Electronic Supplementary Material (ESI) for RSC Advances.

A mild and efficient Zn-catalyzed *C*-glycosylation: Synthesis of C(2)-C(3) unsaturated *C*-linked glycopyranosides

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Supporting Information

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Experimental

General Synthesis Information. Reactions were run in screw capped glass vials (4 mL) stirred with Teflon®-coated magnetic stir bars. Moisture and air-sensitive reactions were performed in flame-dried round bottom flasks, fitted with rubber septa or glass gas adapters, under a positive pressure of nitrogen. Moisture and air-sensitive liquids or solutions were transferred via nitrogen-flushed syringe. Concentration of solvents was accomplished by rotary evaporation using a Büchi rotary evaporator at temperatures between 35 °C and 50 °C. Experiments were monitored by thin layer chromatography (TLC).

Materials. Unless otherwise noted, materials were obtained from commercial suppliers and used without purification. Removal of solvent under reduced pressure refers to distillation with a Büchi rotary evaporator attached to a vacuum pump (~3 mmHg). Products obtained as solids or high boiling oils were dried under vacuum (~1 mmHg).

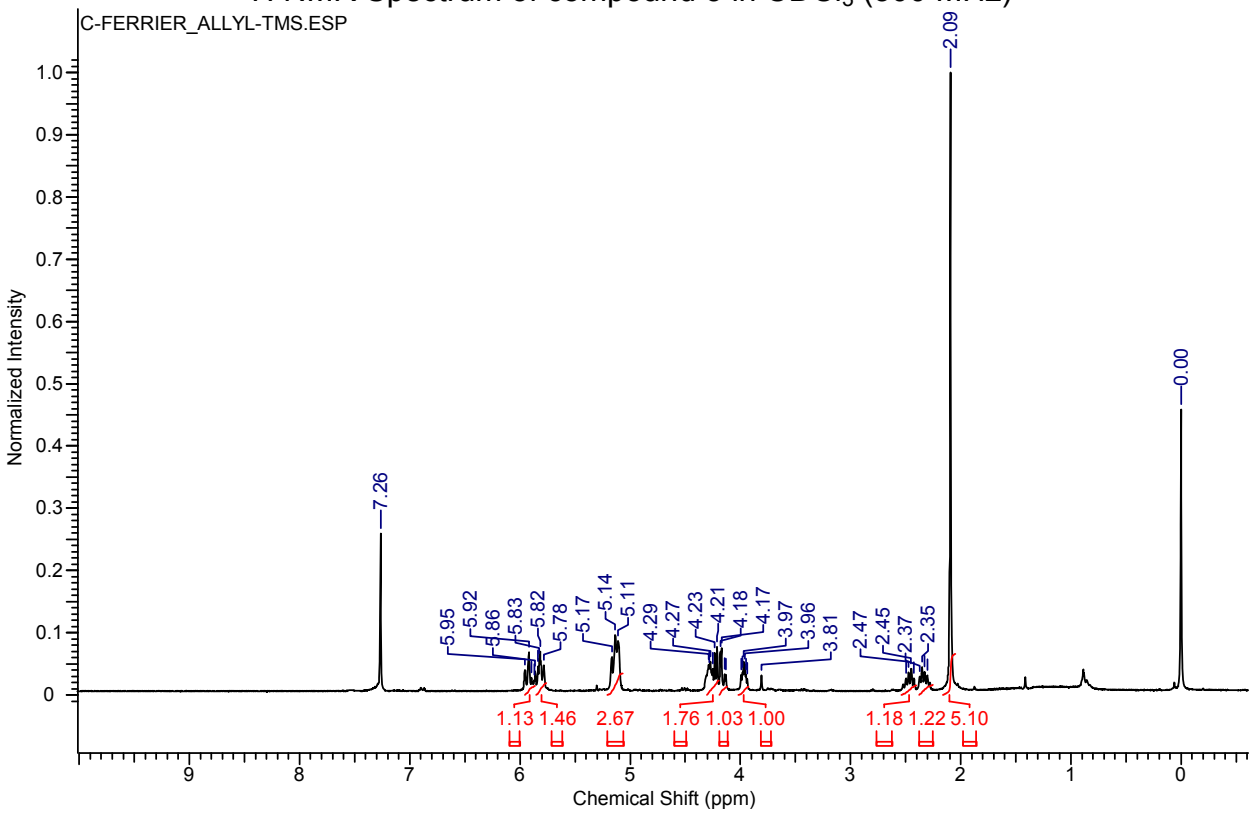
Chromatography. Analytical TLC was performed using Whatman 250 micron aluminum backed UV F254 pre-coated silica gel flexible plates. Subsequent to elution, ultraviolet illumination at 254 nm allowed for visualization of UV active materials. Staining with p-anisaldehyde, basic potassium permanganate solution, or Molisch's reagents allowed for further visualization. The retardation factor (Rf) is the ratio of the distance traveled by the compound to the distance traveled by the eluent.

Physical Data. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Avance 300 or Avance 500 MHz nuclear magnetic resonance spectrometers. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) relative to tetramethylsilane (δ 0.0) using the residual solvent signal as an internal standard or tetramethylsilane itself: chloroform-d (δ 7.26, singlet). The number of protons (n) for a given resonance is indicated by nH. IR spectra were recorded on Bruker Alpha spectrometer and mass analyses (ESI) were performed on Finnegan MAT 1020 mass spectrometer operating at 70 eV.

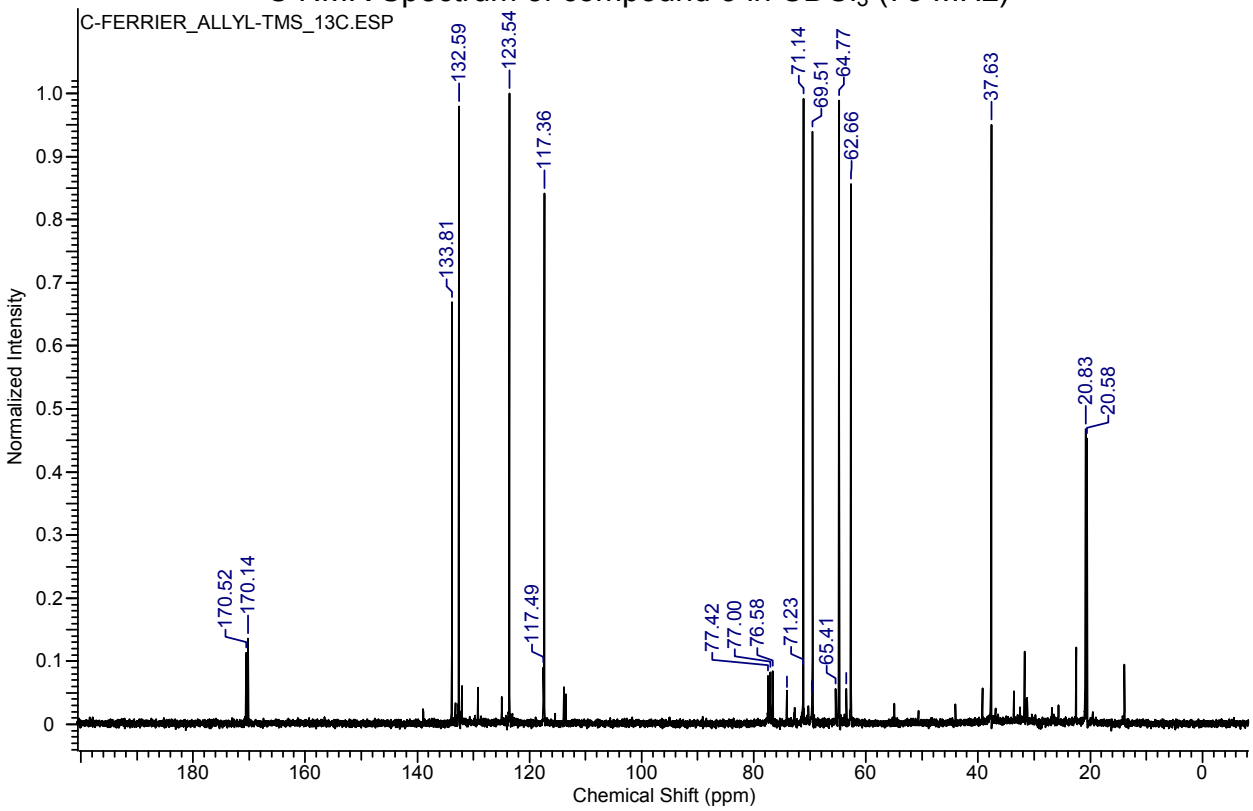
General experimental procedure for the synthesis of glycosides 3-31; To a stirred solution of glycal (1 equiv) and acceptor (1.2 equiv) in anhydrous 1,2-dichloroethane (2 mL/mmol) under an atmosphere of argon was added $Zn(OTf)_2$ (10 mol%) at room temperature. The reaction mixture was stirred at 40 ^{o}C until the complete consumption of the starting material (glycal), adjudged by TLC. The reaction was quenched with saturated $NaHCO_3$ (5 mL), diluted with EtOAc (10 mL), and extracted with EtOAC (3 X 30 mL). The combined organic layers were washed with brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by silica gel column chromatography. All the compounds were confirmed by ^{1}H NMR, ^{13}C NMR and MS/HRMS spectroscopy and overall data were in complete agreement with the assigned structure.

General experimental procedure for the synthesis of glycosides 32-35; To a stirred solution of $Zn(OTf)_2$ (10 mol%) in 1,2-dichloroethane (2 mL/mmol) in a two-necked round-bottom flask under an atmosphere of argon was added a solution of trimethylaluminum (2.0 M in hexanes, 1.5 equiv) at 0 ^{o}C. The reaction mixture was stirred vigorously for 10-15 min at ice-cooled temperature. A preformed solution of glycal (1.0 equiv) in anhydrous 1,2-dichloroethane (2 mL/mmol) was added dropwise to the above-mentioned reaction mixture and reaction mixture was allowed to stirred at room temperature for 1h. The reaction was quenched with saturated $NaHCO_3$ (5 mL), diluted with EtOAc (10 mL), and extracted with EtOAC (3 X 30 mL). The combined organic layers were washed with brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by silica gel column chromatography to obtain the desired methyl glycosides.

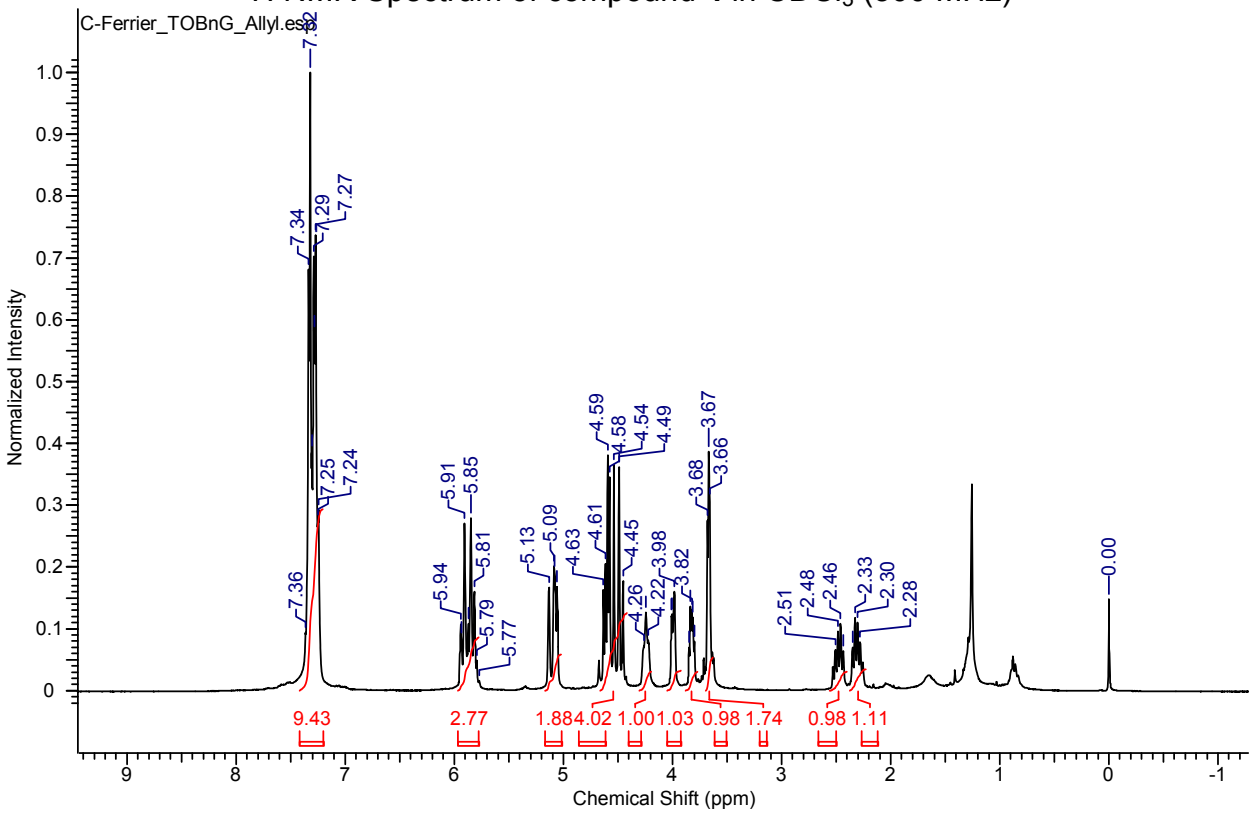
^{1}H NMR Spectrum of compound **3** in $CDCl_3$ (300 MHz)



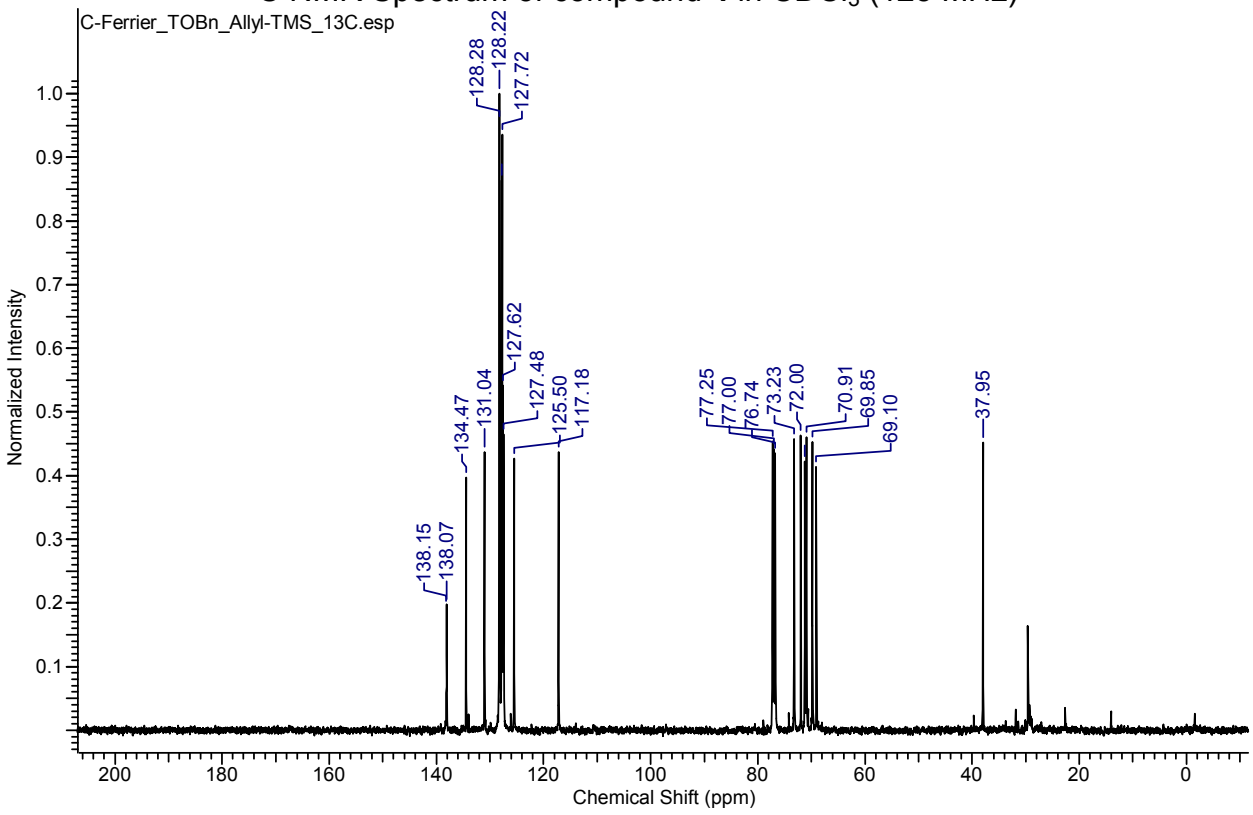
^{13}C NMR Spectrum of compound **3** in $CDCl_3$ (75 MHz)



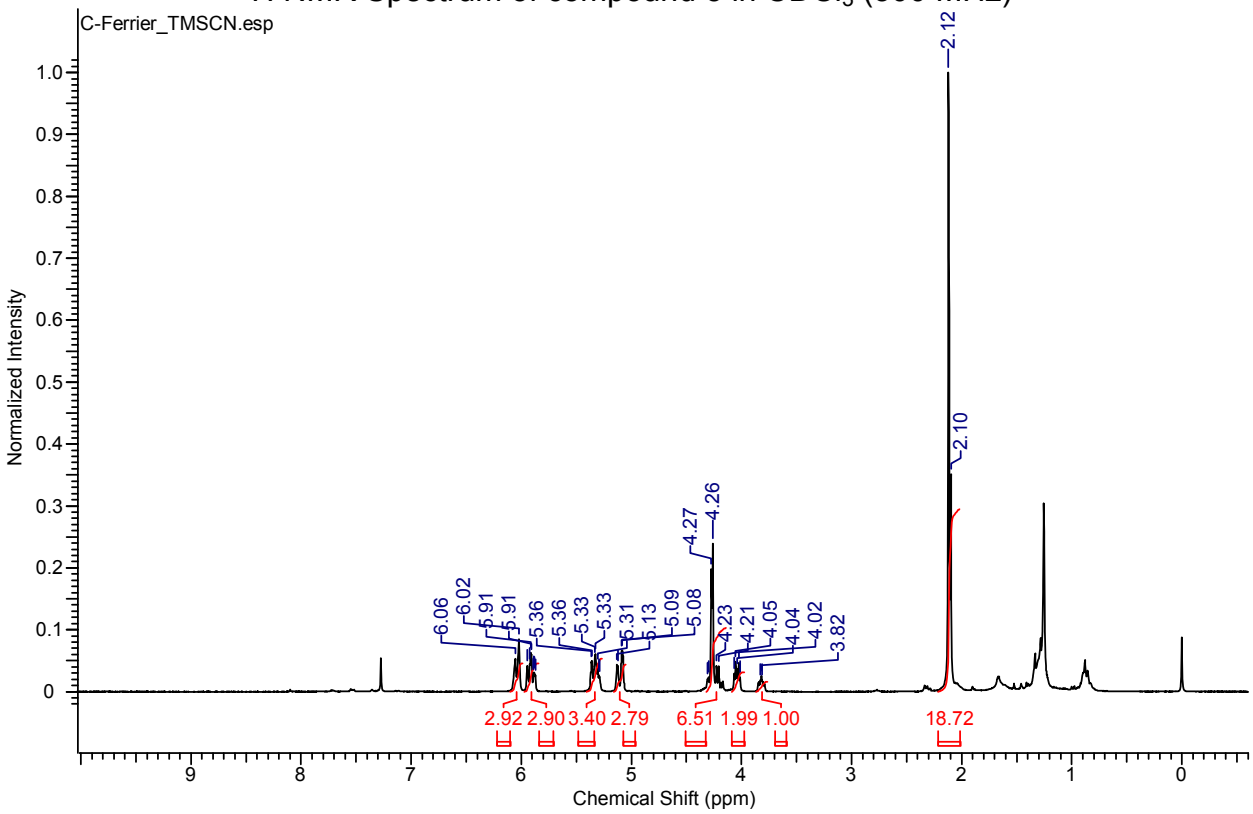
^{1}H NMR Spectrum of compound **4** in $CDCl_3$ (300 MHz)



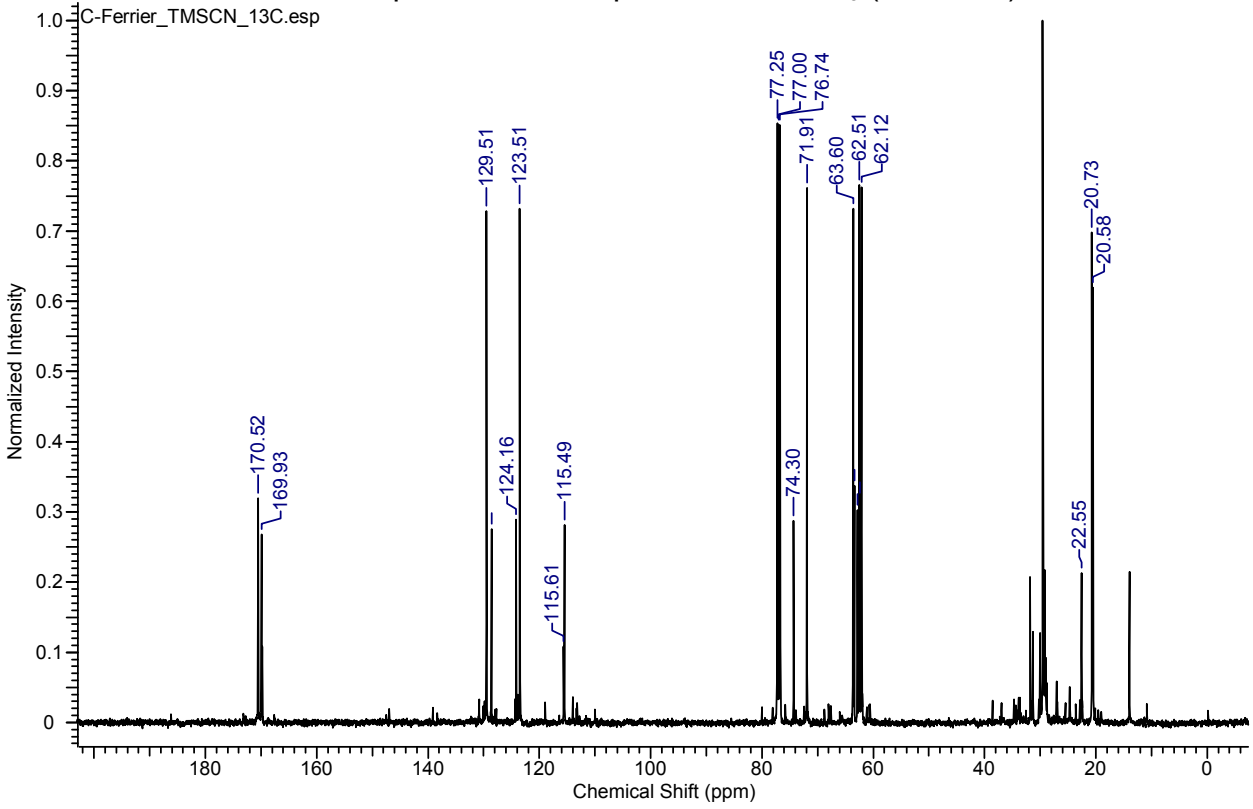
^{13}C NMR Spectrum of compound **4** in $CDCl_3$ (125 MHz)



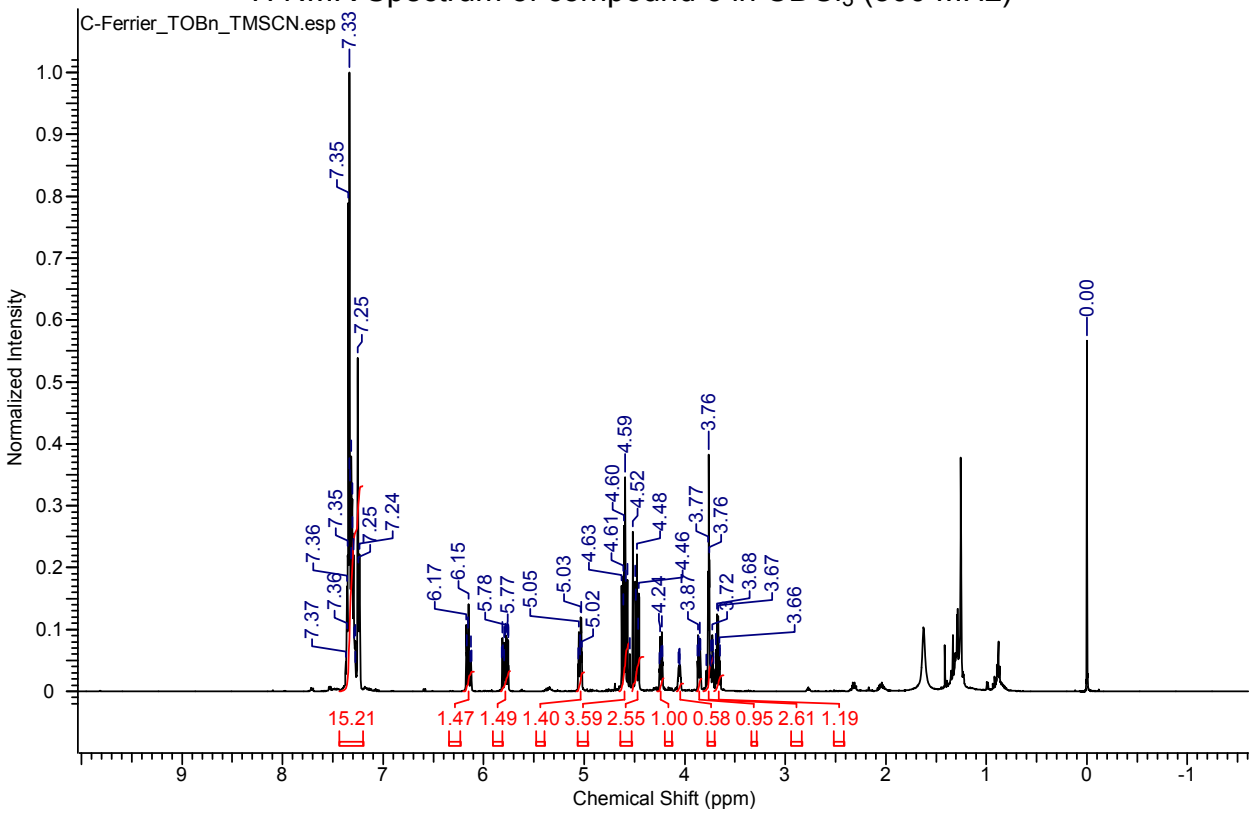
^{1}H NMR Spectrum of compound **5** in $CDCl_3$ (300 MHz)



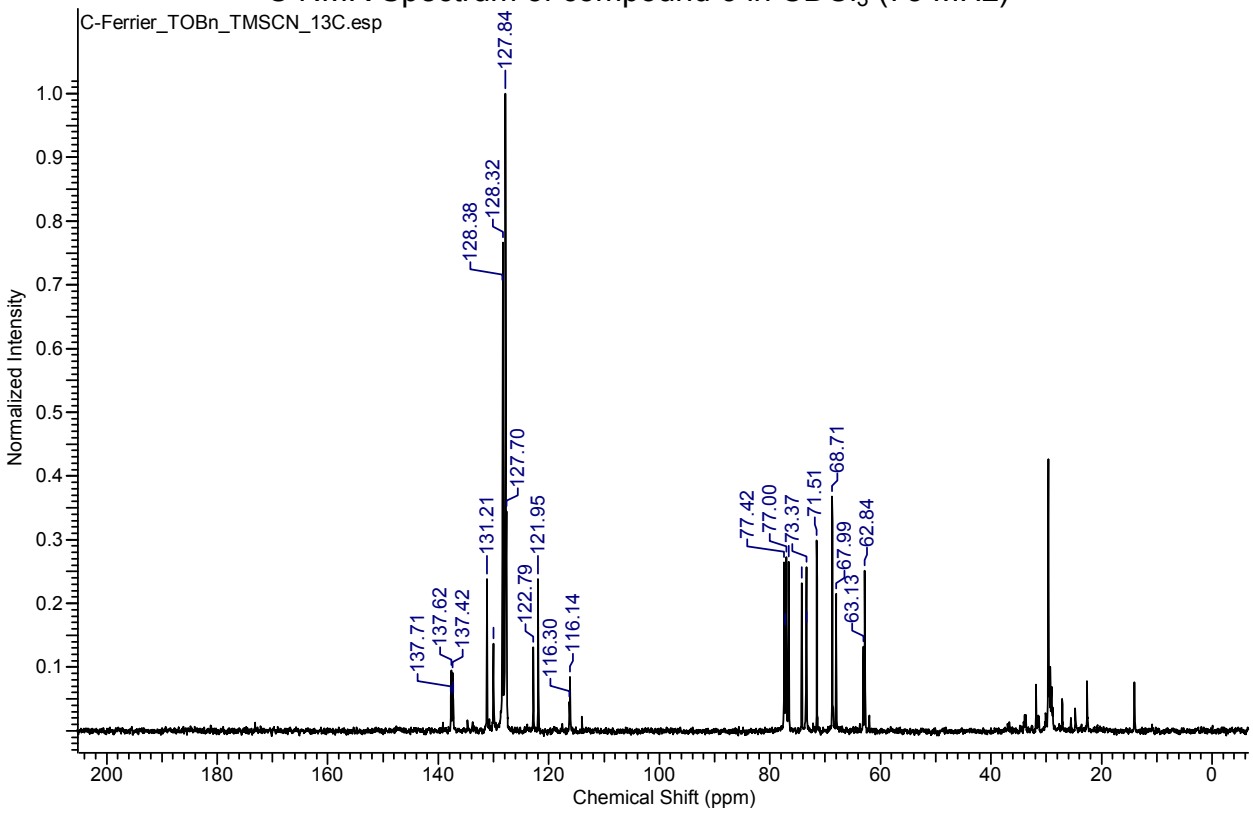
^{13}C NMR Spectrum of compound **5** in $CDCl_3$ (125 MHz)



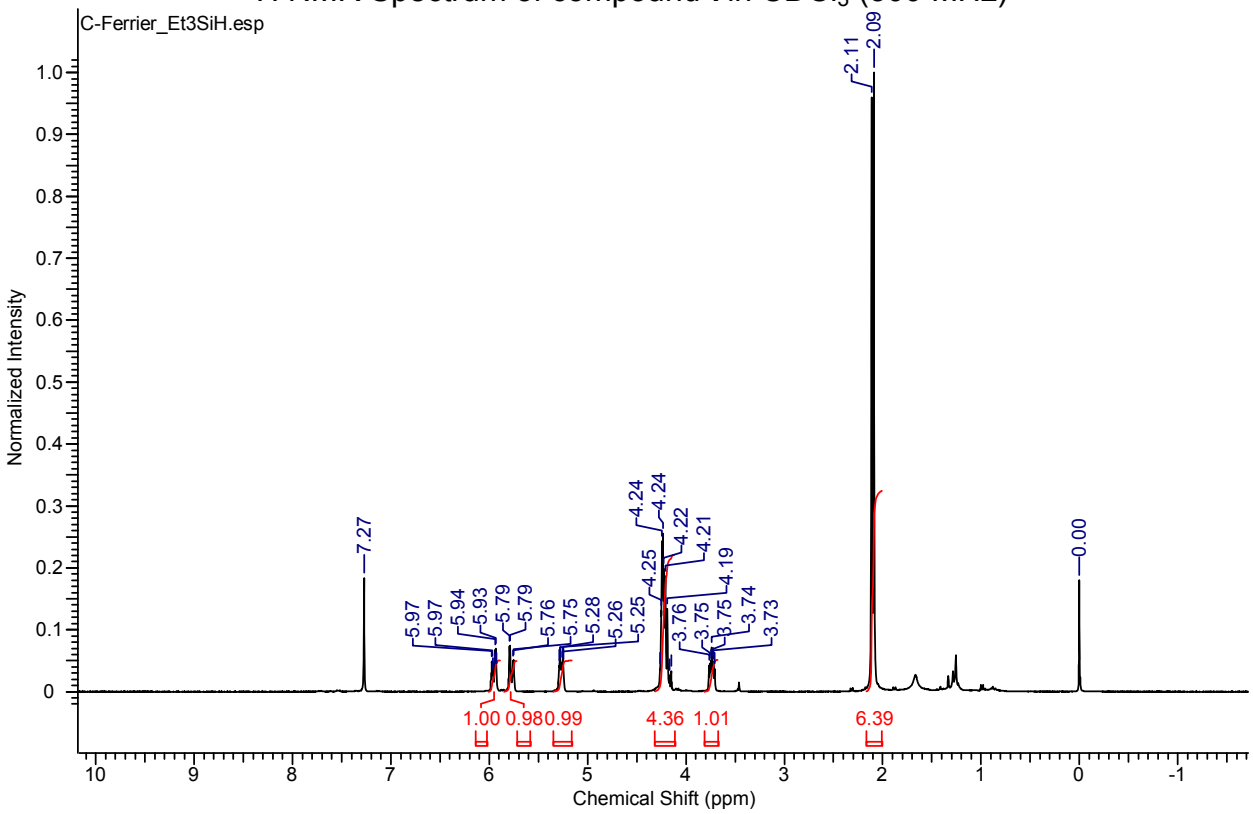
^{1}H NMR Spectrum of compound **6** in $CDCl_3$ (300 MHz)



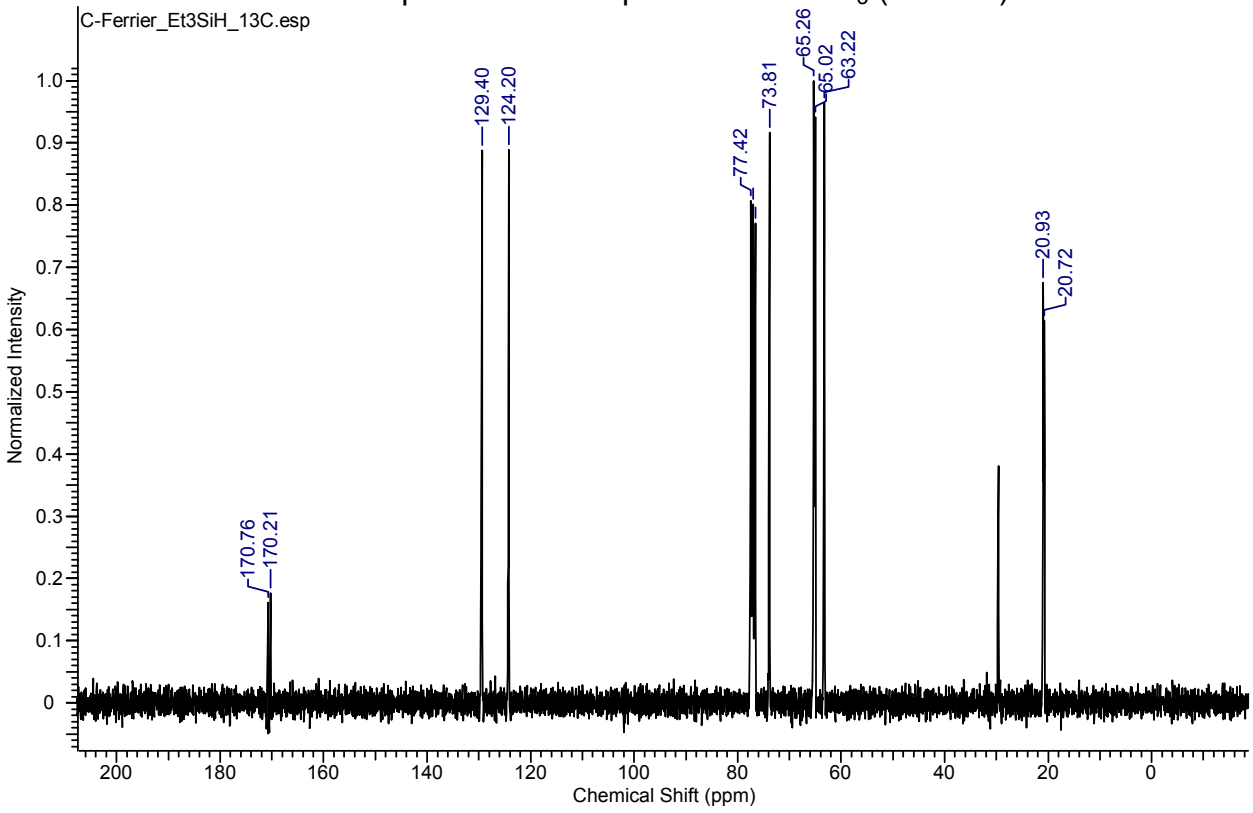
^{13}C NMR Spectrum of compound **6** in $CDCl_3$ (75 MHz)



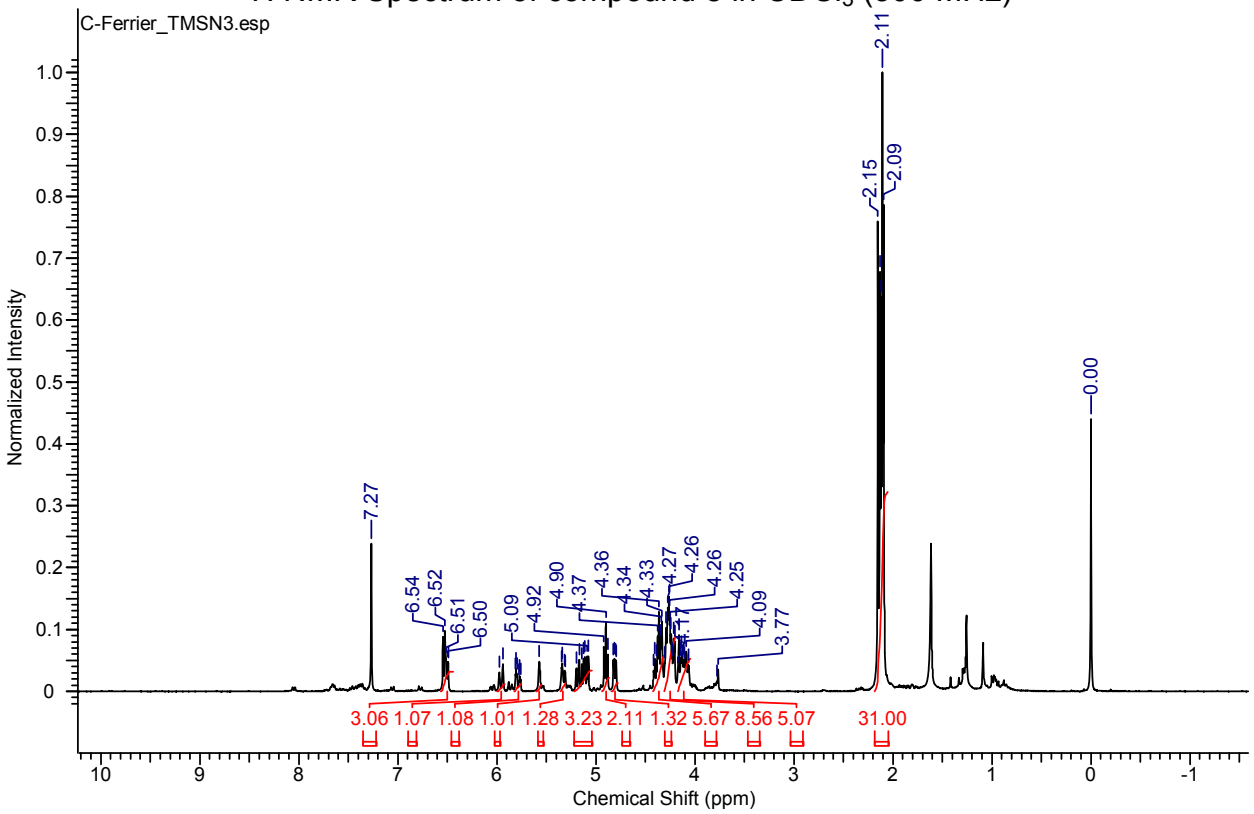
^{1}H NMR Spectrum of compound **7**in $CDCl_3$ (300 MHz)



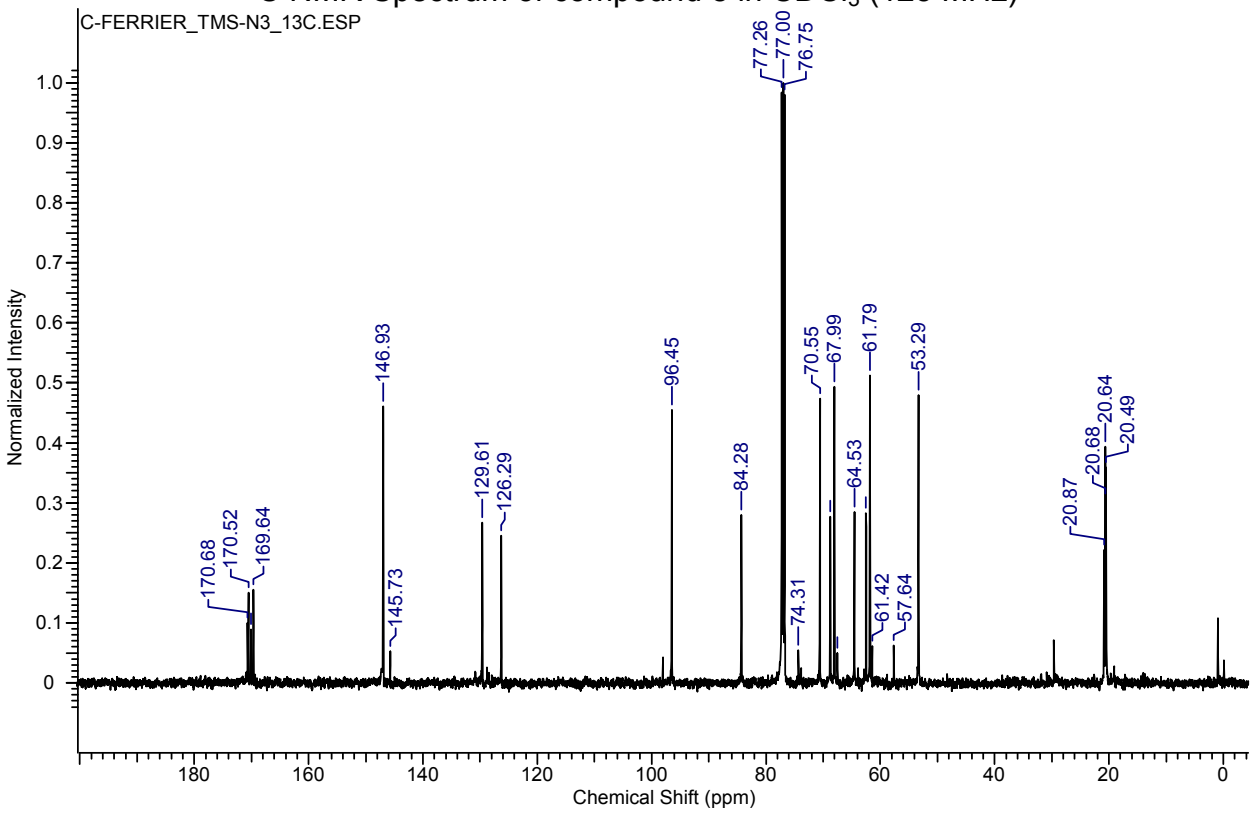
^{13}C NMR Spectrum of compound **7** in $CDCl_3$ (75 MHz)



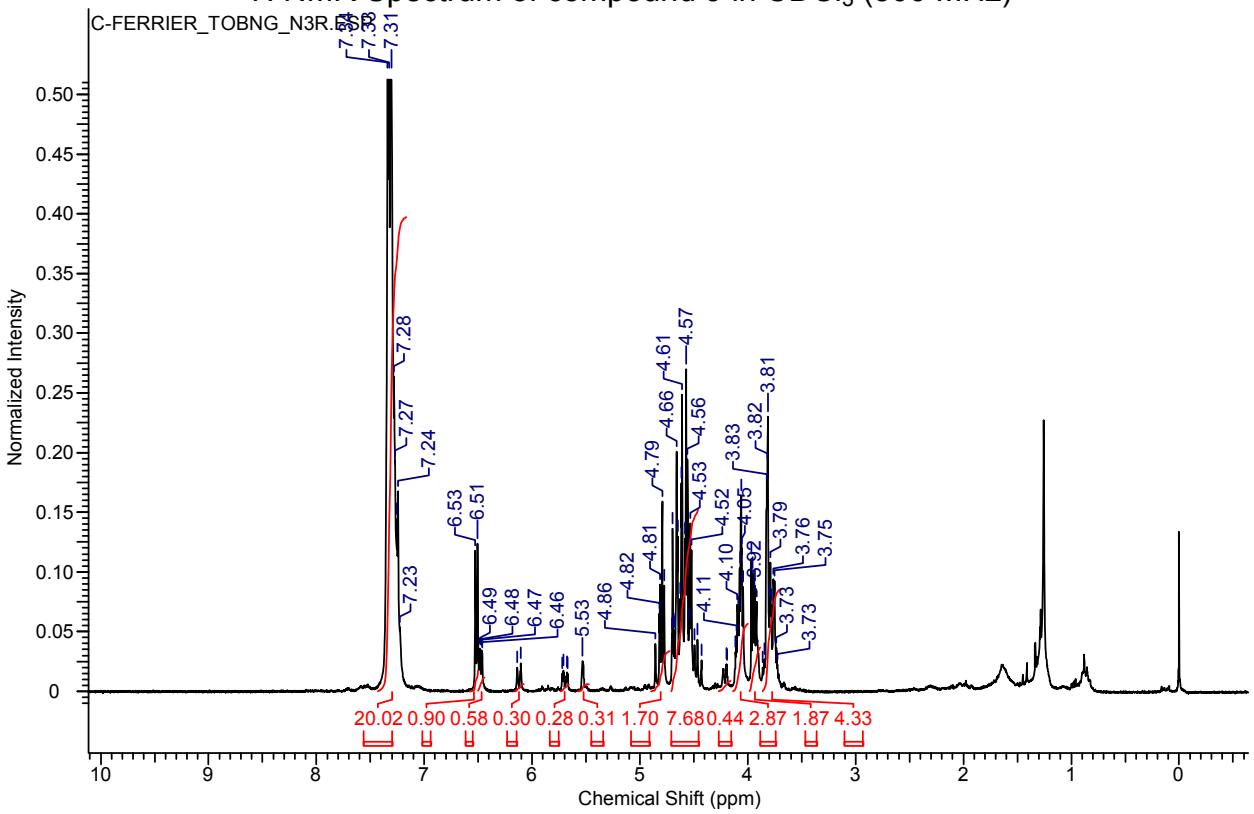
^{1}H NMR Spectrum of compound **8** in $CDCl_3$ (300 MHz)



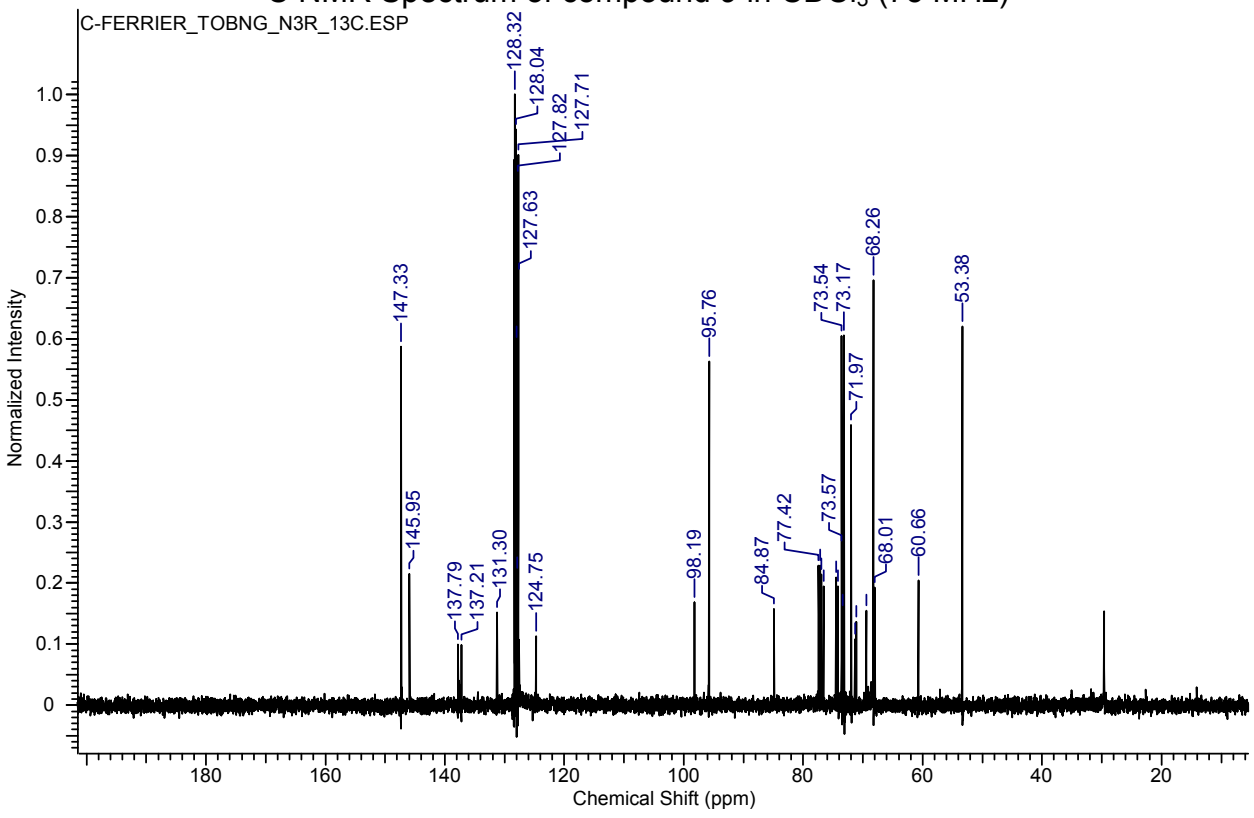
^{13}C NMR Spectrum of compound **8** in $CDCl_3$ (125 MHz)



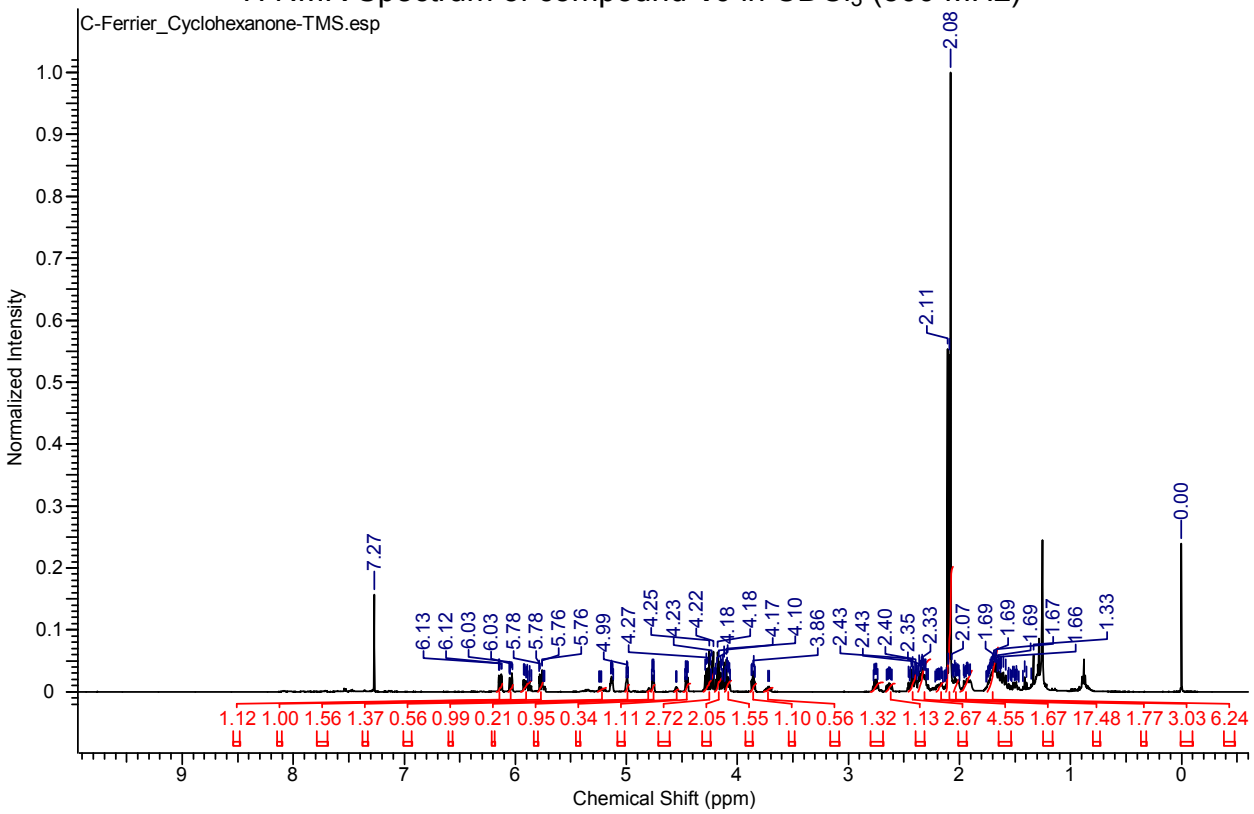
^{1}H NMR Spectrum of compound **9** in $CDCl_3$ (300 MHz)



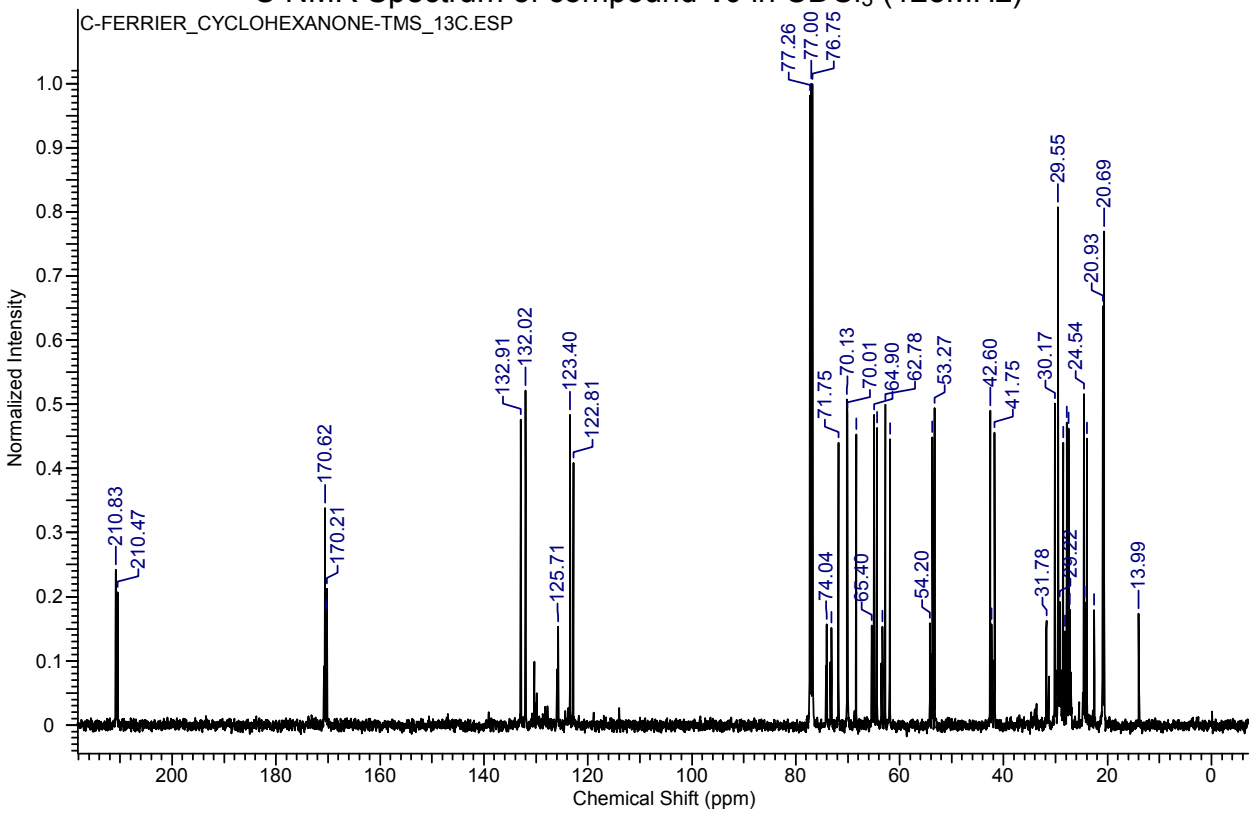
^{13}C NMR Spectrum of compound **9** in $CDCl_3$ (75 MHz)



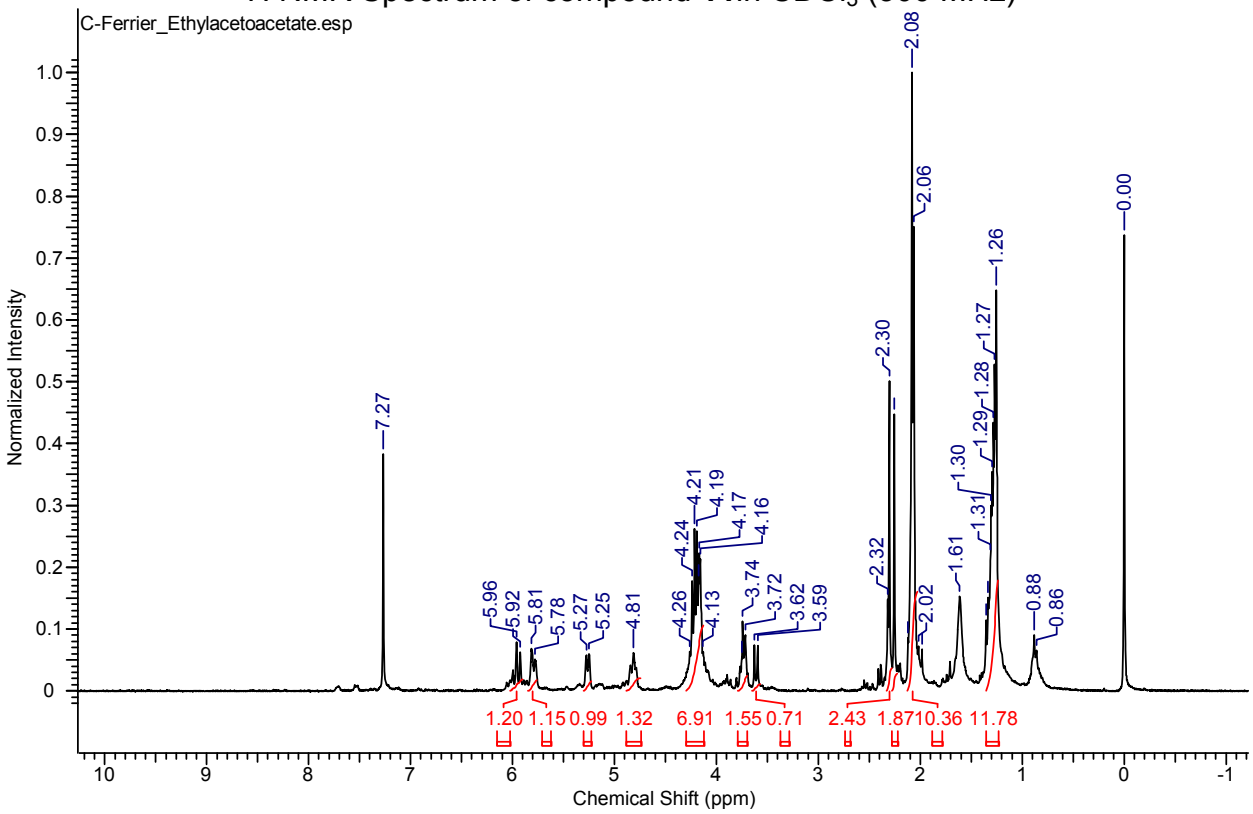
^{1}H NMR Spectrum of compound **10** in $CDCl_3$ (500 MHz)



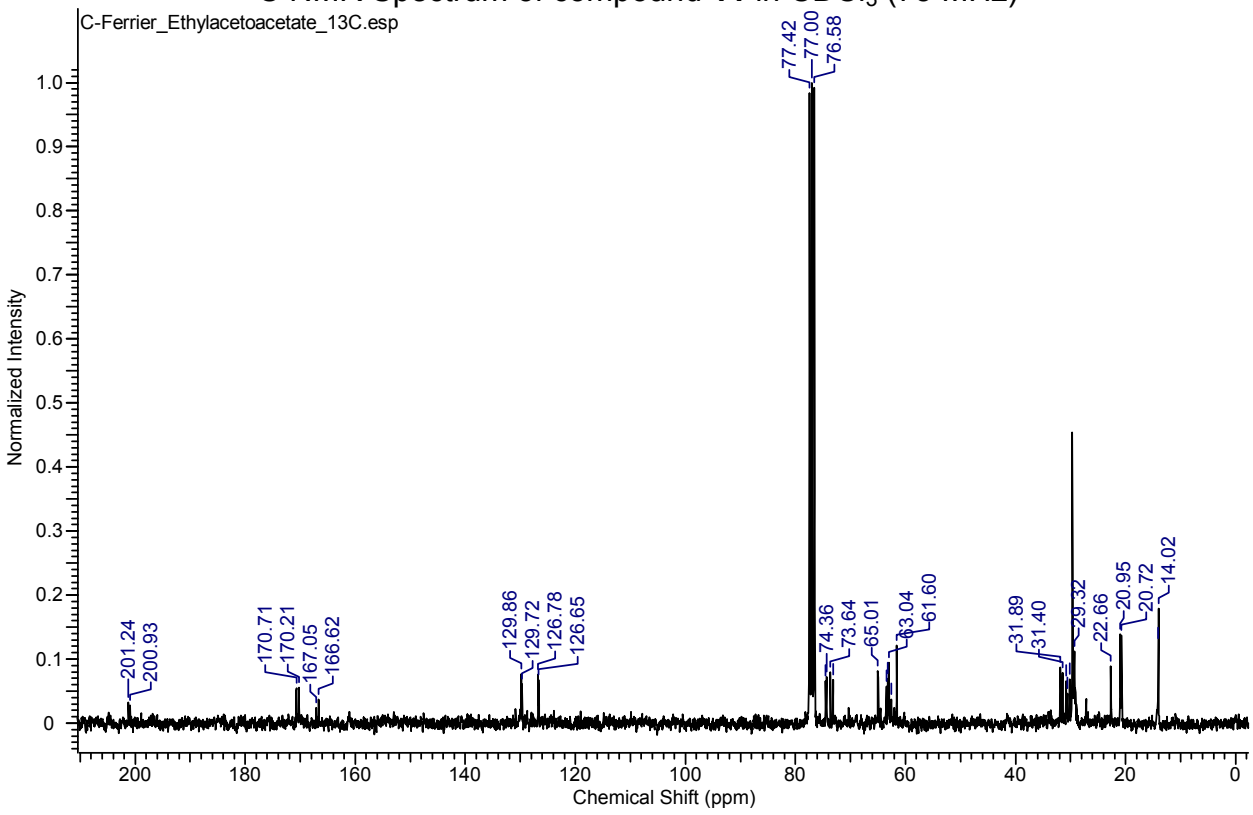
^{13}C NMR Spectrum of compound **10** in $CDCl_3$ (125MHz)



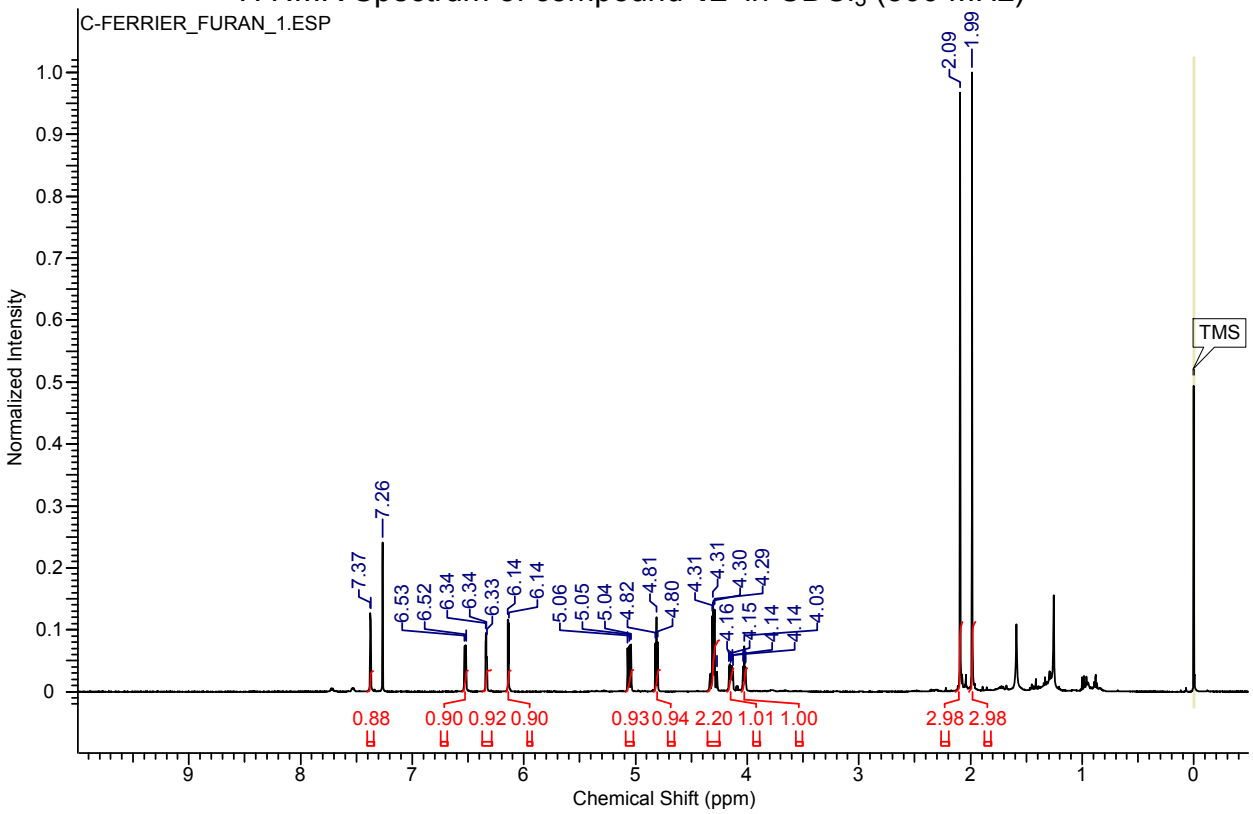
^{1}H NMR Spectrum of compound **11**in $CDCl_3$ (300 MHz)



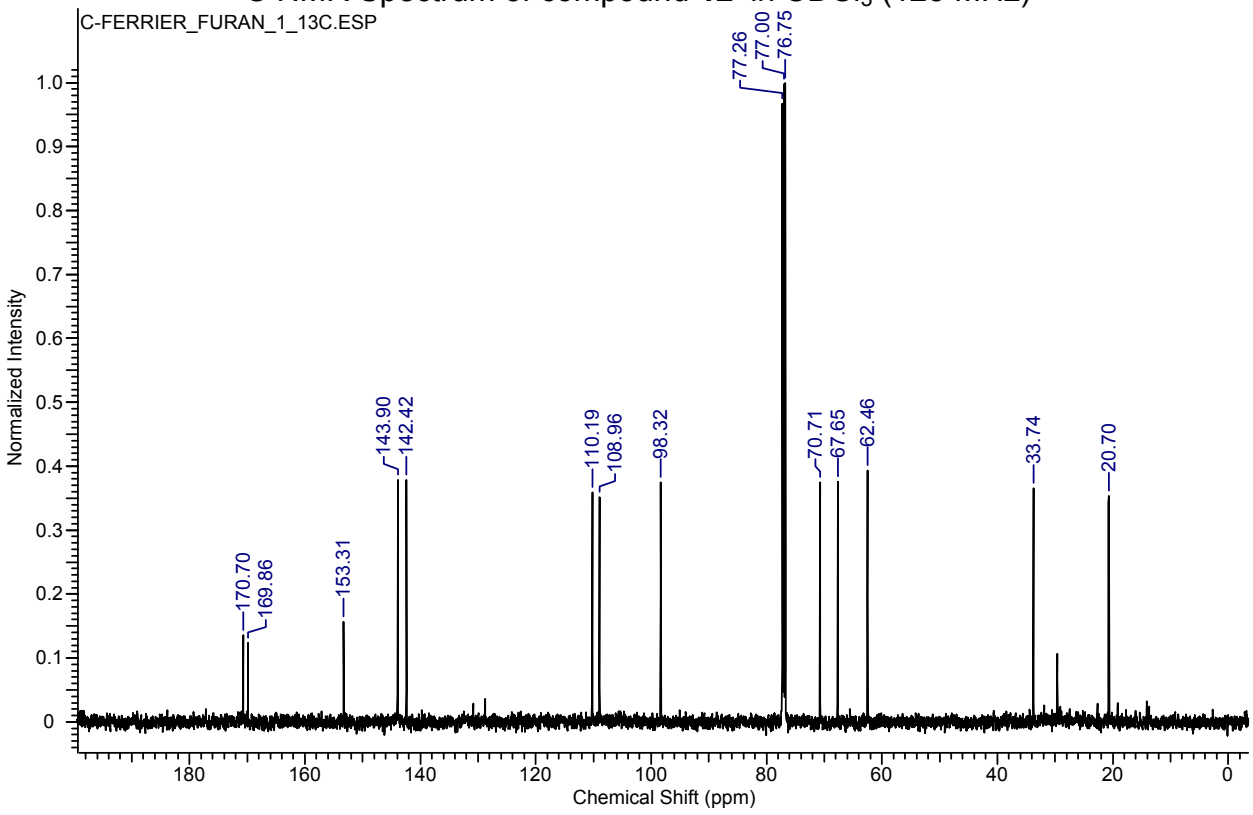
^{13}C NMR Spectrum of compound **11** in $CDCl_3$ (75 MHz)



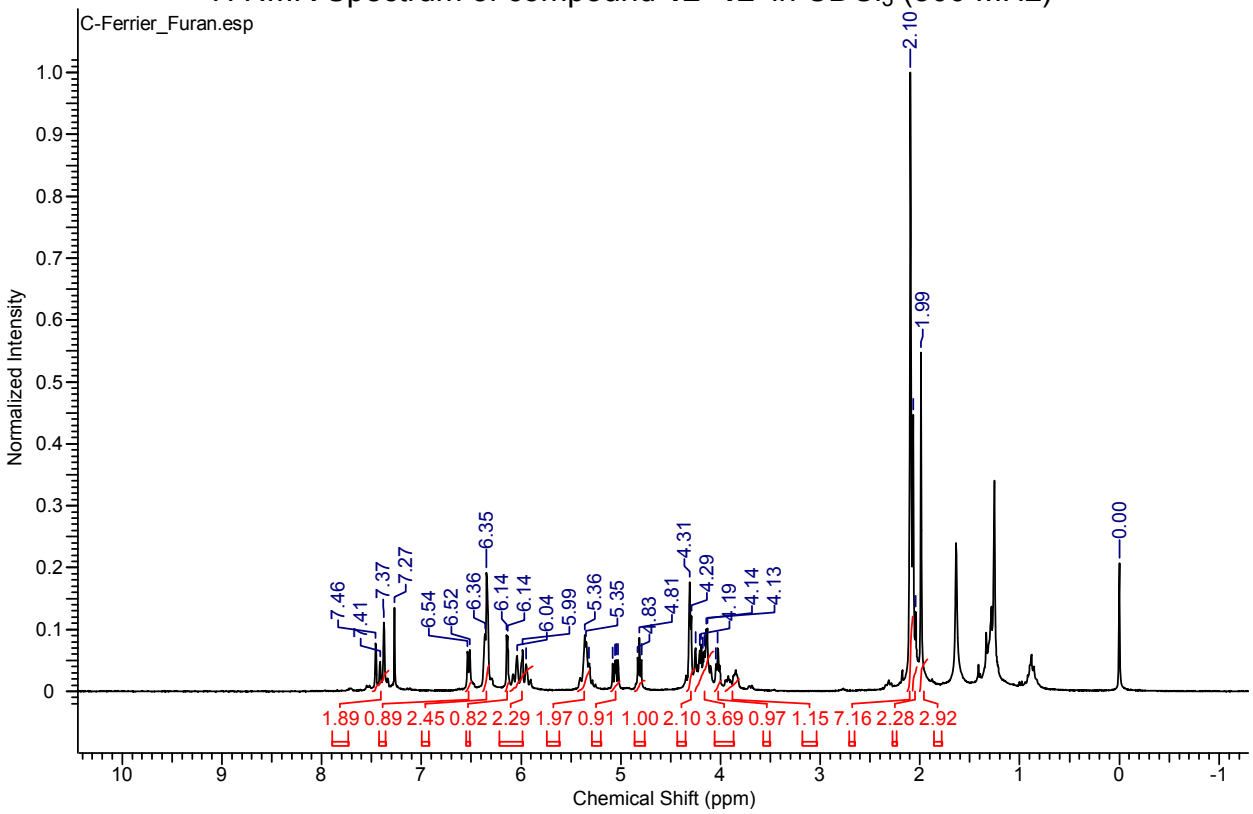
^{1}H NMR Spectrum of compound **12'** in $CDCl_3$ (500 MHz)



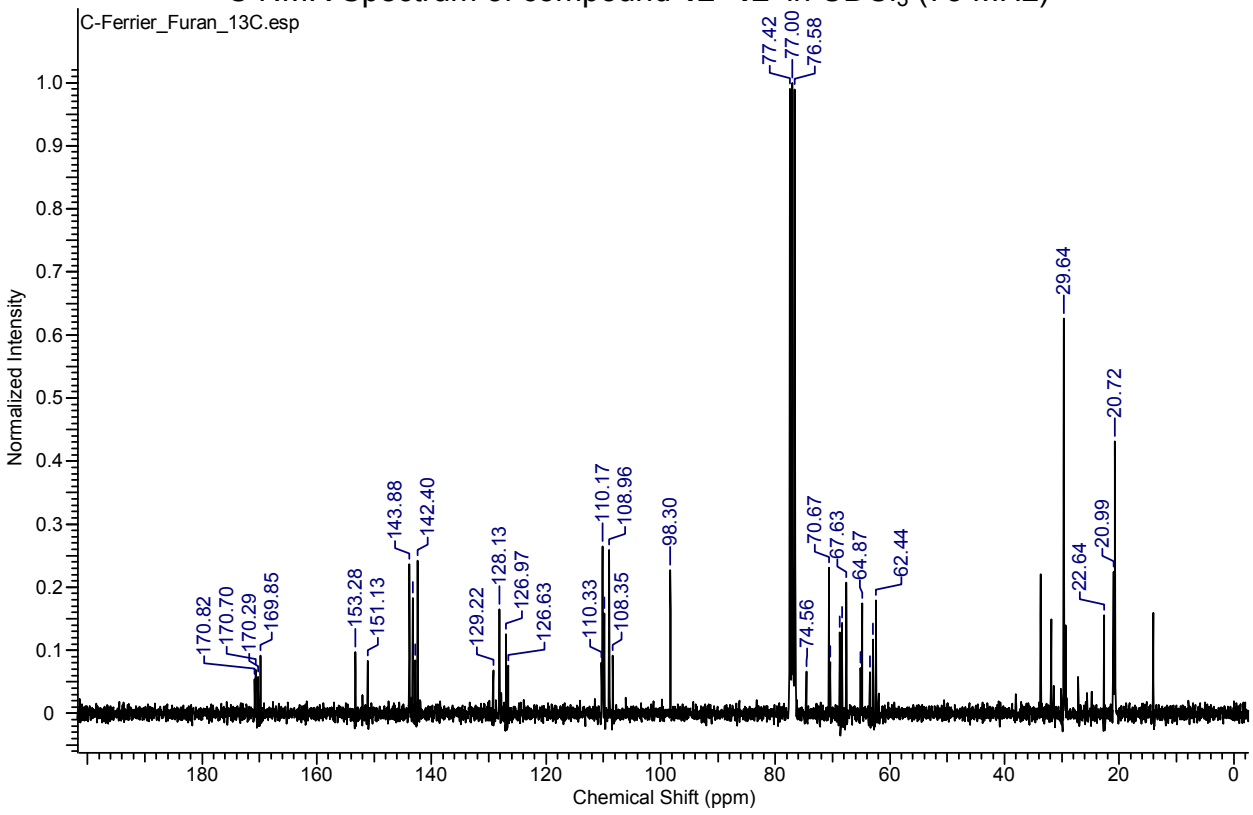
^{13}C NMR Spectrum of compound **12'** in $CDCl_3$ (125 MHz)



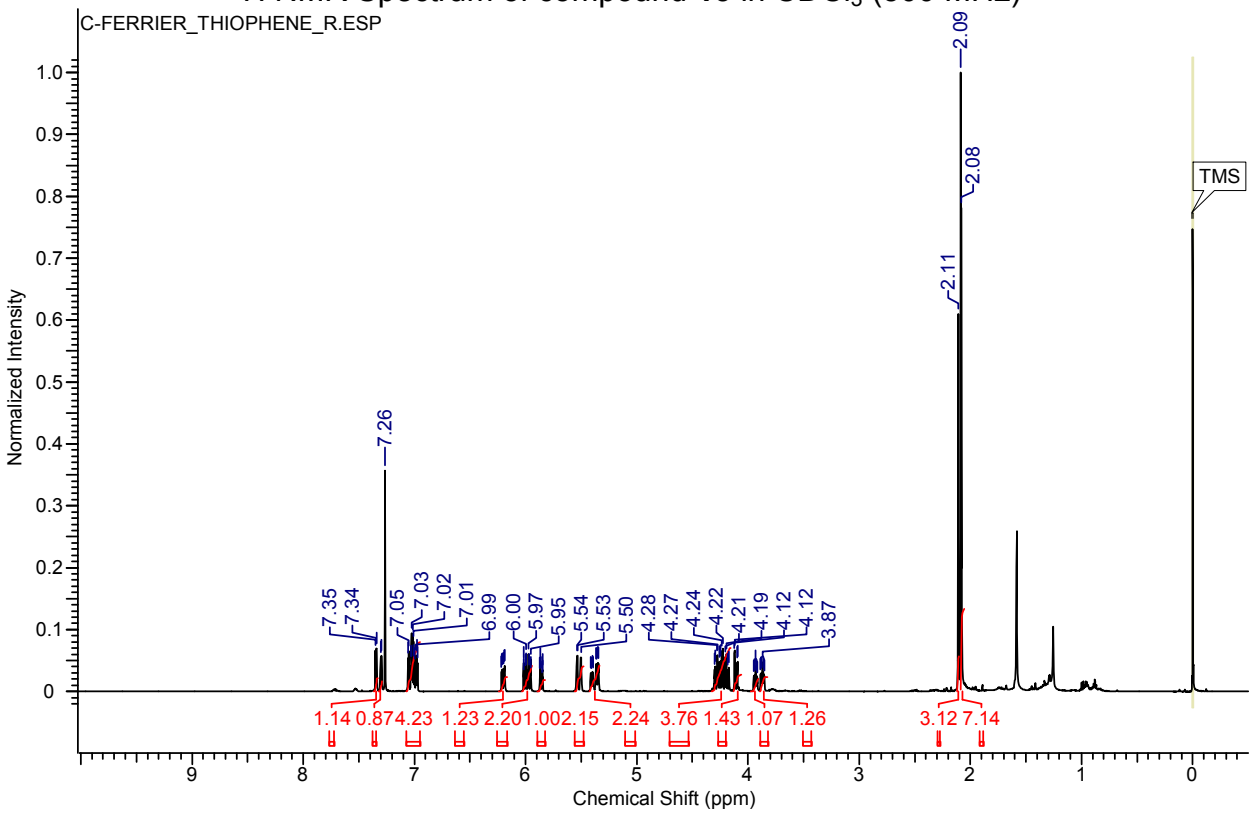
^{1}H NMR Spectrum of compound **12+12'** in $CDCl_3$ (500 MHz)



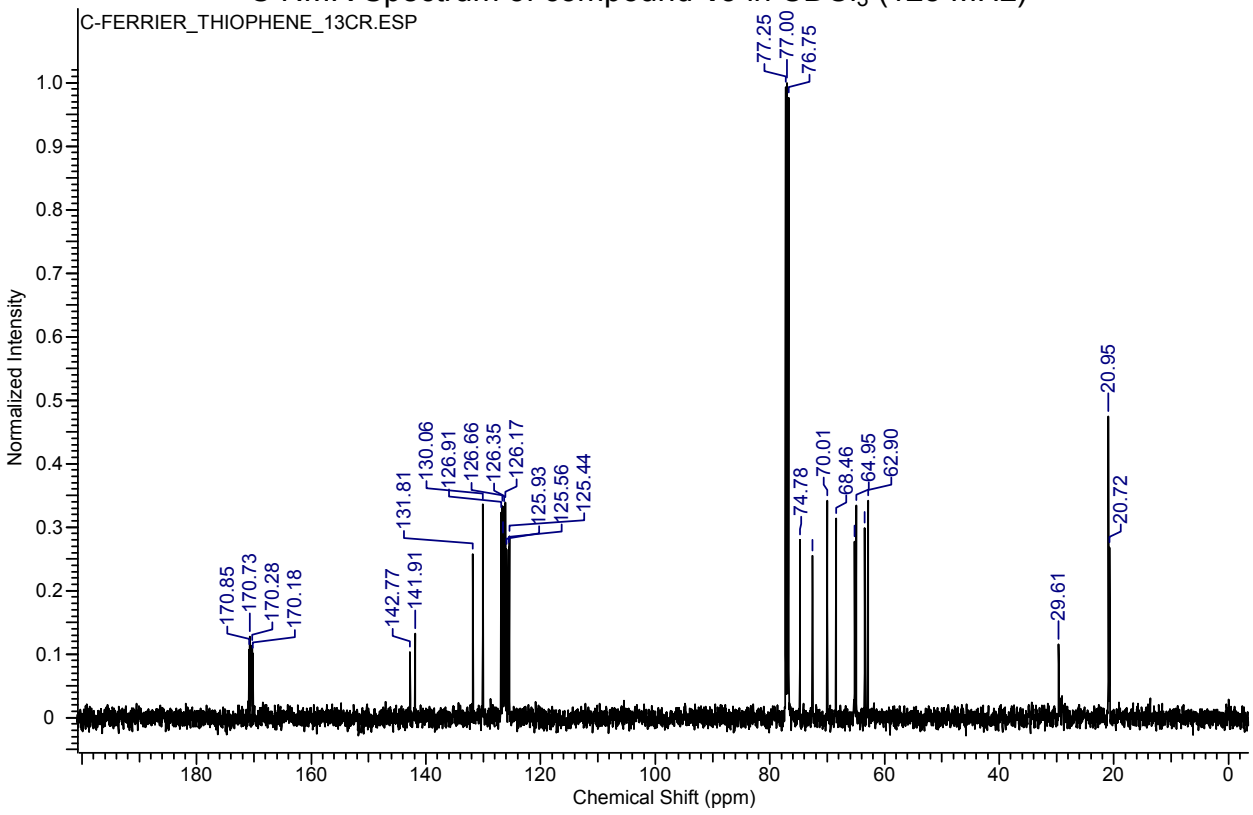
^{13}C NMR Spectrum of compound **12+12'** in $CDCl_3$ (75 MHz)



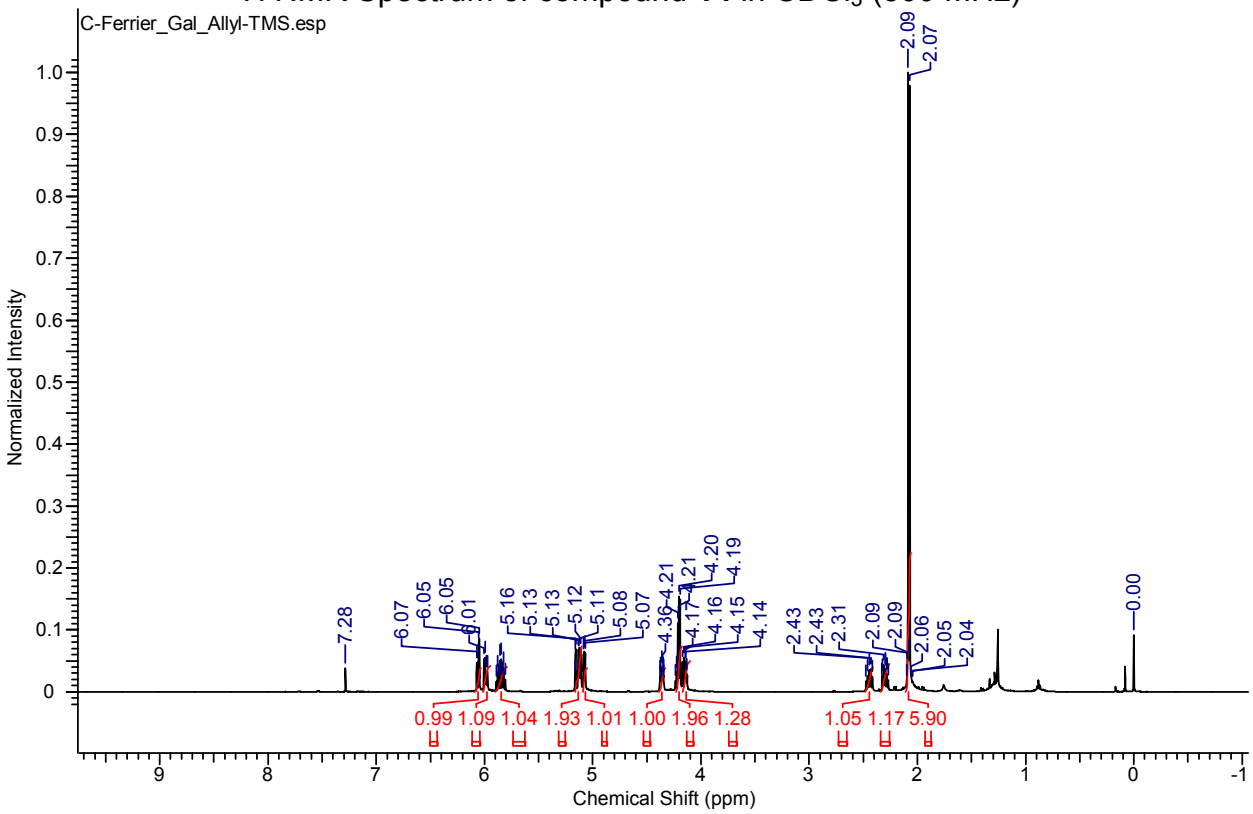
^{1}H NMR Spectrum of compound **13** in $CDCl_3$ (500 MHz)



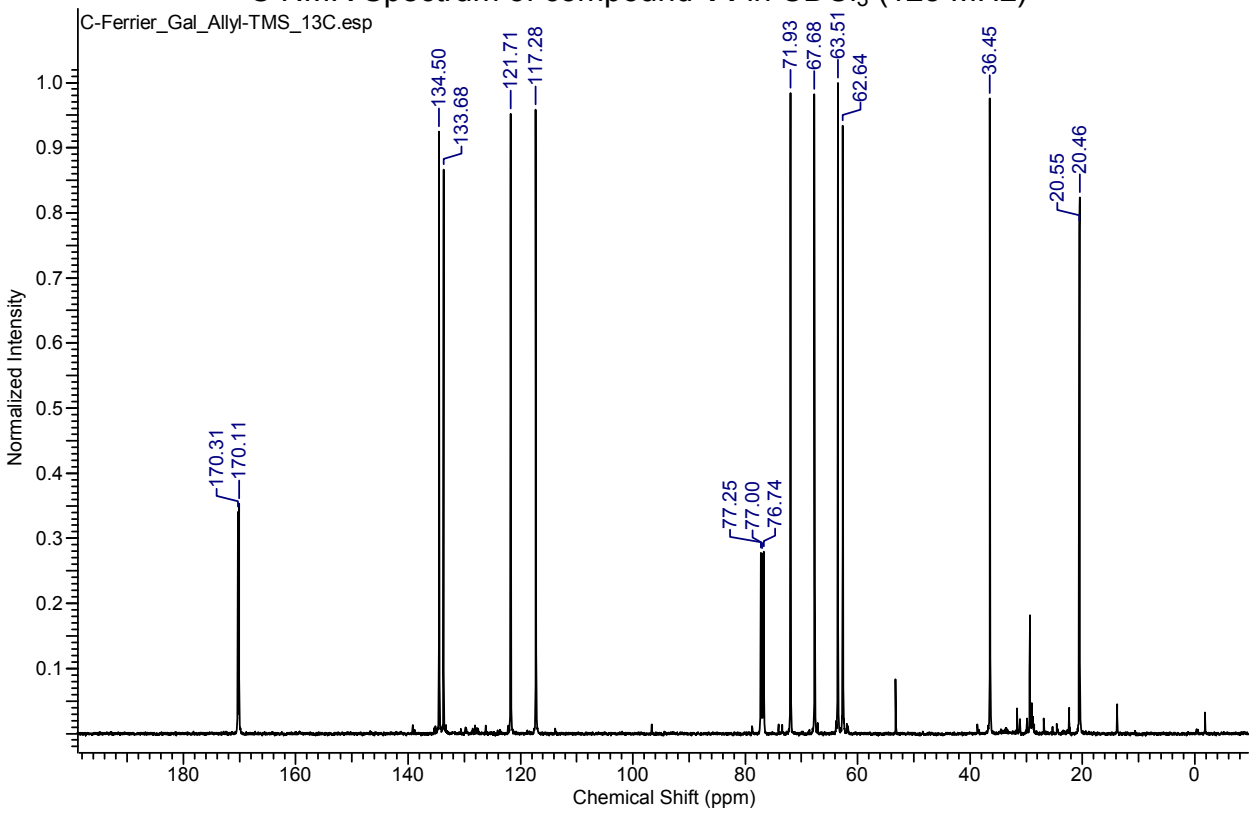
^{13}C NMR Spectrum of compound **13** in $CDCl_3$ (125 MHz)



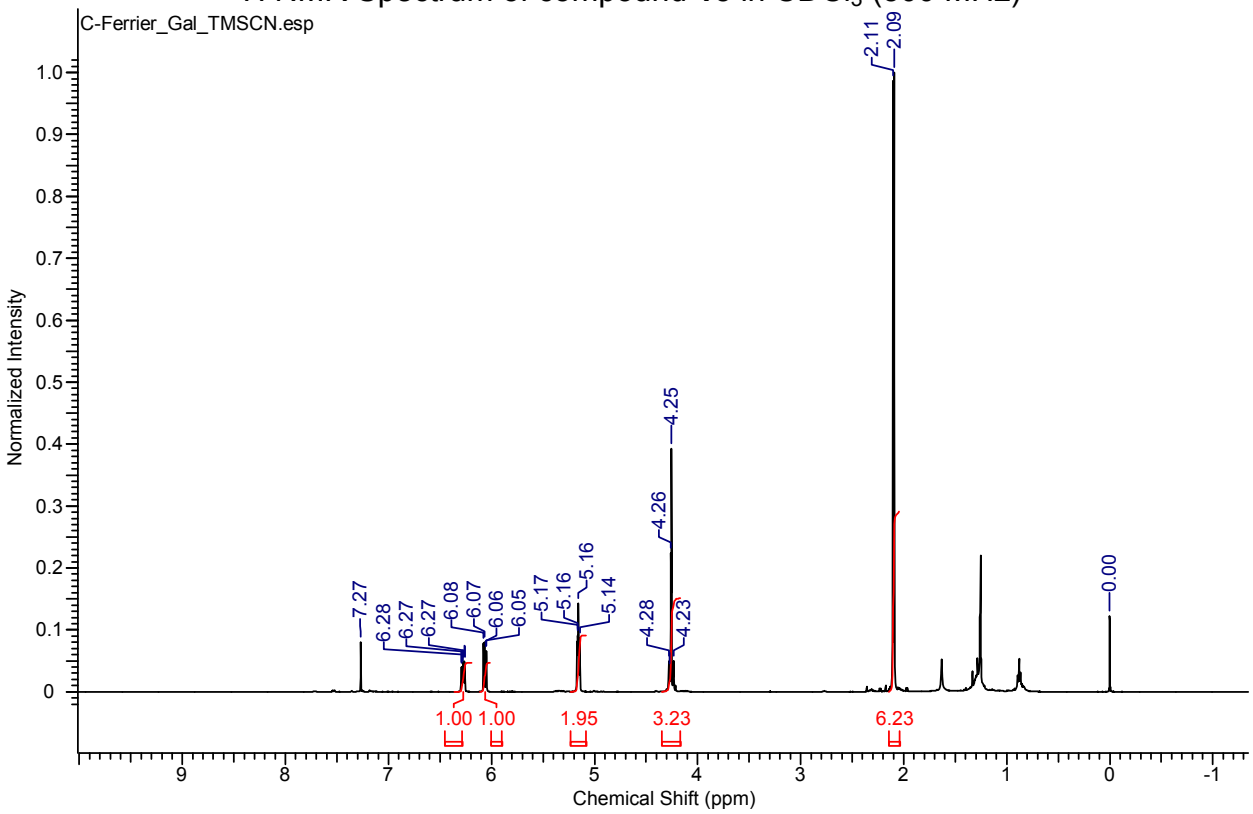
^{1}H NMR Spectrum of compound **14** in $CDCl_3$ (500 MHz)



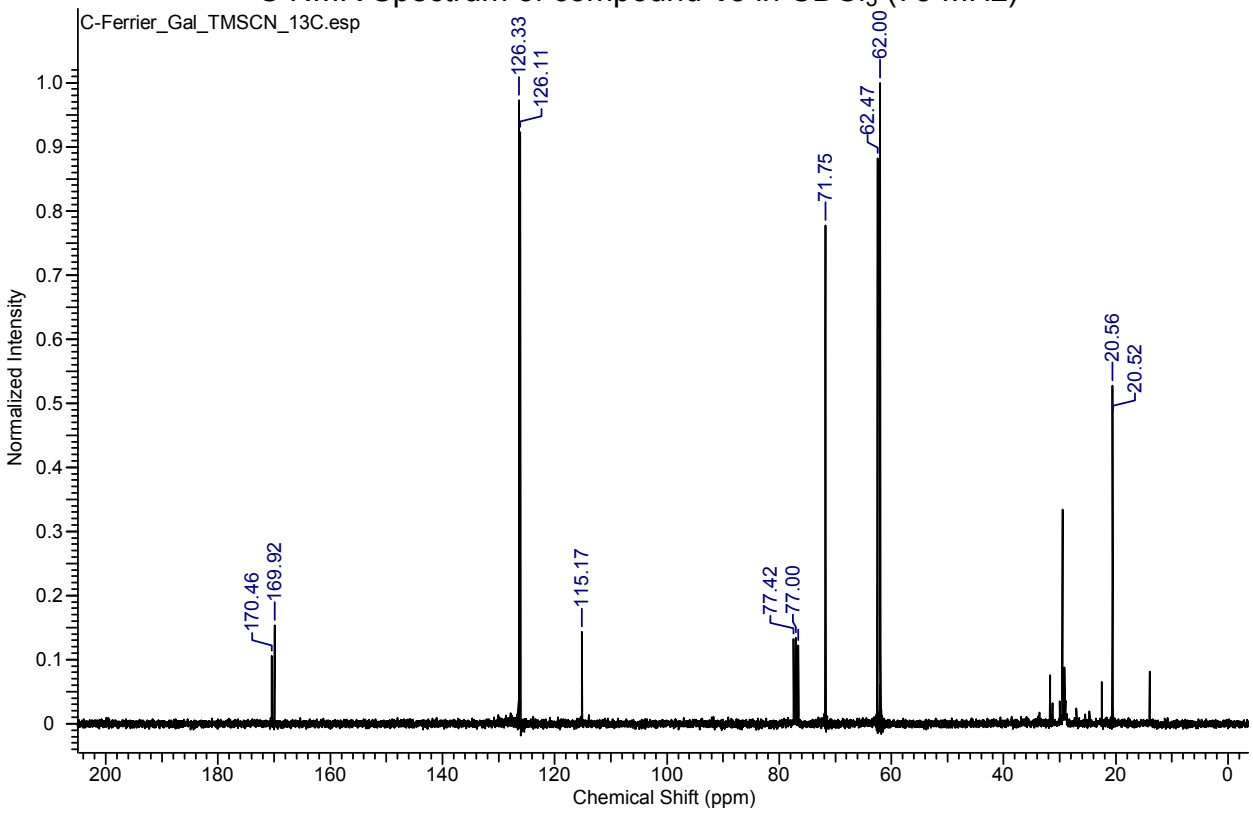
^{13}C NMR Spectrum of compound **14** in $CDCl_3$ (125 MHz)



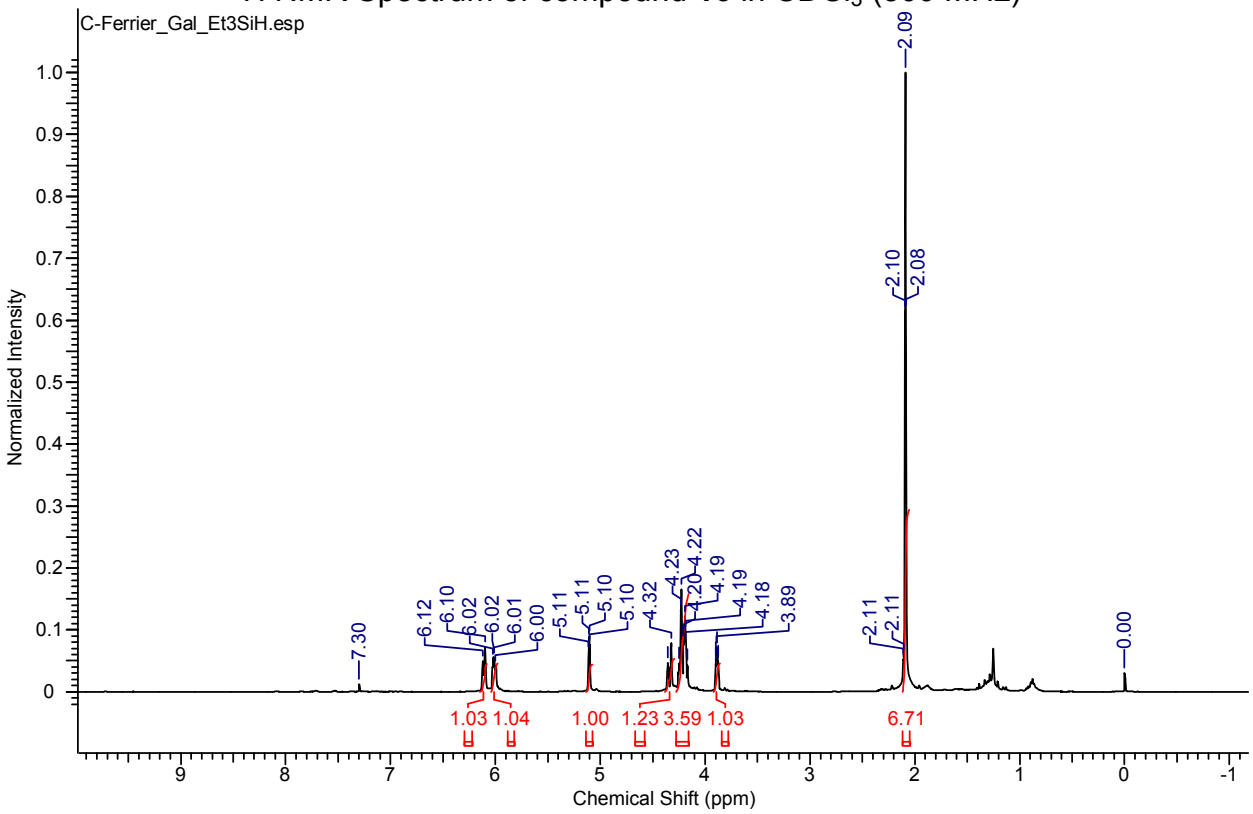
^{1}H NMR Spectrum of compound **15** in $CDCl_3$ (500 MHz)



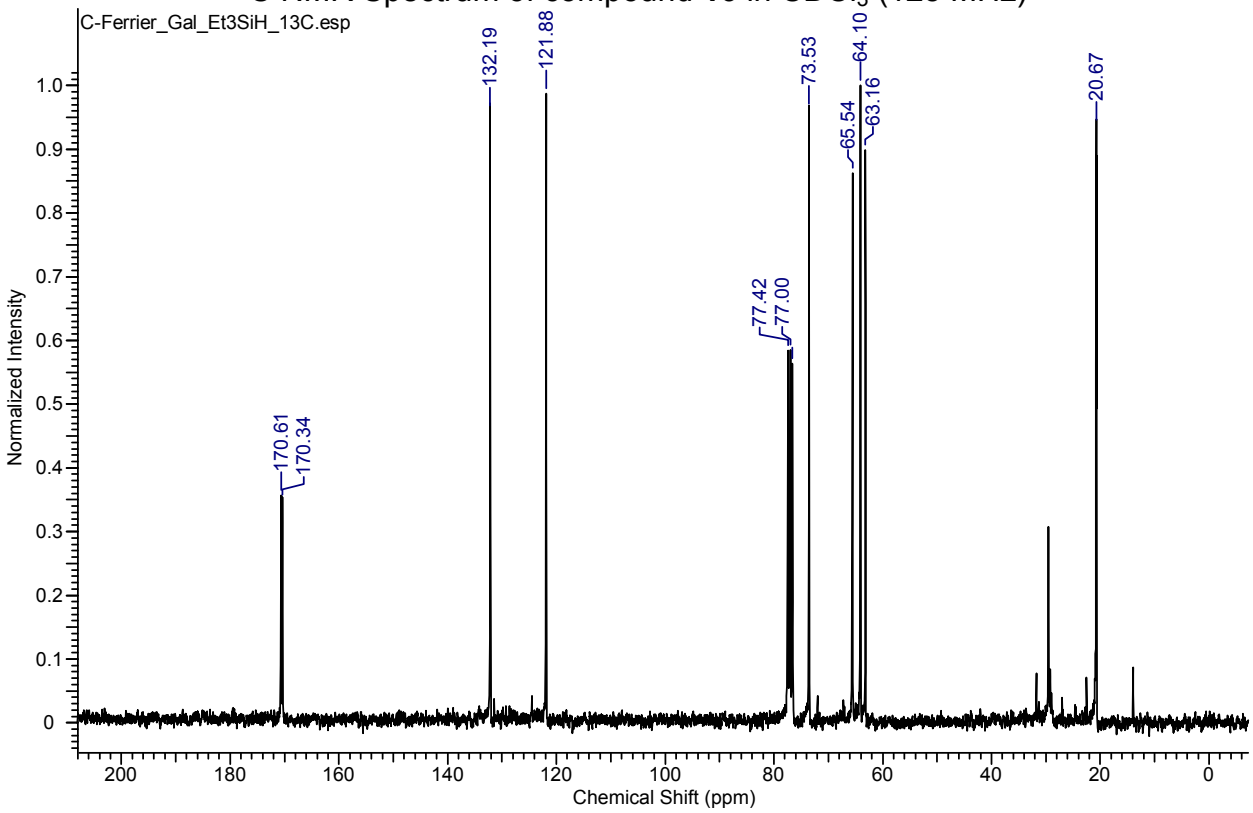
^{13}C NMR Spectrum of compound **15** in $CDCl_3$ (75 MHz)



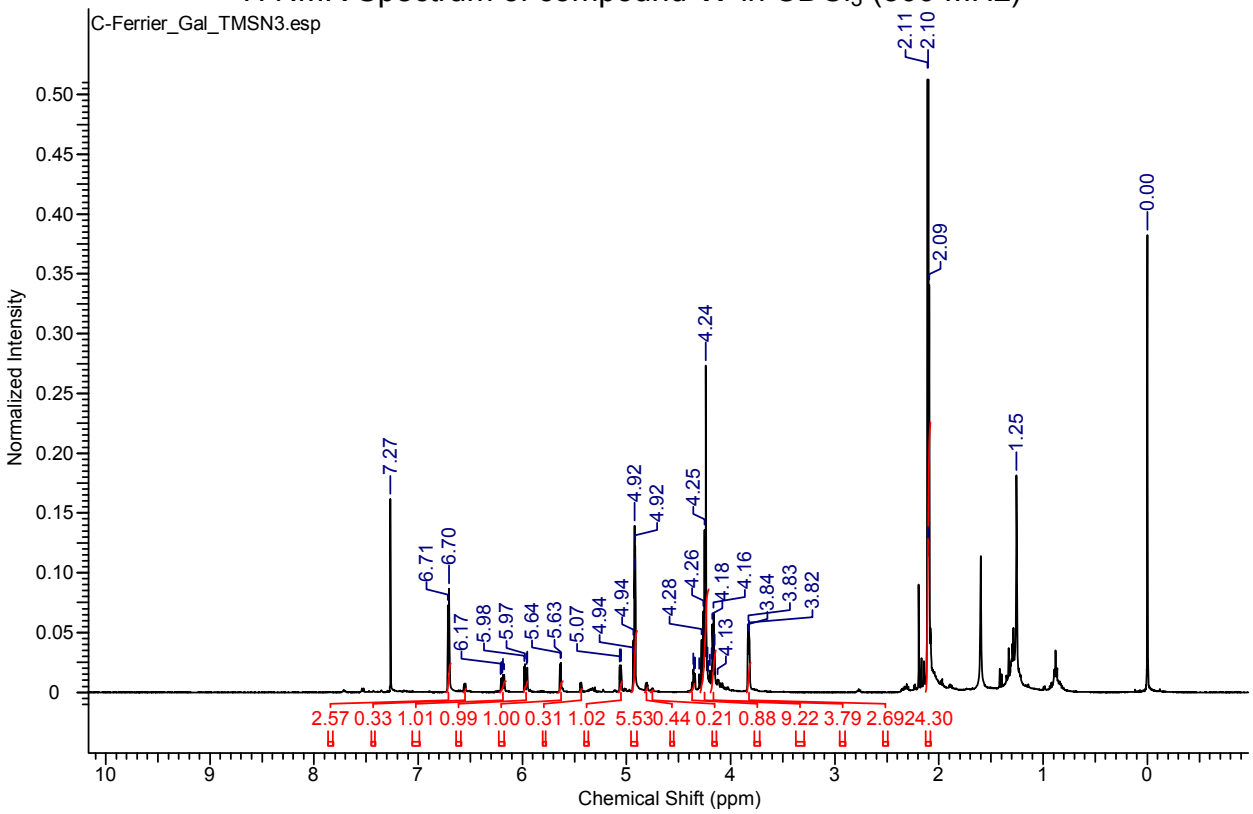
^{1}H NMR Spectrum of compound **16** in $CDCl_3$ (500 MHz)



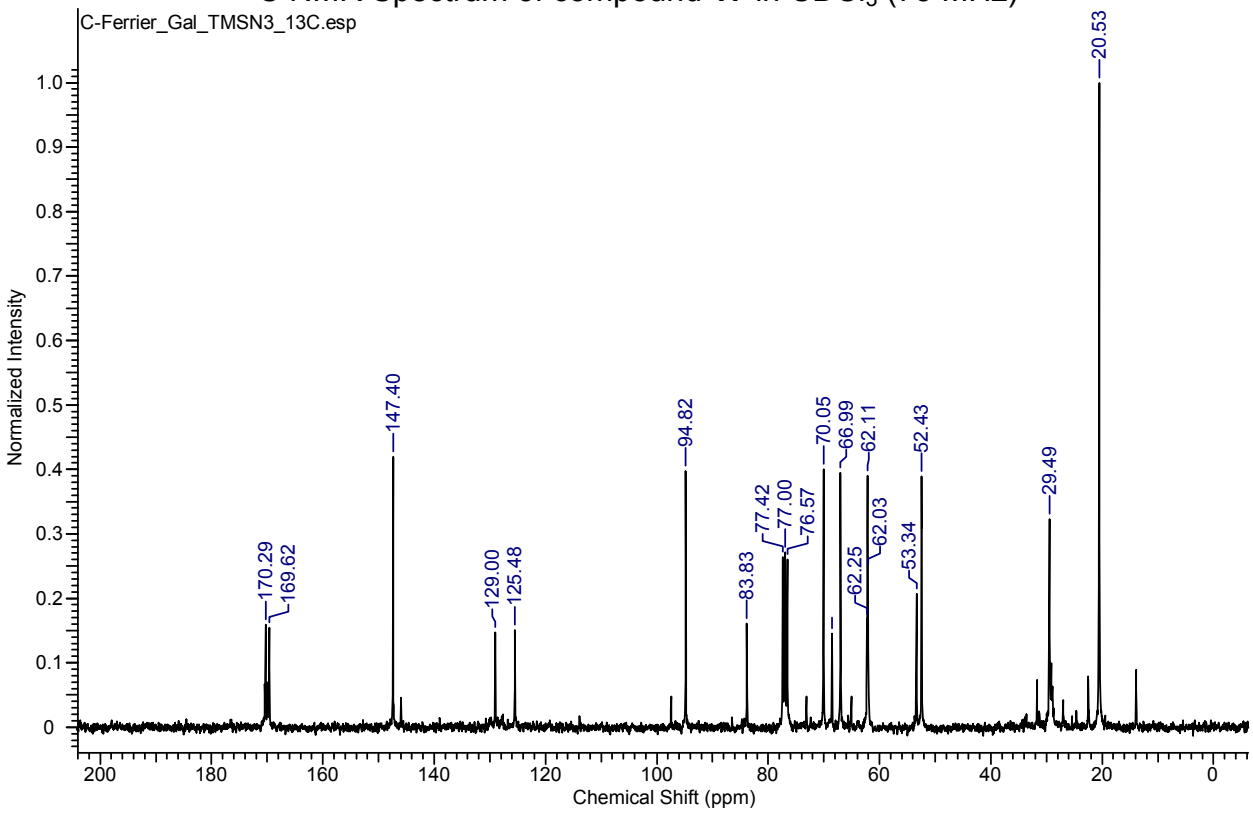
^{13}C NMR Spectrum of compound **16** in $CDCl_3$ (125 MHz)



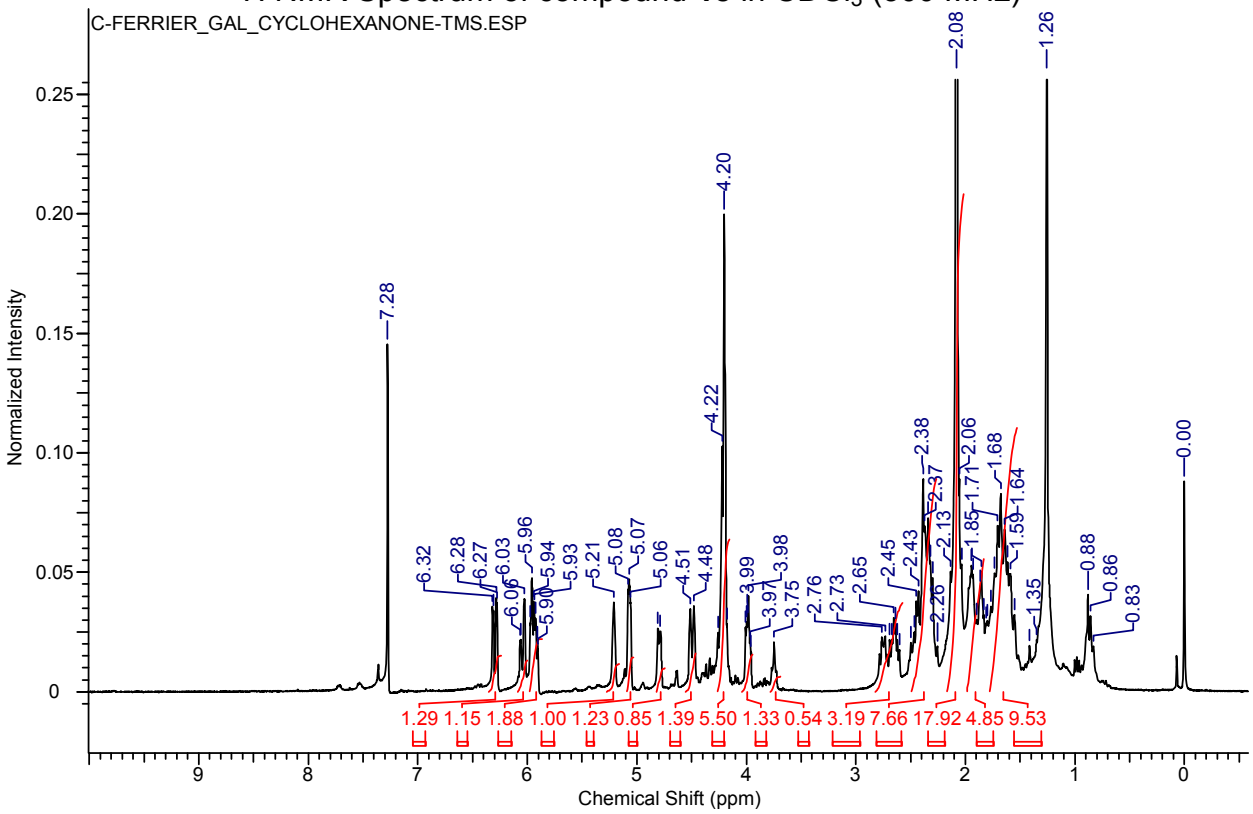
^{1}H NMR Spectrum of compound **17** in $CDCl_3$ (500 MHz)



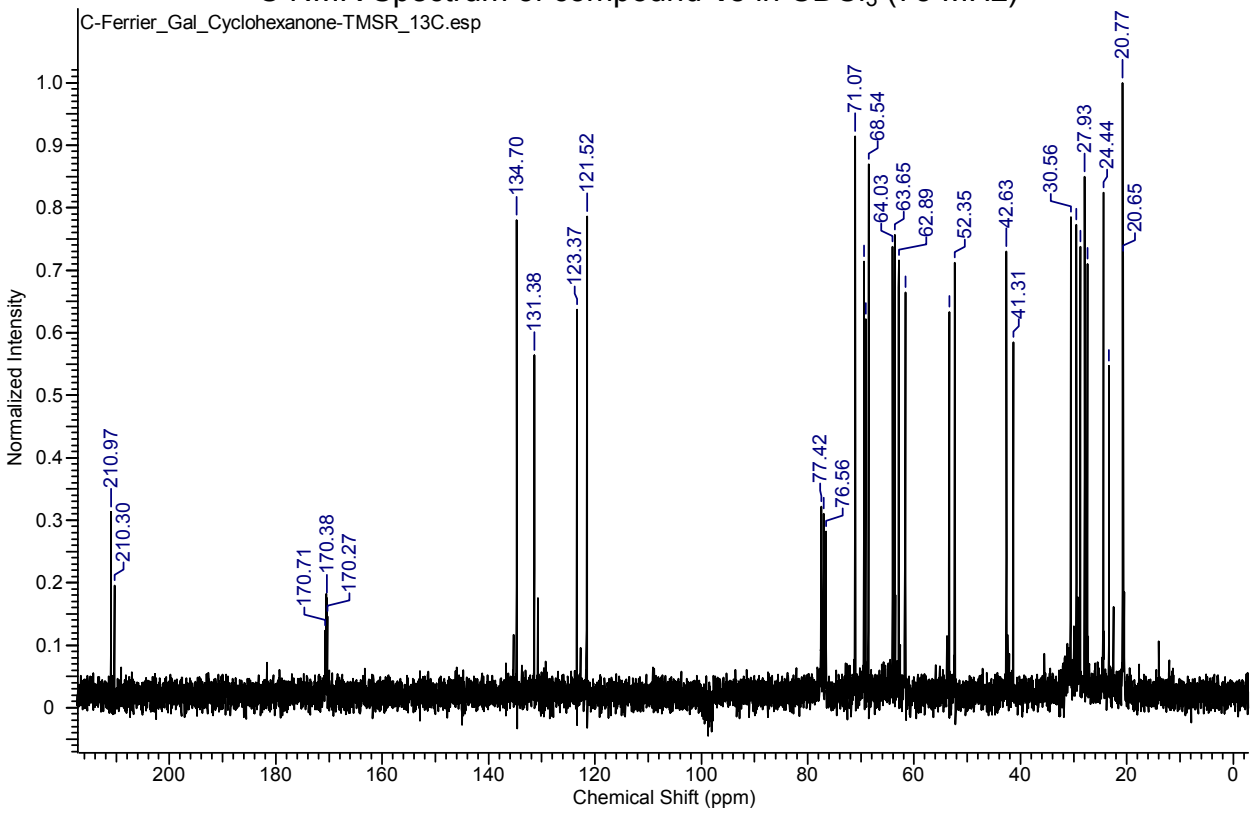
^{13}C NMR Spectrum of compound **17** in $CDCl_3$ (75 MHz)



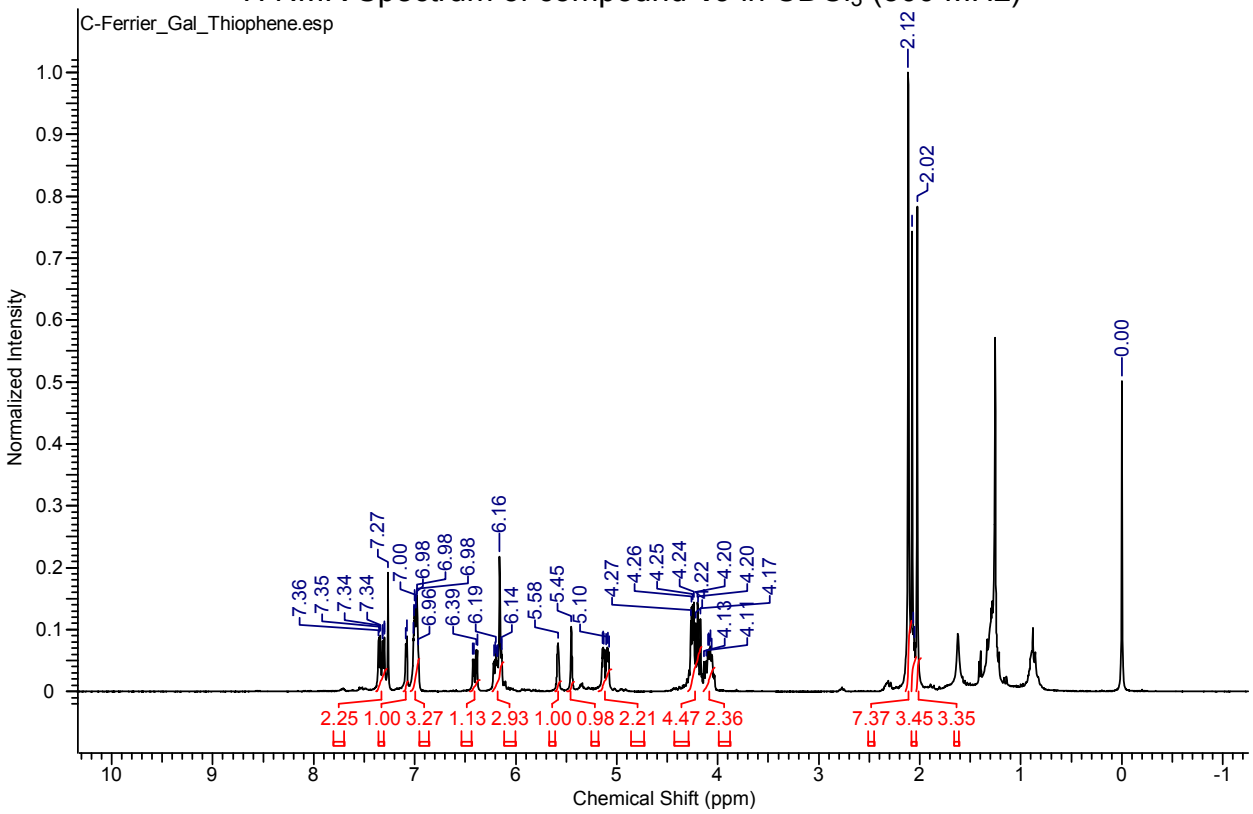
^{1}H NMR Spectrum of compound **18** in $CDCl_3$ (300 MHz)



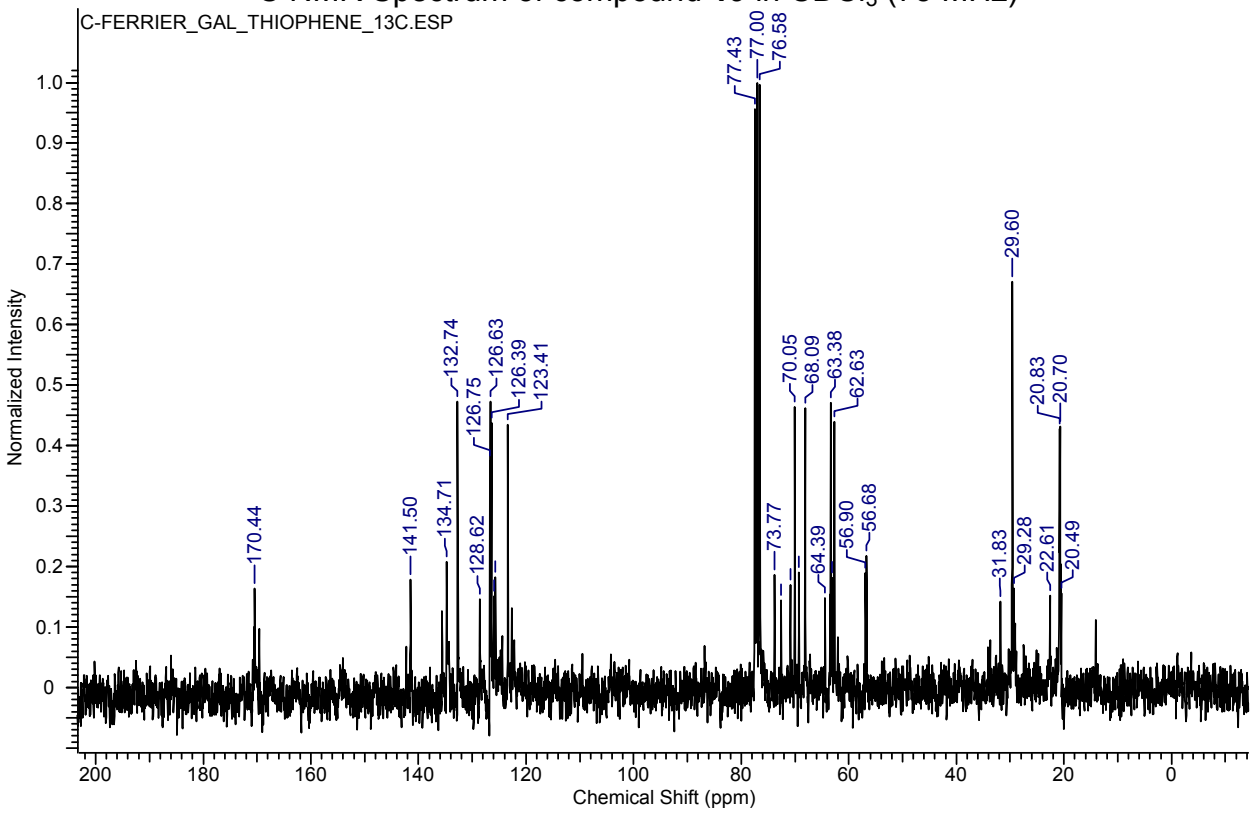
^{13}C NMR Spectrum of compound **18** in $CDCl_3$ (75 MHz)



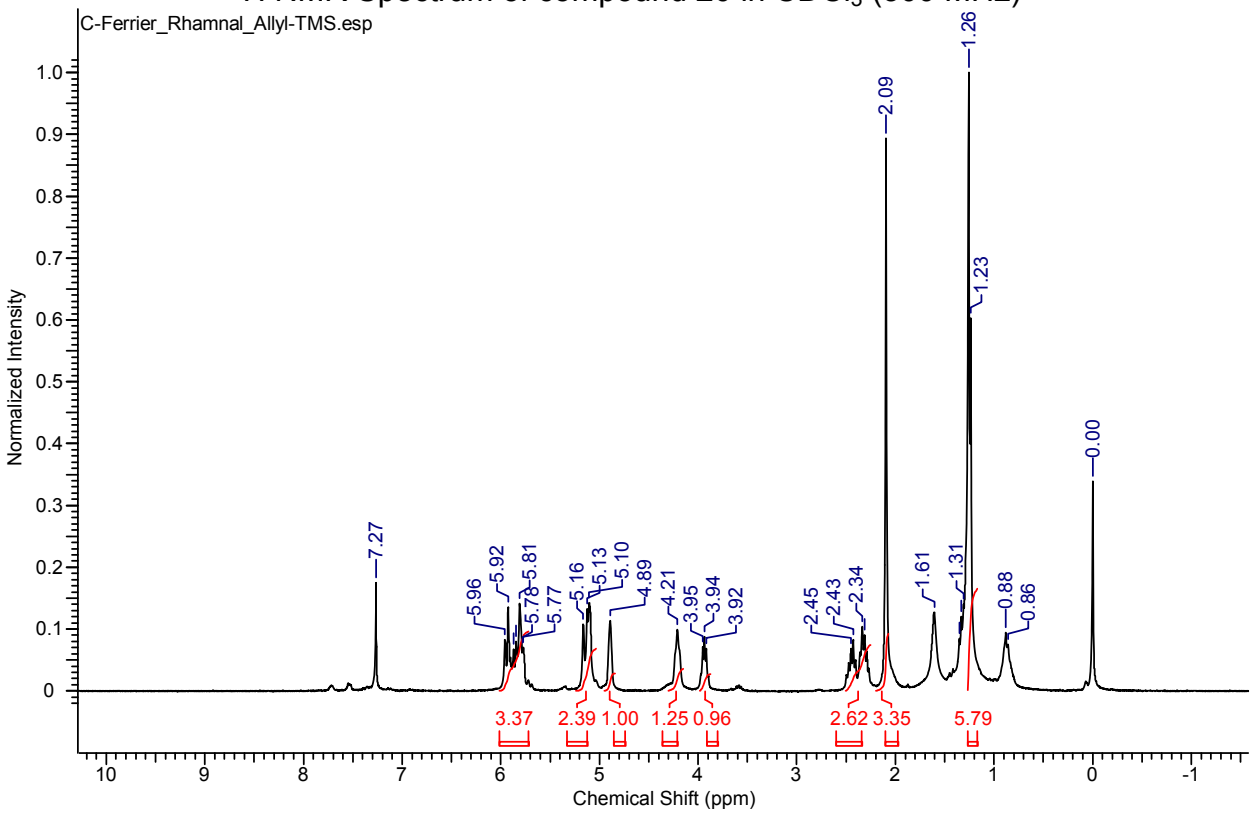
^{1}H NMR Spectrum of compound **19** in $CDCl_3$ (300 MHz)



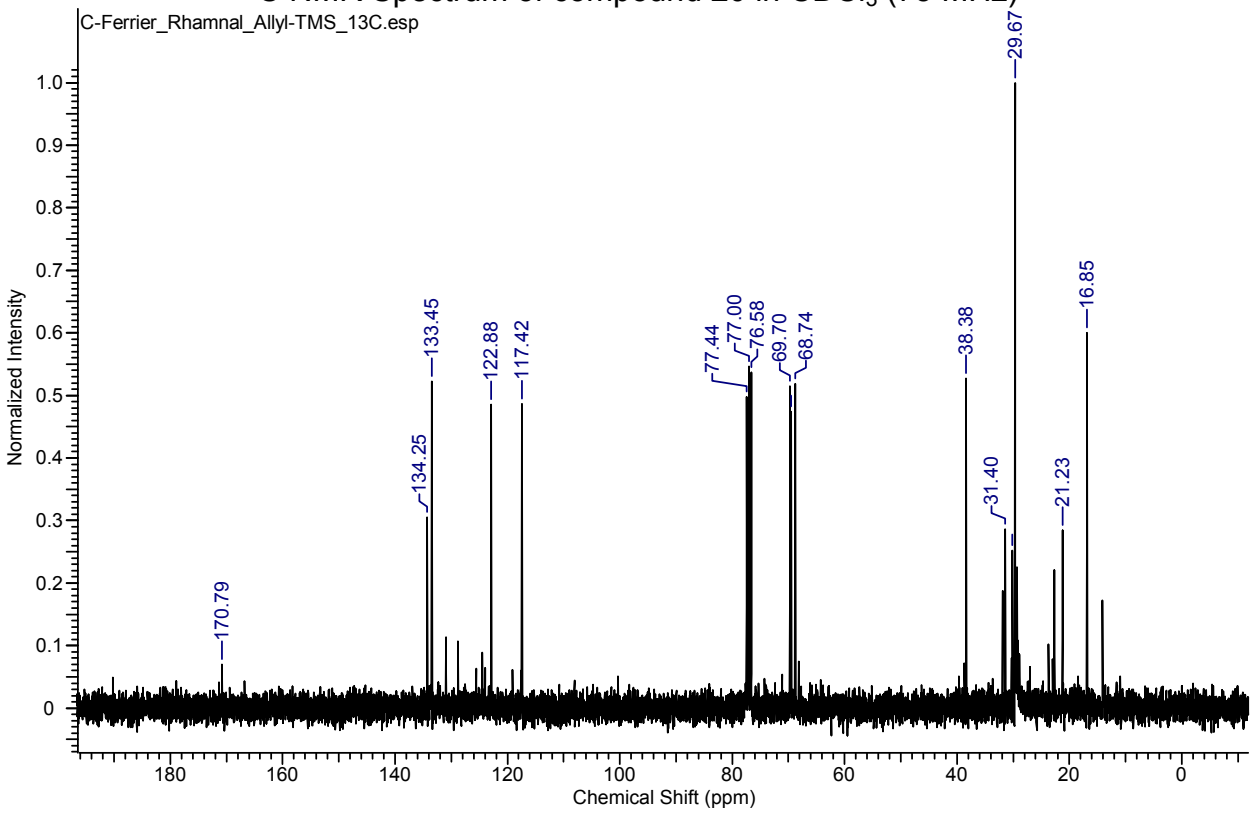
^{13}C NMR Spectrum of compound **19** in $CDCl_3$ (75 MHz)



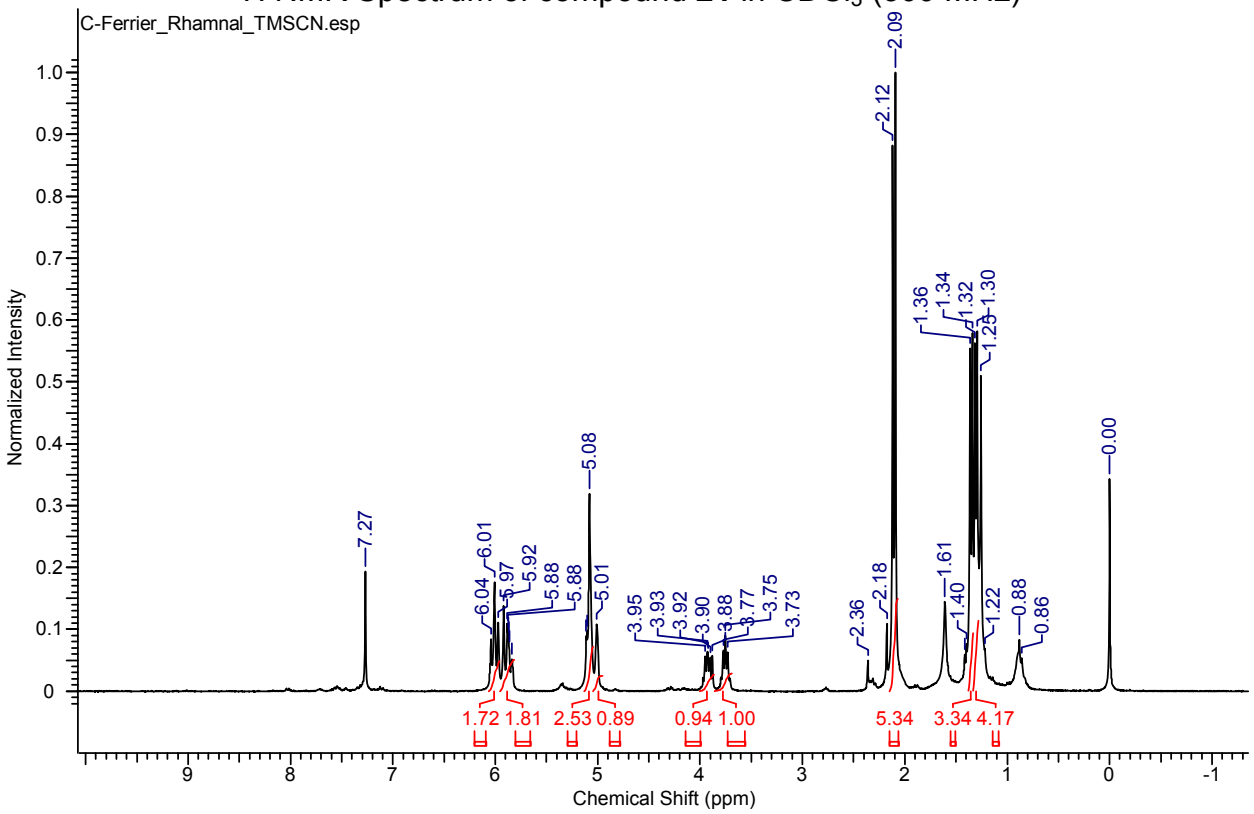
^{1}H NMR Spectrum of compound **20** in $CDCl_3$ (300 MHz)



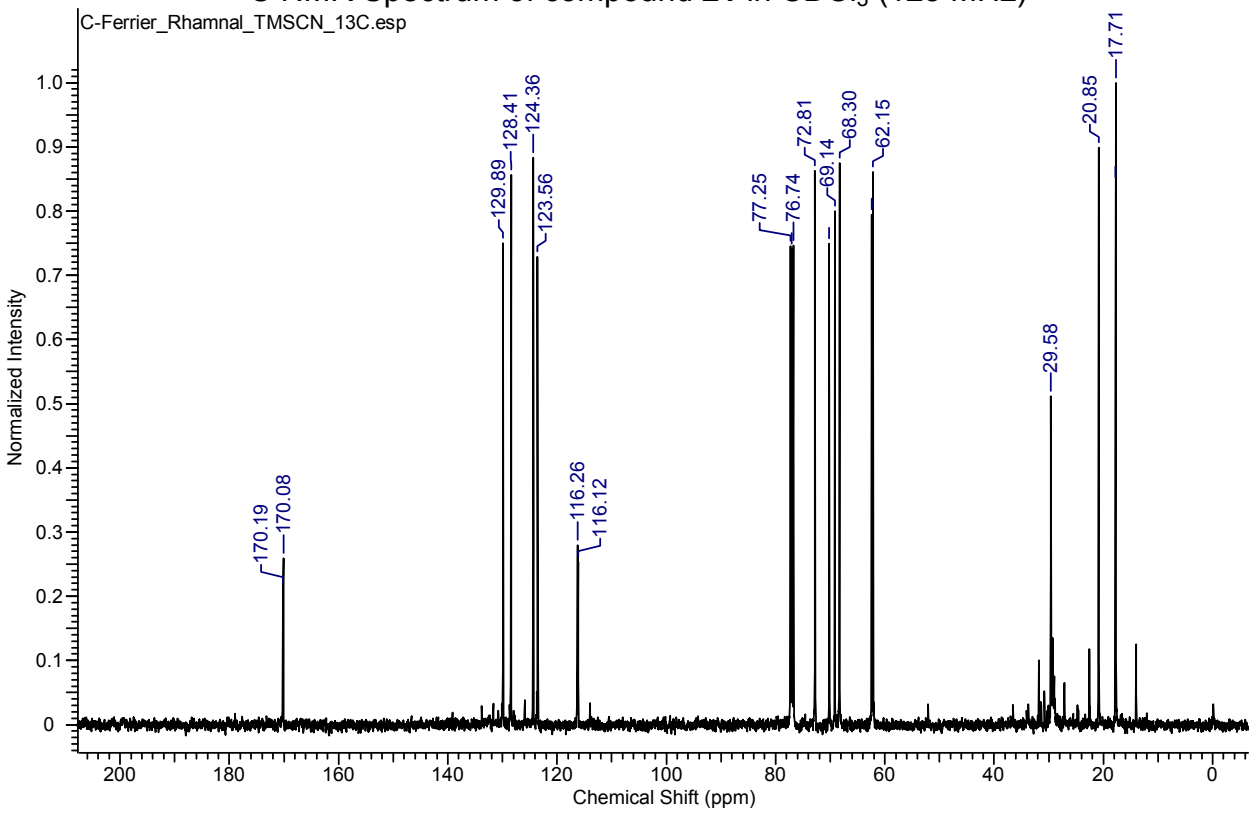
^{13}C NMR Spectrum of compound **20** in $CDCl_3$ (75 MHz)



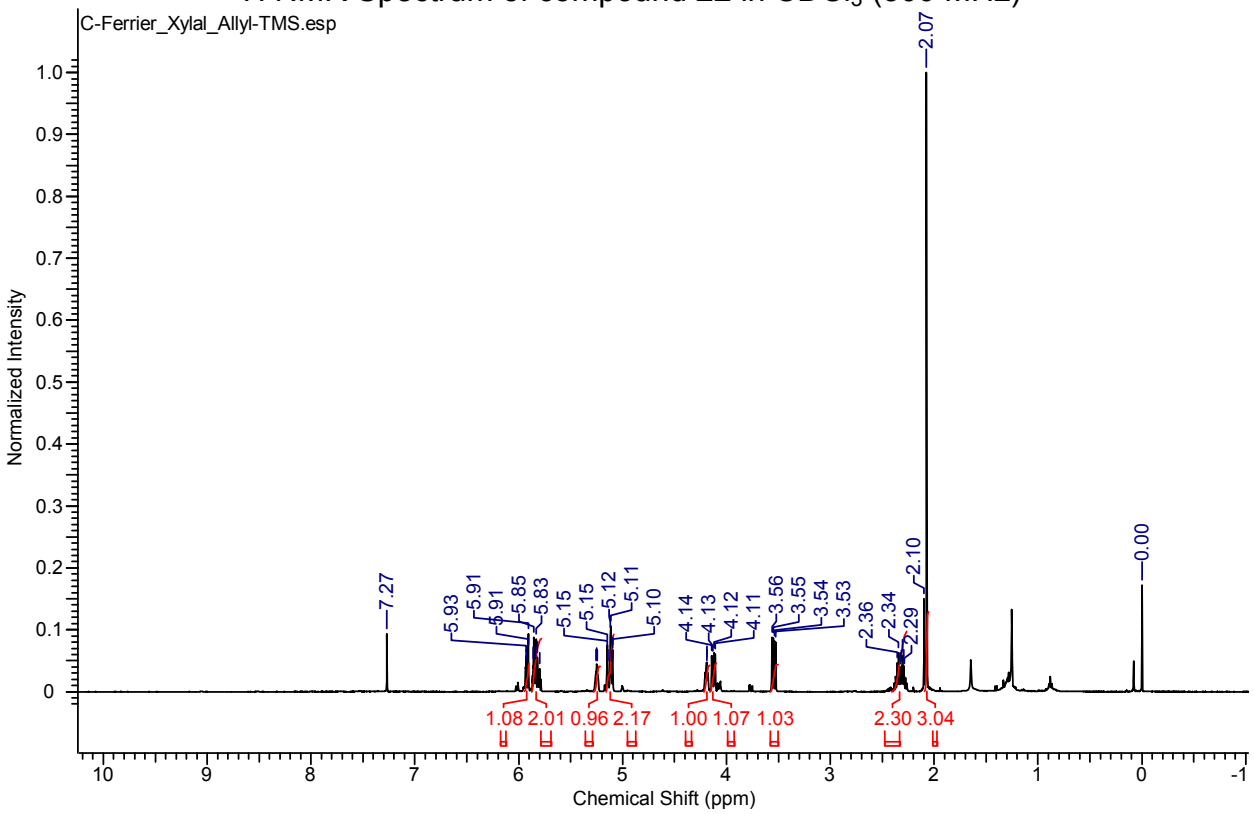
^{1}H NMR Spectrum of compound **21** in $CDCl_3$ (300 MHz)



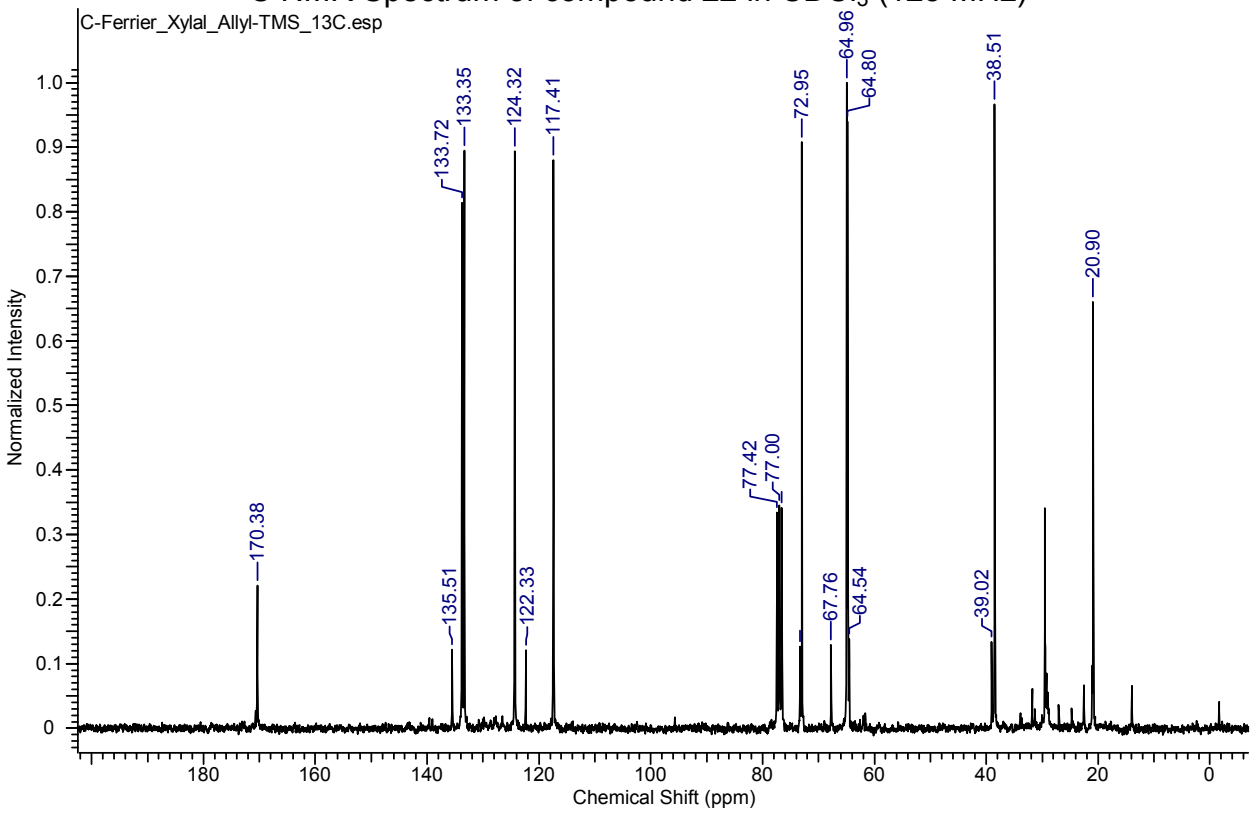
^{13}C NMR Spectrum of compound **21** in $CDCl_3$ (125 MHz)



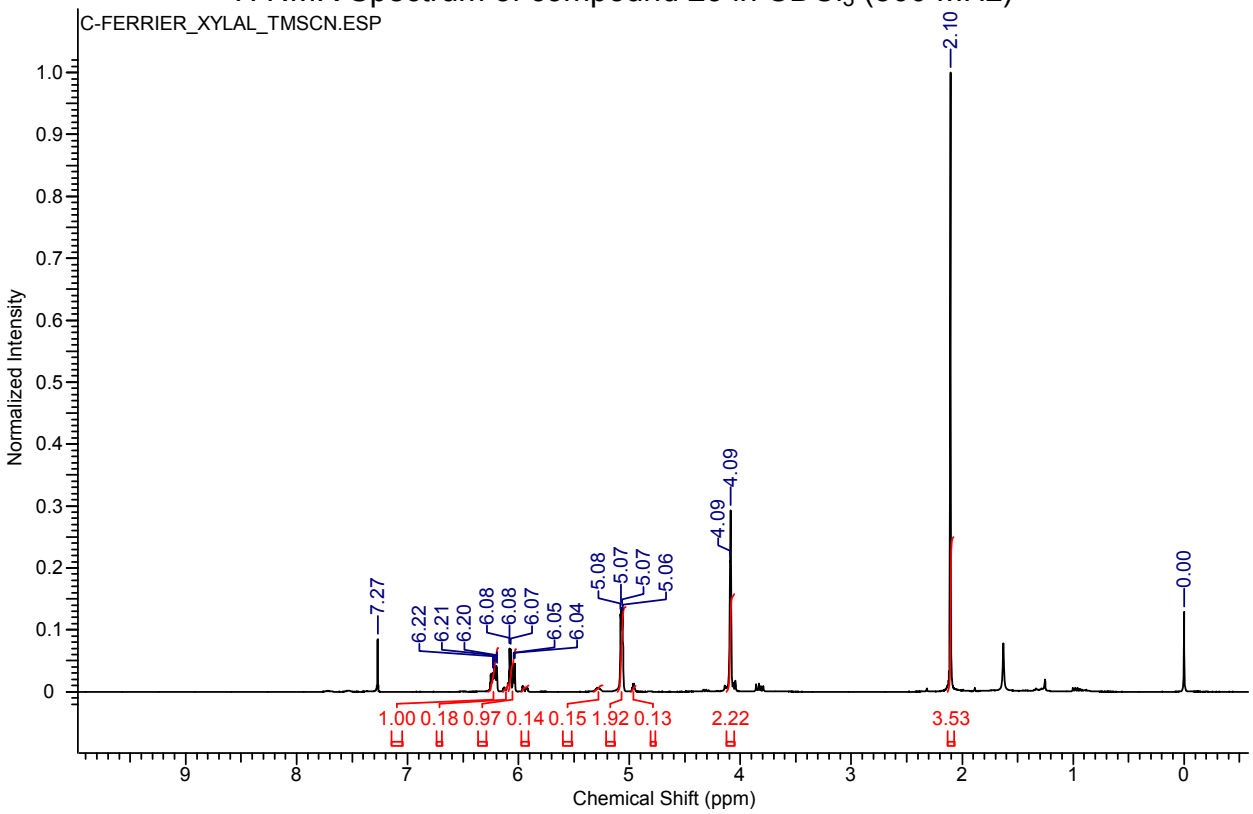
^{1}H NMR Spectrum of compound **22** in $CDCl_3$ (500 MHz)



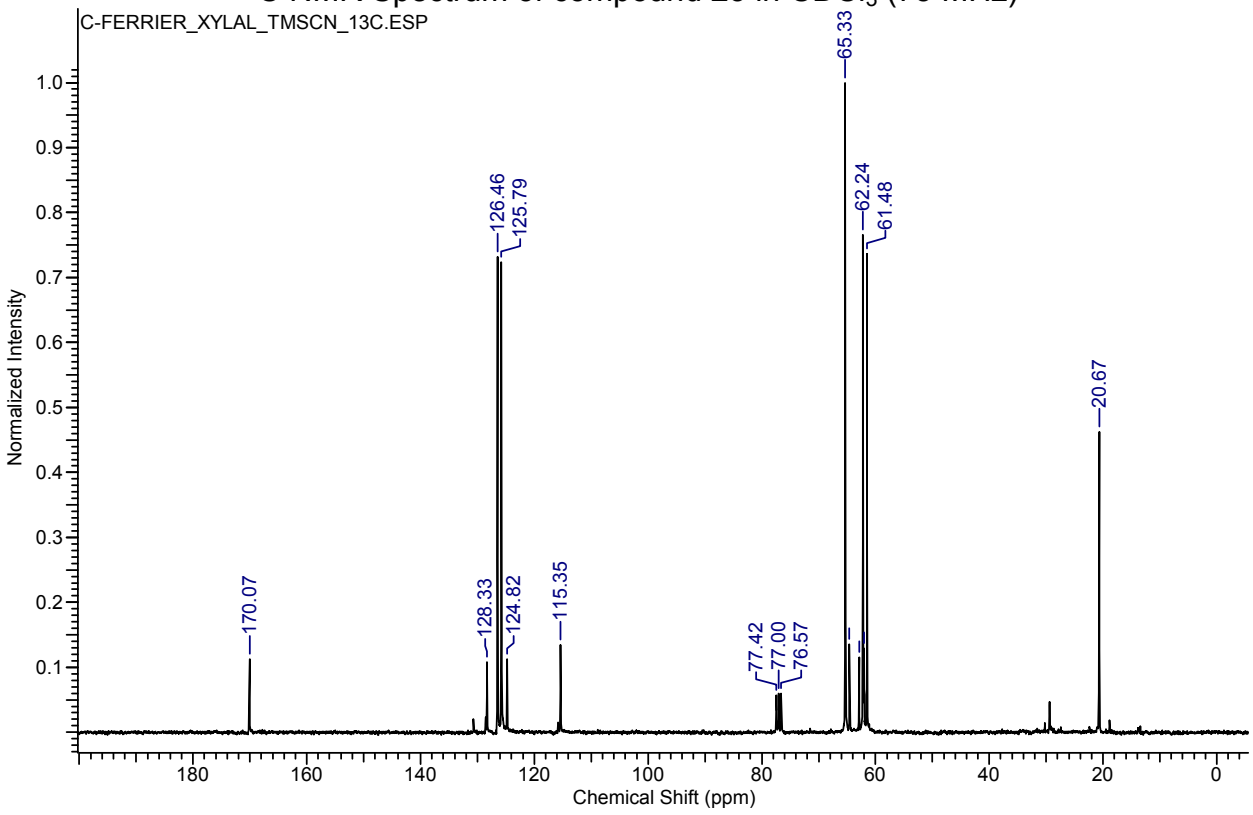
^{13}C NMR Spectrum of compound **22** in $CDCl_3$ (125 MHz)



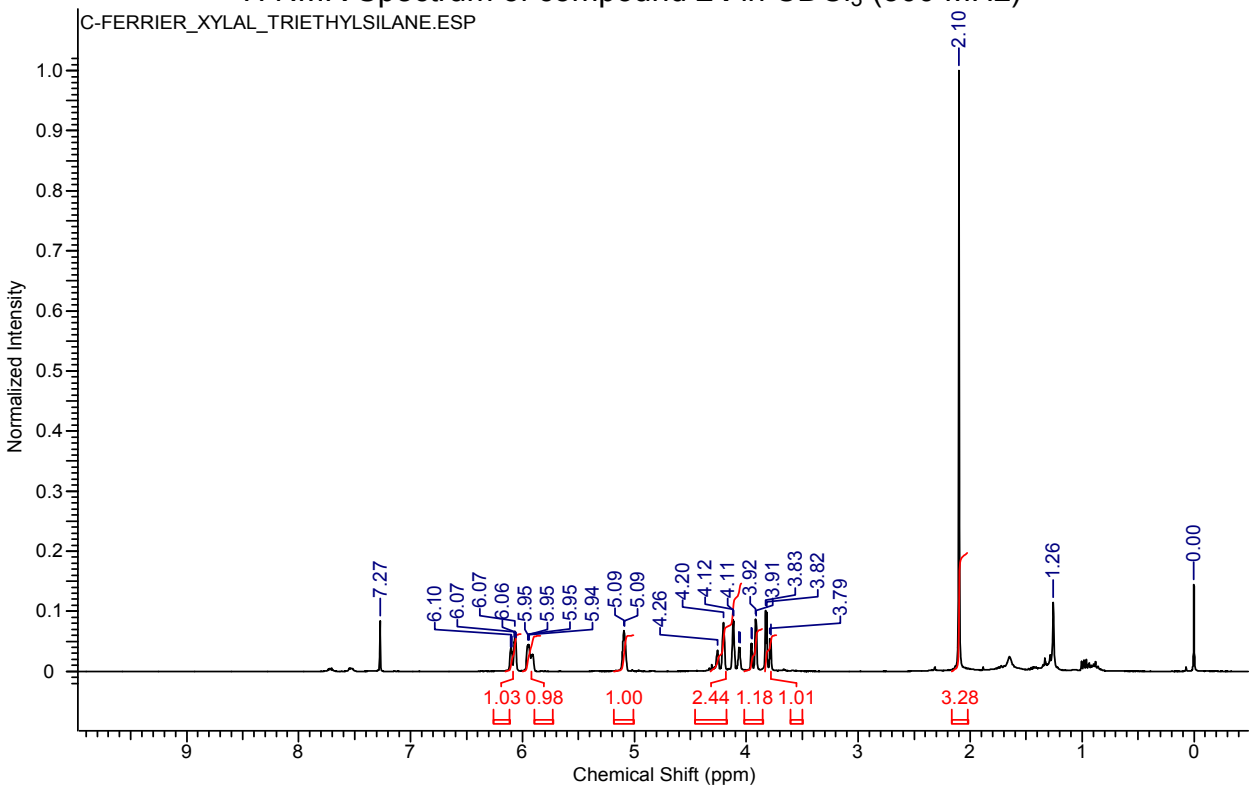
^{1}H NMR Spectrum of compound **23** in $CDCl_3$ (500 MHz)



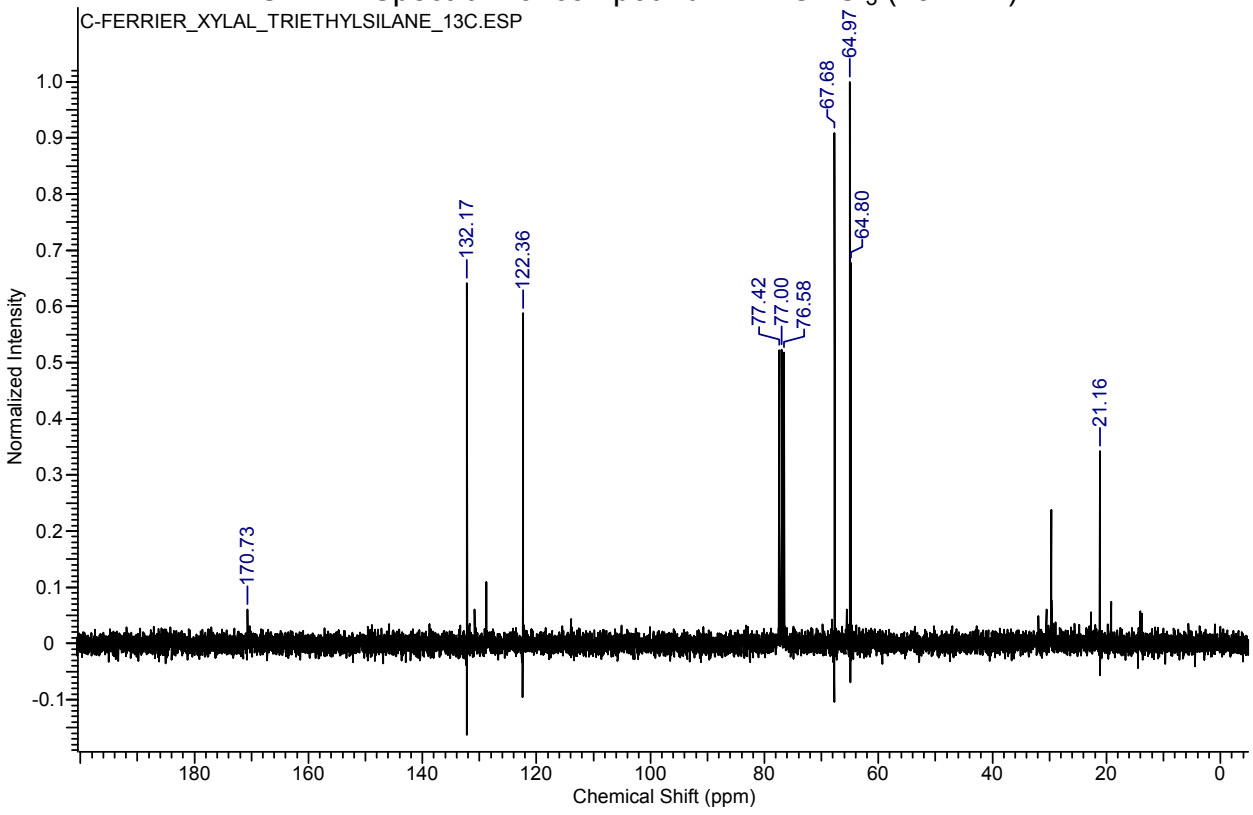
^{13}C NMR Spectrum of compound **23** in $CDCl_3$ (75 MHz)



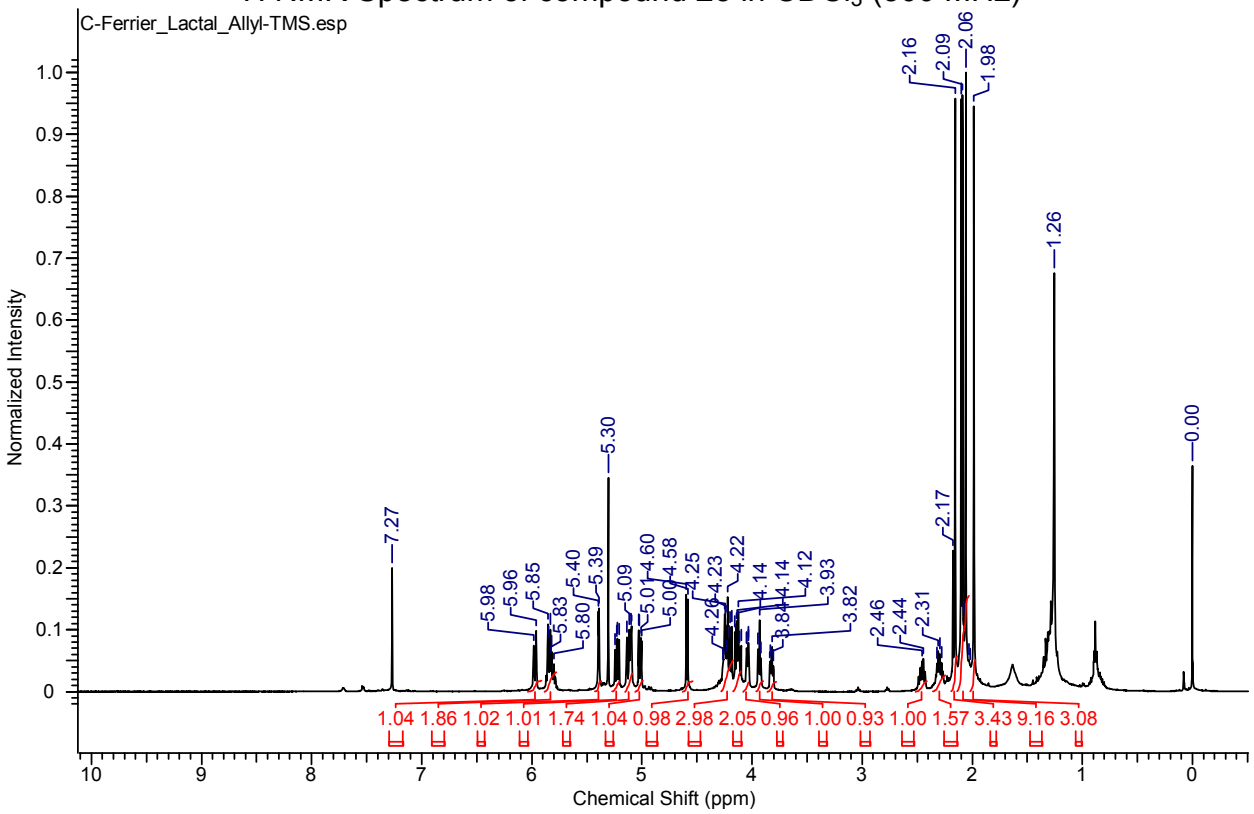
^{1}H NMR Spectrum of compound **24** in $CDCl_3$ (300 MHz)



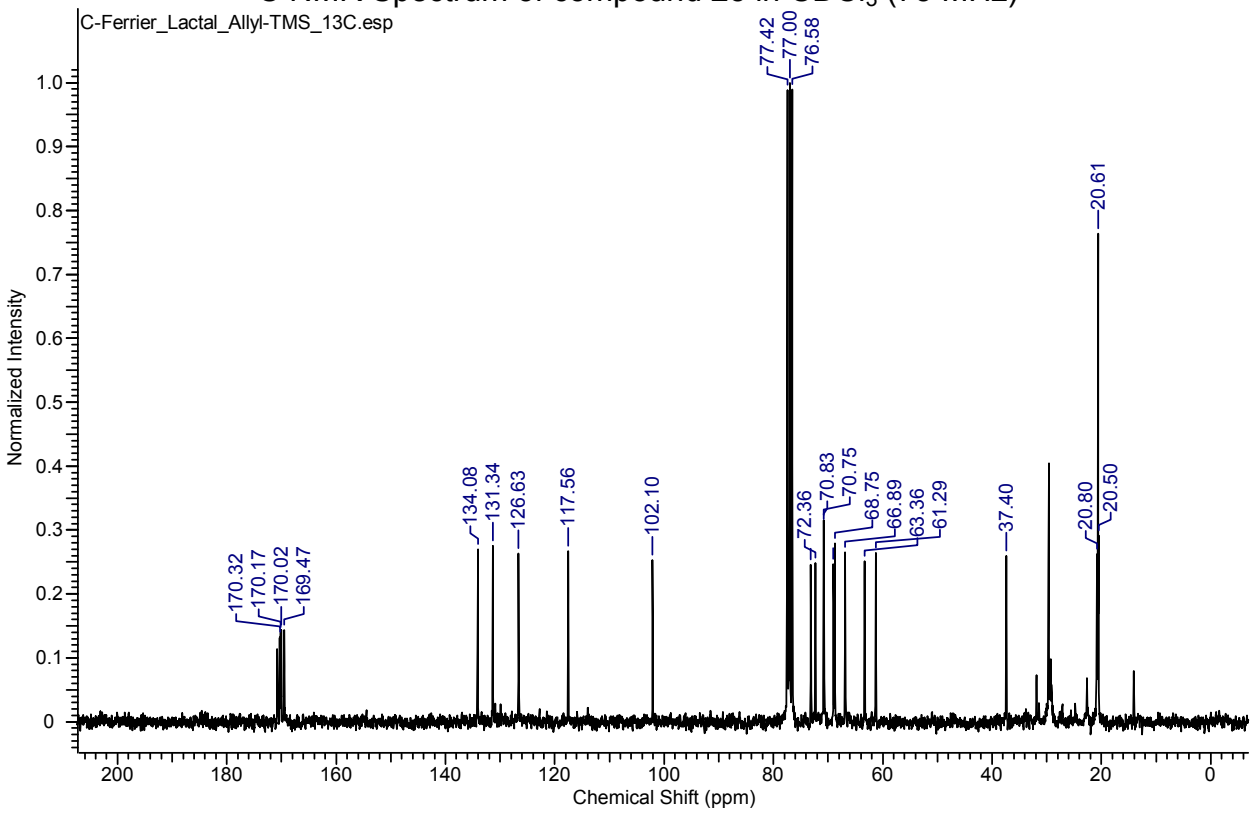
^{13}C NMR Spectrum of compound **24** in $CDCl_3$ (75 MHz)



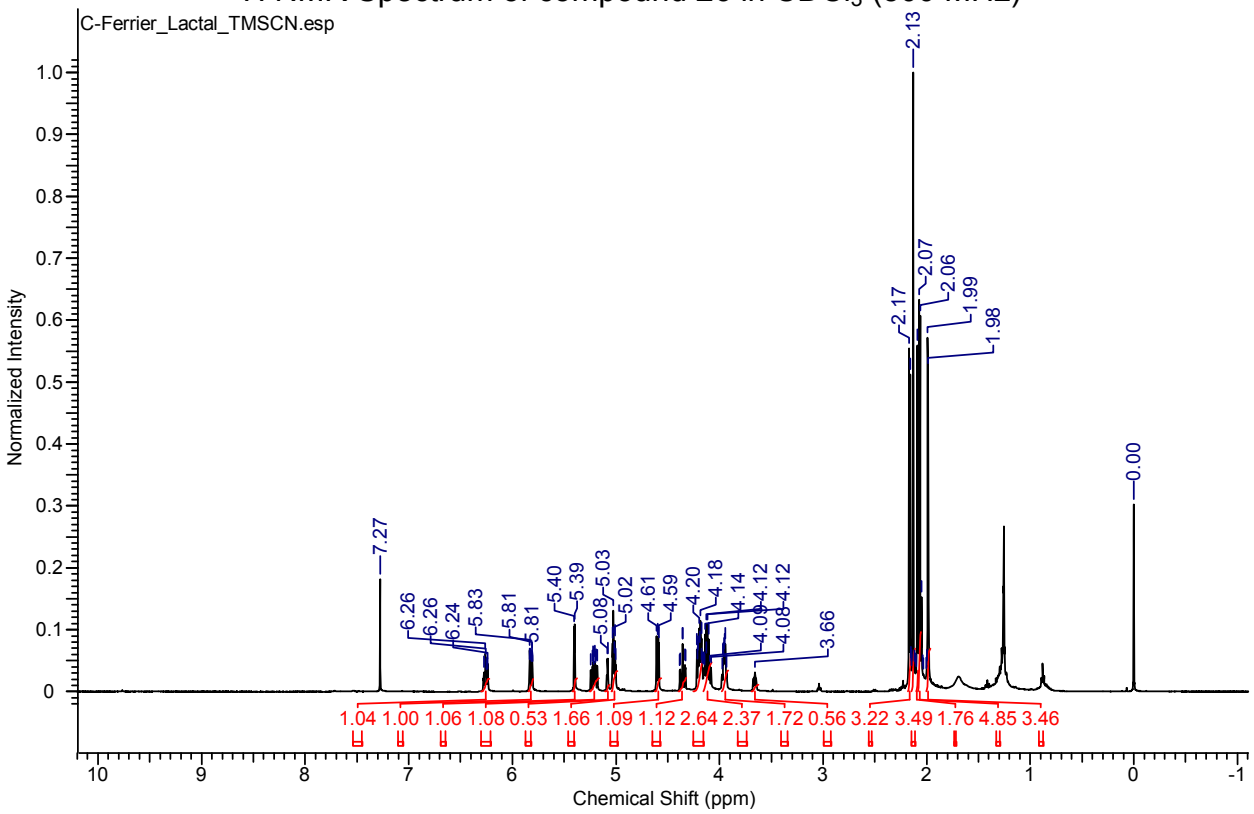
^{1}H NMR Spectrum of compound **25** in $CDCl_3$ (500 MHz)



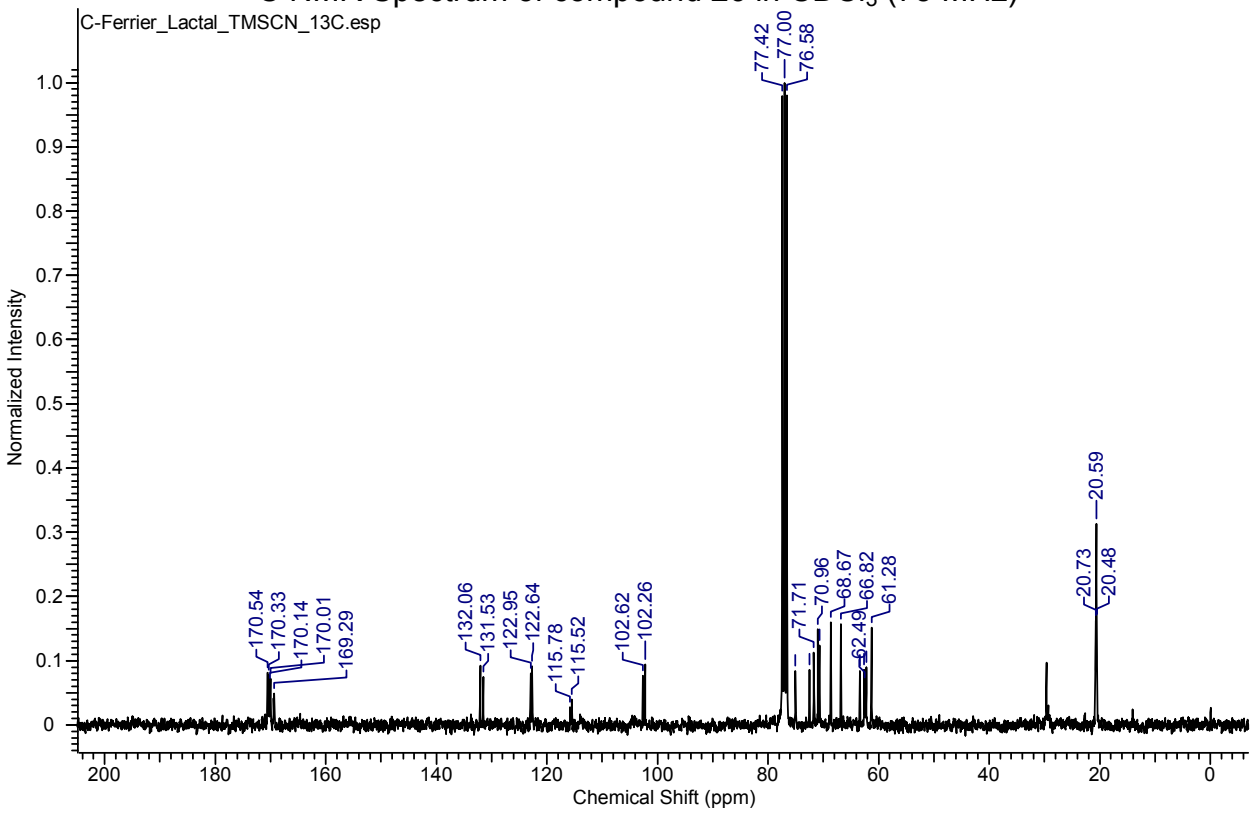
^{13}C NMR Spectrum of compound **25** in $CDCl_3$ (75 MHz)



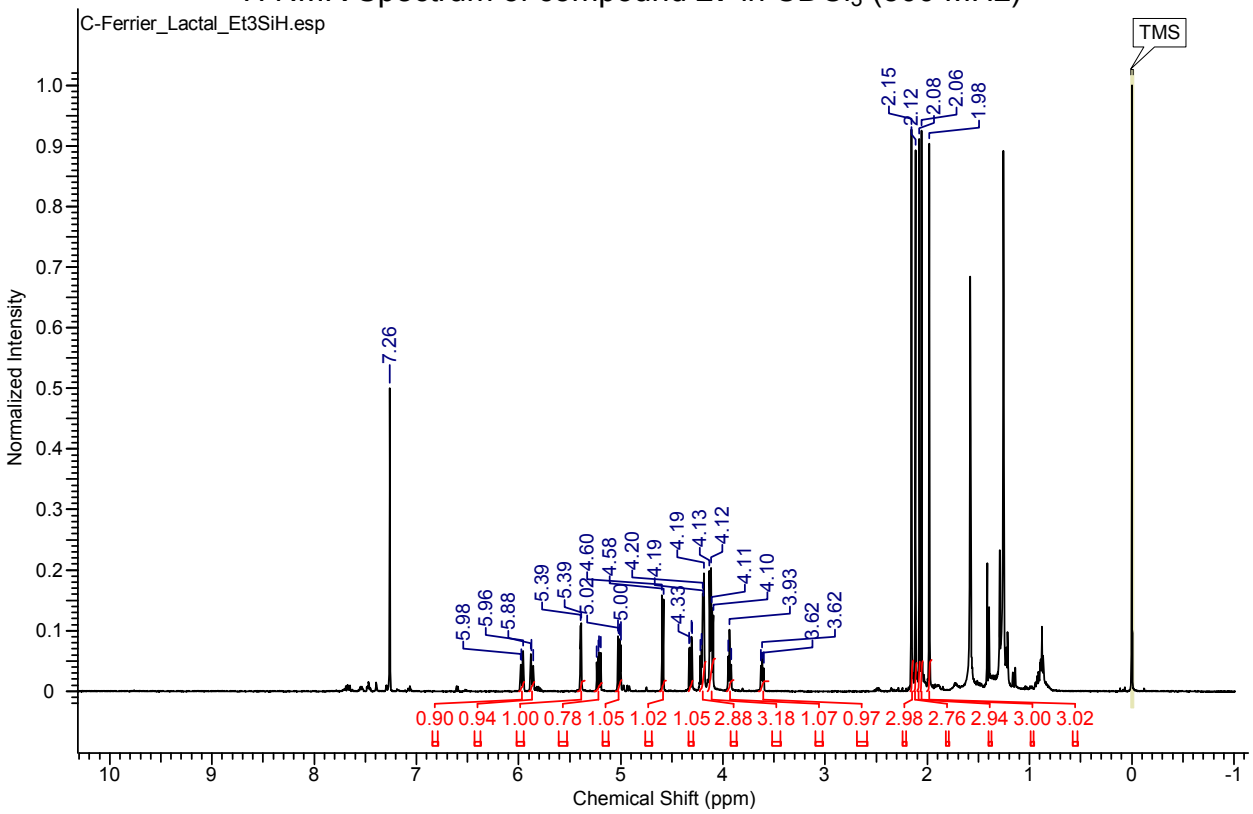
^{1}H NMR Spectrum of compound **26** in $CDCl_3$ (500 MHz)



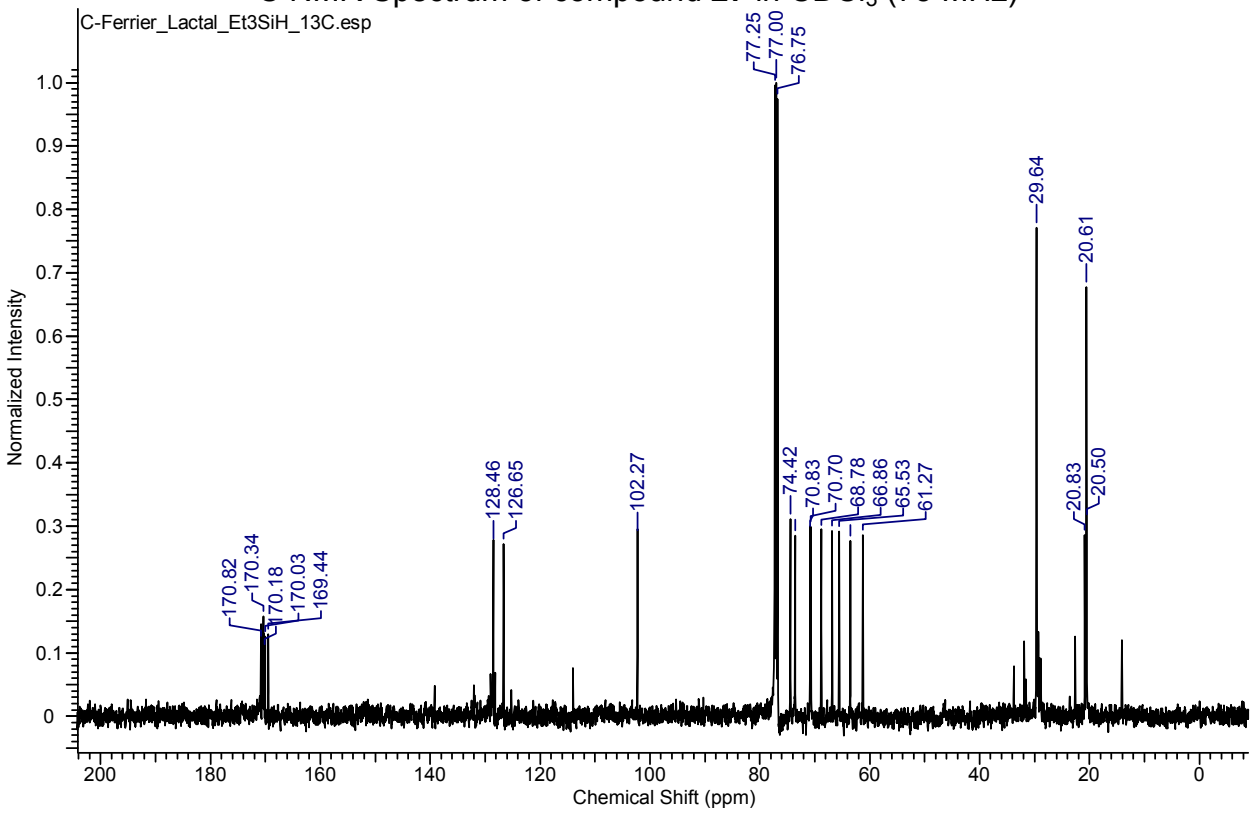
^{13}C NMR Spectrum of compound **26** in $CDCl_3$ (75 MHz)



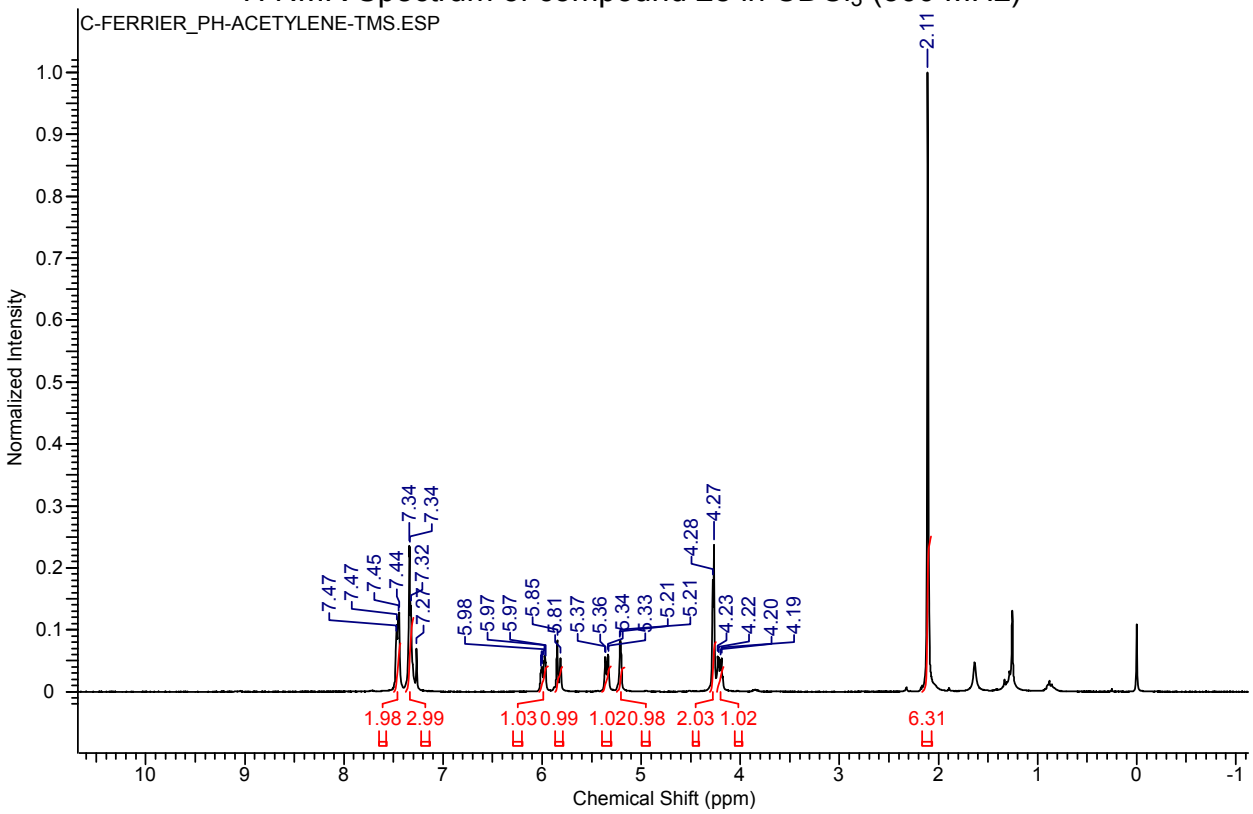
^{1}H NMR Spectrum of compound **27** in $CDCl_3$ (500 MHz)



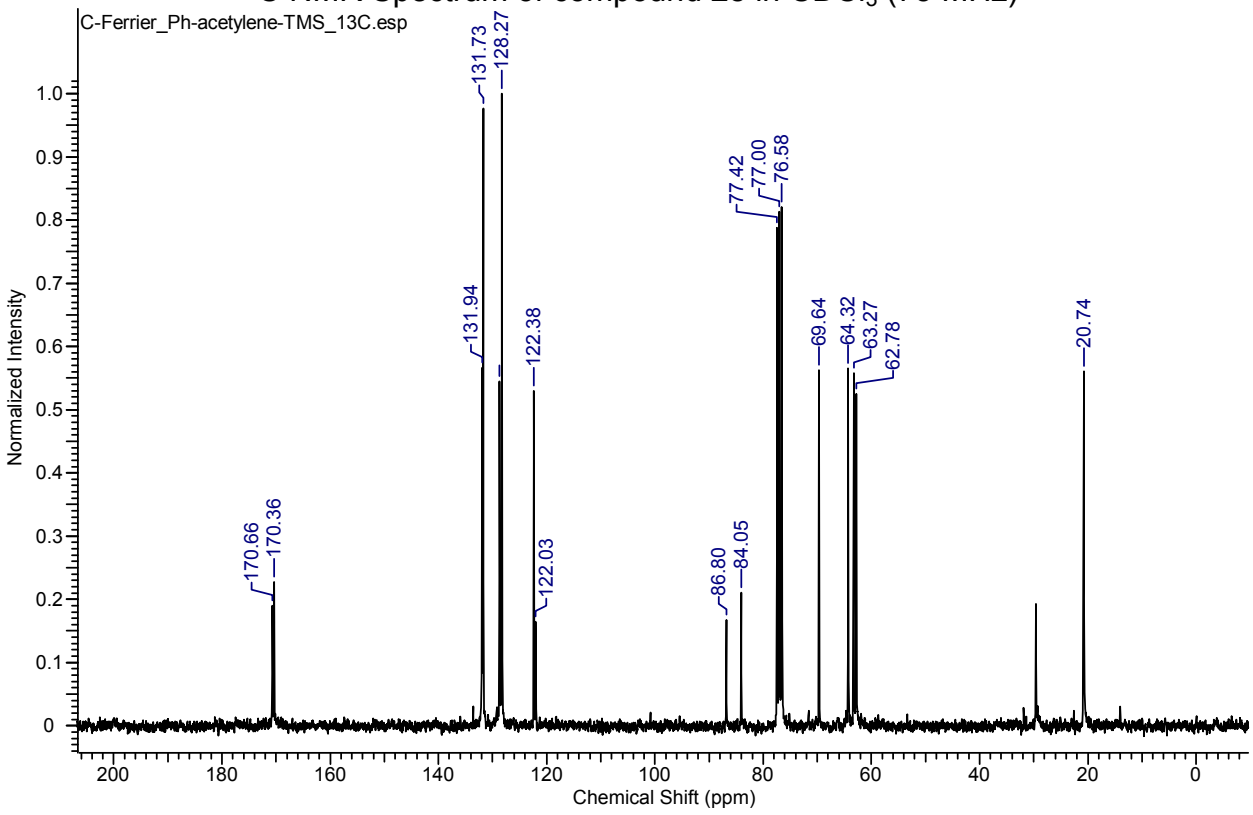
^{13}C NMR Spectrum of compound **27** in $CDCl_3$ (75 MHz)



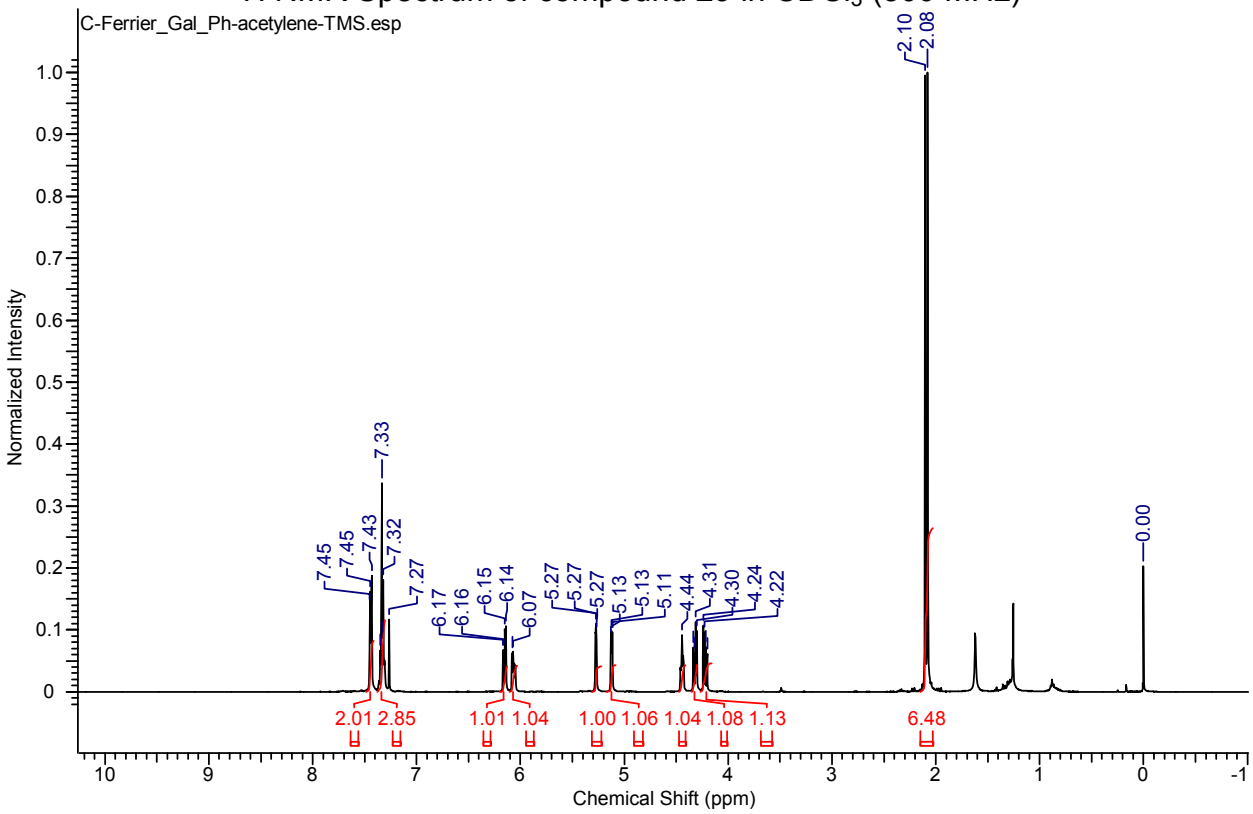
^{1}H NMR Spectrum of compound **28** in $CDCl_3$ (300 MHz)



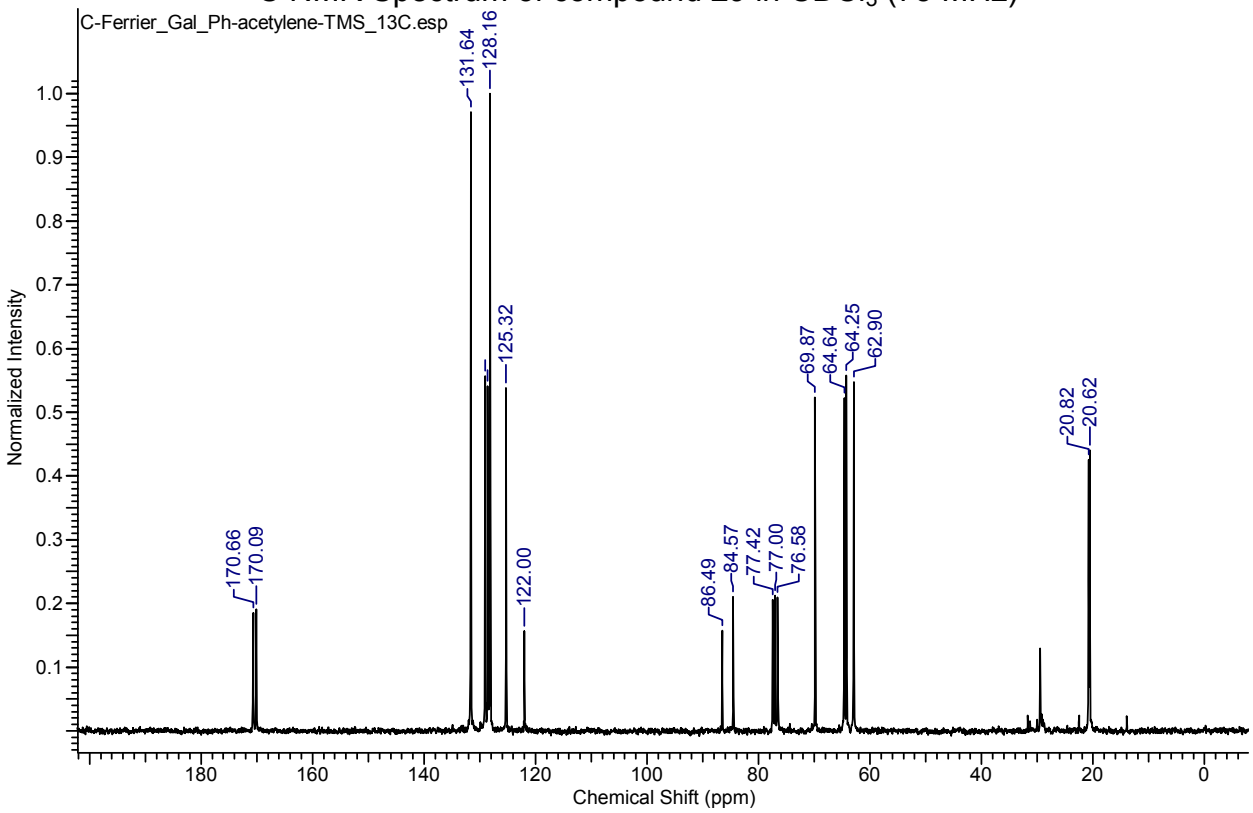
^{13}C NMR Spectrum of compound **28** in $CDCl_3$ (75 MHz)



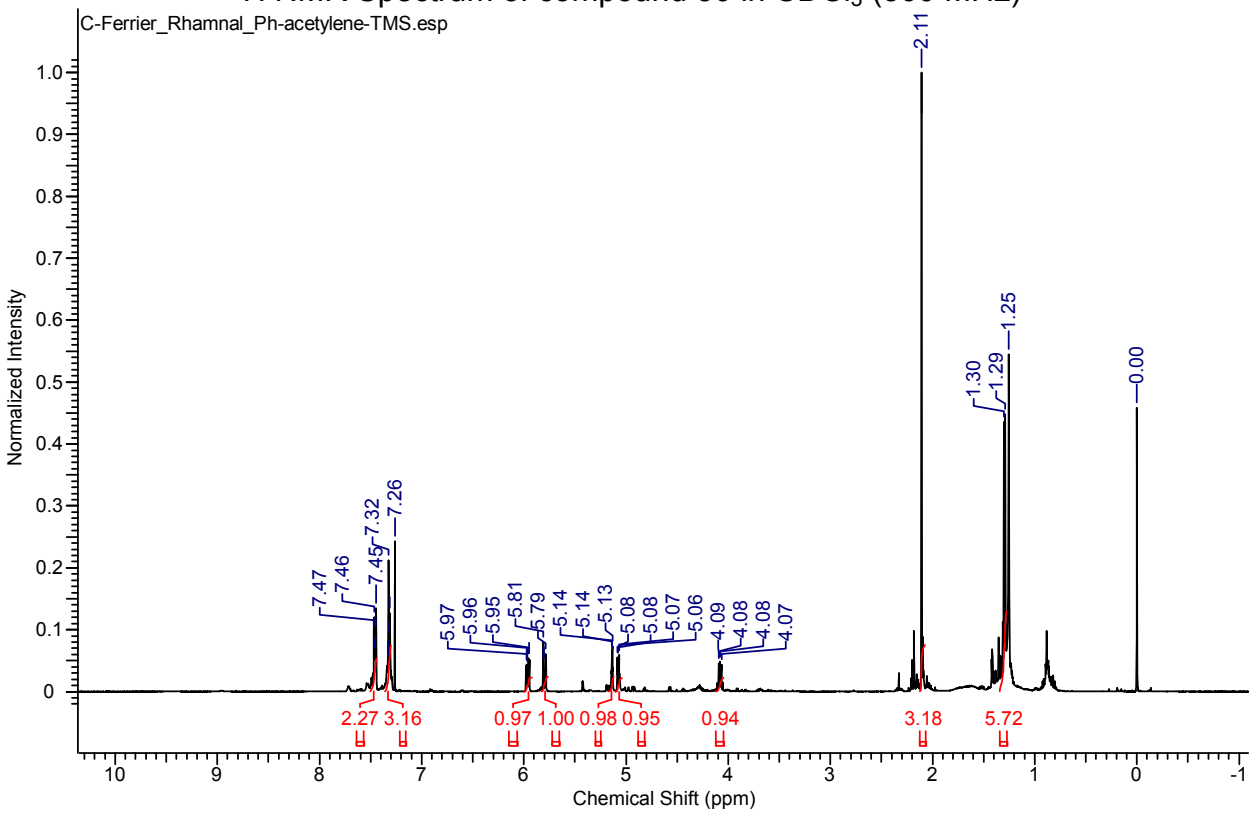
^{1}H NMR Spectrum of compound **29** in $CDCl_3$ (500 MHz)



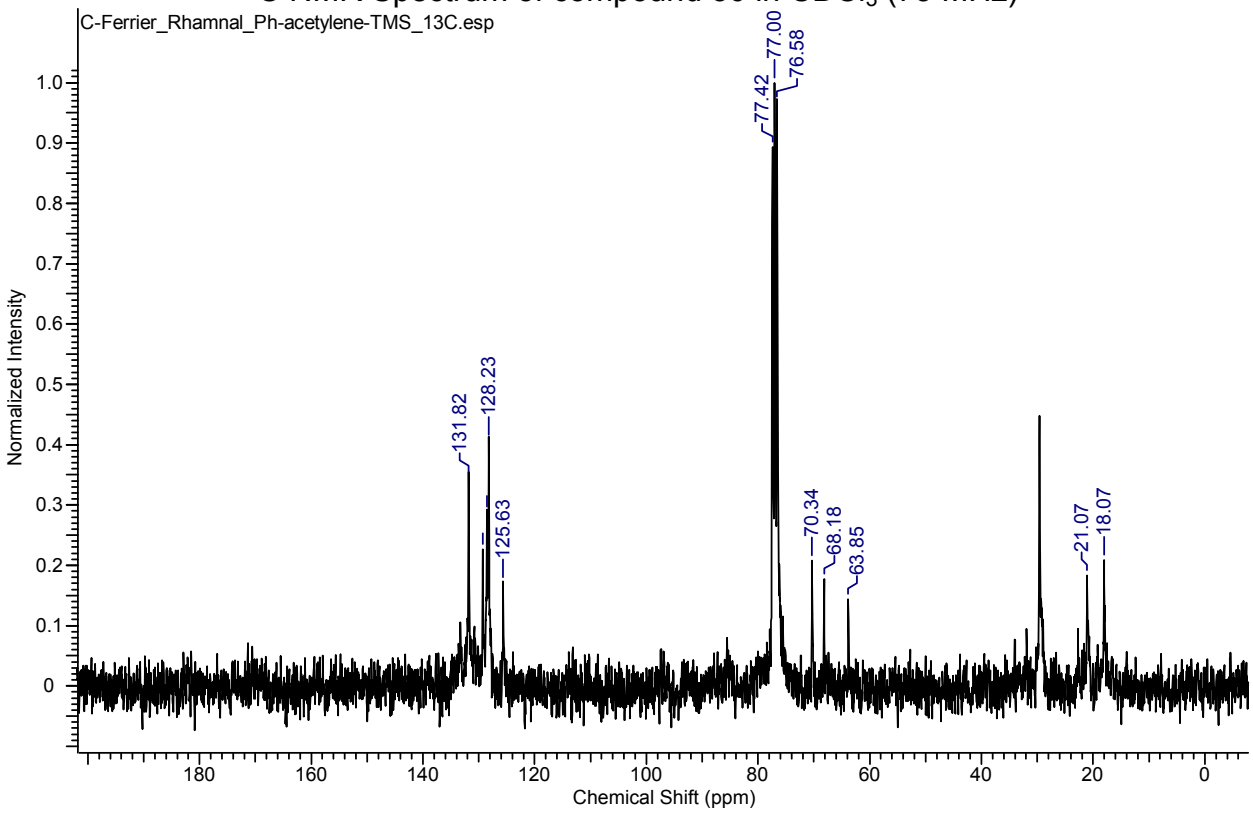
^{13}C NMR Spectrum of compound **29** in $CDCl_3$ (75 MHz)



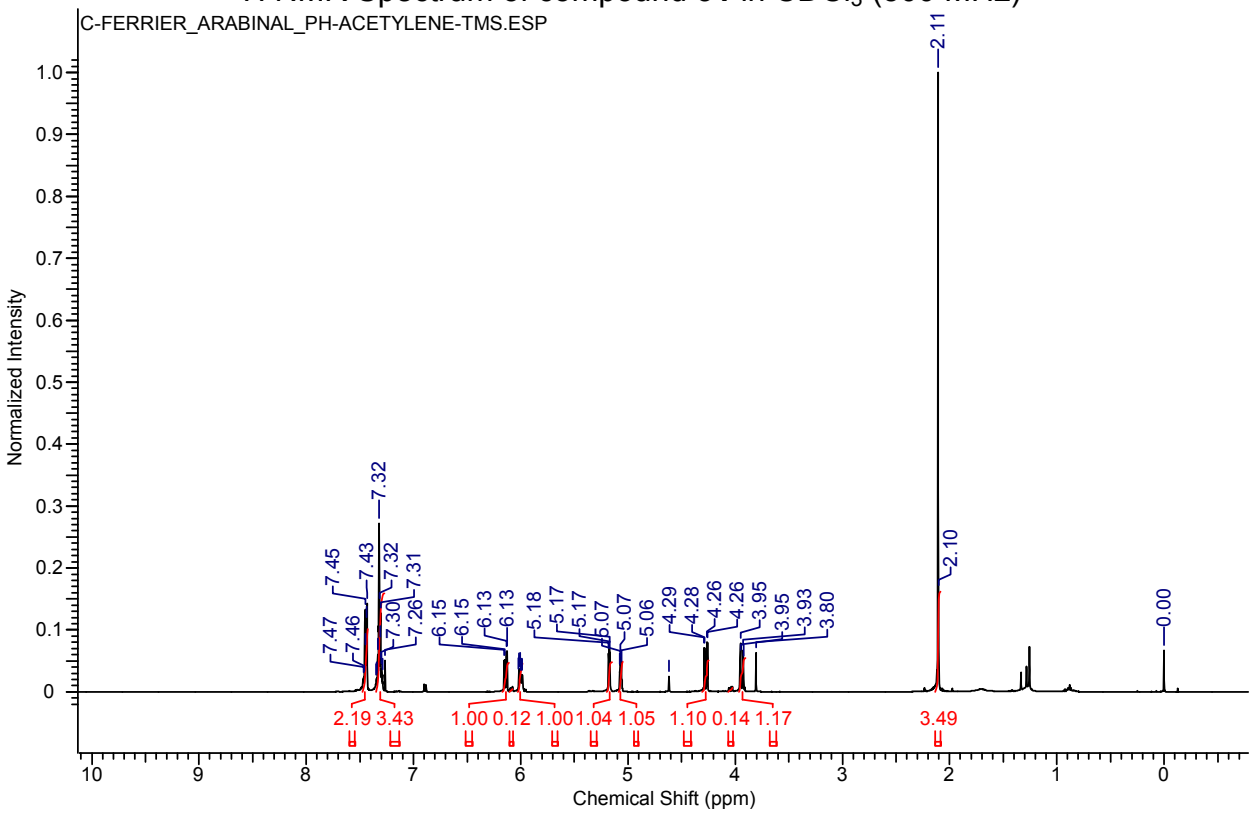
^{1}H NMR Spectrum of compound **30** in $CDCl_3$ (500 MHz)



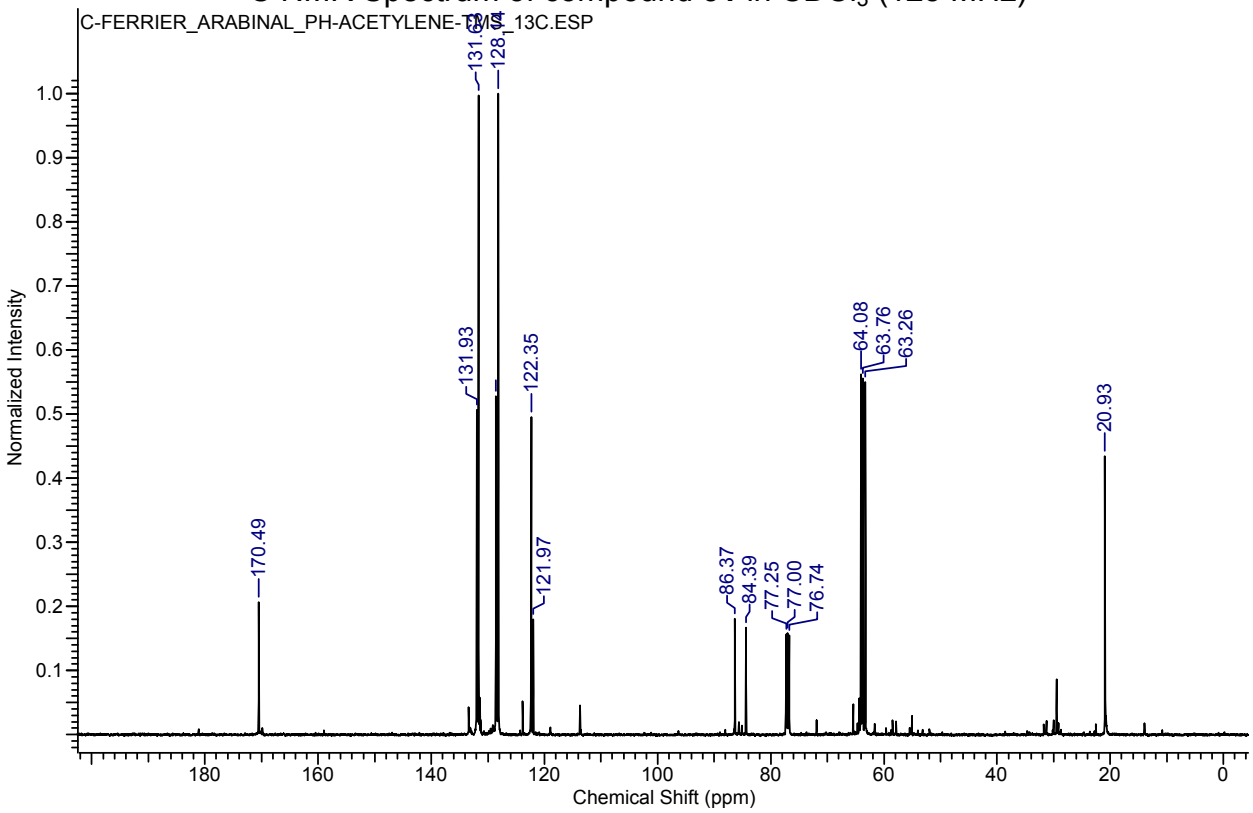
^{13}C NMR Spectrum of compound **30** in $CDCl_3$ (75 MHz)



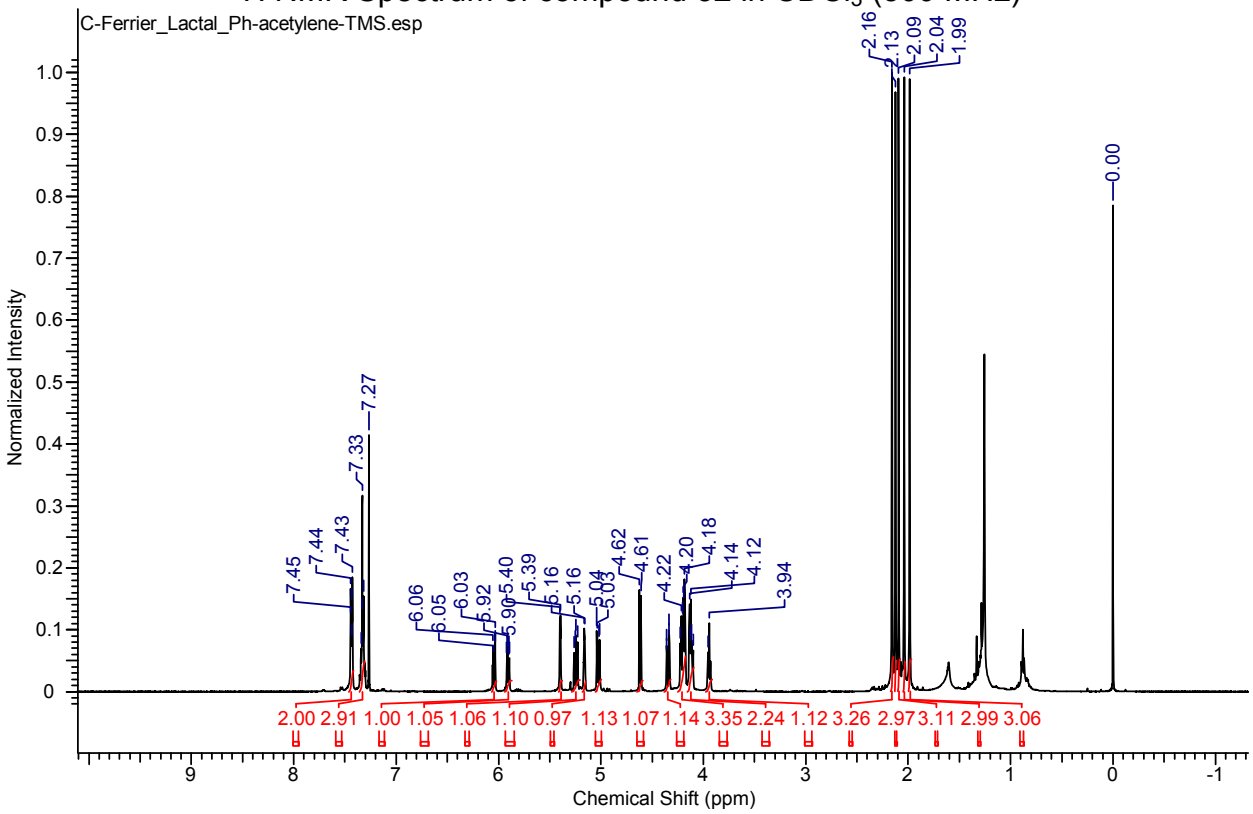
^{1}H NMR Spectrum of compound **31** in $CDCl_3$ (500 MHz)



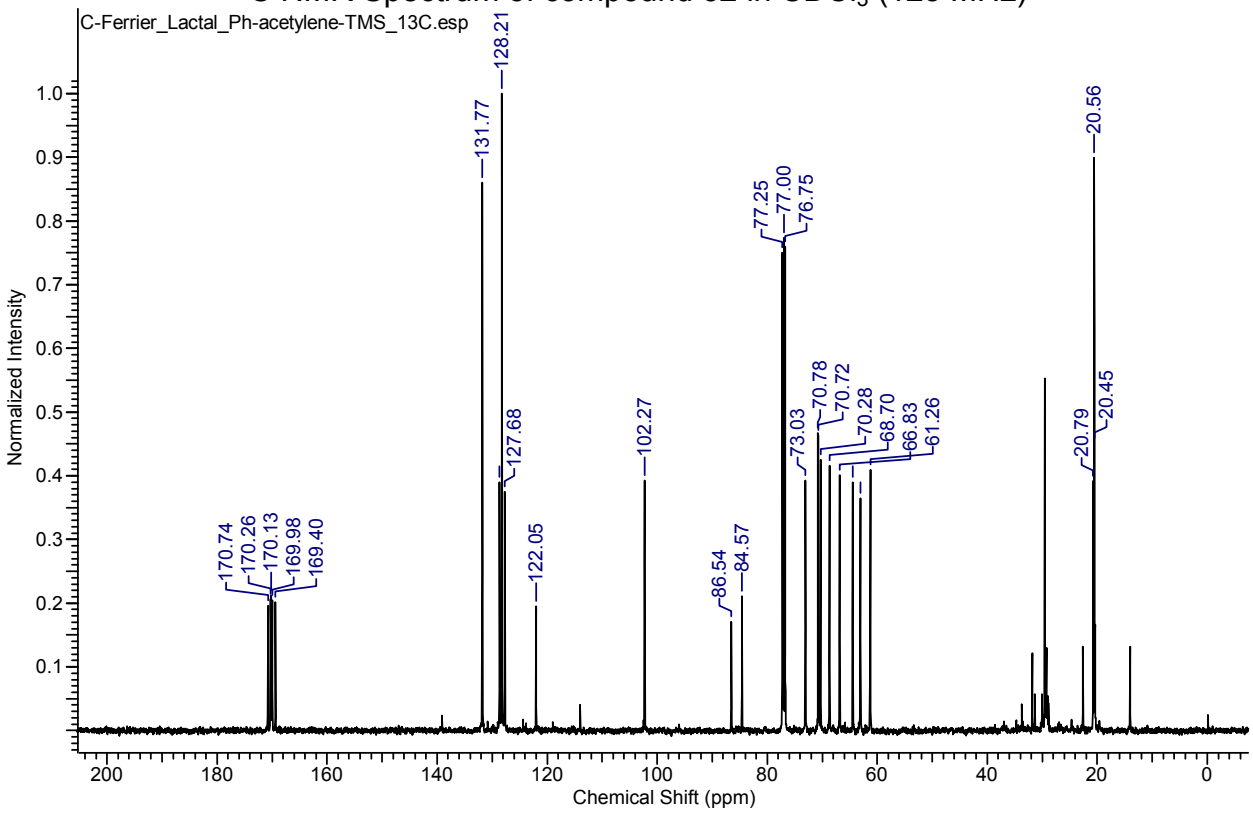
^{13}C NMR Spectrum of compound **31** in $CDCl_3$ (125 MHz)



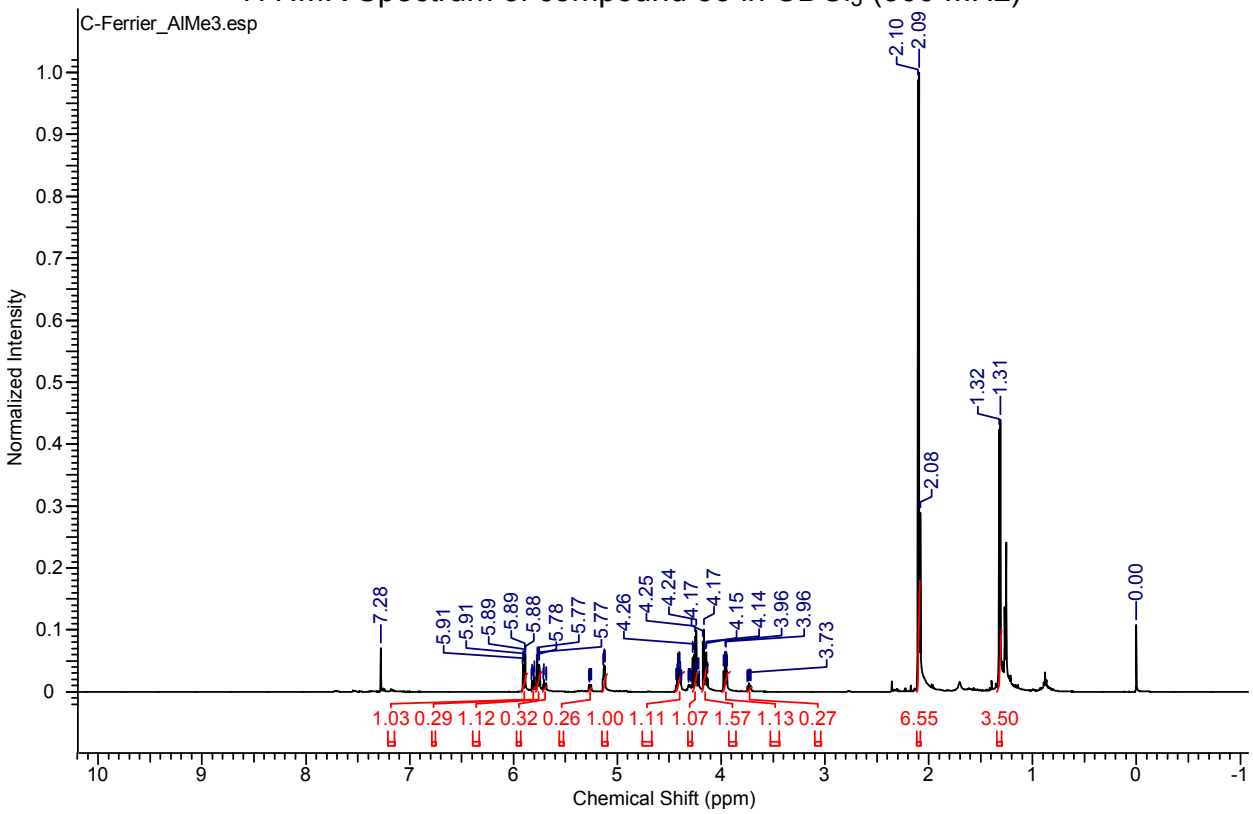
^{1}H NMR Spectrum of compound **32** in $CDCl_3$ (500 MHz)



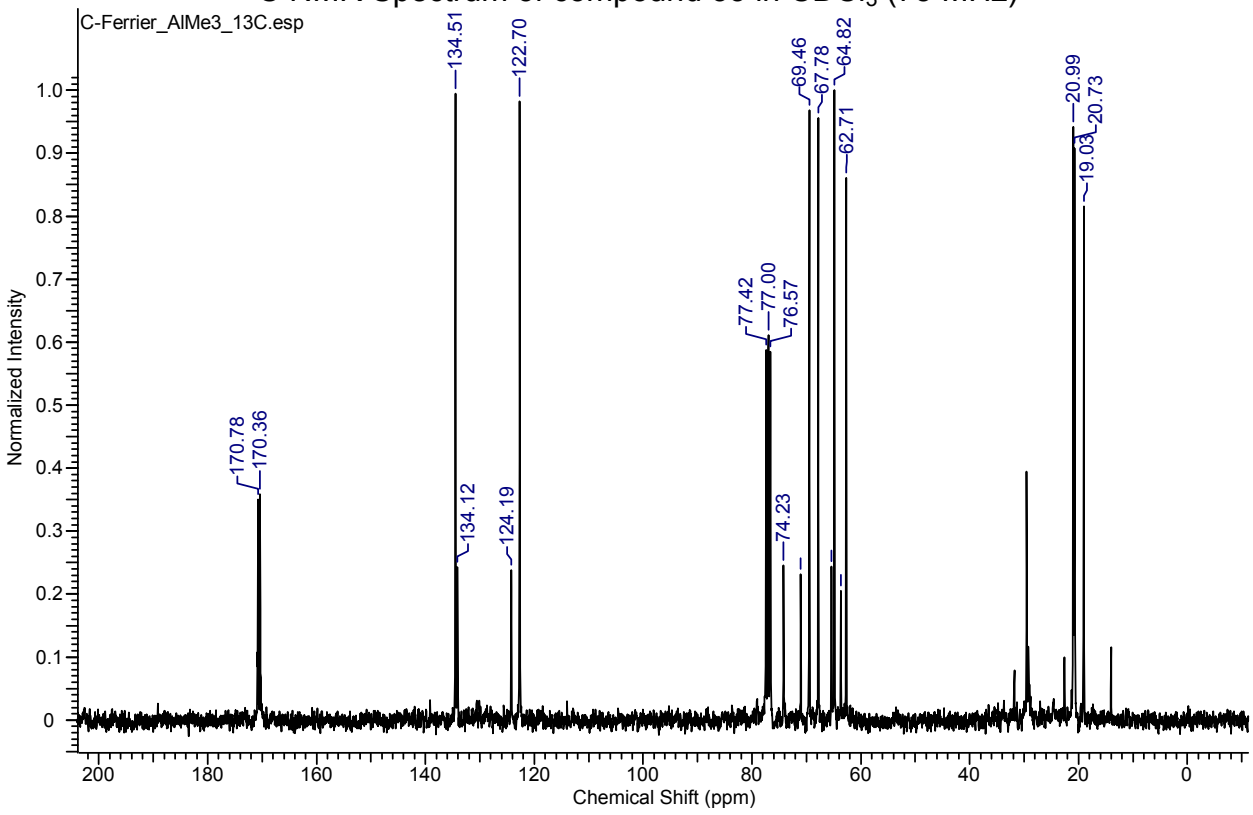
^{13}C NMR Spectrum of compound **32** in $CDCl_3$ (125 MHz)



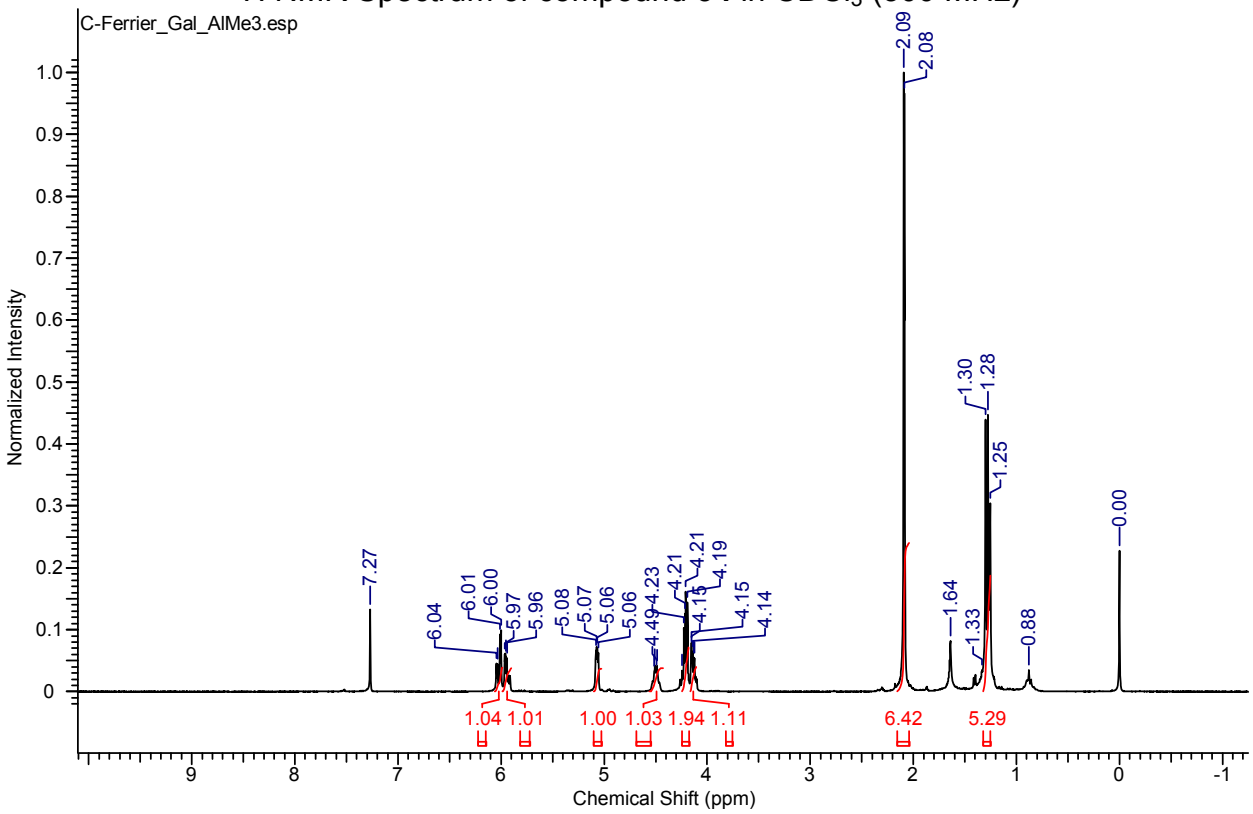
^{1}H NMR Spectrum of compound **33** in $CDCl_3$ (500 MHz)



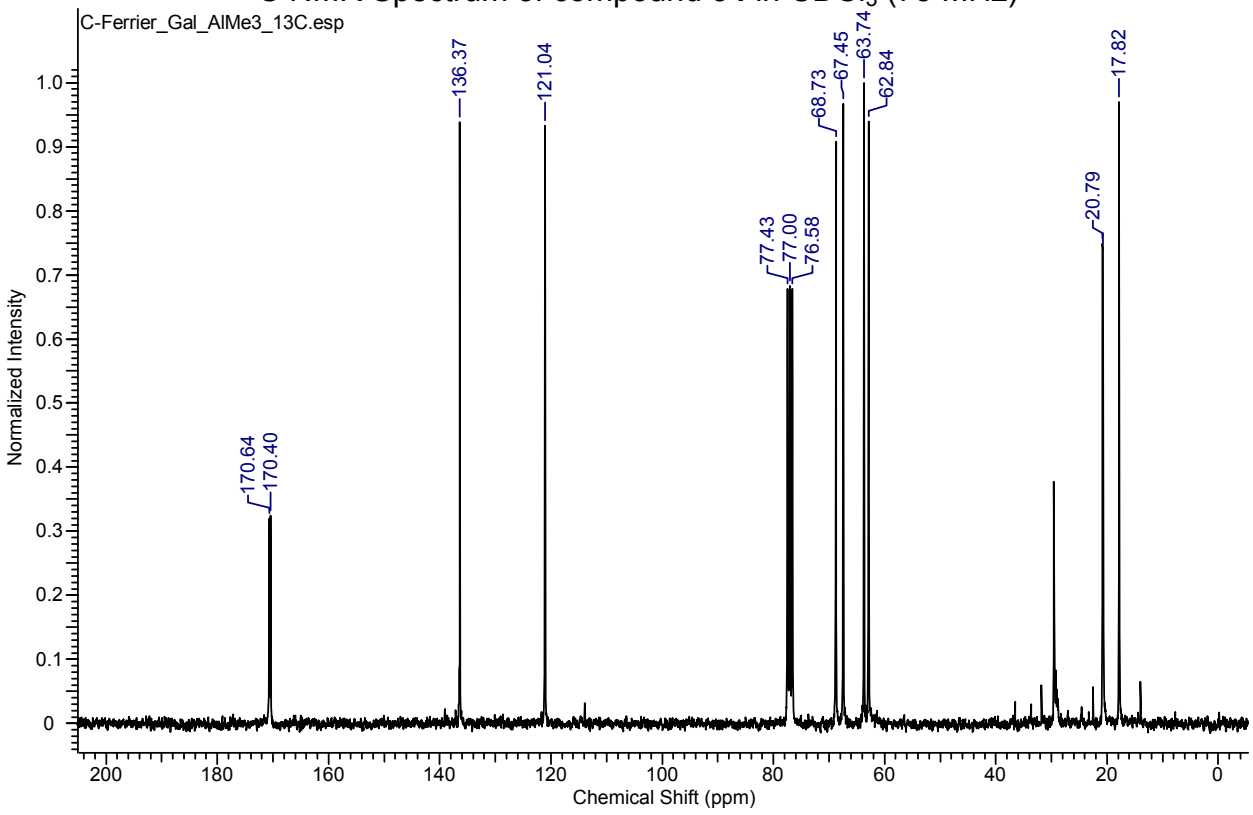
^{13}C NMR Spectrum of compound **33** in $CDCl_3$ (75 MHz)



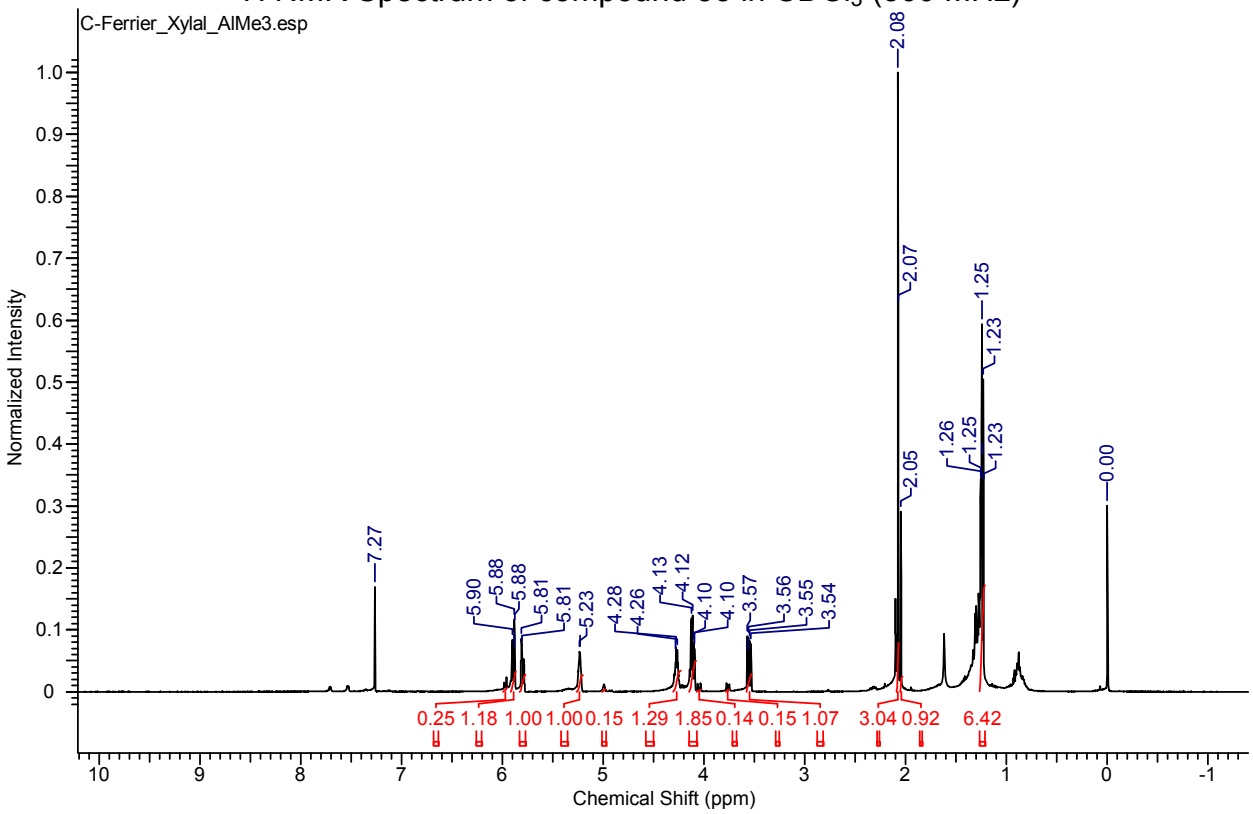
^{1}H NMR Spectrum of compound **34** in $CDCl_3$ (300 MHz)



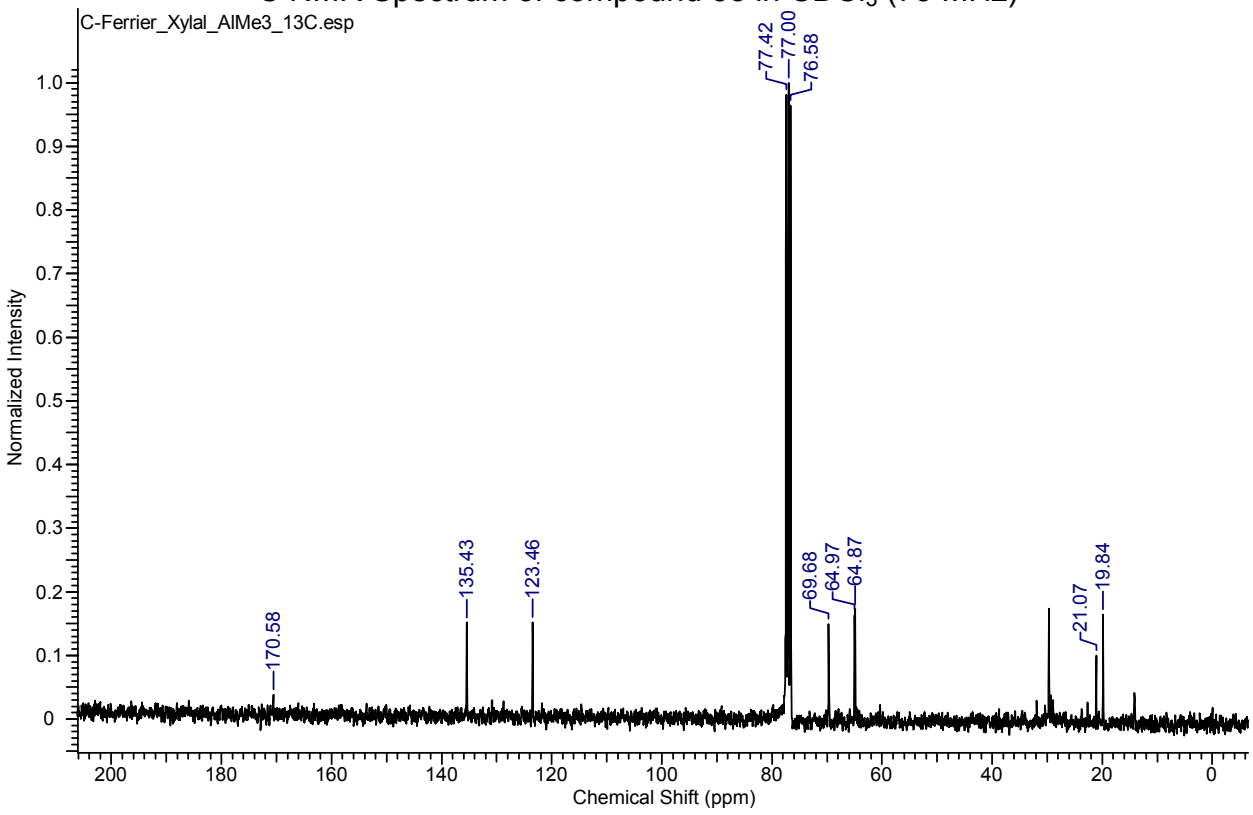
^{13}C NMR Spectrum of compound **34** in $CDCl_3$ (75 MHz)



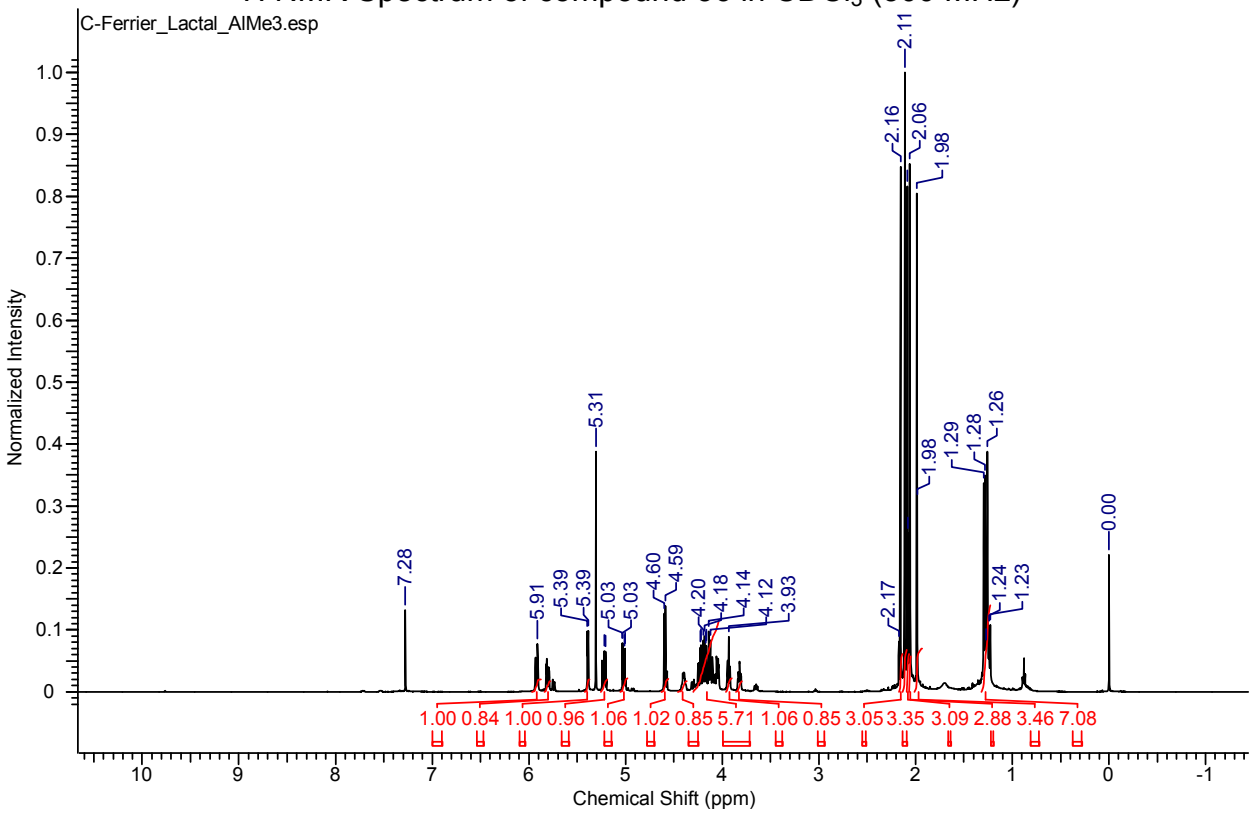
^{1}H NMR Spectrum of compound **35** in $CDCl_3$ (300 MHz)



^{13}C NMR Spectrum of compound **35** in $CDCl_3$ (75 MHz)



^{1}H NMR Spectrum of compound **36** in $CDCl_3$ (300 MHz)



^{13}C NMR Spectrum of compound **36** in $CDCl_3$ (75 MHz)