

## Supporting Information

for

### *A Novel Transition Metal Free, [bis-(trifluoroacetoxy)iodo]benzene (PIFA) Mediated Oxidative ipso Nitration of Organoboronic Acids*

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## 1. General information

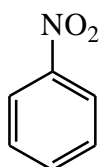
Chemicals and reagents were purchased from commercial suppliers and used without further purification. Anhydrous solvent ( $\text{CH}_3\text{CN}$ ) used in the reactions was dried and freshly distilled before use. Thin layer chromatography (TLC) was performed using pre-coated plates purchased from E. Merck (silica gel 60 PF254, 0.25 mm). Column chromatography was performed using E. Merck silica gel 60 (100–200 mesh). GC-MS analyses were carried out on SHIMADZU GCMS-QP Ultra 2010 instrument. NMR spectra were recorded in  $\text{CDCl}_3$ , on JEOL JNM-ECS spectrometer at operating frequencies of 400 MHz ( $^1\text{H}$ ) or 100 MHz ( $^{13}\text{C}$ ) as indicated in the individual spectrum. Chemical shifts ( $\delta$ ) are given in ppm relative to residual solvent (chloroform,  $\delta= 7.26$  for  $^1\text{H}$  and 77.16 for proton decoupled  $^{13}\text{C}$  NMR) and coupling constants ( $J$ ) in Hz. Multiplicity is tabulated as s for singlet, d for doublet, dd for doublet of doublet, t for triplet, and m for multiplet.

## 2. Syntheses and Characterizations of the Aromatic and Aliphatic Nitro Compounds

### General procedure for syntheses of aromatic, heteroaromatic and aliphatic nitro compounds:

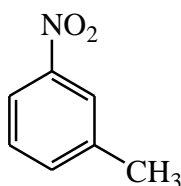
To a stirred solution of appropriate organoboronic acids (0.5 mmol, 1.0 eq.) in CH<sub>3</sub>CN, PIFA (1.5 mmol, 3 eq.), NBS (1 mmol, 2 eq.) and NaNO<sub>2</sub> (1.5 mmol, 3 eq.) were added and the mixture was stirred for 3 h. After completion of the reaction (checked by TLC), the mixture was concentrated under vacuum. It was then washed with distilled water (3×4 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×7 mL). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and after evaporating the solvent, the residue was purified by column chromatography over silica gel using pentane/ether as eluent to provide the pure target product.

### Characterization of compounds:



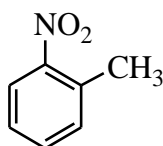
**2a**

**Nitrobenzene (2a)<sup>1</sup>:** **2a** was obtained as a pale yellow liquid (82%, 50.4 mg) following the general procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.20 (dd, *J* = 8.7 Hz, 0.9 Hz, 2H), 7.69 (tt, *J* = 7.3 Hz, 1.4 Hz, 1H), 7.55-7.50 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 148.1, 134.7, 129.4, 123.5; GC-MS (*m/z*): 123 [M<sup>+</sup>]



**2b**

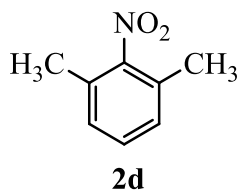
**3-Nitrotoluene (2b)<sup>1</sup>:** **2b** was obtained as a yellowish liquid (93%, 63.7 mg) following the general procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.99 (d, *J* = 8.2, 2H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 148.2, 139.8, 135.4, 129.11, 123.9, 120.4, 21.3; GC-MS (*m/z*): 137 [M<sup>+</sup>].



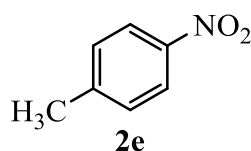
**2c**

**2-Nitrotoluene (2c)<sup>1</sup>:** **2c** was obtained as a pale yellow liquid (90%, 61.6 mg) following the general procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.90 (d, *J* = 8.7, 1H), 7.45 (t, *J* = 7.6, 1H),

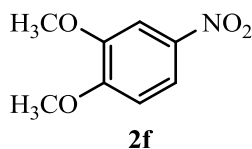
7.27-7.30 (m, 2H), 2.54 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.1, 133.5, 133.0, 132.7, 126.9, 124.5, 20.1; GC-MS ( $m/z$ ): 137 [ $\text{M}^+$ ]



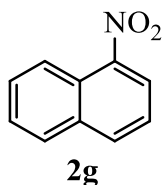
**1, 3 Dimethyl-2-Nitrobenzene (2d)<sup>1</sup>:** **2d** was obtained as a yellow liquid (89%, 67.2 mg) following the general procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.14 (t,  $J = 7.8$  Hz, 1H), 7.00 (d,  $J = 7.8$  Hz, 2H), 2.19(s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.7, 130.0, 129.4, 128.9, 17.4; GC-MS ( $m/z$ ): 151[ $\text{M}^+$ ]



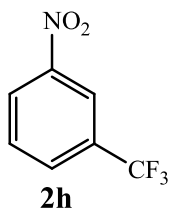
**4-Nitrotoluene (2e)<sup>1</sup>:** **2e** was obtained as a pale yellow crystalline solid (92%, 63.0 mg) following the general procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.10 (d,  $J = 8.7$  Hz, 2H), 7.31 (d,  $J = 8.2$ , 2H), 2.46 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.1, 129.9, 123.6, 21.7; (one peak wasn't observed); GC-MS ( $m/z$ ): 137 [ $\text{M}^+$ ]



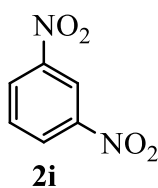
**3,4-Dimethoxy nitrobenzene (2f)<sup>1</sup>:** **2f** was obtained as a yellow crystalline powder (92%, 84.2 mg) following the general procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.91 (dd,  $J = 9.2$  Hz, 0.7 Hz, 1H), 7.74 (d,  $J = 2.3$  Hz, 1H), 6.91 (d,  $J = 9.2$  Hz, 1H), 3.98 (s, 3H), 3.96 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.6, 148.9, 141.5, 117.9, 109.9, 106.4, 56.6, 56.4; GC-MS ( $m/z$ ): 183 [ $\text{M}^+$ ]



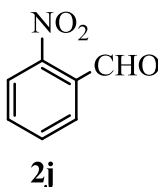
**1-Nitronaphthalene (2g)<sup>1</sup>:** **2g** was obtained as a yellow crystalline powder (88%, 76.1 mg) following the general procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.55 (d,  $J = 8.7$  Hz, 1H), 8.22 (d,  $J = 7.4$  Hz, 1H), 8.11 (d,  $J = 8.2$  Hz, 1H), 7.94 (d,  $J = 8.2$  Hz, 1H), 7.71 (t,  $J = 8.2$  Hz, 1H), 7.61 (t,  $J = 6.9$  Hz, 1H), 7.53(t,  $J = 8.0$  Hz, 1H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.5, 134.8, 134.4, 129.6, 128.7, 127.4, 125.2, 124.2, 124.1, 123.2; GC-MS ( $m/z$ ): 173 [ $\text{M}^+$ ]



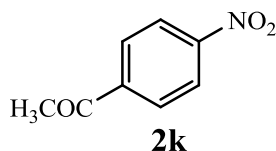
**3-Nitrobenzenetrifluoride (2h)<sup>2</sup>:** **2h** was obtained as a clear yellow liquid (80%, 76.4 mg) following the general procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.40 (d, *J* = 9.2 Hz, 2H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 148.8, 132.2 (q, *J*<sub>C-F</sub> = 34.3 Hz), 131.2 (d, *J*<sub>C-F</sub> = 1.91 Hz), 130.5, 124.3, 121.6, 120.7 (d, *J*<sub>C-F</sub> = 3.82 Hz), 118.9; GC-MS (*m/z*): 191 [M<sup>+</sup>]



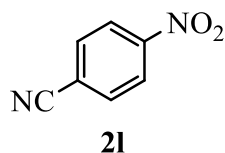
**1, 3-Dinitrobenzene (2i)<sup>2</sup>:** **2i** was obtained as a yellow crystalline powder (87%, 73.1 mg) following the general procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.07 (s, 1H), 8.58 (dd, *J* = 8.2 Hz, 0.5 Hz, 2H), 7.82 (t, *J* = 8.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 148.6, 130.8, 129.0, 119.2; GC-MS (*m/z*): 168 [M<sup>+</sup>]



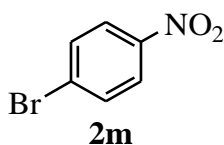
**2-Nitrobenzaldehyde (2j)<sup>3</sup>:** **2j** was obtained as a pale yellow crystalline powder (91%, 68.7 mg) following the general procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.4 (s, 1H), 8.12 (dd, *J* = 7.8 Hz, 1.4 Hz, 1H), 7.95 (dd, *J* = 7.4 Hz, 1.8 Hz, 1H), 7.74-7.82 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 188.8, 134.2, 133.8, 131.5, 129.8, 124.6, 29.8; GC-MS (*m/z*): 151 [M<sup>+</sup>]



**4-Nitroacetophenone (2k)<sup>1</sup>:** **2k** was obtained as a pale yellow semisolid (94%, 77.5 mg) following the general procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.31 (d, *J* = 8.7 Hz, 2H), 8.11 (d, *J* = 8.3 Hz, 2H); GC-MS (*m/z*): 165 [M<sup>+</sup>]



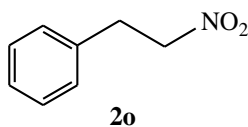
**4-Nitrobenzonitrile (2l)<sup>4</sup>:** **2l** was obtained as a pale yellow crystalline powder (90%, 66.6 mg) following the general procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.36 (d, *J* = 8.9 Hz, 2H), 7.89 (d, *J* = 8.9 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.1, 133.6, 124.5, 118.4, 116.9; GC-MS (*m/z*): 148 [M<sup>+</sup>]



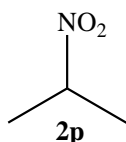
**4-Bromo-1-nitrobenzene (2m)<sup>2</sup>:** **2m** was obtained as a pale yellow semisolid (92%, 92.4 mg) following the general procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.10 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 134.4, 132.8, 130.1, 125.2; GC-MS (*m/z*): 201 [M<sup>+</sup>]



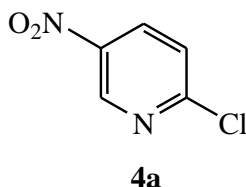
**2-Fluoro-1-nitrobenzene (2n):** **2n** was obtained as a yellowish brown liquid (80%, 56.4 mg) following the general procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.01-8.05 (m, 1H), 7.62-7.68 (m, 1H), 7.28-7.32 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 155.4 (d, *J*<sub>C-F</sub> = 263.2 Hz), 135.8 (d, *J*<sub>C-F</sub> = 8.6 Hz), 126.1 (d, *J*<sub>C-F</sub> = 2.86 Hz), 124.7 (d, *J*<sub>C-F</sub> = 3.82 Hz), 118.4 (d, *J*<sub>C-F</sub> = 20.02 Hz); GC-MS (*m/z*): 141 [M<sup>+</sup>]



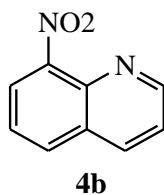
**(2-Nitroethyl) benzene (2o)<sup>5</sup>:** **2o** was obtained as a colourless liquid (90%, 68.0 mg) following the general procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.31-7.35 (m, 2H), 7.27-7.28 (m, 1H), 7.22-7.23 (m, 2H), 4.64 (t, *J* = 6.9 Hz, 2H), 3.02 (t, *J* = 7.3 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 136.3, 128.7, 127.1, 73.4, 33.4, 29.7; GC-MS (*m/z*): 151 [M<sup>+</sup>]



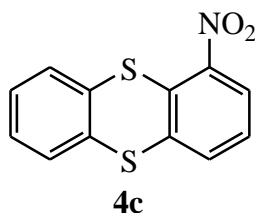
**2-Nitropropane (2p):** **2p** was obtained as a colourless liquid (74%, 131.7 mg) following the general procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 4.56-4.63 (m, 1H), 1.49 (d,  $J = 6.9$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  78.6, 20.7; GC-MS ( $m/z$ ): 89 [ $\text{M}^+$ ]



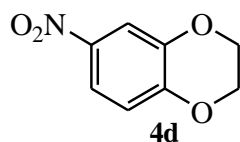
**2-Chloro-5-nitropyridine (4a):** **4a** was obtained as a light yellow solid (83%, 65.6 mg) following the general procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 9.24 (d,  $J = 2.3$  Hz, 1H), 8.45 (dd,  $J = 8.7$  Hz, 2.8 Hz, 1H), 7.54 (d,  $J = 8.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.1, 145.3, 143.7, 133.7, 125.0; GC-MS ( $m/z$ ): 158 [ $\text{M}^+$ ]



**8-Nitroquinoline (4b):** **4b** was obtained as a light yellow crystalline powder (84%, 73.1 mg) following the general procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.06 (dd,  $J = 4.1$  Hz, 1.4 Hz, 1H), 8.26 (dd,  $J = 8.7$  Hz, 1.8 Hz, 1H), 8.04 (d,  $J = 7.8$  Hz, 2H), 7.54-7.63 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.6, 139.6, 136.3, 132.2, 129.3, 125.4, 123.9, 122.9; GC-MS ( $m/z$ ): 174 [ $\text{M}^+$ ]



**1-Nitro-4,10-dihydro-thianthrene (4c):** **4c** was obtained as a dark yellow powder (83%, 108.3 mg) following the general procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.28 (dd,  $J = 7.8$  Hz, 1.4 Hz, 1H), 7.99 (dt, 8.2 Hz, 1.4 Hz, 2H), 7.78 (t,  $J = 7.8$  Hz, 1H), 7.62-7.67 (m, 2H), 7.46-7.50 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  131.0, 130.6, 130.4, 129.6, 129.3, 128.8, 128.2, 126.8, 126.2, 125.1, 124.4, 124.3; GC-MS ( $m/z$ ): 261 [ $\text{M}^+$ ]. This compound could not be obtained in perfectly pure condition; an inseparable impurity always remains there. The reported yield is along with the impurity associated with it.



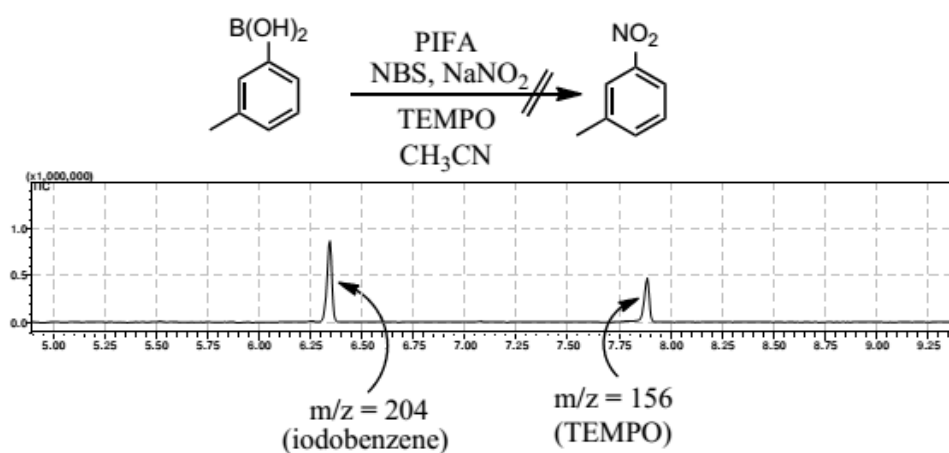
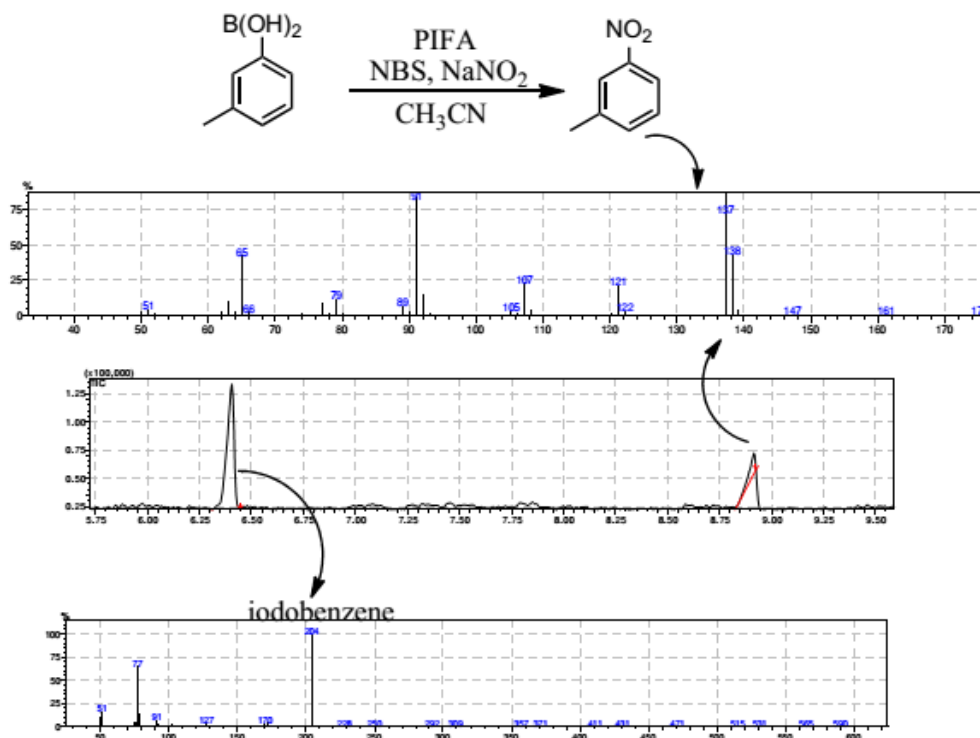
**2,3-Dihydro-6-nitro-1,4-benzodioxin (4d):** **4d** was obtained as a light yellow solid (85%, 76.9 mg) following the general procedure.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.77 (dd,  $J = 7.3$  Hz, 2.3 Hz, 2H), 6.93 (dd,  $J = 7.3$  Hz, 2.8 Hz, 1H), 4.36-4.30 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.8, 143.3, 141.9, 117.8, 117.4, 113.7, 64.8, 64.2; GC-MS ( $m/z$ ): 181 [ $\text{M}^+$ ]

#### References:

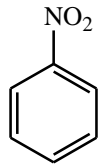
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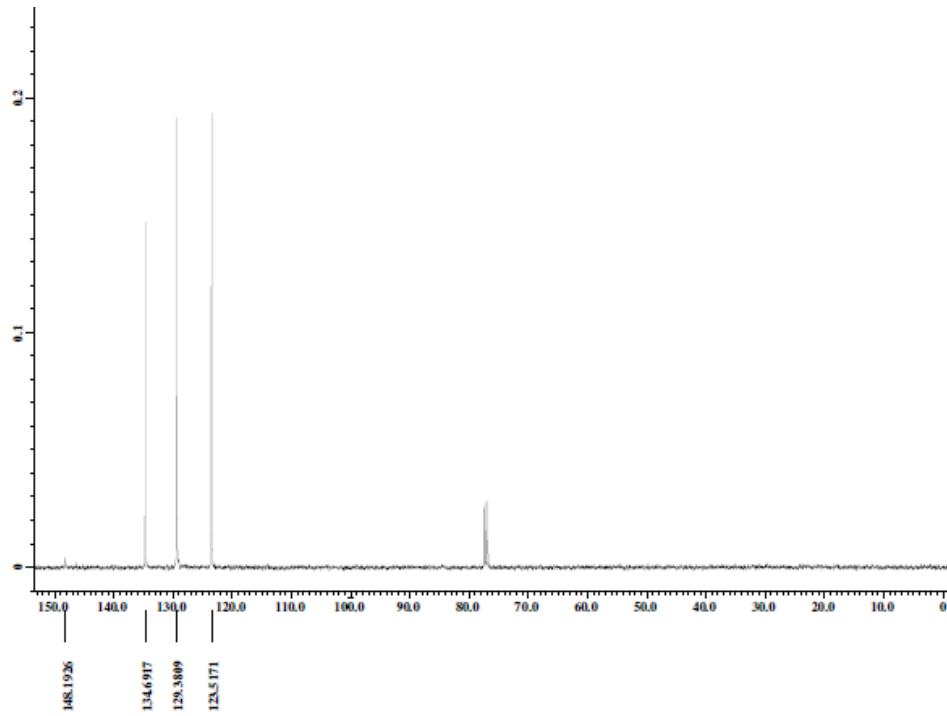
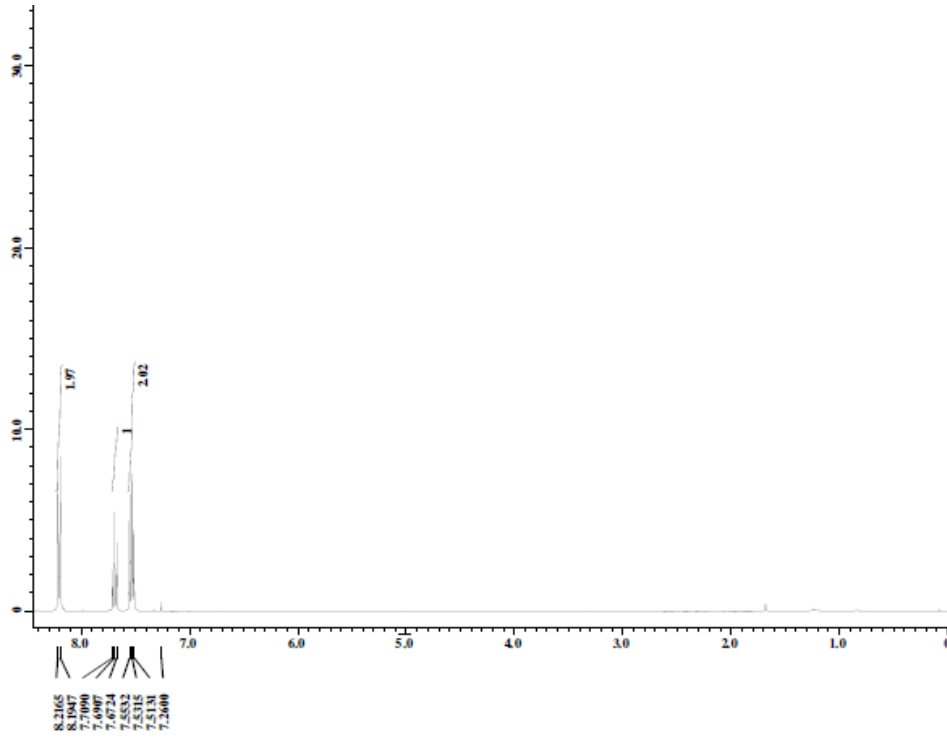
**Radical Scavenging Experiment:** *Successful nitration with PIFA-NBS- $\text{NaNO}_2$  in the absence of TEMPO whereas no nitration took place in the presence of TEMPO with the other reaction conditions remaining unaltered*

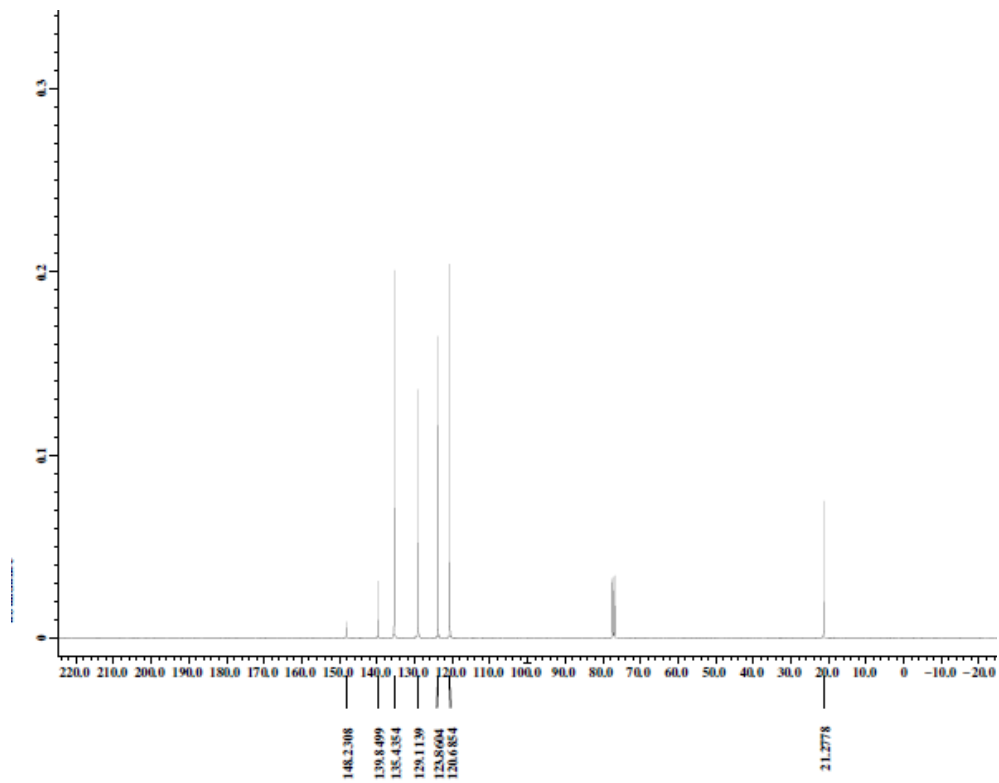
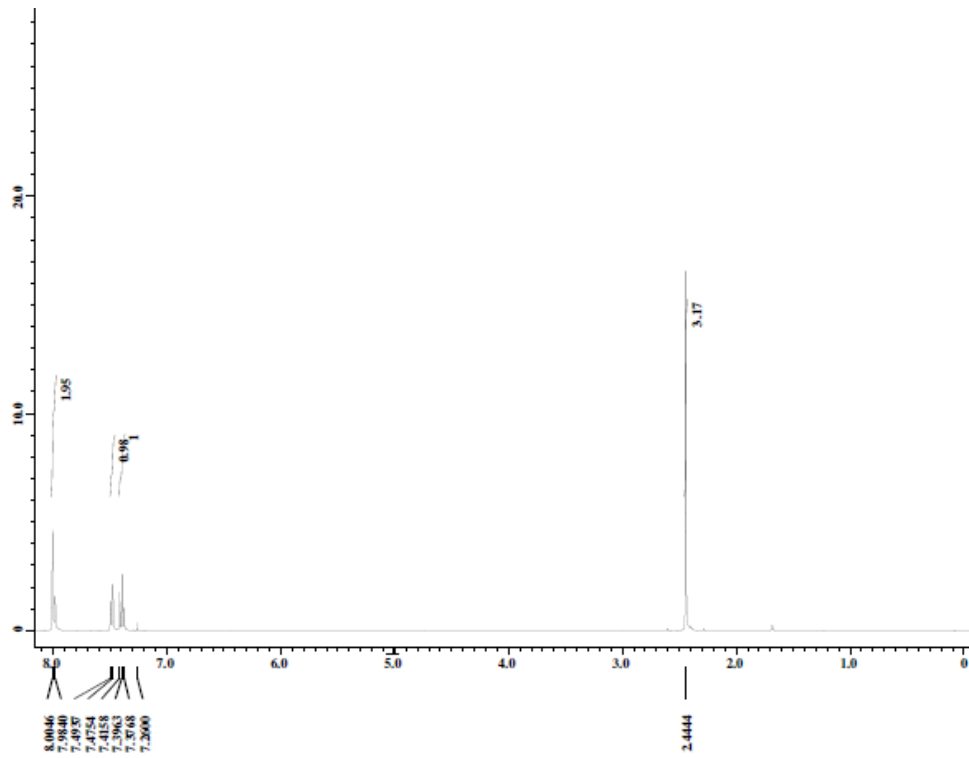
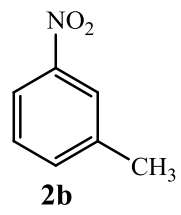


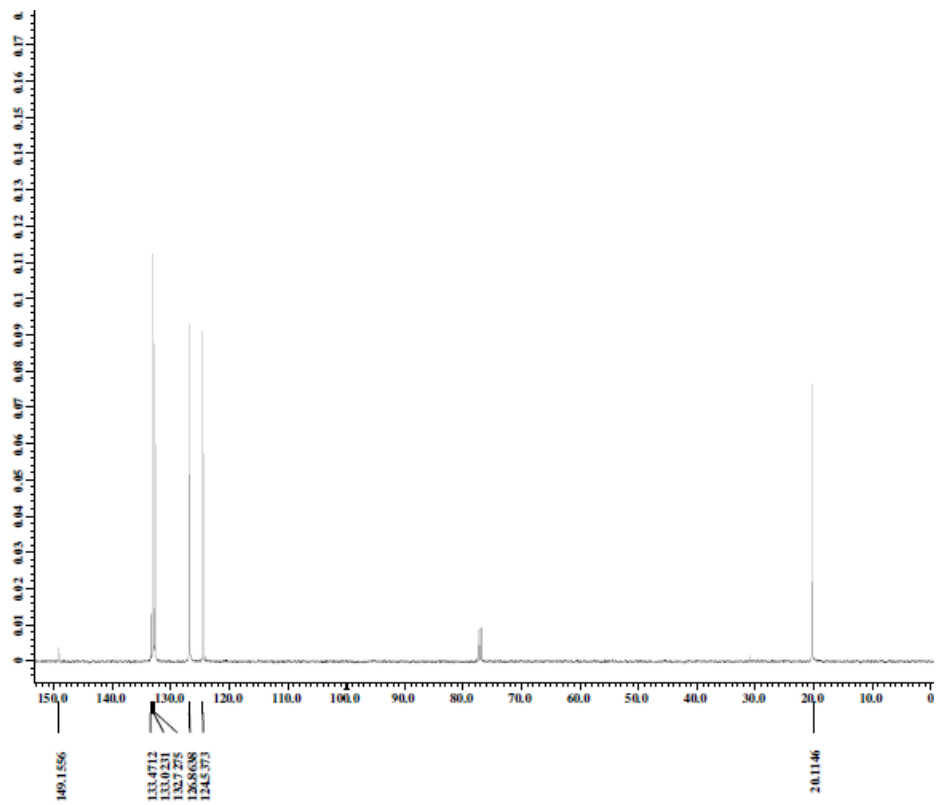
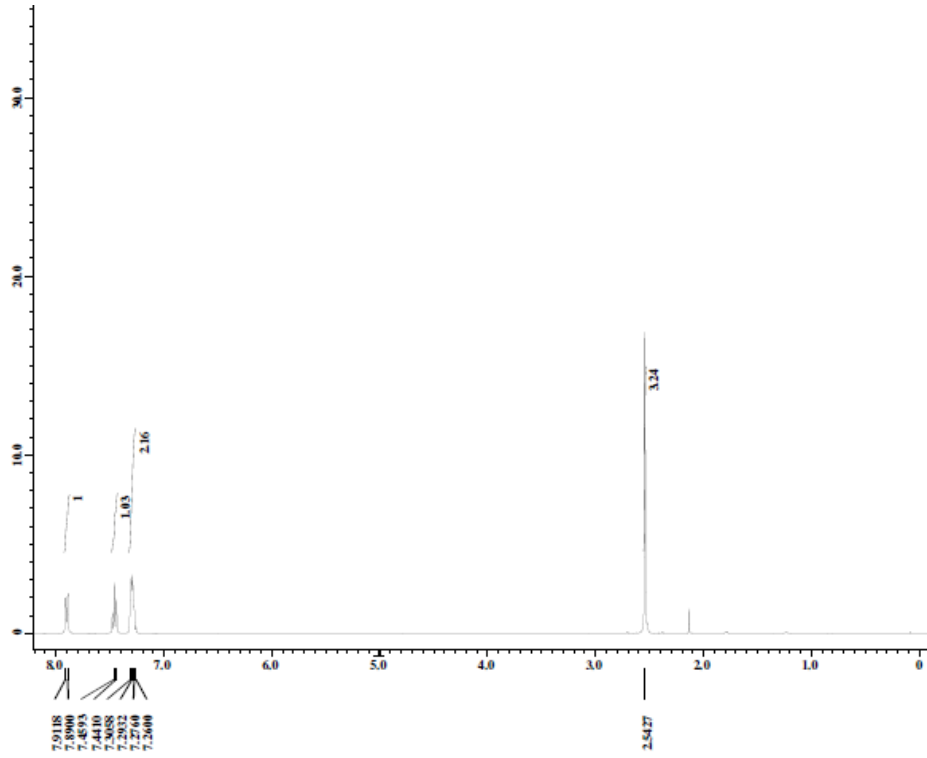
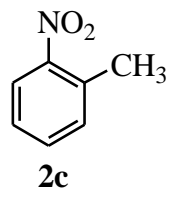
**No peak at  $m/z = 137$ , was observed**

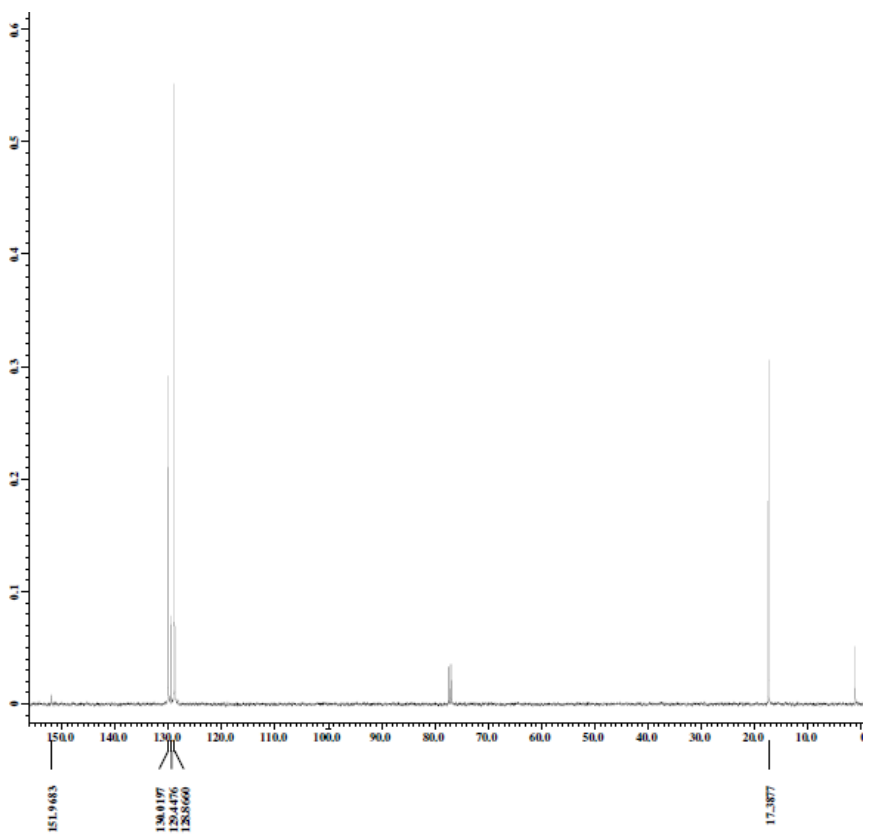
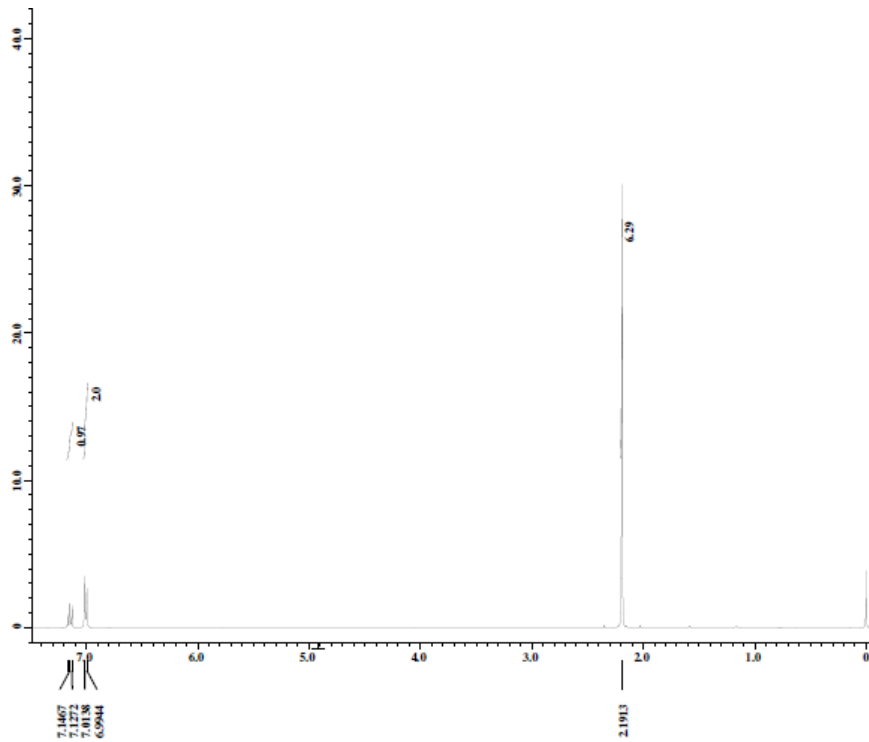
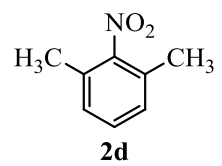


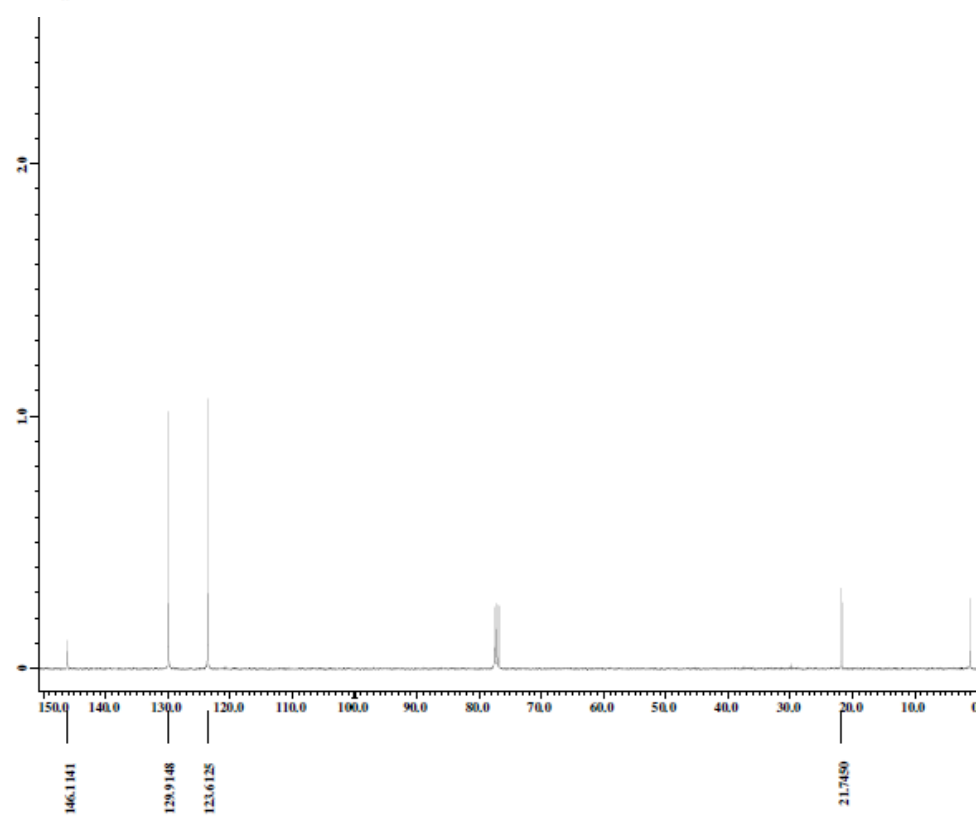
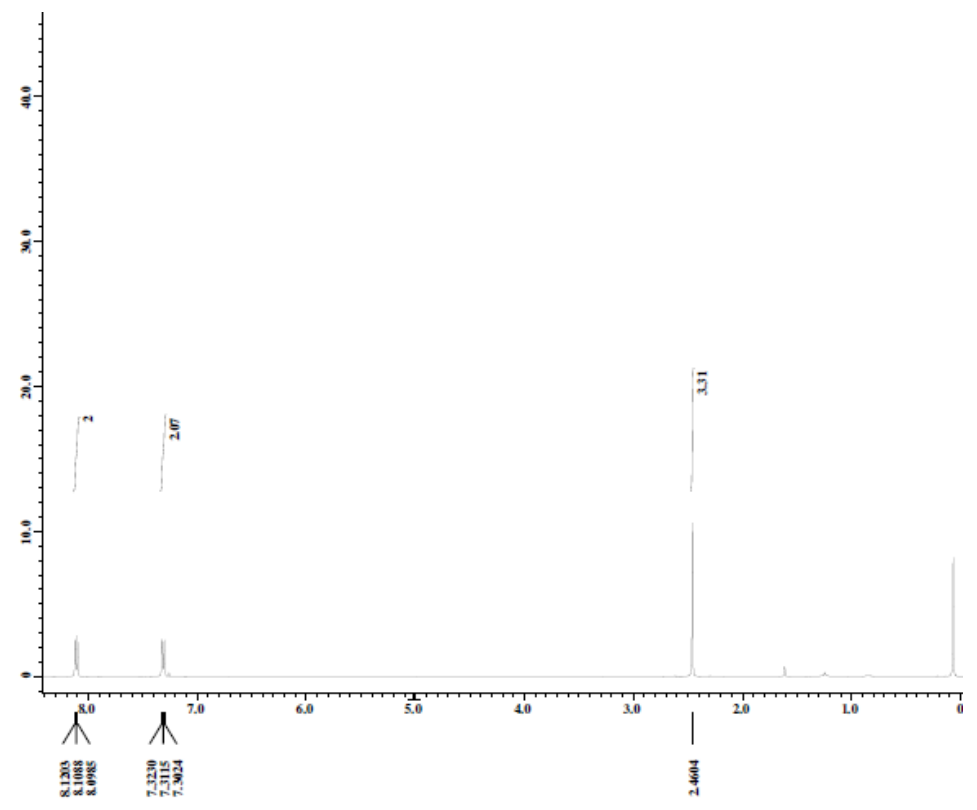
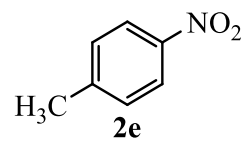
**2a**

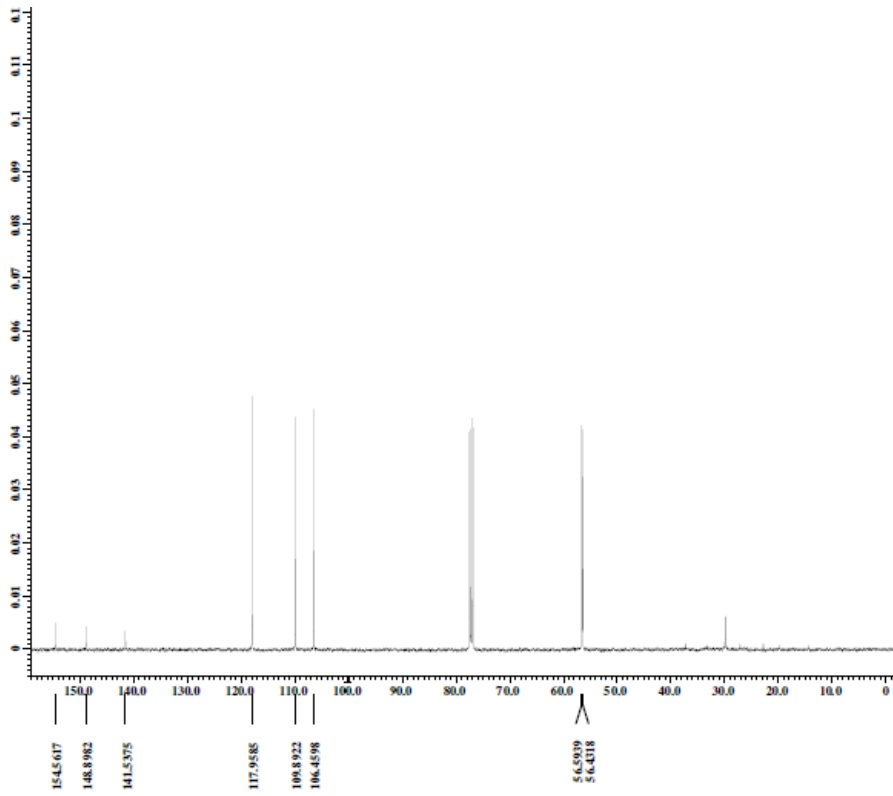
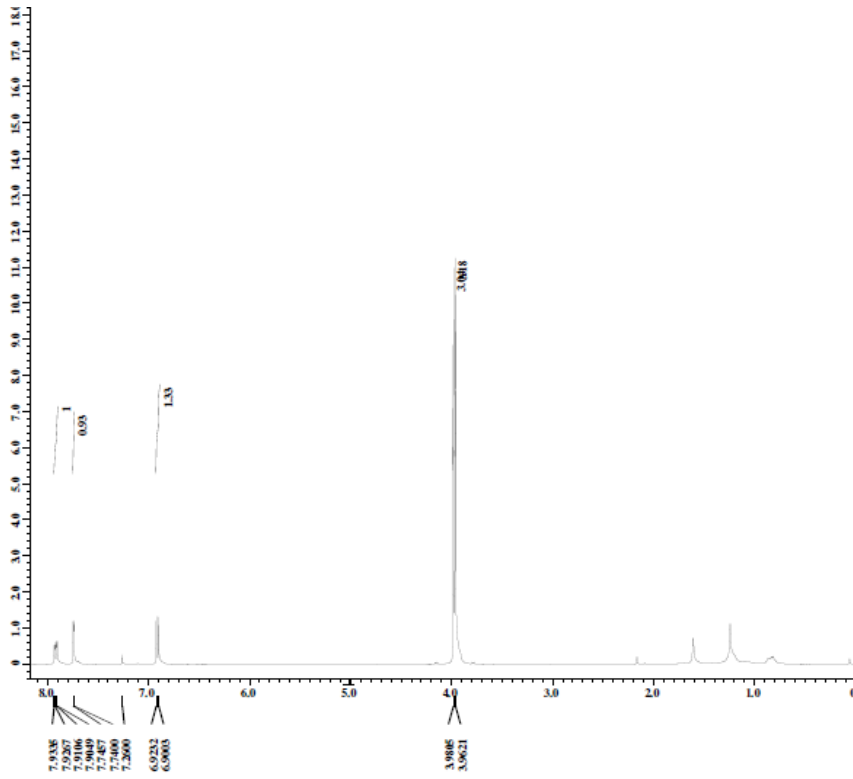
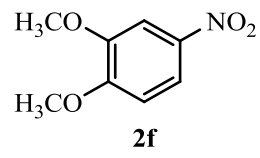


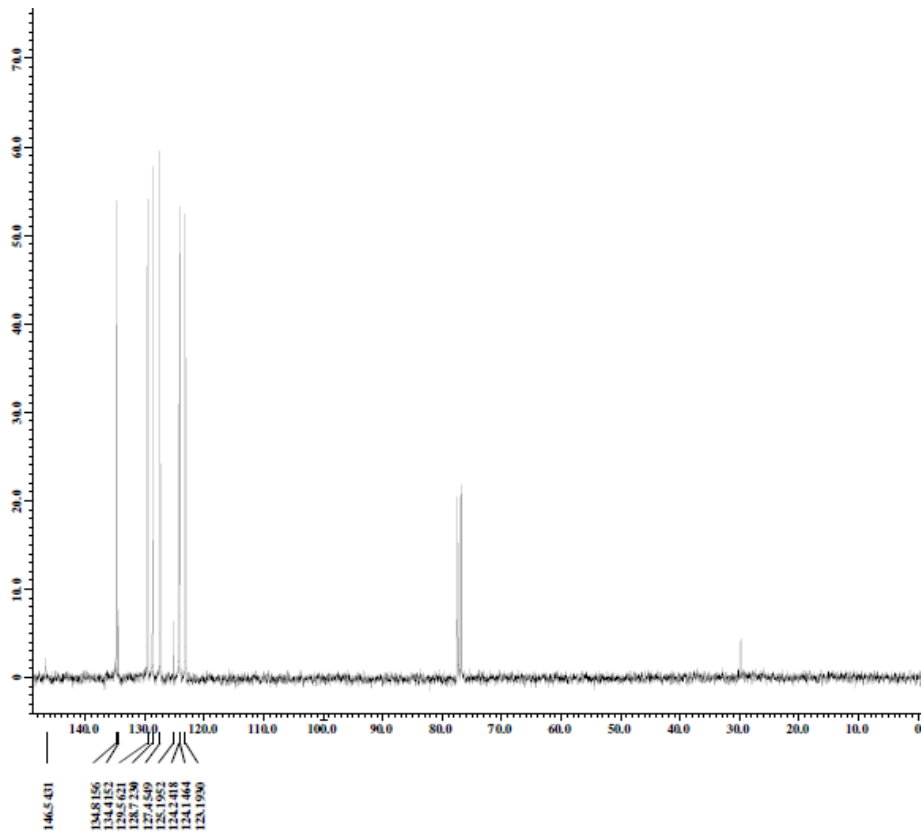
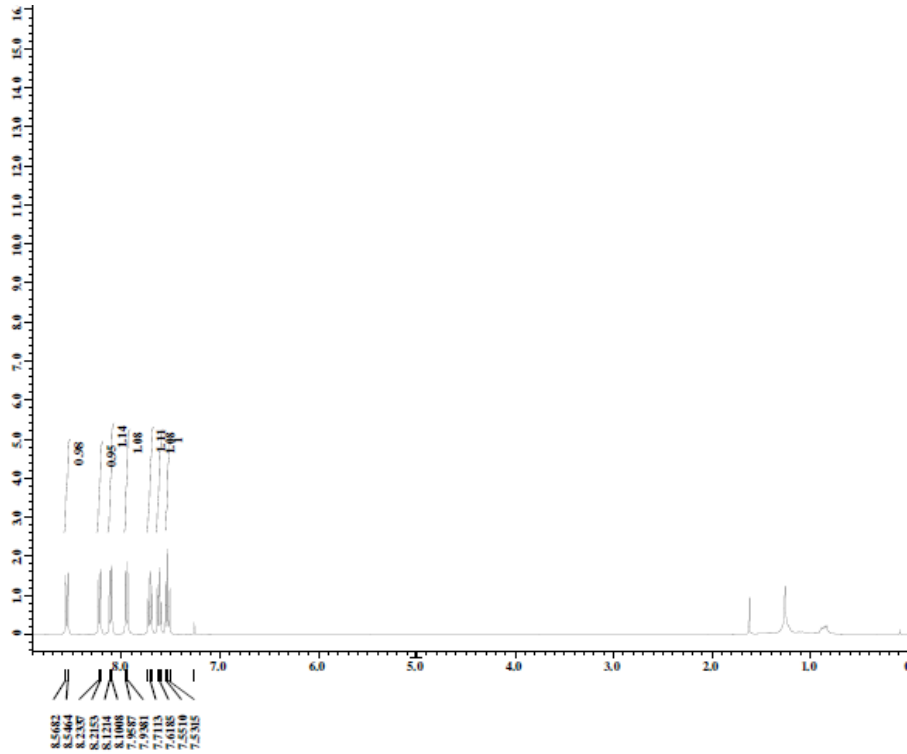
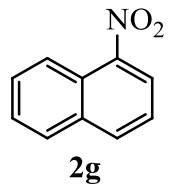




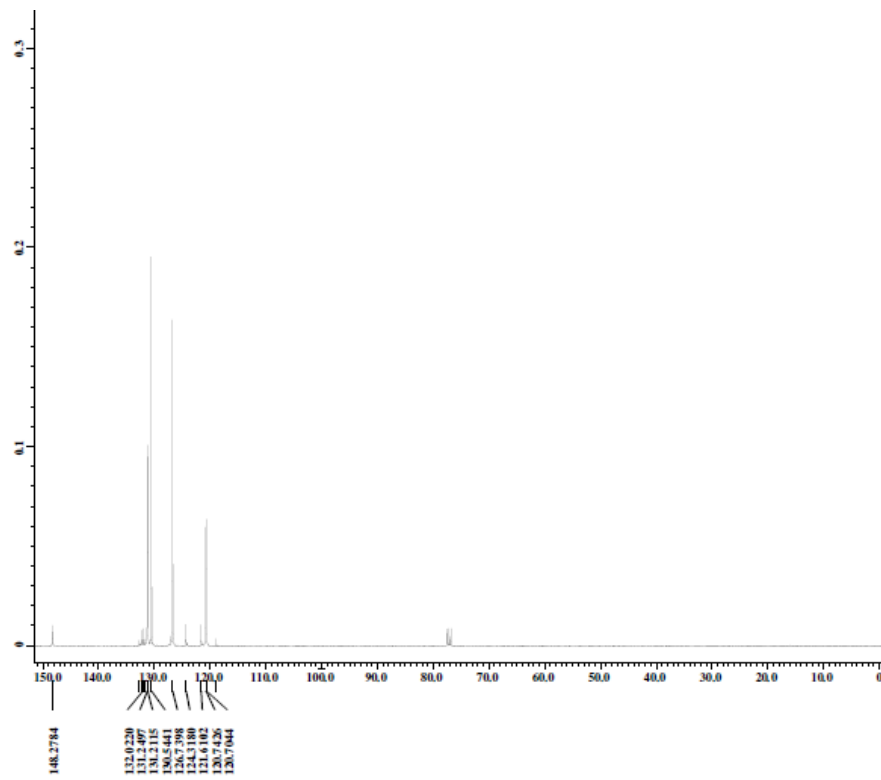
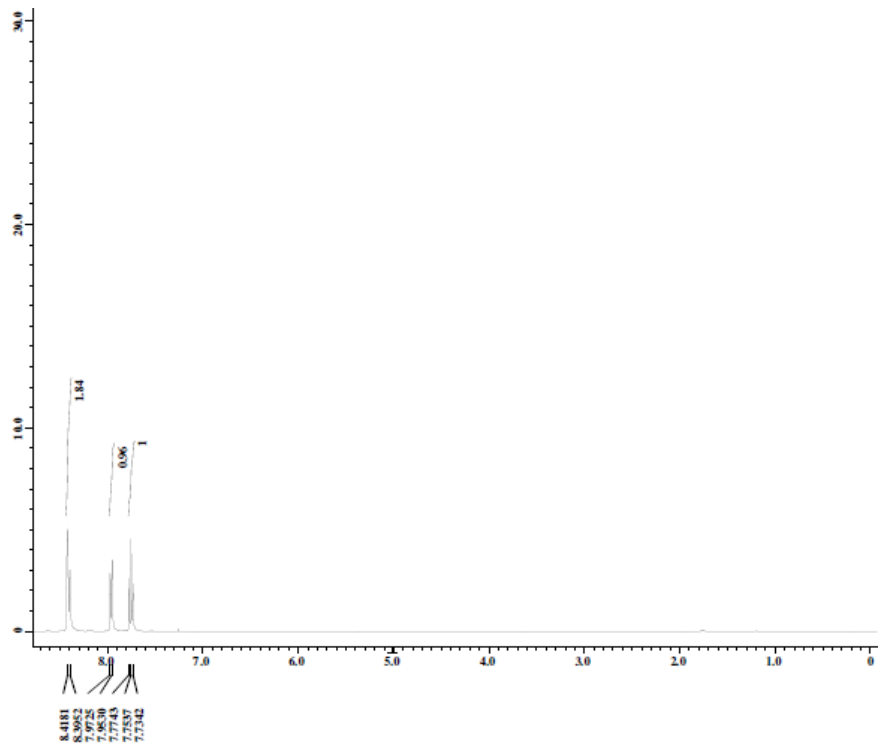
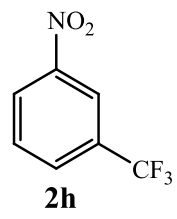


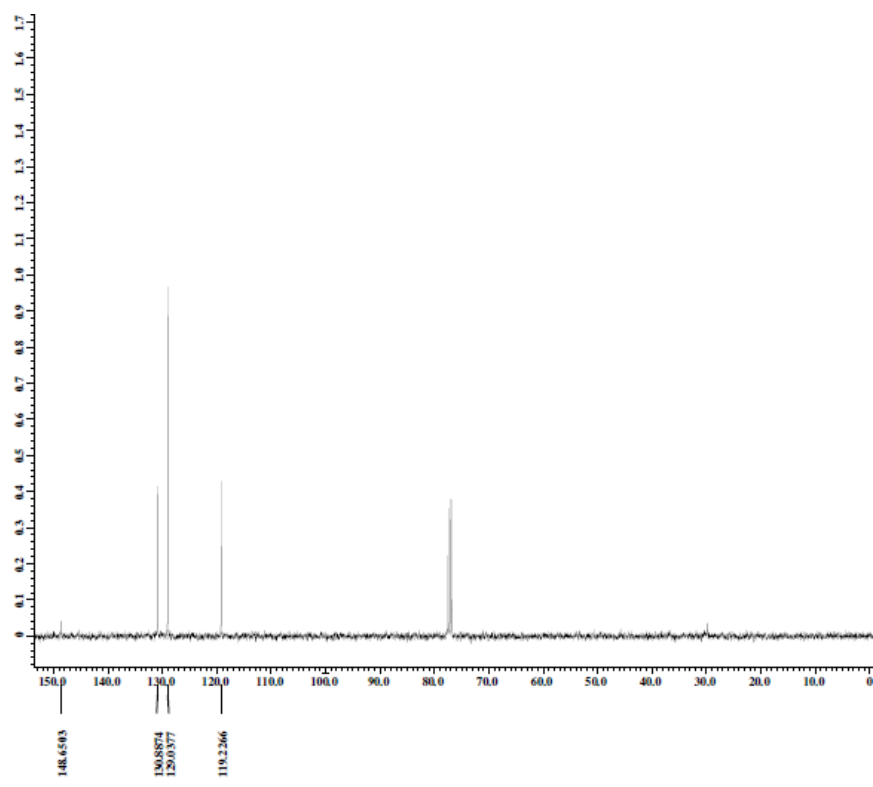
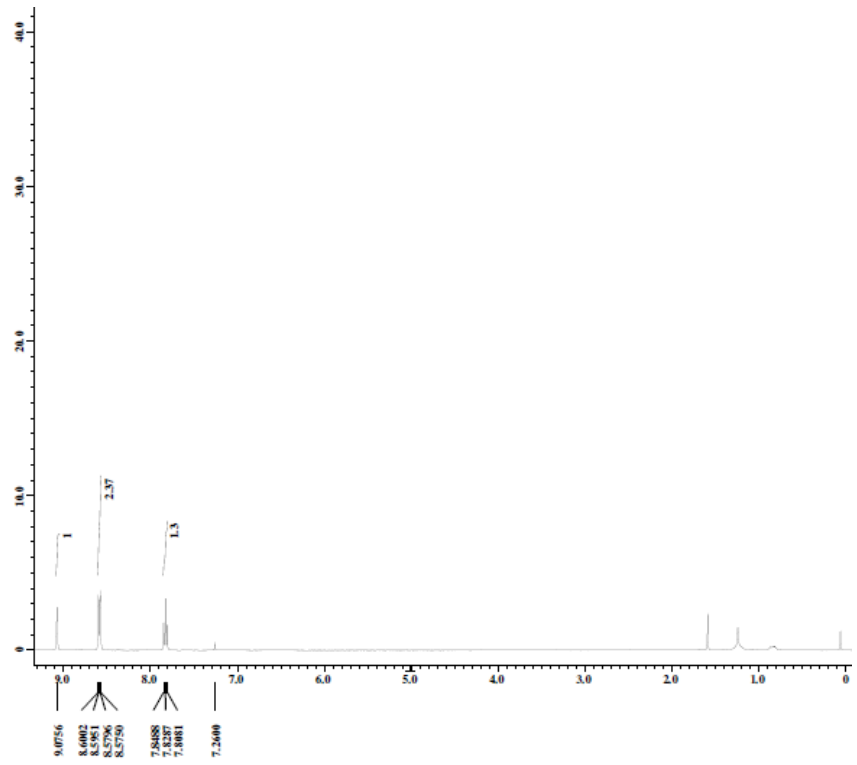
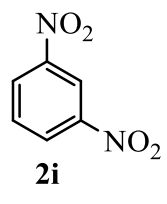


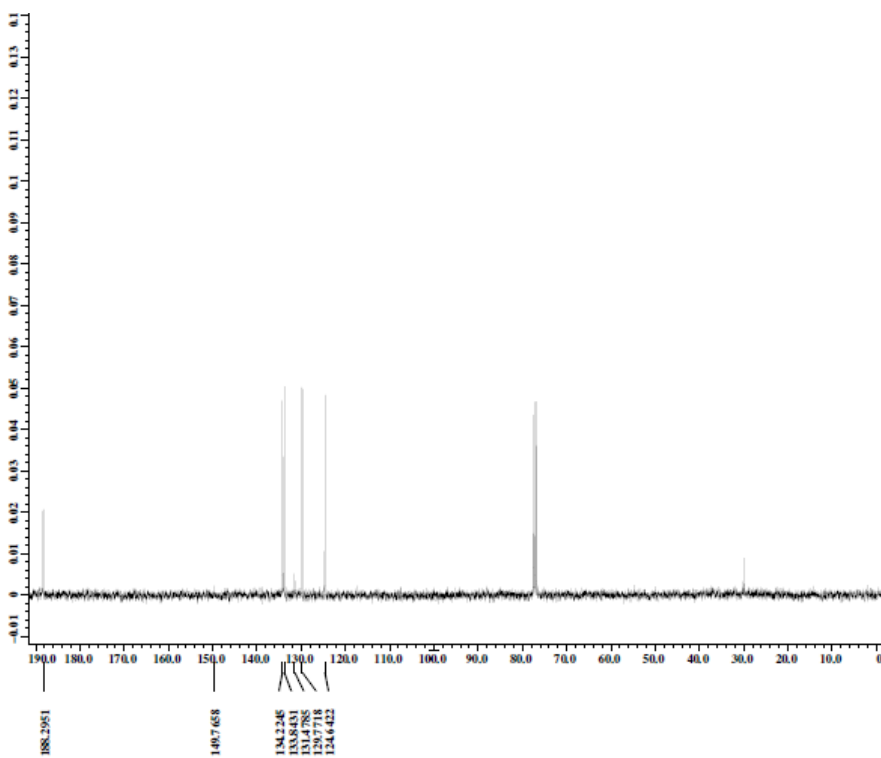
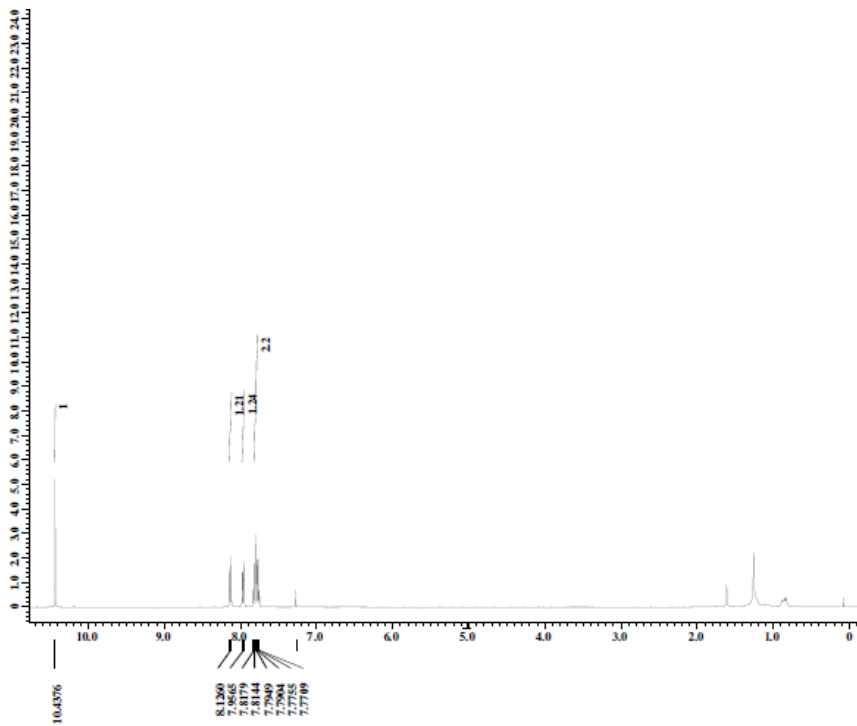
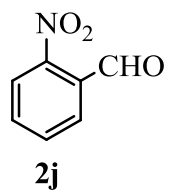


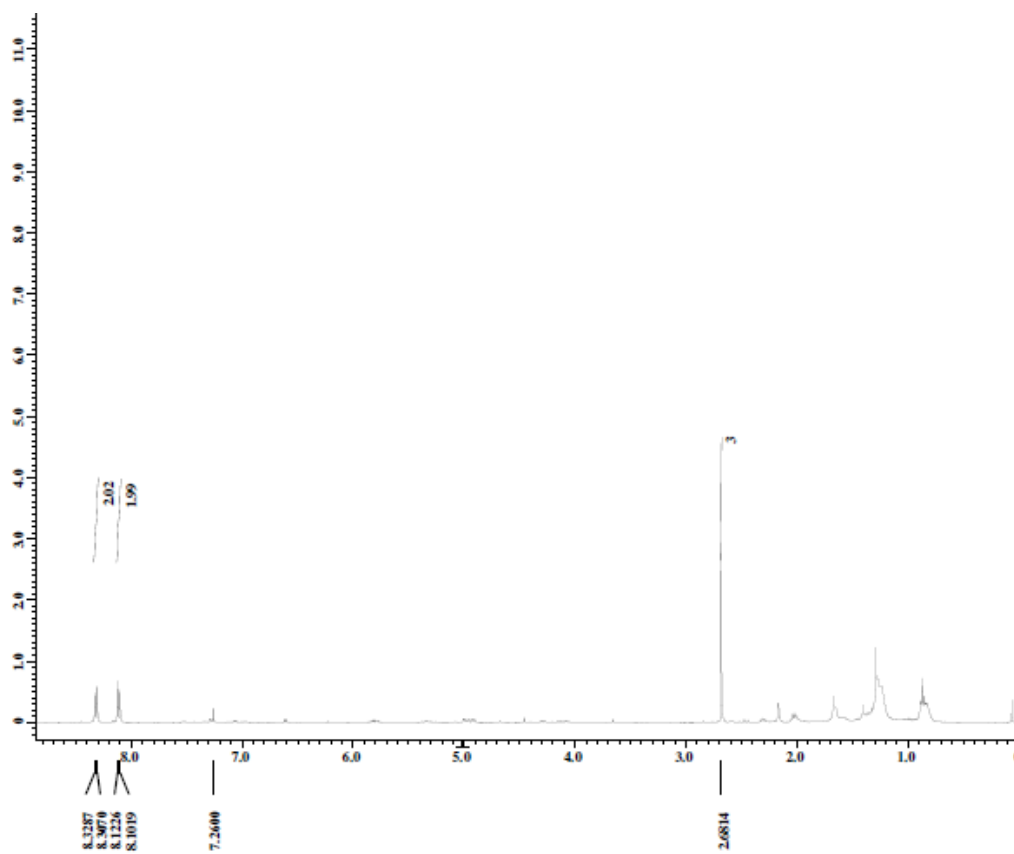
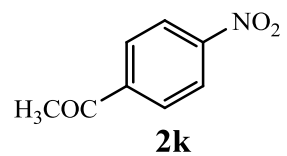


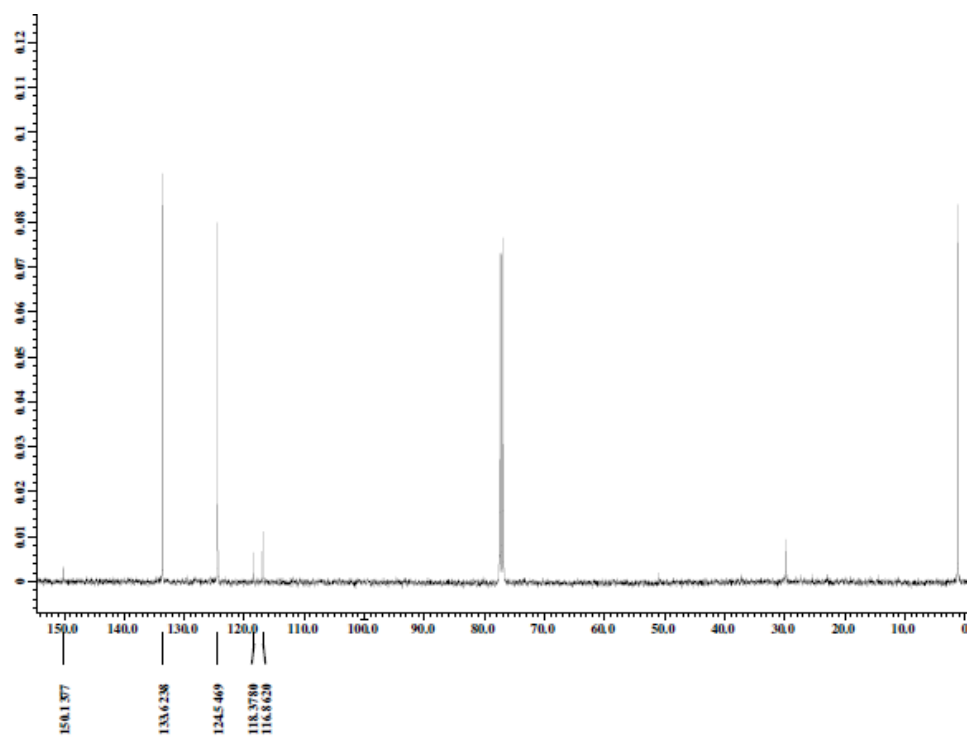
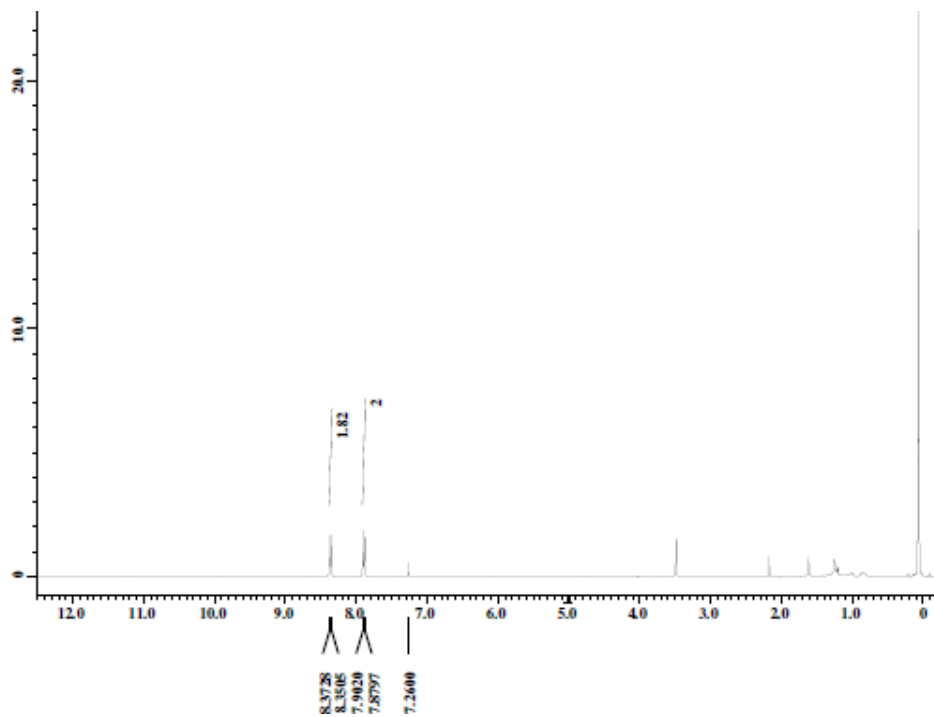
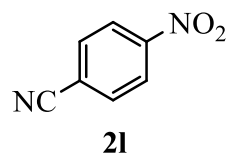


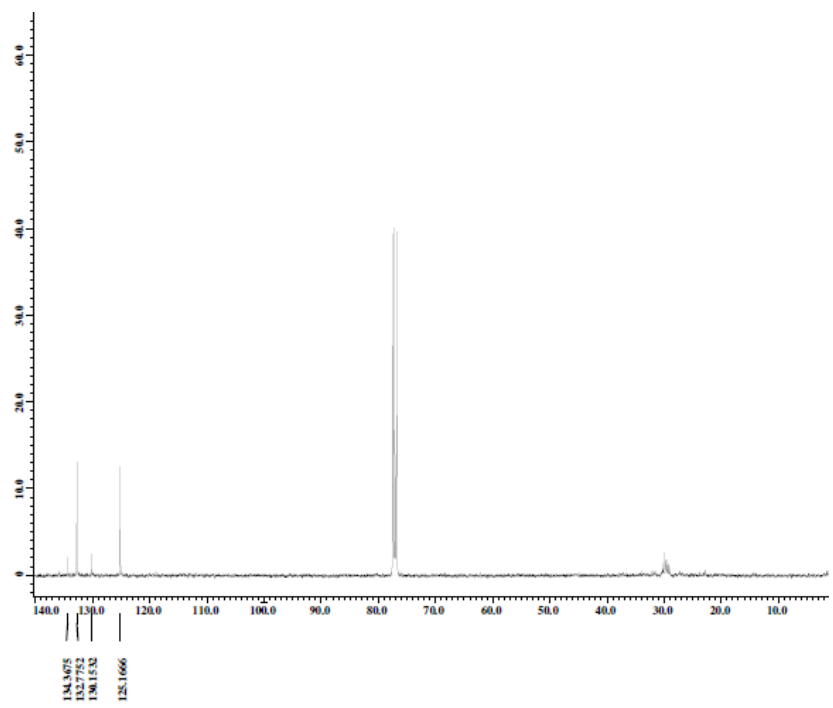
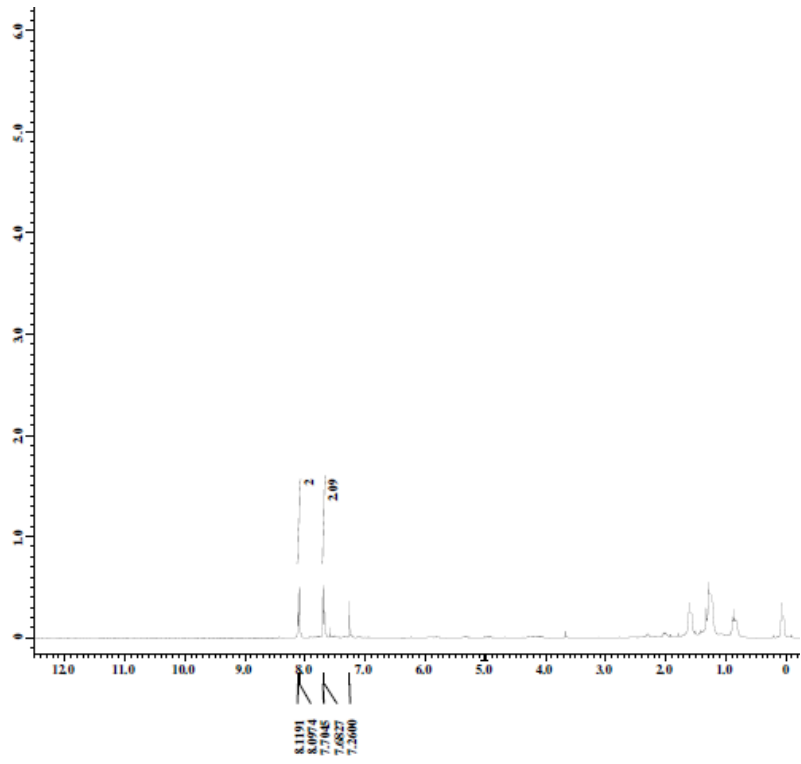
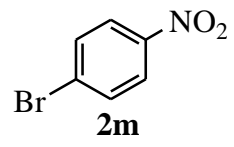


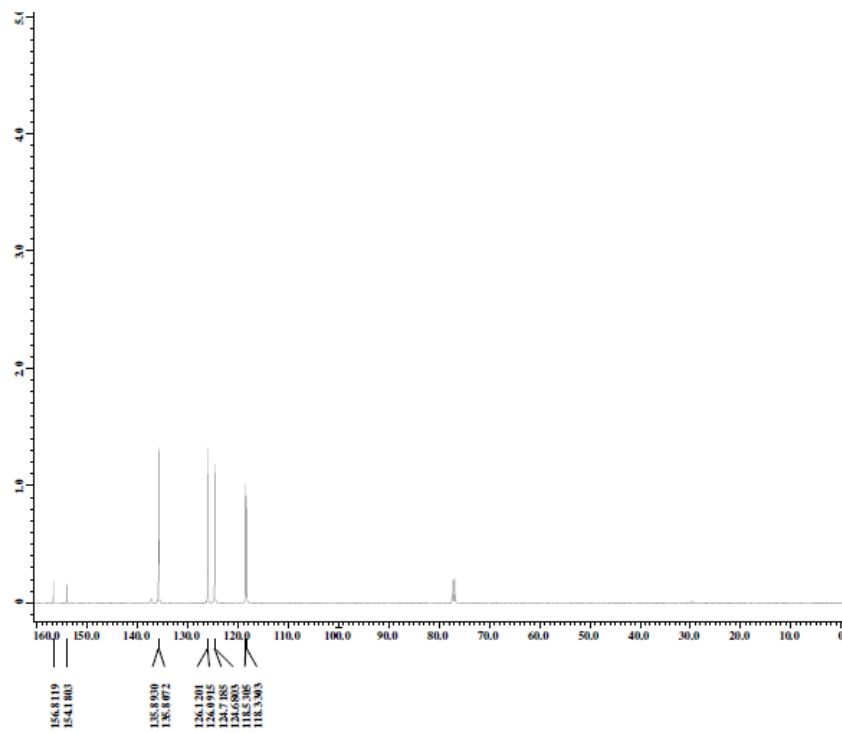
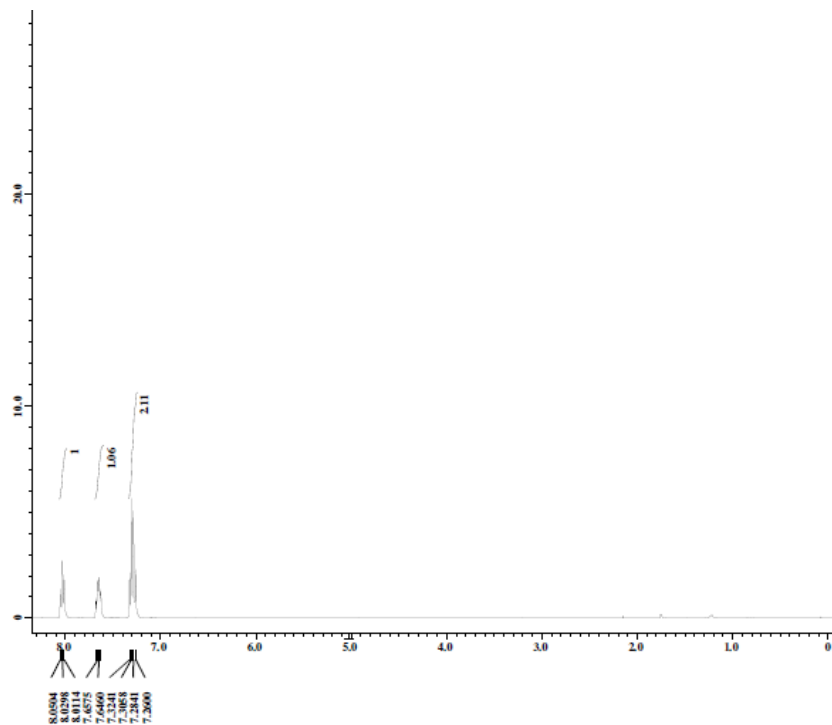
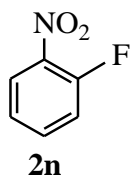


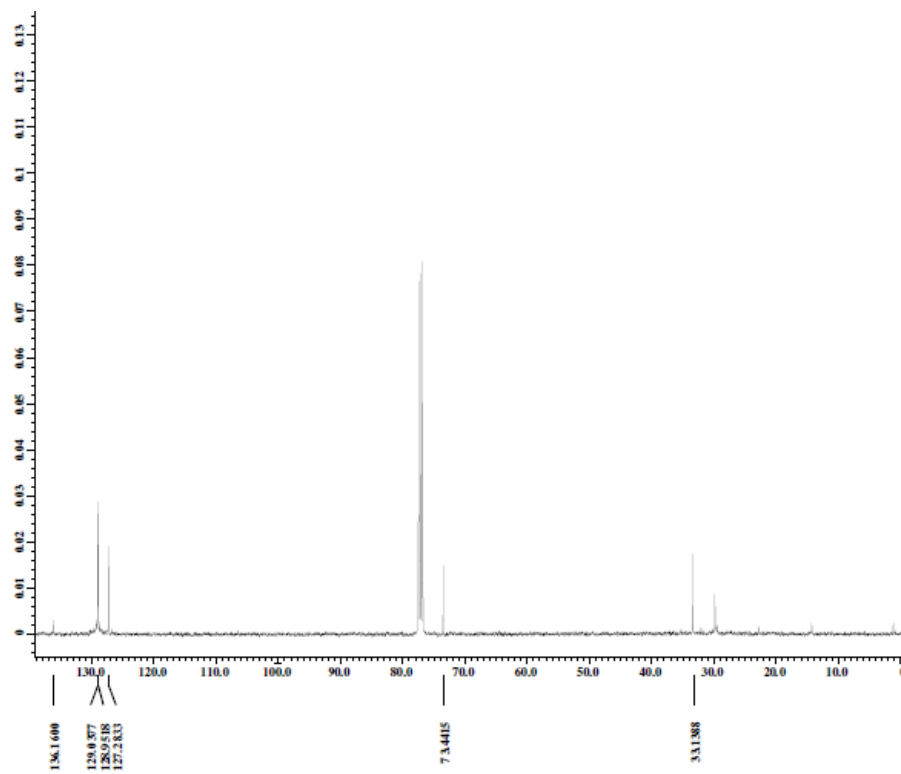
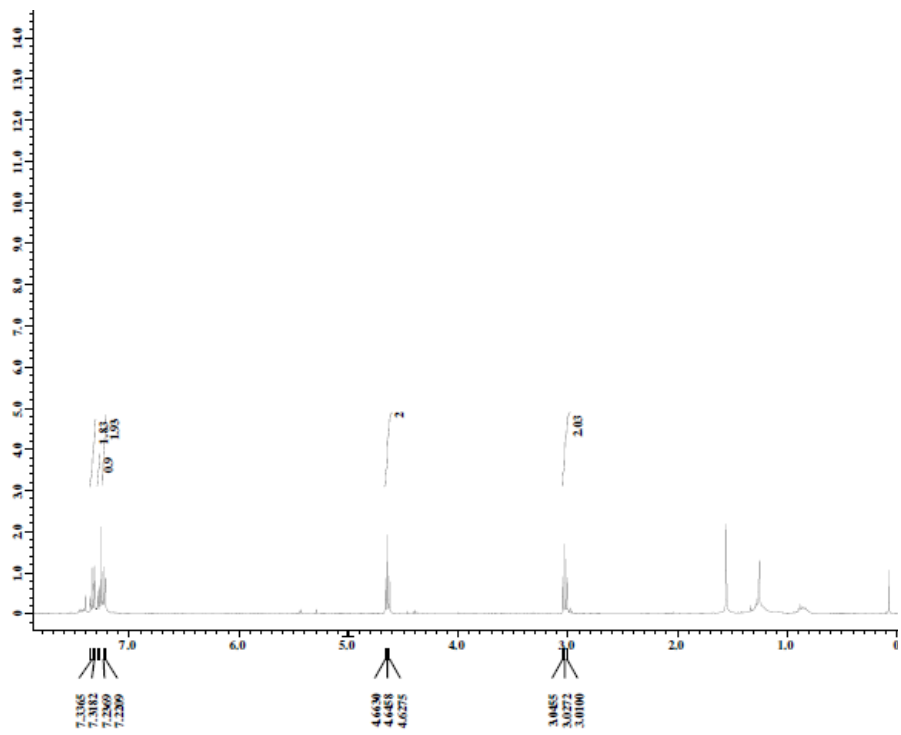
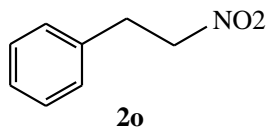




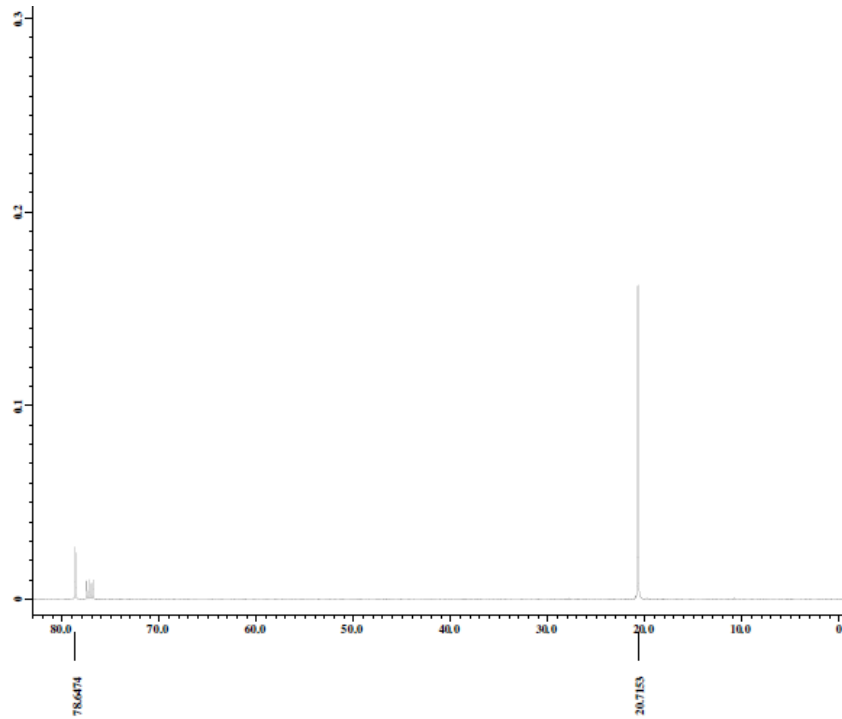
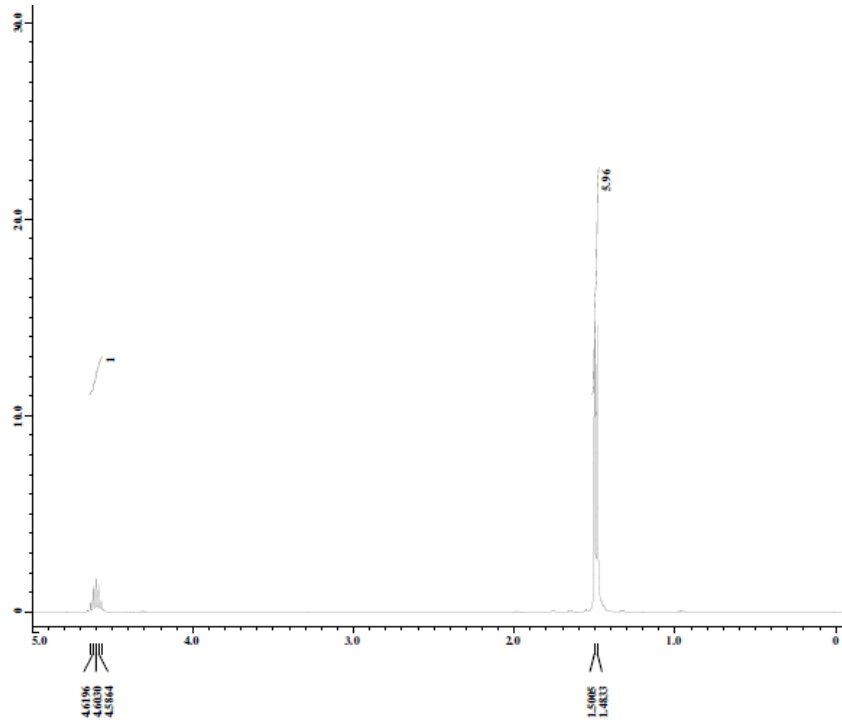
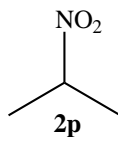


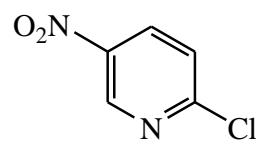




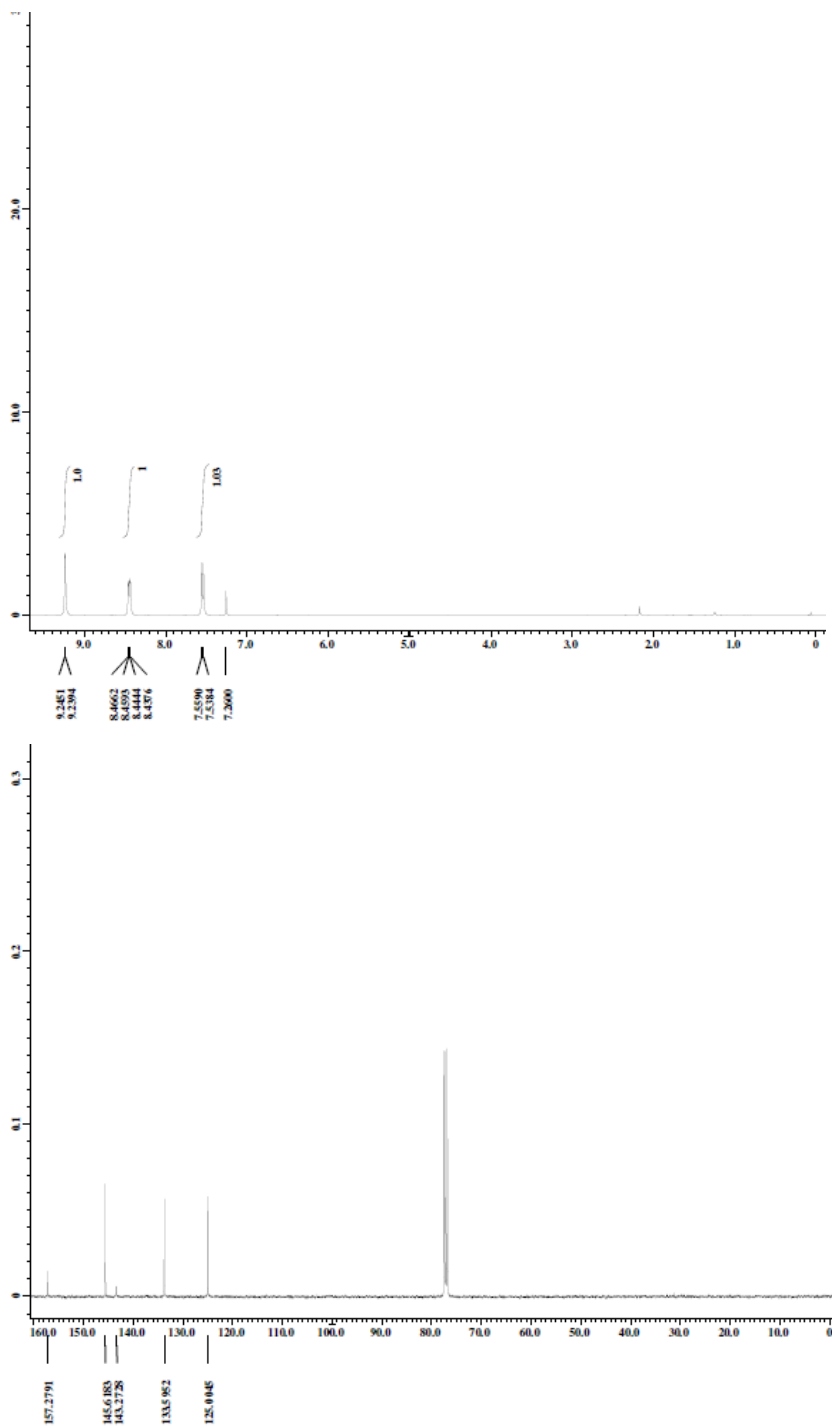


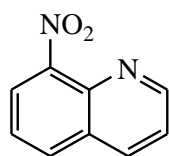




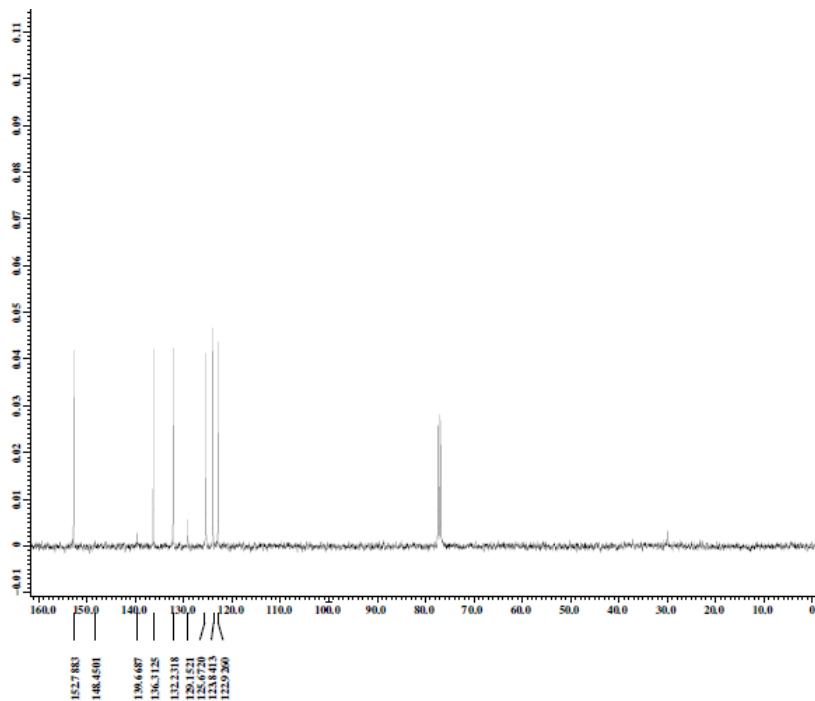
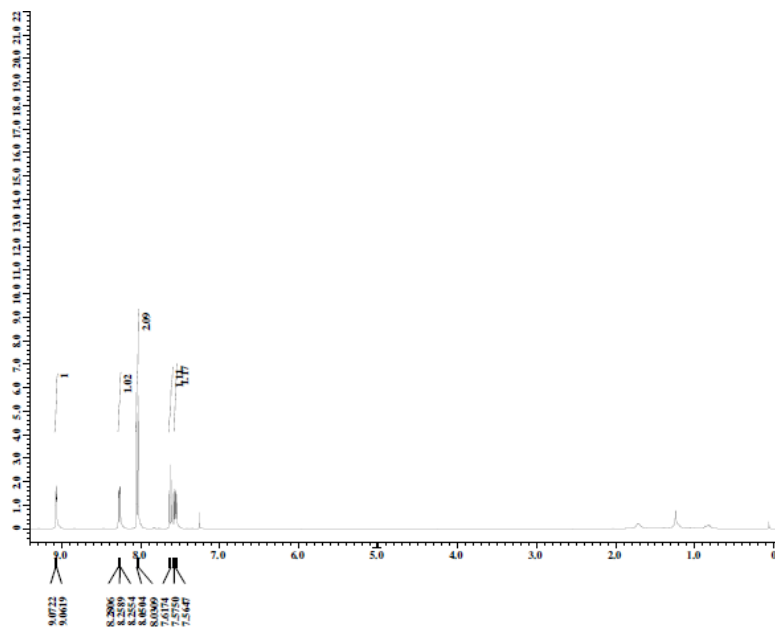


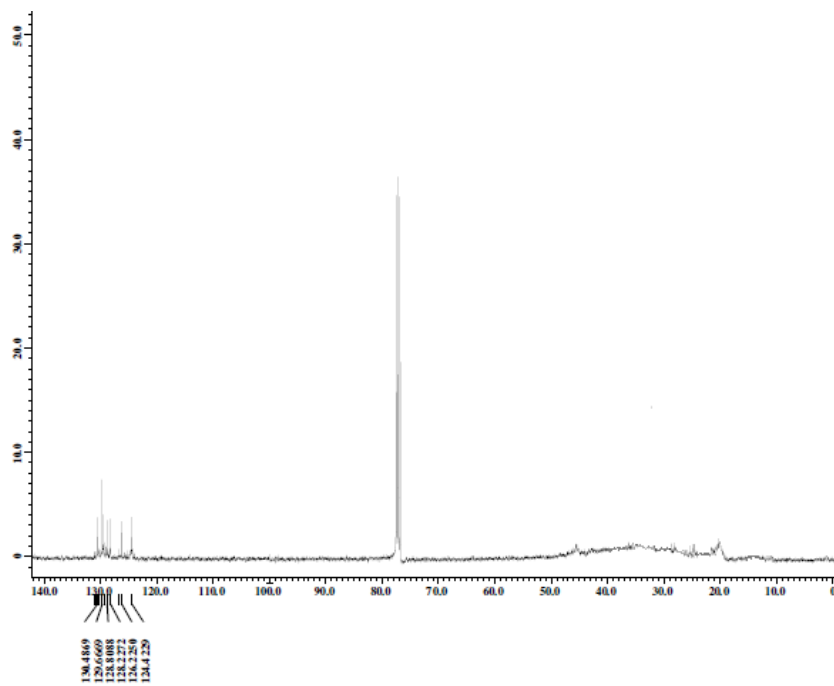
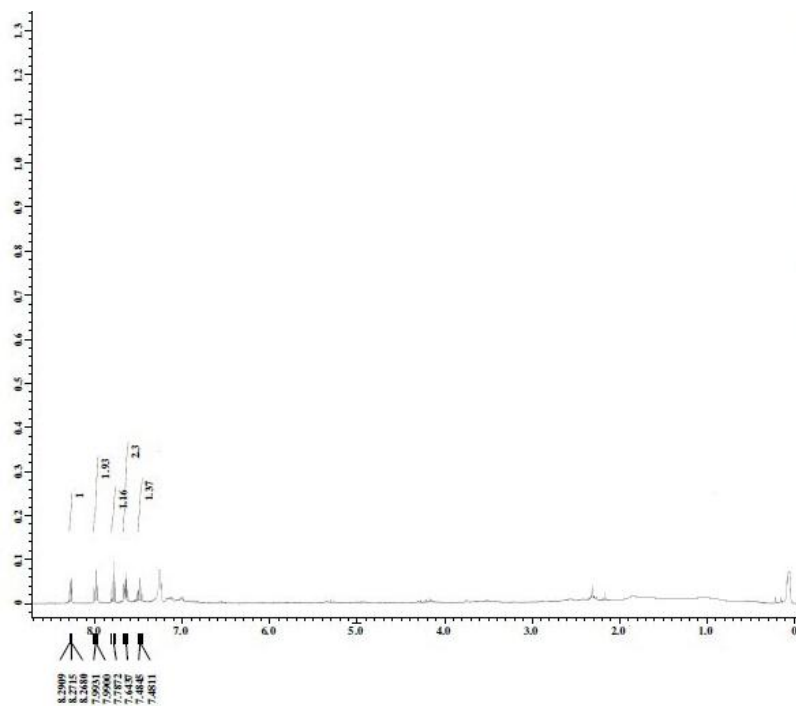
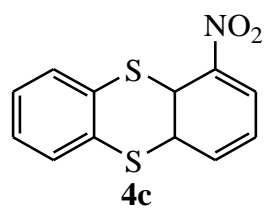
**4a**

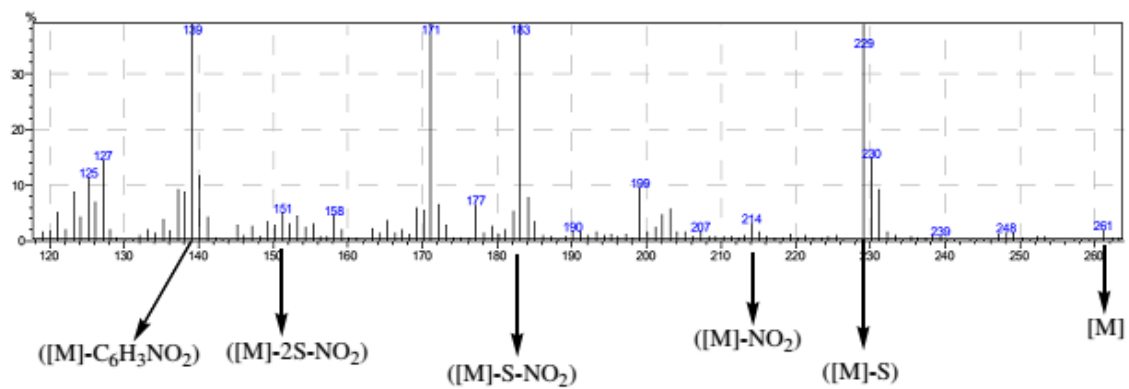
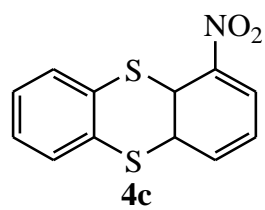




**4b**







(Mass fragmentation of **4c** obtained from GCMS instrument)

