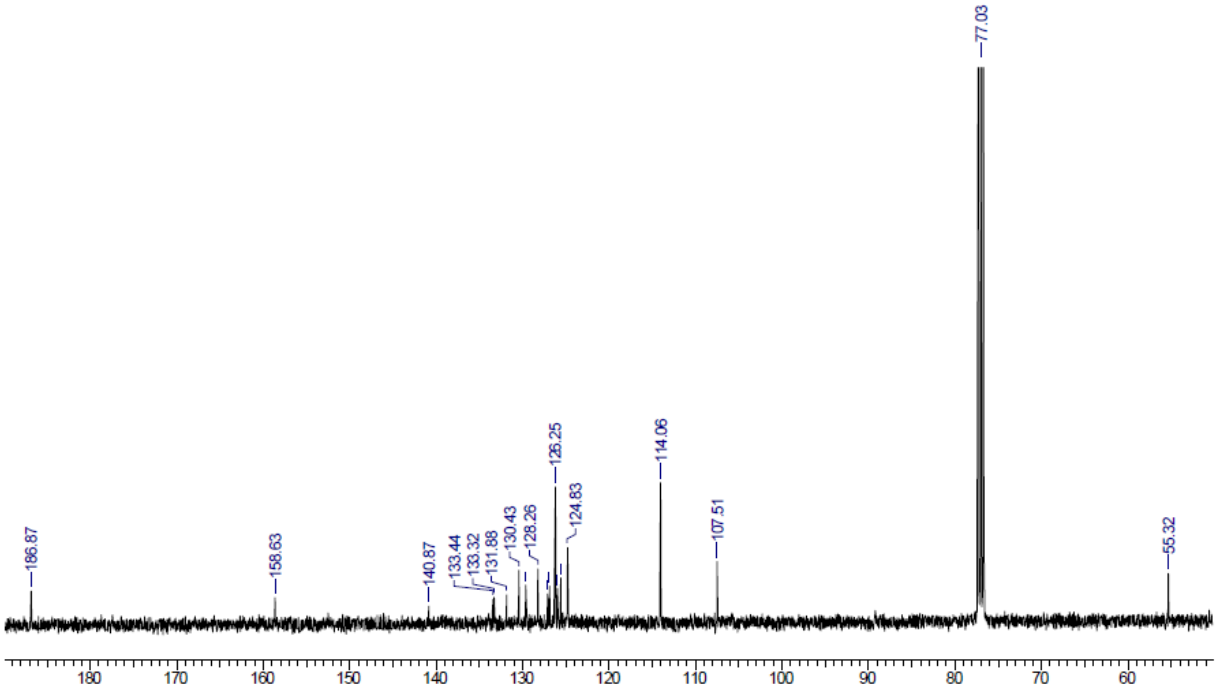

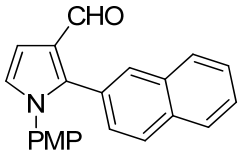
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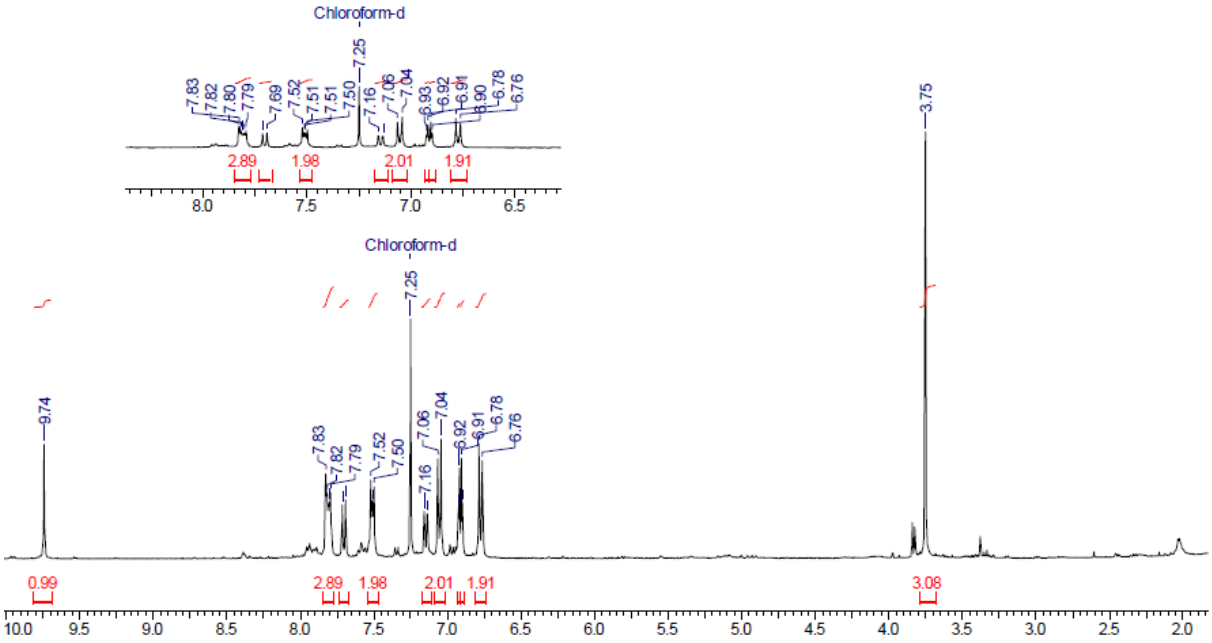
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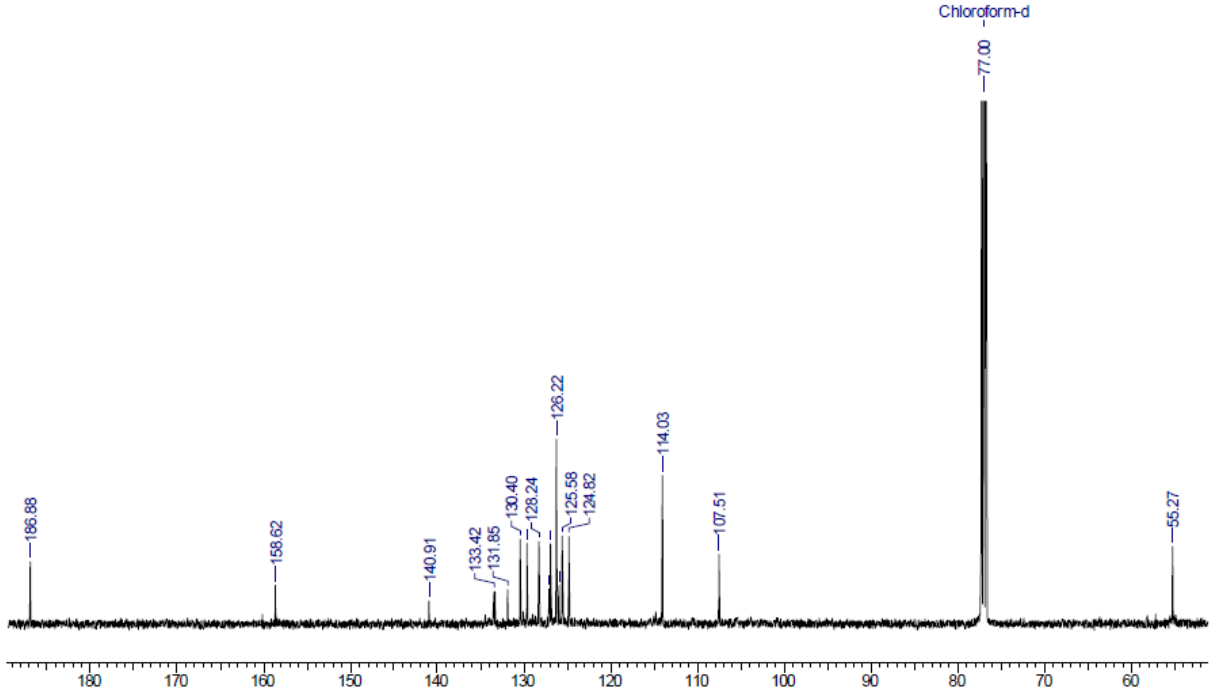
Chloroform-d
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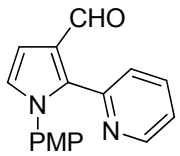
55.27



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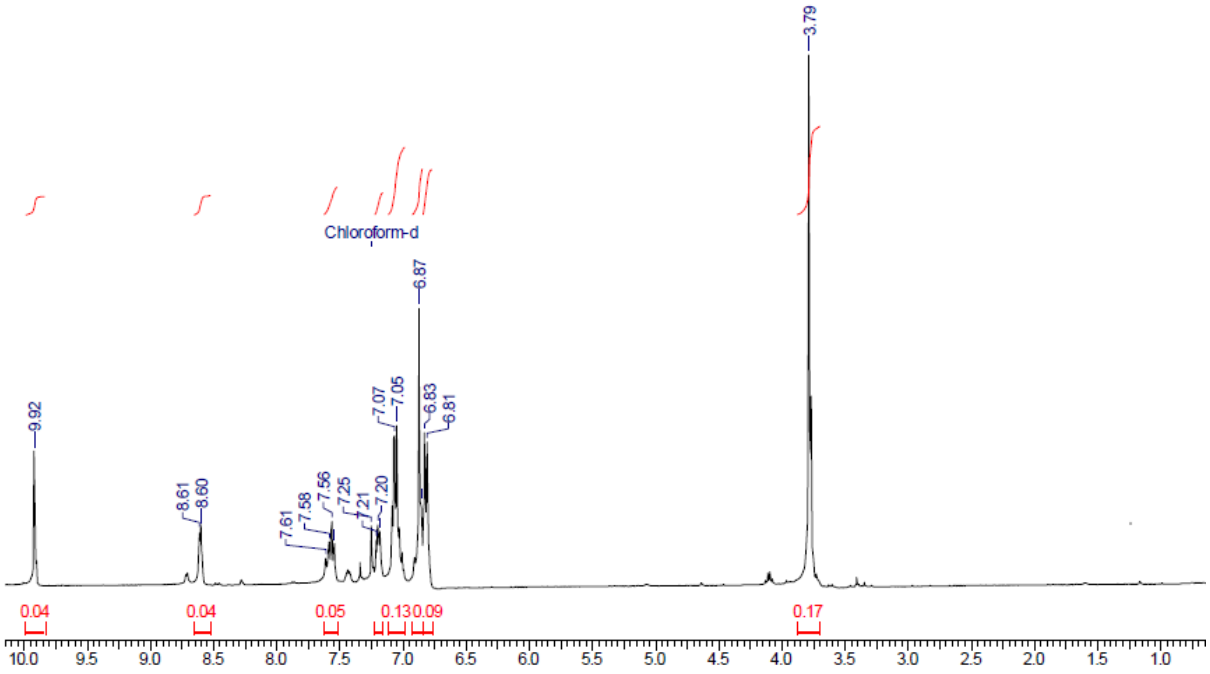

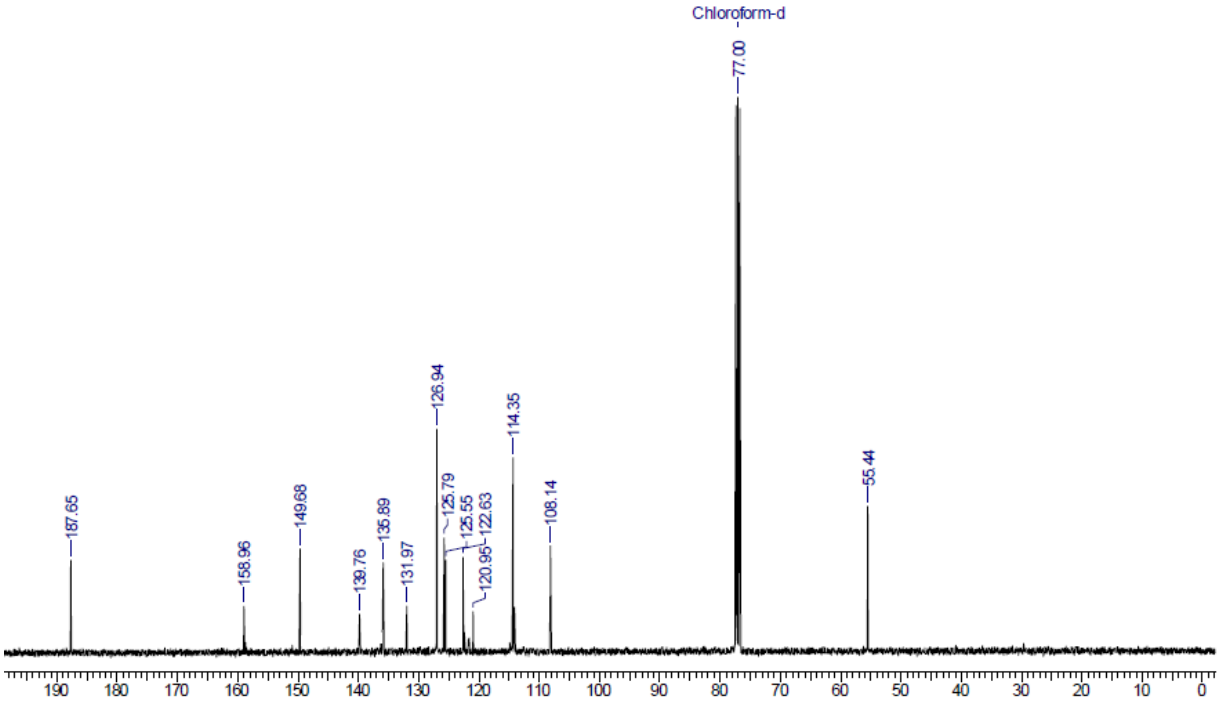

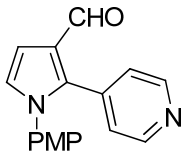

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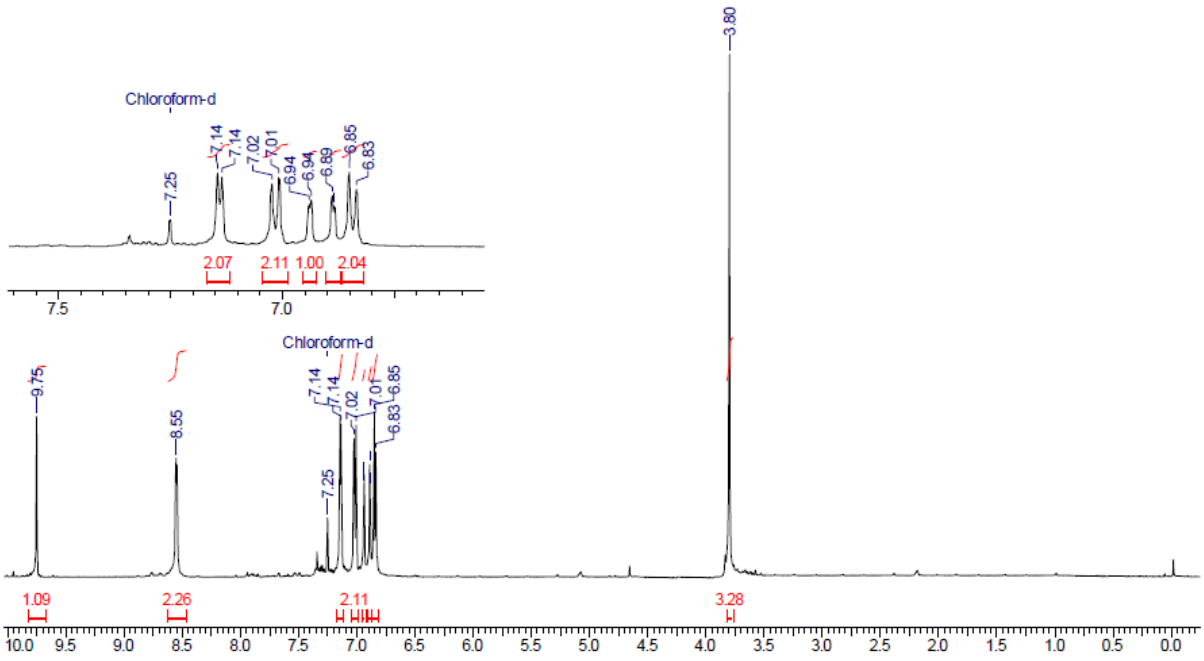

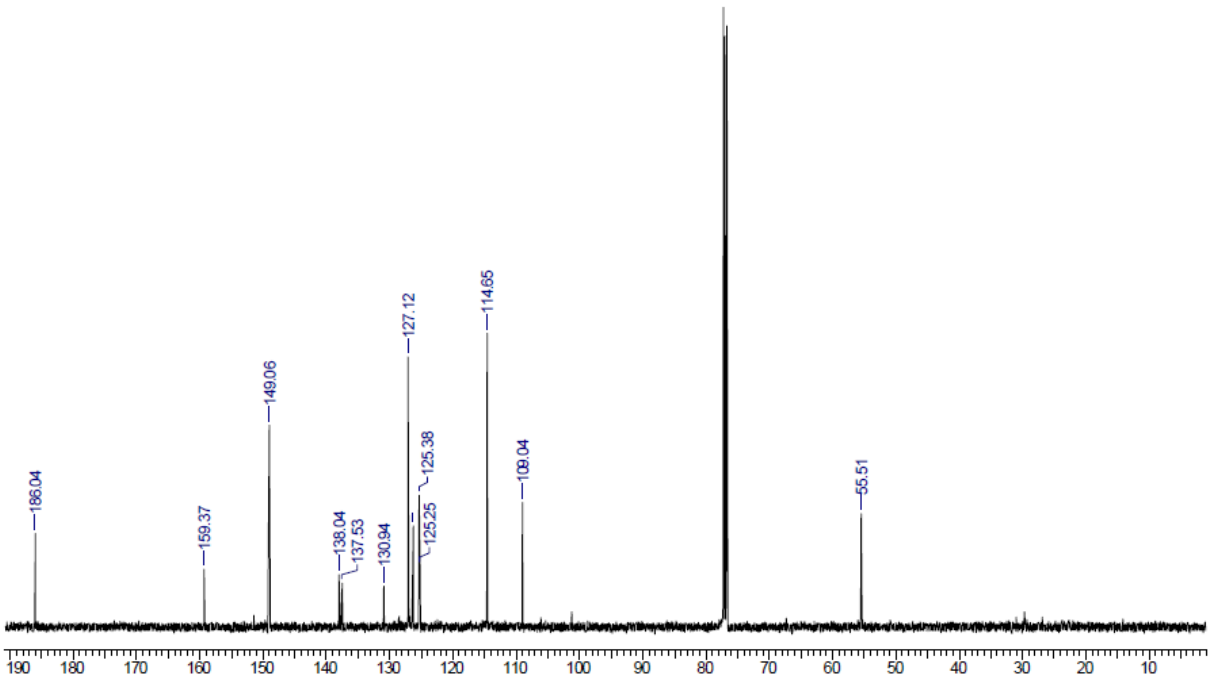

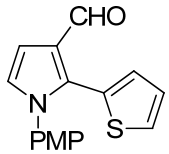
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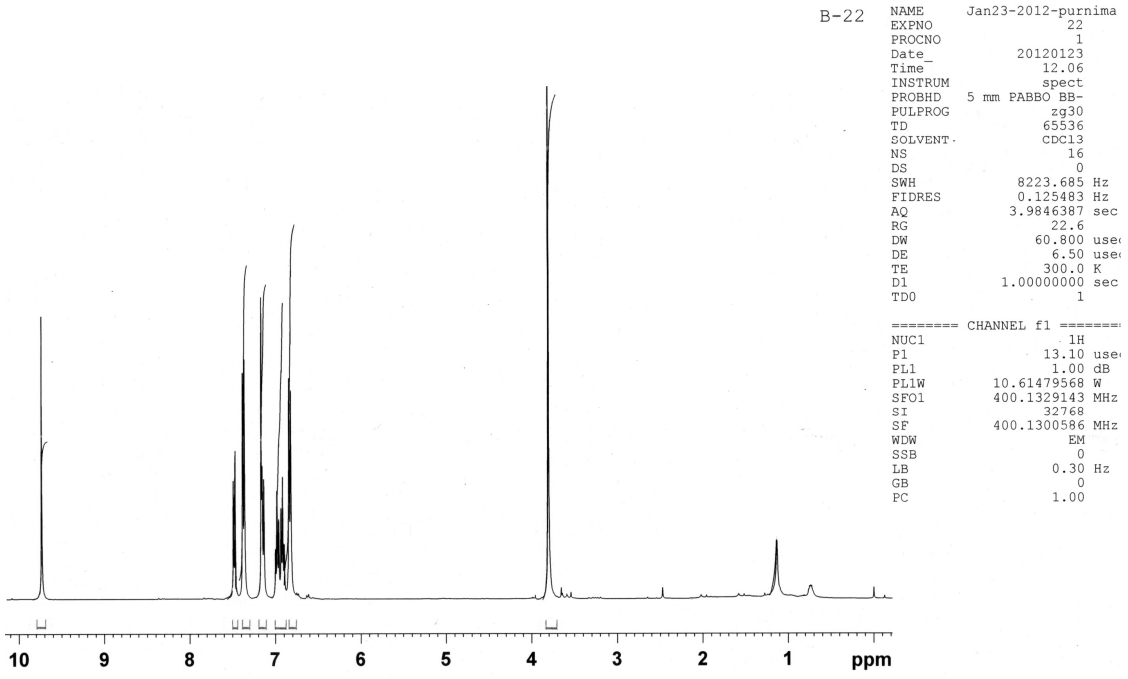
B-22
NAME Jan23-2012-purnima
EXPNO 22
PROCNO 1
Date_ 20120123
Time 12.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 22.6
DW 60.800 use
DE 6.50 use
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.10 use
PL1 1.00 dB
PL1W 10.61479568 W
SFO1 400.1329143 MHz
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LB 0.30 Hz
GB 0
PC 1.00
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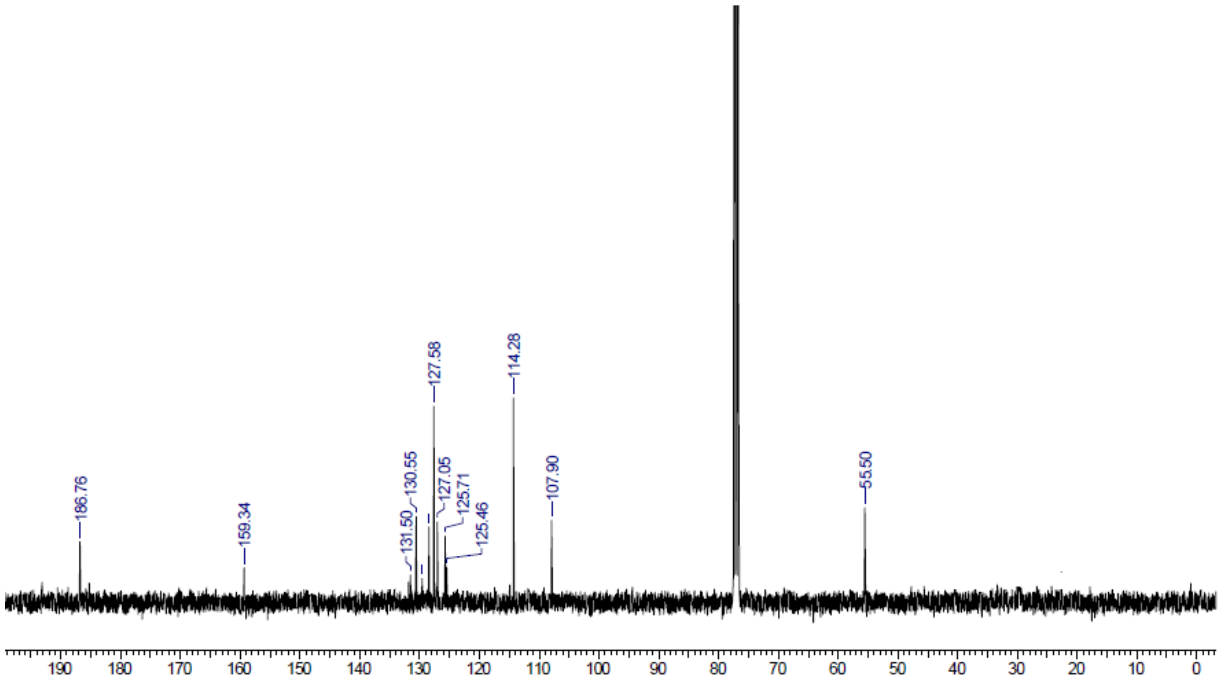
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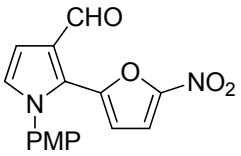

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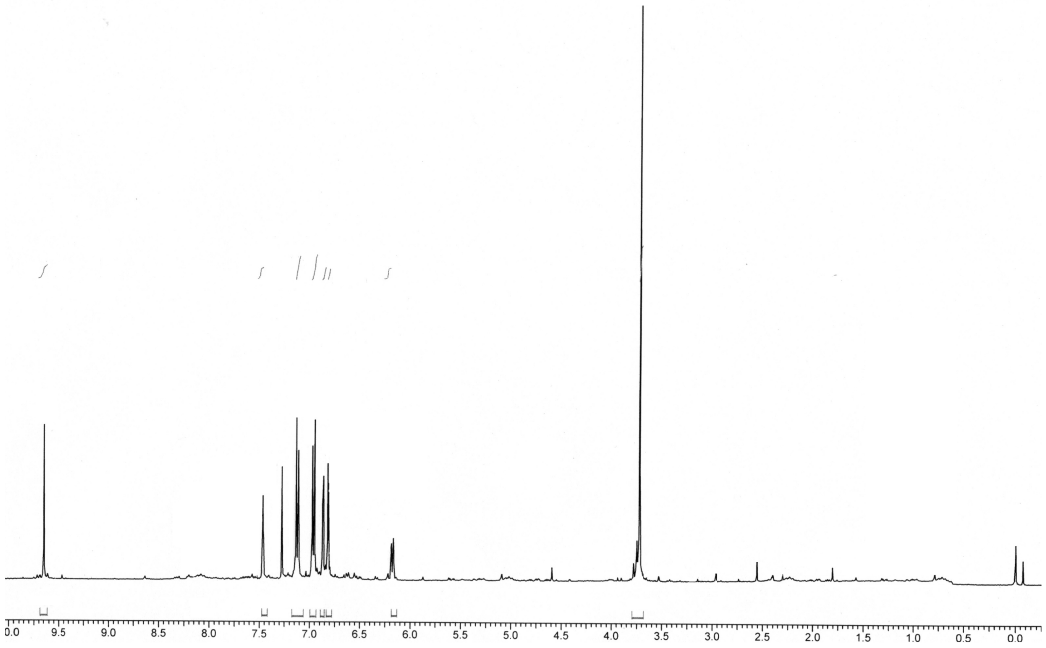

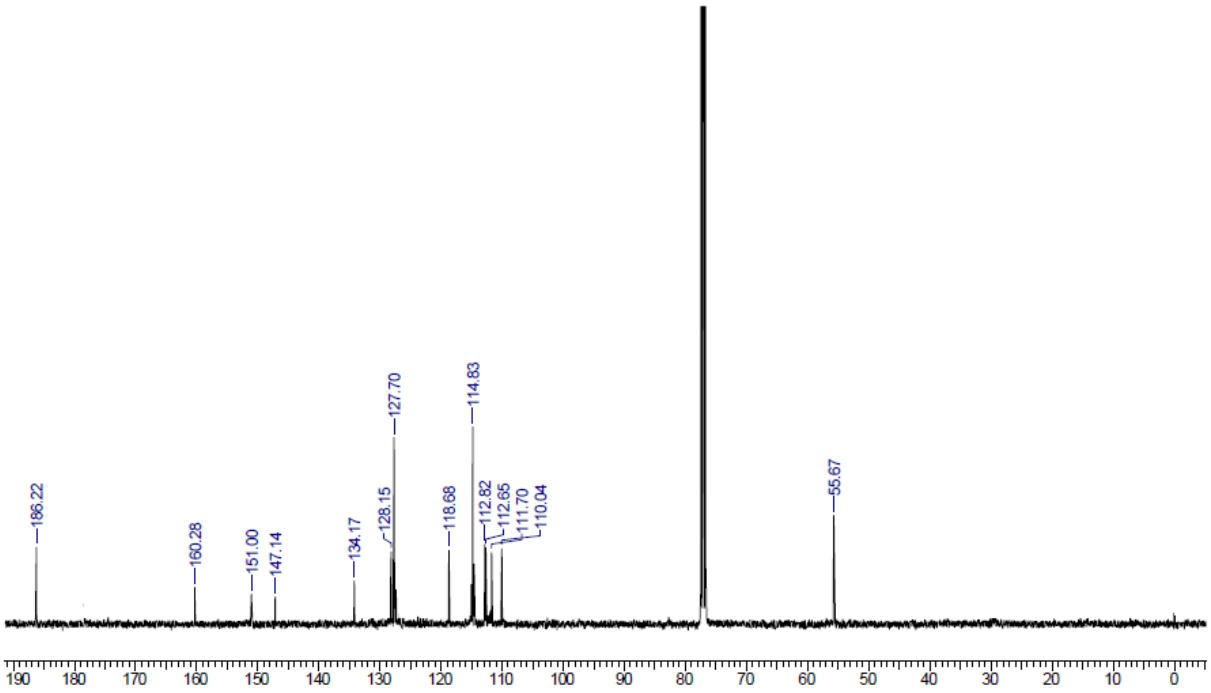

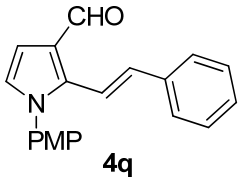

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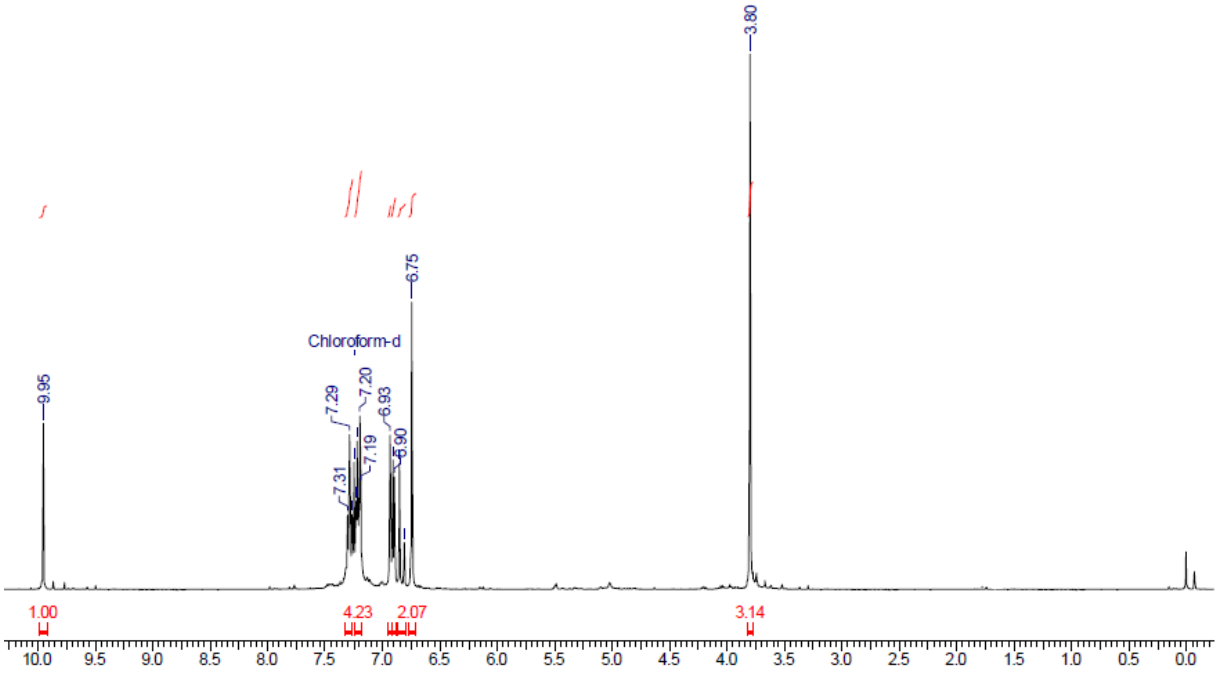
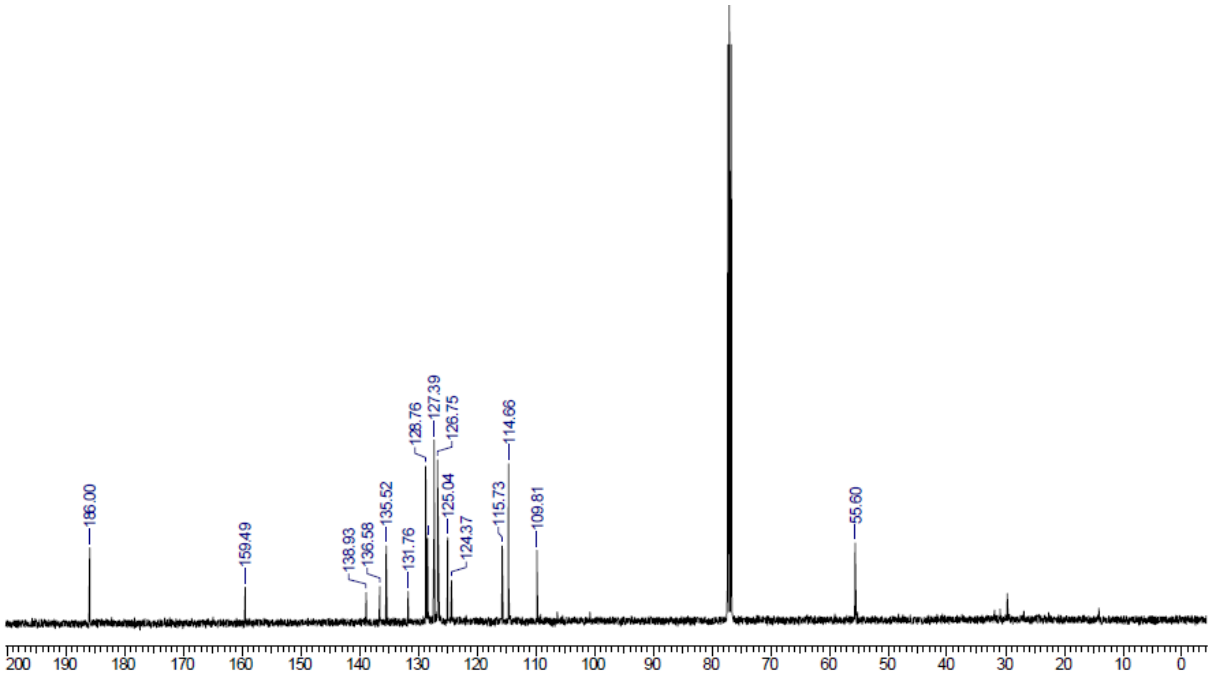
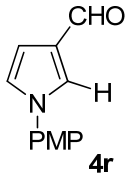
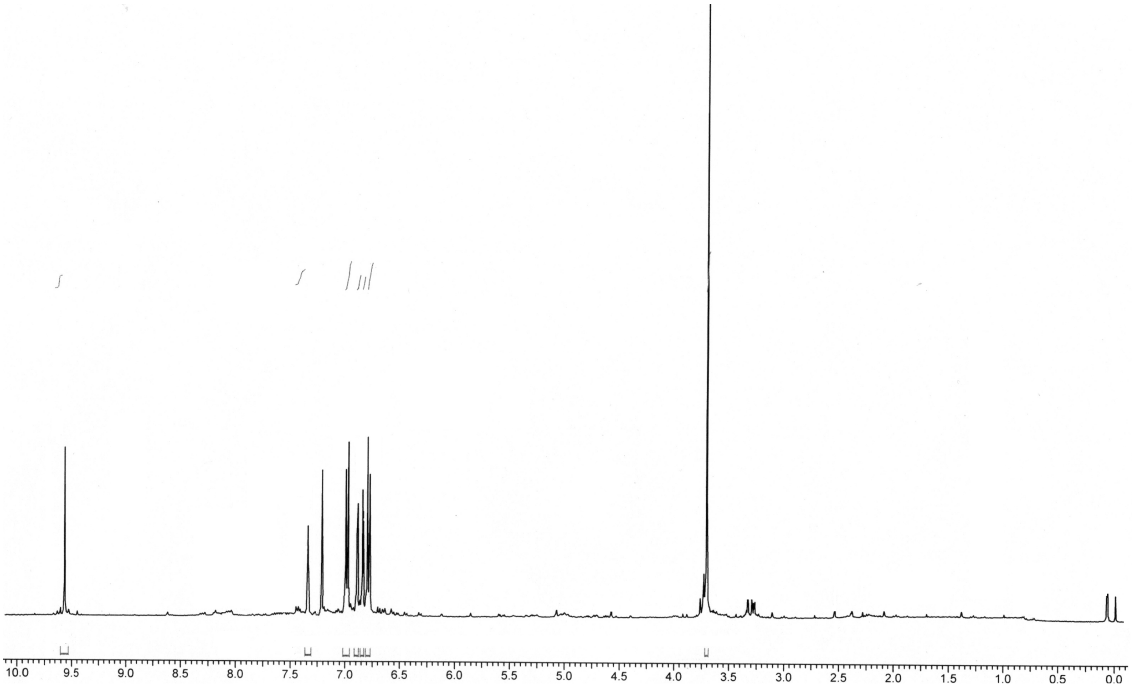
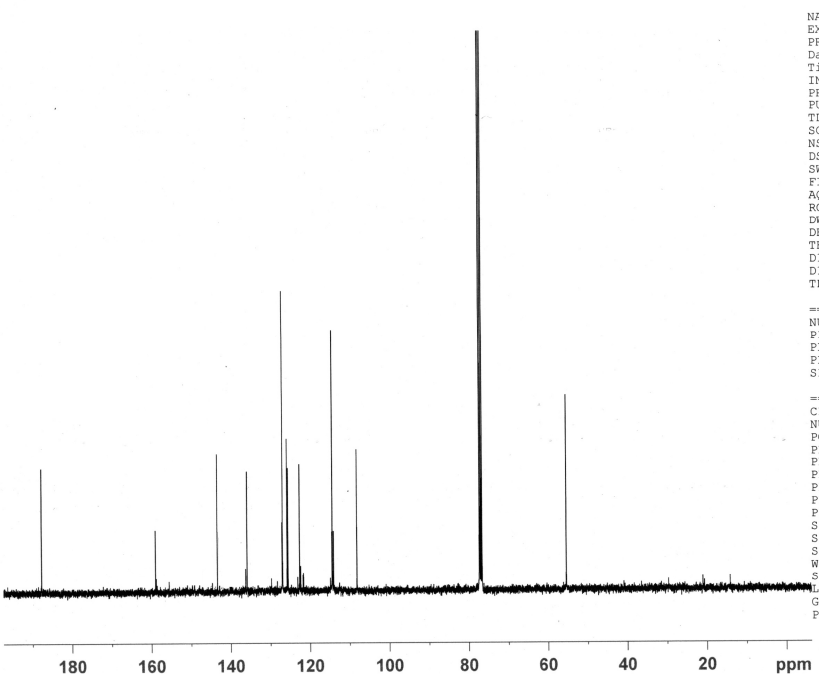




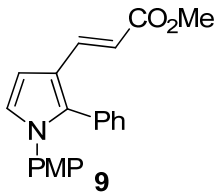


4r





NAME	Dec30-2011-purnima
EXPNO	5
PROCNO	1
Date_	20111230
Time	11.15
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	869
DS	4
SWH	25252.525 Hz
FIDRES	0.385323 Hz
AQ	1.2976629 sec
RG	203
DW	19.800 usec
DE	6.50 usec
TE	300.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	9.20 usec
PL1	-2.40 dB
PL1W	63.73131180 W
SFO1	100.6228298 MHz
========	CHANNEL f2 ========
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.00 dB
PL12	16.72 dB
PL13	20.00 dB
PL2W	10.61479568 W
PL12W	0.28438827 W
PL13W	0.13363236 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



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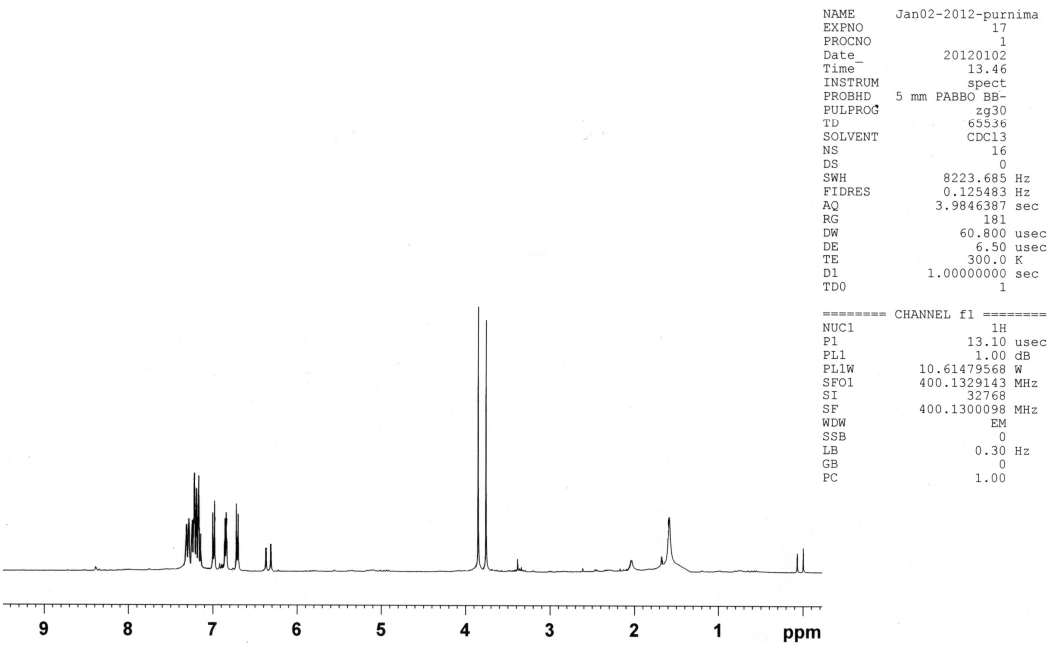

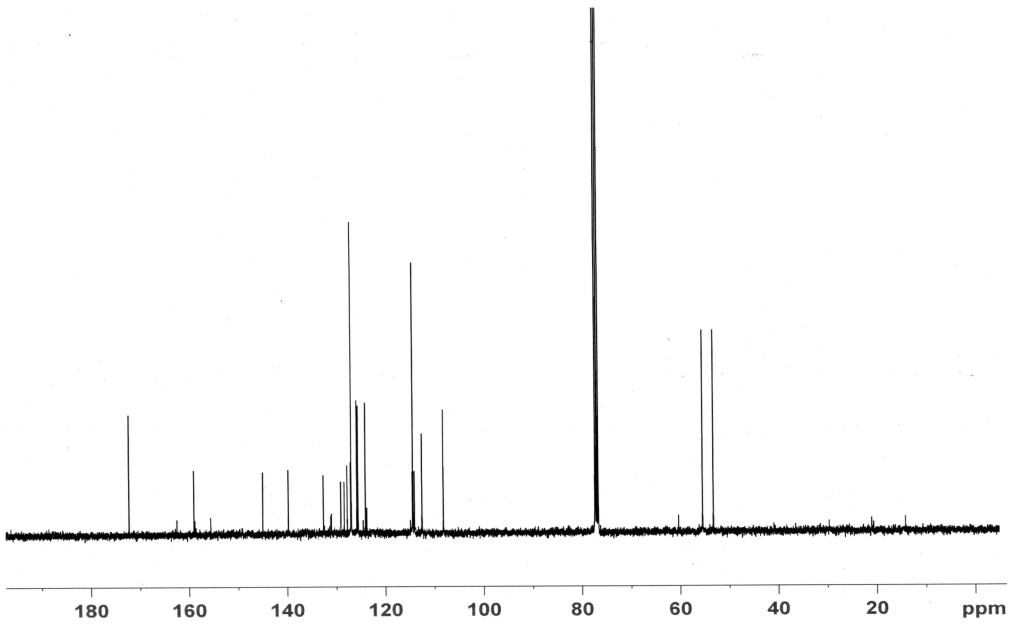

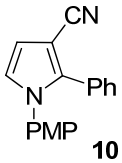

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