

## Supporting Information

### Synthesis of N-Heterocyclic amides from imidazoheterocycles through convergent paired electrolysis

Élise Leclercq, Laura Chevet, Nicolas David, Muriel Durandetti and Laëticia Chausset-Boissarie\*

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## I. Materials and methods

All reagents were purchased from commercial suppliers (Fisher scientific, Sigma-Aldrich or Fluorochem) and were used without further purification unless otherwise indicated. 2-aminopyridine and bromoacetophenone were purchased from commercial suppliers.

**Electrode materials.** The electrodes used in this work for were bought from IKA (<https://www.ika.com/en/Products-Lab-Eq/Electrochemistry-Kit-csp-516/ElectraSyn-20-Package-Accessories-cpacc-20008980/>). For experiments using an ElectraSyn vial (10 mL, for 0.2 mmol scale), the dimensions of the electrodes were  $W8 \times D2 \times H40$  mm (with the submerged exterior surface of the electrode approximately  $W8 \times D2 \times H35$  mm), unless otherwise stated. For experiments using an ElectraSyn flow cell (<https://www.ikaprocess.com/en/Products/Electro-Organic-Synthesis-Systems-cph-45/>) the dimensions of the electrodes were  $W20 \times H60$  mm.

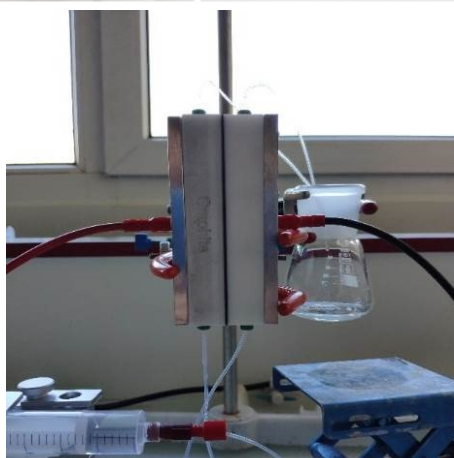
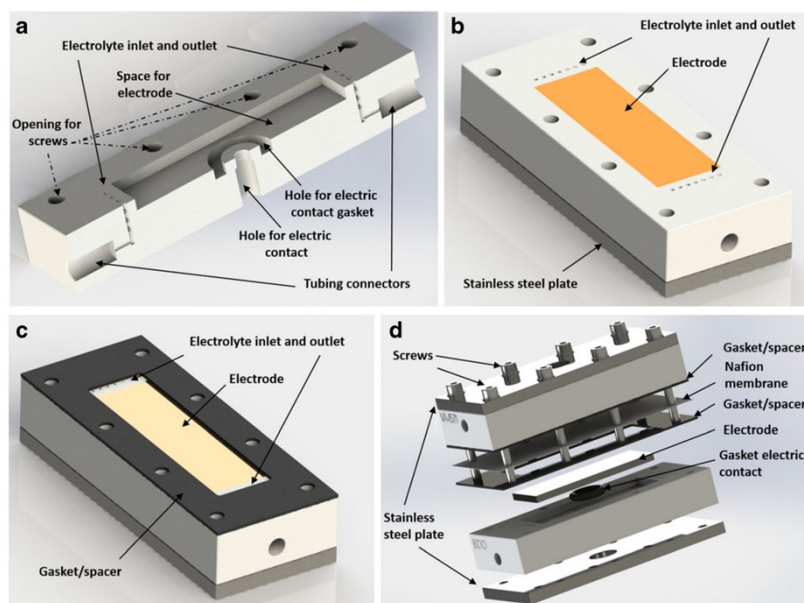


Figure 1. Technical drawings of 2 cm  $\times$  6 cm flow electrolysis cell: a Cross-section of the Teflon piece with connection for tubing, inlet, outlet and free space for electrode. b Complete half-cell containing Teflon piece, the electrode (yellow) and a stainless-steel plate. c Half-cell with gasket/ spacer on top. d Exploded drawing of a complete divided flow electrolysis cell. For the undivided mode, the Nafion membrane and one gasket/spacer is omitted. Reprinted with

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**Power supplies.** Electrolysis in batch was conducted using a DC power supply (OrigaFlex OGFWR-OGF01A) in constant current mode. For the ElectraSyn flow cell a power supply Keysight E36104A was applied.

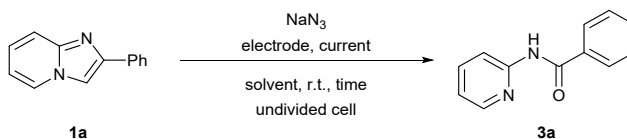
**Pumps.** Flow-rate was regulated as a function of internal volume and residence time of molecules in the reactor thanks to the formula  $Q = V/t_r$ , where  $Q$  is the flow rate ( $\mu\text{L}\cdot\text{min}^{-1}$ ),  $V$  the internal volume of the reactor and  $t_r$  the residence time of molecules in the reactor. The different flow rates of the reactions were regulated using a Chemyx Fusion 200-X syringe pump fitted with 20 mL plastic syringes from HENKE-JECT.

Analytical thin-layer chromatography (TLC) were performed on 0.25 mm E. Merck silica plates (60F-254), using short-wave UV light as the visualizing agent, and  $\text{KMnO}_4$ , phosphomolybdic acid and heat as developing agents. Column chromatography was performed using E. Merck silica gel (60, particle size 0.043–0.063 mm).

NMR spectra were recorded on a Bruker AVANCEIIIHD 300 spectrometer and are calibrated using residual undeuterated solvent ( $\text{CDCl}_3$  at 7.26 ppm  $^1\text{H}$  NMR, 77.16 ppm  $^{13}\text{C}$  NMR). Chemical shifts of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded in parts per million (ppm,  $\delta$ ) relative to solvent signal. The following abbreviations are used for the proton spectra multiplicities: s=singlet; d=doublet; t=triplet; q=quartet; m=multiplet. Coupling constant are reported in hertz (Hz).

High-resolution mass spectra (HRMS) were recorded with a Maxis Bruker 4G instrument and were performed in positive mode with an ESI source on a Q-TOF mass spectrometer with an accuracy tolerance of 2 ppm.

## II. Optimization of the reaction with SODIUM AZIDE



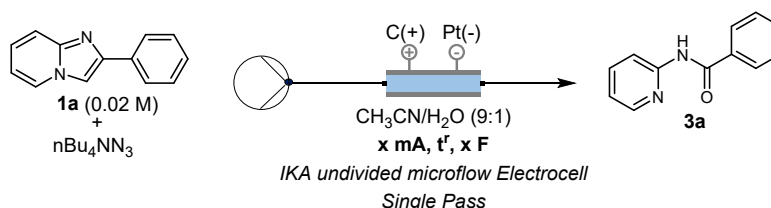
Entry	Electrodes	Solvent	Electrolyte	Time	Current	3a	1a
				(h)	(mA)	Yld (%)	Yld (%)
1	C(+) C(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	LiClO <sub>4</sub>	2	8	62	-
2	C(+) Pt(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	LiClO <sub>4</sub>	2	8	68	-
3	C(+) Ni(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	LiClO <sub>4</sub>	2	8	58	-
4	C(+) Ni foam(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	LiClO <sub>4</sub>	2	8	63	-
5	Pt(+) C(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	LiClO <sub>4</sub>	2	8	21	41
6	Pt(+) Ni(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	LiClO <sub>4</sub>	2	8	15	36
7	Ni(+) C(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	LiClO <sub>4</sub>	2	8	23	32
8	C(+) C(-)	CH <sub>3</sub> CN	LiClO <sub>4</sub>	2	8	12	-
9	C(+) C(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 8:2	LiClO <sub>4</sub>	2	8	45	7
10	C(+) C(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 7:3	LiClO <sub>4</sub>	2	8	53	11
11	C(+) Pt(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	<i>n</i> Bu <sub>4</sub> NClO <sub>4</sub>	2	8	27	-
12	C(+) Pt(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	<i>n</i> Bu <sub>4</sub> NPF <sub>6</sub>	2	8	6	44
13	C(+) Pt(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	<i>n</i> Bu <sub>4</sub> NBF <sub>4</sub>	2	8	traces	42
14	C(+) Pt(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	-	2	8	traces	40
15	C(+) Pt(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	LiClO <sub>4</sub>	1	8	30	-
16	C(+) Pt(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	LiClO <sub>4</sub>	3	8	13	-
17	C(+) Pt(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	LiClO <sub>4</sub>	2	4	10	-
18	C(+) Pt(-)	CH <sub>3</sub> CN/H <sub>2</sub> O 9:1	LiClO <sub>4</sub>	1.5	12	40	-

## III. Optimization of Electrochemical synthesis of N-heterocyclic amides under flow conditions

To transpose the reaction under single-pass continuous flow conditions we used the commercially available microflow electrocell from IKA (Electrasyn Flow cell, V = 0.6 mL, 12 cm<sup>2</sup> surface area, 0.5 mm of interelectrode spacing). A solution of 2-phenylimidazo[1,2-*a*]pyridine **1a** (0.2 mmol, 1 eq) and tetrabutylammonium azide (*n*Bu<sub>4</sub>NN<sub>3</sub>) **2** (1 mmol, 5 eq) in a mixture of acetonitrile/water (9:1, 10 mL, C = 0.02 M) was pumped through the ElectraSyn flow cell equipped with graphite anode

and platinum cathode and prefilled with the reaction mixture at a constant current at room temperature. The reaction mixture was collected in a round-bottom flask as the reactor output after 3 dead volumes of the reactor. The collected reaction mixture was concentrated under vacuum, water was added to the residue and the resulting mixture was extracted with diethyl ether. The combined organics were washed with brine, dried over anhydrous  $\text{MgSO}_4$  and concentrated under reduced pressure. Yield was determined by analysis of  $^1\text{H-NMR}$  spectra of crude reaction product using an internal standard (1,3,5-trimethoxybenzene).

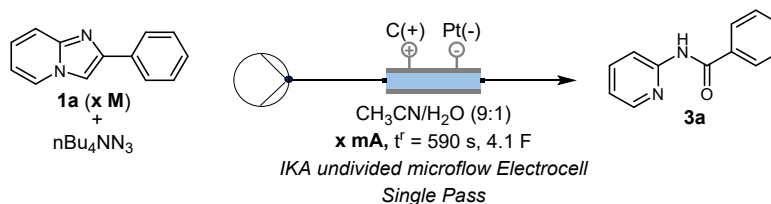
At first, we kept the optimized current (4 mA) and we applied a charge of 4.1 F which corresponds to a residence time of 20 min (Table S1, Entry 1). Then, when increasing the charge at 4.7 F, a slight decrease of the yield to 60% was observed (Entry 2). By applying the same current density as used under batch condition ( $J = 1.25 \text{ mA}\cdot\text{cm}^{-2}$ ) and a residence time of 5 min ( $F = 4.1 \text{ F}$ ), a drop in yield was observed accompanied by degradation (Entry 3). Finally, by dividing the current density, while maintaining the total amount of charge at 4.1 F, the product **3a** was obtained in 63% yield in 9.84 min residence time (Entry 4).



**Table S1: Optimization of electrochemical synthesis of N-heterocyclic amide 3a in micro-flow cell.**

Entry	Current (mA)	Residence time (min)	Flow Rate (mL.min <sup>-1</sup> )	$J$ (mA.cm <sup>-1</sup> )	Charge (F)	Yield (%)
1	4	20	0.030	0.33	4.1	66
2	4	23	0.026	0.33	4.7	60
3	15	5	0.114	1.25	4.1	45
4	8	9.84	0.061	0.66	4.1	63

#### IV. Optimization of the productivity



**Table S2: Optimization of the productivity in micro-flow cell**

Entry	Concentration 1a (M)	Current	Flow Rate (mL.min <sup>-1</sup> )	$J$	Yield	Productivity
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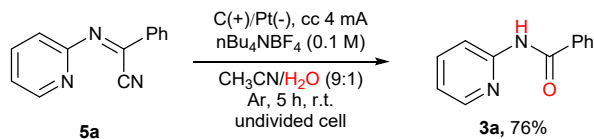
		(mA)		(mA.cm <sup>-1</sup> )	(%)	mg.day <sup>-1</sup>
1	0.02	8	0.061	0.66	63	217
2	0.03	12	0.061	1.00	54	283
3	0.06	24	0.061	1.98	42	436
<b>4</b>	<b>0.08</b>	<b>32</b>	<b>0.061</b>	<b>2.64</b>	<b>38</b>	<b>522</b>
5	0.1	40	0.061	3.3	25	434

## V. Calculation for mass consumption

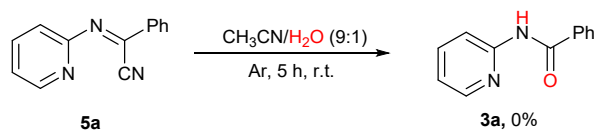
Table S3: Calculation of energy efficiency

Mode	V (mL)	Yld (%)	N <sub>0</sub> (mmol)	N <sub>f</sub> (mmol)	Time (s)	Voltage (V)	Current (A)	P (W) T*V*C	m <sub>3a</sub> (g)	Mass consumption (kW/g)
Batch	10	74	0.2	0.148	18000	4.2	0.004	302.4	0.029	<b>10.32</b>
Flow	10	63	0.2	0.126	9836	2.6	0.008	204.6	0.025	<b>8.20</b>

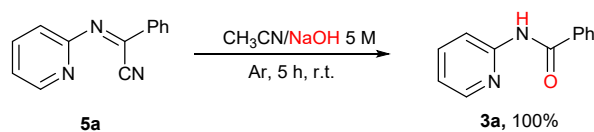
## VI. Control experiments



To a 10 mL undivided ElectroSyn vial equipped with a stirrer bar was added **5a** (0.2 mmol, 1 eq),  $n\text{Bu}_4\text{NBF}_4$  (5 eq), and then a mixture of  $\text{MeCN}:\text{H}_2\text{O}$  (9:1, 10.0 mL). The ElectroSyn vial cap equipped with anode (graphite) and cathode (platinum) was inserted into the mixture. The reaction mixture was carefully degassed for 10 minutes and maintained under an argon atmosphere. The electrolysis was conducted at constant current conditions at room temperature with 4 mA ( $J = 1.25 \text{ mA}\cdot\text{cm}^{-2}$ ) as current during 5 h (3.7 F). After electrolysis, the cap was removed, and the electrodes were taken out and rinsed with diethyl ether into the reaction mixture. The solution was then concentrated under vacuum, water was added to the residue and the resulting mixture was extracted with diethyl ether. The combined organics were washed with brine, dried over anhydrous  $\text{MgSO}_4$  and concentrated under reduced pressure. Product **3a** was obtained in 76% NMR Yield. The yield was determined by analysis of  $^1\text{H-NMR}$  spectra of crude reaction product using an internal standard (1,3,5-trimethoxybenzene).



A solution of **5a** (0.2 mmol, 1 eq) in a mixture of  $\text{MeCN}:\text{H}_2\text{O}$  (9:1, 10.0 mL) was carefully degassed for 10 minutes and stirred under an argon atmosphere for 5 h at room temperature. The solution was then concentrated under vacuum, water was added to the residue and the resulting mixture was extracted with diethyl ether. The combined organics were washed with brine, dried over anhydrous  $\text{MgSO}_4$ , concentrated under reduced pressure and analyzed by  $^1\text{H-NMR}$ . The yield was determined by analysis of  $^1\text{H-NMR}$  spectra of crude reaction product using an internal standard (1,3,5-trimethoxybenzene).



A solution of **5a** (0.2 mmol, 1 eq) in a mixture of  $\text{MeCN}:\text{NaOH}$  5 M (9:1, 10.0 mL) was carefully degassed for 10 minutes and stirred under an argon atmosphere for 5 h at room temperature. The solution was then concentrated under vacuum, water was added to the residue and the resulting mixture was extracted with diethyl ether. The combined organics were washed with brine, dried over anhydrous  $\text{MgSO}_4$ , concentrated under reduced pressure. Product **3a** was obtained in 100 % NMR Yield. The yield was determined by analysis of  $^1\text{H-NMR}$  spectra of crude reaction product using an internal standard (1,3,5-trimethoxybenzene).

## VII. Cyclic voltammetry experiments

Cyclic voltammetry was measured under Ar atmosphere with conventional three electrode system (Reference electrode: Saturated Calomel Electrode (SCE), working electrode: Glassy carbon, counter electrode: Pt wire, Supporting electrolyte: 0.1 M  $n\text{Bu}_4\text{NBF}_4$  in  $\text{MeCN}:\text{H}_2\text{O}$  v/v 9:1) on a BioLogic SP-300 apparatus. Conventional concentrations of 10 mM electroactive species were used. Acquisitions were performed with 200 mV/s scan rates.

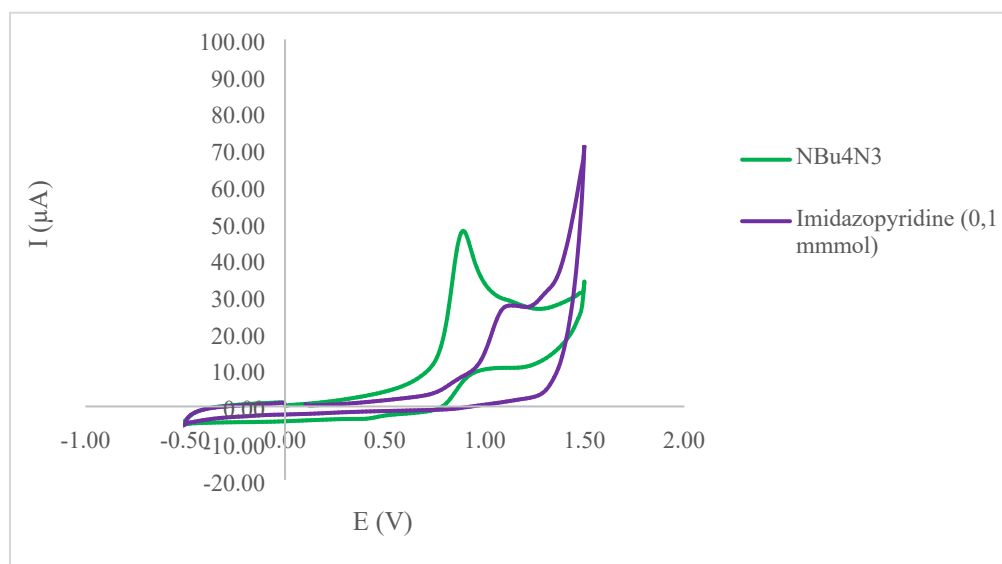


Figure 1 : cyclic voltammetry studies



## VIII. Experimental procedure and characterization data

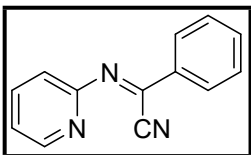
### A. General procedure for the synthesis of imidazoheterocycles

All imidazoheterocycles were synthesized according to literature procedures from condensation of the corresponding  $\alpha$ -bromoketones and 2-aminopyridines in refluxing EtOH<sup>1</sup> with NaHCO<sub>3</sub> and characterized by comparison to literature reports.

### B. General procedure for the synthesis of (Z)-N-(pyridin-2-yl)benzimidoyl cyanide 5a

This procedure was adapted from a similar synthesis of (Z)-N-(pyridin-2-yl)benzimidoyl cyanide <sup>2</sup>

To a solution of solution of 2-phenylimidazo[1,2-*a*]pyridine **1a** (1.0 mmol) in CH<sub>3</sub>CN (9.0 mL) was sequentially added water (1.0 mL), (diacetoxyiodo)-benzene (2.0 mmol), and NaN<sub>3</sub> (3.0 mmol). The reaction mixture was then stirred at room temperature for 3 h. Upon completion, water was added to quench the reaction, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic extracts were dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford a crude residue. The crude product was purified by flash column chromatography (90% Cyclohexane to 8:2 Cyclohexane/EtOAc) to afford (Z)-N-(pyridin-2-yl)benzimidoyl cyanide **5a** in 41% yield. *Caution: Sodium azide (NaN<sub>3</sub>) is highly toxic. It rapidly hydrolyzes in water and acids, producing hydrazoic acid (HN<sub>3</sub>), a highly toxic and volatile liquid. Sodium azide decomposes violently when heated to 275°C and reacts with halogenated organics to form explosive organic azides. When sodium azide or its solutions come into contact with metal surfaces, highly shock-sensitive heavy metal azides can form. Even dilute solutions can accumulate enough azide salts over time to pose a significant explosion risk.*



Brown solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.61 (d, *J* = 4.0 Hz, 1H), 8.23 (d, *J* = 7.3 Hz, 2H), 7.84 (td, *J* = 7.7, 1.8 Hz, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.29 (dd, *J* = 8.0, 4.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.3, 149.1, 141.3, 138.4, 133.8, 133.5, 129.2, 128.9, 123.1, 118.5, 111.7.

HRMS (ESI): *m/z* [M-H]<sup>+</sup> calc. for C<sub>13</sub>H<sub>8</sub>N<sub>3</sub> 206.07182, found 206.07138.

### C. Preparation of tetrabutylammonium azide

This procedure was adapted from a similar synthesis of nBu<sub>4</sub>NN<sub>3</sub>.<sup>3</sup>

A solution of NaN<sub>3</sub> (5.0 g, 77 mmol, 2 eq) in water (11.5 mL) was added to tetrabutylammonium hydroxide (40% aqueous solution, 10.0 g, 38.45 mmol, 1 eq), Dichloromethane (60 mL) was then added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3  $\times$  20 mL). The combined organic layers were dried over anhydrous magnesium sulphate, filtered and concentrated to give the salt as a white crystalline solid (8.2 g, 75%). *Note that tetrabutylammonium azide is extremely hygroscopic.*

<sup>1</sup> a) S. Takizawa, J.-I. Nishida, T. Tsuzuki, S. Tokito, Y. Yamashita, *Inorg. Chem.* **2007**, *46*, 4308–4319; b) E. S. Hand, W. W. Paudler, *Tetrahedron* **1982**, *38*, 49–55; c) S. Mishra, K. Monir, S. Mitra, A. Hajra, *Org. Lett.* **2014**, *16*, 6084.

<sup>2</sup> a) A. H. Kalbandhe, A. C. Kavle, N. N. Karade, *Eur. J. Org. Chem.*, **2017**, 1318-1322.

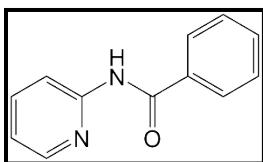
<sup>3</sup> R. W. Bates, R. N. Khanizeman, H. Hirao, Y. S. Tay, P. Sae-Lao *Org. Biomol. Chem.*, **2014**, *12*, 4879–4884

#### D. General Procedure: Electrochemical azidation under batch condition

Unless otherwise specified, the reaction was carried out on 0.2 mmol scale. To a 10 mL undivided ElectroSyn vial equipped with a stirrer bar was added imidazoheterocycles (0.2 mmol, 1 eq), tetrabutylammonium azide (1 mmol, 5 eq), and then a mixture of MeCN:H<sub>2</sub>O (9:1, 10.0 mL). Note that before use, the anode was polished with sandpaper then wiped with a paper. The ElectroSyn vial cap equipped with anode (graphite) and cathode (platinum) was inserted into the mixture. The reaction mixture was carefully degassed for 10 minutes and maintained under an argon atmosphere. The electrolysis was conducted at constant current conditions at room temperature with 4 mA ( $J = 1.25 \text{ mA}\cdot\text{cm}^{-2}$ ) as current during 5 h (3.7 F). After electrolysis, the cap was removed, and the electrodes were taken out and rinsed with diethyl ether into the reaction mixture. The solution was then concentrated under vacuum, water was added to the residue and the resulting mixture was extracted with diethyl ether. The combined organics were washed with brine, dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure [Note: Yield may be determined by analysis of <sup>1</sup>H-NMR spectra of crude reaction product using an internal standard (1,3,5-trimethoxybenzene) at this point]. The crude material was purified by silica gel column chromatography to furnish the desired product.

#### N-(pyridin-2-yl)benzamide 3a

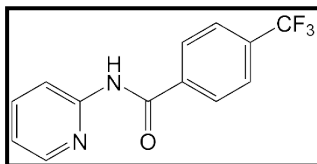
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 29.3 mg (74%) of the title compound **3a**.



White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.88 (s, 1H), 8.44 – 8.35 (m, 1H), 8.22 (ddd,  $J = 4.9, 1.8, 0.8$  Hz, 1H), 7.96 – 7.88 (m, 2H), 7.75 (ddd,  $J = 8.5, 7.5, 1.8$  Hz, 1H), 7.60 – 7.52 (m, 1H), 7.52 – 7.45 (m, 2H), 7.05 (ddd,  $J = 7.3, 4.9, 1.0$  Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165.9, 151.7, 148.1, 138.6, 134.5, 132.4, 129.0 (2), 127.4 (2), 120.1, 114.3. HRMS (ESI):  $m/z$  [M+H]<sup>+</sup> calc. for C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>O 199.086503, found 199.086589.

#### N-(pyridin-2-yl)-4-(trifluoromethyl)benzamide 3b

Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 58.5 mg (80%) of the title compound **3b**.

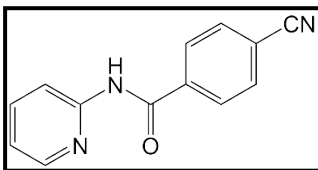


Pale yellow solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.14 (s, 1H), 8.44 – 8.33 (m, 1H), 8.18 (ddd,  $J = 4.9, 1.8, 0.8$  Hz, 1H), 8.04 (d,  $J = 8.1$  Hz, 2H), 7.83 – 7.67 (m, 3H), 7.07 (ddd,  $J = 7.4, 5.0, 1.0$  Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 164.8, 151.5, 147.9, 138.9, 137.7, 133.9 (q,  $J = 32.8$  Hz), 128.0 (2), 125.9 (q,  $J = 7.3$  Hz) (2), 121.9 (q,  $J = 270.9$  Hz), 120.4, 114.7. <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -63.04. HRMS (ESI):  $m/z$  [M+H]<sup>+</sup> calc. for C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>OF<sub>3</sub> 267.073972, found 267.073974.

#### 4-cyano-N-(pyridin-2-yl)benzamide 3c

Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 38.8 mg (87%) of the

title compound **3c**.

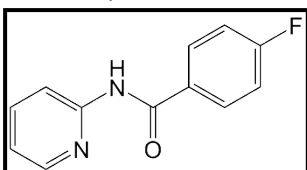


White solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ) 9.09 (s, 1H), 8.43 – 8.32 (m, 1H), 8.24 – 8.15 (m, 1H), 8.08 – 8.00 (m, 2H), 7.85 – 7.74 (m, 3H), 7.09 (ddd,  $J = 7.4, 4.9, 1.0$  Hz, 1H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  164.2, 151.3, 148.0, 138.9, 138.3, 132.8 (2), 128.1 (2), 120.6, 117.9, 115.9, 114.6.

**HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{13}\text{H}_{10}\text{NO}$  224.081791, found 224.081838.

#### 4-fluoro-N-(pyridin-2-yl)benzamide **3d**

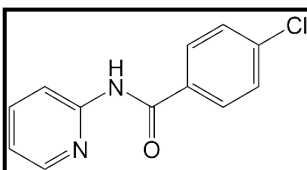
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 35.8 mg (83%) of the title compound **3d**.



White solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ) 8.88 (s, 1H), 8.36 (dt,  $J = 8.4, 0.9$  Hz, 1H), 8.22 (ddd,  $J = 4.9, 1.9, 0.9$  Hz, 1H), 7.98 – 7.91 (m, 2H), 7.75 (ddd,  $J = 8.4, 7.4, 1.9$  Hz, 1H), 7.20 – 7.11 (m, 2H), 7.06 (ddd,  $J = 7.4, 4.9, 1.0$  Hz, 1H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 165.8 (d,  $J = 157.4$  Hz), 151.6, 147.8, 138.6, 129.7 (d,  $J = 9.1$  Hz) (2), 129.7, 120.0, 115.9 (d,  $J = 22.0$  Hz) (2), 114.3.  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -106.78. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{12}\text{H}_{10}\text{FN}_2\text{O}$  217.077092, found 217.077168.

#### 4-chloro-N-(pyridin-2-yl)benzamide **3e**

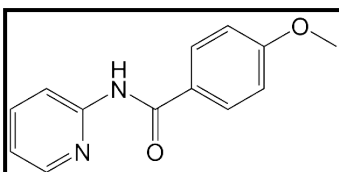
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 19.5 mg (42%) of the title compound **3e**.



White solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 (s, 1H), 8.36 (dt,  $J = 8.4, 0.9$  Hz, 1H), 8.25 (ddd,  $J = 4.9, 1.9, 0.9$  Hz, 1H), 7.91 – 7.84 (m, 2H), 7.76 (ddd,  $J = 8.4, 7.4, 1.9$  Hz, 1H), 7.50 – 7.43 (m, 2H), 7.07 (ddd,  $J = 7.4, 4.9, 1.0$  Hz, 1H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  164.9, 151.6, 148.0, 138.7, 132.8, 129.2 (2), 129.0, 128.9 (2), 120.3, 114.5. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{12}\text{H}_{10}\text{ClN}_2\text{O}$  233.047434, found 233.047617.

#### 4-methoxy-N-(pyridin-2-yl)benzamide **3f**

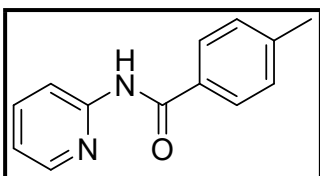
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 37.7 mg (83%) of the title compound **3f**.



Pale yellow solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.56 (s, 1H), 8.37 (d,  $J = 8.4$  Hz, 1H), 8.28 (d,  $J = 4.7$  Hz, 1H), 7.90 (d,  $J = 8.7$  Hz, 2H), 7.75 (t,  $J = 7.8$  Hz, 1H), 7.10 – 7.03 (m, 1H), 6.98 (d,  $J = 8.7$  Hz, 2H), 3.88 (s, 3H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 162.8, 151.8, 147.9, 138.4, 129.2 (2), 126.4, 119.7, 114.1, 114.1 (2), 55.5. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}_2$  228.0899, found 228.0905.

#### 4-methyl-N-(pyridin-2-yl)benzamide **3g**

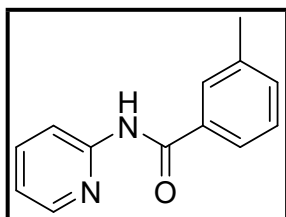
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 33.1 mg (78%) of the title compound **3g**.



Pale yellow solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (s, 1H), 8.36 (dt,  $J$  = 8.4, 0.9 Hz, 1H), 8.20 (ddd,  $J$  = 4.9, 1.9, 0.9 Hz, 1H), 7.86 – 7.77 (m, 2H), 7.71 (ddd,  $J$  = 8.4, 7.4, 1.9 Hz, 1H), 7.31 – 7.20 (m, 2H), 7.01 (ddd,  $J$  = 7.3, 4.9, 1.0 Hz, 1H), 2.38 (s, 3H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 151.9, 147.9, 143.0, 138.6, 131.6, 129.6 (2), 127.4 (2), 120.0, 114.4, 21.6. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}$  213.102118, found 213.102239.

### 3-methyl-N-(pyridin-2-yl)benzamide **3h**

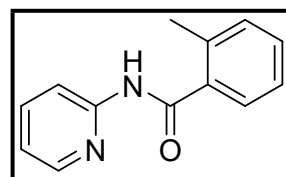
Following General Procedure A on 0.2 mmol scale. Purification by recrystallization in n-pentane afforded 29.7 mg (70%) of the title compound **3h**.



Yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.96 (s, 1H), 8.40 (d,  $J$  = 8.4 Hz, 1H), 8.20 (dd,  $J$  = 4.9, 1.0 Hz, 1H), 7.78 – 7.67 (m, 3H), 7.36 (d,  $J$  = 5.0 Hz, 2H), 7.03 (ddd,  $J$  = 7.3, 4.9, 0.9 Hz, 1H), 2.40 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 151.8, 147.9, 138.8, 138.6, 134.4, 133.1, 128.8, 128.1, 124.4, 119.9, 114.4, 21.5. **HRMS** (ESI):  $m/z$   $[\text{M}]^+$  calc. for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$  212.09496, found 212.09440.

### 2-methyl-N-(pyridin-2-yl)benzamide **3i**

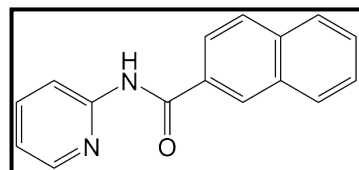
Following General Procedure A on 0.2 mmol scale. Purification by recrystallization in diethyl ether afforded 41.2 mg (97%) of the title compound **3i**.



Yellow solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37 (d,  $J$  = 8.4 Hz, 1H), 8.29 (s, 1H), 8.25 (d,  $J$  = 4.9 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.54 (d,  $J$  = 7.7 Hz, 1H), 7.38 (dd,  $J$  = 10.7, 4.3 Hz, 1H), 7.28 (d,  $J$  = 8.9 Hz, 2H), 7.07 (dd,  $J$  = 6.9, 5.4 Hz, 1H), 2.54 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 149.8, 148.1, 138.6, 136.9, 135.9, 131.6, 130.8, 127.0, 126.1, 120.2, 114.1, 20.1. **HRMS** (ESI):  $m/z$   $[\text{M}]^+$  calc. for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$  212.09496, found 212.09545.

### N-(pyridin-2-yl)-2-naphthamide **3j**

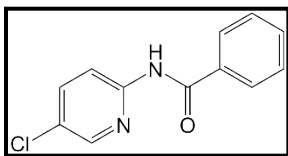
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 20.3 mg (41%) of the title compound **3j**.



White solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.21 (s, 1H), 8.50 – 8.42 (m, 2H), 8.24 (ddd,  $J$  = 4.9, 1.9, 0.9 Hz, 1H), 8.02 – 7.95 (m, 1H), 7.95 – 7.85 (m, 3H), 7.76 (ddd,  $J$  = 8.4, 7.4, 1.9 Hz, 1H), 7.63 – 7.50 (m, 2H), 7.04 (ddd,  $J$  = 7.3, 5.0, 1.0 Hz, 1H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 151.9, 147.9, 138.7, 135.2, 132.7, 131.6, 129.2, 128.8, 128.2 (2), 128.0, 127.1, 123.8, 120.0, 114.5. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}$  249.102223, found 249.102239.

### N-(5-chloropyridin-2-yl)benzamide **3l**

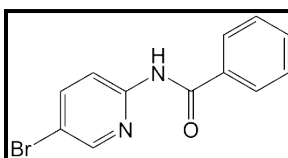
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 34.8 mg (75%) of the title compound **3l**.



Pale yellow solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (s, 1H), 8.38 (dd,  $J = 8.9, 0.5$  Hz, 1H), 8.16 (dd,  $J = 2.5, 0.5$  Hz, 1H), 7.96 – 7.84 (m, 2H), 7.70 (dd,  $J = 8.9, 2.6$  Hz, 1H), 7.57 (ddd,  $J = 6.3, 3.7, 1.4$  Hz, 1H), 7.53 – 7.45 (m, 2H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 150.1, 146.6, 138.2, 134.1, 132.6, 129.0 (2), 127.4 (2), 127.0, 115.0. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{12}\text{H}_{10}\text{ClN}_2\text{O}$  233.047413, found 233.047617.

#### **N-(5-bromopyridin-2-yl)benzamide 3m**

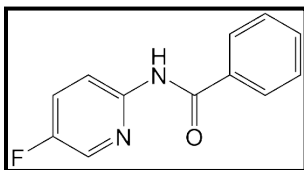
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 36.4 mg (66%) of the title compound **3m**.



Yellow solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ) 8.73 (s, 1H), 8.34 (dd,  $J = 8.9, 0.6$  Hz, 1H), 8.29 (dd,  $J = 2.4, 0.6$  Hz, 1H), 7.94 – 7.88 (m, 2H), 7.84 (dd,  $J = 8.9, 2.4$  Hz, 1H), 7.62 – 7.54 (m, 1H), 7.53 – 7.45 (m, 2H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 150.4, 148.9, 141.0, 134.1, 132.6, 129.0 (2), 127.4 (2), 115.5, 114.9. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{12}\text{H}_{10}\text{BrN}_2\text{O}$  276.996951, found 276.997101.

#### **N-(5-fluoropyridin-2-yl)benzamide 3n**

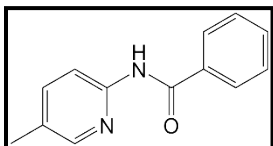
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 36.7 mg (85%) of the title compound **3n**.



White solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.76 (s, 1H), 8.47 – 8.37 (m, 1H), 8.09 (d,  $J = 3.0$  Hz, 1H), 7.97 – 7.88 (m, 2H), 7.62 – 7.43 (m, 4H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 156.6 (d,  $J = 251.3$  Hz), 148.0, 135.5 (d,  $J = 25.6$  Hz), 134.2, 132.5, 129.0 (2), 127.3 (2), 125.5 (d,  $J = 19.4$  Hz), 115.1 (d,  $J = 4.2$  Hz).  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -132.17. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{12}\text{H}_{10}\text{FN}_2\text{O}$  217.077010, found 217.077168.

#### **N-(5-methylpyridin-2-yl)benzamide 3o**

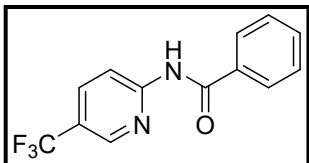
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 29.7 mg (70%) of the title compound **3o**.



White solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (d,  $J = 8.5$  Hz, 1H), 8.04 (dd,  $J = 1.6, 0.8$  Hz, 1H), 7.95 – 7.88 (m, 2H), 7.55 (ddd,  $J = 6.2, 2.8, 1.4$  Hz, 2H), 7.50 – 7.44 (m, 2H), 2.29 (s, 3H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  165.81, 149.6, 147.9, 139.2, 134.6, 132.2, 129.4, 128.9 (2), 127.4 (2), 113.9, 18.0. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$  213.102171, found 213.102239.

#### **N-(5-trifluoromethylpyridin-2-yl)benzamide 3q**

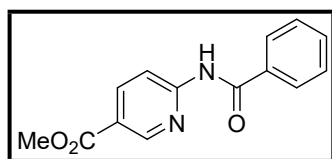
Following General Procedure A on 0.2 mmol scale. Purification by recrystallization in diethyl ether afforded 27.4 mg (51%) of the title compound **3q**.



Brown solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.72 (s, 1H), 8.57 (d,  $J = 0.9$  Hz, 1H), 8.54 (d,  $J = 8.8$  Hz, 1H), 7.99 (dd,  $J = 8.8, 2.4$  Hz, 1H), 7.93 (dd,  $J = 5.2, 3.3$  Hz, 2H), 7.64 – 7.59 (m, 1H), 7.56 – 7.51 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 154.2, 145.6, 145.6, 145.5, 145.5, 136.1, 136.0, 136.0, 136.0, 133.8, 132.9, 129.2, 127.4, 122.3, 113.5.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.88. **HRMS** (ESI):  $m/z$   $[\text{M}]^+$  calc. for  $\text{C}_{13}\text{H}_9\text{F}_3\text{N}_2\text{O}$  266.06670, found 266.06742.

#### **N-(5-methylesterpyridin-2-yl)benzamide 3r**

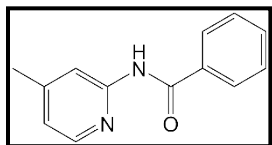
Following General Procedure A on 0.2 mmol scale. Purification by recrystallization in diethyl ether afforded 30.6 mg (60%) of the title compound **3r**.



Yellow solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.96 – 8.92 (m, 1H), 8.73 (s, 1H), 8.47 (dd,  $J = 8.7, 0.5$  Hz, 1H), 8.36 (dd,  $J = 8.7, 2.2$  Hz, 1H), 7.93 (dd,  $J = 5.3, 3.4$  Hz, 2H), 7.60 (ddd,  $J = 6.5, 3.8, 1.2$  Hz, 1H), 7.56 – 7.50 (m, 2H), 3.95 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 165.6, 154.6, 150.3, 140.1, 133.9, 132.8, 129.1, 127.4, 122.4, 113.1, 52.4. **HRMS** (ESI):  $m/z$   $[\text{M}]^+$  calc. for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$  256.08479, found 256.08502.

#### **N-(4-methylpyridin-2-yl)benzamide 3s**

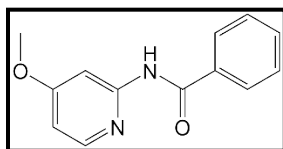
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 38.1 mg (90%) of the title compound **3s**.



White solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.02 (s, 1H), 8.30 – 8.19 (m, 1H), 8.02 (d,  $J = 5.1$  Hz, 1H), 7.98 – 7.89 (m, 2H), 7.59 – 7.51 (m, 1H), 7.47 (ddt,  $J = 8.4, 6.8, 1.5$  Hz, 2H), 6.86 (ddd,  $J = 5.2, 1.4, 0.7$  Hz, 1H), 2.39 (s, 3H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.0, 151.8, 150.2, 147.5, 134.6, 132.3, 128.9 (2), 127.4 (2), 121.2, 114.9, 21.6. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}$  213.102002, found 213.102239.

#### **N-(4-methoxypyridin-2-yl)benzamide 3t**

Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 35.1 mg (77%) of the title compound **3t**.

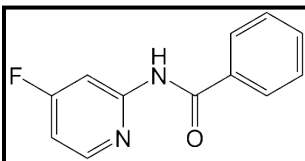


White solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ) 9.14 (s, 1H), 8.05 (d,  $J = 2.4$  Hz, 1H), 7.96 – 7.89 (m, 3H), 7.62 – 7.49 (m, 1H), 7.49 – 7.43 (m, 2H), 6.58 (dd,  $J = 5.8, 2.4$  Hz, 1H), 3.90 (s, 3H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.7, 166.2, 153.5, 148.6, 134.5, 132.3, 128.9 (2), 127.4 (2), 108.0, 99.0, 55.5. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}_2$  229.097367, found 229.097154.

#### **N-(4-fluoropyridin-2-yl)benzamide 3u**

Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 39.3 mg (91%) of the

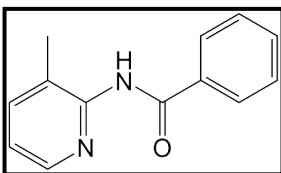
title compound **3u**.



White solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.01 (s, 1H), 8.21 (dd,  $J = 11.2$ , 2.3 Hz, 1H), 8.18 – 8.10 (m, 1H), 7.95 – 7.87 (m, 2H), 7.58 (ddd,  $J = 6.4$ , 3.7, 1.3 Hz, 1H), 7.49 (t,  $J = 7.3$  Hz, 2H), 6.83 – 6.75 (m, 1H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1 (d,  $J = 260.0$  Hz), 166.1, 154.1 (d,  $J = 12.0$  Hz), 150.0 (d,  $J = 9.1$  Hz), 134.1, 132.6, 129.0 (2), 127.4 (2), 108.2 (d,  $J = 18.1$  Hz), 102.4 (d,  $J = 24.1$  Hz).  $^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -98.99. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{12}\text{H}_9\text{FN}_2\text{O}$  217.077308, found 217.077168.

#### **N-(3-methylpyridin-2-yl)benzamide 3v**

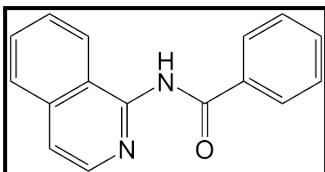
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 34.6 mg (82%) of the title compound **3v**.



White solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.92 (s, 1H), 8.22 (d,  $J = 4.1$  Hz, 1H), 8.01 – 7.89 (m, 2H), 7.60 (dd,  $J = 7.5$ , 0.9 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.45 (dd,  $J = 10.3$ , 4.7 Hz, 2H), 7.12 (dd,  $J = 7.5$ , 4.8 Hz, 1H), 2.33 (s, 3H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 145.5, 140.2, 138.0, 134.2, 132.2, 129.4, 128.8 (2), 127.8 (2), 121.9, 18.6. **HRMS** (ESI):  $m/z$   $[\text{M}]$  calc. for  $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}$ , 212.1070. found 212.1070.

#### **N-(isoquinolin-1-yl)benzamide 4a**

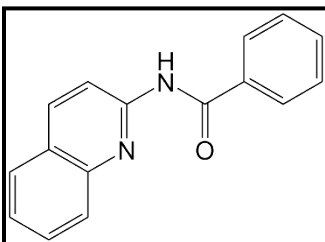
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 12.4 mg (25%) of the title compound **4a**.



Pale yellow solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.00 (s, 1H), 8.58 (d,  $J = 9.0$  Hz, 1H), 8.21 (d,  $J = 8.9$  Hz, 1H), 8.02 – 7.94 (m, 2H), 7.80 (dd,  $J = 13.3$ , 4.9 Hz, 2H), 7.65 (ddd,  $J = 8.4$ , 6.9, 1.5 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.52 – 7.40 (m, 3H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 151.3, 146.7, 138.8, 134.3, 132.5, 130.1, 128.9 (2), 127.7, 127.5 (2), 127.4, 126.5, 125.3, 114.6. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}$ , 249.1022. found 249.1023.

#### **N-(quinolin-2-yl)benzamide 4b**

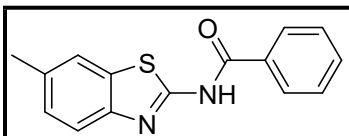
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 12.4 mg (25%) of the title compound **4b**.



Pale yellow solid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.97 (s, 1H), 8.58 (d,  $J = 9.0$  Hz, 1H), 8.21 (d,  $J = 8.9$  Hz, 1H), 8.01 – 7.94 (m, 2H), 7.80 (dd,  $J = 13.5$ , 4.9 Hz, 2H), 7.66 (ddd,  $J = 8.4$ , 6.9, 1.5 Hz, 1H), 7.61 – 7.50 (m, 2H), 7.50 – 7.40 (m, 2H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 151.3, 146.7, 138.8, 134.3, 132.5, 130.2, 128.9 (2), 127.7, 127.5 (2), 127.4, 126.5, 125.4, 114.6. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}$ , 249.1022. found 249.1023.

#### **N-(6-Methyl-2-benzothiazolyl)benzamide 4c**

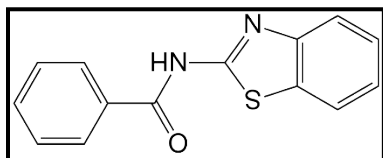
Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 16.0 mg (30%) of the title compound **4c**.



Yellow solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.85 (s, 1H), 8.02 – 7.95 (m, 2H), 7.63 (s, 1H), 7.58 – 7.52 (m, 1H), 7.40 (t,  $J = 7.8$  Hz, 2H), 7.10 – 7.00 (m, 2H), 2.44 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.1, 159.1, 145.8, 134.1, 133.1, 132.3, 132.2, 129.1 (2), 128.1, 127.7 (2), 121.3, 120.4, 21.6. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{15}\text{H}_{13}\text{N}_2\text{OS}$ , 269.0743. found 269.0743.

#### **N-(benzo[d]thiazol-2-yl)benzamide 4d**

Following General Procedure A on 0.2 mmol scale. Purification by silica gel column chromatography (100% Cyclohexane to 6:4 Cyclohexane/EtOAc) afforded 8.6 mg (17%) of the title compound **4d**.



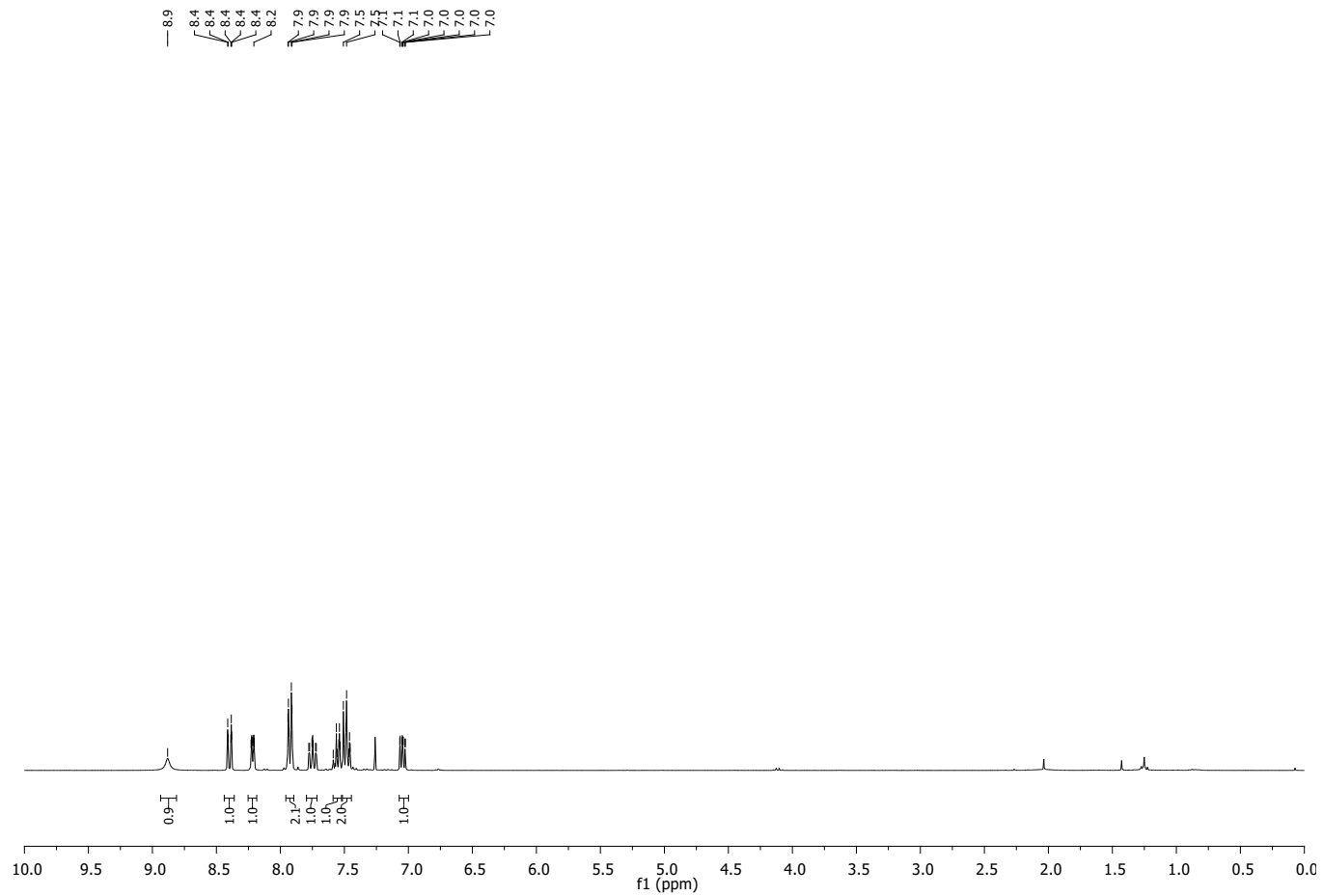
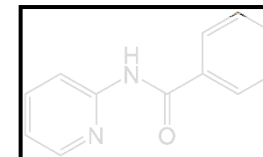
Yellow solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.55 (s, 1H), 7.98 (d,  $J = 7.7$  Hz, 2H), 7.89 – 7.78 (m, 1H), 7.54 (t,  $J = 7.4$  Hz, 1H), 7.40 (t,  $J = 7.7$  Hz, 2H), 7.26 (dd,  $J = 8.6, 4.4$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.0, 159.7, 148.0, 133.2, 132.2, 132.1, 129.2 (2), 128.0 (2), 126.2, 124.1, 121.5, 120.9. **HRMS** (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calc. for  $\text{C}_{14}\text{H}_{11}\text{N}_2\text{OS}$ , 255.0587. found 255.0586.



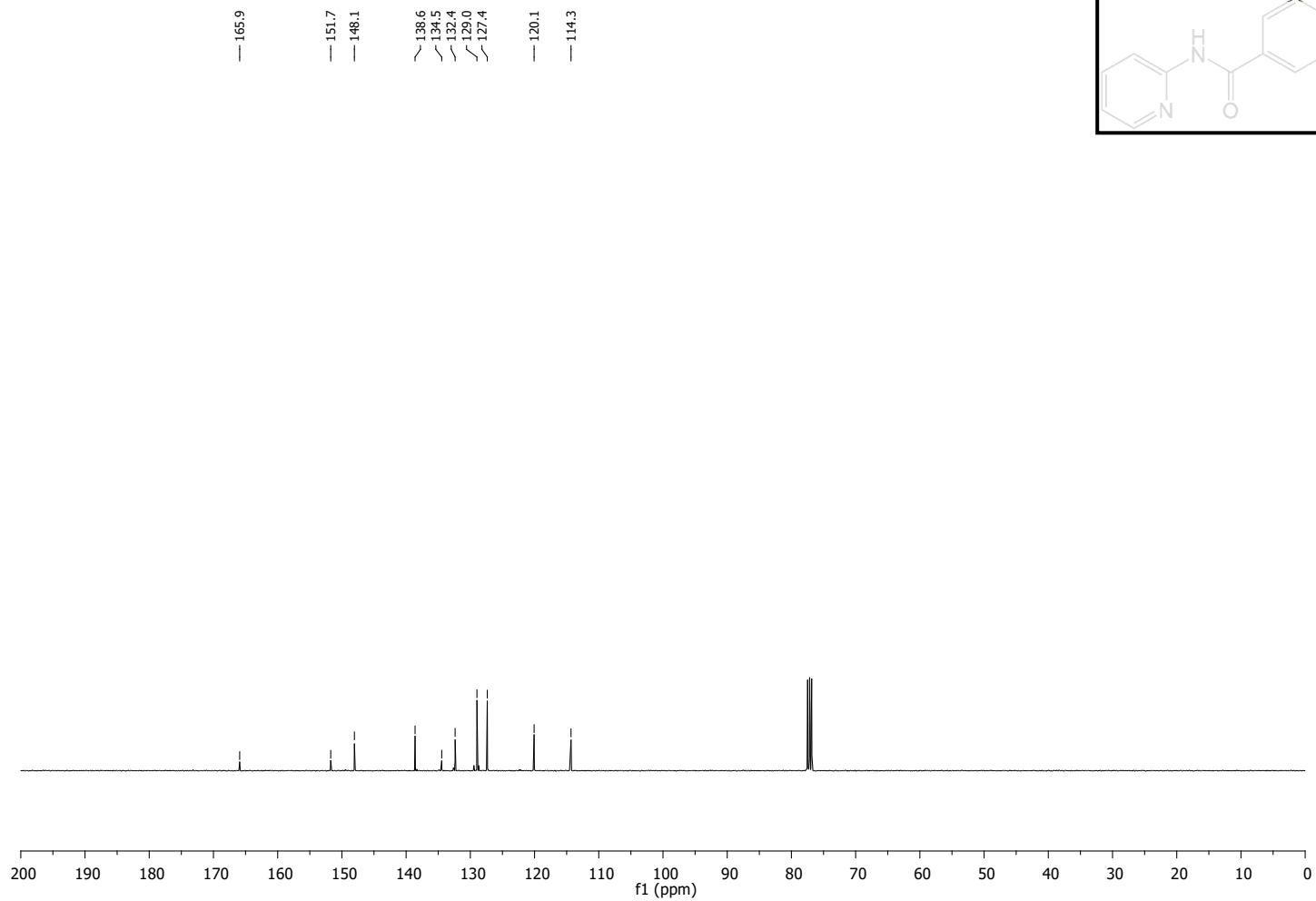
IX. Copies of NMR spectra

N-(pyridin-2-yl)benzamide 3a

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

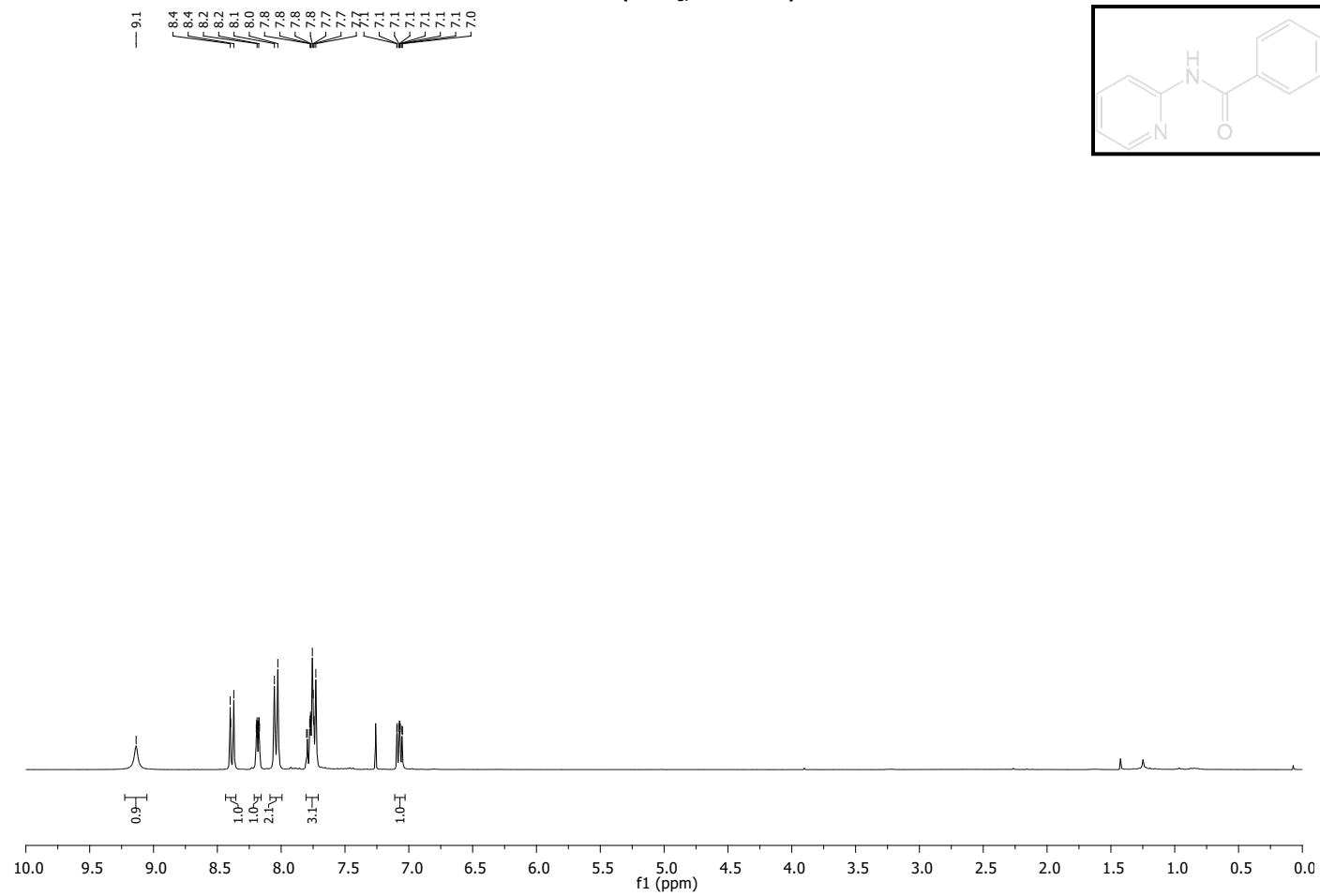
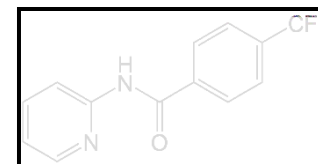


**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)**



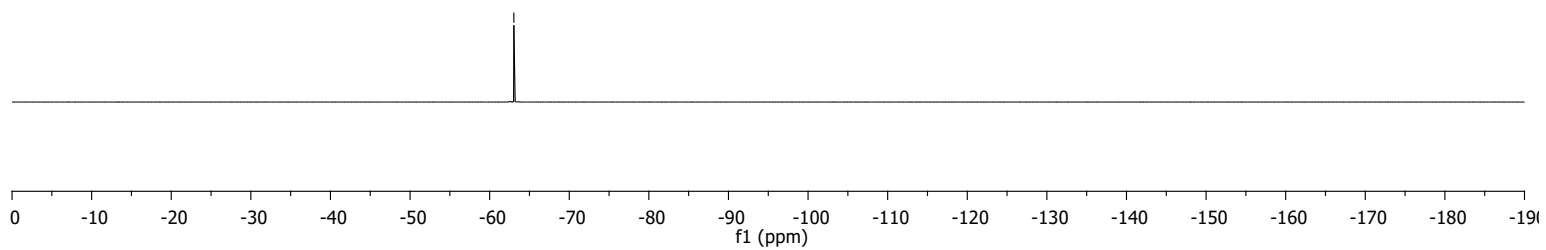
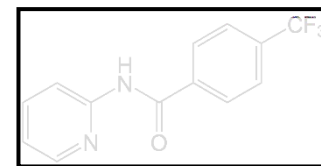
N-(pyridin-2-yl)-4-(trifluoromethyl)benzamide 3b

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

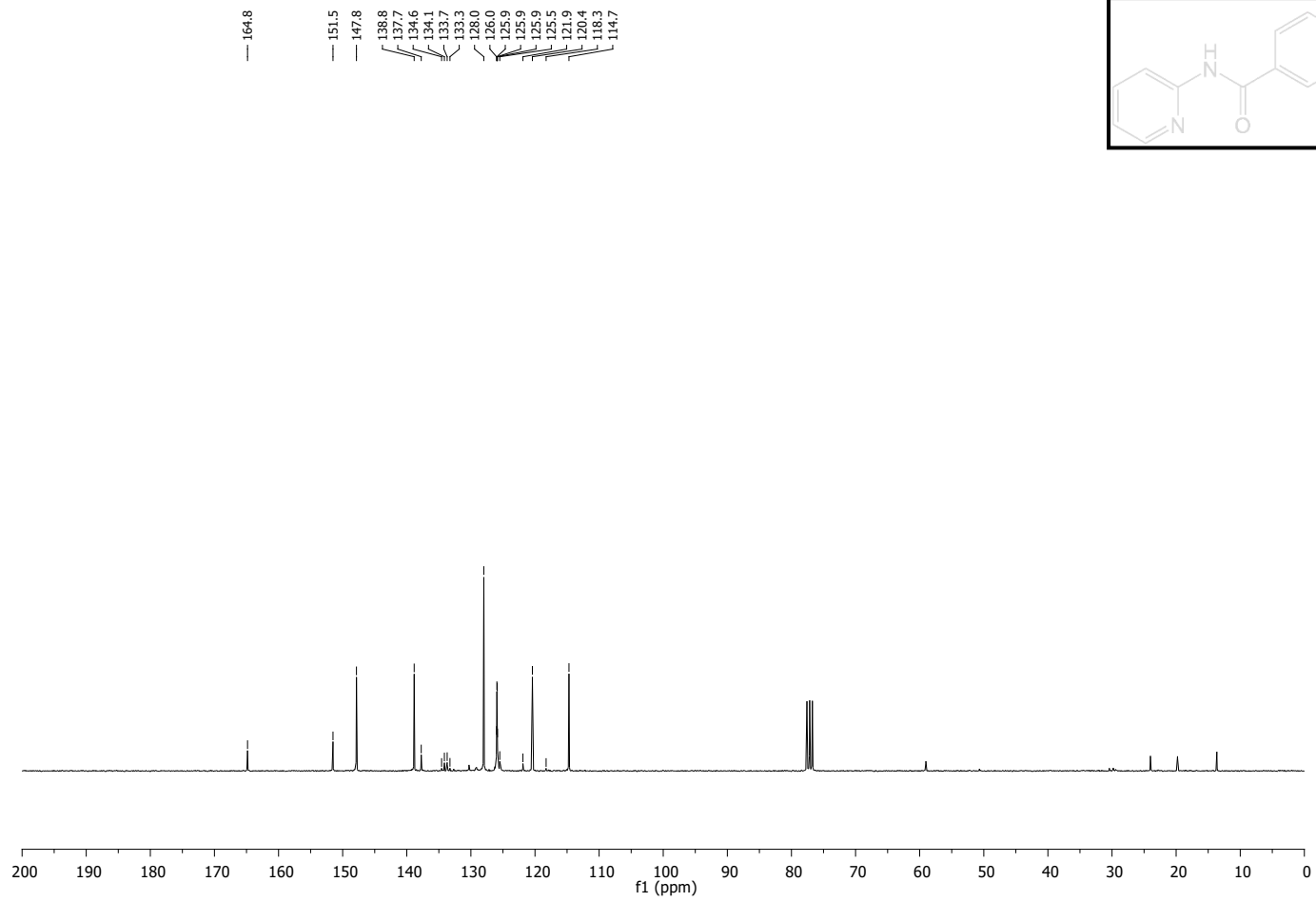
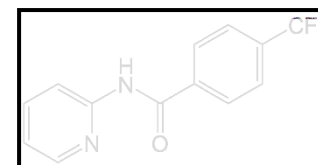


<sup>19</sup>F NMR (CDCl<sub>3</sub>, 75 MHz)

— -63.0

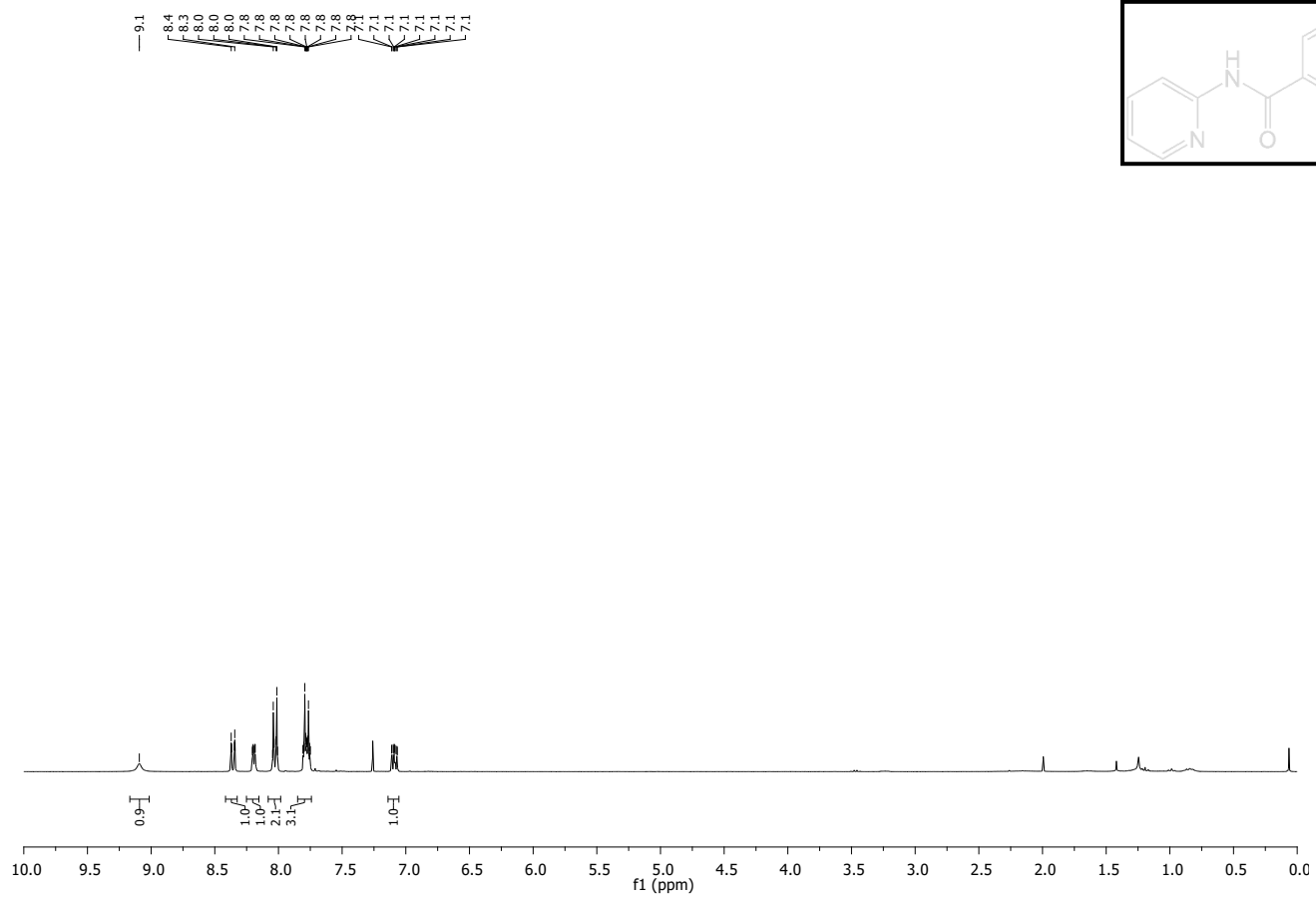


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)



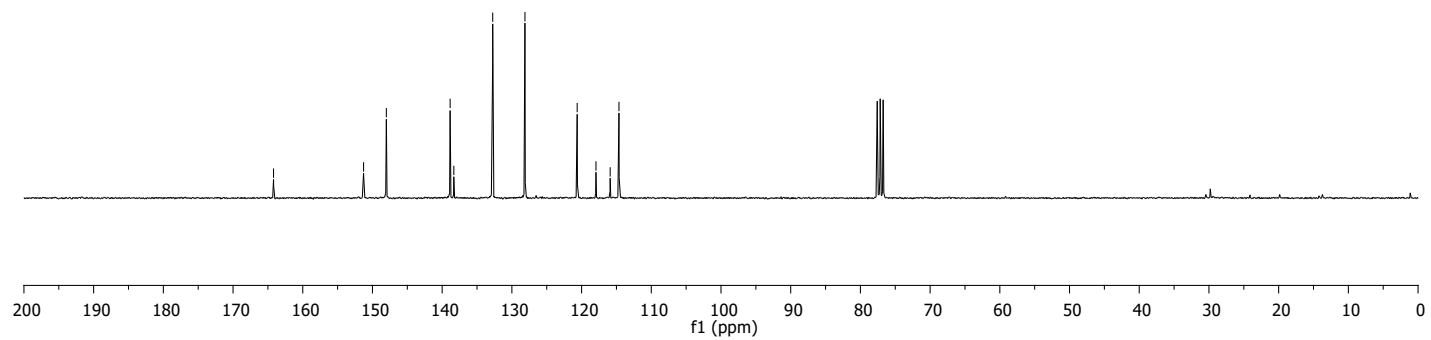
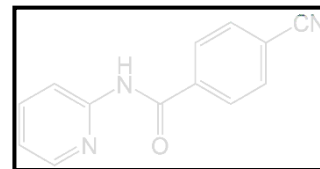
4-cyano-N-(pyridin-2-yl)benzamide 3c

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)



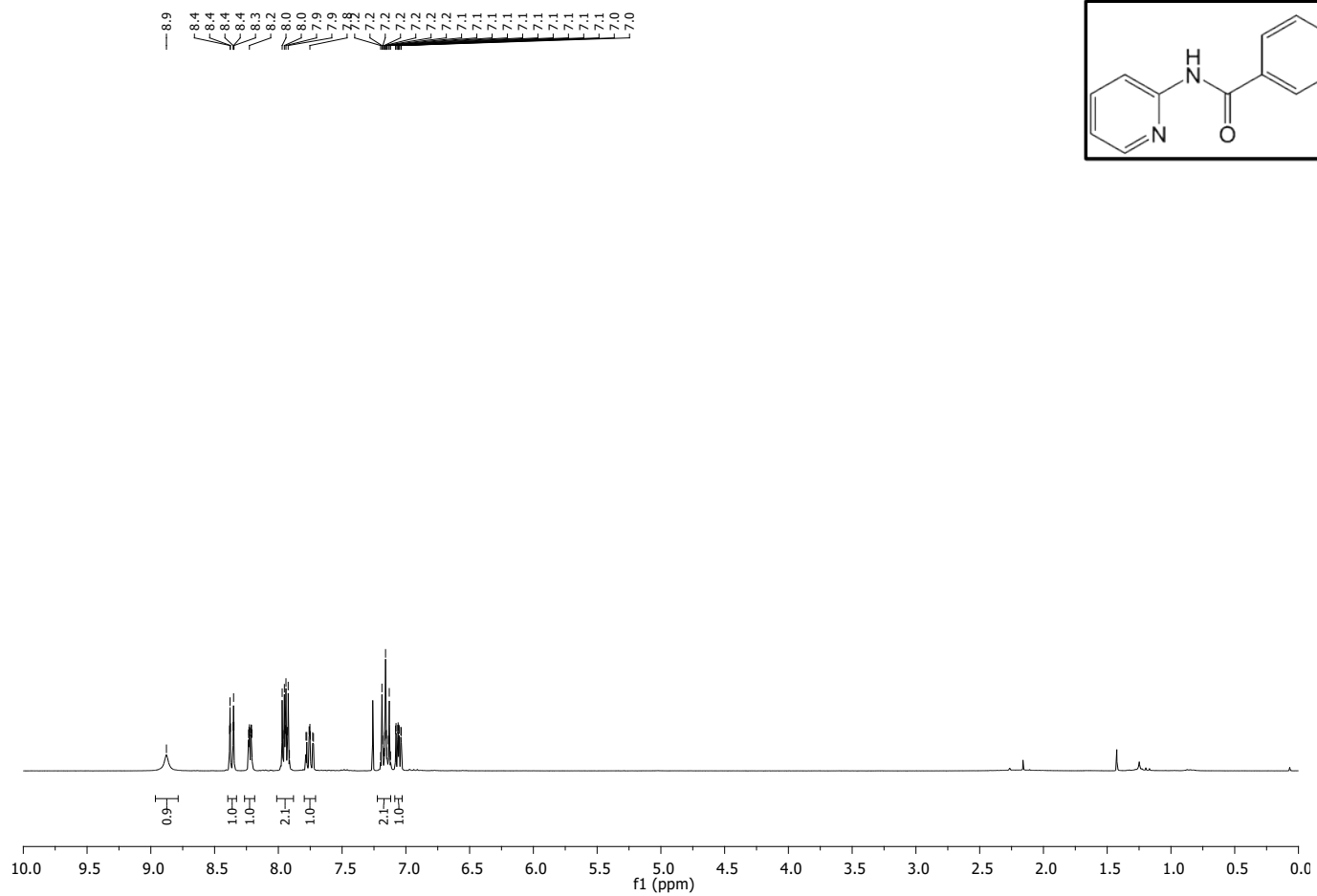
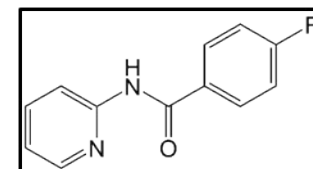
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz)

— 164.2  
— 151.3  
— 148.0  
— 138.9  
— 136.3  
— 132.8  
— 128.1  
— 120.6  
— 117.9  
— 115.9  
— 114.6



4-fluoro-N-(pyridin-2-yl)benzamide 3d

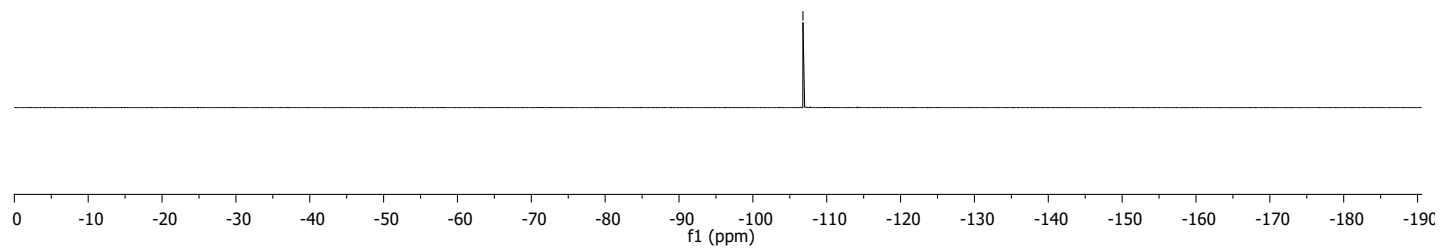
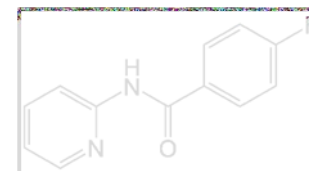
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)





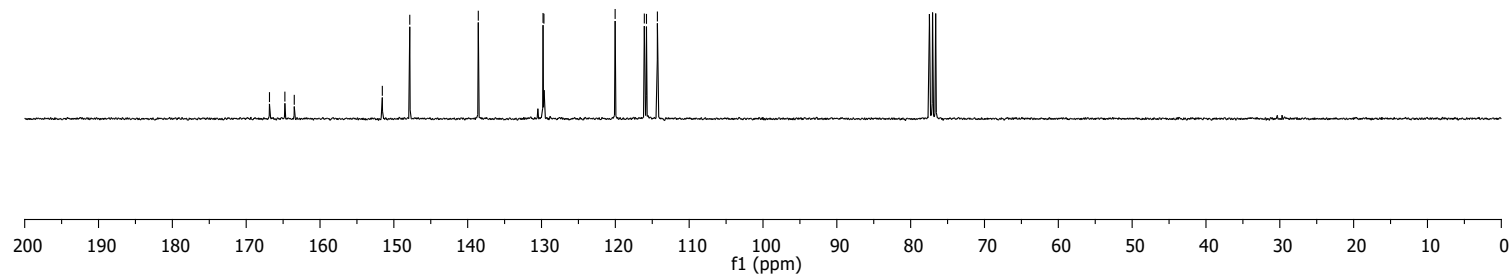
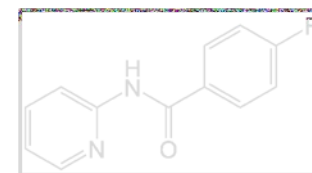
<sup>19</sup>F NMR (CDCl<sub>3</sub>, 300 MHz)

106.8



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

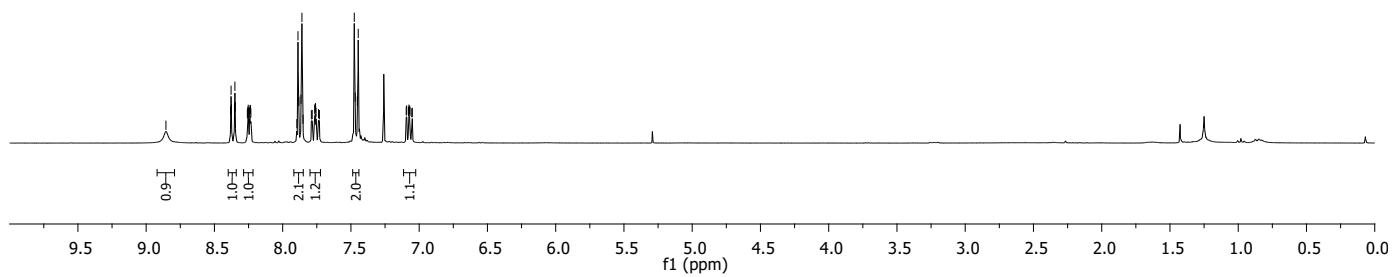
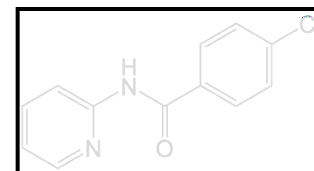
166.8  
164.8  
163.5  
151.6  
147.8  
138.6  
129.8  
129.7  
120.0  
116.1  
115.8  
114.3



4-chloro-N-(pyridin-2-yl)benzamide 3e

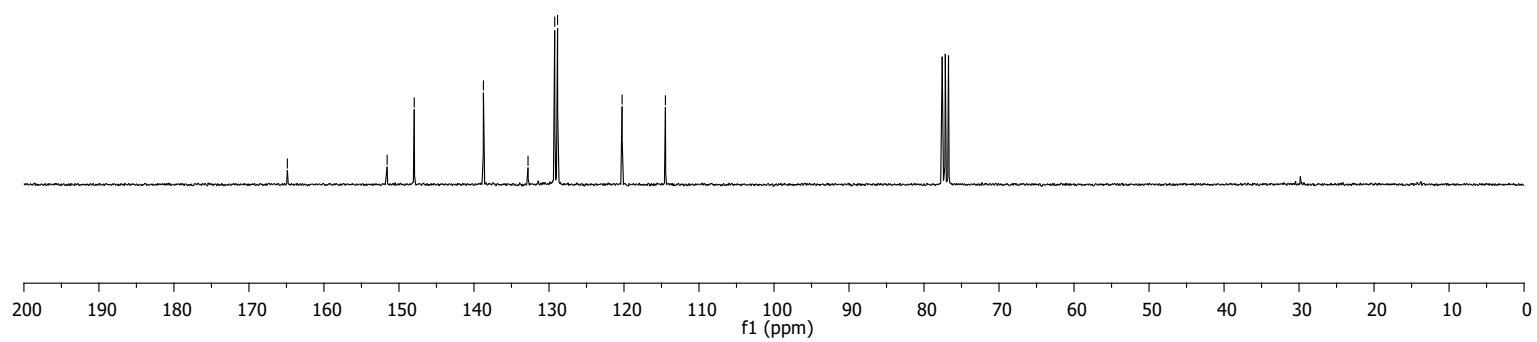
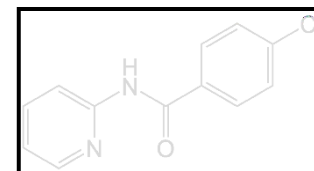
$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)

8.9  
8.4  
8.4  
8.3  
8.3  
7.9  
7.9  
7.5  
7.4  
7.1  
7.1  
7.1  
7.1  
7.1  
7.1  
7.1



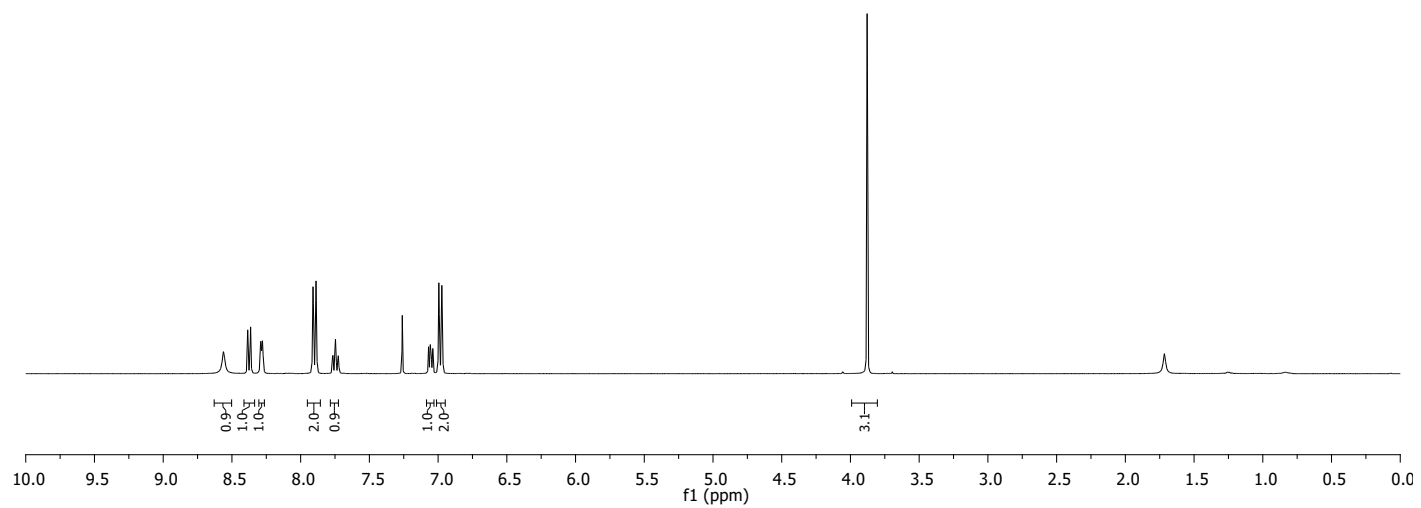
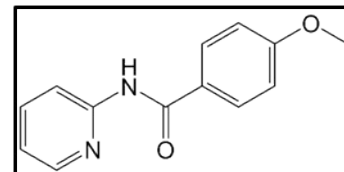
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz)

— 164.9  
— 151.6  
— 148.0  
— 138.7  
— 132.8  
— 129.2  
— 129.0  
— 128.9  
— 120.3  
— 114.5

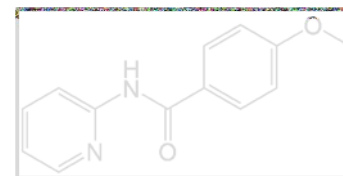
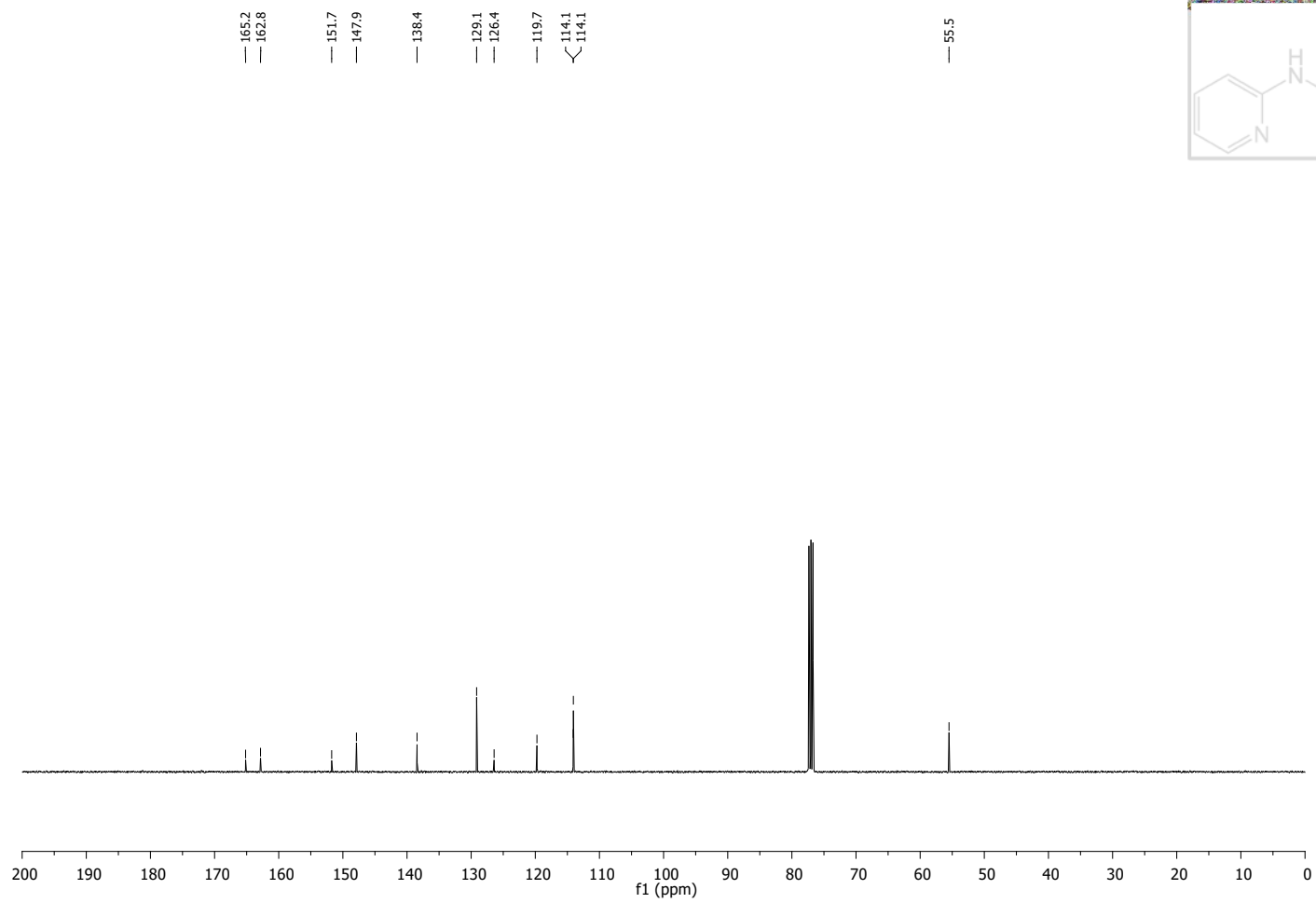


4-methoxy-N-(pyridin-2-yl)benzamide 3f

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz)

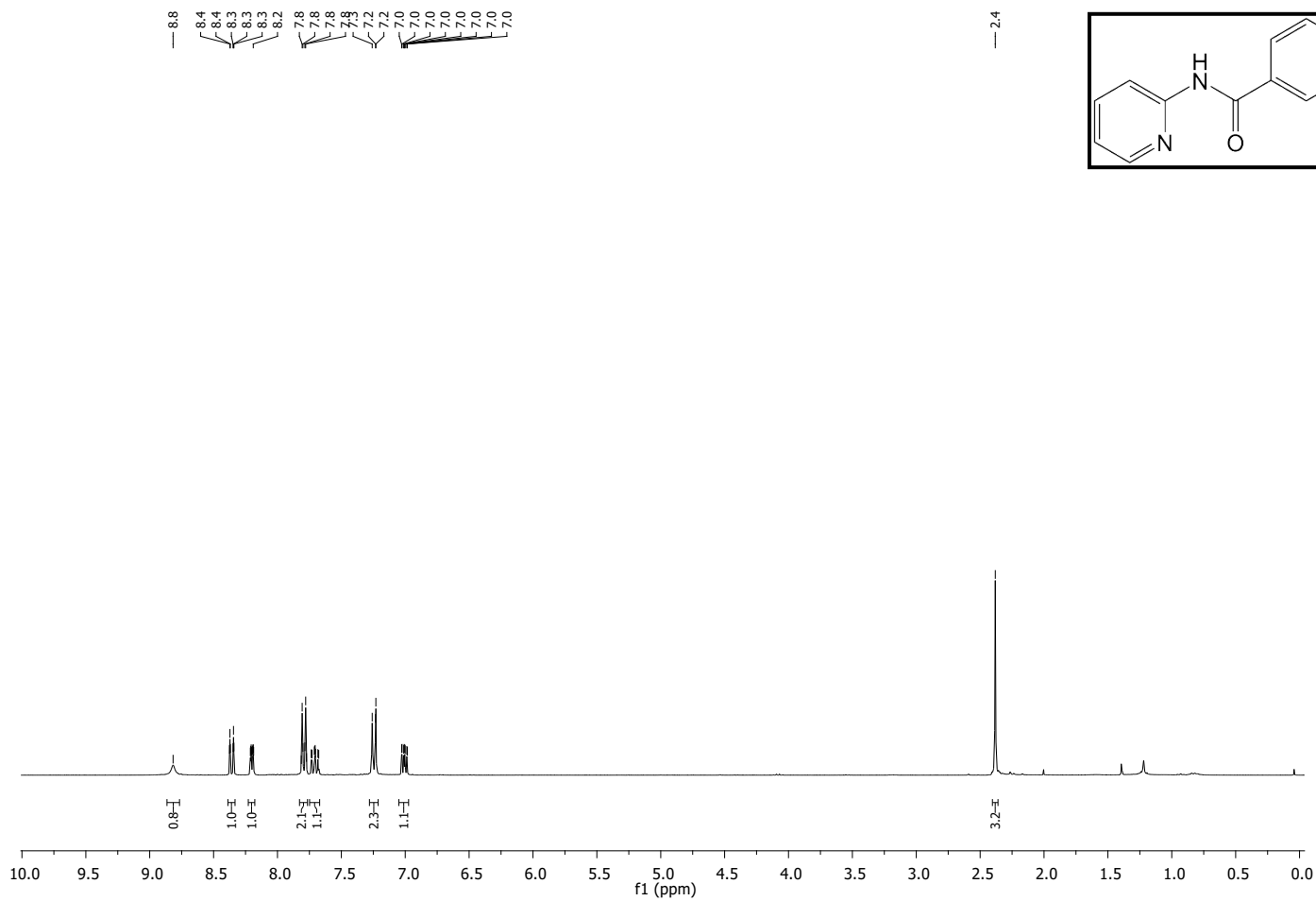


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)



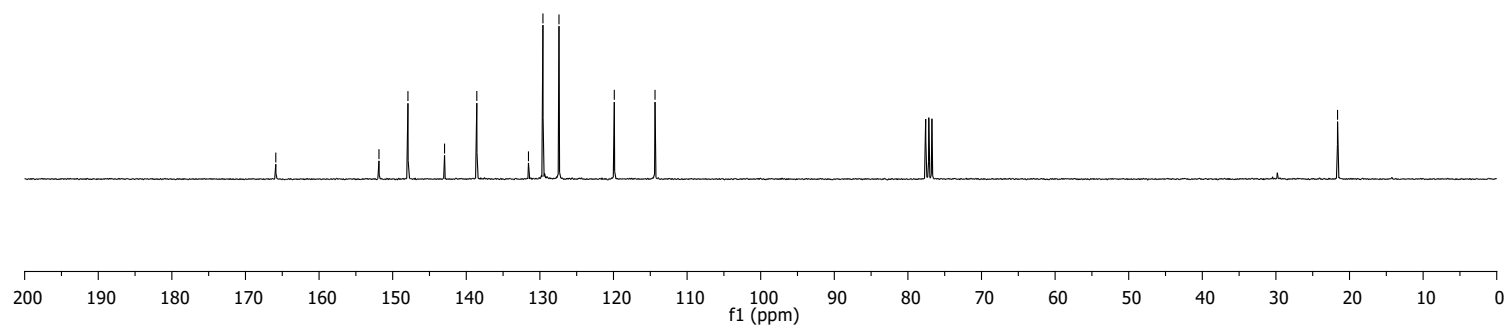
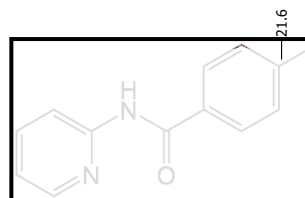
4-methyl-N-(pyridin-2-yl)benzamide 3g

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

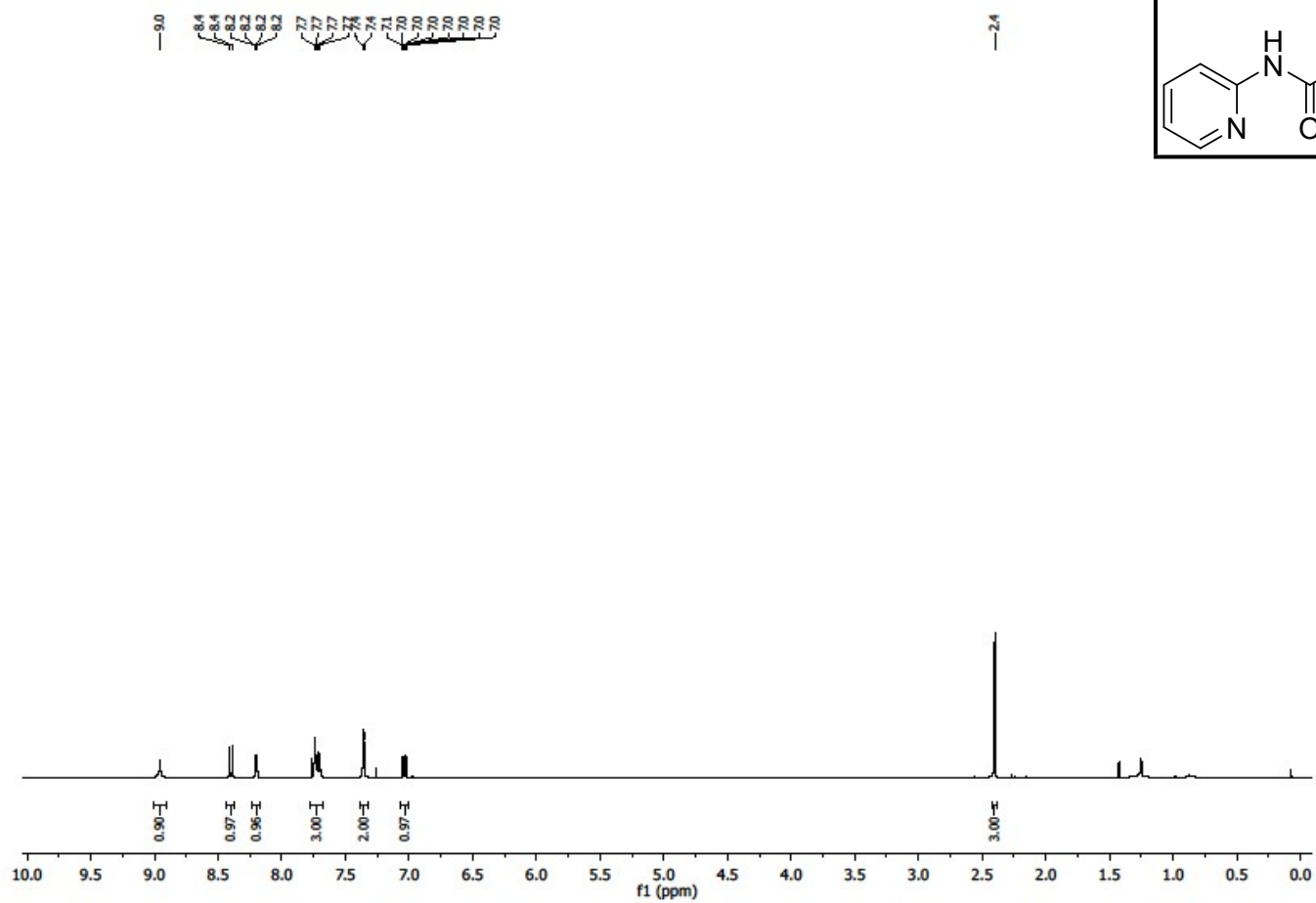
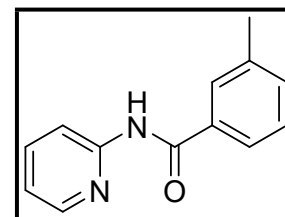
165.9  
151.9  
147.9  
143.0  
138.6  
131.5  
129.6  
127.4  
119.9  
114.4



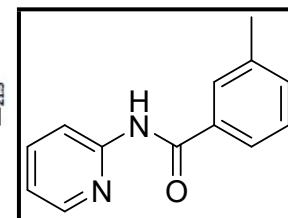
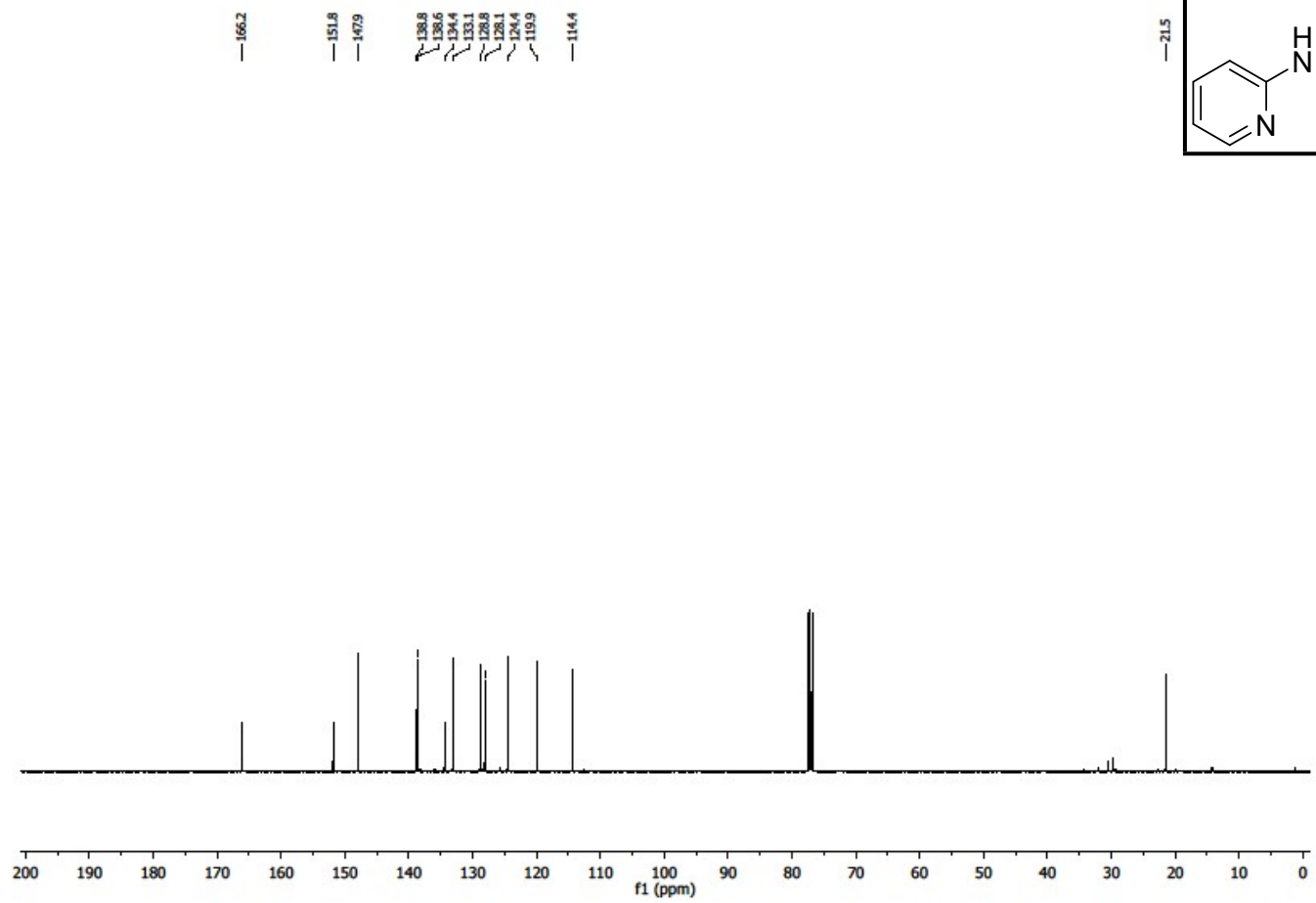


3-methyl-N-(pyridin-2-yl)benzamide 3h

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)

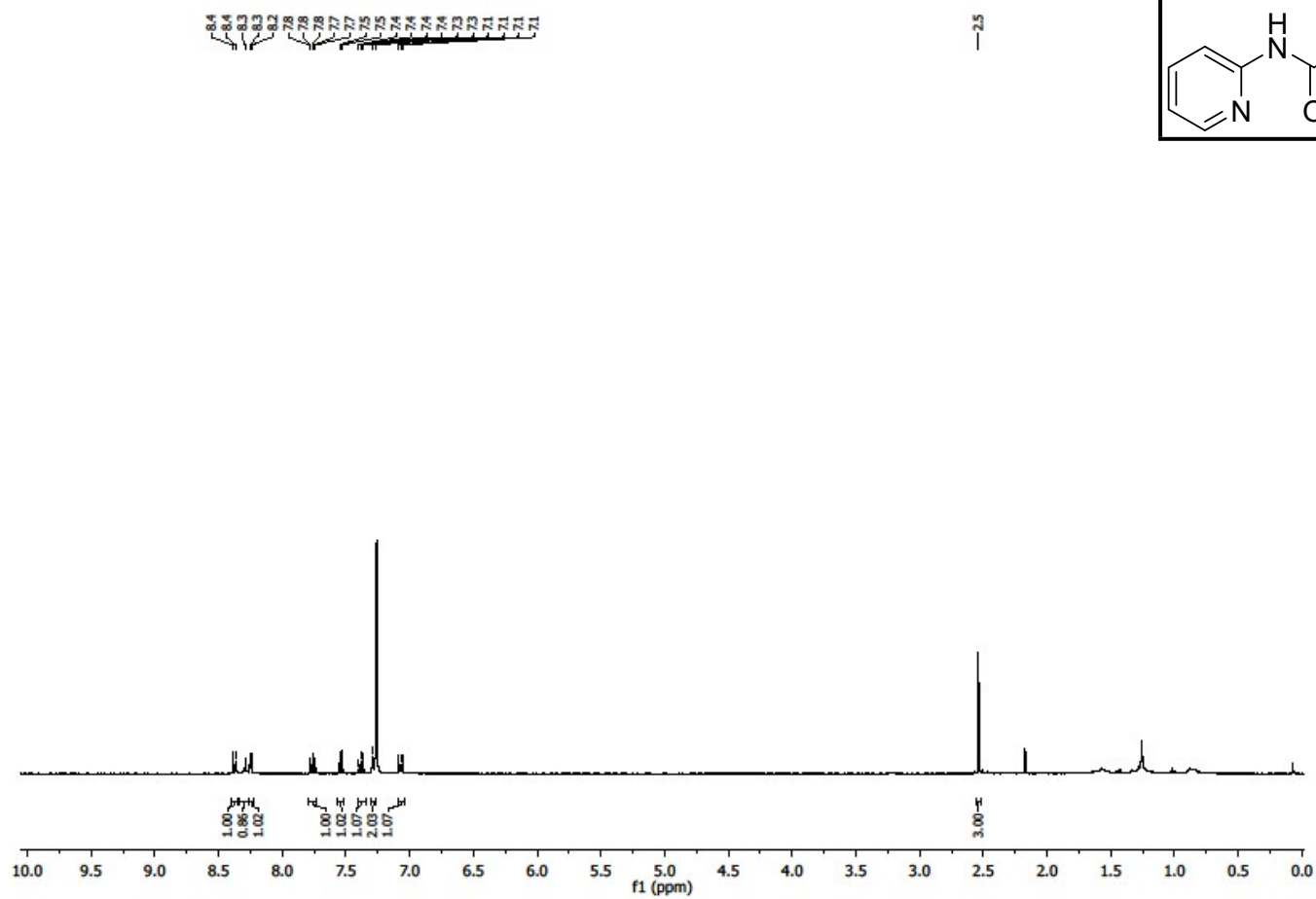
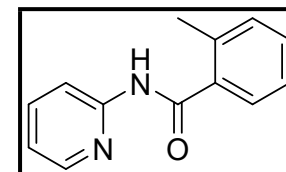


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz)

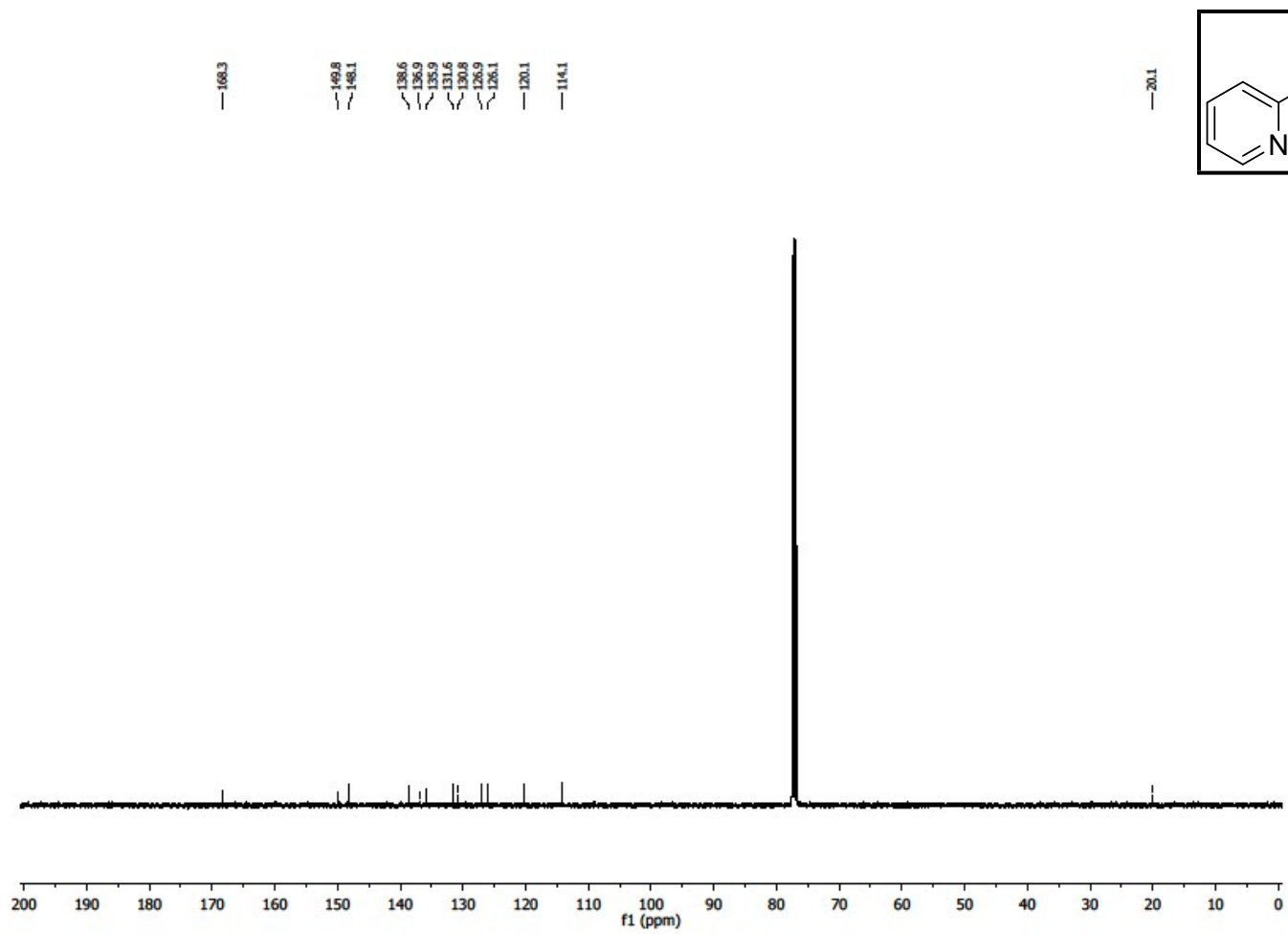


2-methyl-N-(pyridin-2-yl)benzamide 3i

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)

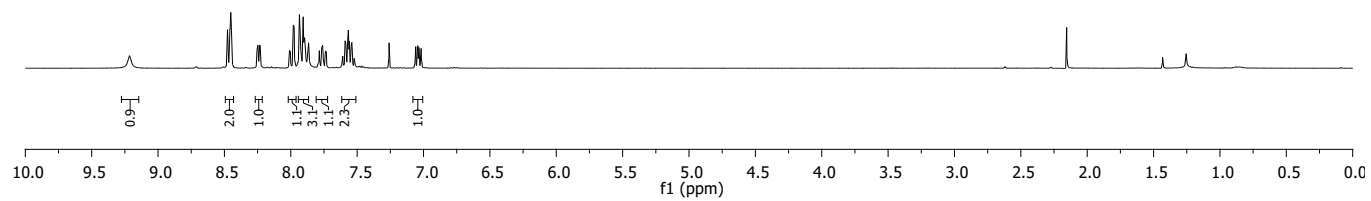
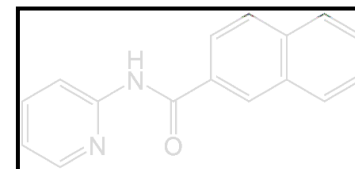


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz)

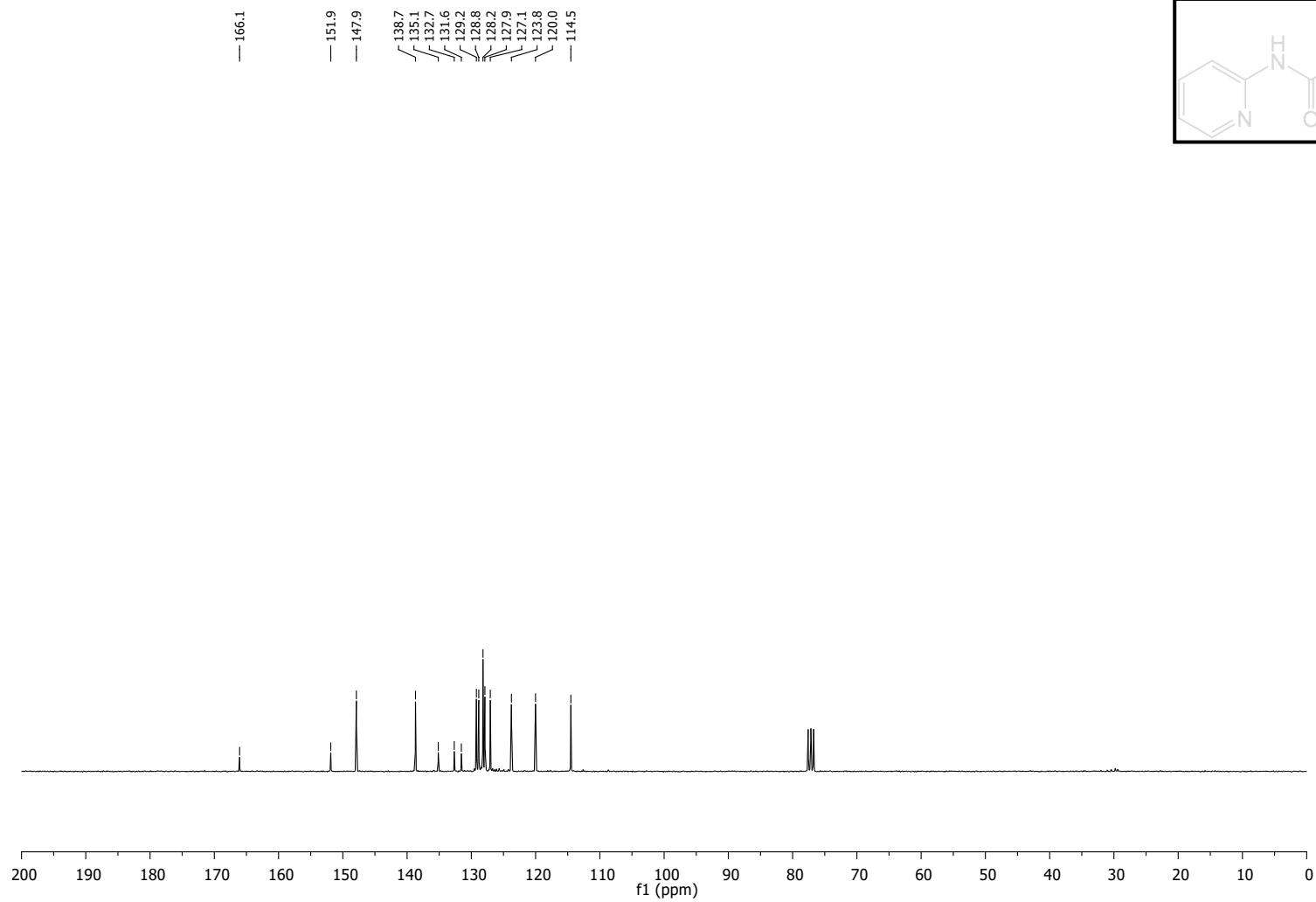
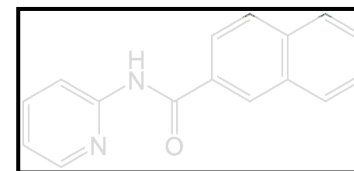


N-(pyridin-2-yl)-2-naphthamide 3j

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

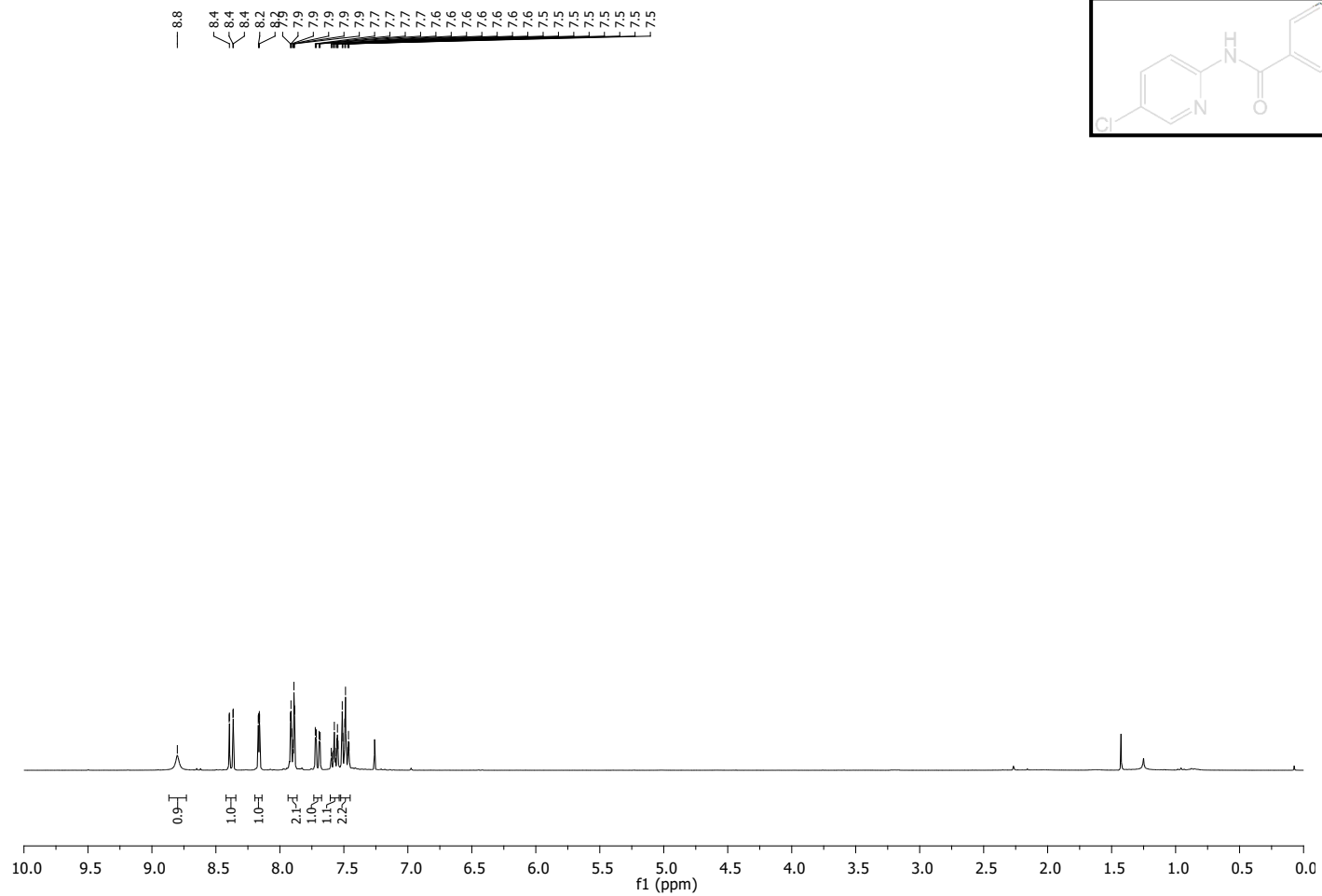
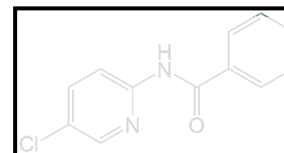


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

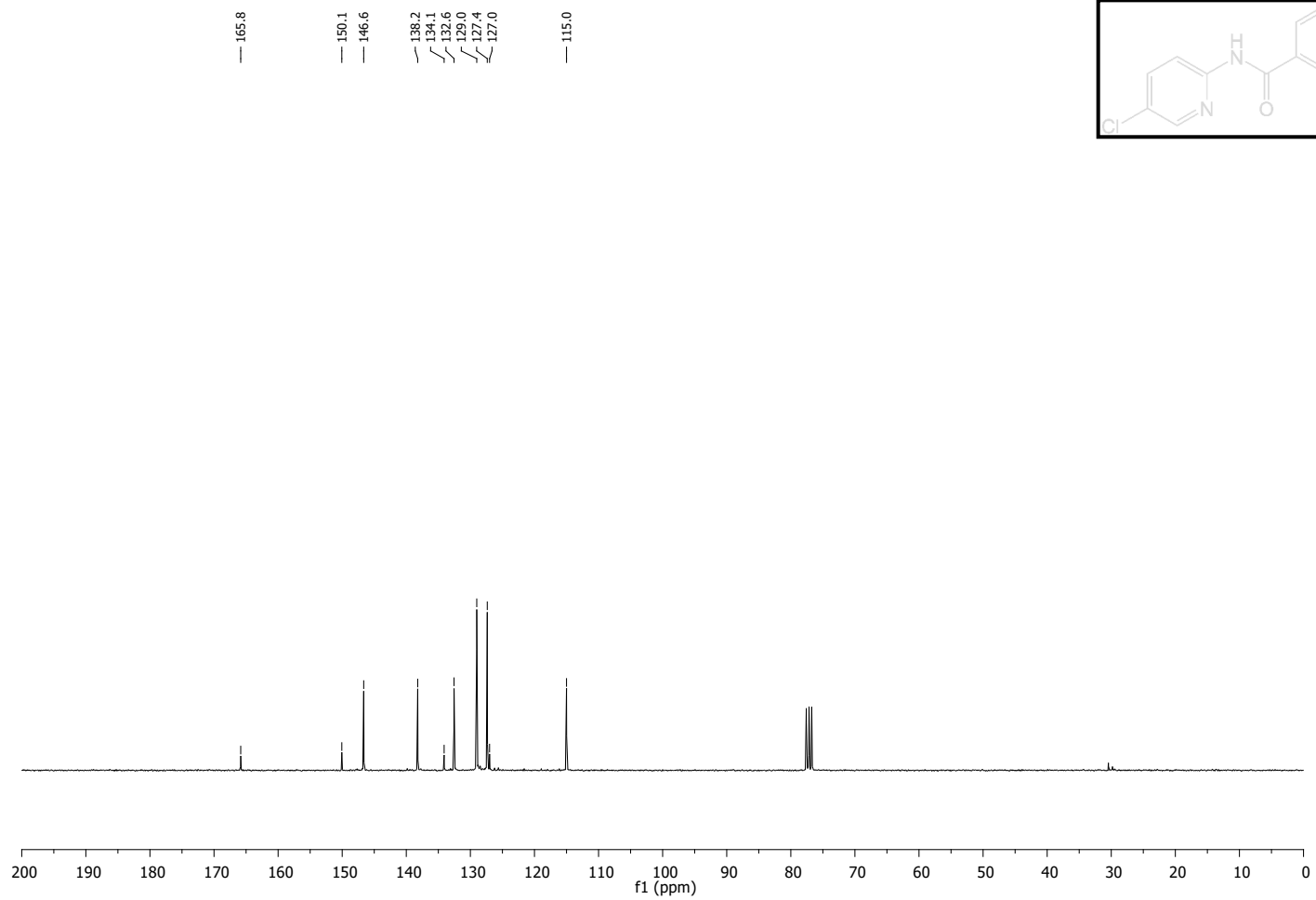


N-(5-chloropyridin-2-yl)benzamide 3I

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)



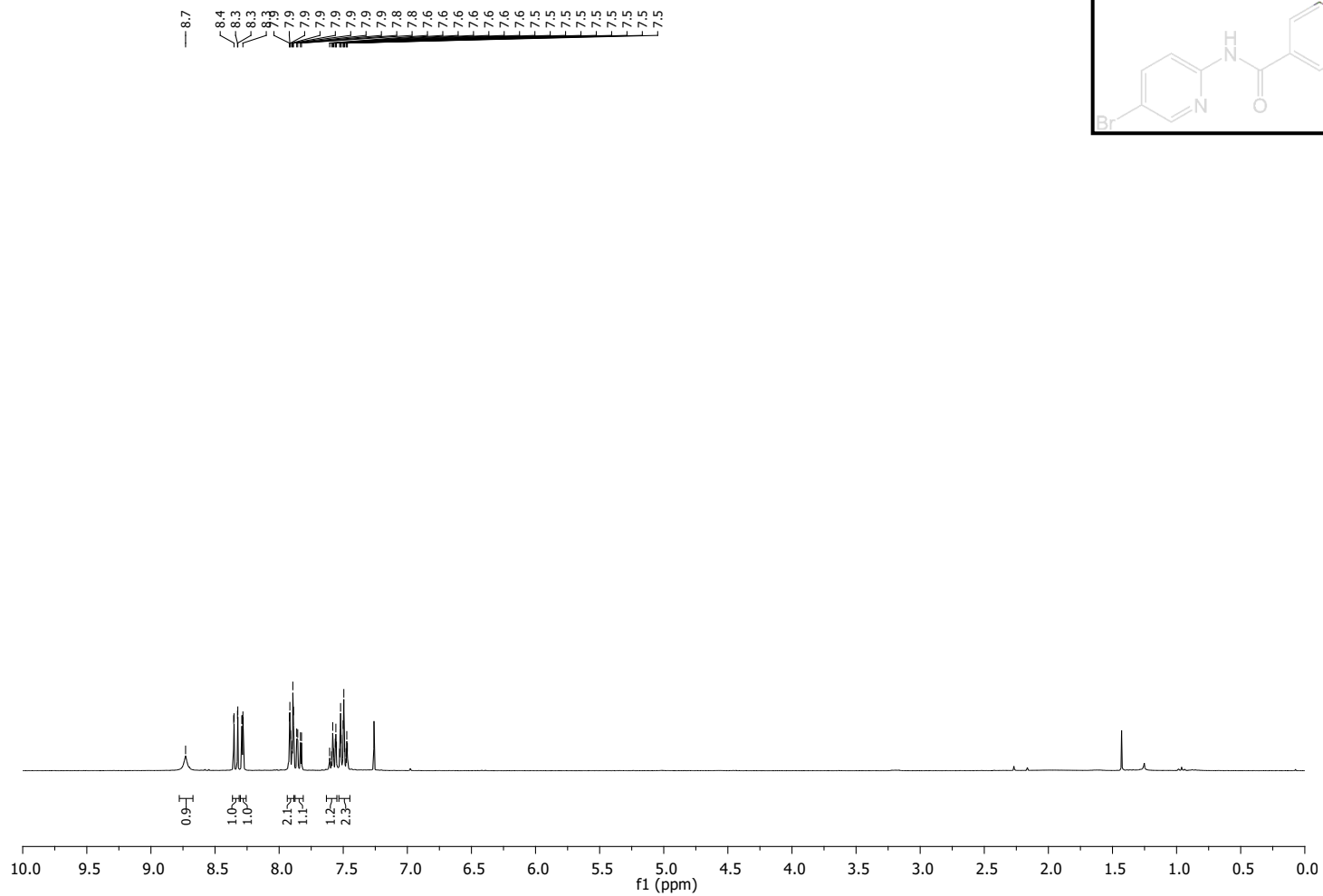
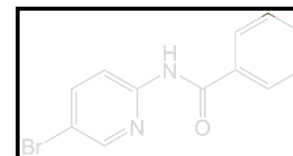
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)



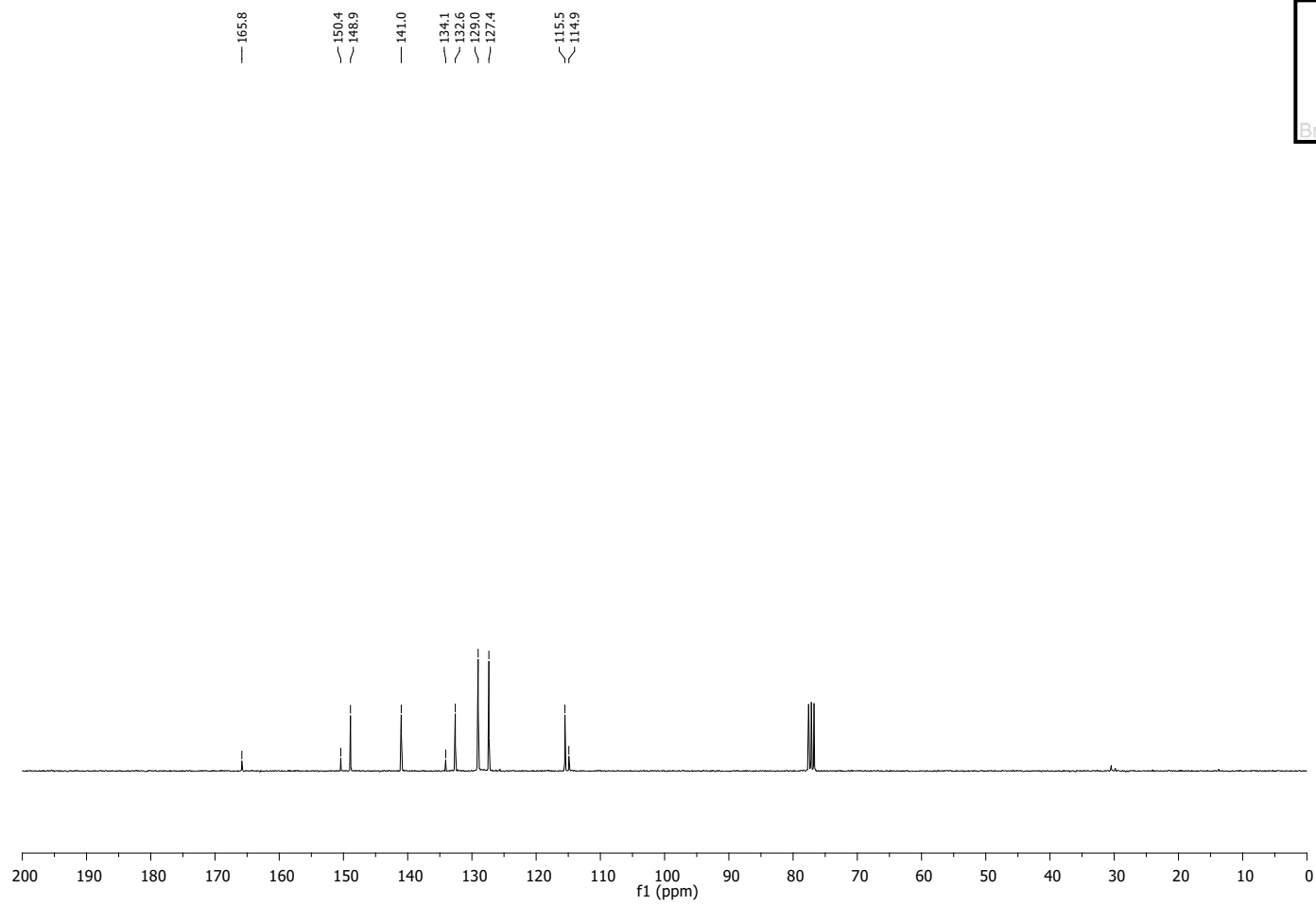
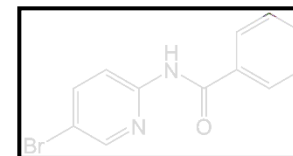


N-(5-bromopyridin-2-yl)benzamide 3m

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

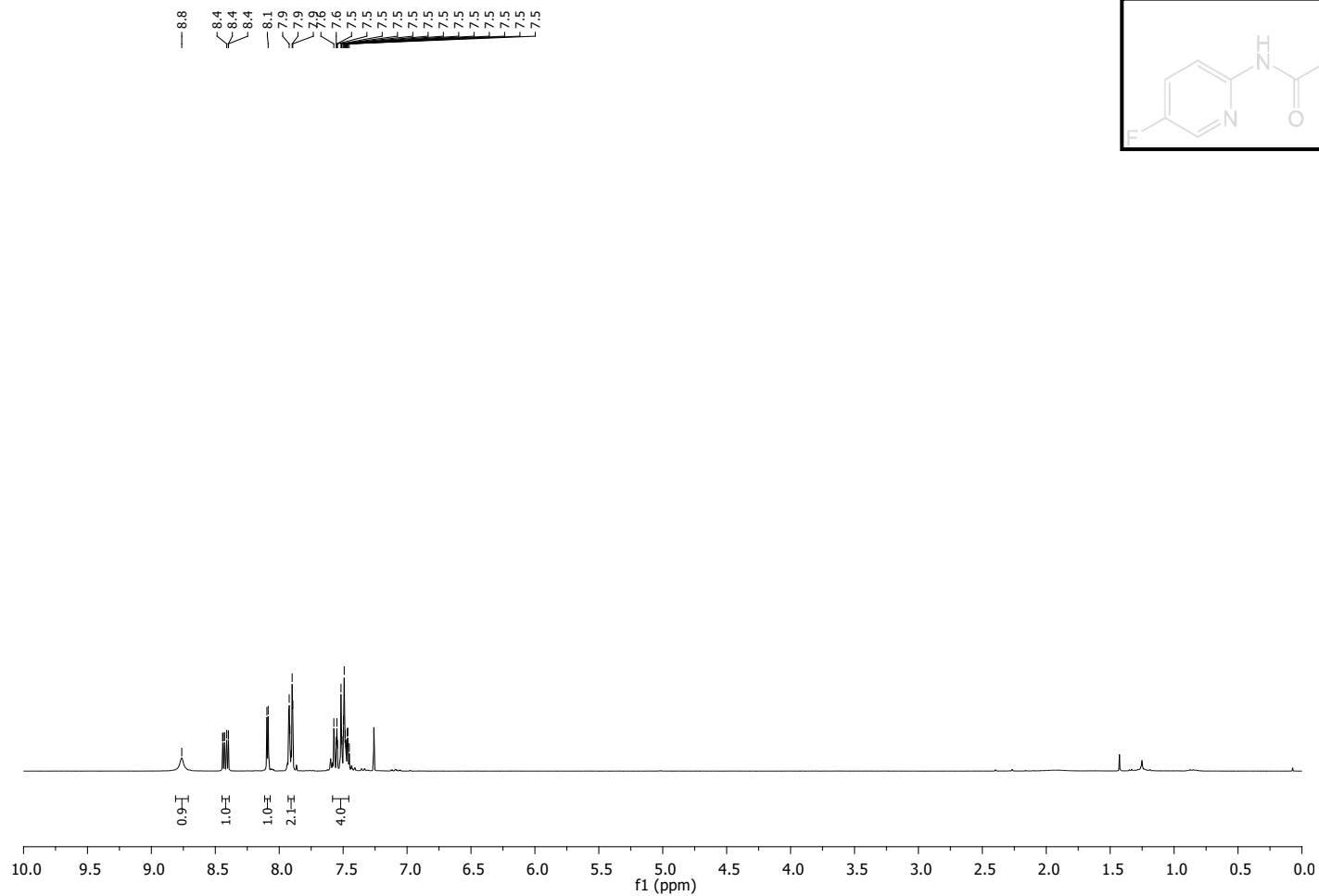
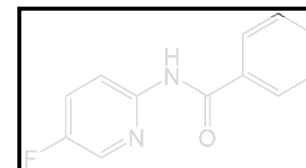


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)



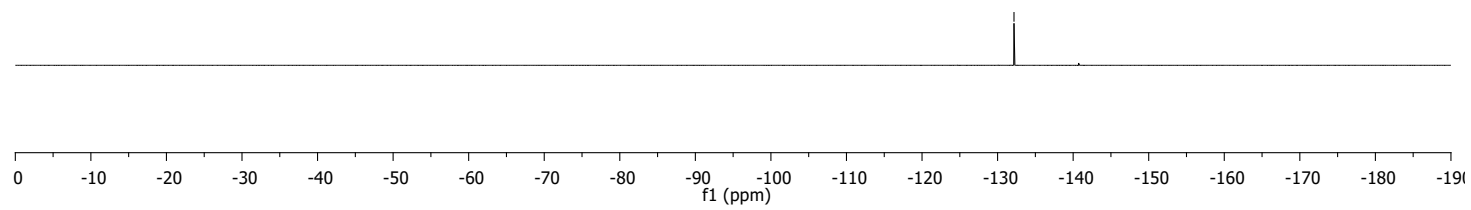
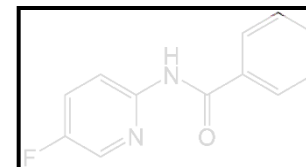
N-(5-fluoropyridin-2-yl)benzamide 3n

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

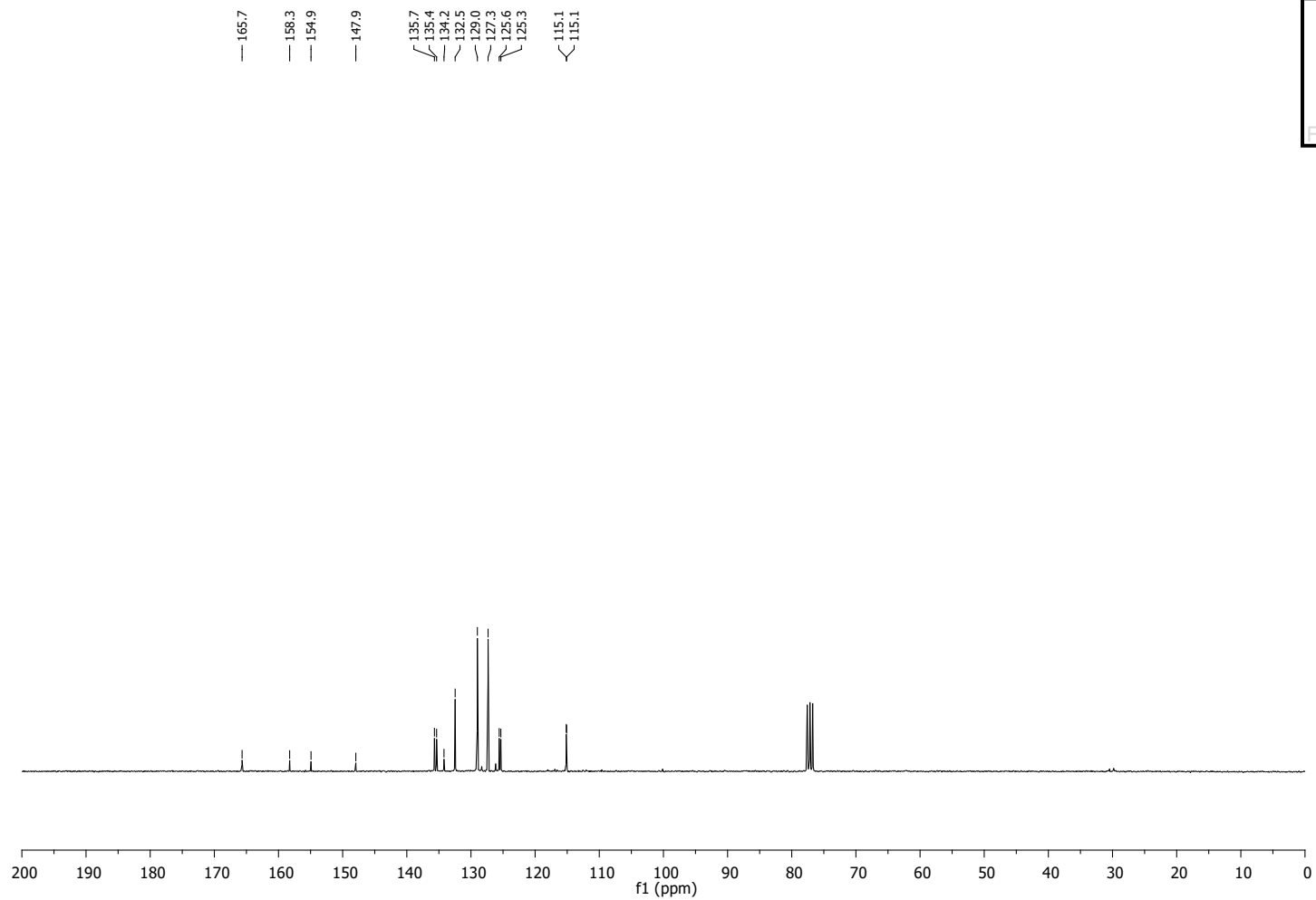
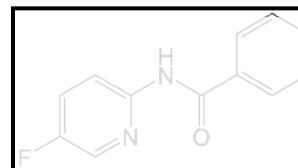


<sup>19</sup>F NMR (CDCl<sub>3</sub>, 300 MHz)

--- -132.2

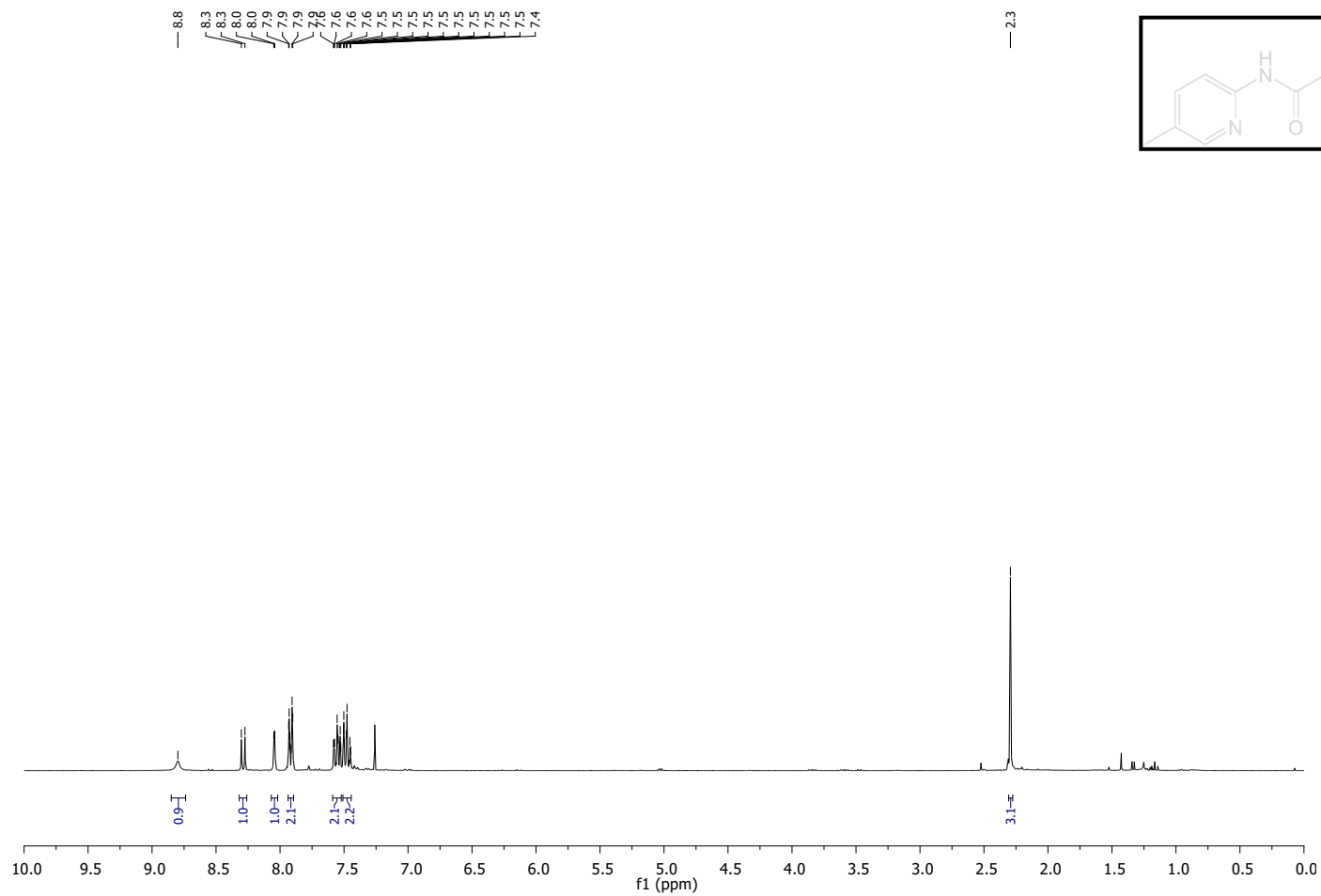


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

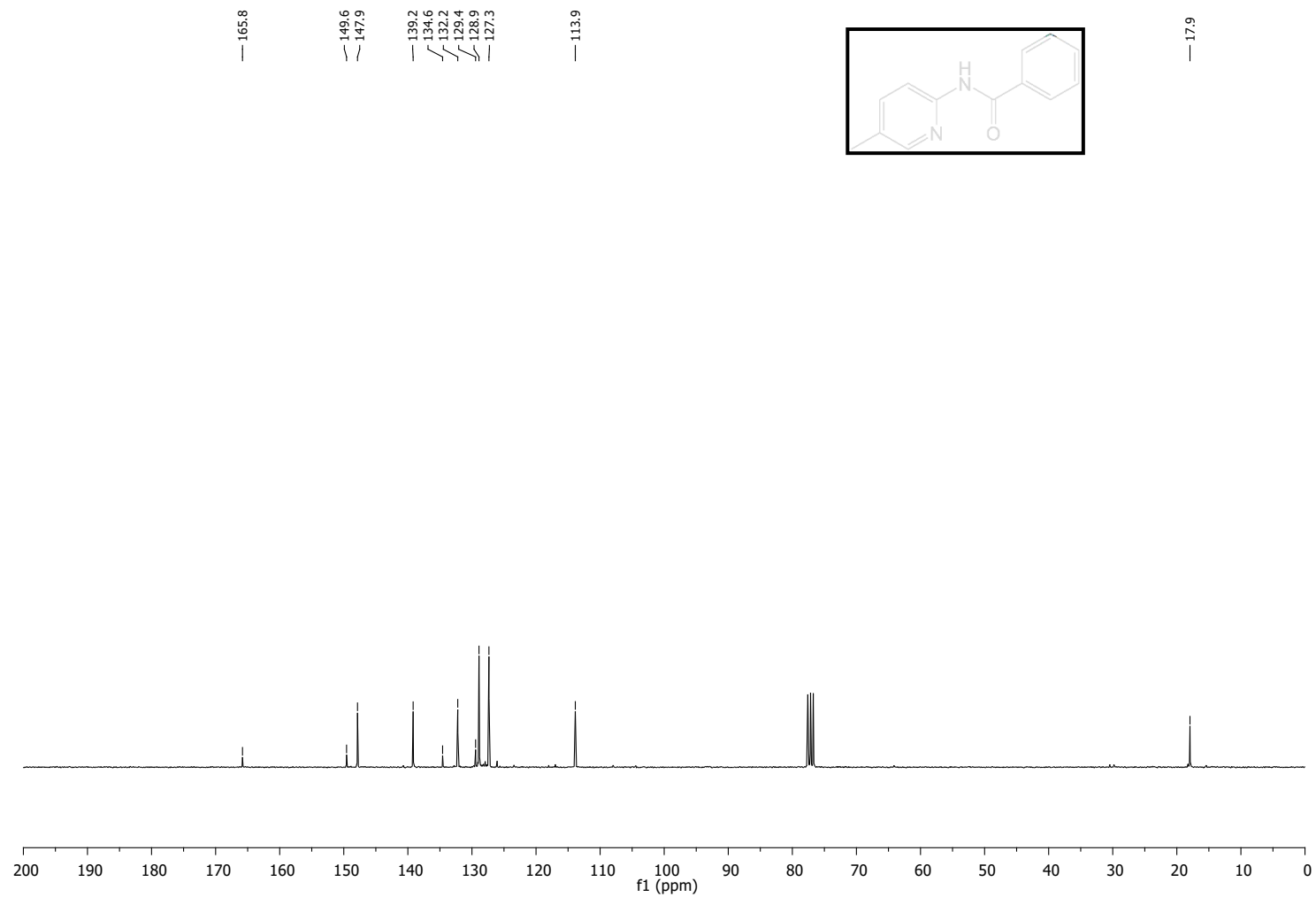


N-(5-methylpyridin-2-yl)benzamide 3o

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

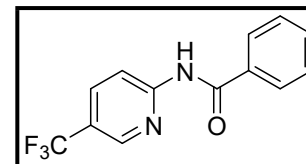


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

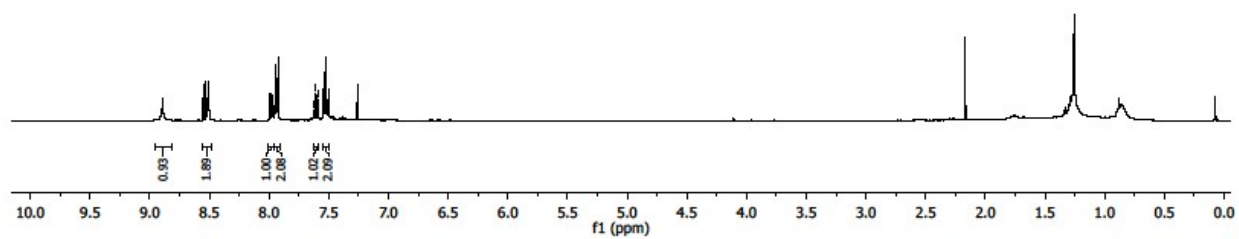


N-(5-trifluoromethylpyridin-2-yl)benzamide 3g

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)

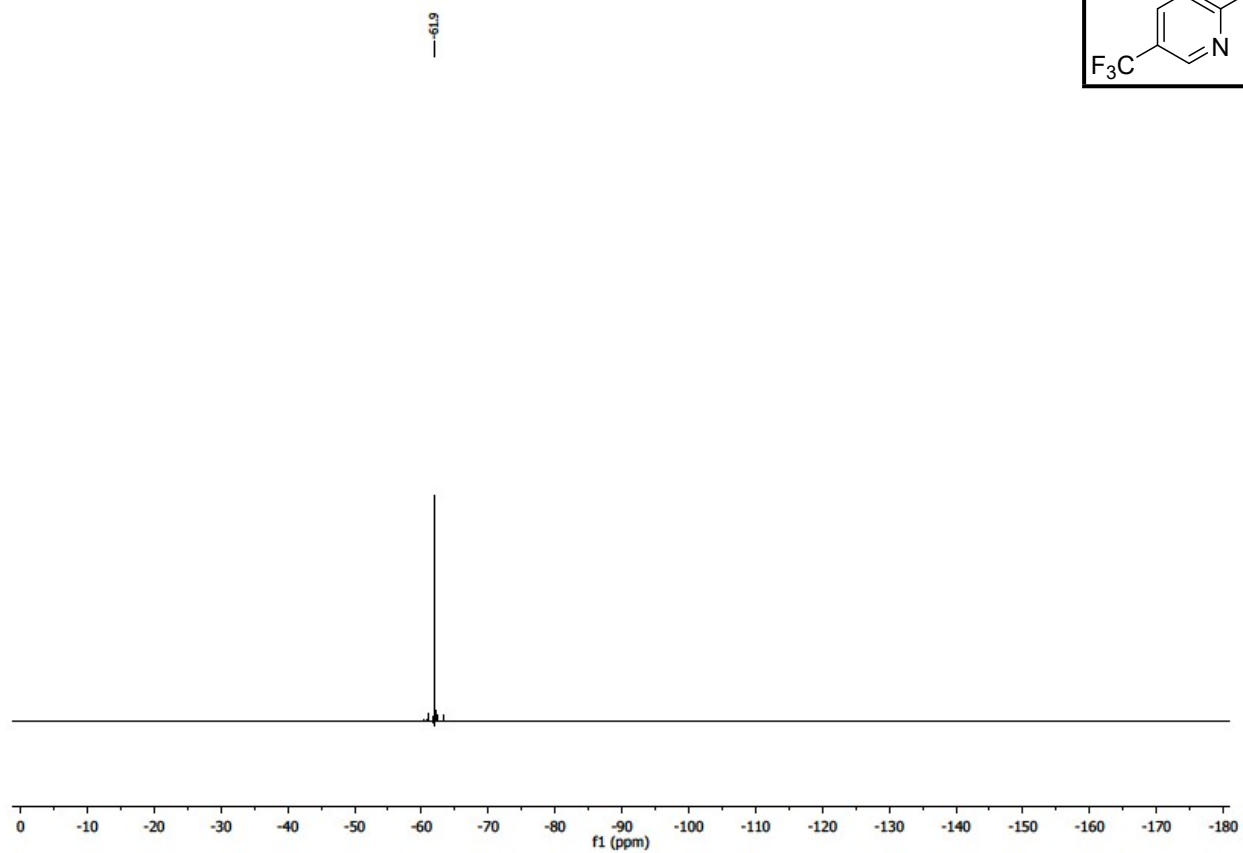
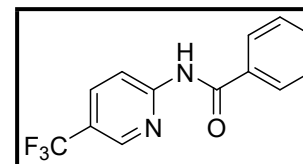


8.9  
8.5  
8.4  
8.3  
8.0  
7.9  
7.9  
7.8  
7.7  
7.6  
7.5  
7.5  
7.5

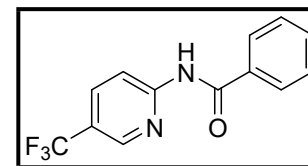
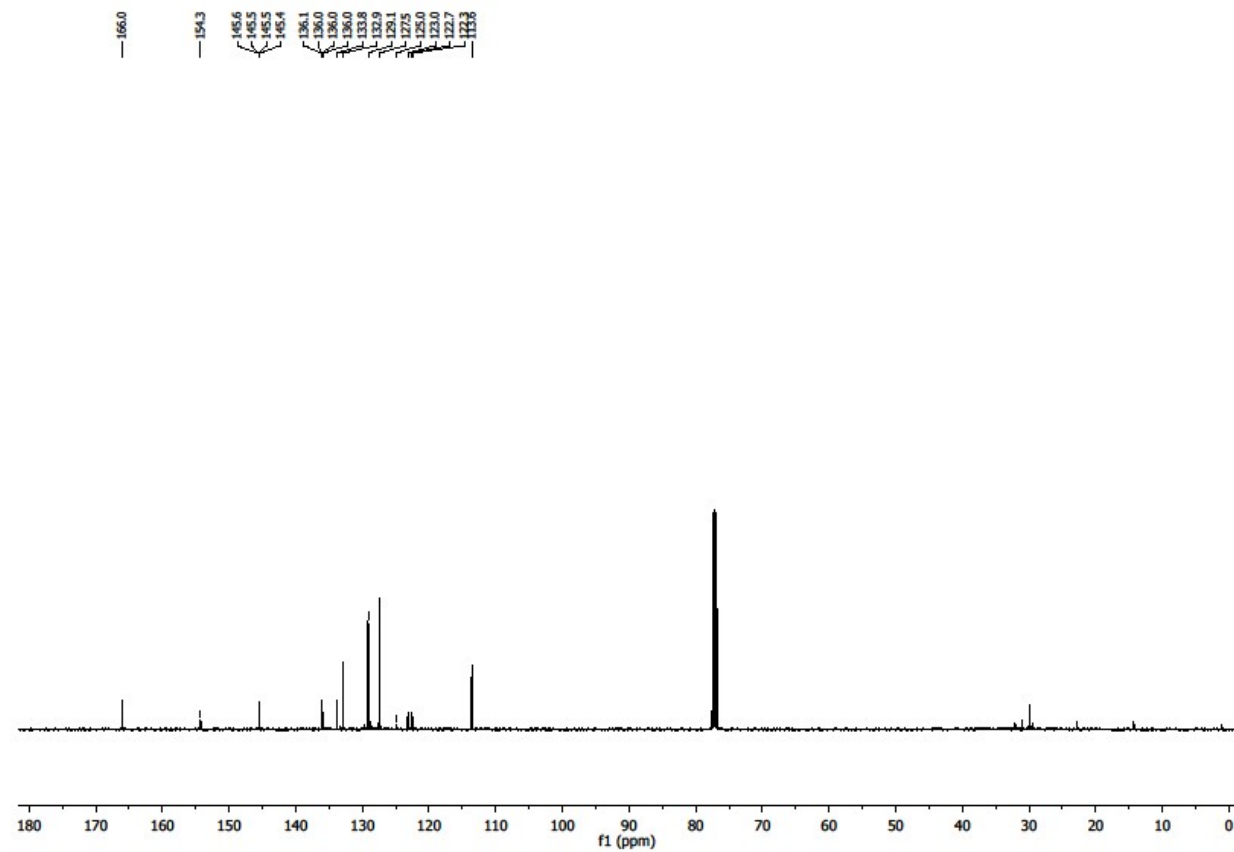




<sup>19</sup>F NMR (CDCl<sub>3</sub>, 377 MHz)

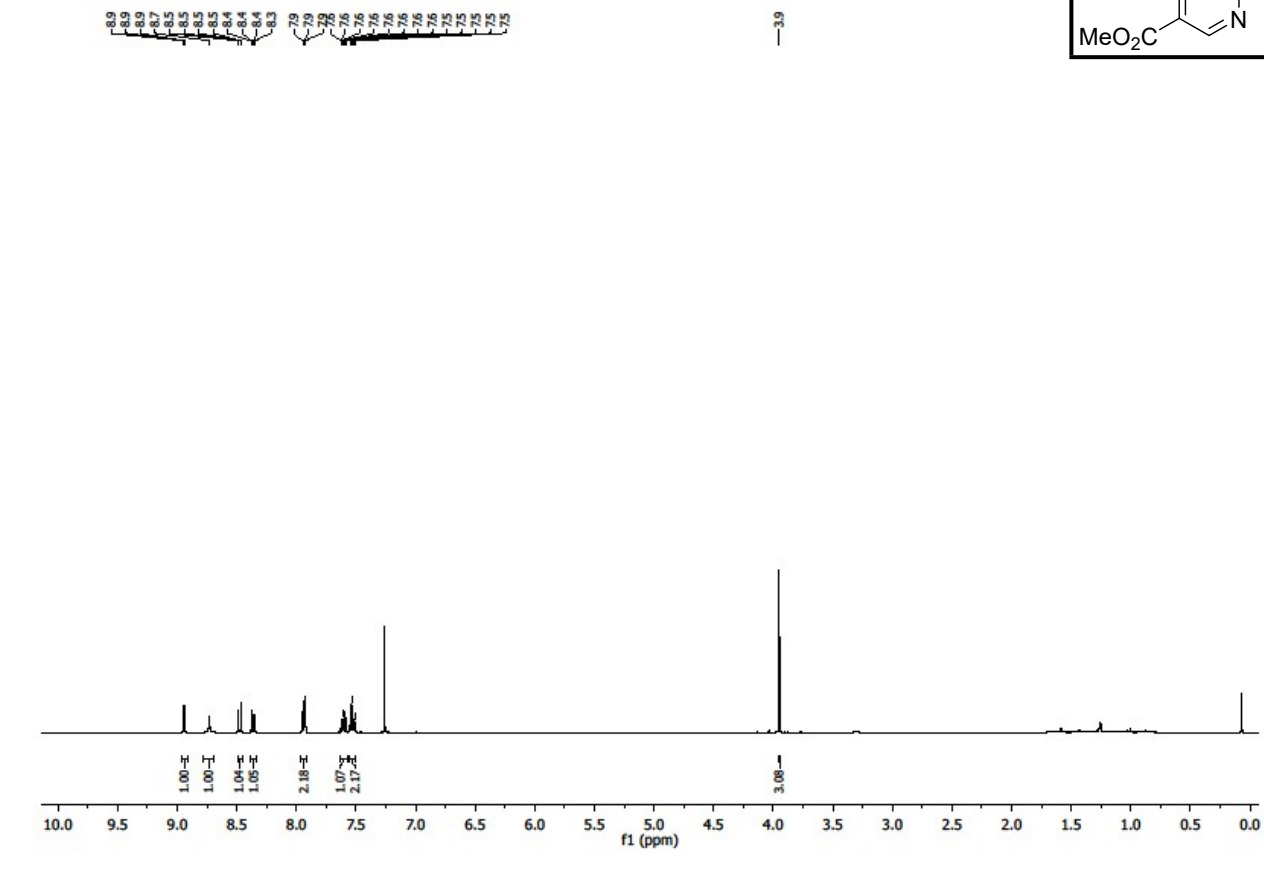
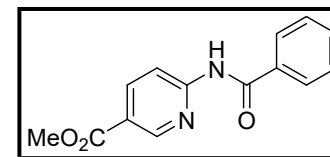


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz)

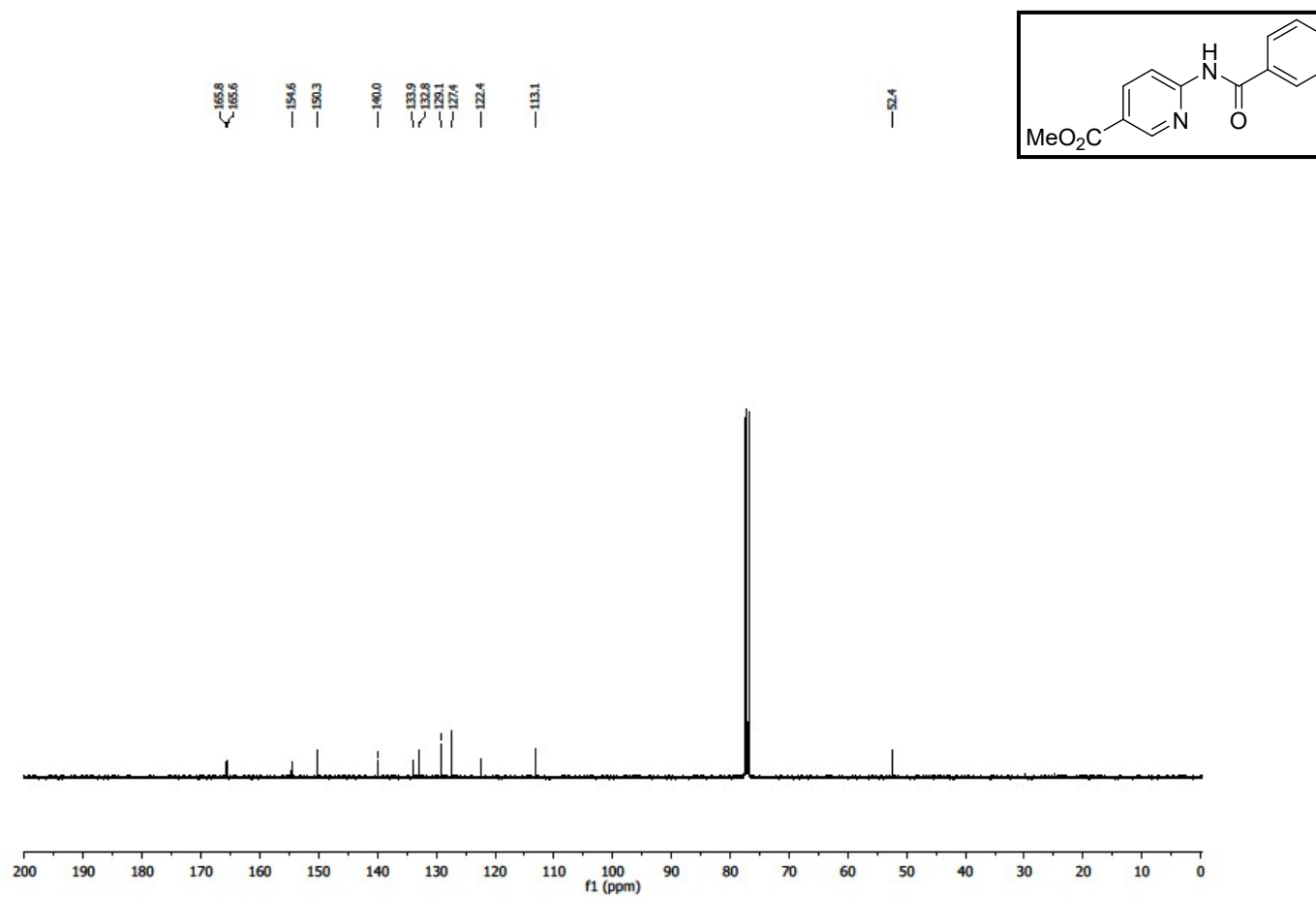


N-(5-methylesterpyridin-2-yl)benzamide 3r

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)

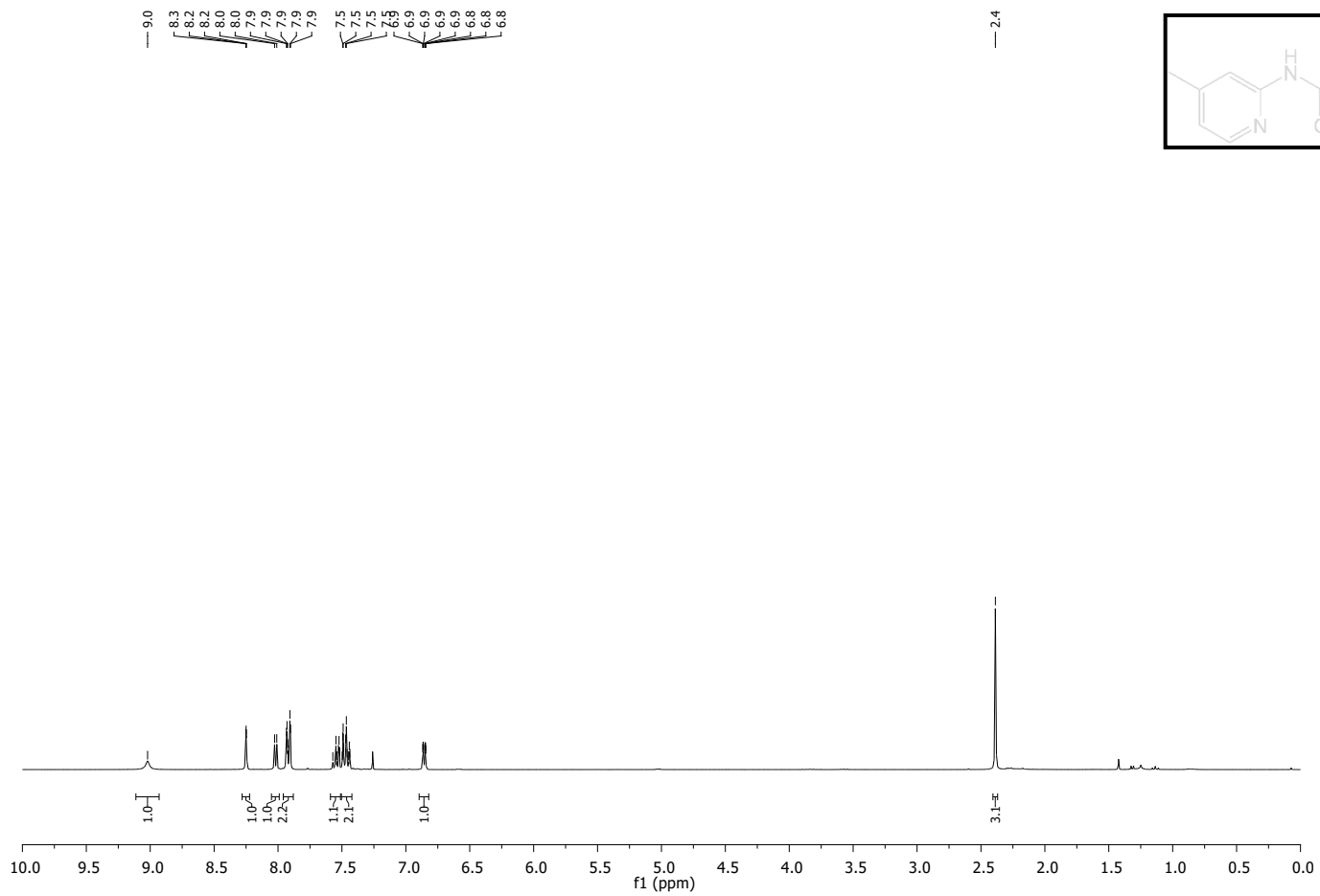


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz)

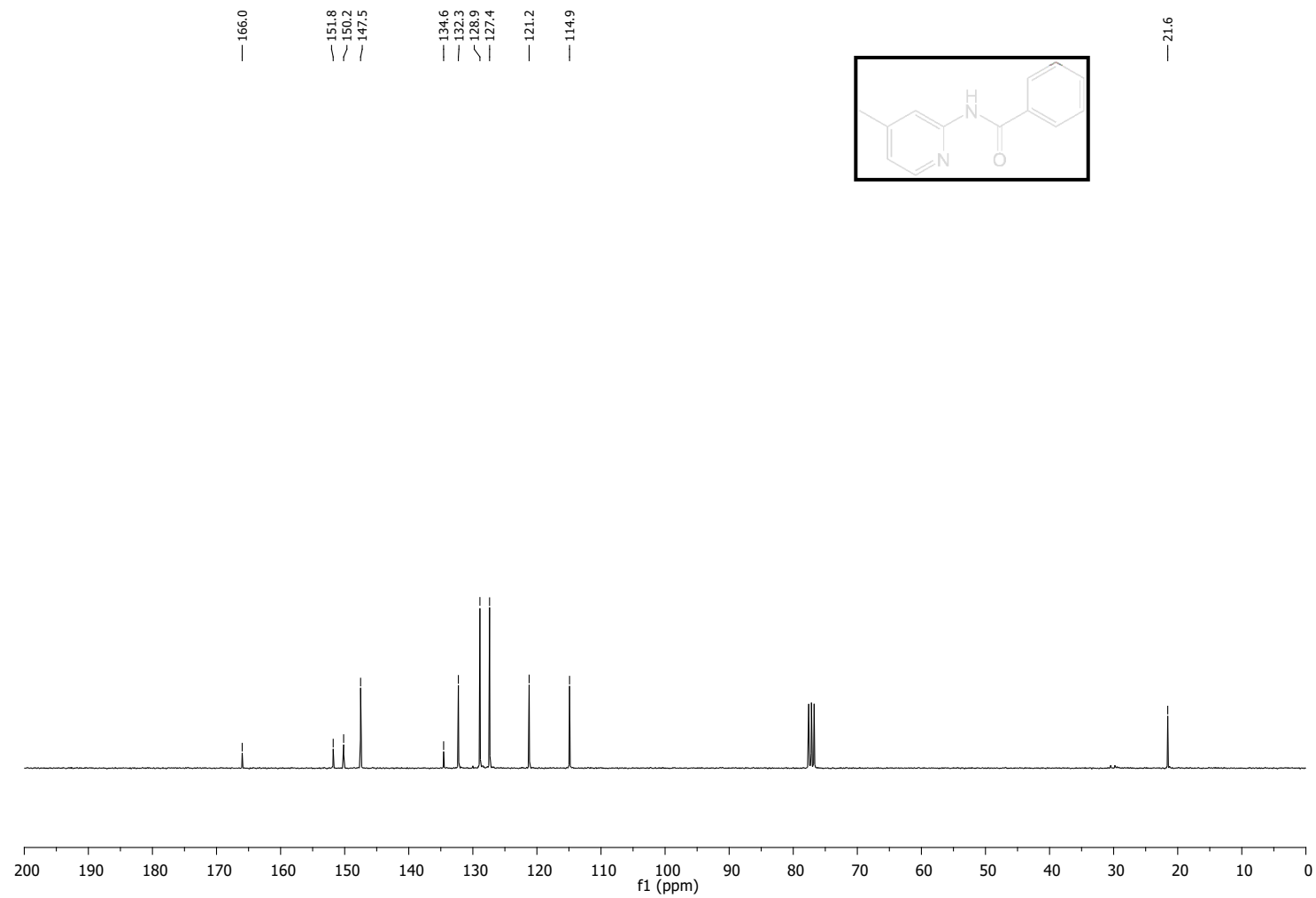


N-(4-methylpyridin-2-yl)benzamide 3s

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

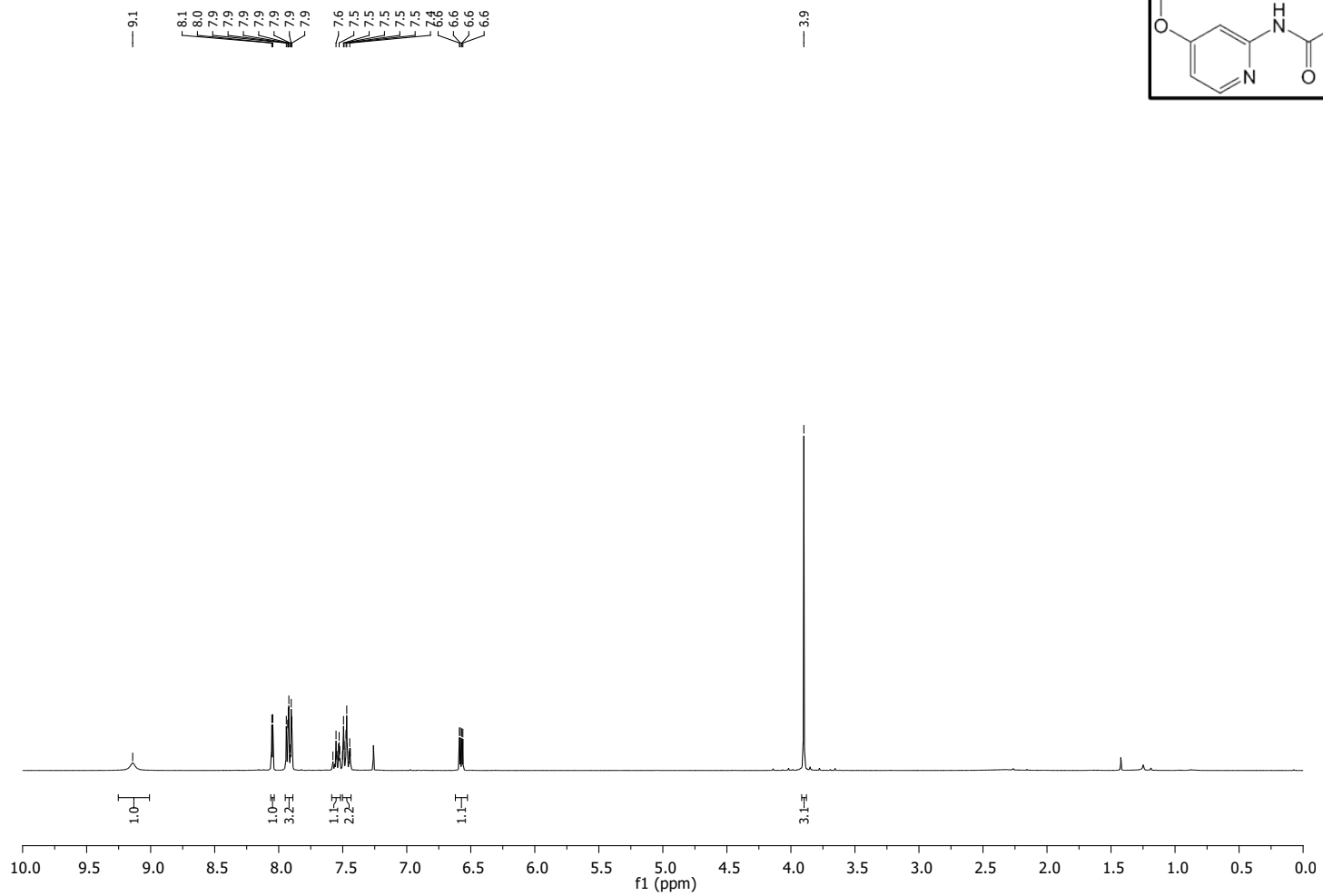
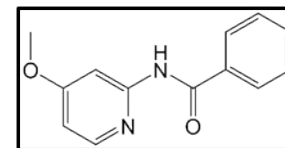


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

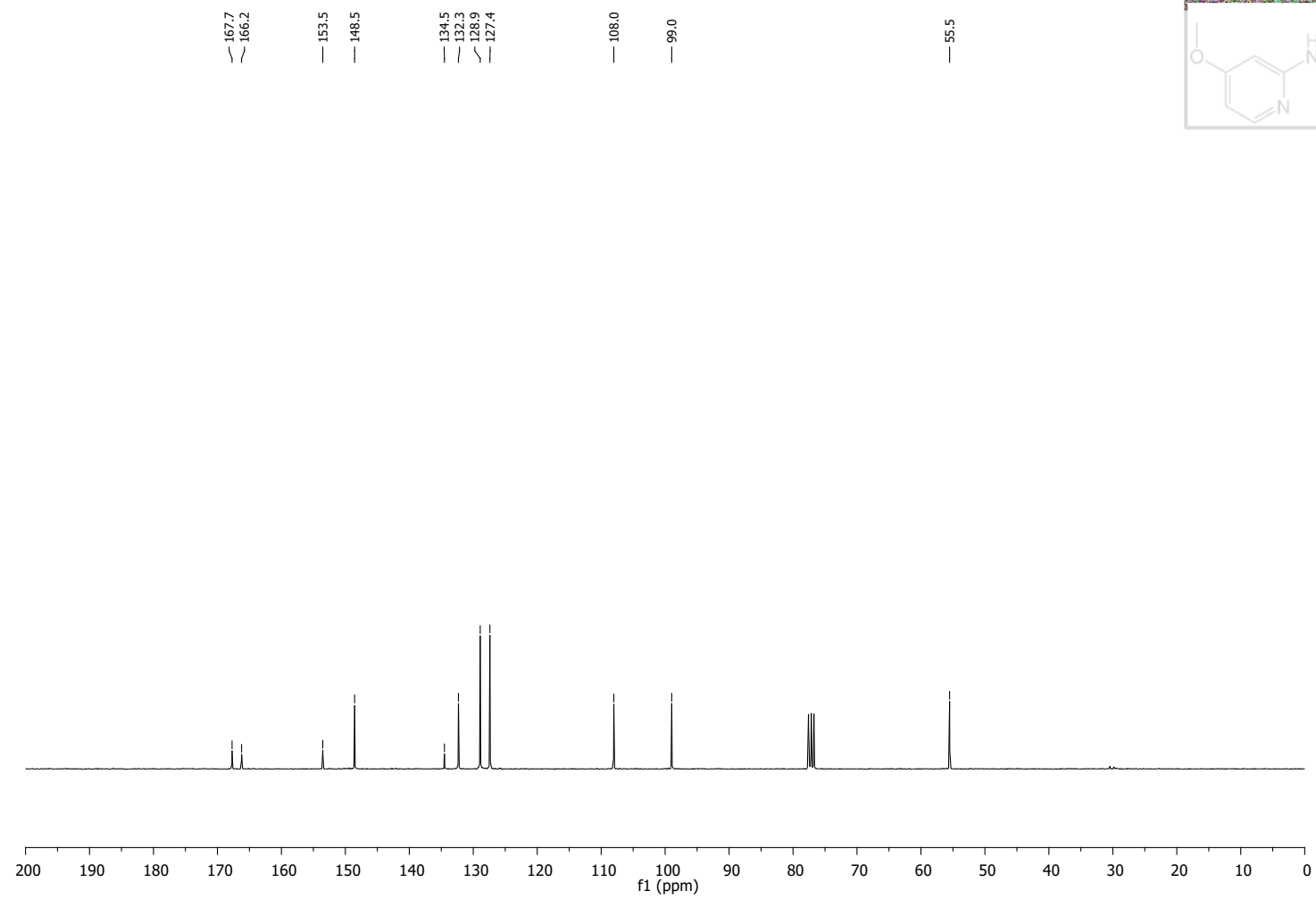


N-(4-methoxypyridin-2-yl)benzamide 3t

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)



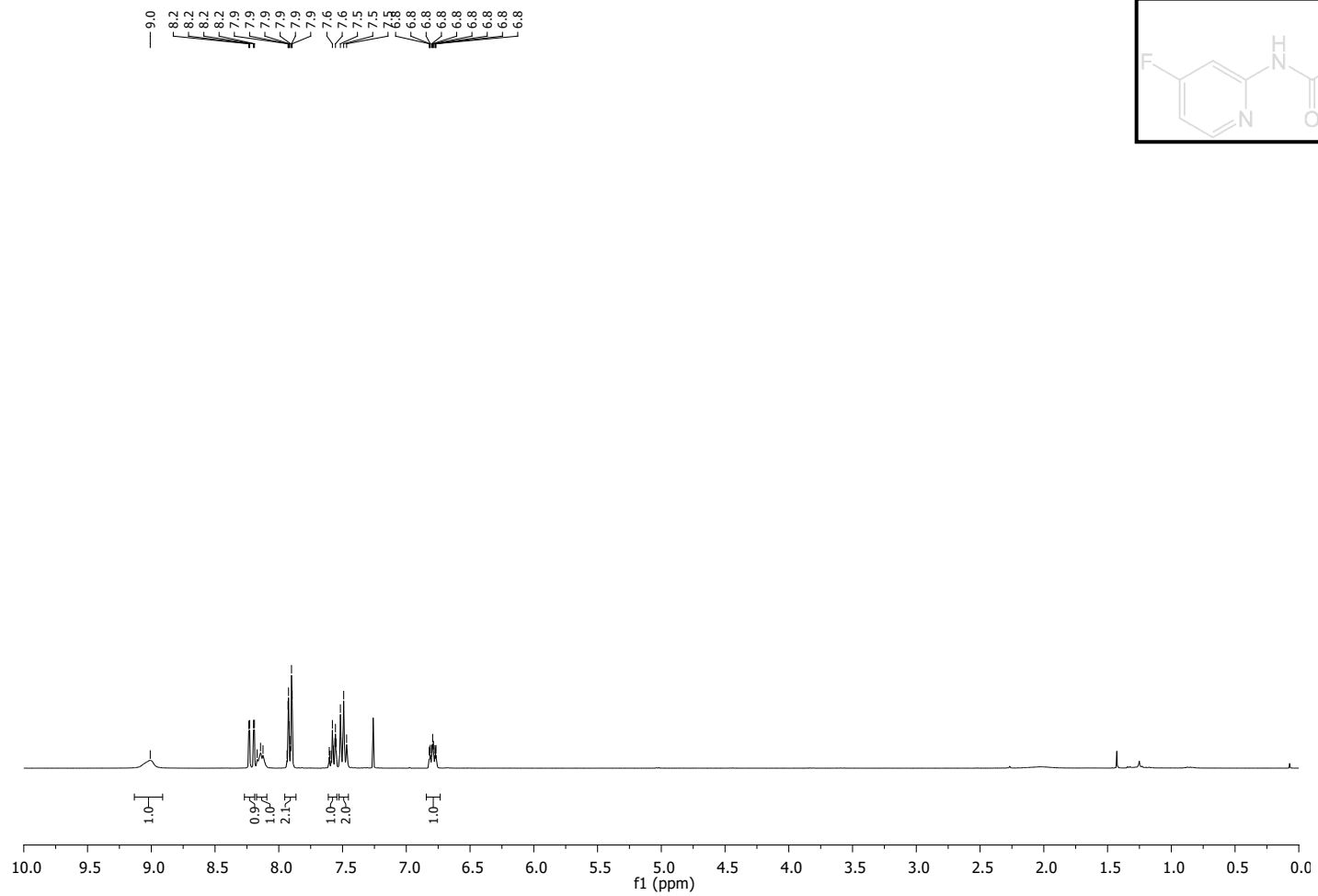
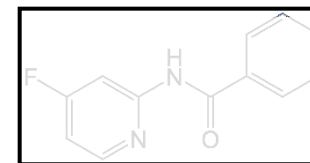
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)





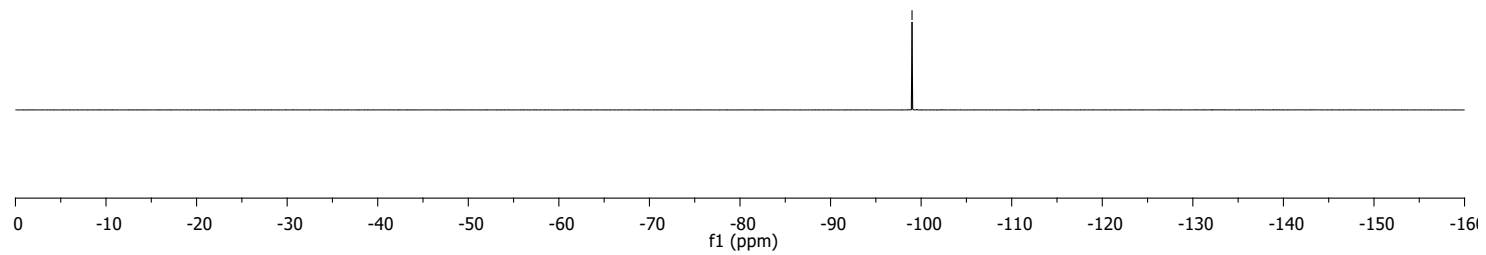
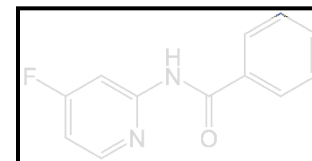
N-(4-fluoropyridin-2-yl)benzamide 3u

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)



<sup>19</sup>F NMR (CDCl<sub>3</sub>, 300 MHz)

— -99.0



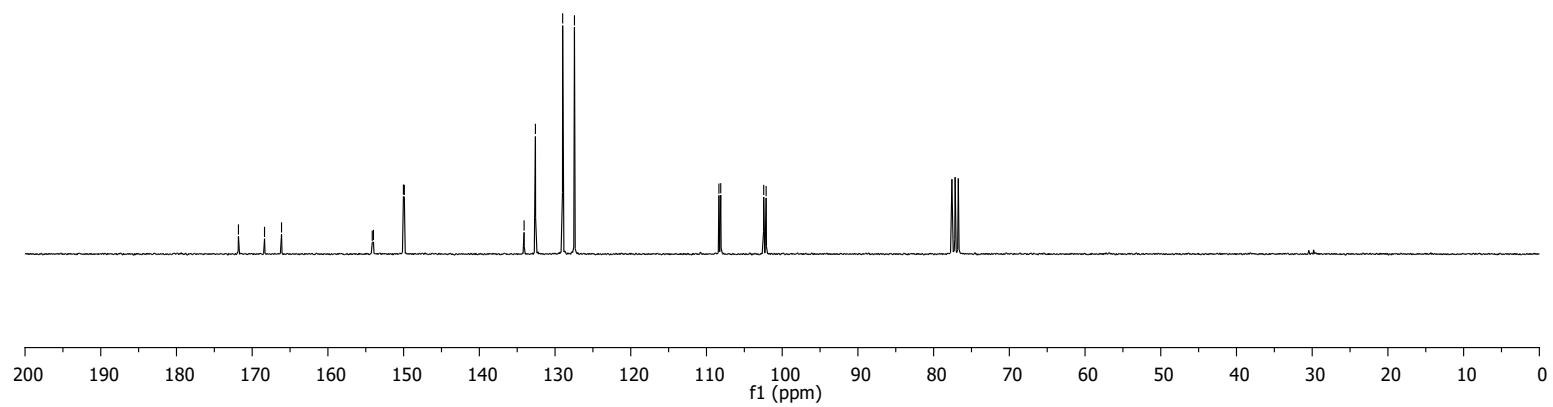
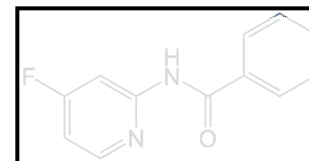
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

171.8  
168.4  
166.1

154.1  
154.0  
150.0  
149.9

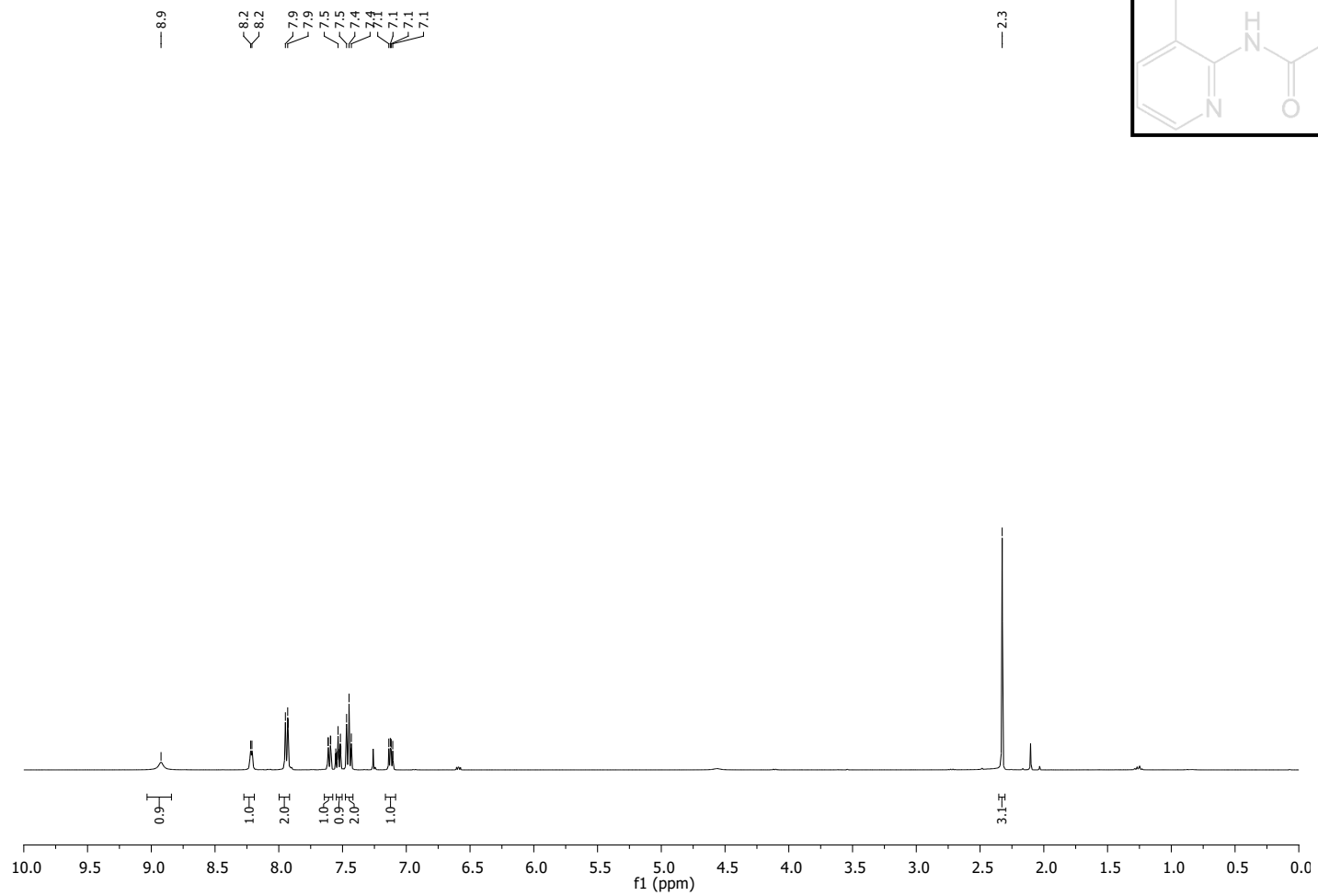
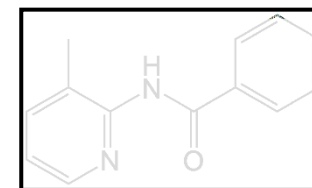
134.1  
132.6  
129.0  
127.4

108.4  
108.1  
102.4  
102.1

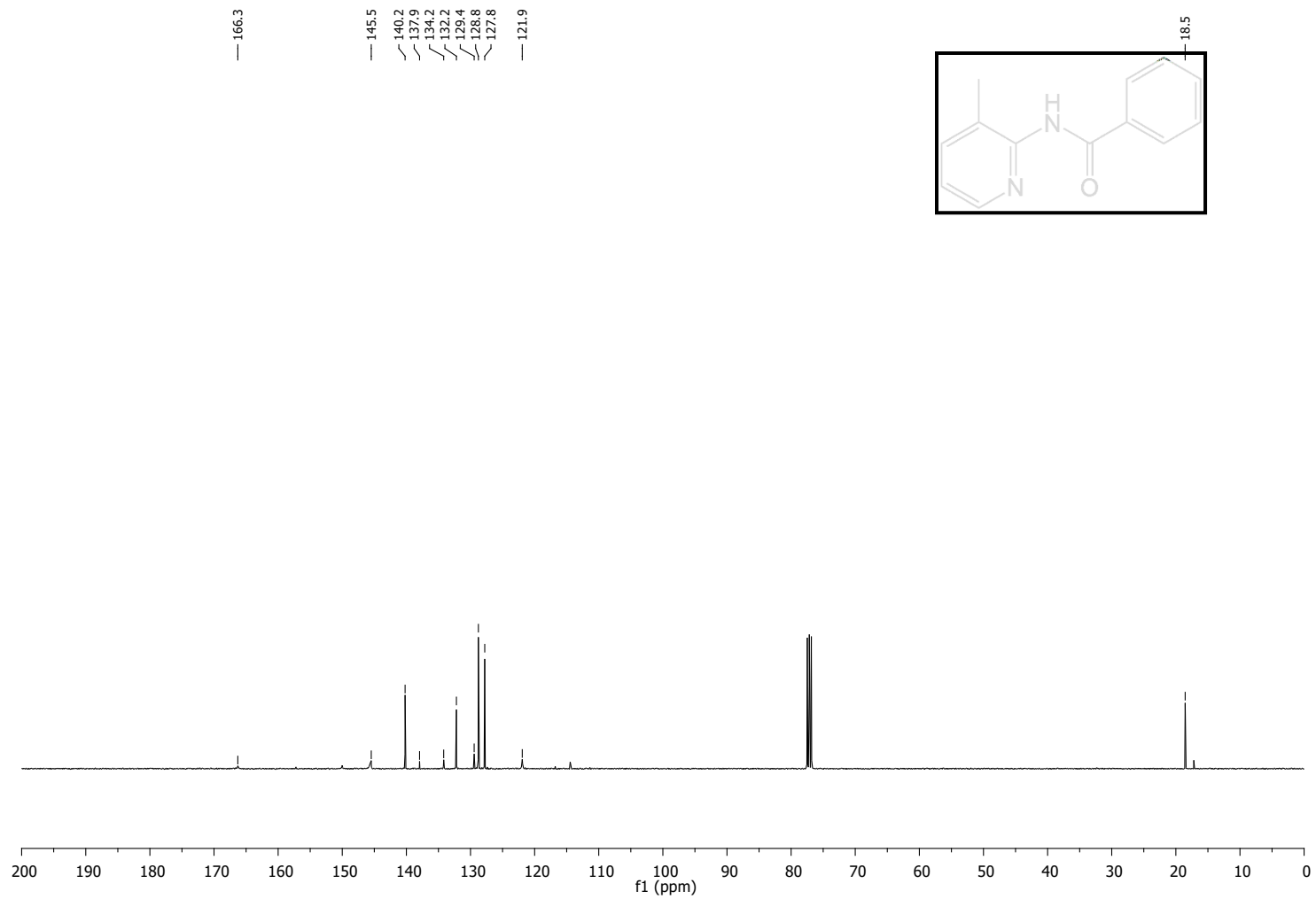


N-(3-methylpyridin-2-yl)benzamide 3v

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

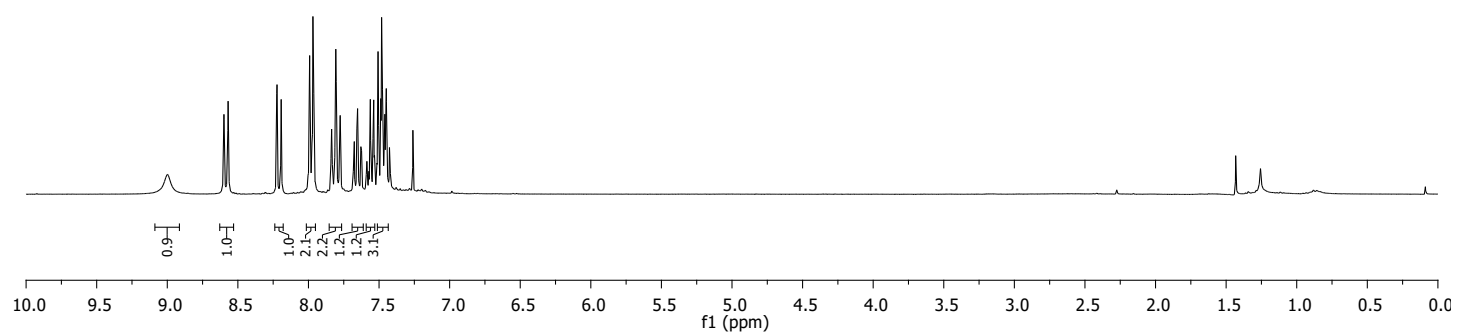
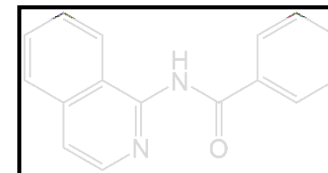


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

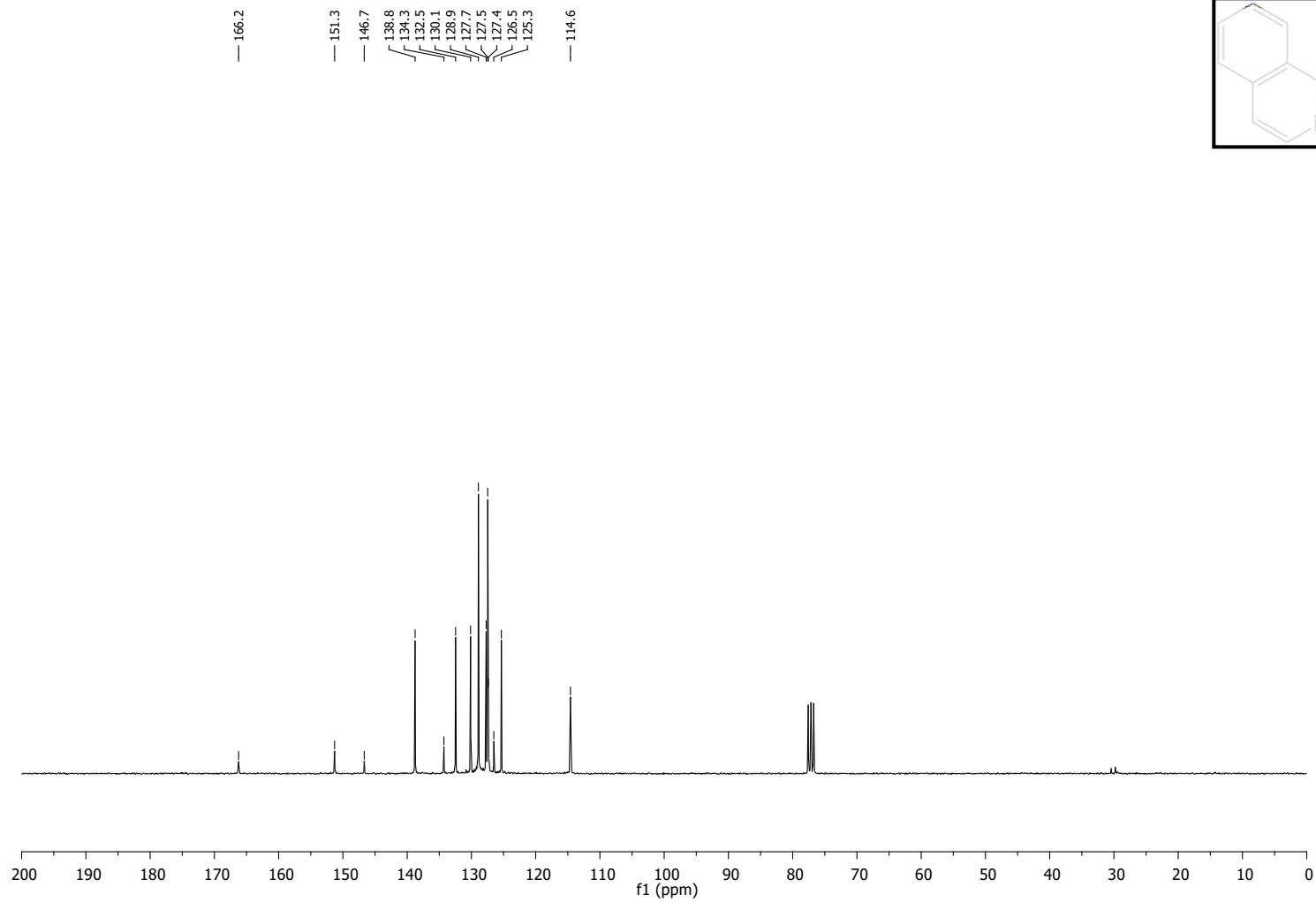
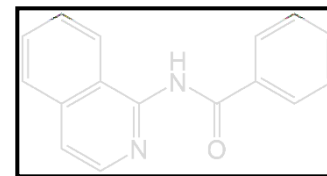


N-(isoquinolin-1-yl)benzamide 4a

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

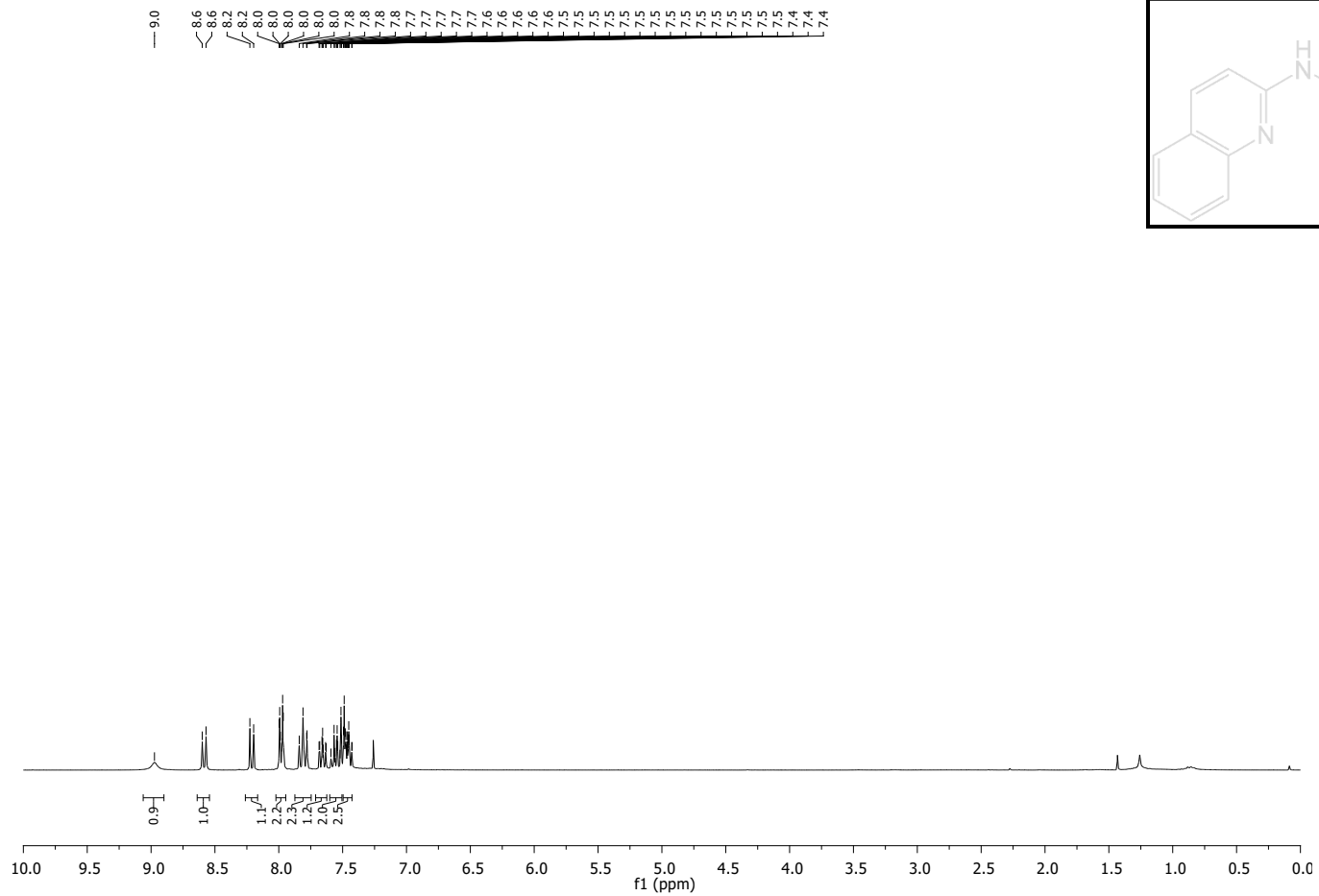


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)



N-(quinolin-2-yl)benzamide 4b

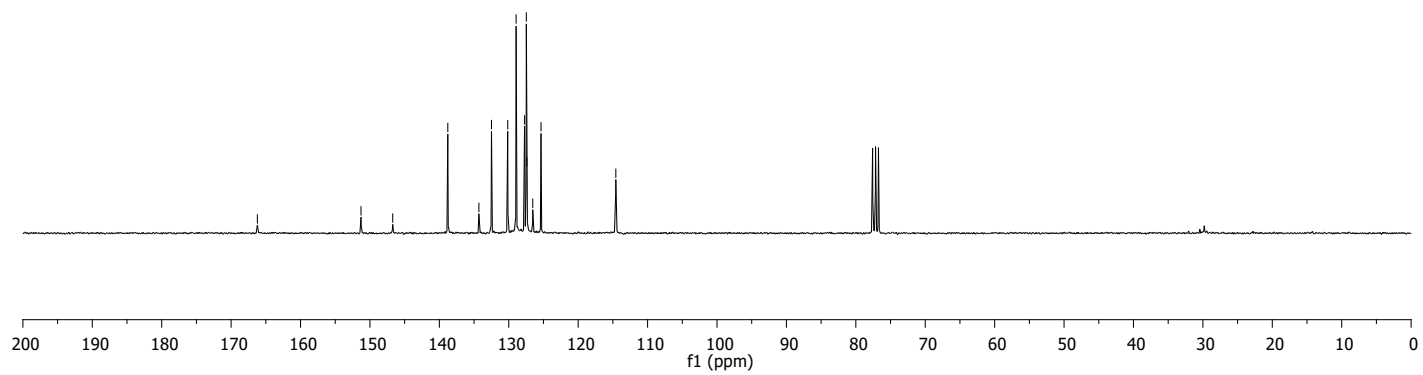
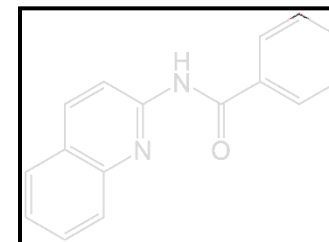
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)





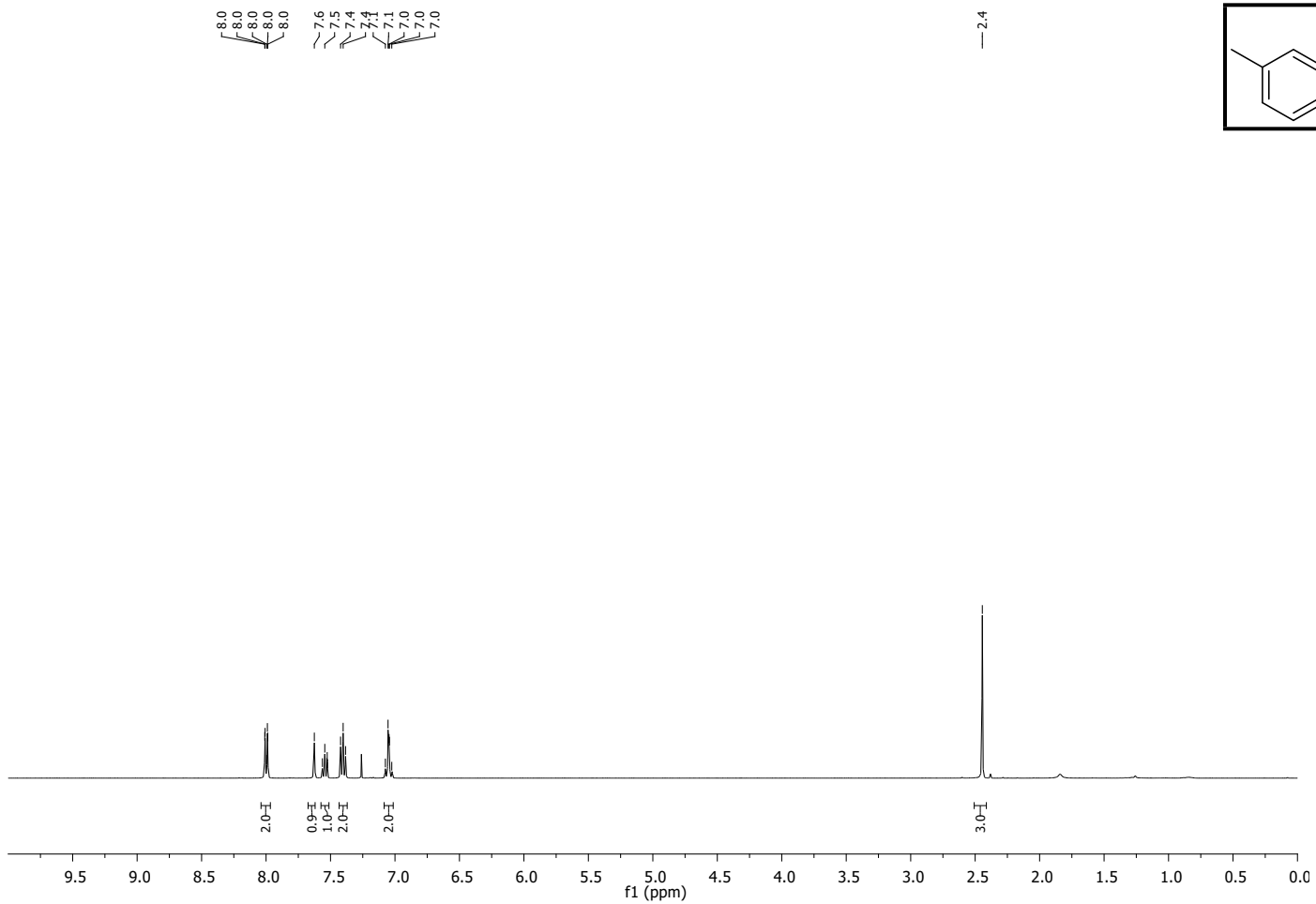
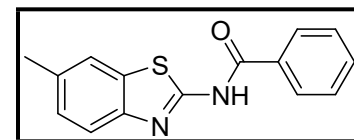
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)

— 166.2  
— 151.3  
— 146.7  
— 138.8  
— 134.3  
— 132.5  
— 130.2  
— 128.9  
— 127.7  
— 127.5  
— 127.4  
— 126.5  
— 125.4  
— 114.6

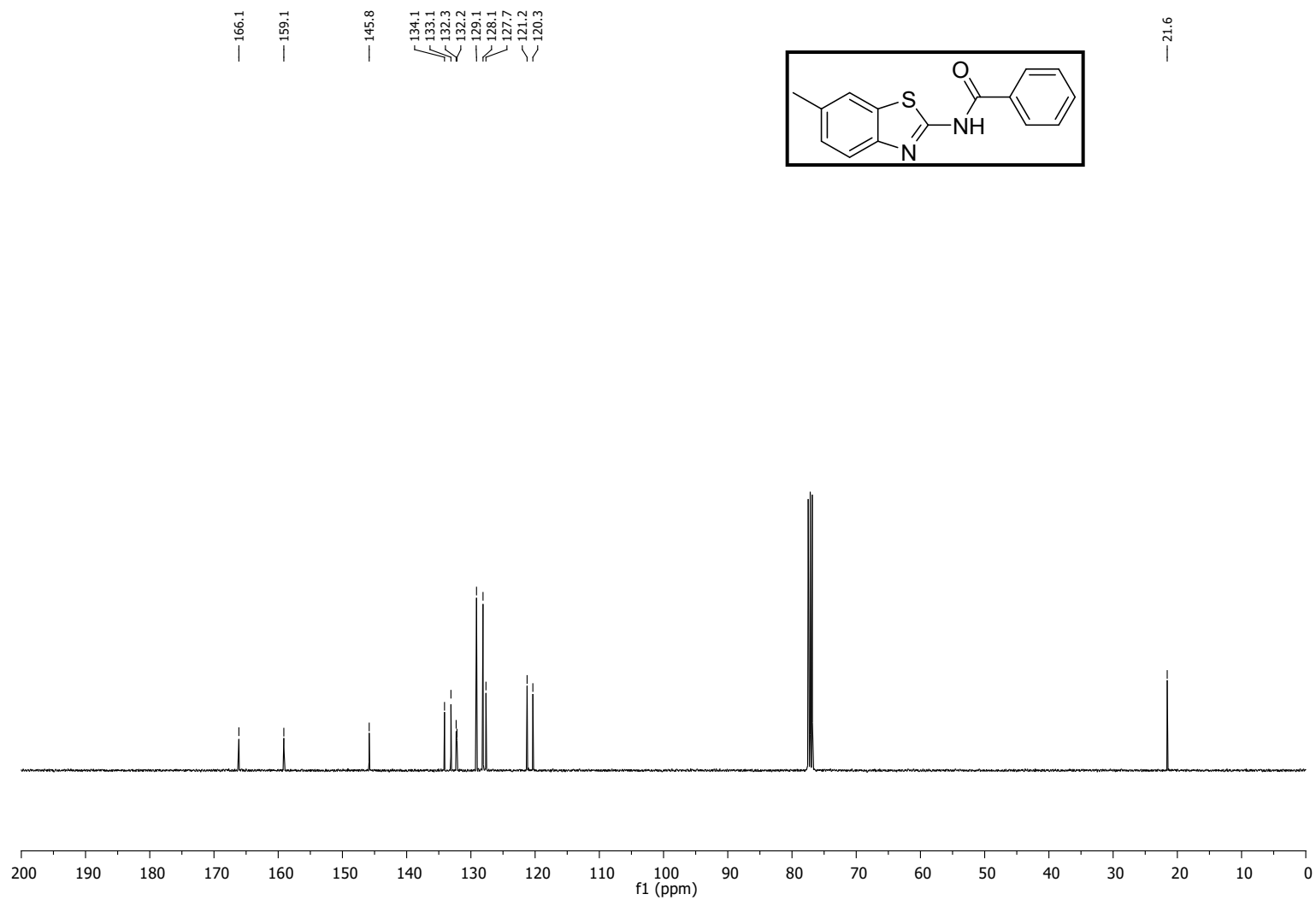


N-(6-Methyl-2-benzothiazolyl)benzamide 4c

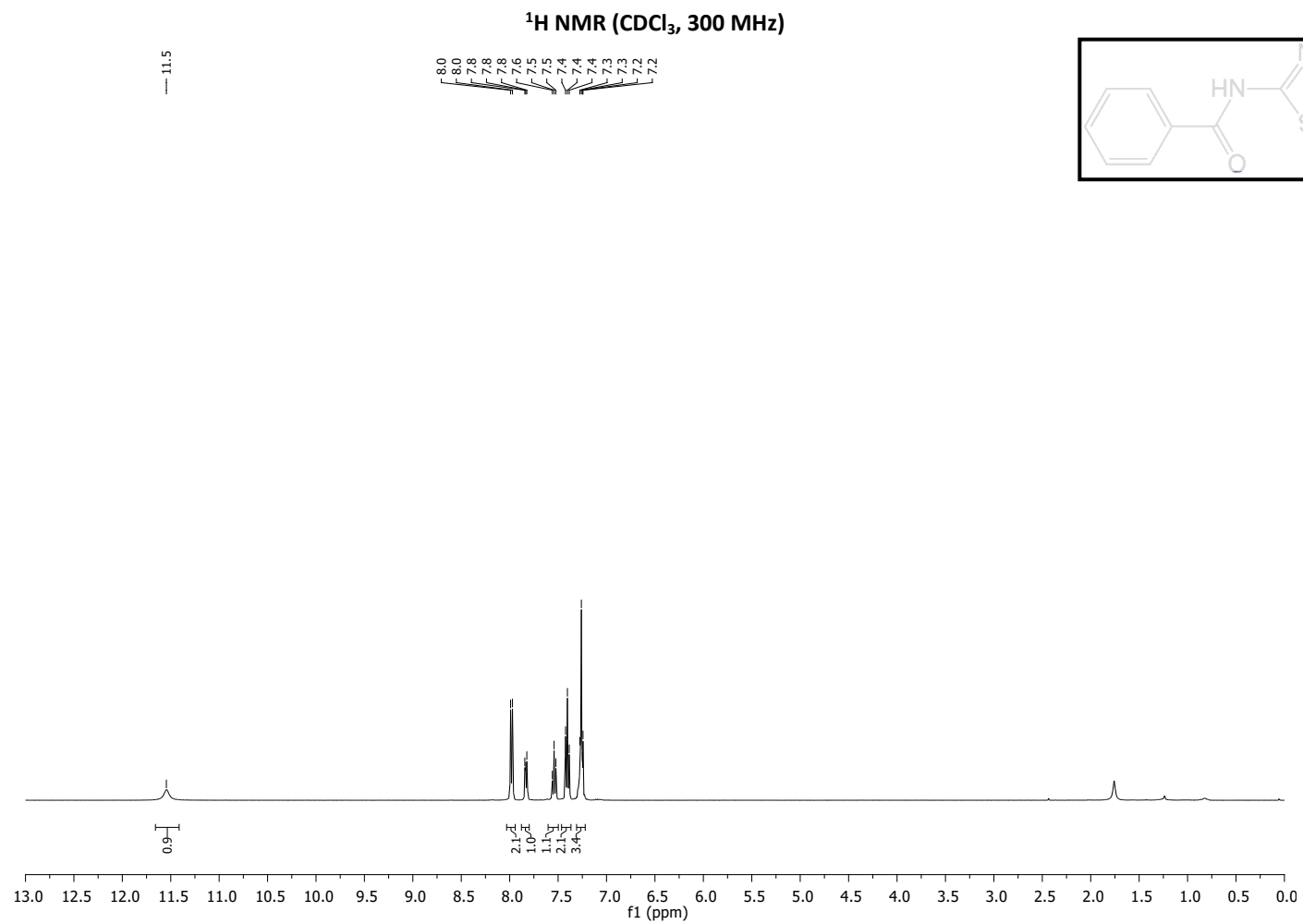
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)



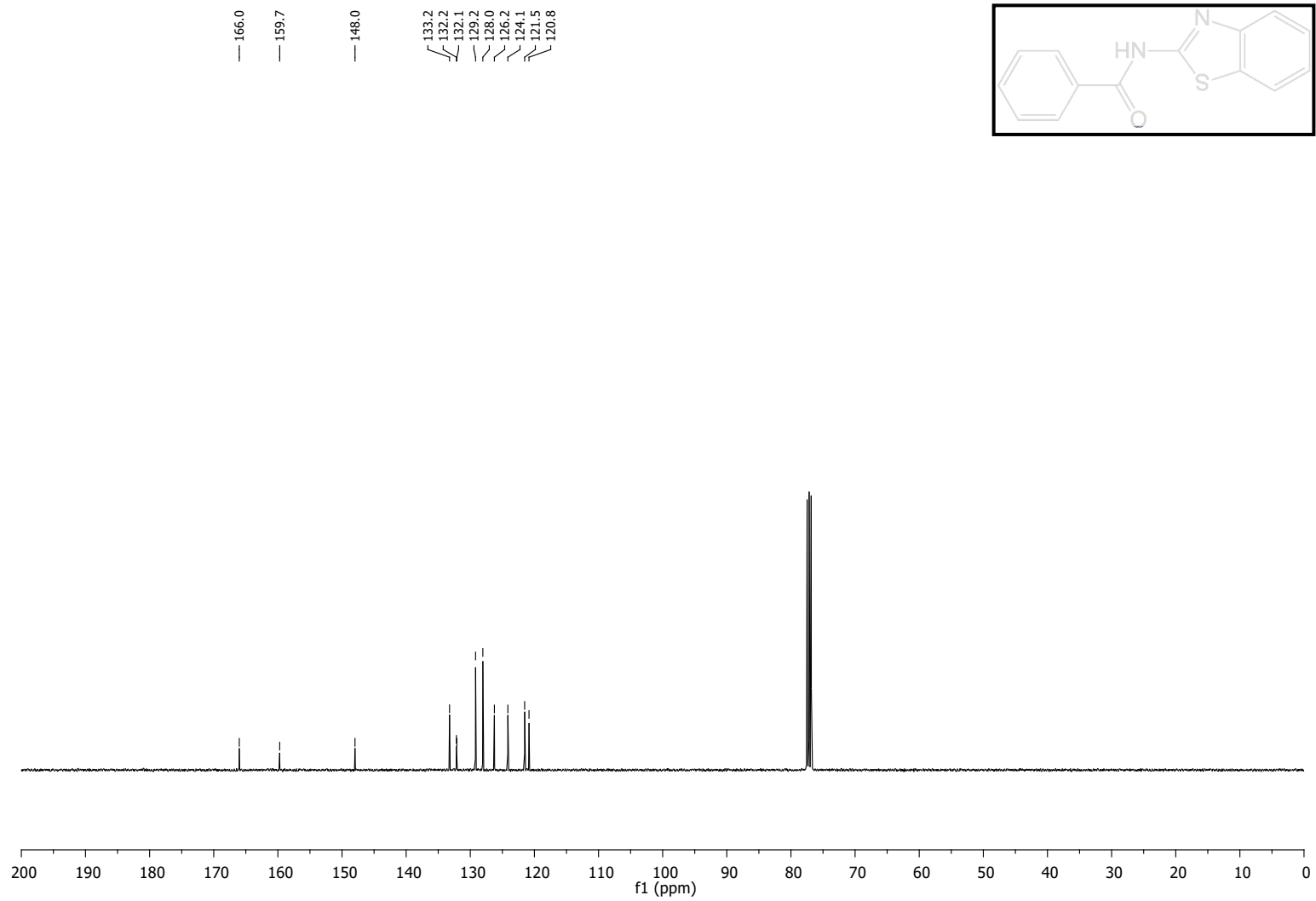
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)



N-(benzo[d]thiazol-2-yl)benzamide 4d

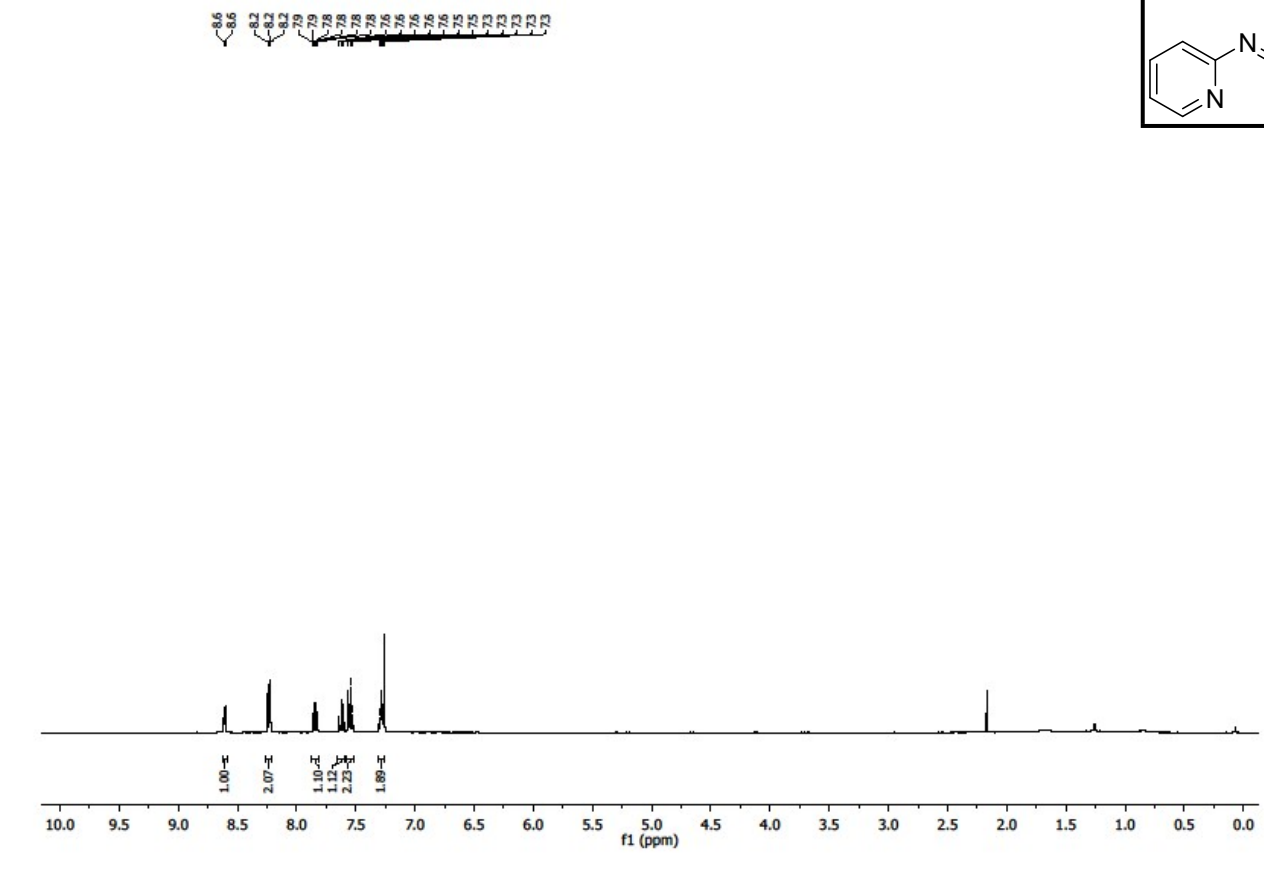
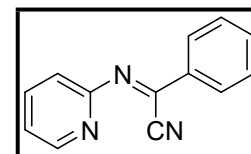


<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)



(Z)-N-(pyridin-2-yl)benzimidoyl cyanide 5a

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz)

159.3  
149.1  
141.3  
138.4  
137.8  
135.5  
133.2  
128.9  
123.1  
118.5  
111.7

