

## Visible-light-induced photocatalytic reductive carbonylation of nitroarenes using formic acid as hydrogen source over a water-dispersible CTF-based palladium catalyst

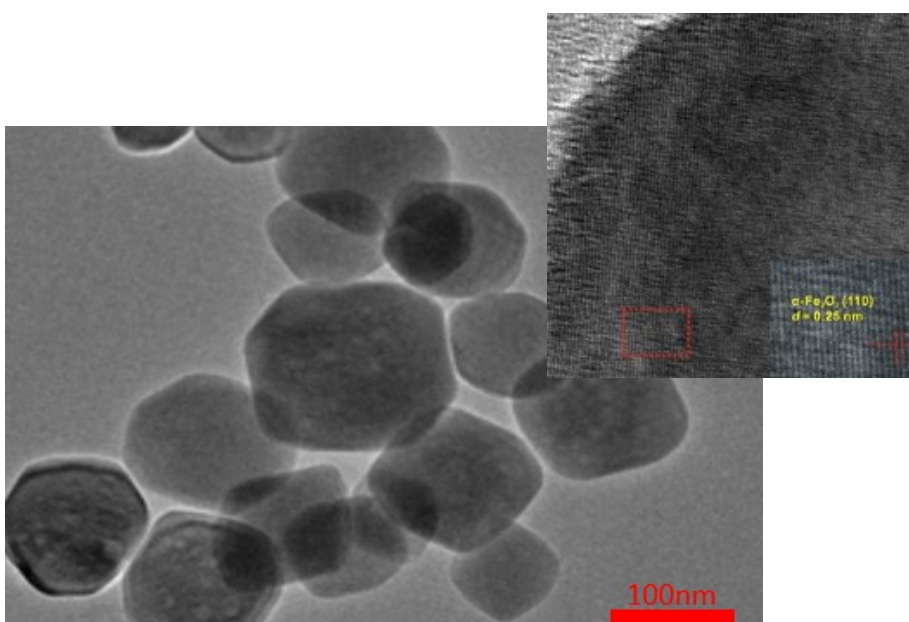
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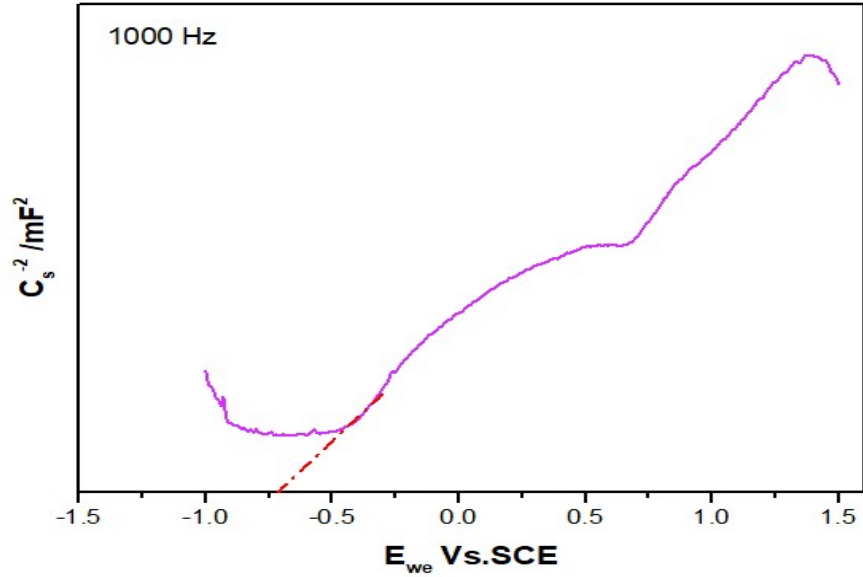
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**Figure S1:** TEM image of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and calculate d-spacing of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> using ImageJ.



**Figure S2:** The Mott-Schottky plot of CTF.

#### Calculation of band edge of $\alpha\text{-Fe}_2\text{O}_3$ :

**$\alpha\text{-Fe}_2\text{O}_3$  material:** The valence band (VB) and conduction band (CB) positions of  $\alpha\text{-Fe}_2\text{O}_3$  were calculated by the following equations:

$$X = (X_{\text{Fe}}^2 * X_{\text{O}}^3)^{1/(2+3)}$$

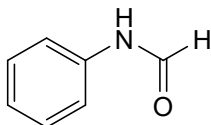
$$E_{\text{CB}} = X - E - 1/2E_g$$

$$E_{\text{VB}} = E_{\text{CB}} + E_g$$

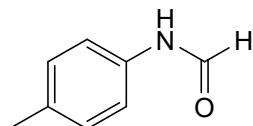
$E$  is the energy of the free electron on the hydrogen scale (4.5 eV), and  $E_g$  is the semiconductor's band gap. Where  $E_{\text{CB}}$  is the CB edge potential,  $E_{\text{VB}}$  is the VB edge potential, and  $X$  is the absolute electronegativity of the semiconductor, expressed as the geometric mean of the absolute electronegativity of the constituent atoms, which is identified as the arithmetic mean of the atomic electron affinity and the first ionization energy. As a result, Supplementary Table 1 displays the values of  $X$ ,  $E_g$ ,  $E_{\text{CB}}$ , and  $E_{\text{VB}}$  of the  $\alpha\text{-Fe}_2\text{O}_3$  samples. The  $E_{\text{CB}}$  and  $E_{\text{VB}}$  of  $\alpha\text{-Fe}_2\text{O}_3$  are therefore 0.31 eV and 2.375 eV, respectively.

Sample	$X_{\text{Fe}}$ (eV)	$X_{\text{O}}$ (eV)	$X$ (eV)	$E_g$	$E_{\text{CB}}$	$E_{\text{VB}}$
$\alpha\text{-Fe}_2\text{O}_3$	4.06	7.45	5.84	2.06	0.31	2.38

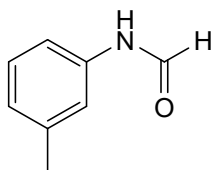
## 1. Characterization of the corresponding N-Arylformamide:



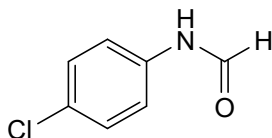
N-phenylformamide (2a)<sup>[1,2]</sup>: White solid; 98% yield (mixture of cis and trans rotamers); Mp: 45-48°C; IR (KBr);  $\nu$  3423, 2926, 2854, 1667, 1542, 1389, 1095  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta_{\text{H}}$  (ppm) = 10.18 (s, 1H, NH), 10.16 (brs, 0.3H, NH), 8.77 (d,  $J=11.0$  Hz, 0.3H, CHO, cis), 8.26 (d,  $J=1.9$  Hz, 1H, CHO, trans), 7.57(d,  $J=7.5$  Hz, 2H), 7.31 (dd,  $J=10.7$  Hz, 5.1 Hz, 3H), 7.18 (d,  $J=7.5$  Hz, 0.8H), 7.1-7.01 (m, 1.4H);  $^{13}\text{CNMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 159.8, 136.9, 136.7, 129.5, 128.7, 125.1, 124.5, 120.1, 110.5; MS (EI, 70eV):  $m/z$ :121.1[M]<sup>+</sup>.



N-p-tolylformamide (2b)<sup>[1,2]</sup>: Yellow solid; 98% yield (mixture of cis and trans rotamers); Mp: 50-52°C; IR (KBr);  $\nu$  3423, 2928, 2890, 1671, 1498, 1388, 1094  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta_{\text{H}}$  (ppm) = 10.06 (brs, 1.17H, NH), 8.7 (d,  $J=11.0$  Hz, 0.26H, CHO, cis), 8.22 (d,  $J=1.9$  Hz, 1H, CHO, trans), 7.46 (d,  $J=8.4$  Hz, 2H), 7.10 (d,  $J=5.5$  Hz, 2H), 7.08 (d,  $J=1.9$  Hz, 1.29H), 2.33 (s, 3.75H);  $^{13}\text{CNMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 159.8, 134.6, 134.4, 134.1, 133.8, 129.9, 129.2, 120.1, 118.7, 20.5, 20.4; MS (EI, 70eV):  $m/z$ :135.3 [M]<sup>+</sup>.

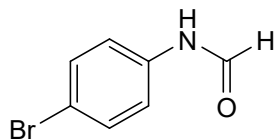


N-m-tolylformamide (2c)<sup>[2]</sup>: White solid; 97% yield (mixture of cis and trans rotamers); Mp 182-187 °C; IR (KBr);  $\nu$  3425, 2980, 2885, 1669, 1490, 1375  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta_{\text{H}}$  (ppm) = 10.2-10.08 (brs, 2H, NH), 8.78 (d,  $J=11.1$  Hz, 1H, CHO, cis), 8.27 (d,  $J=1.8$  Hz, 1H, CHO, trans), 7.97(s, 2H), 7.44 (s, 2H), 7.39(d,  $J=8.3$  Hz, 1H), 7.21 (t,  $J=7.8$  Hz, 1H), 7.01 (d,  $J=8.7$  Hz, 1H), 6.91 (d,  $J=7.5$  Hz, 1H), 2.53 (s, 3H), 2.53 (s, 3H);  $^{13}\text{CNMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 159.6, 139.5, 138.8, 136.8, 136.6, 129.4, 128.7, 125.8, 125.4, 120.6, 119.3, 117.2, 115.5; MS (EI, 70eV):  $m/z$ :135.4 [M]<sup>+</sup>.

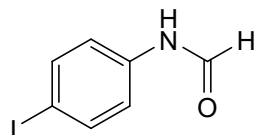


N-(4-chlorophenyl)formamide (2d)<sup>[1,2]</sup>: White solid, 95% yield (mixture of cis and trans rotamers); Mp:103-105 °C; IR (KBr);  $\nu$  3422, 2927, 2850, 1666, 1598,1493,1388,1092  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (500 MHz,

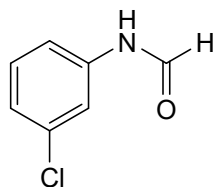
DMSO-d<sub>6</sub>):  $\delta_{\text{H}}$  (ppm) = 10.3 (s, 1H, NH), 10.23-10.09 (m, 1H, NH), 8.77 (d, J= 10.8 Hz, 1H, CHO, cis), 8.29 (d, J= 1.8 Hz, CHO, trans), 7.63 (d, J=8.5 Hz, 2H), 7.59-7.56 (m, 2H), 7.36 (d, J= 8.5 Hz, 2H), 7.30-7.28 (m, 2H); <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.7, 159.4, 135.4, 135.3, 130.7, 129.8, 129.2, 121.4, 119.9; MS (EI, 70eV): m/z:155.0 [M]<sup>+</sup>.



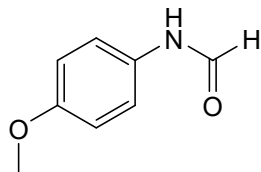
N-(4-bromophenyl)formamide (2e)<sup>[2]</sup>: Light brown solid; 93% yield (mixture of cis and trans rotamers); Mp: 115-118 °C; IR (KBr);  $\nu$  3420, 2924, 2852, 1670, 1542, 1398, 1275, 1073 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta_{\text{H}}$  (ppm) = 10.34 (s, 1H, NH), 10.23 (d, J= 11.5 Hz, 1H, NH), 8.81 (d, J= 10.8 Hz, 1H, CHO, cis), 8.31 (s, 1H, CHO, trans), 7.81-7.65 (m, 2H), 7.55-7.53 (m, 4H), 7.14-7.12 (m, 2H); MS (EI, 70eV): m/z:198.8[M]<sup>+</sup>.



N-(4-iodophenyl)formamide (2f): Light brown solid; 90% yield (mixture of cis and trans rotamers); Mp: 100-105 °C; IR (KBr);  $\nu$  3670, 3274, 2922, 1678, 1587, 1393, 1291, 1060 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta_{\text{H}}$  (ppm) = 10.28 (s, 1H, NH), 10.19 (d, J= 11.2 Hz, 1H, NH), 8.79 (d, J= 11.1 Hz, 1H, CHO, cis), 8.29 (s, 1H, CHO, trans), 7.66 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 7.1 Hz, 0.58H), 7.43 (d, J = 7.9 Hz, 2H), 7.02 (d, J = 8.4 Hz, 0.38H); MS (EI, 70eV): m/z:246.9[M]<sup>+</sup>.

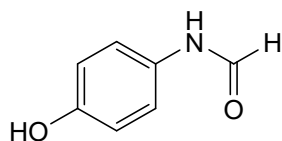


N-(3-chlorophenyl)formamide (2g)<sup>[3]</sup>: White solid; 91% yield (mixture of cis and trans rotamers); Mp: 47-49 °C; IR (KBr);  $\nu$  3420, 2916, 2849, 1683, 1596, 1405, 1275 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  (ppm) = 8.71 (brs, 1H, CHO), 8.38 (s, 1H, CHO), 7.66 (s, 2H, NH), 7.37 (d, J = 7.8 Hz, 2H), 7.18-7.08 (m, 4H), 6.96 (d, J = 4.3 Hz, 2H); MS (EI, 70eV): m/z:155.2[M]<sup>+</sup>.

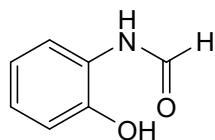


N-(4-methoxyphenyl)formamide (2h)<sup>[1, 2]</sup>: White solid; 97% yield (mixture of cis and trans rotamers); Mp: 75-77 °C; IR (KBr);  $\nu$  3380, 2923, 1664, 1515, 1458, 1399, 1260, 1038 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta_{\text{H}}$  (ppm) = 10 (brs, 1H, NH), 9.93 (d, J= 10.9 Hz, 1H, NH), 8.58 (d, J=11.1 Hz, 1H, CHO, cis), 8.19 (s, 1H, CHO, trans), 7.49 (d, J=8.8 Hz, 2H), 7.10 (d, J= 8.6 Hz, 2H), 6.89 (d, J= 8.5 Hz, 2H), 6.87 (d, J=

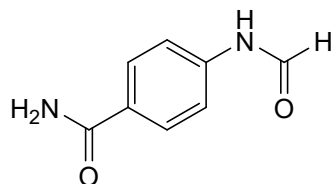
8.7 Hz, 2H), 3.71 (s, 6H, OCH<sub>3</sub>); <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>) δ 163.4, 159.5, 157.3, 156.4, 130.1, 129.6, 121.8, 121.2, 114.7, 113.9, 55.5, 55.4; MS (EI, 70eV): m/z:151.1[M]<sup>+</sup>.



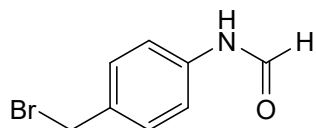
N-(4-hydroxyphenyl)formamide (2i)<sup>[1, 2]</sup>: Light brown solid, 90% yield (mixture of cis and trans rotamers); Mp: 134-136 °C; IR (KBr); ν 3429, 2924, 2853, 1664, 1515, 1458, 1399, 1260, 1038 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): δ<sub>H</sub> (ppm) = 9.87 (s, 1H, NH, trans), 9.81 (d, J = 11.1 Hz, 1H, NH, cis), 8.50 (d, J = 11 Hz, 1H, CHO, cis), 8.17 (d, J = 1.8 Hz, 1H, CHO, trans), 8.12 (s, 1H), 7.98 (s, 1H), 7.36 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 7.8 Hz, 1H), 6.69 (d, J = 7.5 Hz, 1H), 6.71 (d, J = 4.5 Hz, 1H); MS (EI, 70eV): m/z:137.2 [M]<sup>+</sup>.



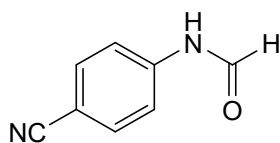
N-(2-hydroxyphenyl)formamide (2j)<sup>[3]</sup>: Light brown solid; 83% yield (No cis / trans mixture of rotamers); Mp: 44-48 °C; IR (KBr); ν 3430, 2922, 2851, 1637, 1562, 1400, 1275 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> (ppm) = 8.26 (s, 1H), 8.09 (s, 1H), 7.14 (d, J = 6.9 Hz, 2H), 7.01 (d, J = 7.9 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H).



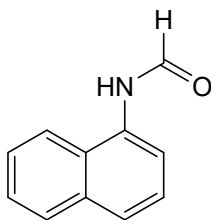
4-formamidobenzamide (2k)<sup>[2]</sup>: Light brown solid, 75% yield (mixture of cis and trans rotamers); IR (KBr); ν 3420, 2980, 2850, 1686, 1665, 1482, 1350, 1220 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): δ<sub>H</sub> (ppm) = 10.42 (s, 1H, NH, trans), 10.35 (d, J = 10.8 Hz, 1H, NH, cis), 8.94 (d, J = 10.8 Hz, CHO, cis), 8.36 (s, 1H, CHO, trans), 8.02 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 6.8 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H), 6.85 (brs, 2.68 H, NH).



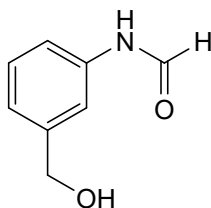
N-(4-(bromomethyl)phenyl)formamide (2n): Yellow oil; 75% yield (No cis /trans mixture of rotamers); IR (KBr); ν 3417, 2927, 2862, 1665, 1519, 1386, 1345, 1259 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): δ<sub>H</sub> (ppm) = 8.22 (d, J=8.6, 2H), 8.16 (s, 1H), 7.61 (d, J= 8.7 Hz, 2H), 4.66 (s, 2H).



N-(4-cyanophenyl)formamide (2m)<sup>[2]</sup>: White solid; 76% yield (mixture of cis and trans rotamers); Mp:180-183 °C; IR (KBr);  $\nu$  3424, 2924, 2853, 2225, 1607, 1459, 1275,1260  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 8.82 (d,  $J$  = 10.2 Hz, 1H, CHO, cis), 8.44 (s, 1H, CHO, trans), 8.02 (d,  $J$  = 8.1 Hz, 1H), 7.65 (m, 6H), 7.36 (s, 1H), 7.15 (d,  $J$  = 7.5 Hz, 1H); MS (EI, 70eV):  $m/z$ : 146.3  $[\text{M}]^+$ .

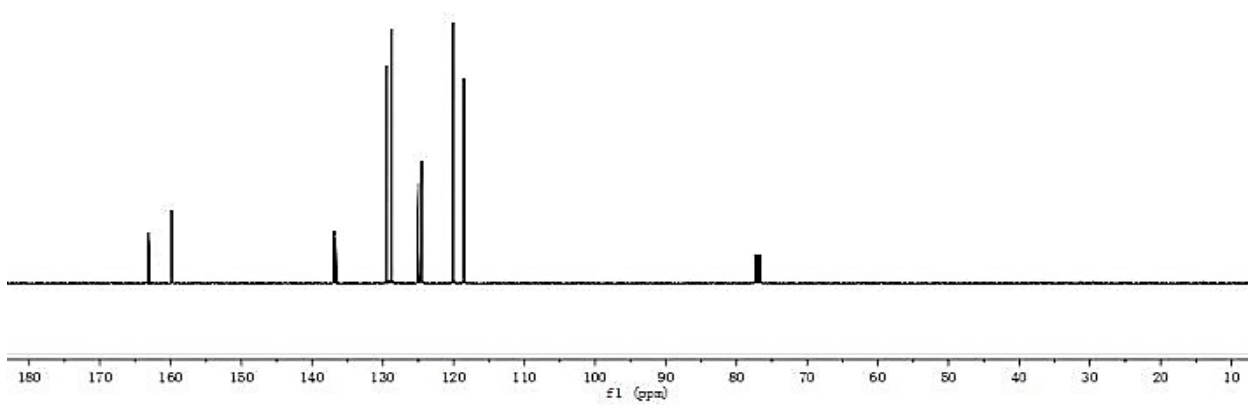
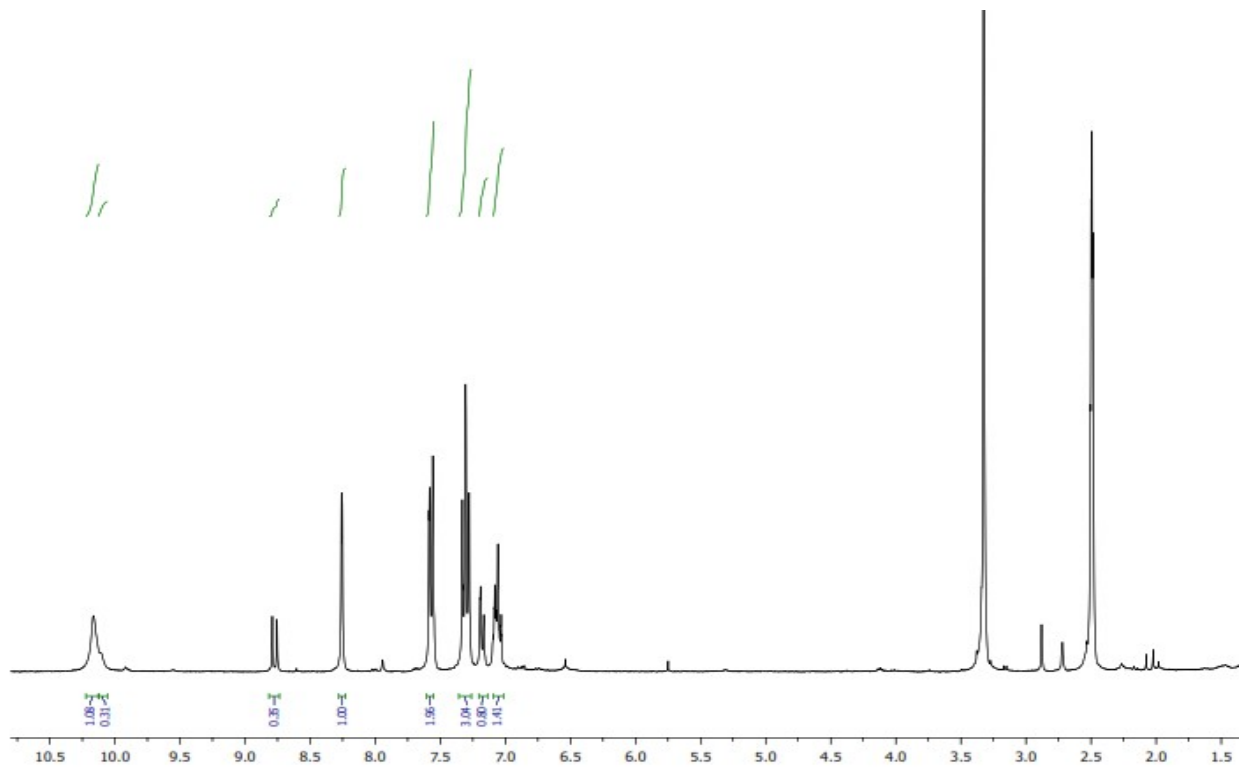
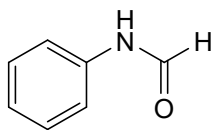


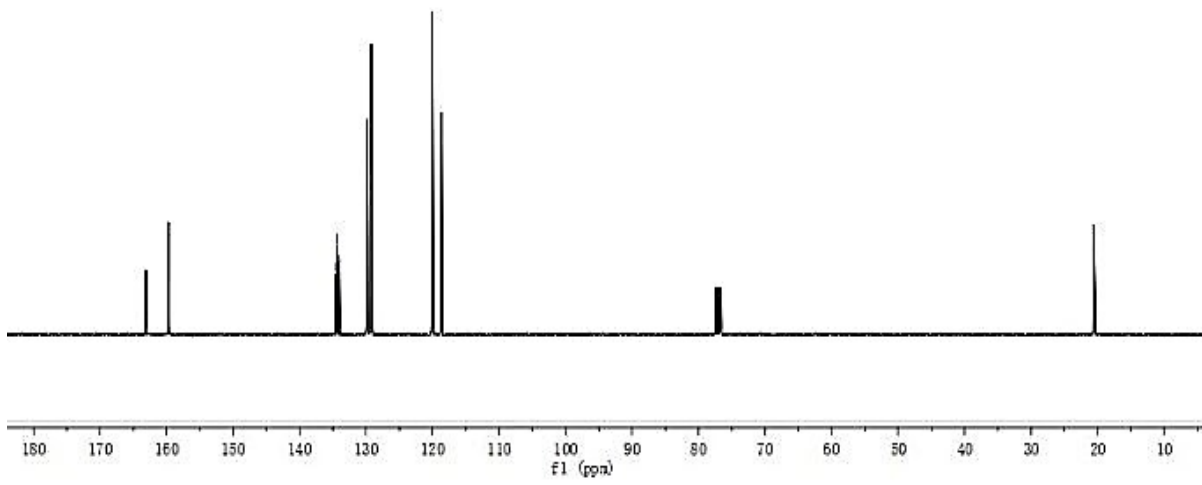
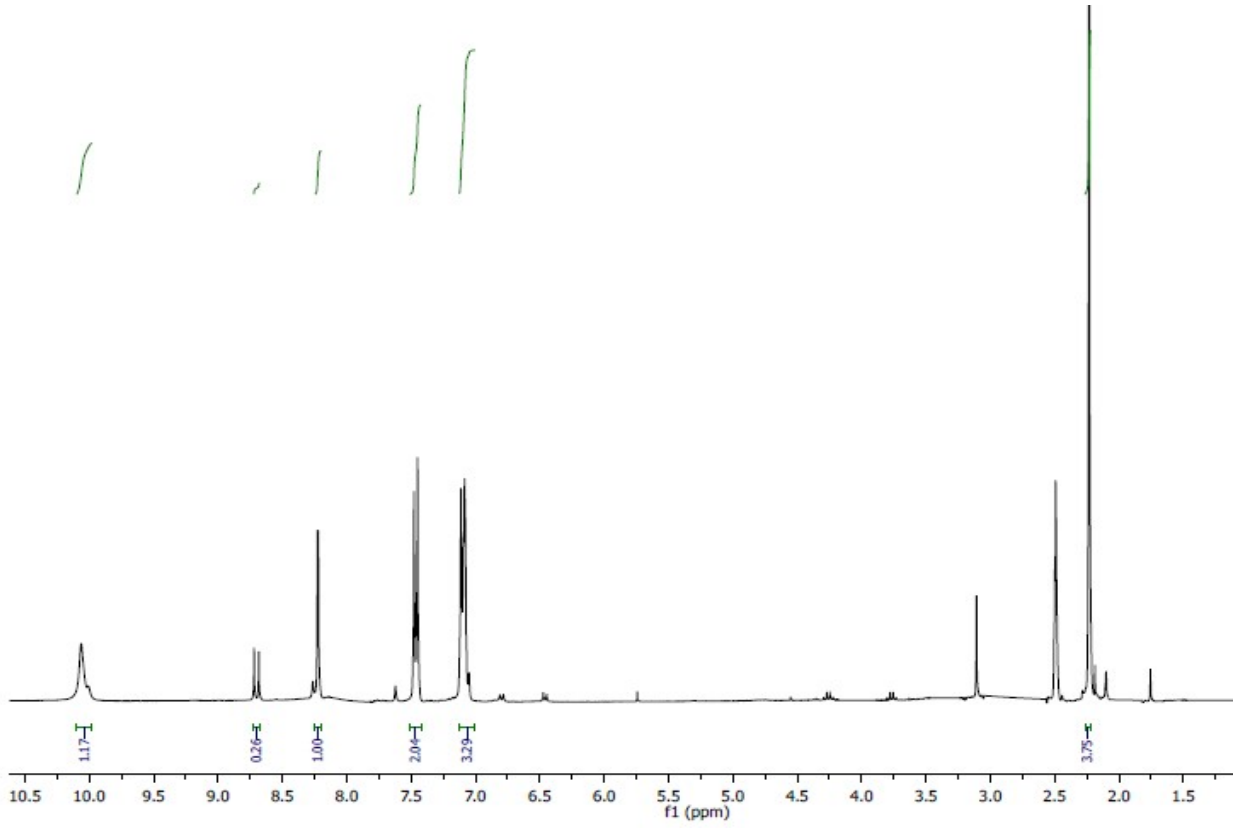
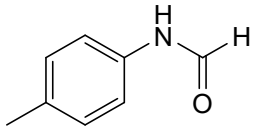
N-(naphthalen-1-yl)formamide (2n): Yellow solid; 84% yield (mixture of cis and trans rotamers); Mp:145-149 °C; IR (KBr);  $\nu$  3429, 3137, 1652, 1402, 1274,1100  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta_{\text{H}}$  (ppm) = 10.51 (d,  $J$  = 9.1 Hz, 0.59H, NH), 10.33 (s, 1H, NH), 8.59 (d,  $J$  = 8.9 Hz, 0.52H, CHO, cis), 8.49 (d,  $J$  = 1.6 Hz, 1H, CHO, trans), 8.14 (d,  $J$  = 7.2 Hz, 1.47H), 8.01 (d,  $J$  = 7.5 Hz, 1.6H), 7.79-7.7 (m, 2.6H), 7.62-7.53 (m, 3H), 7.52-7.42 (m, 2H);  $^{13}\text{CNMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 159.7, 134.3, 134.1, 132.0, 131.2, 128.9, 128.8, 128.6, 127.8, 127.1, 126.8, 126.7, 126.5, 126.3, 126.1, 125.8, 125.5, 121.3, 120.9, 120.4, 119.1; MS (EI, 70eV):  $m/z$ : 171.2  $[\text{M}]^+$ .



N-(3-(hydroxymethyl)phenyl)formamide (2o)<sup>[3]</sup>: White solid; 85% yield (mixture of cis and trans rotamers); Mp:67-70 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta_{\text{H}}$  (ppm) = 10.17 (s, 1H, NH), 10.13 (s, 1H, NH), 8.79 (d,  $J$  = 11 Hz, 1H, CHO, cis), 8.28 (s, 1H, CHO, trans), 7.49 (d,  $J$  = 8 Hz, 2H), 7.37-7.24 (m, 2H), 7.13 (d,  $J$  = 8.3 Hz, 2H), 7.07-6.97 (m, 2H), 4.49 (d,  $J$  = 8.3 Hz, 2H), 1.26 (s, 1H).

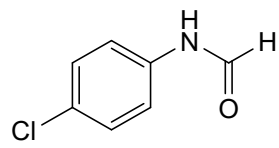
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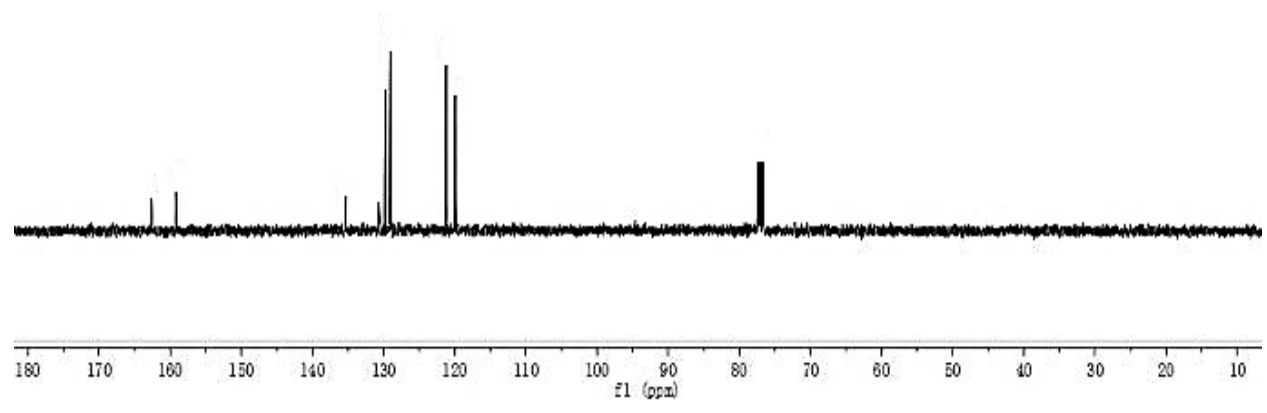
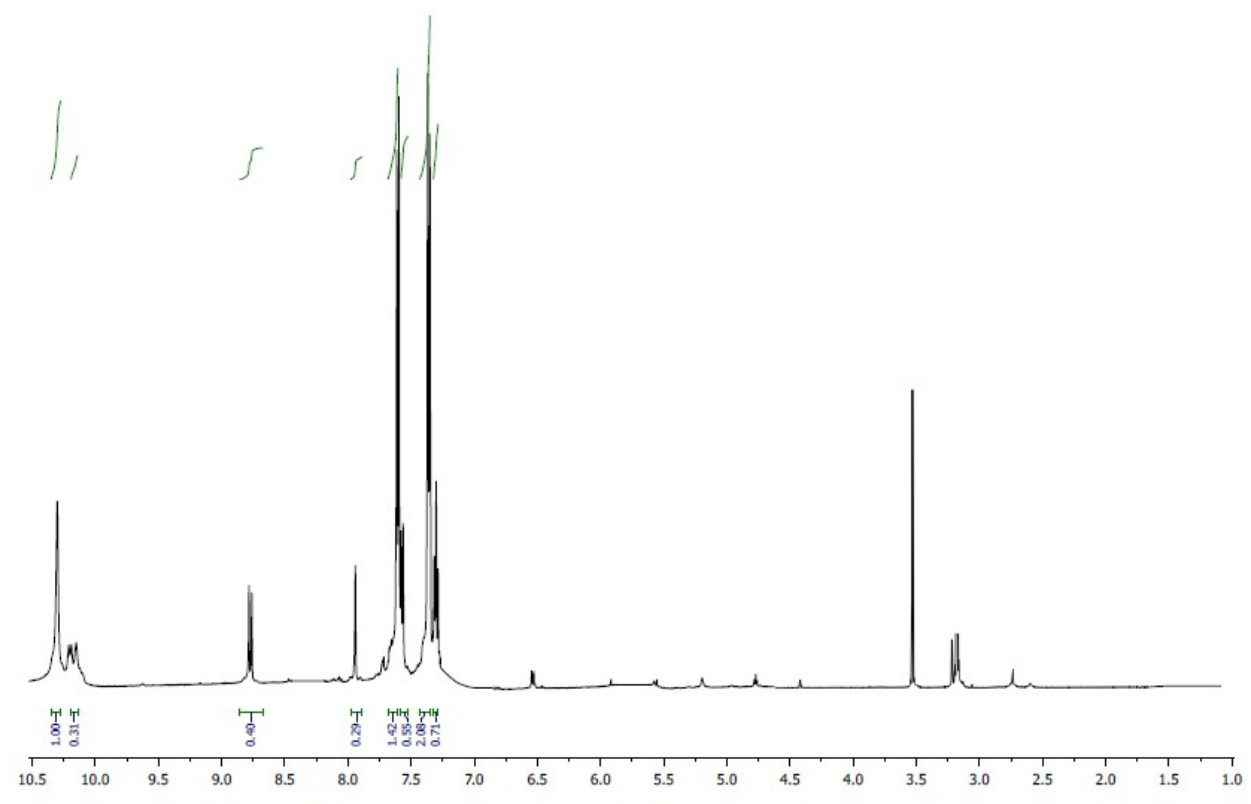


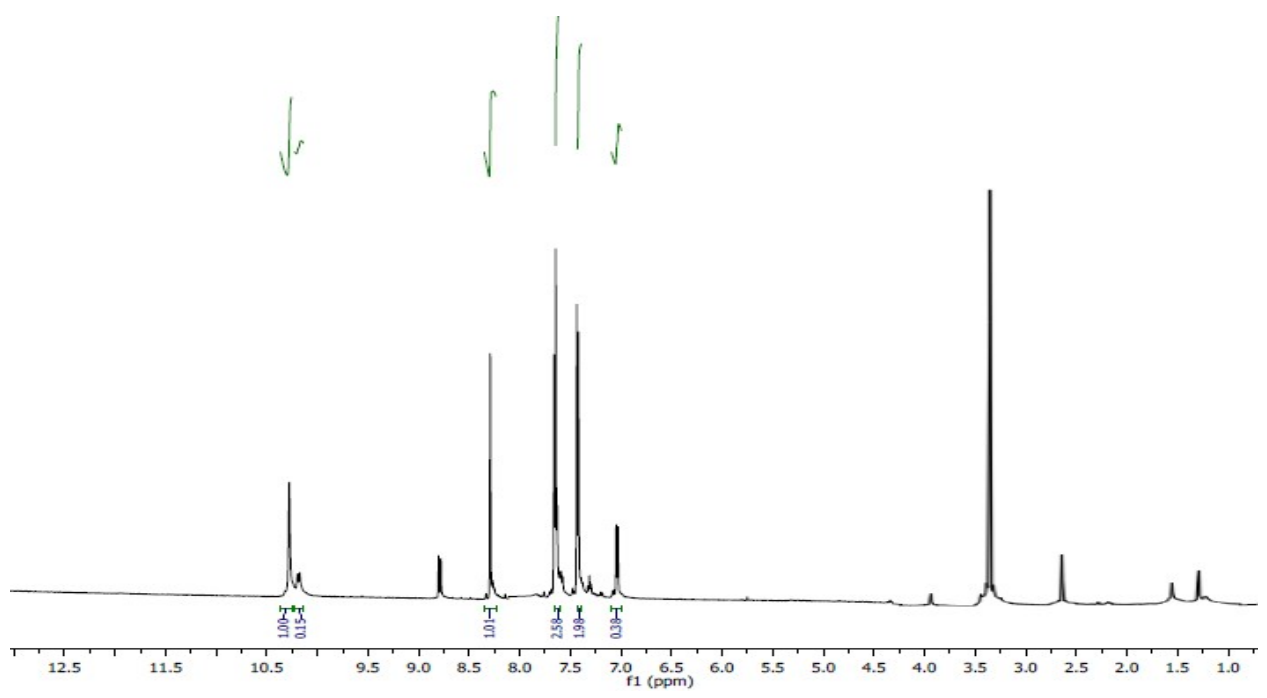
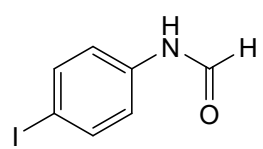
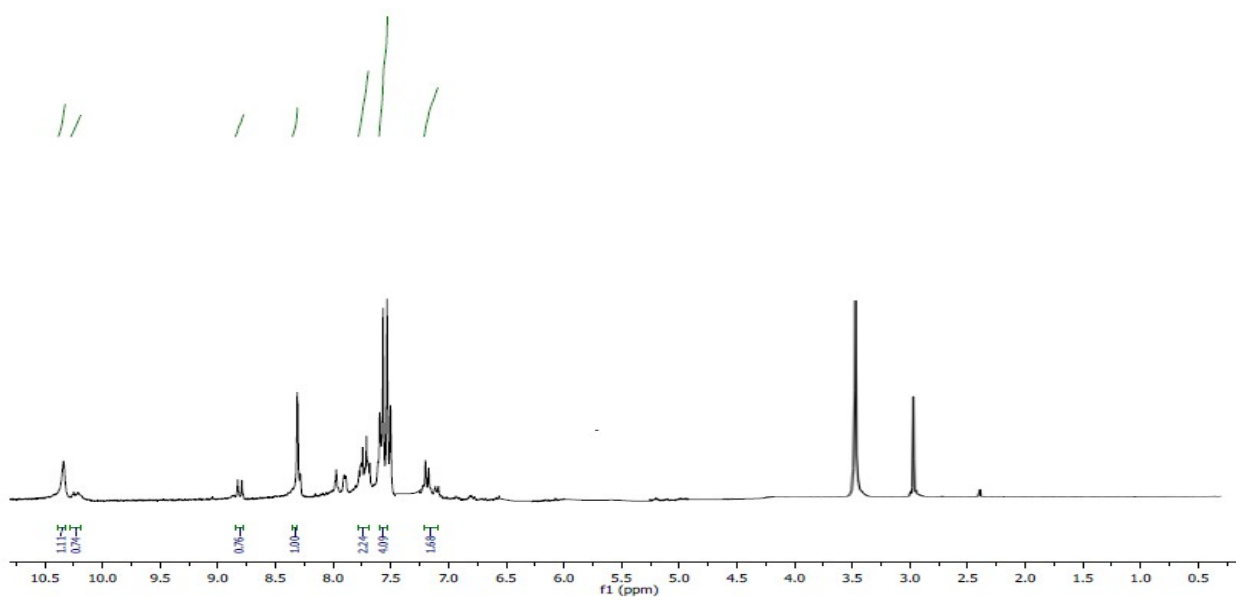
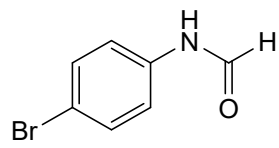


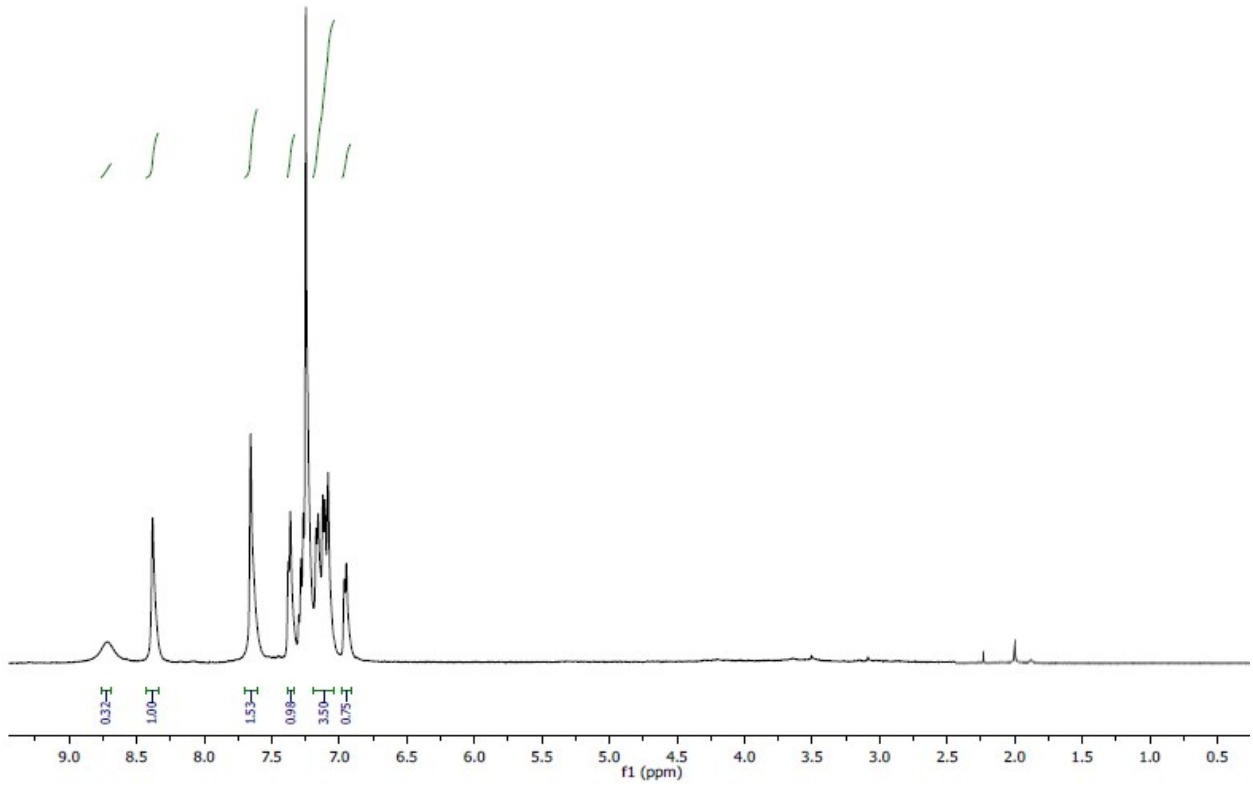
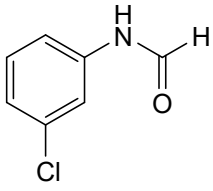


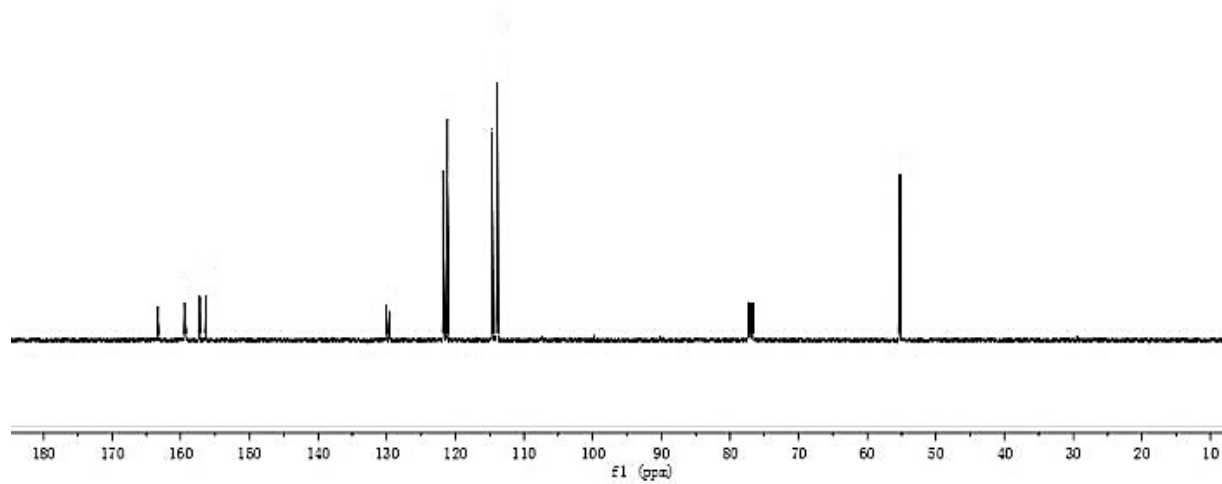
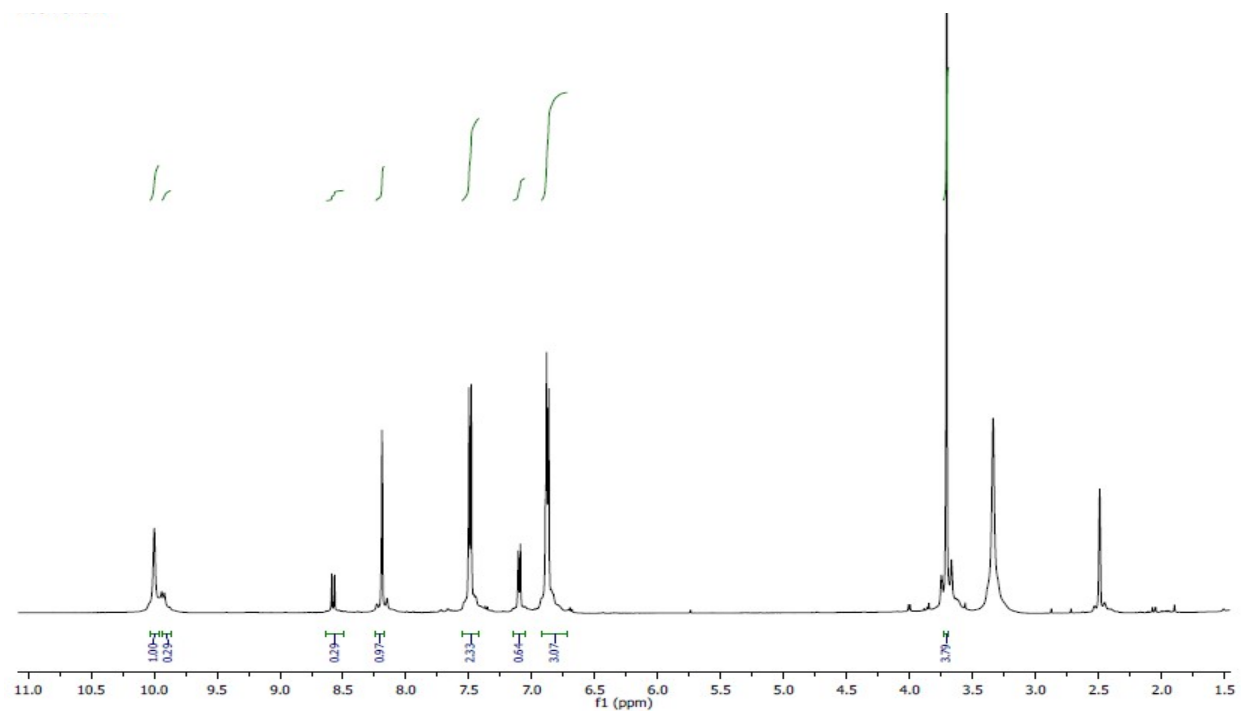
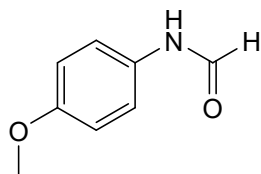


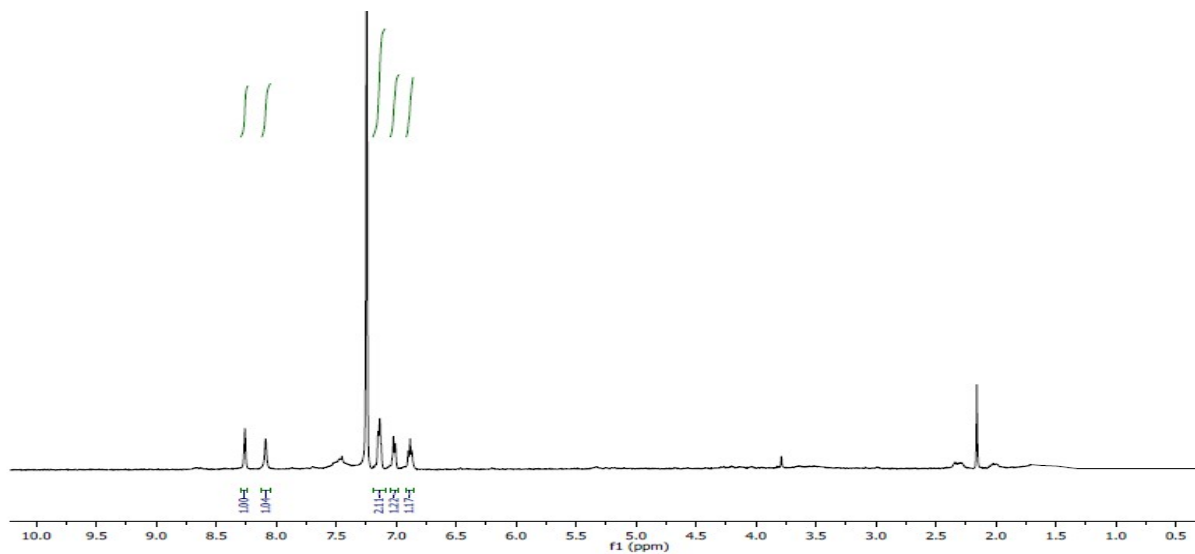
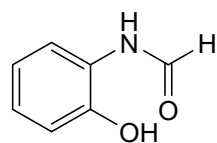
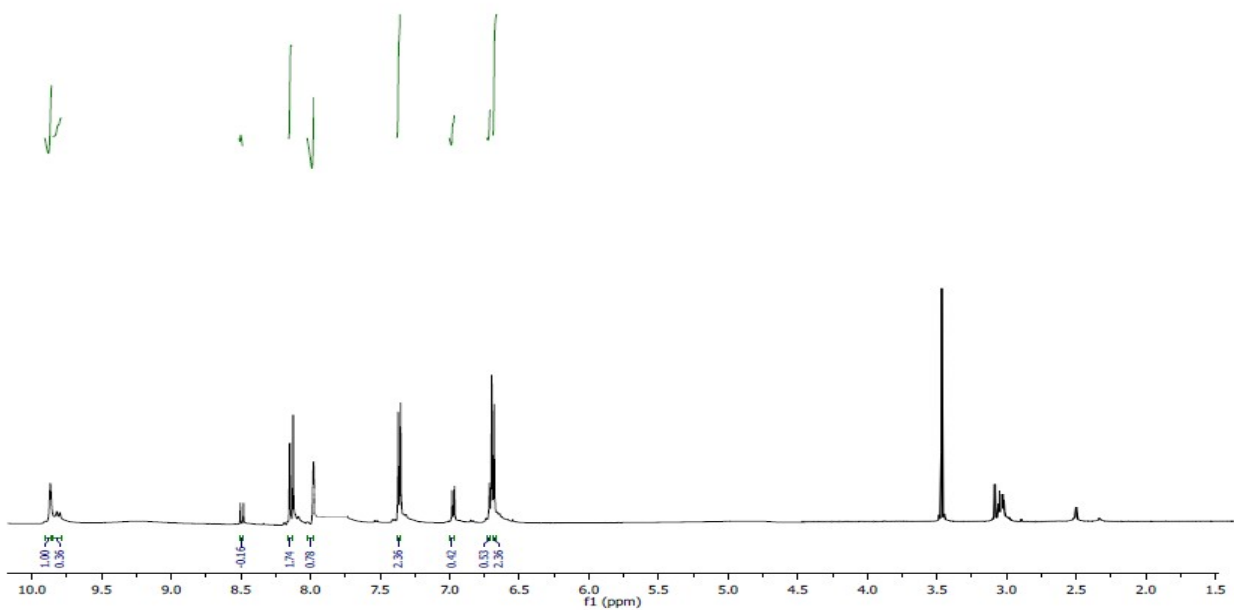
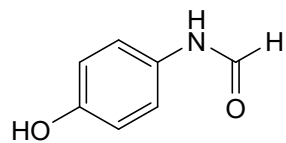
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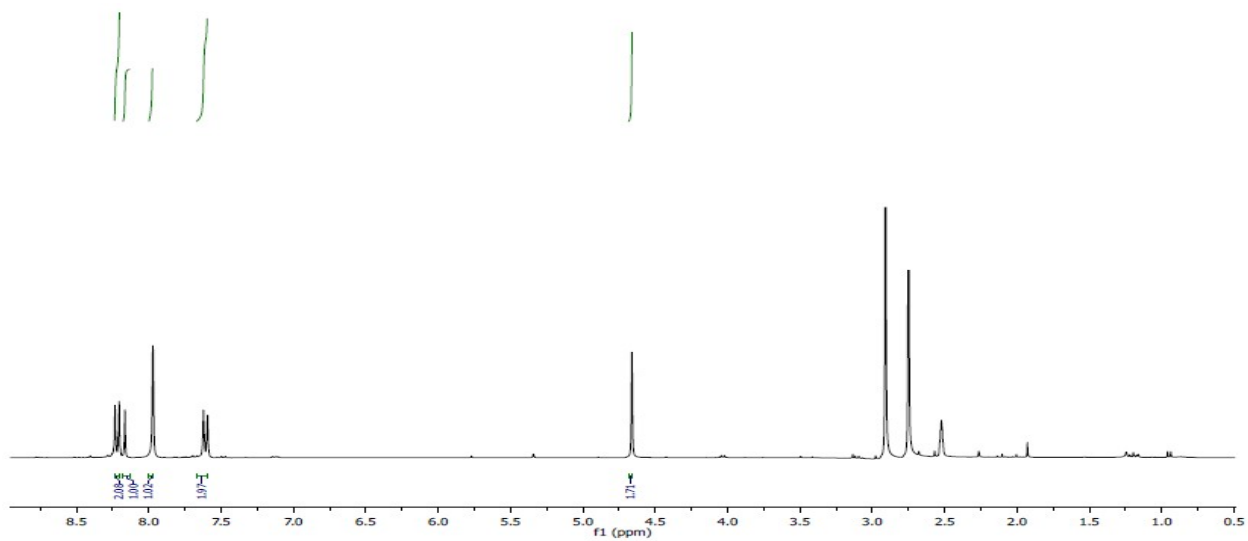
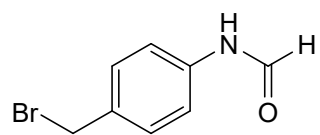
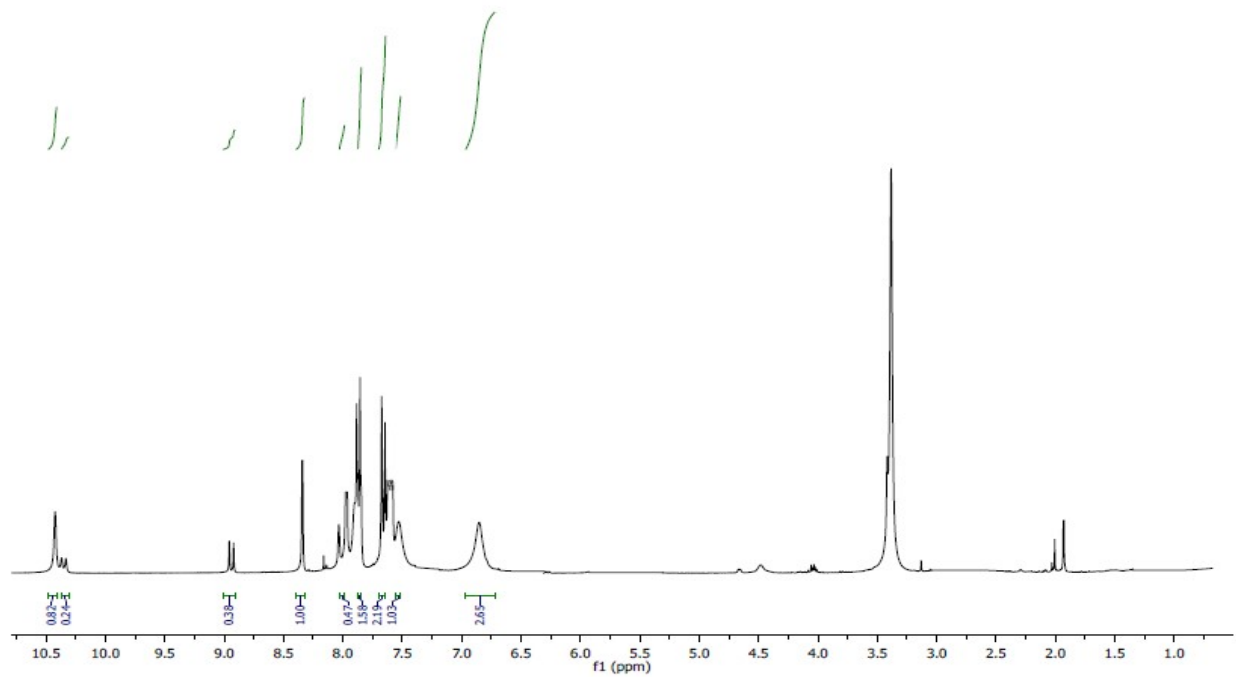
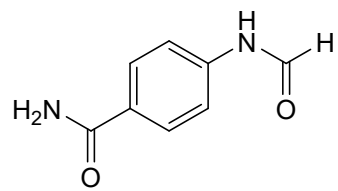


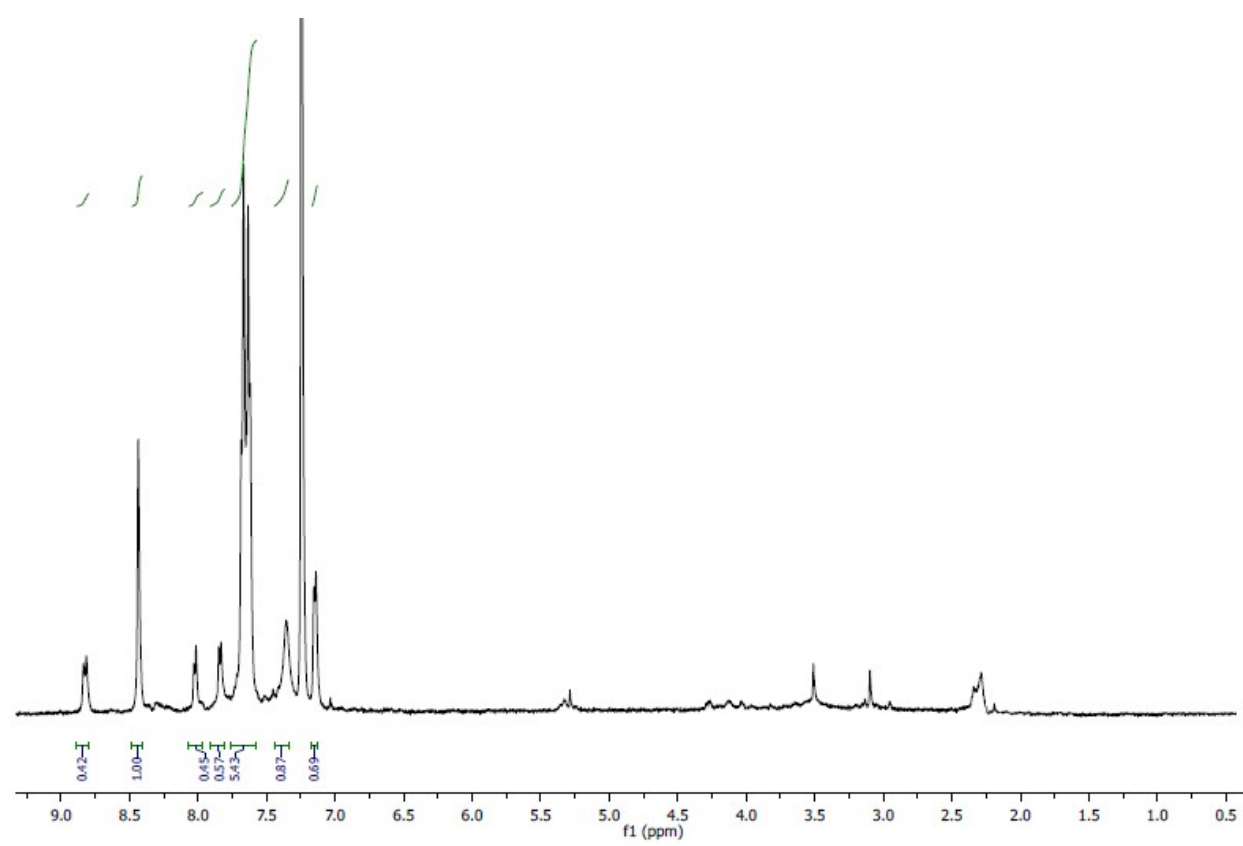
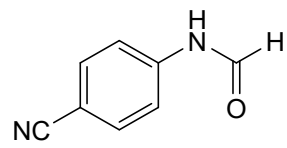




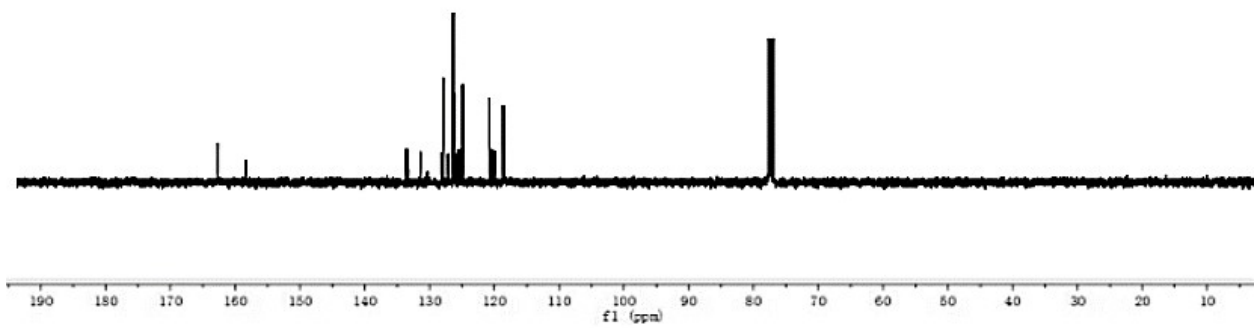
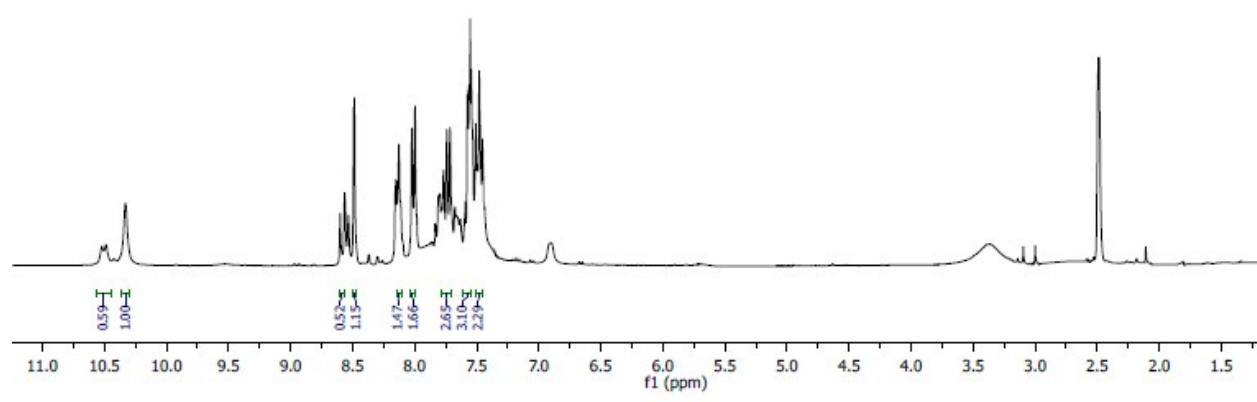
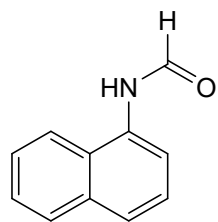


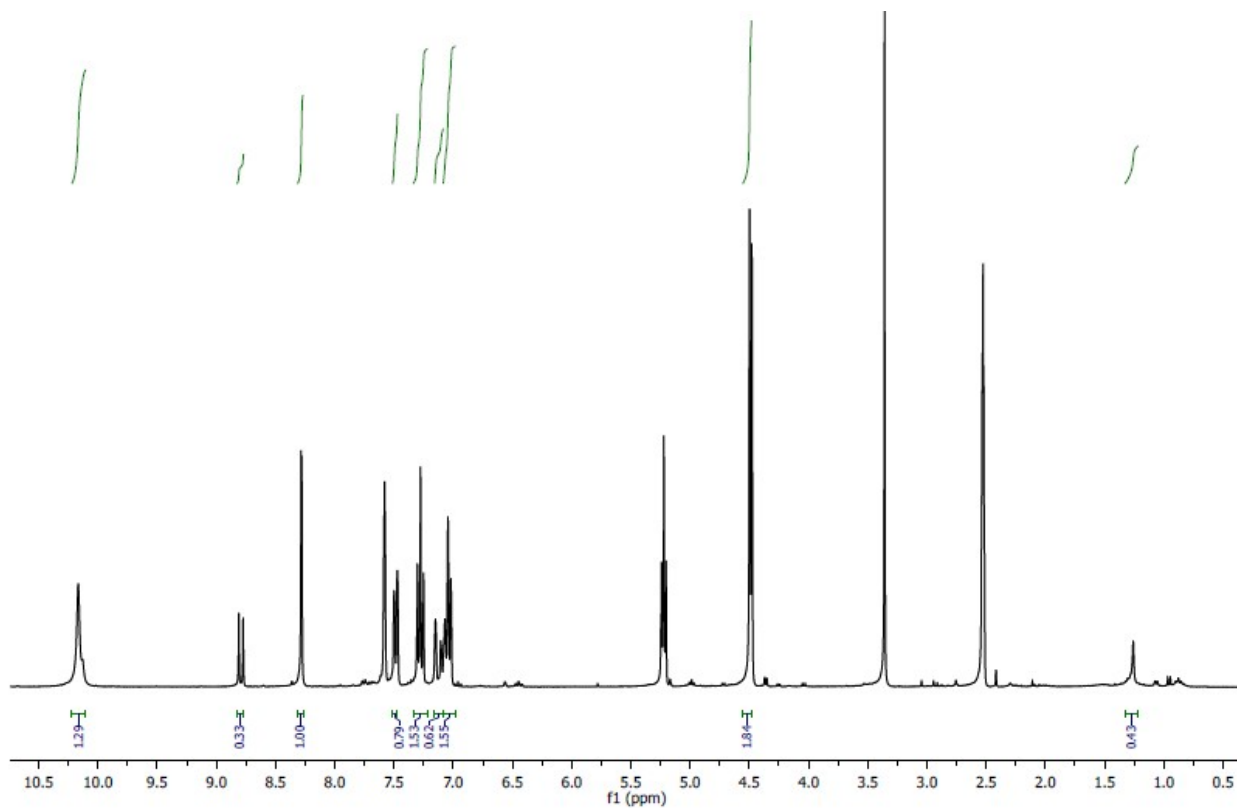
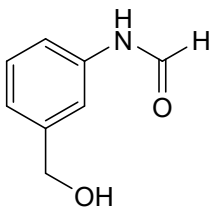












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