

## **Supporting Information**

### **Addition of Terminal Alkynes to 1,3-Dicarbonyl Compounds and $\beta$ -Ketoesters Catalyzed by a Cationic Cobalt(III) Complex**

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# NMR Spectra:

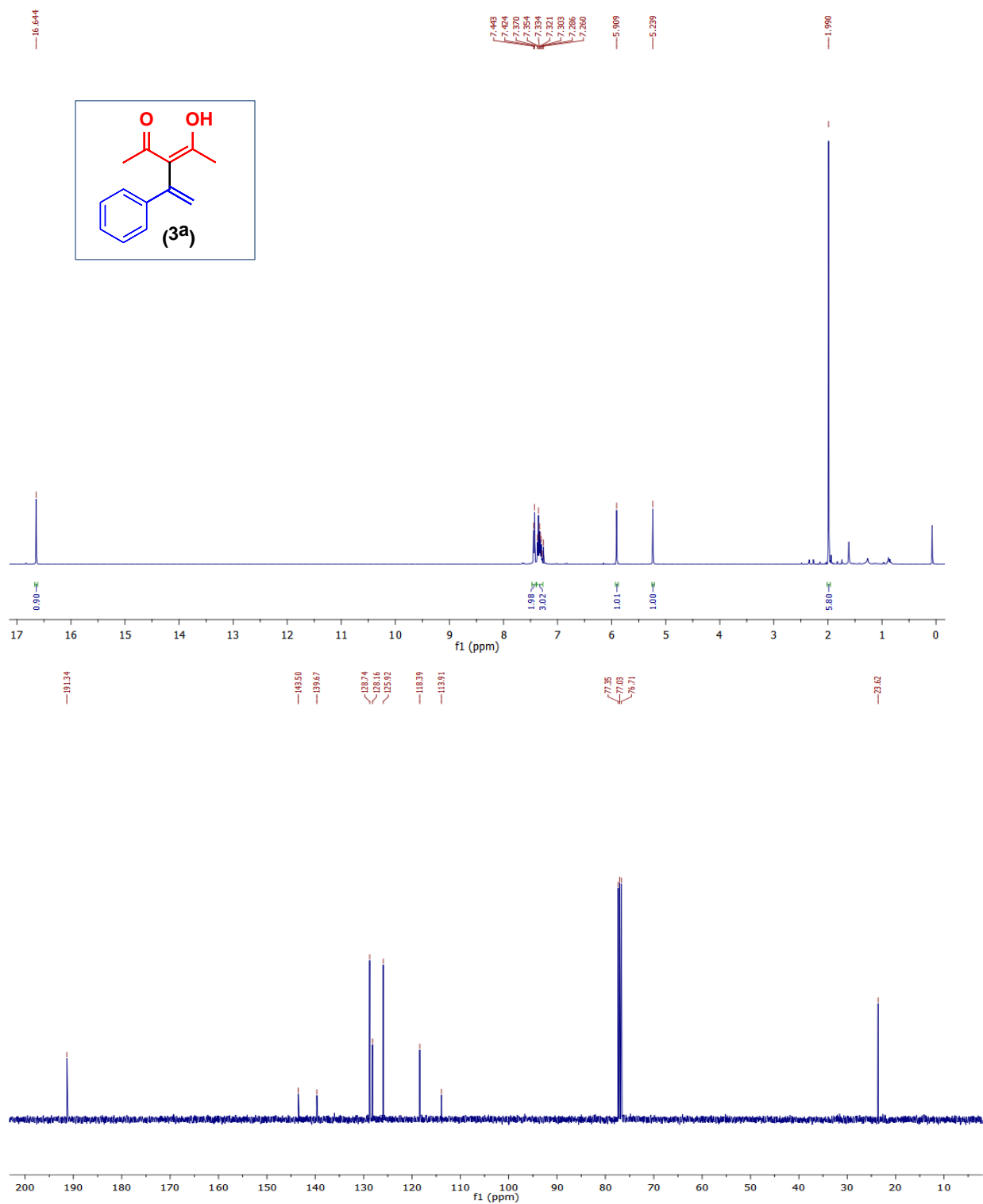
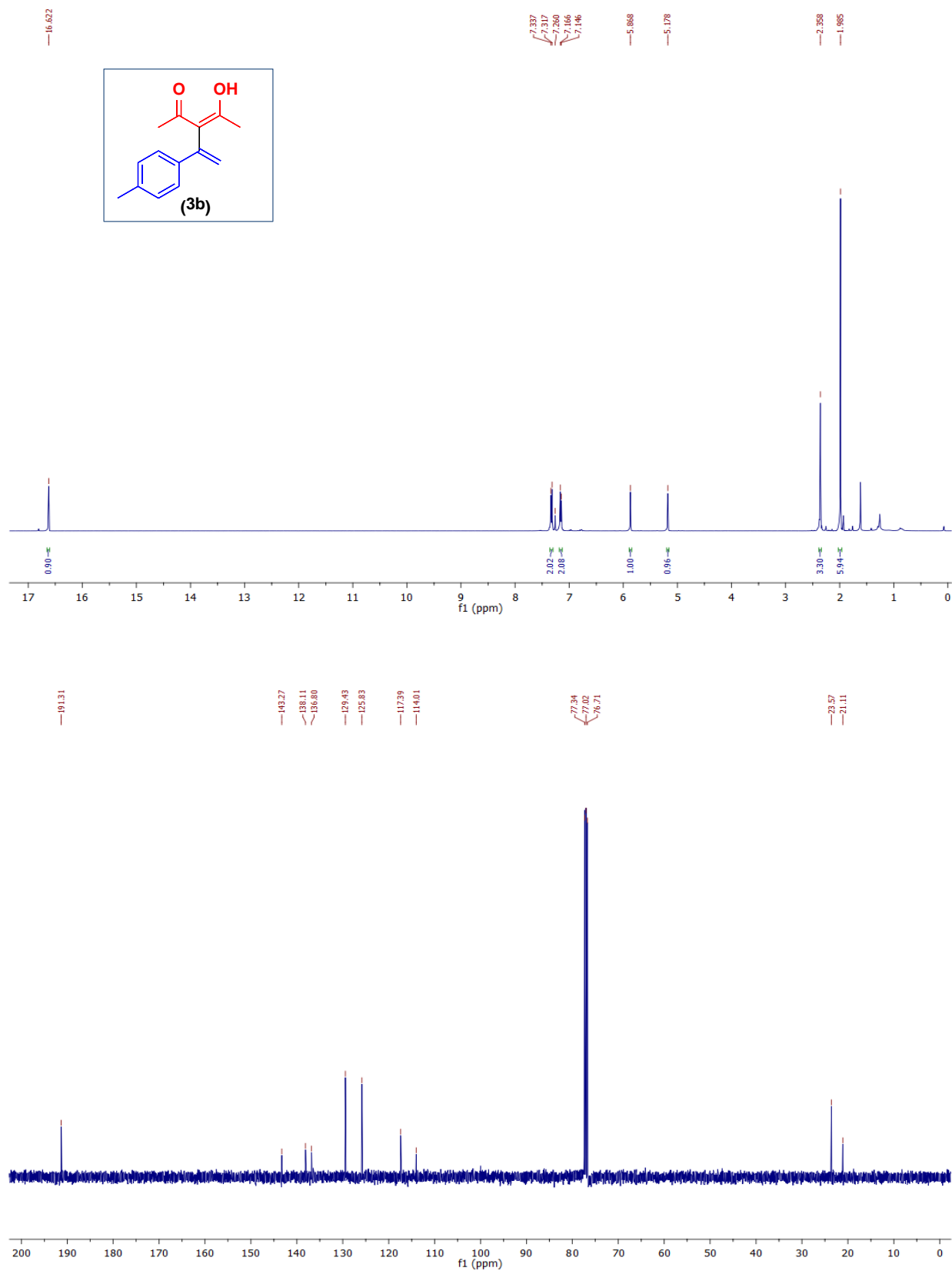
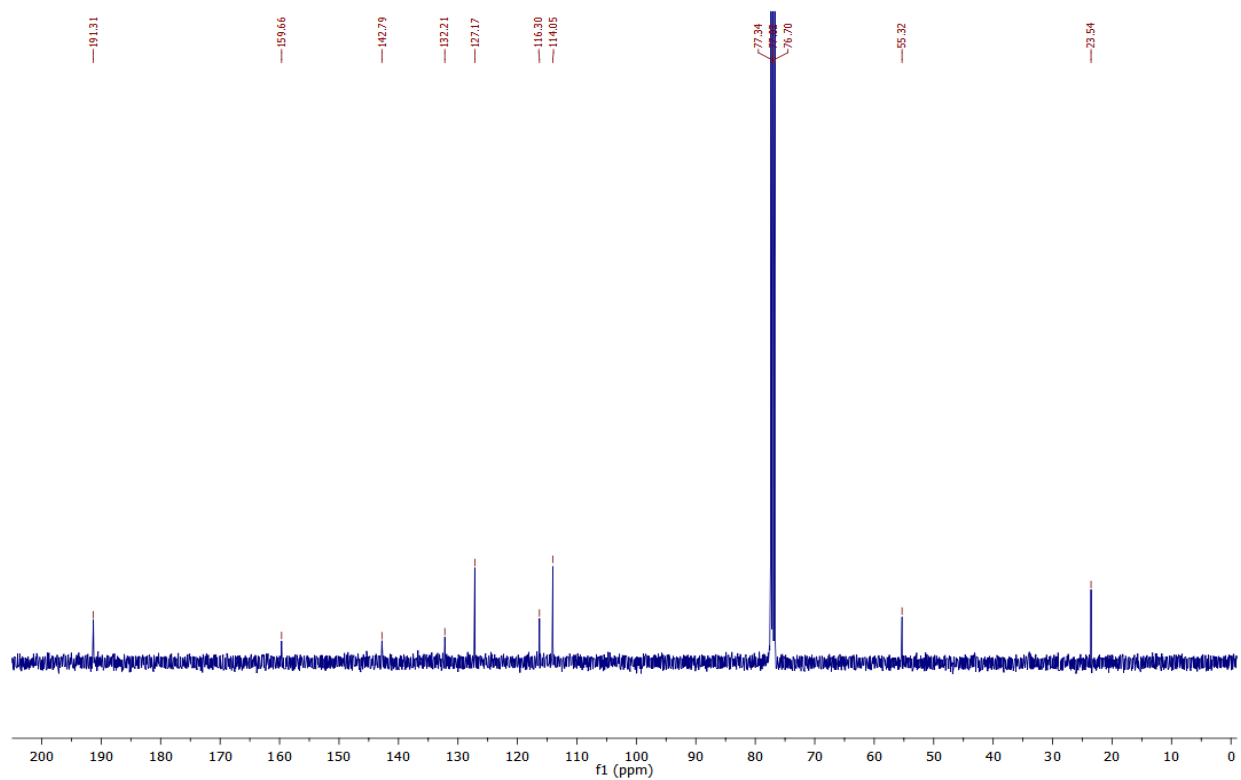
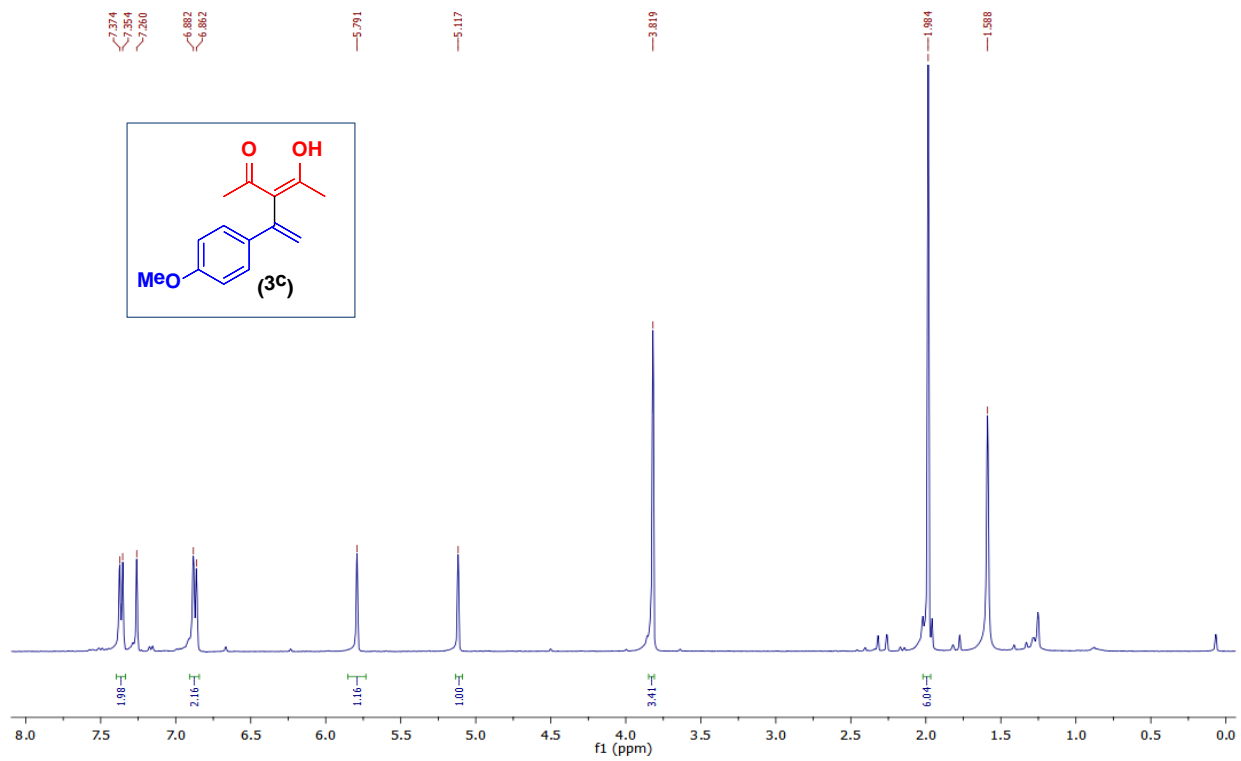


Figure S1 <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **3a**



**Figure S2** <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **3b**



**Figure S3** <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **3c**

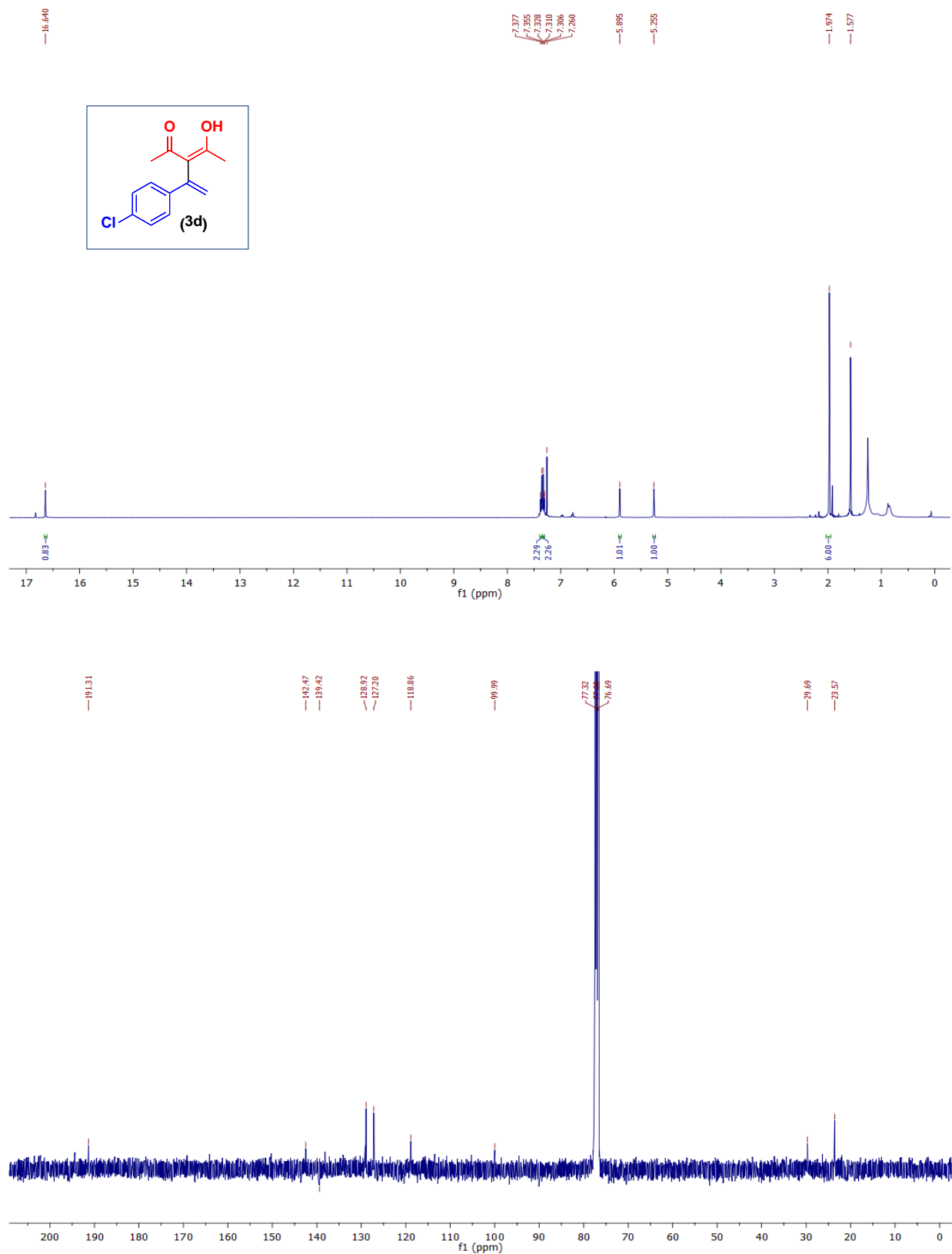
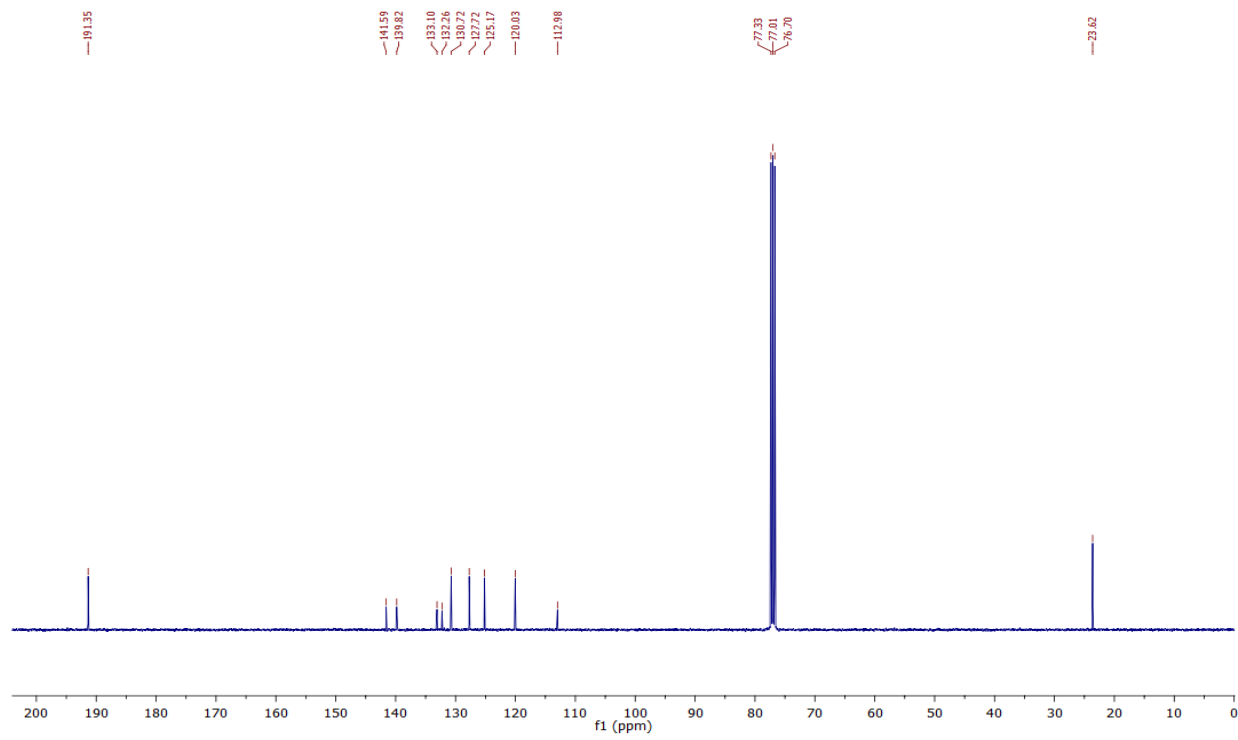
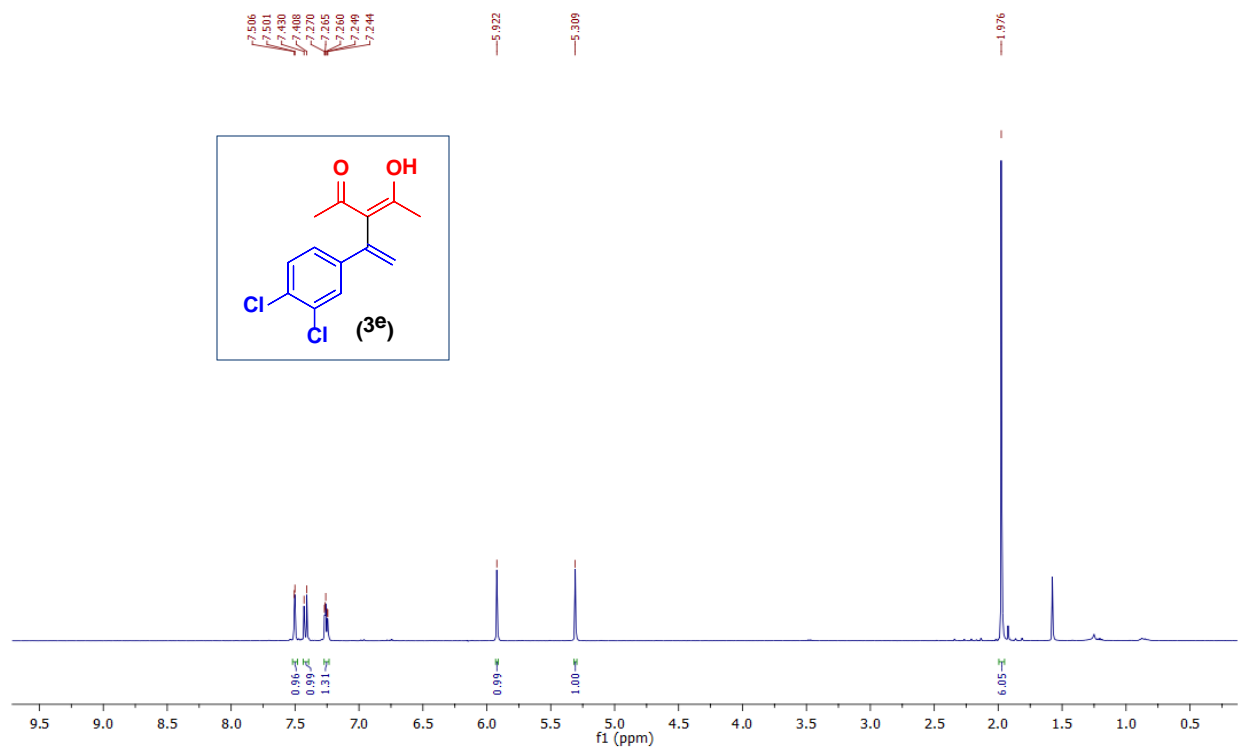
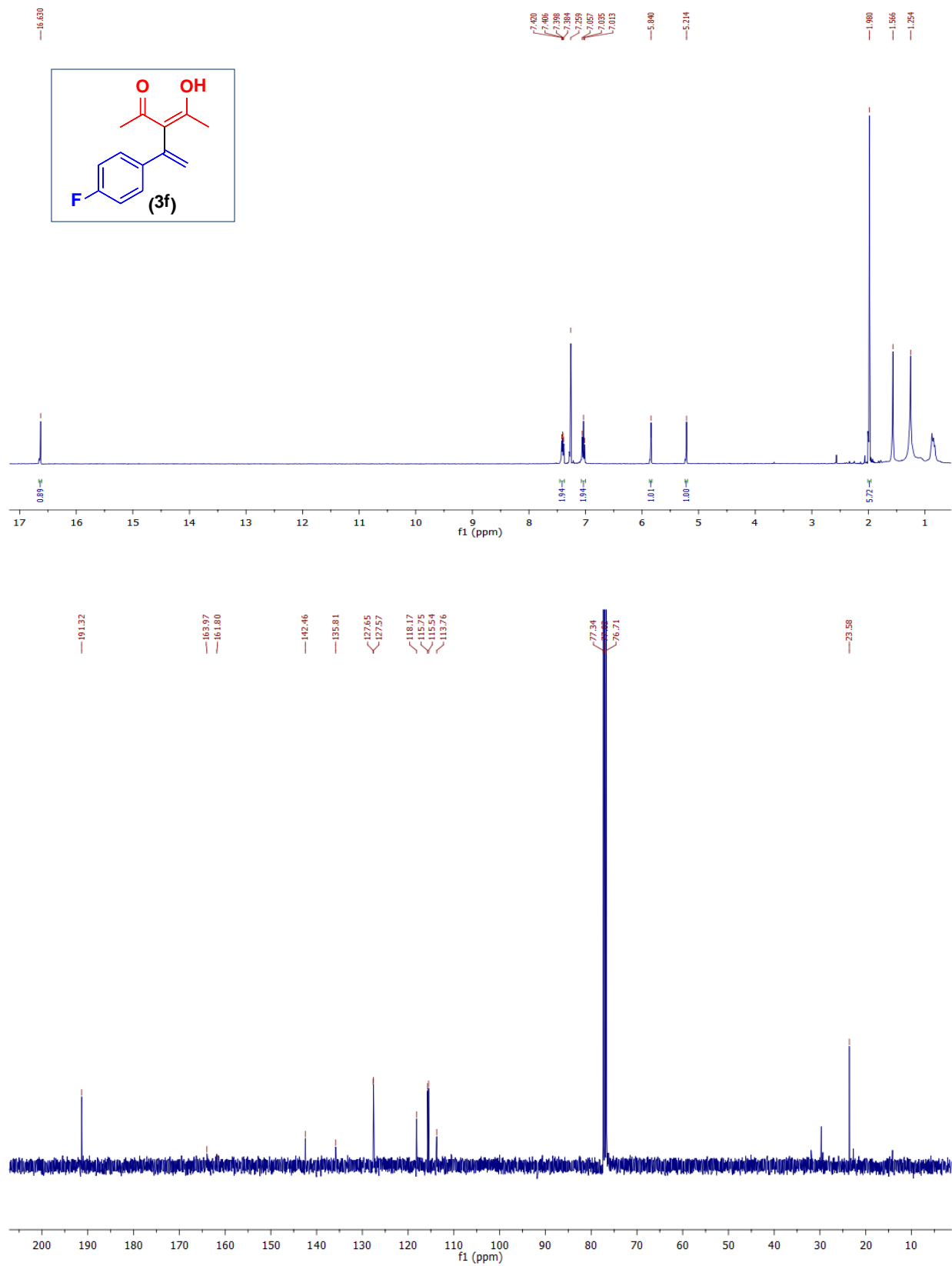


Figure S4  $^1\text{H}$  &  $^{13}\text{C}$  NMR Spectra of compound **3d**



**Figure S5** <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **3e**



**Figure S6** <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **3f**

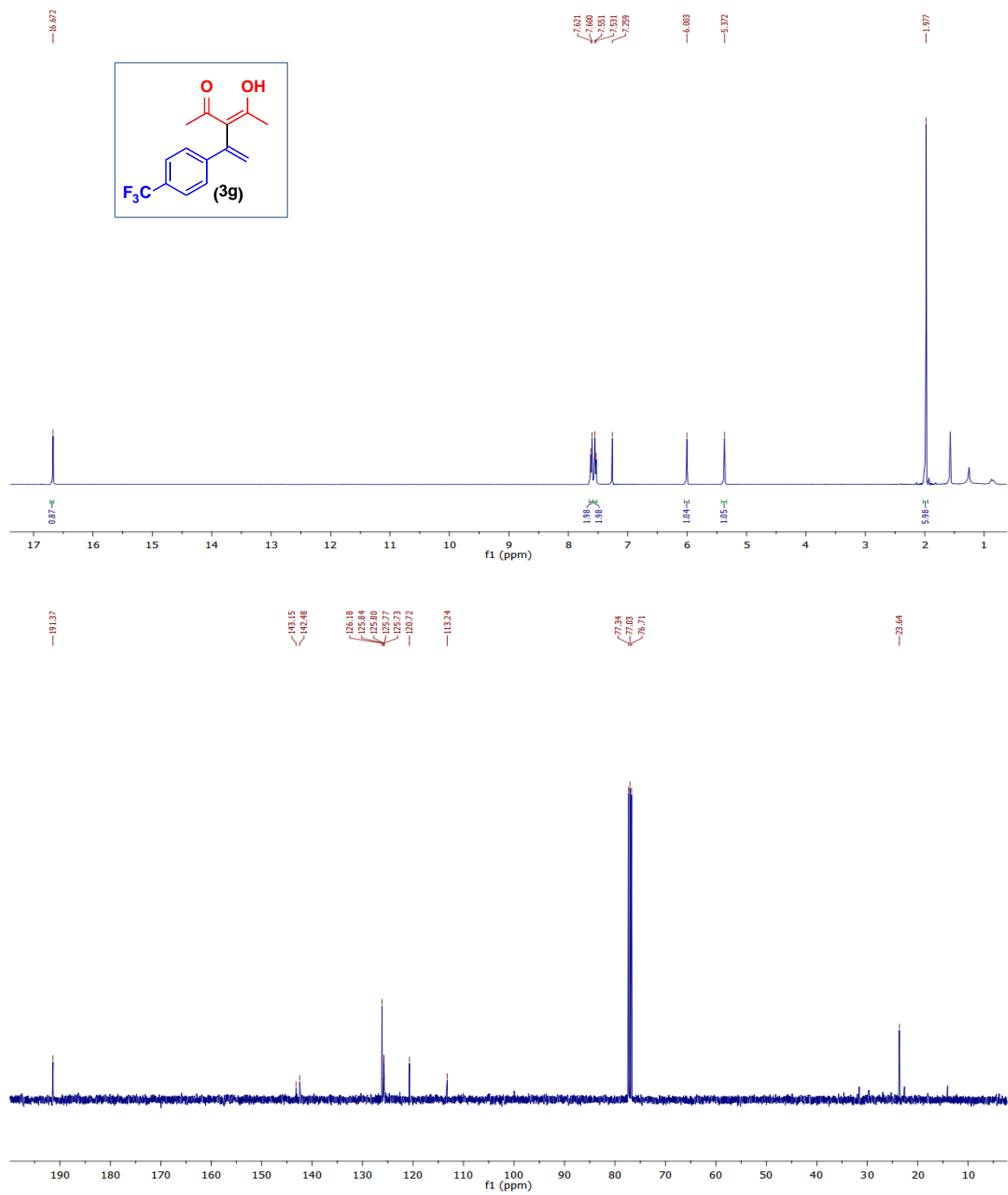


Figure S7  $^1\text{H}$  &  $^{13}\text{C}$  NMR Spectra of compound **3g**



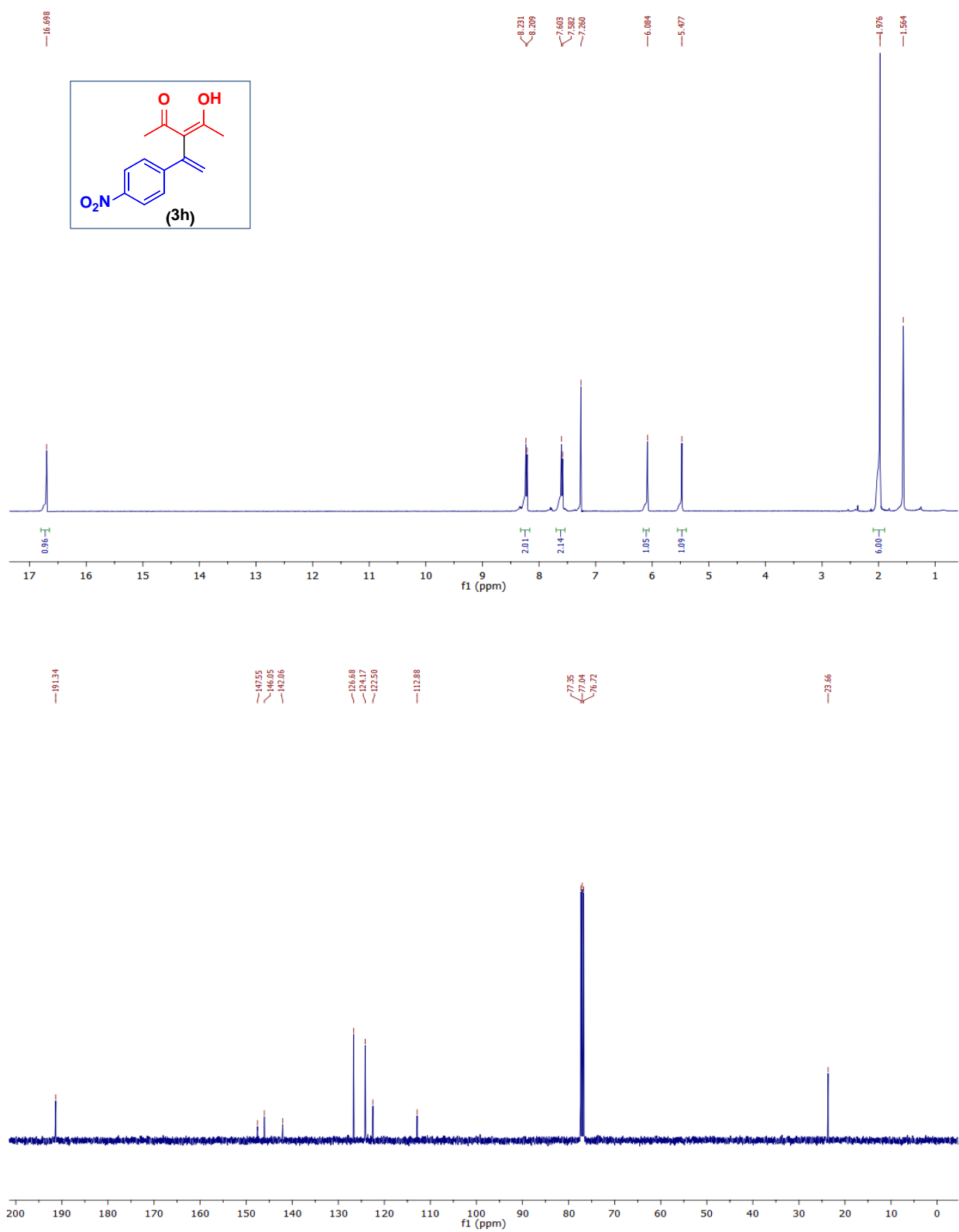


Figure S8 <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **3h**

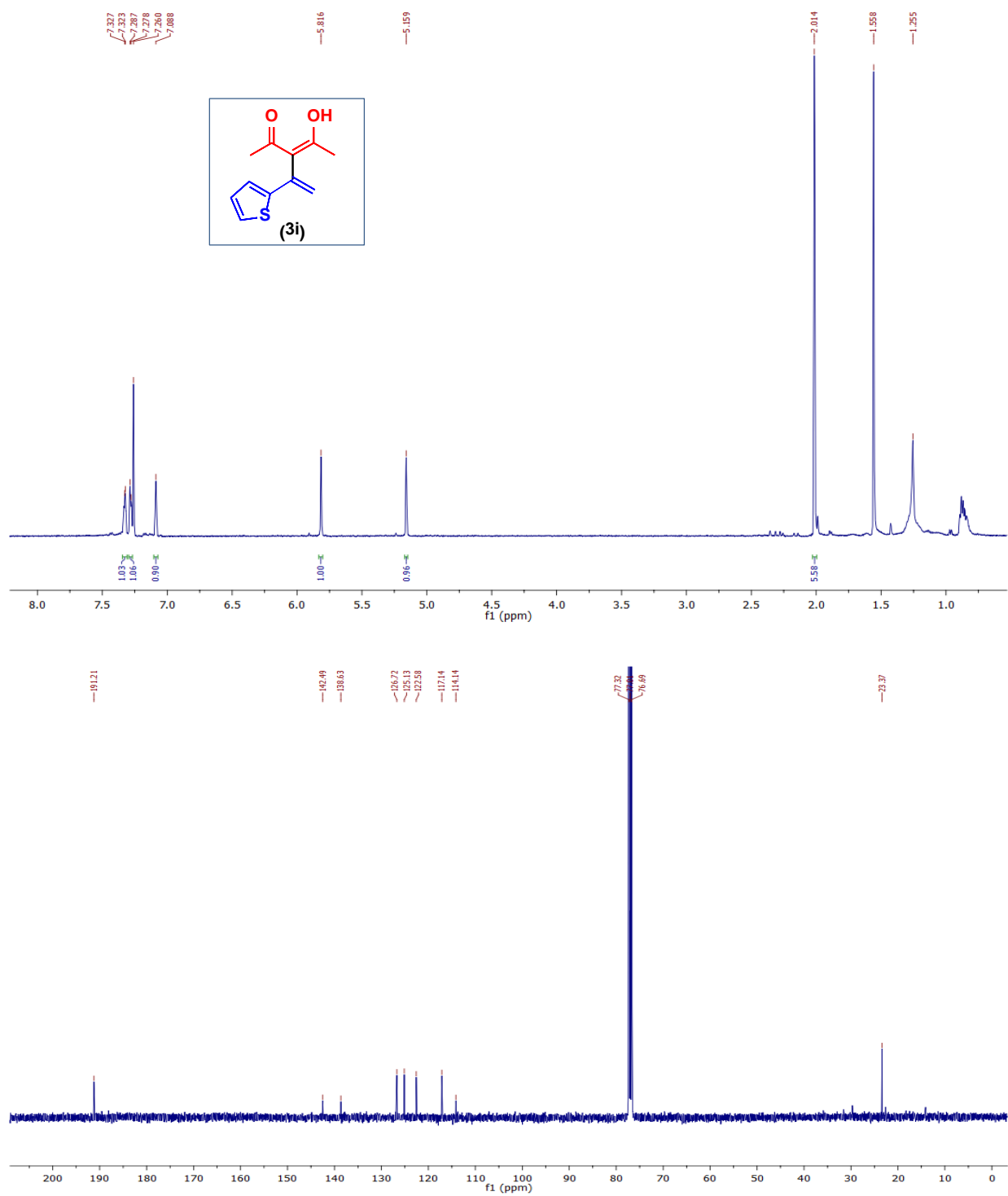


Figure S9  $^1\text{H}$  &  $^{13}\text{C}$  NMR Spectra of compound **3i**

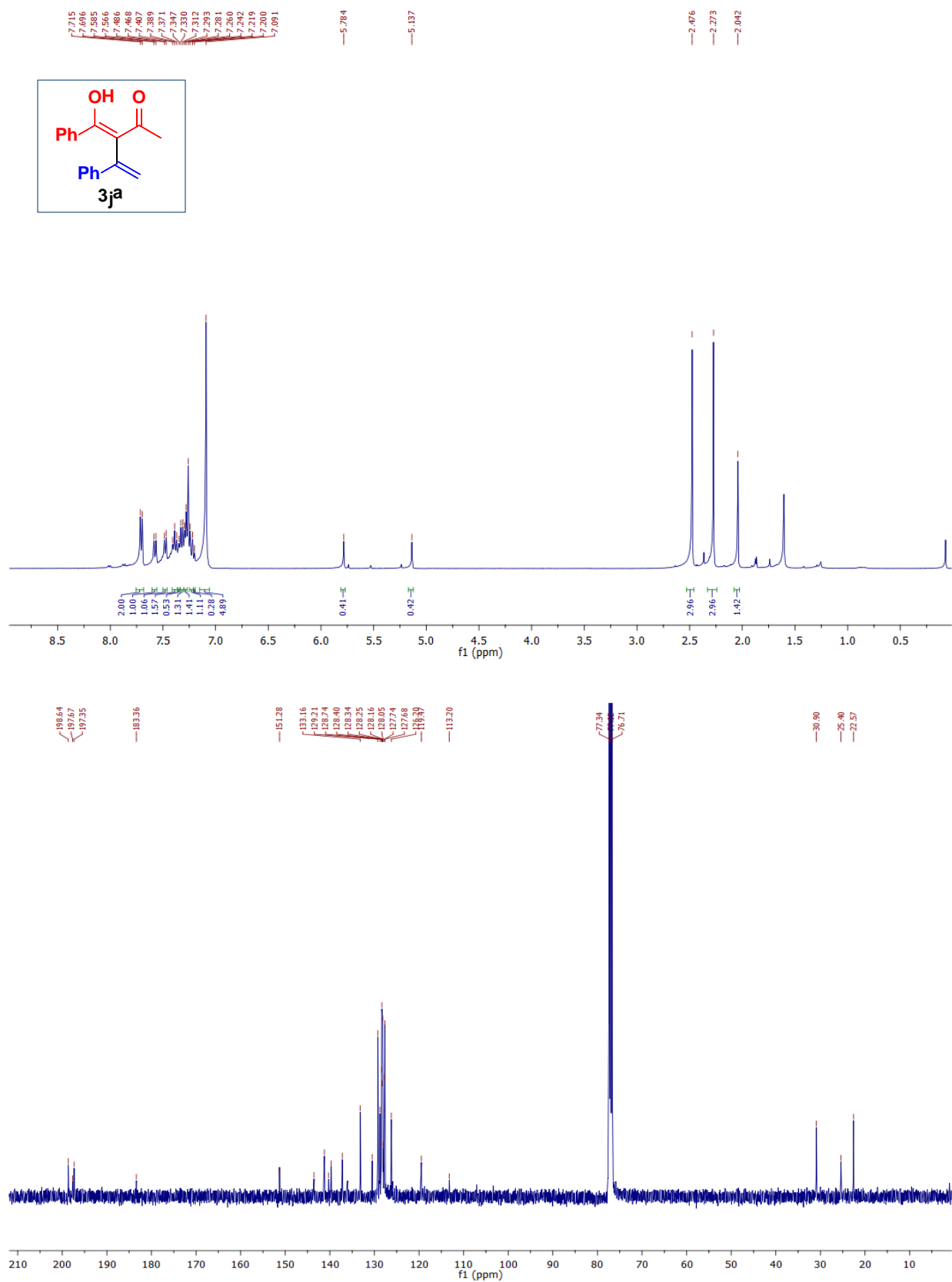


Figure S10a <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **3ja** (mixed with **3jb** Z-isomer)

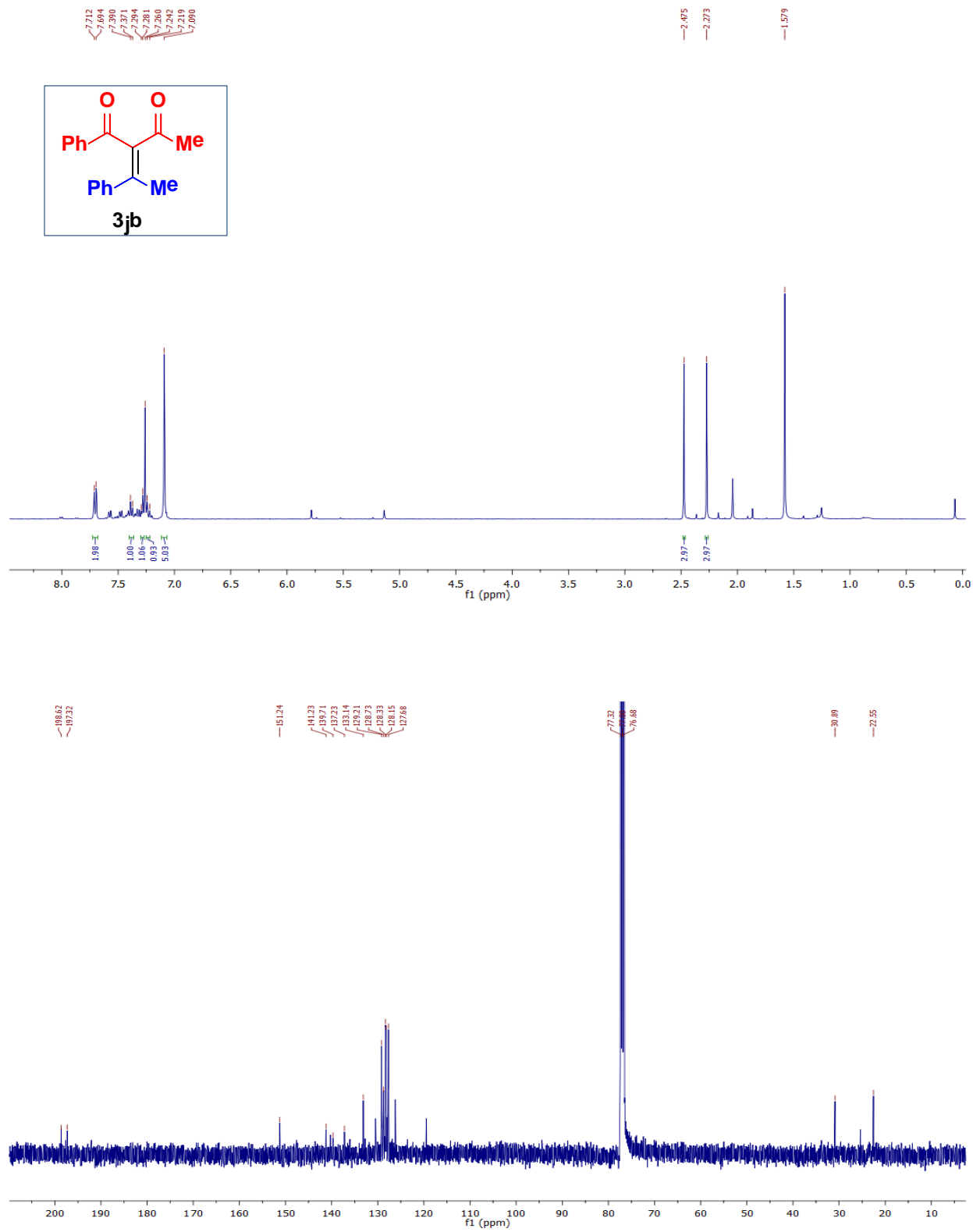
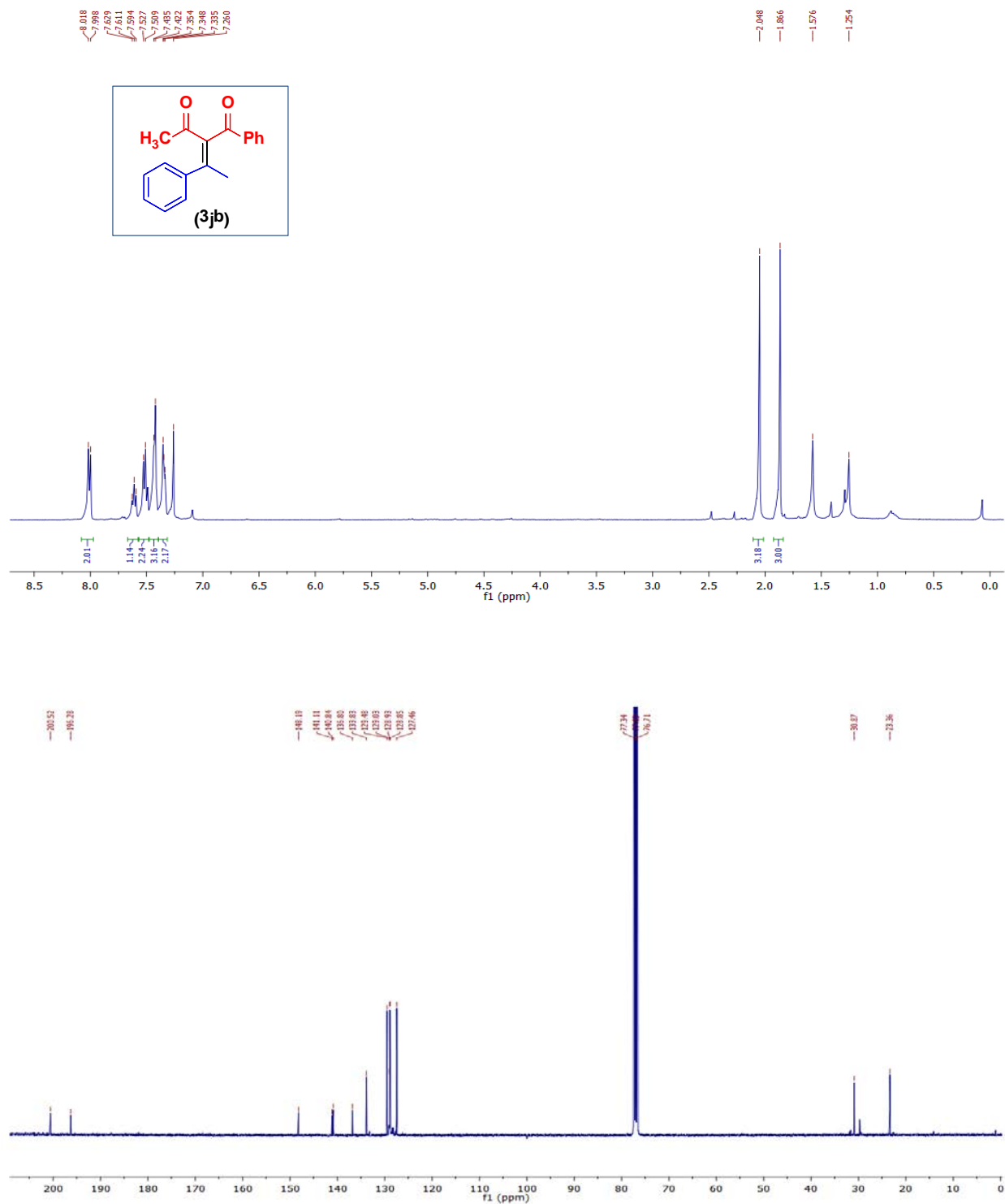
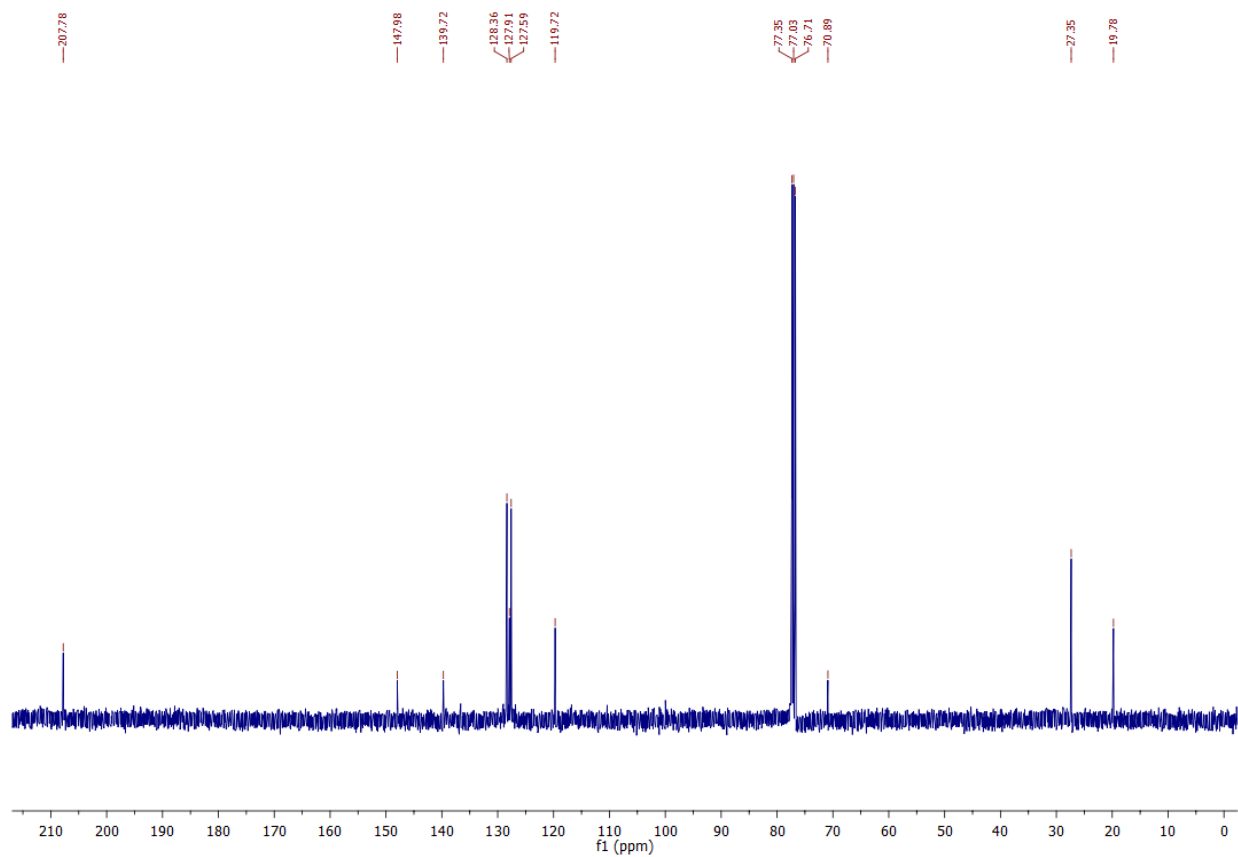
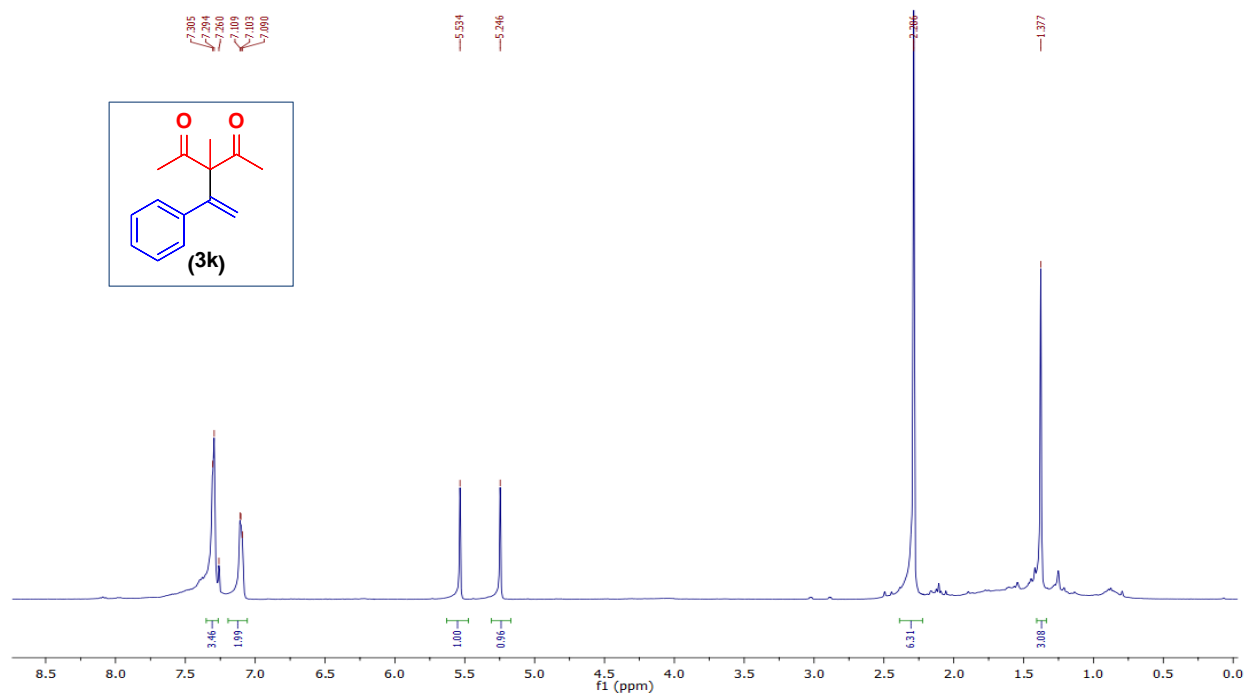


Figure S10b  $^1\text{H}$  &  $^{13}\text{C}$  NMR Spectra of compound **3jb** (Z-isomer)



**Figure S10c** <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **3jb** (E-isomer)



**Figure S11** <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **3k**

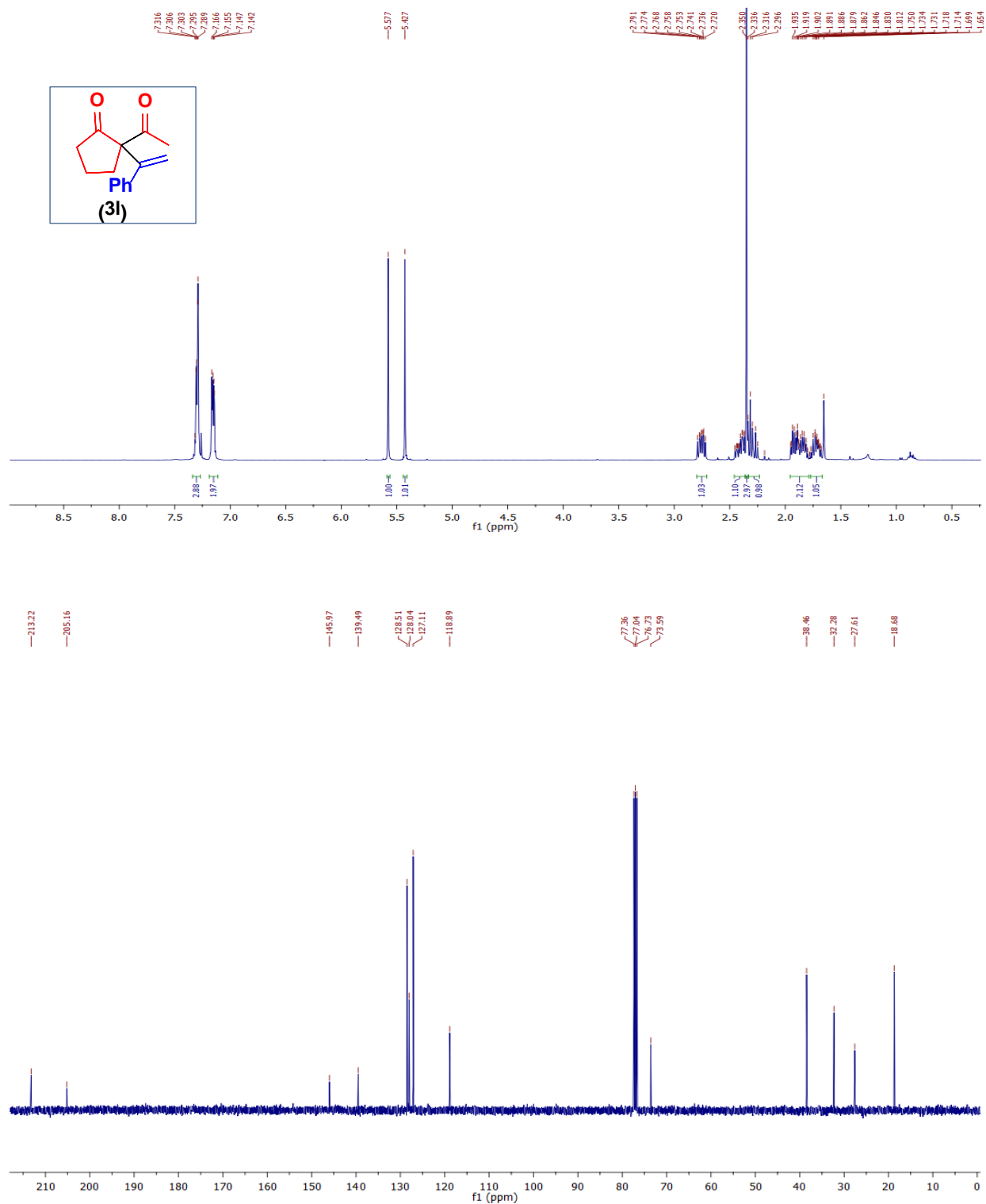


Figure S12 <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound 3I

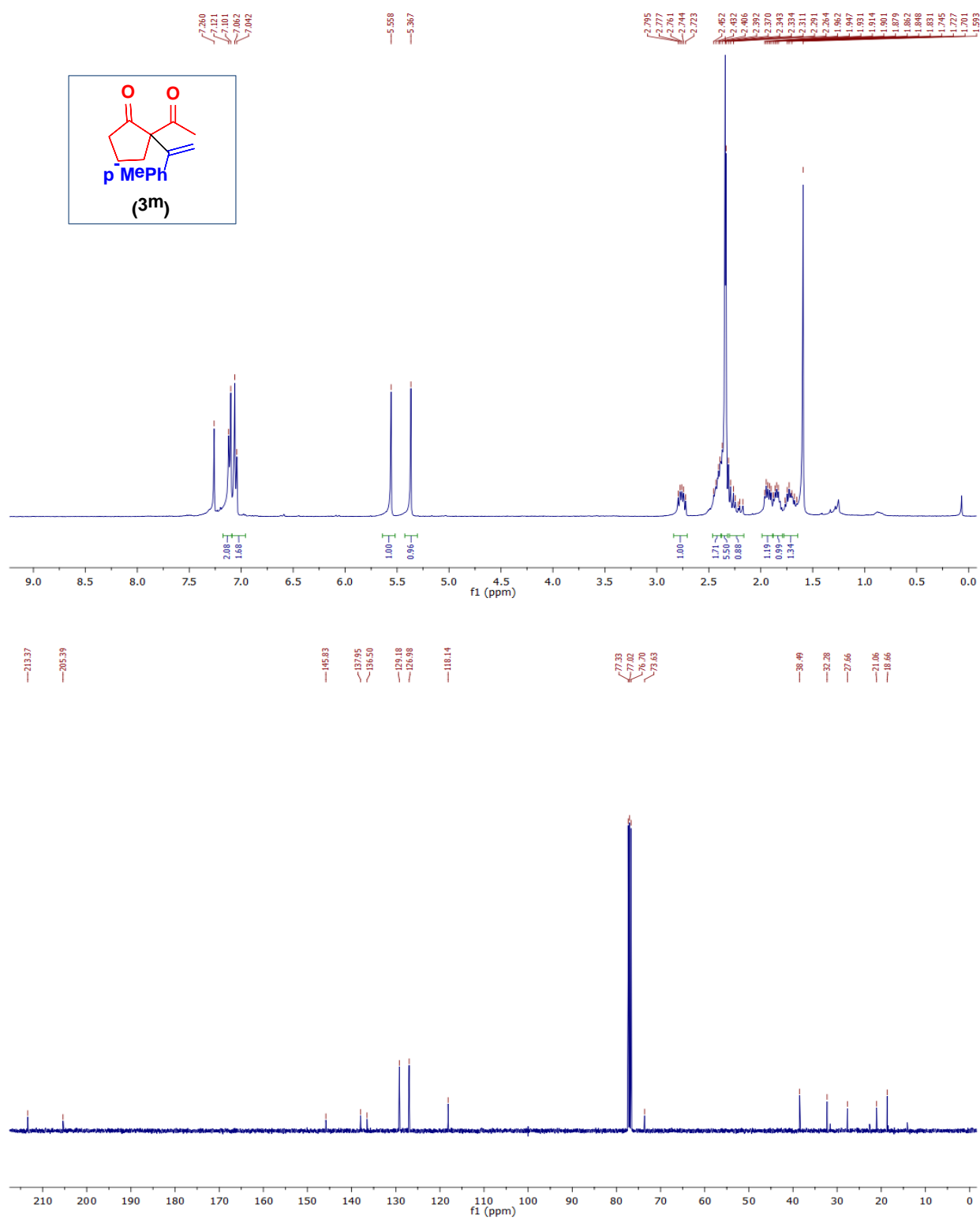


Figure S13 <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **3m**



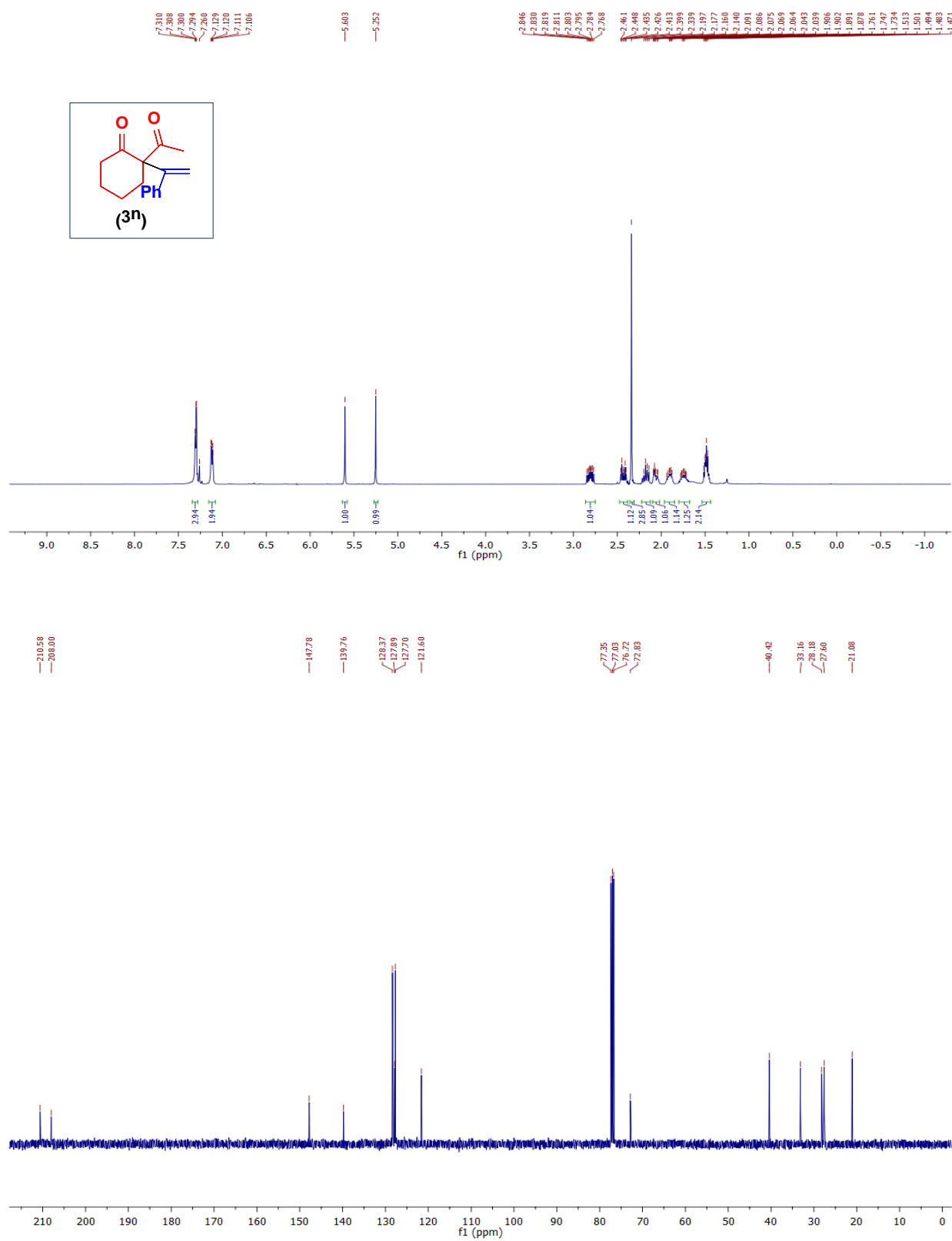


Figure S14 <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound 3n

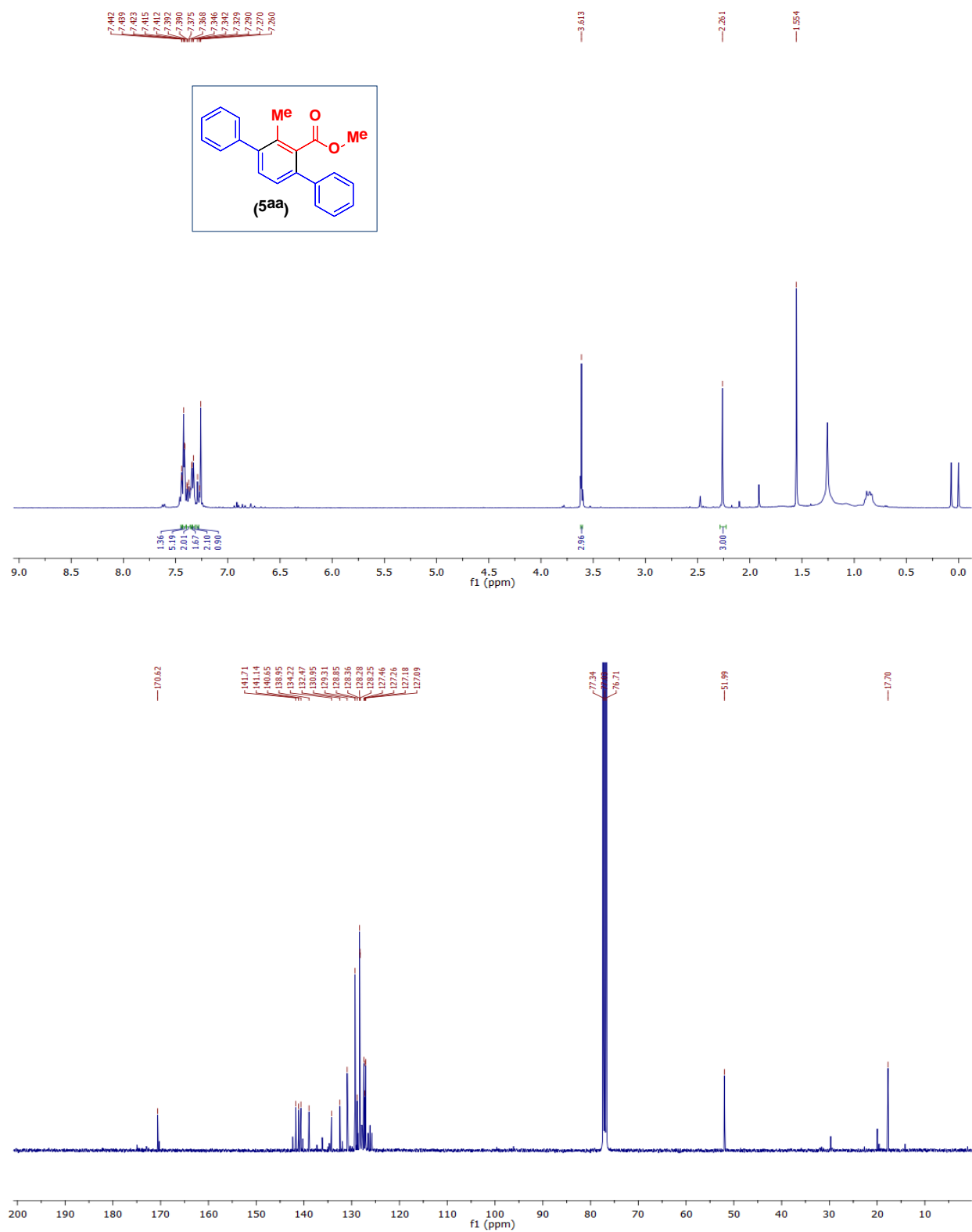


Figure S15a <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound 5aa

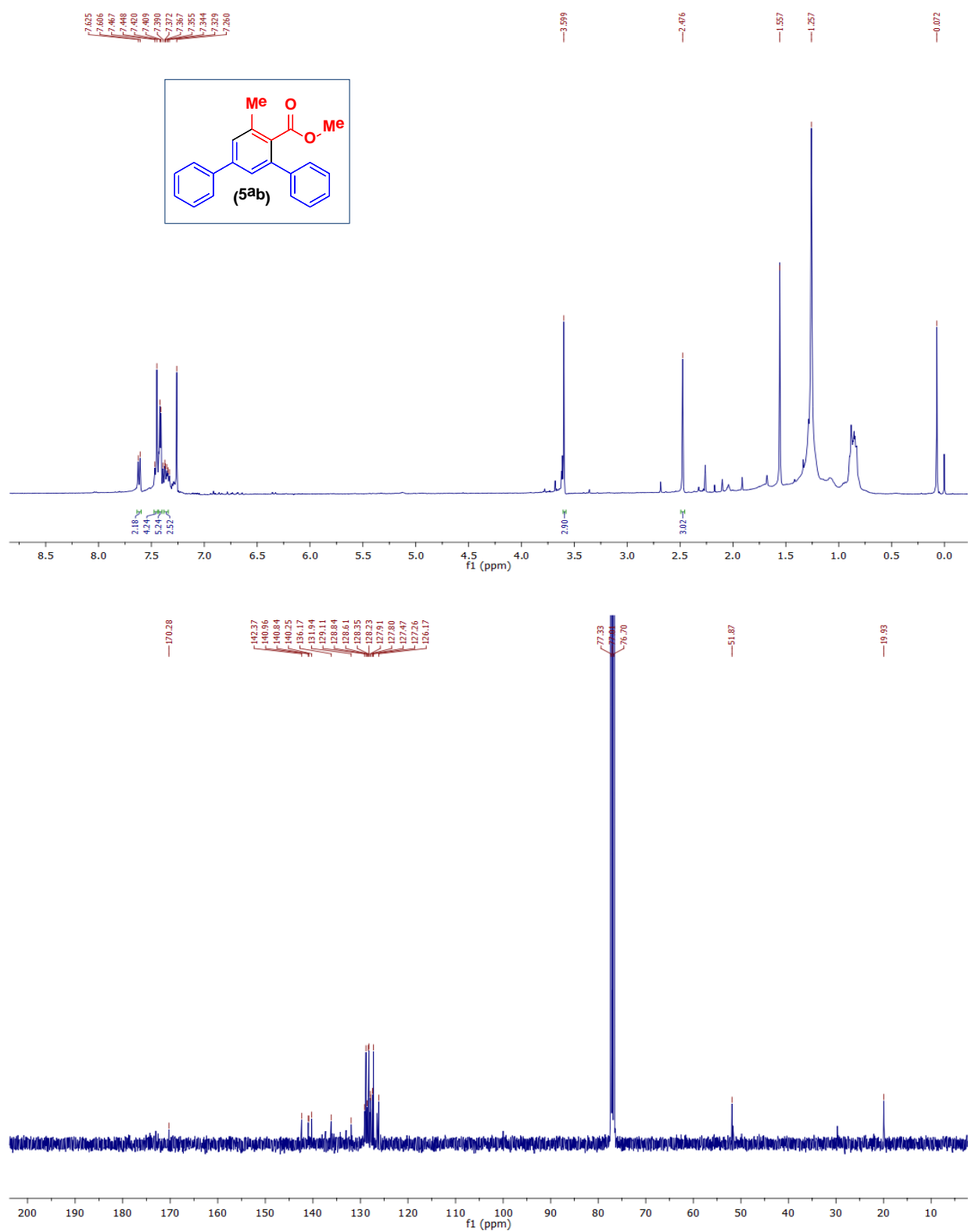


Figure S15b <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound 5ab

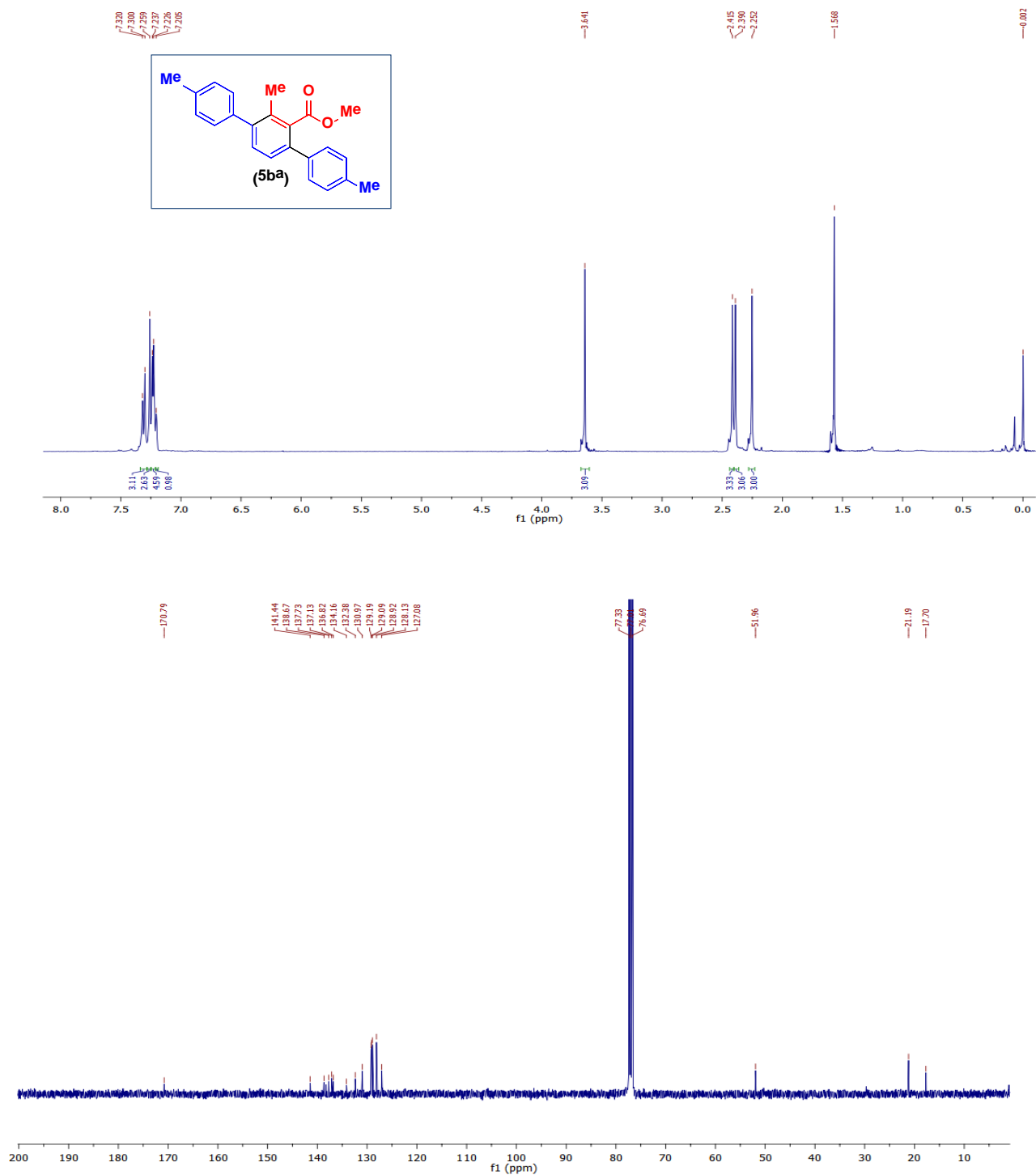


Figure S16a <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound 5ba

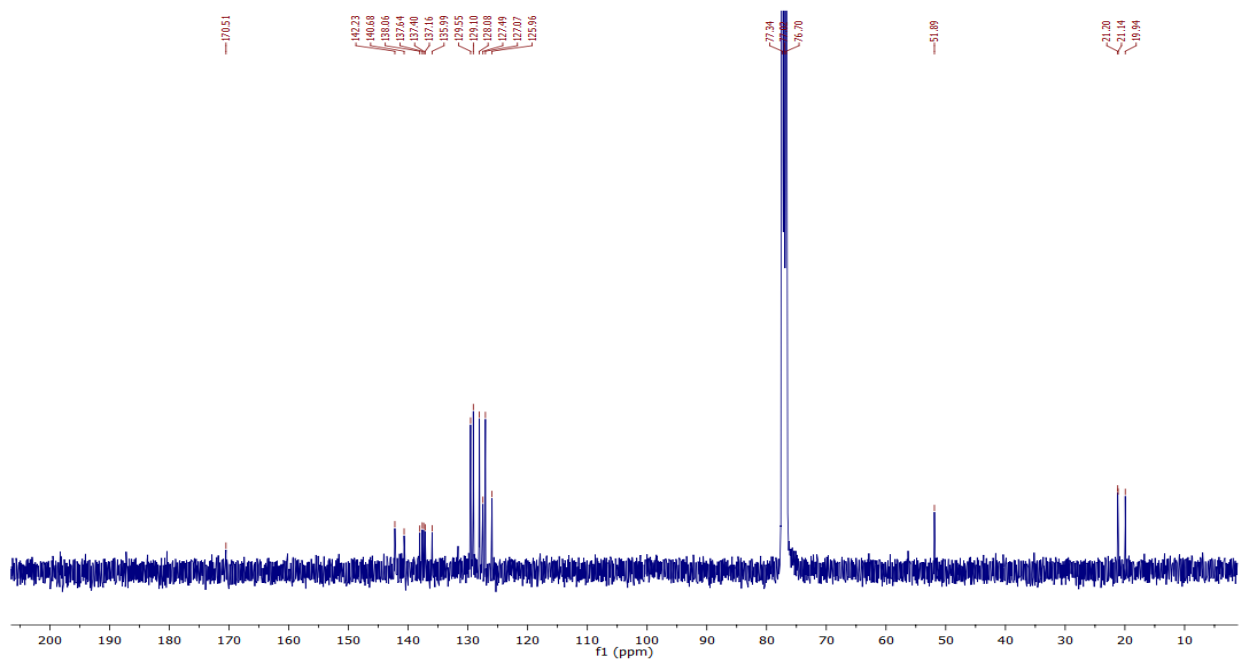
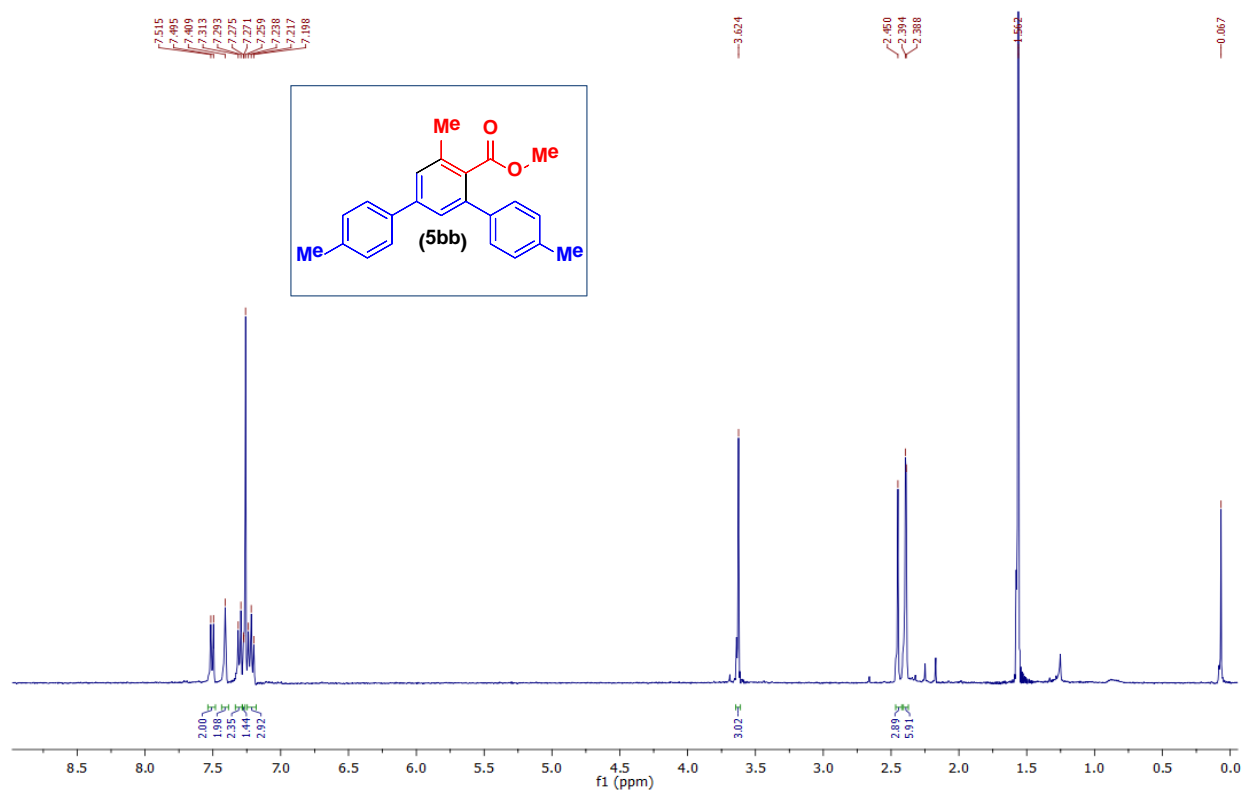
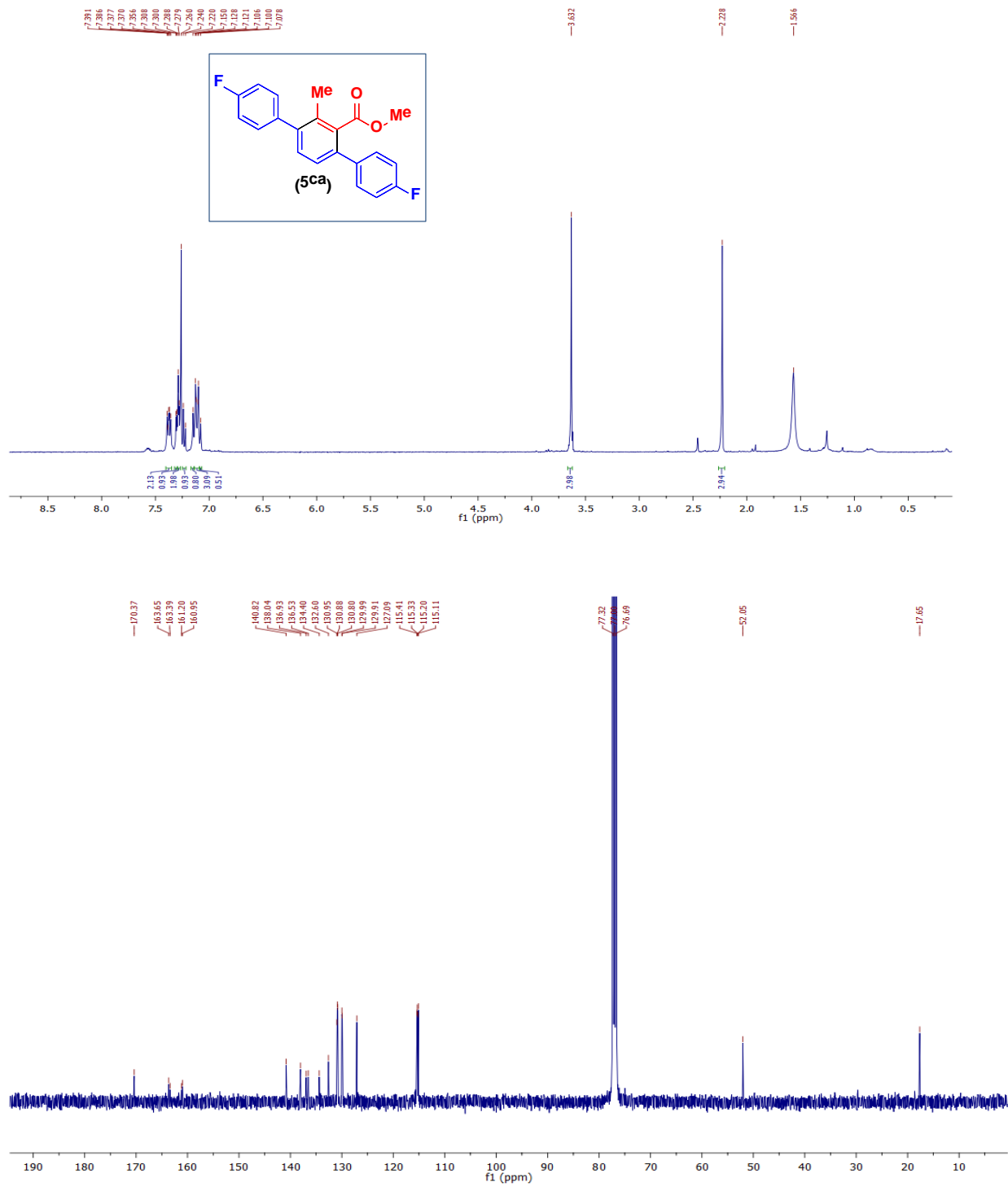


Figure S16b  $^1\text{H}$  &  $^{13}\text{C}$  NMR Spectra of compound **5bb**



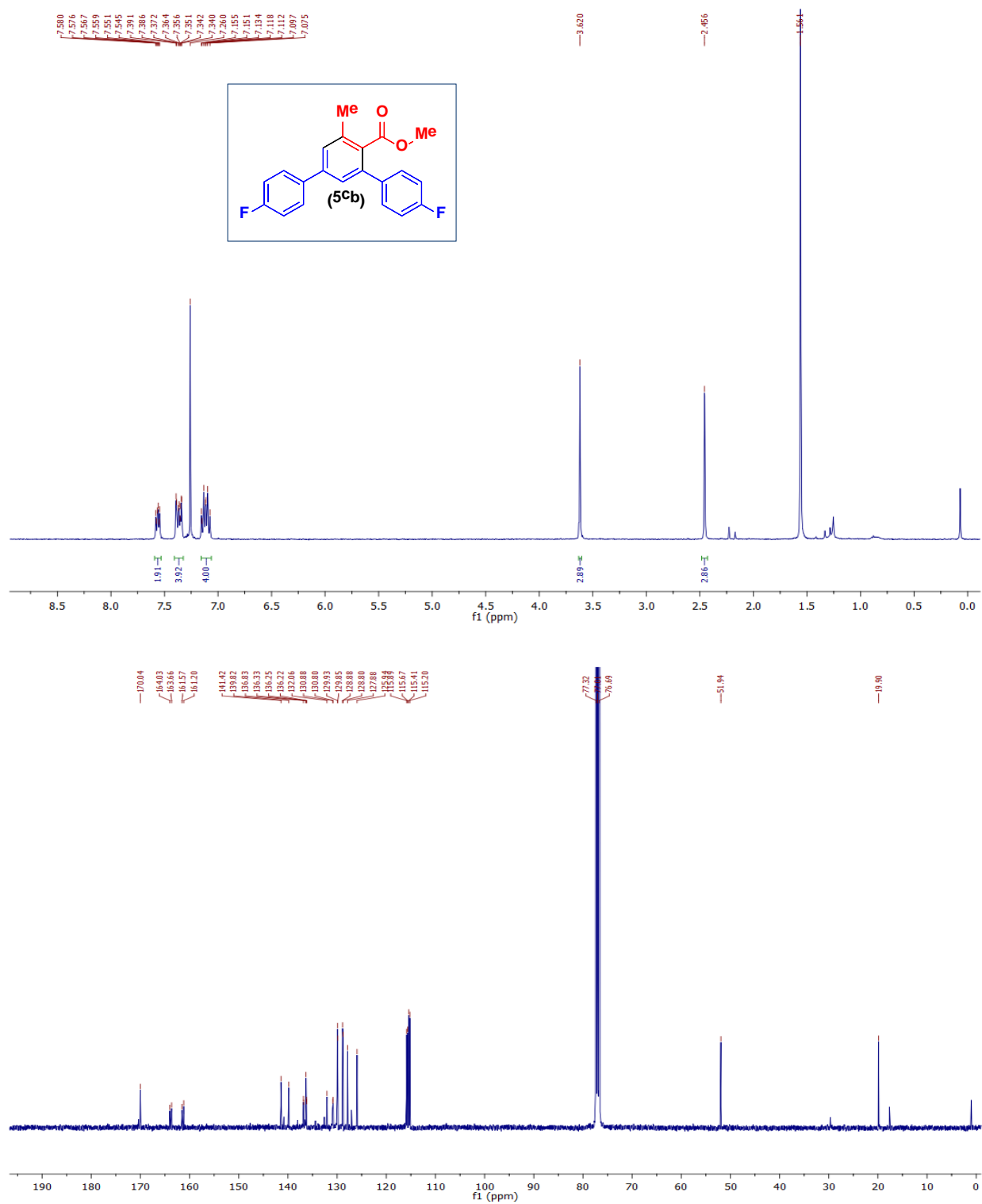
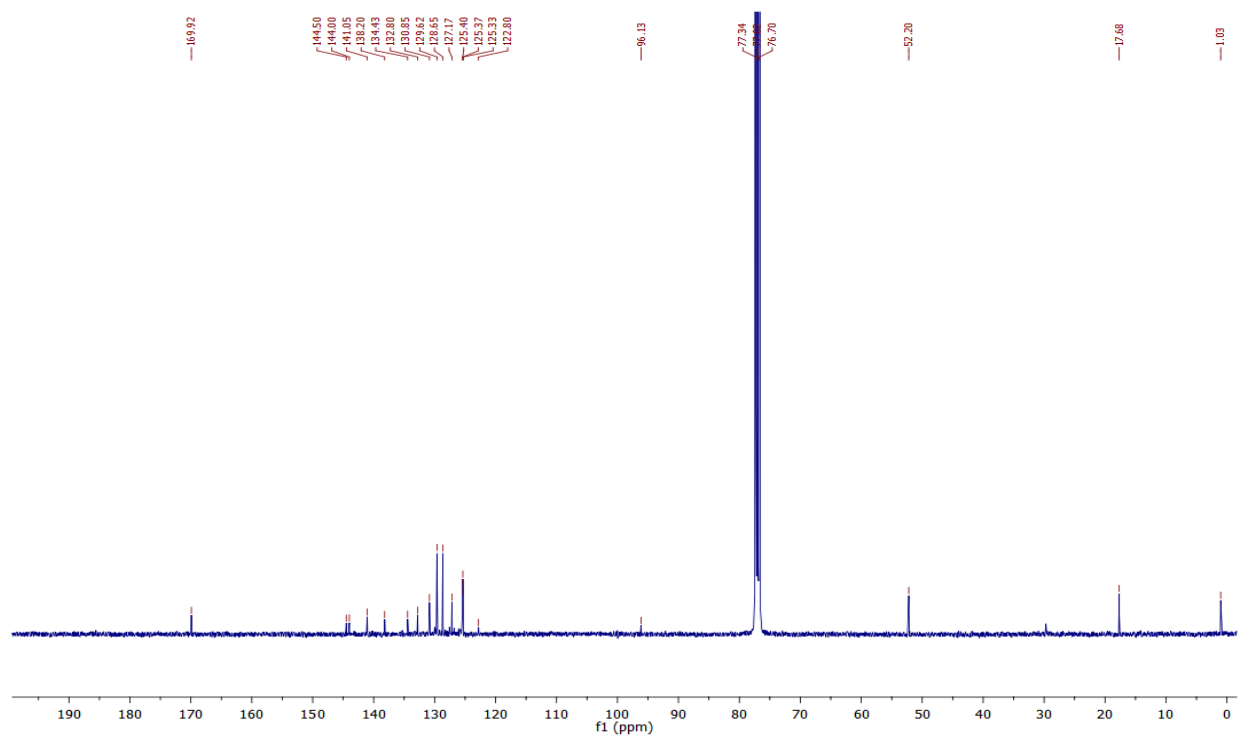
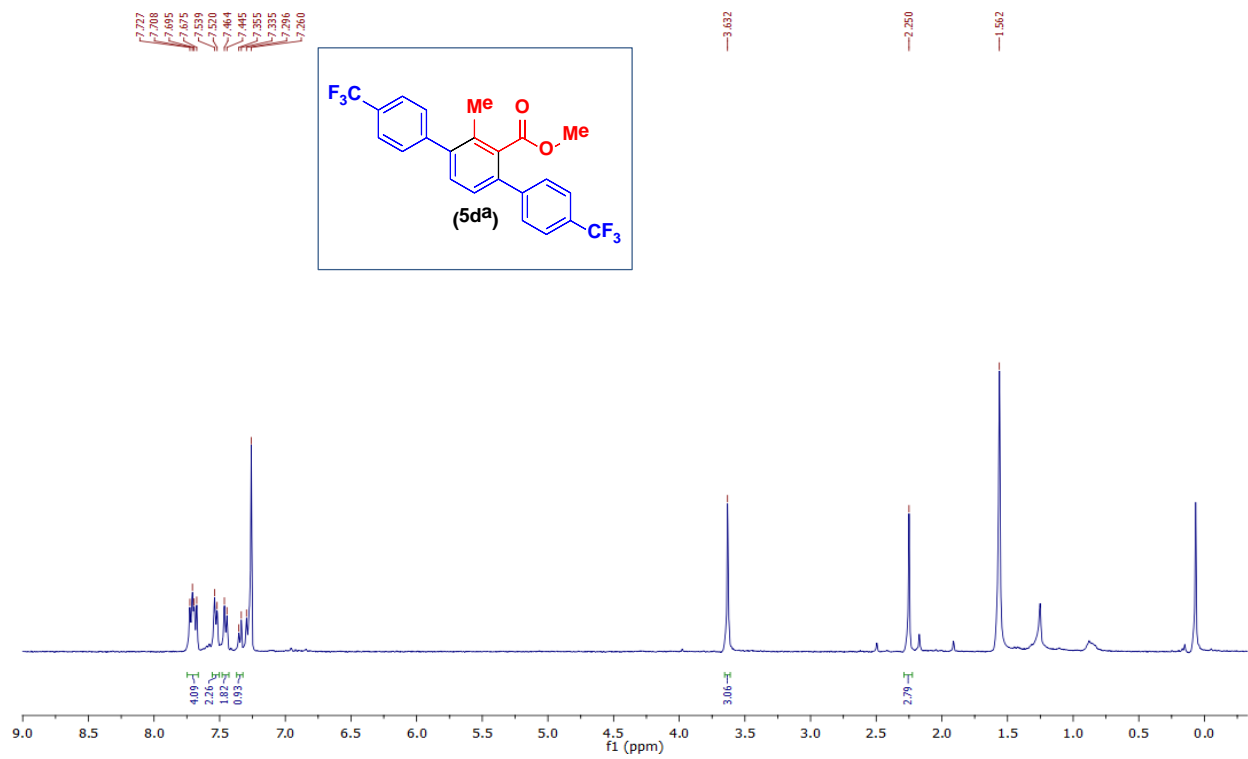


Figure S17b <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **5cb**



**Figure S18a** <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **5da**



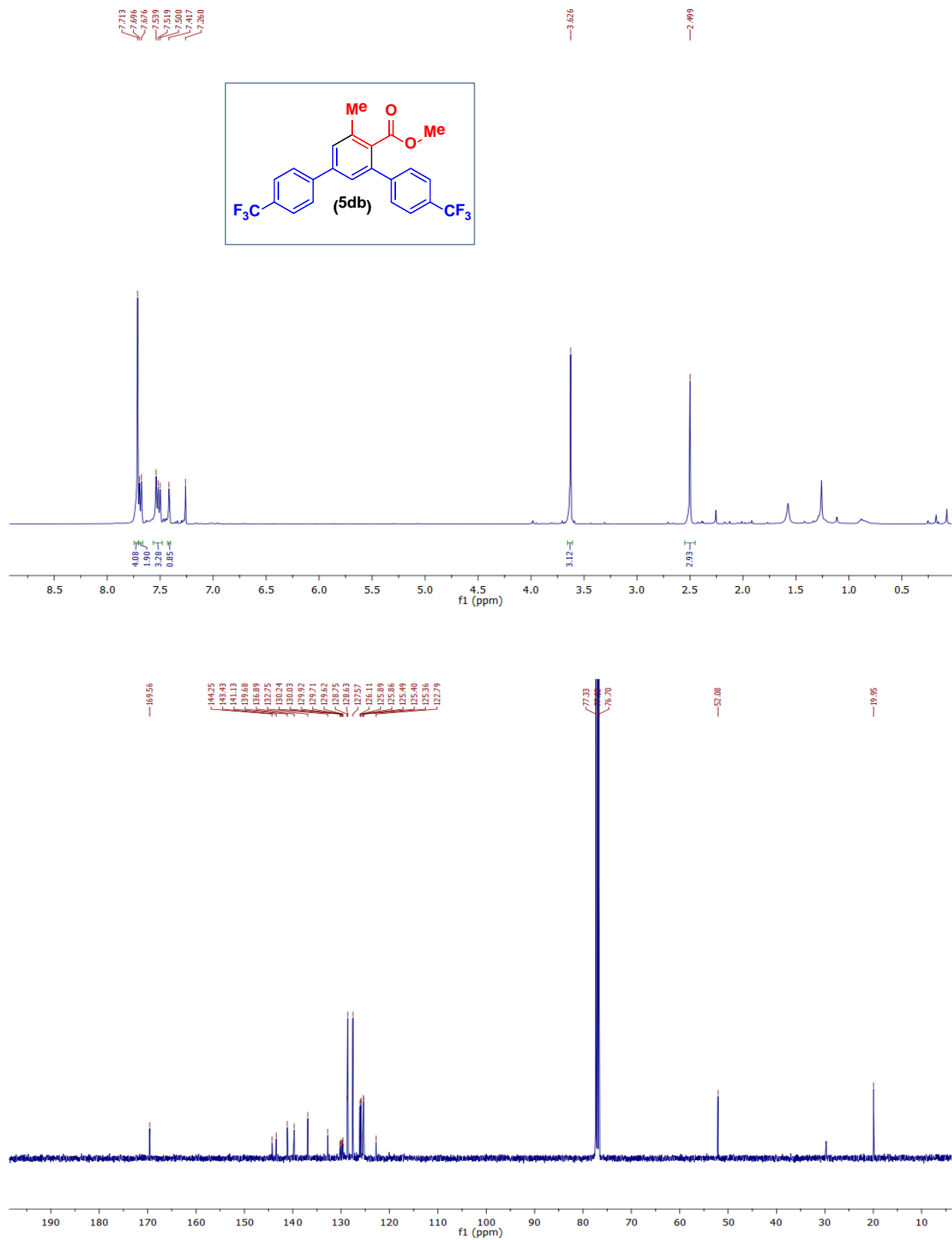


Figure S18b <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **5db**

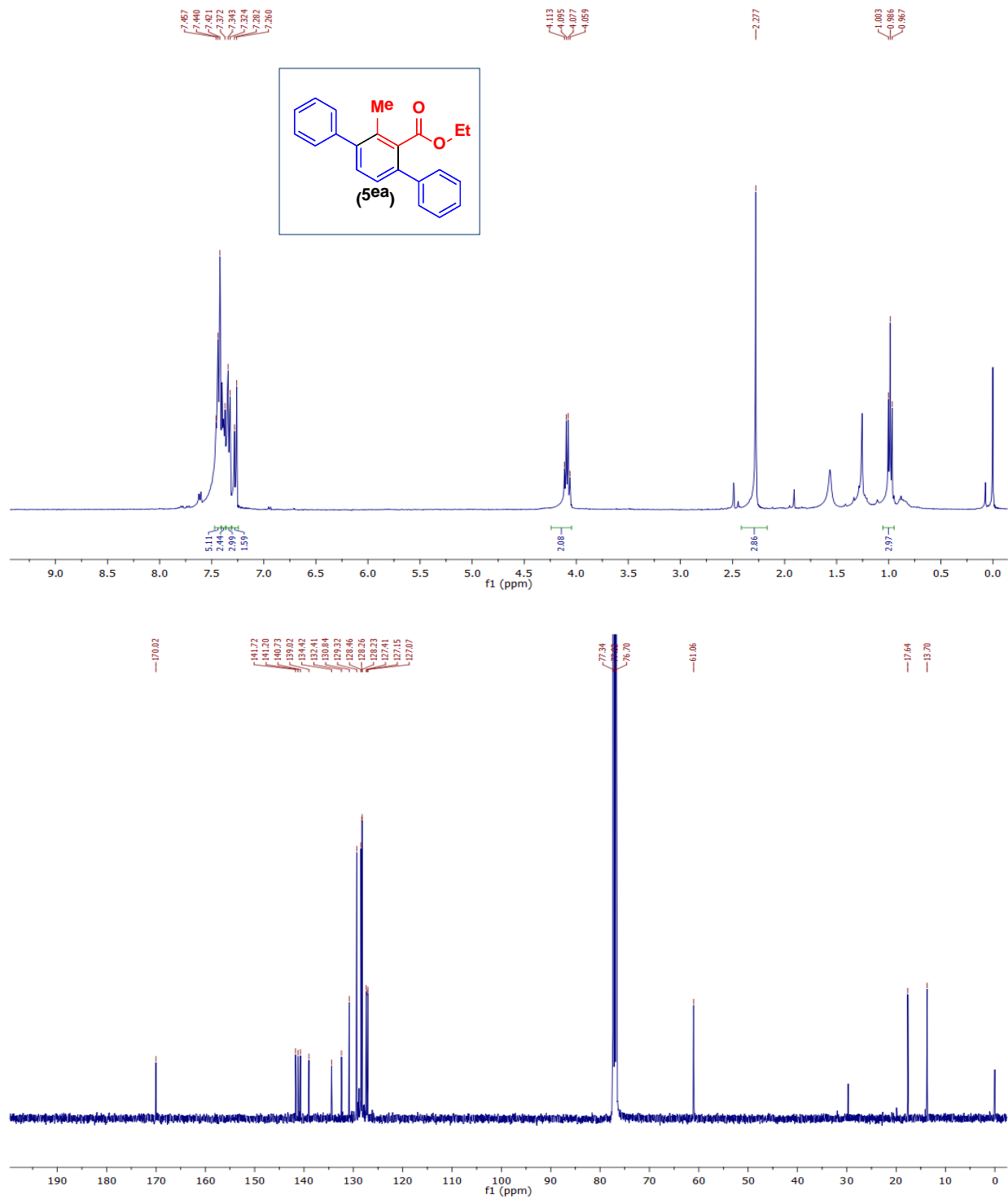


Figure S19a <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound 5ea

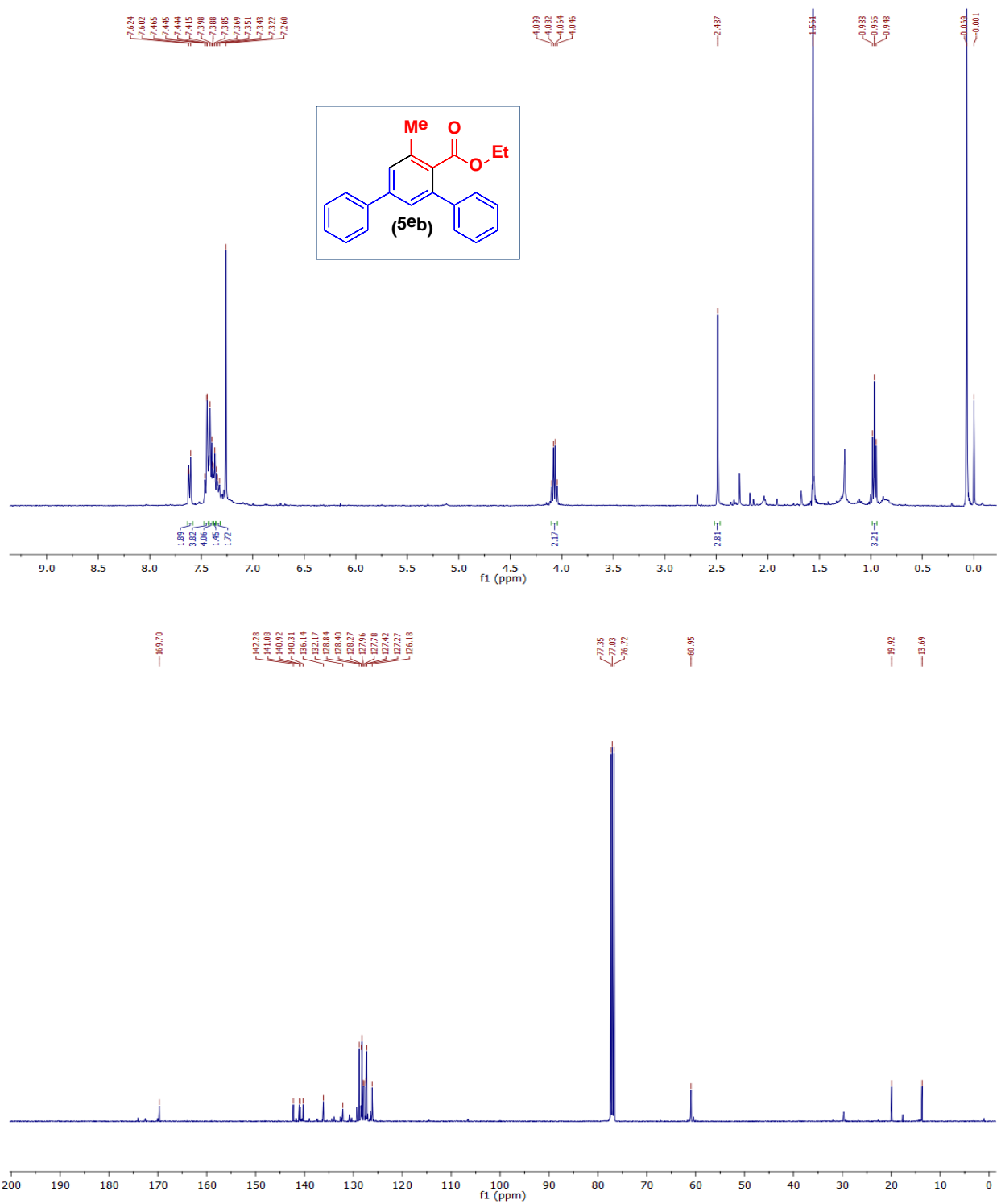


Figure S19b <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **5eb**

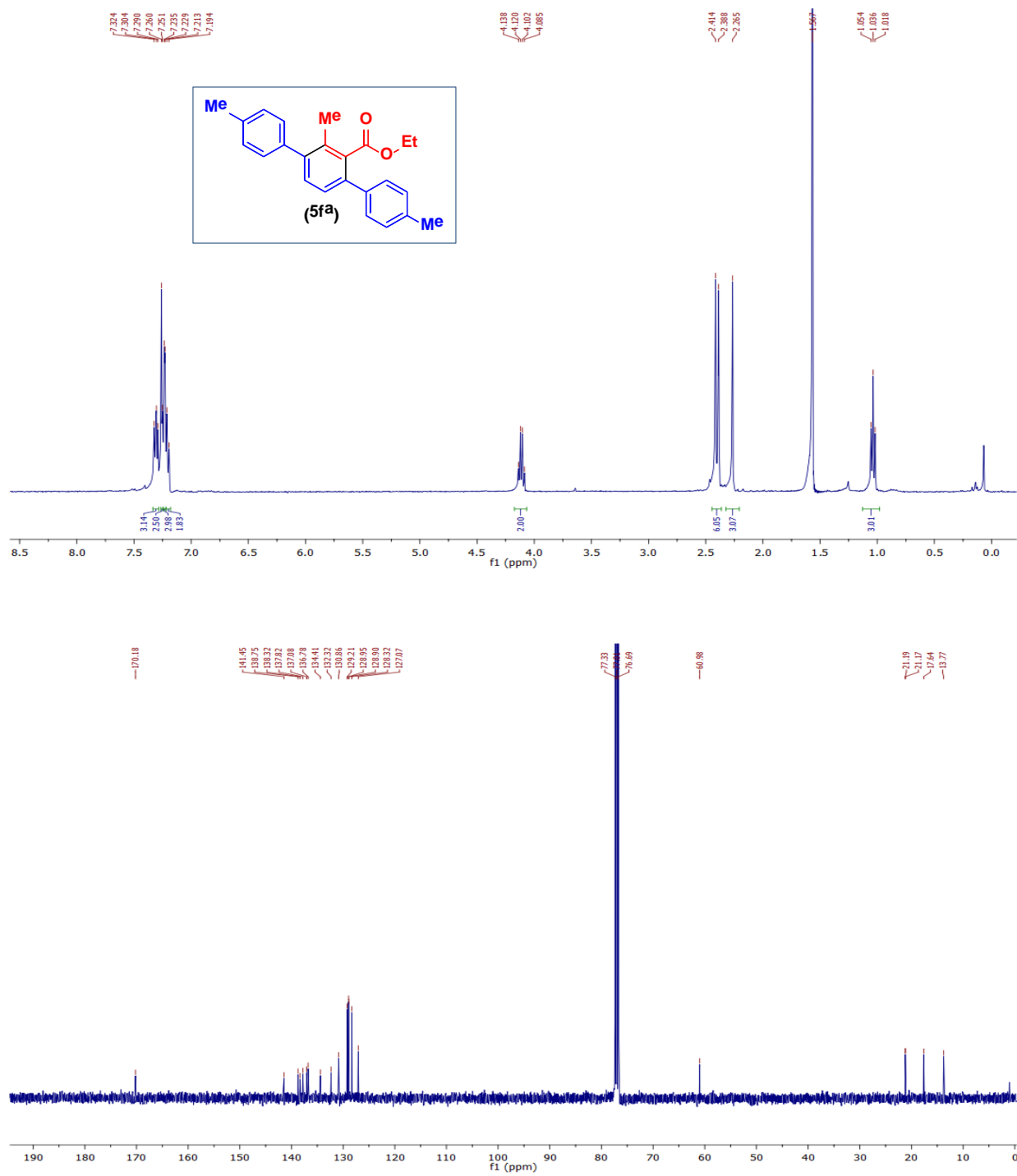


Figure S20a <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound 5fa

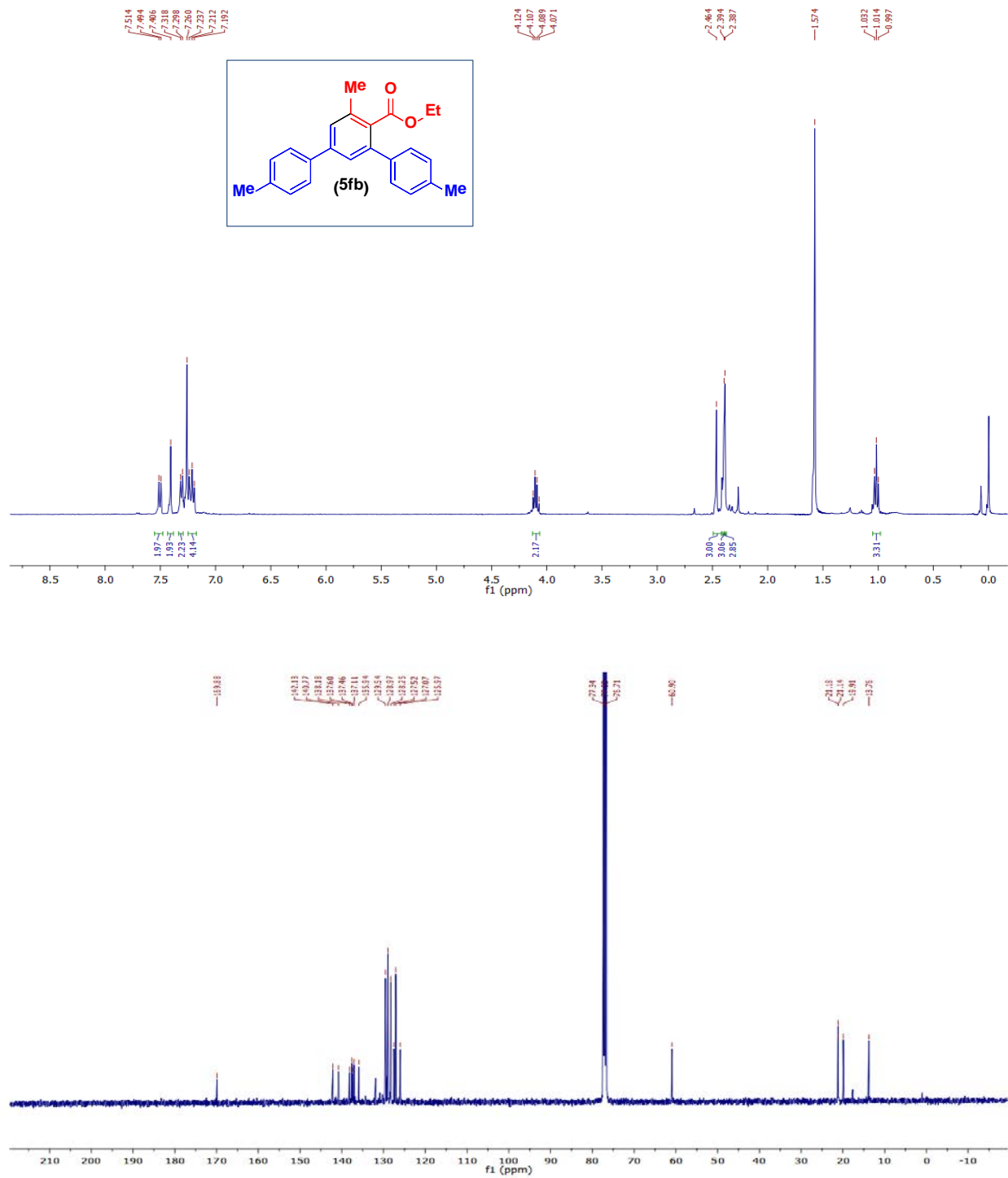


Figure S20b <sup>1</sup>H & <sup>13</sup>C NMR Spectra of compound **5fb**

## High Resolution Mass Spectra

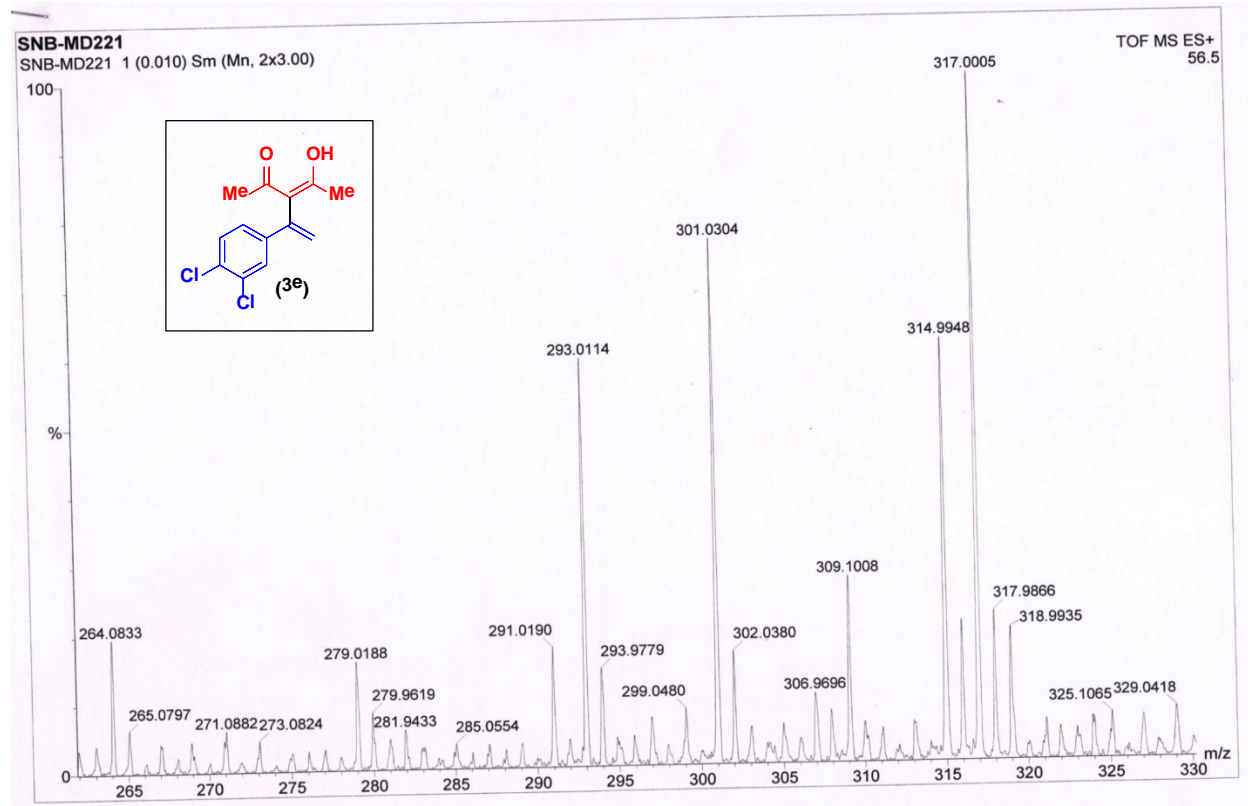


Figure S21 HRMS data of the compound **3e**

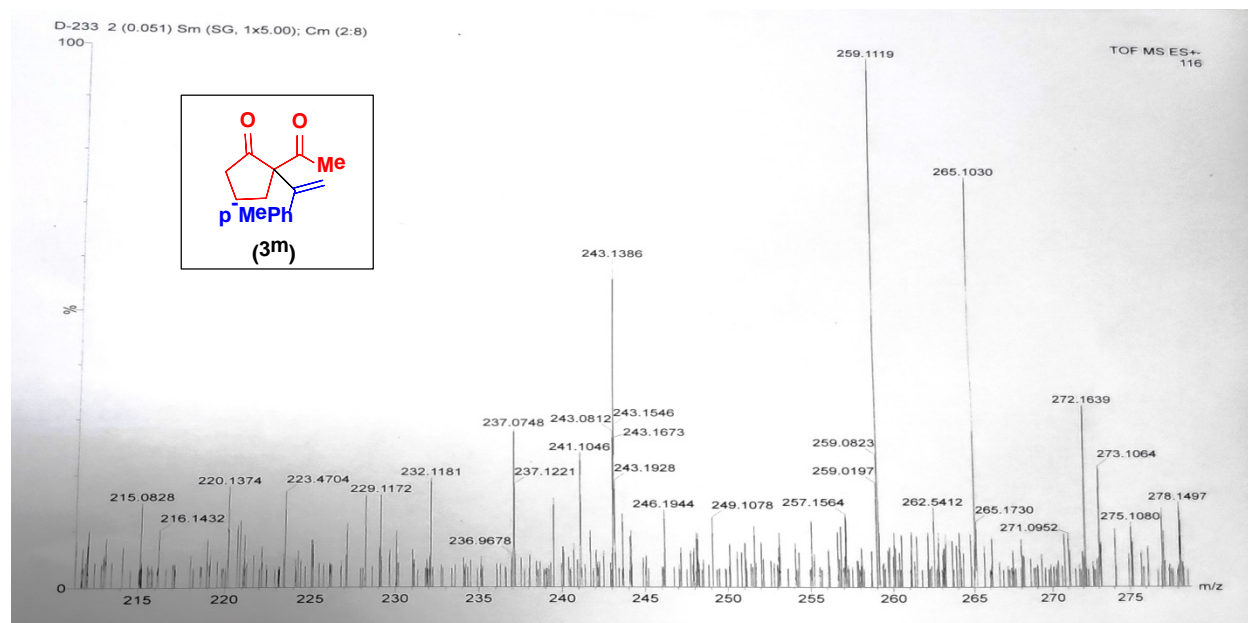


Figure S22 HRMS data of the compound **3m**

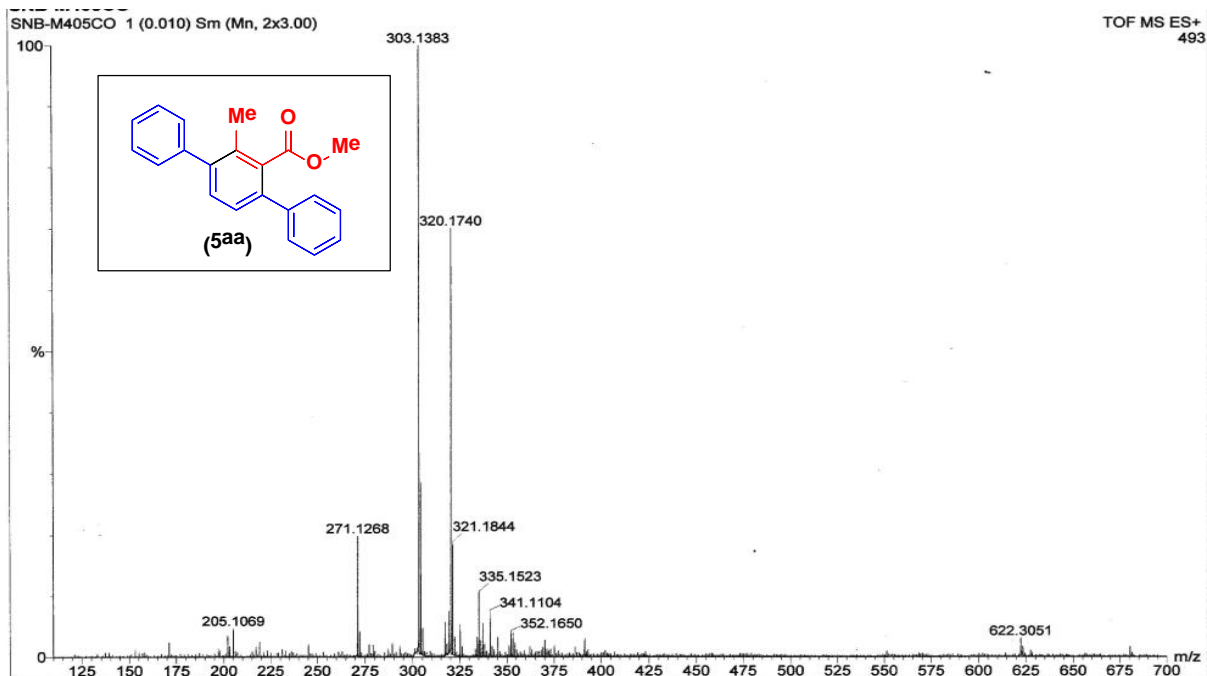


Figure S23 HRMS data of the compound 5aa

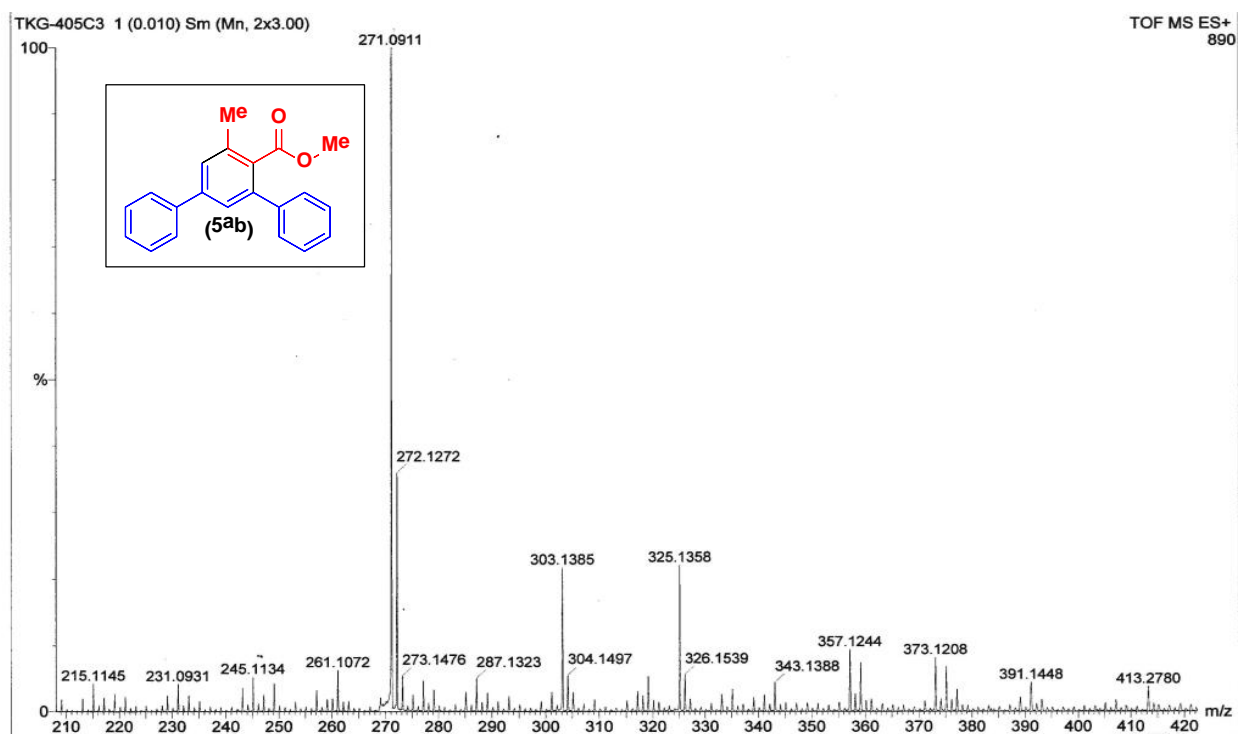


Figure S24 HRMS data of the compound 5ab

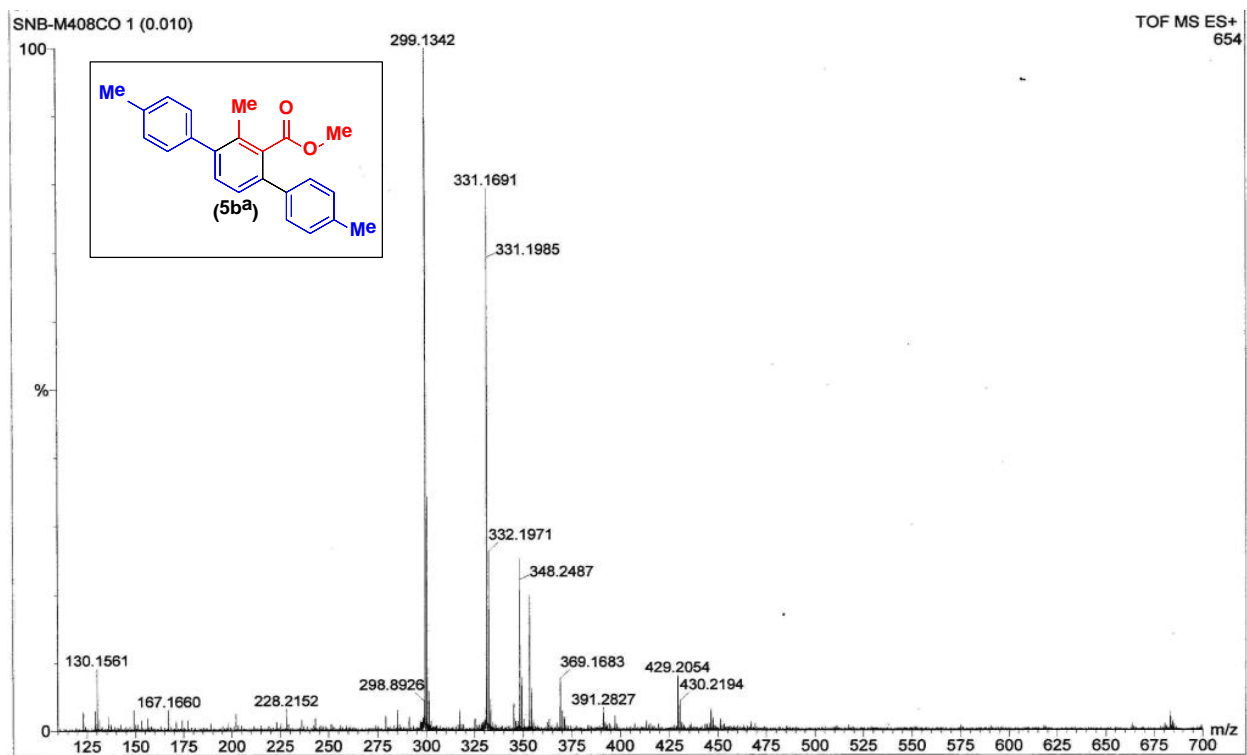


Figure S25 HRMS data of compound 5ba

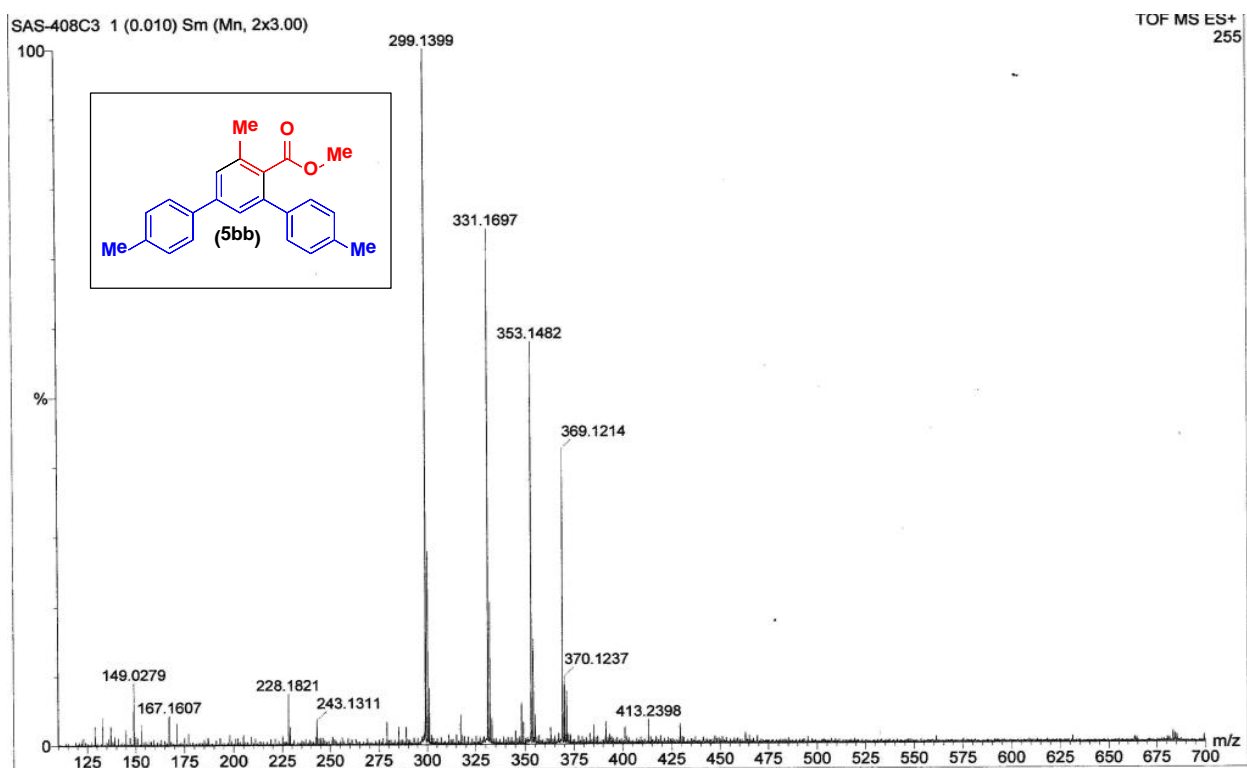


Figure S26 HRMS data of the compound 5bb



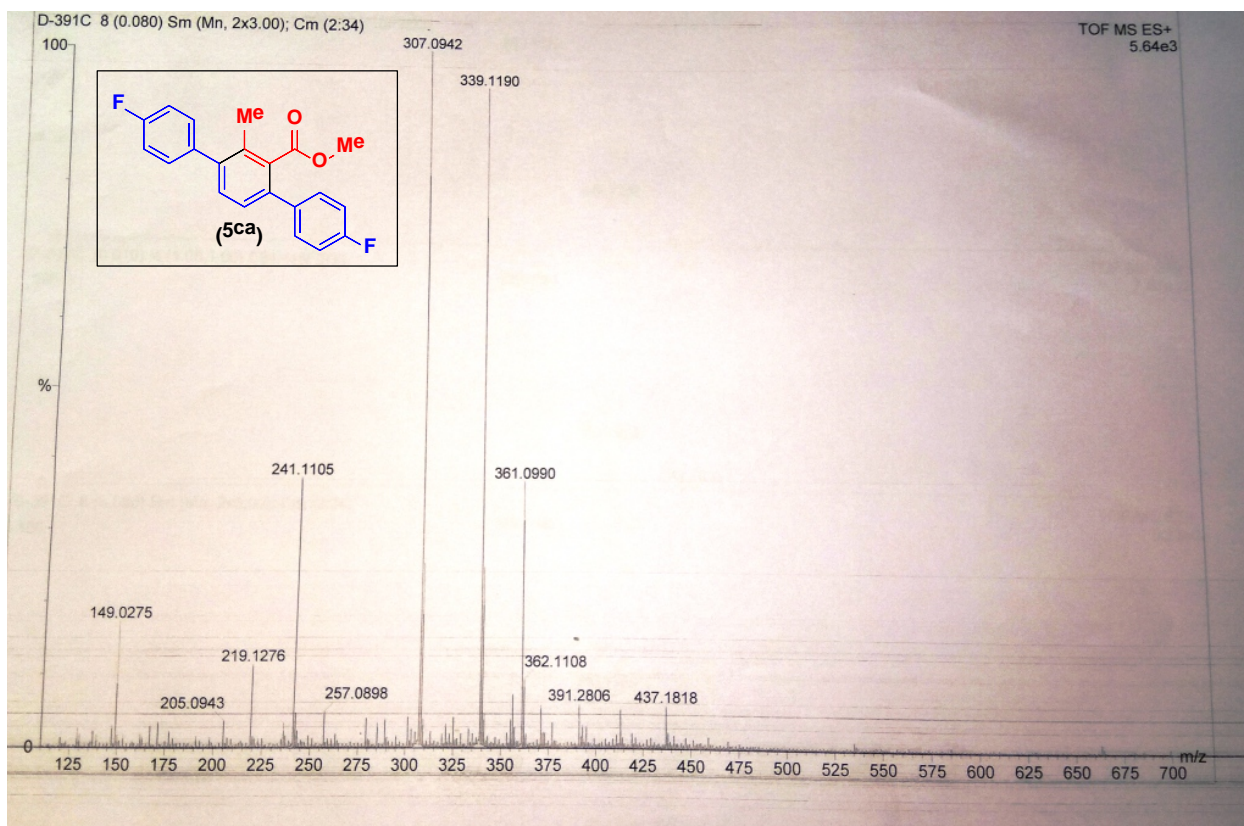


Figure S27 HRMS data of compound 5ca

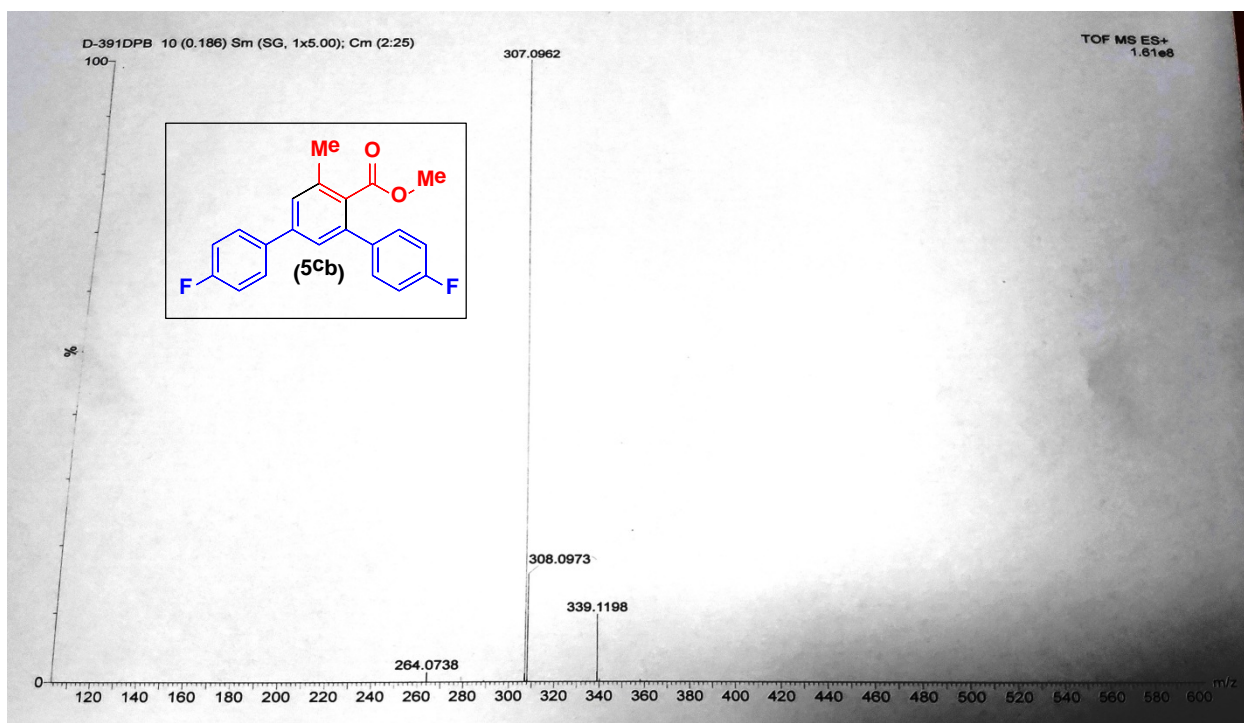


Figure S28 HRMS data of the compound 5cb

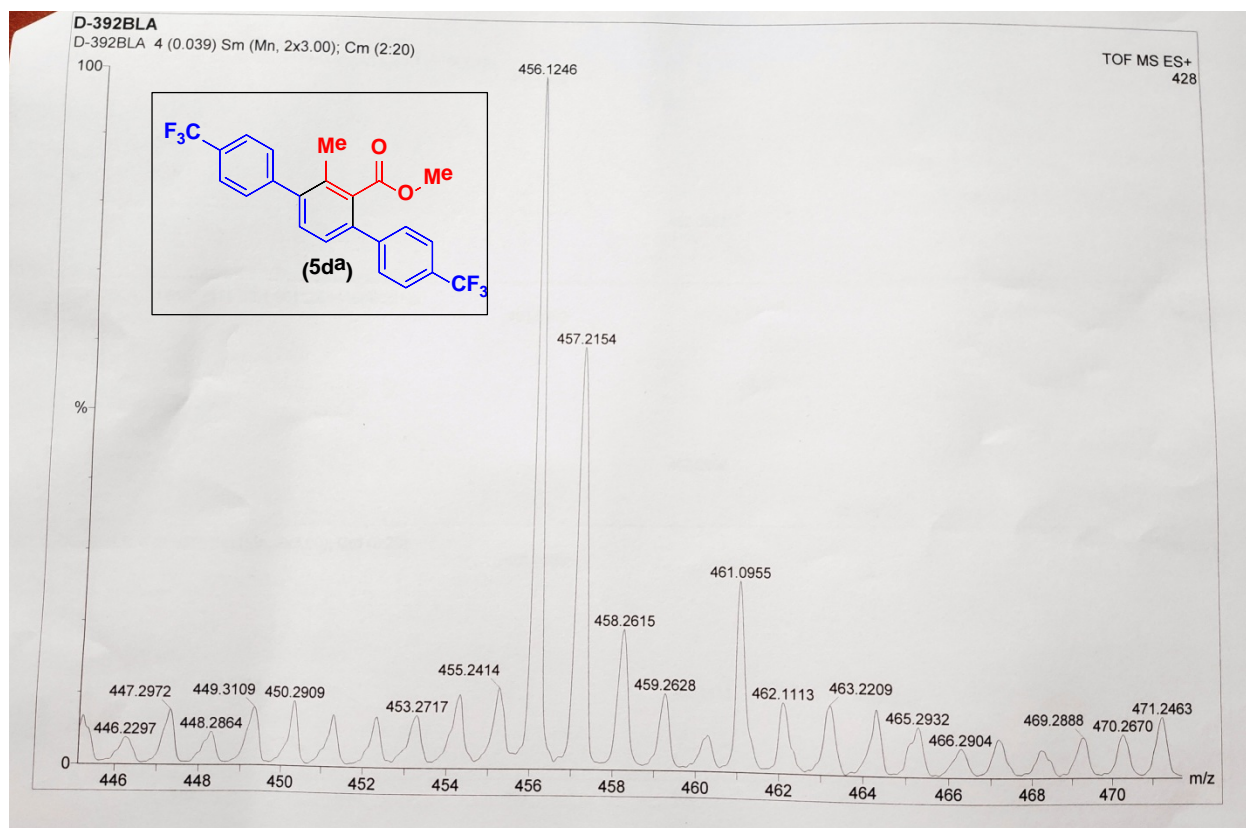


Figure S29 HRMS data of the compound 5da

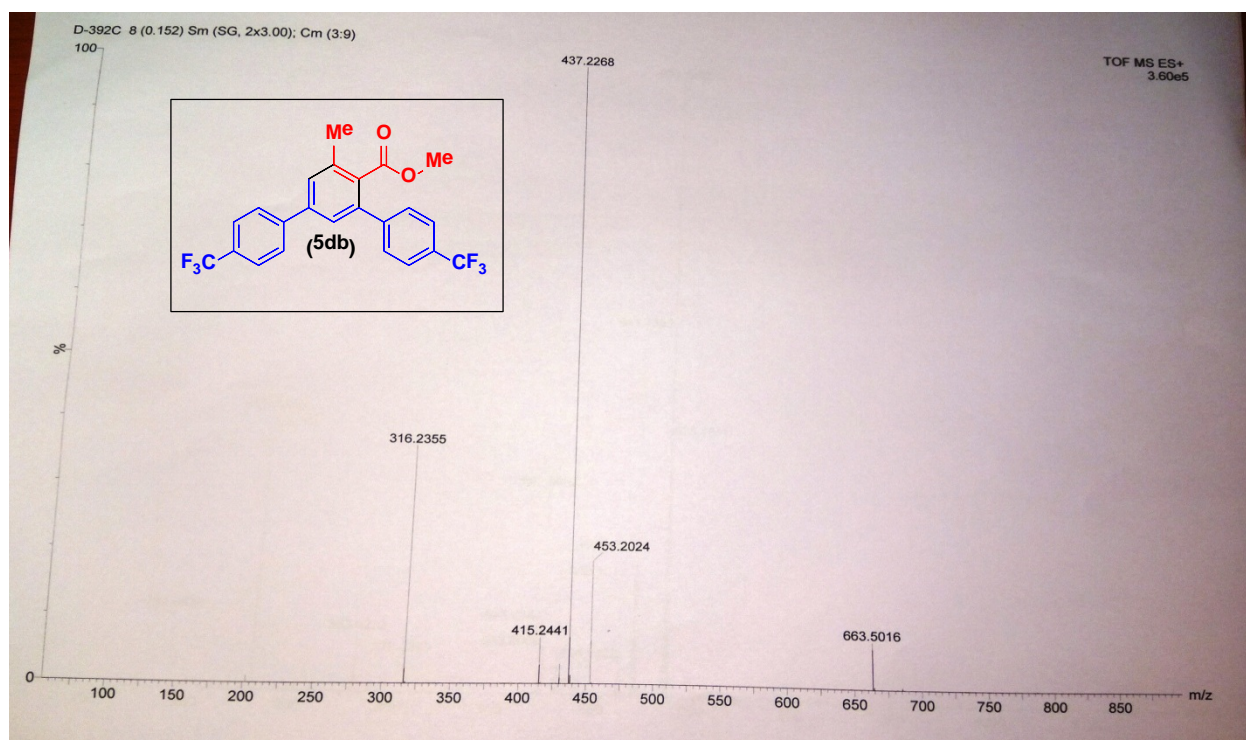


Figure S30 HRMS data of the compound 5db

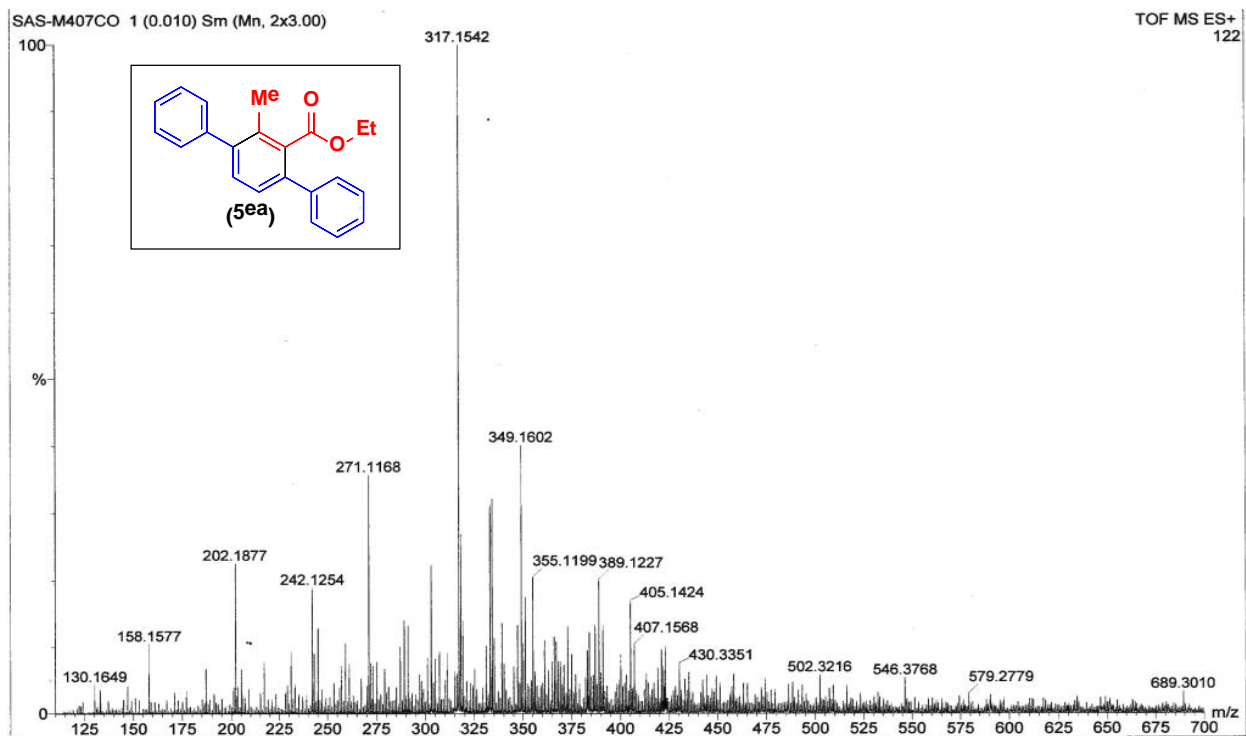


Figure S31 HRMS data of the compound **5ea**

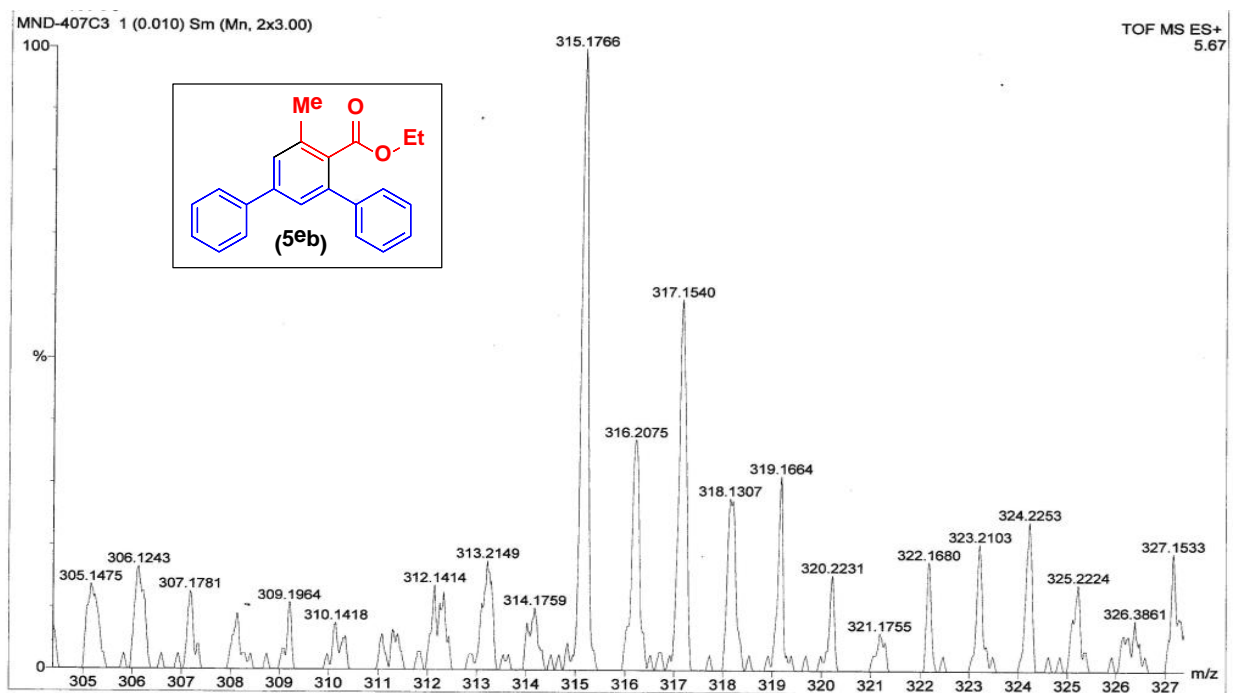


Figure S32 HRMS data of the compound of **5eb**



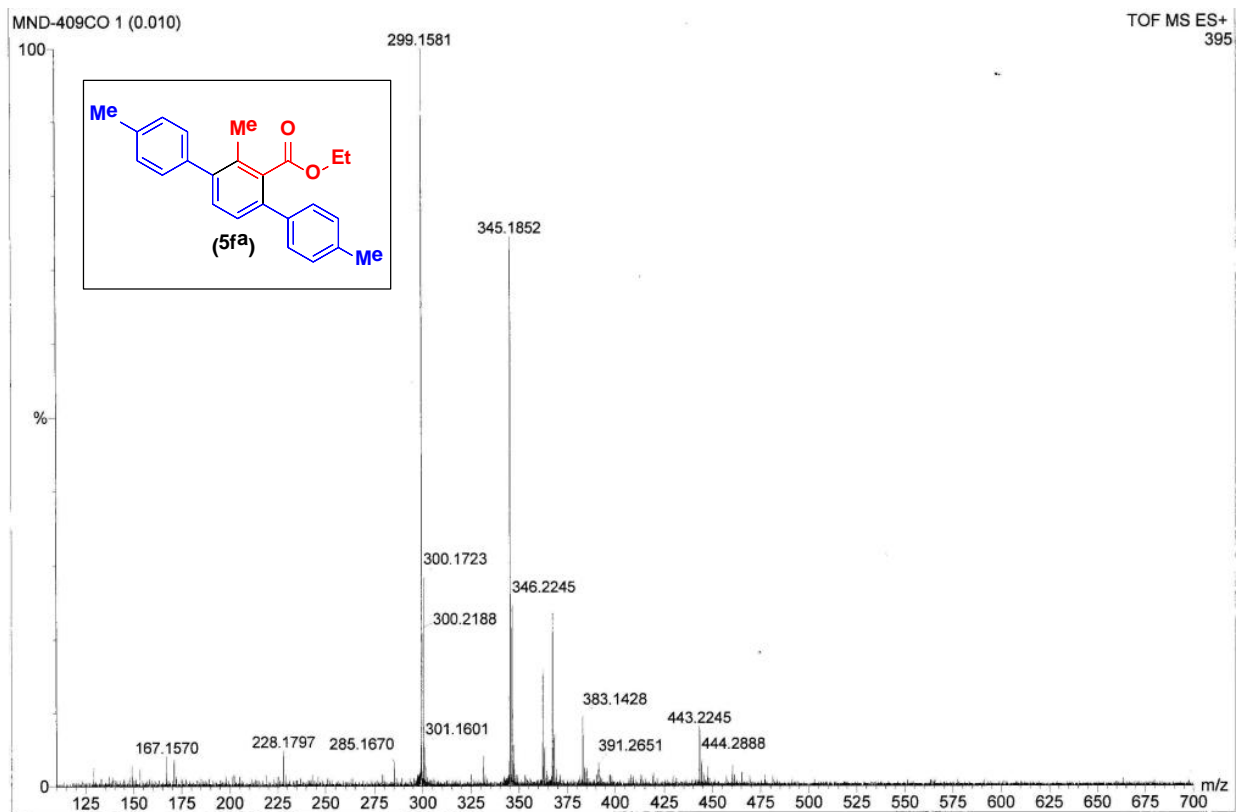


Figure S33 HRMS data of the compound **5fa**

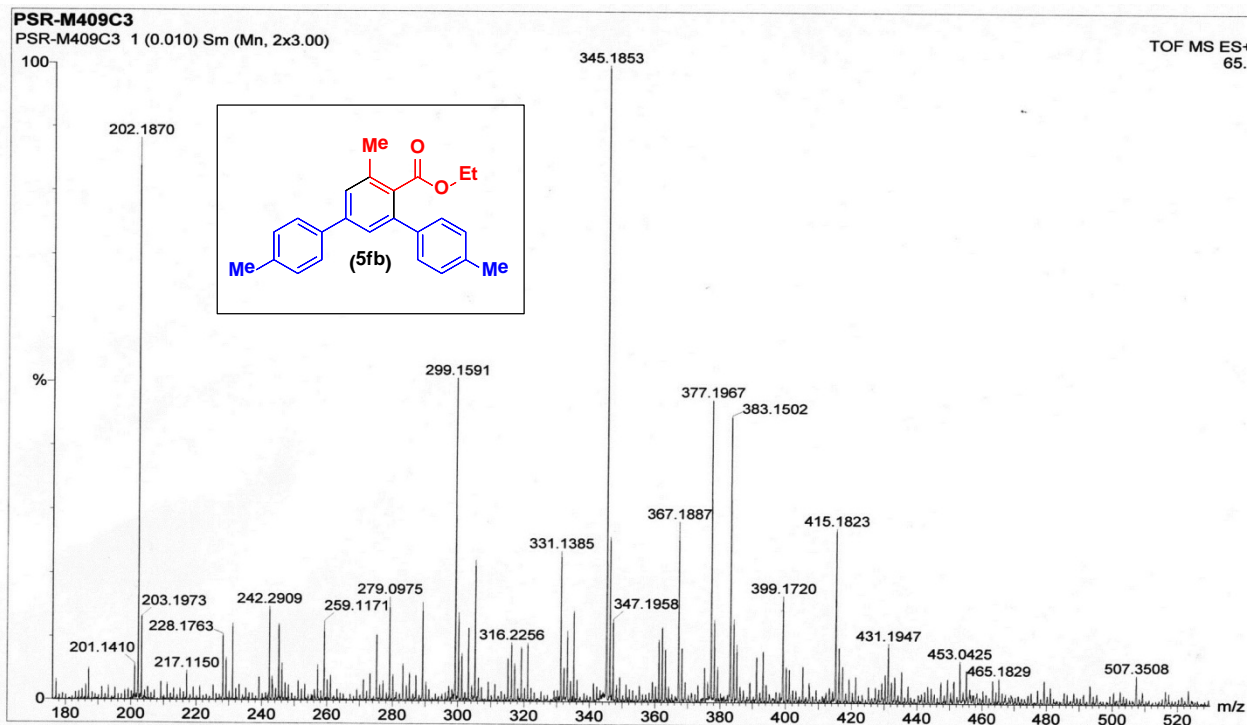
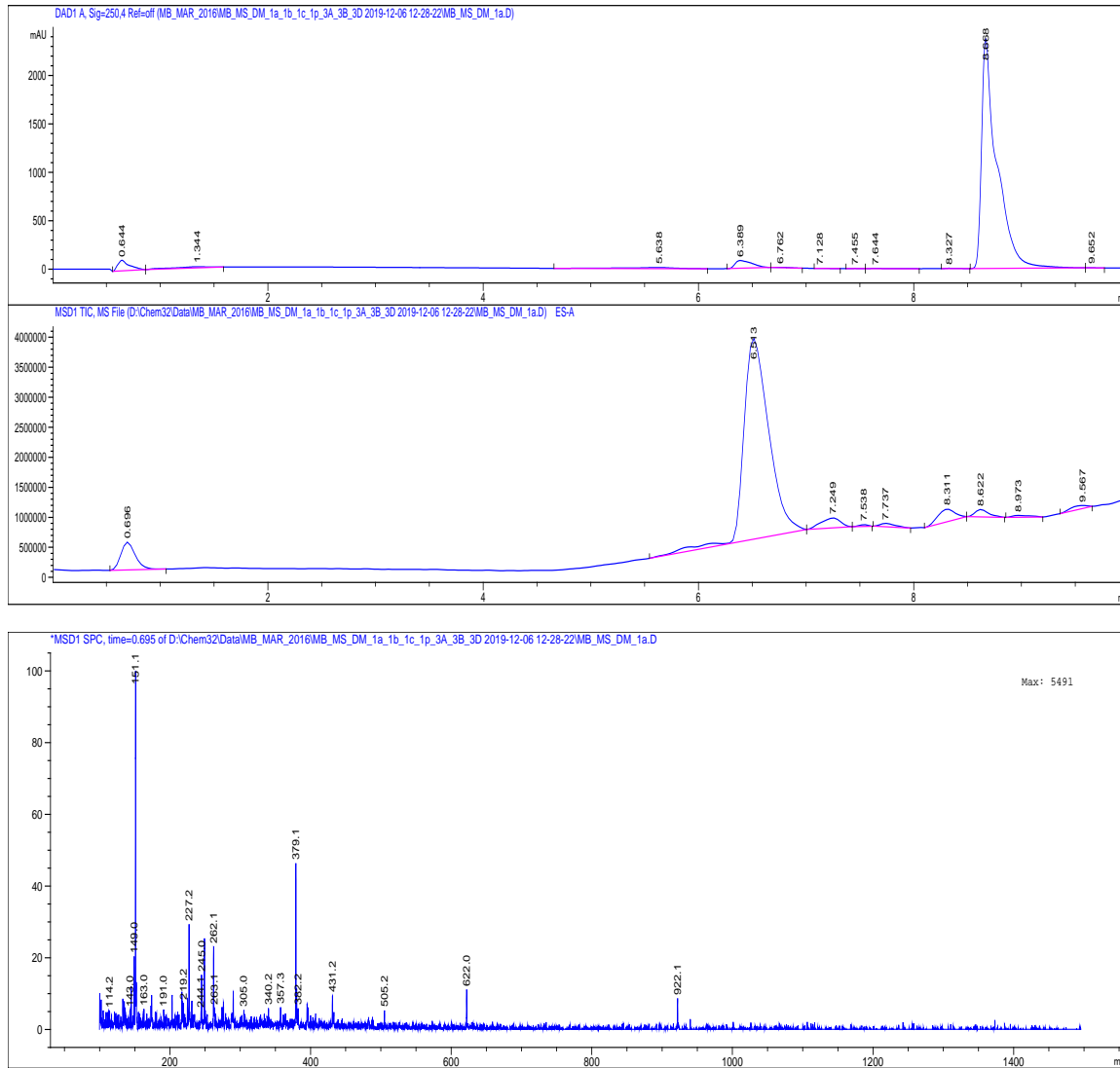
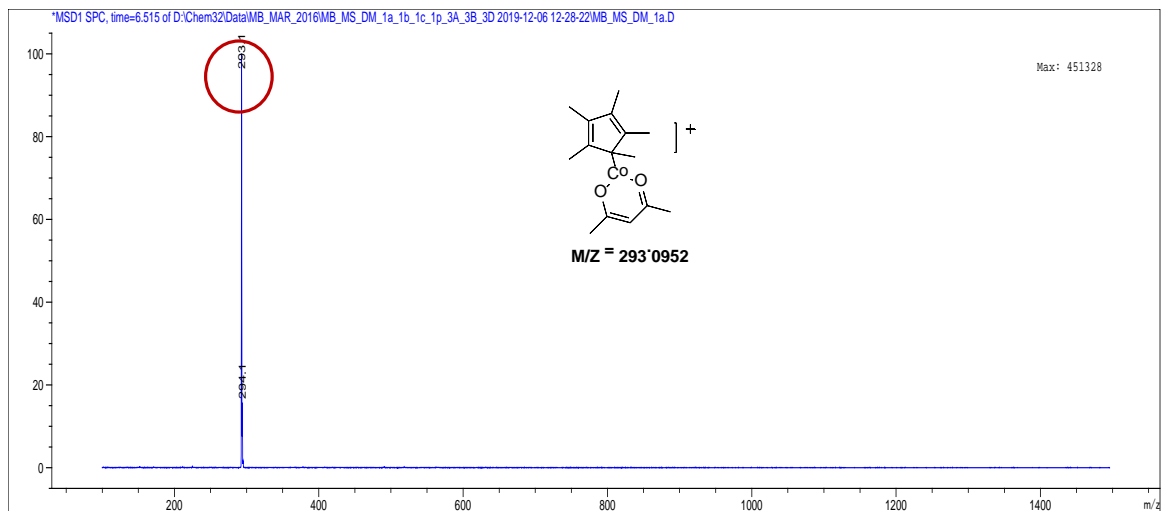


Figure S34 HRMS data of the compound **5fb**

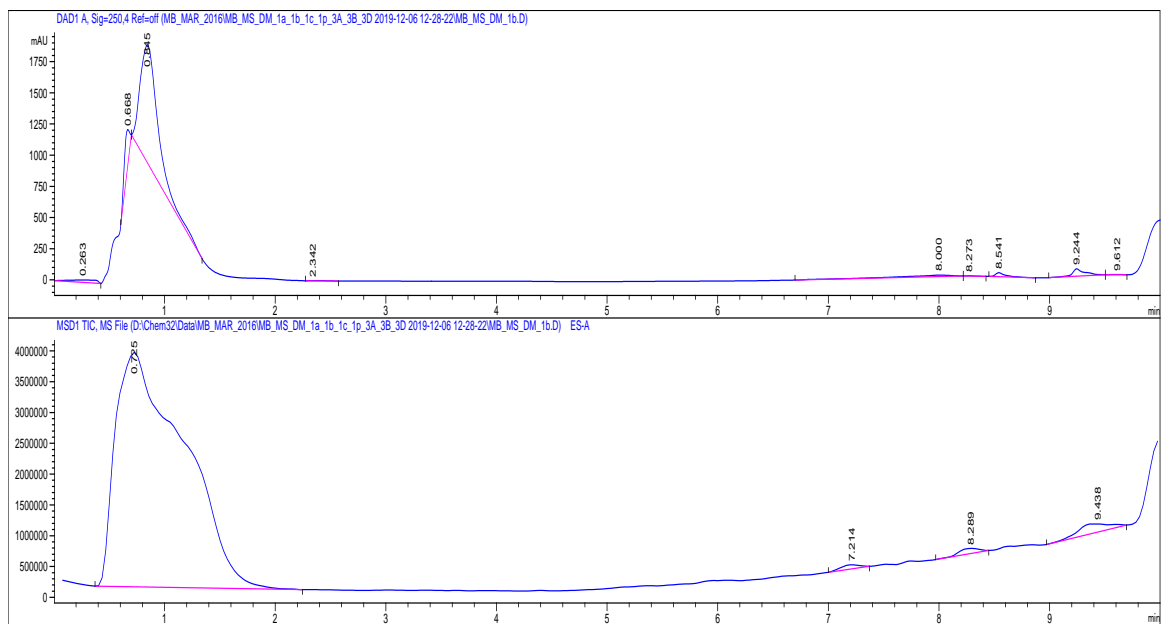
# In Situ LCMS Chromatograms and Mass Spectra

After 1 hour of reaction with catalyst (mol%) and acetylacetone





After 45 minutes of alkyne addition on the above reaction mixture (catalyst+acetylacetone+toluene)

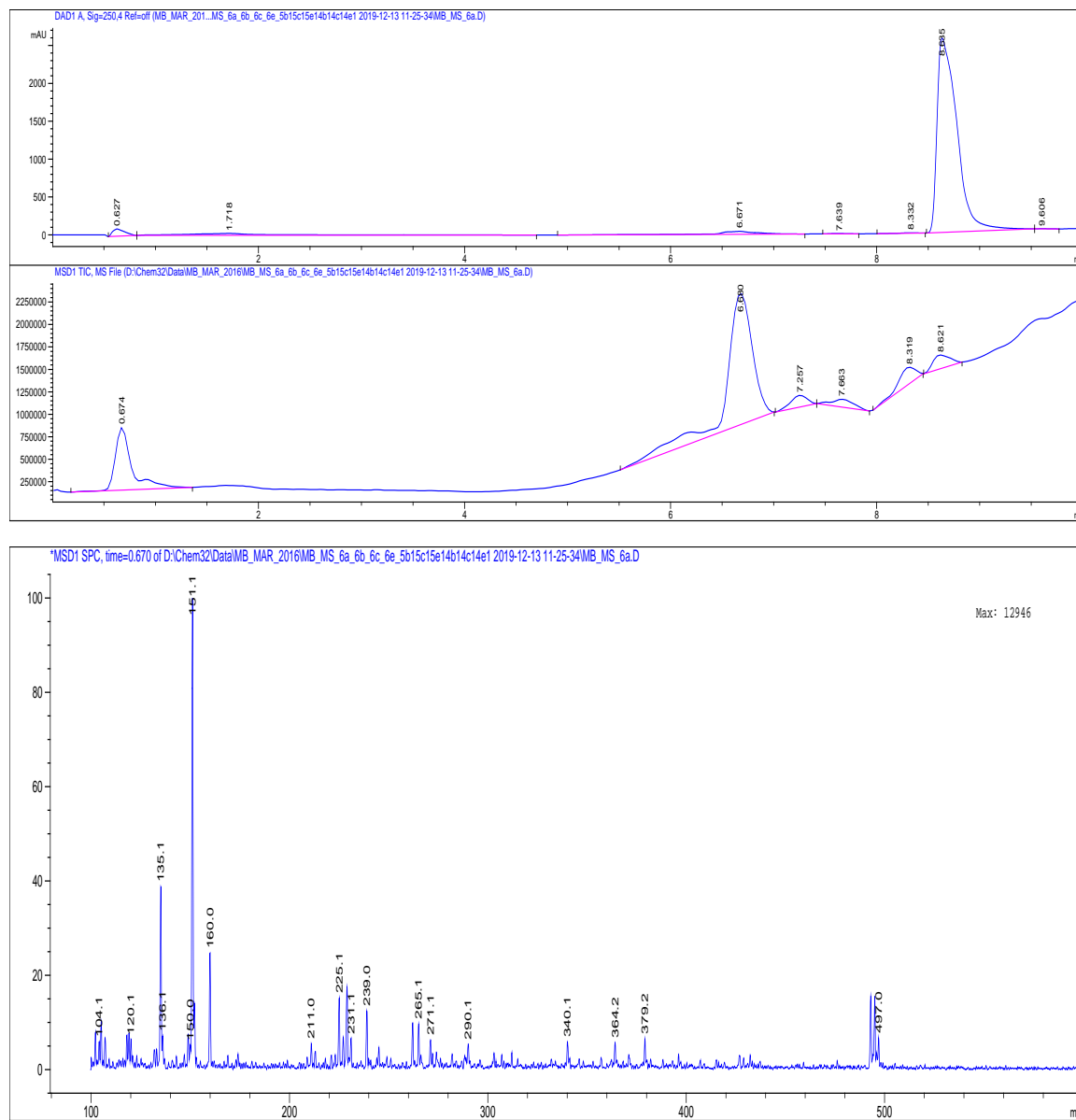


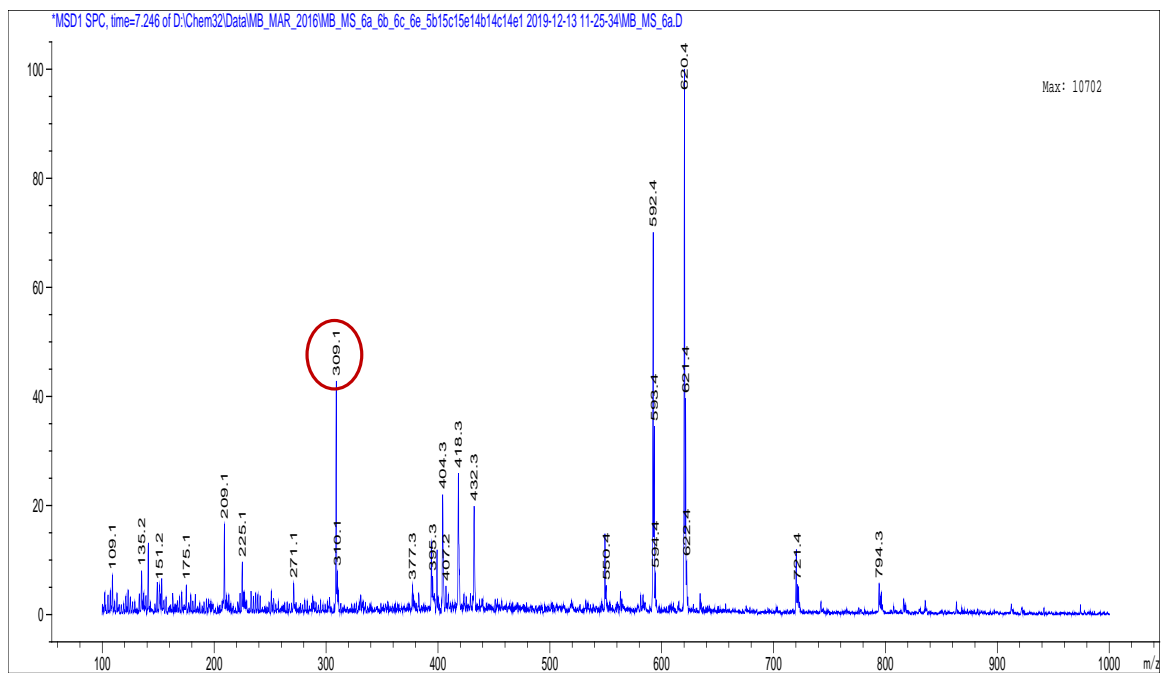
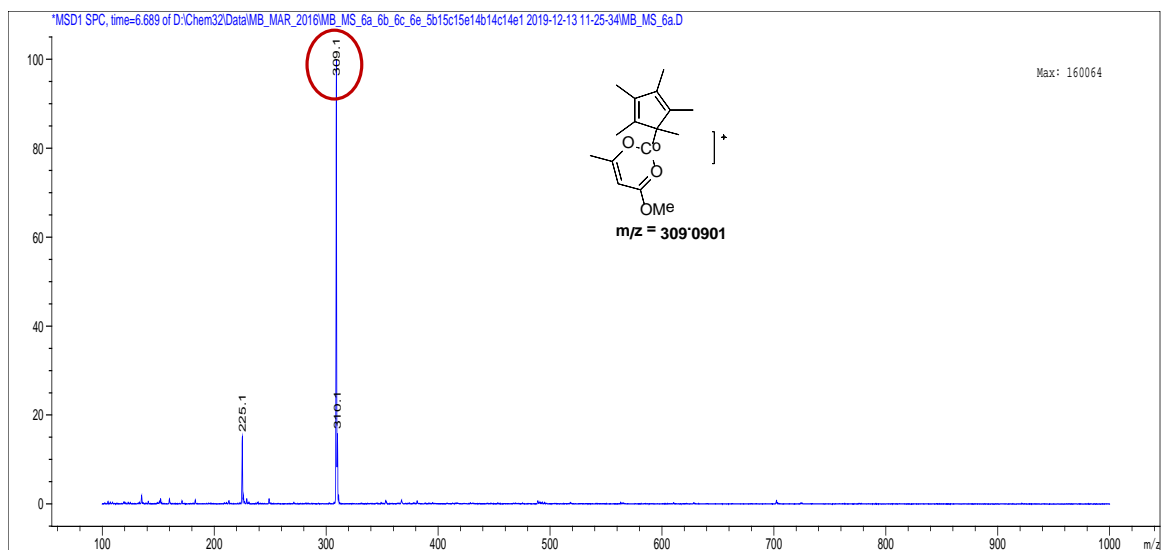




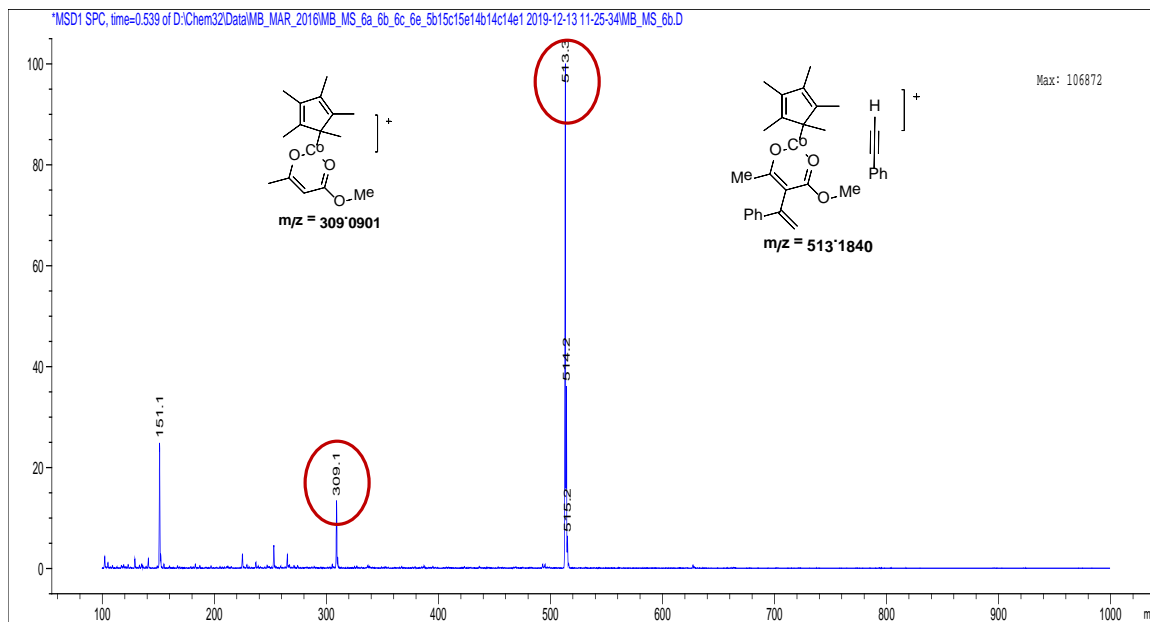
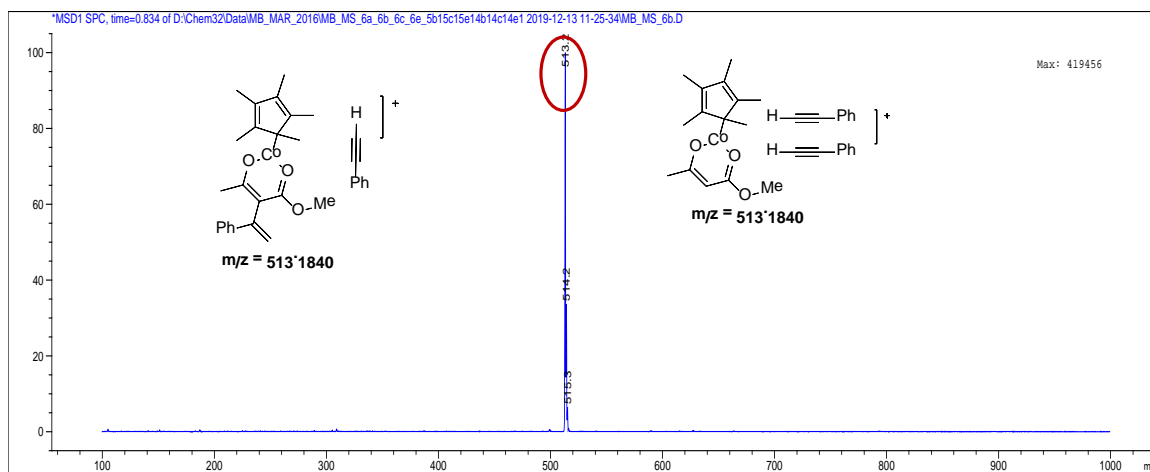
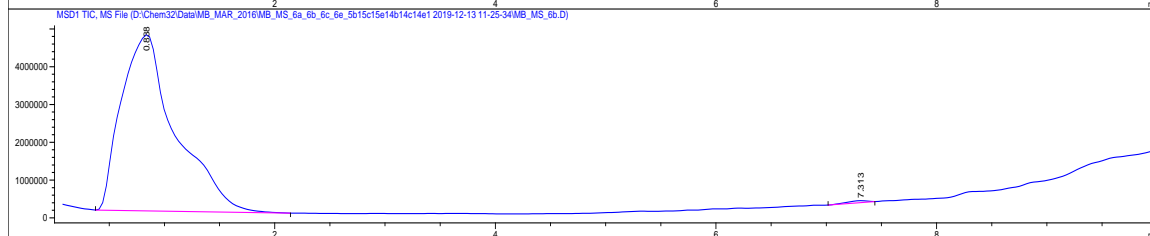
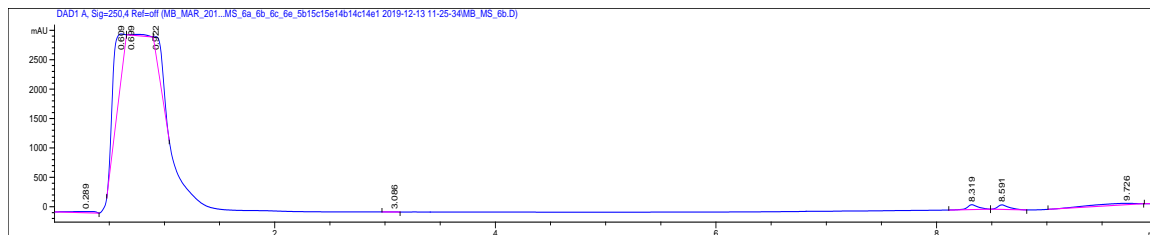


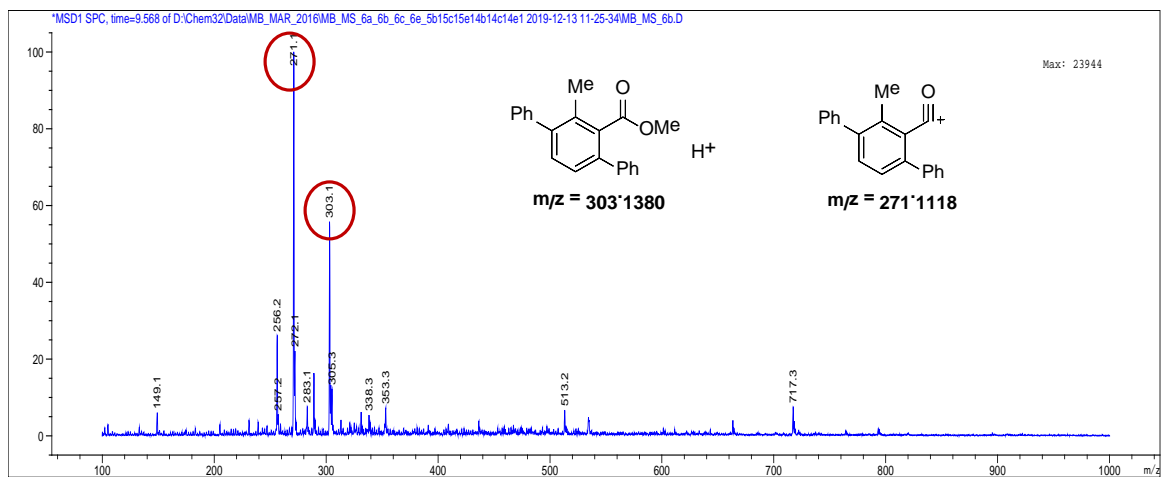
# LCMS data of catalyst (mol%) and methyl acetoacetate reaction mixture in toluene after 1h



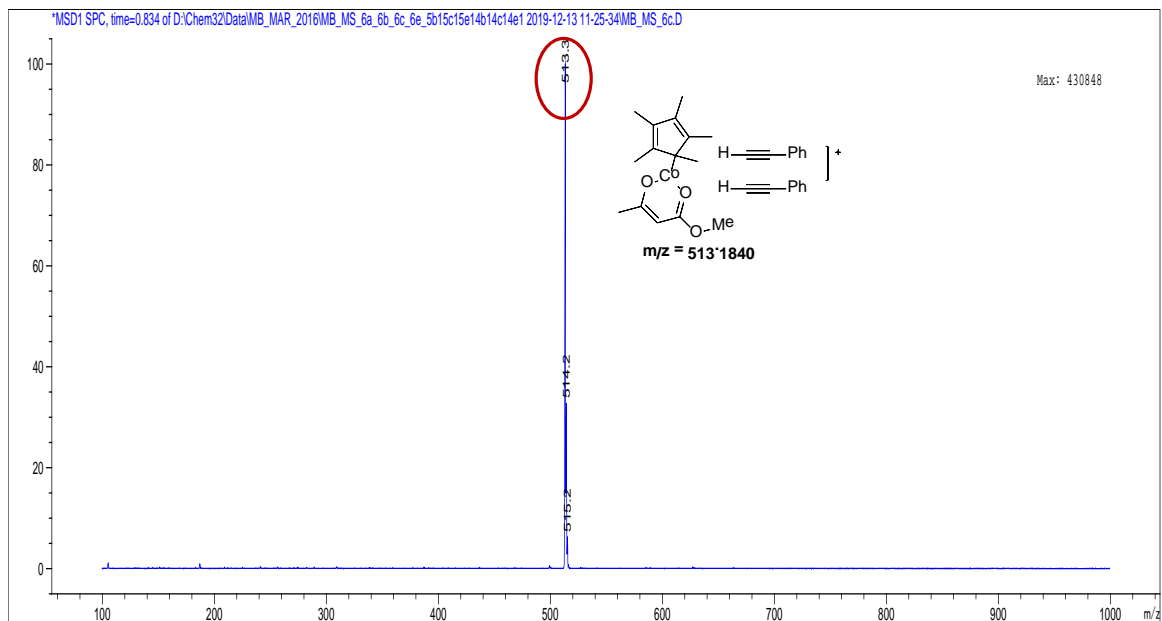
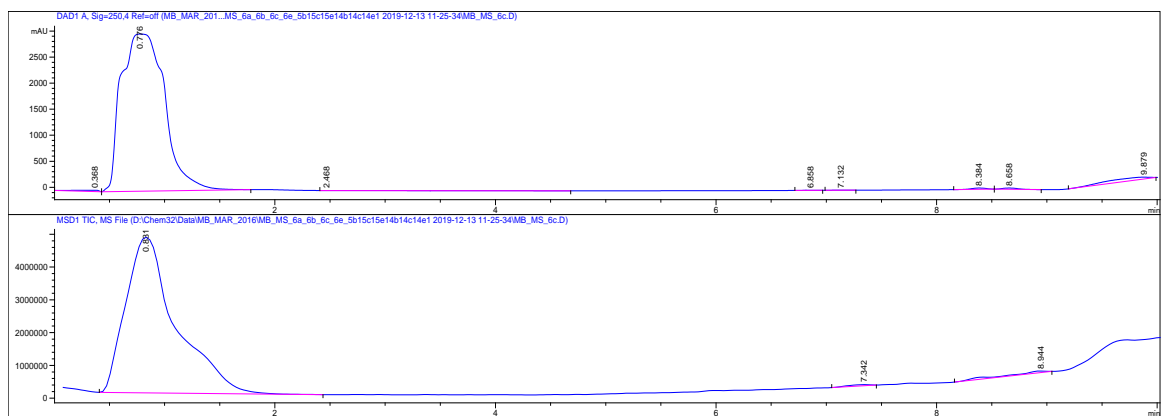


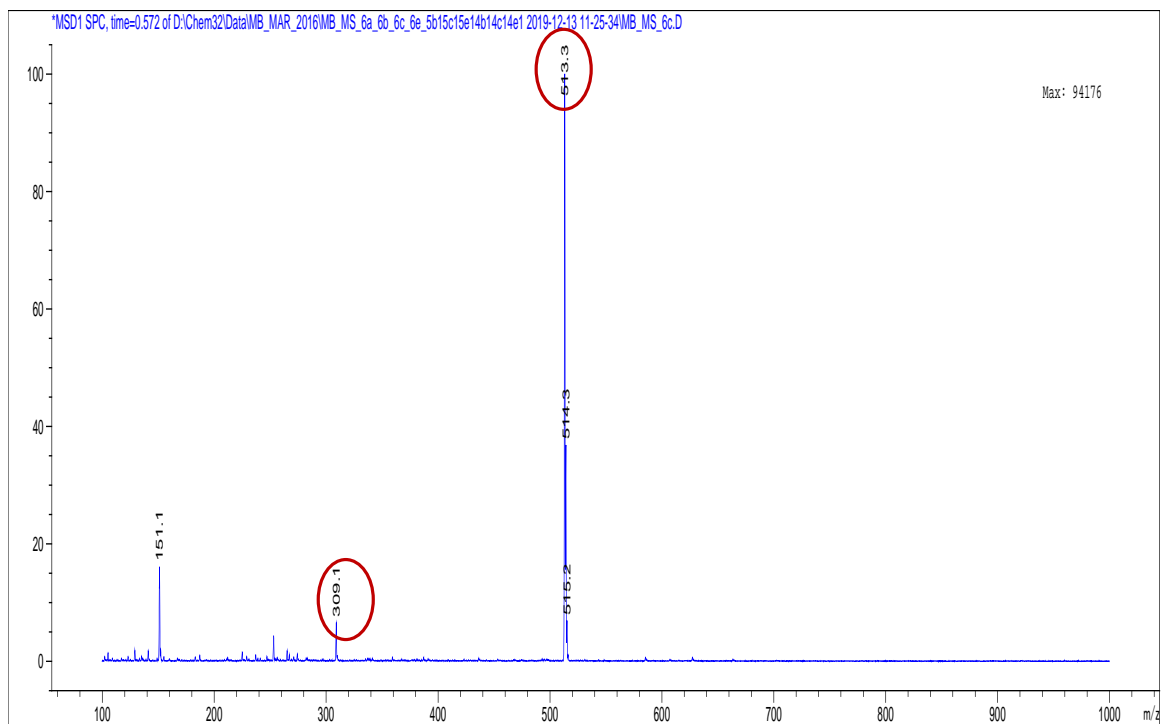
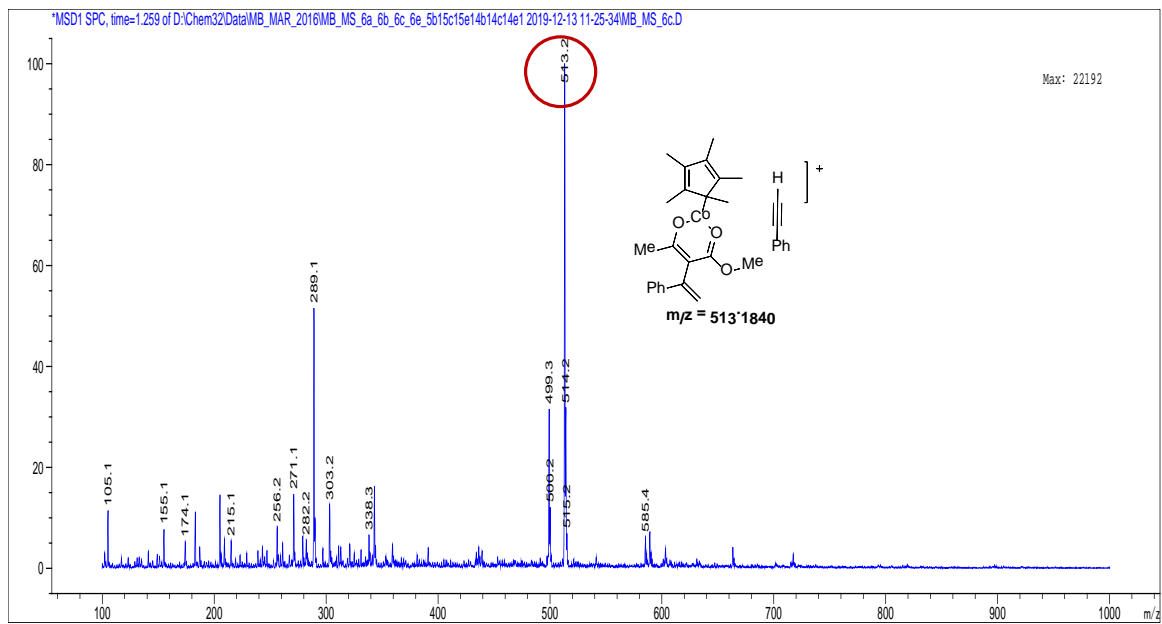
After 1h of alkyne addition; LCMS of catalyst and methyl acetoacetate and phenylacetylene reaction mixture in toluene





After 3h of alkyne addition; LCMS of catalyst and methyl acetoacetate and phenylacetylene reaction mixture in toluene





After 16h of alkyne addition LCMS of catalyst (mol%) and methyl acetoacetate and phenylacetylene reaction mixture in toluene

