

## SUPPORTING INFORMATION

### Access to Fluorazones by Intramolecular Dehydrative Cyclization of Aromatic Tertiary Amides: A Synthetic and Mechanistic Study

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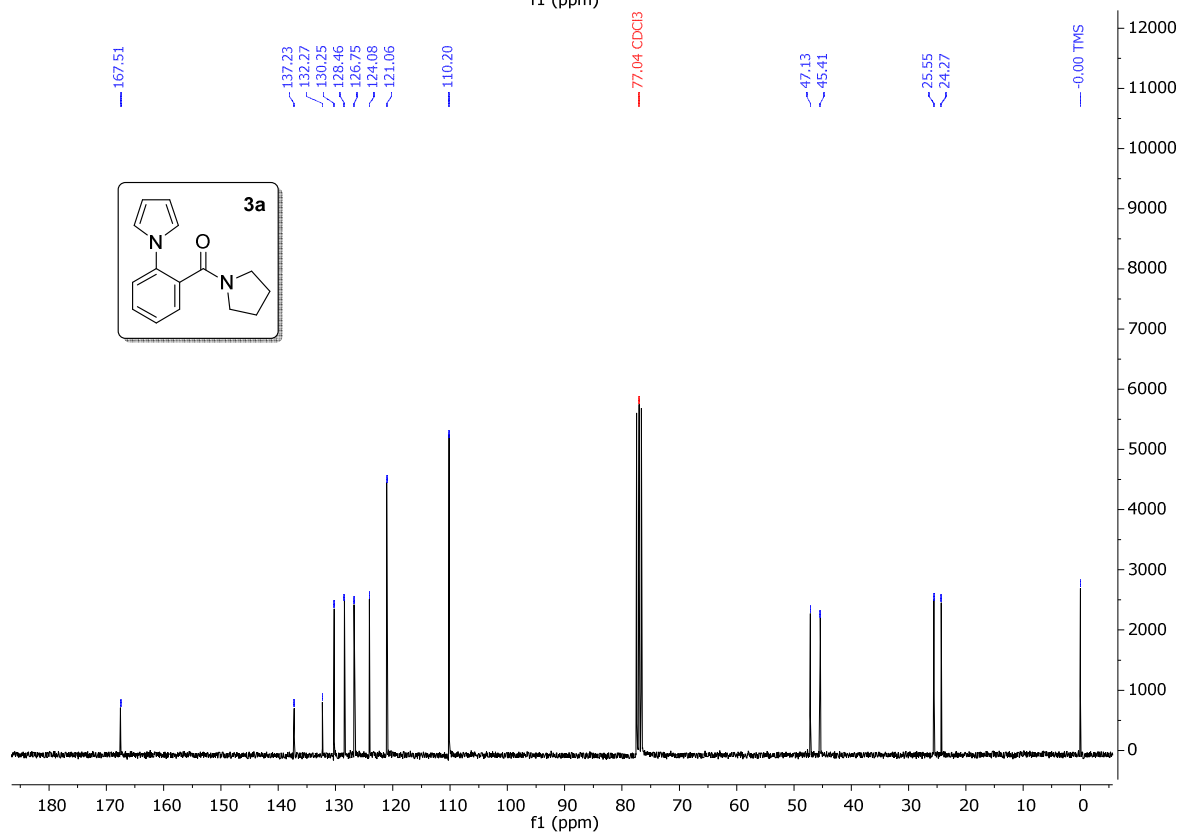
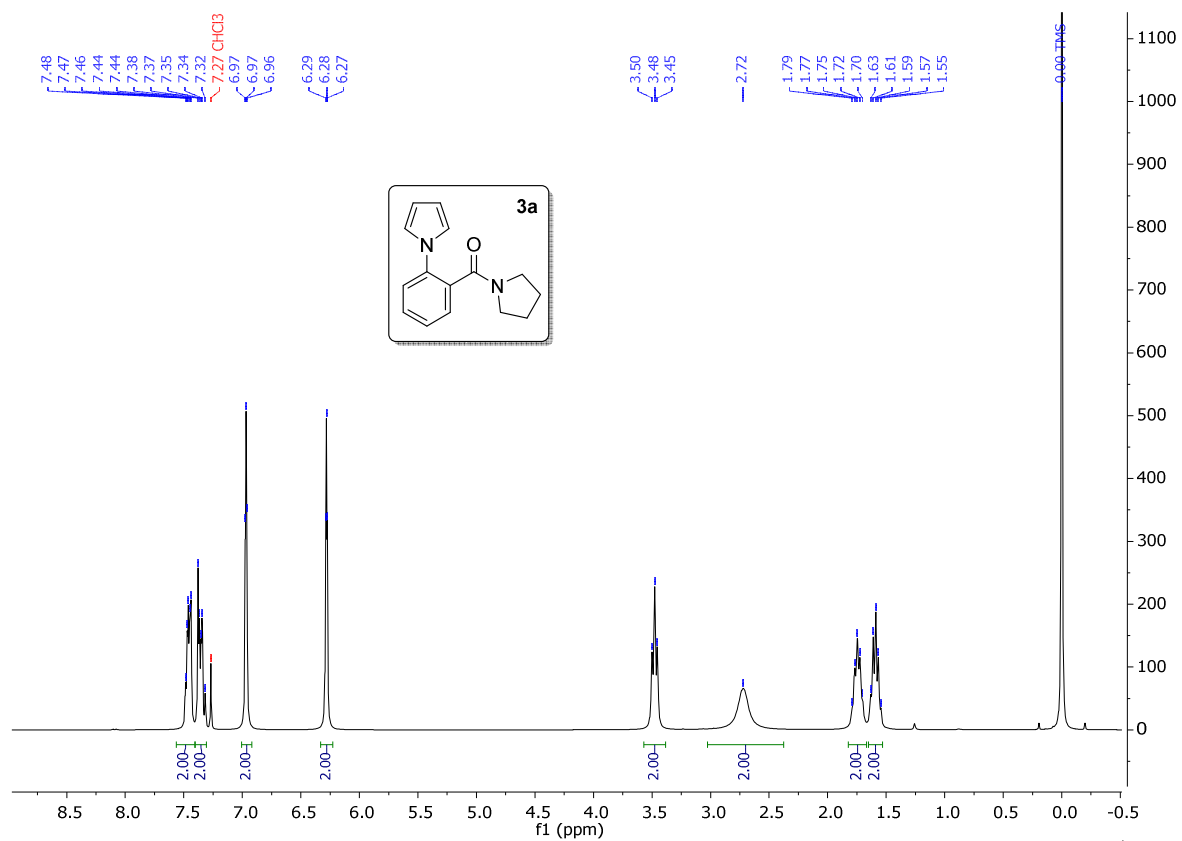
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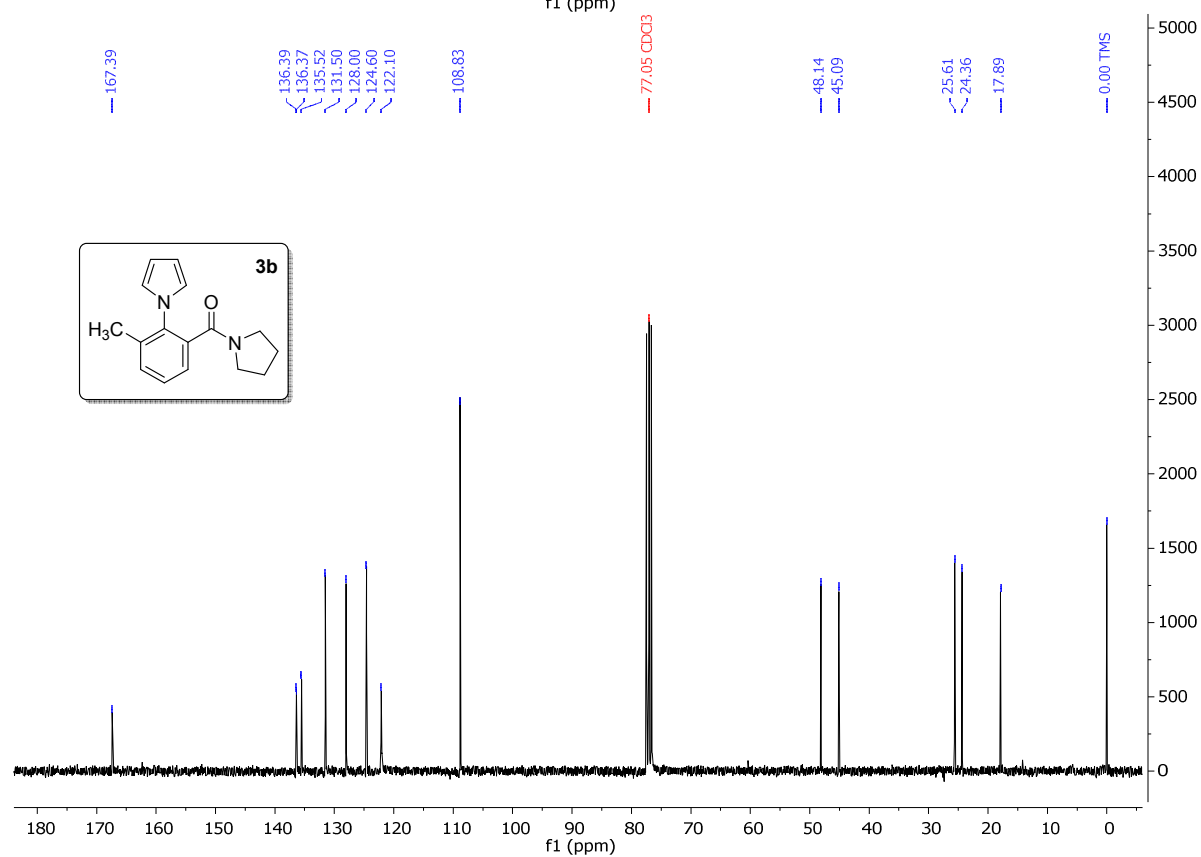
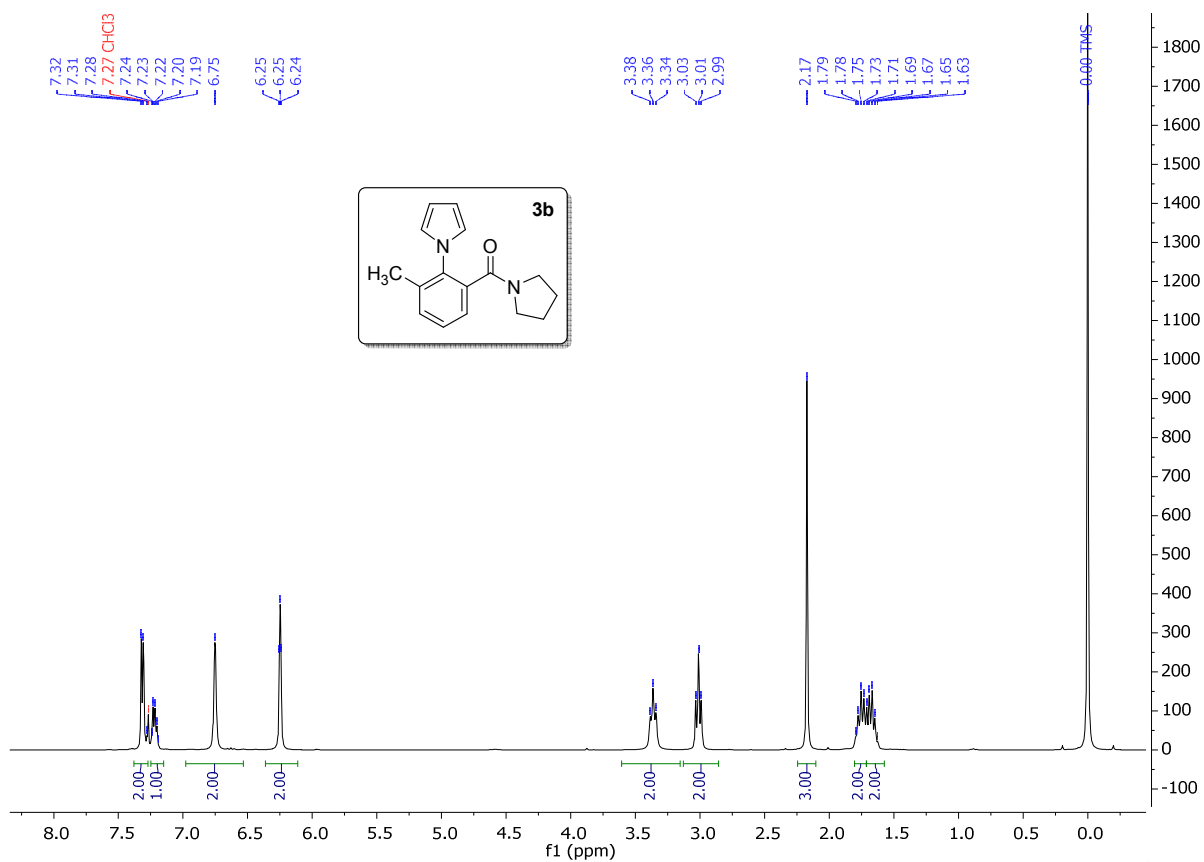
<sup>\*</sup>E-mail: bmatravolgyi@mail.bme.hu

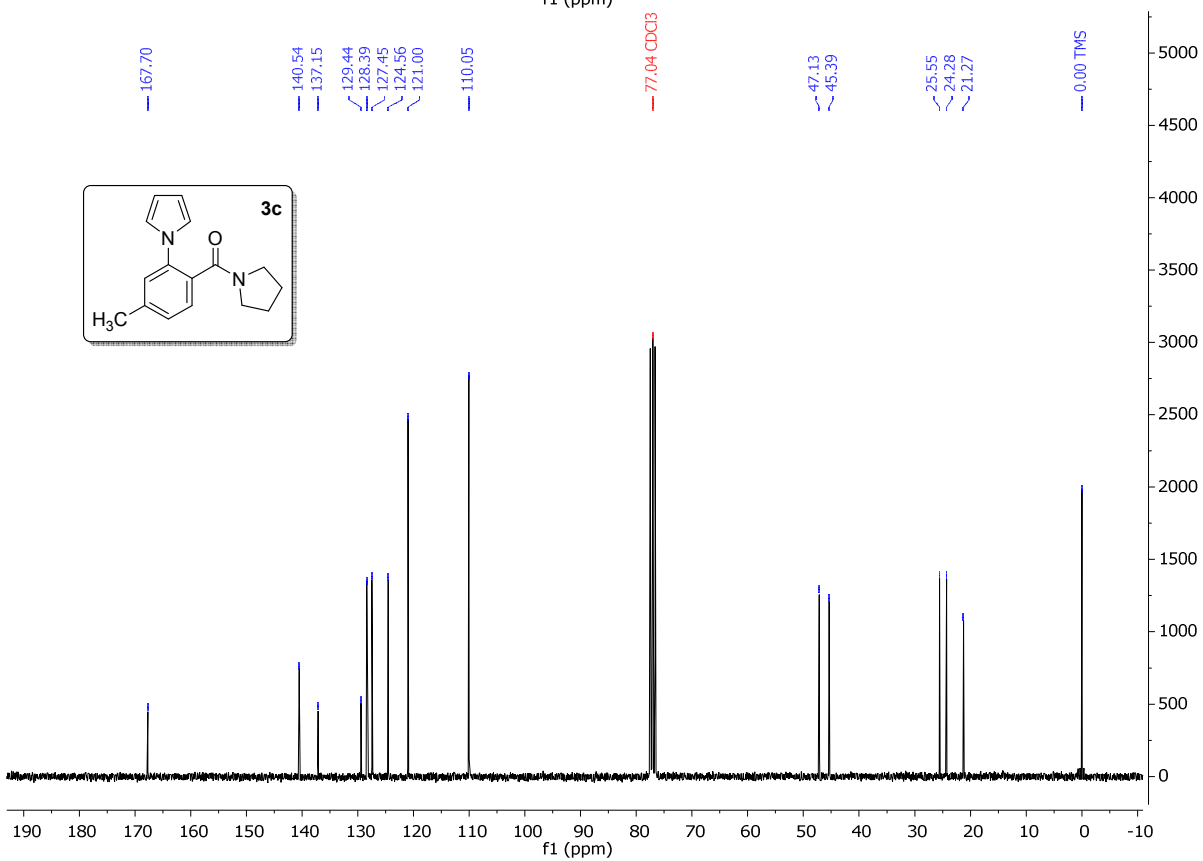
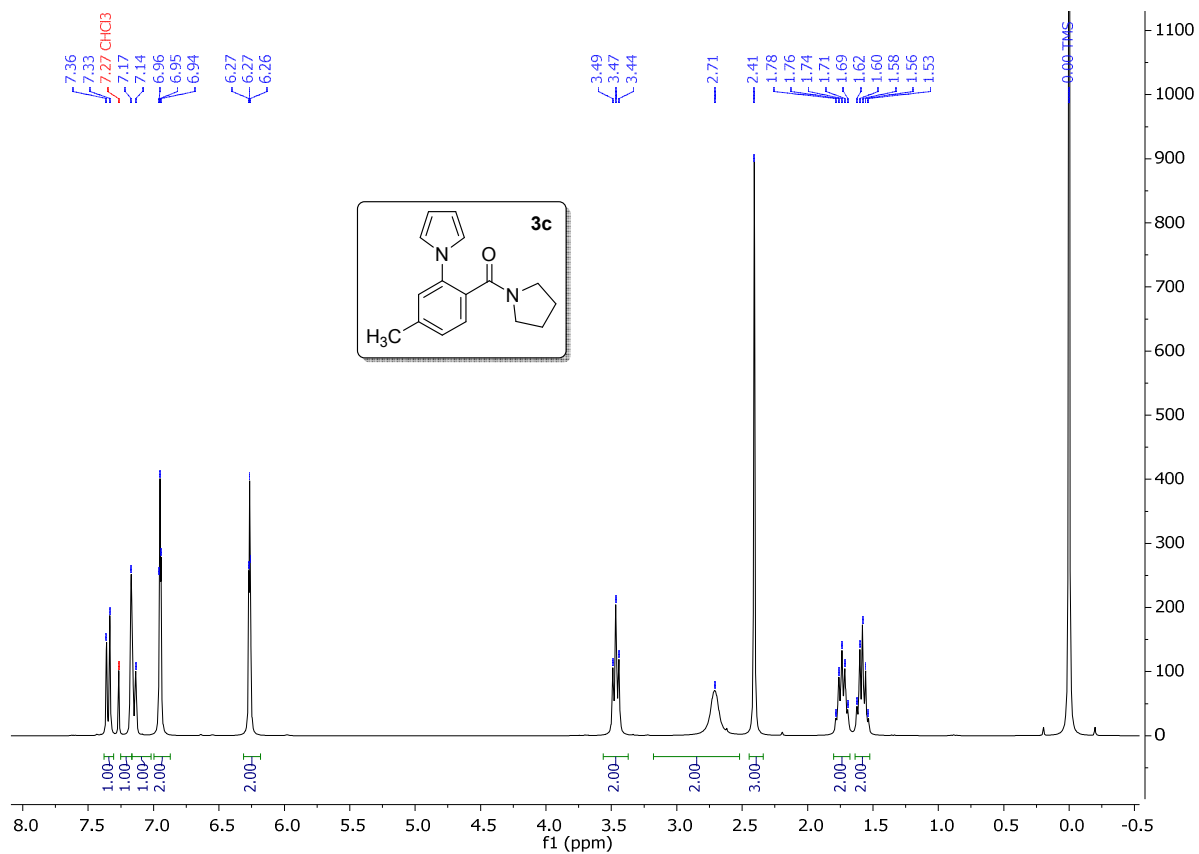
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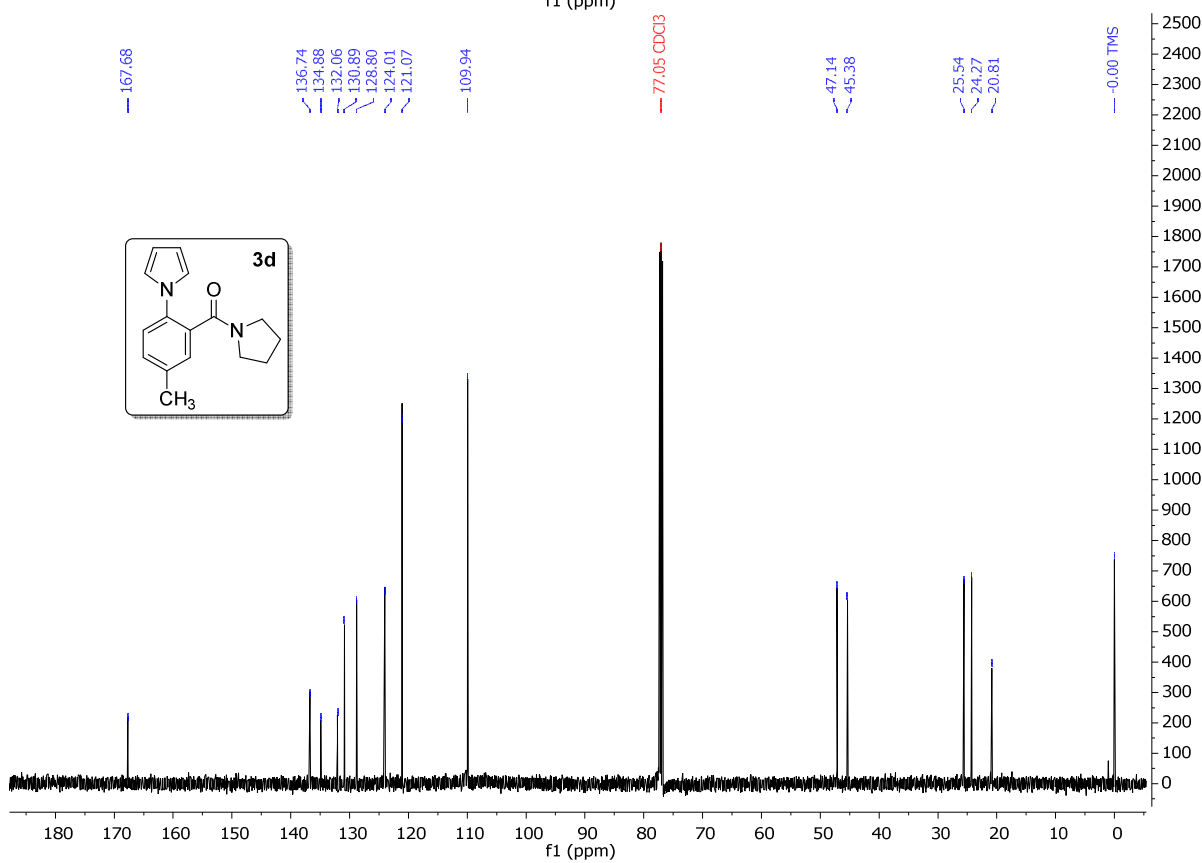
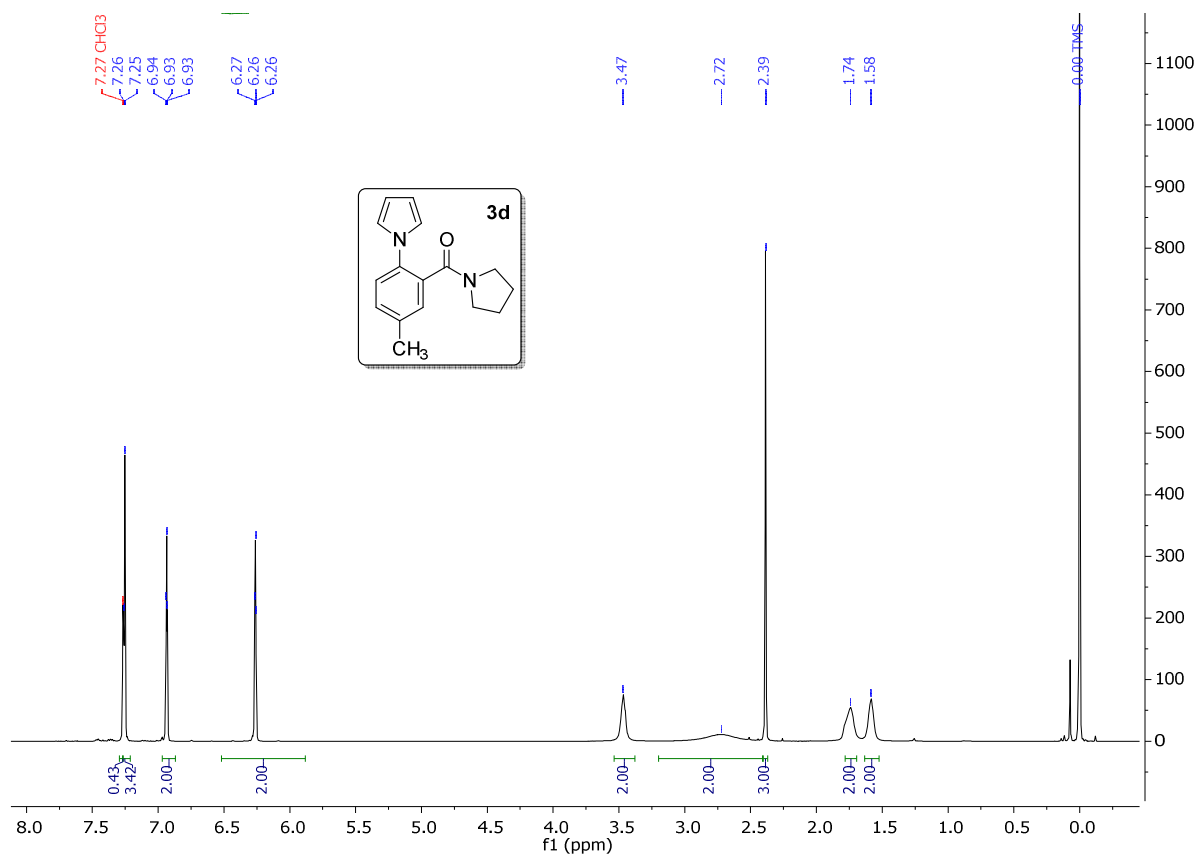
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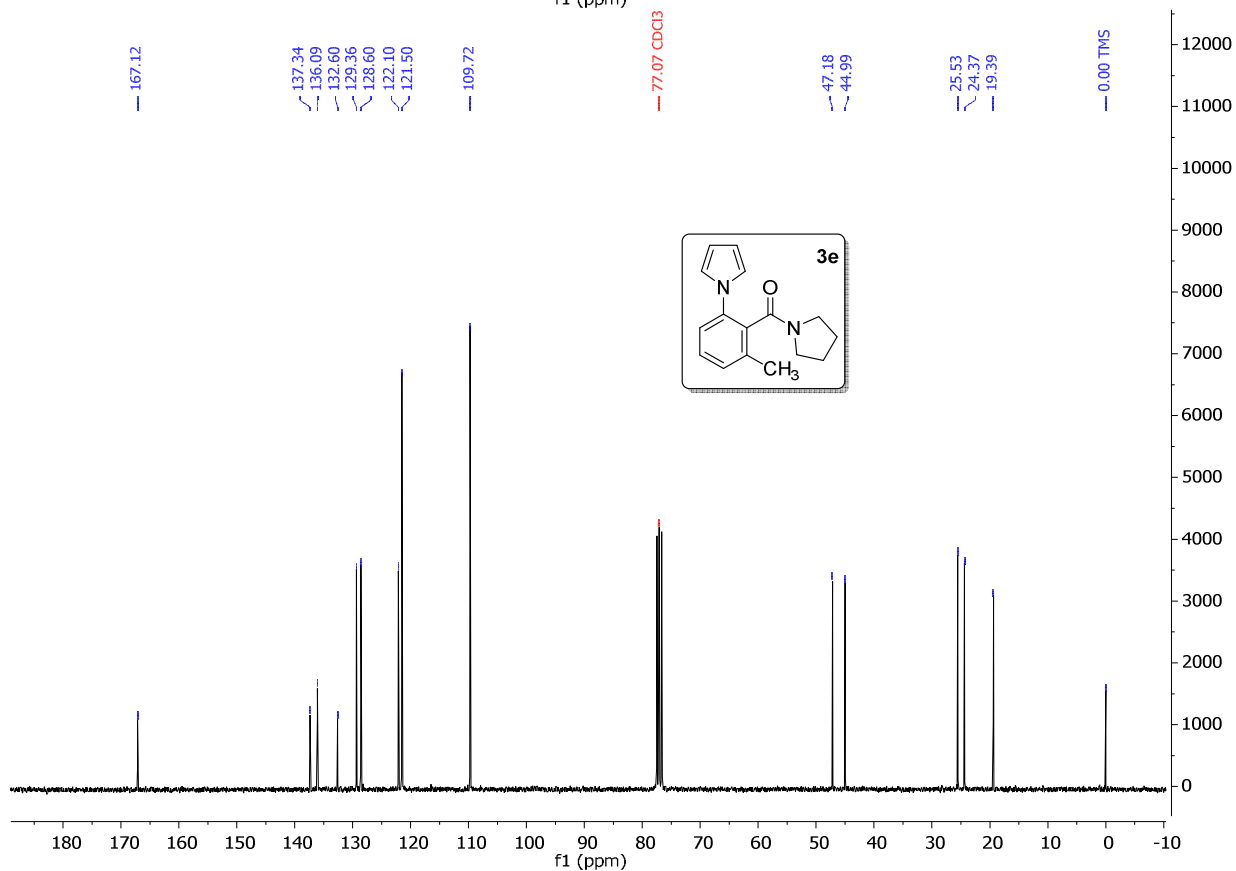
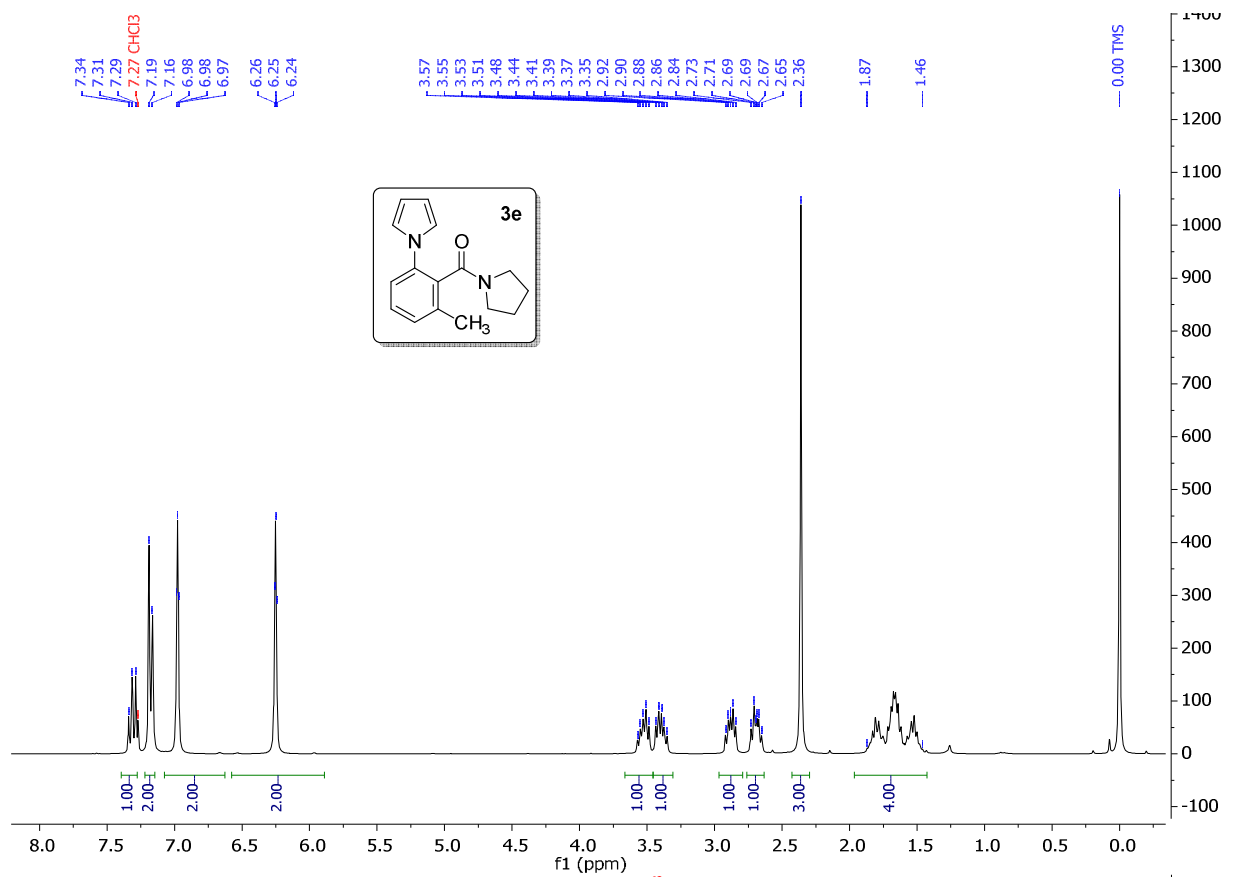
# $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of compounds

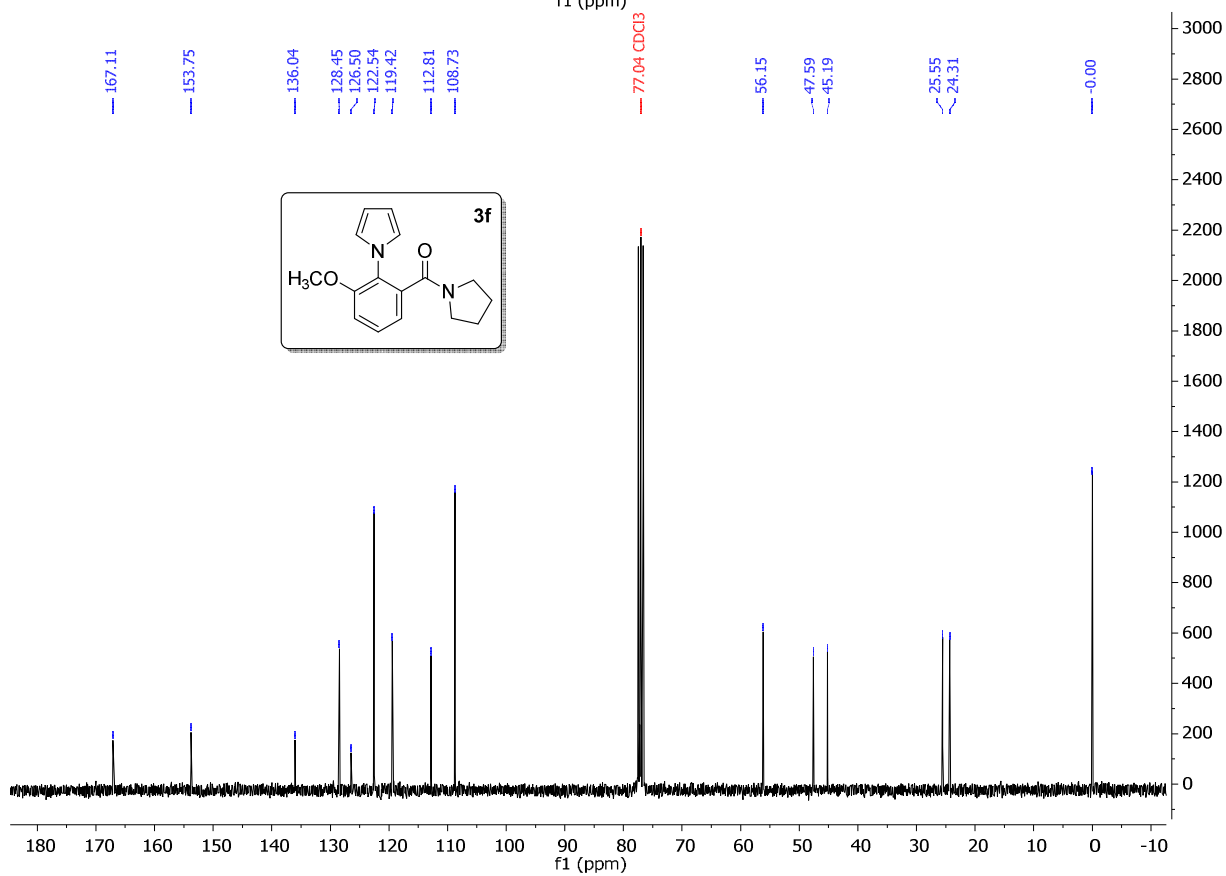
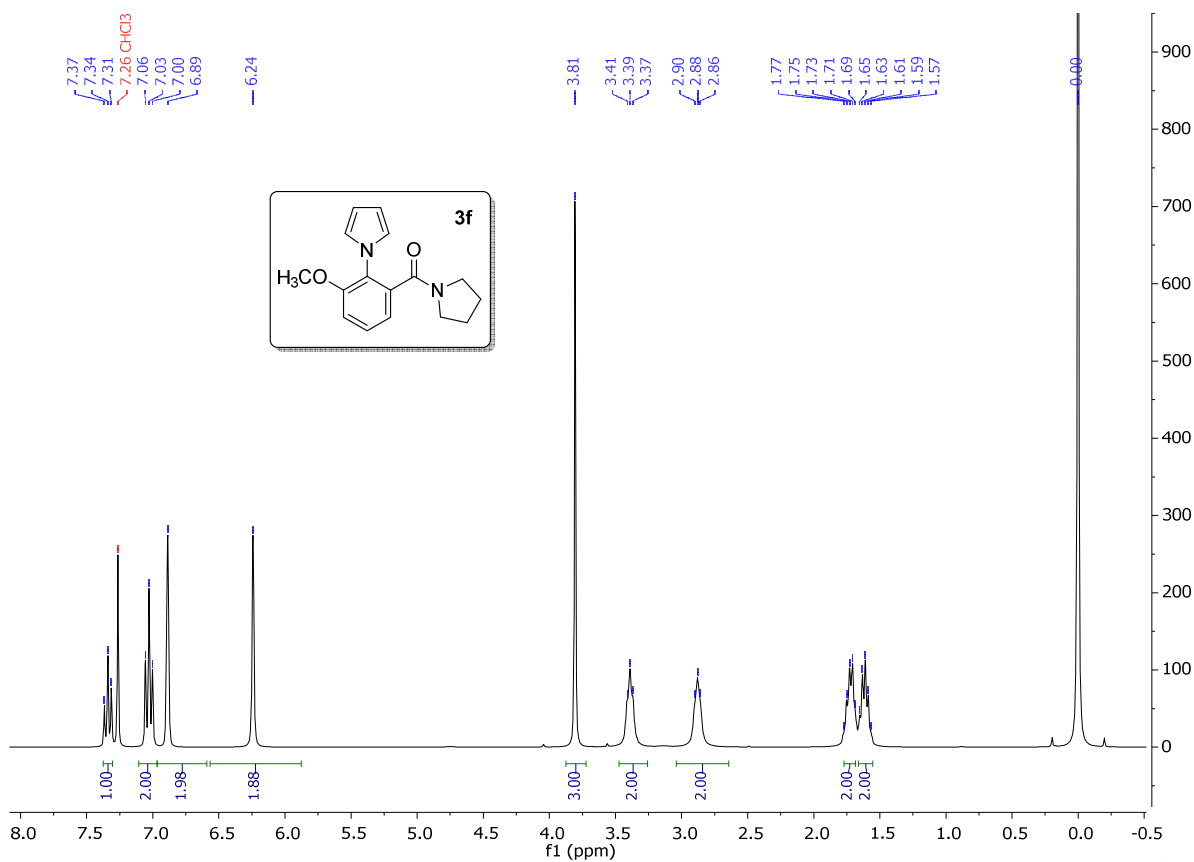


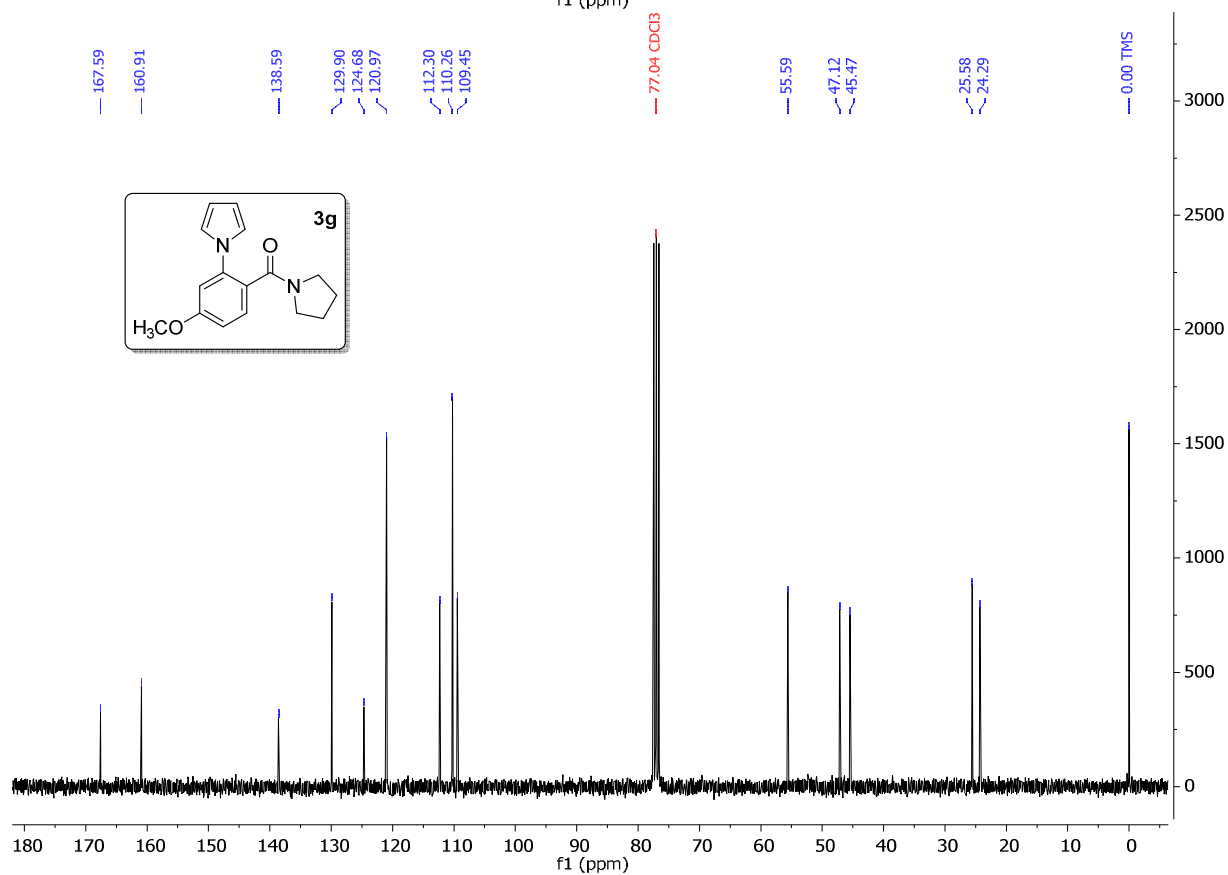
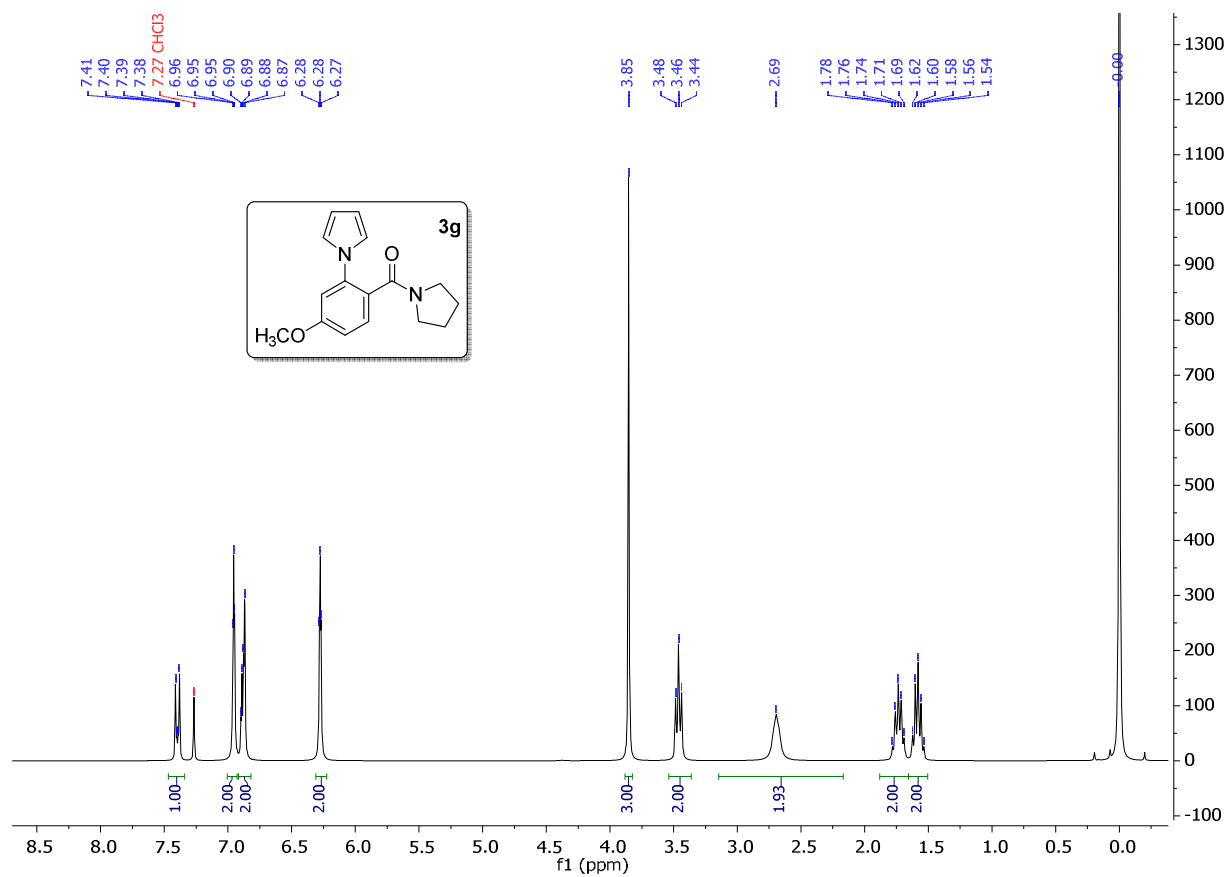




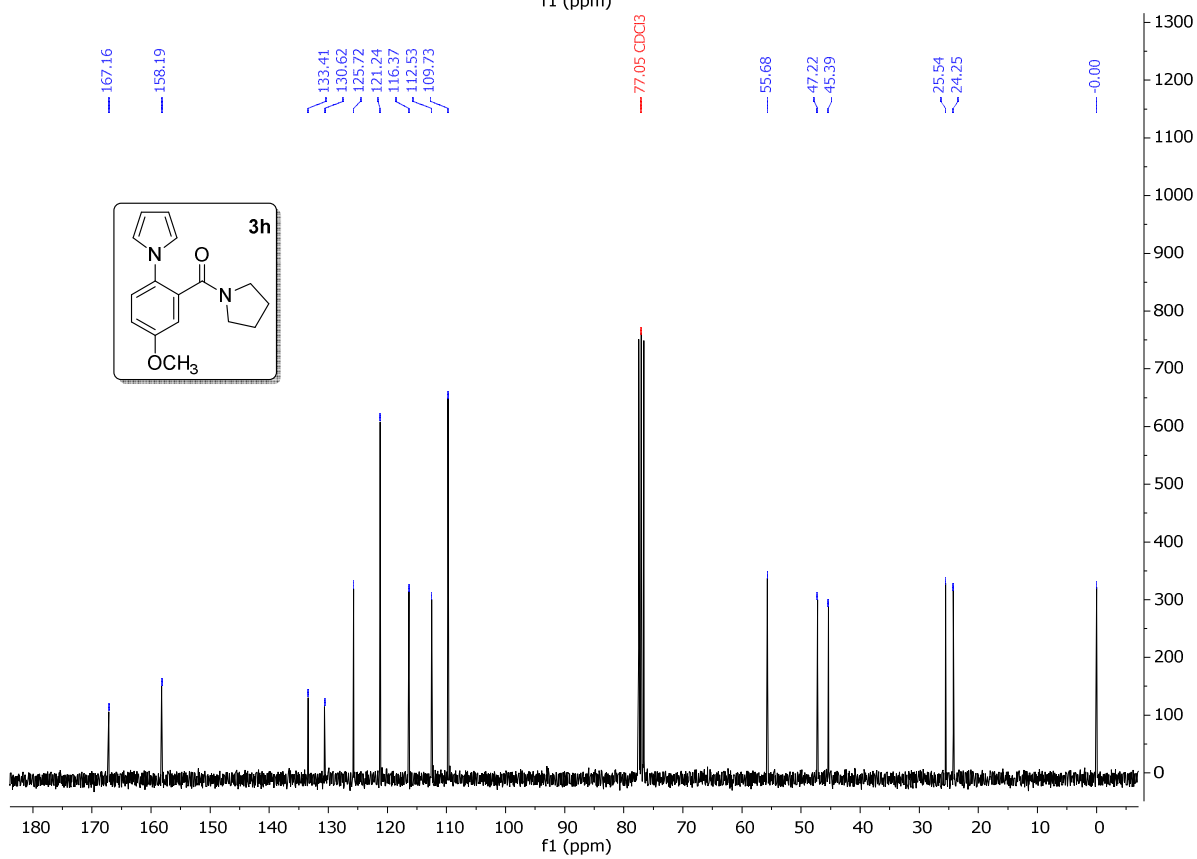
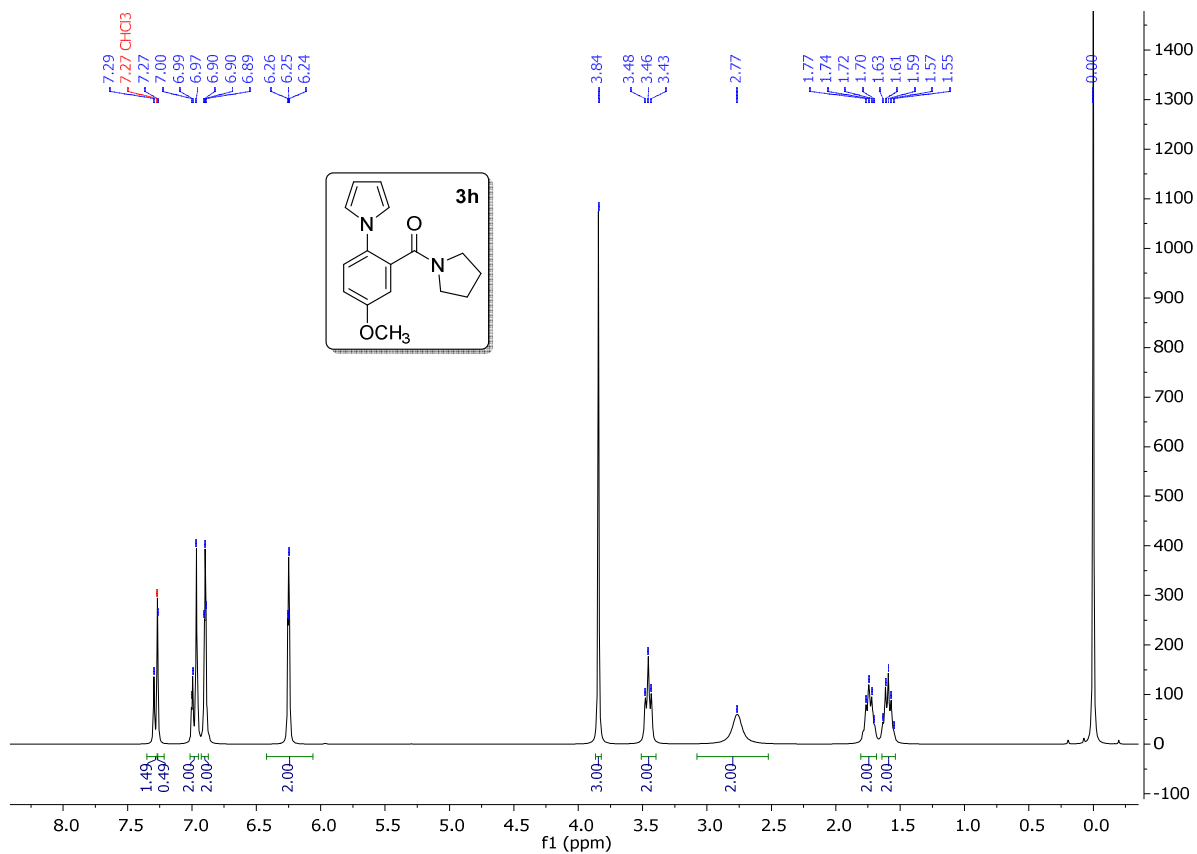


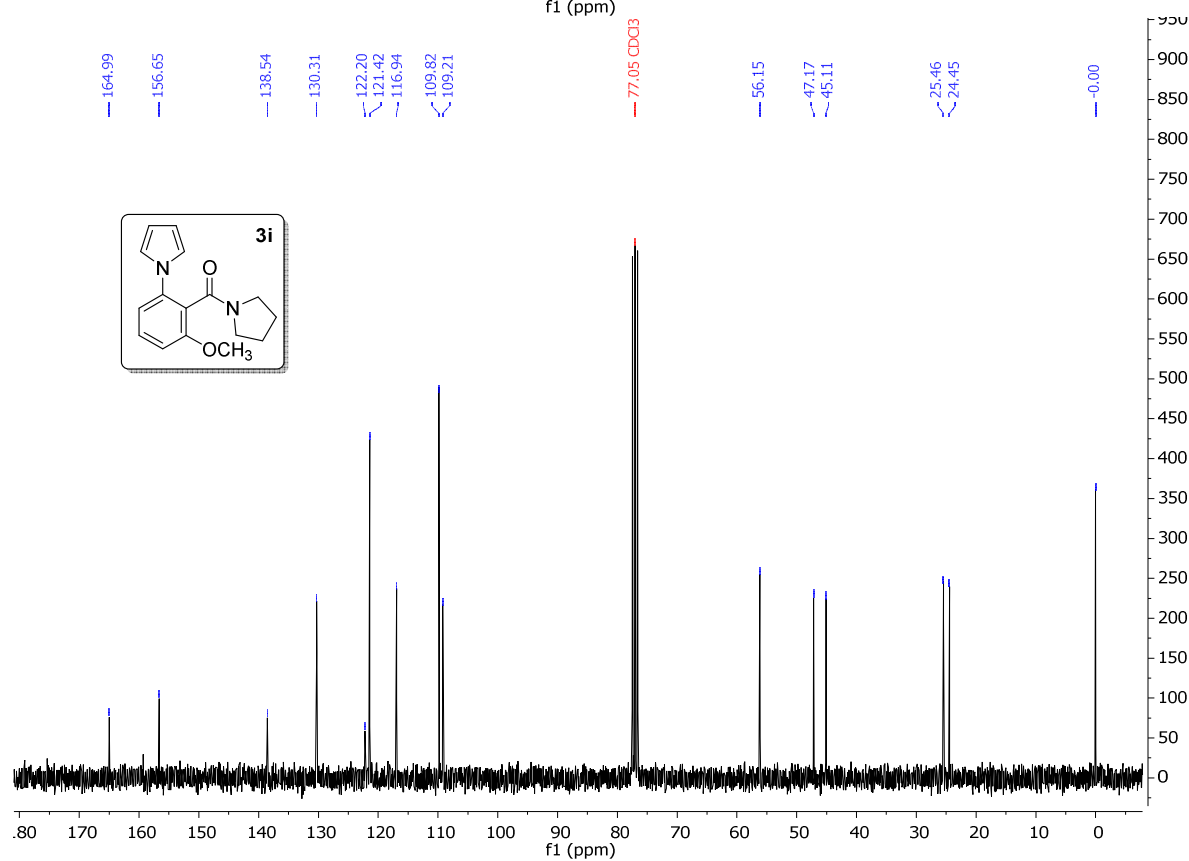
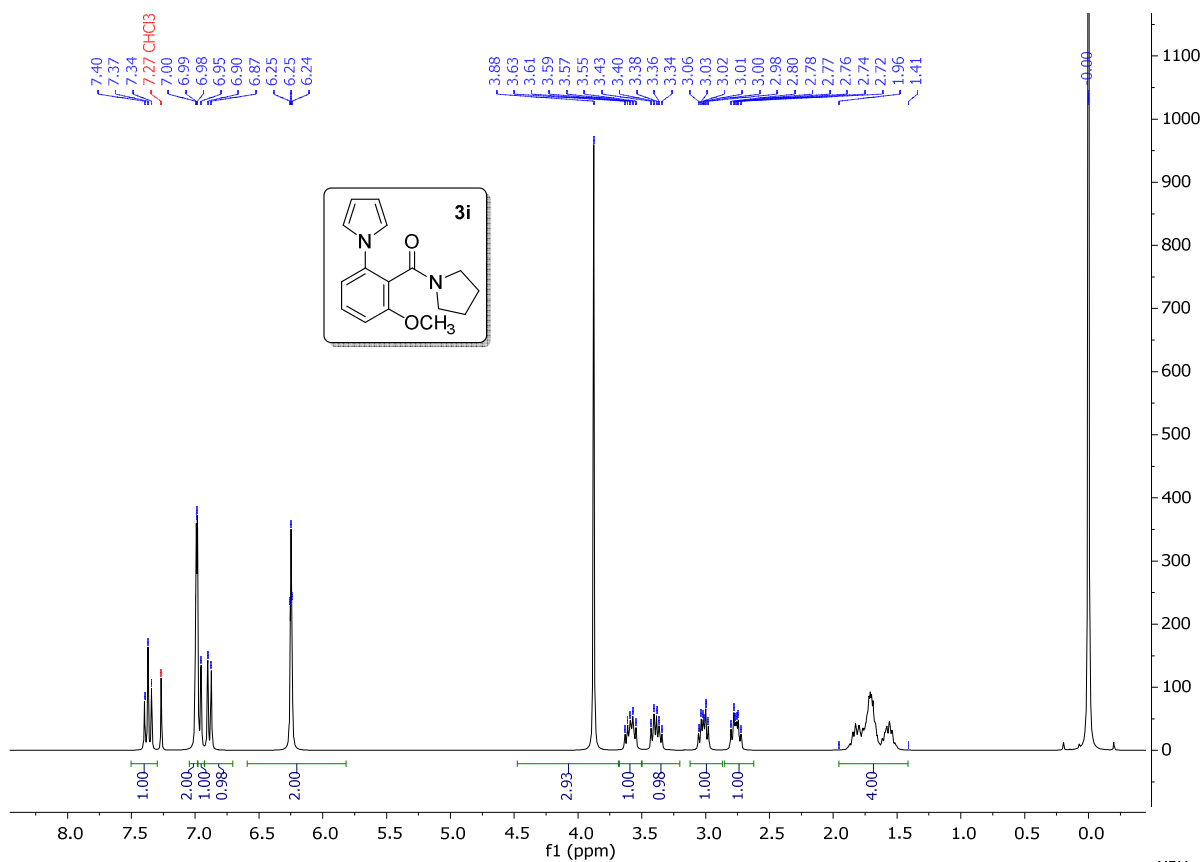


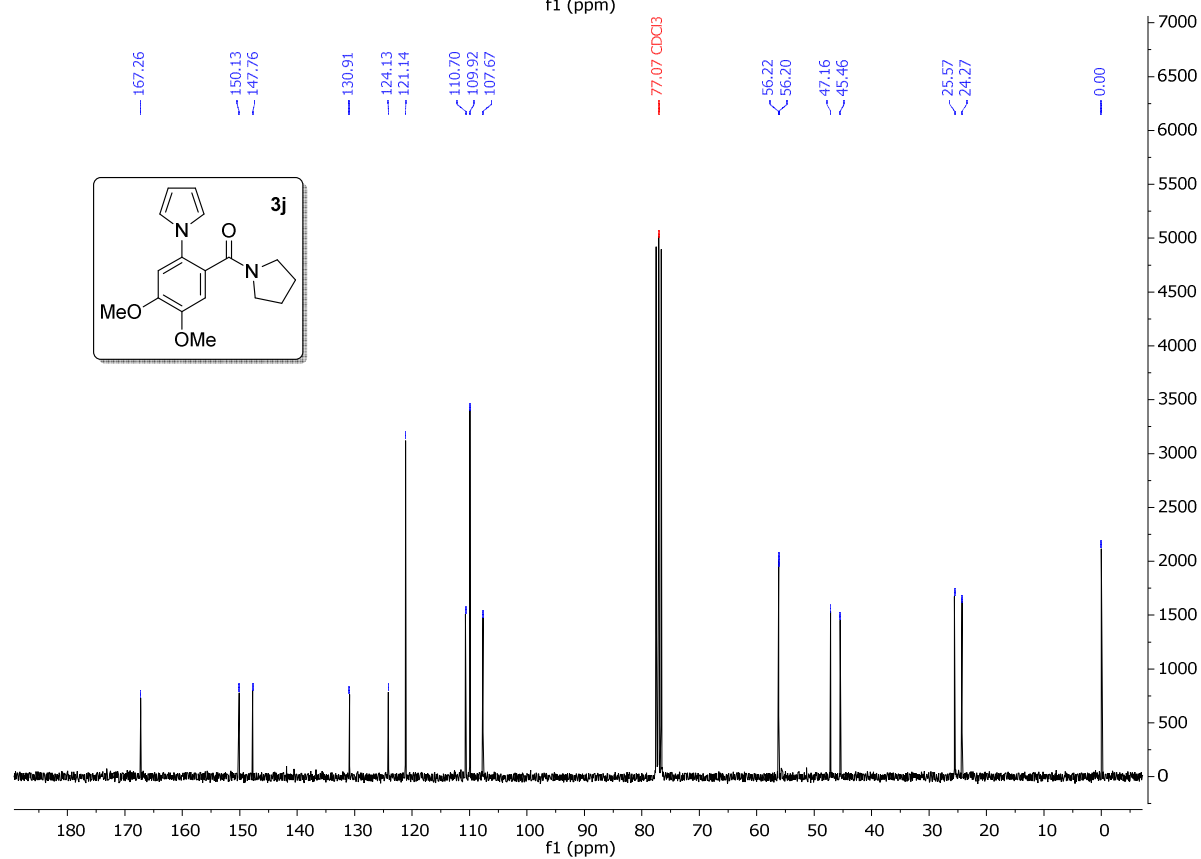
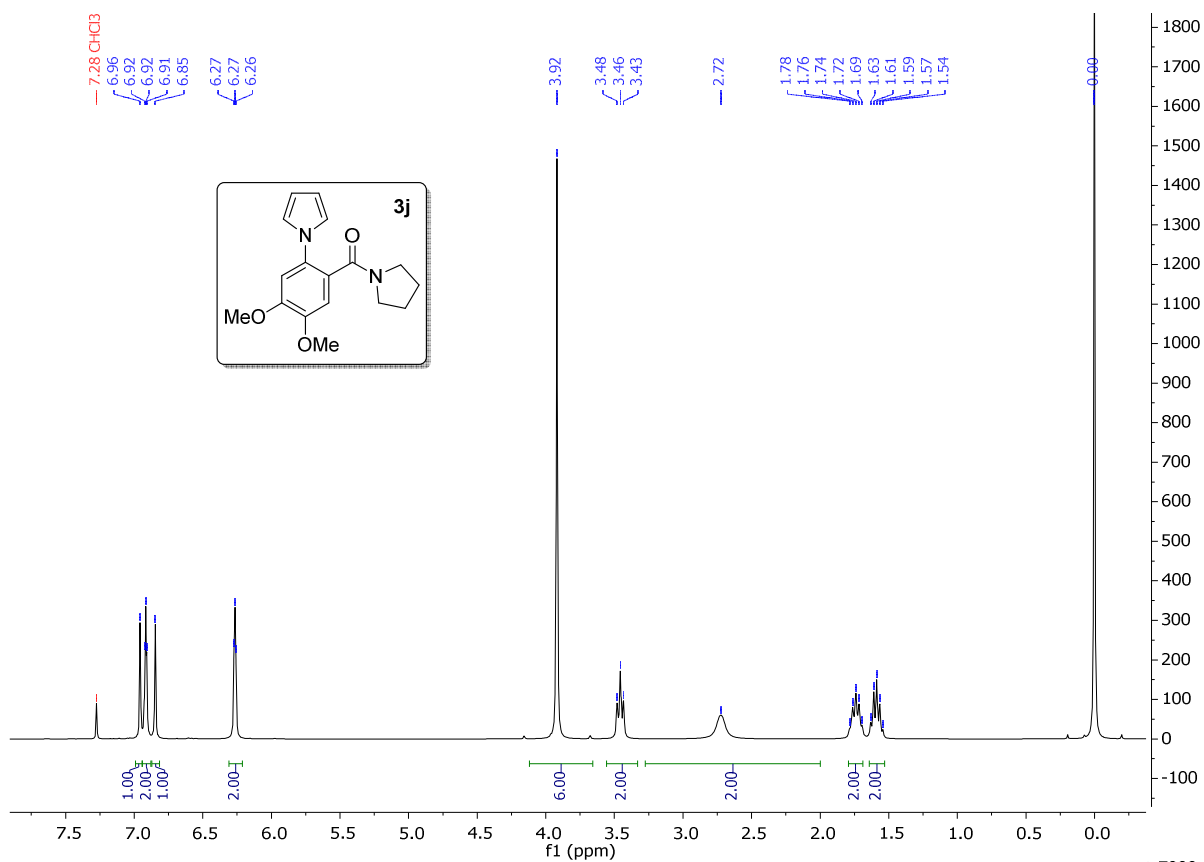


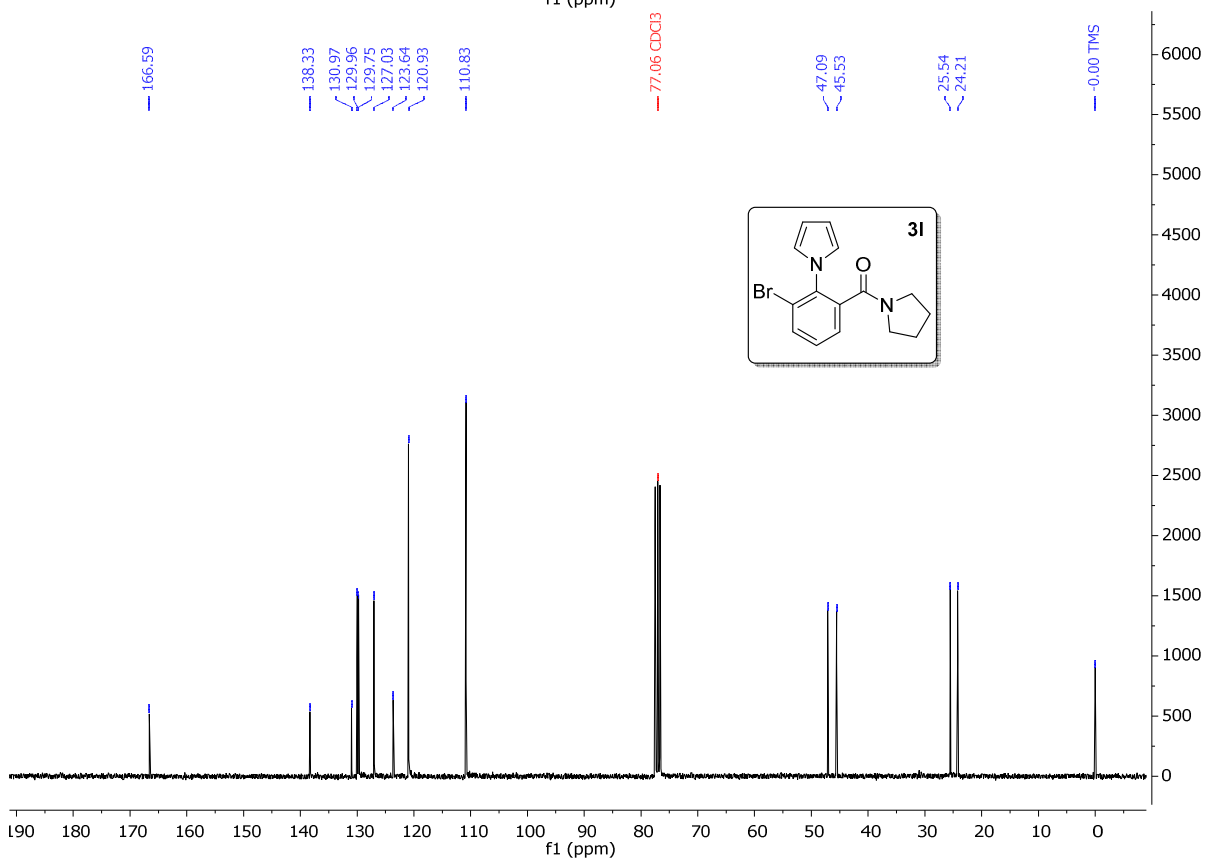
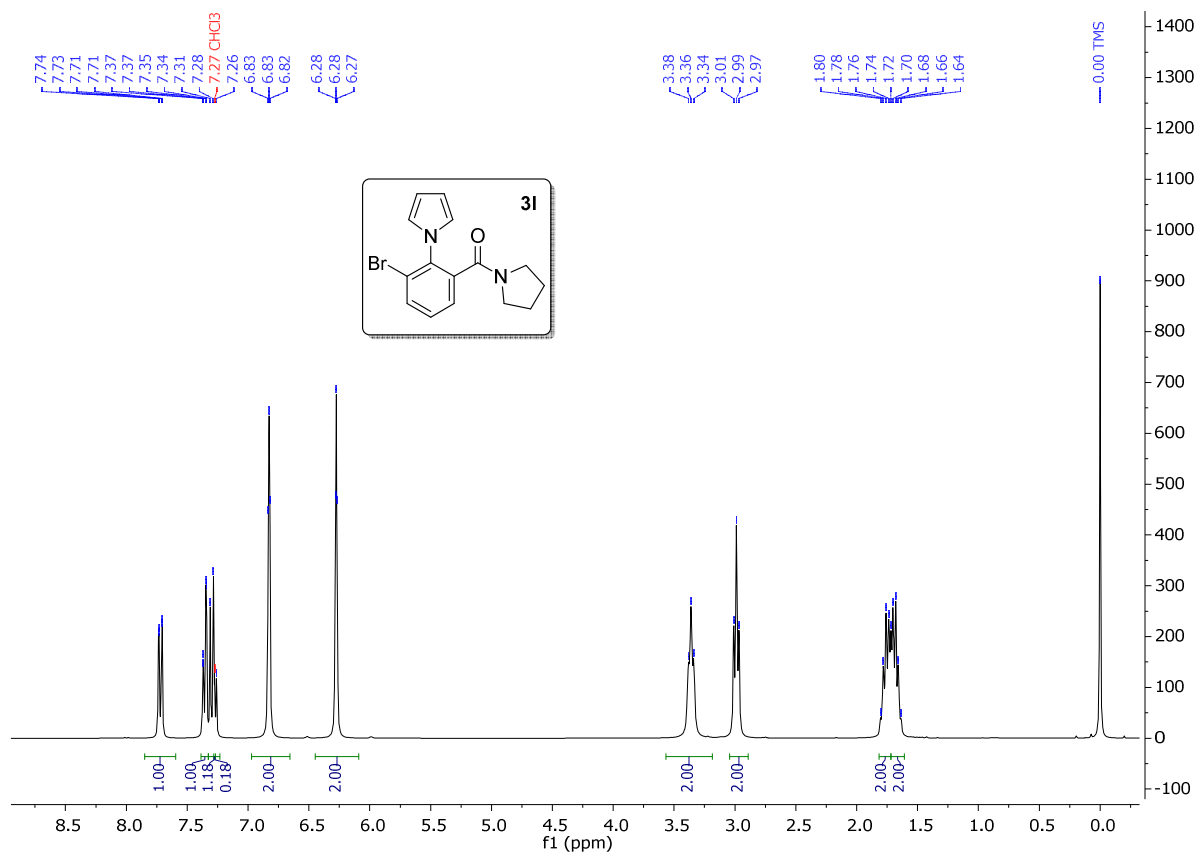


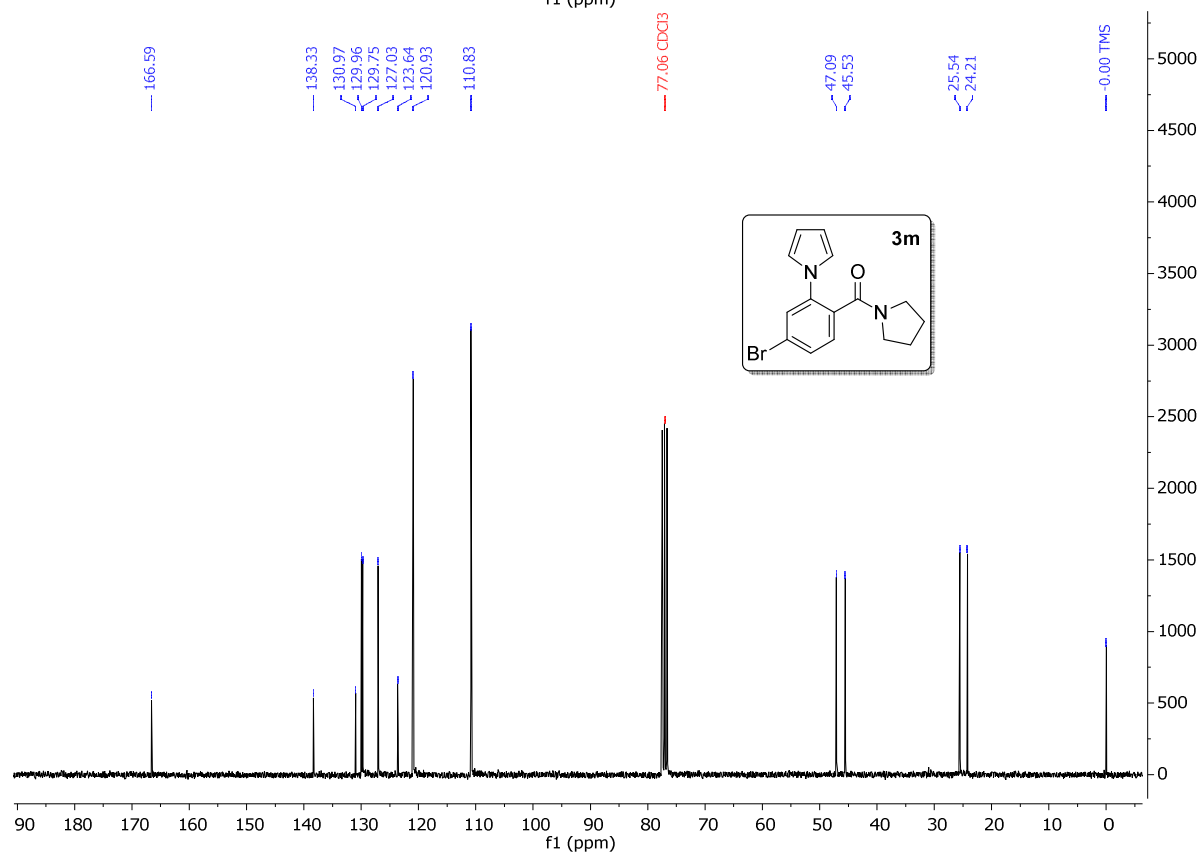
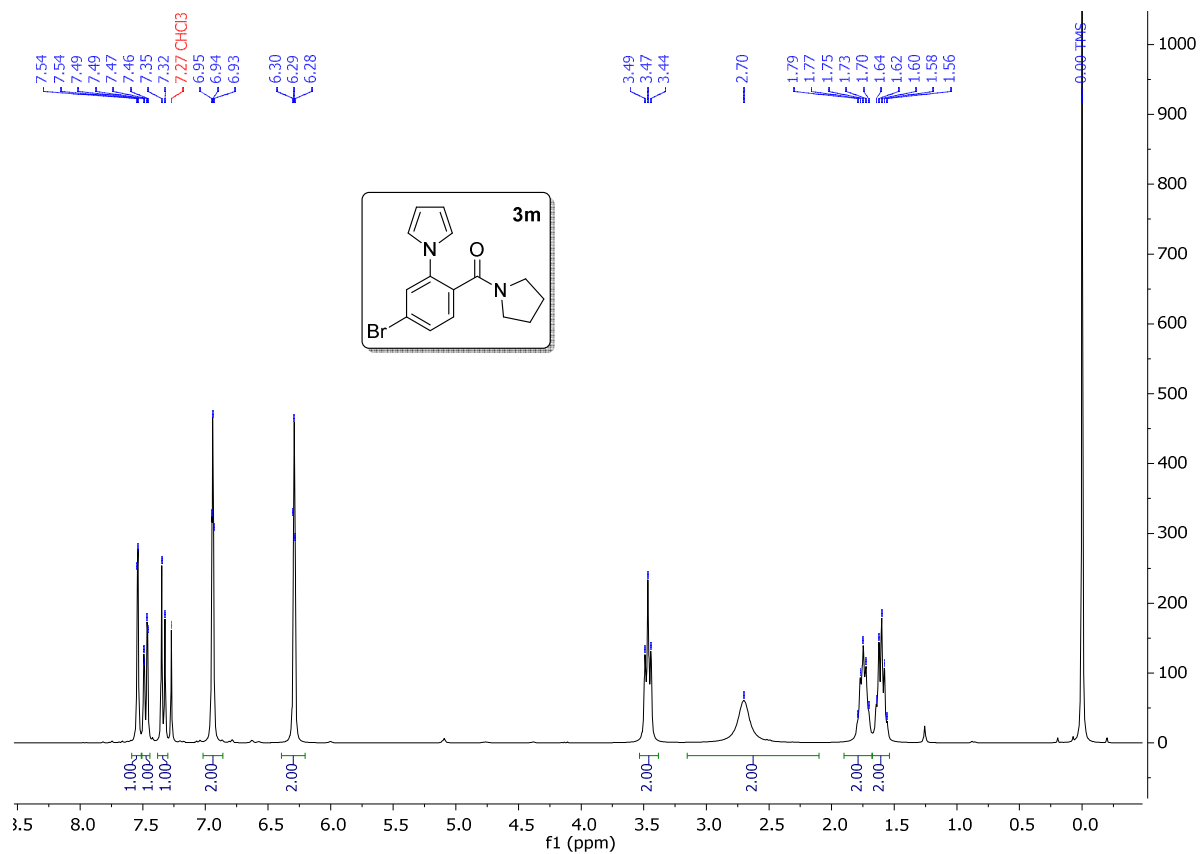


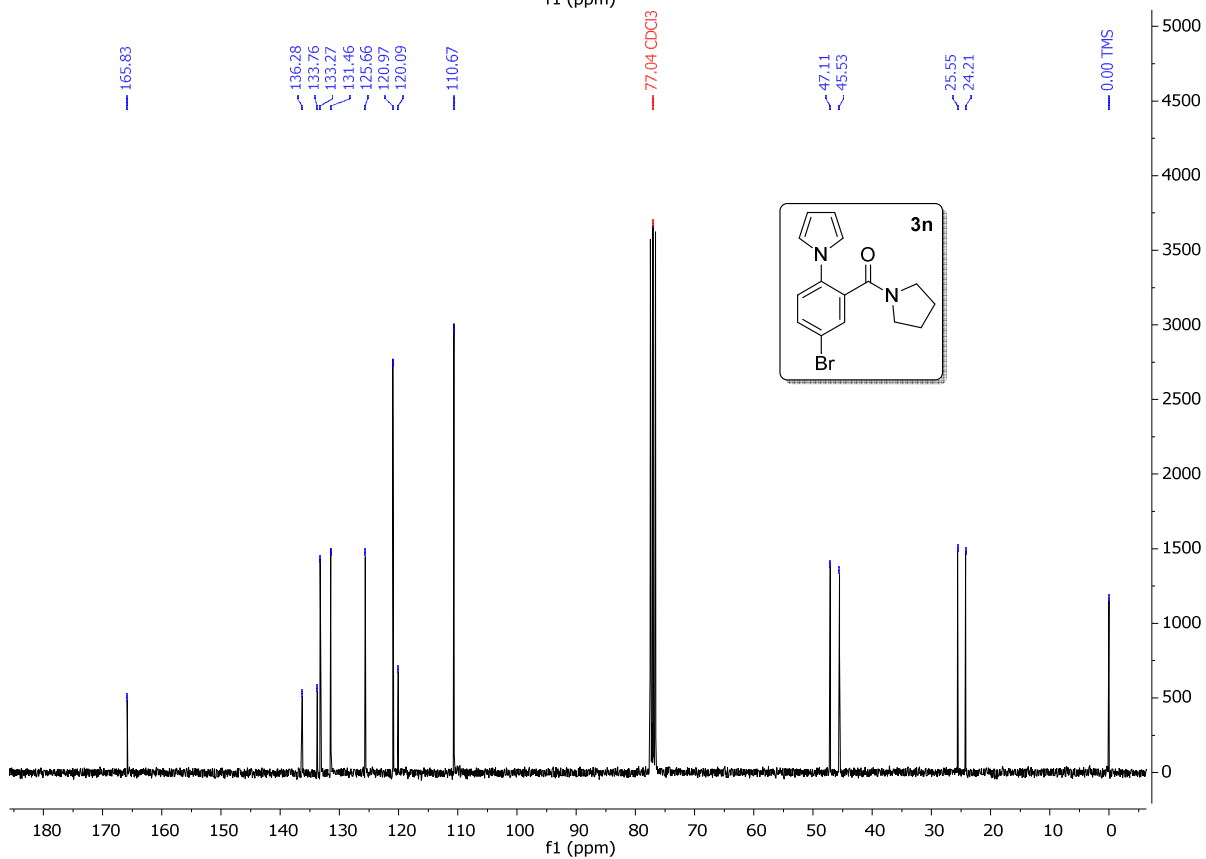
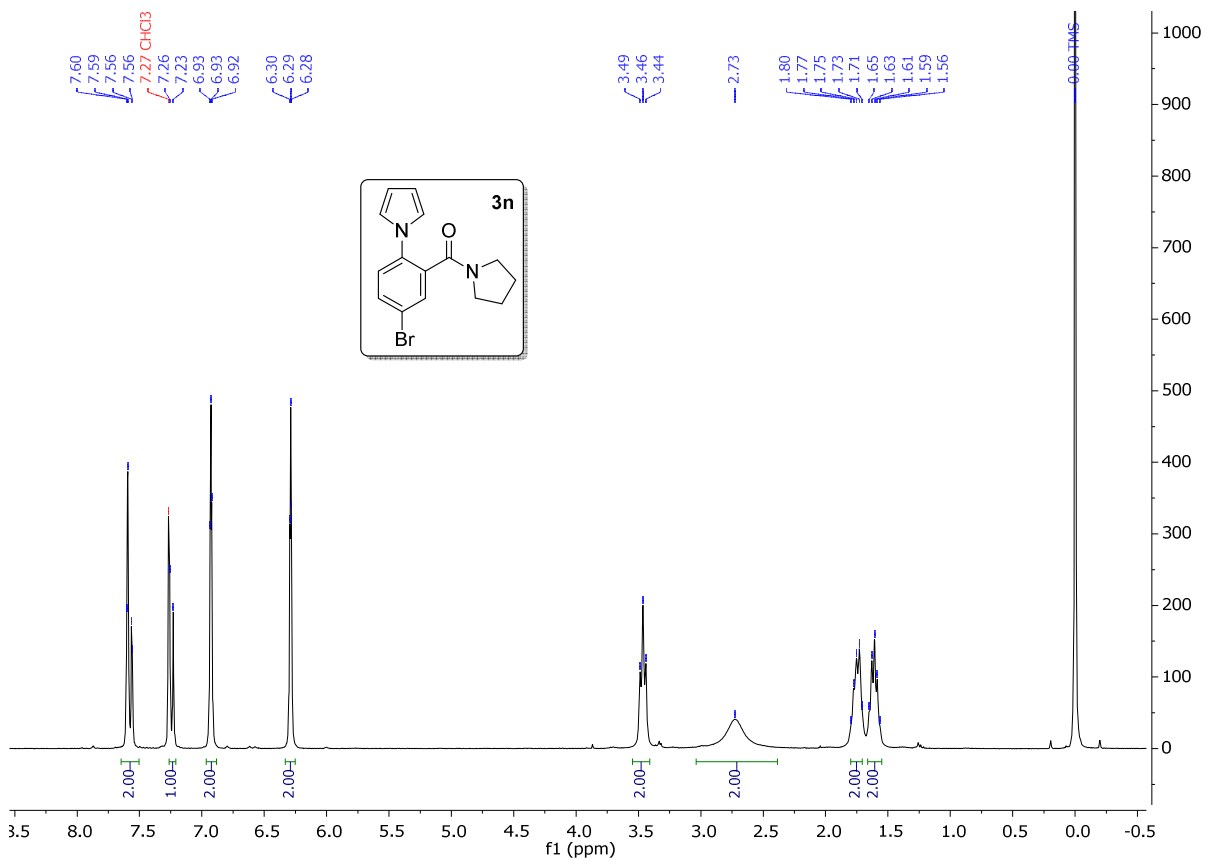


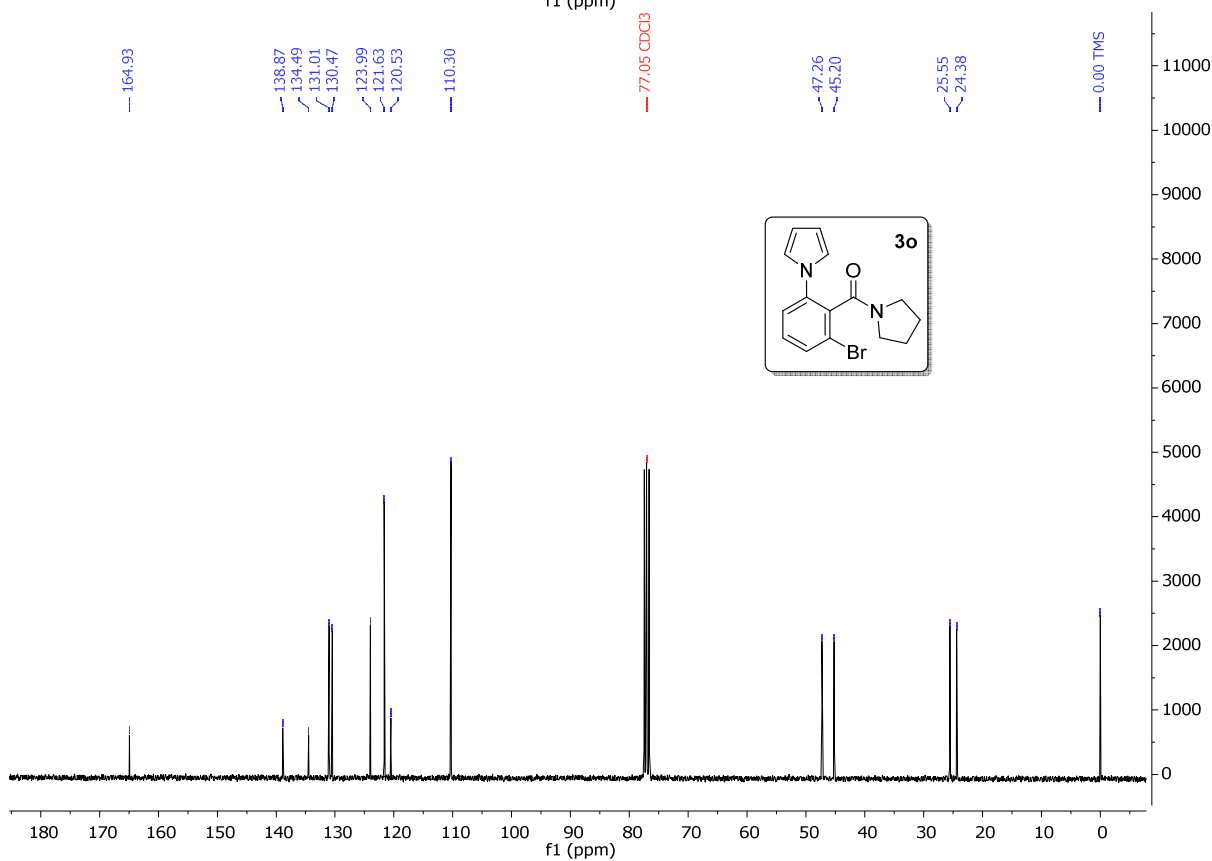
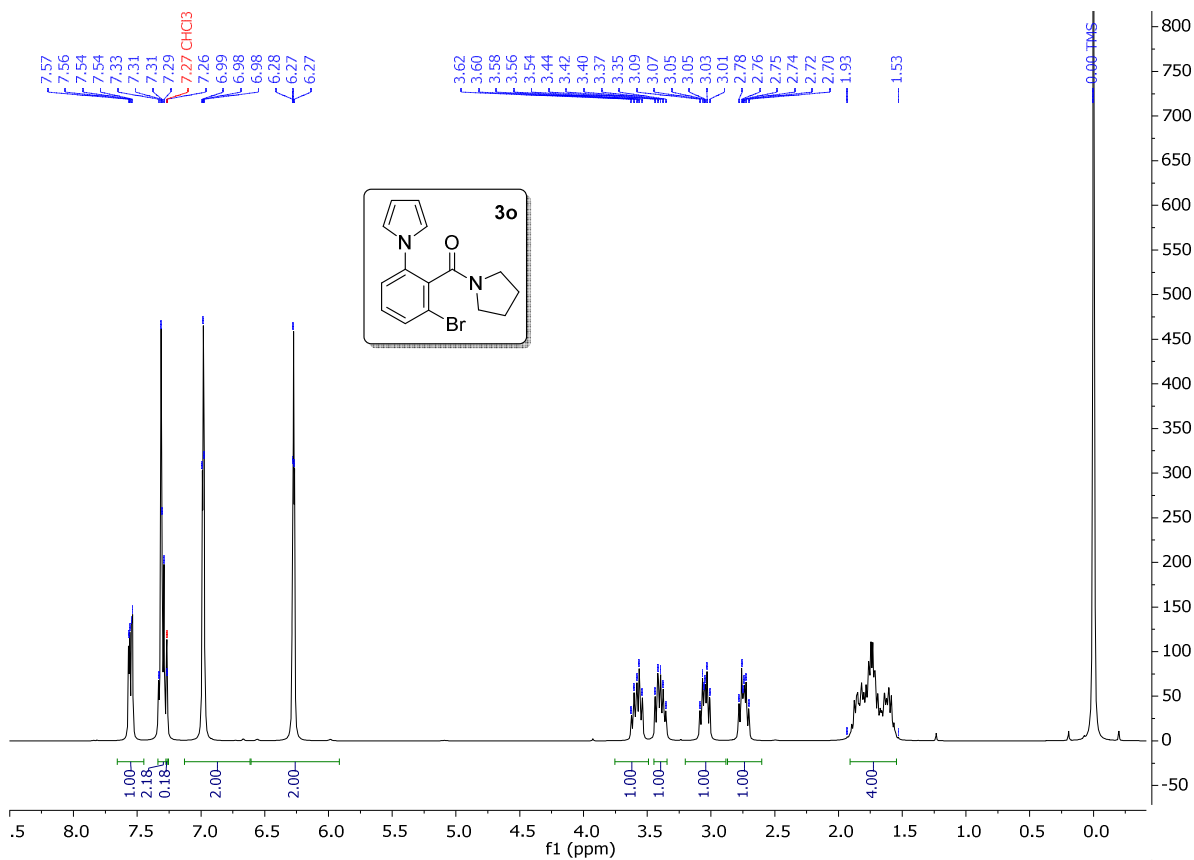


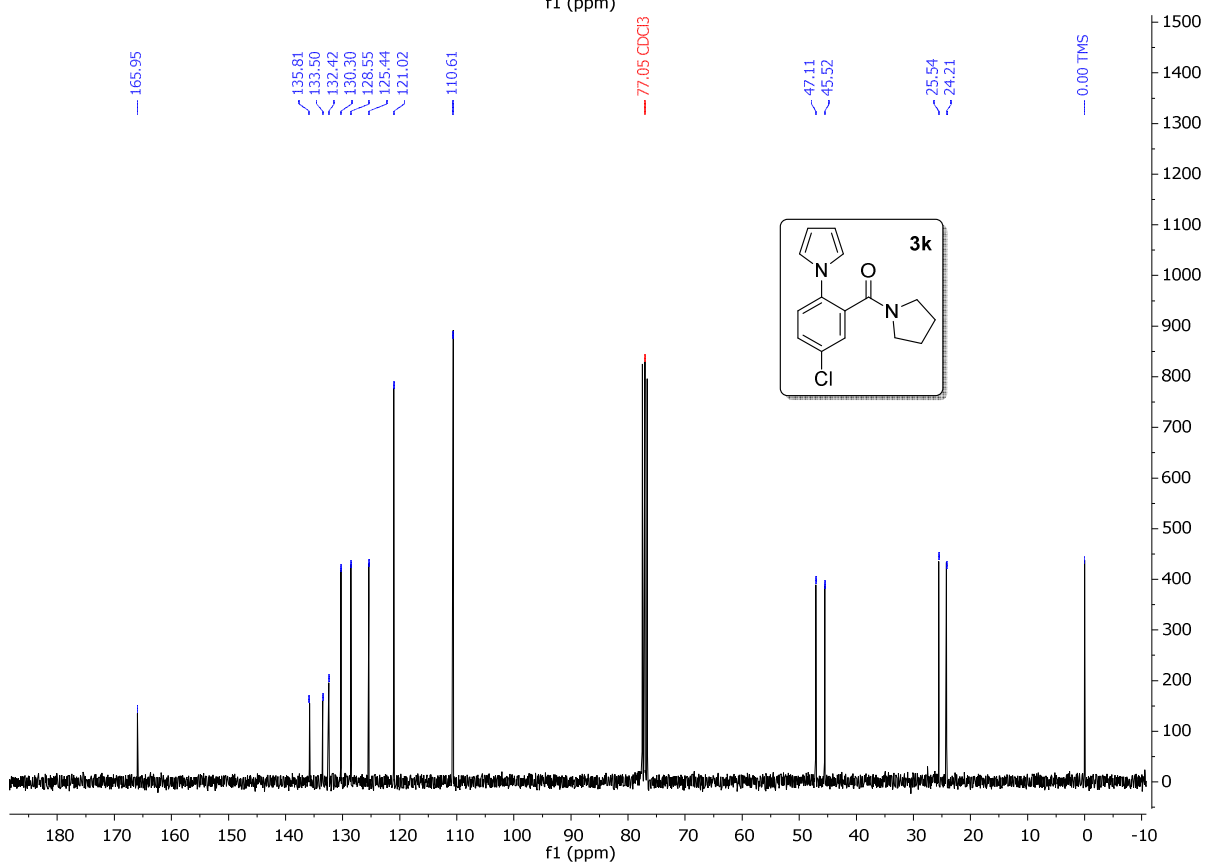
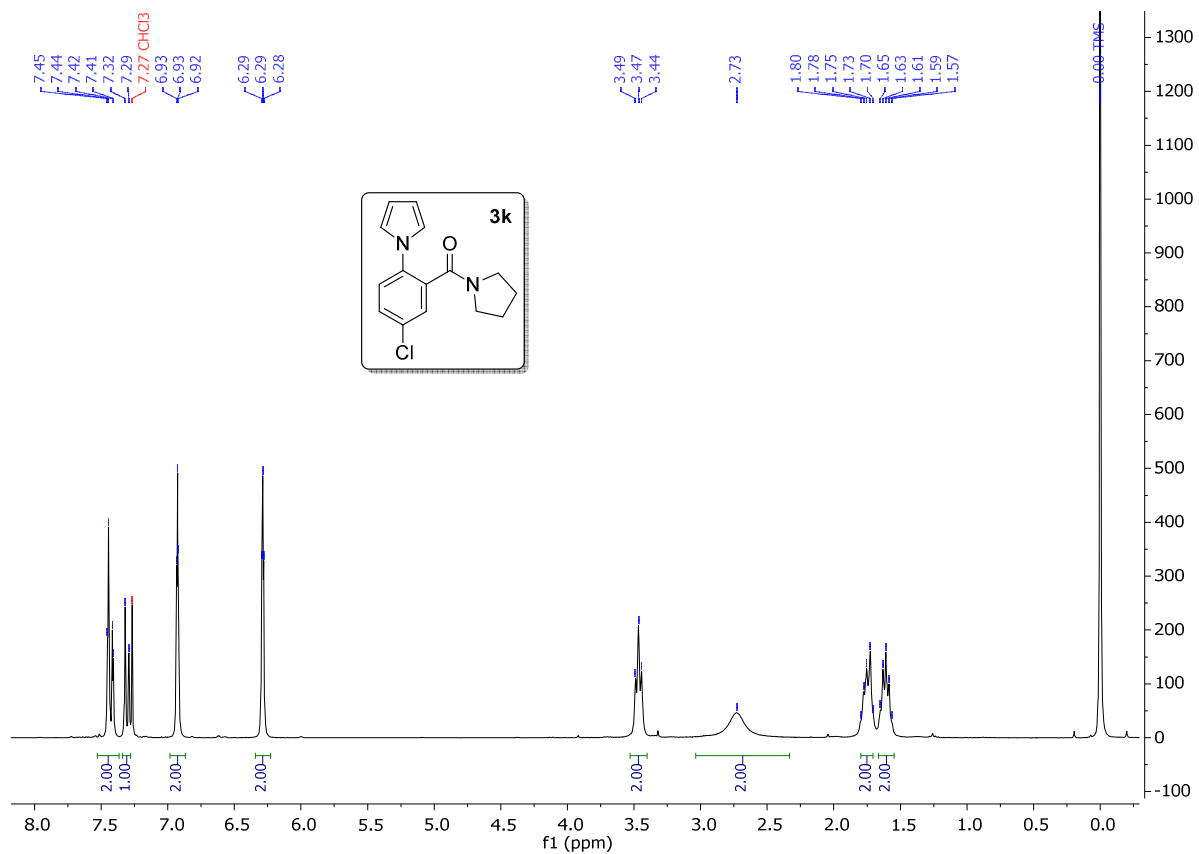




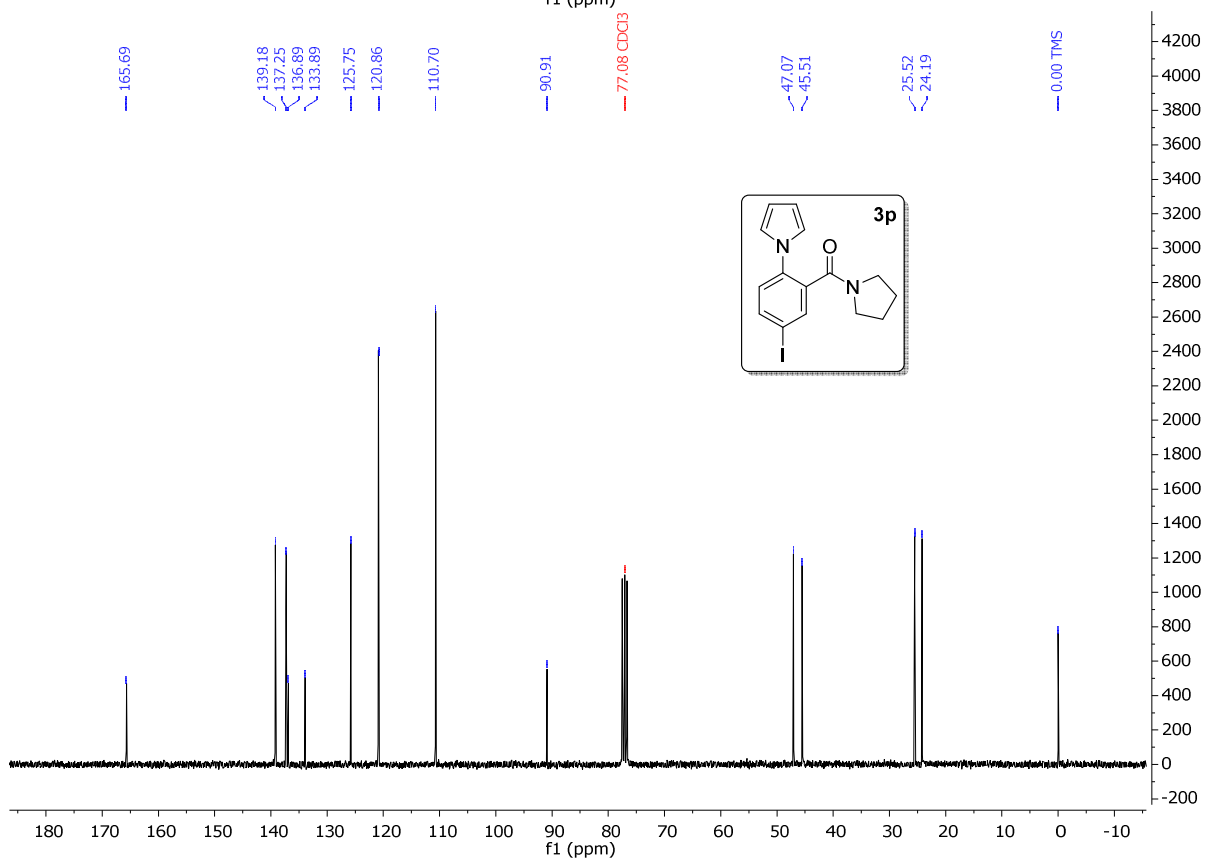
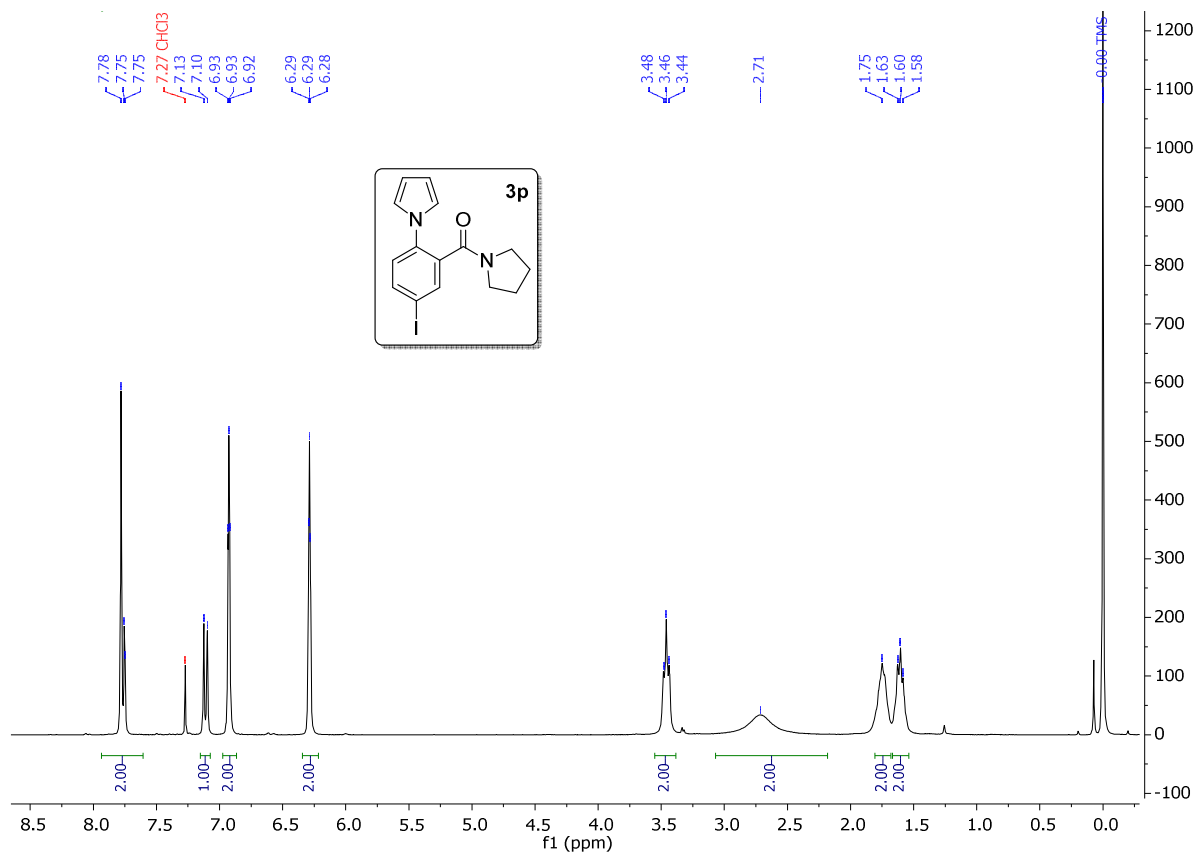


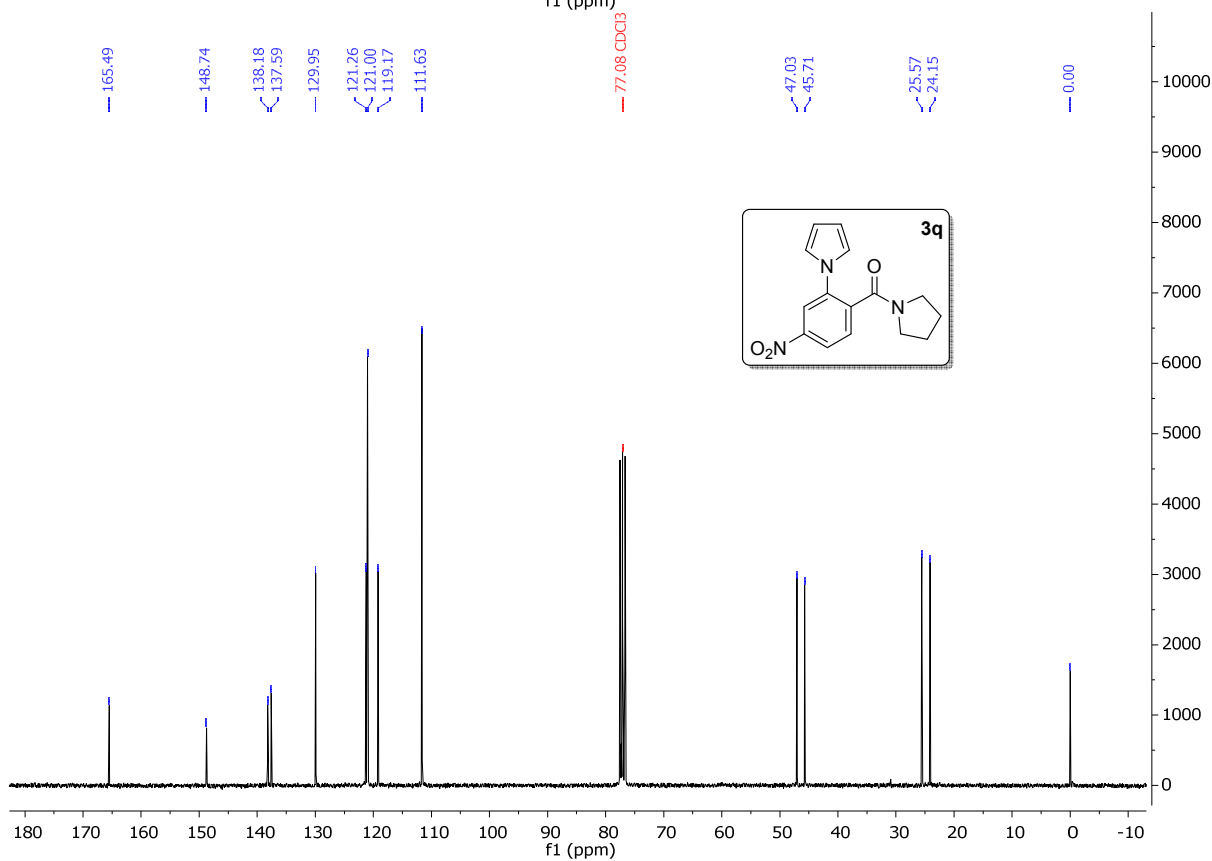
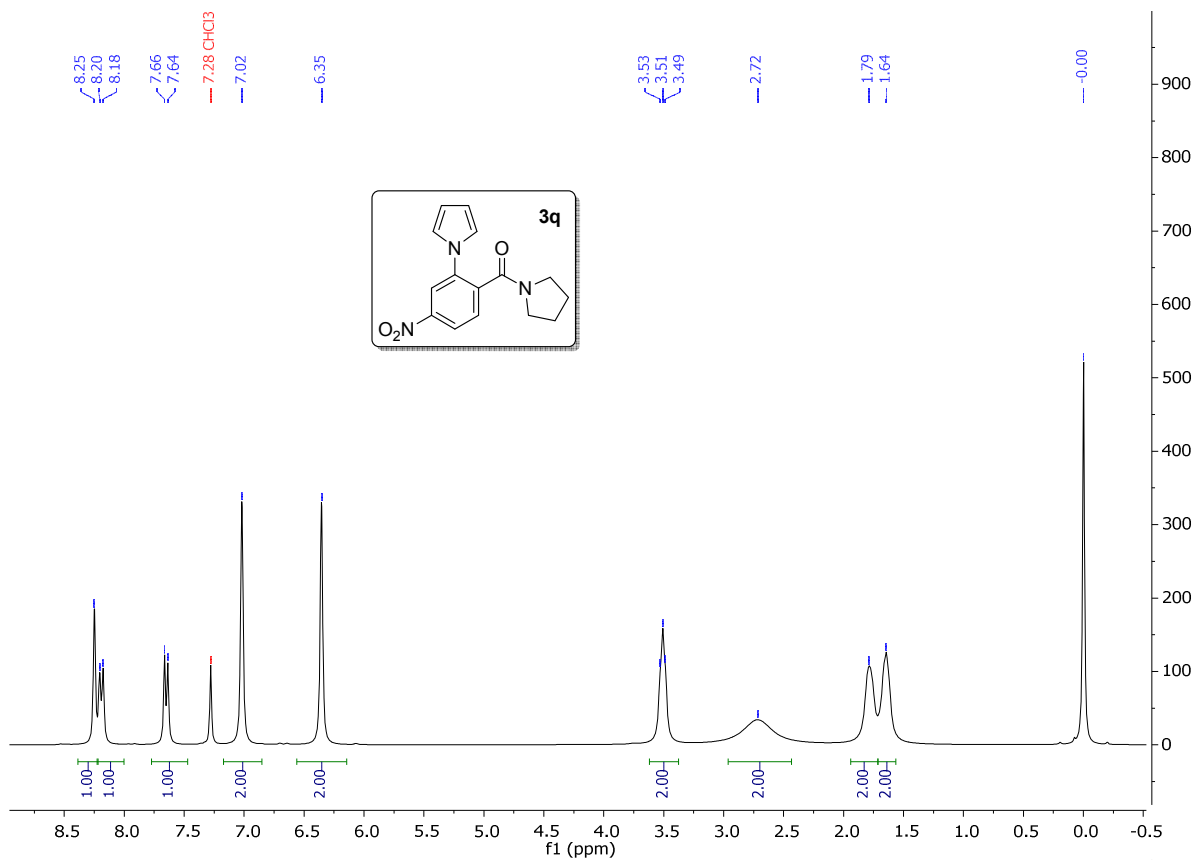


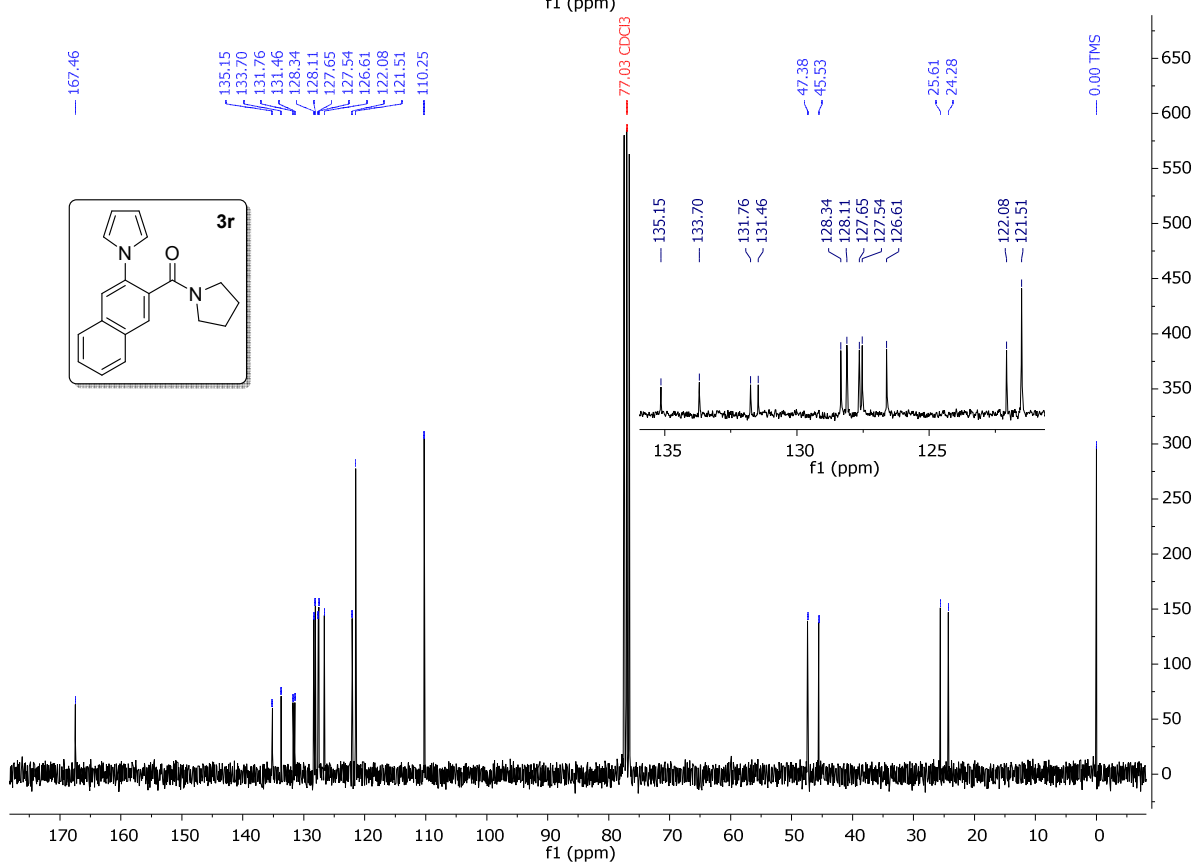
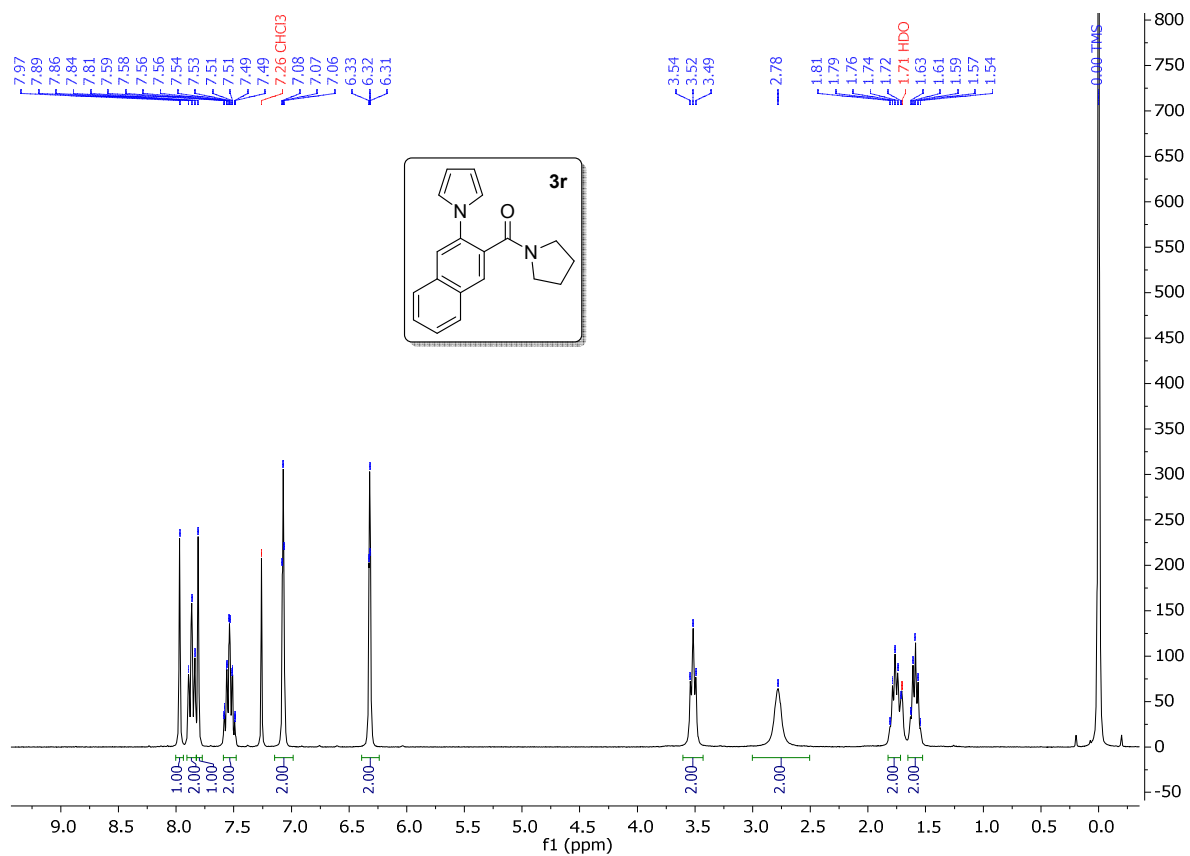


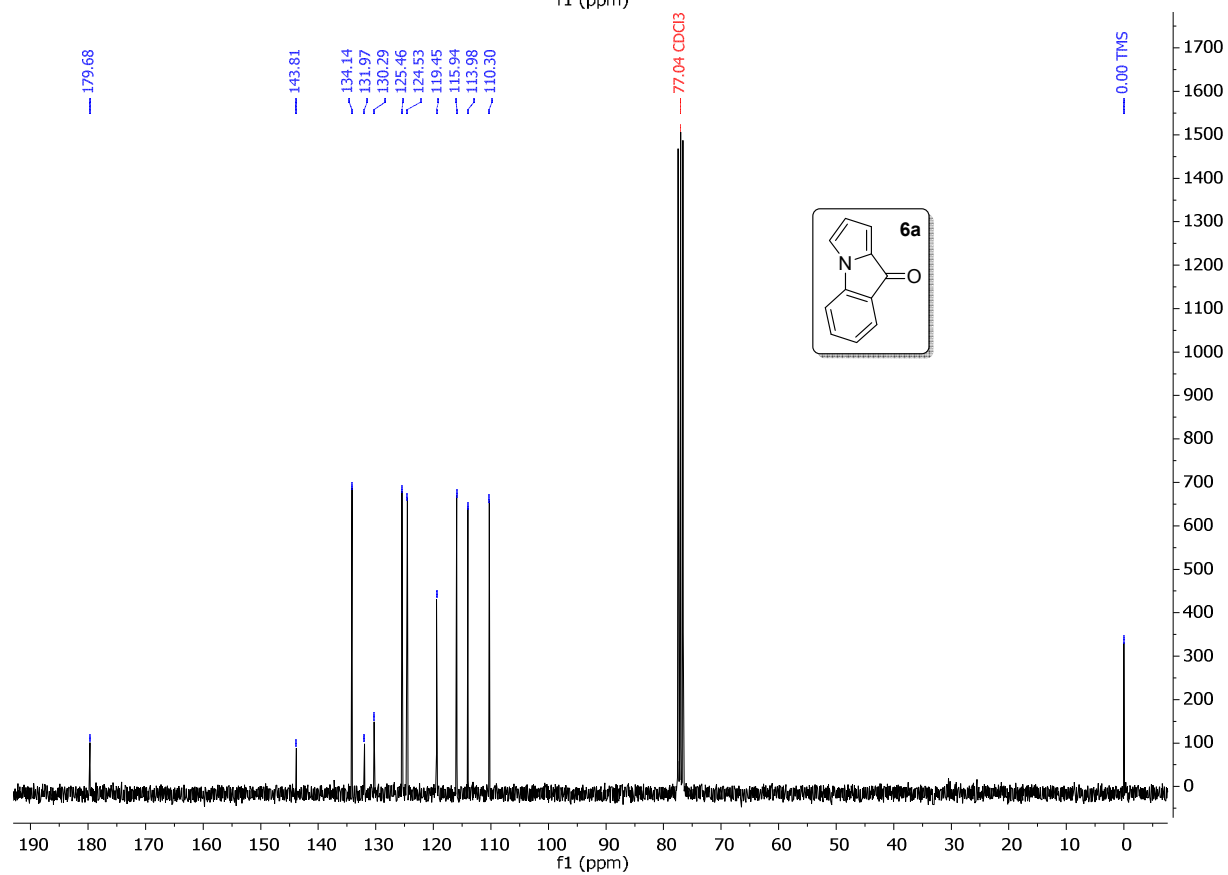
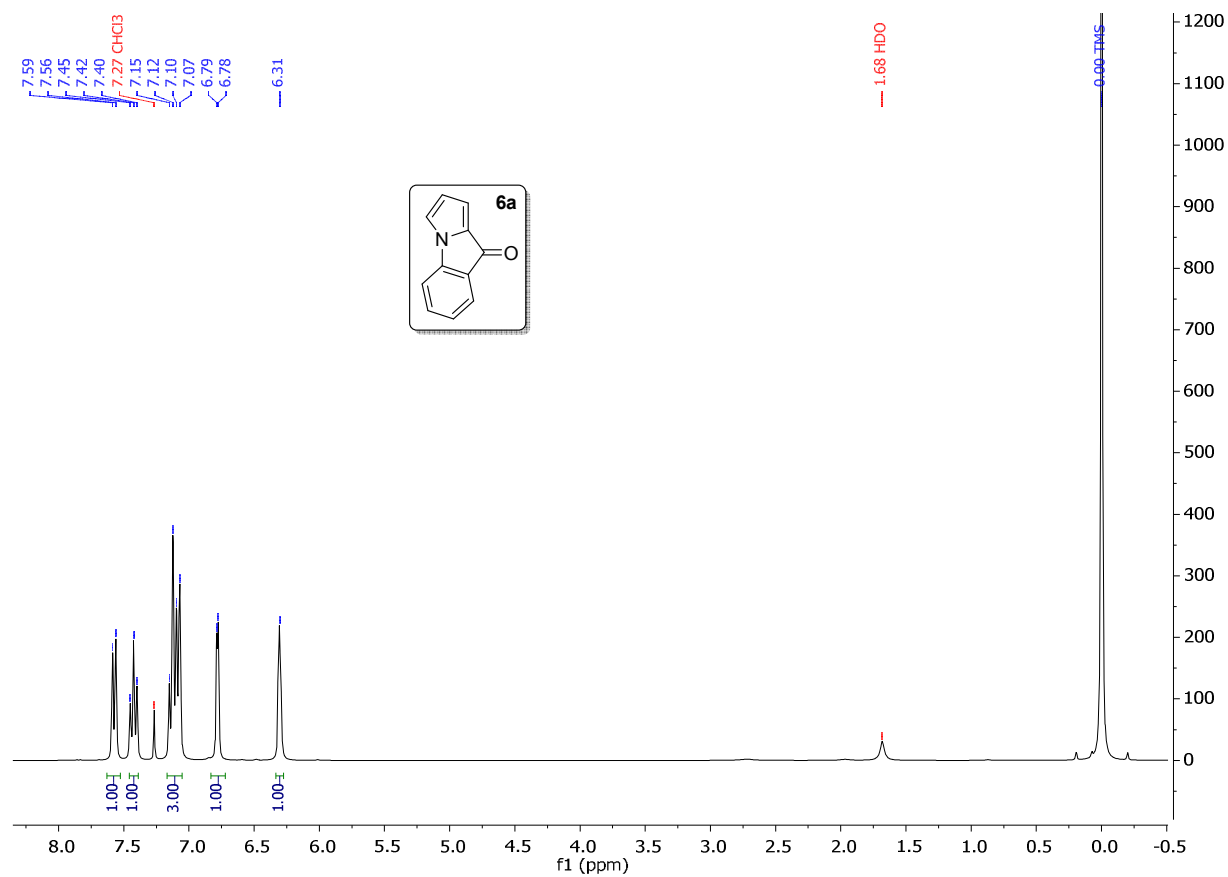


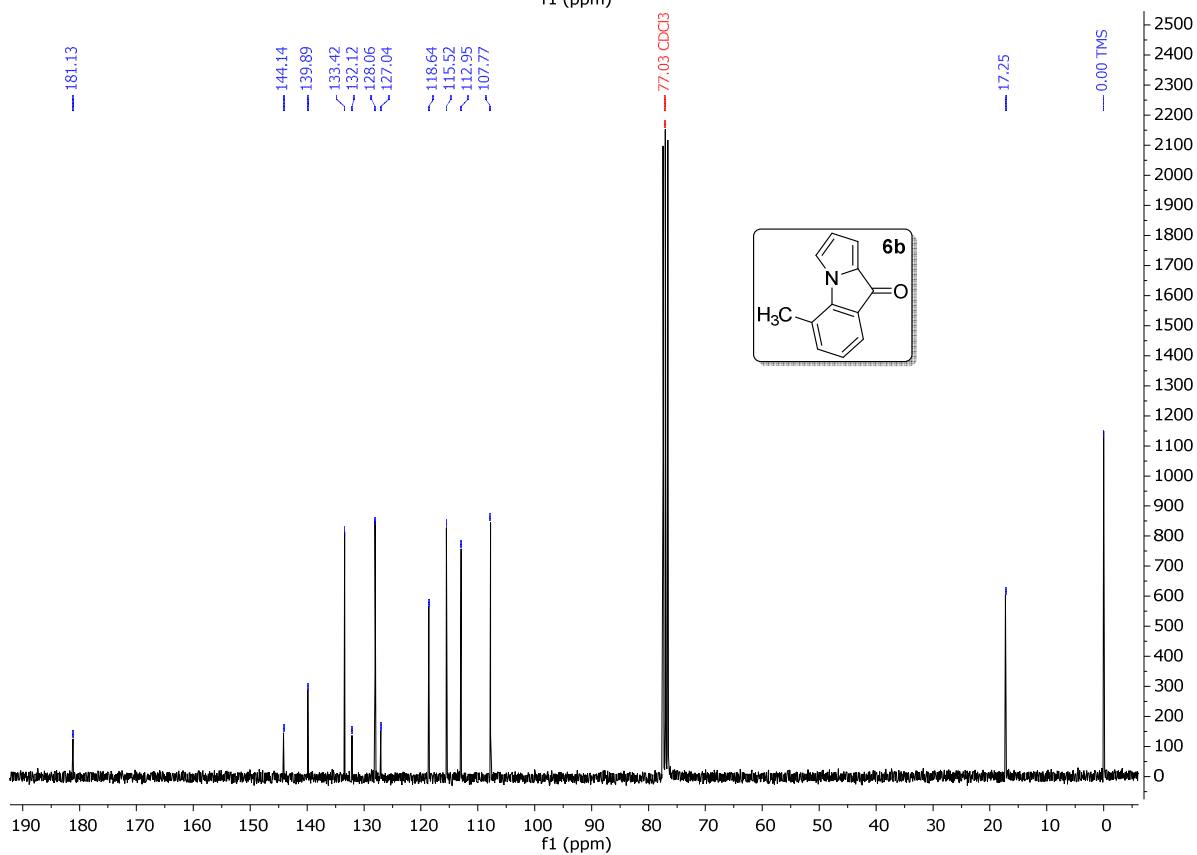
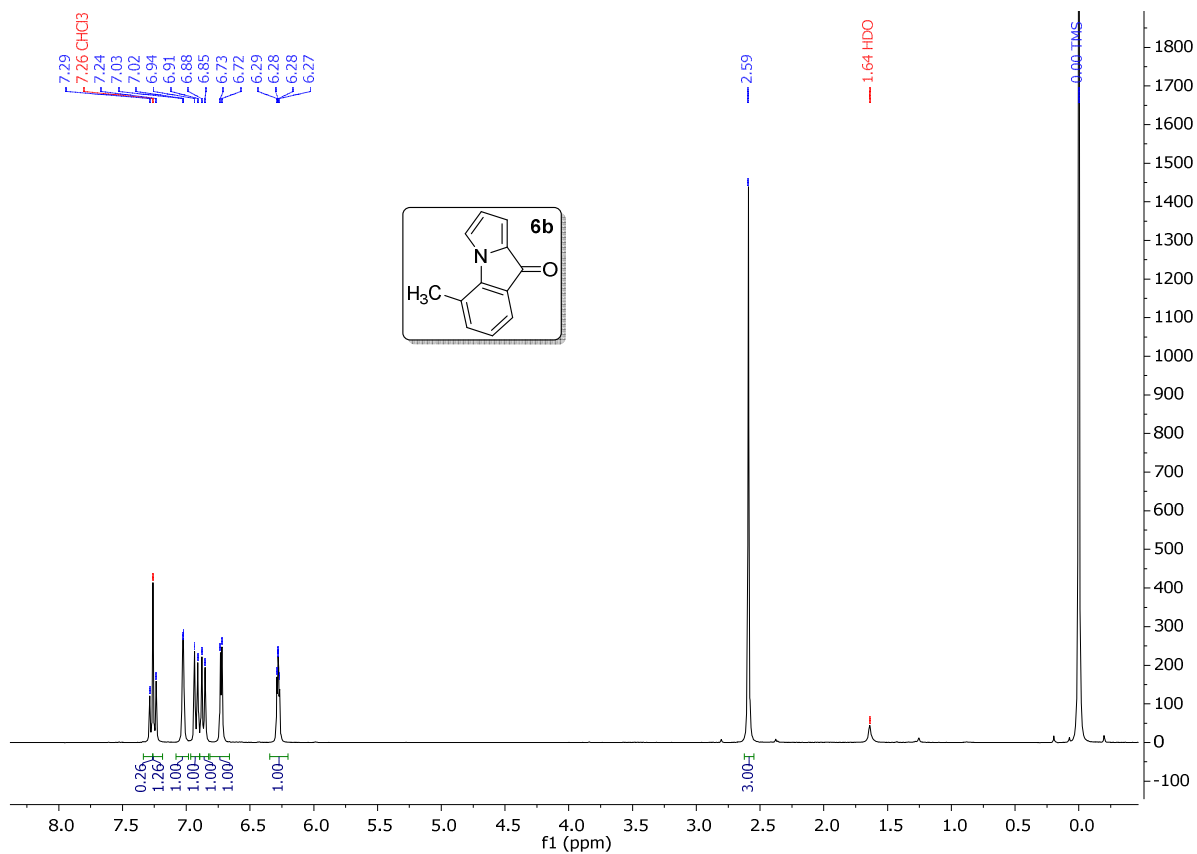


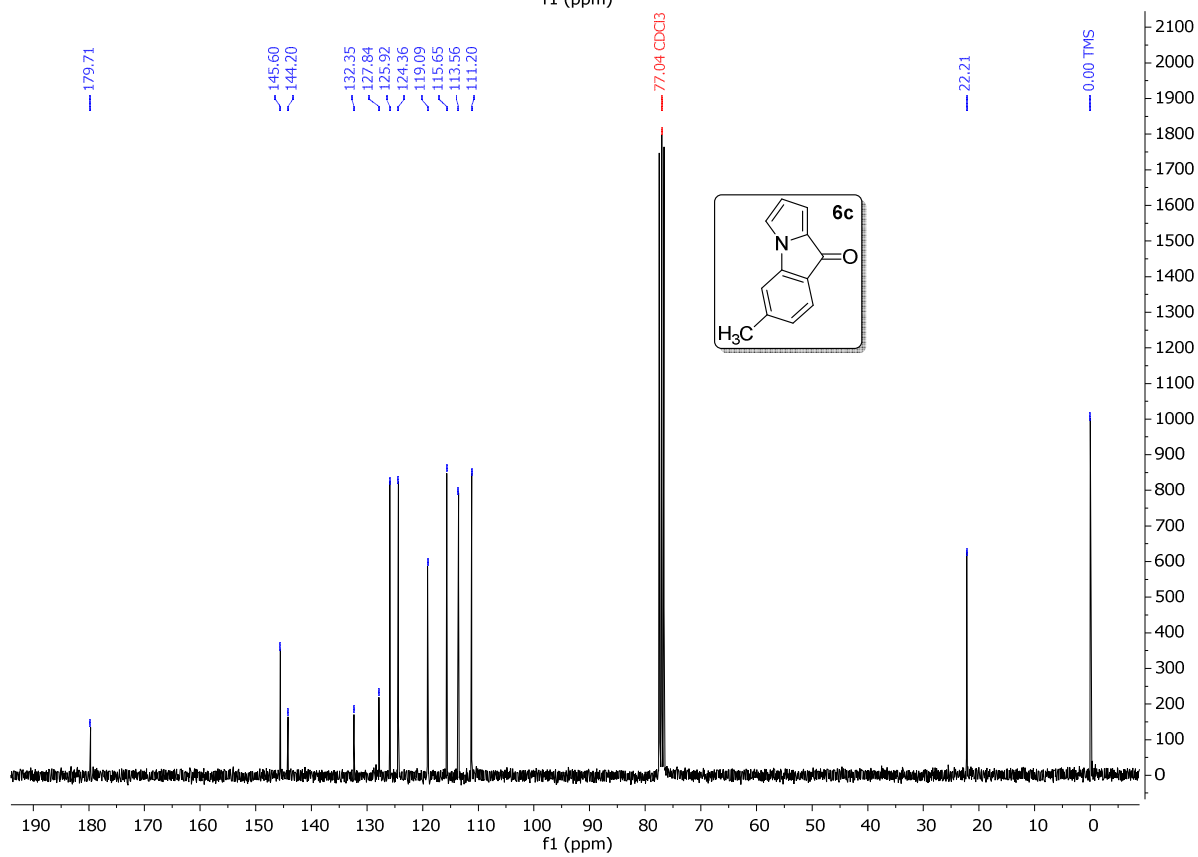
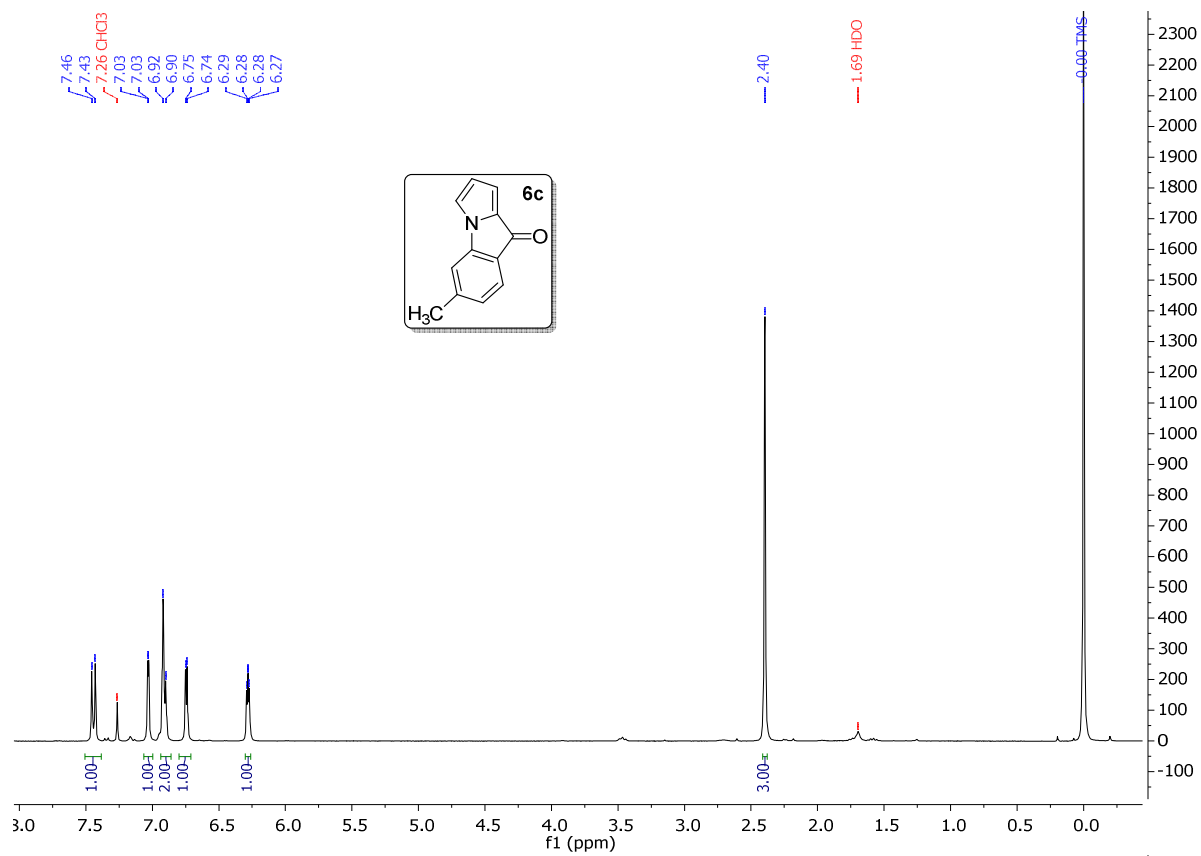


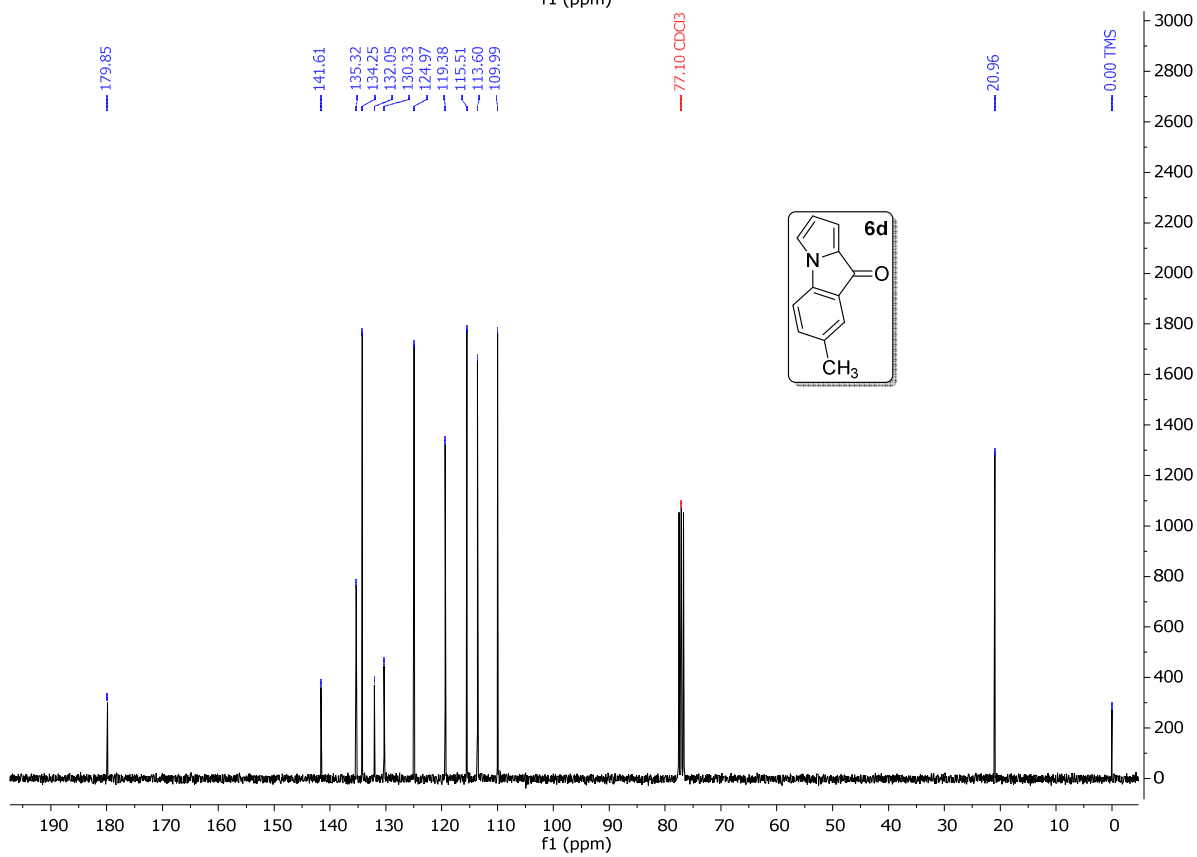
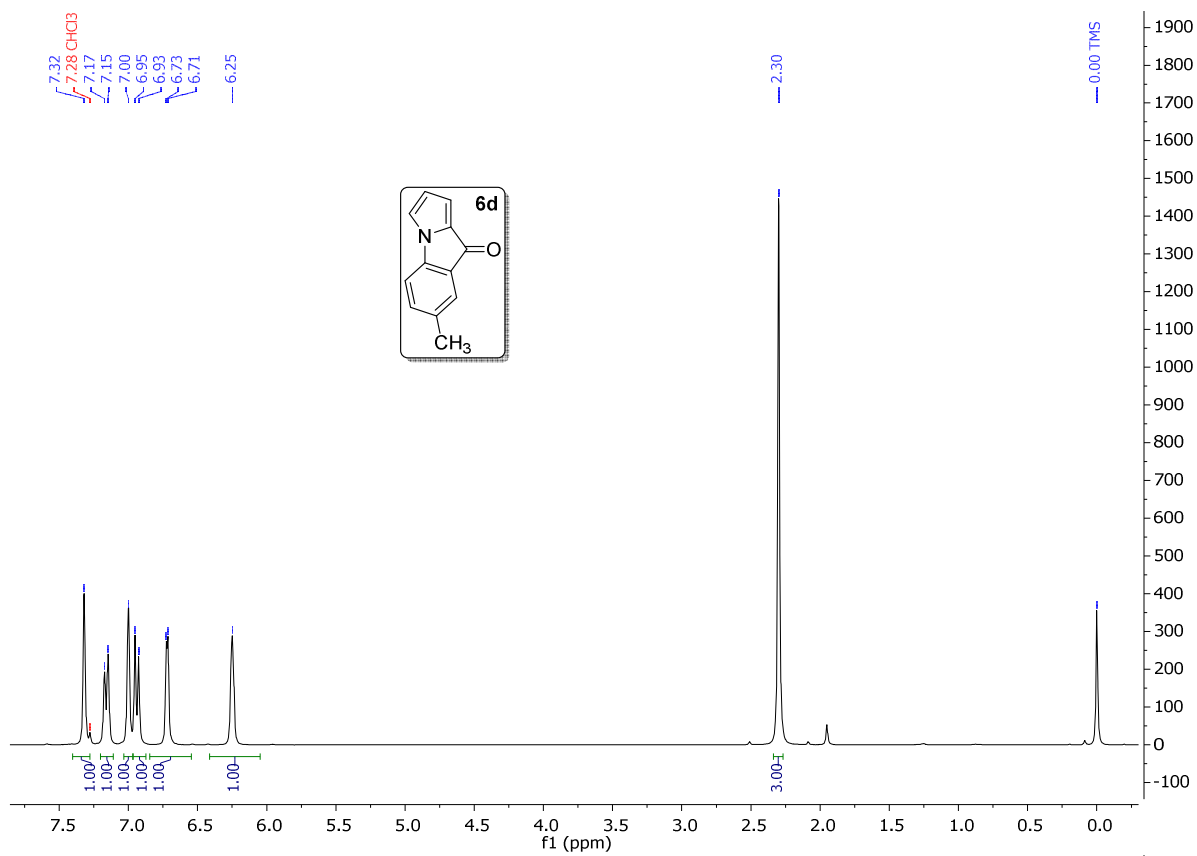


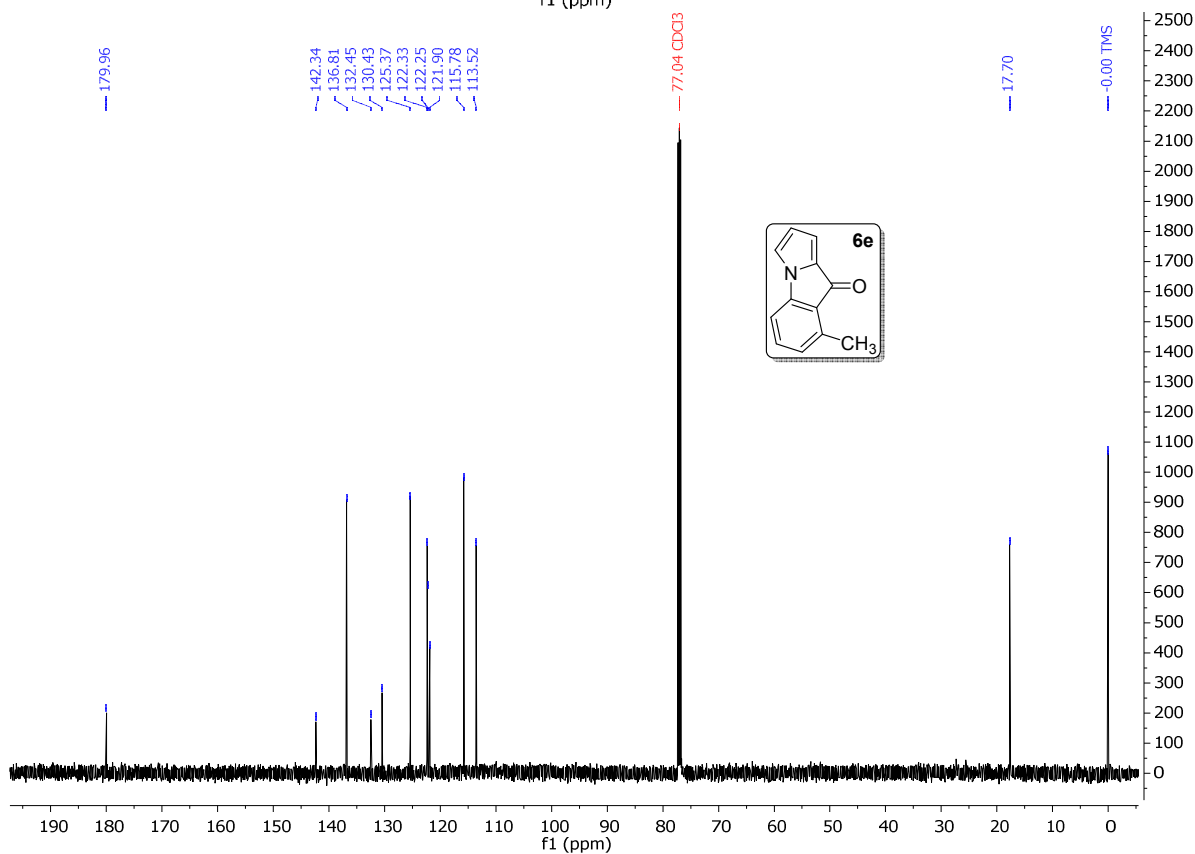
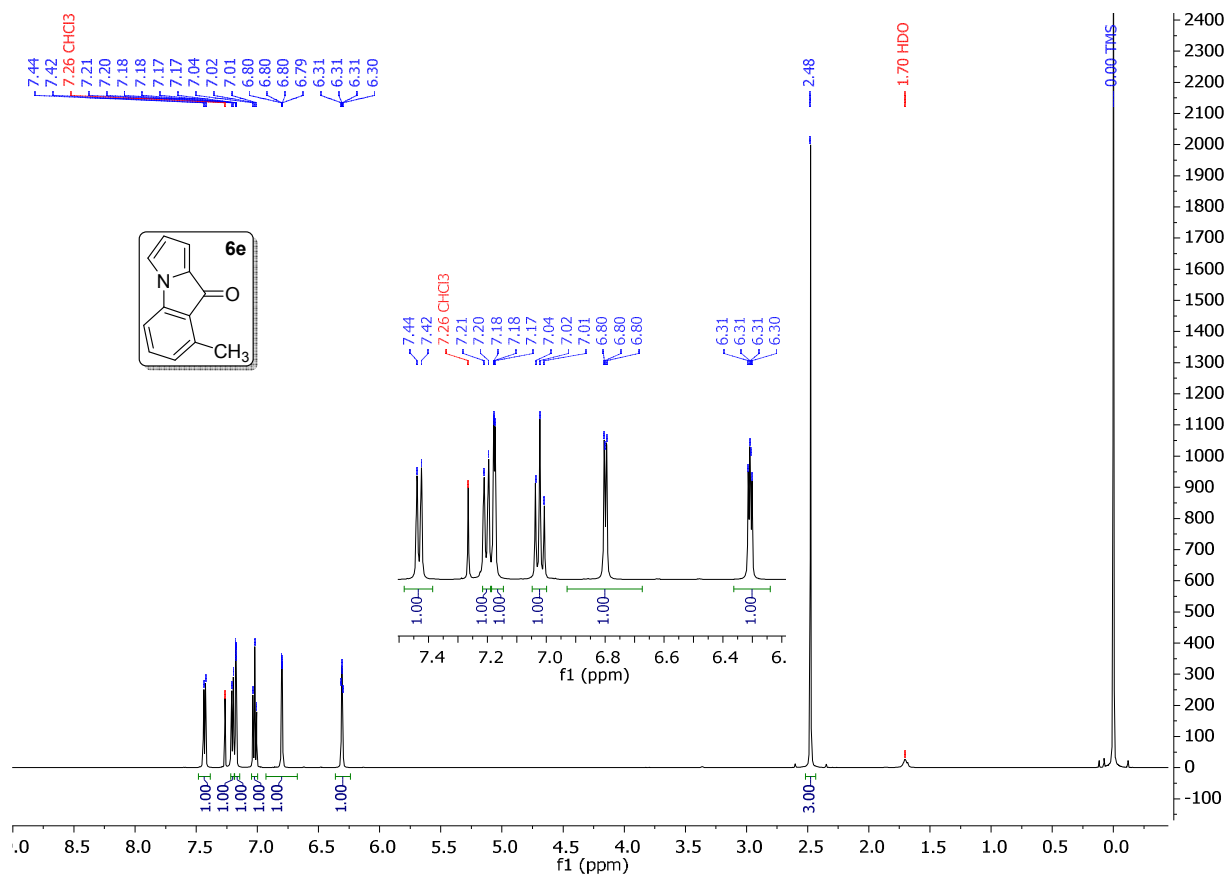




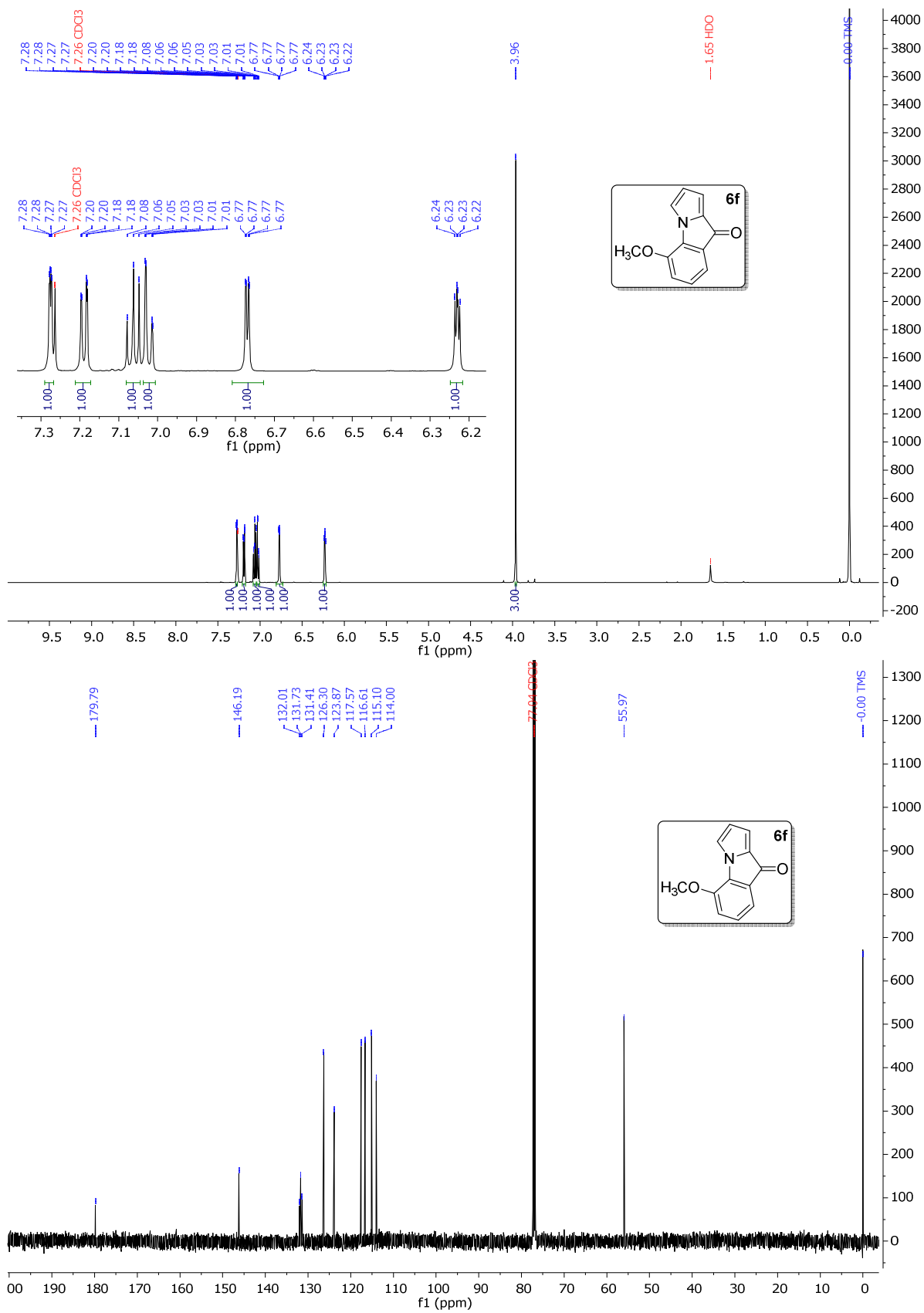


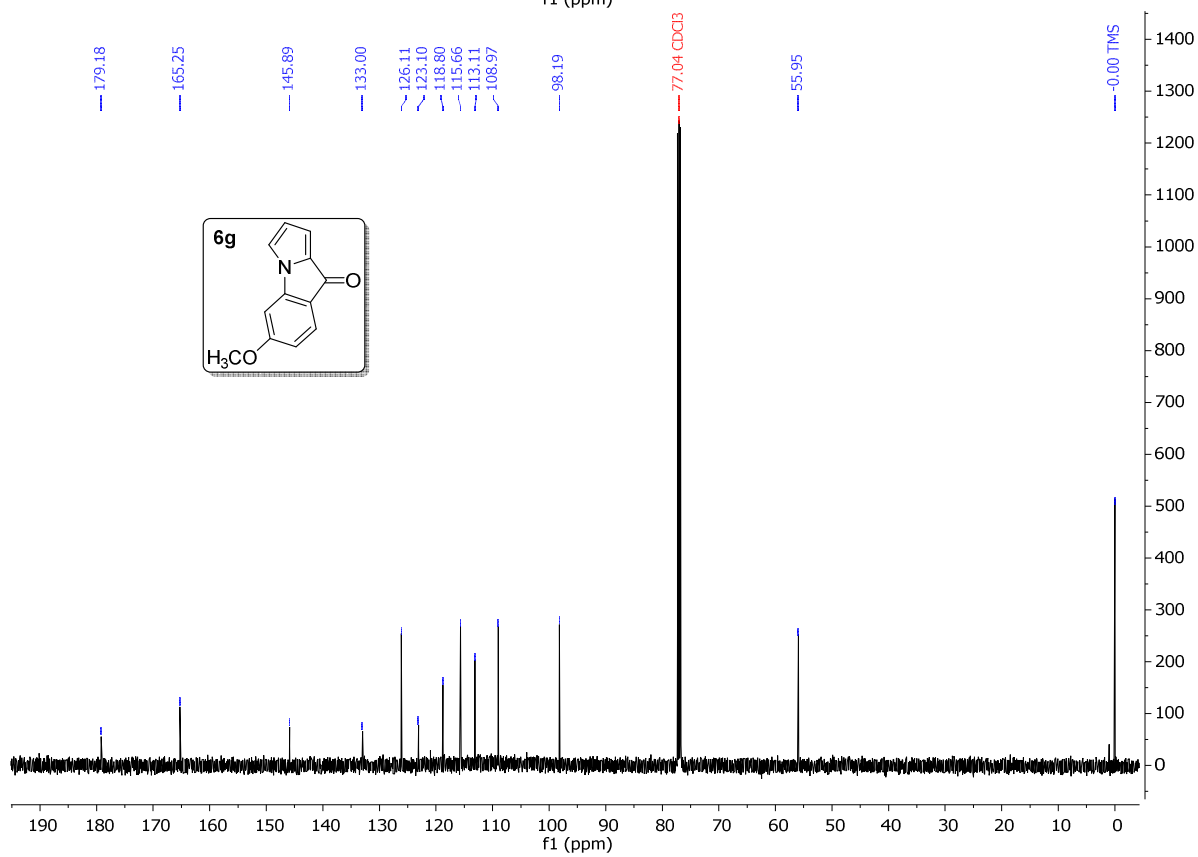
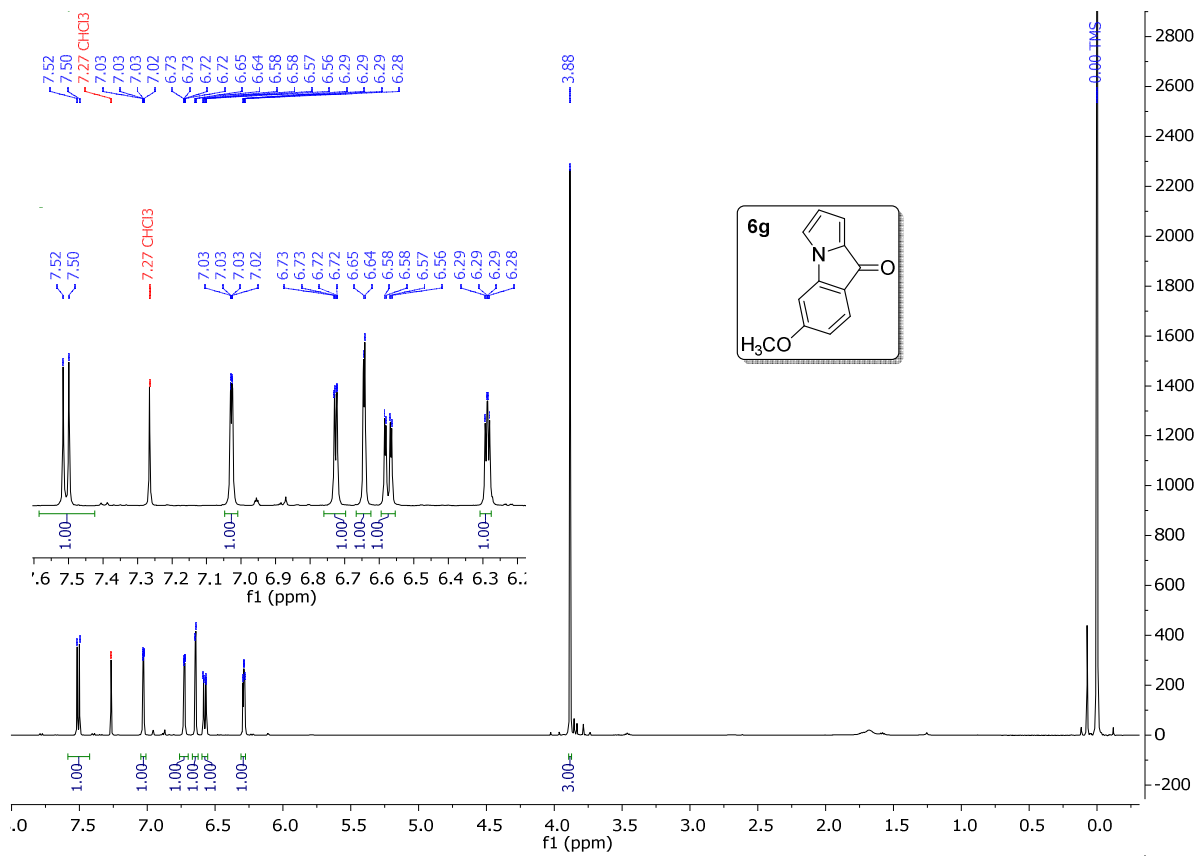


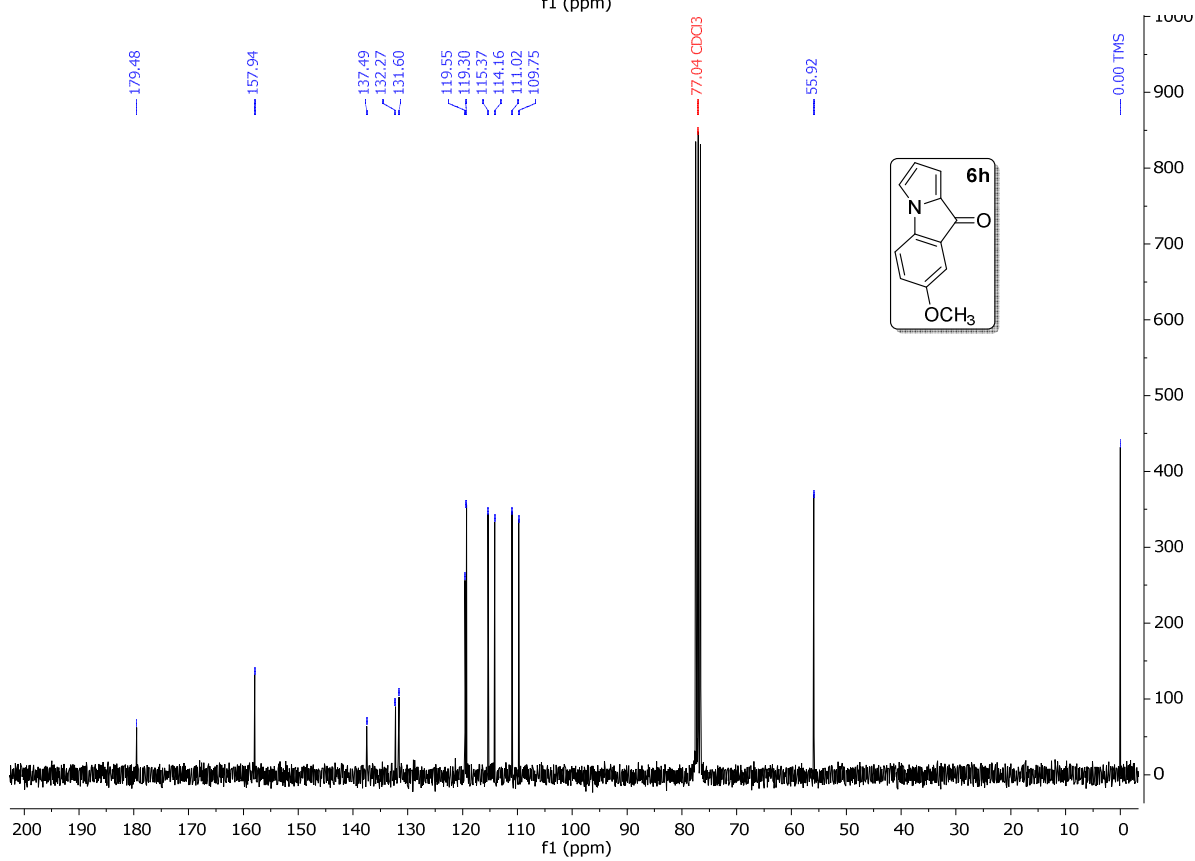
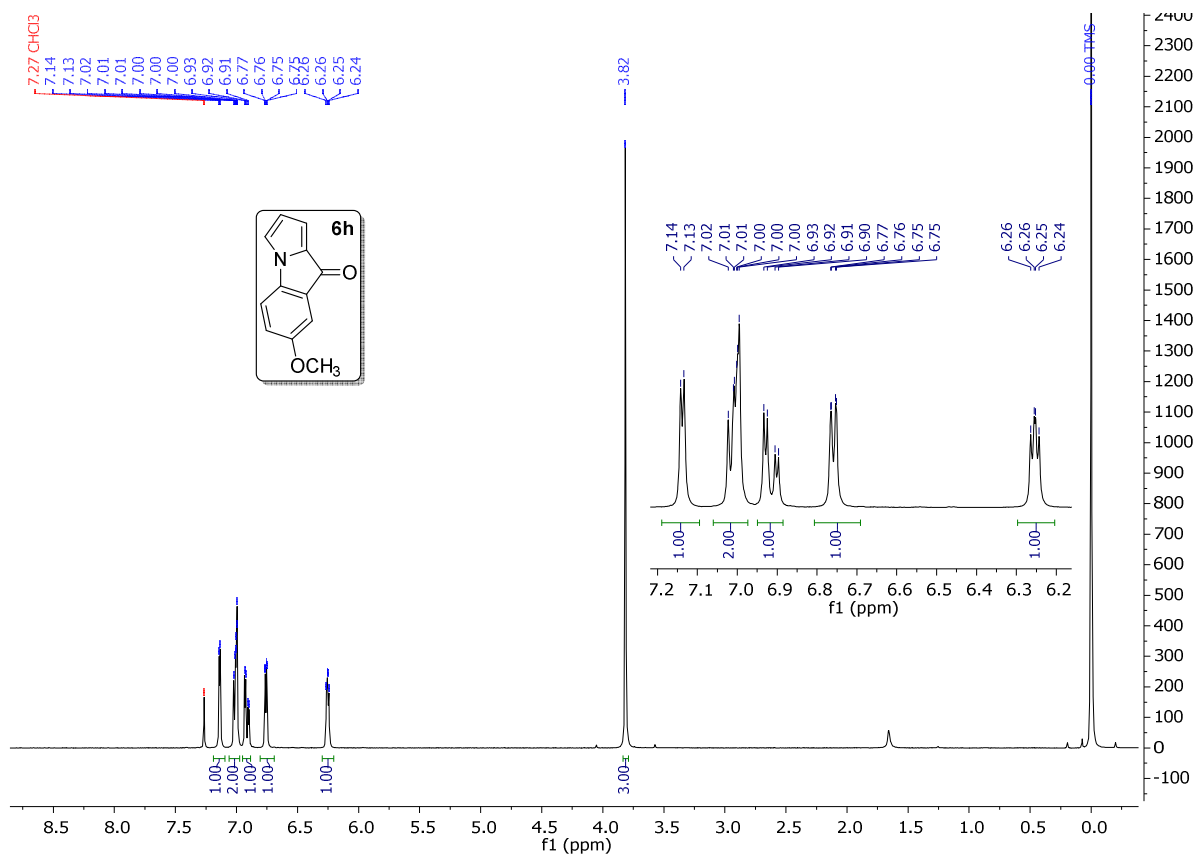


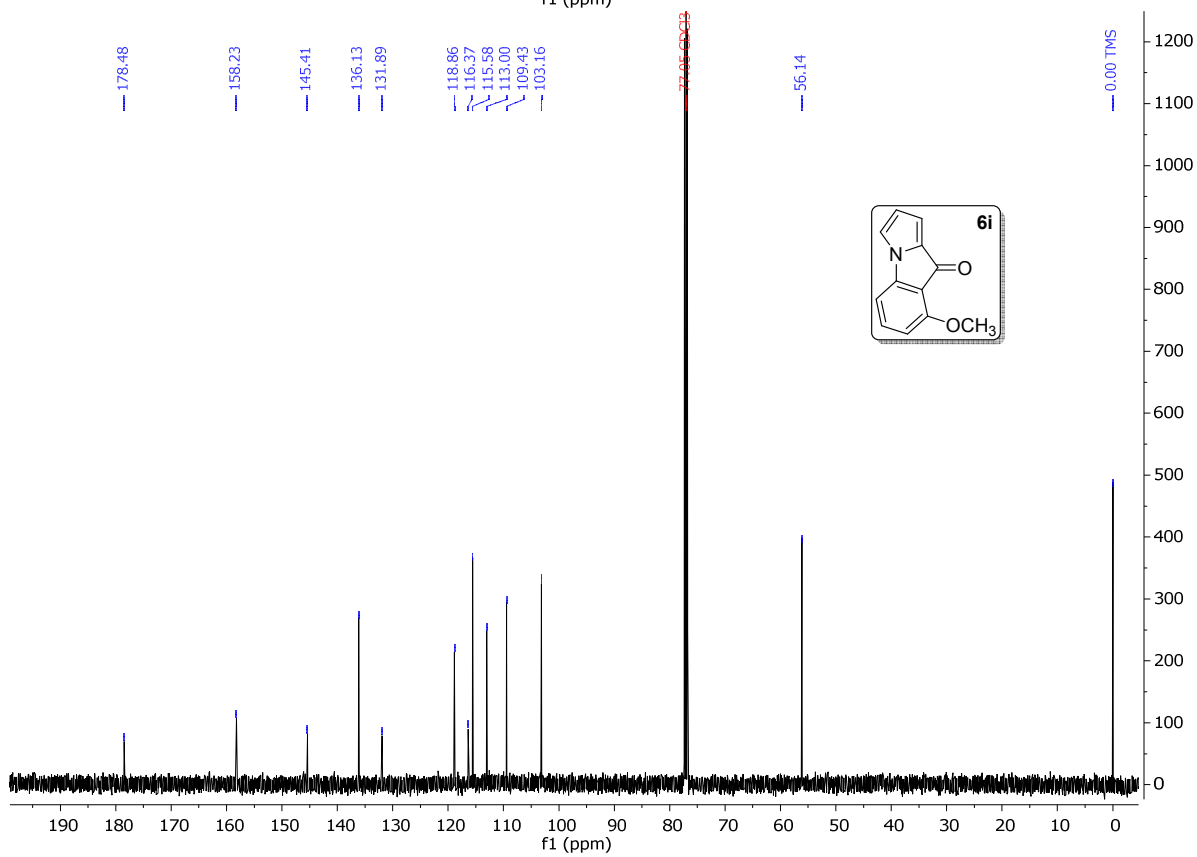
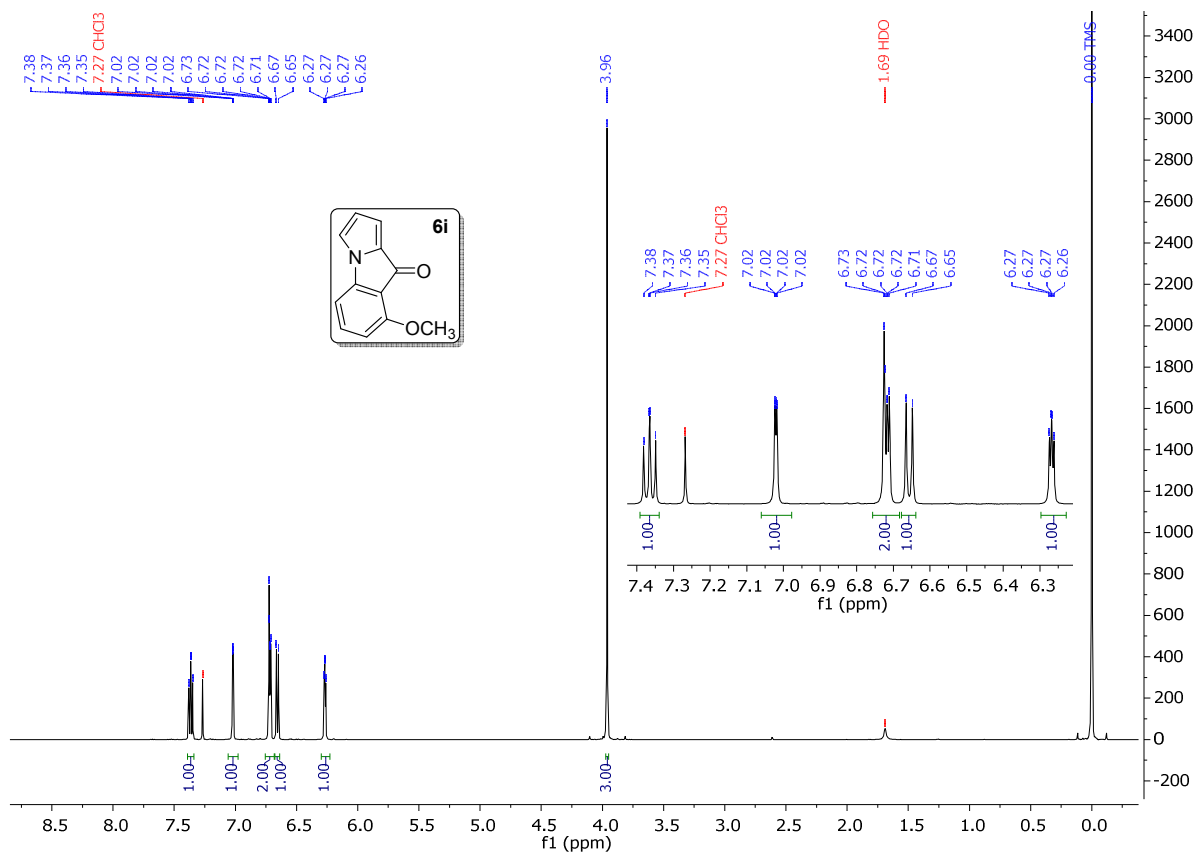


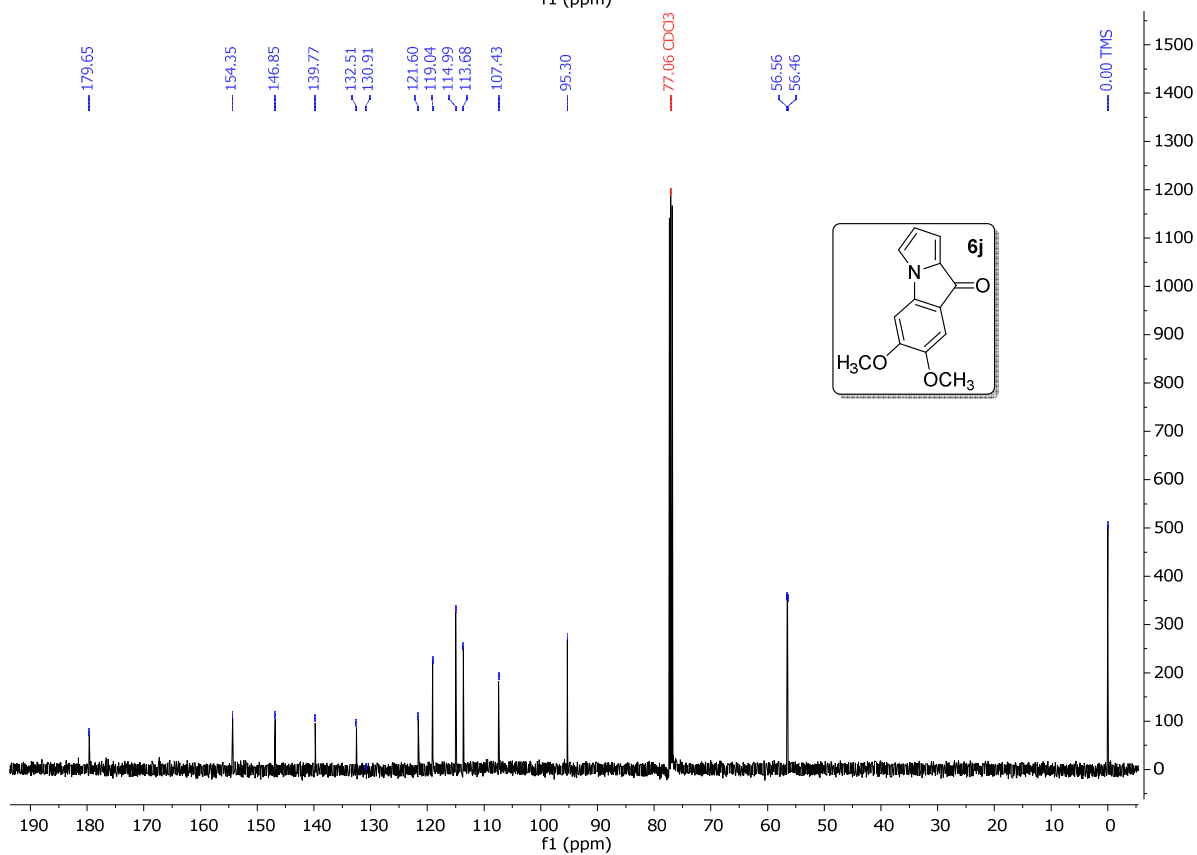
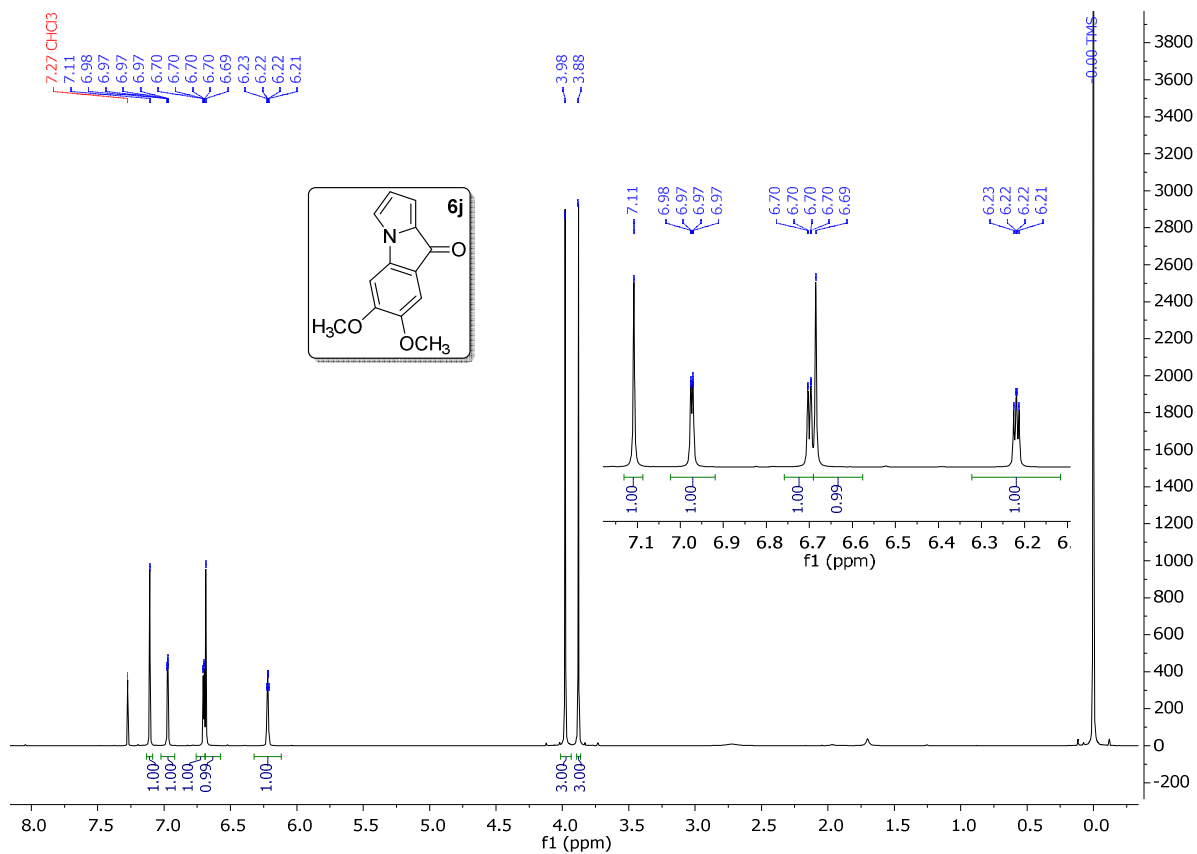


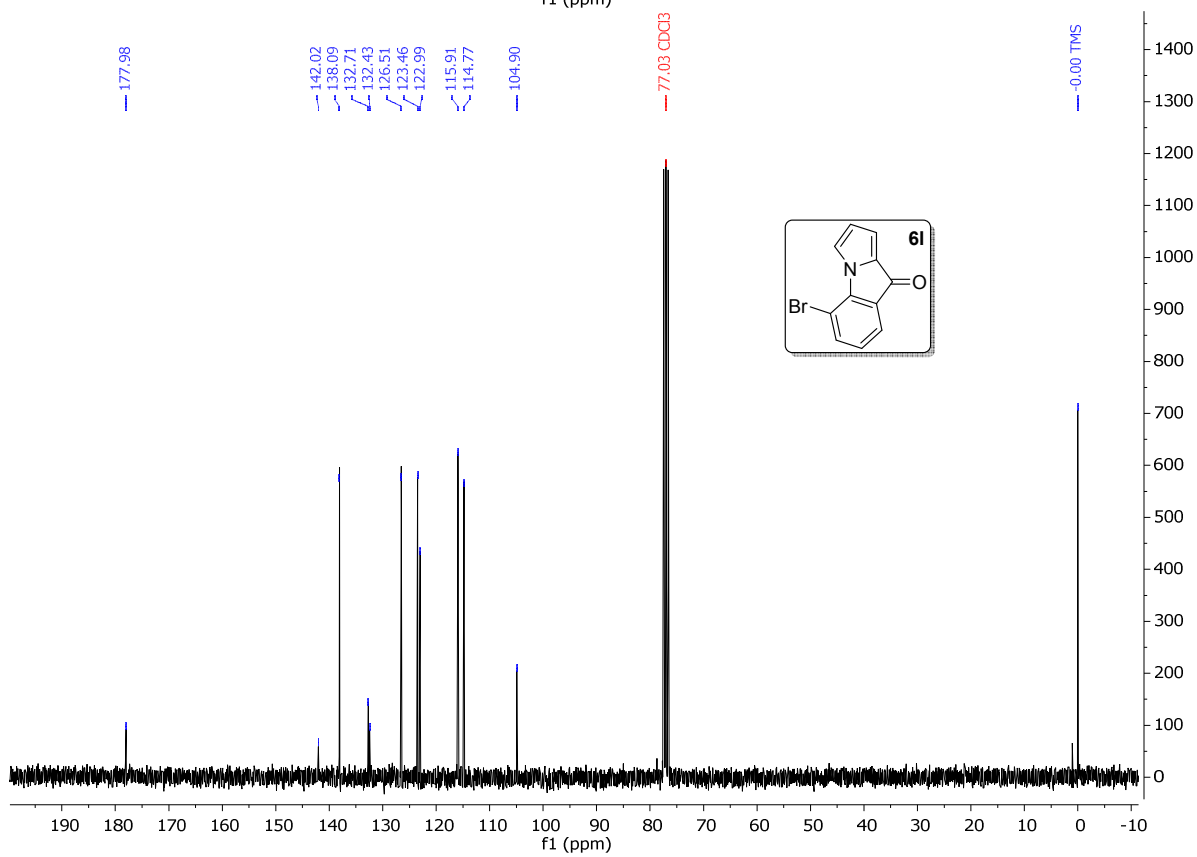
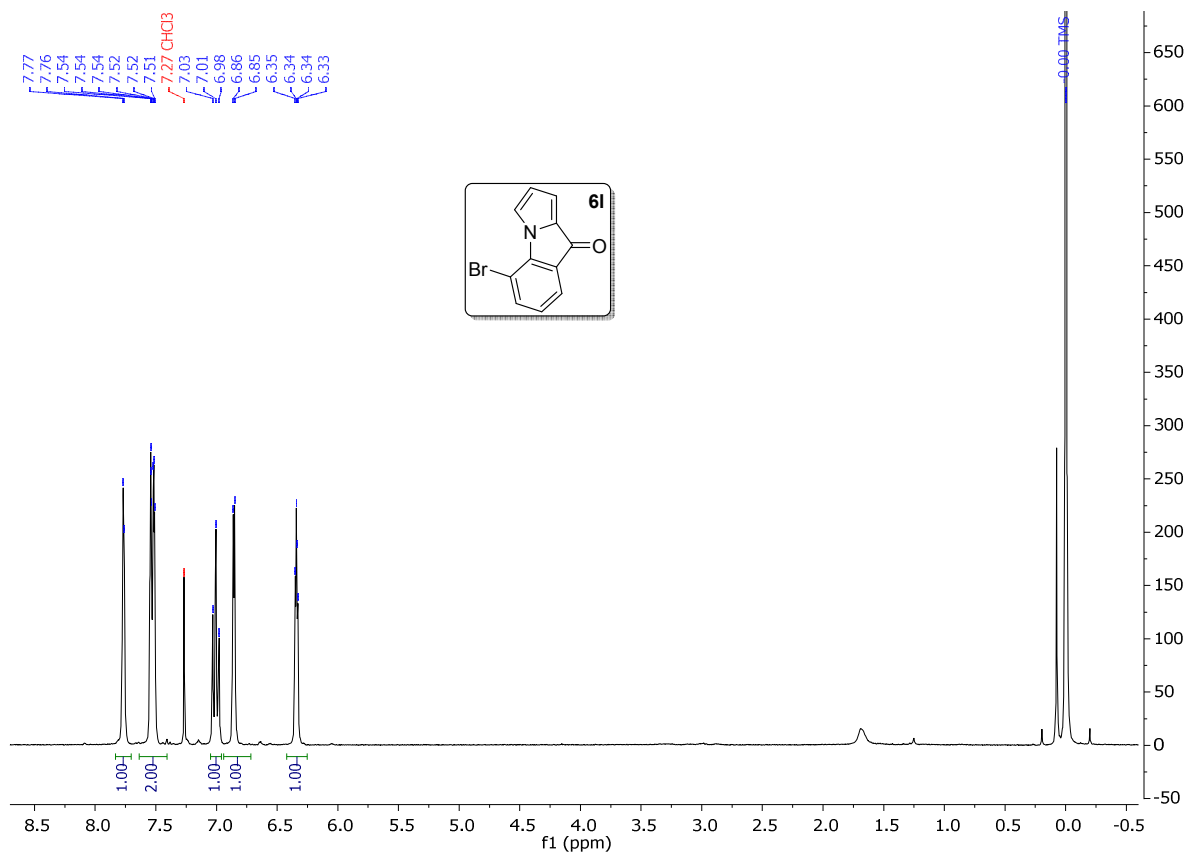


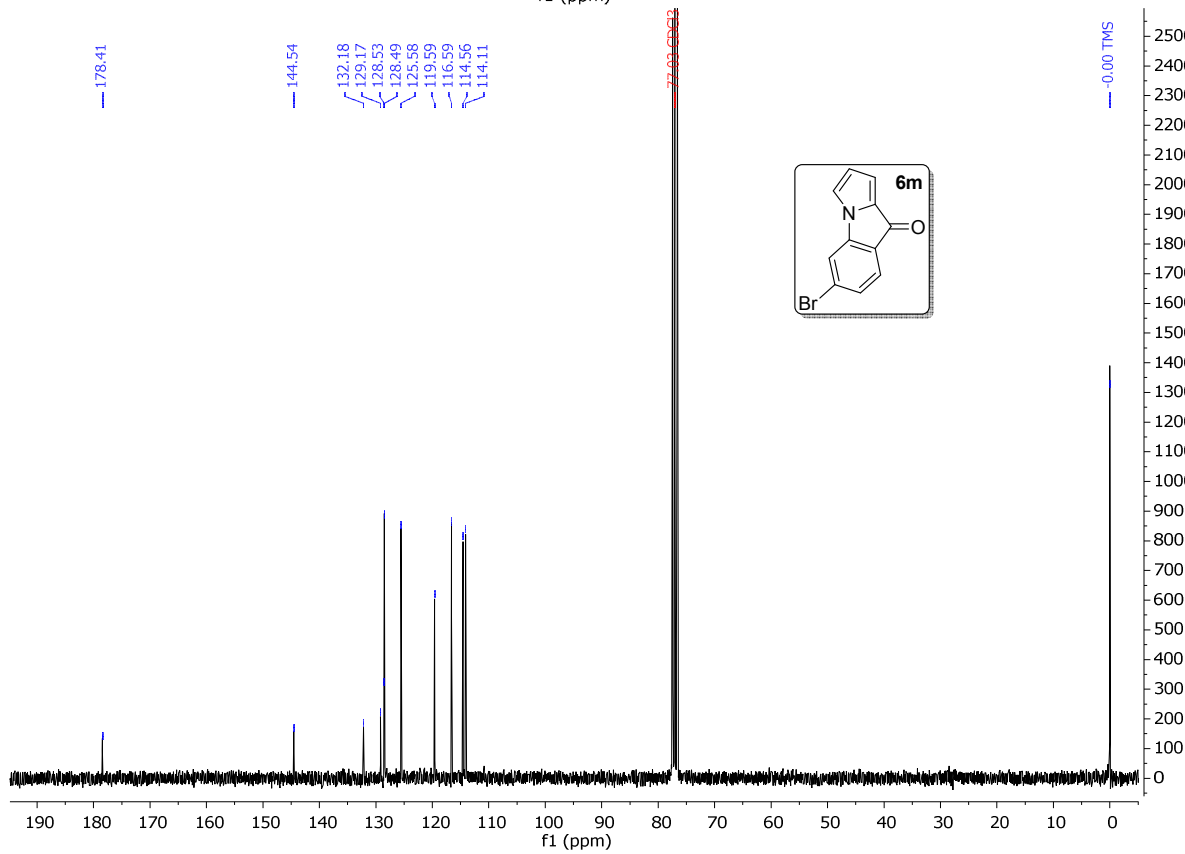
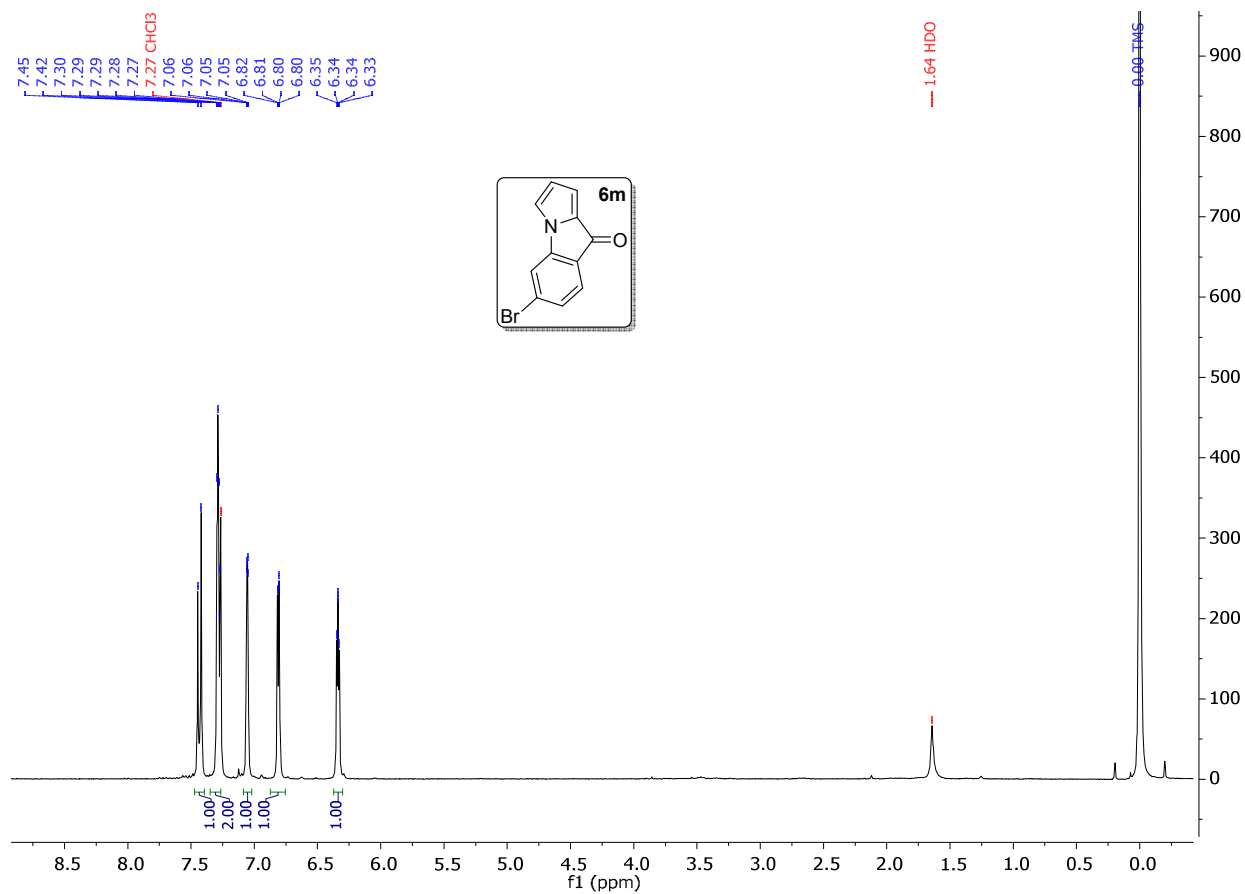


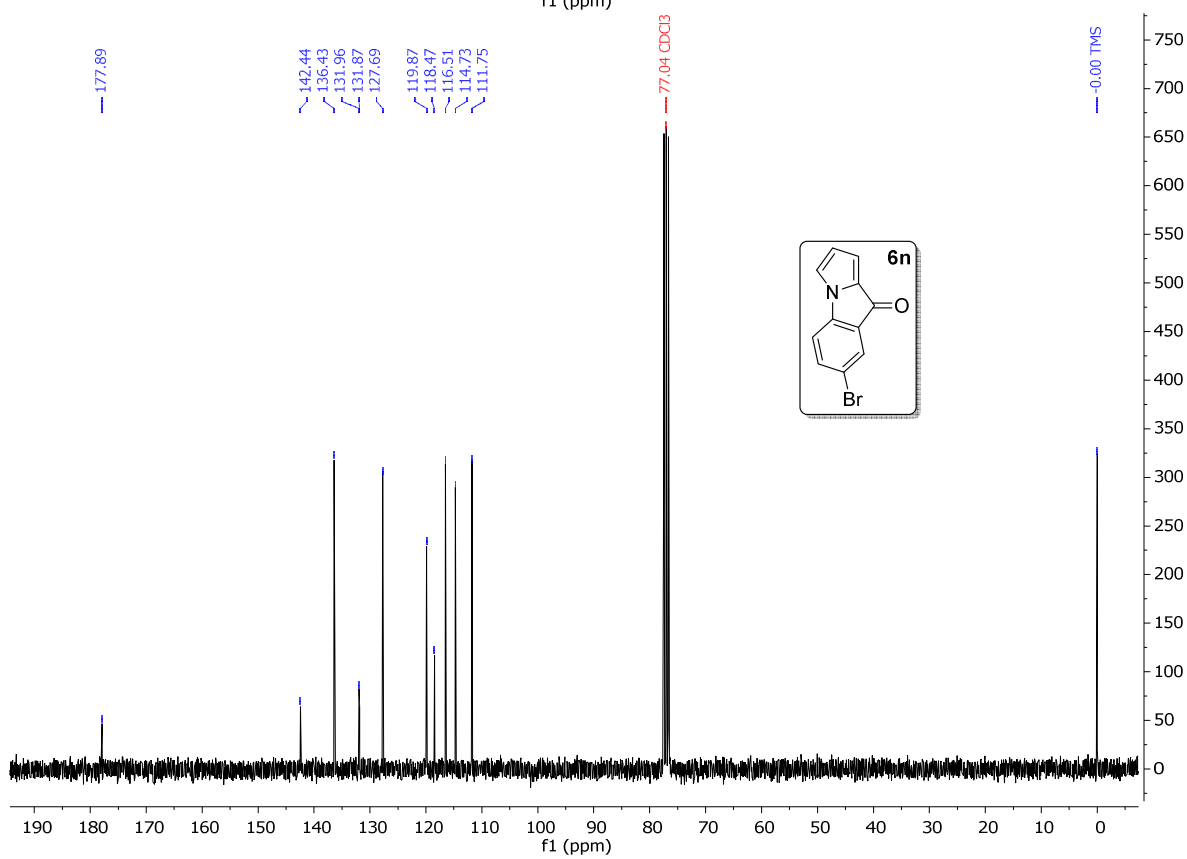
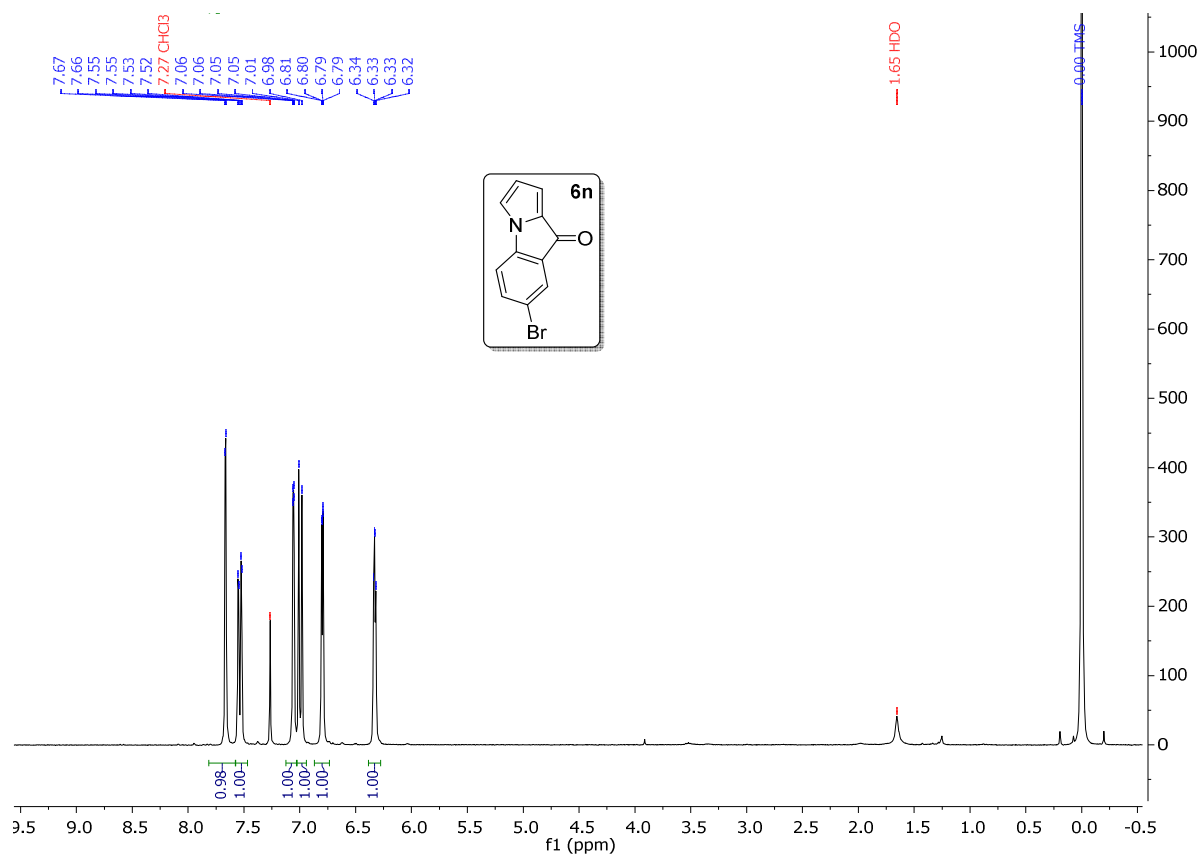




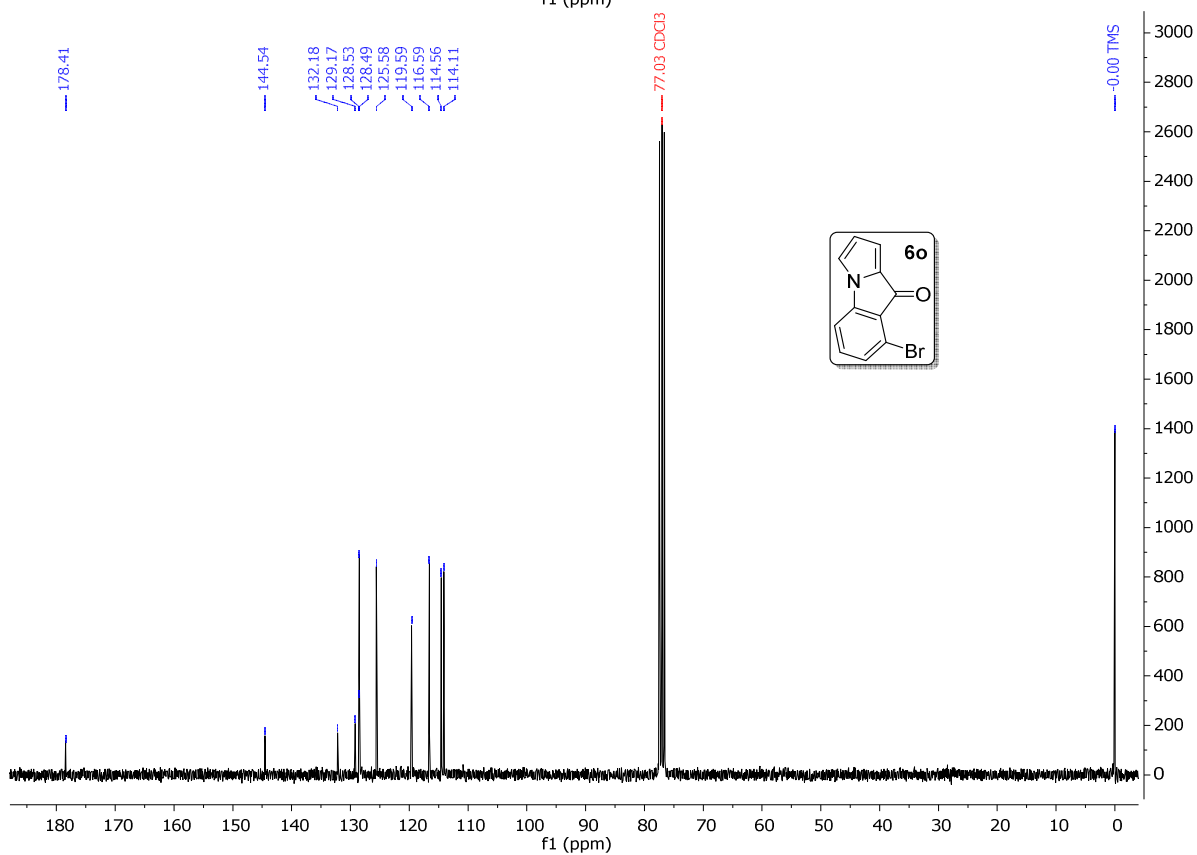
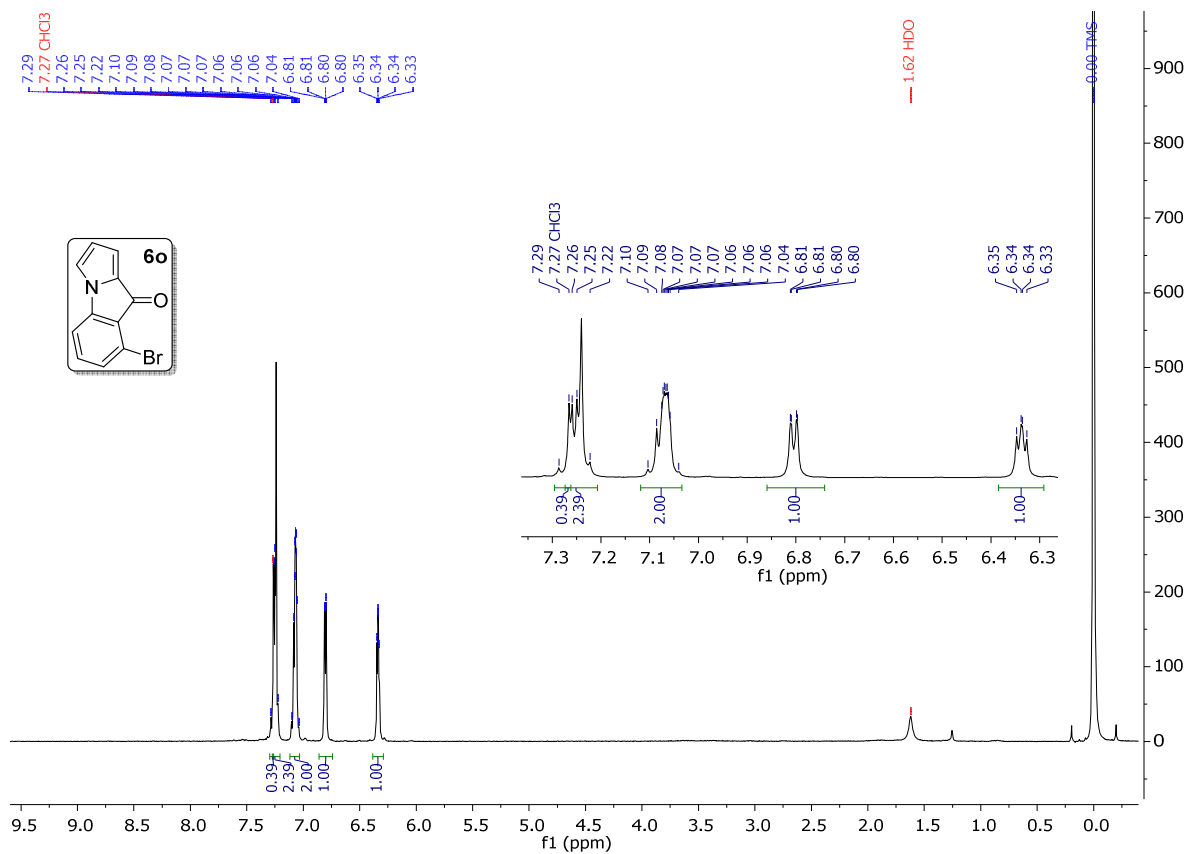


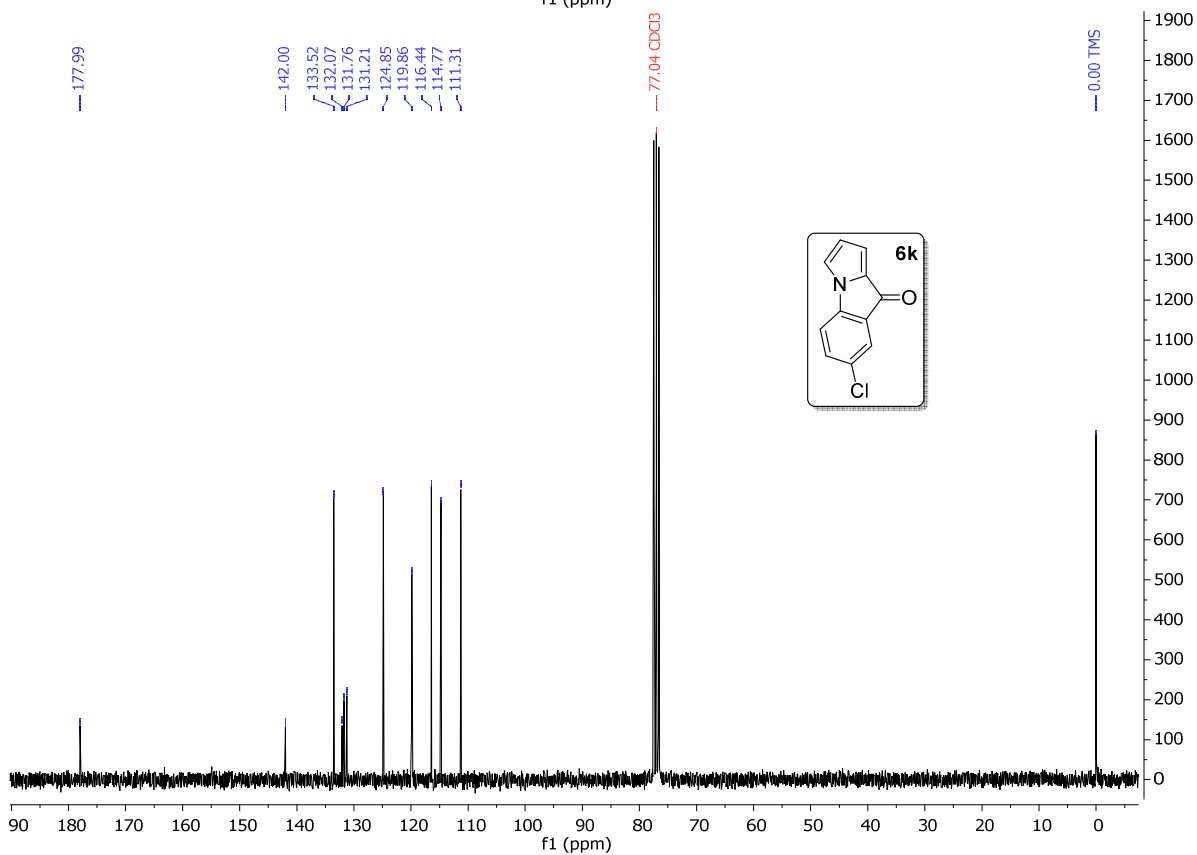
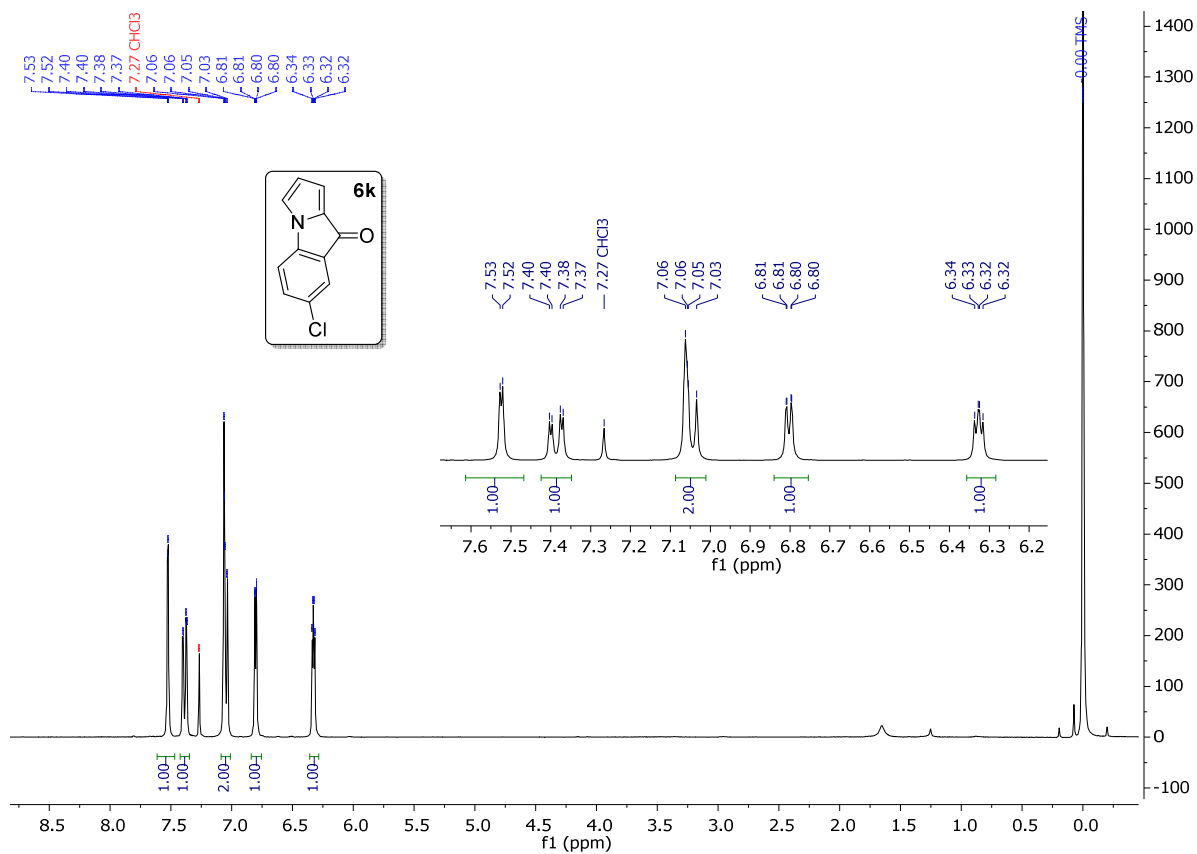


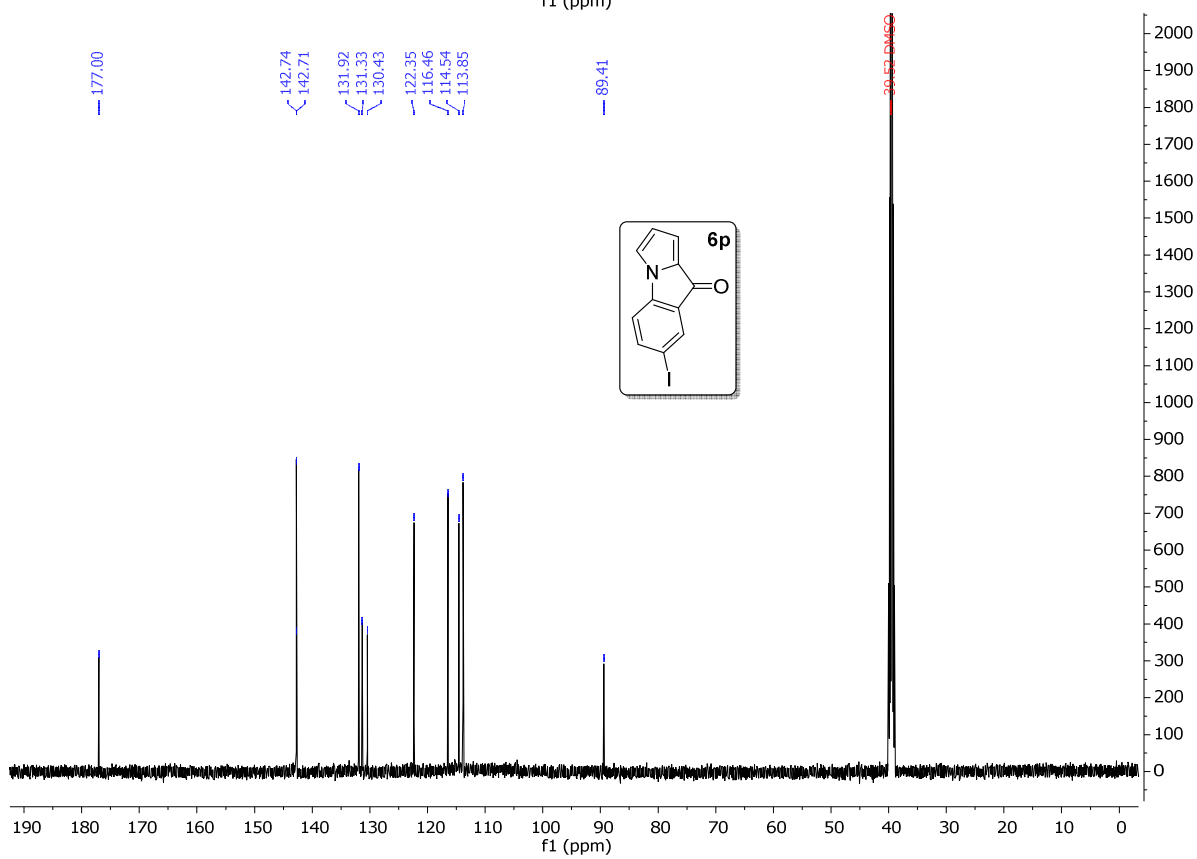
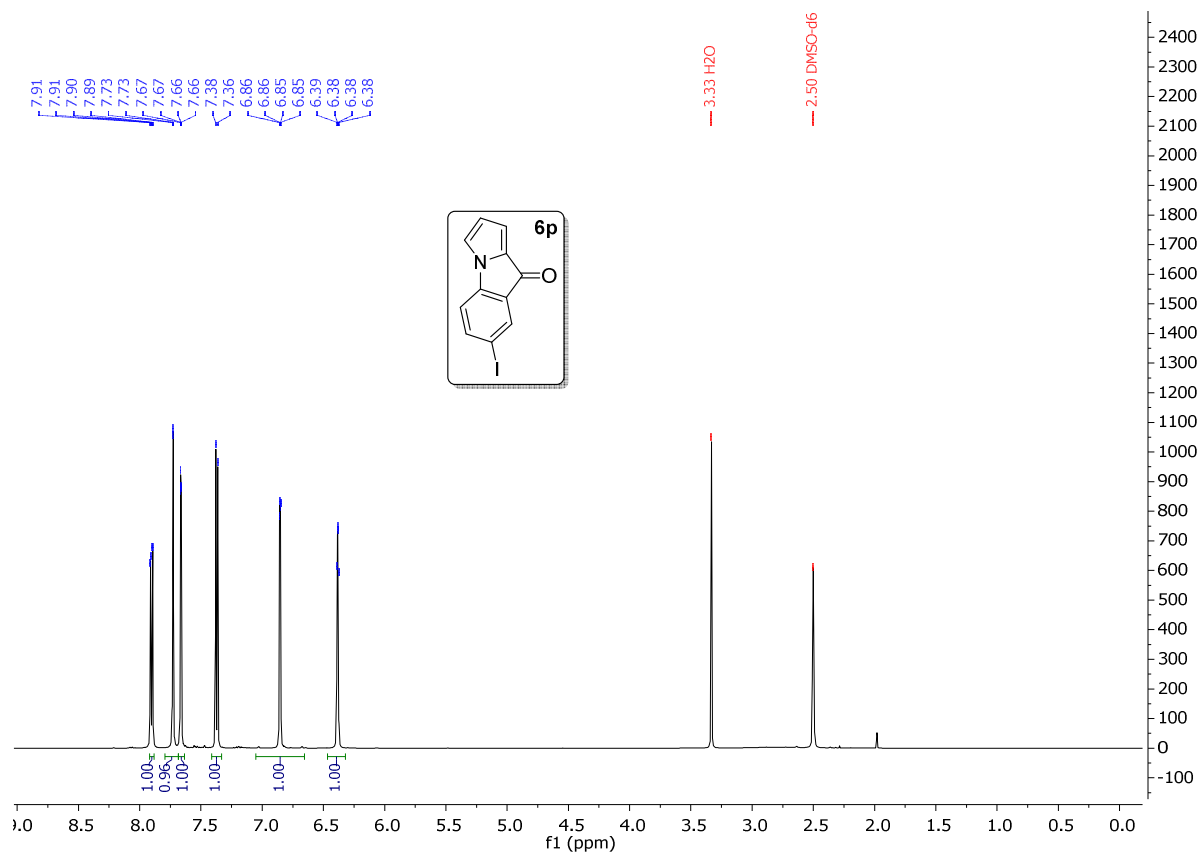


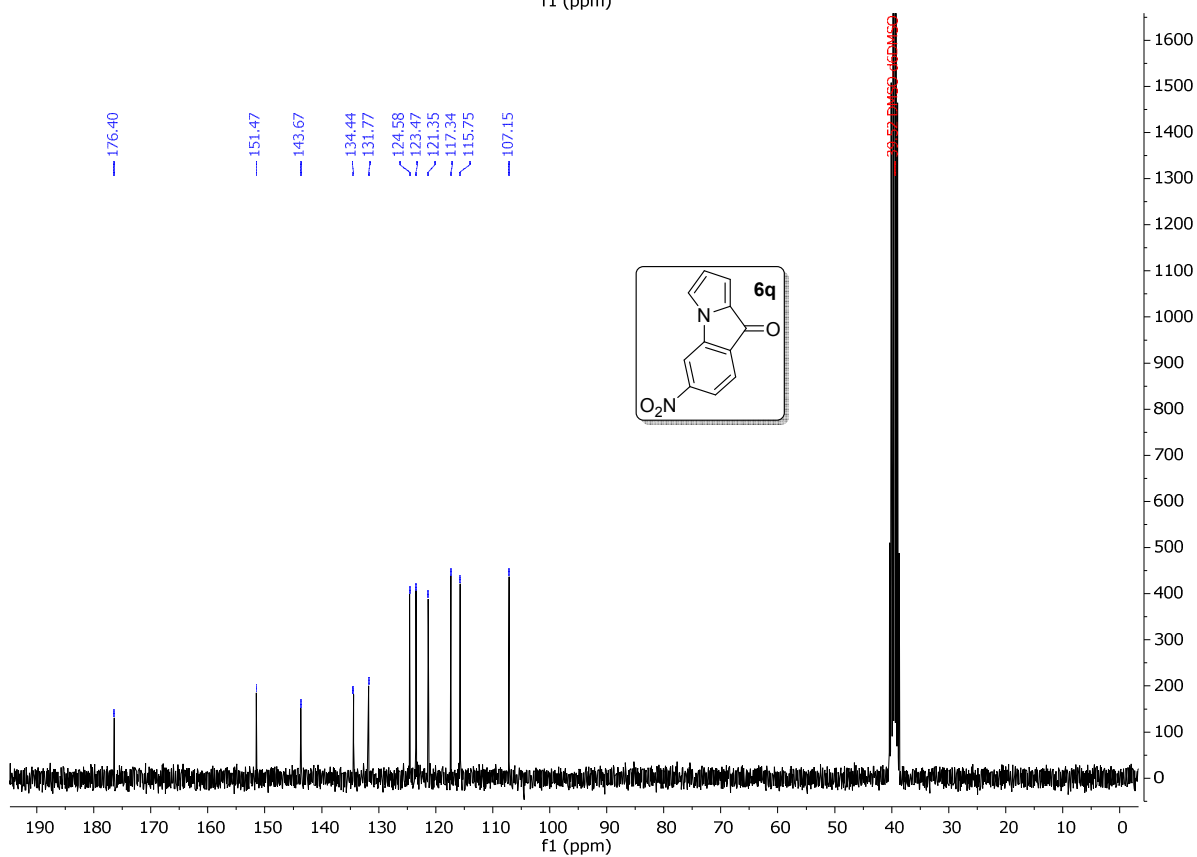
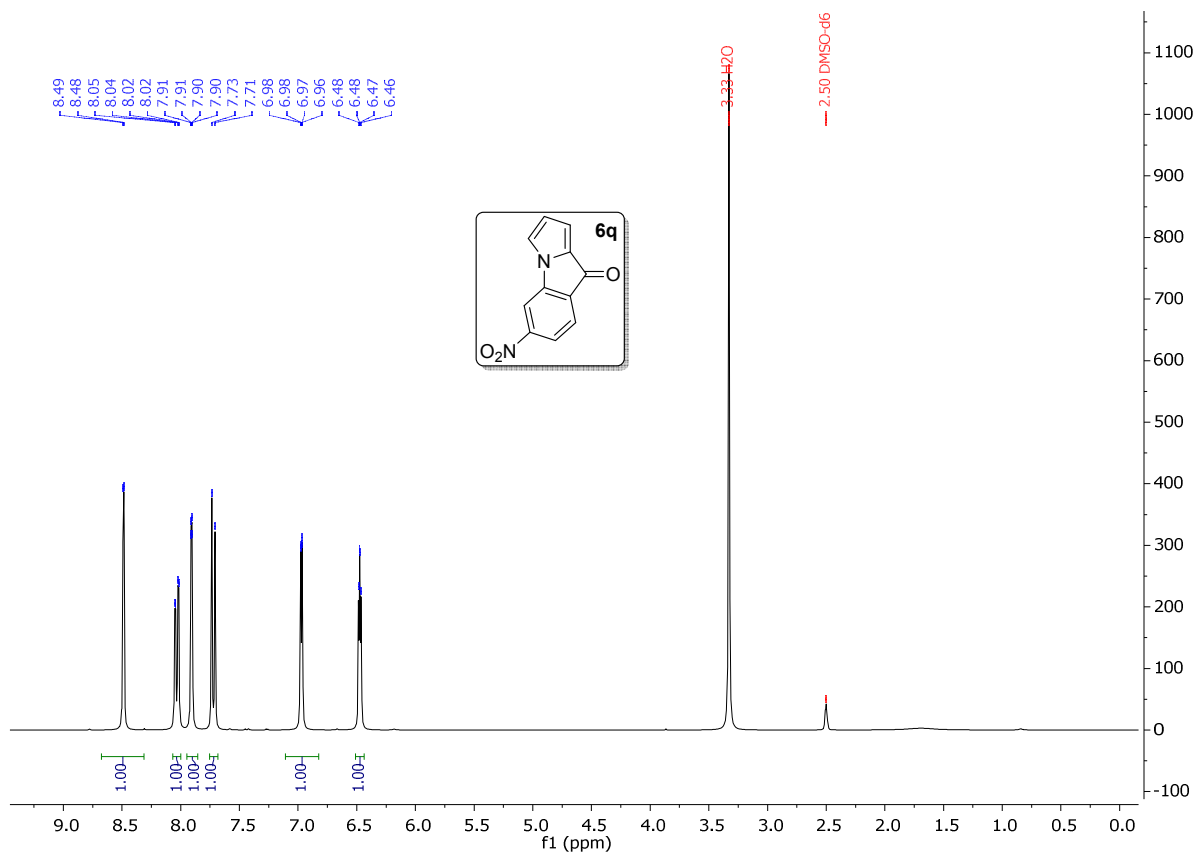


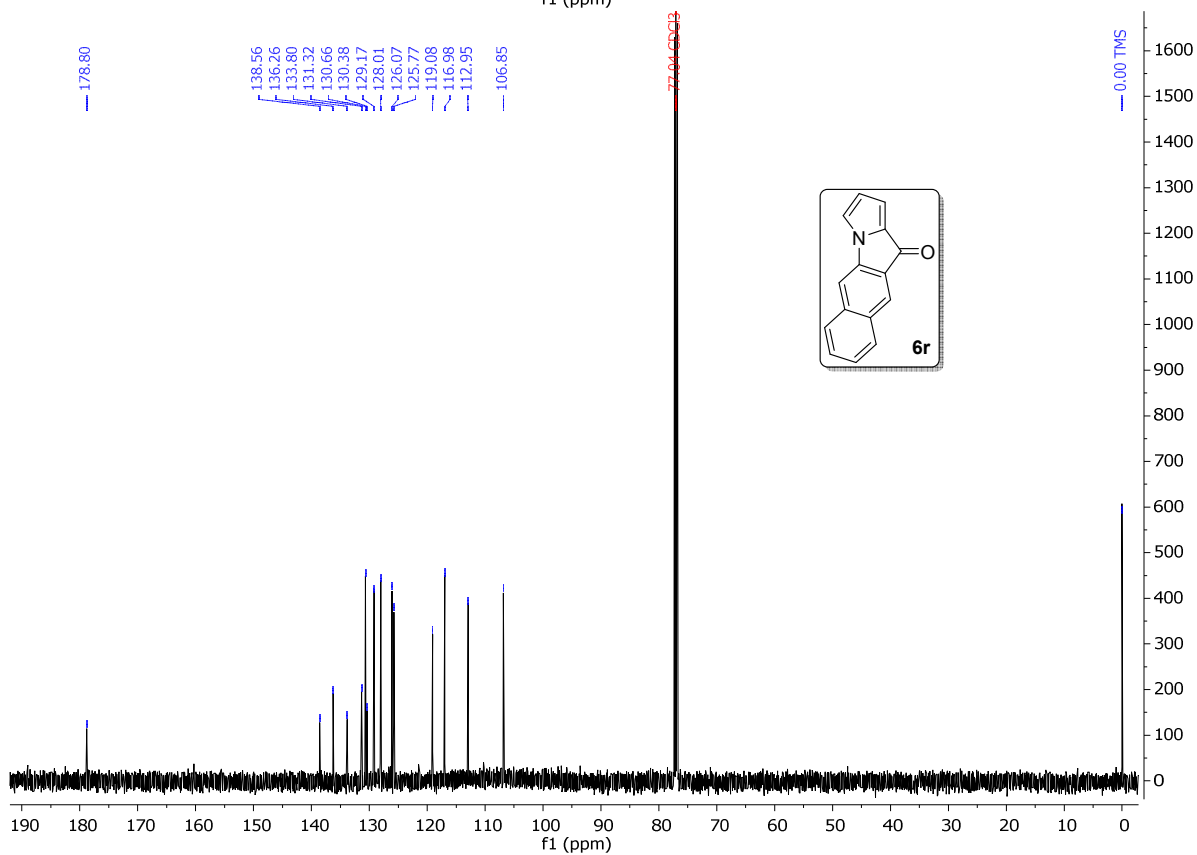
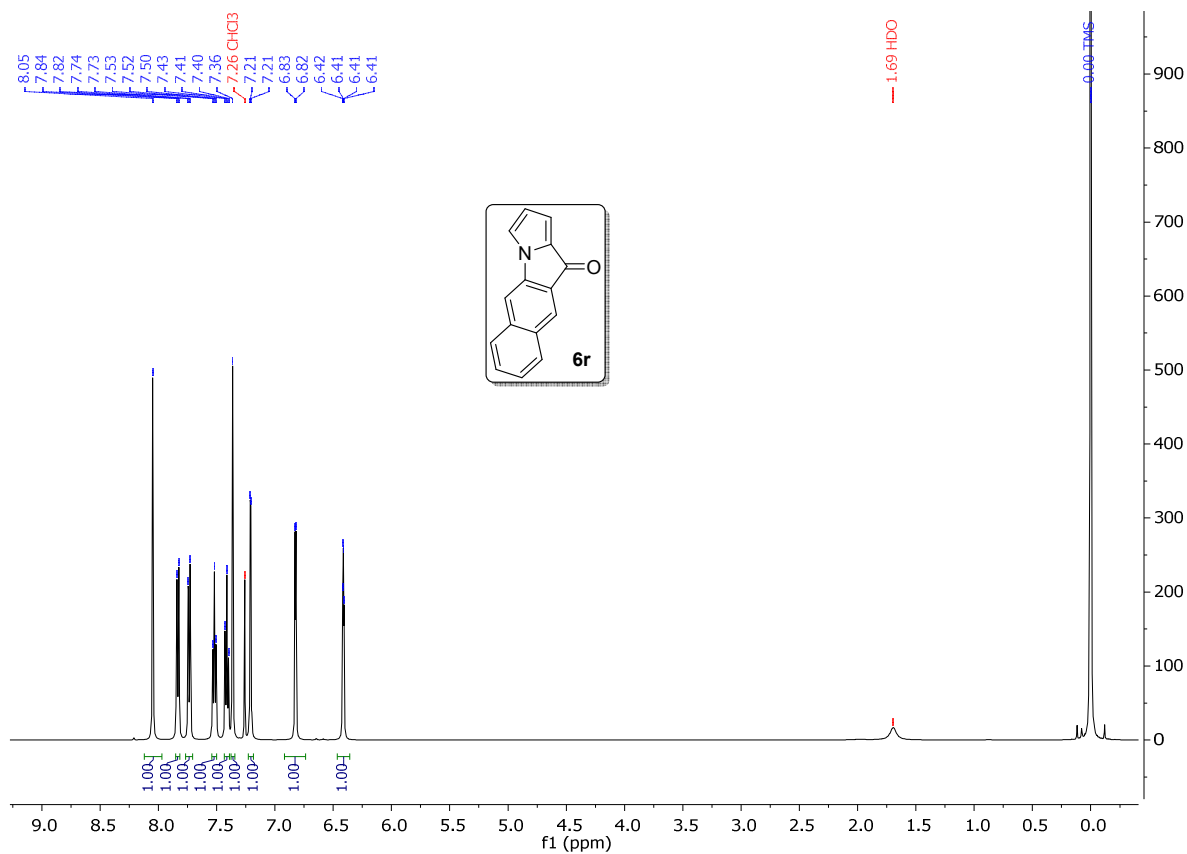






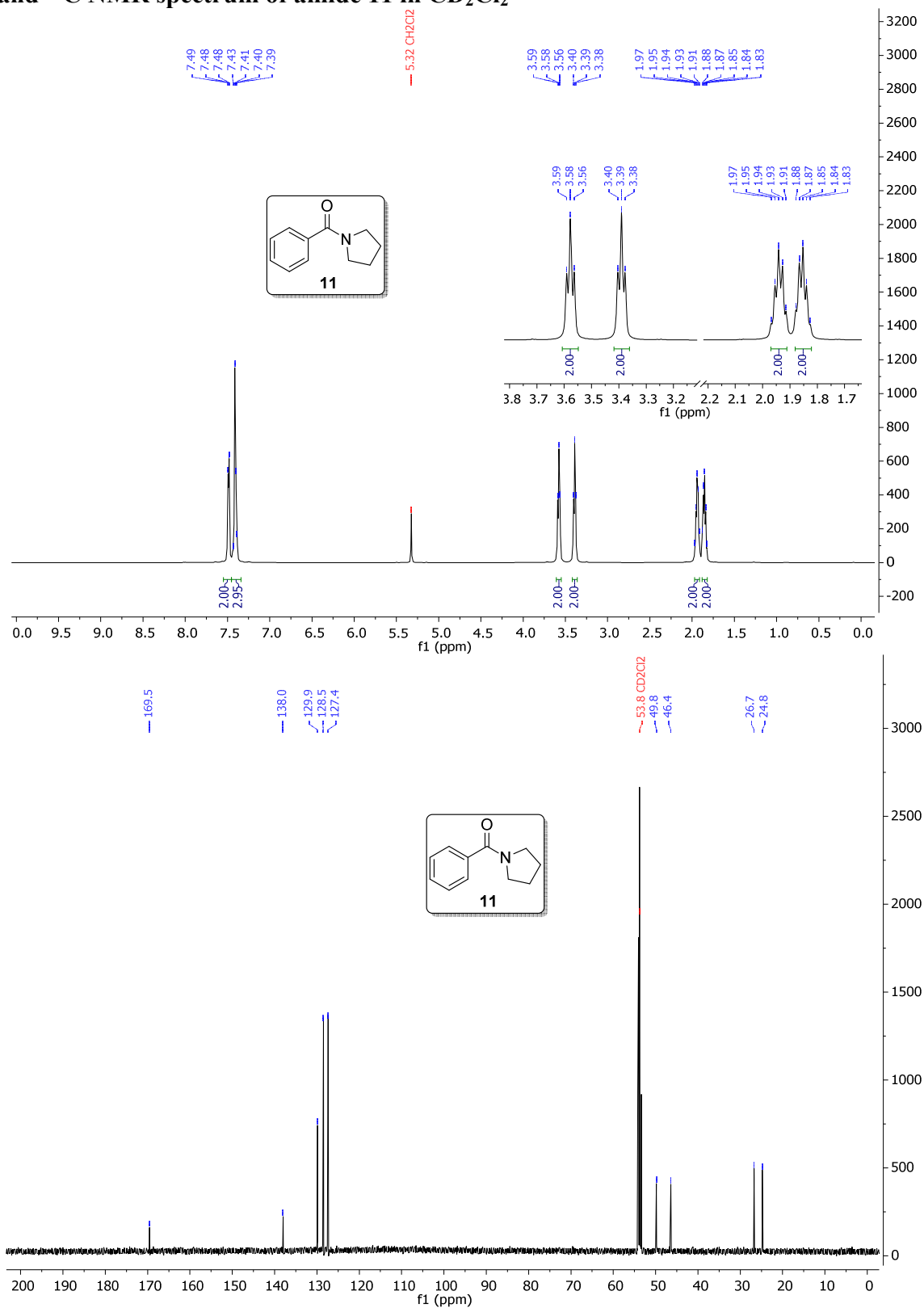




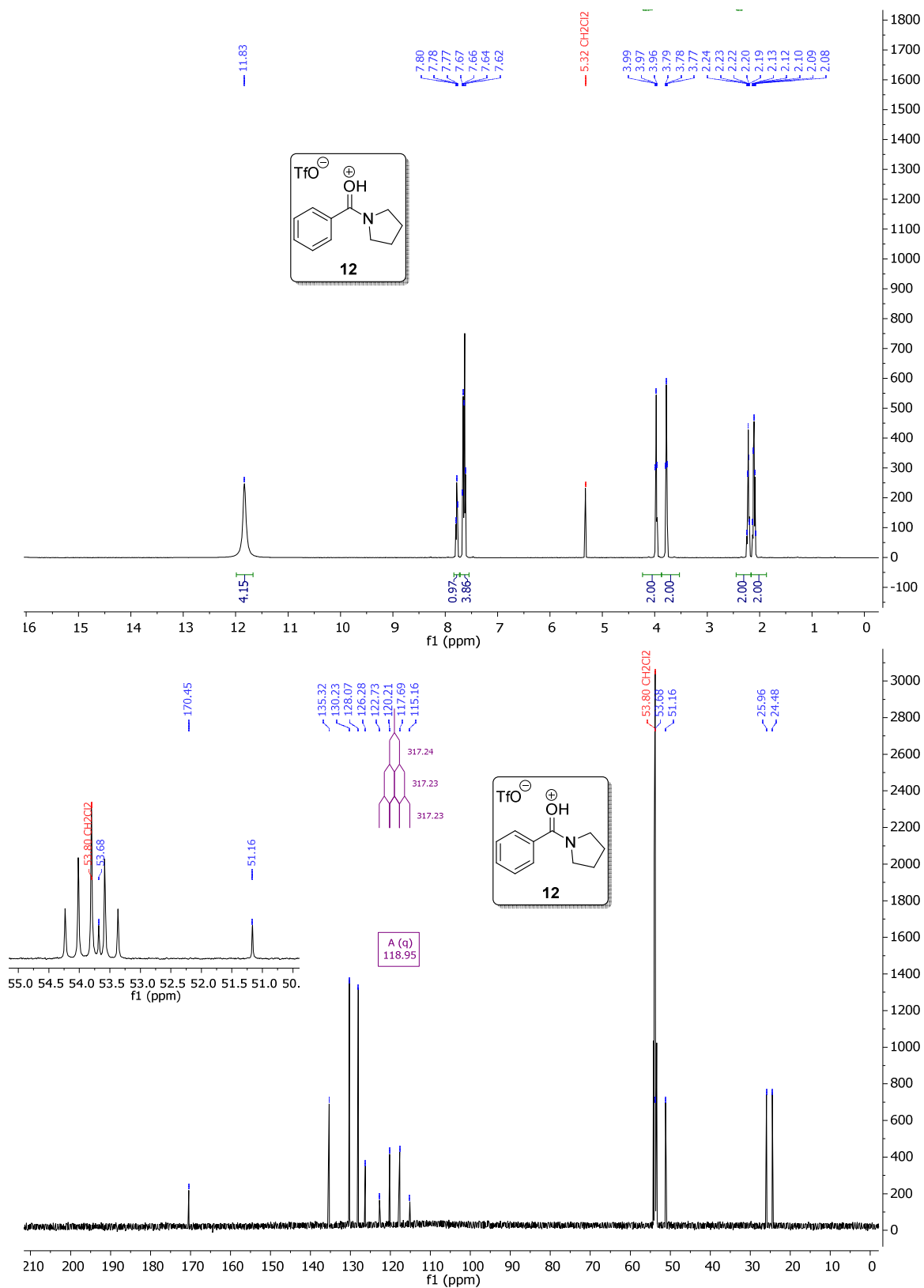


## NMR Spectra Obtained by the Study of the Reaction Mechanism

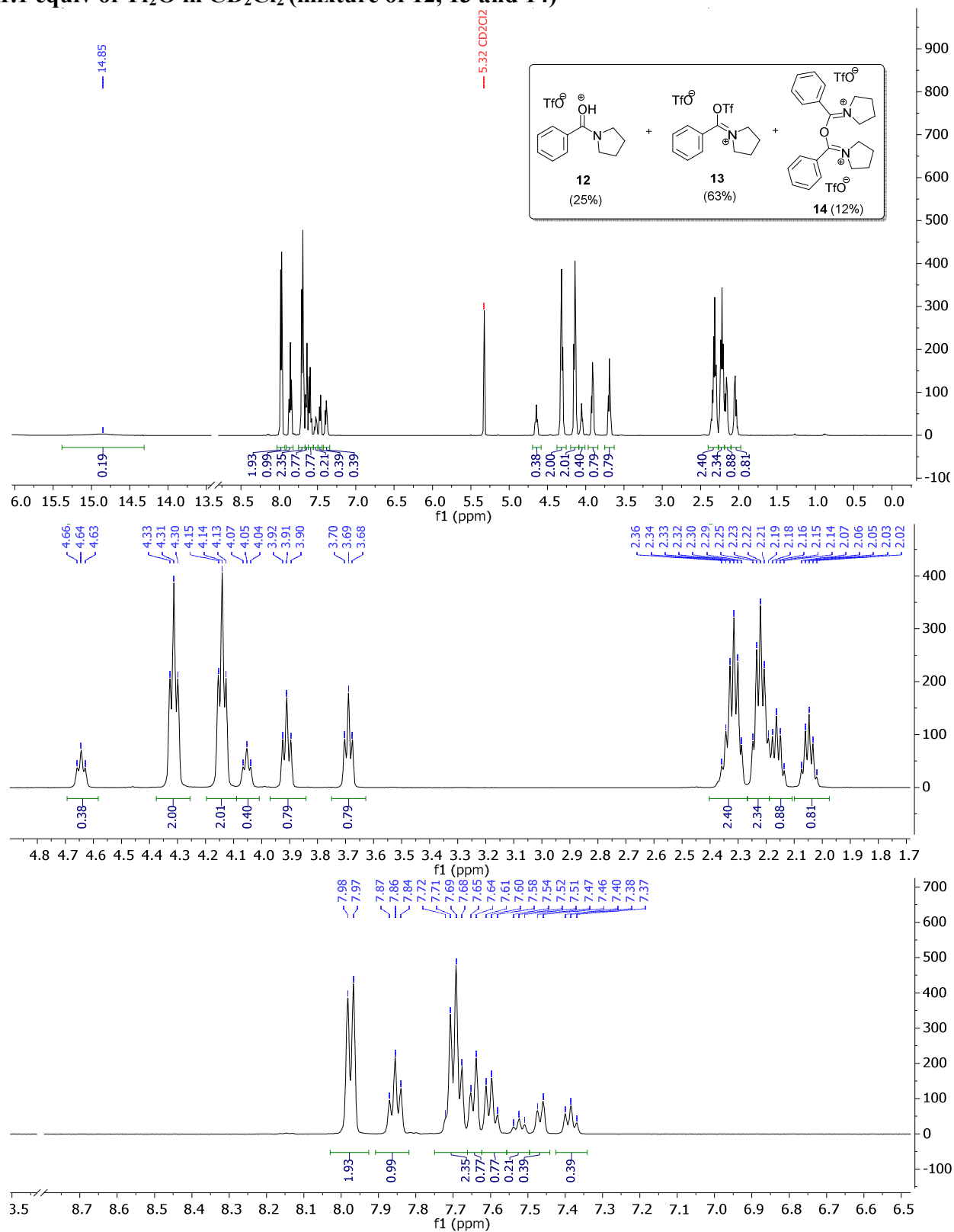
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of amide **11** in  $\text{CD}_2\text{Cl}_2$



**$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the mixture of amide 11 with 4.0 equiv of TfOH in  $\text{CD}_2\text{Cl}_2$  (12)**

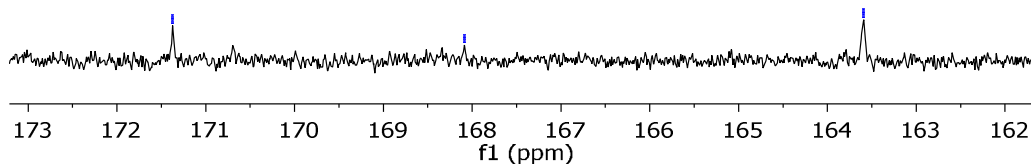
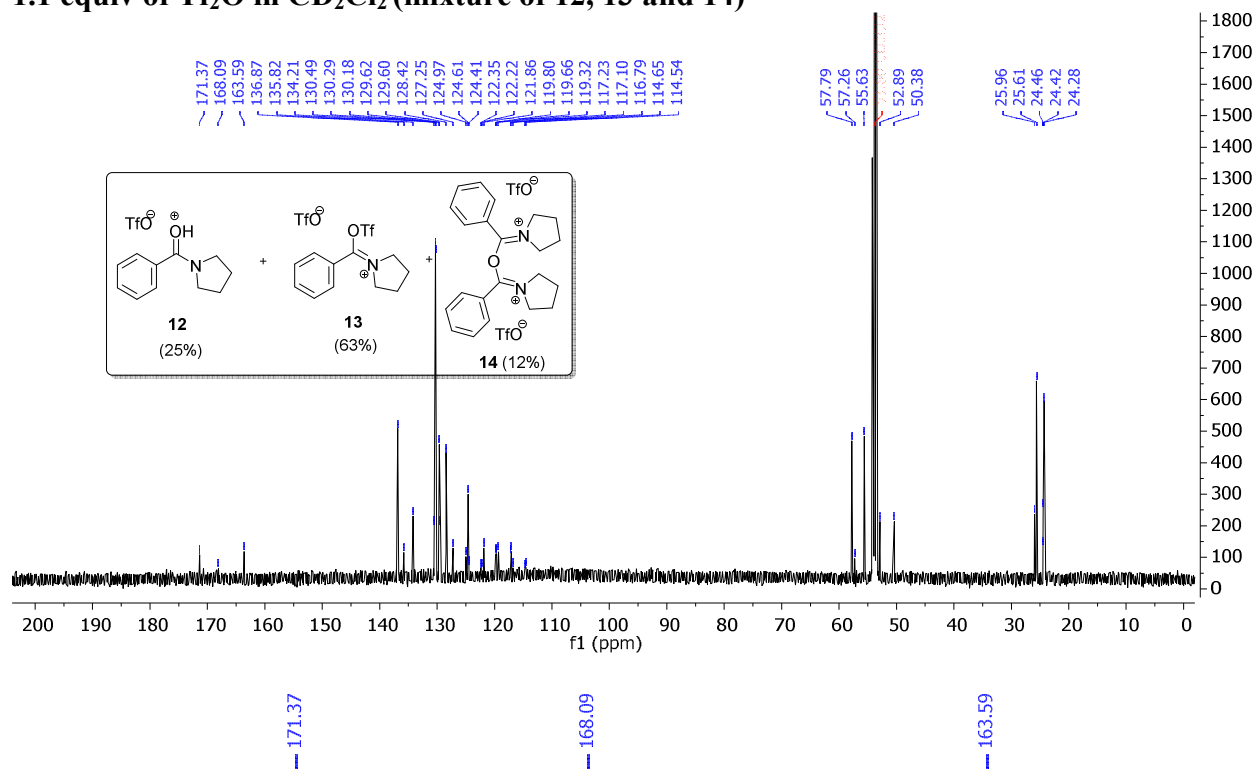


**$^1\text{H}$  and spectrum of the reaction mixture of amide 11 with 0.25 equiv of TfOH followed by 1.1 equiv of Tf<sub>2</sub>O in CD<sub>2</sub>Cl<sub>2</sub> (mixture of 12, 13 and 14)**

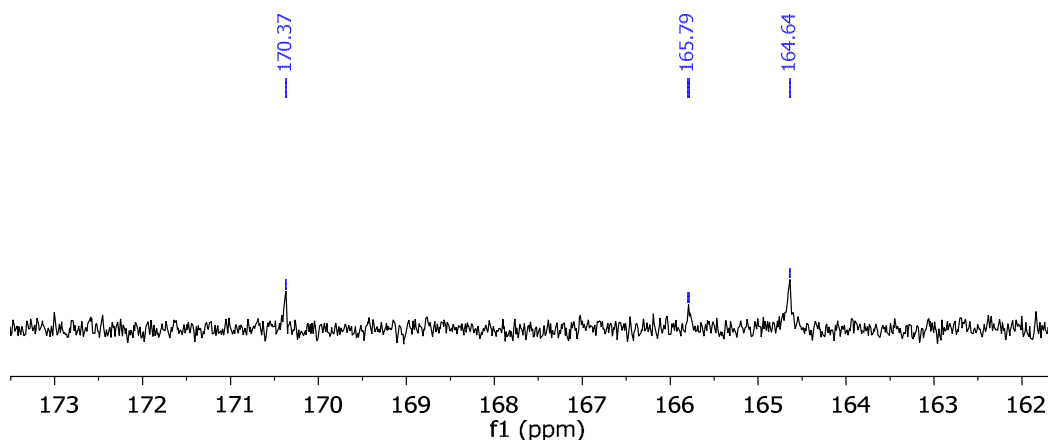




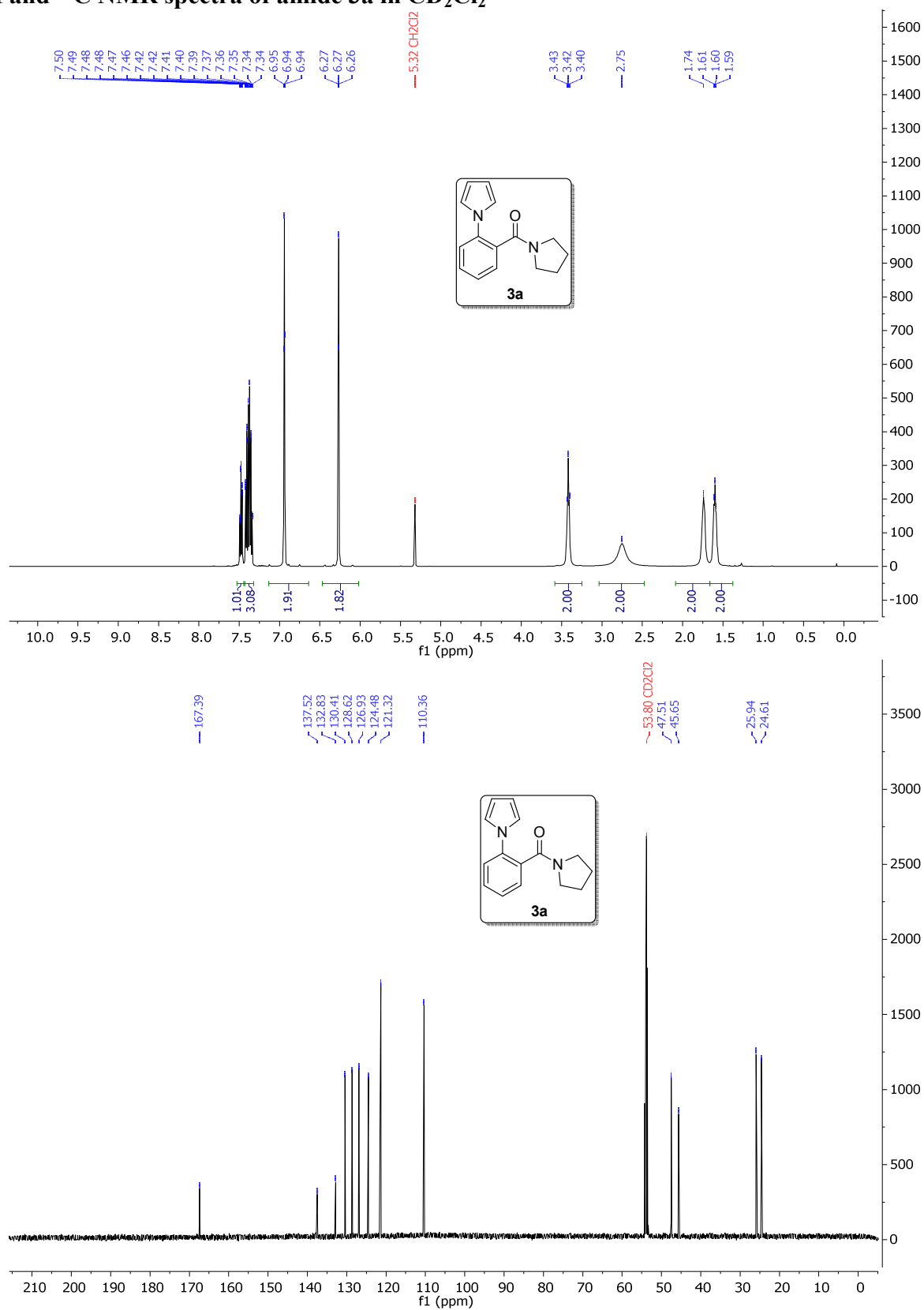
<sup>13</sup>C and spectrum of the reaction mixture of amide 11 with 0.25 equiv of TfOH followed by 1.1 equiv of Tf<sub>2</sub>O in CD<sub>2</sub>Cl<sub>2</sub> (mixture of 12, 13 and 14)



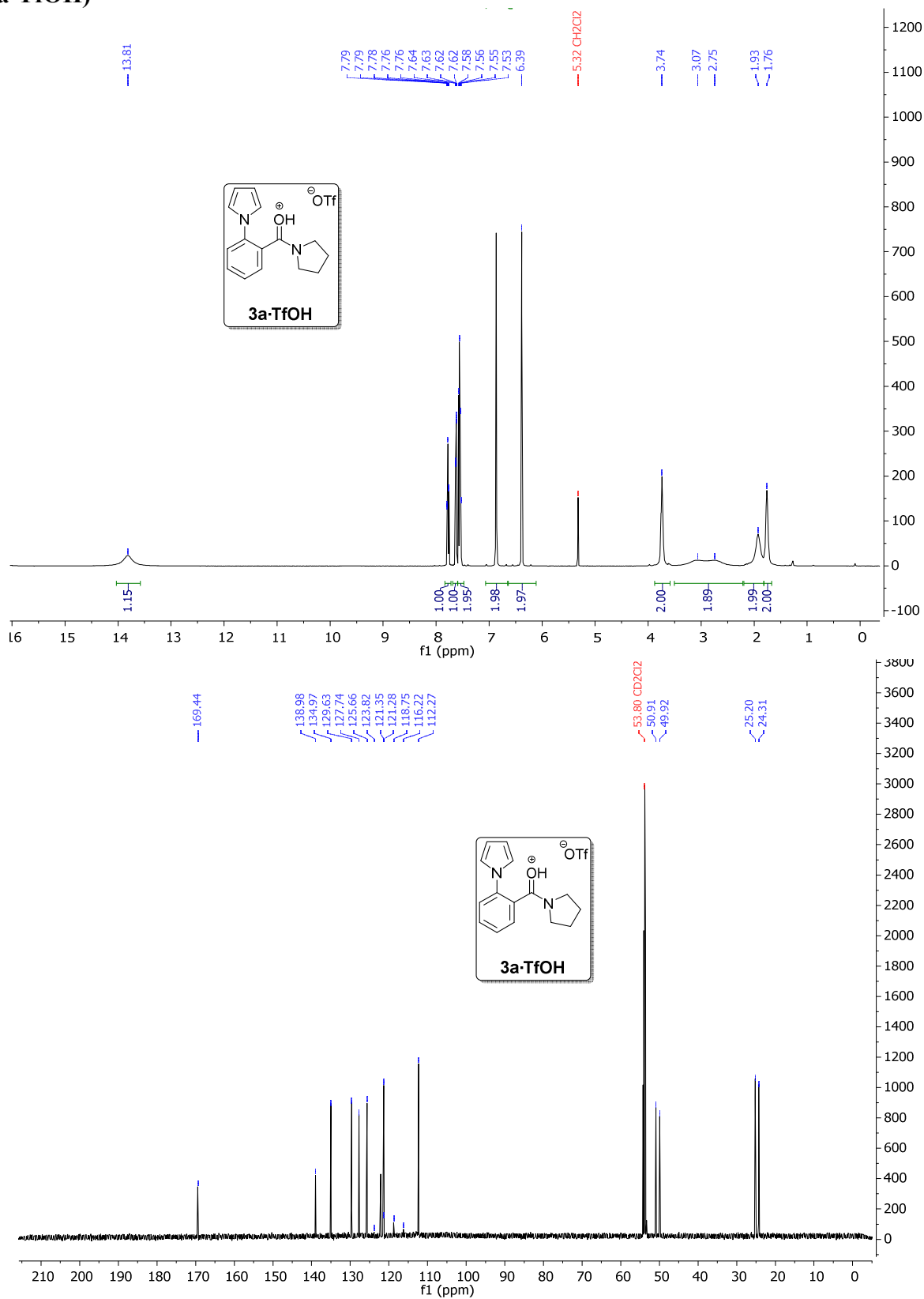
<sup>13</sup>C and spectrum of the reaction mixture of amide 11 with 0.25 equiv of TfOH followed by 1.1 equiv of Tf<sub>2</sub>O in CD<sub>2</sub>Cl<sub>2</sub> + 4.0 equiv TfOH (mixture of 12, 13 and 14)



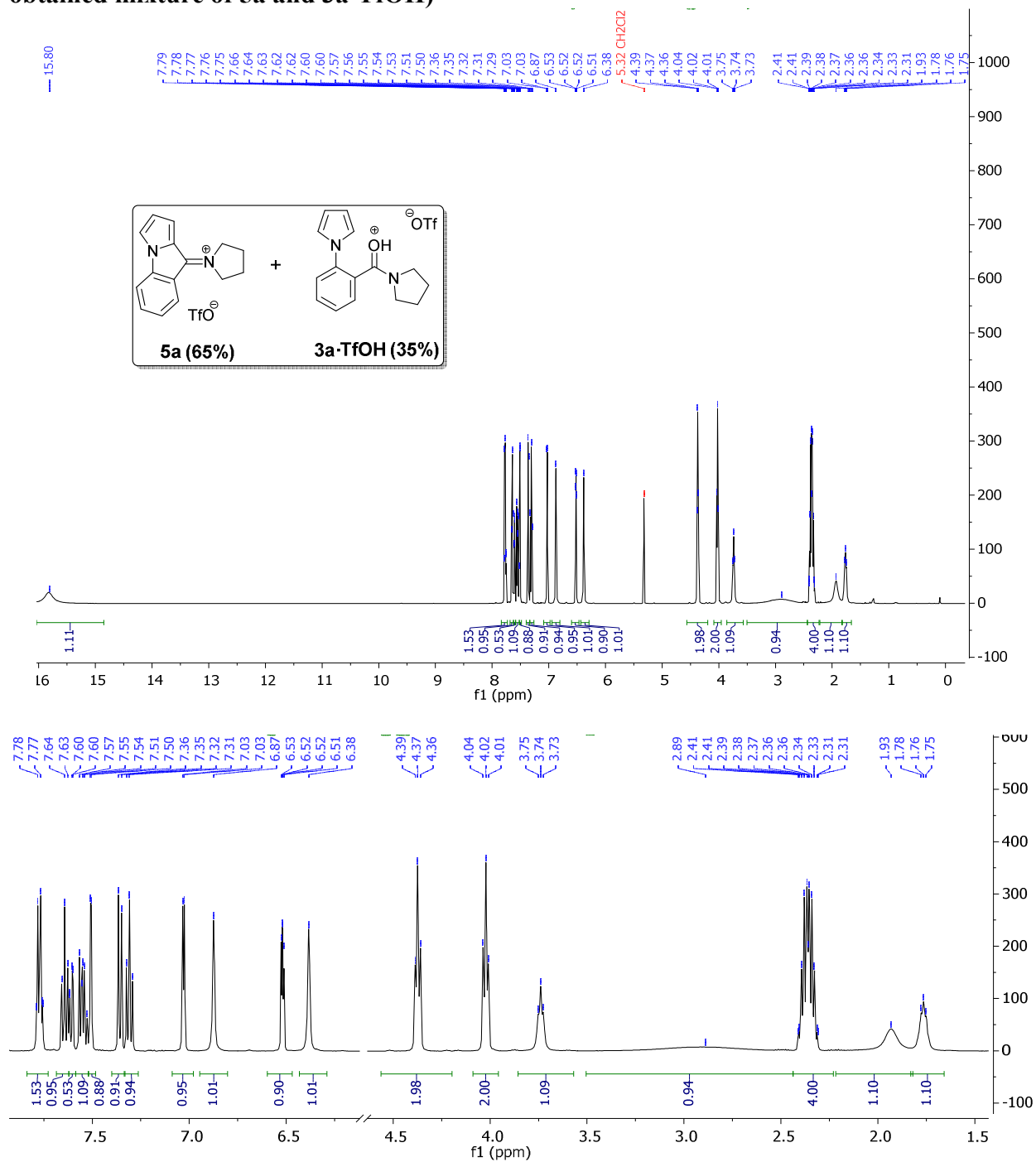
**$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of amide 3a in  $\text{CD}_2\text{Cl}_2$**



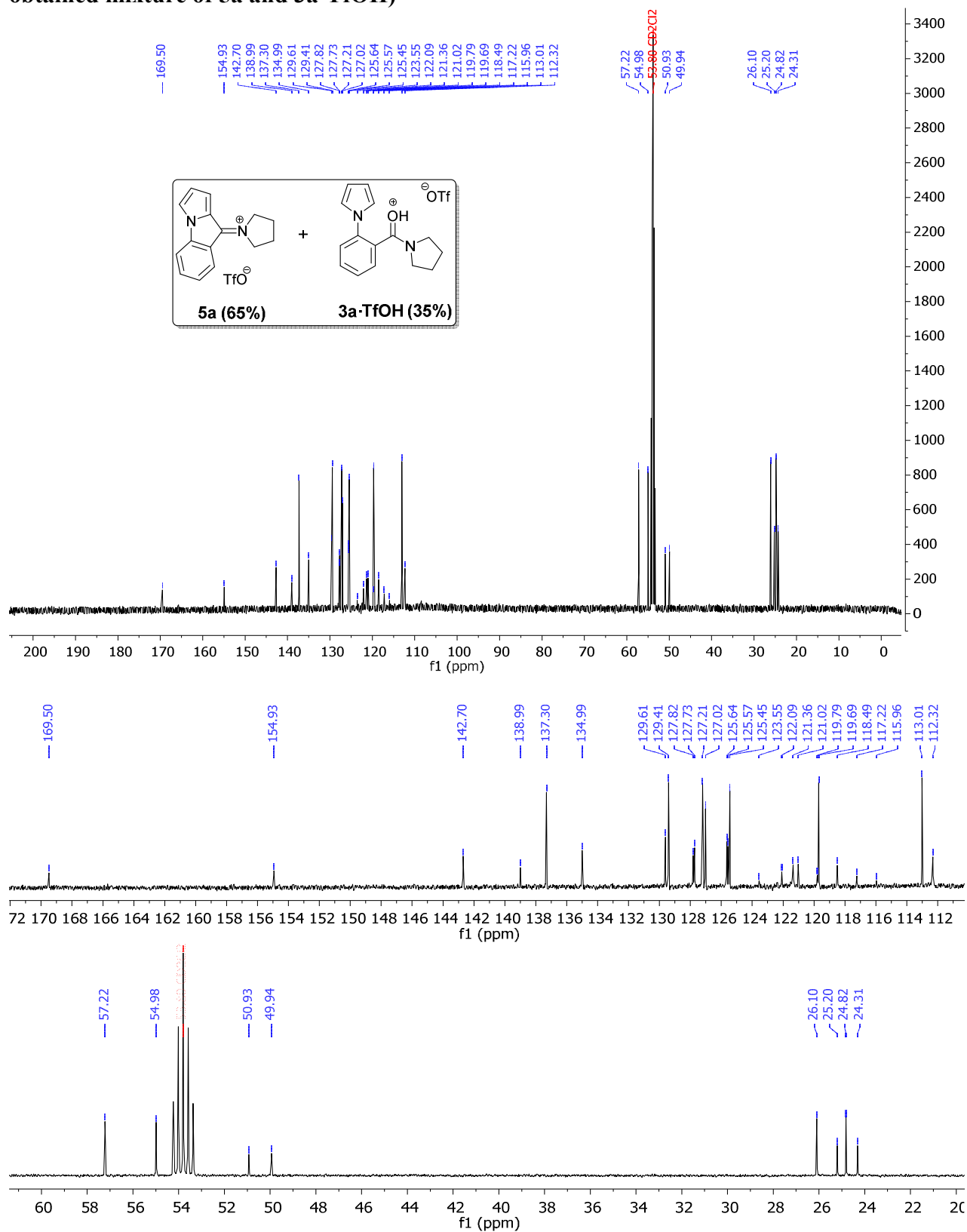
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of the mixture of amide **3a** with 1.1 equiv of TfOH in  $\text{CD}_2\text{Cl}_2$  (**3a**·TfOH)



**$^1\text{H}$  NMR spectrum of the reaction mixture of amide 3a with 1.1 equiv of  $\text{TiF}_2\text{O}$  in  $\text{CD}_2\text{Cl}_2$  (the obtained mixture of 5a and 3a·TfOH)**



**$^{13}\text{C}$  NMR spectrum of the reaction mixture of amide 3a with 1.1 equiv of  $\text{Ti}_2\text{O}$  in  $\text{CD}_2\text{Cl}_2$  (the obtained mixture of 5a and 3a·TfOH)**

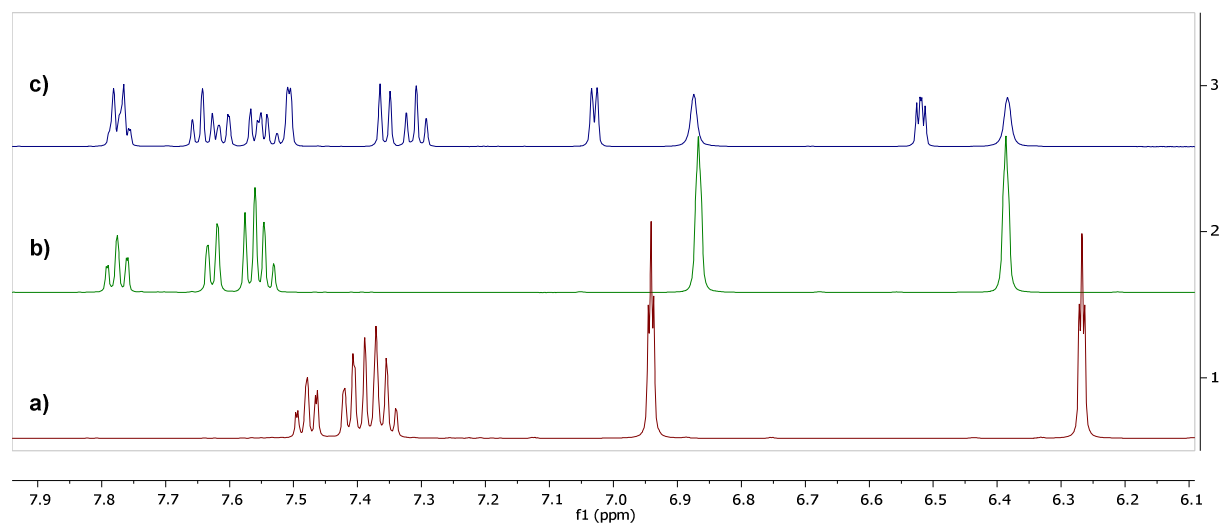
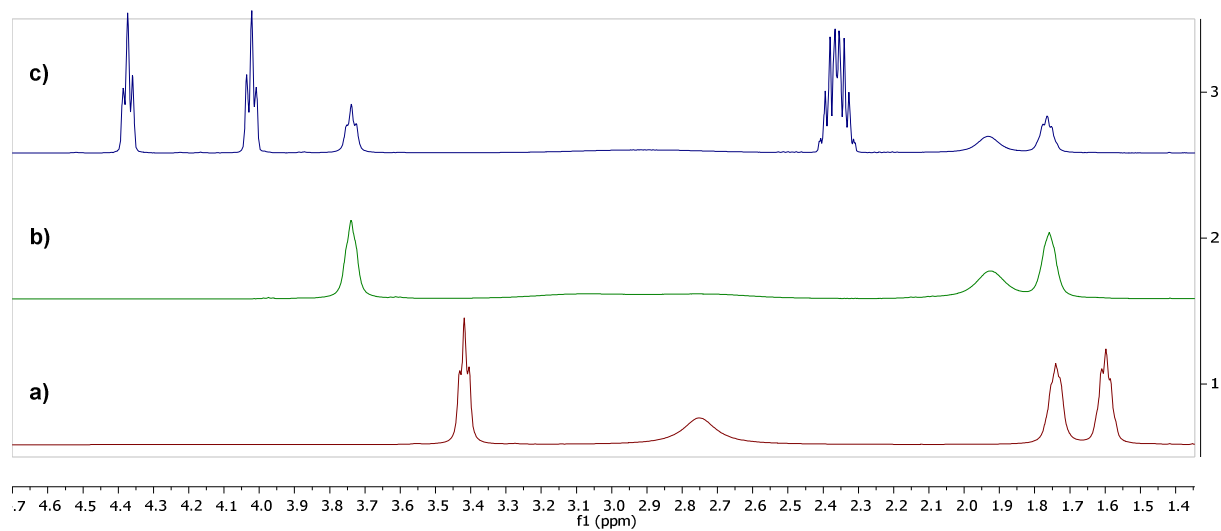


Sections of stacked view of  $^1\text{H}$  NMR spectra obtained by the study of  $\text{Tf}_2\text{O}$ -mediated activation of amide **3a** in  $\text{CD}_2\text{Cl}_2$ . (for full view of stacked spectra see article Figure 1)

a) spectrum of **3a**

b) spectrum of the mixture of **3a** and 1.1 equiv of  $\text{TfOH}$

c) spectrum of the reaction mixture of **3a** and 1.1 equiv  $\text{Tf}_2\text{O}$

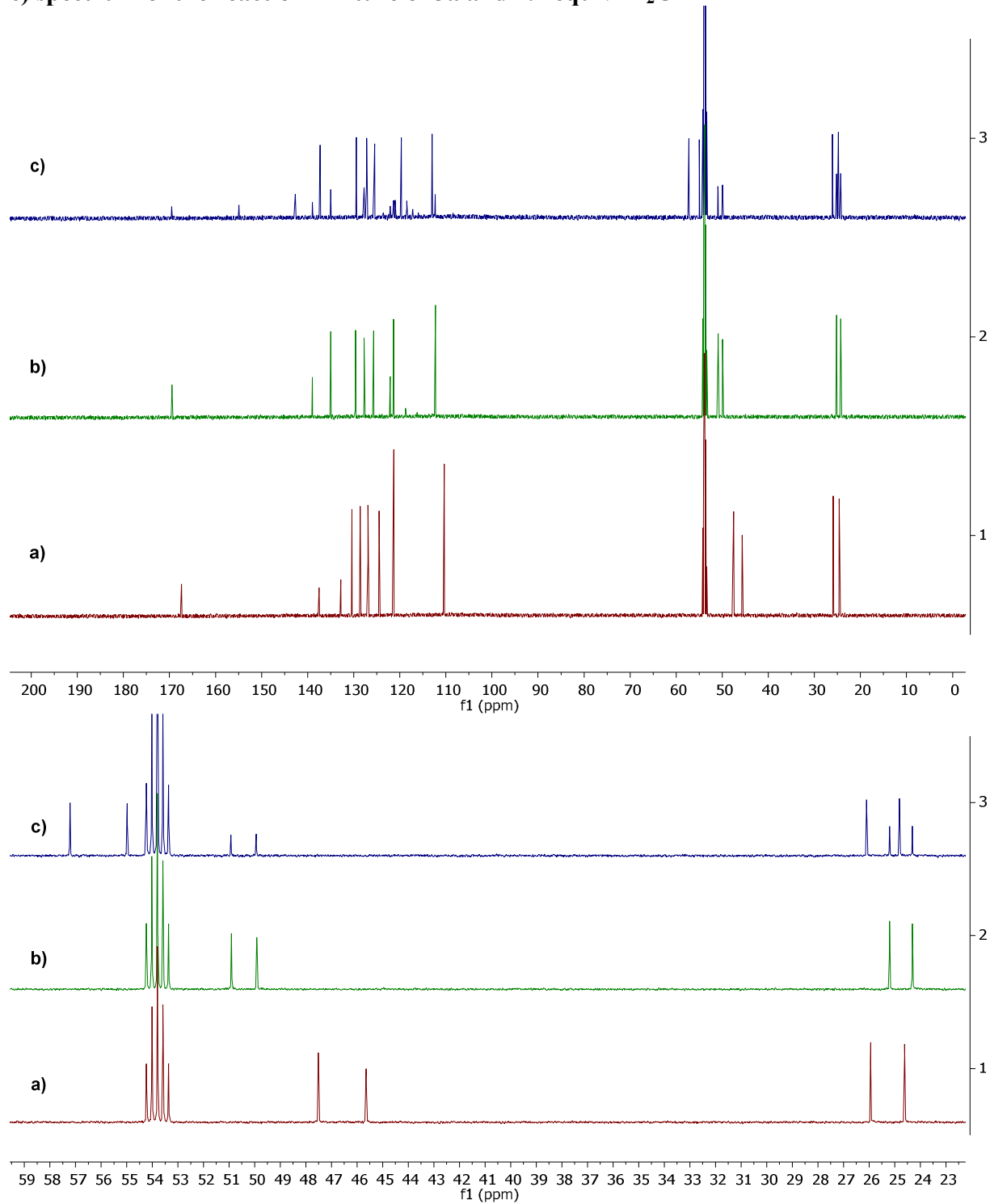


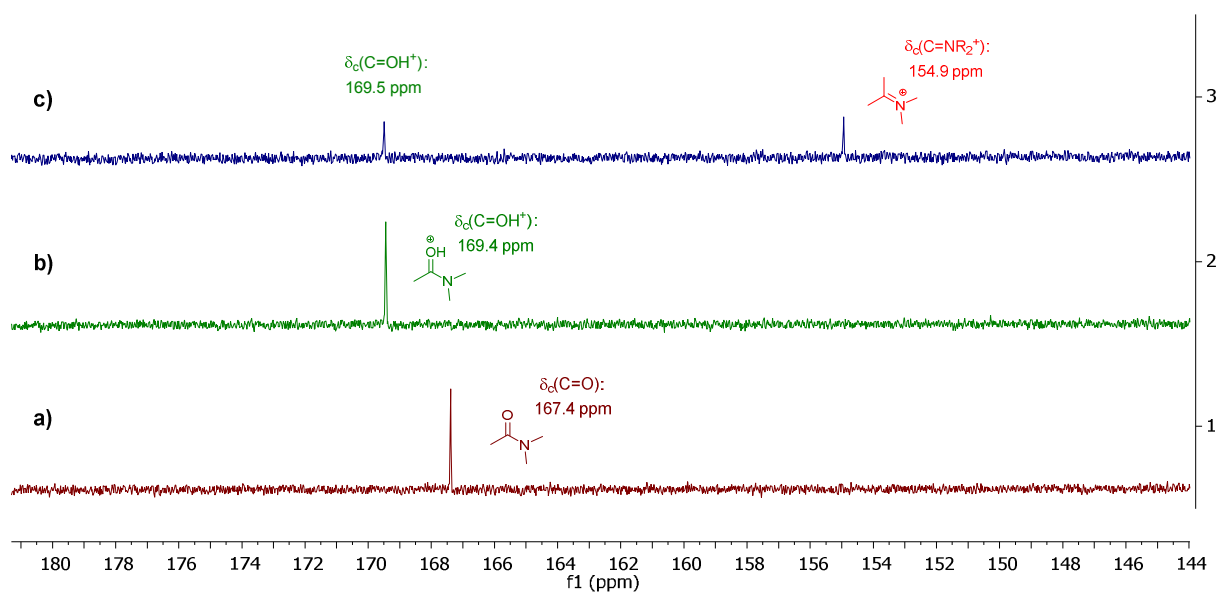
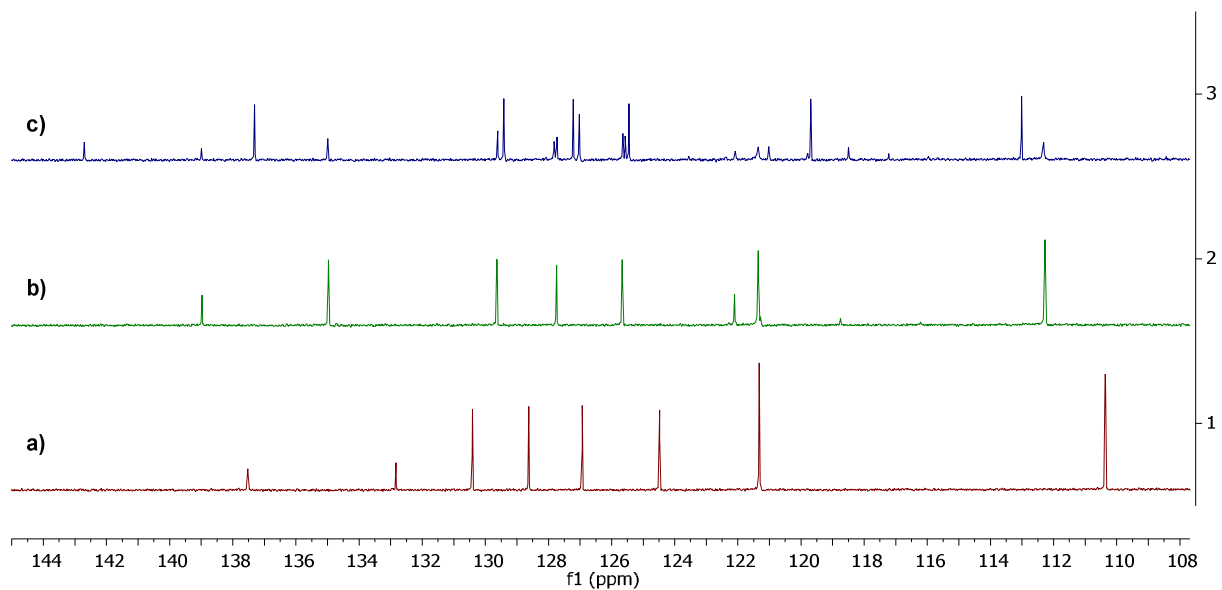
Stacked view of  $^{13}\text{C}$  NMR spectra obtained by the study of  $\text{Tf}_2\text{O}$ -mediated activation of amide 3a in  $\text{CD}_2\text{Cl}_2$ .

a) spectrum of 3a

b) spectrum of the mixture of 3a and 1.1 equiv of  $\text{TfOH}$

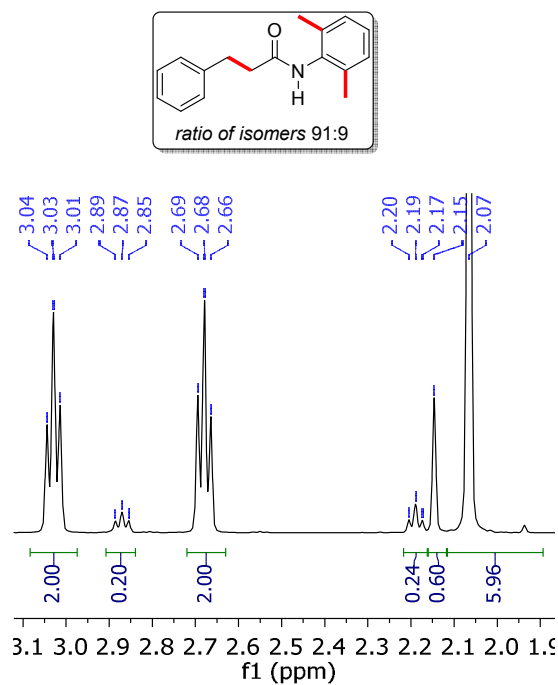
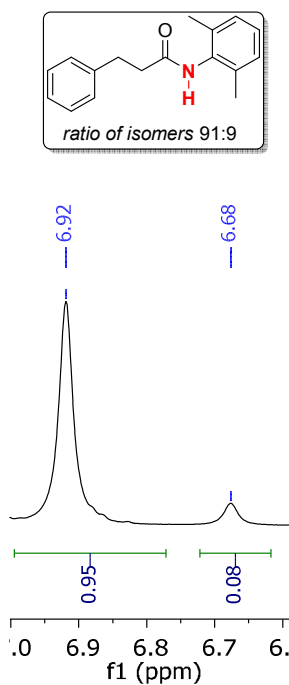
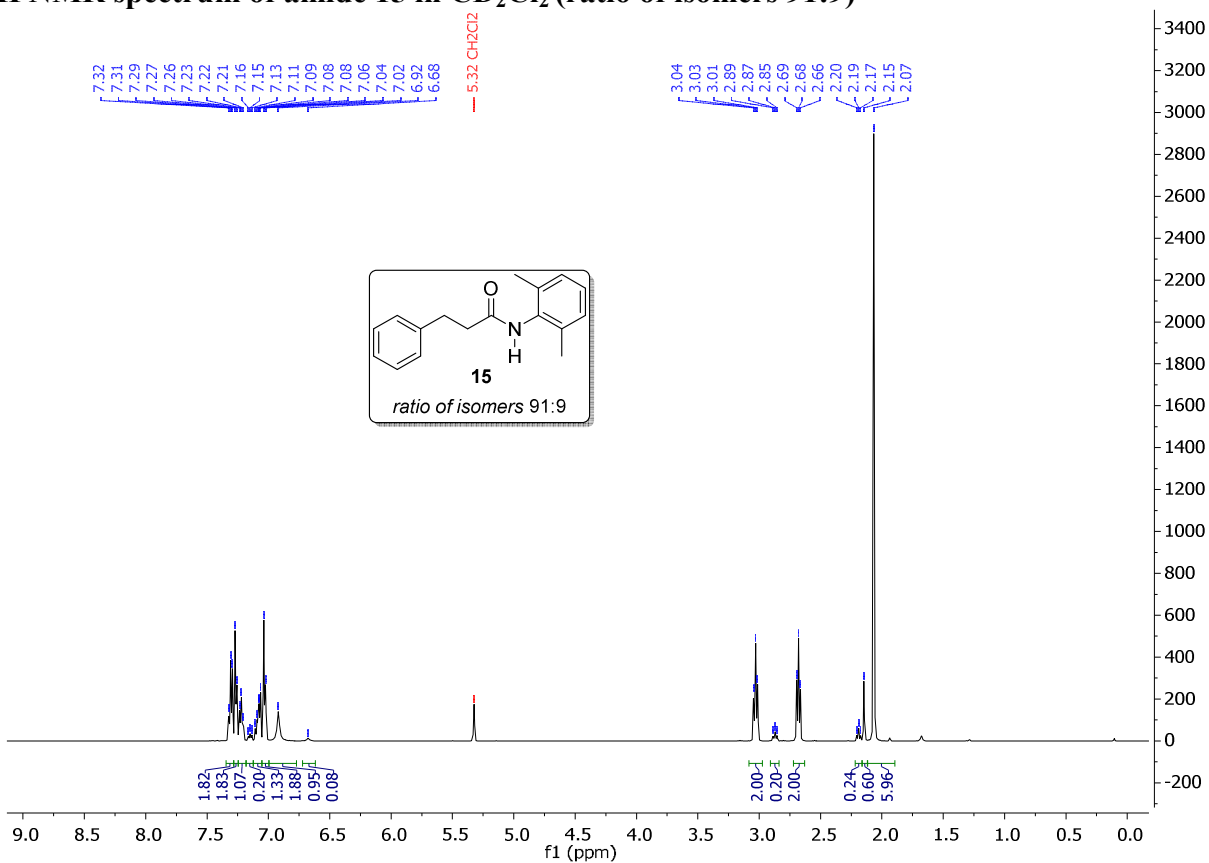
c) spectrum of the reaction mixture of 3a and 1.1 equiv  $\text{Tf}_2\text{O}$



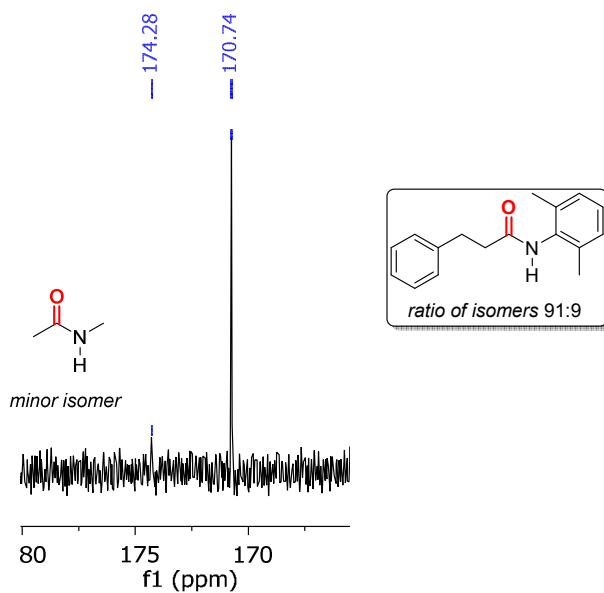
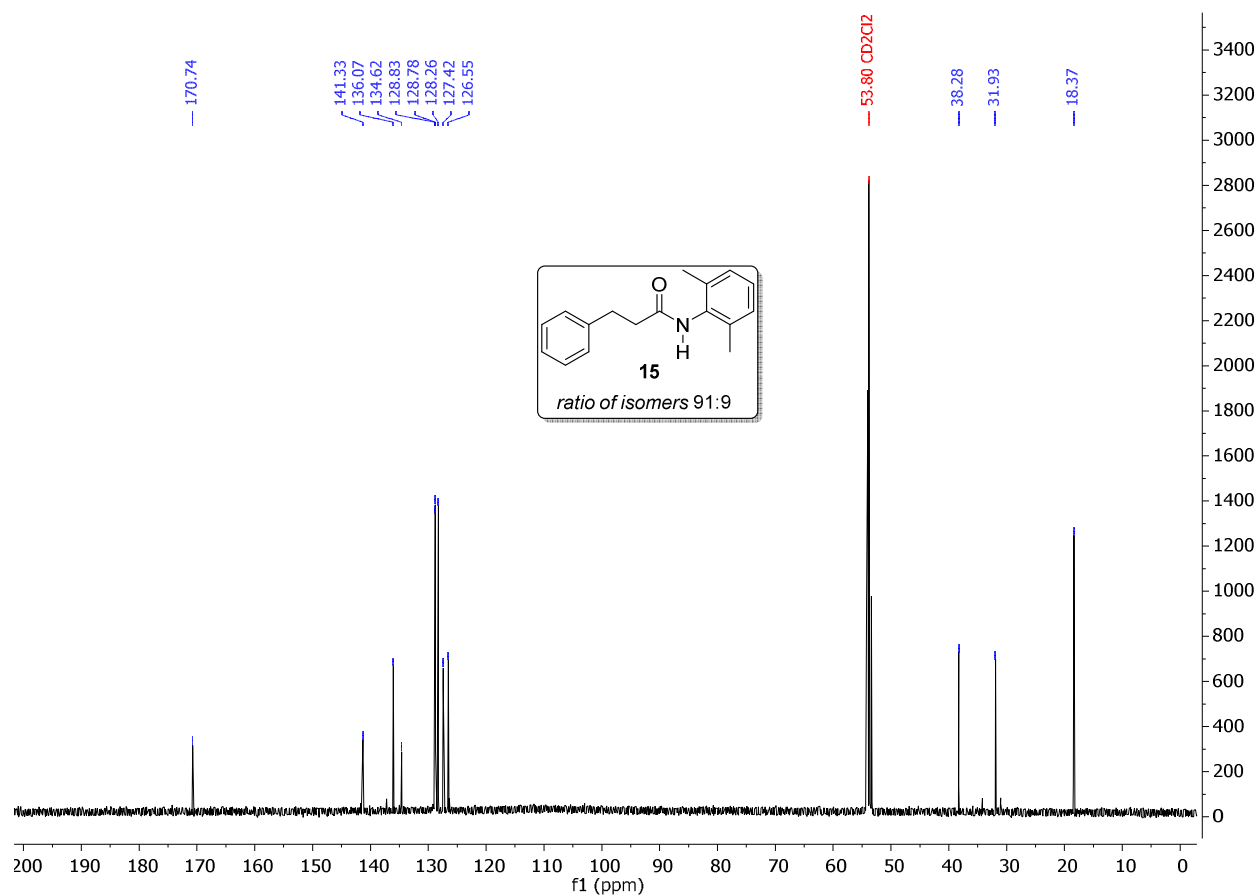




**$^1\text{H}$  NMR spectrum of amide 15 in  $\text{CD}_2\text{Cl}_2$  (ratio of isomers 91:9)**



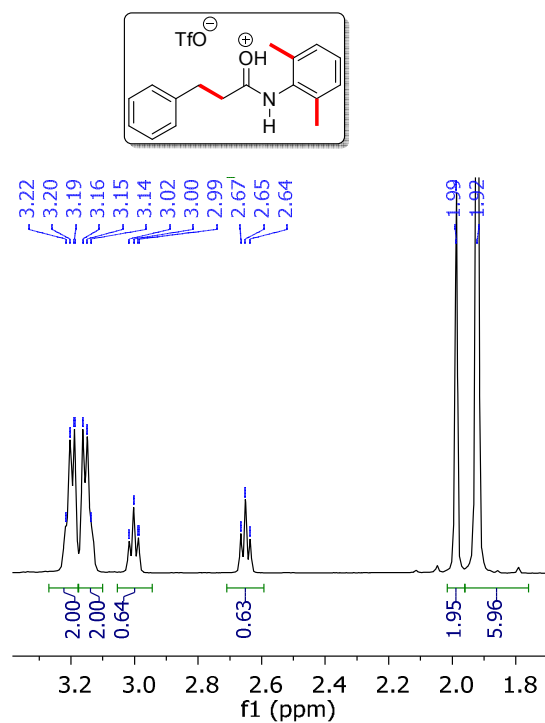
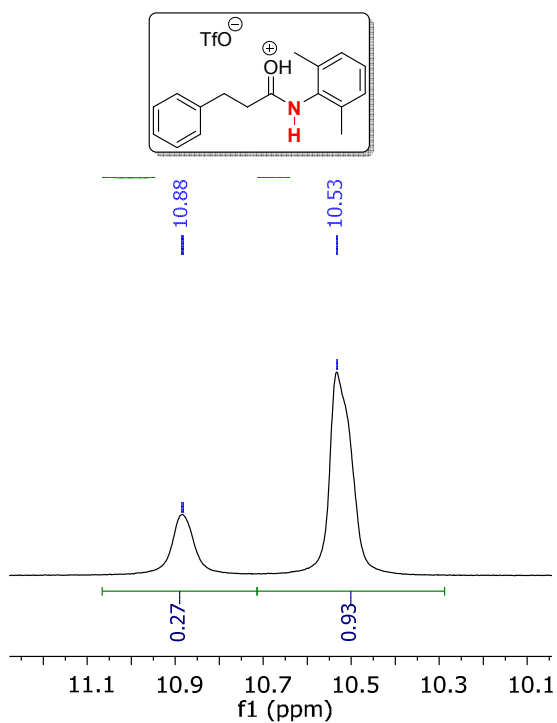
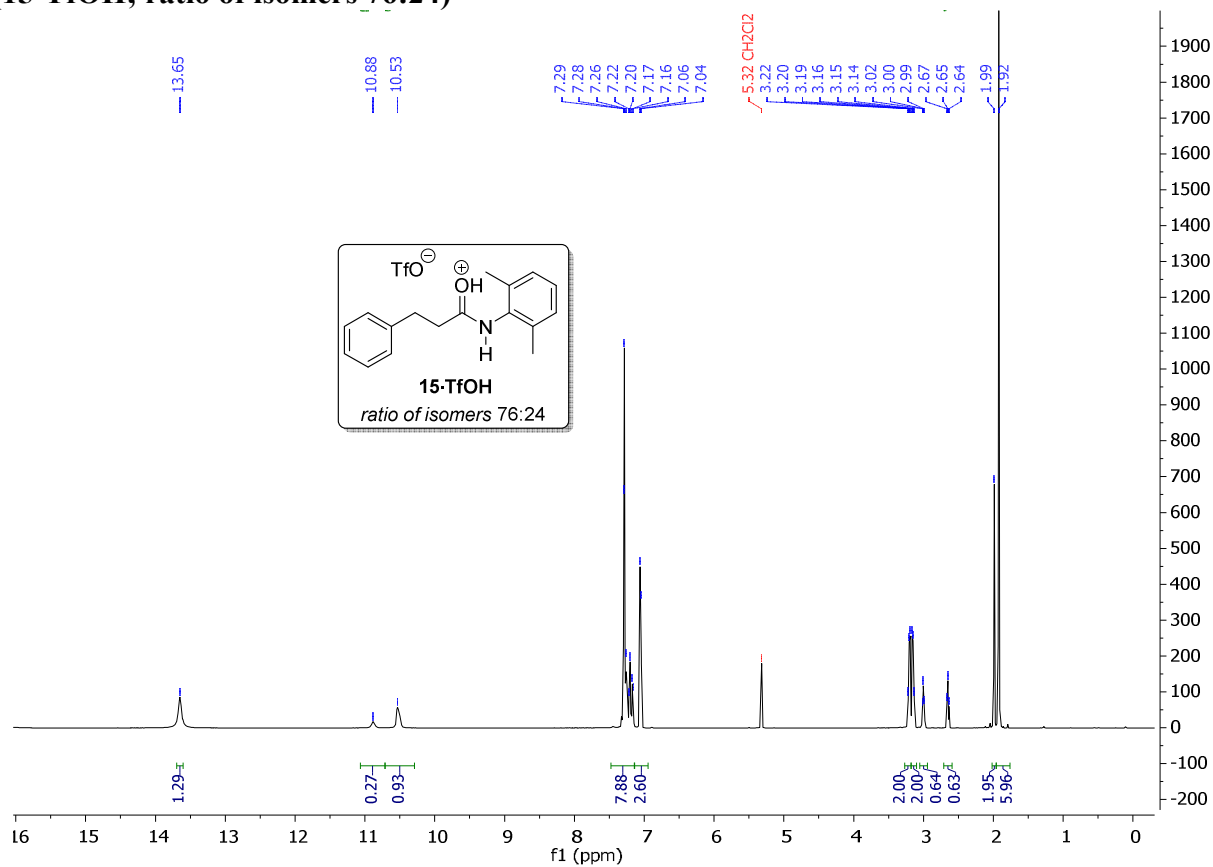
**$^{13}\text{C}$  NMR spectrum of amide **15** in  $\text{CD}_2\text{Cl}_2$  (ratio of isomers 91:9)**



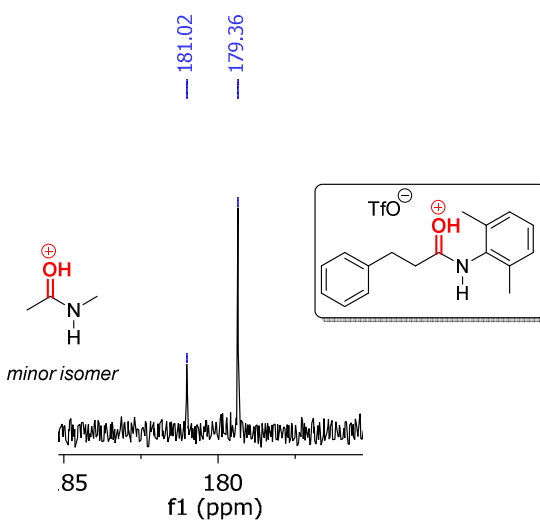
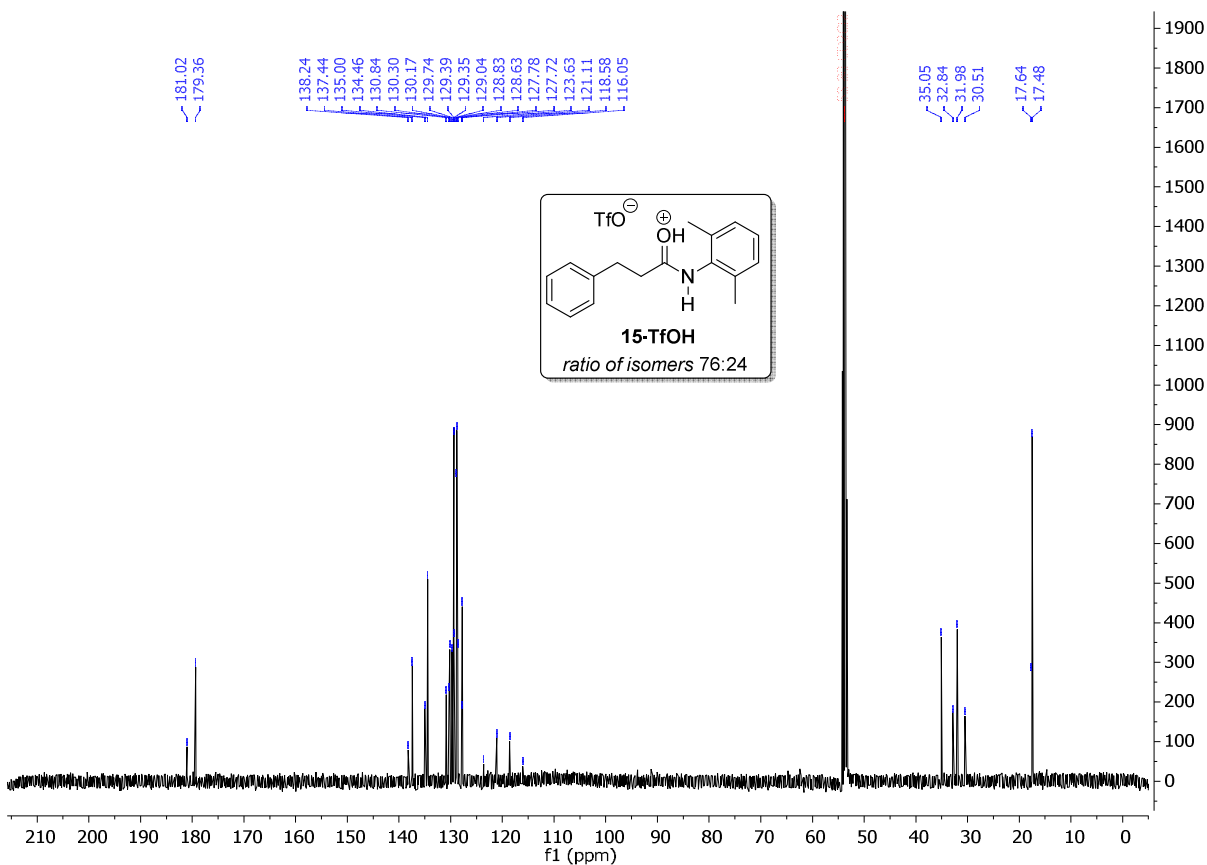
**Note:**

The existence of two isomers of amide **15** can also be observed in the spectra of **15** made by Huang and co-workers.<sup>1</sup>

**$^1\text{H}$  NMR spectrum of the mixture of amide 15 with 1.1 equiv of TfOH in  $\text{CD}_2\text{Cl}_2$   
(15·TfOH; ratio of isomers 76:24)**



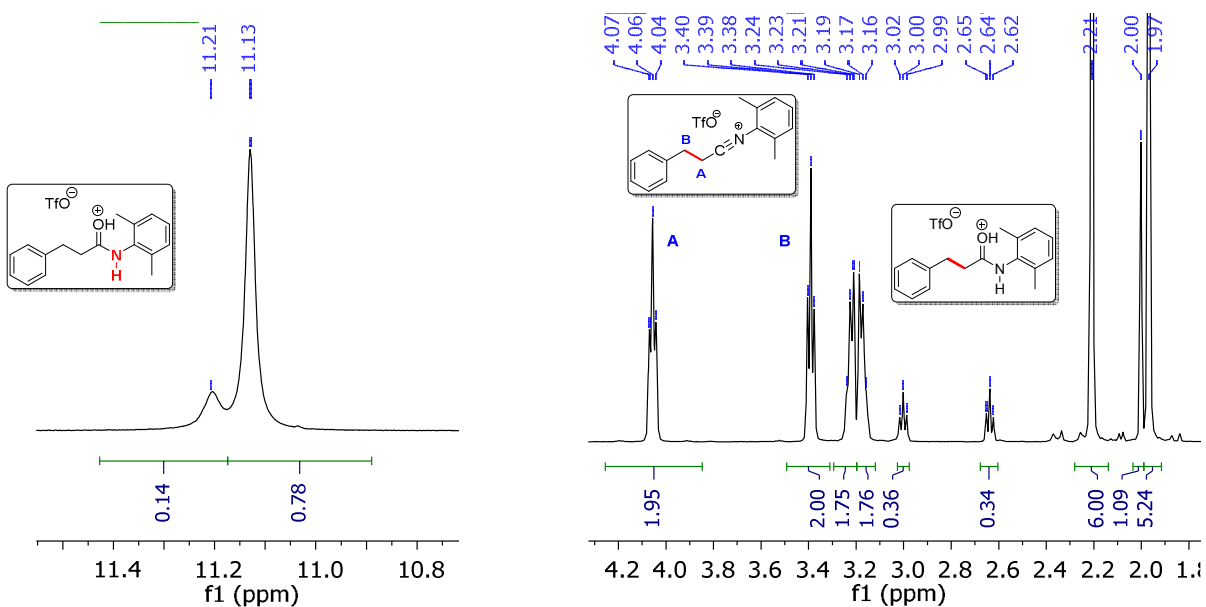
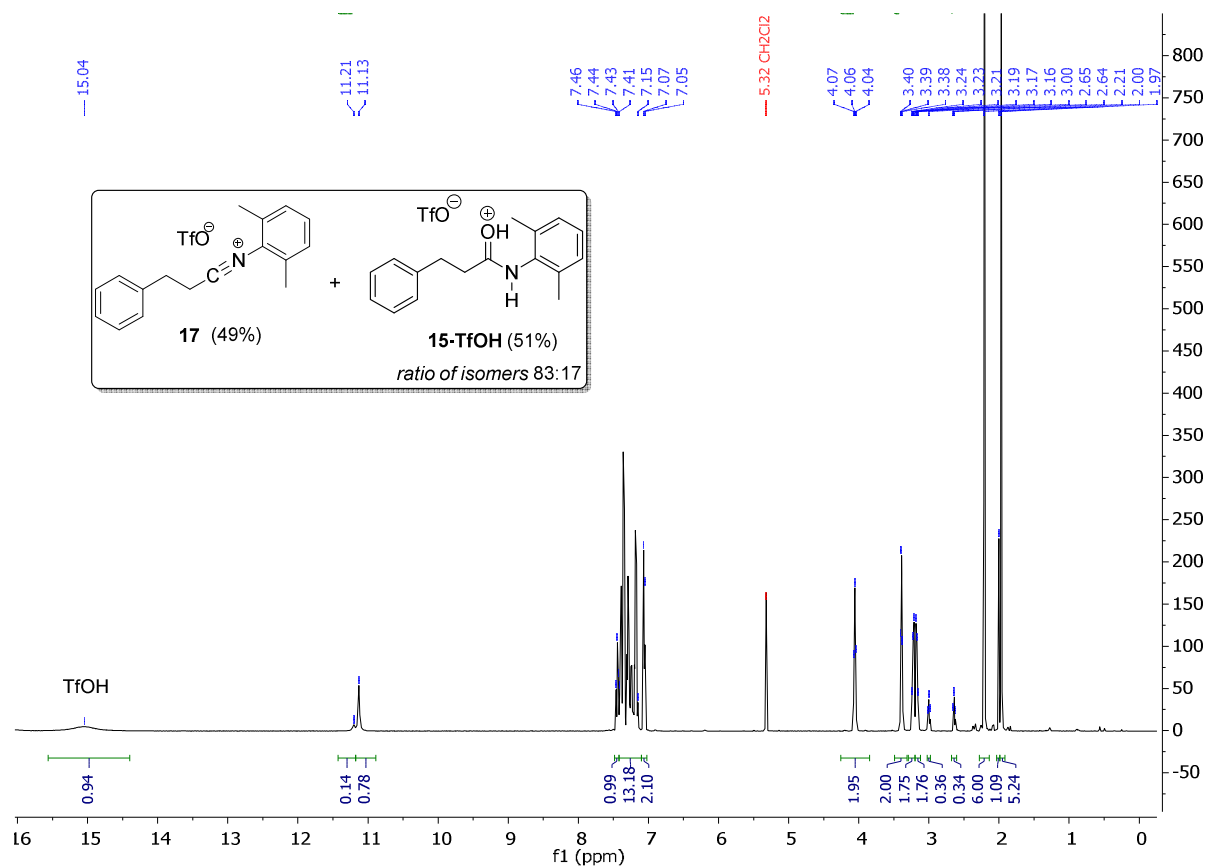
$^{13}\text{C}$  NMR spectrum of the mixture of amide **15** with 1.1 equiv of TfOH in  $\text{CD}_2\text{Cl}_2$  (**15**·TfOH; ratio of isomers 76:24)



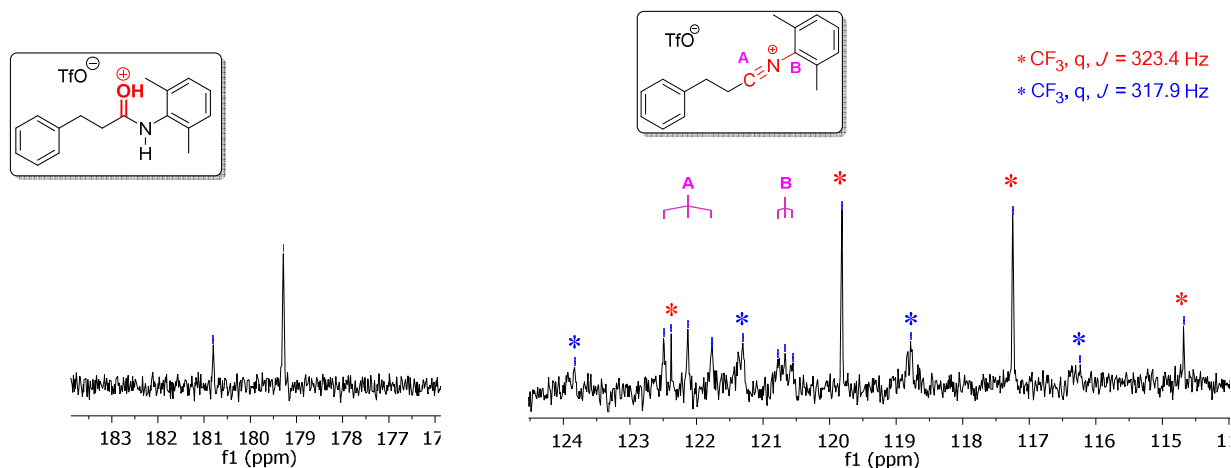
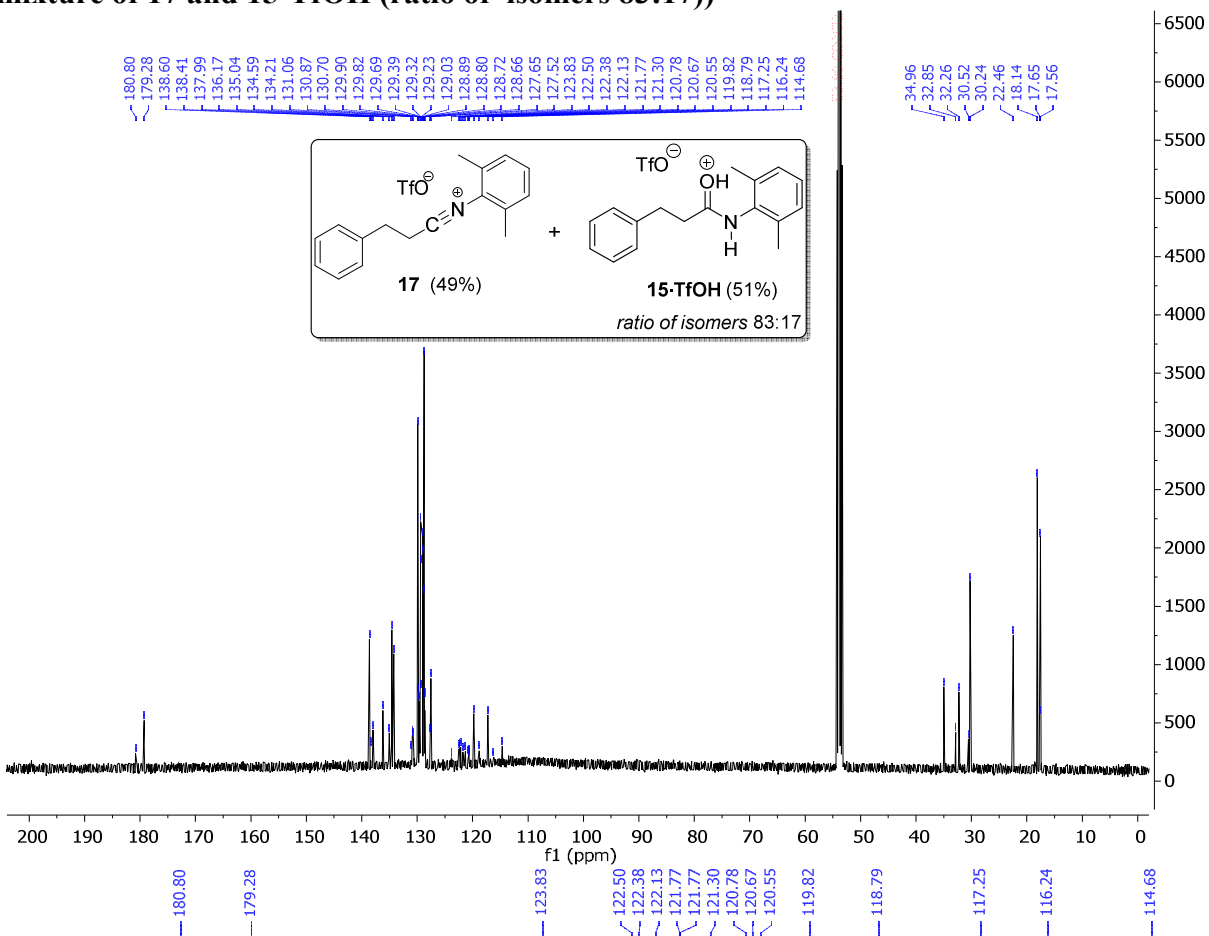
### Note

Based on spectra of **15** and spectra of **15**·TfOH it can be concluded, that the ratio of isomers and the NMR chemical shifts of signals are strongly depends on the pH of the solvent. Moreover, the addition of TfOH increased the ratio of minor isomer of **15** significantly.

**$^1\text{H}$  NMR spectrum of the reaction mixture of amide 15 with 1.1 equiv of  $\text{Tf}_2\text{O}$  in  $\text{CD}_2\text{Cl}_2$  (mixture of 17 and 15·TfOH (ratio of isomers 83:17))**



**$^{13}\text{C}$  NMR spectrum of the reaction mixture of amide 15 with 1.1 equiv of  $\text{Tf}_2\text{O}$  in  $\text{CD}_2\text{Cl}_2$  (mixture of 17 and 15·TfOH (ratio of isomers 83:17))**



$$\delta_{\text{C(A)}} = 122.1 \text{ (t, } J_{13\text{C-14N}} = 45.4 \text{ Hz)}$$

$$\delta_{\text{C(B)}} = 120.7 \text{ (t, } J_{13\text{C-14N}} = 14.4 \text{ Hz)}$$

### Note

Lit.: nitrilium carbon at  $\delta_{\text{C(A)}} = 123.4 \text{ (t, } J_{13\text{C-14N}} = 45.6 \text{ Hz)}^1$

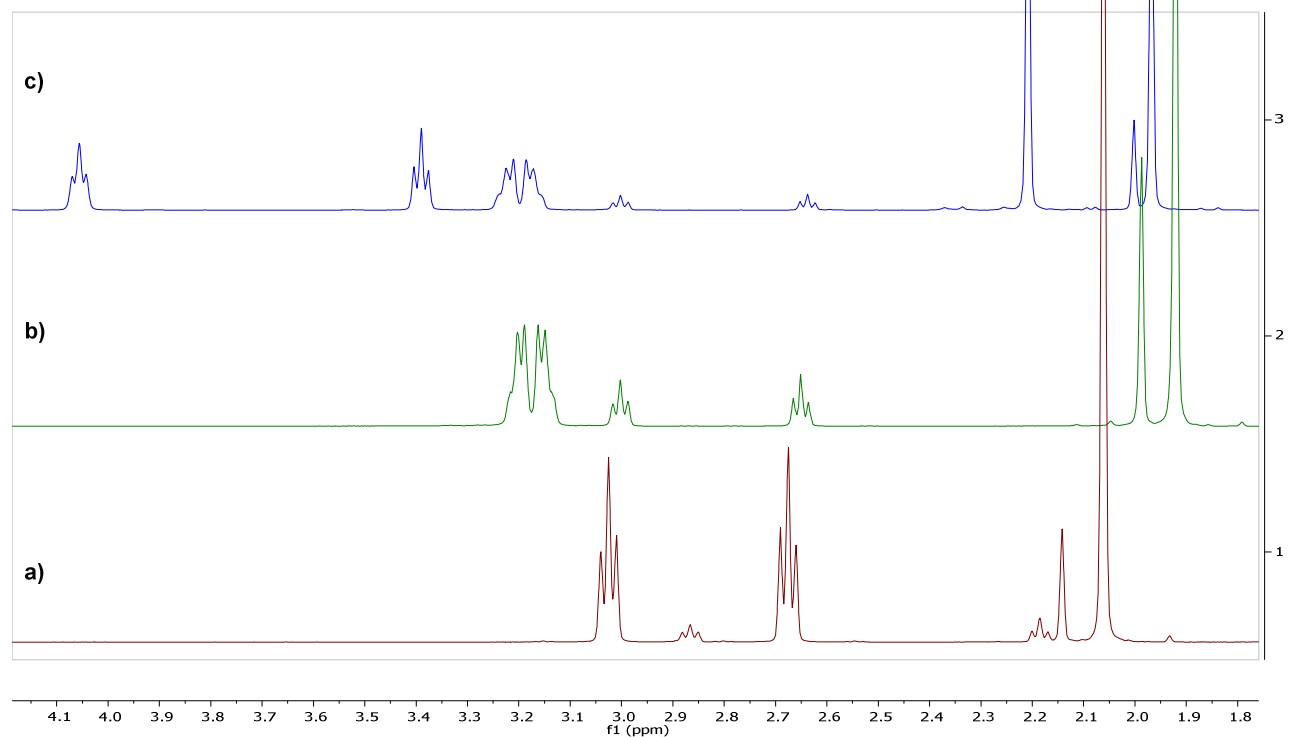
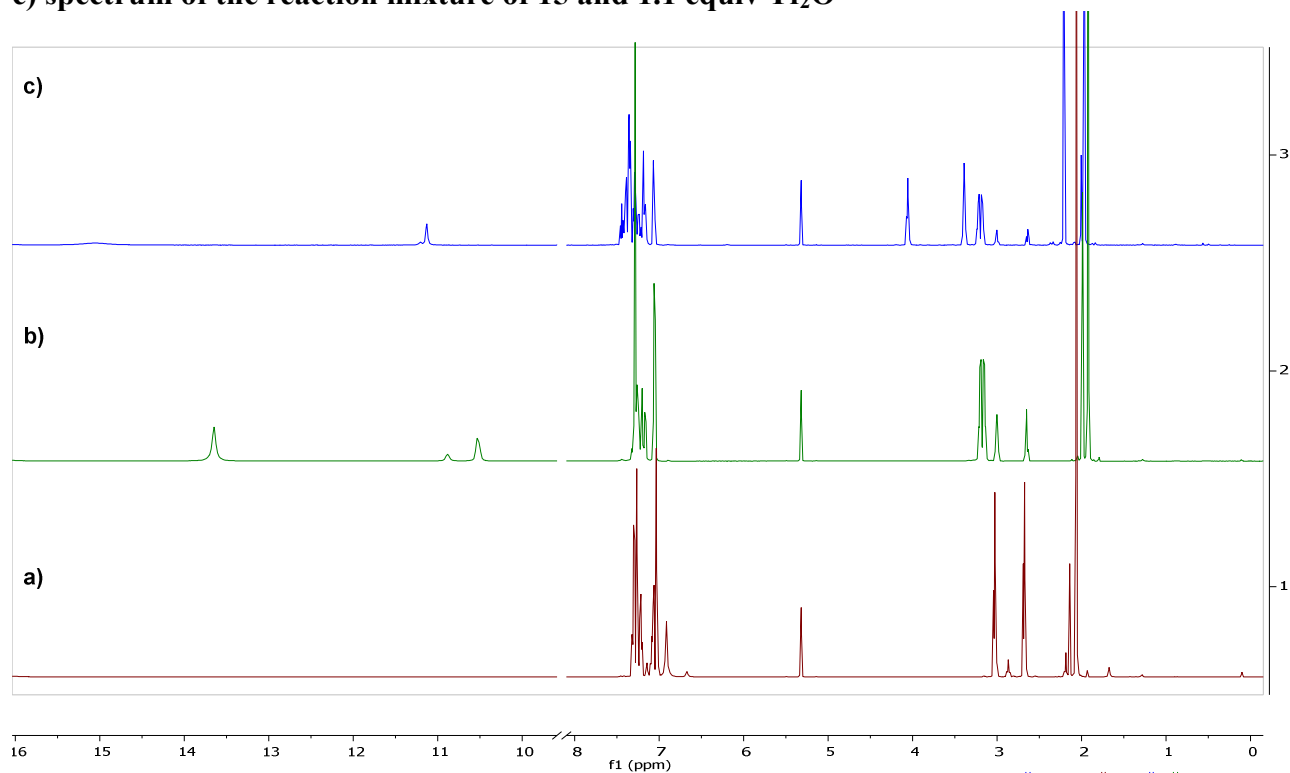
nitrilium *N*- $\alpha$  aromatic carbon at  $\delta_{\text{C(B)}} = 121.9 \text{ (t, } J_{13\text{C-14N}} = 13.5 \text{ Hz)}^1$

Stacked view of  $^1\text{H}$  NMR spectra obtained by the study of  $\text{Tf}_2\text{O}$ -mediated activation of amide **15** in  $\text{CD}_2\text{Cl}_2$ .

a) spectrum of **15**

b) spectrum of the mixture of **15** and 1.1 equiv of  $\text{TfOH}$

c) spectrum of the reaction mixture of **15** and 1.1 equiv  $\text{Tf}_2\text{O}$

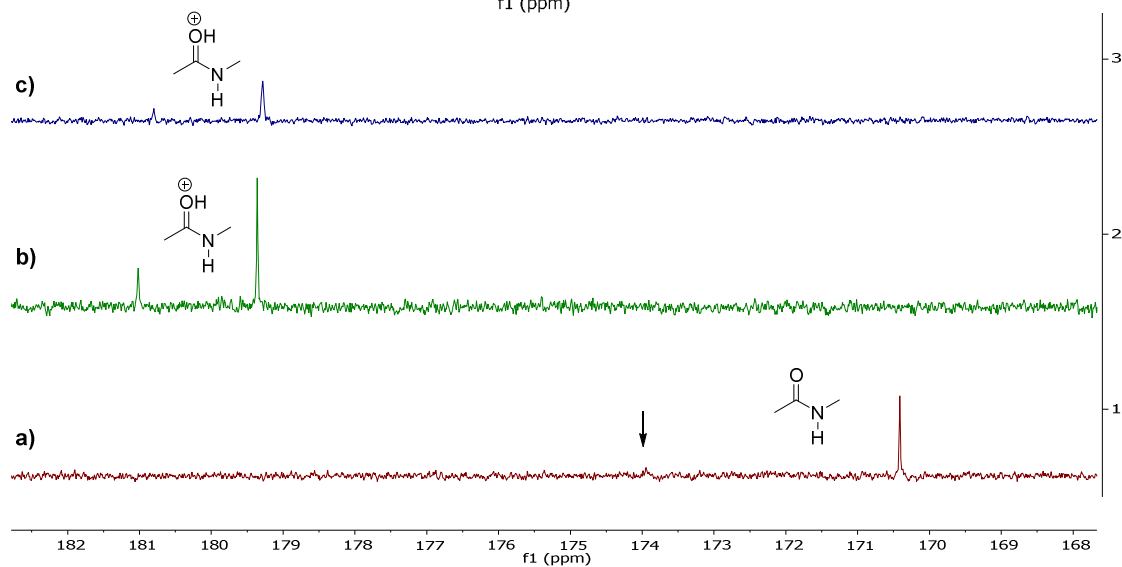
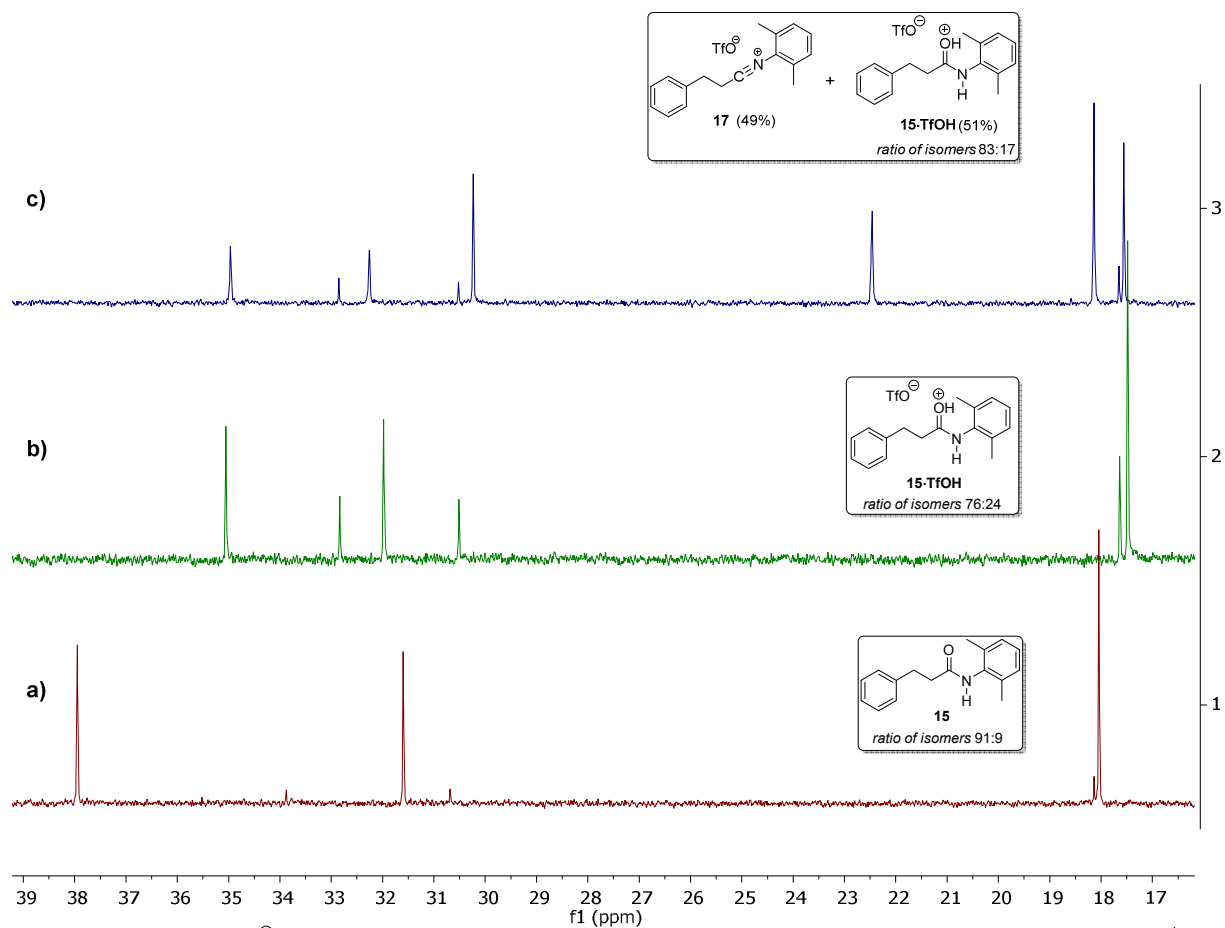


Stacked view of  $^{13}\text{H}$  NMR spectra obtained by the study of  $\text{Tf}_2\text{O}$ -mediated activation of amide 15 in  $\text{CD}_2\text{Cl}_2$ . (aliphatic section of spectra)

a) spectrum of 15

b) spectrum of the mixture of 15 and 1.1 equiv of TfOH

c) spectrum of the reaction mixture of 15 and 1.1 equiv  $\text{Tf}_2\text{O}$





## References

- (1) Huang, P.-Q.; Huang, Y.-H.; Geng, H.; Ye, J.-L. *Sci. Rep.* **2016**, *6*, 28801-28811.