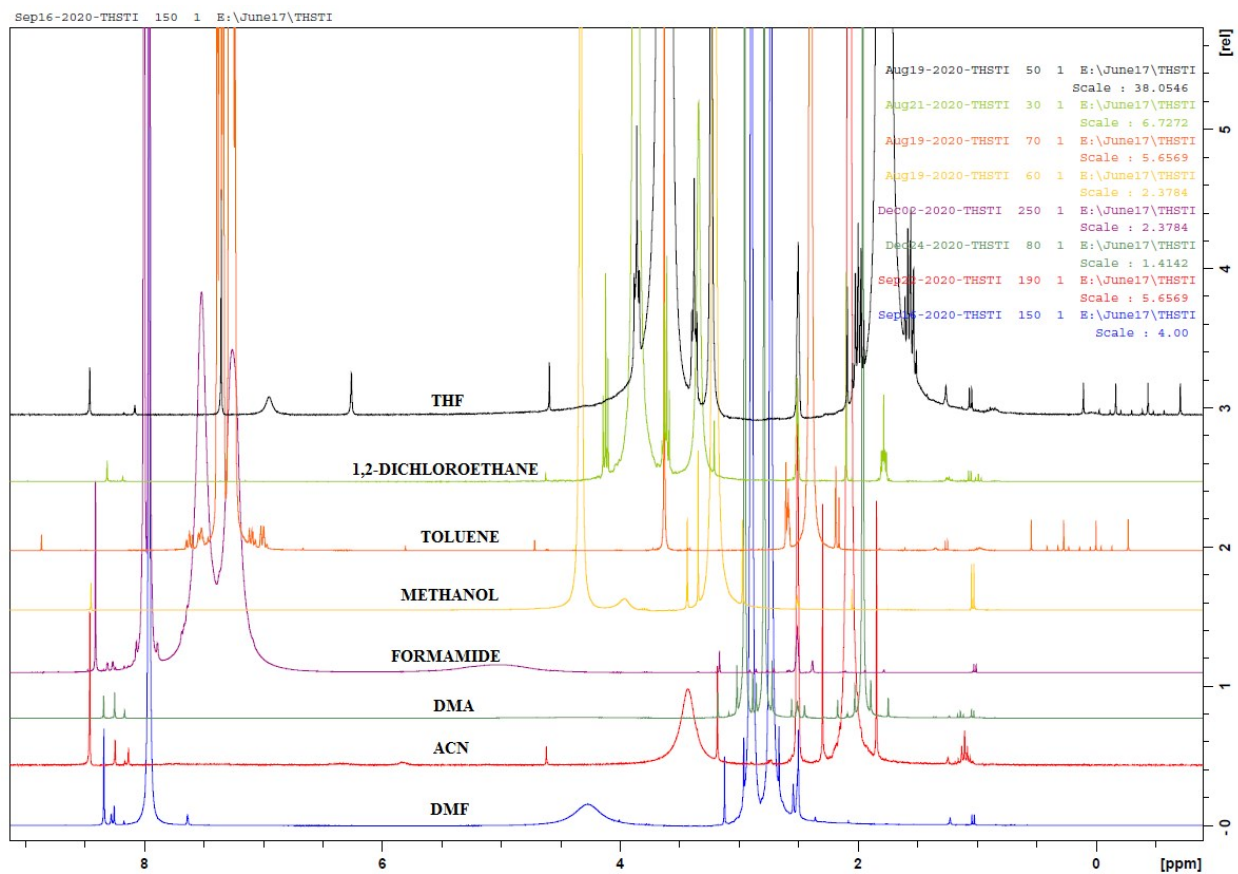


## Catalyst free *N*-formylation of aromatic and aliphatic amines exploiting reductive formylation of CO<sub>2</sub> using NaBH<sub>4</sub>

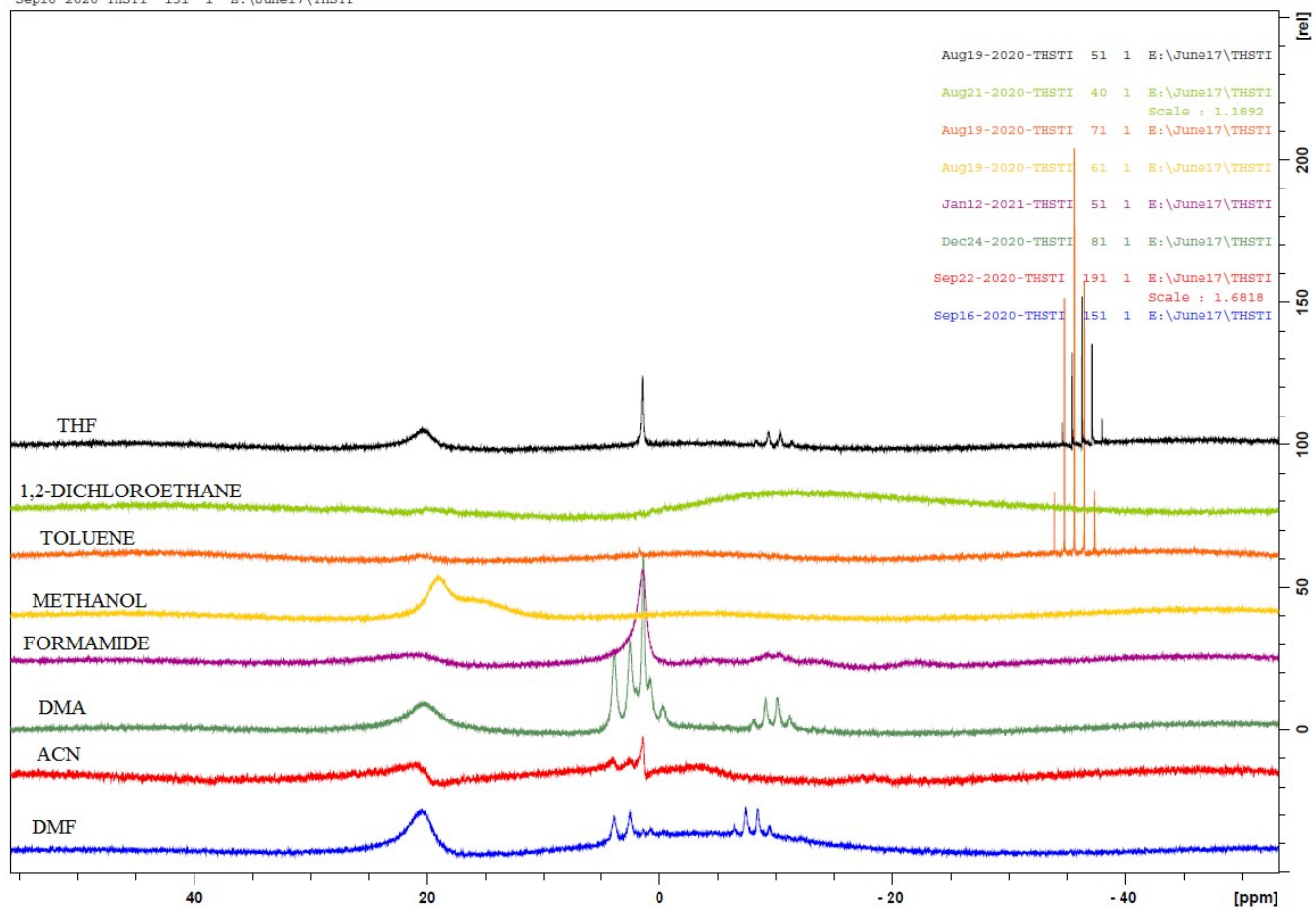
Arun Kumar, Pankaj Sharma, Nidhi Sharma, Yashwant Kumar and Dinesh Mahajan\*

### Table of Contents

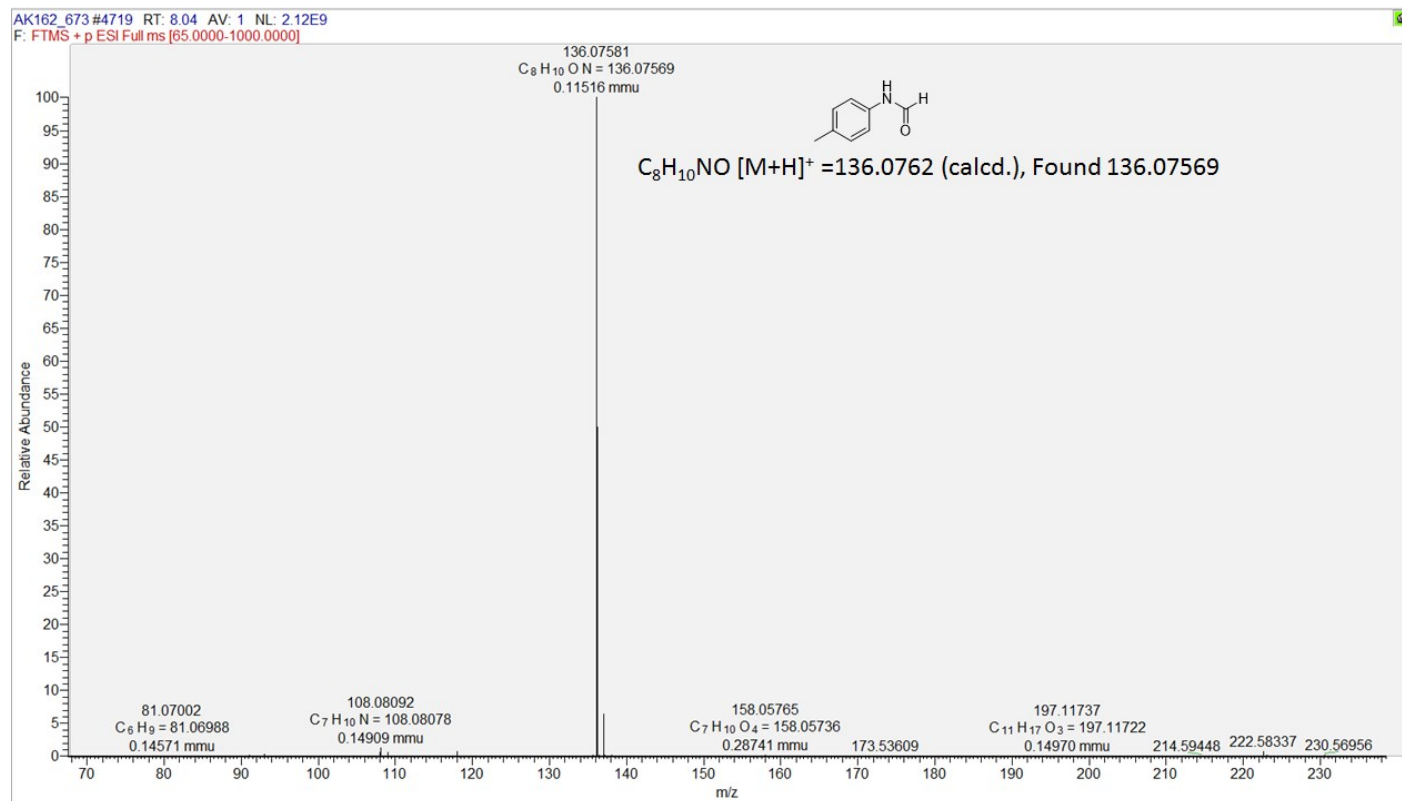
<b>S.NO.</b>	<b>Content</b>	<b>Pages</b>
1	Figure S1	2
2	Figure S2	3
3	Figure S3-S11	4-12
4	Figure S12	13
5	Figure S13-S60	14-61
6	Figure S61-S64	62-64



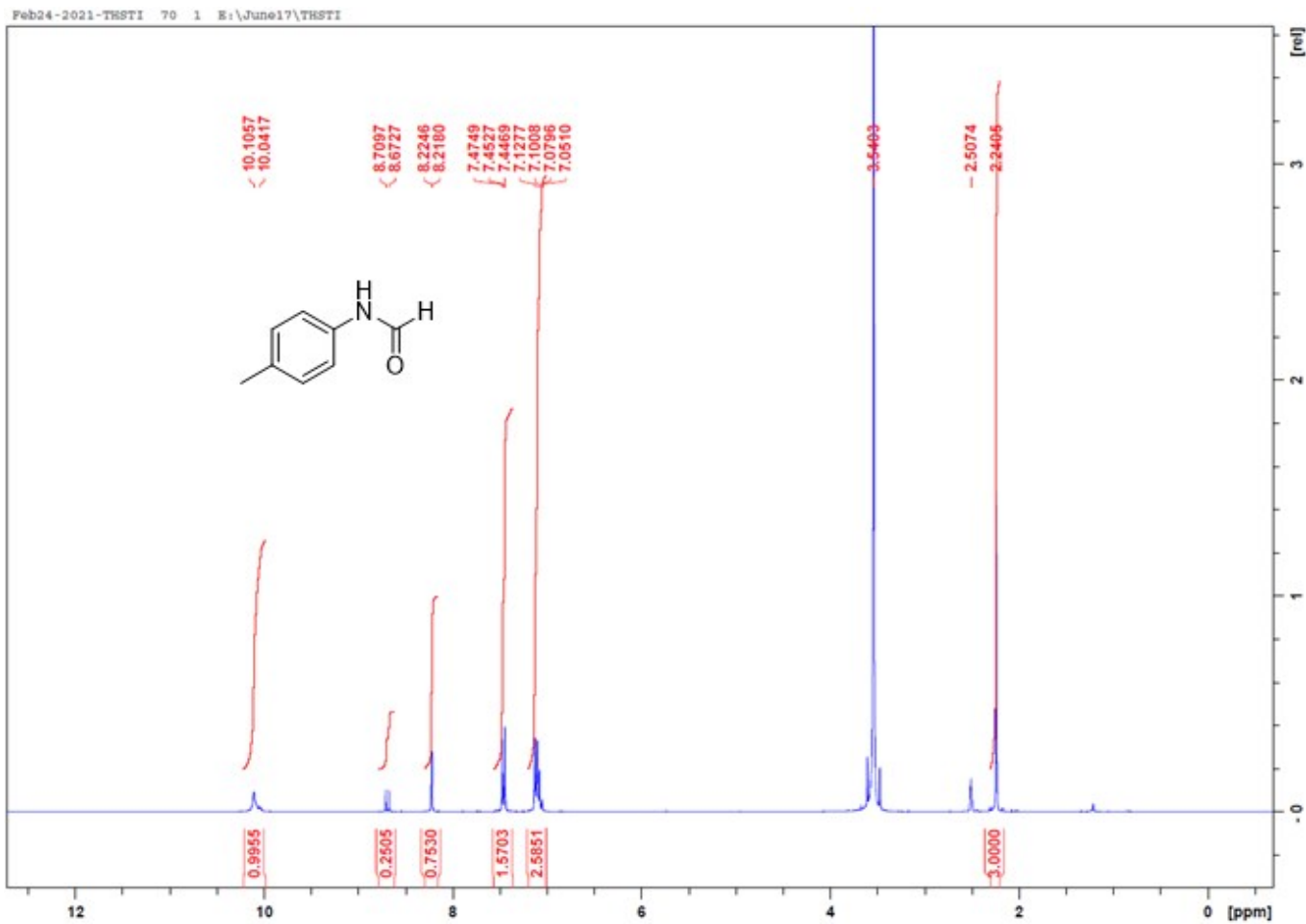
**Figure S1:**  $^1\text{H}$  NMR spectrum of reaction mixture after dissolving  $\text{NaBH}_4$  in different solvents followed by sparging of  $\text{CO}_2$  gas.



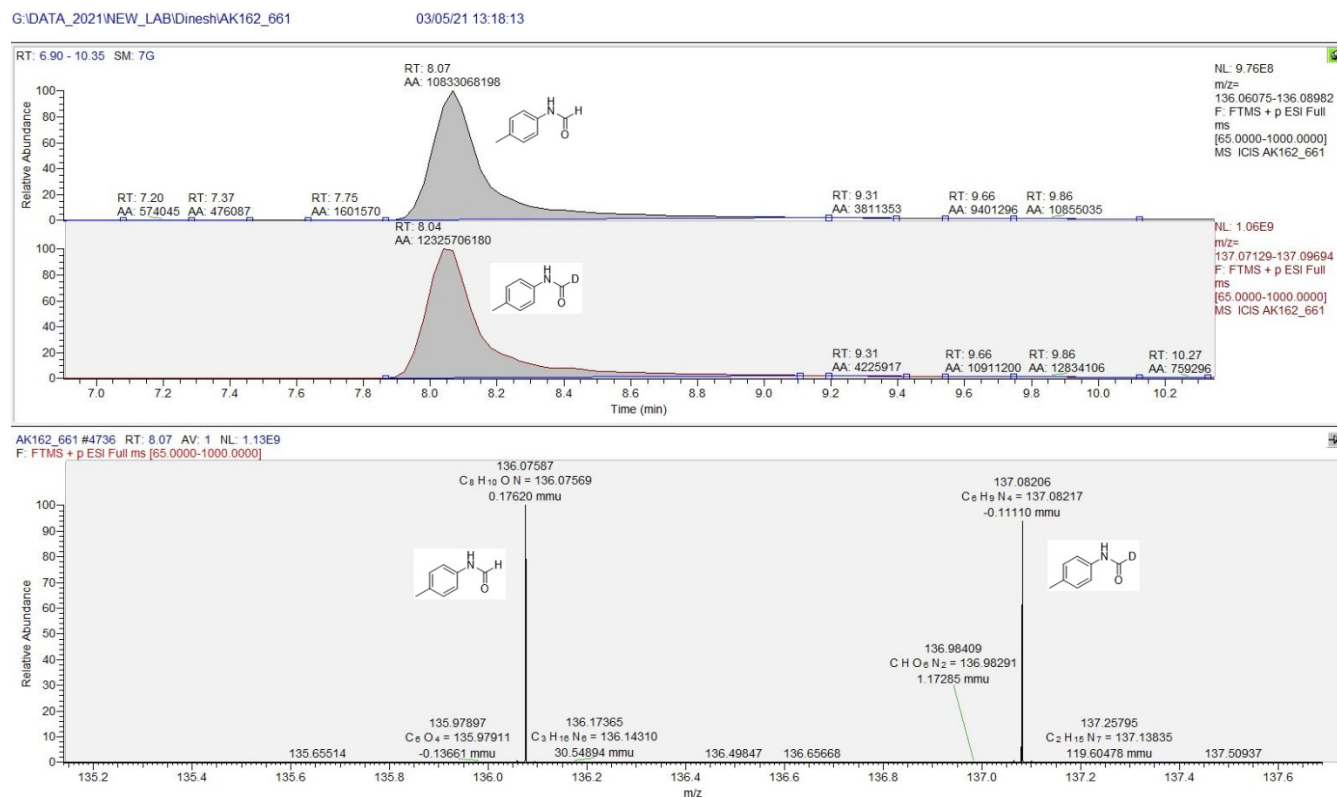
**Figure S2:**  $^{11}\text{B}$  NMR spectrum of reaction mixture after dissolving  $\text{NaBH}_4$  in different solvents followed by sparging of  $\text{CO}_2$  gas.



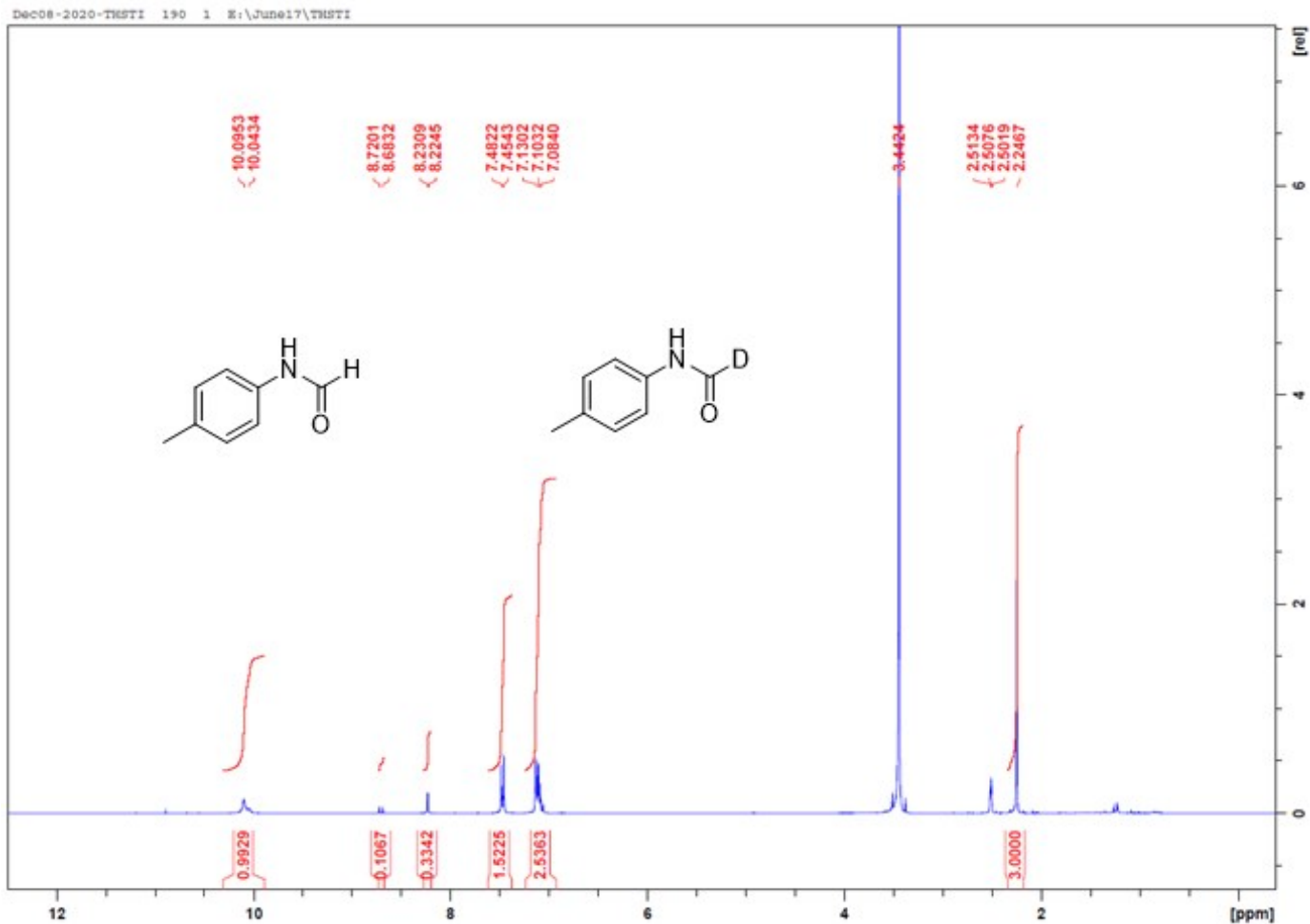
**Figure S3:** MS spectrum of N-*p*-tolylformamide (**16**) synthesized in DMF solvent using NaBH<sub>4</sub> and CO<sub>2</sub>.



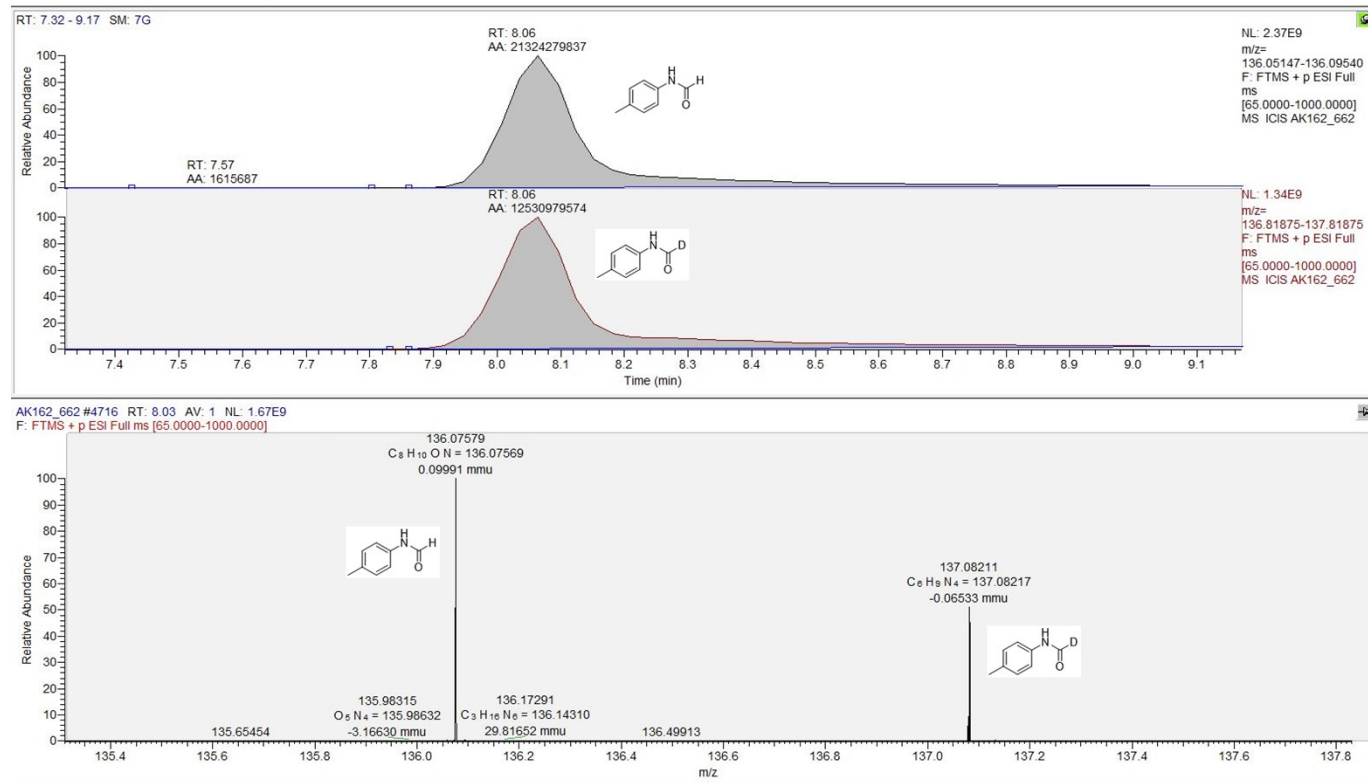
**Figure S4:**  $^1\text{H}$  NMR spectrum of N-p-tolylformamide (**16**) synthesized in DMF using  $\text{NaBH}_4$  and  $\text{CO}_2$ .



**Figure S5:** LCMS spectrum of N-p-tolylformamide enriched with deuterium (**16D**) i.e. synthesized in DMF using sodium borodeuteride (NaBD<sub>4</sub>) and CO<sub>2</sub> (refer figure 4a in main text).

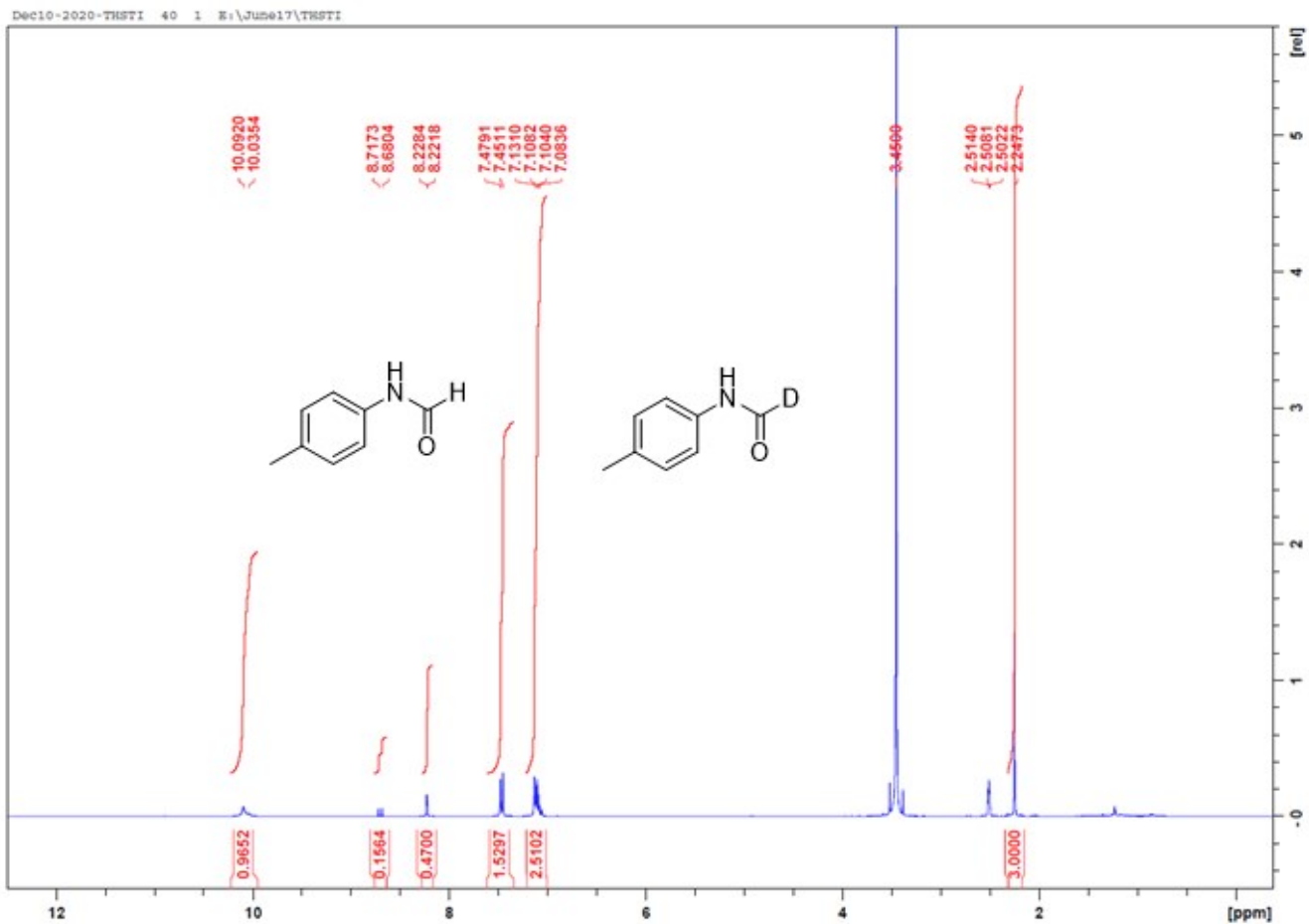


**Figure S6:**  $^1\text{H}$  NMR spectrum of N-p-tolylformamide enriched with deuterium (**16D**) i.e. synthesized using DMF, sodium borodeuteride ( $\text{NaBD}_4$ ) and  $\text{CO}_2$  (refer figure 4a in main text).

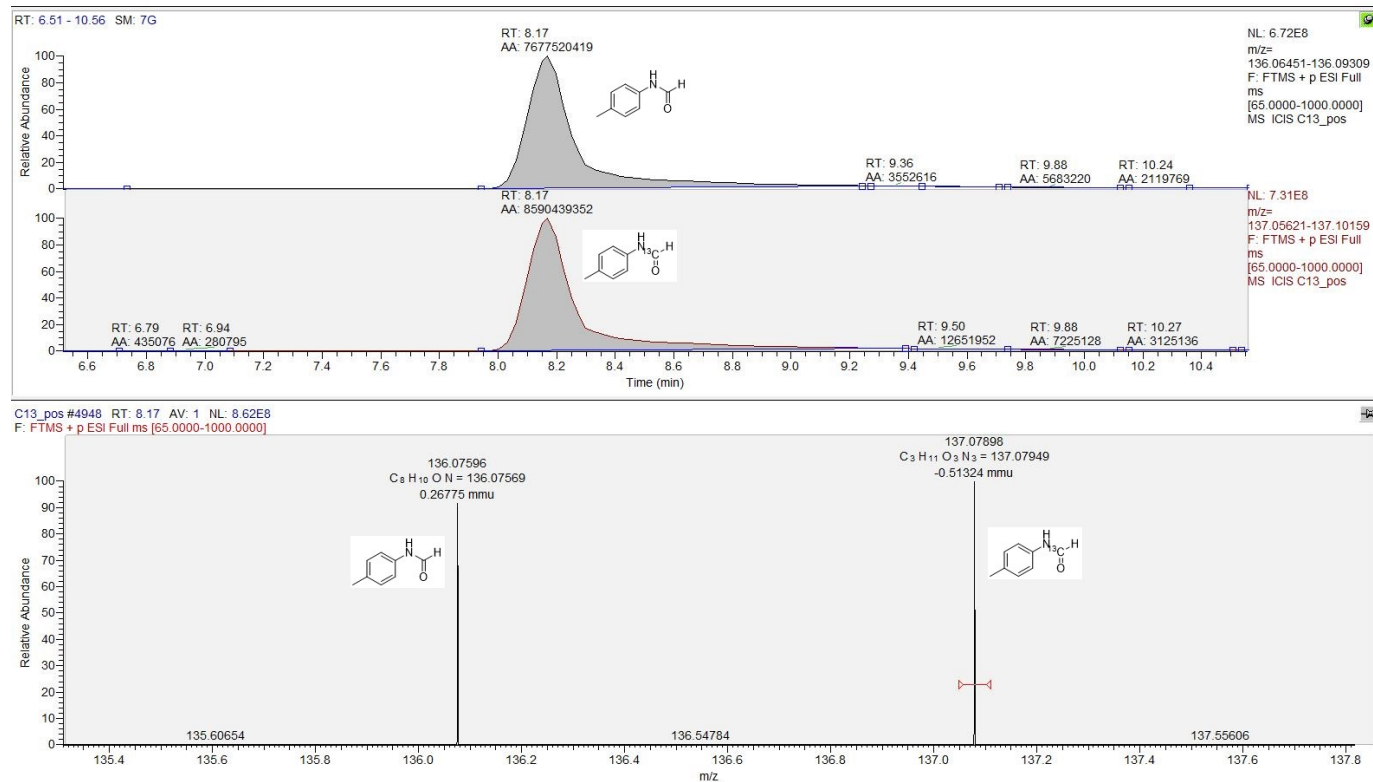


**Figure S7:** LCMS spectrum of N-p-tolylformamide enriched with deuterium (**16D**) i.e. synthesized in DMF-d<sub>7</sub> solvent using NaBH<sub>4</sub> and CO<sub>2</sub> (refer figure 4c in main text).

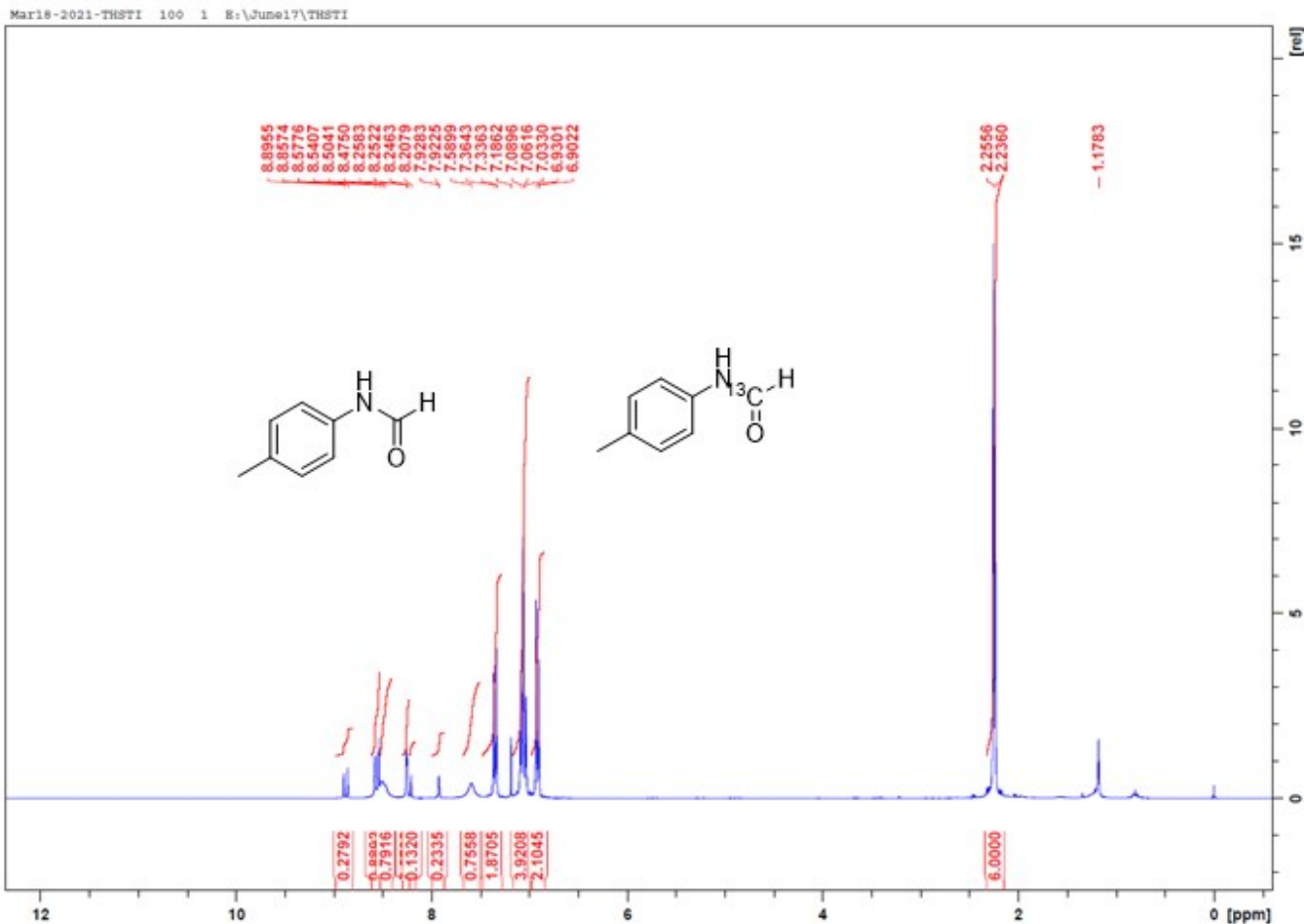




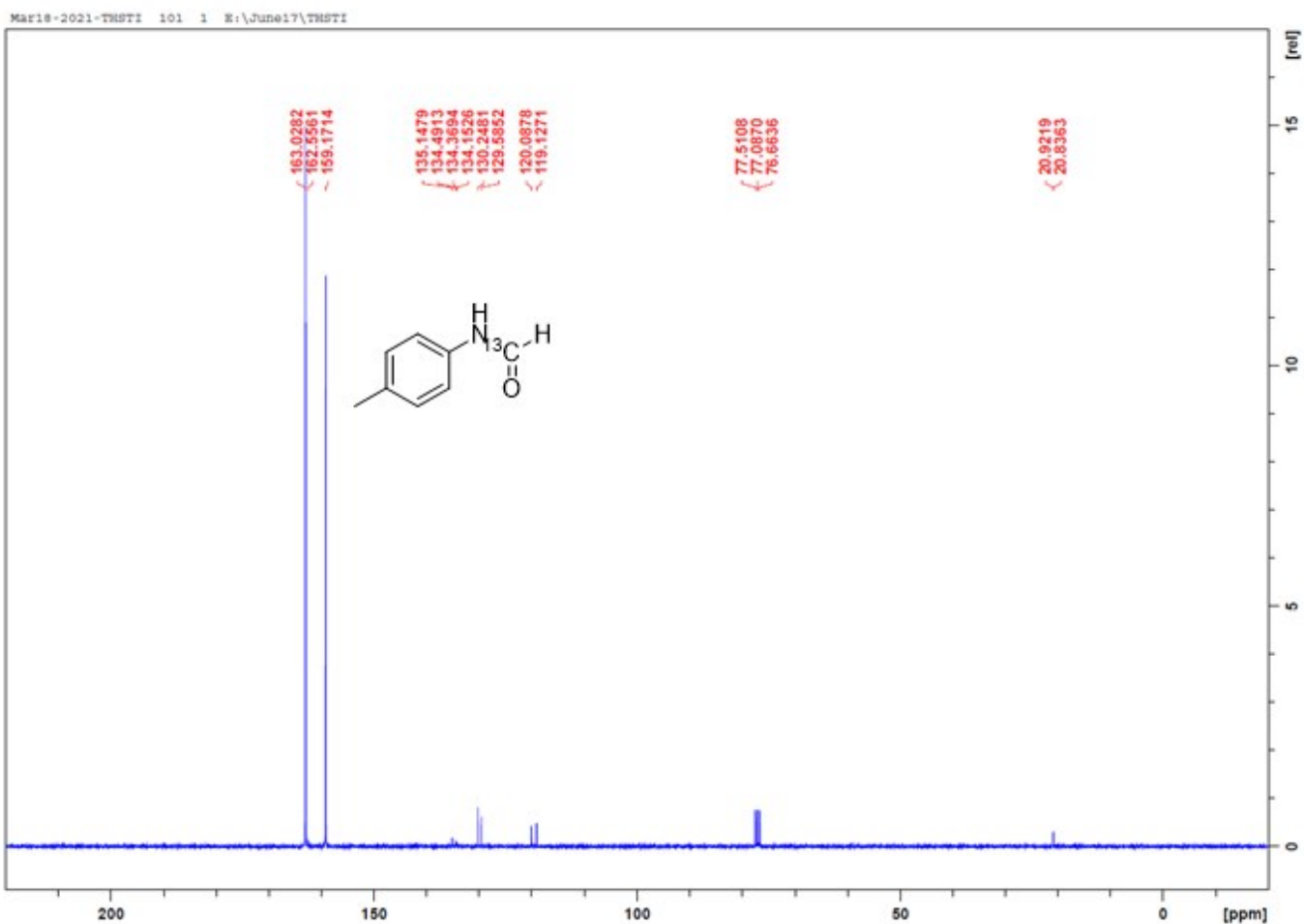
**Figure S8:**  $^1\text{H}$  NMR spectrum of N-p-tolylformamide enriched with deuterium (**16D**) i.e. synthesized in  $\text{DMF-d}_7$  using  $\text{NaBH}_4$  and  $\text{CO}_2$  (refer figure 4c in main text).



**Figure S9:** LCMS spectrum of N-p-tolylformamide enriched with  $^{13}C$  (\*16) i.e. synthesized in DMF using  $NaBH_4$ , and  $^{13}CO_2$  (refer figure 4b in main text).

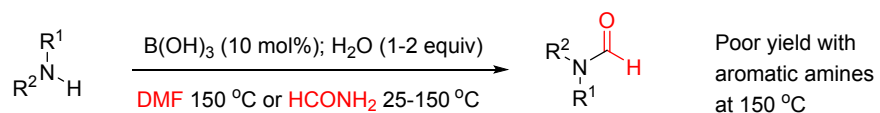


**Figure S10:**  $^1\text{H}$  NMR spectrum of N-p-tolylformamide enriched with  $^{13}\text{C}$  (\***16**) i.e. synthesized in DMF using  $\text{NaBH}_4$ , and  $^{13}\text{CO}_2$  (refer figure 4b in main text).

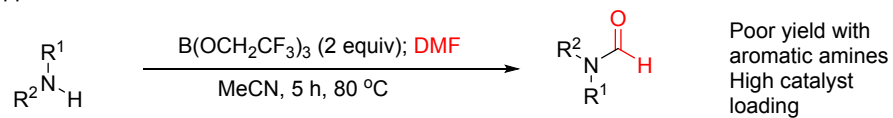


**Figure S11:**  $^{13}\text{C}$  NMR spectrum of N-p-tolylformamide enriched with  $^{13}\text{C}$  (\*16) i.e. synthesized in DMF using  $\text{NaBH}_4$ , and  $^{13}\text{CO}_2$  (refer figure 4b in main text).

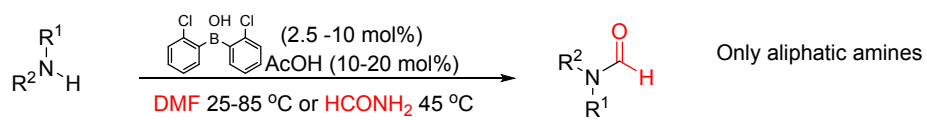
Nguyen *et al.* 2012



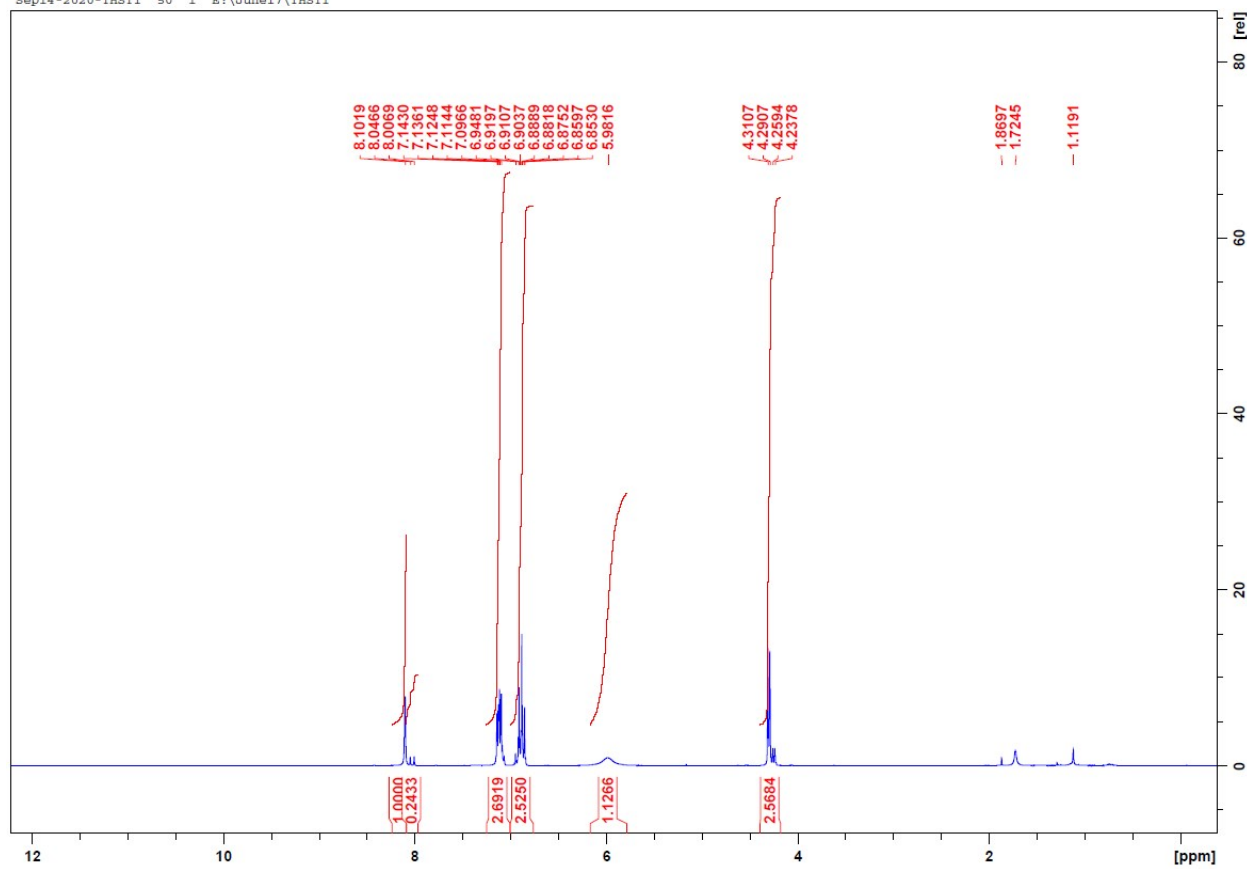
Sheppard *et al.* 2013



Blanchet *et al.* 2016



**Figure S12:** Literature summary on transamidation reactions catalysed by boron based reagents.



**Figure S13:** <sup>1</sup>H NMR spectra of compound 2.

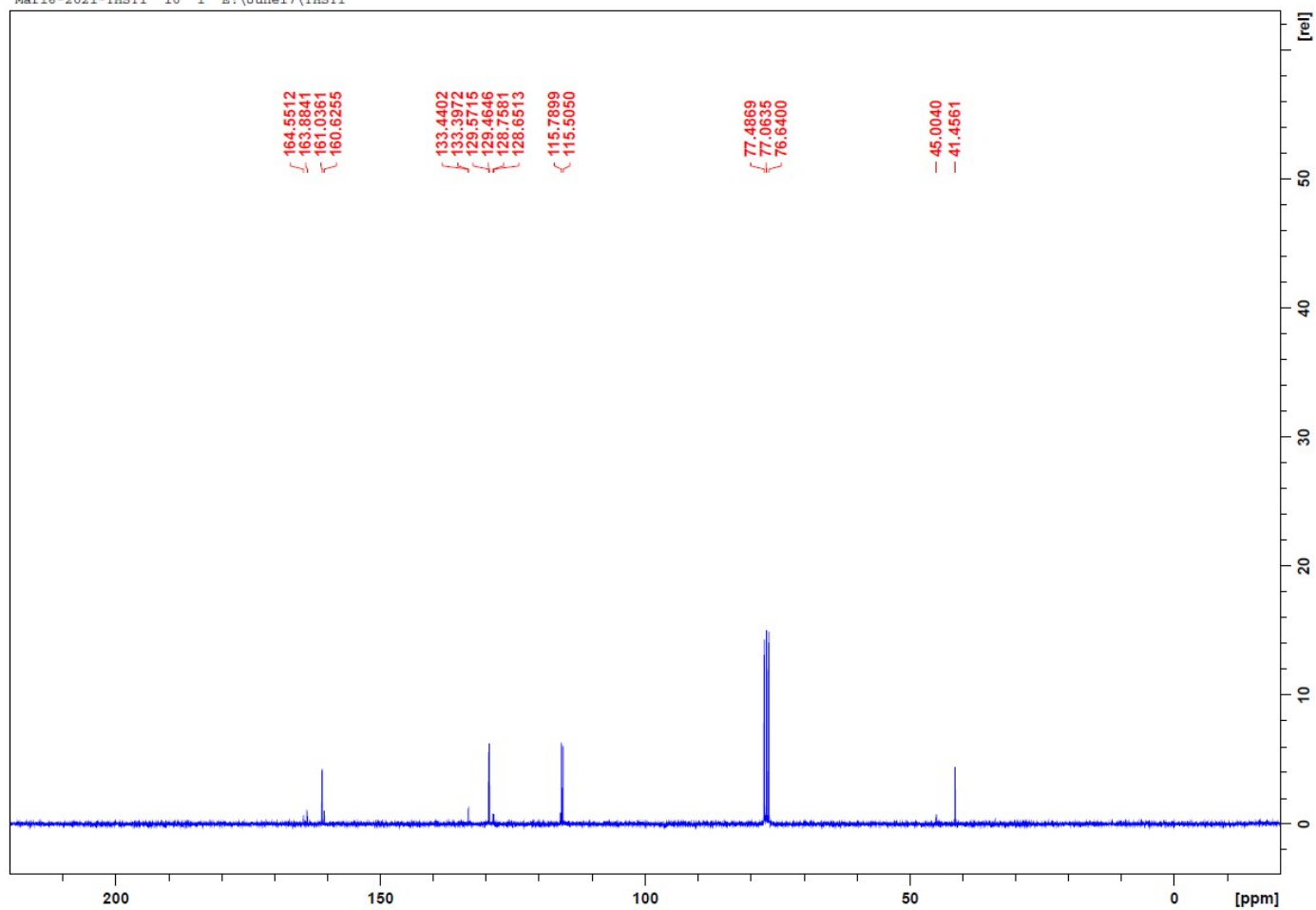


Figure S14: <sup>13</sup>C NMR spectra of compound 2.

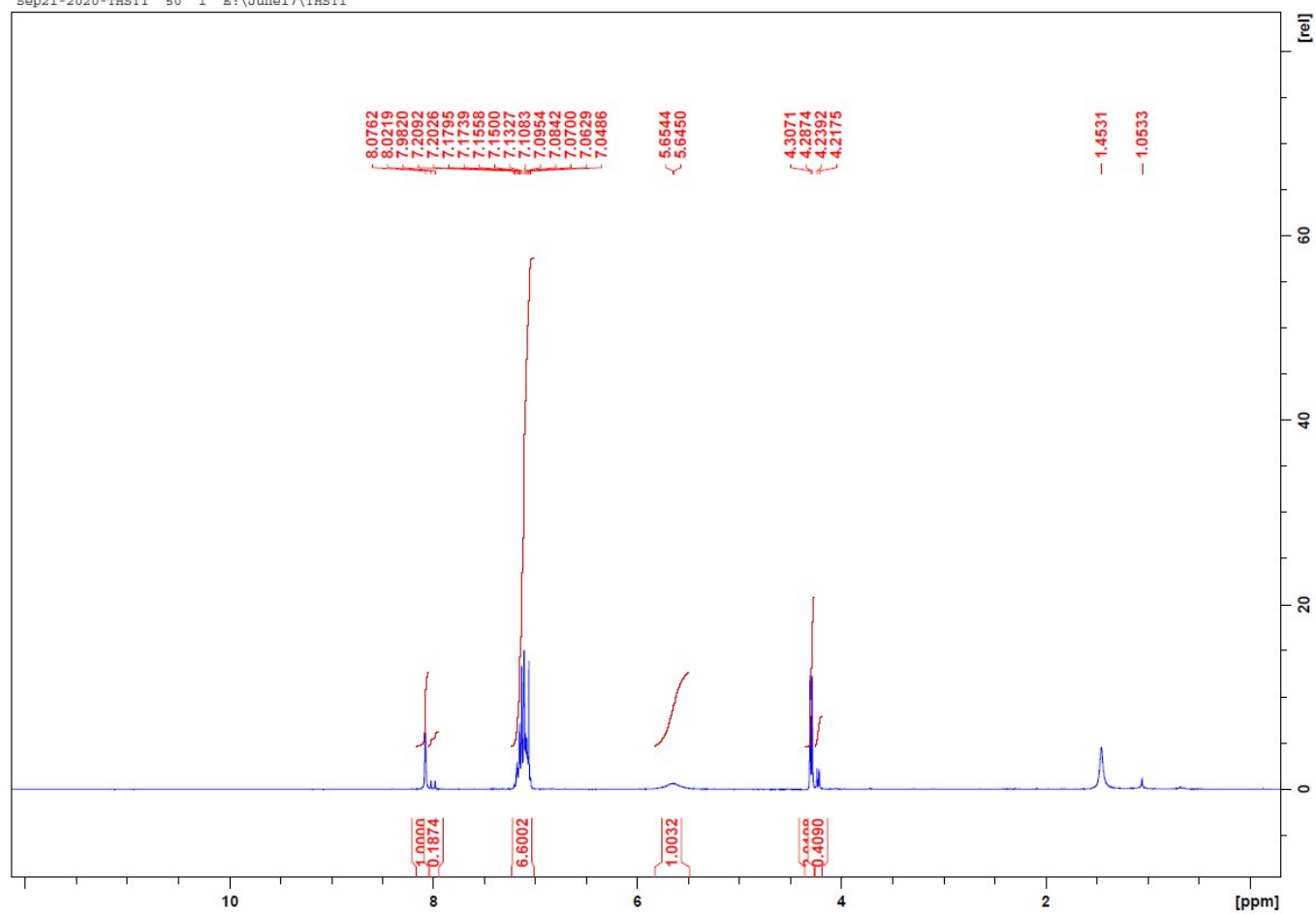


Figure S15: <sup>1</sup>H NMR spectra of compound 3.



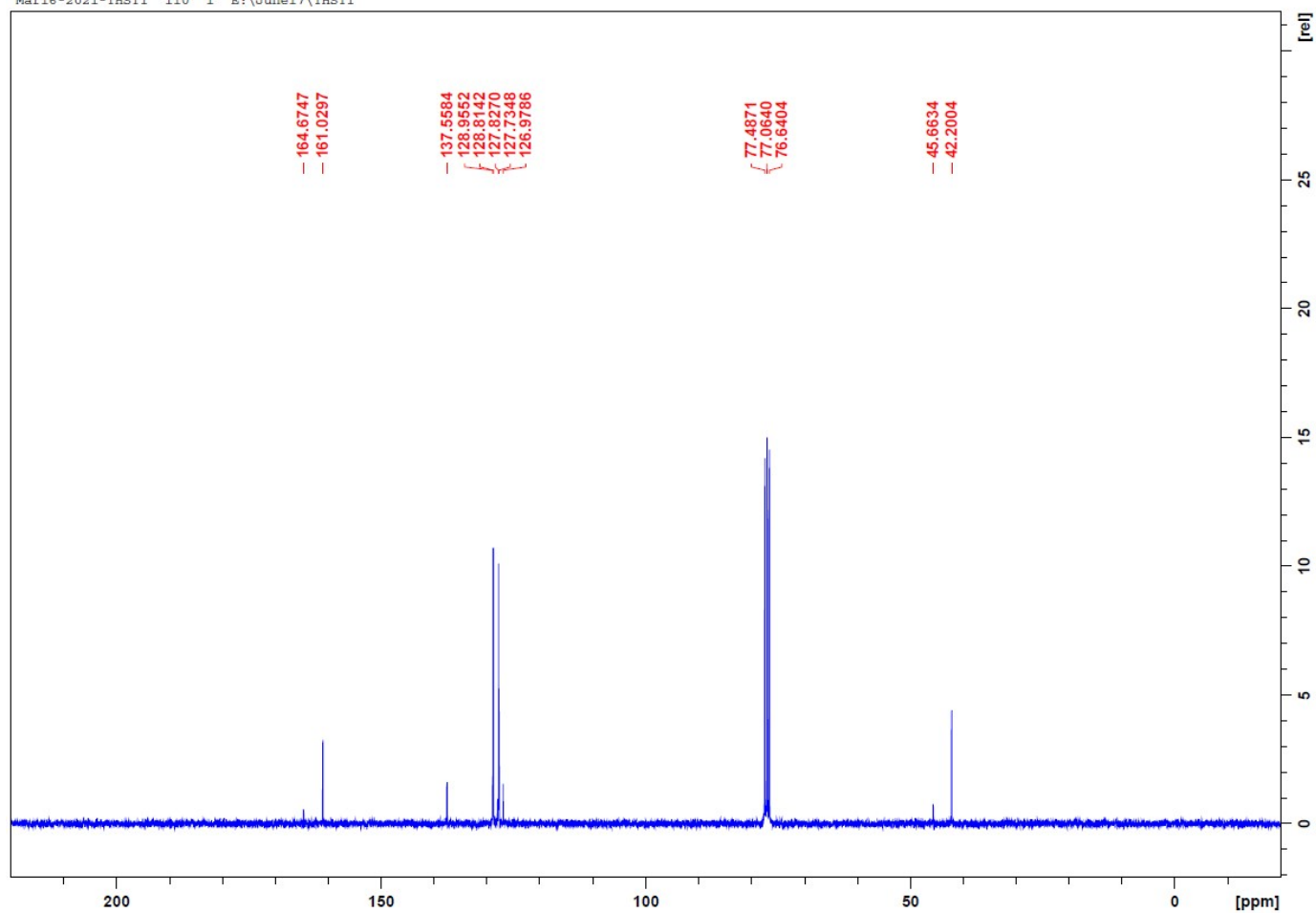


Figure S16:  $^{13}\text{C}$  NMR spectra of compound 3.

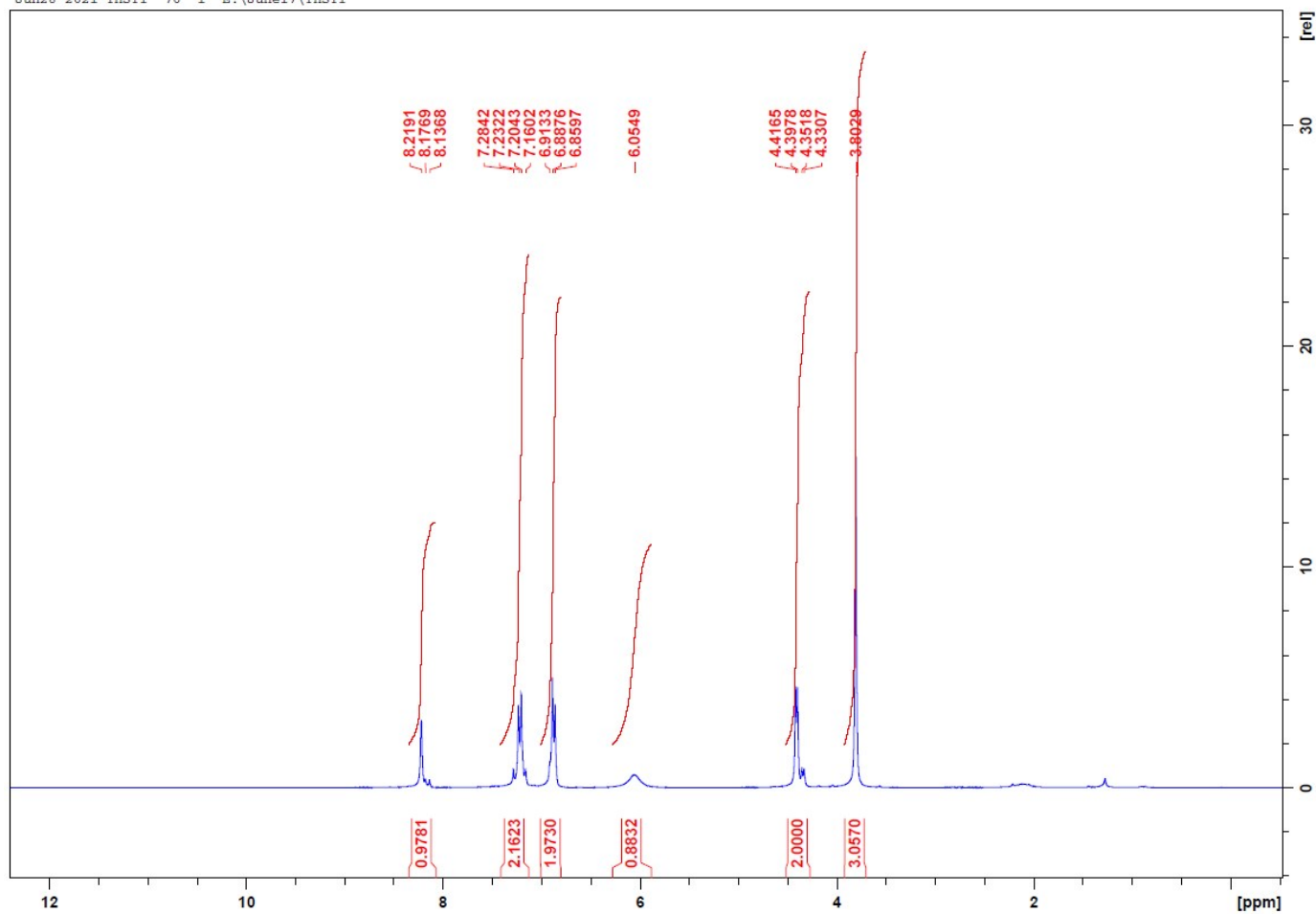


Figure S17: <sup>1</sup>H NMR spectra of compound 4.

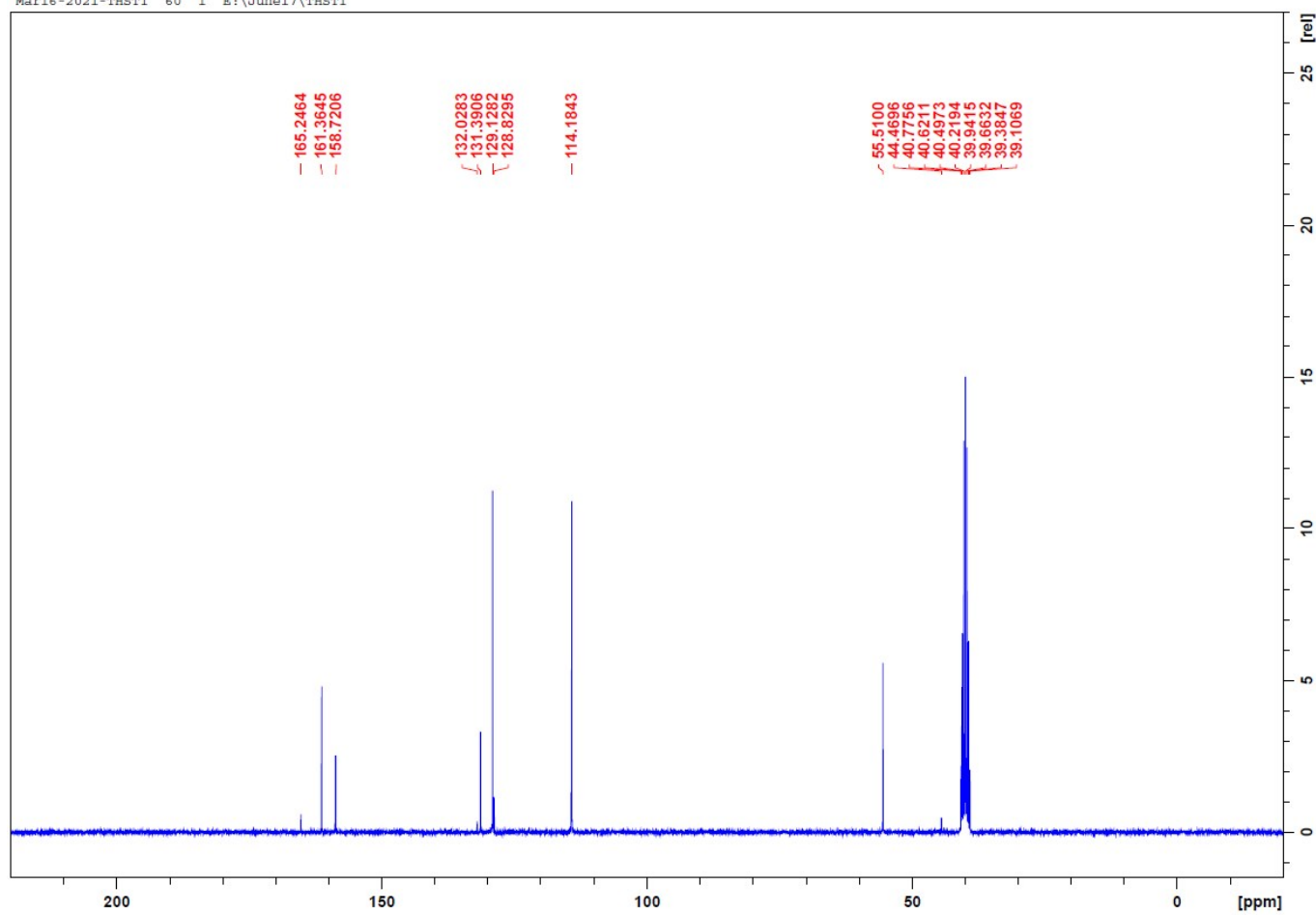


Figure S18:  $^{13}\text{C}$  NMR spectra of compound 4.

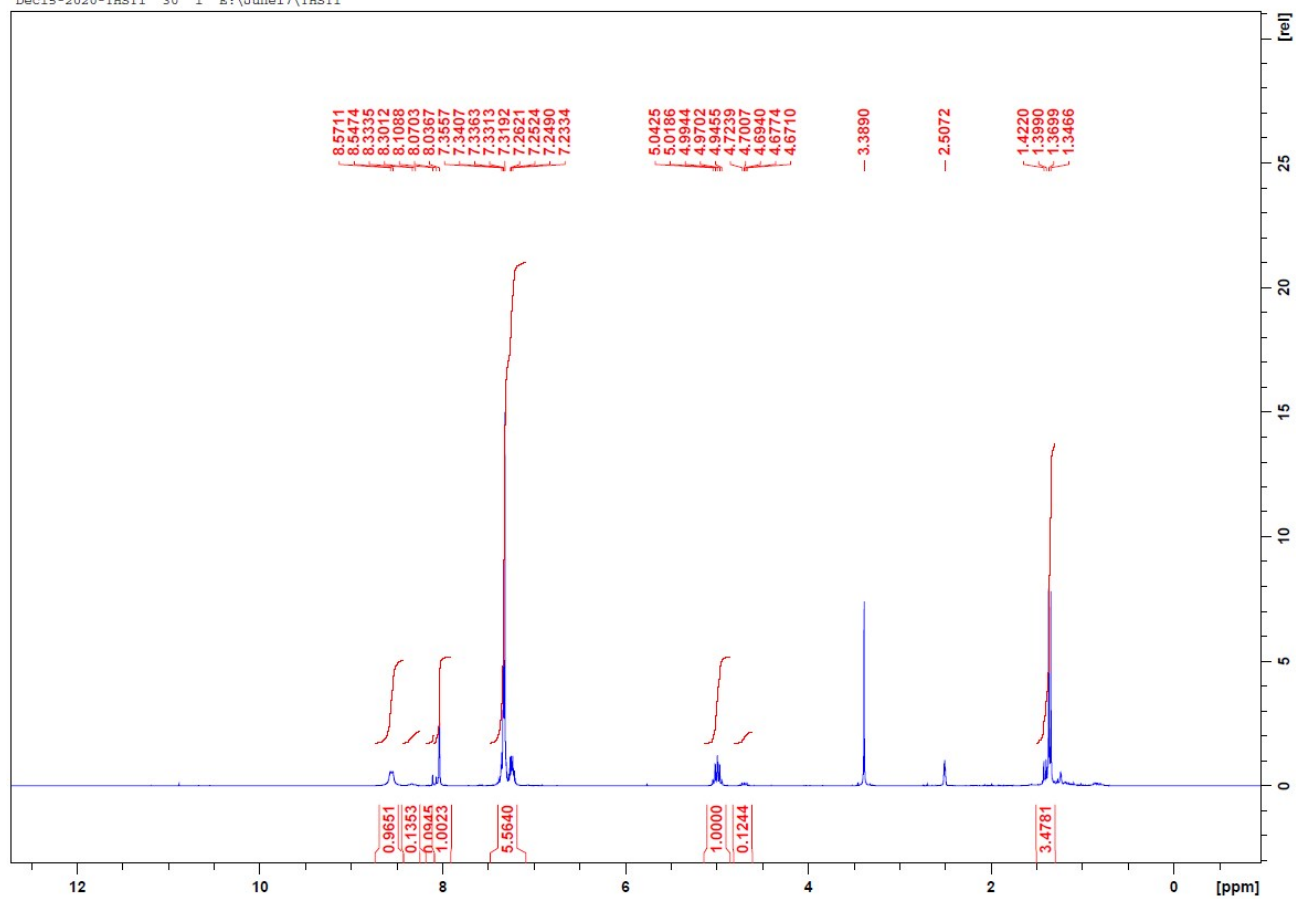


Figure S19: <sup>1</sup>H NMR spectra of compound 5.

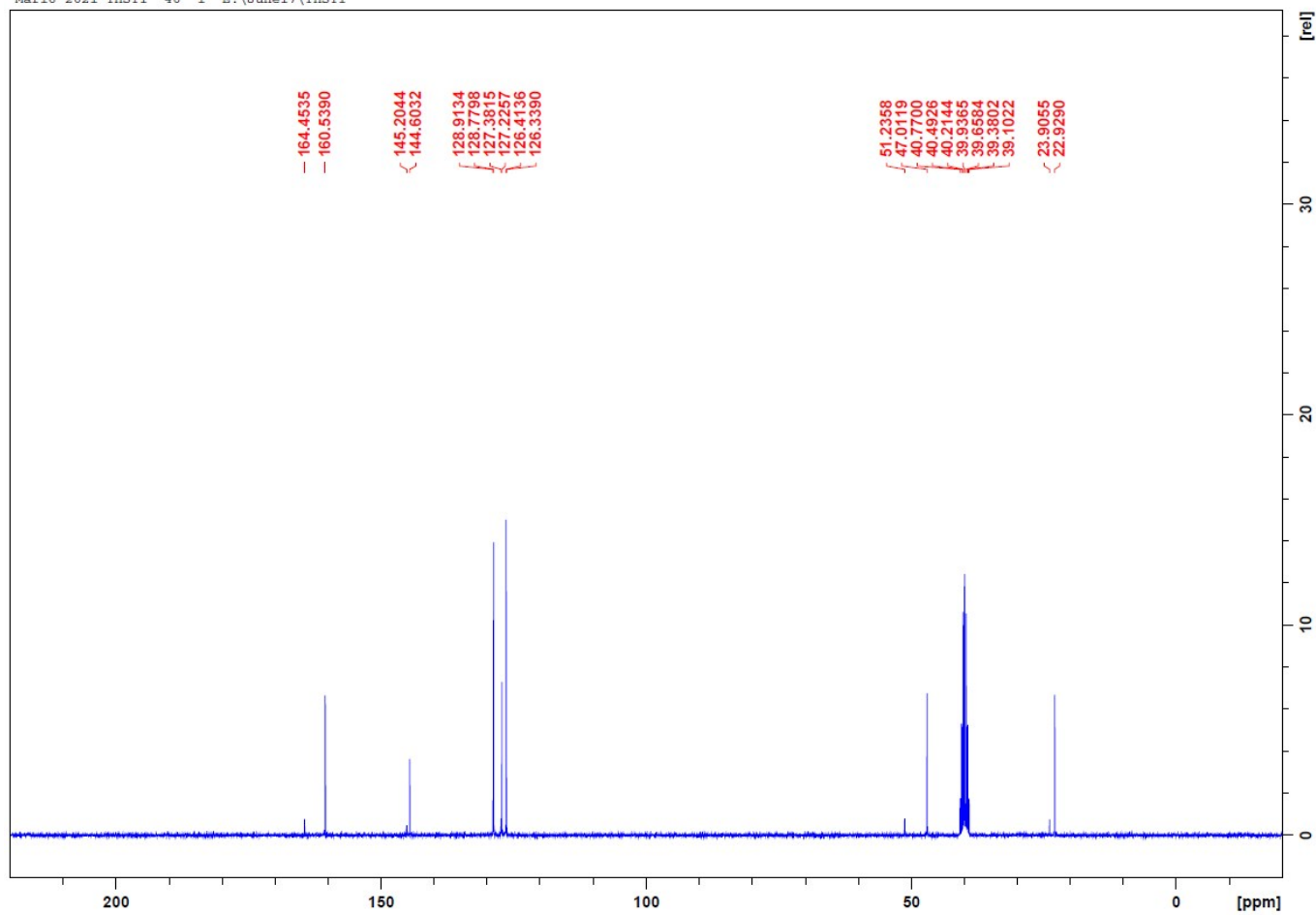


Figure S20:  $^{13}\text{C}$  NMR spectra of compound 5.

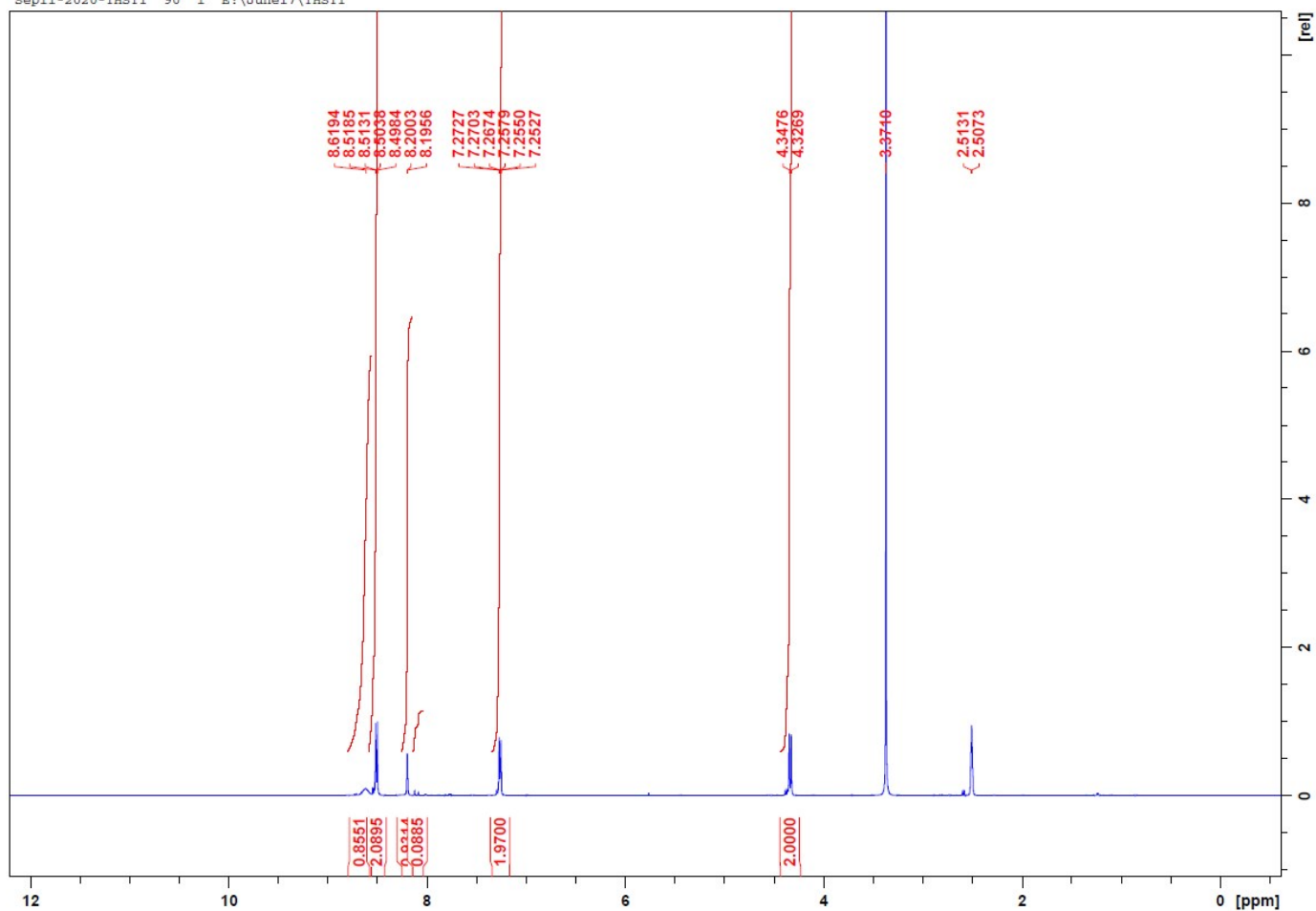


Figure S21: <sup>1</sup>H NMR spectra of compound 6.

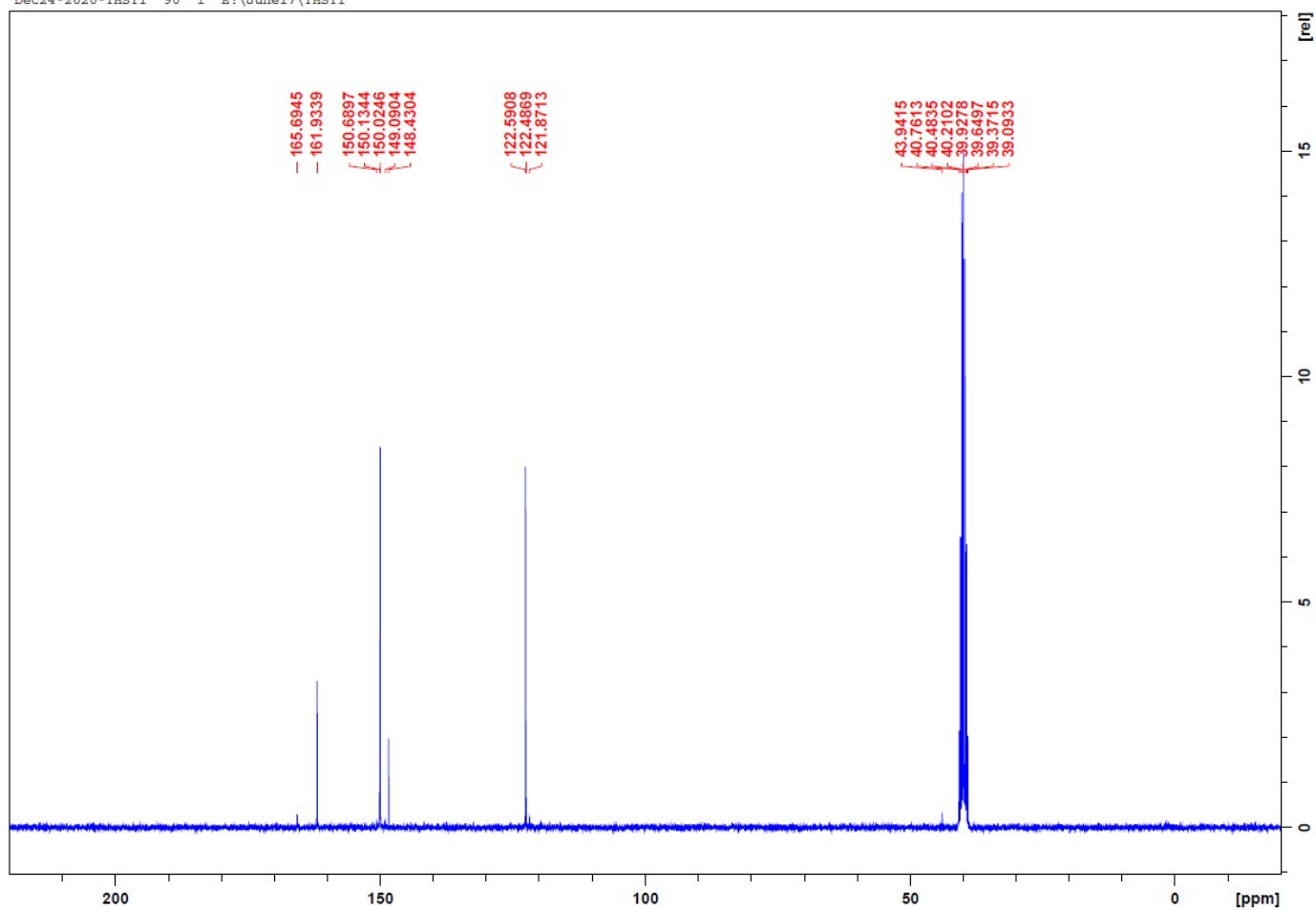


Figure S22:  $^{13}\text{C}$  NMR spectra of compound 6.

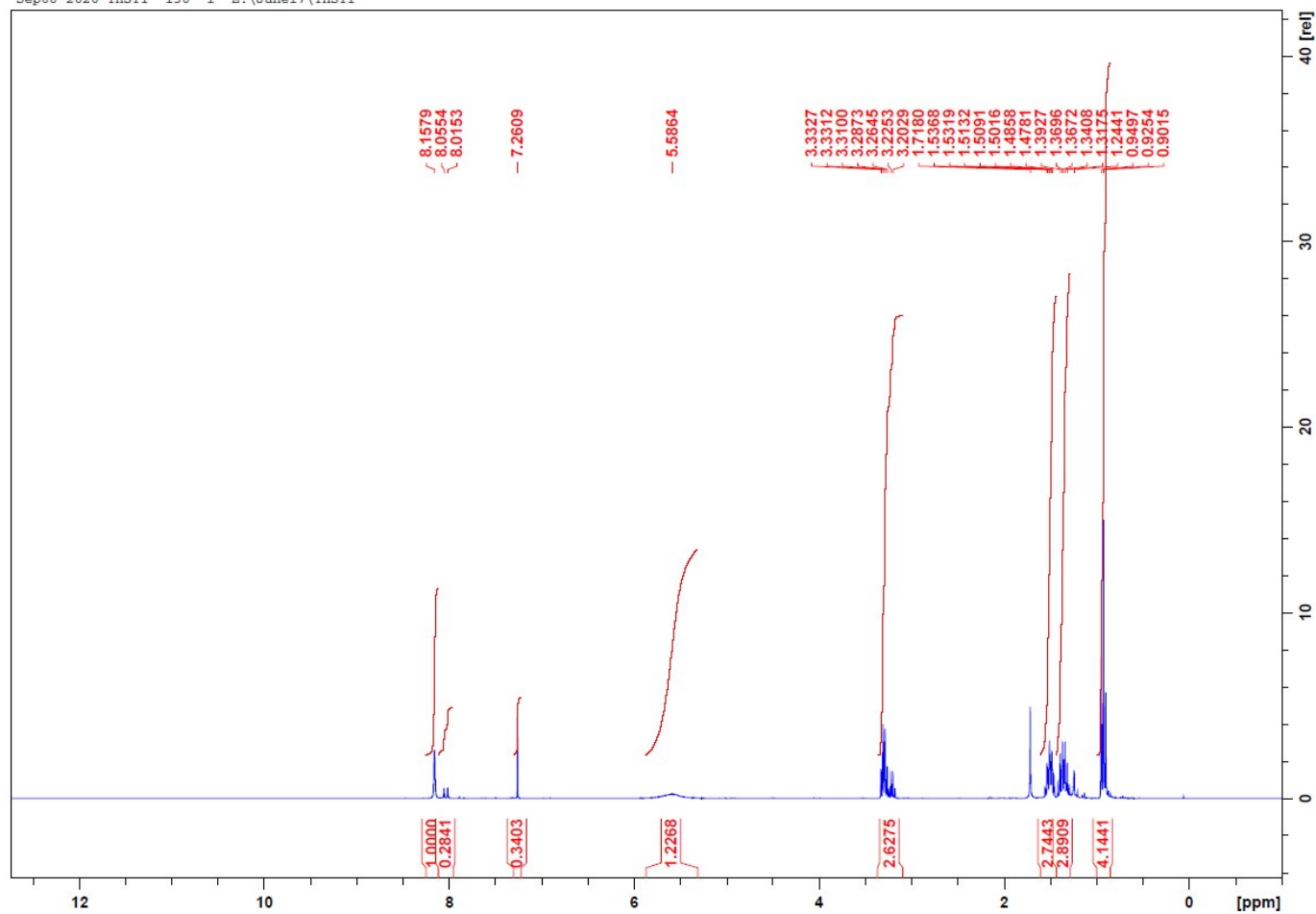


Figure S23: <sup>1</sup>H NMR spectra of compound 7.



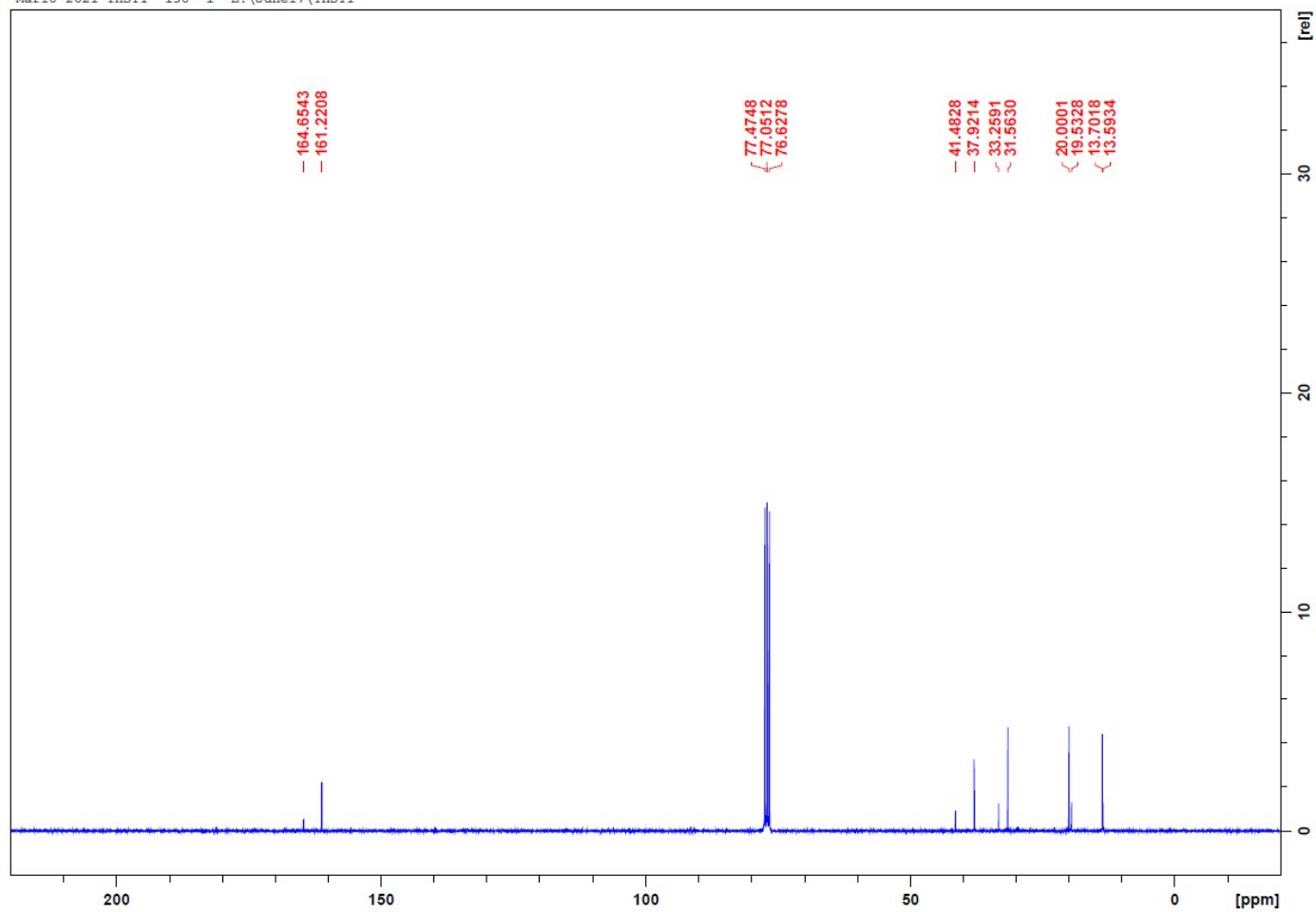


Figure S24: <sup>13</sup>C NMR spectra of compound 7.

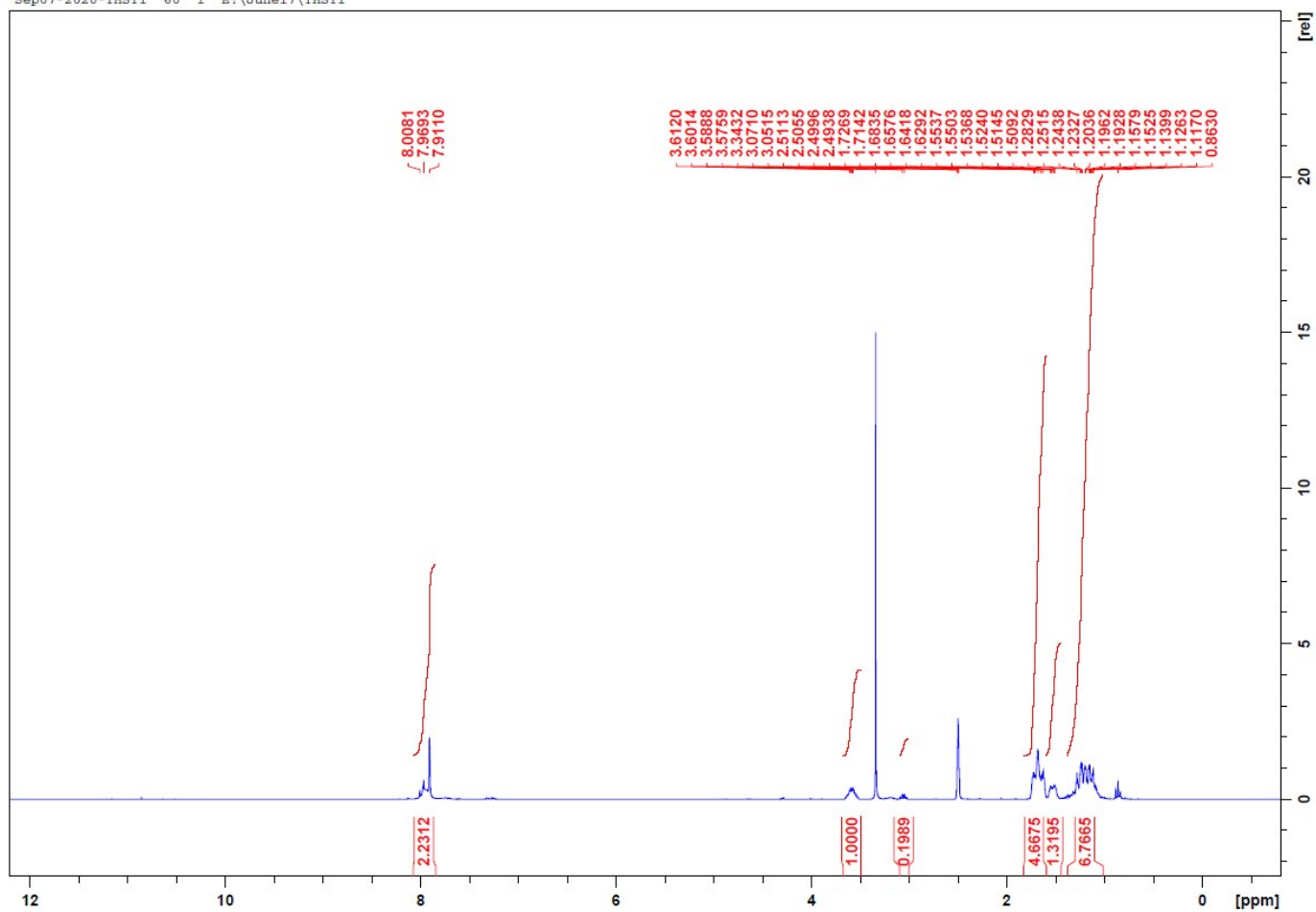


Figure S25: <sup>1</sup>H NMR spectra of compound **8**.

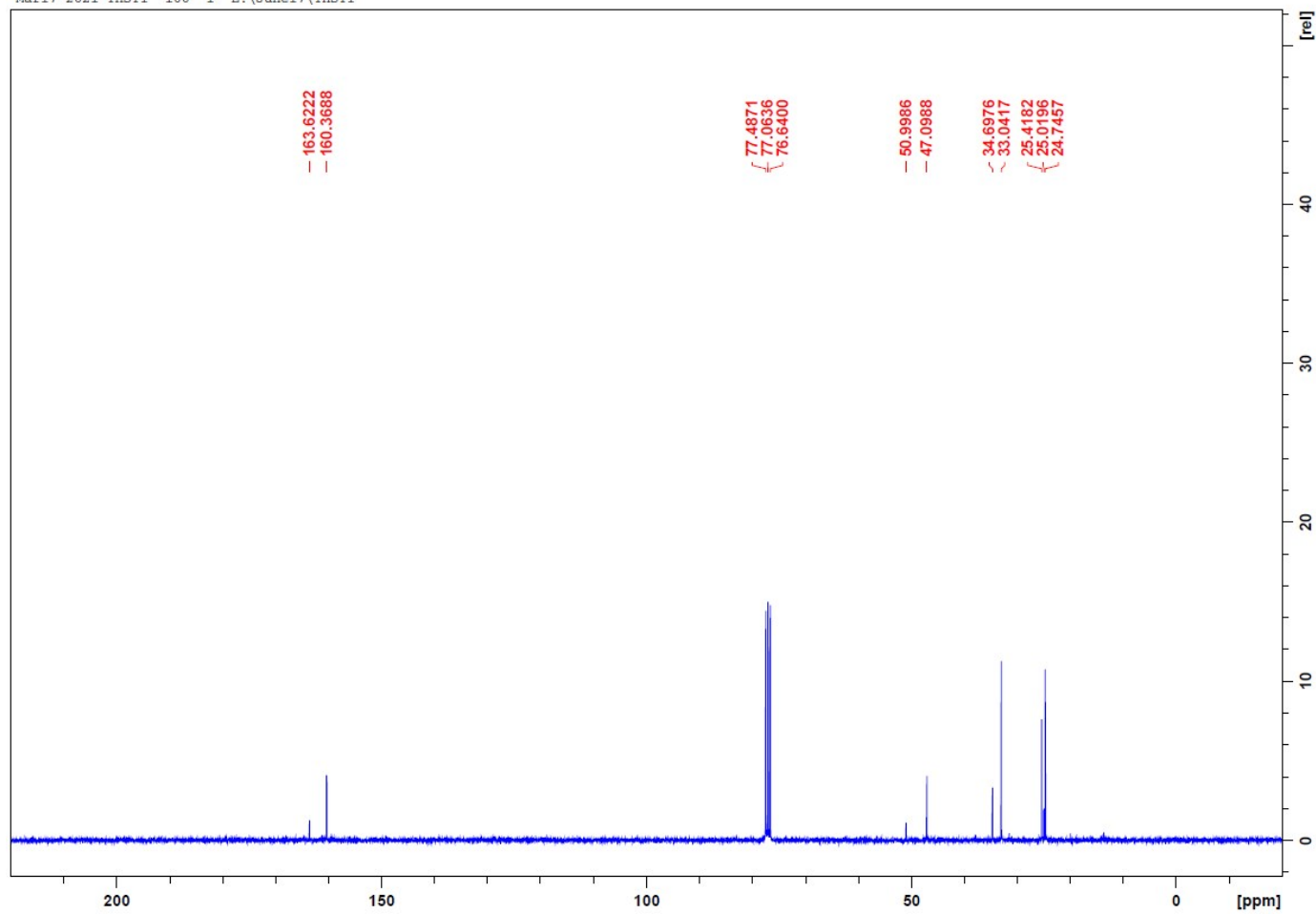


Figure S26:  $^{13}\text{C}$  NMR spectra of compound 8.

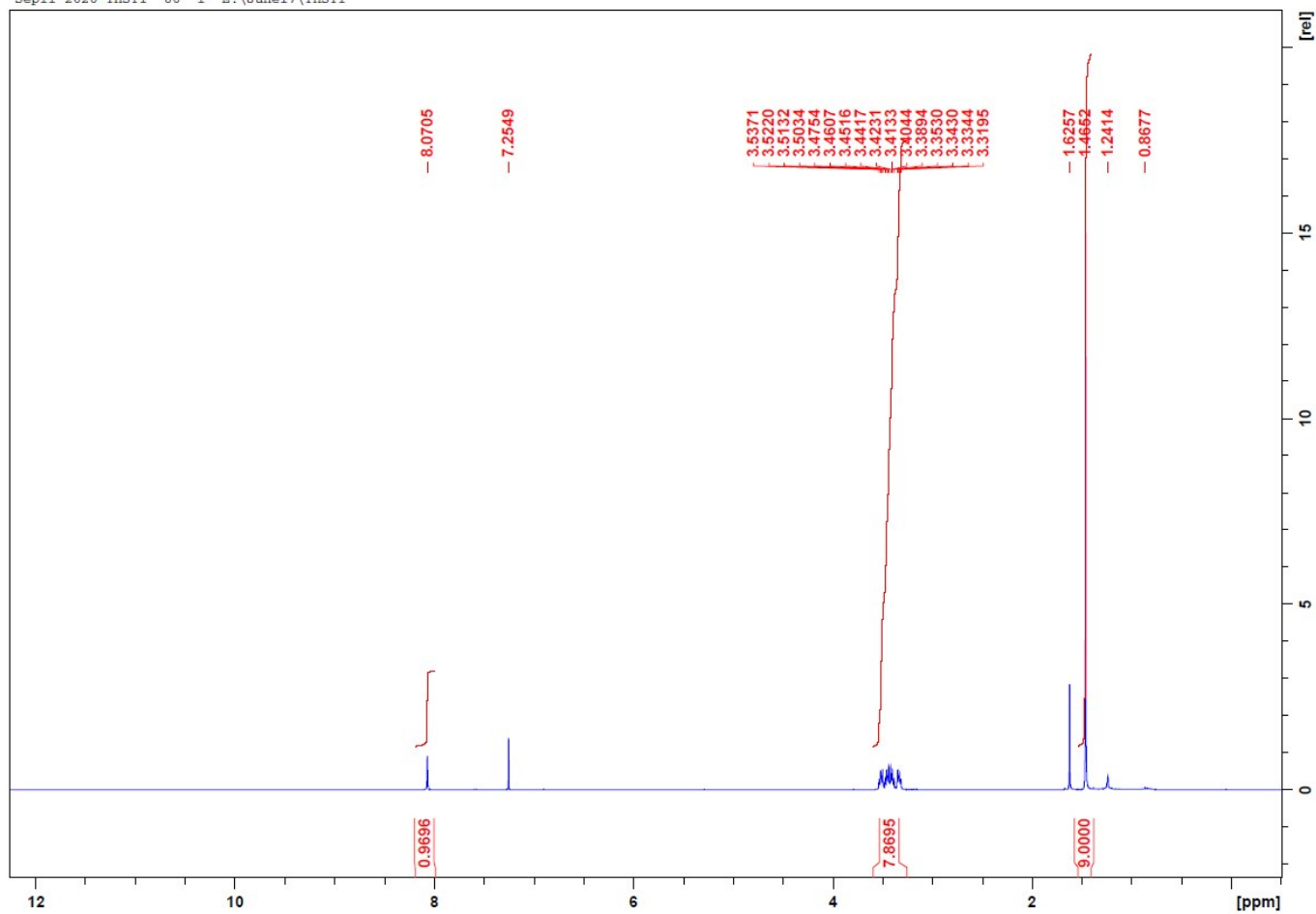
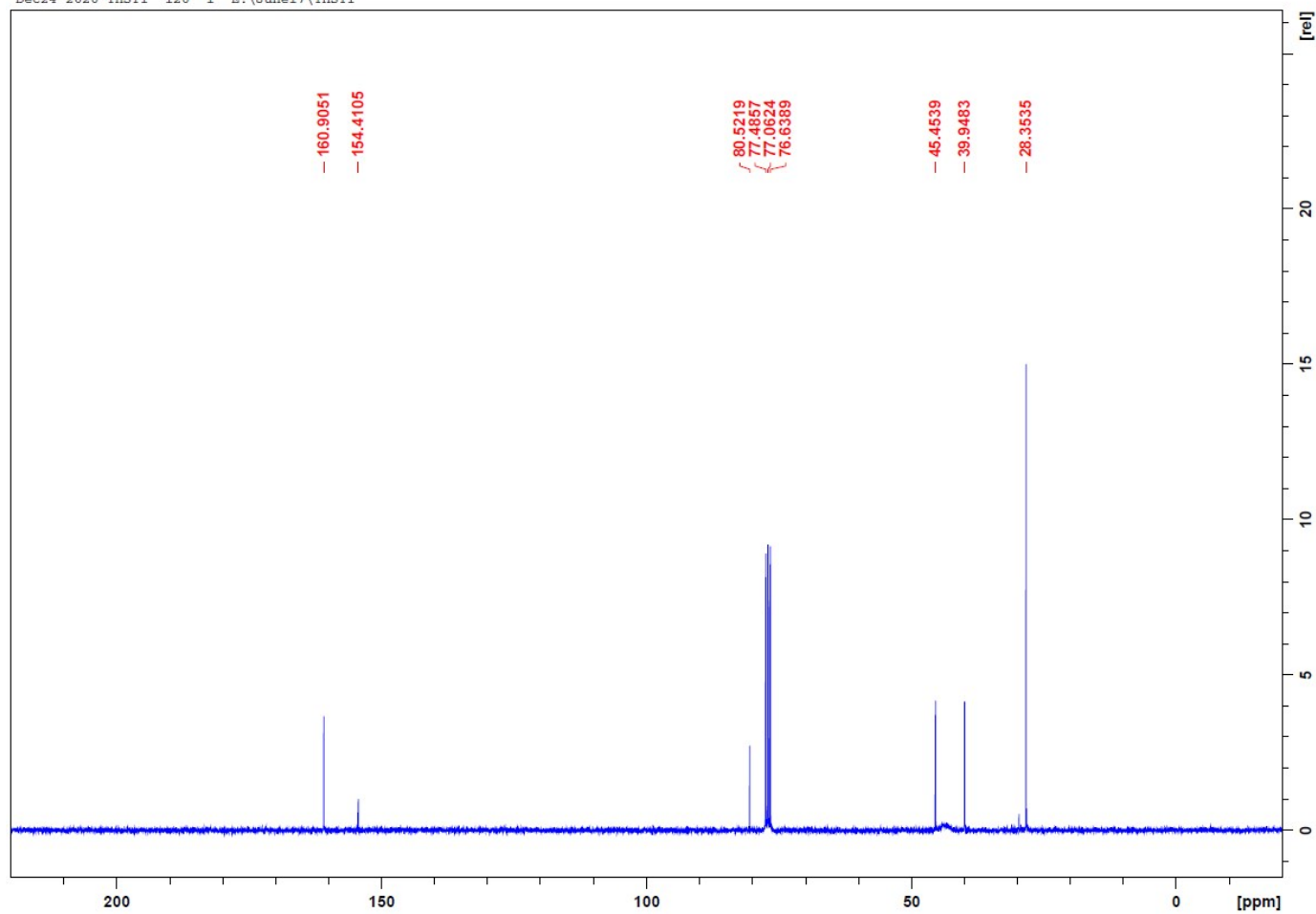


Figure S27: <sup>1</sup>H NMR spectra of compound 9.



**Figure S28:** <sup>13</sup>C NMR spectra of compound **9**.

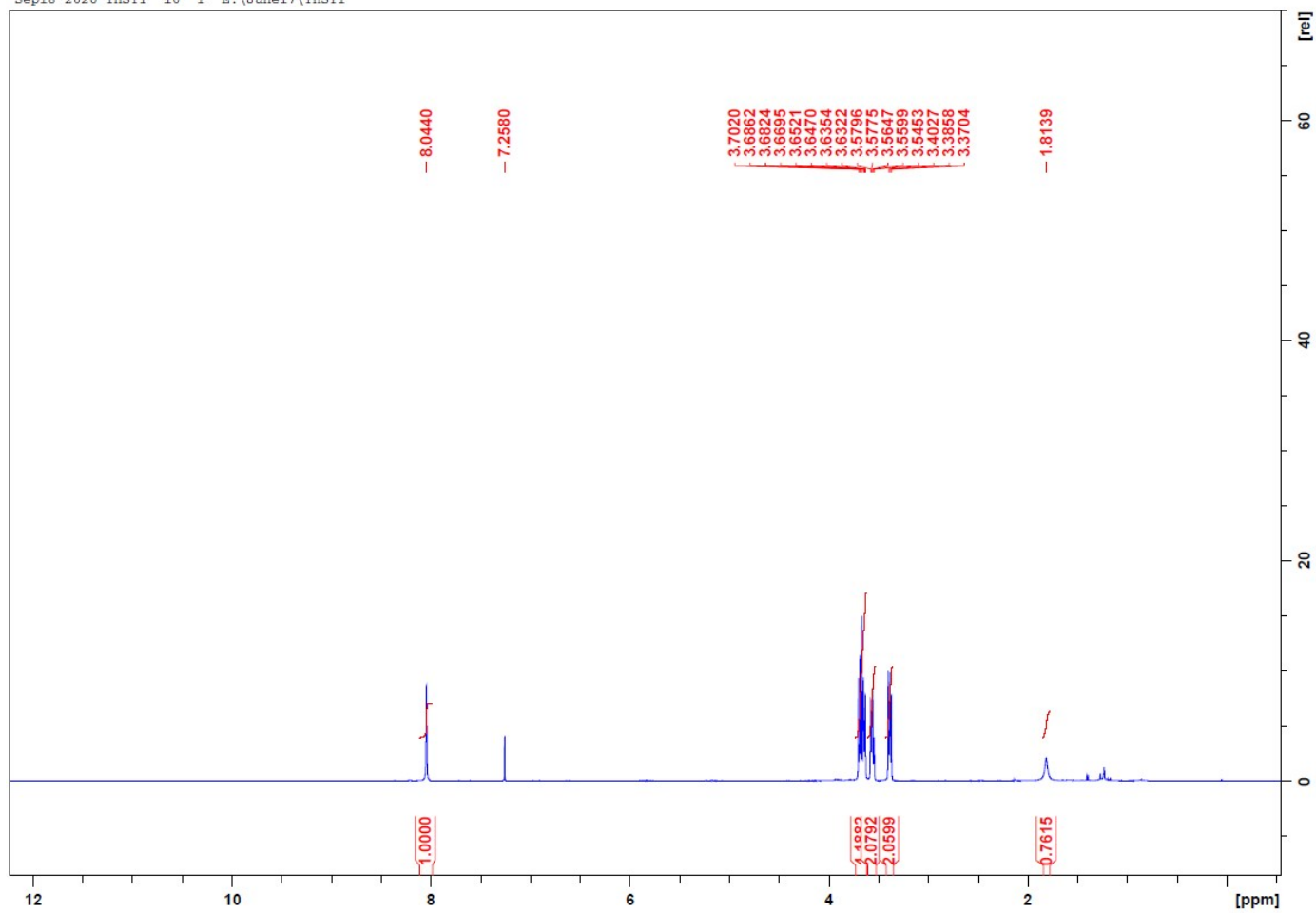


Figure S29: <sup>1</sup>H NMR spectra of compound 10.

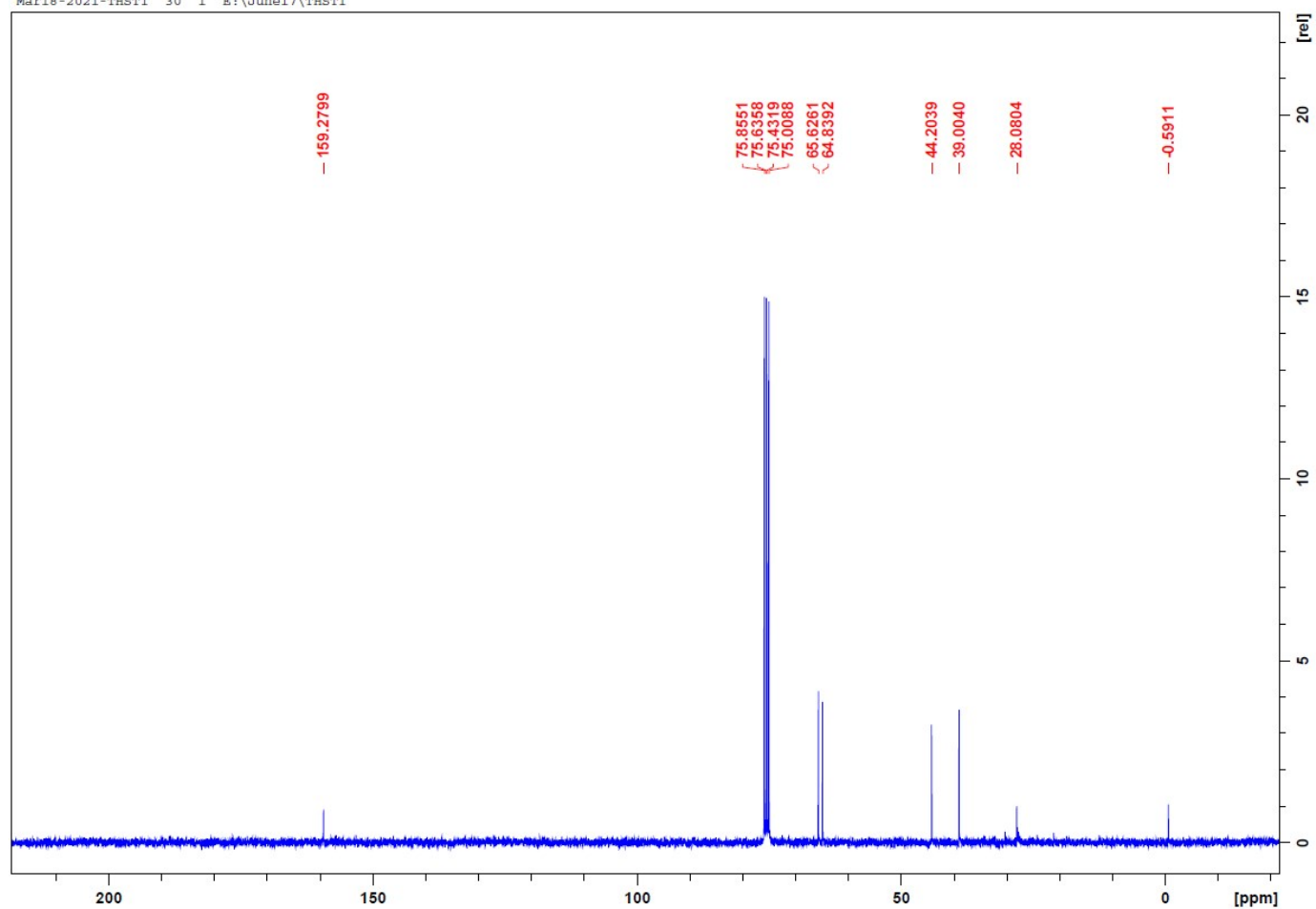


Figure S30: <sup>13</sup>C NMR spectra of compound 10.

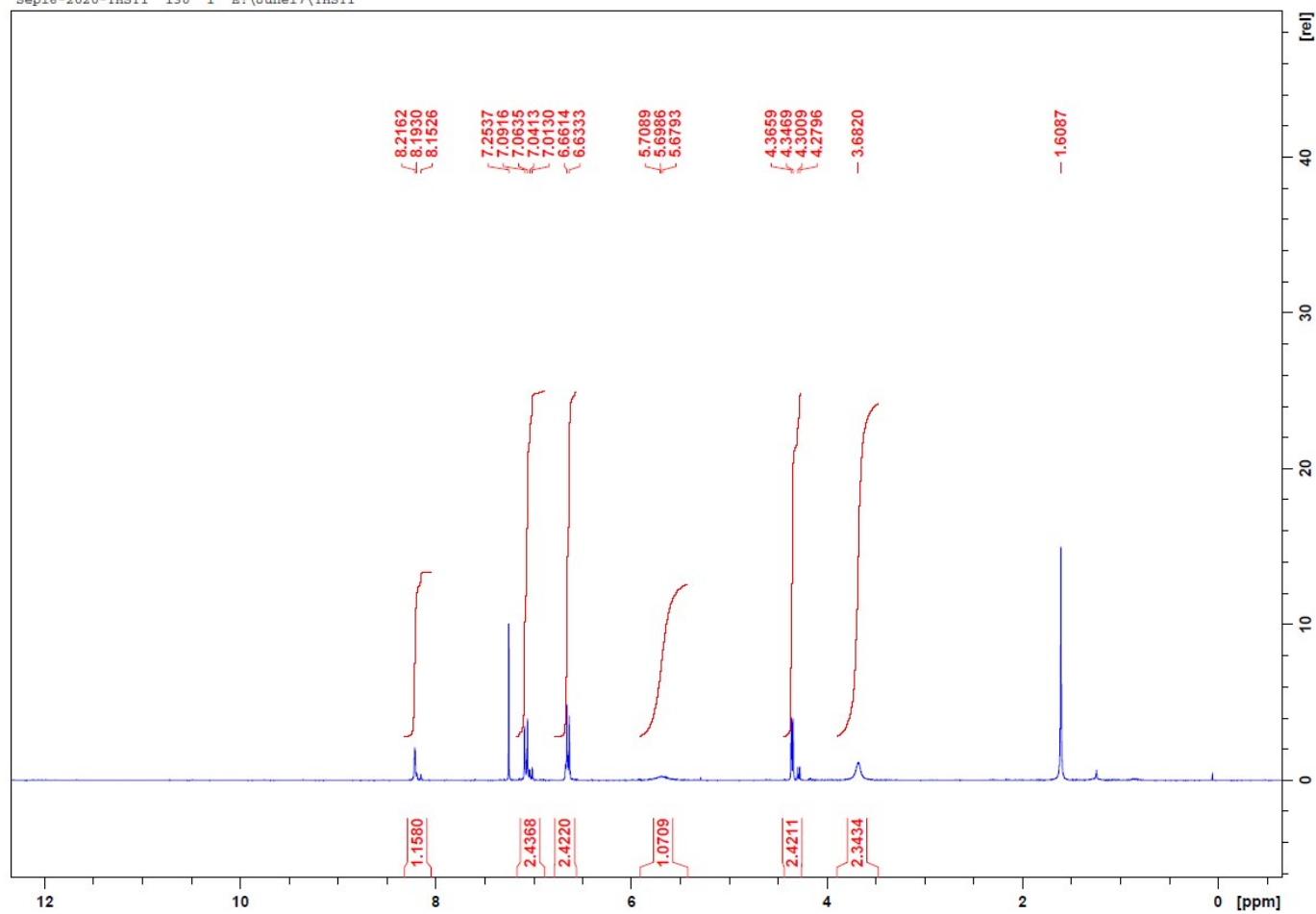
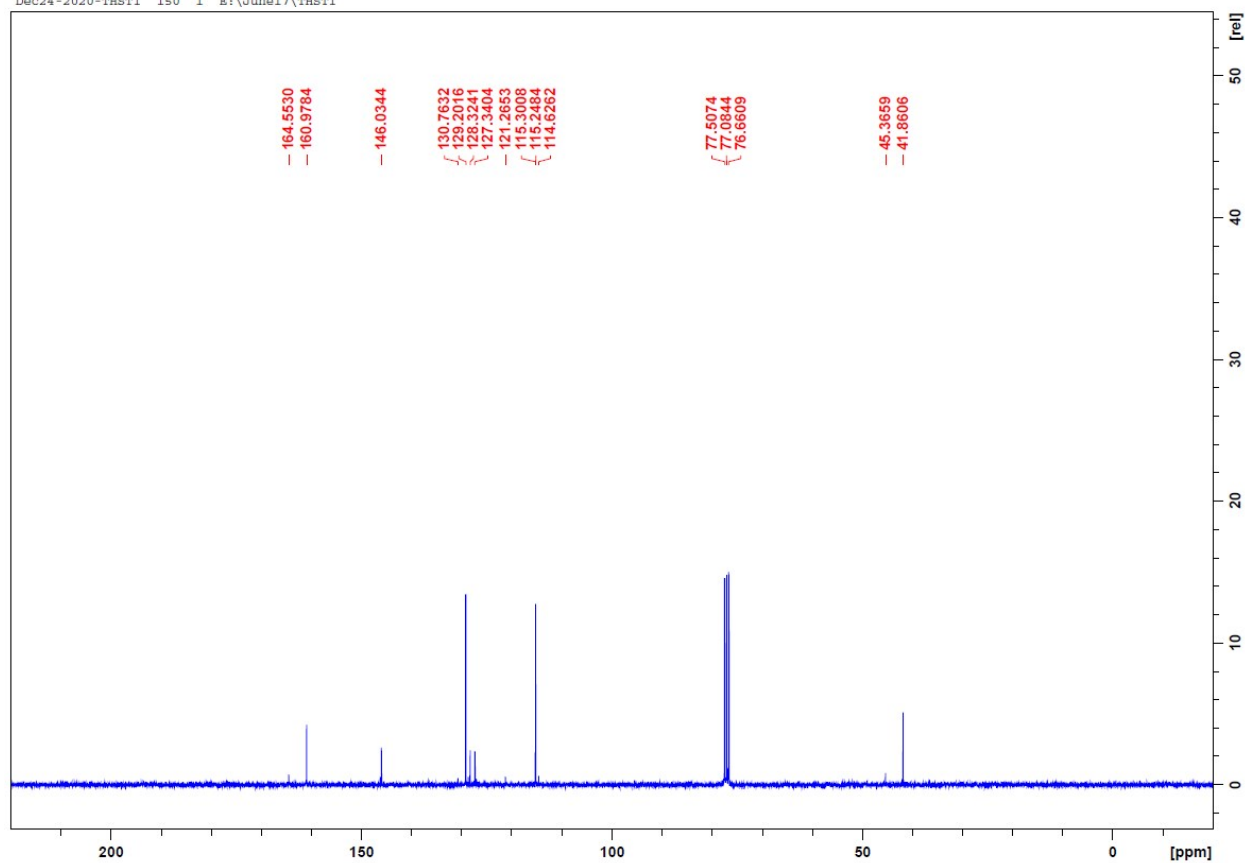


Figure S31: <sup>1</sup>H NMR spectra of compound 11.





**Figure S32:**  $^{13}\text{C}$  NMR spectra of compound **11**.

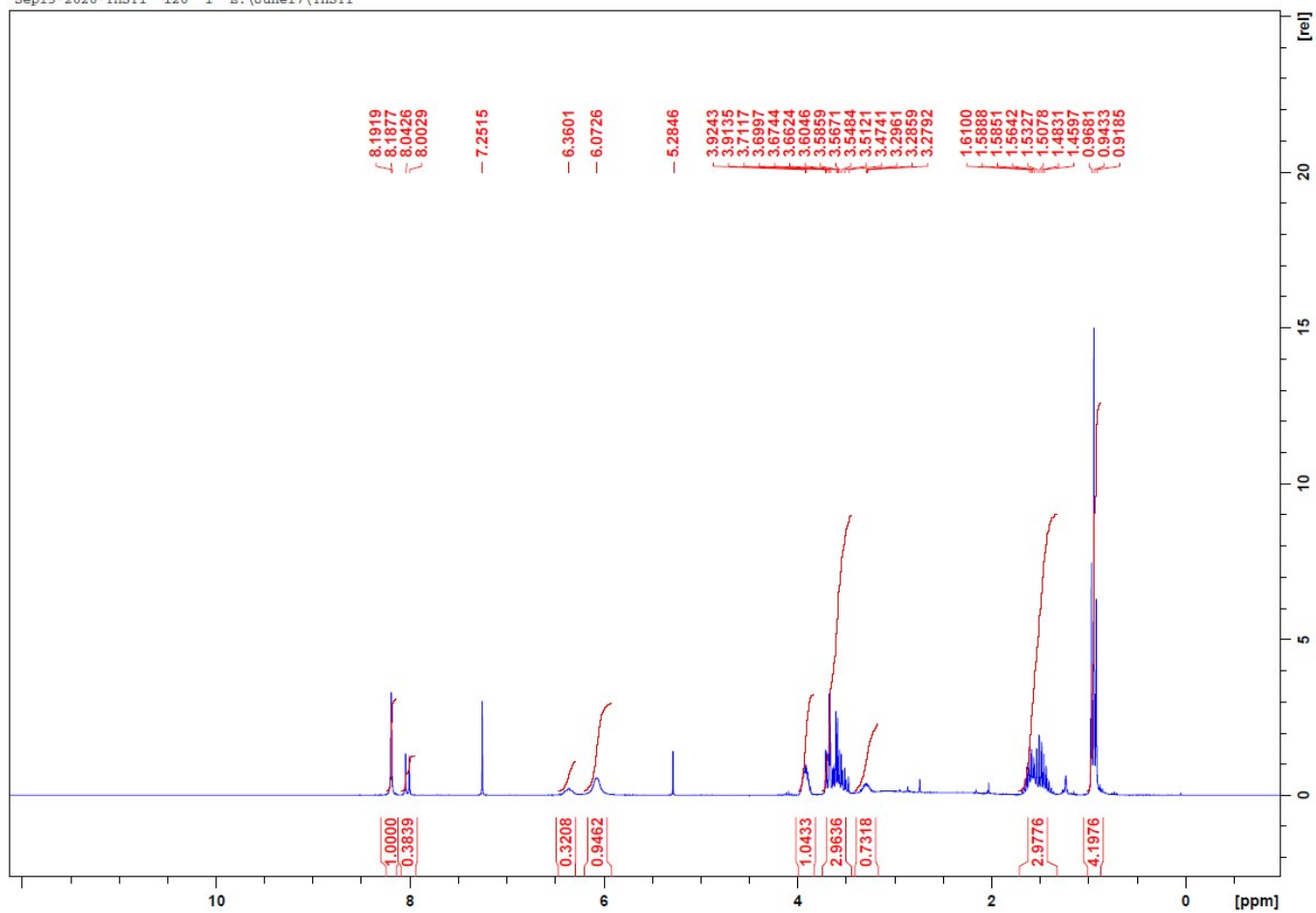
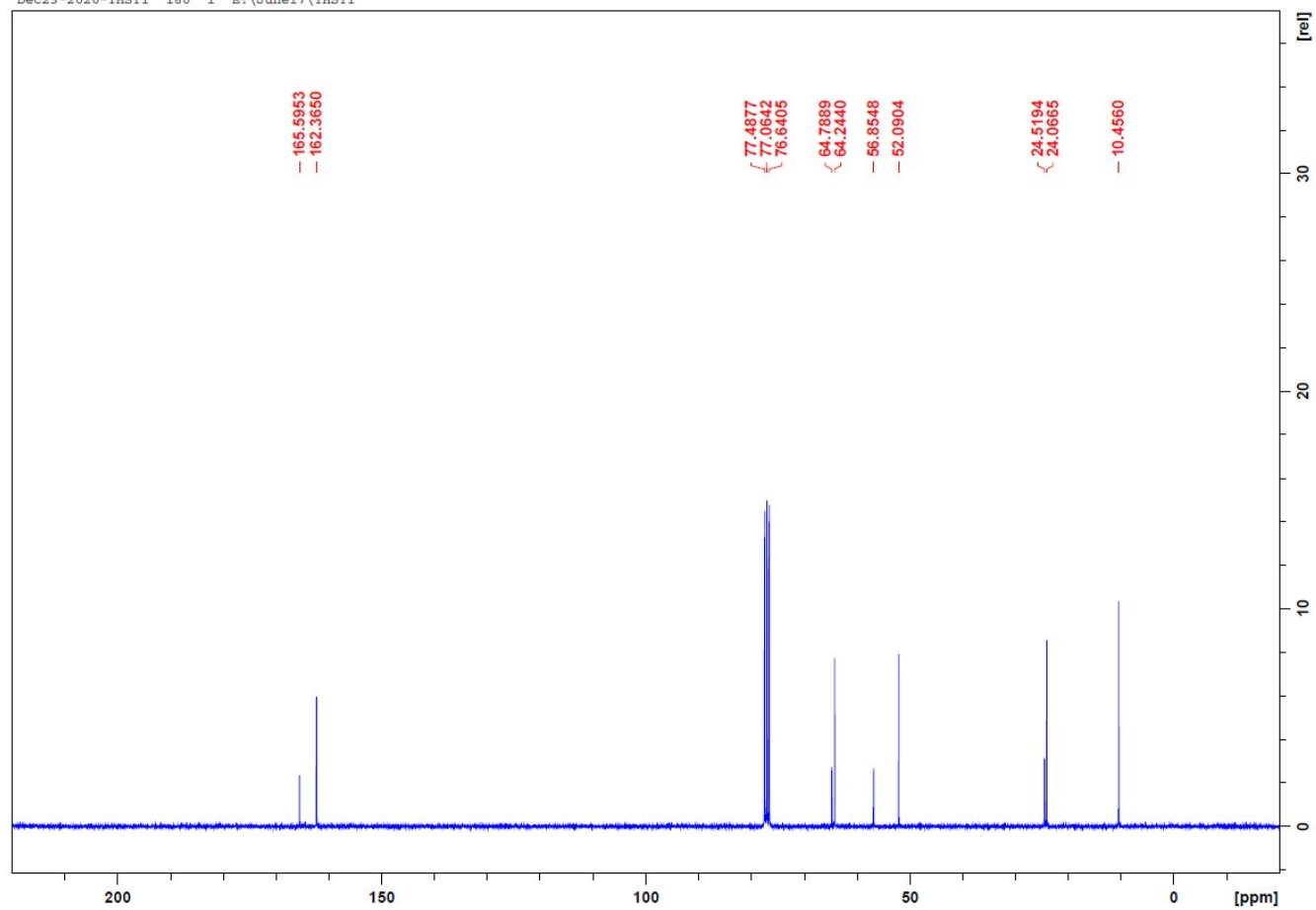


Figure S33: <sup>1</sup>H NMR spectra of compound 12.



**Figure S34:** <sup>13</sup>C NMR spectra of compound 12.

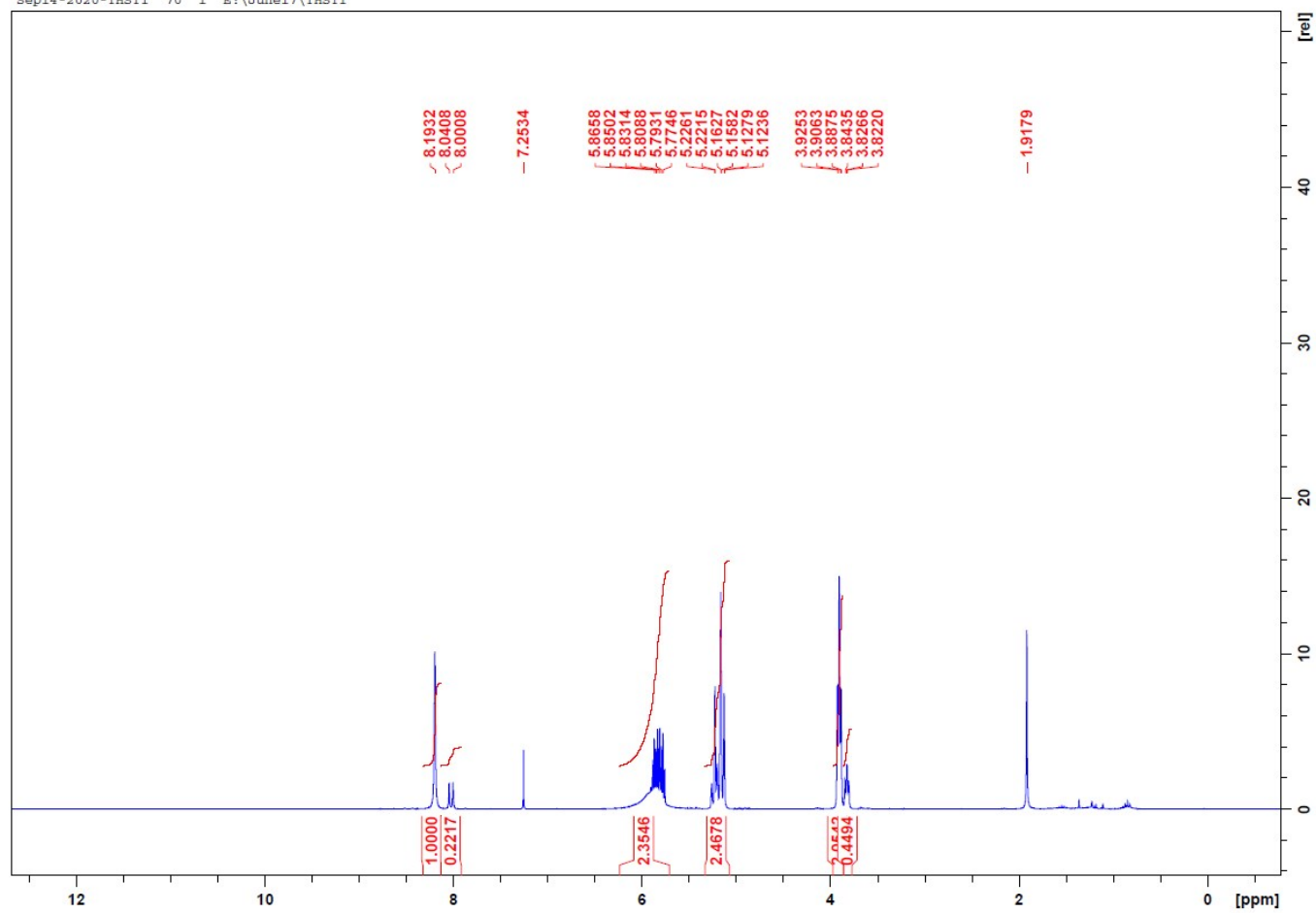


Figure S35: <sup>1</sup>H NMR spectra of compound 13.

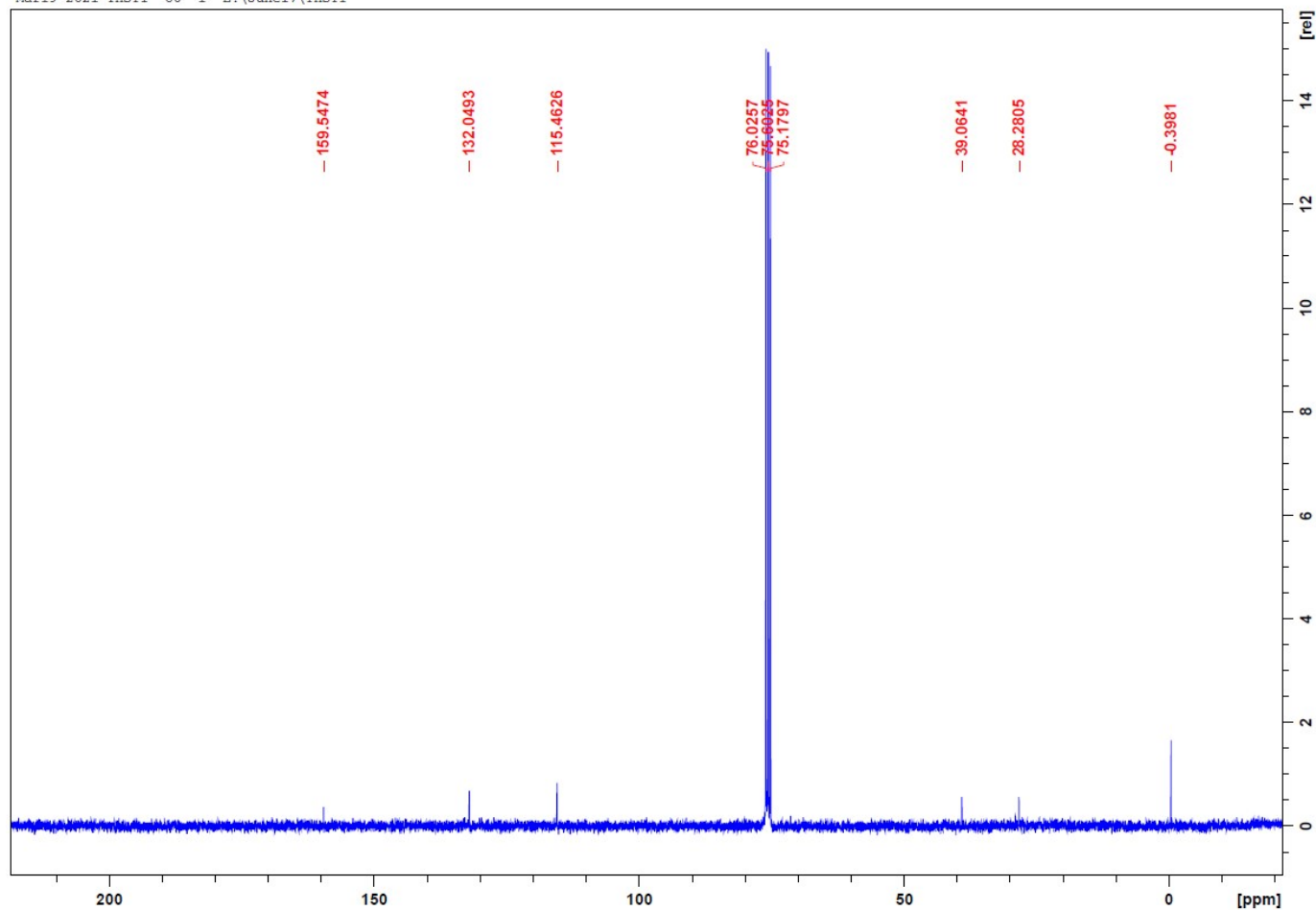


Figure S36: <sup>13</sup>C NMR spectra of compound 13.

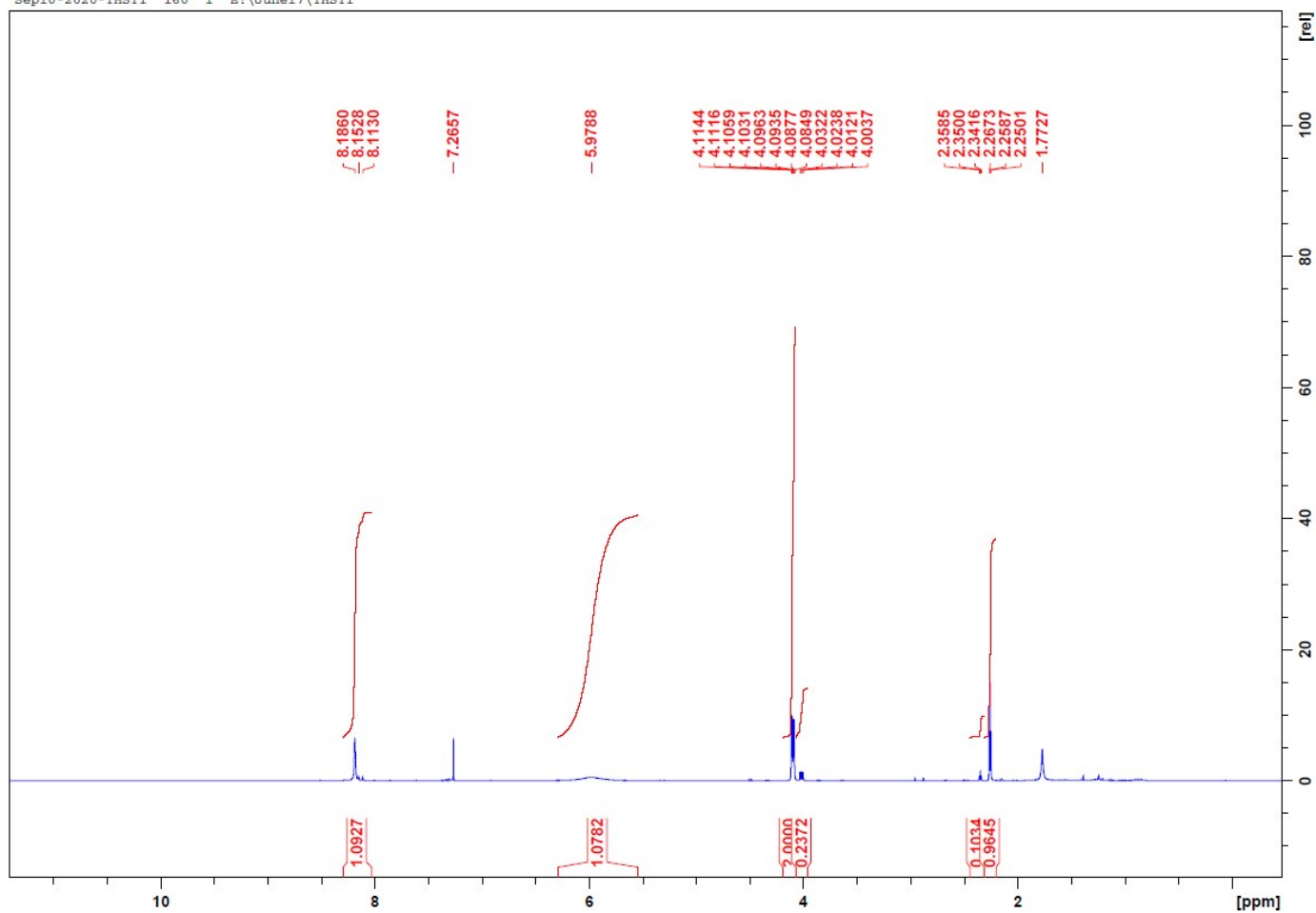
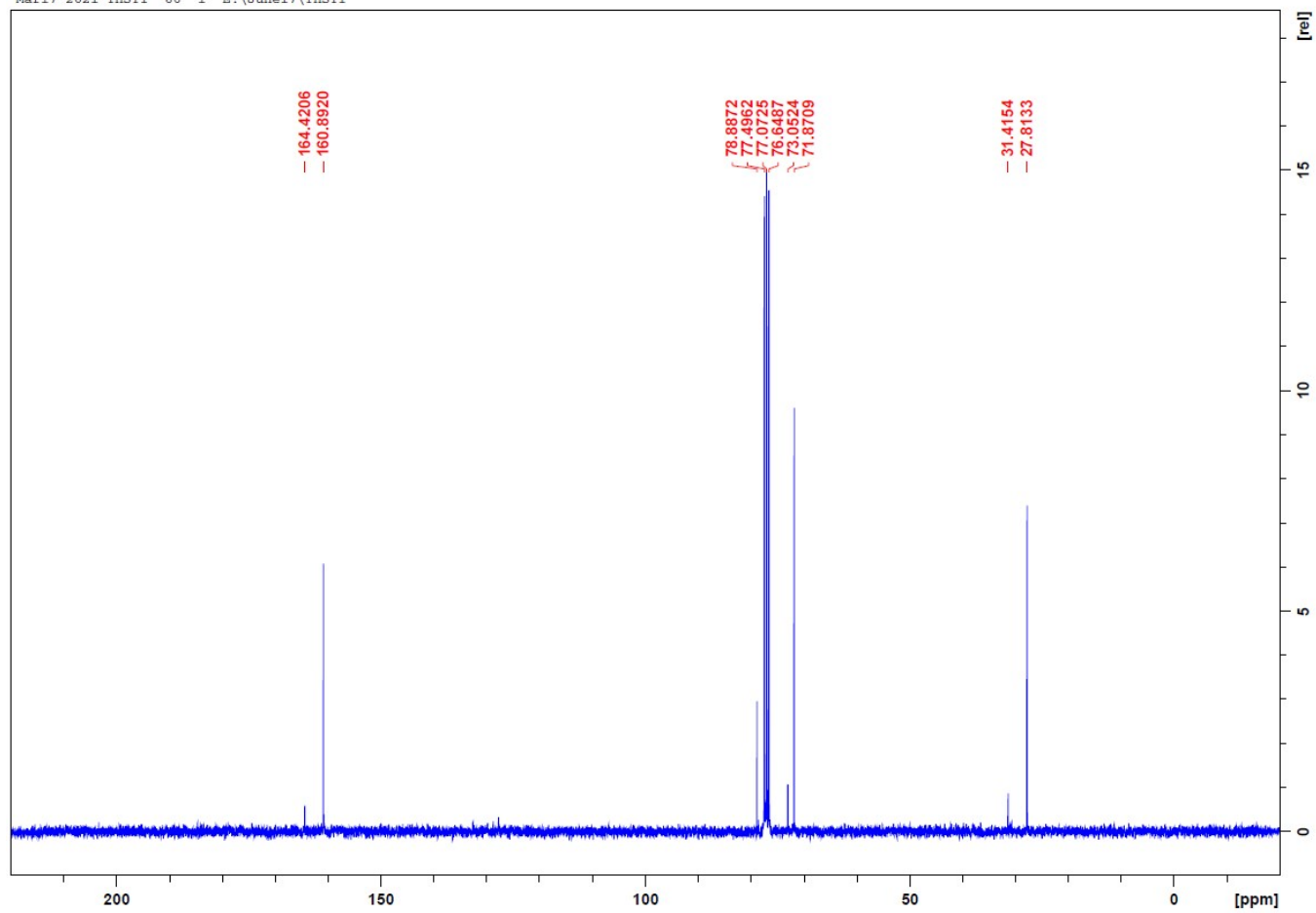


Figure S37: <sup>1</sup>H NMR spectra of compound 14.



**Figure S38:** <sup>13</sup>C NMR spectra of compound 14.

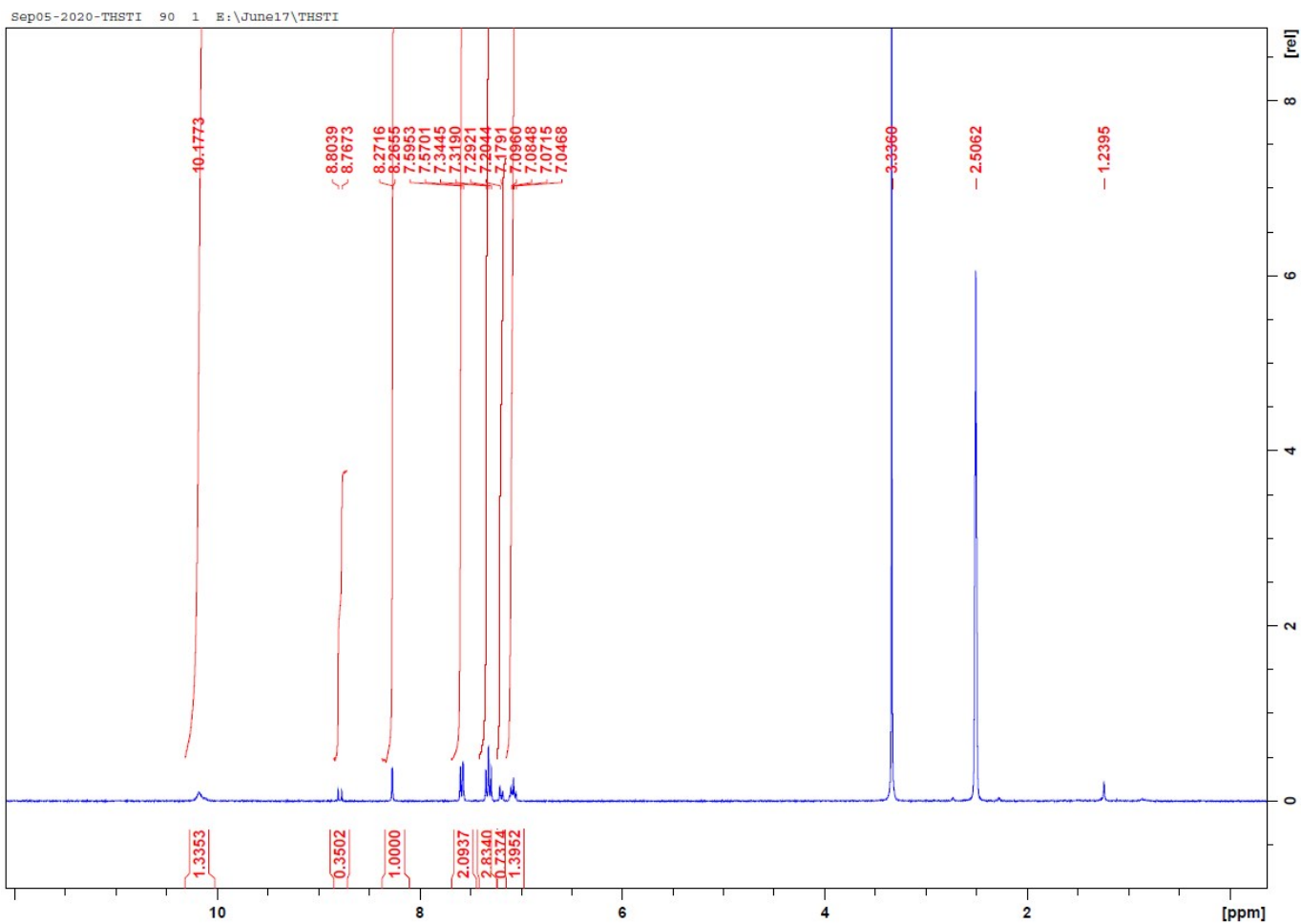
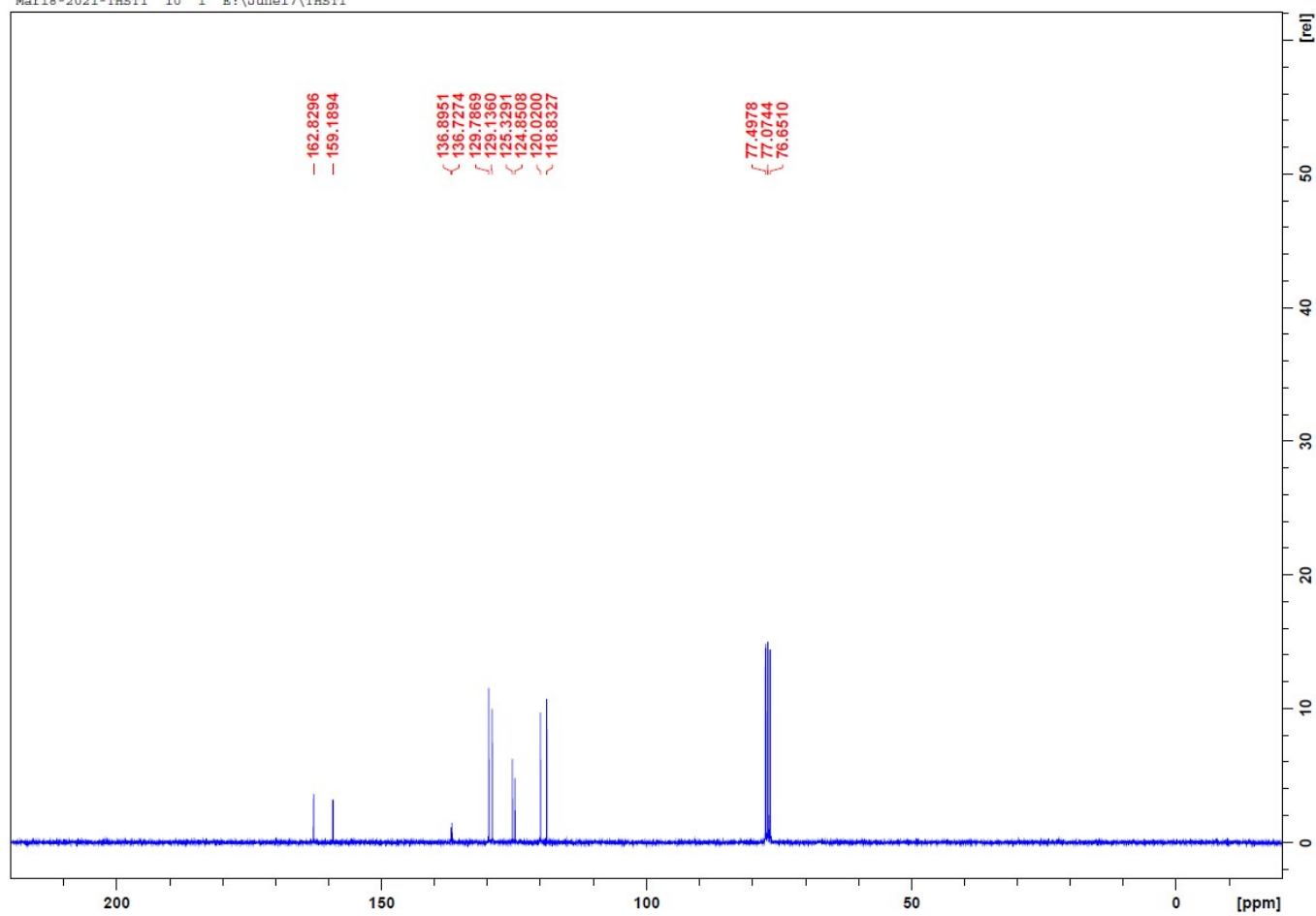


Figure S39:  $^1\text{H}$  NMR spectra of compound 15.





**Figure S40:**  $^{13}\text{C}$  NMR spectra of compound **15**.

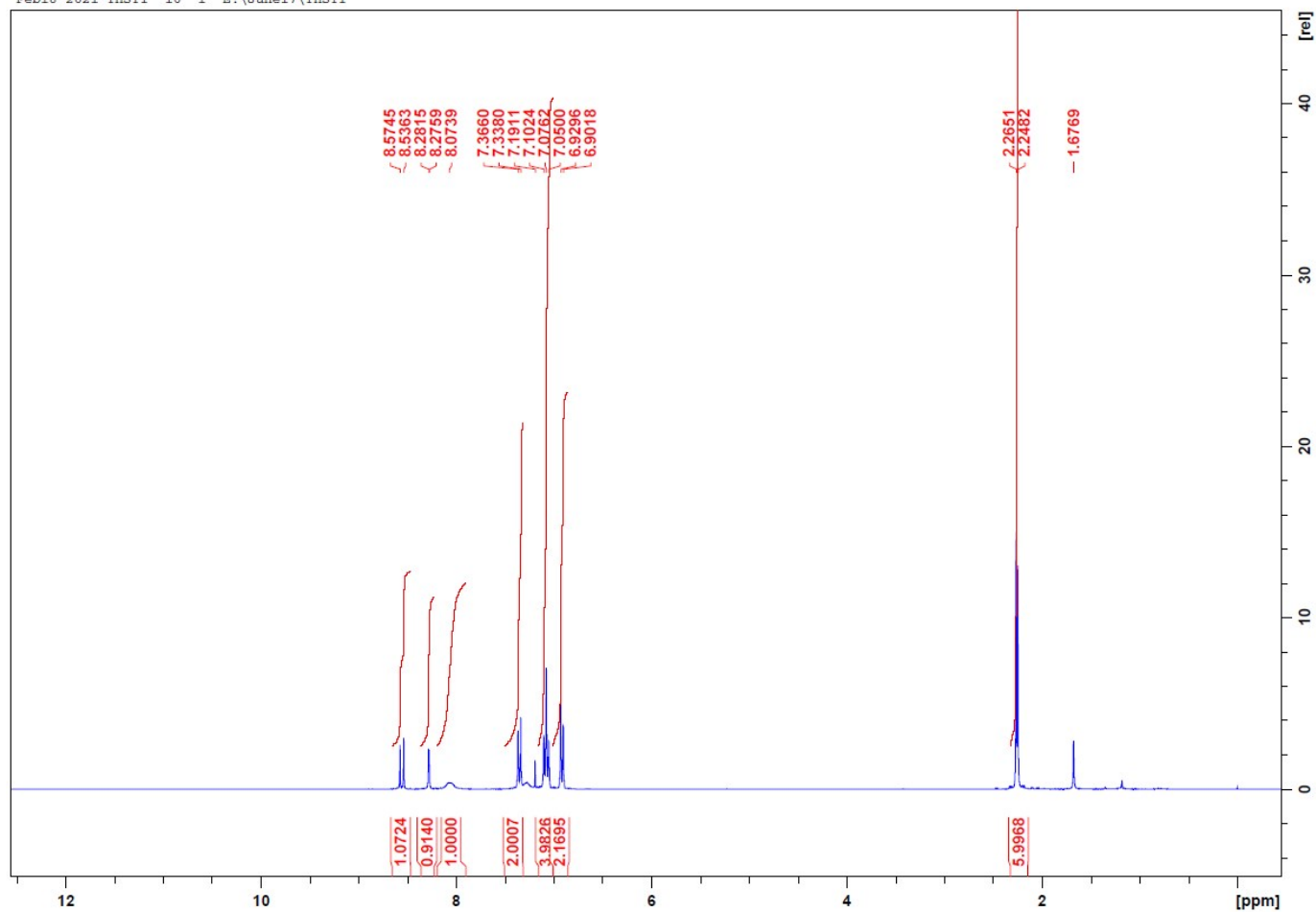


Figure S41: <sup>1</sup>H NMR spectra of compound 16.

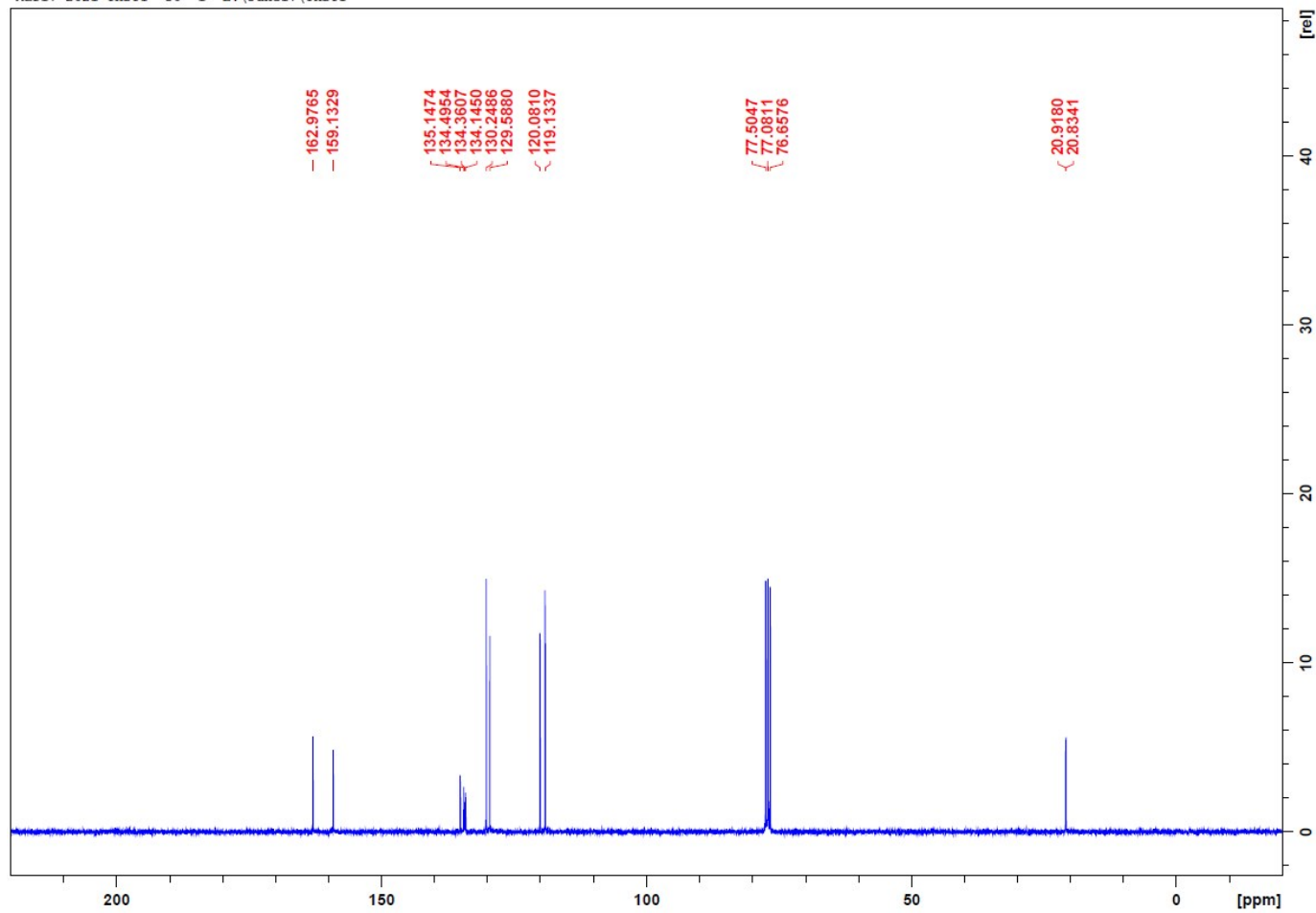


Figure S42: <sup>13</sup>C NMR spectra of compound 16.

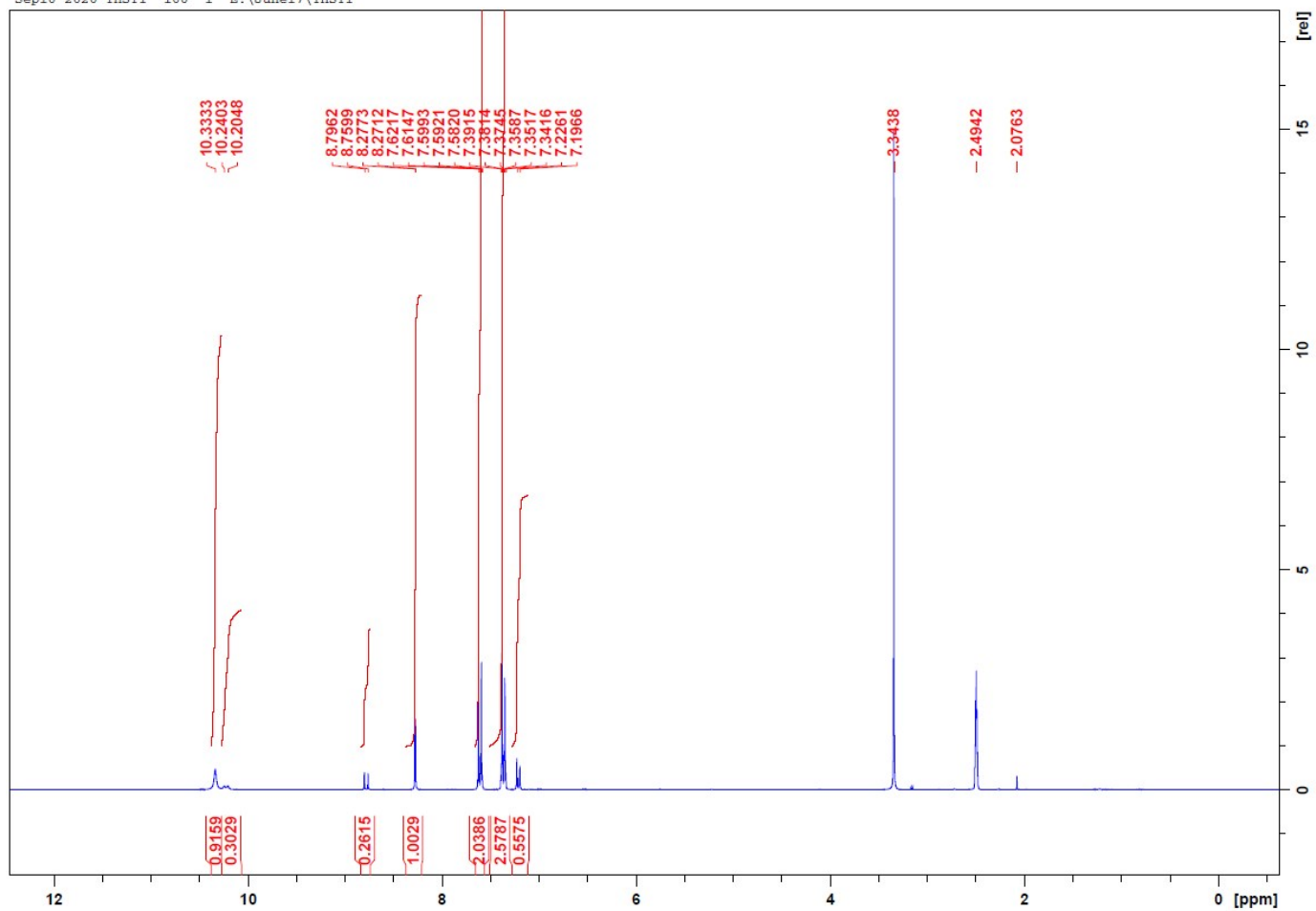


Figure S43: <sup>1</sup>H NMR spectra of compound 17.

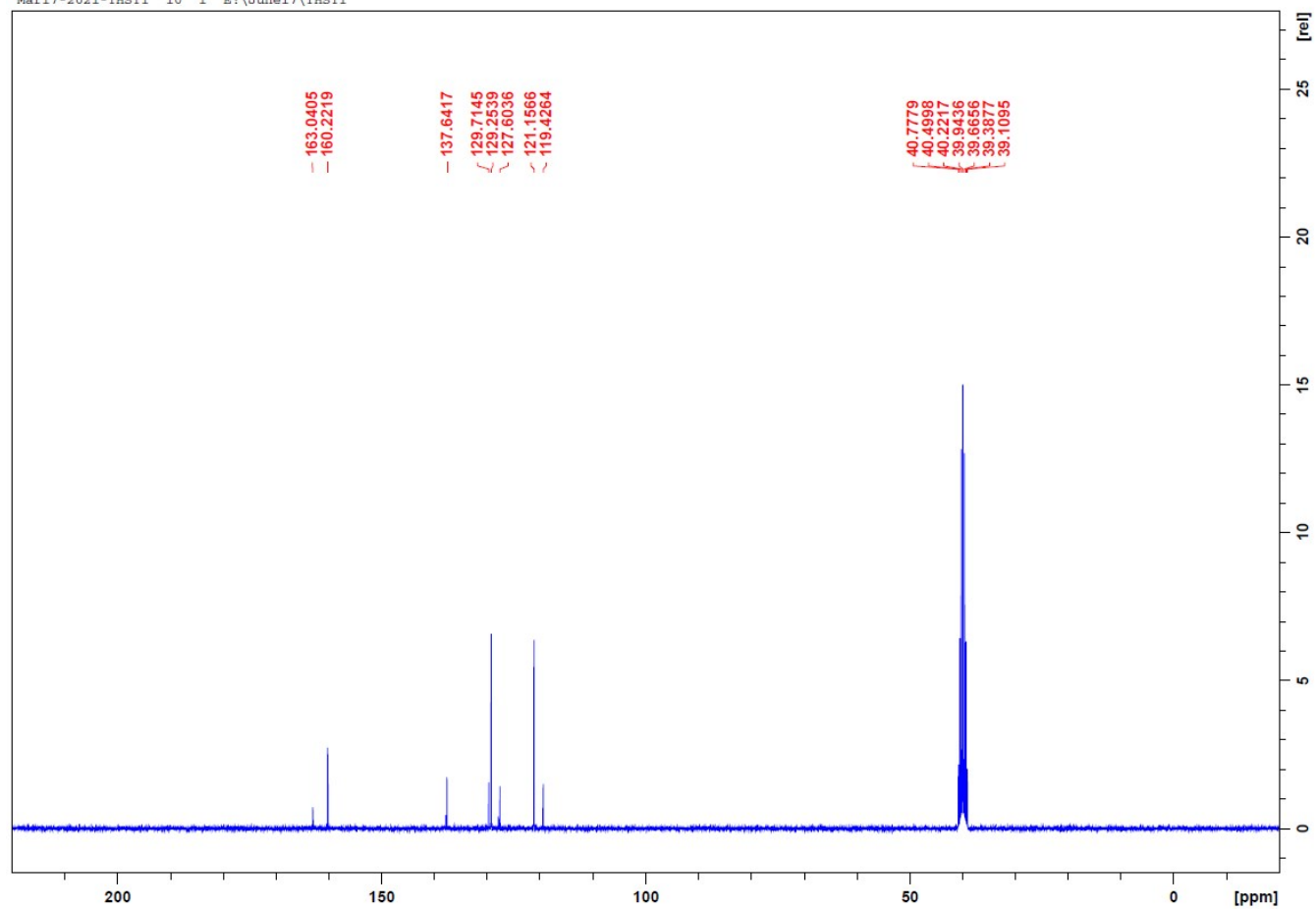


Figure S44:  $^{13}\text{C}$  NMR spectra of compound 17.

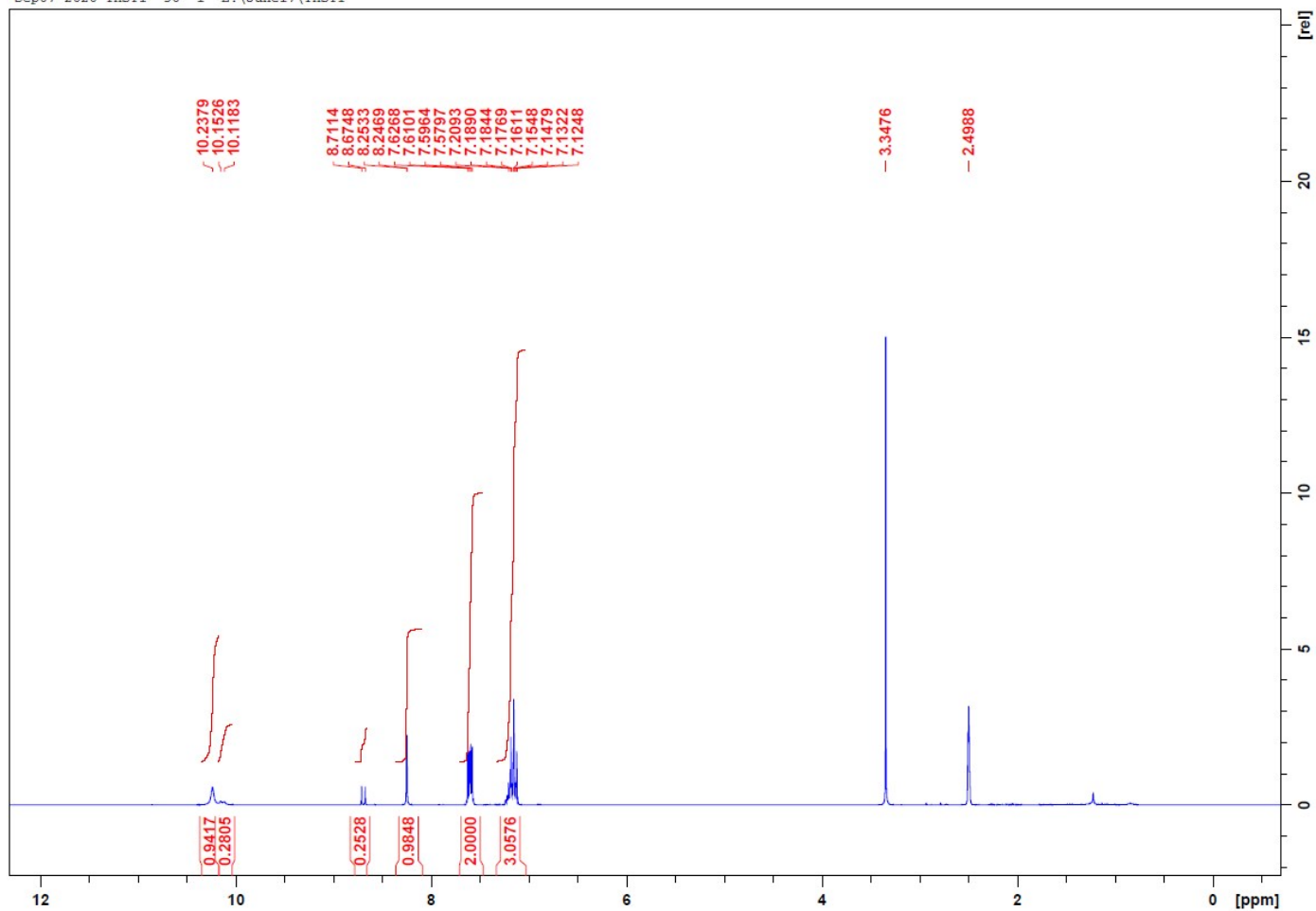


Figure S45: <sup>1</sup>H NMR spectra of compound 18.

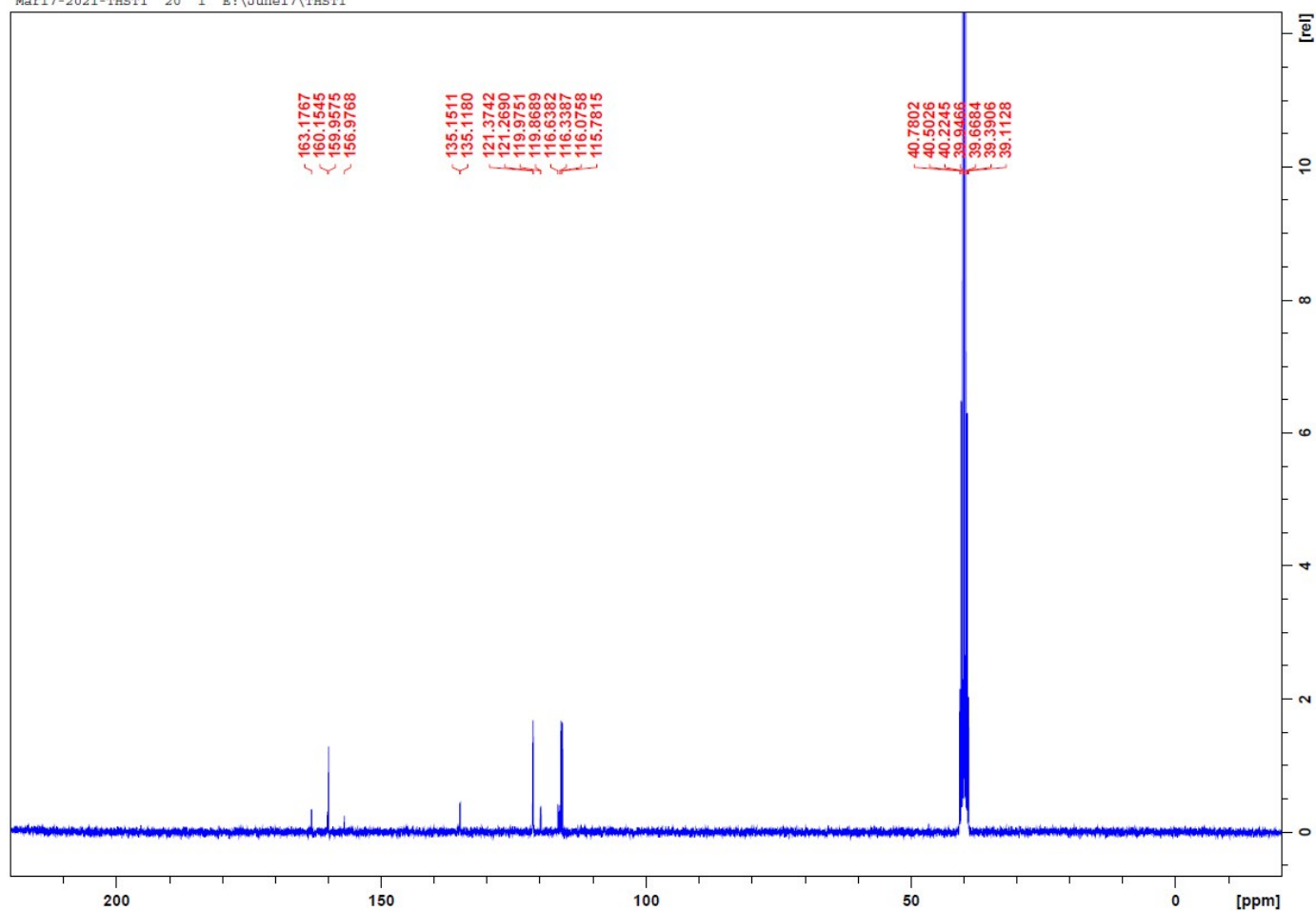


Figure S46: <sup>13</sup>C NMR spectra of compound 18.

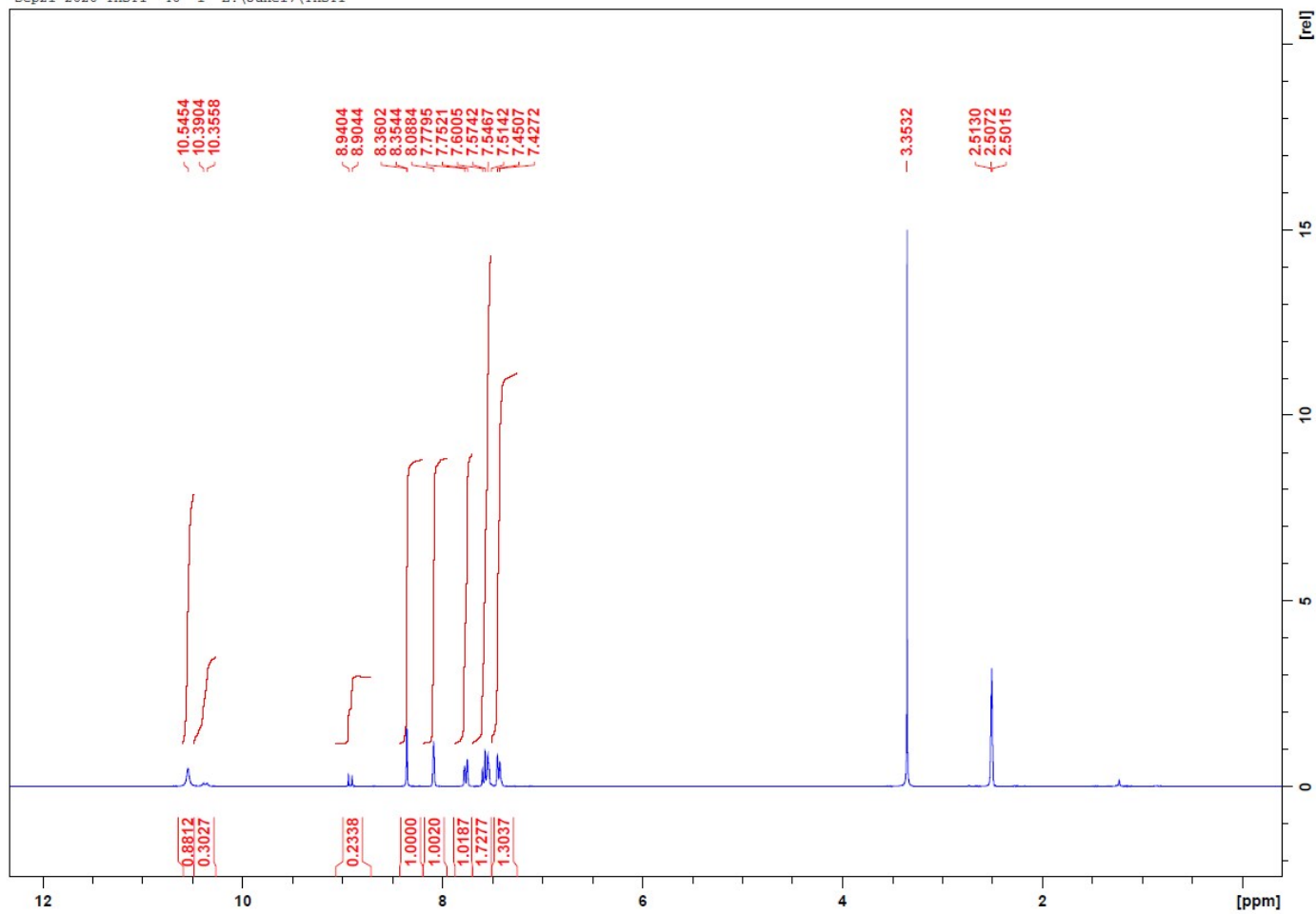


Figure S47: <sup>1</sup>H NMR spectra of compound 19.



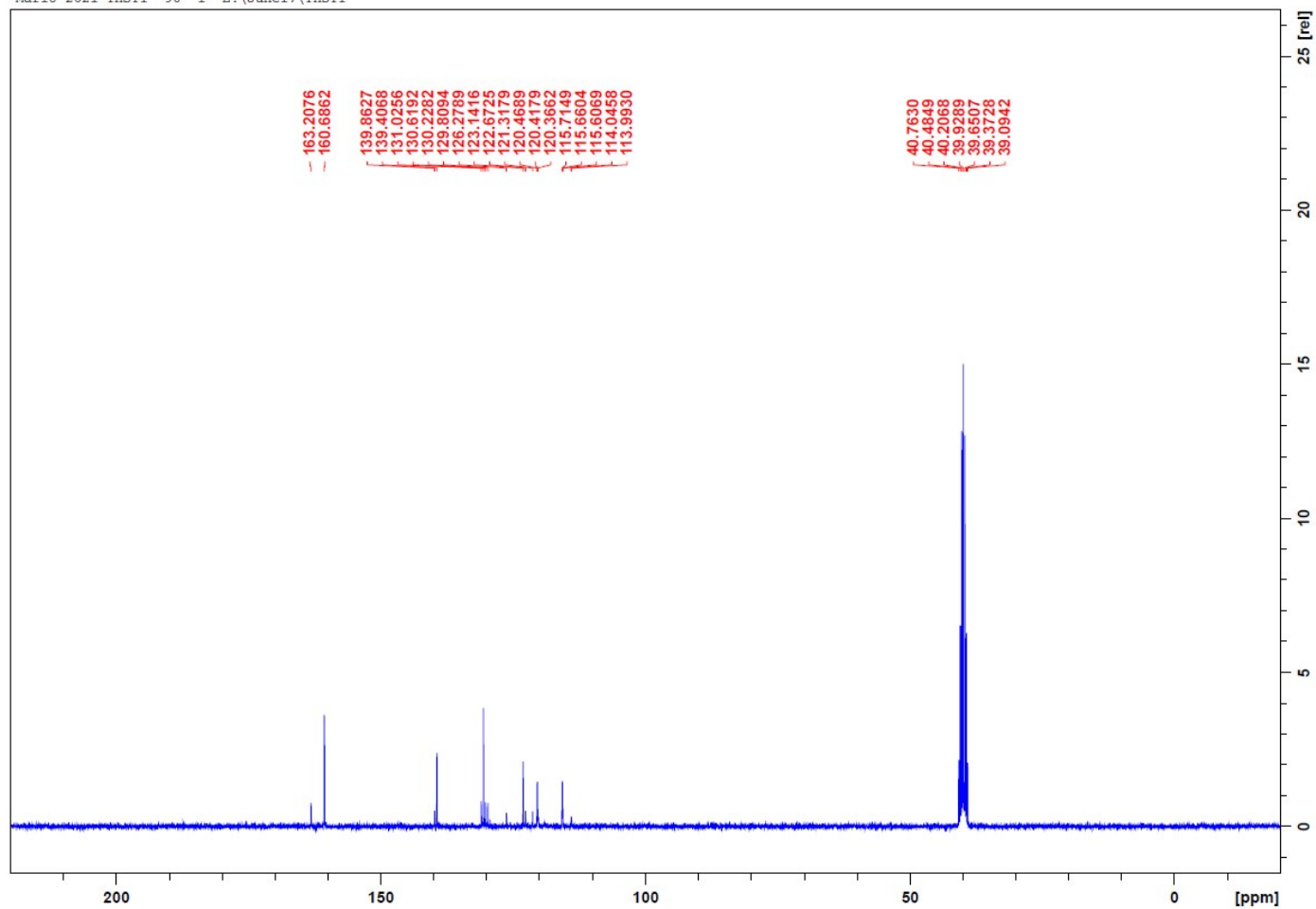


Figure S48: <sup>13</sup>C NMR spectra of compound 19.

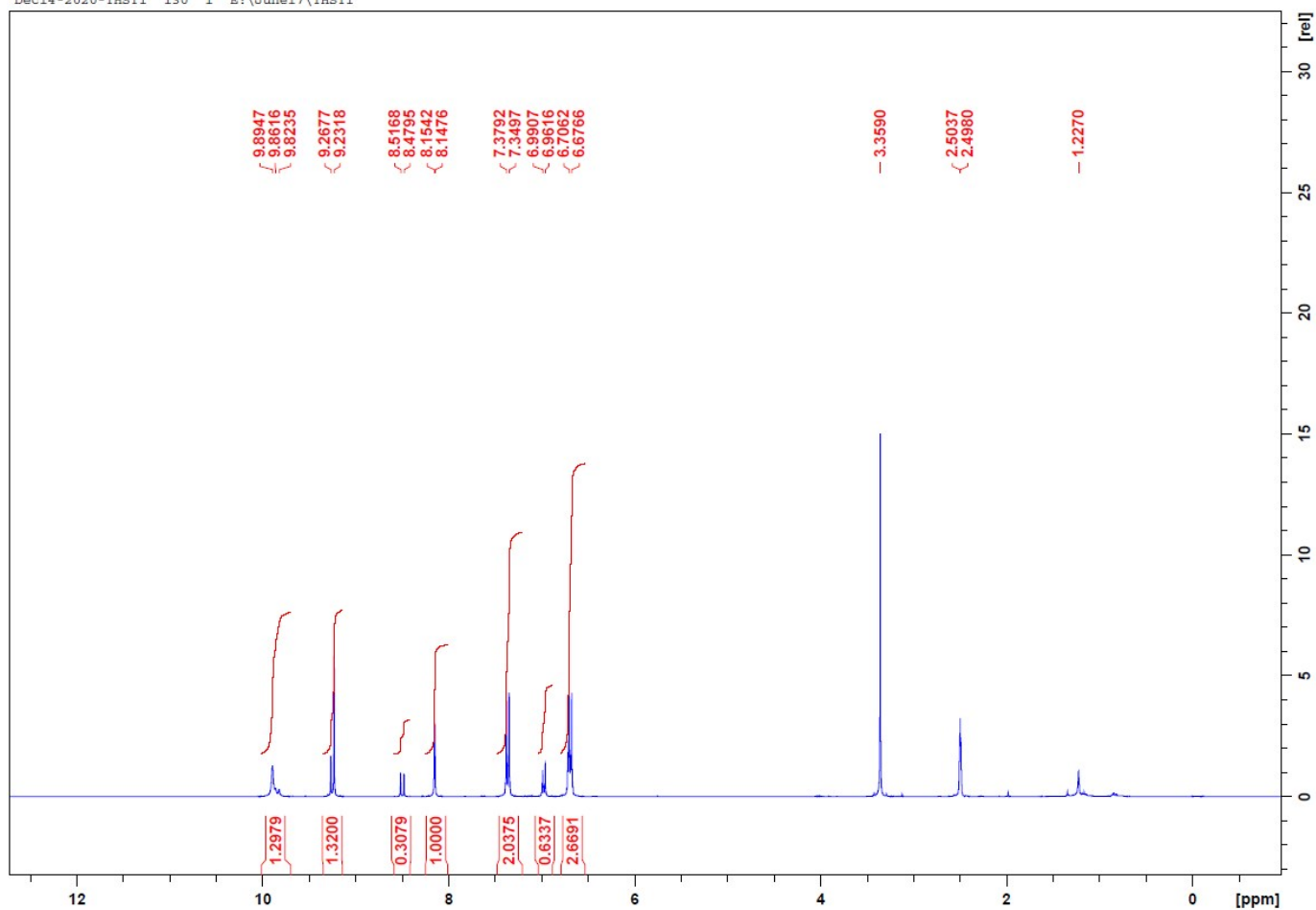
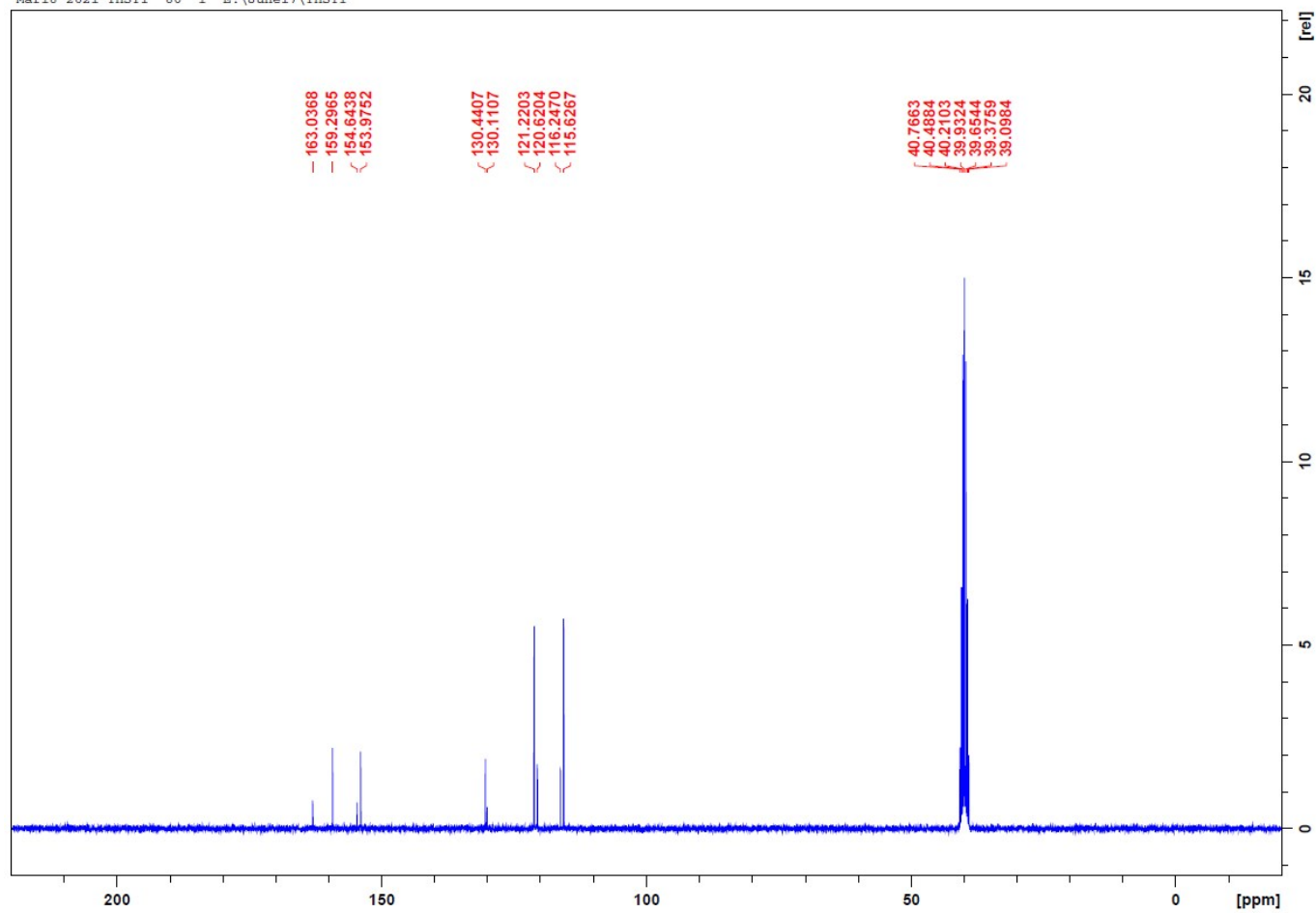


Figure S49: <sup>1</sup>H NMR spectra of compound 20.



**Figure S50:**  $^{13}\text{C}$  NMR spectra of compound 20.

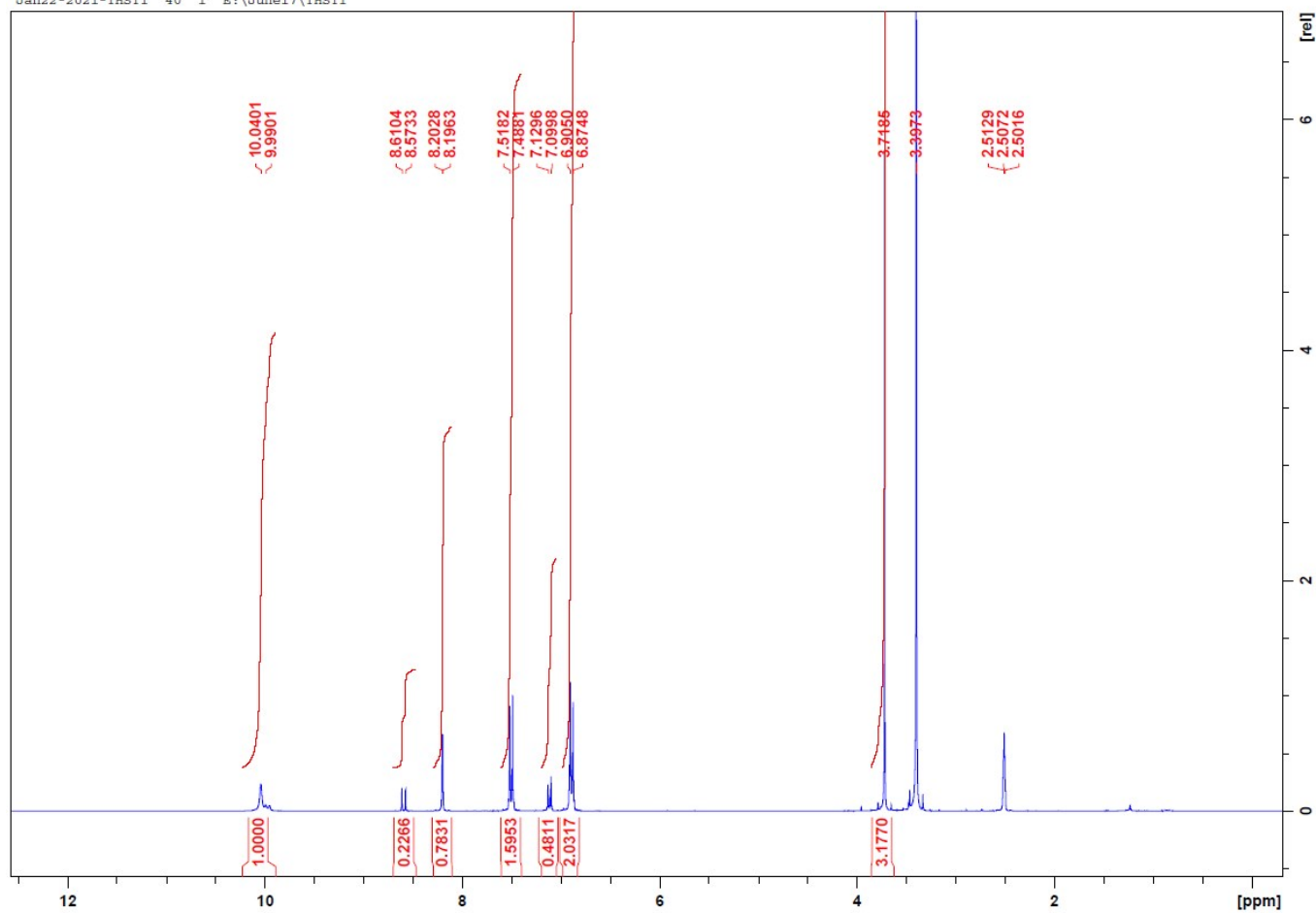


Figure S51:  $^1\text{H}$  NMR spectra of compound 21.

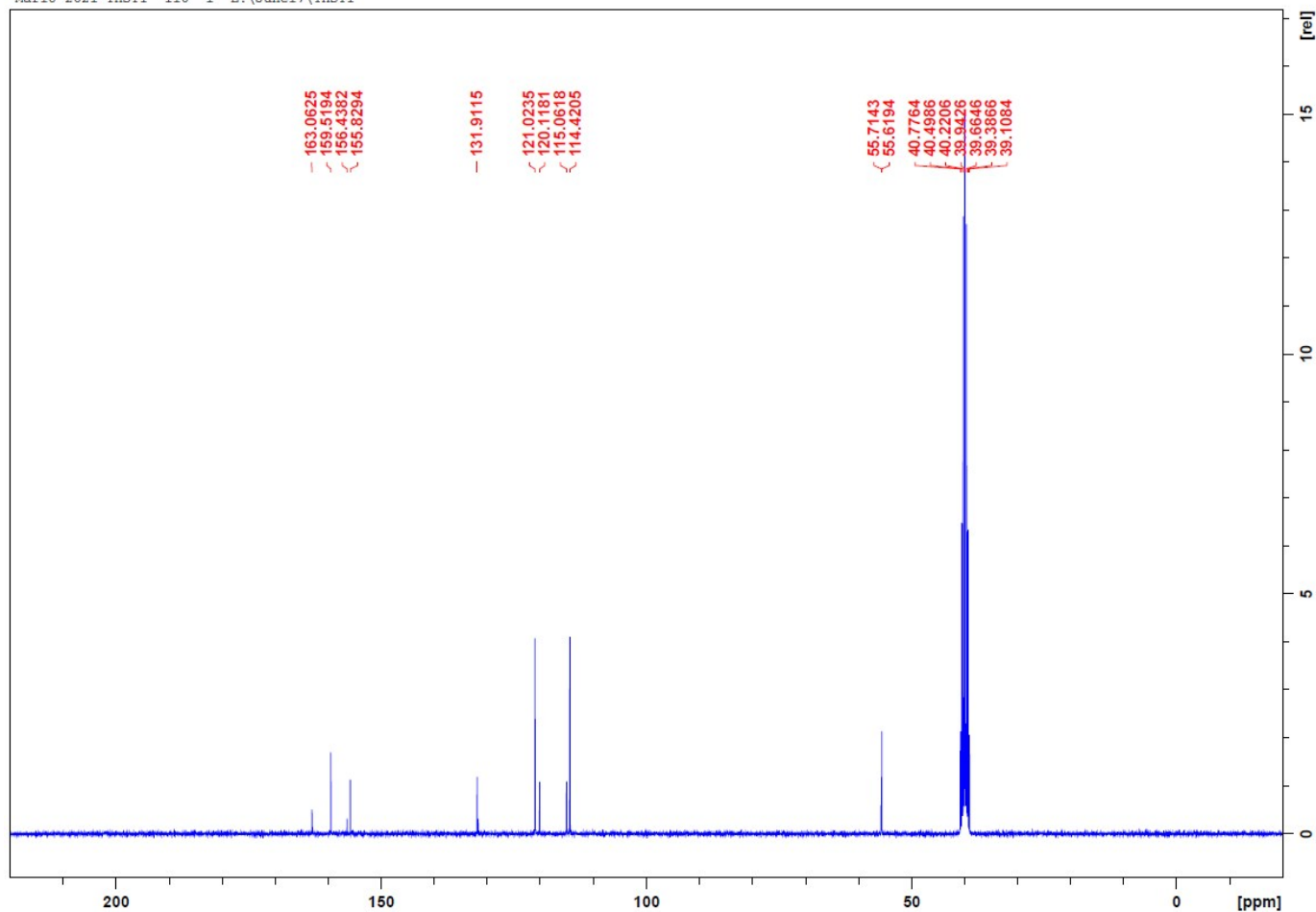


Figure S52:  $^{13}\text{C}$  NMR spectra of compound **21**.

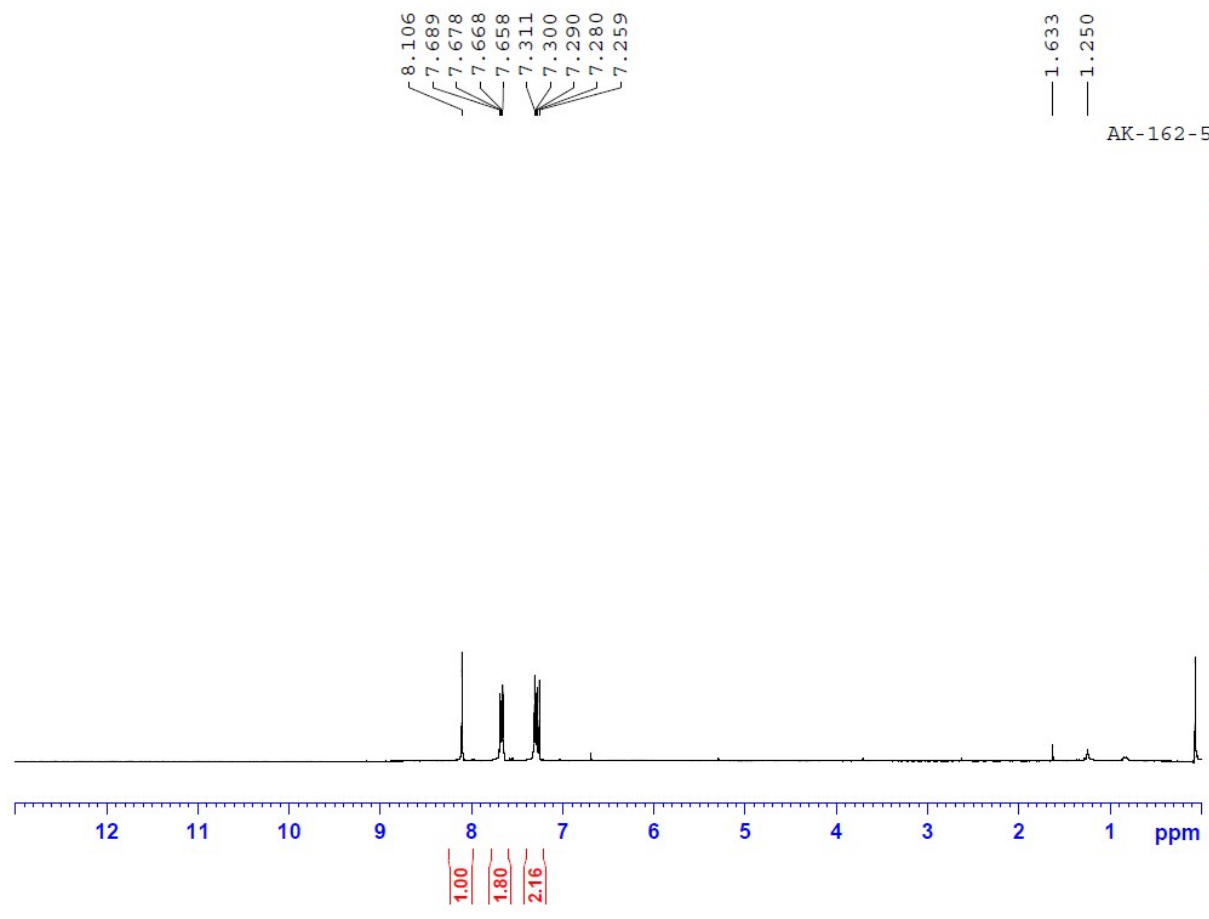
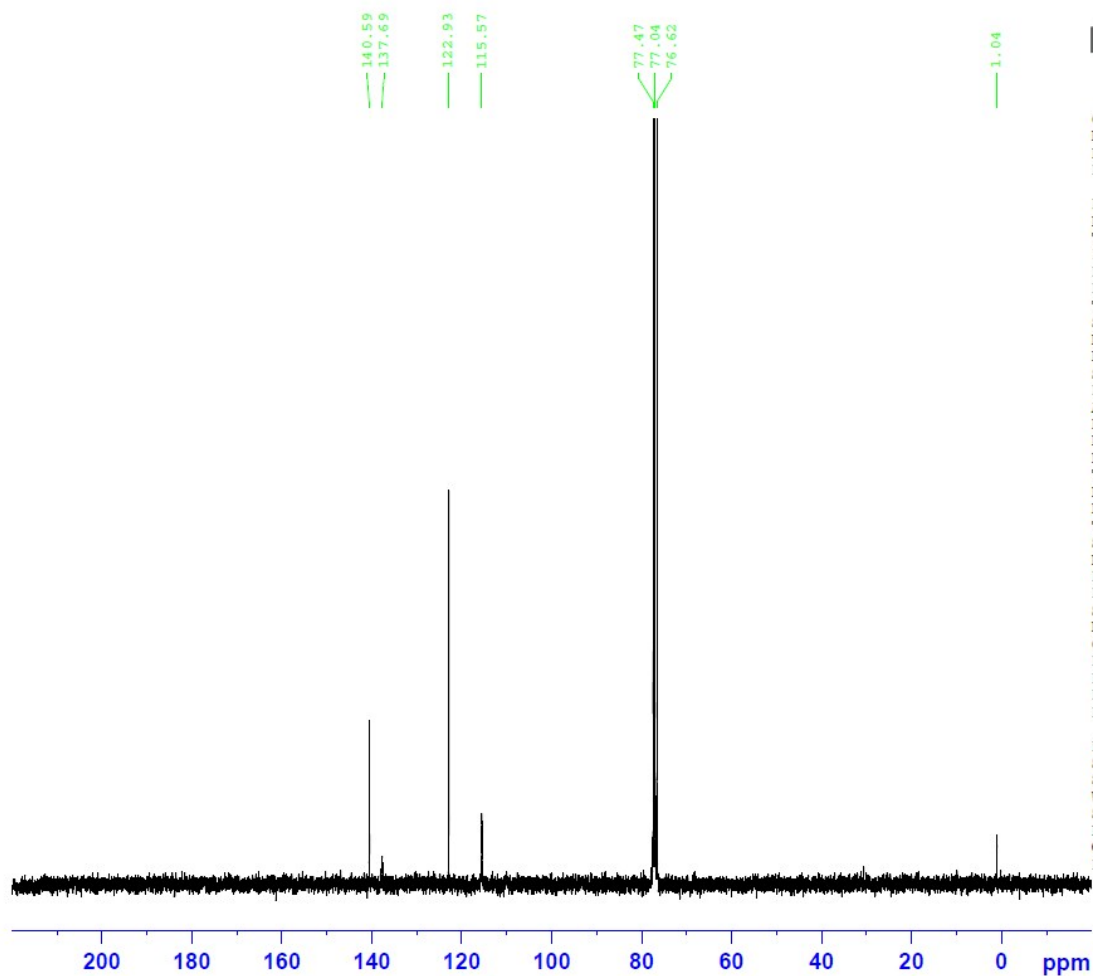


Figure S53: <sup>1</sup>H NMR spectra of compound 22.

AK-162-567-P 22-13 C



Current Data Parameters  
NAME Jul15-2021-THSTI  
EXPNO 20  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20210715  
Time\_ 11.34 h  
INSTRUM spect  
PROBHD Z104275\_0363 (  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 1024  
DS 4  
SWH 18115.941 Hz  
FIDRES 0.552855 Hz  
AQ 1.8087935 sec  
RG 14.65  
DW 27.600 usec  
DE 6.50 usec  
TE 294.9 K  
D1 2.00000000 sec  
D11 0.03000000 sec  
TD0 1  
SFO1 75.5180461 MHz  
NUC1 13C  
P1 10.00 usec  
PLW1 44.50699997 W  
SFO2 300.3012012 MHz  
NUC2 1H  
CPDPRG2 waltz16  
PCPD2 90.00 usec  
PLW2 8.38599968 W  
PLW12 0.20043489 W  
PLW13 0.10045800 W

F2 - Processing parameters  
SI 32768  
SF 75.5104951 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

Figure S54:  $^{13}\text{C}$  NMR spectra of compound 22.

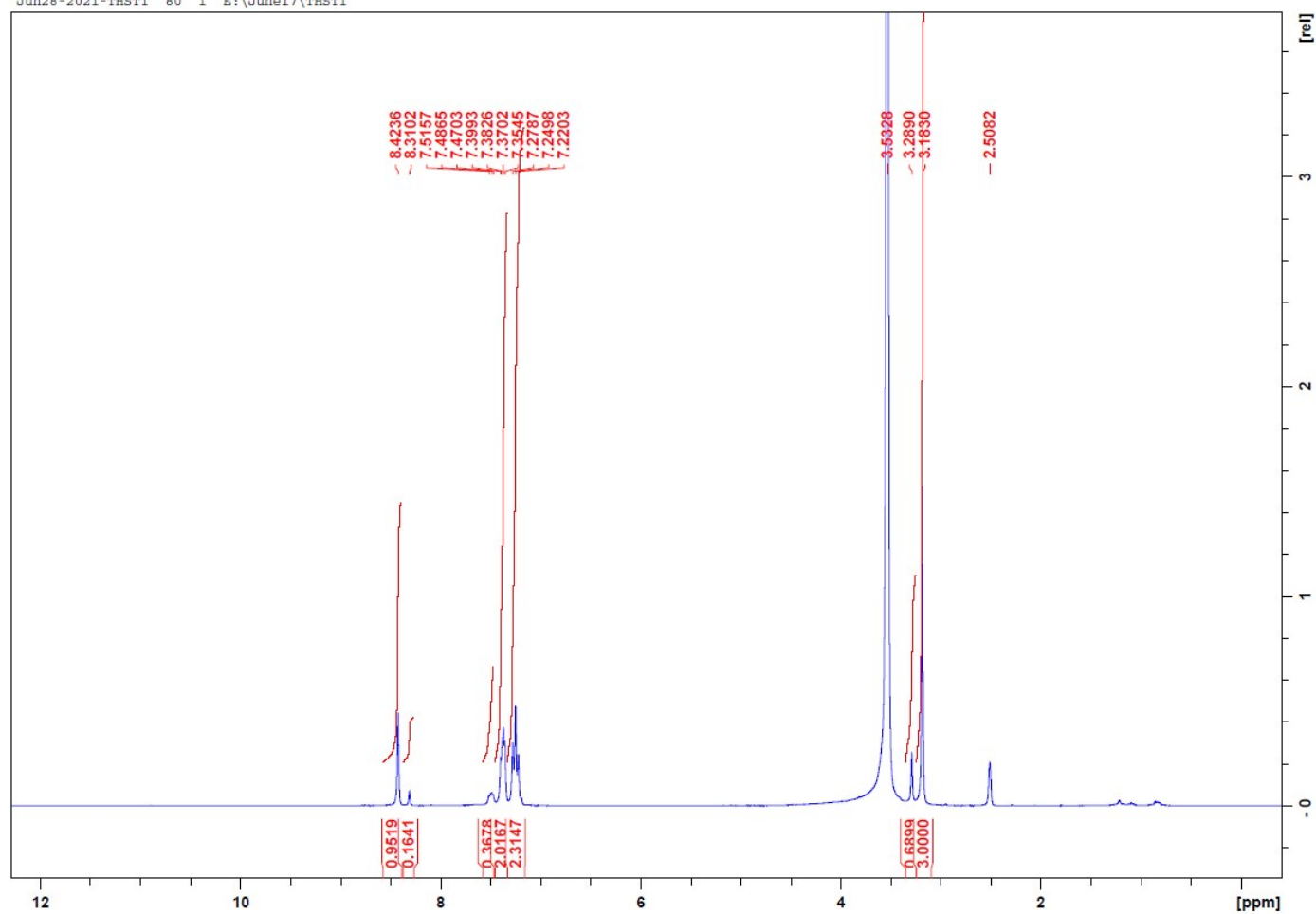
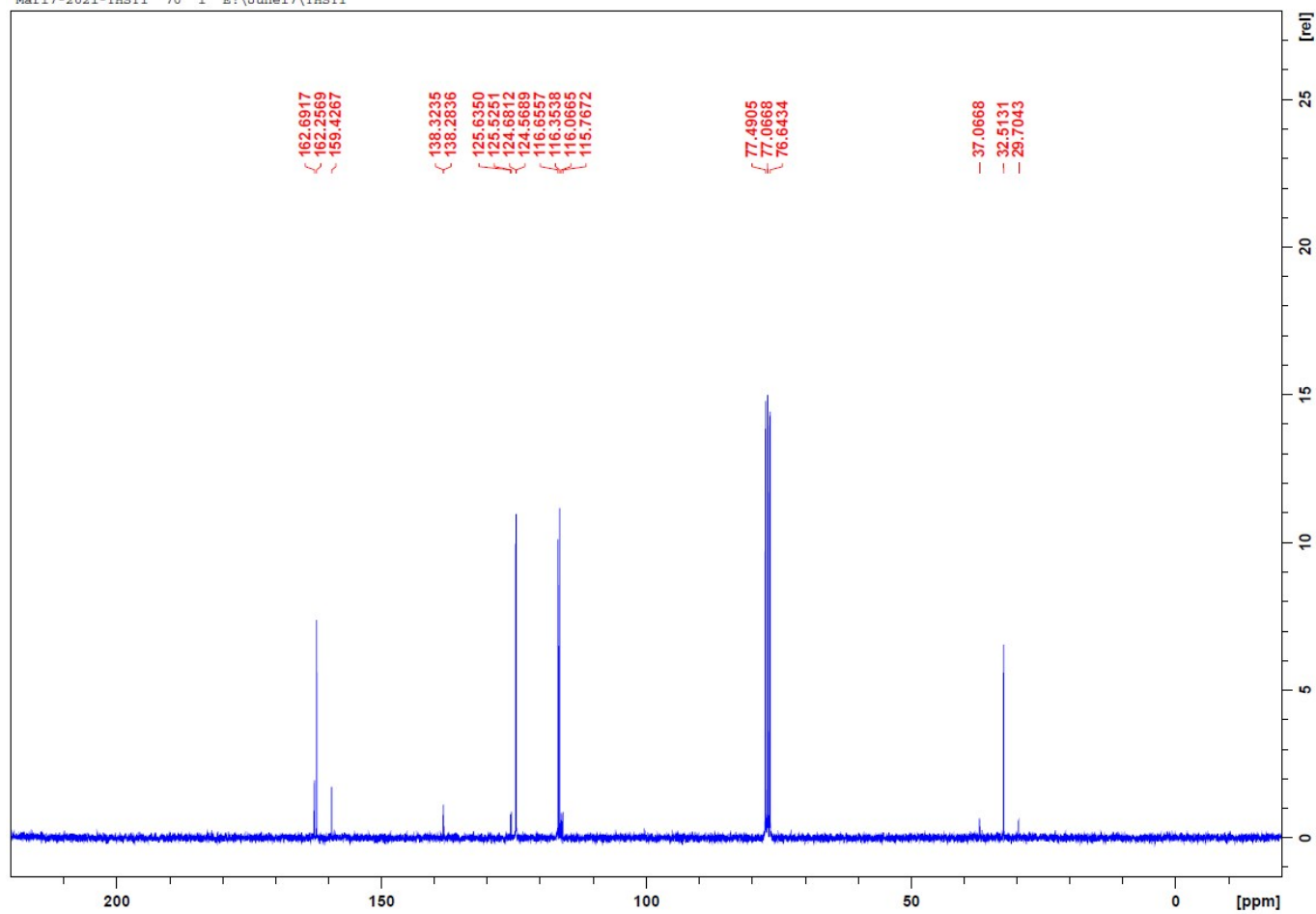


Figure S55: <sup>1</sup>H NMR spectra of compound 23.





**Figure S56:**  $^{13}\text{C}$  NMR spectra of compound 23.

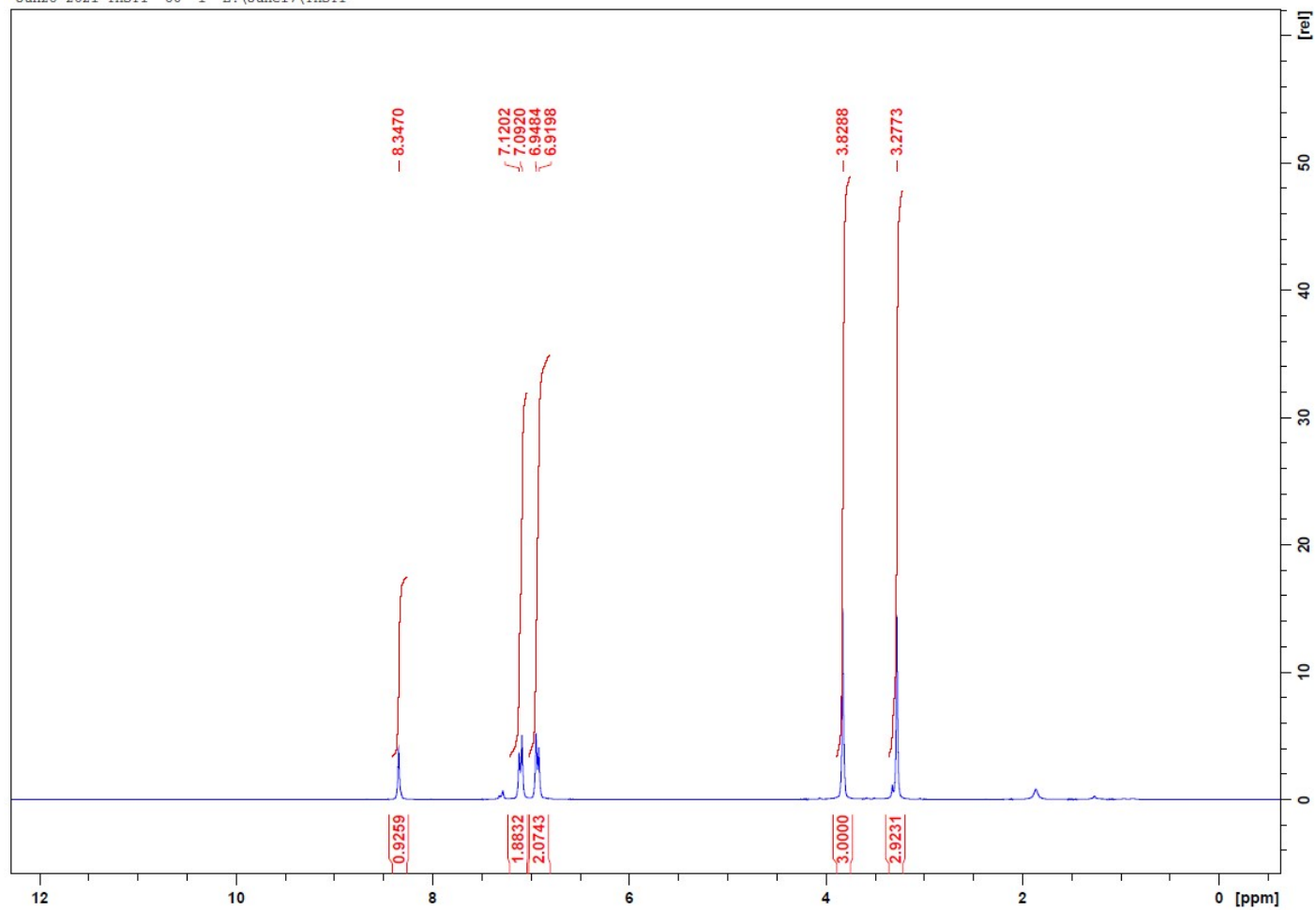
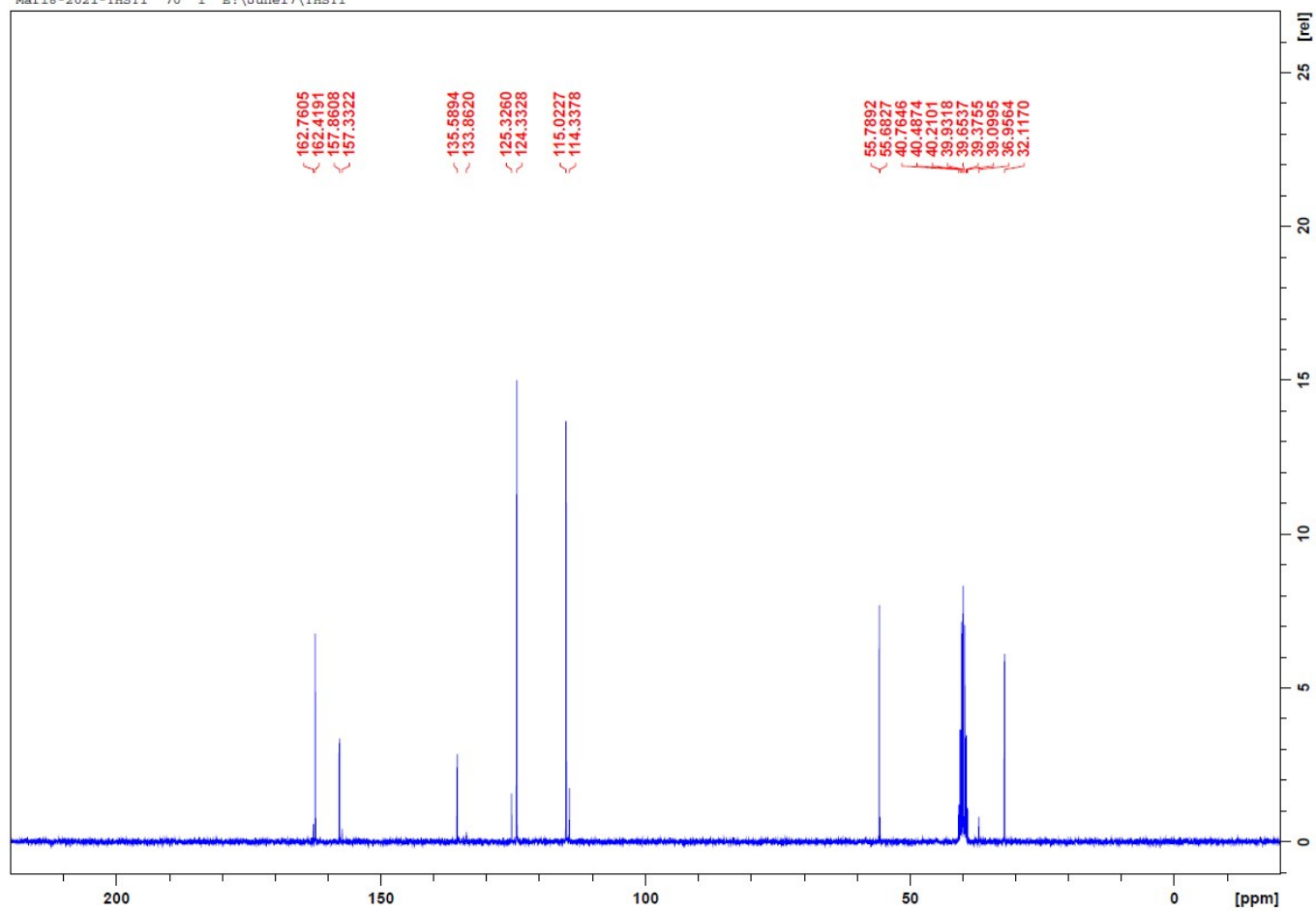


Figure S57: <sup>1</sup>H NMR spectra of compound 24.



**Figure S58:**  $^{13}\text{C}$  NMR spectra of compound 24.

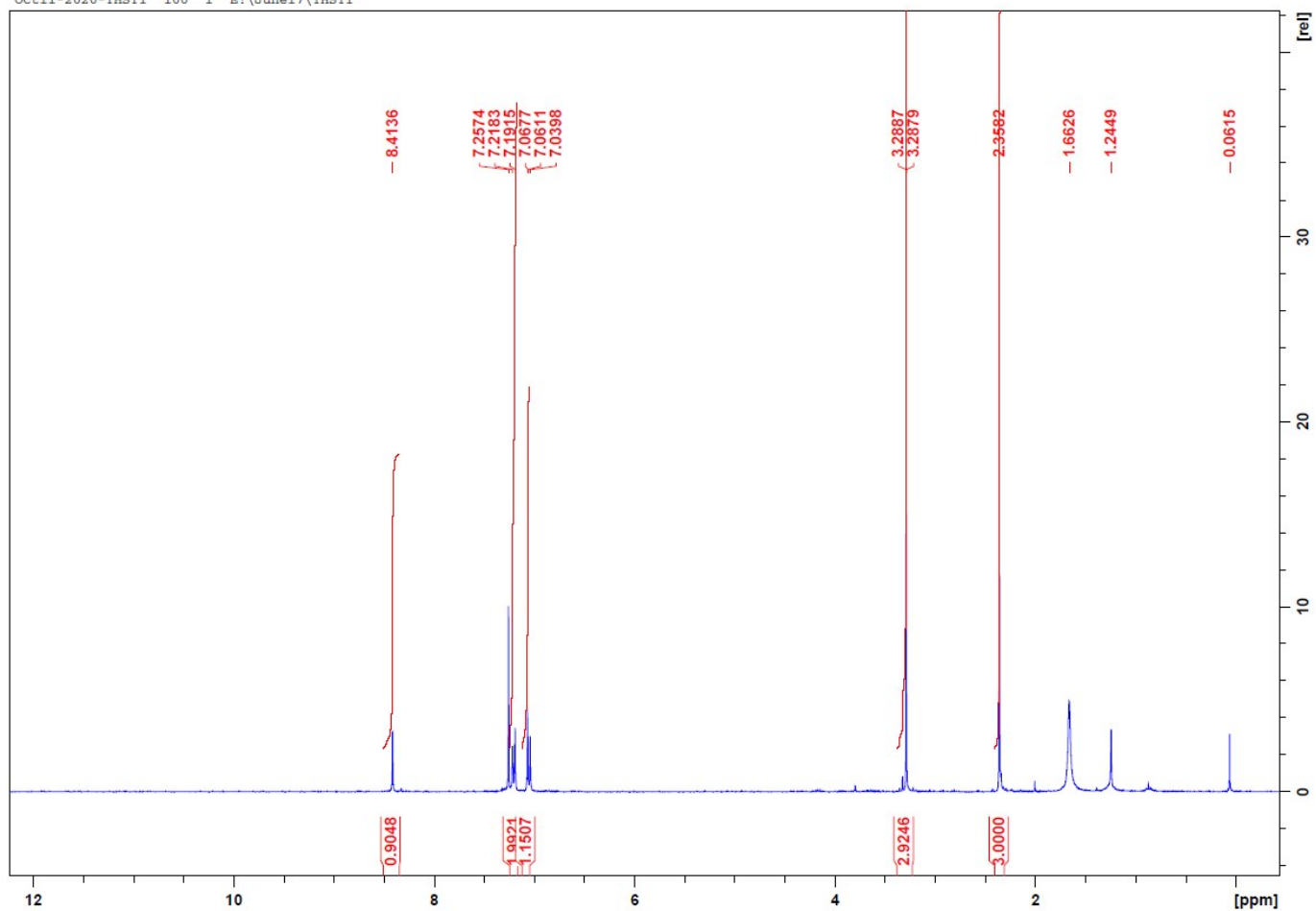
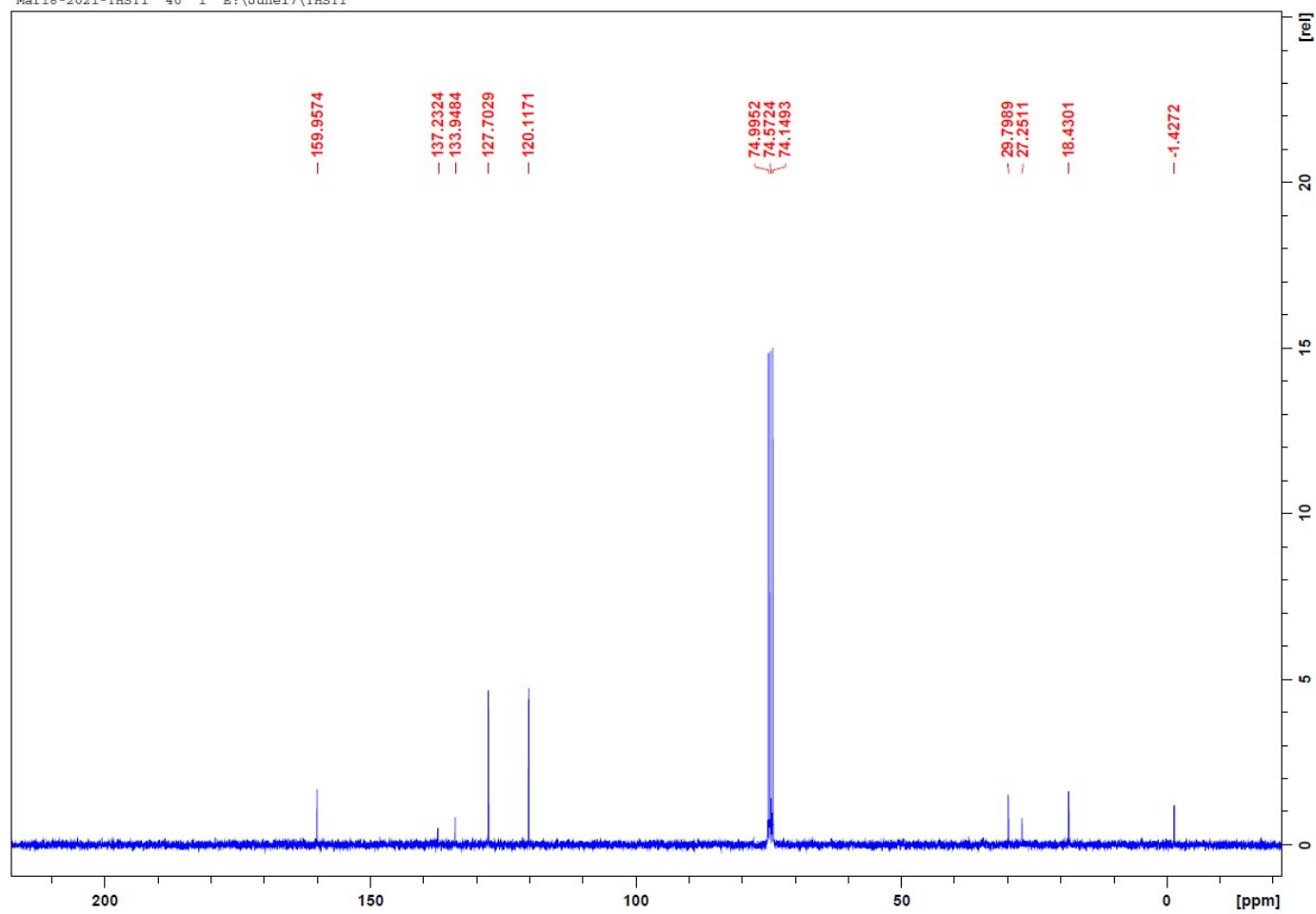
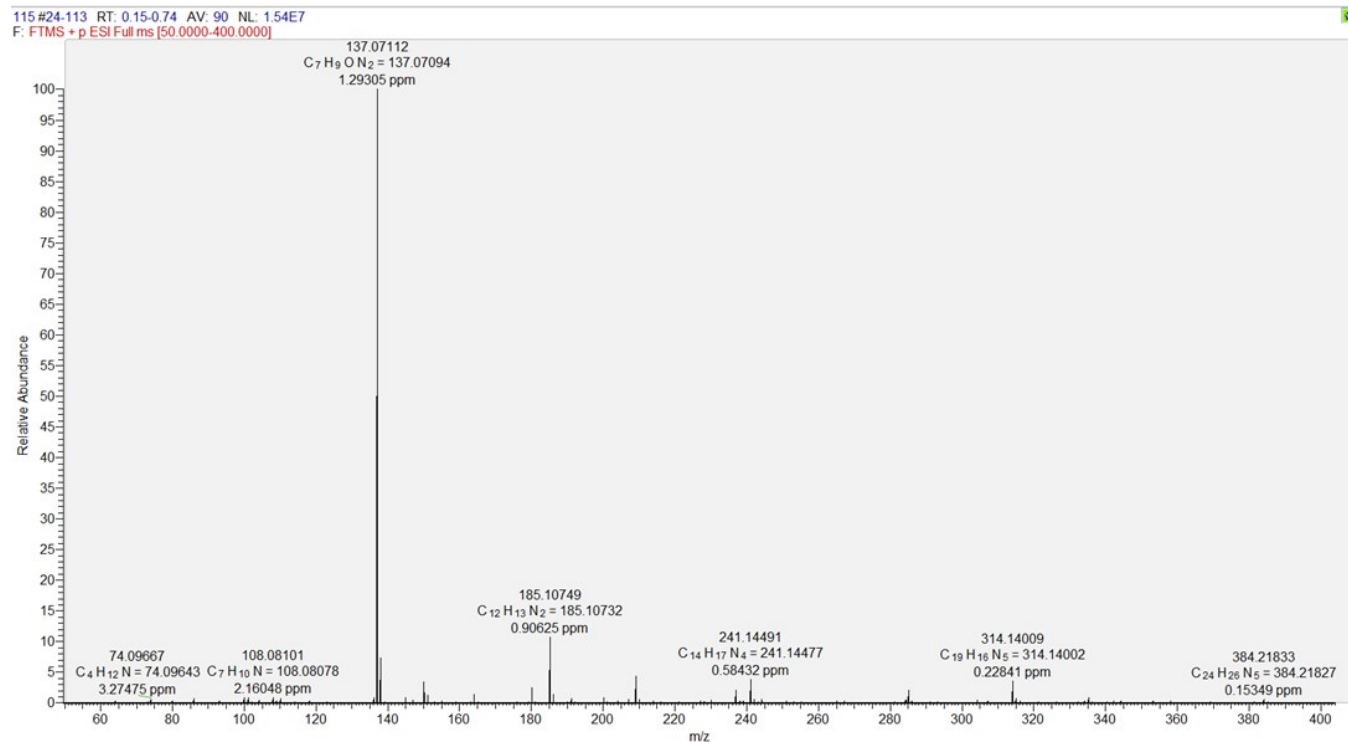


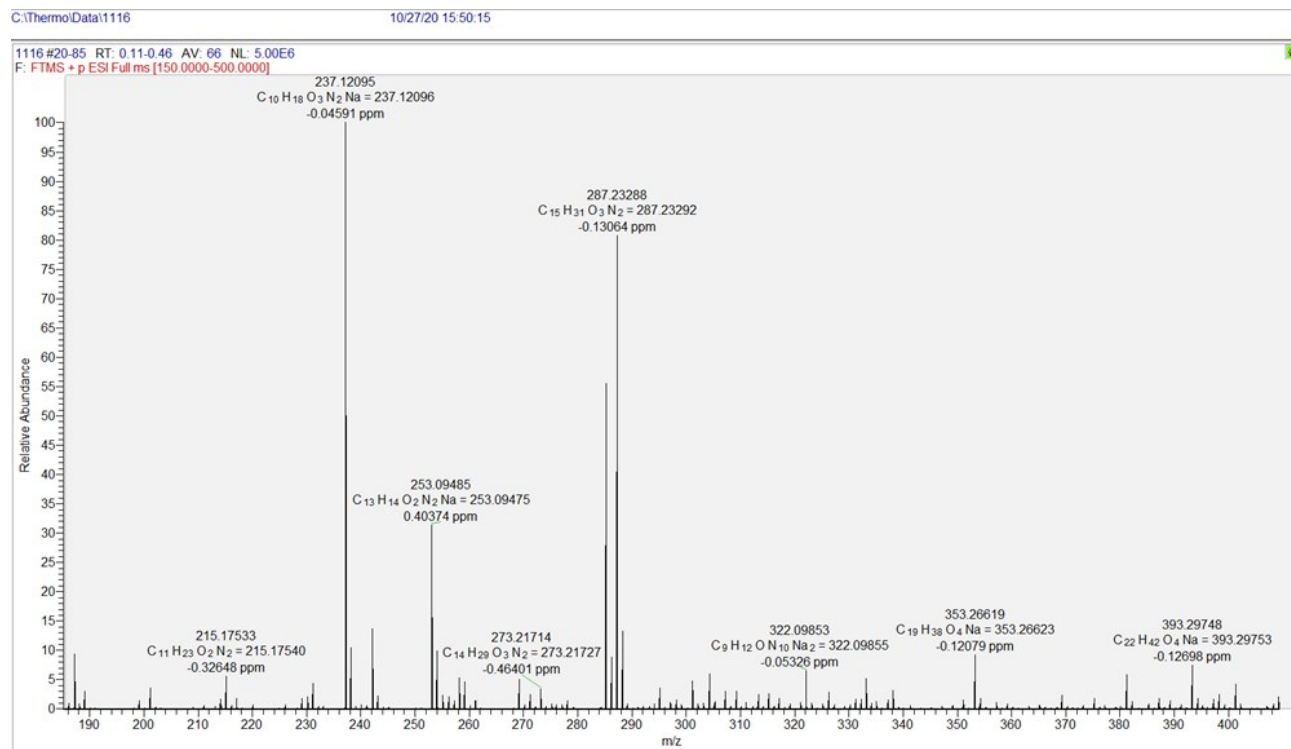
Figure S59: <sup>1</sup>H NMR spectra of compound 25.



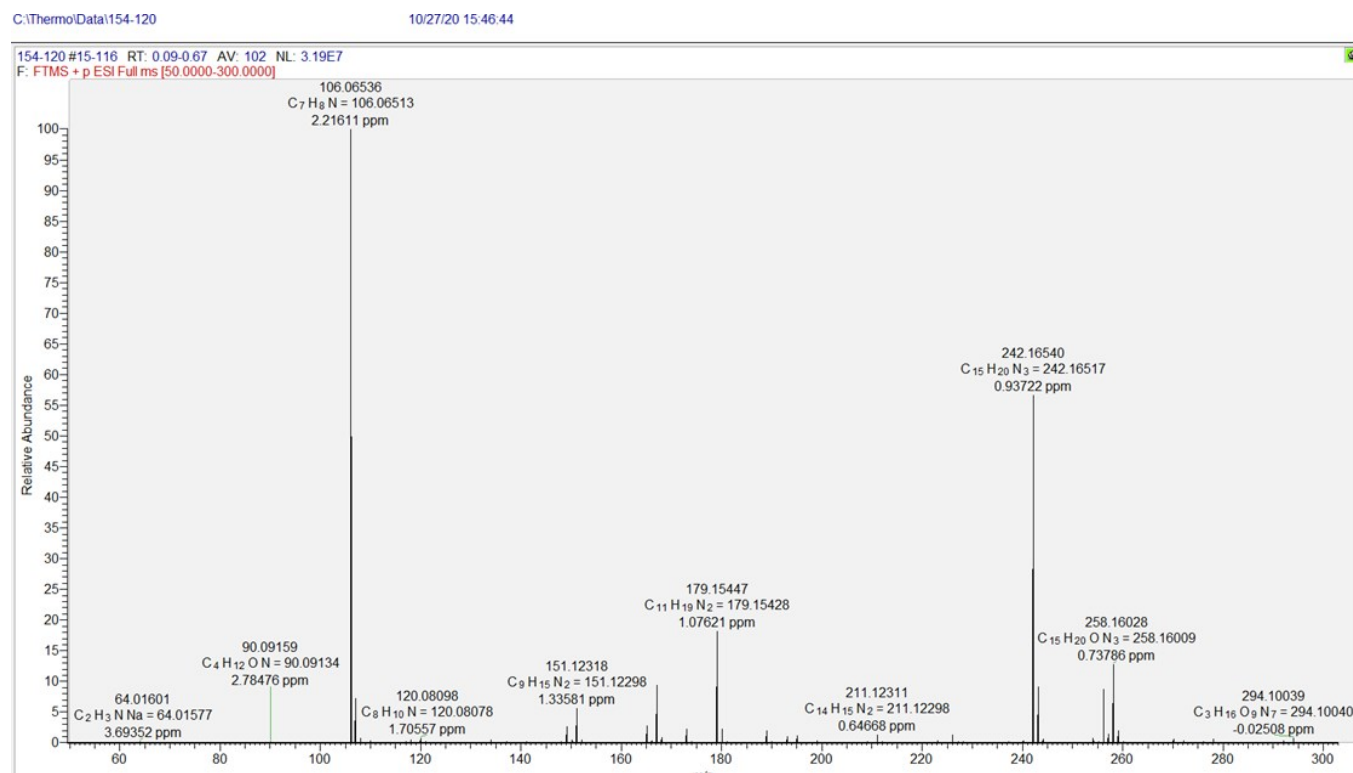
**Figure S60:** <sup>13</sup>C NMR spectra of compound 25.



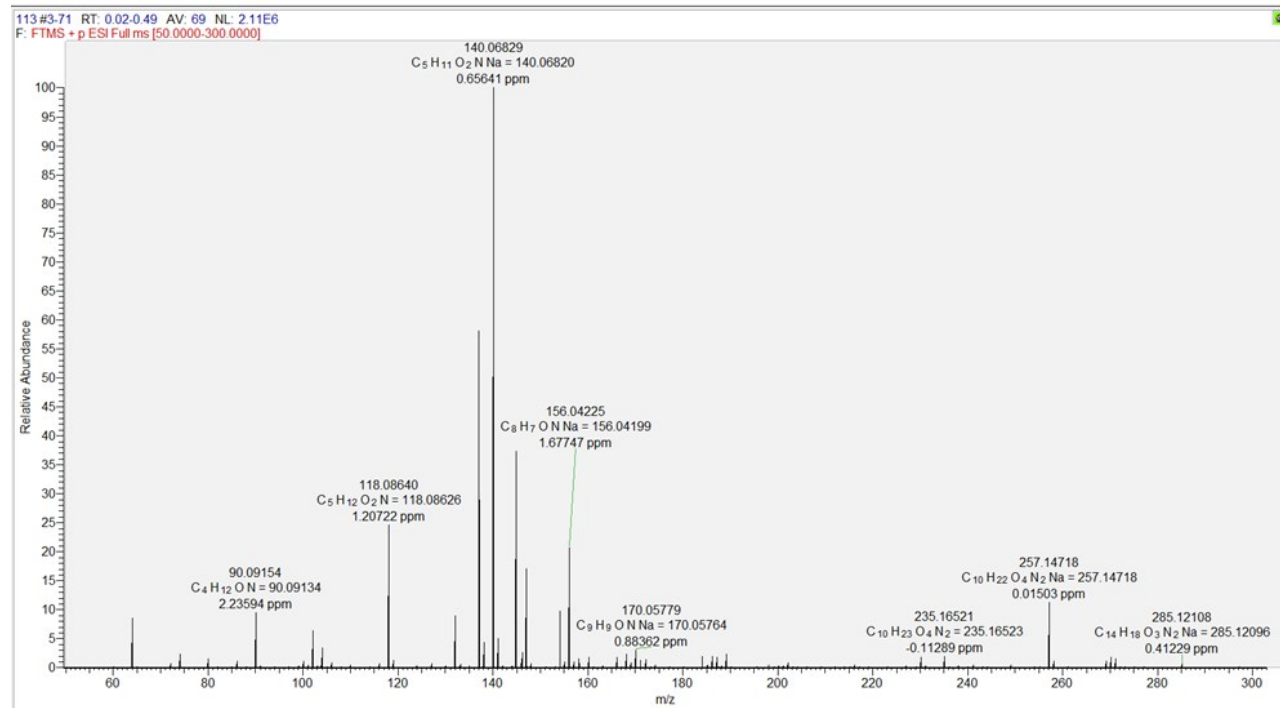
**Figure S61:** HRMS spectrum of compound **6**.



**Figure S62:** HRMS spectrum of compound **9**.



**Figure S63:** HRMS spectrum of compound **11**.



**Figure S64:** HRMS spectrum of compound **12**.