

*Supporting Information for*

**Transition Metal-Free Direct Trifluoromethylthiolation of  
Indoles using Trifluoromethanesulfonyl Chloride in the  
Presence of Triphenylphosphine**

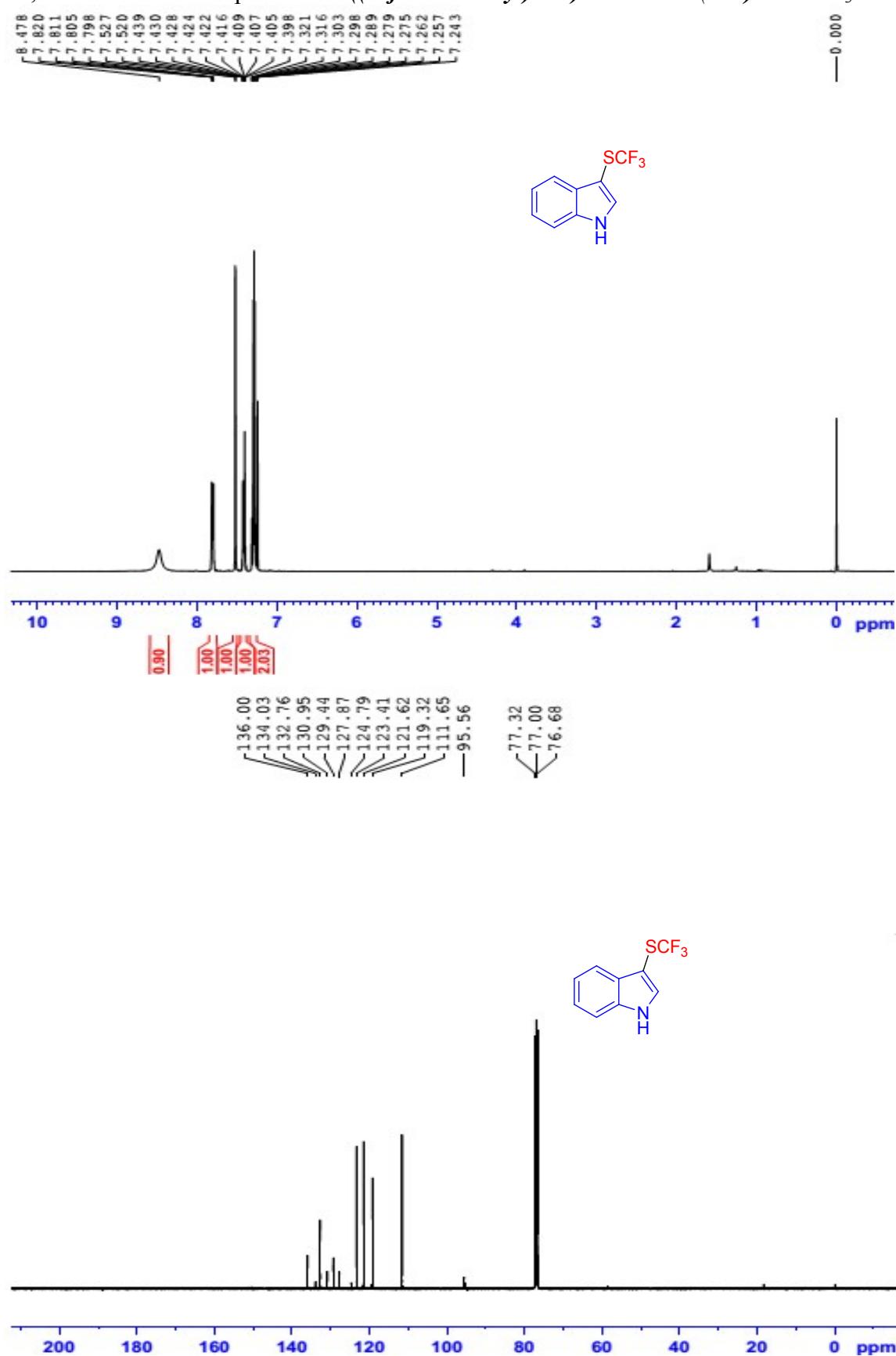
Kui Lu, <sup>\*a</sup>Zhijie Deng, <sup>b</sup>Ming Li, <sup>a</sup>Tianjiao Li <sup>b</sup>and Xia Zhao <sup>\*b</sup>

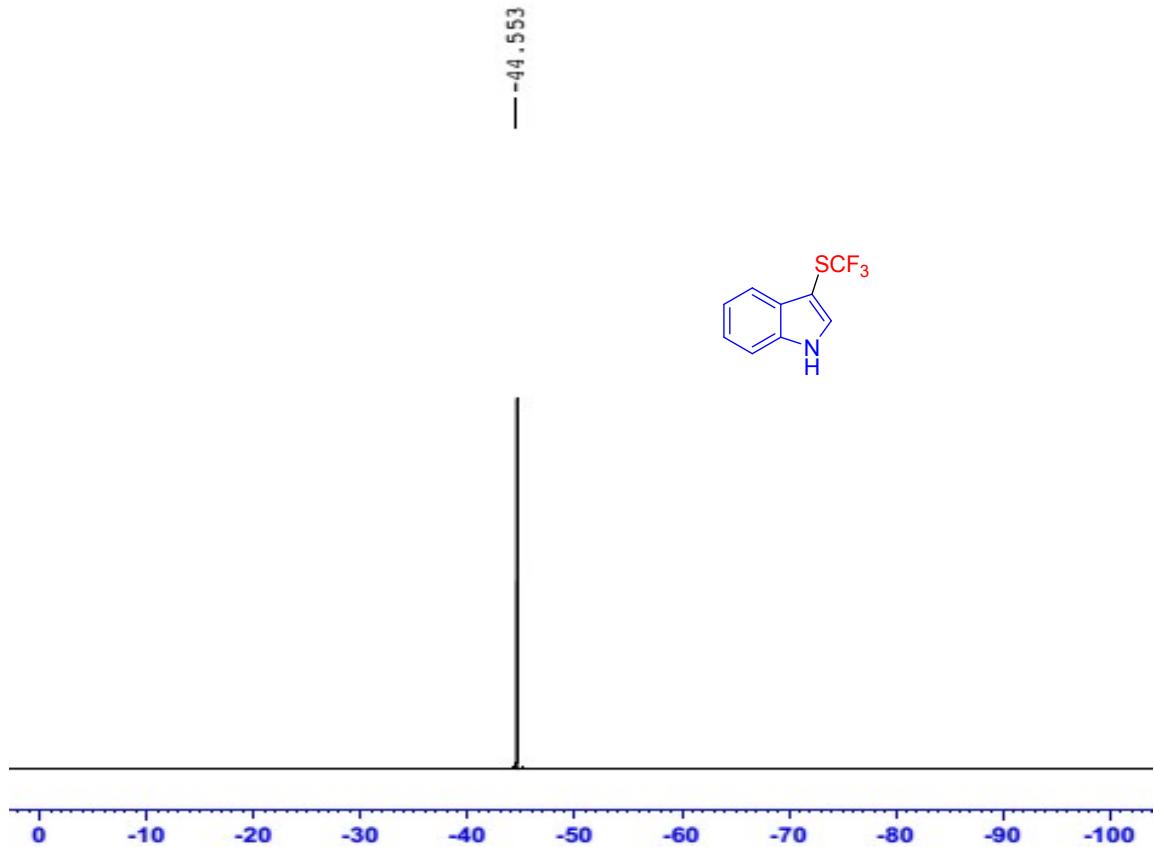
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<sup>b</sup> College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Key laboratory of Inorganic-organic Hybrid Functional Material Chemistry, Ministry of Education, Tianjin Normal University, Tianjin 300387, China

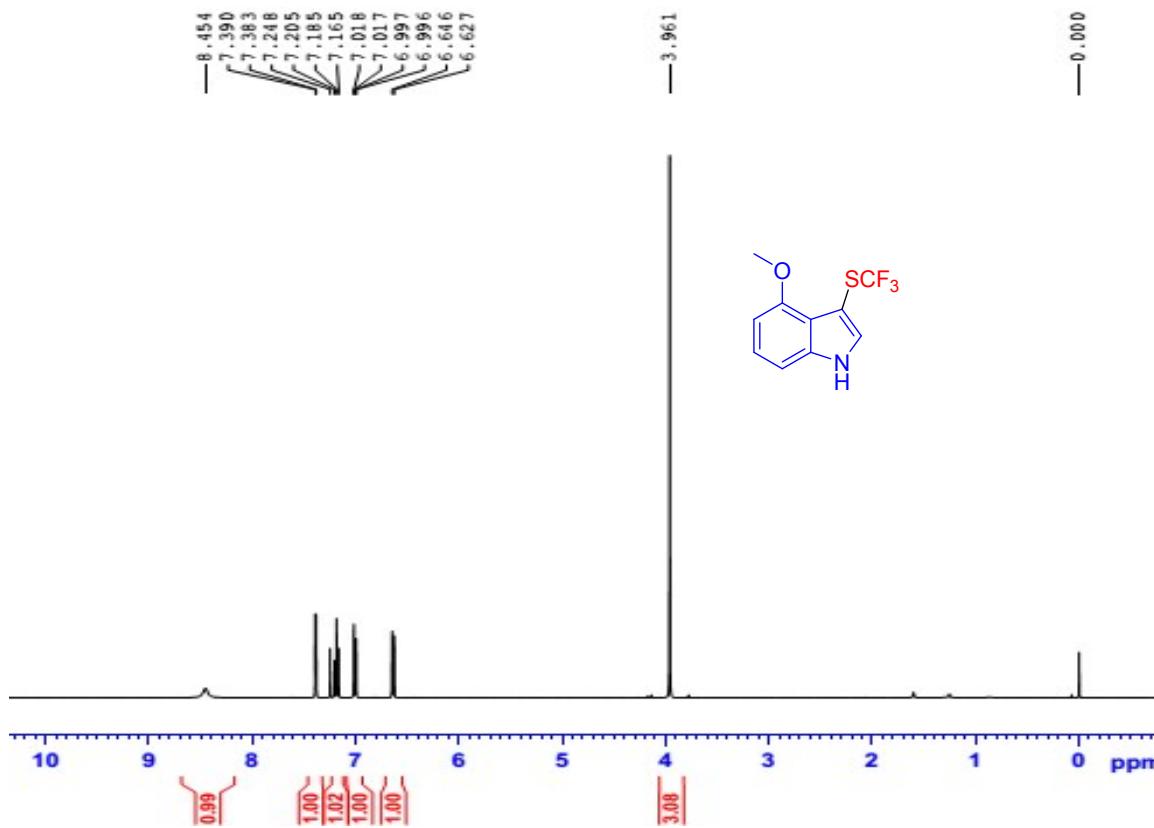
\*E-mail: [lukui@tust.edu.cn](mailto:lukui@tust.edu.cn); [hxxxyzhx@mail.tjnu.edu.cn](mailto:hxxxyzhx@mail.tjnu.edu.cn);

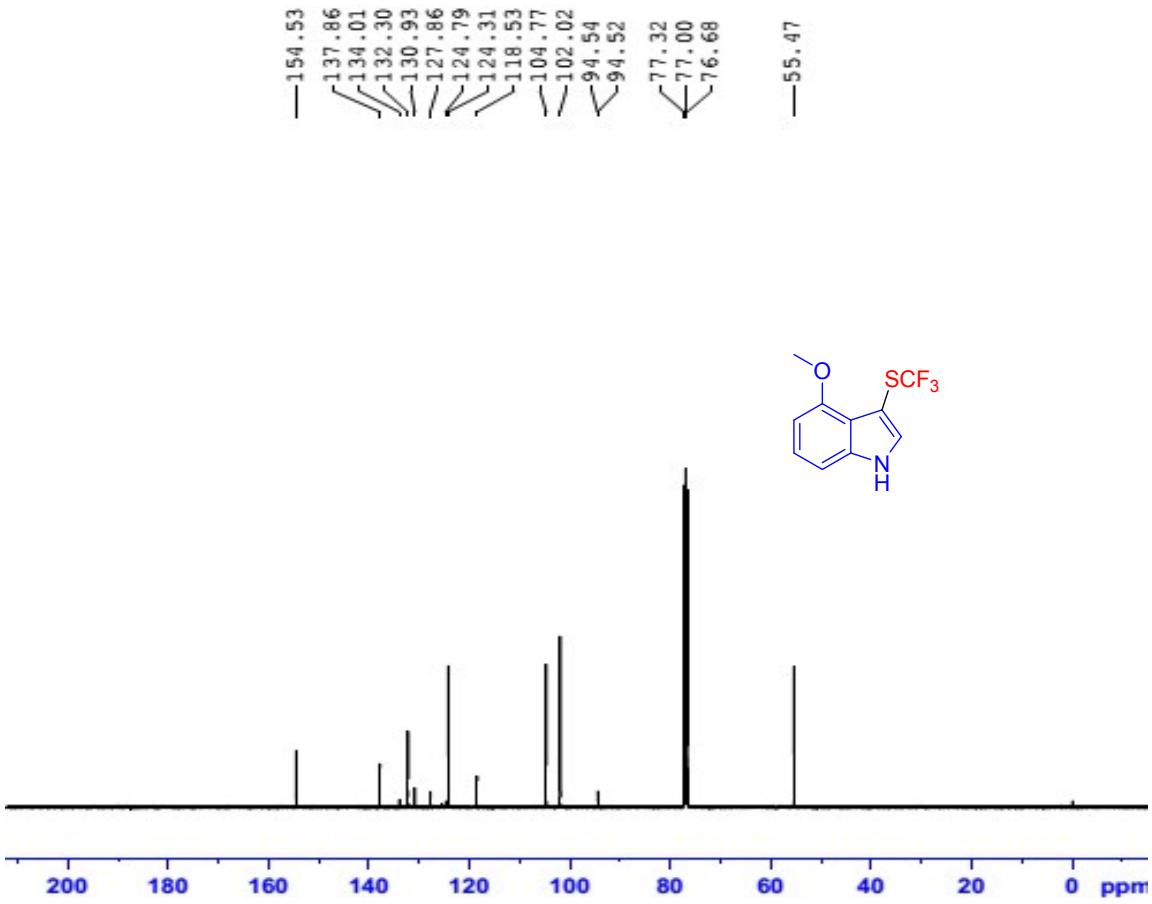
<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra of **3-((trifluoromethyl)thio)-1H-indole (11a)** in CDCl<sub>3</sub>



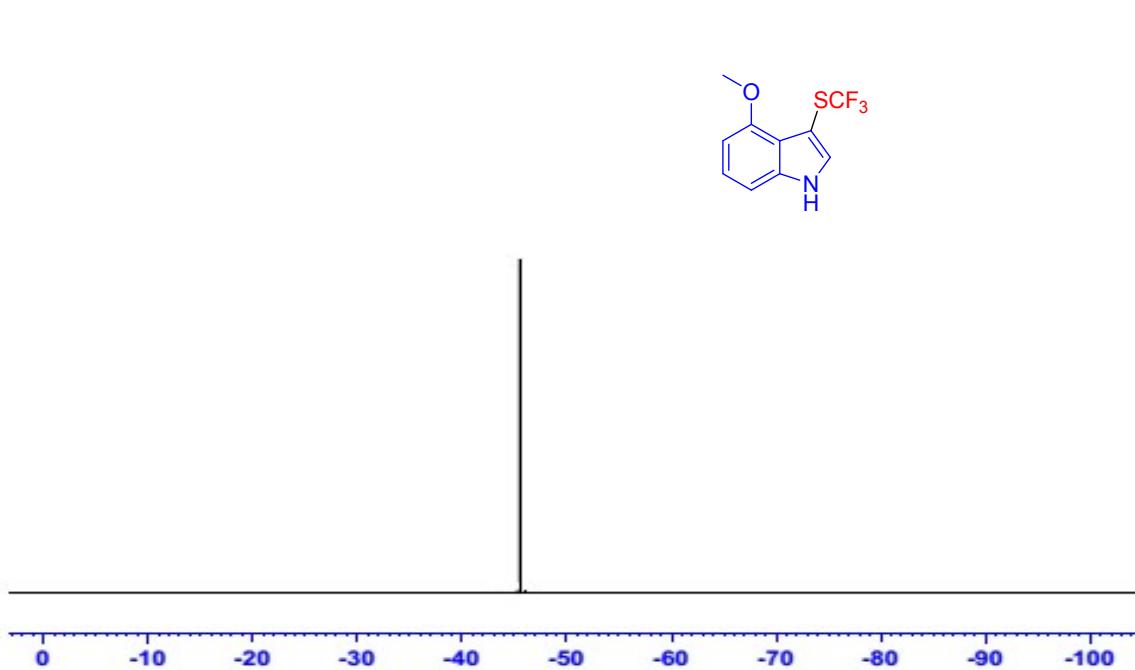
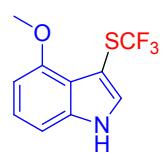


<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra of **4-methoxy-3-((trifluoromethyl)thio)-1H-indole (11b)** in CDCl<sub>3</sub>

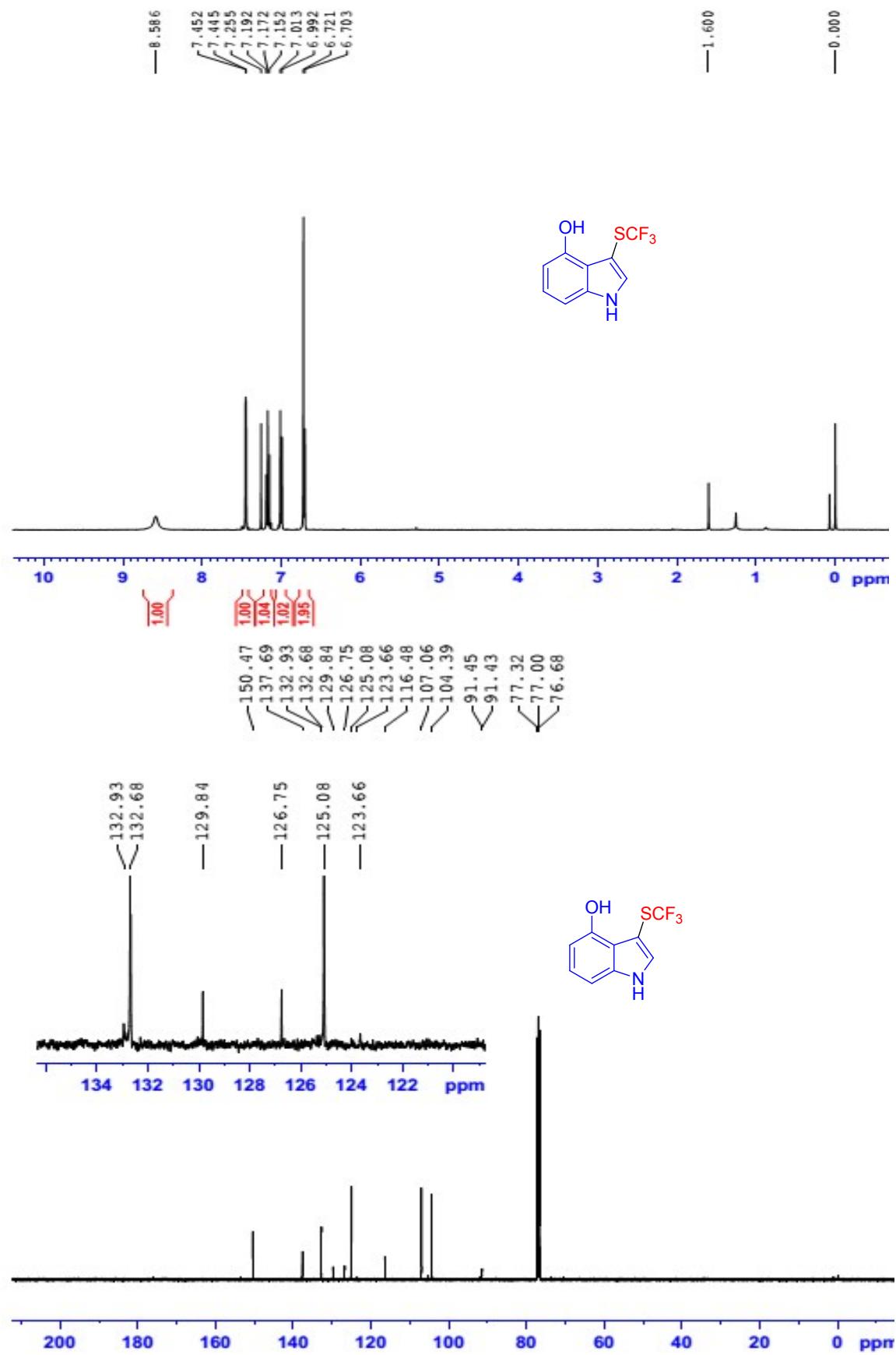


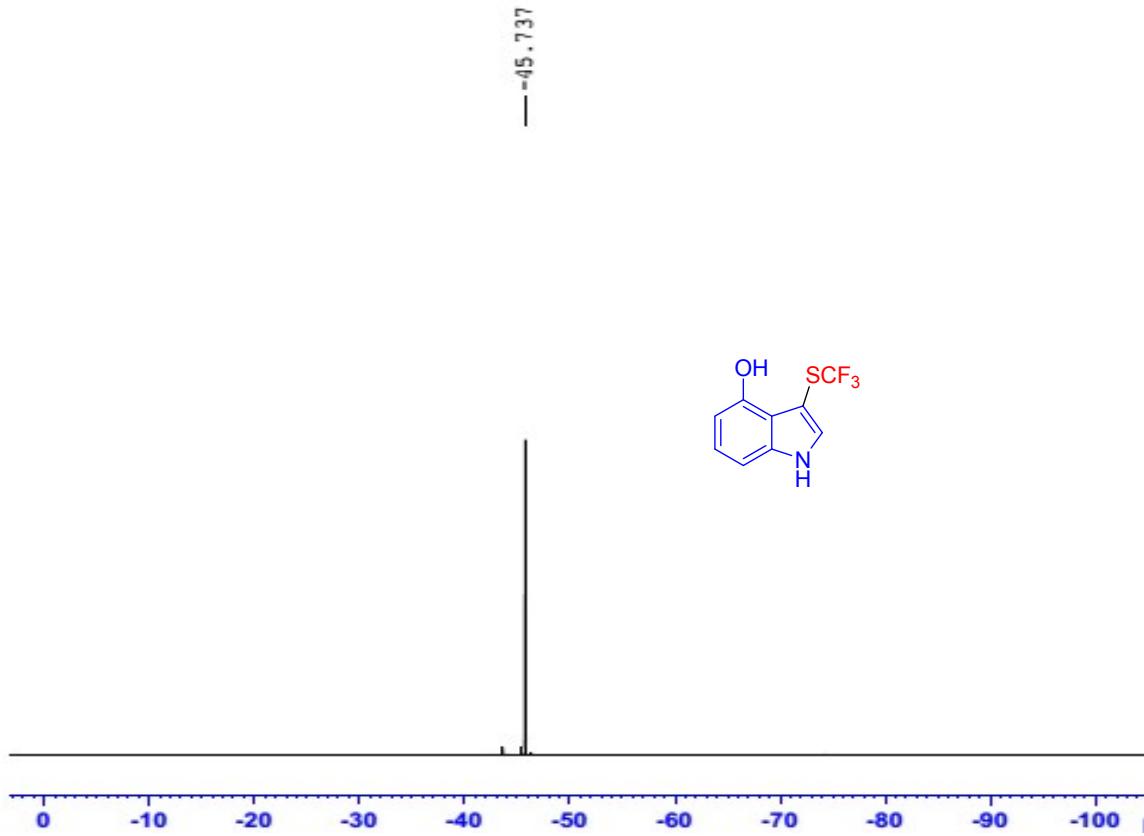


—45.476

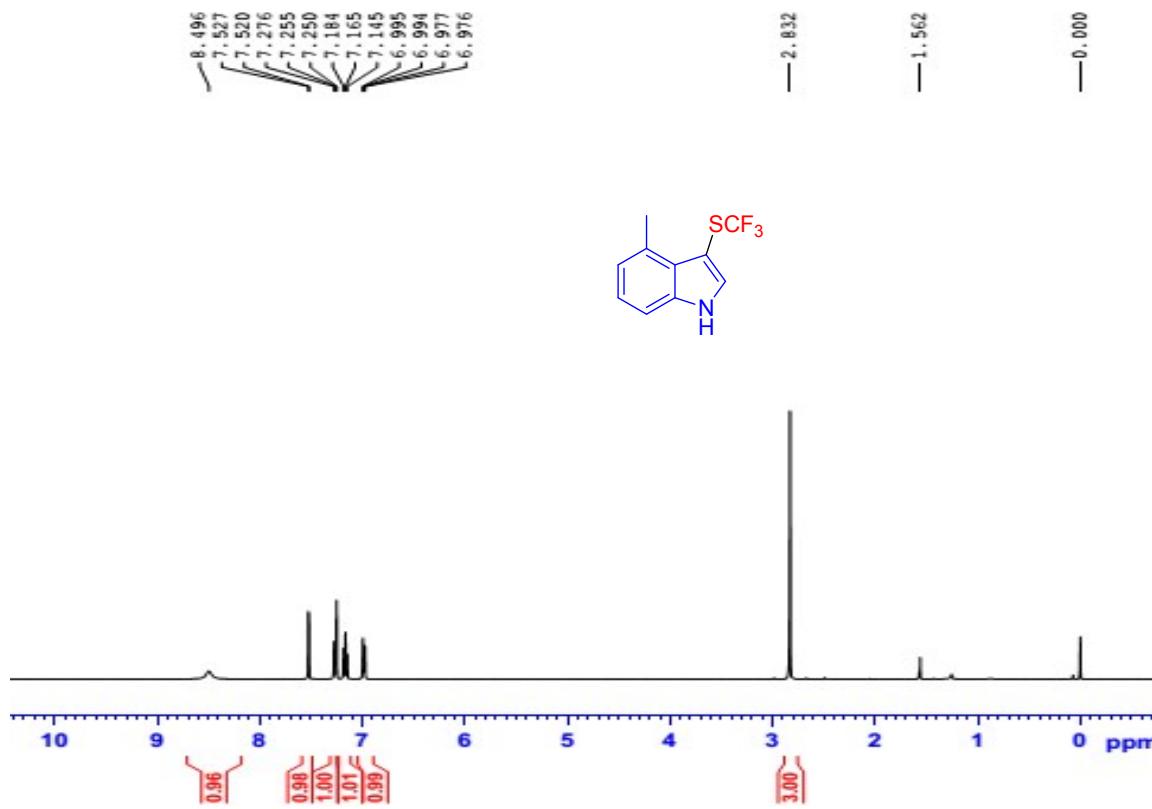


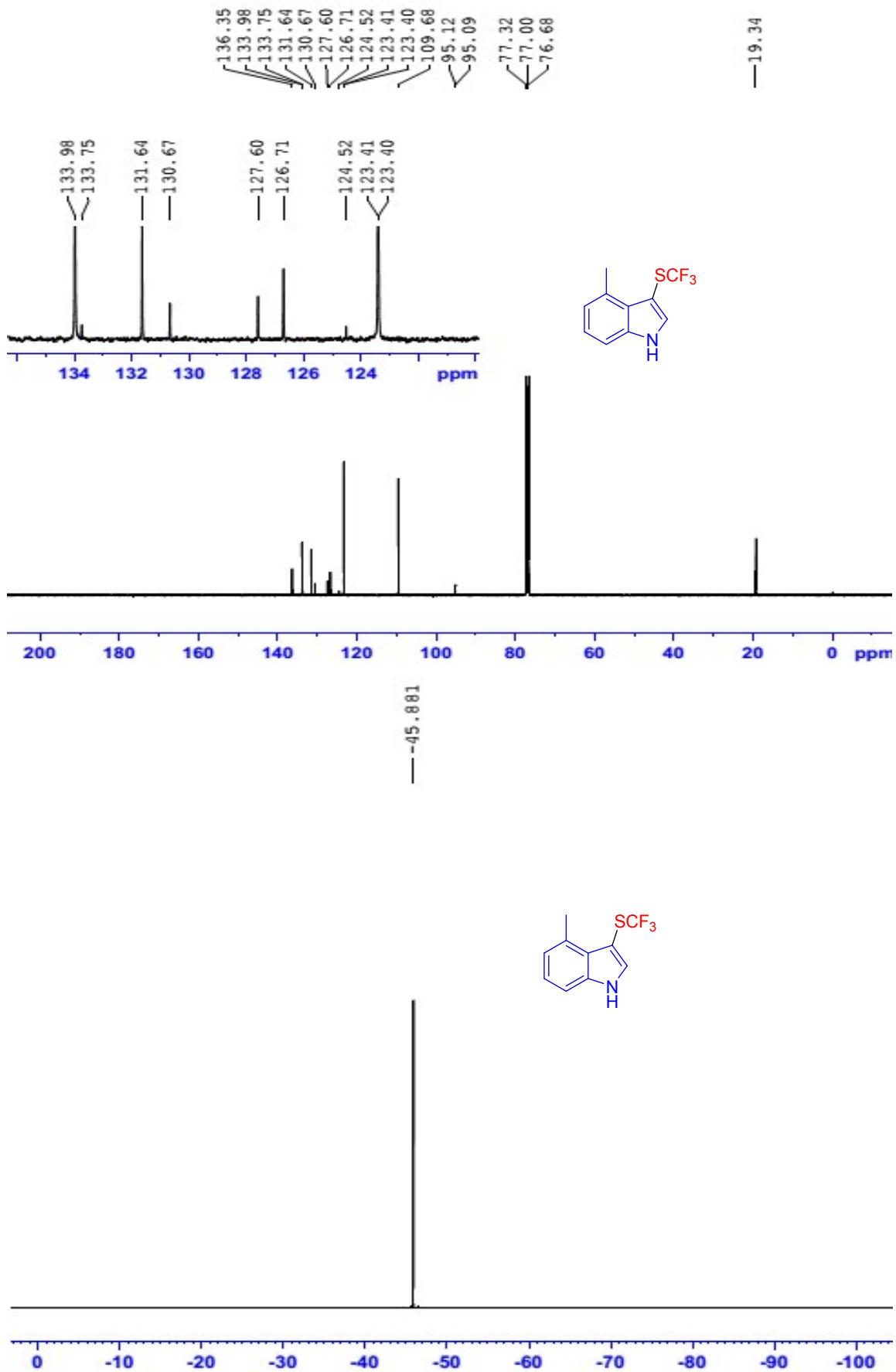
<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra of **3-((trifluoromethyl)thio)-1H-indol-4-ol (11c)** in CDCl<sub>3</sub>



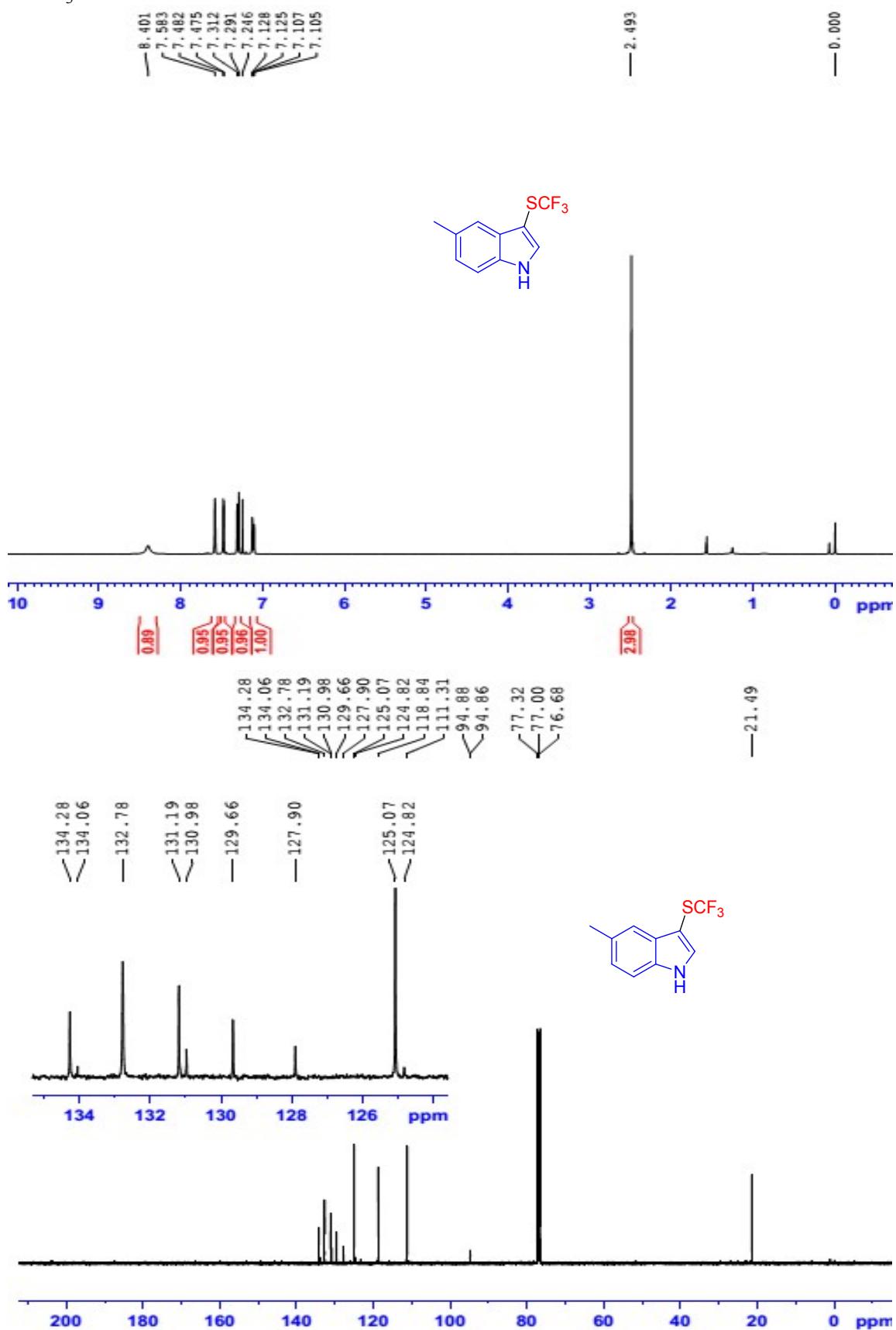


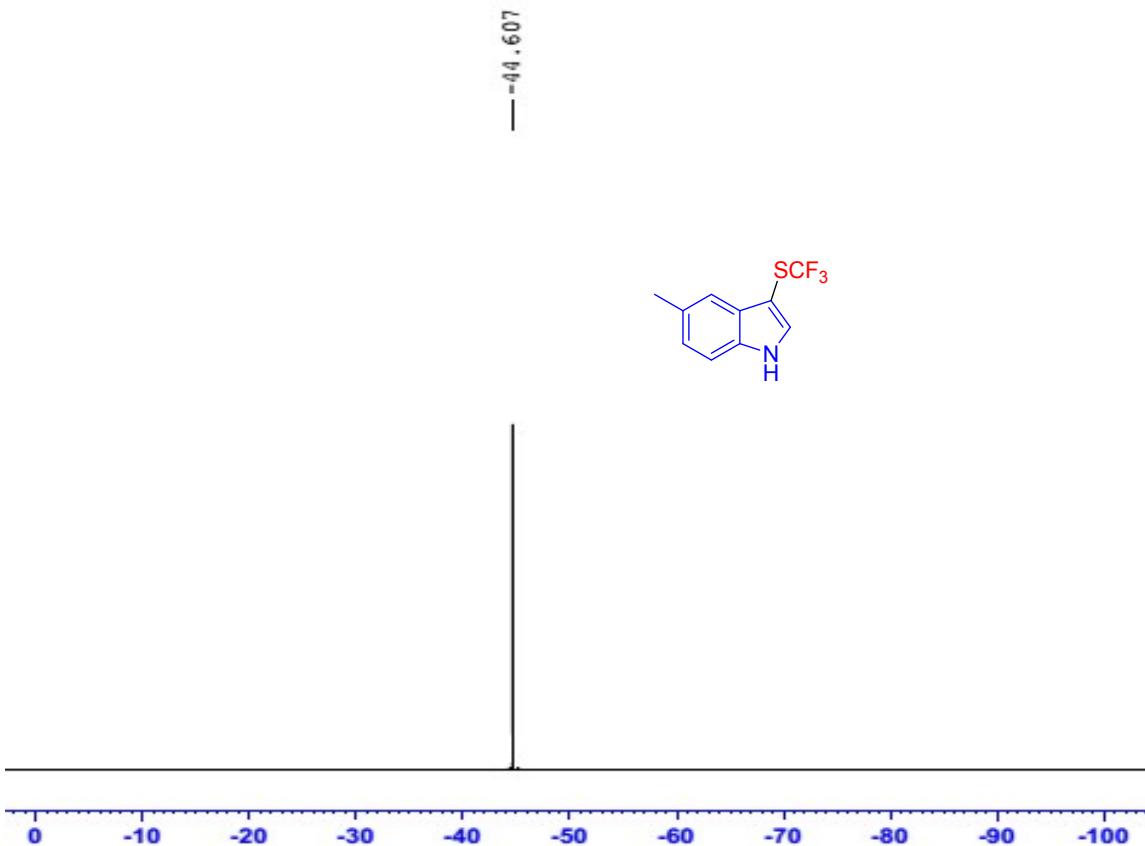
<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra of **4-methyl-3-((trifluoromethyl)thio)-1H-indole (11d)** in CDCl<sub>3</sub>



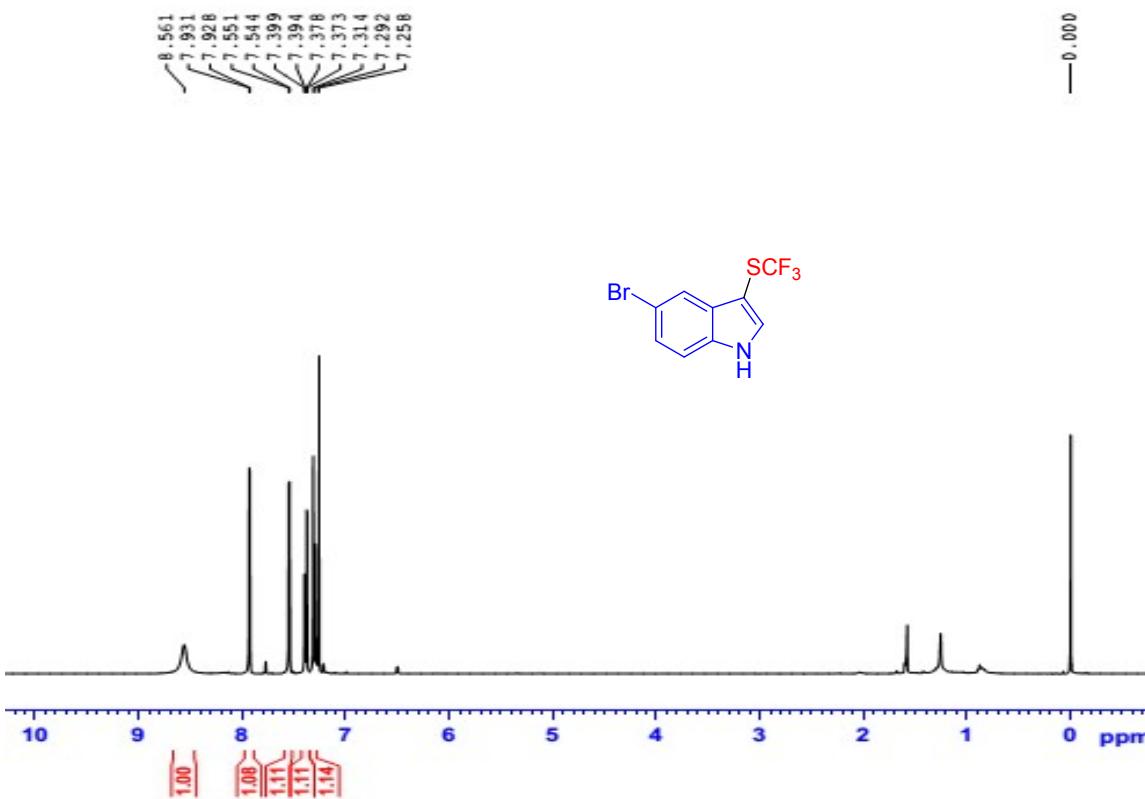


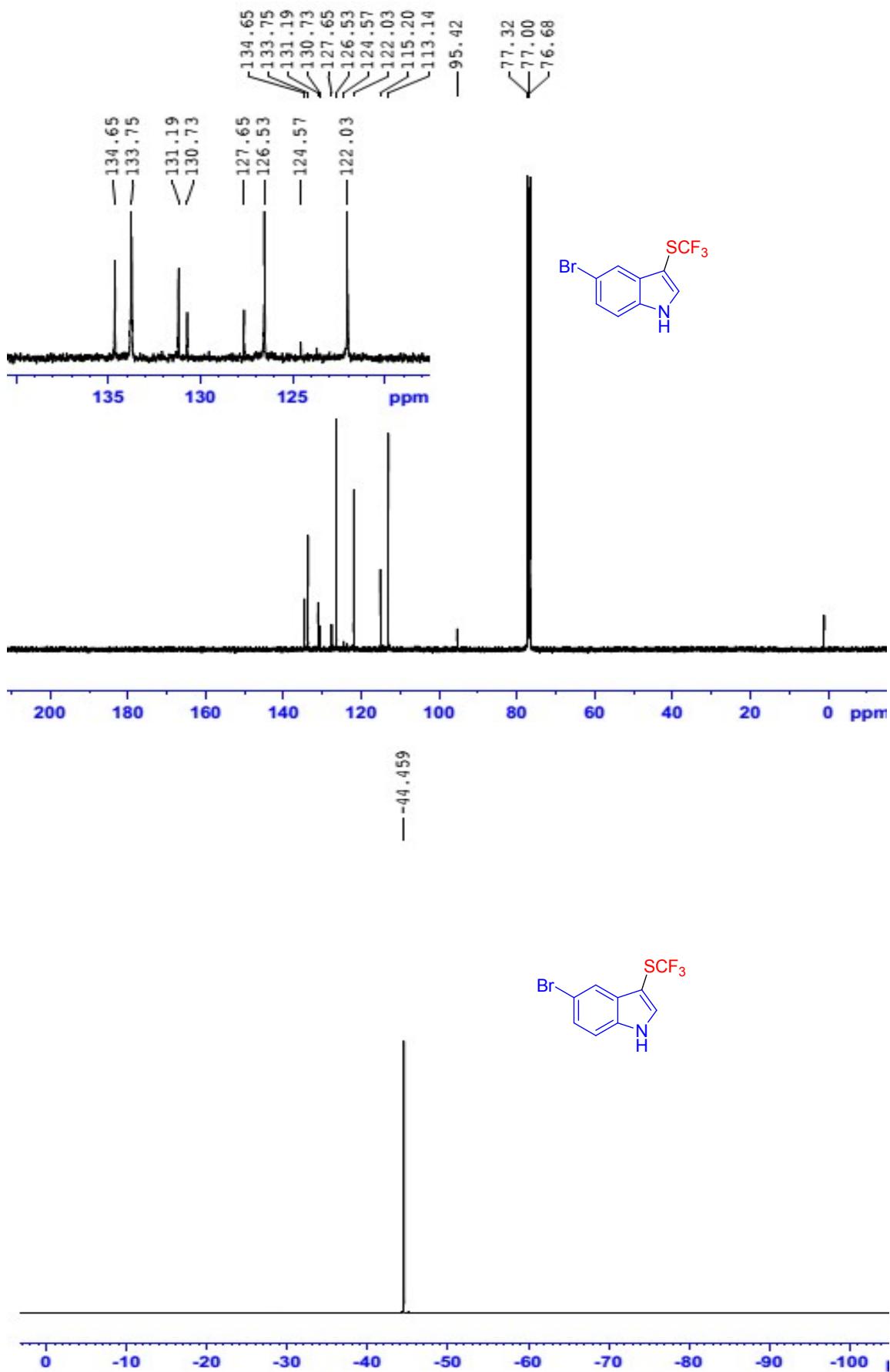
<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra of **5-methyl-3-((trifluoromethyl)thio)-1H-indole (11e)** in CDCl<sub>3</sub>



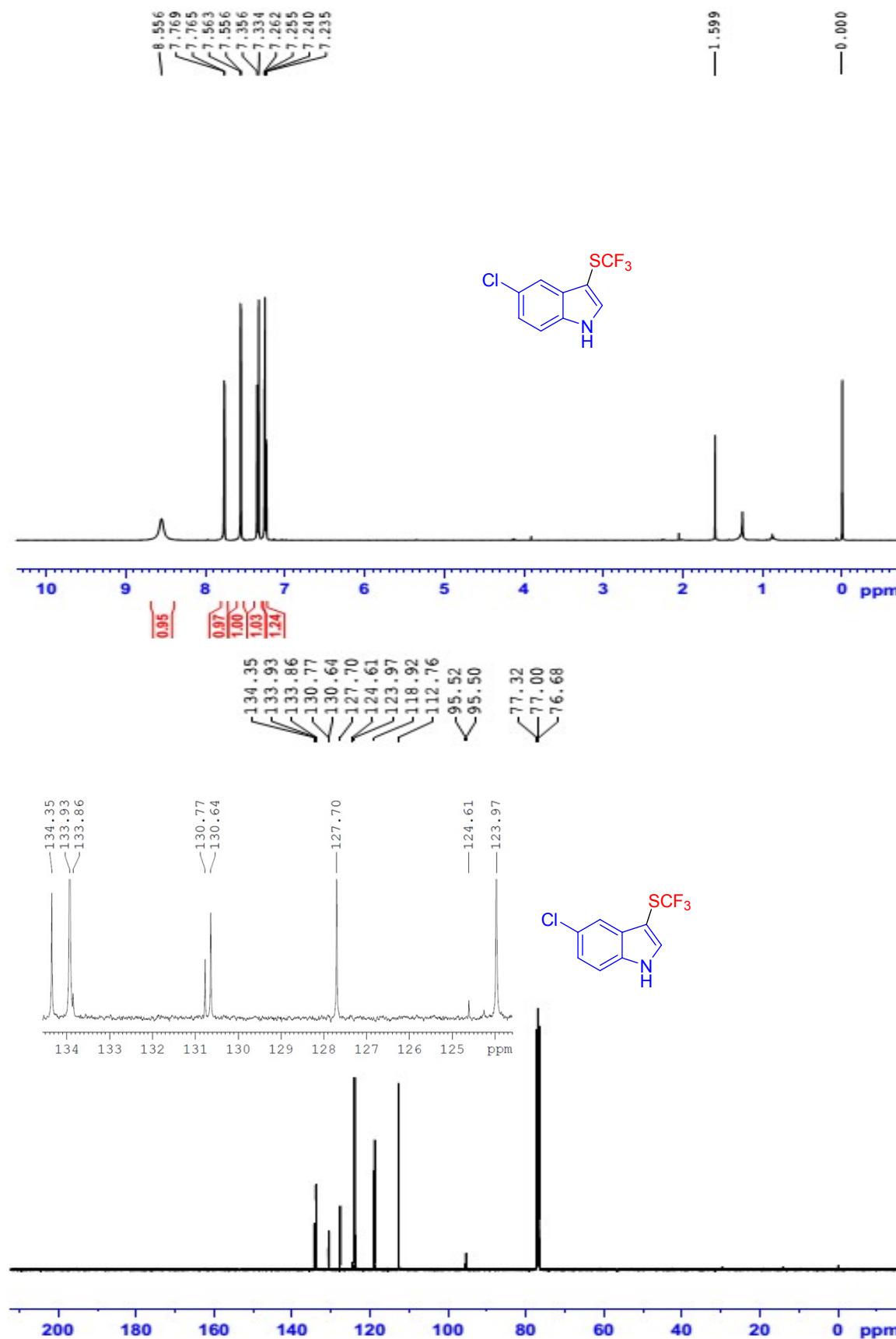


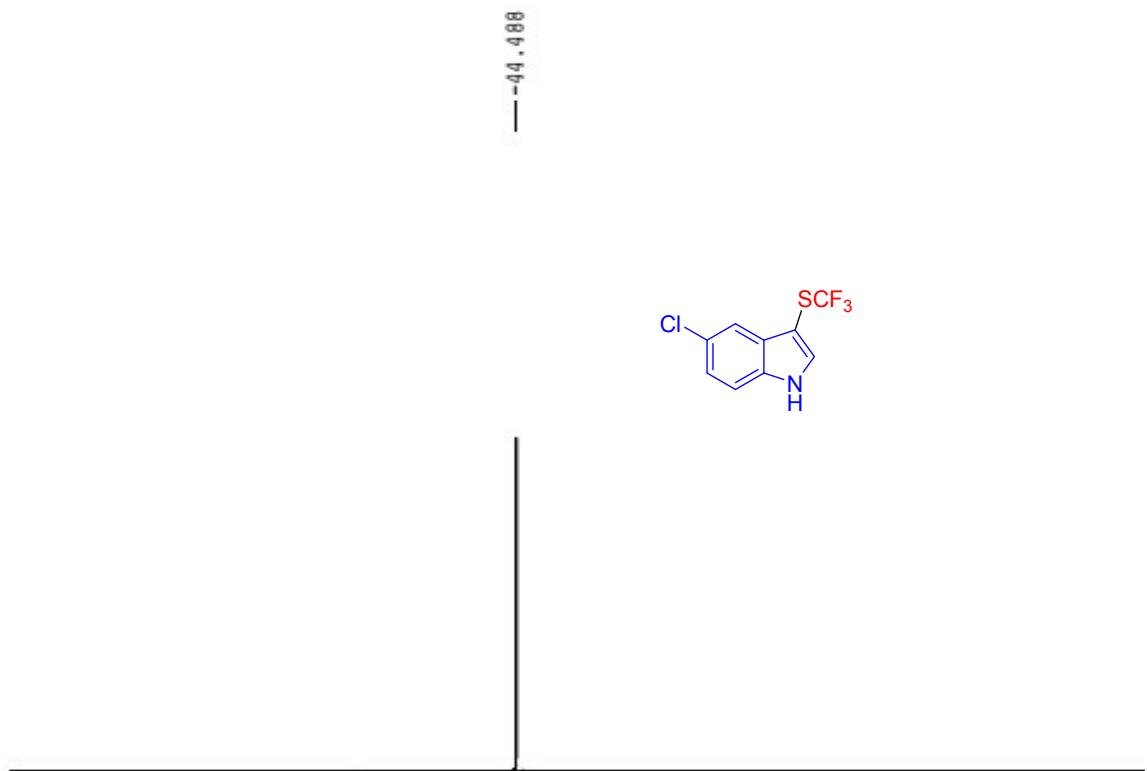
<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra of **5-bromo-3-((trifluoromethyl)thio)-1H-indole (11f)** in CDCl<sub>3</sub>



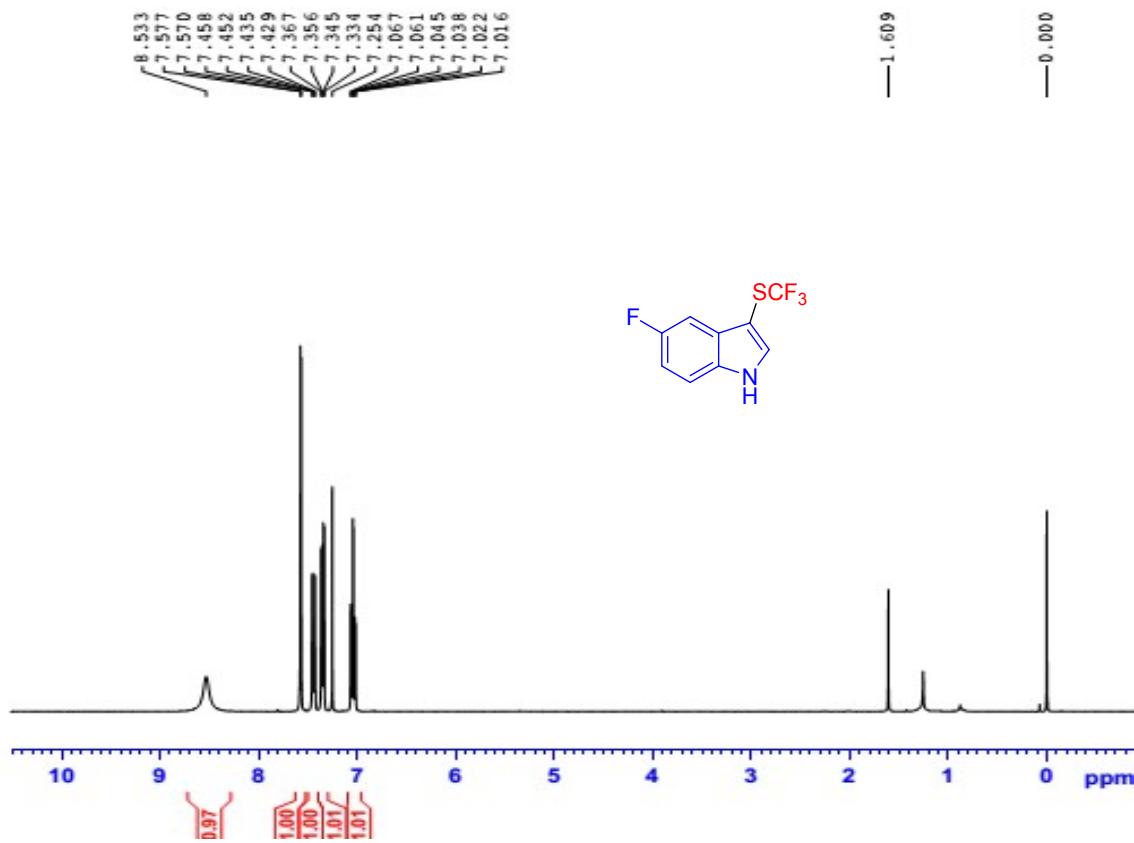


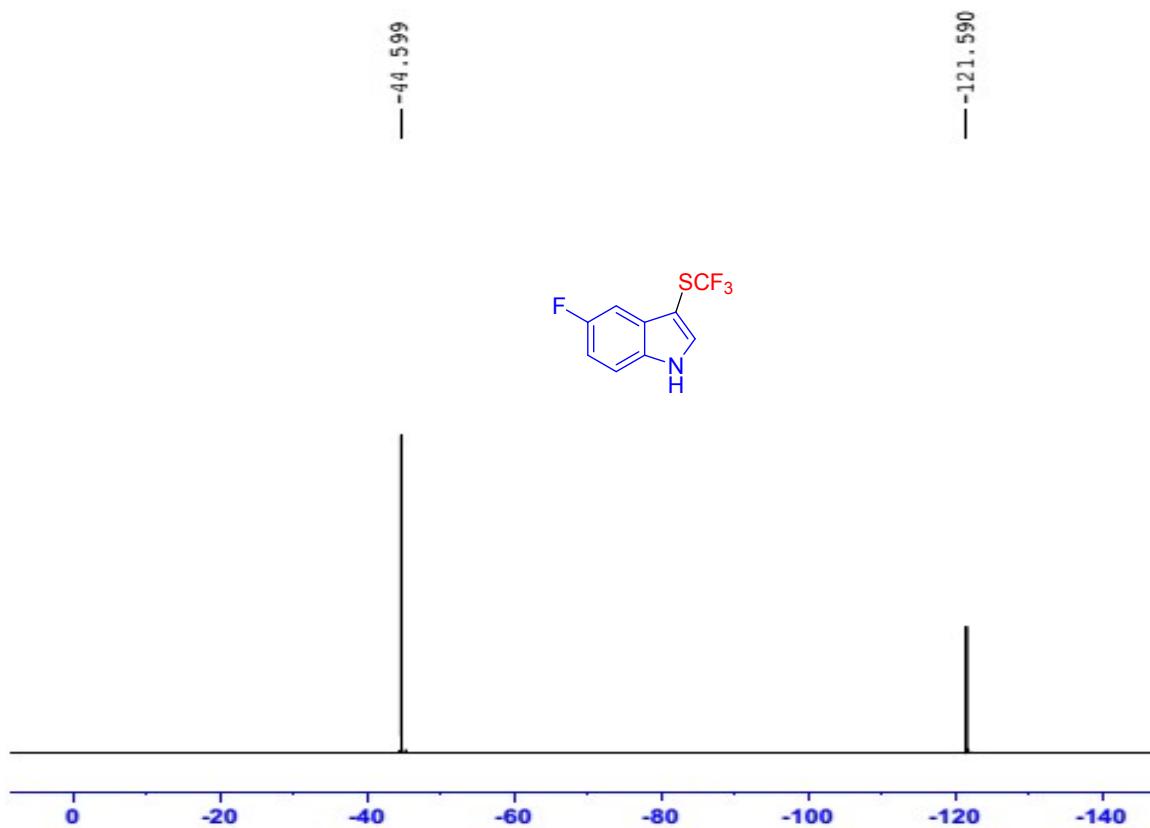
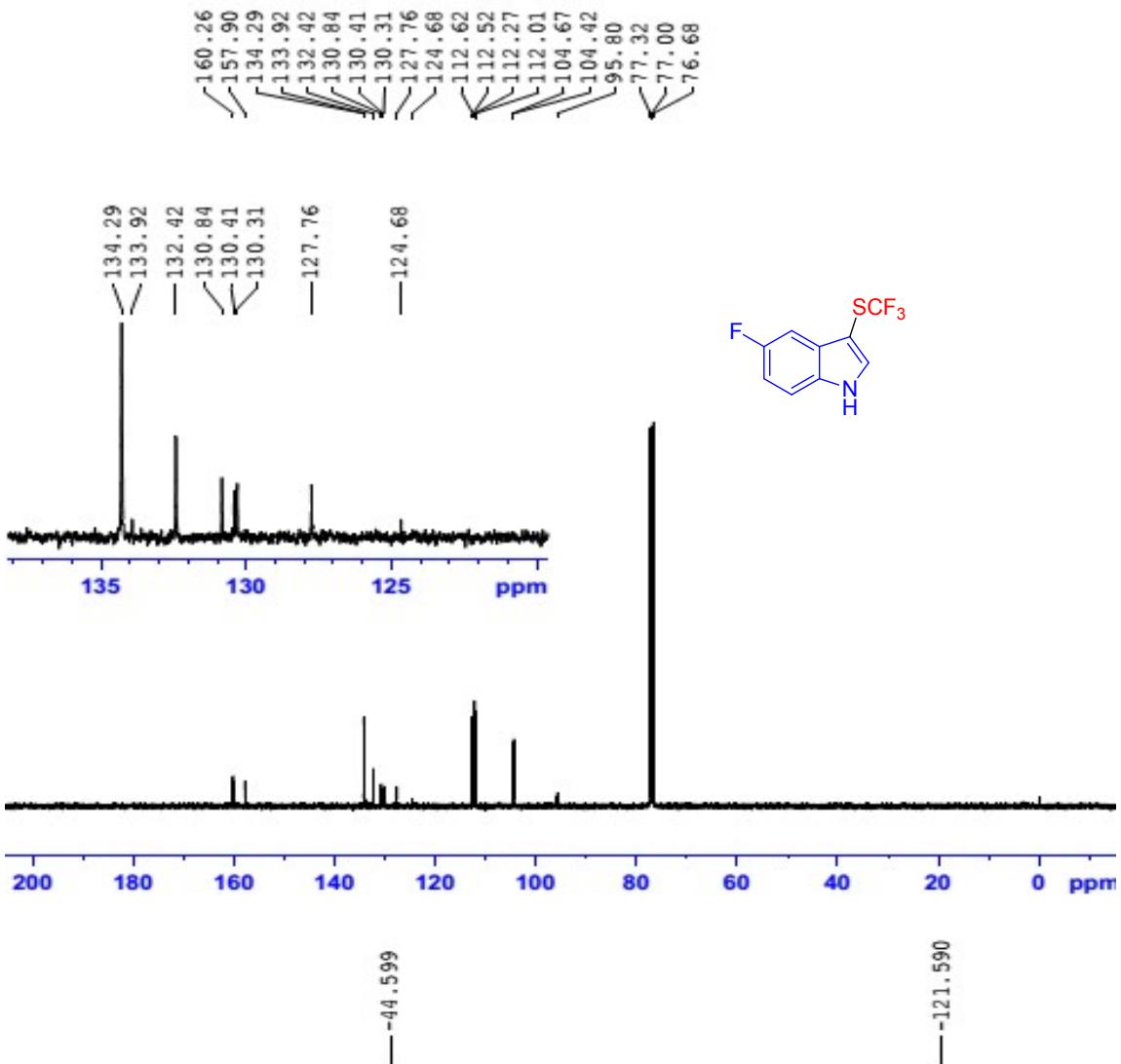
<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra of **5-chloro-3-((trifluoromethyl)thio)-1H-indole (11g)** in CDCl<sub>3</sub>



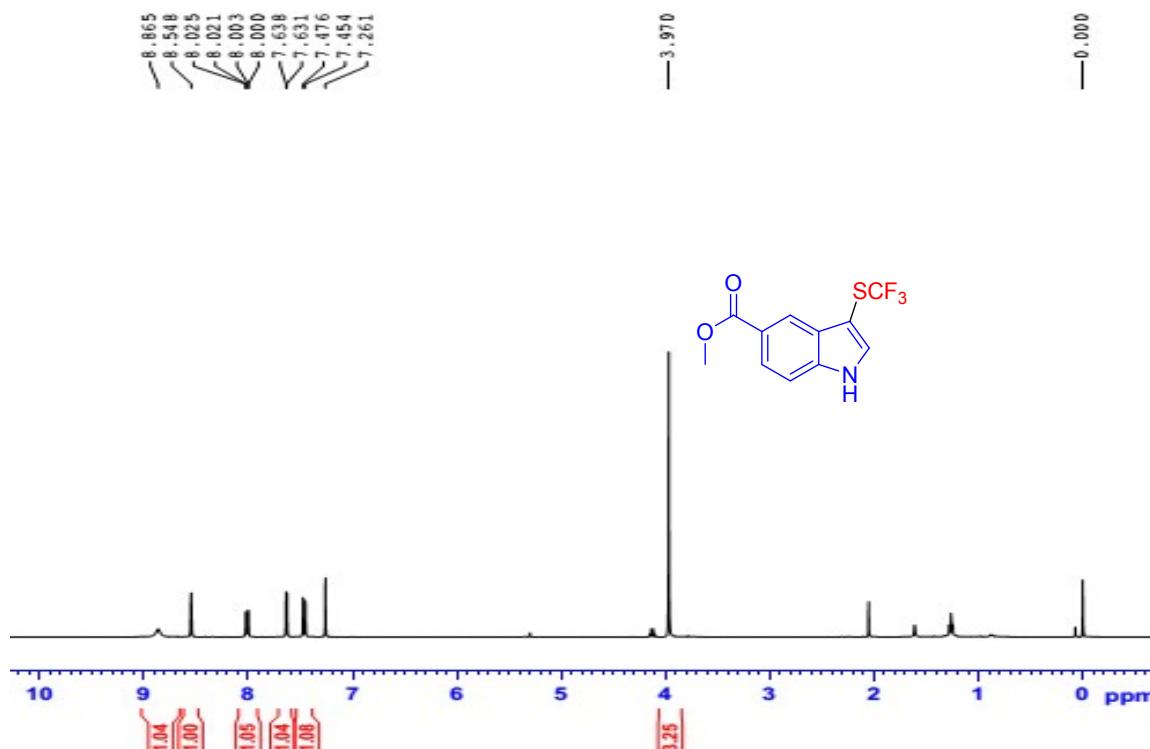


$^1\text{H}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR spectra of *5-fluoro-3-((trifluoromethyl)thio)-1H-indole (11h)* in  $\text{CDCl}_3$

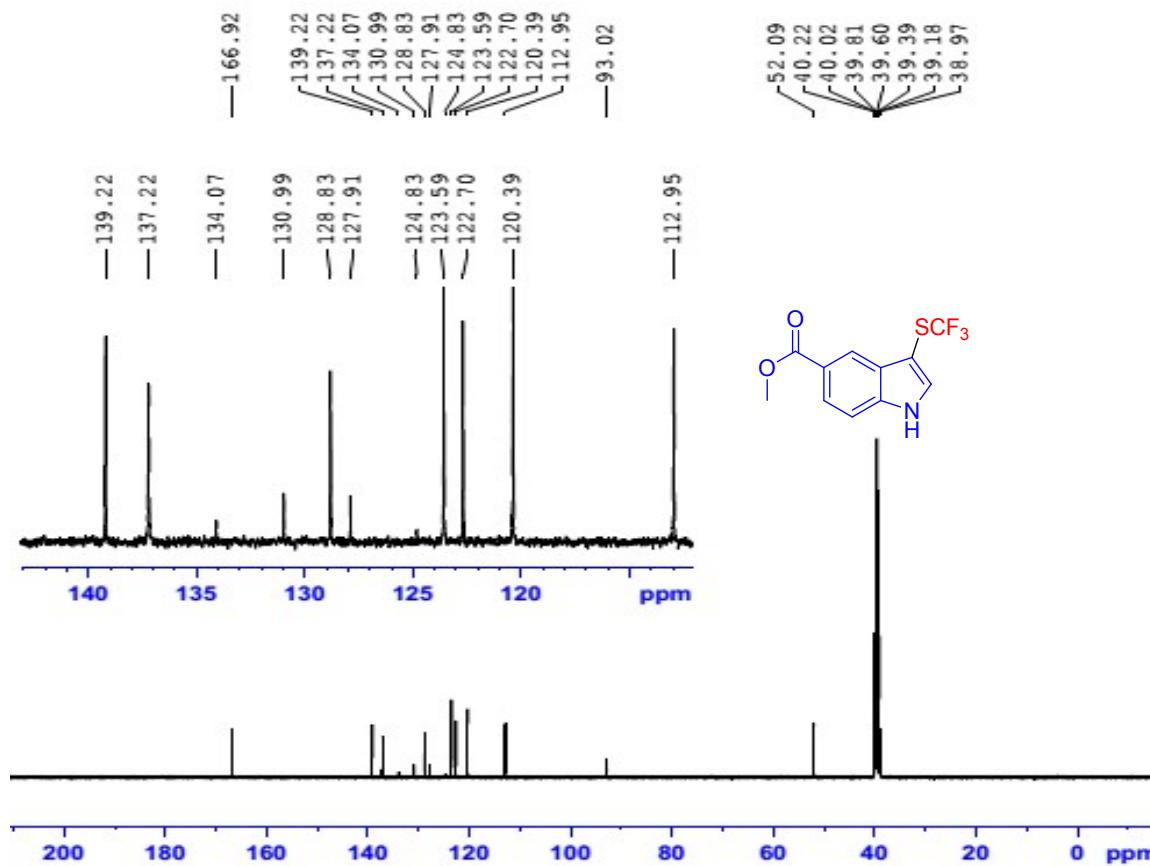




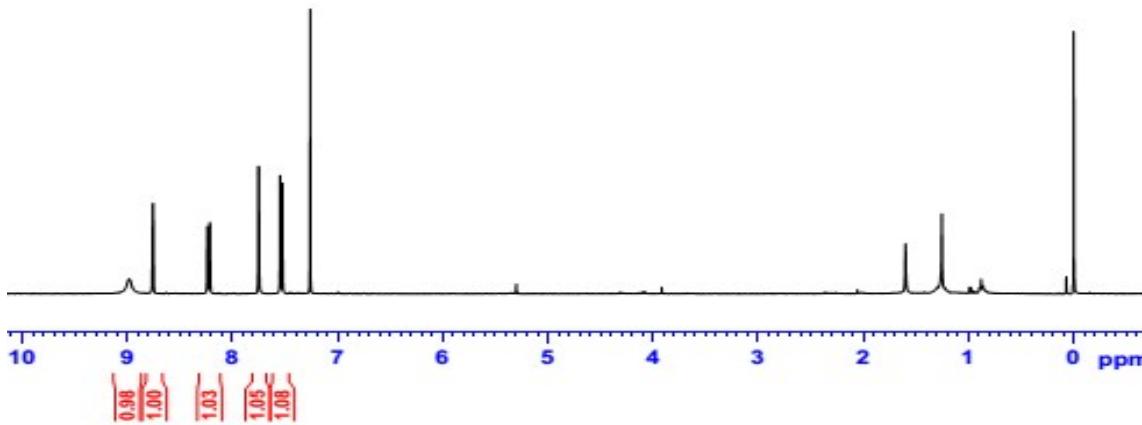
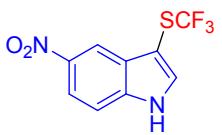
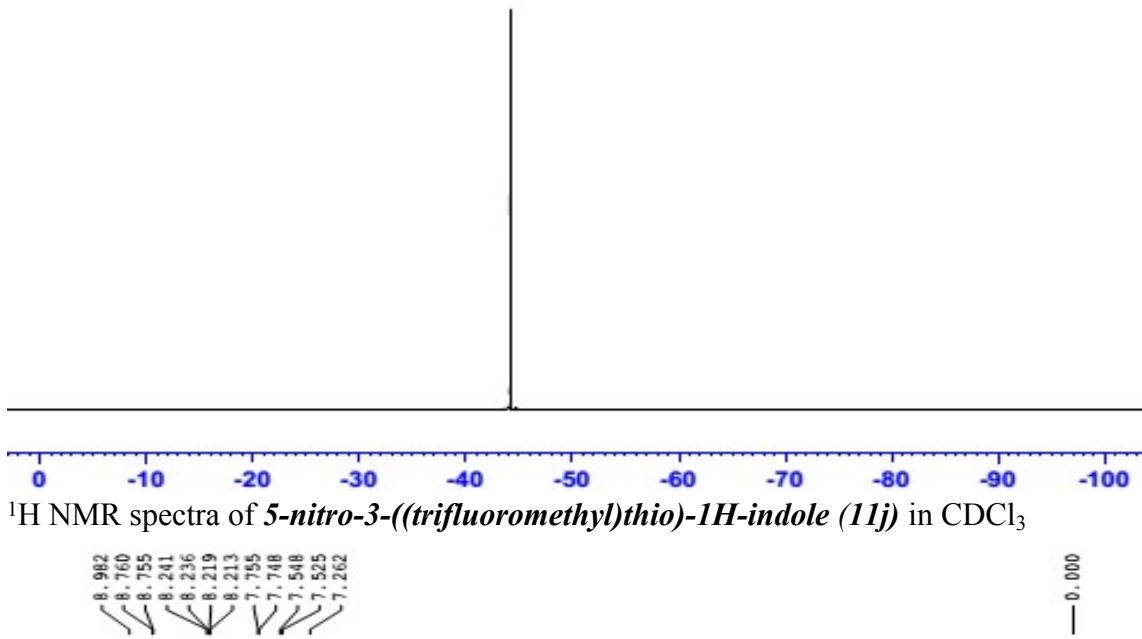
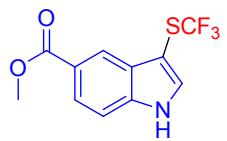
<sup>1</sup>H NMR spectra of *methyl 3-((trifluoromethyl)thio)-1H-indole-5-carboxylate (11i)* in CDCl<sub>3</sub>



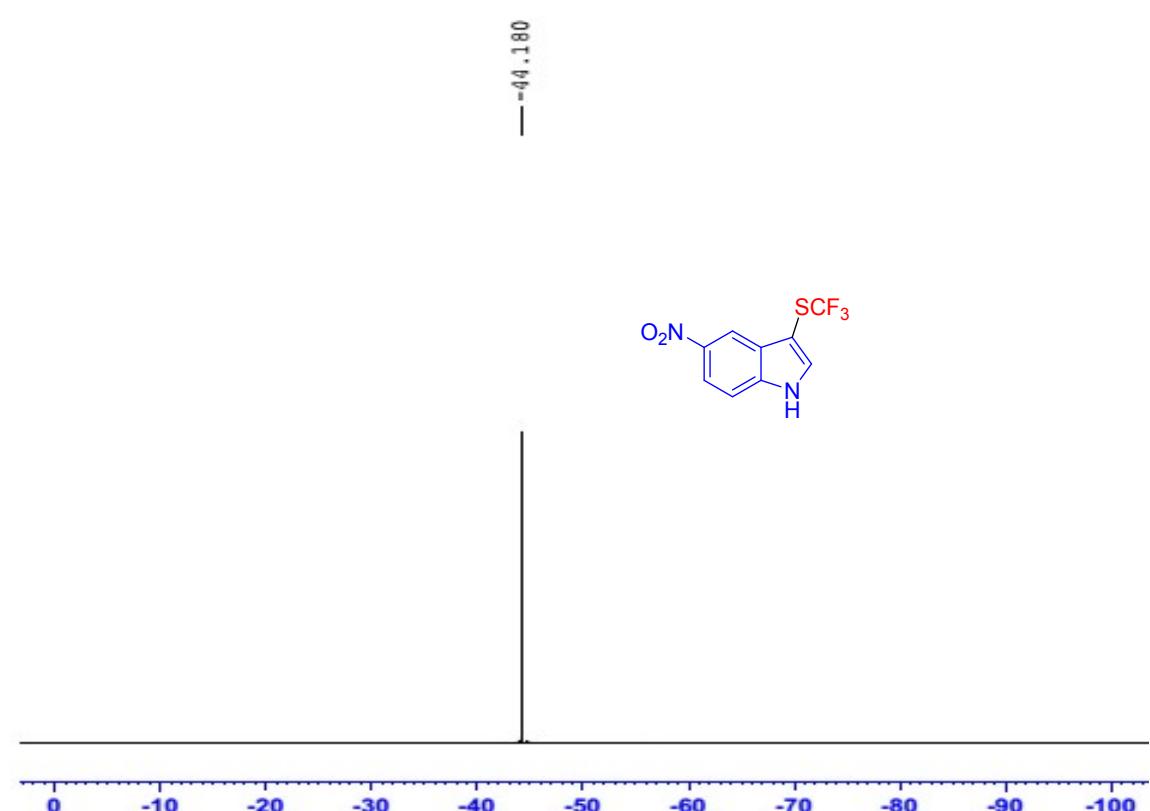
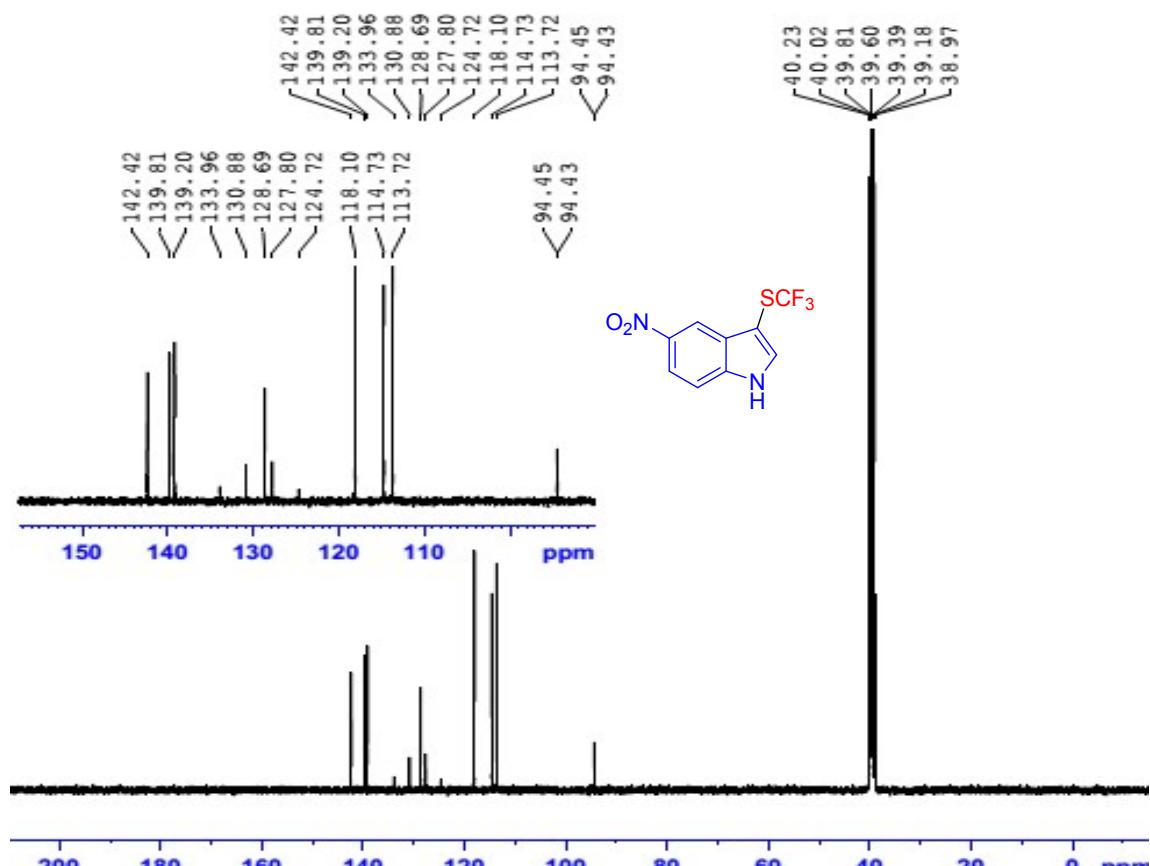
<sup>13</sup>C NMR and <sup>19</sup>F NMR spectra of *methyl 3-((trifluoromethyl)thio)-1H-indole-5-carboxylate (11i)* in DMSO-d6



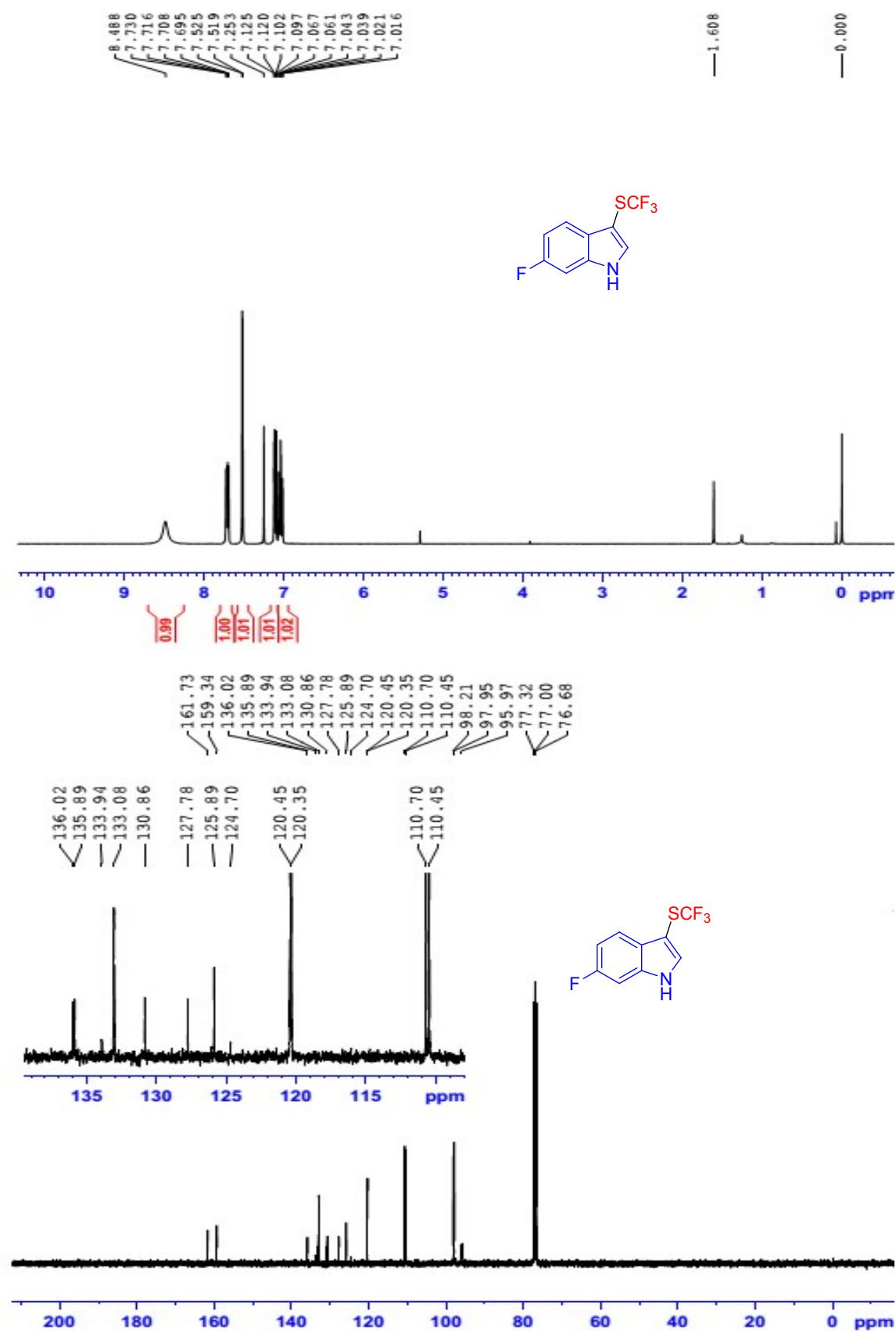
— -44.178

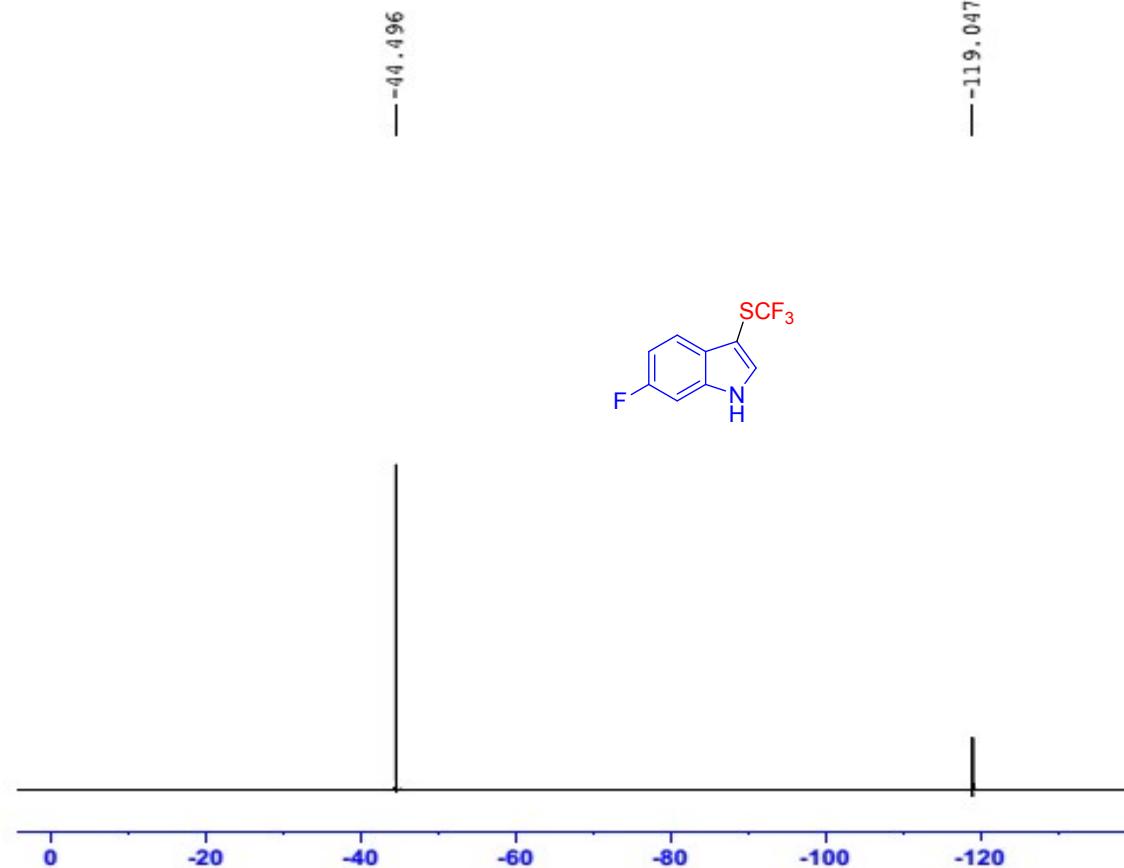


<sup>19</sup>F and <sup>13</sup>C NMR spectra of **5-nitro-3-((trifluoromethyl)thio)-1H-indole (11j)** in DMSO<sup>46</sup>

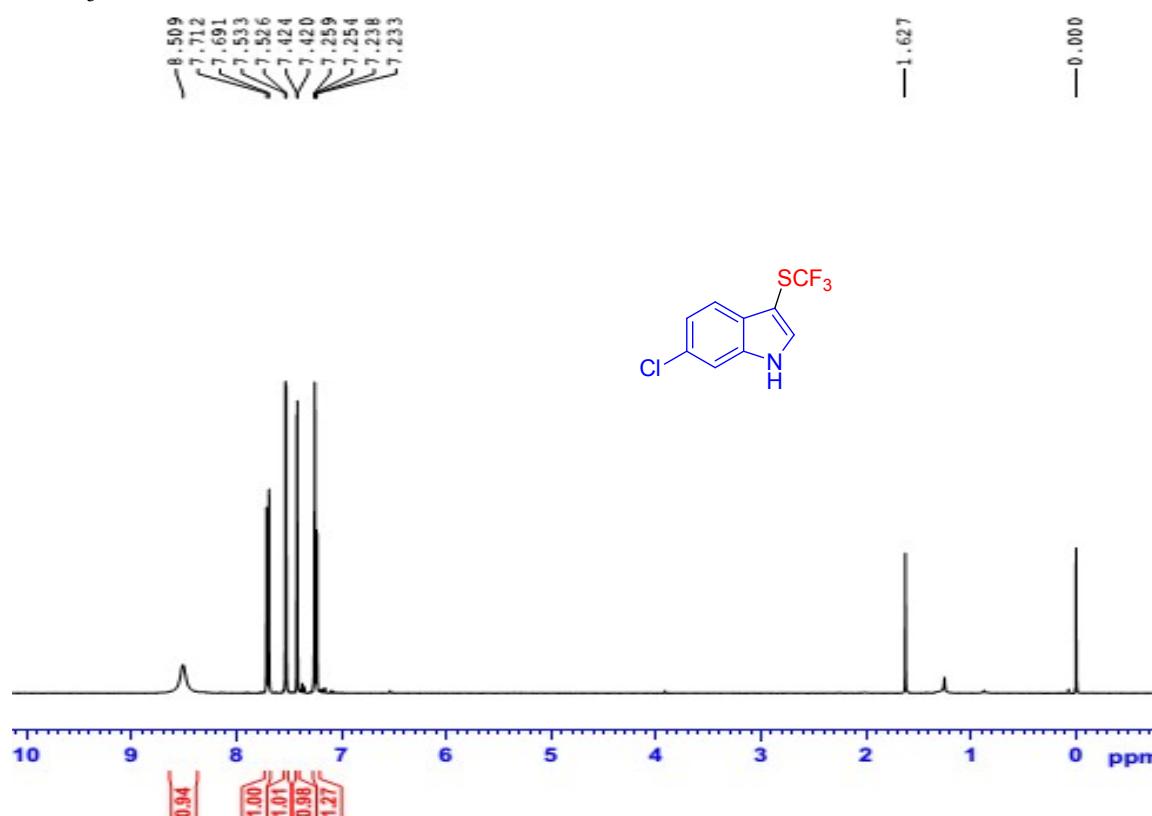


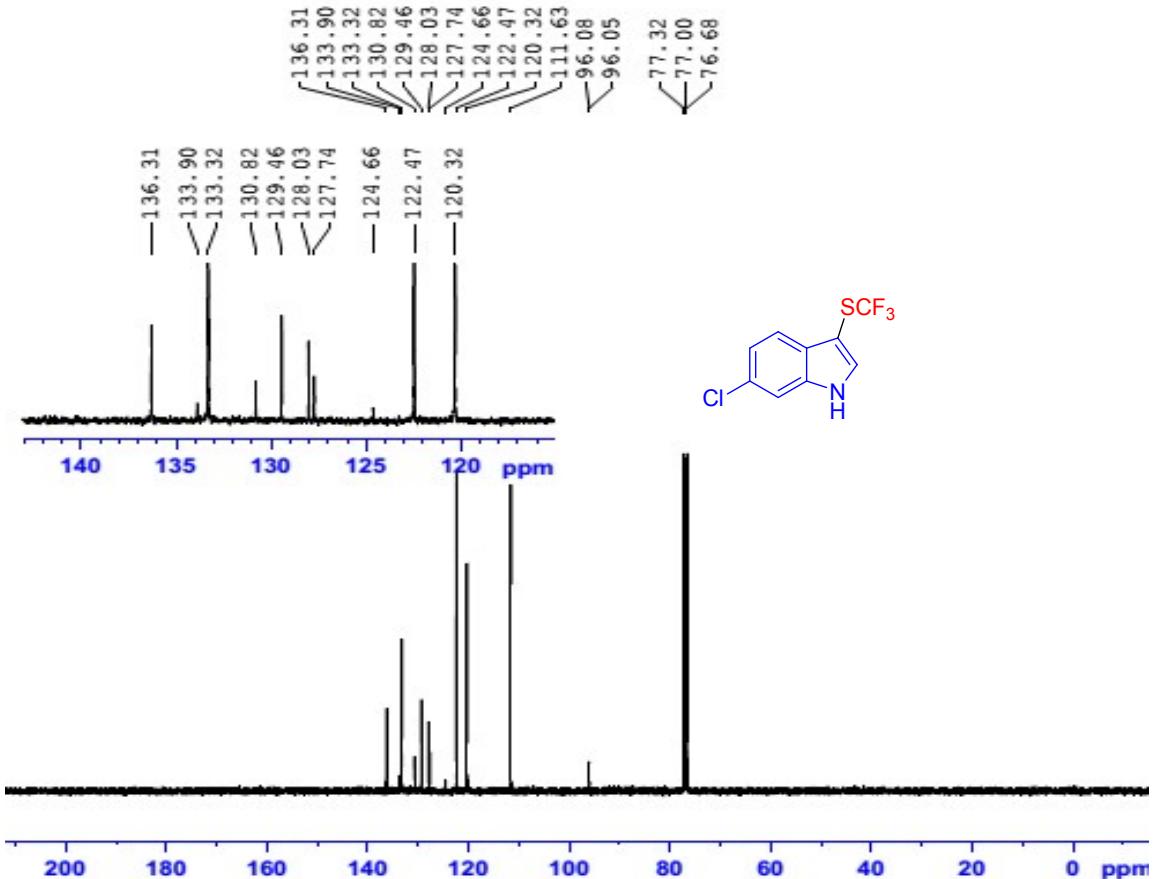
<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra of **6-fluoro-3-((trifluoromethyl)thio)-1H-indole (11k)** in CDCl<sub>3</sub>



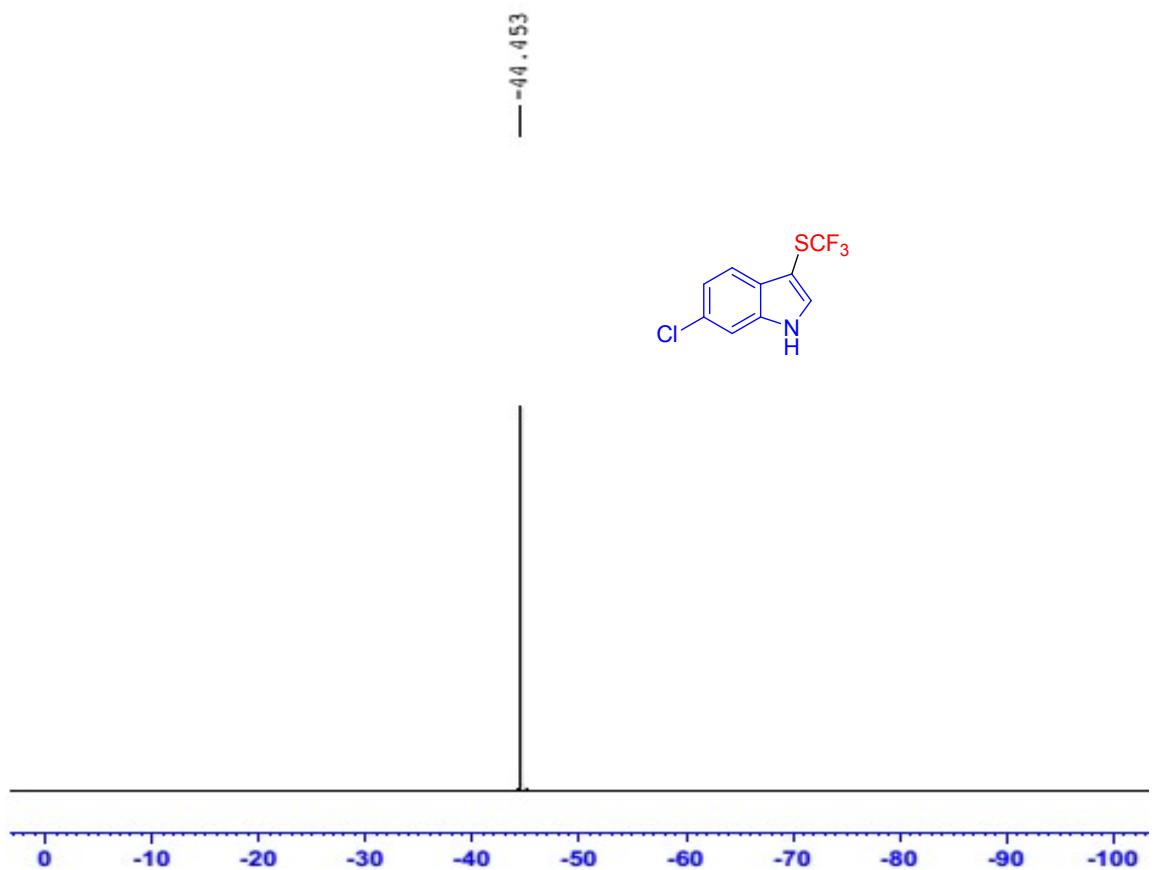


$^1\text{H}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR spectra of **6-chloro-3-((trifluoromethyl)thio)-1H-indole (11l)** in  $\text{CDCl}_3$

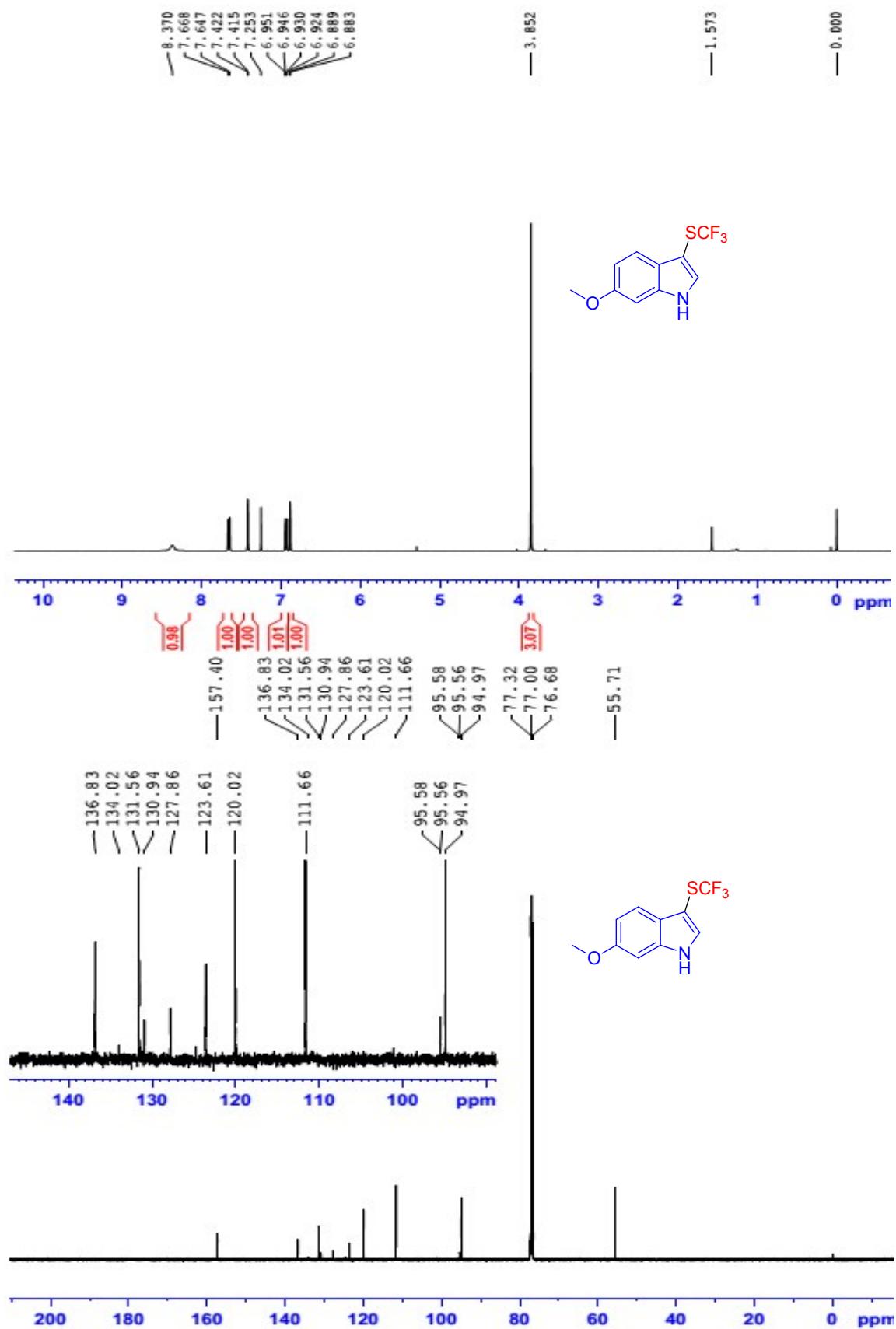


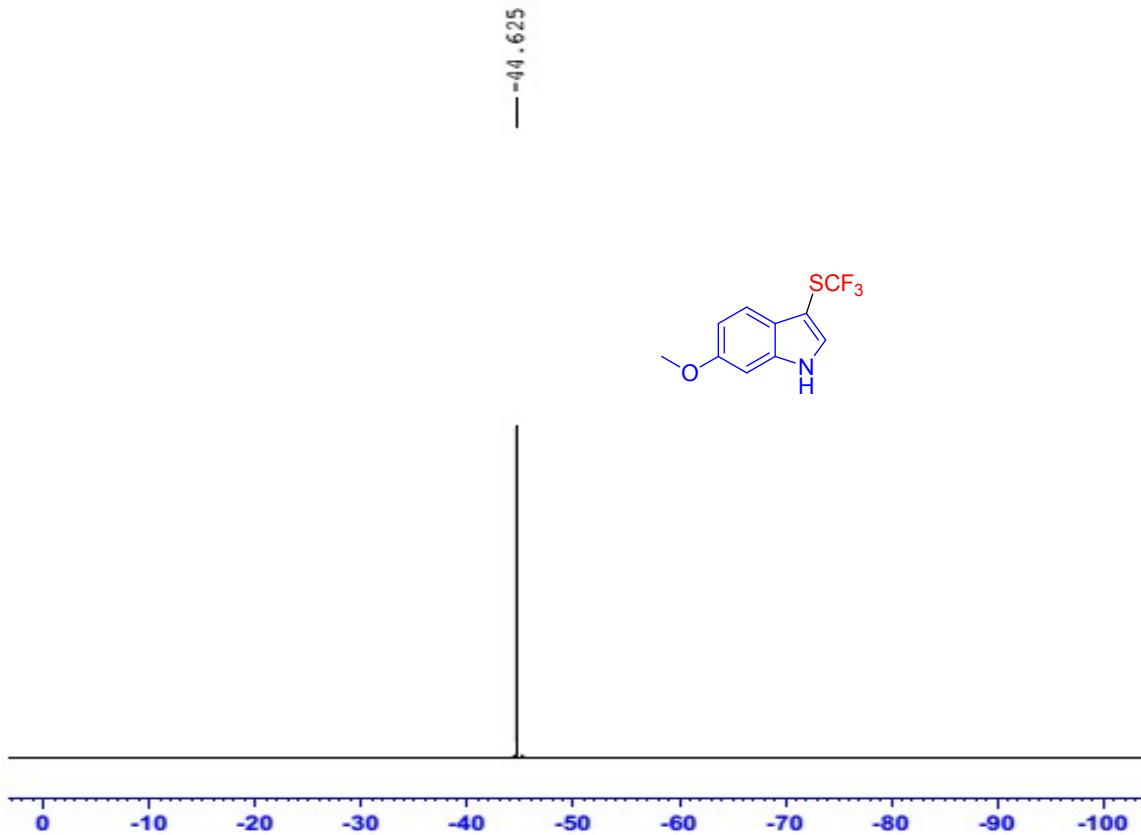


-44.453

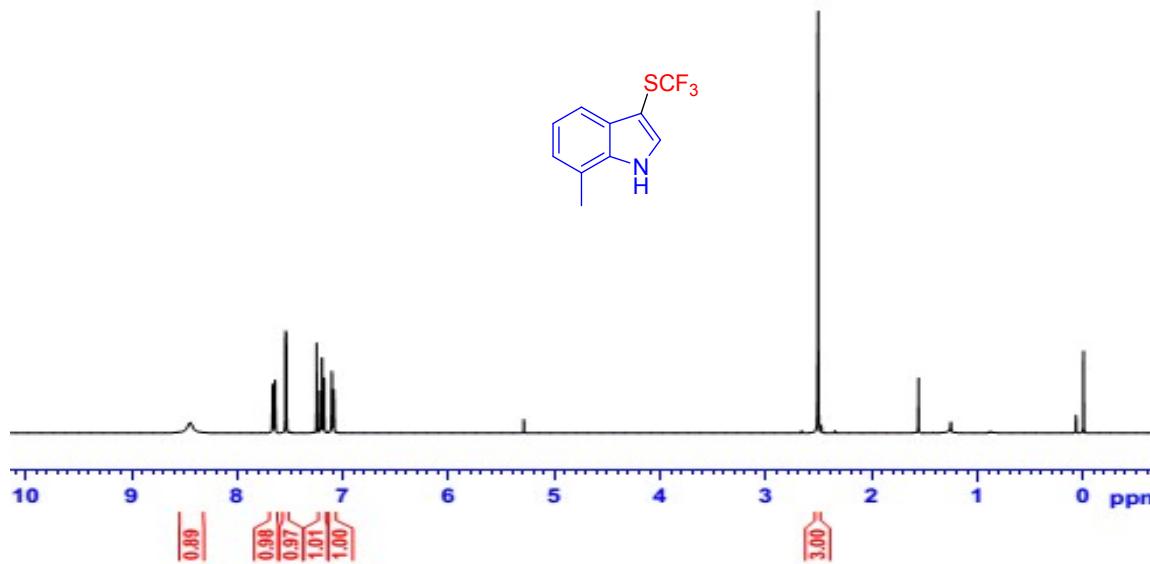


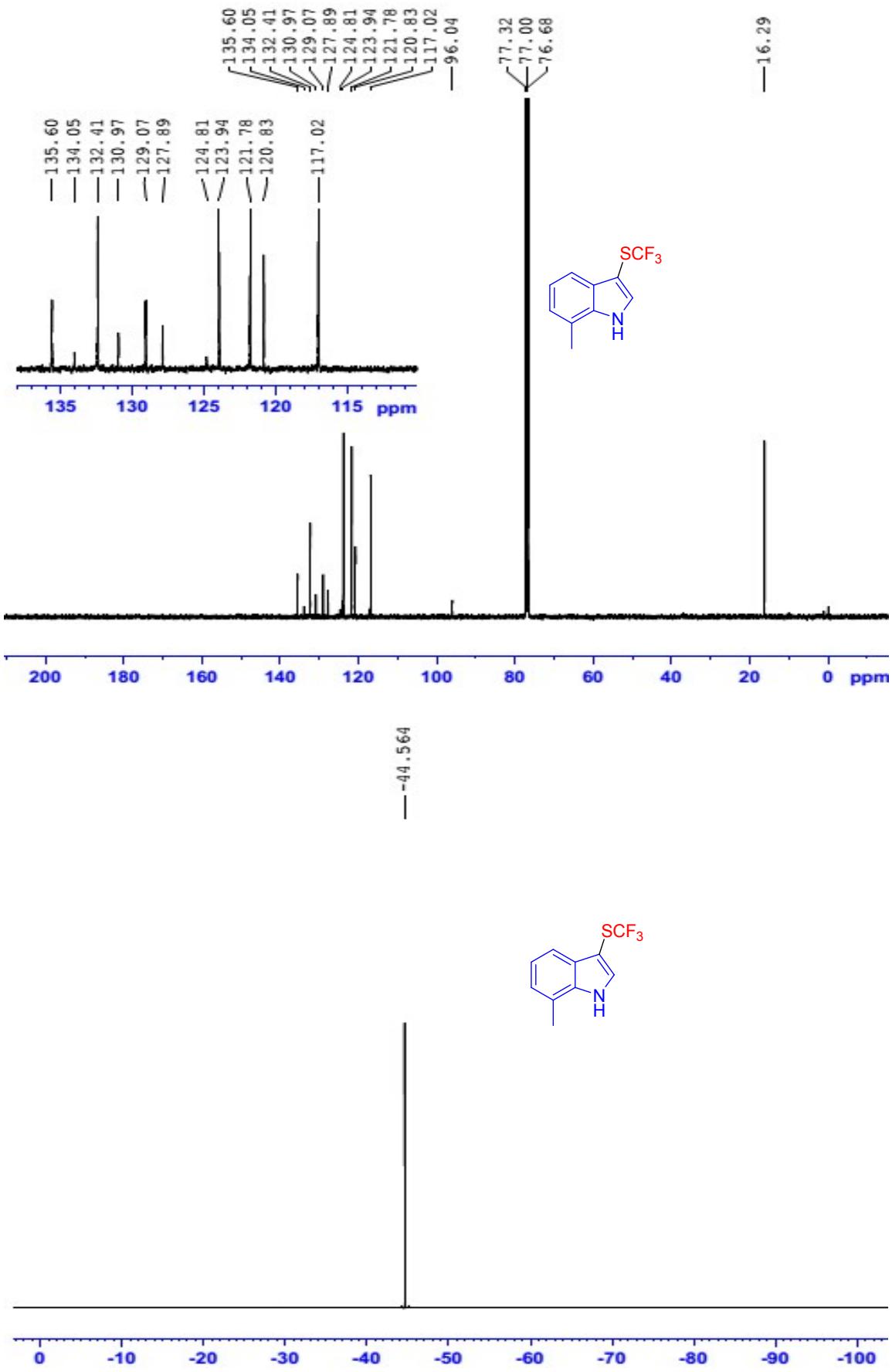
<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra of **6-methoxy-3-((trifluoromethyl)thio)-1H-indole (11m)** in CDCl<sub>3</sub>



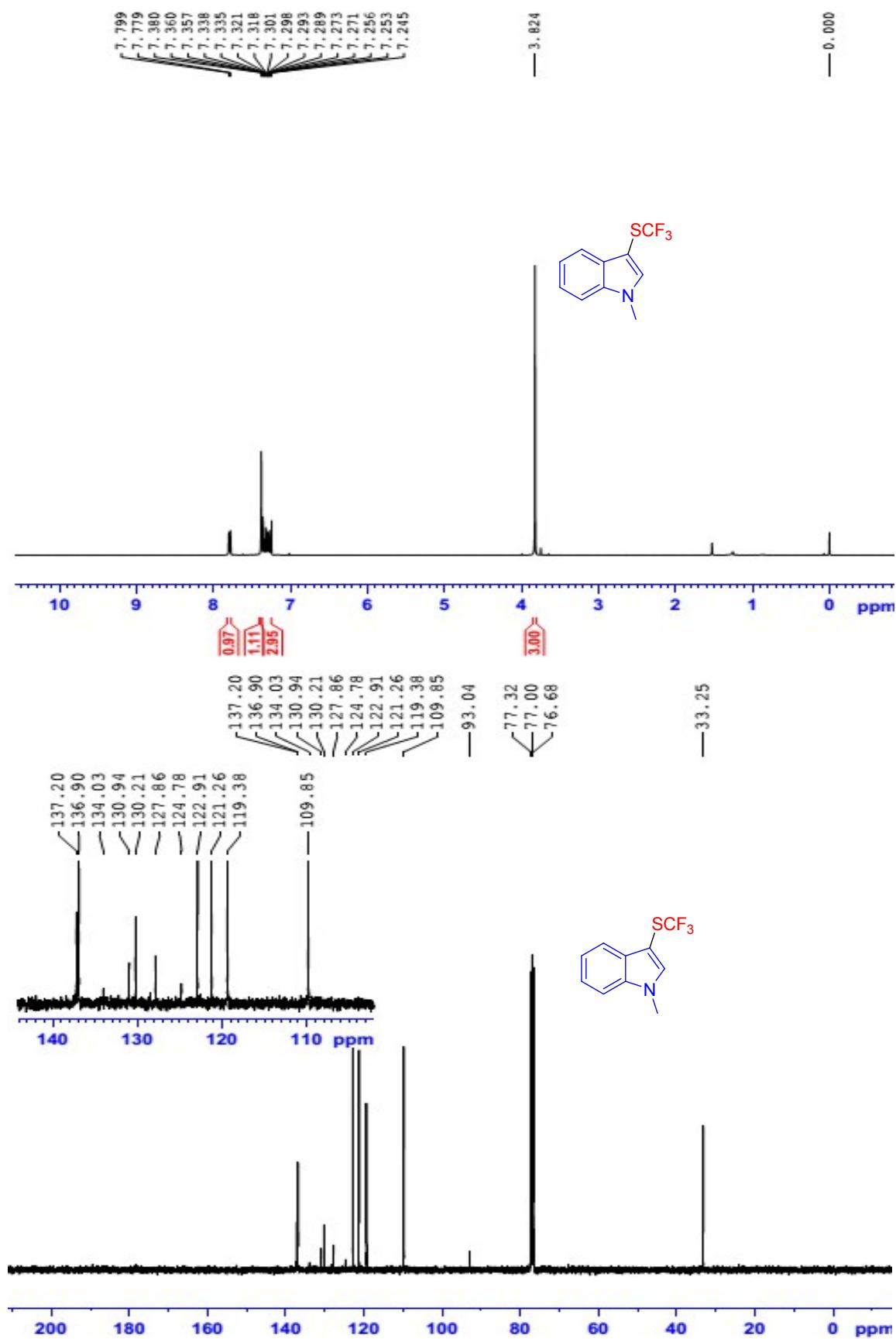


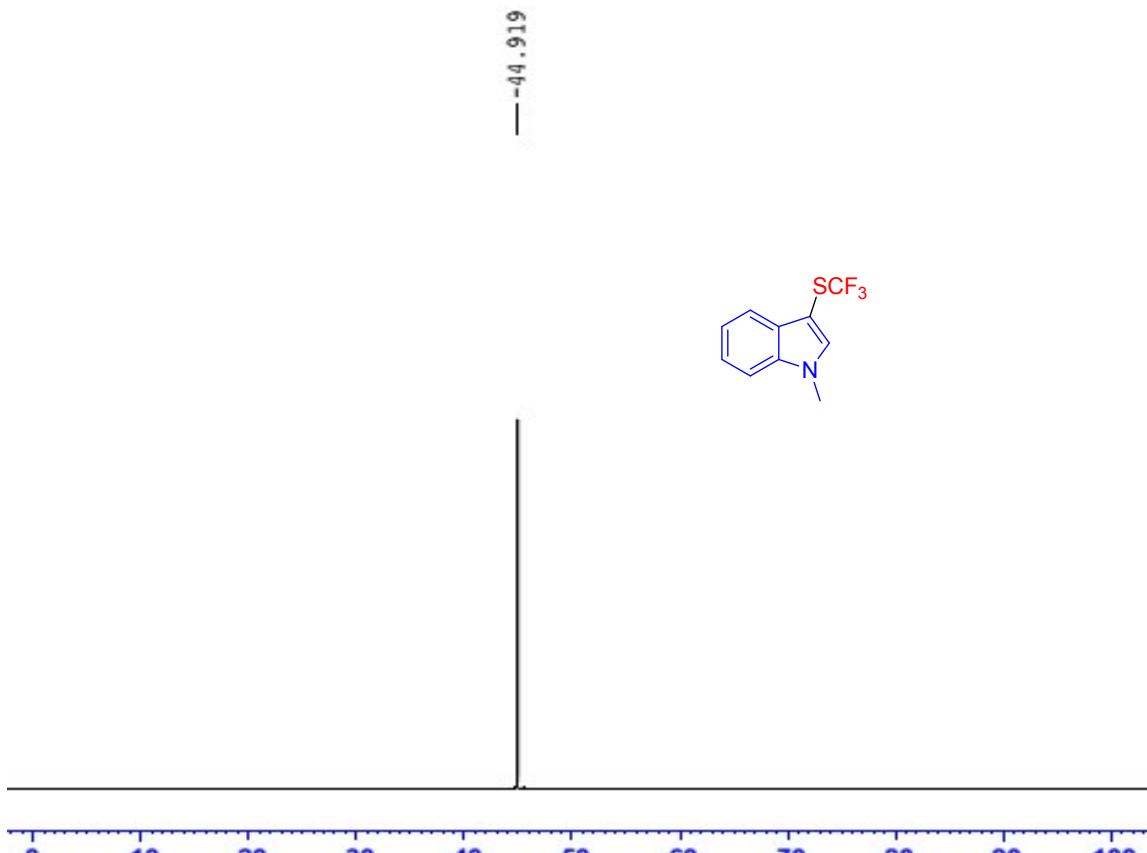
$^1\text{H}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR spectra of *7-methyl-3-((trifluoromethyl)thio)-1H-indole (11n)* in  $\text{CDCl}_3$



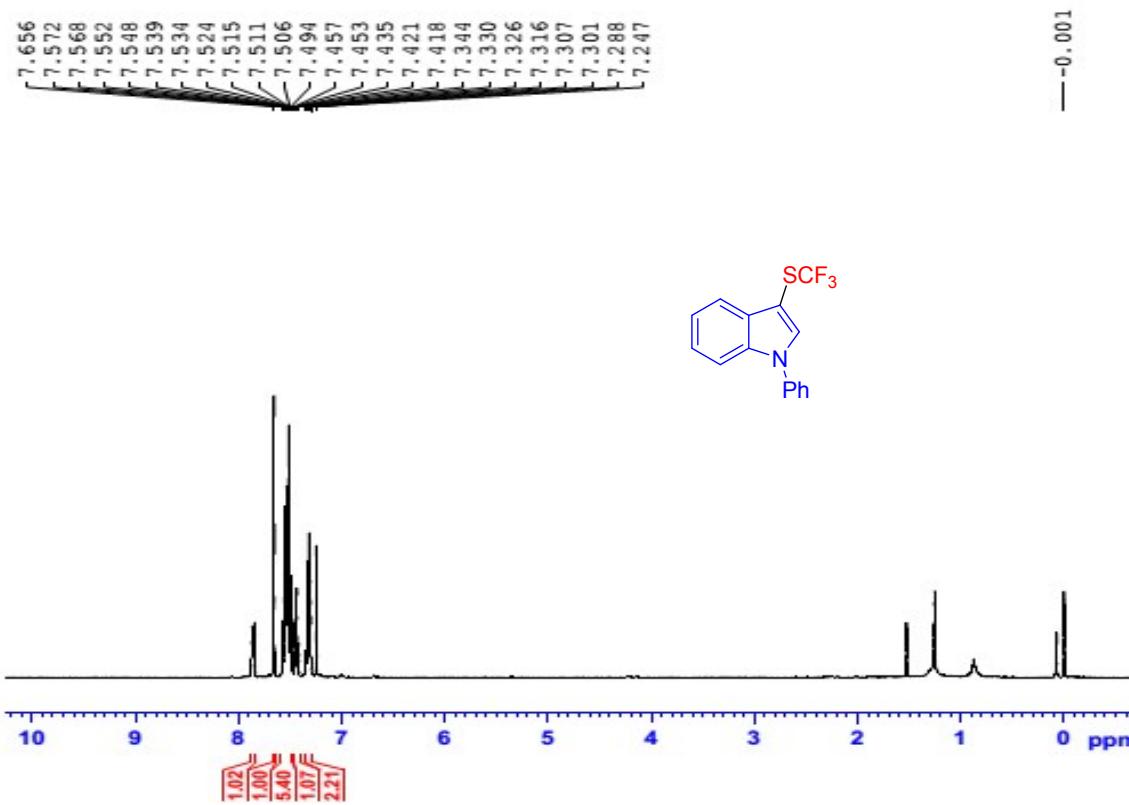


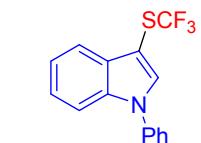
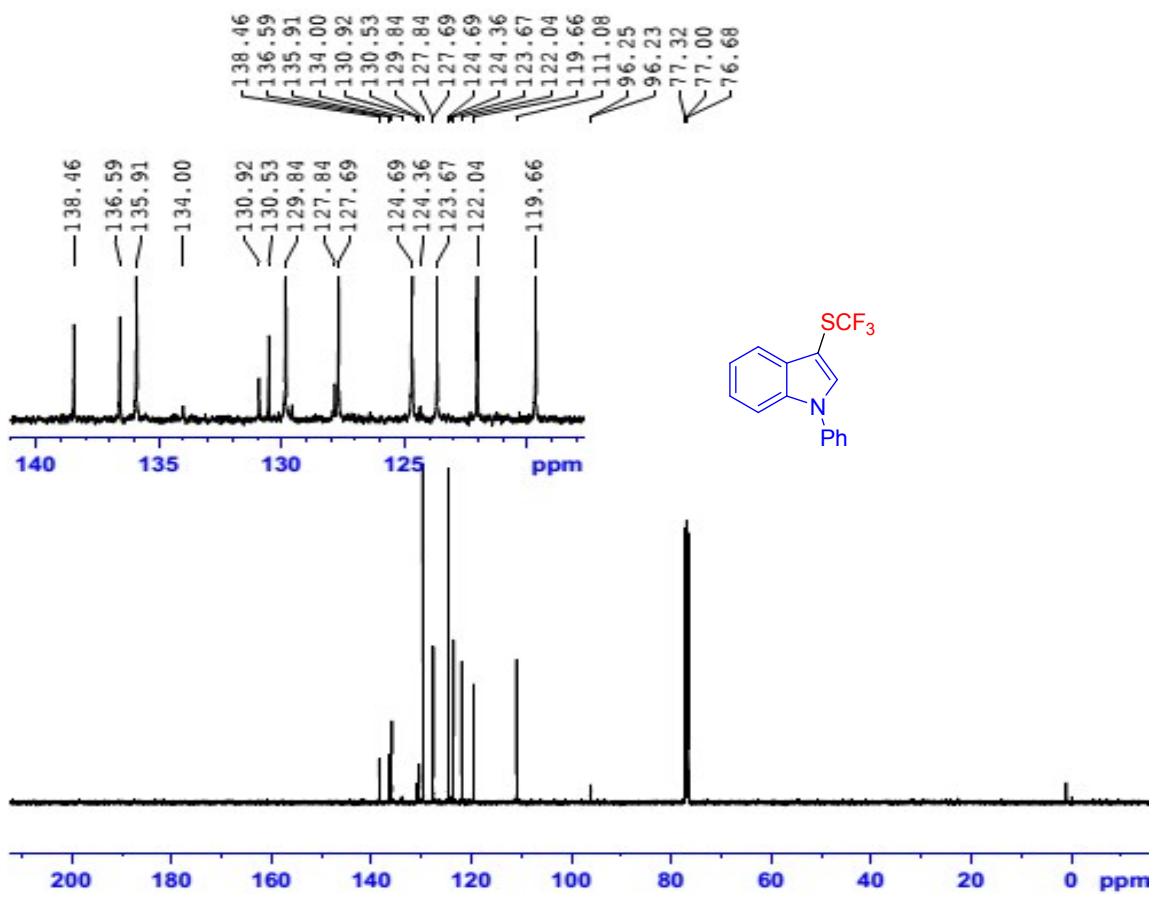
<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra of **1-methyl-3-((trifluoromethyl)thio)-1H-indole (11o)** in CDCl<sub>3</sub>



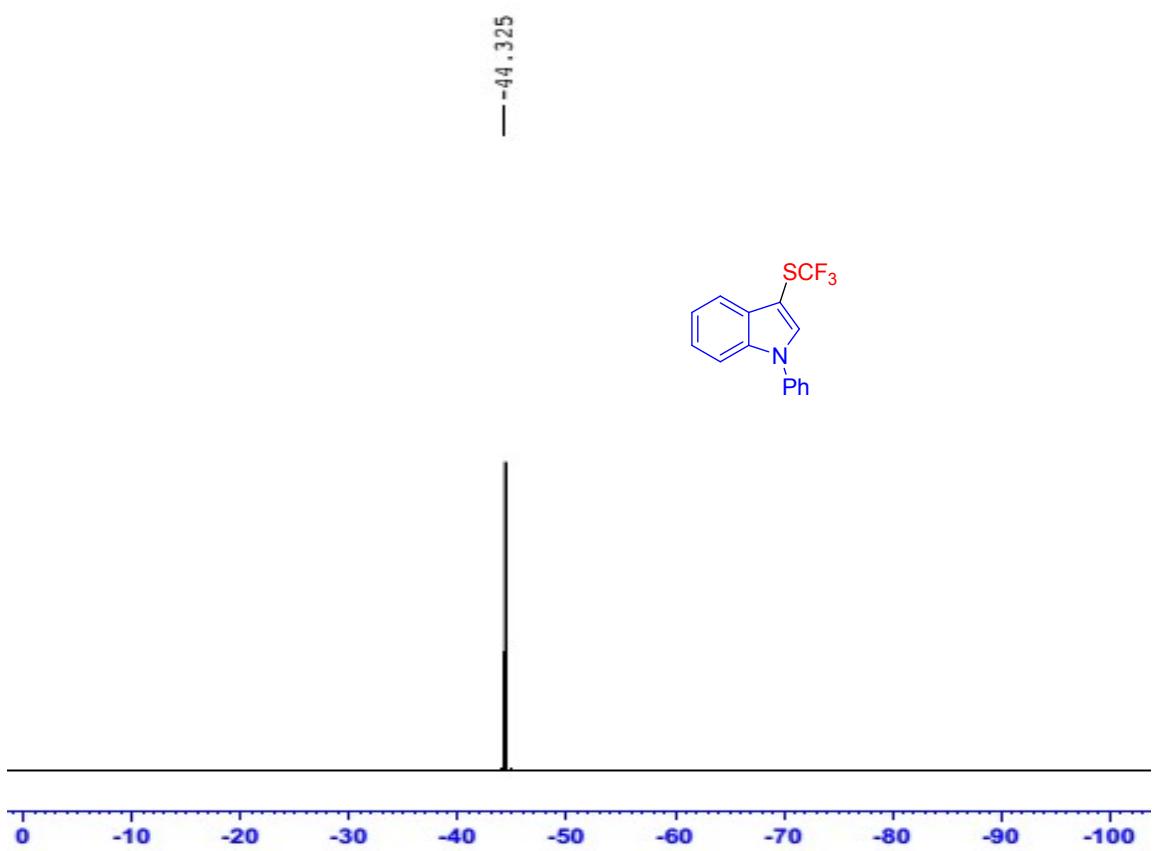
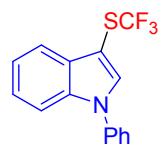


$^1\text{H}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR spectra of *1-phenyl-3-((trifluoromethyl)thio)-1H-indole* (*11p*) in  $\text{CDCl}_3$

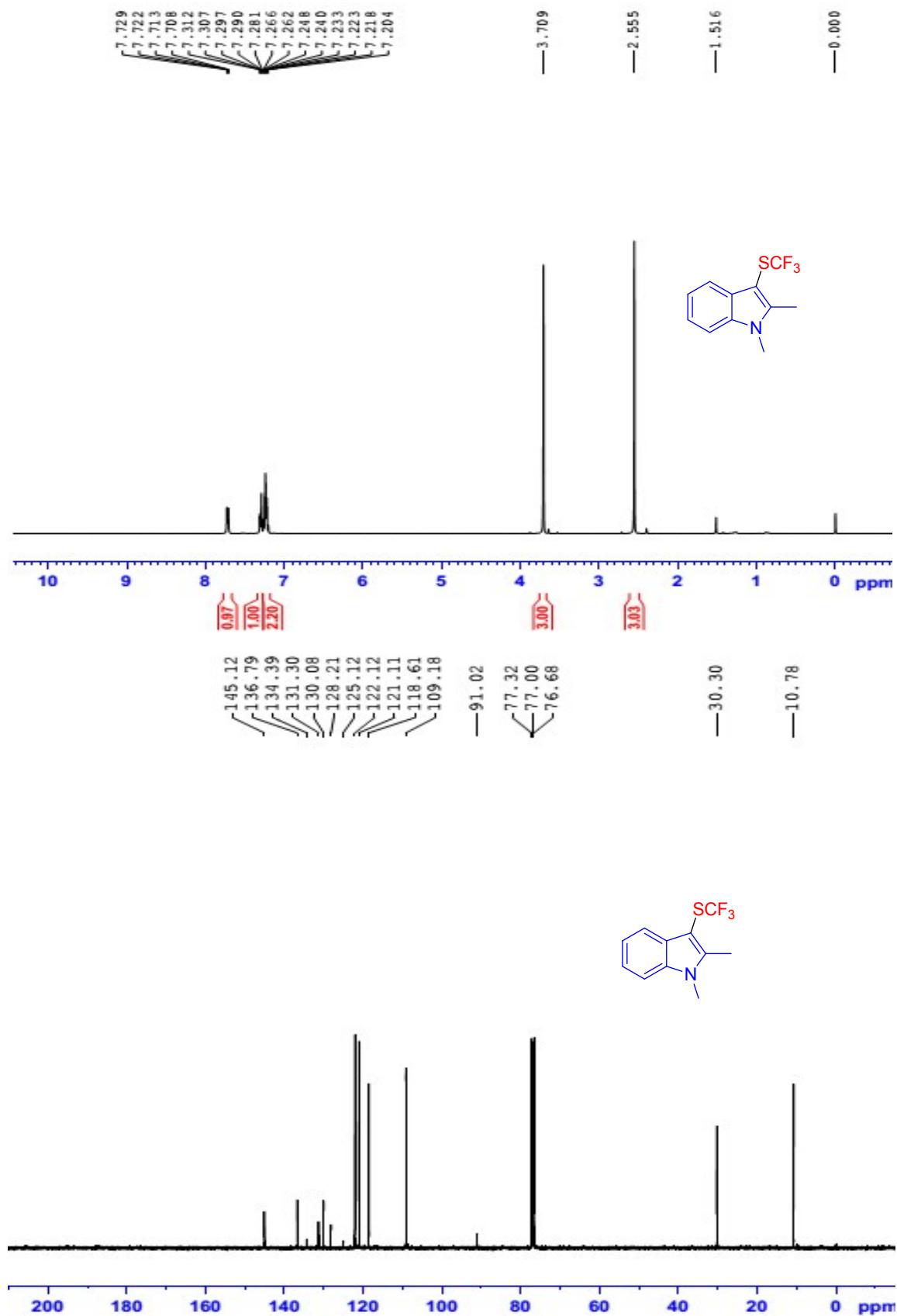


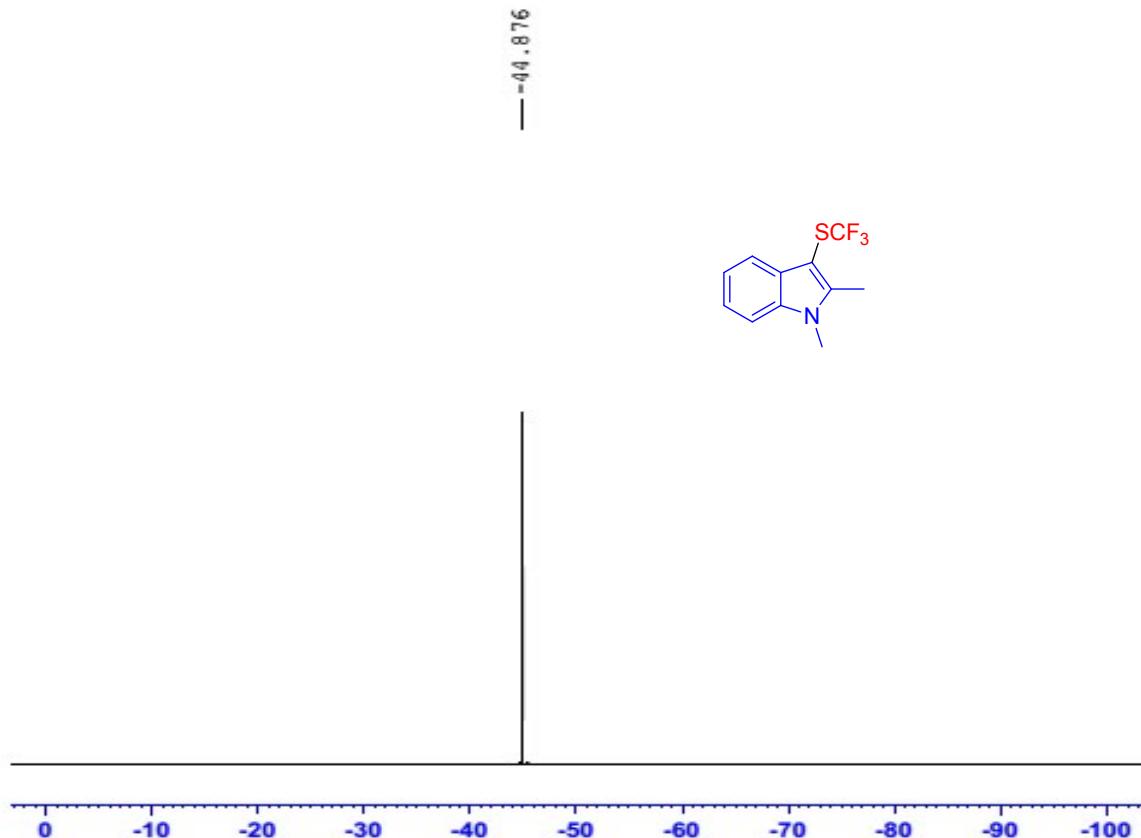


-44.325

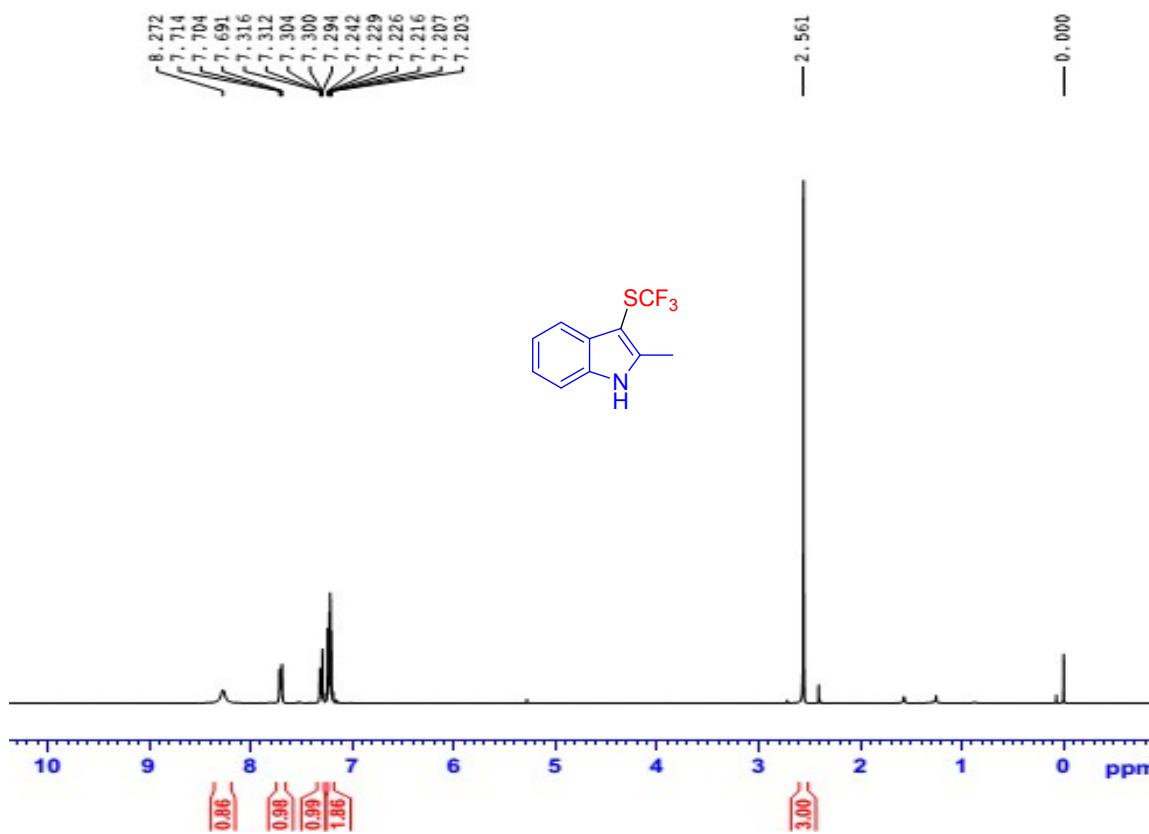


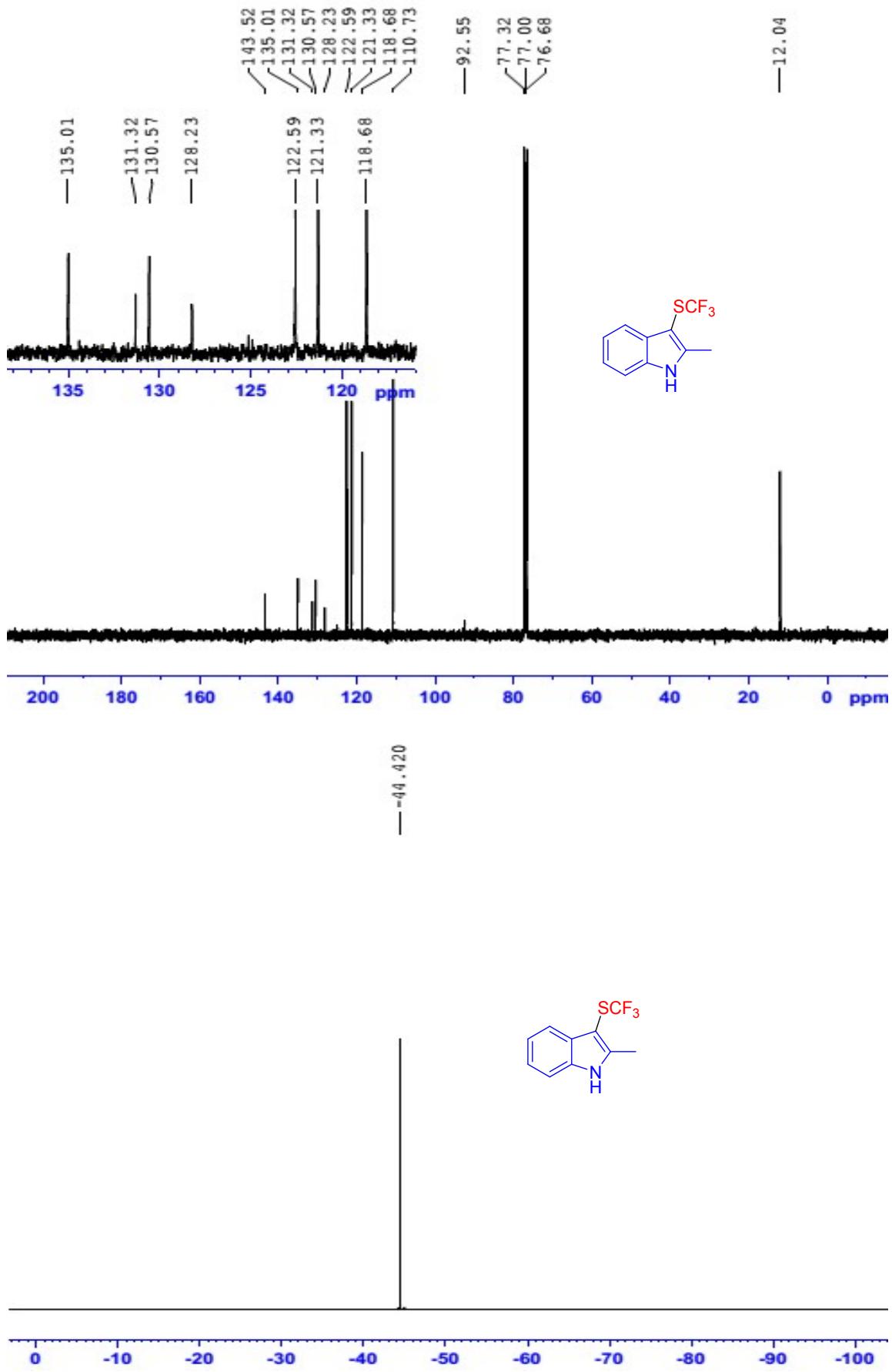
<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra of *1,2-dimethyl-3-((trifluoromethyl)thio)-1H-indole (11q)* in CDCl<sub>3</sub>



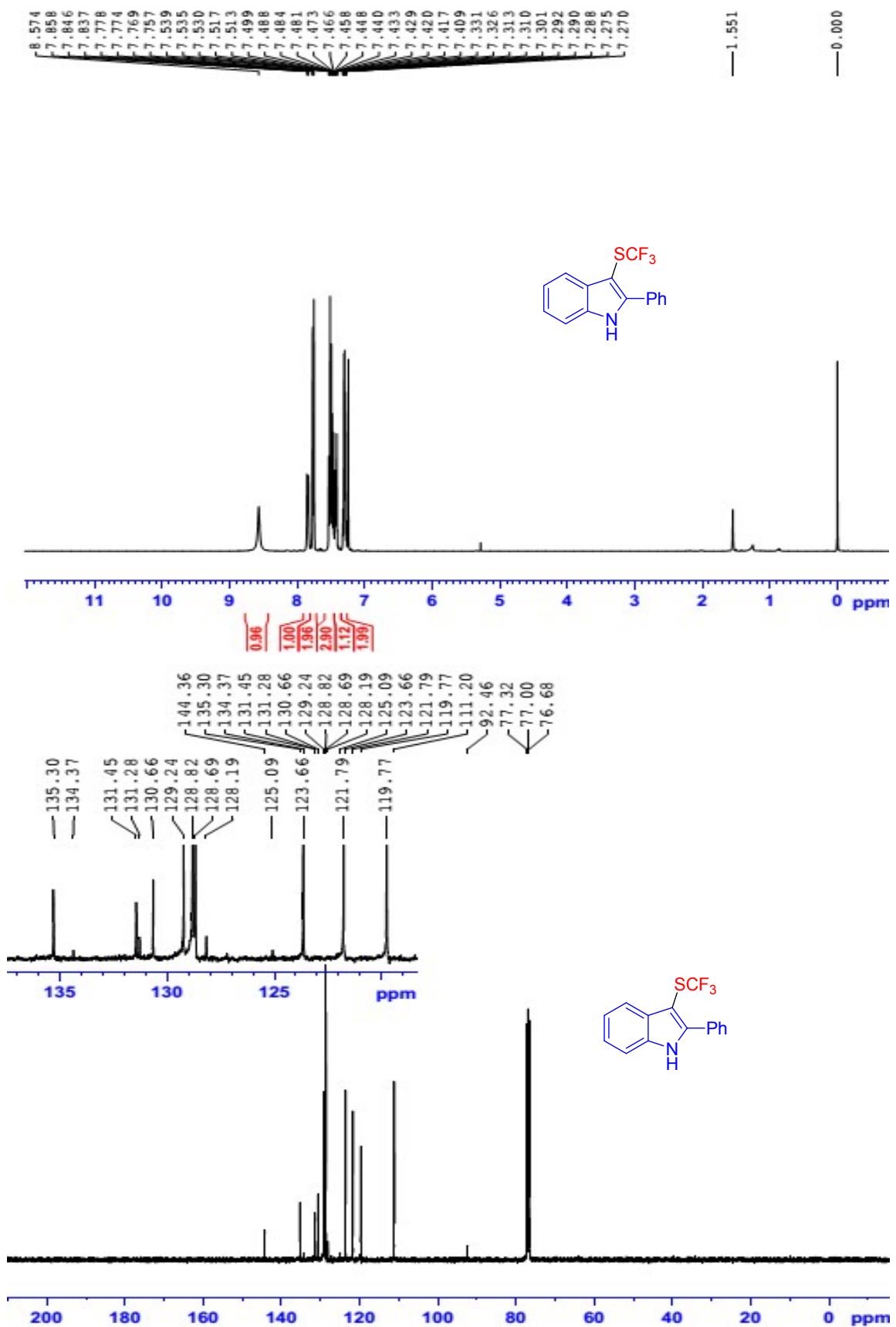


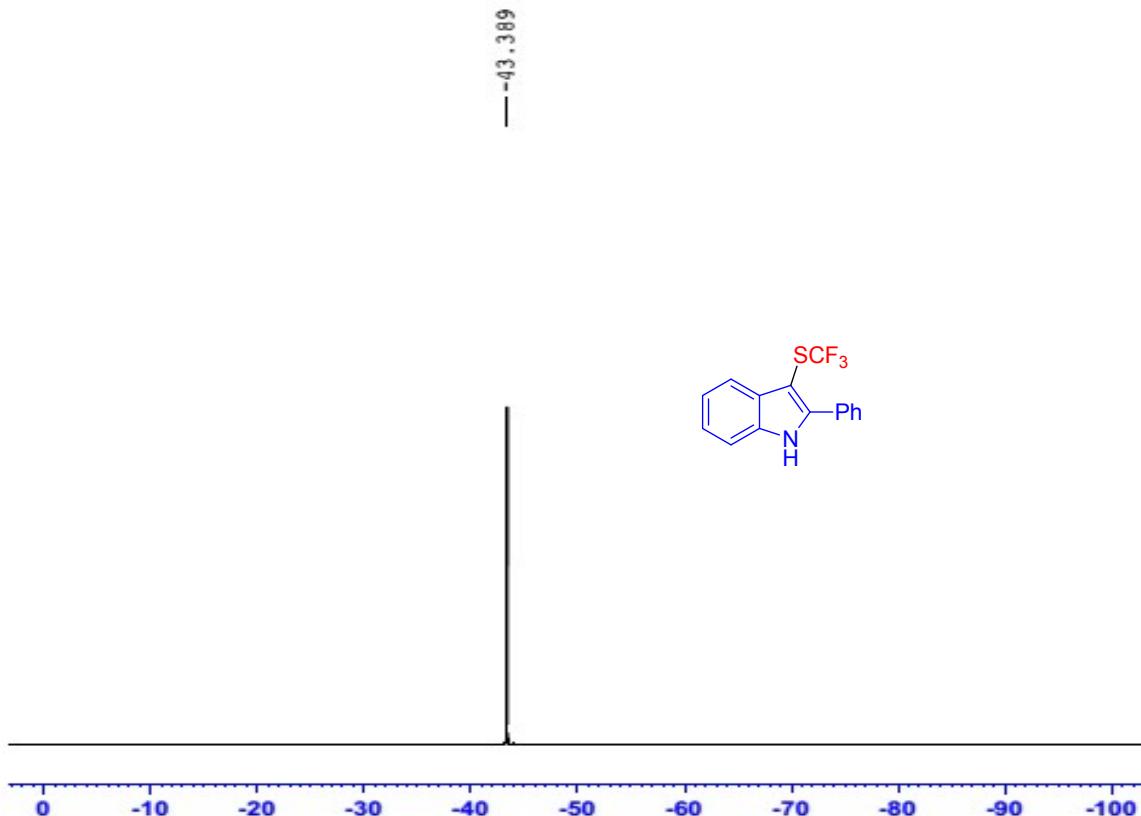
$^1\text{H}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR spectra of **2-methyl-3-((trifluoromethyl)thio)-1H-indole (11r)** in  $\text{CDCl}_3$



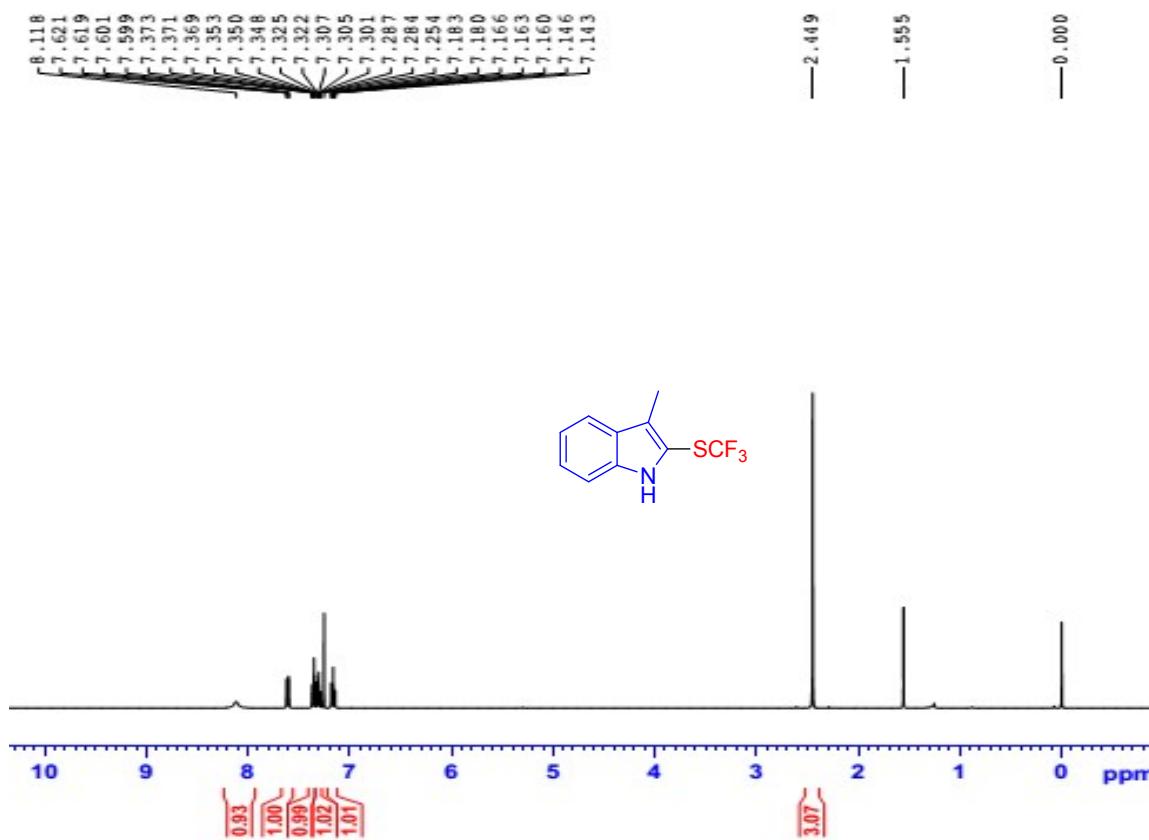


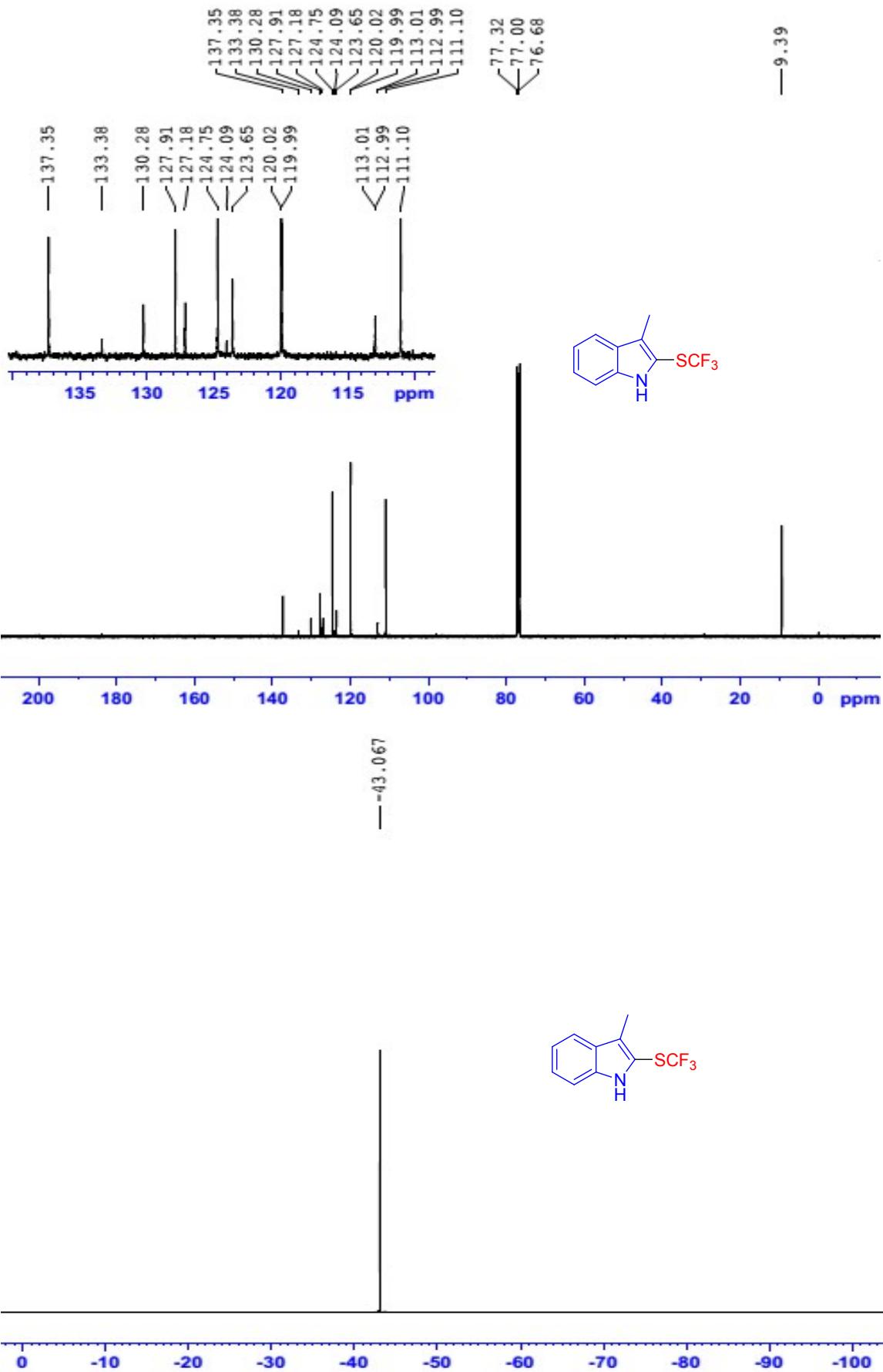
<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra of **2-phenyl-3-((trifluoromethyl)thio)-1H-indole (11s)** in CDCl<sub>3</sub>





$^1\text{H}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR spectra of **3-methyl-2-((trifluoromethyl)thio)-1H-indole (11t)** in  $\text{CDCl}_3$





<sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra of *S*-(trifluoromethyl) 1*H*-indole-3-sulfinothioate (**18a**) in DMSO-d<sub>6</sub>

