

## Electronic Supplementary Information

# Green synthesis of primary, secondary, and tertiary amides through oxidative amidation of methyl groups with amine hydrochlorides over recyclable $\text{CoFe}_2\text{O}_4$ NPs

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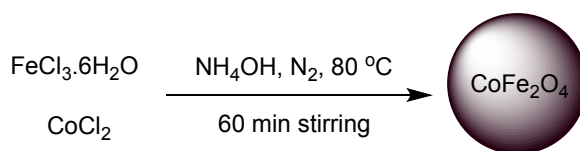
## 1. General

All chemical reagents used in our experiments were purchased from Merck or Aldrich Chemical Company with high purity. All solvents were distilled, dried and purified using standard procedures. Melting points were measured on an Electrothermal 9100 apparatus.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance (DPX 500 MHz and DPX 125 MHz) in pure deuterated  $\text{CDCl}_3$  solvent using tetramethylsilane (TMS) as an internal reference. Fourier transform infrared (FT-IR) spectra were recorded using KBr pellets on a Nicolet IR-100 infrared spectrometer. The powder X-ray diffraction spectrum was recorded at room temperature using a Philips X-Pert 1710 diffractometer. The latter appeared with  $\text{Co K}\alpha$  ( $\alpha=1.79285 \text{ \AA}$ ) voltage: 40 kV, current: 40 mA and was in the range of  $20^\circ\text{--}80^\circ$  ( $2\theta$ ) with a scan speed of  $0.02^\circ/\text{s}$ . The particle morphology was examined by scanning electron microscopy using SEM (HITACHI S-4160) on gold coated samples. Magnetic properties were obtained by a vibrating magnetometer/Alternating Gradient Force Magnetometer (VSM/AGFM, MDK Co., Iran).

## 2. Experimental Section

### 2.1 Preparation of magnetic $\text{CoFe}_2\text{O}_4$ nanoparticles (MNPs)

Magnetic  $\text{CoFe}_2\text{O}_4$  nanoparticles were prepared by chemical co-precipitation chlorine salt of  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  ions with a molar ratio of 2:1. Typically,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (5.8g, 0.02mol) and  $\text{CoCl}_2$  (1.3g, 0.01mol) were dissolved in 100 mL deionized water at  $80^\circ\text{C}$  under  $\text{N}_2$  atmosphere and vigorous stirring. Then, 10 mL of 25%  $\text{NH}_4\text{OH}$  was quickly injected into the reaction mixture in one portion. The addition of the base to the  $\text{Co}^{2+}/\text{Fe}^{3+}$  salt solution results in immediate formation of a black precipitate of MNPs. The reaction was continued for another 60 min and the mixture was cooled to room temperature. The black precipitate was washed with doubly warm distilled water (Scheme 4).

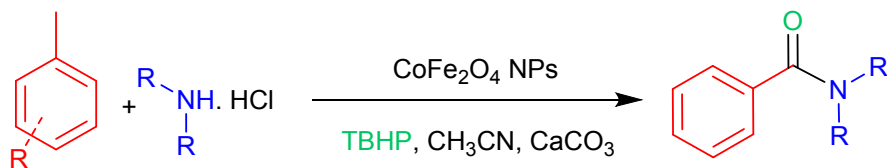


Preparation of magnetic  $\text{CoFe}_2\text{O}_4$  nanocatalyst.

### 2.2 General procedure for direct amidation of methylarenes with amine hydrochloride salts

A mixture was made that consisted of catalyst (20 mg), an amine hydrochloride salt (1.5 mmol),  $\text{CaCO}_3$  (3 equiv.), methylarenes (1 mmol), and *t*-BuOOH (70 wt% in  $\text{H}_2\text{O}$ , 6 equiv.), in  $\text{CH}_3\text{CN}$  (2 mL), under an argon atmosphere for appropriate time at  $80^\circ\text{C}$ . After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with EtOAc. The catalyst was separated using an external magnet, washed several times with EtOAc and dried under vacuum at room temperature to be ready for a later run. The mixture was extracted with EtOAc, then the combined organic phases were dried over anhydrous  $\text{MgSO}_4$  and the solvent was

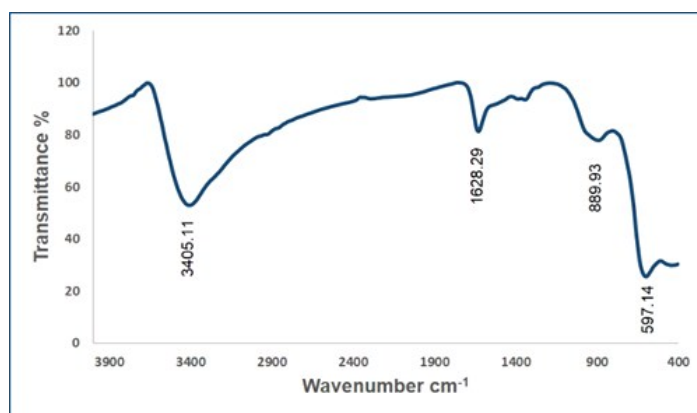
evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to provide the desired amides.



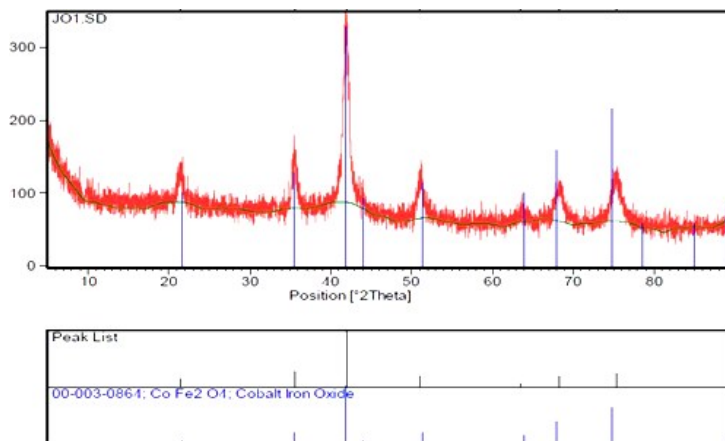
Oxidative amidation of methylenes catalysed by CoFe<sub>2</sub>O<sub>4</sub> NPs.

### 3. Catalyst Characterization

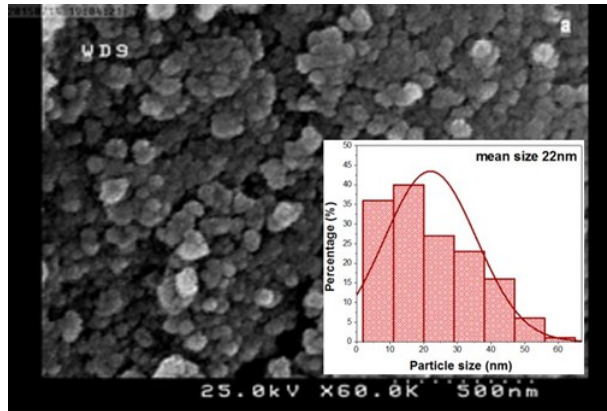
Characterization of CoFe<sub>2</sub>O<sub>4</sub> NPs is done via fourier transform infrared (FT-IR), vibrating sample magnetometry (VSM), Energy-dispersive spectrum (EDS), scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), and X-ray diffraction (XRD) analyses.



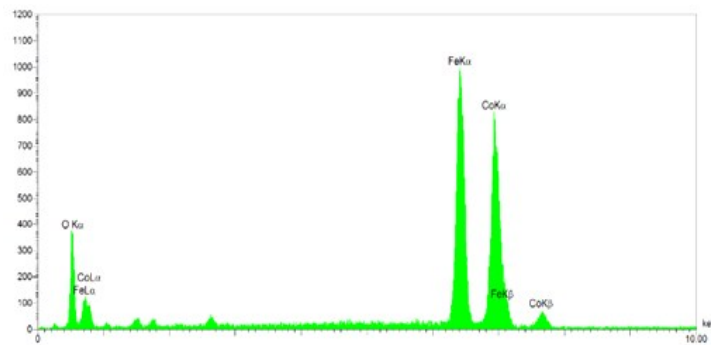
FT-IR Spectrum of CoFe<sub>2</sub>O<sub>4</sub> NPs.



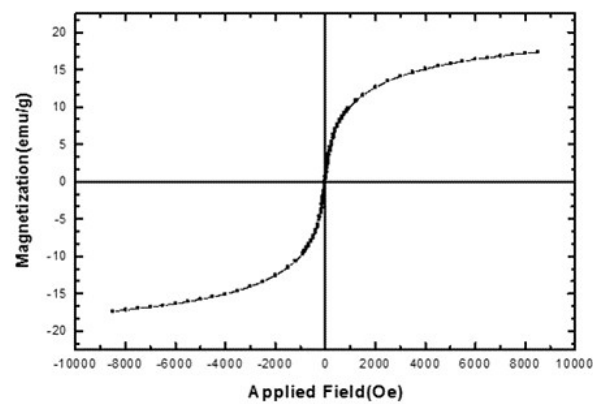
XRD Pattern of the catalyst CoFe<sub>2</sub>O<sub>4</sub> NPs.



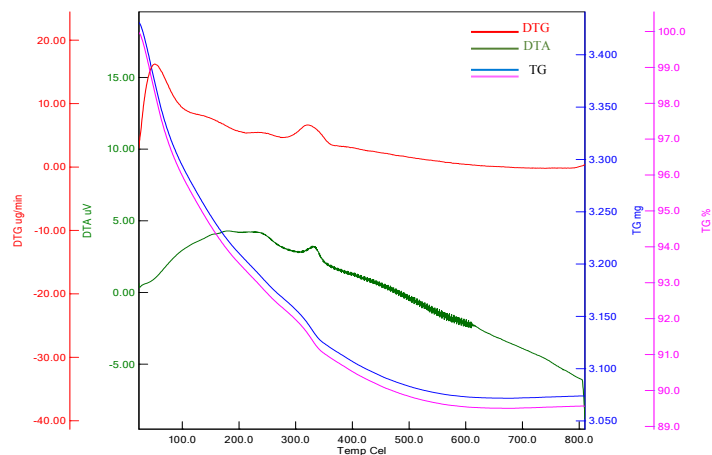
SEM analysis of the catalyst CoFe<sub>2</sub>O<sub>4</sub> NPs



Energy-dispersive spectrum (EDS) of CoFe<sub>2</sub>O<sub>4</sub> NPs.



Vibrating sample magnetometer (VSM) curve for CoFe<sub>2</sub>O<sub>4</sub> NPs.



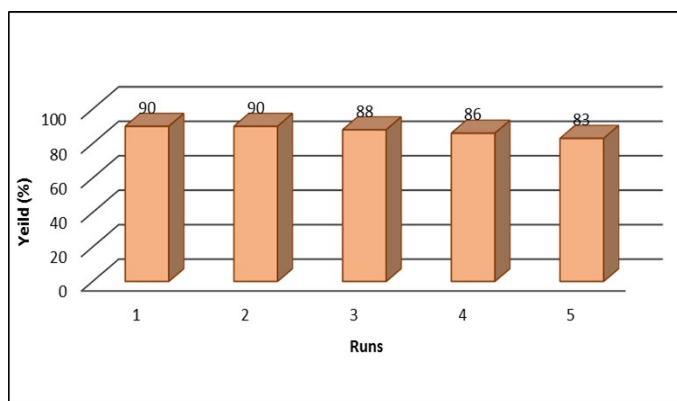
TGA/DTA/DTG analysis of  $\text{CoFe}_2\text{O}_4$  NPs.

#### 4. Recyclability of the catalyst

Reusability of the catalyst is evaluated under the reaction conditions described above for the model reaction. After completion of the reaction, the catalyst is easily recovered by applying a strong external permanent magnet, followed by washing with ethanol to remove the residual product(s). Then the recovered catalyst is dried under vacuum, and reused directly for the next cycle without further treatment. The catalyst is used over five runs, and no obvious loss in the catalytic activity is observed.

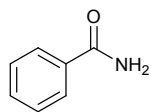


Separation of the catalyst from the reaction mixture by an external magnet.

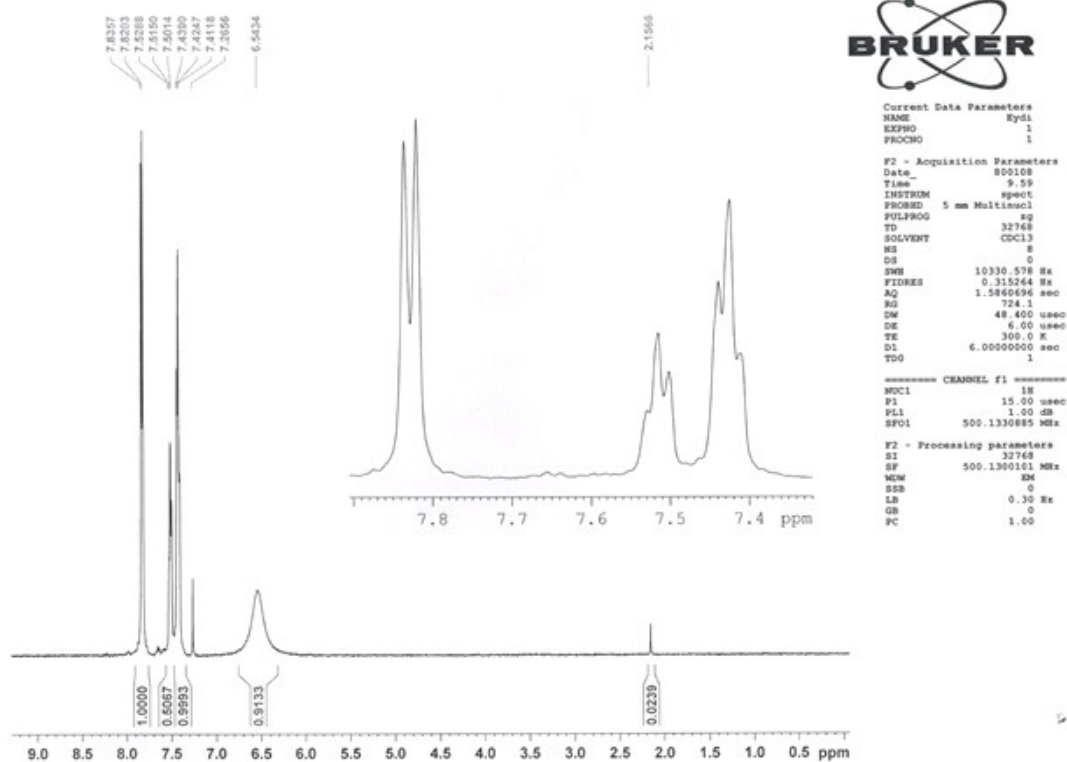


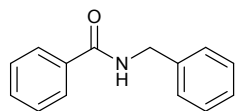
Reusability of  $\text{CoFe}_2\text{O}_4$  nanoparticles in synthesis of amides.

## 5. Characterization of the corresponding amides

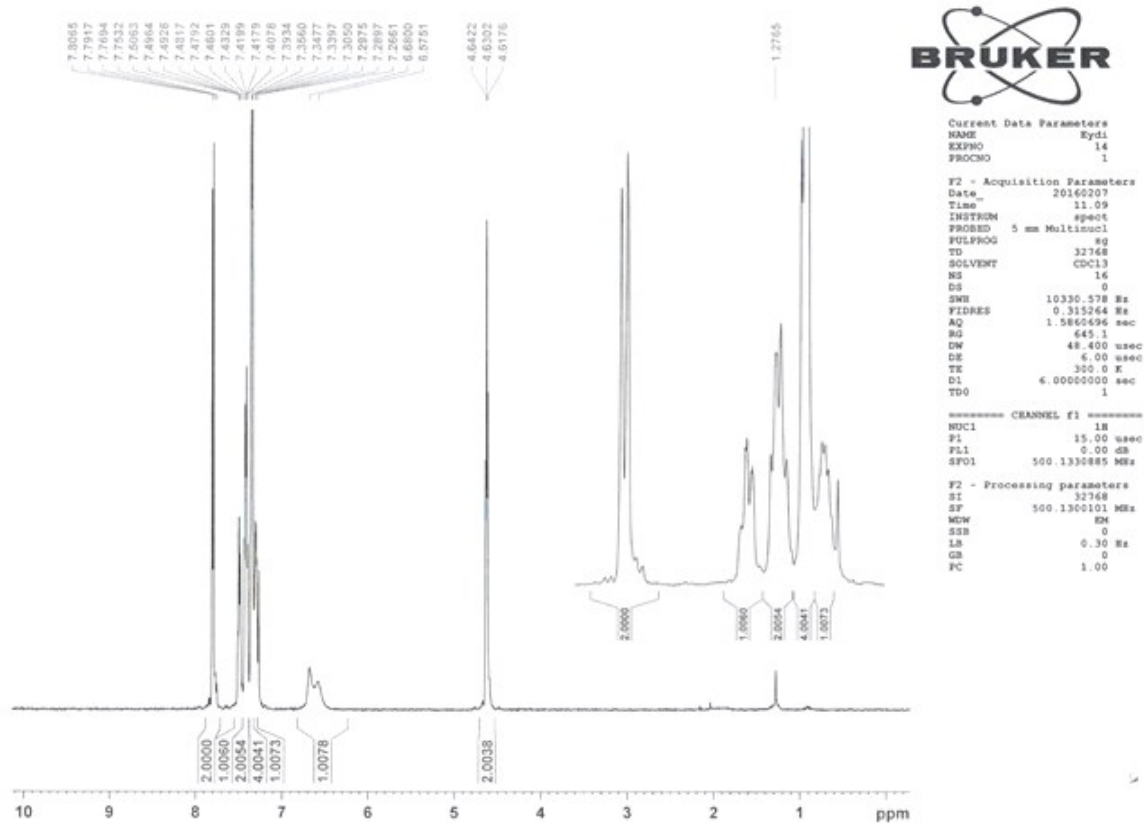


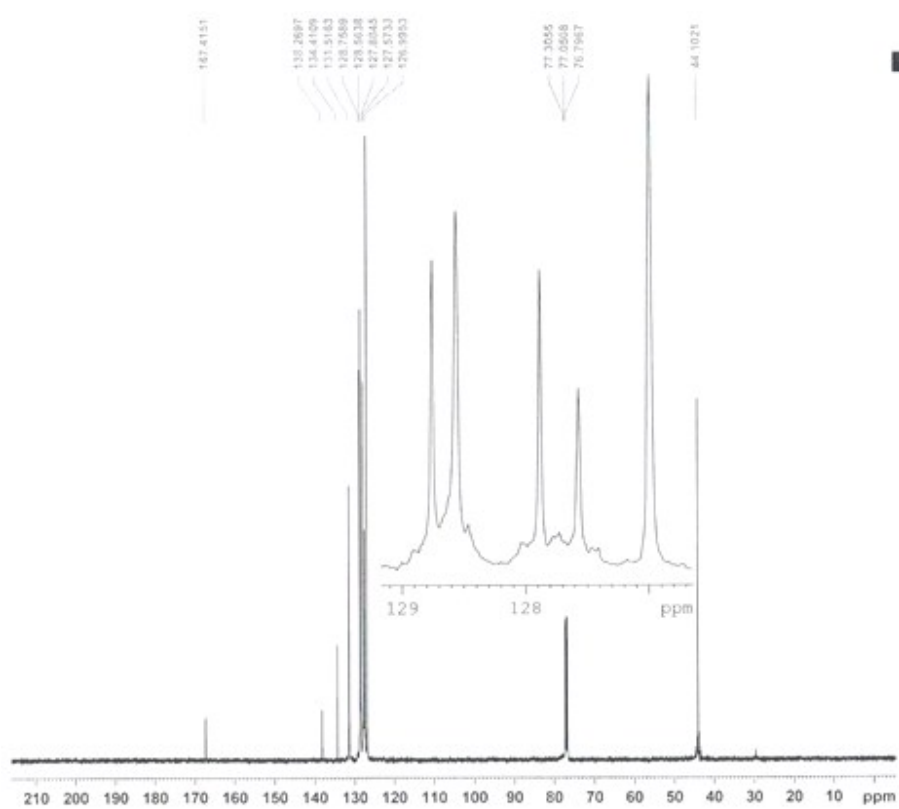
benzamide: Isolated yield = 78%;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.80-7.75 (m, 2H), 7.50- 7.27 (m, 8H), 6.6 (br s, 1H), 4.63 (m, 2H); FT-IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3371, 3175, 1659, 1399, 1121.





N-benzylbenzamide: Isolated yield = 90%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.80-7.75 (m, 2H), 7.50-7.27 (m, 8H), 6.6 (br s, 1H), 4.63 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 167.4, 138.3, 134.4, 131.5, 128.8, 128.6, 127.9, 127.6, 127.0, 44.1; FT-IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3288, 3064, 2922, 1639, 1549, 1488, 1317, 1259.





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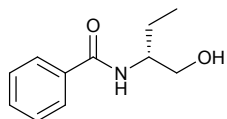
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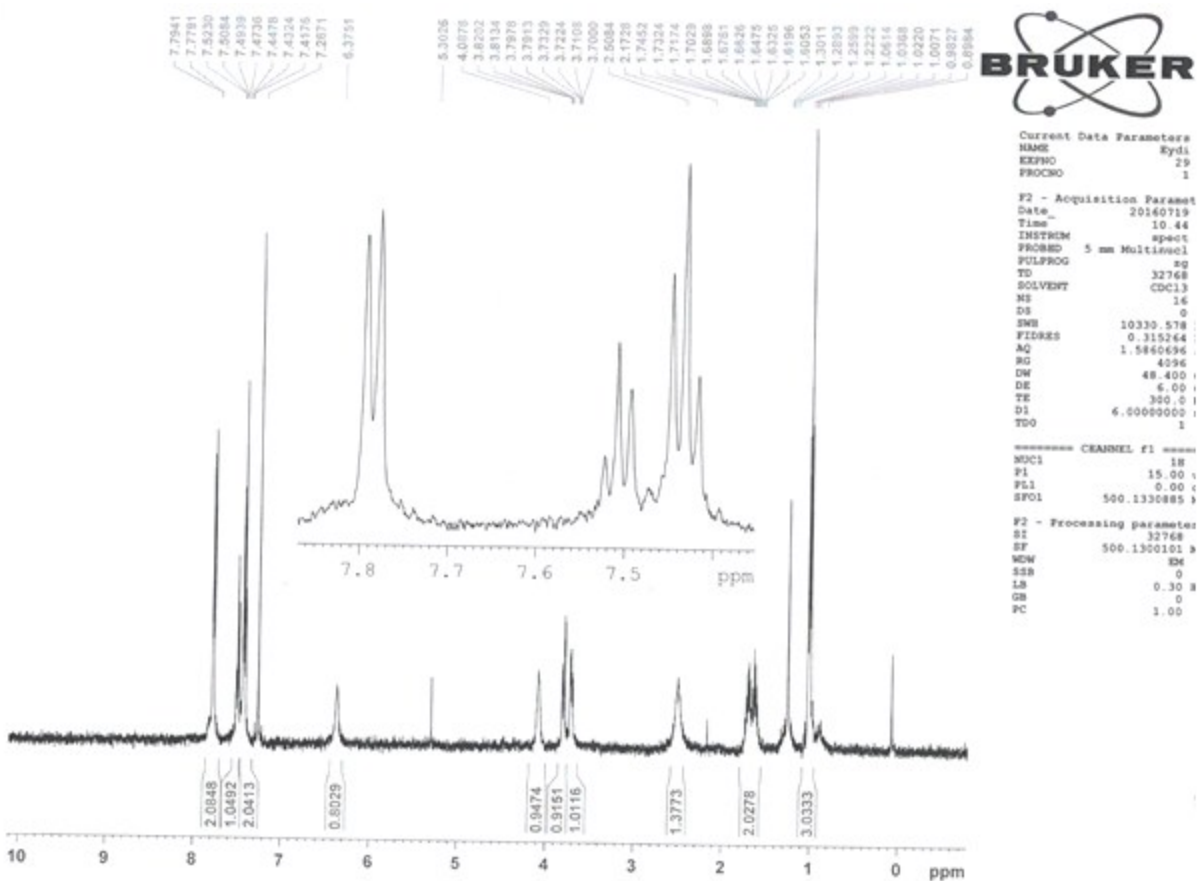
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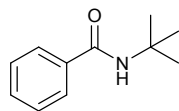
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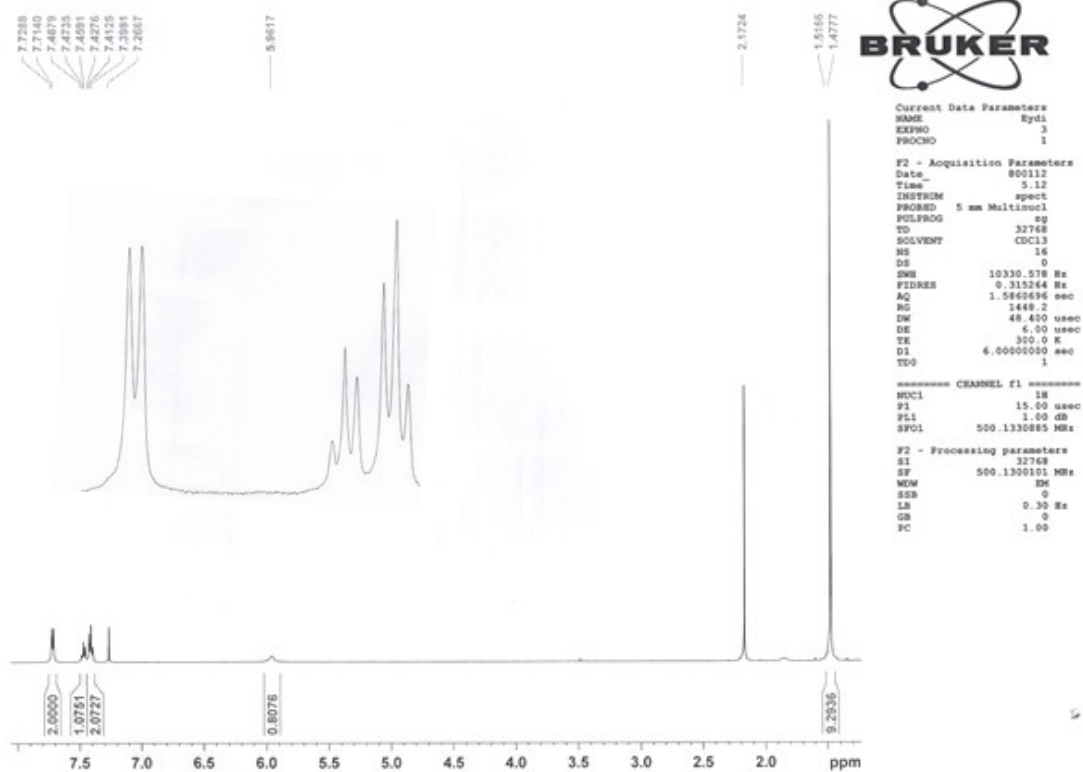


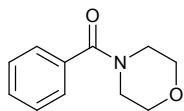
(*R*)-*N*-(1-hydroxybutan-2-yl)benzamide: Isolated yield = 73%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.9 (d, 2H), 7.51 (t, 1H), 7.43 (t, 2H), 6.37 (s, 1H), 4.08 (br s, 1H), 3.82-3.79 (m, 1H), 3.73-3.70 (dd, 1H), 2.51 (br s, 1H), 1.74-1.60 (m, 2H), 1.02 (t, 3H).; IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3301, 3067, 2958, 2930, 2868, 1636, 1539, 1454, 1048.



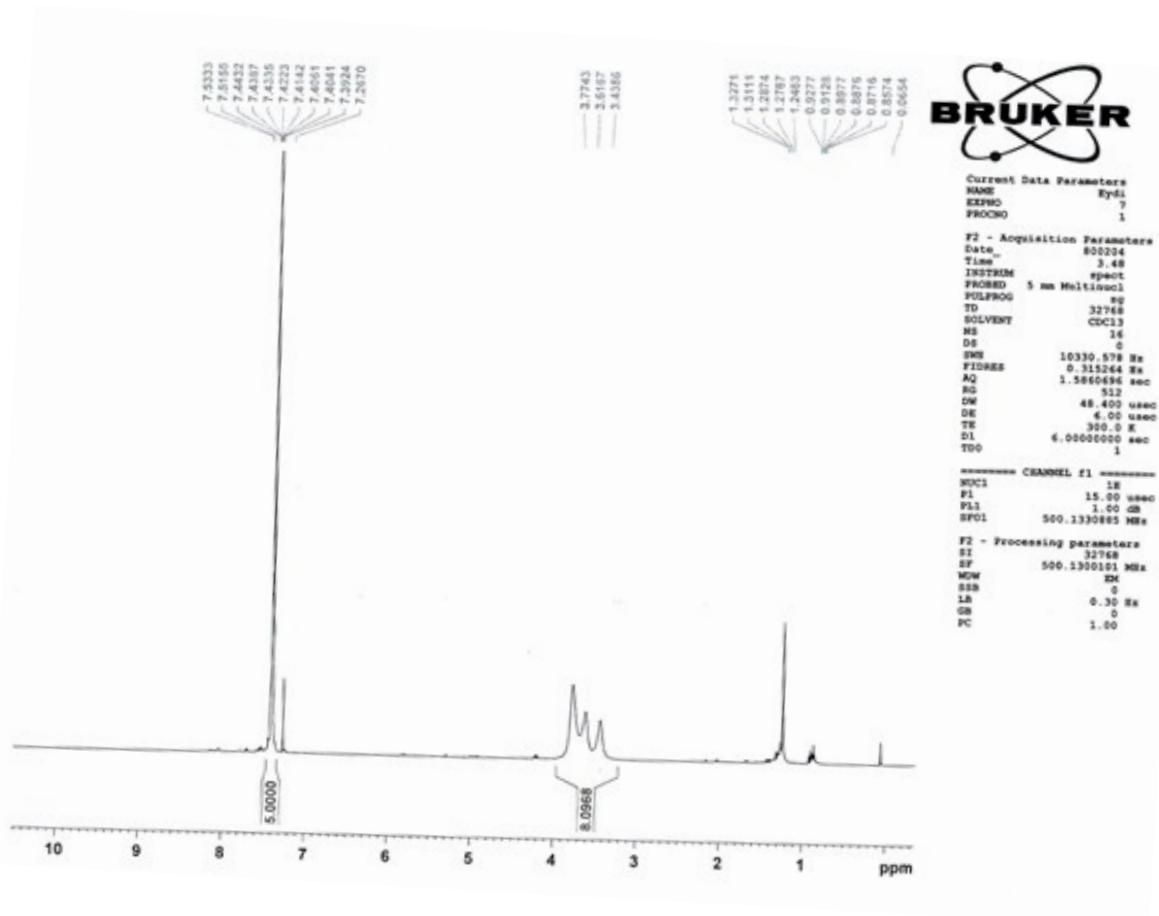


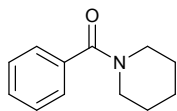
*N*-(*tert*-butyl)benzamide: Isolated yield = 64%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.73-7.71 (d, 2H), 7.50- 7.40 (m, 3H), 5.96 (br s, 1H), 1.48 (s, 9H).; IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3323, 3061, 2970, 1638, 1537, 1450, 1310, 1219.



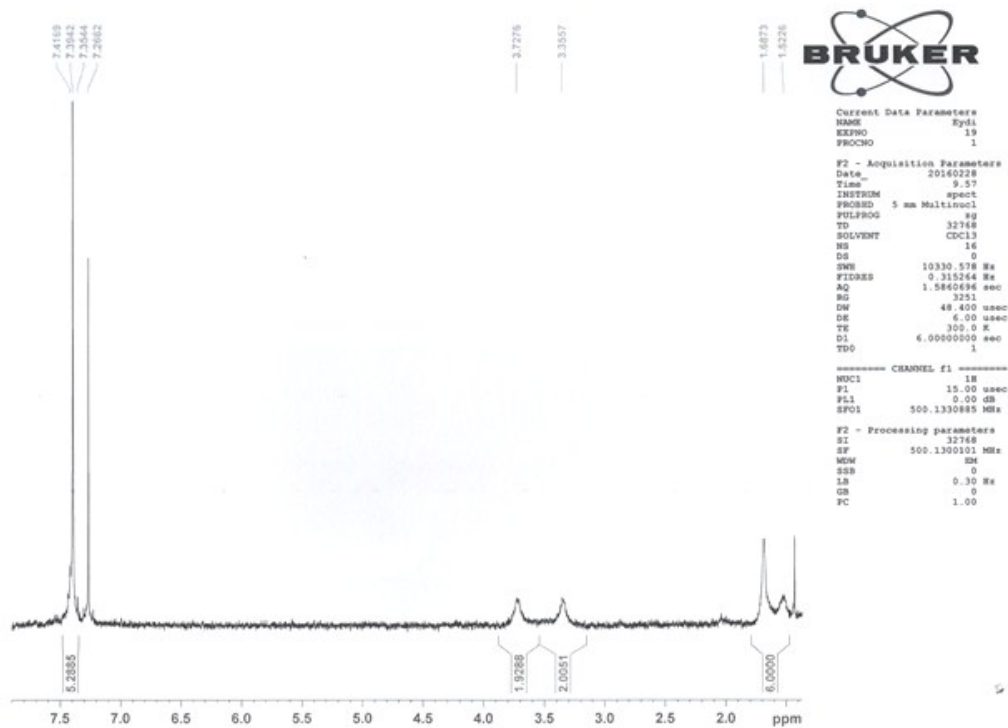


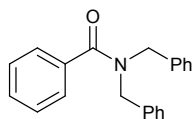
morpholino(phenyl)methanone: Isolated yield = 80%;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.42 (m, 5H), 3.78-3.44 (m, 8H).; IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) = 3060, 2915, 2856, 1633, 1433, 1268.



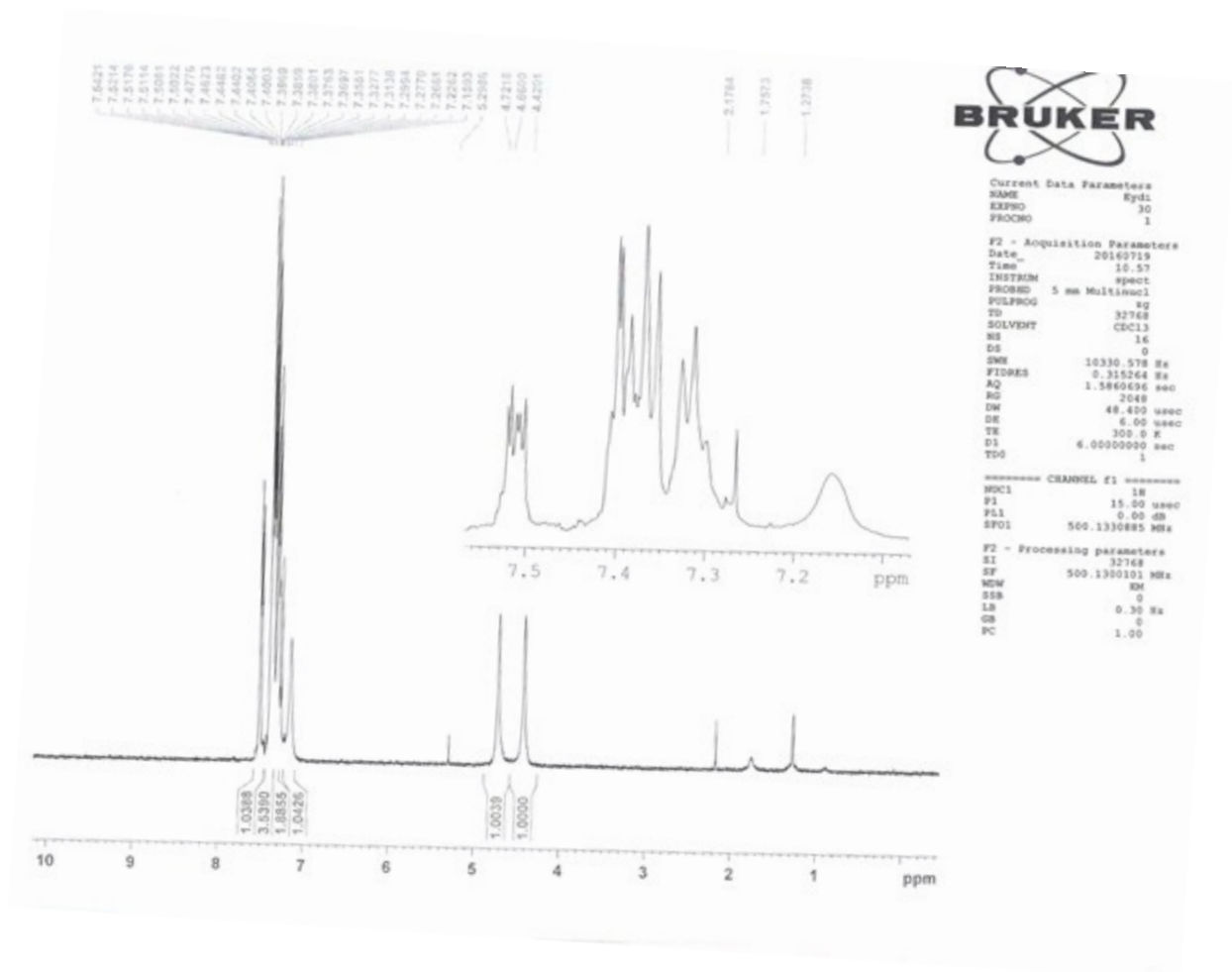


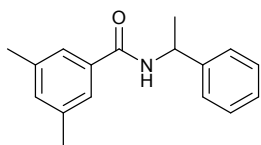
Phenyl(piperidin-1-yl)methanone: Isolated yield = 78%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.39 (m, 5H), 3.72 (m, 2H), 3.35 (m, 2H), 1.68-1.52 (m, 6H); FT-IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) = 3058, 2923, 2860, 1630, 1437, 1263.



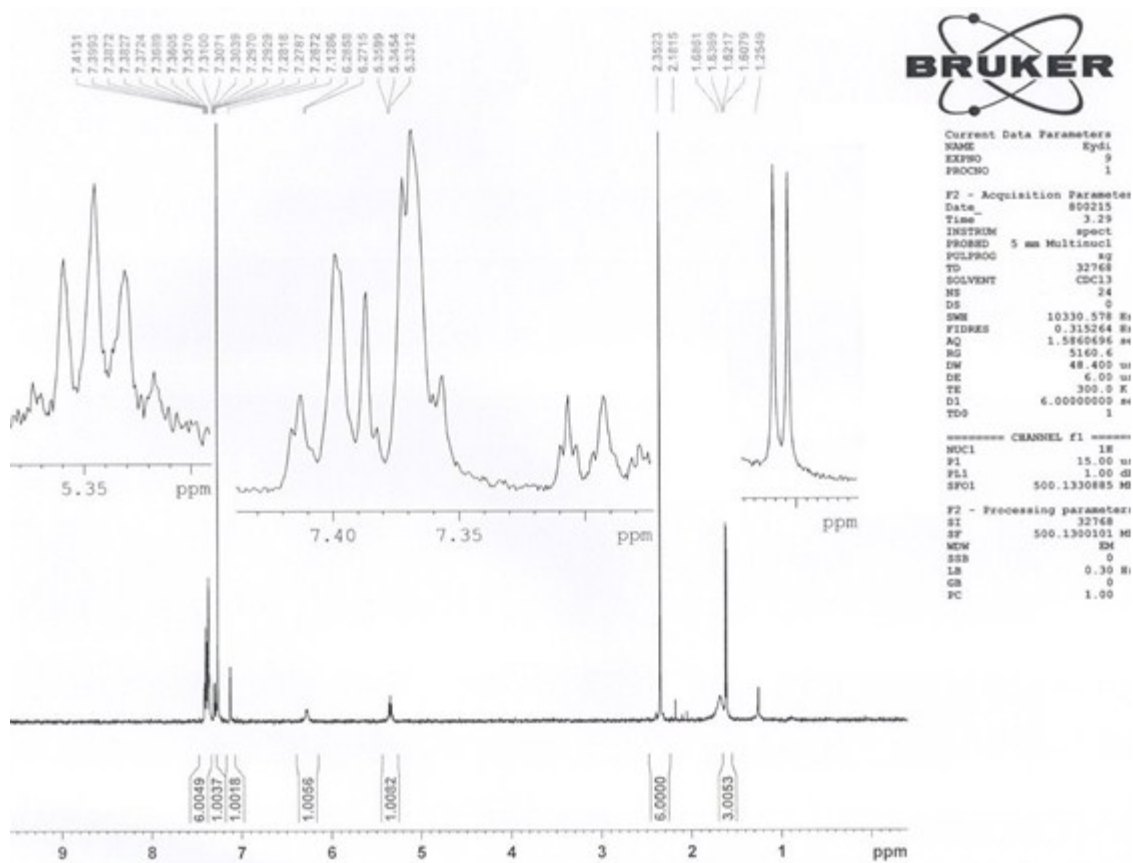


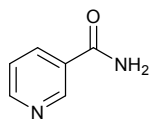
*N,N*-dibenzylbenzamide: Isolated yield = 71%;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.54–7.16 (m, 15H), 4.72 (s, 2H), 4.42 (s, 2H); IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3062, 2928, 1625, 1431, 1254.



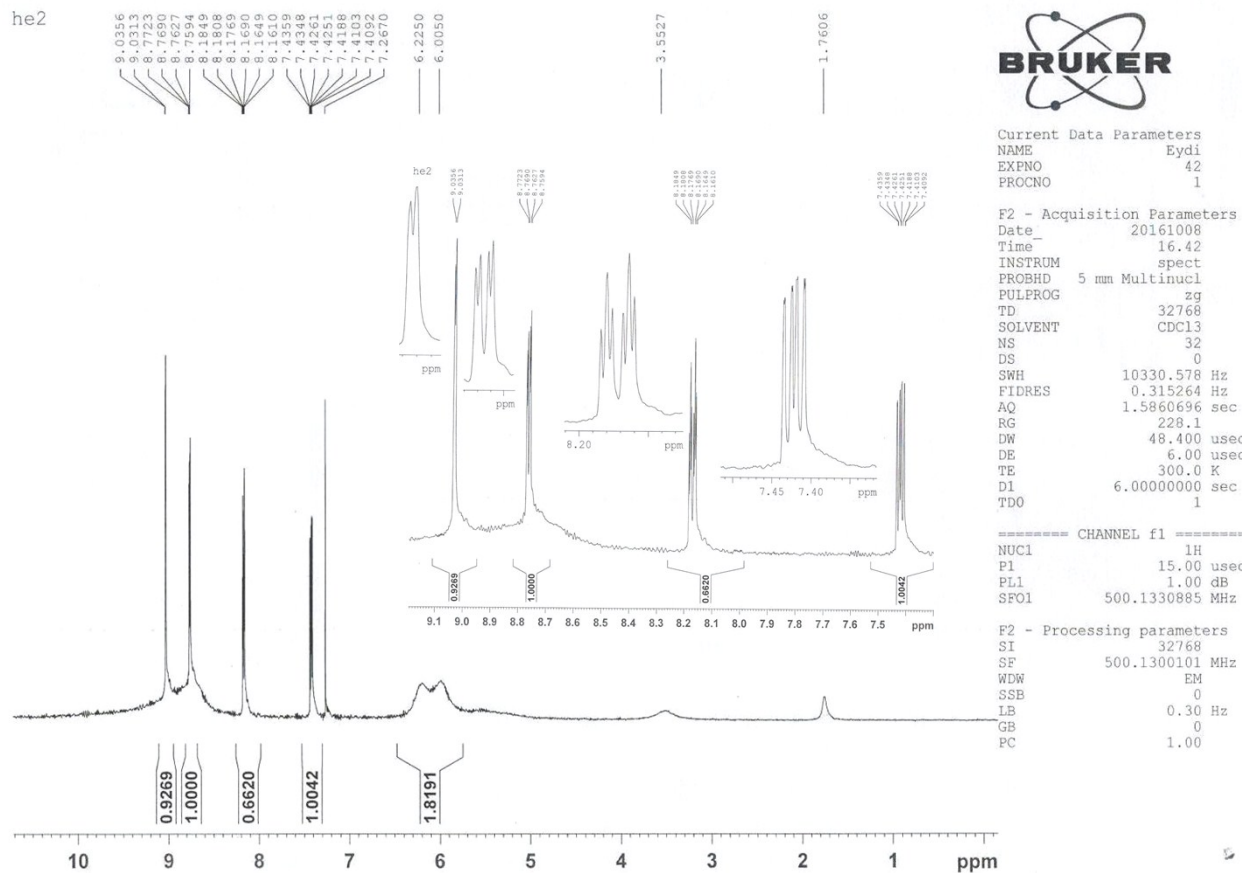


3,5-dimethyl-*N*-(1-phenylethyl)benzamide: Isolated yield = 68%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 7.41–7.13 (m, 8H), 6.28 (d, 1H), 5.35 (quintet, 1H), 2.35 (s, 6H), 1.63 (d, 3H); IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3343, 2927, 1637, 1521, 1251.

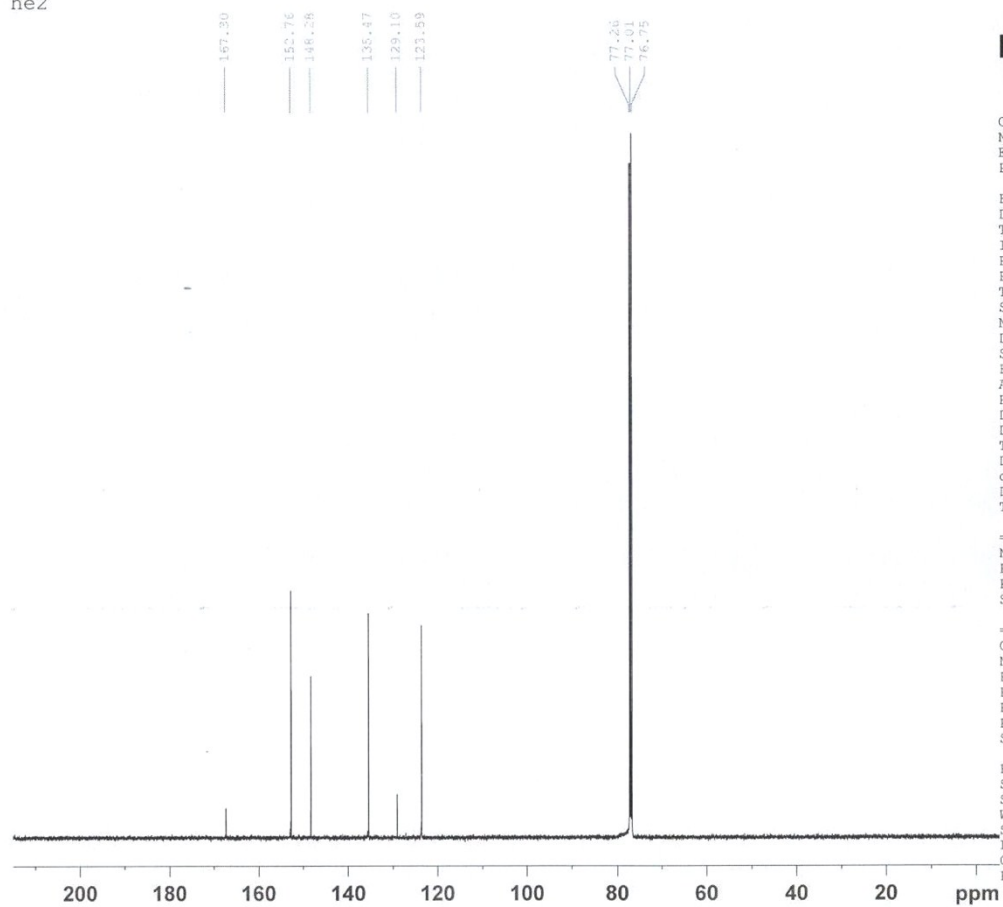




nicotinamide: Isolated yield = 53%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 9.03 (d, 1H), 8.77 (m, 1H), 8.17 (m, 1H), 7.43 (m, 1H), 6.00-6.22 (br, 2H,  $\text{NH}_2$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 167.3, 152.8, 148.3, 135.5, 129.1, 123.6; FT-IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3363, 3158, 2778, 1683, 1615, 1480, 1396.



he2



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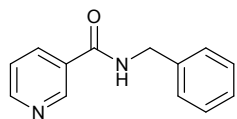
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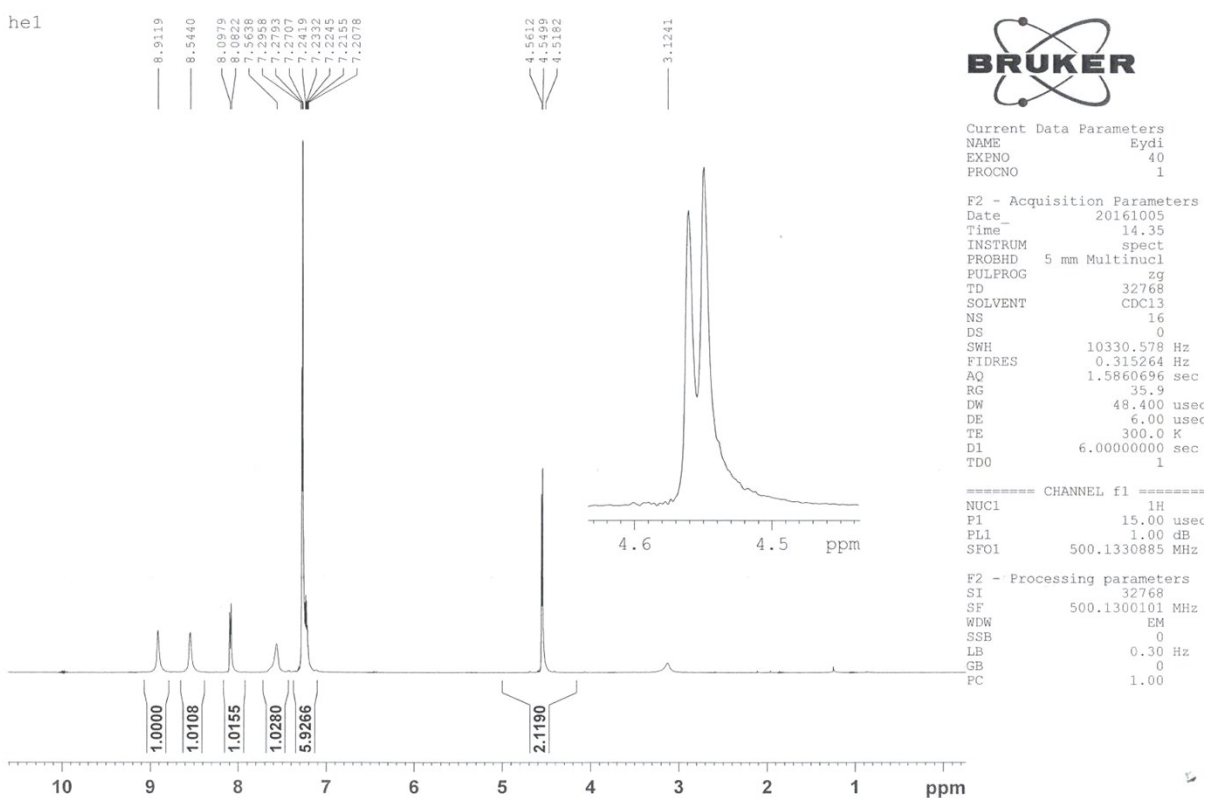
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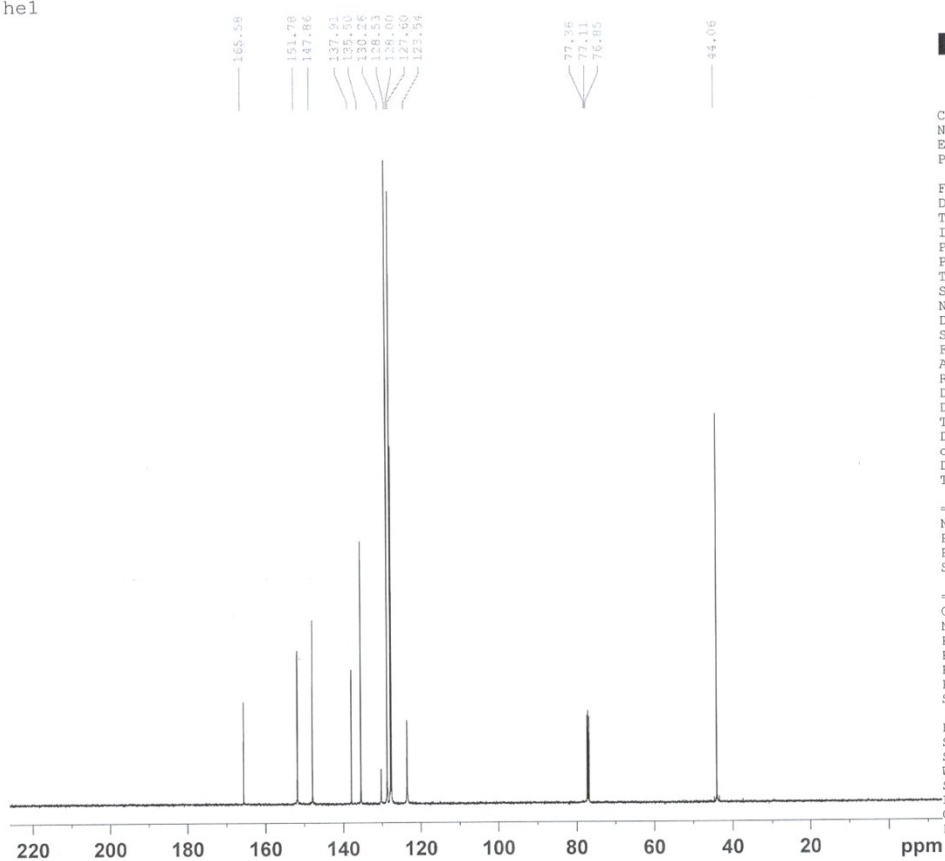




N-benzylnicotinamide: Isolated yield = 55%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 8.91 (s, 1H), 8.54 (d, 1H), 8.09 (d, 1H), 7.56 (br s, 1H, NH), 7.29-7.20 (m, 6H), 4.55 (d, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 165.6, 151.8, 147.9, 137.9, 135.5, 130.3, 128.5, 128.0, 127.6, 123.5, 44.1; FT-IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3297, 3037, 2929, 1635, 1547, 1420, 1304, 1231.



hel



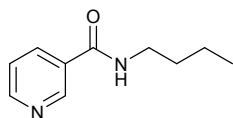
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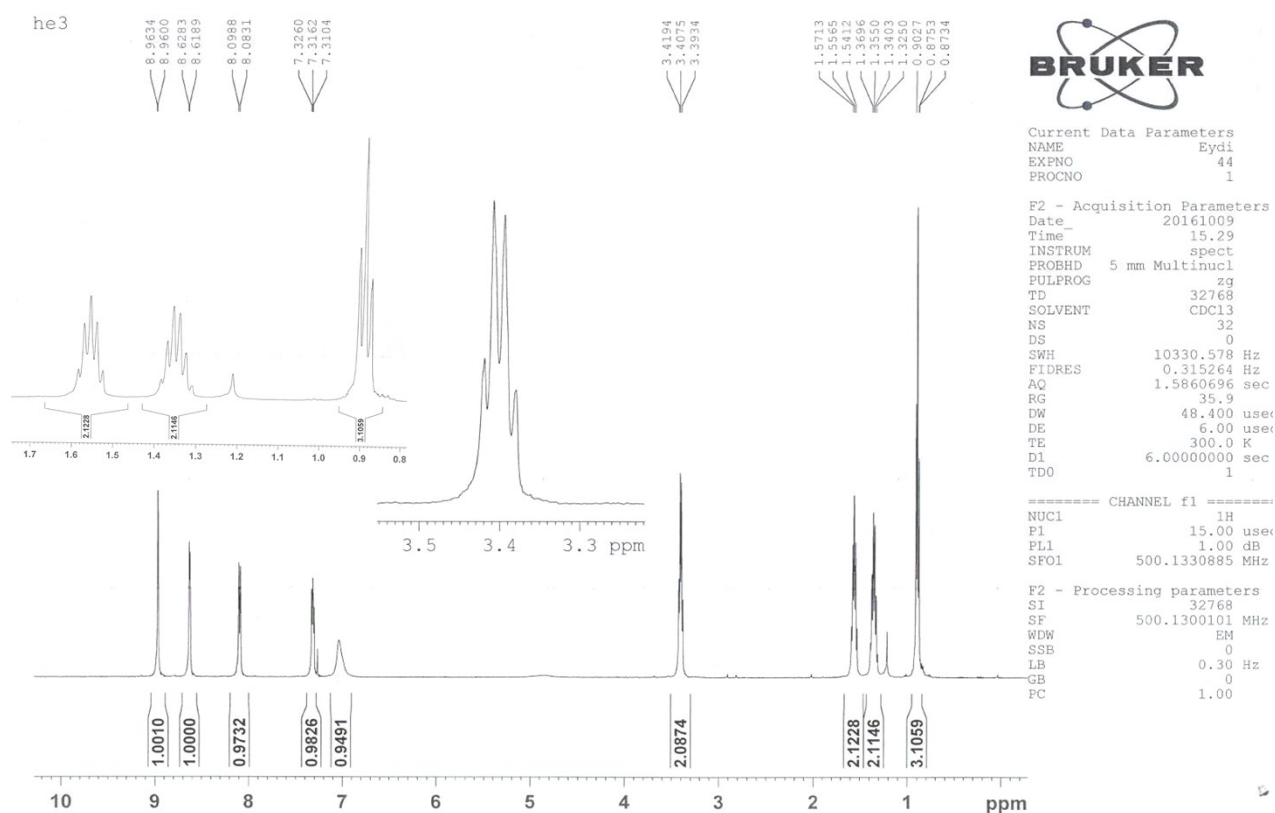
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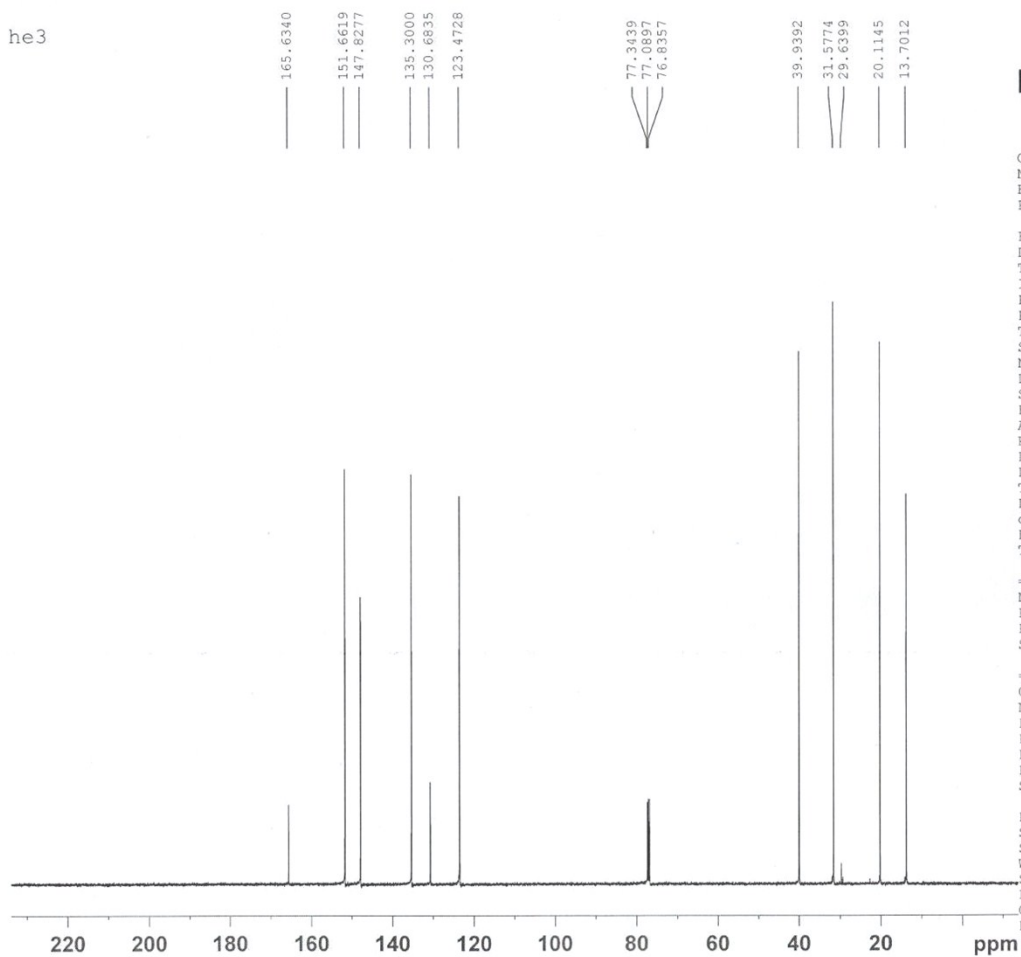
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N-butylnicotinamide: Isolated yield = 46%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (ppm) = 8.96 (s, 1H), 8.62 (d, 1H), 8.09 (d, 1H), 7.31 (m, 1H), 7.05 (br s, 1H, NH), 3.40 (q, 2H), 1.56 (quintet, 2H), 1.35 (sextet, 2H), 0.87 (t, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  (ppm) = 165.6, 151.7, 147.8, 135.3, 130.7, 123.5, 39.9, 31.6, 20.1, 13.7; FT-IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3300, 3067, 2953, 1646, 1545, 1468, 1310.



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