

Supporting Information

Copper (II)-Catalyzed Stereoselective 1,2-Addition vs Ferrier Glycosylation of “Armed” and “Disarmed” Glycal Donors

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and

*Dr. Sudhir Kashyap**

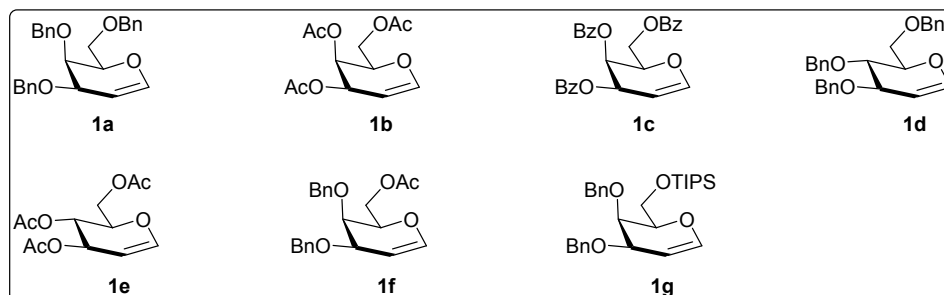
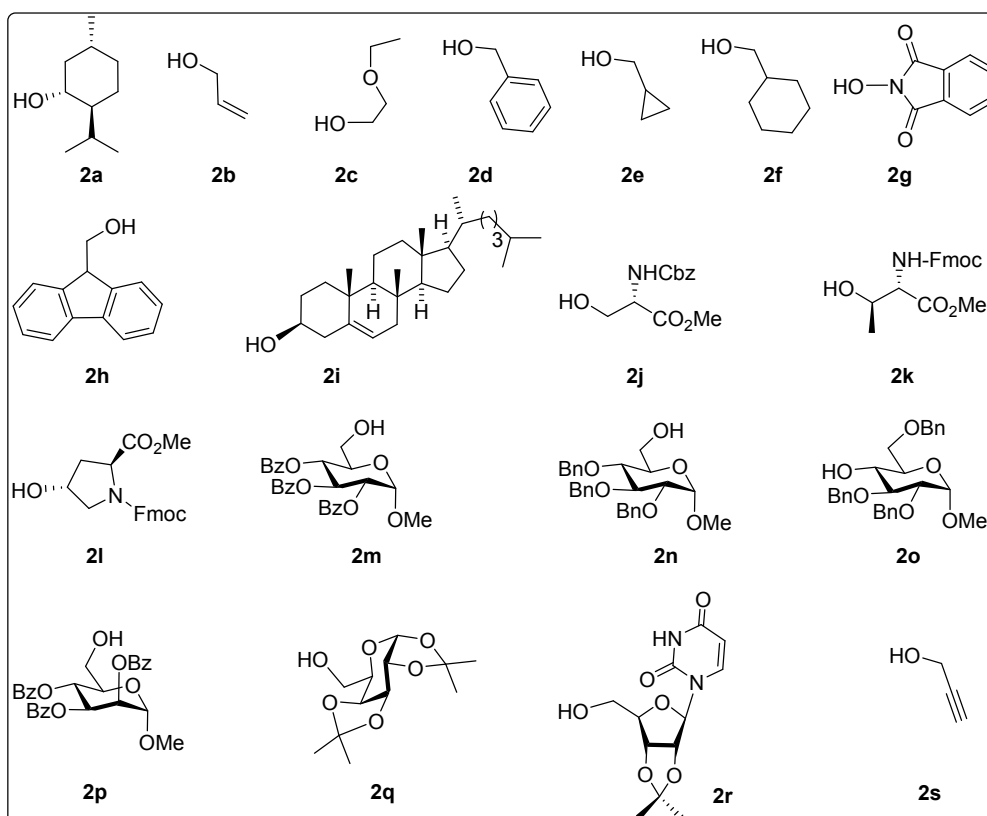
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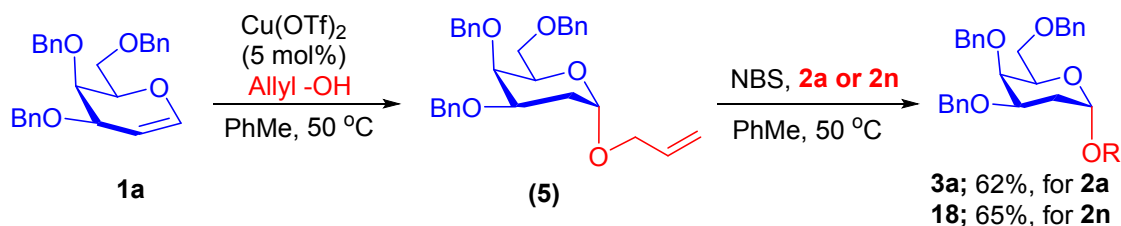
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Content

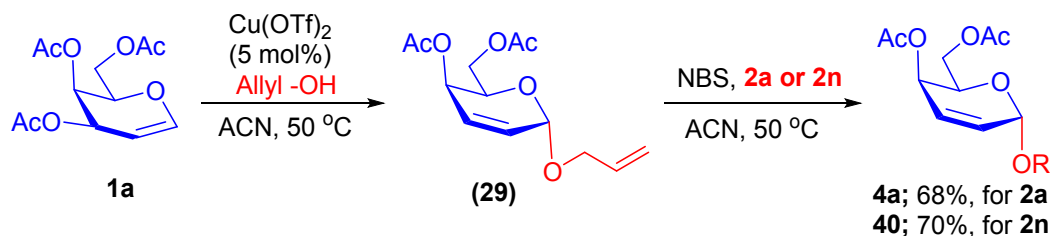
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A. Glycals Donors and Glycals Acceptors Used:**Glycals Donors****Acceptors**

B. Control-Experiments for Mechanistic Studies:**(i) Direct addition reaction of armed glycal **1a** and anomeric activation in One-pot:**

To a solution of glycal donor **1a** (100 mg, 0.240 mmol, 1.0 equiv.) and allyl alcohol **2b** (19 μL , 17 mg, 0.288 mmol, 1.2 equiv.) in Toluene (2 mL) was added 5 mol% $\text{Cu}(\text{OTf})_2$ and the resulting mixture was stirred at 50 °C temperature under N_2 atmosphere. After the completion of the reaction the resulted allyl glycoside **5** was treated with L-Menthol (45 mg, 0.288 mmol, 1.2 equiv.) and NBS (51 mg, 0.288 mmol, 1.2 equiv.). The reaction mixture was stirred at 50 °C under inert atmosphere for 3 h. The reaction mixture after extraction with ethyl acetate, usual workup, purified by silica gel column chromatography to obtain pure compound **3a** in 62% yield over two-steps with α/β ; 97:03.

Similarly, one-pot sequential glycosylation-anomeric activation employing **2n** as the acceptor in second step, purified by silica gel column chromatography to obtain the glycoside **18** in 65% yield with α/β ; 96:04.

(ii) Ferrier Glycosylation of disarmed glycal **1b and anomeric activation in One-pot:**

To a solution of glycal donor **1b** (100 mg, 0.367 mmol, 1.0 equiv.) and allyl alcohol (30 μL , 25 mg, 0.440 mmol, 1.2 equiv.) in Acetonitrile (2 mL) was added 5 mol% $\text{Cu}(\text{OTf})_2$ and the resulting mixture was stirred at 50 °C temperature under N_2 atmosphere. After the completion of

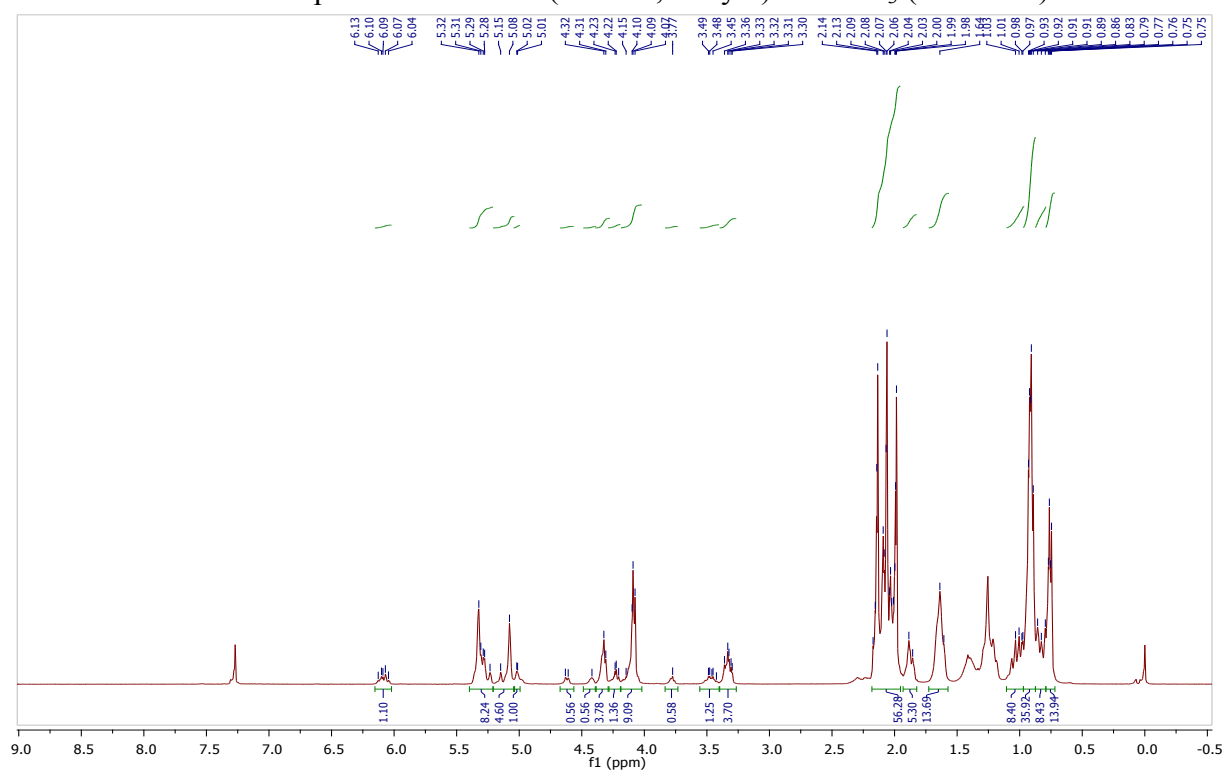
the reaction the resulted allyl glycoside **29** was treated with L-Menthol (68 mg, 0.440 mmol, 1.2 equiv.) and NBS (78 mg, 0.440 mmol, 1.2 equiv.). After the completion of starting material, the reaction mixture was extracted with ethyl acetate and purification through column chromatography on silica to afford glycoside **4a** in 68% yield with α/β ; 98:02.

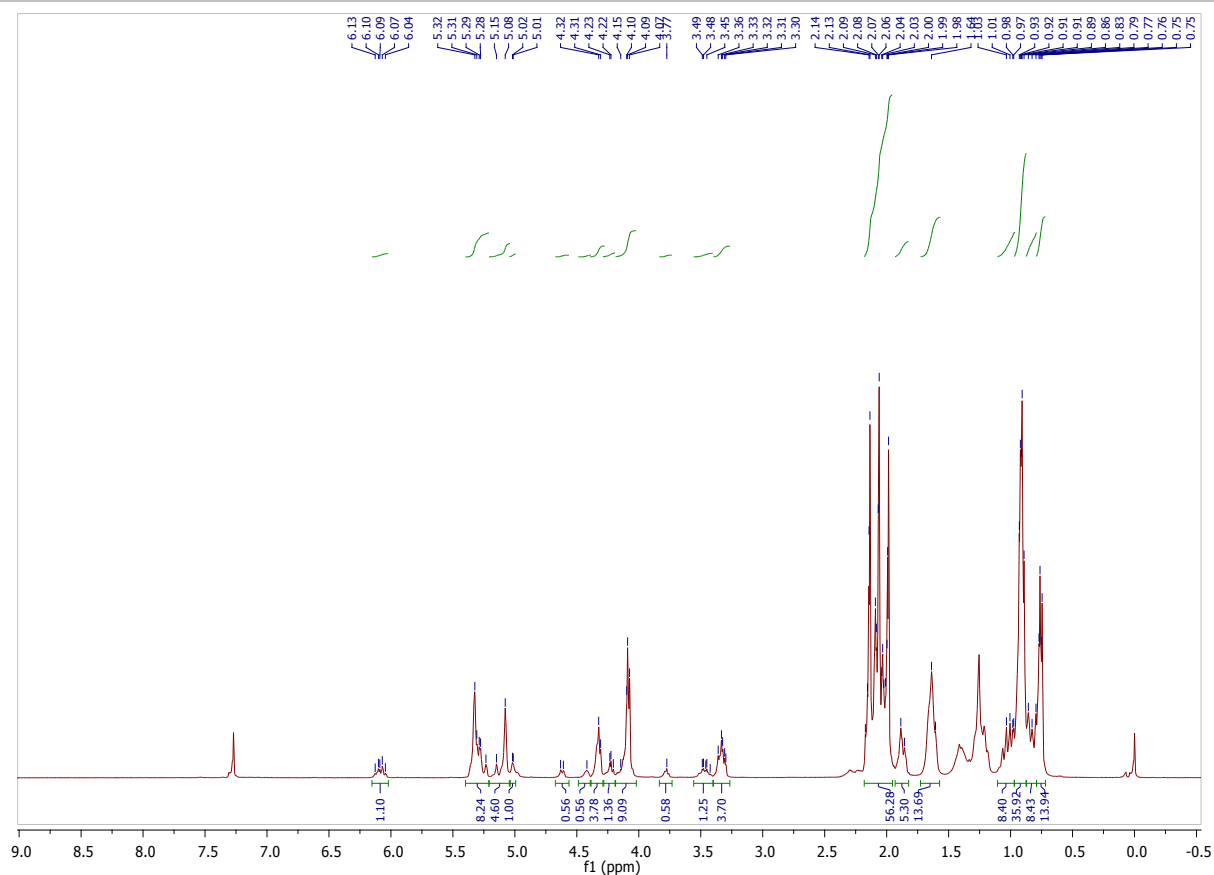
Similarly, one-pot sequential Ferrier glycosylation-anomeric activation employing **2n** as the acceptor in second step, purified by silica gel column chromatography to obtain the 2,3-unsaturated disaccharide **40** in 70% yield with complete α -selectivity.

C. References:

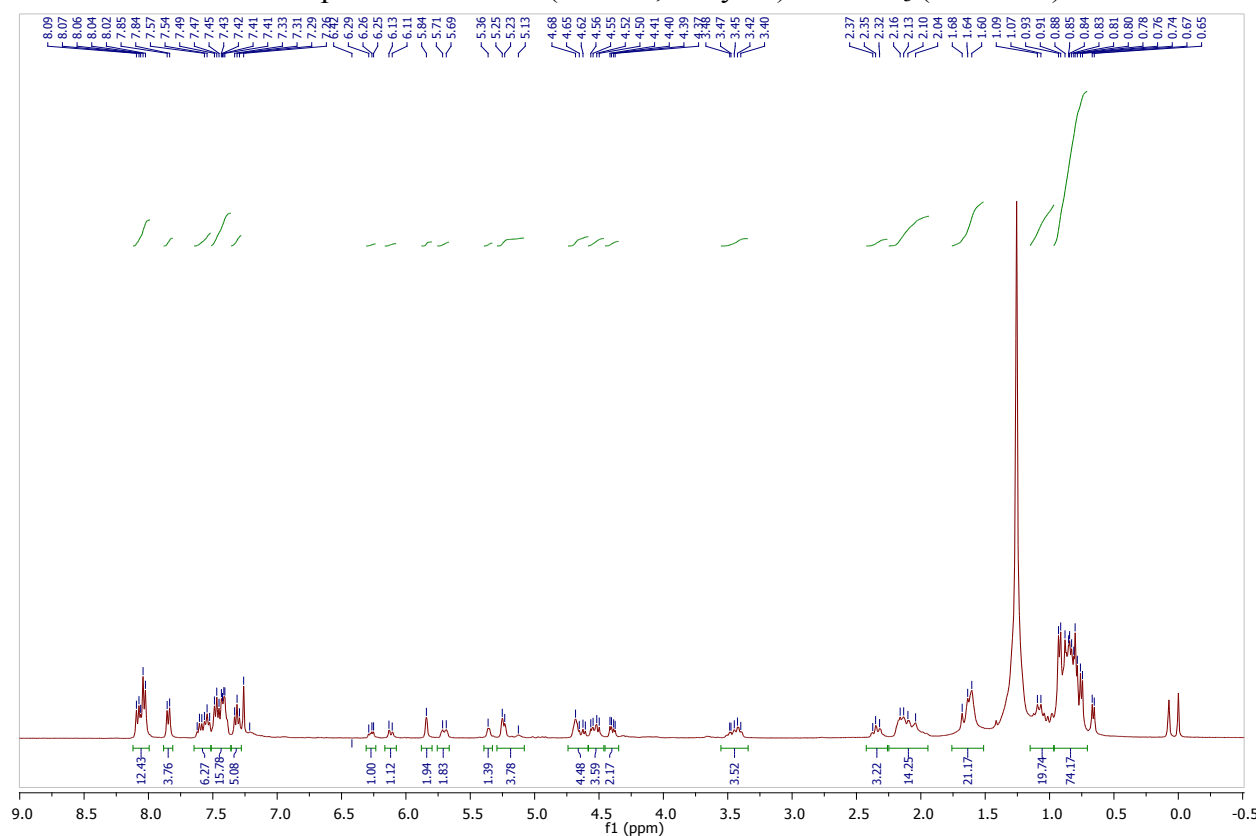
- (1) Thombal, R. S.; Jadhav, V. H. *RSC Adv.* **2016**, *6*, 30846. (Facile O-Glycosylation of Glycals Using Glu-Fe₃O₄-SO₃H, a Magnetic Solid Acid Catalyst).
- (2) Pachamuthu, K.; Vankar, Y. D. *J. Org. Chem.* **2001**, *66*, 7511. (Ceric Ammonium Nitrate-Catalyzed Tetrahydropyranylation of Alcohols and Synthesis of 2-Deoxy-O-Glycosides).
- (3) Rosati, O.; Curini, M.; Messina, F.; Marcotullio, M. C.; Cravotto, G. *Catal. Lett.* **2013**, *143*, 169. (Ferrier Rearrangement and 2-Deoxy Sugar Synthesis from D-Glycals Mediated by Layered α -Zirconium Sulfophenyl phosphonate-Methanphosphonate as Heterogeneous Catalyst).
- (4) Sau, A.; Palo-Nieto, C.; Galan, M. C. *J. Org. Chem.* **2019**, *84*, 2415. (Substrate-controlled direct α -stereoselective synthesis of deoxyglycosides from glycals using B(C₆F₅)₃ as Catalyst).
- (5) Palo-Nieto, C.; Sau, A.; Galan, M. C. *J. Am. Chem. Soc.* **2017**, *139*, 14041. (Gold(I)-Catalysed Direct Stereoselective Synthesis of Deoxyglycosides from Glycals).
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- (7) Bandi, R.; Chalapala, S.; Chandrasekaran, S. *Org. Biomol. Chem.* **2018**, *16*, 2248. (2-Deoxyglycosyl 3-benzoylpropionates as novel donors for the direct and stereoselective synthesis of 2-deoxy-glycosides).

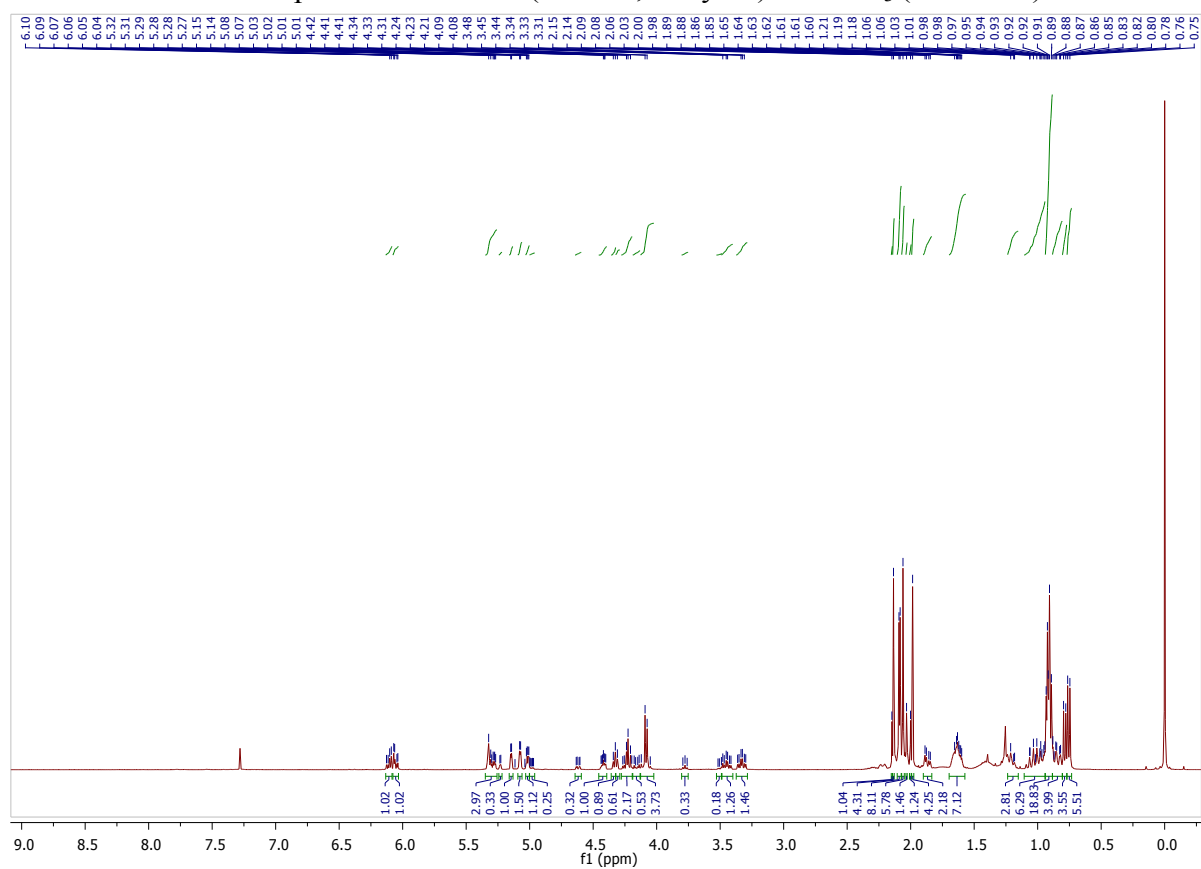
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- (8) Zhao, G.; Wang, T. *Angew. Chem.* **2018**, *51*, 6120. (Stereoselective Synthesis of 2-Deoxyglycosides from Glycals via Visible-Light-Induced Photoacid Catalysis).
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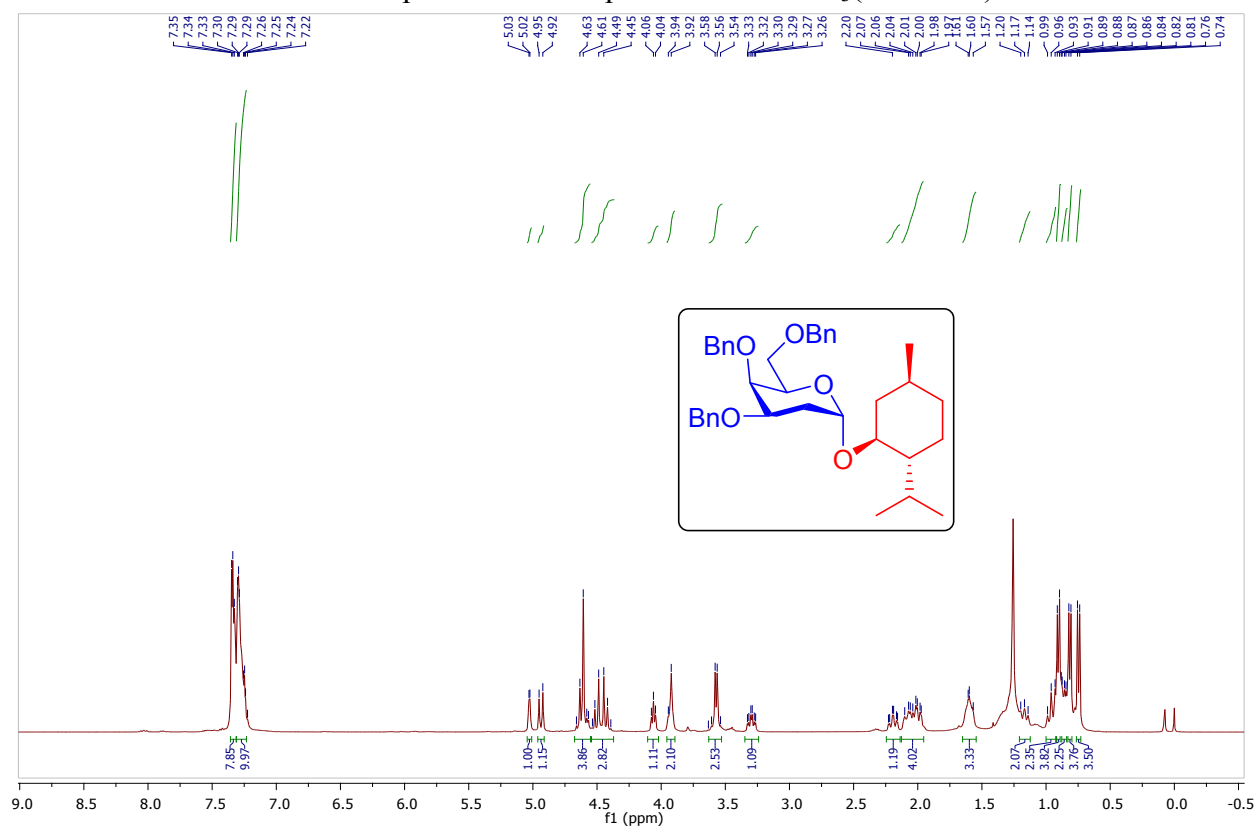
D. ^1H and ^{13}C NMR Spectra ^1H NMR spectrum of **3b:4b** (Table 1, entry 6) in CDCl_3 (400 MHz) ^1H NMR spectrum of **3b:4b** (Table 1, entry 7) in CDCl_3 (400 MHz)

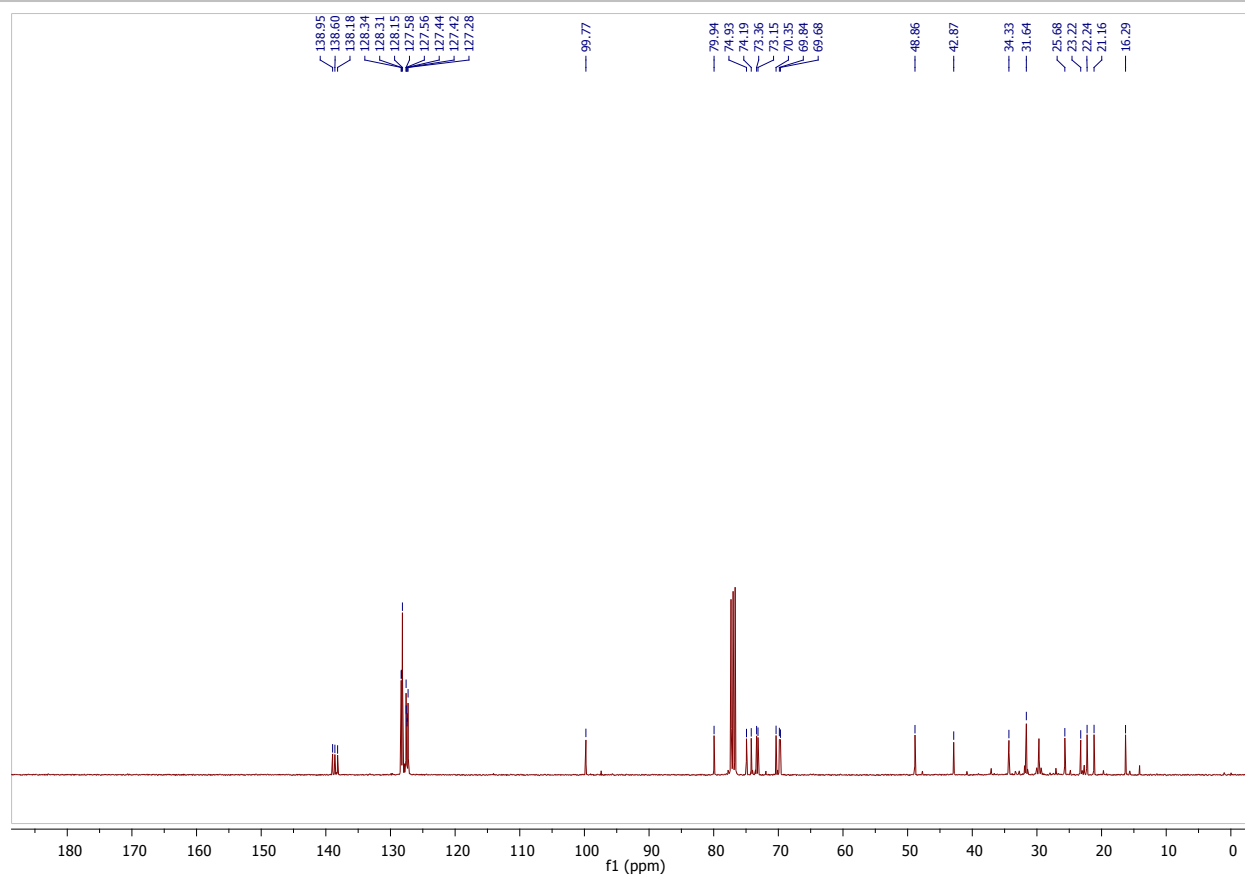


¹H NMR spectrum of 3c:4c (Table 1, entry 10) in CDCl₃ (400 MHz)

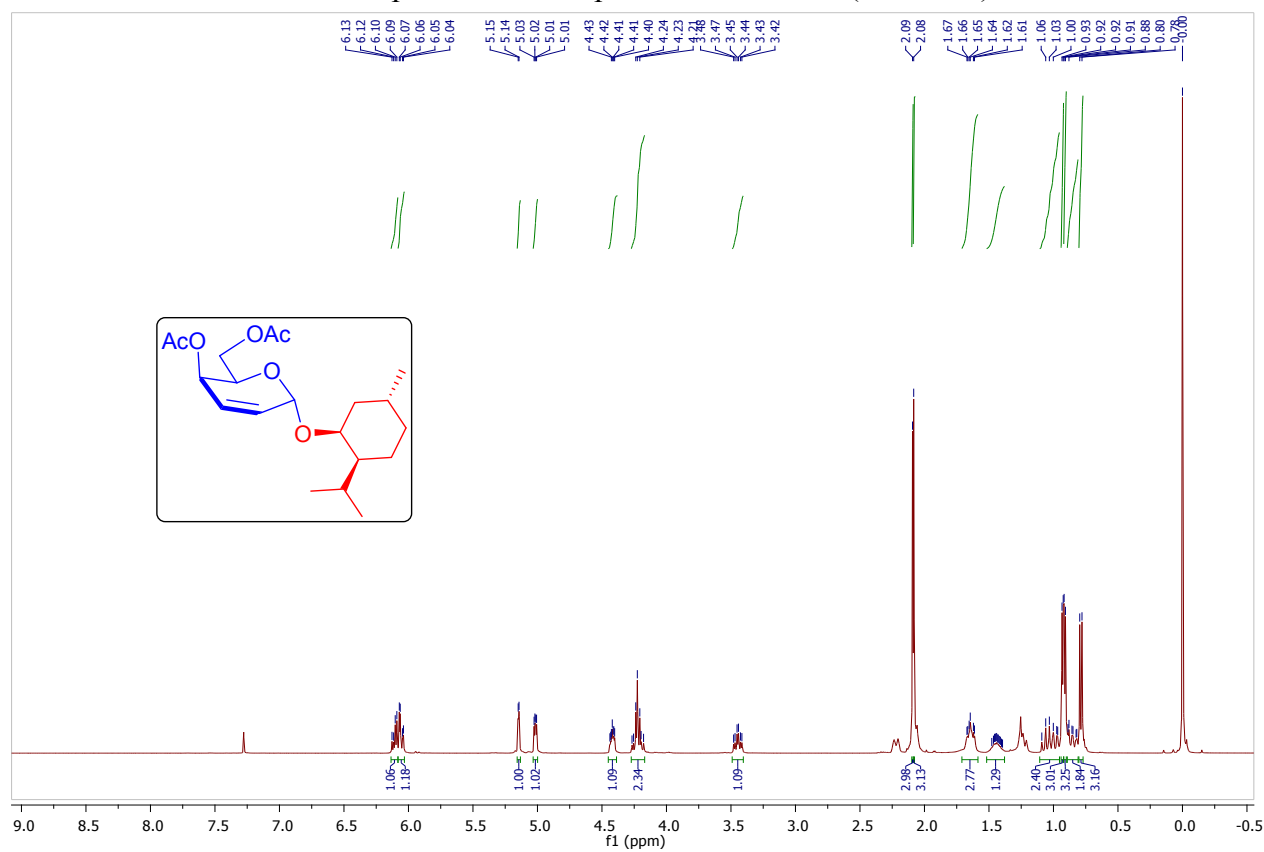


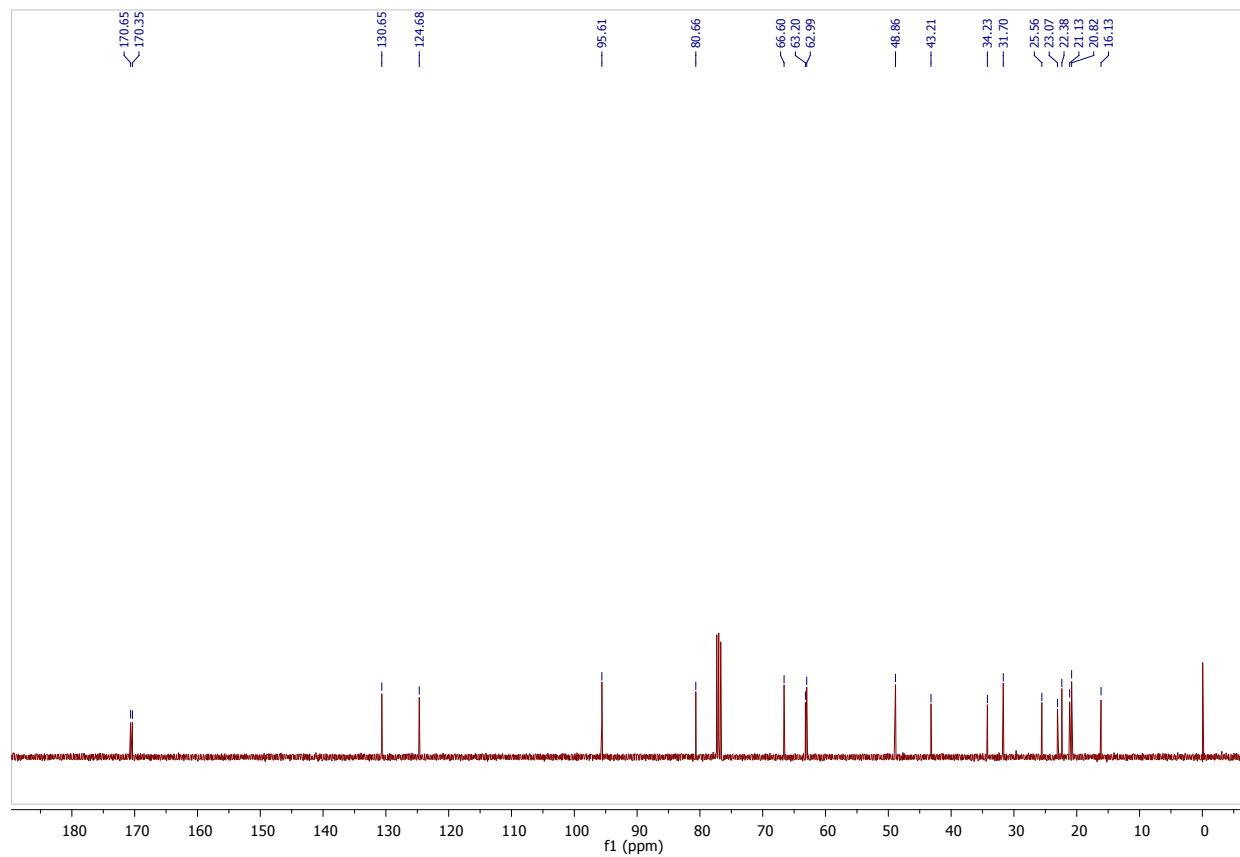
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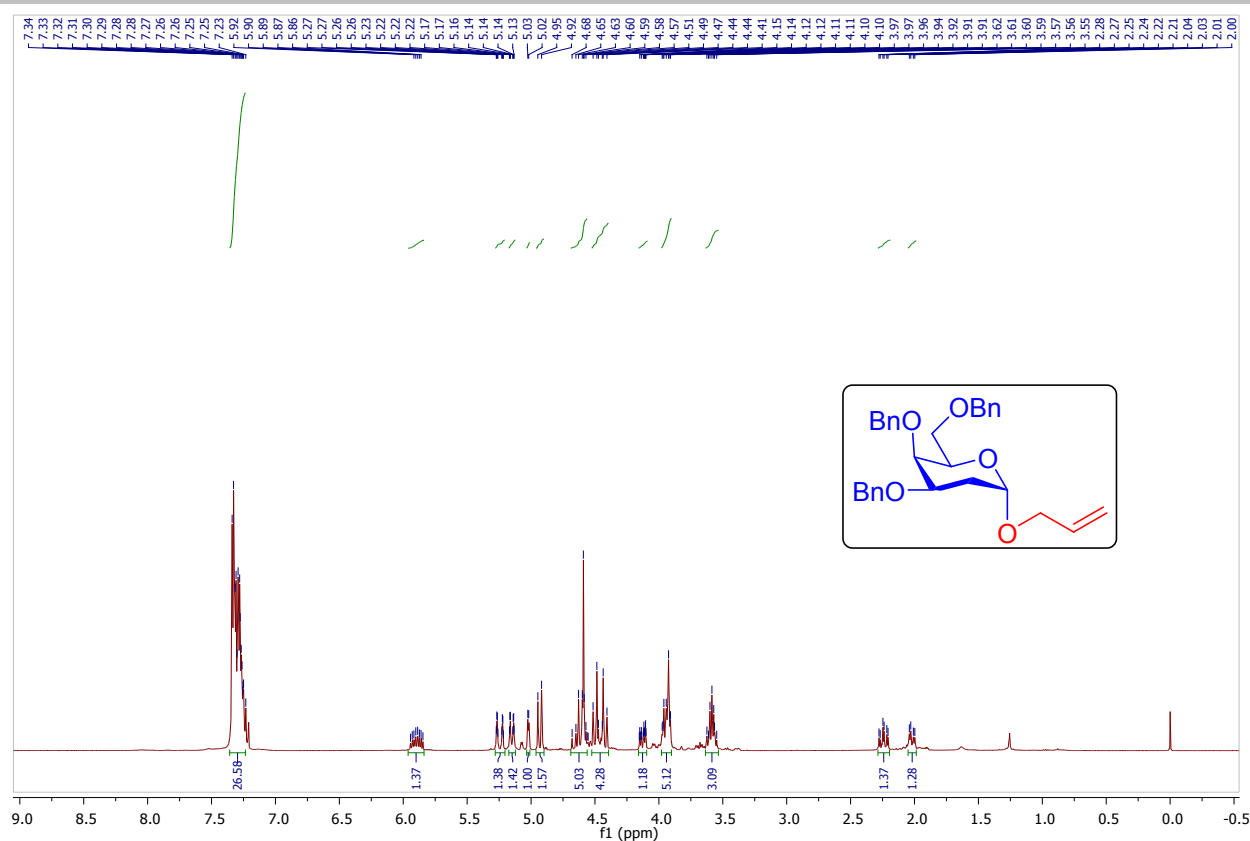
^1H NMR spectrum of compound **3a** in CDCl_3 (400 MHz) ^{13}C NMR spectrum of compound **3a** in CDCl_3 (101 MHz)



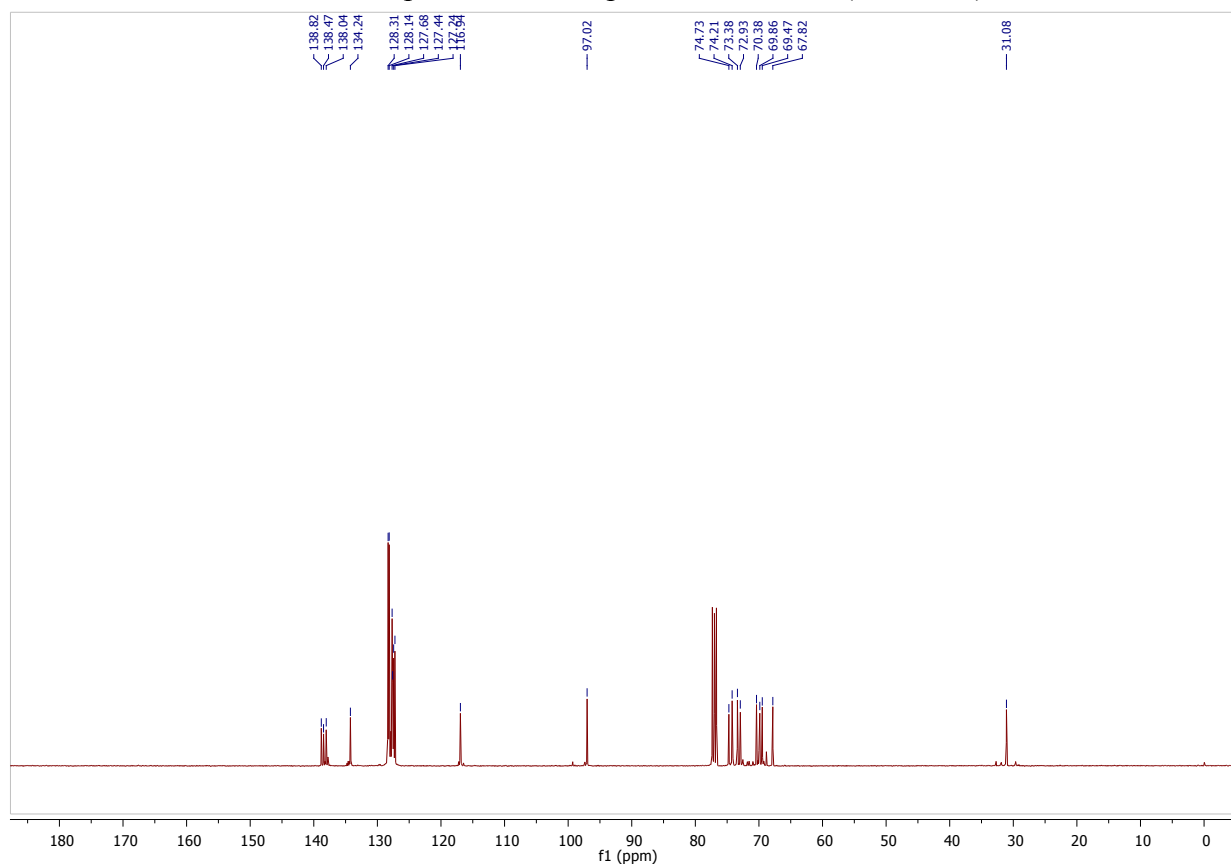
¹H NMR spectrum of compound **4b** in CDCl₃ (400 MHz)

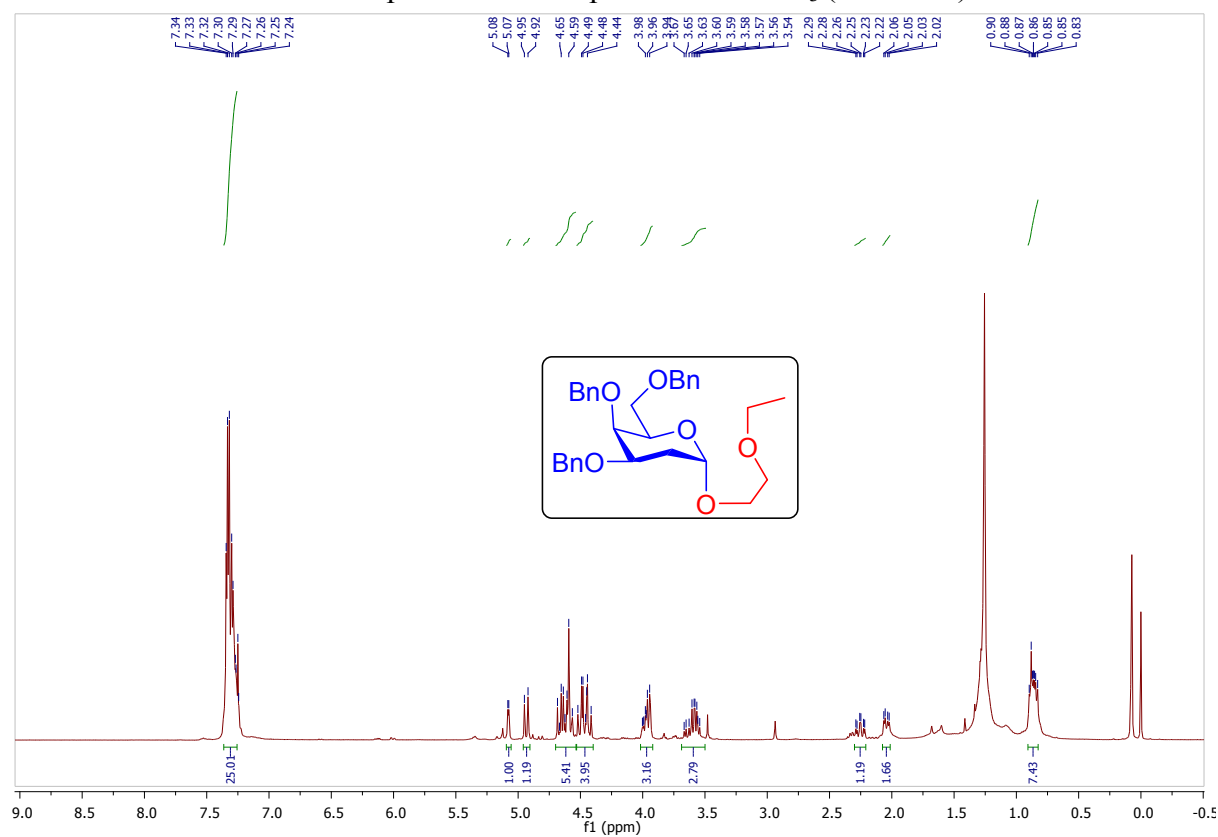
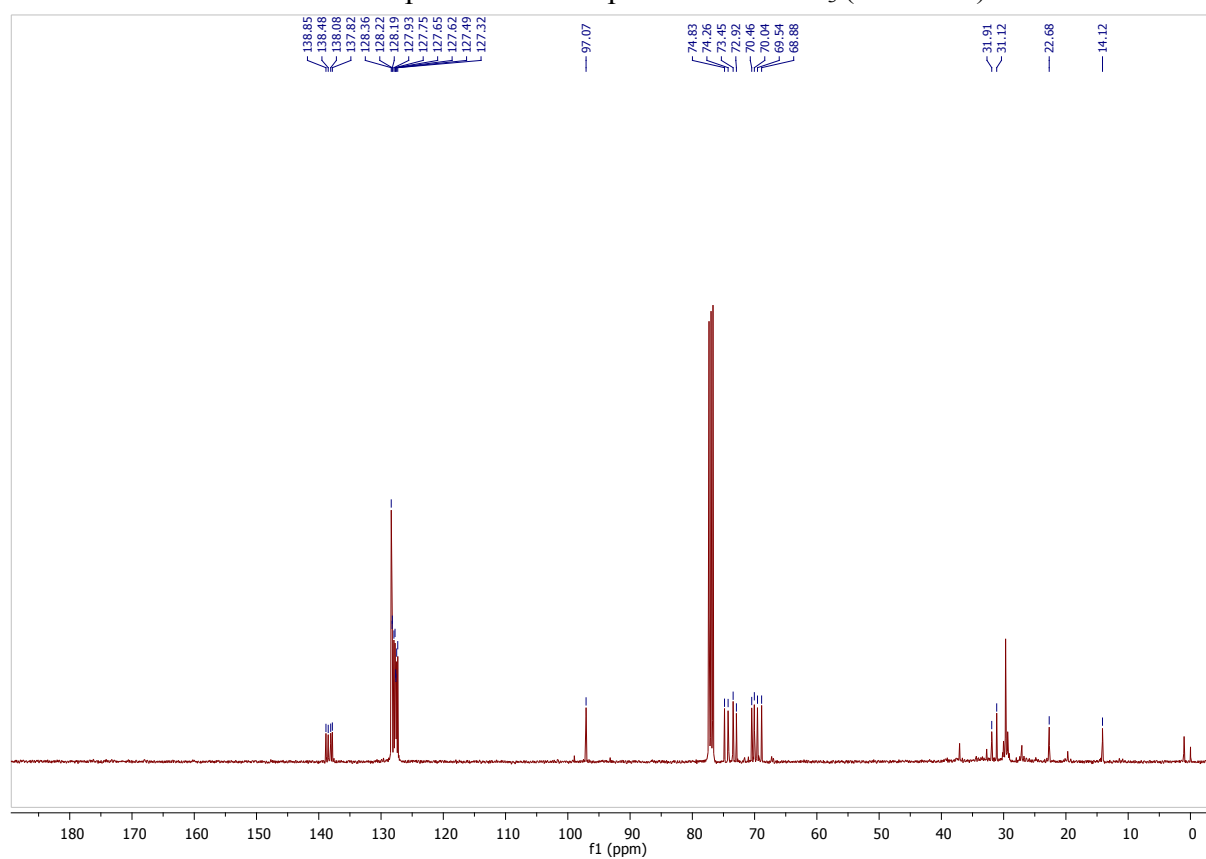


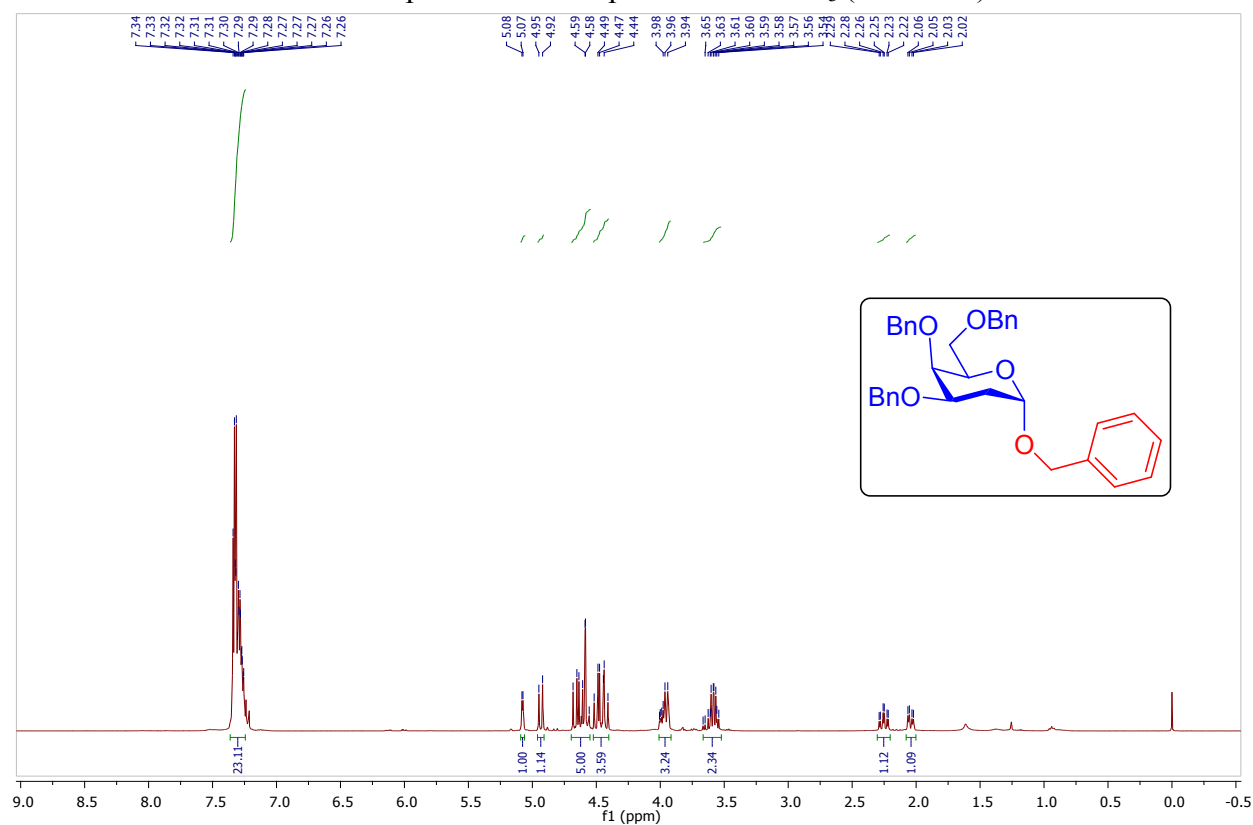
^{13}C NMR spectrum of compound **4b** in CDCl_3 (101 MHz) ^1H NMR spectrum of compound **5** in CDCl_3 (400 MHz)

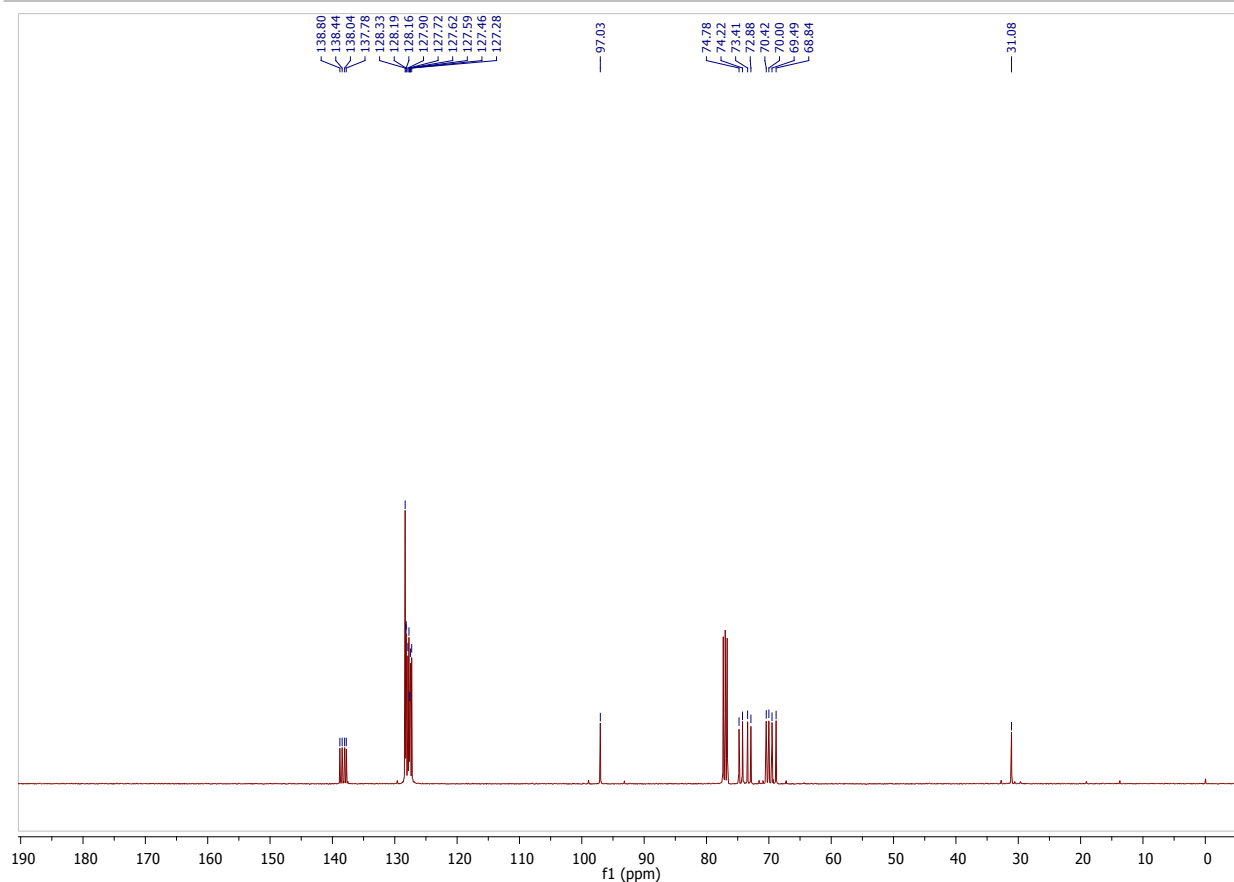


¹³C NMR spectrum of compound 5 in CDCl₃ (101 MHz)

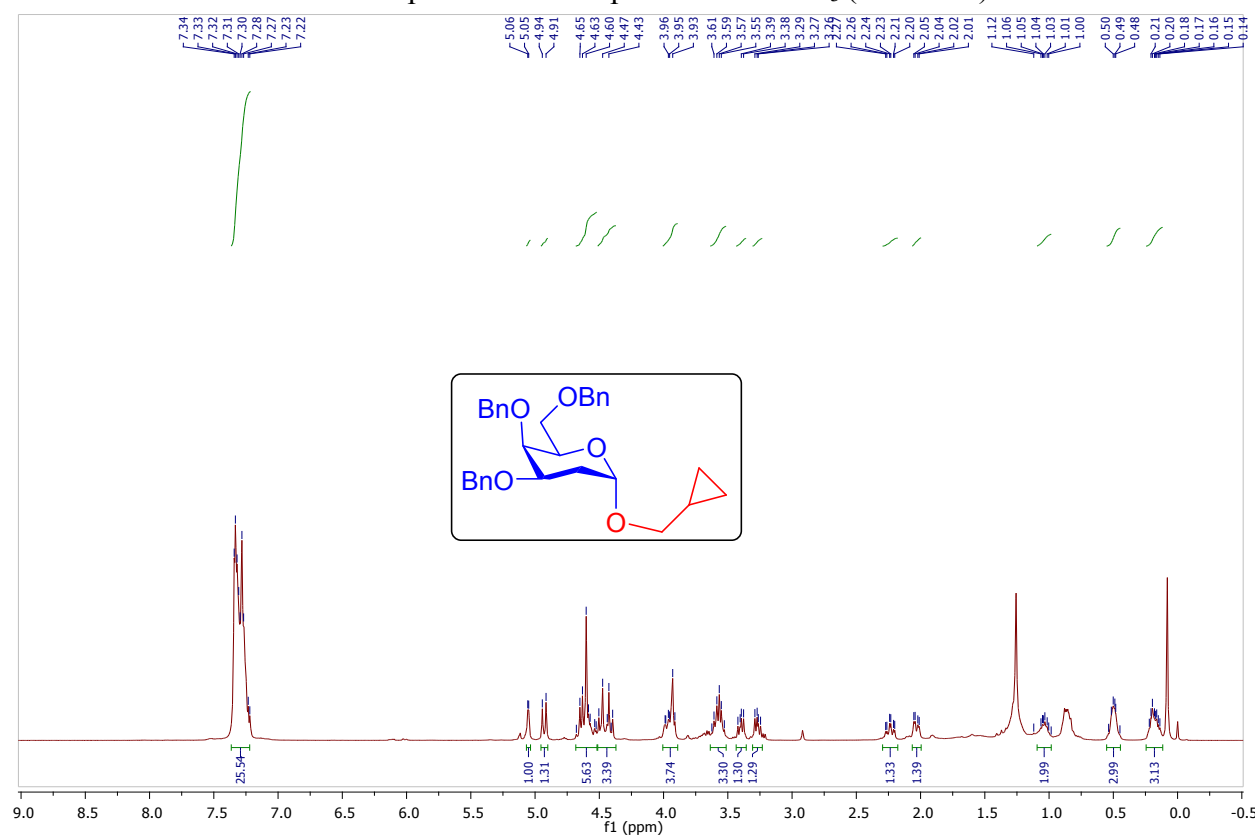


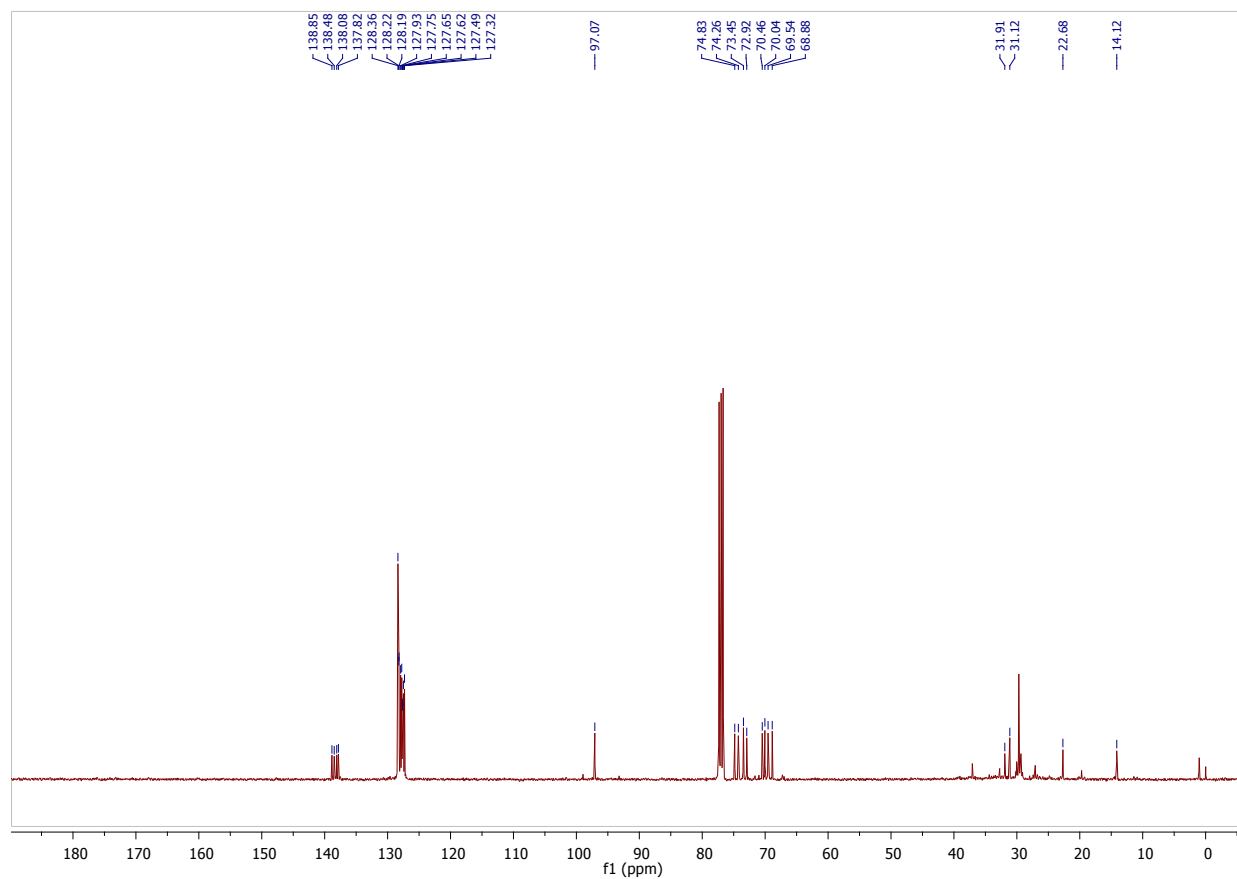
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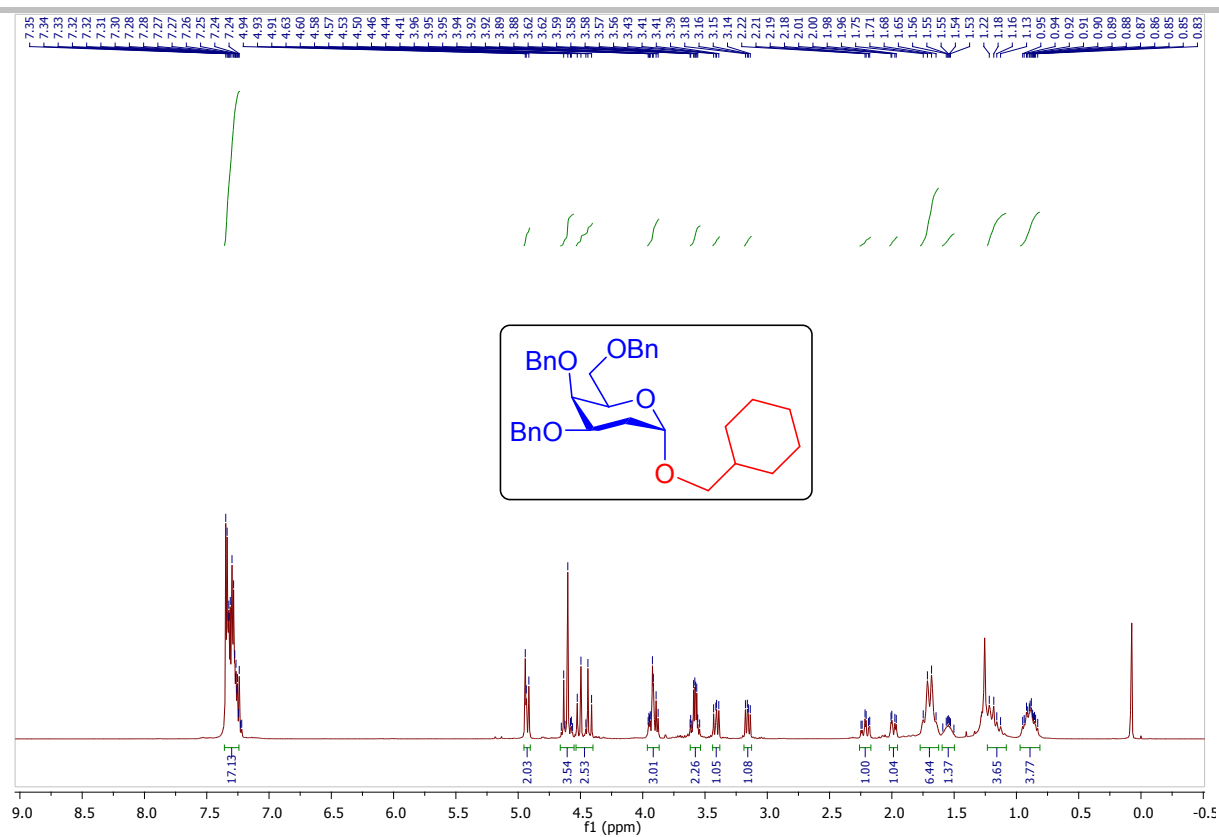
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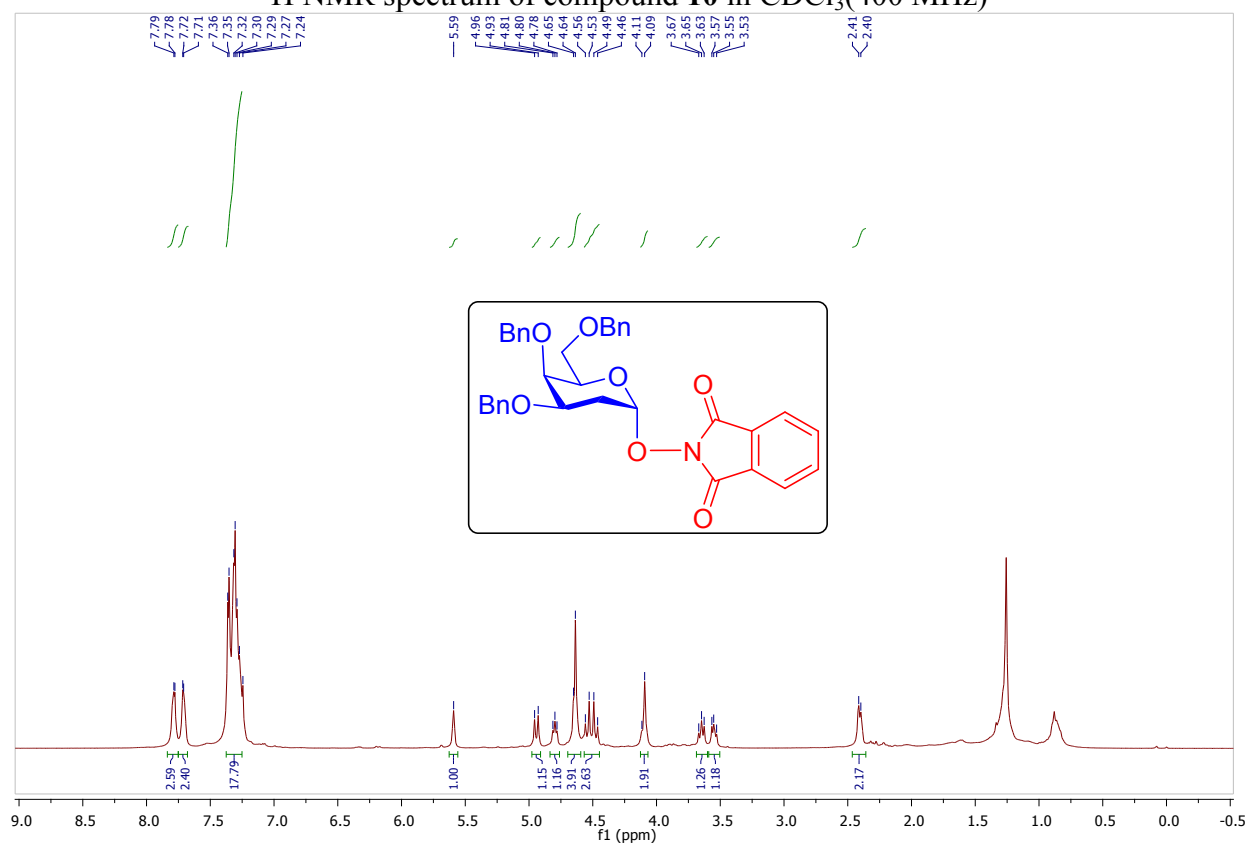


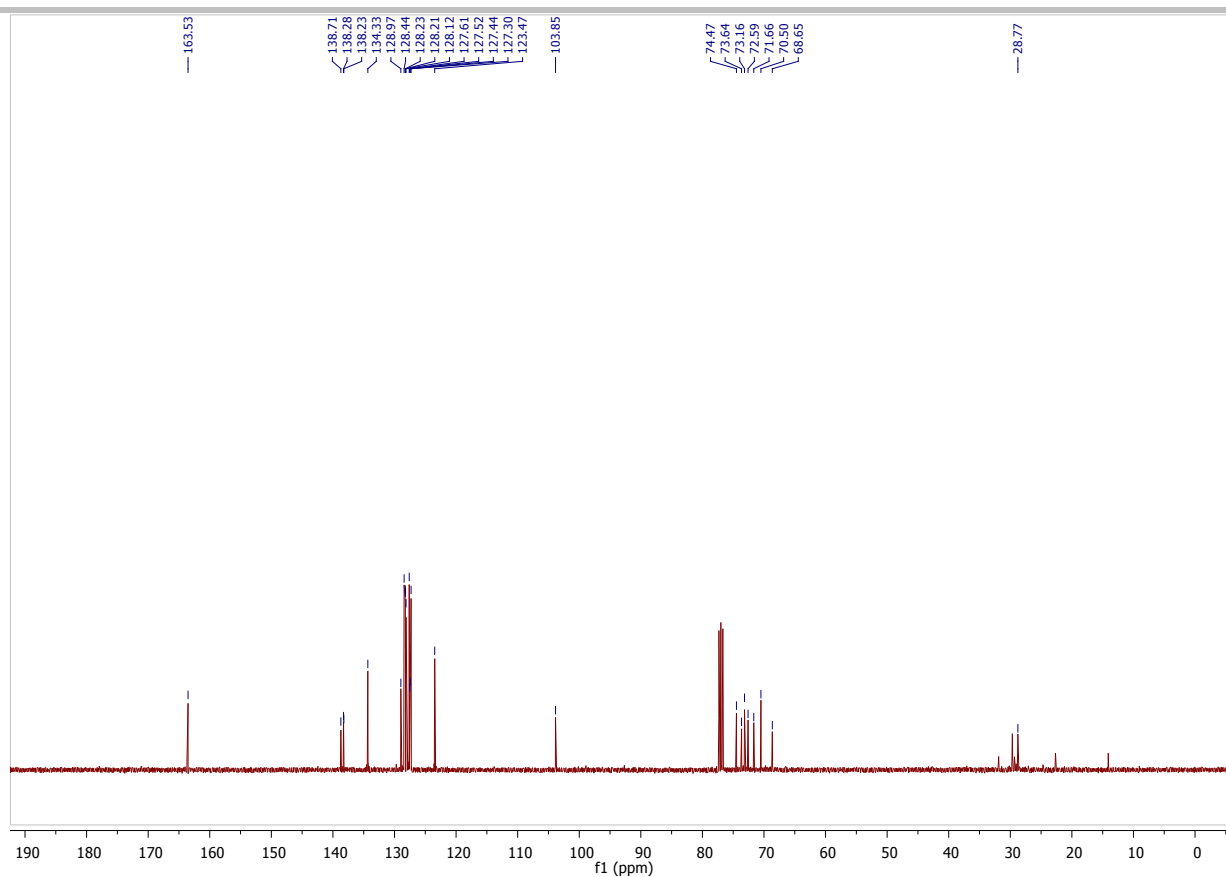
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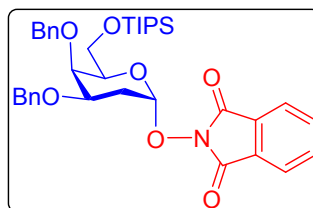
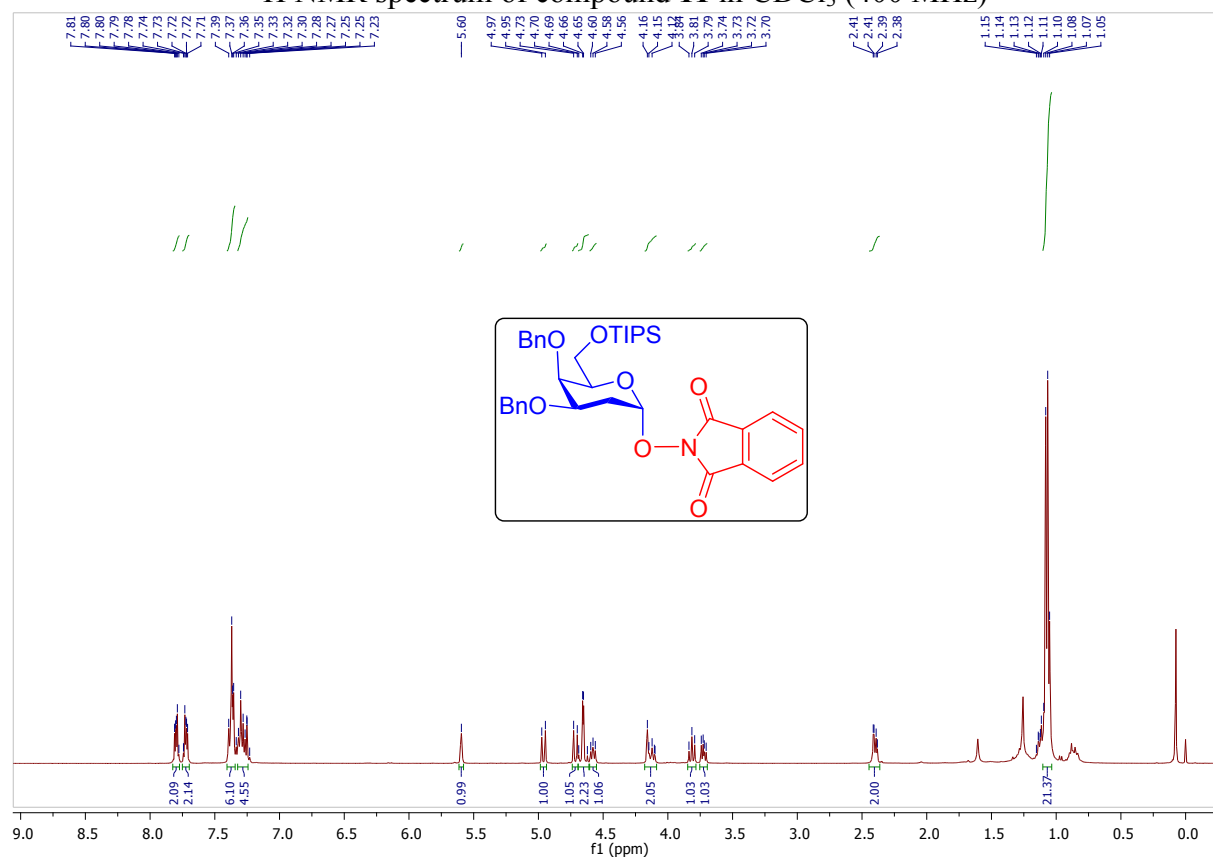
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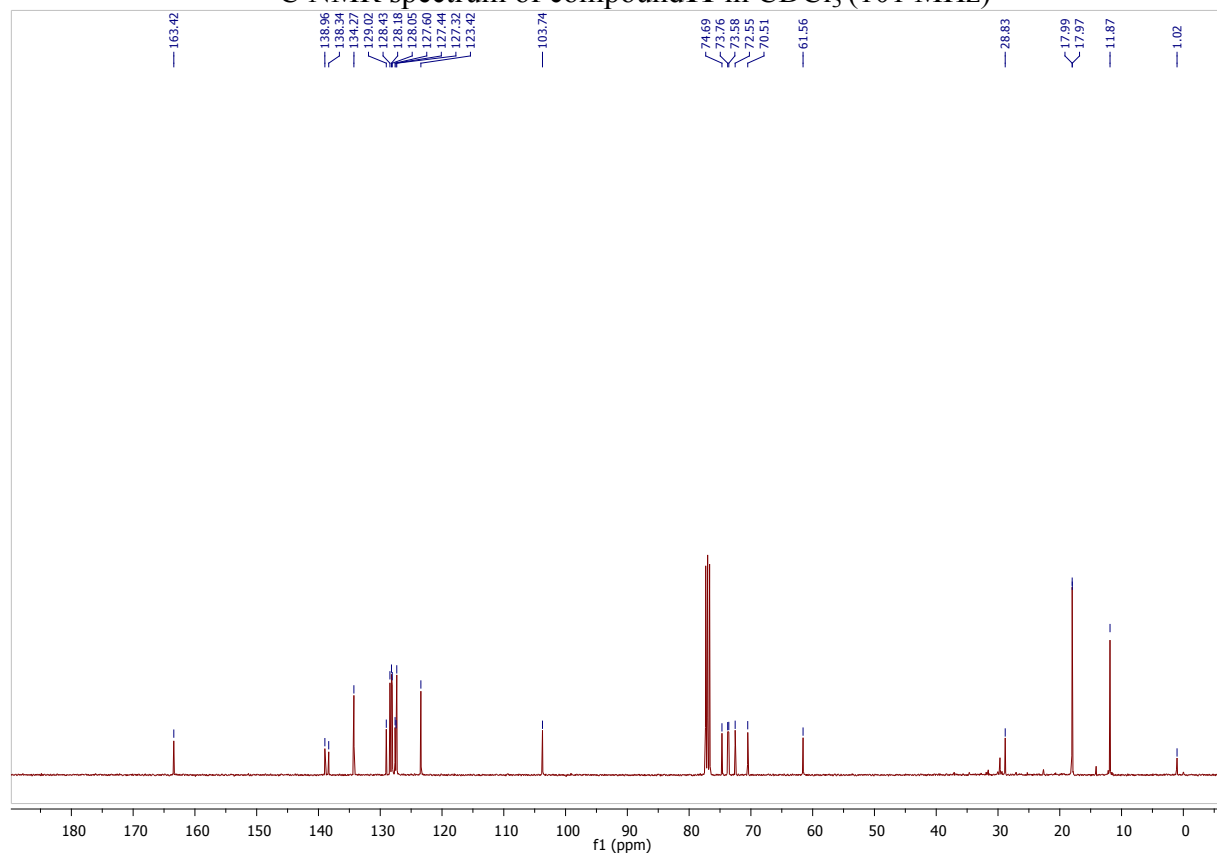


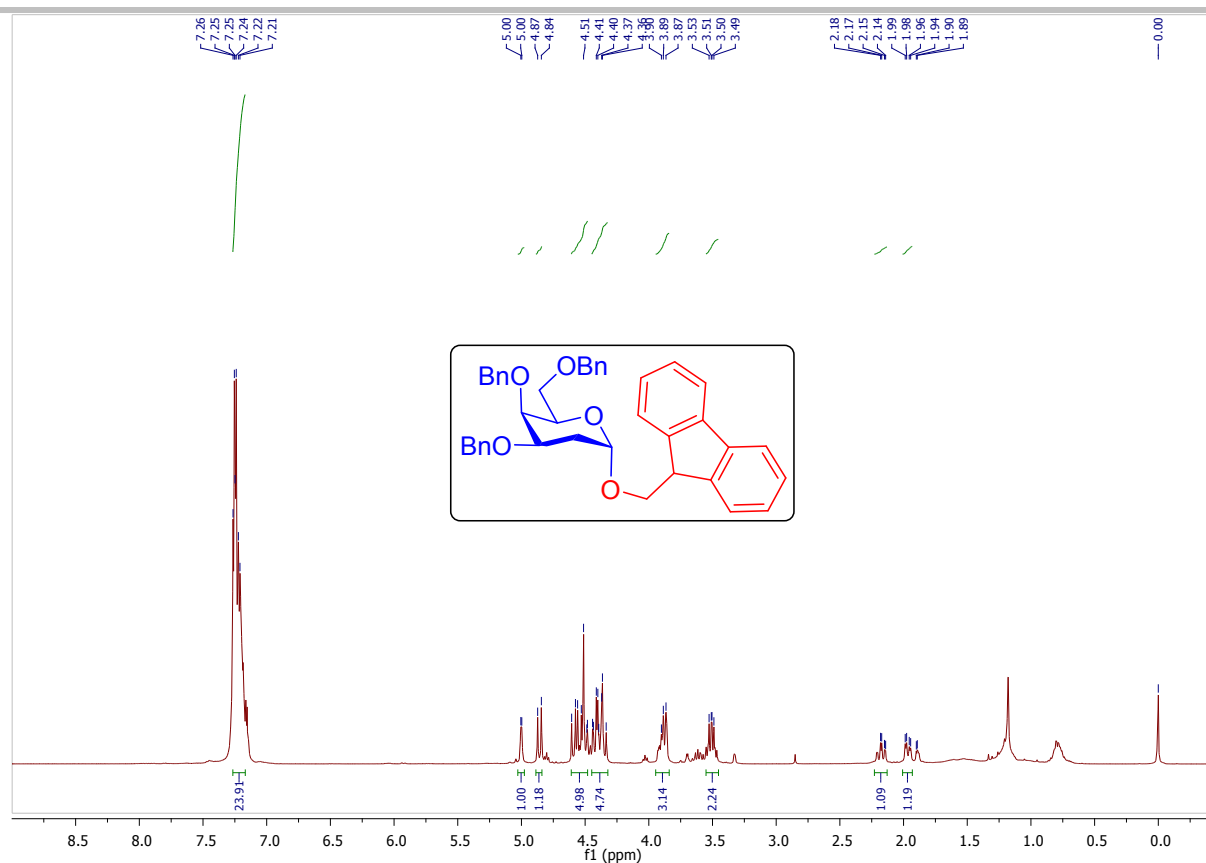
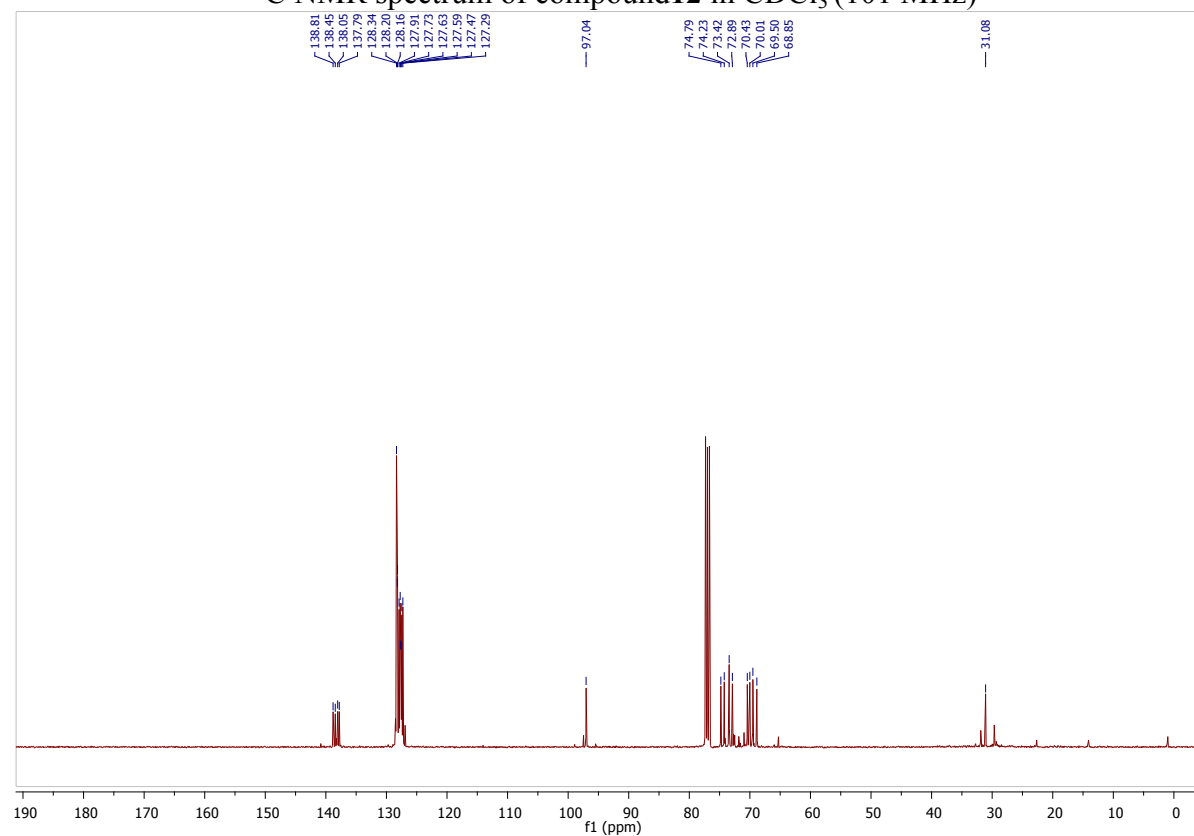
¹H NMR spectrum of compound **10** in CDCl₃ (400 MHz)¹³C NMR spectrum of compound **10** in CDCl₃ (101 MHz)

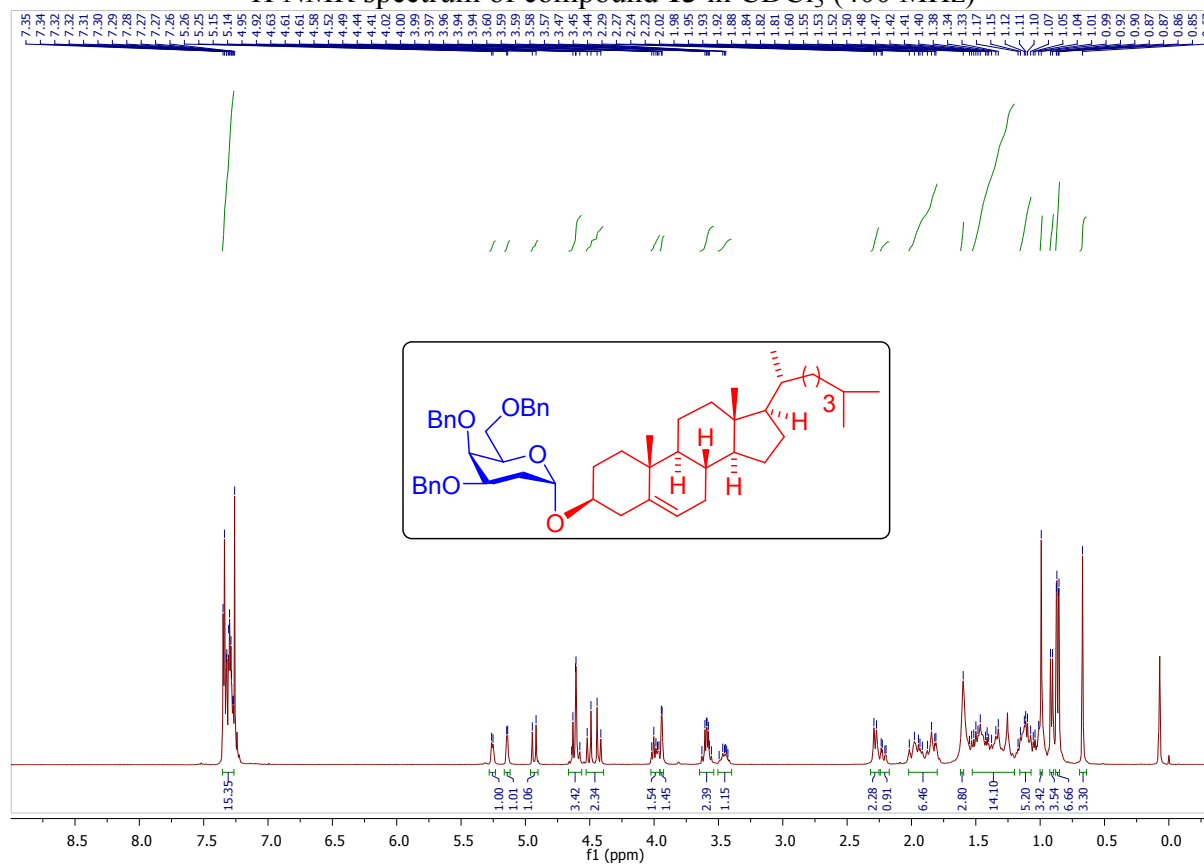
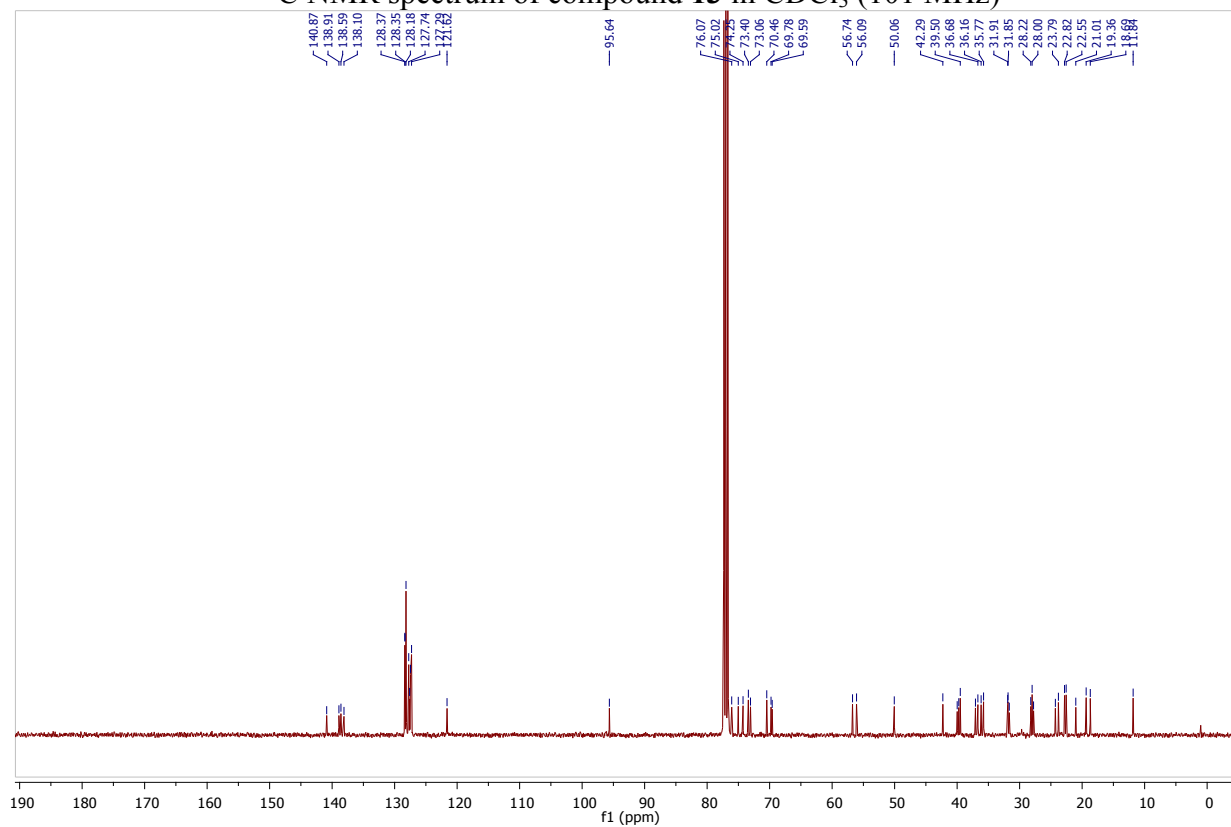


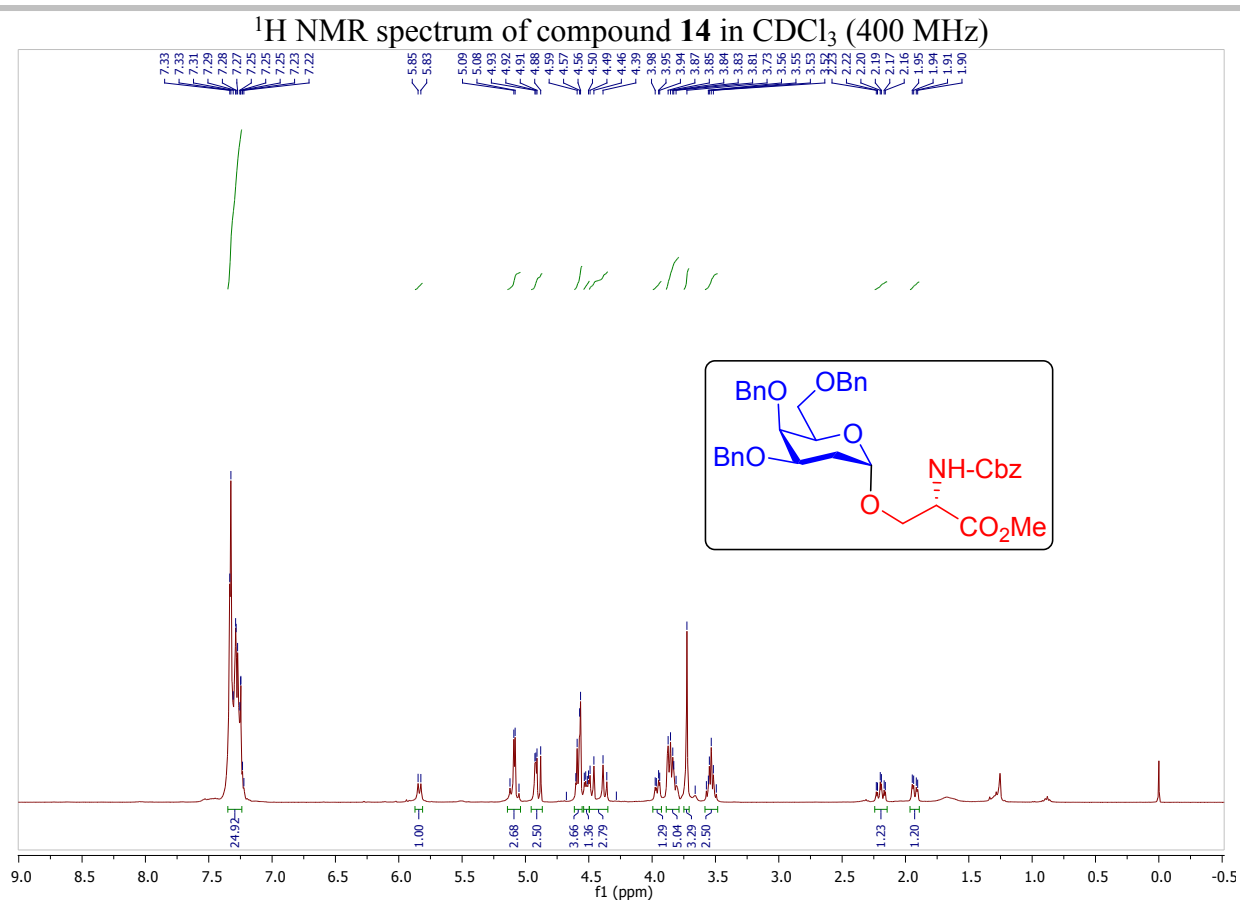
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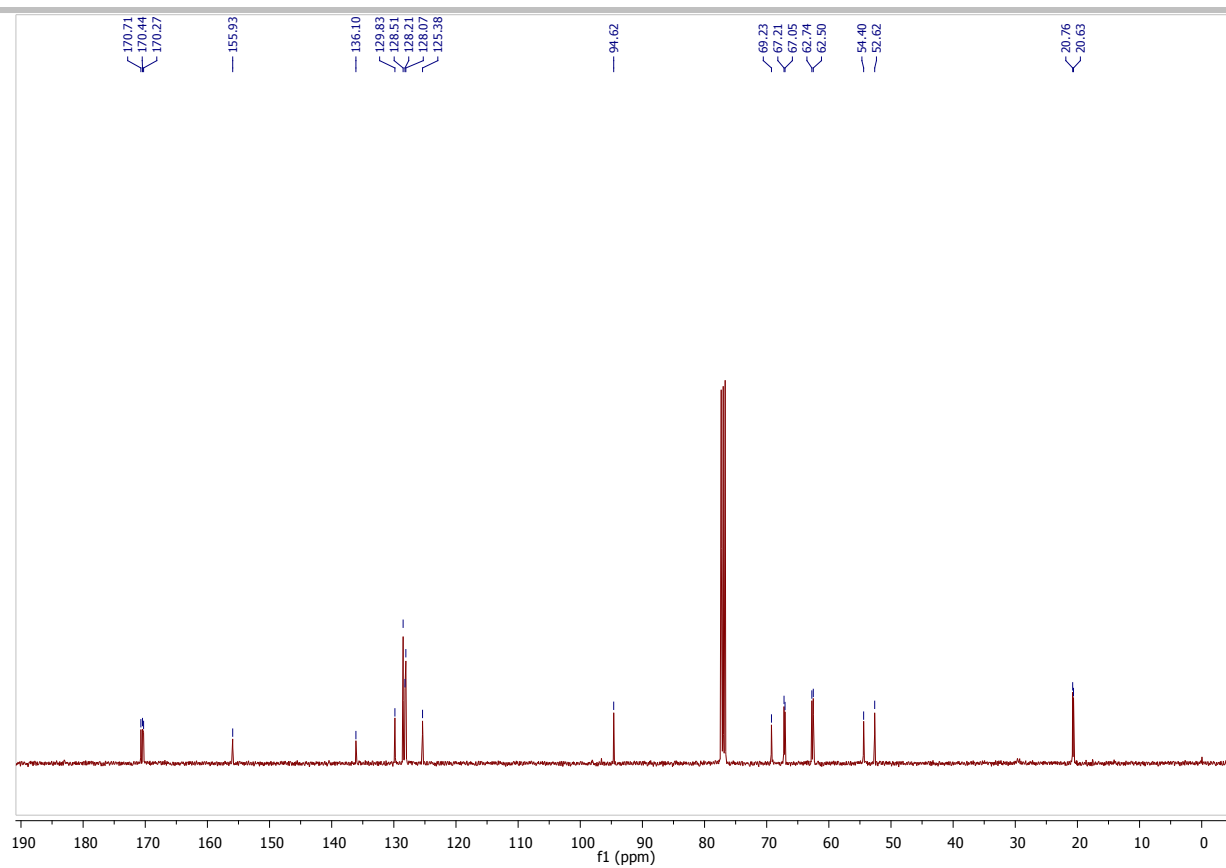
^{13}C NMR spectrum of compound **11** in CDCl_3 (101 MHz) ^1H NMR spectrum of compound **12** in CDCl_3 (400 MHz)

¹³C NMR spectrum of compound **12** in CDCl₃ (101 MHz)

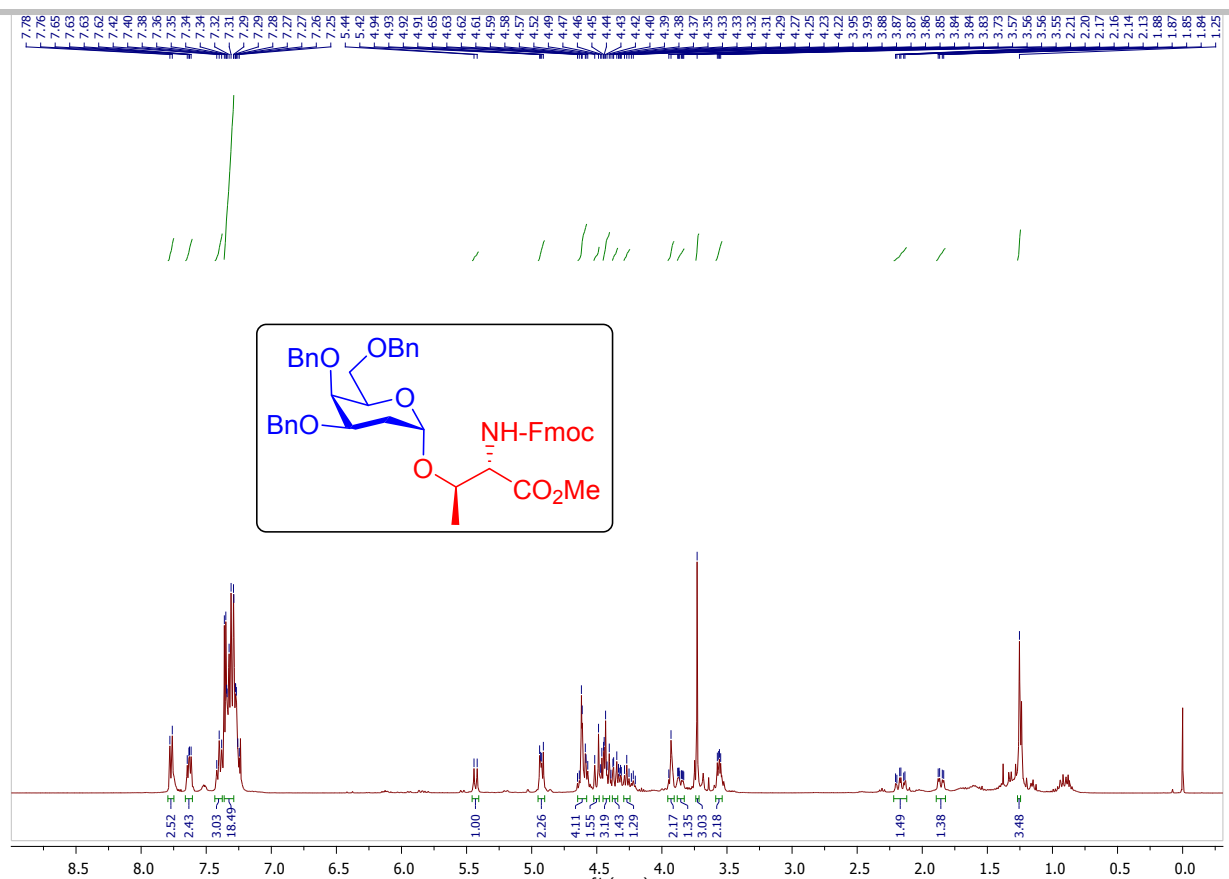
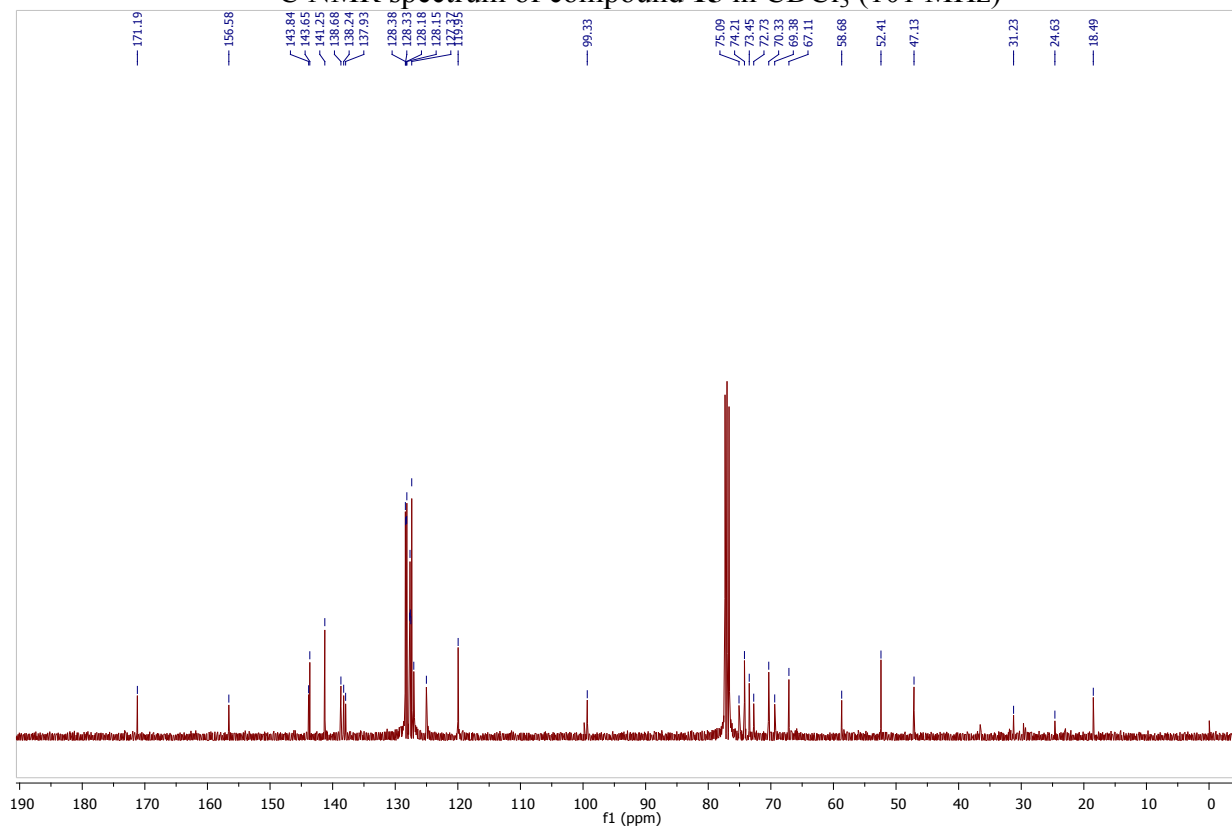
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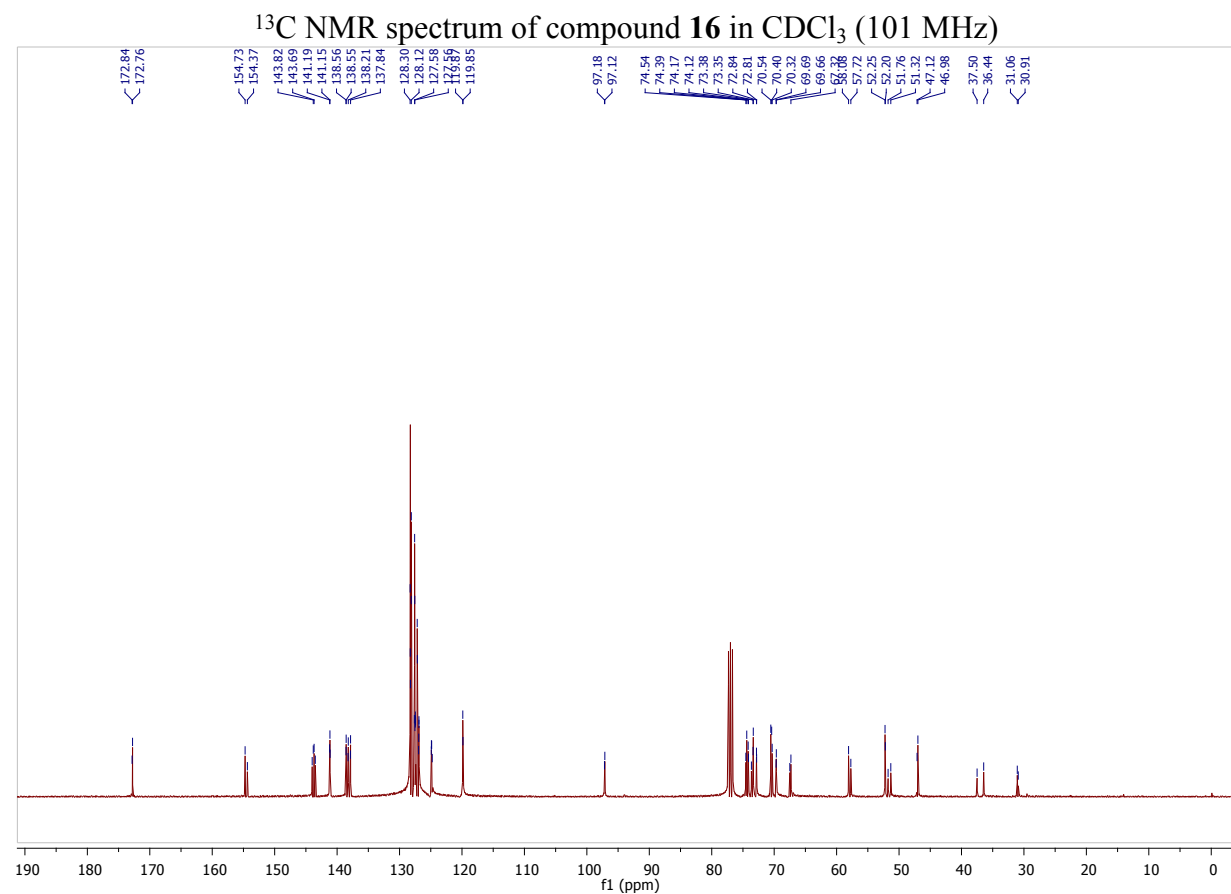
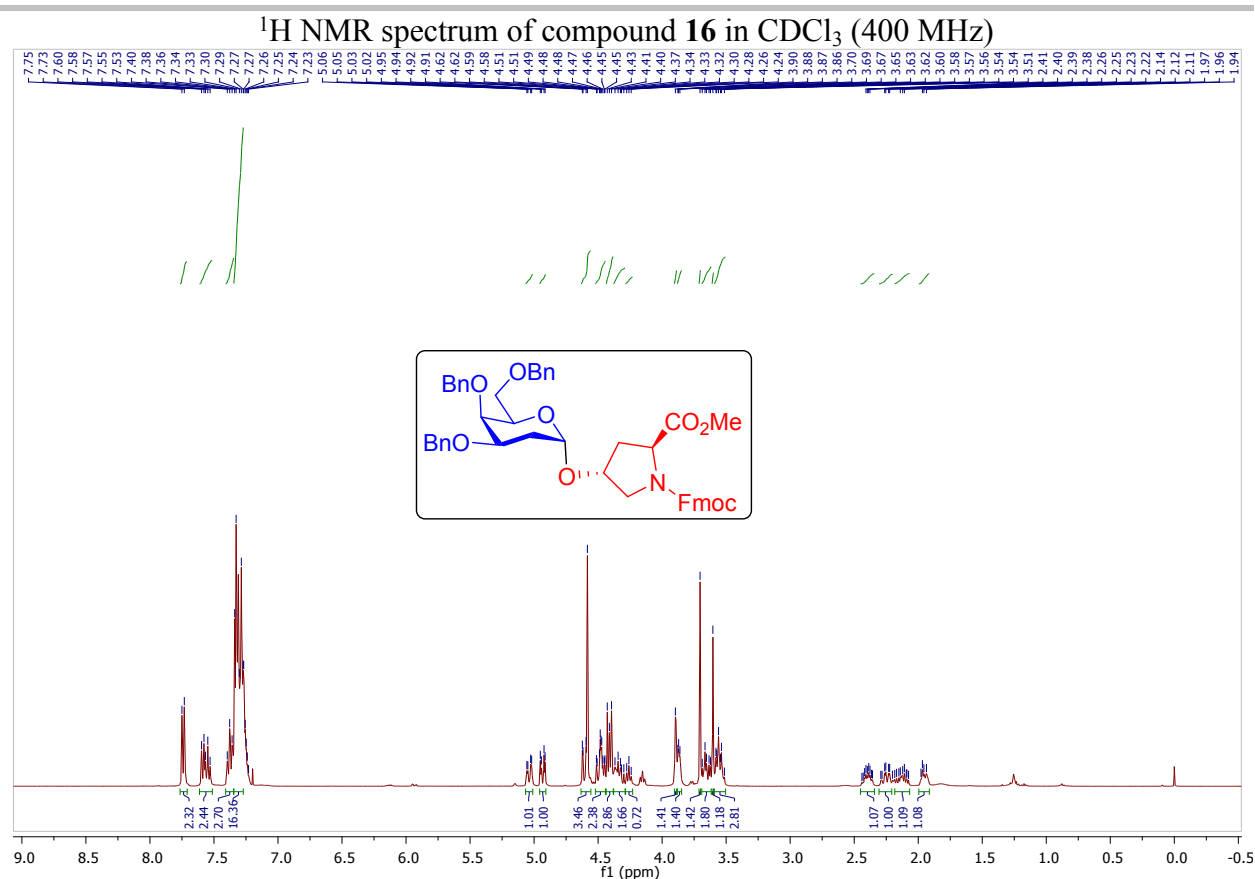


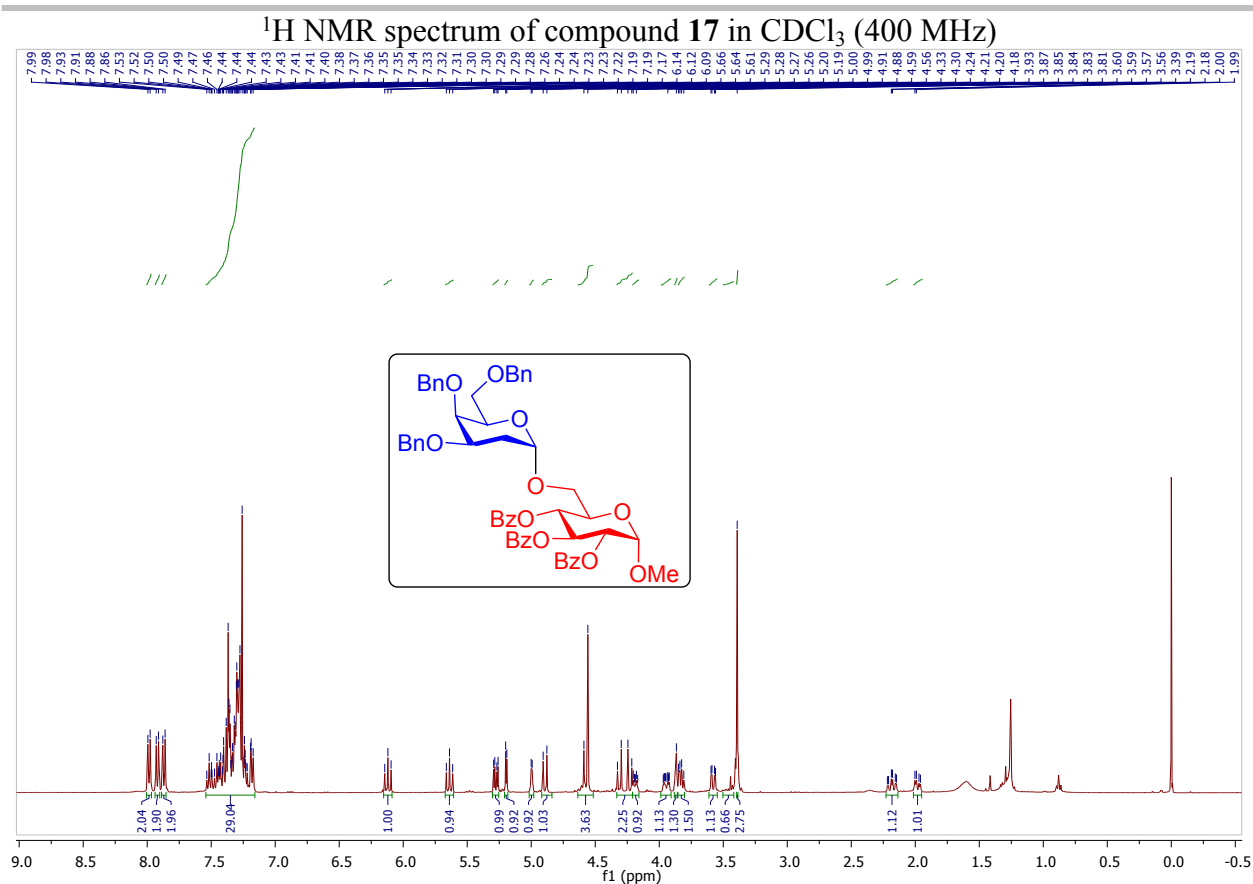
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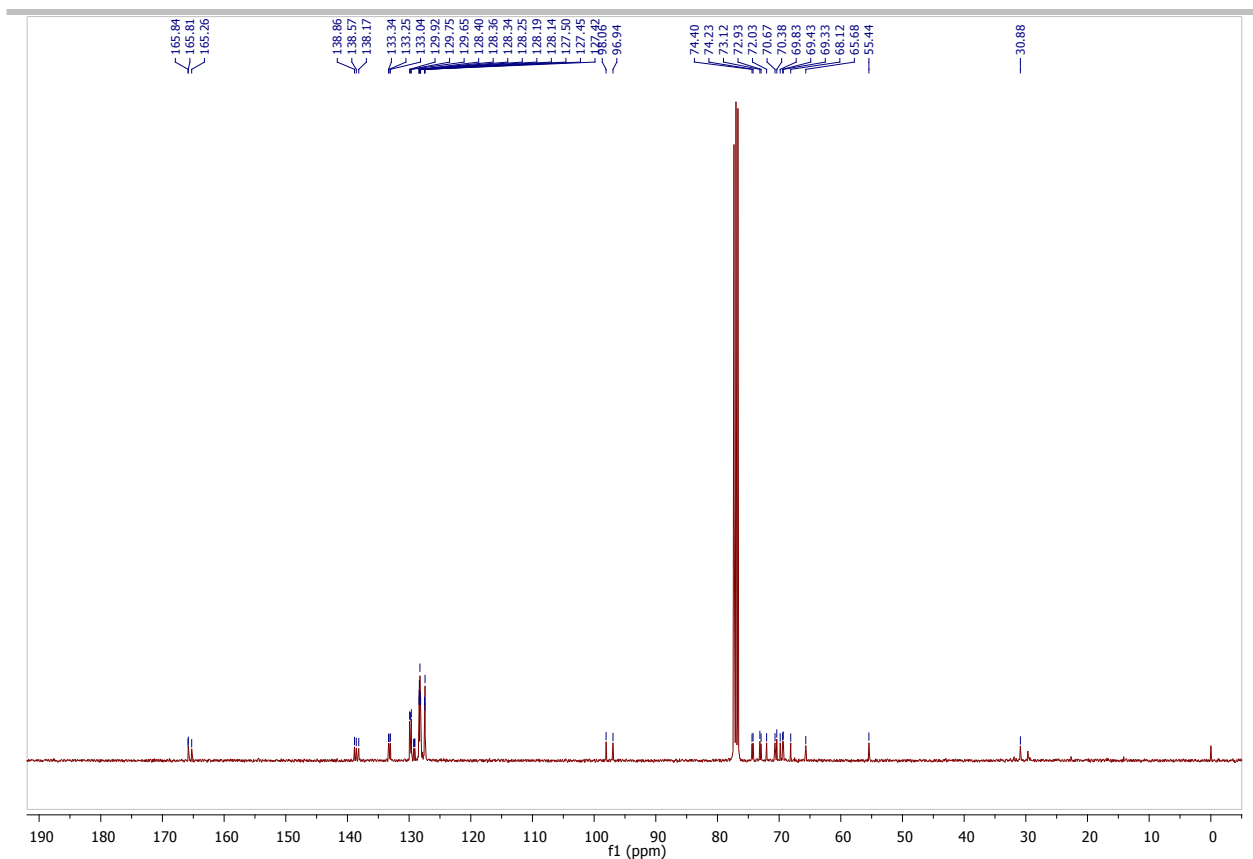
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¹³C NMR spectrum of compound **15** in CDCl₃ (101 MHz)

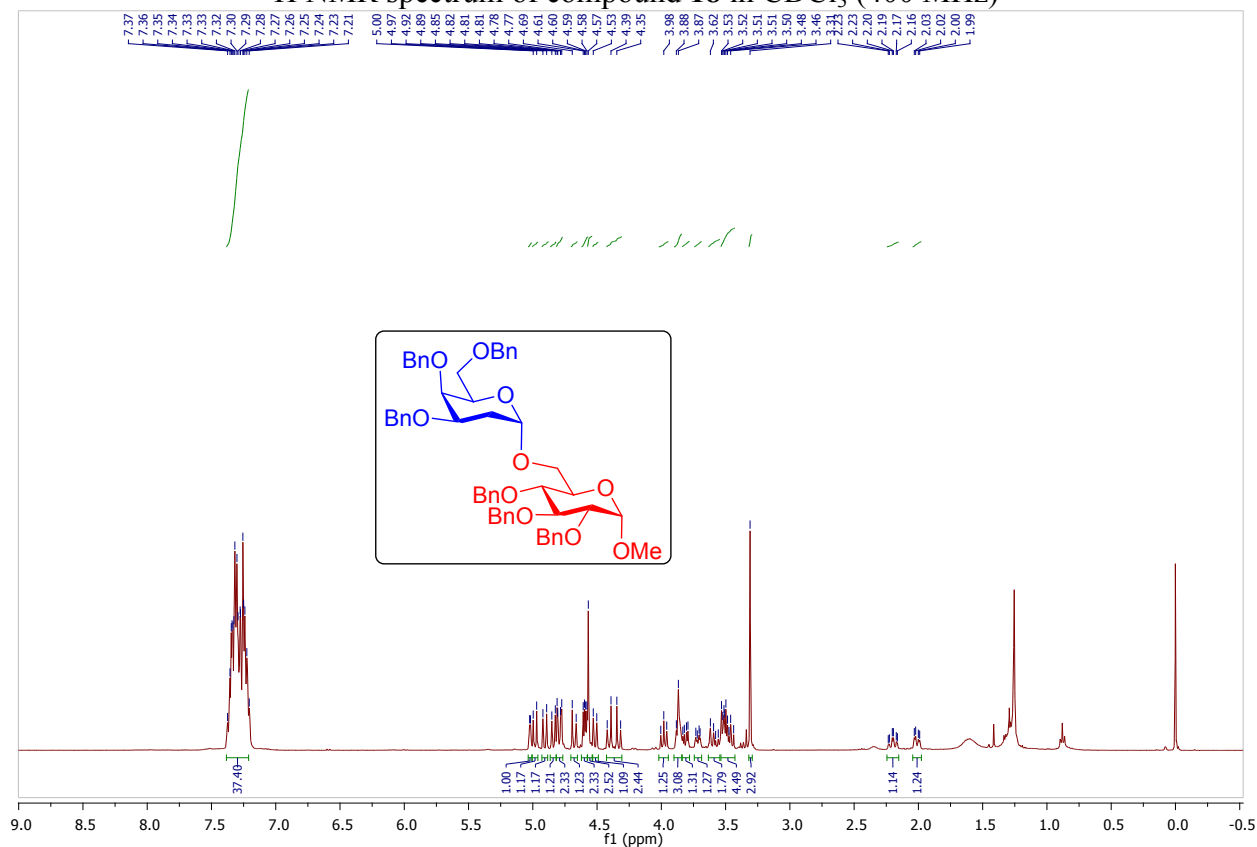


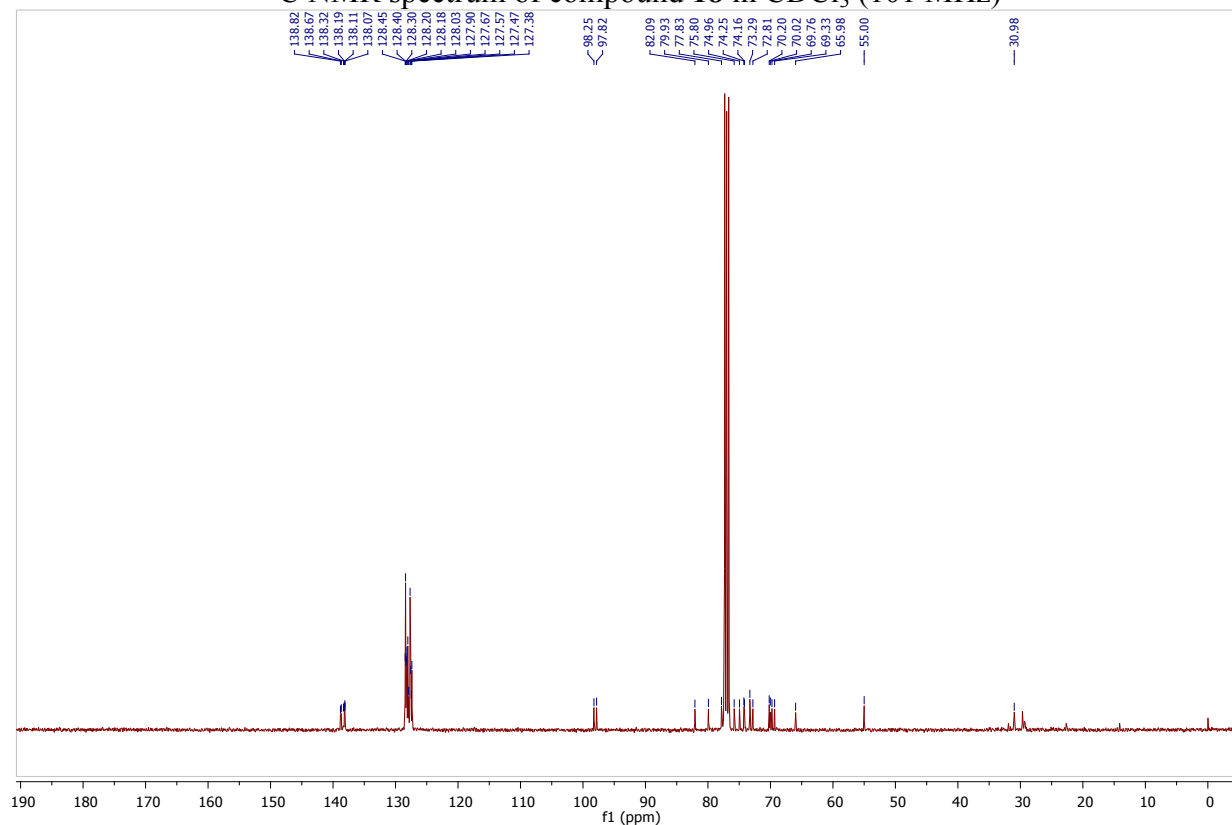
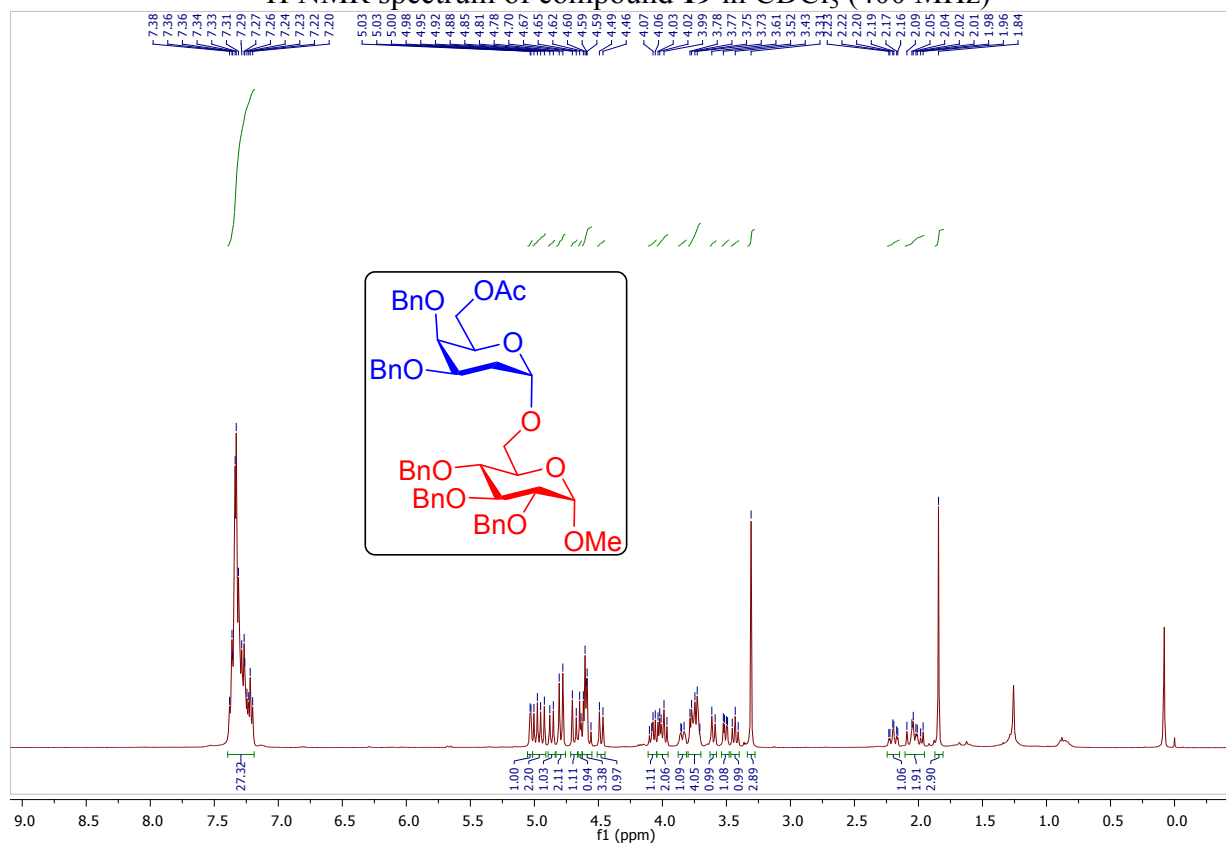


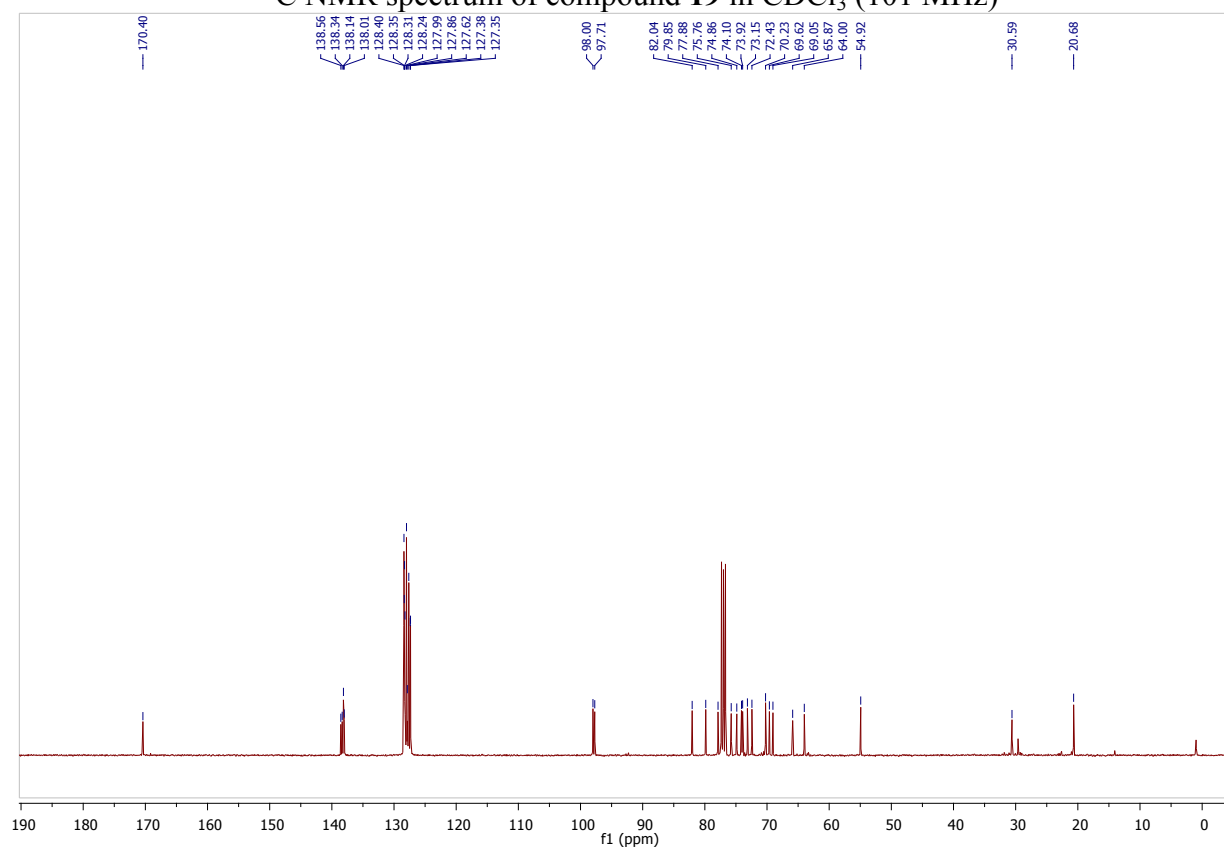
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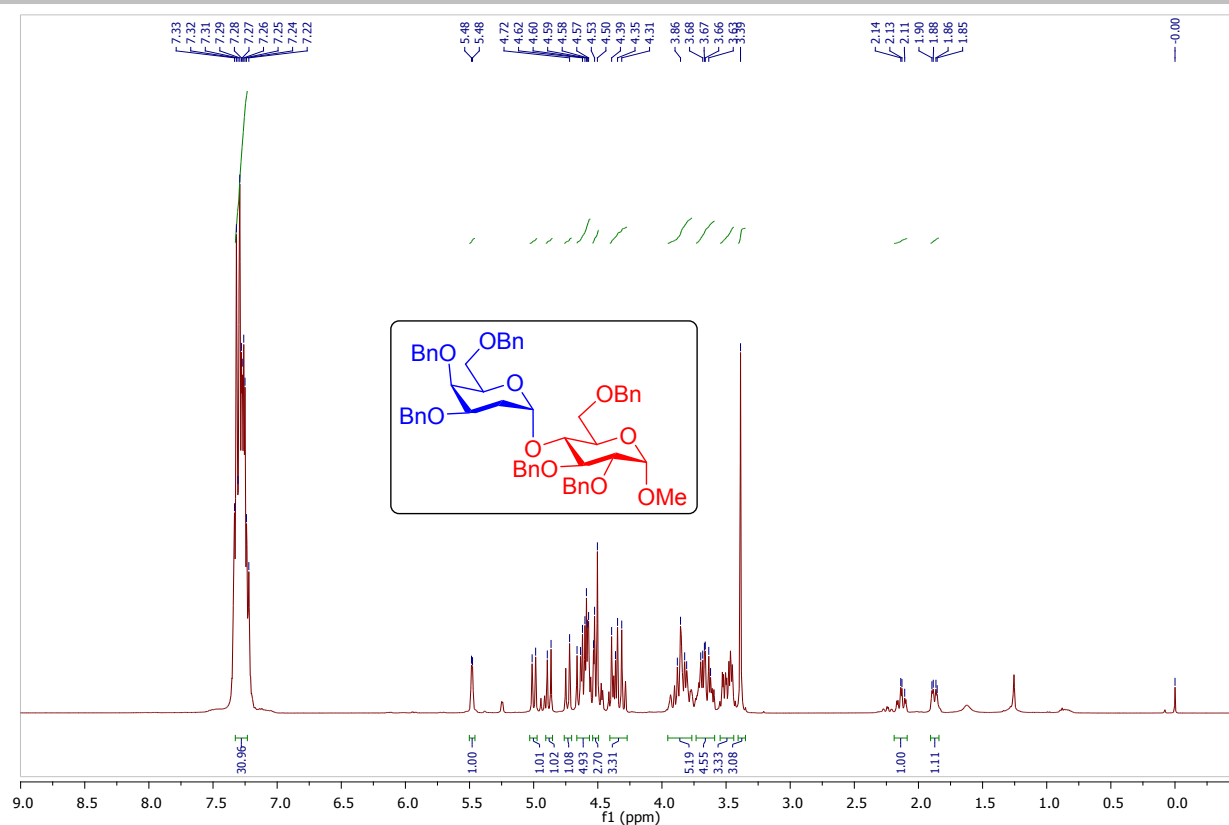


¹H NMR spectrum of compound **18** in CDCl₃ (400 MHz)

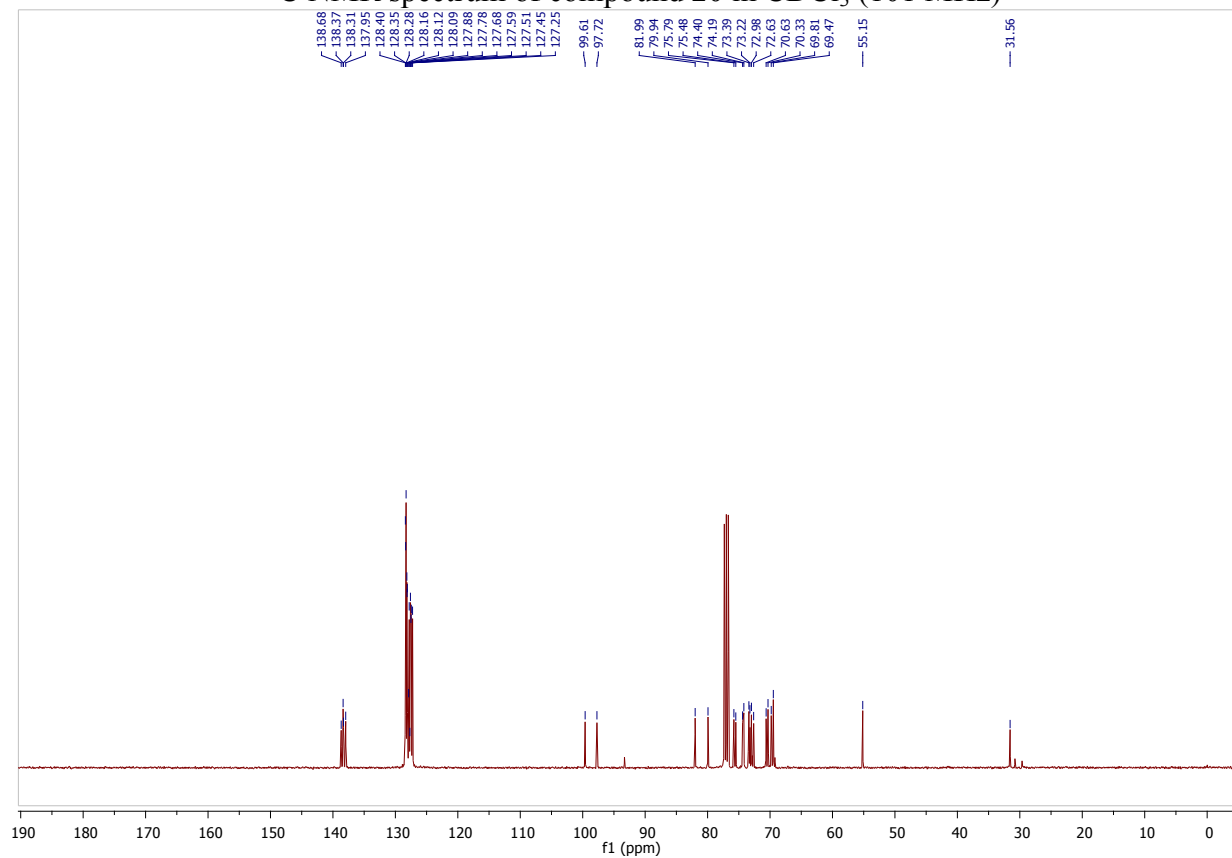


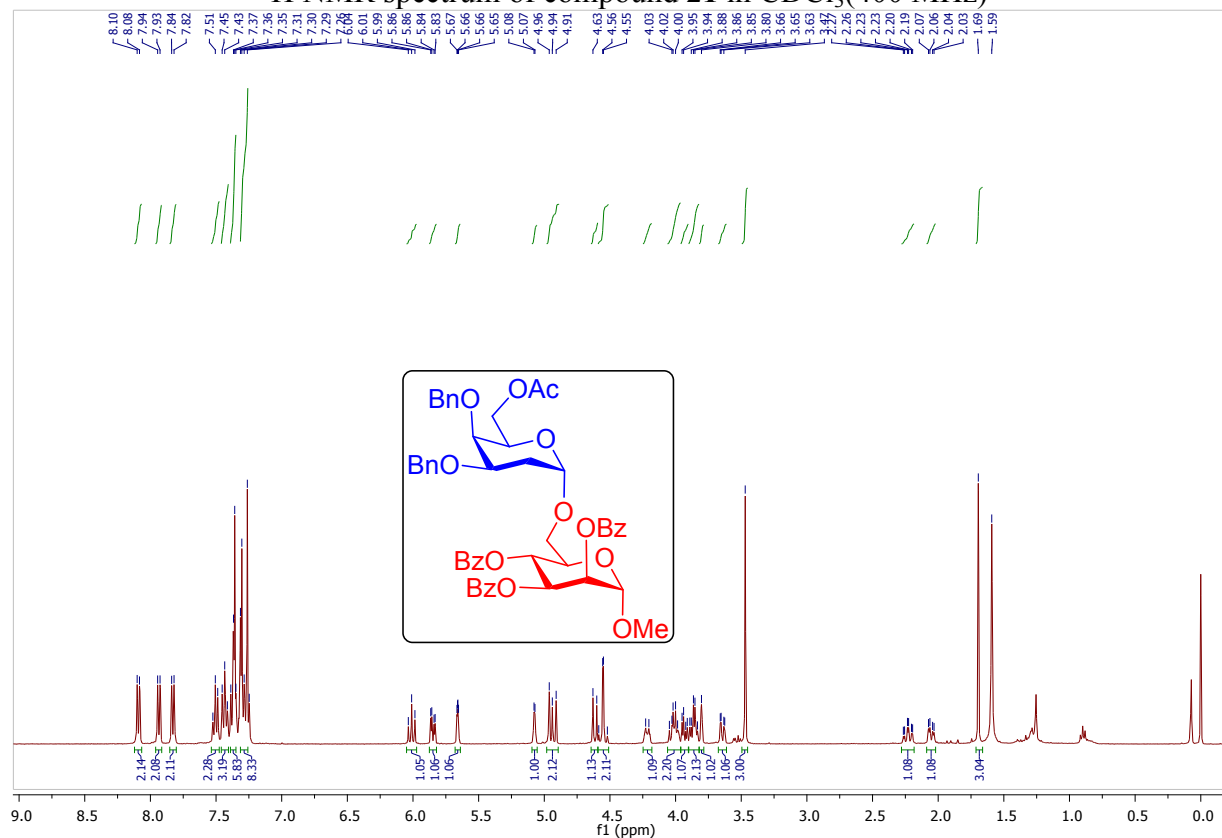
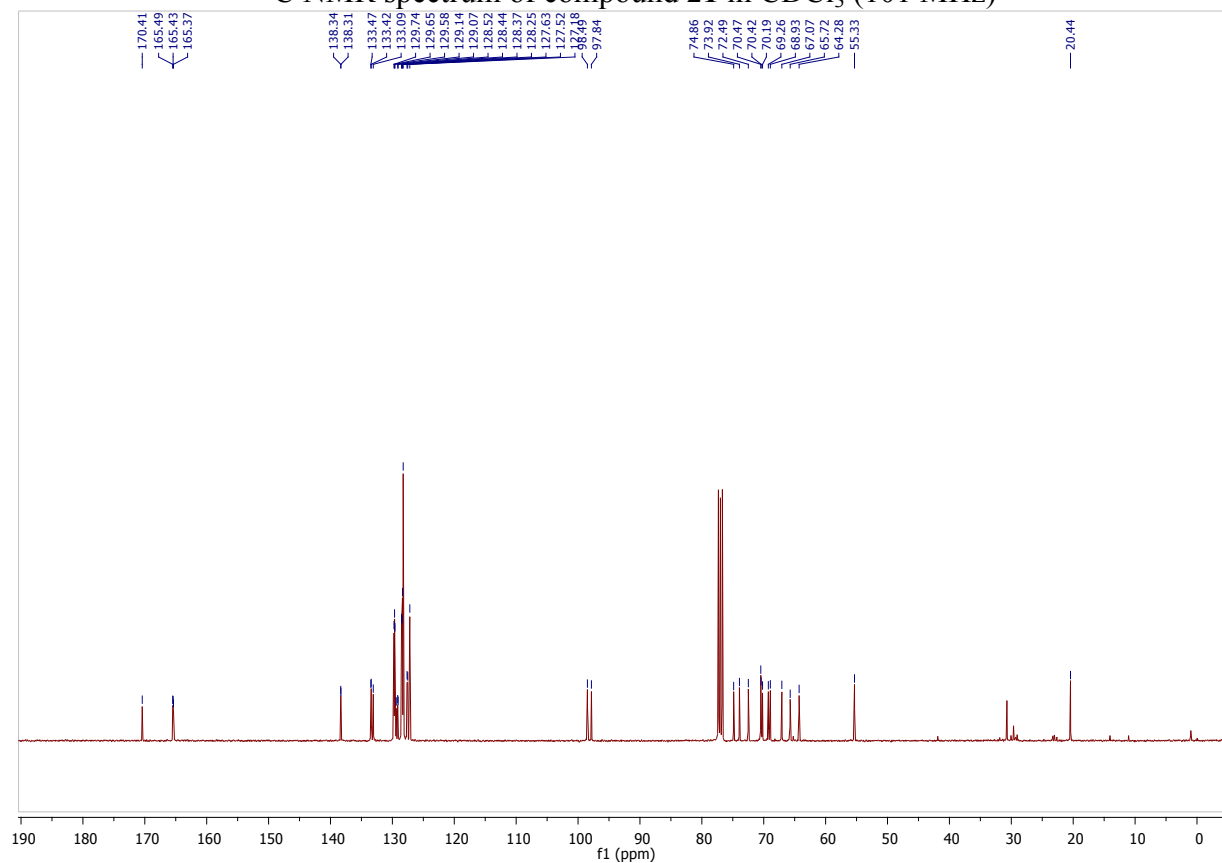
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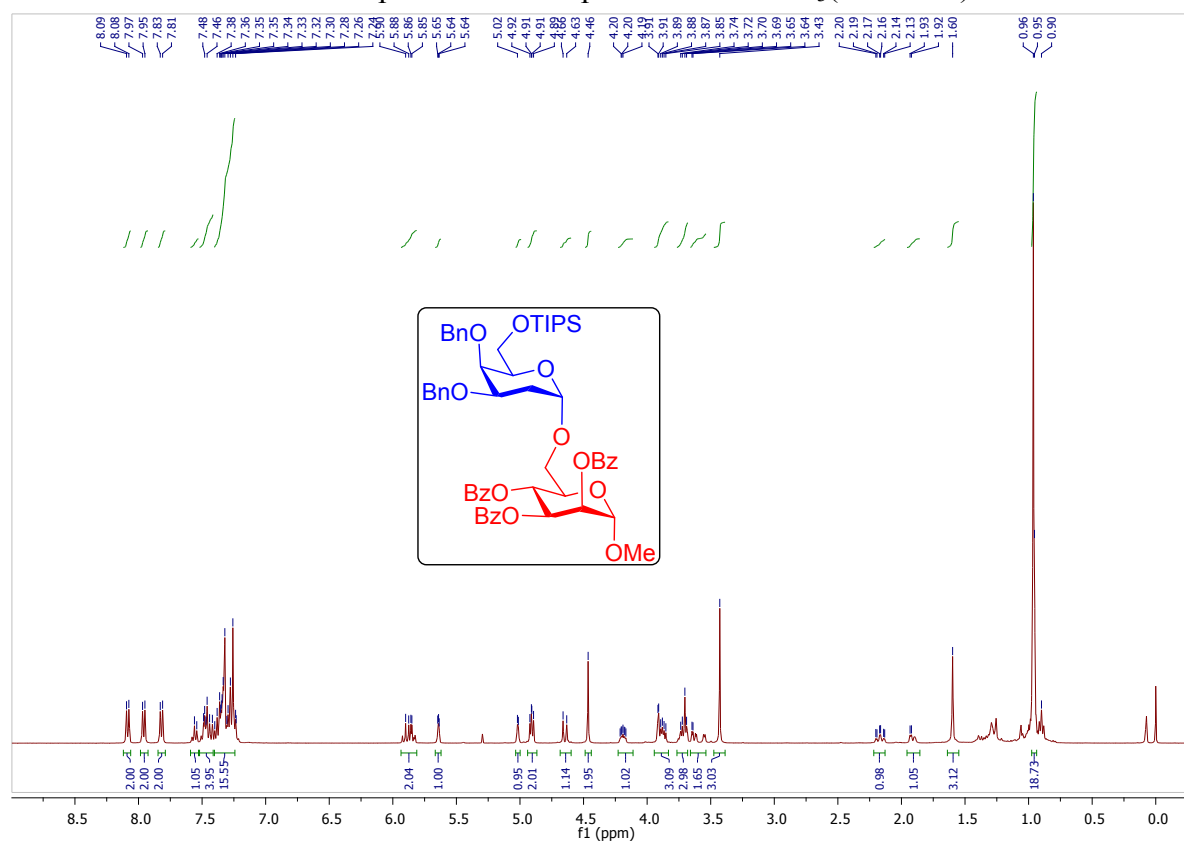
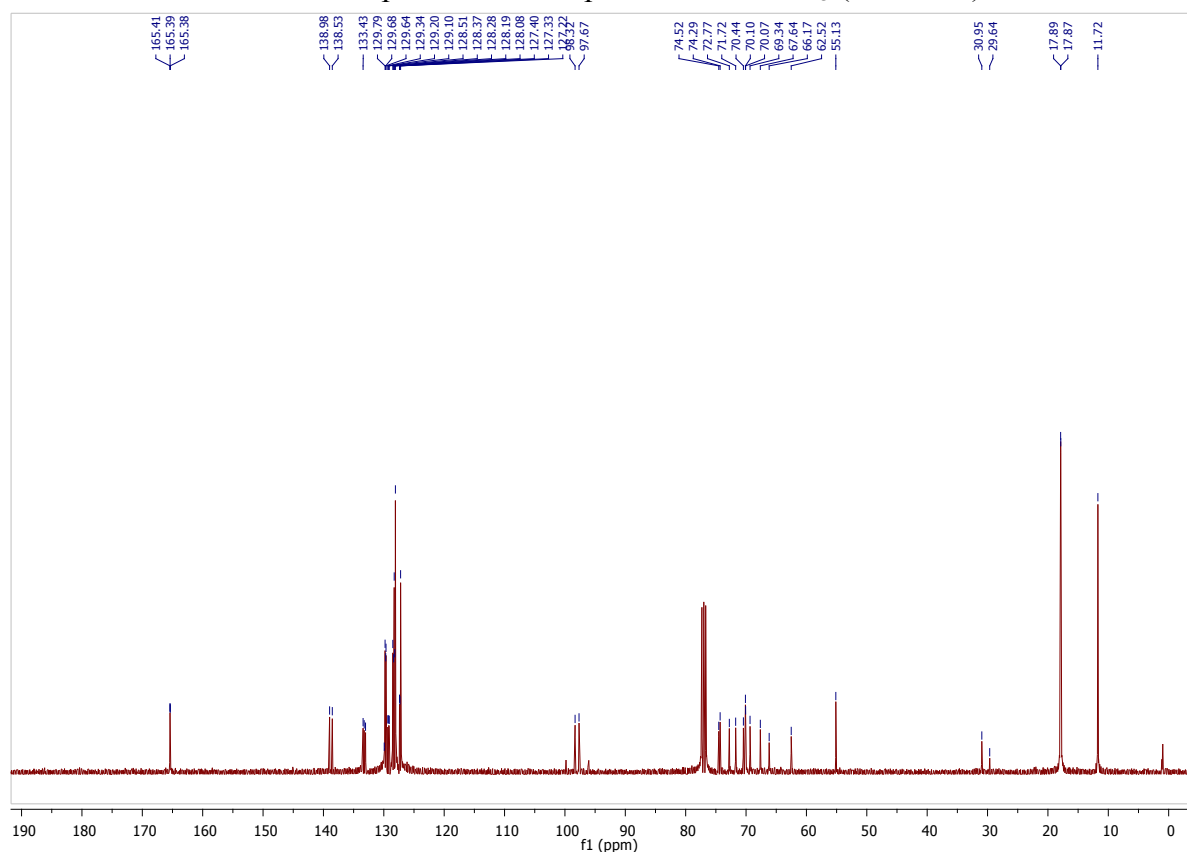
^{13}C NMR spectrum of compound **19** in CDCl_3 (101 MHz) ^1H NMR spectrum of compound **20** in CDCl_3 (400 MHz)

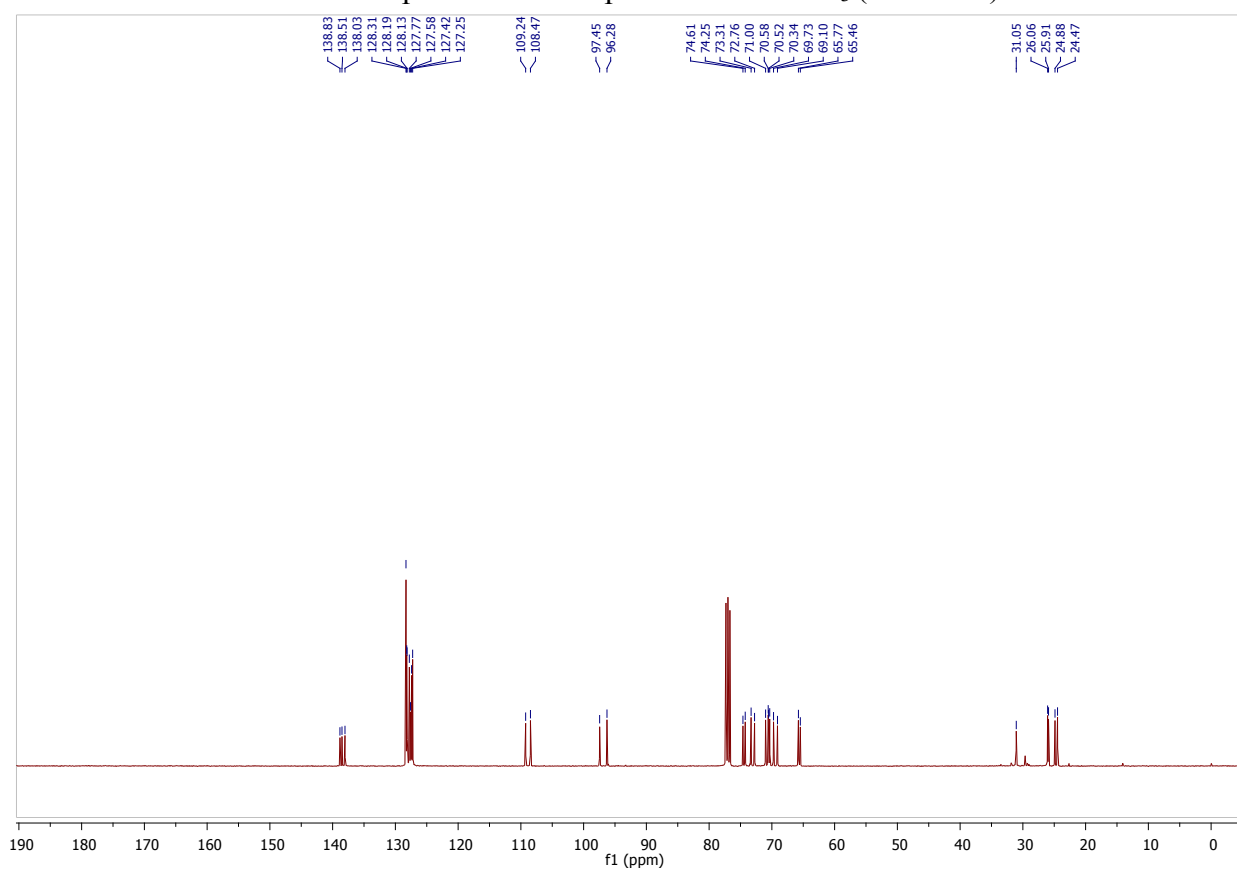


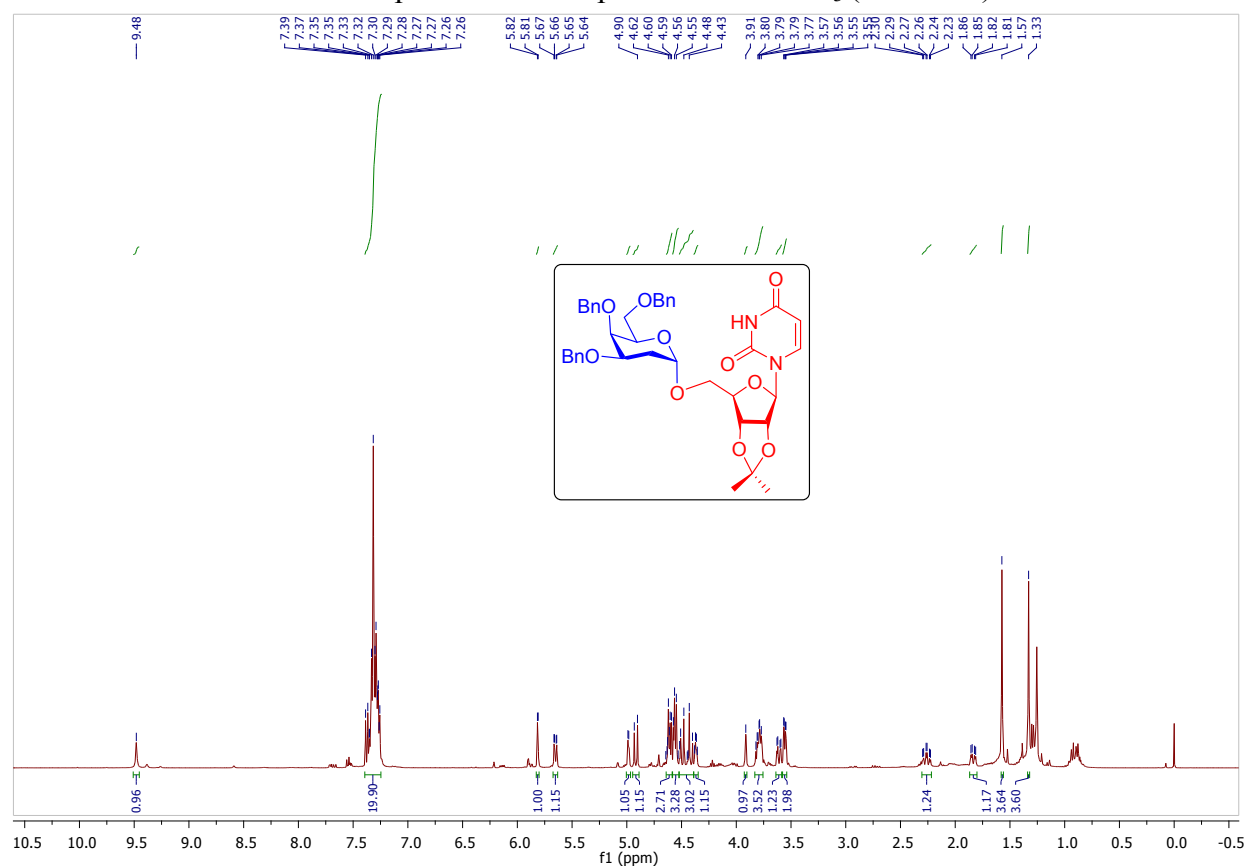
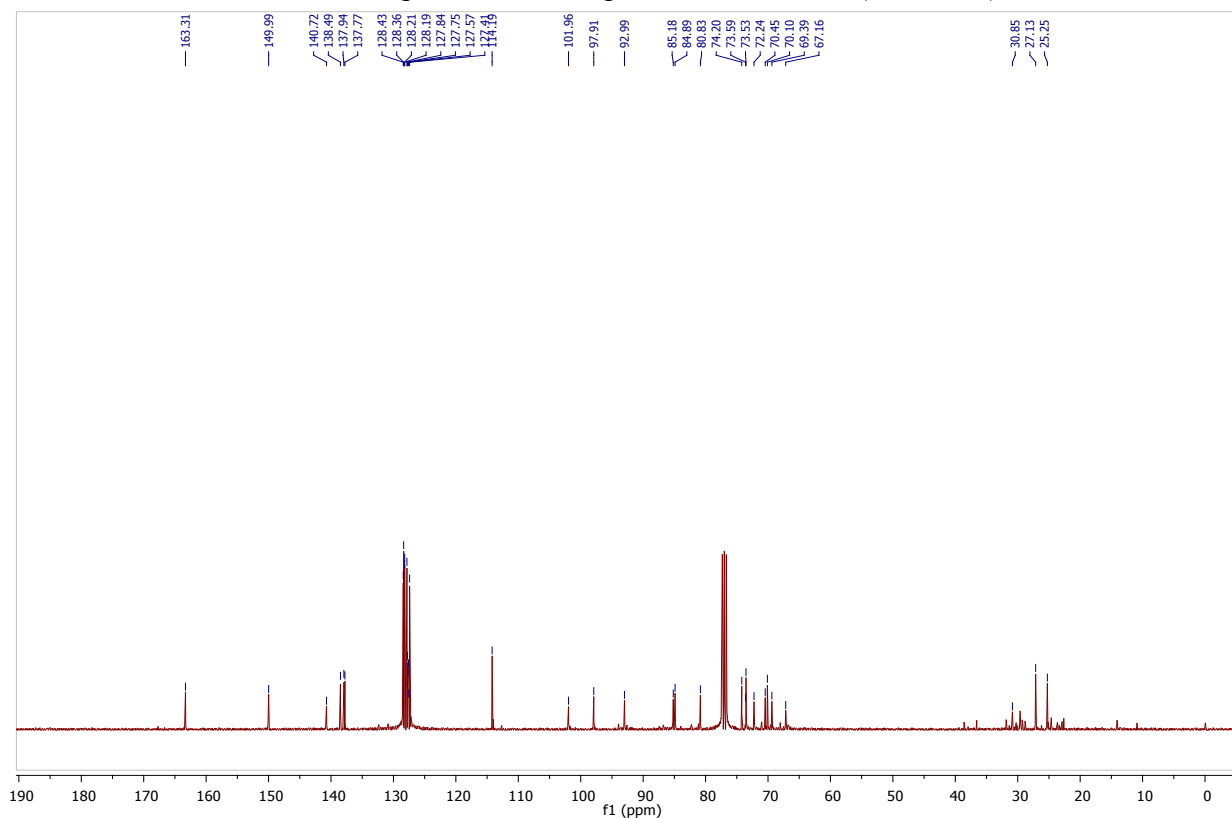
¹³C NMR spectrum of compound **20** in CDCl₃ (101 MHz)

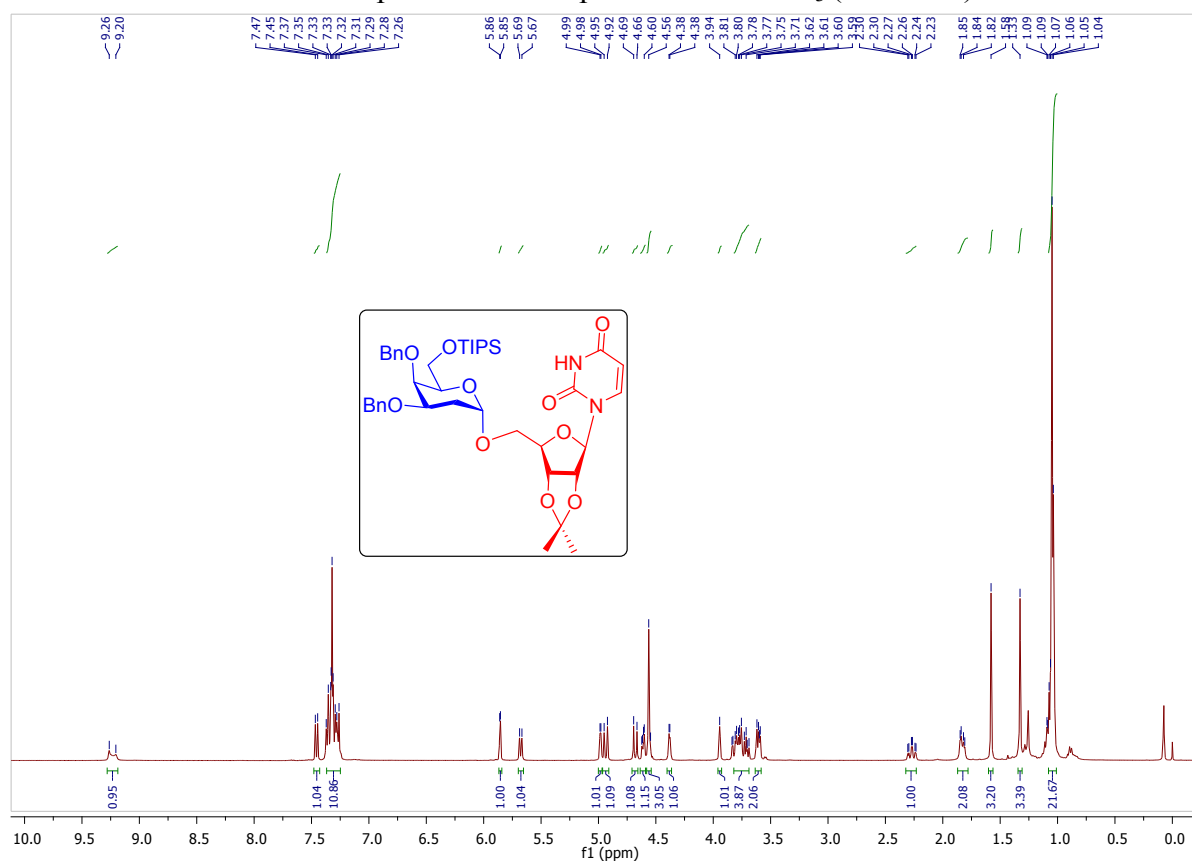


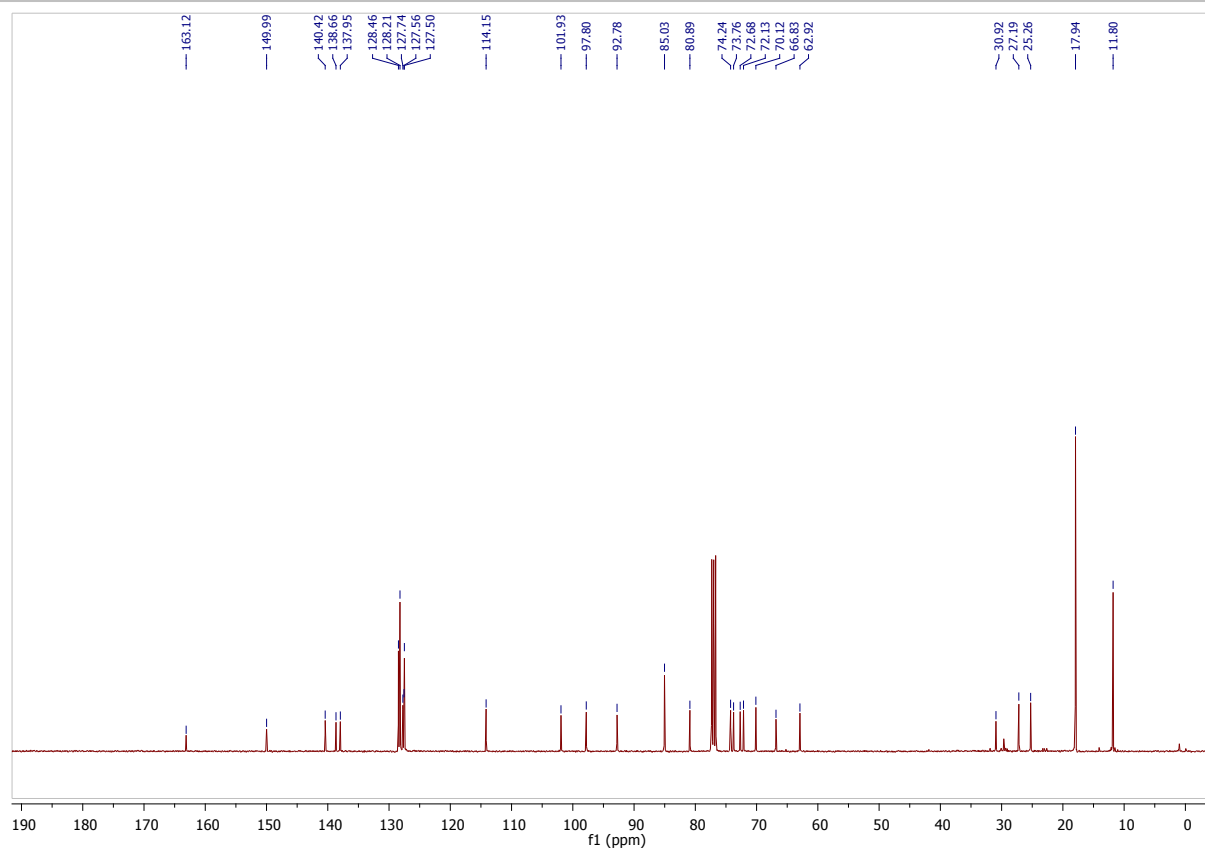
¹H NMR spectrum of compound **21** in CDCl₃ (400 MHz)¹³C NMR spectrum of compound **21** in CDCl₃ (101 MHz)

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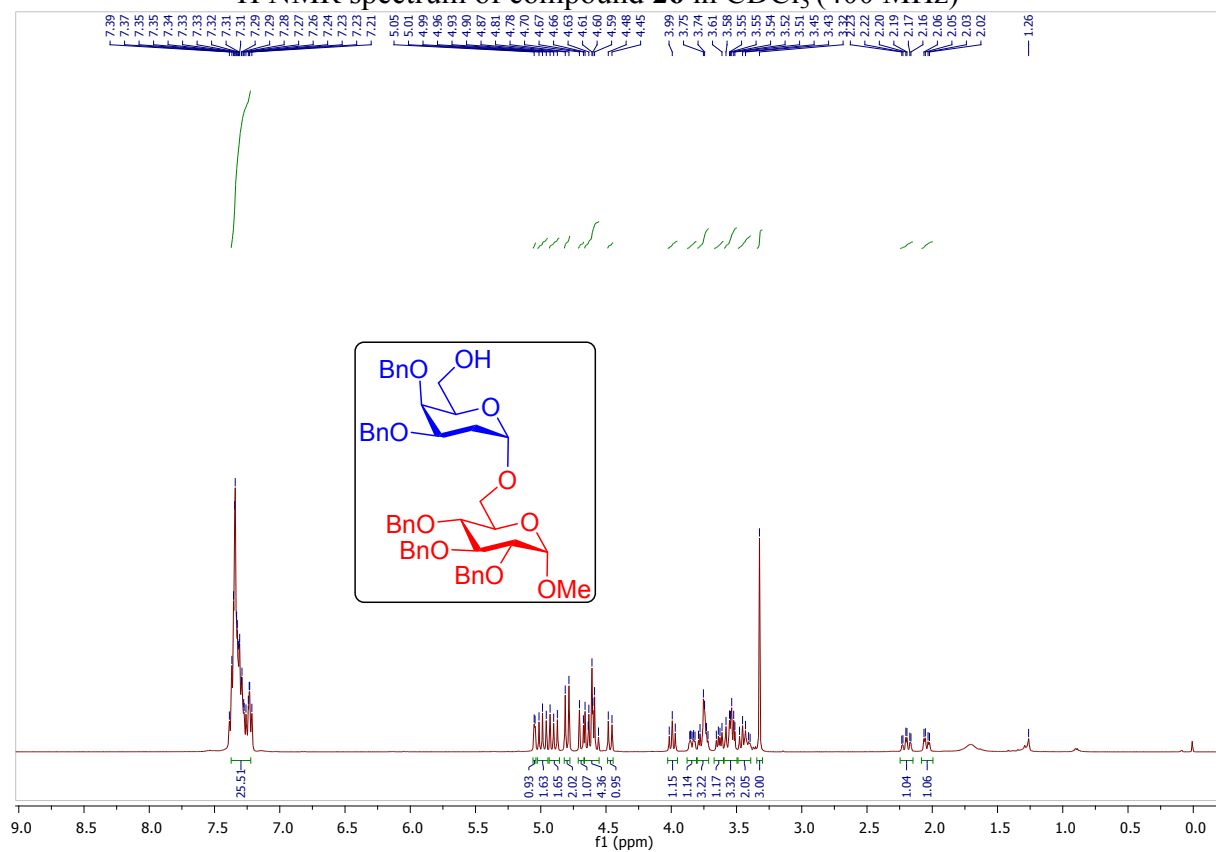


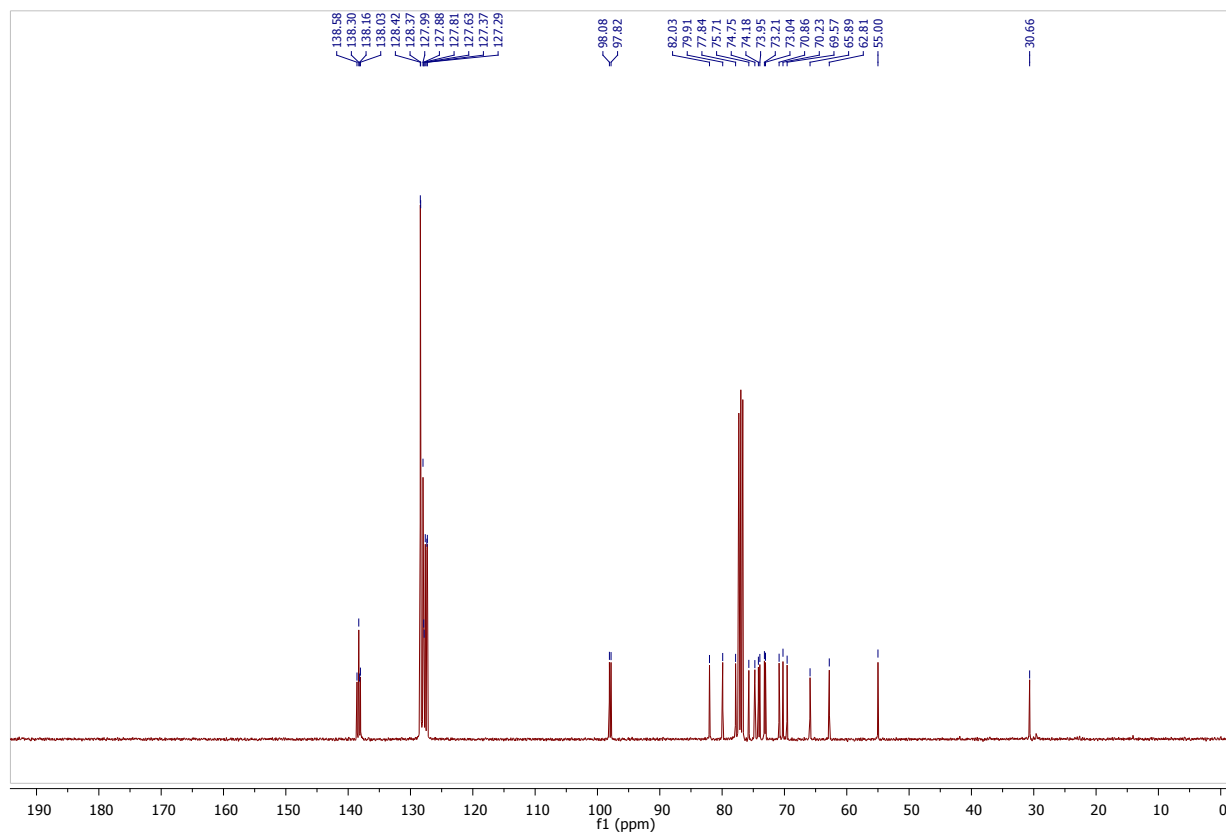
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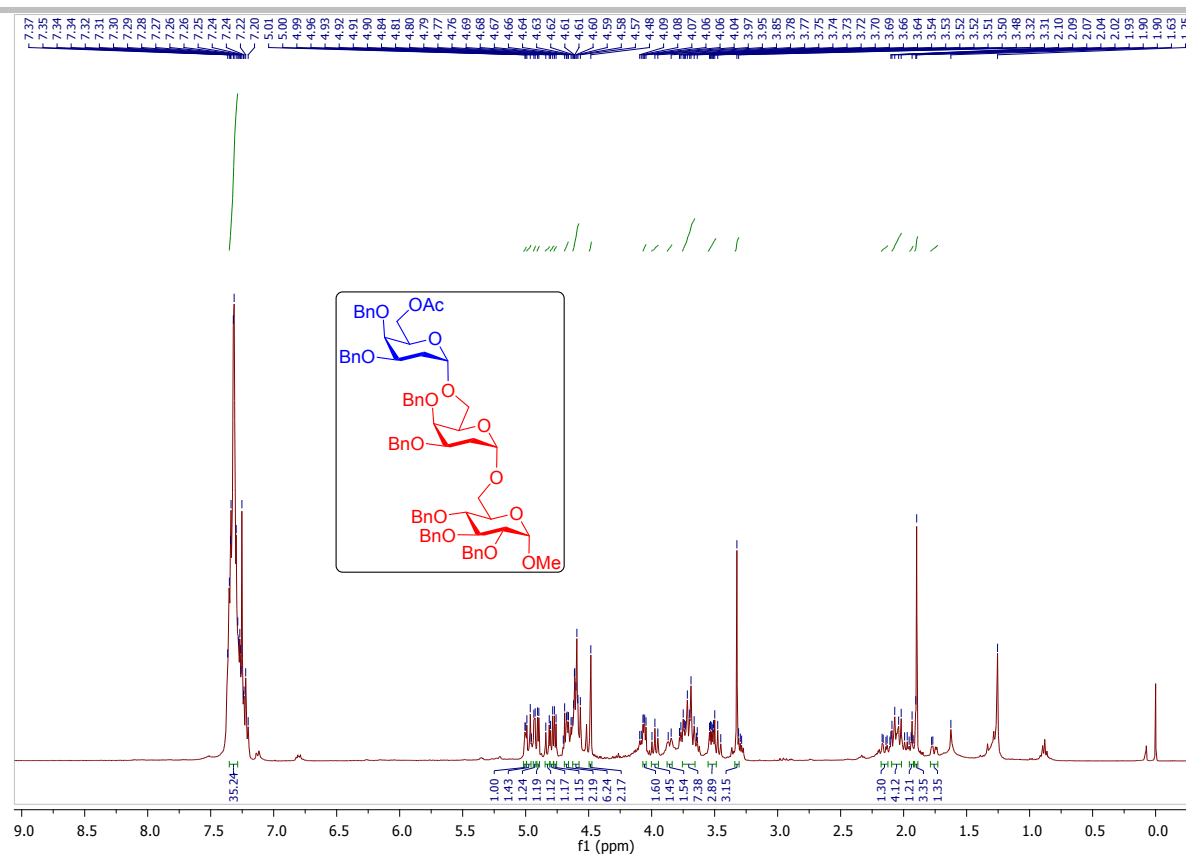
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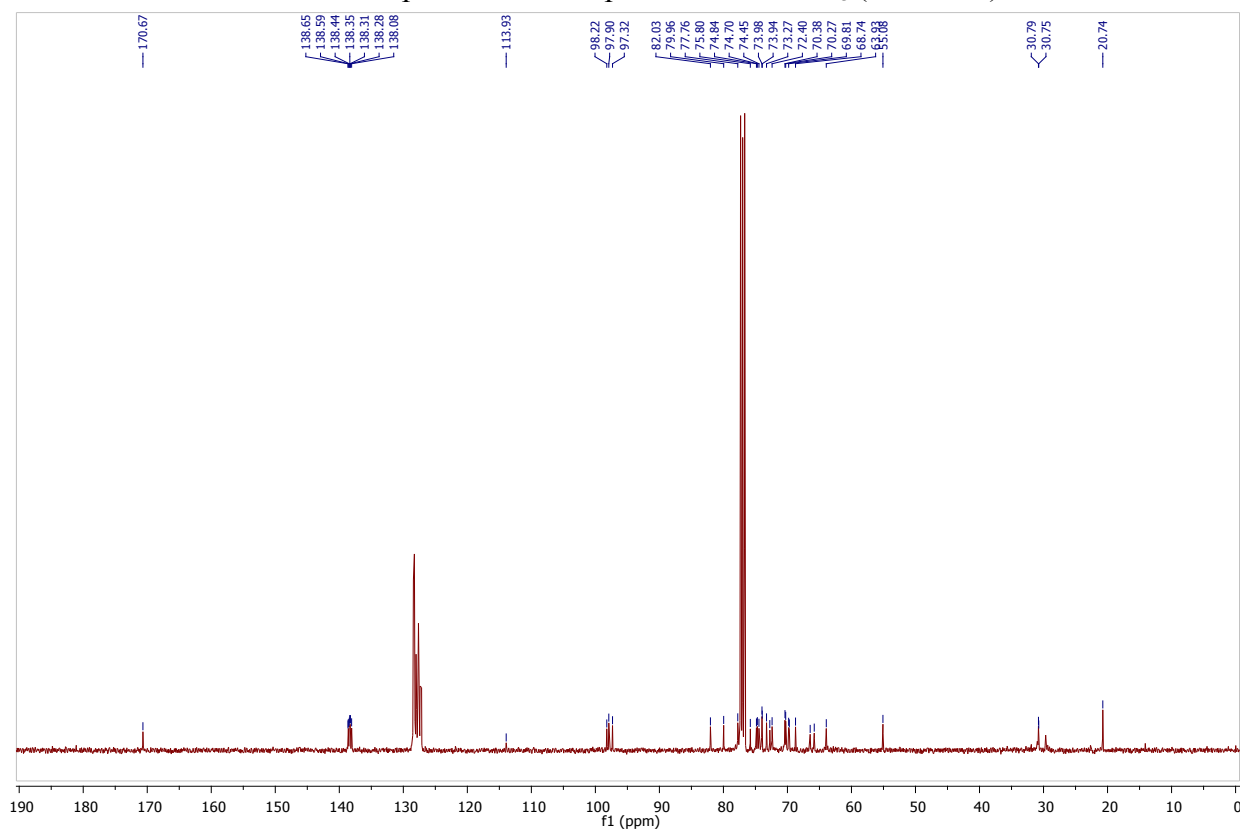
¹H NMR spectrum of compound 26 in CDCl₃ (400 MHz)

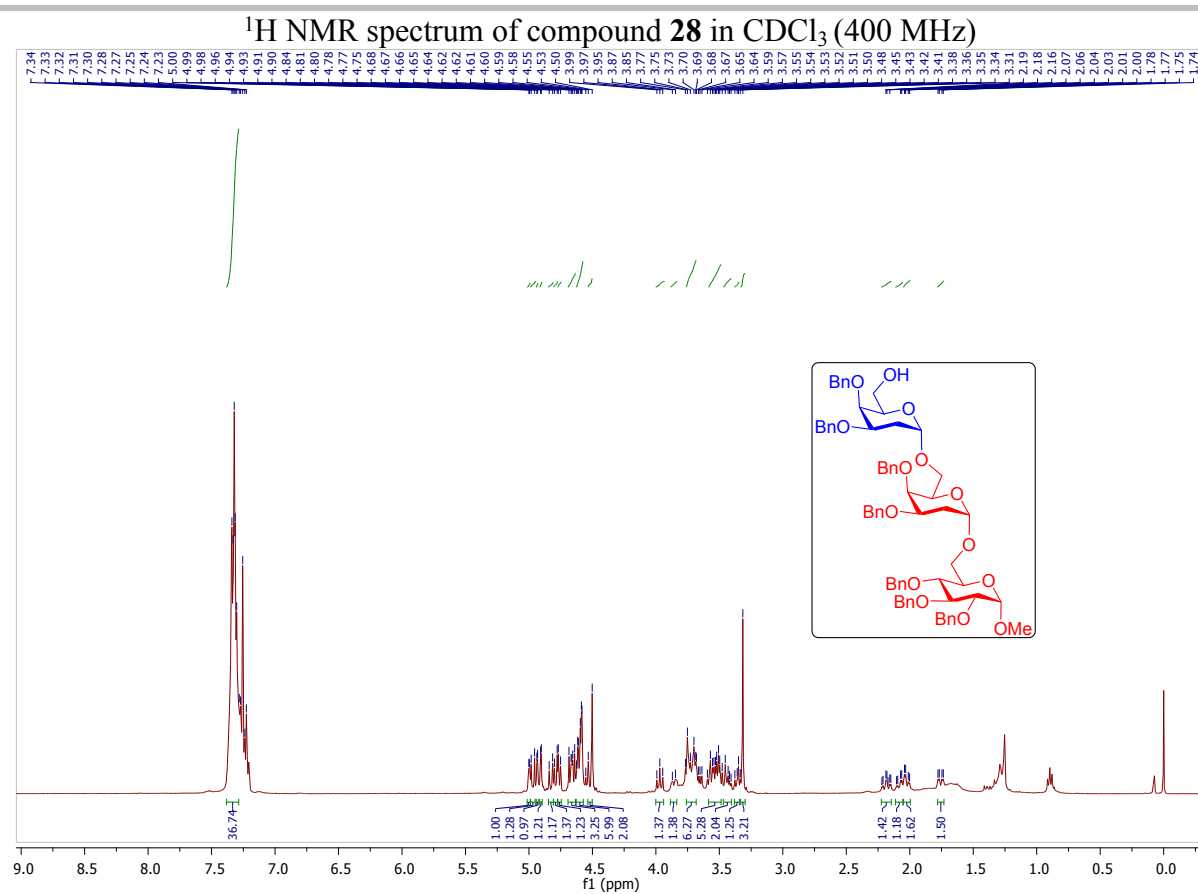


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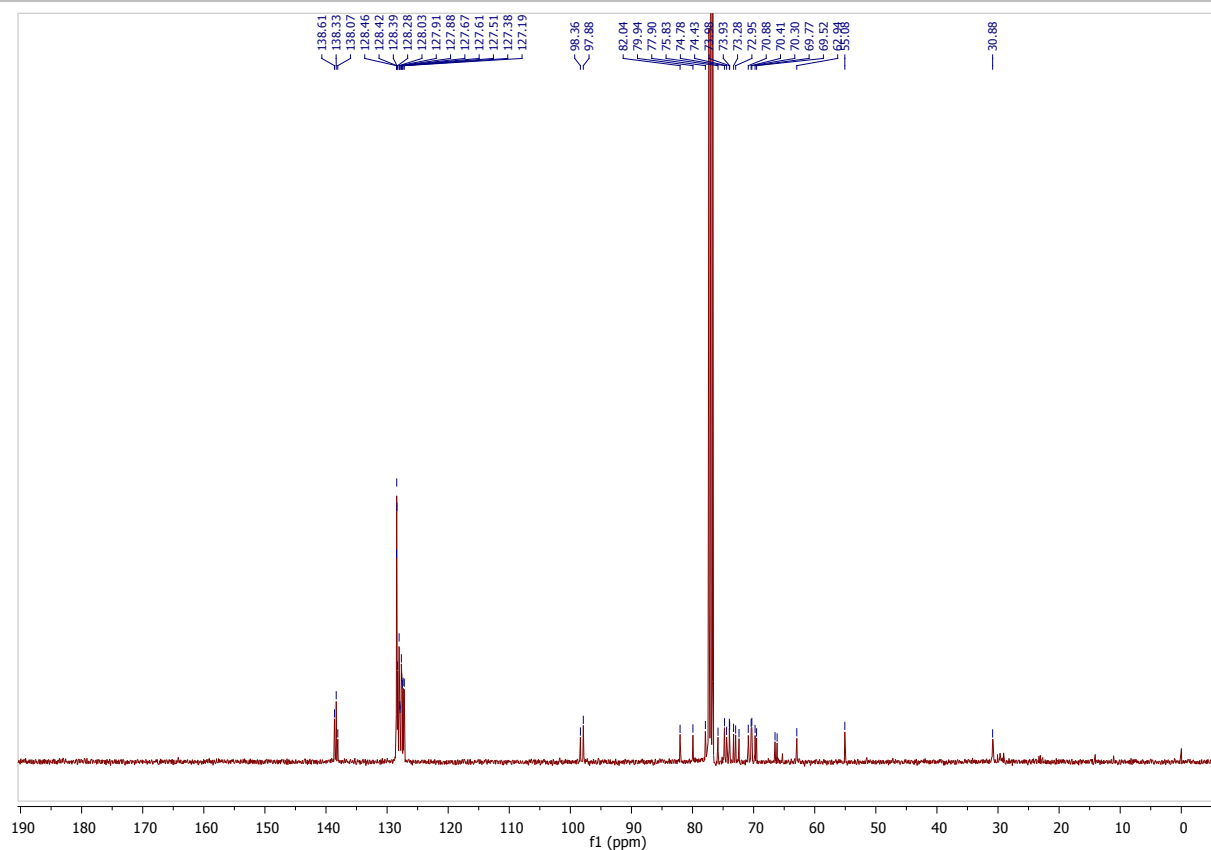


¹³C NMR spectrum of compound **27** in CDCl₃ (101 MHz)

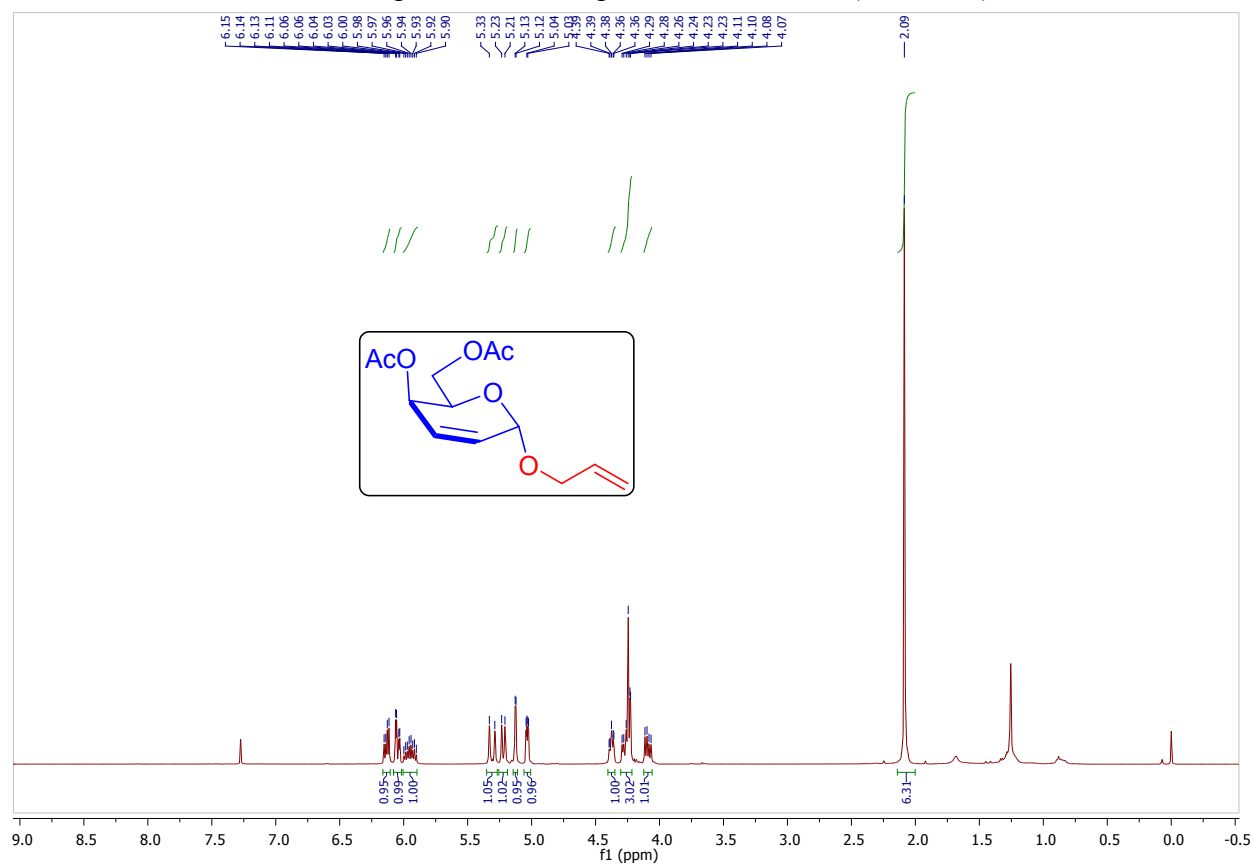


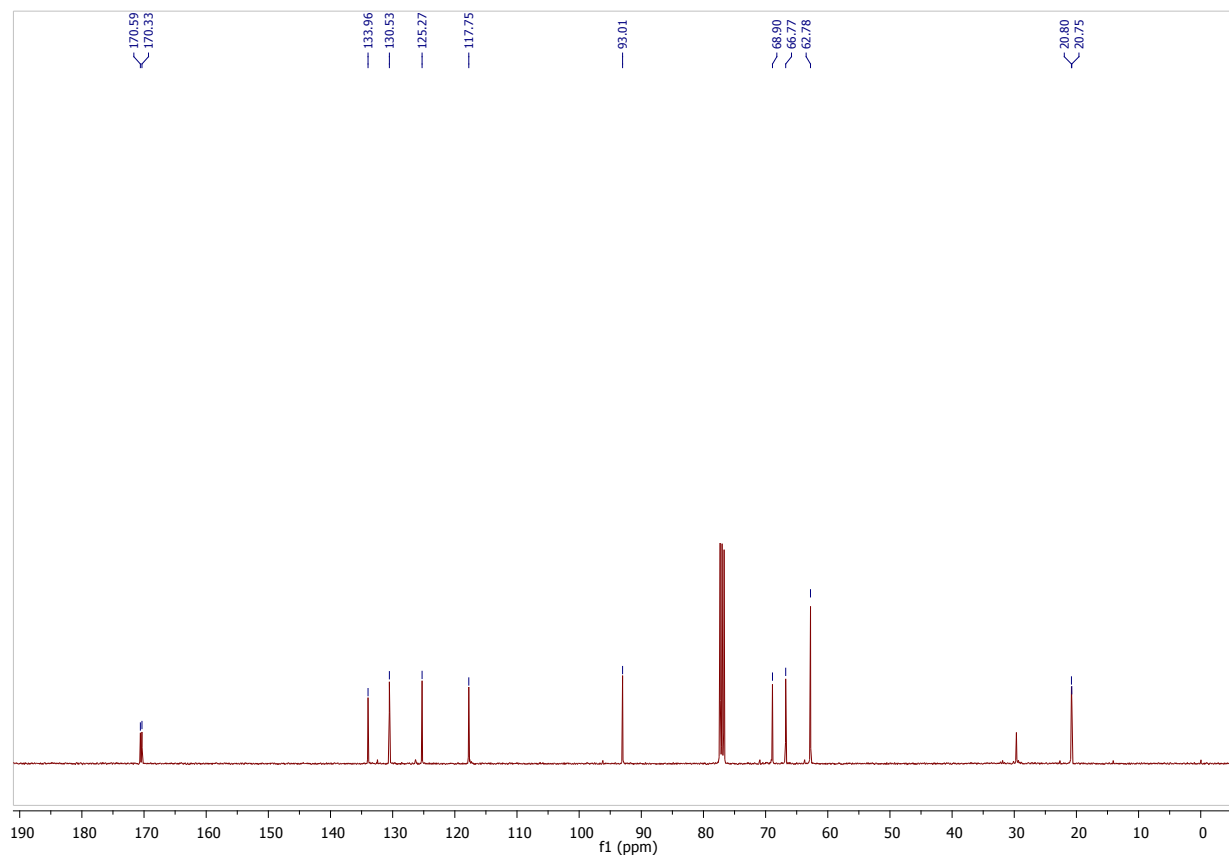


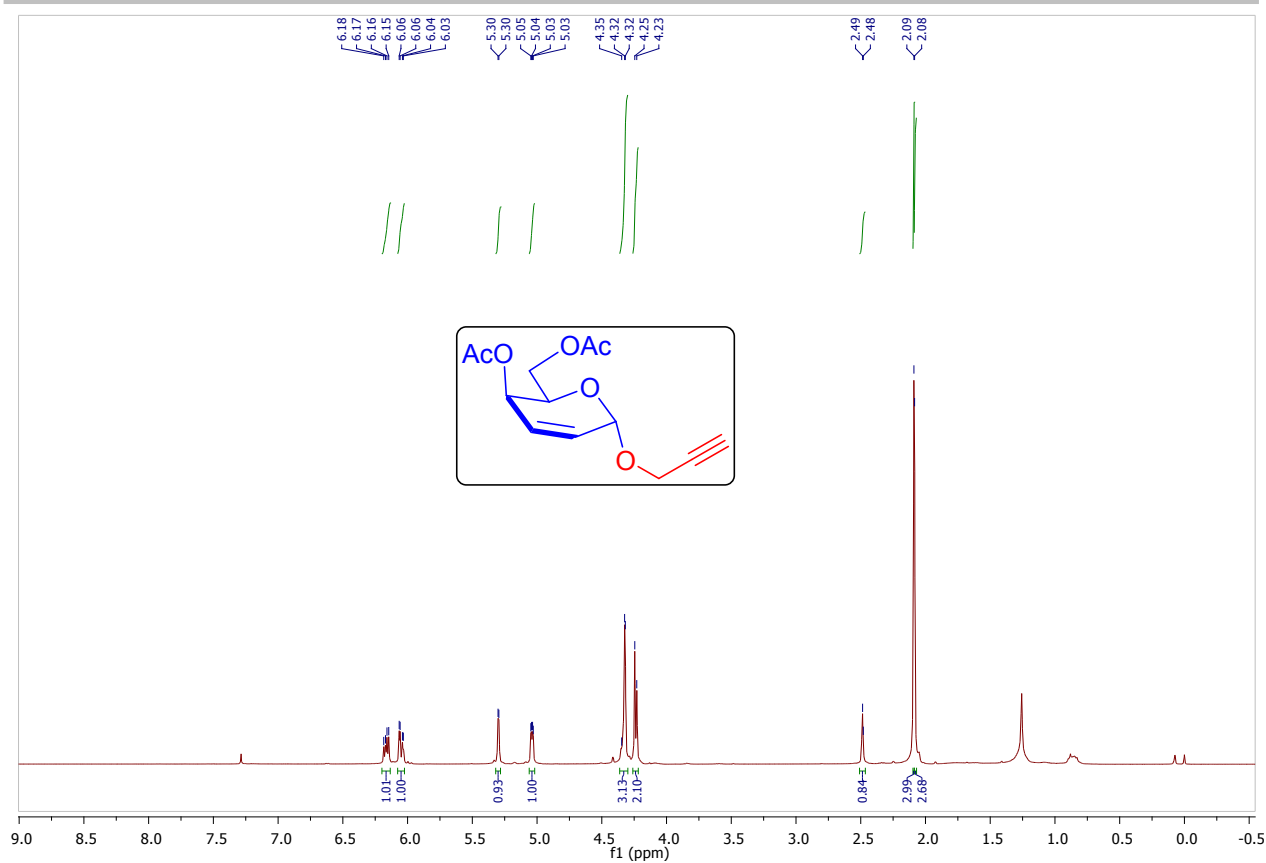
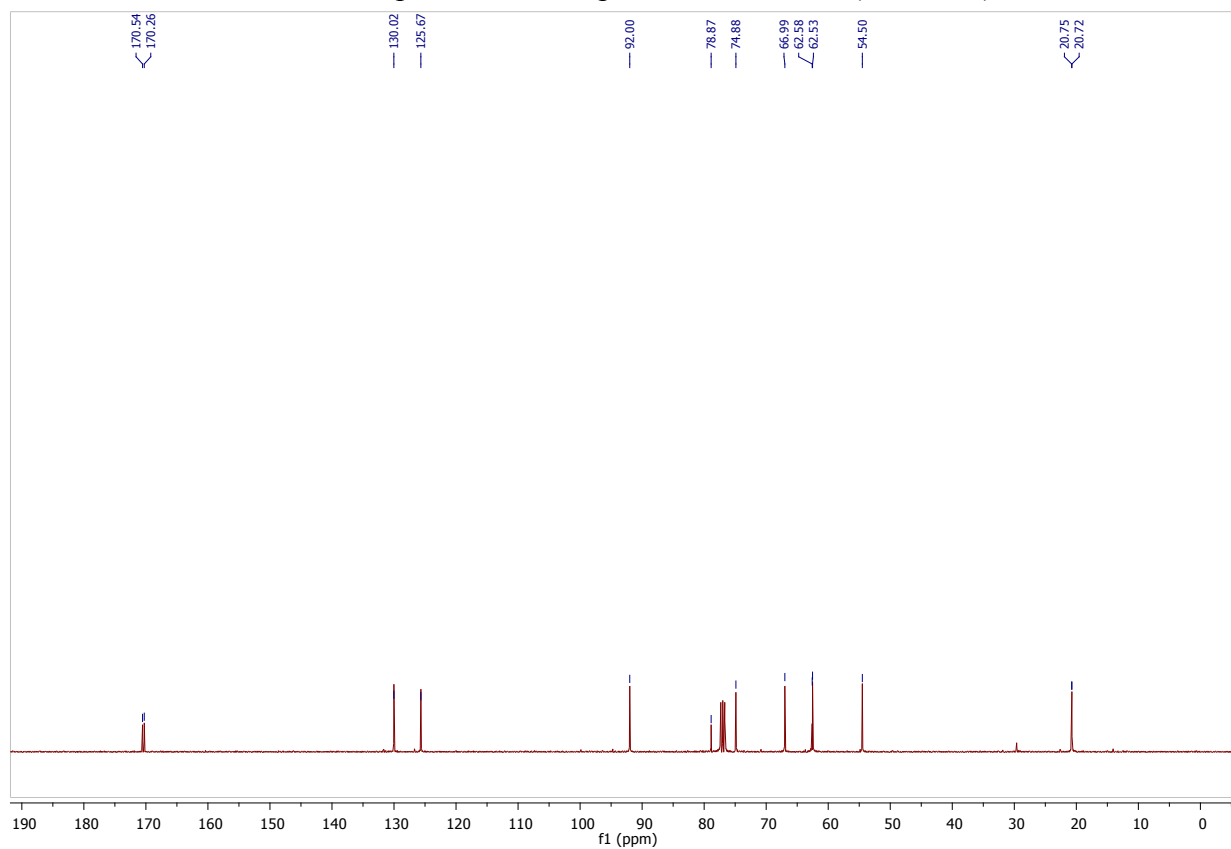
¹³C NMR spectrum of compound **28** in CDCl₃ (101 MHz)

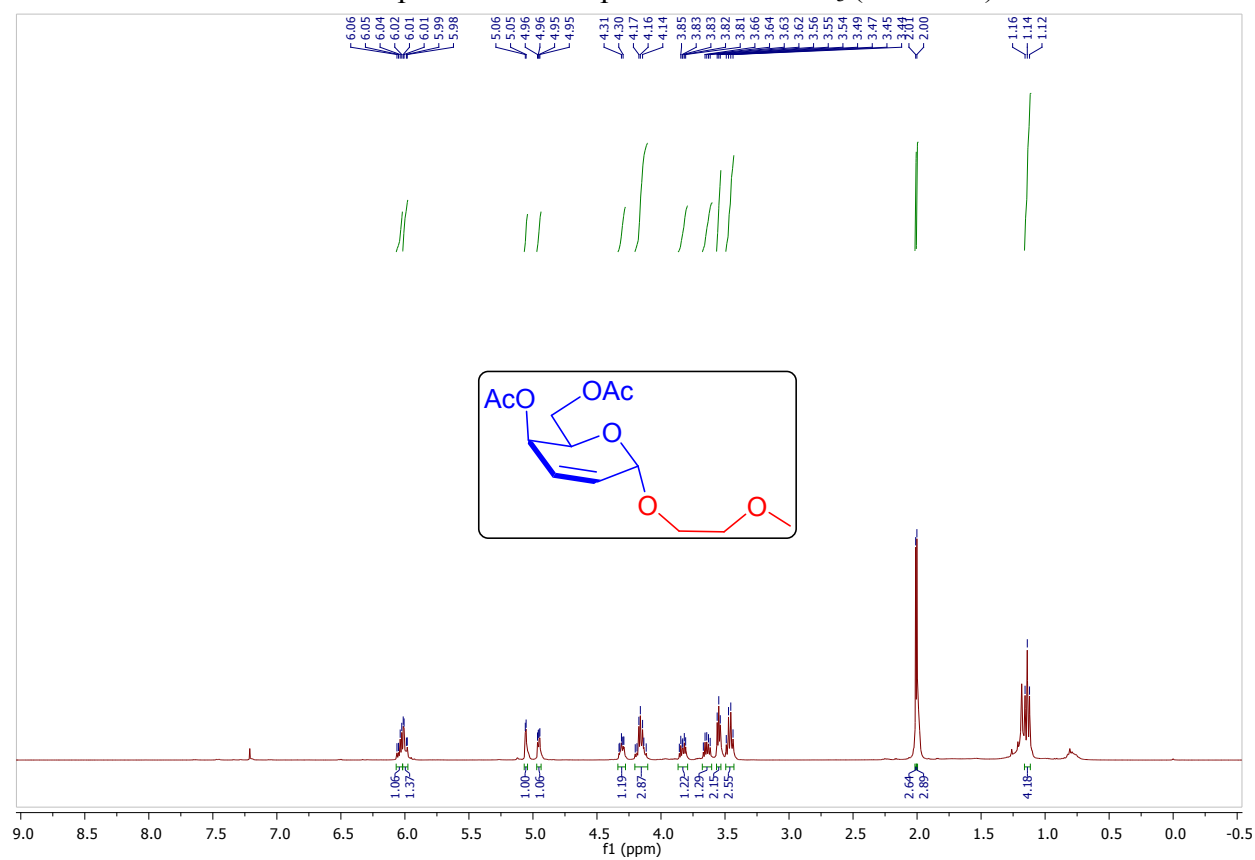
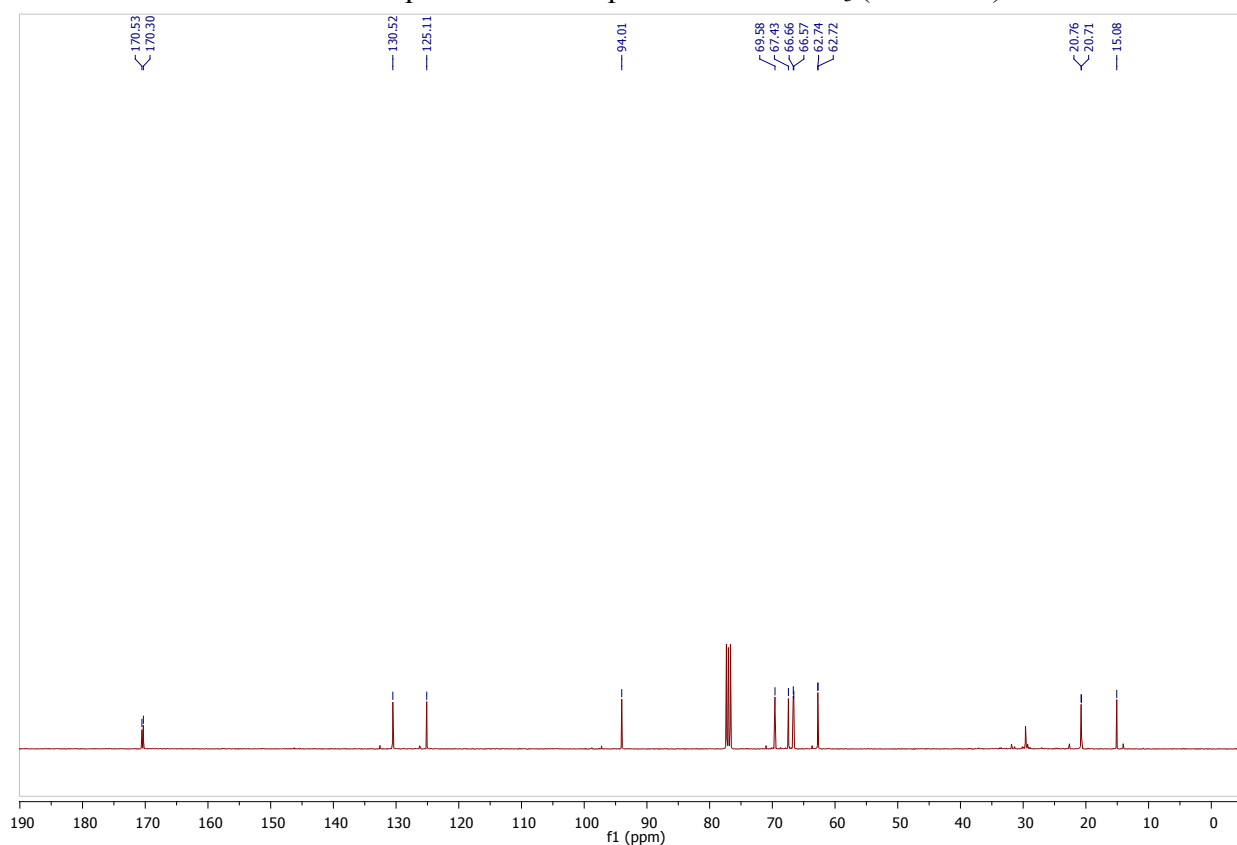


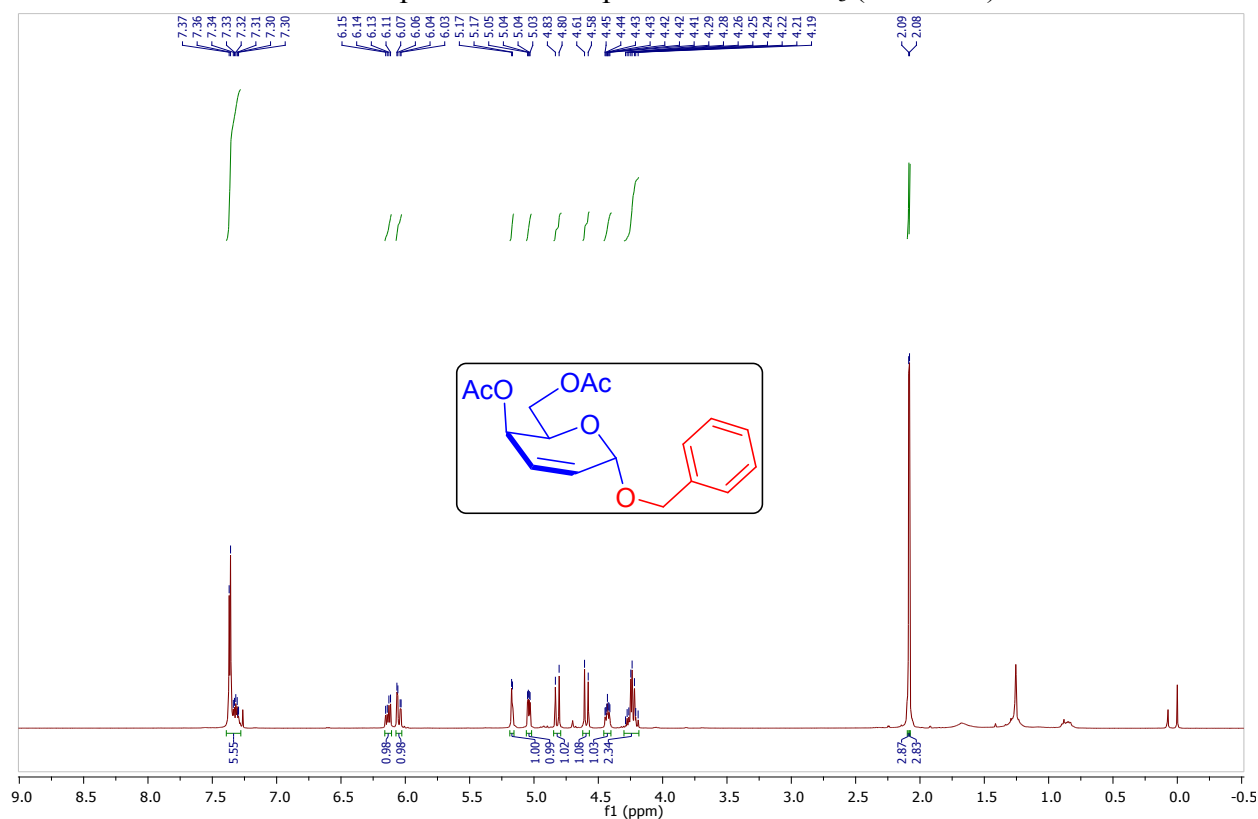
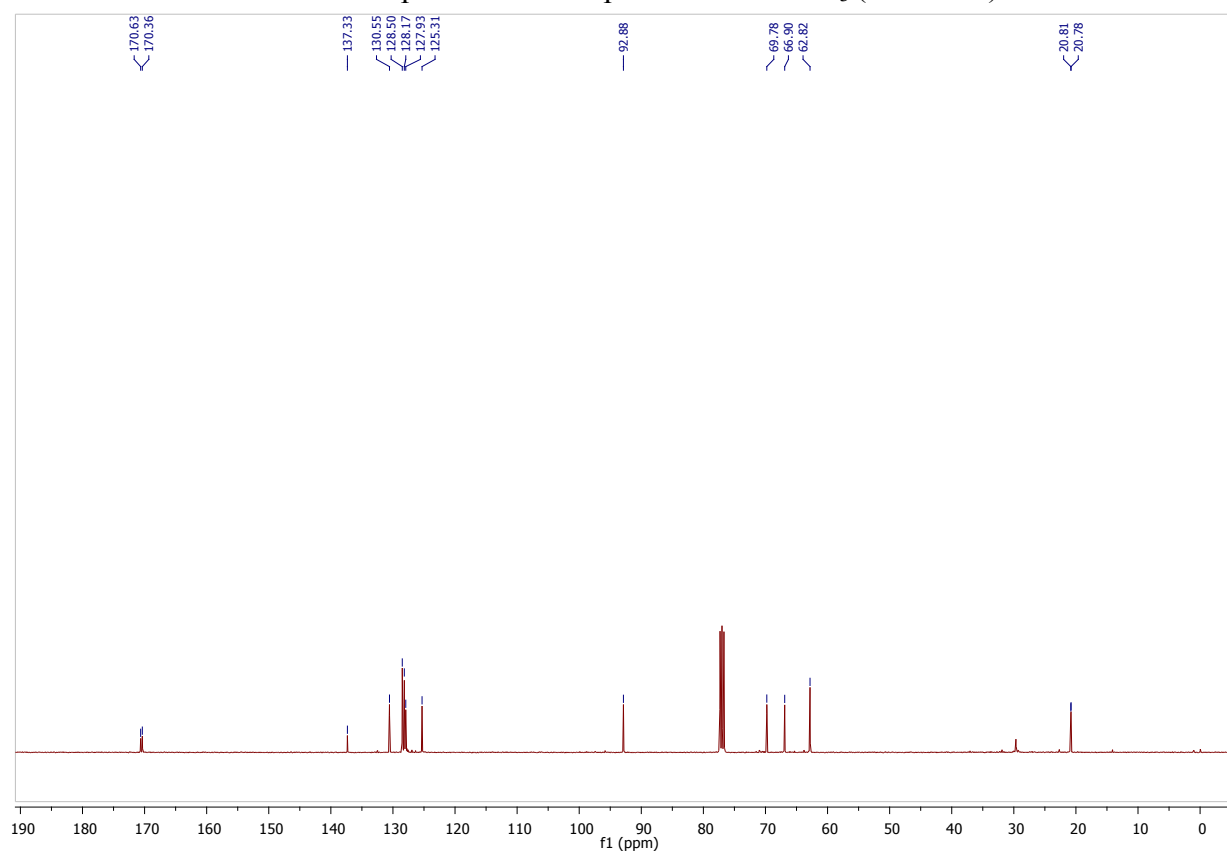
¹H NMR spectrum of compound **29** in CDCl₃ (400 MHz)

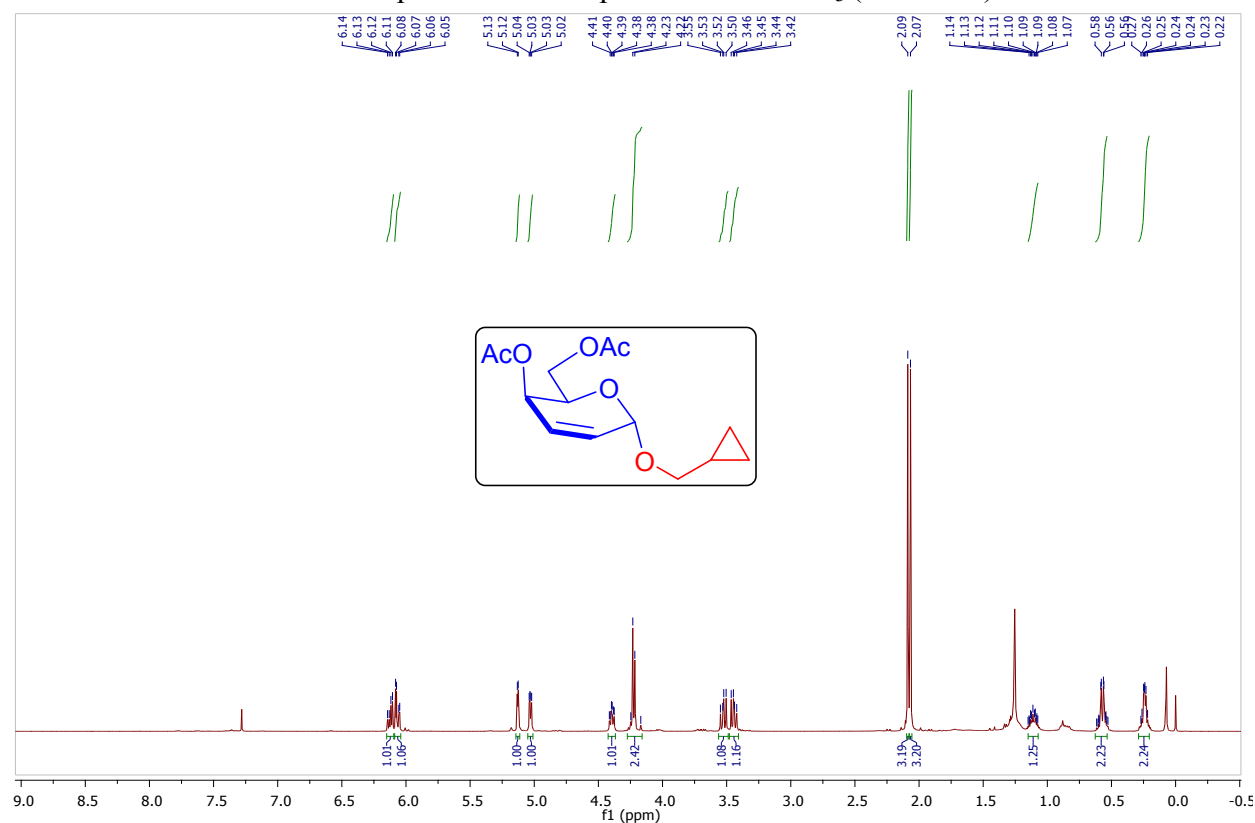
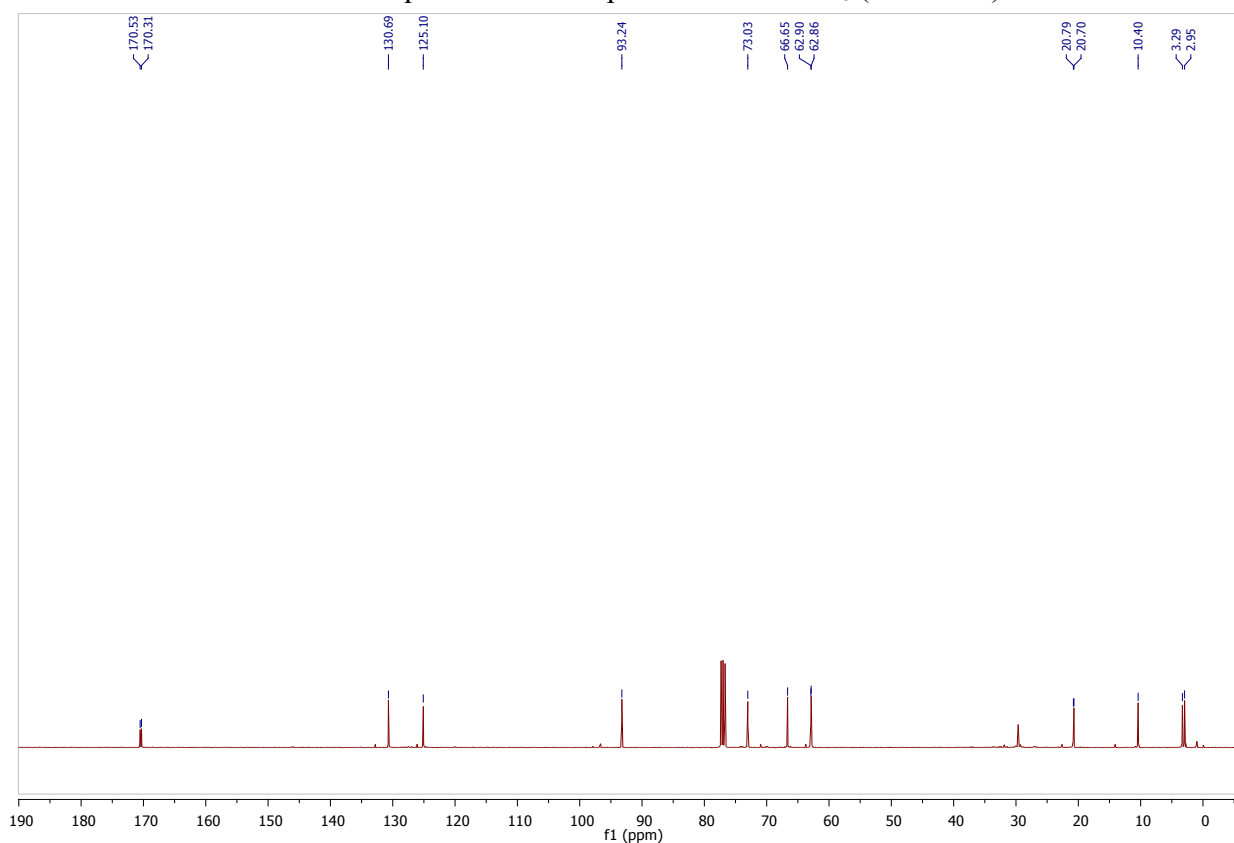


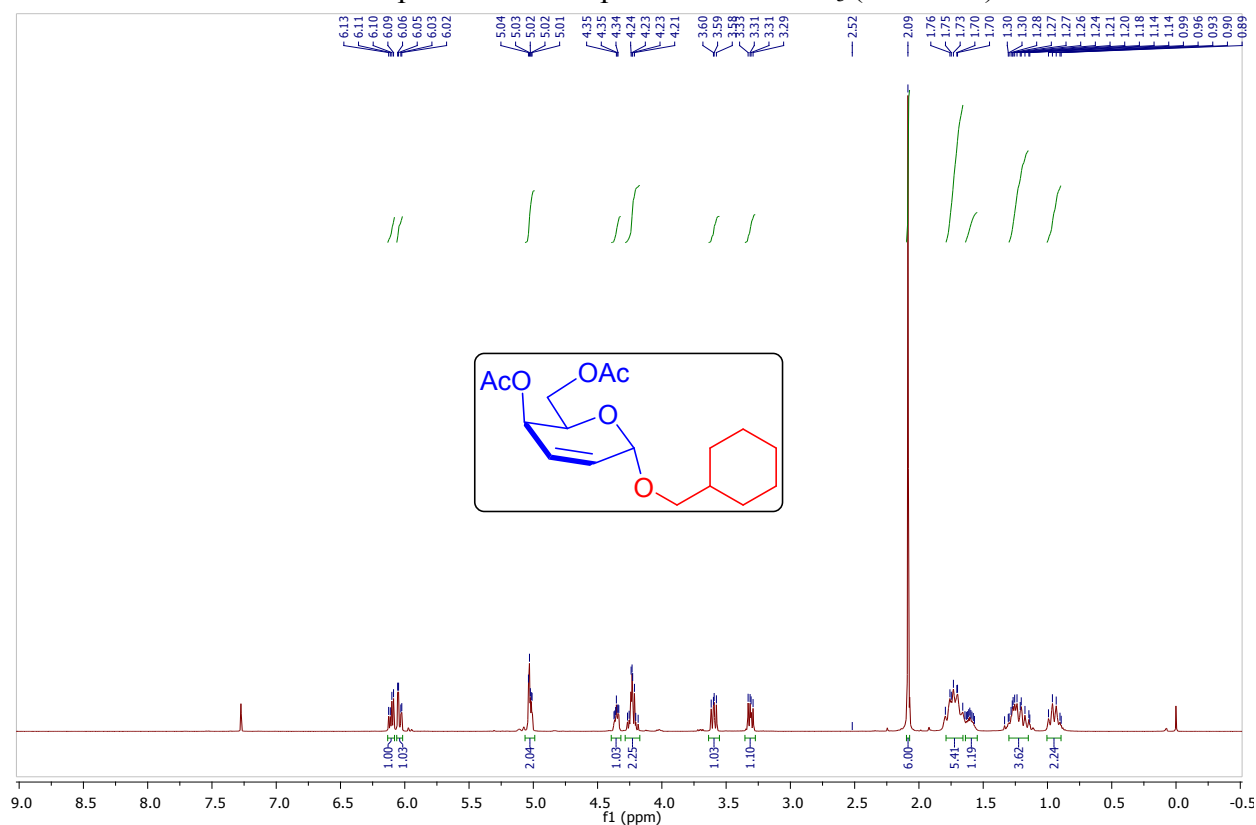
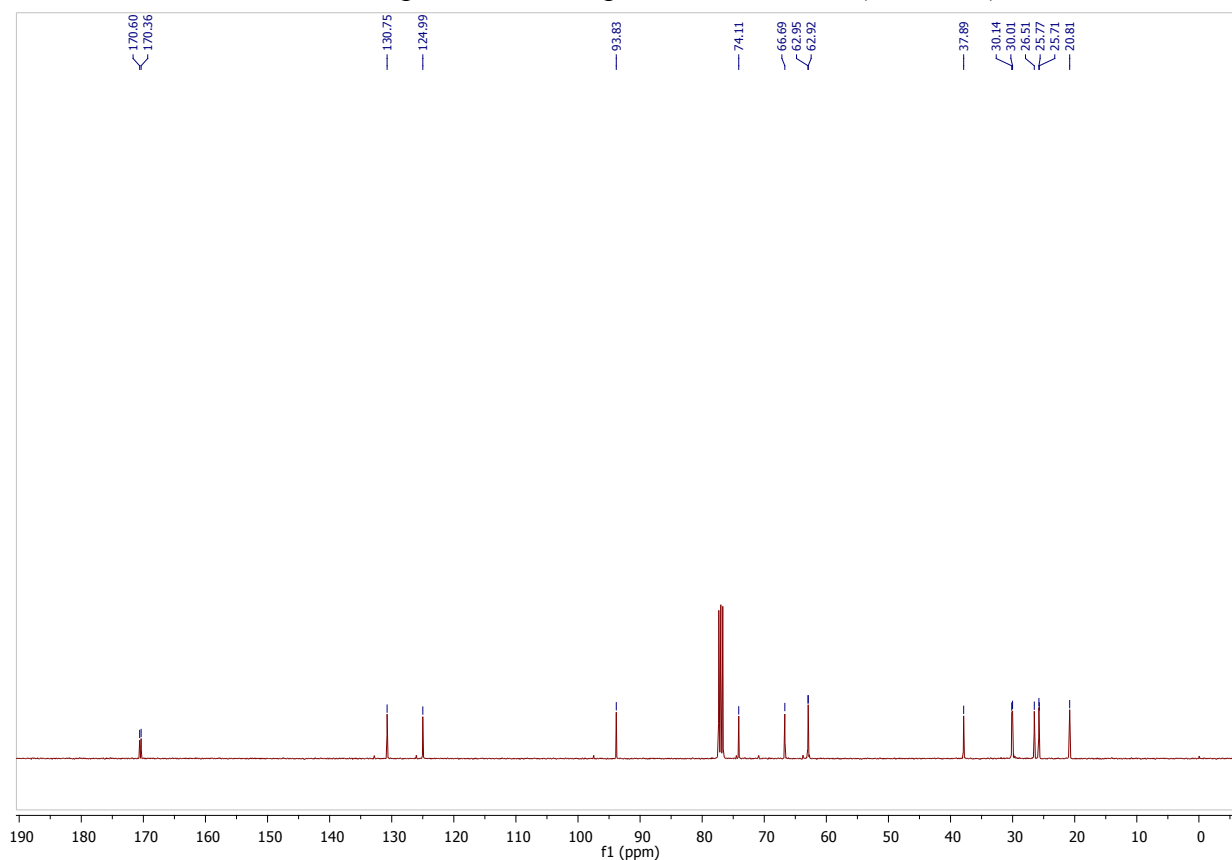
^{13}C NMR spectrum of compound **29** in CDCl_3 (101 MHz) ^1H NMR spectrum of compound **30** in CDCl_3 (400 MHz)

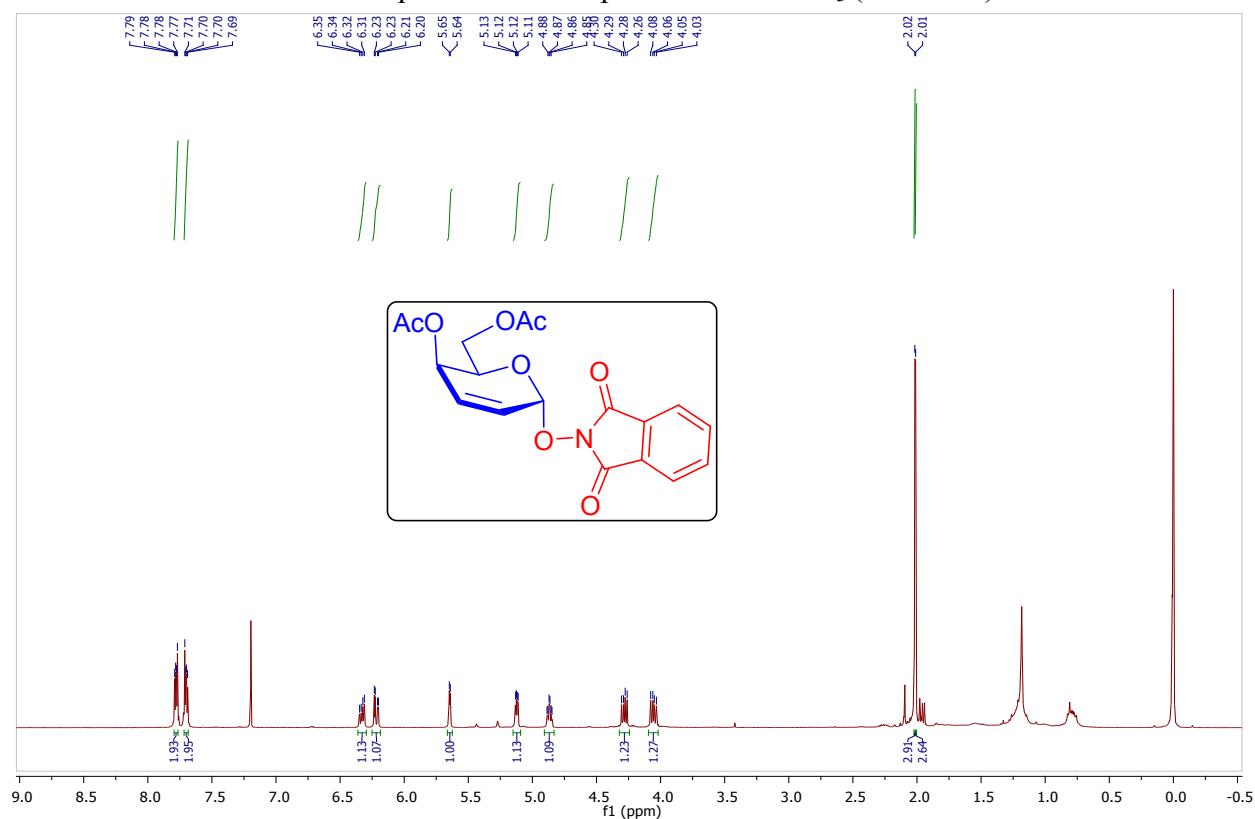
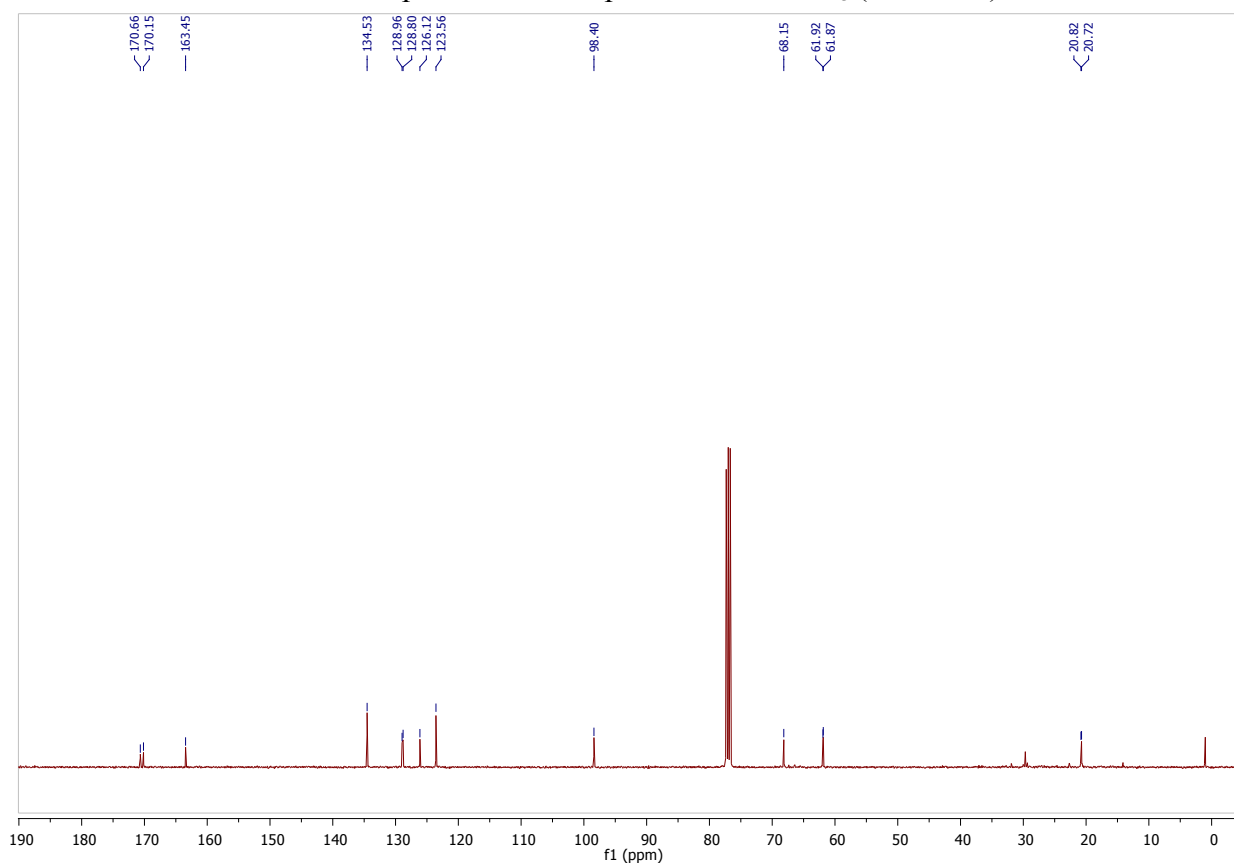
¹³C NMR spectrum of compound **30** in CDCl₃ (101 MHz)

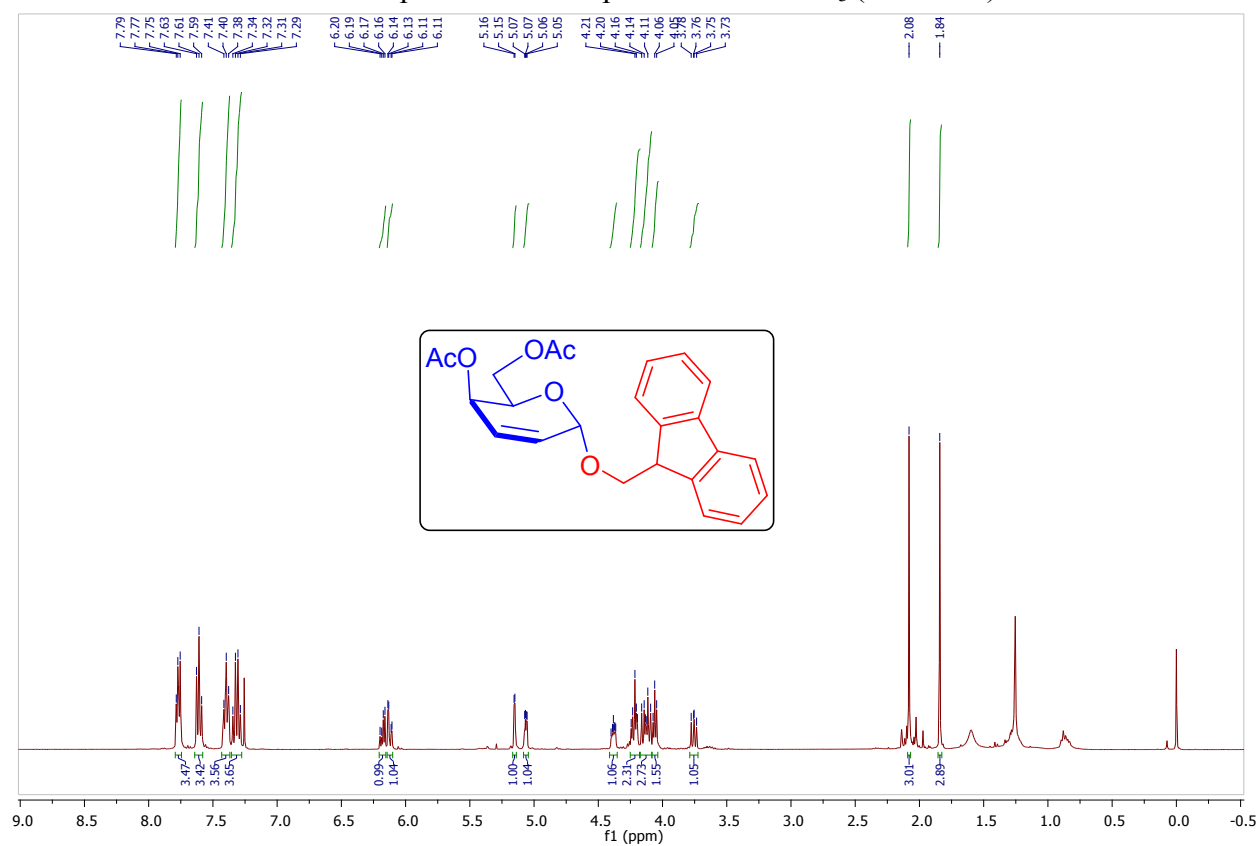
¹H NMR spectrum of compound **31** in CDCl₃ (400 MHz)¹³C NMR spectrum of compound **31** in CDCl₃ (101 MHz)

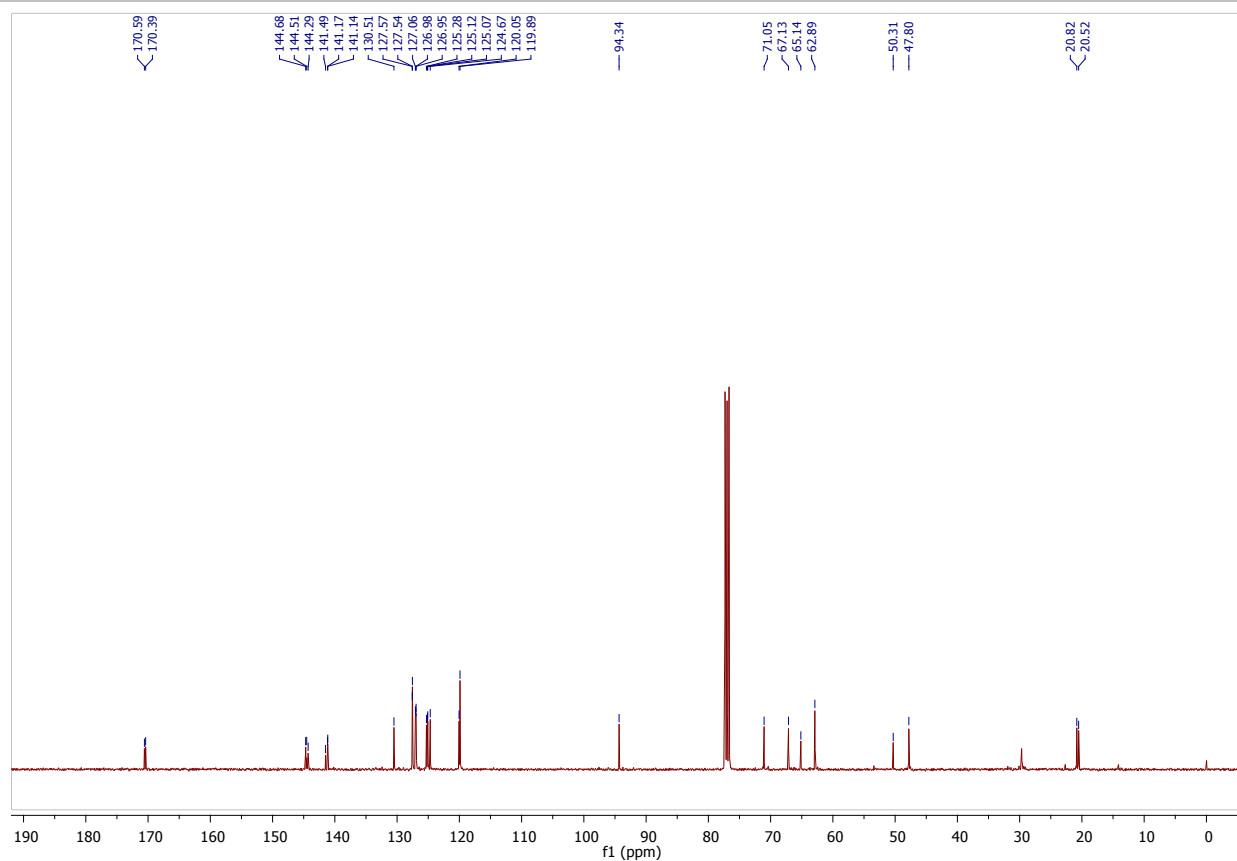
^1H NMR spectrum of compound **32** in CDCl_3 (400 MHz) ^{13}C NMR spectrum of compound **32** in CDCl_3 (101 MHz)

^1H NMR spectrum of compound **33** in CDCl_3 (400 MHz) ^{13}C NMR spectrum of compound **33** in CDCl_3 (101 MHz)

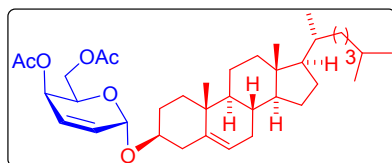
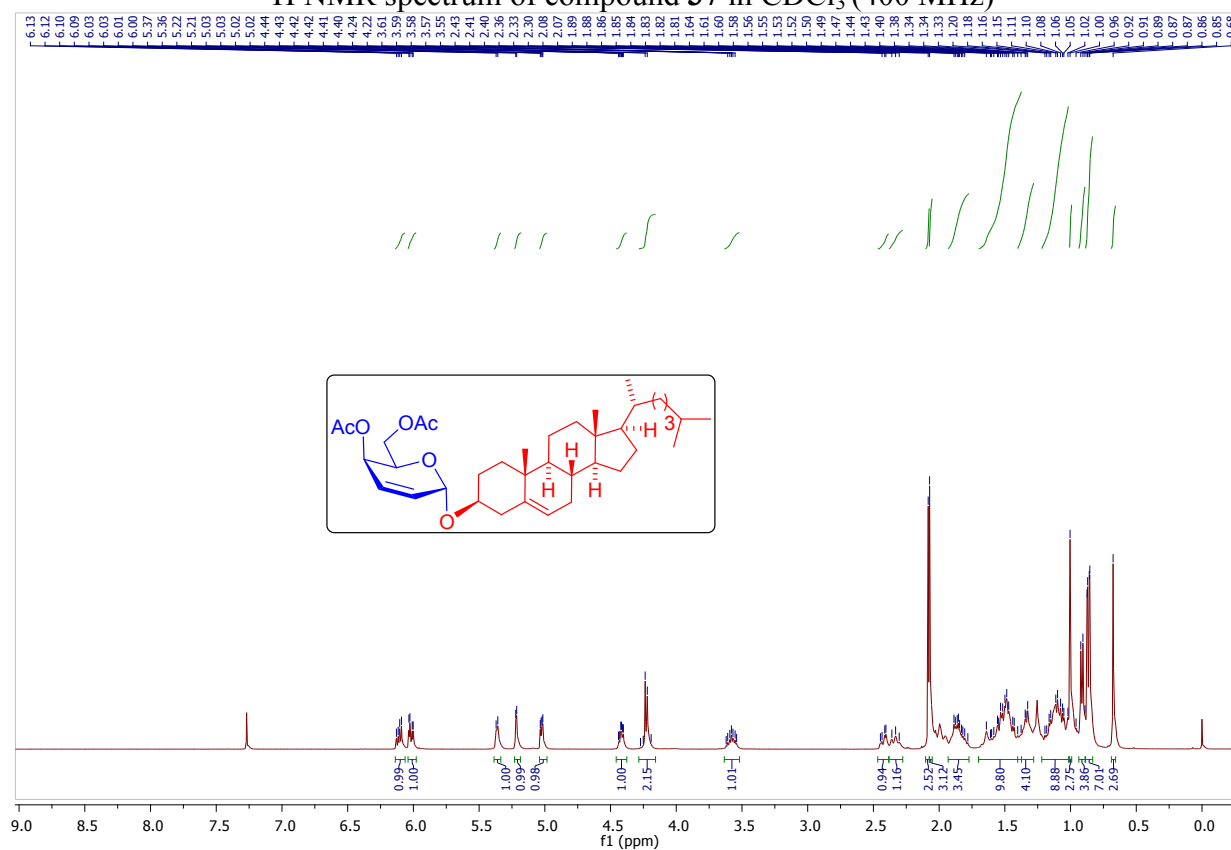
^1H NMR spectrum of compound **34** in CDCl_3 (400 MHz) ^{13}C NMR spectrum of compound **34** in CDCl_3 (101 MHz)

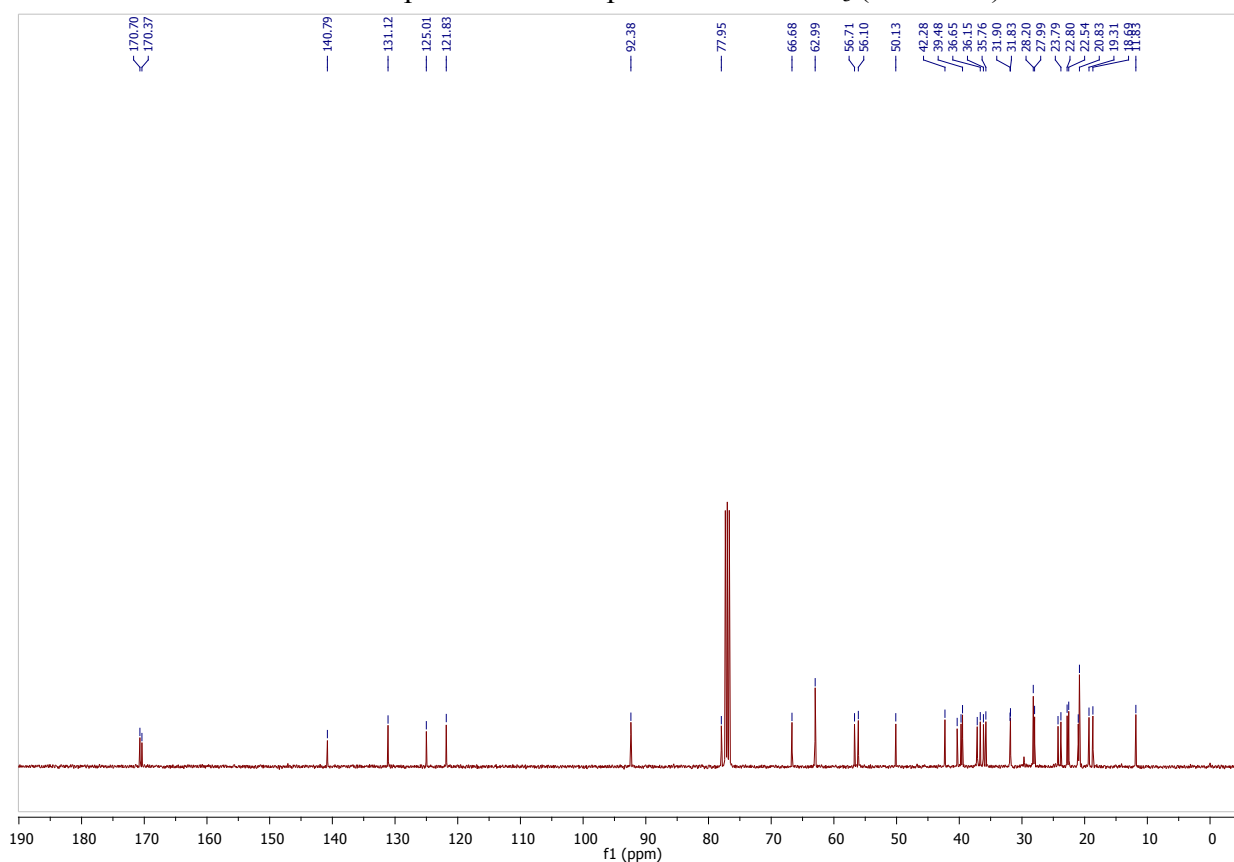
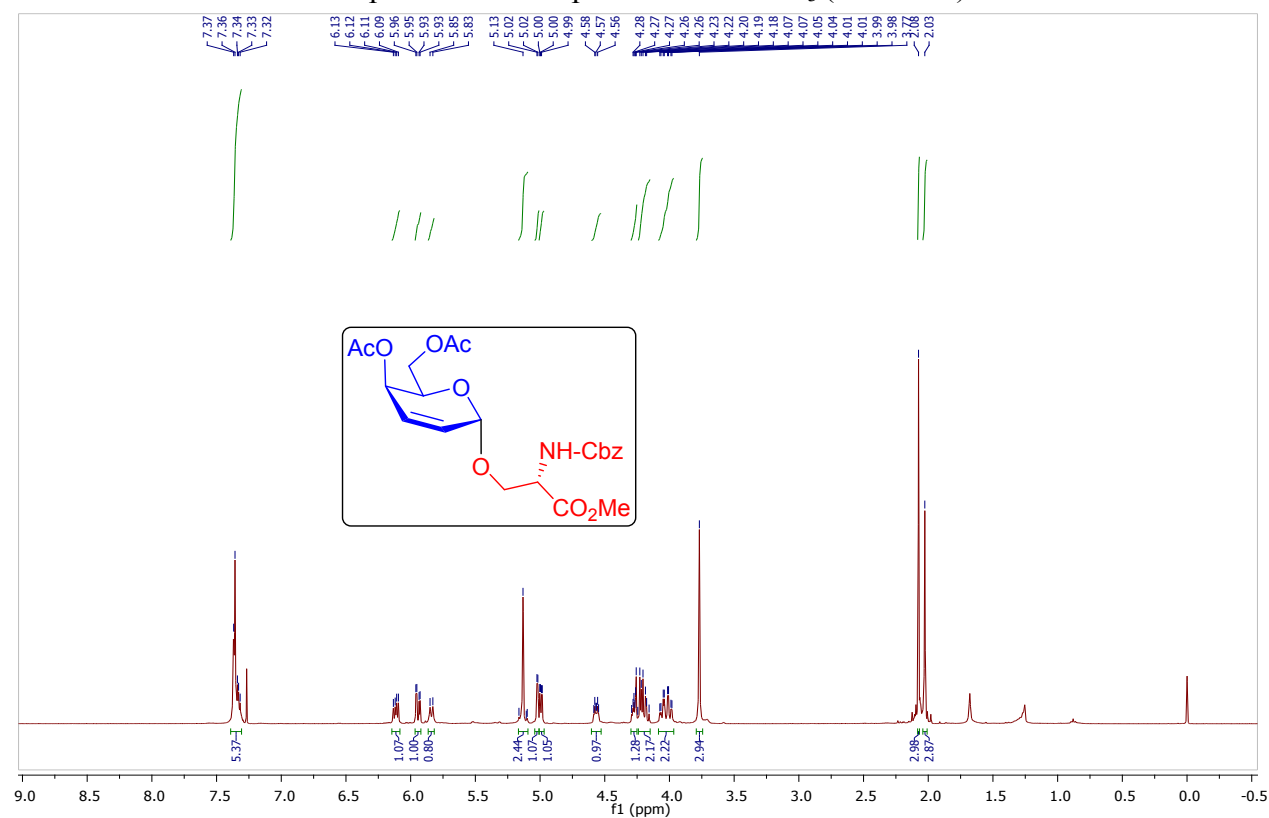
^1H NMR spectrum of compound **35** in CDCl_3 (400 MHz) ^{13}C NMR spectrum of compound **35** in CDCl_3 (101 MHz)

^1H NMR spectrum of compound **36** in CDCl_3 (400 MHz) ^{13}C NMR spectrum of compound **36** in CDCl_3 (101 MHz)

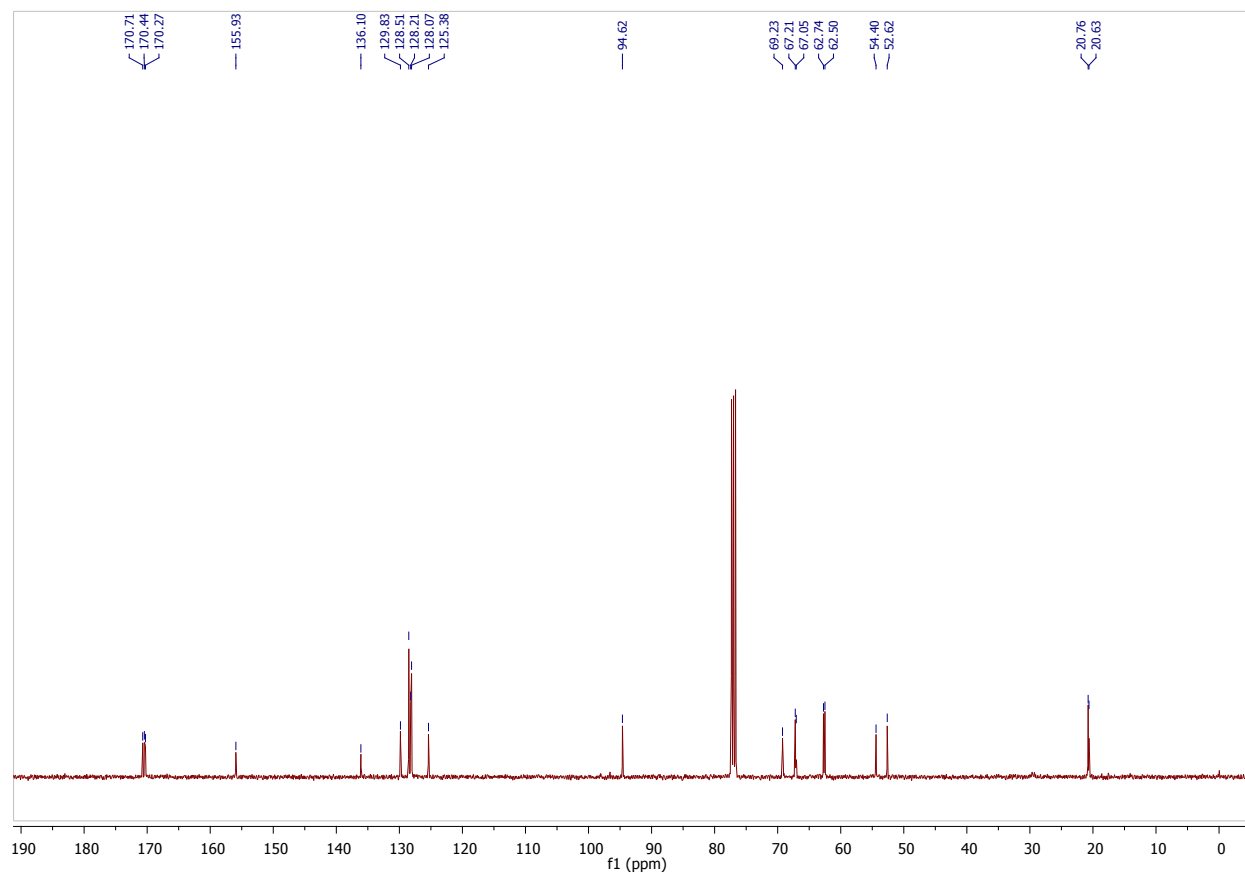


¹H NMR spectrum of compound **37** in CDCl₃ (400 MHz)

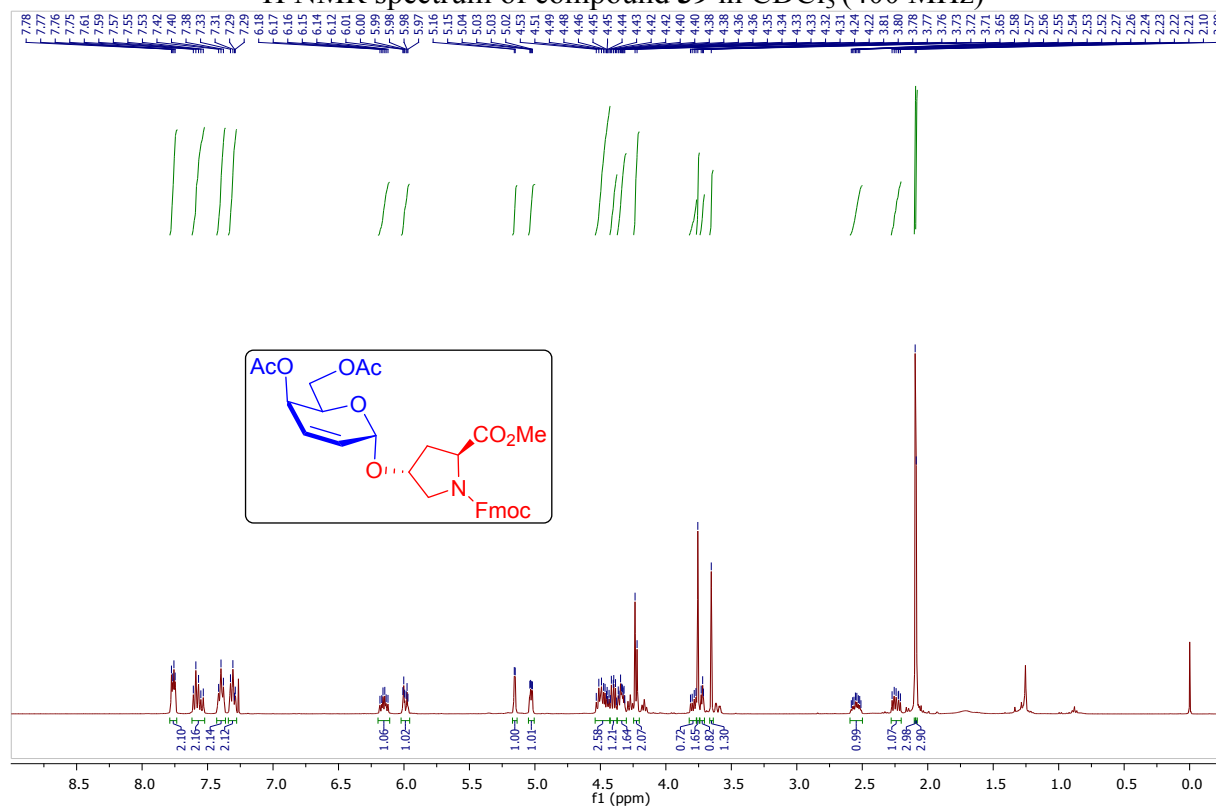


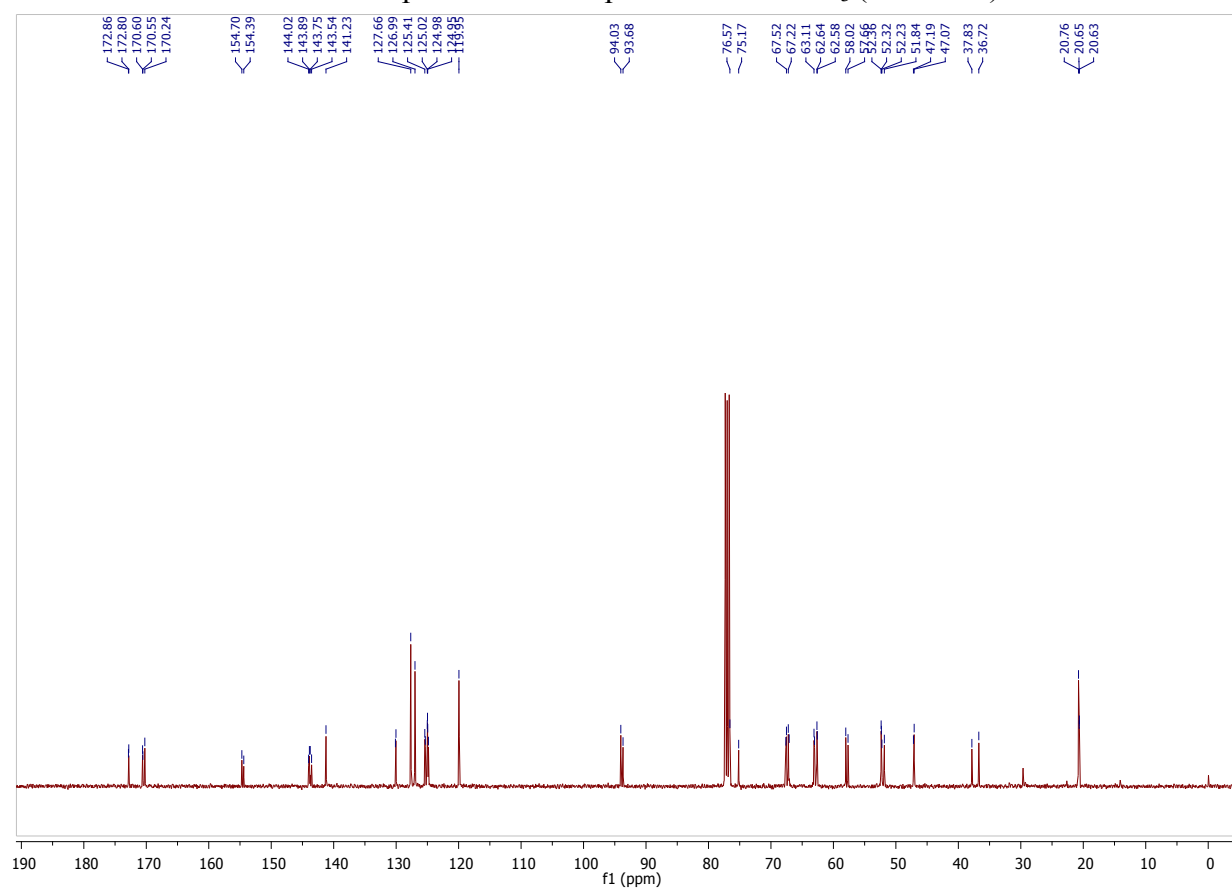
^{13}C NMR spectrum of compound **37** in CDCl_3 (101 MHz) ^1H NMR spectrum of compound **38** in CDCl_3 (400 MHz)

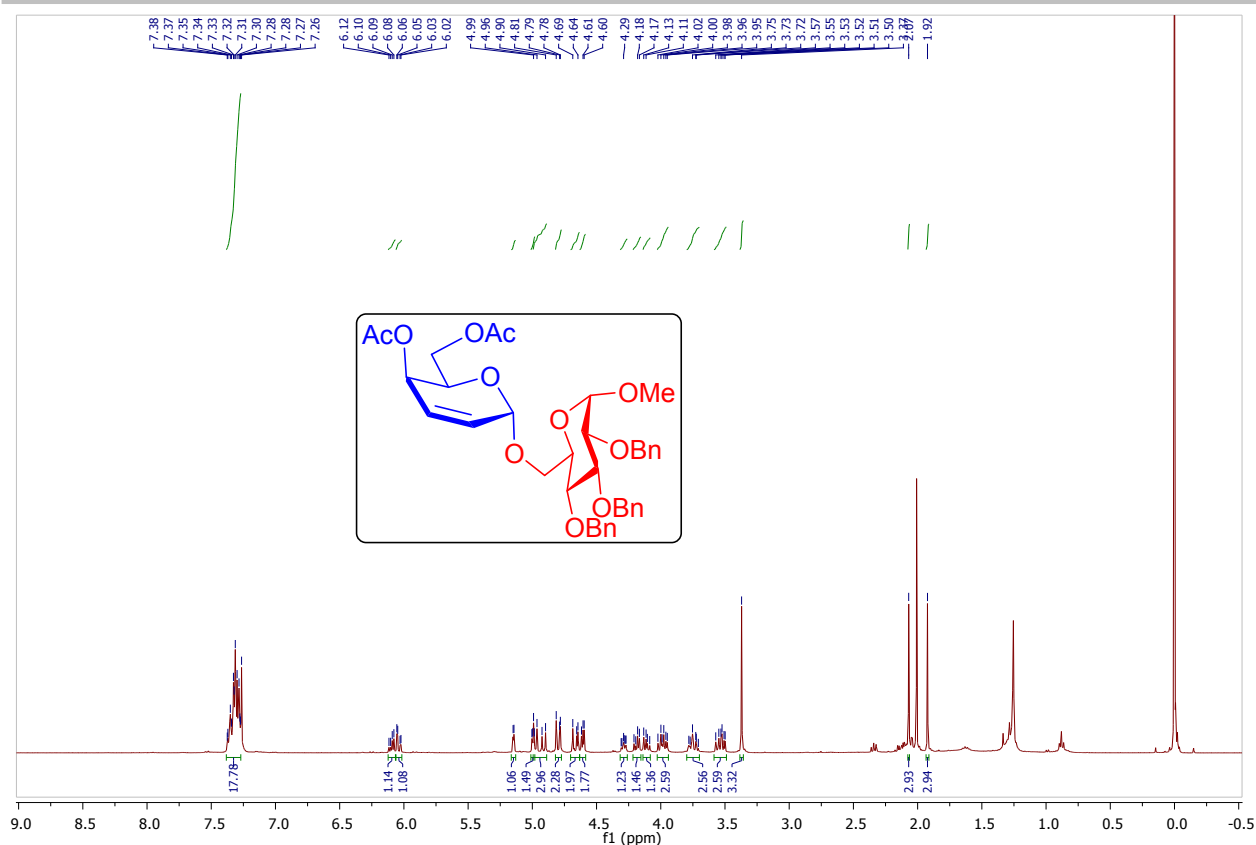
^{13}C NMR spectrum of compound **38** in CDCl_3 (101 MHz)



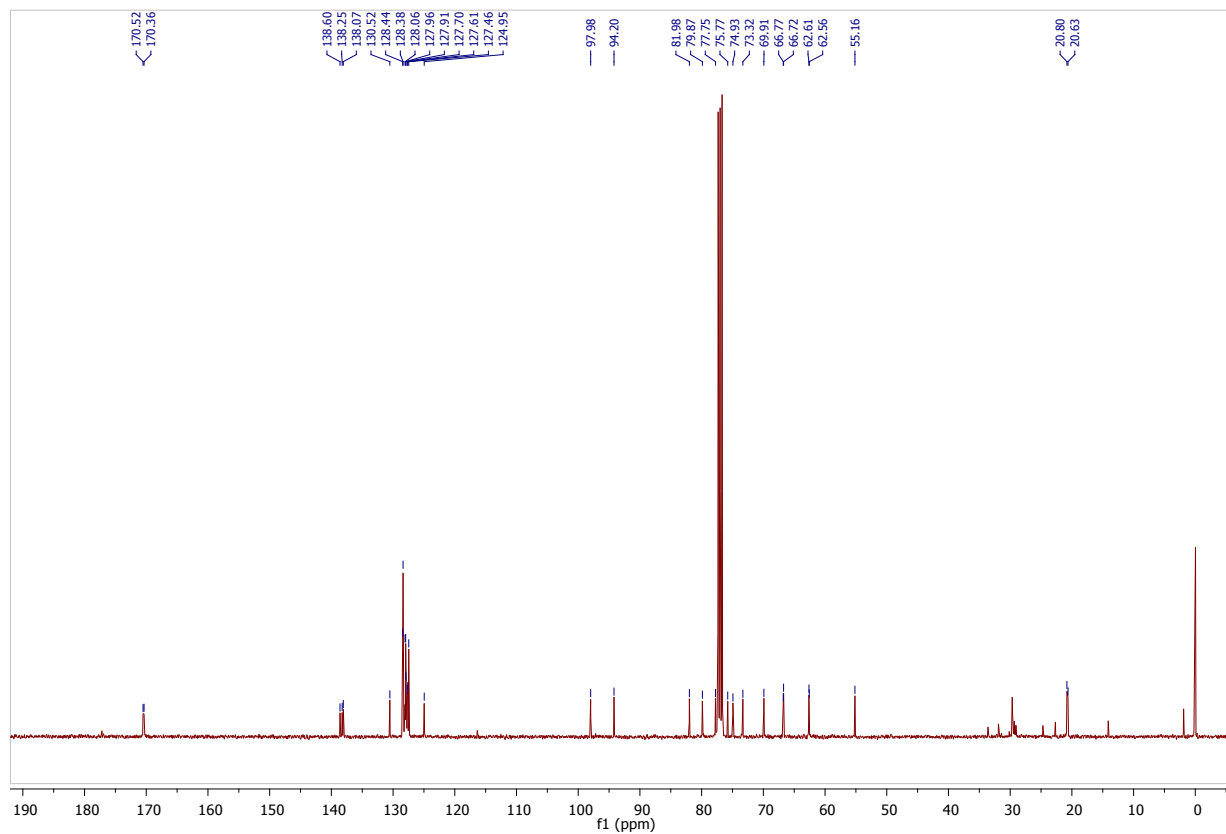
^1H NMR spectrum of compound **39** in CDCl_3 (400 MHz)



^{13}C NMR spectrum of compound **39** in CDCl_3 (101 MHz) ^1H NMR spectrum of compound **40** in CDCl_3 (400 MHz)



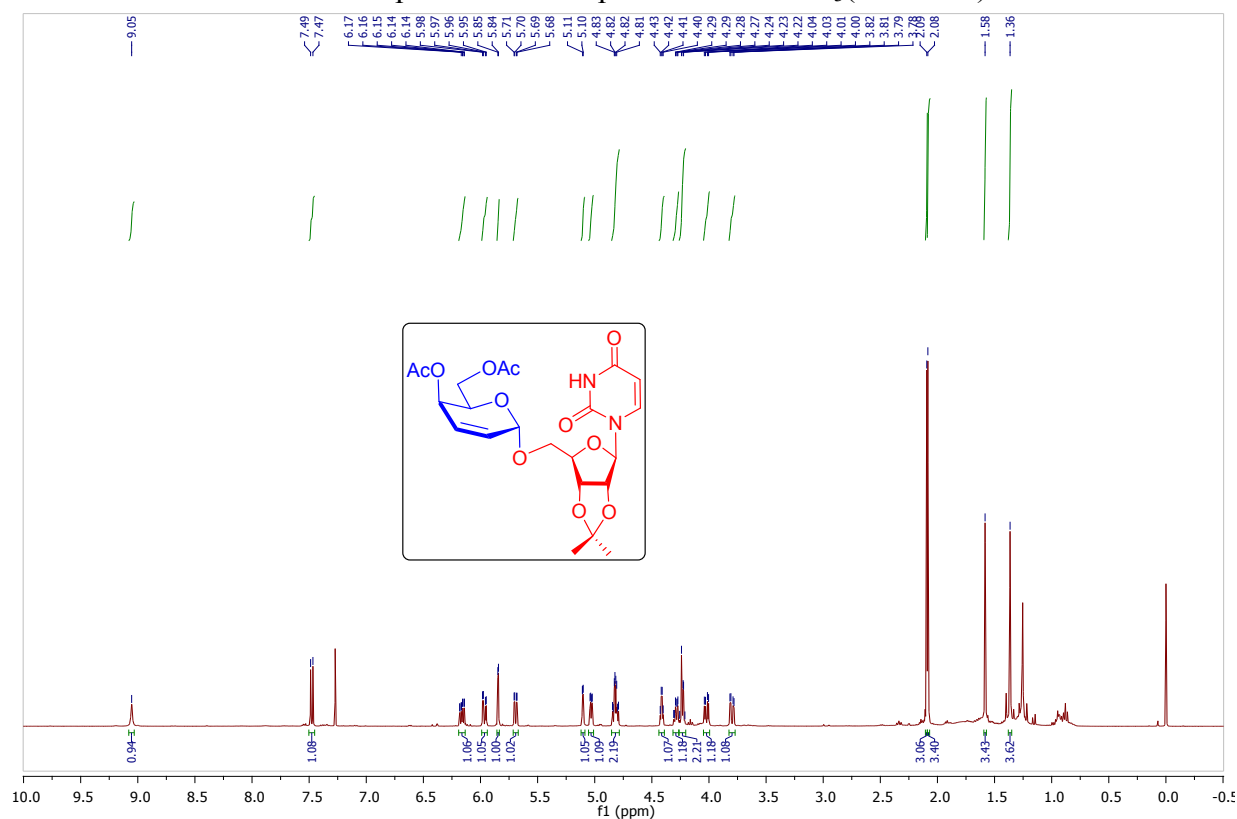
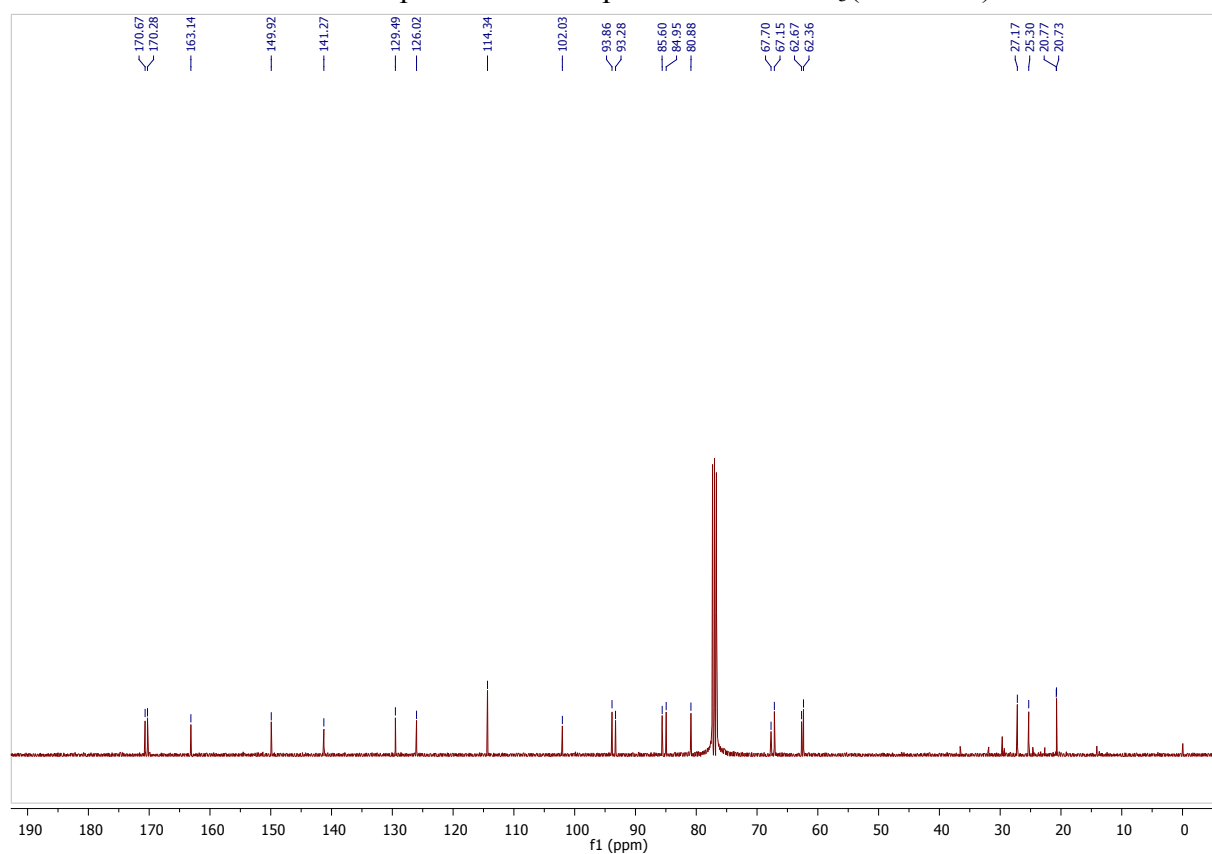
¹³C NMR spectrum of compound **40** in CDCl₃ (101 MHz)

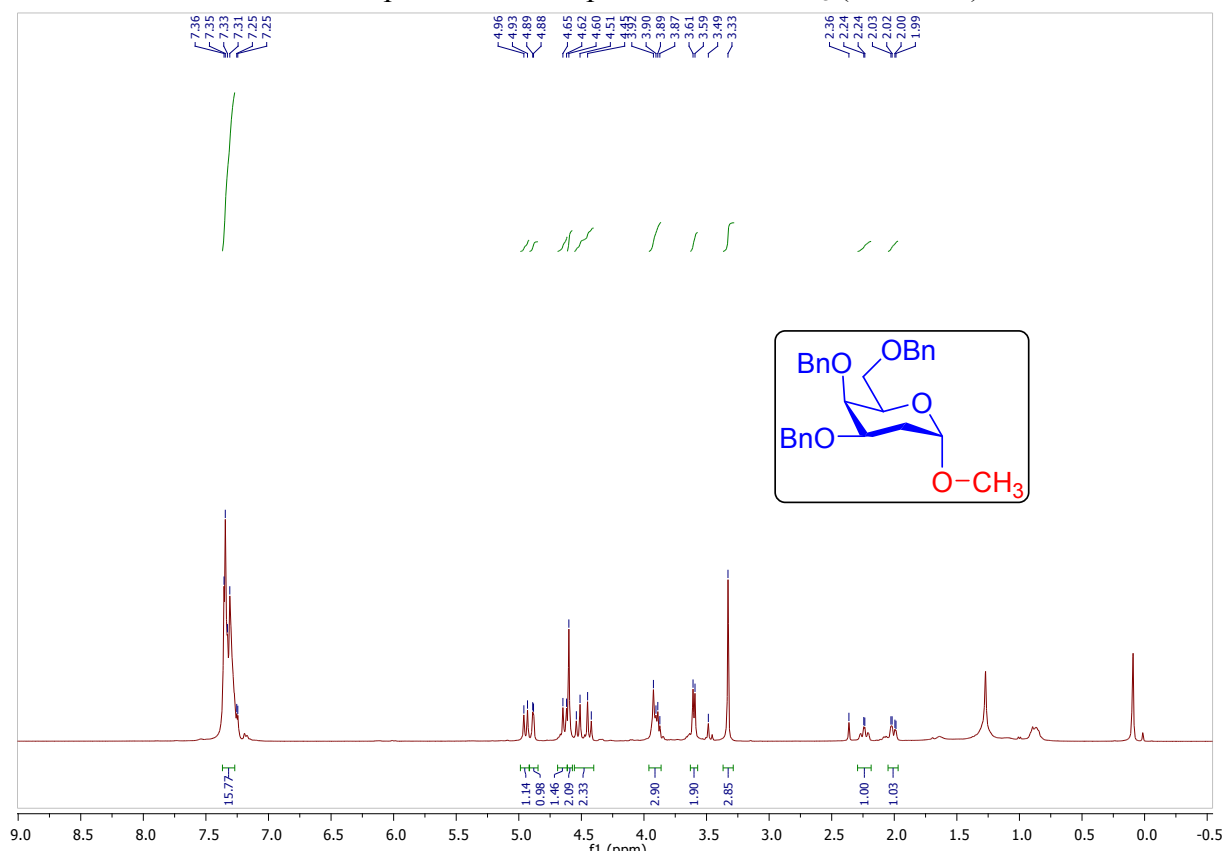


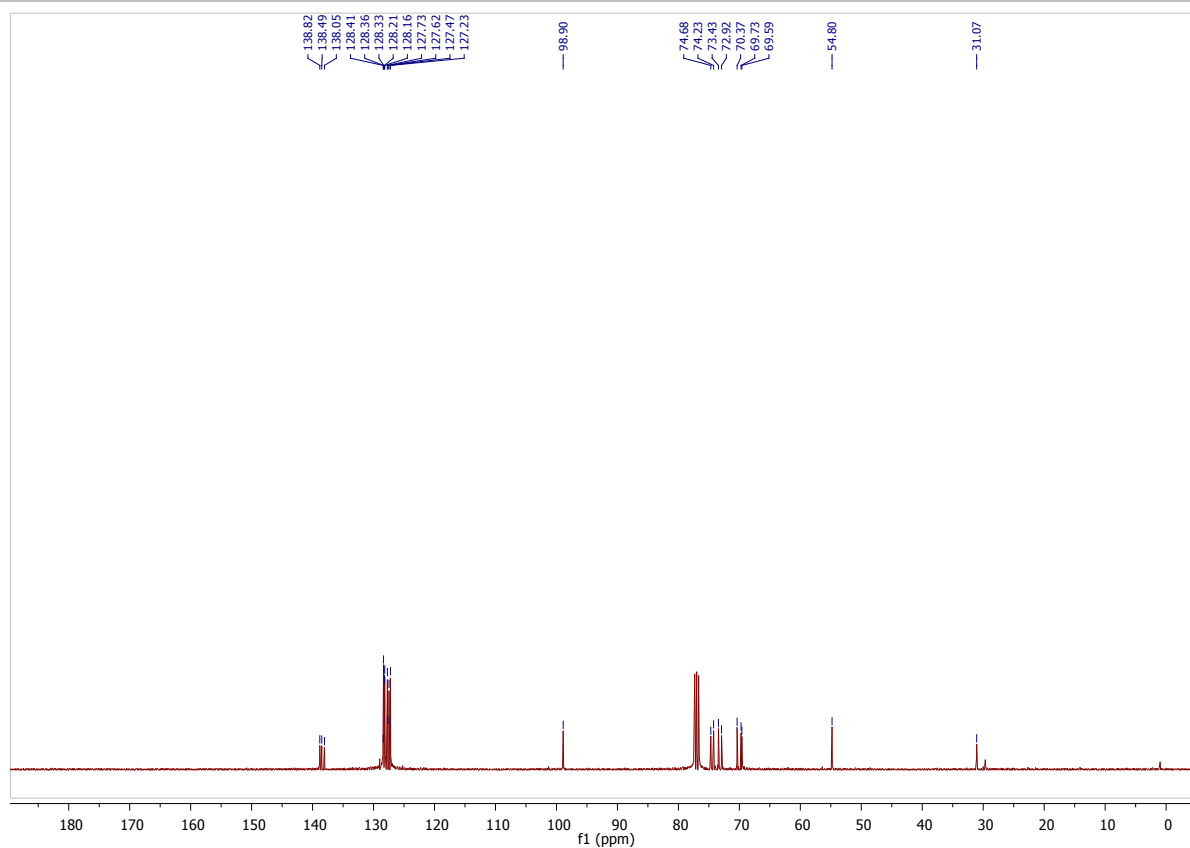
Chemical Structure of Compound 10:

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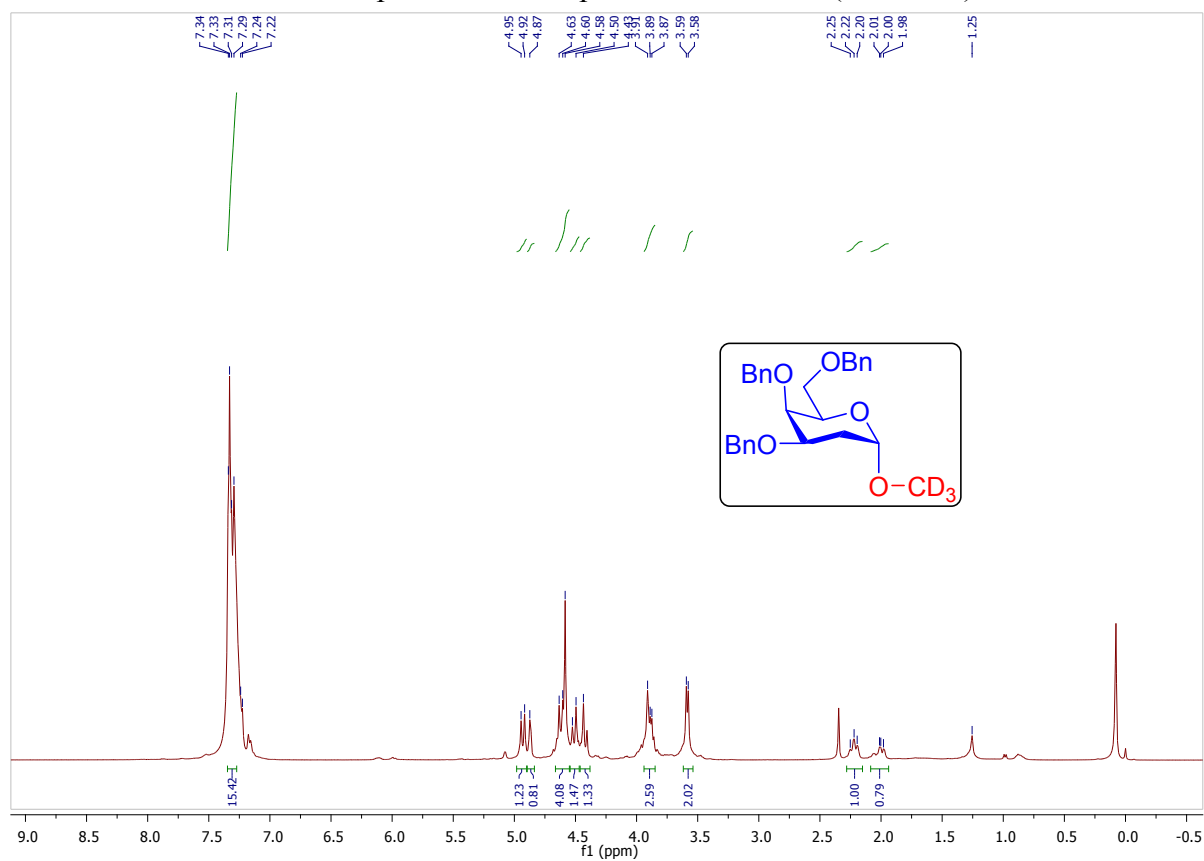
13C NMR spectrum of compound 10b in CDCl₃. The x-axis represents the chemical shift in ppm, ranging from 0 to 190. The spectrum shows several sharp peaks. Key peaks are labeled with their chemical shifts: 170.43, 170.29, 138.47, 138.23, 137.82, 130.46, 128.44, 128.44, 128.11, 127.95, 127.57, 127.50, 127.47, 127.44, 124.41, 97.61, 95.06, 81.82, 81.82, 81.82, 76.07, 75.50, 73.17, 72.94, 69.49, 69.45, 66.78, 62.57, 62.34, 55.15, 31.87, 22.64, 20.77, 20.72, and 14.08.

¹H NMR spectrum of compound **42** in CDCl₃(400 MHz)¹³C NMR spectrum of compound **42** in CDCl₃(101 MHz)

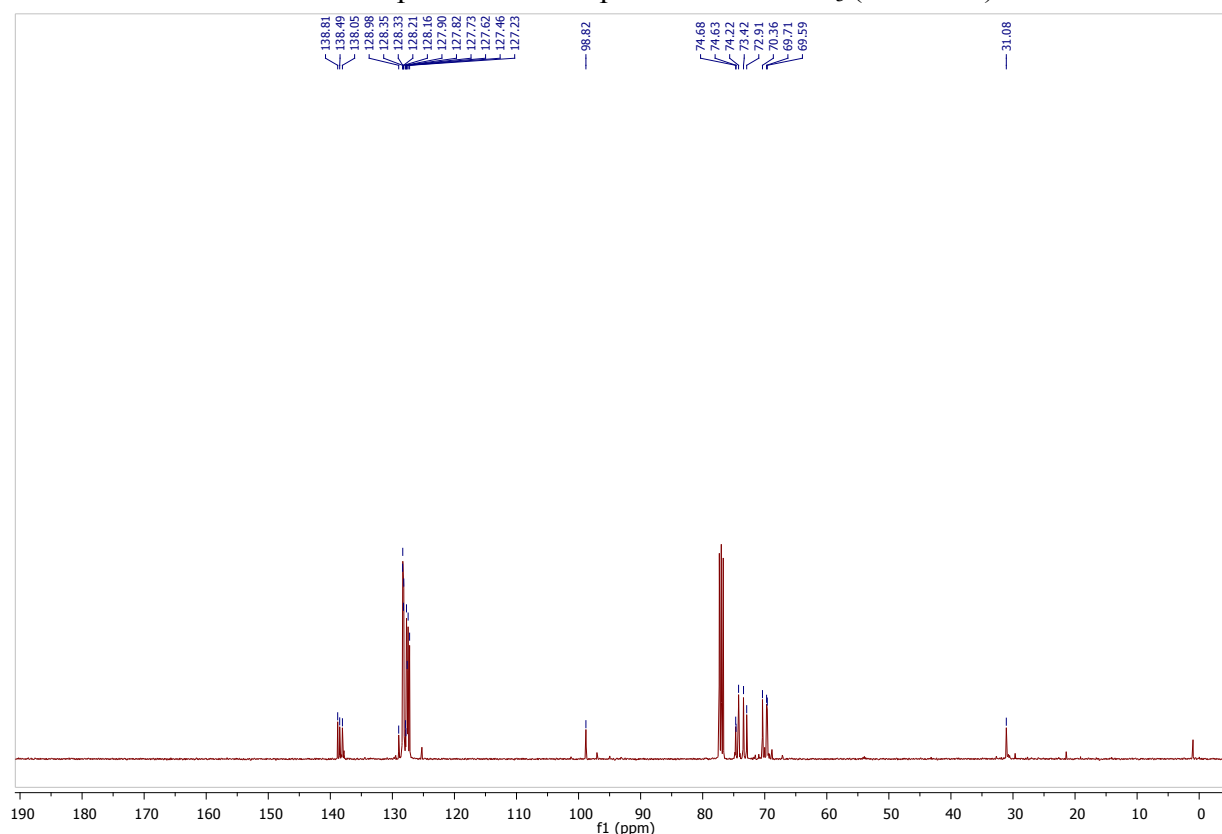
¹H NMR spectrum of compound **43** in CDCl₃ (400 MHz)¹³C NMR spectrum of compound **43** in CDCl₃ (101 MHz)



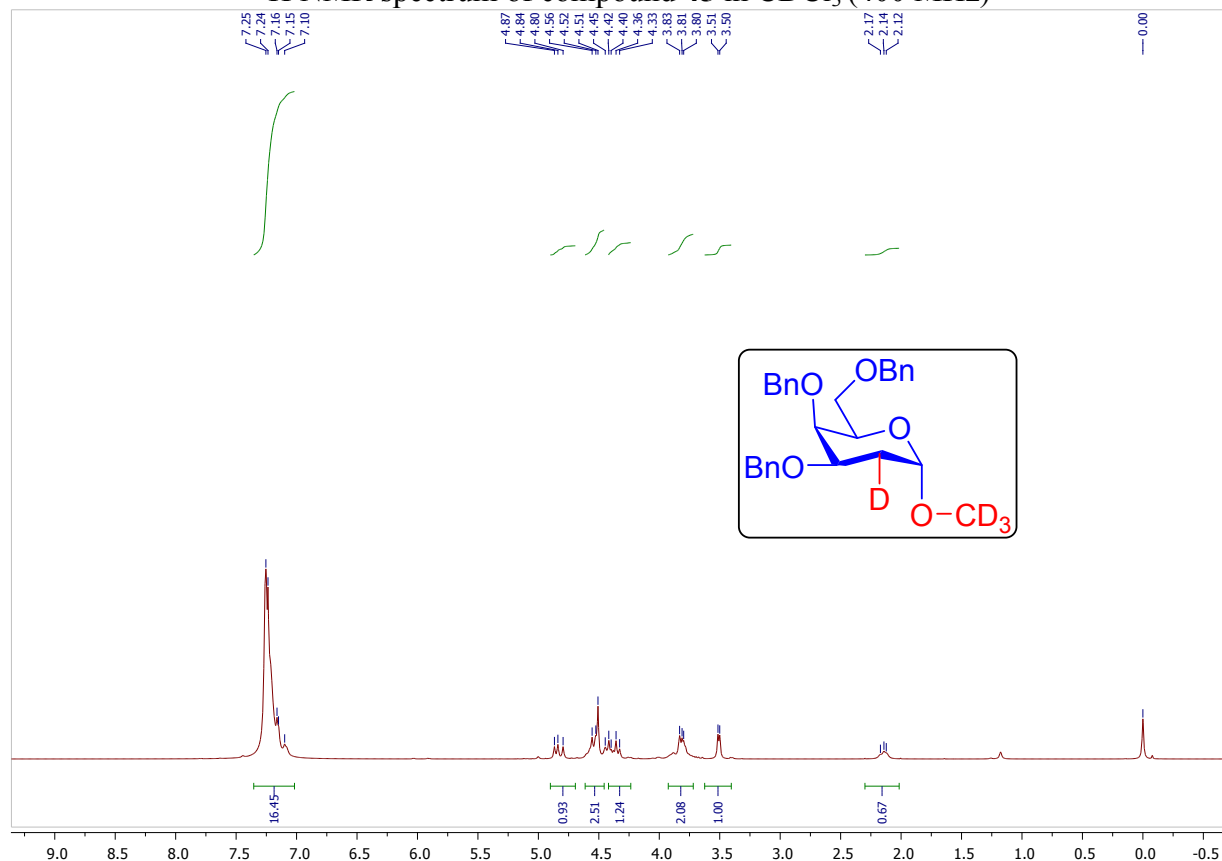
¹H NMR spectrum of compound **44** in CDCl₃ (400 MHz)



^{13}C NMR spectrum of compound **44** in CDCl_3 (101 MHz)



^1H NMR spectrum of compound **45** in CDCl_3 (400 MHz)



^{13}C NMR spectrum of compound **45** in CDCl_3 (101 MHz)