

## Facile Synthesis of Unusual Glycosyl Carbamates and Amino Acid Glycosides from Propargyl 1,2-Orthoesters as Glycosyl Donors

Ashif Y. Shaikh,<sup>a</sup> Gopalsamy Sureshkumar,<sup>a</sup> Debasis Pati,<sup>b</sup> Sayam Sen Gupta<sup>b</sup> and Srinivas Hotha<sup>\*a,c</sup>

<sup>a</sup> *Division of Organic Chemistry, Combi Chem - BioResource Center, <sup>b</sup>Chemical Engineering & Process Development National Chemical Laboratory (CSIR), Dr. Homi Bhabha Road, PUNE – 411 008, India;*  
<sup>c</sup> *Department of Chemistry, Indian Institute of Science Education & Research, PUNE – 411 008, India.*

*s.hotha@iiserpune.ac.in*

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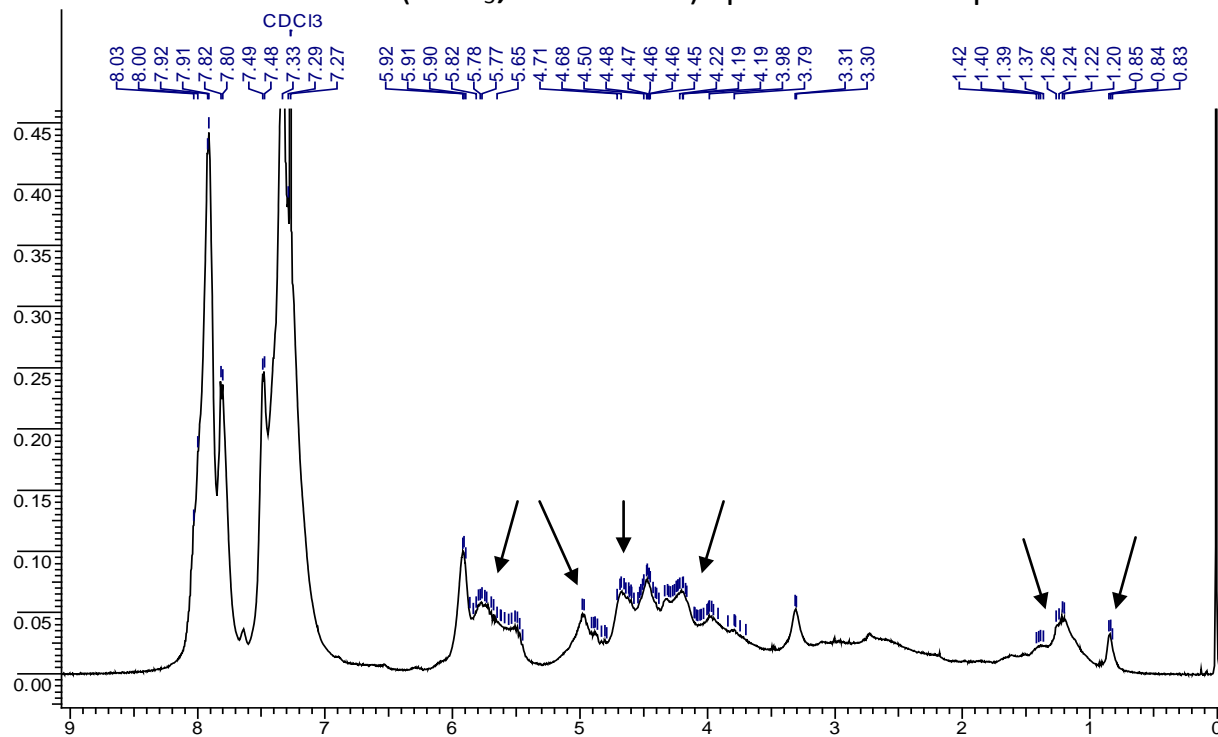
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## General Experimental Techniques and Apparatus

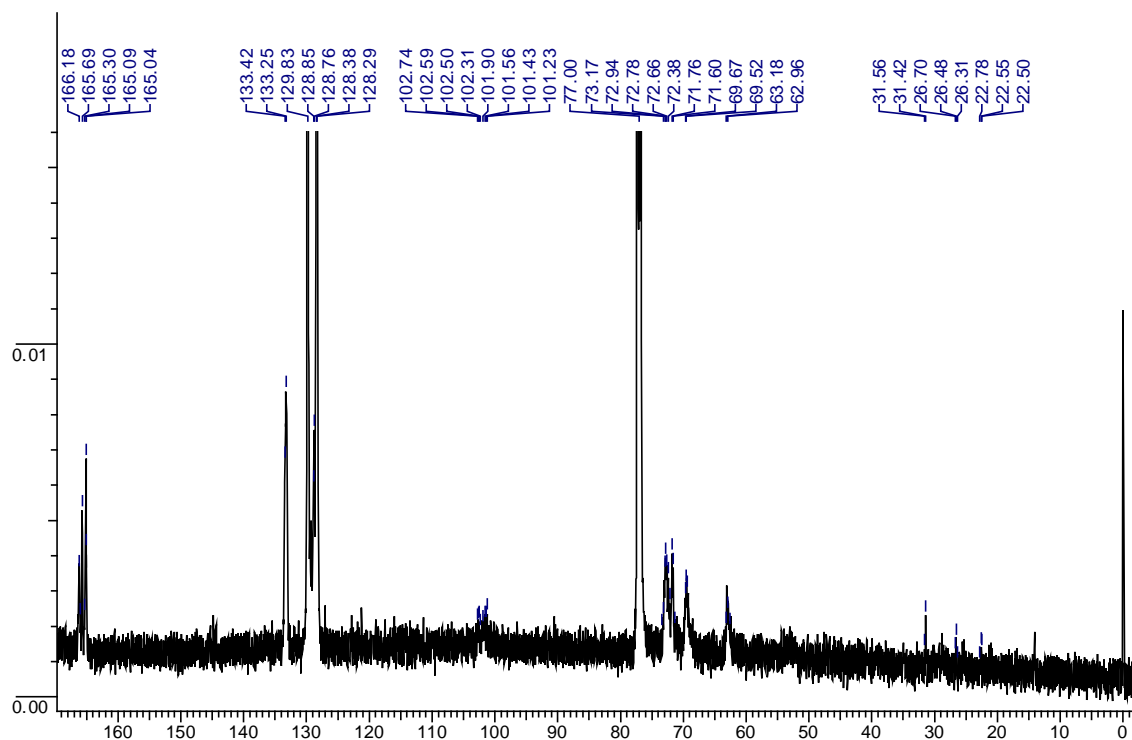
Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Unless otherwise reported all reactions were performed under argon atmosphere. Removal of solvent *in vacuo* refers to distillation using a rotary evaporator attached to an efficient vacuum pump. Products obtained as solids or syrups were dried under high vacuum. AuCl<sub>3</sub> was purchased from multi-national commercial vendors. Analytical thin-layer chromatography was performed on pre-coated silica plates (F<sub>254</sub>, 0.25 mm thickness); compounds were visualized by UV light or by staining with anisaldehyde spray. <sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded on 200 MHz for <sup>1</sup>H and 50 MHz for <sup>13</sup>C NMR or 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C NMR or 500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C NMR spectrometers. HRMS data was recorded on MALDI-TOF using 2,5-dihydroxybenzoic acid as the solid matrix. Chemical shifts ( $\delta_{\text{H}}$ ) are quoted in ppm and are referenced to tetramethylsilane (internal). Size-exclusion chromatography of the glycopolypeptides was performed using an instrument equipped with Waters 590 pump with an Spectra System RI-150 RI detector. Separations were effected by 10<sup>5</sup> and 10<sup>3</sup> Å Phenomenex 5 $\mu$  columns using 0.1M LiBr in DMF eluent at 60 °C at the samples concentrations of 5mg/ml. A constant flow rate of 1 mL/min was maintained, and the instrument was calibrated using polystyrene standards.

### Characterization of glycopeptide 7b:

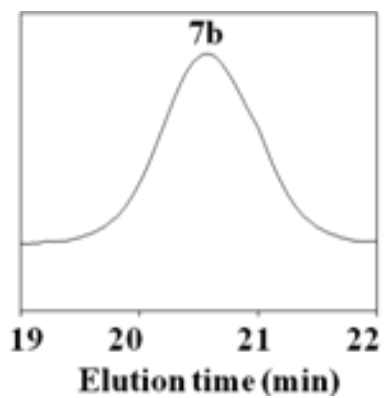
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500.13MHz) Spectrum of Compound 7b



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 124.32 MHz) Spectrum of Compound 7b

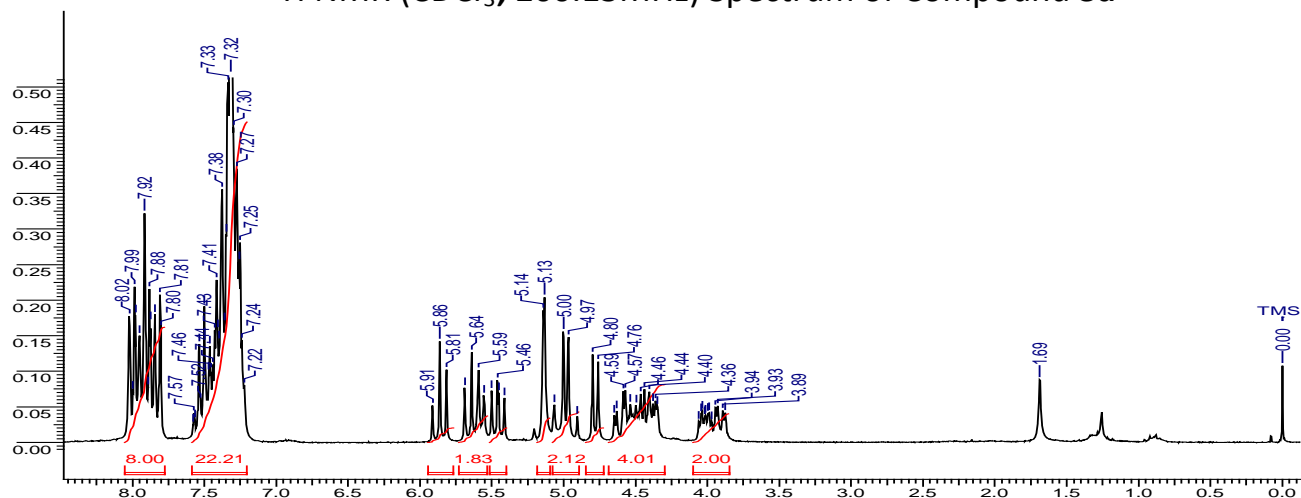


Size Exclusion Chromatogram of Glycopolypeptide **7b**

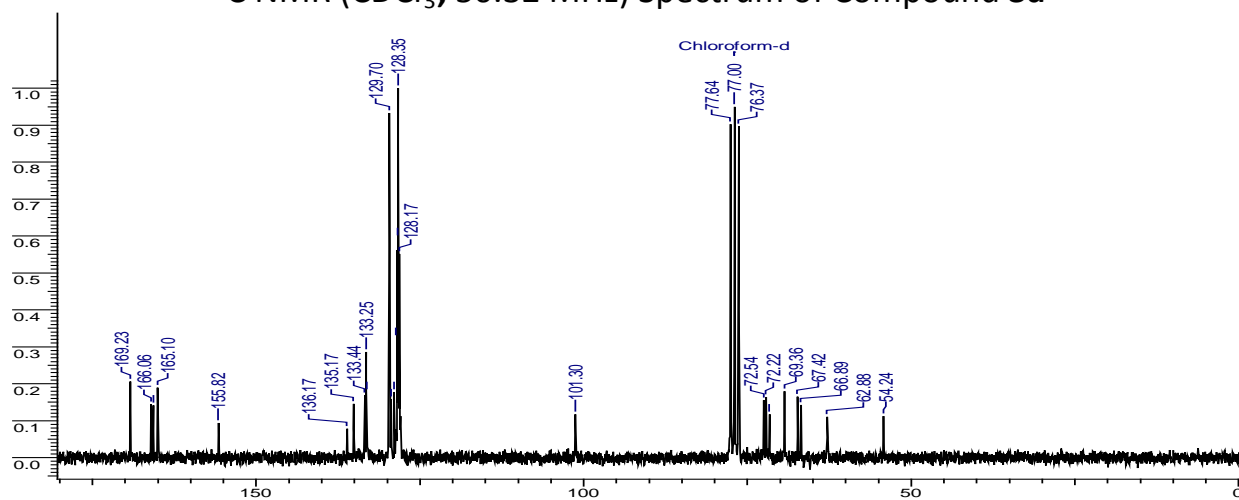


GPC of polymer **7b** (DMF/0.1M LiBr, 60 °C, RI)

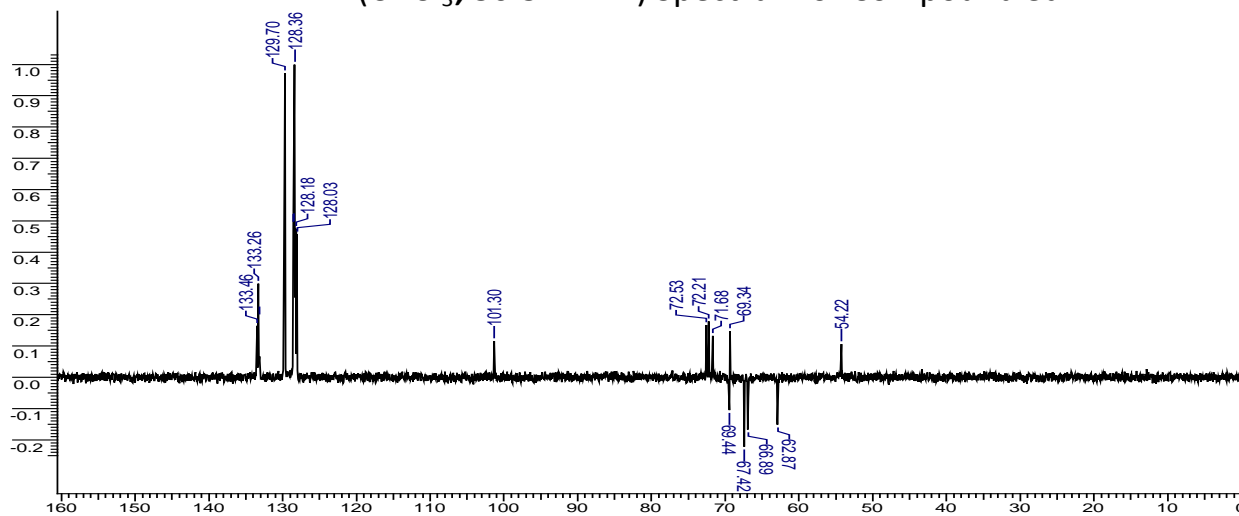
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 200.13MHz) Spectrum of Compound **3a**



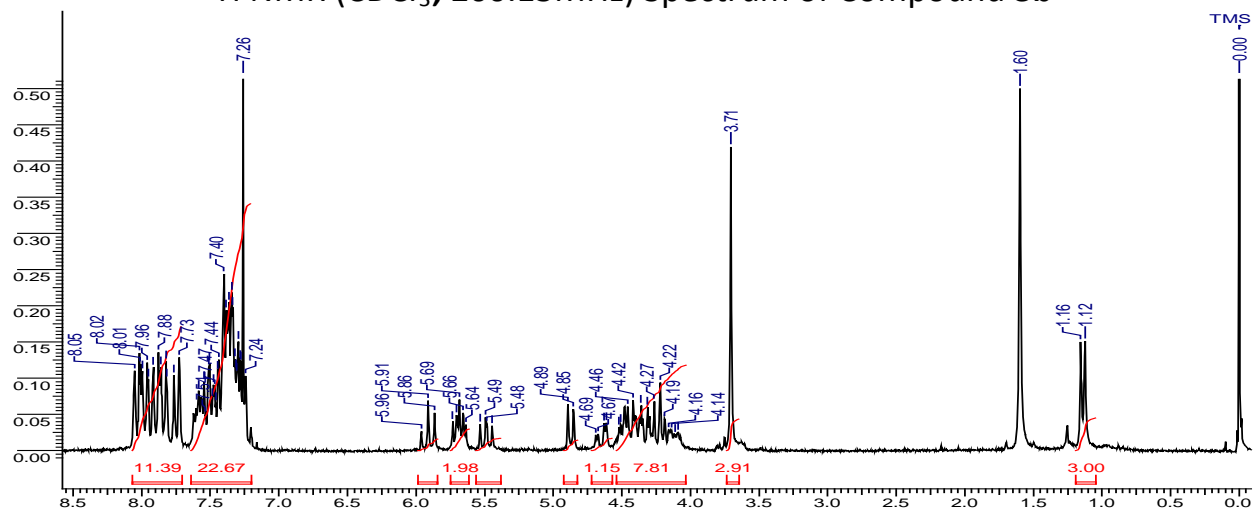
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **3a**



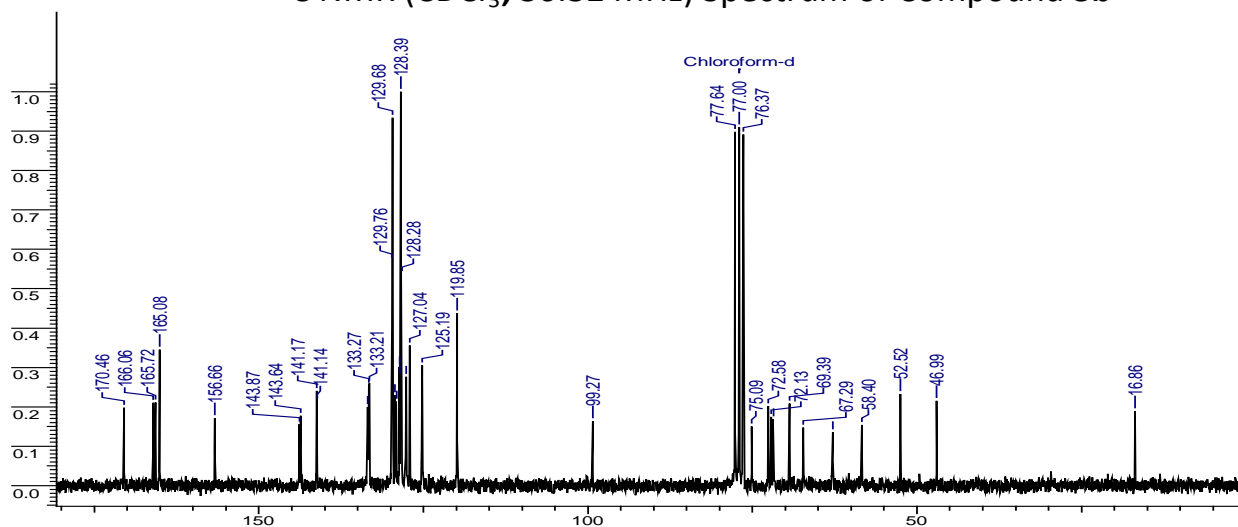
### DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **3a**



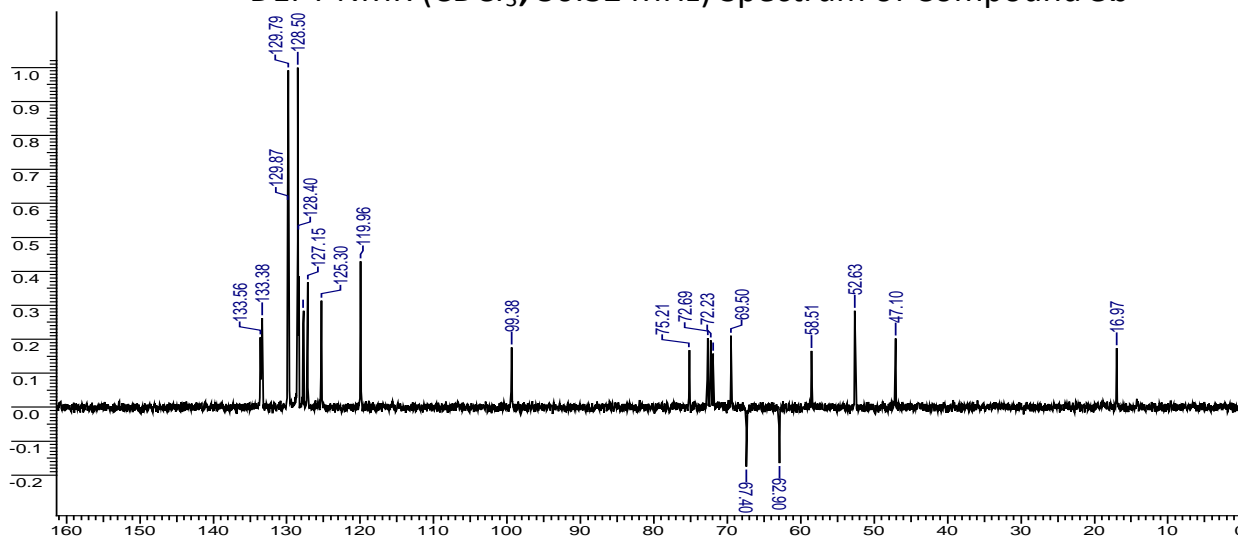
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200.13MHz) Spectrum of Compound **3b**



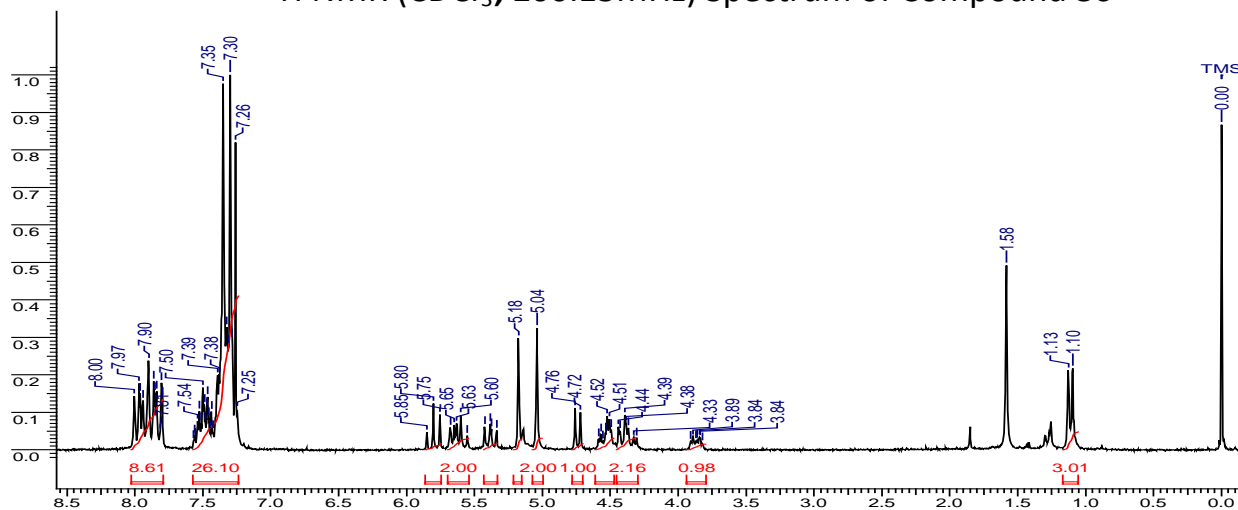
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 50.32 MHz) Spectrum of Compound **3b**



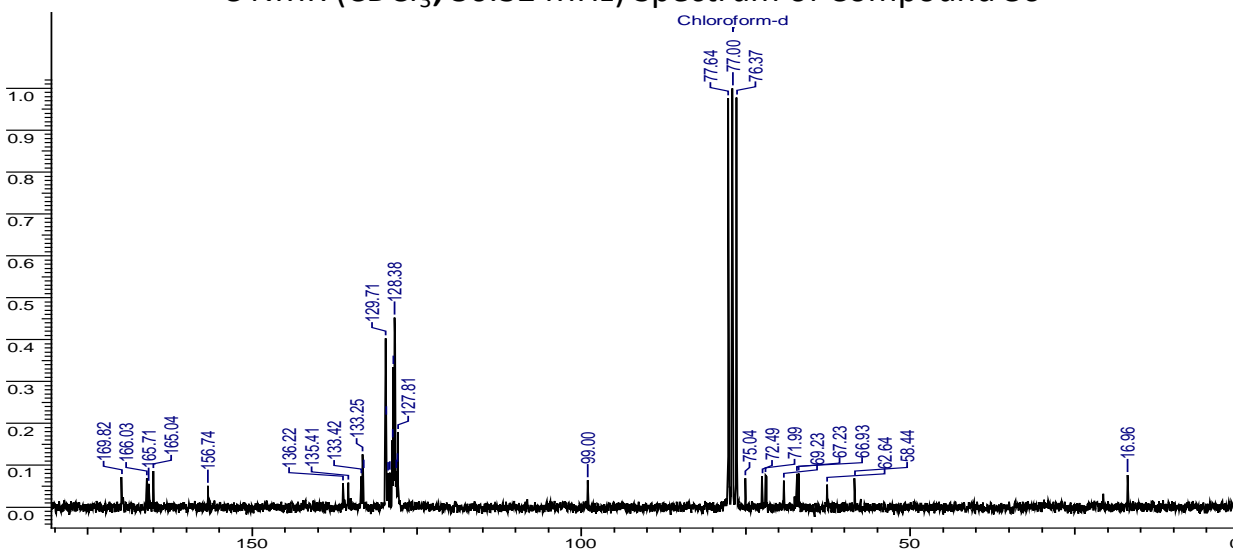
DEPT NMR (CDCl<sub>3</sub>, 50.32 MHz) Spectrum of Compound **3b**



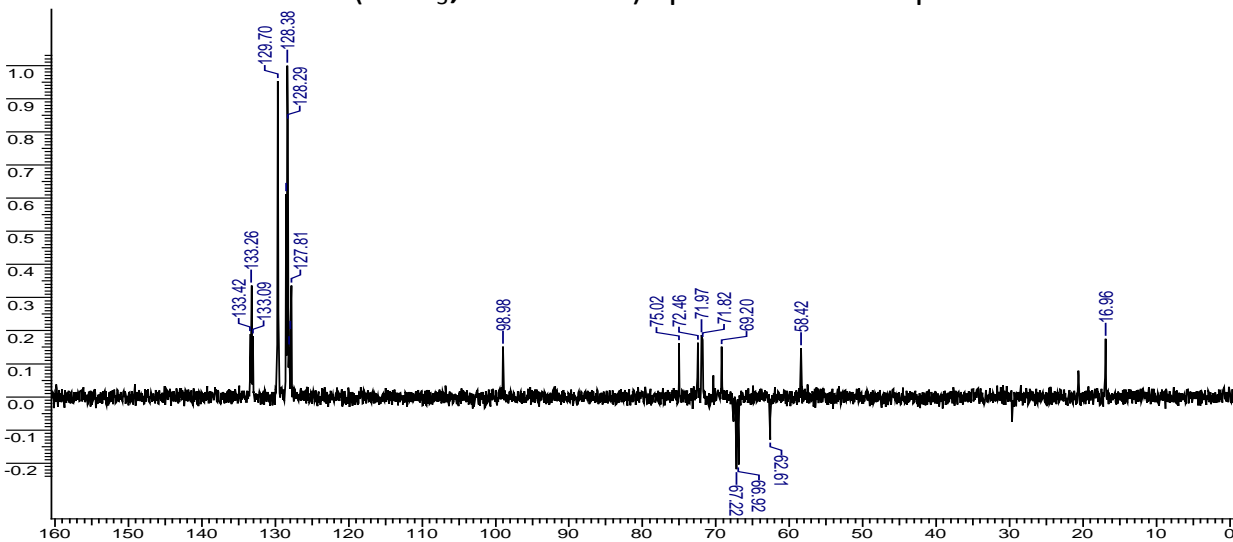
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 200.13MHz) Spectrum of Compound **3c**



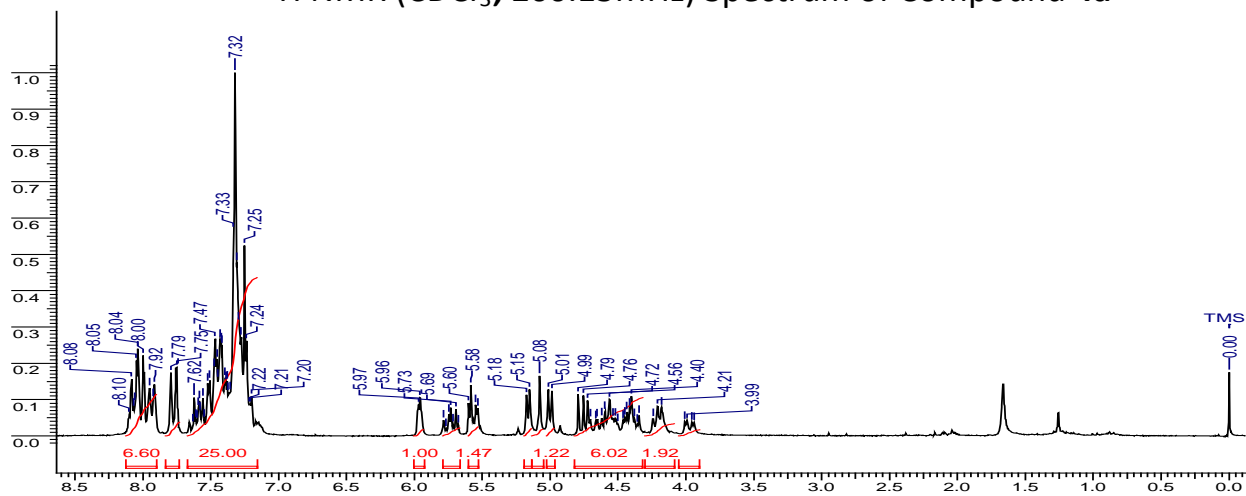
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **3c**



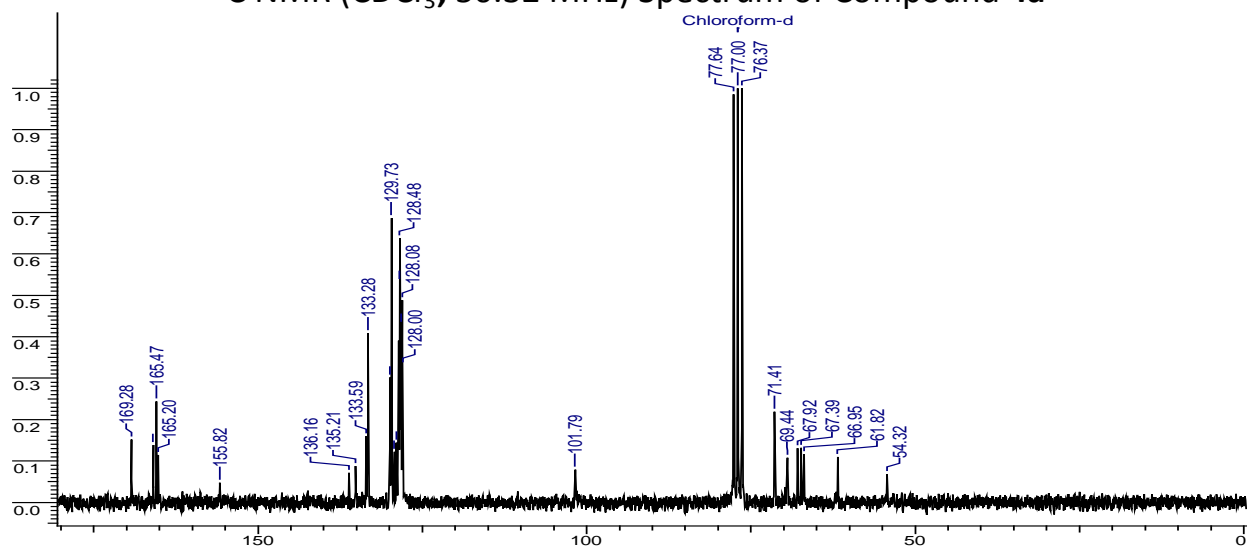
### DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **3c**



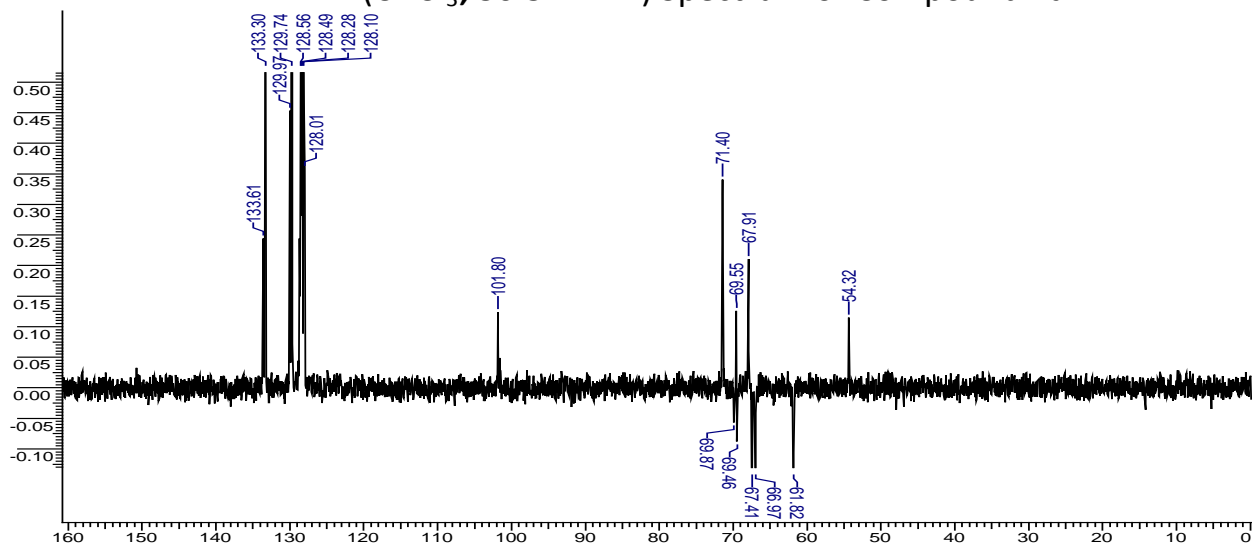
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 200.13MHz) Spectrum of Compound 4a



### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound 4a

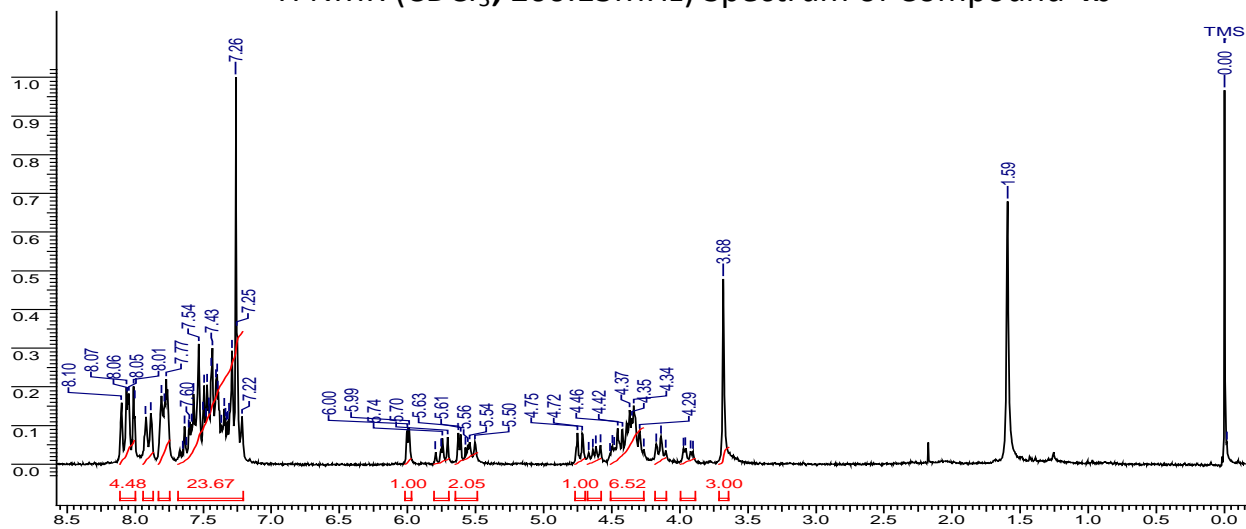


### DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound 4a

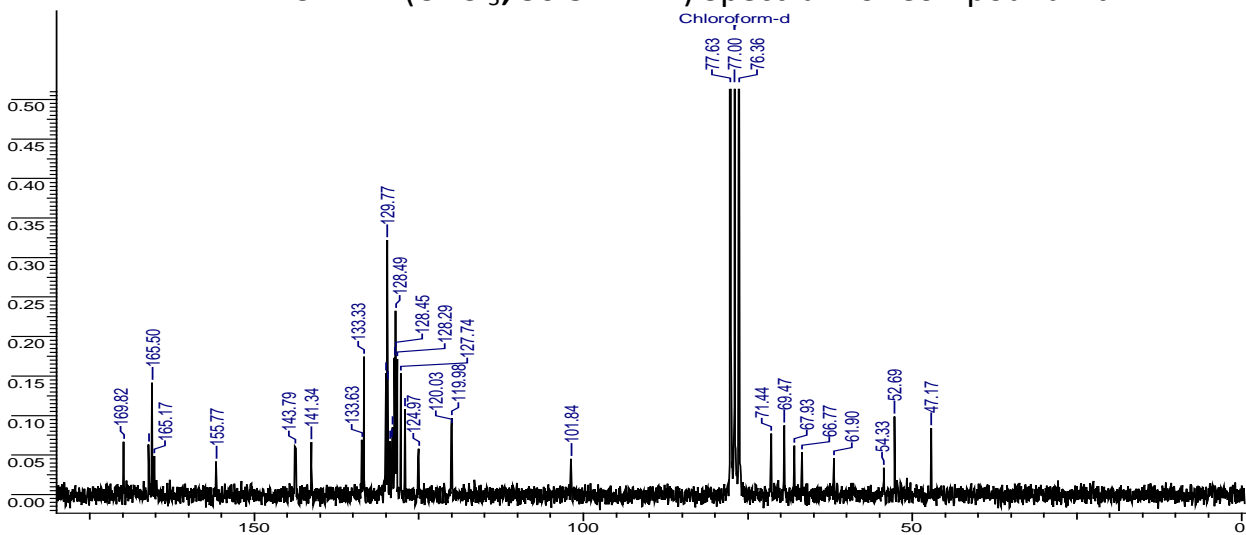




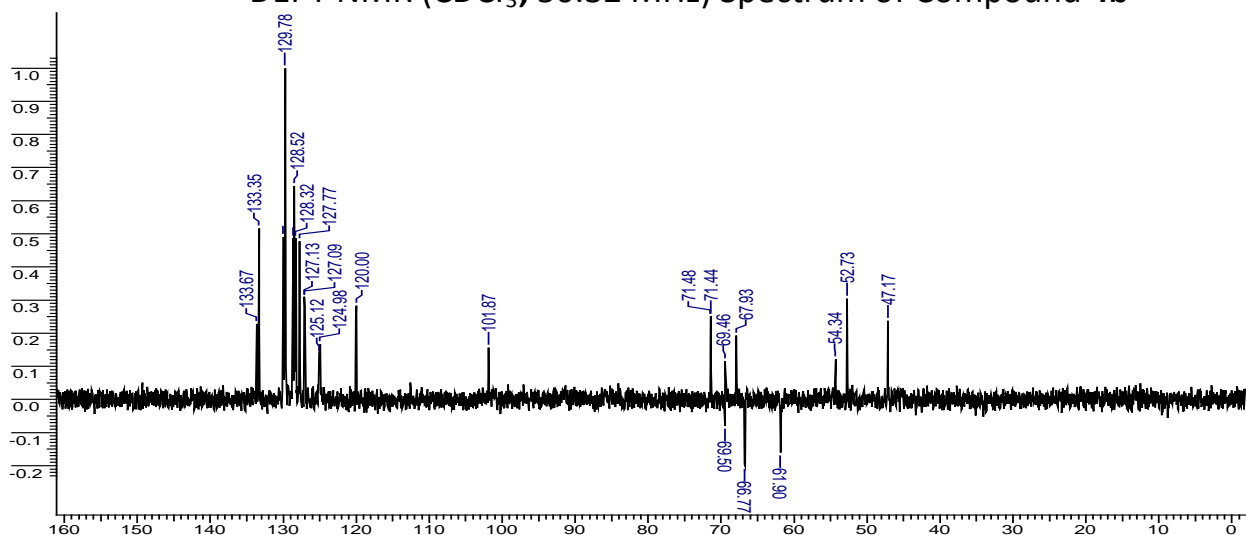
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 200.13MHz) Spectrum of Compound **4b**



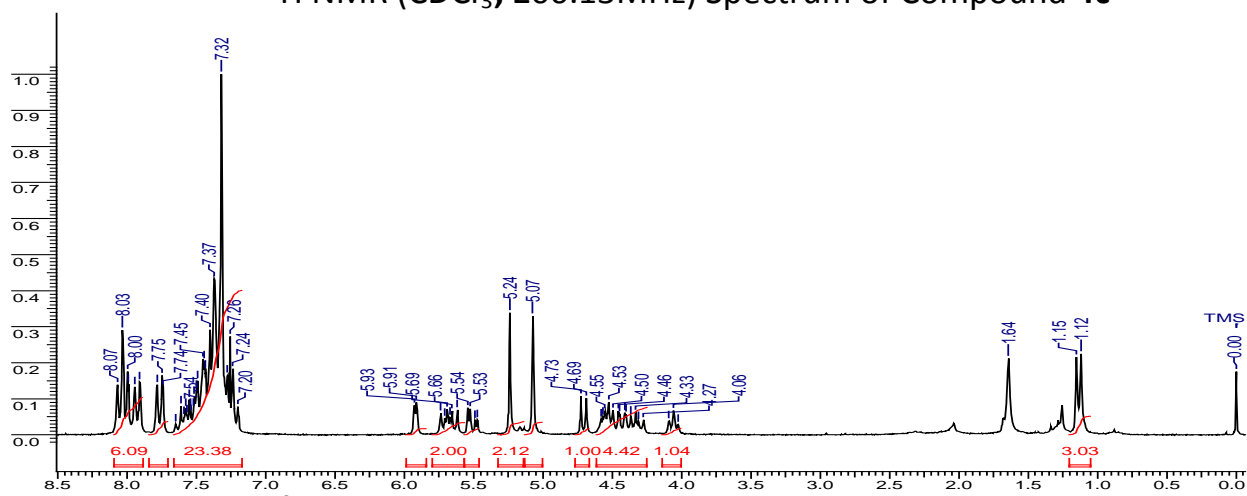
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **4b**



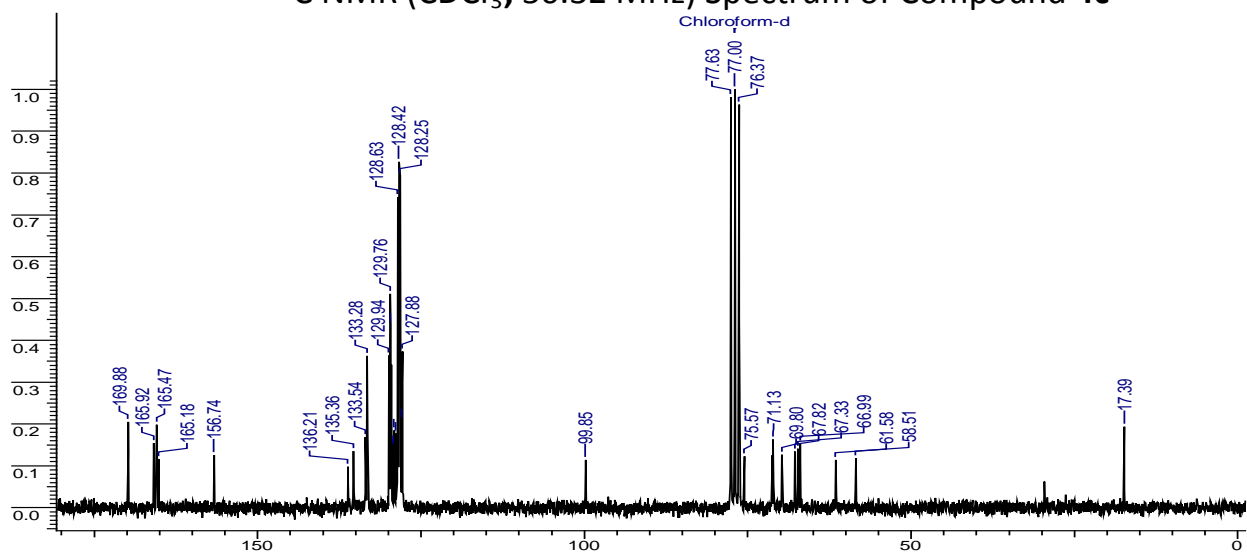
### DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **4b**



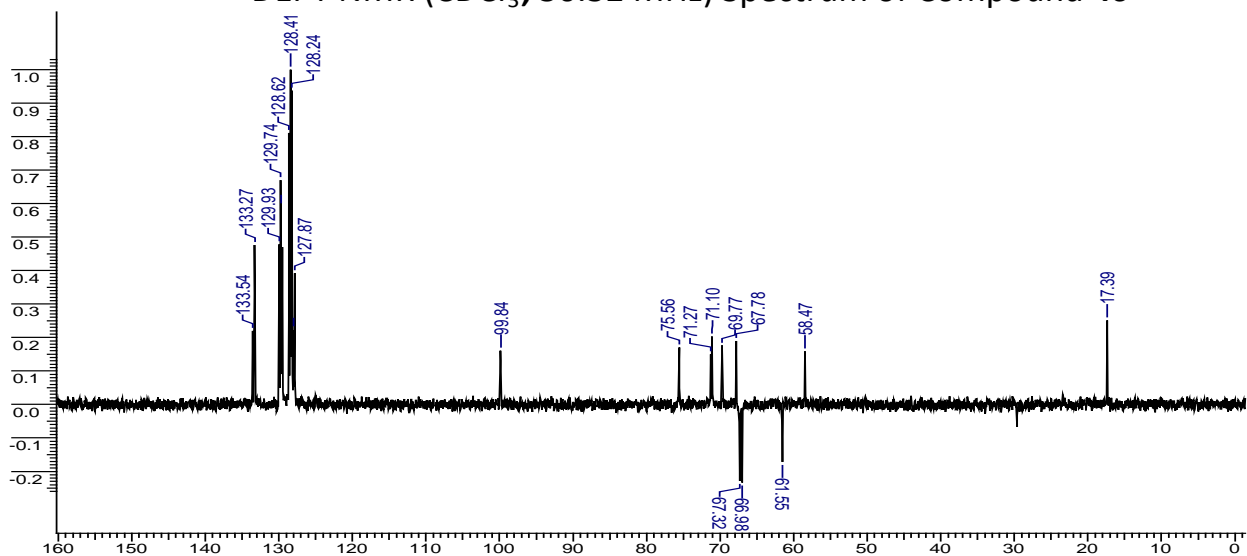
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 200.13MHz) Spectrum of Compound 4c



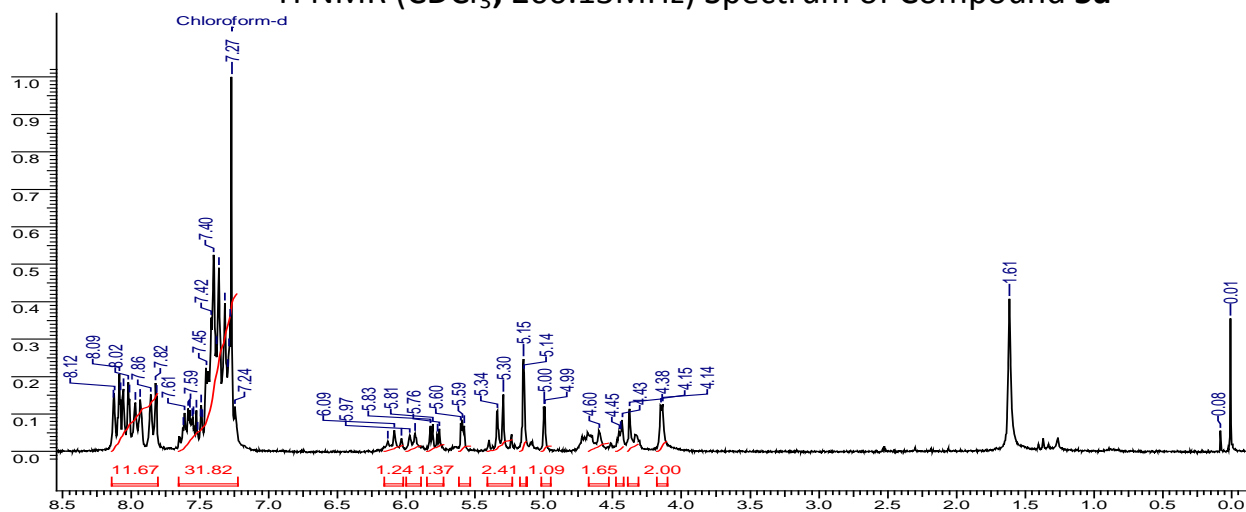
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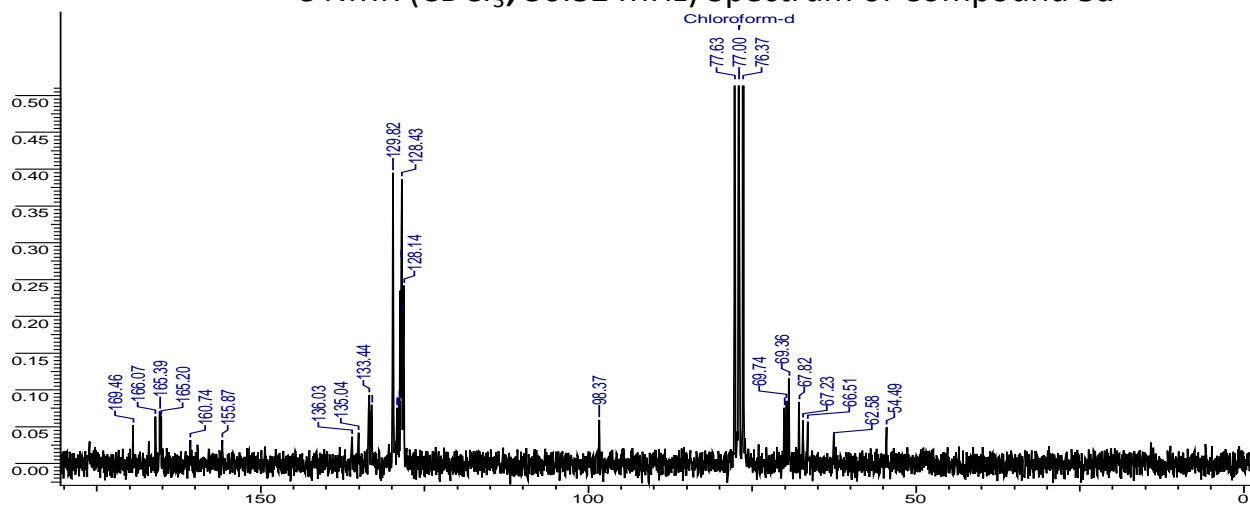
### DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound 4c



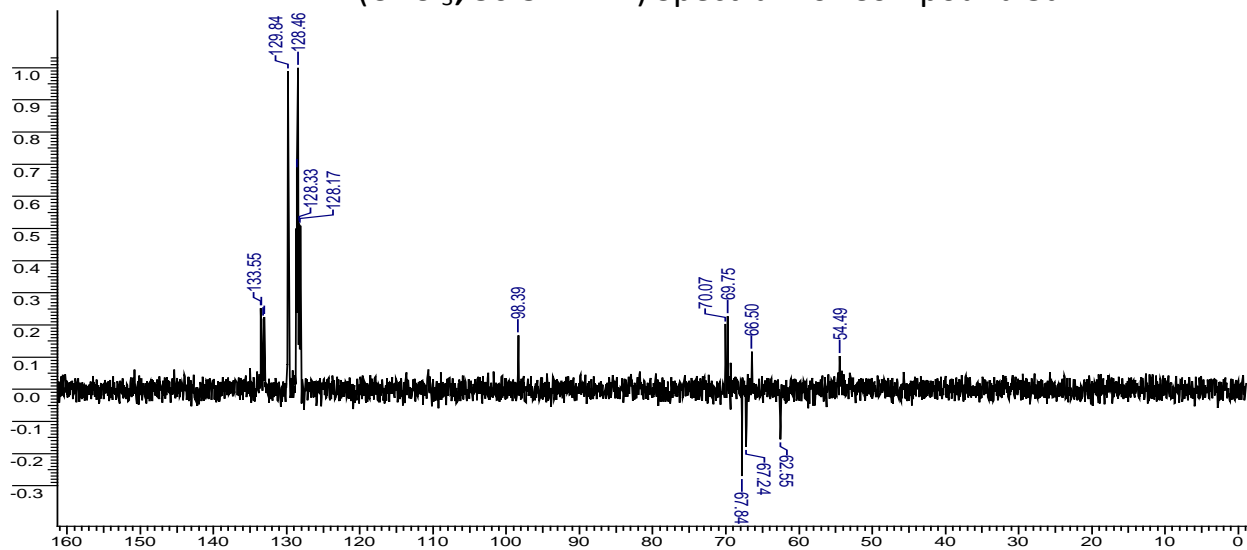
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 200.13MHz) Spectrum of Compound 5a



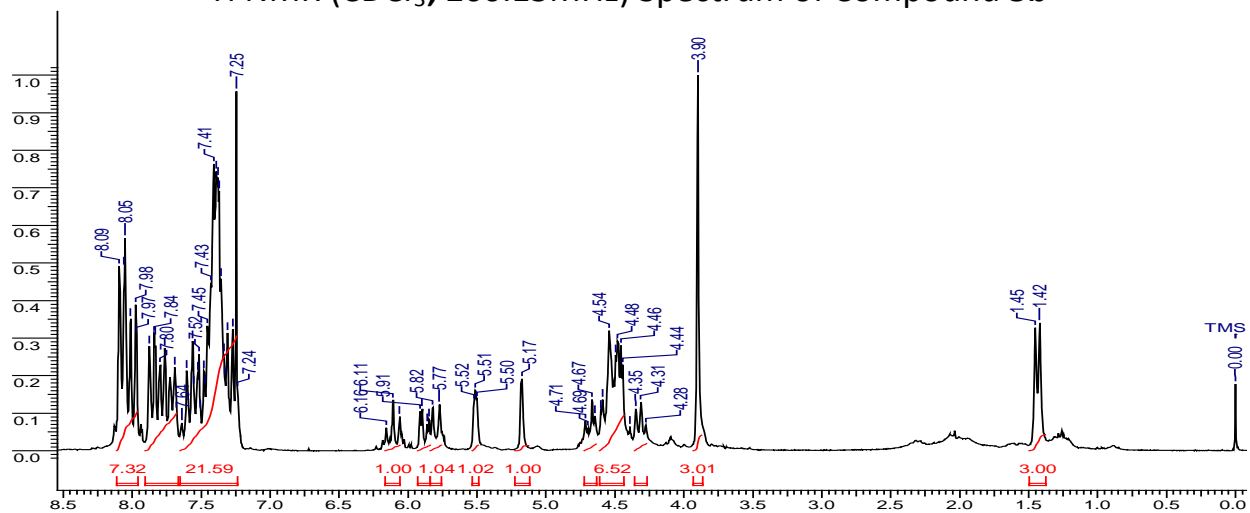
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound 5a



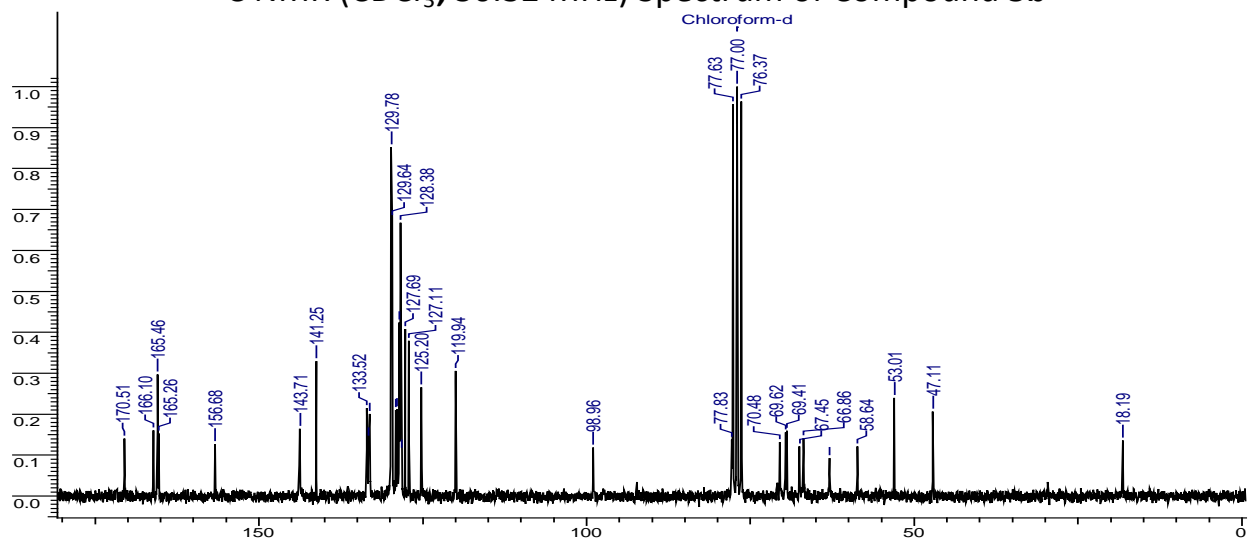
### DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound 5a



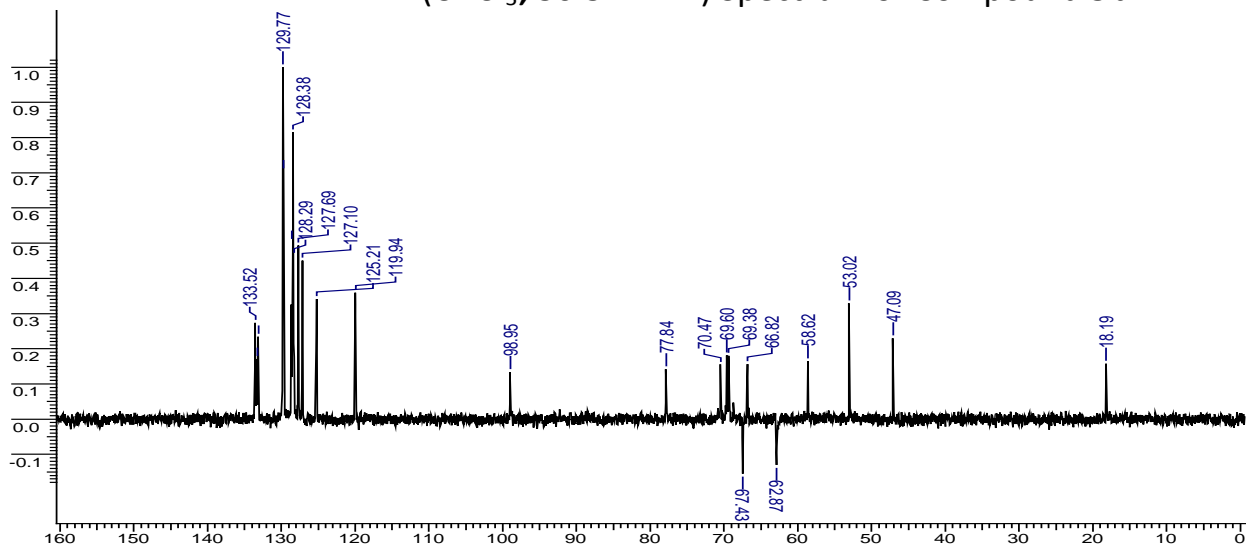
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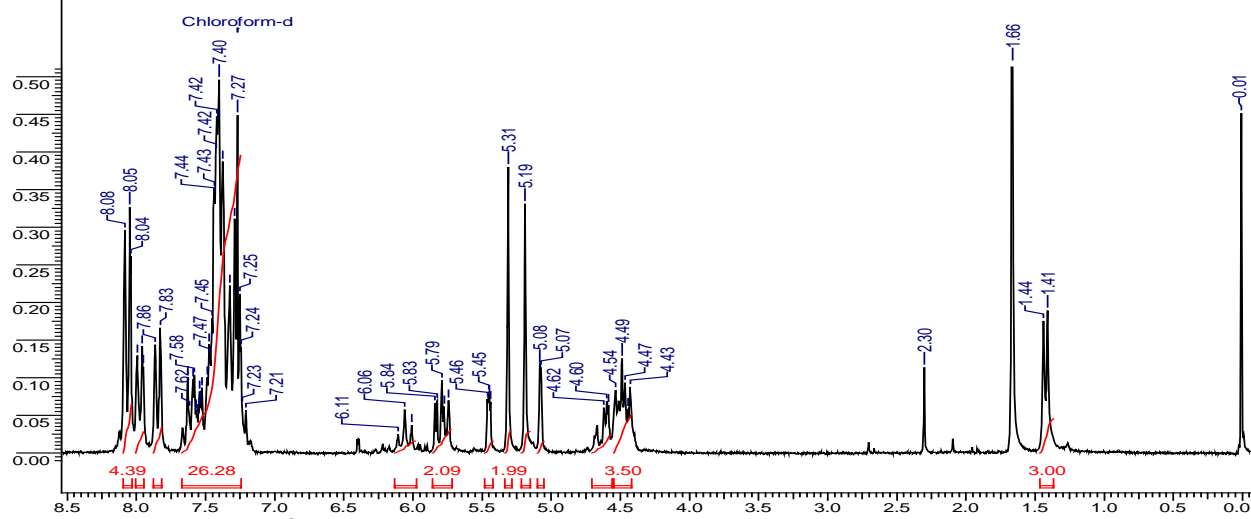
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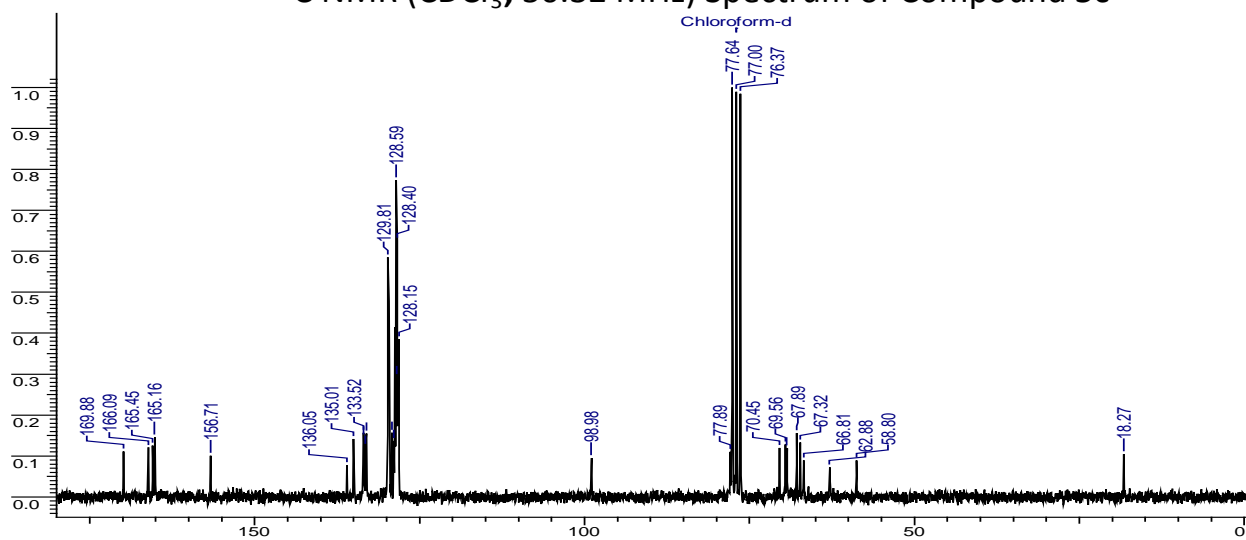
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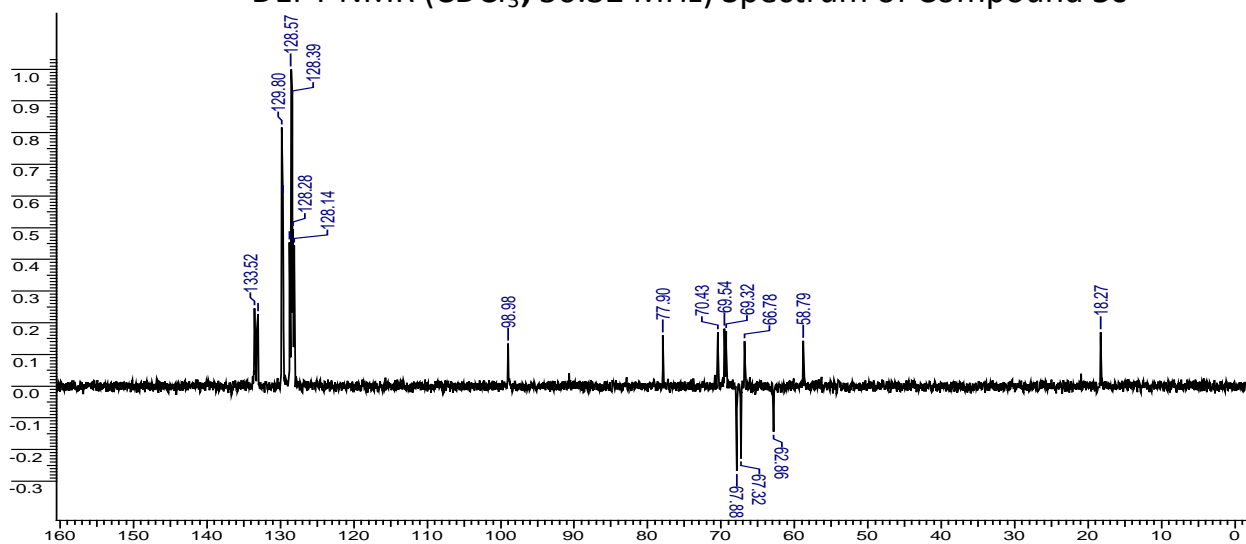
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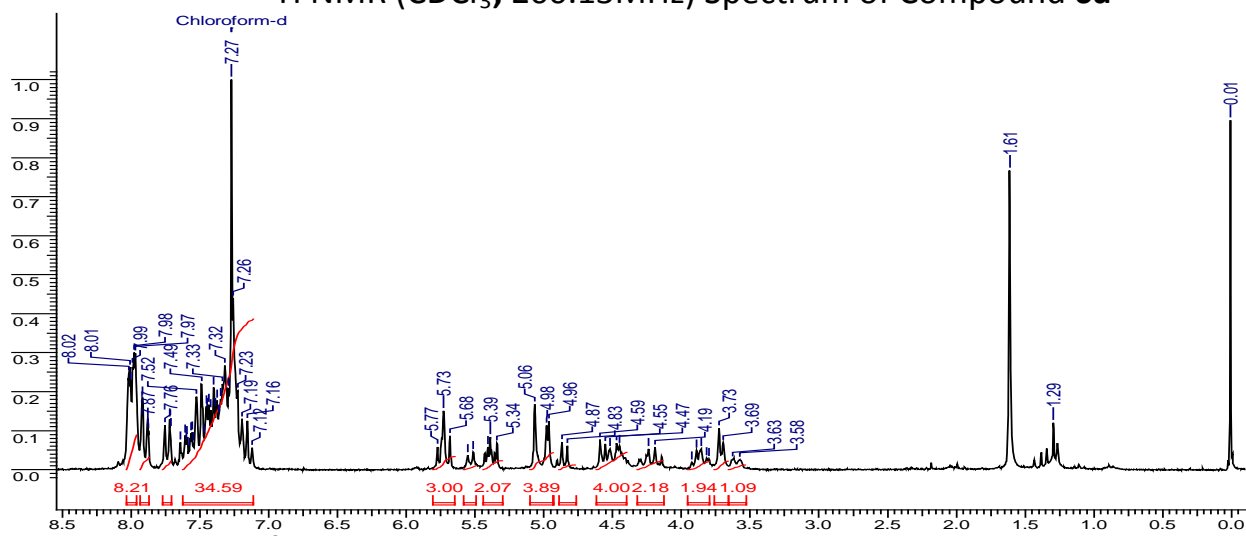
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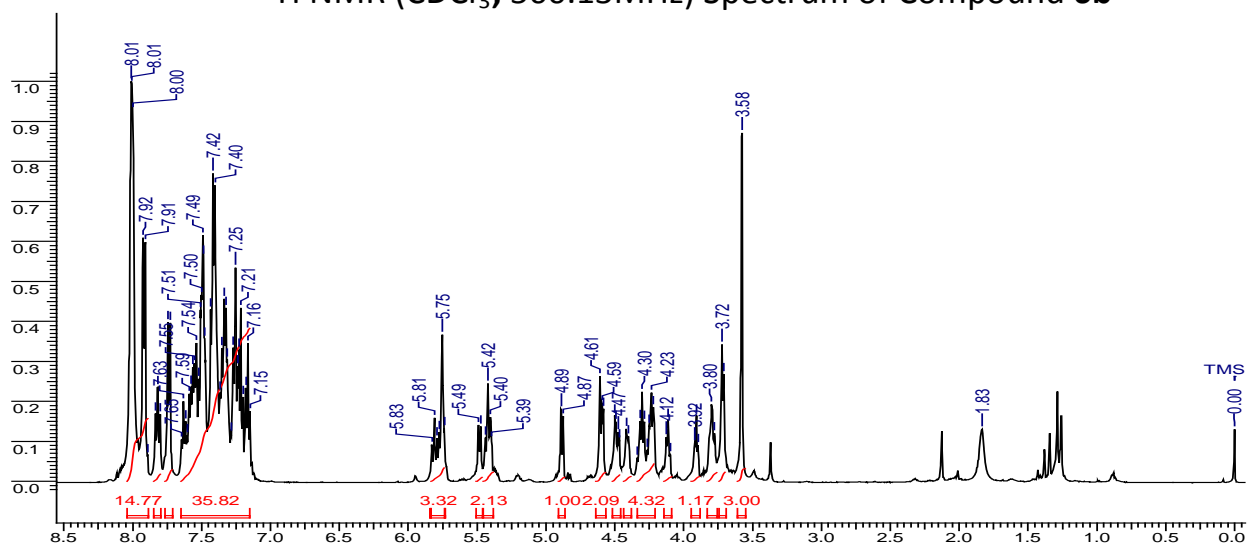
### DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound 5c



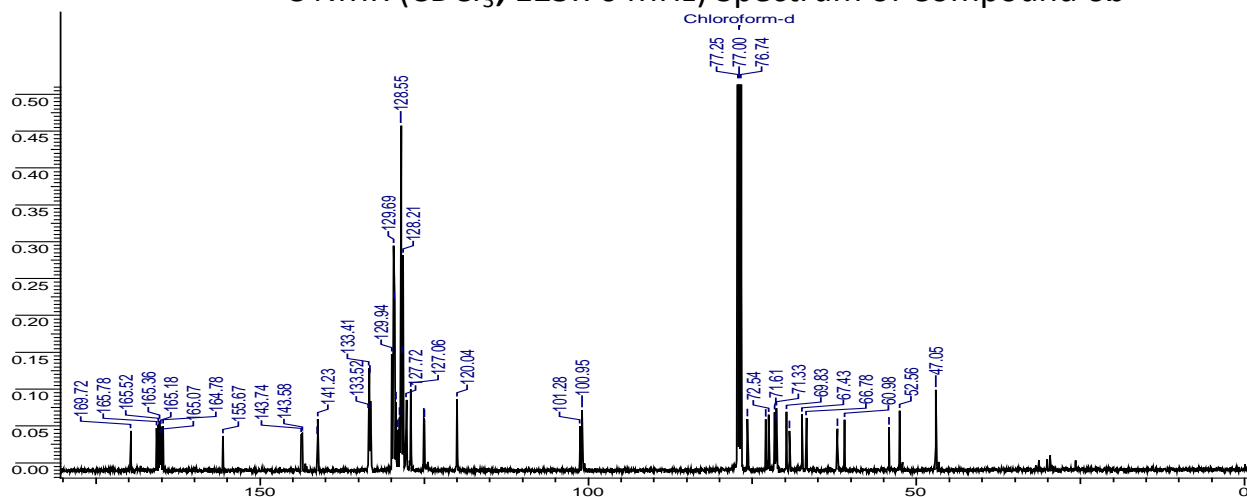
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 200.13MHz) Spectrum of Compound 6a



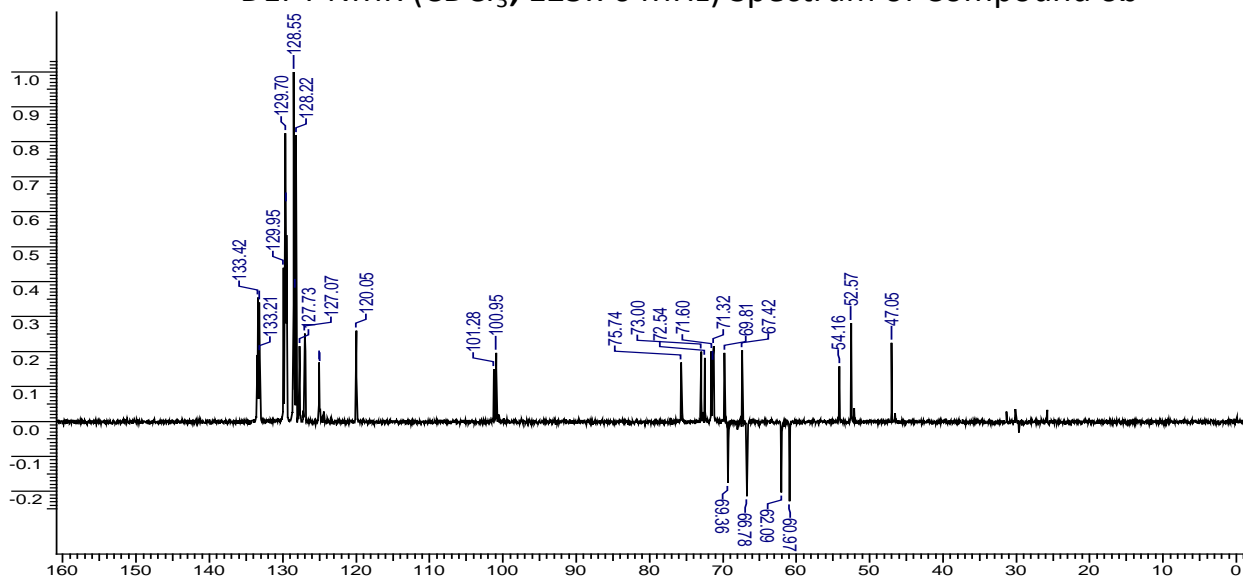
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500.13MHz) Spectrum of Compound **6b**



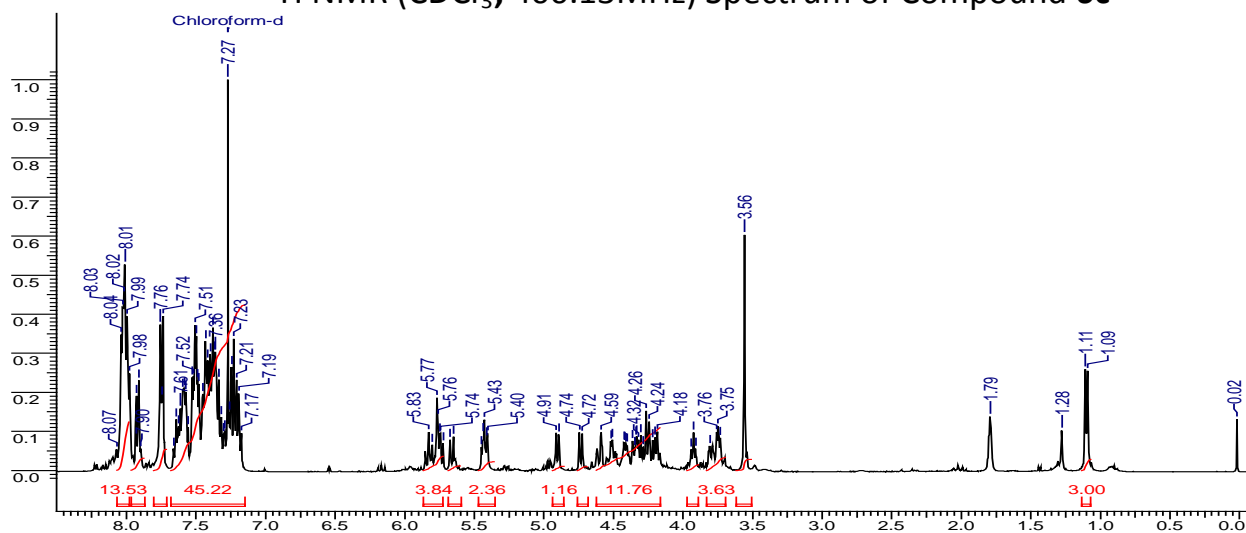
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 125.76 MHz) Spectrum of Compound **6b**



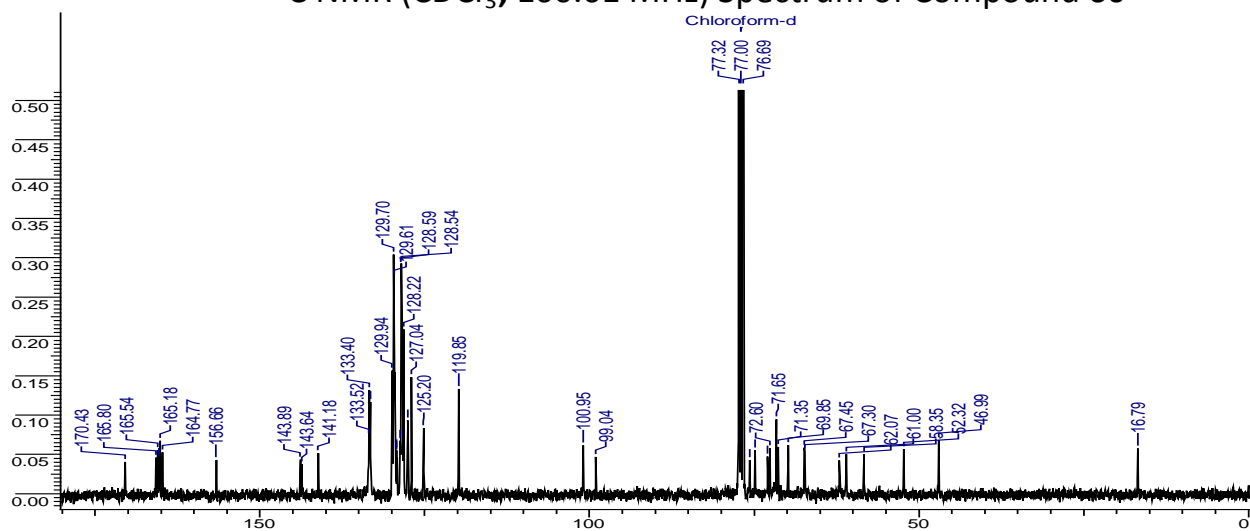
### DEPT NMR ( $\text{CDCl}_3$ , 125.76 MHz) Spectrum of Compound **6b**



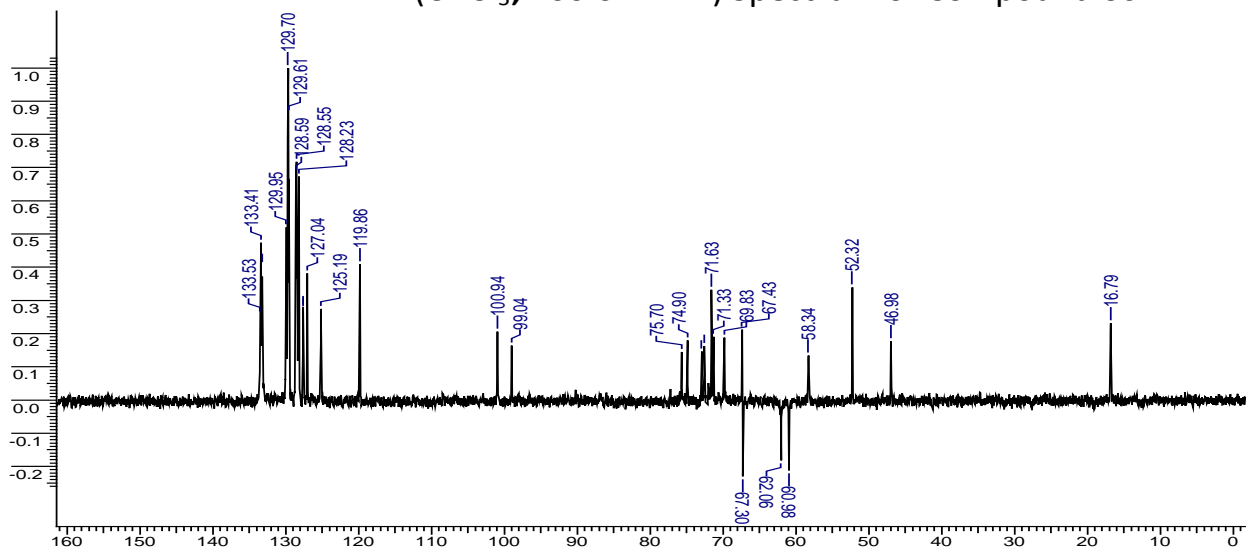
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400.13MHz) Spectrum of Compound **6c**



### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100.61 MHz) Spectrum of Compound **6c**

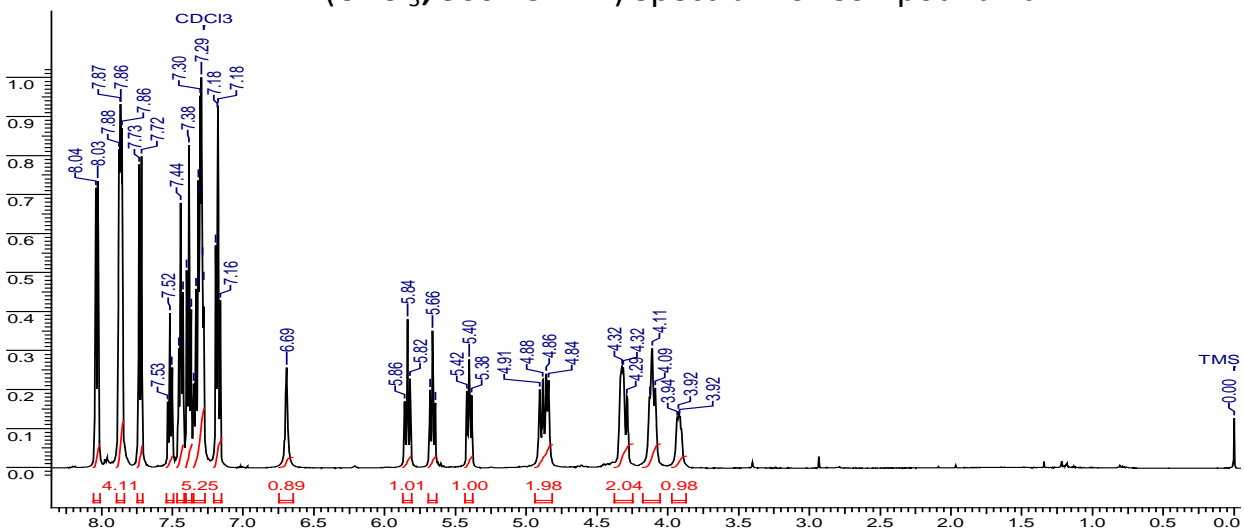


### DEPT NMR ( $\text{CDCl}_3$ , 100.61 MHz) Spectrum of Compound **6c**

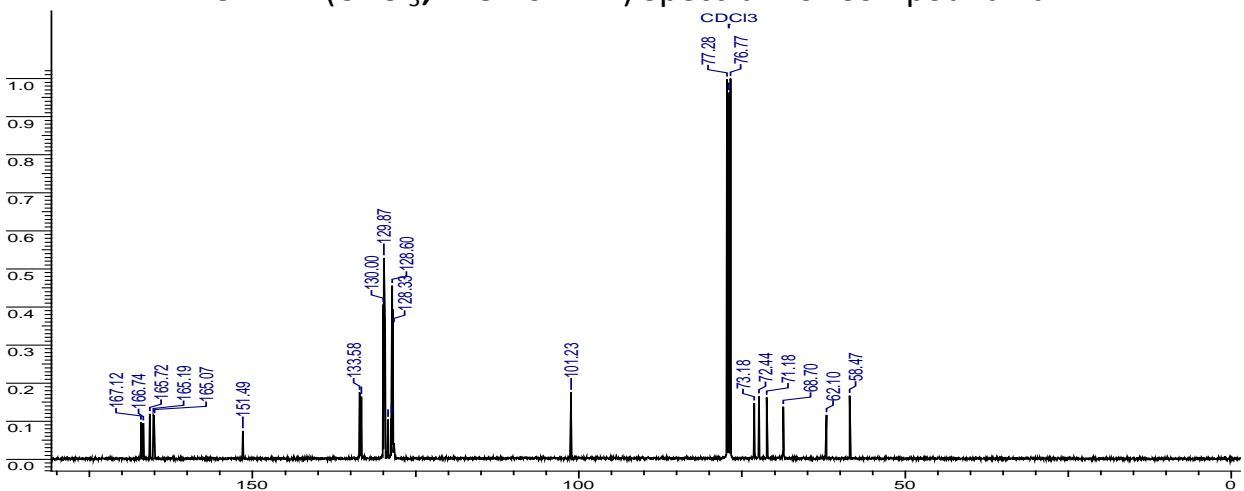




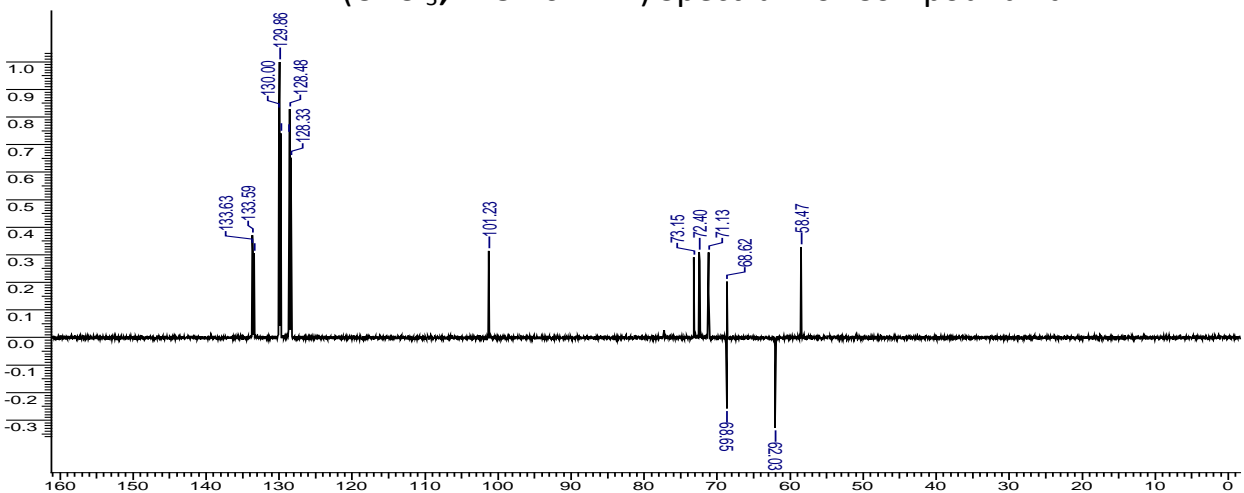
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500.13MHz) Spectrum of Compound 7a



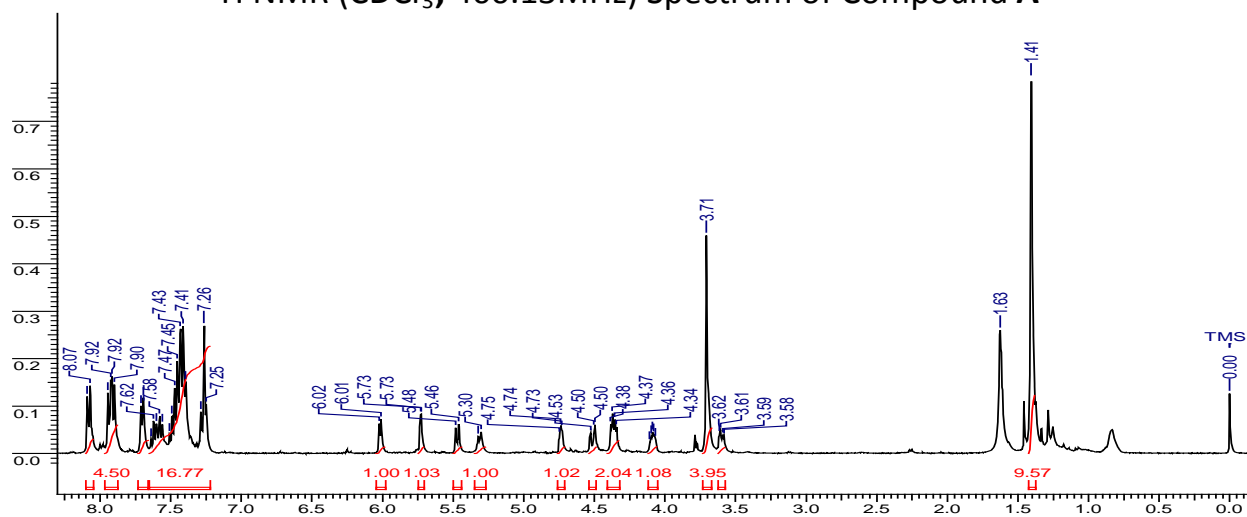
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.76 MHz) Spectrum of Compound 7a



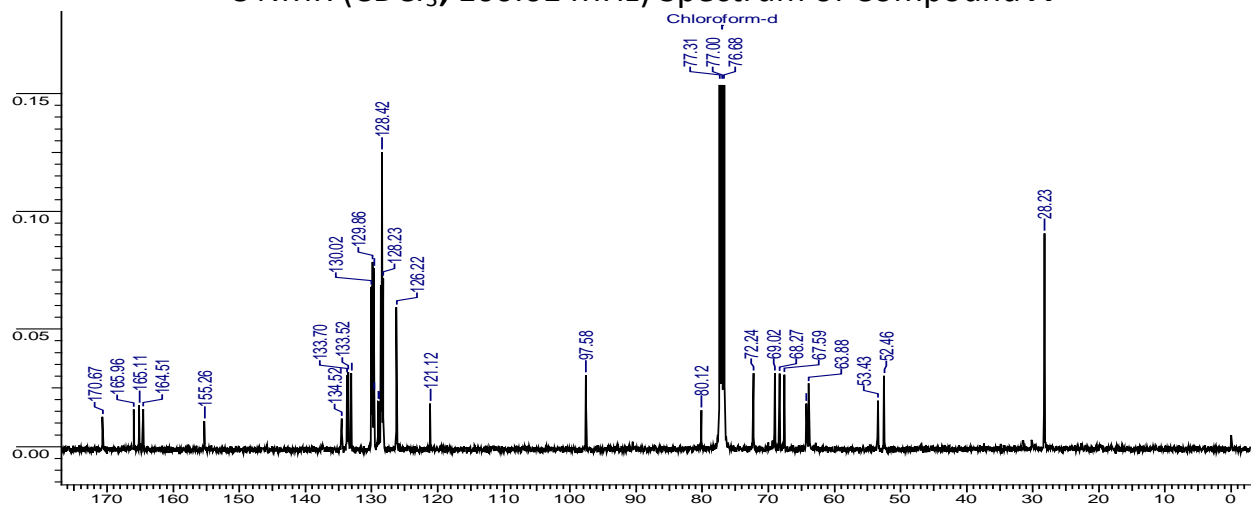
DEPT NMR (CDCl<sub>3</sub>, 125.76 MHz) Spectrum of Compound 7a



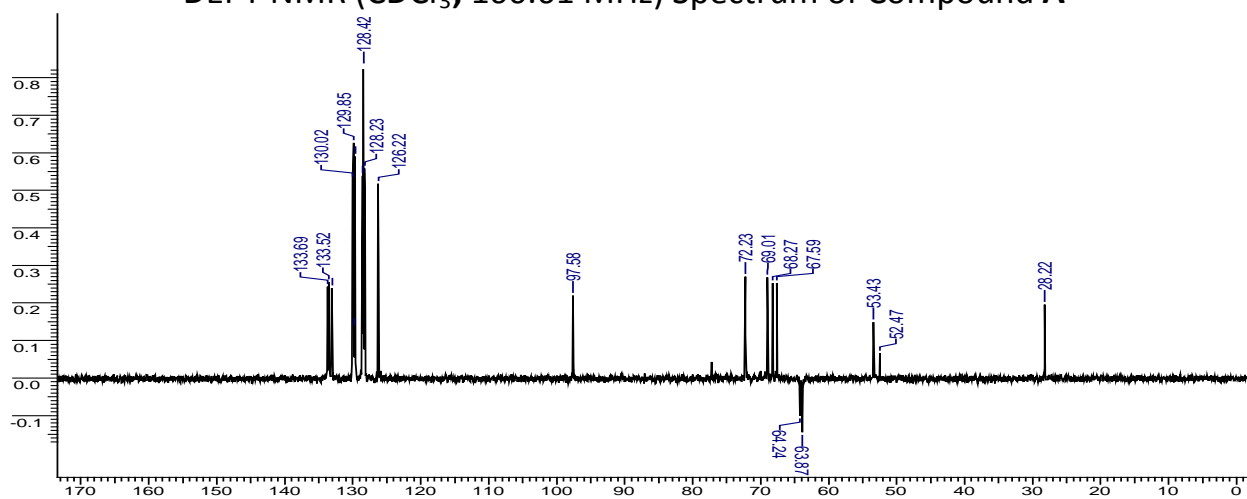
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400.13MHz) Spectrum of Compound A



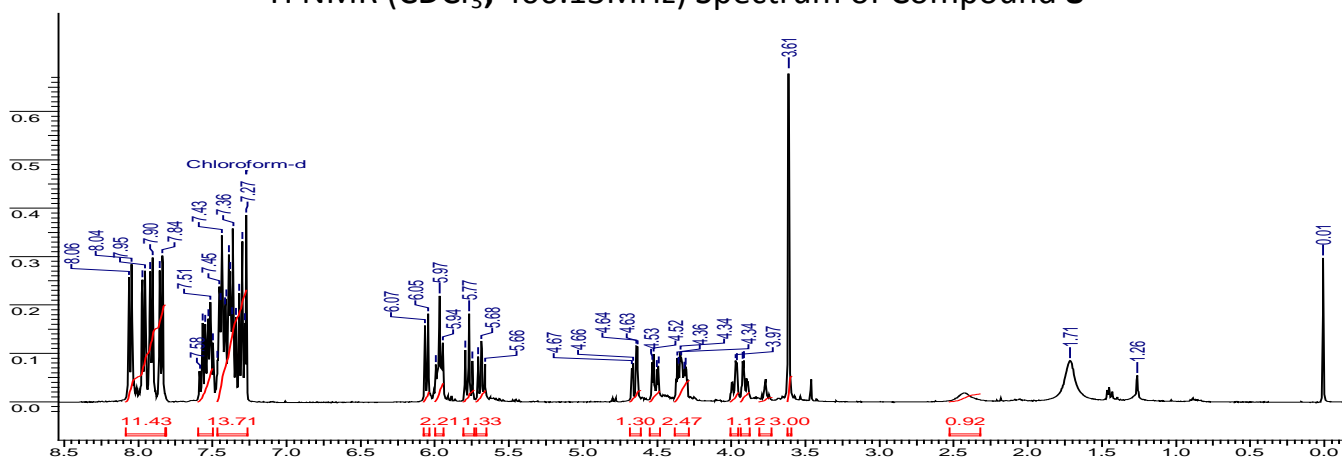
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100.61 MHz) Spectrum of Compound A



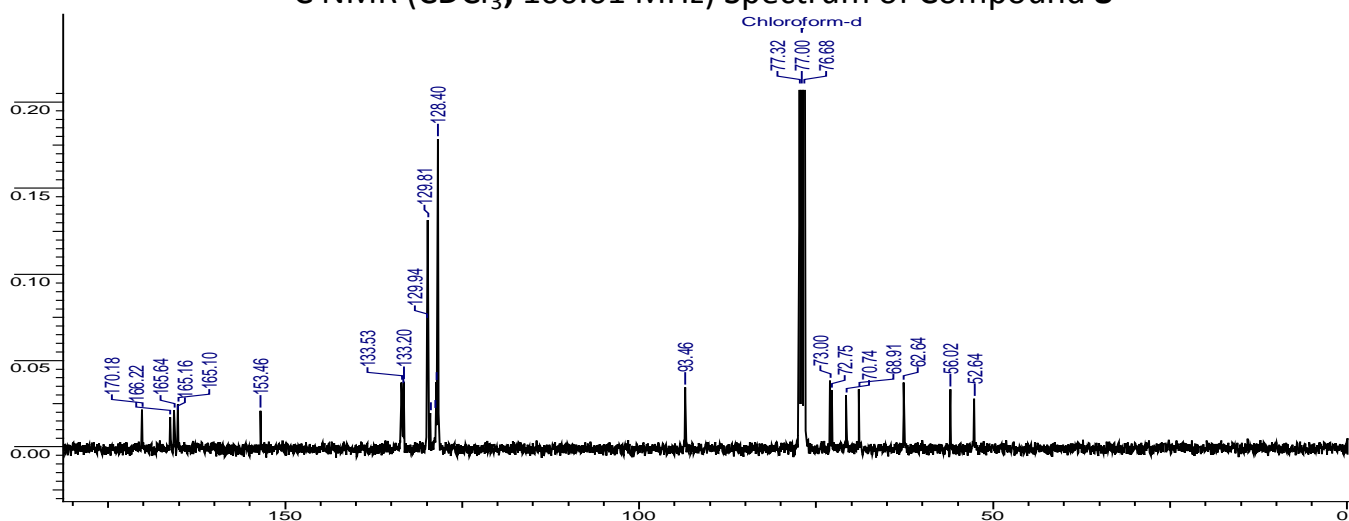
### DEPT NMR ( $\text{CDCl}_3$ , 100.61 MHz) Spectrum of Compound A



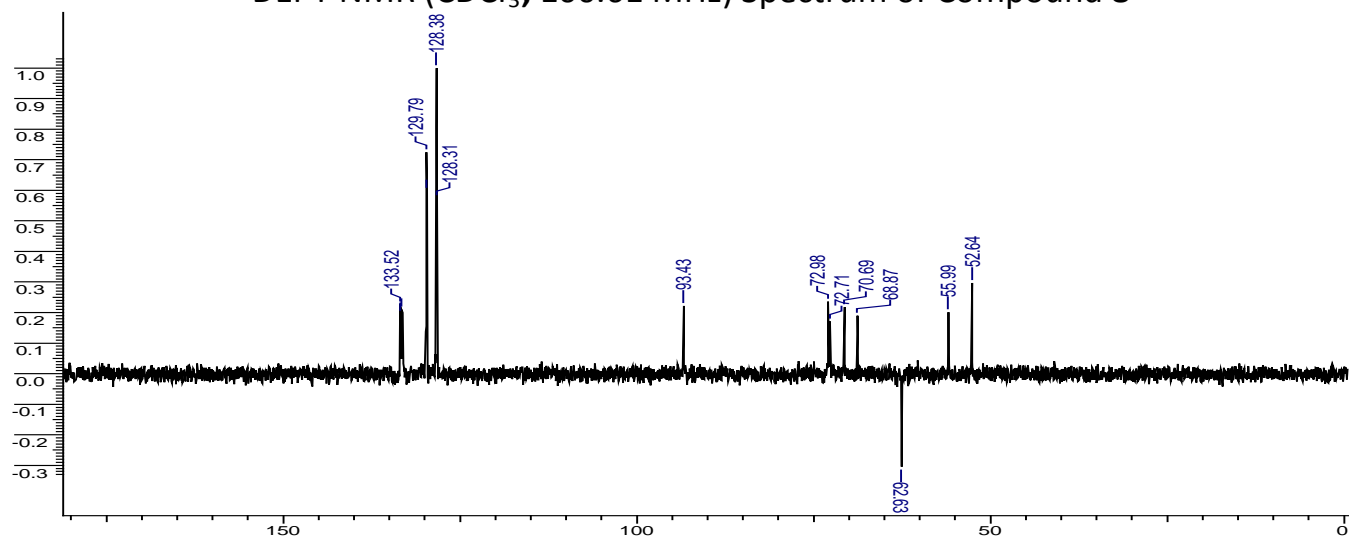
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400.13MHz) Spectrum of Compound **8**



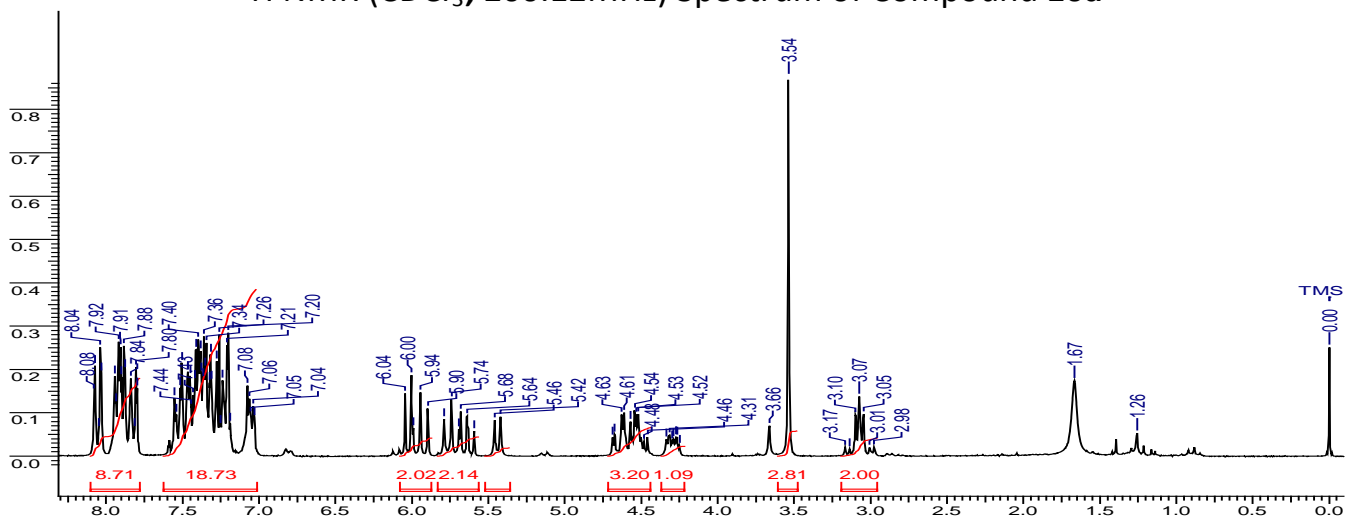
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100.61 MHz) Spectrum of Compound **8**



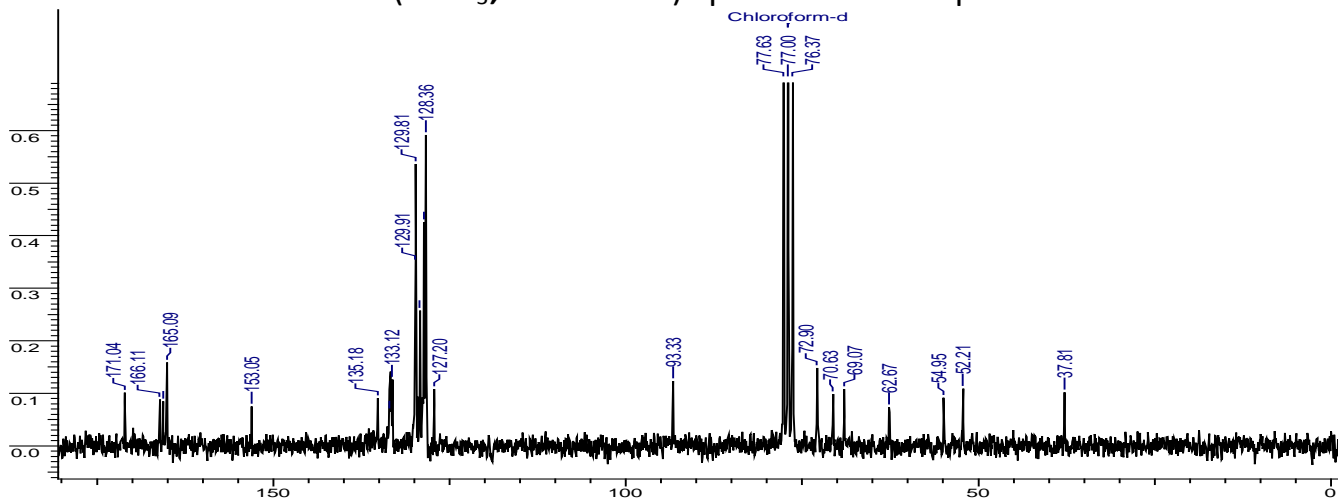
### DEPT NMR ( $\text{CDCl}_3$ , 100.61 MHz) Spectrum of Compound **8**



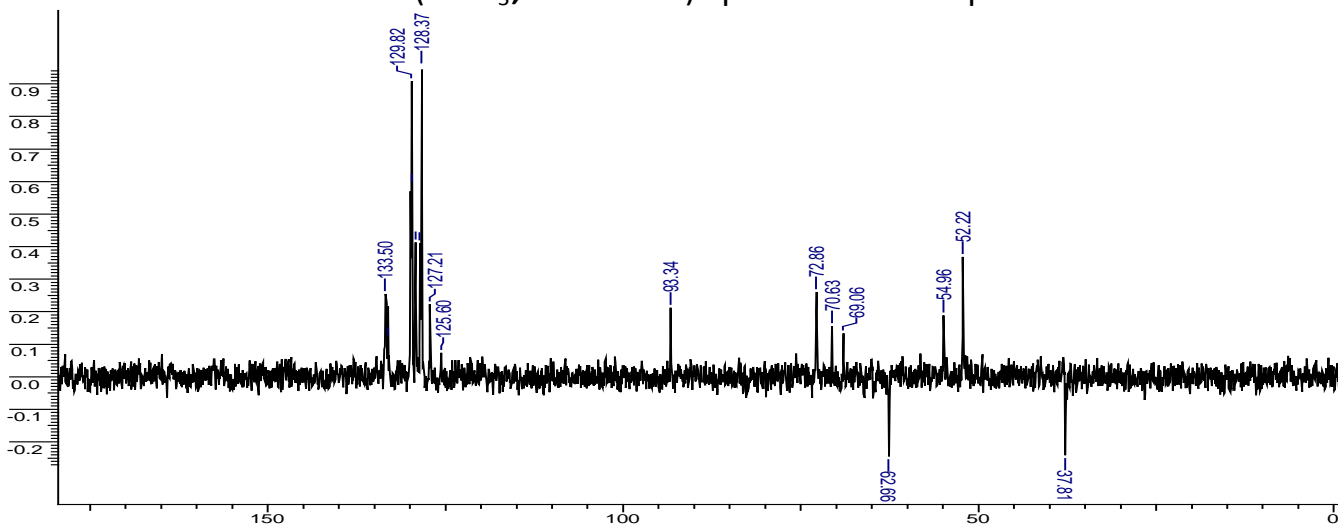
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 200.12MHz) Spectrum of Compound **10a**



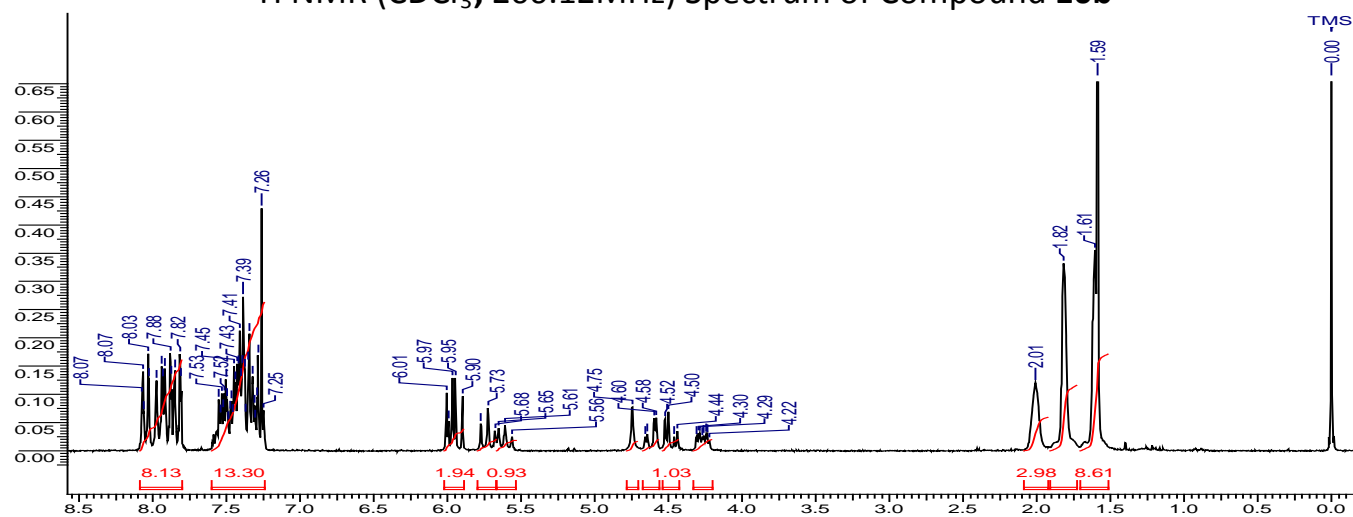
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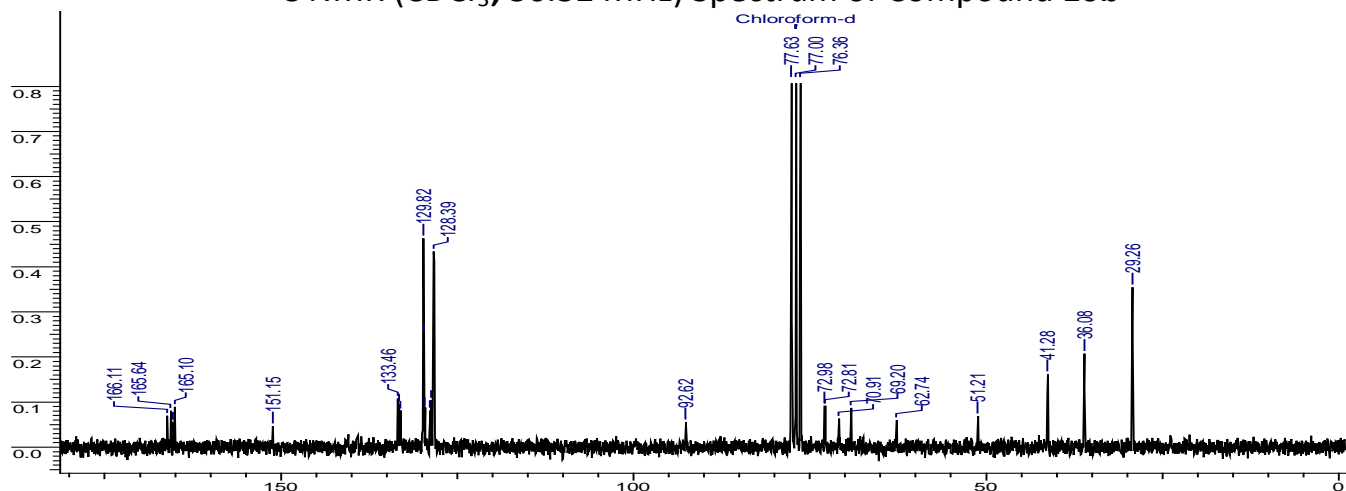
### DEPT NMR ( $\text{CDCl}_3$ , 50.32MHz) Spectrum of Compound **10a**



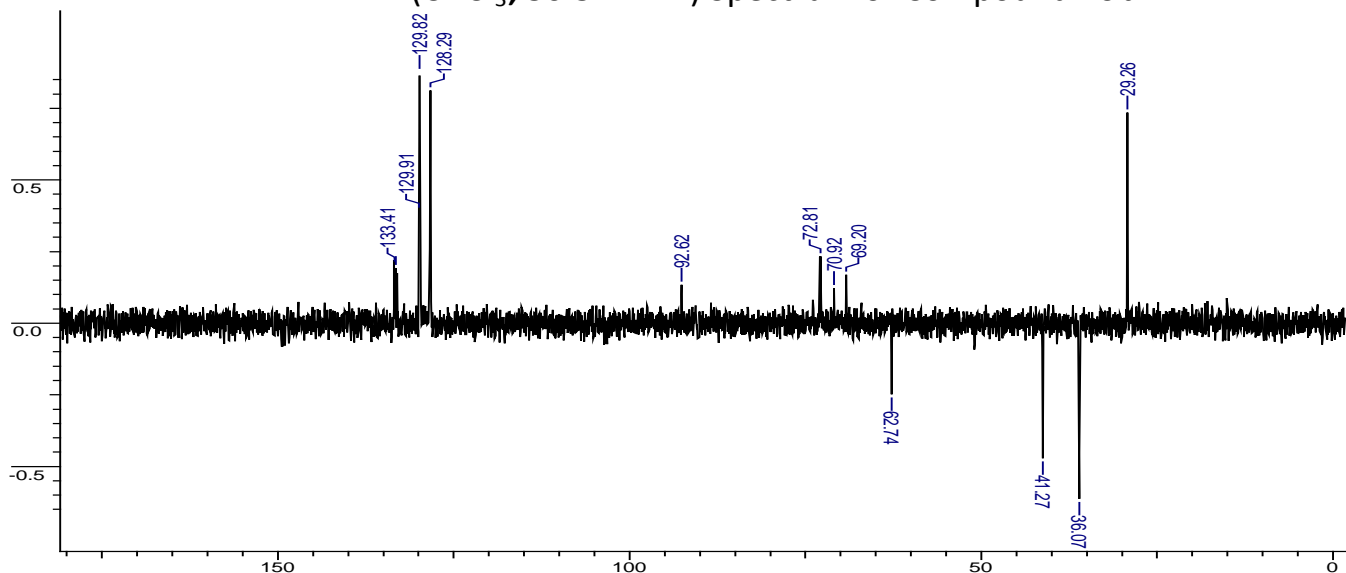
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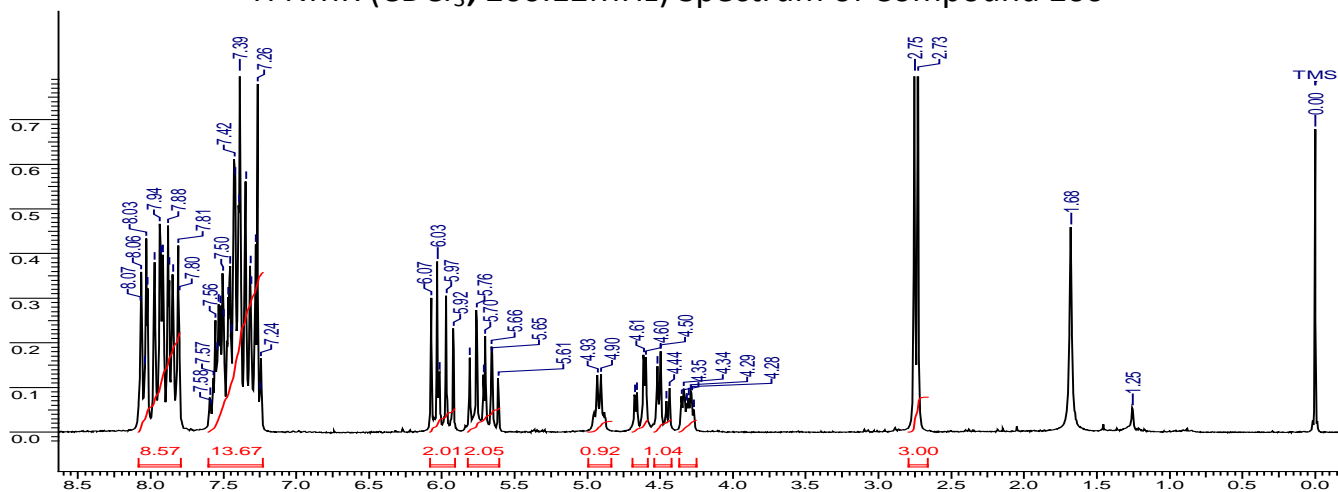
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **10b**



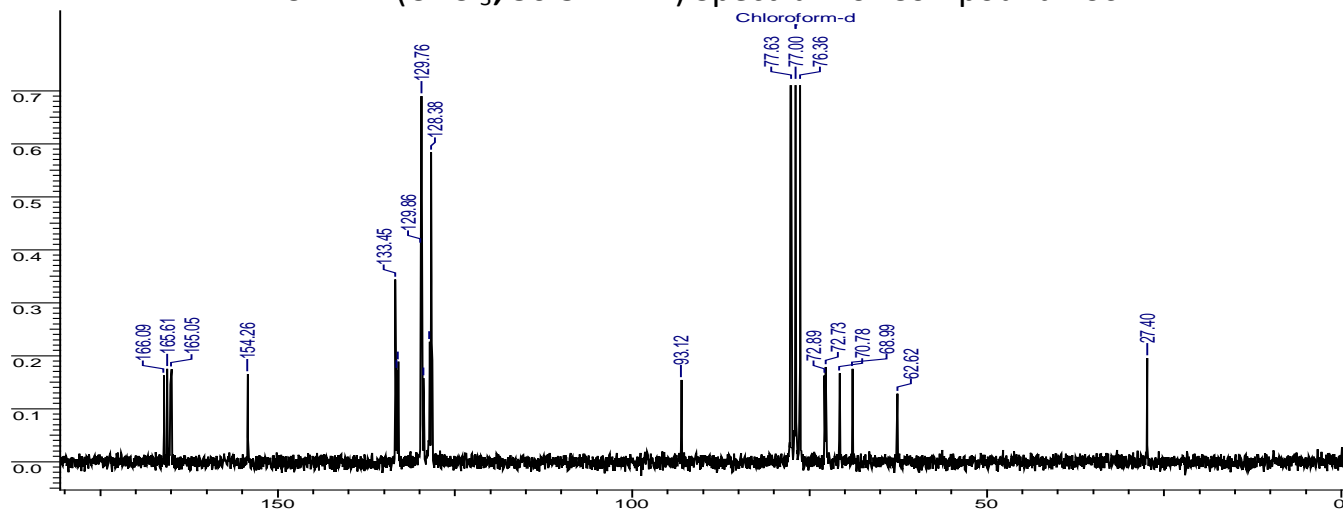
### DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **10b**



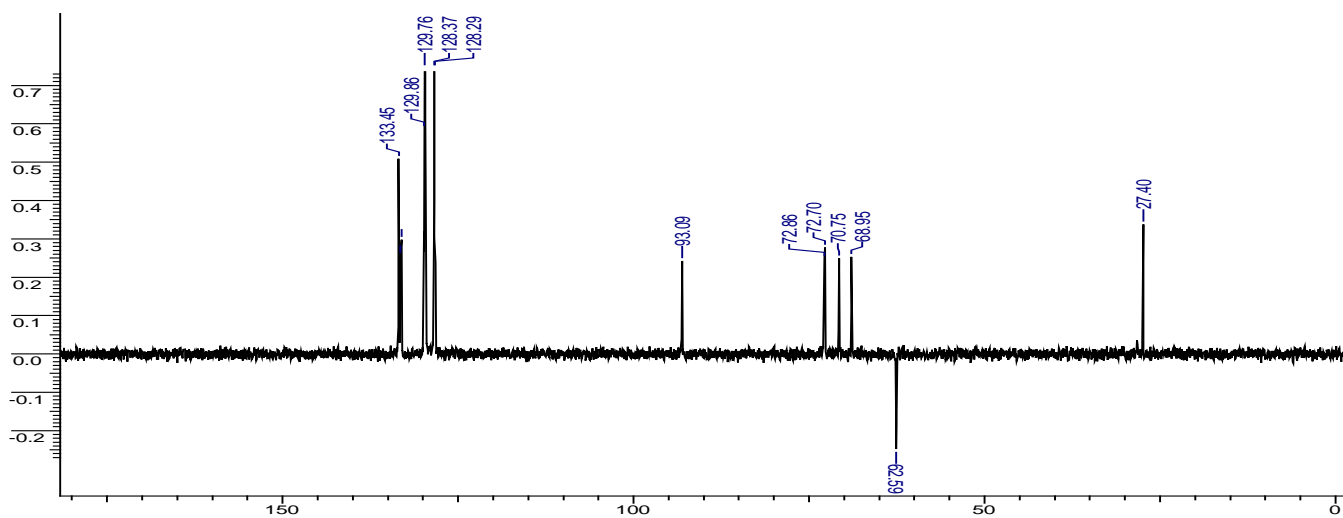
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200.12MHz) Spectrum of Compound **10c**



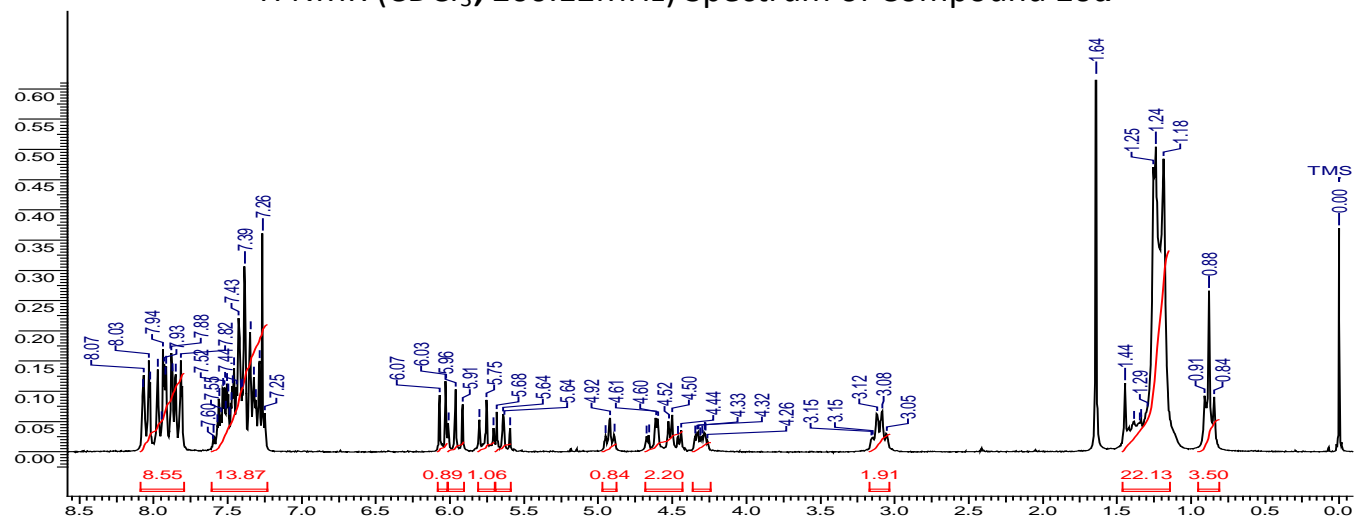
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **10c**



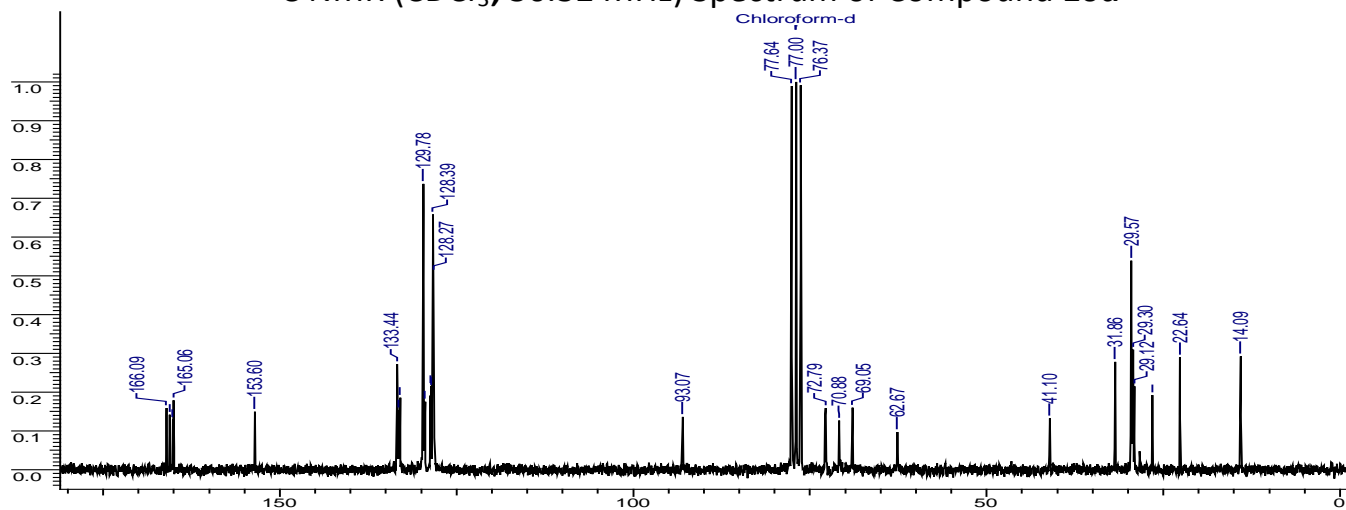
DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **10c**



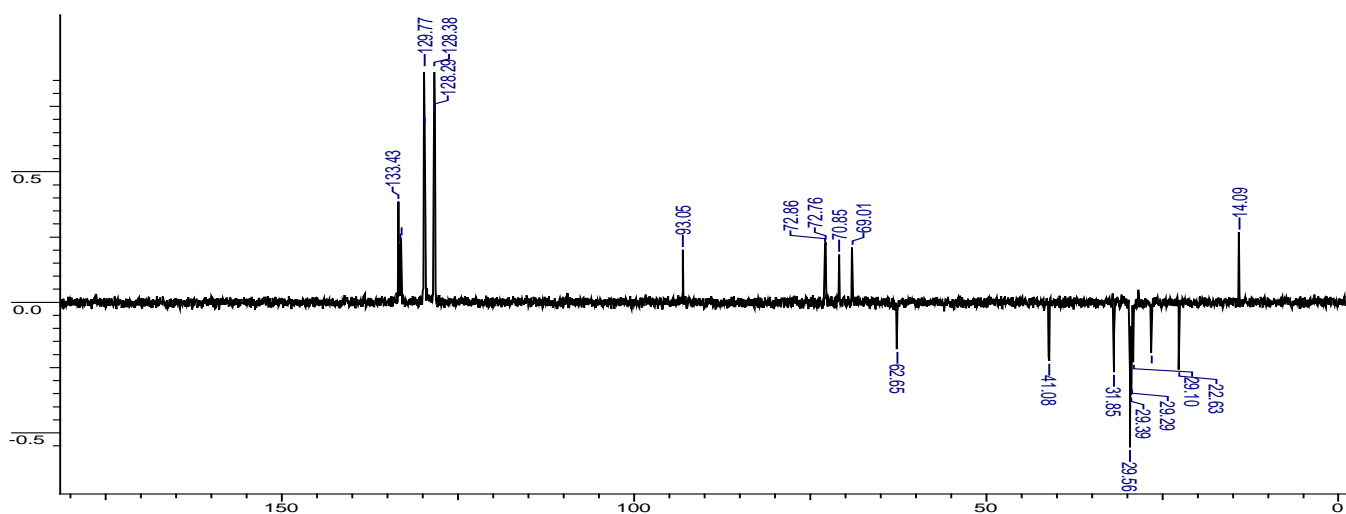
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 200.12MHz) Spectrum of Compound **10d**



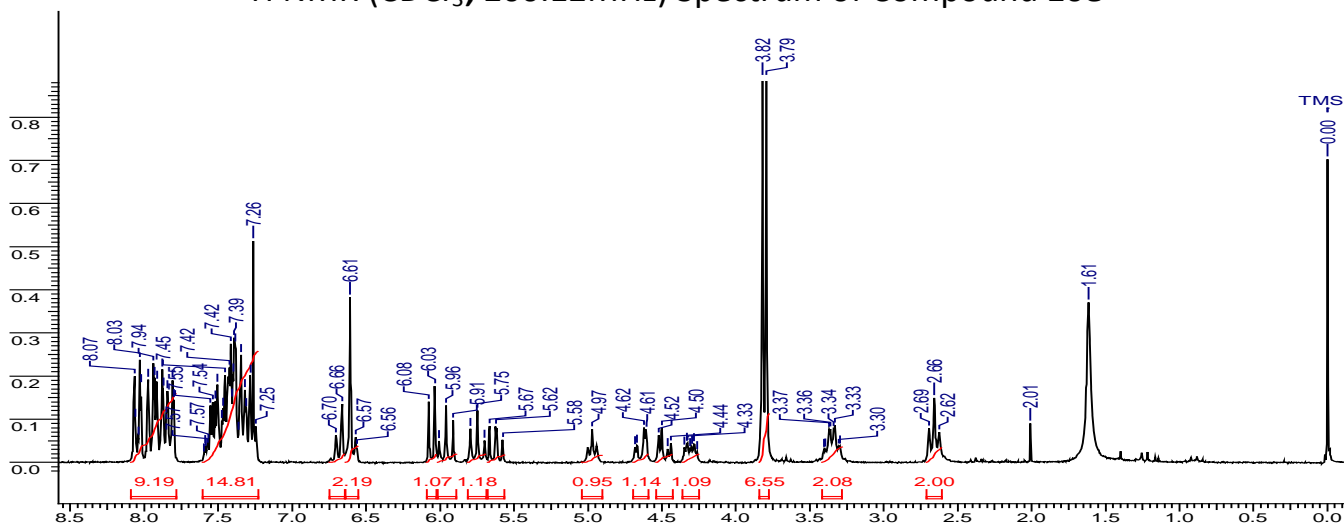
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **10d**



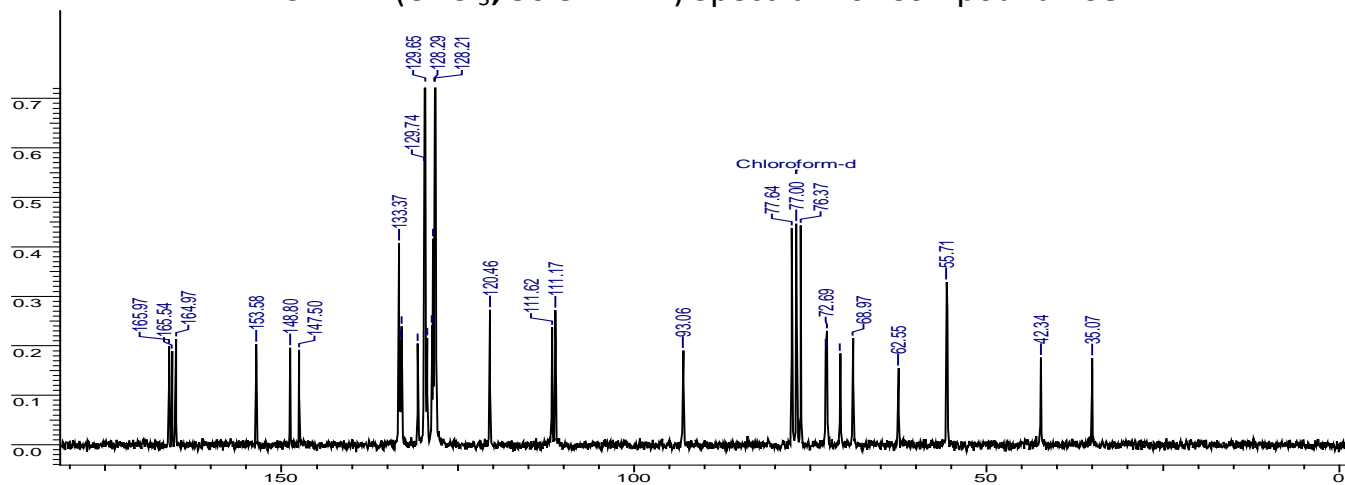
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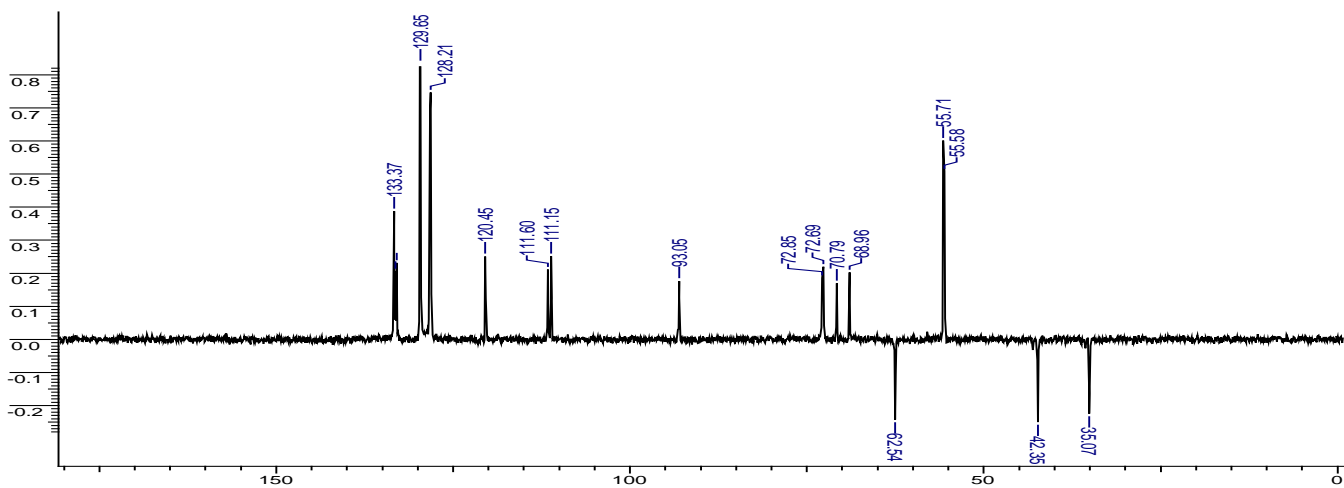
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200.12MHz) Spectrum of Compound **10e**



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **10e**

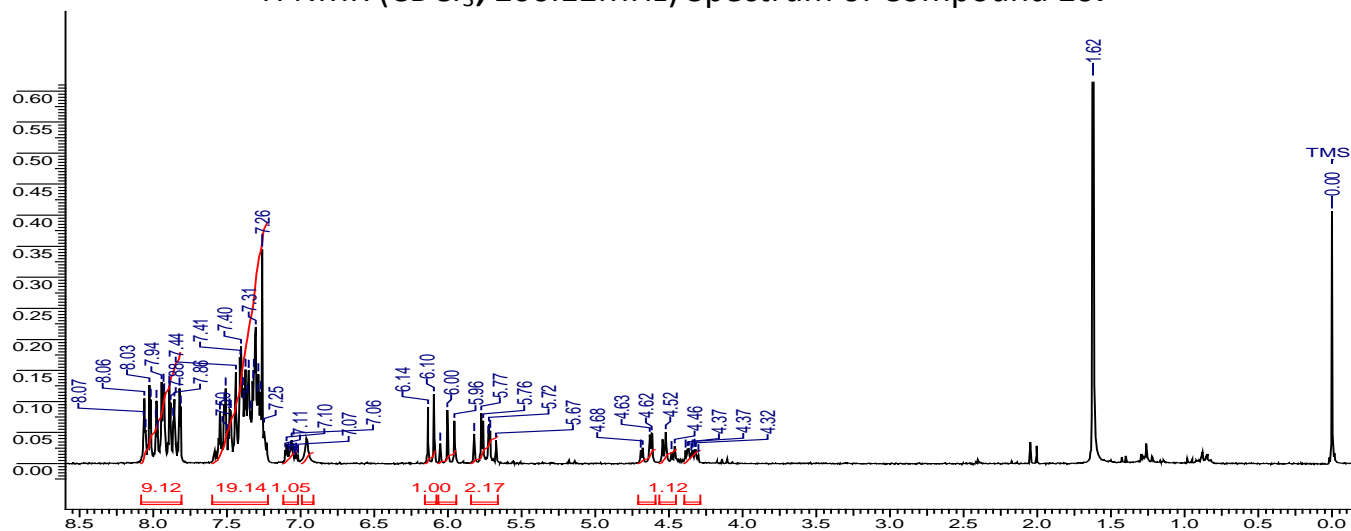


DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **10e**

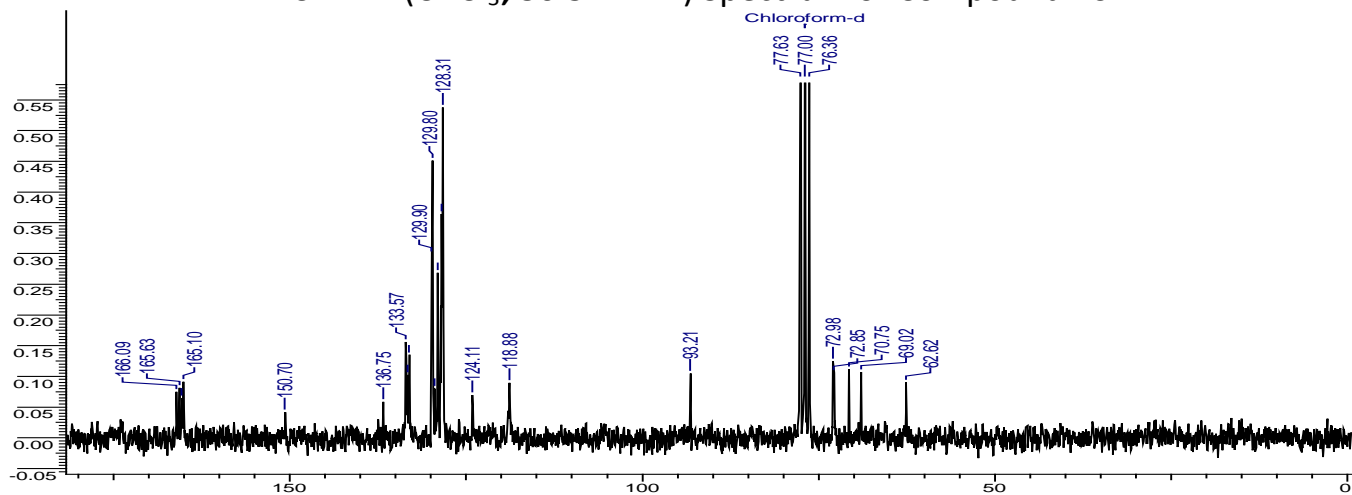




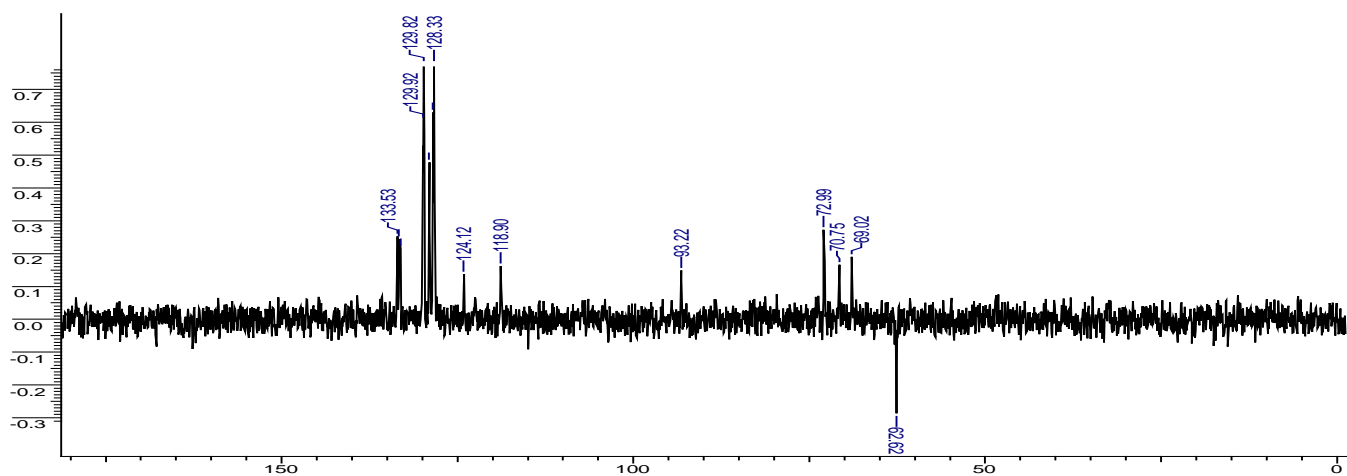
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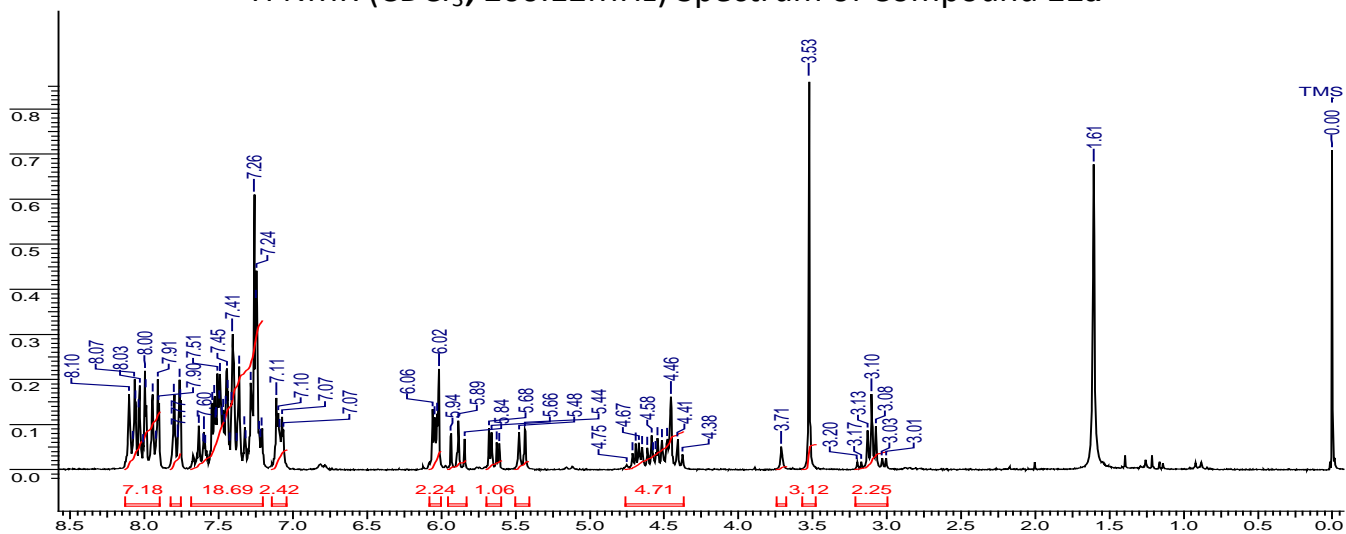
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **10f**



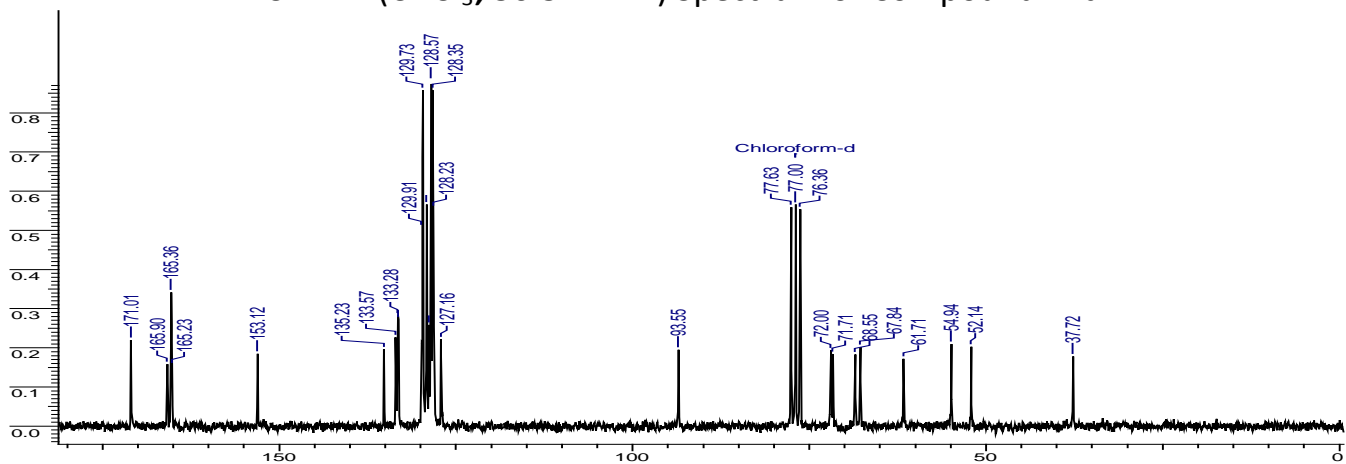
### DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **10f**



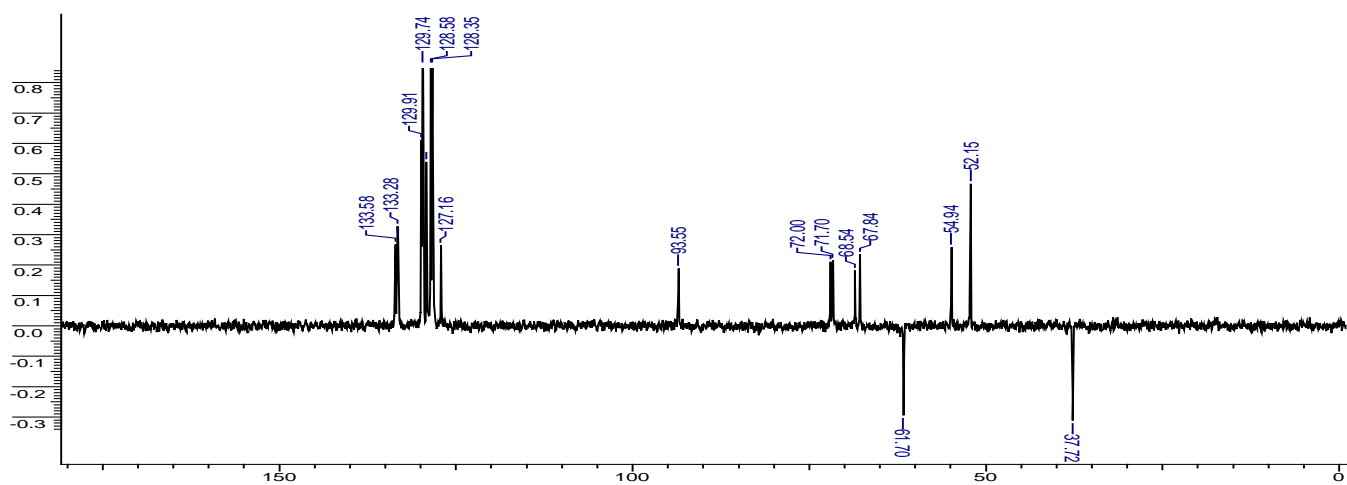
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 200.12MHz) Spectrum of Compound **11a**



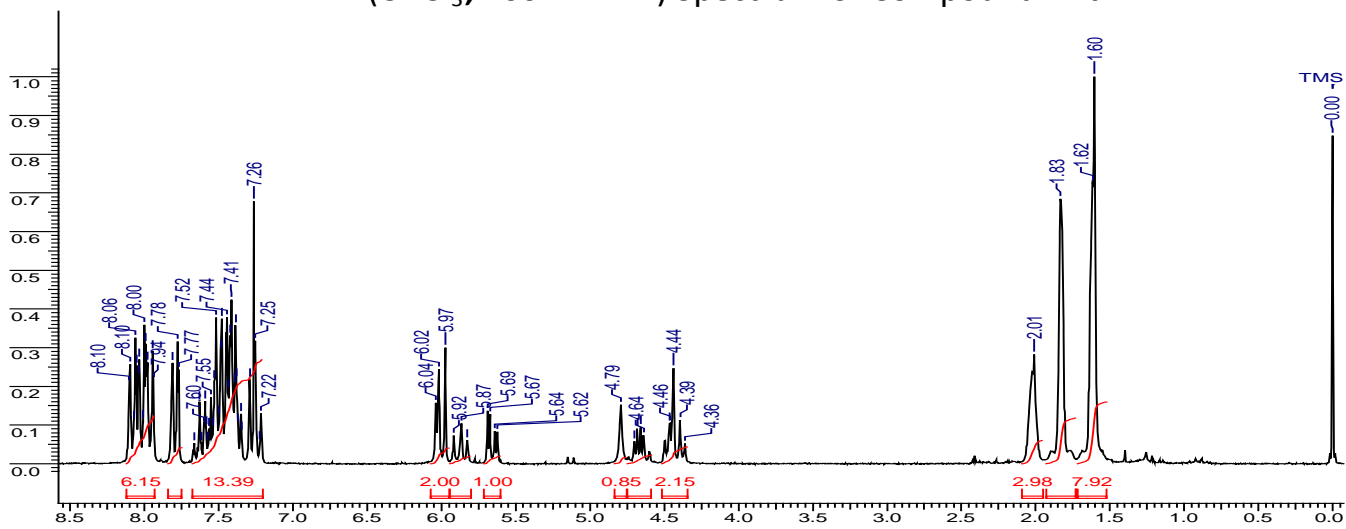
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **11a**



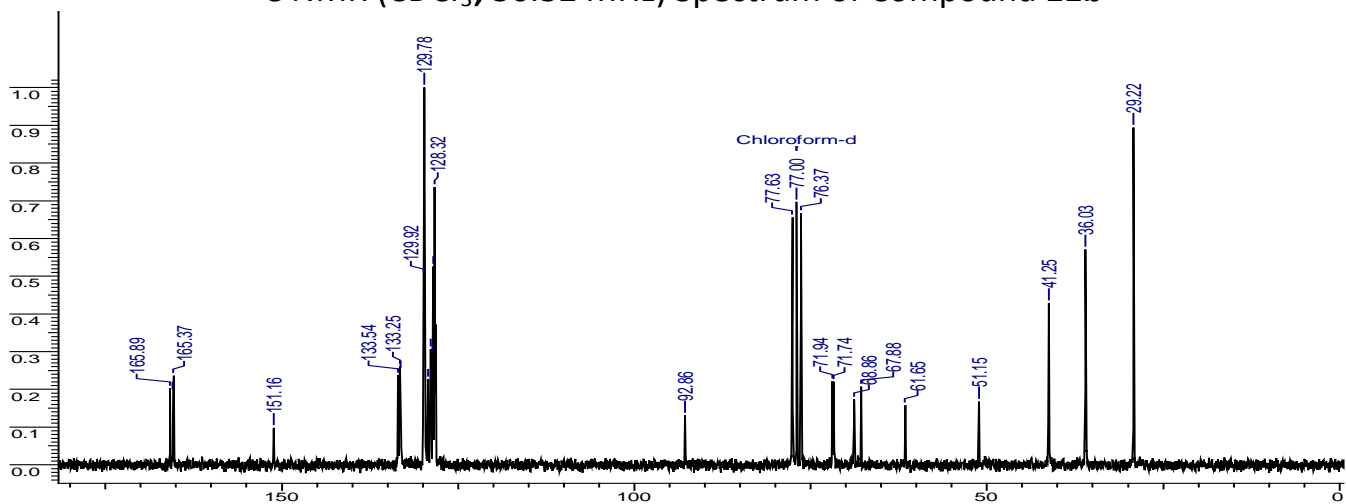
### DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **11a**



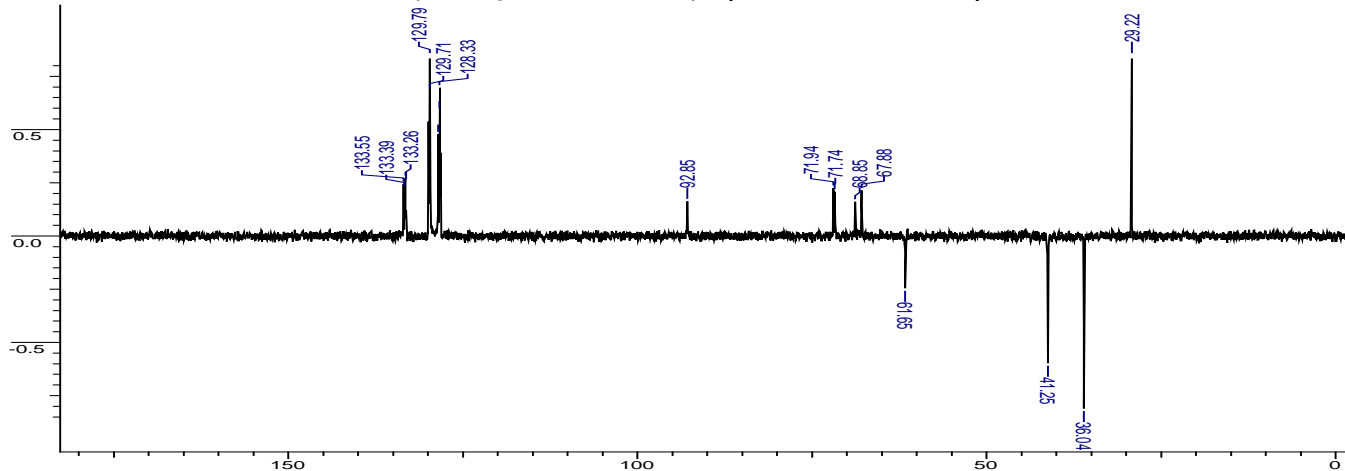
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200.12MHz) Spectrum of Compound **11b**



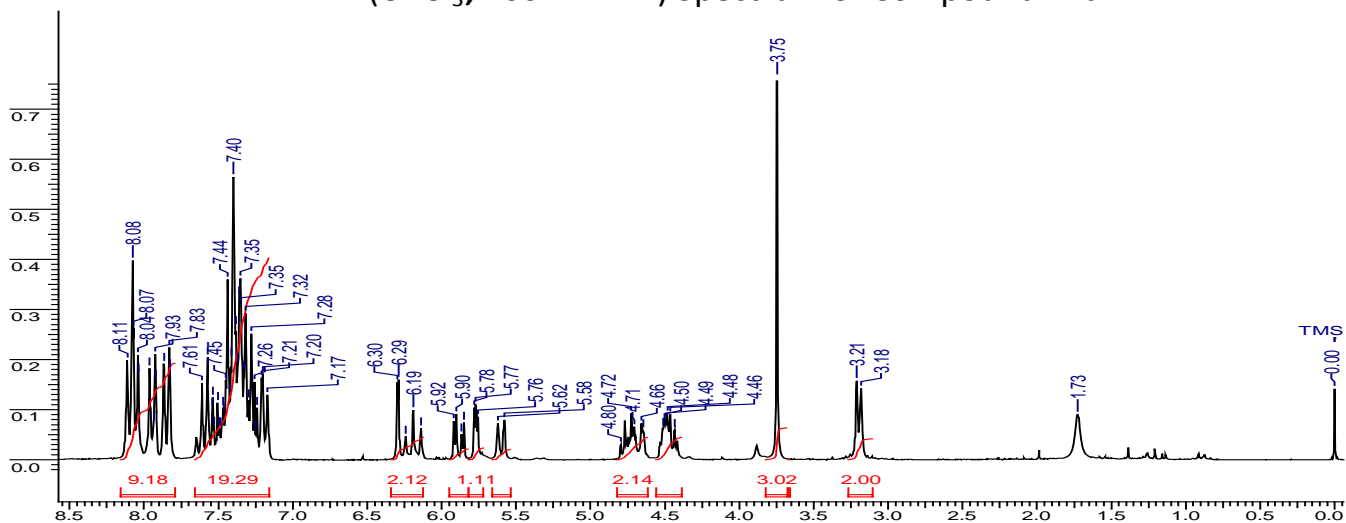
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **11b**



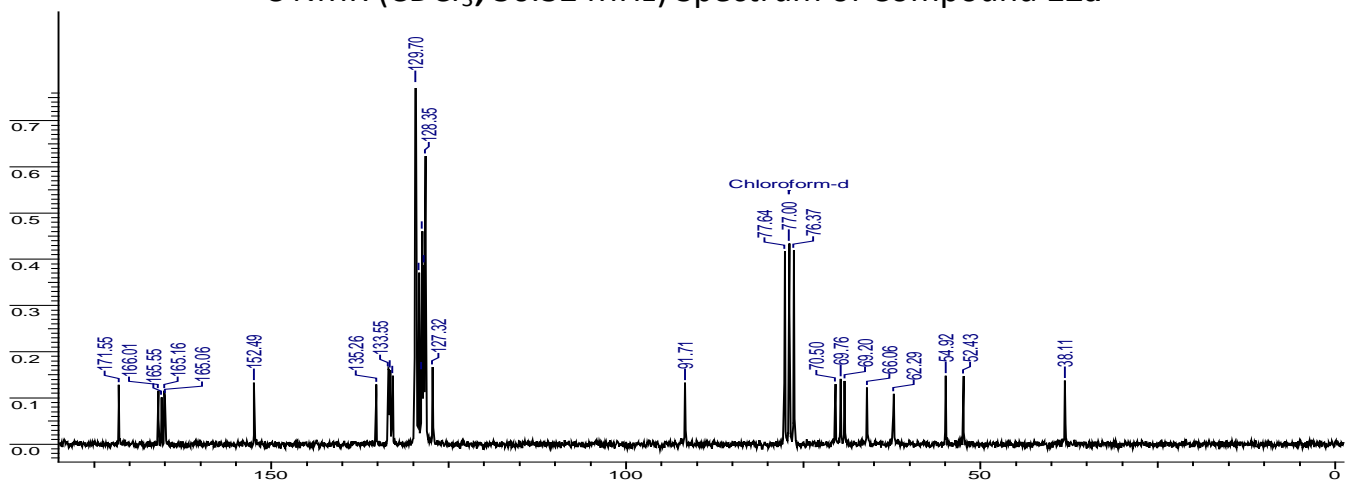
DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **11b**



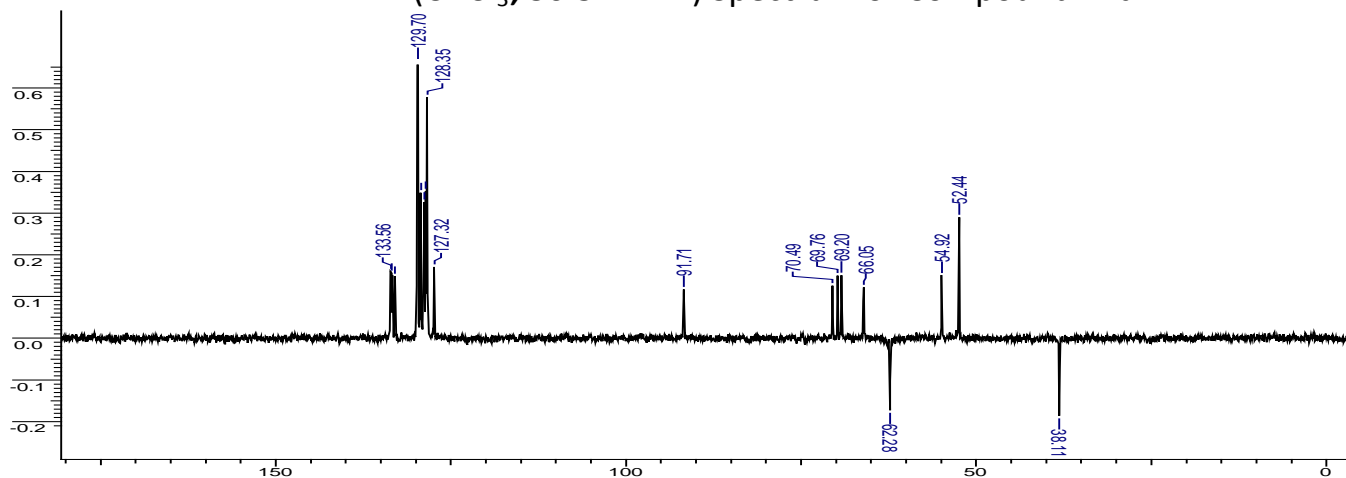
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200.12MHz) Spectrum of Compound **12a**



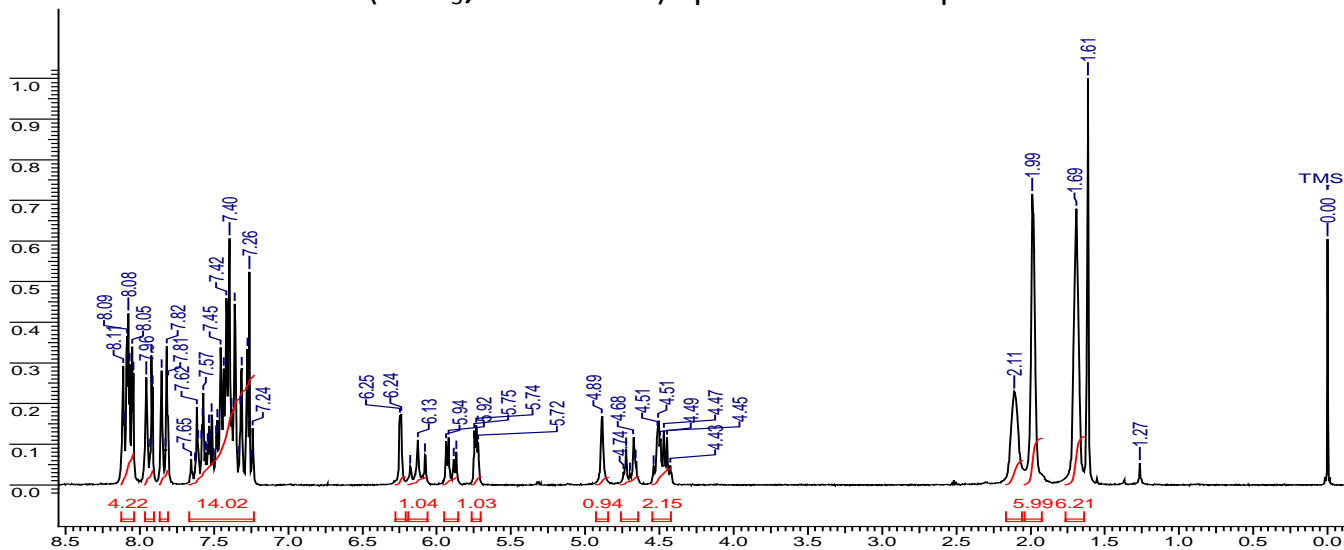
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **12a**



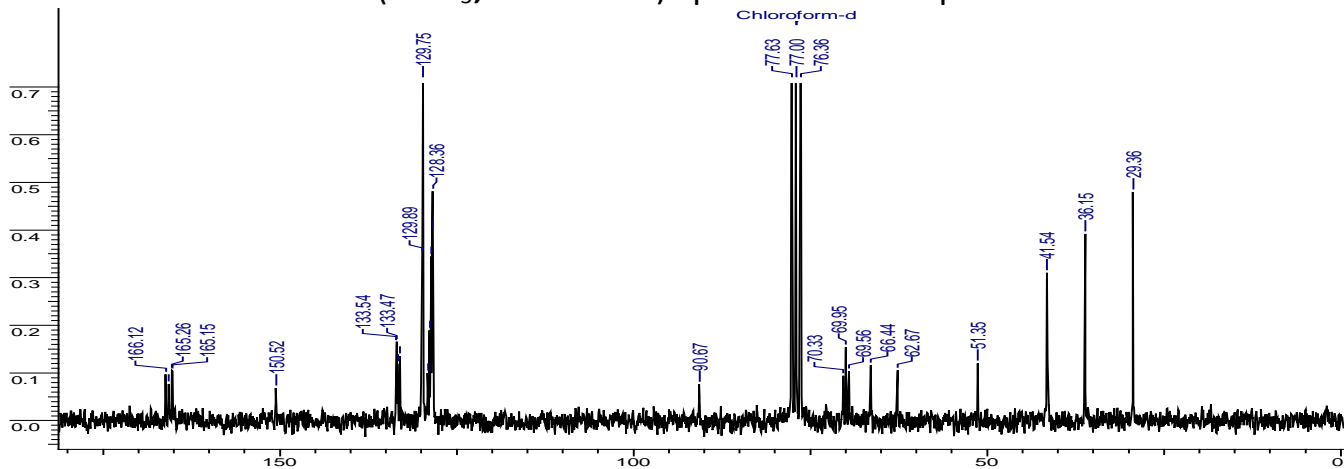
DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **12a**



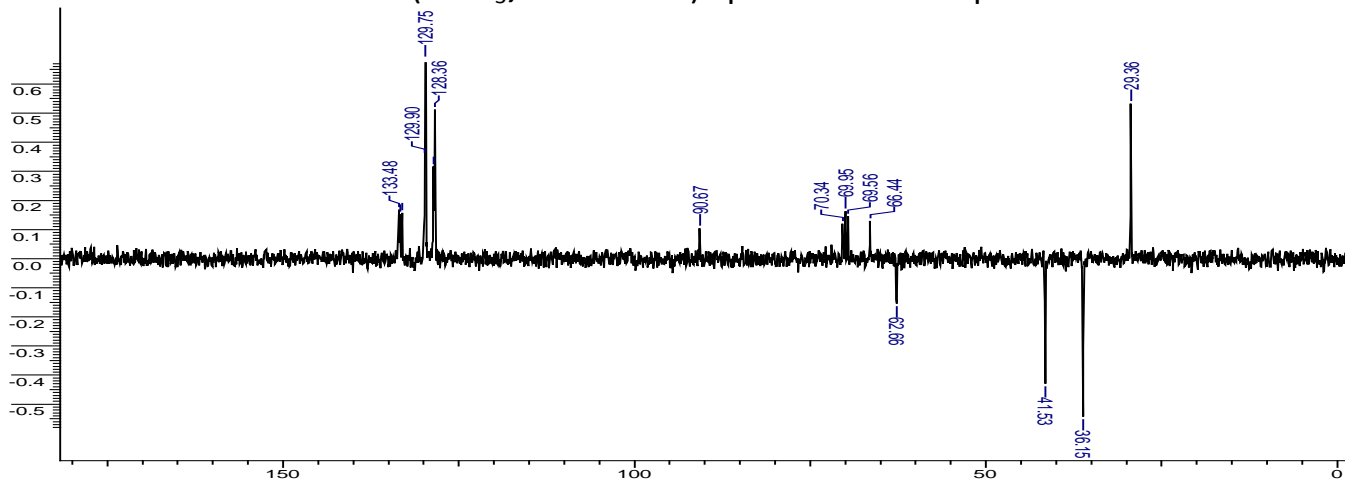
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 200.12MHz) Spectrum of Compound **12b**



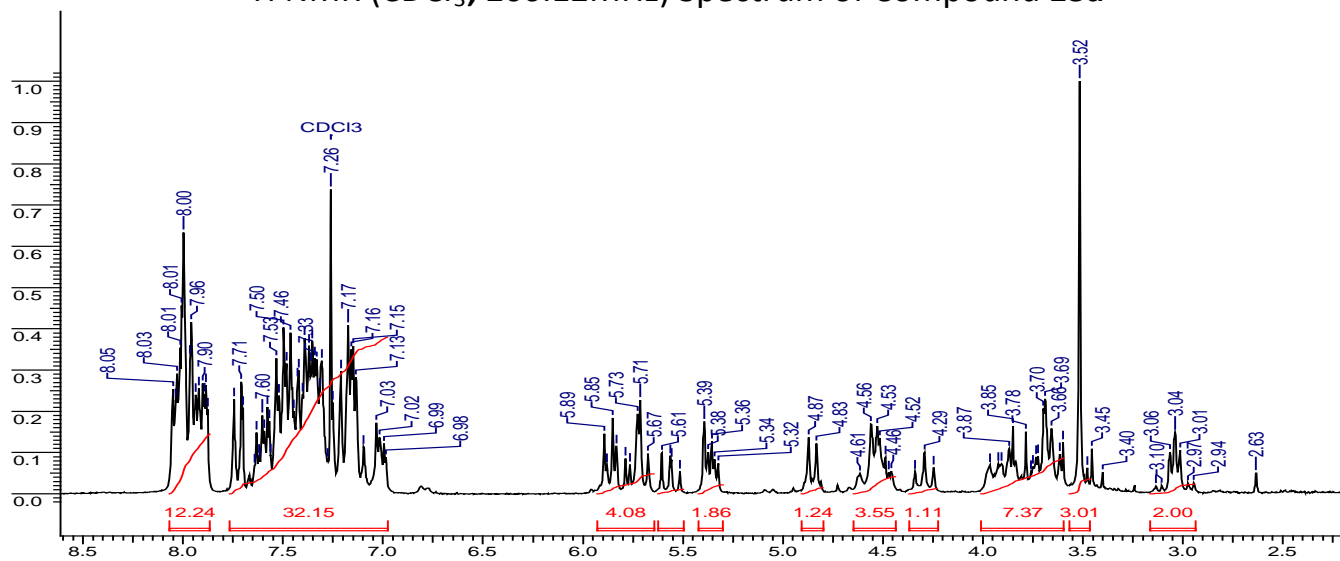
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **12b**



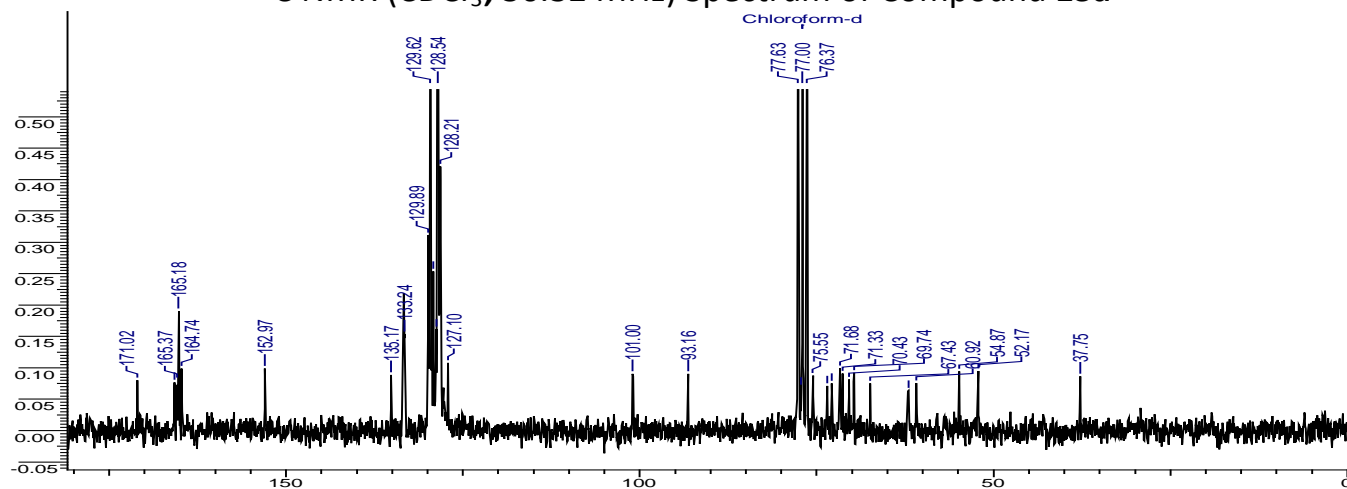
### DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **12b**



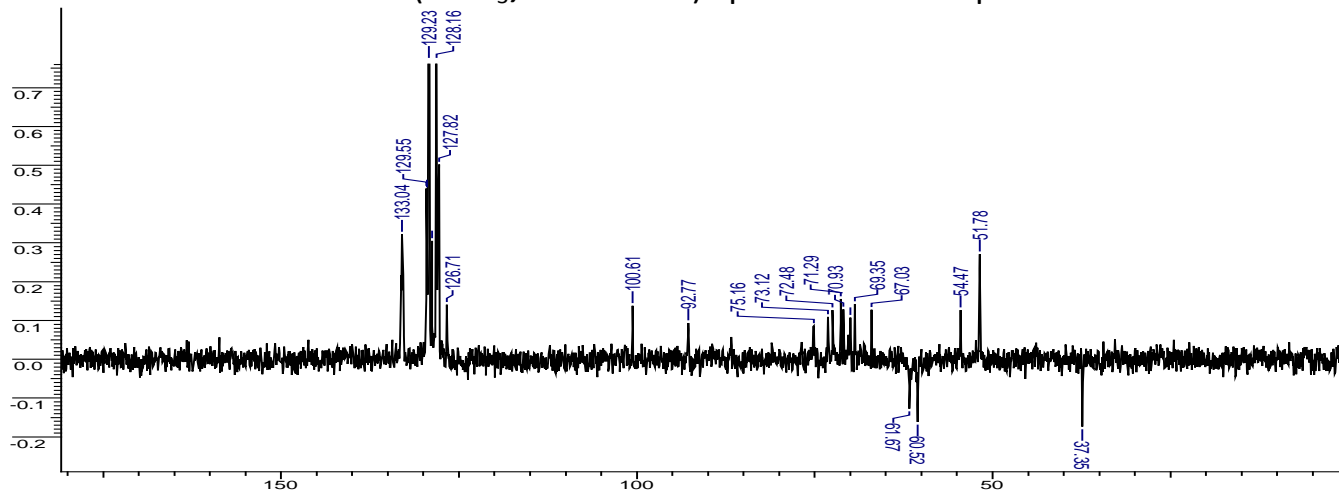
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 200.12MHz) Spectrum of Compound **13a**



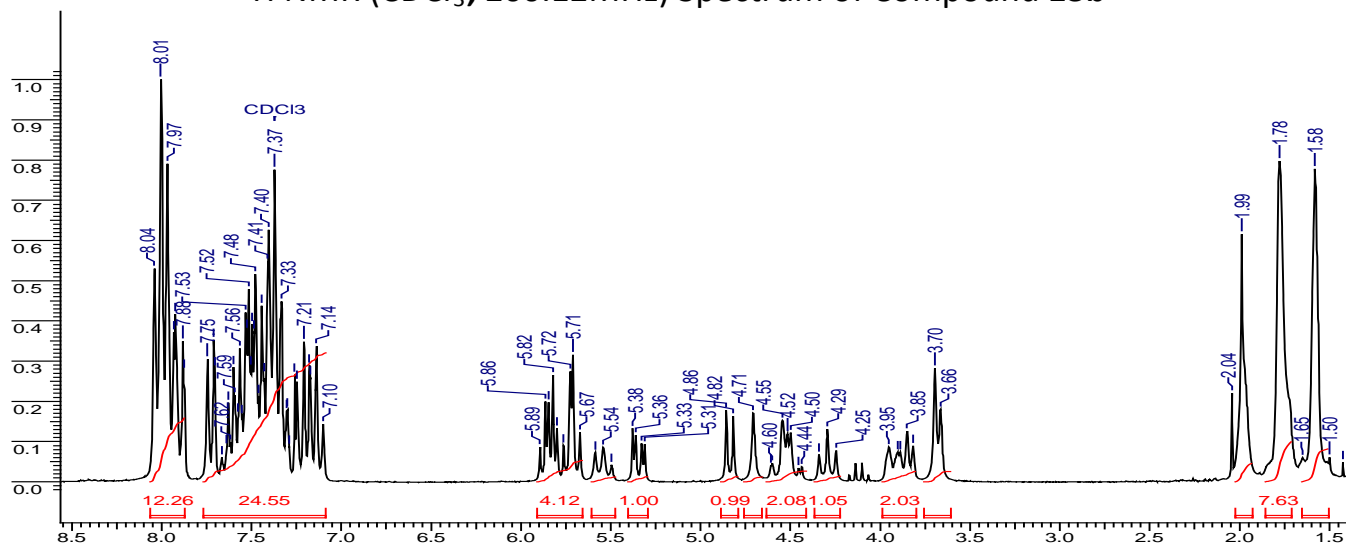
### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **13a**



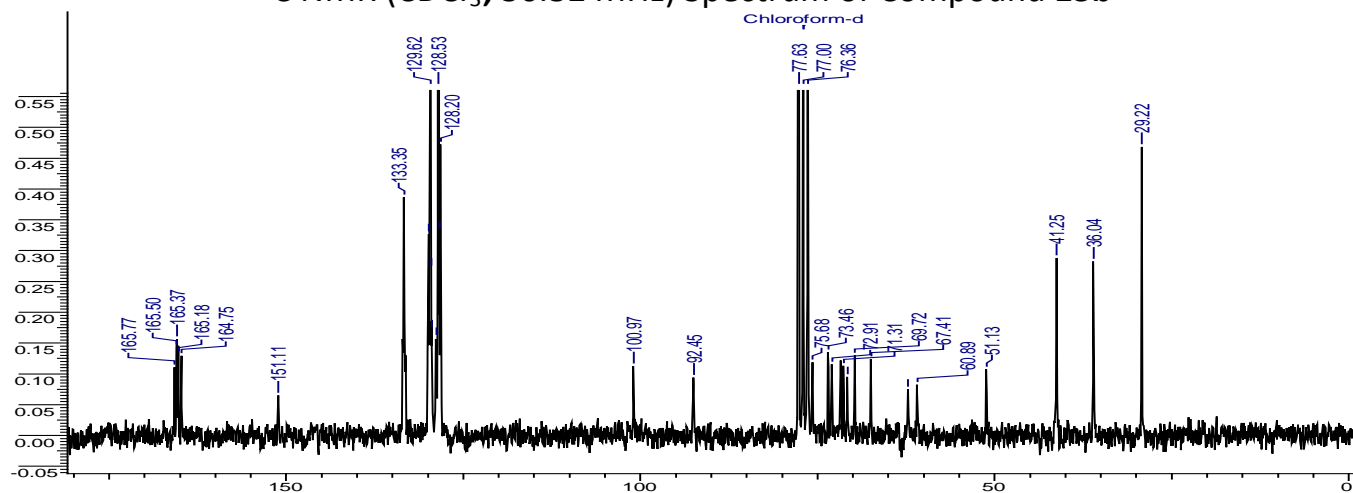
### DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **13a**



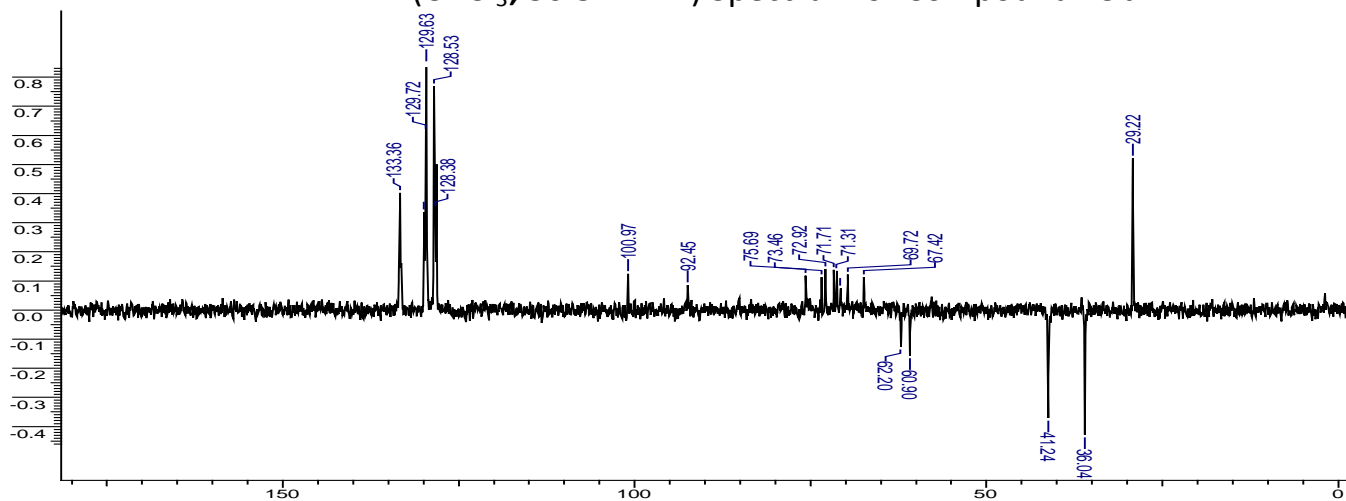
### $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 200.12MHz) Spectrum of Compound **13b**



### $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **13b**



### DEPT NMR ( $\text{CDCl}_3$ , 50.32 MHz) Spectrum of Compound **13b**



### Mass Spectral Data of All New Compounds

Compound No.	Molecular Formula	Calculated Mol. Wt.	Observed Mol. Wt.	Optical rotation $[\alpha]_D^{25}$ in CHCl <sub>3</sub> at 25°C; c 1.0
<b>3a</b>	C <sub>52</sub> H <sub>45</sub> NO <sub>14</sub> Na	930.2738	930.2742	+14.0°
<b>3b</b>	C <sub>54</sub> H <sub>47</sub> NO <sub>14</sub> Na	956.2894	956.2889	+12.0°
<b>3c</b>	C <sub>53</sub> H <sub>47</sub> NO <sub>14</sub> Na	944.2894	944.2899	+4.0°
<b>4a</b>	C <sub>52</sub> H <sub>45</sub> NO <sub>14</sub> Na	930.2738	930.2735	+58.0°
<b>4b</b>	C <sub>53</sub> H <sub>45</sub> NO <sub>14</sub> Na	942.2738	942.2736	+66.0°
<b>4c</b>	C <sub>53</sub> H <sub>47</sub> NO <sub>14</sub> Na	944.2894	944.2890	+36.0°
<b>5a</b>	C <sub>52</sub> H <sub>45</sub> NO <sub>14</sub> Na	930.2738	930.2740	-42.0°
<b>5b</b>	C <sub>54</sub> H <sub>47</sub> NO <sub>14</sub> Na	956.2894	956.2893	-30.0°
<b>5c</b>	C <sub>53</sub> H <sub>47</sub> NO <sub>14</sub> Na	944.2894	944.2897	-40.0°
<b>6a</b>	C <sub>79</sub> H <sub>67</sub> NO <sub>22</sub> Na	1405.4052	1404.4048	+46.0°
<b>6b</b>	C <sub>80</sub> H <sub>67</sub> NO <sub>22</sub> Na	1416.4052	1416.4056	+48.0°
<b>6c</b>	C <sub>81</sub> H <sub>69</sub> NO <sub>22</sub> Na	1431.4209	1431.4212	+42.0°
<b>A</b>	C <sub>43</sub> H <sub>43</sub> NO <sub>14</sub> Na	820.2581	820.2577	+3.8°
<b>8</b>	C <sub>39</sub> H <sub>35</sub> NO <sub>14</sub> Na	764.1955	764.1960	+32.9°
<b>10a</b>	C <sub>45</sub> H <sub>39</sub> NO <sub>13</sub> Na	824.2319	824.2320	+46.5°
<b>10b</b>	C <sub>45</sub> H <sub>43</sub> NO <sub>11</sub> Na	796.2734	796.2730	+34.6°
<b>10c</b>	C <sub>36</sub> H <sub>31</sub> NO <sub>11</sub> Na	676.1795	676.1790	+47.3°
<b>10d</b>	C <sub>47</sub> H <sub>53</sub> NO <sub>11</sub> Na	830.3516	830.3520	+34.4°
<b>10e</b>	C <sub>45</sub> H <sub>41</sub> NO <sub>13</sub> Na	826.2476	826.2480	+30.2°
<b>10f</b>	C <sub>41</sub> H <sub>33</sub> NO <sub>11</sub> Na	738.1951	738.1950	+29.2°
<b>11a</b>	C <sub>45</sub> H <sub>39</sub> NO <sub>13</sub> Na	824.2319	824.2320	+96.6°
<b>11b</b>	C <sub>45</sub> H <sub>43</sub> NO <sub>11</sub> Na	796.2734	796.2730	+97.3°
<b>12a</b>	C <sub>45</sub> H <sub>39</sub> NO <sub>13</sub> Na	824.2319	824.2320	-17.8°
<b>12b</b>	C <sub>45</sub> H <sub>43</sub> NO <sub>11</sub> Na	796.2734	796.2730	-41.7°
<b>13a</b>	C <sub>72</sub> H <sub>61</sub> NO <sub>21</sub> Na	1298.3634	1298.3630	+54.2°
<b>13b</b>	C <sub>72</sub> H <sub>65</sub> NO <sub>19</sub> Na	1270.4048	1270.4050	+48.0°