

Supporting information for:

“Corroles that “Click”: Modular Synthesis of Azido- and Propargyl- Functionalized Metallocorrole Complexes and Convergent Synthesis of a bis-Corrole Scaffold”

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A. Cyclic voltammetry of compounds **7**, **9**, **14** and **15**

Cyclic voltammetric measurements were performed with a Gamry Reference 600 potentiostat, using either 0.1 M tetraethylammonium tetrafluoroborate (TEABF₄) in acetonitrile or 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) in CH₂Cl₂. A three-electrode cell was used, with a glassy carbon working electrode (3 mm diameter), a platinum mesh counter electrode, and a Ag/Ag⁺ reference electrode. The reference electrode consisted of a silver wire in a solution of 0.01 M AgNO₃ and 0.1 M TEABF₄ in acetonitrile, separated from the bulk solution by a Vycor frit. Electrolyte solutions were deoxygenated with nitrogen for at least 10 minutes before any compounds were added and were kept under a blanket of nitrogen during analysis. Between measurements, the working electrode was polished with 0.05 μm alumina and rinsed with distilled water and acetonitrile.

All potentials are referenced to Ag/Ag⁺ (0.01 M Ag⁺). Potentials reproduced from other publications have been converted from SCE to Ag/Ag⁺ by subtracting 298 mV.¹ All scans shown were taken at 100 mV/s, except for **15** (the Cu-Fe complex), which was not sufficiently soluble in acetonitrile (although solubility was better in acetonitrile than in CH₂Cl₂) and had to be measured at 500 mV/s to observe well-resolved peaks. Currents are reported as current densities, calculated using an electrode area of 0.071 cm². Arrows on the voltammograms (in text and SI) indicate the direction of the first potential sweep.

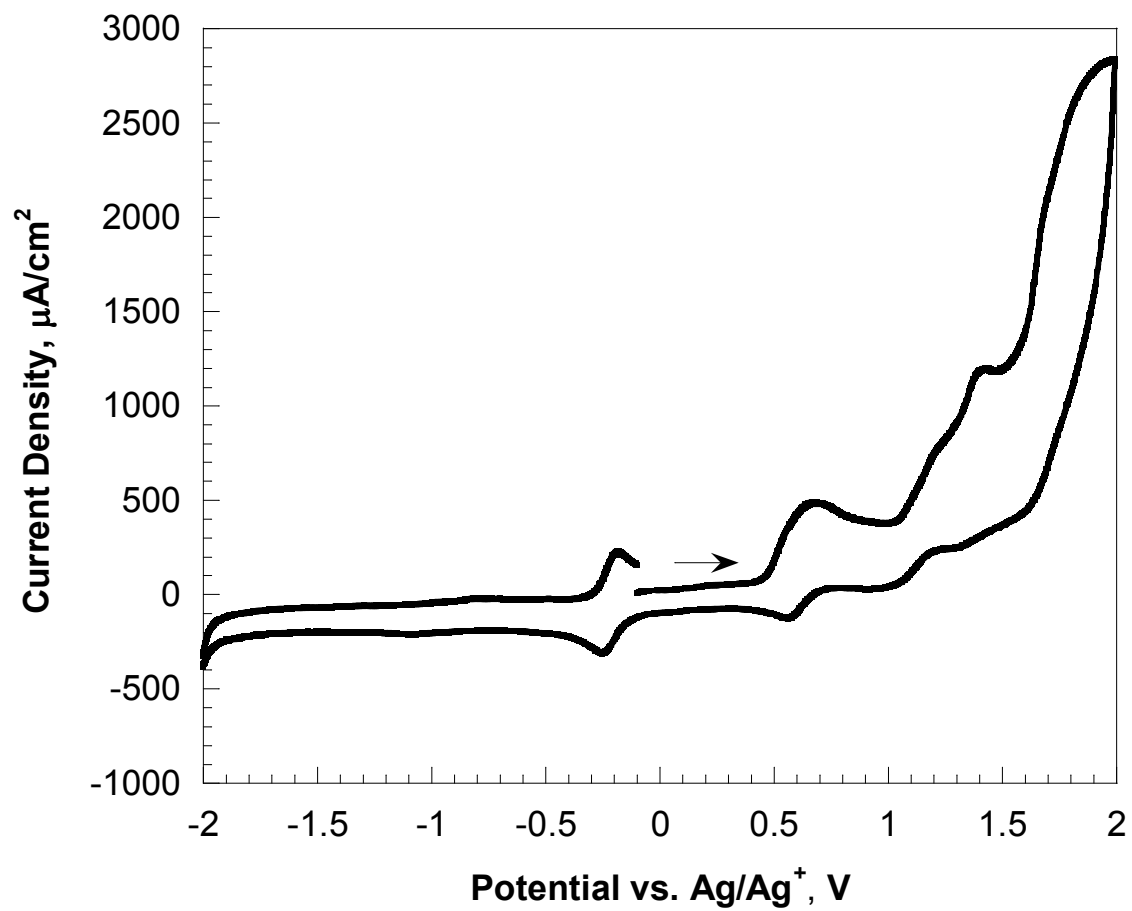


Figure S1. Cyclic voltammogram of 1 mM $(\text{C}_6\text{F}_5)_2(p\text{-OMePh})\text{corroleCu}$ (**7**) in acetonitrile, 100 mV/s.

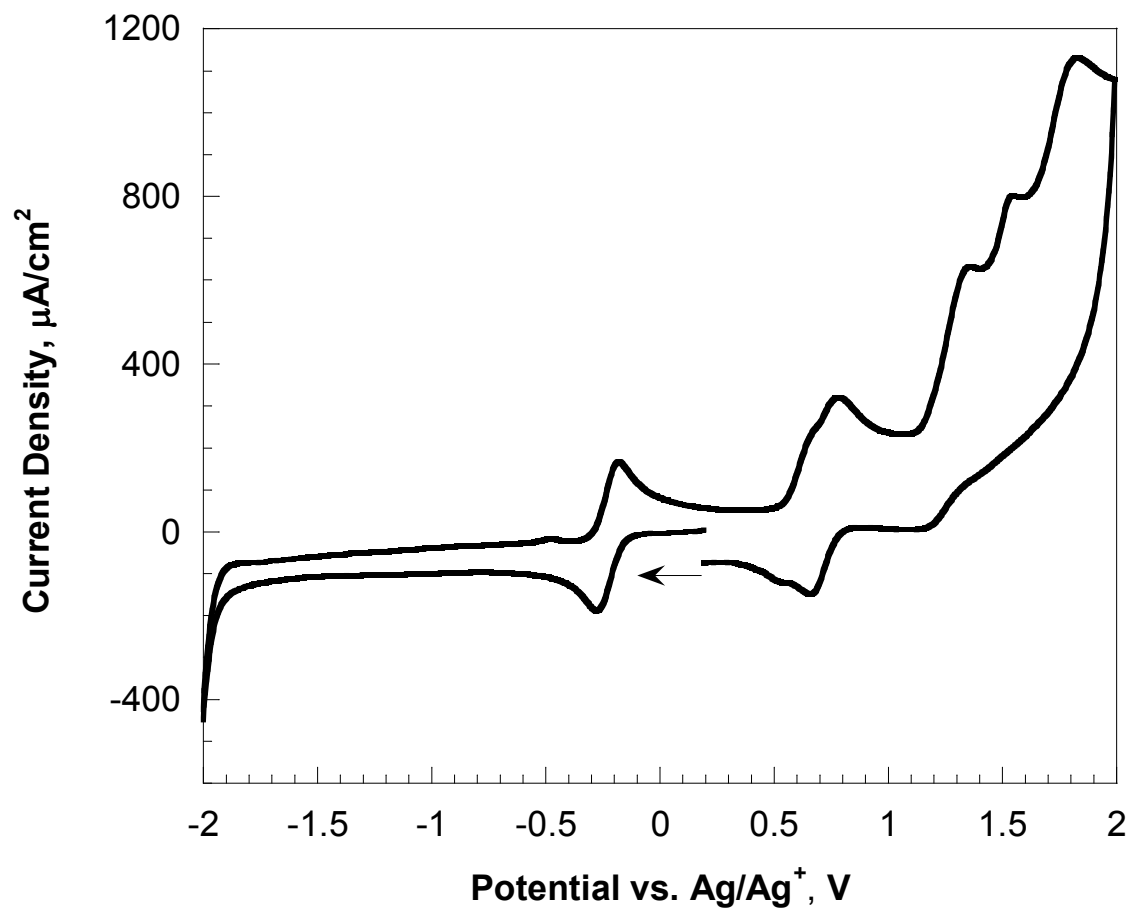


Figure S2. Cyclic voltammogram of 1 mM $(\text{C}_6\text{F}_5)_2(p\text{-OMePh})\text{corroleCu}$ (**7**) in CH_2Cl_2 , 100 mV/s.

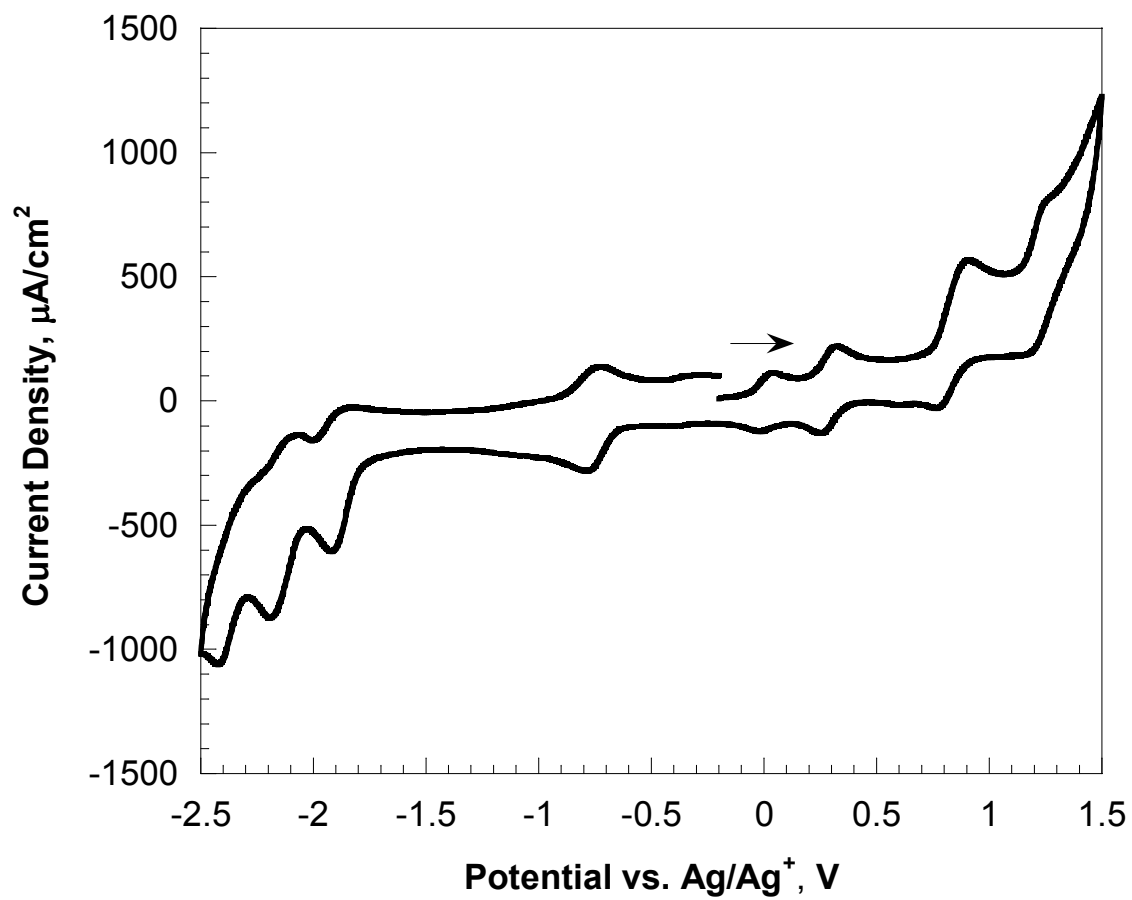


Figure S3. Cyclic voltammogram of 1 mM $((\text{C}_6\text{F}_5)_2(p\text{-OMePh})\text{corroleFe}(\text{Et}_2\text{O})_2)$ (**9**) in acetonitrile, 100 mV/s.

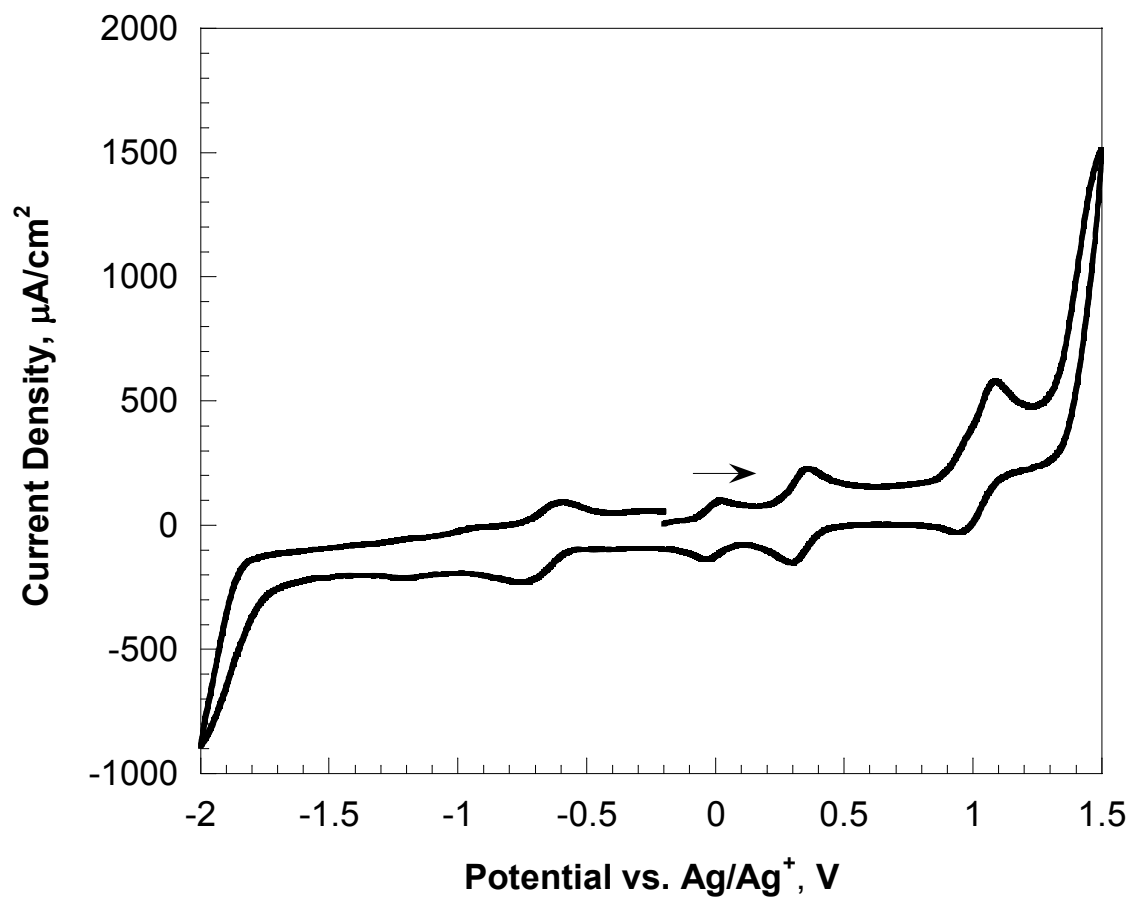


Figure S4. Cyclic voltammogram of 1 mM $((\text{C}_6\text{F}_5)_2(p\text{-OMePh})\text{corroleFe}(\text{Et}_2\text{O})_2)$ (**9**) in CH_2Cl_2 , 100 mV/s.

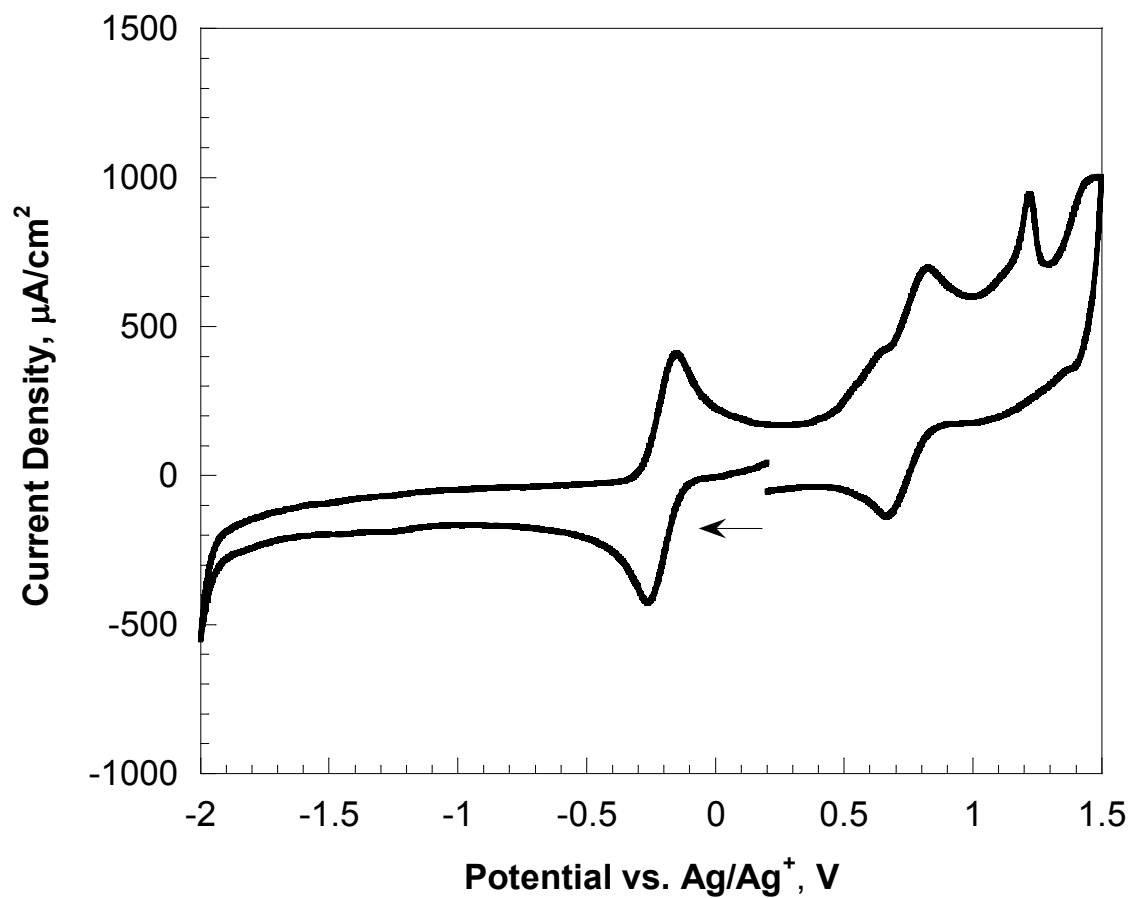


Figure S5. Cyclic voltammogram of 1 mM $\text{Cu}(\text{corrole}((\text{C}_6\text{F}_5)_2(\text{Ph}))-p\text{-O}-(\text{CH}_2)(\text{C}_2\text{HN}_3)(\text{CH}_2)-m-(\text{Ph}(\text{C}_6\text{F}_5)_2\text{corrole})\text{Cu}$ (**14**) corrole in CH_2Cl_2 , 100 mV/s.

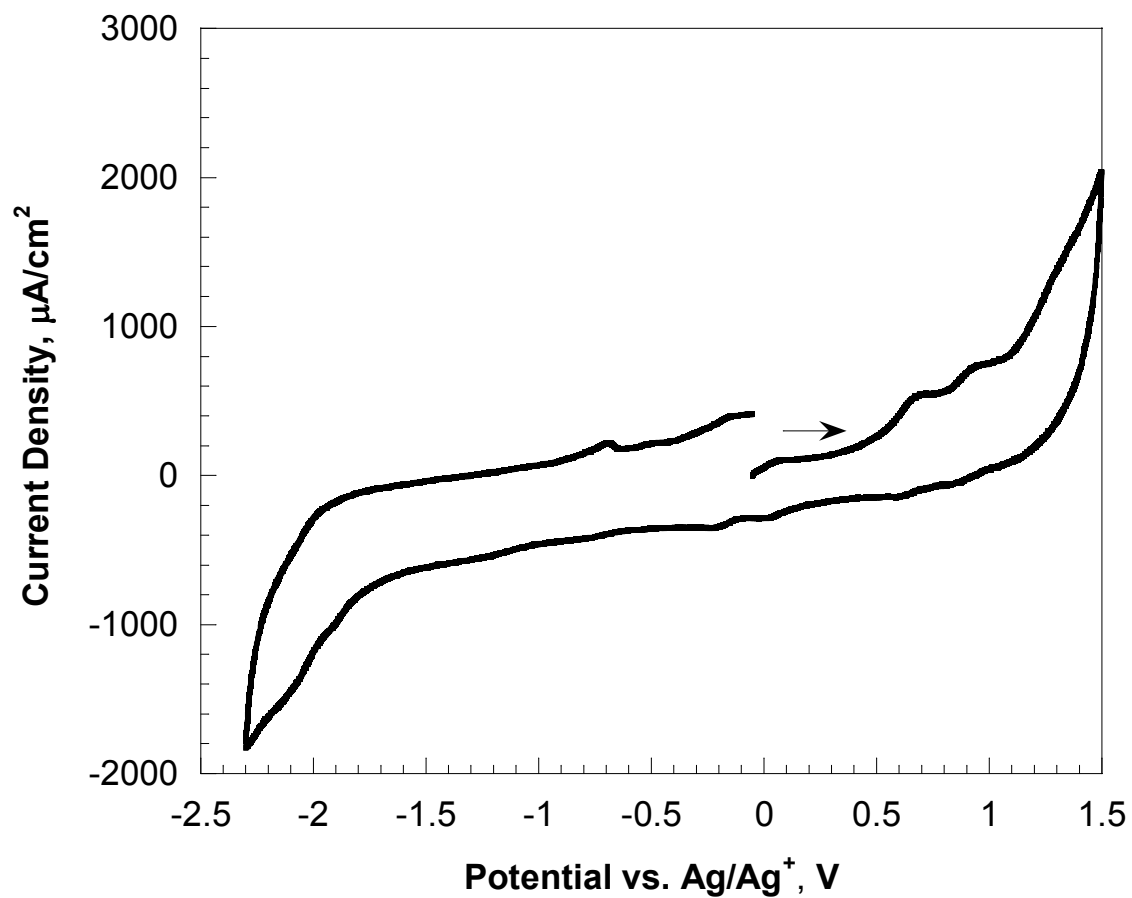


Figure S6. Cyclic voltammogram of $<1 \text{ mM Fe}(\text{CH}_3\text{CN})_2(\text{corrole}((\text{C}_6\text{F}_5)_2(\text{Ph}))-p\text{-O}-(\text{CH}_2)(\text{C}_2\text{HN}_3)(\text{CH}_2)-m-(\text{Ph}(\text{C}_6\text{F}_5)_2\text{corrole})\text{Cu}$ (**15**) in acetonitrile, 500 mV/s.

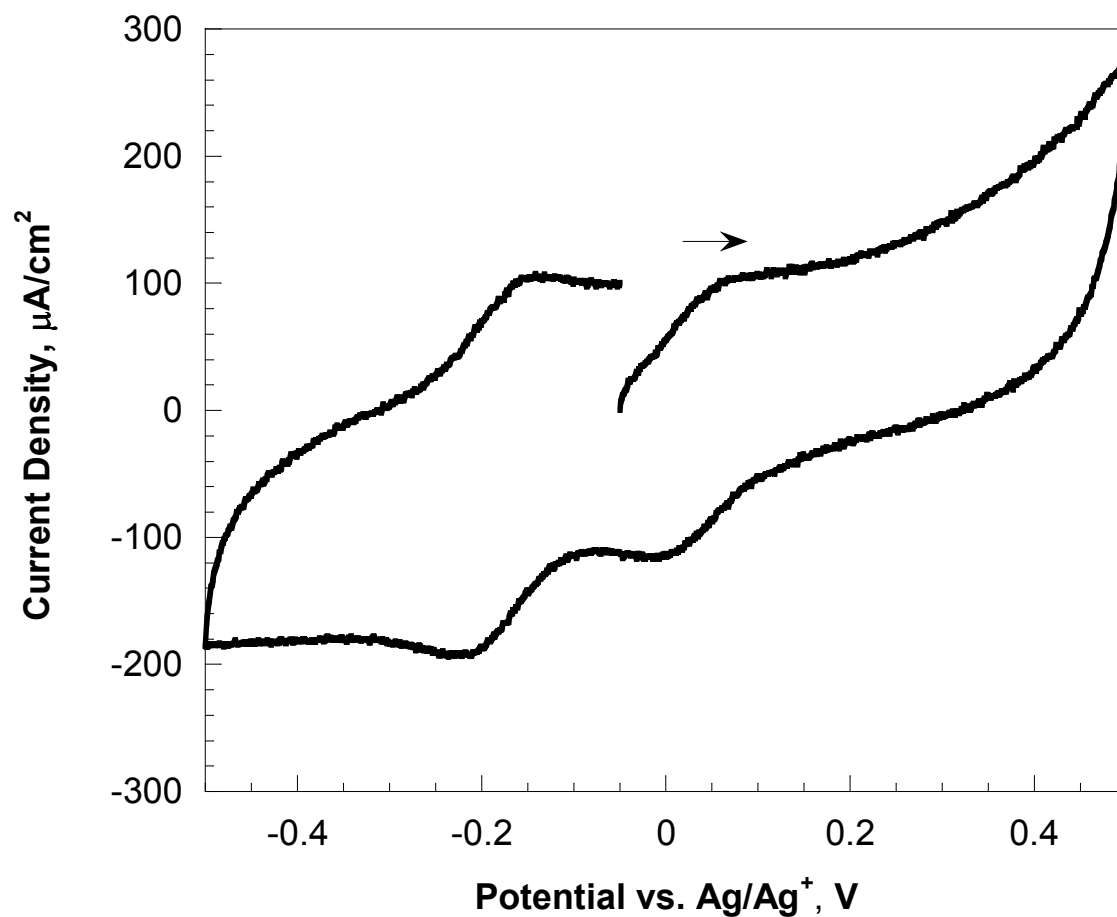


Figure S7. Cyclic voltammogram of <1 mM $\text{Fe}(\text{CH}_3\text{CN})_2(\text{corrole}((\text{C}_6\text{F}_5)_2(\text{Ph}))-p\text{-O}-(\text{CH}_2)(\text{C}_2\text{HN}_3)(\text{CH}_2)-m-(\text{Ph}(\text{C}_6\text{F}_5)_2\text{corrole})\text{Cu}$ (**15**) in acetonitrile, focus on Cu and Fe peaks, 500 mV/s.

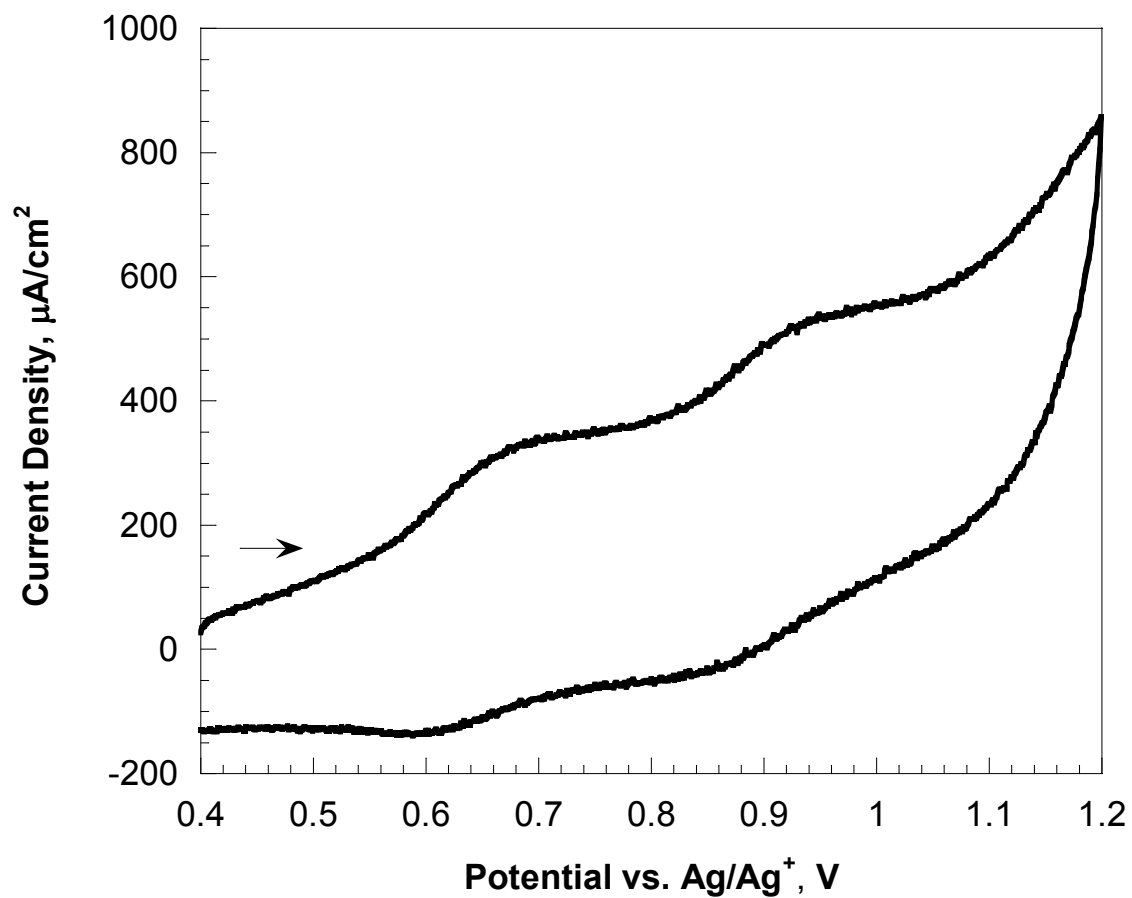


Figure S8. Cyclic voltammogram of <1 mM $\text{Fe}(\text{CH}_3\text{CN})_2(\text{corrole}((\text{C}_6\text{F}_5)_2(\text{Ph}))-p\text{-O}-(\text{CH}_2)(\text{C}_2\text{HN}_3)(\text{CH}_2)-m-(\text{Ph}(\text{C}_6\text{F}_5)_2\text{corrole})\text{Cu}$ (**15**) in acetonitrile, focus on ligand oxidation, 500 mV/s.

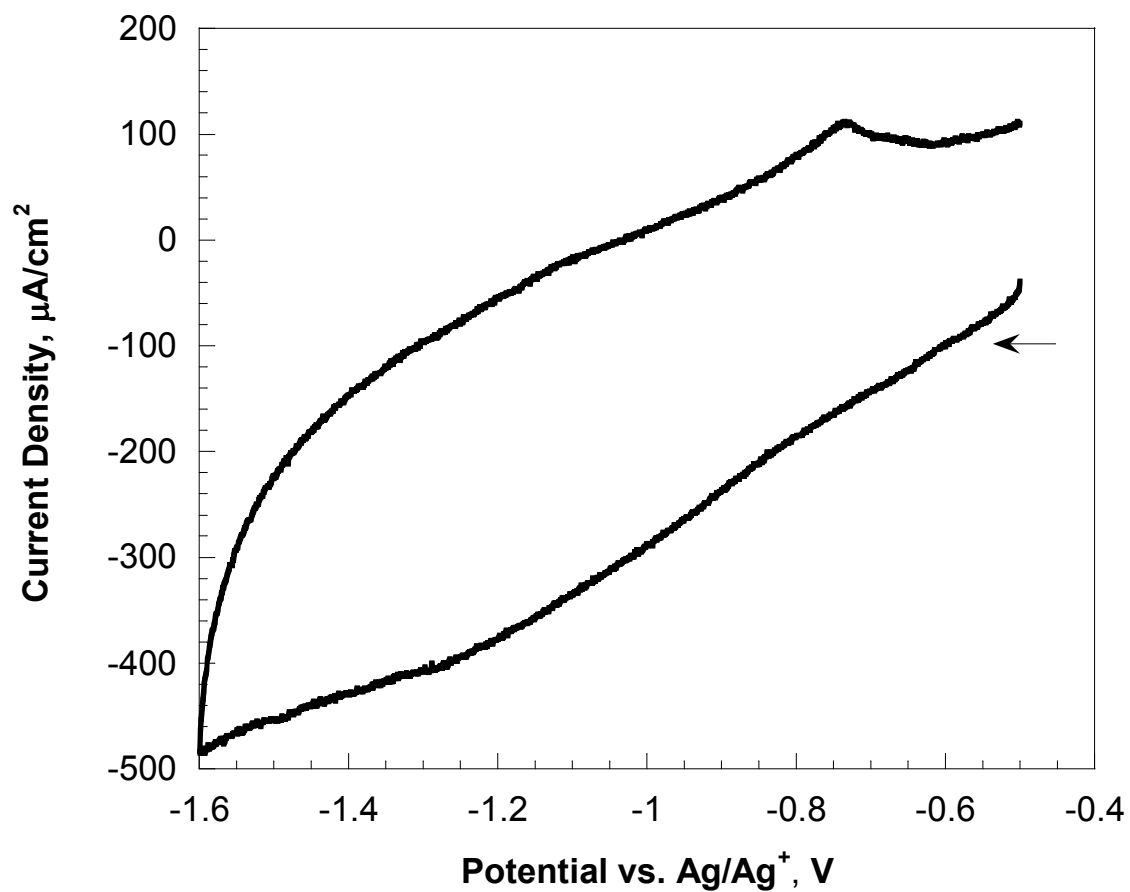


Figure S9. Cyclic voltammogram of <1 mM $\text{Fe}(\text{CH}_3\text{CN})_2(\text{corrole}((\text{C}_6\text{F}_5)_2(\text{Ph}))\text{-}p\text{-O}-(\text{CH}_2)(\text{C}_2\text{HN}_3)(\text{CH}_2)\text{-}m\text{-}(\text{Ph}(\text{C}_6\text{F}_5)_2\text{corrole})\text{Cu}$ (**15**) in acetonitrile, focus on oxidative adsorption peak, 500 mV/s.

B. NMR Spectroscopy of compounds 1-3, 5-15

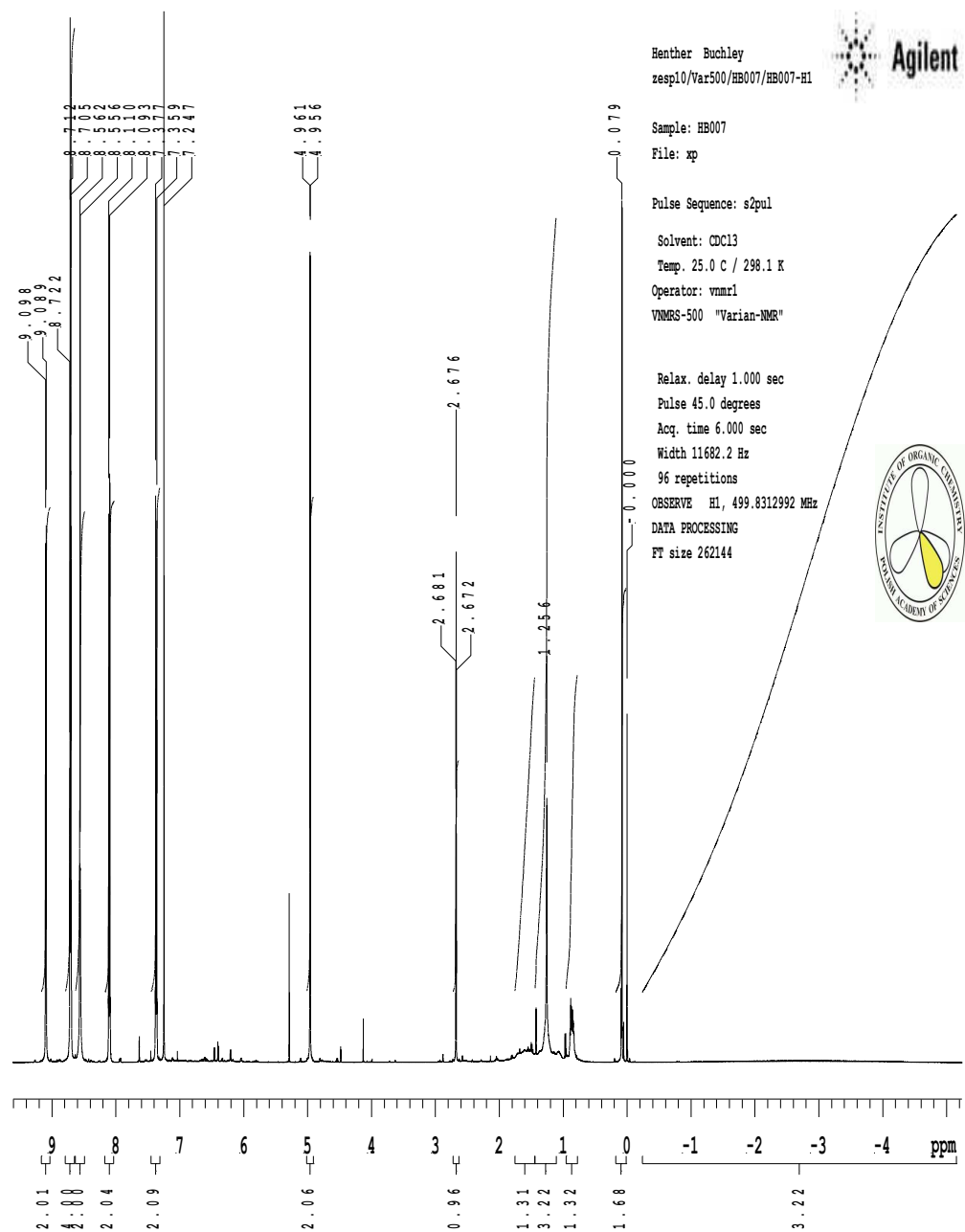


Figure S10. ¹H NMR spectrum of **1** in CDCl₃.

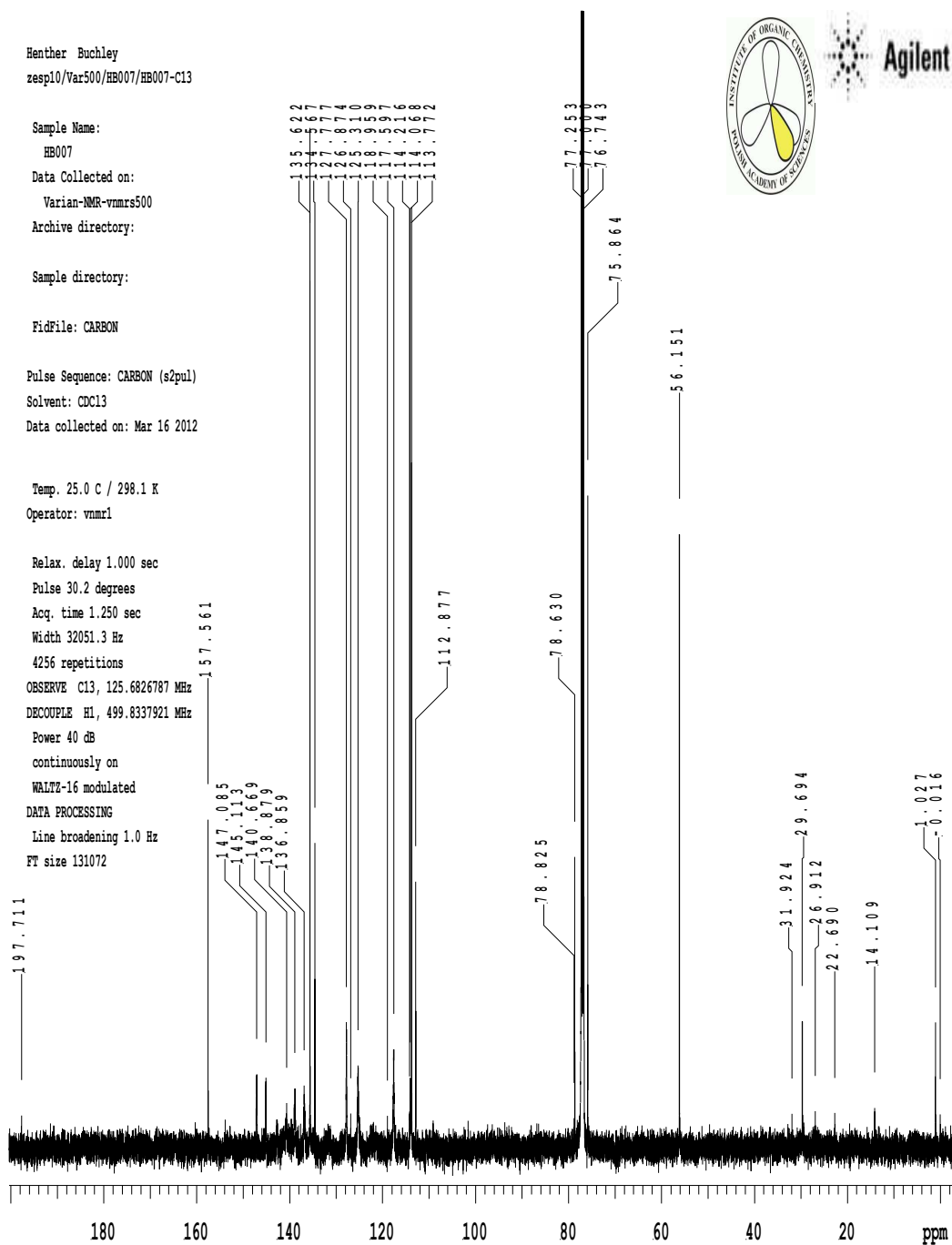


Figure S11. ¹³C NMR spectrum of **1** in CDCl₃.

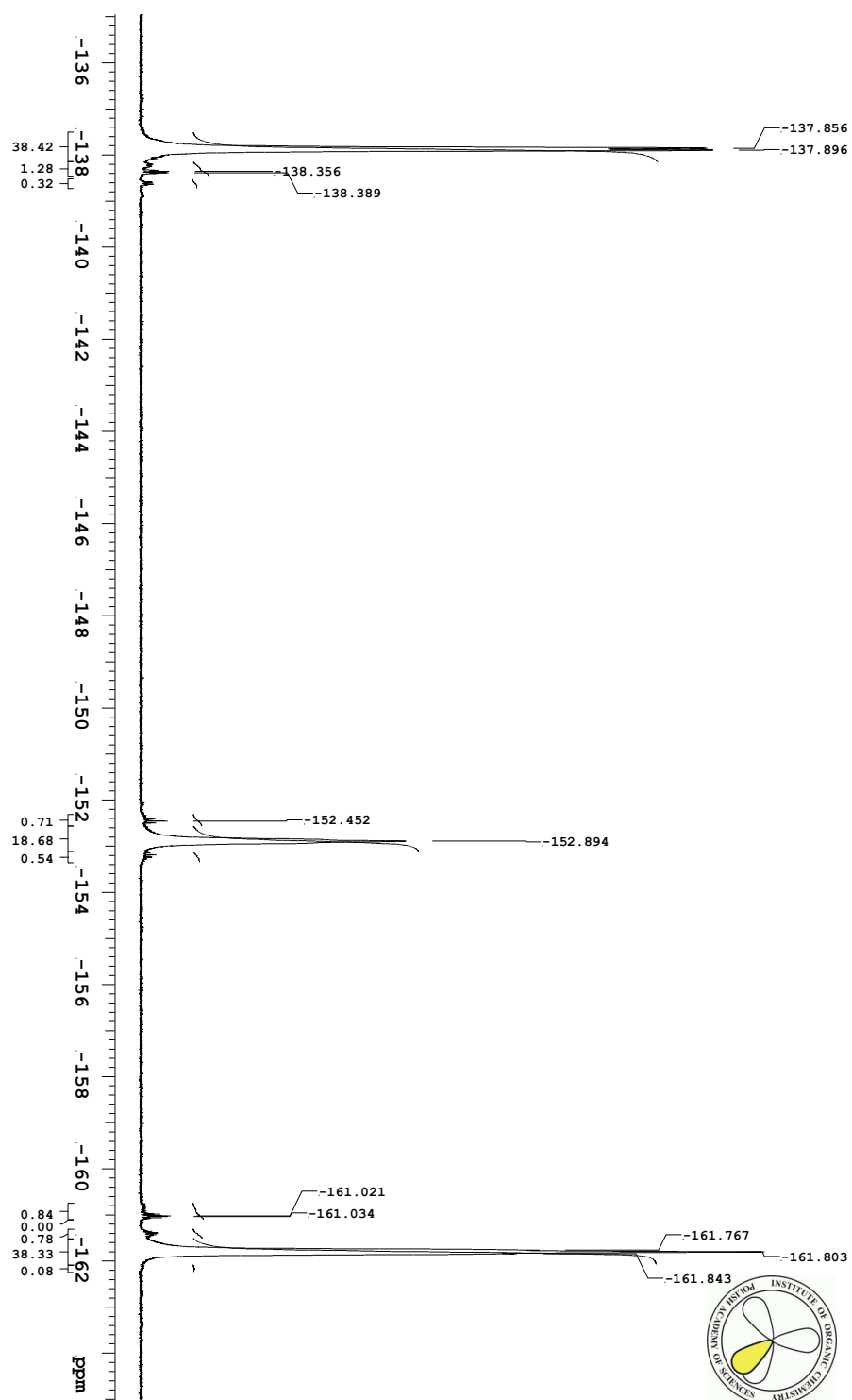


Figure S12. ¹⁹F NMR spectrum of **1** in CDCl₃.

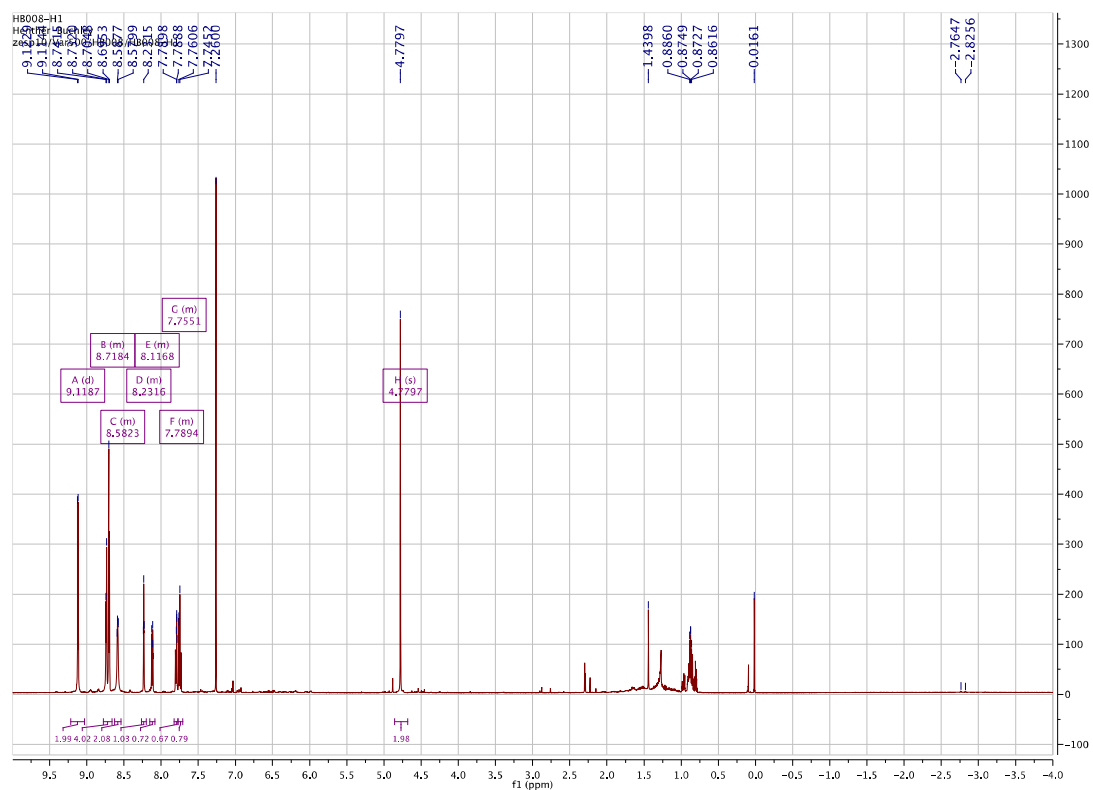
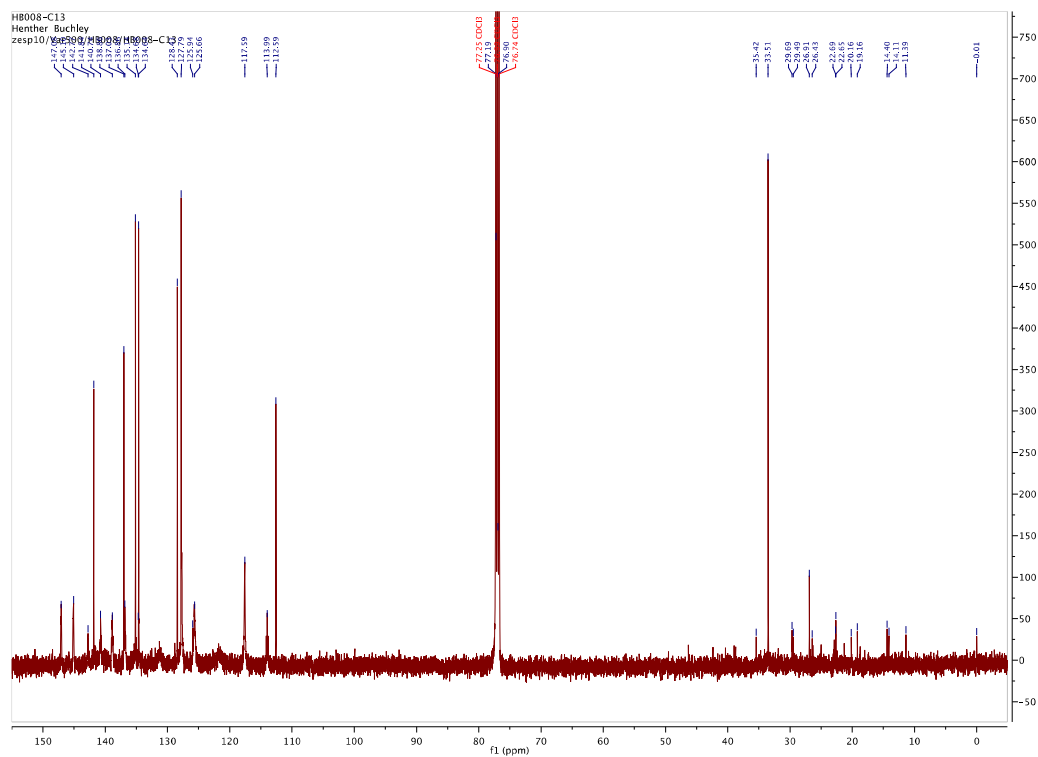


Figure S13. ¹H NMR spectrum of **2** in CDCl₃.



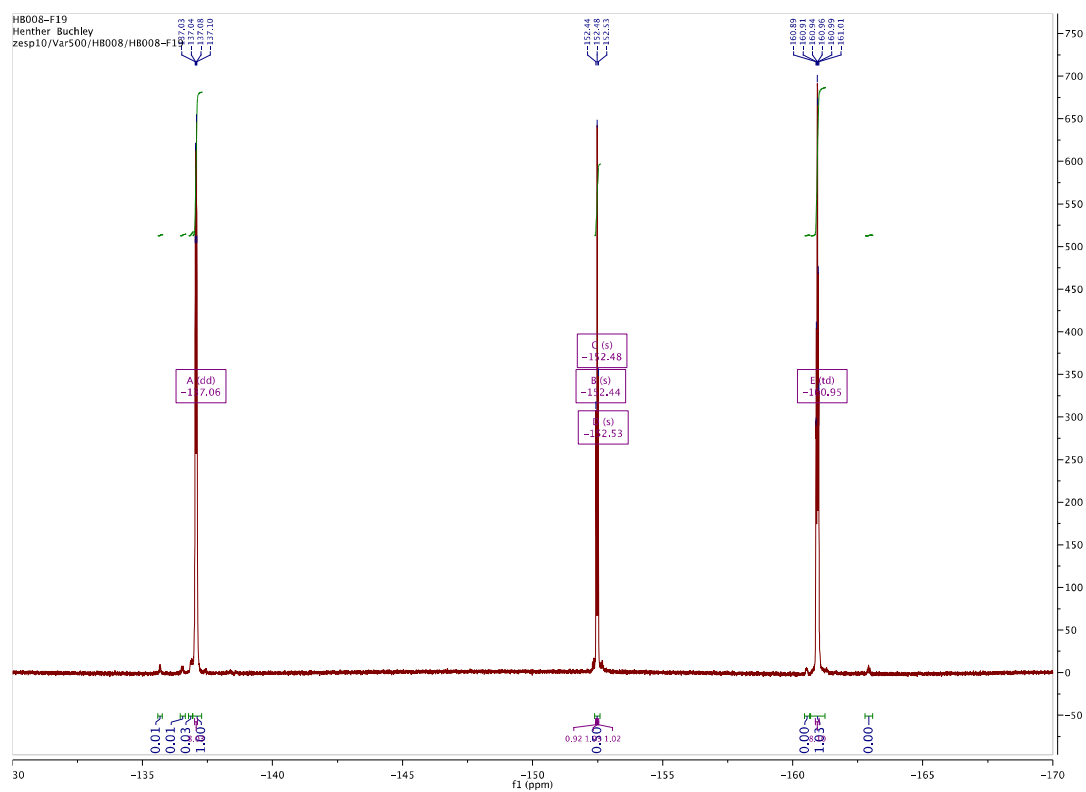


Figure S15. ^{19}F NMR spectrum of **2** in CDCl_3 .

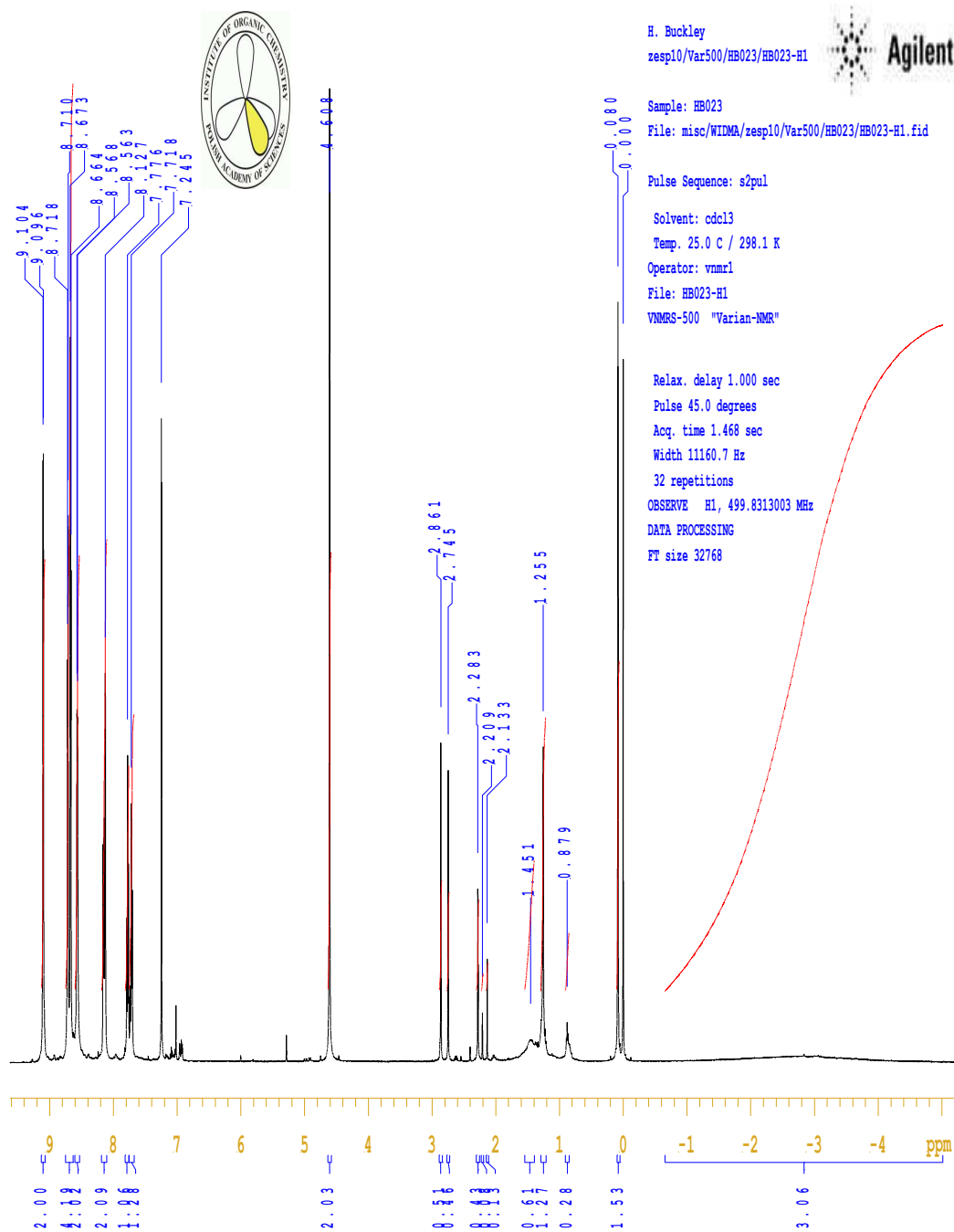


Figure S16. ^1H NMR spectrum of **3** in CDCl_3 .

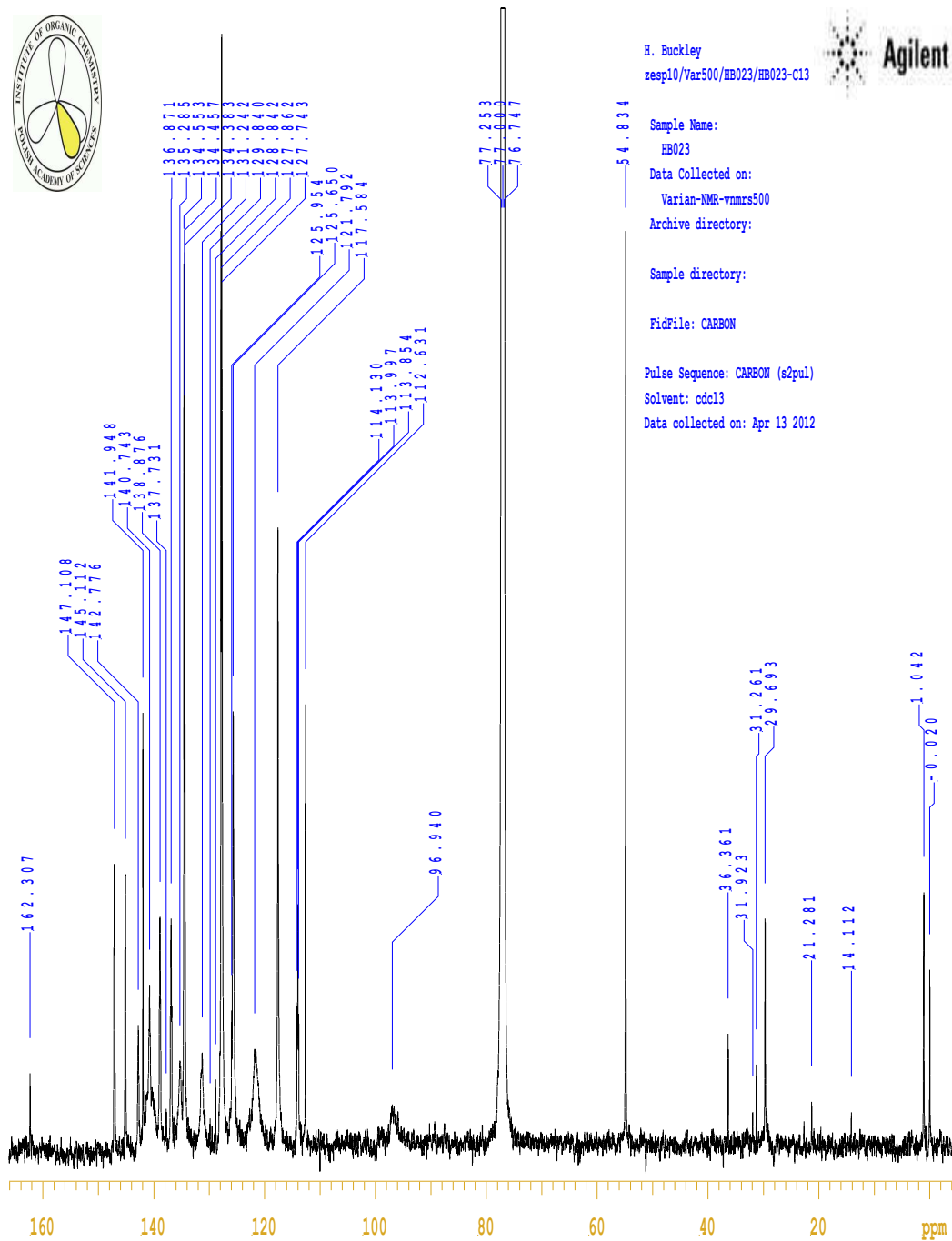


Figure S17. ^{13}C NMR spectrum of **3** in CDCl_3 .



H. Buckley
zespl0/Var500/HB023/HB023-F19
zespl0/Var500/HB023/HB023-F19



Sample Name:
302-148-19-01
Data Collected on:
Varian-NMR-vnmrs500
Archive directory:

Sample directory:

FidFile: FLUORINE

Pulse Sequence: FLUORINE (s2pul)
Solvent: dmsd
Data collected on: Apr 13 2012

Temp. 25.0 C / 298.1 K
Operator: vnmr1

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.524 sec
Width 15625.0 Hz
128 repetitions
OBSERVE F19, 470.3135458 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 16384

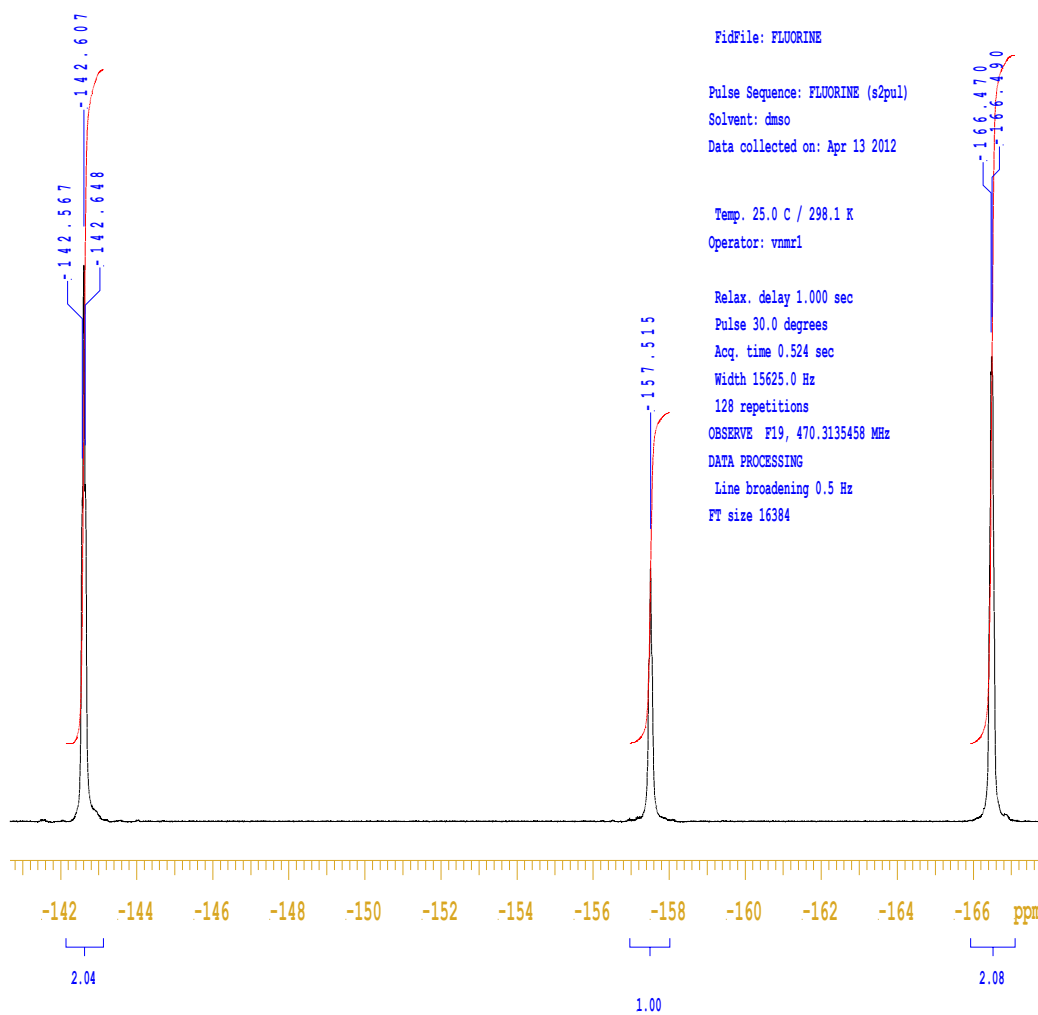
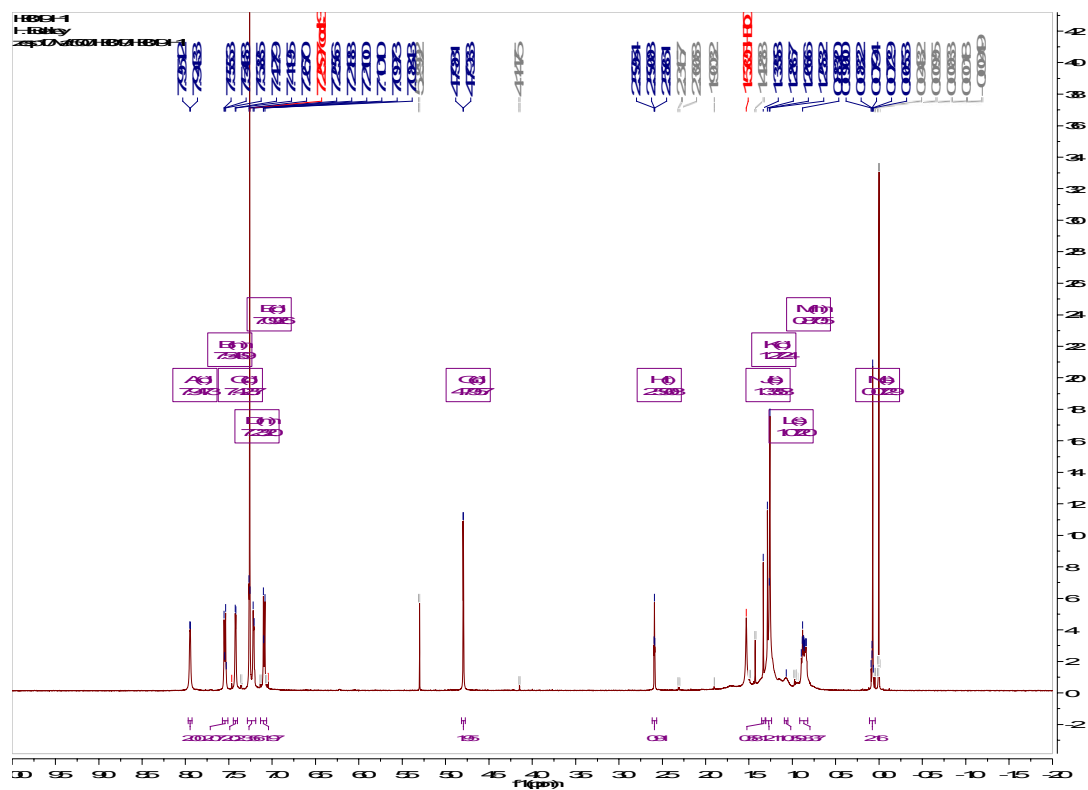


Figure S18. ^{19}F NMR spectrum of **3** in CDCl_3 .



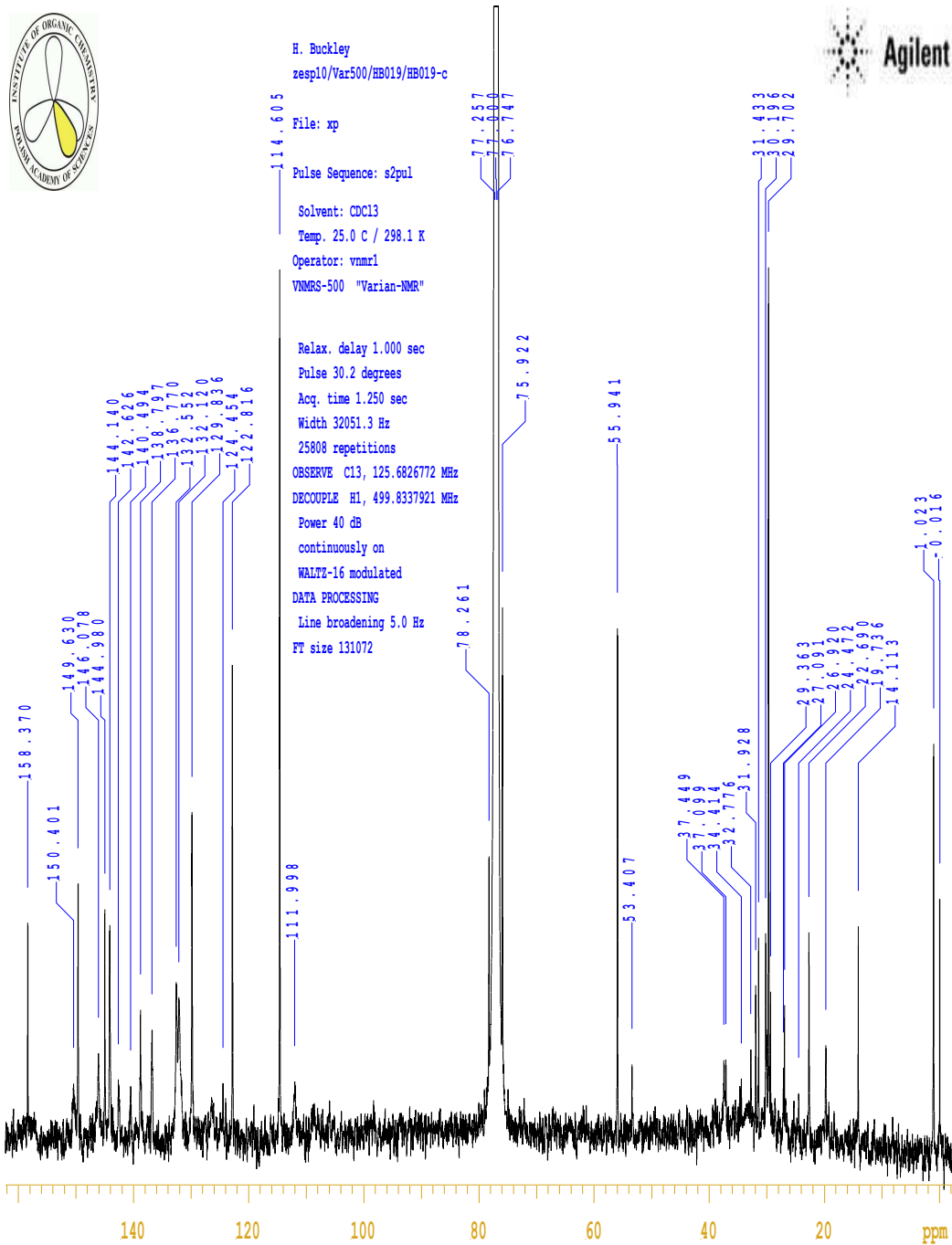


Figure S20. ^{13}C NMR spectrum of **5** in CDCl_3 .

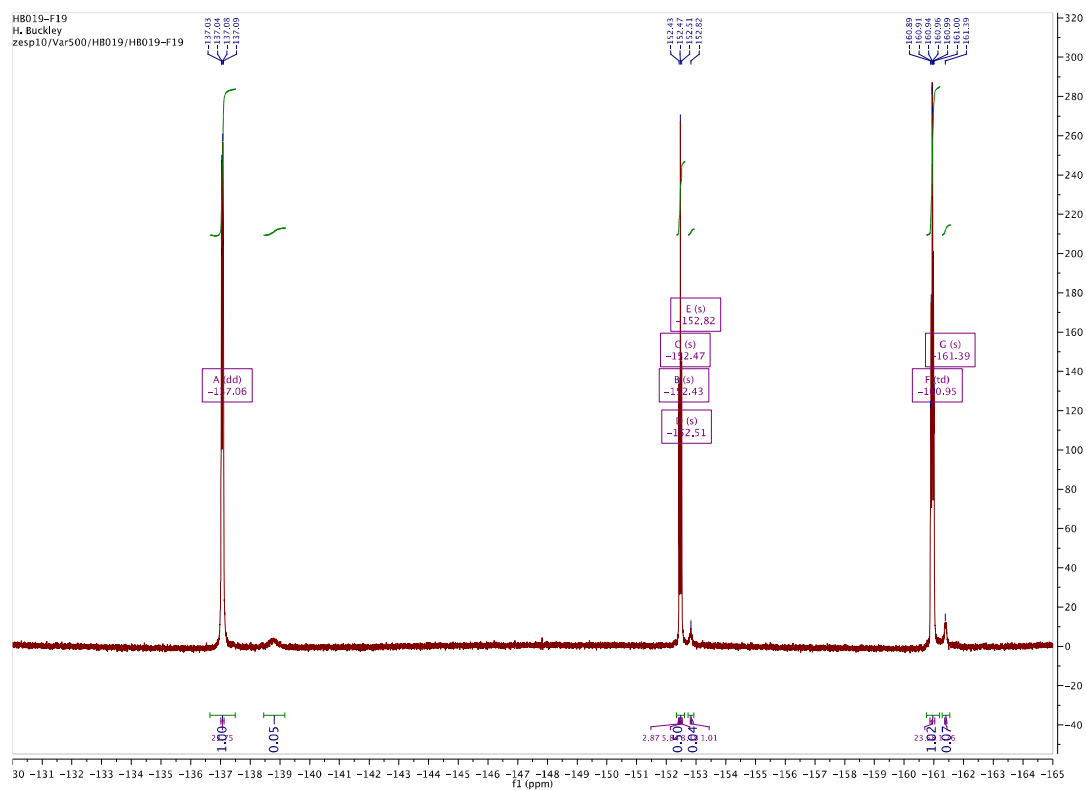


Figure S21. ^{19}F NMR spectrum of **5** in CDCl_3 .

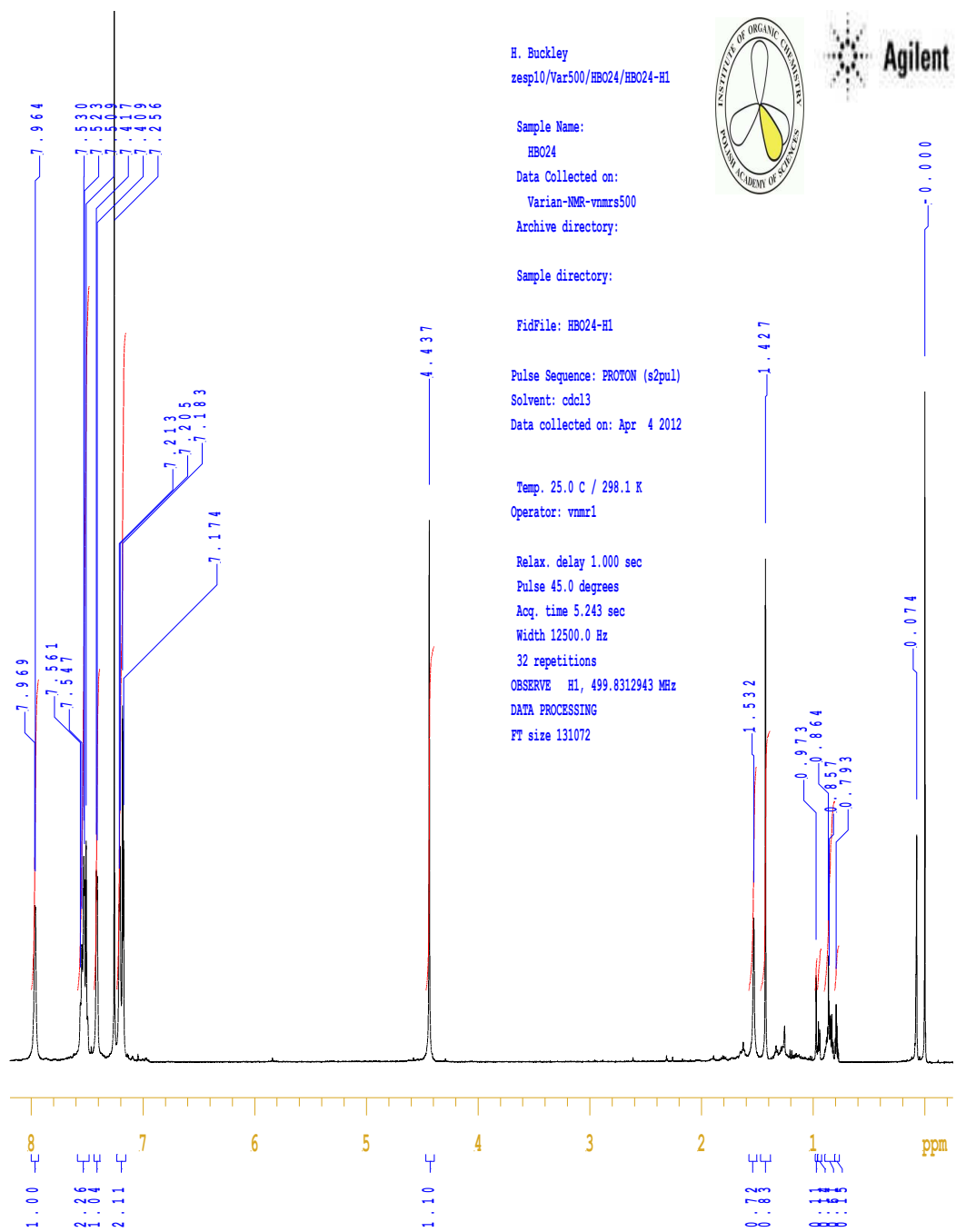


Figure S22. ^1H NMR spectrum of **6** in CDCl_3 .

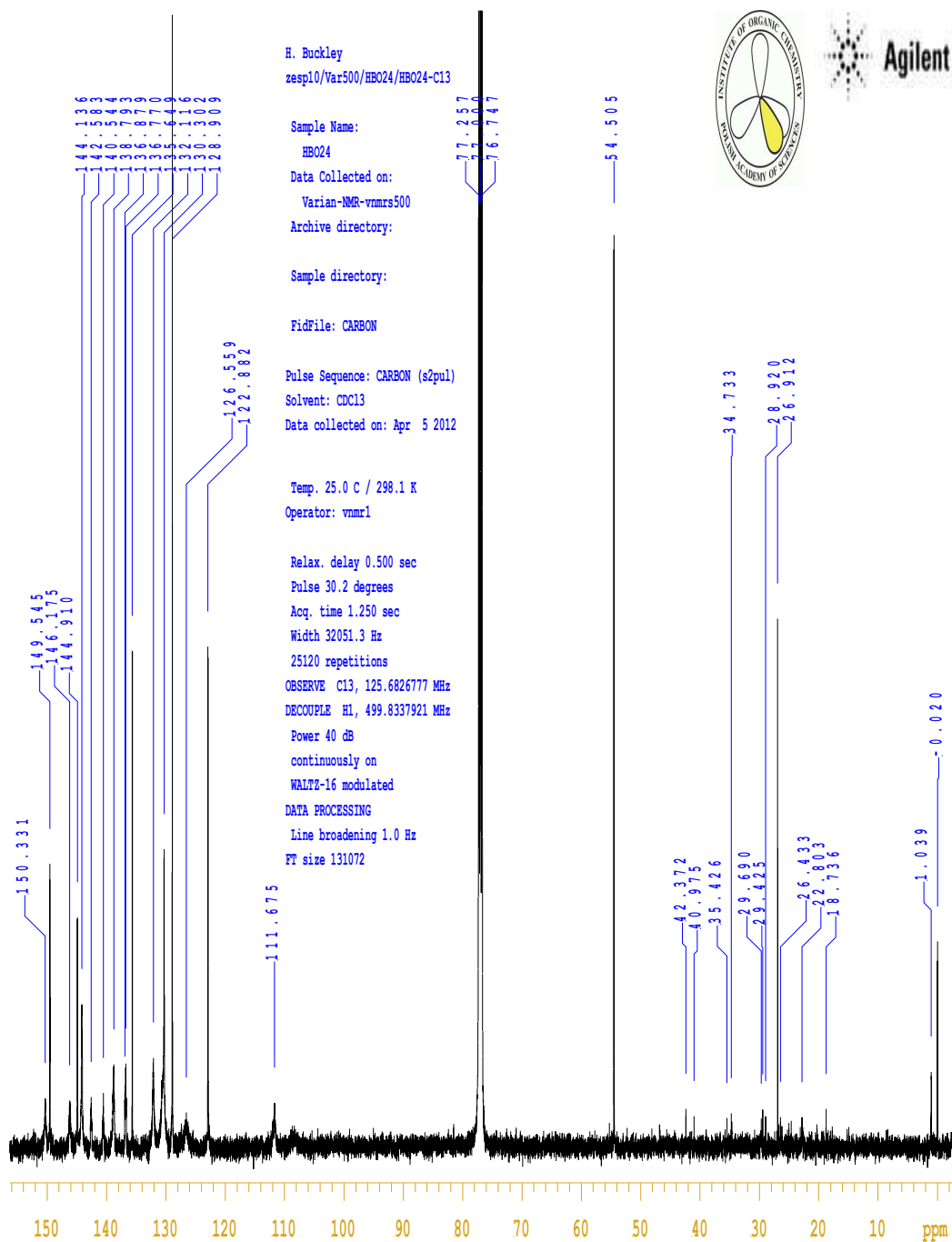


Figure S23. ^{13}C NMR spectrum of **6** in CDCl_3 .

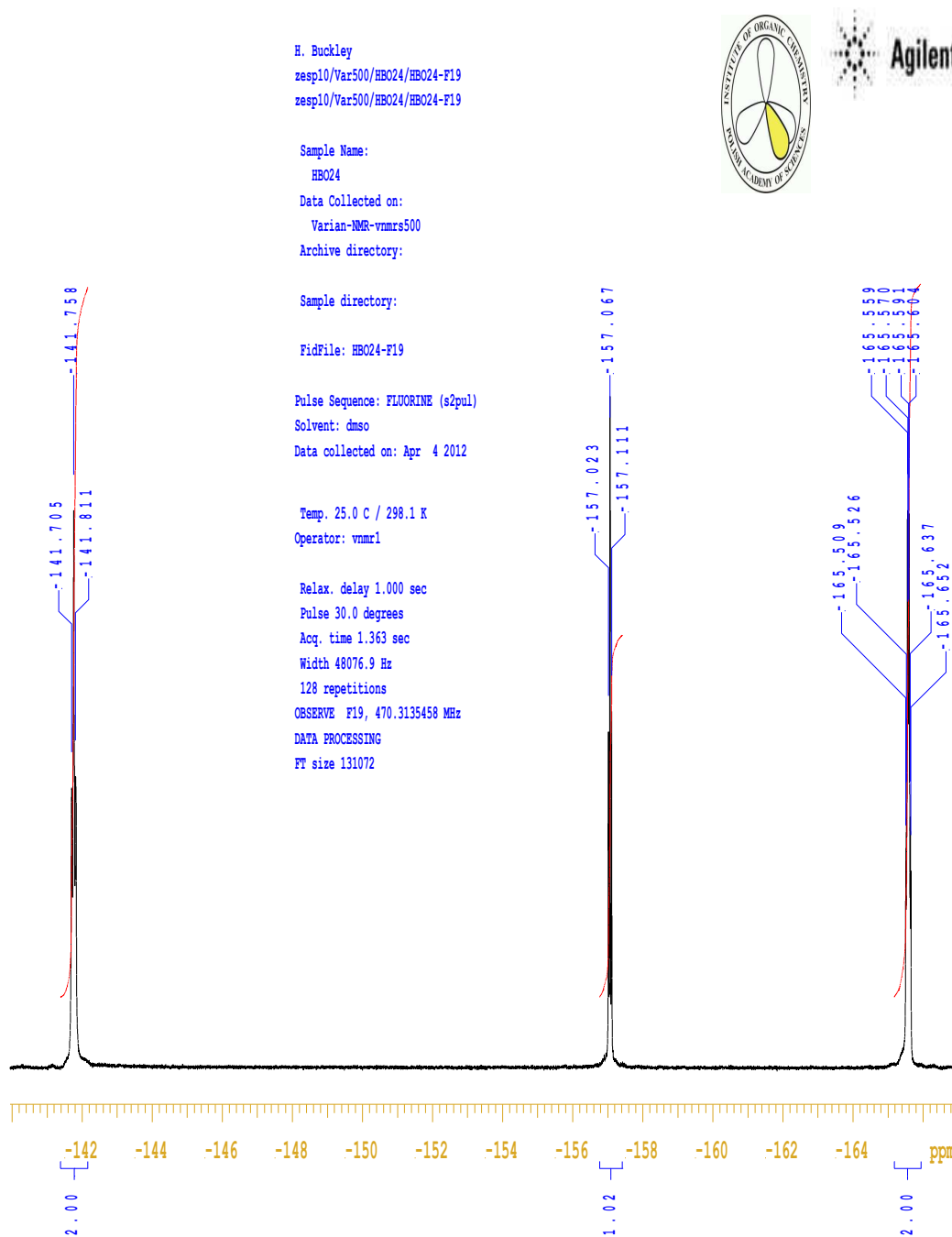


Figure S24. ^{19}F NMR spectrum of **6** in CDCl_3 .

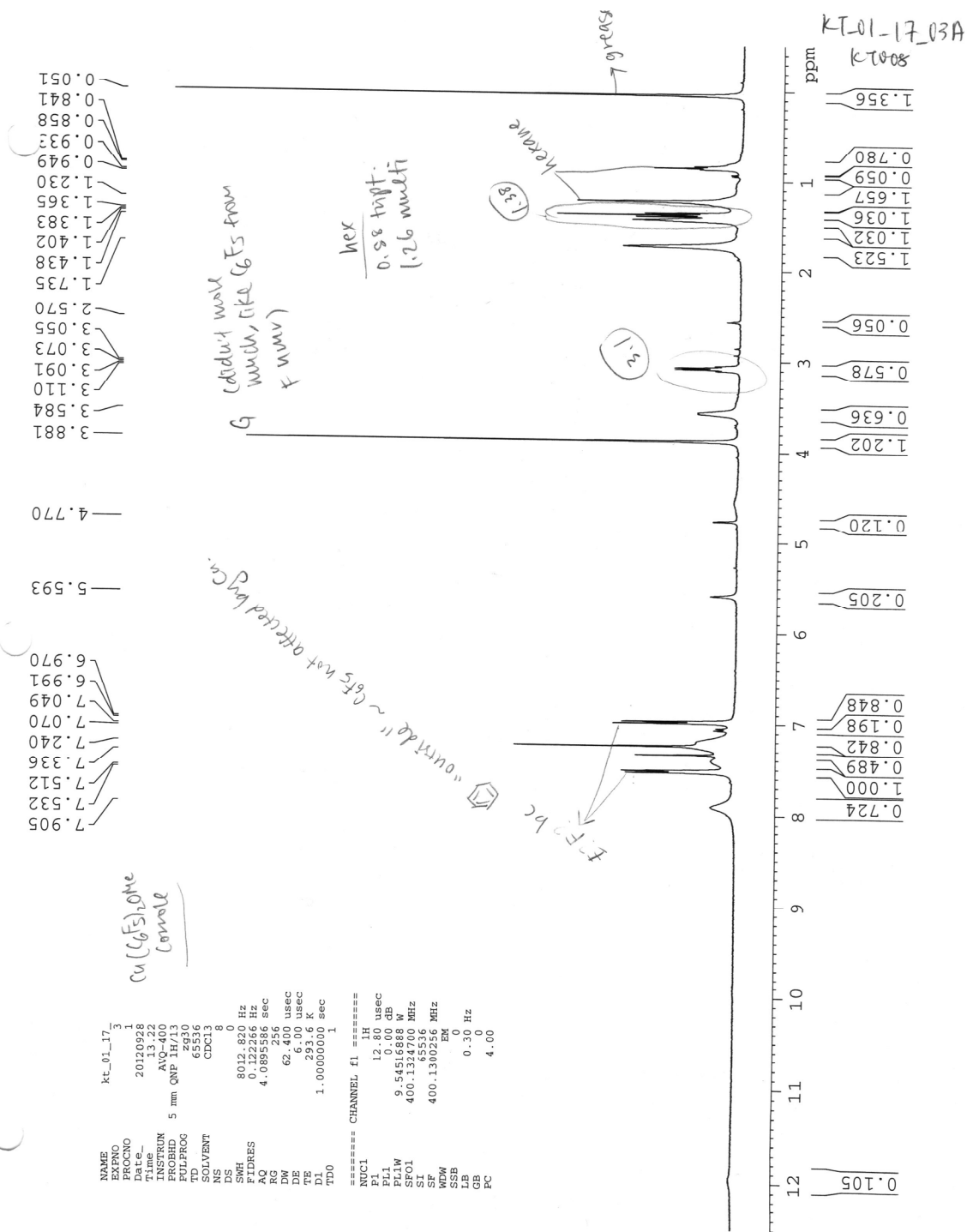
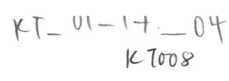


Figure S25. ¹H NMR spectrum of **7** in CDCl₃.



28

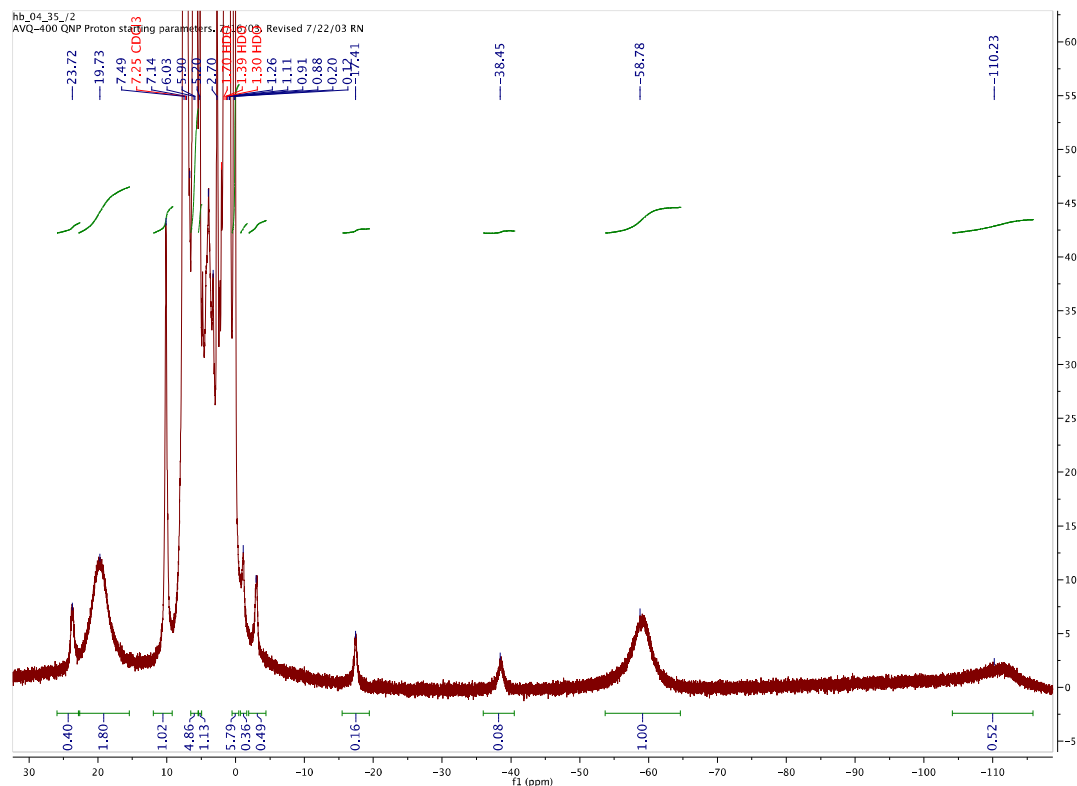


Figure S27. ^1H NMR spectrum of **8** in C_6D_6 (broad window).

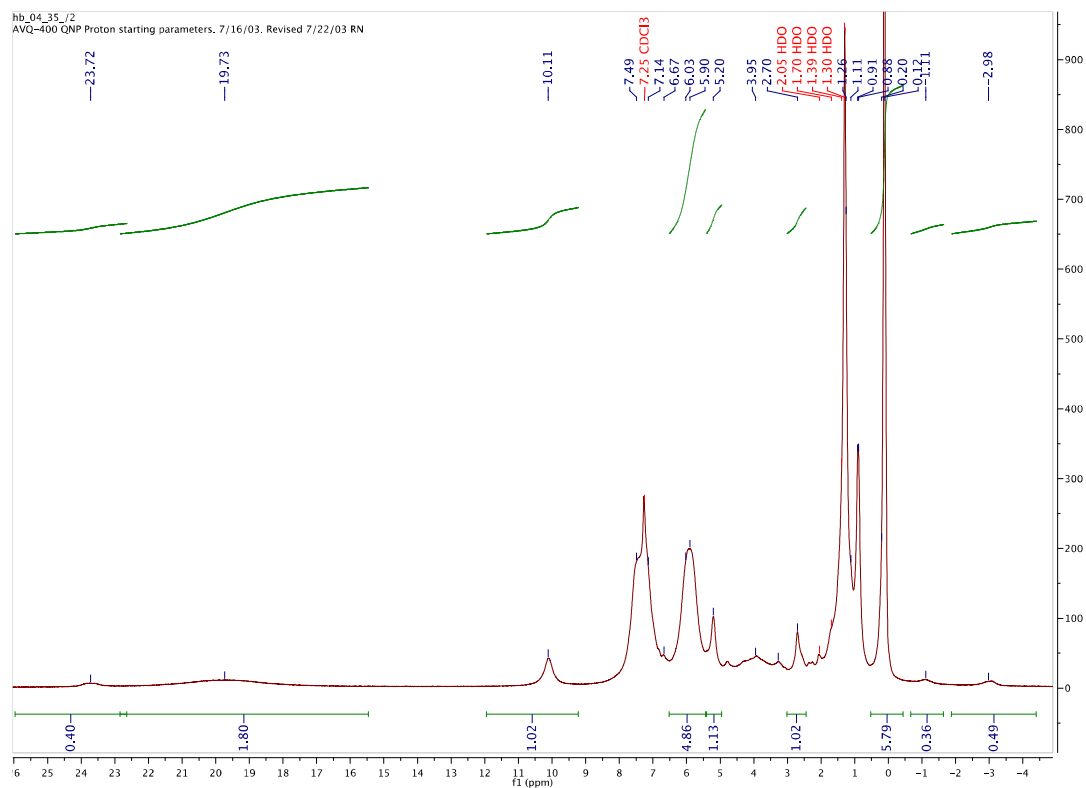


Figure S28. ^1H NMR spectrum of **8** in C_6D_6 (narrow window).

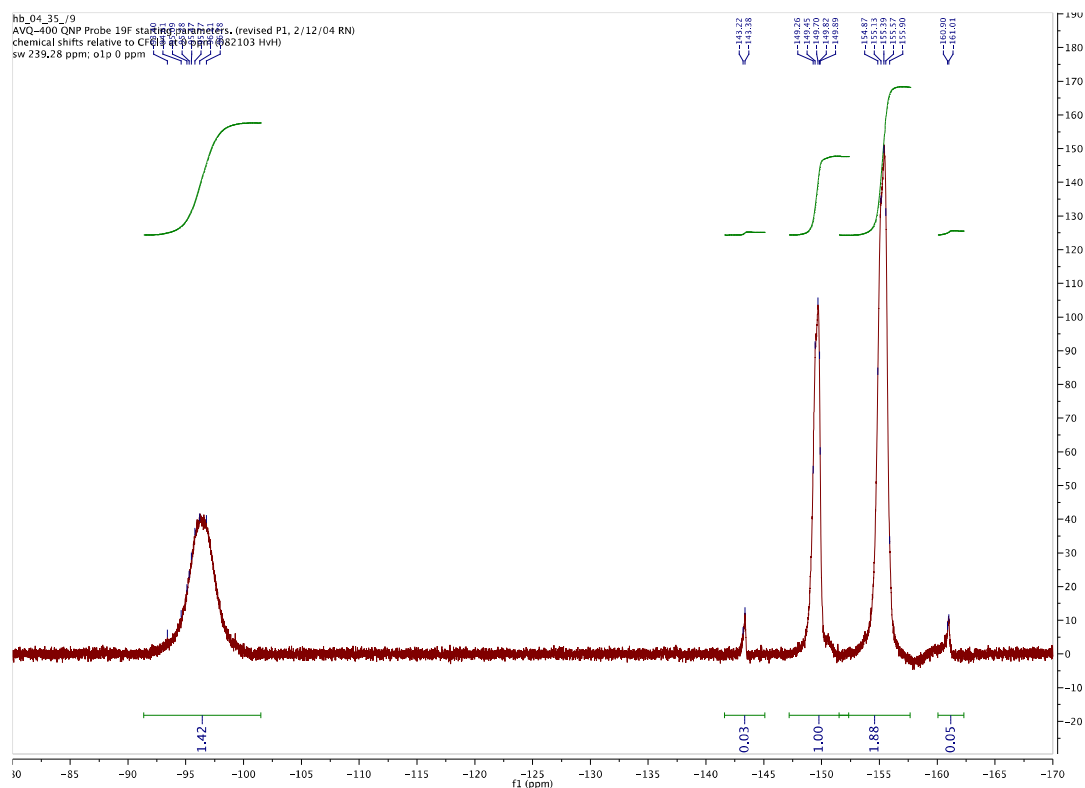


Figure S29. ^{19}F NMR spectrum of **8** in C_6D_6 .

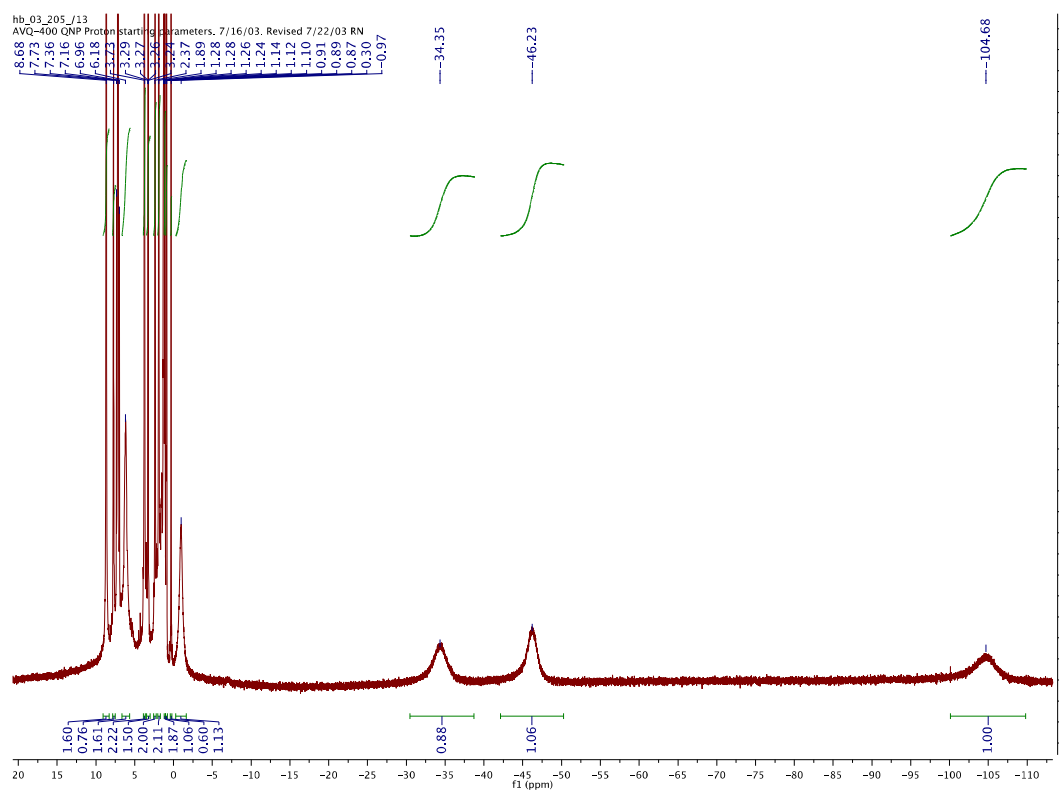


Figure S30. ^1H NMR spectrum of **9** in C_6D_6 (broad window)

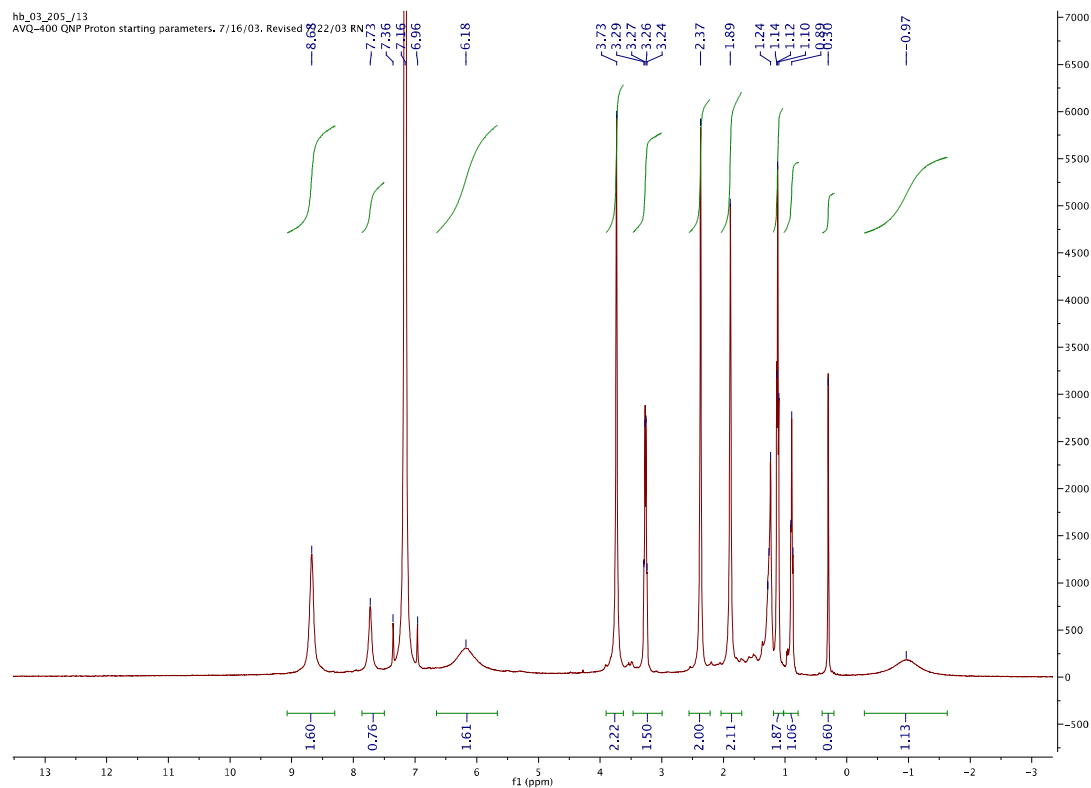


Figure S31. ^1H NMR spectrum of **9** in C_6D_6 (narrow window).

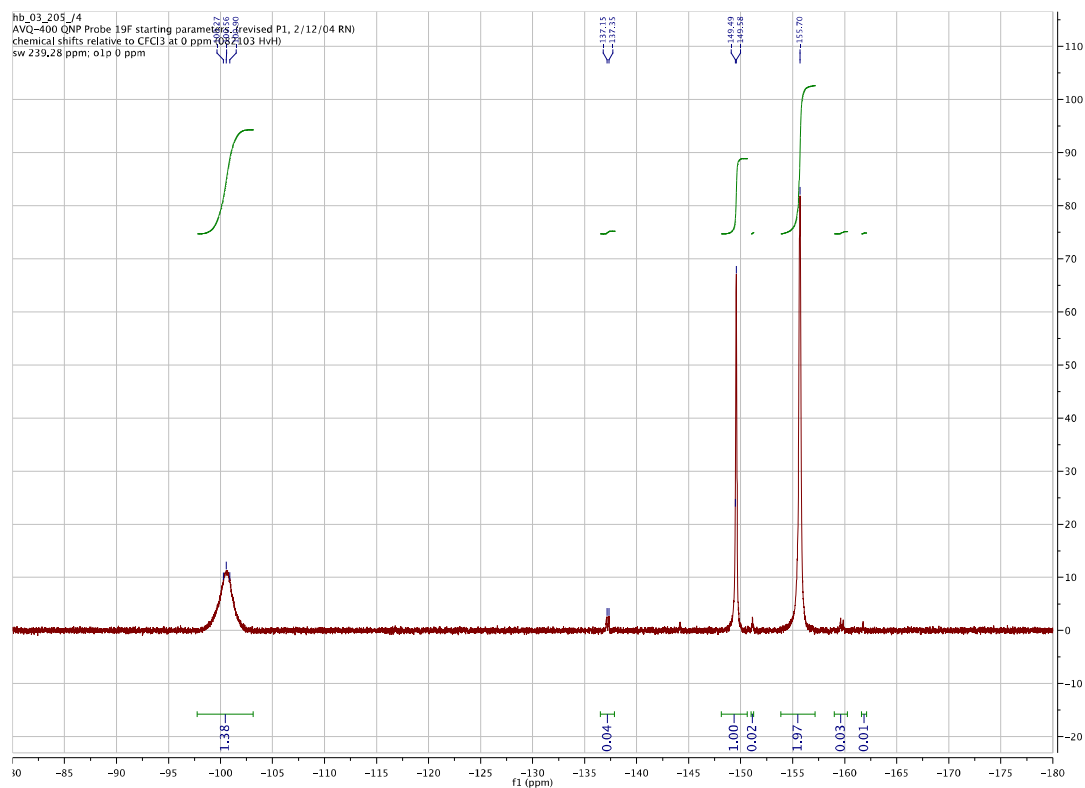


Figure S32. ^{19}F NMR spectrum of **9** in C_6D_6 .

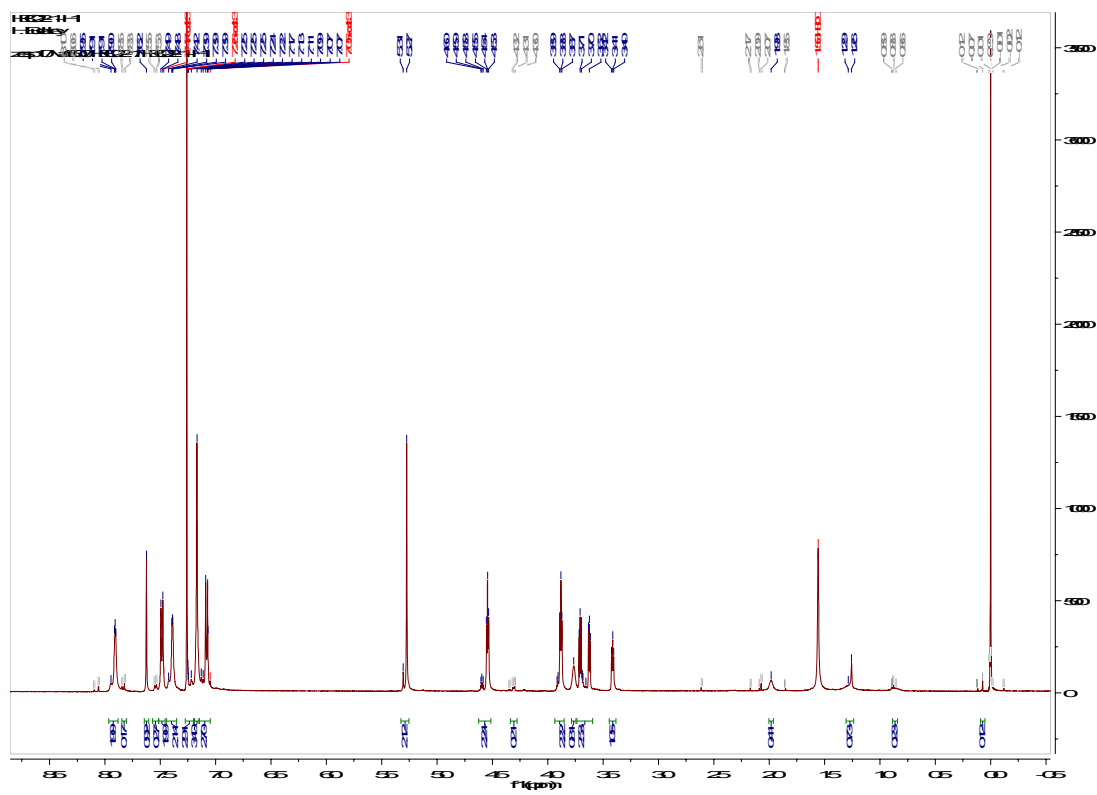


Figure S33. ^1H NMR spectrum of **10** in CDCl_3 .

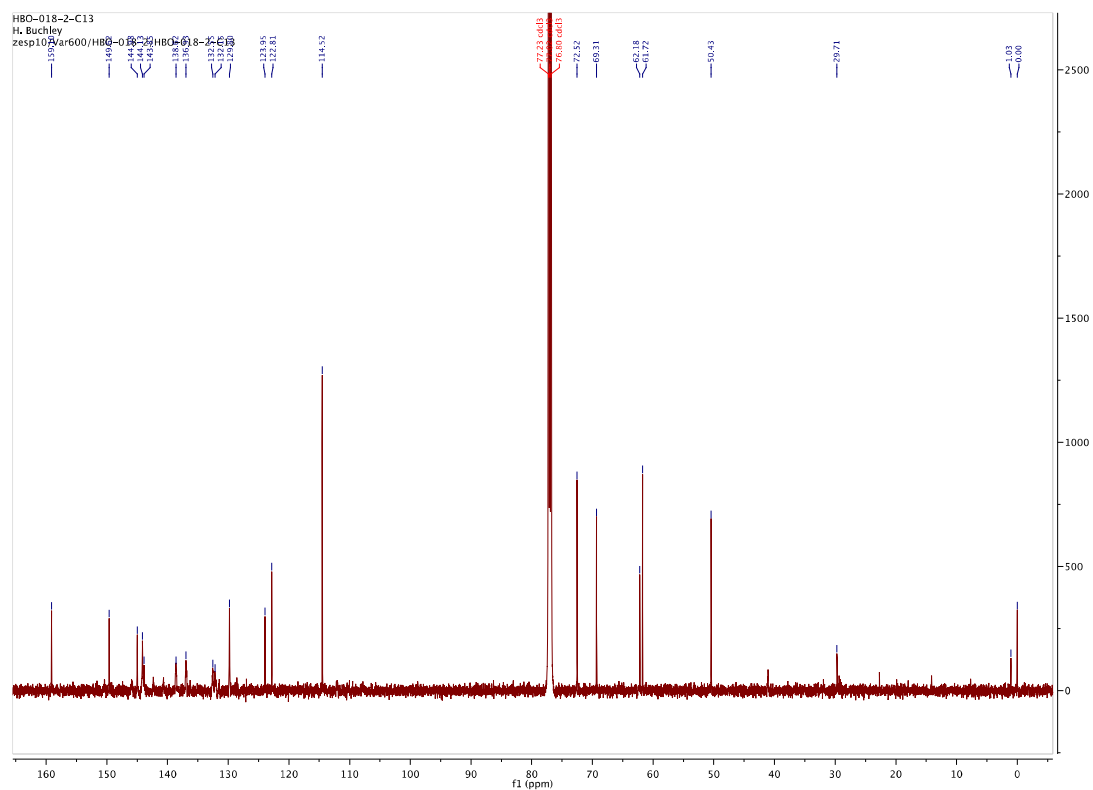


Figure S34. ^{13}C NMR spectrum of **10** in CDCl_3 .

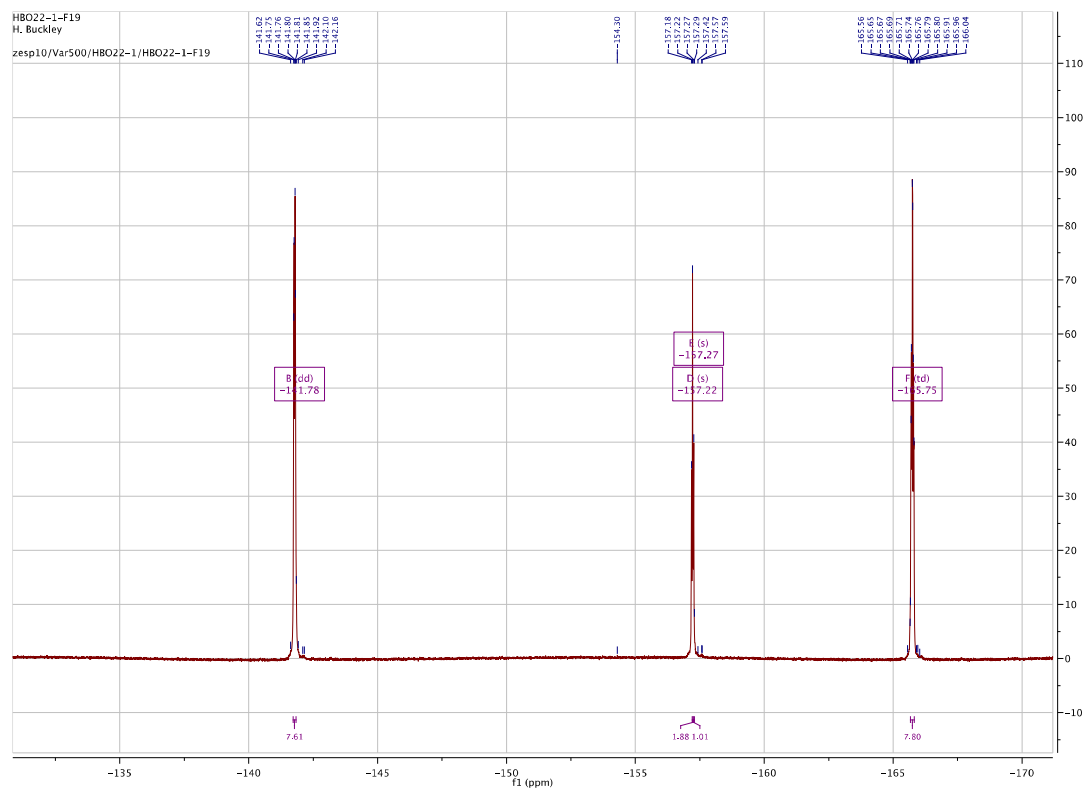


Figure S35. ^{19}F NMR spectrum of **10** in CDCl_3 .

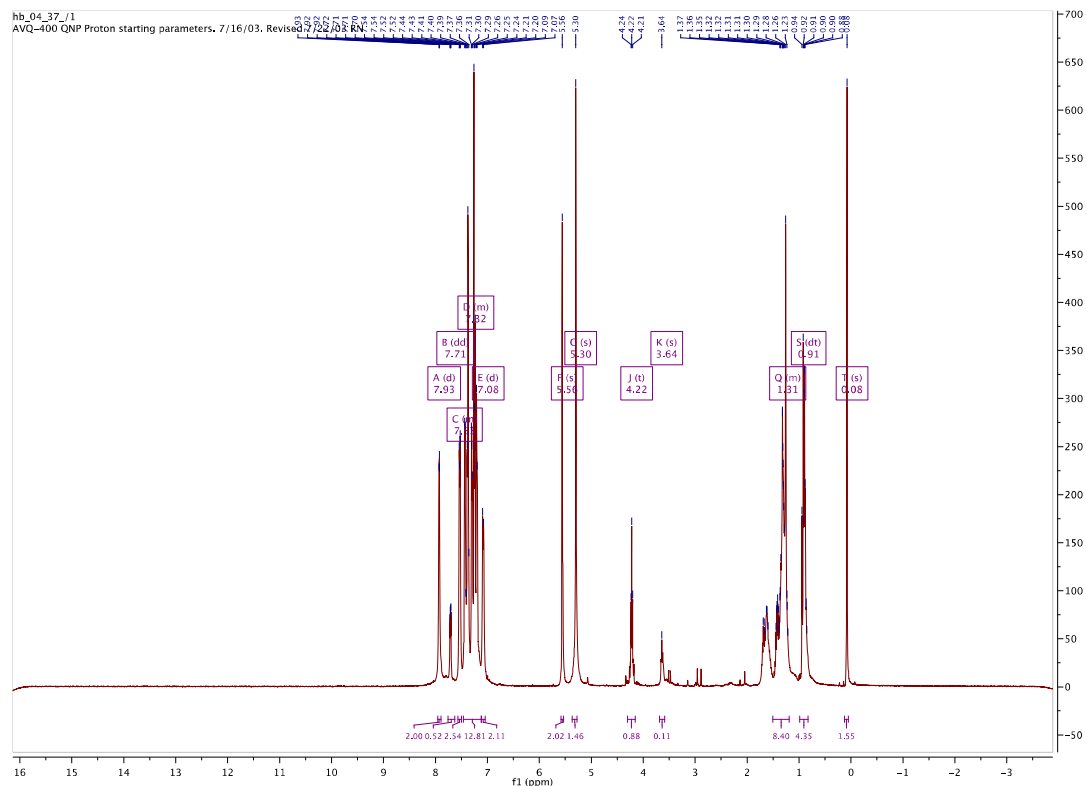


Figure S36. ^1H NMR spectrum of **11** in CDCl_3 .

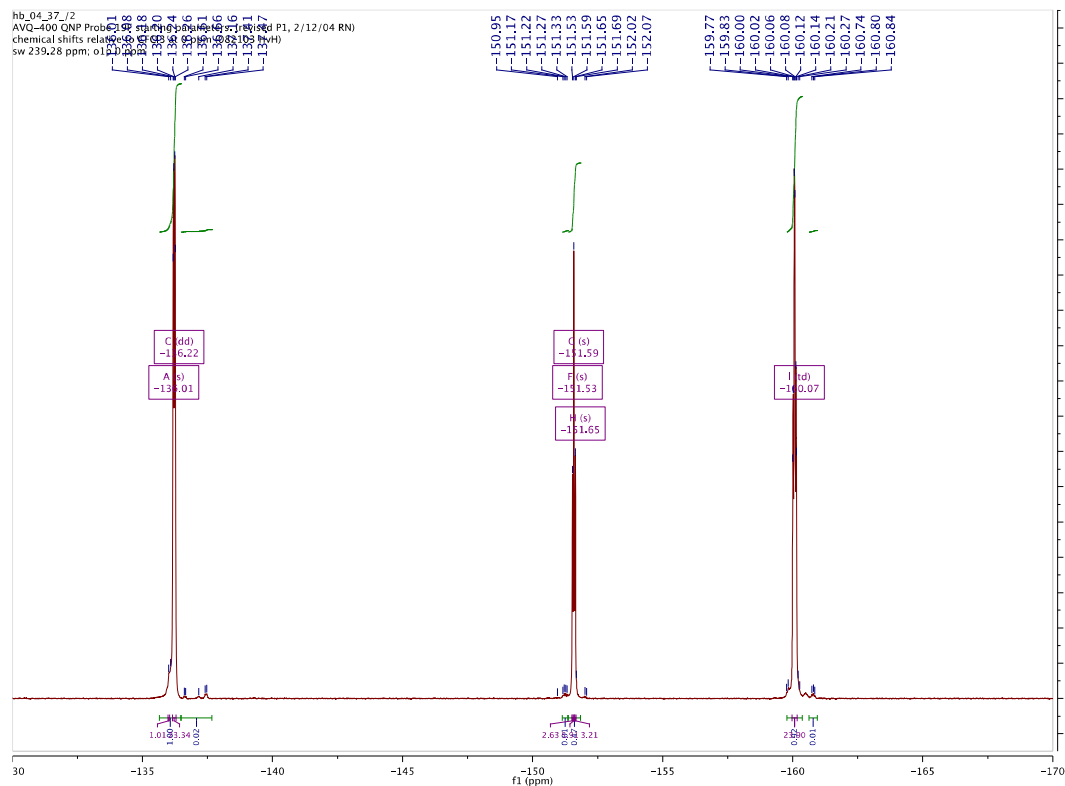


Figure S37. ^{19}F NMR spectrum of **11** in CDCl_3 .

NO FIGURE. DATA IS MISSING. WE APOLOGIZE FOR THE INCONVENIENCE

Figure S38. ^1H NMR spectrum of **12**.

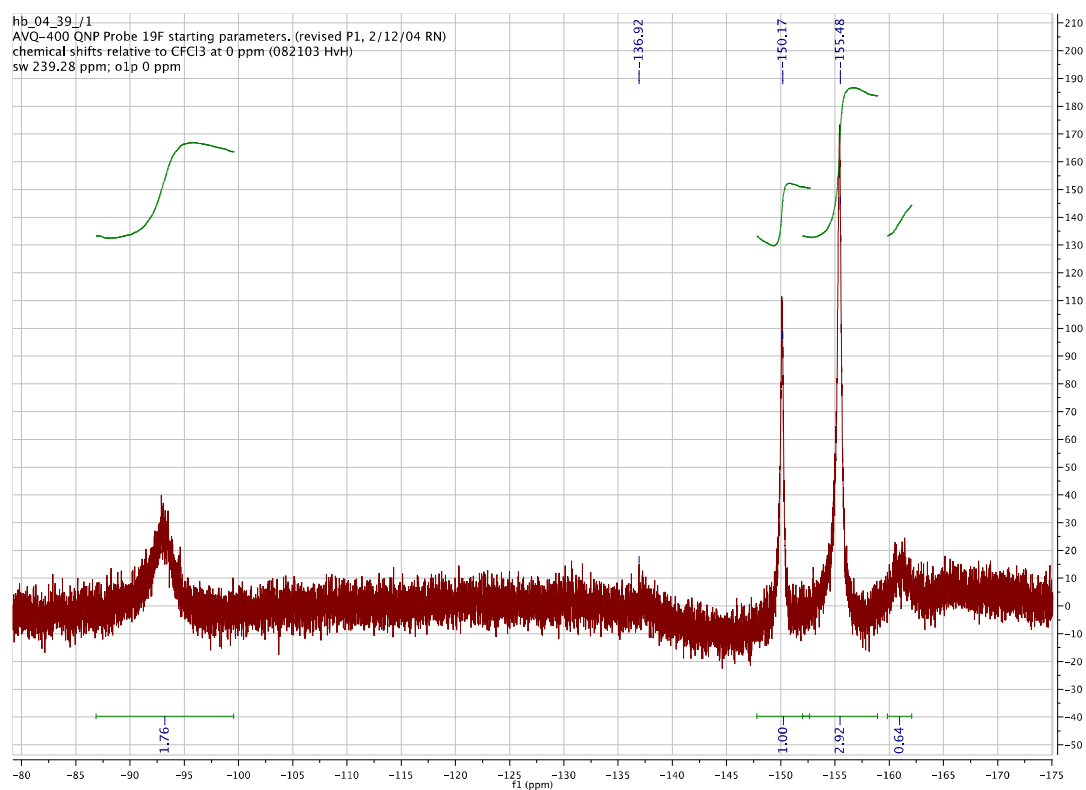


Figure S39. ^{19}F NMR spectrum of **12** in C_6D_6 .

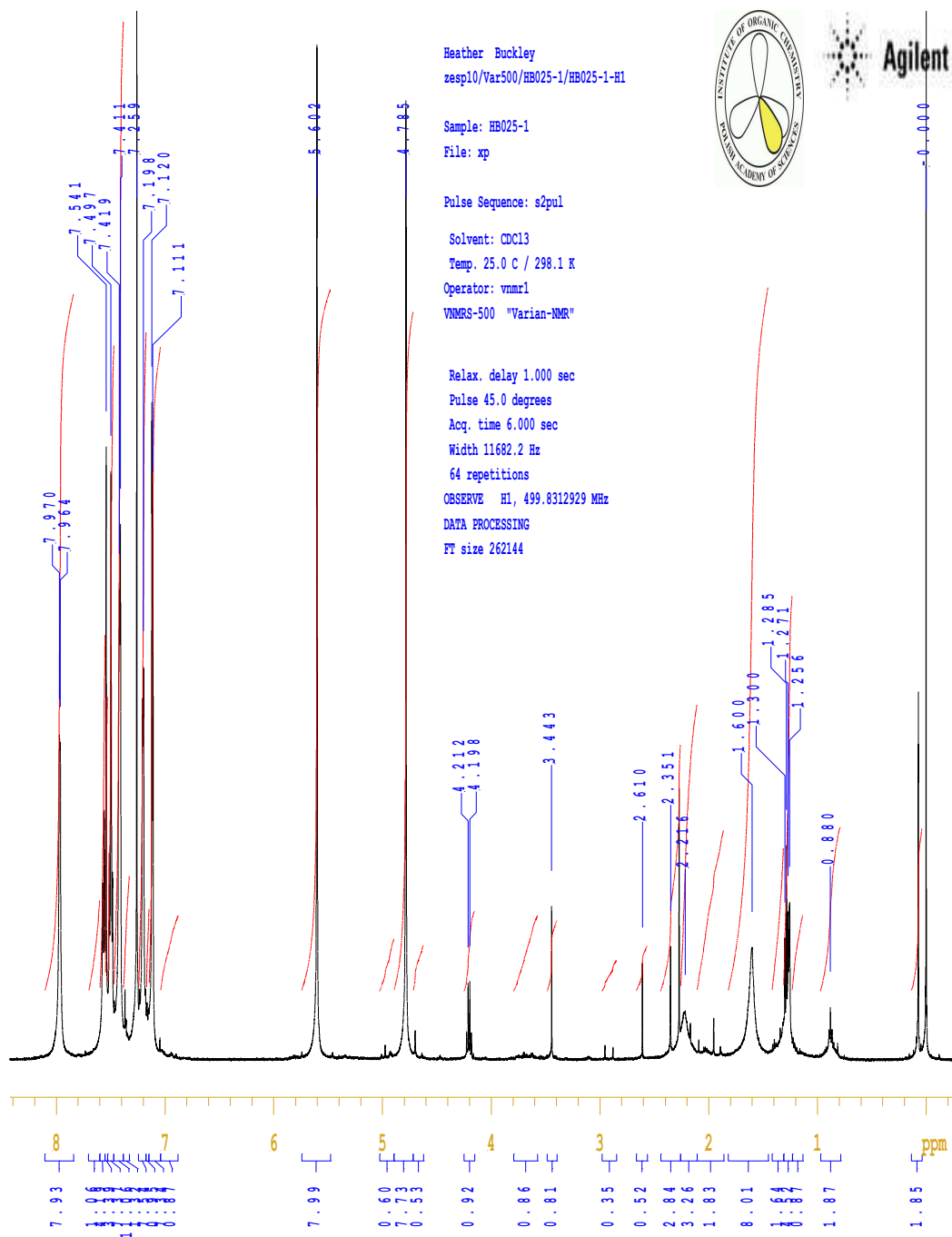


Figure S40. ^1H NMR spectrum of **13** in CDCl_3 .

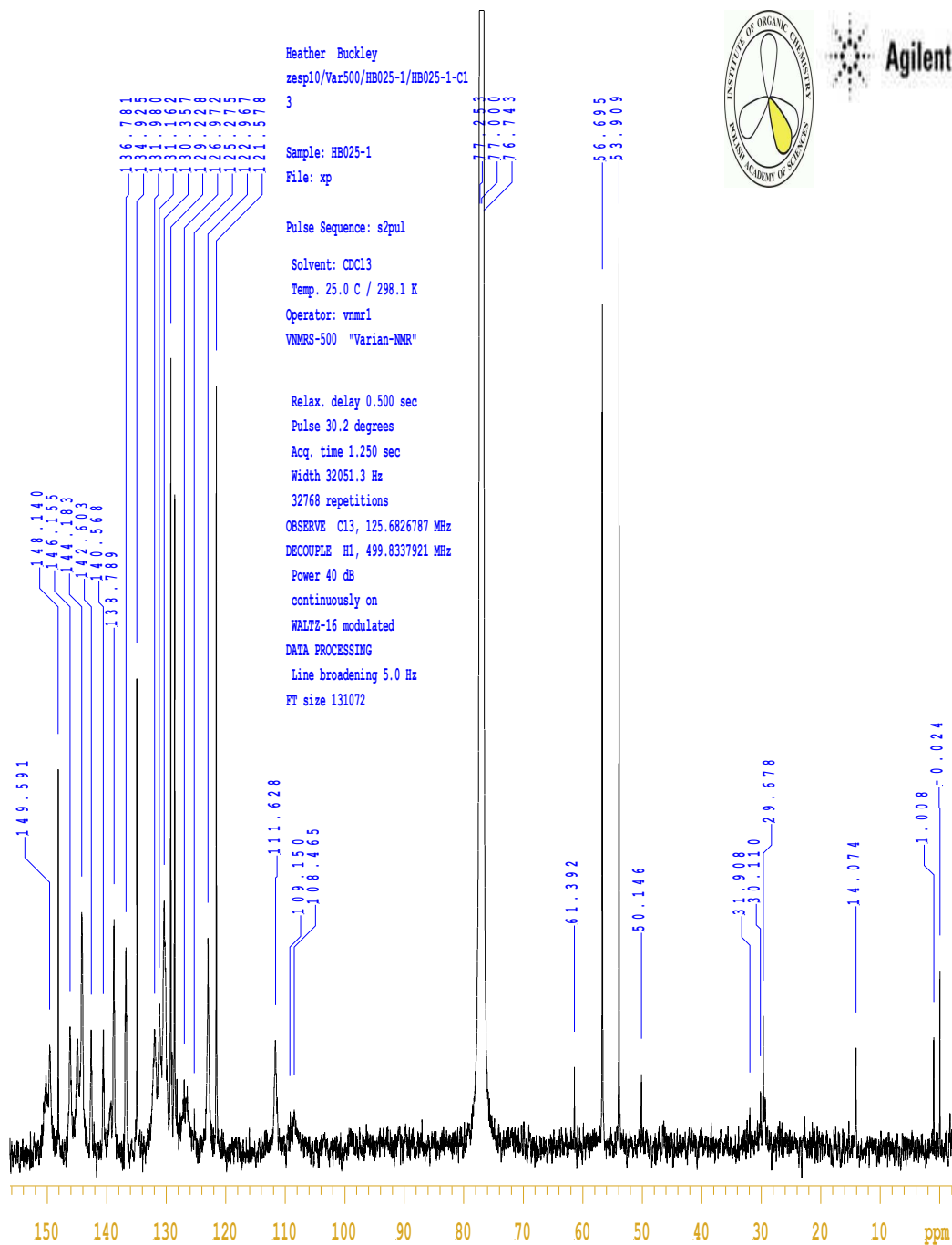
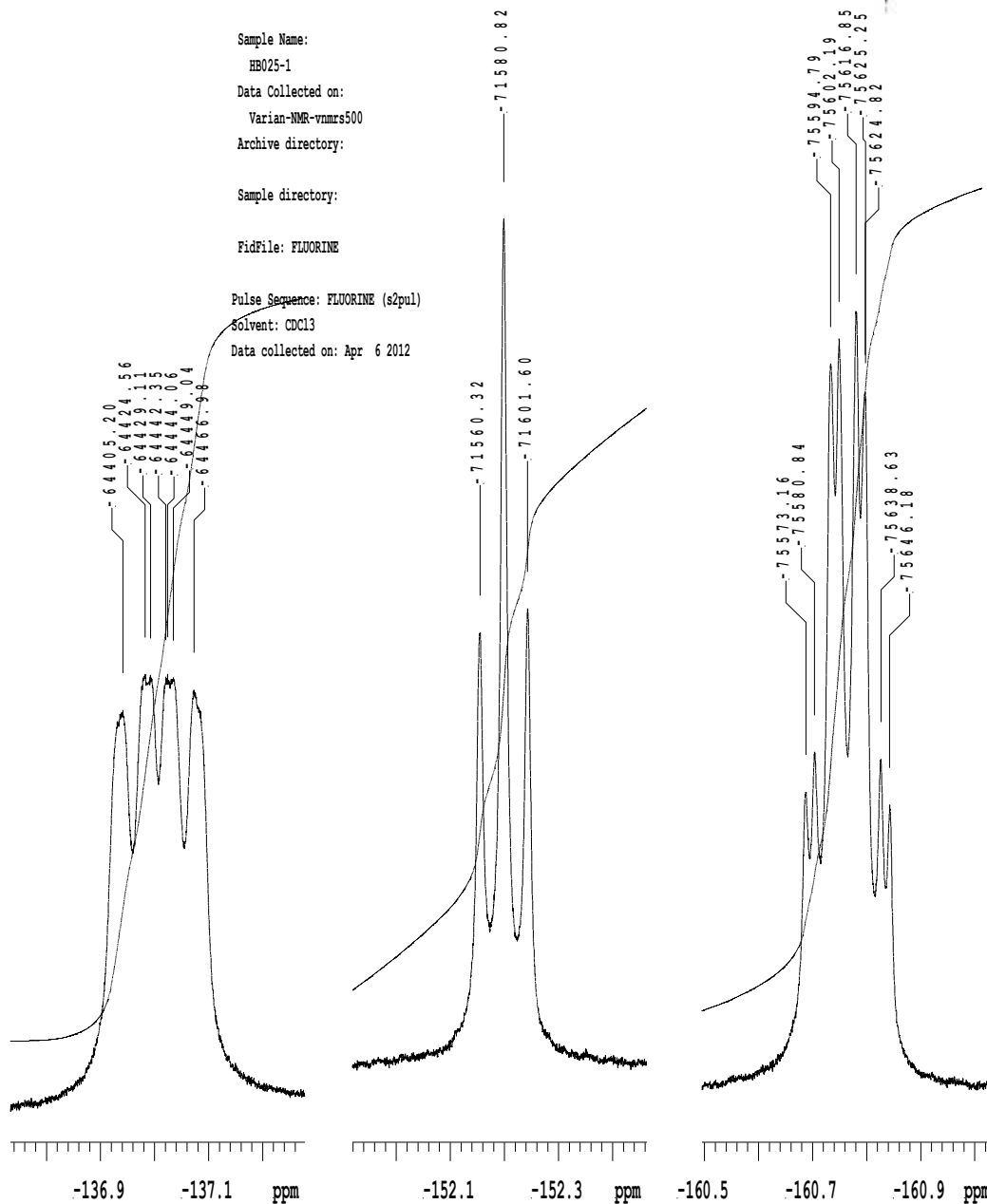


Figure S41. ¹³C NMR spectrum of **13** in CDCl₃.



Pulse Sequence: FLUORINE (s2pul)
Solvent: CDCl3
Data collected on: Apr 6 2012



38

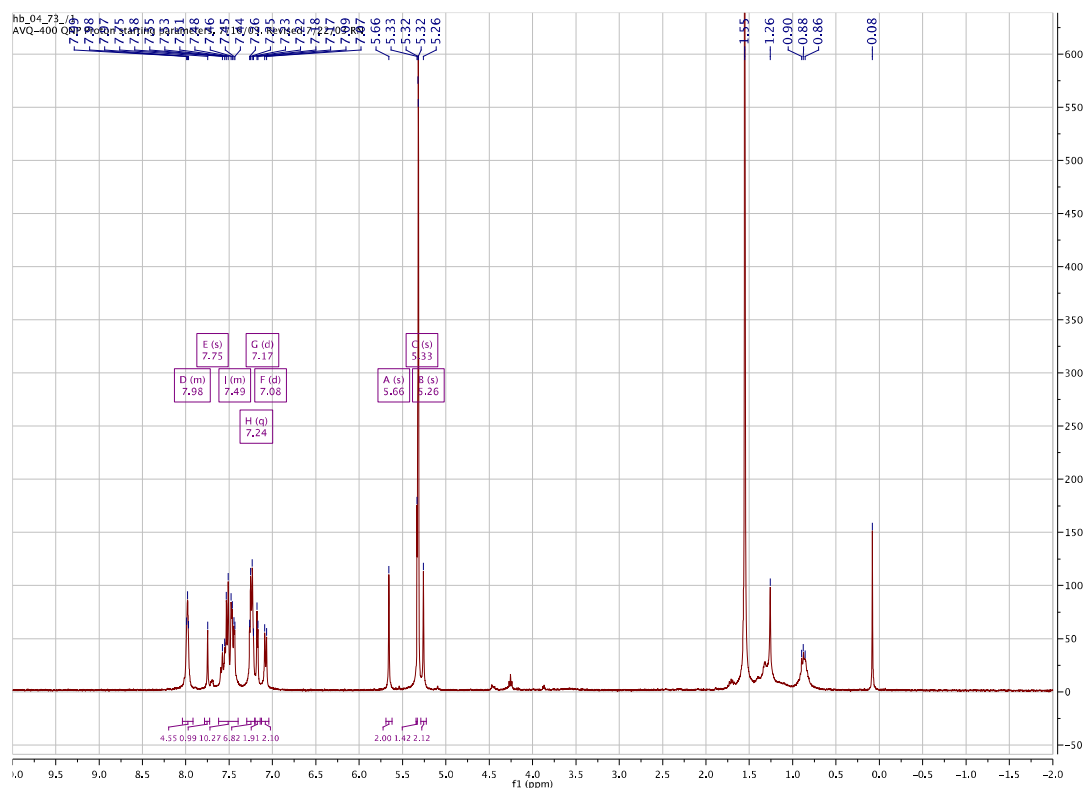
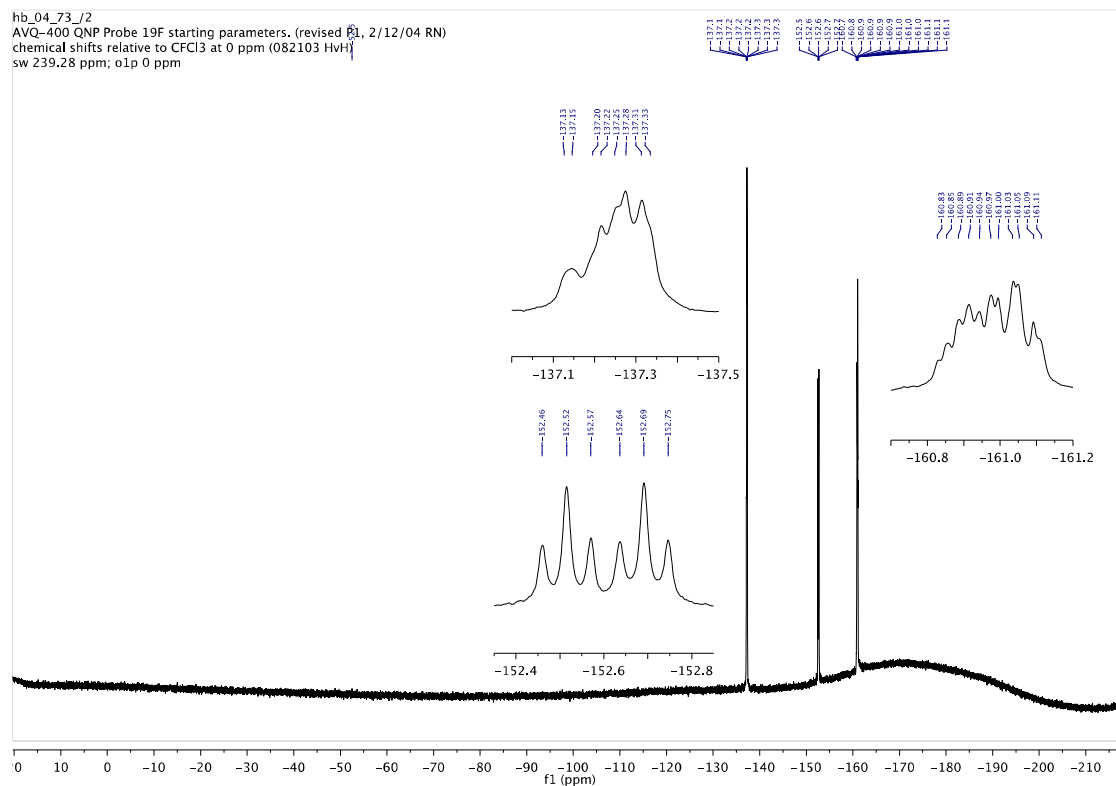


Figure S43. ^1H NMR spectrum of **14** in CD_2Cl_2 .



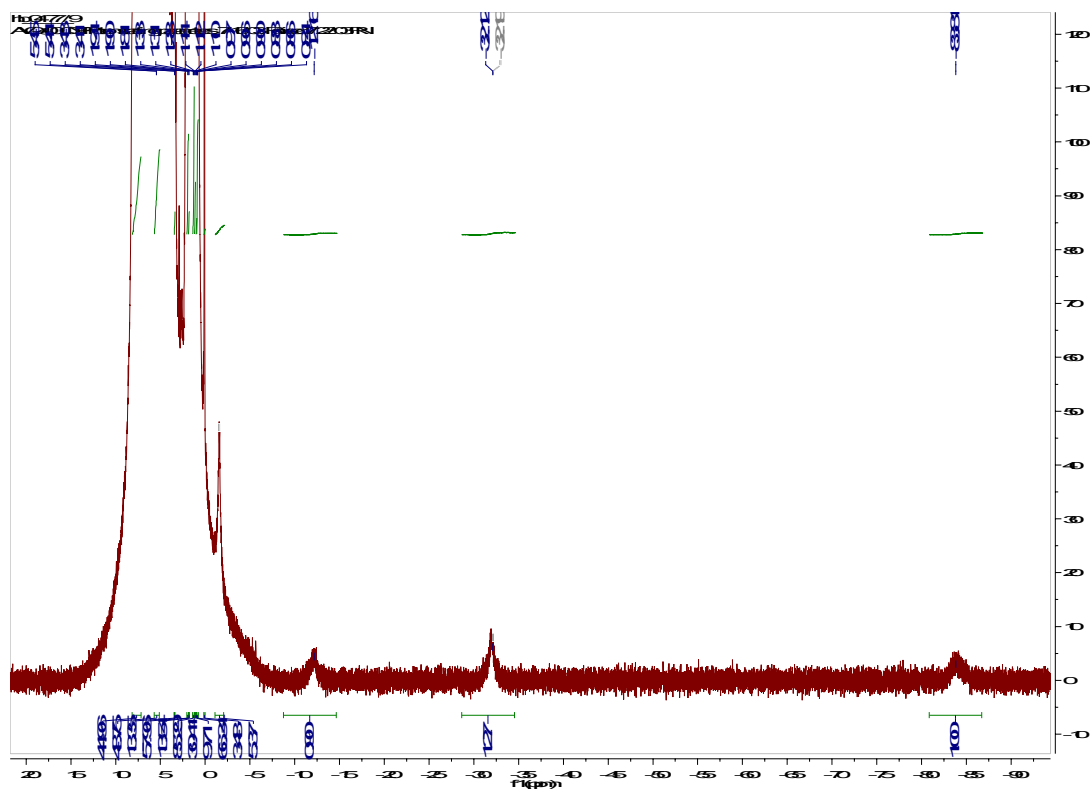


Figure S45. ^1H NMR spectrum of **15** in CD_3CN (broad window).

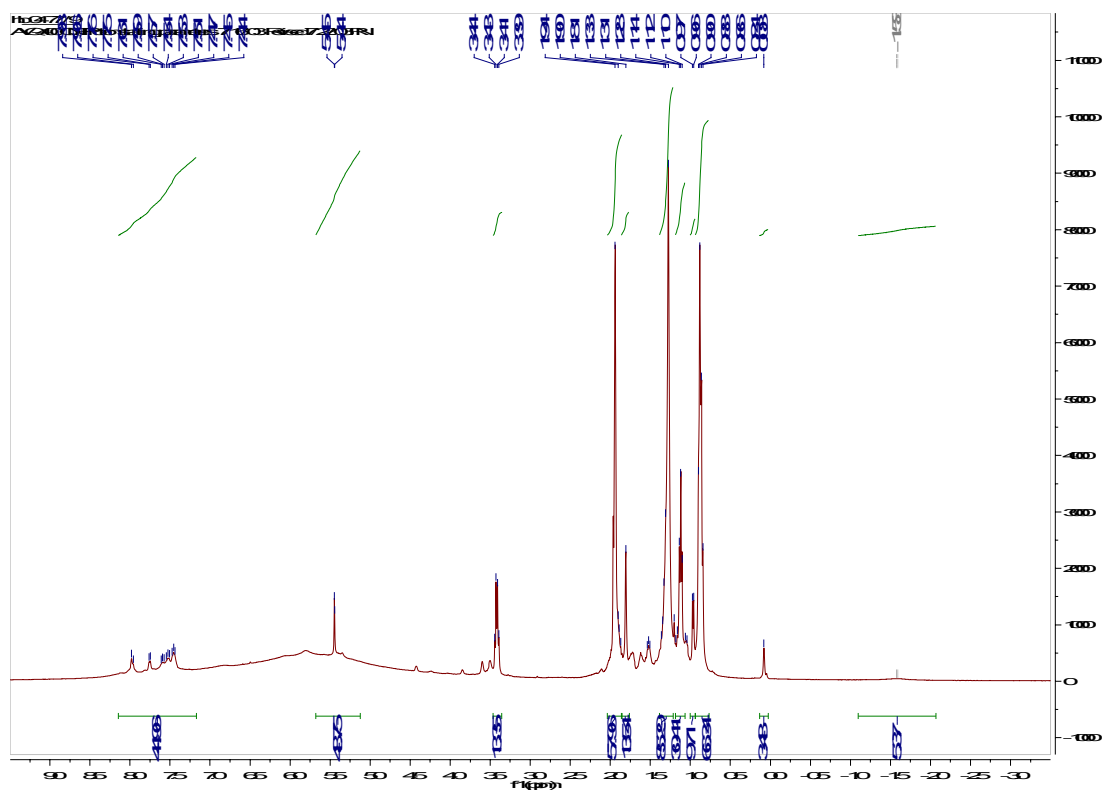


Figure S46. ^1H NMR spectrum of **15** in CD_3CN (narrow window).

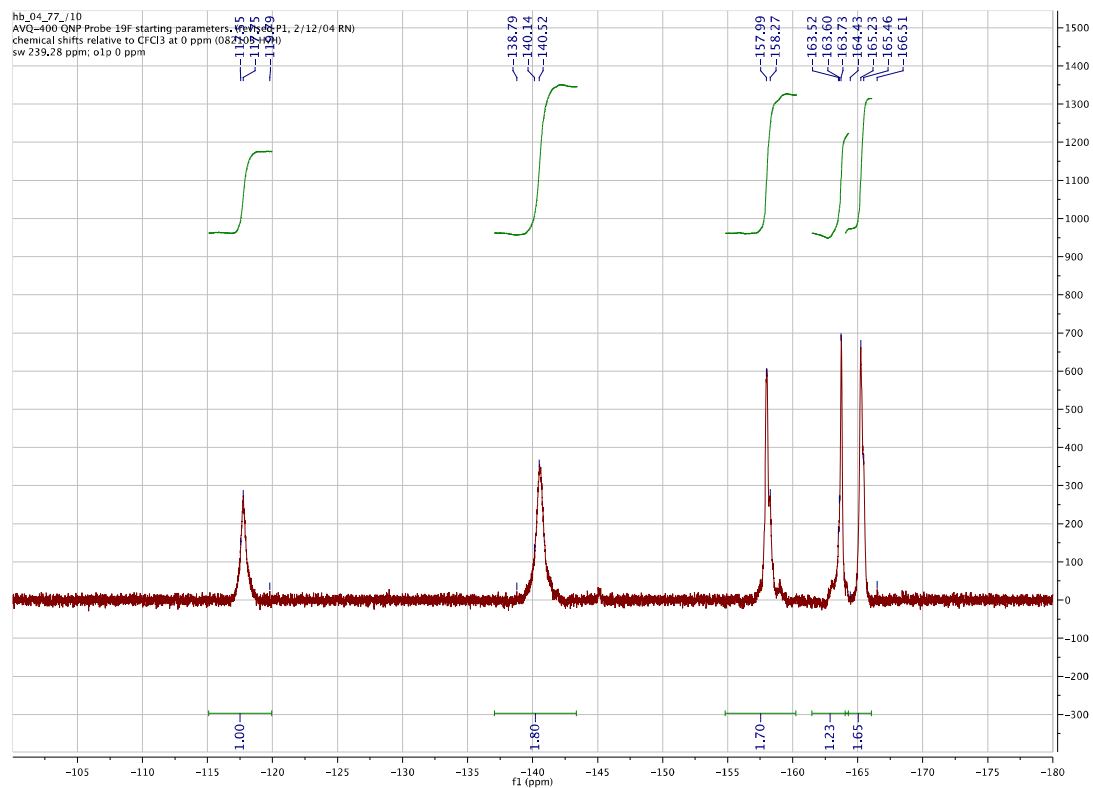


Figure S47. ^{19}F NMR spectrum of **15** in CD_3CN .

C. References

- (1) Pavlishchuk, V. V.; Addison, A. W. *Inorg. Chim. Acta* **2000**, 298, 97–102.