

# Direct, rapid, solvent-free conversion of unactivated esters to amides using lithium hydroxide as a catalyst

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### Key to Abbreviated Terms:

CDCl<sub>3</sub>: deuterated chloroform  
DCM: dichloromethane  
EtOAc: ethyl acetate  
Hex: hexanes

## General Considerations:

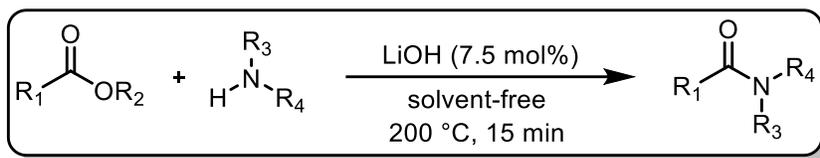
### General:

Reactions were performed using a CEM Discover microwave unit. NMR Spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ ) were performed at 298 K on either a Bruker Avance Ultra Shield 300 MHz NMR, Bruker DRX-400 400 MHz NMR, or Bruker Avance 500 MHz NMR.  $^1\text{H}$ -NMR Spectra obtained in  $\text{CDCl}_3$  were referenced to residual non-deuterated chloroform (7.26 ppm) in the deuterated solvent.  $^{13}\text{C}$ - NMR Spectra obtained in  $\text{CDCl}_3$  were referenced to chloroform (77.3 ppm). Flash chromatography and silica plugs utilized Dynamic Adsorbents Inc. Flash Silica Gel (60Å porosity, 32-63  $\mu\text{m}$ ).

### Chemicals:

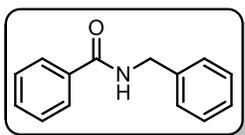
Deuterated chloroform was purchased from Cambridge Isotope Laboratories and stored over 4Å molecular sieves. Ethyl benzoate, benzylamine, pyrrolidine, and cyclohexylamine were purchased from Sigma-Aldrich. Lithium hydroxide and 1,2,3,4-tetrahydroisoquinoline were purchased from Acros Organic. Ethyl-*p*-nitrobenzoate, ethyl-4-bromobenzoate, *n*-octylamine, and  $\delta$ -valerolactone were purchased from Alfa Aesar. Aniline was purchased from Fisher Scientific. Ethyl-4-(trifluoromethyl)benzoate and 4-methoxybenzylamine were purchased from Oakwood Chemicals. Ethyl hexanoate and benzyl benzoate were purchased from Chem Service.

## Synthesis of Amides



### TYPICAL PROCEDURE

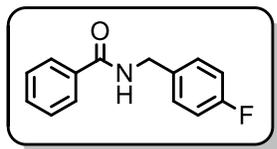
#### *N*-Benzylbenzamide (3a)



To a 10-mL capacity glass microwave tube equipped with a stir bar was added ethyl benzoate (0.75 g, 5 mmol, 1 equiv), benzylamine (0.80 g, 7.5 mmol, 1.5 equiv), and lithium hydroxide (0.009 g, 0.375 mmol, 0.075 equiv). The tube was sealed with a septum and placed into the microwave cavity. The reaction mixture was heating to 200 °C using an initial microwave power of 200 W and setting a pressure cut-off of 250 psi for safety purposes. Once at temperature, the contents of the tube were maintained at 200 °C for 30 min. After completion of the heating time, the reaction vessel was cooled to 50 °C before removing from the microwave unit. Product conversion was then determined by <sup>1</sup>H NMR. To isolate the product, the contents of the tube were triturated with hexanes, filtered through a fritted funnel, and washed with more hexanes. The solid precipitate was dissolved in EtOAc and filtered through a pad of Celite. The ethyl acetate was removed *in vacuo* by rotary evaporation to afford the pure amide product, *N*-benzyl benzamide as a white solid (0.823 g, 78%).<sup>1-6</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 4.56 (d, *J*=5.84 Hz, 2 H) 7.26 - 7.32 (m, 5 H) 7.35 (t, *J*=7.59 Hz, 2 H) 7.46 (t, *J*=1.00 Hz, 1 H) 7.81 (d, *J*=7.79 Hz, 2 H)

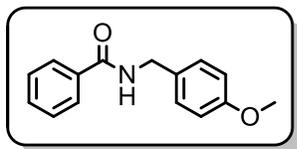
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ ppm 44.01 (CH<sub>2</sub>) 127.24 (CH) 127.45 (CH) 127.82 (CH) 128.56 (CH) 128.72 (CH) 131.52 (CH) 134.48 (C) 138.56 (C) 167.73 (C)



*N*-(4-Fluorobenzyl) benzamide (**3b**) (0.915 g, 80%) was prepared from 4-fluorobenzylamine and ethyl benzoate using the typical procedure. The crude compound was filtered through a silica plug with a gradient of 9:1 Hex: EtOAc then 1:1 Hex: EtOAc basified with 10% triethylamine as the eluent to afford the product as a brown solid.<sup>5</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 4.56 (d, *J*=5.76 Hz, 2 H) 6.77 (br. s., 1 H) 6.99 (tt, *J*=1.00 Hz, 2 H) 7.26 - 7.33 (m, 2 H) 7.35 - 7.44 (m, 2 H) 7.49 (tt, *J*=1.00 Hz, 1 H) 7.74 - 7.82 (m, 2 H)

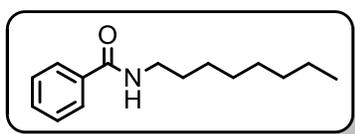
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ ppm 43.55 (CH<sub>2</sub>) 115.61 - 115.96 (d, *J*<sub>C-C-F</sub>=1.00 Hz, CH) 127.24 (CH) 128.82 (CH) 129.74 (d, *J*<sub>C-C-F</sub>=8.09 Hz, CH) 131.85 (CH) 134.36 (d, *J*<sub>C-C-C-F</sub>=8.09 Hz, C) 134.49 (C) 161.15 - 163.70 (d, *J*<sub>C-F</sub>=1.00 Hz, C) 167.69 (C)



**N-(4-Methoxybenzyl)-benzamide (3c)** (0.974 g, 81%) was prepared from 4-methoxybenzylamine and ethyl benzoate using the typical procedure. The crude compound was filtered through a silica plug with a gradient of 9:1 Hex: EtOAc then 1:1 Hex: EtOAc basified with 10% triethylamine as the eluent to afford the product as a white solid.<sup>5</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 3.79 (s, 3 H) 4.56 (d, *J*=5.21 Hz, 2 H) 6.75 (br. s., 1 H) 6.87 (d, *J*=8.42 Hz, 2 H) 7.27 (d, *J*=8.27 Hz, 2 H) 7.40 (t, *J*=1.00 Hz, 2 H) 7.49 (t, *J*=1.00 Hz, 1 H) 7.79 (q, *J*=1.00 Hz, 1 H)

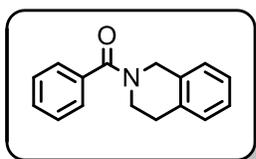
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ ppm 43.71 (CH<sub>2</sub>) 55.41 (CH<sub>3</sub>) 114.26 (2 x CH) 127.17 (CH) 128.67 (CH) 129.39 (CH) 130.53 (C) 131.60 (CH) 134.59 (C) 159.20 (C) 167.55 (C)



**N-Octylbenzamide (3d)** (0.949 g, 81%) was prepared from *n*-octylamine and ethyl benzoate using the typical procedure. The crude compound was filtered through a silica plug with a gradient of 95:5 Hex: EtOAc then 1:1 Hex: EtOAc basified with 1% triethylamine as the eluent to afford the product as a white solid.<sup>7</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 0.79 - 0.94 (m, 3 H) 1.14 - 1.43 (m, 10 H) 1.52 - 1.66 (m, 2 H) 3.36 - 3.48 (m, 2 H) 6.34 (br. s., 1 H) 7.31 - 7.51 (m, 3 H) 7.69 - 7.82 (m, 2 H)

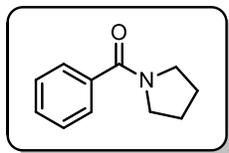
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ ppm 14.22 (CH<sub>3</sub>) 22.78 (CH<sub>2</sub>) 27.19 (CH<sub>2</sub>) 29.37 (CH<sub>2</sub>) 29.46 (CH<sub>2</sub>) 29.81 (CH<sub>2</sub>) 31.94 (CH<sub>2</sub>) 40.31 (CH<sub>2</sub>) 127.13 (CH) 128.52 (CH) 131.29 (CH) 135.03 (C) 167.78 (C)



**2-Benzoyl-1,2,3,4-tetrahydroisoquinoline (3e)** (0.693 g, 58%) was prepared was prepared from 1,2,3,4-tetrahydroisoquinoline and ethyl benzoate using the typical procedure. The crude product was triturated with a 3:1 hex: EtOAc mixture, filtered through a fritted funnel, and washed with more hexanes. The solid precipitate was dissolved in EtOAc and filtered through a pad of Celite. The ethyl acetate was removed *in vacuo* by rotary evaporation to afford the pure amide product to afford 2-benzoyl-1,2,3,4-tetrahydro-isoquinoline as a white solid.<sup>2</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 3.05 (br. s., 2 H) 3.44 (br. s., 2 H) 4.34 (br. s., 2 H) 7.02 - 7.45 (m, 7 H) 7.84 (d, *J*=5.50 Hz, 2 H)

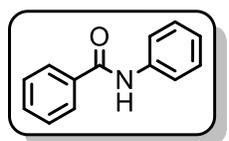
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ ppm 26.23 (CH<sub>2</sub>) 41.51 (CH<sub>2</sub>) 44.75 (CH<sub>2</sub>) 126.96 (CH) 127.63 (CH) 127.96 (CH) 129.23 (CH) 129.48 (CH) 129.91 (CH) 130.85 (C) 132.57 (C) 136.26 (1 C) 173.92 (C)



**N-Benzoylpyrrolidine (3f)** (0.607 g, 70%) was prepared from pyrrolidine and ethyl benzoate using the typical procedure. The crude compound was filtered through a silica plug with a gradient of 9:1 Hex: EtOAc then 1:1 Hex: EtOAc basified with 10% triethylamine as the eluent to afford the product as a brown oil.<sup>2</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 1.72 (q, *J*=1.00 Hz, 2 H) 1.81 (q, *J*=1.00 Hz, 2 H) 3.28 (t, *J*=6.59 Hz, 2 H) 3.51 (t, *J*=6.93 Hz, 2 H) 7.26 - 7.31 (m, 3 H) 7.38 - 7.44 (m, 2 H)

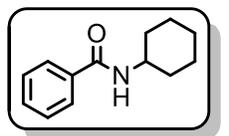
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ ppm 24.31 (CH<sub>2</sub>) 26.26 (CH<sub>2</sub>) 46.01 (CH<sub>2</sub>) 49.43 (CH<sub>2</sub>) 126.94 (CH) 128.09 (CH) 129.60 (C) 137.18 (C)



**Benzoylaminobenzene (3g)** (0.067 g, 7%) was prepared from aniline and ethyl benzoate using the typical procedure. The crude compound was triturated with hexanes, filtered through a fritted funnel, and washed with more hexanes. The solid precipitate was dissolved in EtOAc and filtered through a pad of Celite. The solvent was removed *in vacuo* by rotary evaporation to afford the product as a white solid.<sup>7</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 7.11 - 7.20 (m, 1 H) 7.38 (t, *J*=7.90 Hz, 2 H) 7.45 - 7.60 (m, 3 H) 7.65 (d, *J*=7.74 Hz, 2 H) 7.82 (br. s., 1 H) 7.84 - 7.92 (m, 2 H)

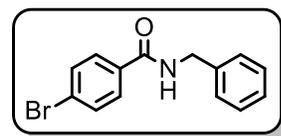
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ ppm 120.51 (CH) 124.84 (CH) 127.30 (CH) 129.05 (CH) 129.36 (CH) 132.10 (CH) 135.29 (C) 138.22 (C) 166.05 (C)



**N-Cyclohexylbenzamide (3h)** (24% by <sup>1</sup>H NMR) was prepared from cyclohexylamine and ethyl benzoate using the typical procedure. The crude compound was triturated with hexanes, filtered through a fritted funnel, and washed with more hexanes. The solid precipitate was dissolved in EtOAc and filtered through a pad of Celite. The solvent was removed *in vacuo* by rotary evaporation to afford the product as a tan solid.<sup>7</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 1.14 - 1.31 (m, 3 H) 1.36 - 1.50 (m, 2 H) 1.65 (dt, *J*=12.94, 3.80 Hz, 1 H) 1.75 (dt, *J*=13.66, 3.73 Hz, 2 H) 1.99 - 2.09 (m, 2 H) 3.91 - 4.04 (m, 1 H) 5.97 (br. s., 1 H) 7.33 - 7.52 (m, 3 H) 7.69 - 7.79 (m, 2 H)

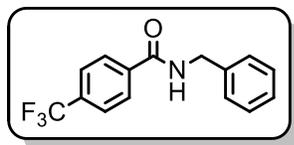
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ ppm 25.01 - 25.32 (CH<sub>2</sub>) 25.79 (CH<sub>2</sub>) 33.42 (CH<sub>2</sub>) 48.92 (CH) 127.09 (CH) 128.68 (CH) 131.40 (CH) 135.34 (C) 166.87 (C)



**N-Benzyl-4-bromobenzamide (3j)** (0.906 g, 62%) was prepared from benzylamine and ethyl-4-bromobenzoate using the typical procedure. The crude compound was filtered through a silica plug with a gradient of 9:1 then 6:4 Hex: EtOAc as the eluent to afford the product as a white solid.<sup>5</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 4.60 (d, *J*=5.35 Hz, 2 H) 6.59 (br. s., 1 H) 7.29 - 7.40 (m, 5 H) 7.53 (d, *J*=8.08 Hz, 2 H) 7.65 (d, *J*=8.08 Hz, 2 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ ppm 44.46 (CH<sub>2</sub>) 127.96 (C) 128.17 (CH) 128.89 (CH) 129.07 (CH) 132.05 (CH) 133.45 (C) 138.21 (C) 166.70 (C)

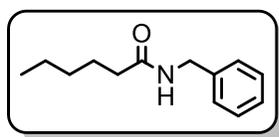


**N-benzyl-4-(trifluoromethyl) benzamide (3k)** (1.082 g, 78%) was prepared from benzylamine and ethyl-4-trifluoromethylbenzoate using the typical procedure. The crude compound was triturated with hexanes, filtered through a fritted funnel, and washed with more hexanes. The solid precipitate was dissolved in

EtOAc and filtered through a pad of Celite. The solvent was removed *in vacuo* by rotary evaporation to afford the product as a white solid.<sup>5</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 4.63 (d, *J*=5.69 Hz, 2 H) 6.64 (br. s., 1 H) 7.29 - 7.38 (m, 5 H) 7.66 (d, *J*=8.17 Hz, 2 H) 7.88 (d, *J*=8.08 Hz, 2 H)

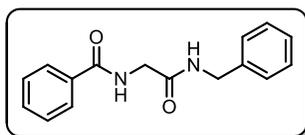
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ ppm 44.58 (CH<sub>2</sub>) 125.91 (q, *J*=3.70 Hz, 1 CF<sub>3</sub>) 127.74 (CH) 128.09 (CH) 128.21 (CH) 129.15 (CH) 133.57 (d, *J*<sub>C-F</sub>=1.00 Hz) 137.91 (C) 138.01 (C) 166.38 (C)



**N-Benzylhexanamide (3l)** (0.593 g, 58%) was prepared from benzylamine and ethyl hexanoate using the typical procedure. The crude compound was filtered through a silica plug with a gradient of 9:1 Hex: EtOAc then 1:1 Hex: EtOAc basified with 1% triethylamine as the eluent to afford the product as a white solid.<sup>6</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 0.89 (t, *J*=6.69 Hz, 3 H) 1.23 - 1.37 (m, 4 H) 1.64 (quin, *J*=7.32 Hz, 2 H) 2.18 (t, *J*=7.61 Hz, 2 H) 4.40 (d, *J*=5.74 Hz, 2 H) 6.11 (br. s., 1 H) 7.24 (br. s., 1 H) 7.26 - 7.28 (m, 1 H) 7.28 - 7.35 (m, 2 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ ppm 14.14 (CH<sub>3</sub>) 22.60 (CH<sub>2</sub>) 25.67 (CH<sub>2</sub>) 31.69 (CH<sub>2</sub>) 36.89 (CH<sub>2</sub>) 43.69 (CH<sub>2</sub>) 127.59 (CH) 127.95 (CH) 128.84 (CH) 138.74 (C) 173.33 (C)



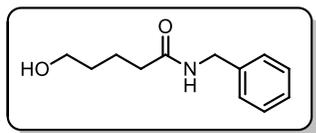
**N-(2-(benzylamino)-2-oxoethyl)benzamide (3o)** (0.450 g, 76%) was prepared from the benzyl ester of benzoyl glycine and benzylamine using the typical procedure, but with modified conditions of 90 °C with 50 W for 30 min. The crude compound was triturated with chilled hexanes, filtered through a fritted funnel, and washed with more chilled

hexanes. The solid precipitate was dissolved in DCM and filtered through a pad of Celite. The solvent was removed *in vacuo* by rotary evaporation to afford the product as a white solid.<sup>8</sup>

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm 4.17 (d, *J*=5.06 Hz, 2 H) 4.43 (d, *J*=5.69 Hz, 2 H) 7.20 - 7.31 (m, 5 H) 7.38 (t, *J*=7.61 Hz, 3 H) 7.48 (t, *J*=7.37 Hz, 2 H) 7.75 (d, *J*=7.30 Hz, 2 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ ppm 43.90 (CH<sub>2</sub>) 44.13 (CH<sub>2</sub>) 127.43 (CH) 127.77 (CH) 127.99 (CH) 128.84 (CH) 128.94 (CH) 132.12 (CH) 133.63 (C) 138.09 (C) 168.16 (C) 169.32 (C)

**5-Hydroxy-N-(phenylmethyl)pentanamide (3o)** (5.404 g, 87%) was prepared from was prepared from benzylamine and  $\delta$ -valerolactone using the typical procedure. The crude compound was



trituated with hexanes, filtered through a fritted funnel, and washed with more hexanes. The solid precipitate was dissolved in EtOAc and filtered through a pad of Celite. The solvent was removed *in vacuo* by rotary evaporation to afford the product as a white solid.<sup>8</sup>

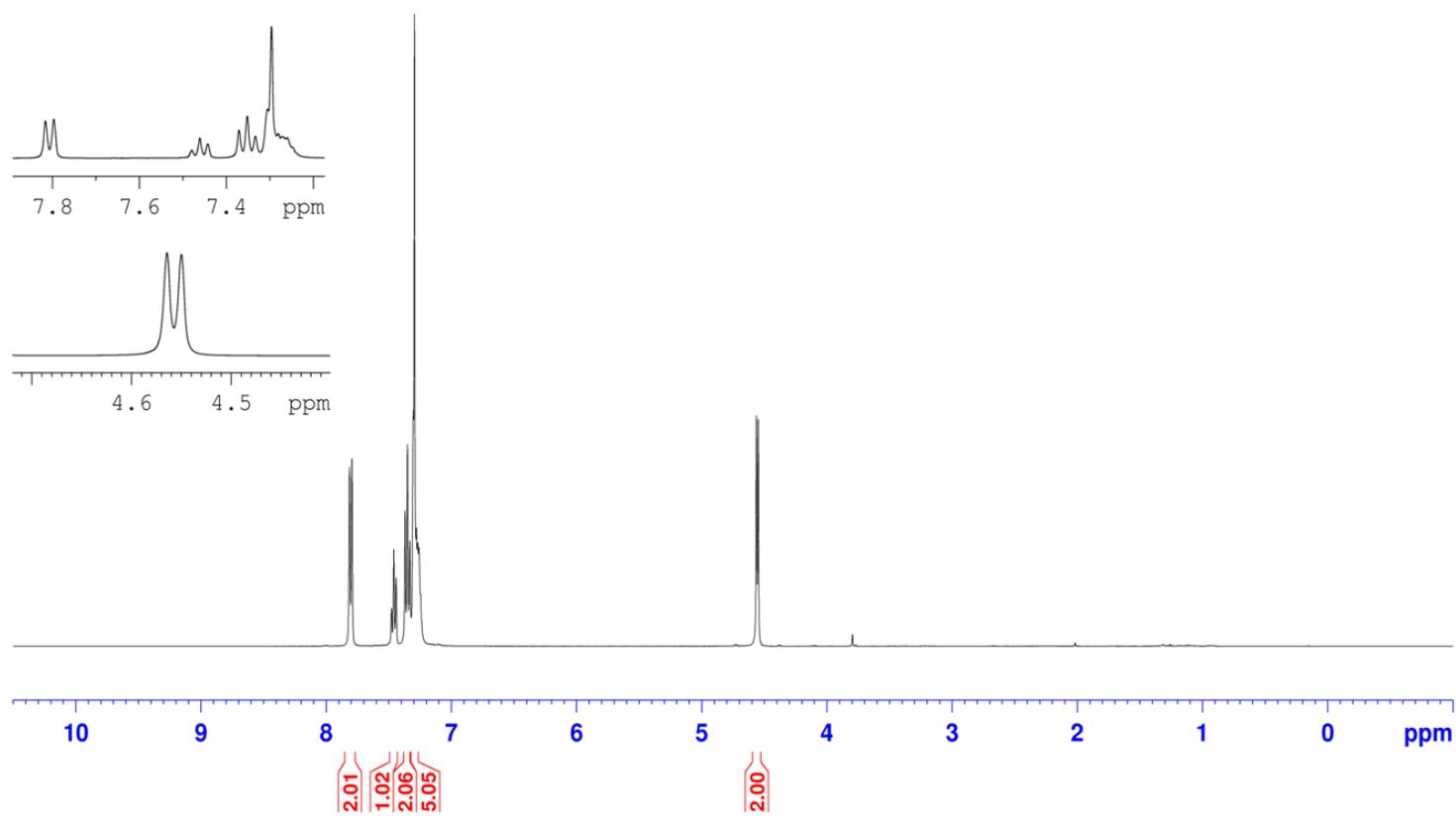
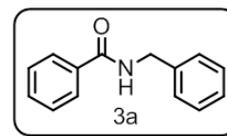
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 1.52 - 1.64 (m, 2 H) 1.69 - 1.81 (m, 2 H) 2.25 (t,  $J=7.20$  Hz, 2 H) 3.62 (t,  $J=6.14$  Hz, 2 H) 4.42 (d,  $J=5.70$  Hz, 2 H) 6.02 (br. s., 1 H) 7.21 - 7.37 (m, 5 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz)  $\delta$  ppm 21.96 (CH<sub>2</sub>) 32.26 (CH<sub>2</sub>) 36.27 (CH<sub>2</sub>) 43.88 (CH<sub>2</sub>) 62.28 (CH<sub>2</sub>) 127.78 (CH) 128.07 (CH) 128.97 (CH) 138.56 (C) 173.28 (C)

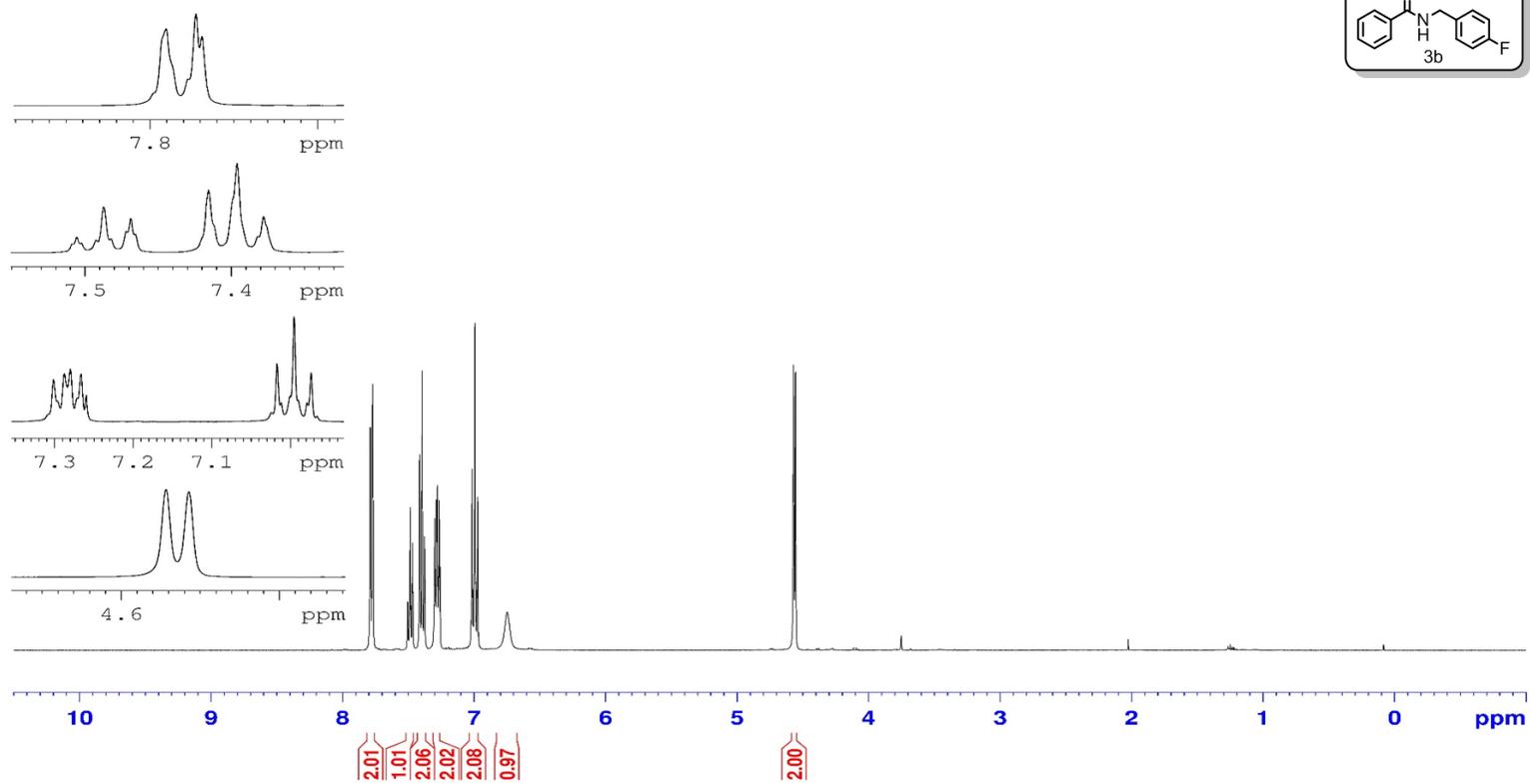
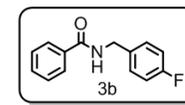
## References

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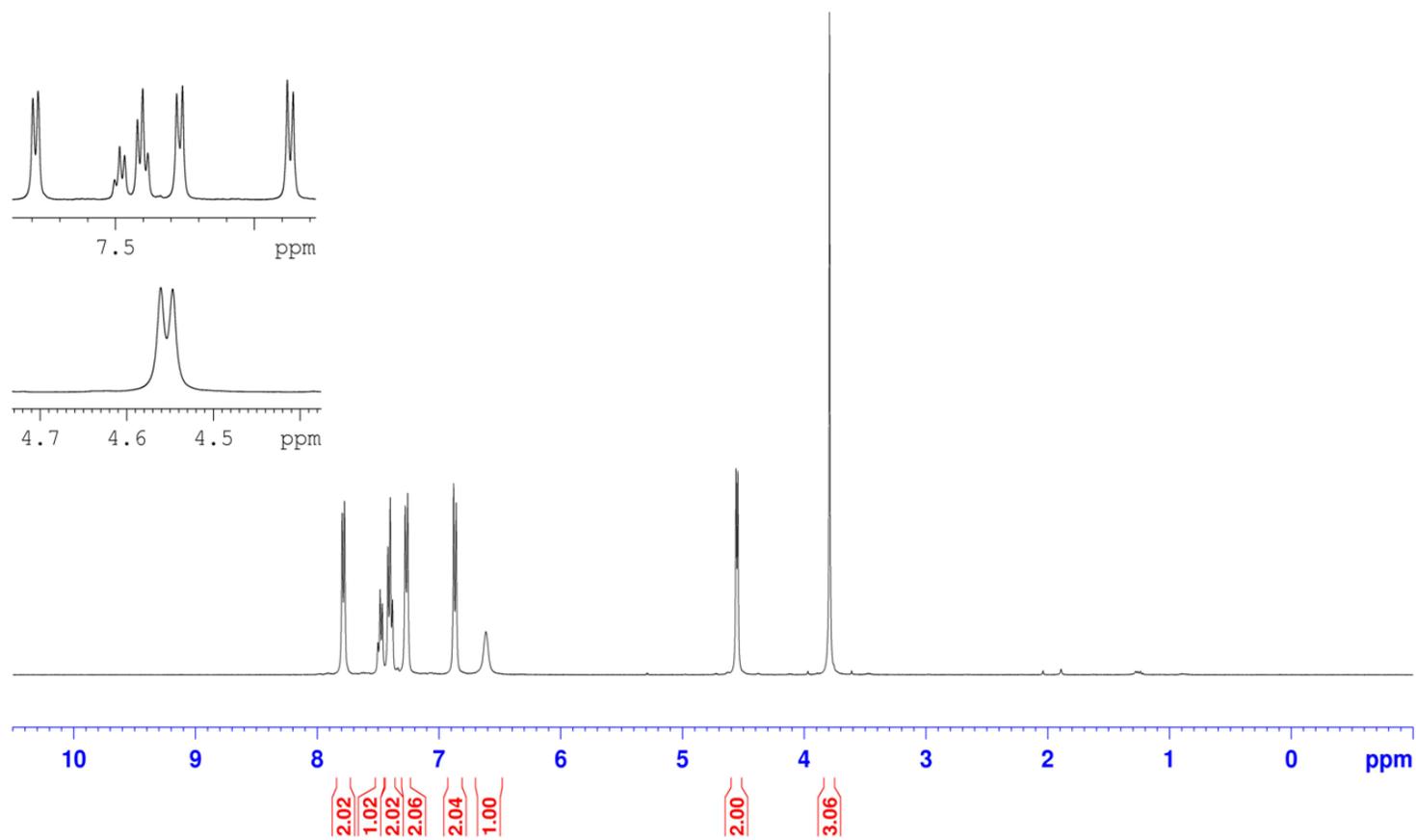
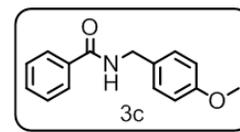
N-Benzyl benzamide  
400 MHz, CDCl<sub>3</sub>



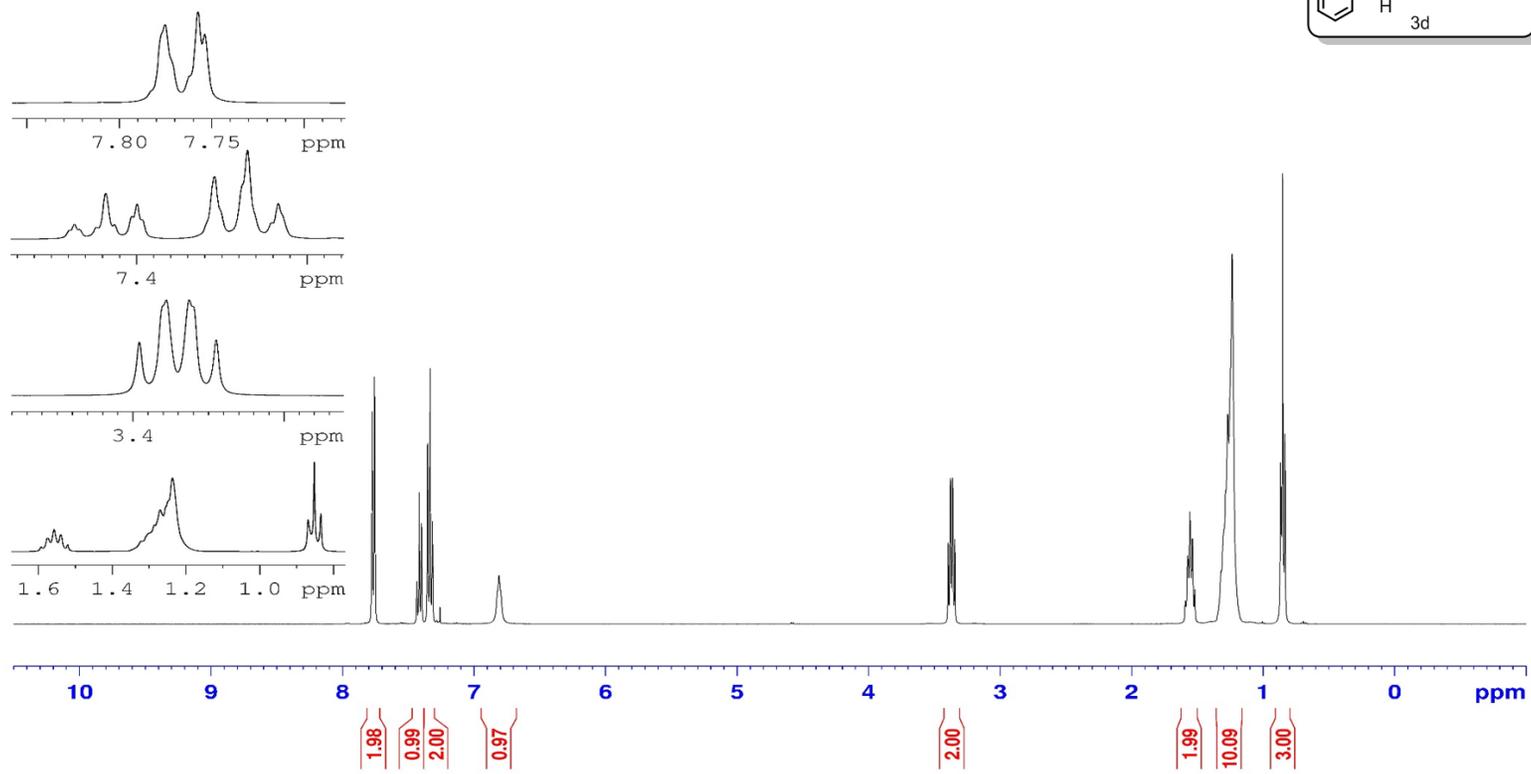
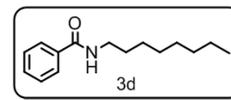
**N-(4-Fluorobenzyl) benzamide**  
400 MHz, CDCl<sub>3</sub>



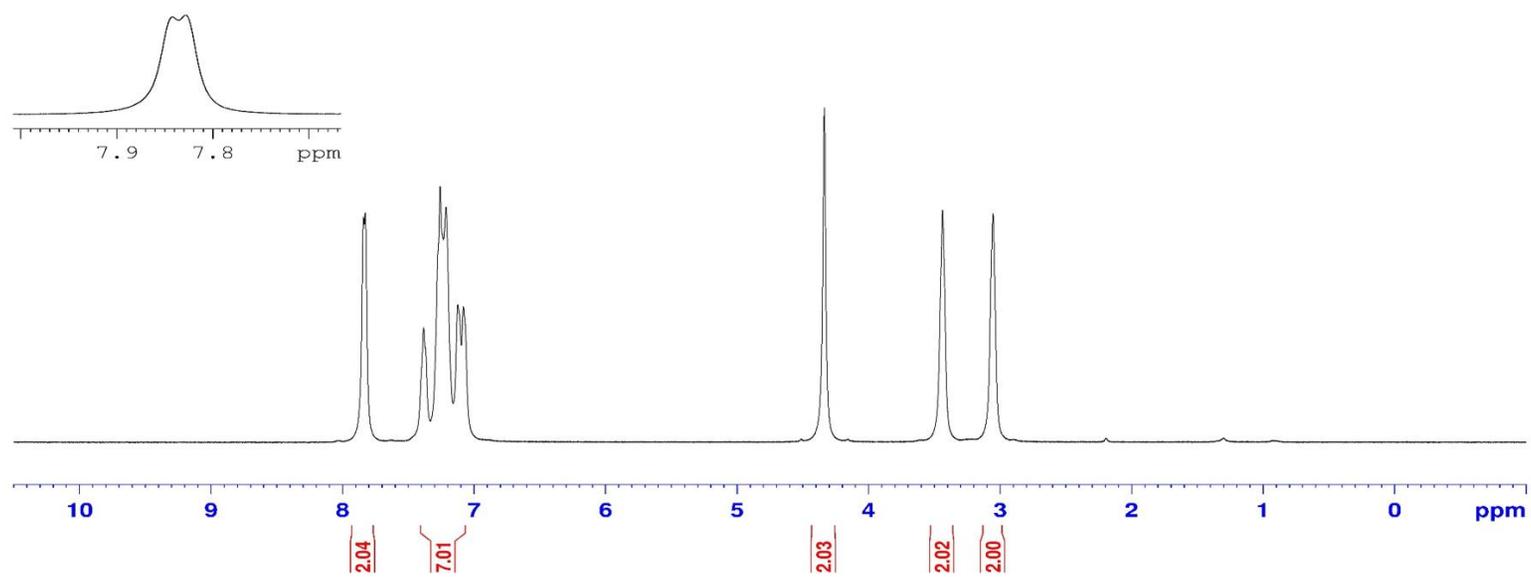
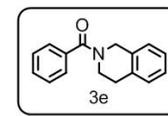
N-(4-Methoxybenzyl)-benzamide  
400 MHz, CDCl<sub>3</sub>



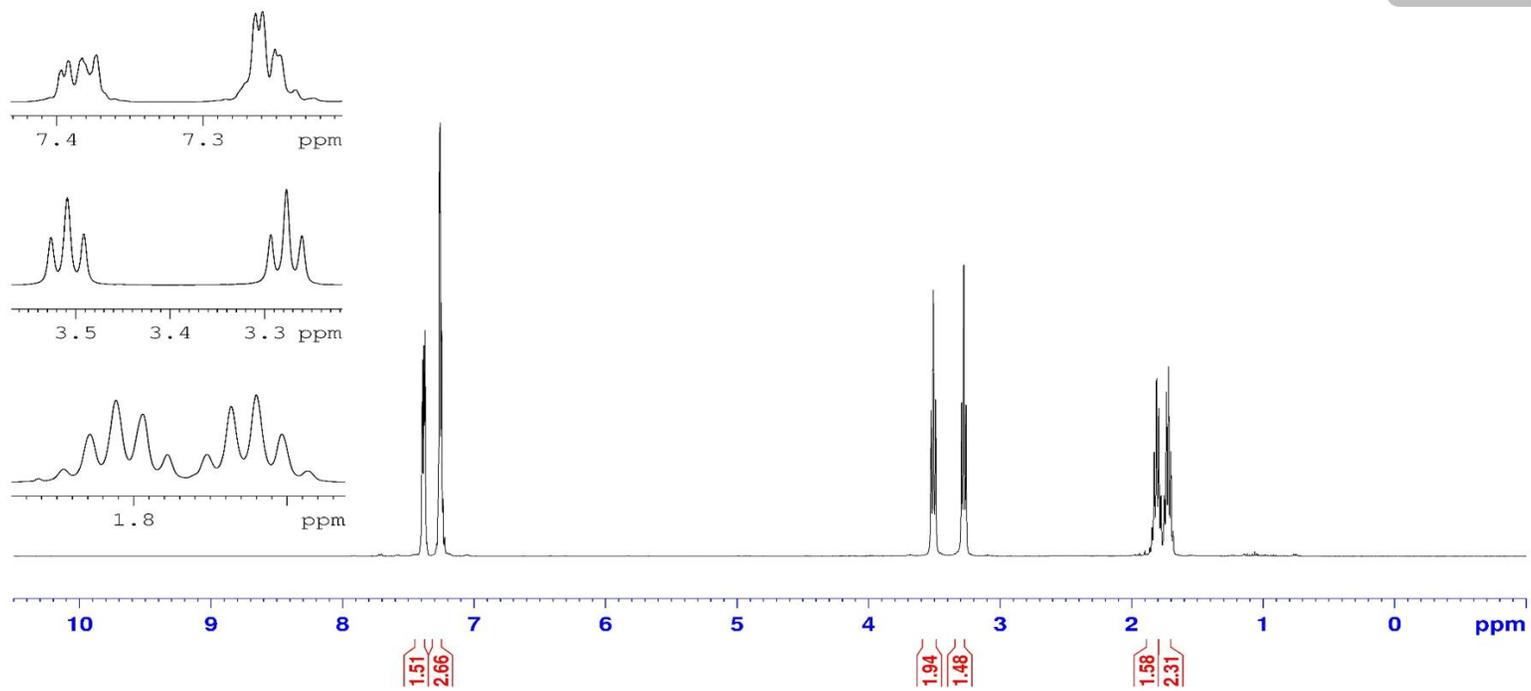
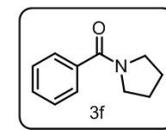
**N-Octylbenzamide**  
400 MHz, CDCl<sub>3</sub>



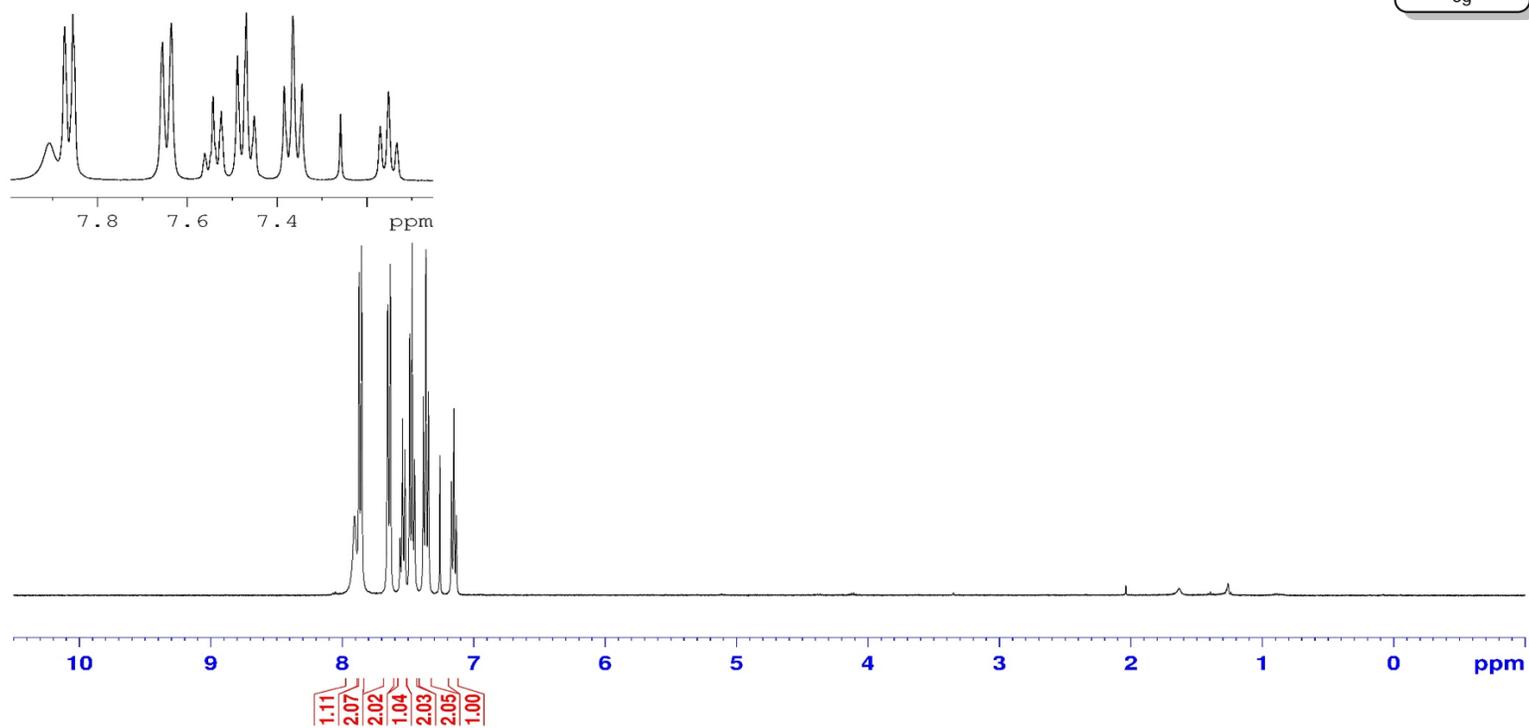
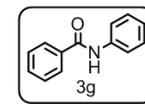
2-Benzoyl-1,2,3,4-tetrahydroisoquinoline  
400 MHz, CDCl<sub>3</sub>



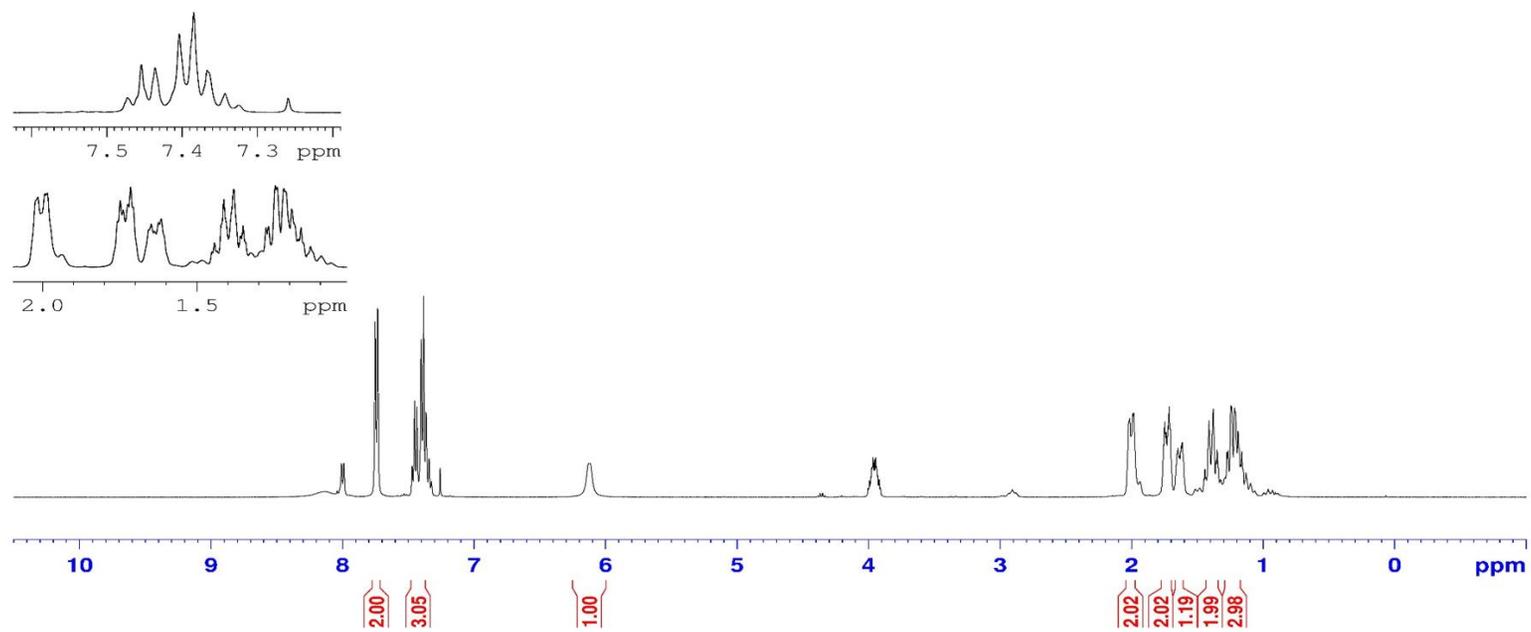
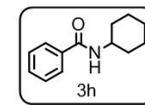
**N-Benzoylpyrrolidine**  
400 MHz, CDCl<sub>3</sub>



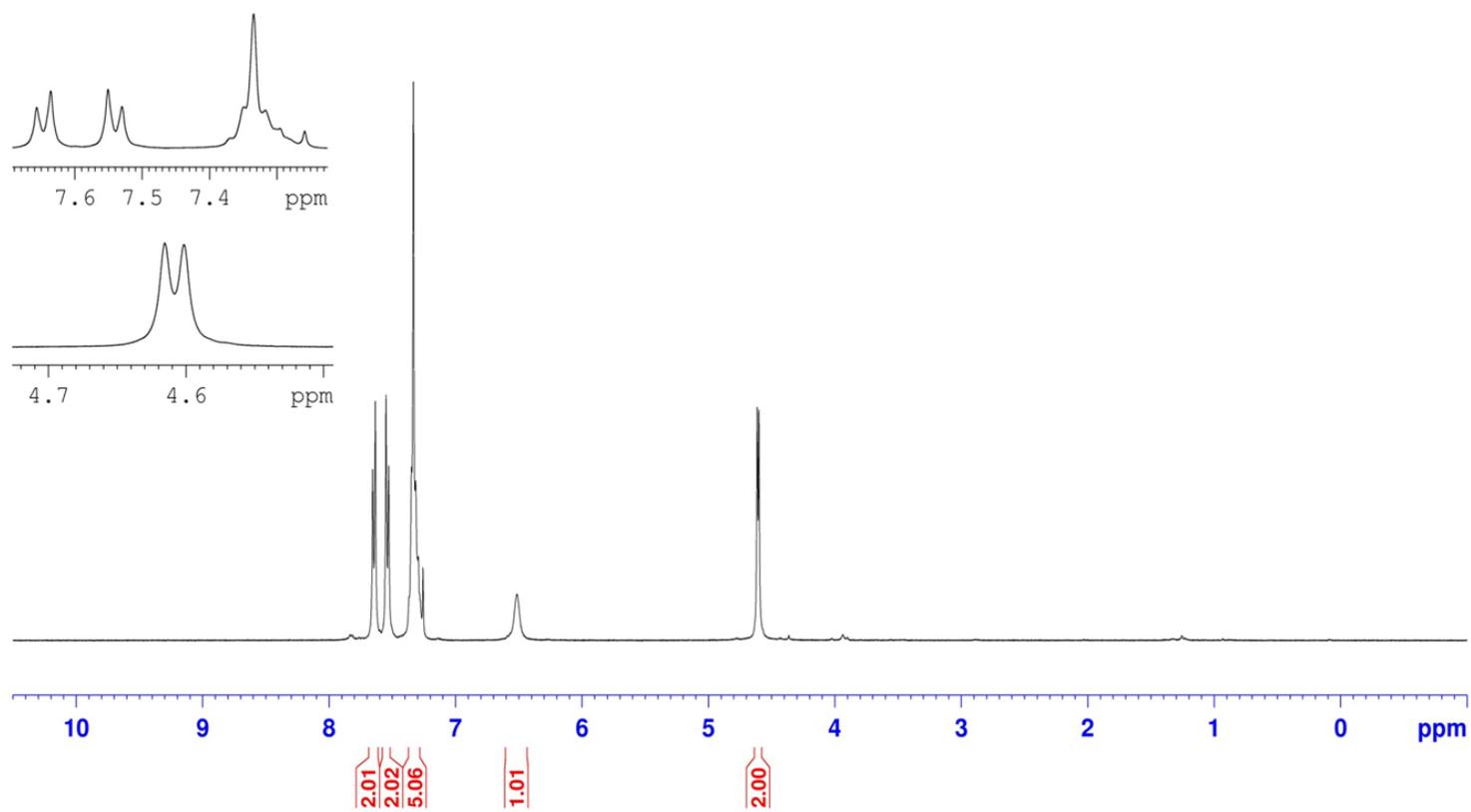
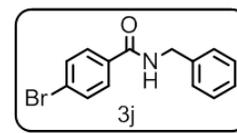
**Benzoylaminobenzene**  
400 MHz, CDCl<sub>3</sub>



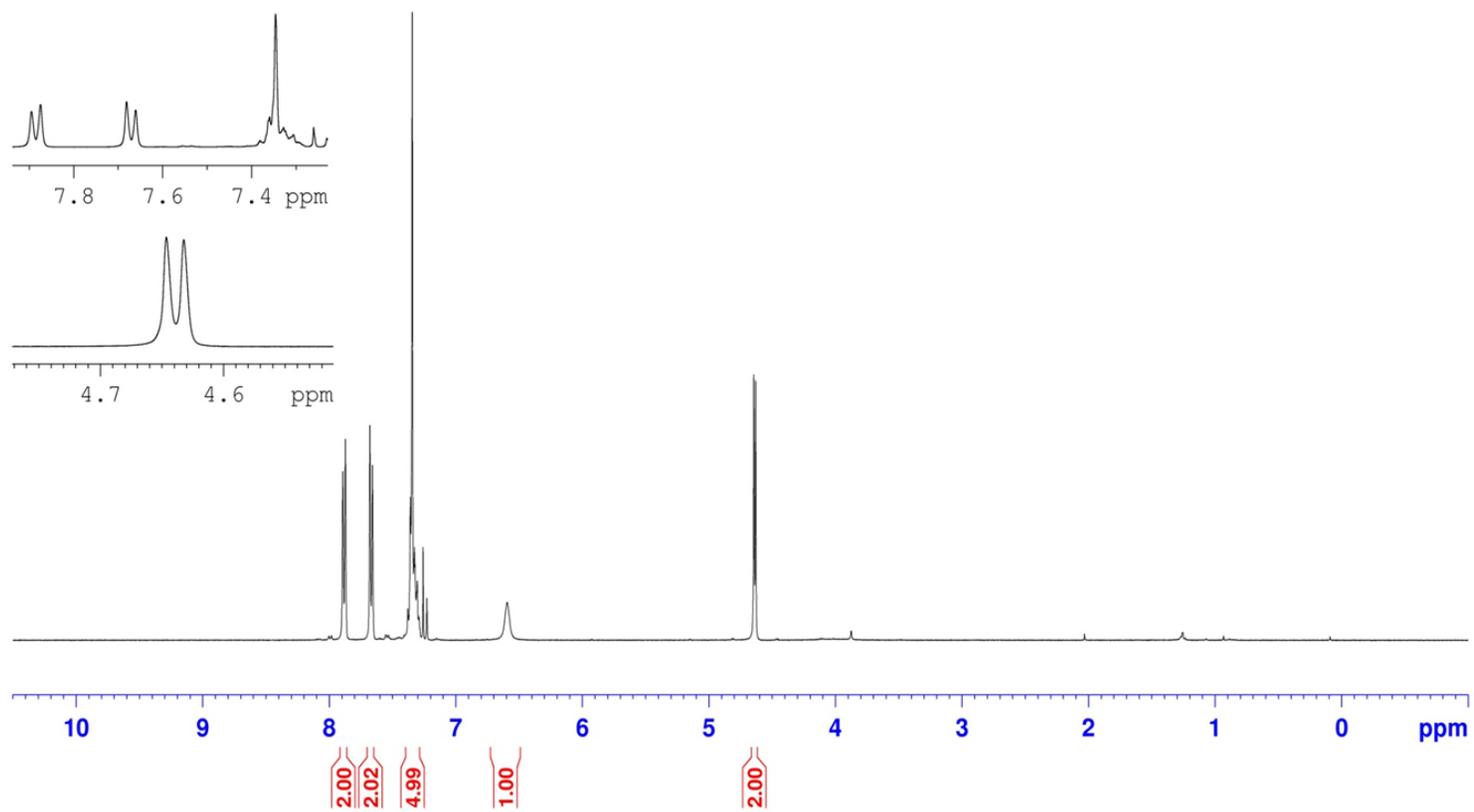
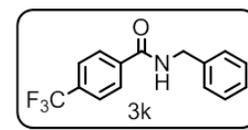
**N-Cyclohexylbenzamide**  
400 MHz, CDCl<sub>3</sub>



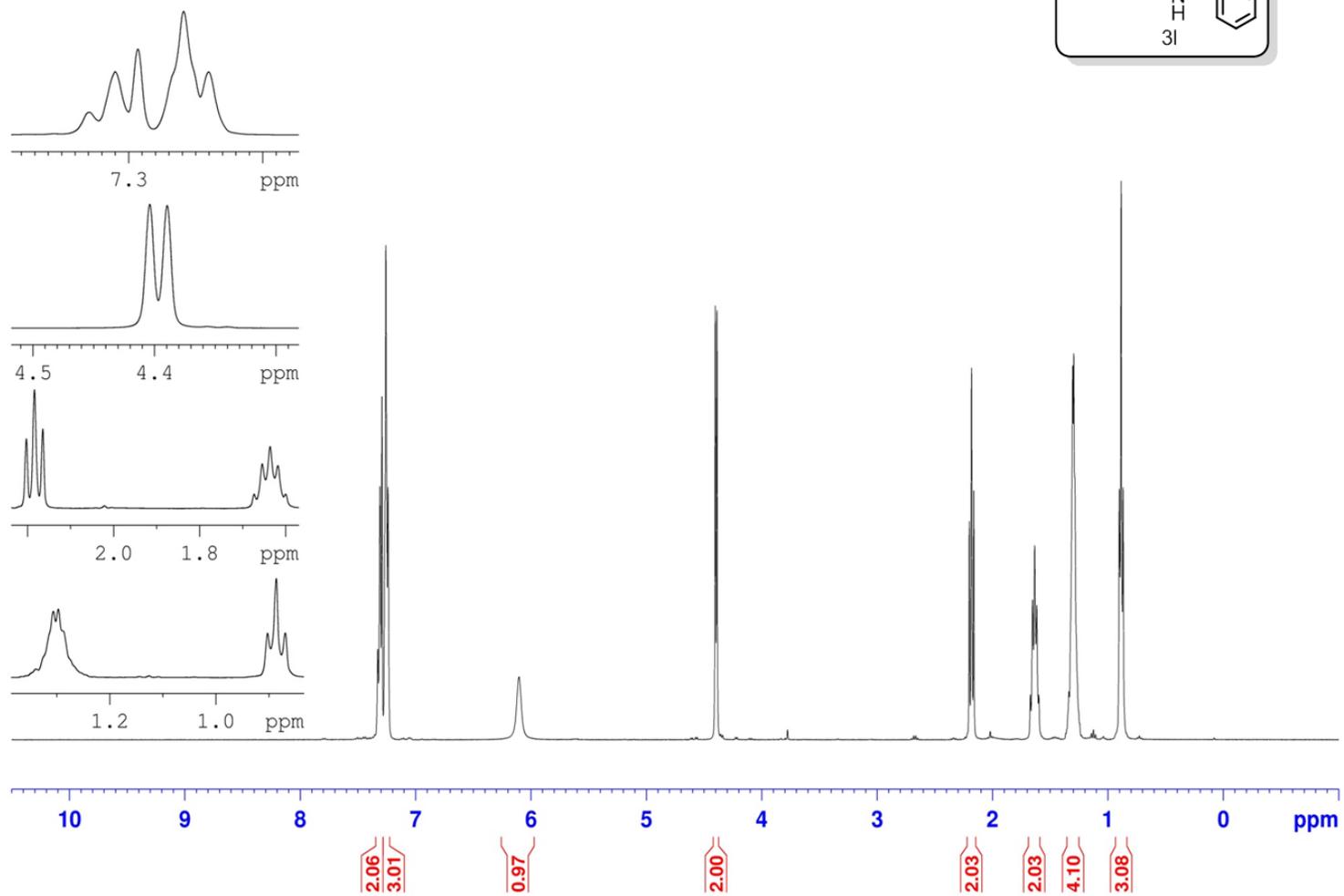
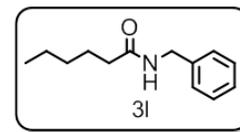
N-Benzyl-4-bromo-benzamide  
400 MHz, CDCl<sub>3</sub>



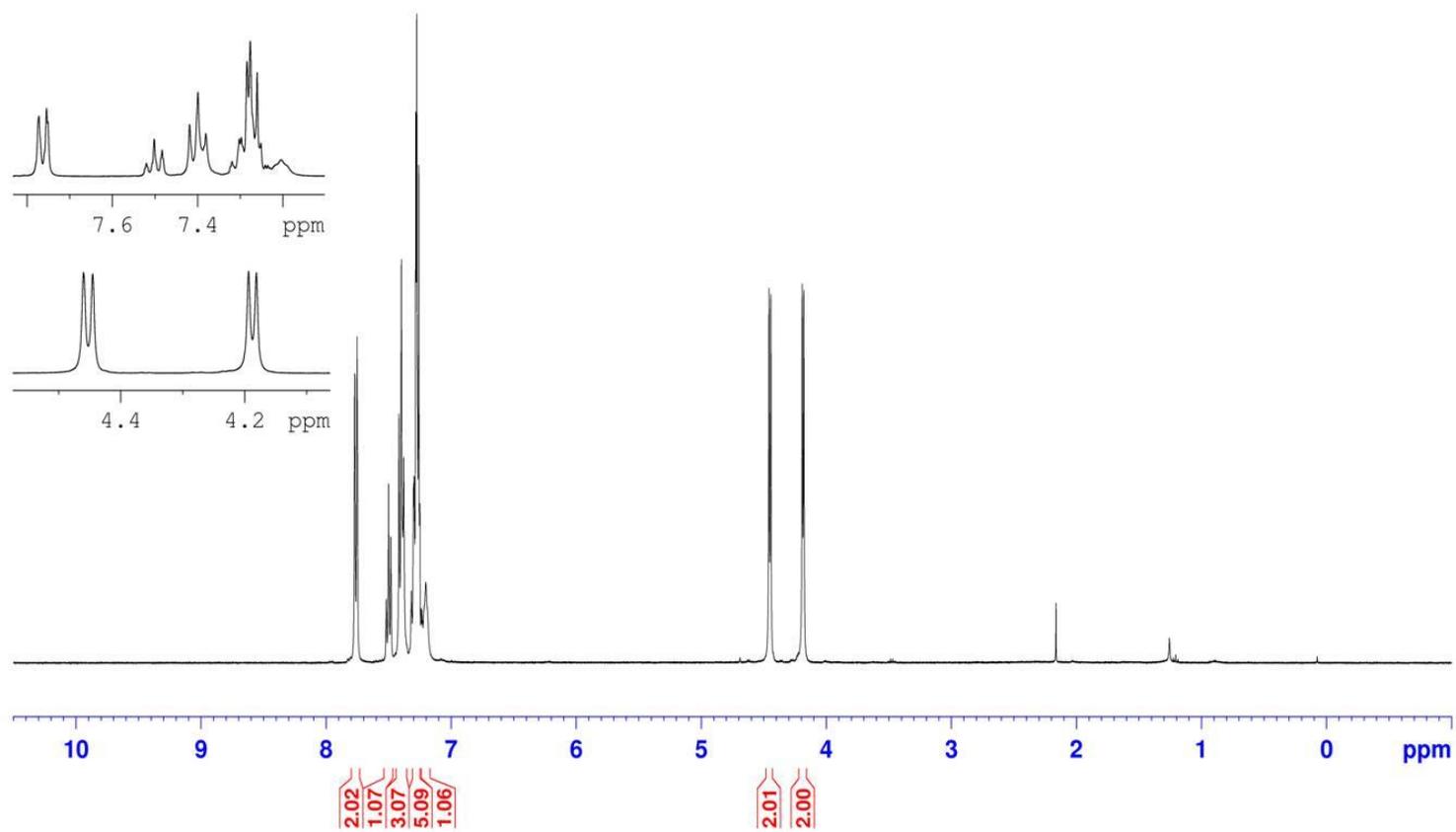
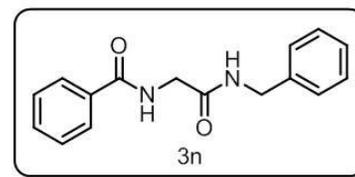
N-Benzyl-4-(trifluoromethyl) benzamide  
400 MHz, CDCl<sub>3</sub>



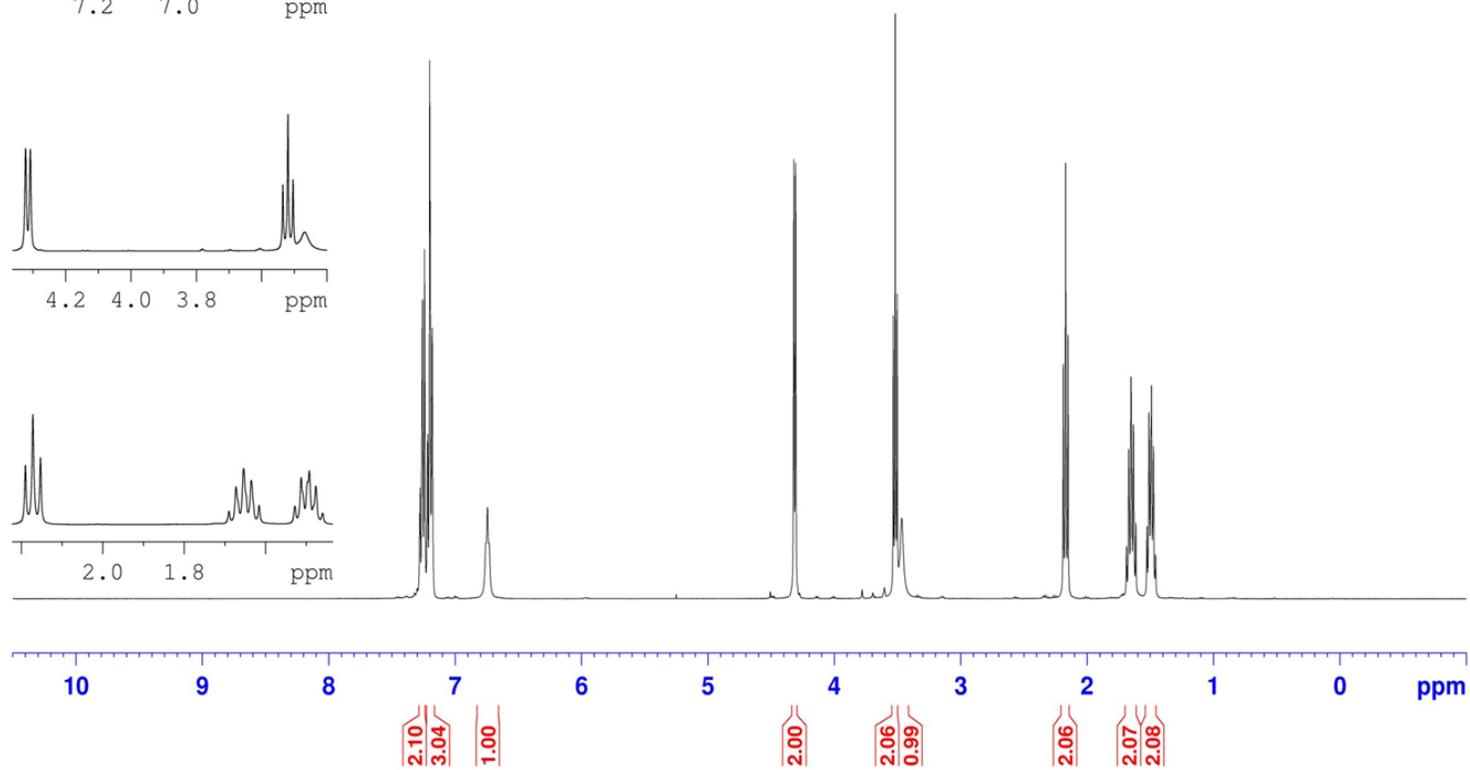
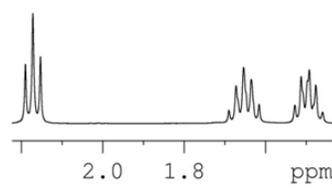
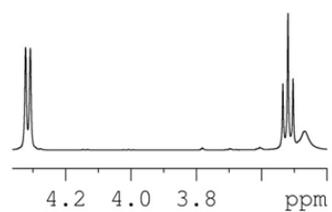
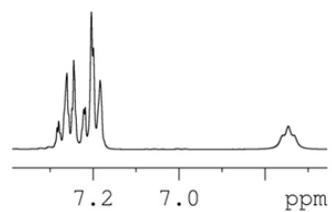
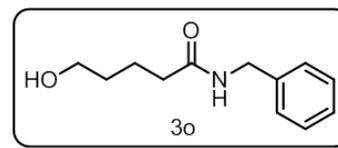
**N-Benzylhexanamide**  
400 MHz, CDCl<sub>3</sub>

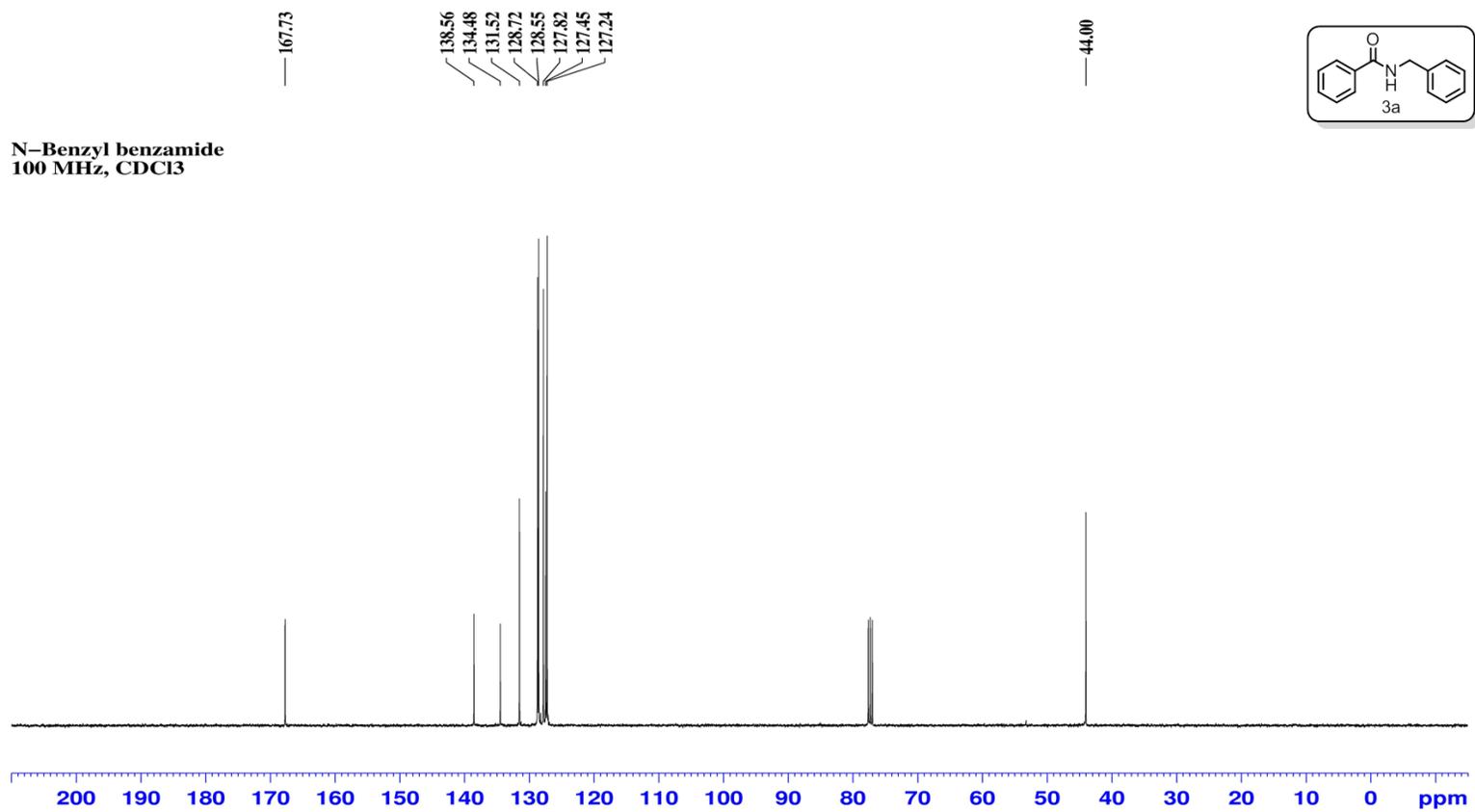


N-(2-(benzylamino)-2-oxoethyl)benzamide  
400MHz, CDCl<sub>3</sub>



5-Hydroxy-N-(phenylmethyl)pentanamide  
400 MHz, CDCl<sub>3</sub>

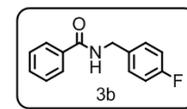




167.68  
163.64  
161.20

134.48  
134.36  
134.33  
131.84  
129.77  
129.69  
128.81  
127.23  
115.87  
115.66

43.53



**N-(4-Fluorobenzyl) benzamide**  
**100 MHz, CDCl<sub>3</sub>**

