Supporting Information

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

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and

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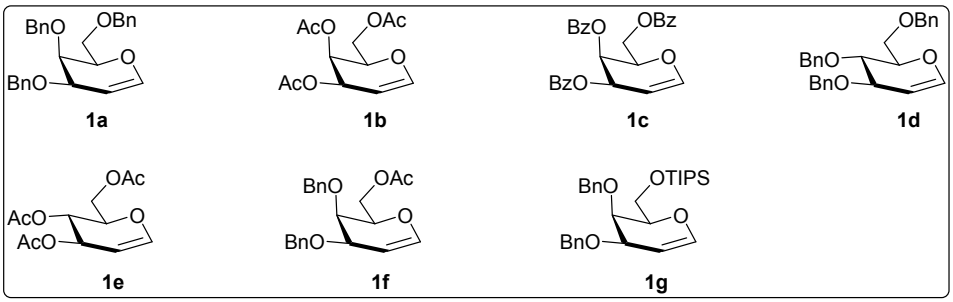
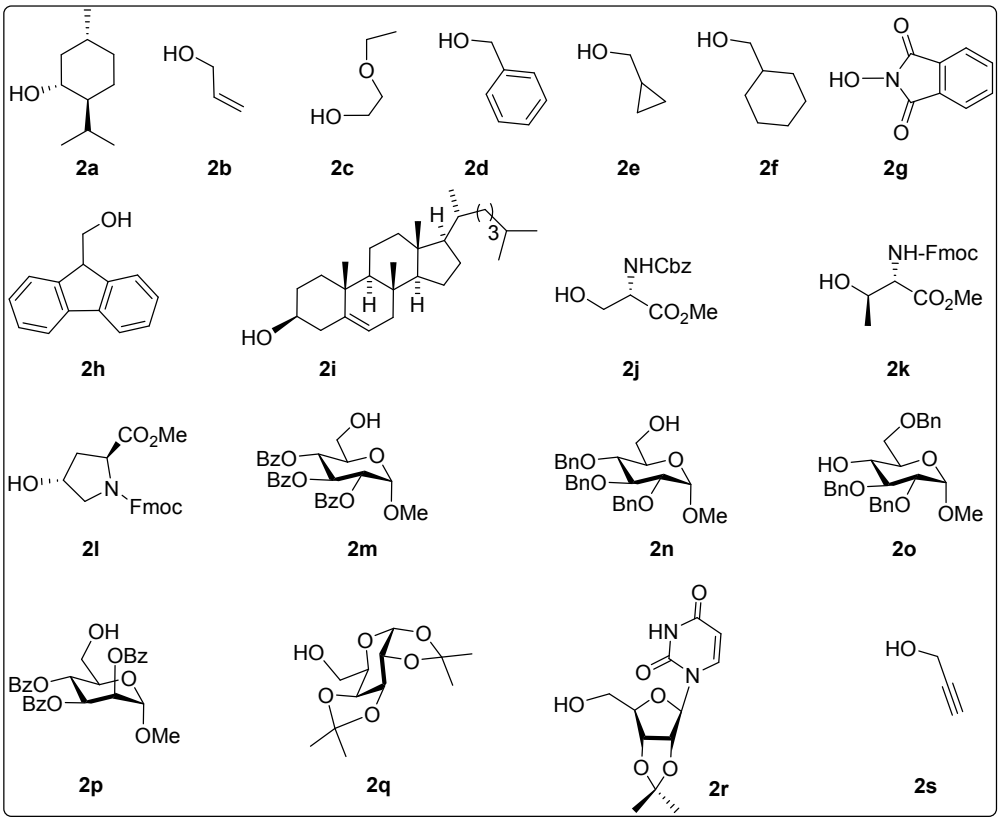
Content

A. Glycals Donors and Glycals Acceptors Used:

Glycals Donors

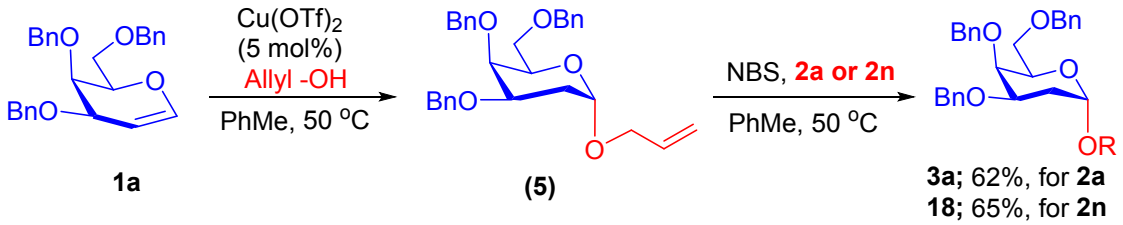


Acceptors



B. Control-Experiments for Mechanistic Studies:

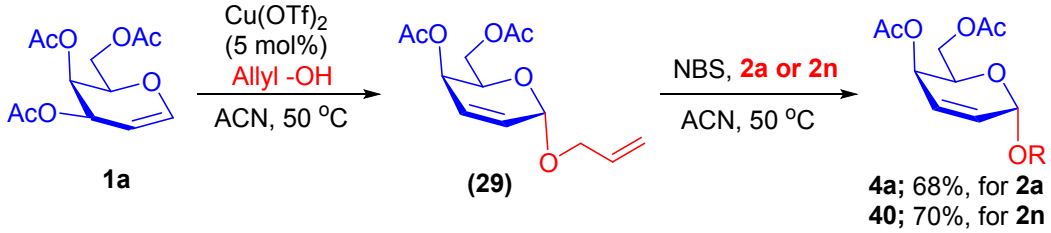
(i) Direct addition reaction of armed glycal 1a and anomeric activation in One-pot:



To a solution of glycal donor **1a** (100 mg, 0.240mmol, 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% $Cu(OTf)_2$ 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% $Cu(OTf)_2$ 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 mixturewasextrated with ethyl acetateand 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-Fe_3O_4-SO_3H, 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 $B(C_6F_5)_3$ 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).

(6) Palo-Nieto,C.; Sau, A.; Williams, R.; Galan, M. C. *J. Org. Chem.* **2017**, *82*, 407. (Cooperative Brønsted Acid-Type Organocatalysis for the Stereoselective Synthesis of Deoxyglycosides).

(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).

(8) Zhao, G.; Wang, T. *Angew. Chem.***2018**, *51*, 6120. (Stereoselective Synthesis of 2-Deoxyglycosides from Glycals via Visible-Light-Induced Photoacid Catalysis).

(9) Sau, A.; Williams, R.; Palo-Nieto, C.; Franconetti, A.; Medina, S.; Galan, M. C. *Angew. Chem. Int. Ed.* **2017**, *56*, 1. (Palladium-Catalyzed Direct Stereoselective Synthesis of Deoxyglycosides from Glycals).

(10) Balmond, E. I.; Coe, D. M.; Galan, M. C.; McGarrigle, E. M. *Angew. Chem. Int. Ed.* **2012**, *51*, 1. (α-Selective Organocatalytic Synthesis of 2-Deoxygalactosides).

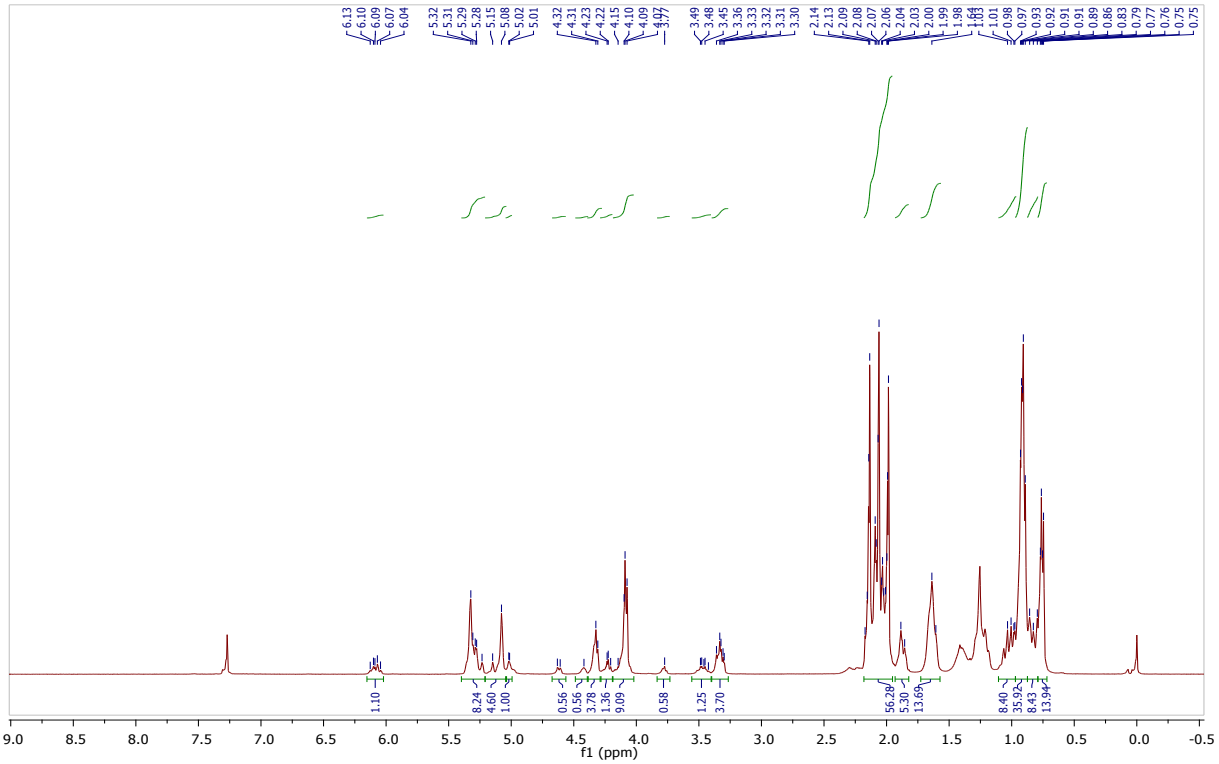
(11) Sherry, B. D.; Loy, R. N.; Toste, F. D. *J. Am. Chem. Soc*. **2004**, *126*, 4510. (Rhenium(V)-Catalyzed Synthesis of 2-Deoxy-α-glycosides).

(12) Das, S.; Pekel, D.; Neudçrfl, J. M.; Berkessel, A. *Angew. Chem. Int. Ed.* **2015**, *54*, 12479. (Organocatalytic Glycosylation by Using Electron-Deficient Pyridinium Salts).

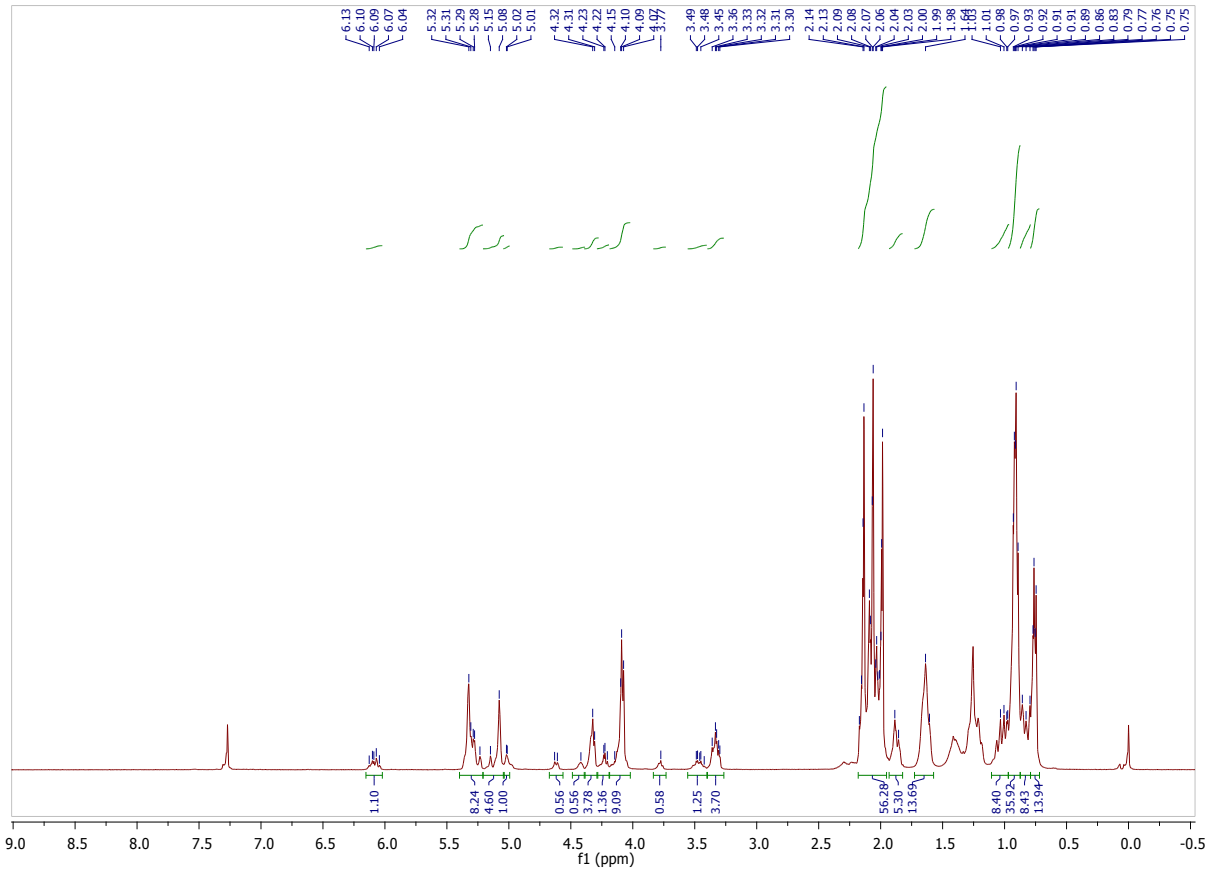
(13) Balamurugan, R.; Koppolu, S. R. *Tetrahedron Lett*. **2009**, *65*, 8139. (Scope of $AuCl_3$ in The Activation of Per-*O*-Acetyl Glycals).

D. ^{1}H and ^{13}C NMR Spectra

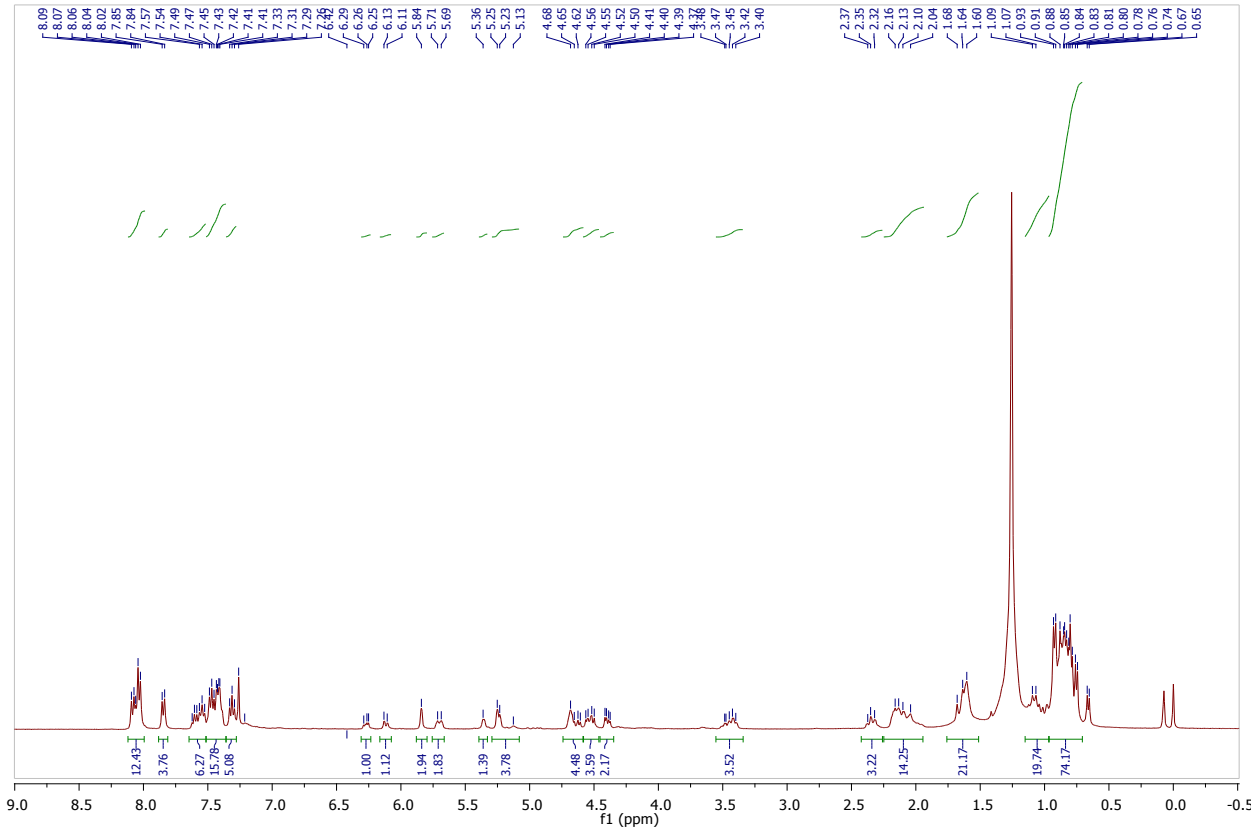
^{1}HNMR spectrum of **3b:4b** (Table 1, entry 6) in $CDCl_3$ (400 MHz)



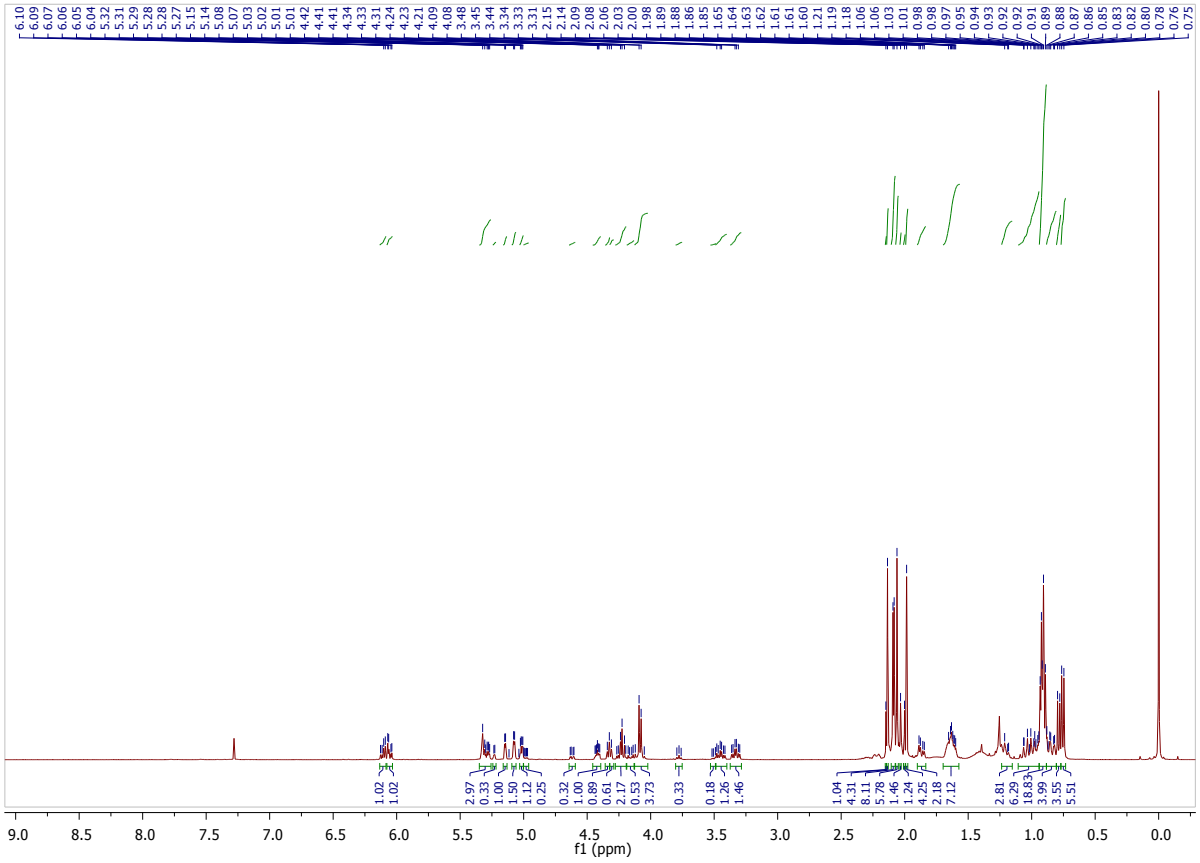
^{1}HNMR spectrum of **3b:4b** (Table 1, entry 7) in $CDCl_3$ (400 MHz)



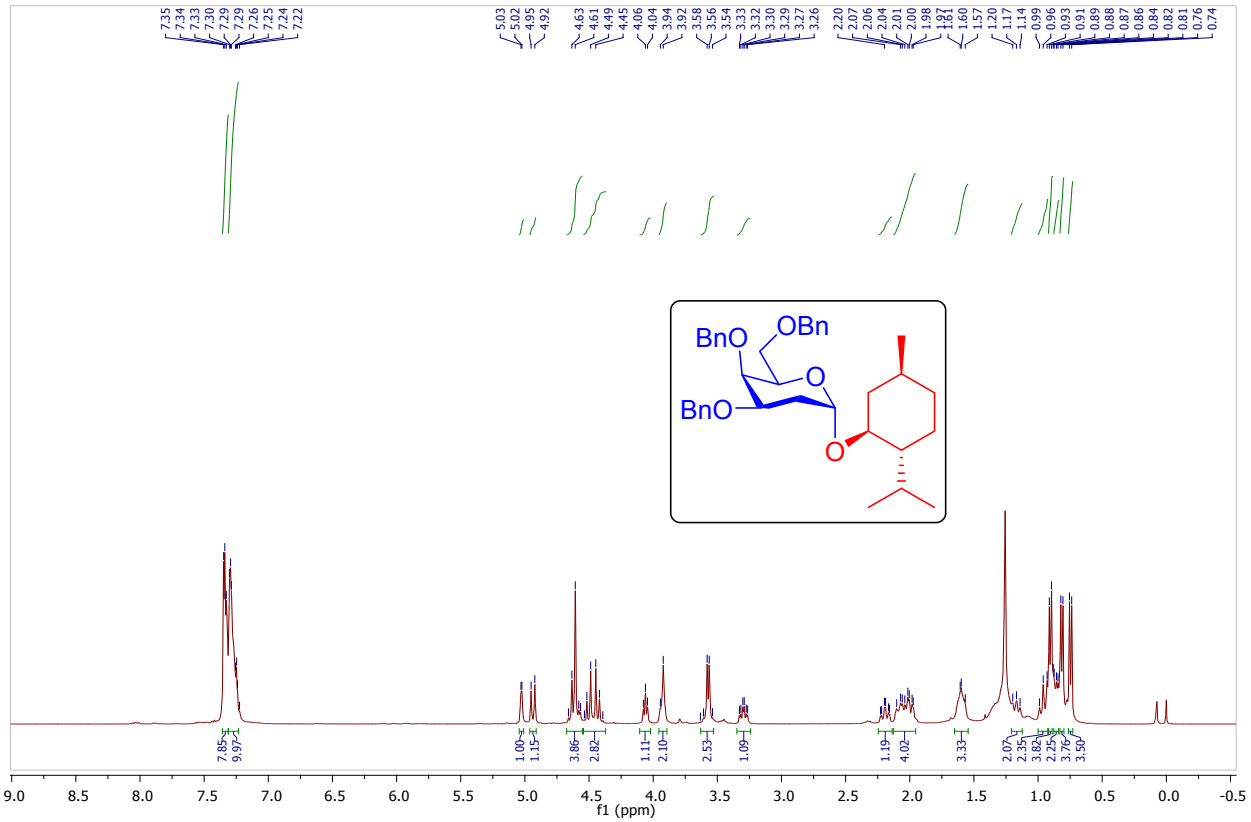
^{1}HNMR spectrum of **3c:4c** (Table 1, entry 10) in $CDCl_3$ (400 MHz)



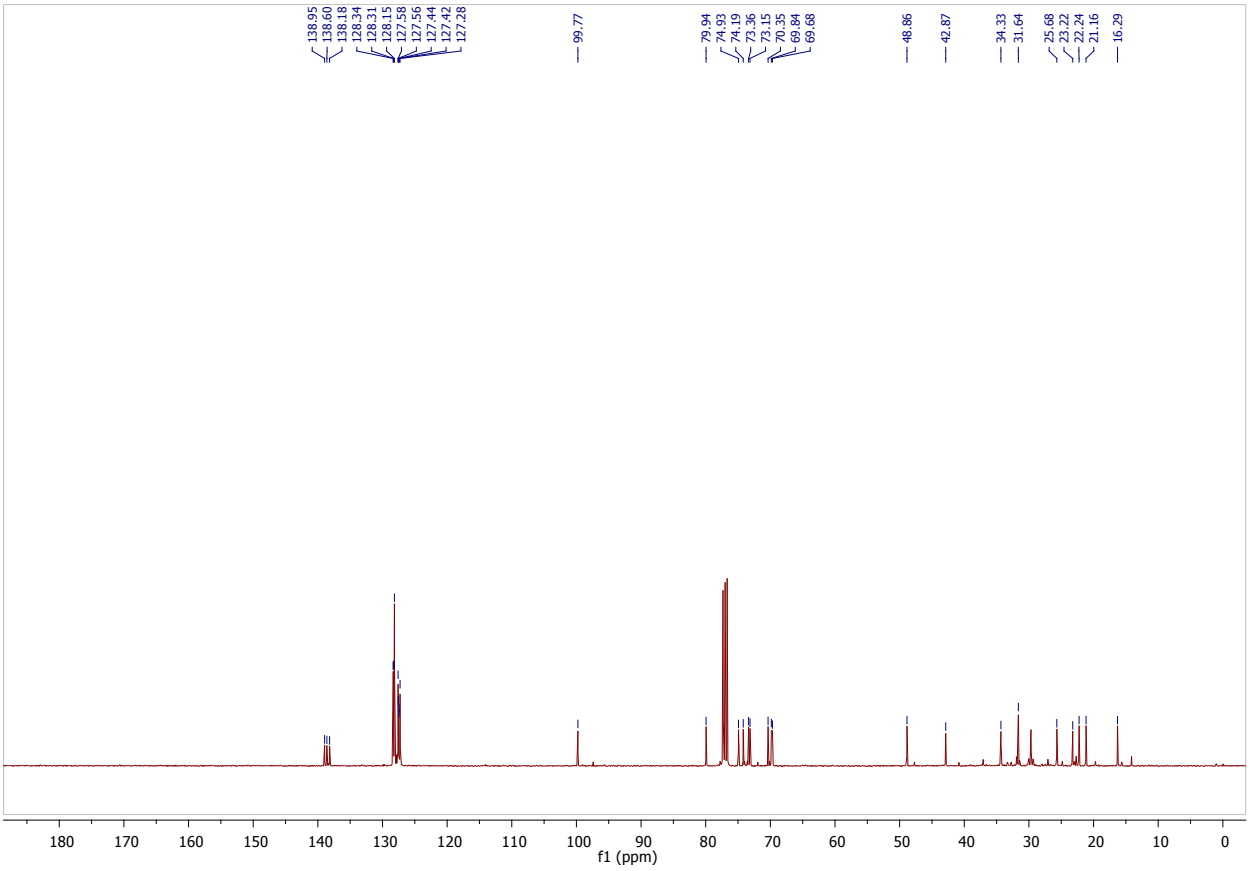
^{1}HNMR spectrum of **3b:4b** (Table 1, entry 17) in $CDCl_3$ (400 MHz)



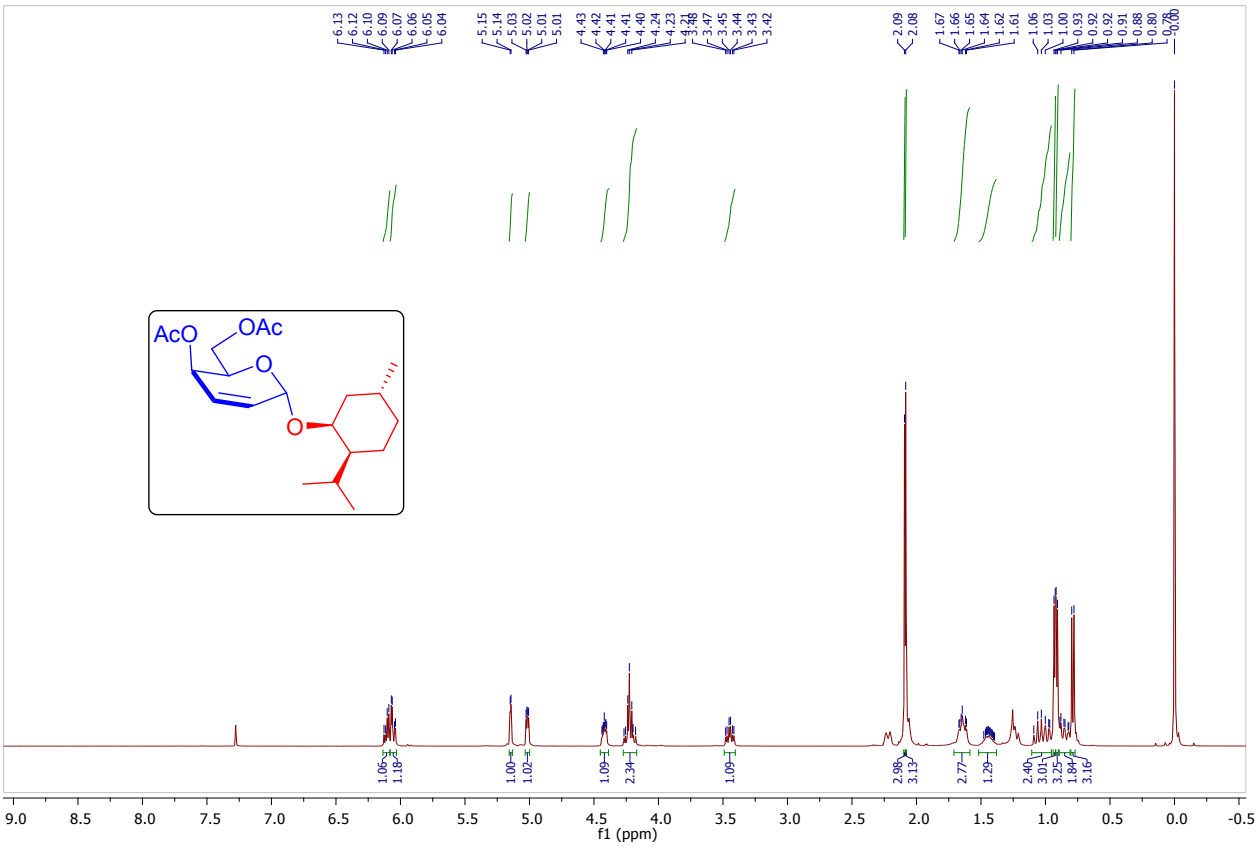
^{1}H NMR spectrum of compound **3a** in $CDCl_3$(400 MHz)



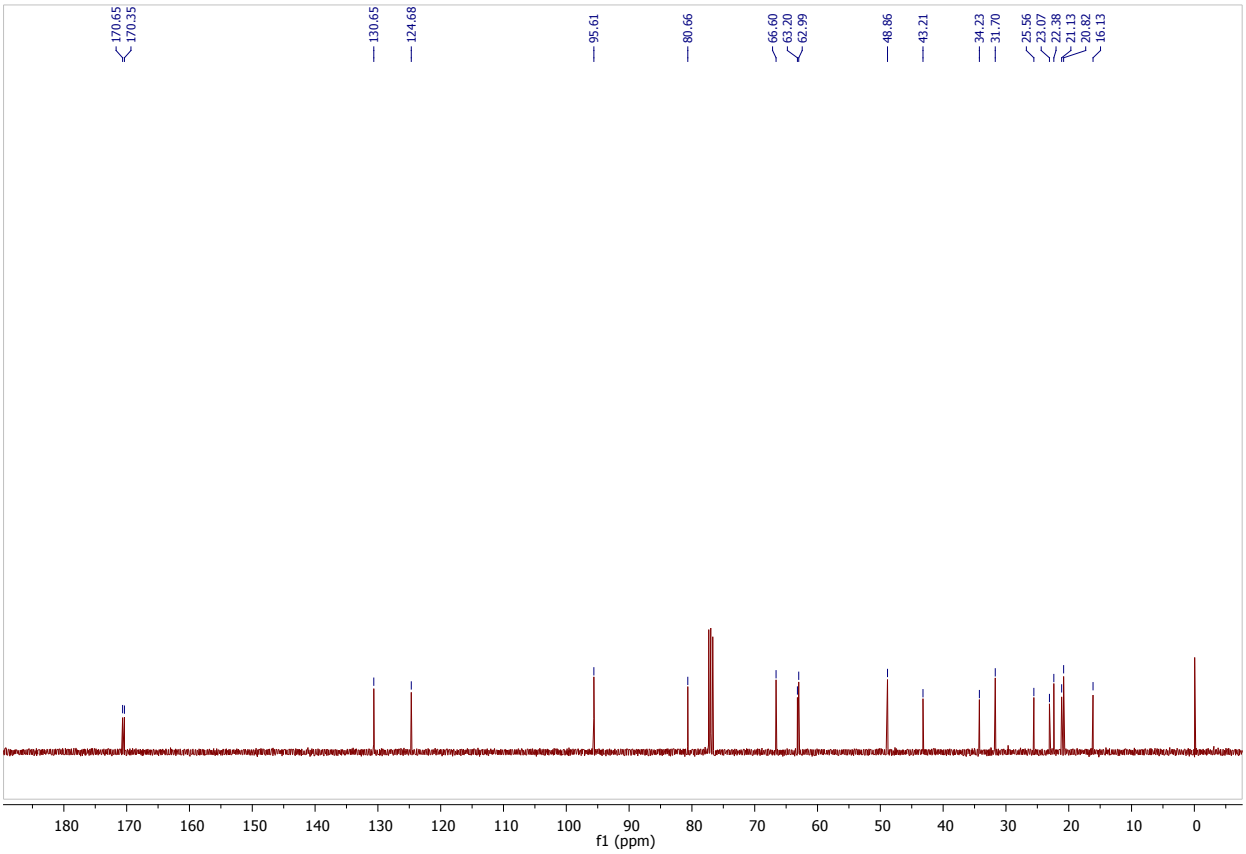
^{13}C NMR spectrum of compound**3a** in $CDCl_3$(101 MHz)



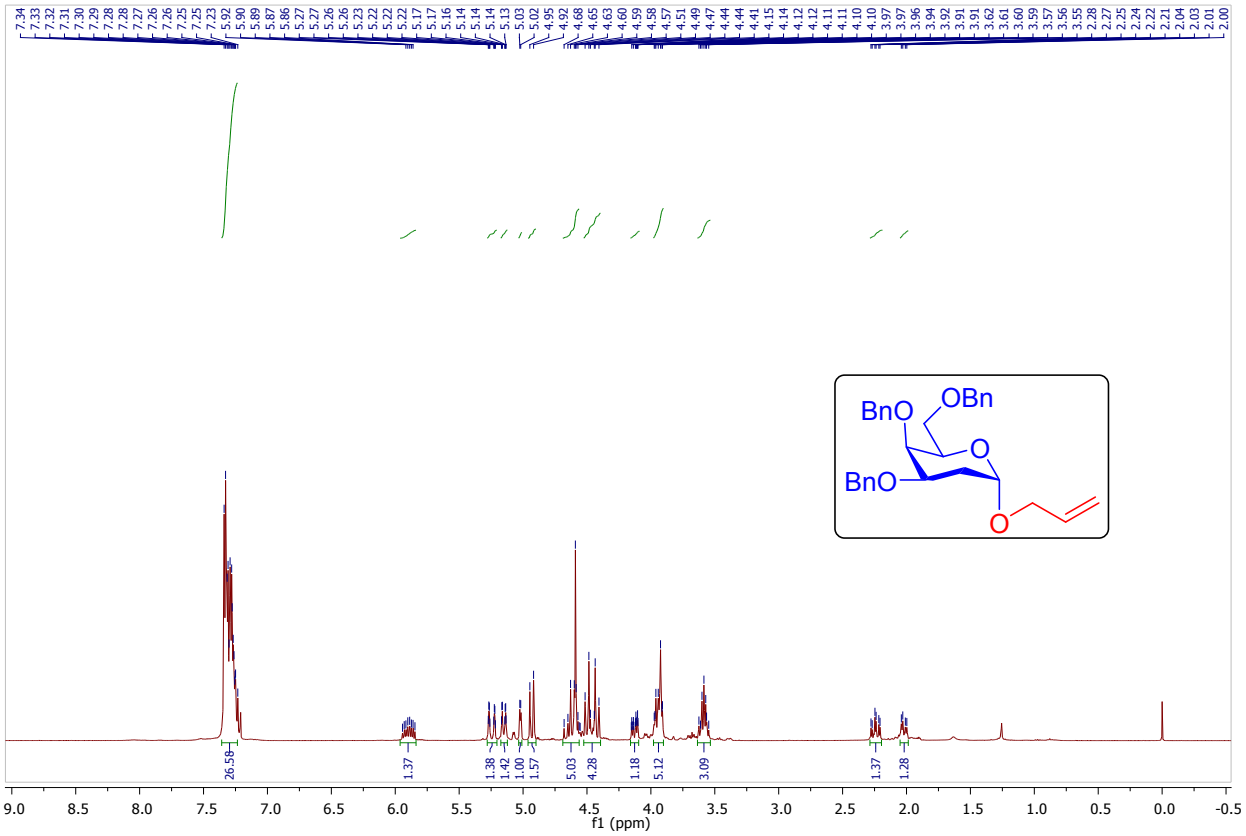
^{1}H NMR spectrum of compound **4b** in $CDCl_3$ (400 MHz)



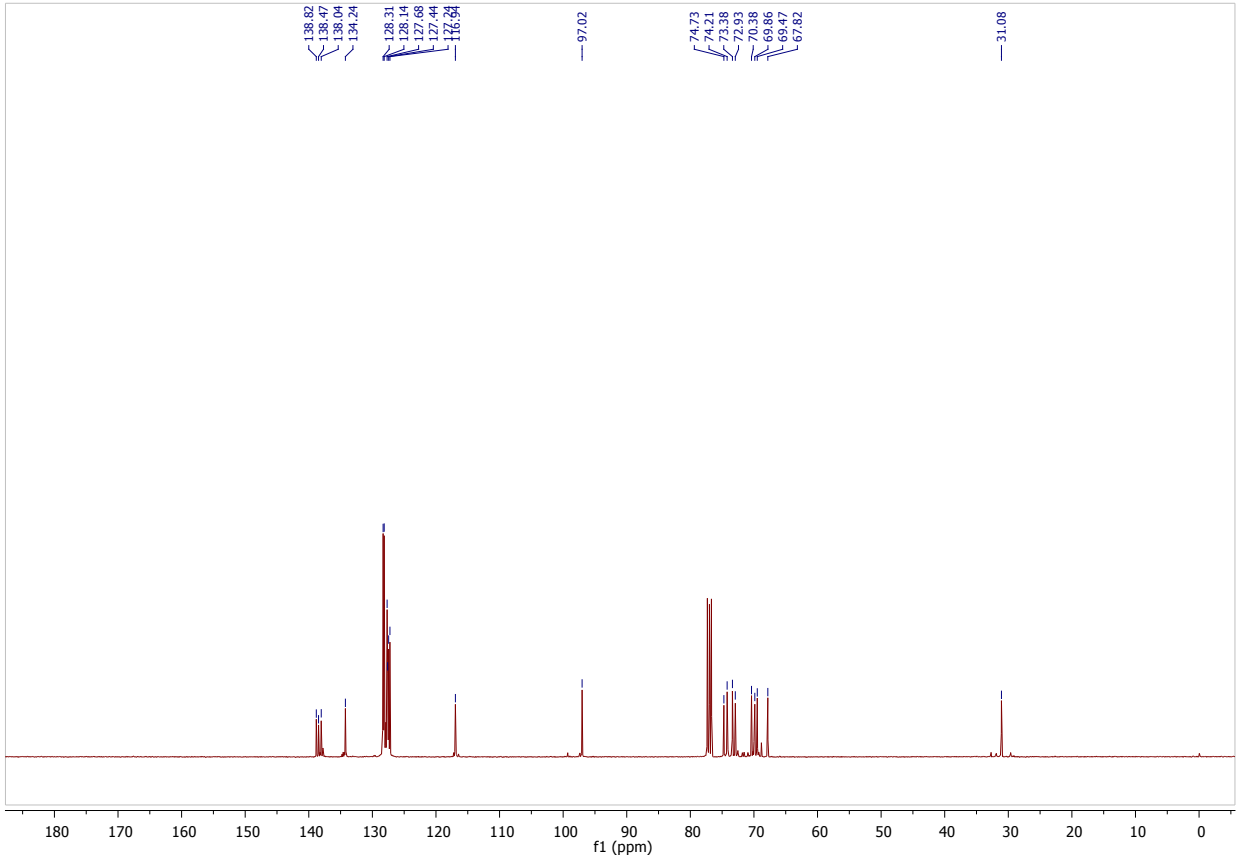
^{13}C NMR spectrum of compound **4b** in $CDCl_3$(101 MHz)



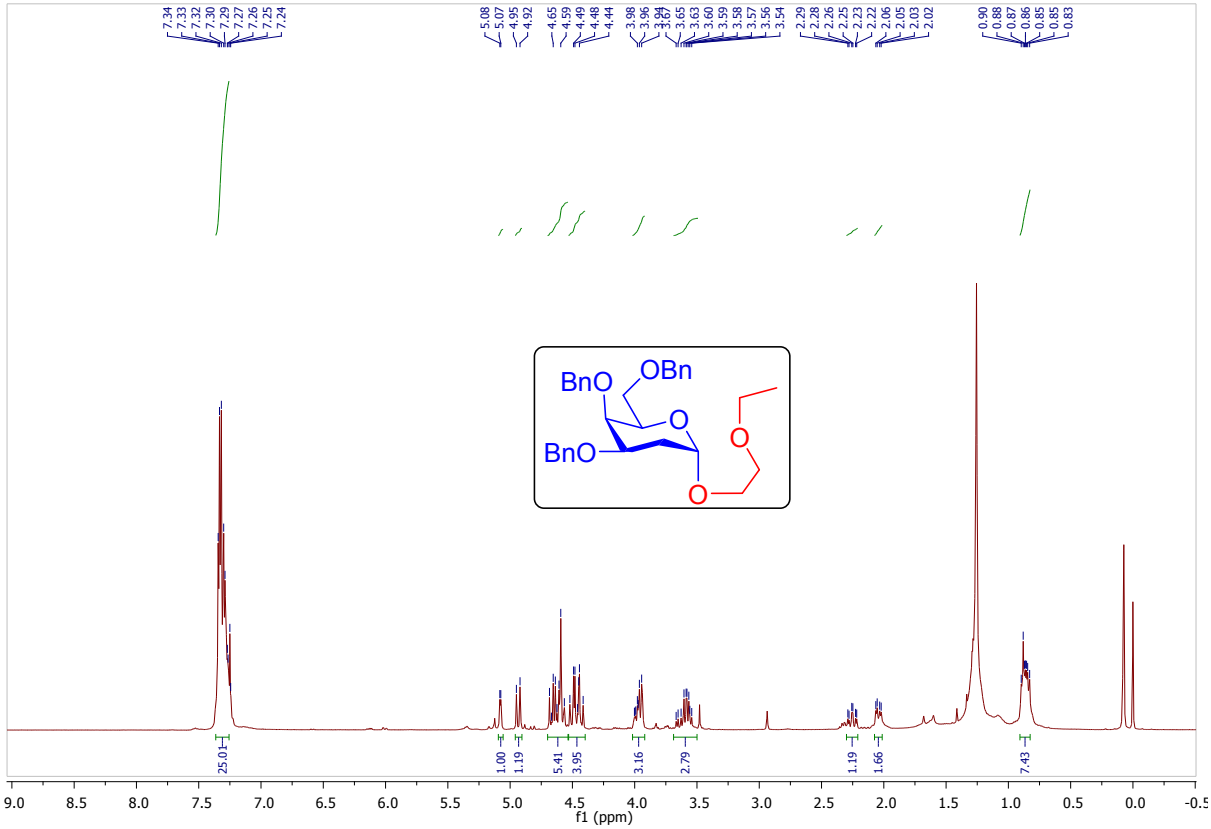
^{1}H NMR spectrum of compound **5** in $CDCl_3$(400 MHz)



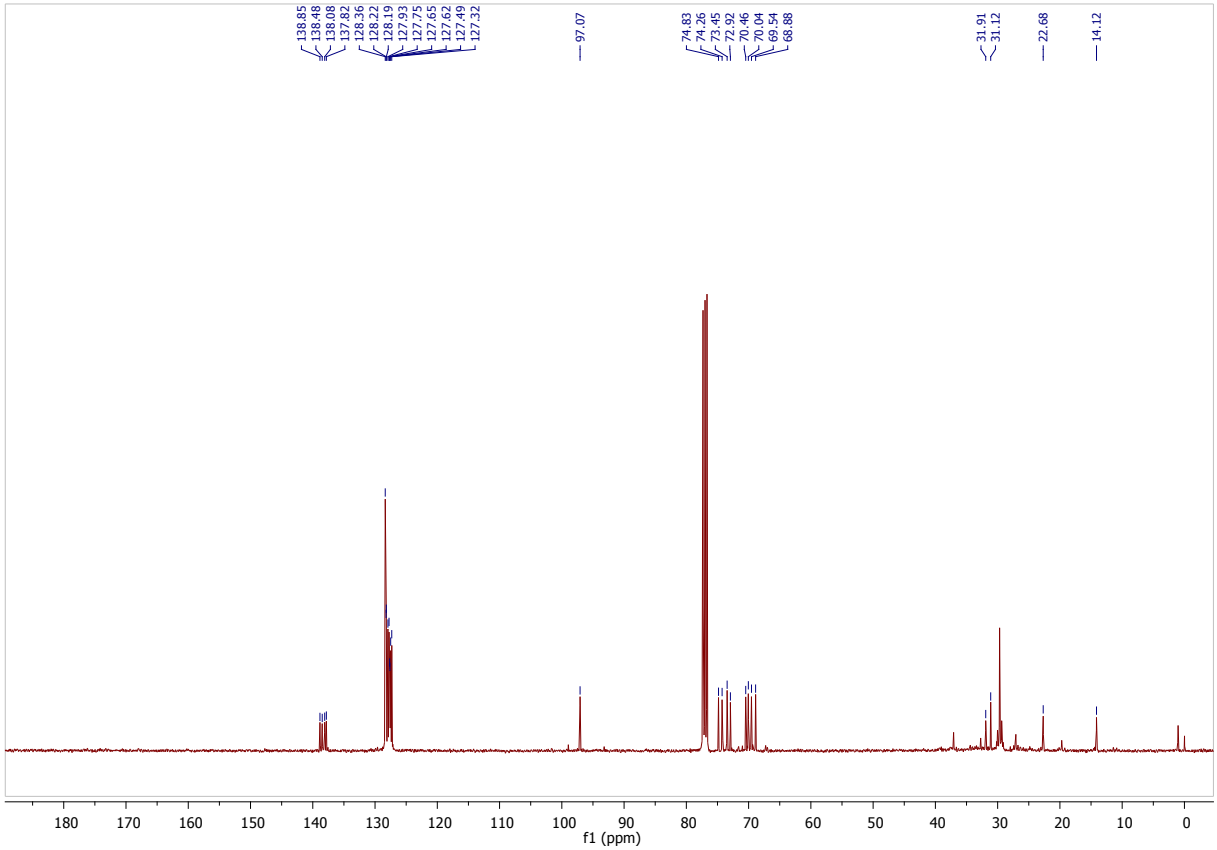
^{13}C NMR spectrum of compound **5** in $CDCl_3$ (101 MHz)



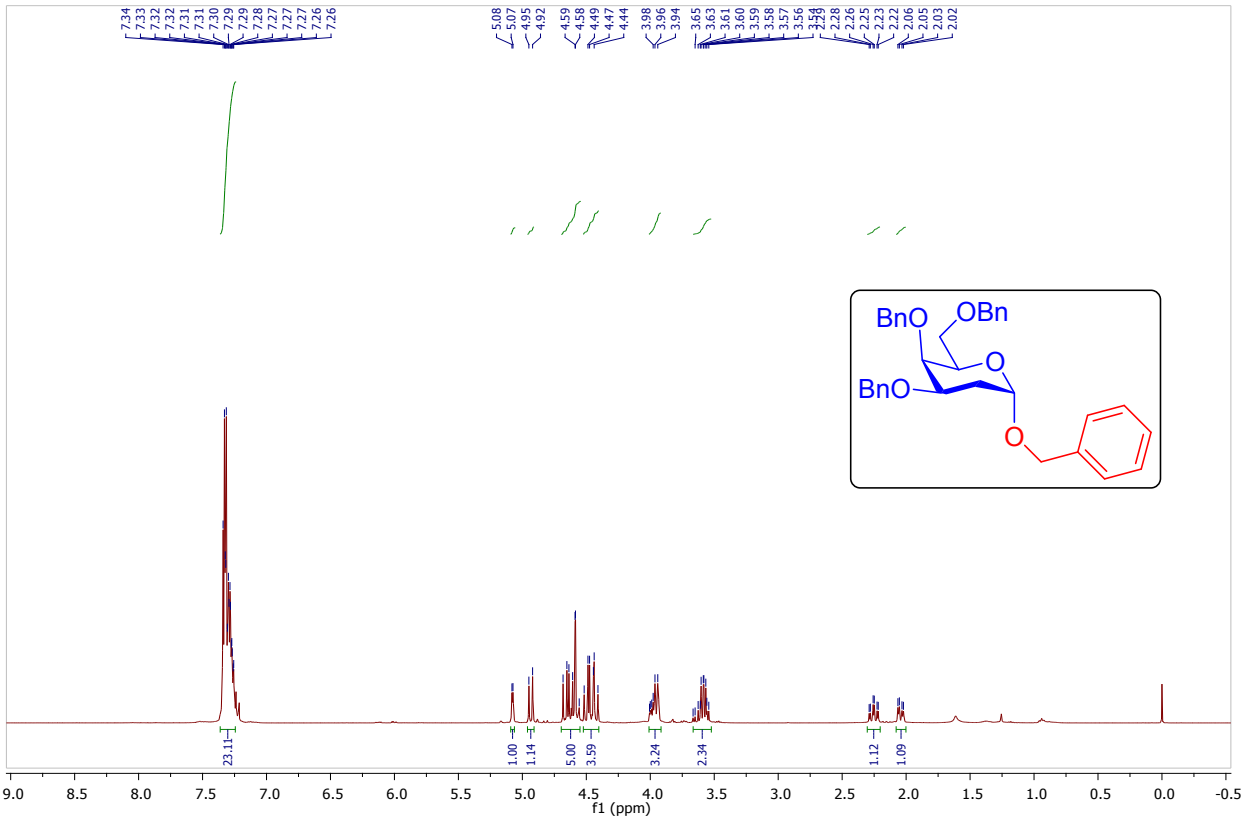
^{1}H NMR spectrum of compound **6** in $CDCl_3$ (400 MHz)



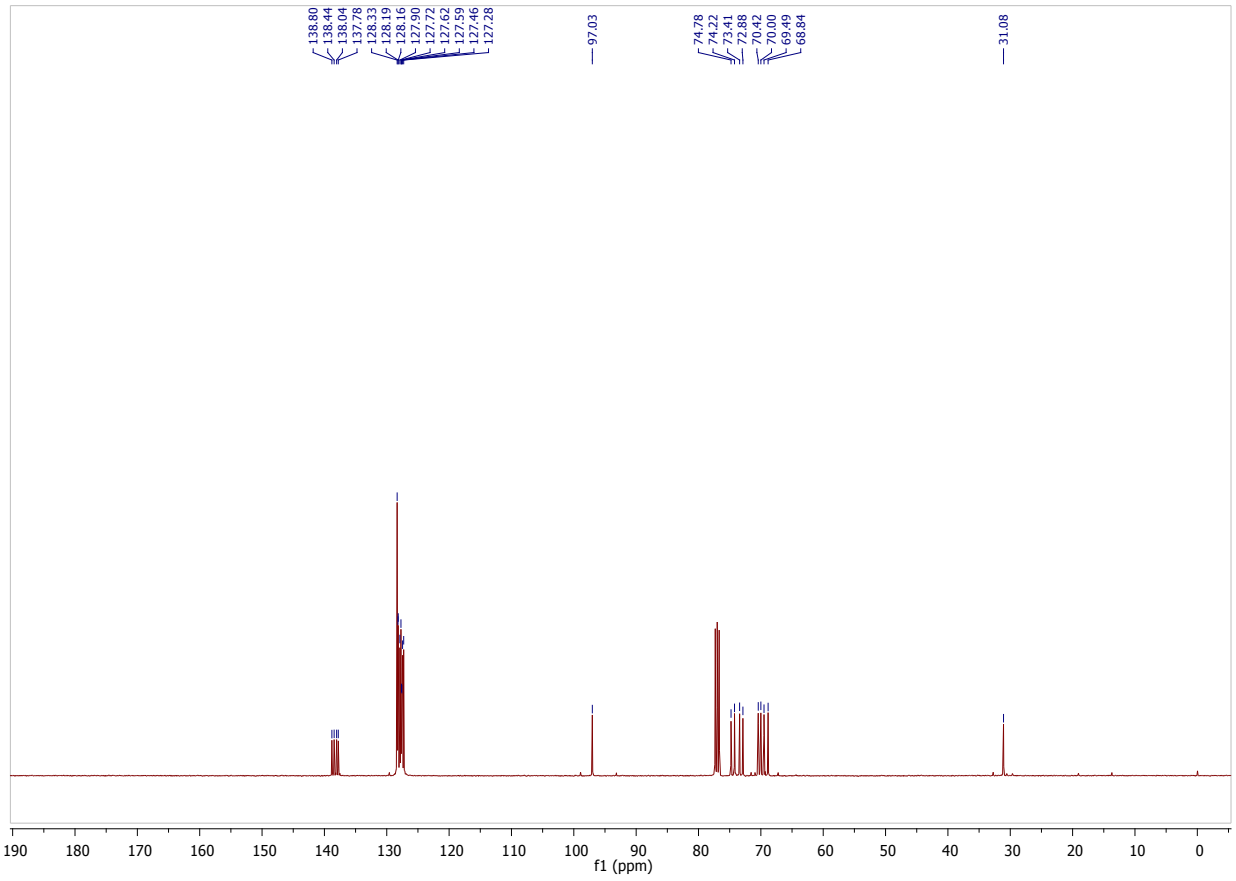
^{13}C NMR spectrum of compound **6** in $CDCl_3$ (101 MHz)



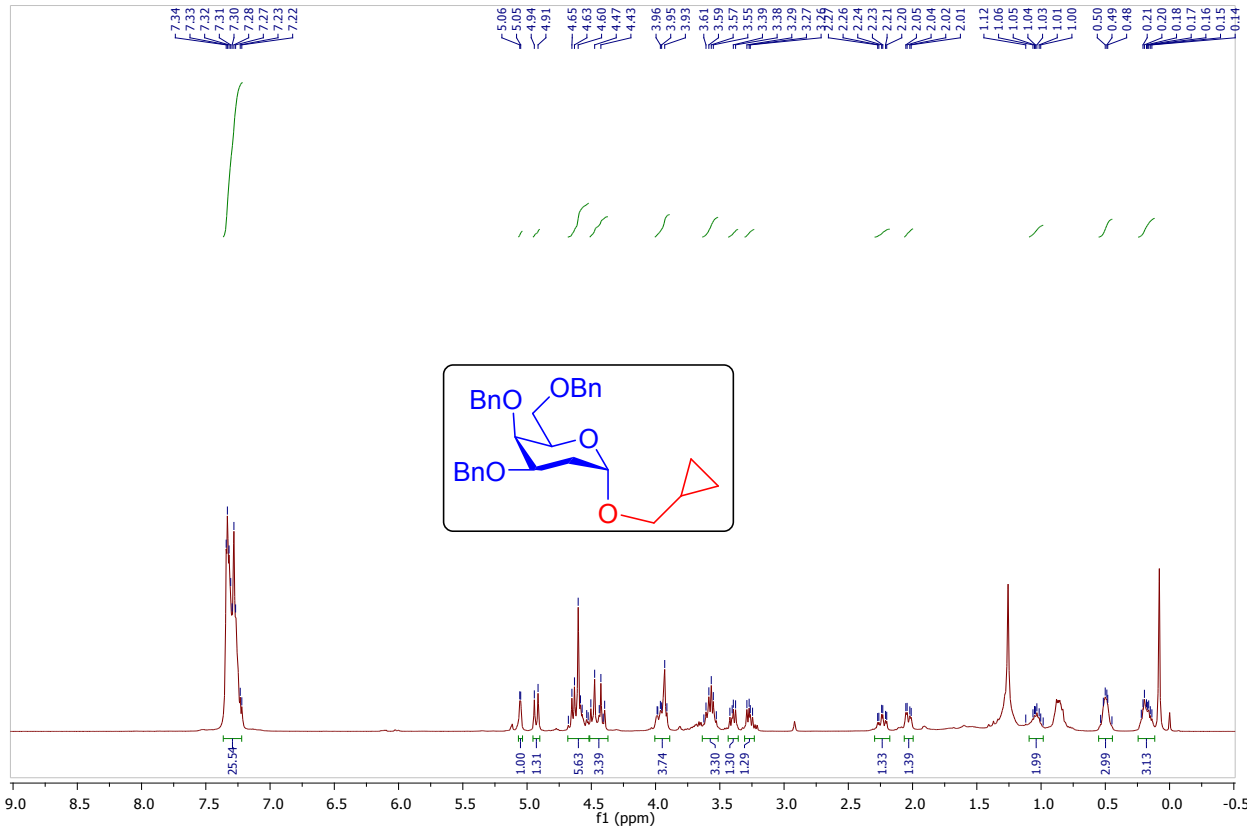
^{1}H NMR spectrum of compound **7** in $CDCl_3$ (400 MHz)



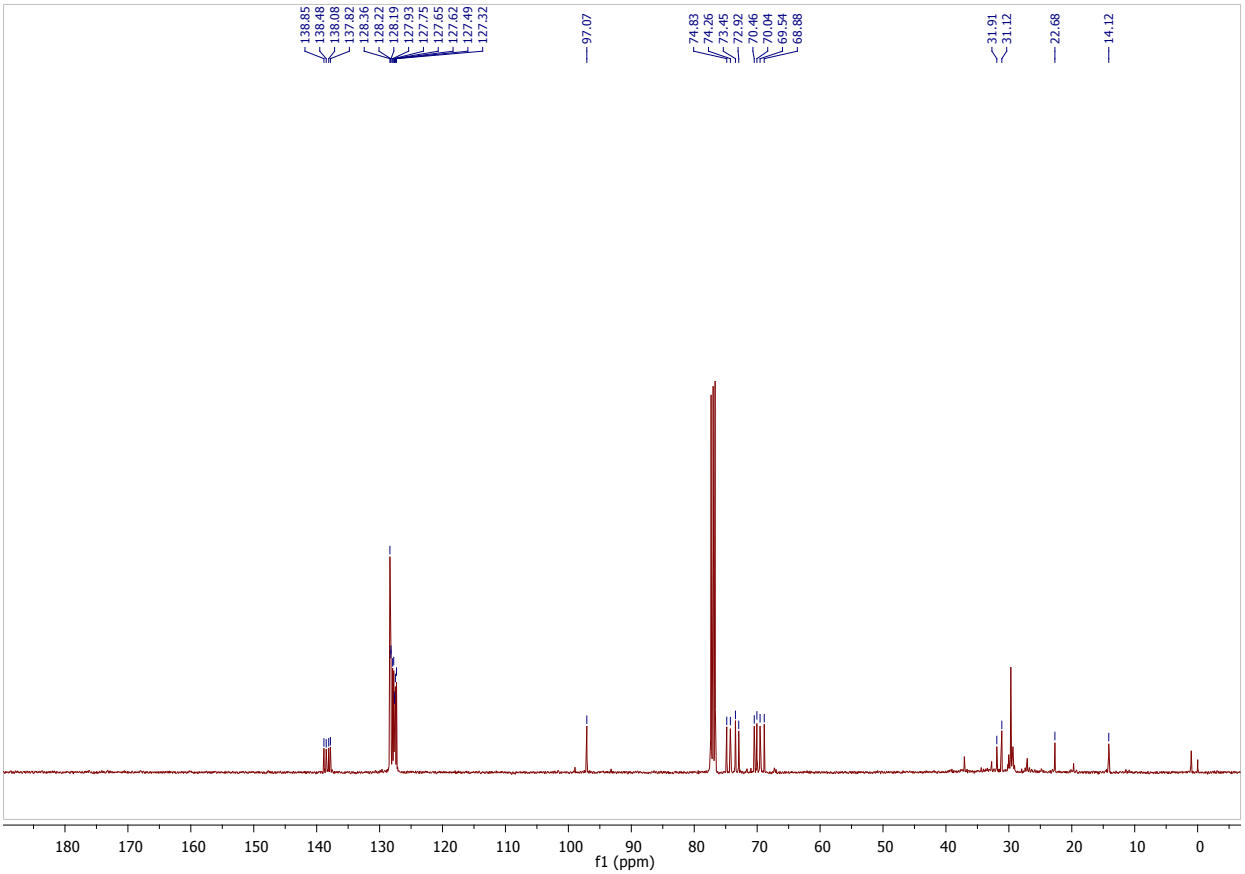
^{13}C NMR spectrum of compound **7** in $CDCl_3$ (101 MHz)



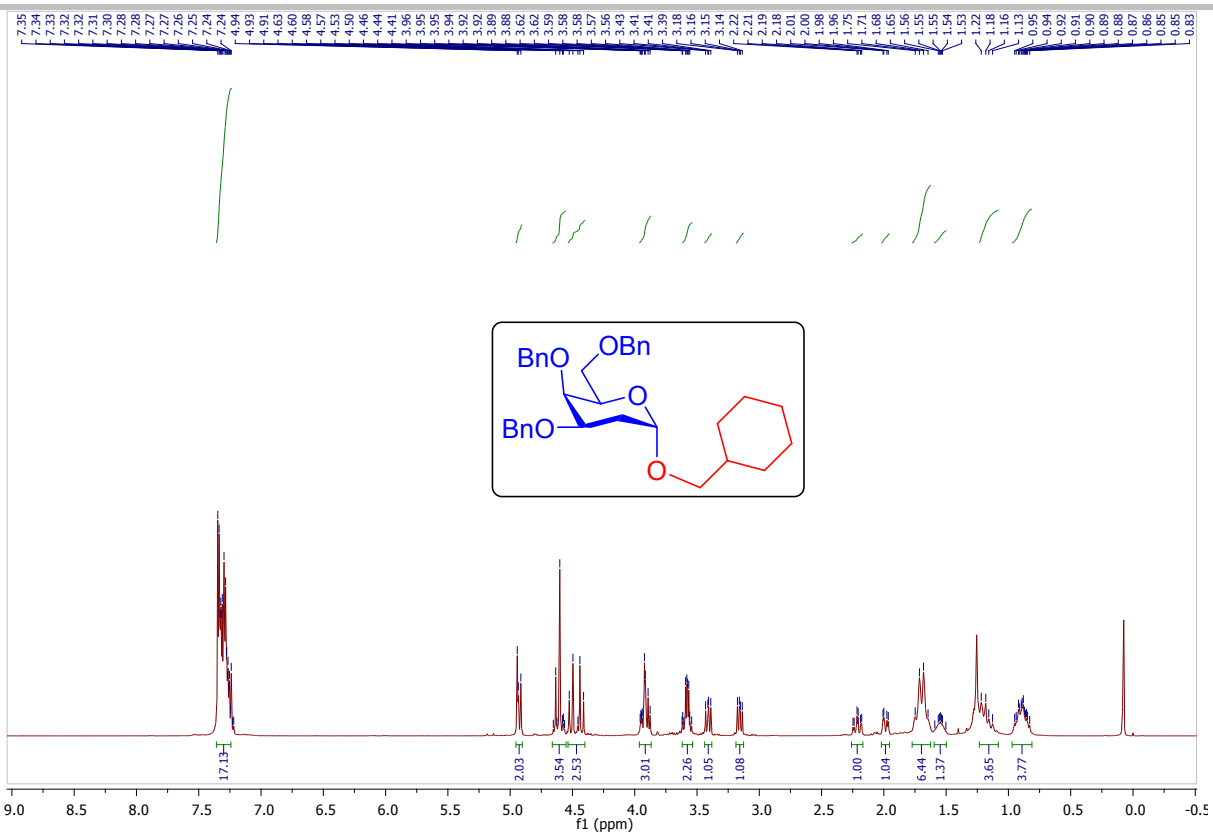
^{1}H NMR spectrum of compound **8** in $CDCl_3$ (400 MHz)



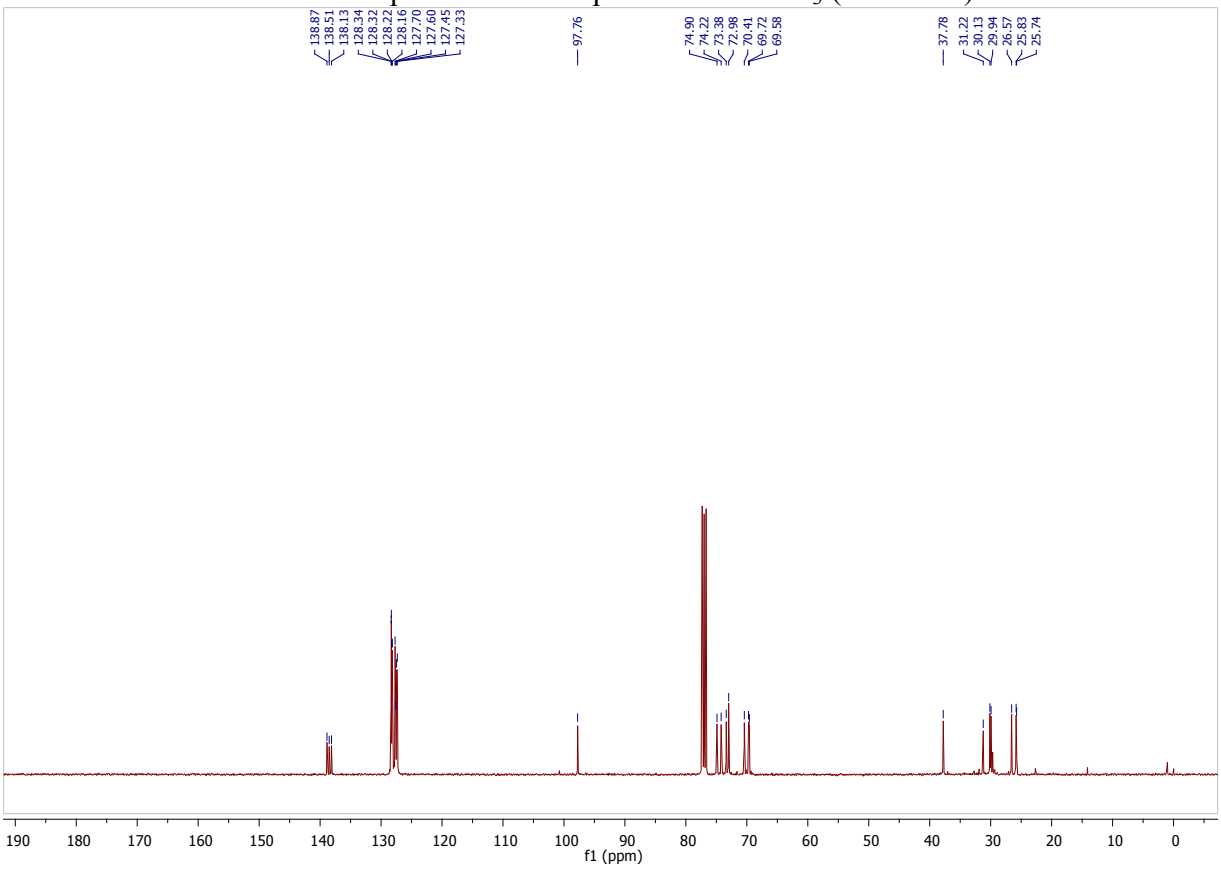
^{13}C NMR spectrum of compound **8** in $CDCl_3$ (101 MHz)



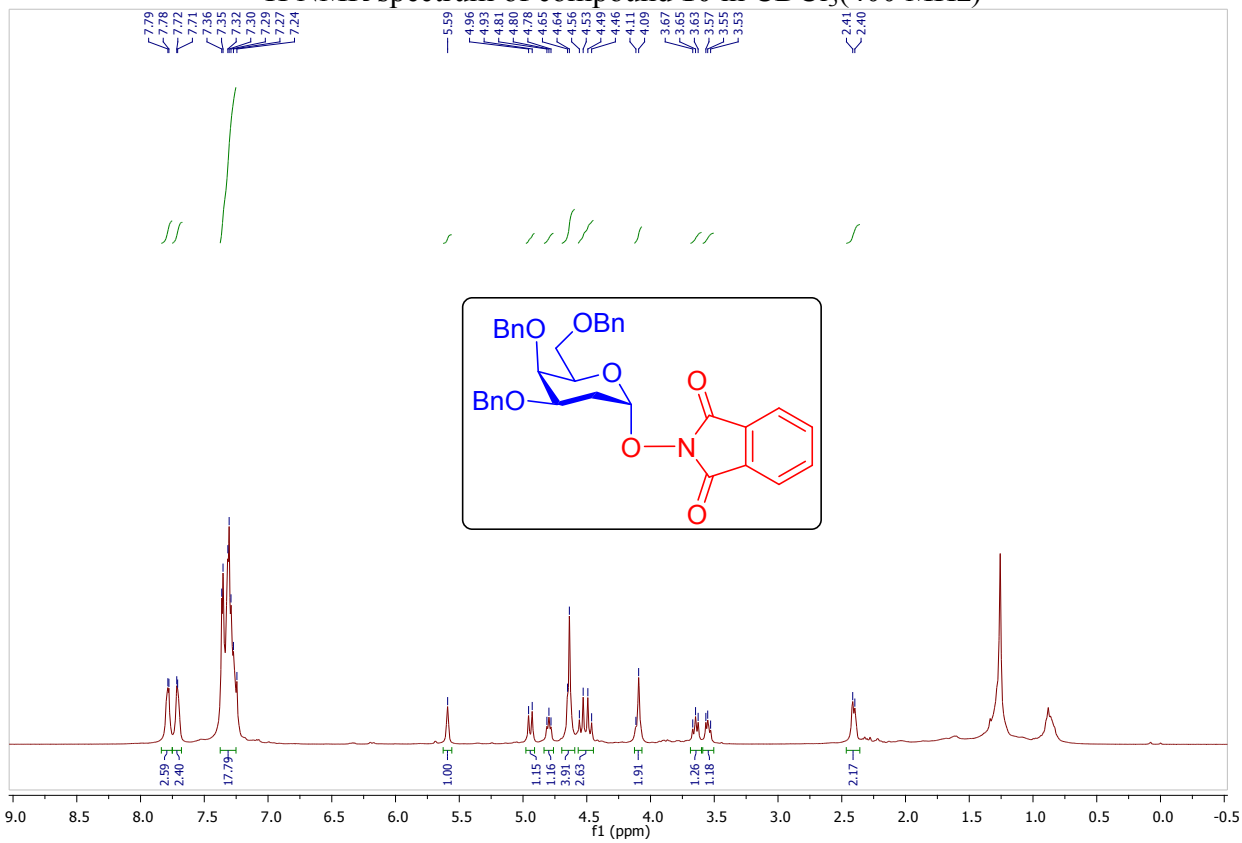
^{1}H NMR spectrum of compound **9** in $CDCl_3$ (400 MHz)



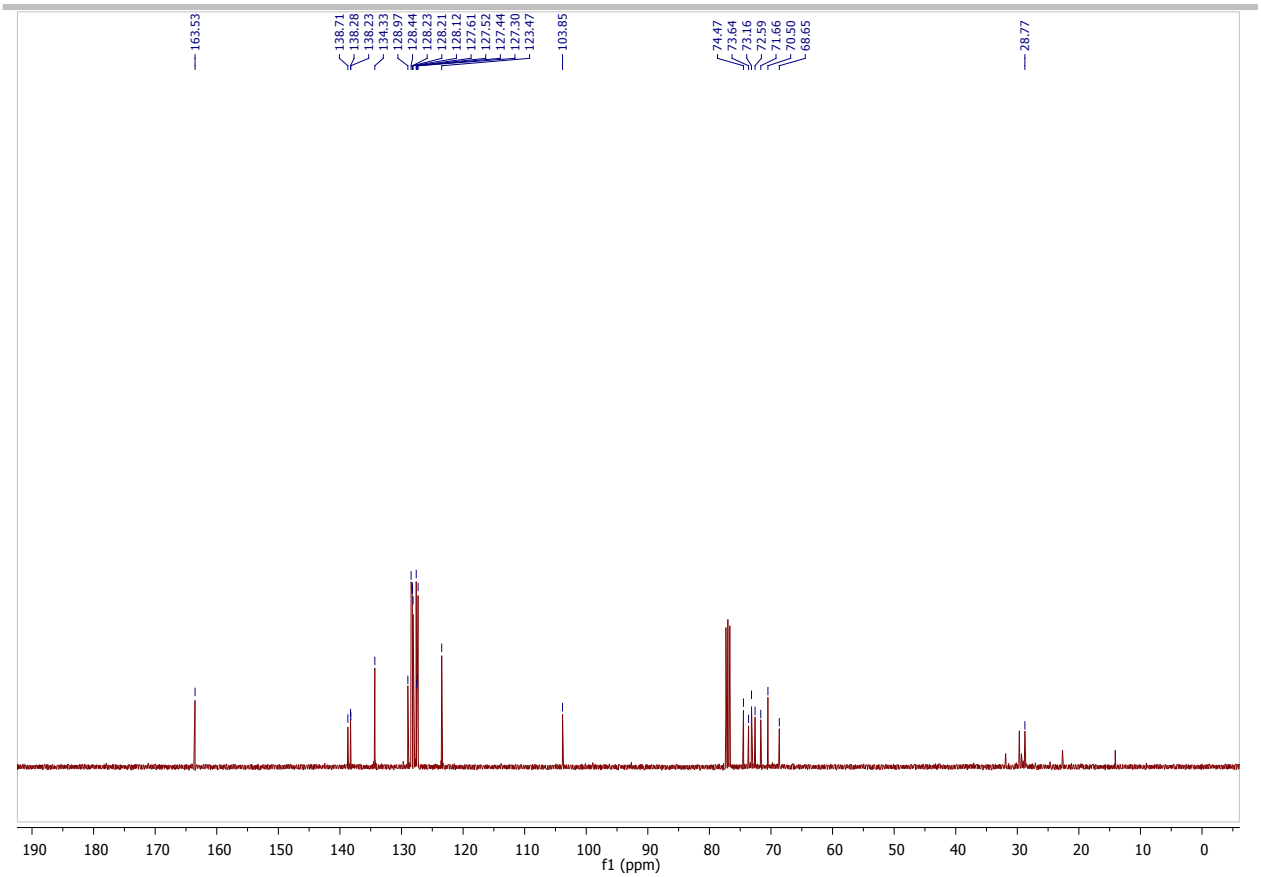
^{13}C NMR spectrum of compound **9** in $CDCl_3$ (101 MHz)



^{1}H NMR spectrum of compound **10** in $CDCl_3$(400 MHz)



^{13}CNMR spectrum of compound **10**in $CDCl_3$ (101 MHz)



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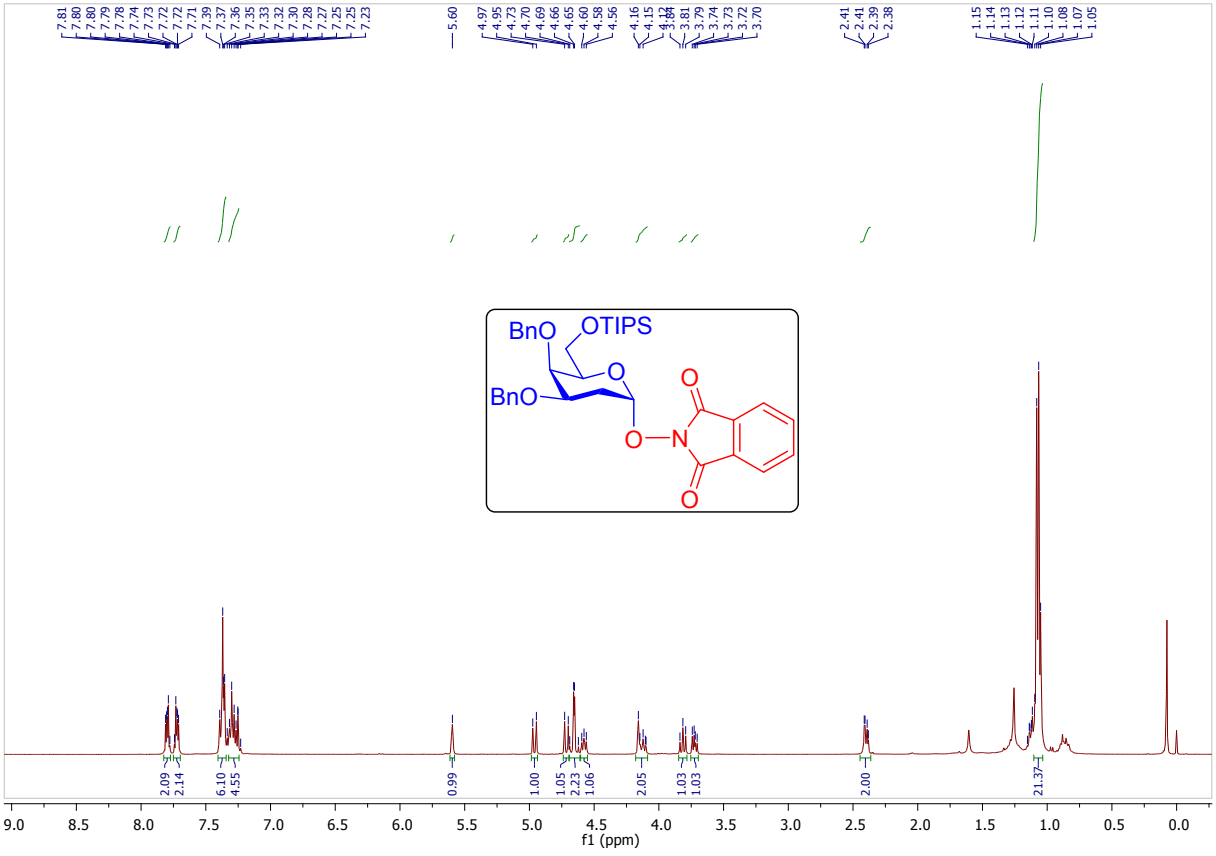
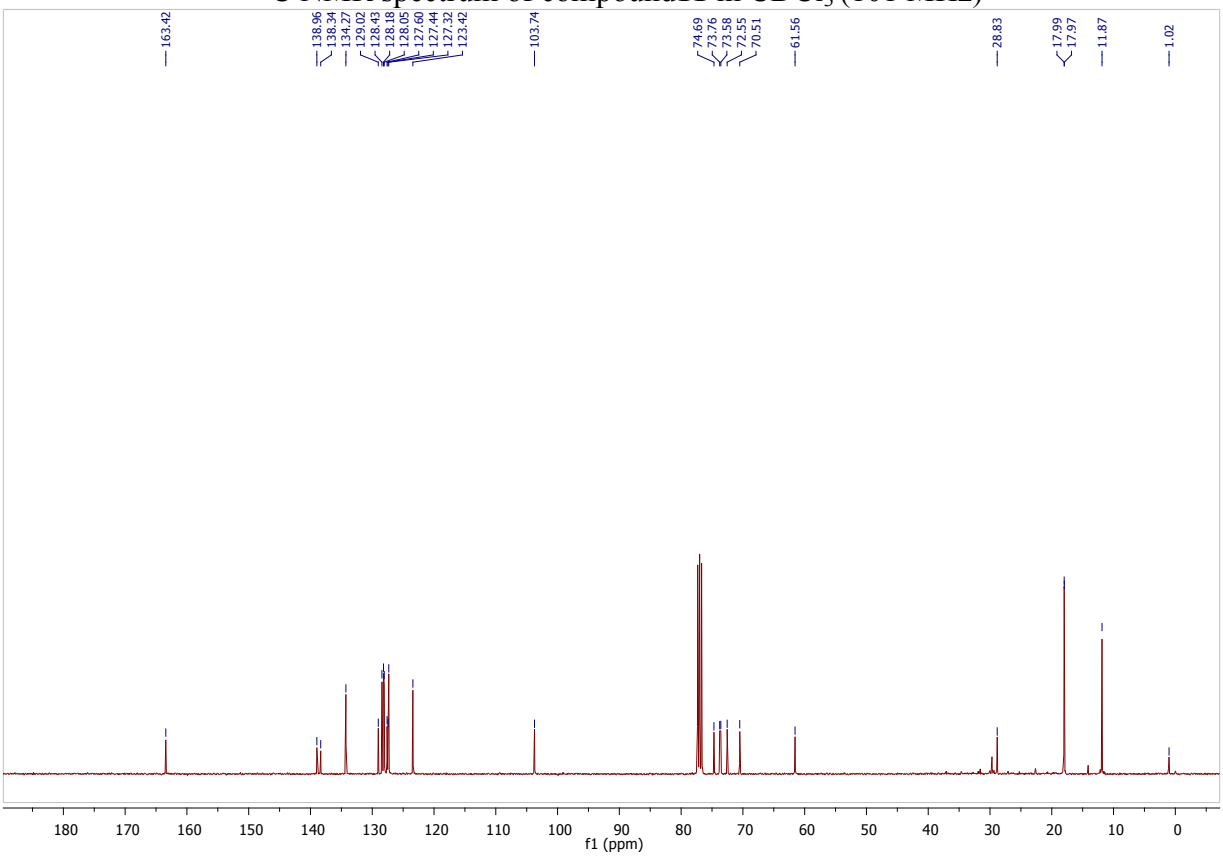
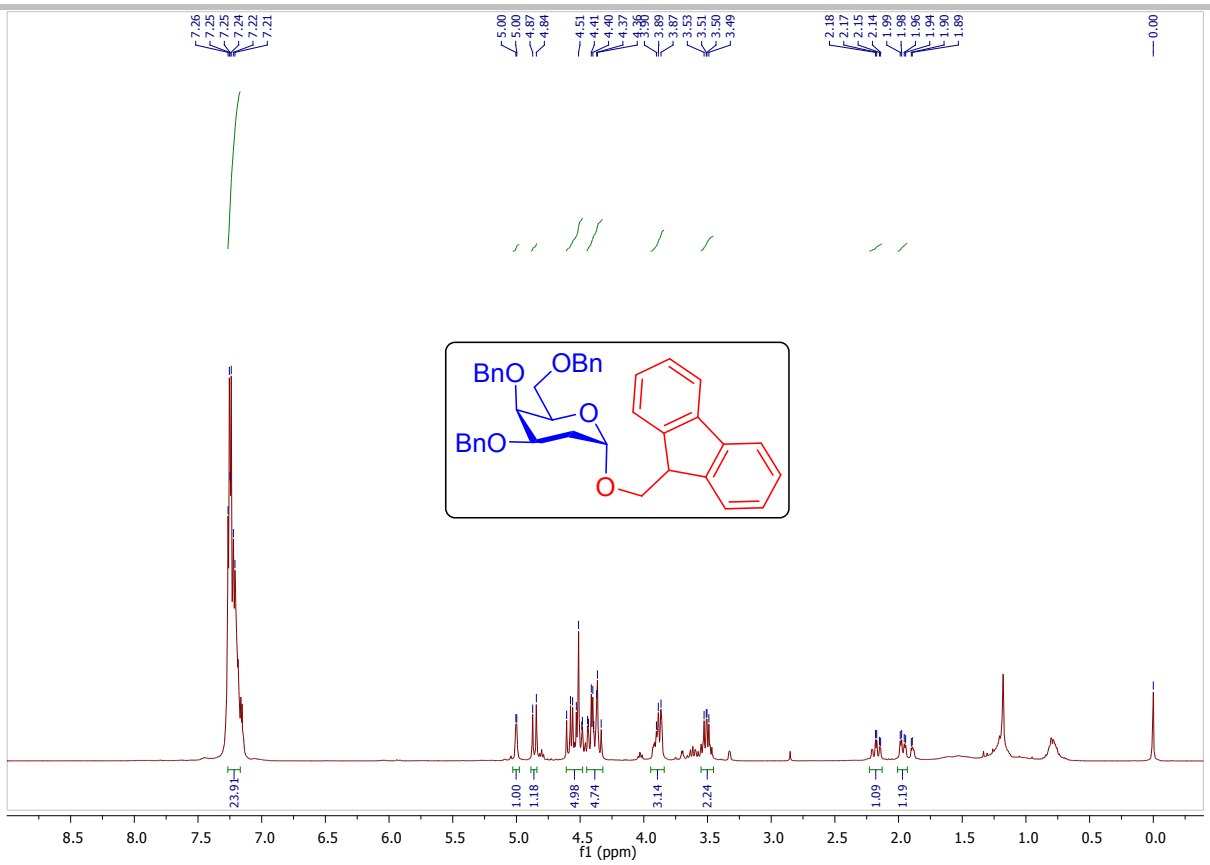


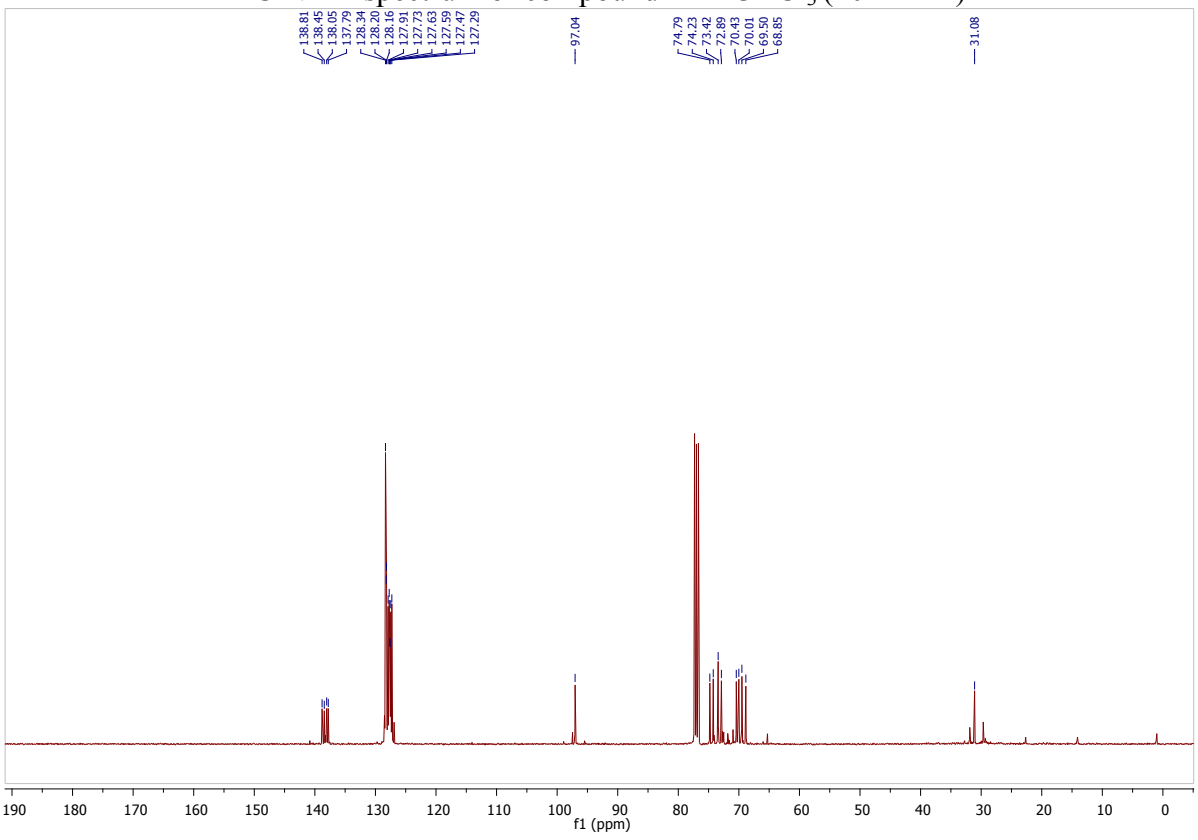
^{13}C NMR spectrum of compound**11** in $CDCl_3$ (101 MHz)



^{1}H NMR spectrum of compound **12** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **12** in $CDCl_3$ (101 MHz)



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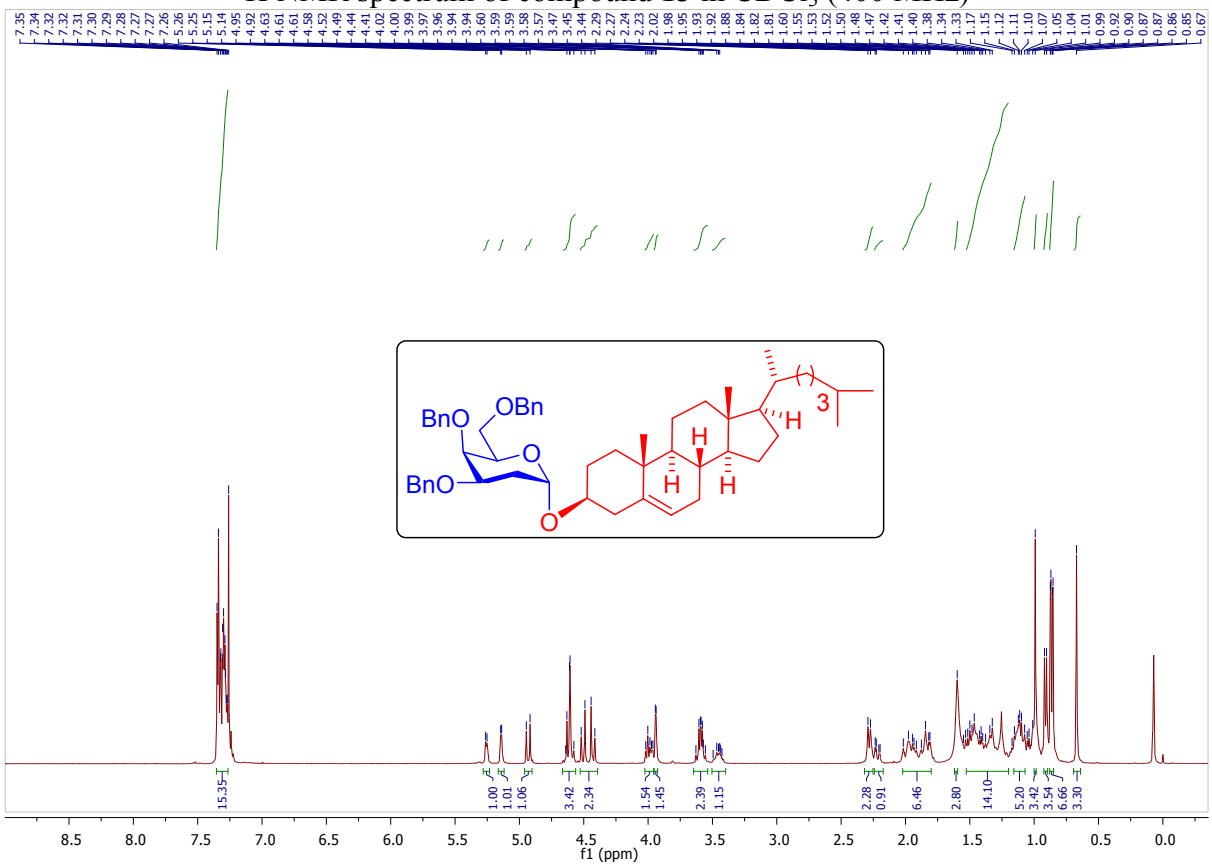
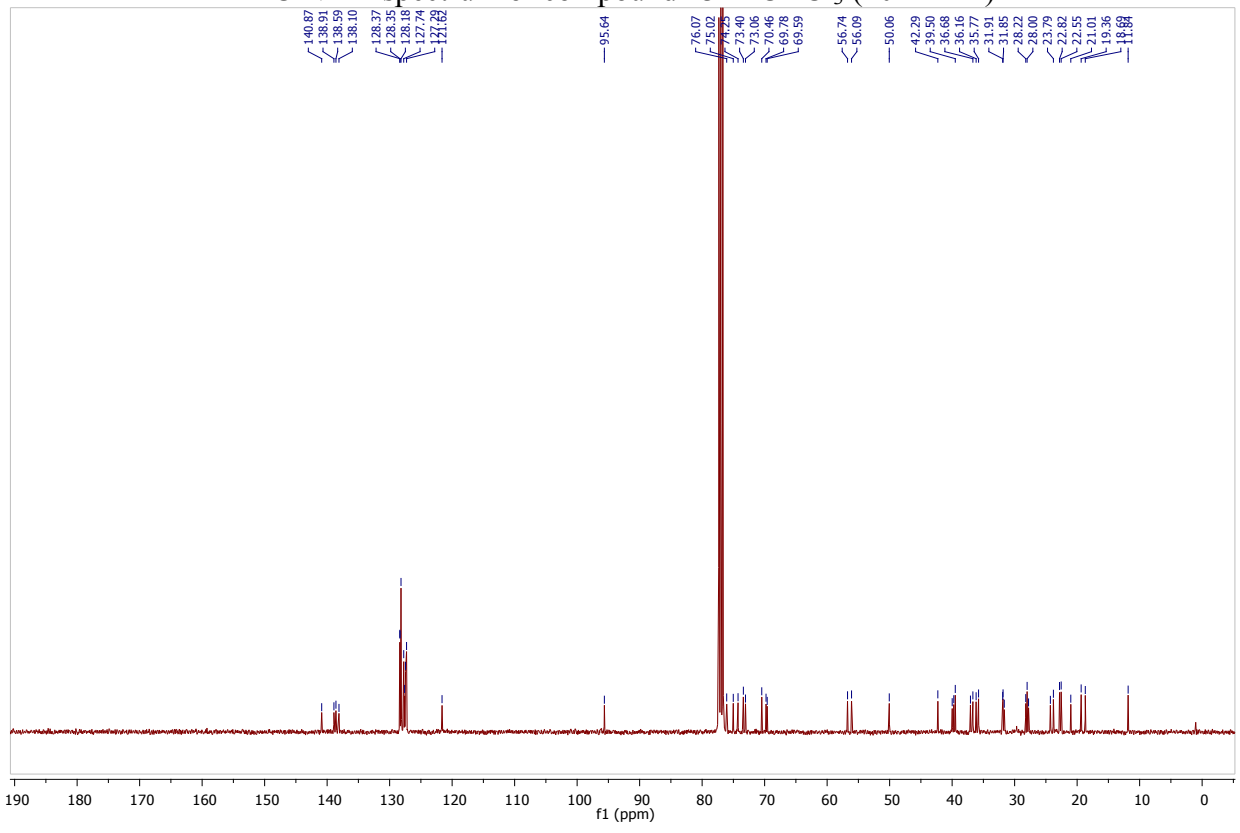
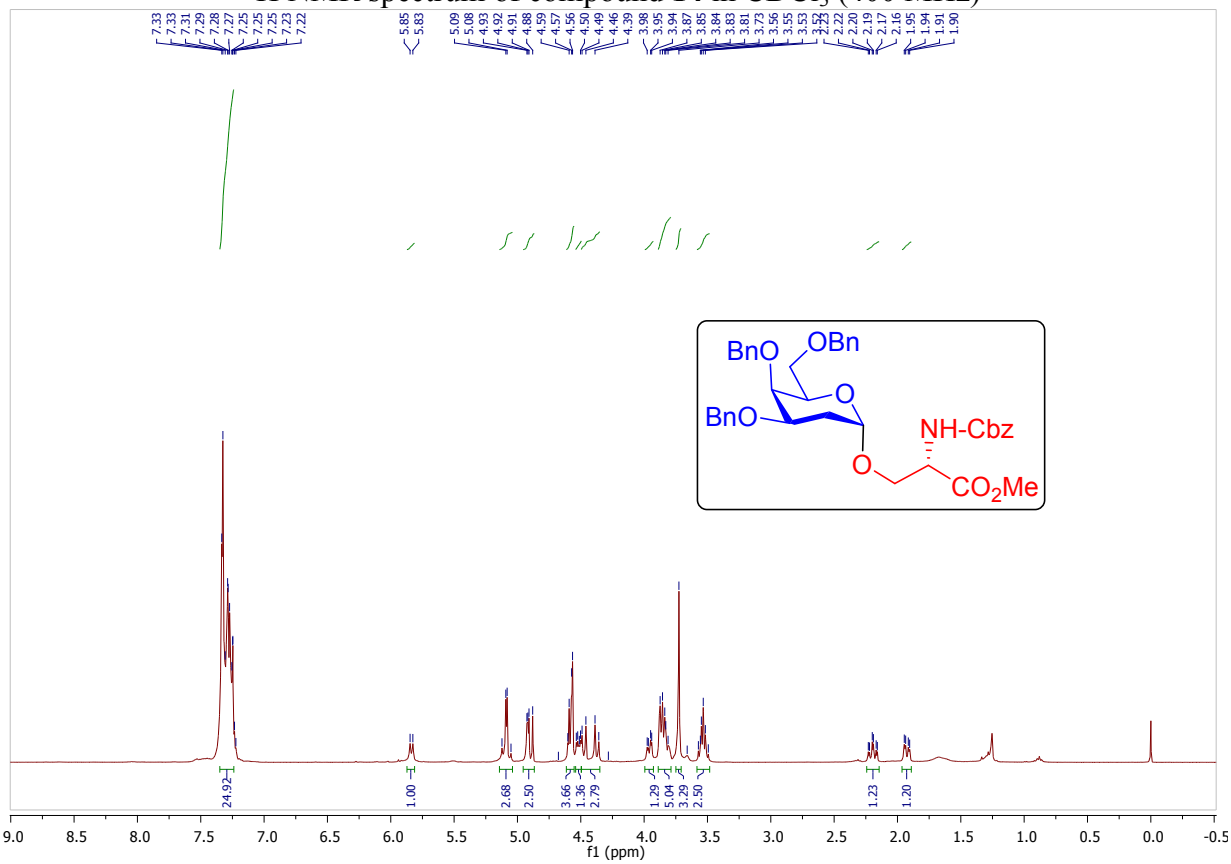


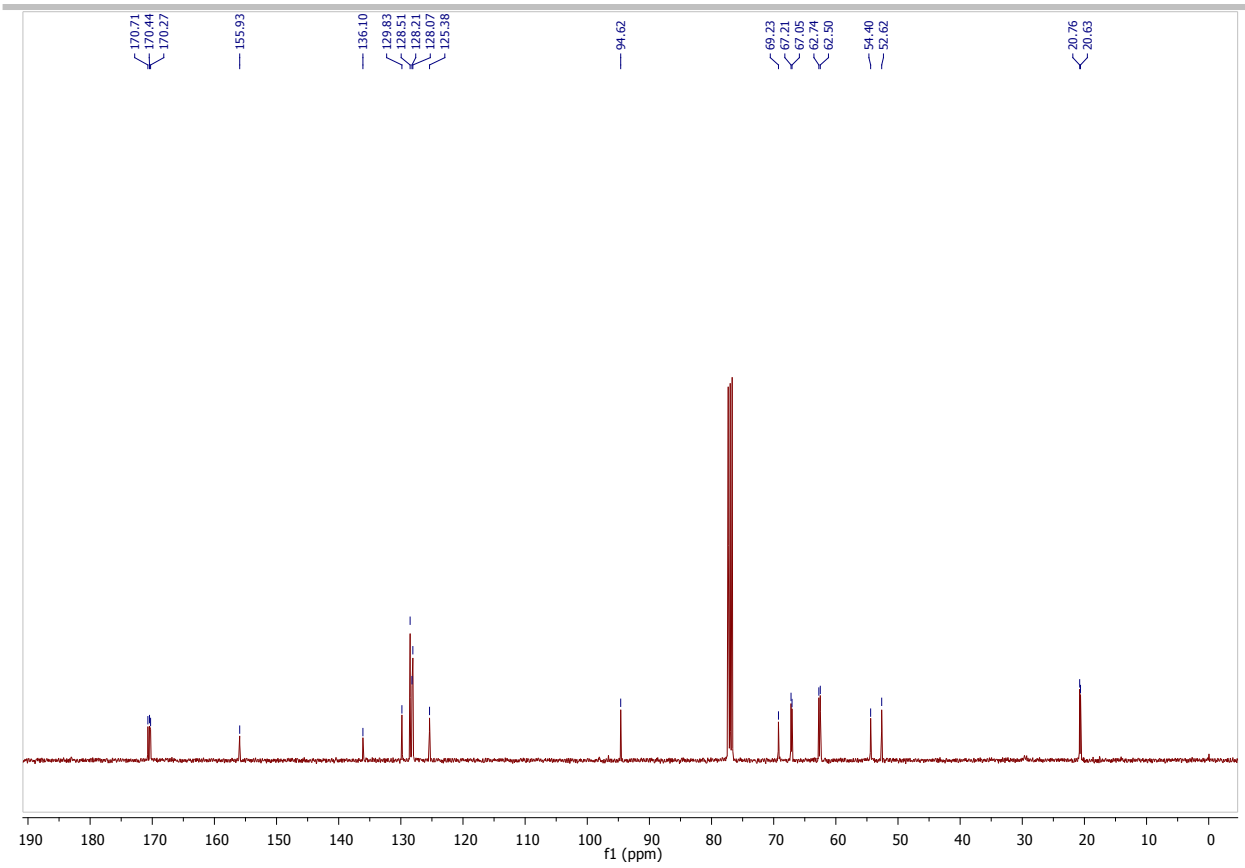
^{13}C NMR spectrum of compound **13** in $CDCl_3$ (101 MHz)



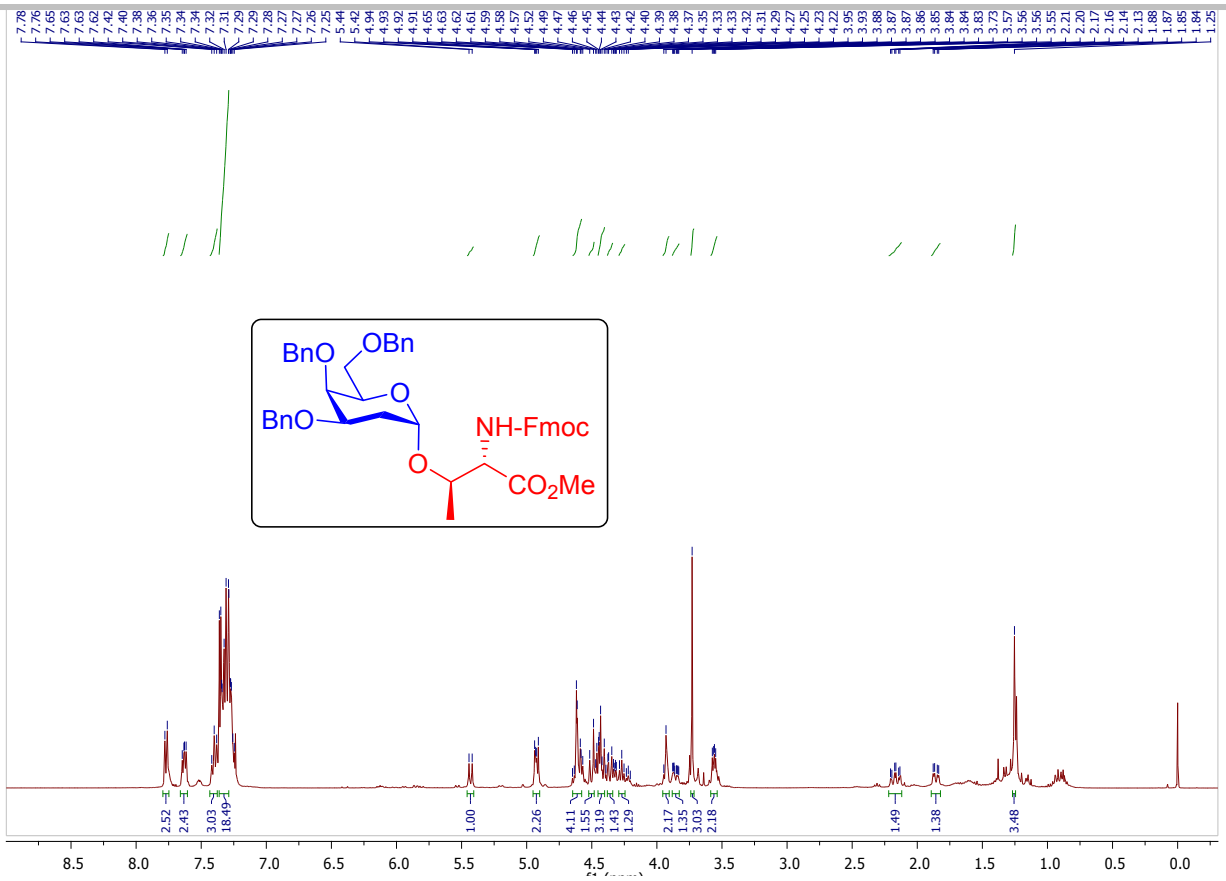
^{1}H NMR spectrum of compound **14** in $CDCl_3$ (400 MHz)



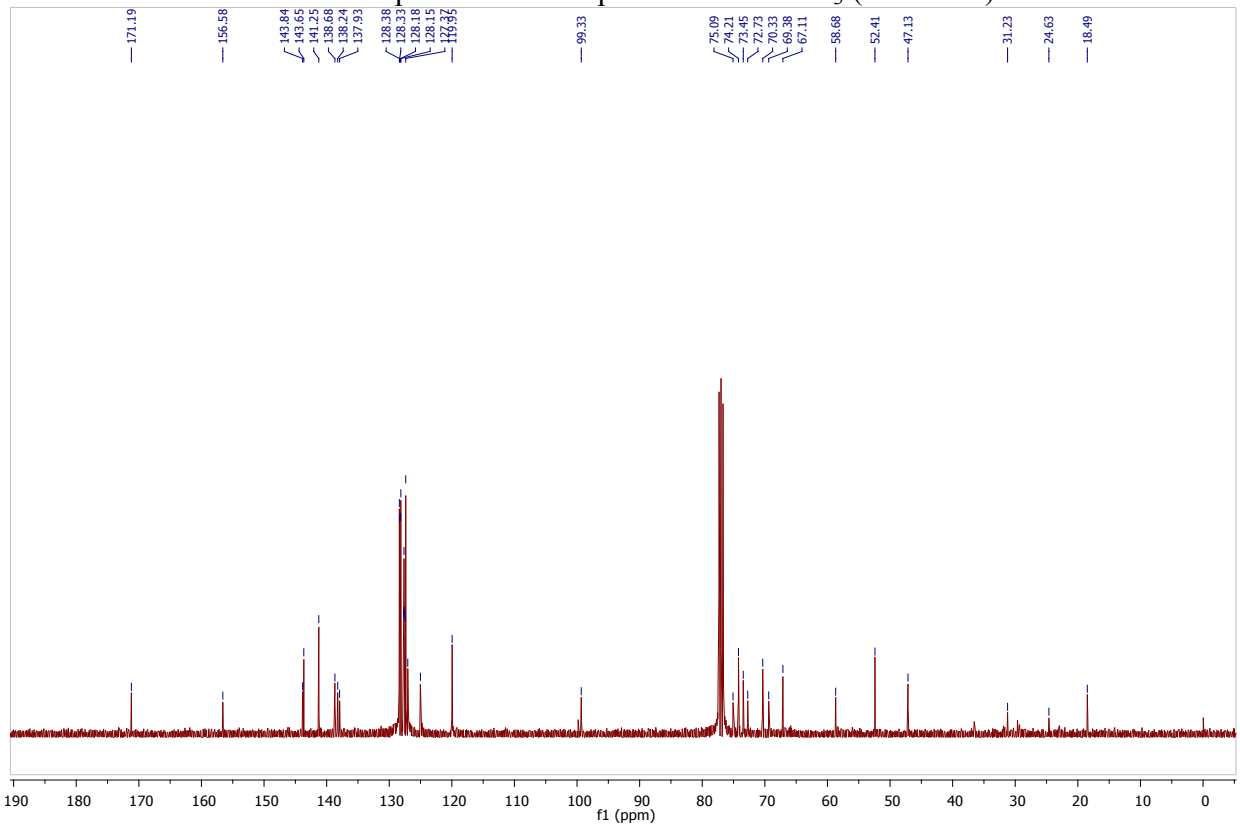
^{13}C NMR spectrum of compound **14** in $CDCl_3$ (101 MHz)



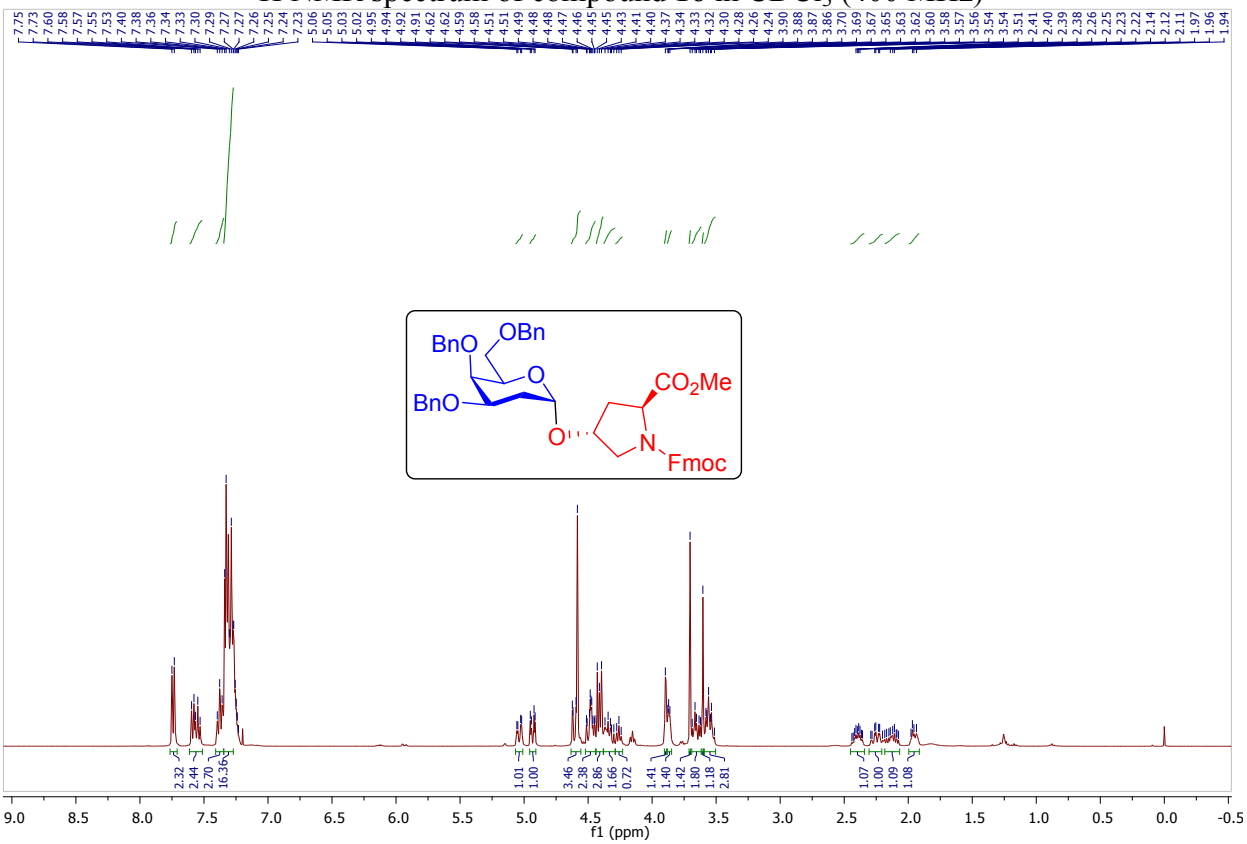
^{1}H NMR spectrum of compound **15** in $CDCl_3$ (400 MHz)



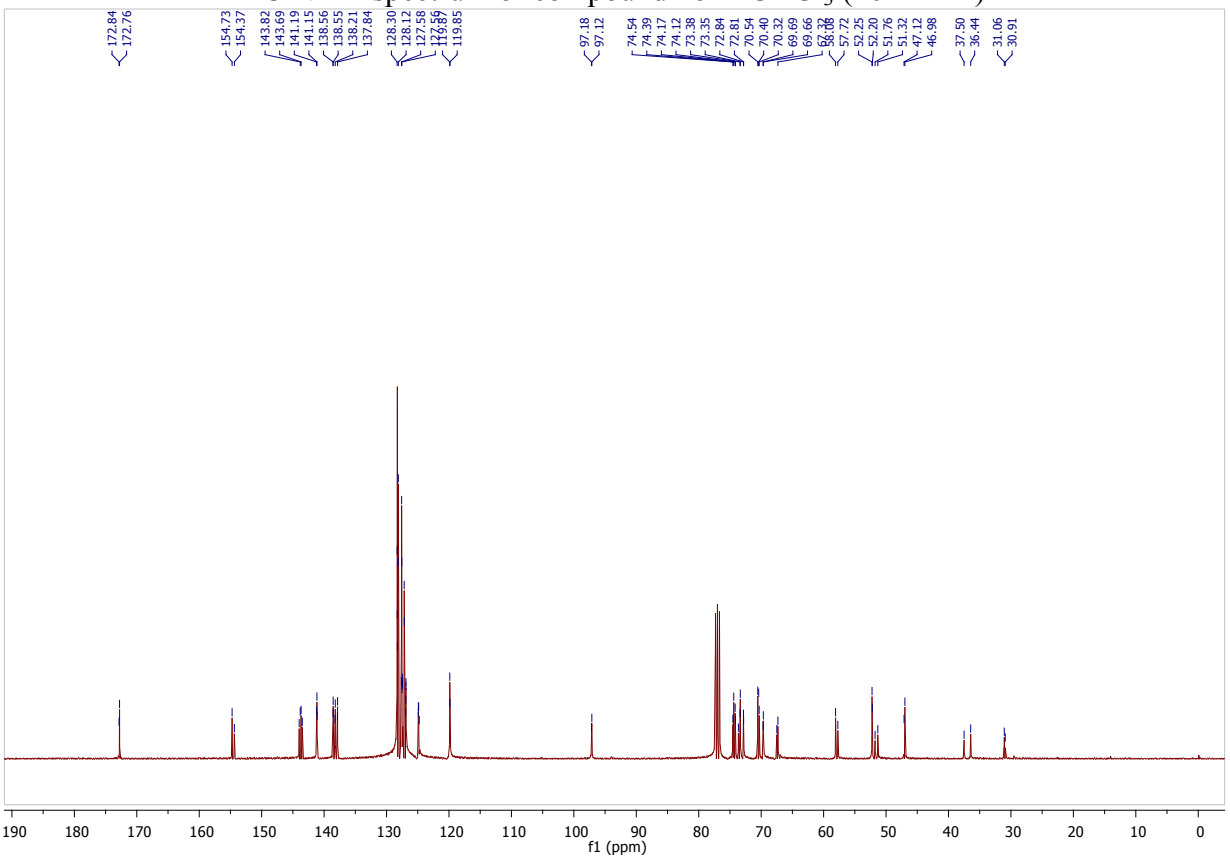
^{13}C NMR spectrum of compound **15** in $CDCl_3$ (101 MHz)



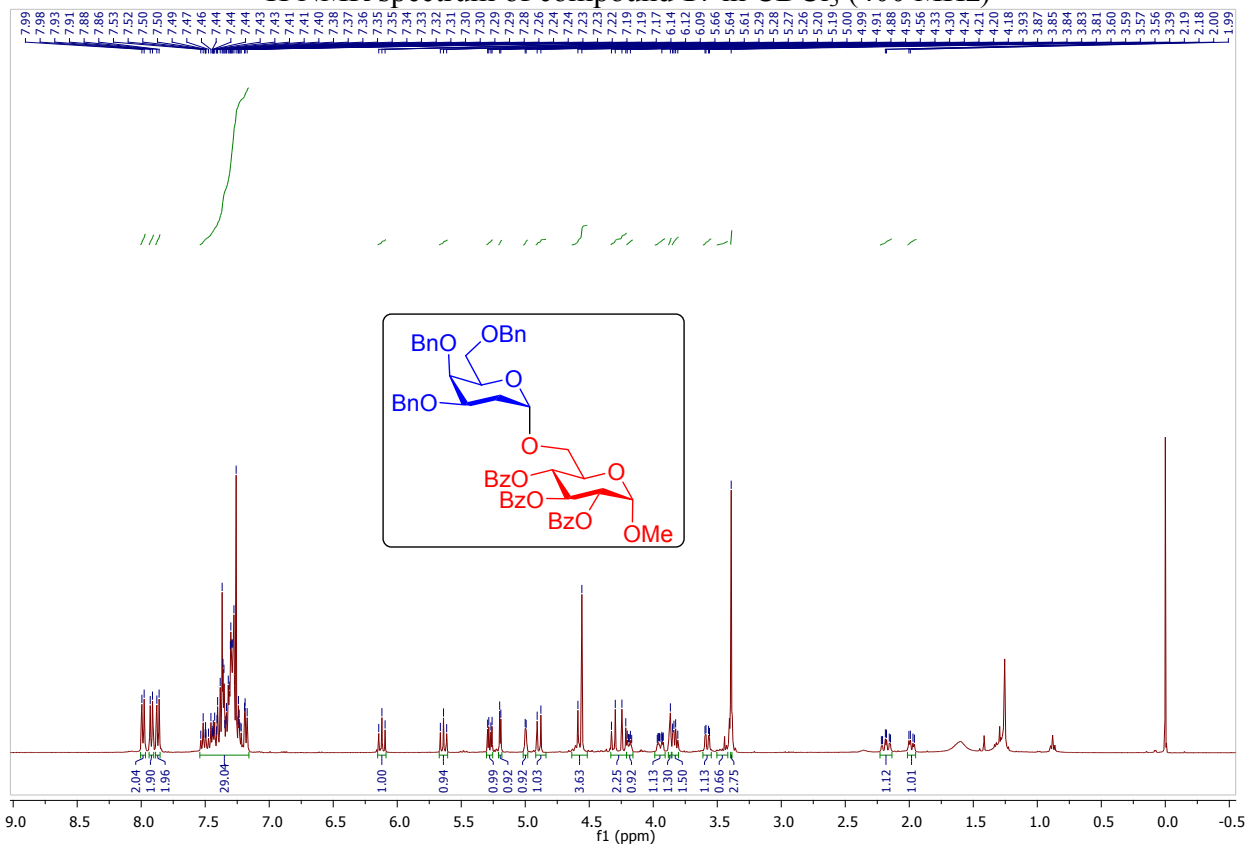
^{1}H NMR spectrum of compound **16** in $CDCl_3$ (400 MHz)



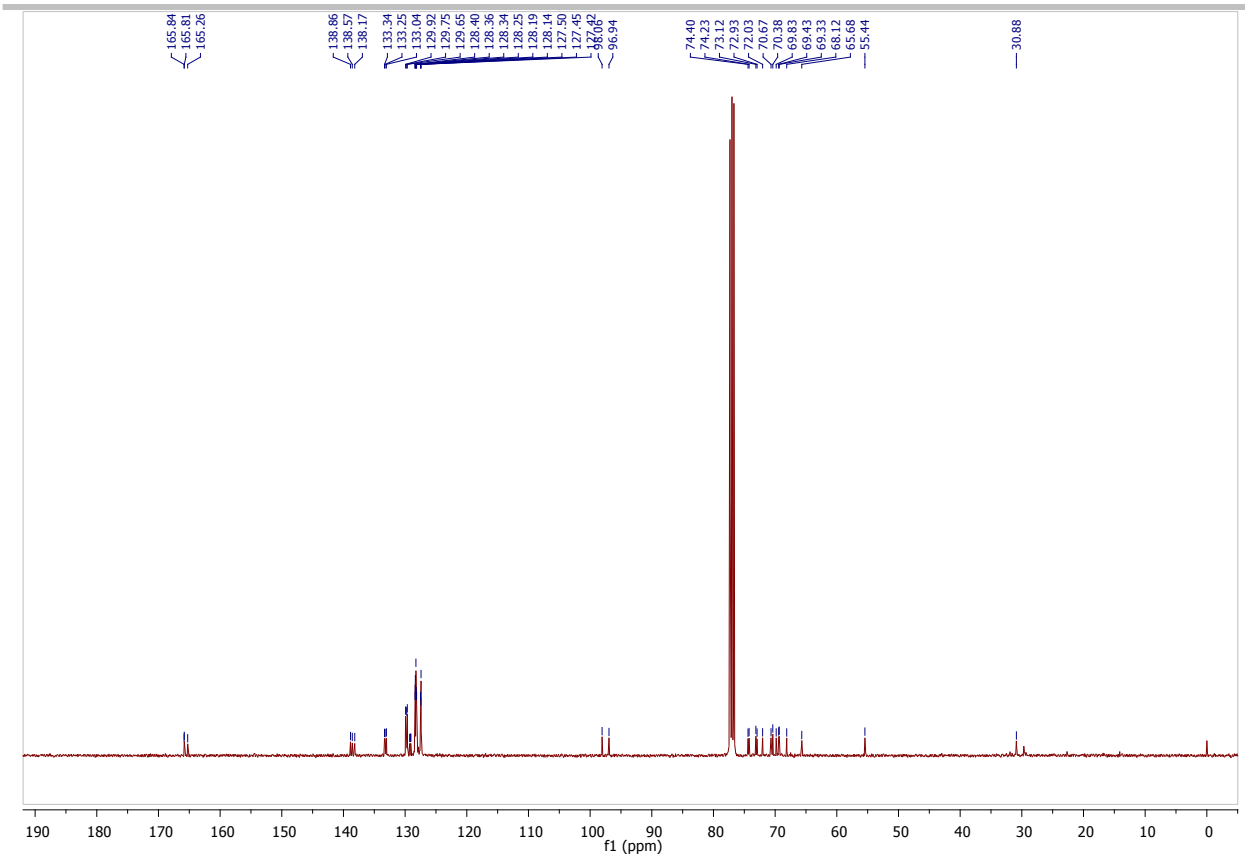
^{13}C NMR spectrum of compound **16** in $CDCl_3$ (101 MHz)



^{1}H NMR spectrum of compound **17** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **17** in $CDCl_3$ (101 MHz)



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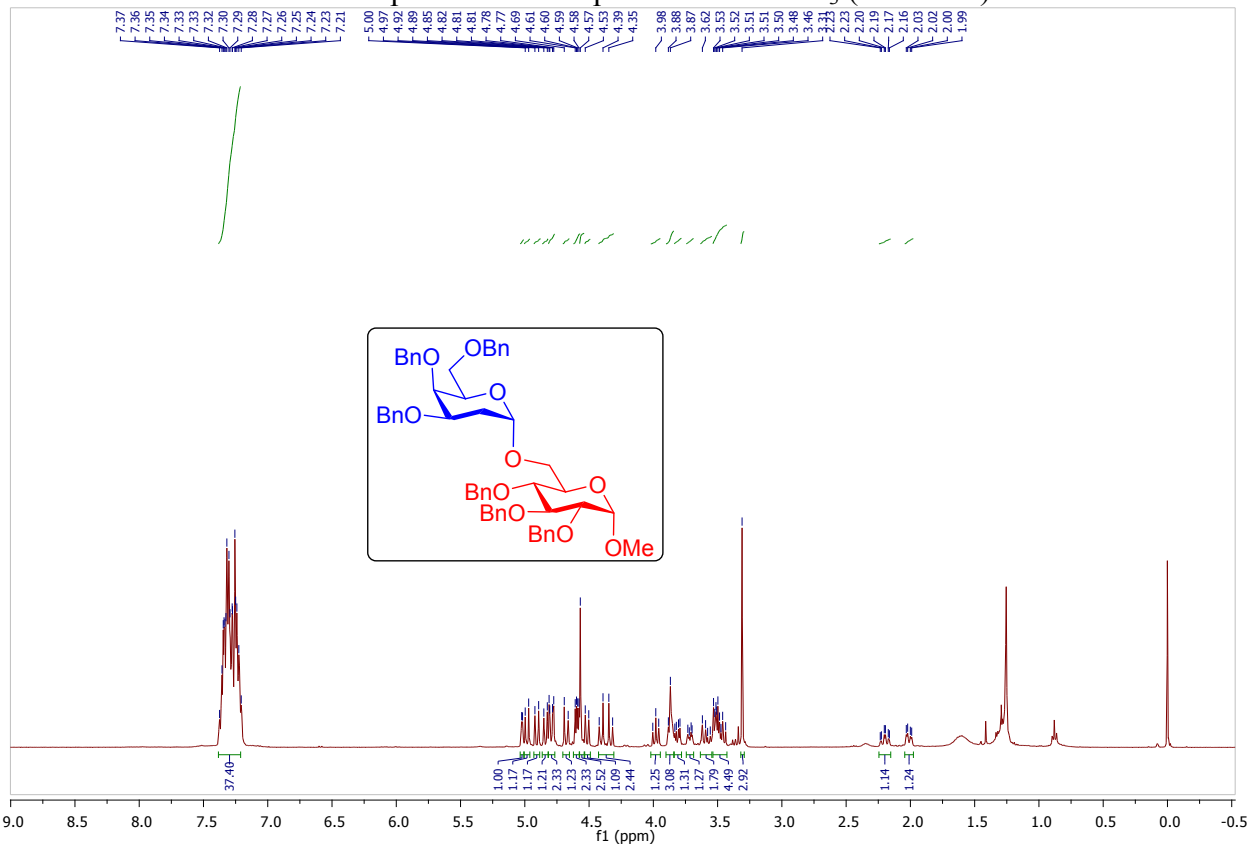
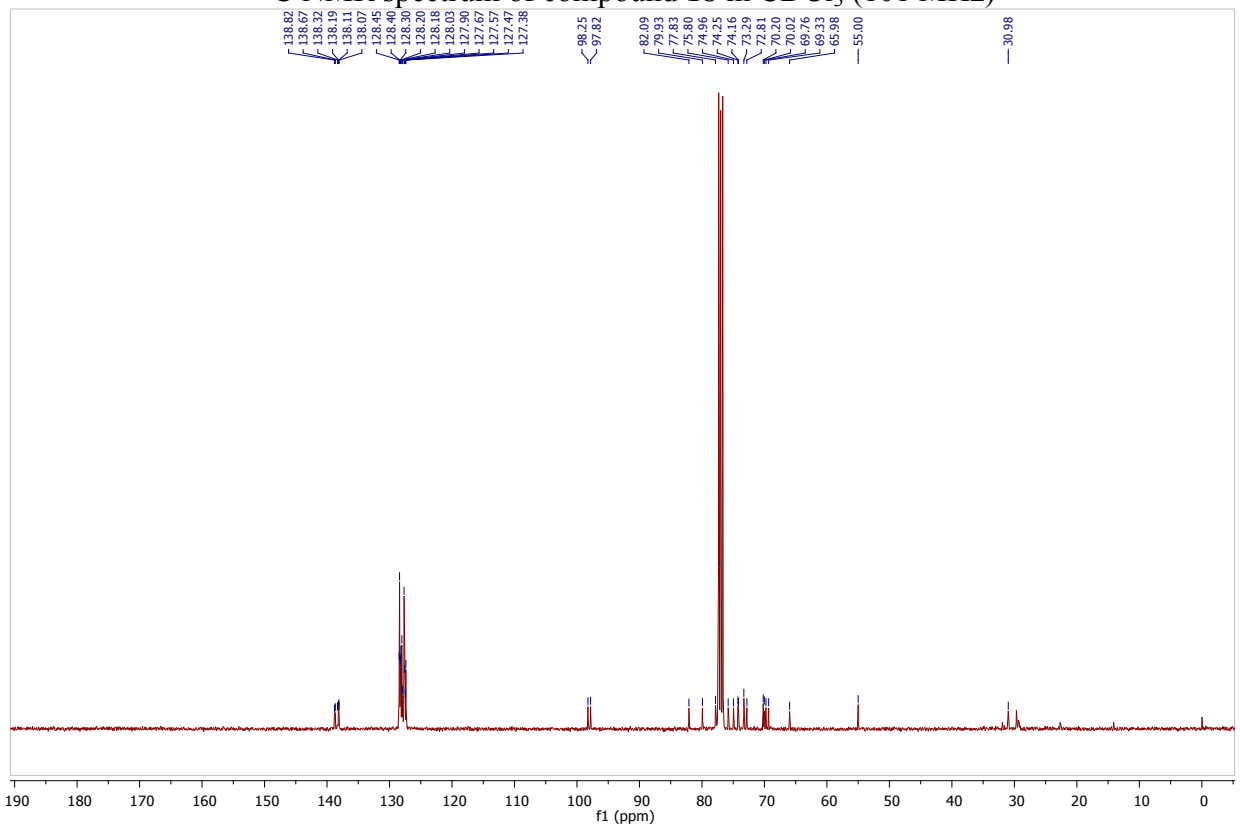
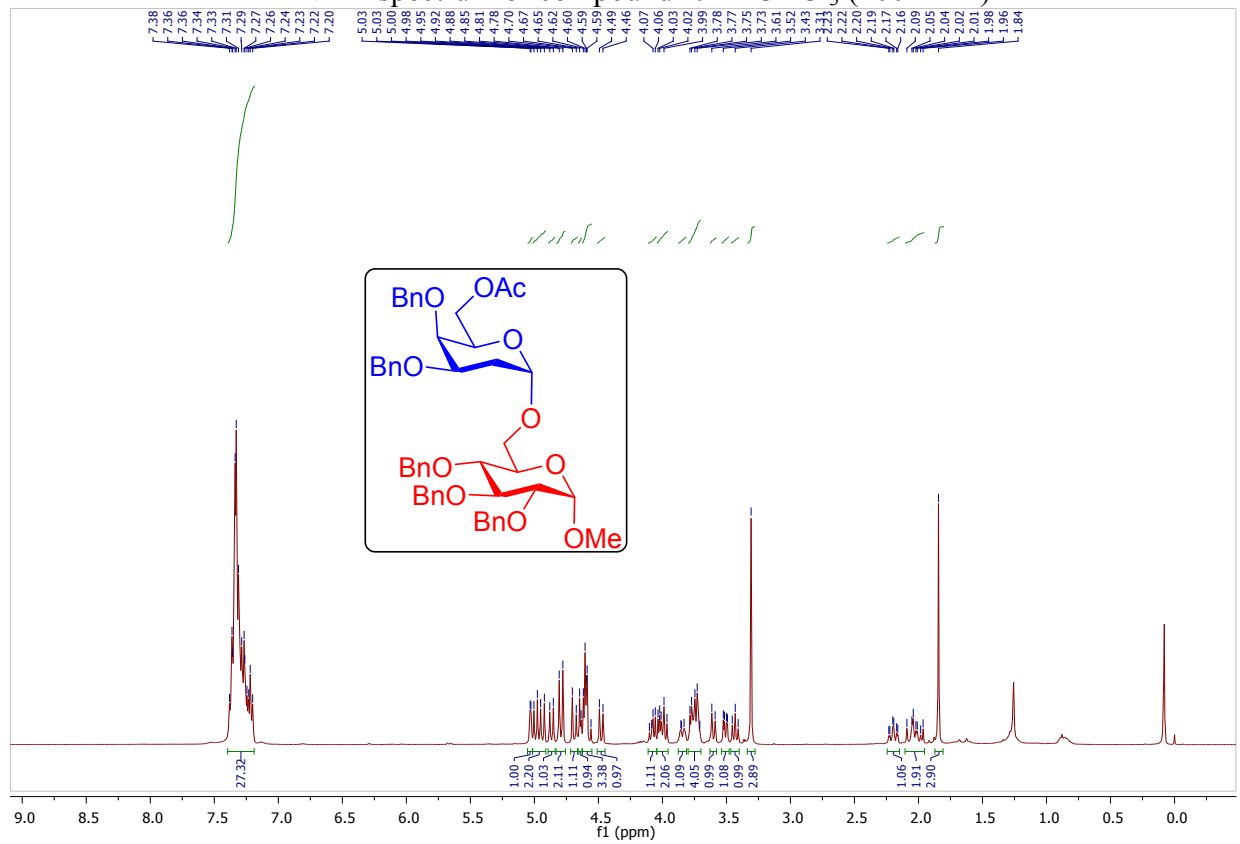


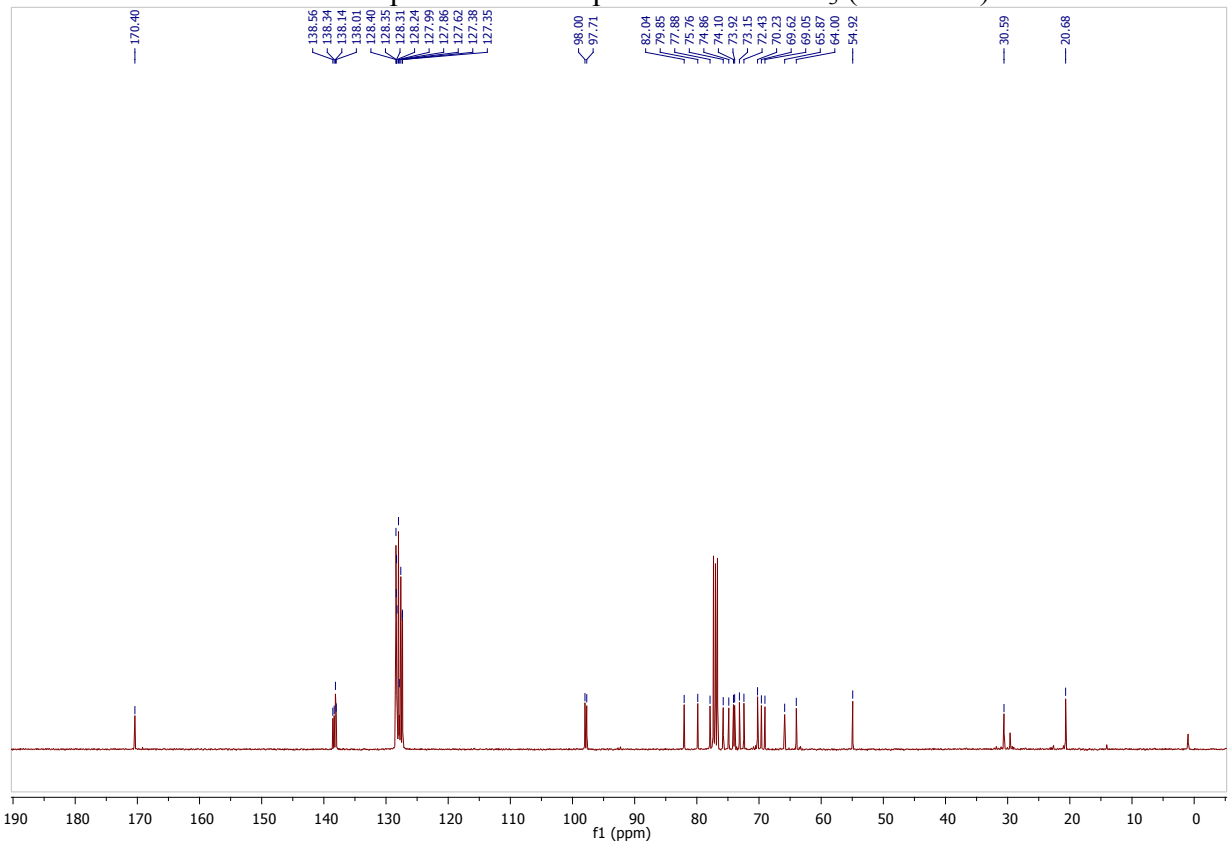
^{13}C NMR spectrum of compound **18** in $CDCl_3$ (101 MHz)



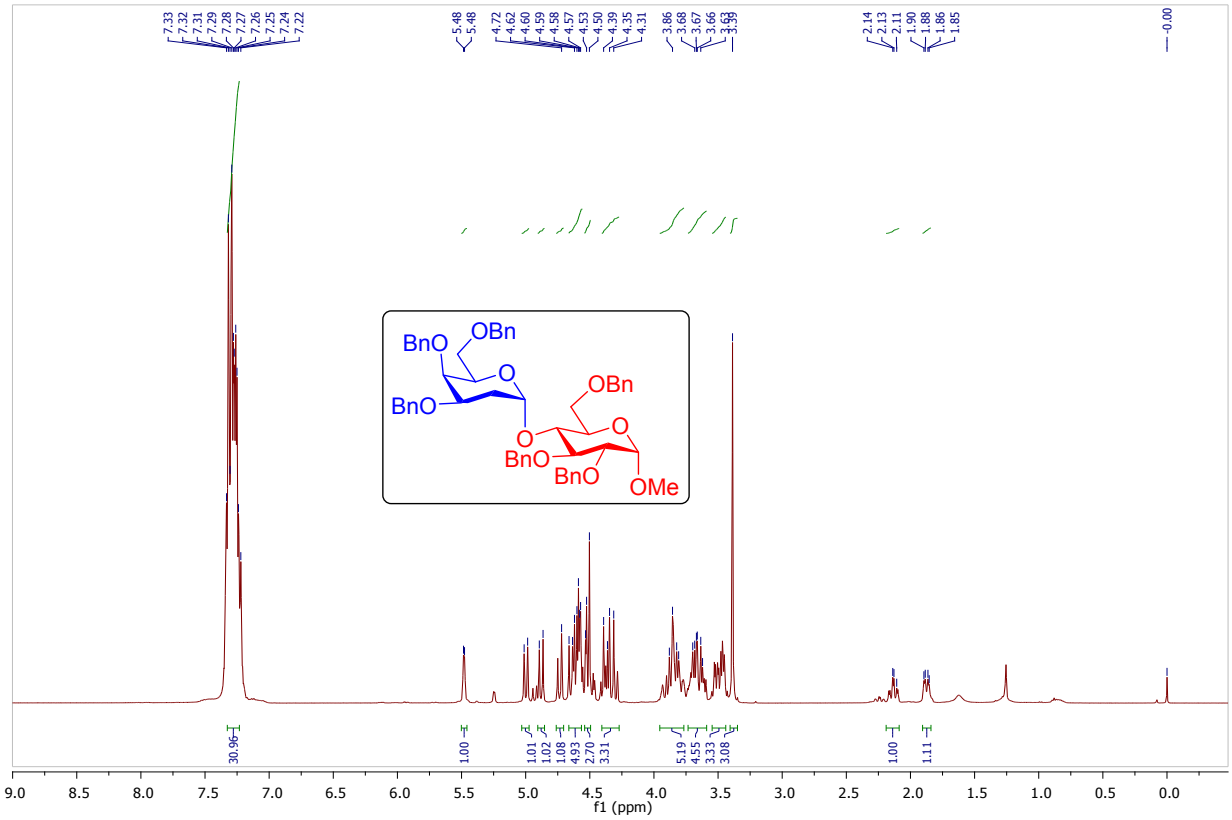
^{1}H NMR spectrum of compound **19** in $CDCl_3$ (400 MHz)



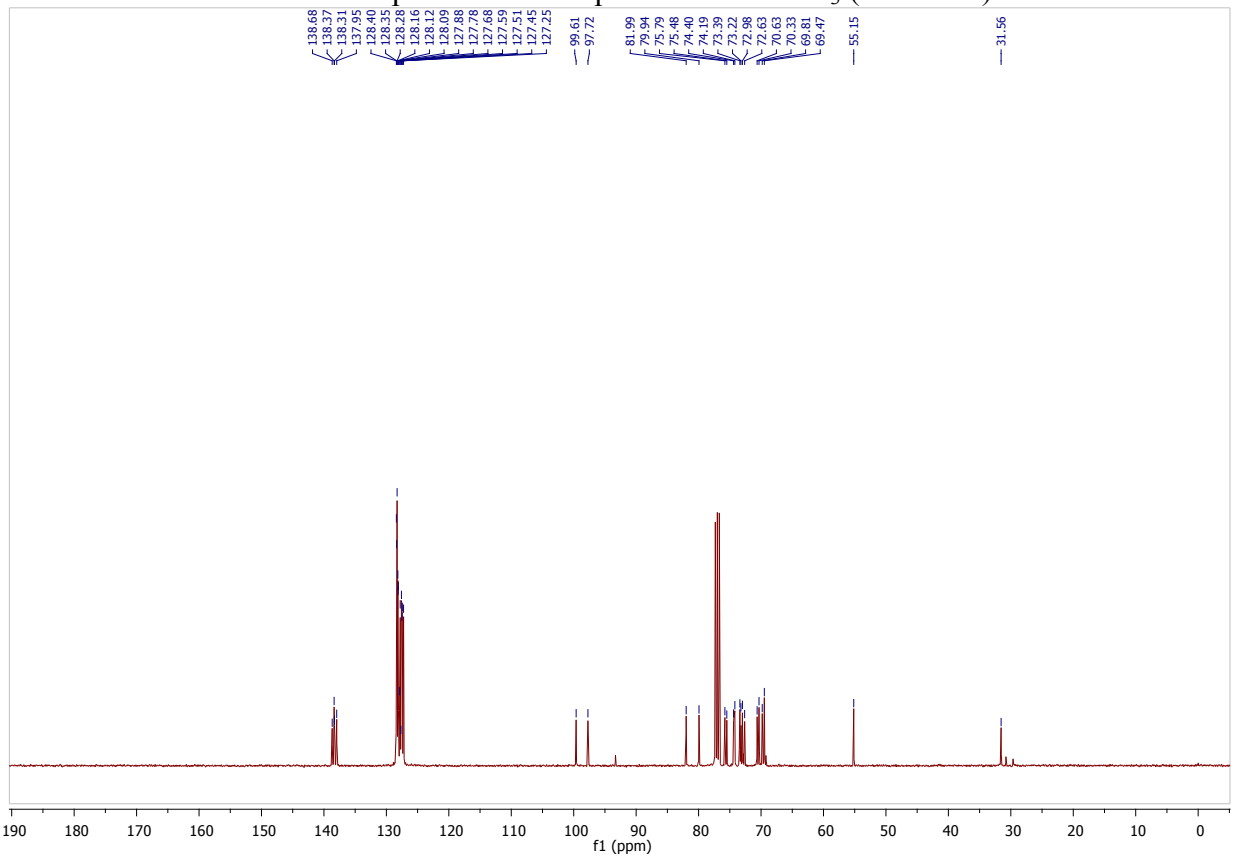
^{13}C NMR spectrum of compound **19** in $CDCl_3$ (101 MHz)



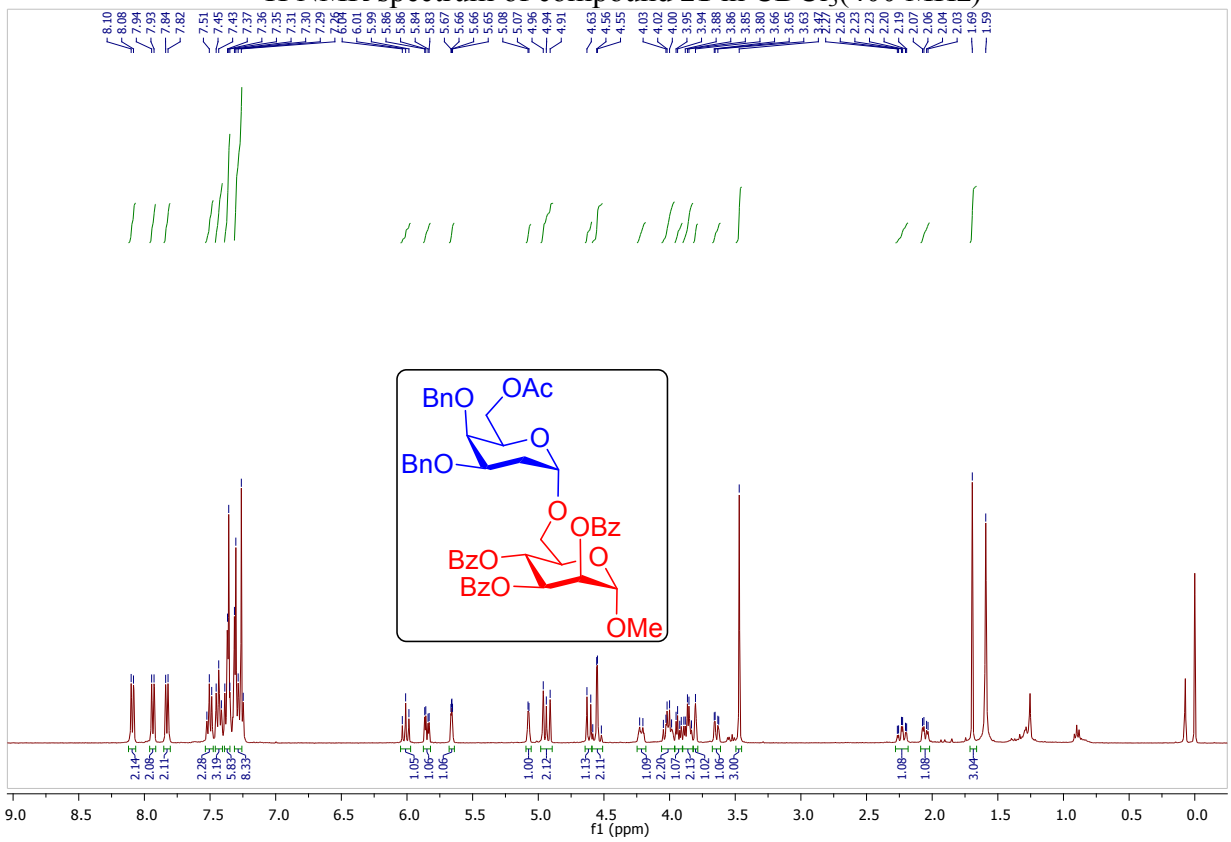
^{1}H NMR spectrum of compound **20** in $CDCl_3$ (400 MHz)



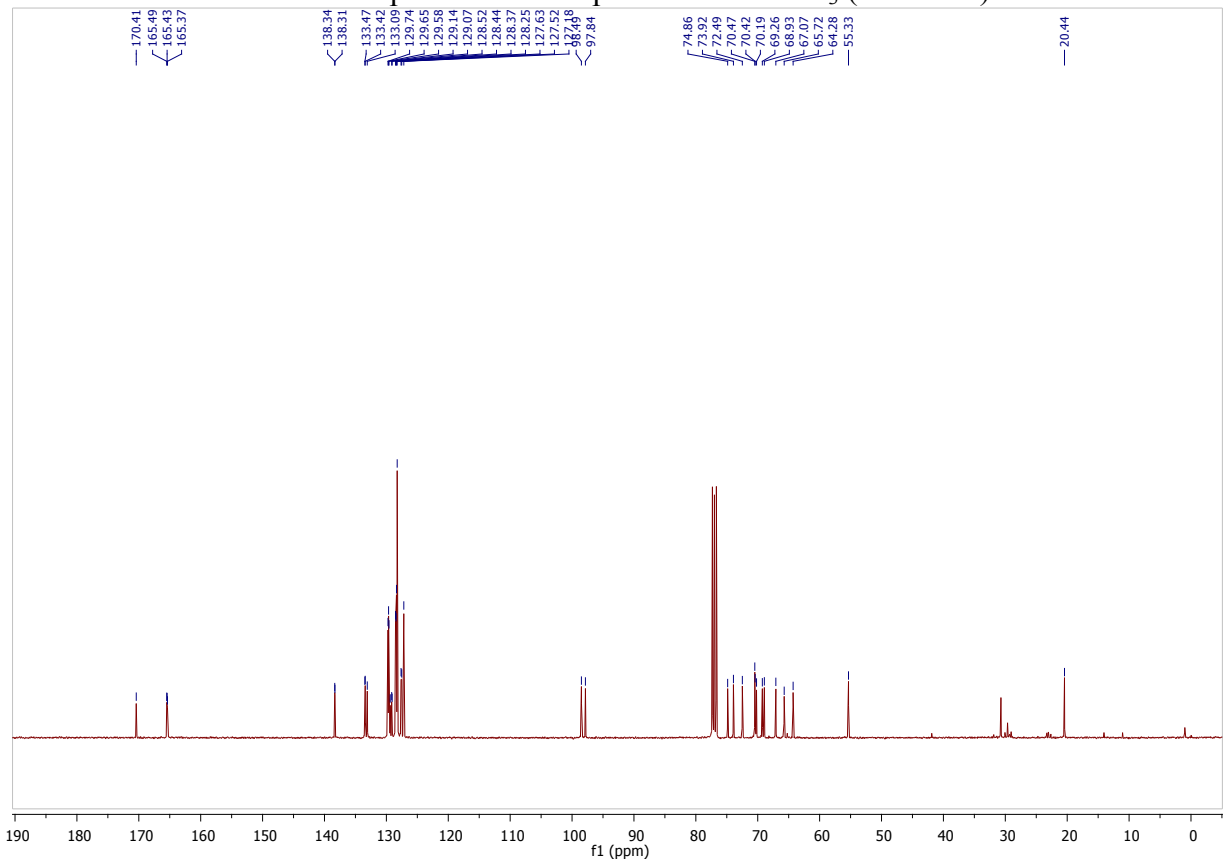
^{13}C NMR spectrum of compound **20** in $CDCl_3$ (101 MHz)



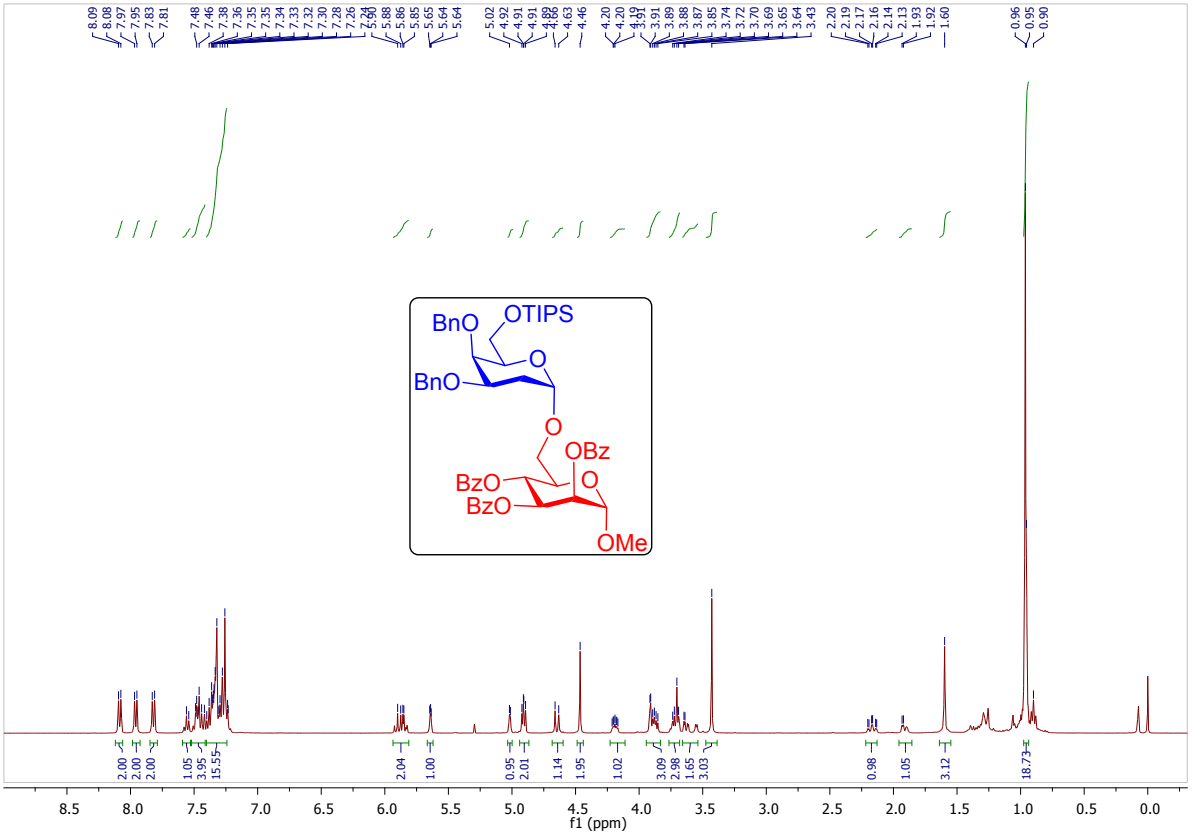
^{1}H NMR spectrum of compound **21** in $CDCl_3$(400 MHz)



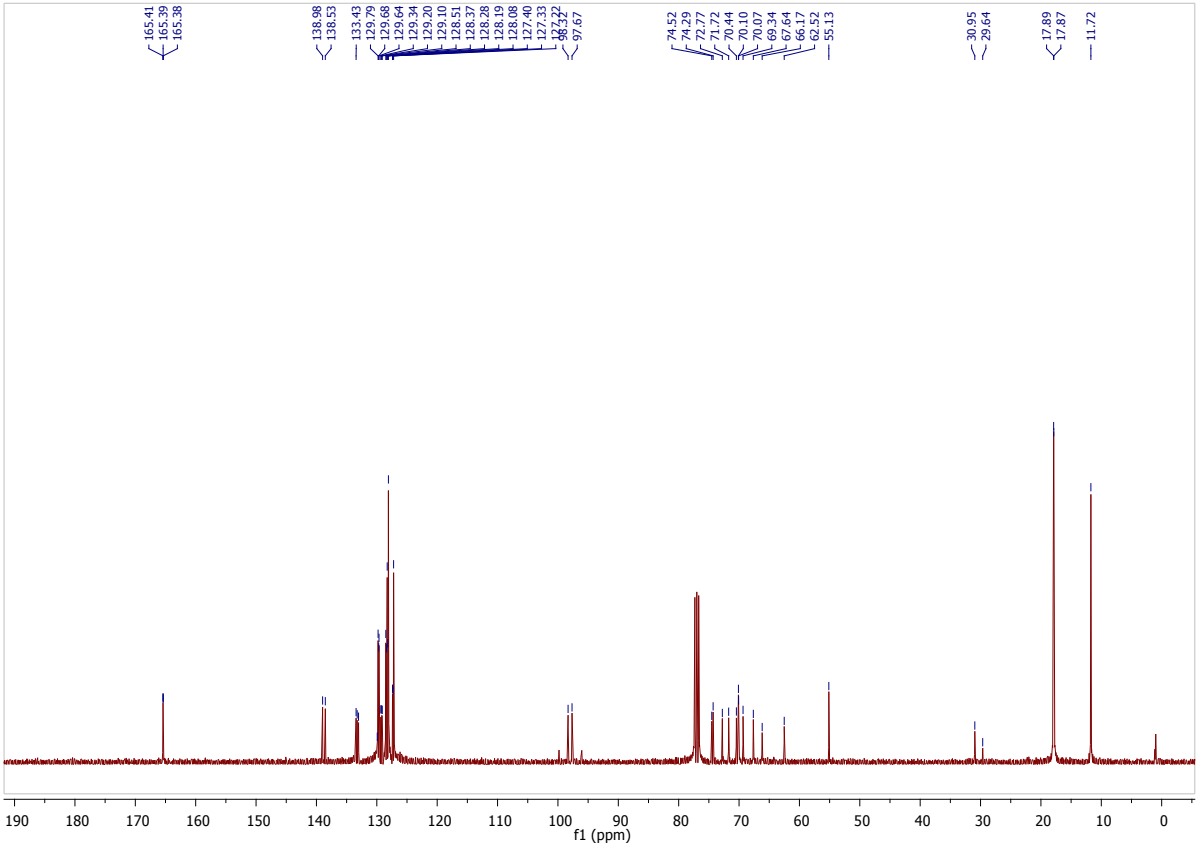
^{13}C NMR spectrum of compound **21** in $CDCl_3$ (101 MHz)



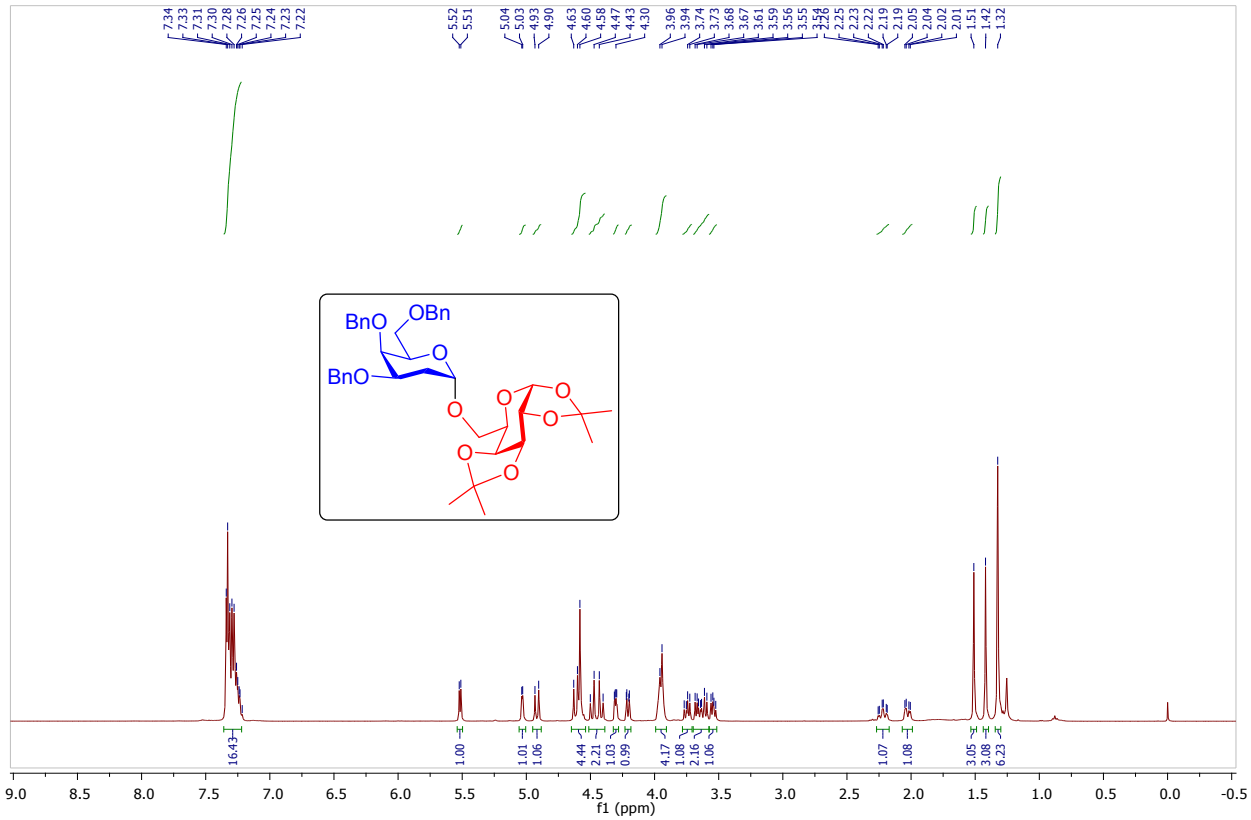
^{1}H NMR spectrum of compound **22** in $CDCl_3$(400 MHz)



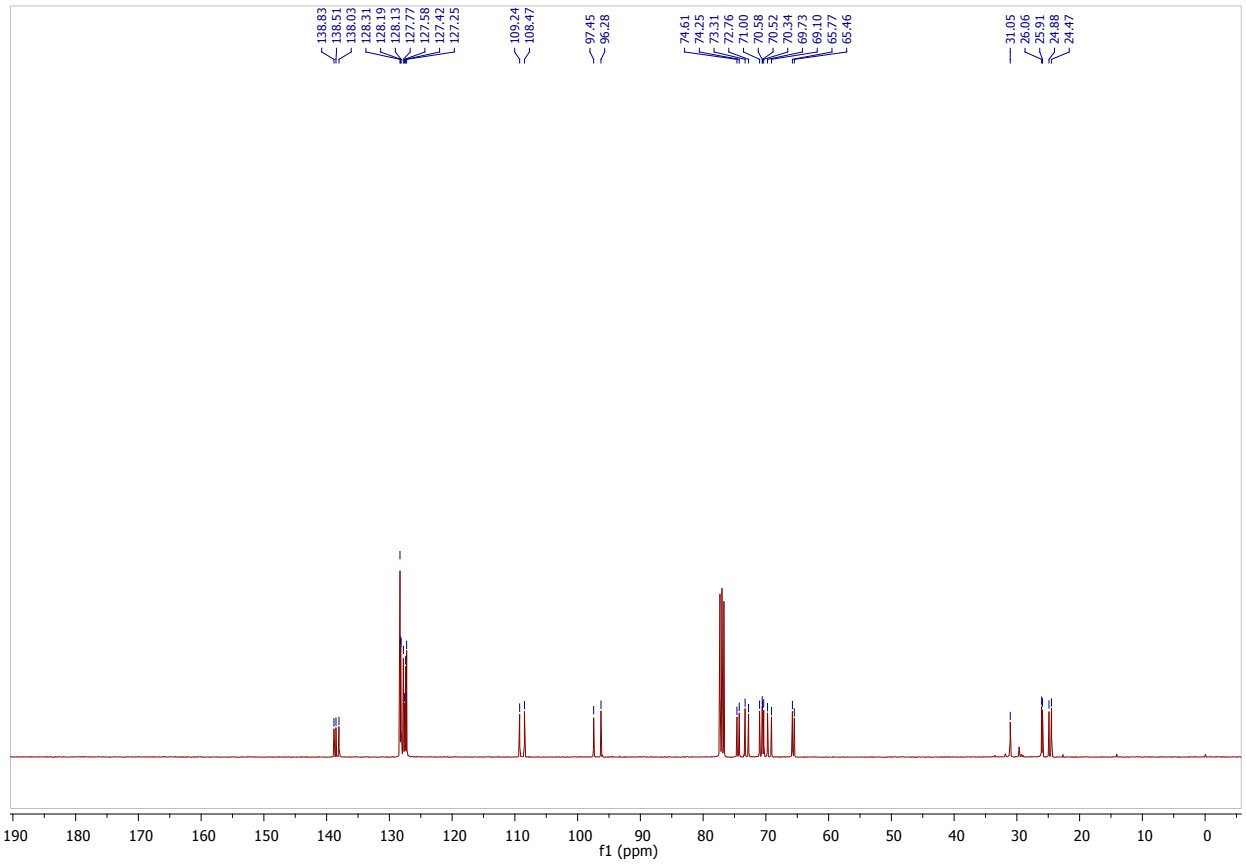
^{13}C NMR spectrum of compound **22** in $CDCl_3$ (101 MHz)



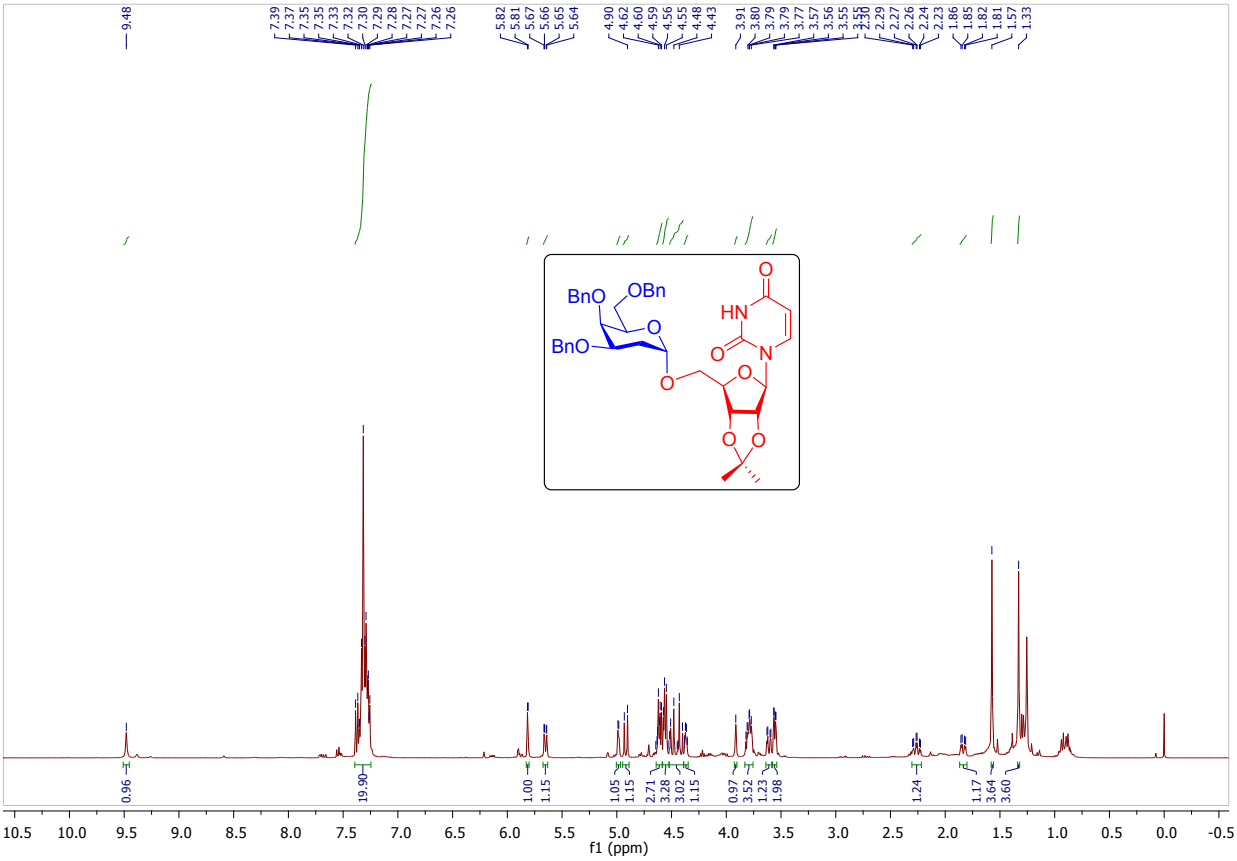
^{1}H NMR spectrum of compound **23** in $CDCl_3$ (400 MHz)



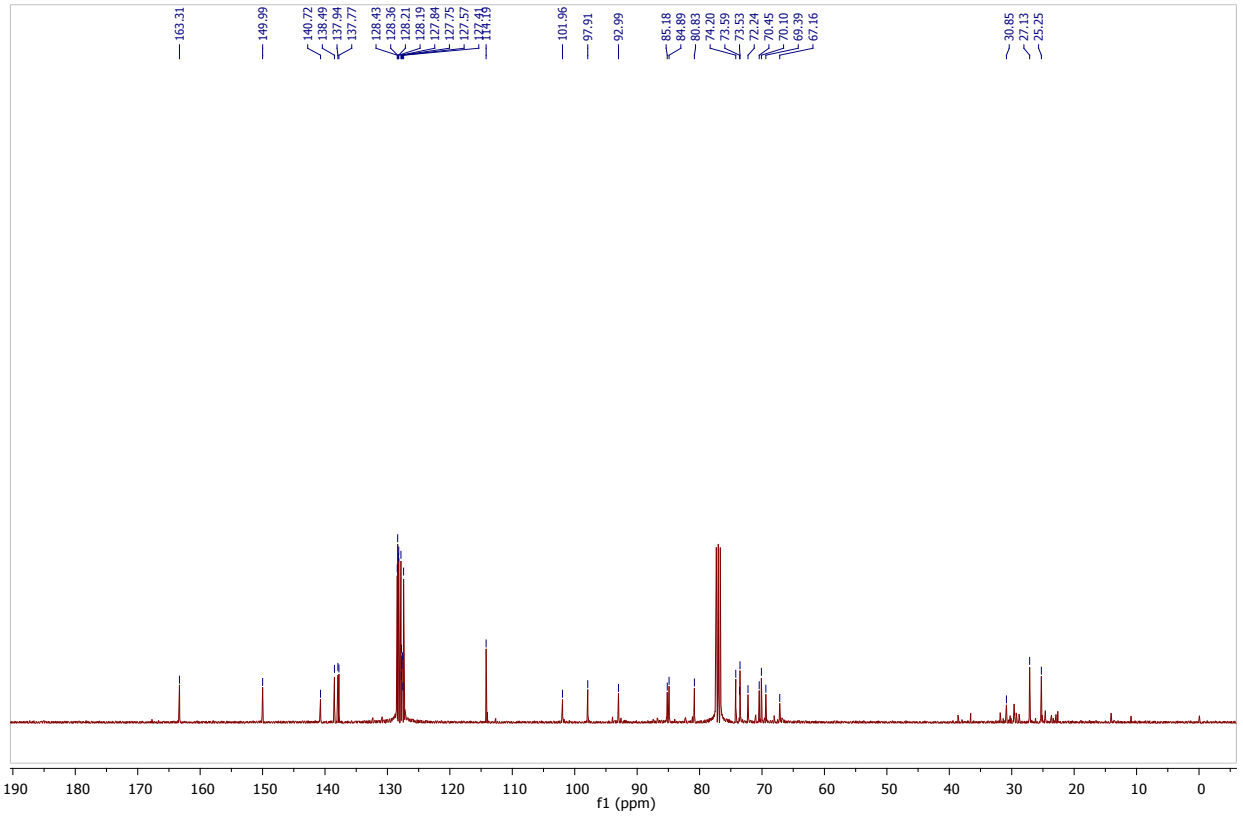
^{13}C NMR spectrum of compound **23** in $CDCl_3$ (101 MHz)



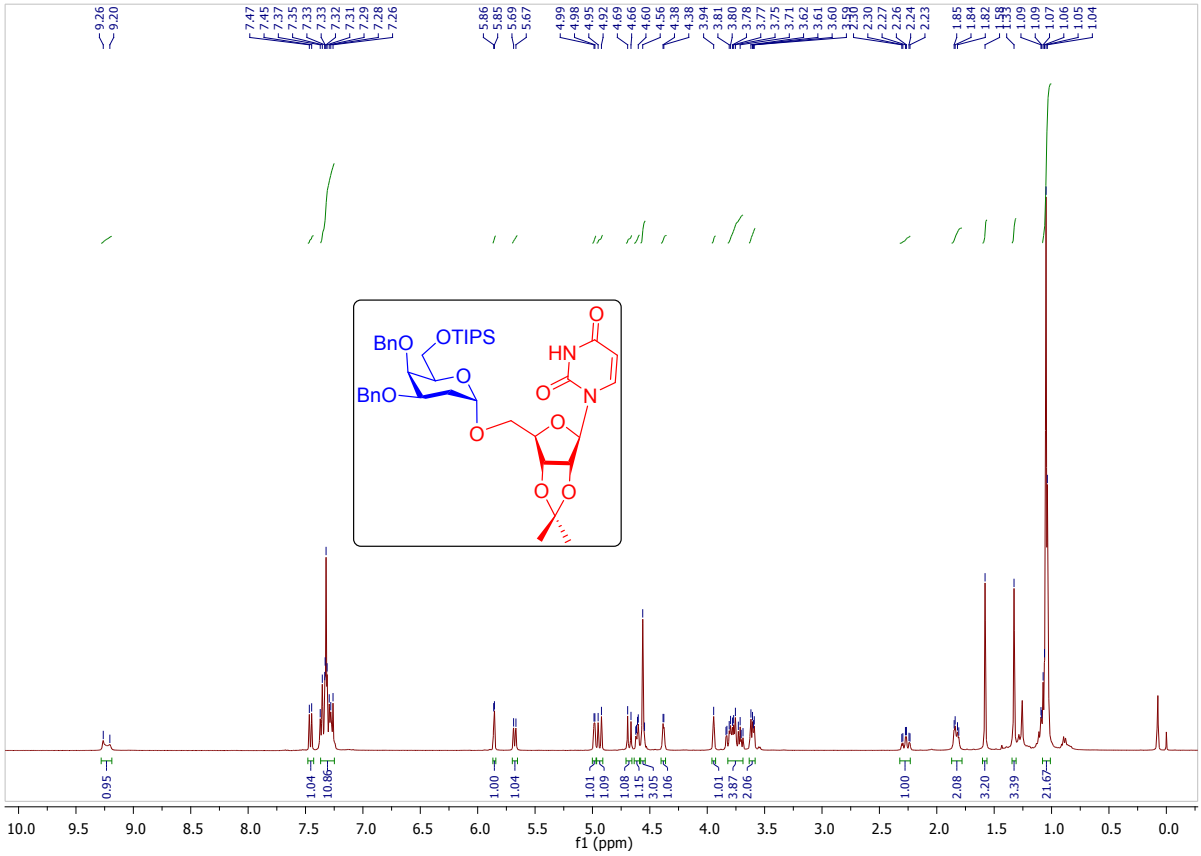
^{1}H NMR spectrum of compound **24** in $CDCl_3$ (400 MHz)



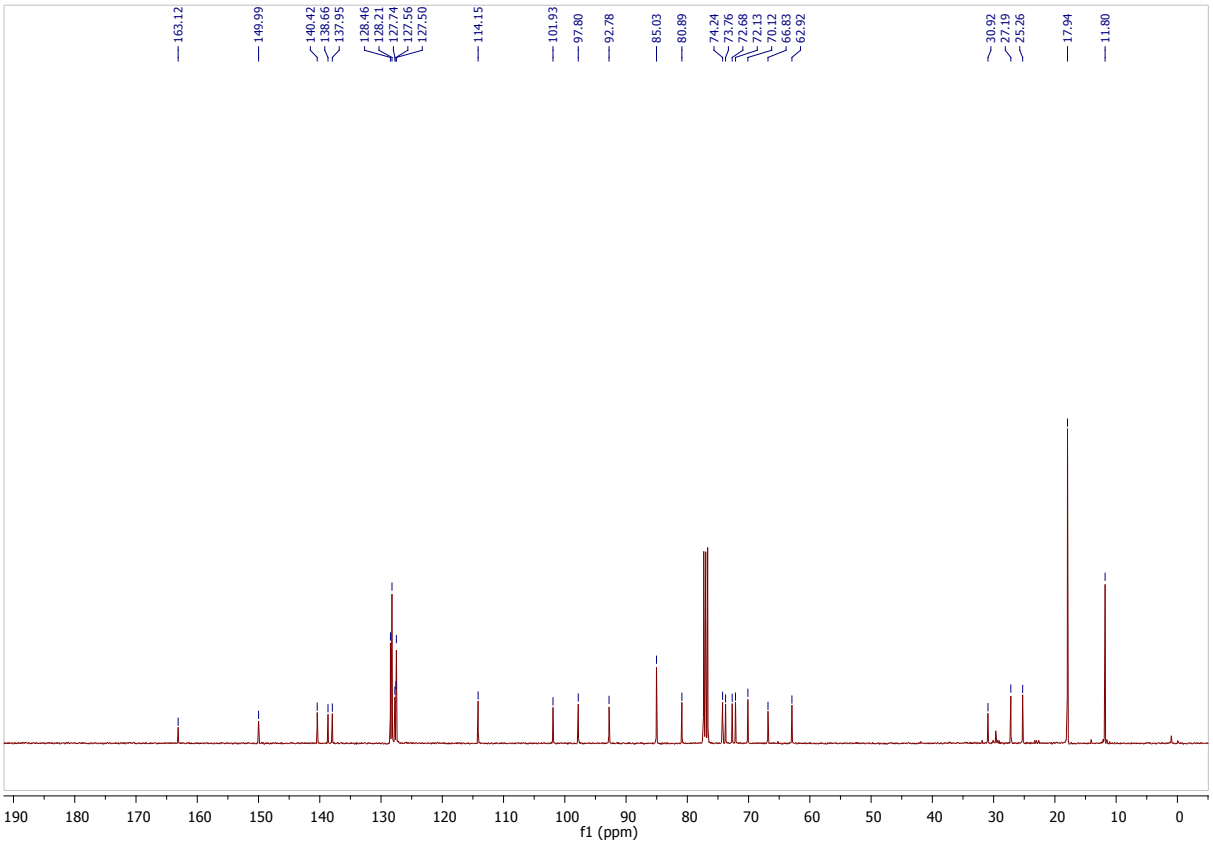
^{13}C NMR spectrum of compound **24** in $CDCl_3$ (101 MHz)



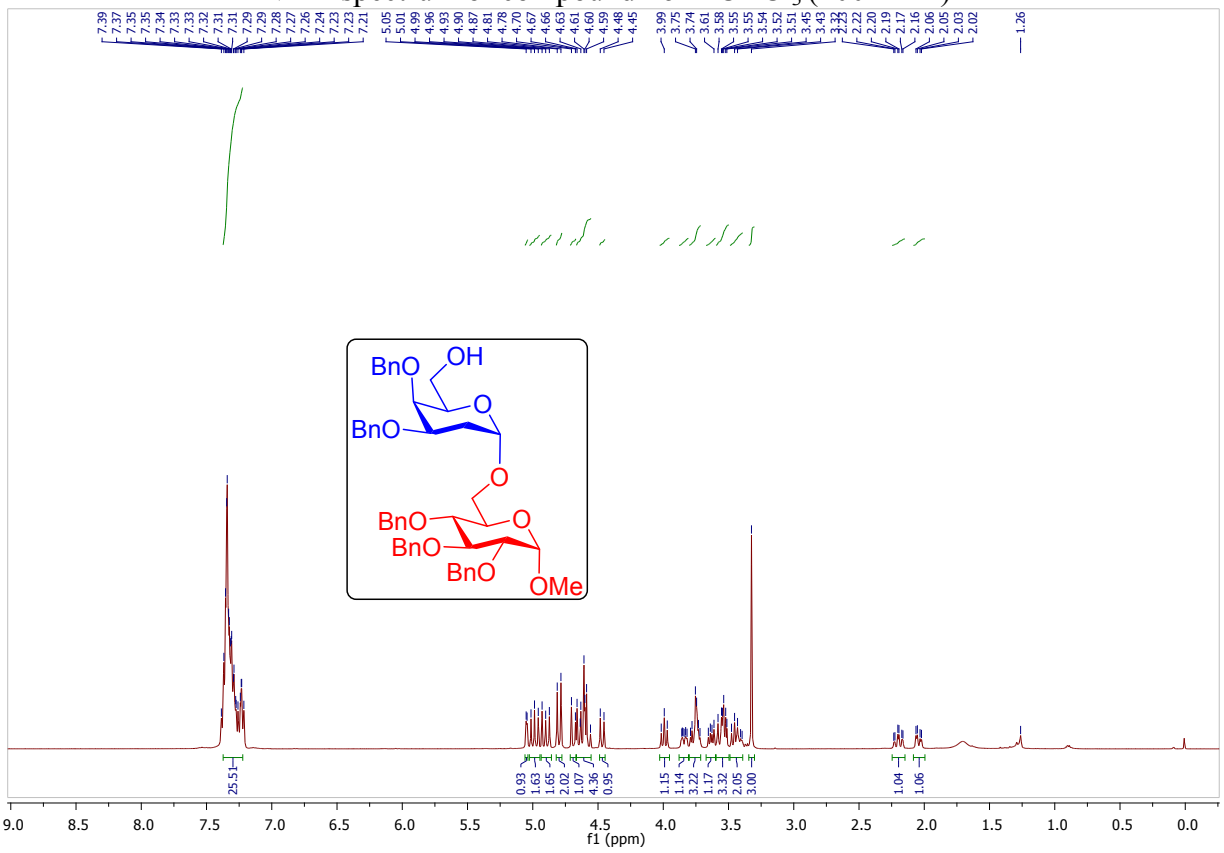
^{1}H NMR spectrum of compound **25** in $CDCl_3$ (400 MHz)



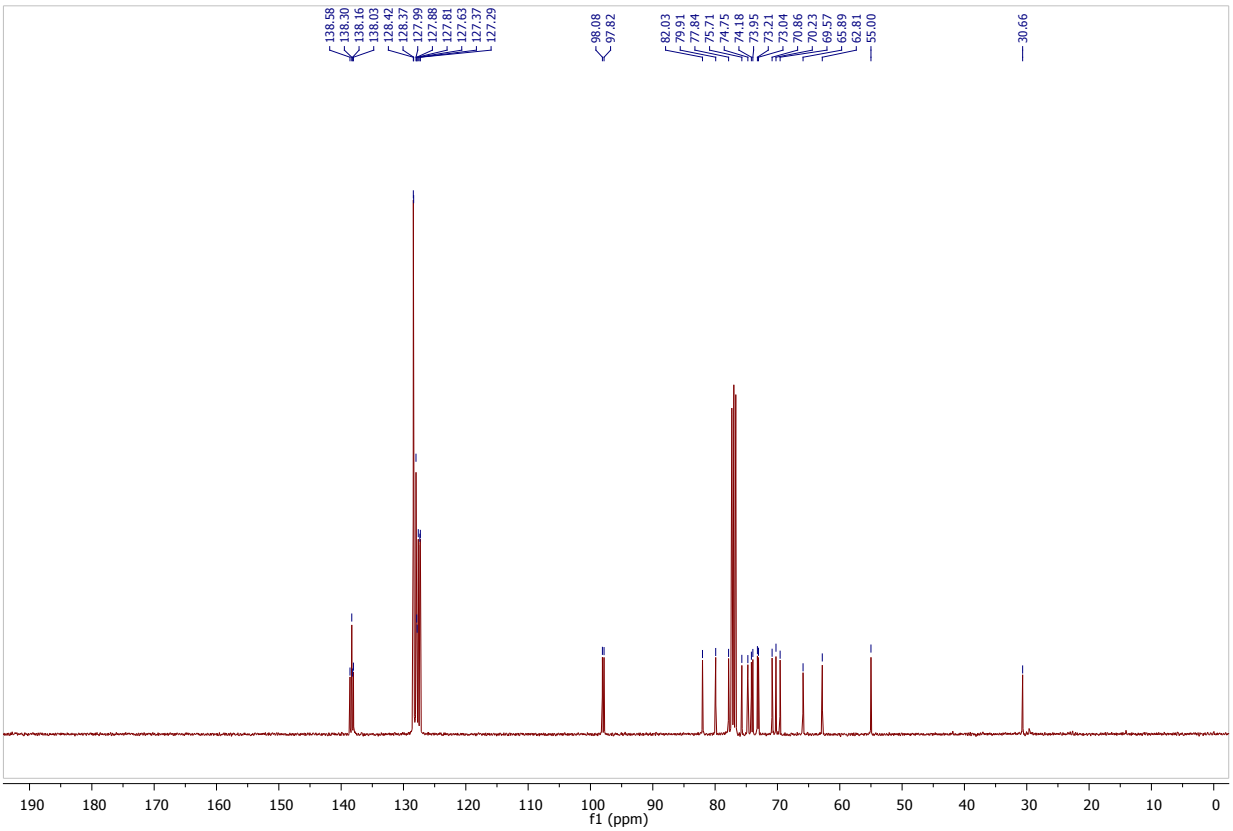
^{13}C NMR spectrum of compound **25** in $CDCl_3$ (101 MHz)



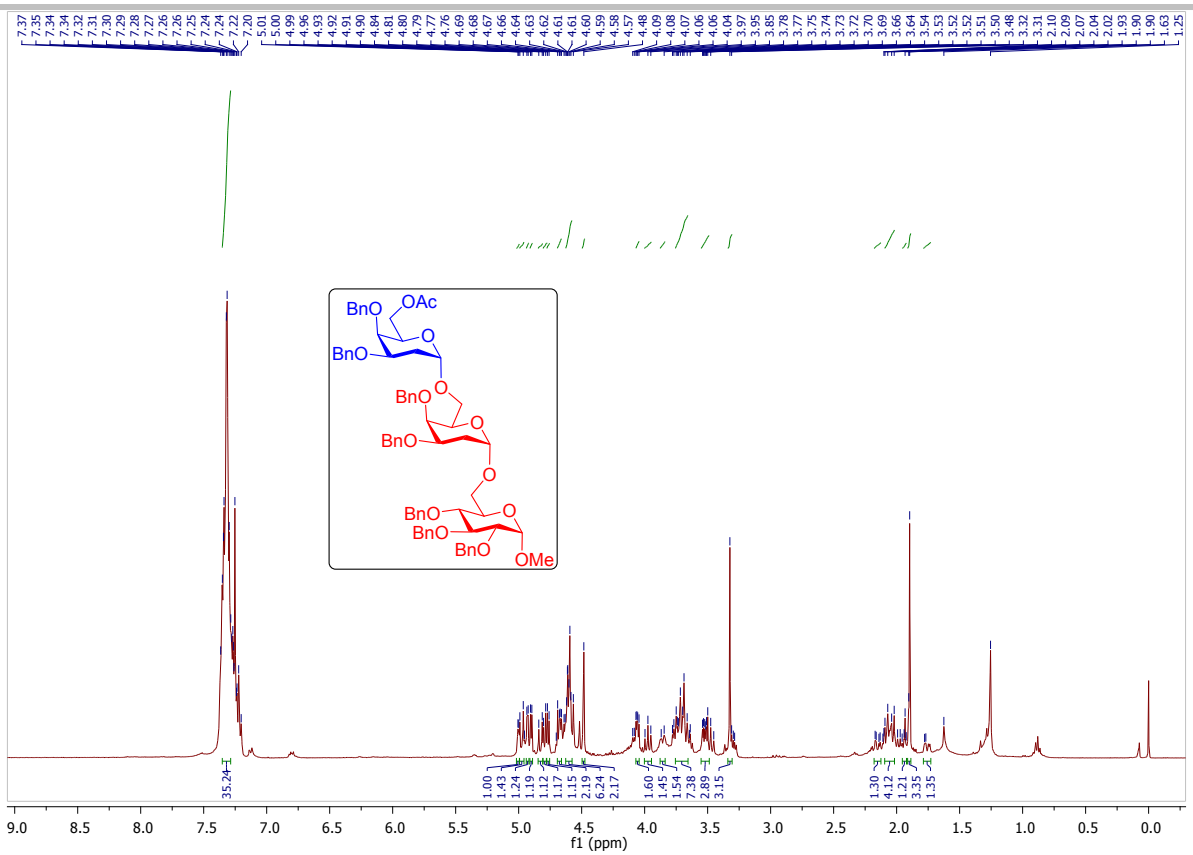
^{1}H NMR spectrum of compound **26** in $CDCl_3$ (400 MHz)



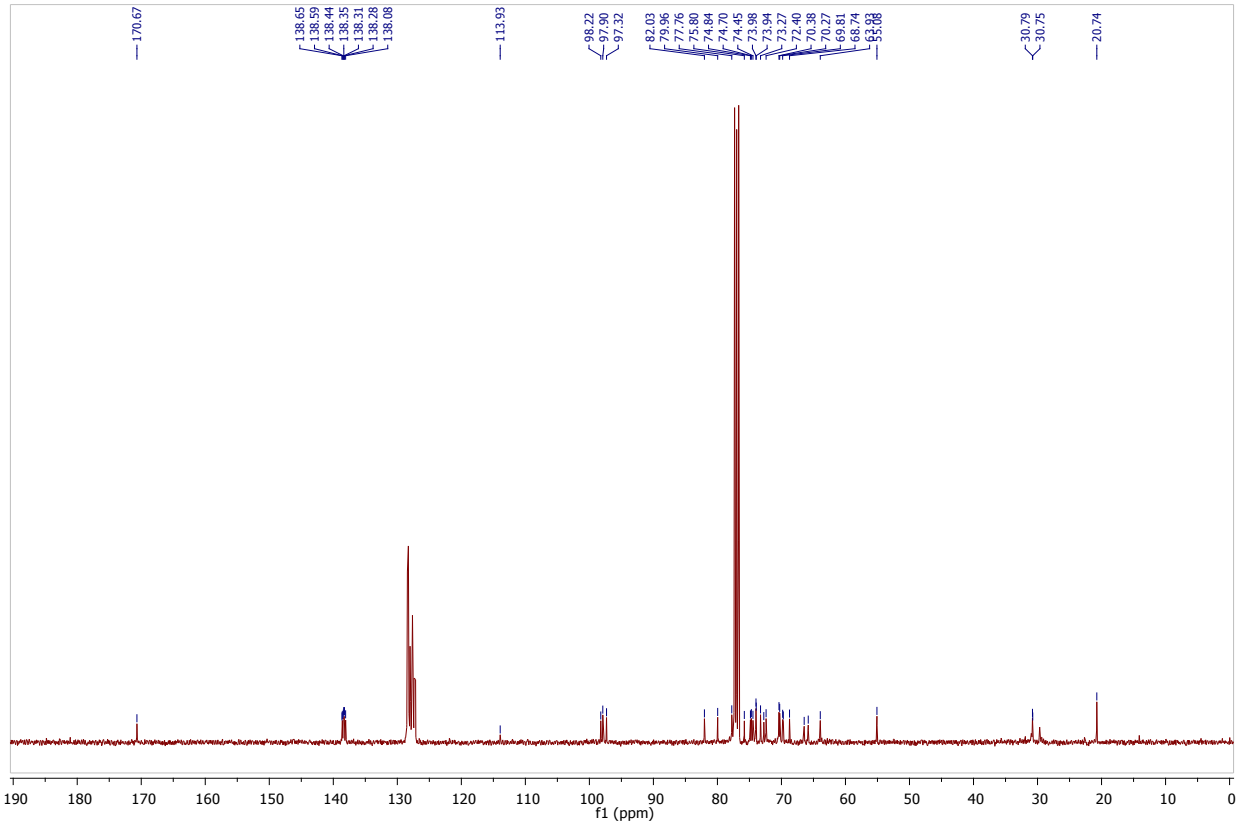
^{13}C NMR spectrum of compound **26** in $CDCl_3$ (101 MHz)



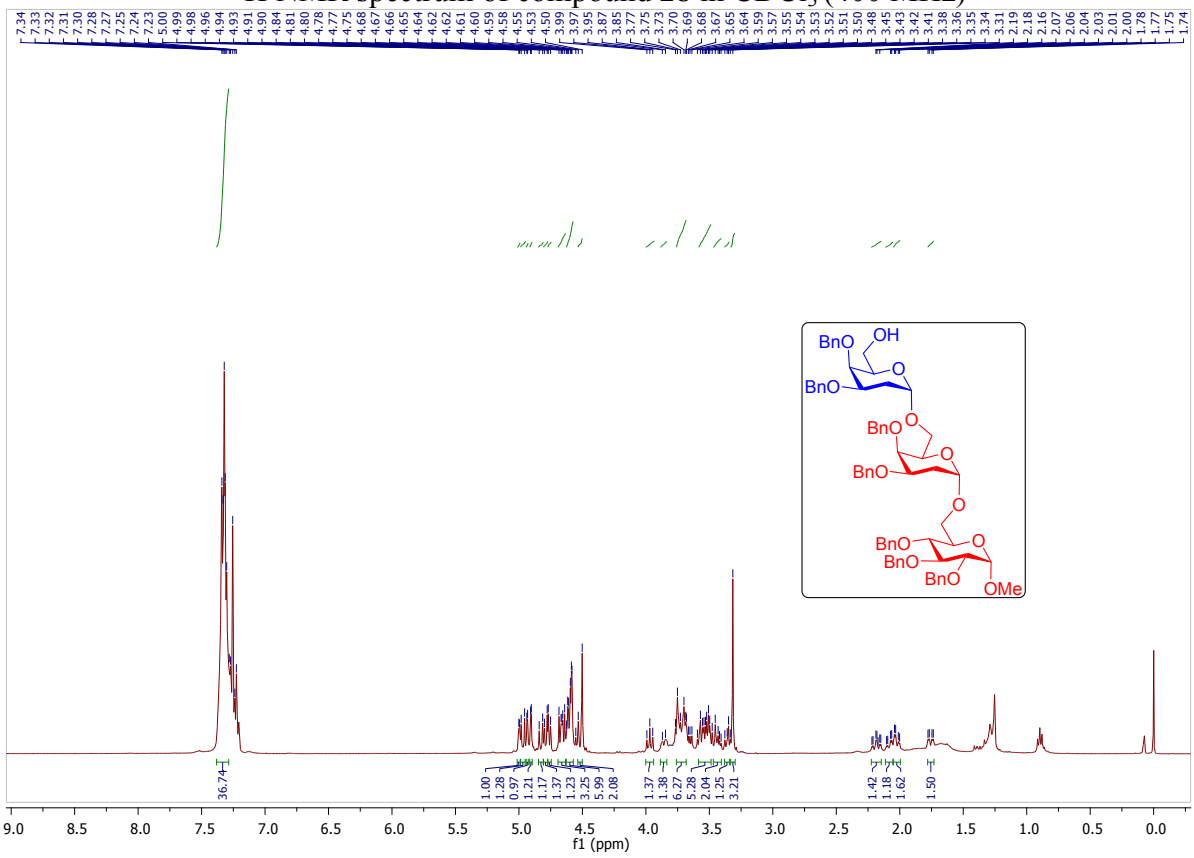
^{1}H NMR spectrum of compound **27** in $CDCl_3$ (400 MHz)



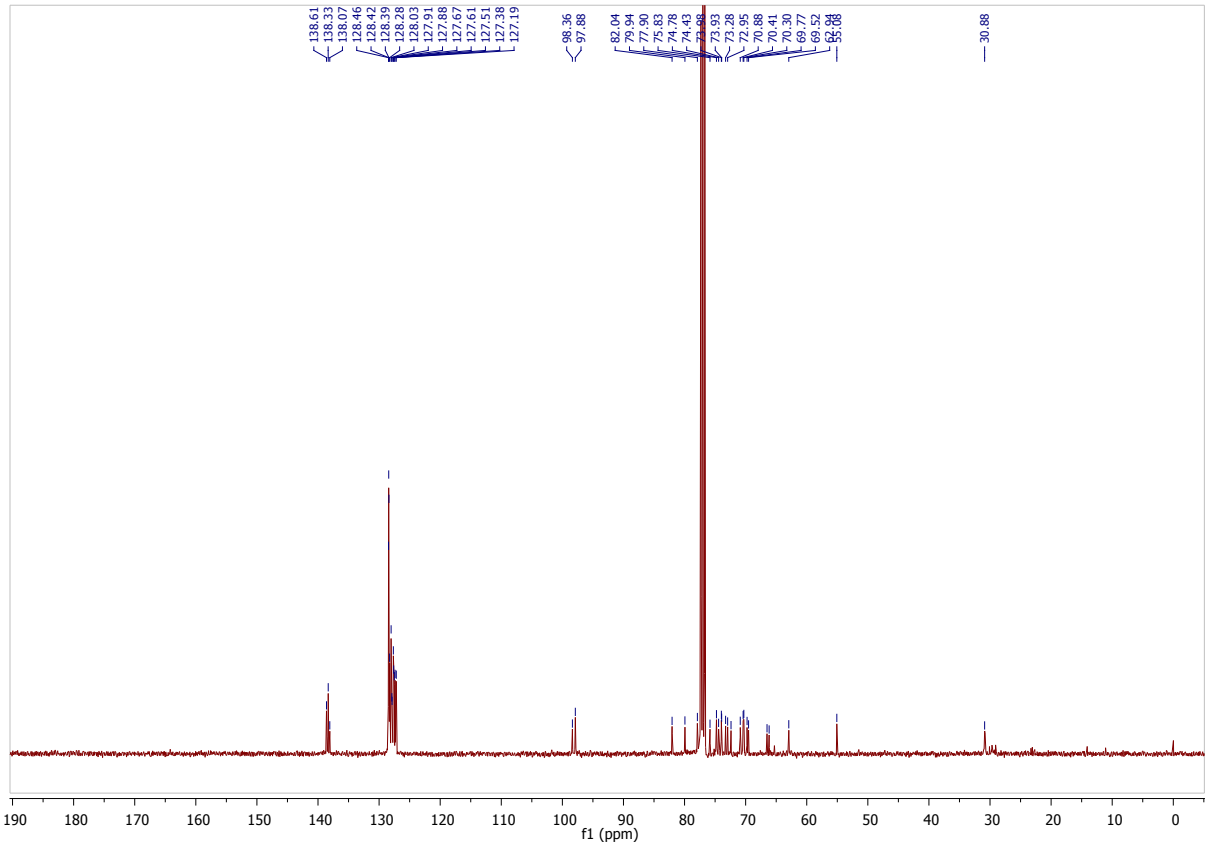
^{13}C NMR spectrum of compound **27** in $CDCl_3$ (101 MHz)



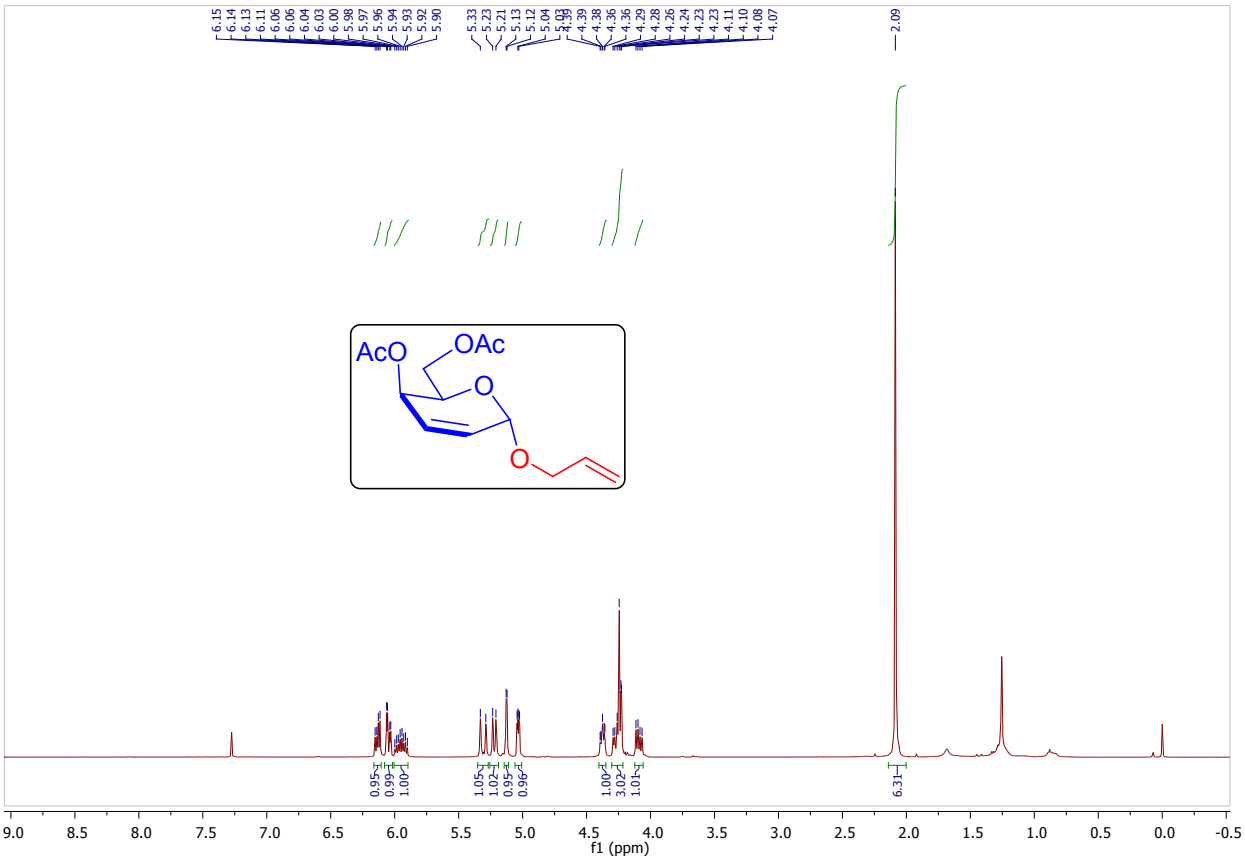
^{1}H NMR spectrum of compound **28** in $CDCl_3$ (400 MHz)



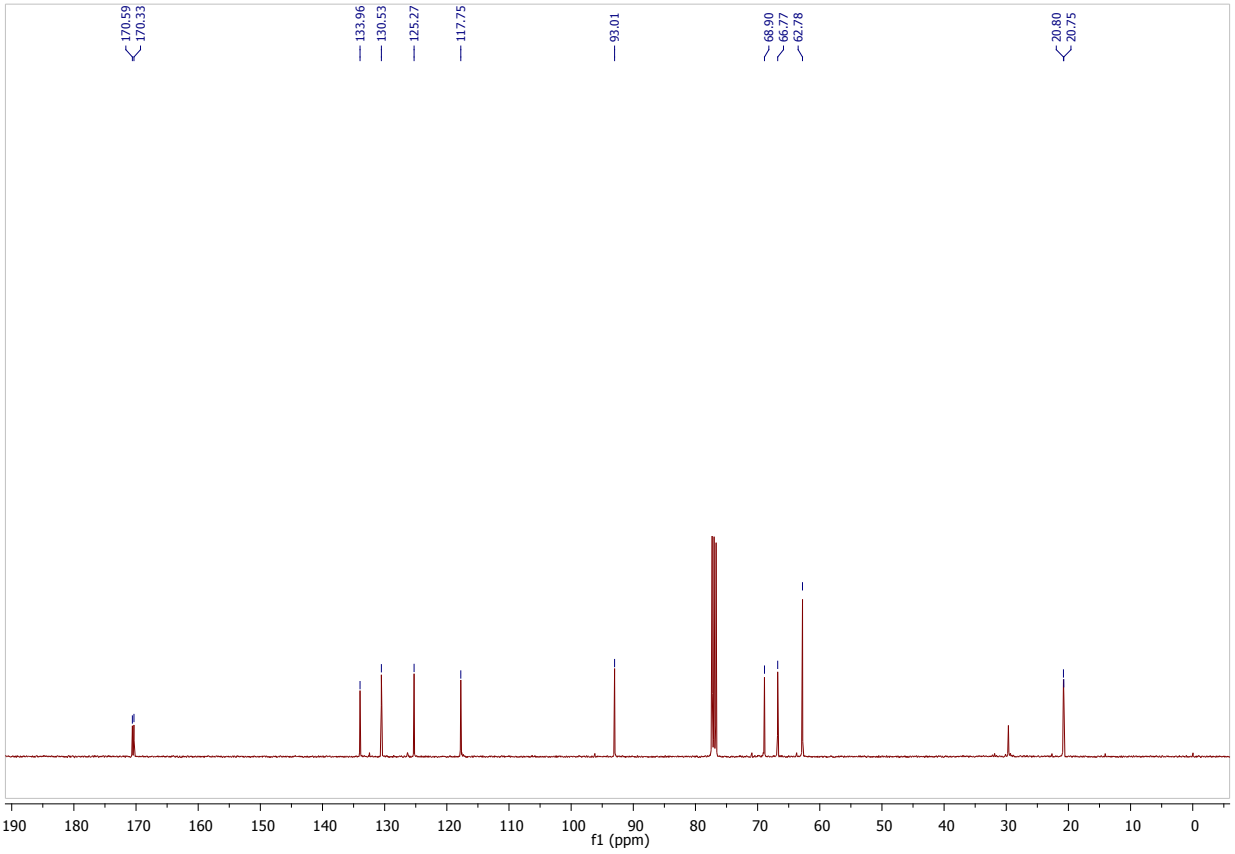
^{13}C NMR spectrum of compound **28** in $CDCl_3$ (101 MHz)



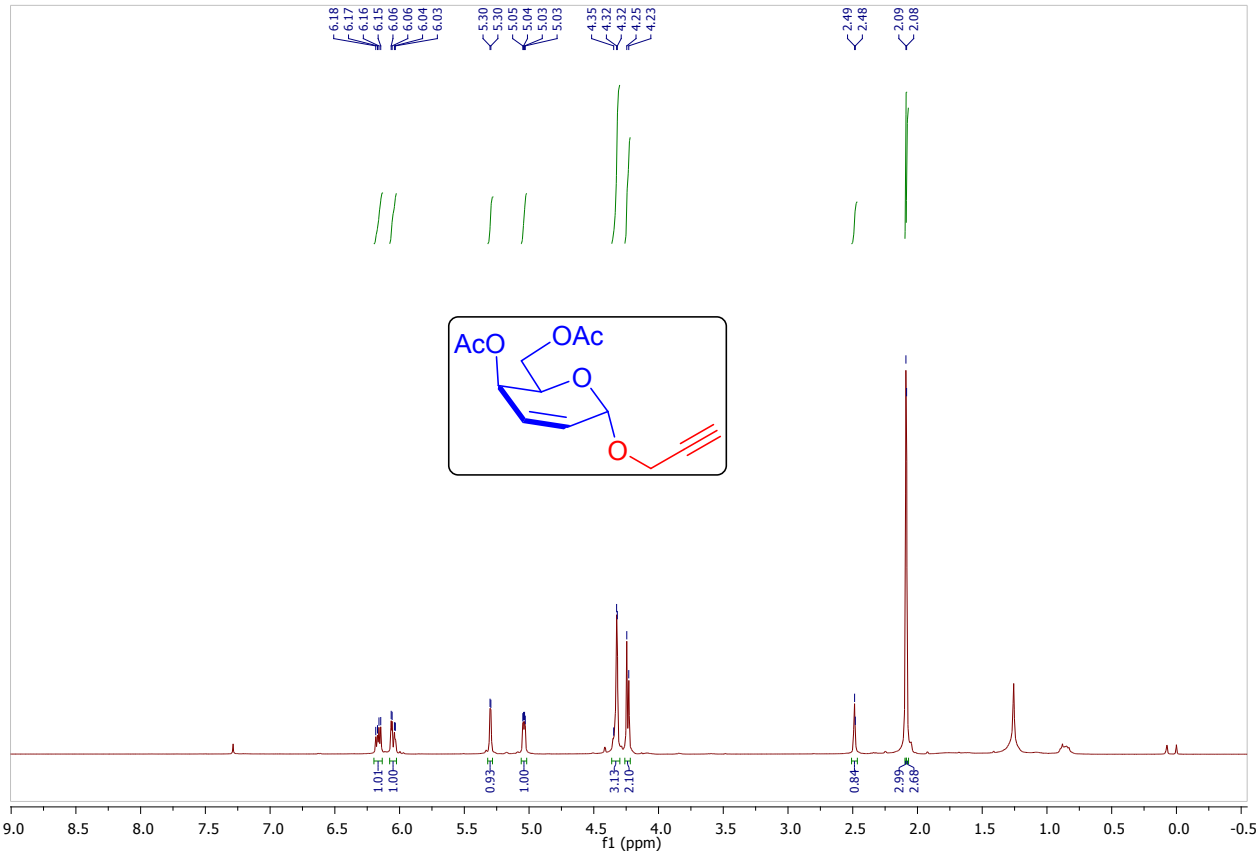
^{1}H NMR spectrum of compound **29** in $CDCl_3$ (400 MHz)



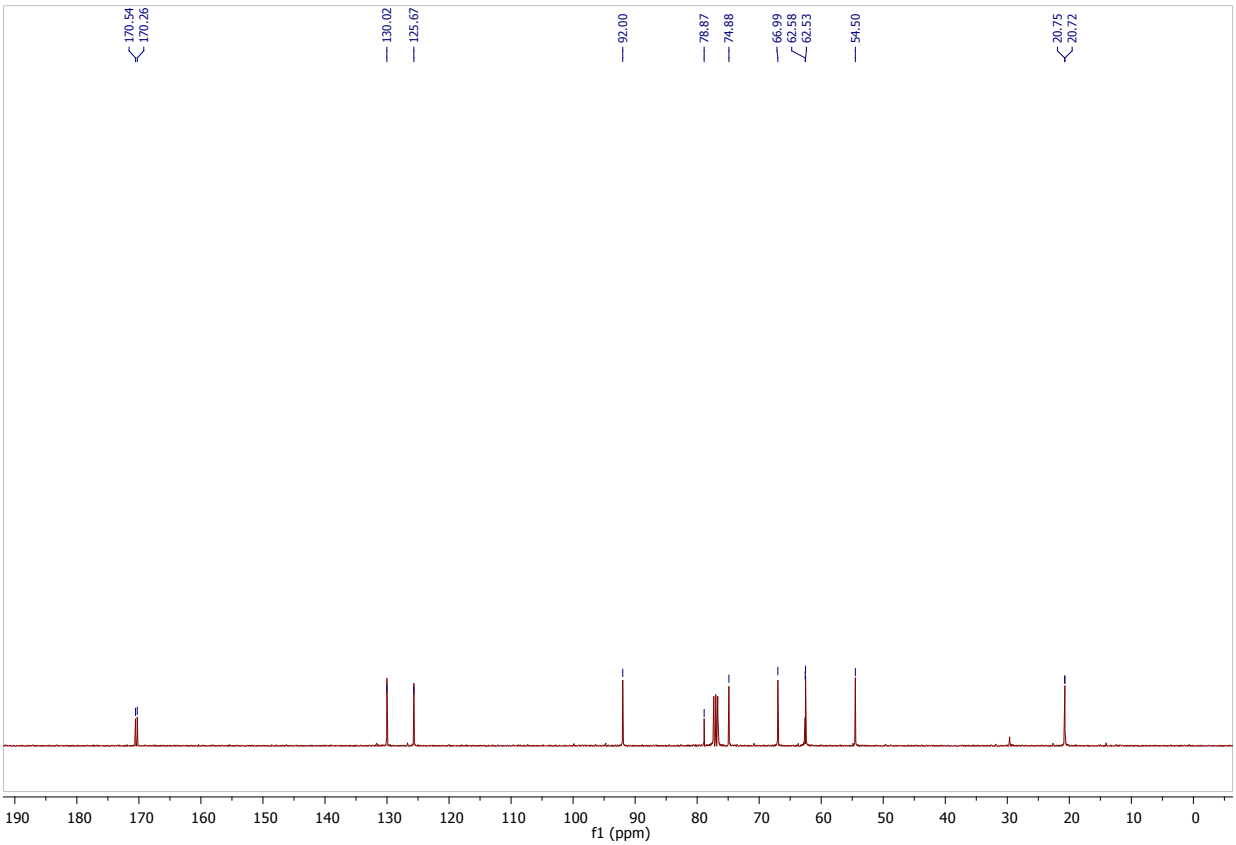
^{13}C NMR spectrum of compound **29** in $CDCl_3$ (101 MHz)



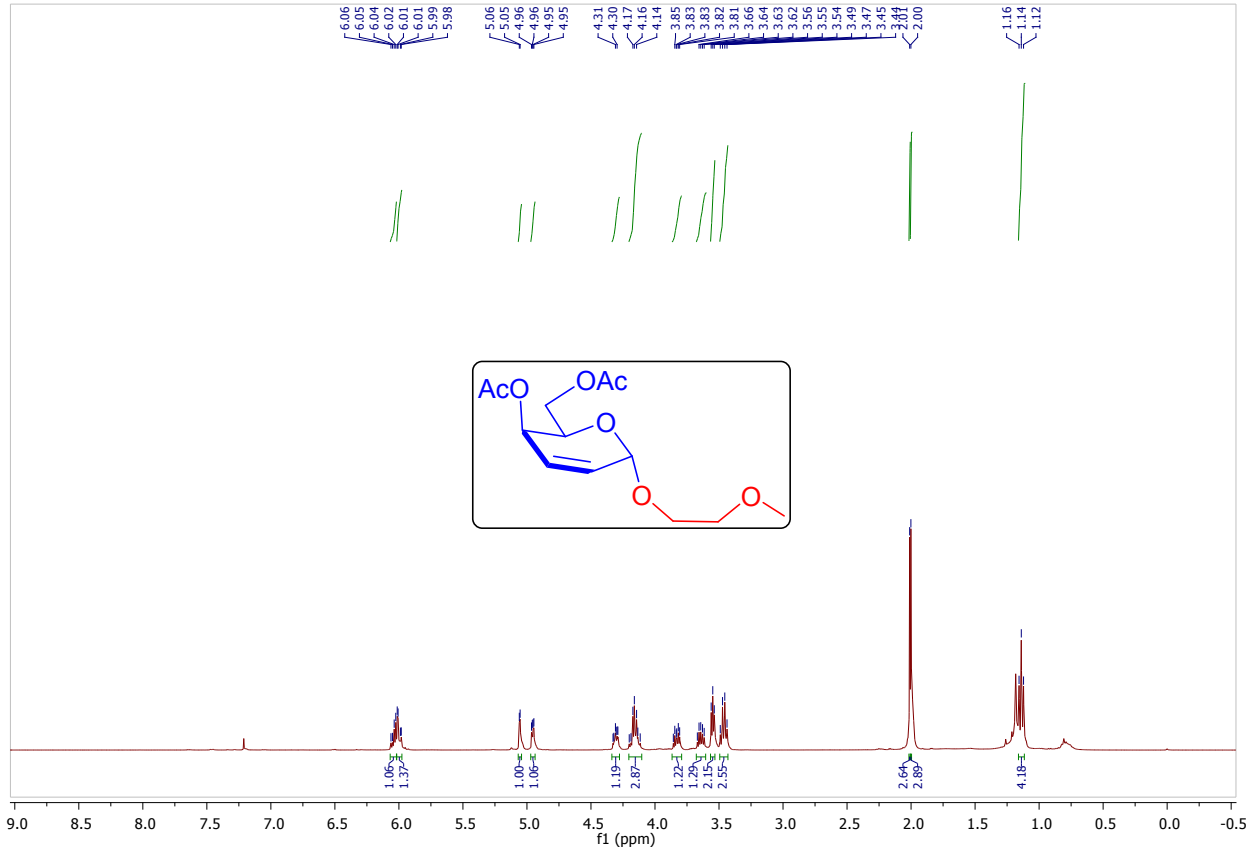
^{1}H NMR spectrum of compound **30** in $CDCl_3$ (400 MHz)



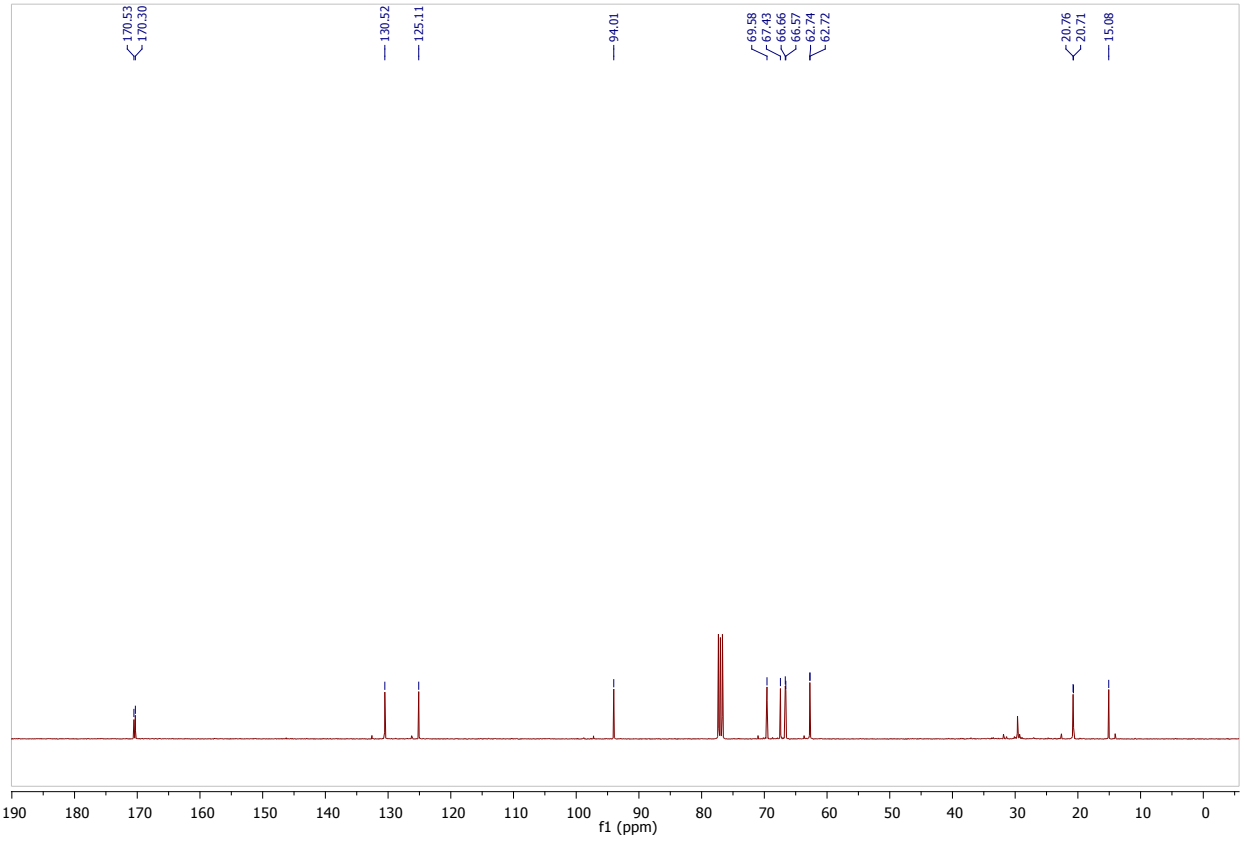
^{13}C NMR spectrum of compound **30** in $CDCl_3$ (101 MHz)



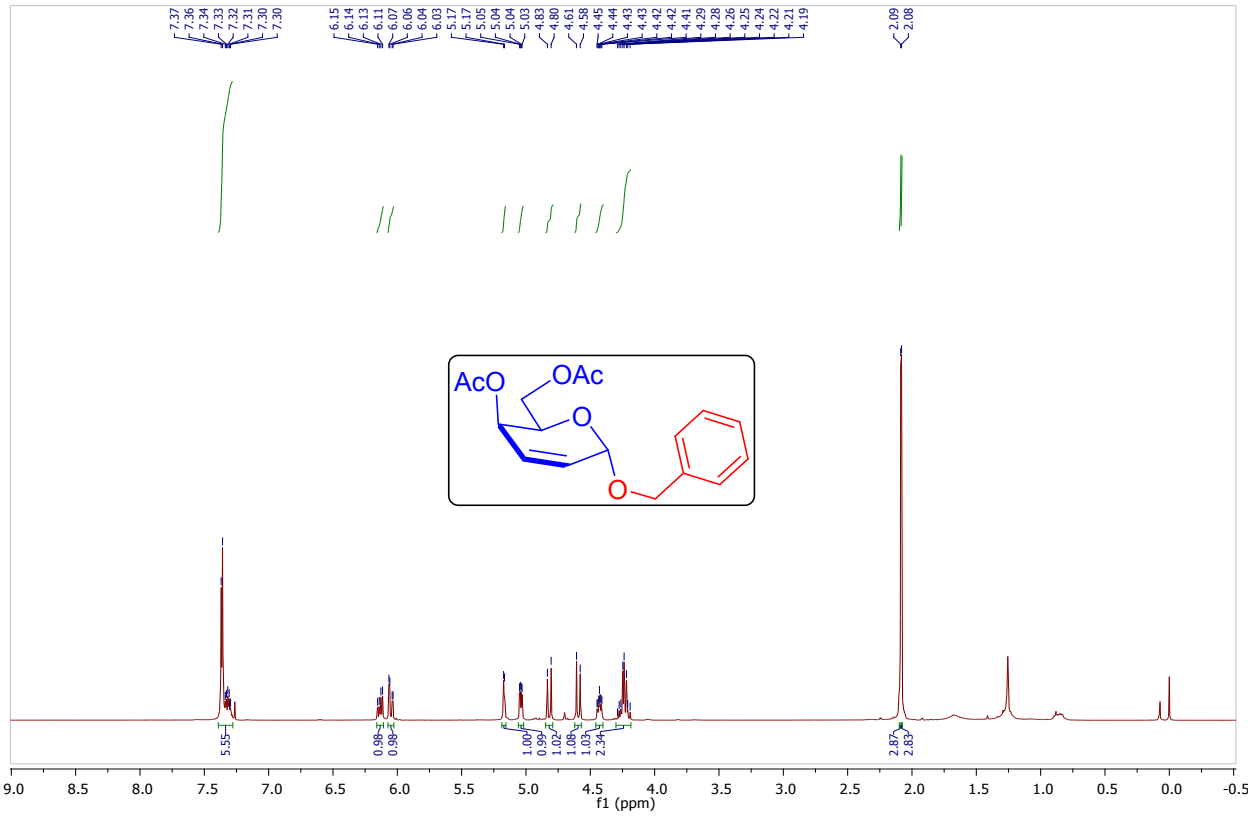
^{1}H NMR spectrum of compound **31** in $CDCl_3$ (400 MHz)



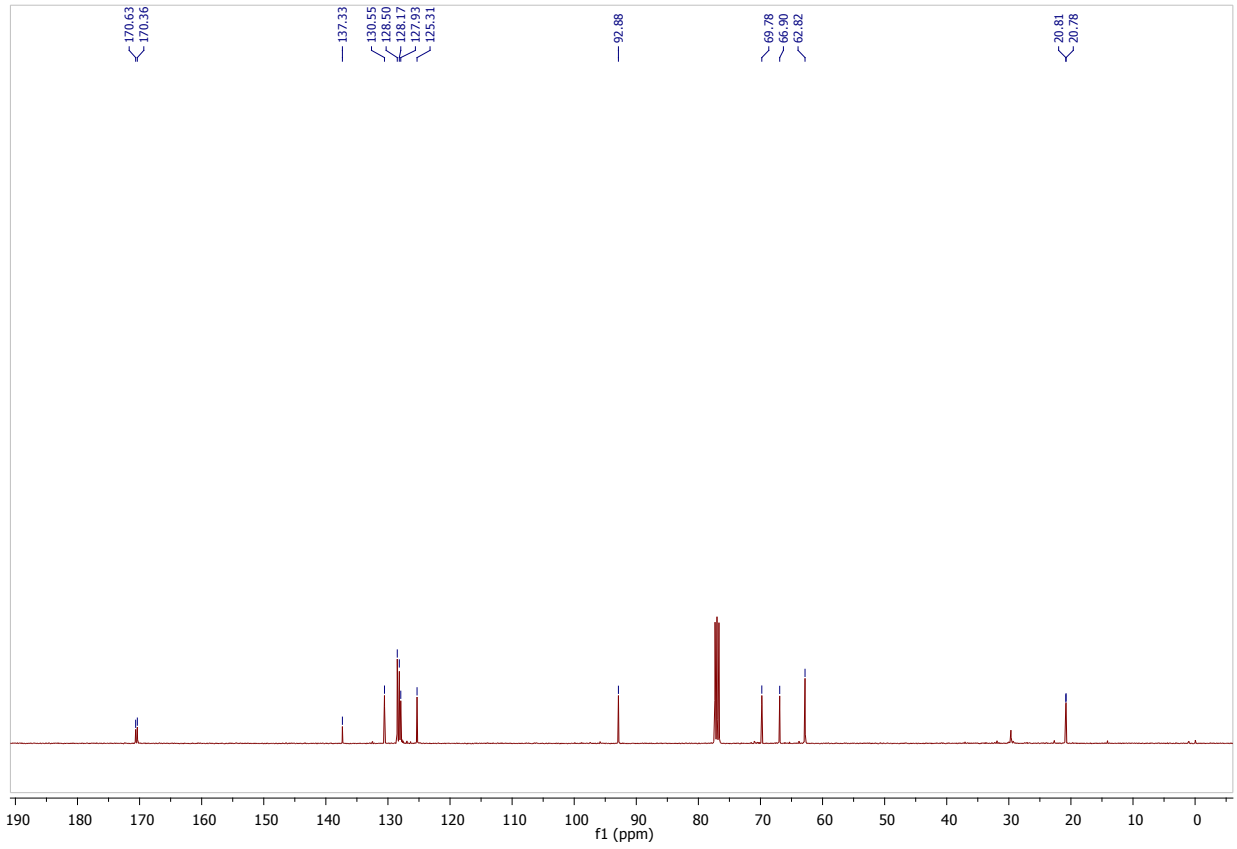
^{13}C NMR spectrum of compound **31** in $CDCl_3$ (101 MHz)



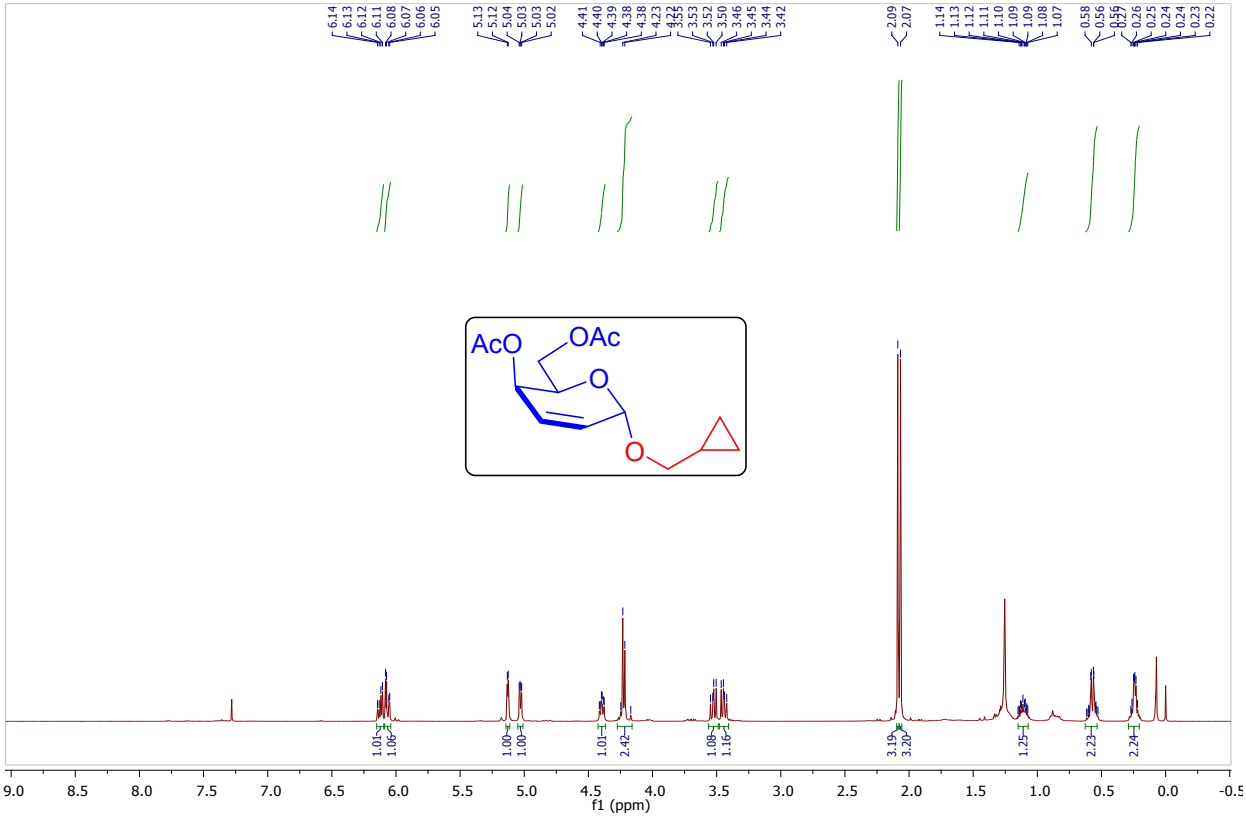
^{1}H NMR spectrum of compound **32** in $CDCl_3$ (400 MHz)



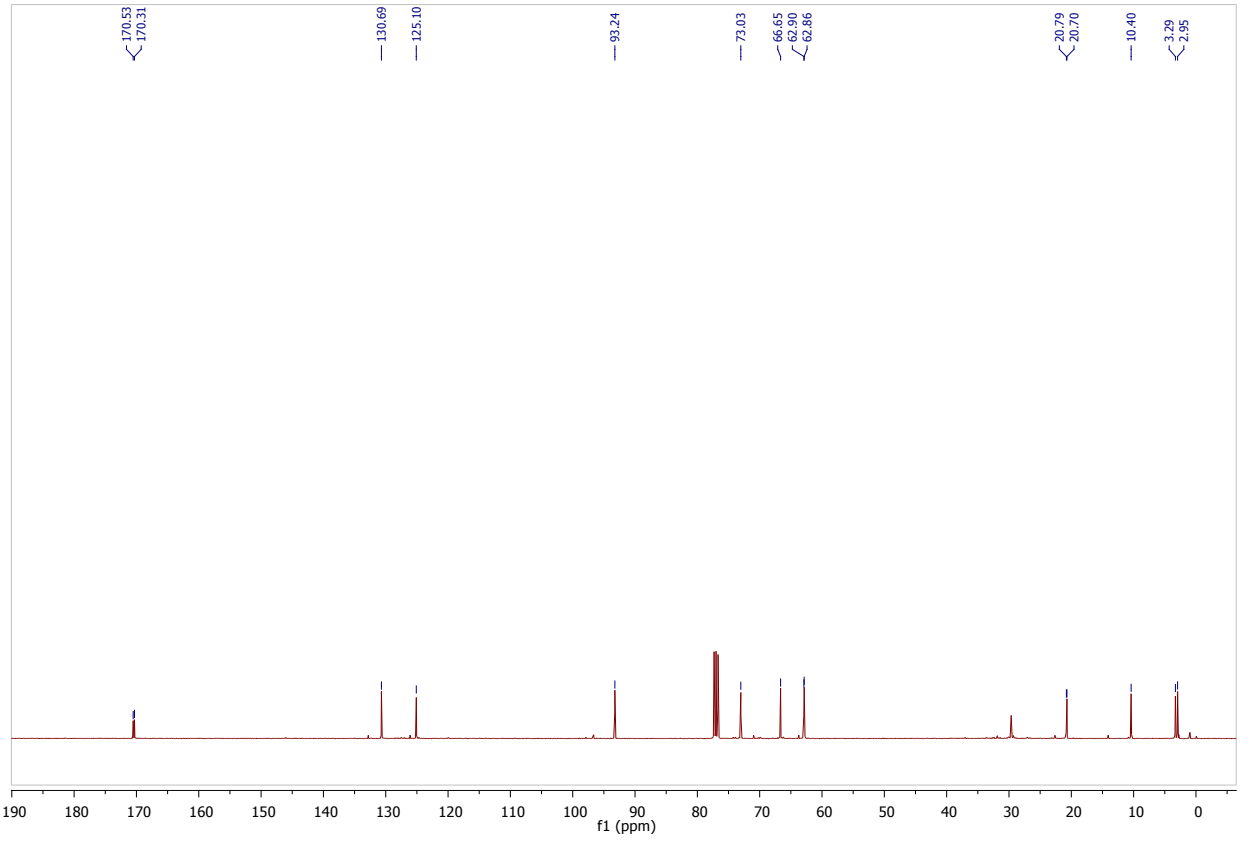
^{13}C NMR spectrum of compound **32** in $CDCl_3$ (101 MHz)



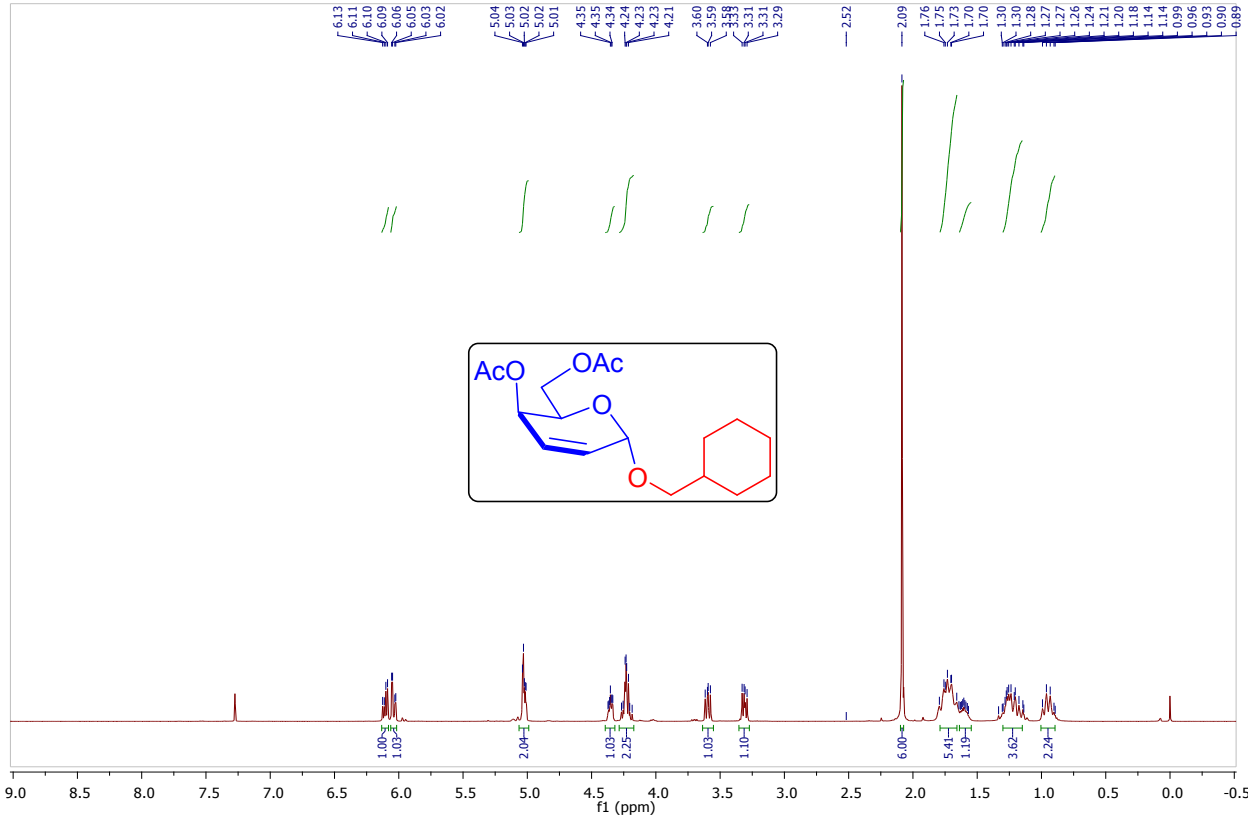
^{1}H NMR spectrum of compound **33** in $CDCl_3$ (400 MHz)



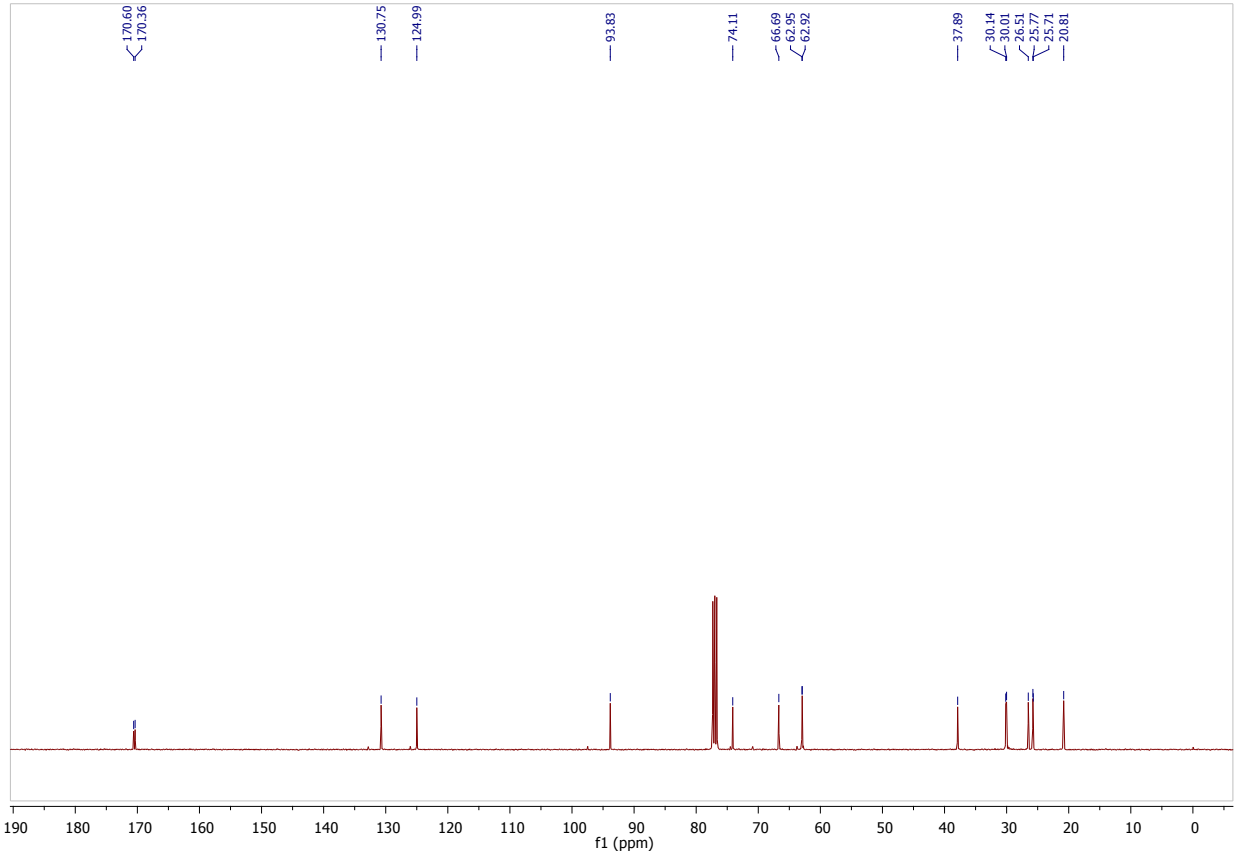
^{13}C NMR spectrum of compound **33** in $CDCl_3$ (101 MHz)



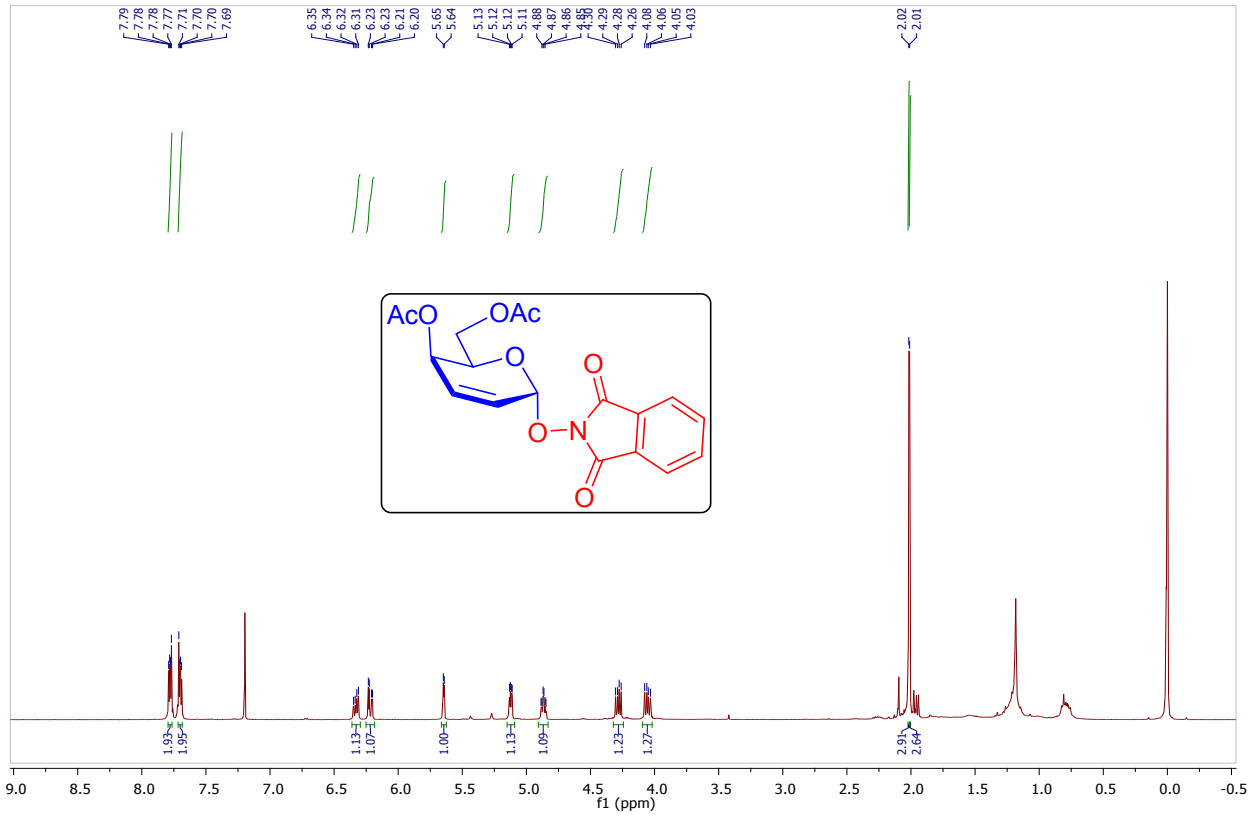
^{1}H NMR spectrum of compound **34** in $CDCl_3$ (400 MHz)



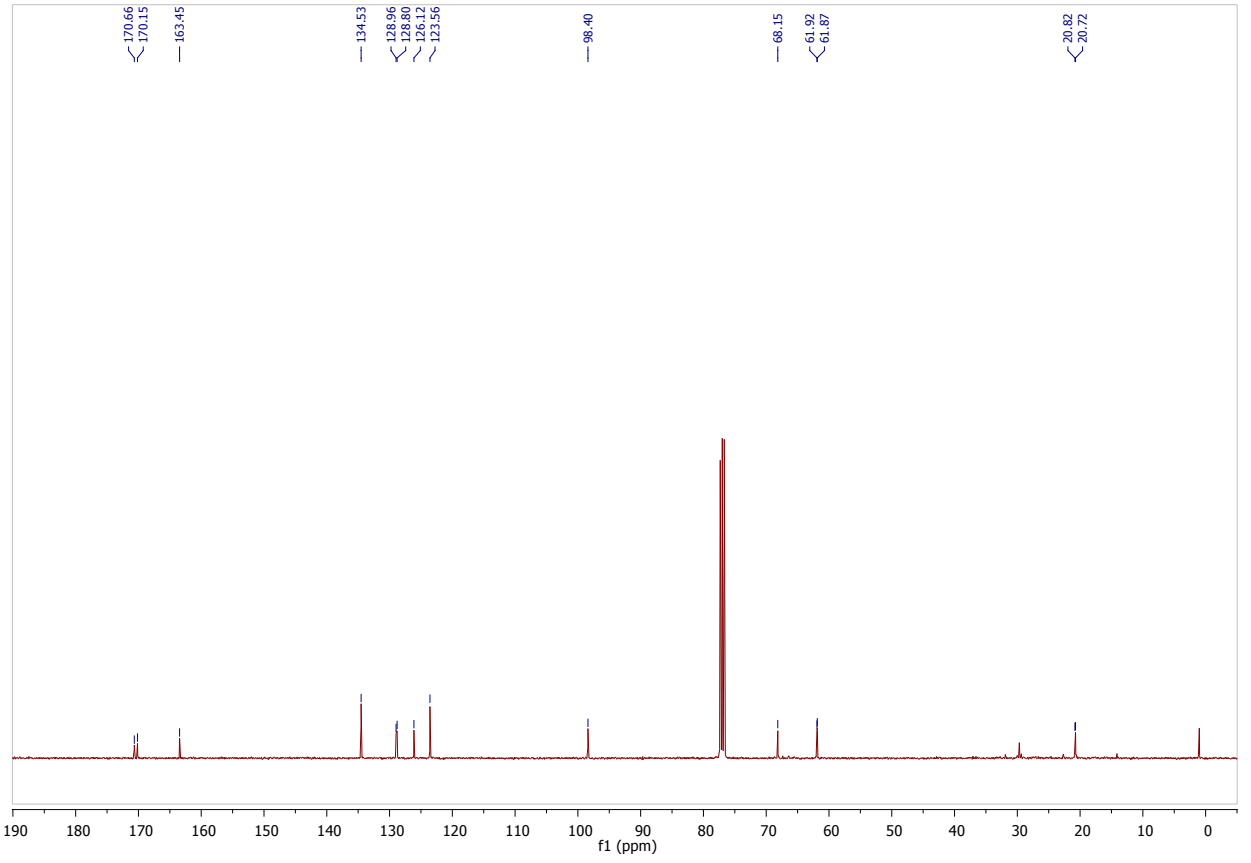
^{13}C NMR spectrum of compound **34** in $CDCl_3$ (101 MHz)



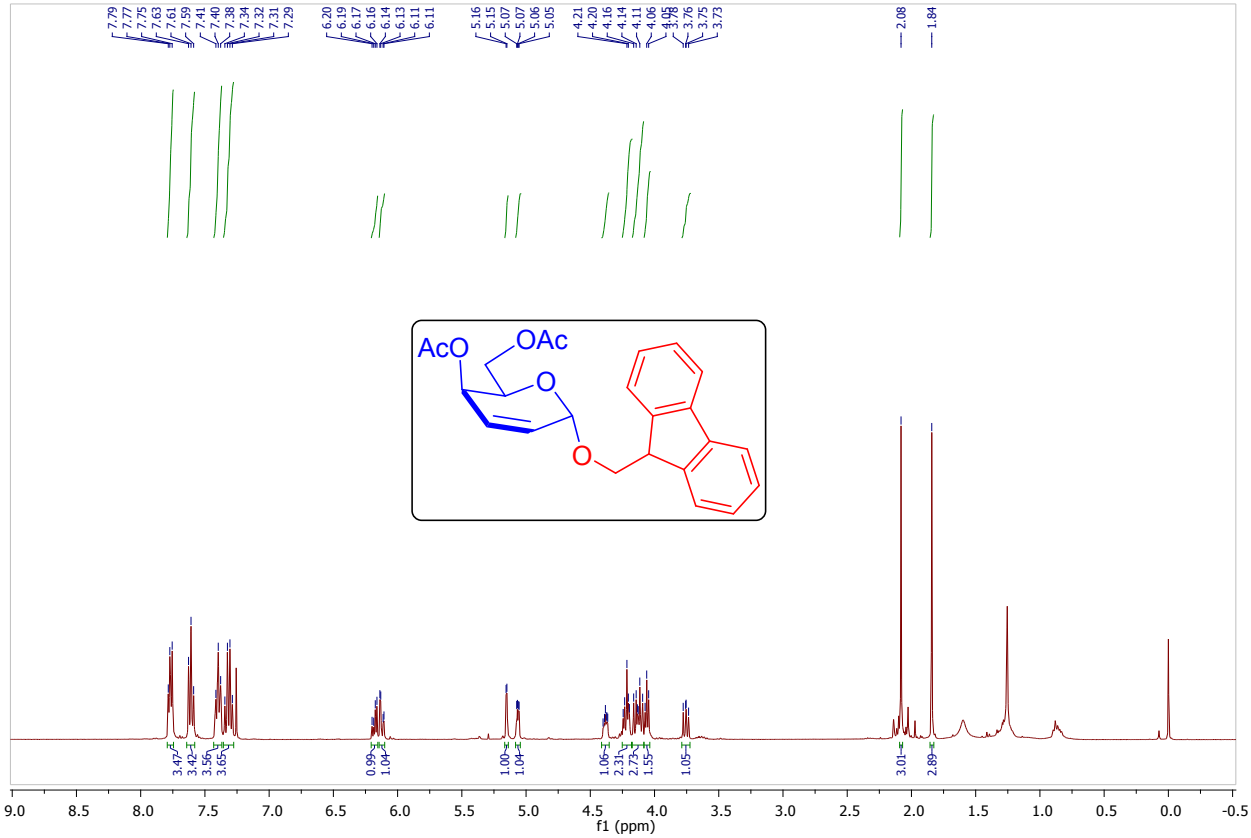
^{1}H NMR spectrum of compound **35** in $CDCl_3$ (400 MHz)



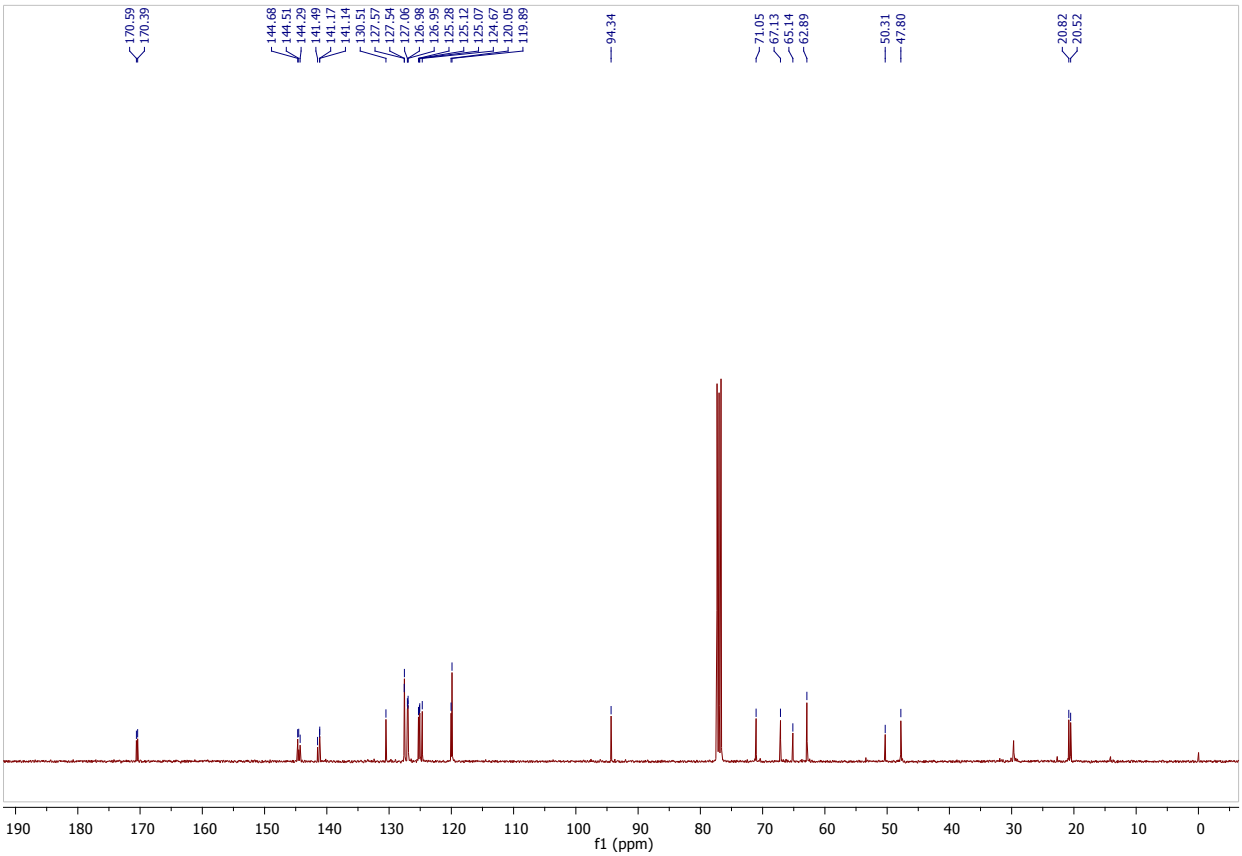
^{13}C NMR spectrum of compound **35** in $CDCl_3$ (101 MHz)



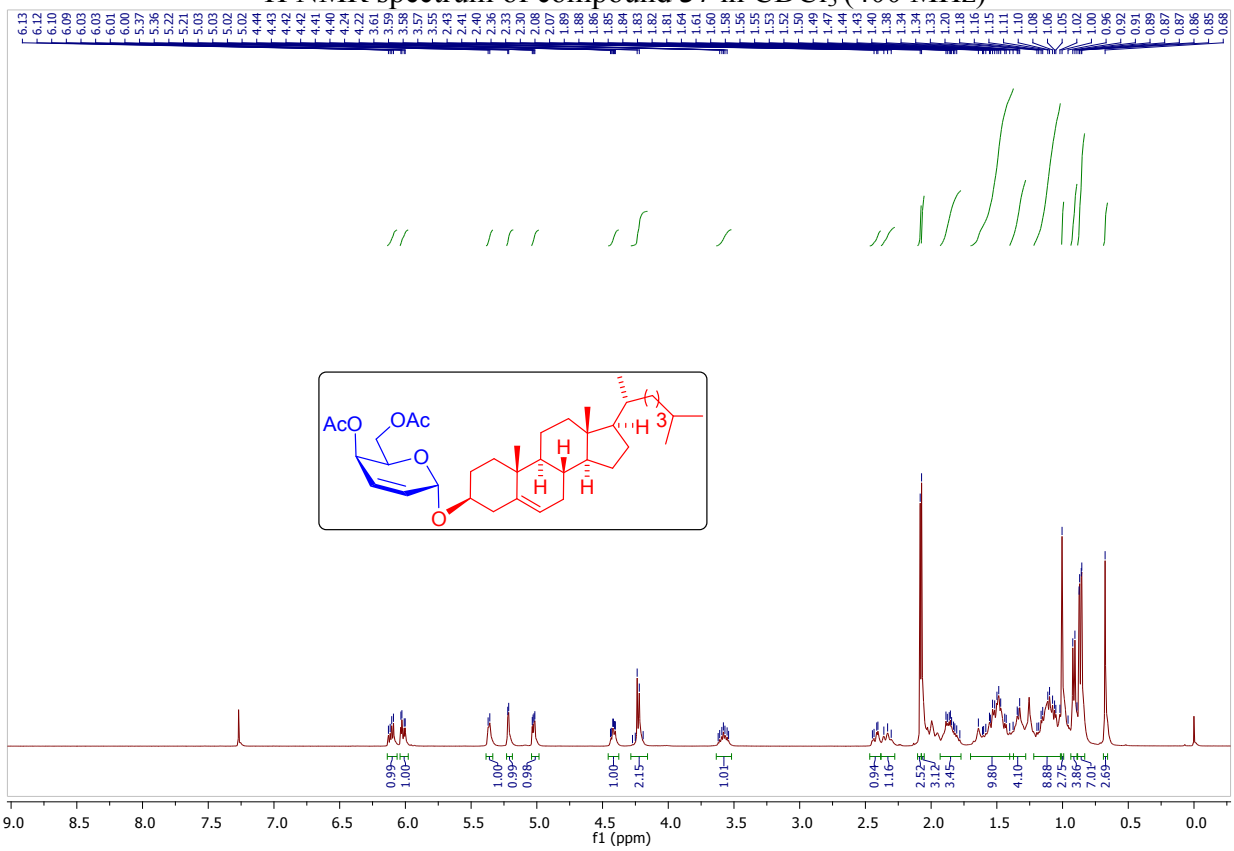
^{1}H NMR spectrum of compound **36** in $CDCl_3$ (400 MHz)



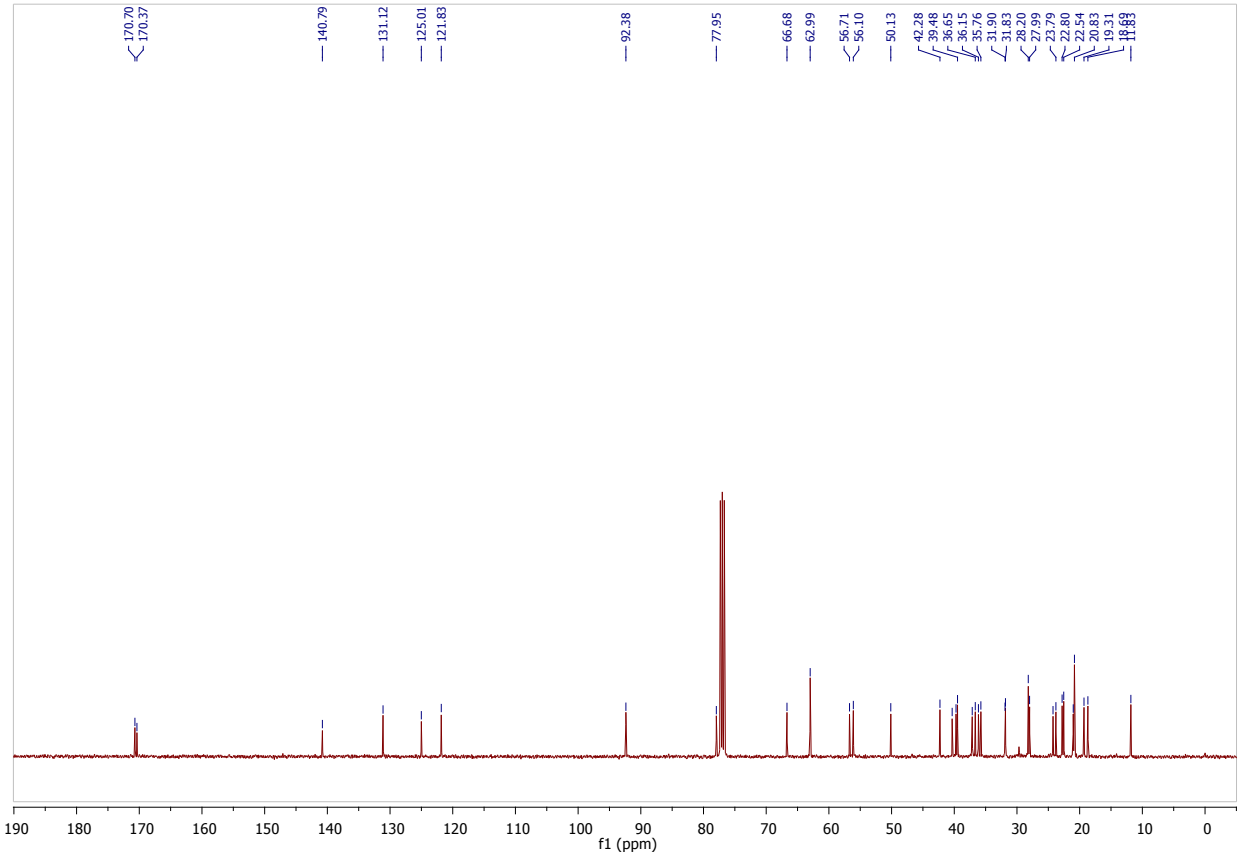
^{13}C NMR spectrum of compound **36** in $CDCl_3$ (101 MHz)



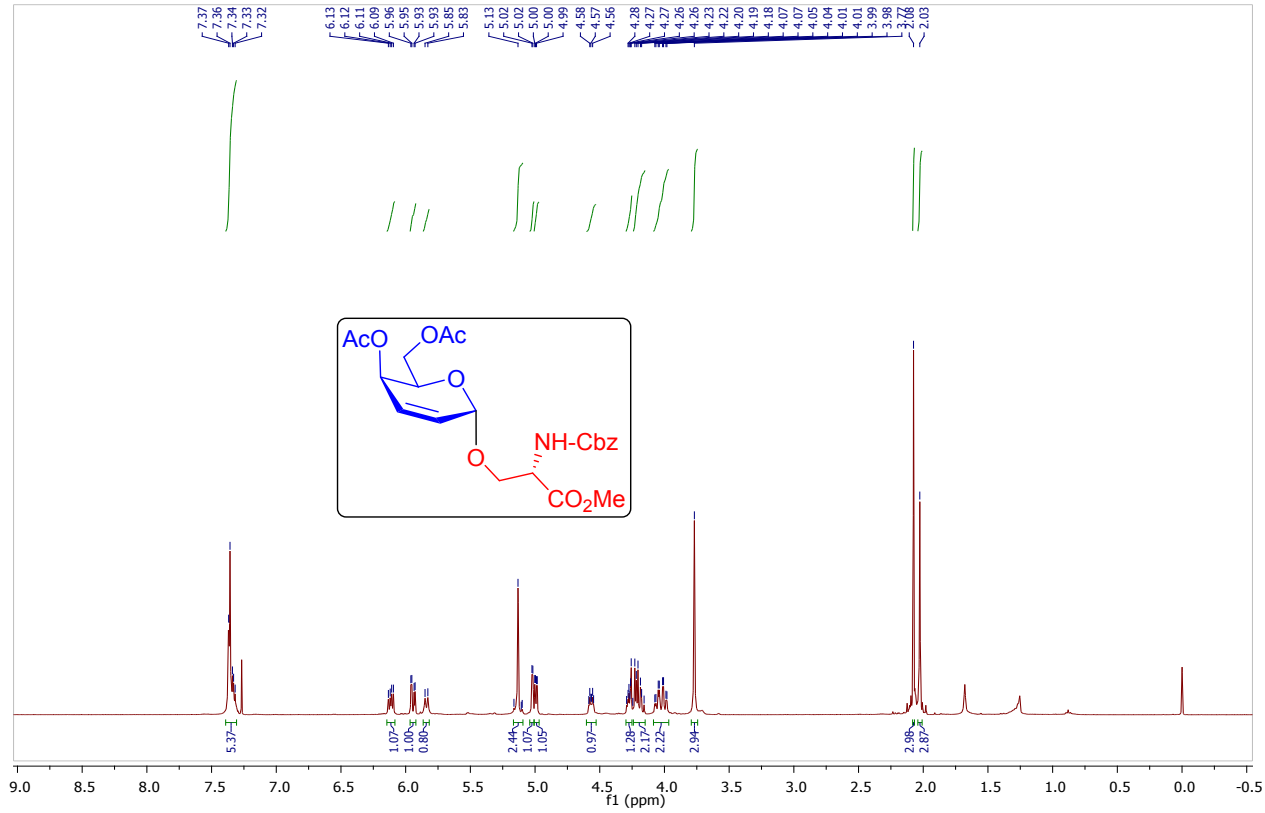
^{1}H NMR spectrum of compound **37** in $CDCl_3$ (400 MHz)



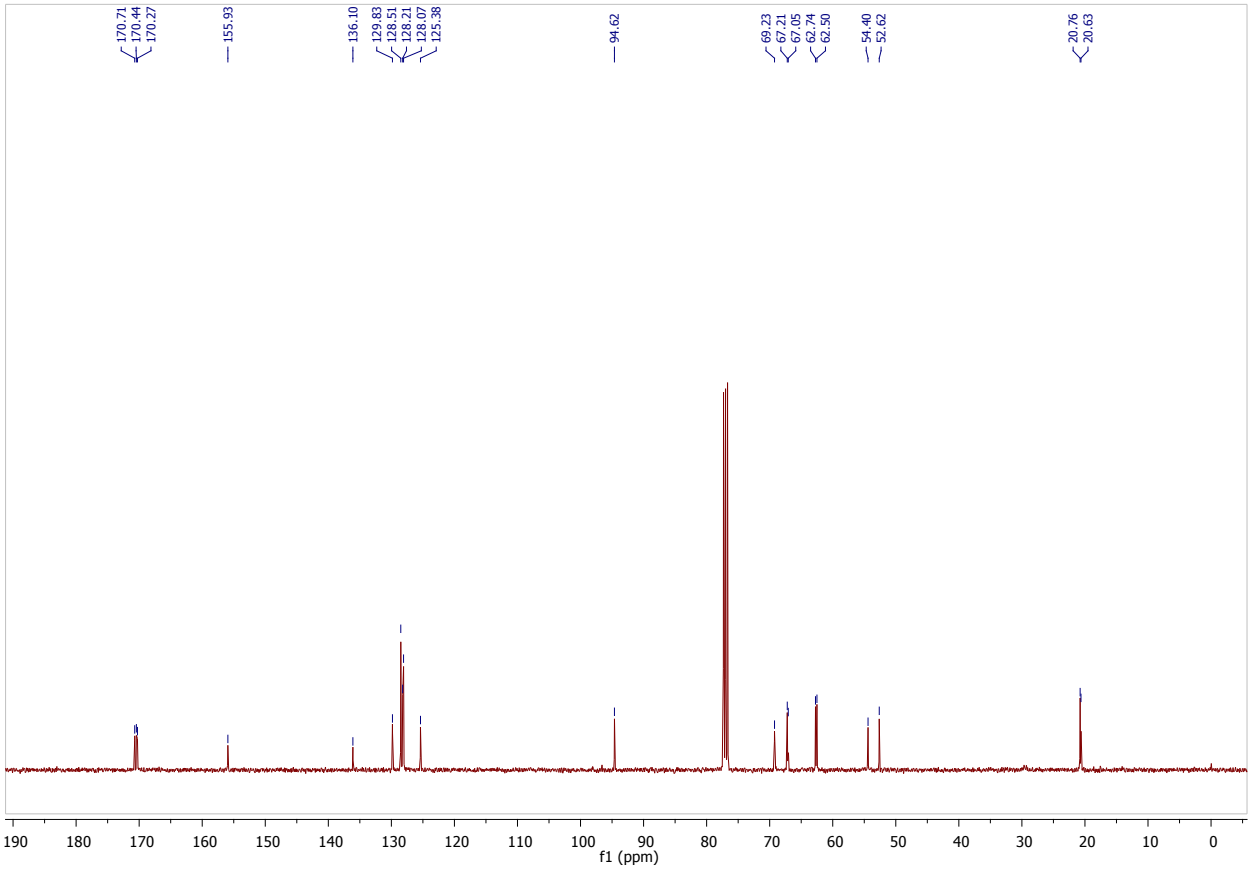
^{13}C NMR spectrum of compound **37** in $CDCl_3$ (101 MHz)



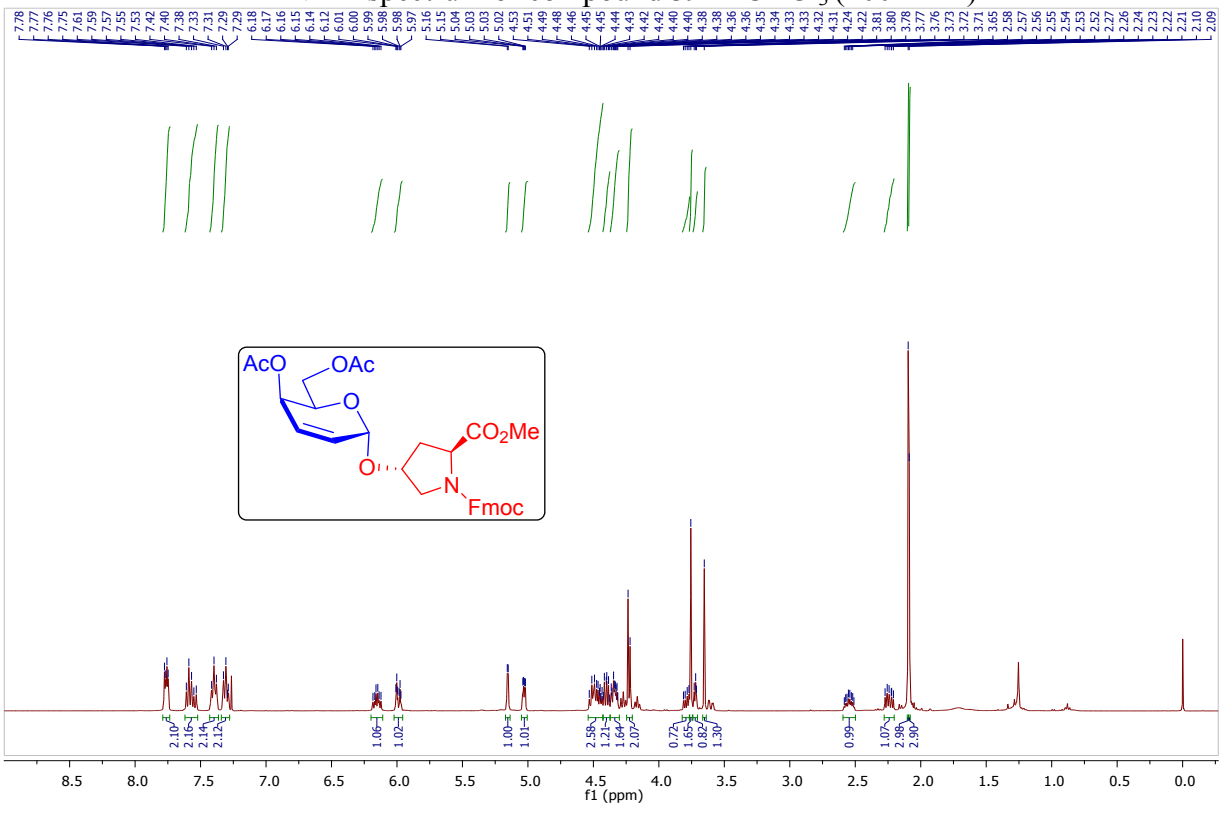
^{1}H NMR spectrum of compound **38** in $CDCl_3$ (400 MHz)



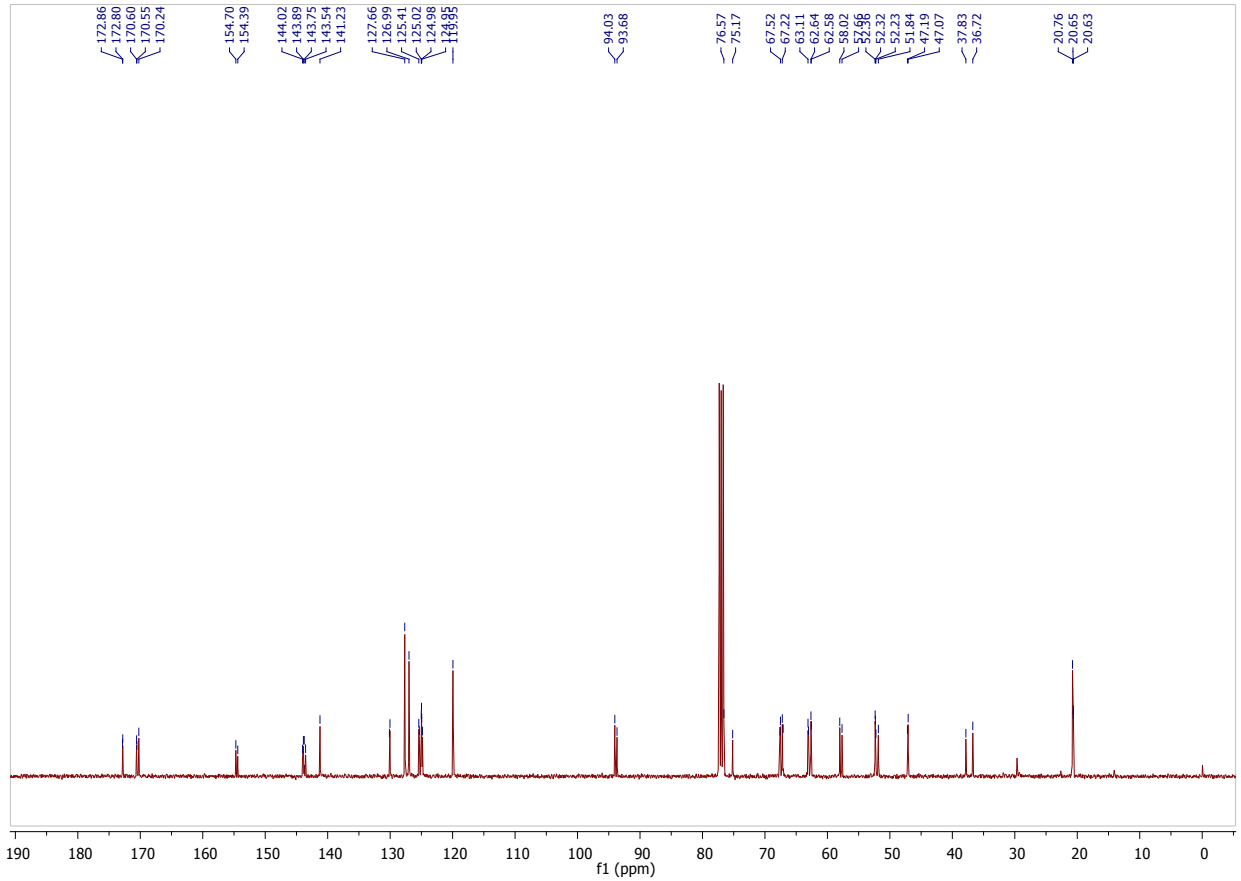
^{13}C NMR spectrum of compound **38** in $CDCl_3$ (101 MHz)



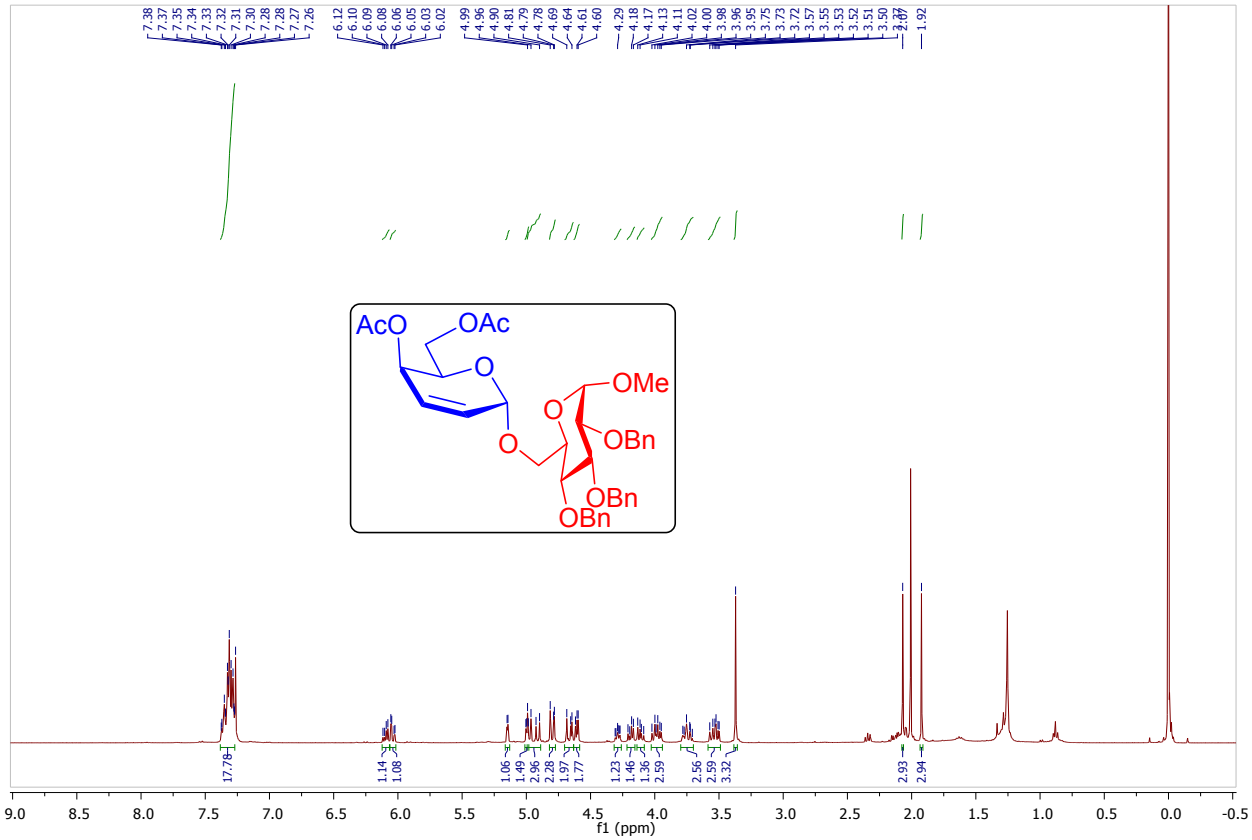
^{1}H NMR spectrum of compound **39** in $CDCl_3$ (400 MHz)



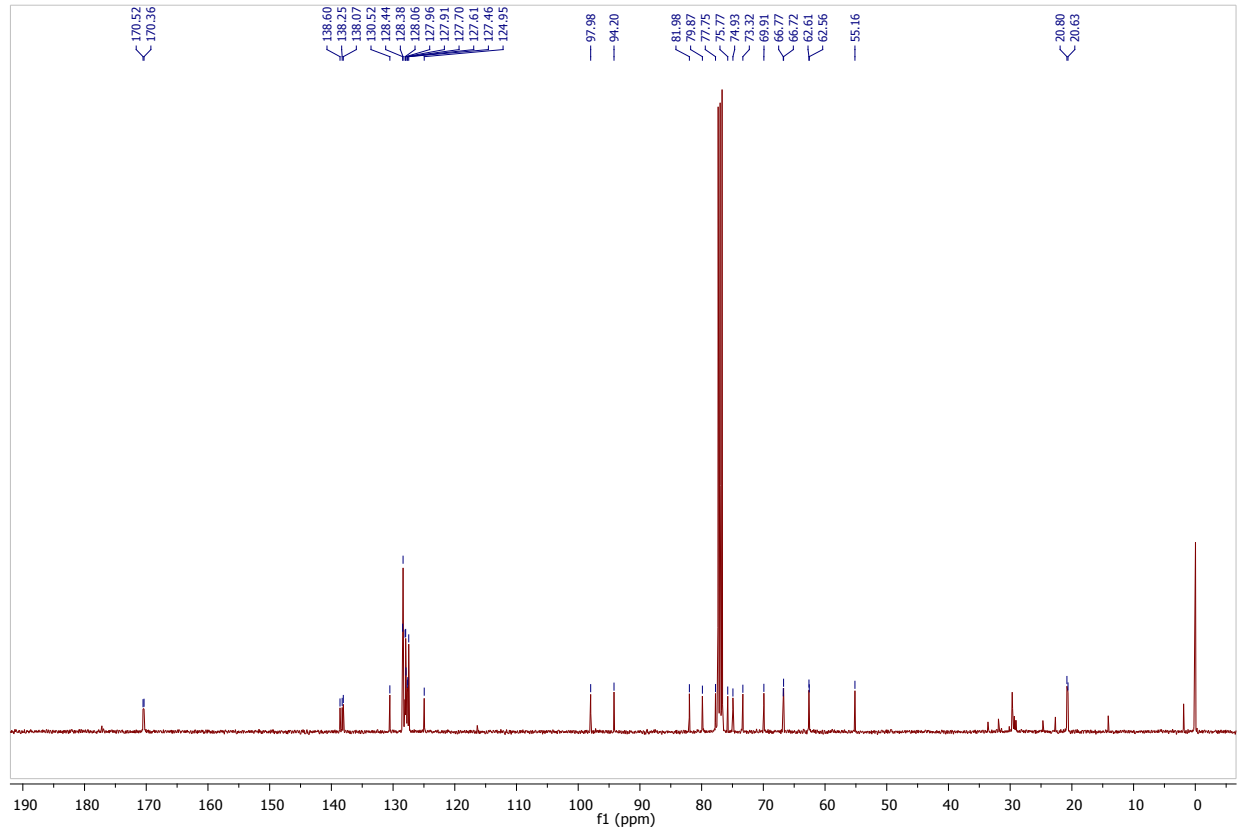
^{13}C NMR spectrum of compound **39** in $CDCl_3$ (101 MHz)



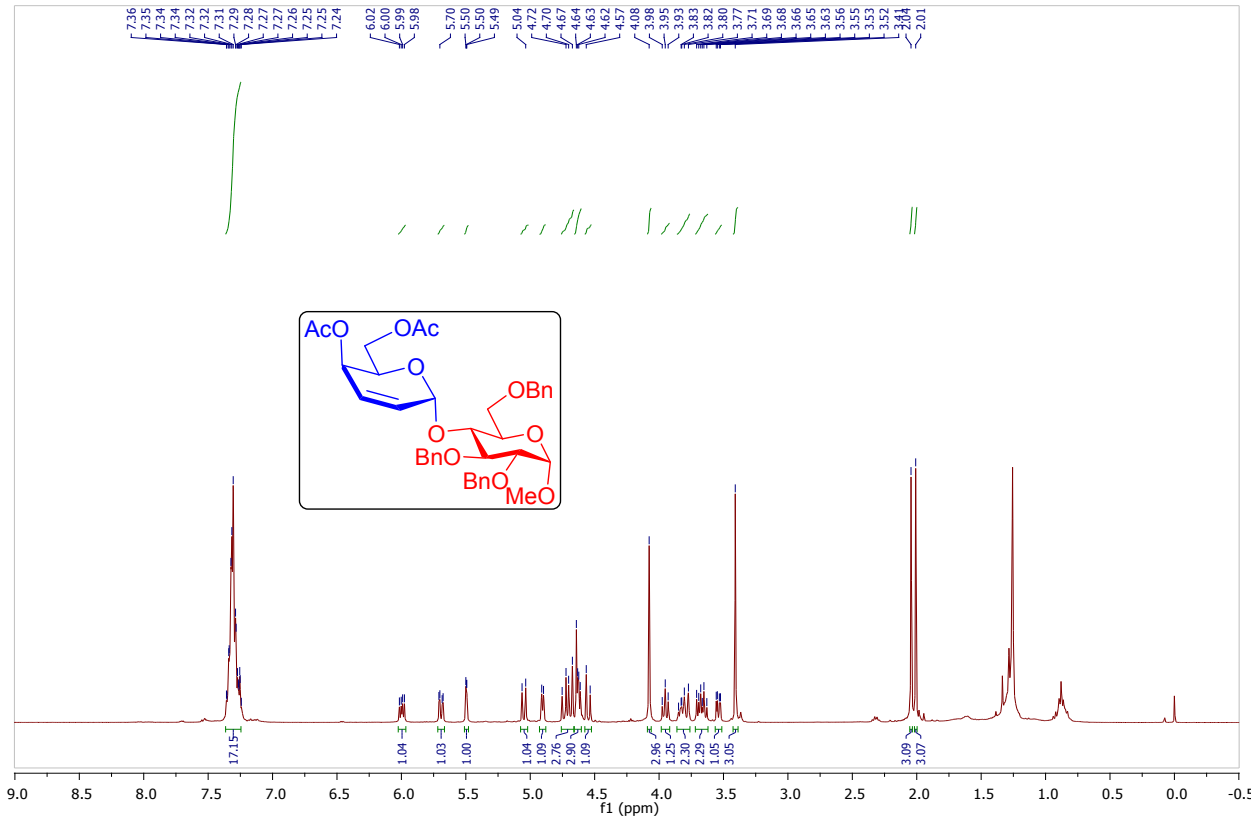
^{1}H NMR spectrum of compound **40** in $CDCl_3$ (400 MHz)



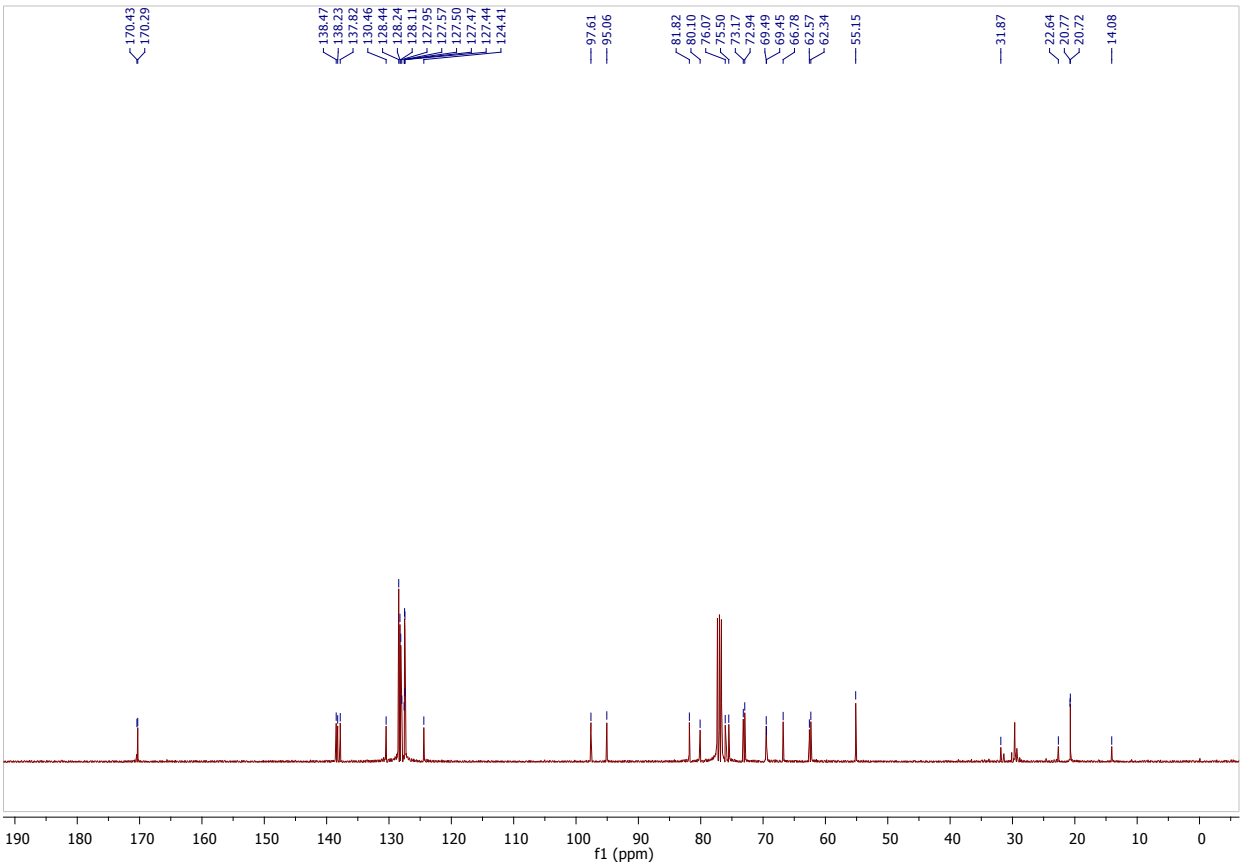
^{13}C NMR spectrum of compound **40** in $CDCl_3$ (101 MHz)



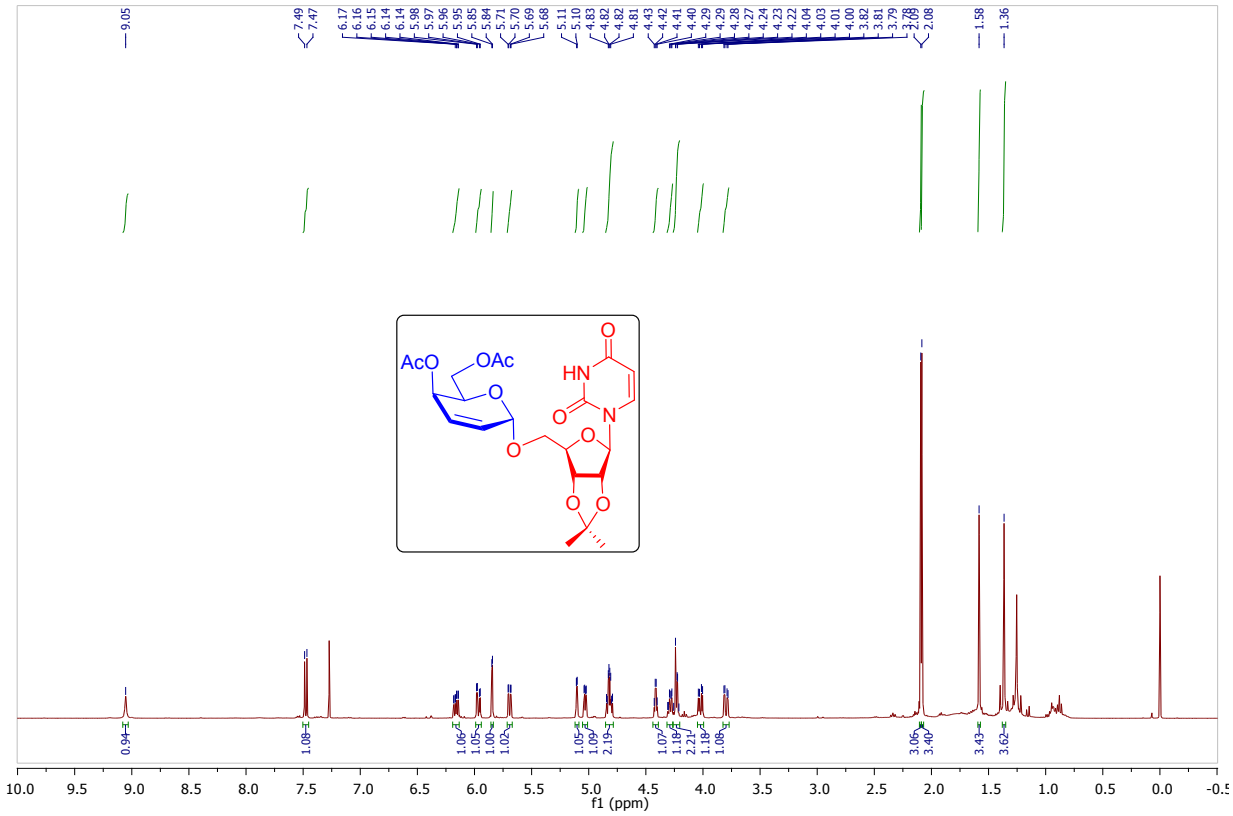
^{1}H NMR spectrum of compound **41** in $CDCl_3$ (400 MHz)



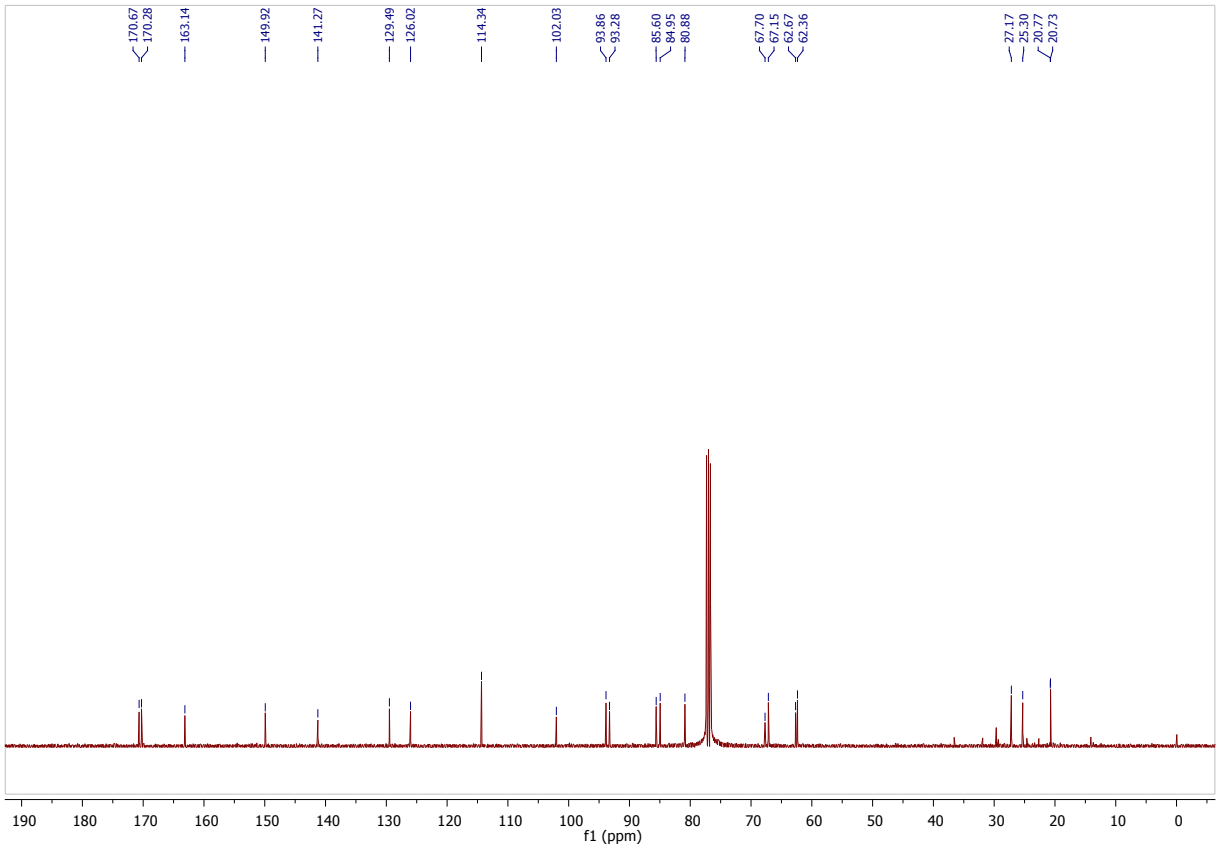
^{13}C NMR spectrum of compound **41** in $CDCl_3$ (101 MHz)



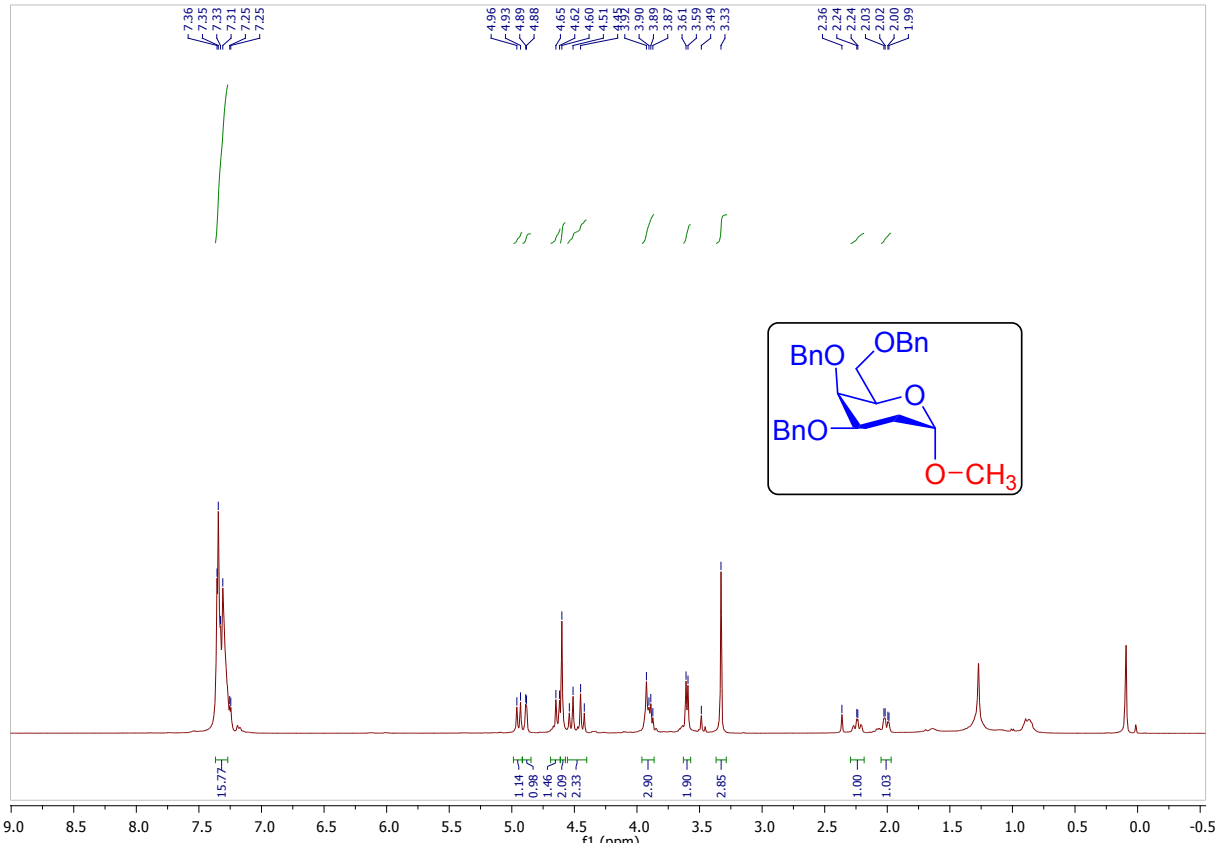
^{1}H NMR spectrum of compound **42** in $CDCl_3$(400 MHz)



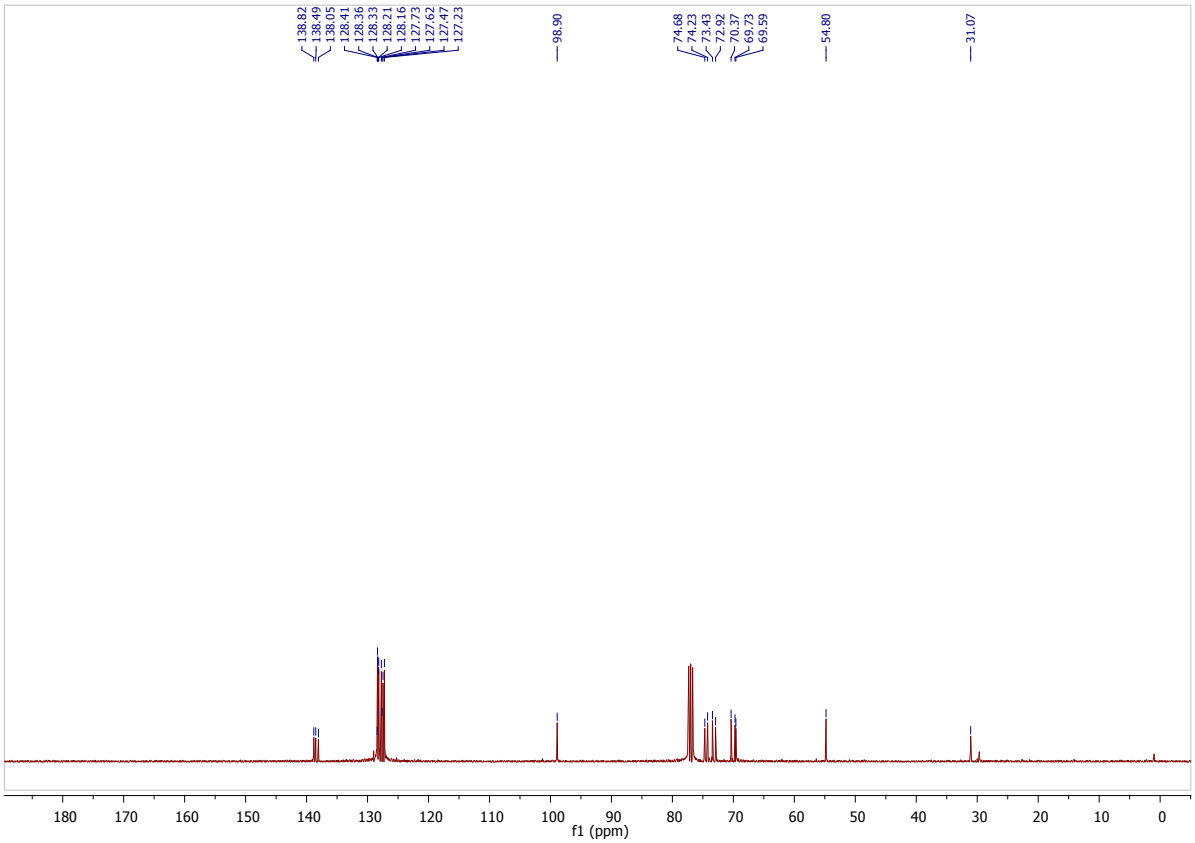
^{13}C NMR spectrum of compound **42** in $CDCl_3$(101 MHz)



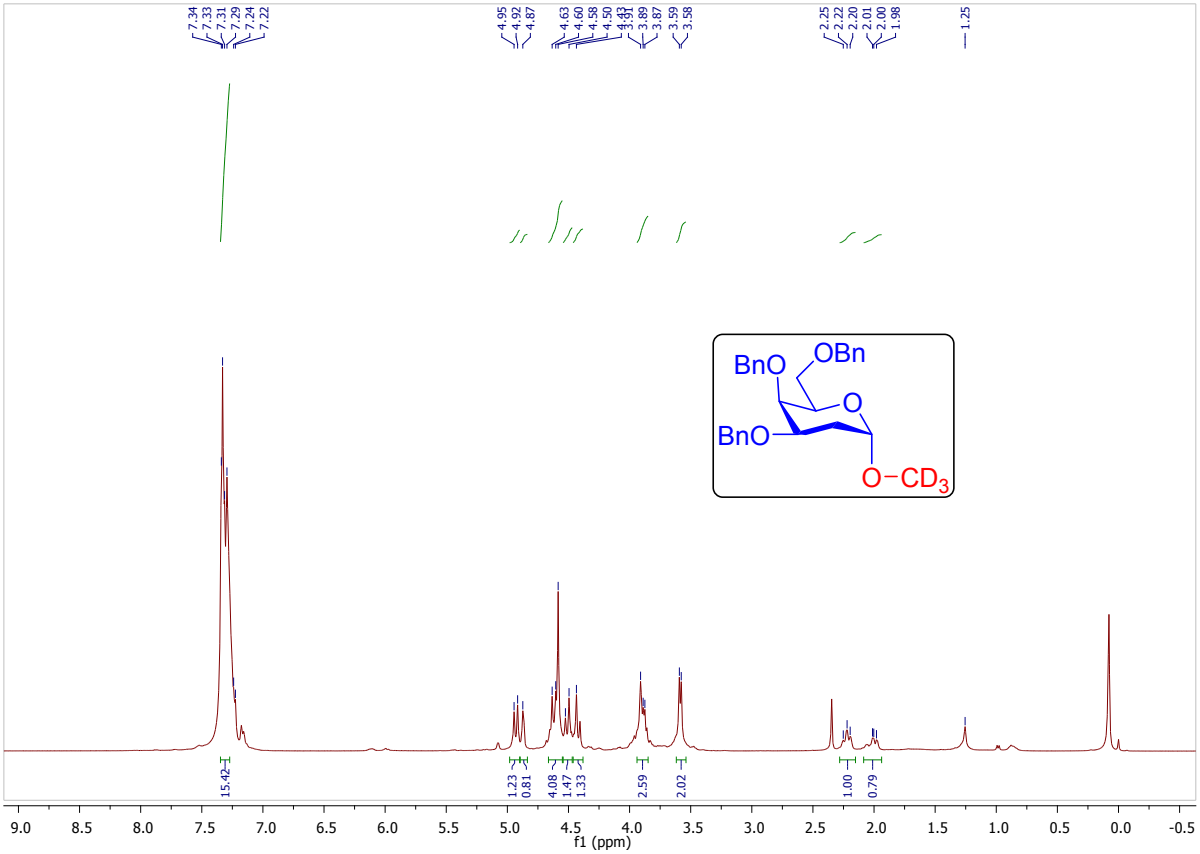
^{1}H NMR spectrum of compound **43** in $CDCl_3$ (400 MHz)



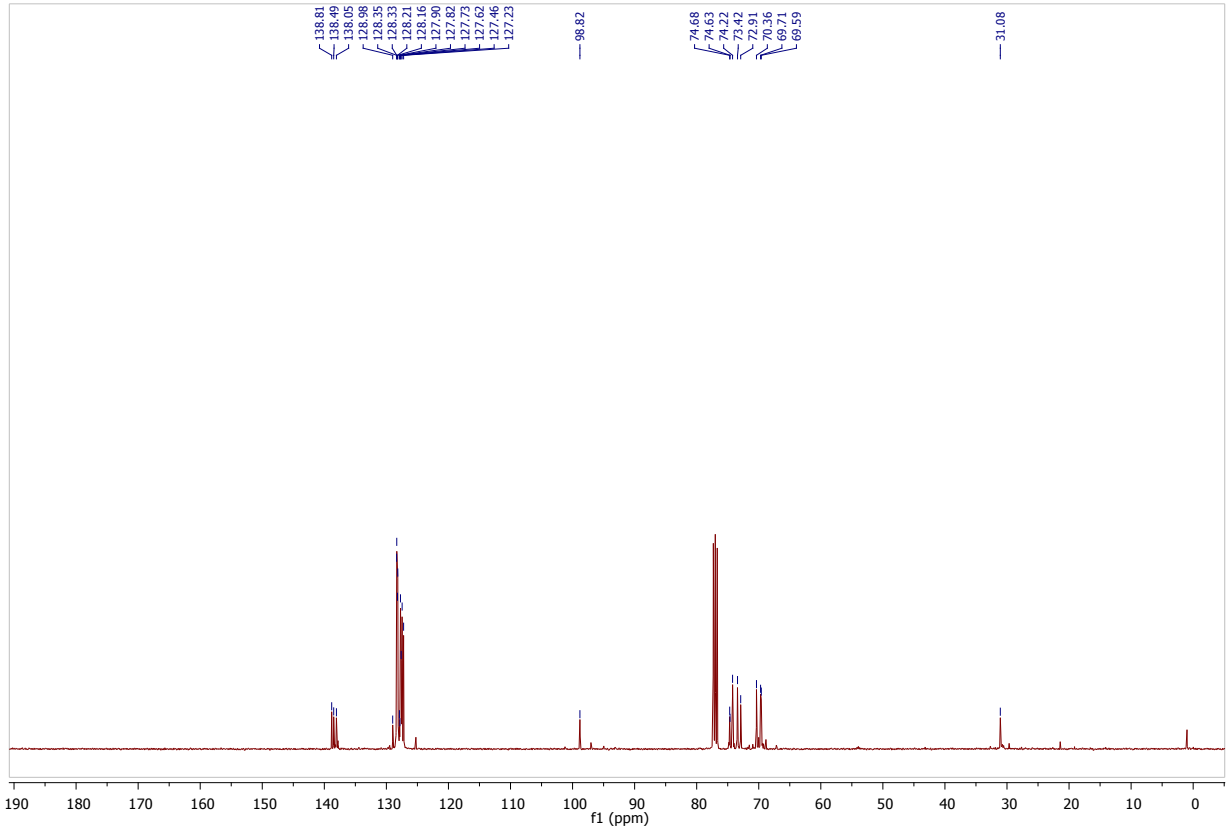
^{13}C NMR spectrum of compound **43** in $CDCl_3$ (101 MHz)



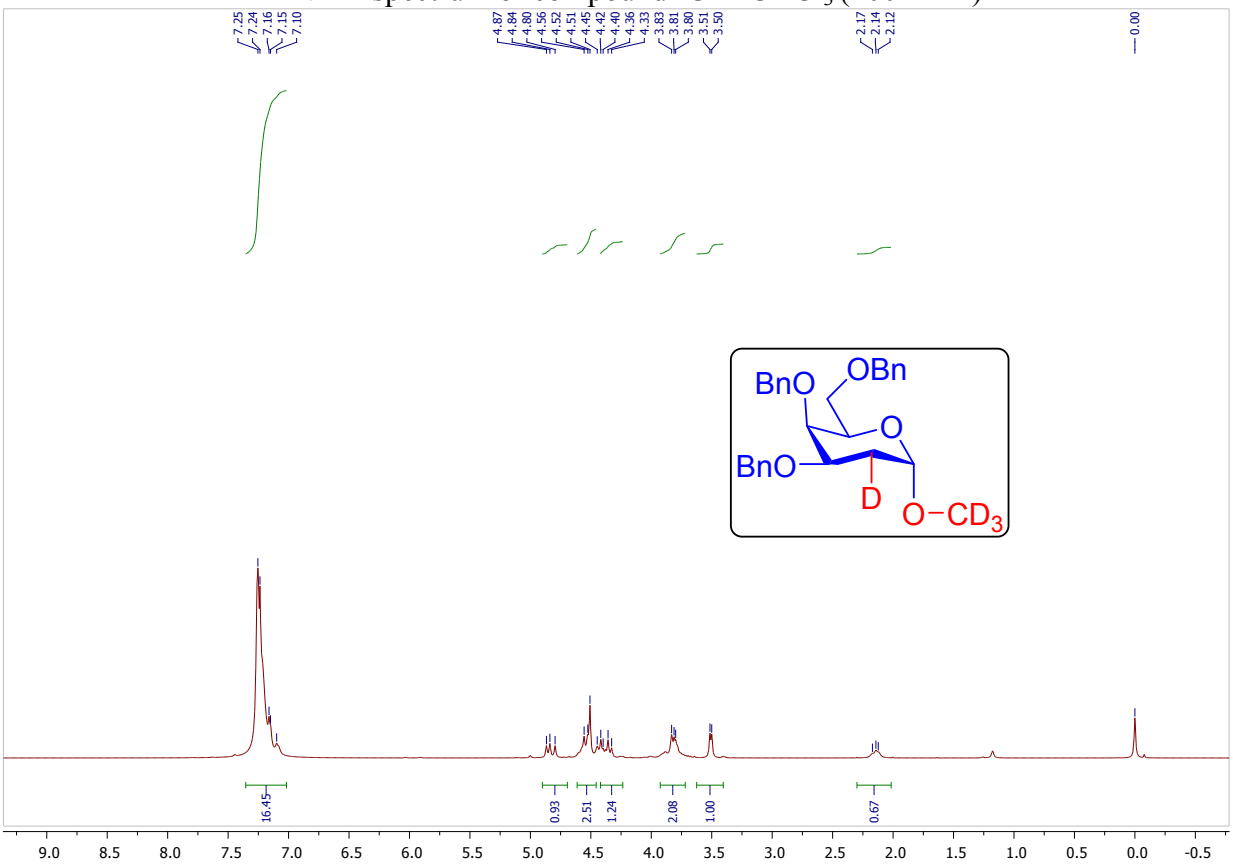
^{1}H NMR spectrum of compound **44** in $CDCl_3$ (400 MHz)



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



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



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