

## **Superparamagnetic Fe(OH)<sub>3</sub>@Fe<sub>3</sub>O<sub>4</sub> Nanoparticles: An Efficient and Recoverable Catalyst for Tandem Oxidative Amidation of Alcohols with Amine Hydrochloride Salts**

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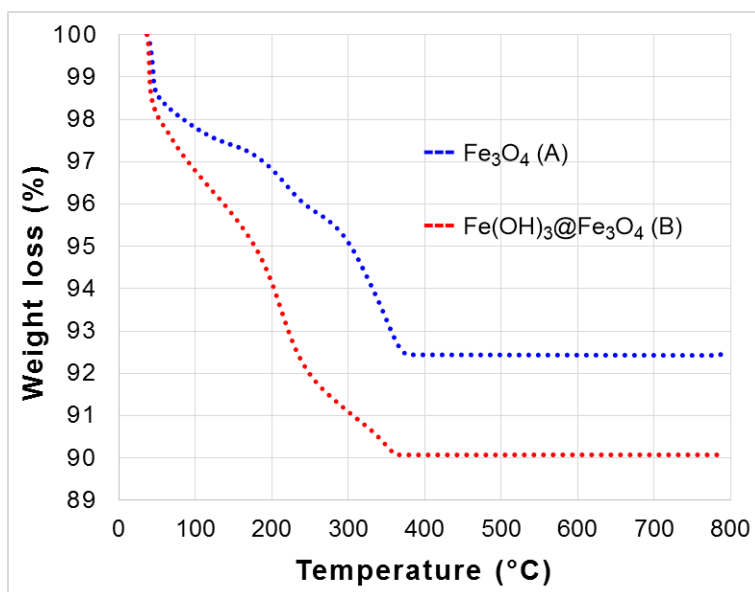
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## 1. General remarks

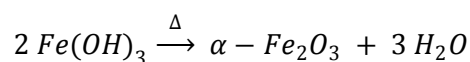
All experiments were carried out under argon. All chemicals and solvents were purchased from commercial suppliers and used without further purification. FT-IR spectra were obtained over the region 400–4000  $\text{cm}^{-1}$  with a Nicolet IR100 FT-IR with spectroscopic grade KBr. The powder X-ray diffraction spectrum was recorded at room temperature using a Philips X-Pert 1710 diffractometer with Co  $K\alpha$  ( $\lambda=1.79285 \text{ \AA}$ ) voltage: 40 kV, current: 40 mA and in the range  $20^\circ$ – $80^\circ$  ( $2\theta$ ) with a scan speed of  $0.02^\circ/\text{s}$ . The morphology of catalyst was studied with scanning electron microscopy using SEM (Philips XL 30 and S-4160) on gold coated samples. The magnetic properties of  $\text{Fe}(\text{OH})_3@ \text{Fe}_3\text{O}_4$  were obtained by a vibrating magnetometer/Alternating Gradient Force Magnetometer (VSM/AGFM, MDK Co., Iran, [www.mdk-magnetic.com](http://www.mdk-magnetic.com)). Transmission electron microscopy (TEM) were carried out at 120 kV (Philips model CM120). Thermal gravimetric analysis (TGA) was performed on a Thermal Analyzer with a heating rate of  $20^\circ \text{C min}^{-1}$  over a temperature range of  $25$ – $1100^\circ \text{C}$  under flowing compressed  $\text{N}_2$ .  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance (DPX 250 MHz and DRX 400 MHz) in pure deuterated  $\text{CDCl}_3$  solvent with tetramethylsilane (TMS) as internal standard.

## 2. Detailed explanation of the TG analysis



**Figure S1:** TGA results of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}(\text{OH})_3@ \text{Fe}_3\text{O}_4$ .

Figure S1 represents the TGA diagram of the  $\text{Fe}(\text{OH})_3@ \text{Fe}_3\text{O}_4$  nanoparticles besides pristine magnetite for comparison. Above  $400^\circ \text{C}$ , where lines are horizontal, some 2.37% difference in weight loss of the two samples is seen. This difference can be attributed to the dehydroxylation of the loaded  $\text{Fe}(\text{OH})_3$  according to the equation below.



Considering this equation, the amount of ferric hydroxide loading in the Fe(OH)<sub>3</sub>@Fe<sub>3</sub>O<sub>4</sub> nanoparticles is calculable as follows:

$$\frac{2.37 \text{ g } H_2O}{100 \text{ g cat.}} \times \frac{1 \text{ mol } H_2O}{18 \text{ g } H_2O} \times \frac{2 \text{ mol } Fe(OH)_3}{3 \text{ mol } H_2O} \times \frac{106.87 \text{ g } Fe(OH)_3}{1 \text{ mol } Fe(OH)_3} = \frac{9.4 \text{ g } Fe(OH)_3}{100 \text{ g cat.}} = 9.4 \% \text{ } Fe(OH)_3$$

### 3. Experimental procedures

#### 3.1. Preparation of the Fe(OH)<sub>3</sub>@Fe<sub>3</sub>O<sub>4</sub> catalyst

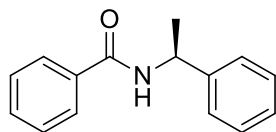
The nano-sized Fe(OH)<sub>3</sub>@Fe<sub>3</sub>O<sub>4</sub> was synthesized via a modified procedure reported by Song *et al.*<sup>1</sup>. The Superparamagnetic catalyst was prepared by dissolving the mixture of 4 mmol FeCl<sub>3</sub>·6H<sub>2</sub>O and 2 mmol FeCl<sub>2</sub>·4H<sub>2</sub>O salts in 40 mL deionized water under vigorous stirring. An ammonia solution (25% (w/w)) was added in drop-wise manner over 5 min to the stirring mixture to maintain the reaction pH about 11. The resulting black dispersion was stirred vigorously for 1h at room temperature and then was refluxed for 1h. Fe<sub>3</sub>O<sub>4</sub> nanoparticles were magnetically gathered and the residue was repeatedly washed with water and ethanol. Subsequently, as-prepared Fe<sub>3</sub>O<sub>4</sub> nanoparticles and 15 mmol of FeCl<sub>3</sub>·6H<sub>2</sub>O were ultrasonically dispersed into 10 ml of ethanol. After totally dissolution and dispersion, the nanoparticles were separated from the ethanol solution by magnetic decantation and dried at 80 °C for 4h. Fe(OH)<sub>3</sub>@Fe<sub>3</sub>O<sub>4</sub> nanoparticles were obtained by drop-wise addition of aqueous ammonia (25% (w/w), 5 mL) to the dried brown nanoparticles under vigorous stirring. Finally, the products of Fe(OH)<sub>3</sub>@Fe<sub>3</sub>O<sub>4</sub> were magnetically separated, washed with water, and dried in an oven at 373 K overnight for further usage.

#### 3.2. General procedure for the direct amidation of alcohols with amine hydrochloride salts

To a mixture of catalyst (20 mg, 3.5 mol%), amine hydrochloride salt (0.75 mmol, 1.5 equiv.) and CaCO<sub>3</sub> (75.1 mg, 1.5 equiv.) in CH<sub>3</sub>CN (1 mL) were added alcohol (0.5 mmol, 1 equiv.), and *t*-BuOOH (70 wt% in H<sub>2</sub>O, 3 equiv.) under argon atmosphere. The mixture was stirred at 80 °C for 6 h. After completion, the reaction mixture was allowed to cool to room temperature. It was then diluted with EtOAc and the catalyst was separated with an external magnet and washing twice with EtOAc. The mixture was extracted with EtOAc, the volatiles were removed under reduced pressure, and the crude product was purified by column chromatography to afford the desired product.

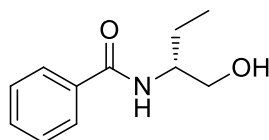
#### 4. Characterization of the corresponding amide

##### (S)-N-(1-phenylethyl)benzamide 3{1,6}



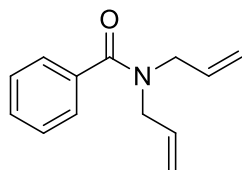
Isolated yield = 89%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.79-7.81 (m, 2H), 7.30-7.54 (m, 8H), 6.34 (d,  $J$  = 5.2 Hz, 1H), 5.32-5.41 (m, 2H), 1.64 (d,  $J$  = 7.2 Hz, 3H).;  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 166.6, 143.1, 134.6, 131.5, 128.8, 128.6, 127.5, 126.9, 126.3, 49.2, 21.7; IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3329, 3030, 2967, 1635, 1525, 1449, 1080; MS (EI, 70 eV):  $m/z$  (%) = 225 ( $\text{M}^+$ , 40), 210 (12), 120 (10), 105 (100), 91 (3), 77 (80).

##### (R)-N-(1-hydroxybutan-2-yl)benzamide 3{1,7}



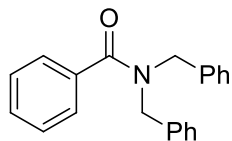
Isolated yield = 73%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.70 (d,  $J$  = 7.6 Hz, 2H), 7.42 (t,  $J$  = 7.2 Hz, 1H), 7.34 (dd,  $J$  = 7.6 Hz,  $J$  = 7.2 Hz, 2H), 6.36 (s, 1H), 4.0 (br s, 1H), 3.71 (dd,  $J$  = 10.7 Hz,  $J$  = 2.8 Hz, 1H), 3.62 (dd,  $J$  = 10.7 Hz,  $J$  = 5.2 Hz, 1H), 2.96 (br s, 1H), 1.51-1.67 (m, 2H), 0.94 (t,  $J$  = 7.2 Hz, 3H).;  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 168.3, 134.4, 131.6, 128.6, 127.0, 65.2, 53.7, 24.3, 10.7; IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3301, 3067, 2958, 2930, 2868, 1636, 1539, 1454, 1048; MS (EI, 70 eV):  $m/z$  (%) = 193 ( $\text{M}^+$ , 3), 175 (6), 162 (98), 150 (10), 122 (48), 105 (100), 77 (50).

##### N, N-diallylbenzamide 3{1,11}



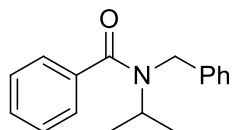
Isolated yield = 64%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.43 (d,  $J$  = 7.2, 2H), 7.27-7.43 (m, 3H), 5.89 (br s, 1H), 5.74 (br s, 1H), 5.18-5.26 (m, 4H), 4.15 (br s, 2H), 3.84 (br s, 2H).;  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 171.8, 136.3, 133.2, 132.8, 129.6, 128.4, 126.6, 117.6, 50.7, 46.9; IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) = 3074, 2924, 2800, 1637, 1416, 1261; MS (EI, 70 eV):  $m/z$  (%) = 201 ( $\text{M}^+$ , 18), 160 (34), 105 (100), 96 (14), 77 (50).

***N,N*-dibenzylbenzamide 3{1,9}**



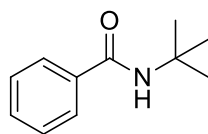
Isolated yield = 75%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.51 (dd,  $J=5.2$  Hz,  $J=1.6$  Hz, 2H), 7.39 (dd,  $J=6.8$  Hz,  $J=5.2$  Hz, 2H), 7.35–7.40 (m, 7H), 7.31 (t,  $J=6.8$  Hz, 2H), 7.16 (d,  $J=7.2$  Hz, 2H), 4.72 (s, 2H), 4.42 (s, 2H).;  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 172.35, 136.93, 136.45, 136.24, 129.74, 128.92, 128.75, 128.62, 128.53, 127.75, 127.62, 127.14, 126.71, 51.53, 46.93; IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3059, 2927, 1622, 1489, 1429, 1251; MS (EI, 70 eV):  $m/z$  (%) = 301 ( $\text{M}^+$ , 10), 210 (86), 105 (100), 91 (88), 77 (90).

***N*-benzyl-*N*-isopropylbenzamide 3{1,12}**



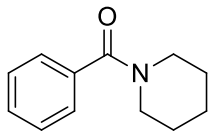
Isolated yield = 80%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.42–7.45 (m, 5H), 7.33–7.36 (m, 5H), 4.70 (s, 2H), 4.15 (br s, 1H), 1.12 (br s, 6H).;  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 168.9, 137.3, 133.2, 129.9, 129.2, 128.6, 128.4, 127.0, 126.2, 50.8, 43.4, 21.5; IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) = 3061, 2978, 2850, 1633, 1421, 1344, 1179; MS (EI, 70 eV):  $m/z$  (%) = 253 ( $\text{M}^+$ , 15), 210 (24), 162 (20), 105 (100), 91 (68), 77 (80).

***N*-(*tert*-butyl)benzamide 3{1,4}**



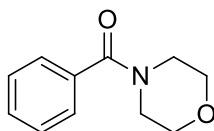
Isolated yield = 49%;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.74 (d,  $J = 8.0$  Hz, 2H), 6.97 - 7.12 (m, 3H), 5.92 (br s, 1H), 1.48 (s, 9H).;  $^{13}\text{C}$ -NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 167.0, 136.1, 131.2, 128.6, 126.8, 51.7, 29.0; IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3323, 3061, 2970, 1638, 1537, 1450, 1310, 1219; MS (EI, 70 eV):  $m/z$  (%) = 177 ( $\text{M}^+$ , 60), 162 (60), 122 (50), 105 (100), 77 (88), 57 (10).

**Phenyl(piperidin-1-yl)methanone 3{1,13}**



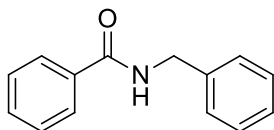
Isolated yield = 70%;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.39 (s, 5H), 3.72 (s, 2H), 3.35 (s, 2H), 1.42-1.68 (m, 6H).;  $^{13}\text{C}$ -NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 170.4, 136.6, 129.5, 128.5, 126.9, 48.8, 43.2, 26.8, 25.8, 24.7; IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) = 3059, 2931, 2858, 1625, 1565, 1433, 1277; MS (EI, 70 eV):  $m/z$  (%) = 189 ( $\text{M}^+$ , 18), 160 (4), 133 (4), 111 (46), 105 (86), 84 (18), 77 (100).

**Morpholino(phenyl)methanone 3{1,15}**



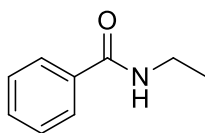
Isolated yield = 79%;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.37-7.43 (m, 5H), 3.46-3.71 (m, 8H).;  $^{13}\text{C}$ -NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 170.6, 135.4, 130.0, 128.7, 127.2, 67.0, 48.2, 42.7; IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) = 3058, 2925, 2862, 1630, 1436, 1259; MS (EI, 70 eV):  $m/z$  (%) = 191 ( $\text{M}^+$ , 8), 176 (5), 148 (5), 114 (5), 105 (100), 86 (11), 77 (87).

**N-benzylbenzamide 3{1,5}**



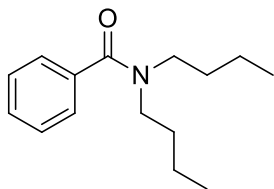
Isolated yield = 87%;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.79-7.81 (m, 2H), 7.31-7.79 (m, 8H), 6.40 (br s, 1H), 4.66 (d,  $J$  = 4.7 Hz, 2H); IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3295, 3060, 2978, 1644, 1540, 1488, 1260; MS (EI, 70 eV):  $m/z$  (%) = 211 ( $\text{M}^+$ , 61), 121 (4), 105 (100), 91 (12), 77 (65).

**N-ethylbenzamide 3{1,2}**



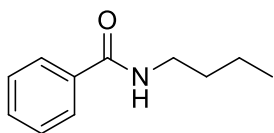
Isolated yield = 89%;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.39-7.78 (m, 5H), 6.12 (br s, 1H), 3.45-3.57 (m, 2H), 1.26 (t,  $J$  = 7.2 Hz, 3H); IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3318, 3074, 2977, 1637, 1546, 1430, 1308; MS (EI, 70 eV):  $m/z$  (%) = 149 ( $\text{M}^+$ , 60), 134 (3), 105 (100), 77 (42).

***N,N*-dibutylbenzamide 3{1,10}**



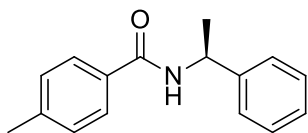
Isolated yield = 68%;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.28-7.39 (m, 5H), 3.18-3.49 (m, 4H), 1.11-1.64 (m, 8H), 0.77-1.00 (m, 6H); IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) = 3070, 2952, 2869, 1635, 1523, 1438, 1349.

***N*-butylbenzamide 3{1,3}**



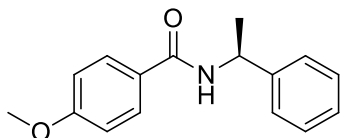
Isolated yield = 77%;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.29-8.00 (m, 5H), 6.32 (br s, 1H), 3.32-3.40 (m, 2H), 1.18-1.57 (m, 4H), 0.87 (t,  $J$  = 7.5 Hz, 3H); IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3302, 3081, 2958, 2870, 1635, 1548, 1488, 1315.

**(*S*)-4-methyl-*N*-(1-phenylethyl)benzamide 3{6,6}**



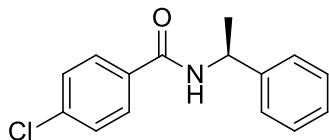
Isolated yield = 70%;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.77 (d,  $J$  = 7.7 Hz, 2H), 7.31-7.47 (m, 7H), 6.31 (br s, 1H), 5.31-5.37 (m, 1H), 2.41 (s, 3H), 1.61 (d,  $J$  = 6.7 Hz, 3H); IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3331, 3032, 2973, 2925, 1632, 1522, 1450, 1270.

**(*S*)-4-methoxy-*N*-(1-phenylethyl)benzamide 3{5,6}**



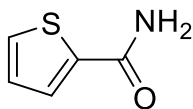
Isolated yield = 87%;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.74 (d,  $J$  = 8.7 Hz, 2H), 7.30-7.39 (m, 5H), 6.89-6.93 (m, 2H), 6.23 (br s, 1H), 5.31-5.36 (m, 1H), 3.84 (s, 3H), 1.60 (d,  $J$  = 6.7 Hz, 3H); IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3434, 3337, 2818, 2849, 1622, 1526, 1502, 1257.

**(S)-4-chloro-*N*-(1-phenylethyl)benzamide 3{2,6}**



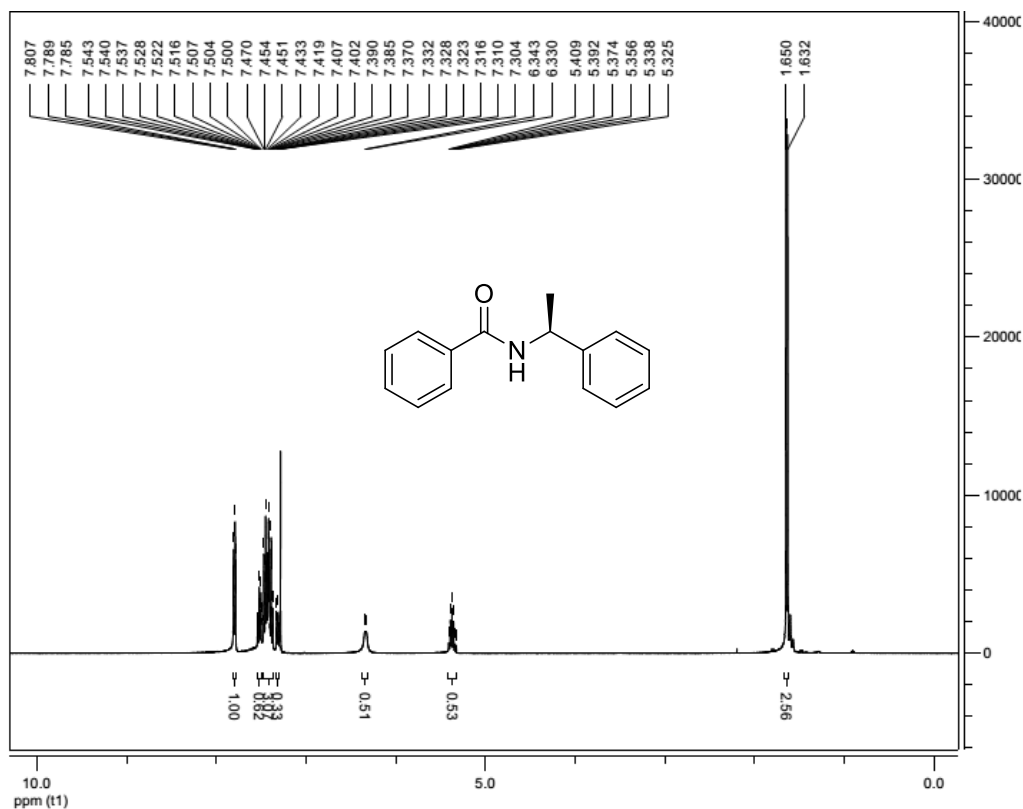
Isolated yield = 60%;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.71 (d,  $J$  = 8.2 Hz, 2H), 7.30-7.40 (m, 7H), 6.39 (br s, 1H), 5.28-5.34 (m, 1H), 1.60 (d,  $J$  = 7.0, 3H); IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3421, 3338, 2980, 1636, 1529, 1485, 1268.

**Thiophene-2-carboxamide 3{10,1}**

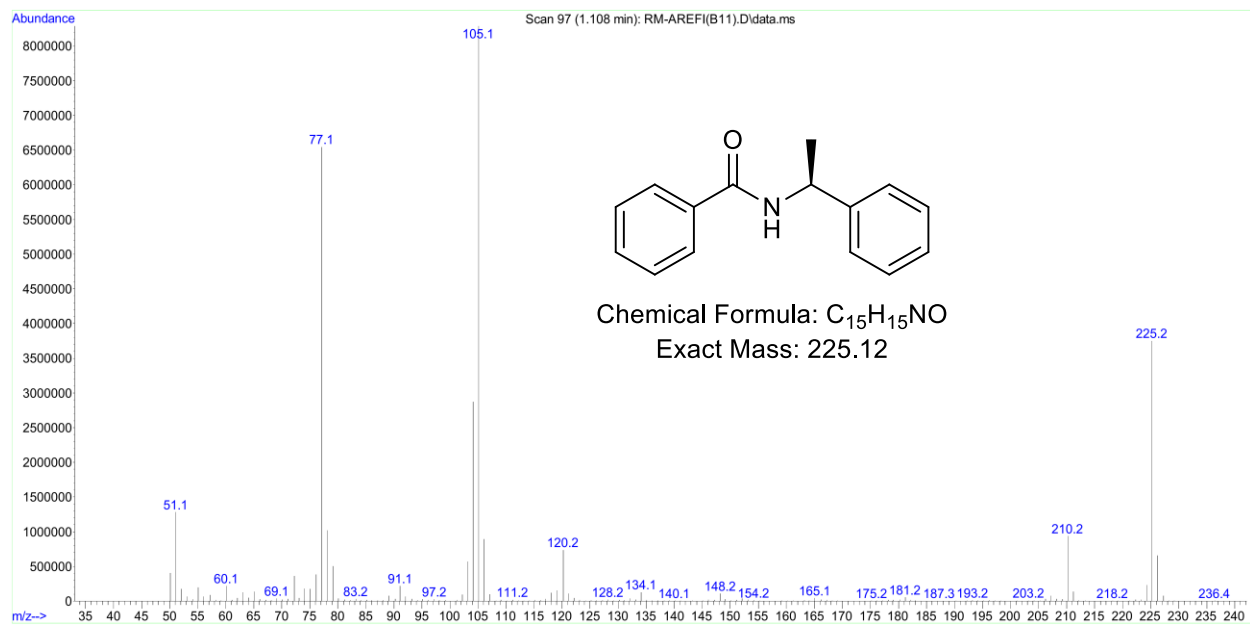
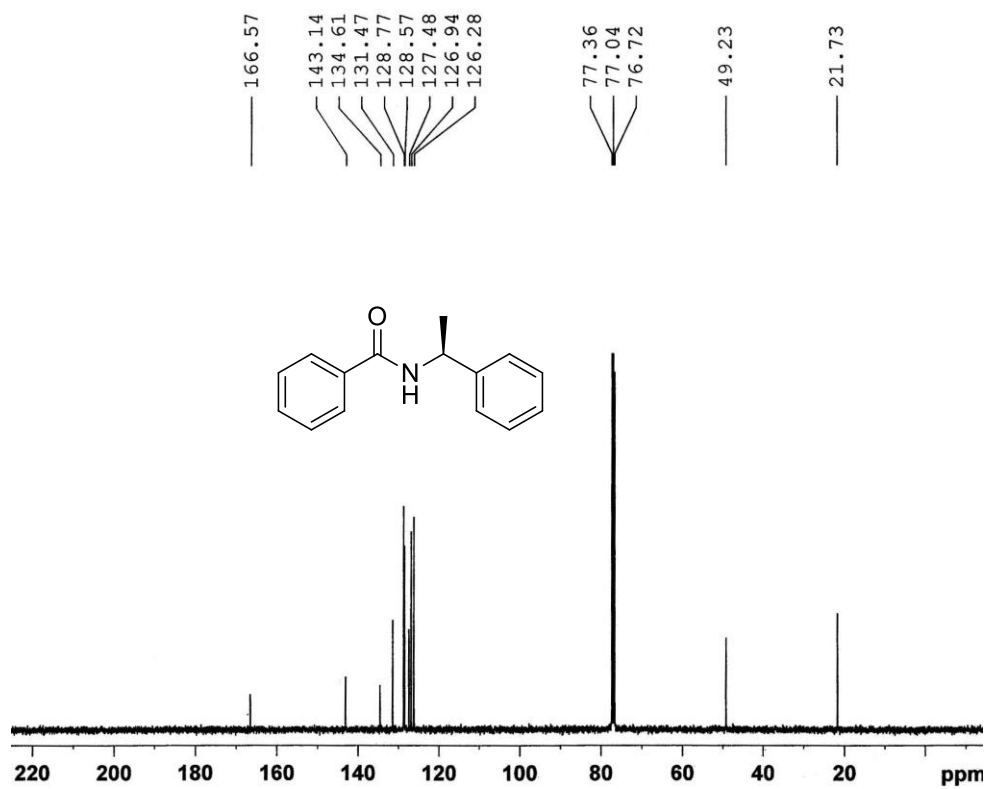


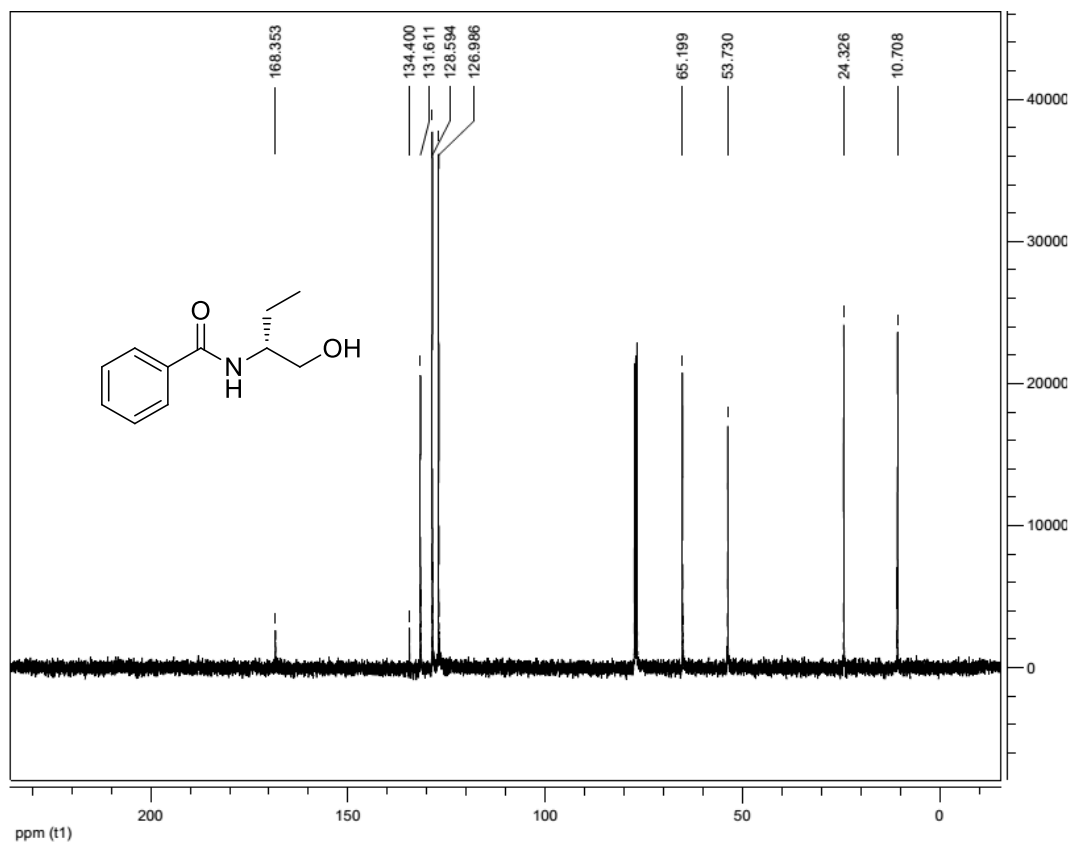
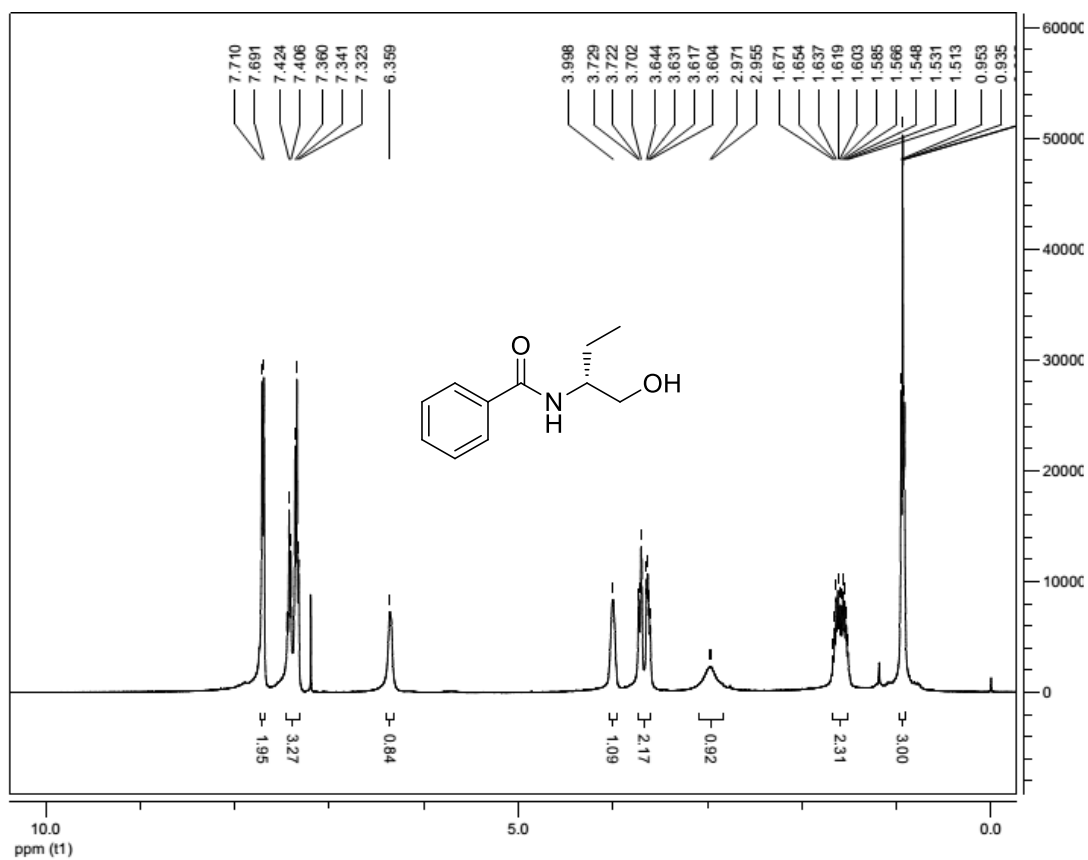
Isolated yield = 54%;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.45-7.47 (m, 2H), 7.03 (dd,  $J$  = 4.8 Hz,  $J$  = 4.8 Hz, 1H), 5.72 (br s, 2H); IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) = 3362, 3173, 2924, 1653, 1606, 1432, 1119; MS (EI, 70 eV):  $m/z$  (%) = 127 ( $\text{M}^+$ , 42), 111 (100), 83 (18), 69 (12), 57 (49).

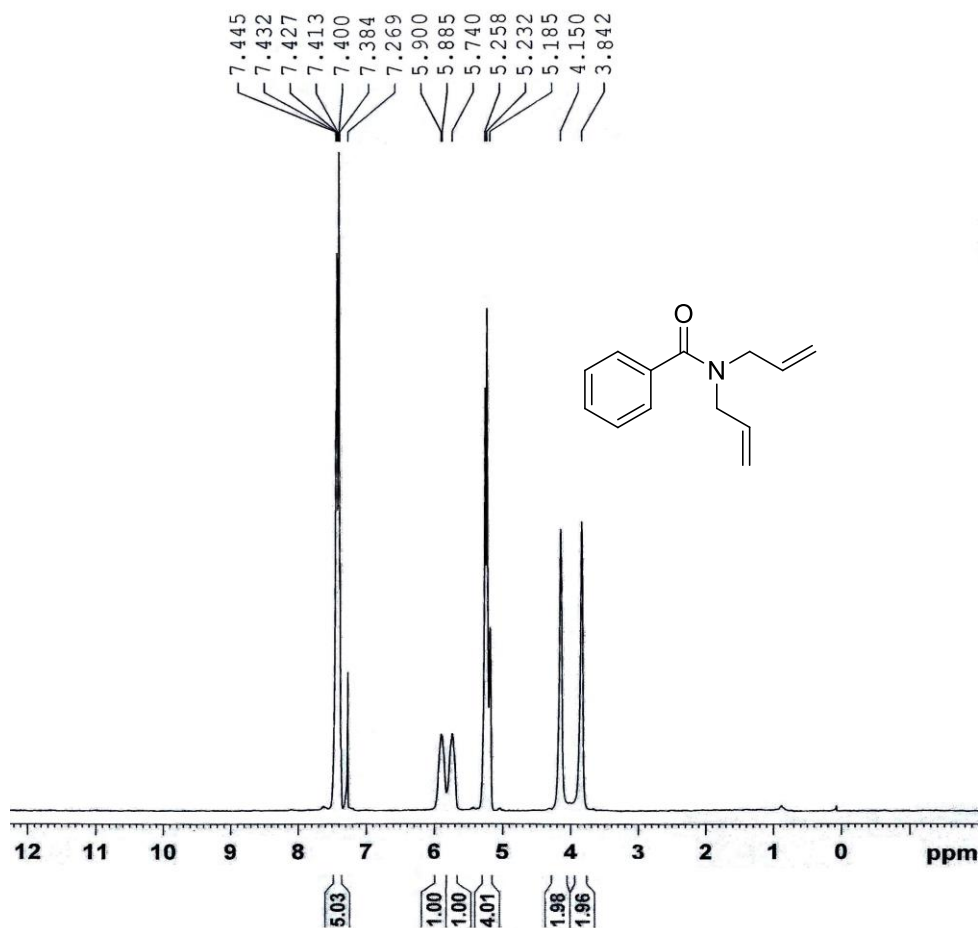
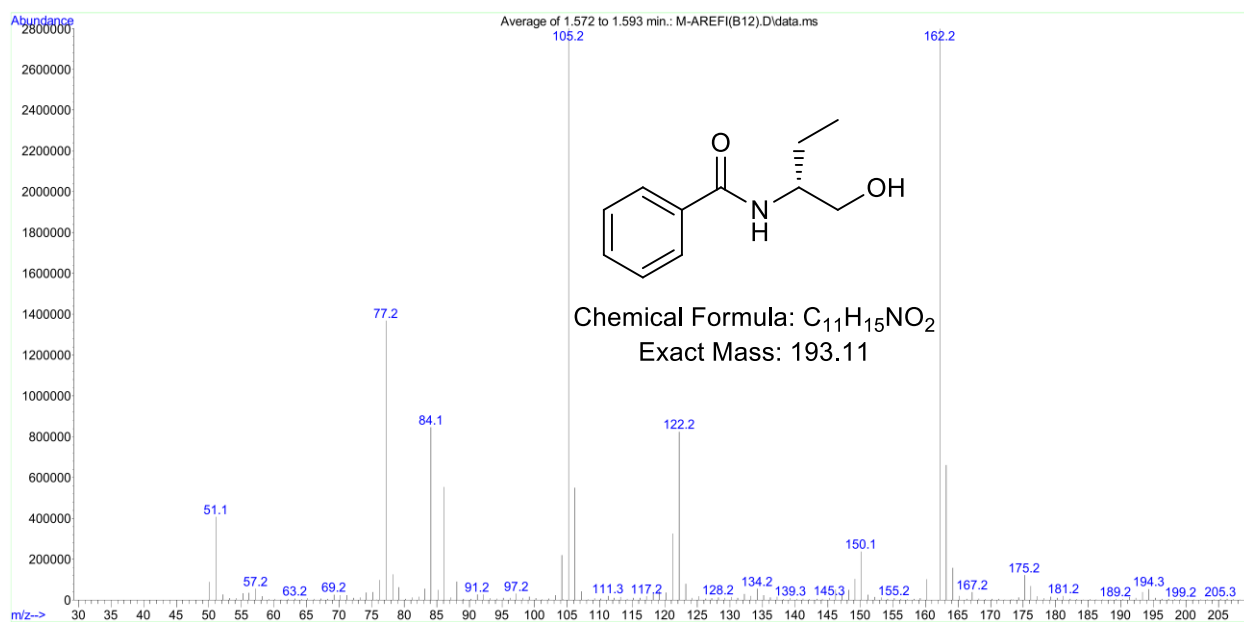
**5. Copy of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectra of amide derivatives**

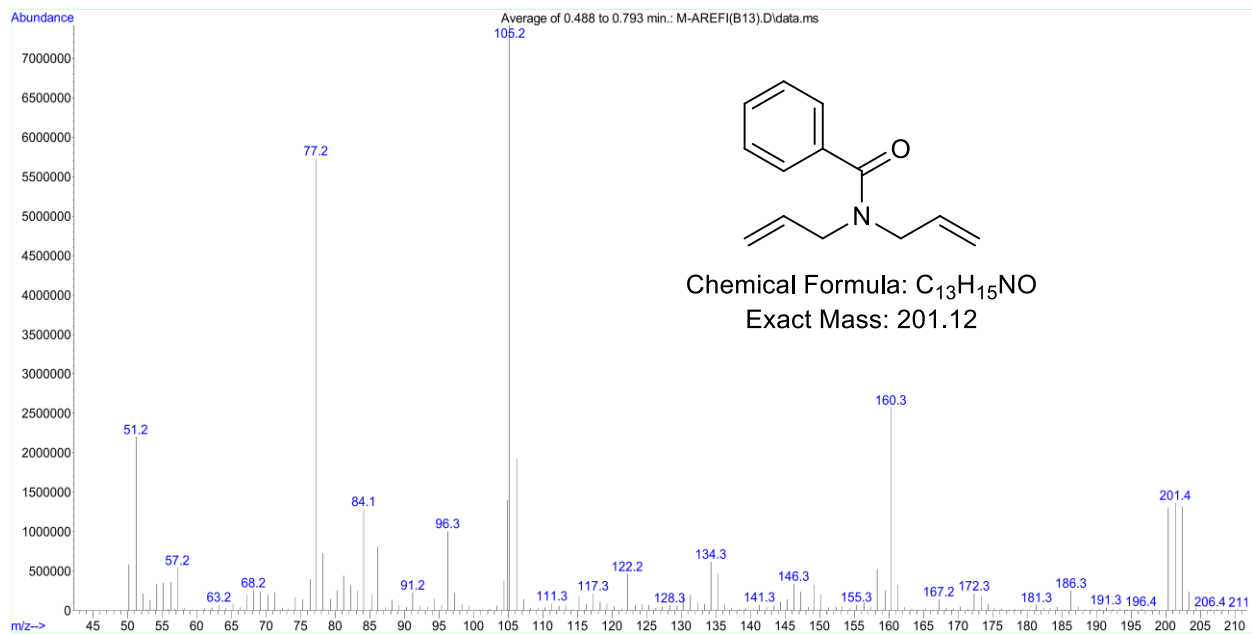
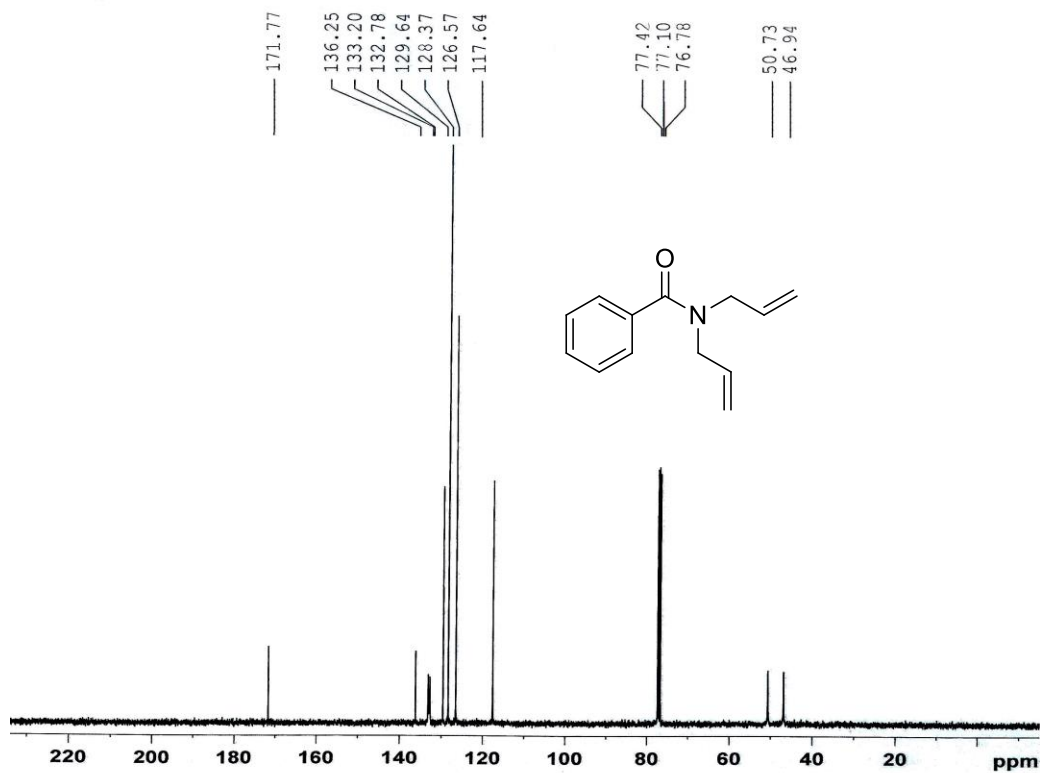


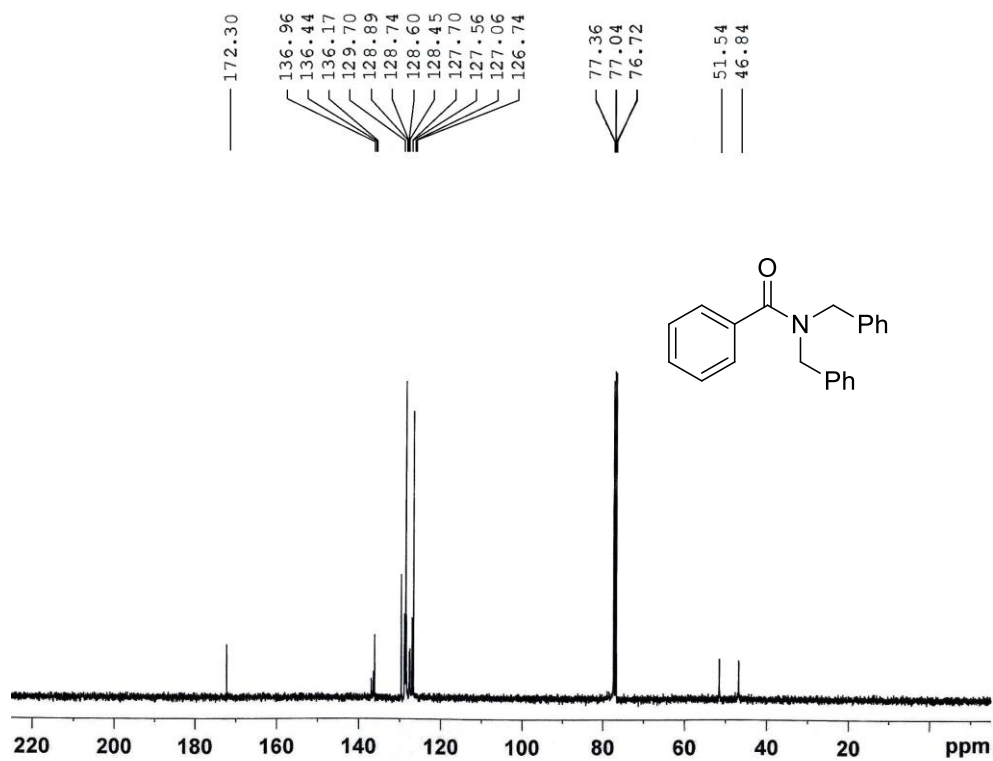
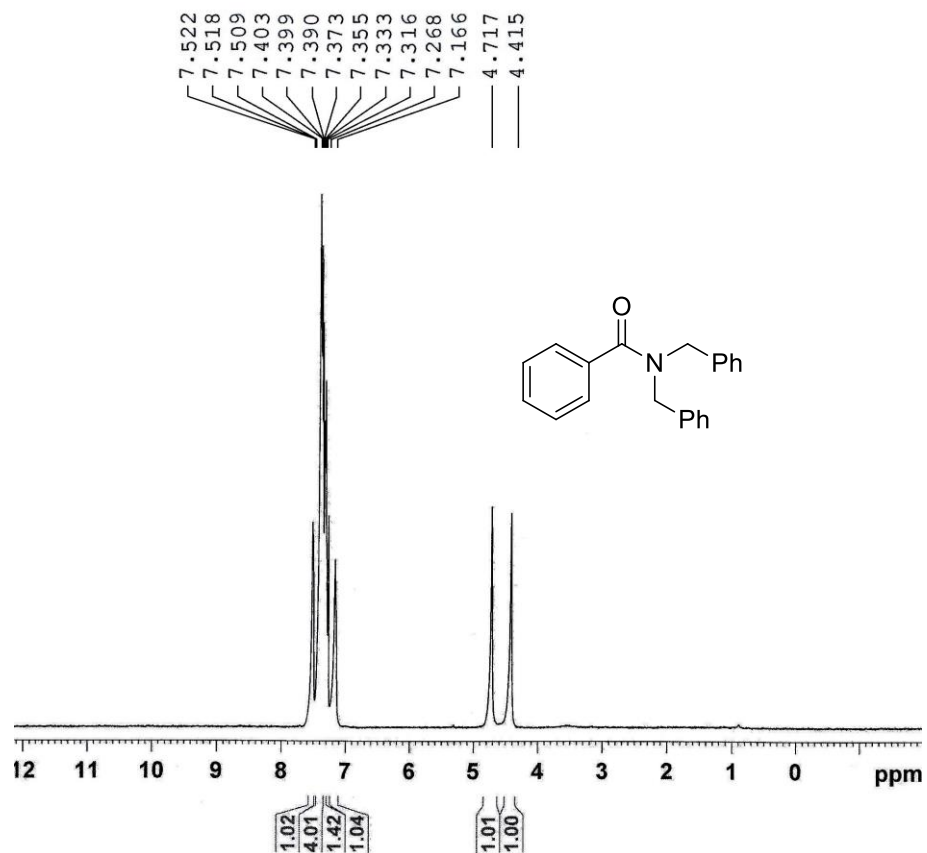


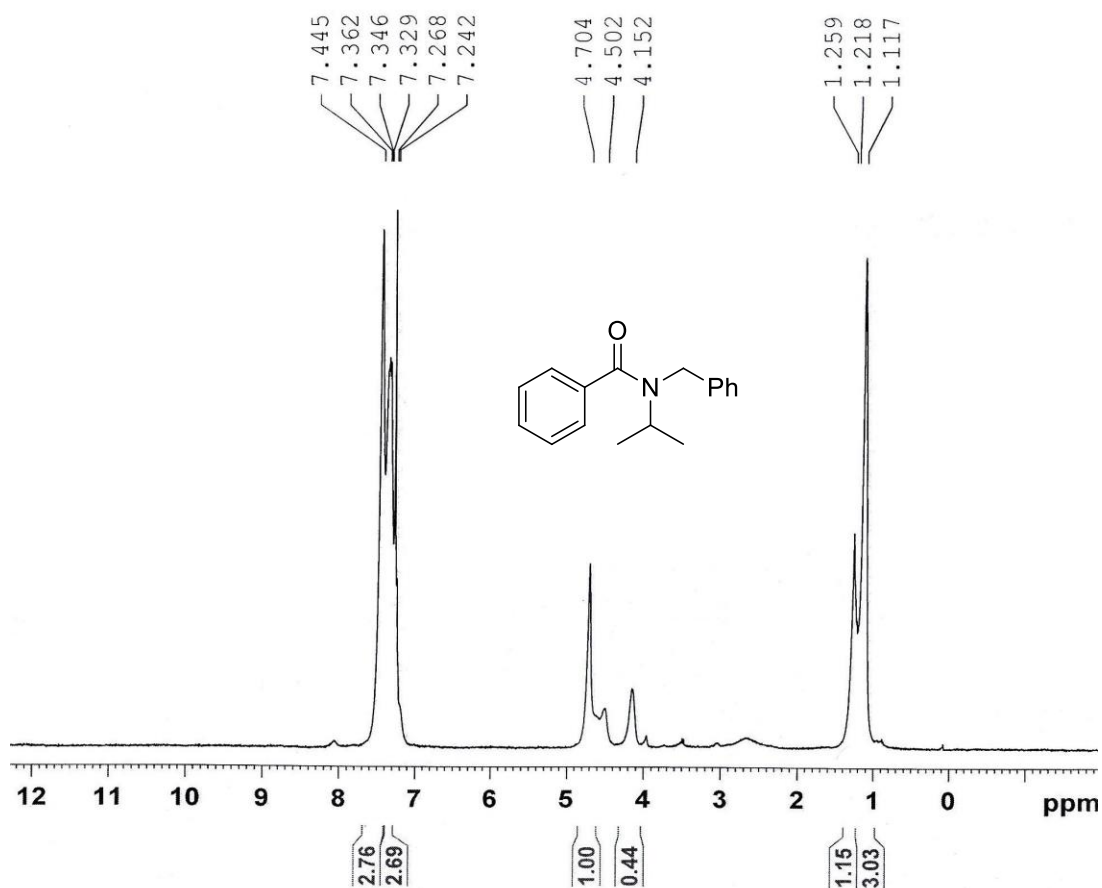
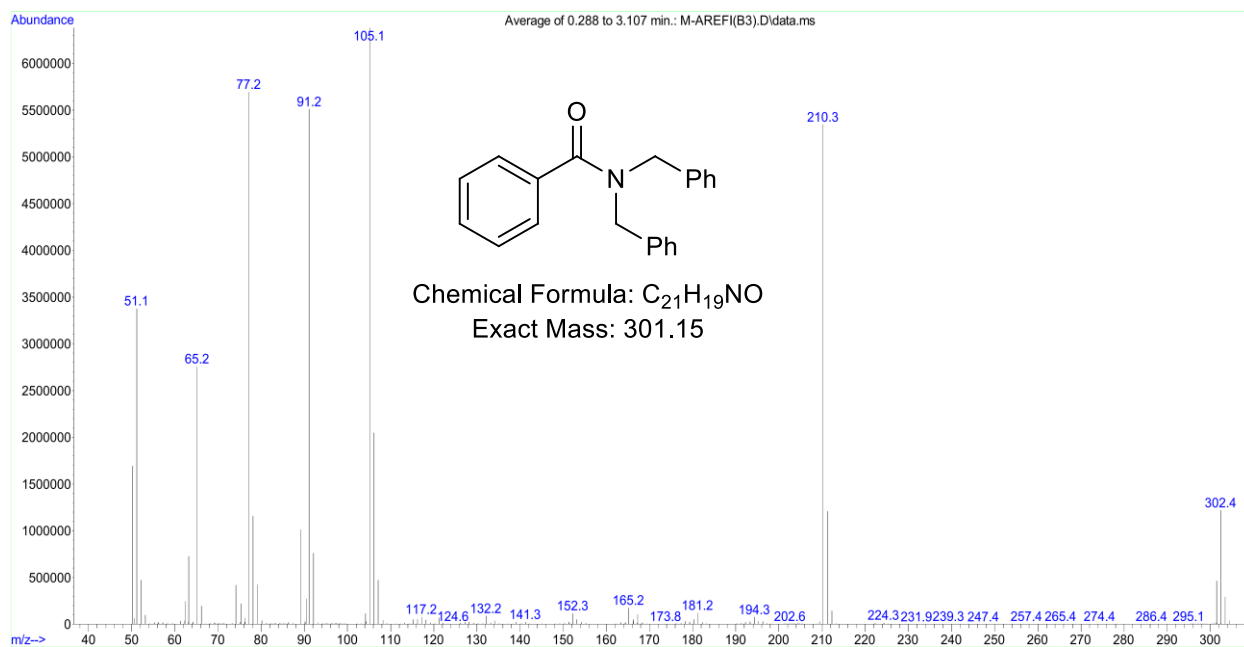


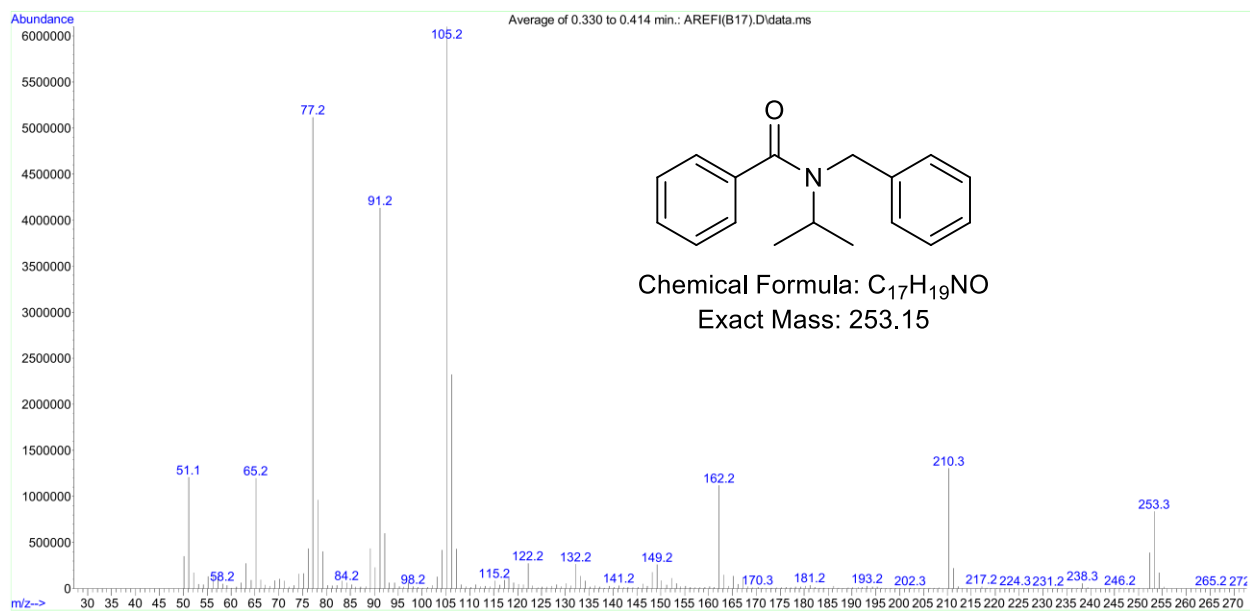
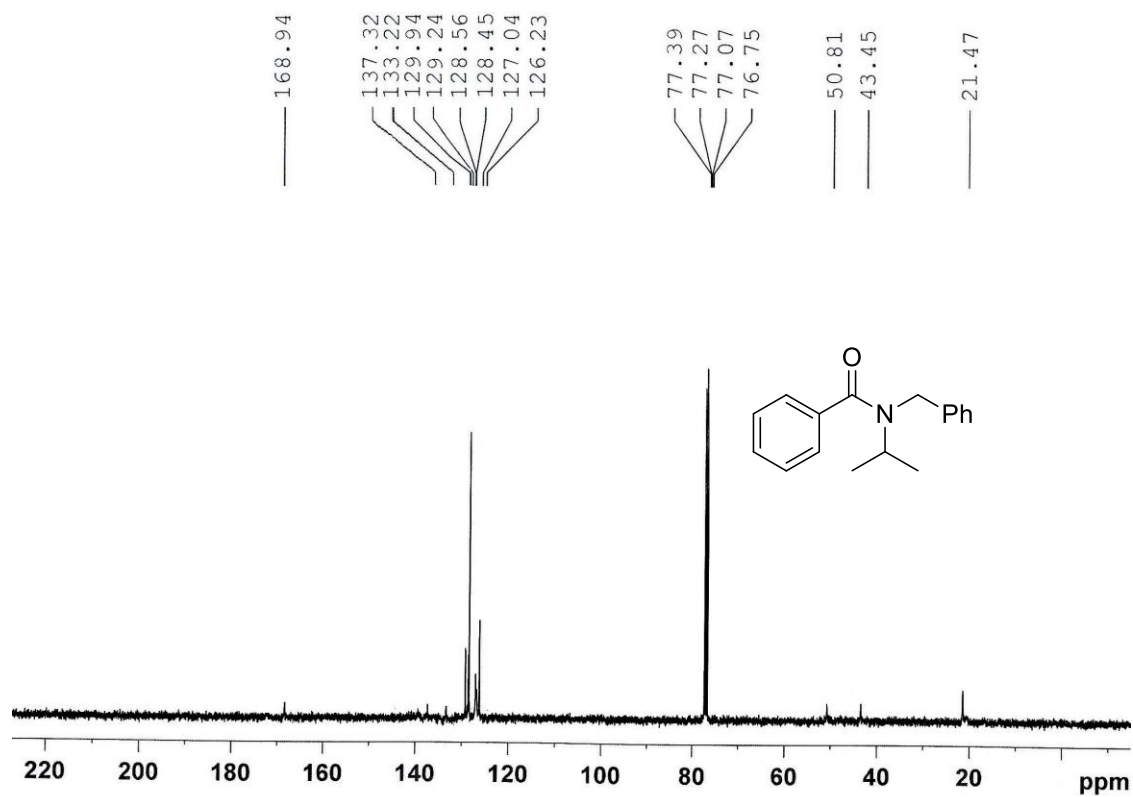


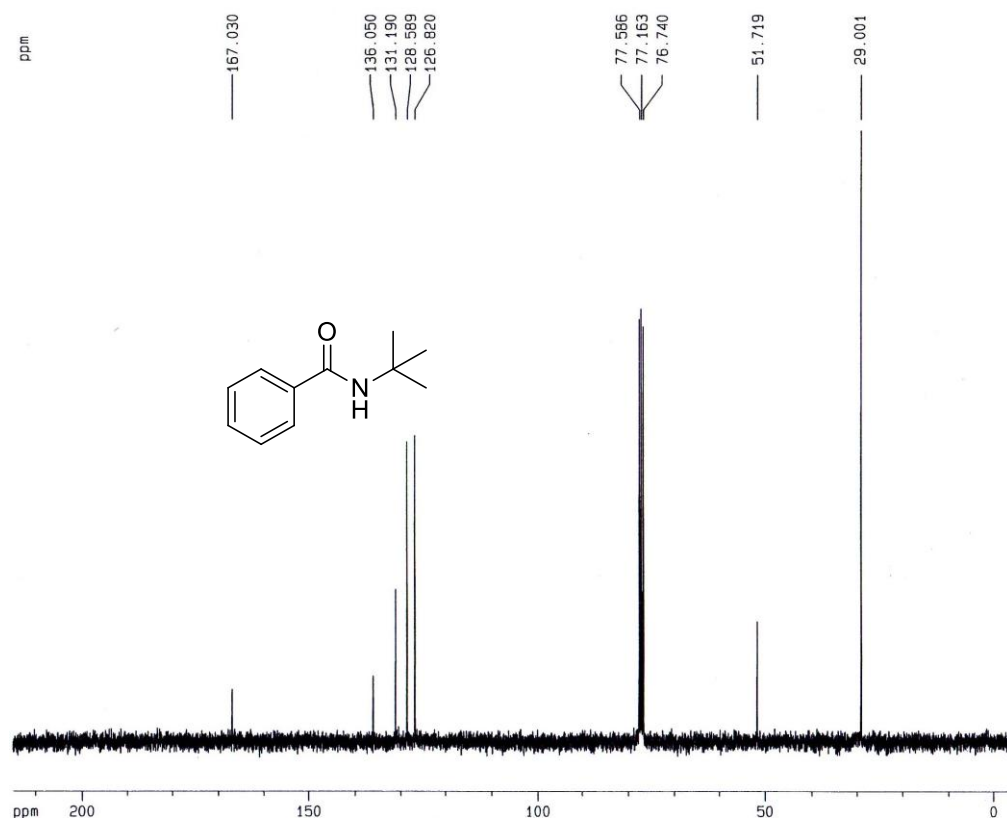
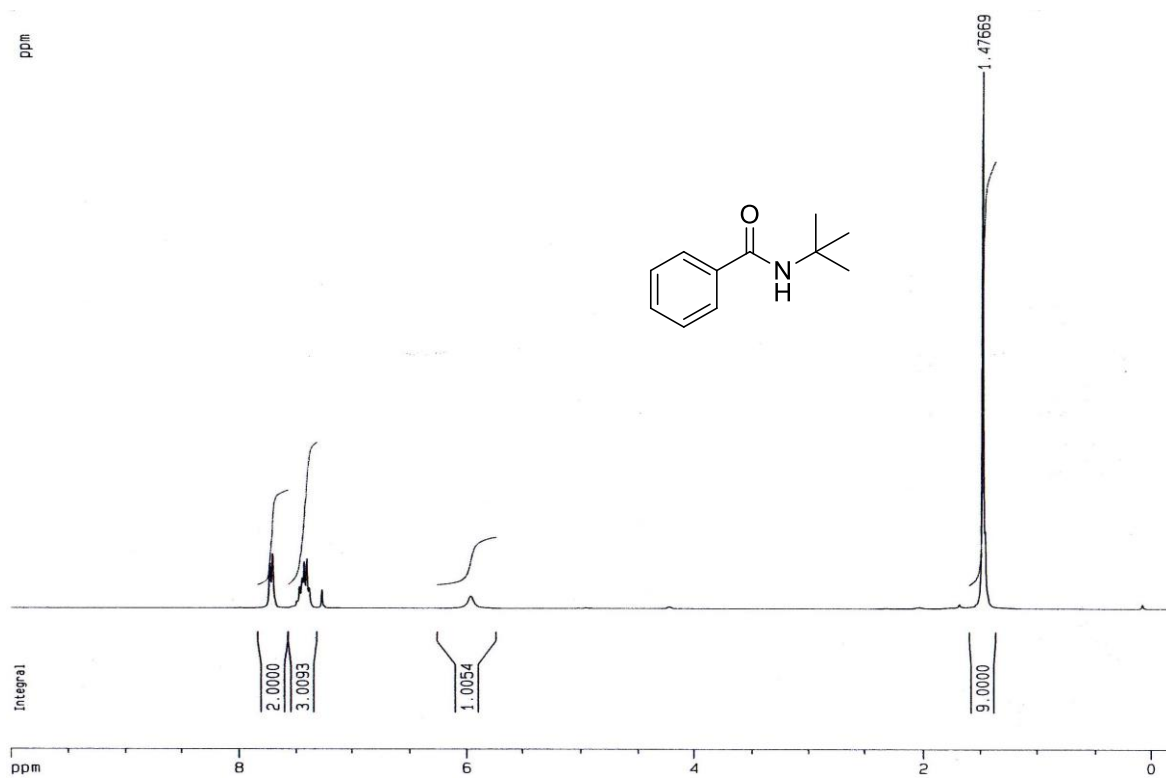




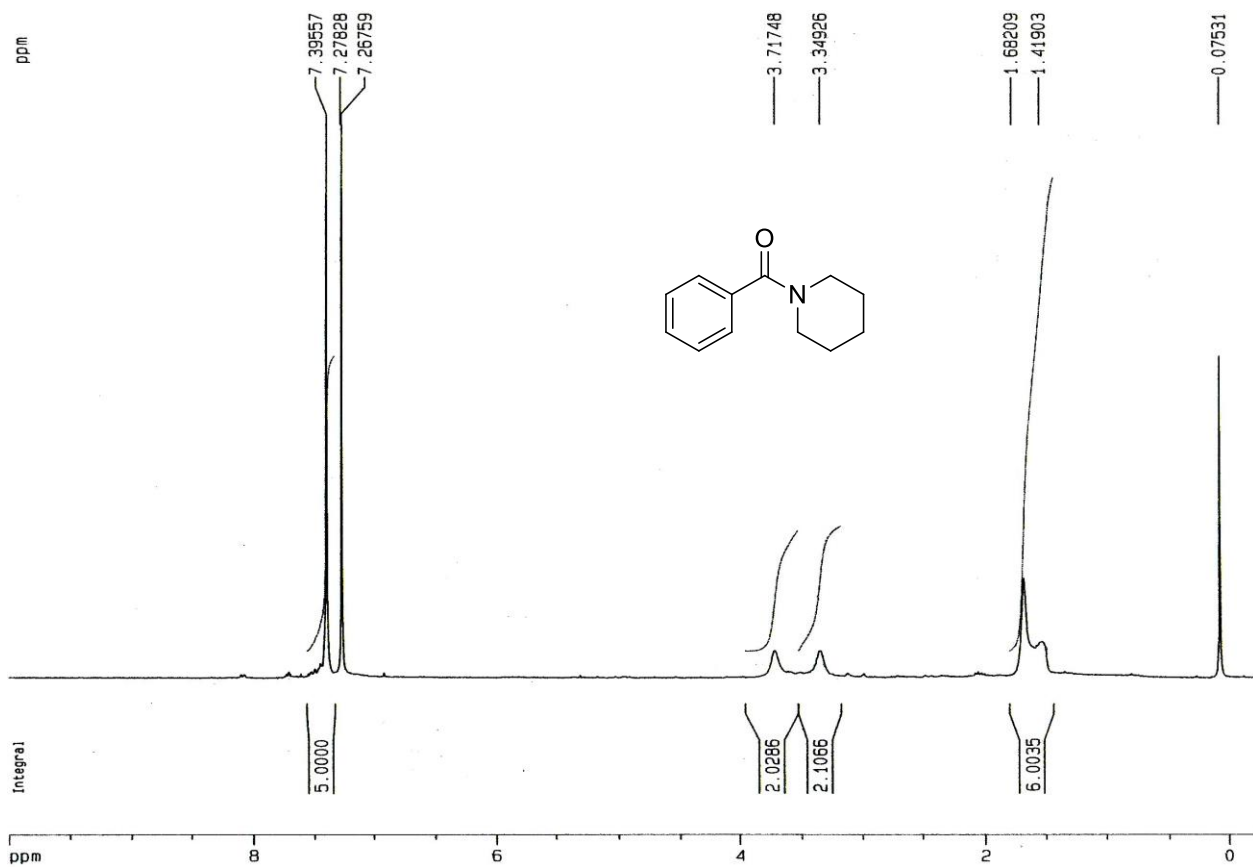
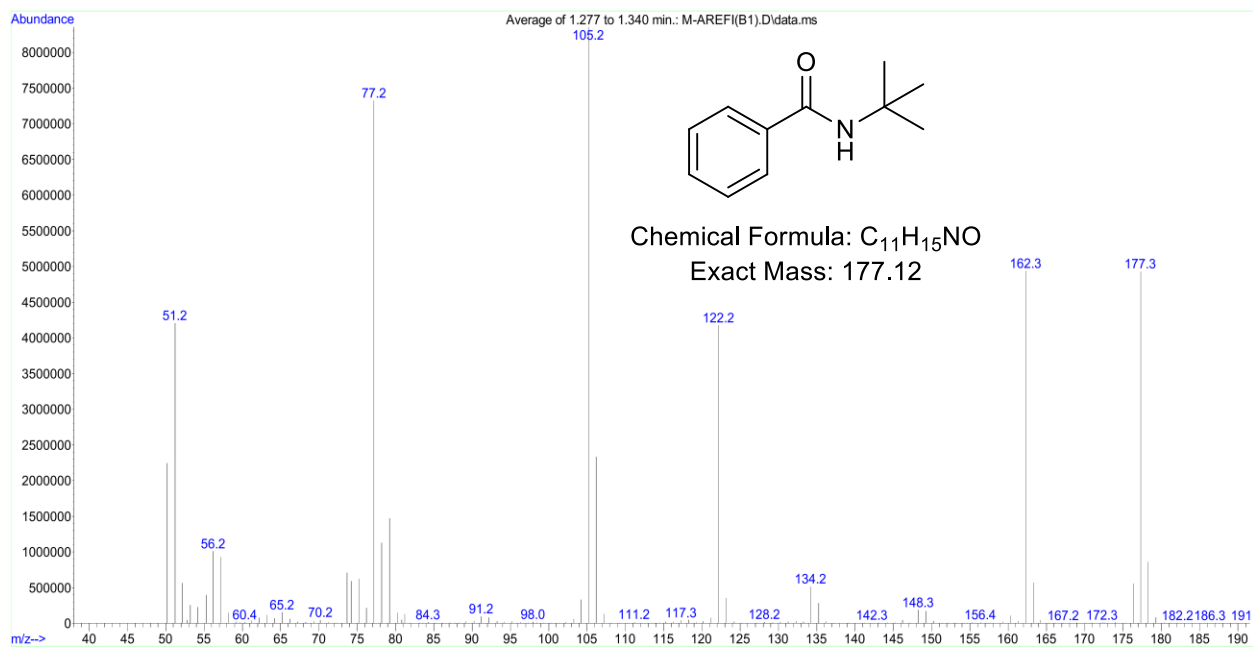


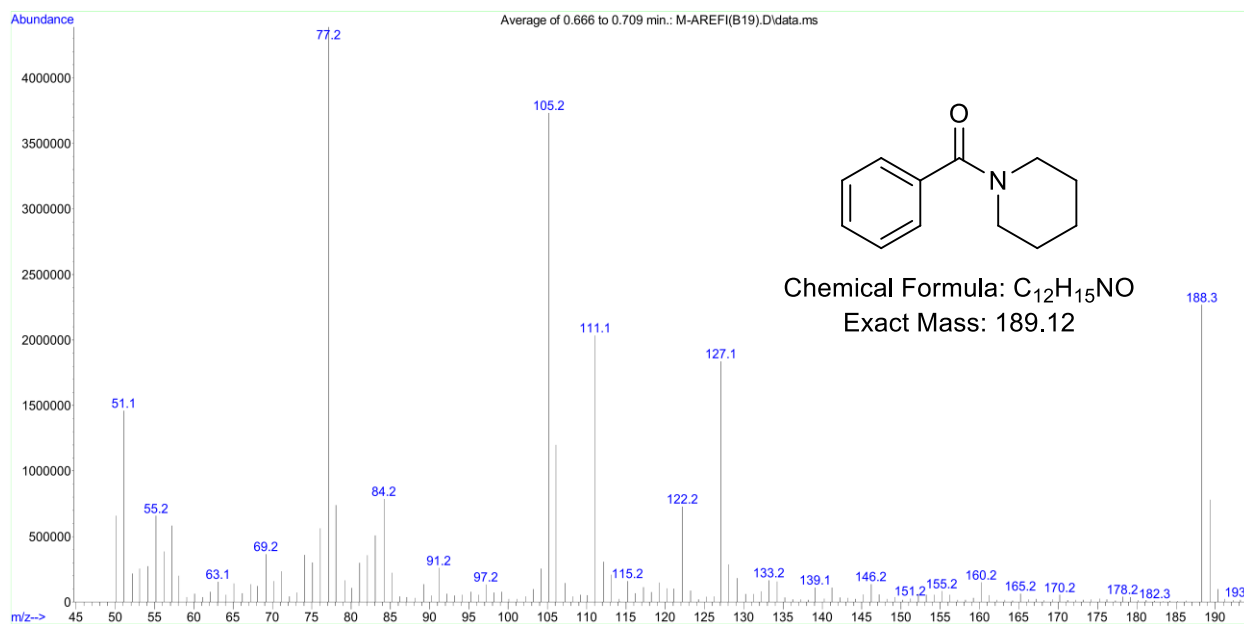
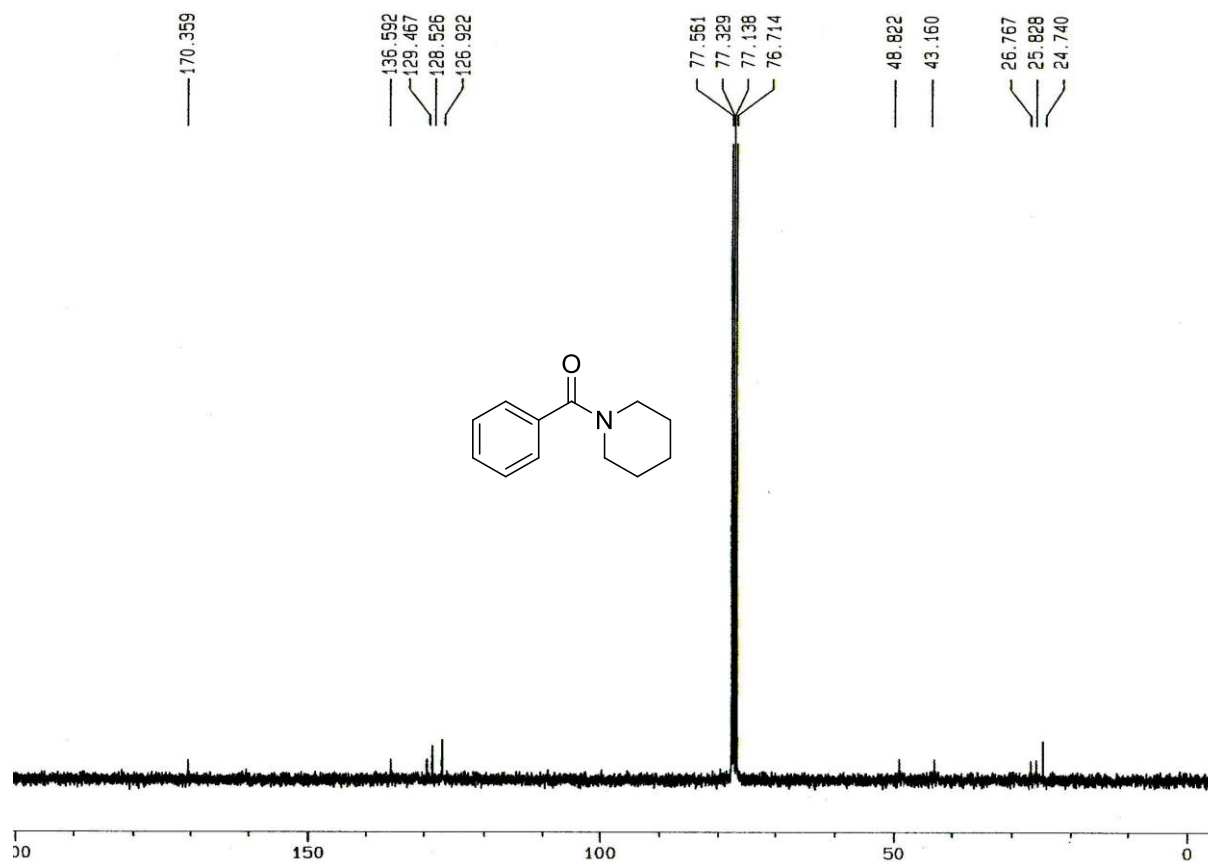


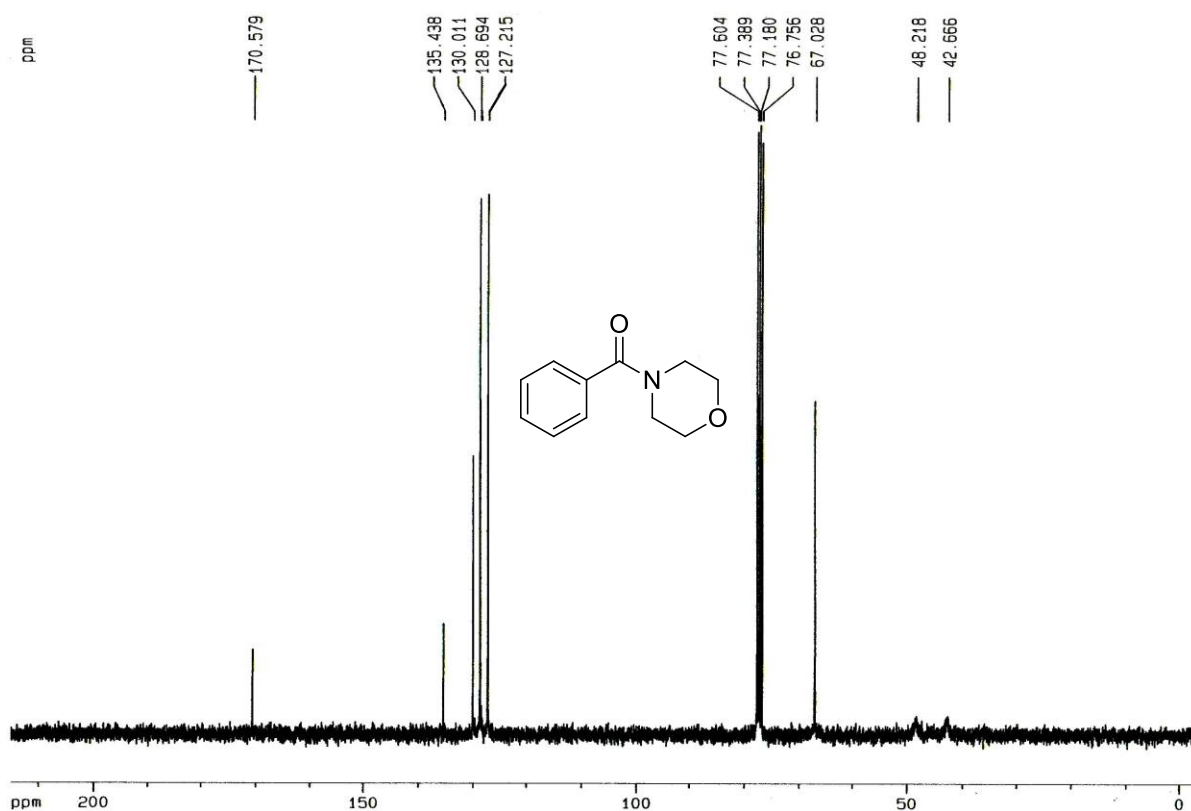


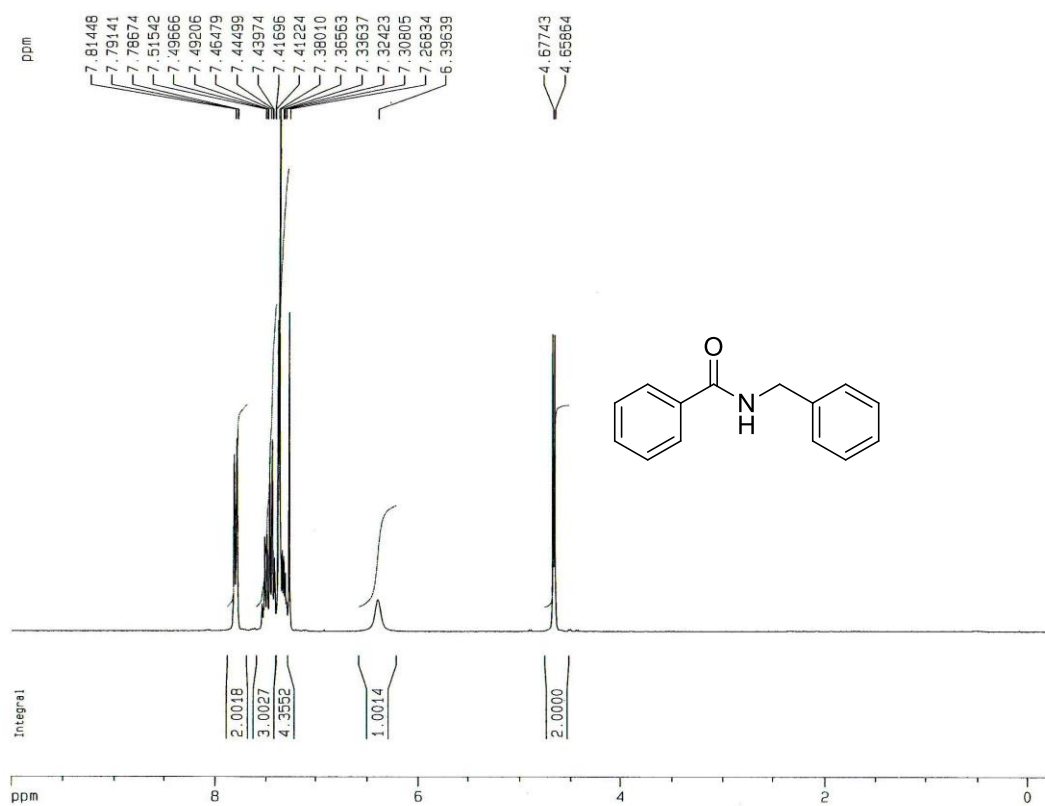
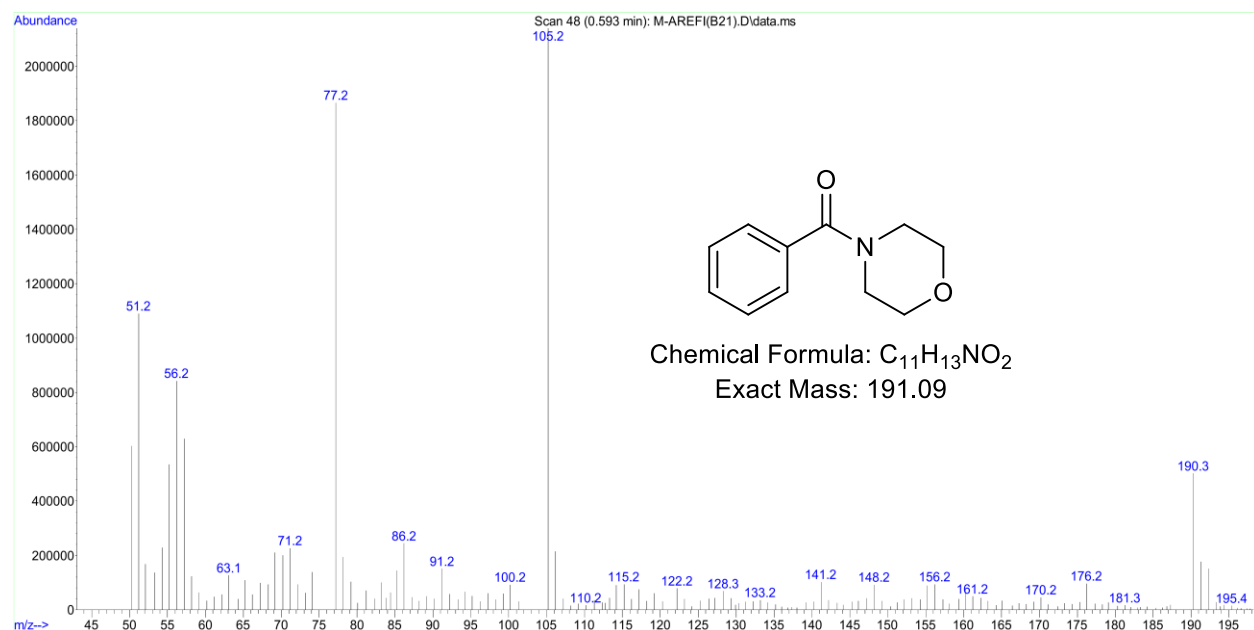


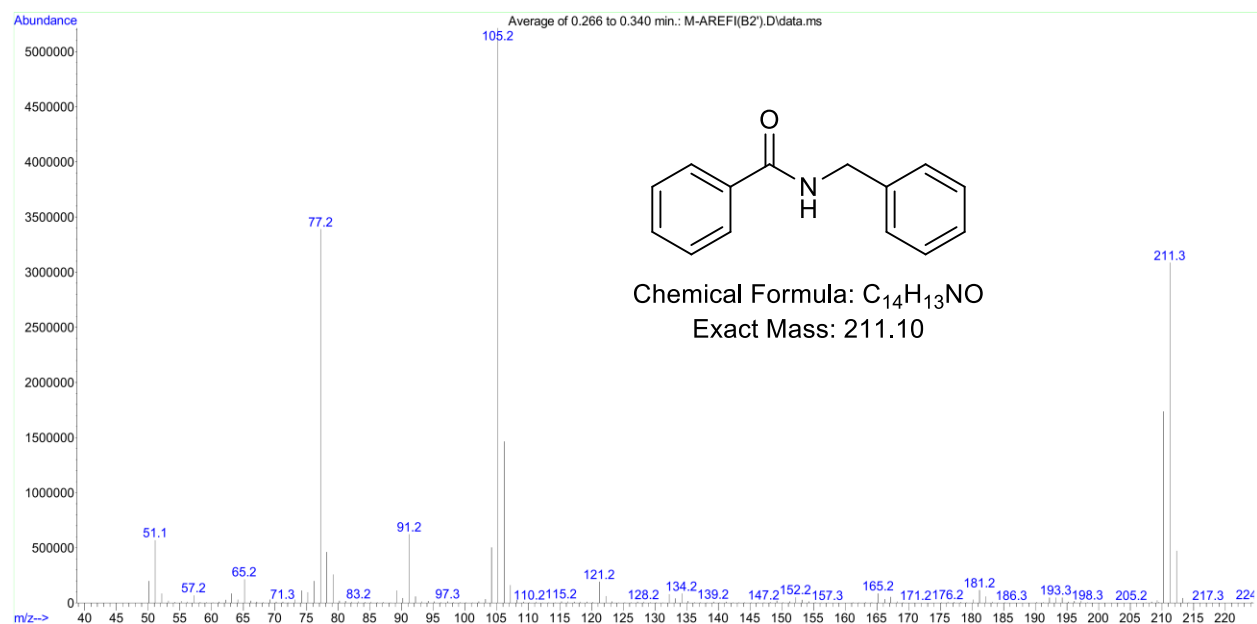


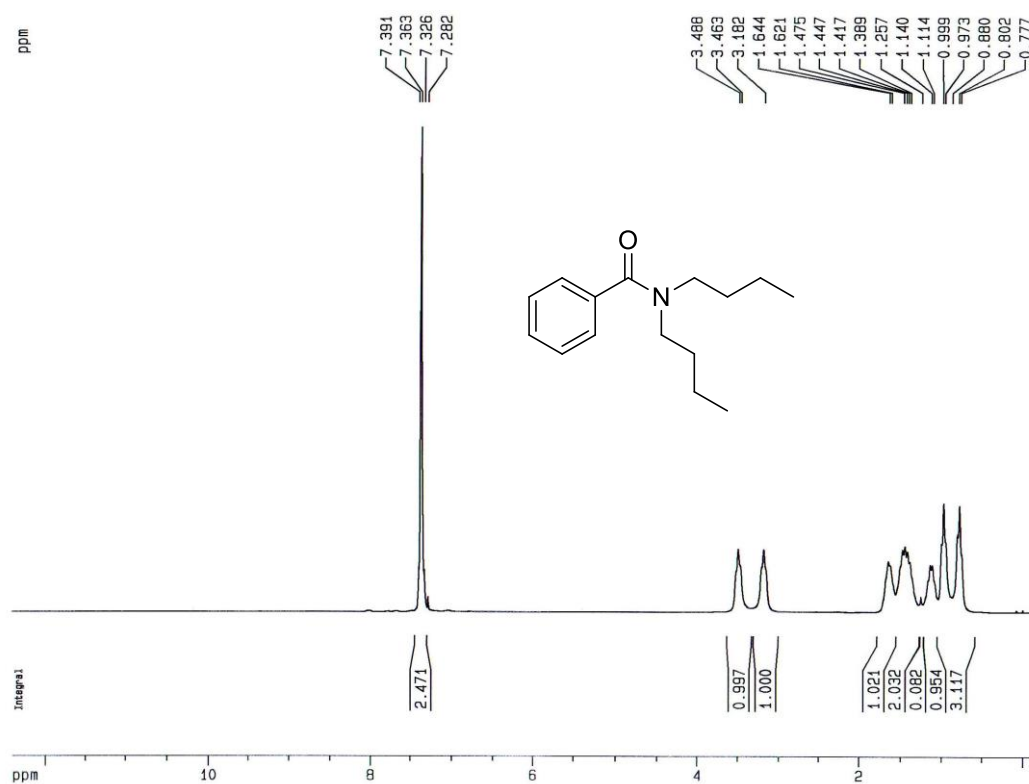
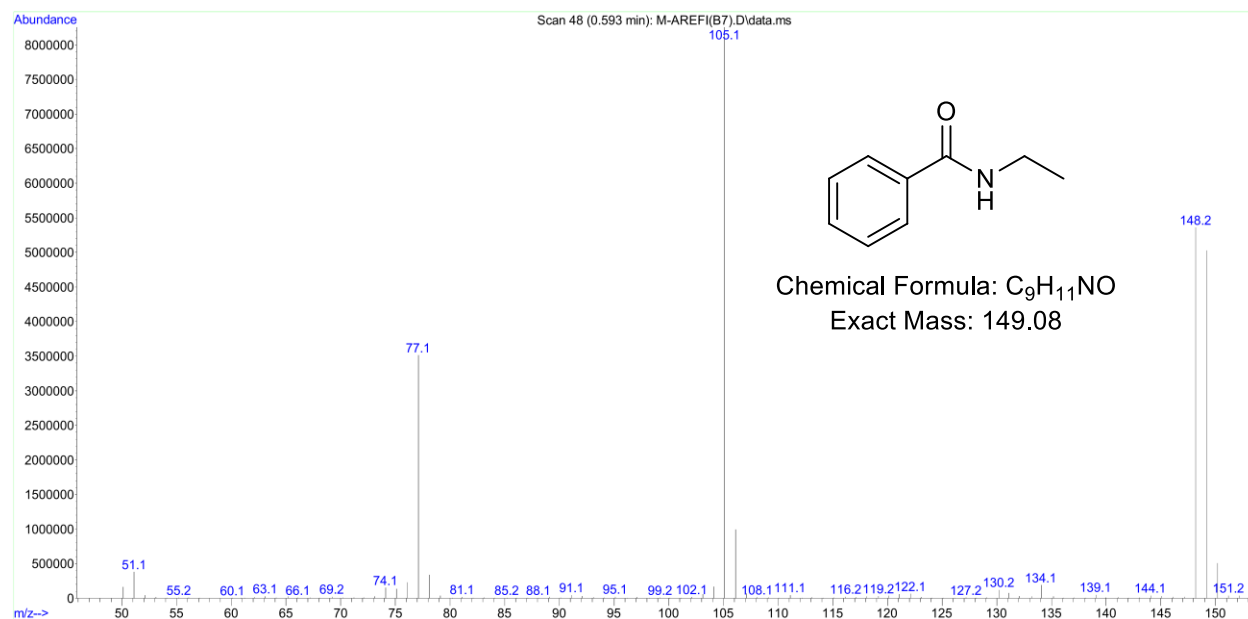


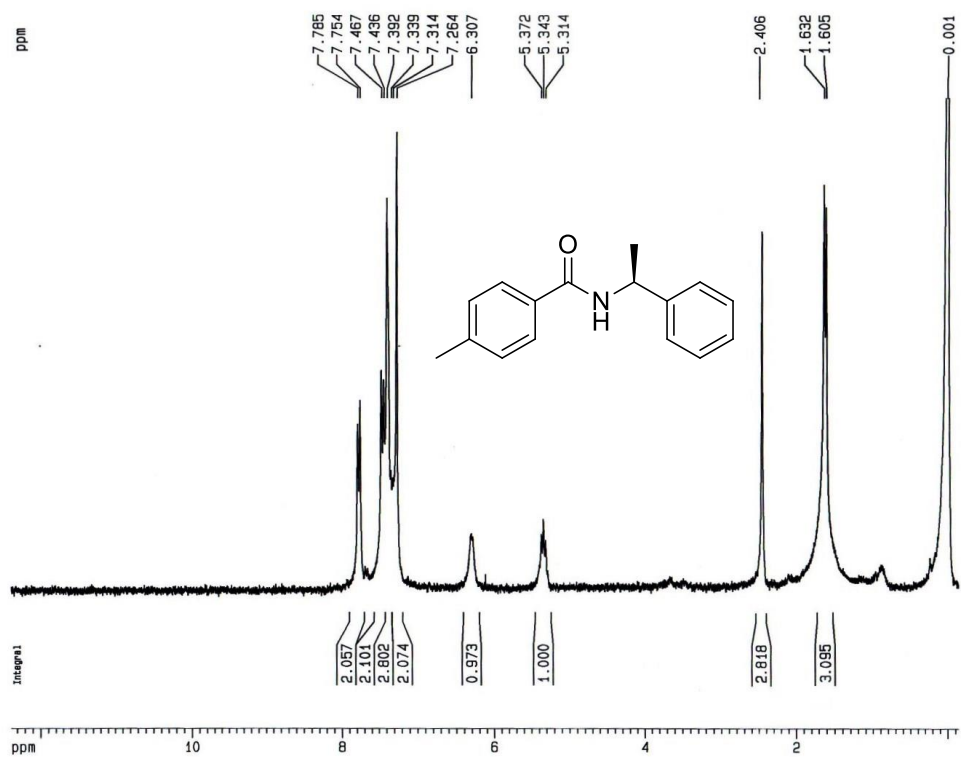
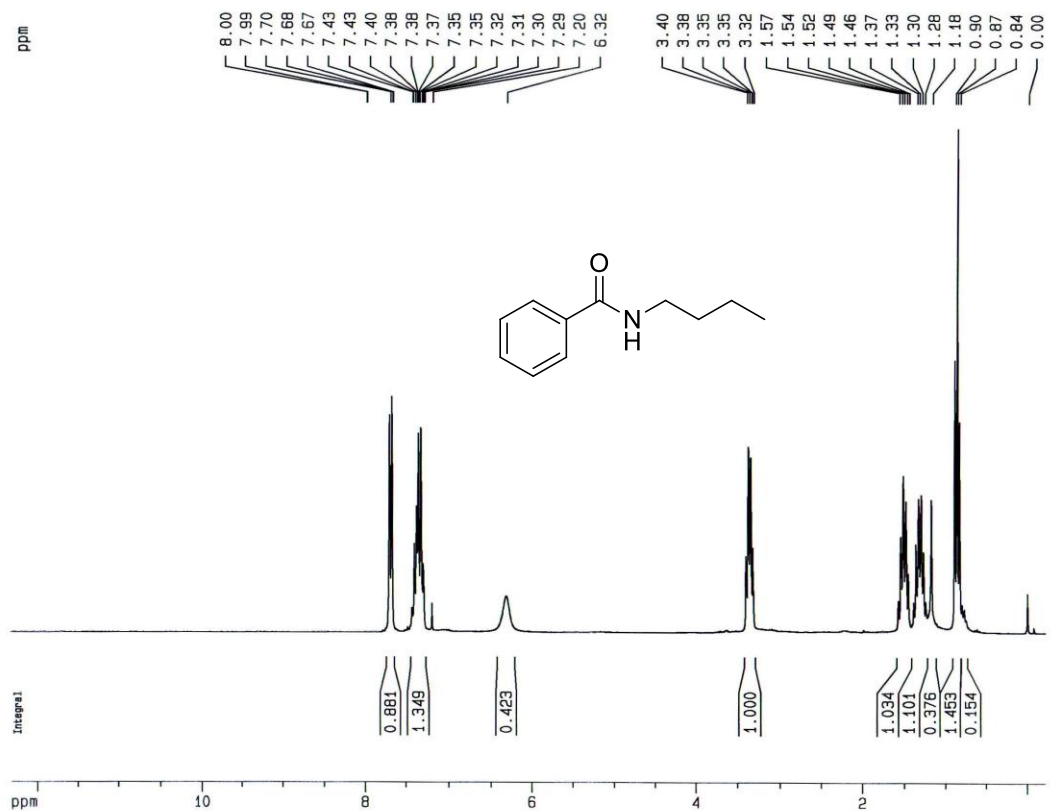


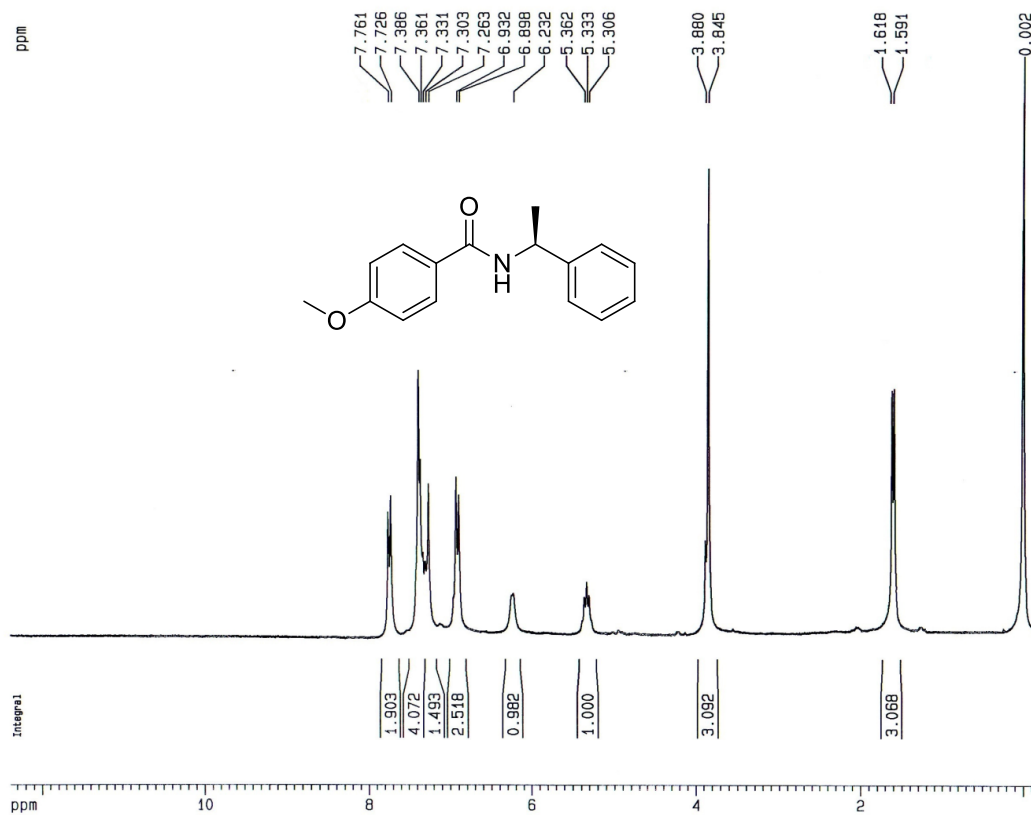




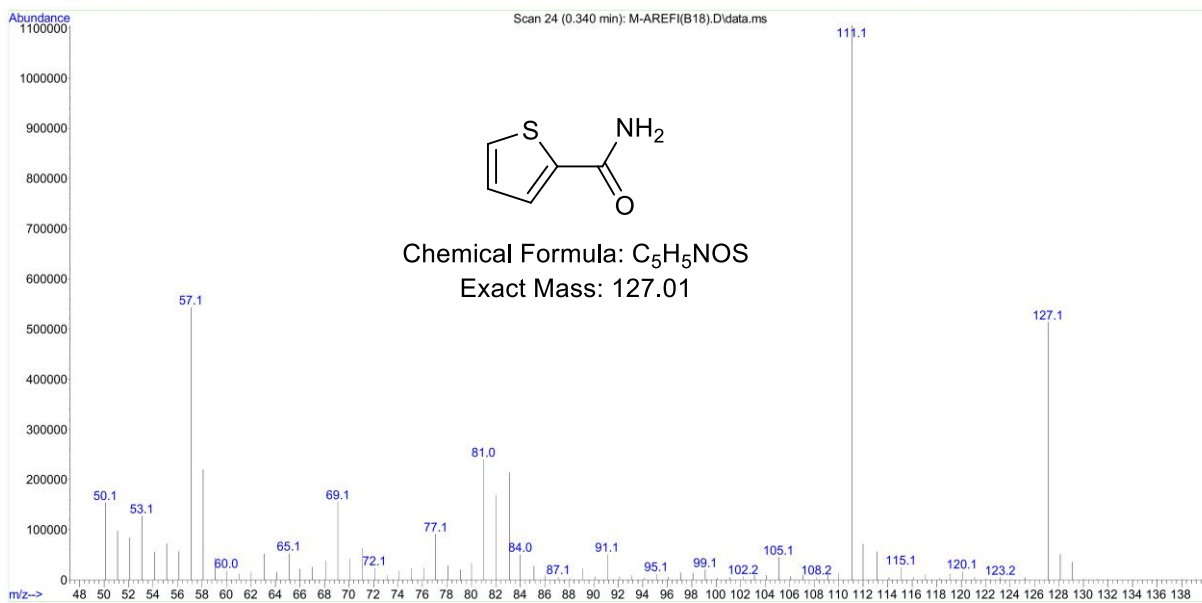
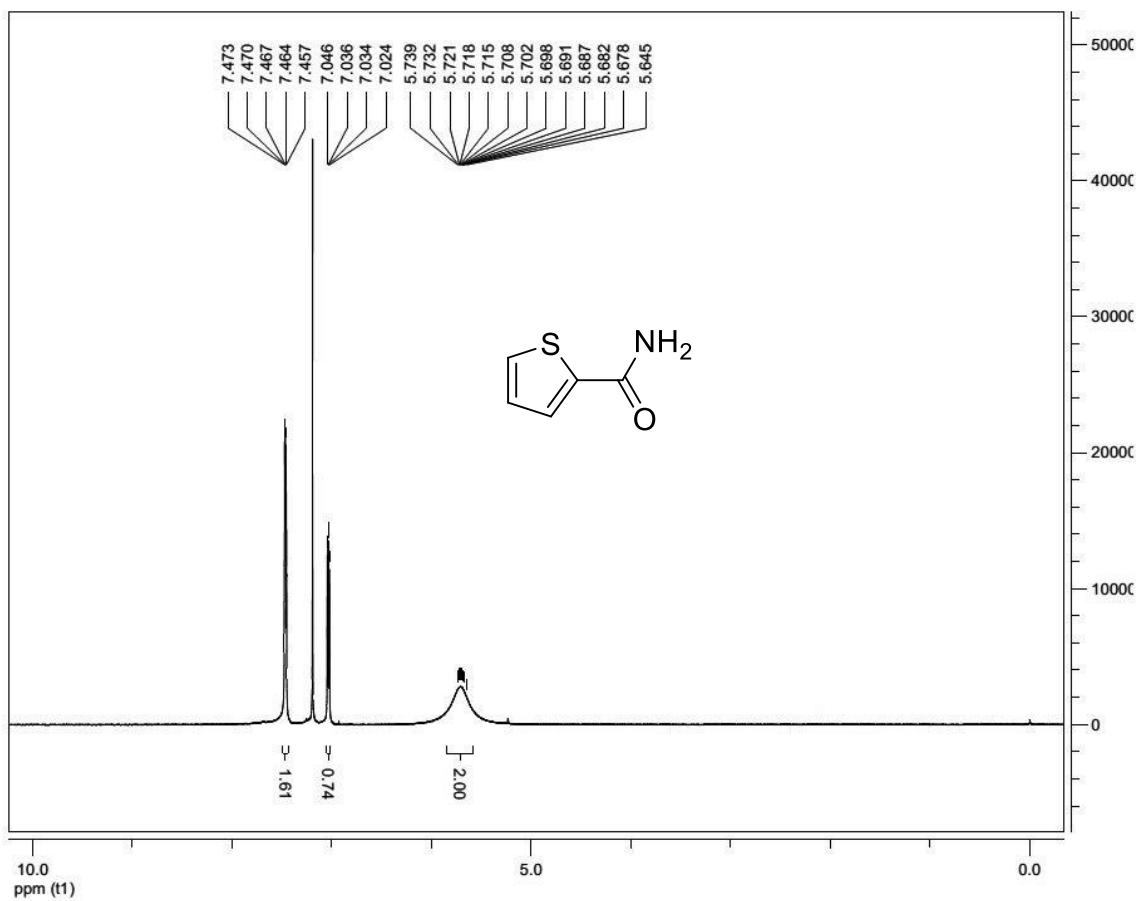








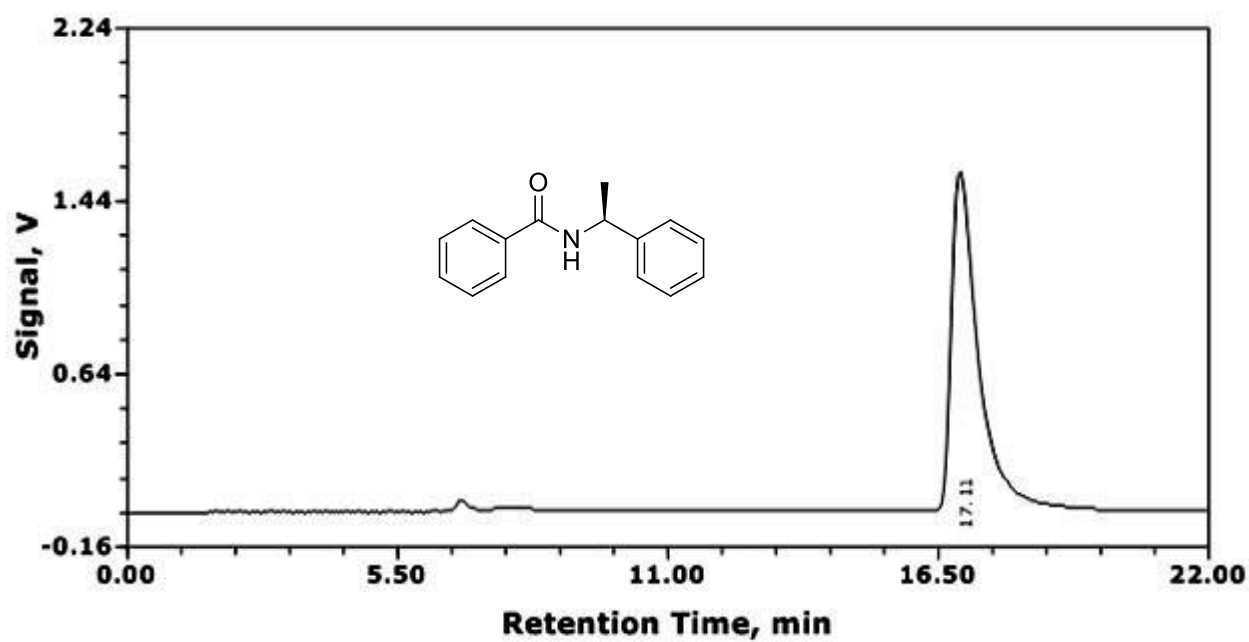




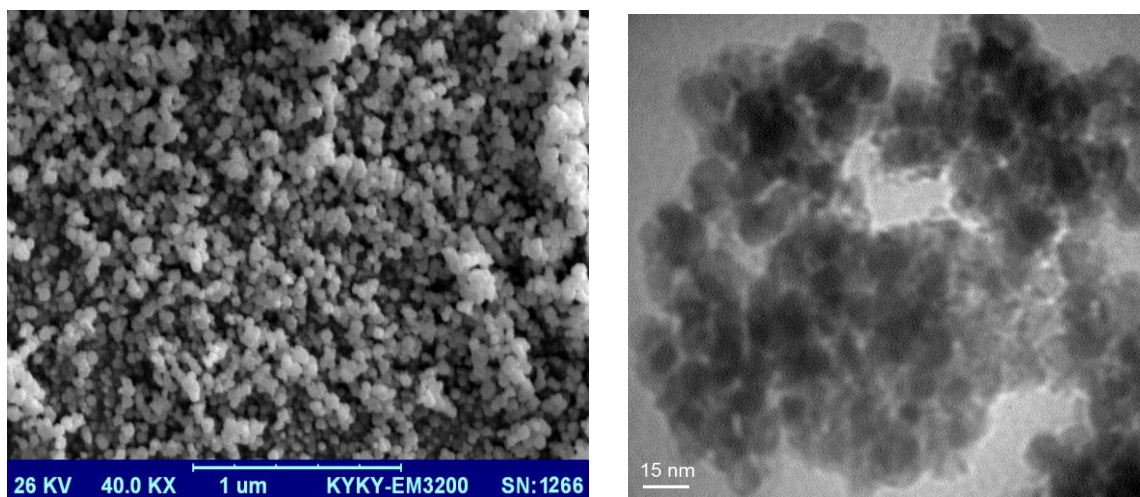
## 6. Chiral HPLC

Chiral HPLC data on compound (S)-*N*-(1-phenylethyl)benzamide **3**{1,6}:

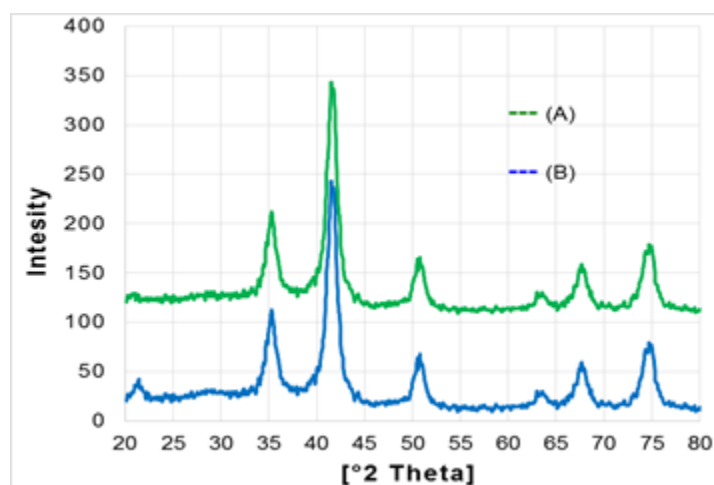
Method: Chiralcel OD-H, Hexane/iPrOH 90:10, Flow rate: 1 mL/min, UV 214 nm,  $t_R = 17.11$  min. Chromatogram was compared to previously reported literature.<sup>2</sup> In addition, no racemization was observed for this compound.



## 7. Data of the reused catalyst after six consecutive runs



**Figure S2:** SEM (left) and TEM (right) images of reused  $\text{Fe}(\text{OH})_3@ \text{Fe}_3\text{O}_4$  catalyst after being reused six times



**Figure S3:** XRD pattern of the  $\text{Fe}(\text{OH})_3@ \text{Fe}_3\text{O}_4$  before using (B) and after being reused six times (A).

1. Niu, F.; Zhang, L.; Luo, S.-Z.; Song, W.-G. Room temperature aldol reactions using magnetic  $\text{Fe}_3\text{O}_4@ \text{Fe}(\text{OH})_3$  composite microspheres in hydrogen bond catalysis. *Chem. Commun.* **2010**, *46*, 1109-1111.
2. Bantreil, X.; Fleith, C.; Martinez, J.; Lamaty, F. Copper-Catalyzed Direct Synthesis of Benzamides from Alcohols and Amines. *ChemCatChem* **2012**, *4*, 1922-1925.