Electronic Supplementary Material (ESI) for New Journal of Chemistry.
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$B(C_6F_5)_3$: a Robust Catalyst for the Activation of CO_2 and Dimethylamine Borane for the N-Formylation Reactions

Vitthal B. Saptal, Gaurav Juneja and Bhalchandra M. Bhanage*[a]

Department of Chemistry, Institute of Chemical Technology, Mumbai, 400019

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Experimental Section

1) General

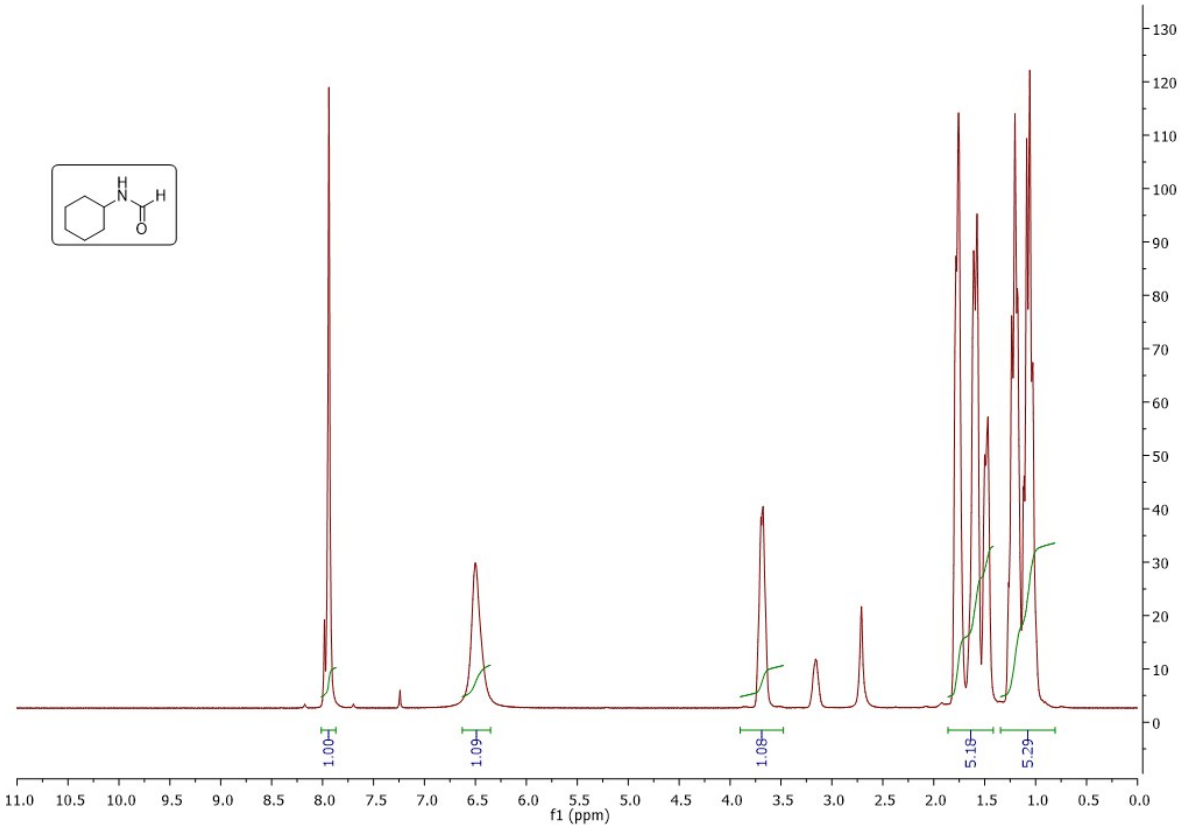
All chemicals and solvents were purchased from different commercial sources and used as received without further purifications. The progress of the reaction was monitored by GC–MS. A QP2010 GC–MS instrument [Rtx-17 column, 30 m × 25 mm i.d, film thickness (df) = 0.25 μm; column flow 2 mL min^{-1}, 100 to 240 °C at a rate of 10 °C min^{-1}] was used for the mass spectrometric analysis of the products. The products were purified by column chromatography with 100–200 mesh silica gel. The 1 H NMR spectra were recorded with a 400 MHz spectrometer with samples in $CDCl_3$. The ^{13}C NMR spectra were recorded with a 100 MHz spectrometer with the samples in $CDCl_3$.

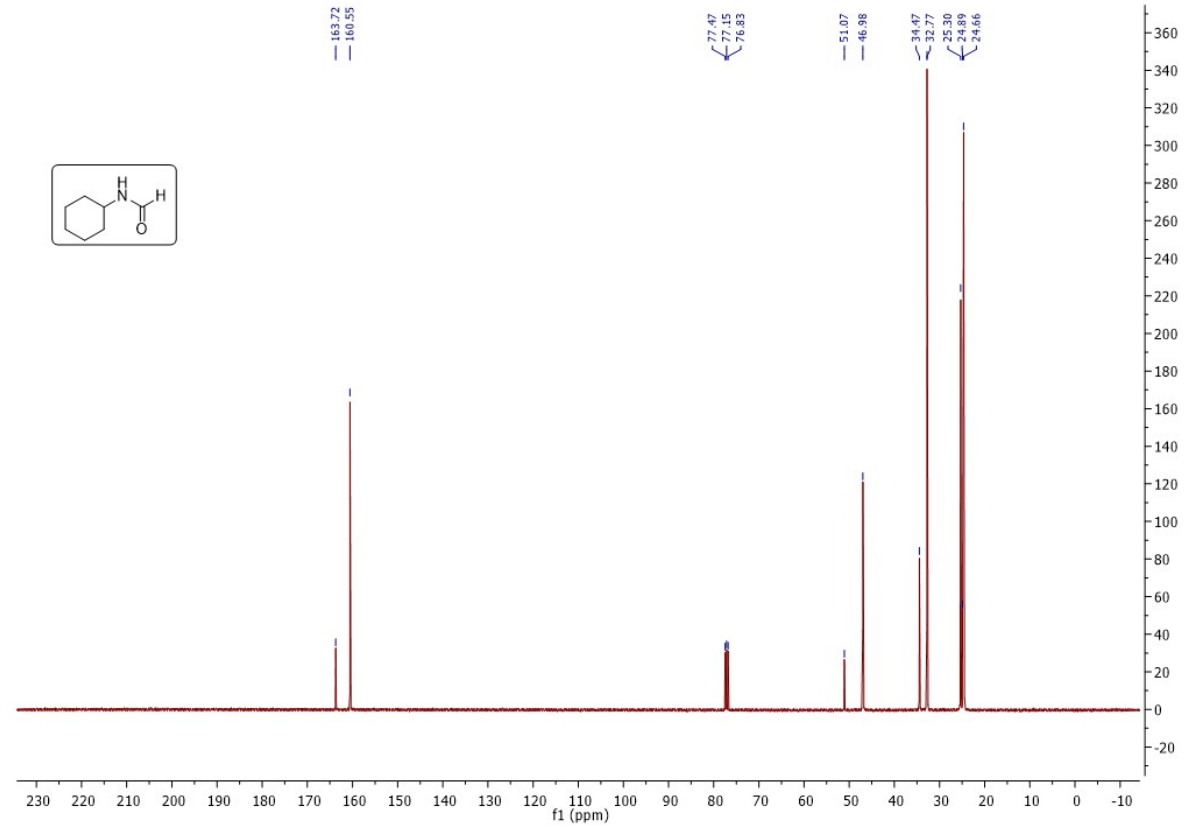
2) Experimental procedure for the formylation and cyclization reactions

The N-formylation and cyclized product were synthesized by the reaction amines with CO_2 and dimethylamine borane (DMAB) in the presence of catalyst. All the reactions were carried out in a 100 mL stainless-steel autoclave with stirring at 650 rpm and equipped with an automatic stirrer and temperature control system. In a typical procedure, the $B(C_6F_5)_3$ (2 mg) was introduced into the reactor containing amine (5 mmol), CH_3CN (3 mL) and DMAB (10 mmol) at room temperature and then pressurized to the respective pressure of CO_2 and heated to a particular temperature. After completion the reaction, the reactor was cooled in an ice-cold water bath and then CO_2 was released slowly. The synthesized products were extracted and then purified by using the pet ether and ethyl acetate by using column chromatography and then H^1 & C^{13} spectra were recorded, for additional spectra refer references.[1-3]

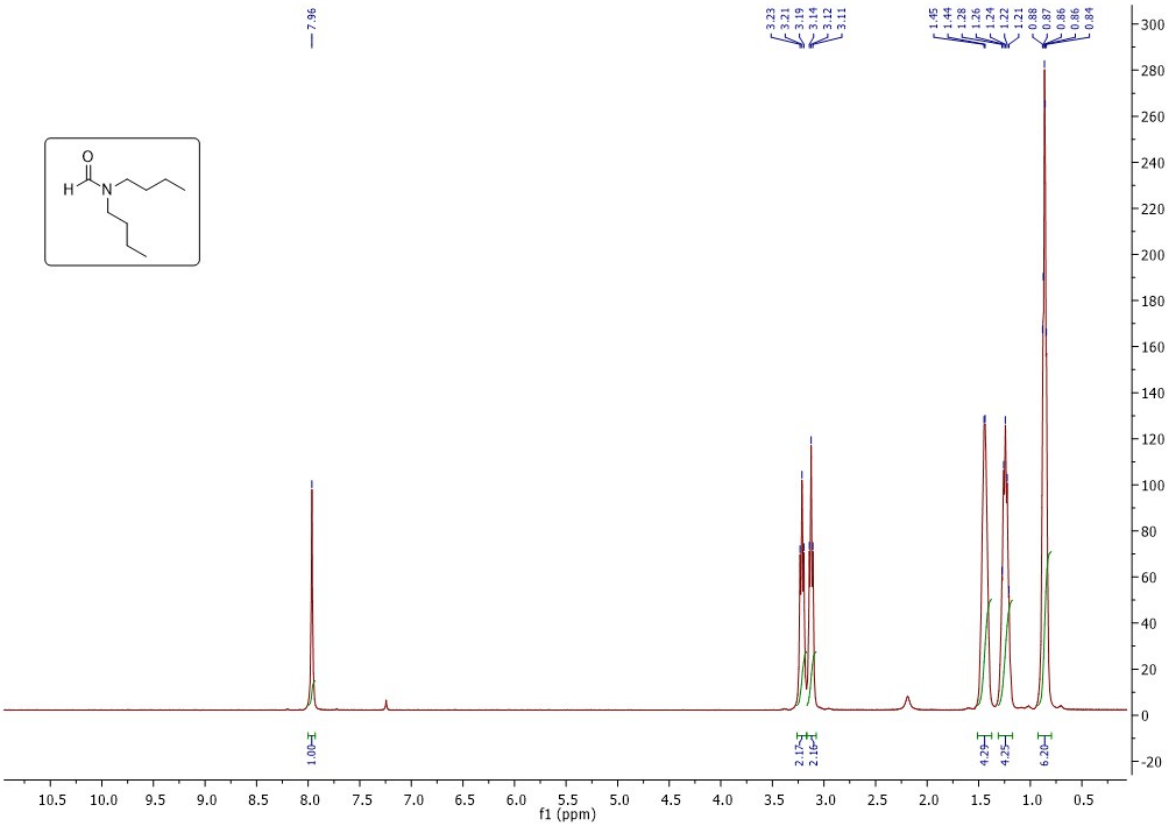
3) NMR Spectra

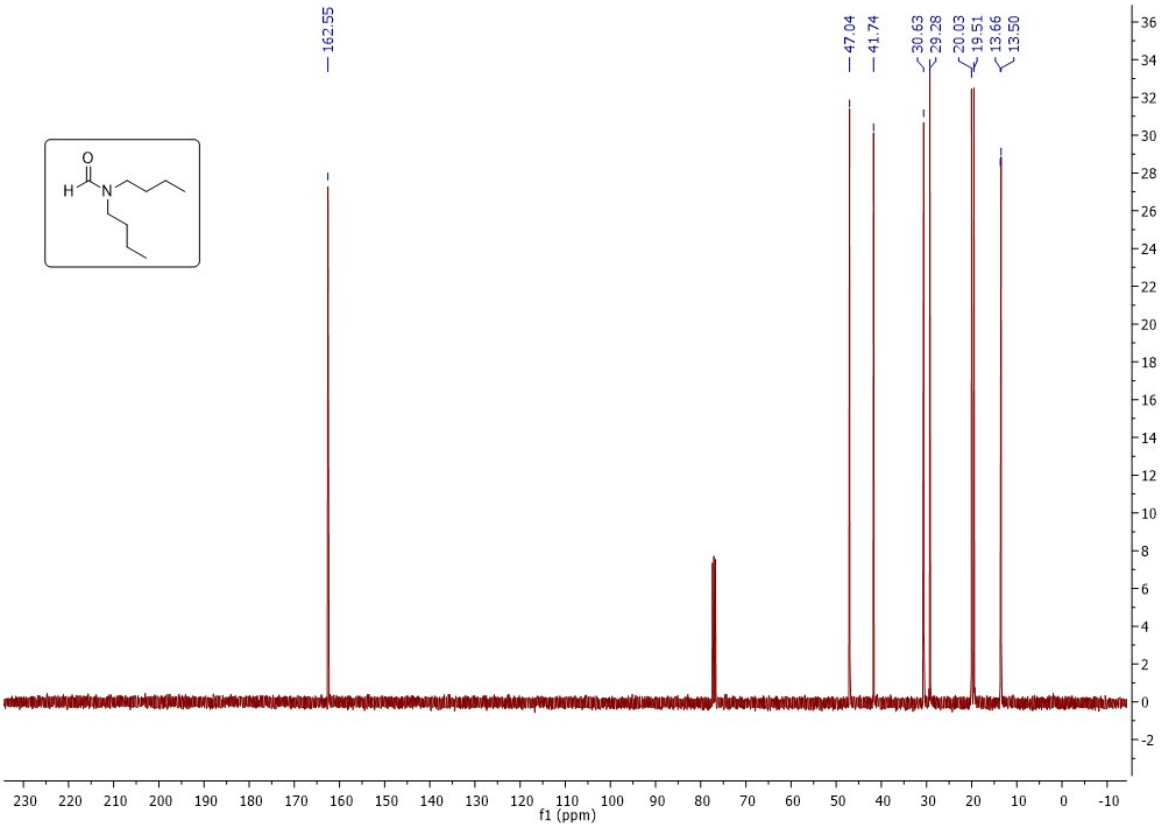
3.1 N-cyclohexylformamide (6a)



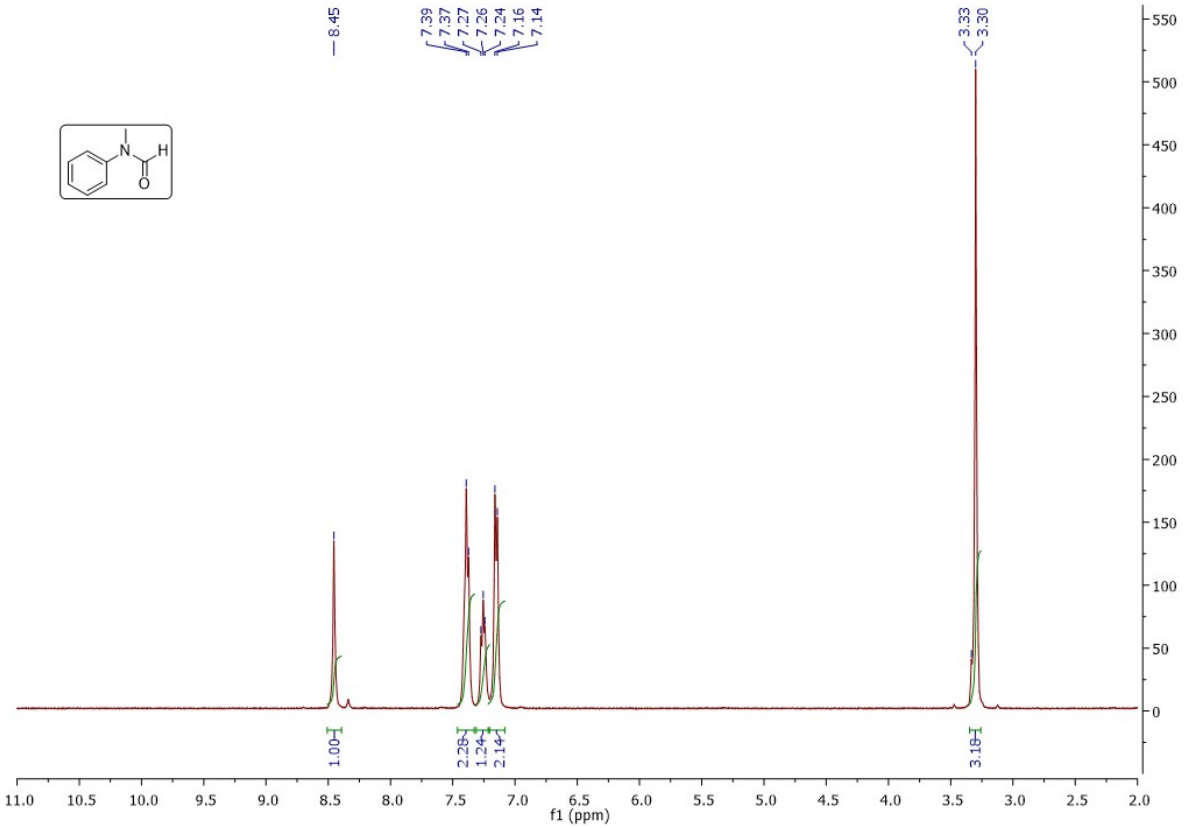


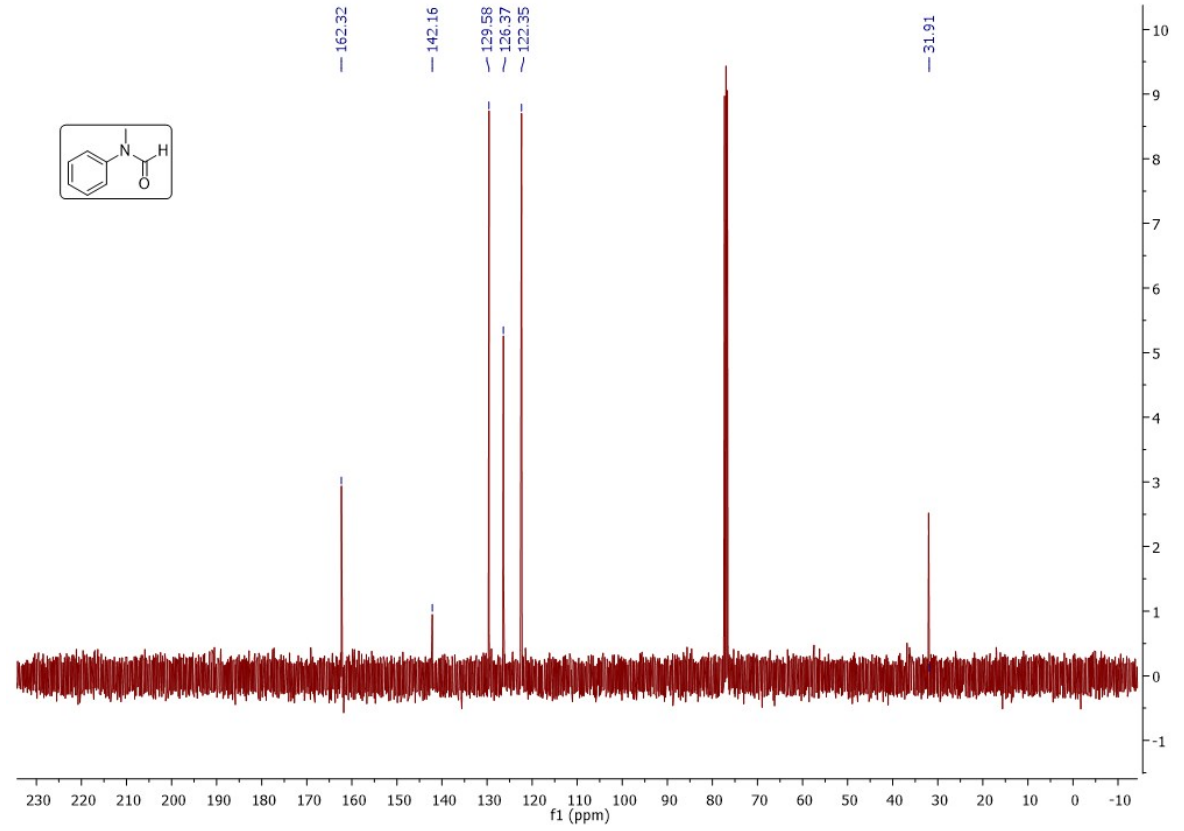
3.2 N,N-dibutylformamide (7a)



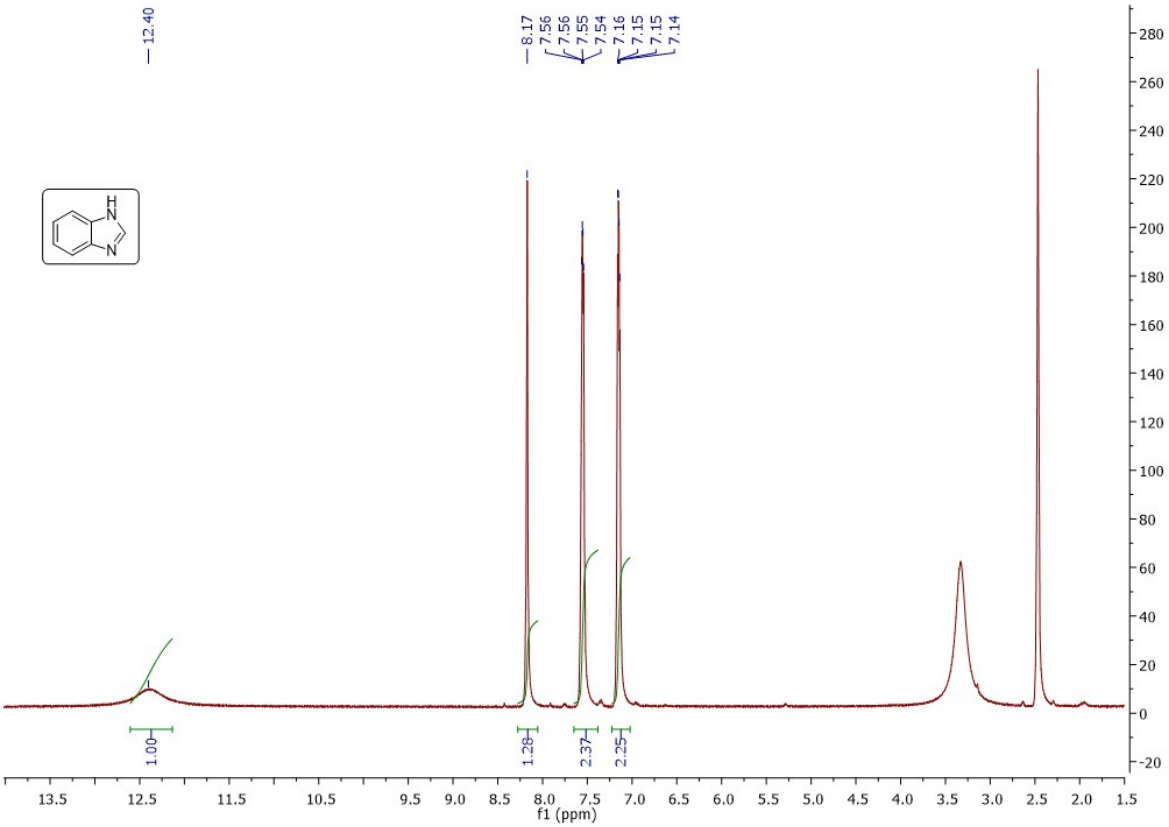


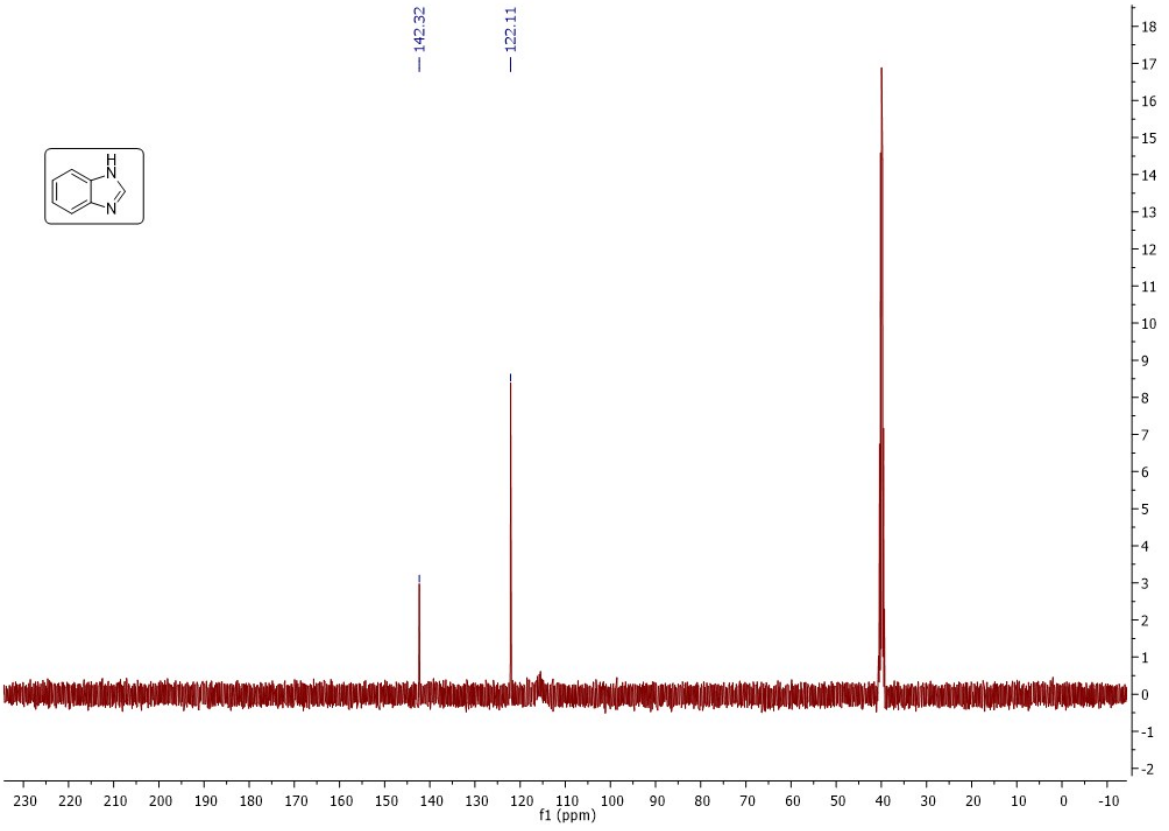
3.3 N-methyl-N-phenylformamide (12a)



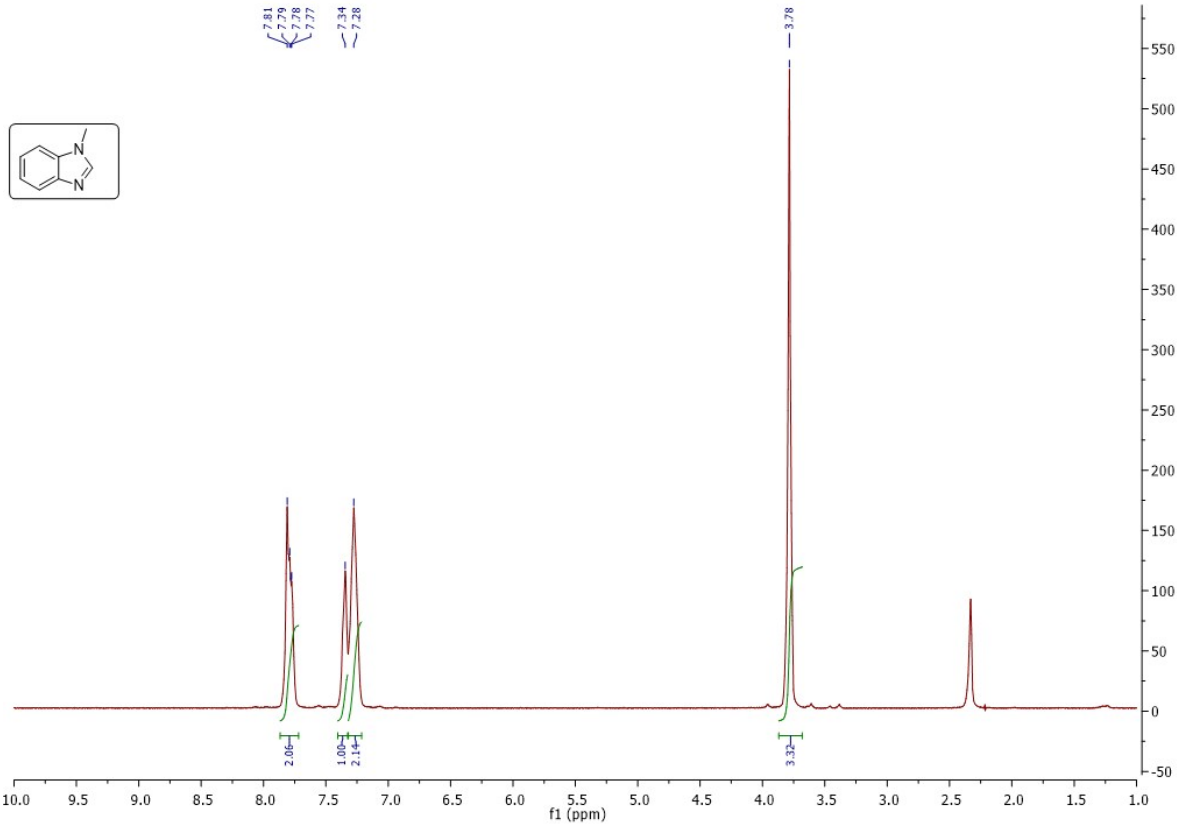


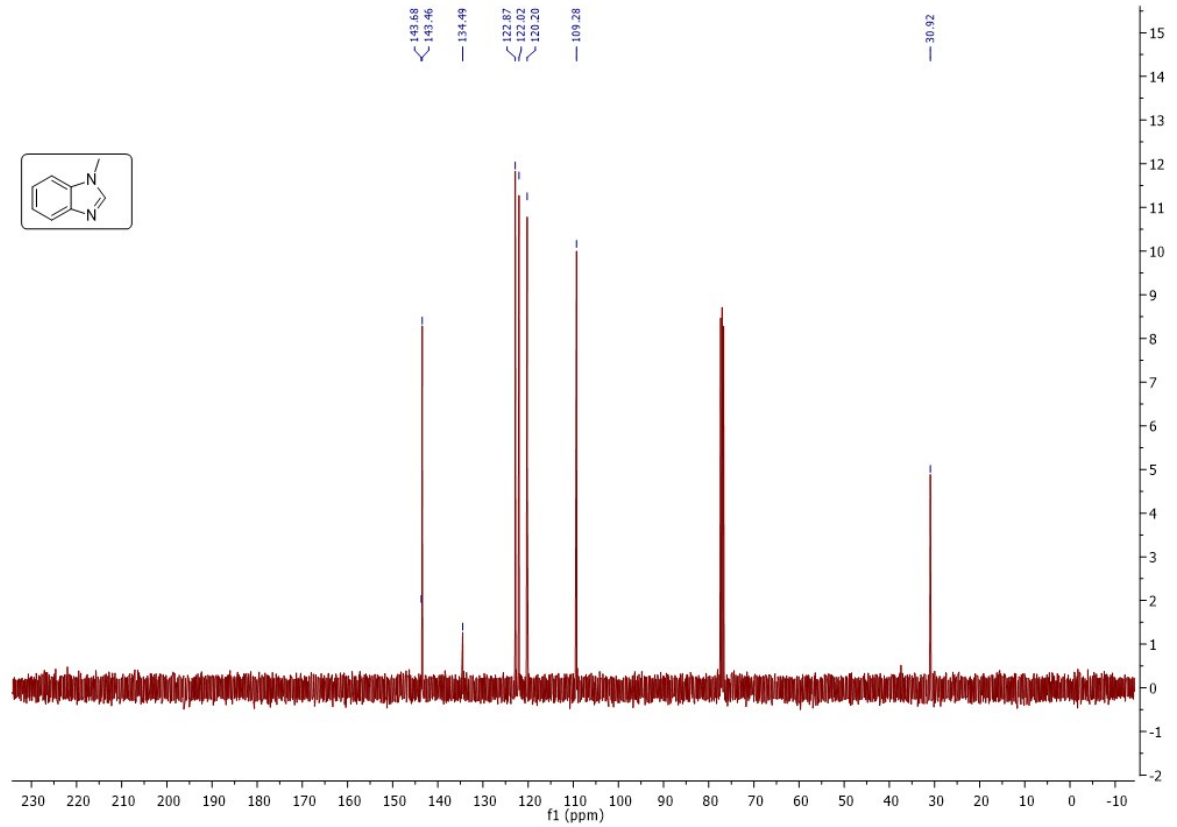
3.4 1H-benzo[d]imidazole(3b)



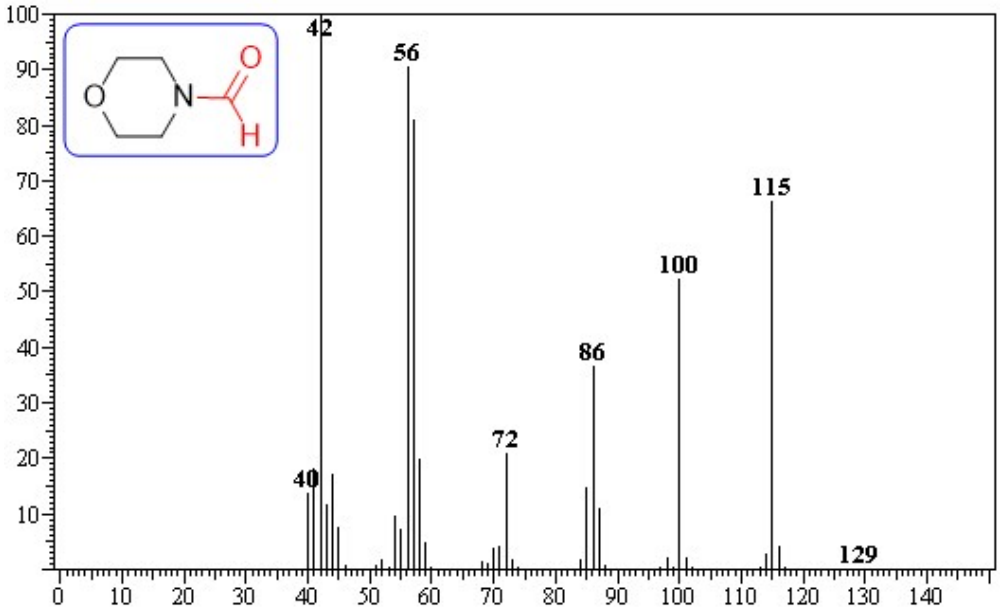


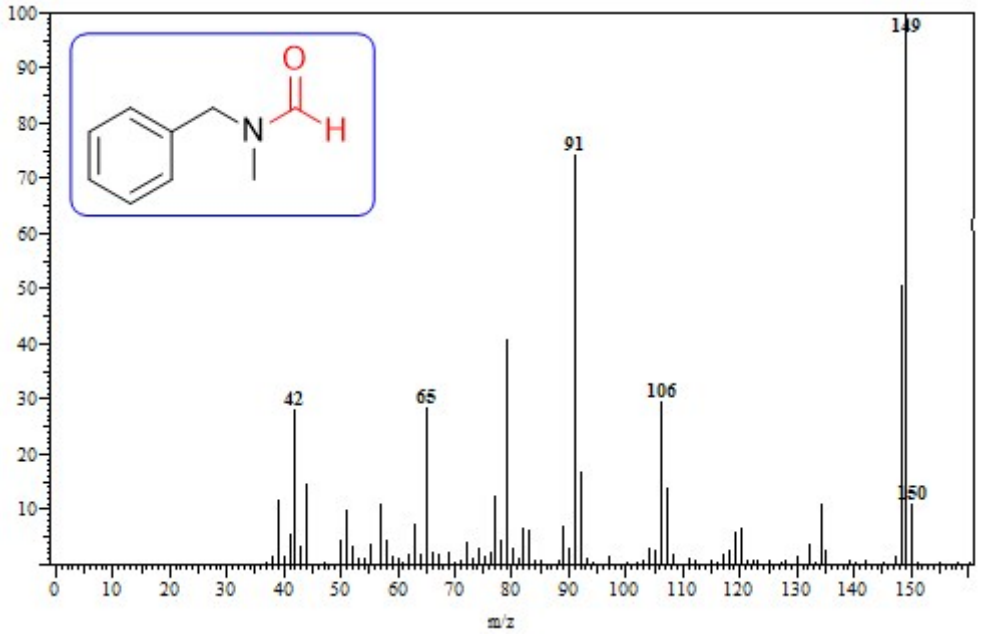
3.5 1-methyl-1H-benzo[d]imidazole (4b)

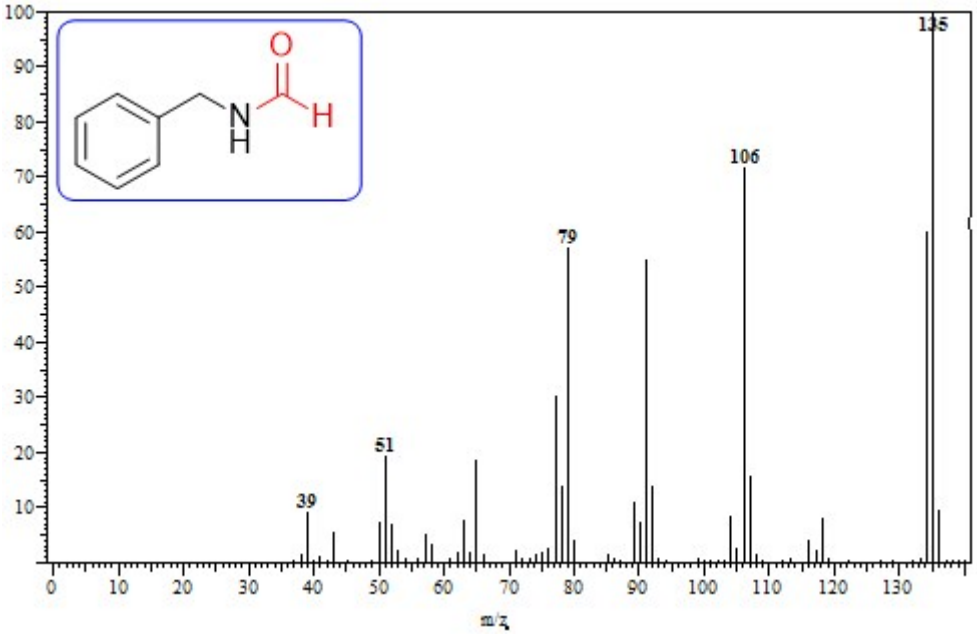




4) Mass spectra



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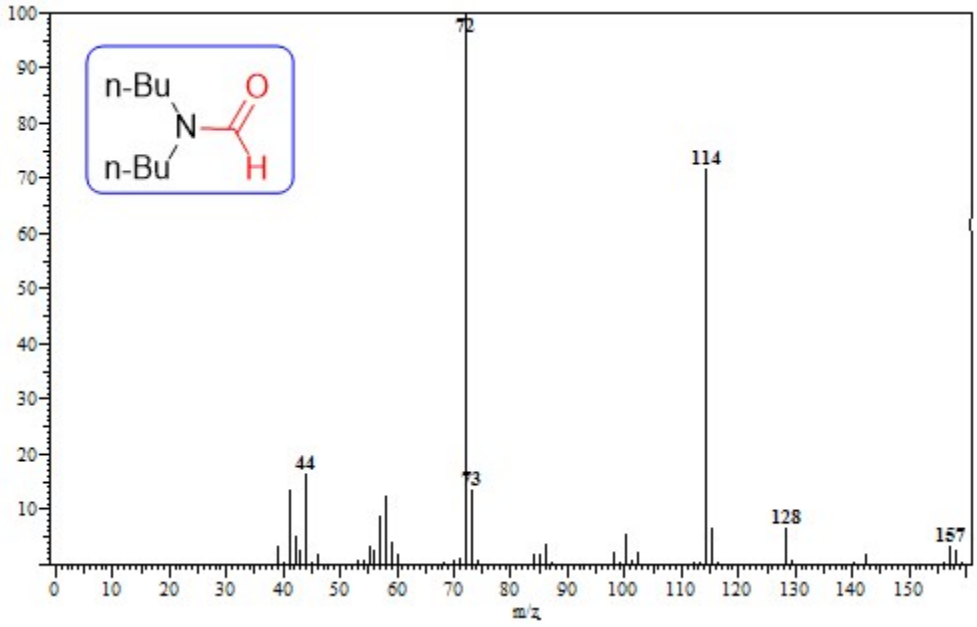
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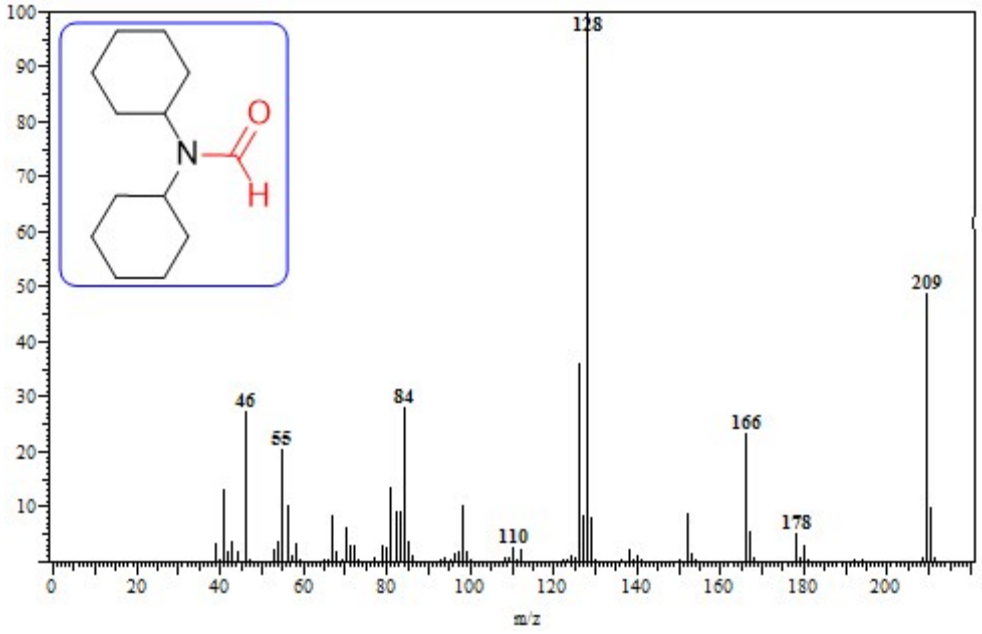
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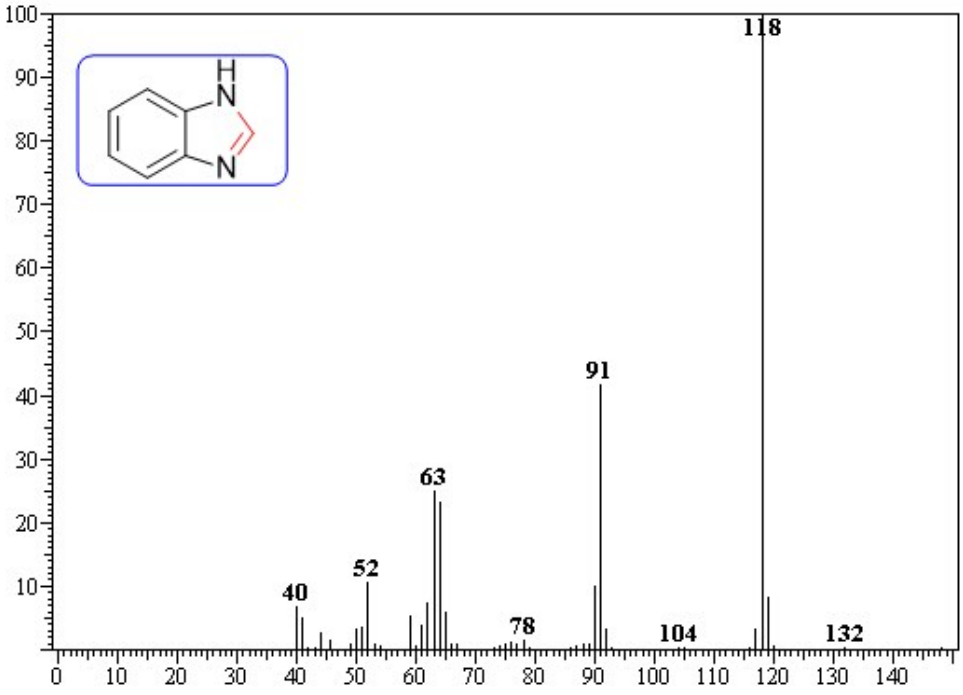
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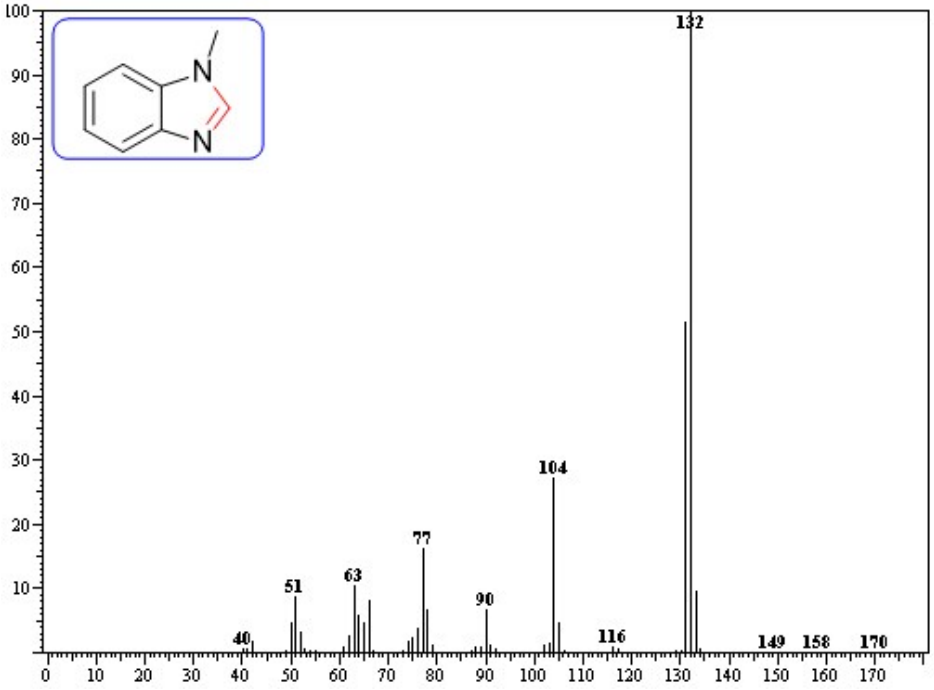

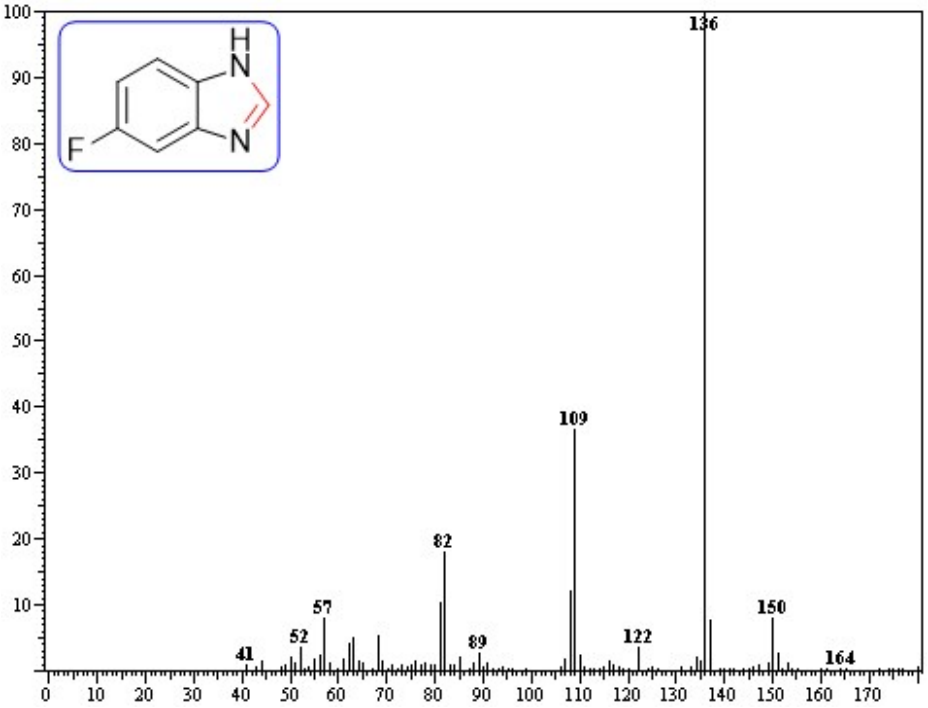

5) References

1) Vitthal B. Saptal, Bhalchandra M Bhanage, *ChemSusChem*, **2016**, *9*, 1980-1985.

2) Vitthal B. Saptal, Takehiko Sasaki, Bhalchandra M. Bhanage, ChemCatChem, 2018, DOI: 10.1002/cctc.201800185.

3) Tian-Xiang Zhao, Gao-Wen Zhai, Jian Liang, Ping Li, Xing-Bang Hu and You-Ting Wu, *Chem. Commun.*, **2017**,*53*, 8046-8049.