

## Supporting Information

### Singlet Oxygen Mediated Dual C-C and C-N bond cleavage in Visible Light

Ritu, Charu Sharma, Sharvan Kumar and Nidhi Jain\*

Department of Chemistry, Indian Institute of Technology, New Delhi-110016

\*E-mail: [njain@chemistry.iitd.ac.in](mailto:njain@chemistry.iitd.ac.in); Fax: +91 11 26581102; Tel: +91 11 26591562

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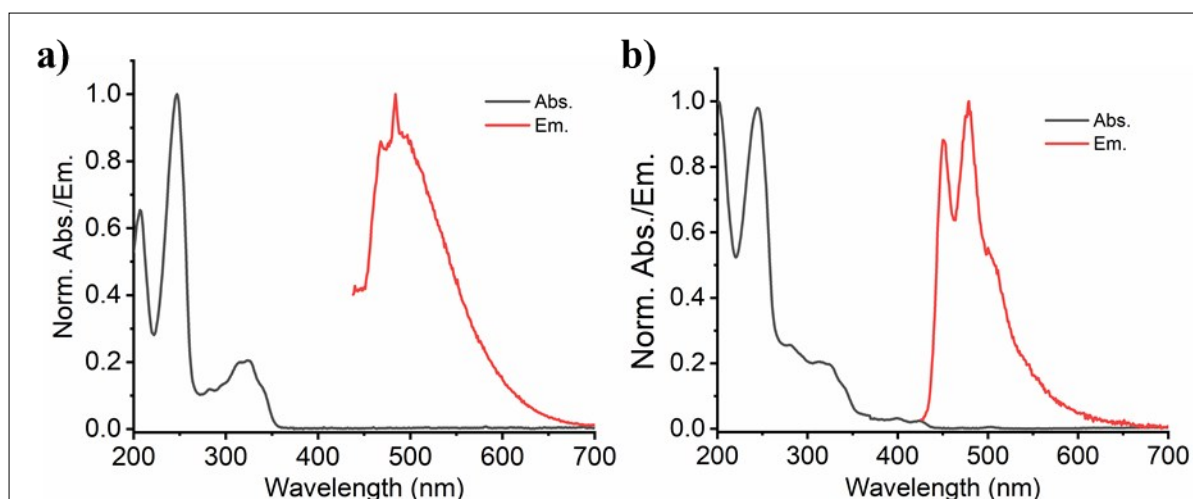
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## Experimental Details

**UV-visible and PL spectroscopy:** UV-visible spectra were recorded with a T90+UV-visible spectrophotometer in acetonitrile (ACN) solution ( $5 \times 10^{-5}$  M). Photoluminescence spectra were measured using Shimadzu RF5301PC spectrofluorophotometer.

**Cyclic and Differential Pulse Voltammetry (CV/DPV):** CV and DPV were carried out using a computer controlled potentiostat (CHI 650C) and a standard three electrode arrangement that consisted of both platinum working and auxiliary electrodes and standard calomel electrode (SCE) as reference electrode. All the electrochemical measurements were carried out in Ar-purged solvents with n-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte. The scan rate for the measurements were typically 200-300 mV/s. DPV was carried out keeping peak amplitude 50 mV, peak width 0.01 sec, pulse period 0.05 sec and increment E at 20 mV.

**Crystallographic Description:** Data Collection and Refinement Single-crystal X-ray data of compounds was collected on Bruker APEX-II CCD Diffractometer using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). Frames were collected at T = 303 K by  $\omega$ ,  $\phi$ , and  $2\theta$ -rotations with full quadrant data collection strategy (four domains each with 600 frames) at 10s per frame. The measured intensities were reduced to F<sup>2</sup> and corrected for absorption with SADABS-2016/2.<sup>1</sup> Structure solution, refinement, and data output were carried out with the SHELXTL package by direct methods.<sup>2,3</sup> Non-hydrogen atoms were refined anisotropically using the Olex2.<sup>4</sup> All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms using SHELX default parameters. Molecular structures have drawn using ORTEP software. Further information on the crystal structure determination (excluding structure factors) has been given as table S1 and also deposited in the Cambridge Crystallographic Data Centre as CCDC-1946046. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk) or via internet.

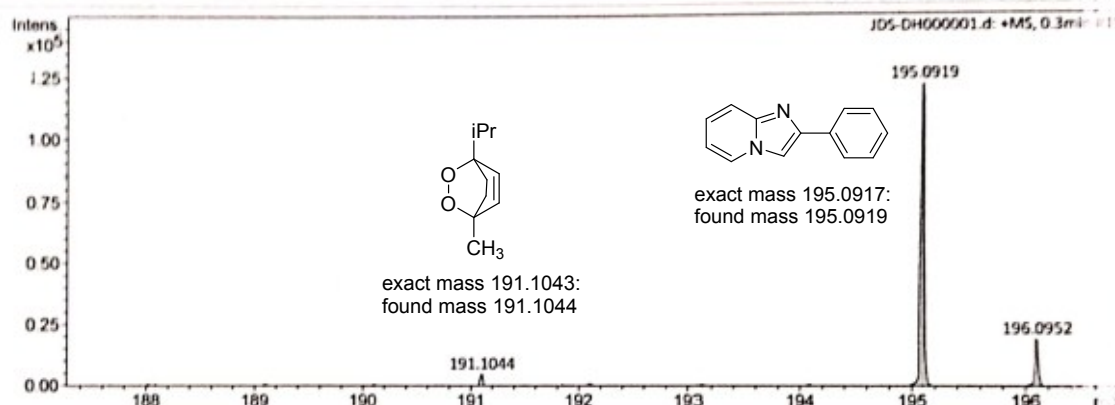


**Fig. S1:** Normalized absorption (black) and emission (red) spectra of 2-phenylimidazopyridine (**1a**) (a) In acetonitrile excitation wavelength 325 nm. (b) In acetonitrile after 30 min. irradiation of blue LED excitation wavelength 420 nm.

The UV-vis spectra of **1a** in MeCN exhibited absorption bands at 246, 282, 325 nm and a small hump at 340 nm. We found that after 30 minutes of irradiation of the sample in blue light, the absorption spectrum changed and peaks at 240, 281, 325, 399 and 425 nm were observed. On excitation at 420 nm, **1a** gave an emission peak at  $\lambda_{\text{max}}$  480 nm. The above results suggested that imidazo [1,2-a] pyridines can undergo ISC upon excitation and display fluorescence with lifetimes in the millisecond–second. The triplet state energies of some derivatives of imidazo [1,2-a] pyridines are reported in the range of ~46-49 kcal/mol.<sup>5</sup> This energy is significantly larger than that of the  $^3\text{O}_2$  to  $^1\text{O}_2$  [ $E(^1\Delta-^3\Sigma) = 22.5$  kcal/mol and sufficient for photosensitization of  $^3\text{O}_2$  to  $^1\text{O}_2$ .

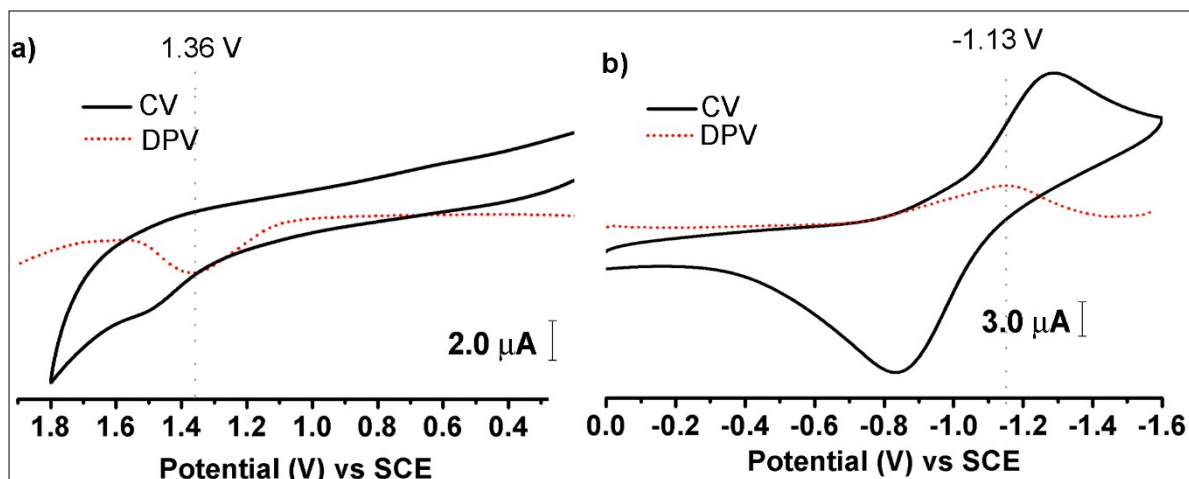
## Display Report

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Method	Tune_Low_New.m	Instrument	micrOTOF-Q 228888.10212		
Sample Name	tm 1 100	Comment			
Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste



**Fig. S2:** HRMS spectrum for  $\alpha$ -terpinene adduct with singlet oxygen

A control reaction of **1a** and  $\alpha$ -terpinene under  $O_2$  atmosphere (in the absence of eosin Y) in blue light quenched the product formation and showed formation of peroxide adduct of  $\alpha$ -terpinene.

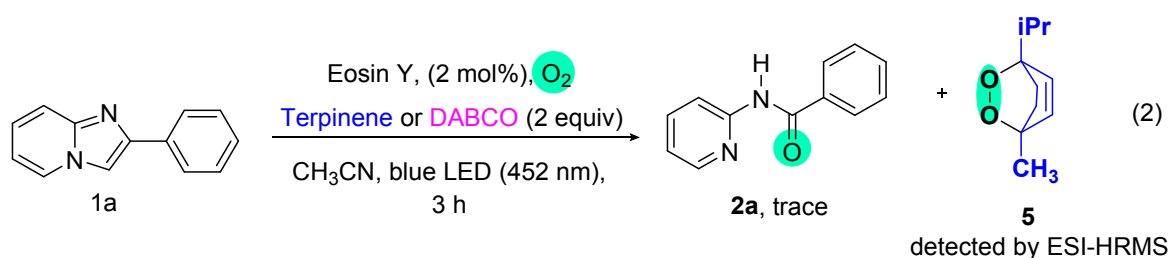


**Fig. S3:** Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) shows oxidation and reduction potential values of 2-phenylimidazopyridine (**1a**).

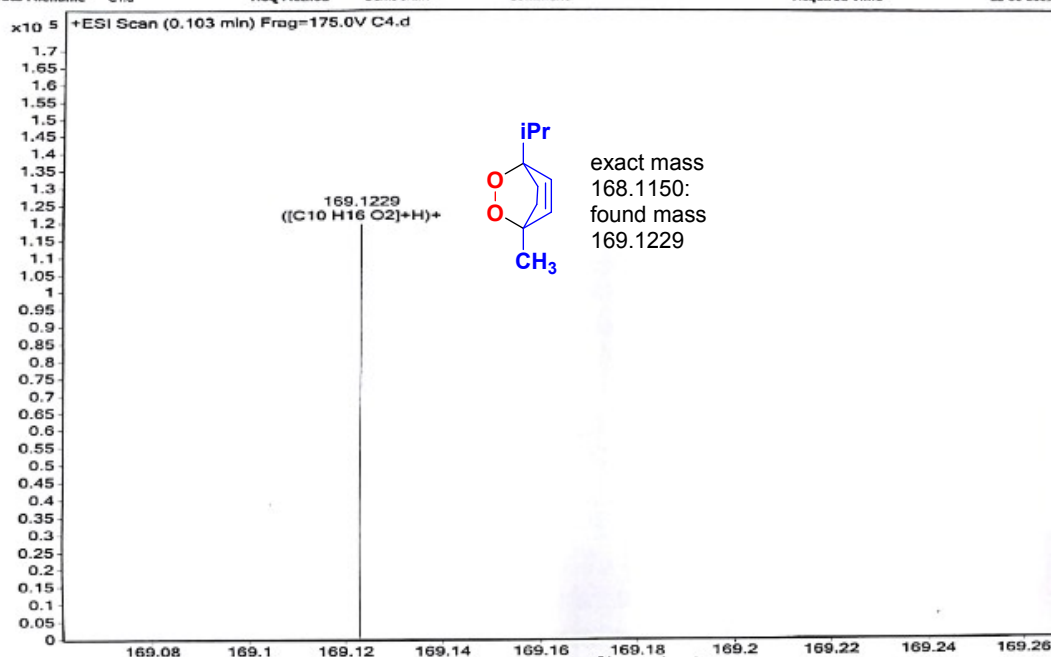
## Experiments for mechanistic study

### 1. Singlet oxygen quenching experiments:

A reaction tube was charged with 2-phenylimidazo[1,2-*a*] pyridine (**1a**) (97 mg, 0.5 mmol), terpinene/DABCO (136 mg/112 mg, 1.0 mmol) and eosin Y (2 mol%) dissolved in MeCN (4.0 mL). The reaction mixture was stirred under blue LED (10 W) irradiation in O<sub>2</sub> atmosphere at RT for 3 h. The reaction mixture was monitored by thin layer chromatography. The desired product **2a** was formed in trace. Further, a small aliquot of the reaction mixture was injected into the mass spectrometer. Peak corresponding to terpinene adduct (**5**) was seen in the mass spectrum given below. HRMS (ESI, *m/z*) calcd. for C<sub>10</sub>H<sub>17</sub>O<sub>2</sub> [M+H]<sup>+</sup> 169.1223, found 169.1229.

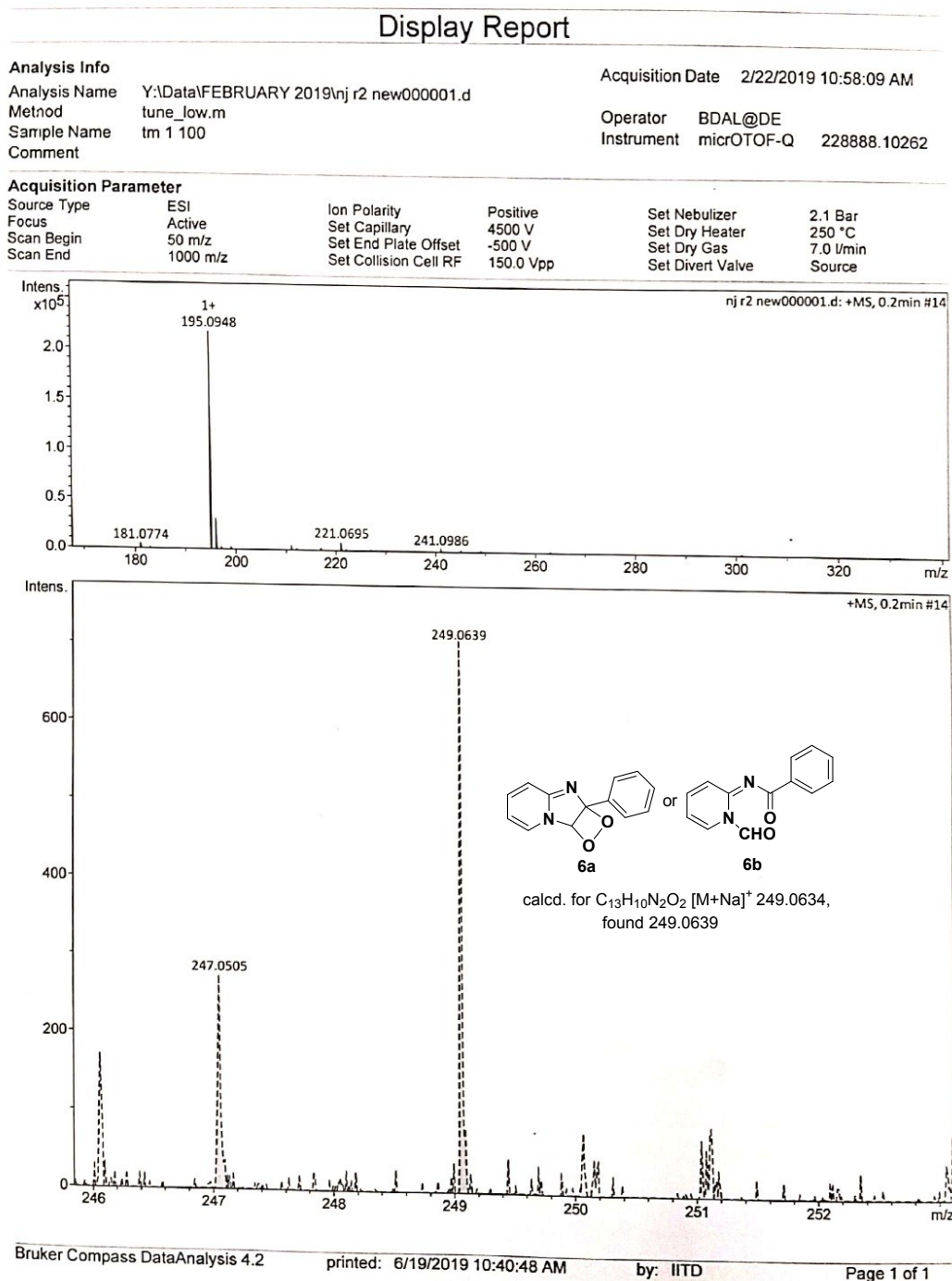


Sample Name	C4	Position	P1-85	Instrument Name	Instrument 1	User Name	
Inj Vol	1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	C4.d	ACQ Method	Damo JK.m	Comment		Acquired Time	22-01-2019 14:06:50

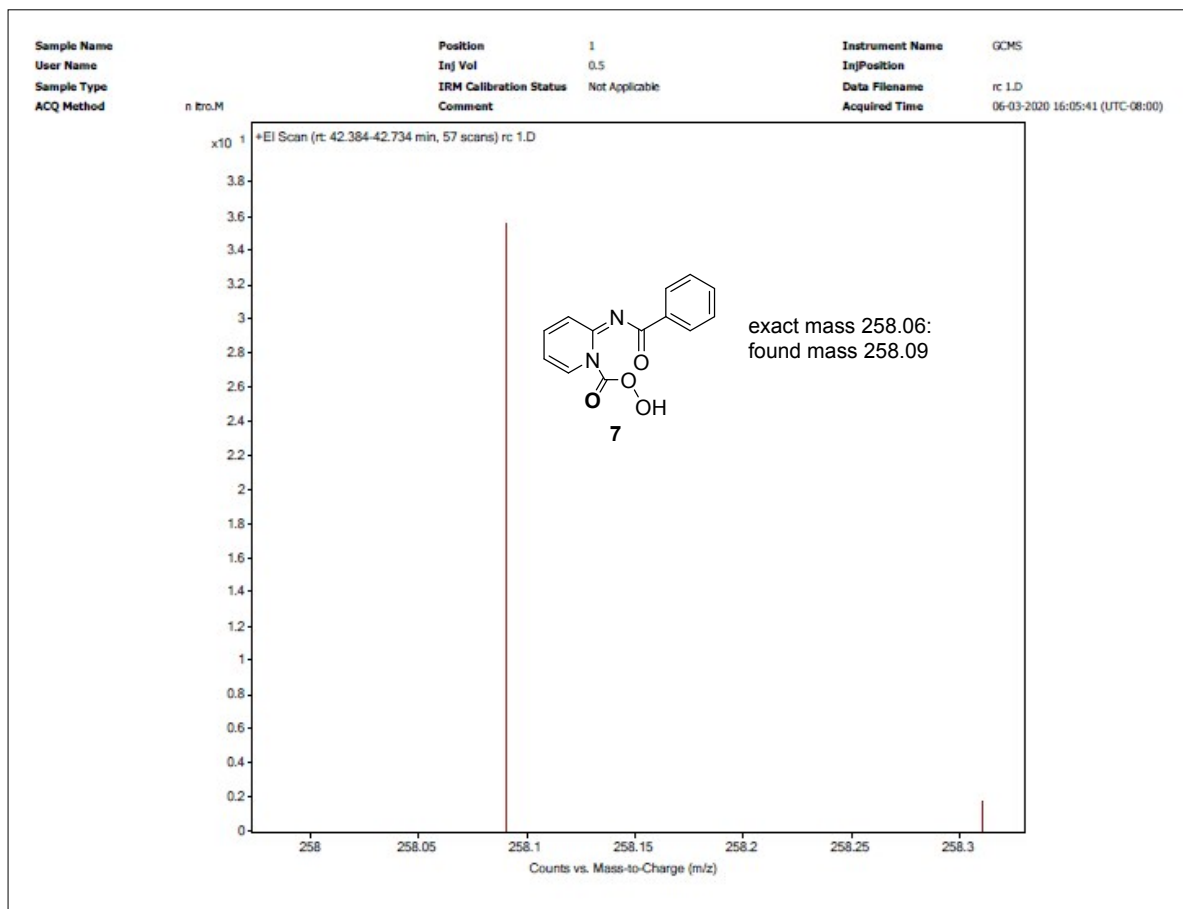


## 2. Experimental procedure for analysis of reaction mixture by mass spectrometry

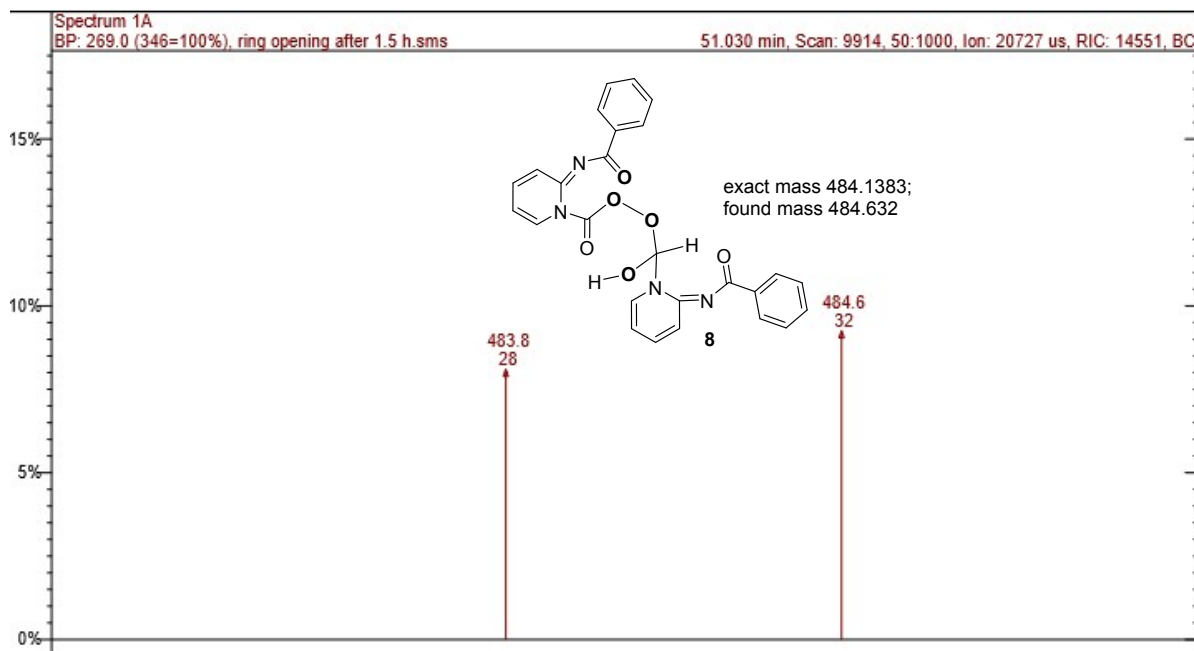
A reaction tube was charged with 2-phenylimidazo[1,2-*a*]pyridine (**1a**) (97 mg, 0.5 mmol) and eosin Y (2 mol %) dissolved in MeCN (4.0 mL). The reaction mixture was stirred under blue LED (10 W) irradiation in O<sub>2</sub> atmosphere at RT for 1 h. 30 μL of the mixture was quickly taken out into a small tube and analysed by HRMS and GCMS (**Fig. S4, S5 and S6**).



**Fig. S4:** HRMS spectrum of the reaction mixture.



**Fig. S5:** GCMS spectrum of the reaction mixture after 1 h.



**Fig. S6:** GCMS spectrum of the reaction mixture after 1 h.

### 3. Detection of CO<sub>2</sub>.

A sealed tube was charged with 2-phenylimidazo[1,2-*a*] pyridine (**1a**) (97 mg, 0.5 mmol) and eosin Y (2 mol %) dissolved in MeCN (4.0 mL). The reaction mixture was stirred under blue LED (10 W) irradiation in O<sub>2</sub> atmosphere at RT. The gases produced in the reaction mixture were taken into 1 ml syringe from headspace and injected into a glass chromatograph. A calibration curve was drawn between concentration of CO<sub>2</sub> injected and area of the CO<sub>2</sub> peak obtained at different concentrations (Fig. S7).

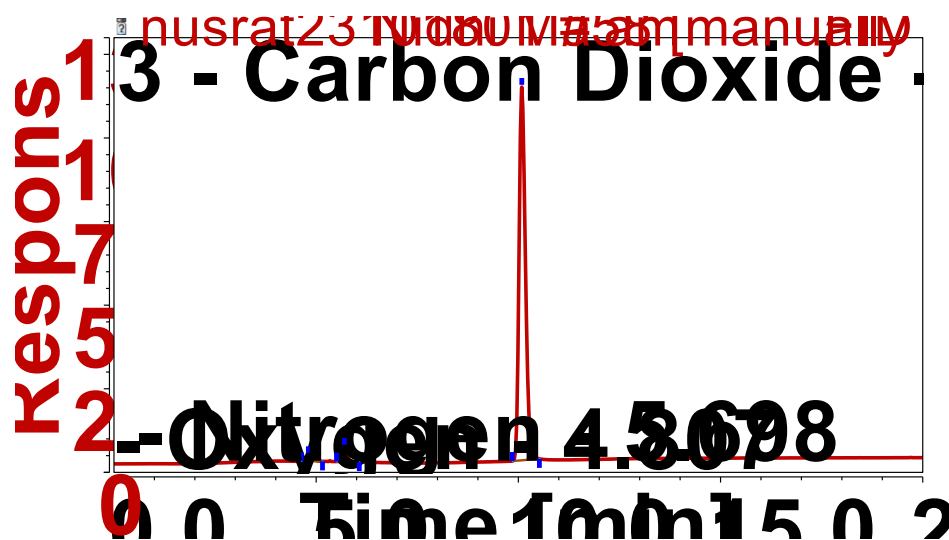


Fig. S7: Calibration curve for CO<sub>2</sub> estimation.

The area obtained in the test sample was equal to a concentration of 5000 ppm CO<sub>2</sub> in the standard samples. Presence of O<sub>2</sub> and N<sub>2</sub> may be due to their natural abundance in atmospheric air.

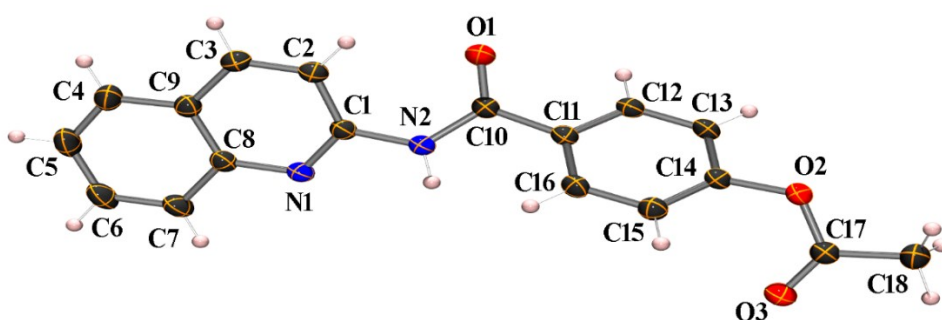


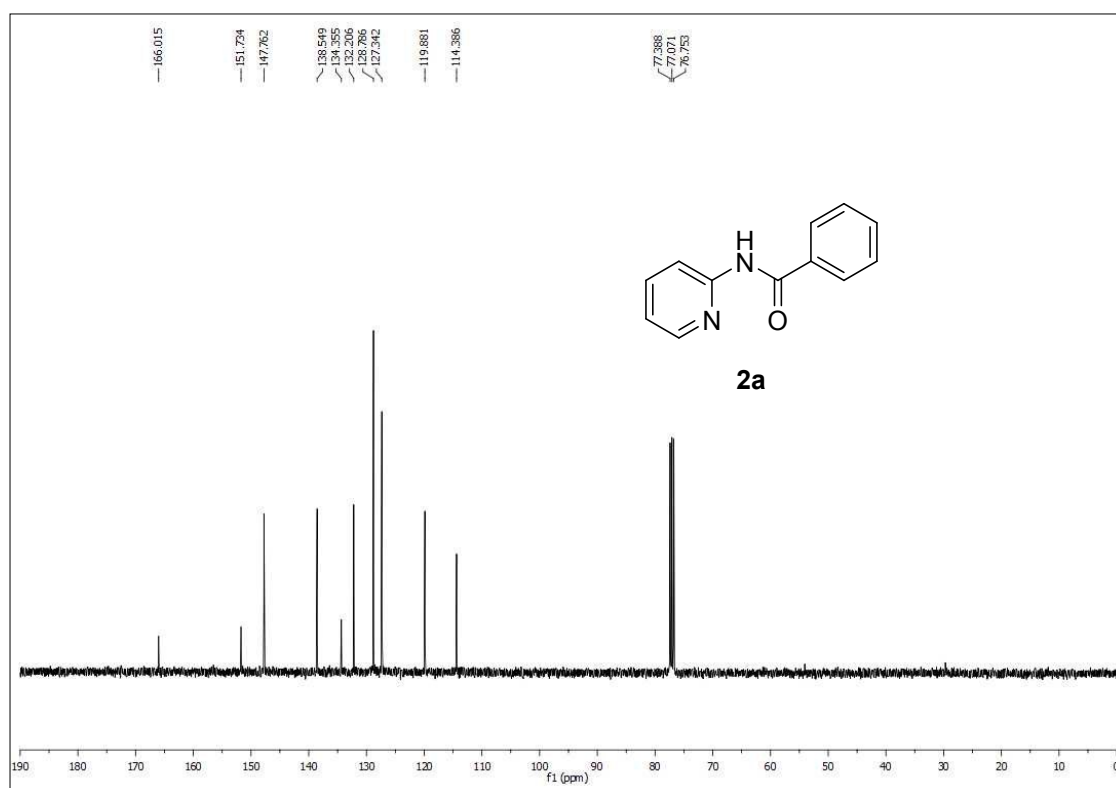
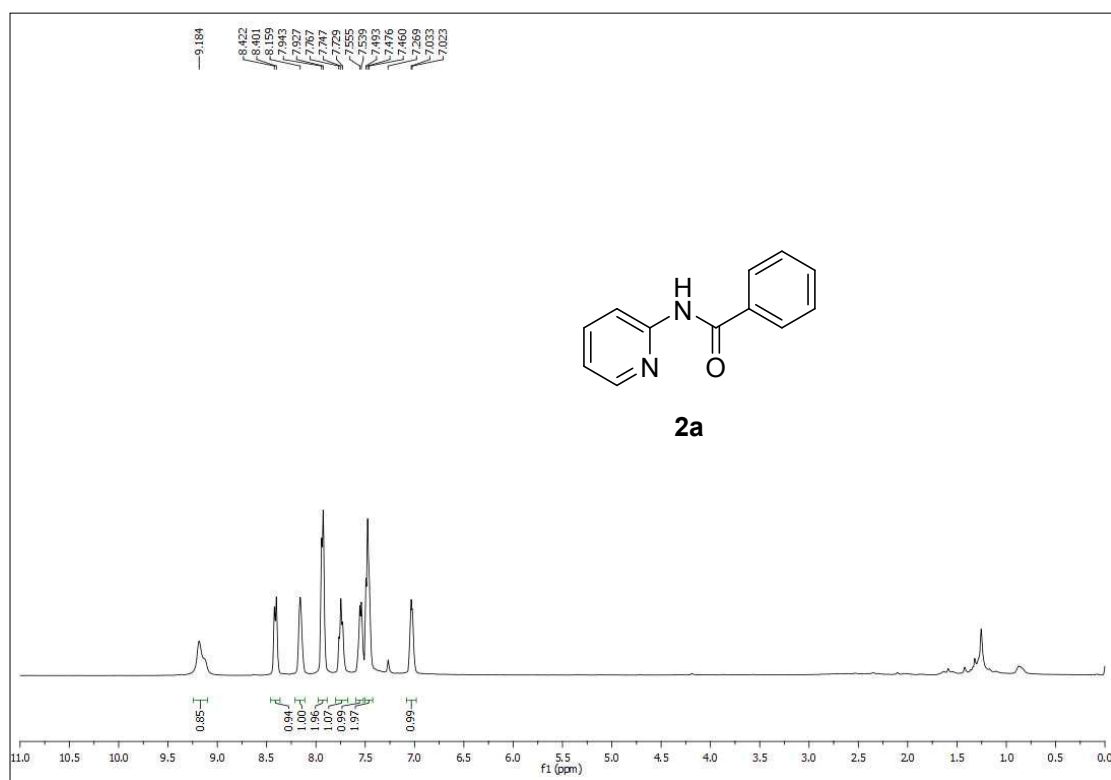
Fig. S8: Single crystal X-ray molecular structure of compound **4g**. Thermal ellipsoids are set at 50% probability.

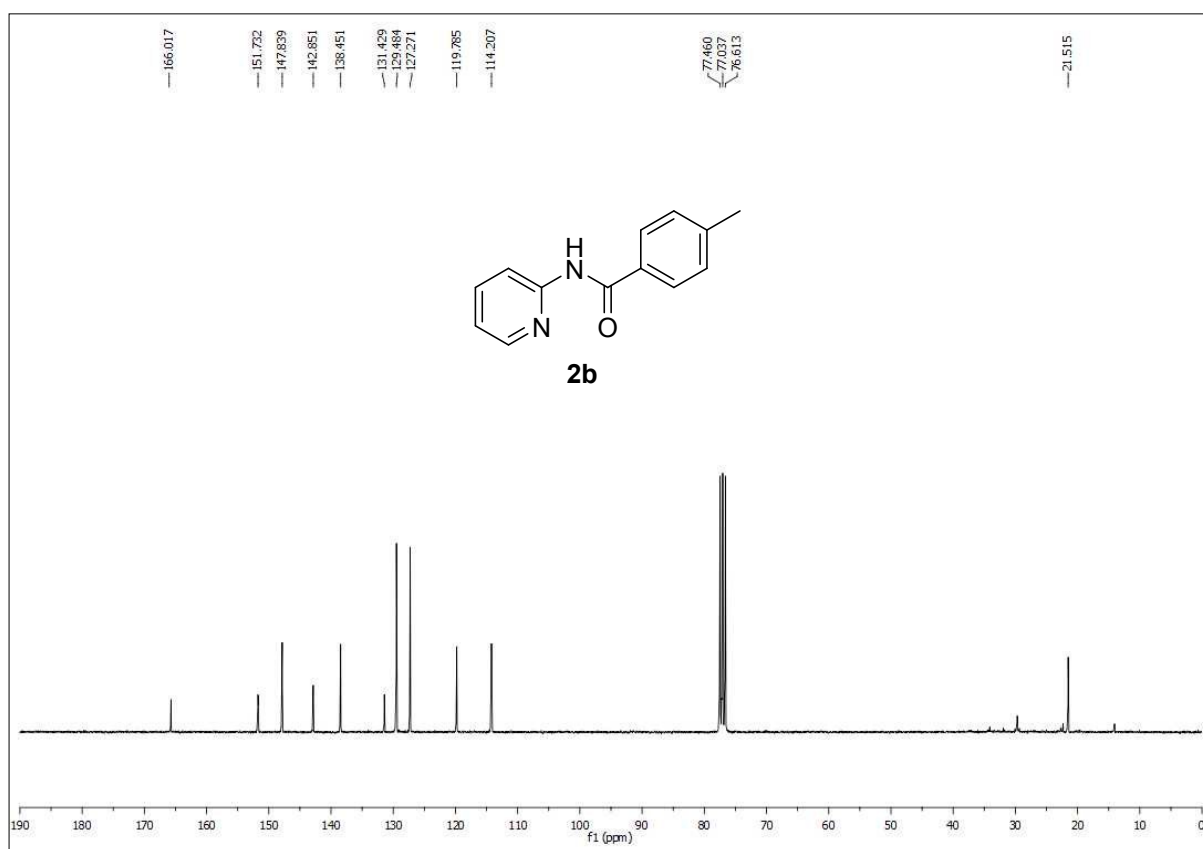
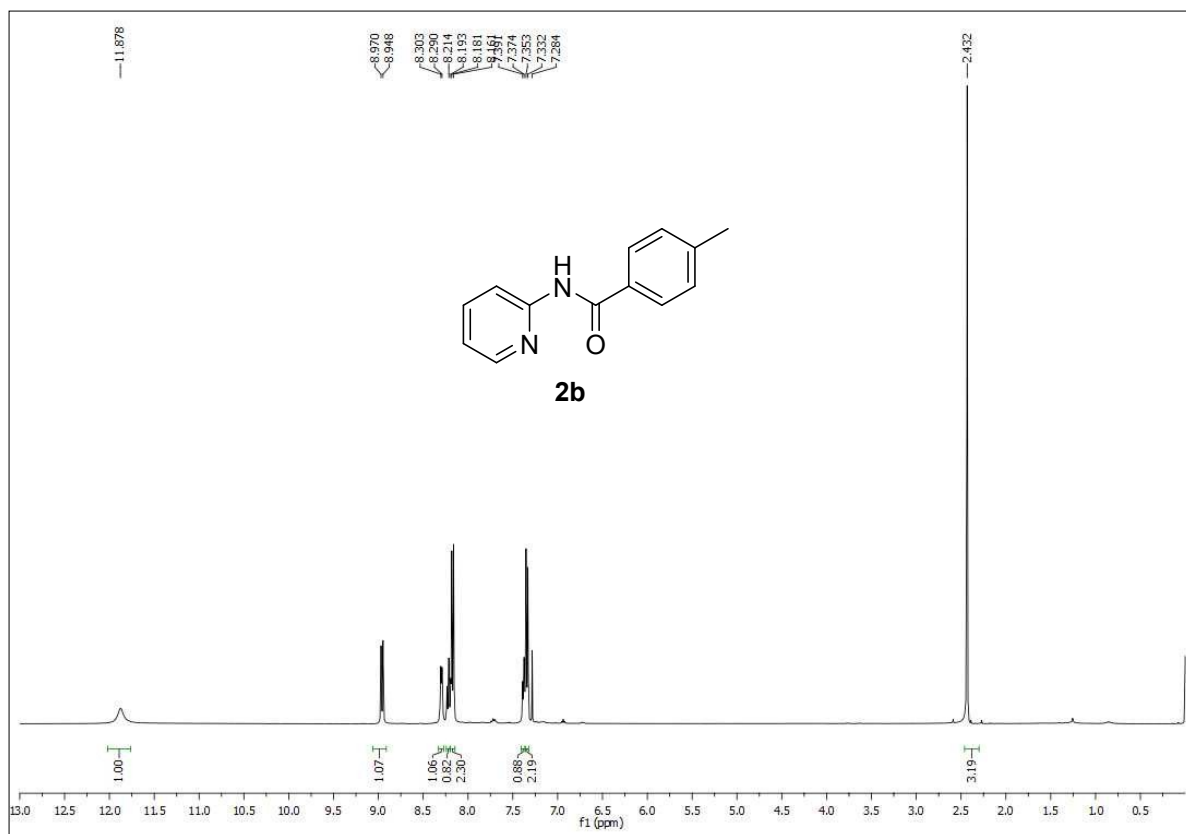


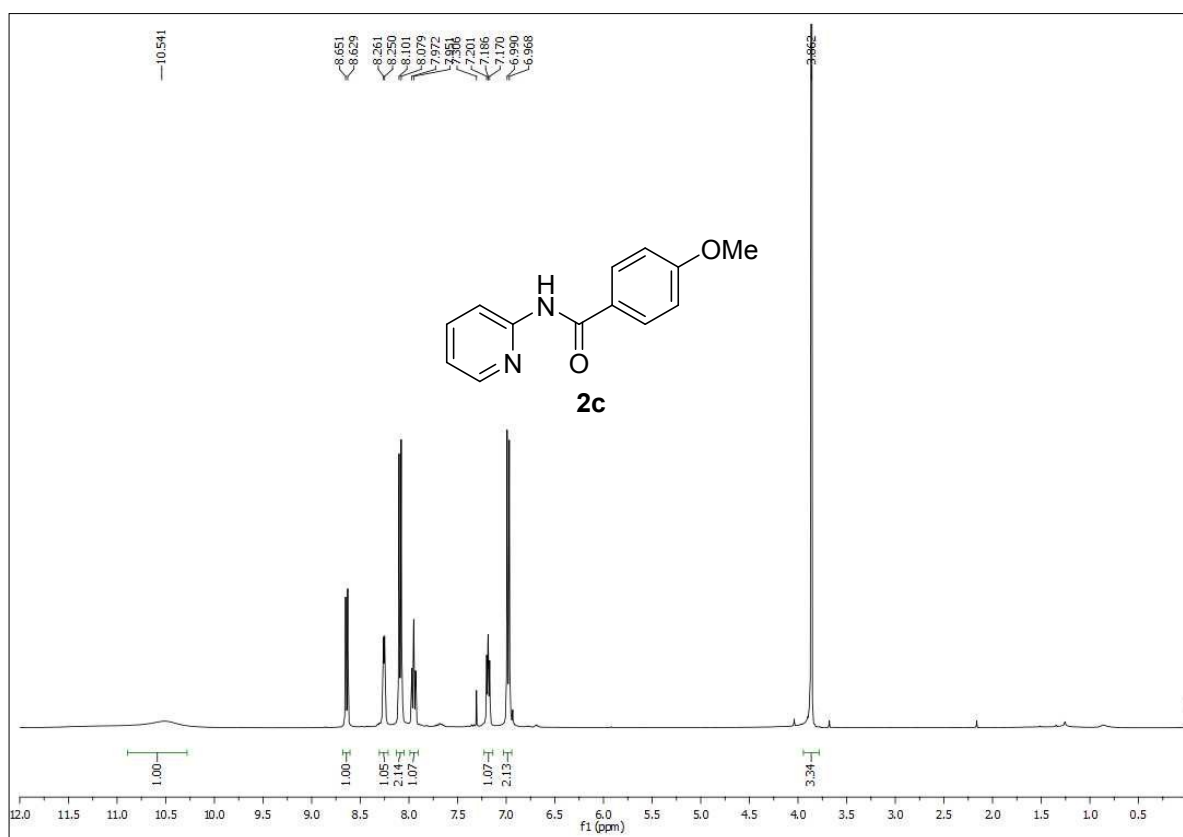
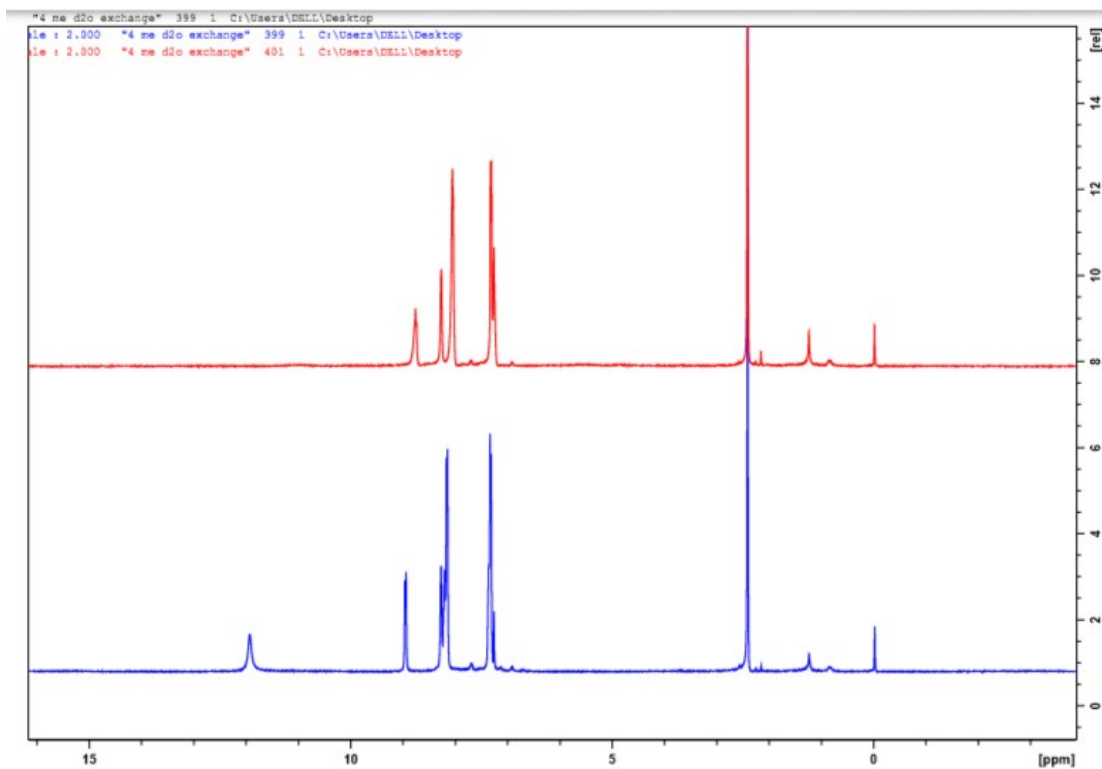
**Crystallographic description of 4-(quinolin-2-ylcarbamoyl)phenyl acetate (4g) (Table S1):**

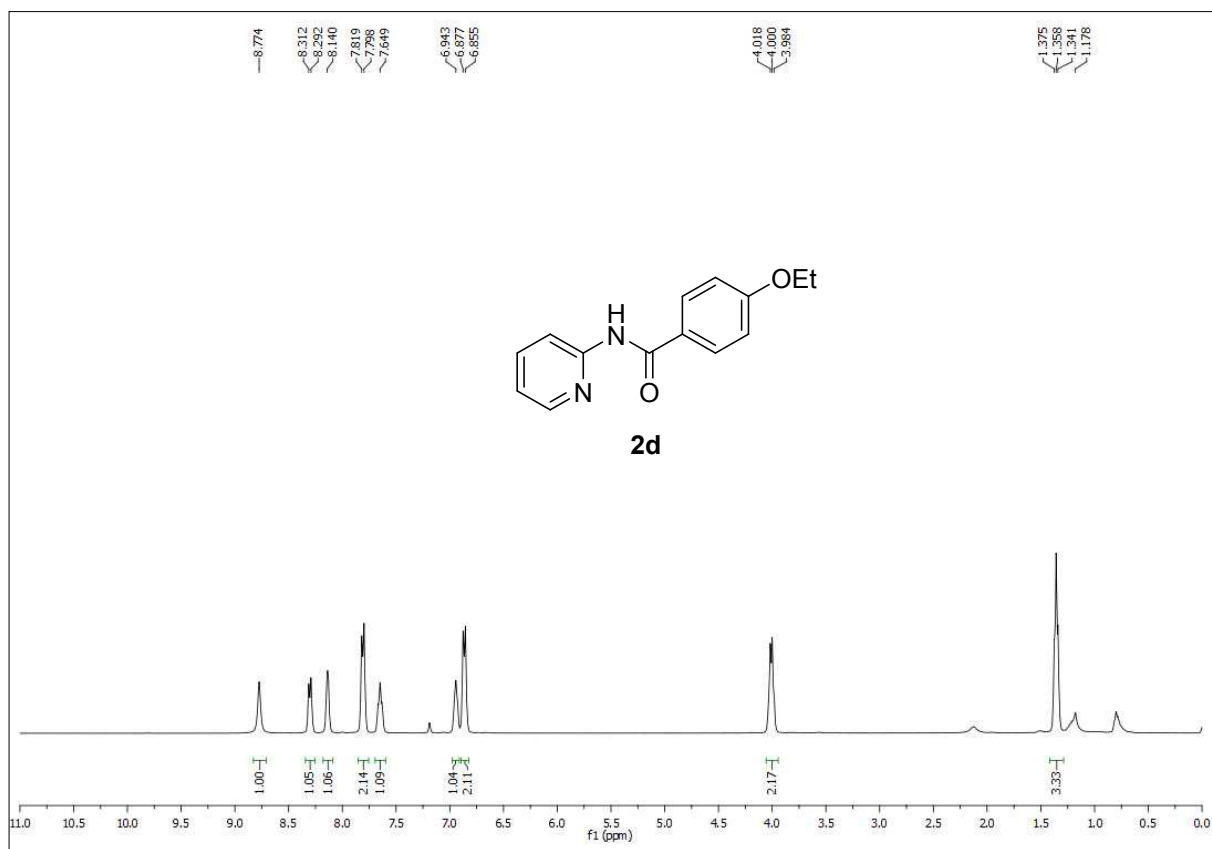
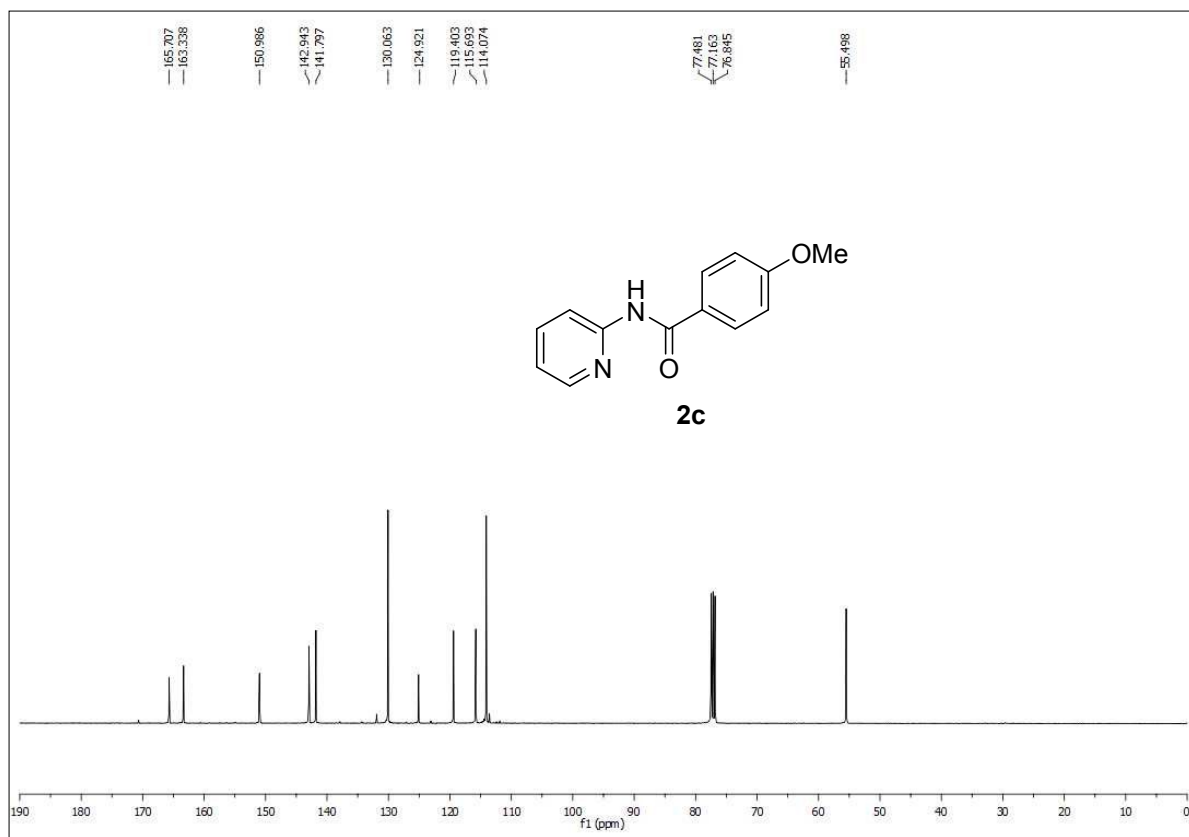
Identification code	new7_1_0m_a	
Empirical formula	C <sub>18</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>	
Formula weight	306.31	
Temperature	303 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 9.5310 (5) Å	a = 90°.
	b = 7.0315 (4) Å	b = 93.267 (2)°.
	c = 21.6758 (12) Å	g = 90°.
Volume	1450.29 (14) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.403 Mg/m <sup>3</sup>	
Absorption coefficient	0.097 mm <sup>-1</sup>	
F(000)	640.0	
Crystal size	0.16 x 0.10 x 0.08 mm <sup>3</sup>	
Theta range for data collection	3.12 to 24.99°.	
Index ranges	-12 ≤ h ≤ 12, -9 ≤ k ≤ 9, -28 ≤ l ≤ 28	
Reflections collected	9023	
Independent reflections	3304 [R(int) = 0.0510]	
Completeness to theta = 28.30°	98.6 %	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	3561 / 0 / 210	
Goodness-of-fit on F <sup>2</sup>	1.069	
Final R indices [I > 2σ(I)]	R1 = 0.0538, wR2 = 0.1454	
R indices (all data)	R1 = 0.0510, wR2 = 0.1482	

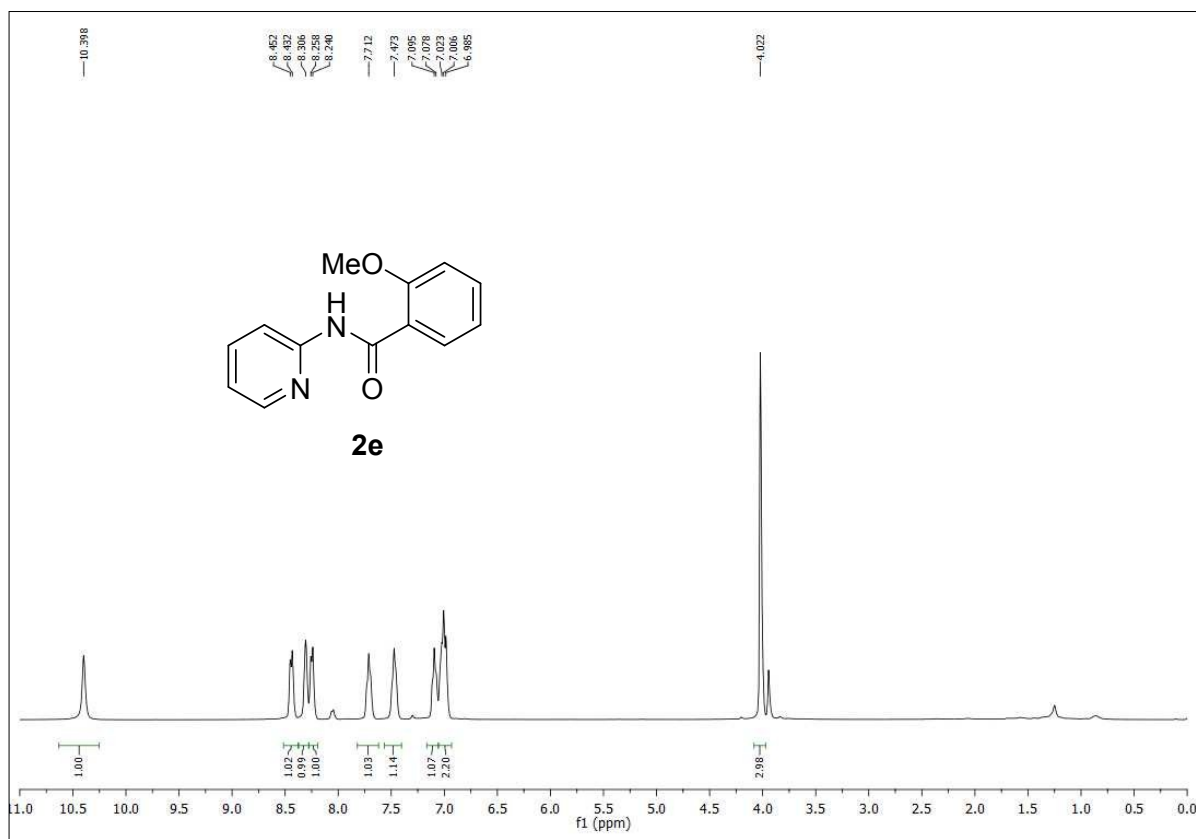
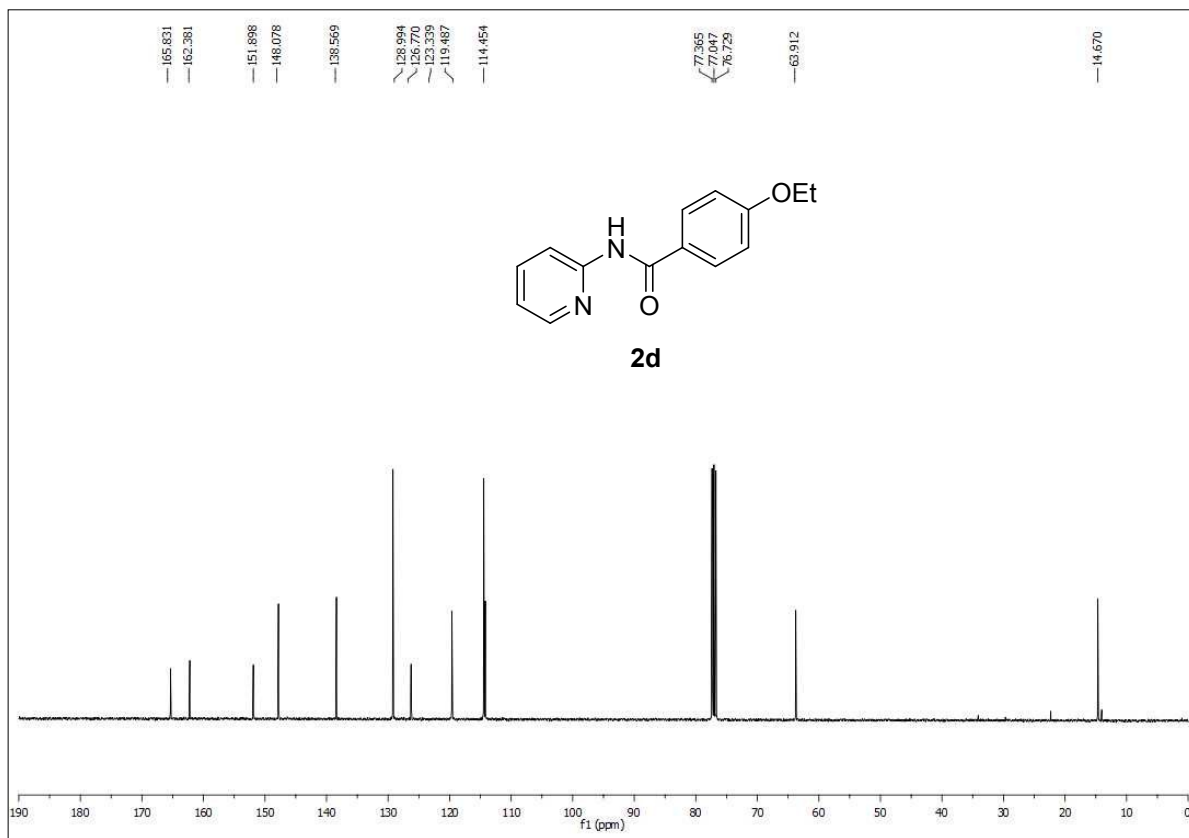
# Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra.

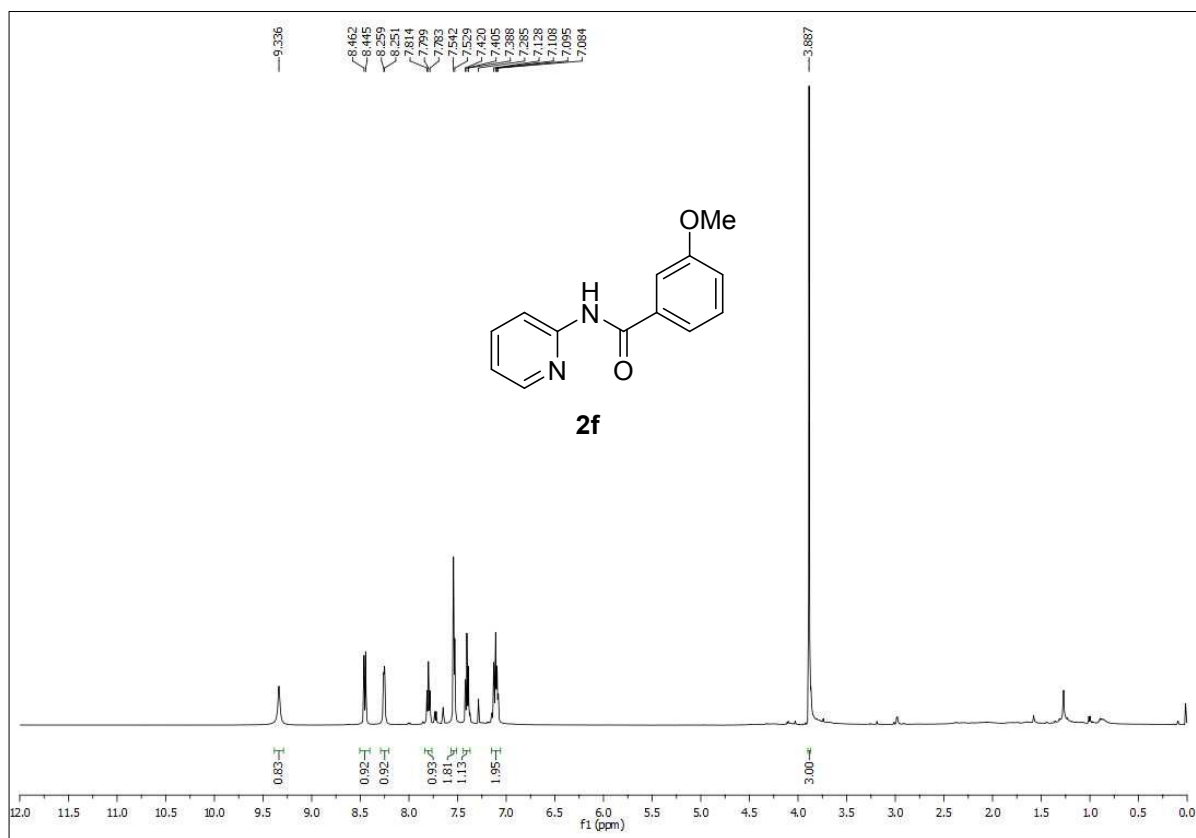
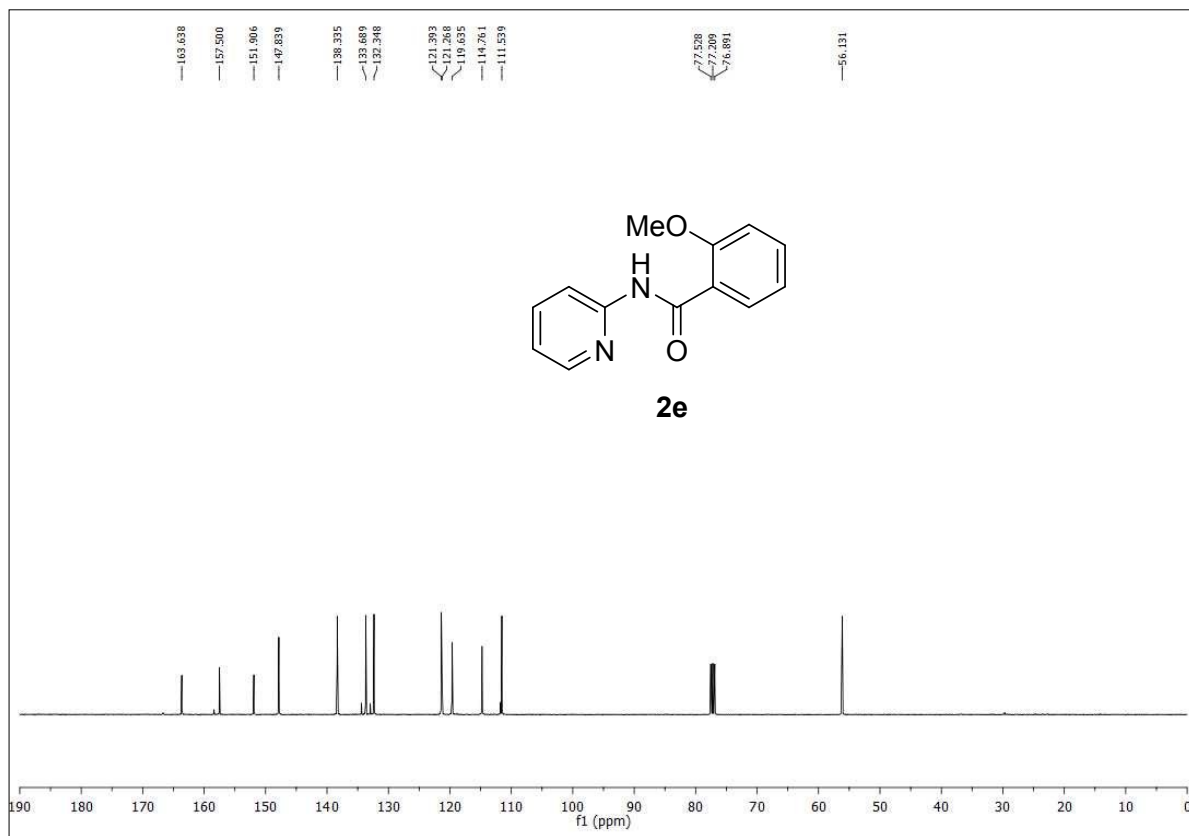


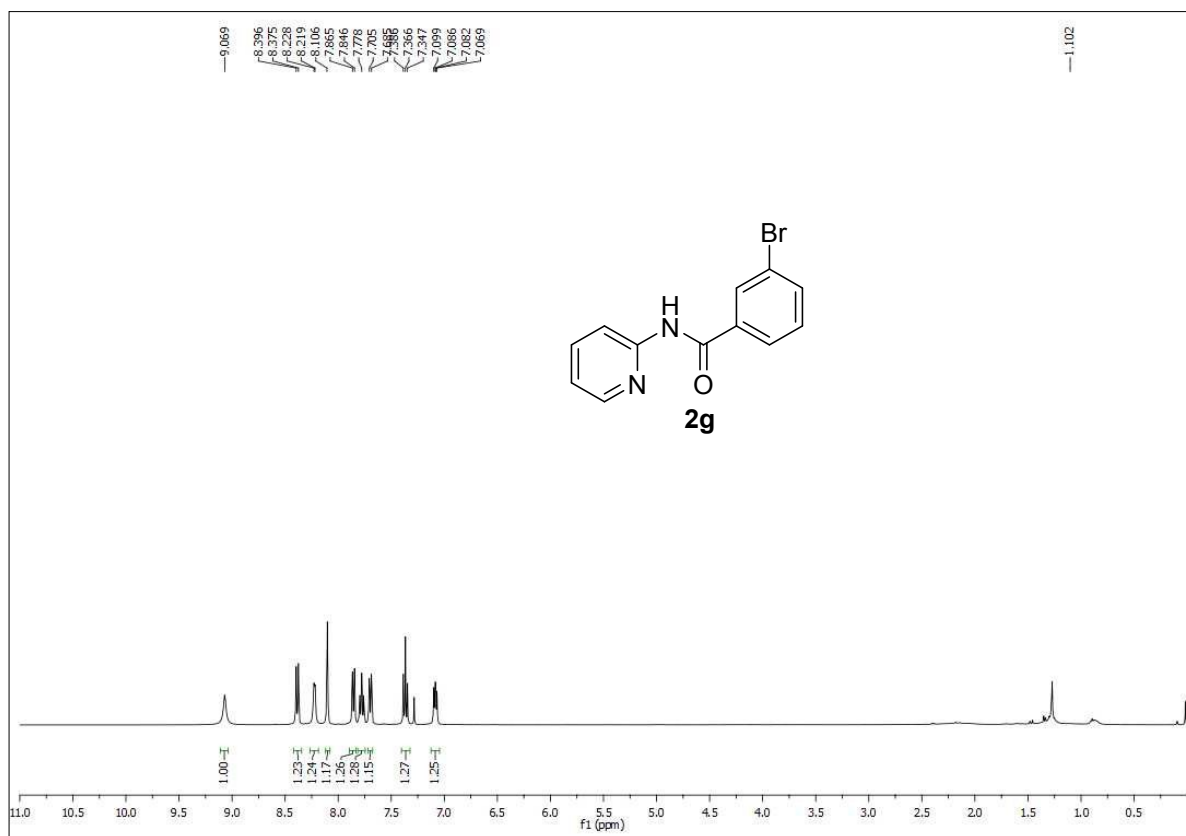
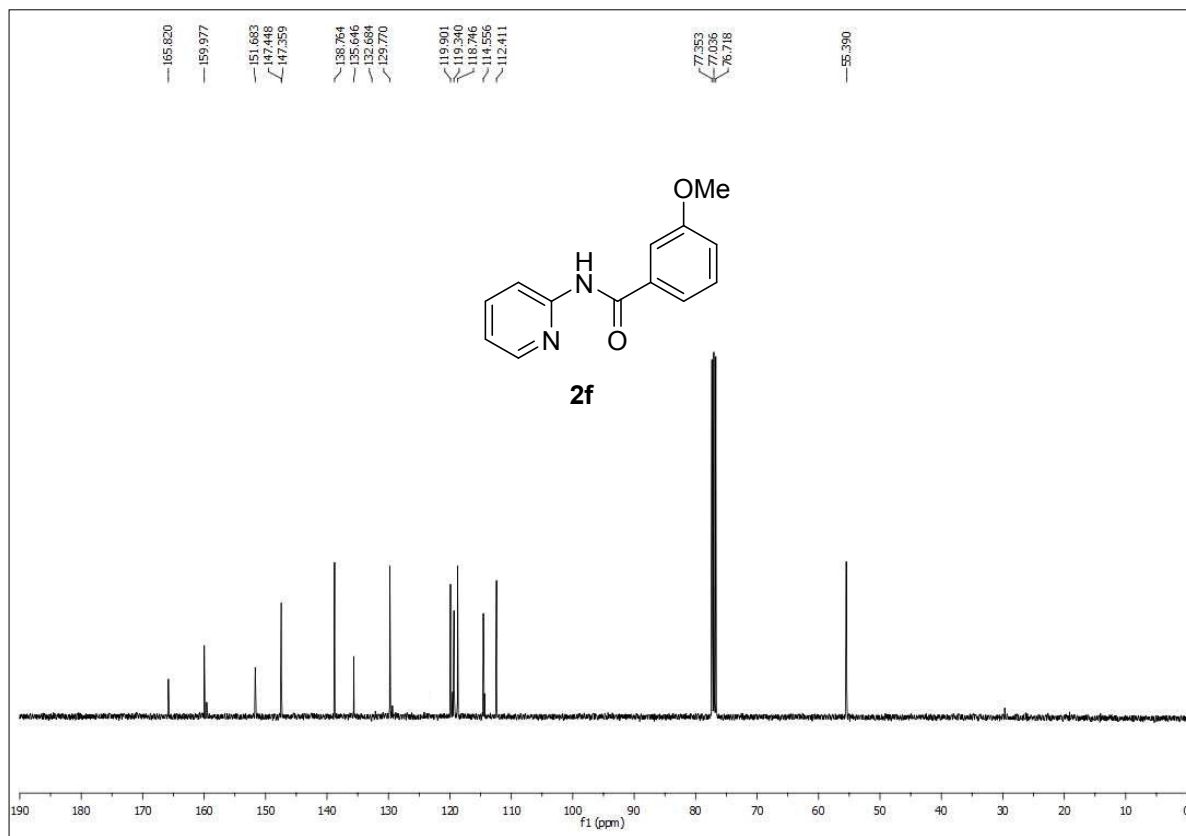




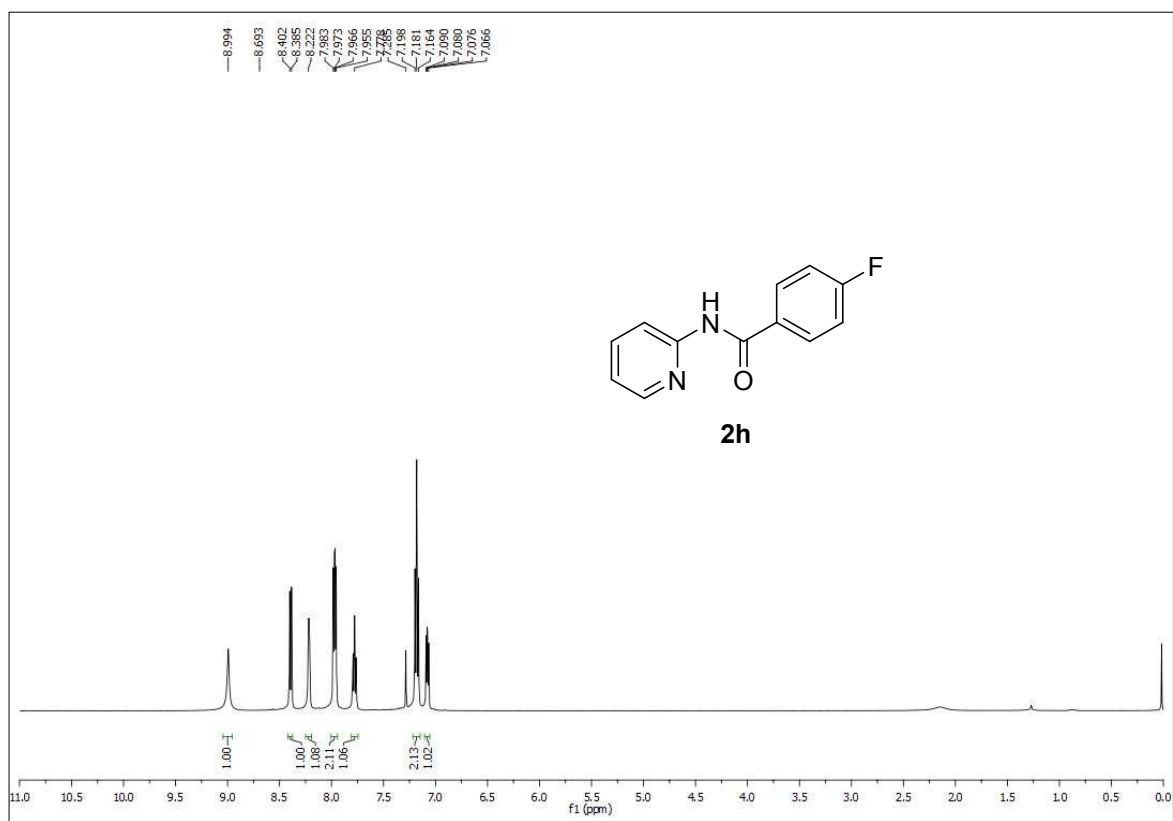
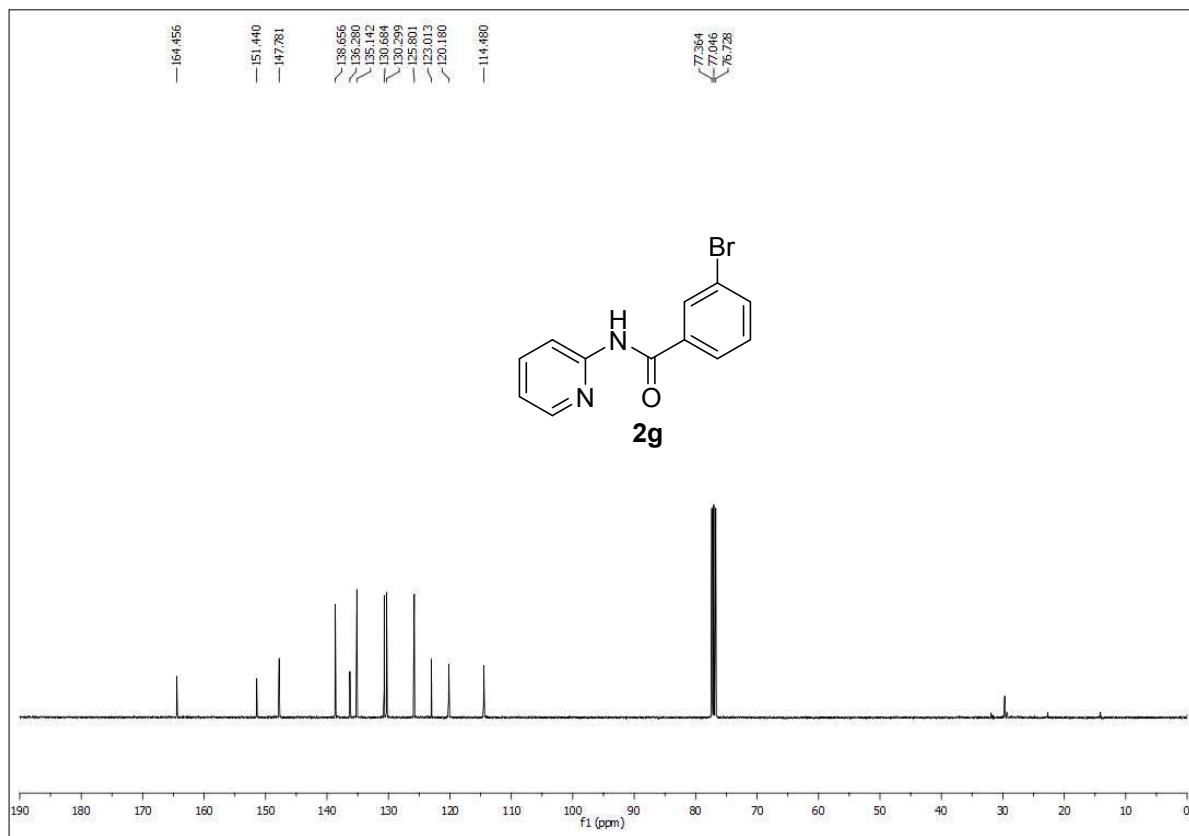


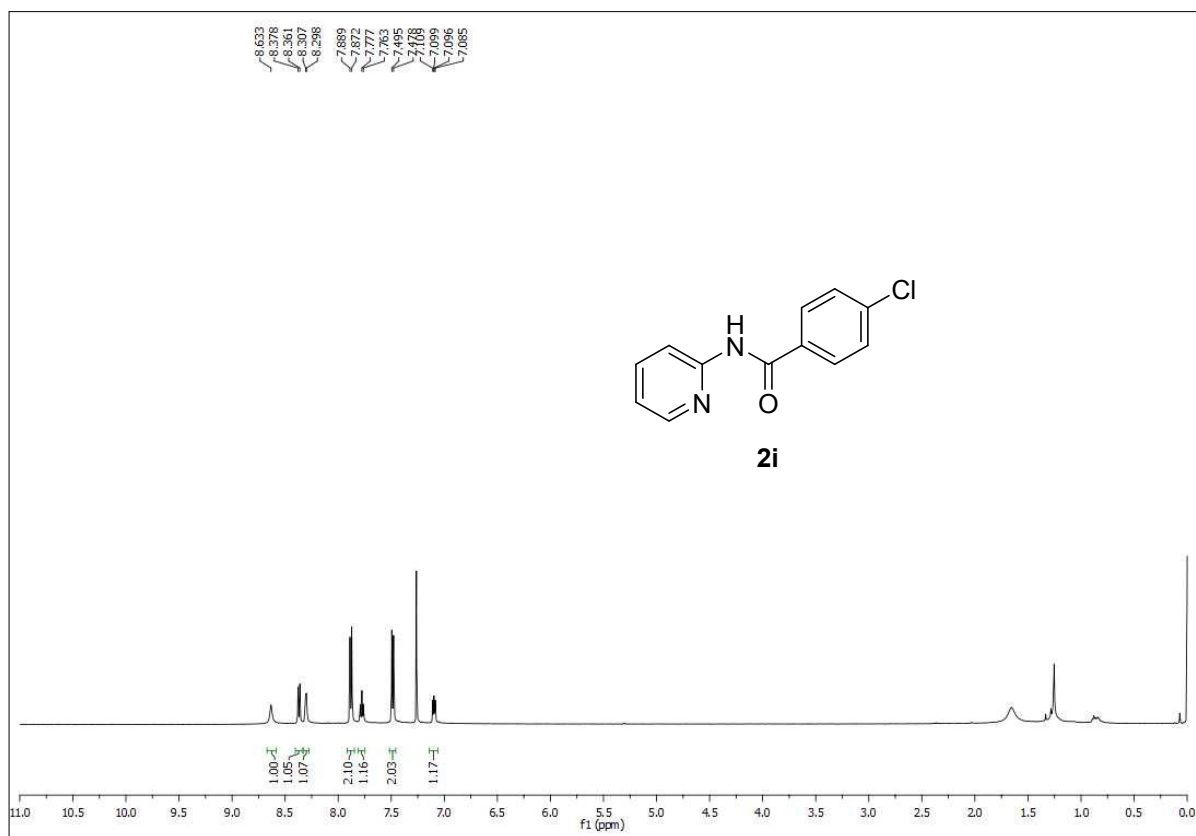
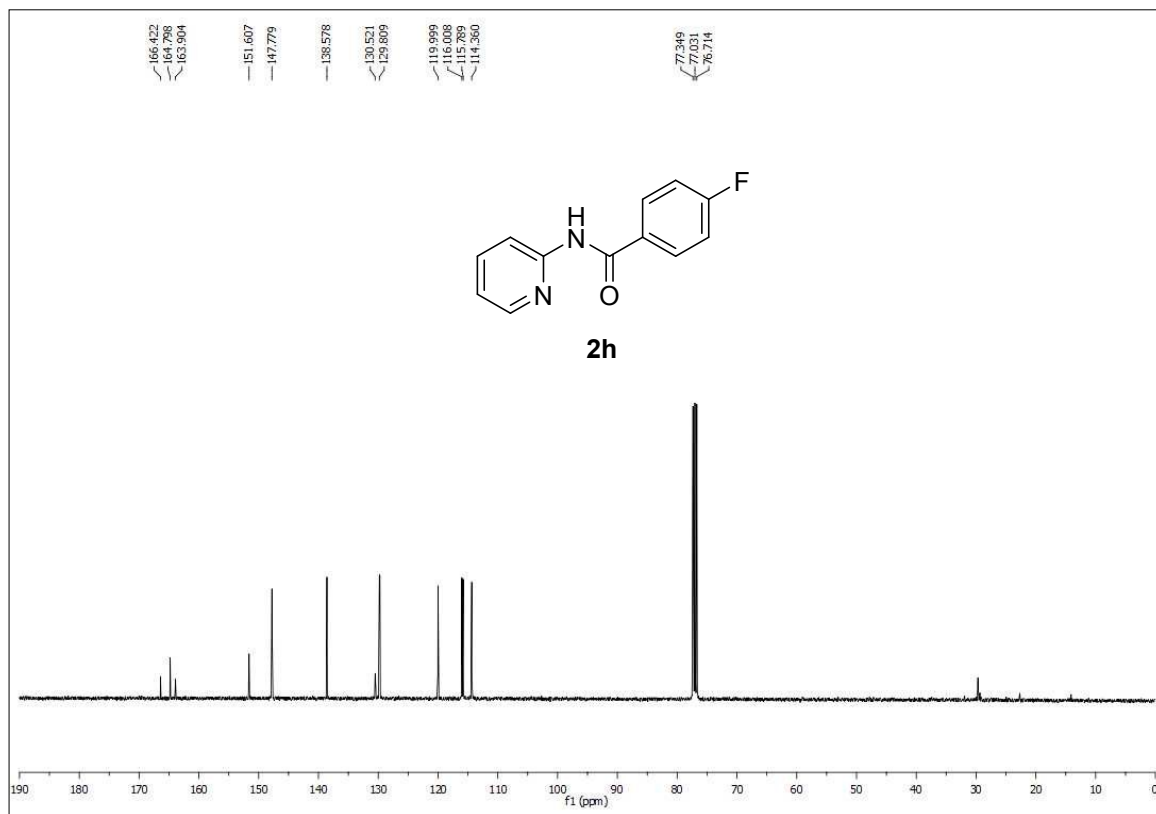


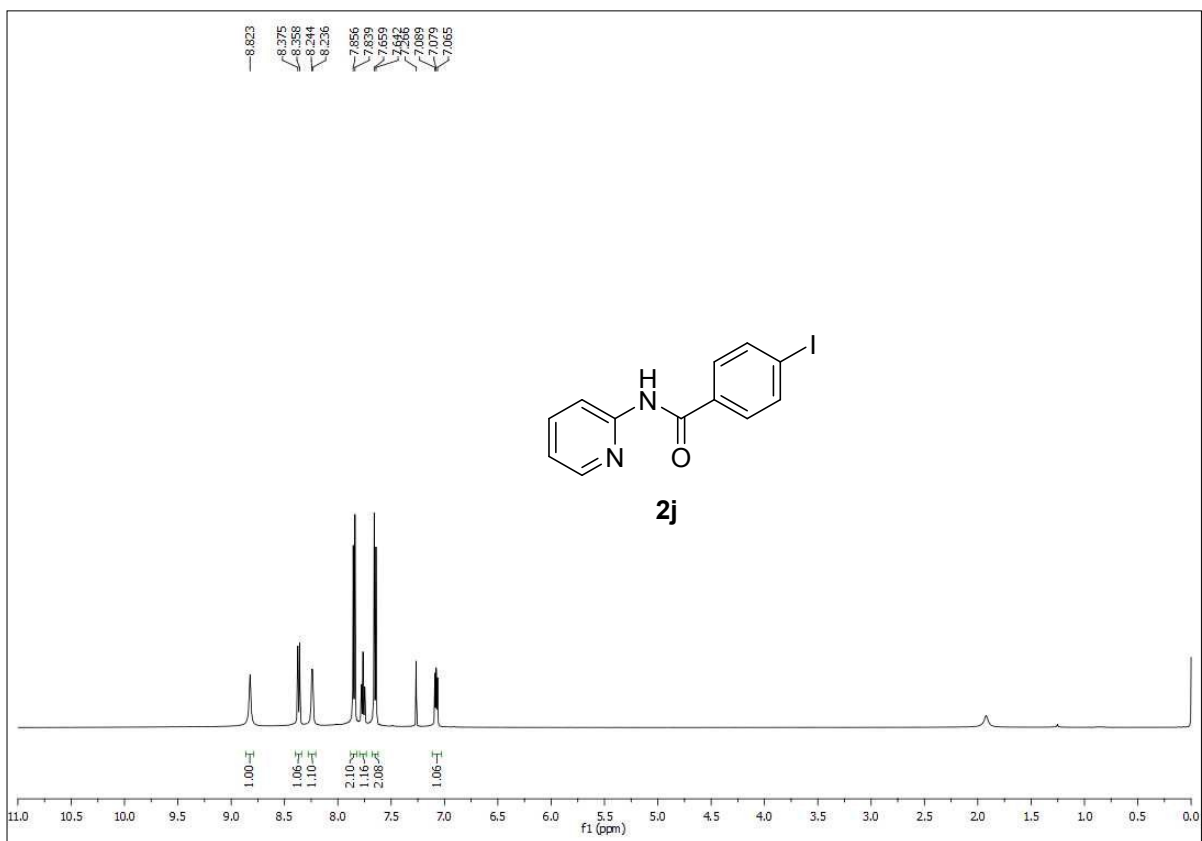
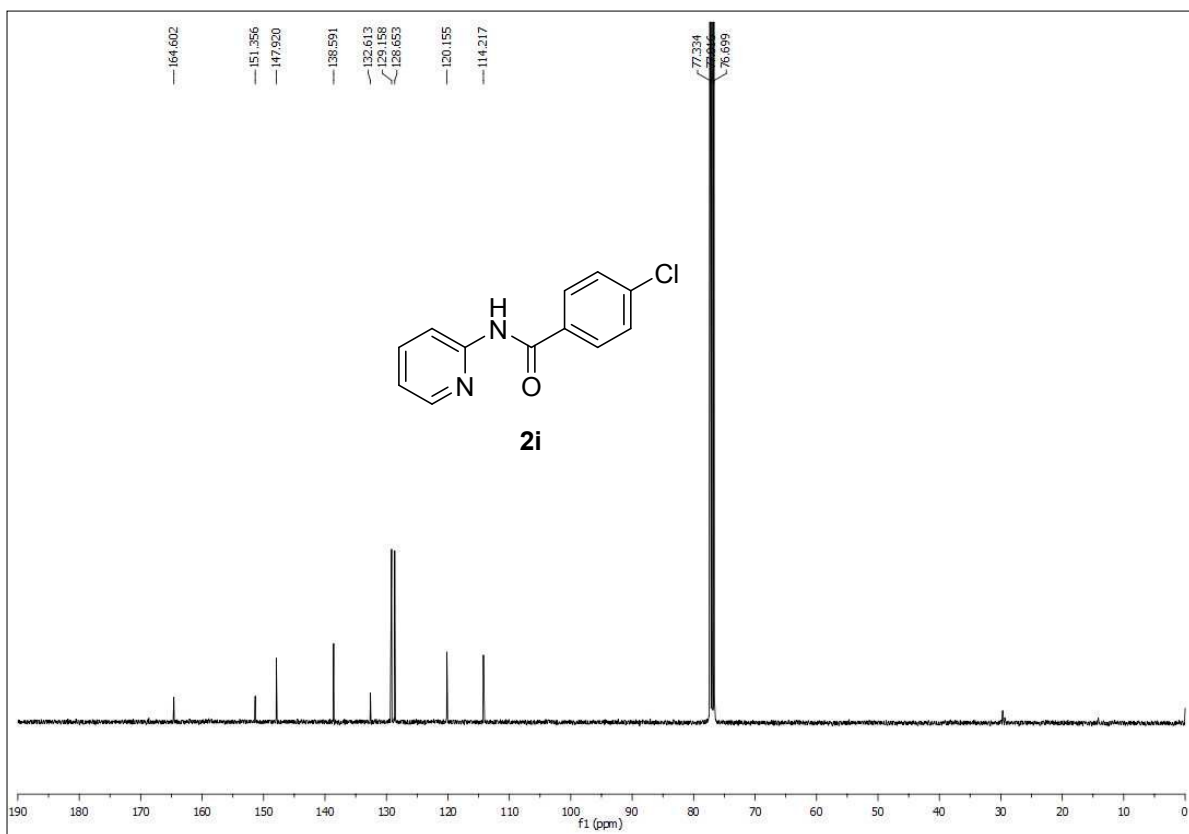


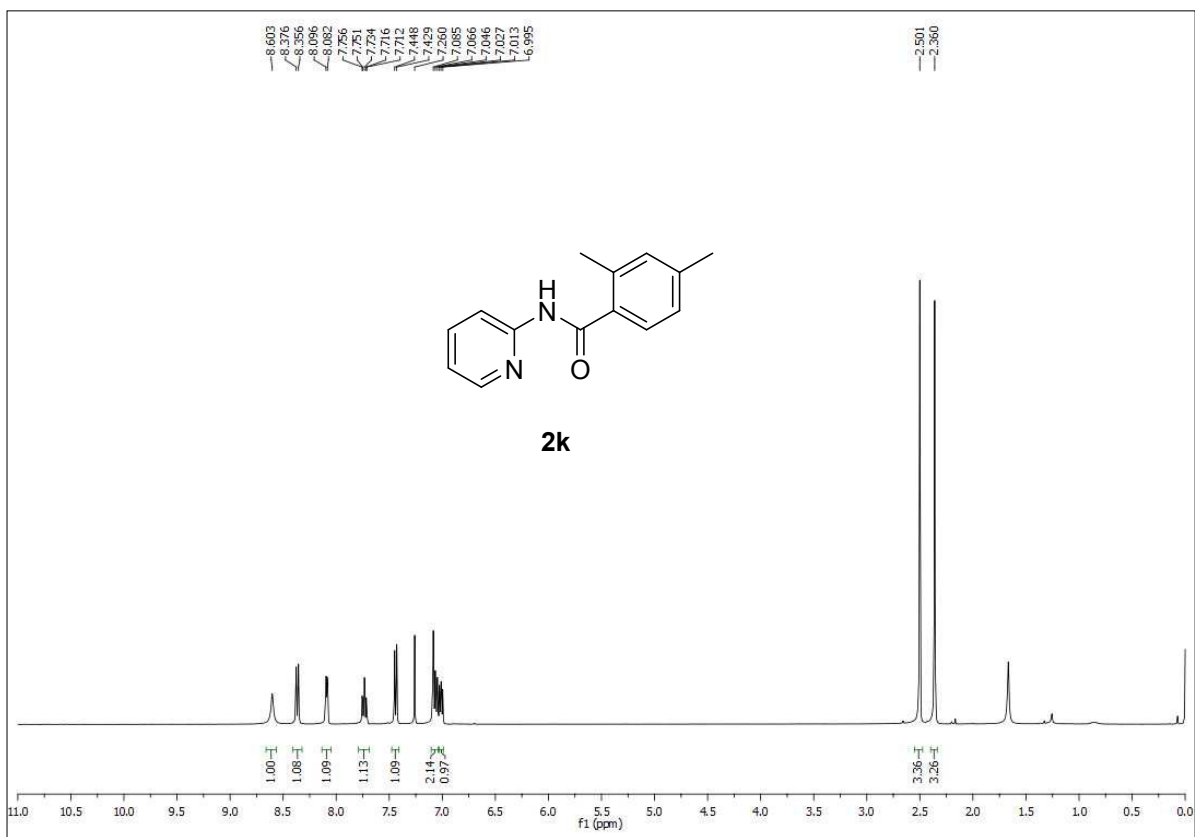
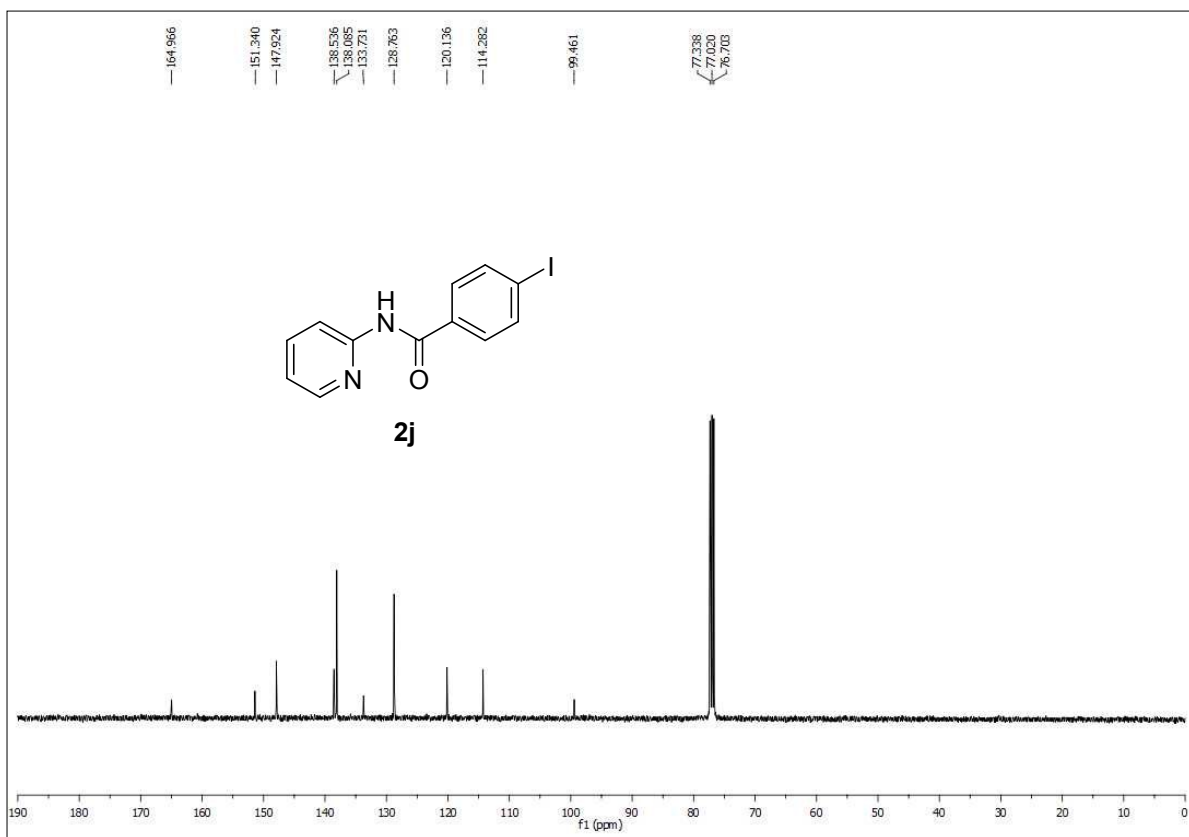


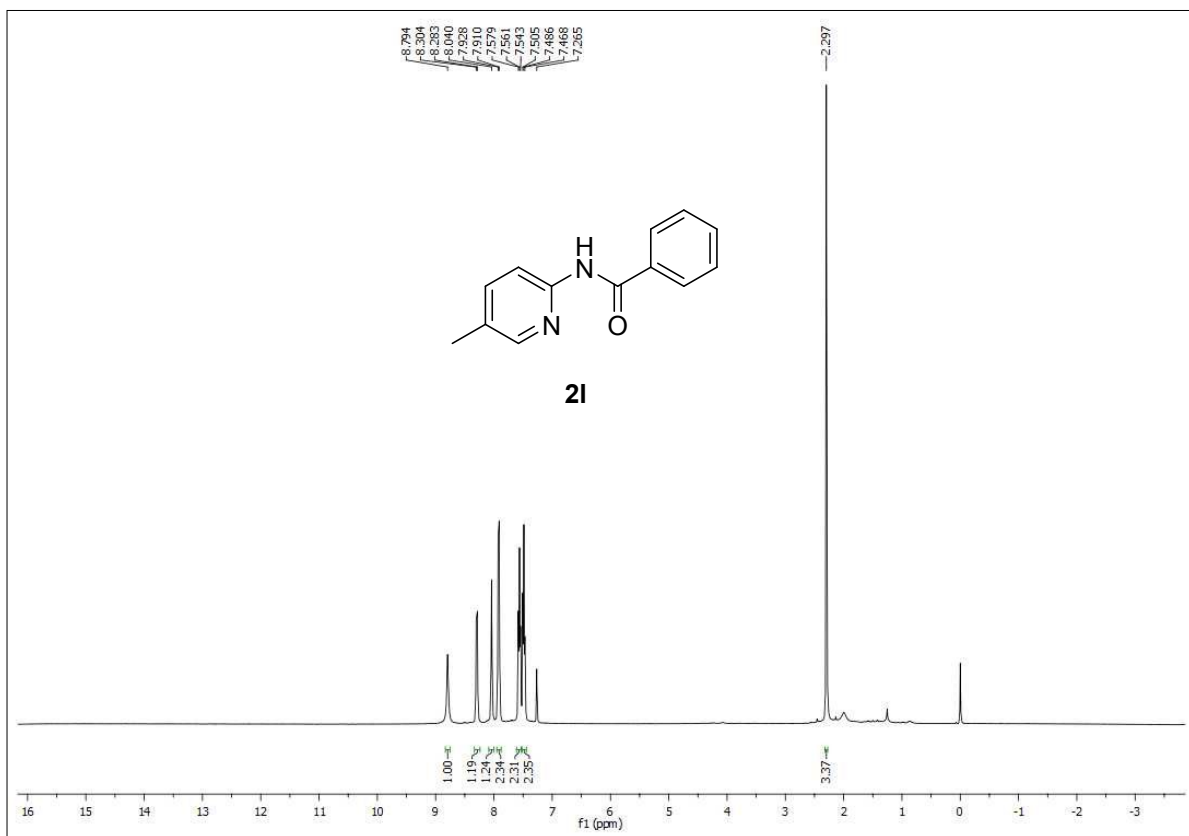
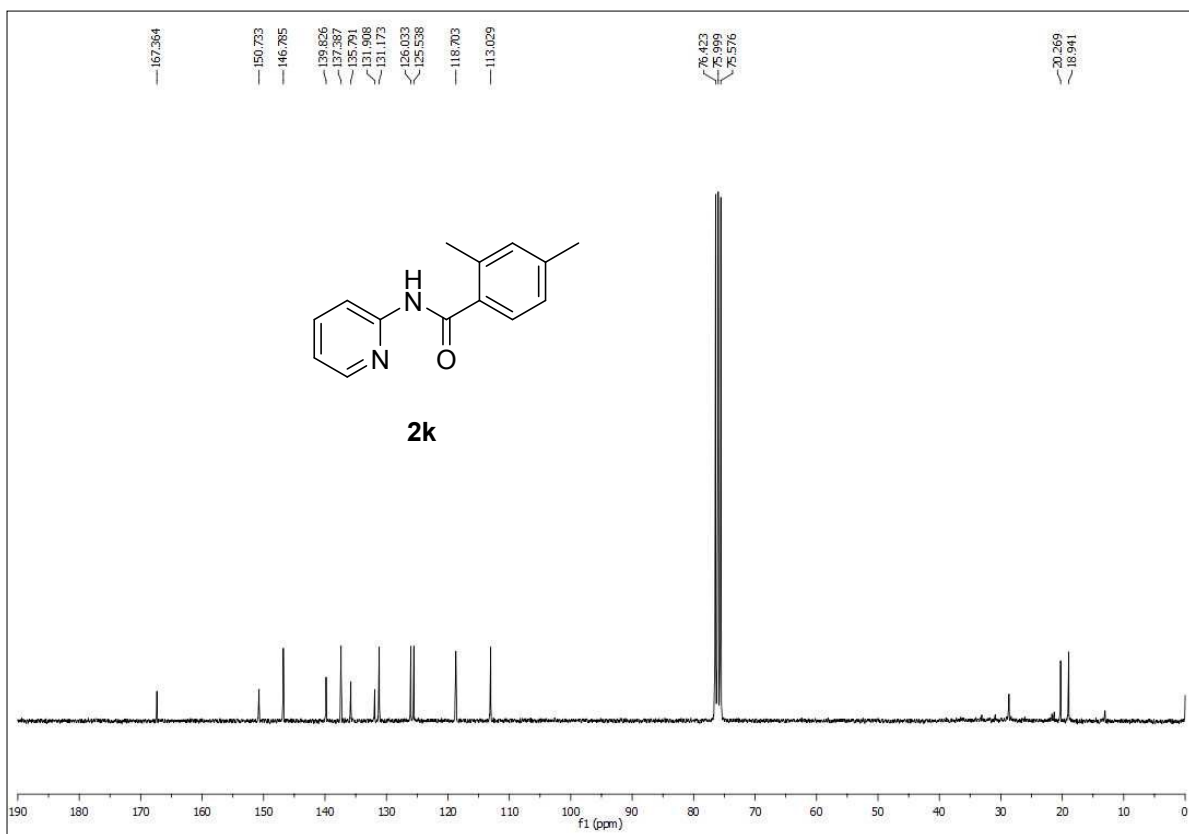


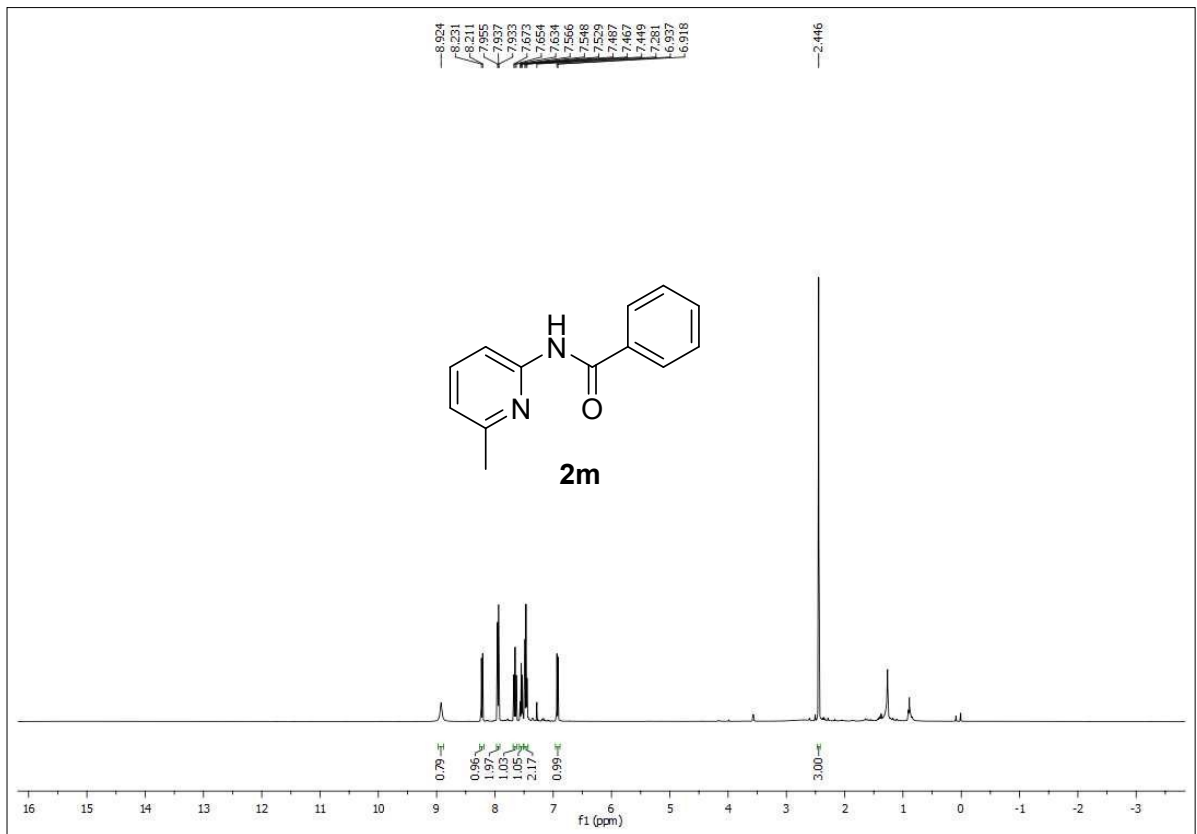
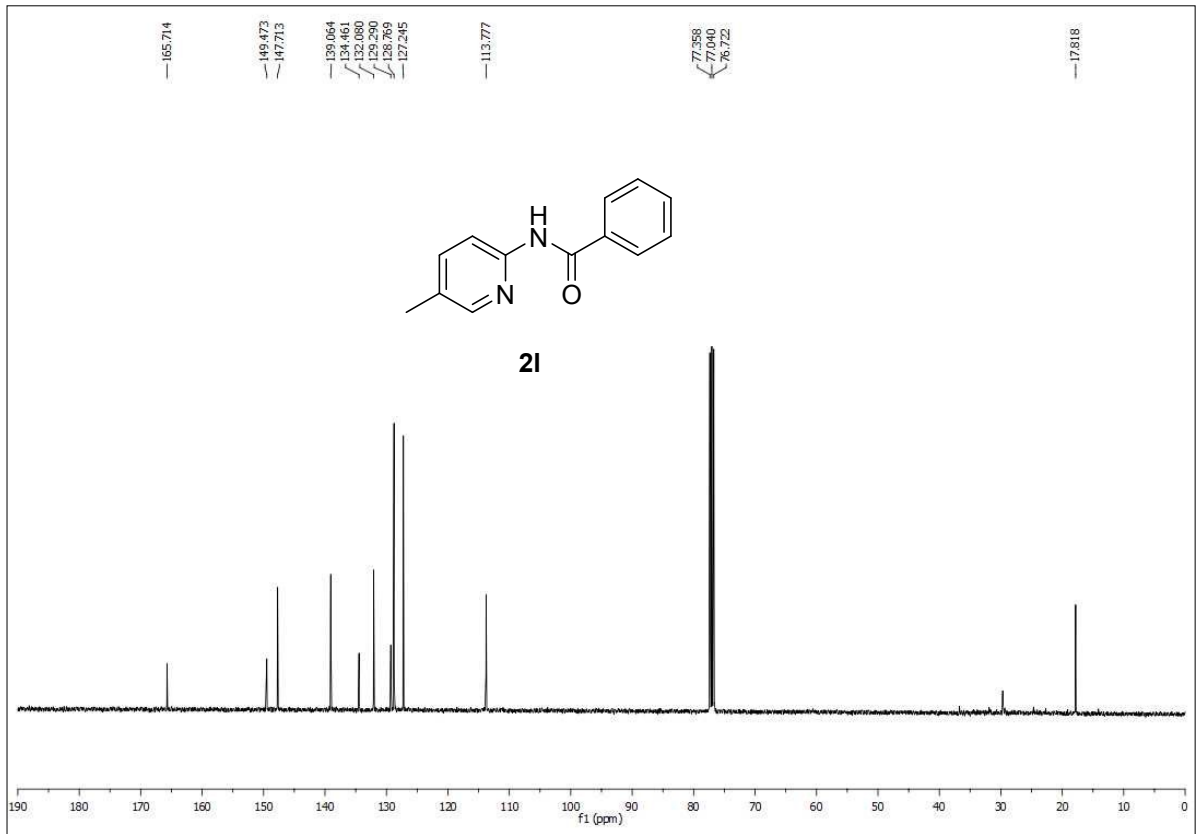


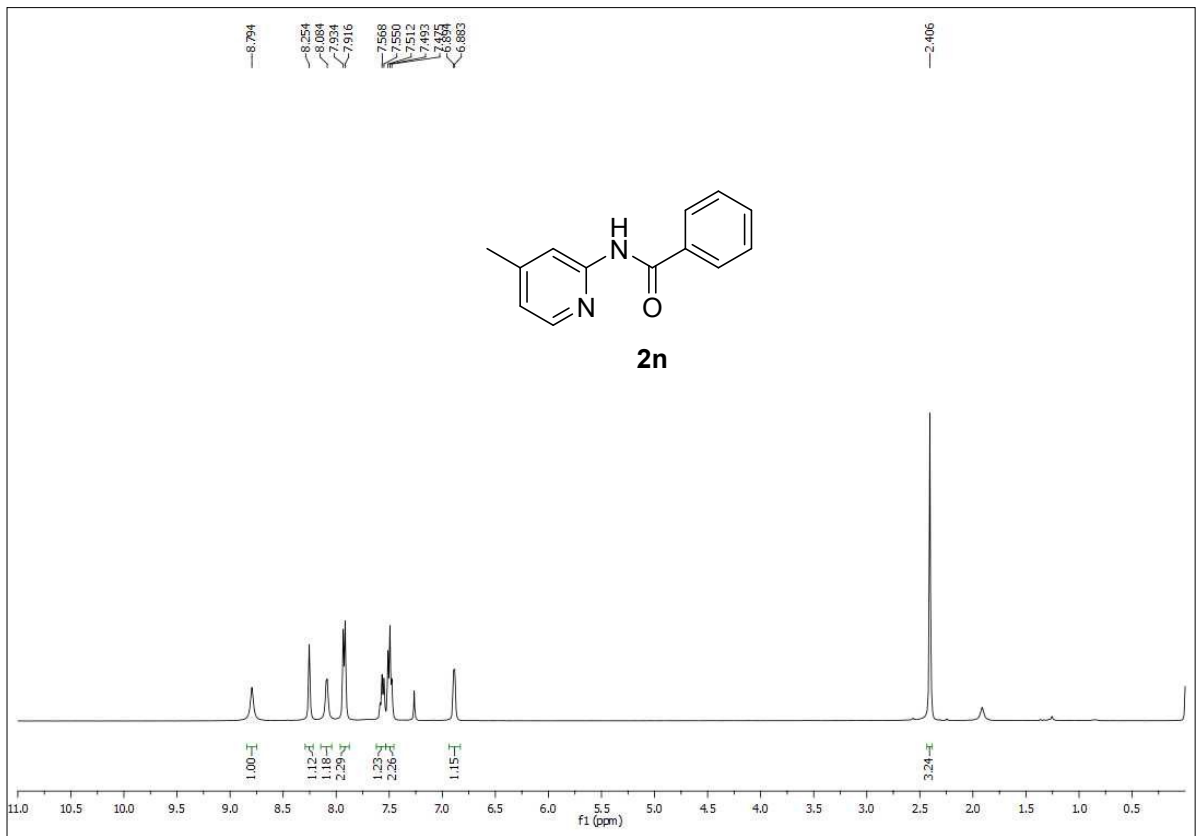
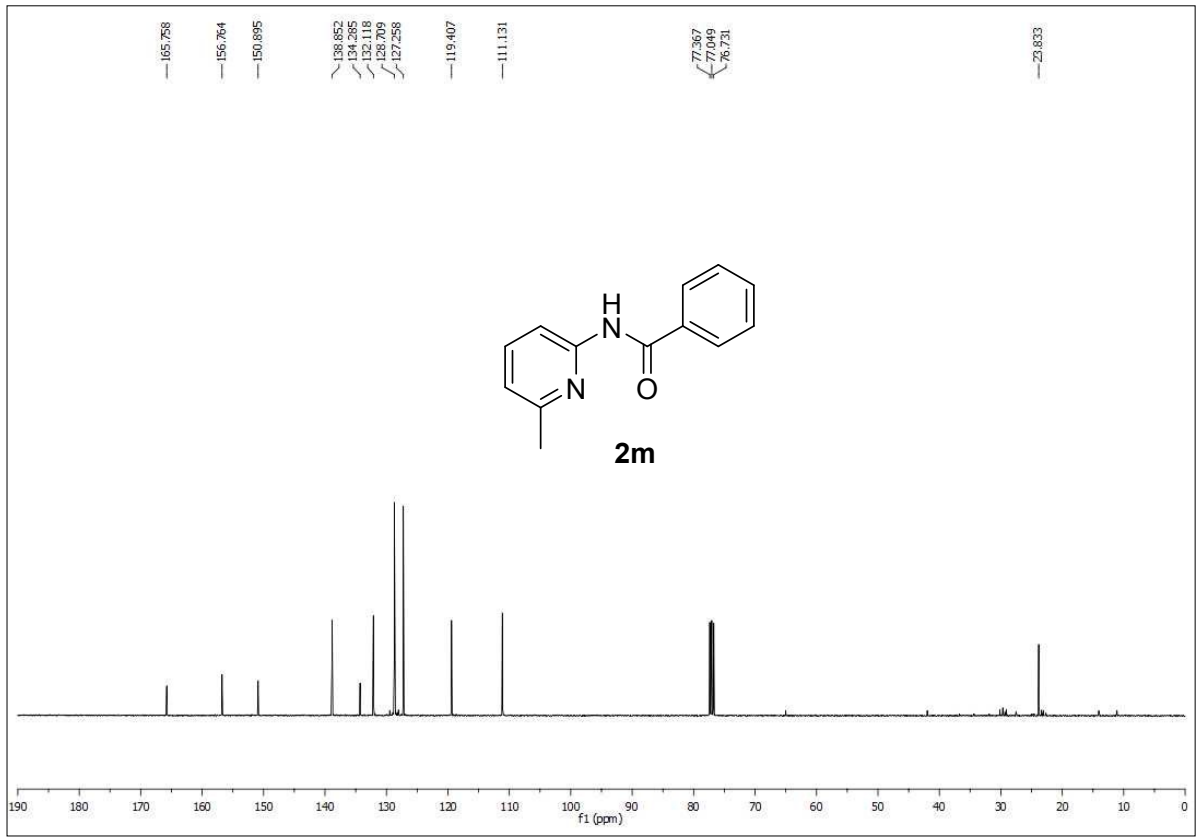


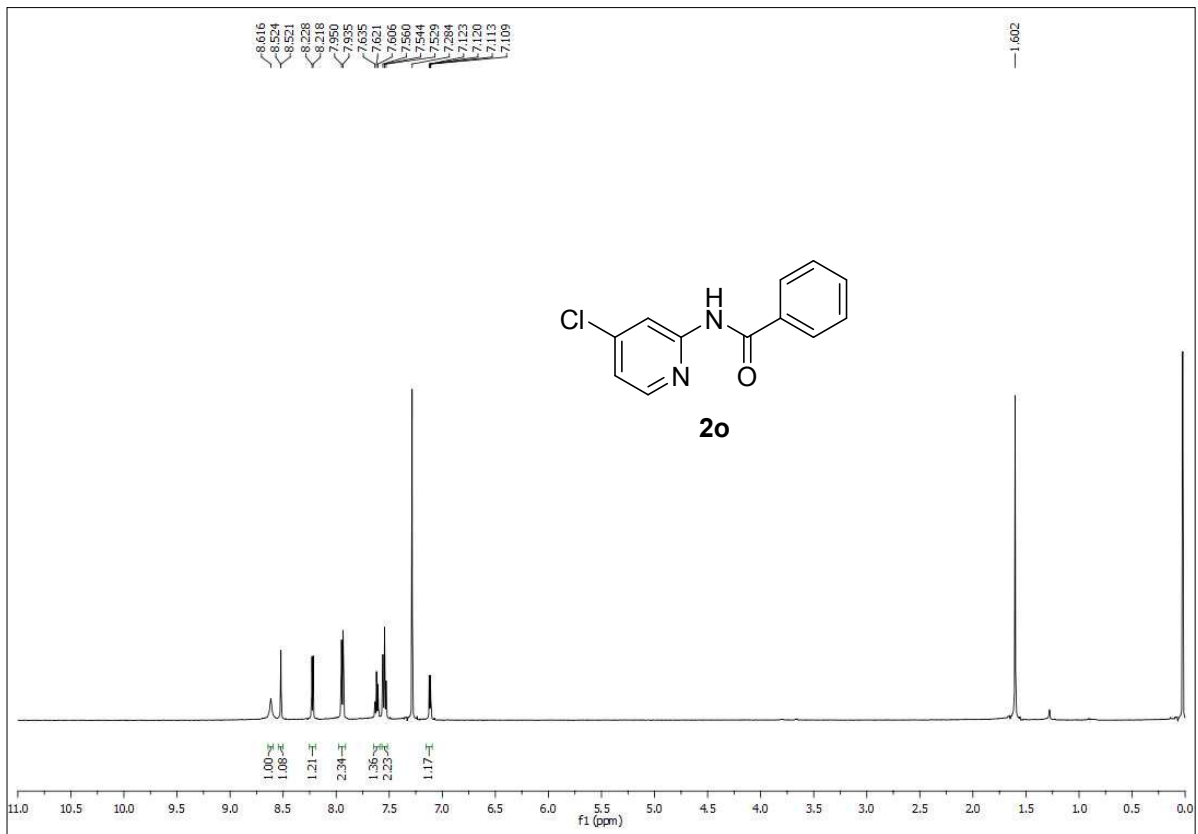
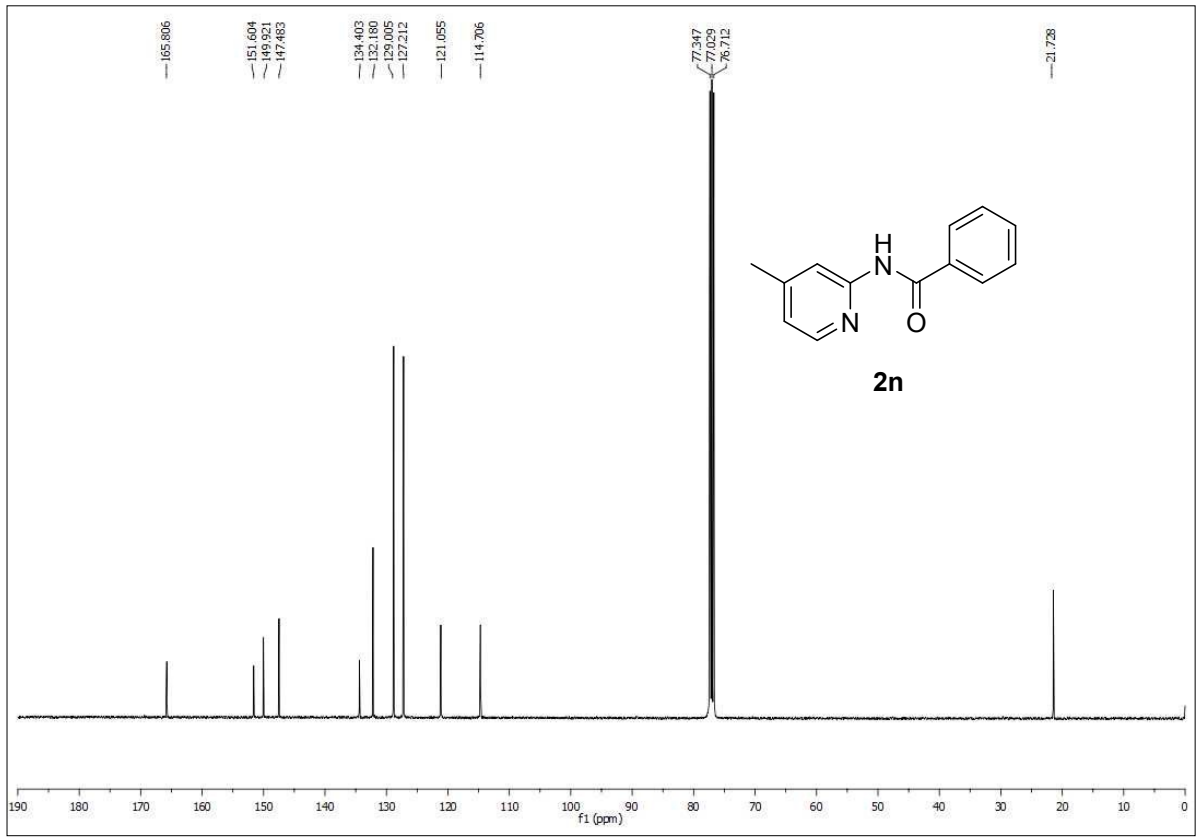




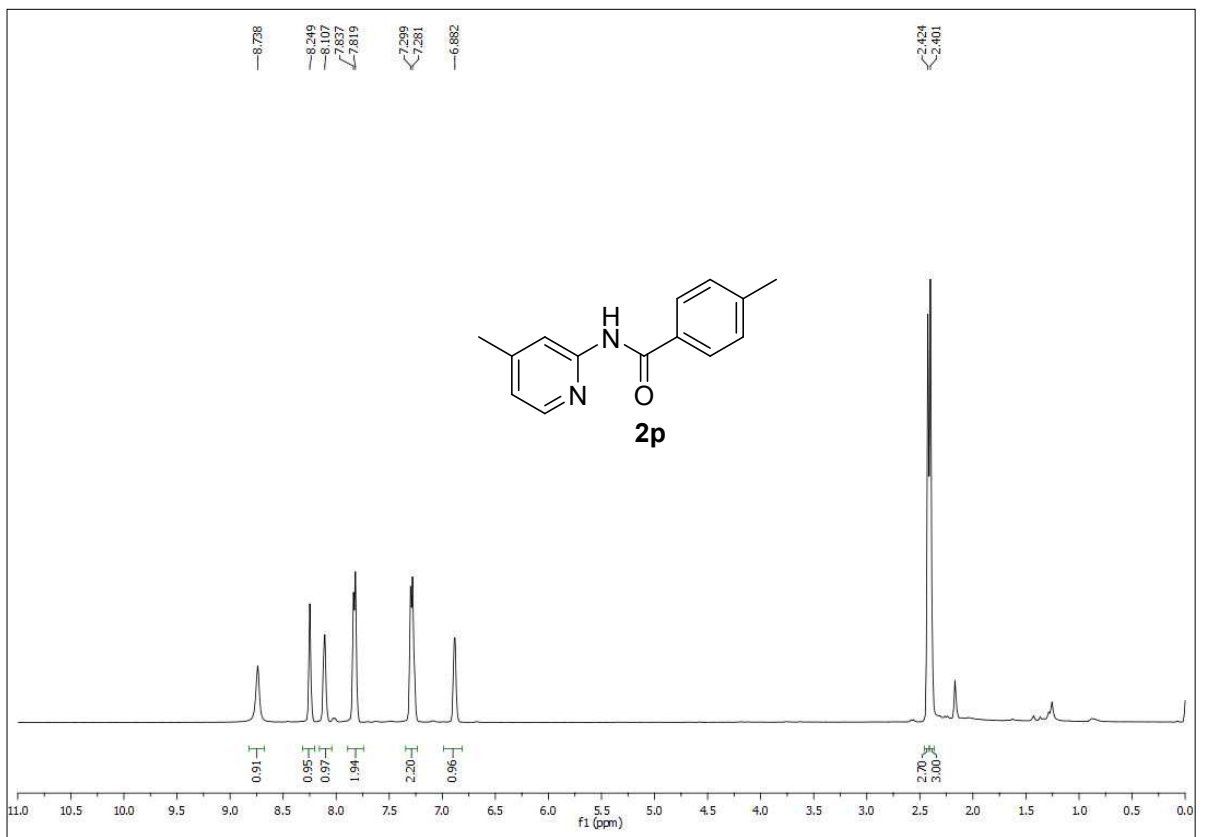
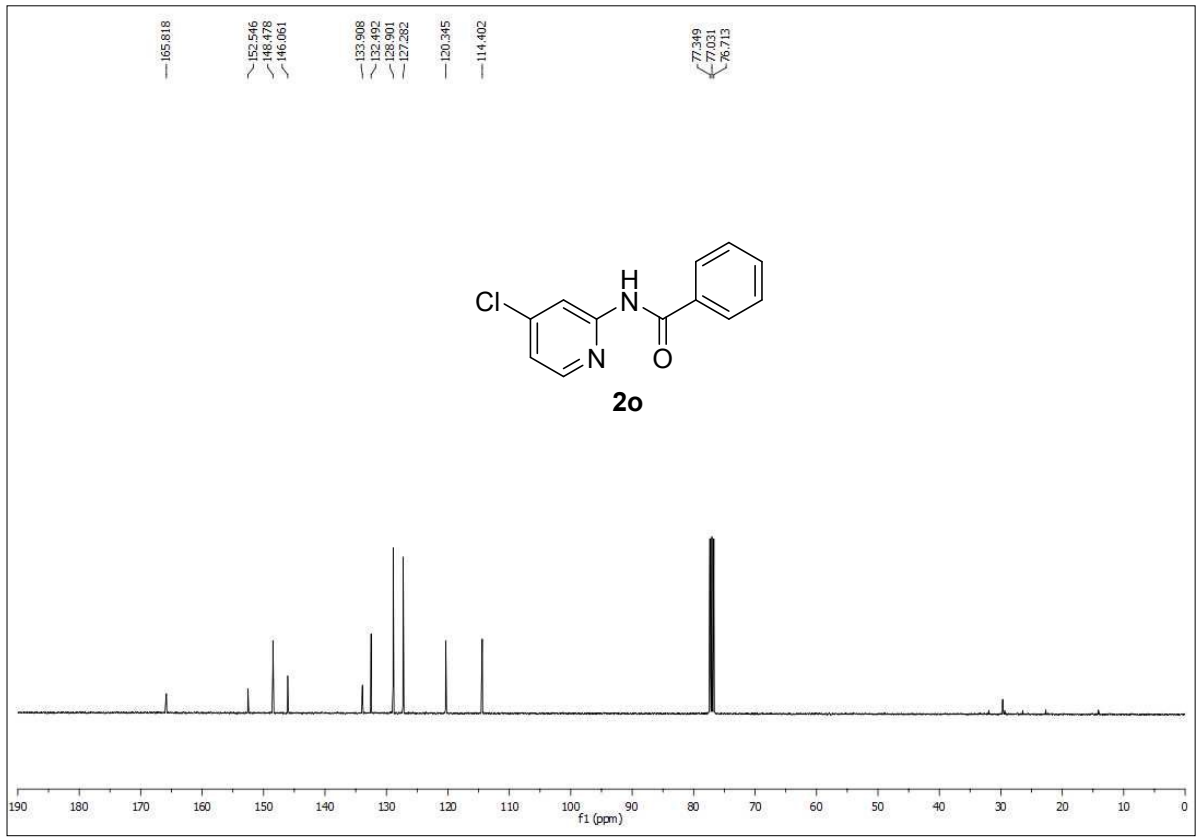


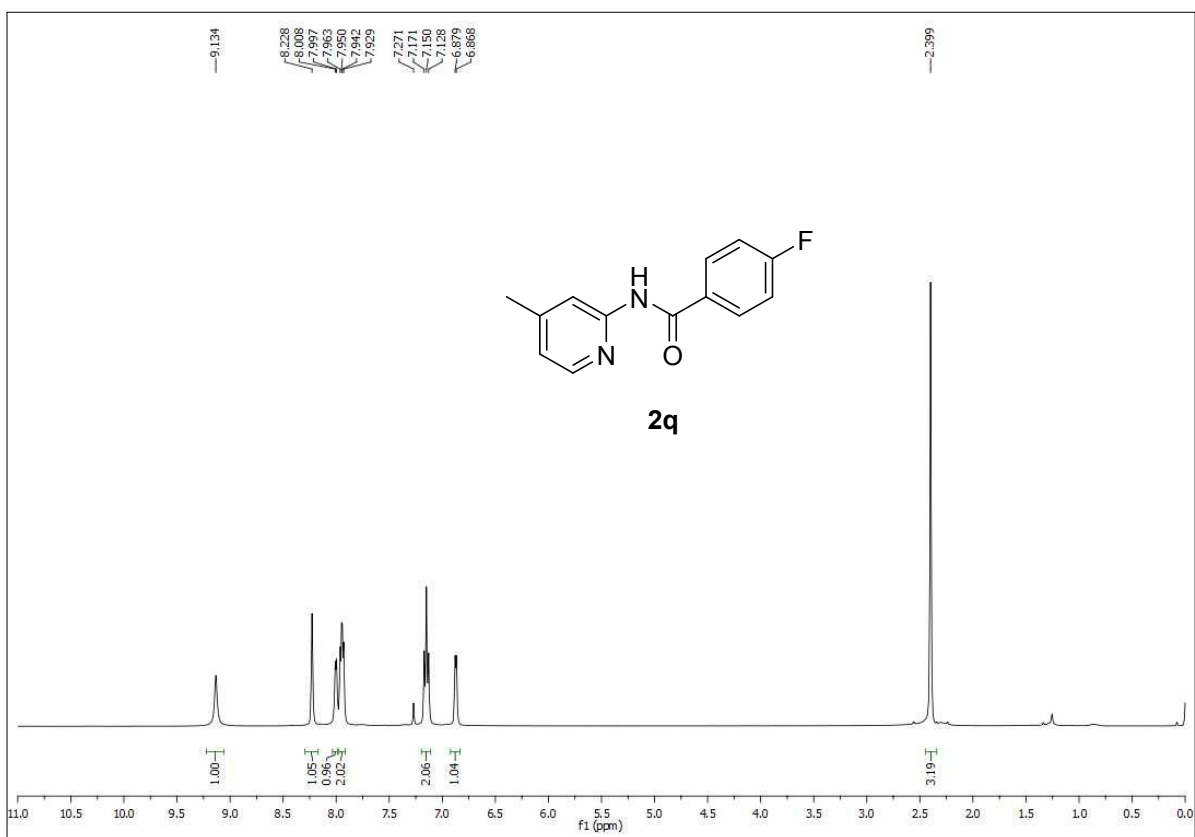
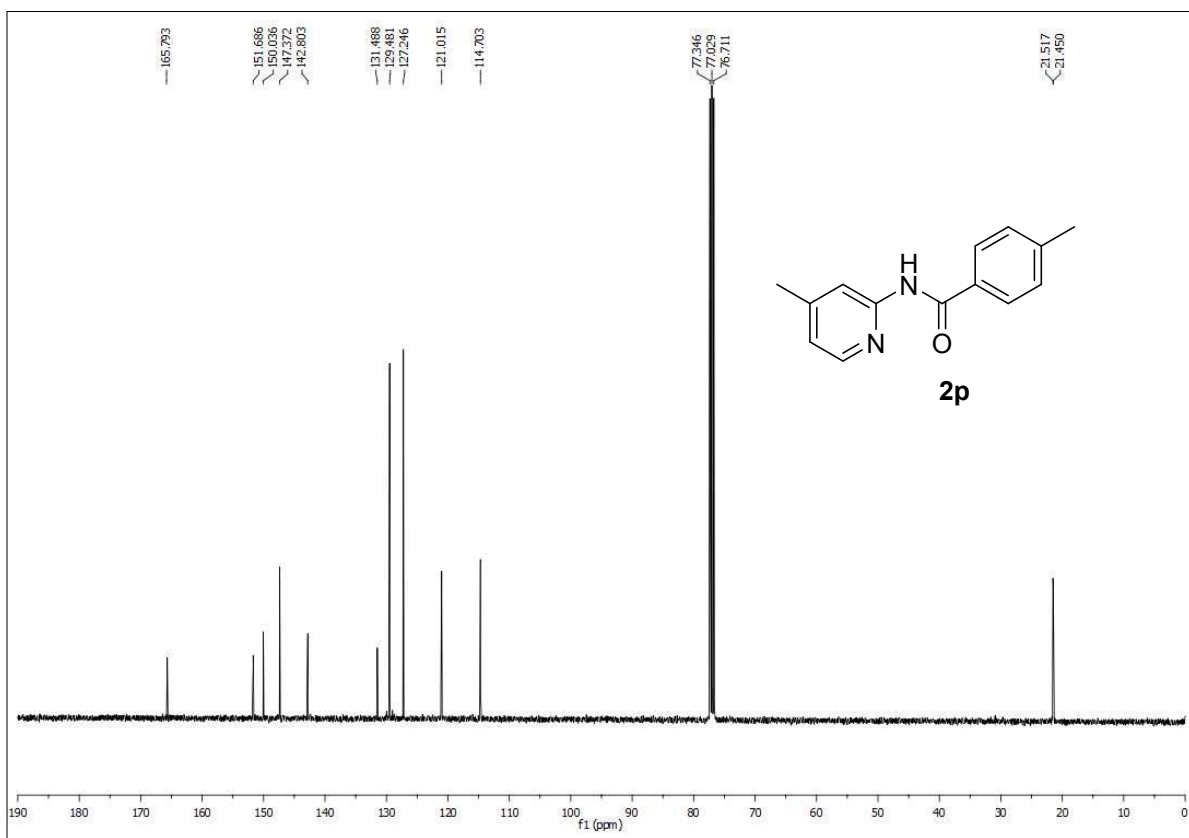


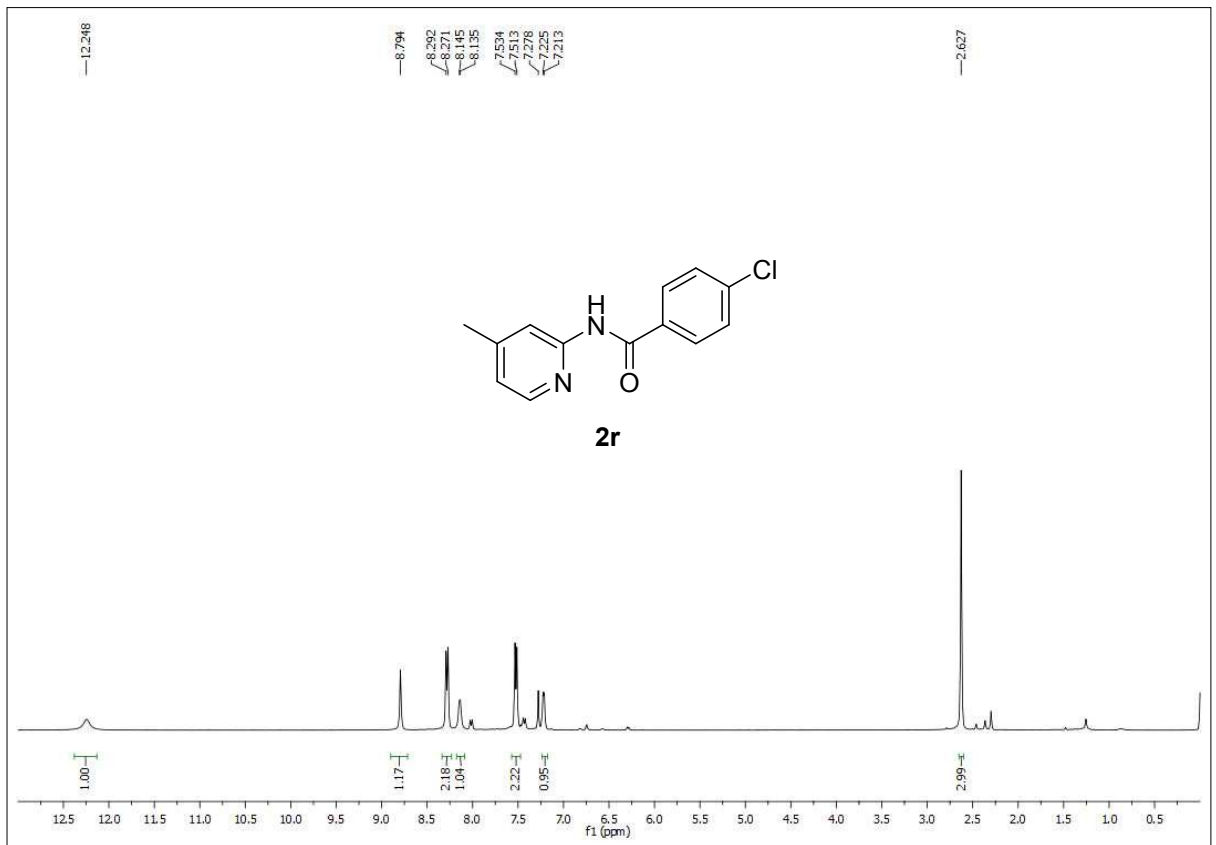
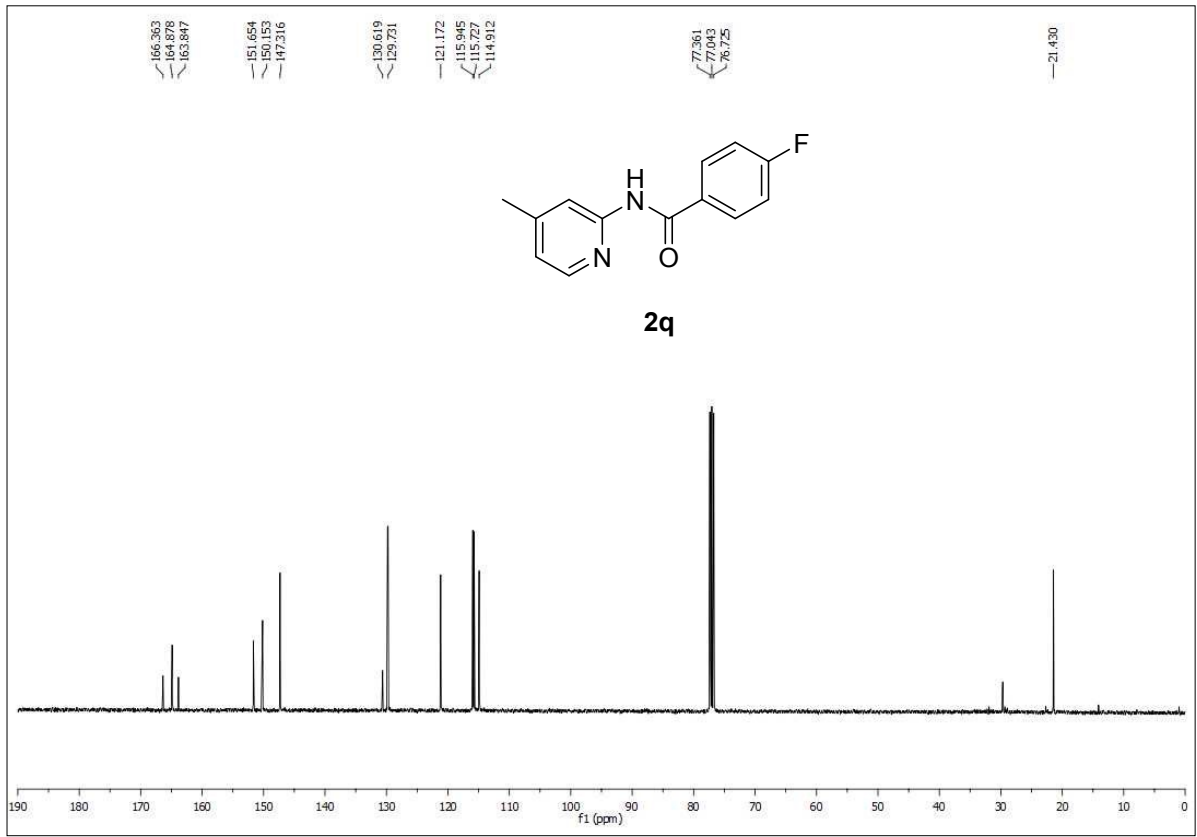


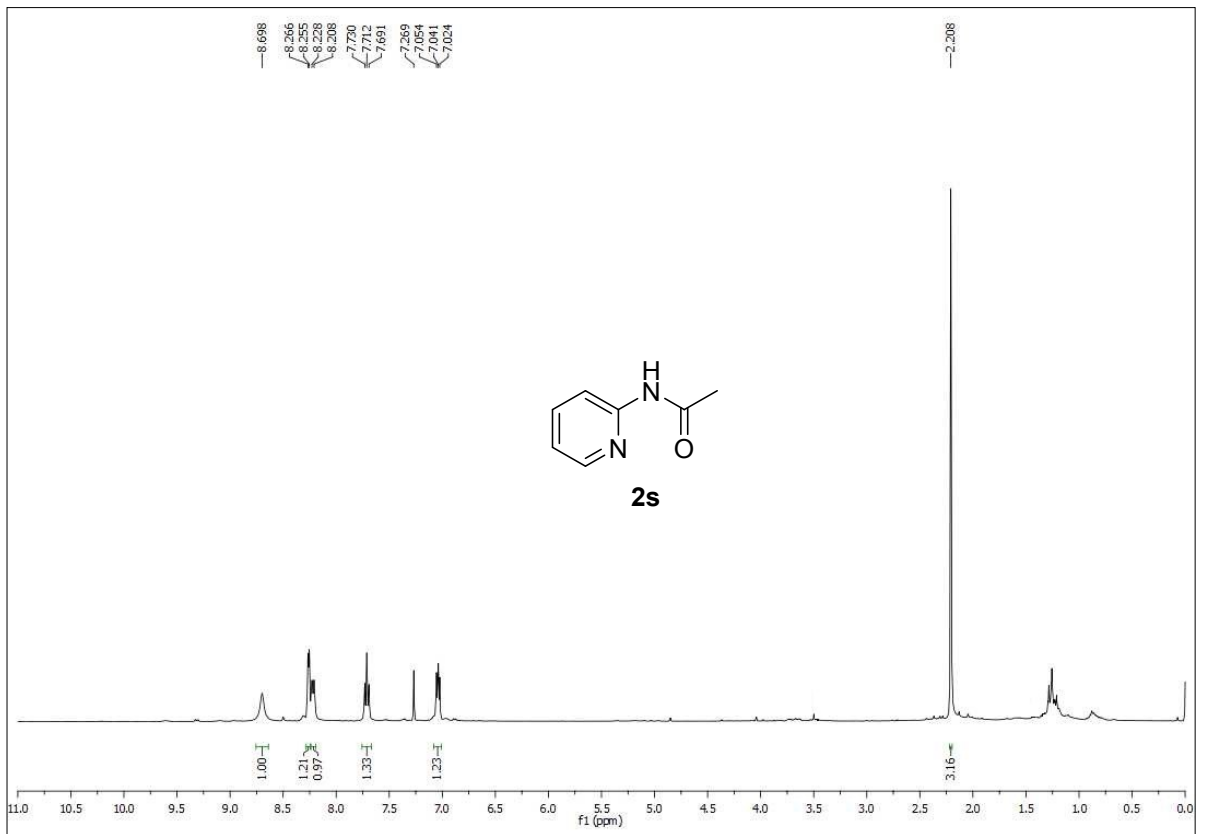
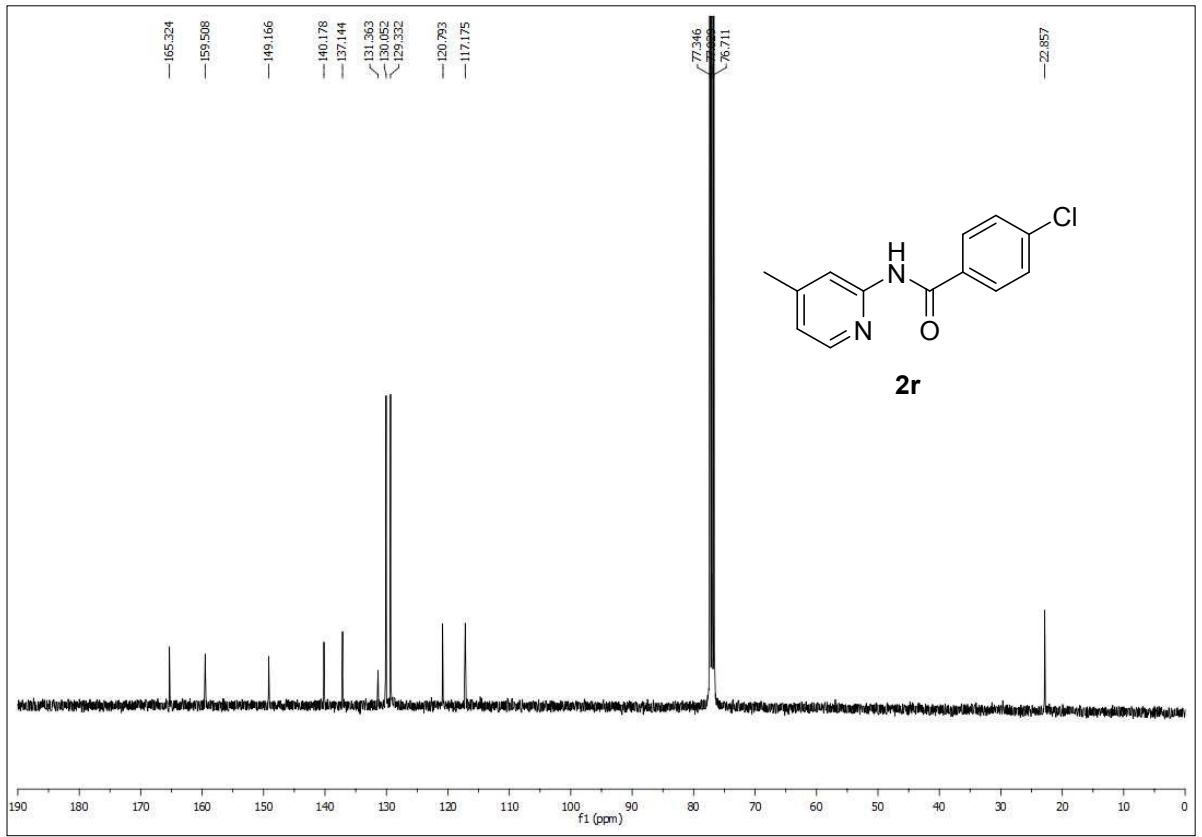


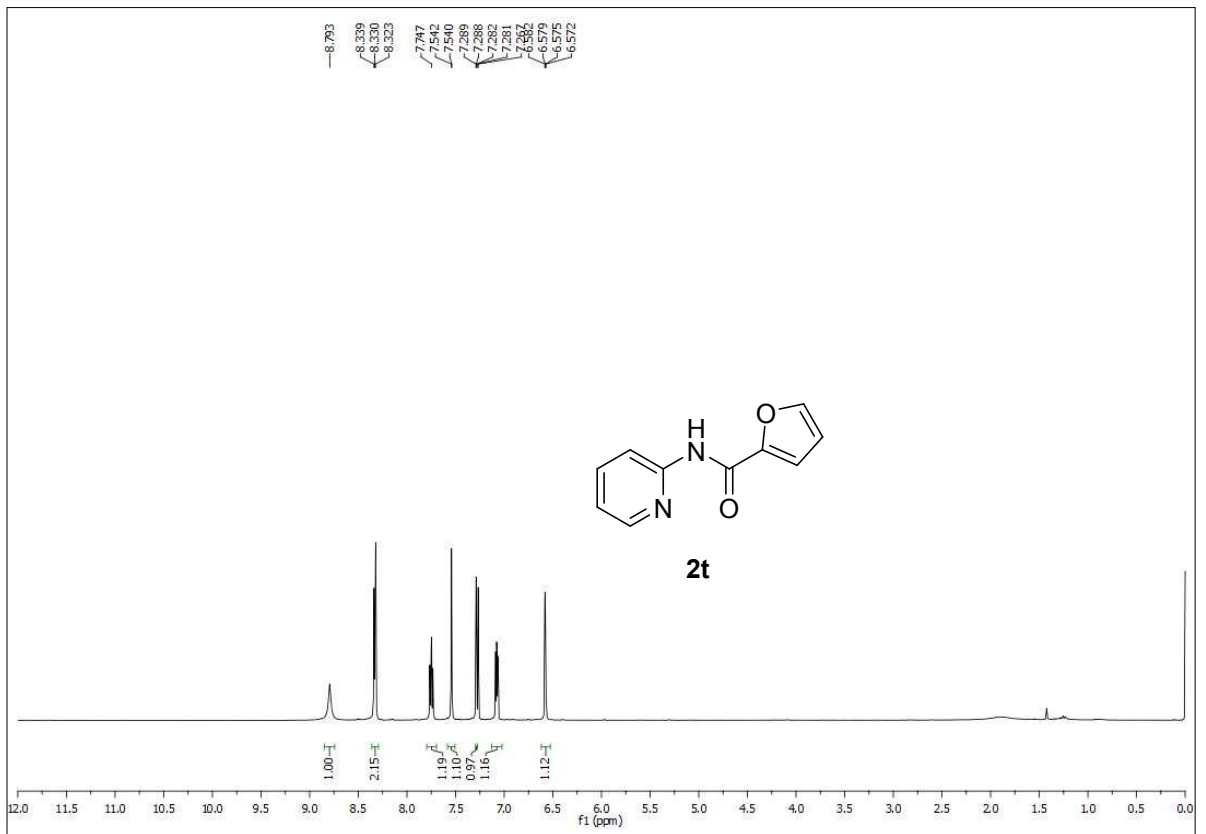
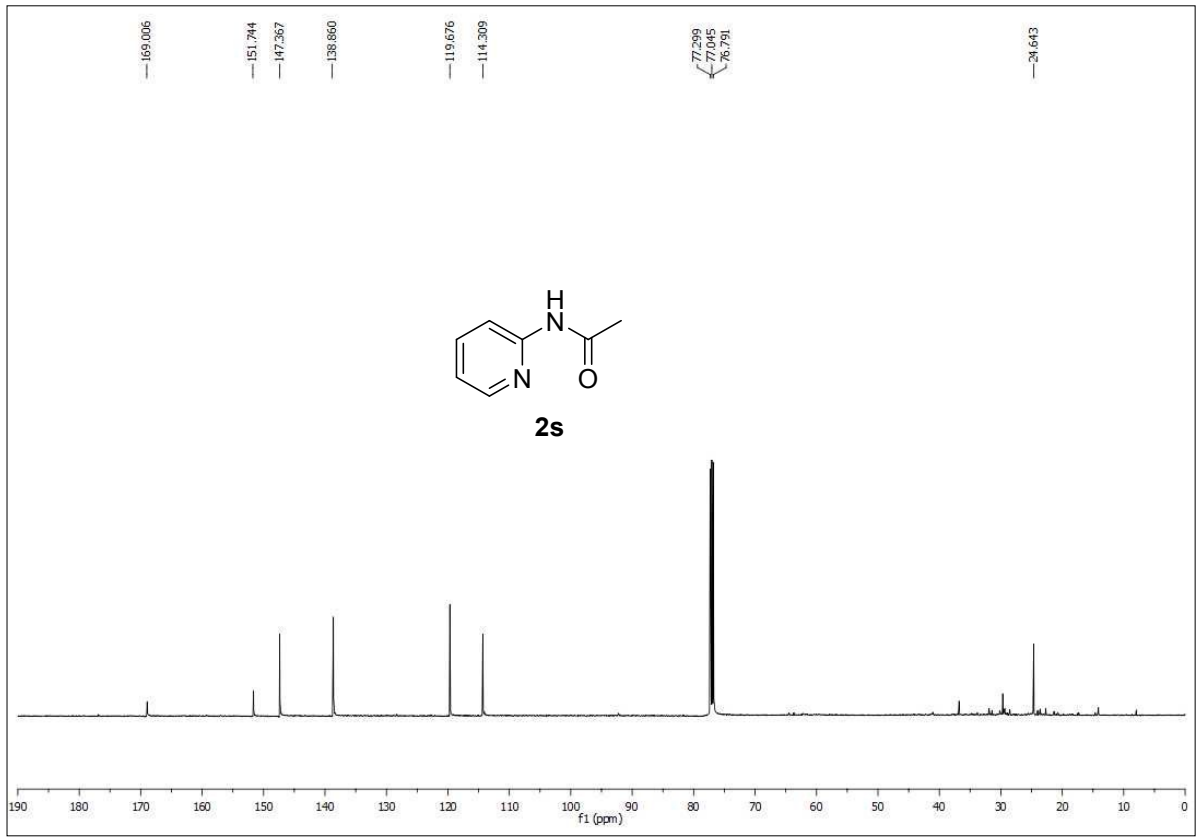


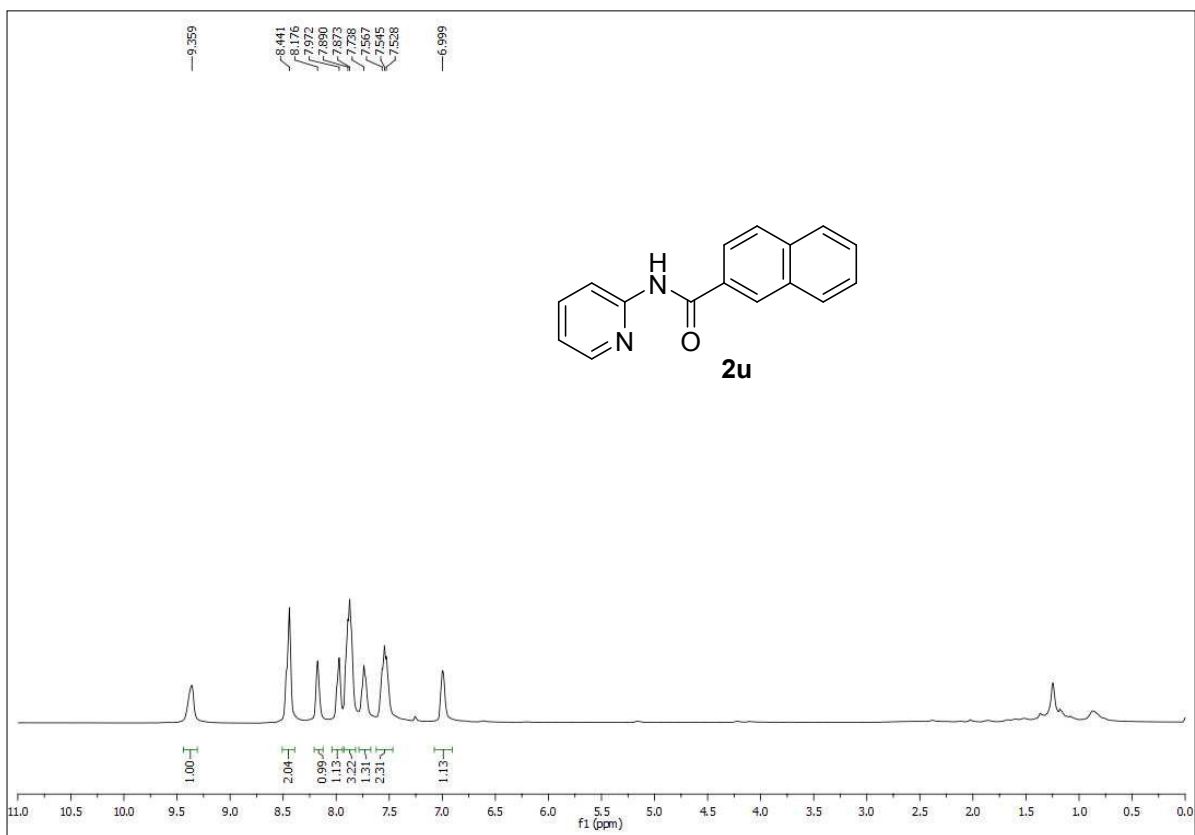
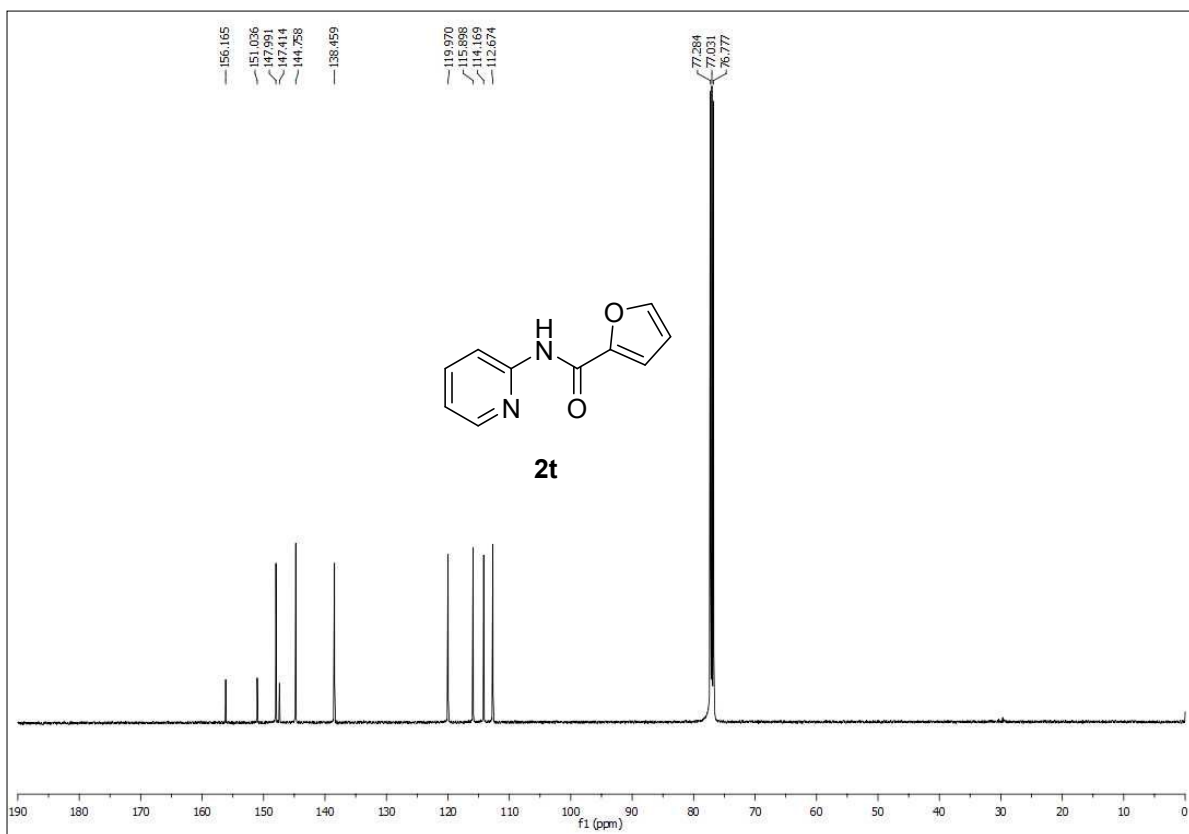


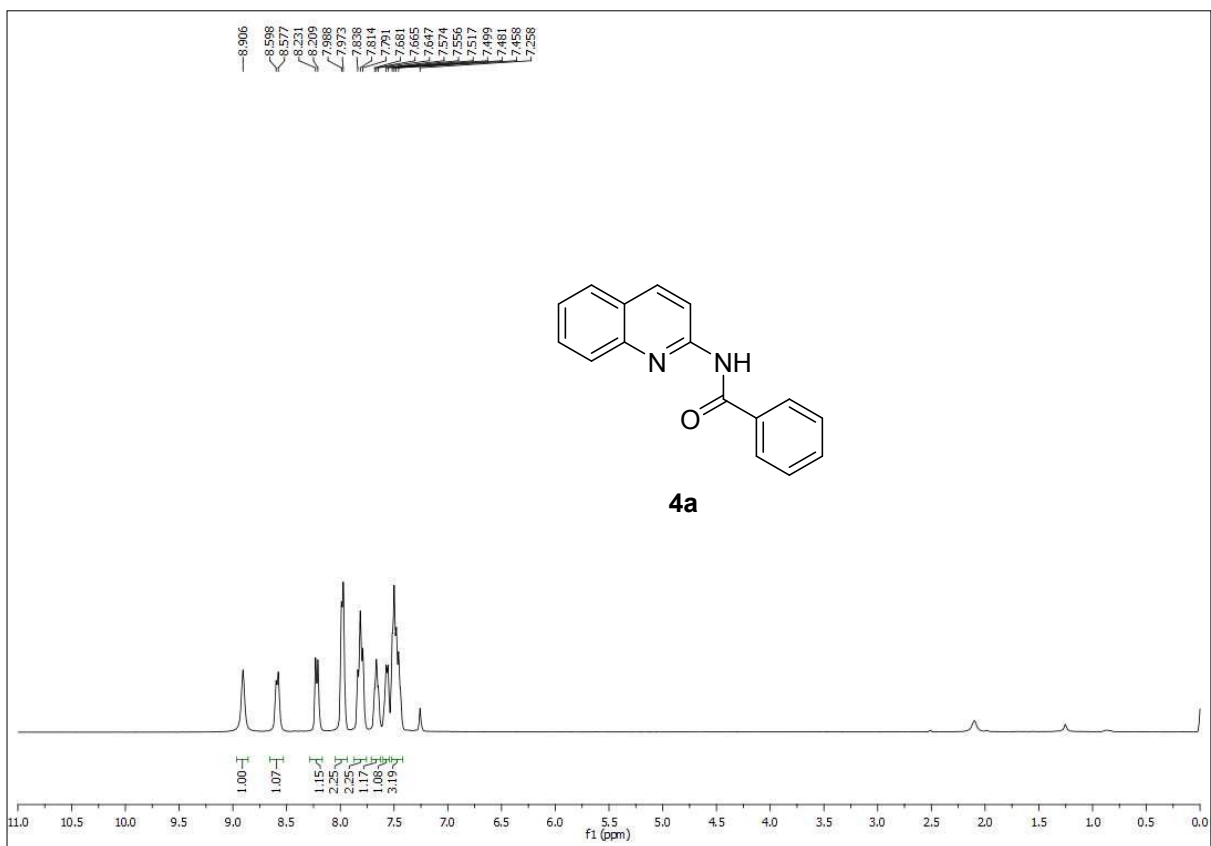
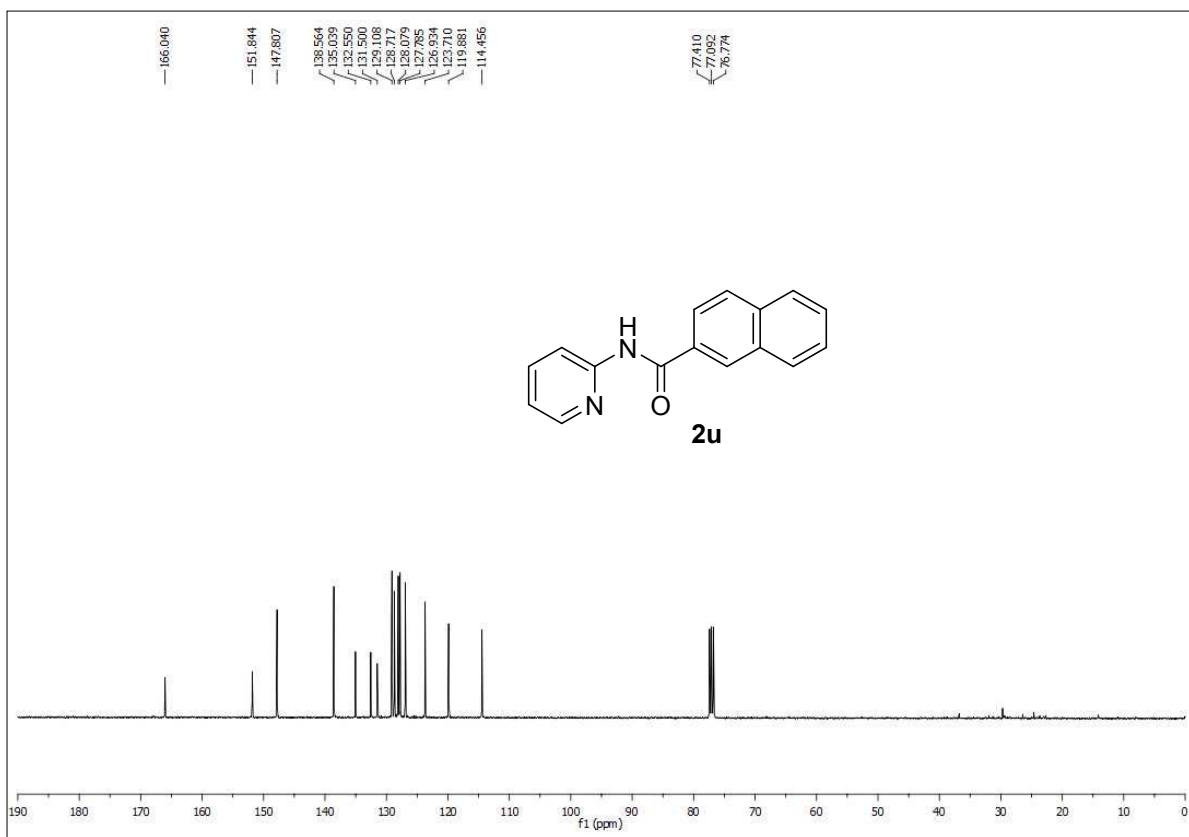


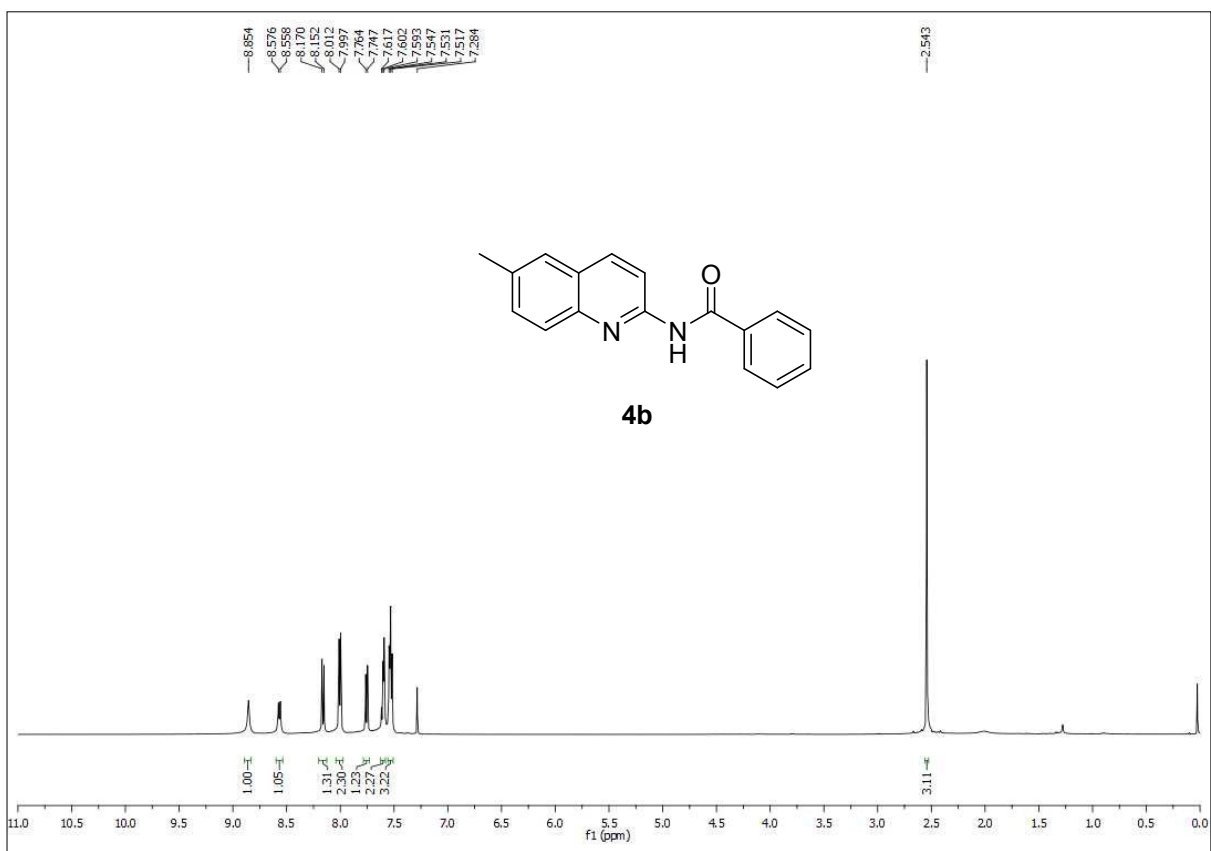
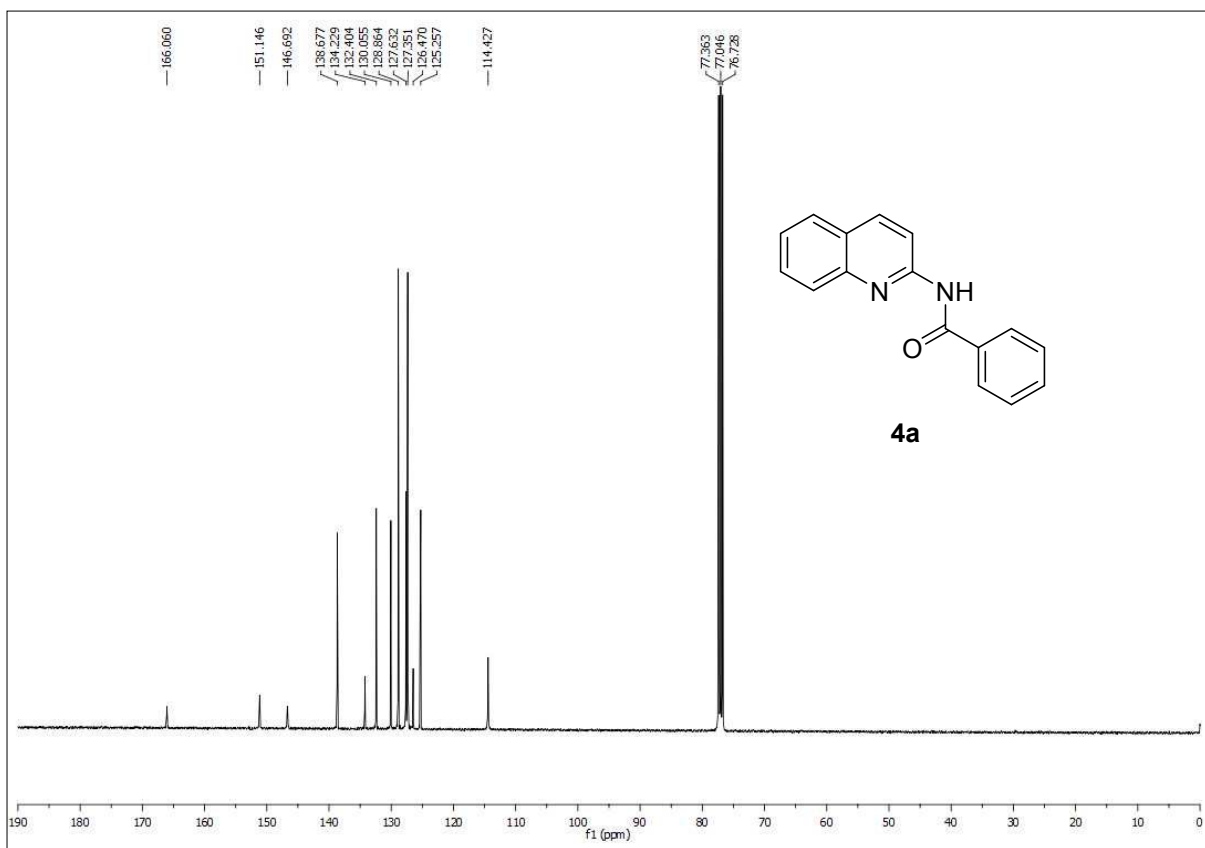




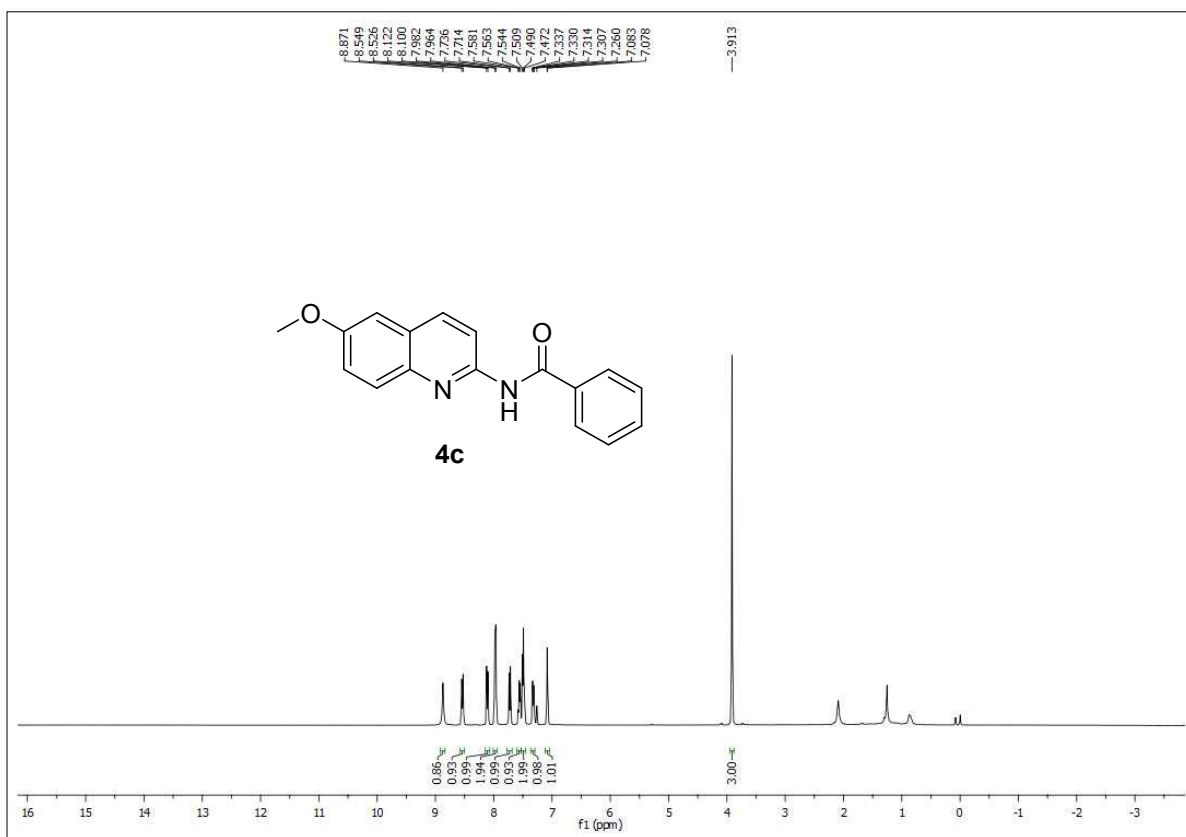
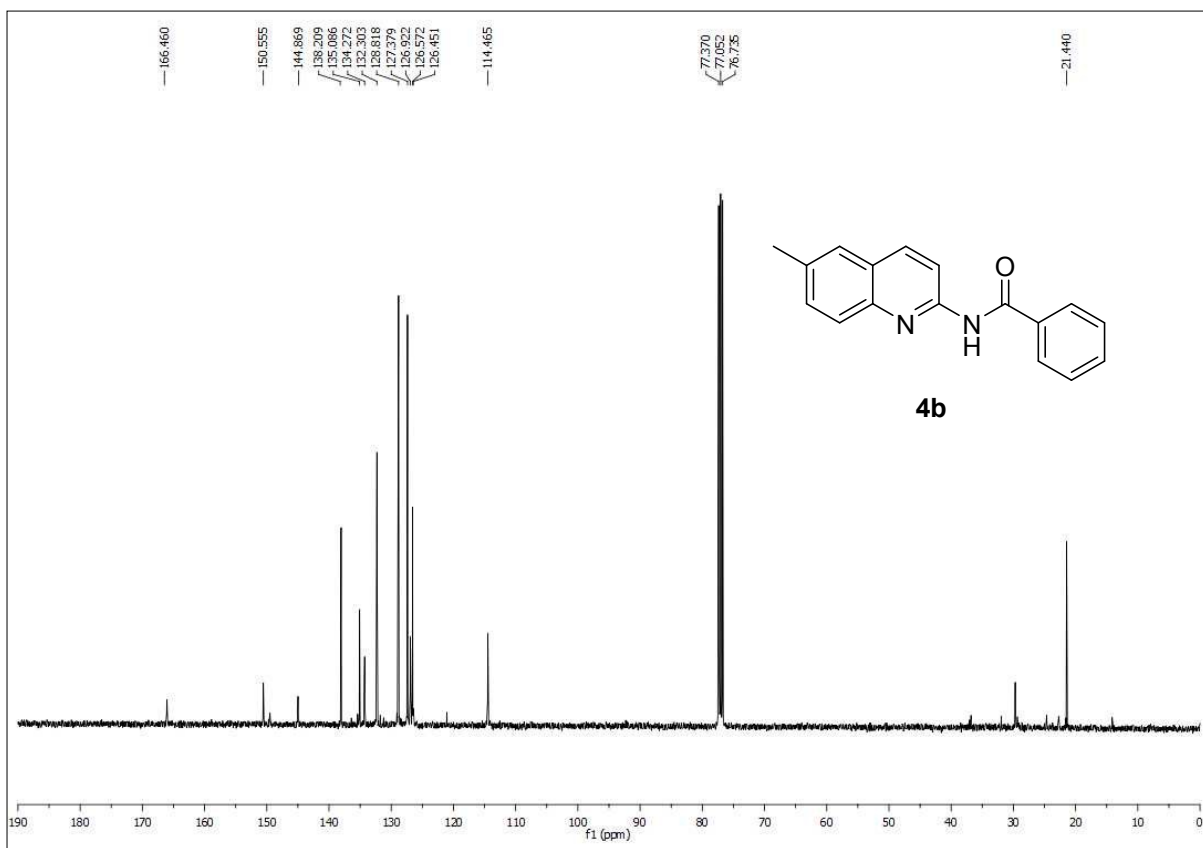


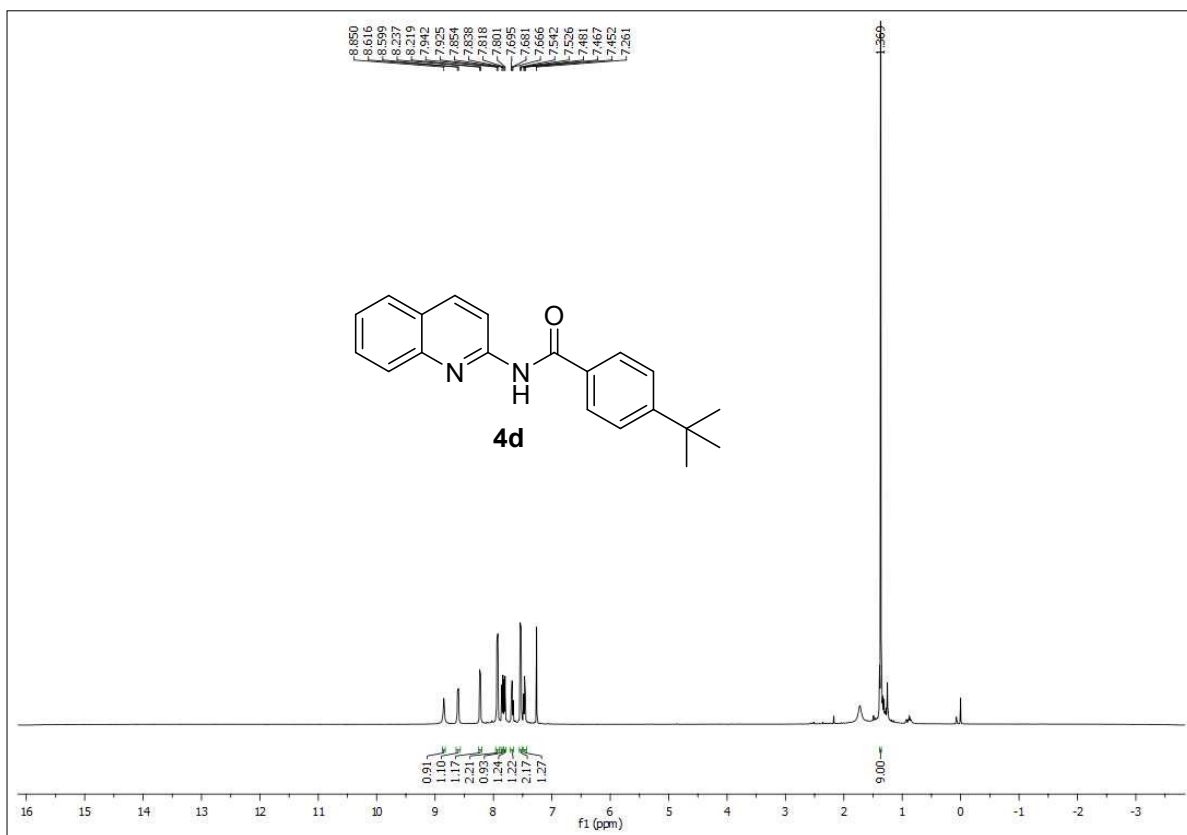
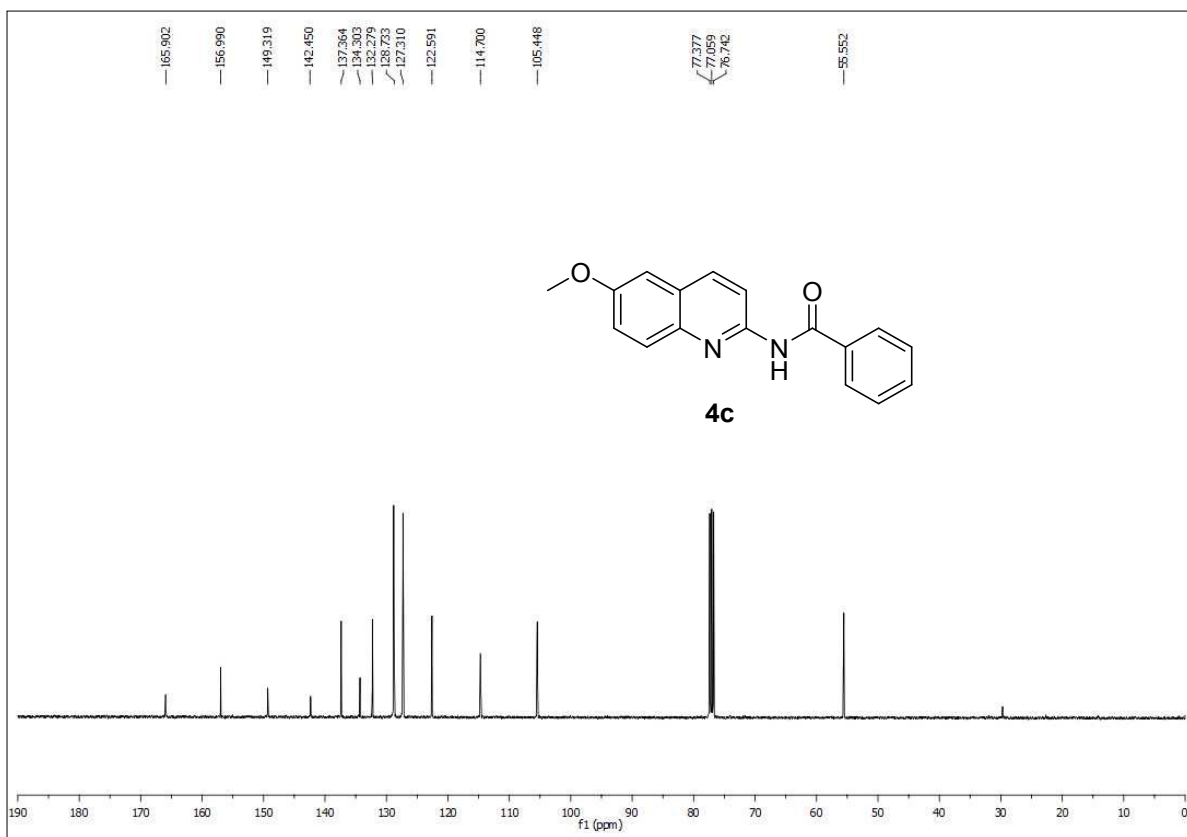


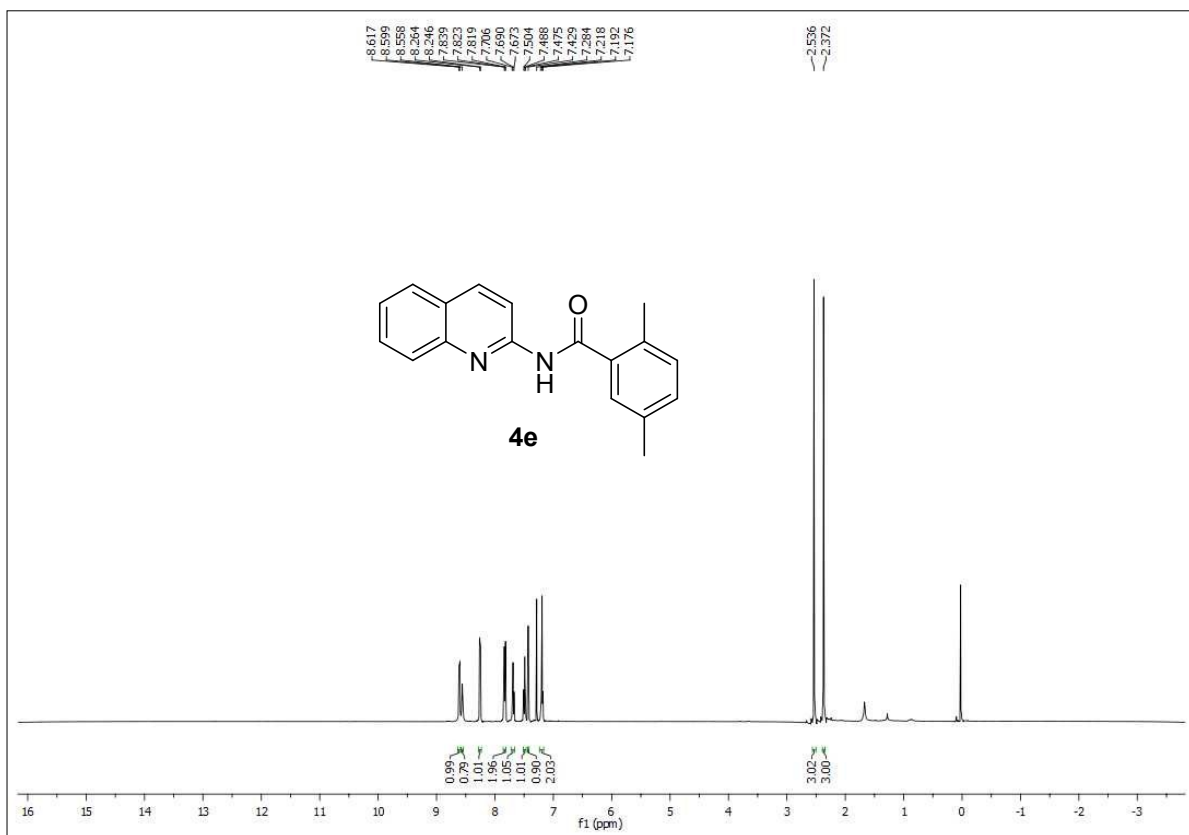
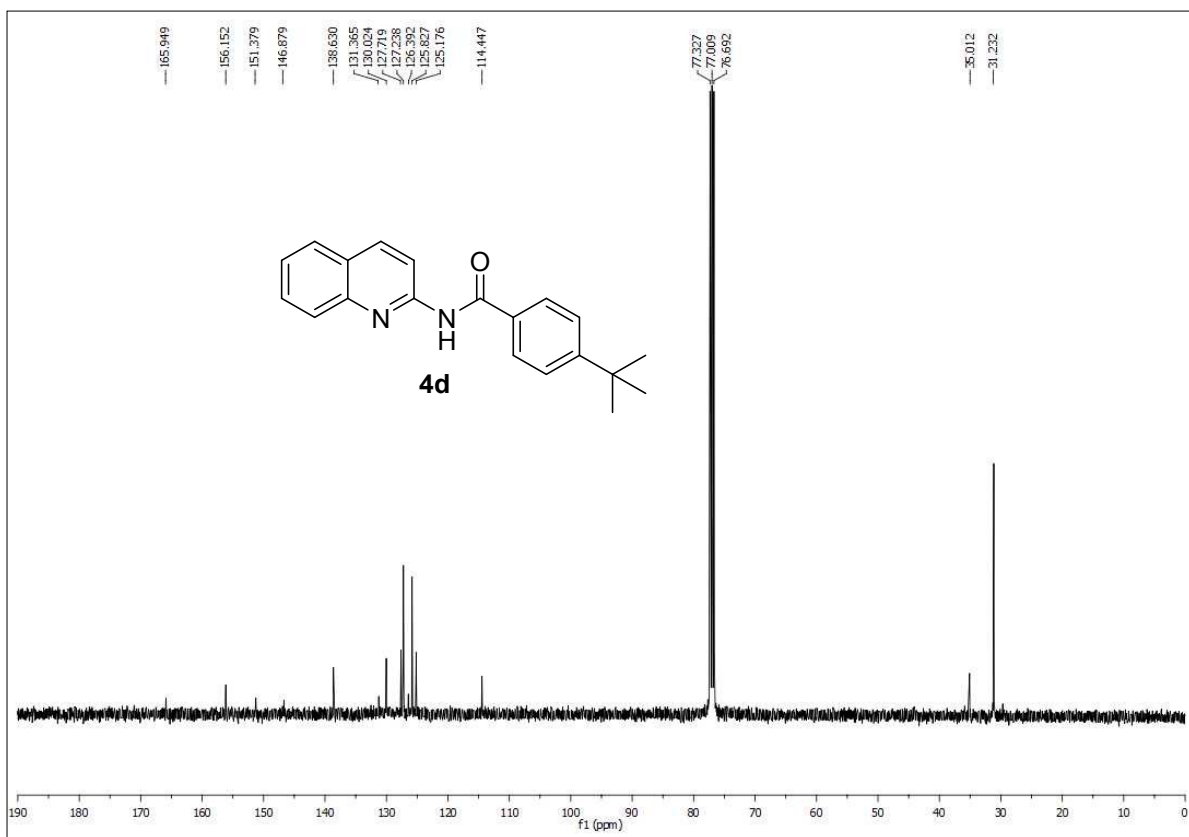


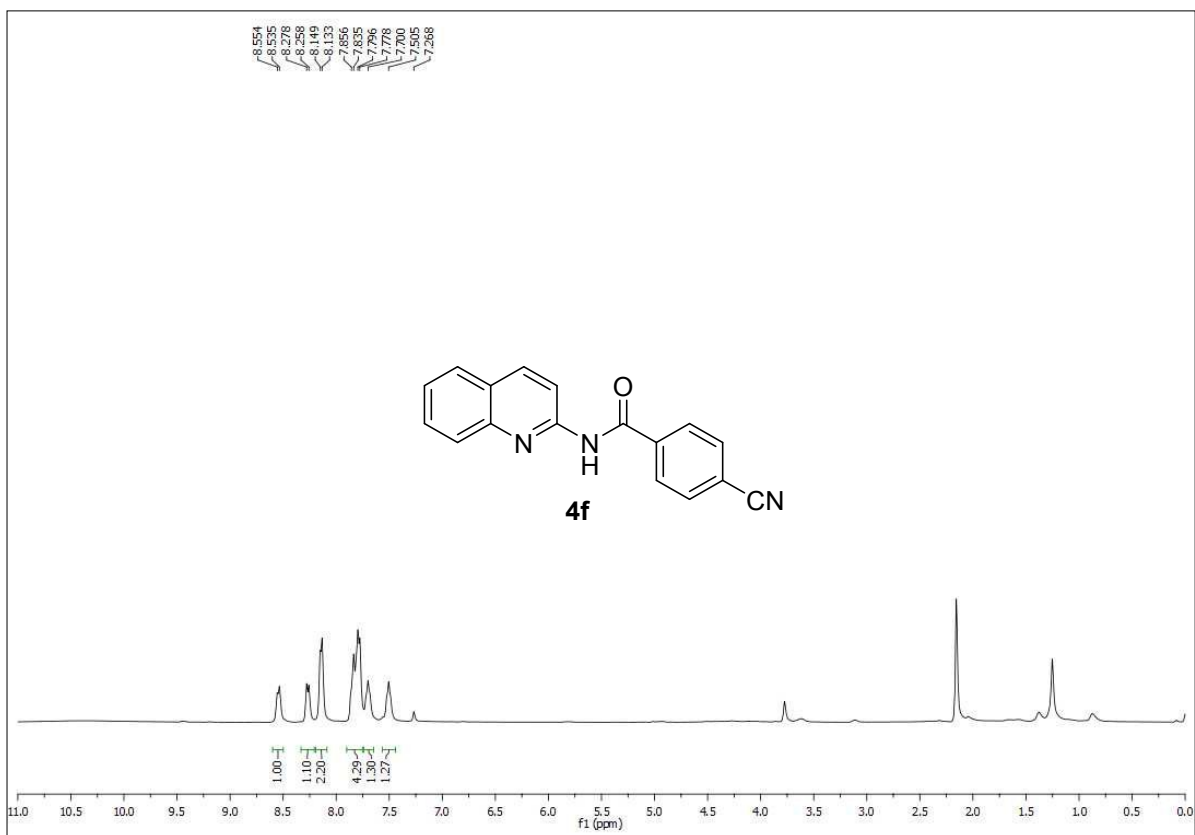
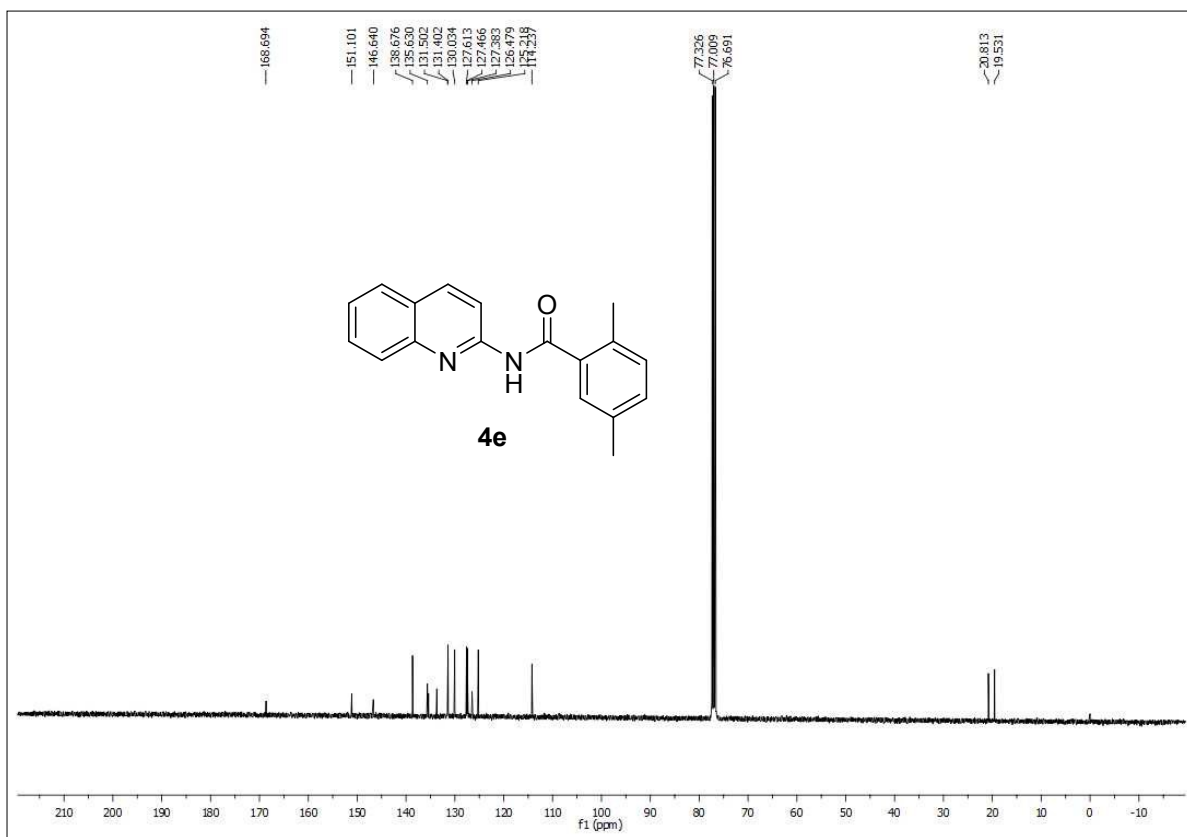


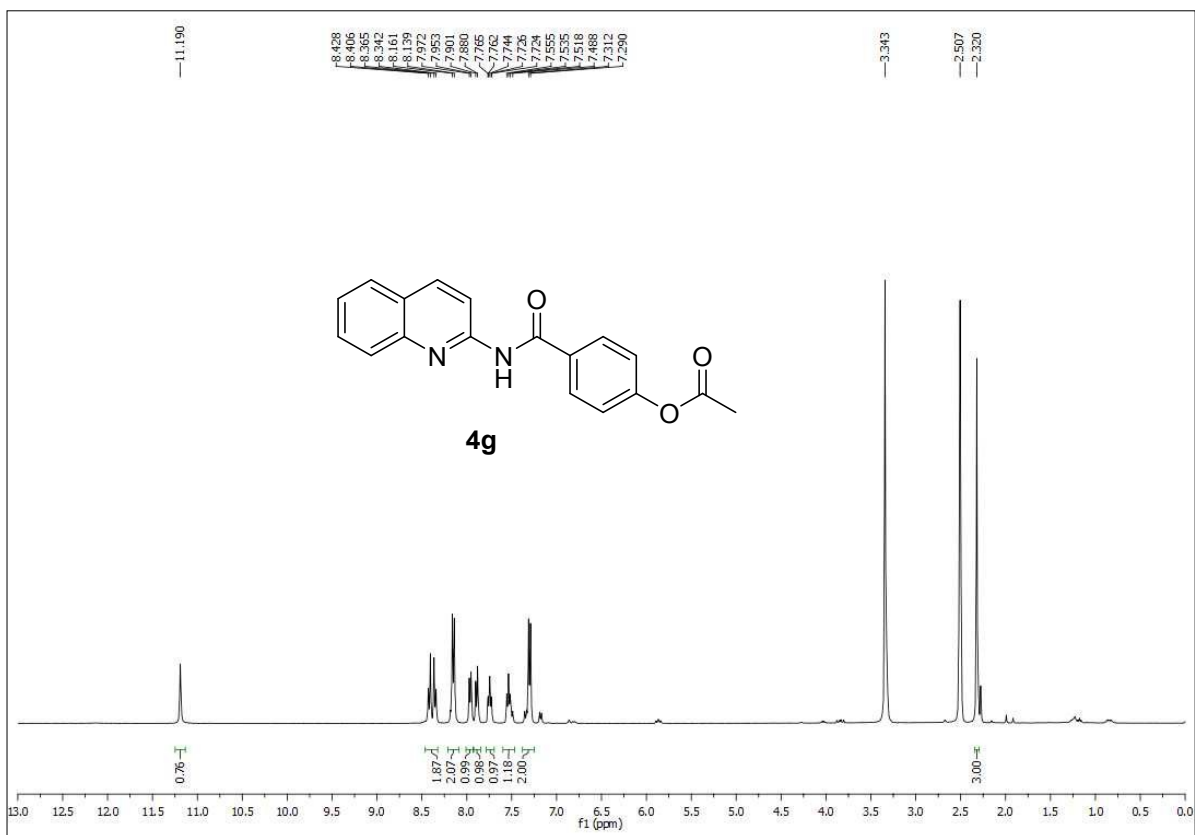
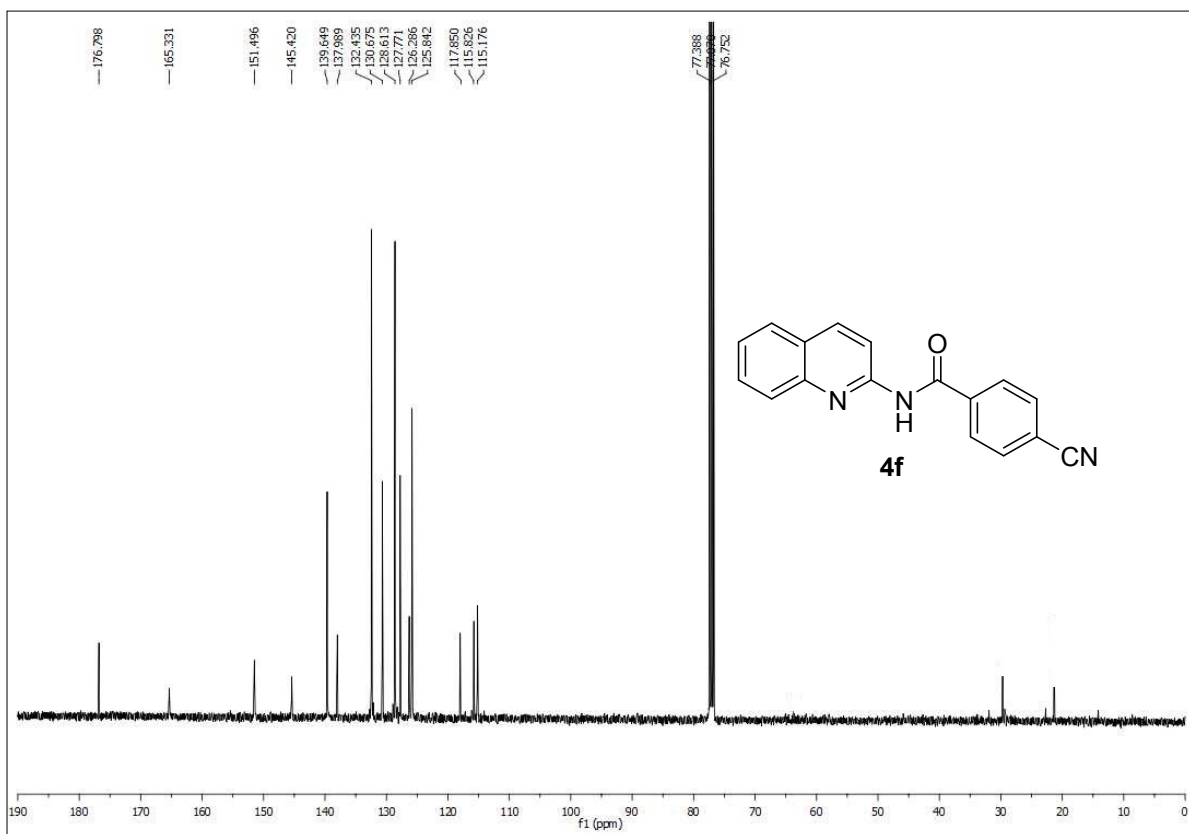


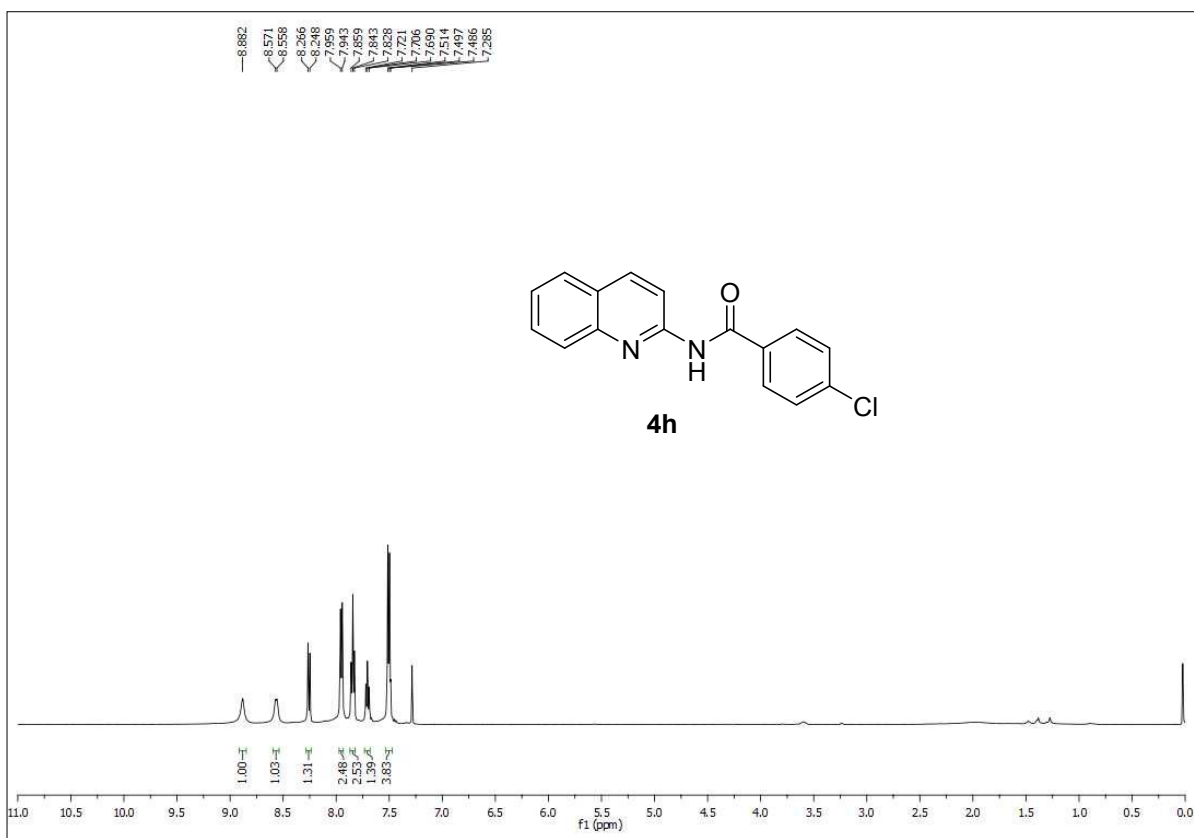
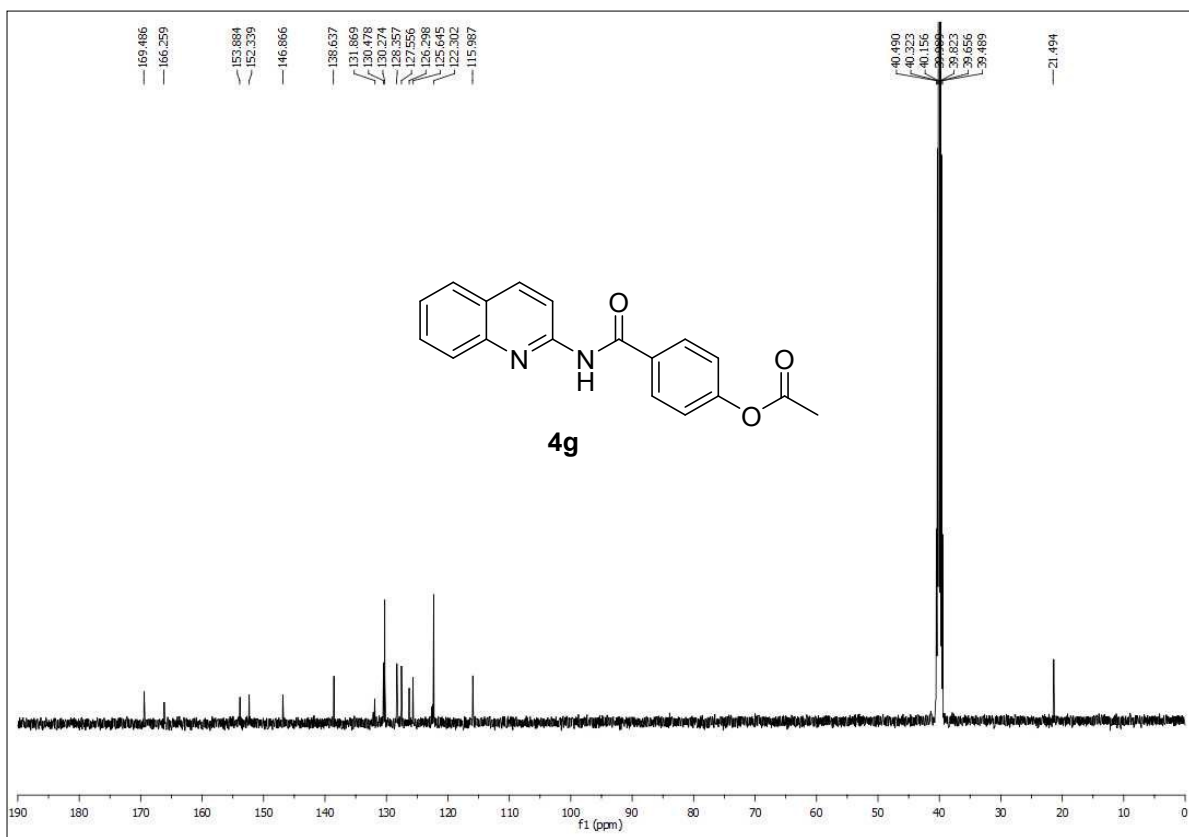


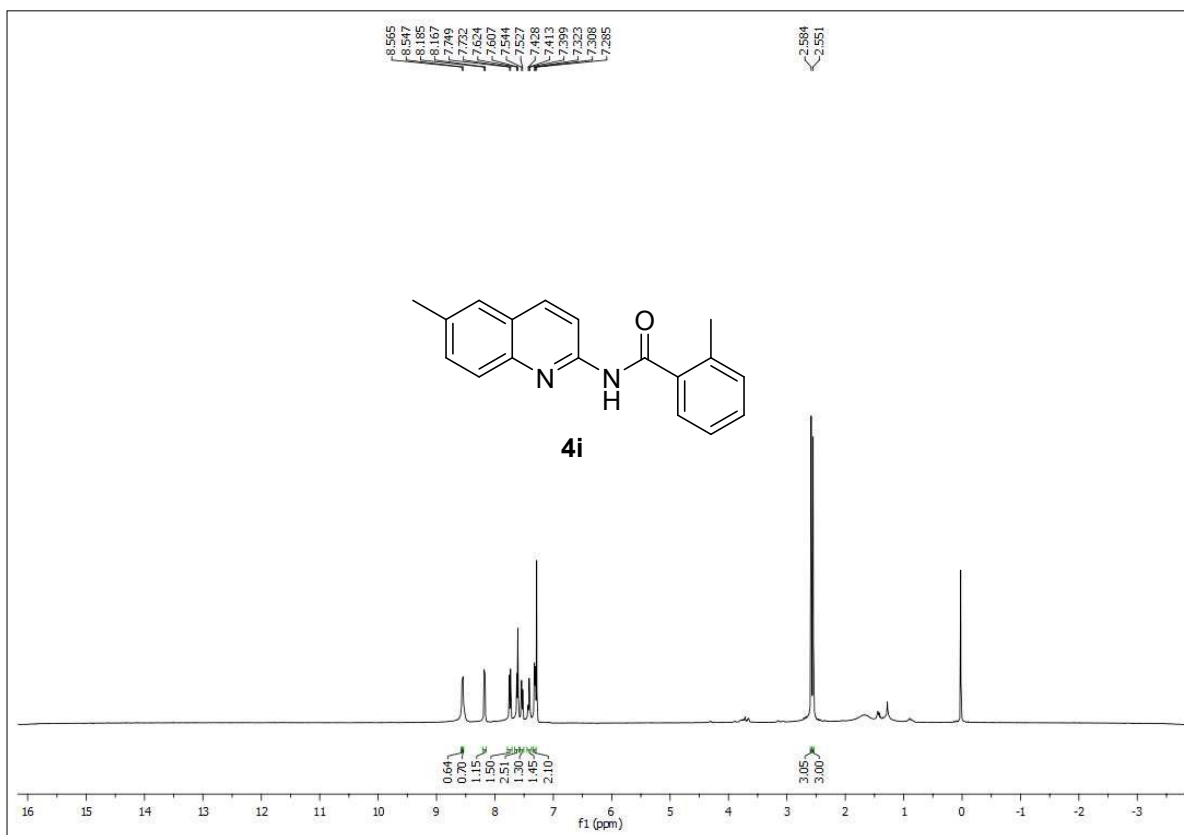
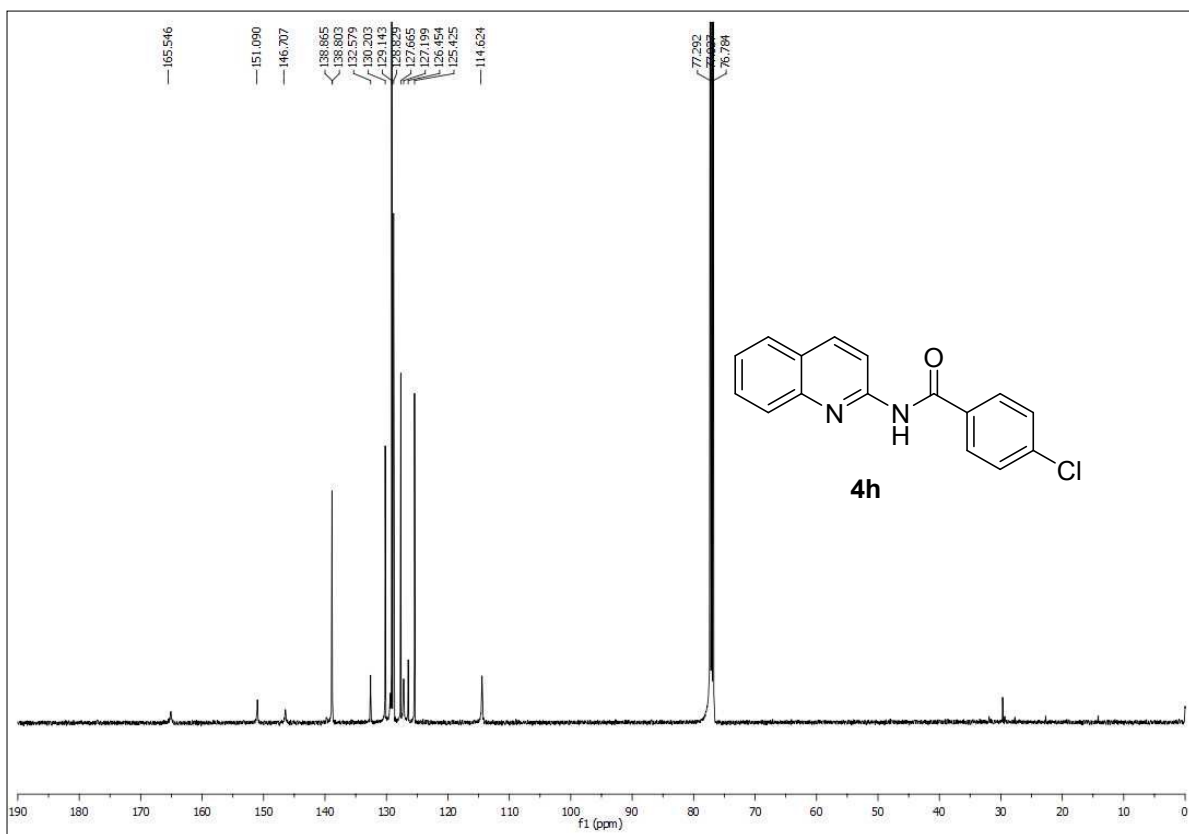


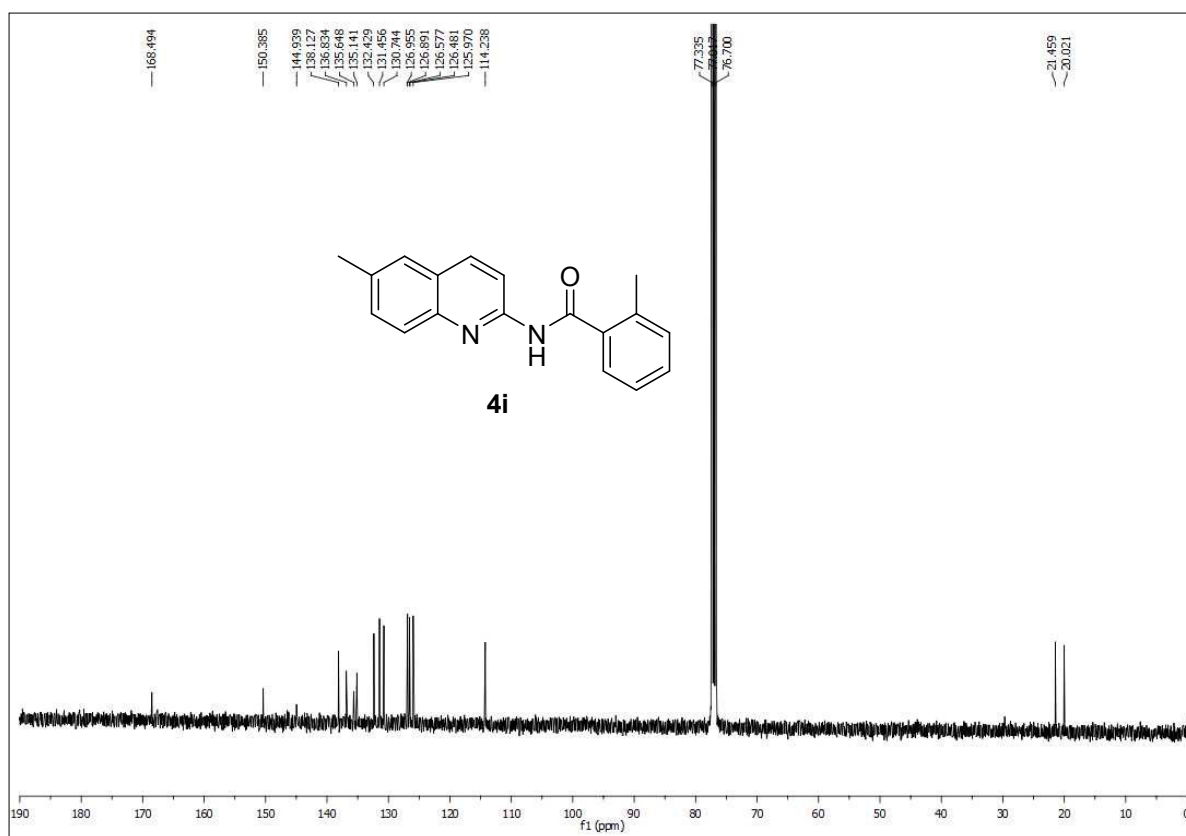












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