

# **Metalated N-Heterocyclic Reagents Prepared by the Frustrated Lewis Pair $\text{TMPMgCl}\cdot\text{BF}_3$ and their Addition to Aromatic Aldehydes and Activated Ketones**

Sophia M. Manolikakes, Milica Jaric, Konstantin Karaghiosoff and Paul Knochel

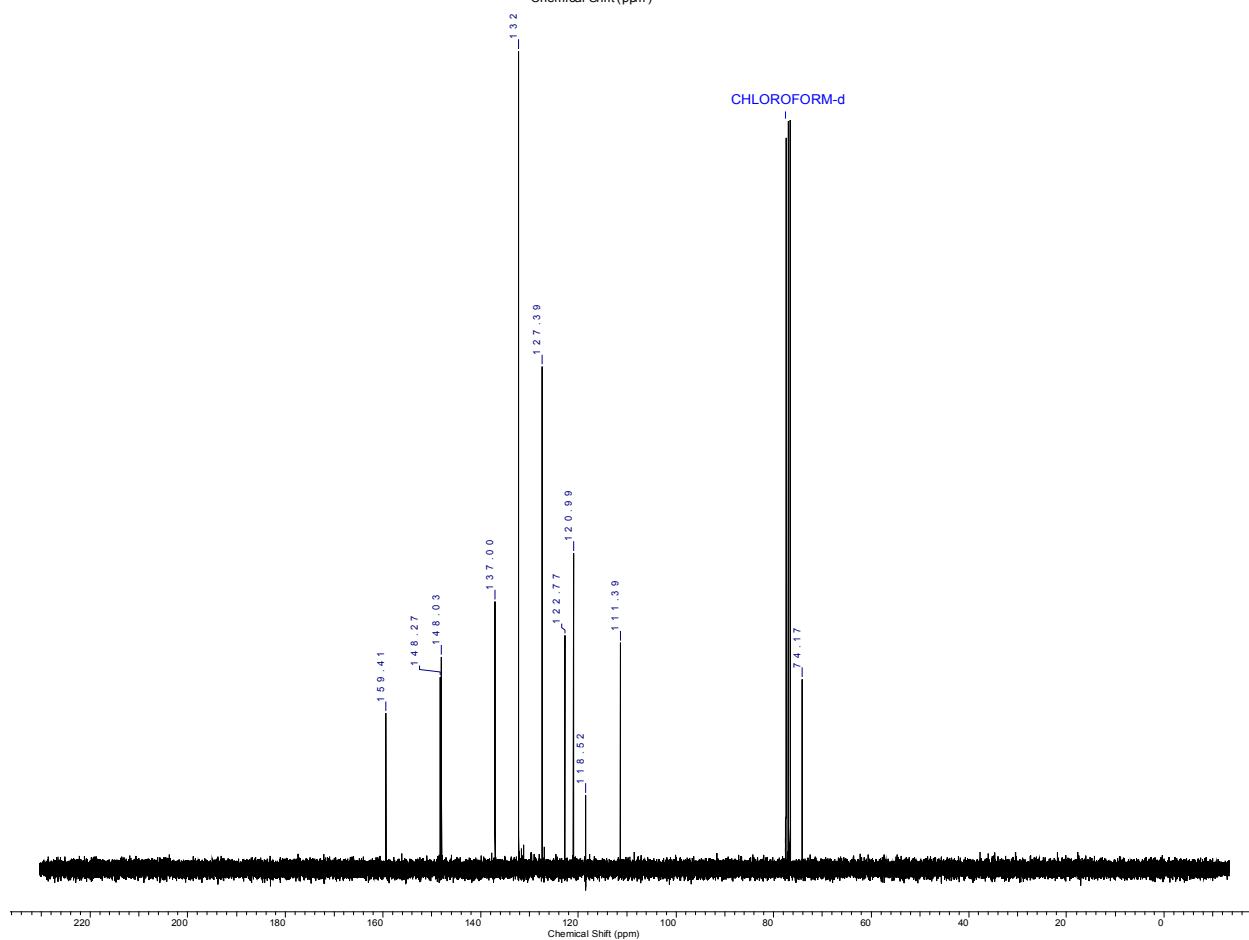
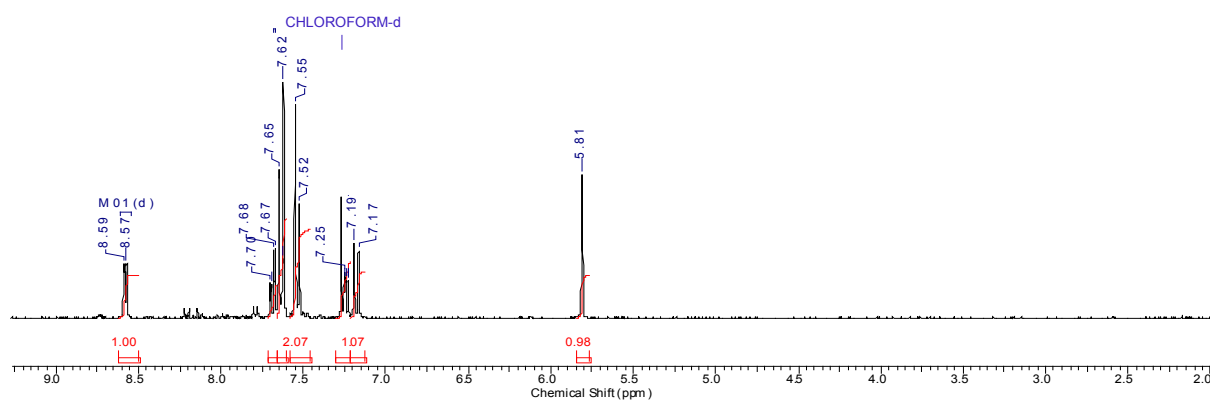
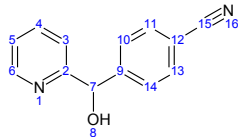
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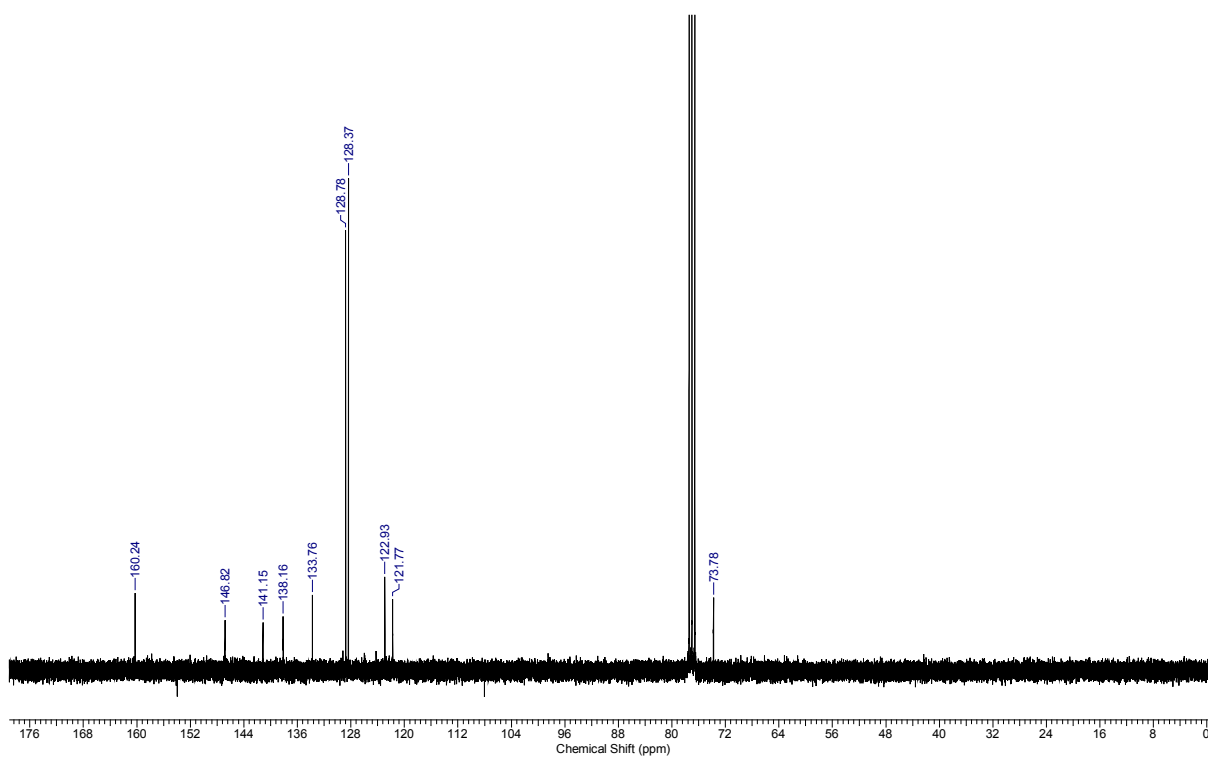
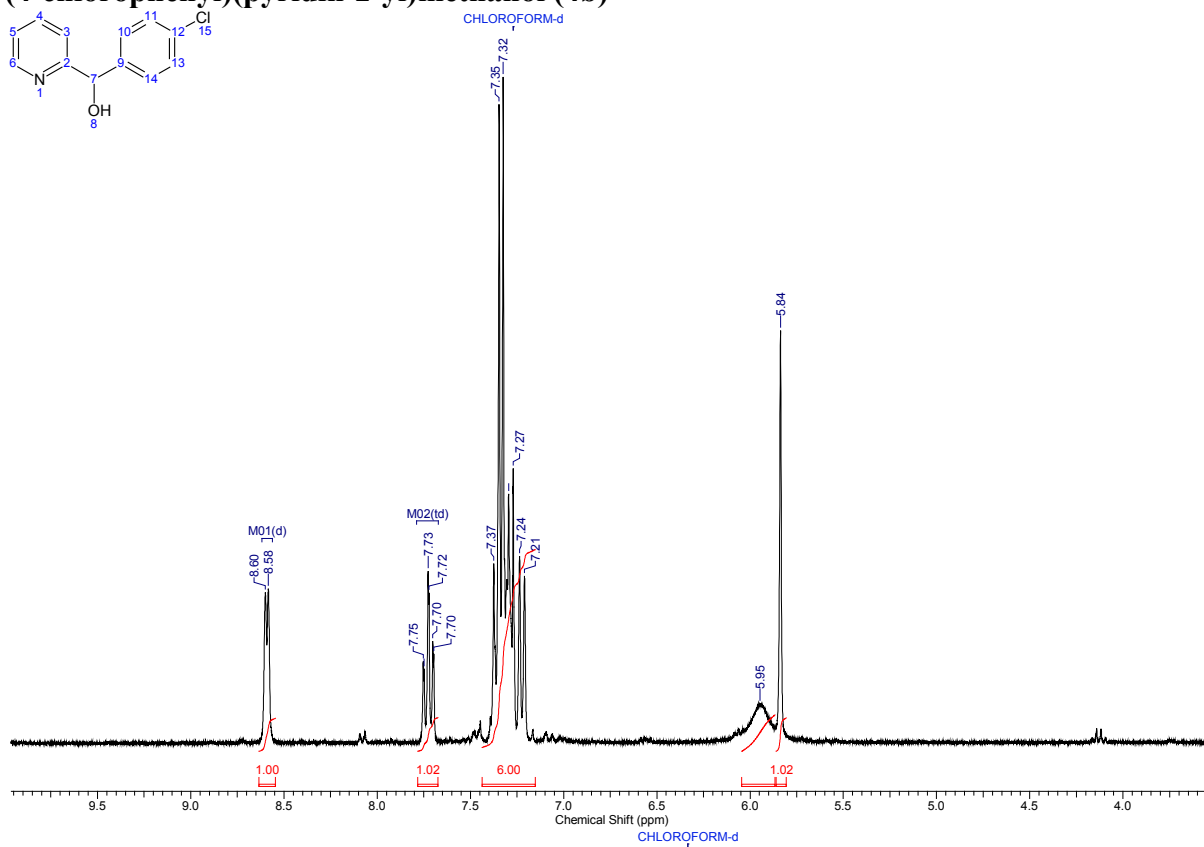
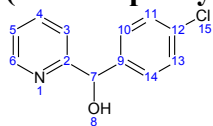
**Supporting Information**

**NMR spectra**

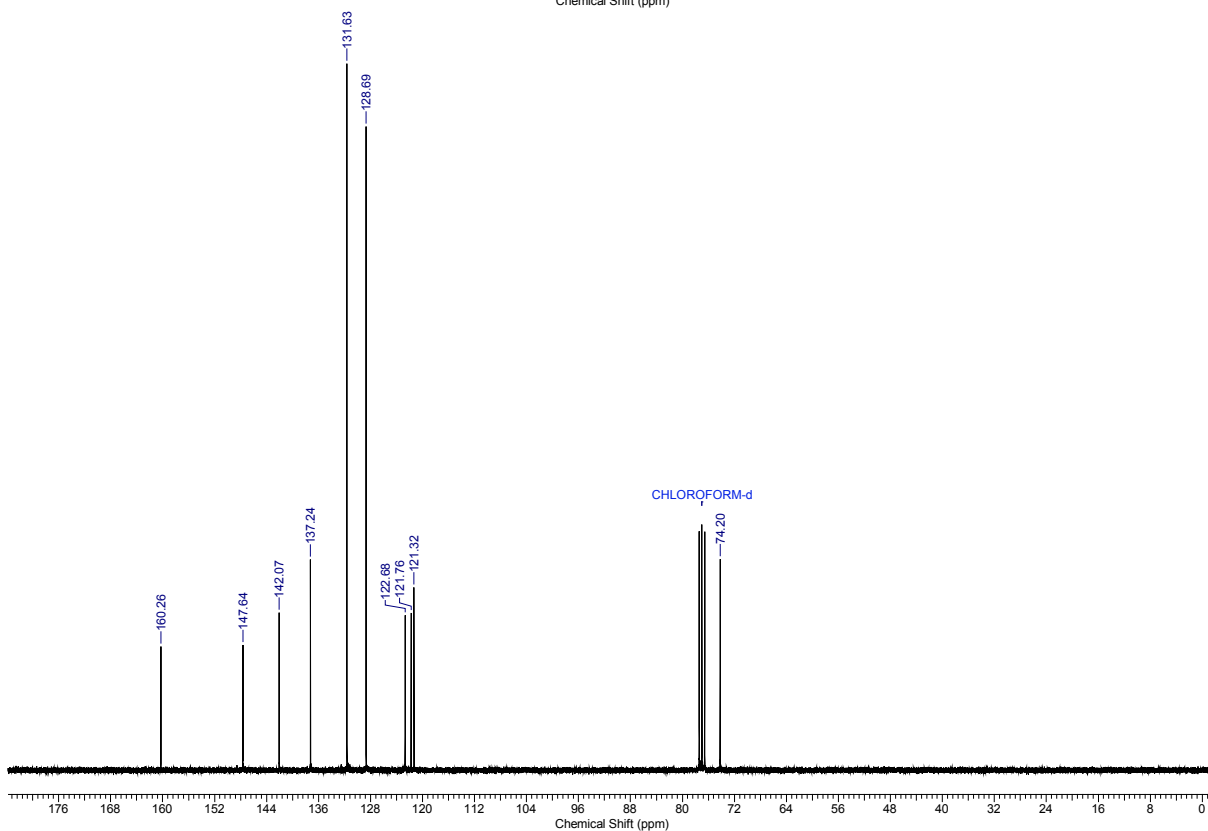
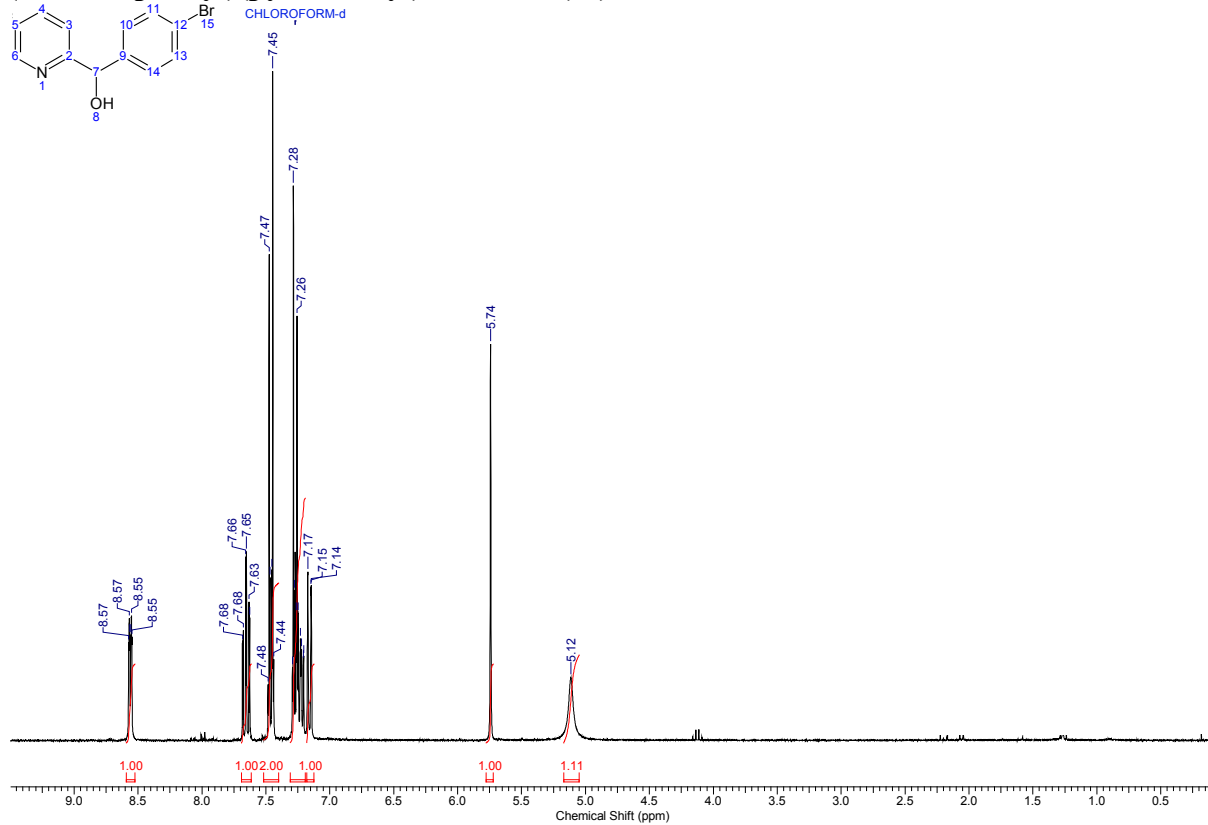
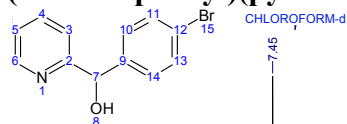
### 4-[hydroxy(pyridin-2-yl)methyl]benzonitrile (4a)



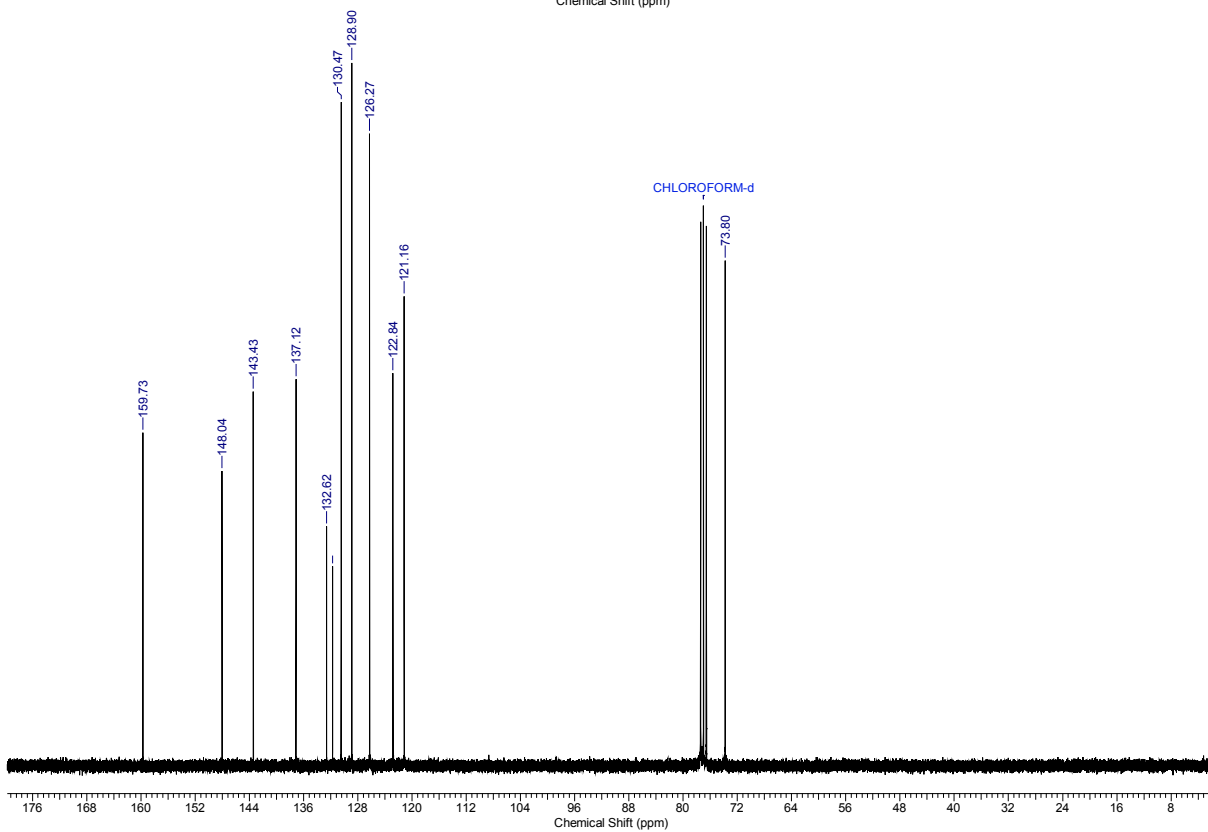
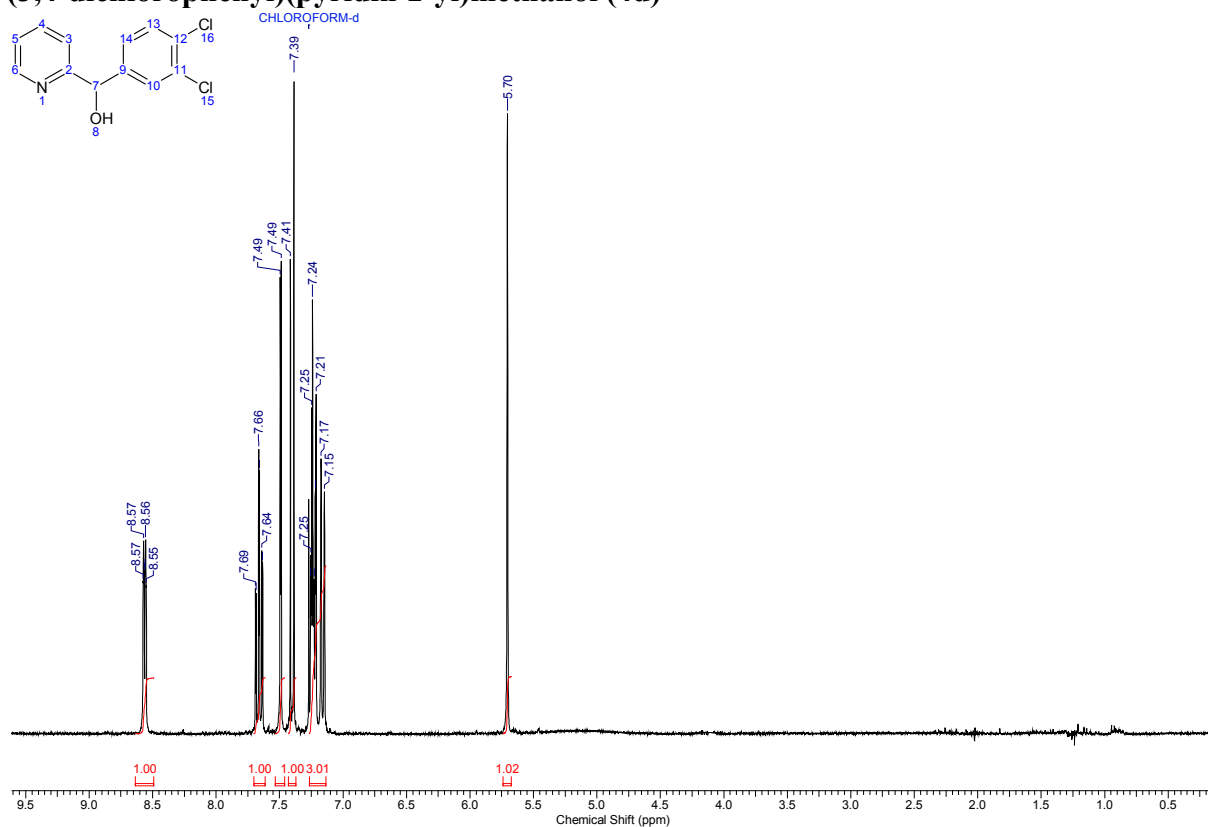
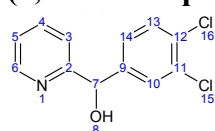
### (4-chlorophenyl)(pyridin-2-yl)methanol (4b)



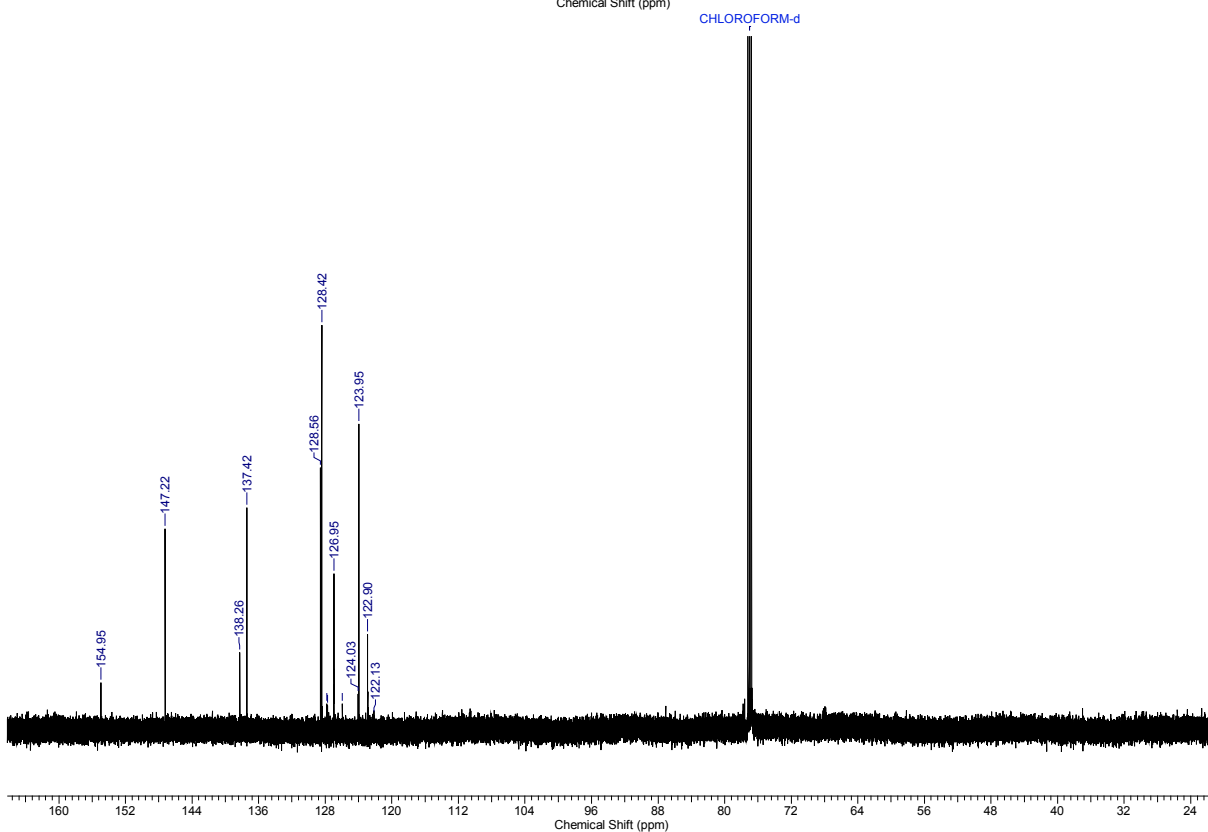
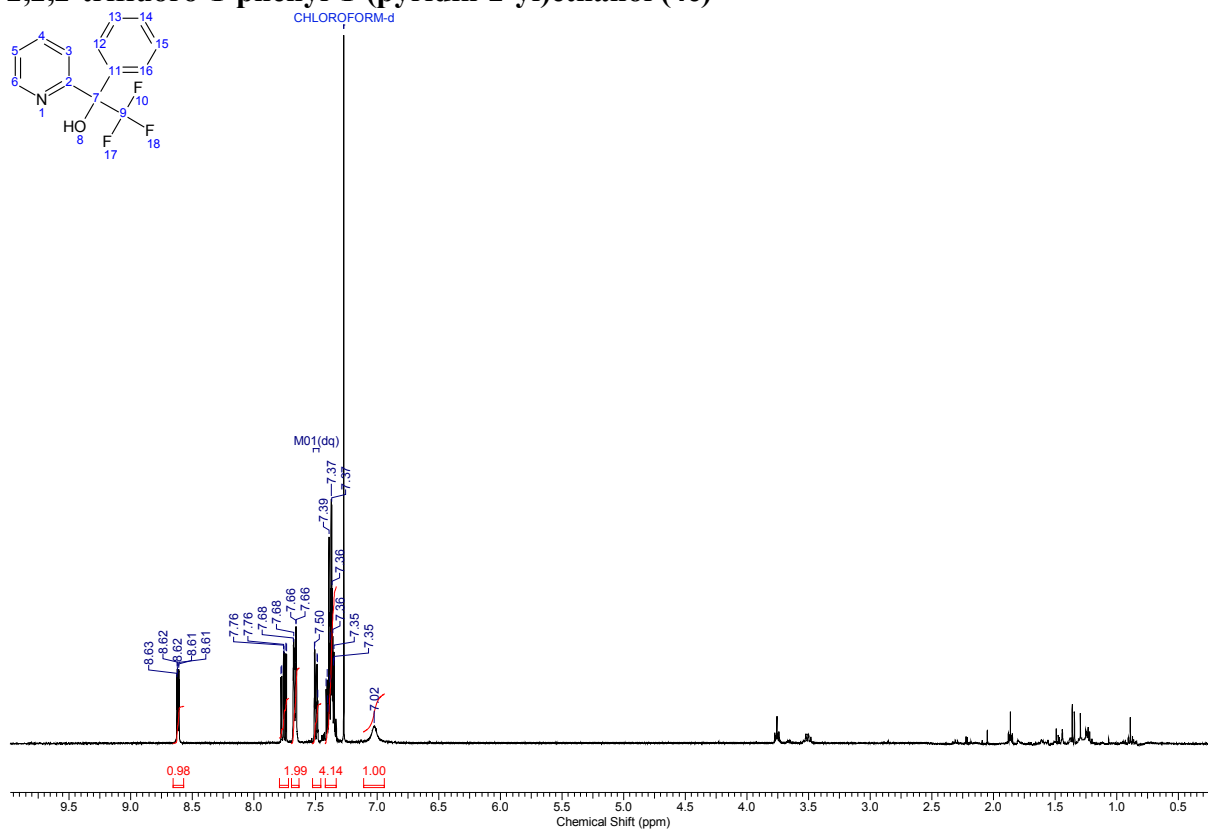
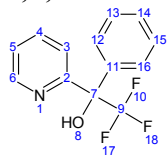
**(4-bromophenyl)(pyridin-2-yl)methanol (4c)**



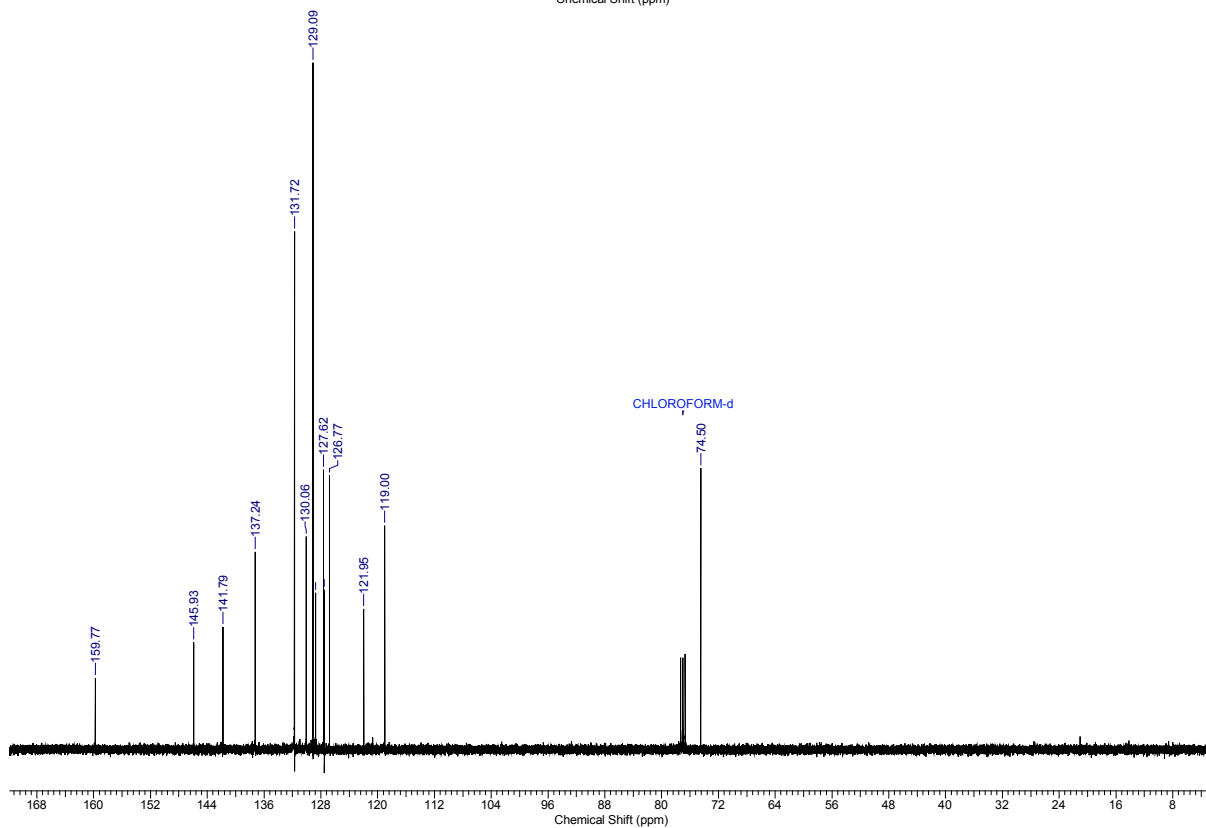
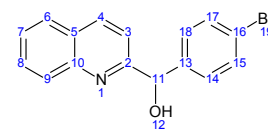
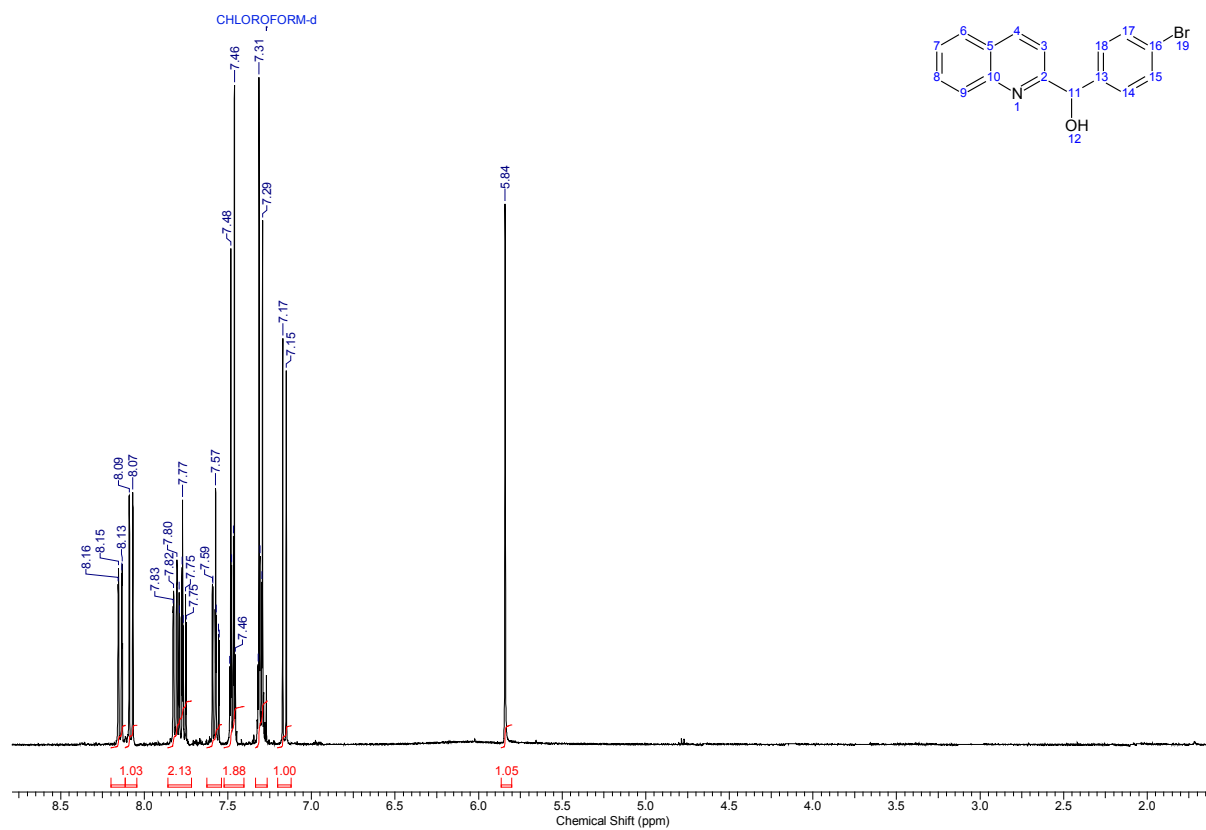
### (3,4-dichlorophenyl)(pyridin-2-yl)methanol (4d)



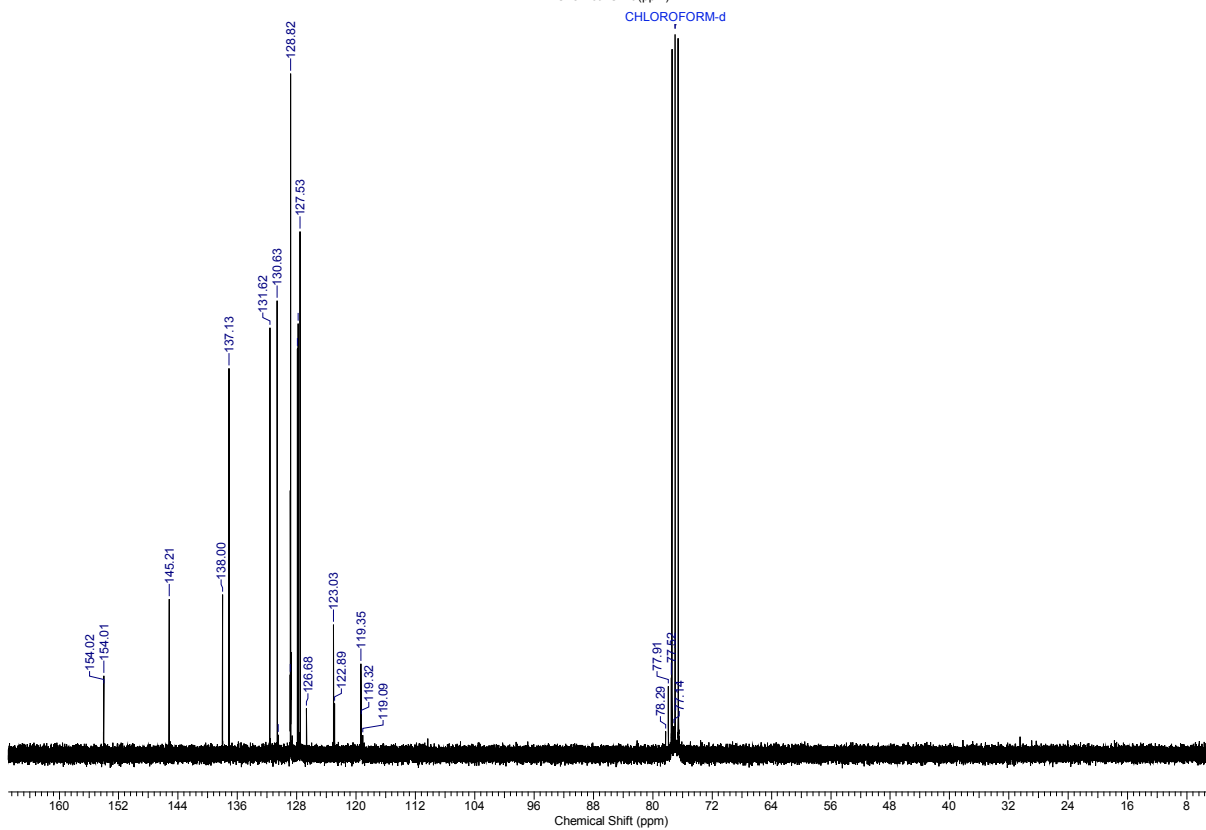
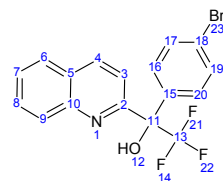
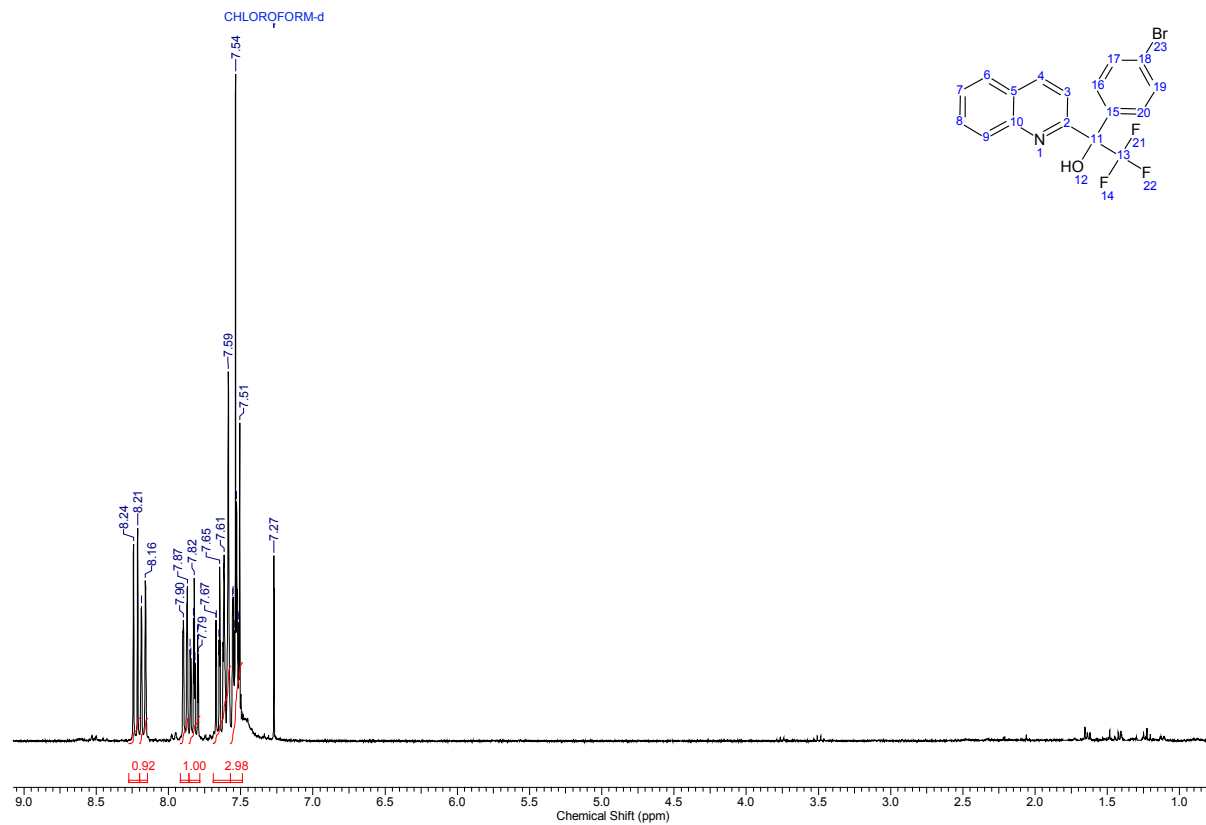
### 2,2,2-trifluoro-1-phenyl-1-(pyridin-2-yl)ethanol (4e)



### (4-bromophenyl)(quinolin-2-yl)methanol (4f)

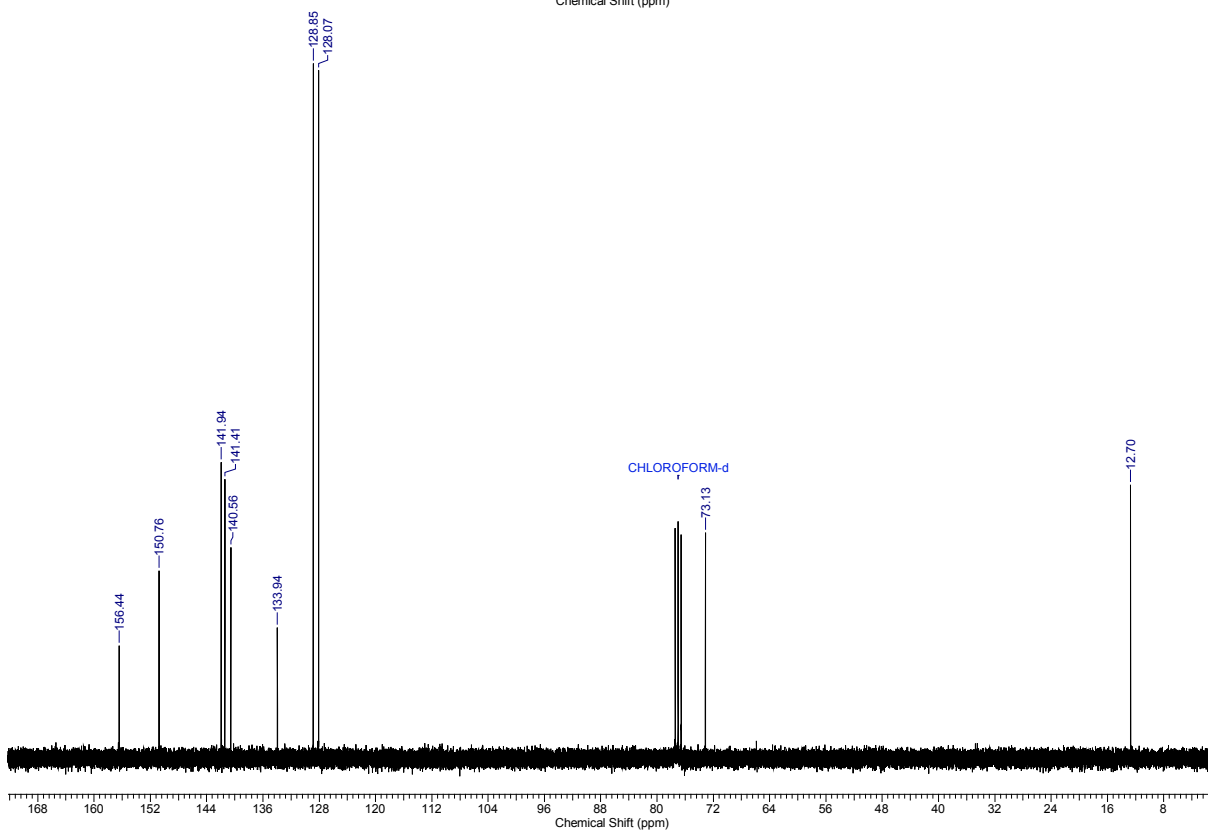
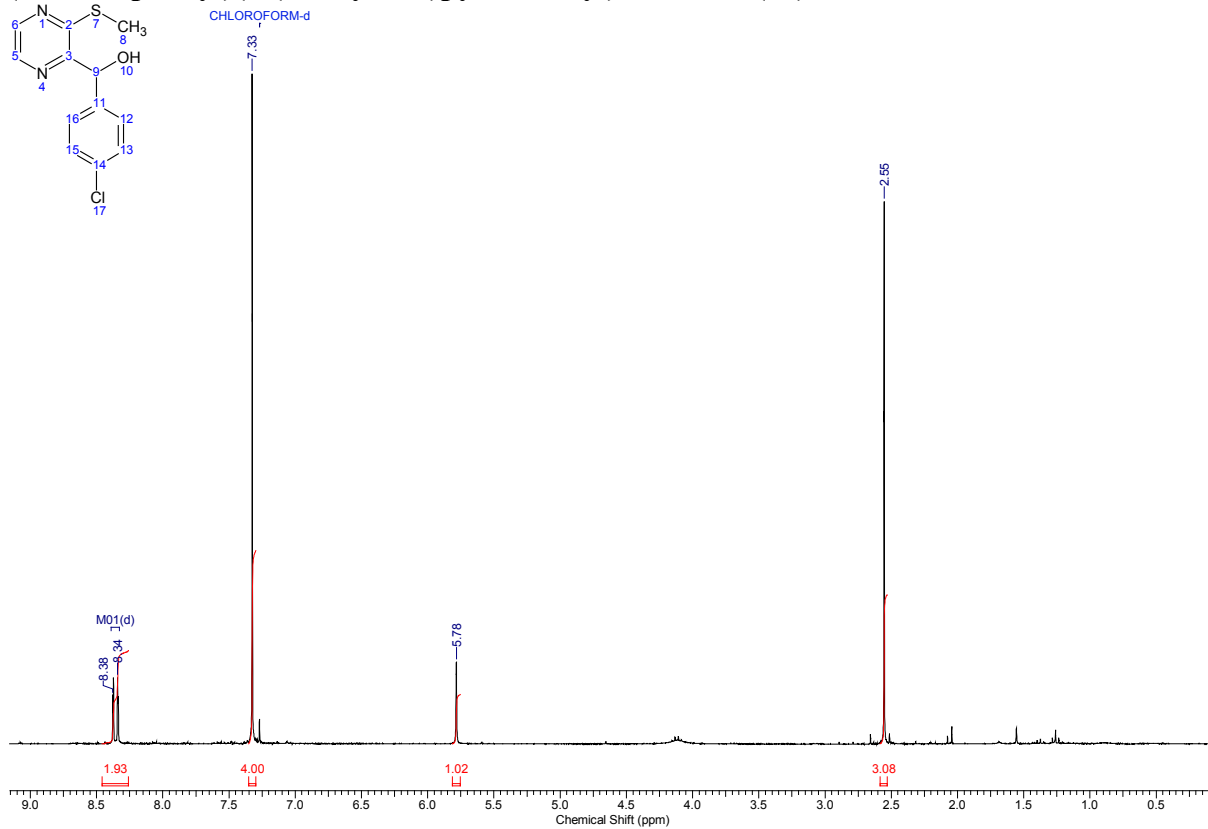
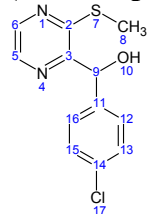


### 1-(4-bromophenyl)-2,2,2-trifluoro-1-(quinolin-2-yl)ethanol (4g)

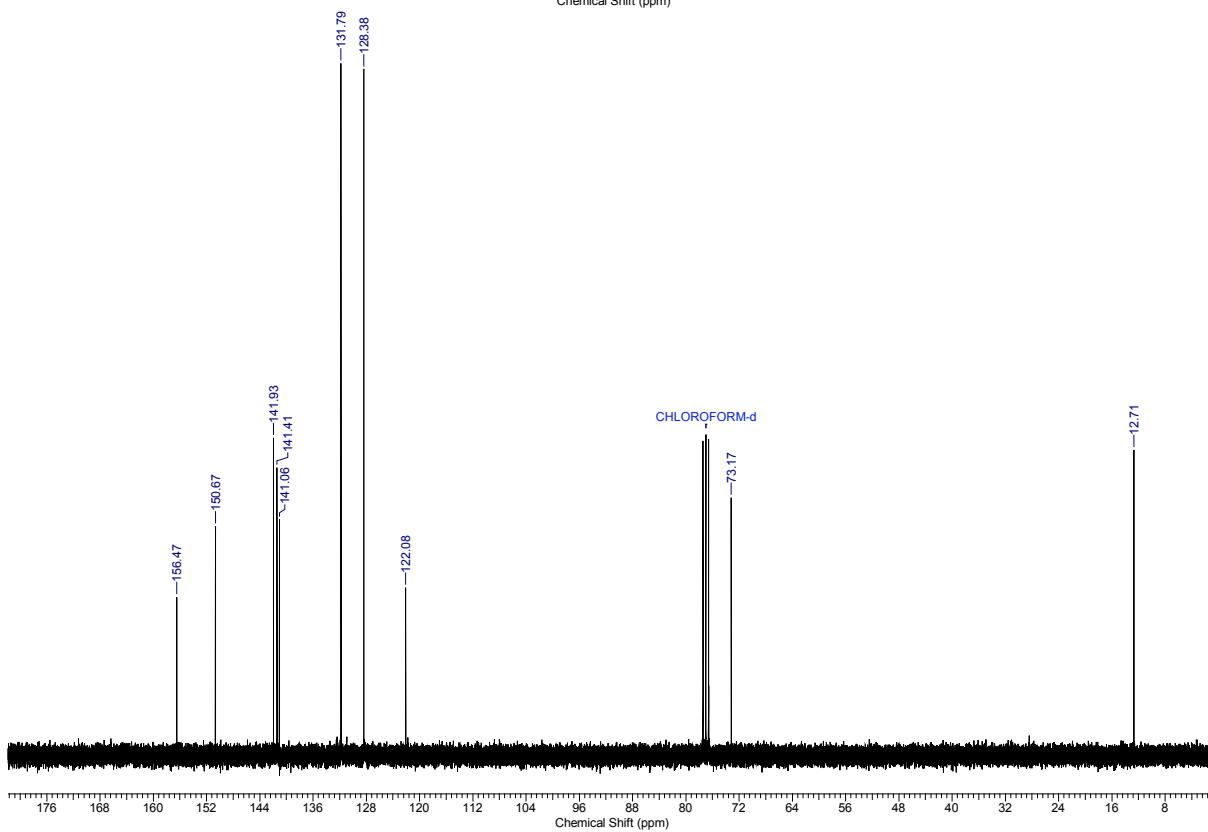
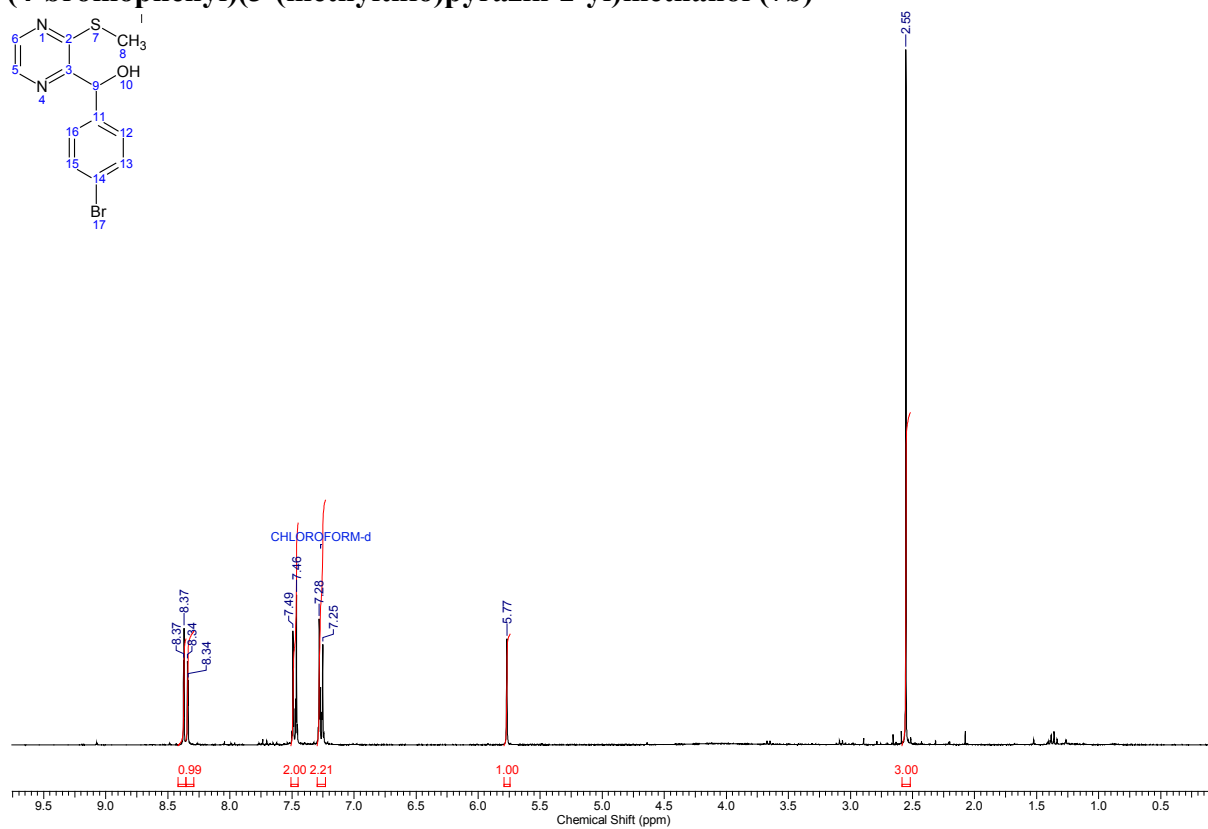
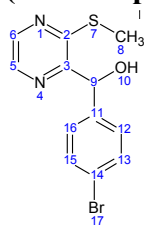




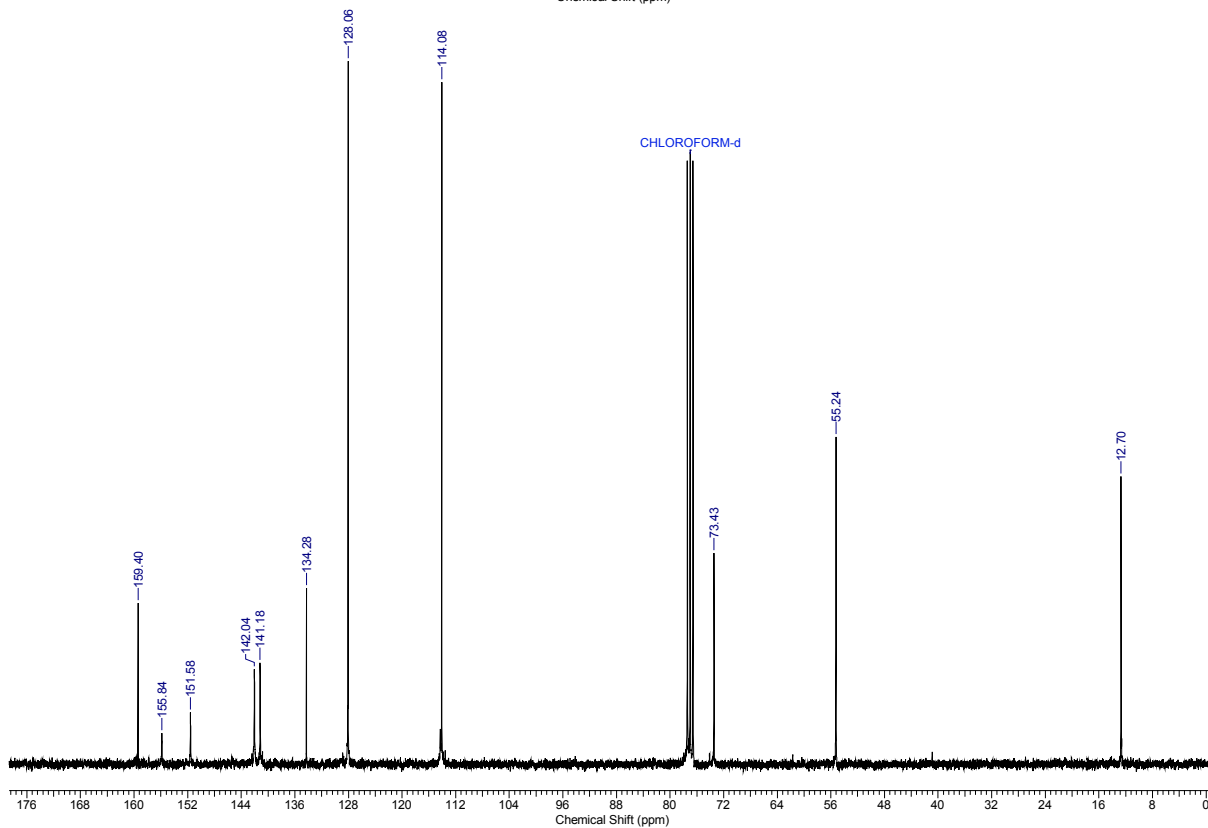
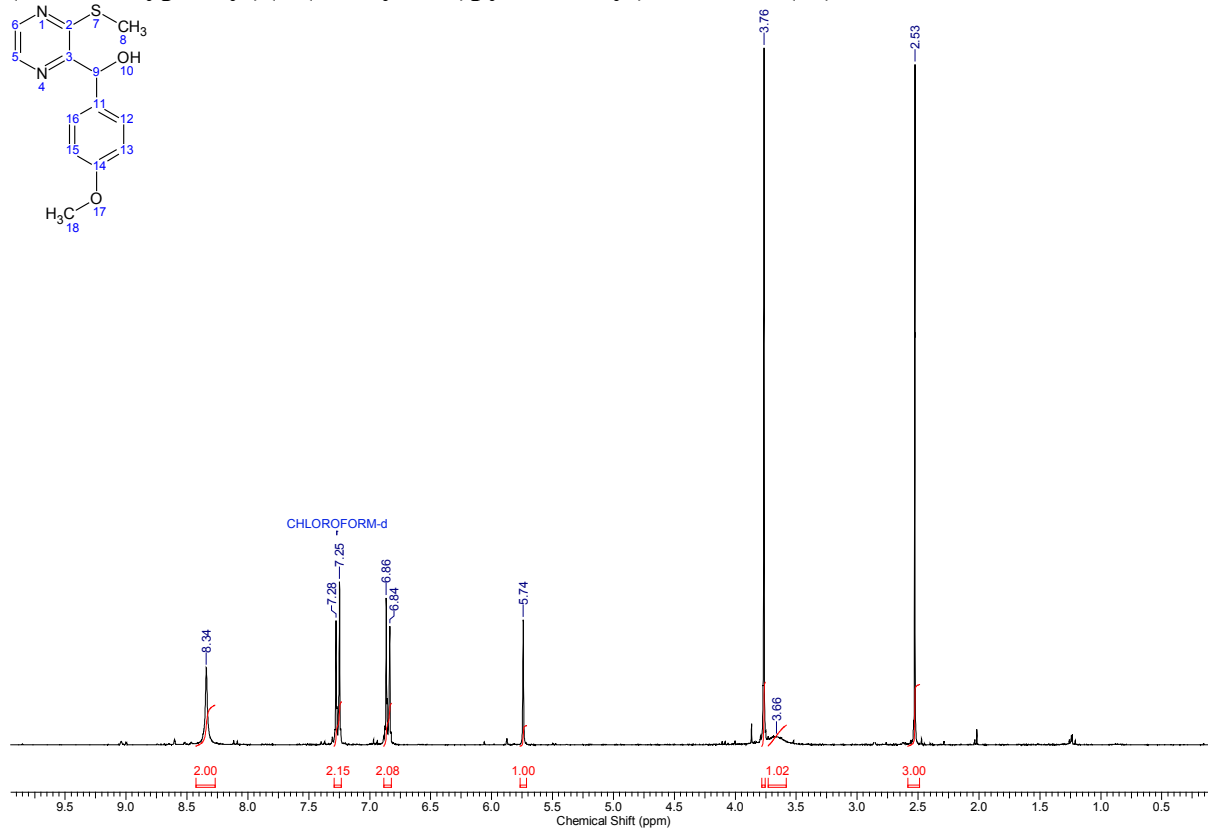
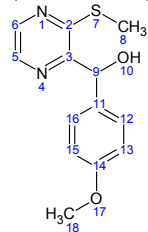
### (4-chlorophenyl)(3-(methylthio)pyrazin-2-yl)methanol (7a)



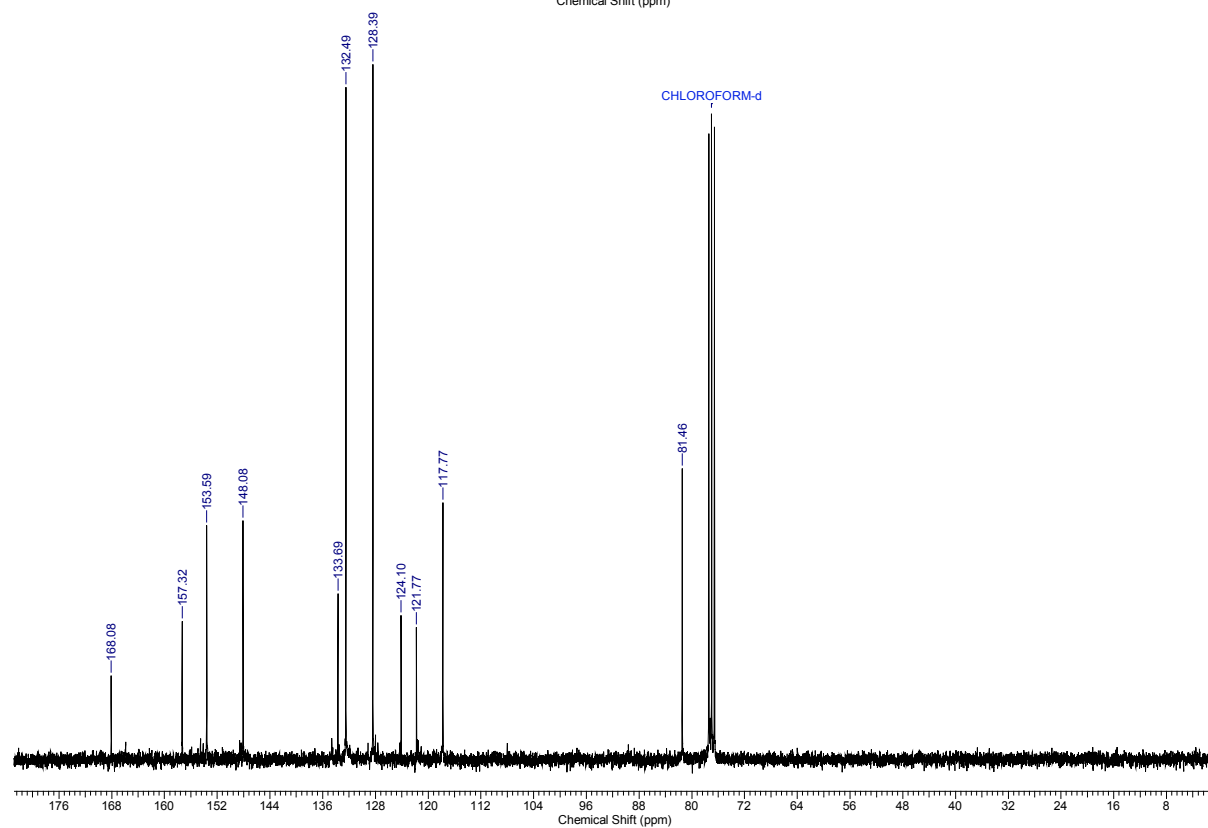
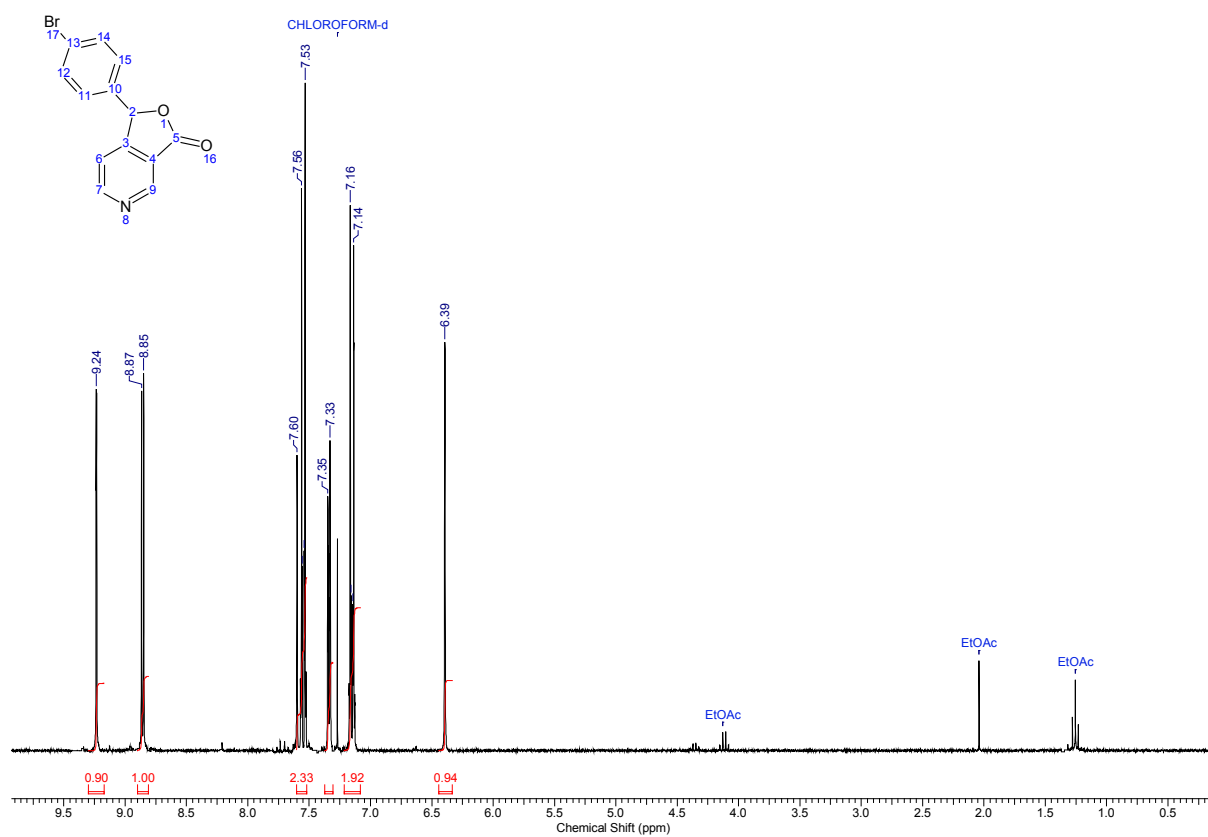
### (4-bromophenyl)(3-(methylthio)pyrazin-2-yl)methanol (7b)



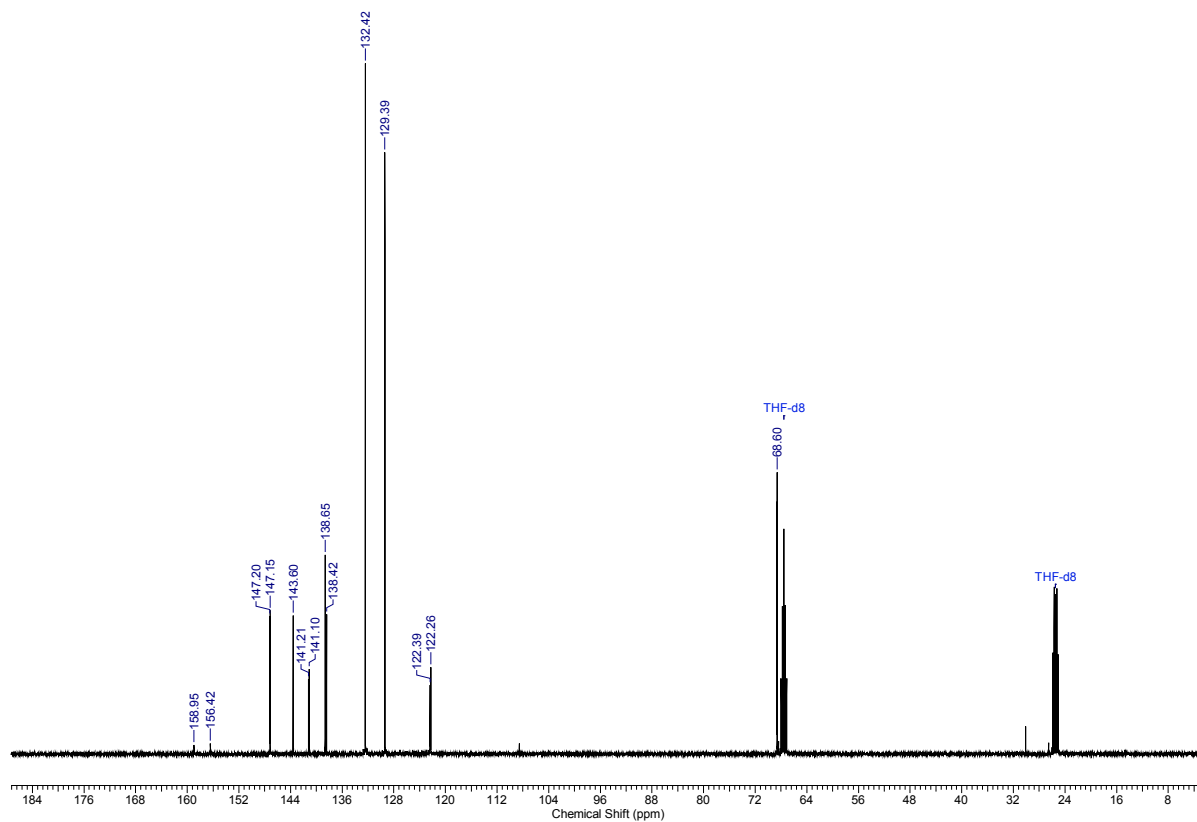
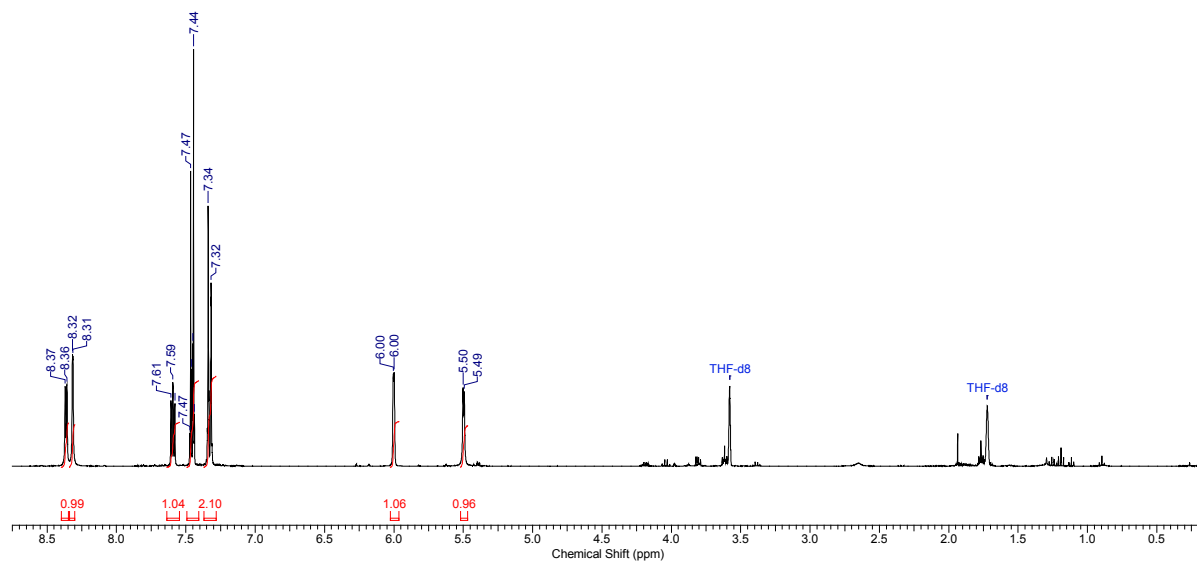
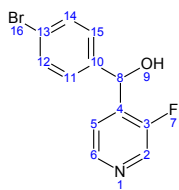
**(4-methoxyphenyl)(3-(methylthio)pyrazin-2-yl)methanol (7c)**



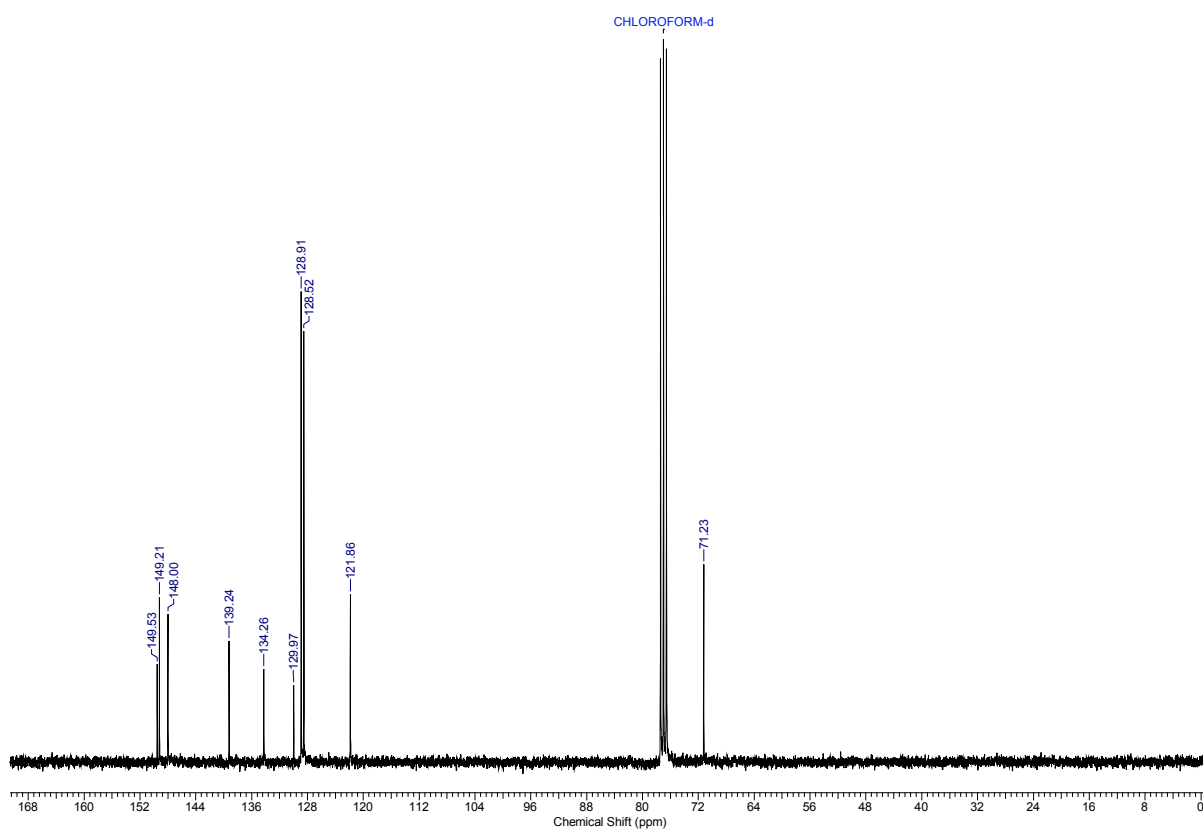
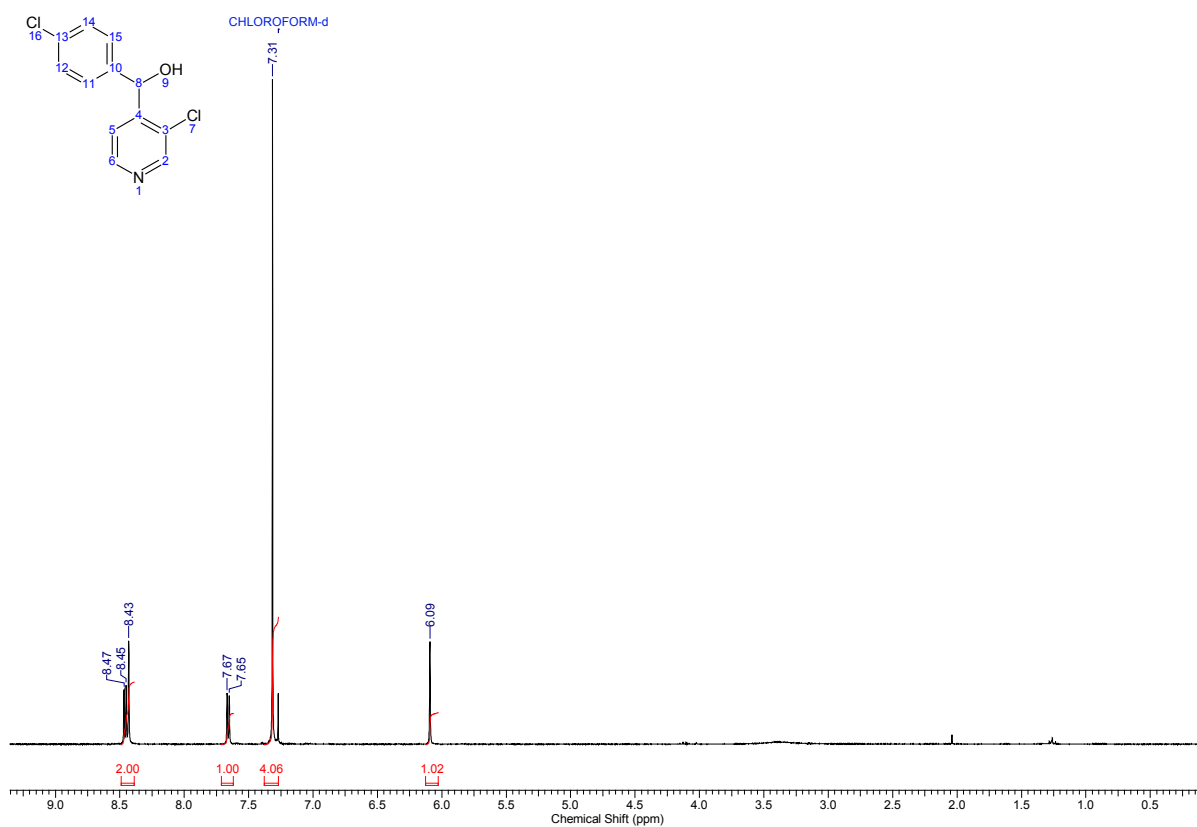
### 1-(4-bromophenyl)furo[3,4-c]pyridin-3(1H)-one (10a)



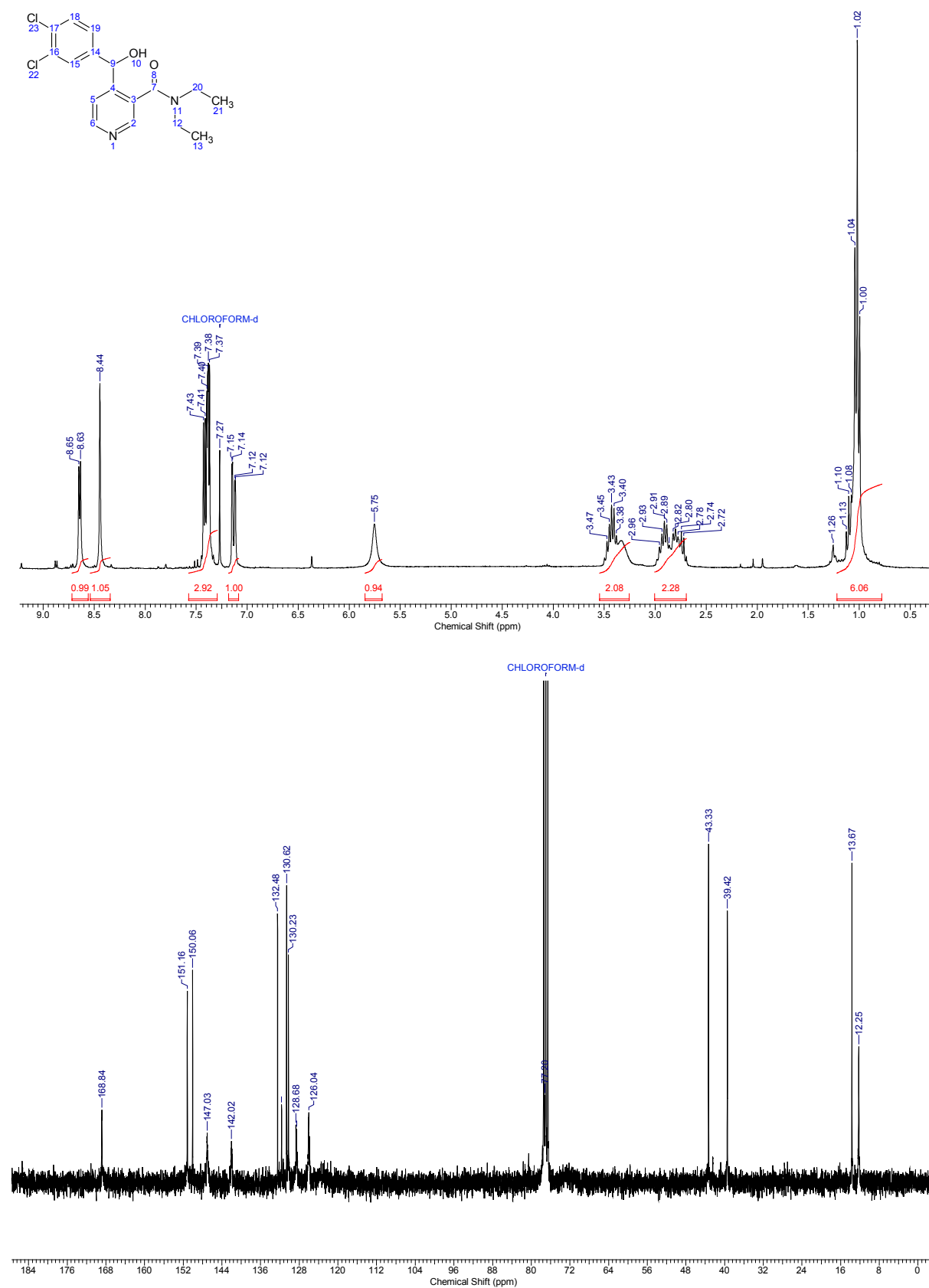
### (4-bromophenyl)(3-fluoropyridin-4-yl)methanol (10b)



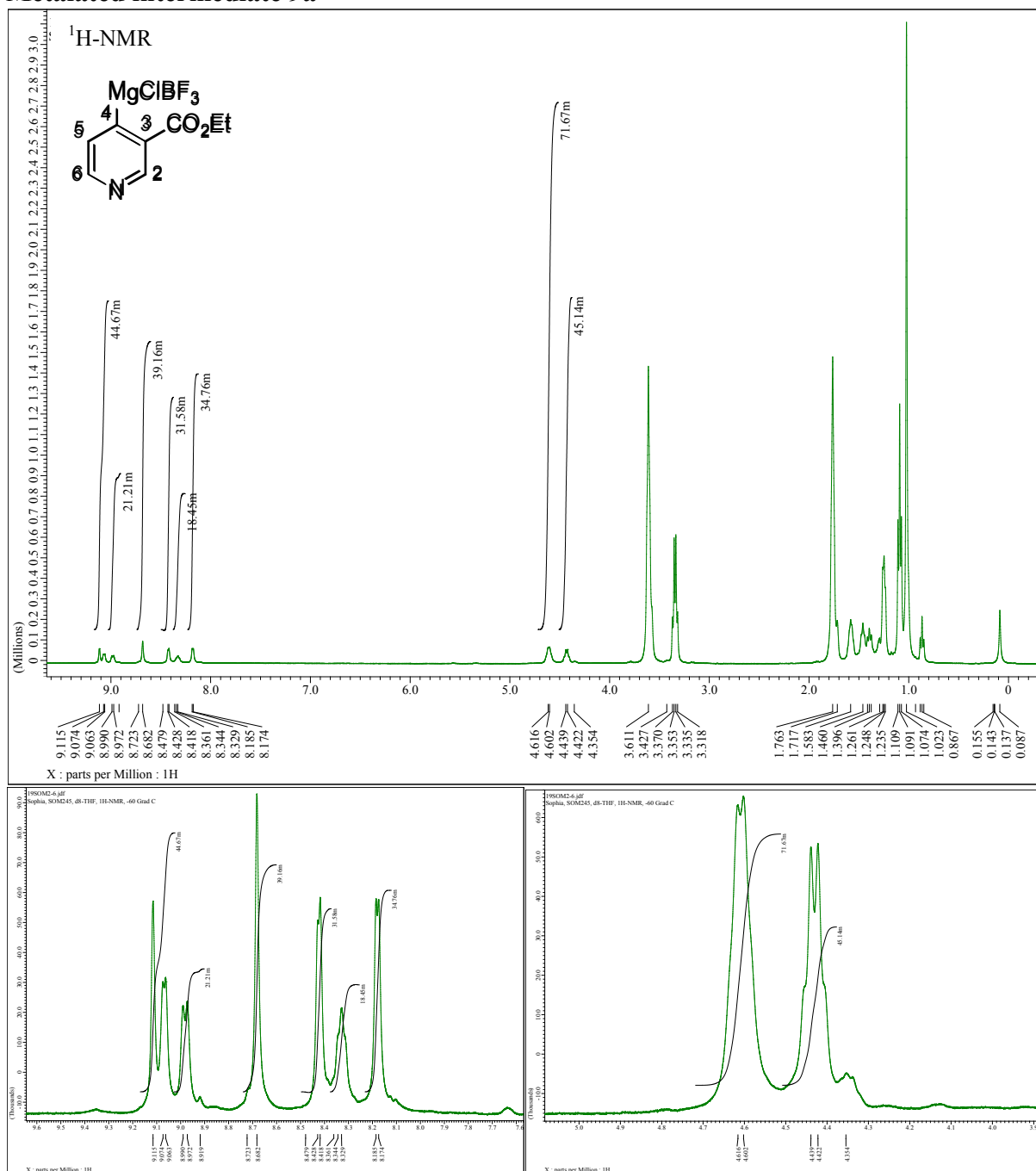
### (4-chlorophenyl)(3-chloropyridin-4-yl)methanol (10c)



### 4-((3,4-dichlorophenyl)(hydroxy)methyl)-*N,N*-diethylnicotinamide (10d)

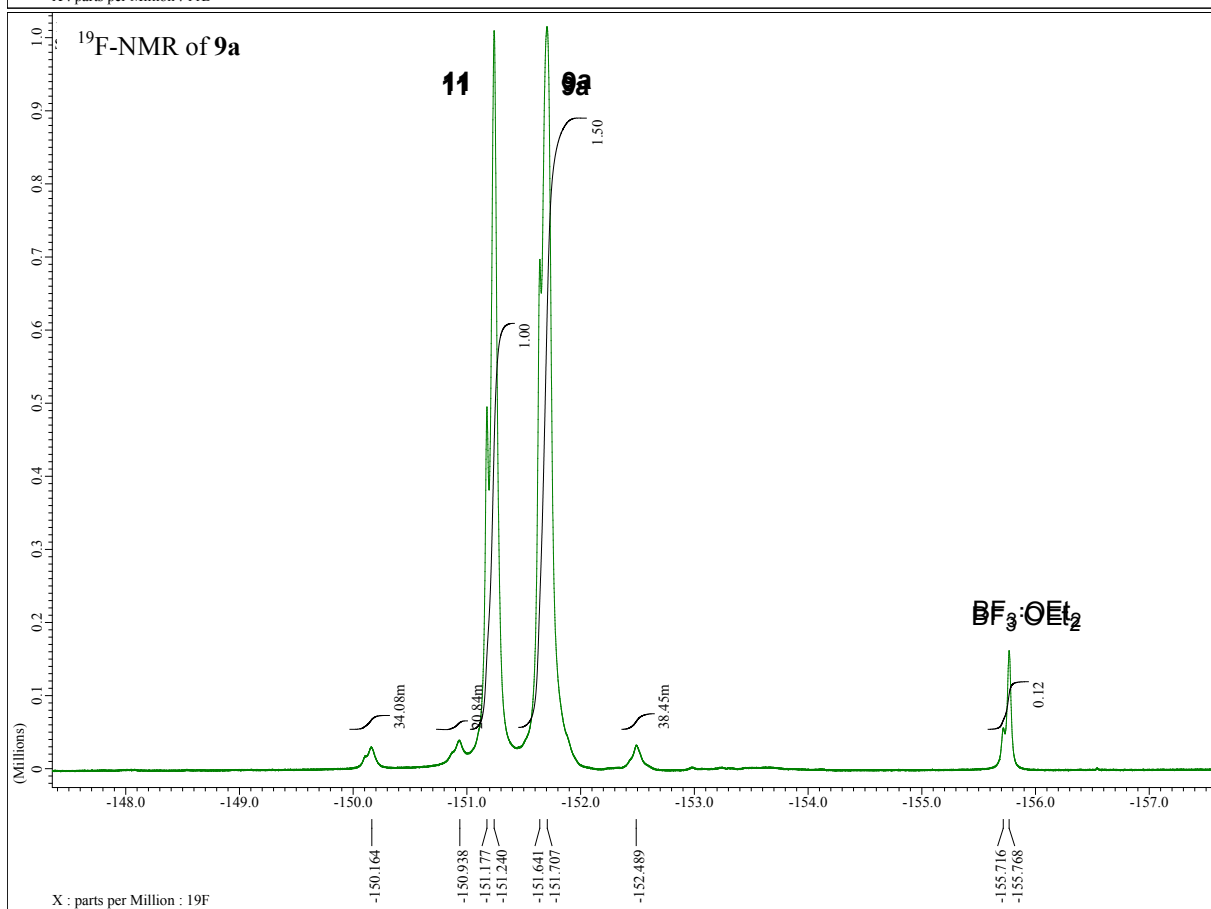
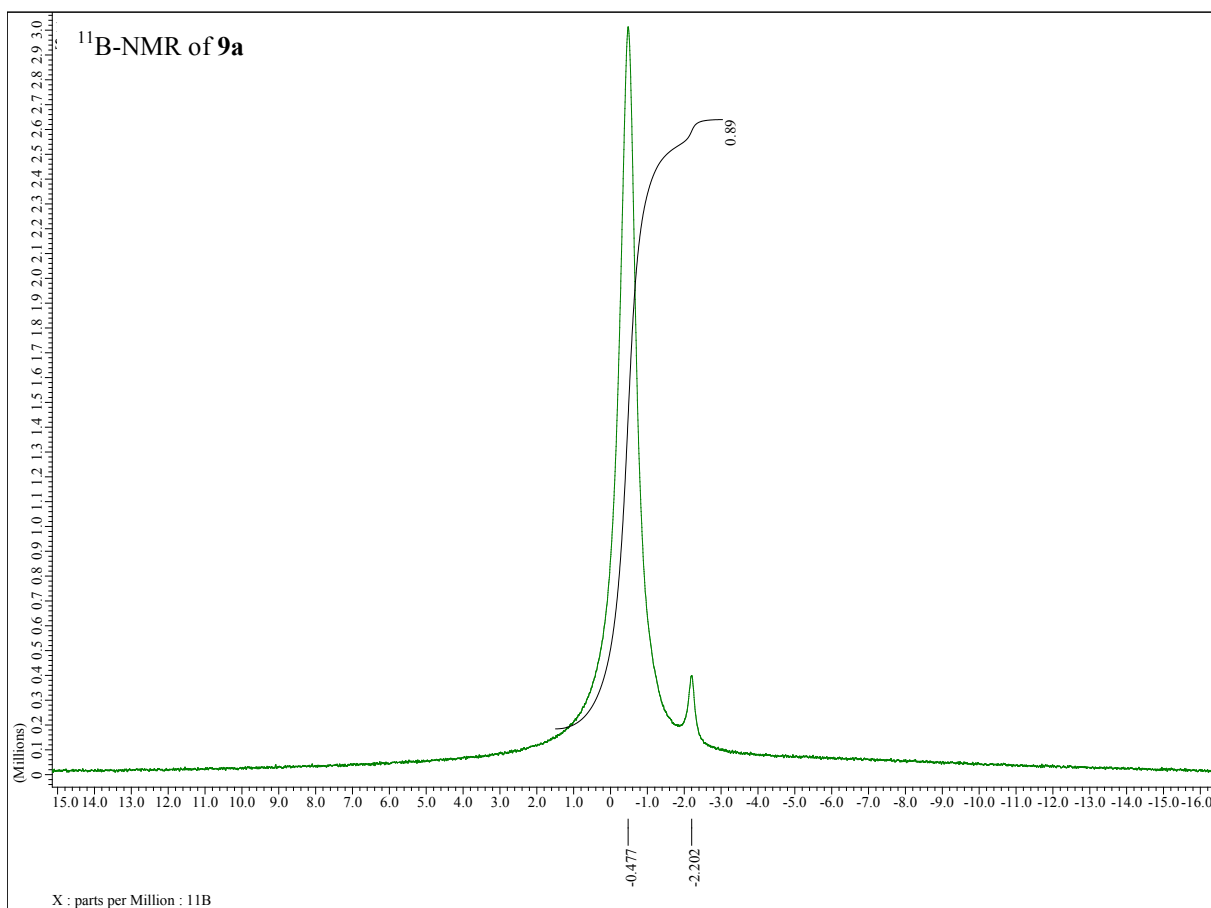


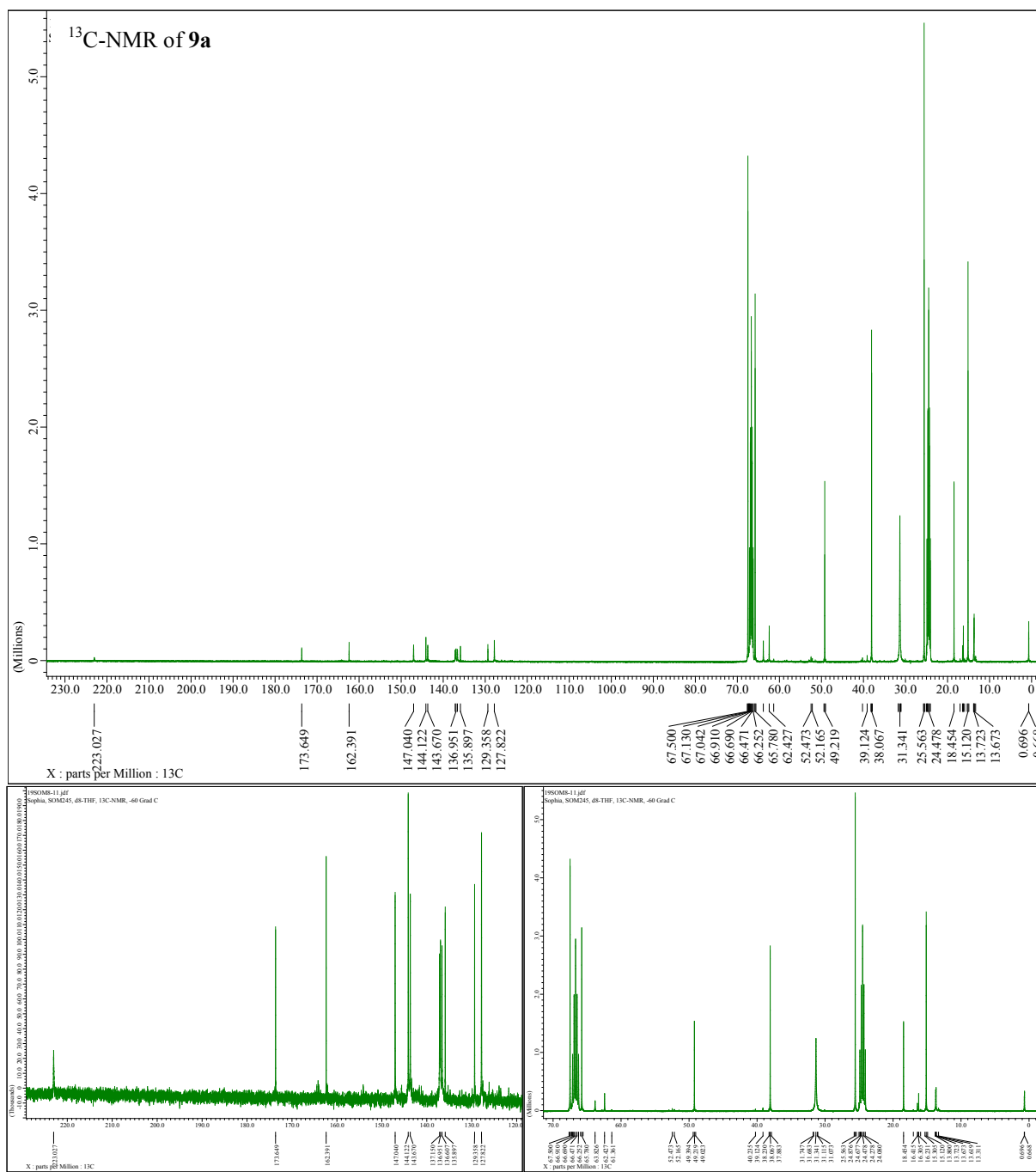
### Metalated intermediate **9a**



**<sup>1</sup>H-NMR** expansions of intermediate **9a** of the aromatic region (left) and the CH<sub>2</sub> signal region (right).

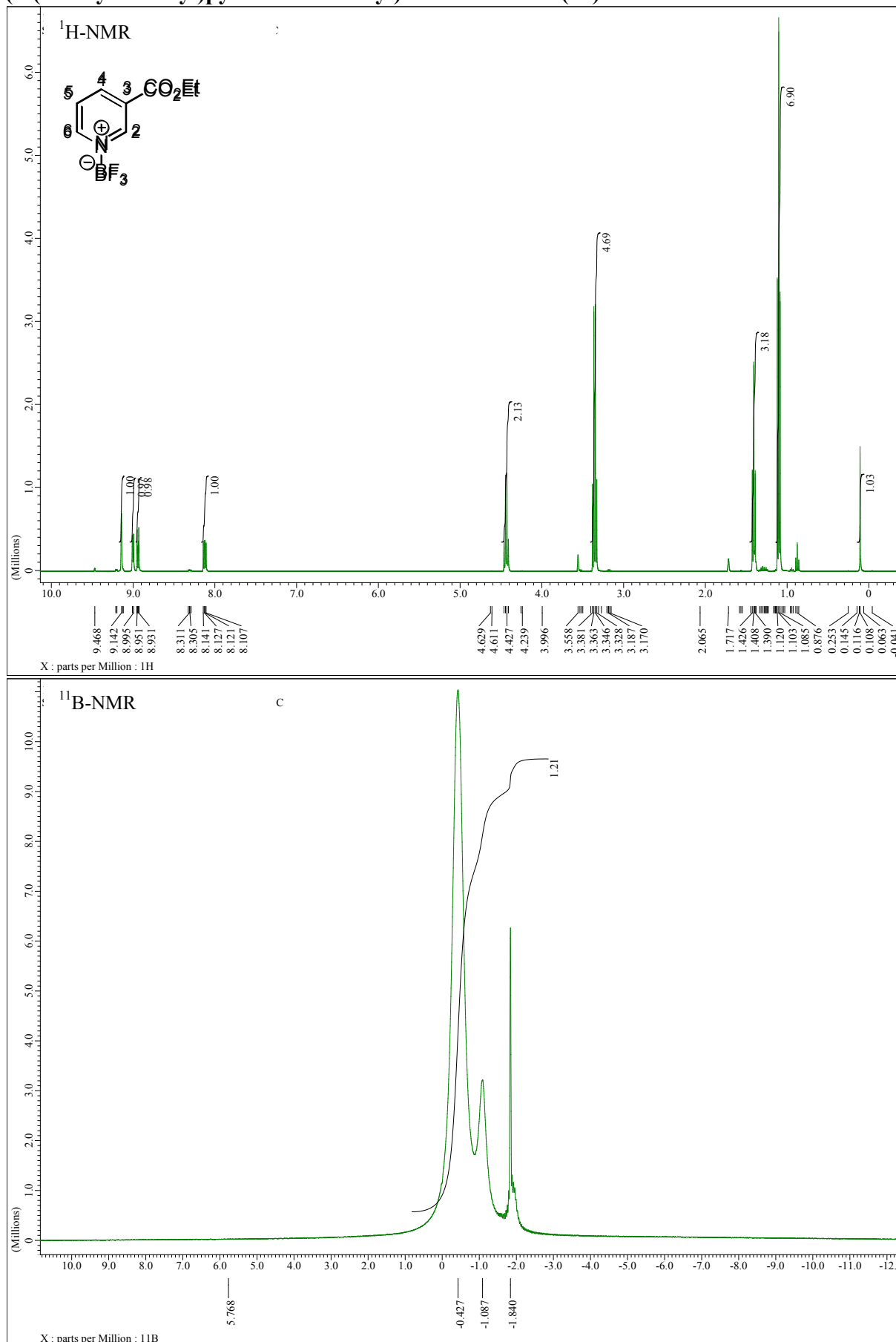


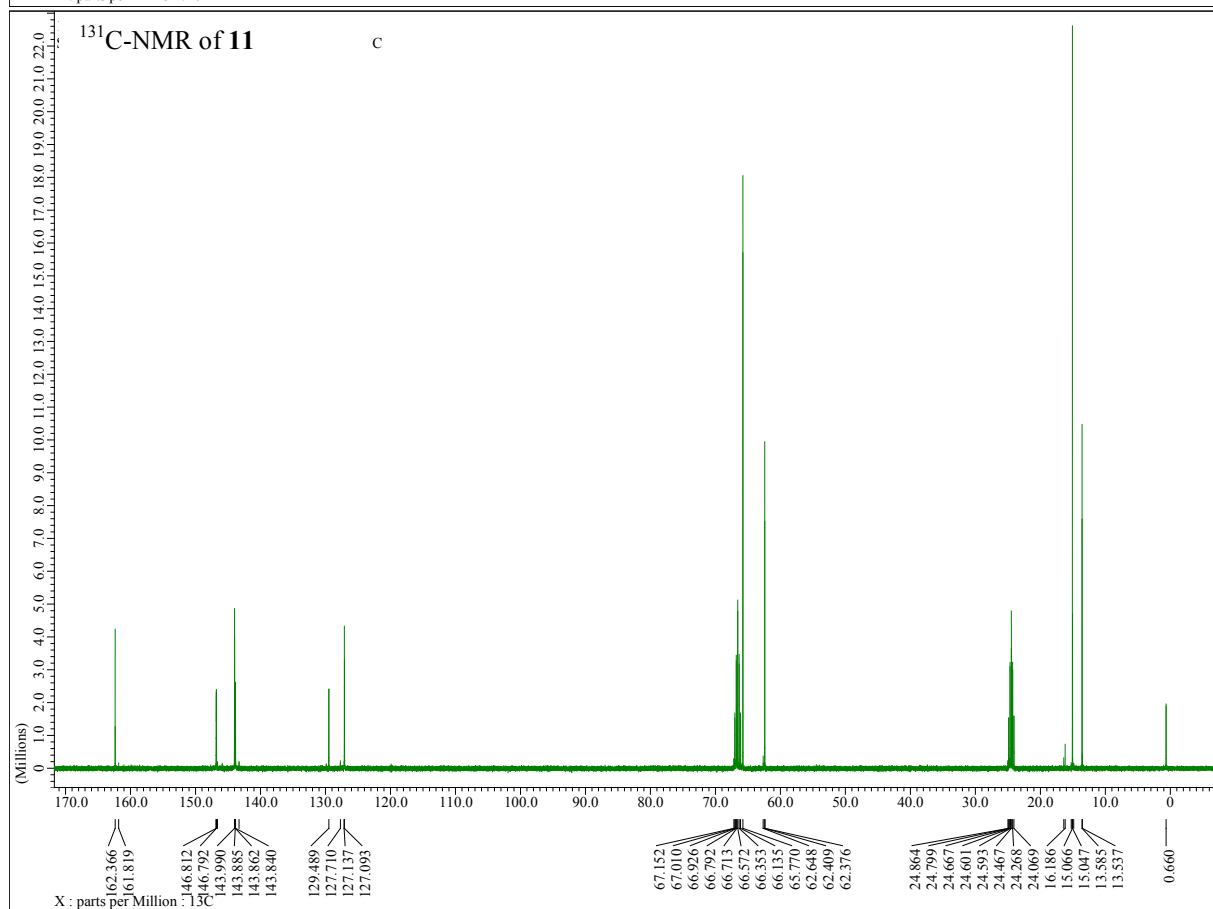
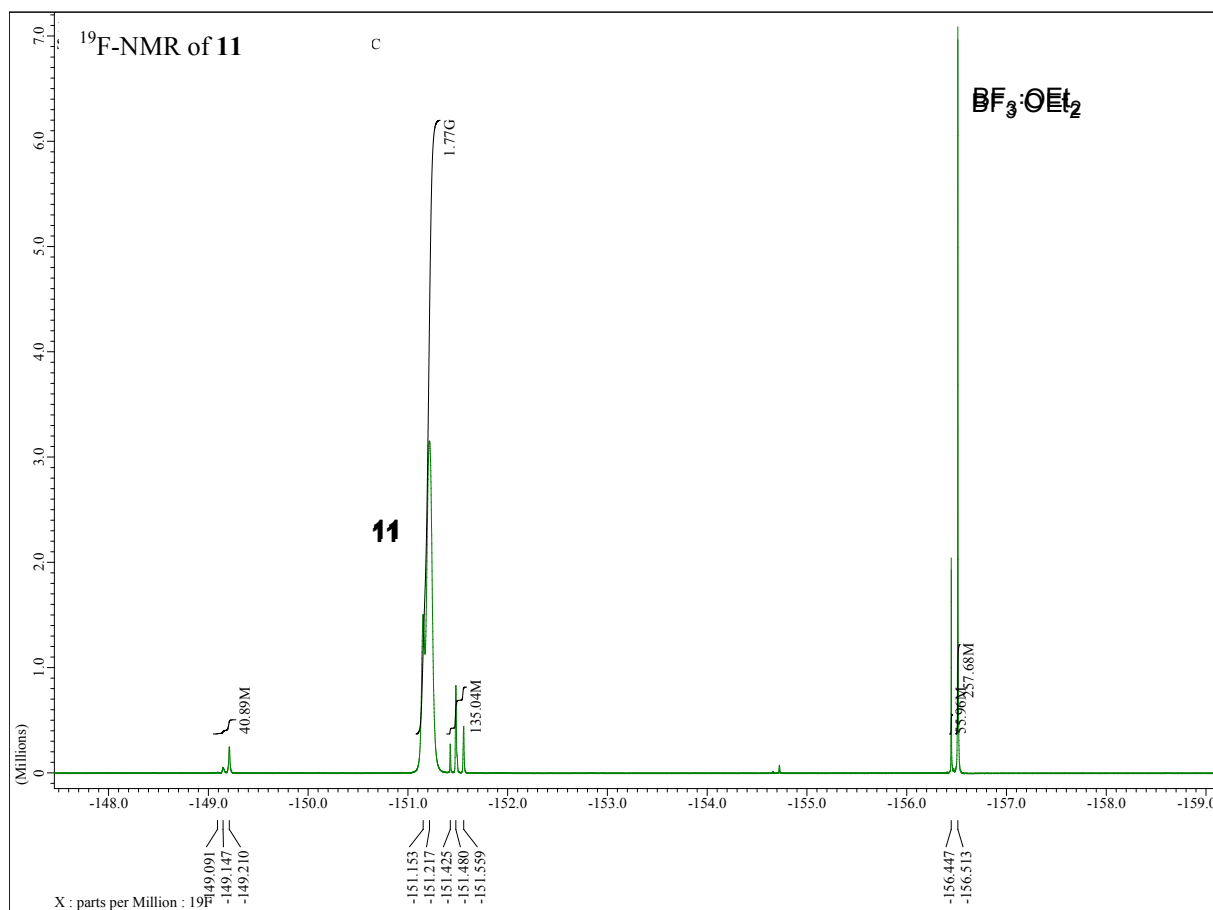




<sup>13</sup>C-NMR expansions of the intermediate **9a** of the aromatic region (120-230 ppm, left) and the aliphatic region (0-70 ppm) right).

### (3-(ethoxycarbonyl)pyridin-1-ium-1-yl)trifluoroborate (11)





### Trifluoro(2,2,6,6-tetramethylpiperidin-1-ium-1-yl)borate (12)

