

# **A four-step cascade reaction involving O[1,3] sigmatropic shift and Smiles rearrangements as key steps**

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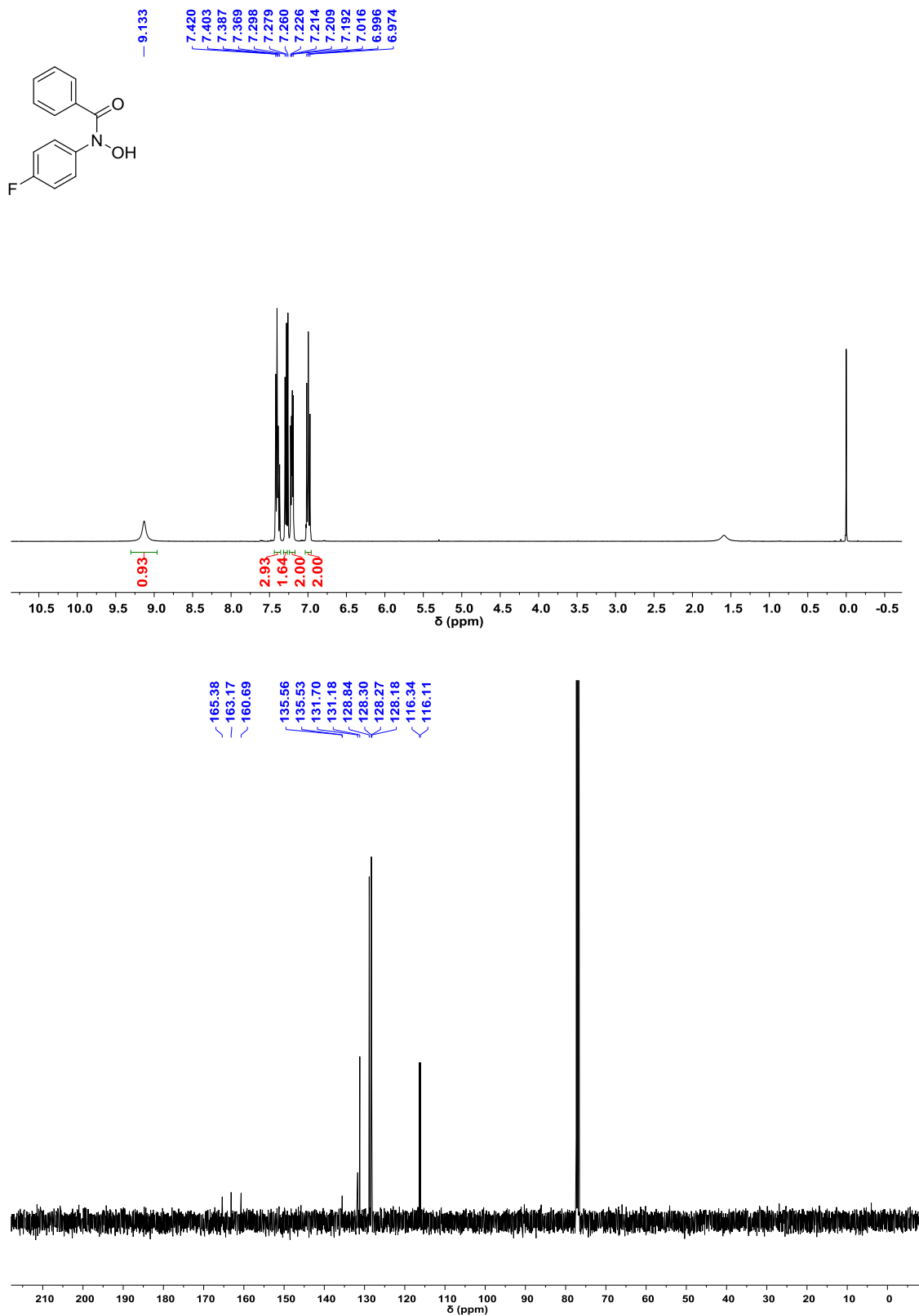
## **Supplementary Information**

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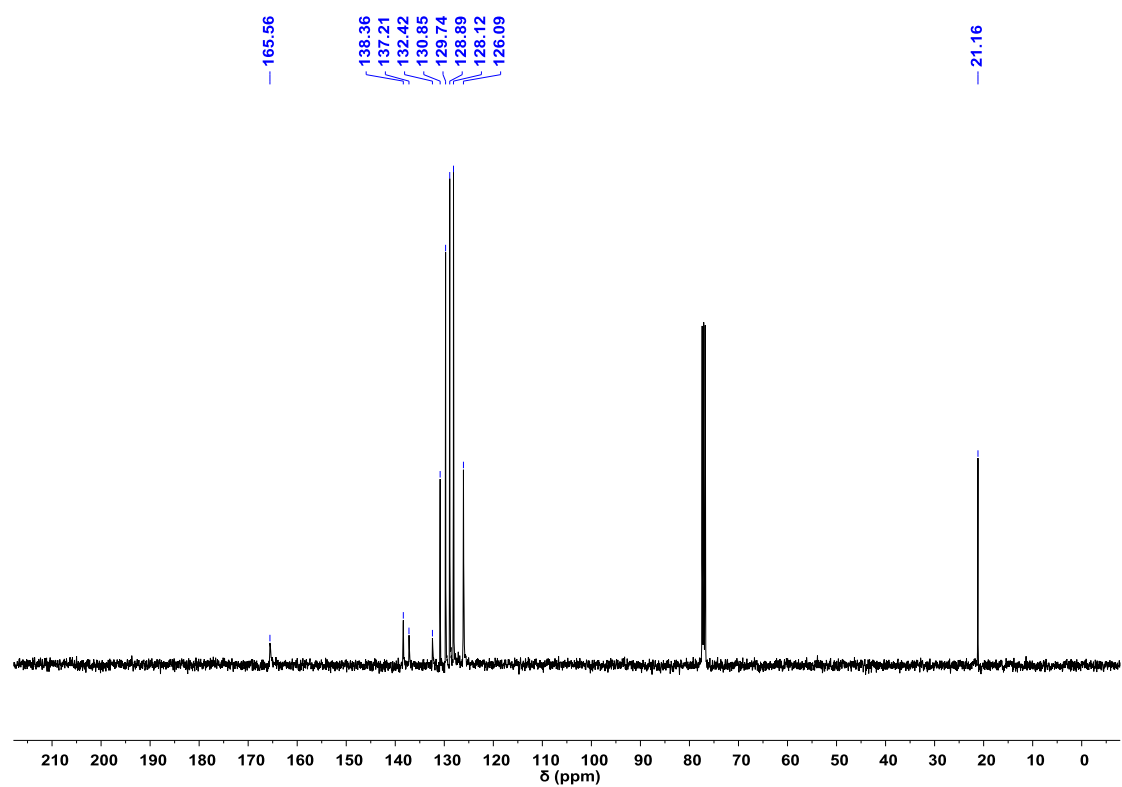
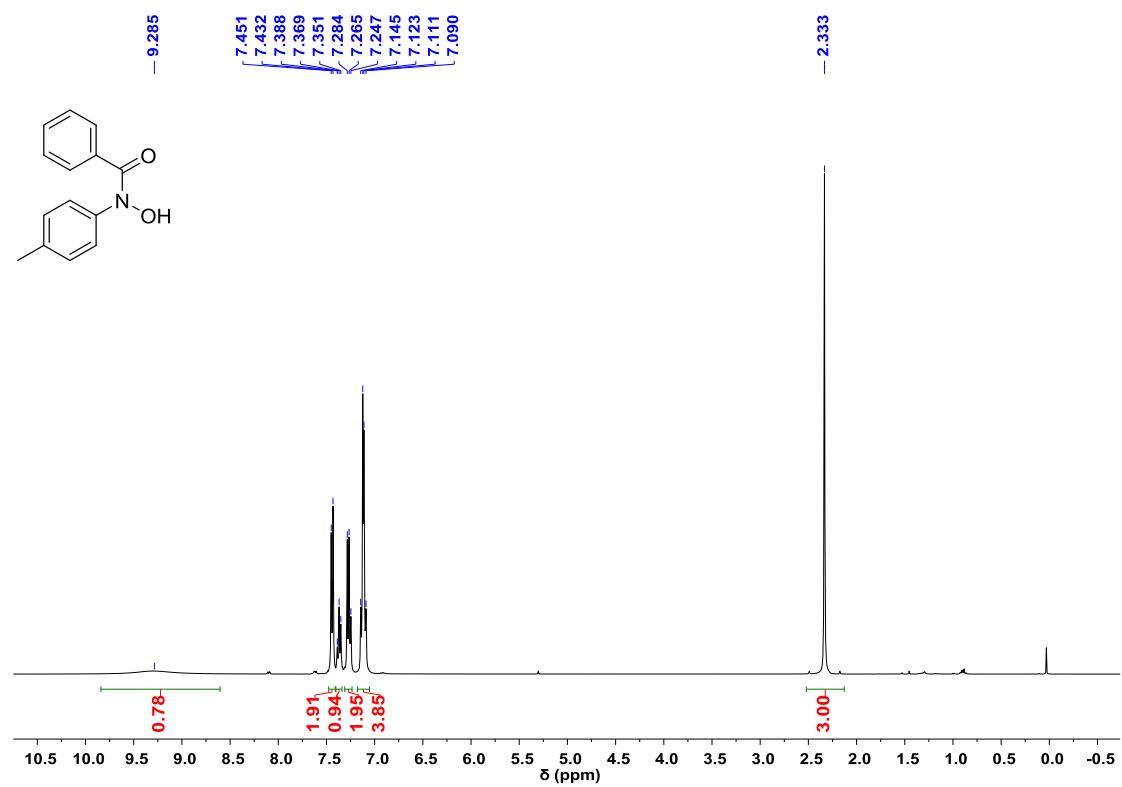
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# Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of products **1**

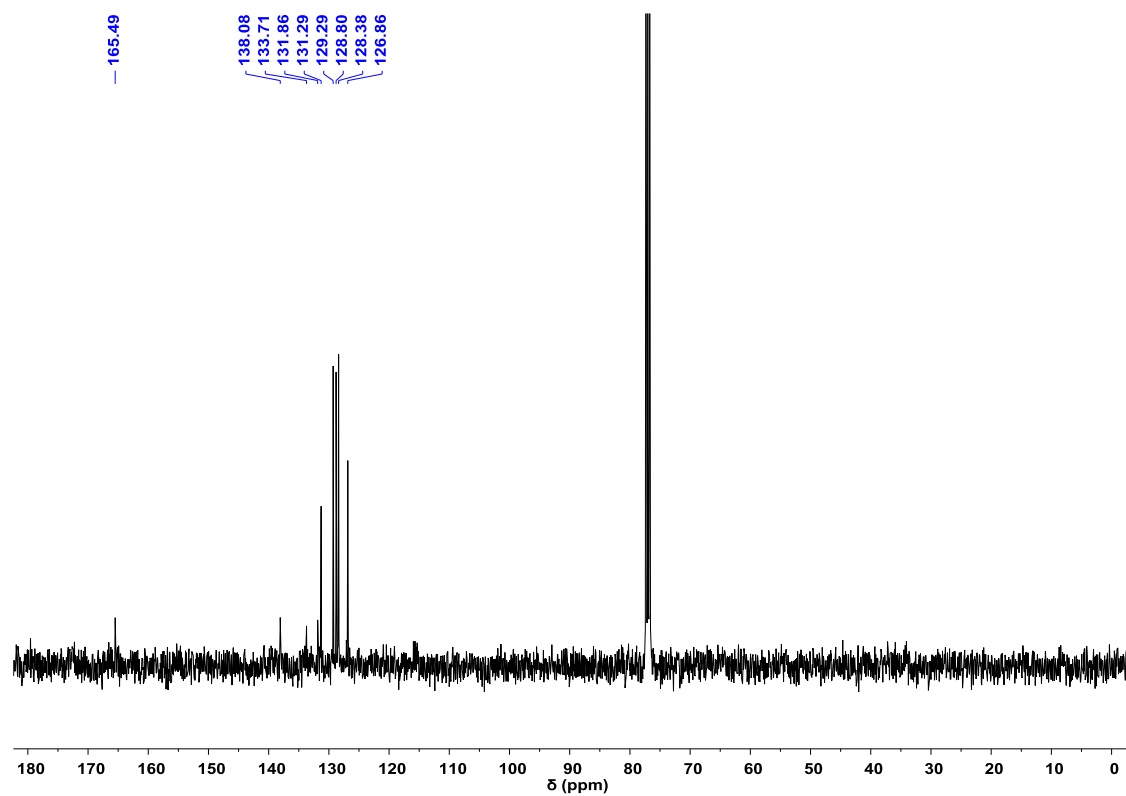
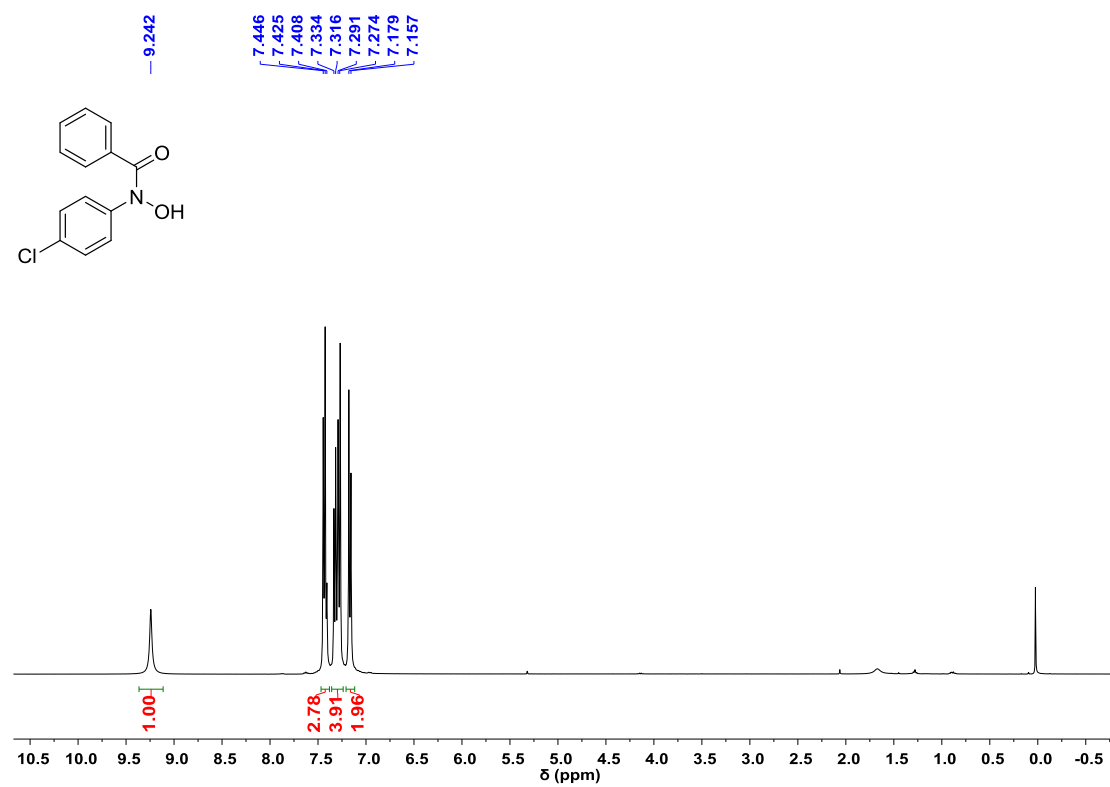
## *N*-(4-Fluorophenyl)-*N*-hydroxybenzamide (**1a**)



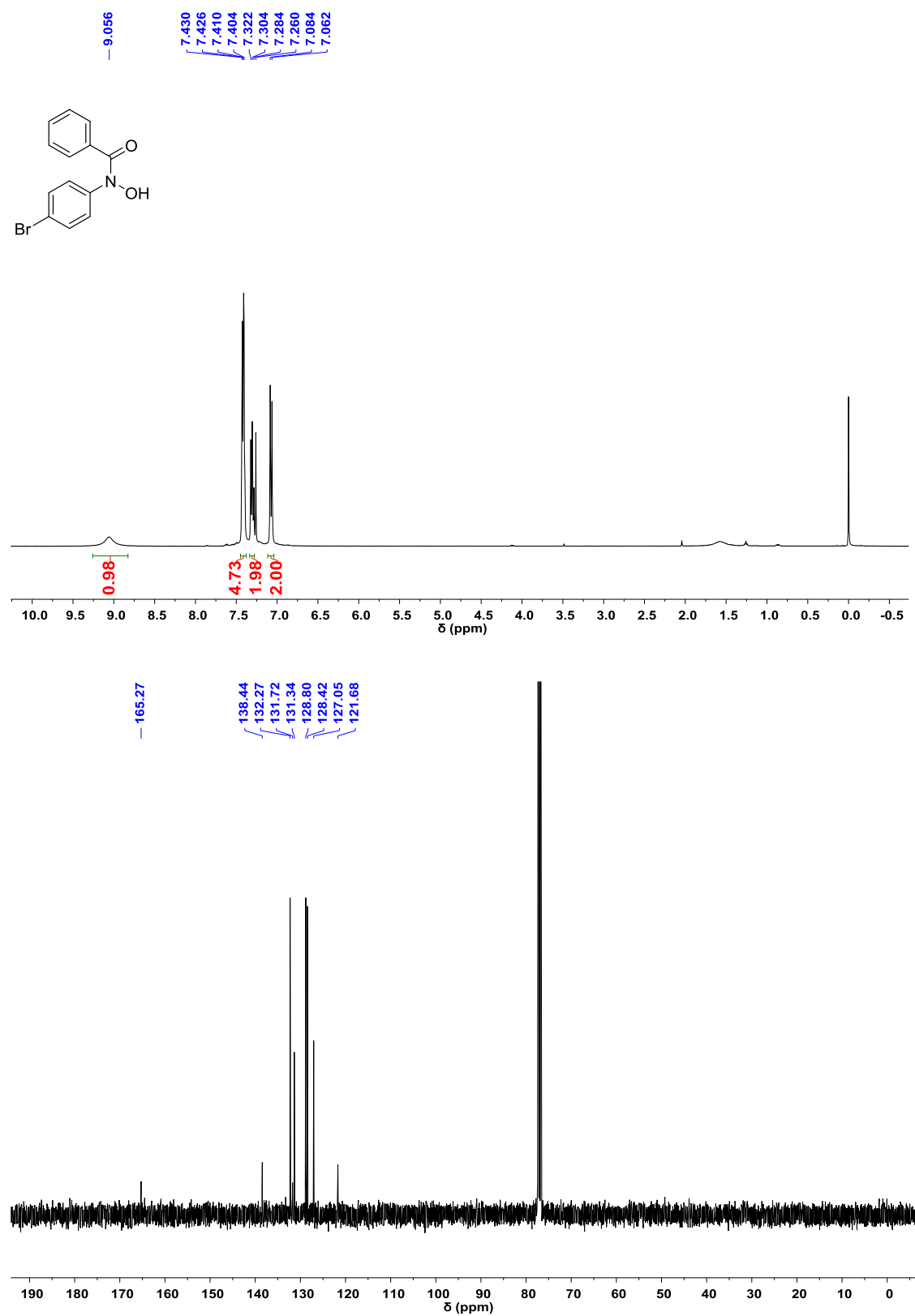
*N*-Hydroxy-*N*-(4-methylphenyl)benzamide (**1b**)



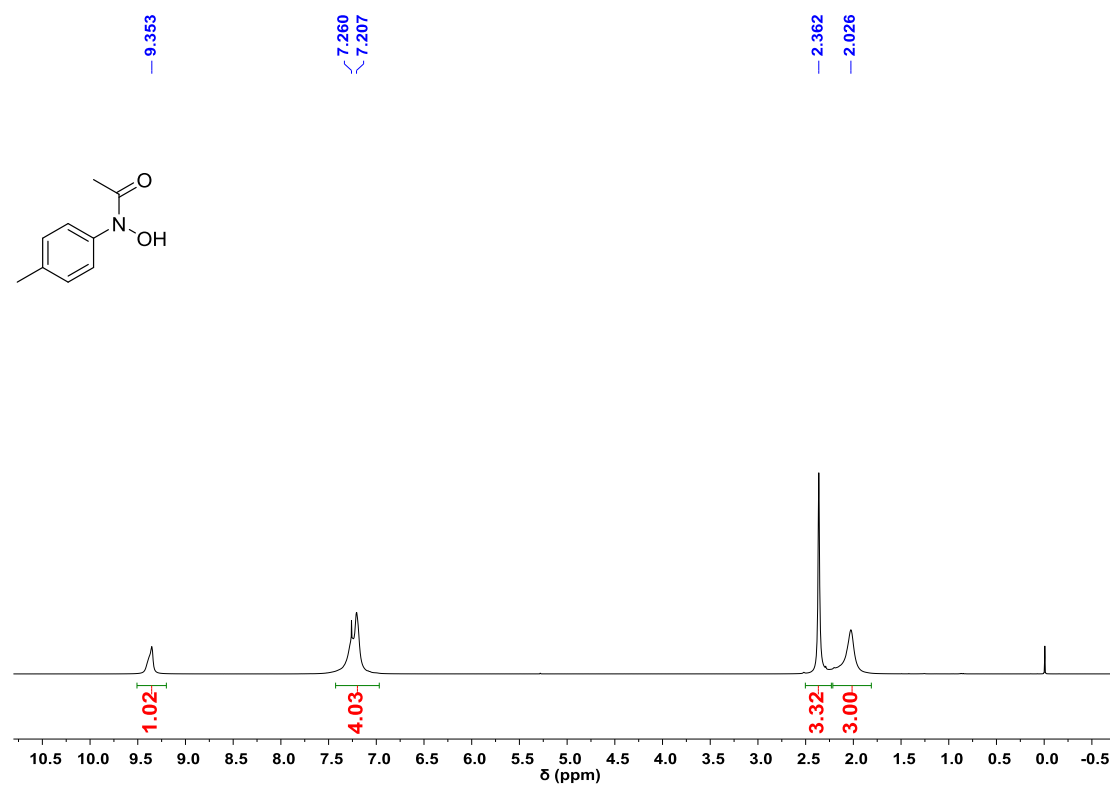
*N*-(4-Chlorophenyl)-*N*-hydroxybenzamide (**1c**)



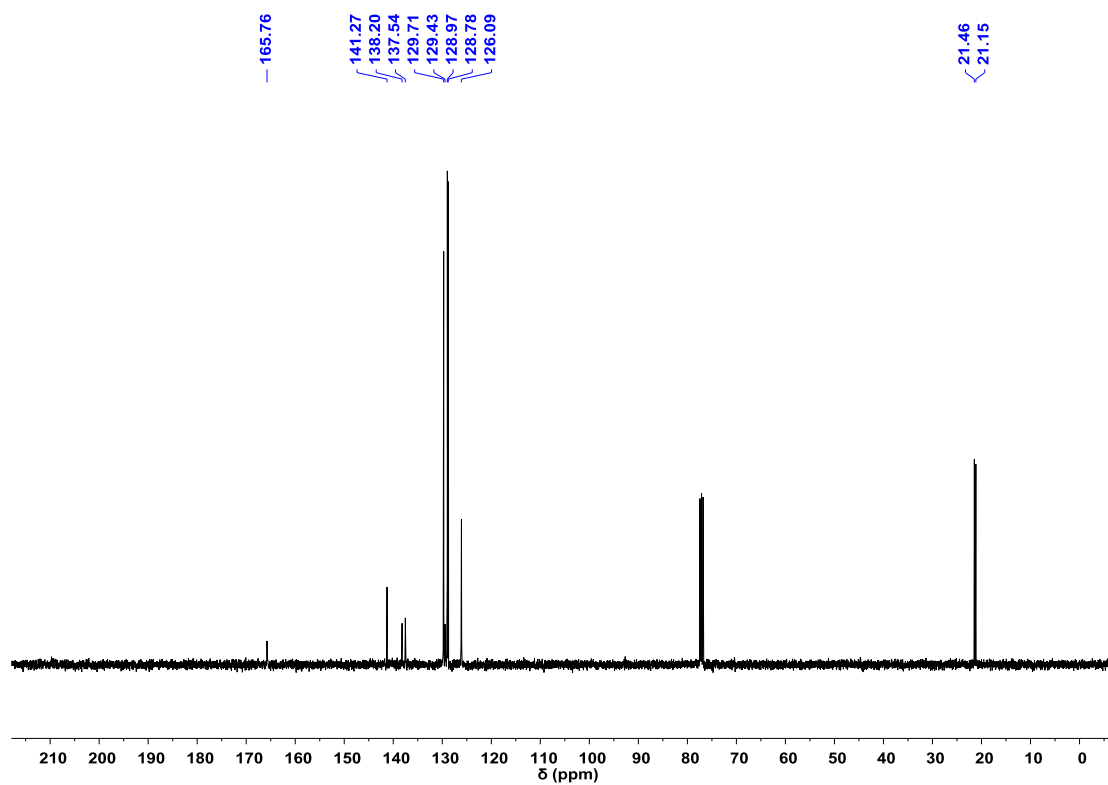
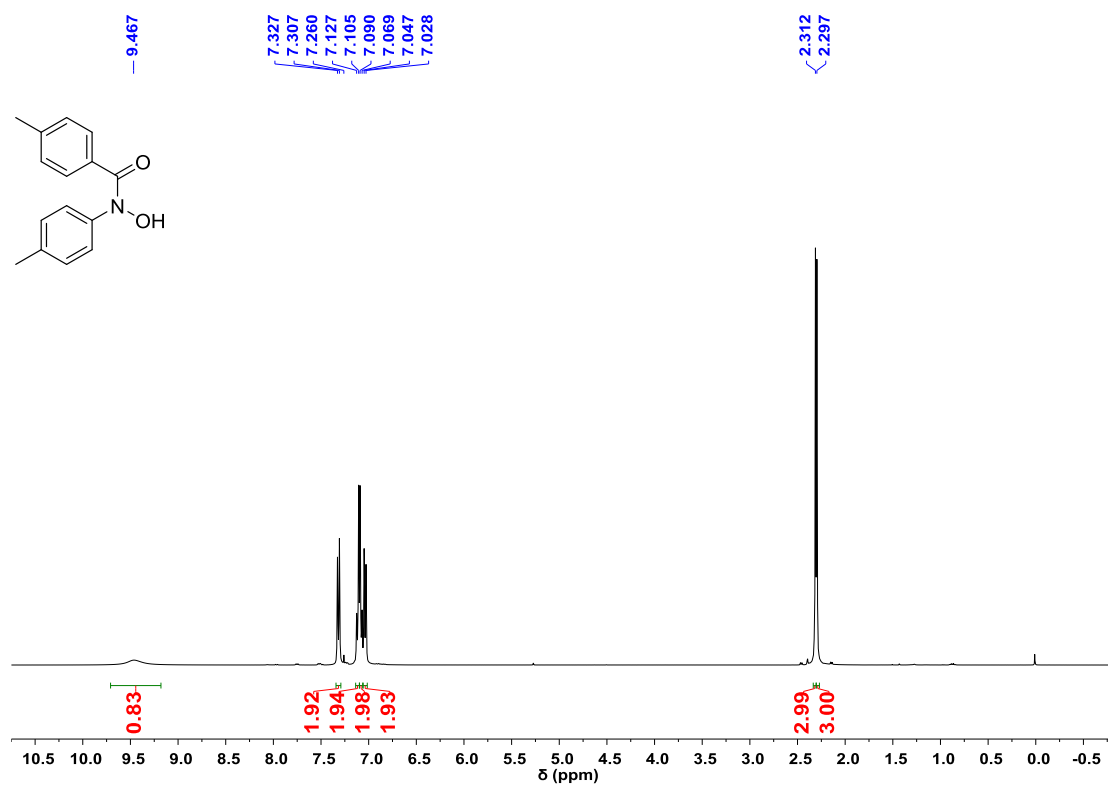
*N*-(4-Bromophenyl)-*N*-hydroxybenzamide (**1d**)



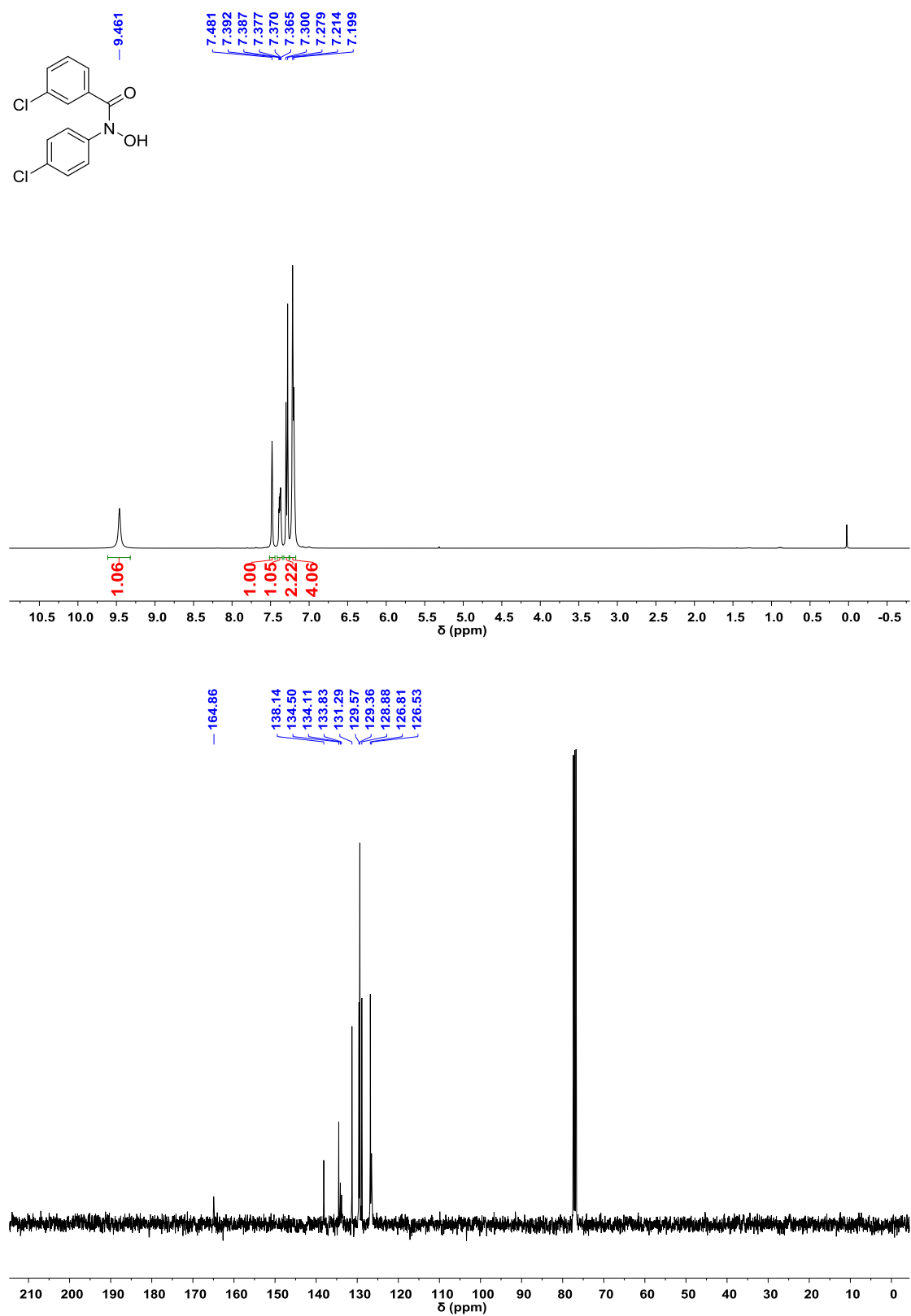
*N*-Hydroxy-*N*-(*p*-tolyl)acetamide (**1e**)



*N*-Hydroxy-4-methyl-*N*-(*p*-tolyl)benzamide (**1f**)

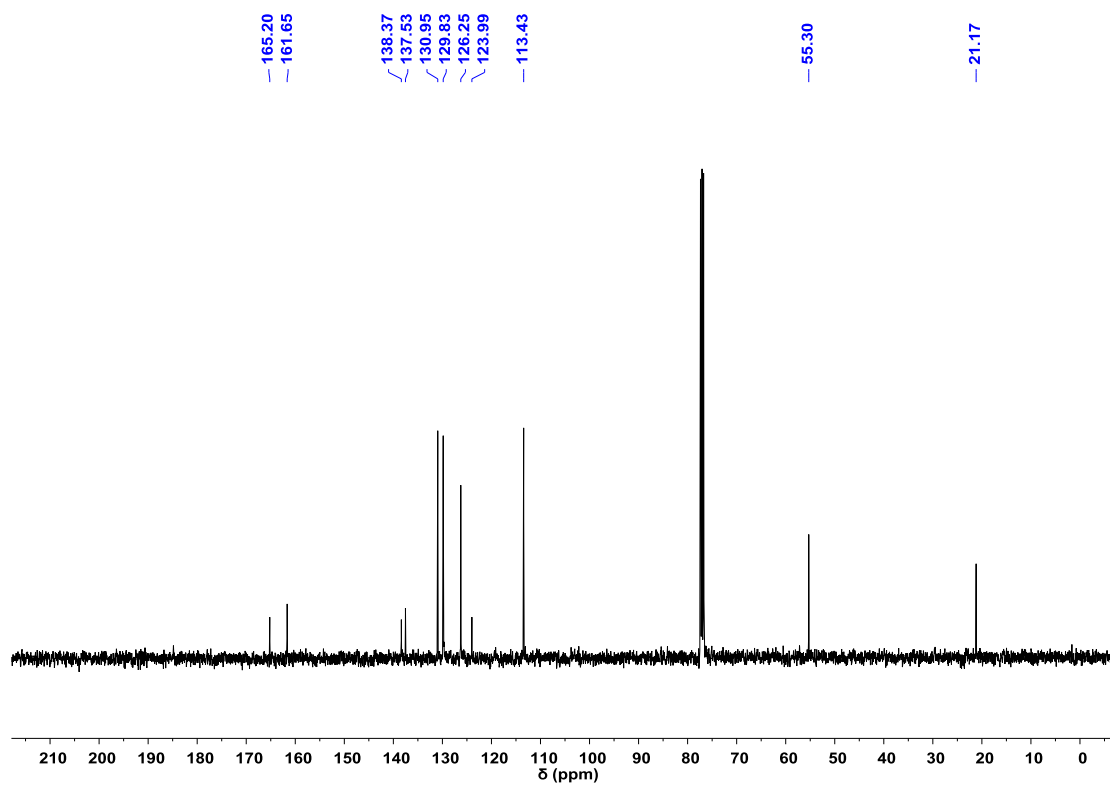
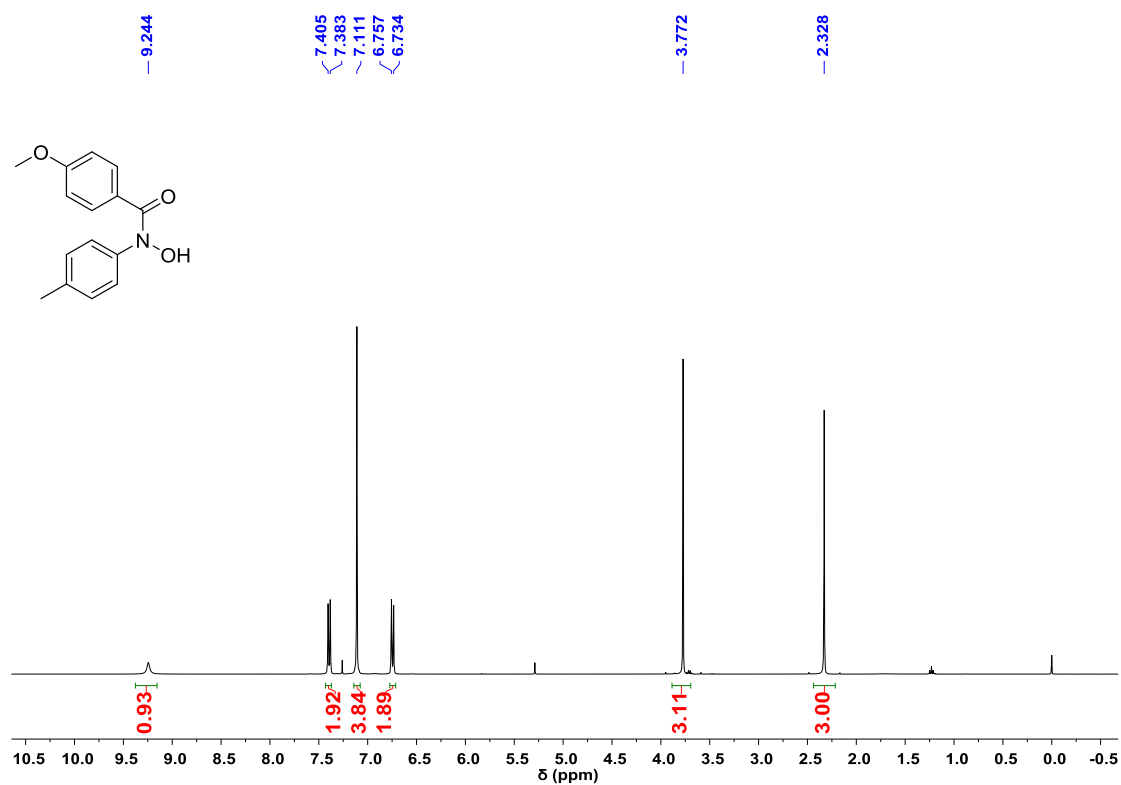


3-Chloro-*N*-(4-chlorophenyl)-*N*-hydroxybenzamide (**1g**)



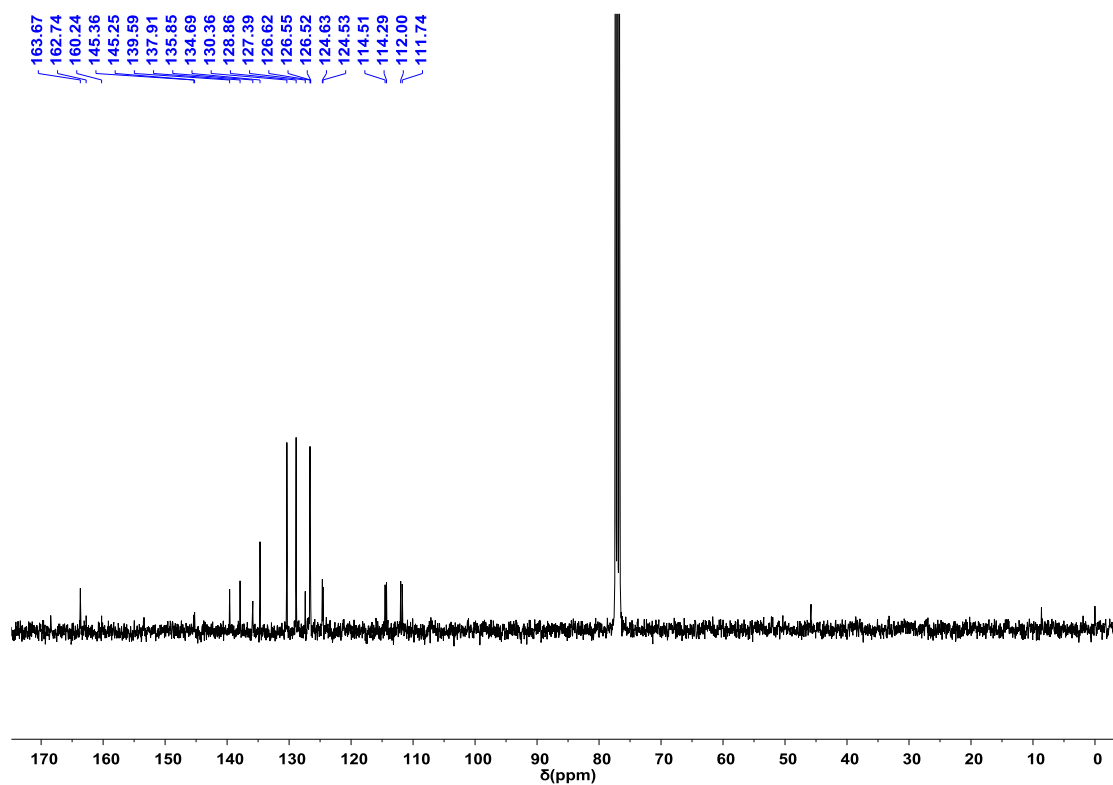
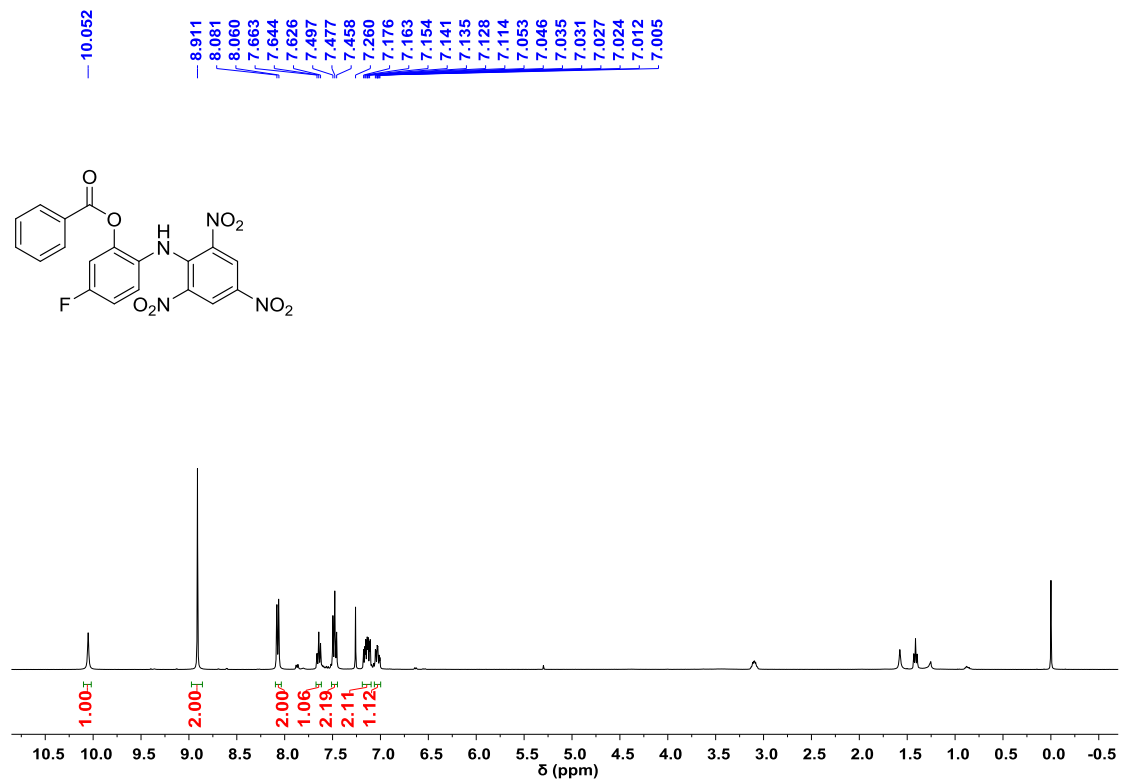


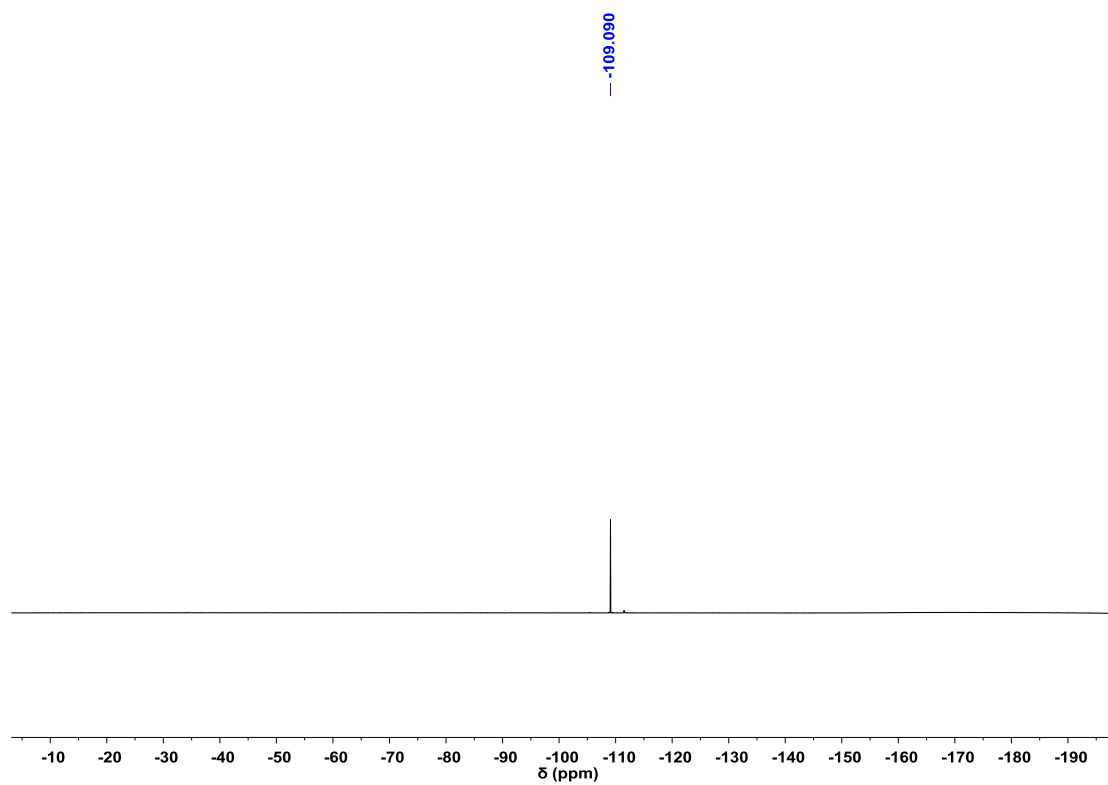
*N*-Hydroxy-4-methoxy-*N*-(*p*-tolyl)benzamide (**1h**)



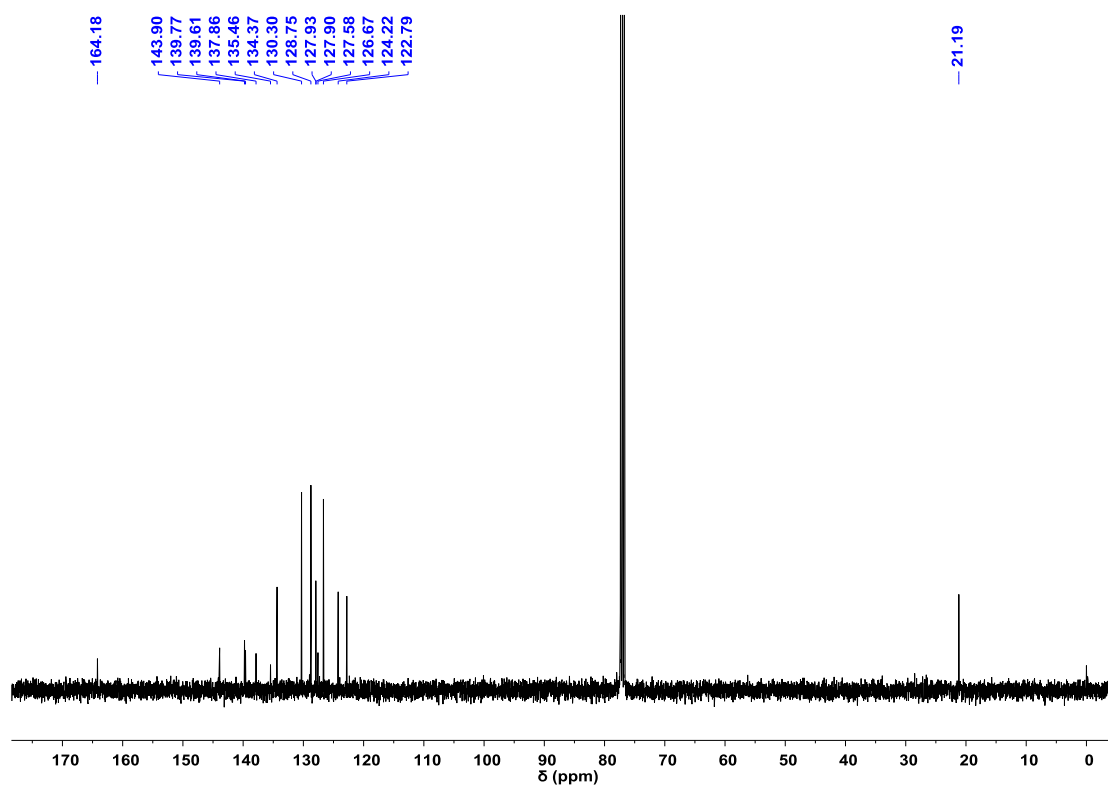
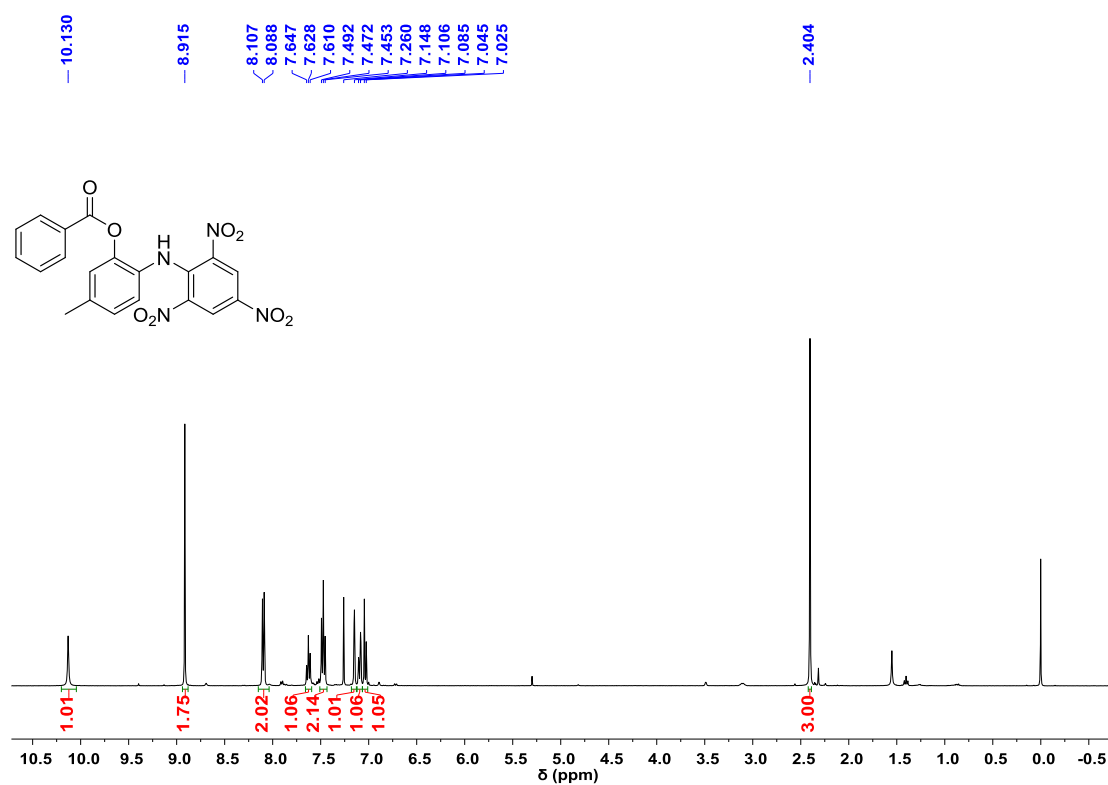
# Copies of $^1\text{H}$ , $^{13}\text{C}$ , and $^{19}\text{F}$ NMR spectra of products **3**

## 5-Fluoro-2-((2,4,6-trinitrophenyl)amino)phenyl benzoate (**3aa**)

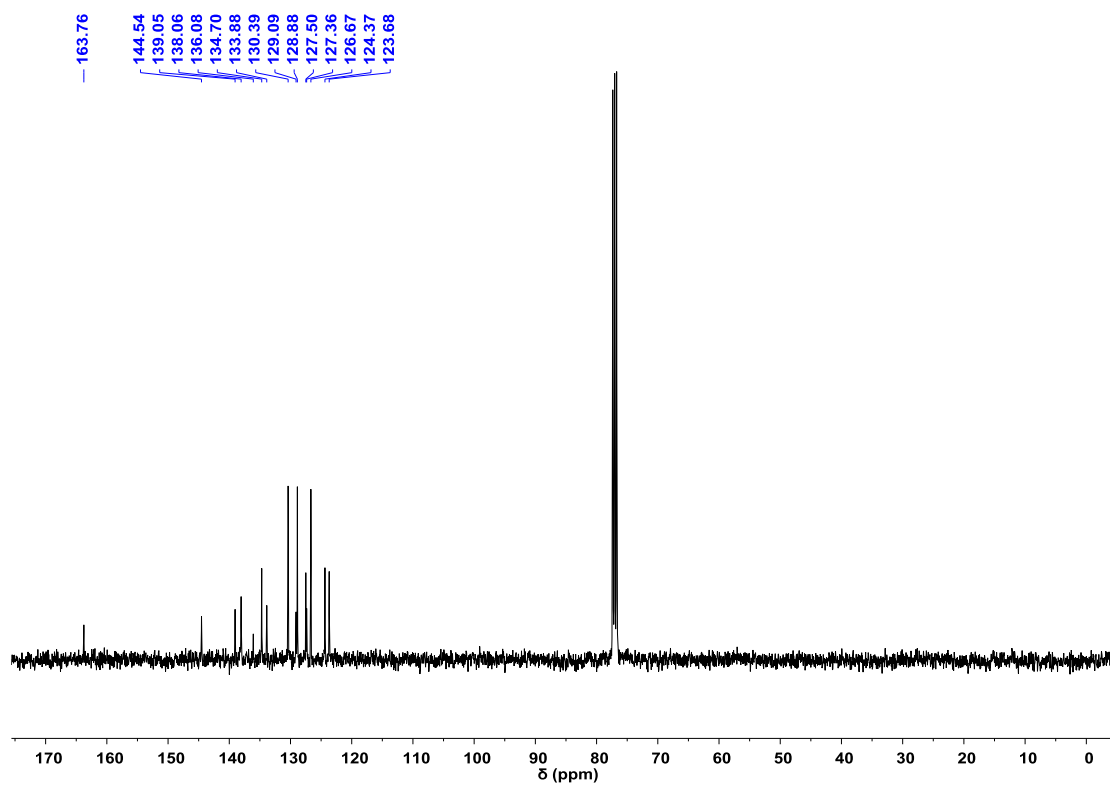
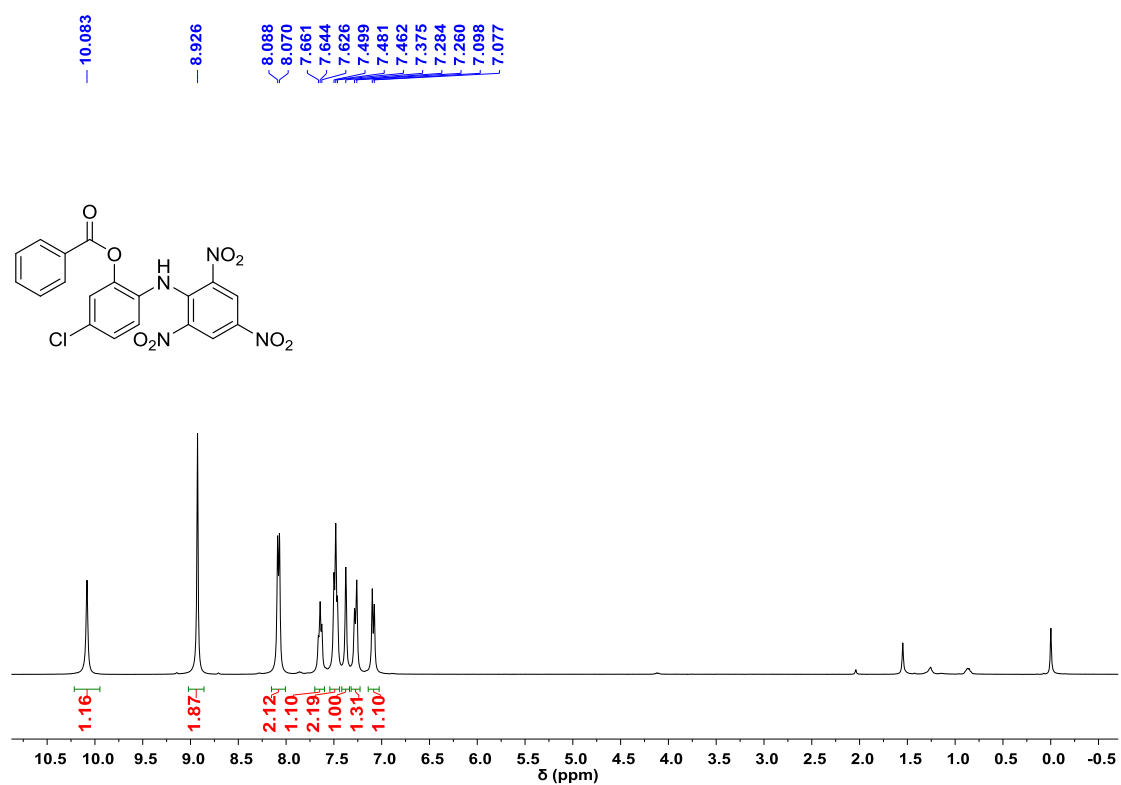




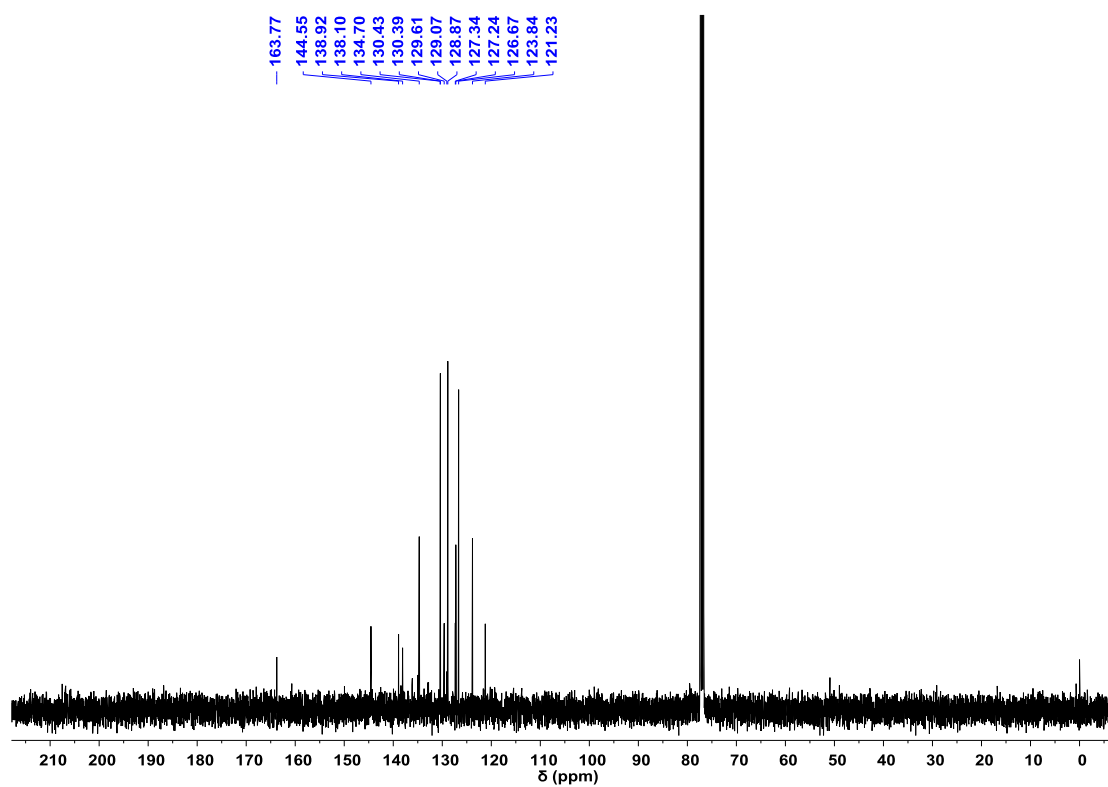
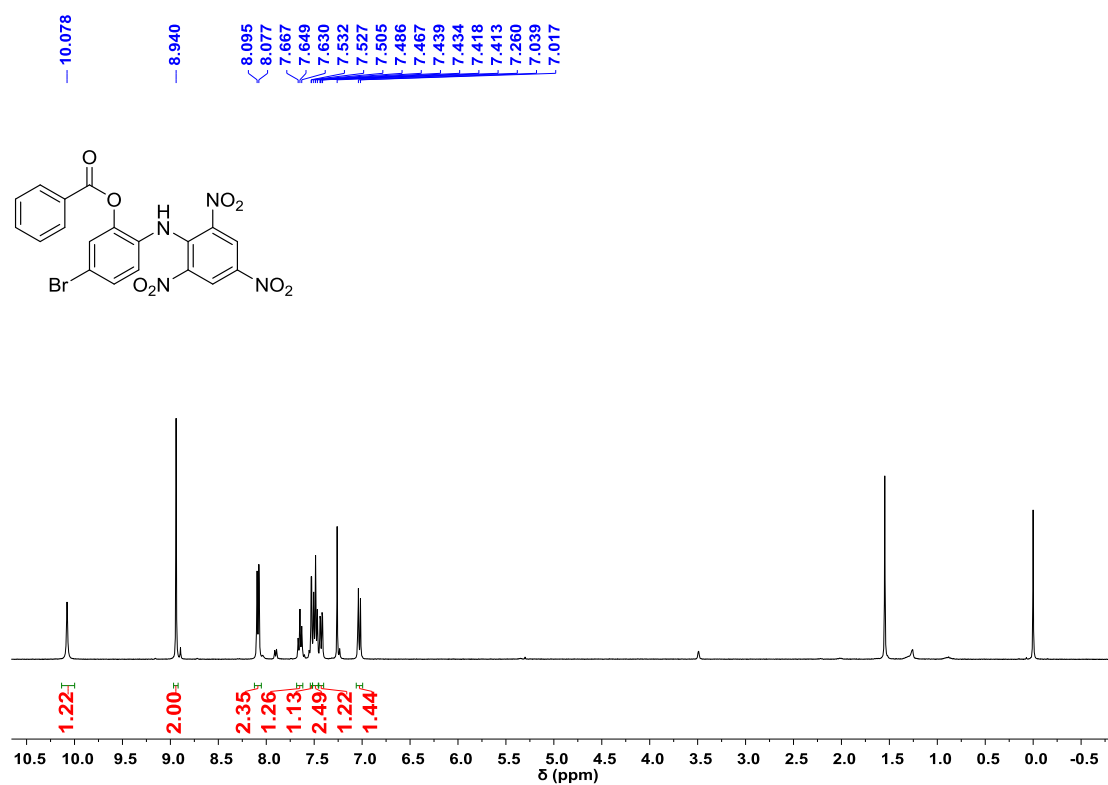
5-Methyl-2-((2,4,6-trinitrophenyl)amino)phenyl benzoate (**3ba**)



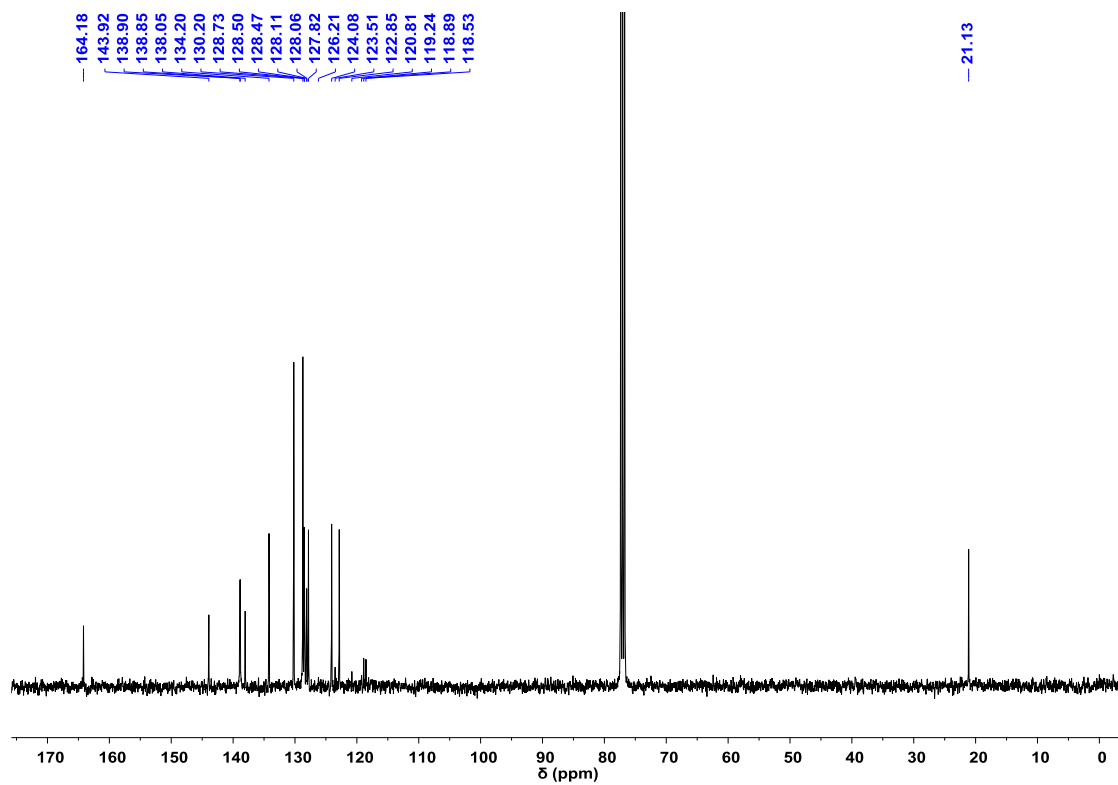
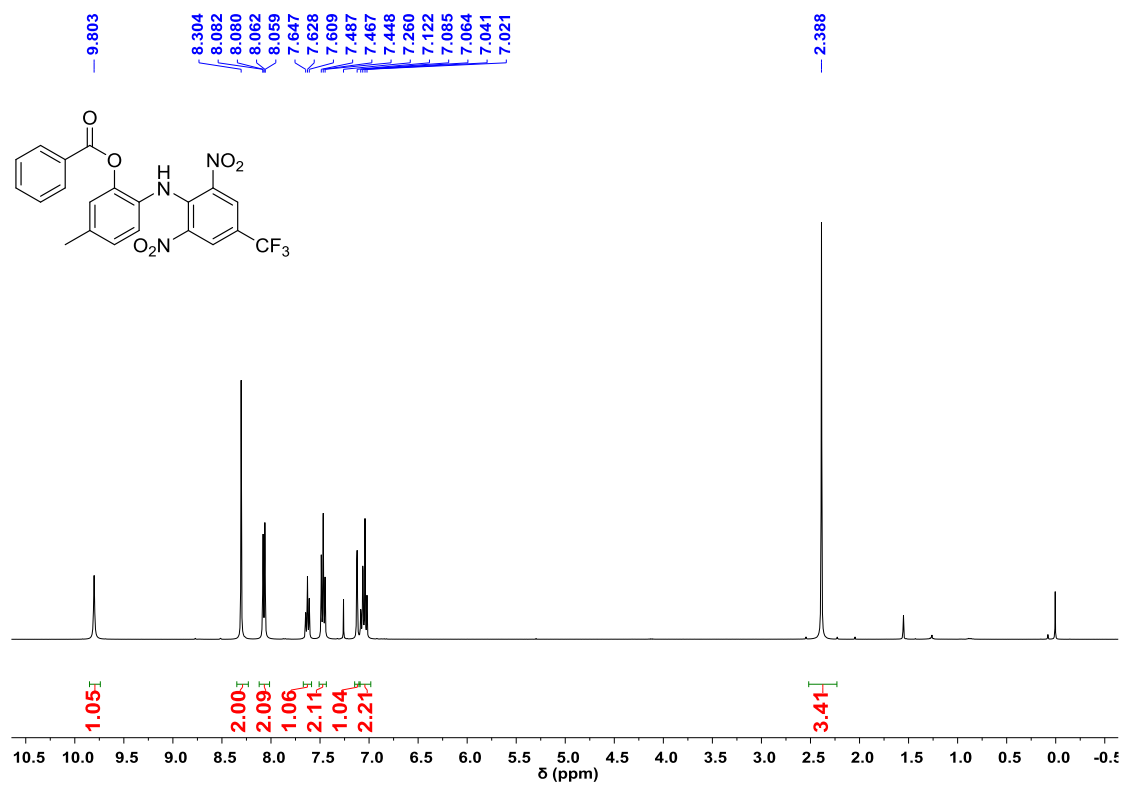
5-Chloro-2-((2,4,6-trinitrophenyl)amino)phenyl benzoate (**3ca**)

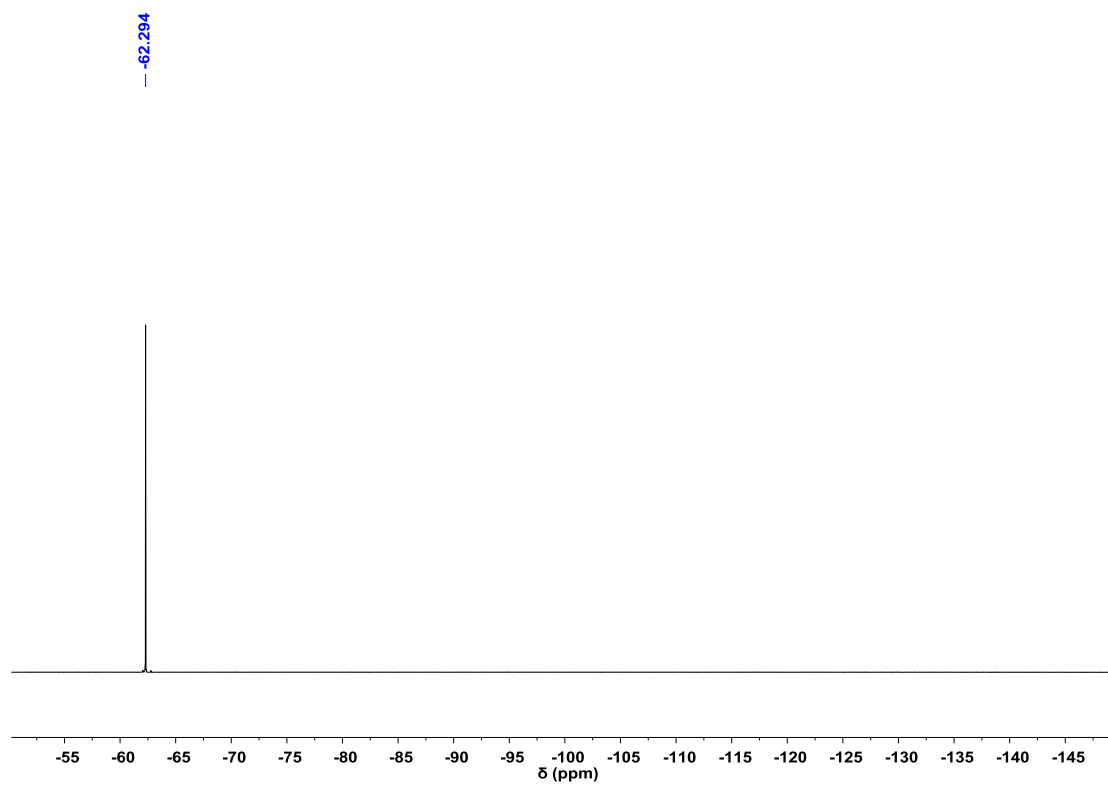


5-Bromo-2-((2,4,6-trinitrophenyl)amino)phenyl benzoate (**3da**)



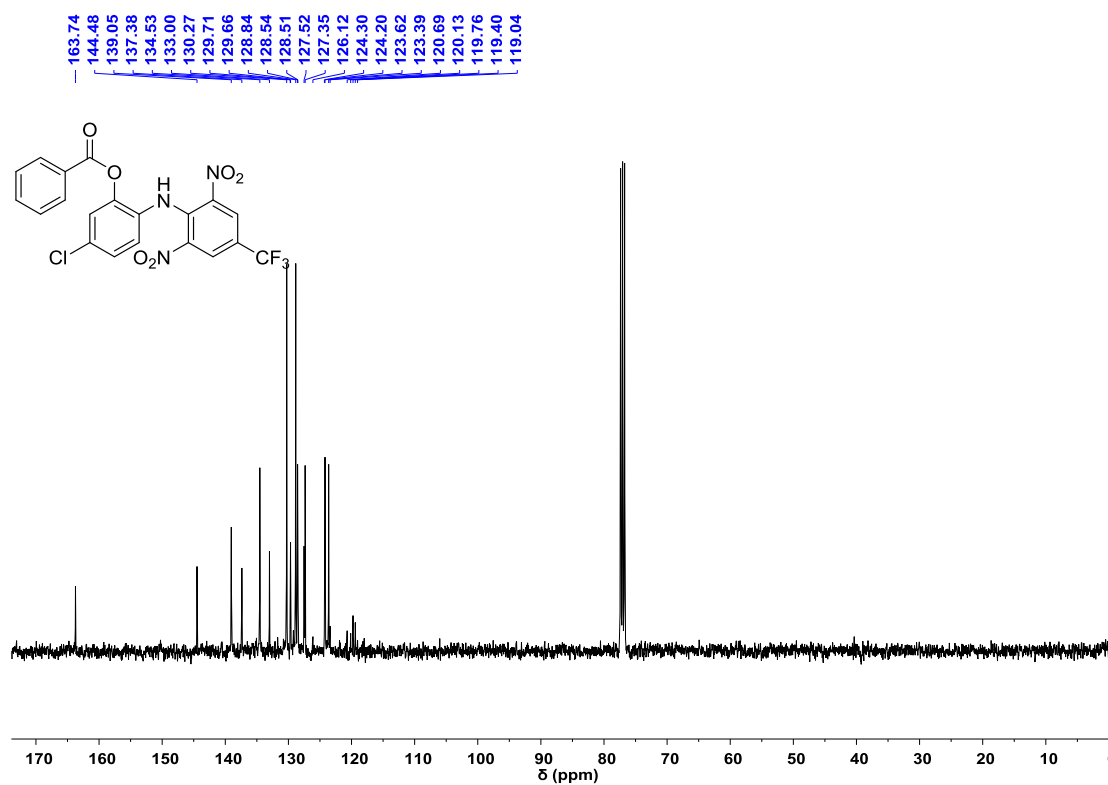
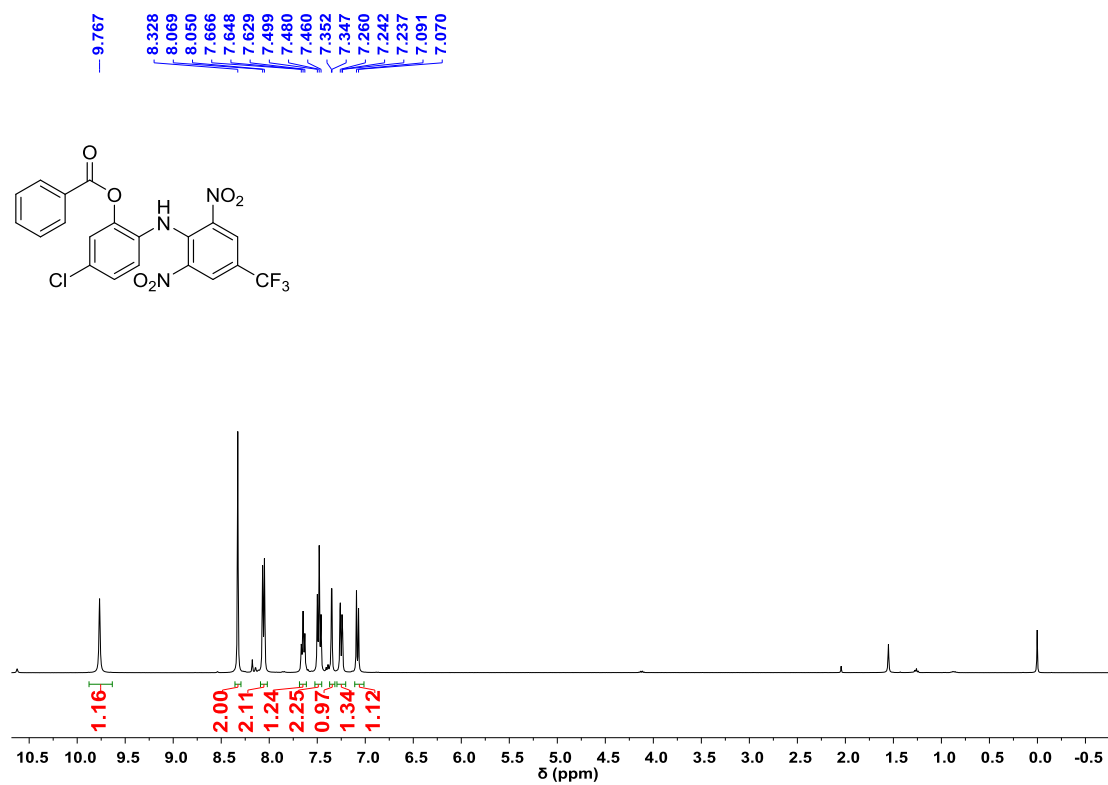
$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR of 2-((2,6-Dinitro-4-(trifluoromethyl)phenyl)amino)-5-methylphenyl benzoate (**3bb**)

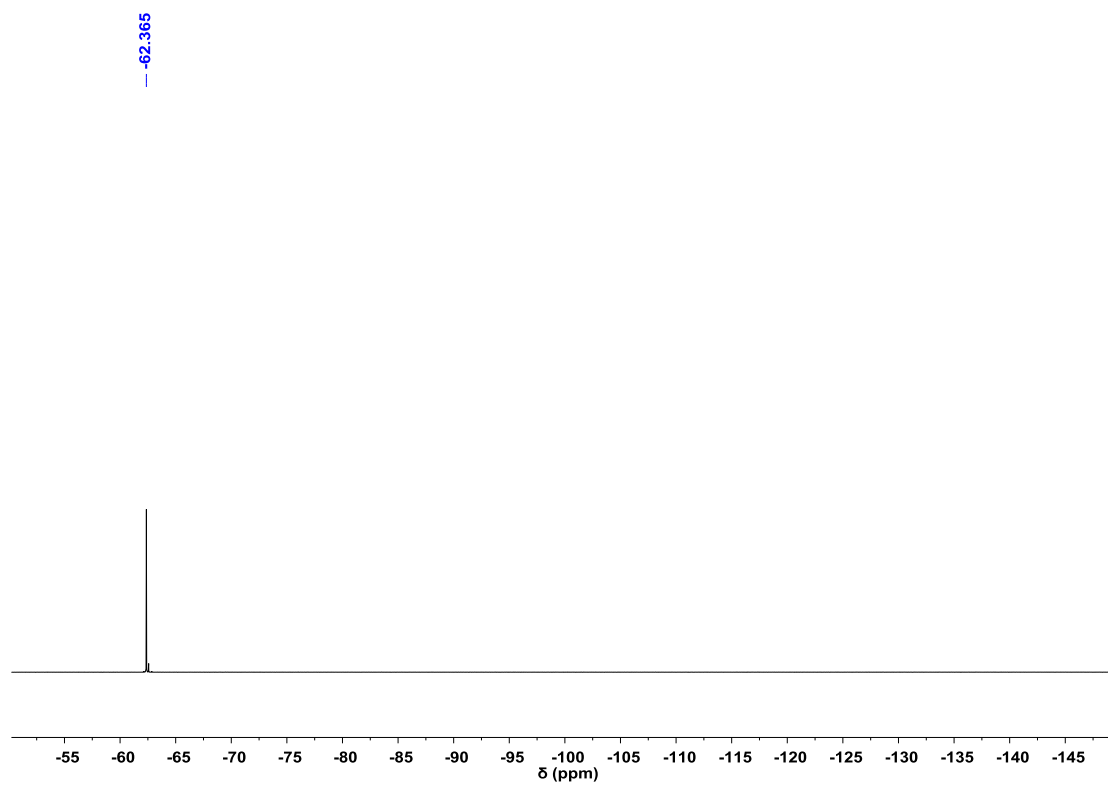




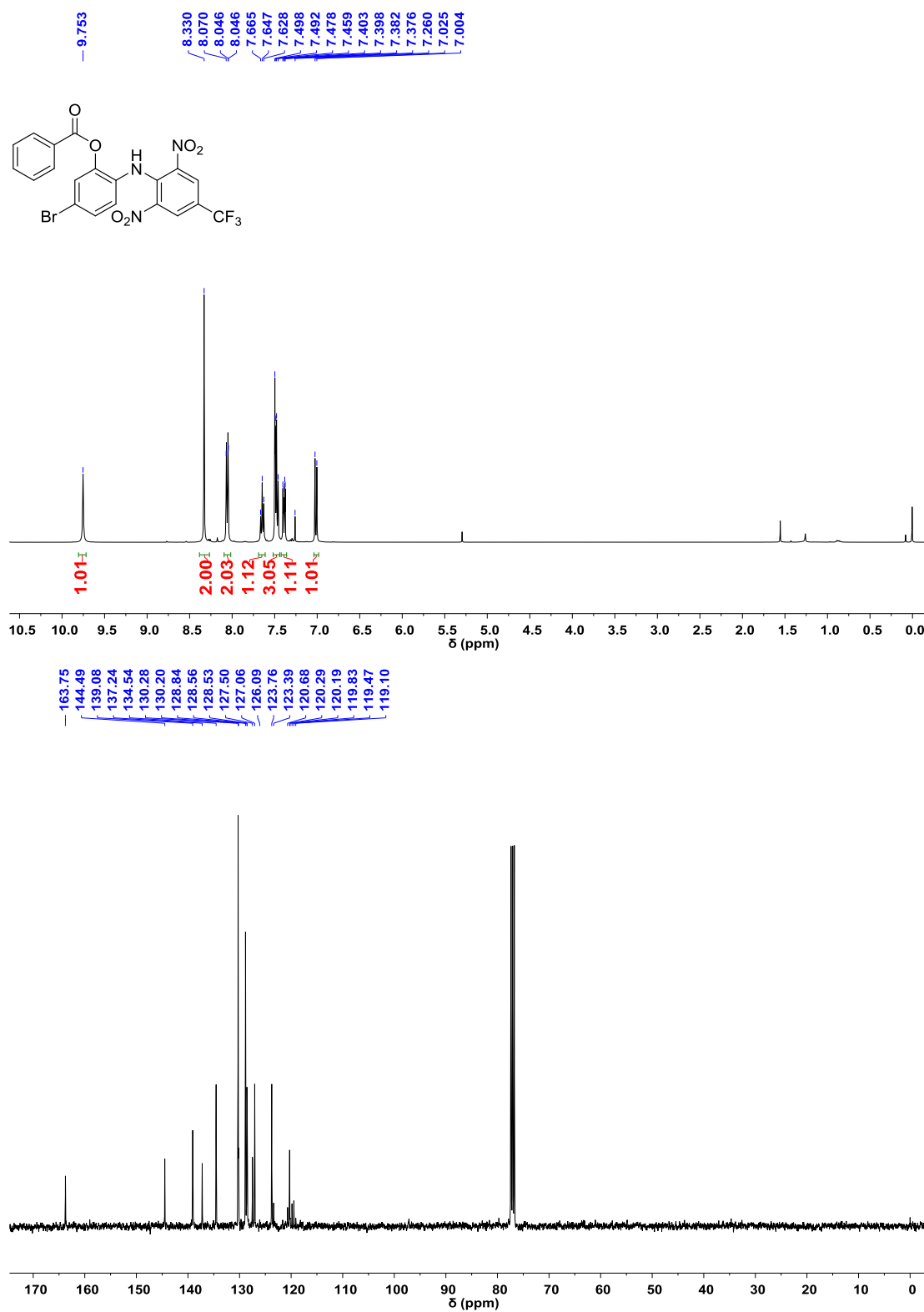


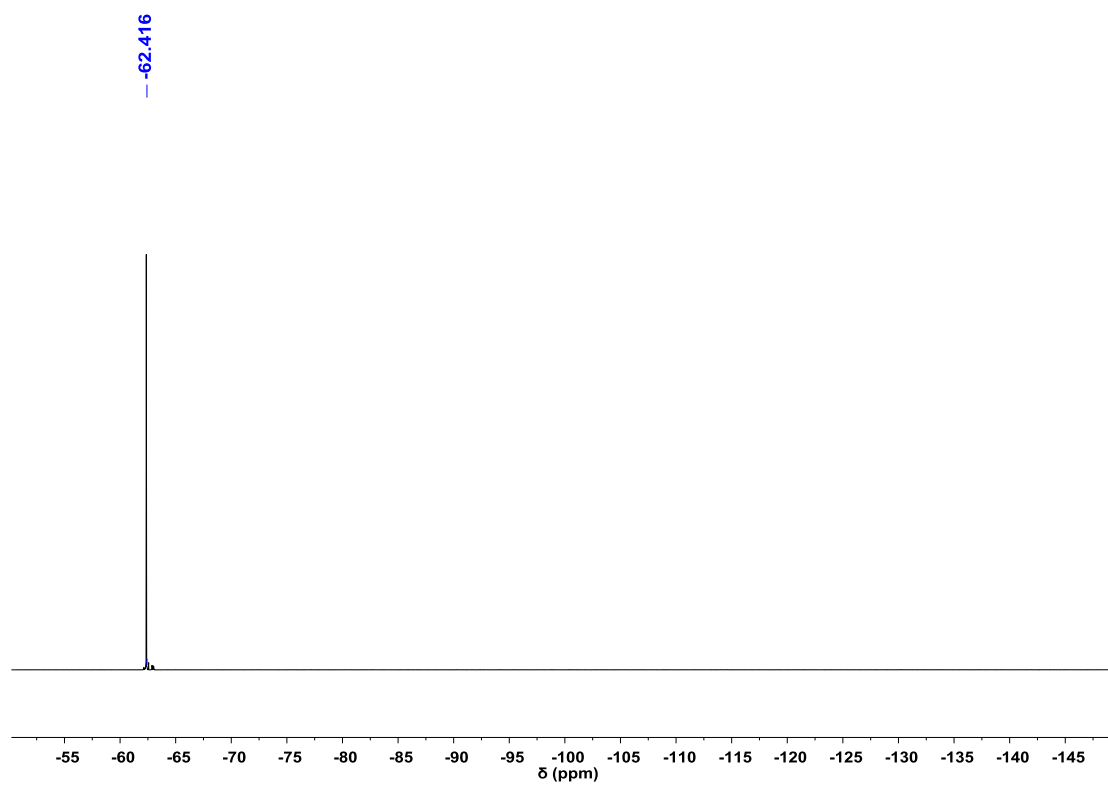
$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR of 5-Chloro-2-((2,6-dinitro-4-(trifluoromethyl)phenyl)amino)phenyl benzoate (**3cb**)



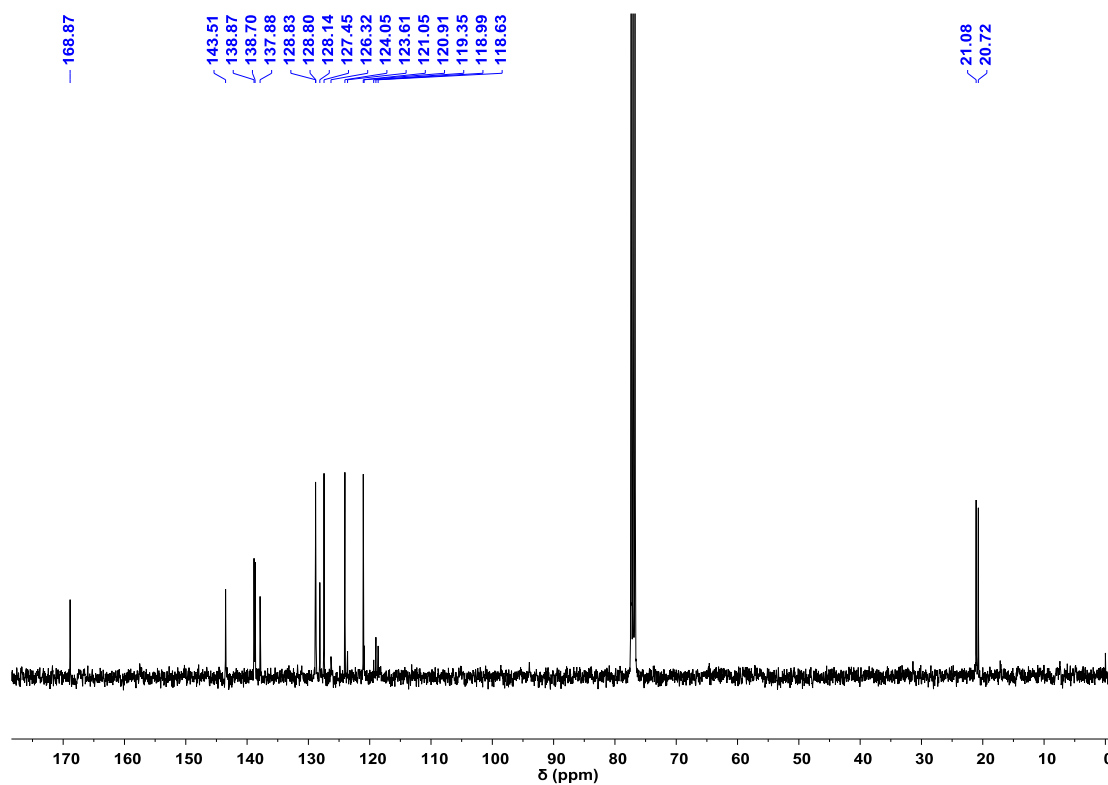
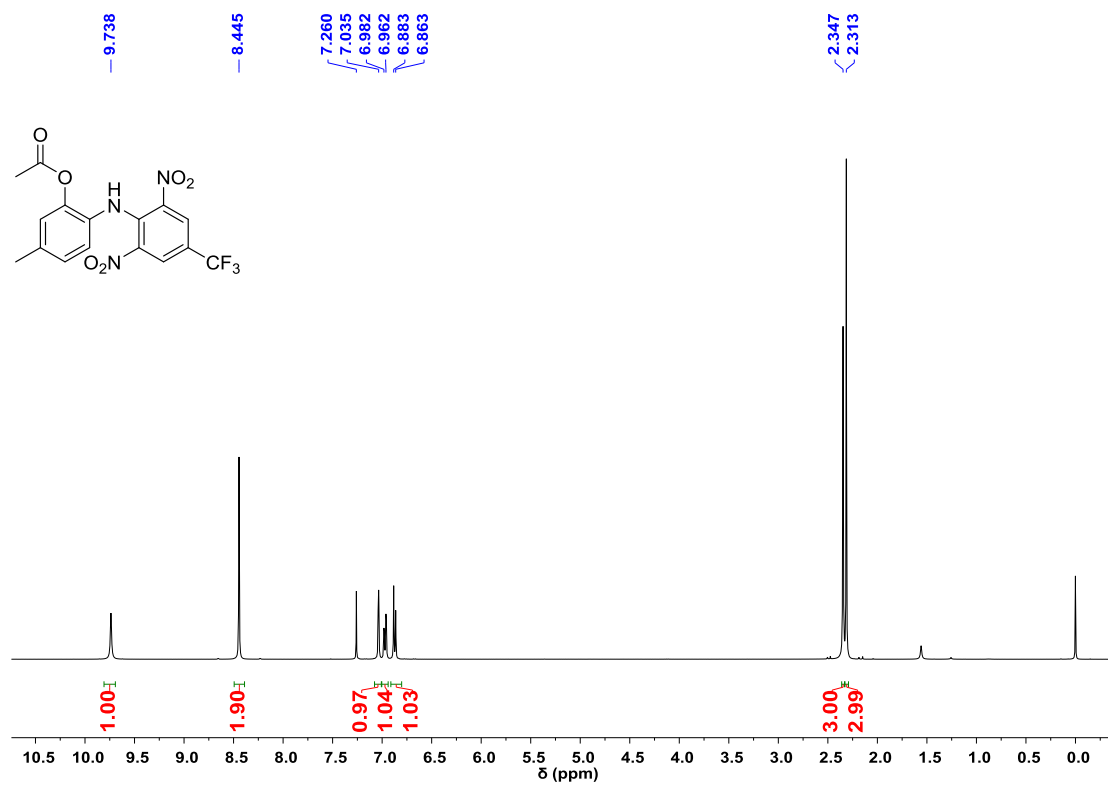


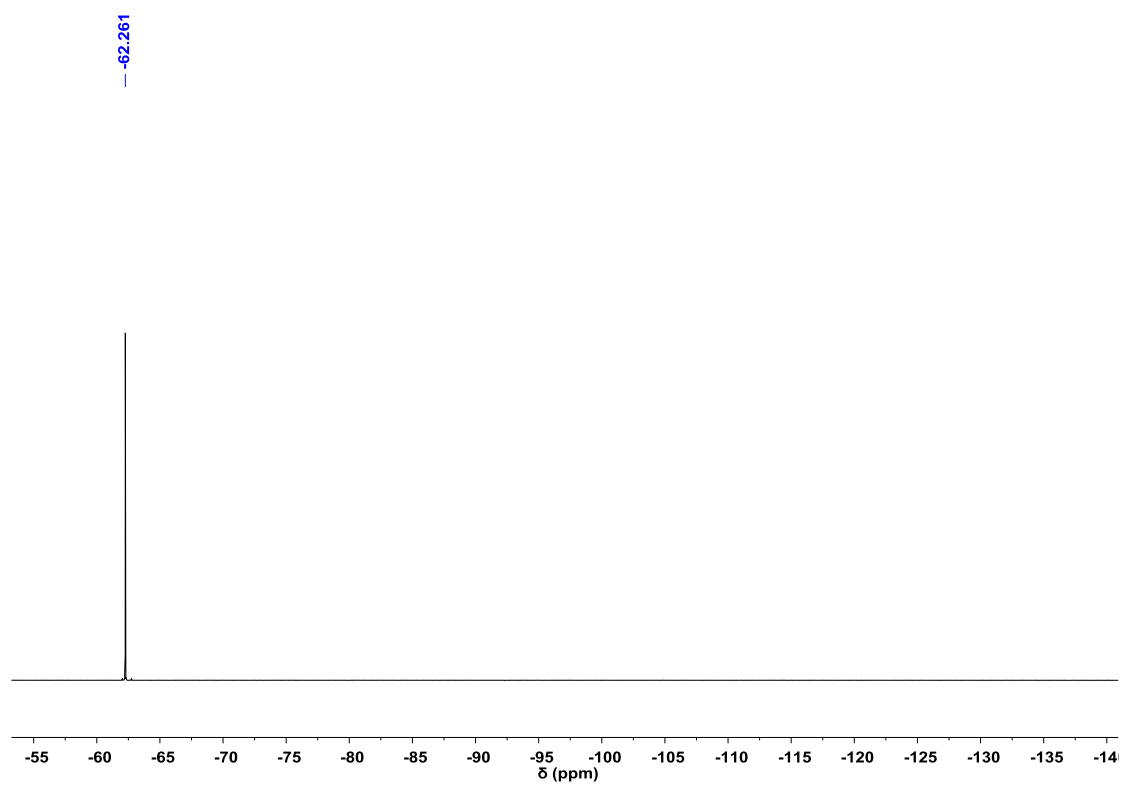
$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR of 5-Bromo-2-((2,6-dinitro-4-(trifluoromethyl)phenyl)amino)phenyl benzoate (**3db**)



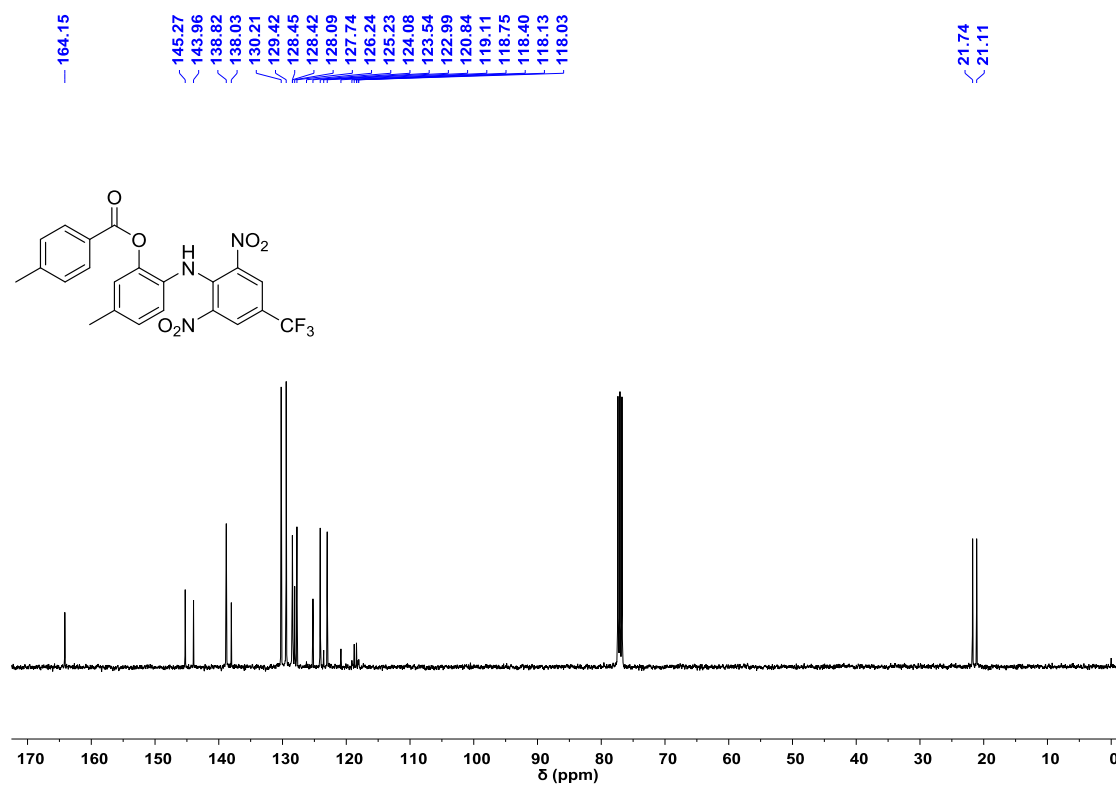
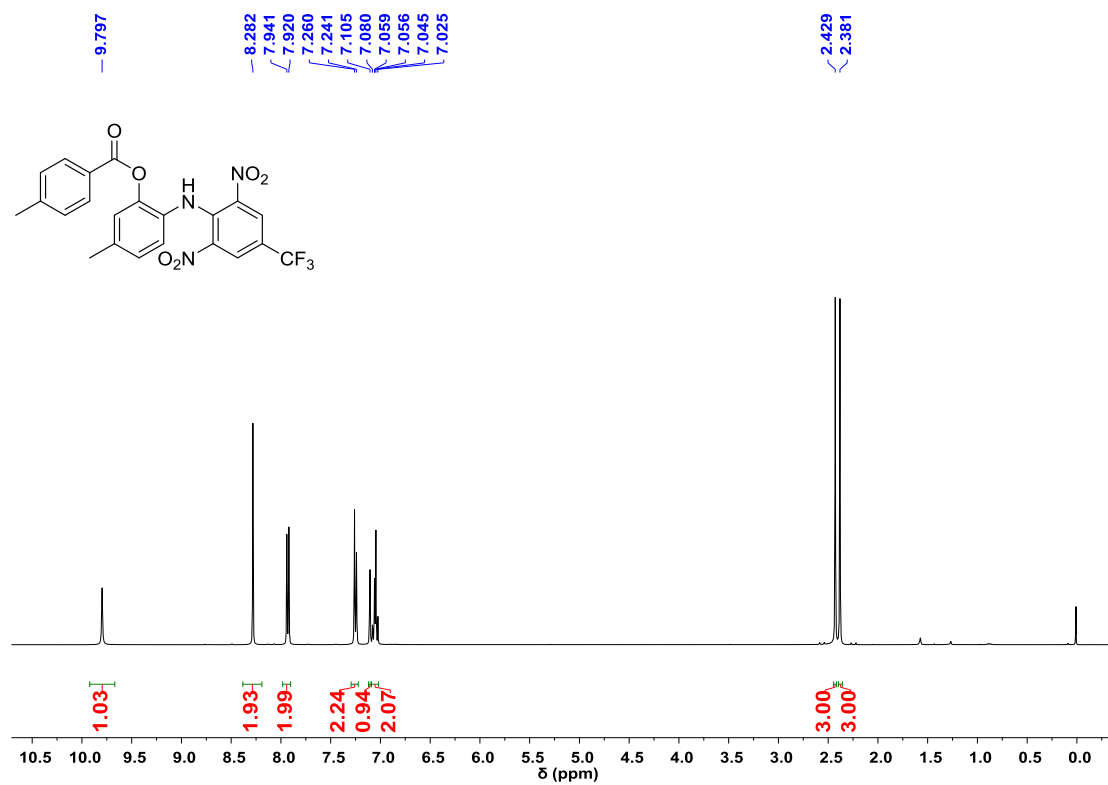


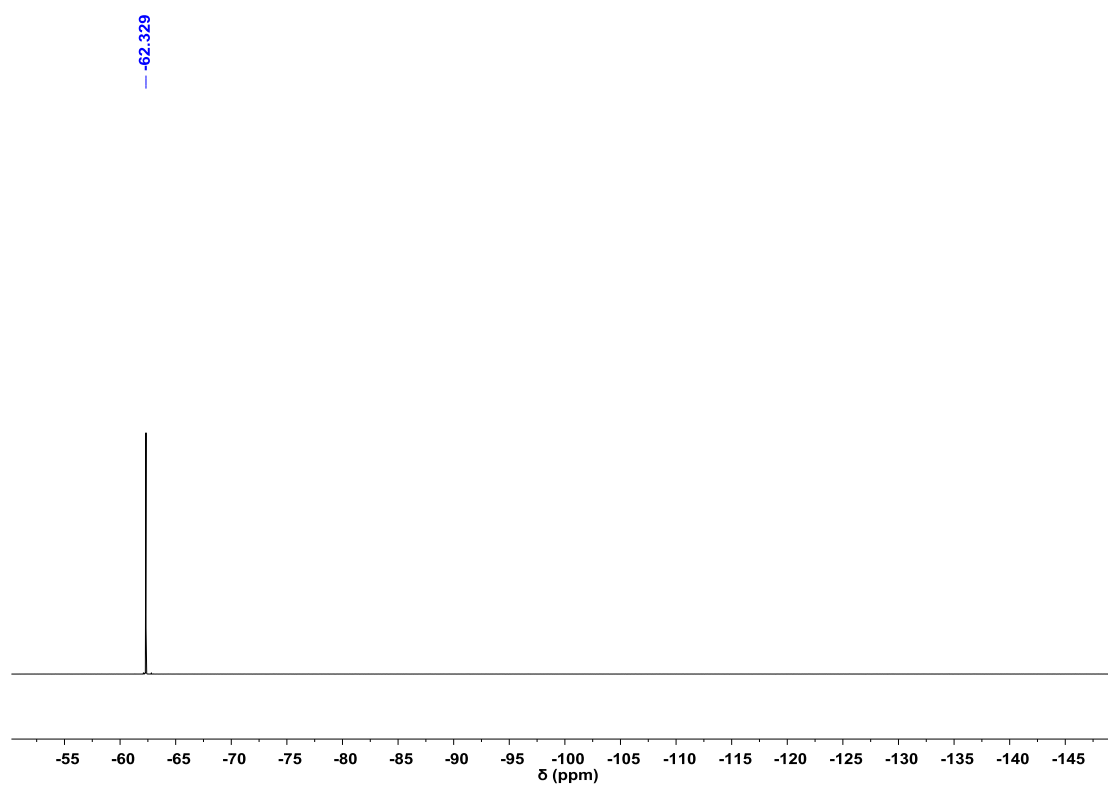
$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR of 2-((2,6-Dinitro-4-(trifluoromethyl)phenyl)amino)-5-methylphenyl acetate (**3eb**)





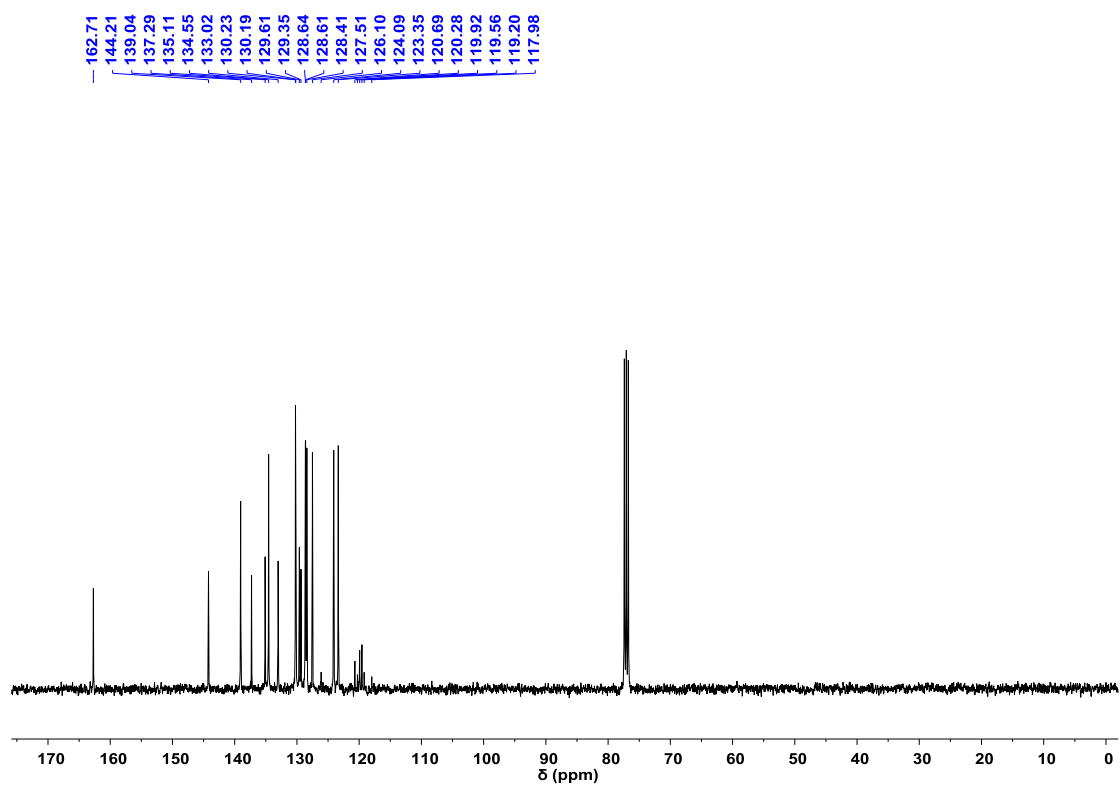
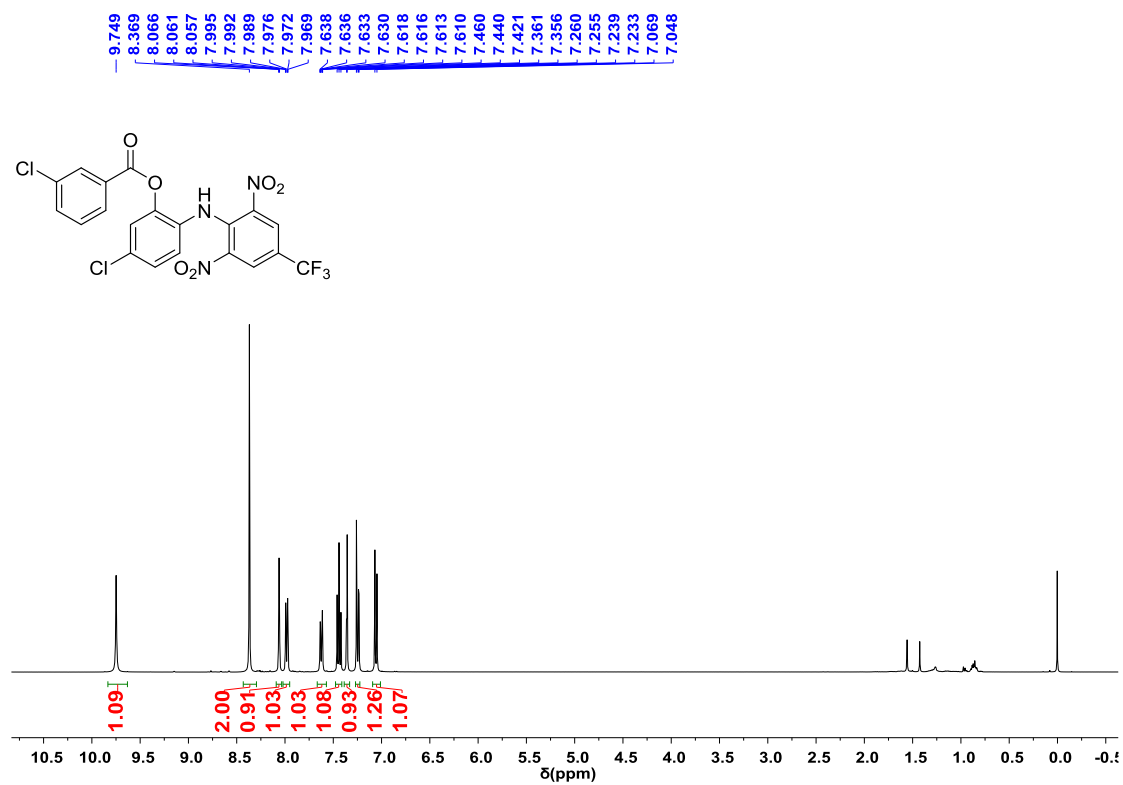
$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR of 2-((2,6-Dinitro-4-(trifluoromethyl)phenyl)amino)-5-methylphenyl 4-methylbenzoate (**3fb**)

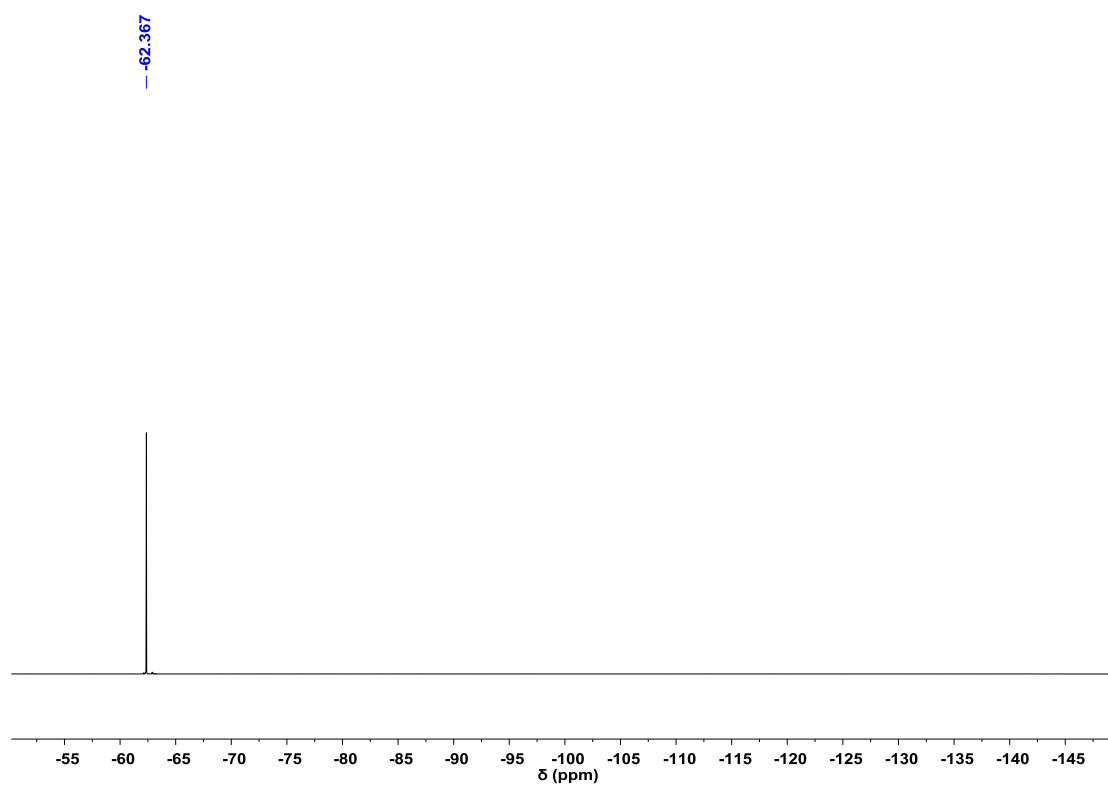




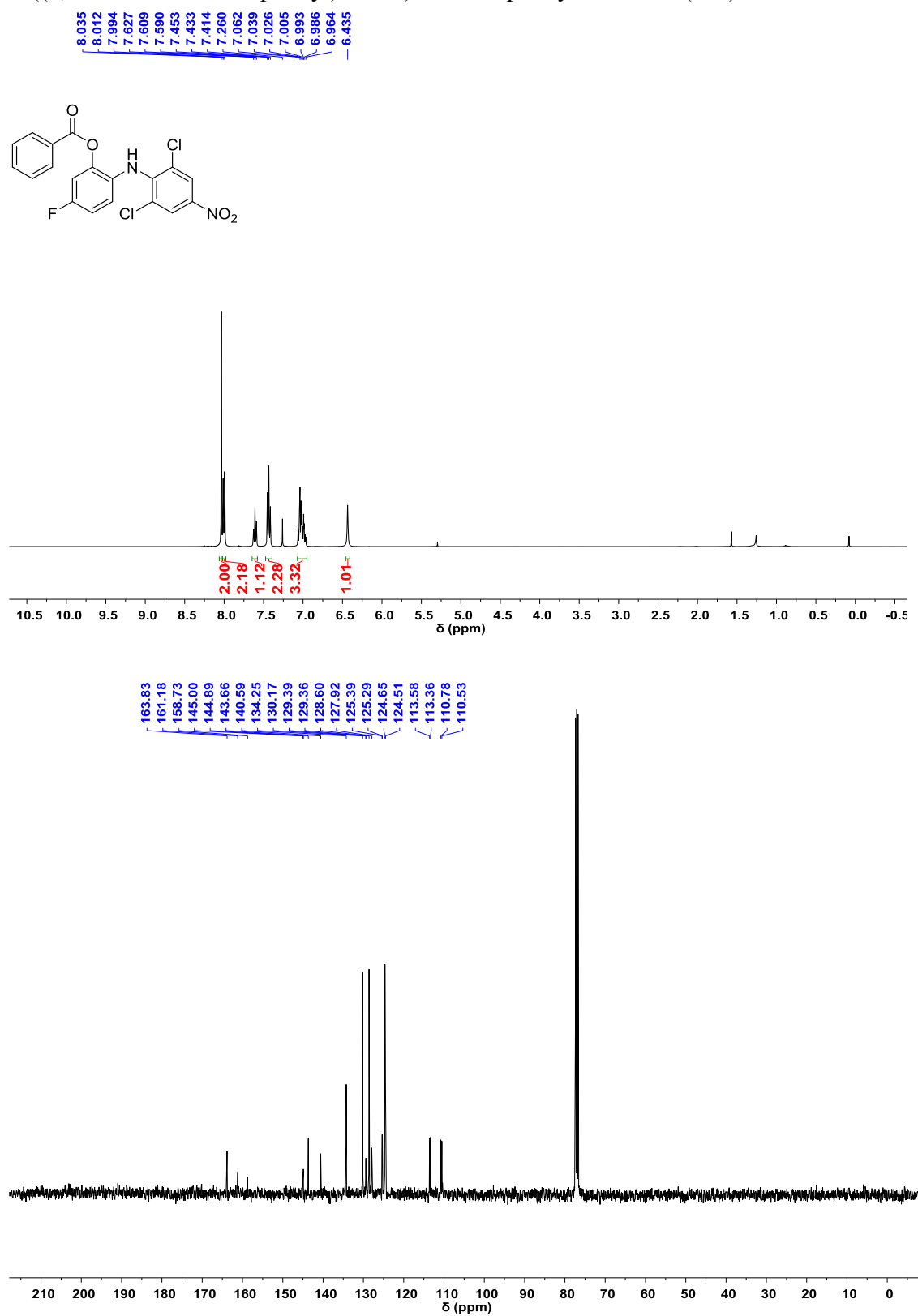


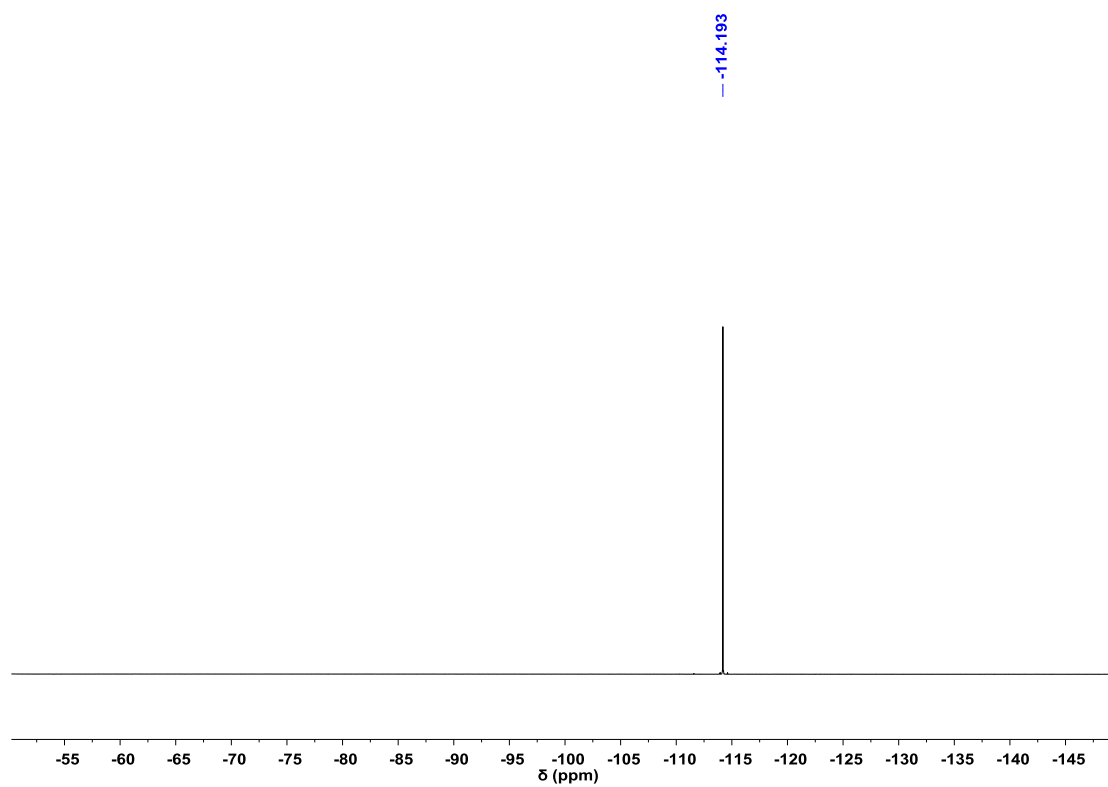
$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR of 5-Chloro-2-((2,6-dinitro-4-(trifluoromethyl)phenyl)amino)phenyl 3-chlorobenzoate (**3gb**)



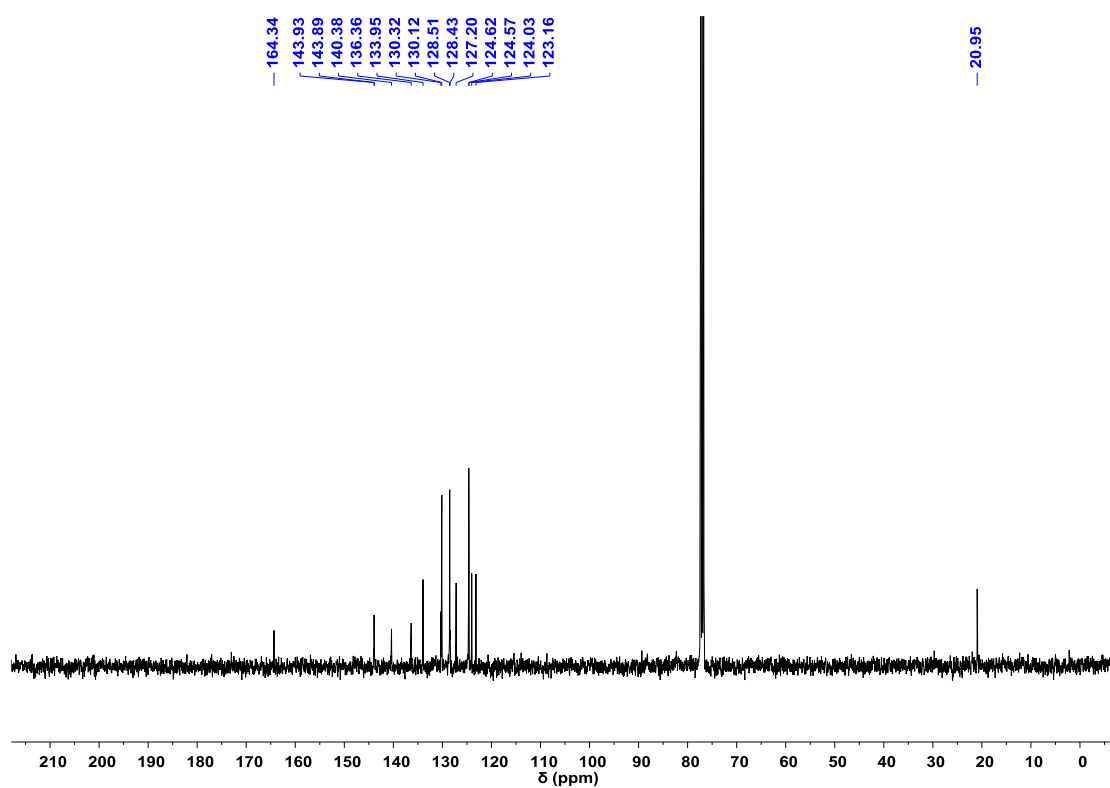
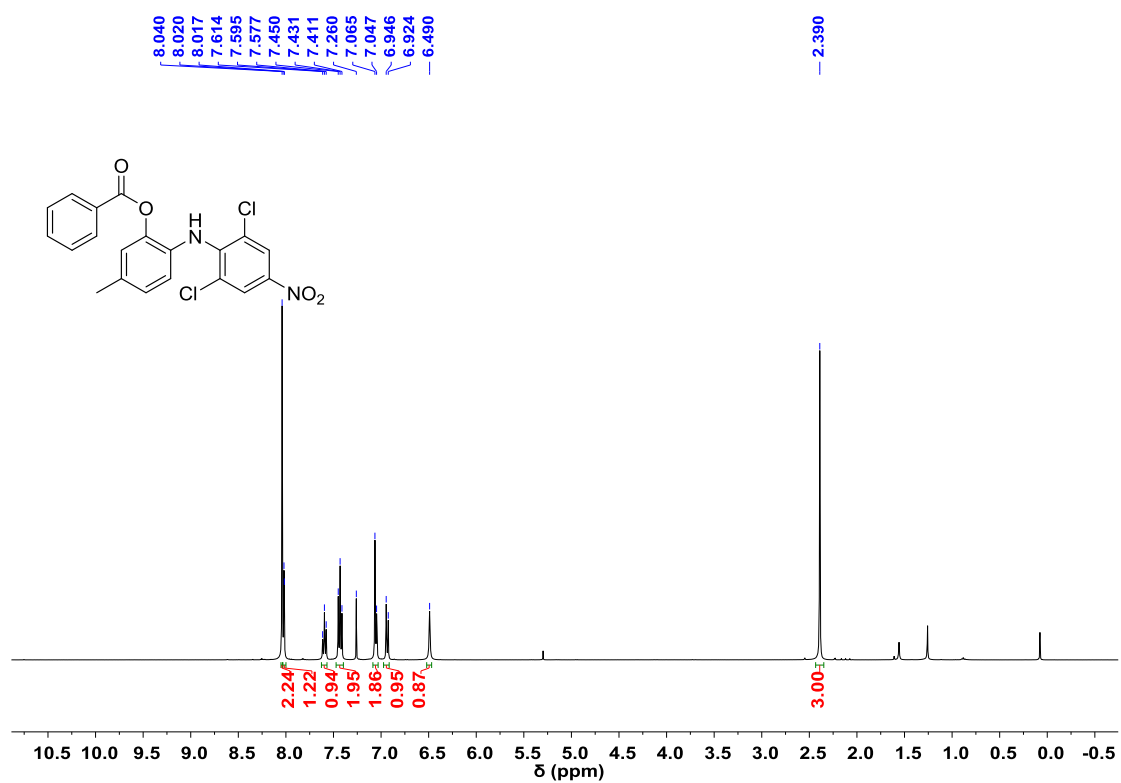


2-((2,6-Dichloro-4-nitrophenyl)amino)-5-fluorophenyl benzoate (**3ac**)

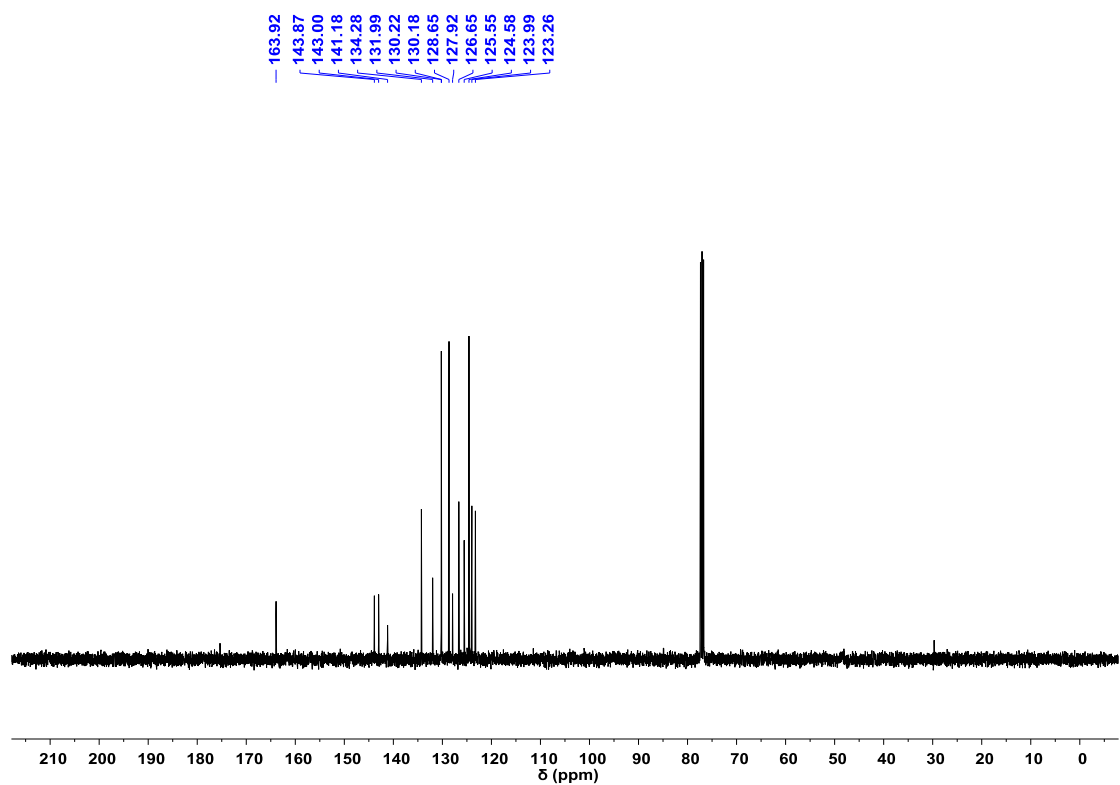
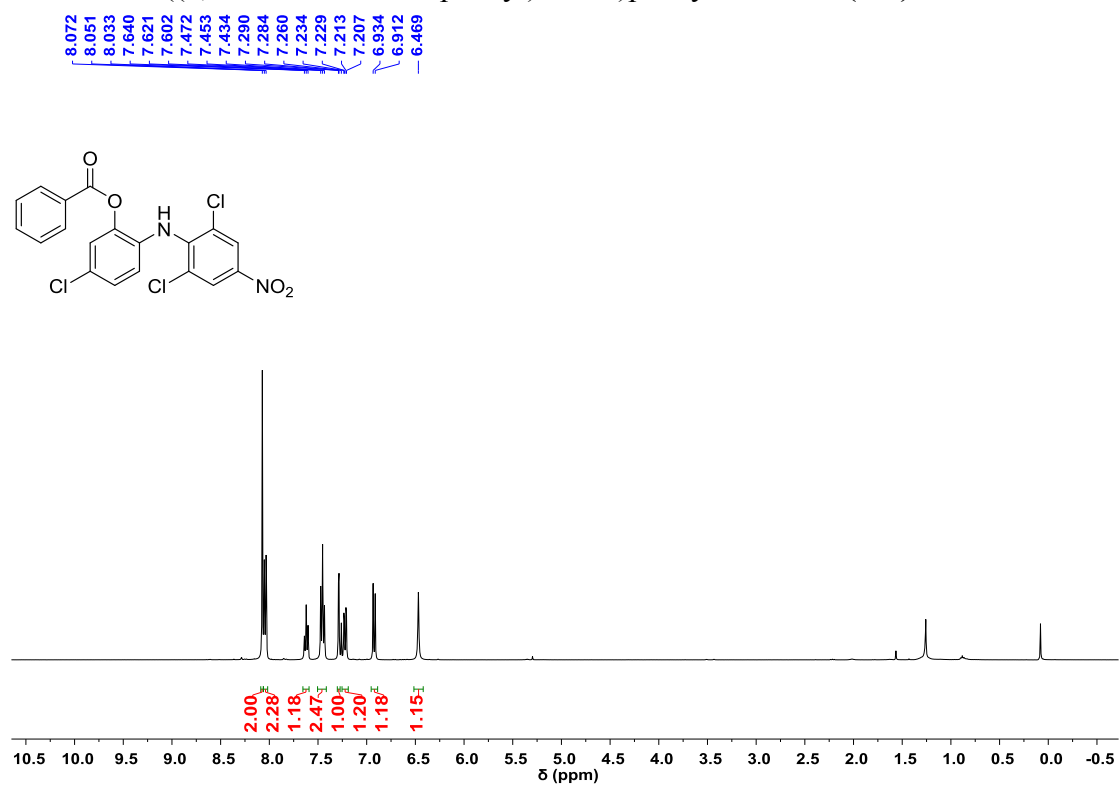




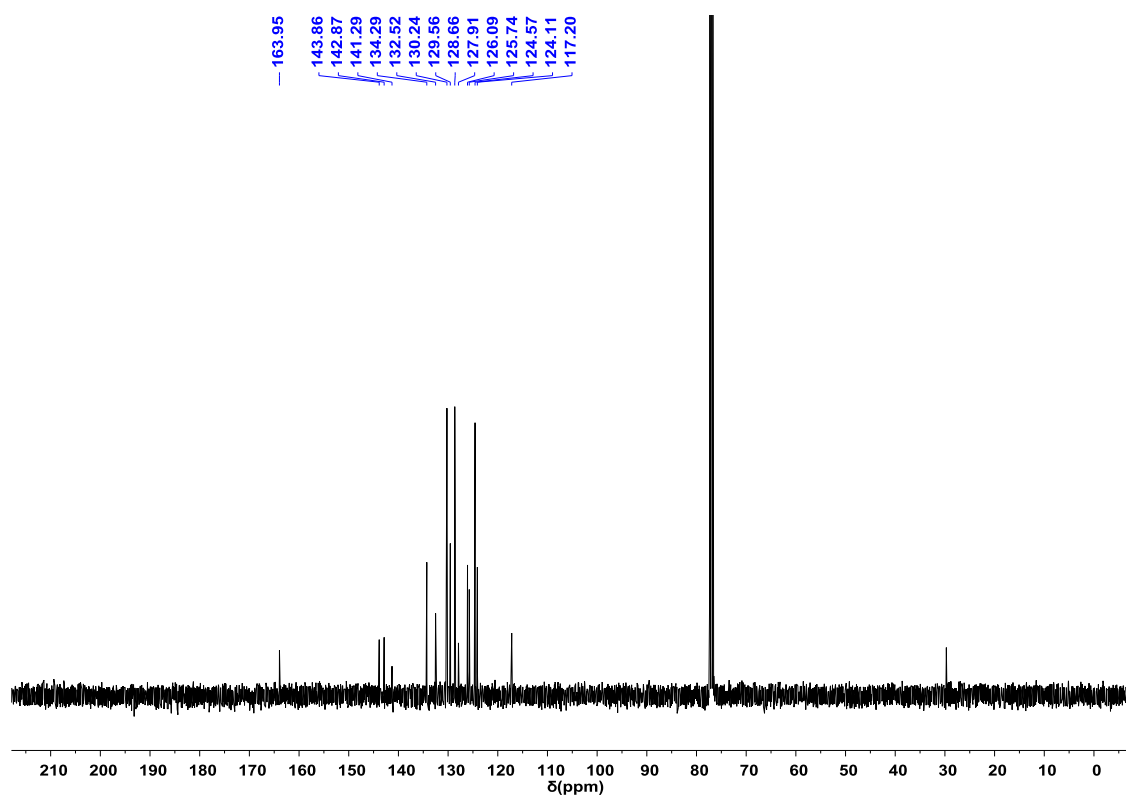
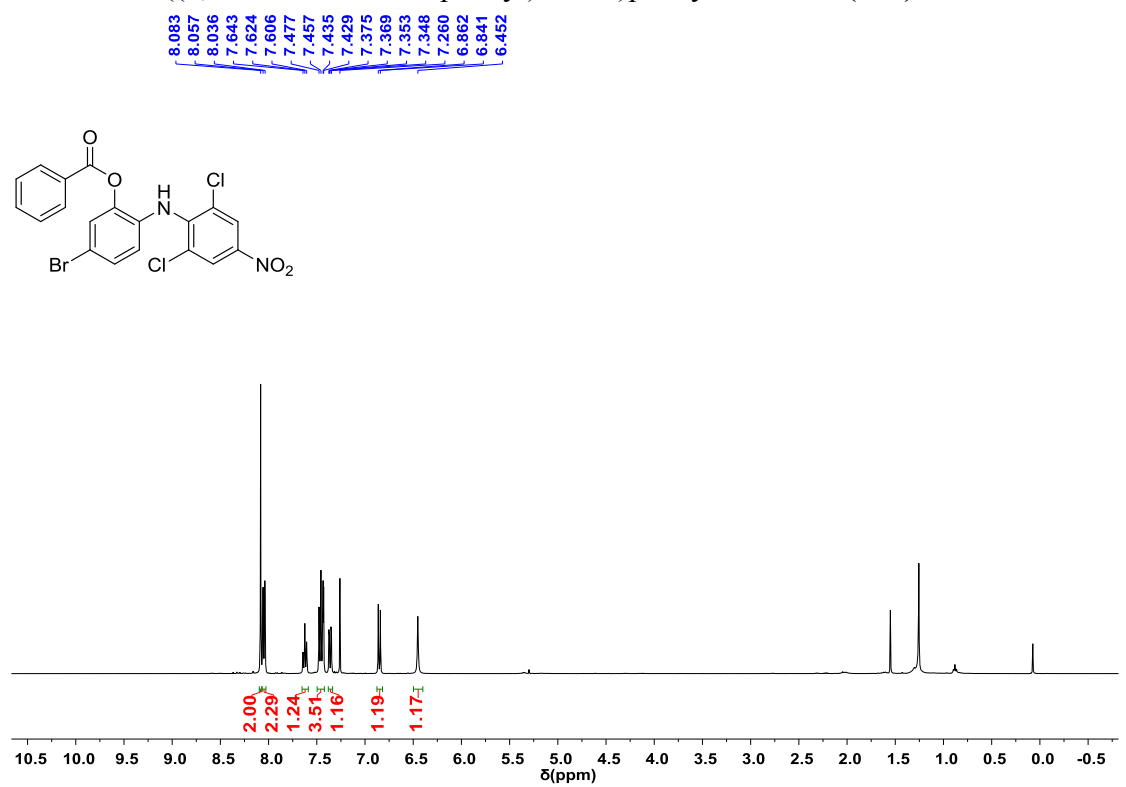
2-((2,6-Dichloro-4-nitrophenyl)amino)-5-methylphenyl benzoate (**3bc**)



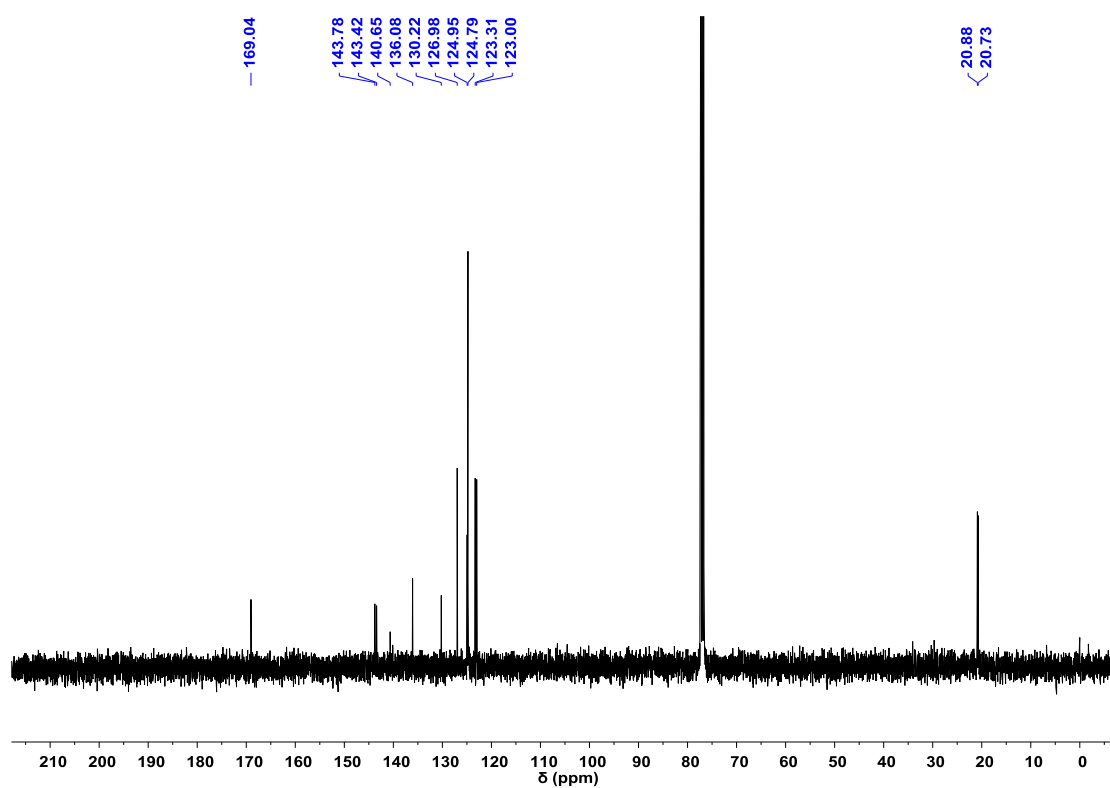
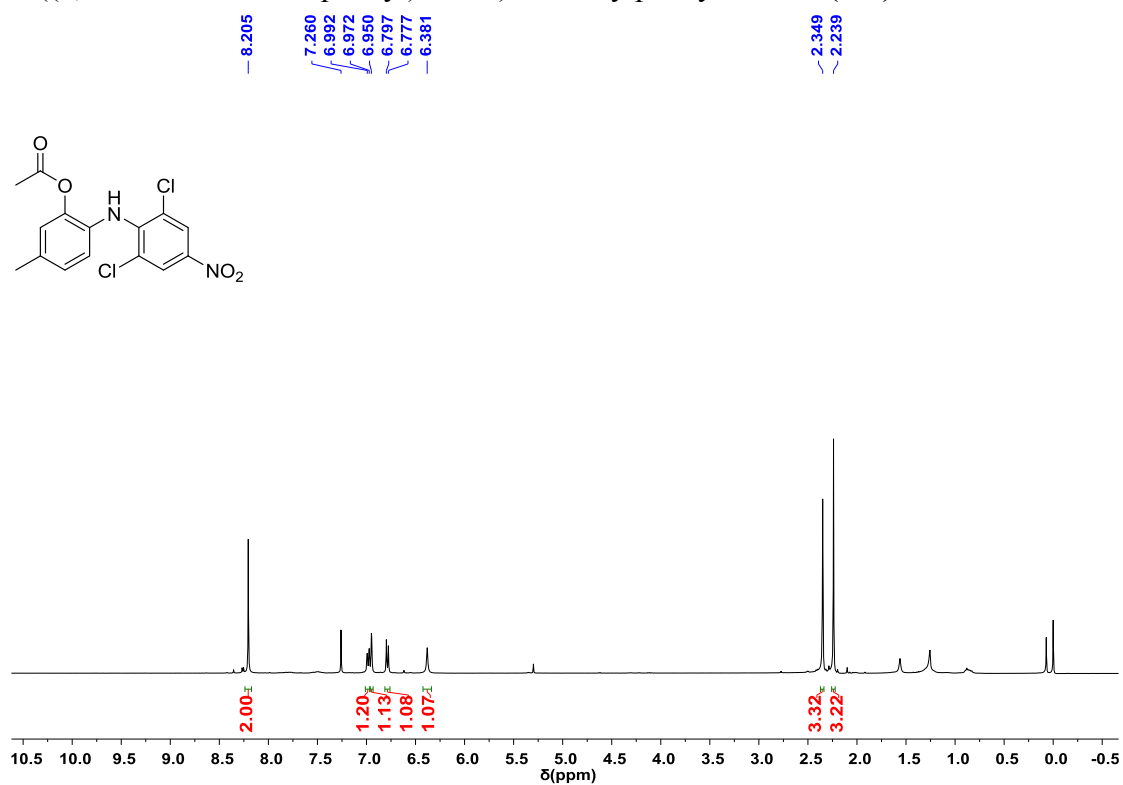
5-Chloro-2-((2,6-dichloro-4-nitrophenyl)amino)phenyl benzoate (**3cc**)



5-Bromo-2-((2,6-dichloro-4-nitrophenyl)amino)phenyl benzoate (**3dc**)

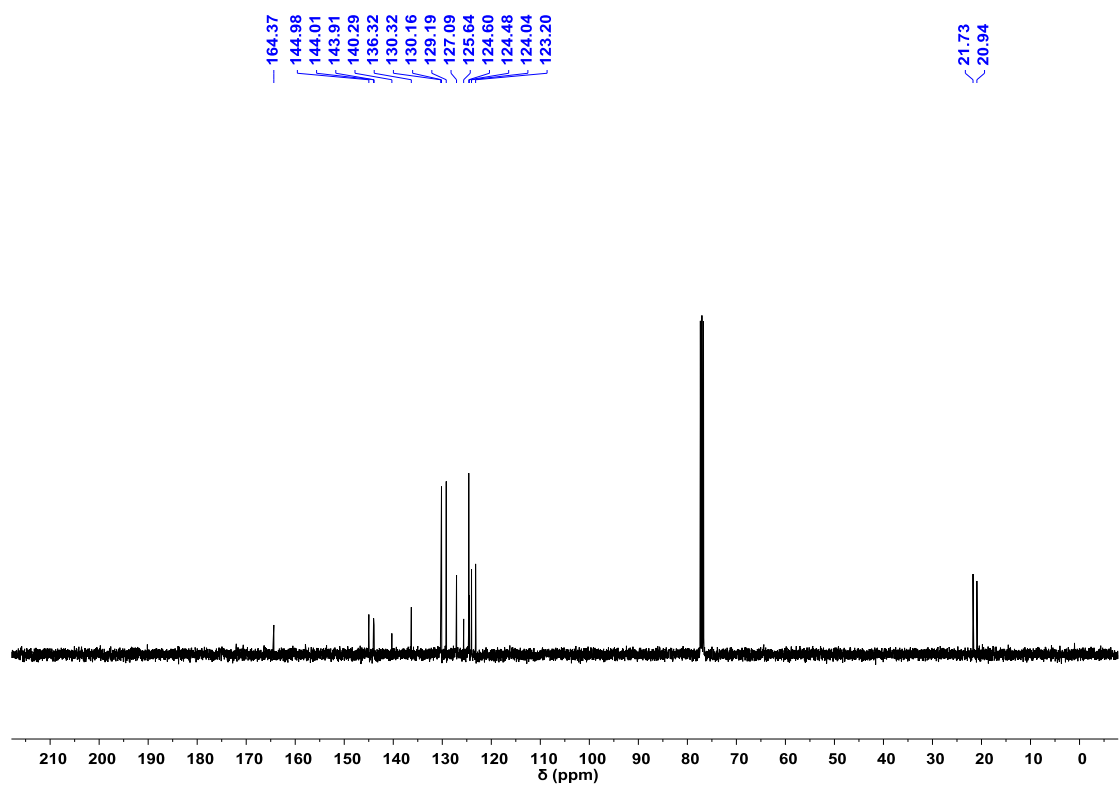
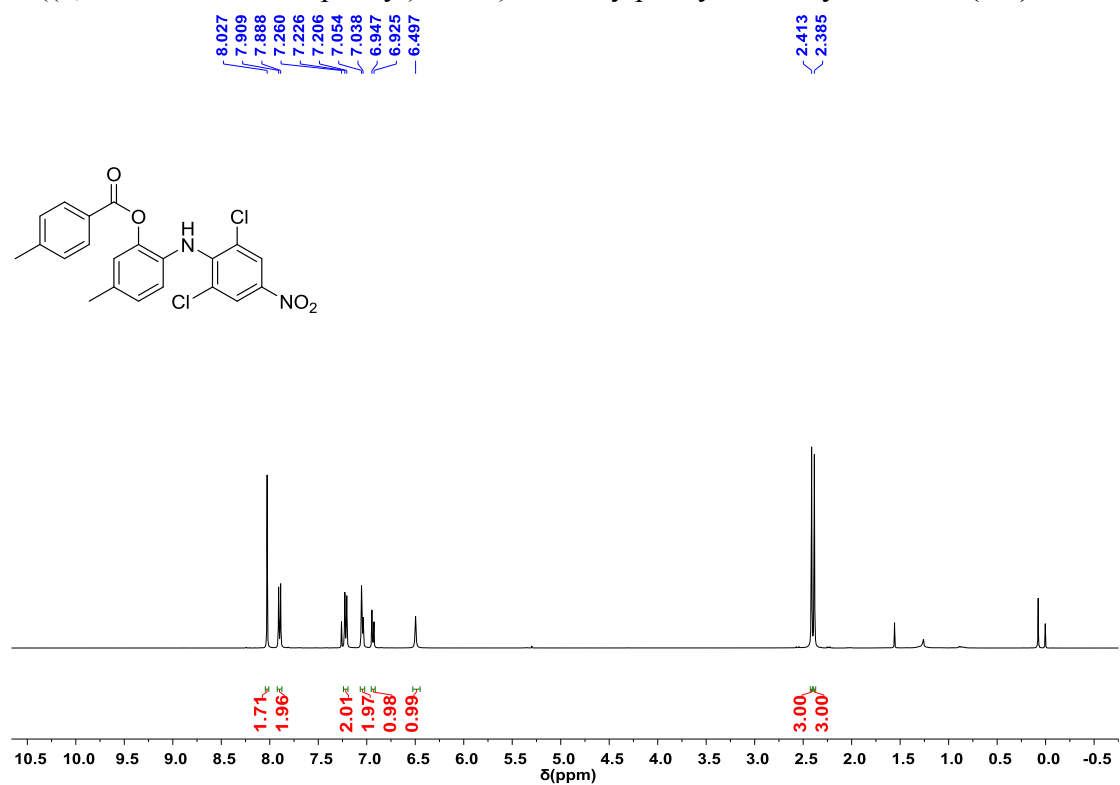


2-((2,6-Dichloro-4-nitrophenyl)amino)-5-methylphenyl acetate (**3ec**)

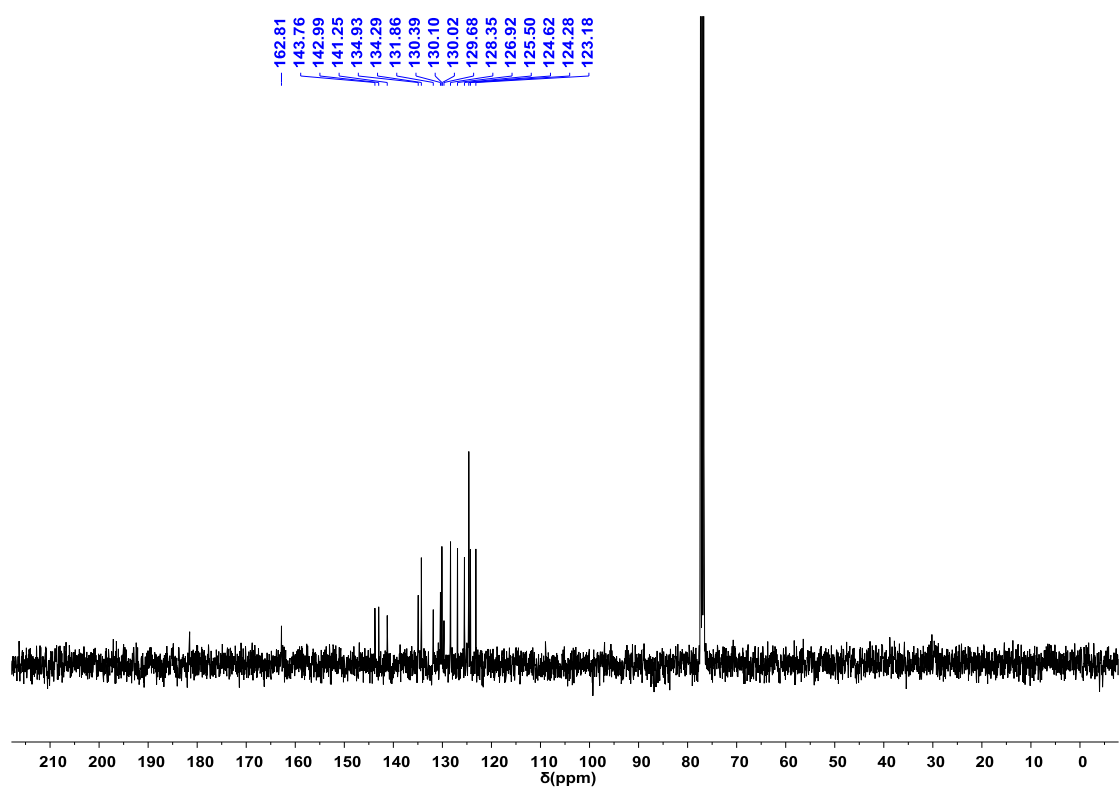
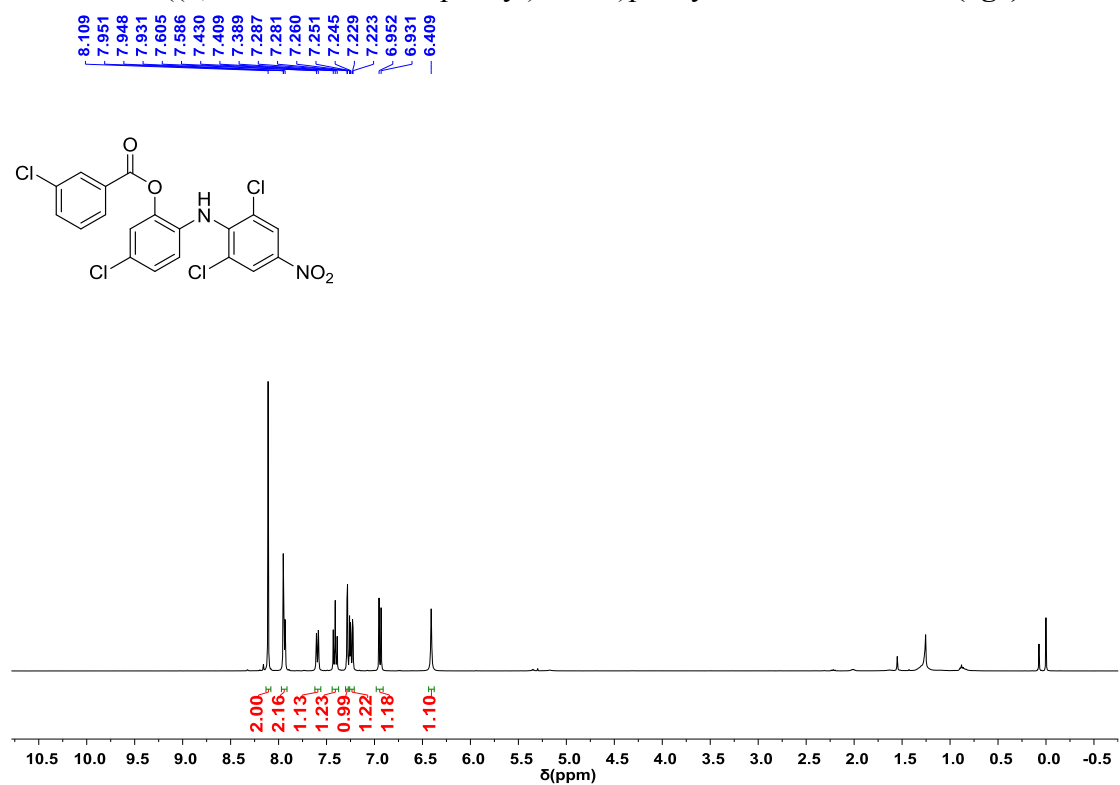




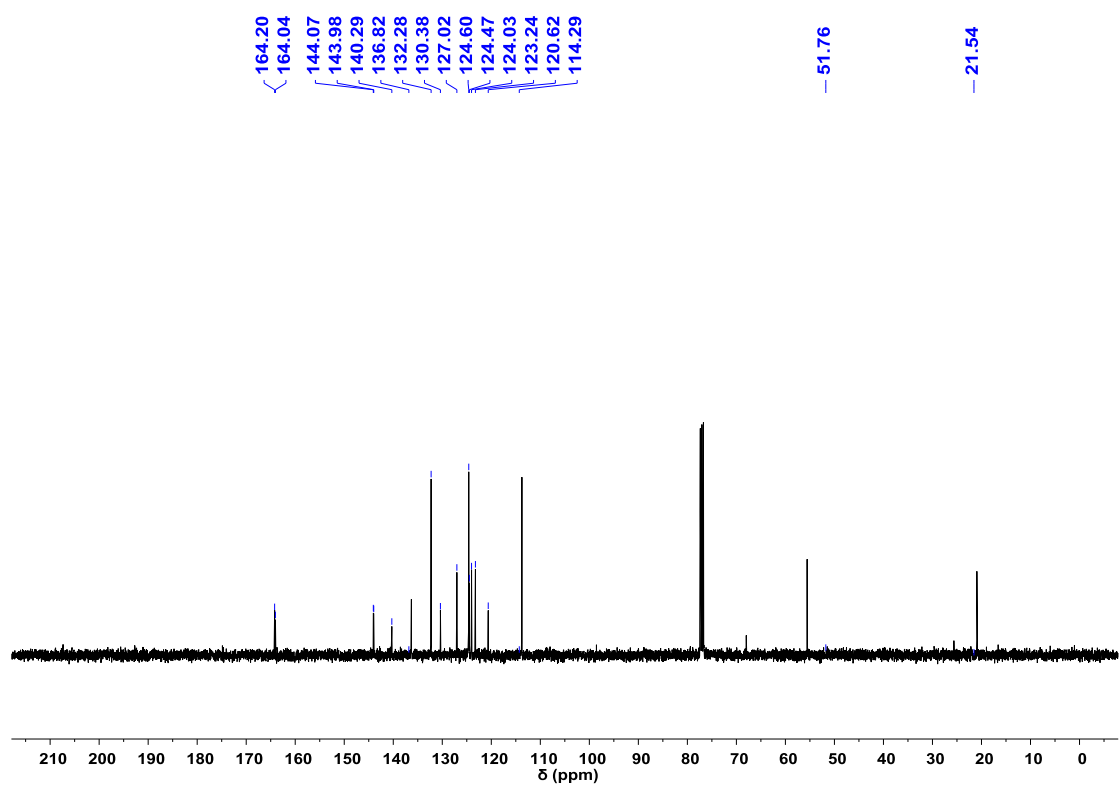
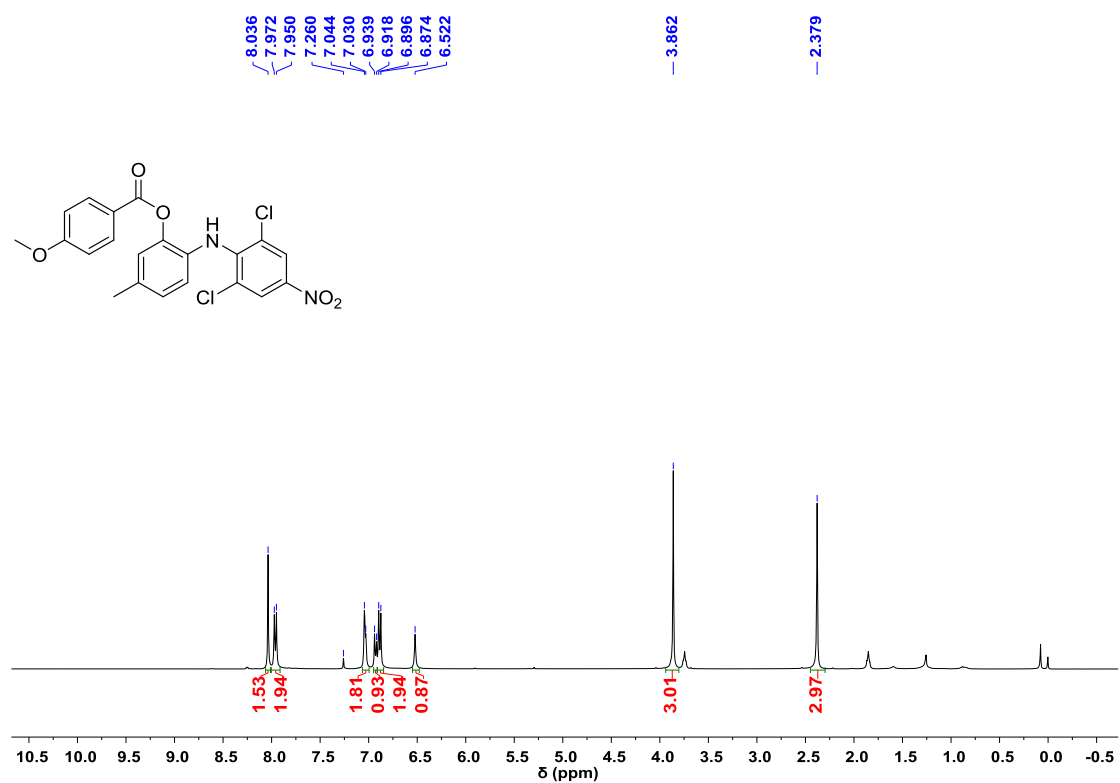
2-((2,6-Dichloro-4-nitrophenyl)amino)-5-methylphenyl 4-methylbenzoate (**3fc**)



5-Chloro-2-((2,6-dichloro-4-nitrophenyl)amino)phenyl 3-chlorobenzoate (**3gc**)

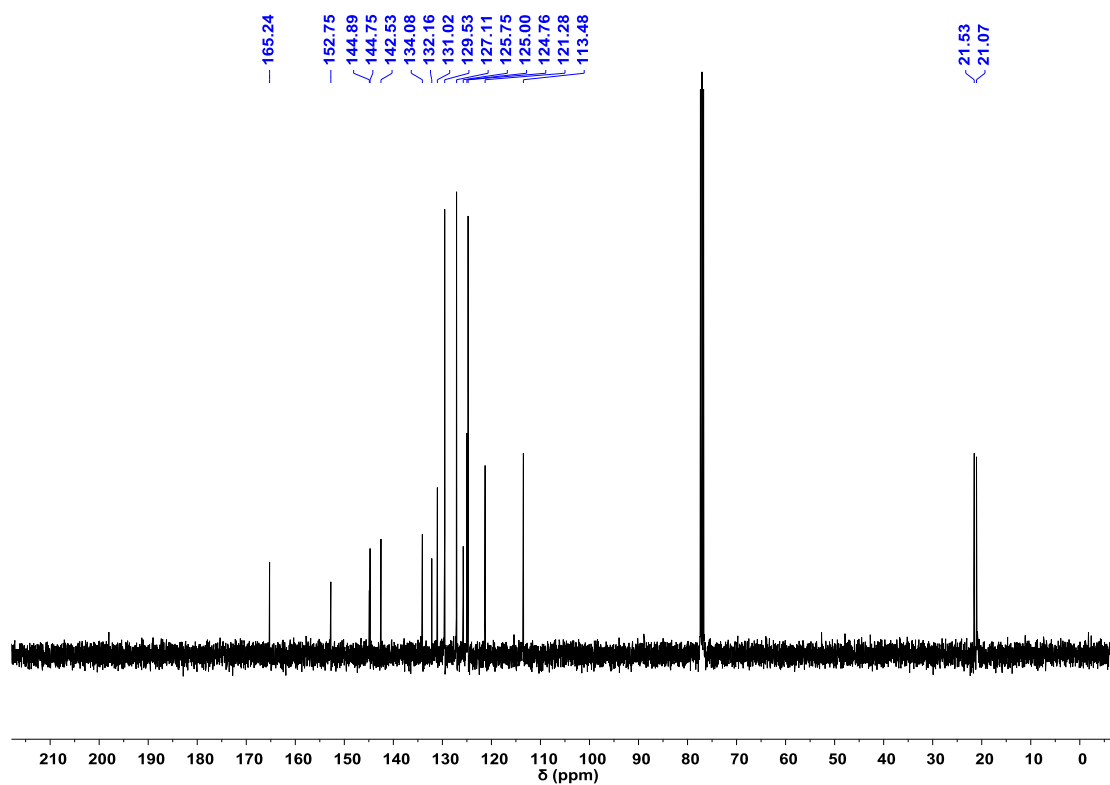
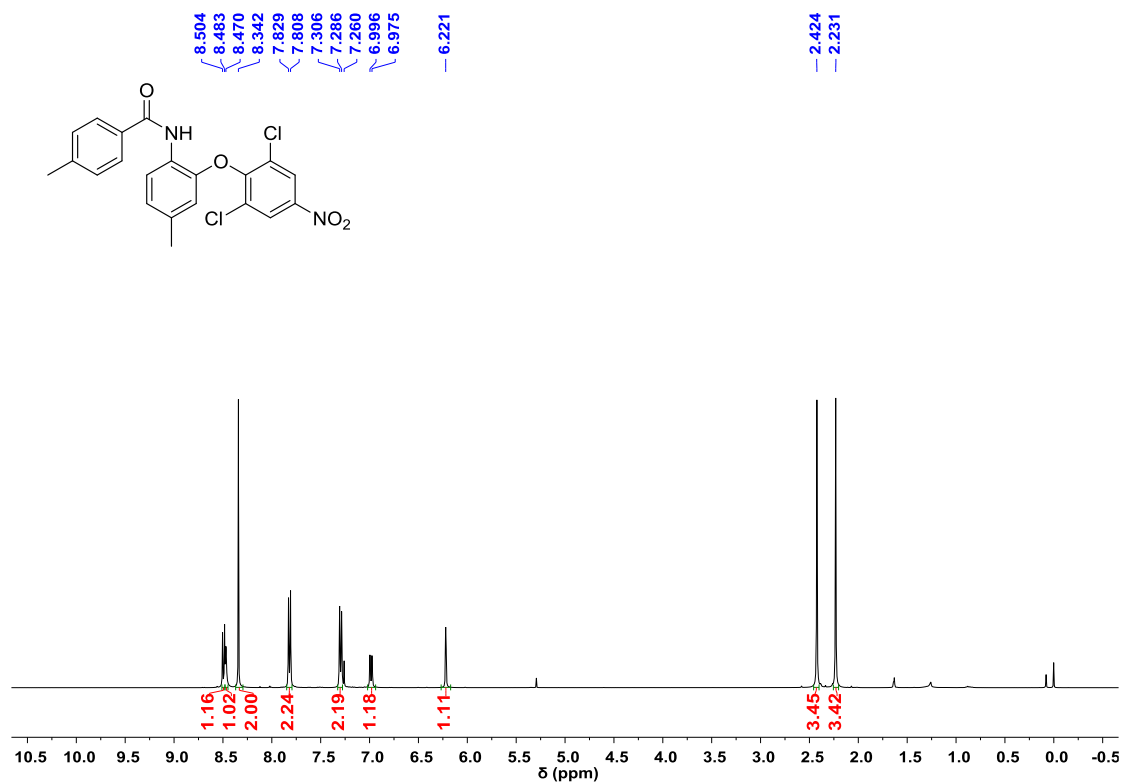


2-((2,6-Dichloro-4-nitrophenyl)amino)-5-methylphenyl 4-methoxybenzoate (**3hc**)



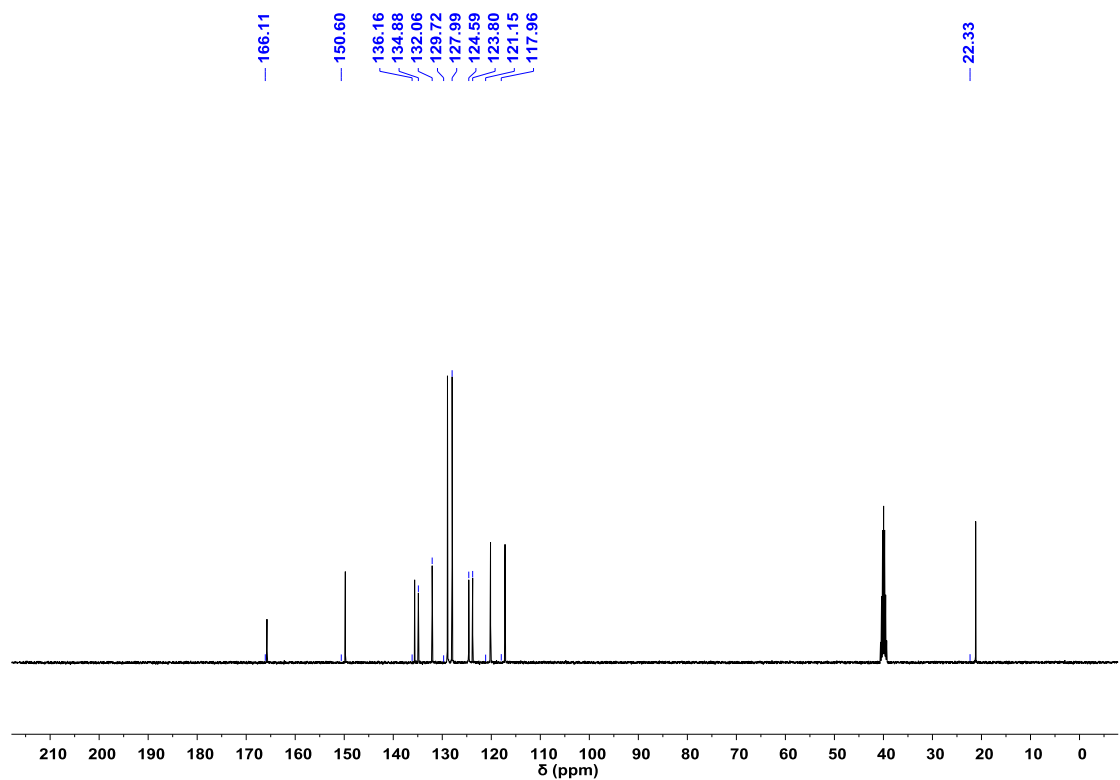
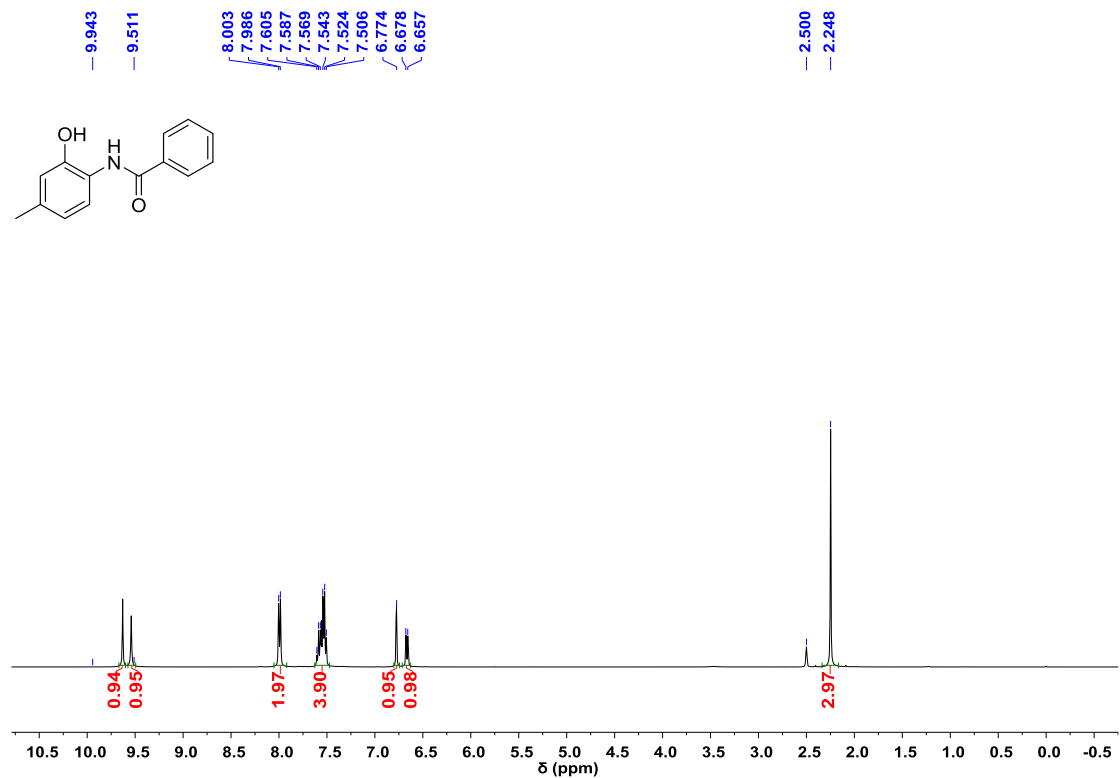
# Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of product **4**

*N*-(2-(2,6-Dichloro-4-nitrophenoxy)-4-methylphenyl)-4-methylbenzamide (**4fc**)



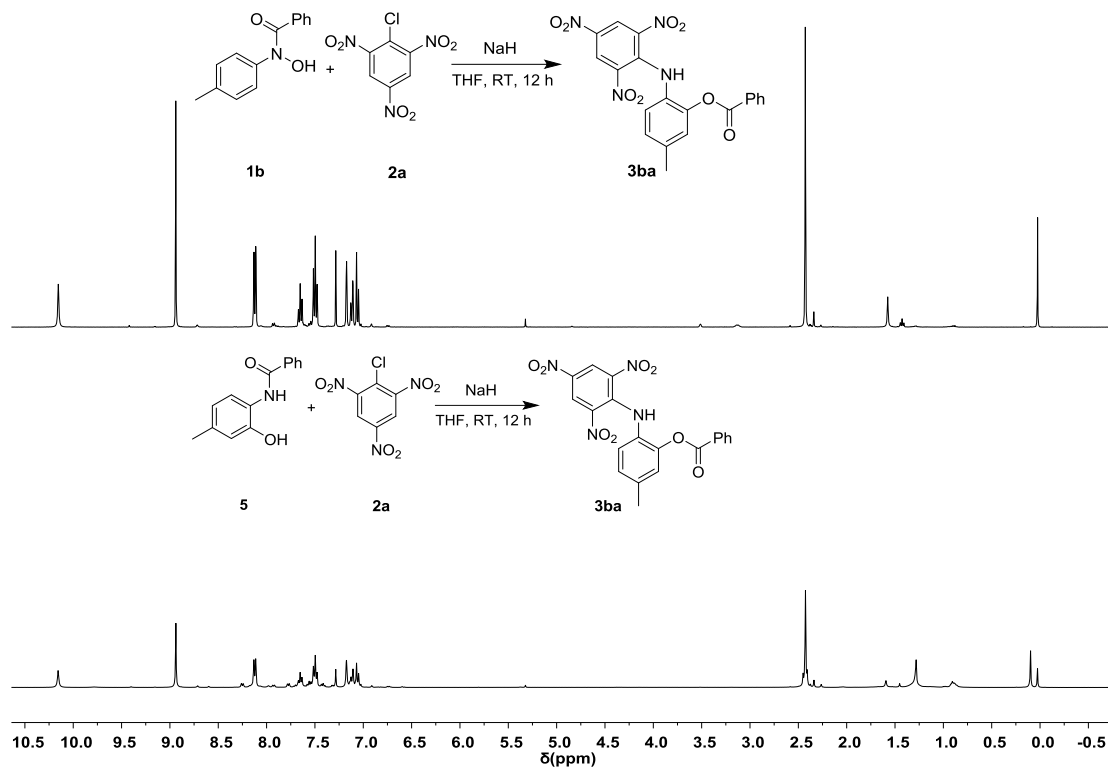
# Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of product **5**

*N*-(2-Hydroxy-4-methylphenyl)benzamide (**5**)

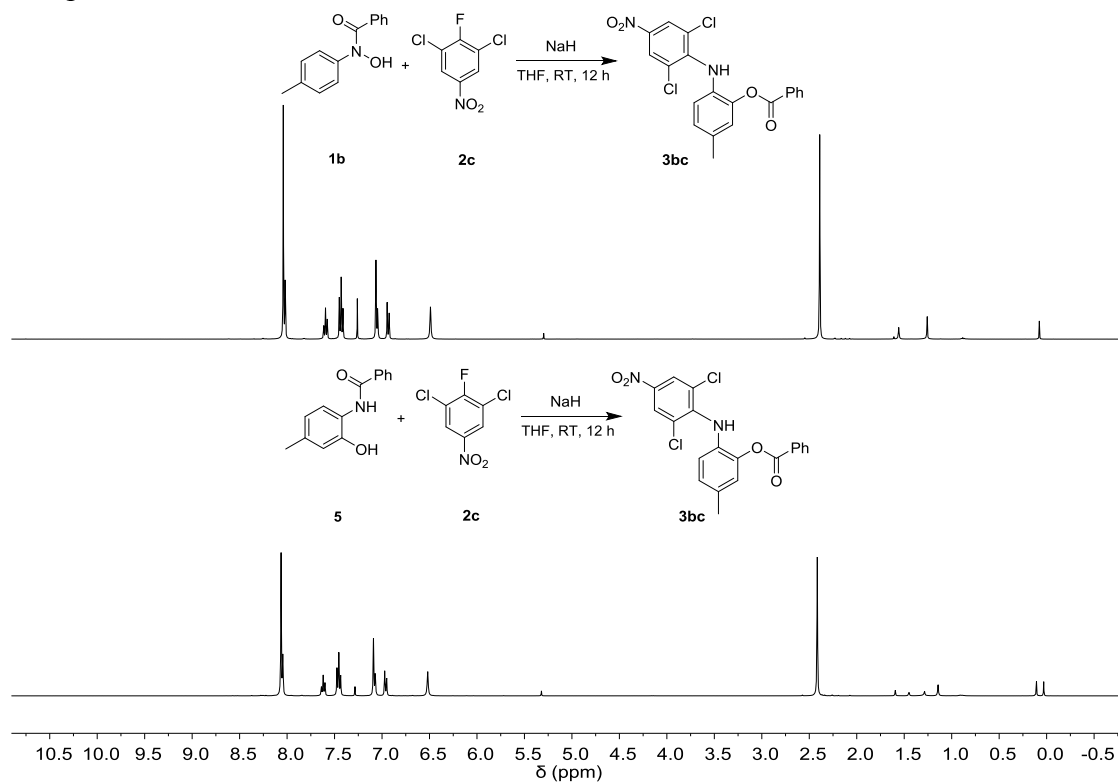


Copies of  $^1\text{H}$  NMR spectra of products **3** produced from the reactions of **5** and **2a,c**

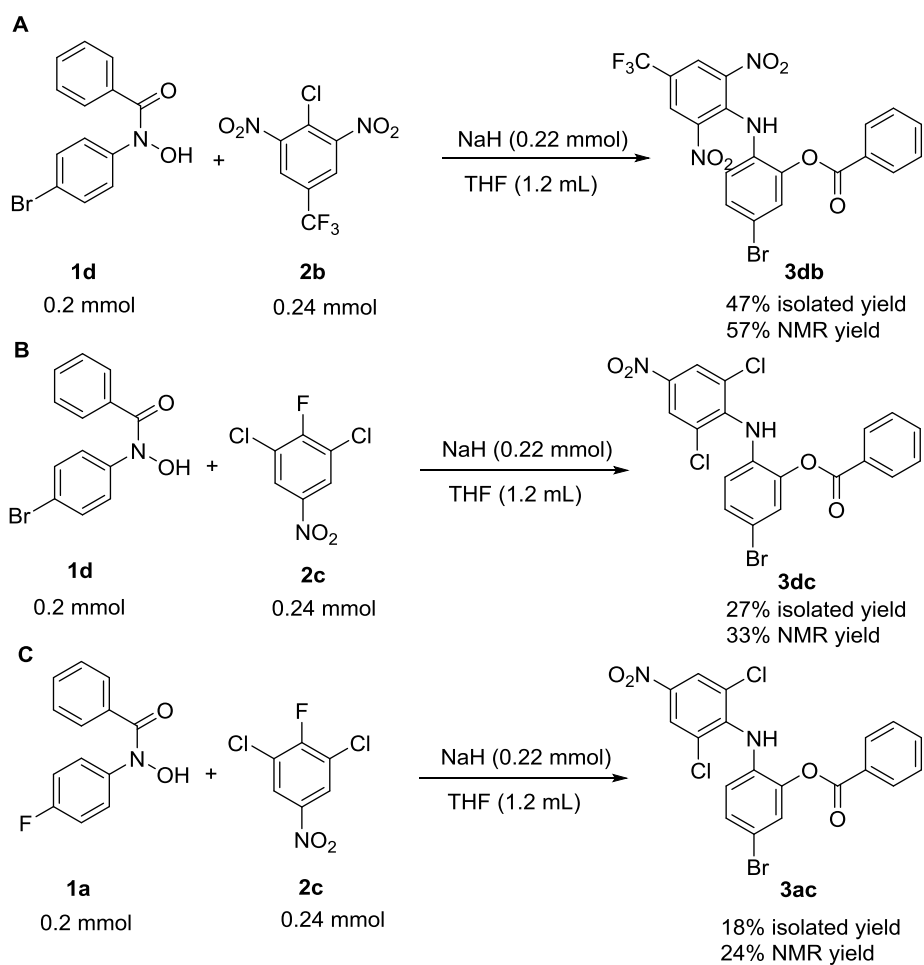
**3ba** produced from the reactions of **1b** and **5** with **2a**



**3bc** produced from the reactions of **1b** and **5** with **2c**



## Copies of $^1\text{H}$ NMR spectra in tracing reaction mixtures



Scheme 1S.  $^1\text{H}$  NMR tracing reactions with NMR and isolated yields.

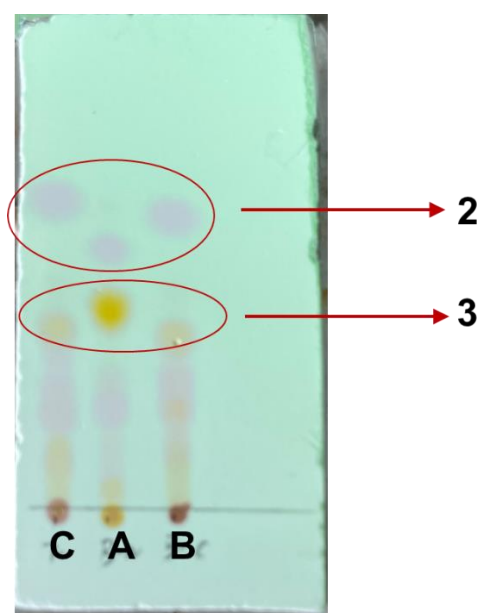
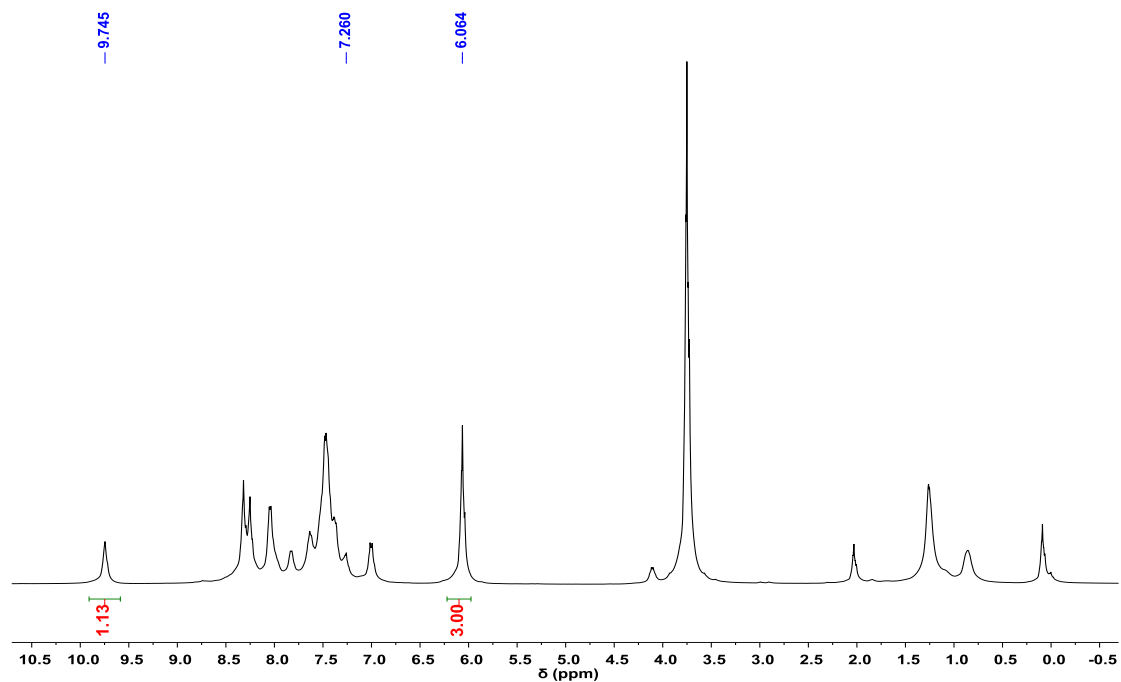
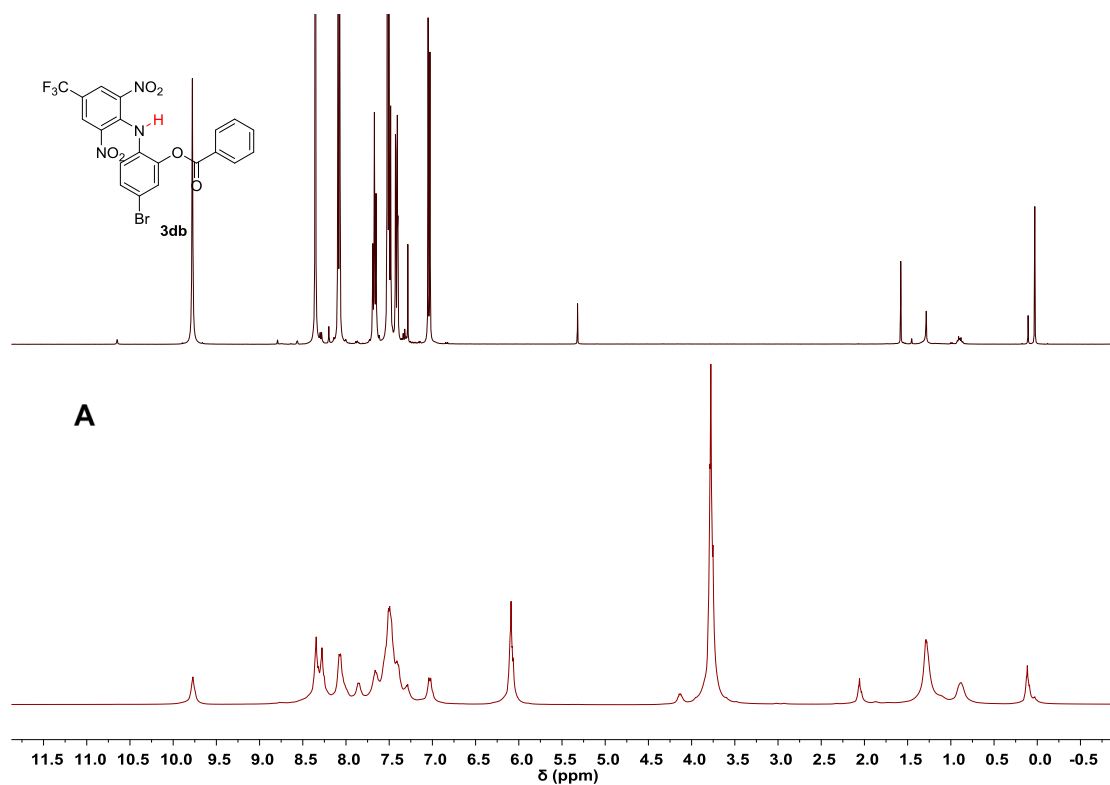


Figure 1S. TLC tracing results of reactions A, B, and C

Copies of  $^1\text{H}$  NMR spectra in tracing reaction mixture for reaction A  
**1d** (0.2 mmol) with 1,3,5-trimethoxybenzene (0.1 mmol) as an internal standard



$^1\text{H}$  NMR spectrum of reaction mixture A

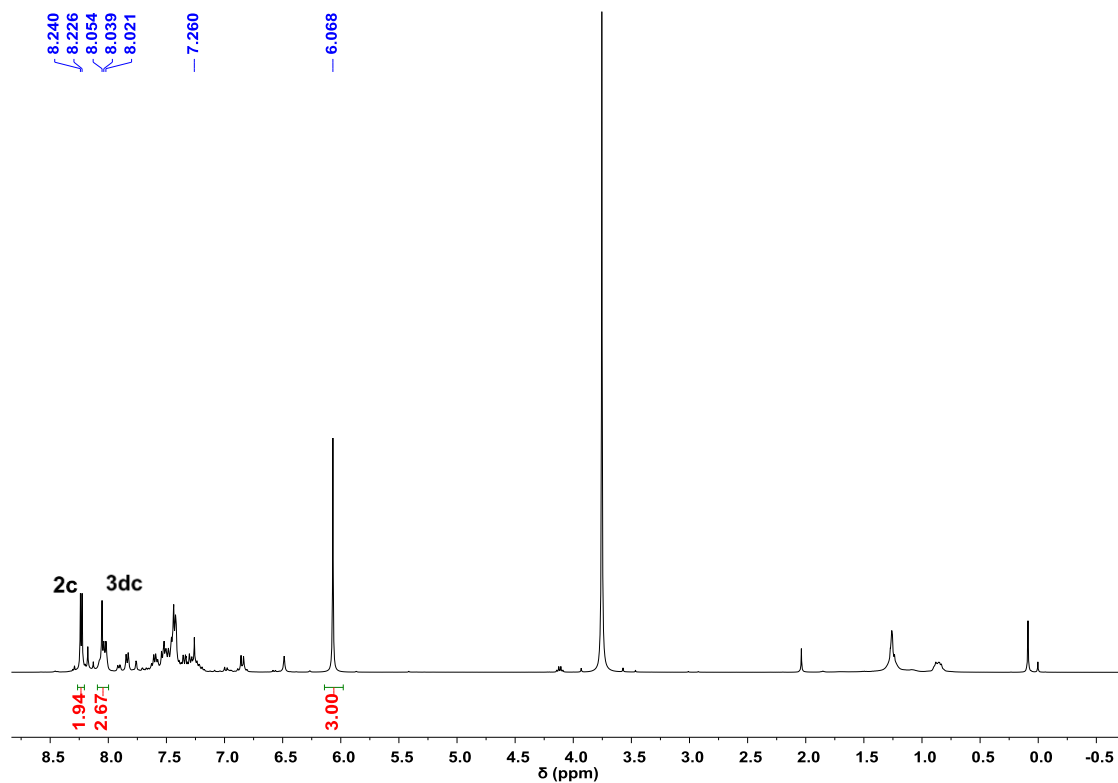


$^1\text{H}$  NMR spectra of product **3db** and reaction mixture A

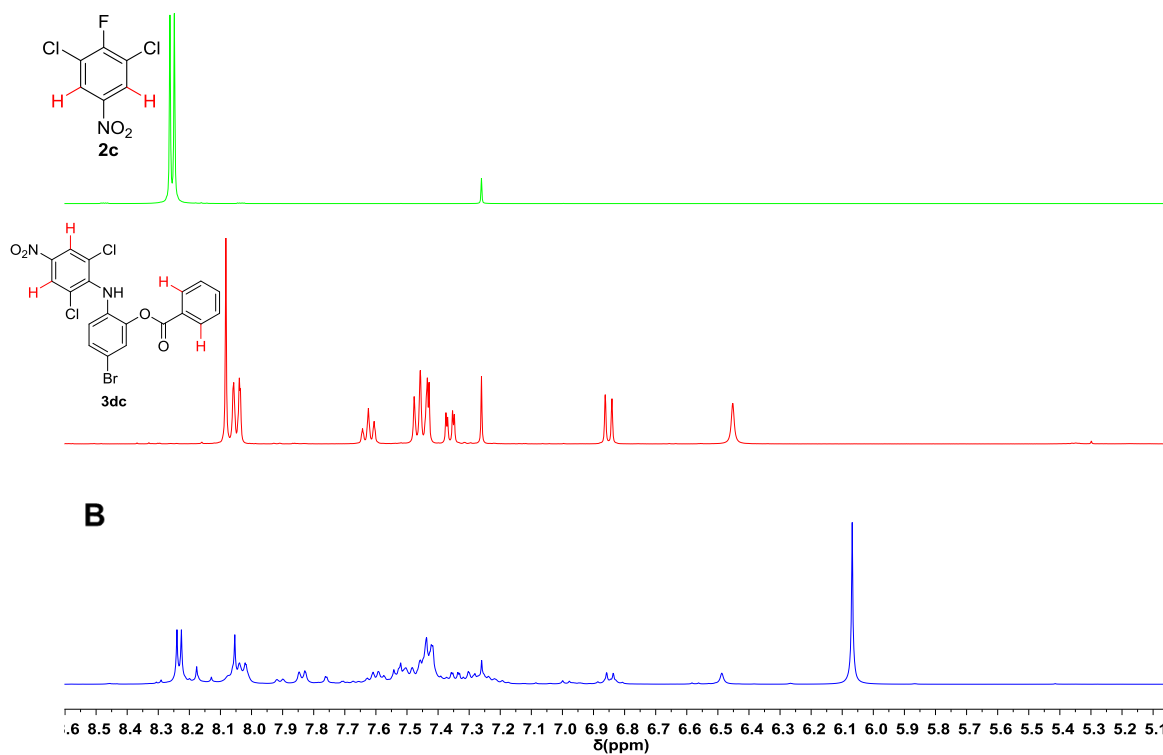


Copies of  $^1\text{H}$  NMR spectra in tracing reaction mixture for reaction B

**1d** (0.2 mmol) with 1,3,5-trimethoxybenzene (0.1 mmol) as an internal standard



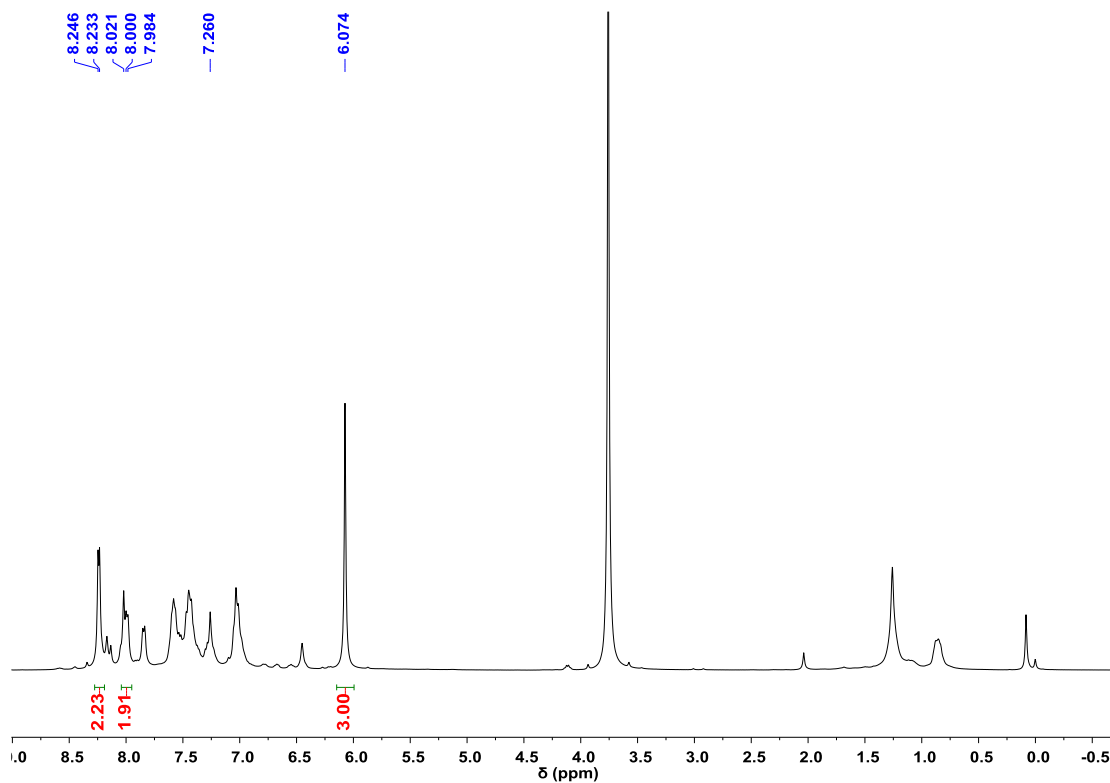
$^1\text{H}$  NMR spectrum of reaction mixture B



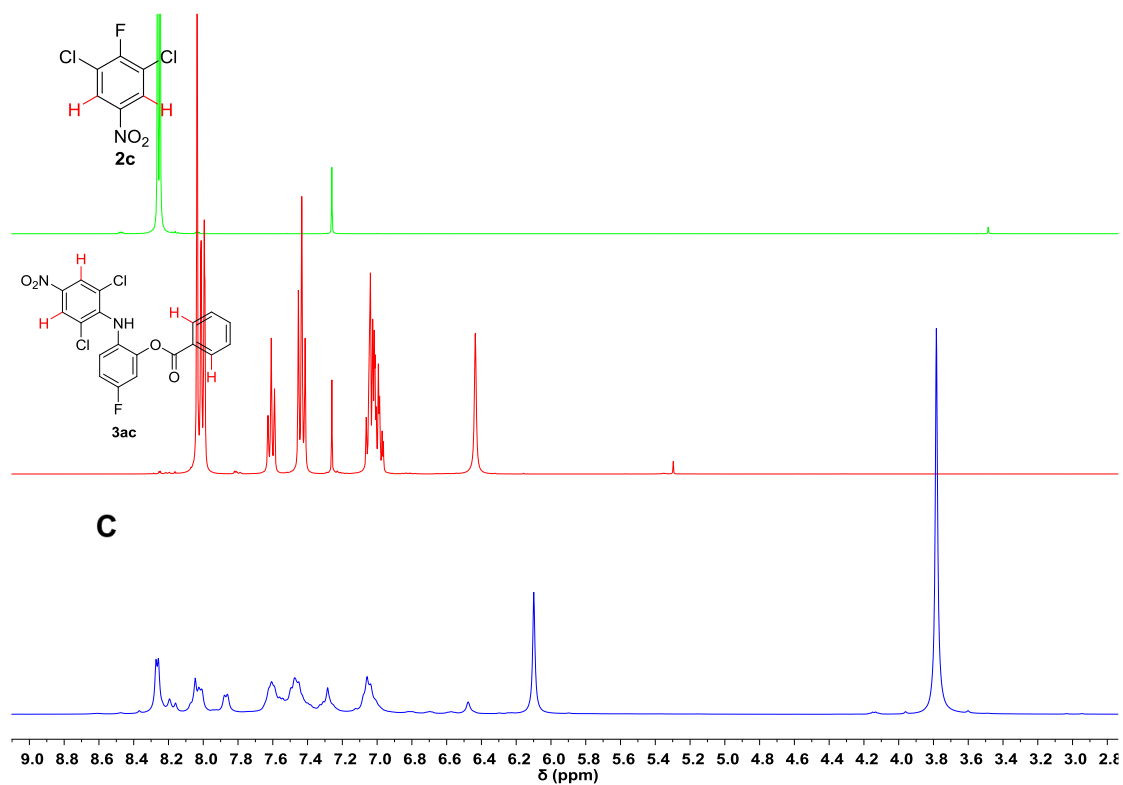
$^1\text{H}$  NMR spectra of reactant **2c**, product **3db** and reaction mixture B

Copies of  $^1\text{H}$  NMR spectra in tracing reaction mixture for reaction C

**1a** (0.2 mmol) with 1,3,5-trimethoxybenzene (0.1 mmol) as an internal standard



$^1\text{H}$  NMR spectrum of reaction mixture C



$^1\text{H}$  NMR spectra of reactant **2c**, product **3ac** and reaction mixture C