

Supporting Information

Synthesis and structures of tridentate ketoiminate zinc complexes bearing trifluoromethyl substituents that act as L-lactide ring opening polymerization initiators

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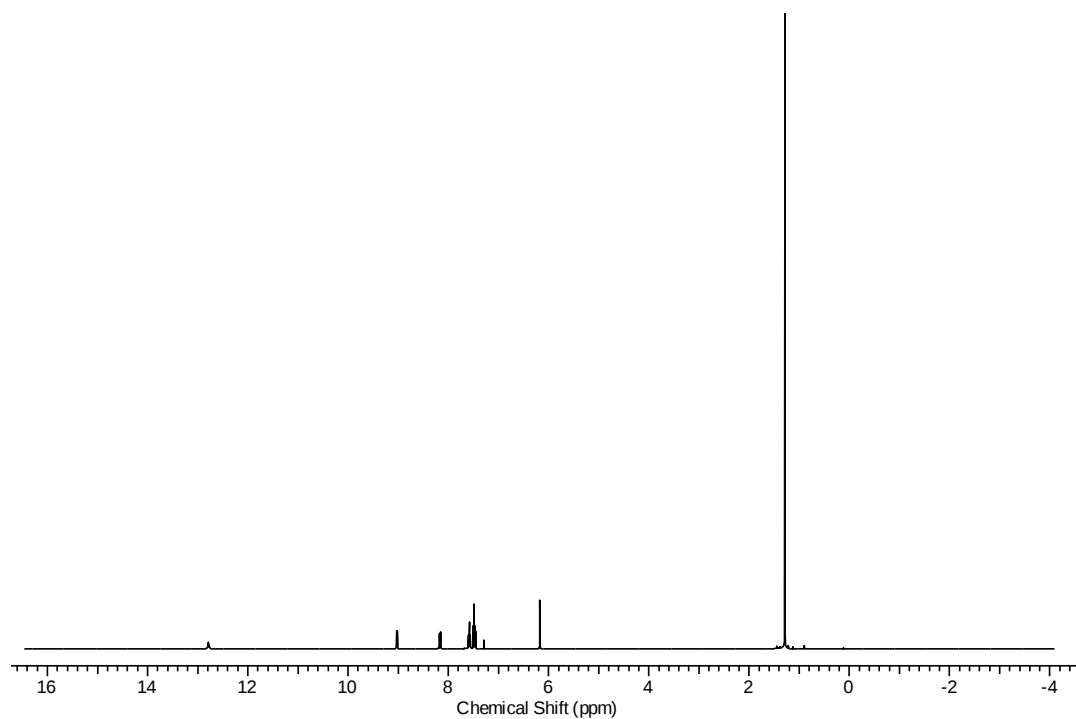
^bDepartment of Chemistry, University of California, San Diego

Table of contents

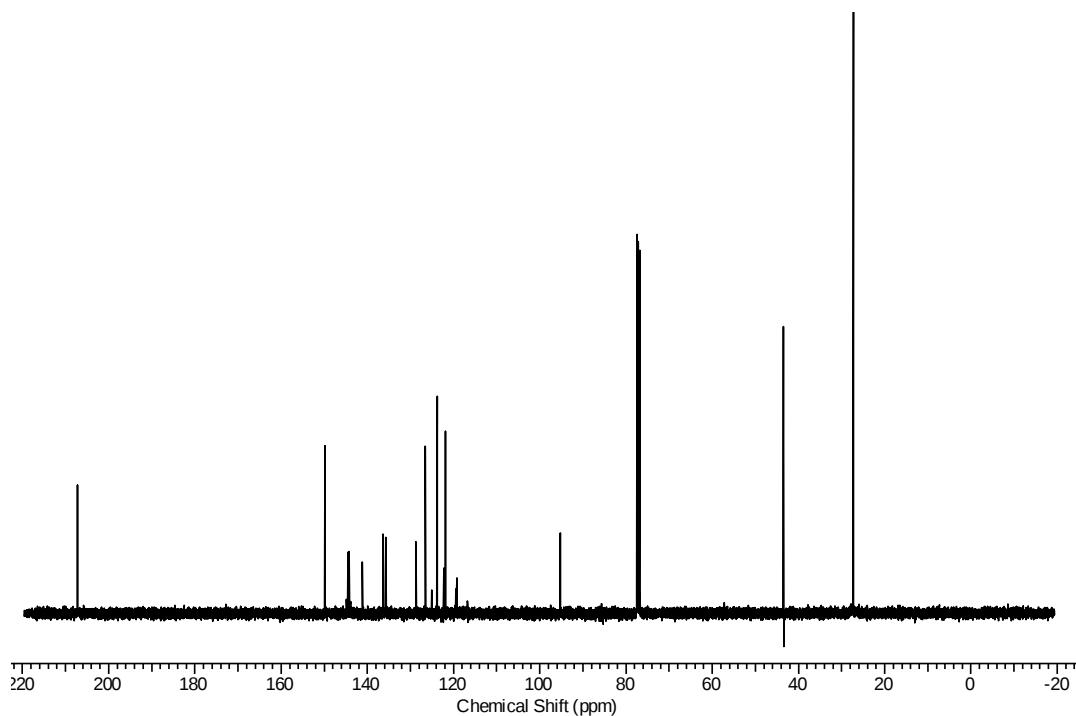
SI Figures 1-10. ¹ H, ¹³ C, and ¹⁹ F NMR spectra of ketoimines 1 - 8	2-21
SI Figures 11-16. ¹ H, ¹³ C, and ¹⁹ F NMR spectra of zinc phenoxide complexes 1a – 6a	22-33
SI Figures 17. ¹ H, ¹³ C, and ¹⁹ F NMR spectra of zinc amide complex 2b	34-35
SI Figure 18. ORTEP diagram of 2a	36
SI Figure 19. ¹ H NMR spectrum of isolated PLLA	37
SI Figure 20. { ¹ H} ¹ H NMR spectrum of isolated PLLA	38
SI Figure 21. Linear relationship between M_n and monomer/initiator ratio	39
SI Figure 22. PLA M_n versus percentage conversion	39
SI Figure 23. GPC-ELSD chromatograms of PLA isolated from double feed	40

SI Figure 1. NMR spectra of compound **1**.

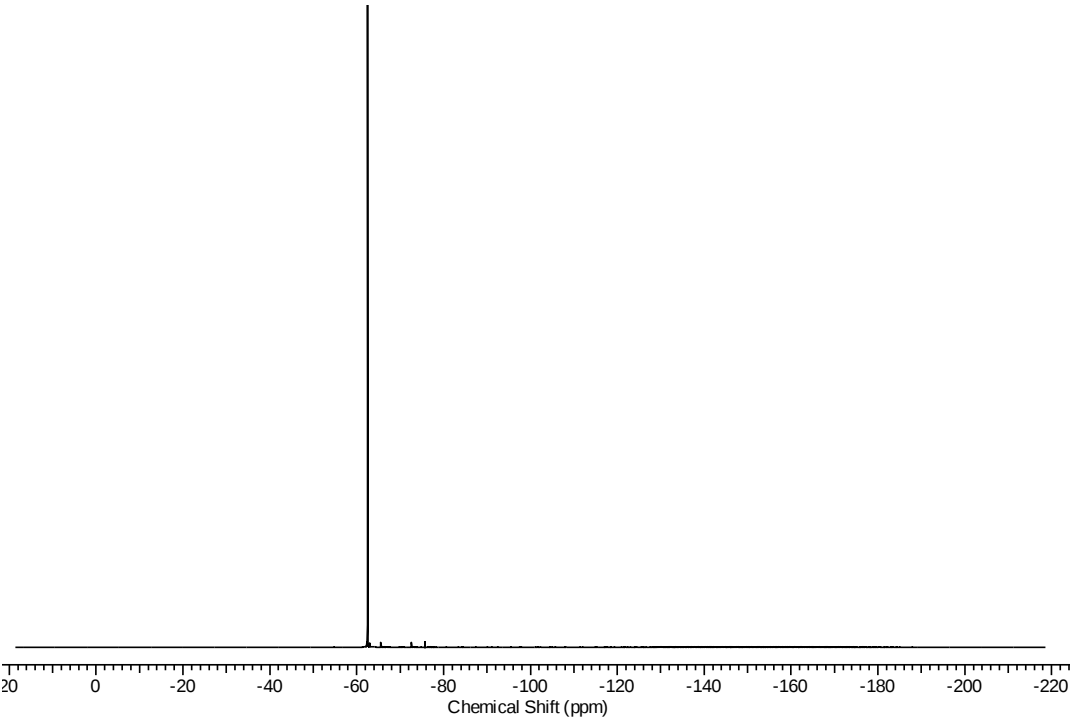
^1H NMR spectrum of **1**



^{13}C NMR spectrum of **1**

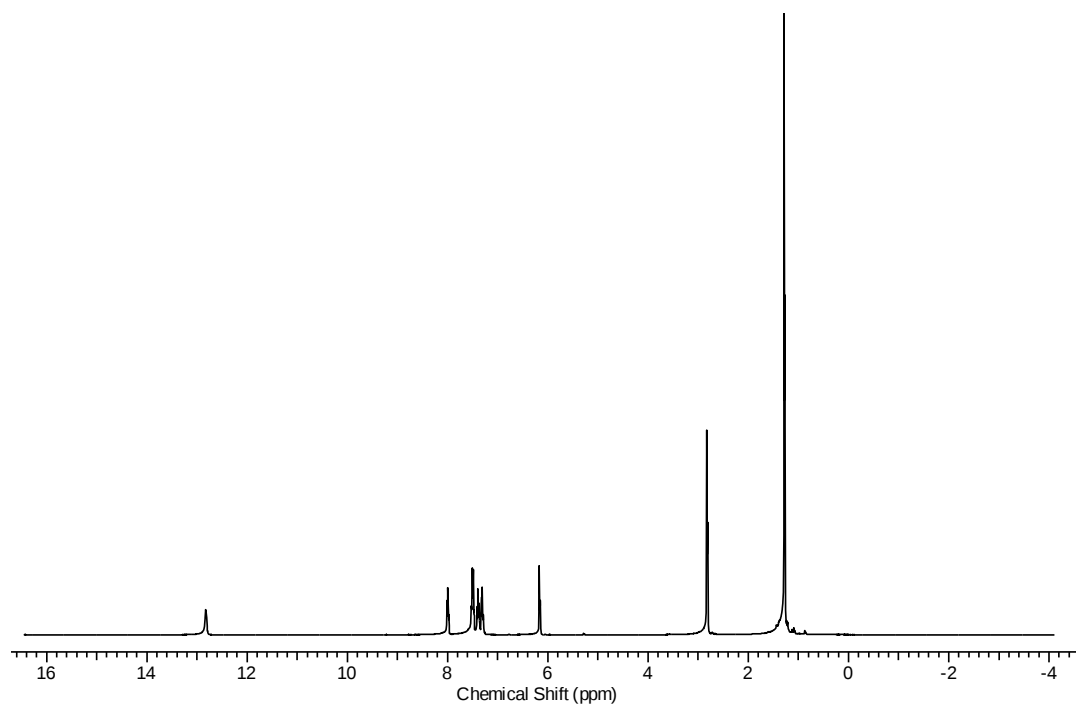


^{19}F NMR spectrum of **1**

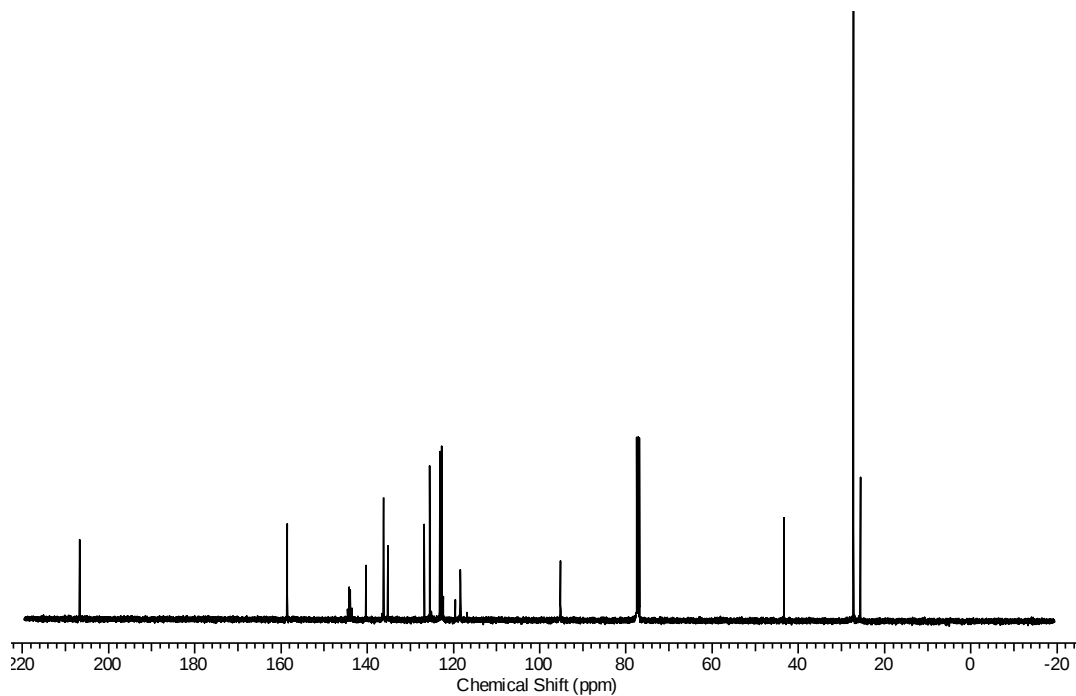


SI Figure 2. NMR spectra of compound 2.

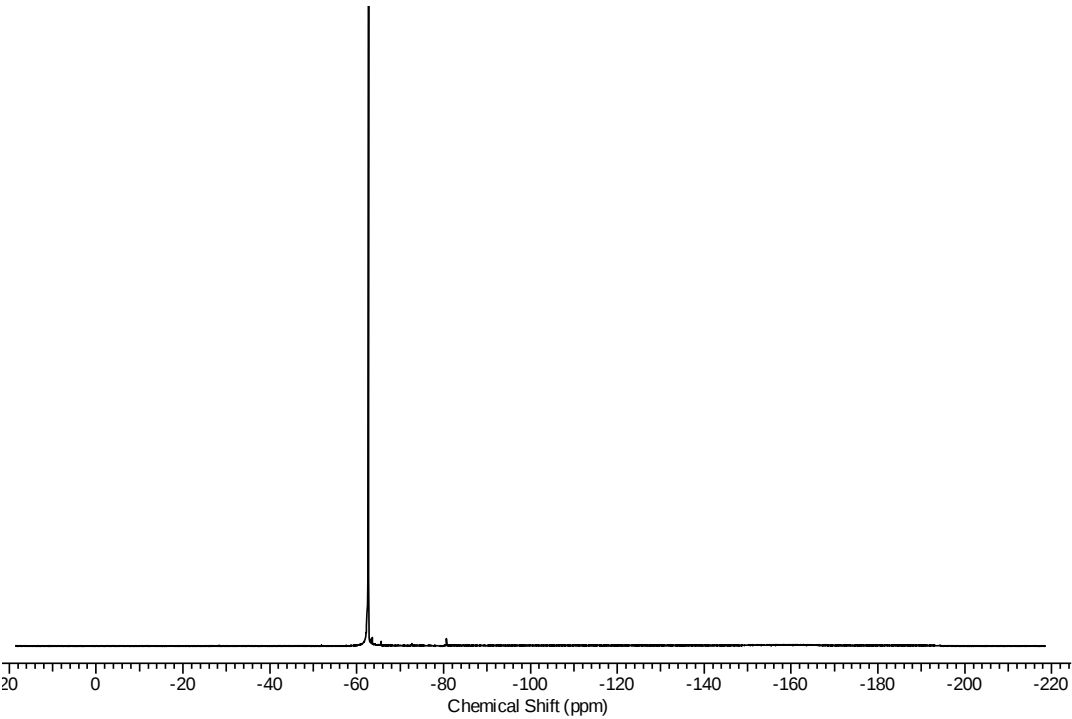
^1H NMR spectrum of 2



^{13}C NMR spectrum of 2

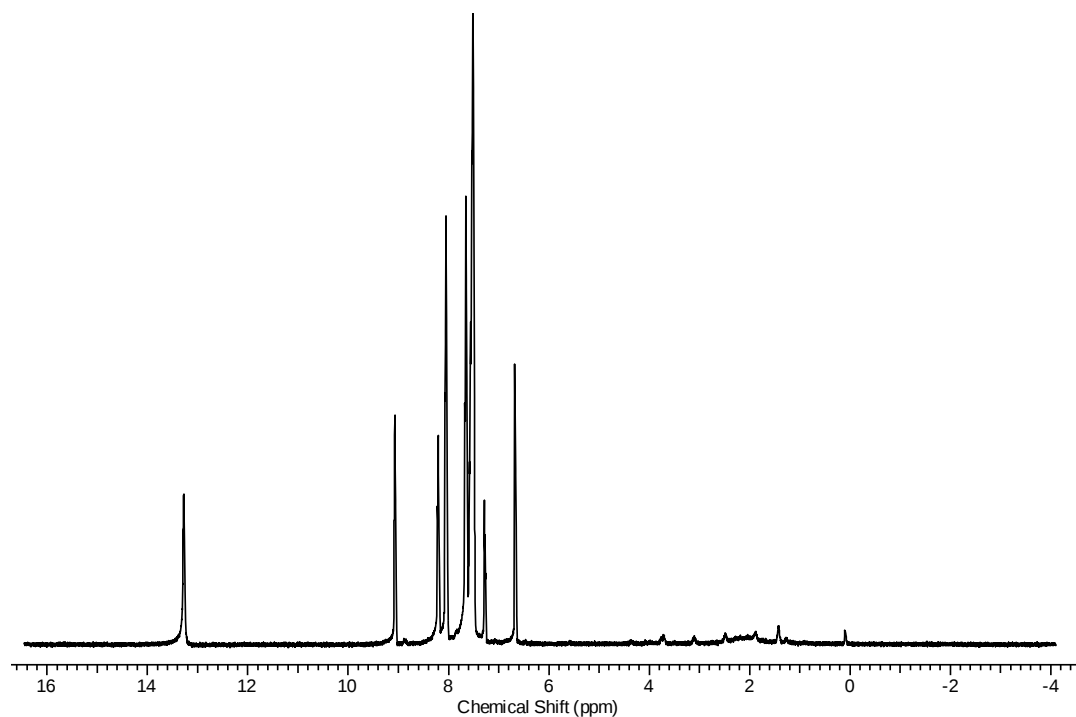


^{19}F NMR spectrum of **2**

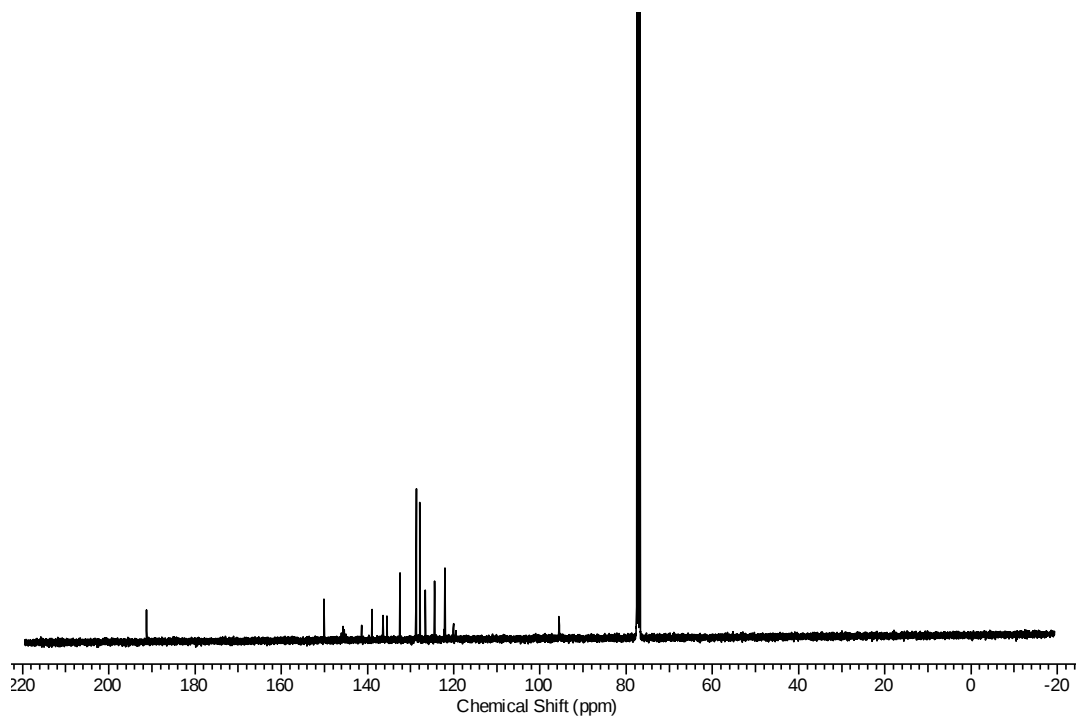


SI Figure 3. NMR spectra of compound **3**.

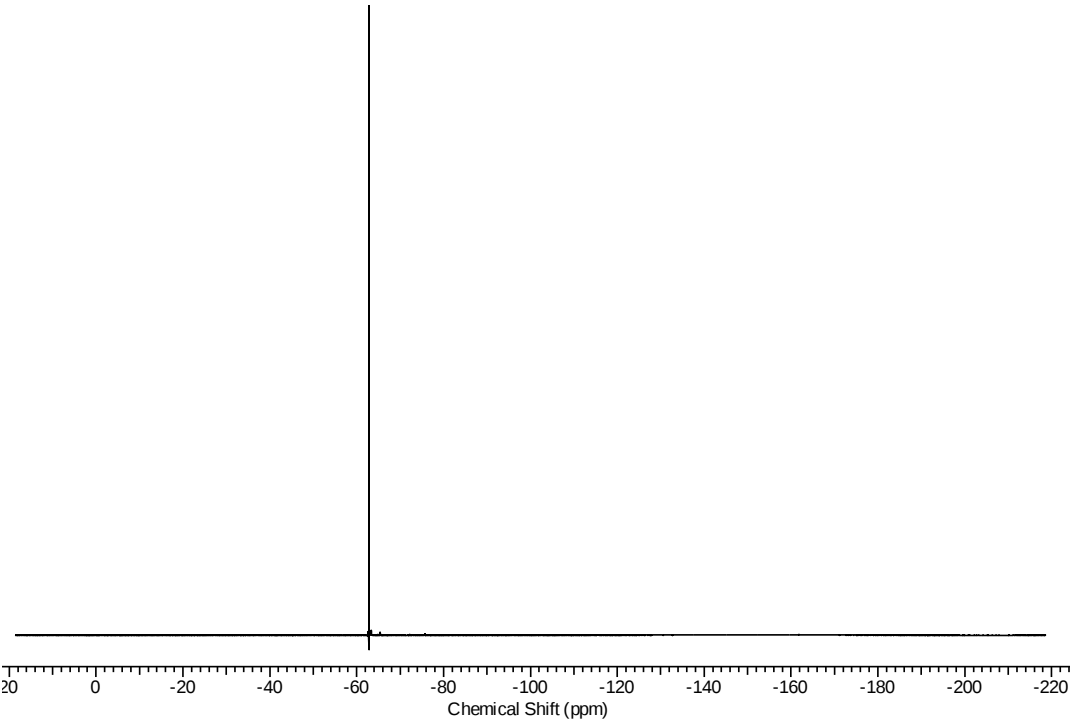
^1H NMR spectrum of **3**



^{13}C NMR spectrum of **3**

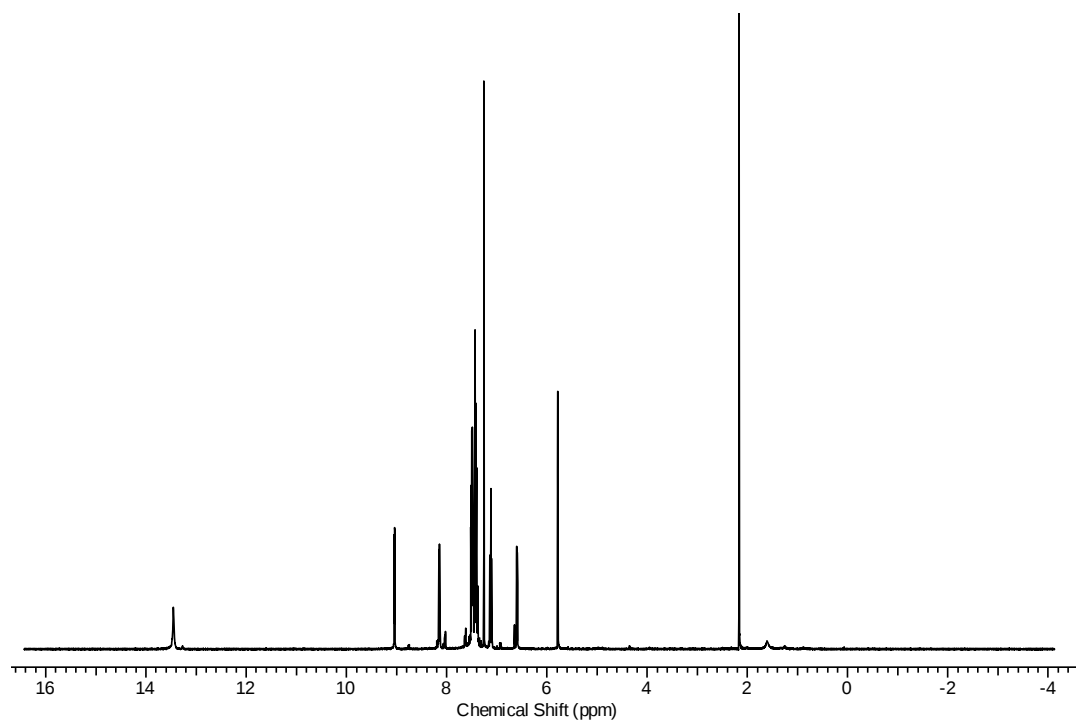


^{19}F NMR spectrum of **3**

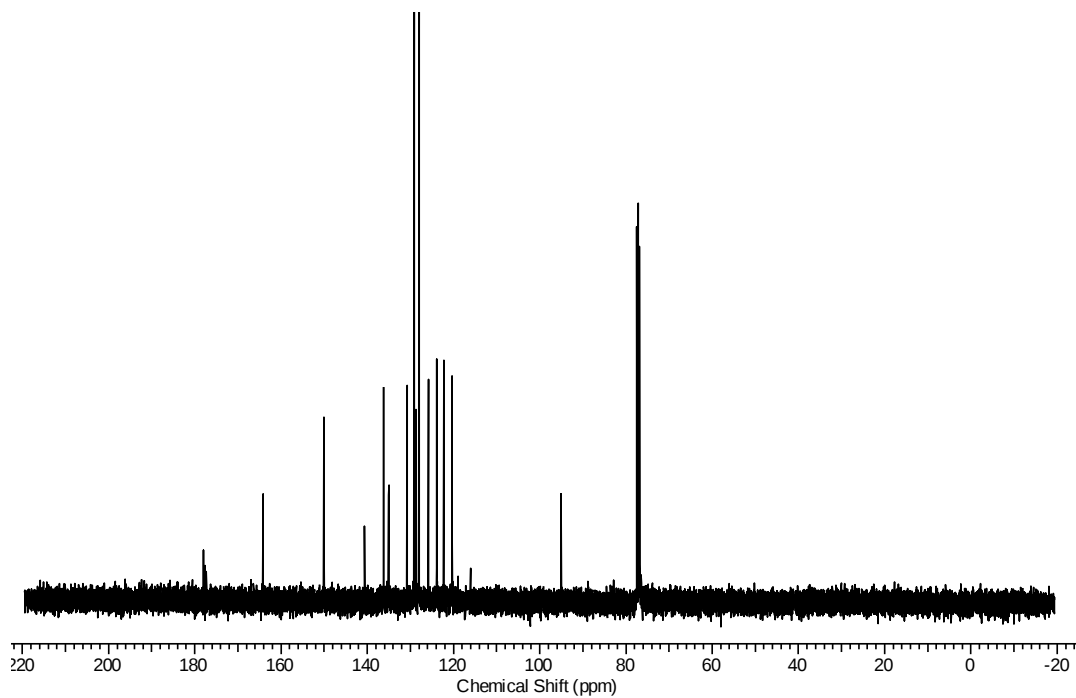


SI Figure 4. NMR spectra of compound **3'**.

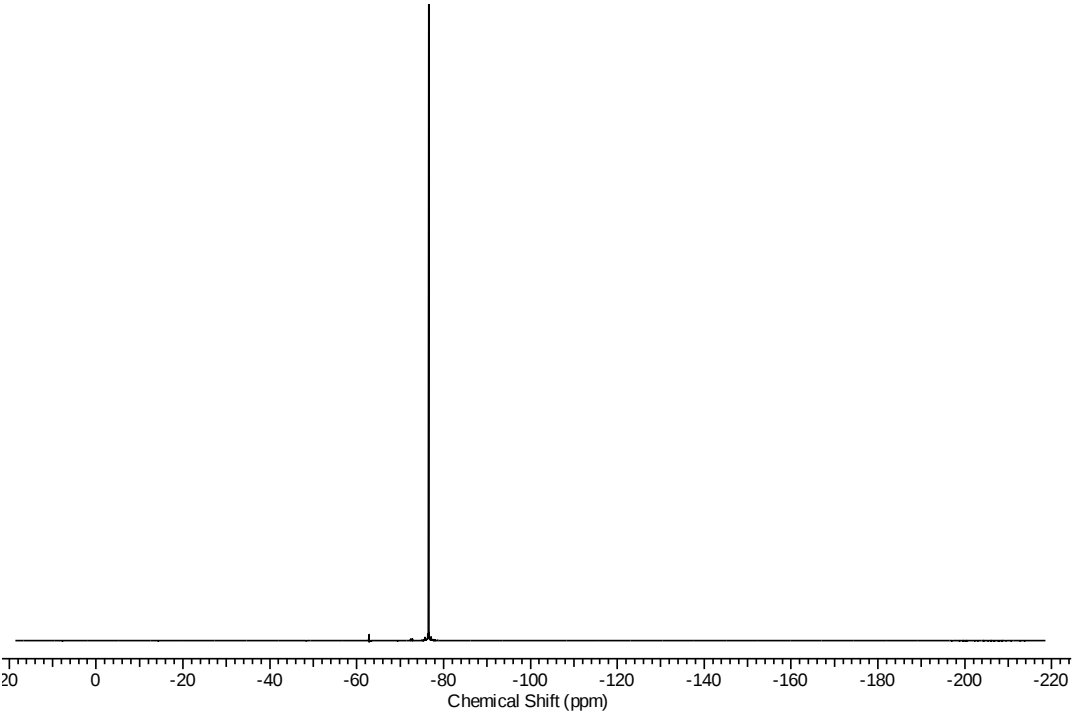
^1H NMR spectrum of **3'**



^{13}C NMR spectrum of **3'**

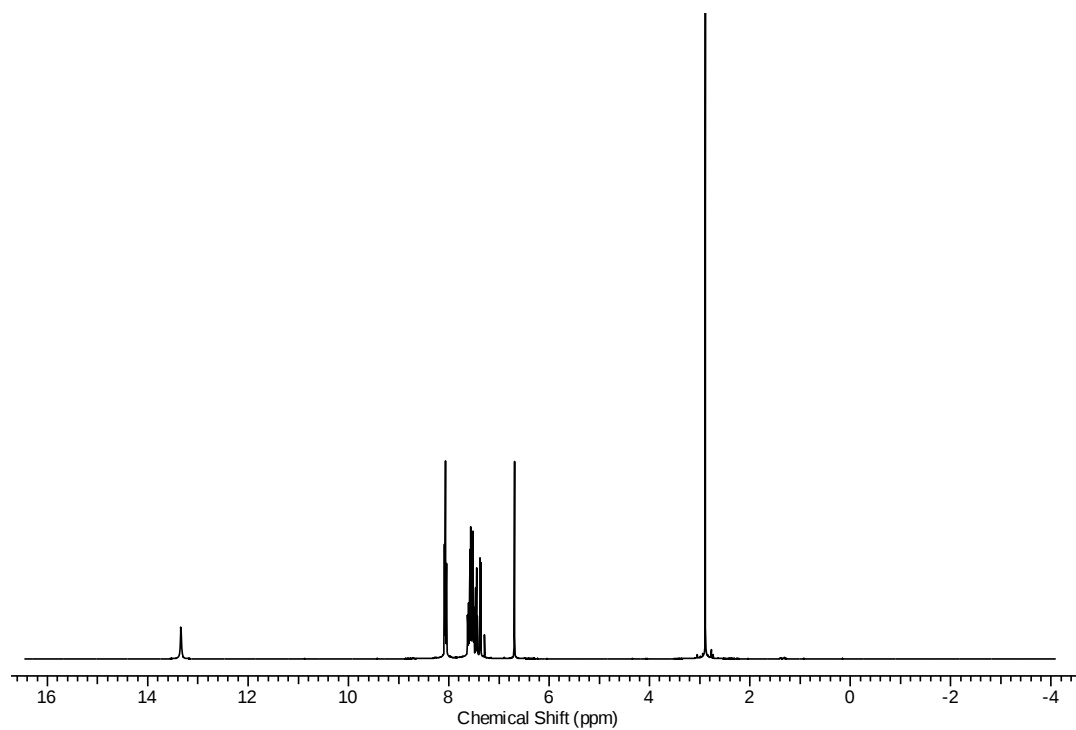


^{19}F NMR spectrum of **3'**

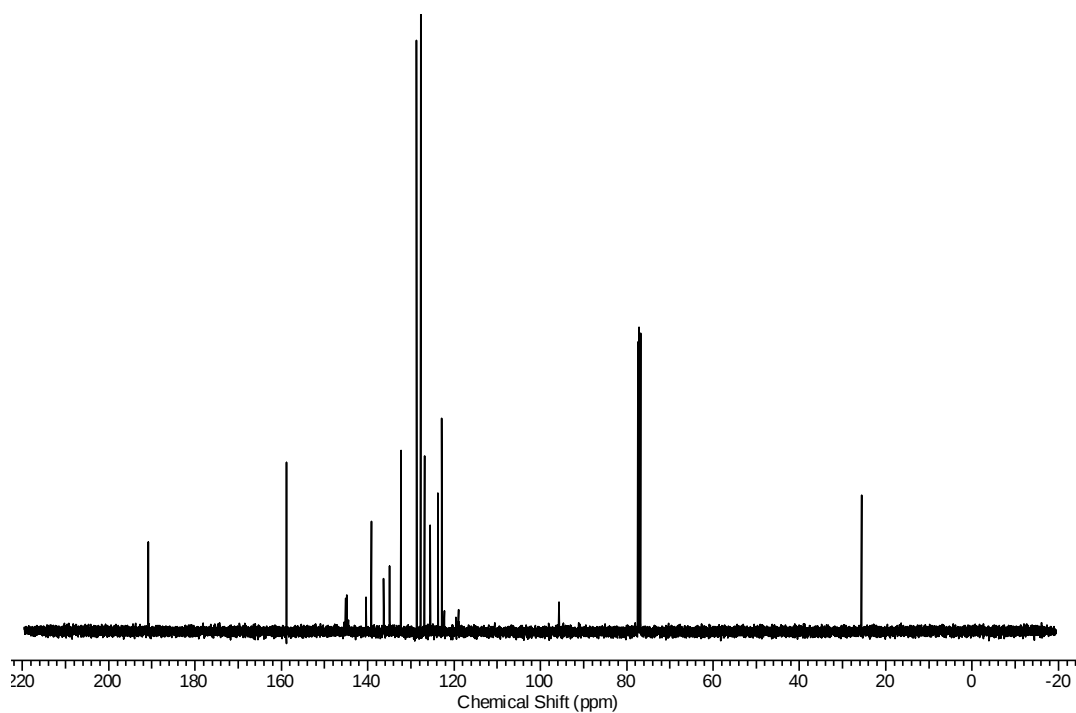


SI Figure 5. NMR spectra of compound **4**.

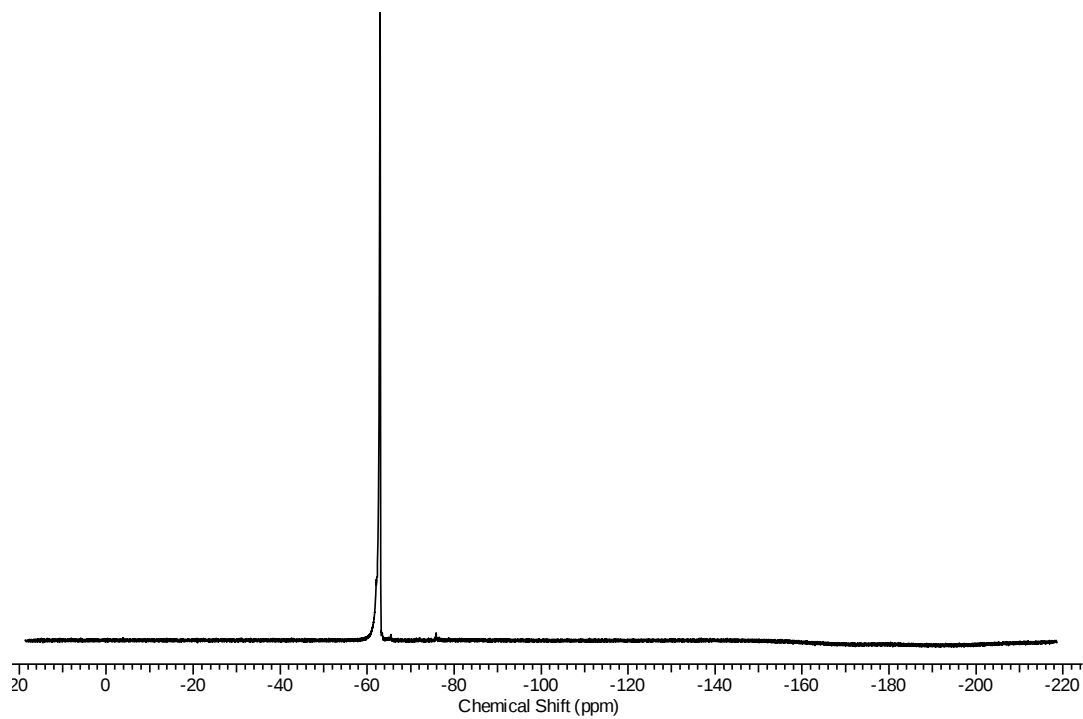
^1H NMR spectrum of **4**



^{13}C NMR spectrum of **4**

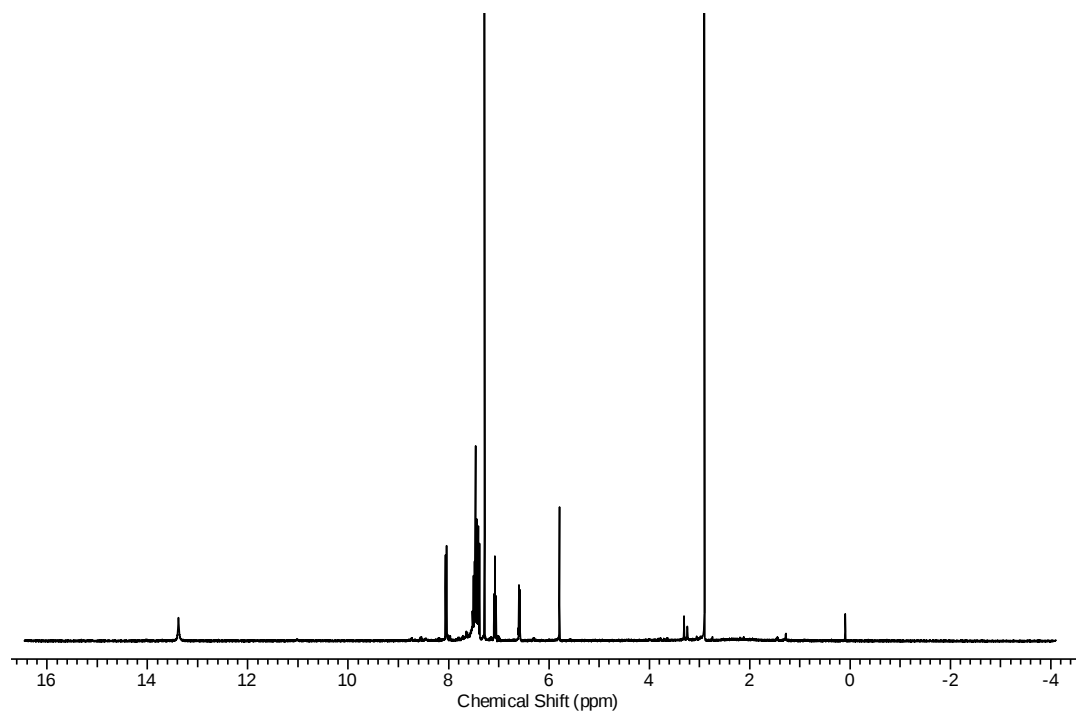


^{19}F NMR spectrum of **4**

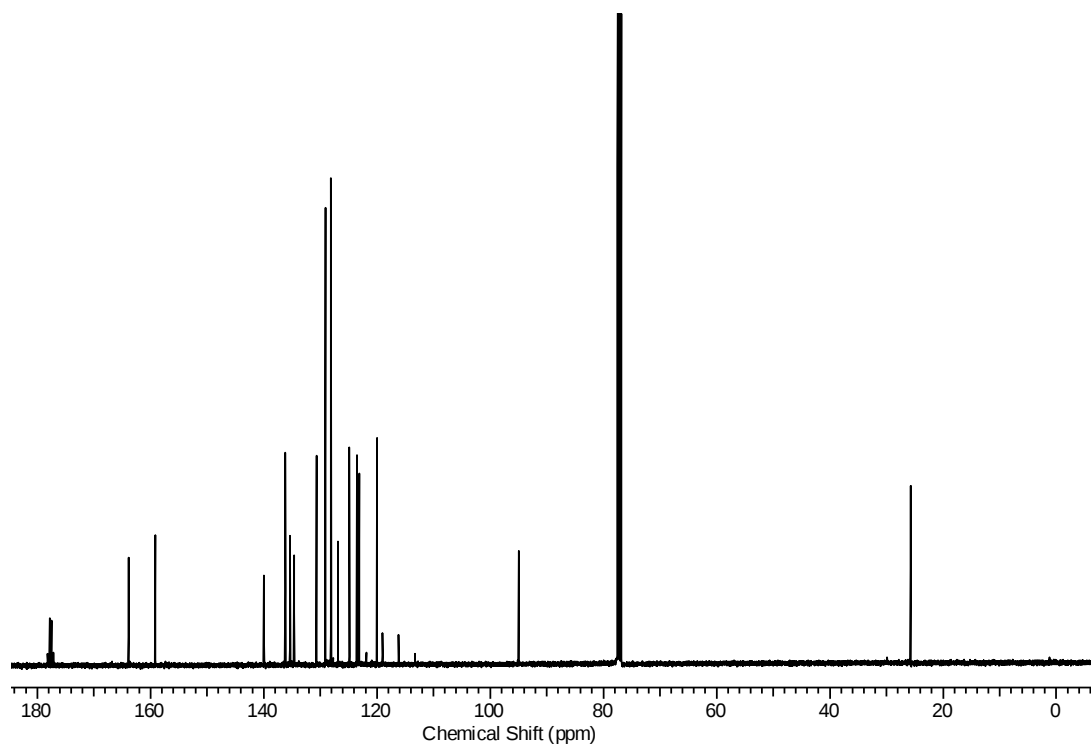


SI Figure 6. NMR spectra of compound **4'**.

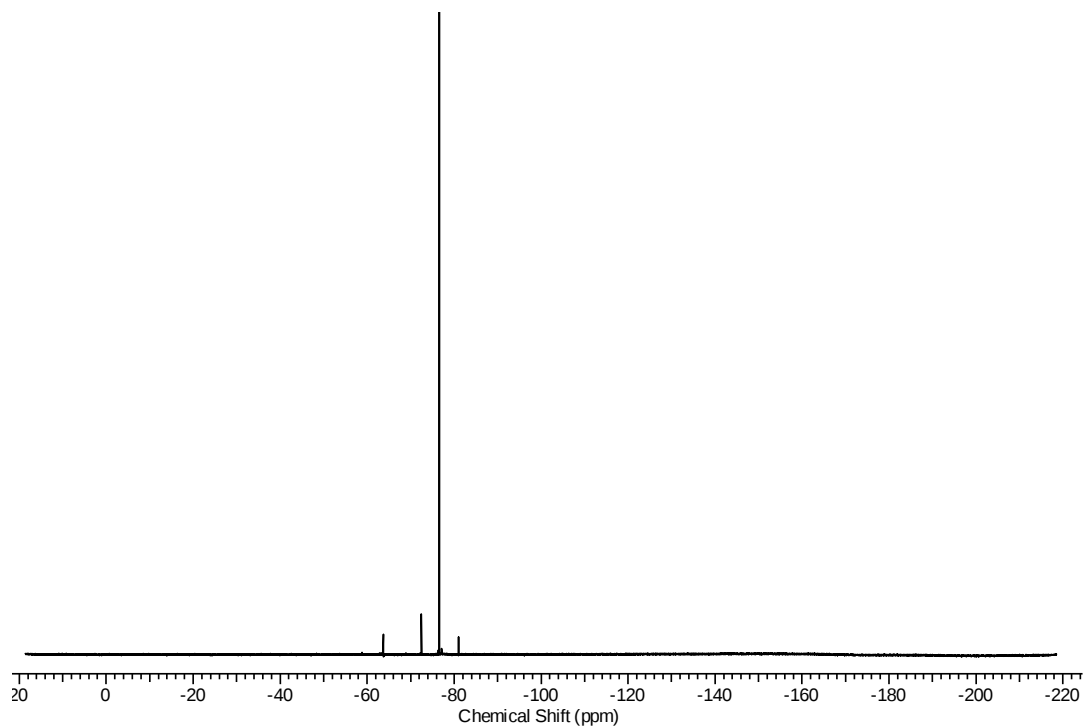
^1H NMR spectrum of **4'**



^{13}C NMR spectrum of **4'**

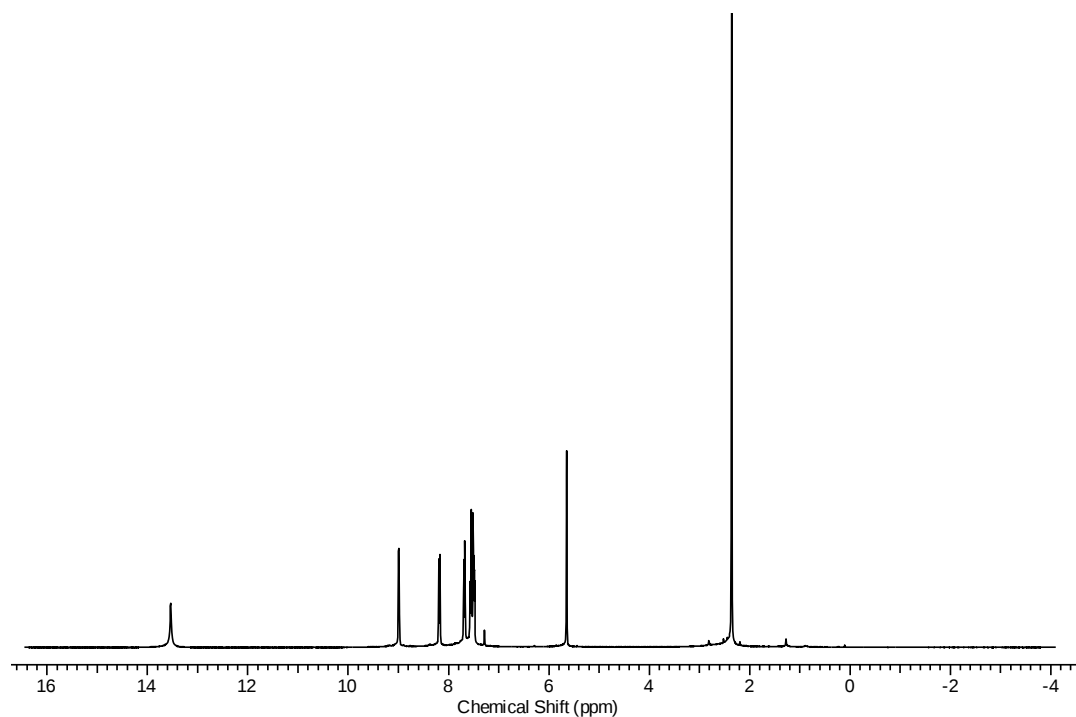


^{19}F NMR spectrum of **4'**

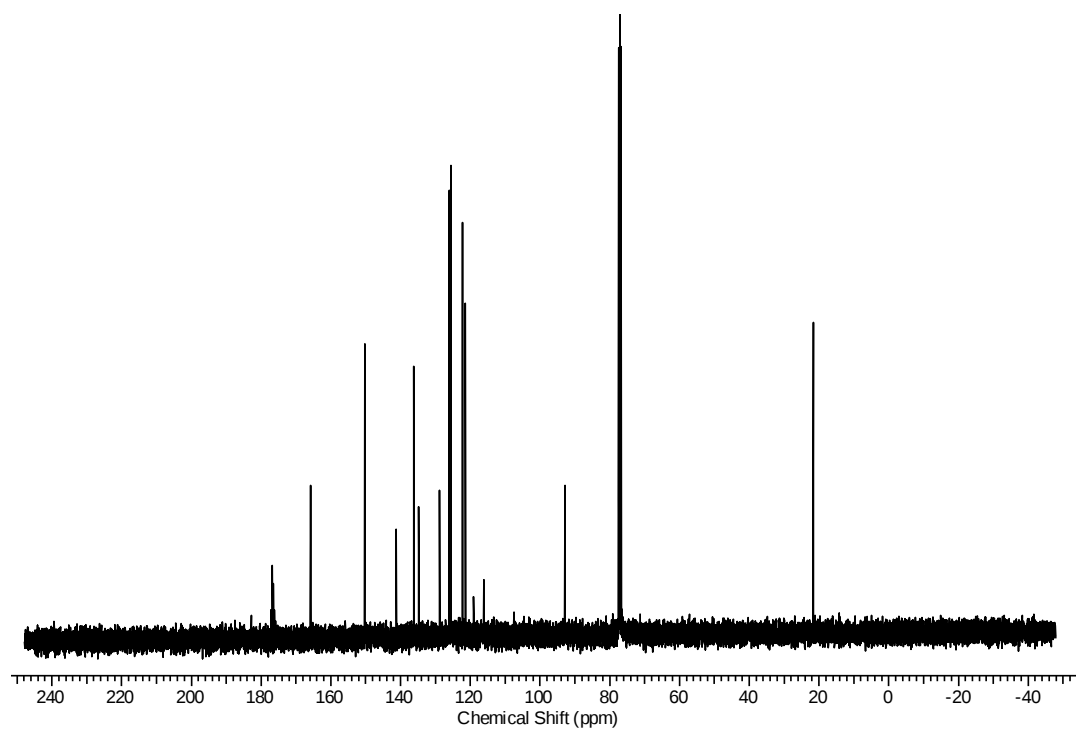


SI Figure 7. NMR spectra of compound 5.

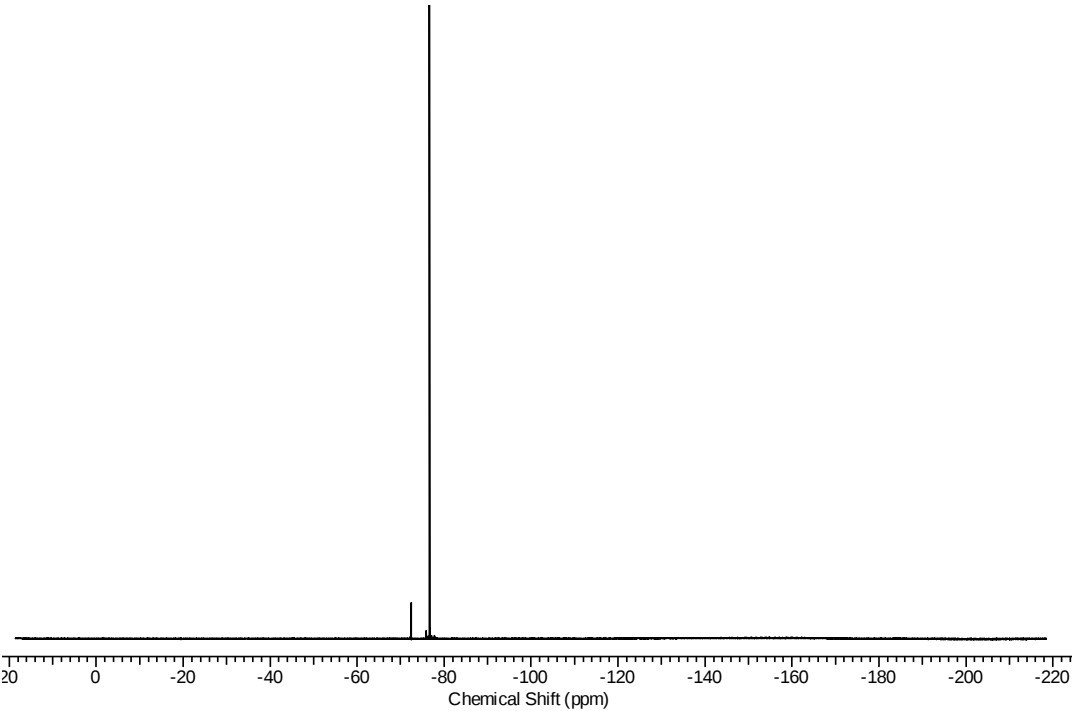
^1H NMR spectrum of 5



^{13}C NMR spectrum of 5

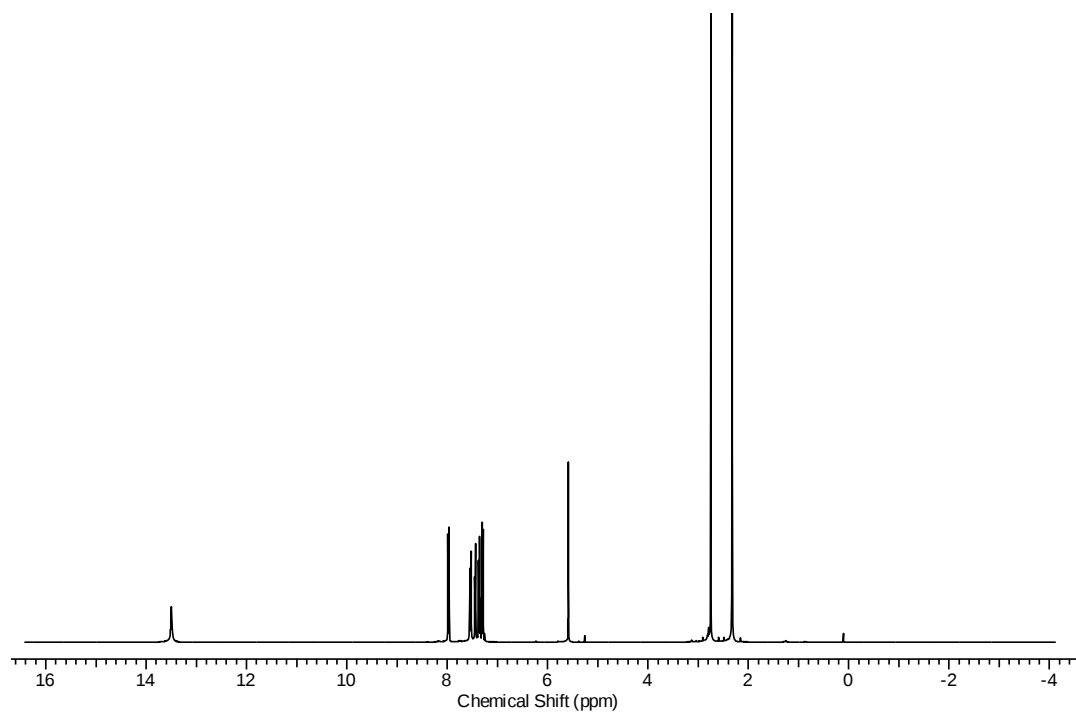


¹⁹F NMR spectrum of 5

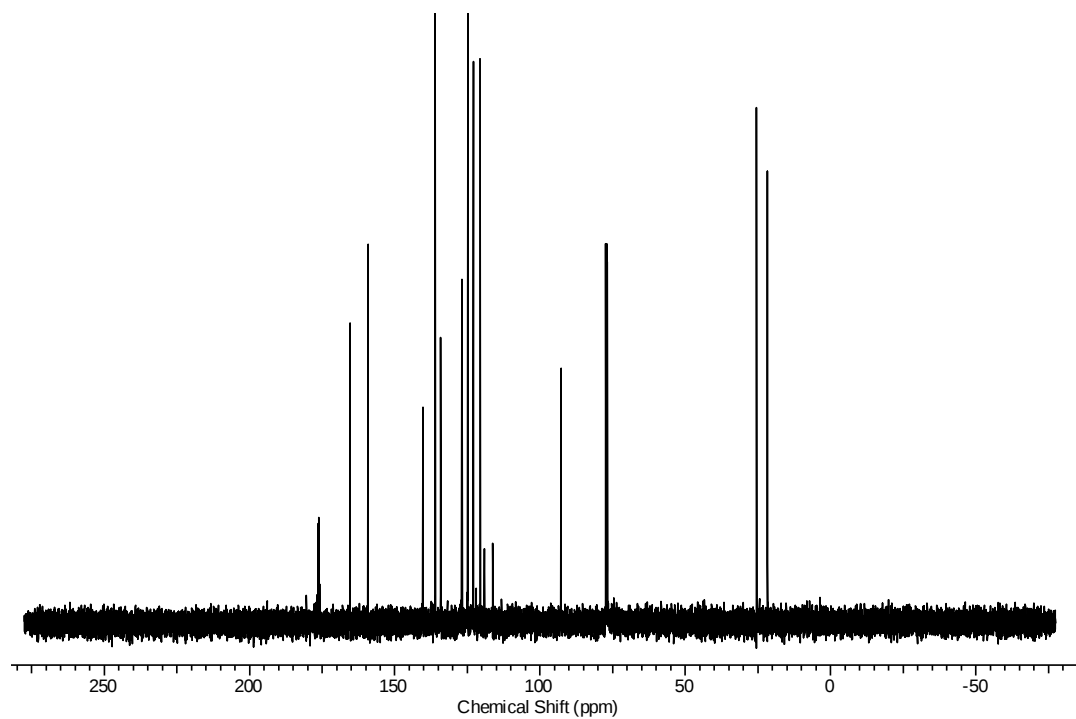


SI Figure 8. NMR spectra of compound **6**.

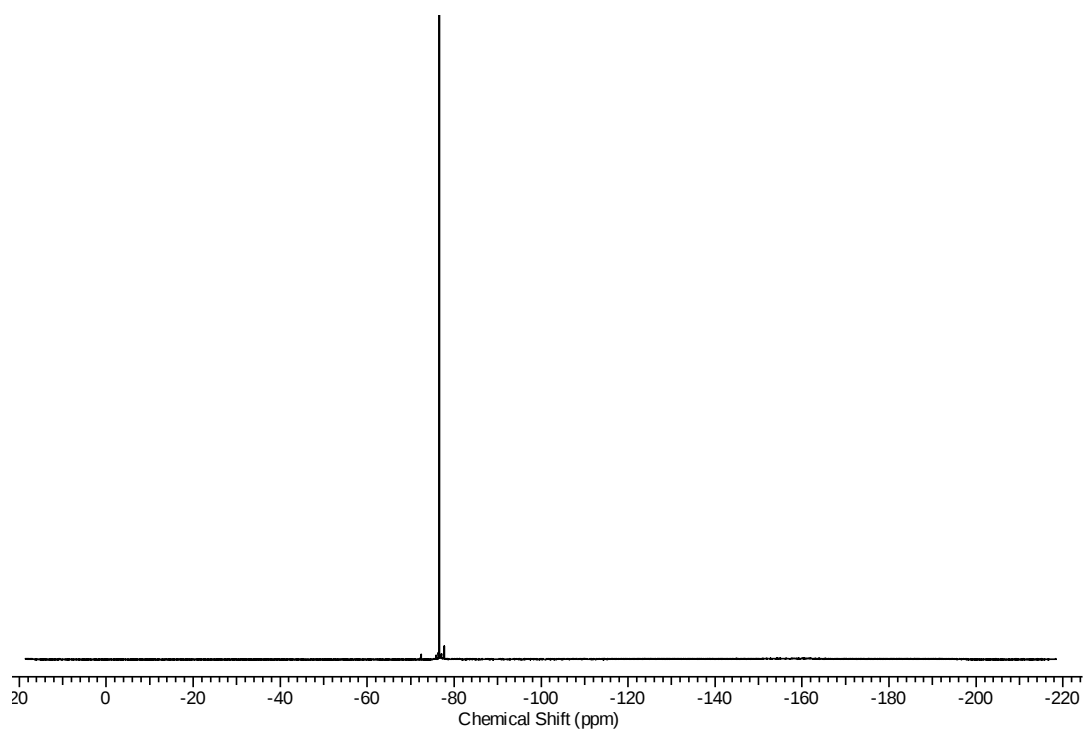
^1H NMR spectrum of **6**



^{13}C NMR spectrum of **6**

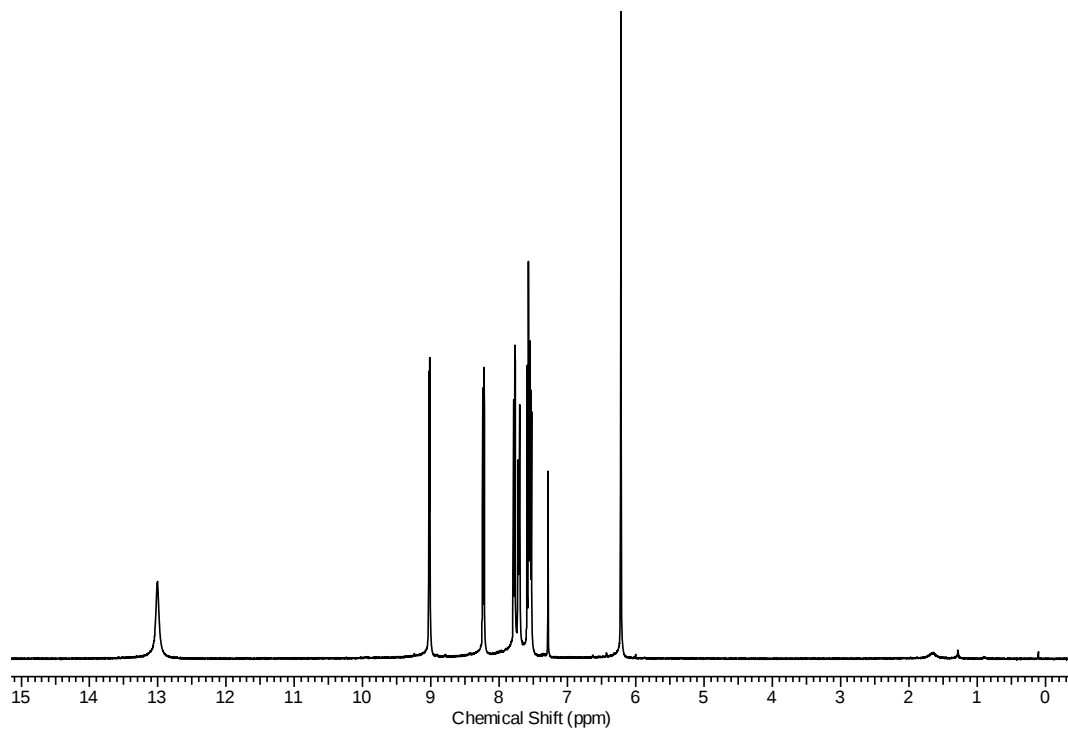


^{19}F NMR spectrum of **6**

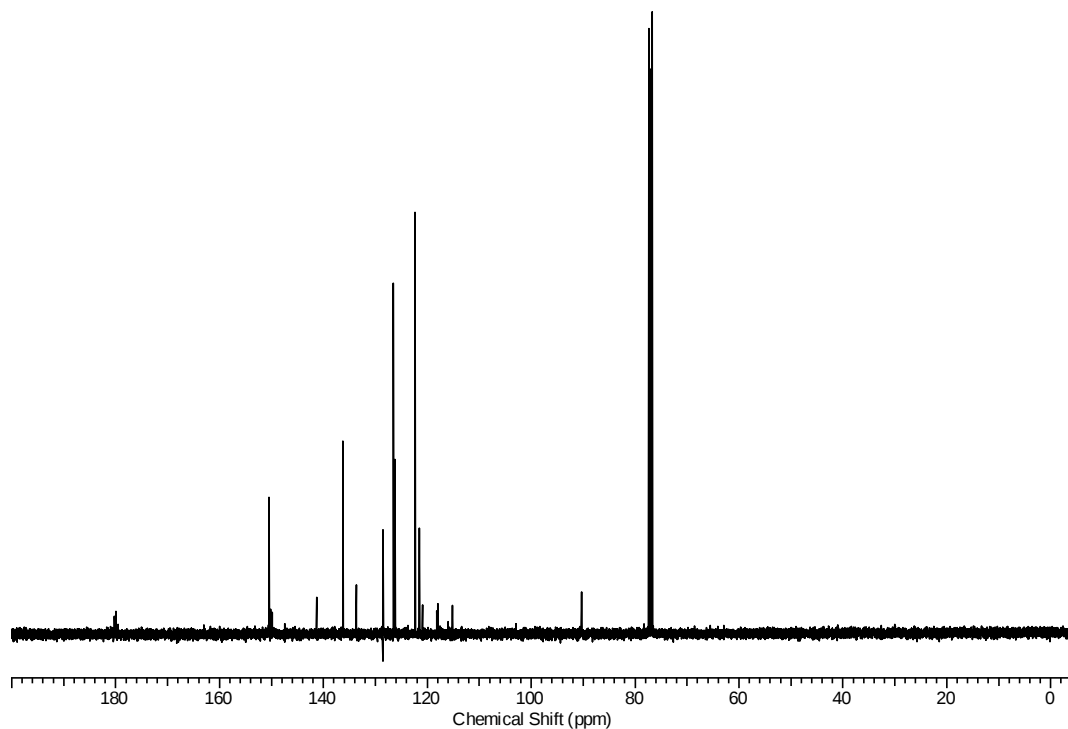


SI Figure 9. NMR spectra of compound 7.

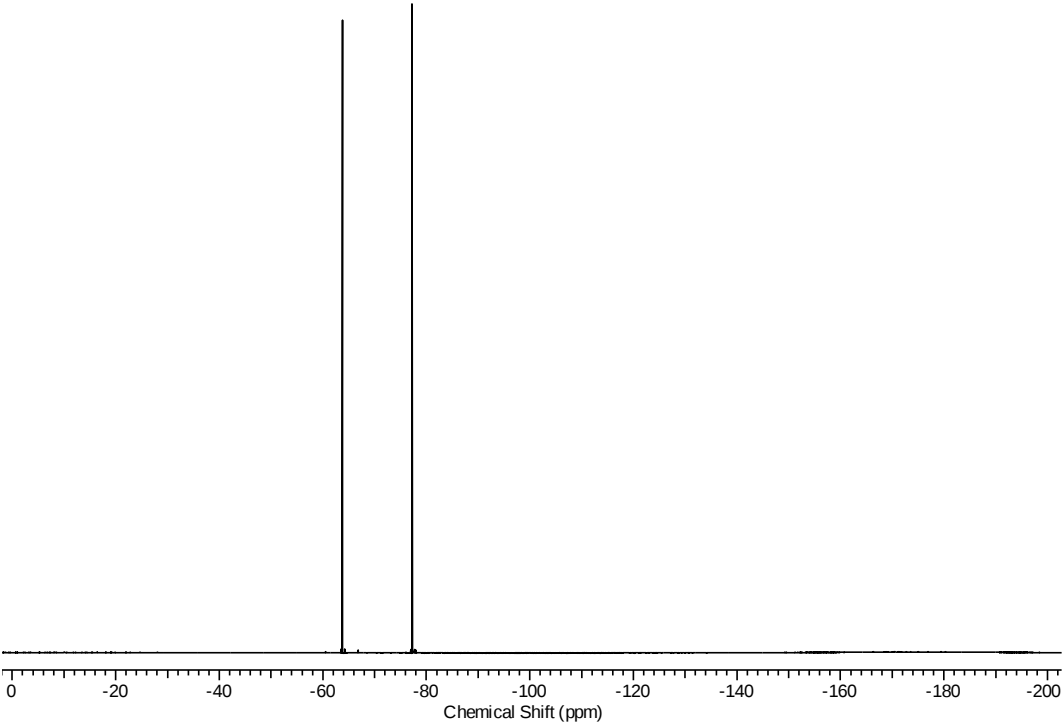
^1H NMR spectrum of 7



^{13}C NMR spectrum of 7

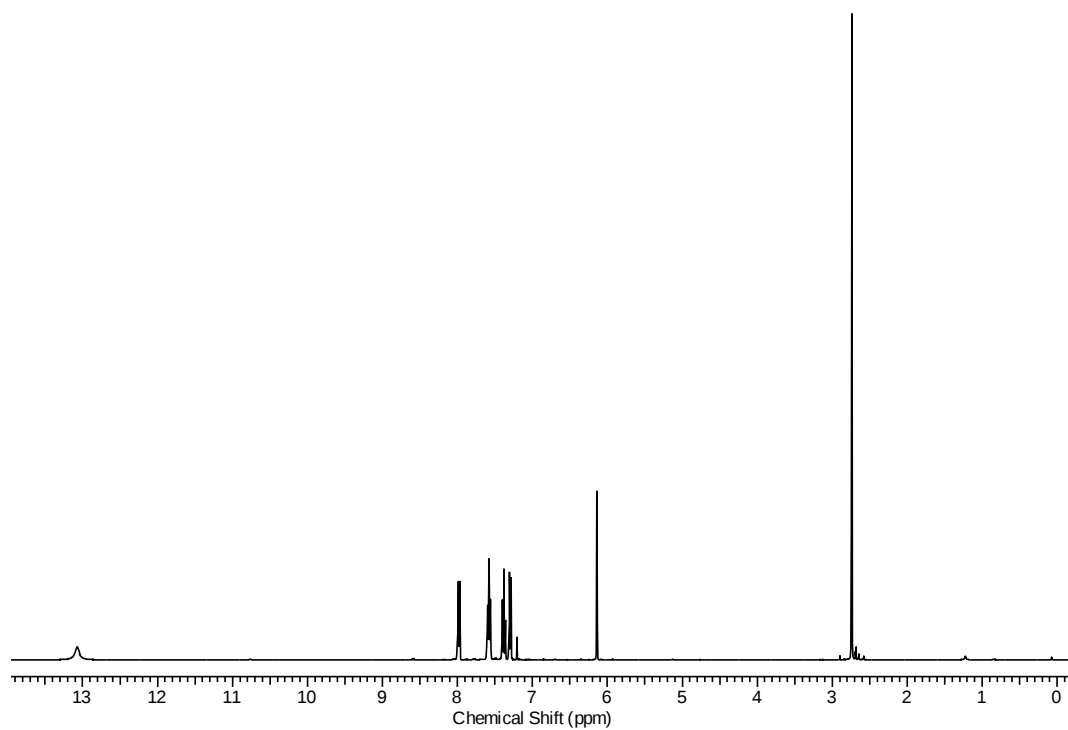


^{19}F NMR spectrum of **7**

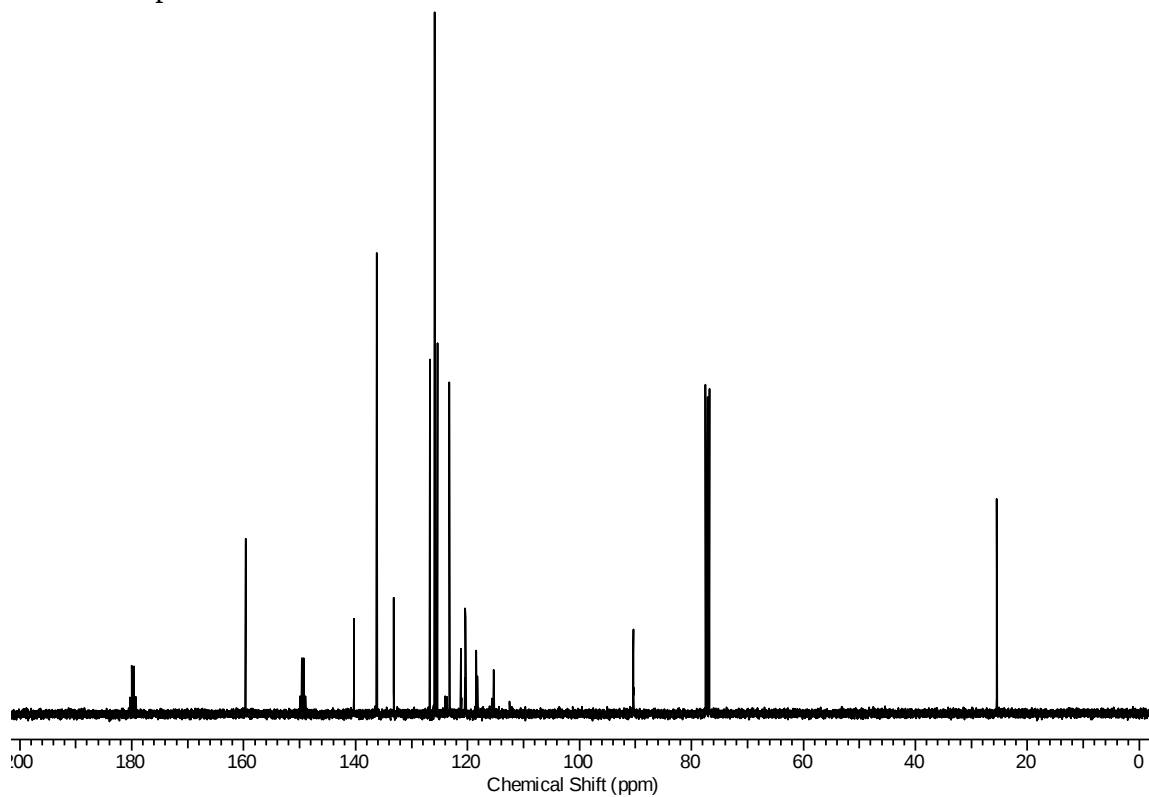


SI Figure 10. NMR spectra of compound **8**.

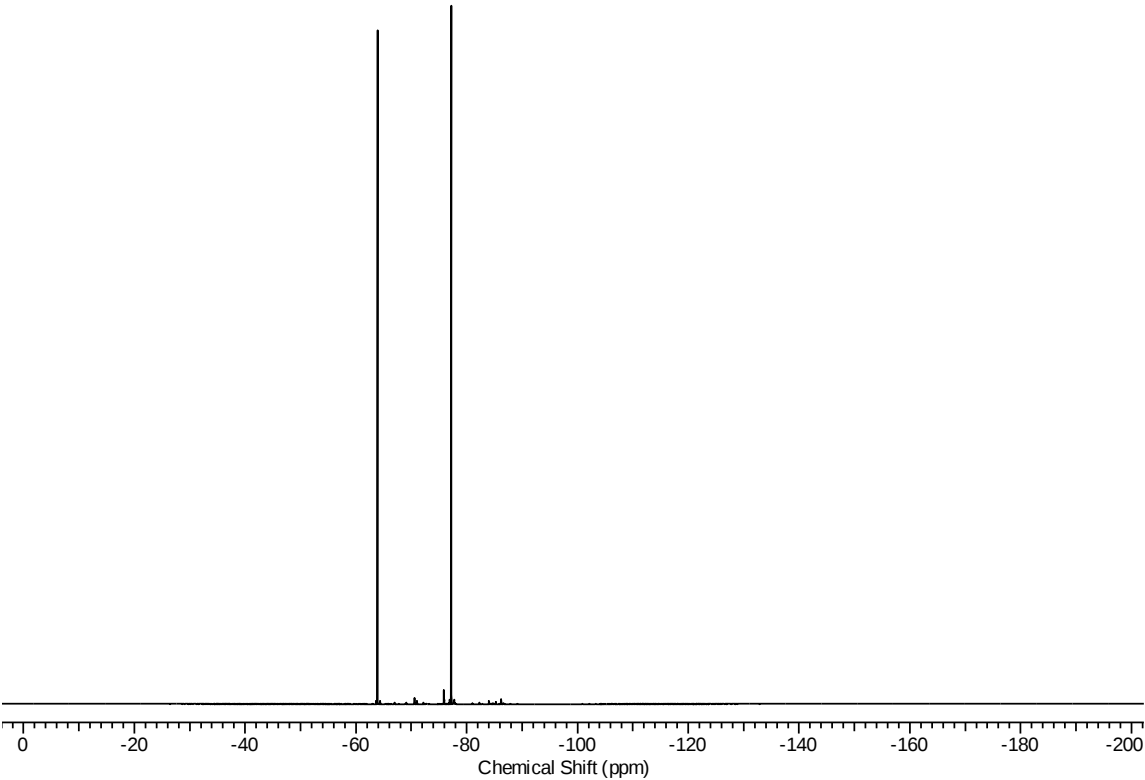
^1H NMR spectrum of **8**



^{13}C NMR spectrum of **8**

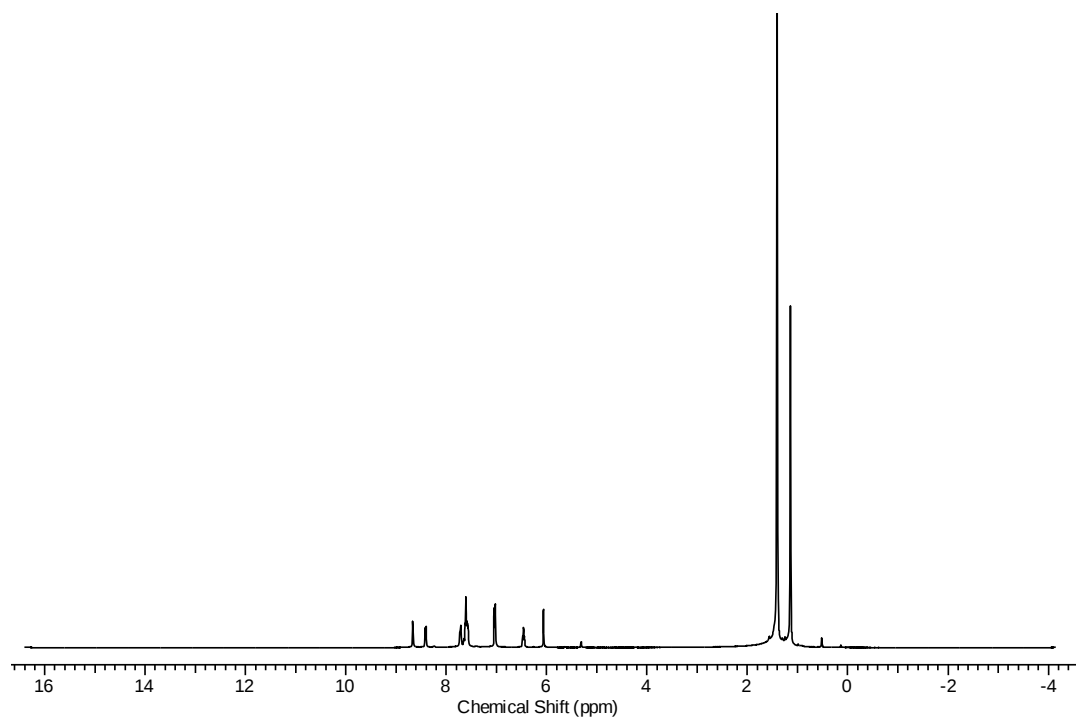


¹⁹F NMR spectrum of **8**

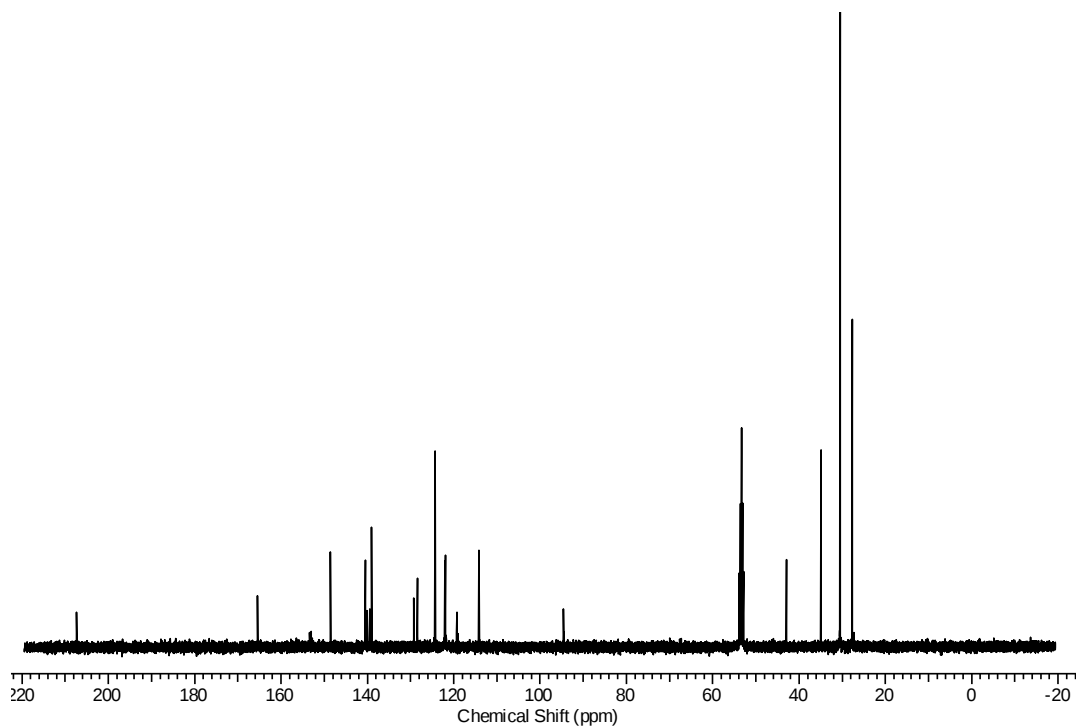


SI Figure 11. NMR spectra of compound **1a**.

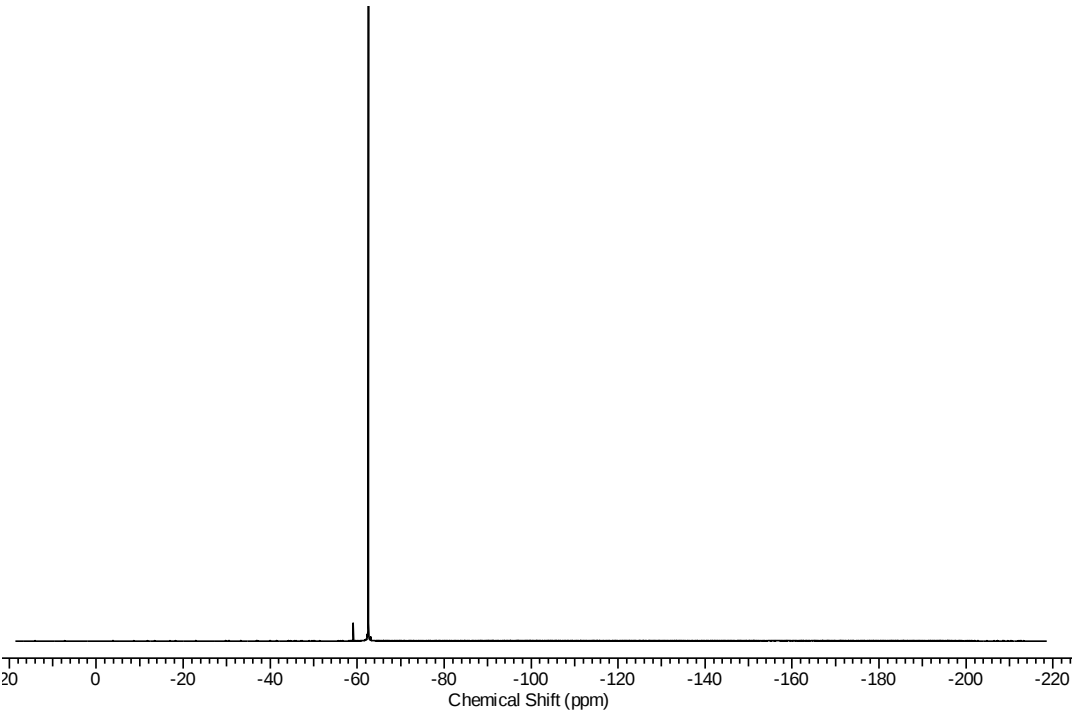
^1H NMR spectrum of **1a**



^{13}C NMR spectrum of **1a**

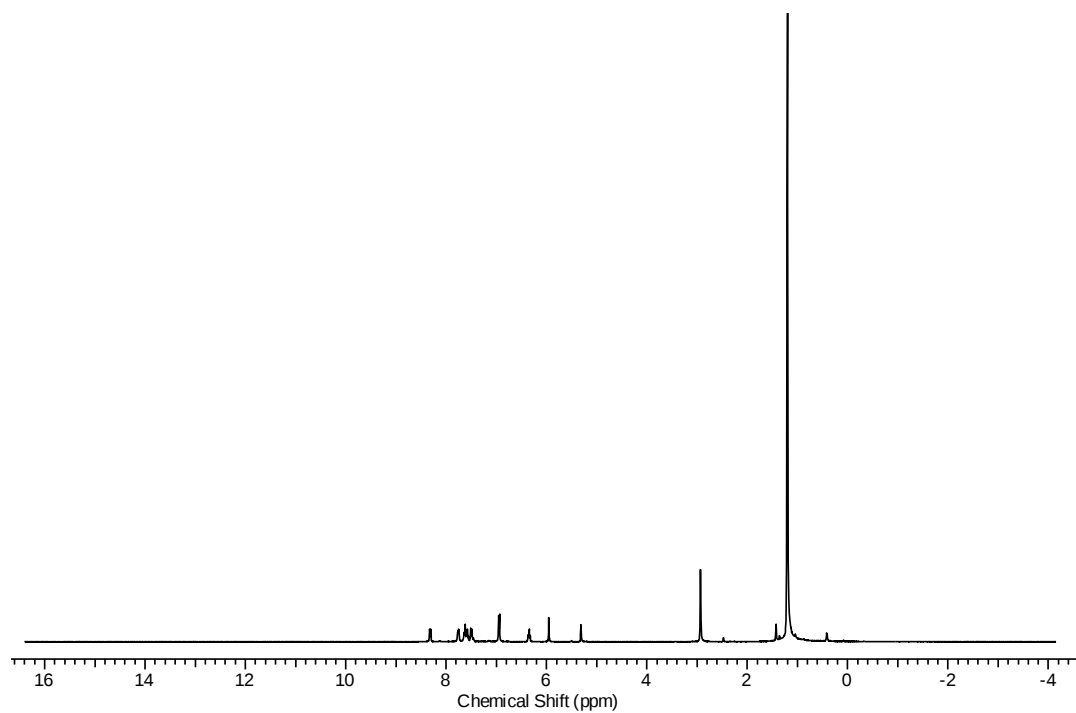


^{19}F NMR spectrum of **1a**

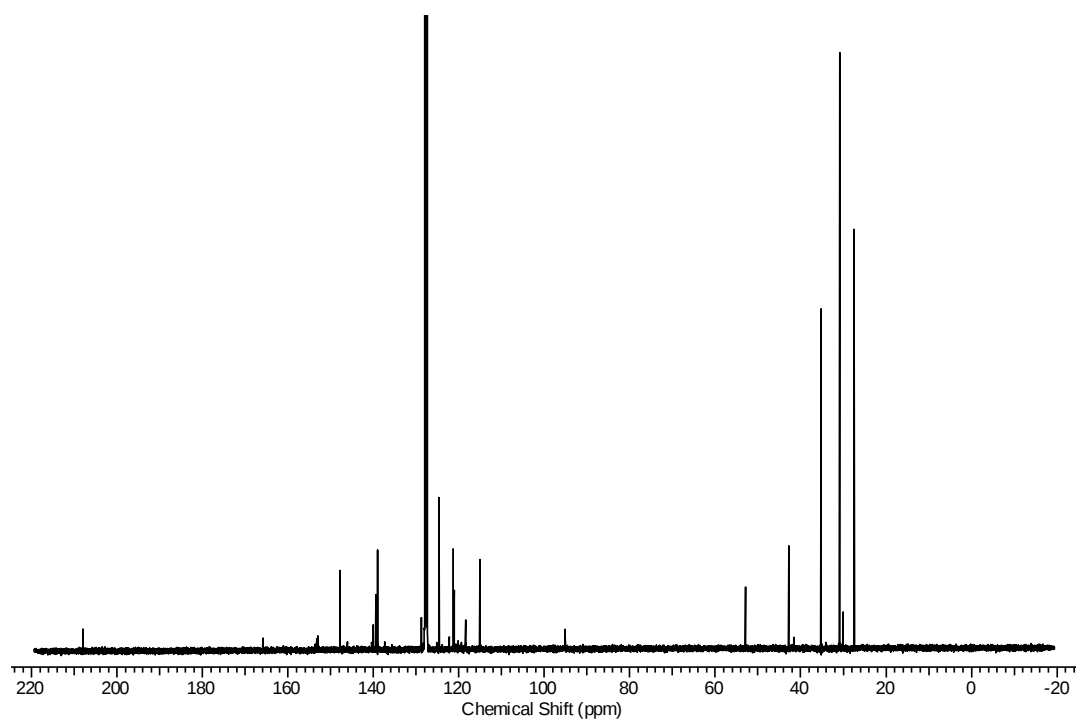


SI Figure 12. NMR spectra of compound **2a**.

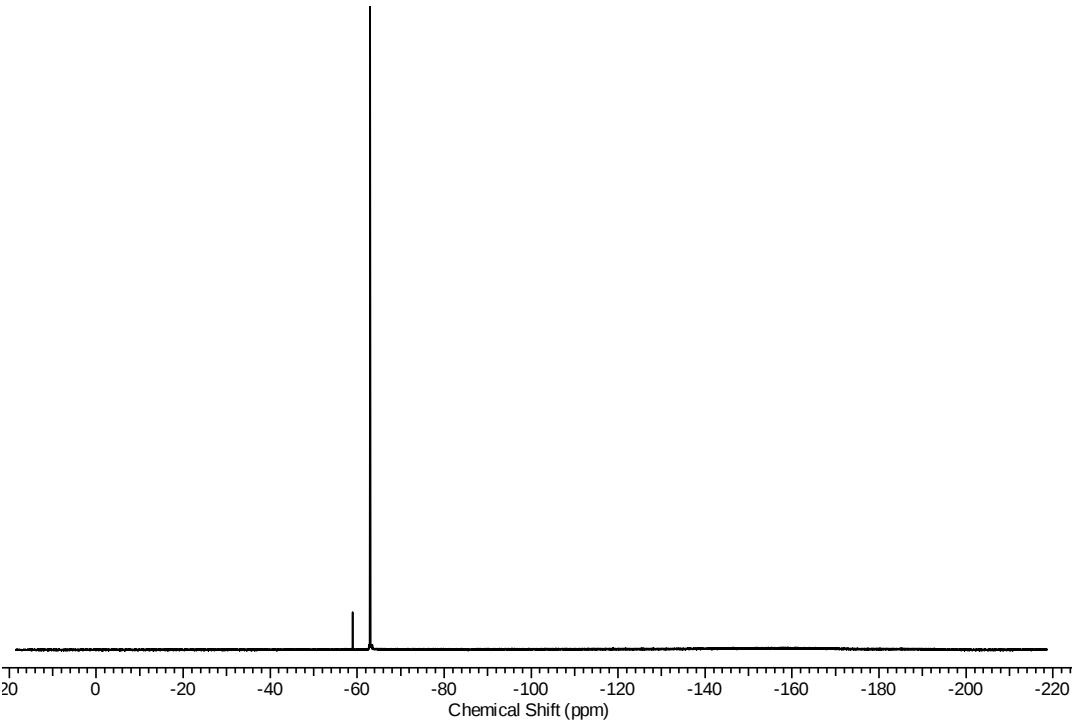
^1H NMR spectrum of **2a**



^{13}C NMR spectrum of **2a**

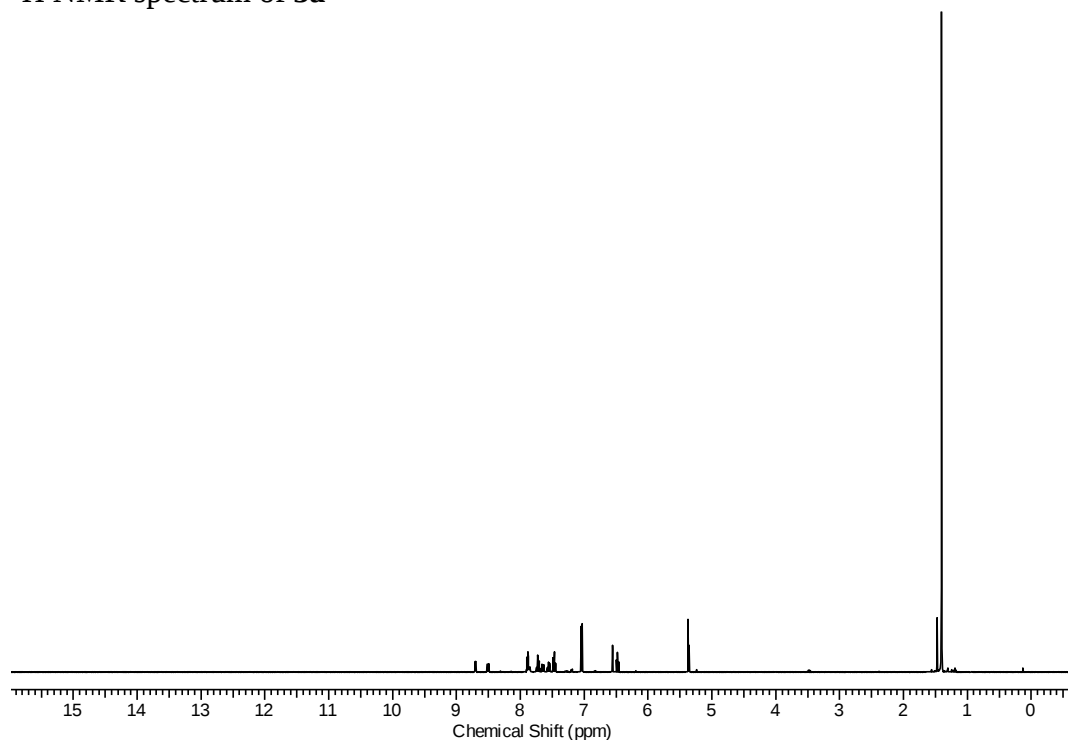


¹⁹F NMR spectrum of **2a**

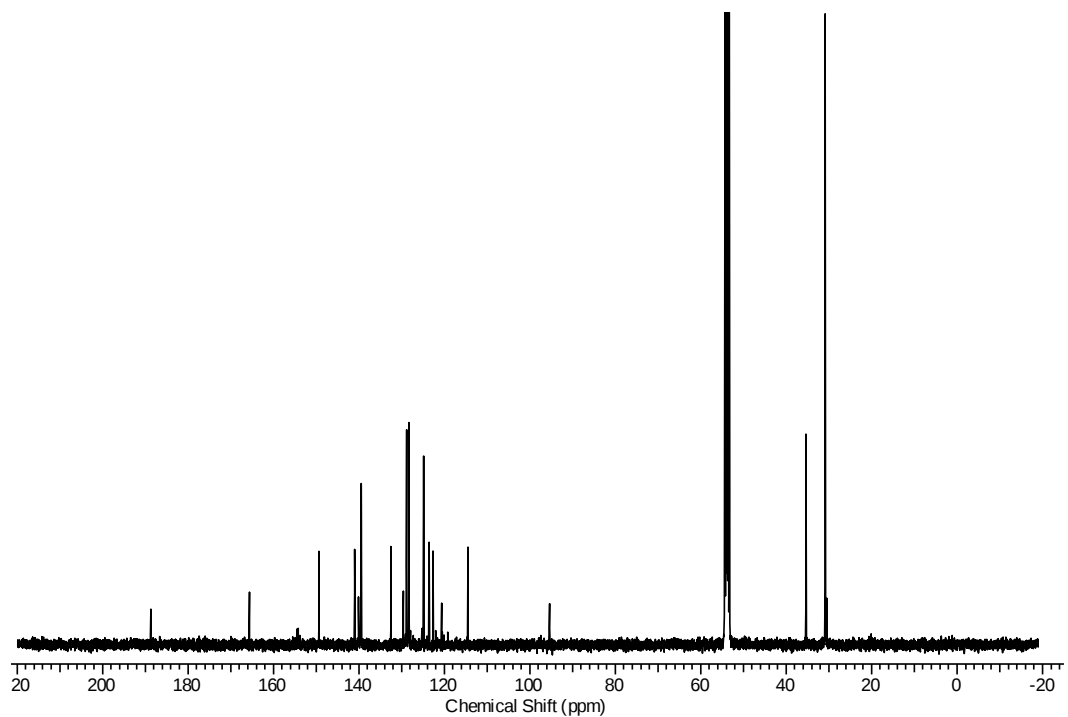


SI Figure 13. NMR spectra of compound **3a**.

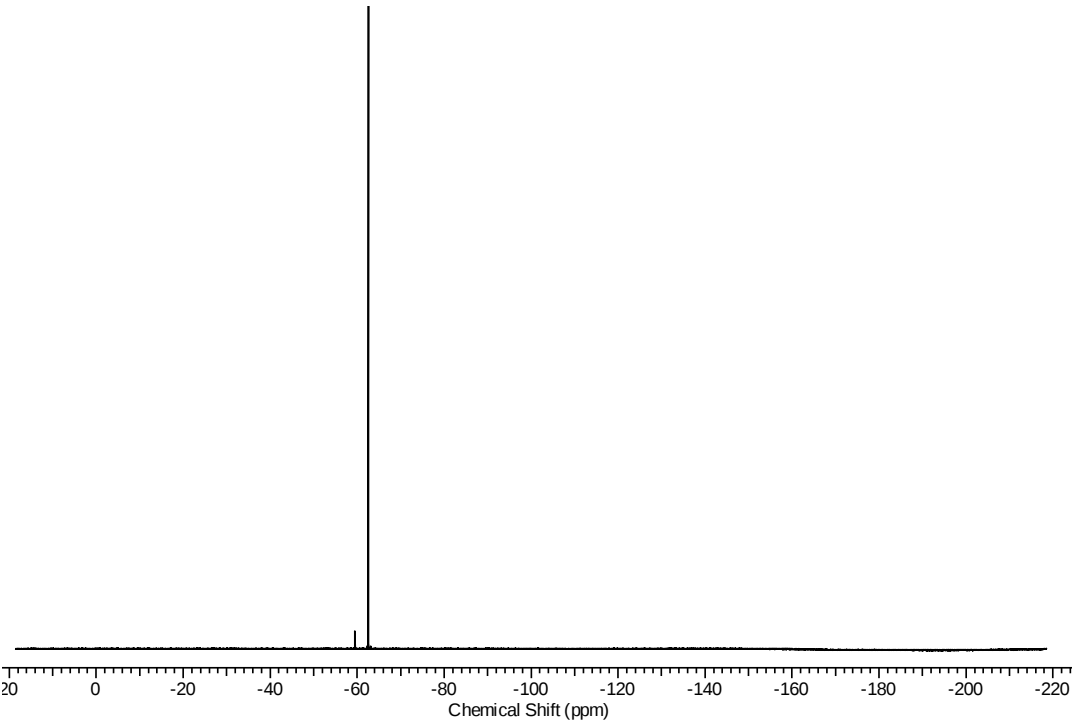
^1H NMR spectrum of **3a**



^{13}C NMR spectrum of **3a**

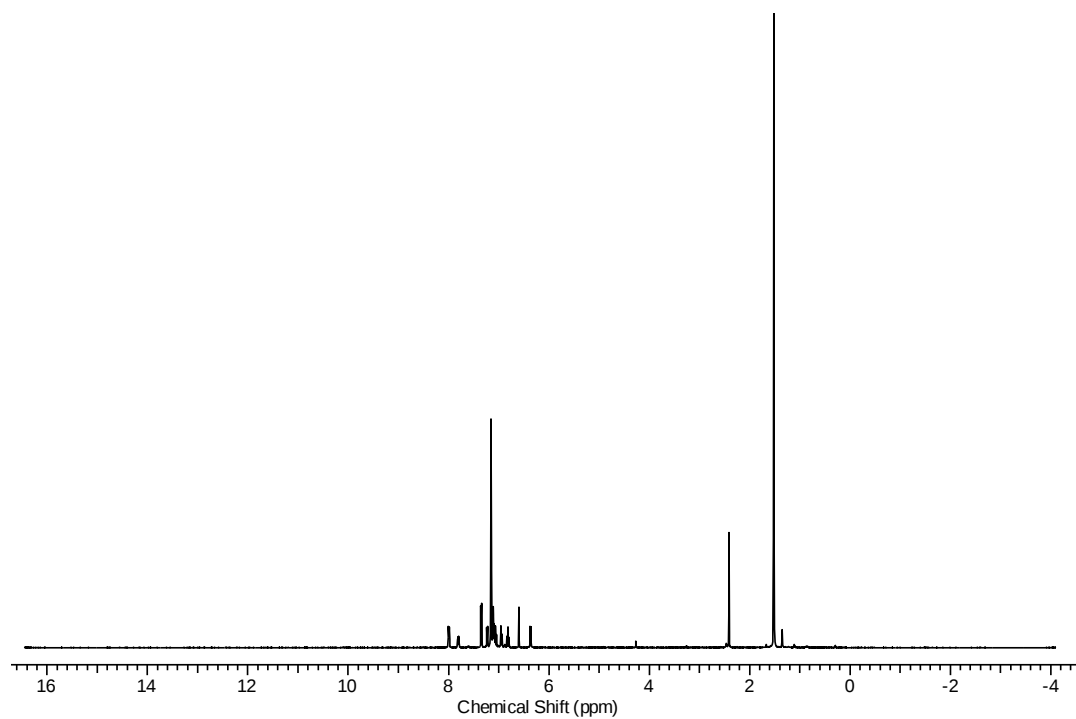


¹⁹F NMR spectrum of **3a**

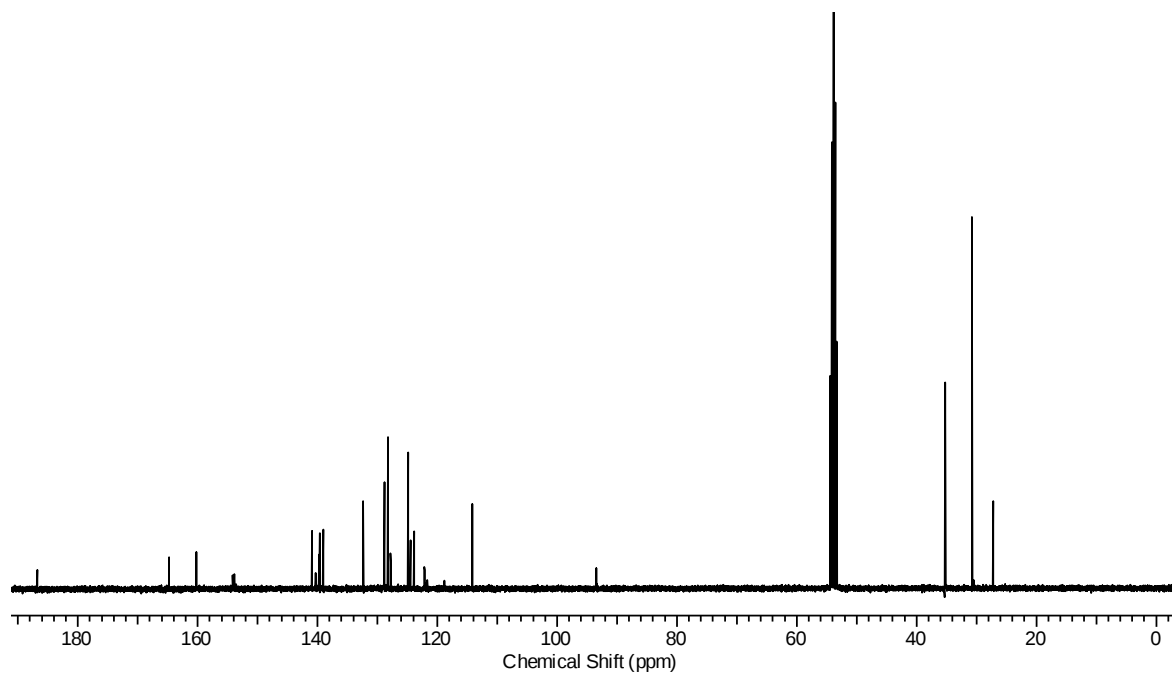


SI Figure 14. NMR spectra of compound **4a**.

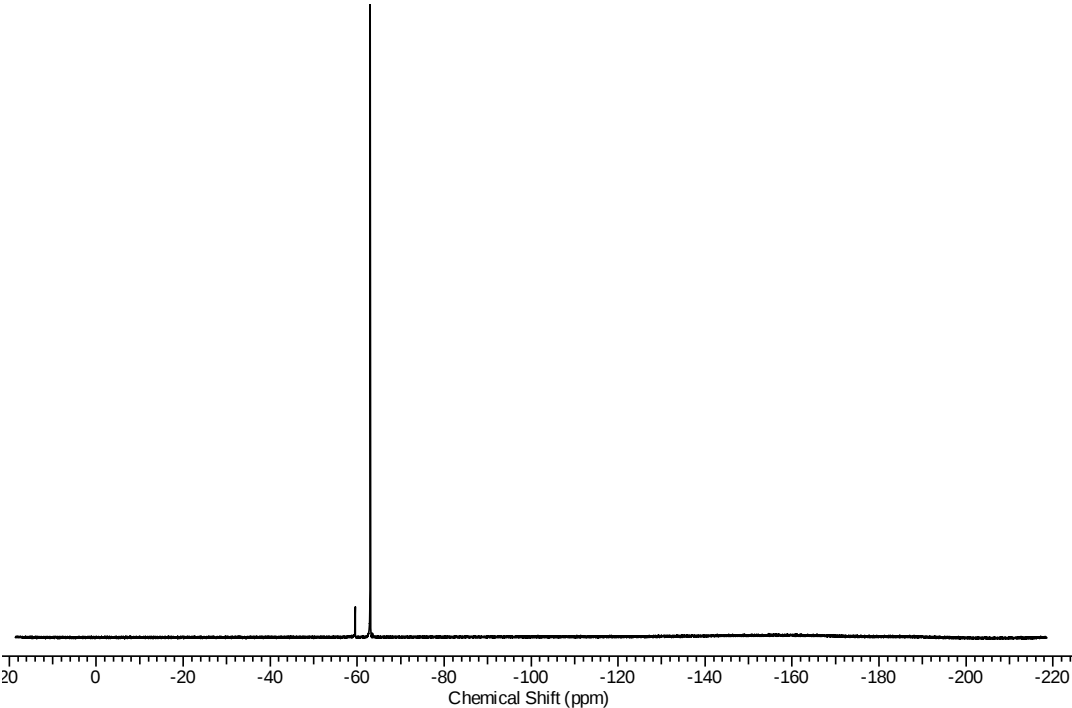
^1H NMR spectrum of **4a**



^{13}C NMR spectrum of **4a**

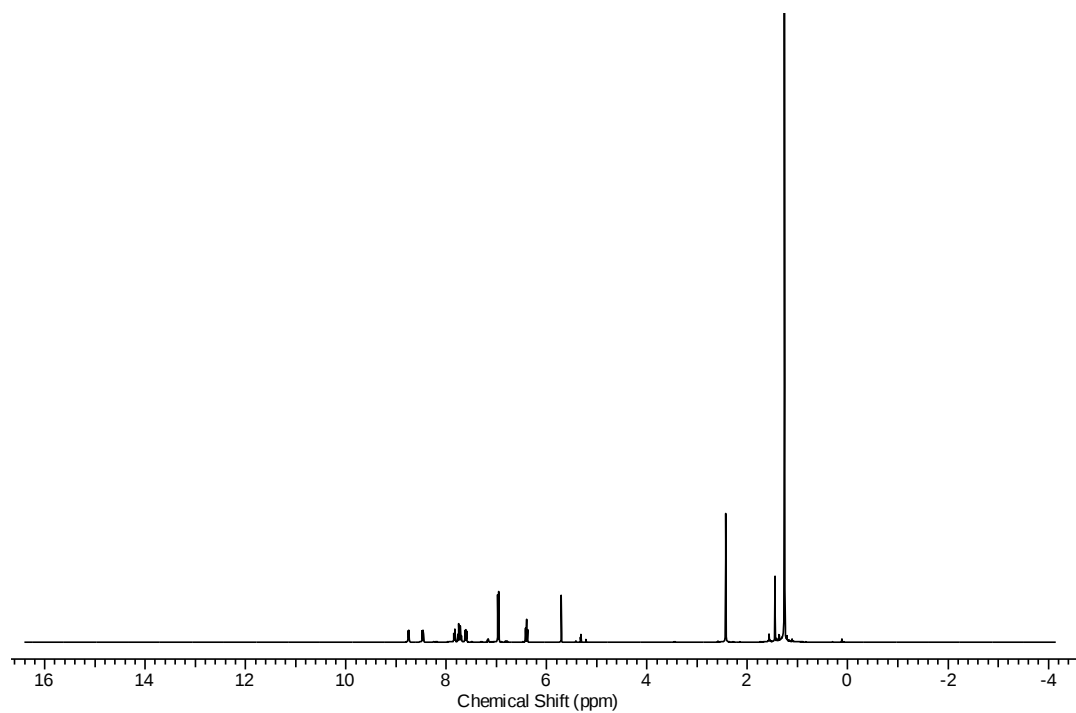


¹⁹F NMR spectrum of **4a**

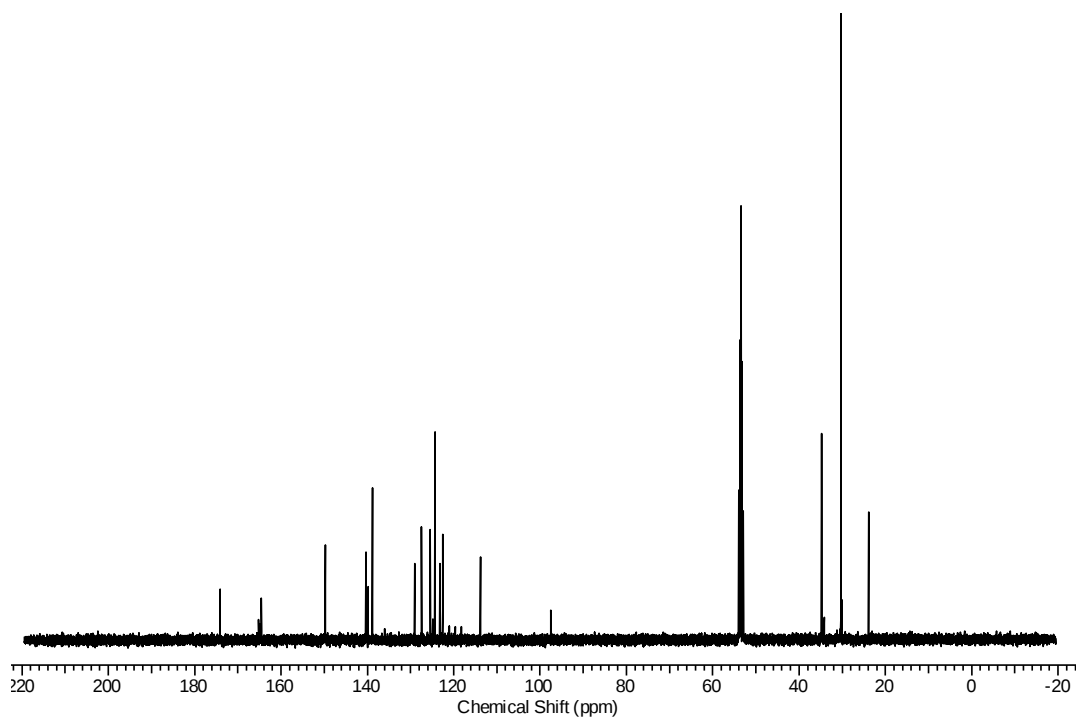


SI Figure 15. NMR spectra of compound **5a**.

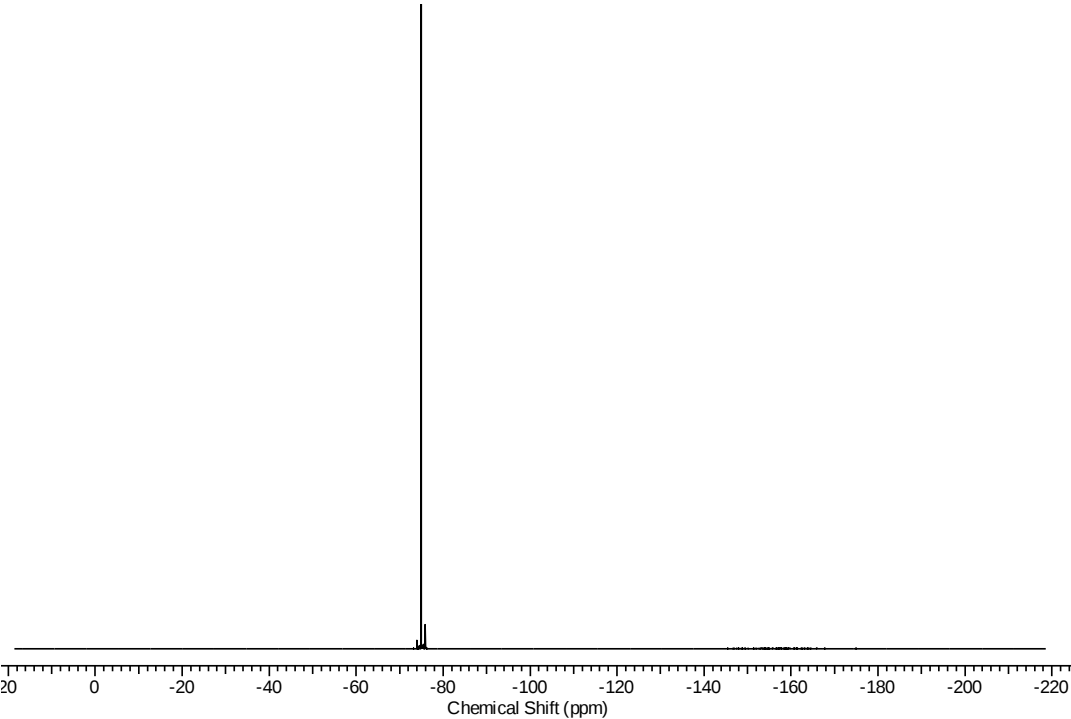
^1H NMR spectrum of **5a**



^{13}C NMR spectrum of **5a**

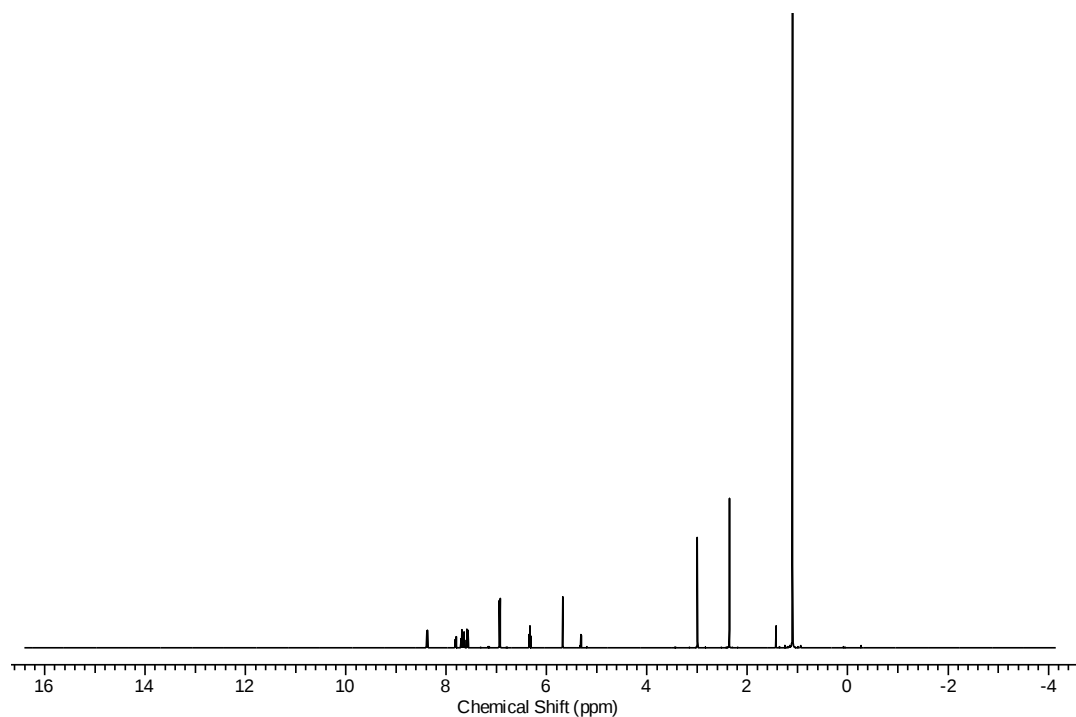


^{19}F NMR spectrum of **5a**

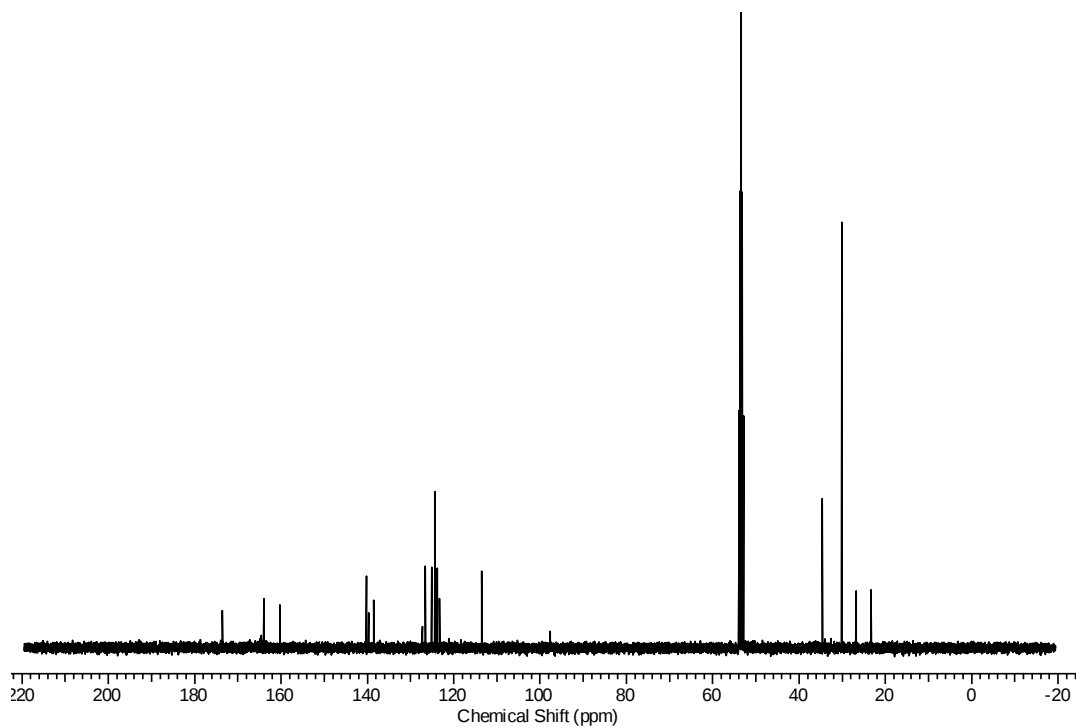


SI Figure 16. NMR spectra of compound **6a**.

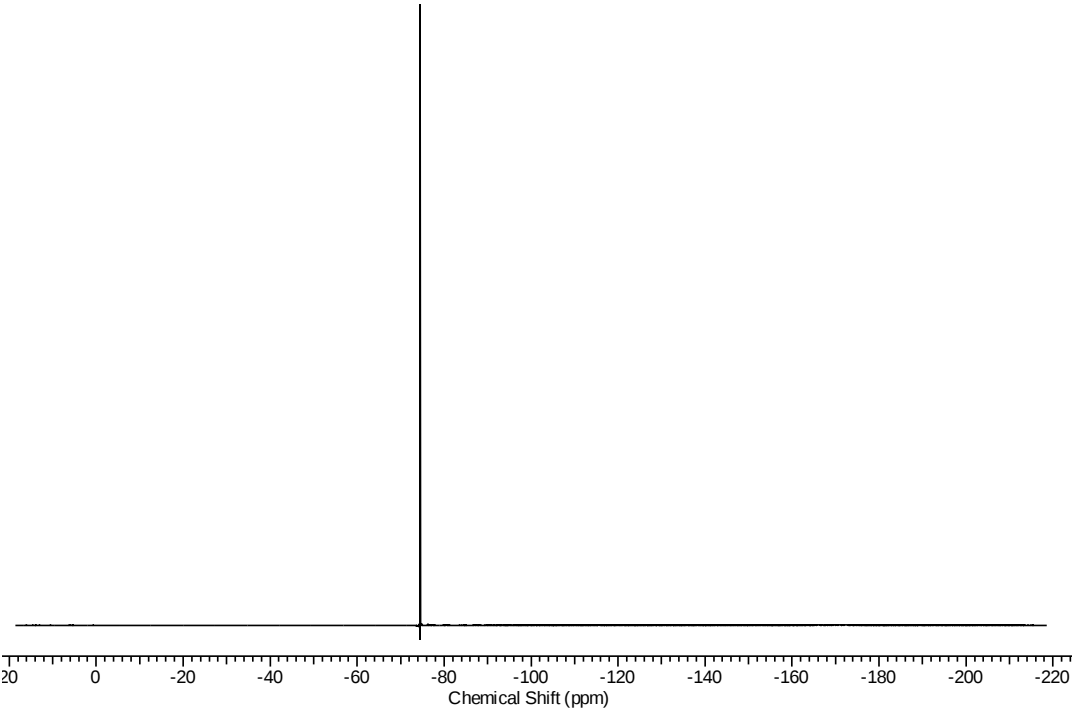
^1H NMR spectrum of **6a**



^{13}C NMR spectrum of **6a**

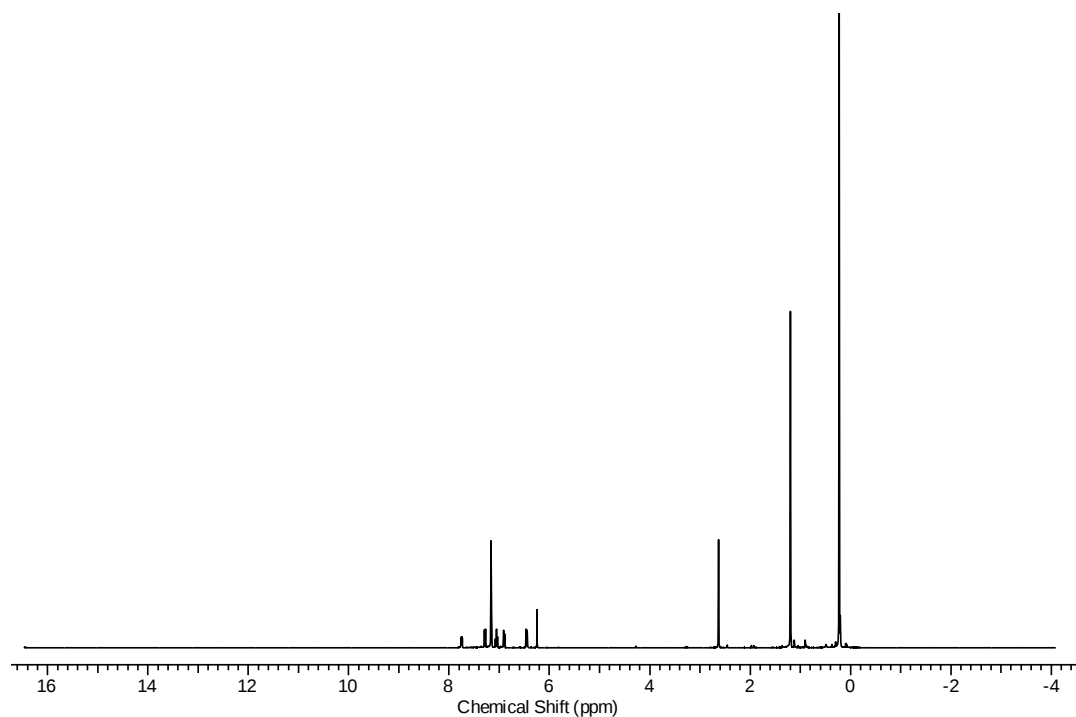


^{19}F NMR spectrum of **6a**

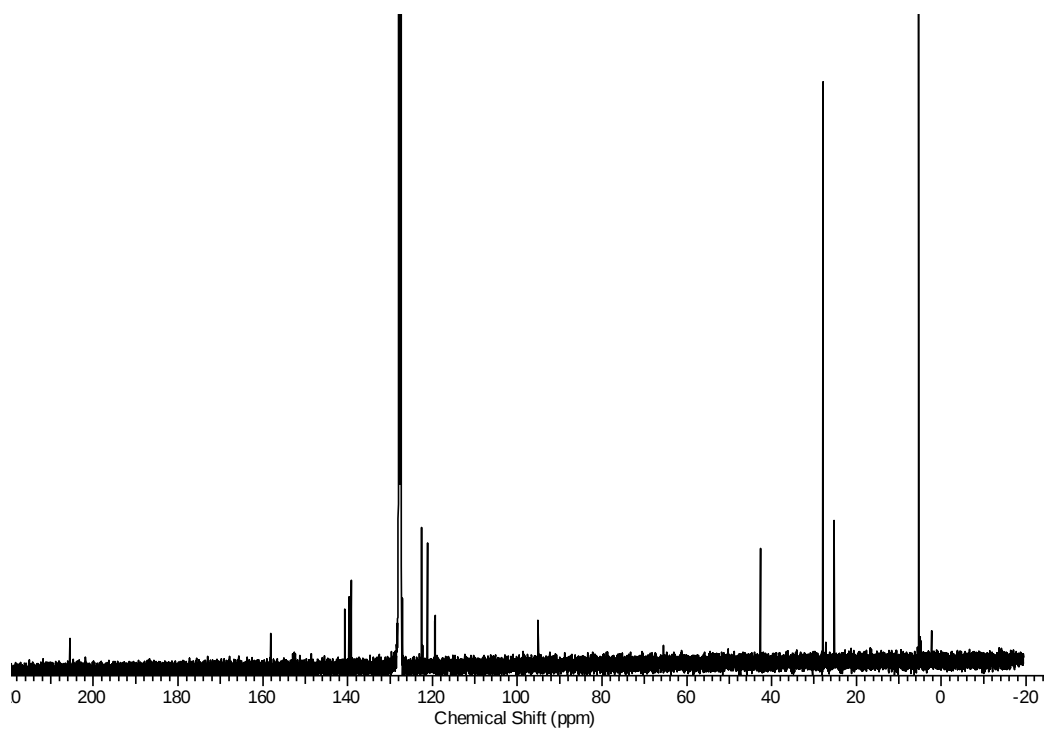


SI Figure 17. NMR spectra of compound **2b**.

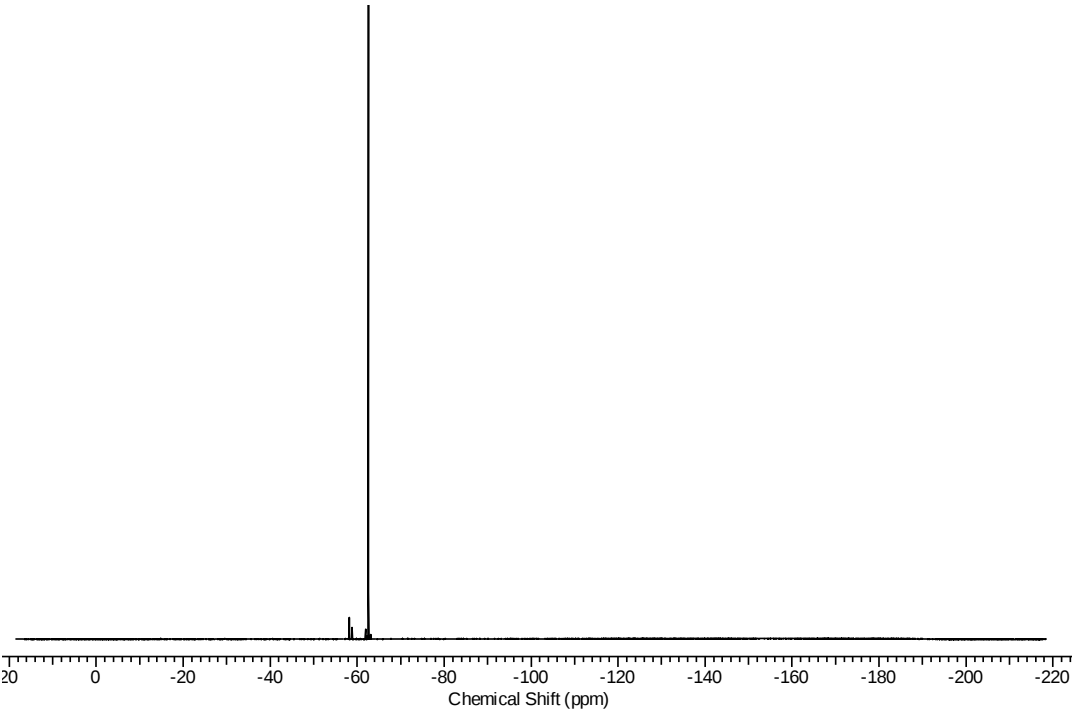
^1H NMR spectrum of **2b**



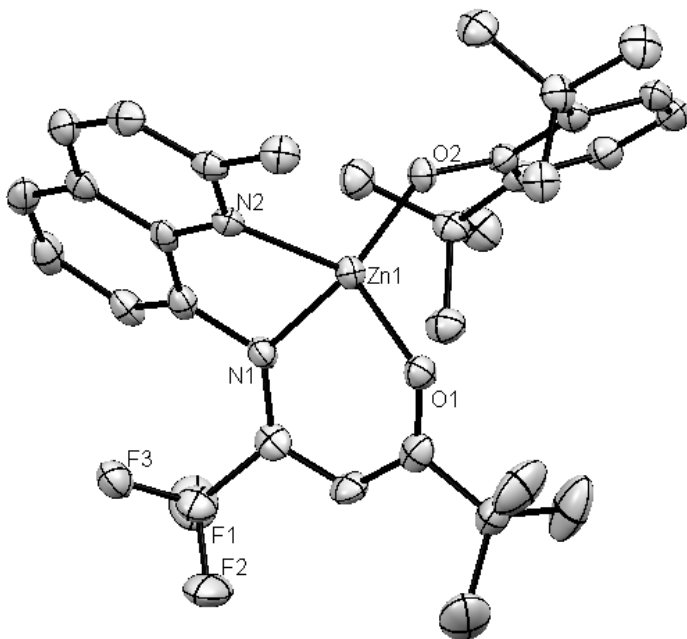
^{13}C NMR spectrum of **2b**



^{19}F NMR spectrum of **2b**

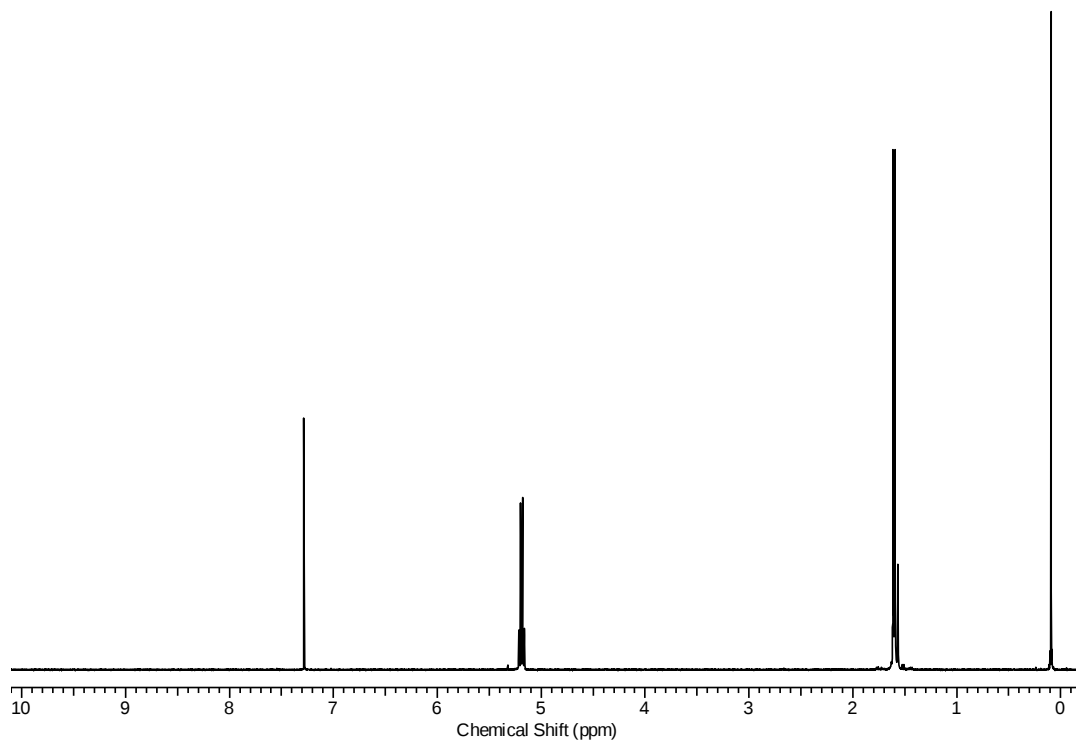


SI Figure 18. ORTEP diagram of the molecular structure of **2a** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

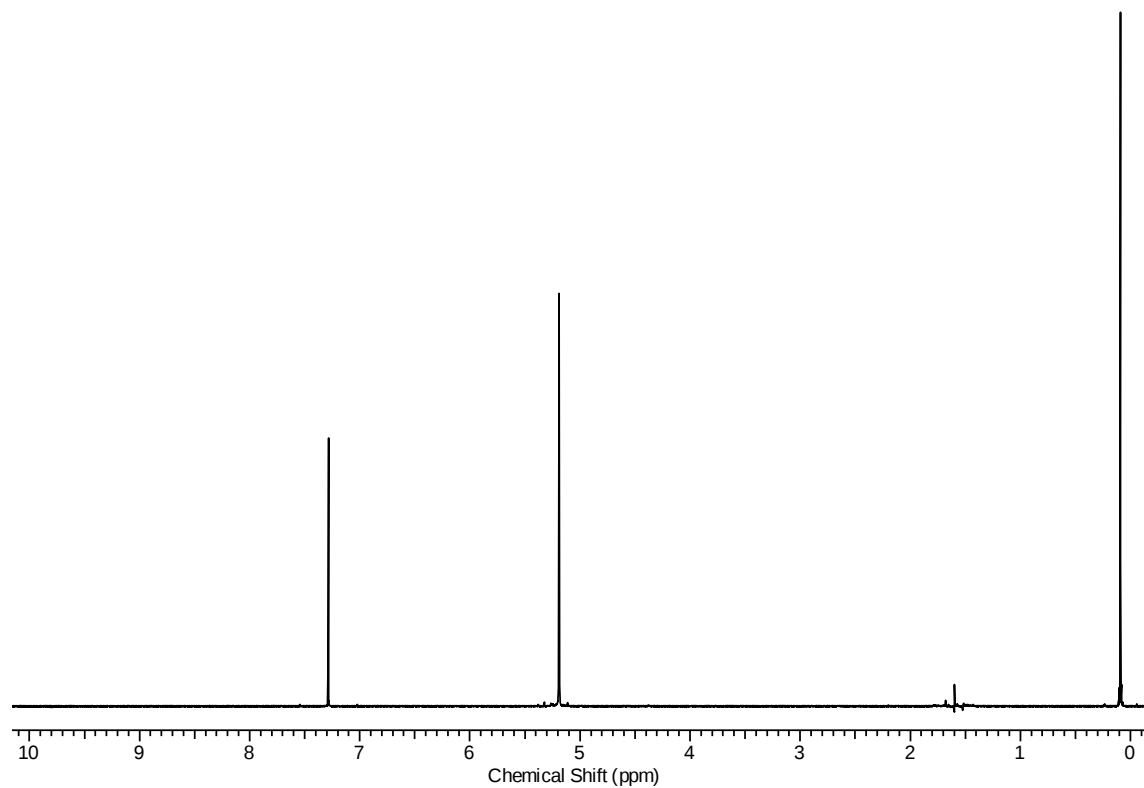


Data on isolated Poly-lactic acid

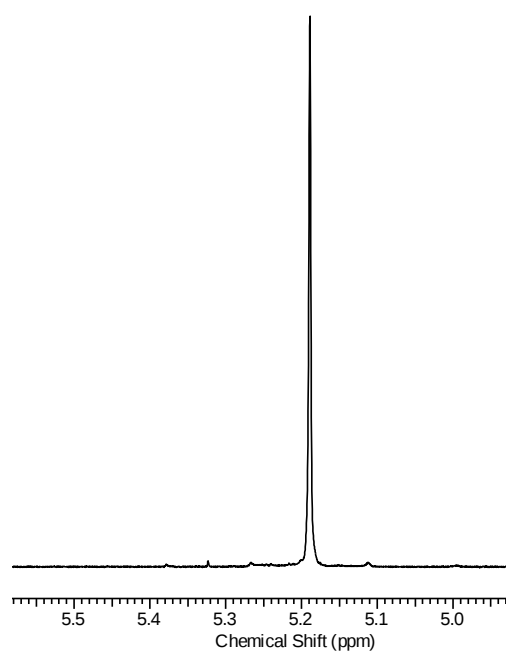
SI Figure 19. ^1H NMR spectrum of isolated PLLA from $[\text{L-lac}]:[\mathbf{1a}]=500$ to 1, Table 4 entry 4



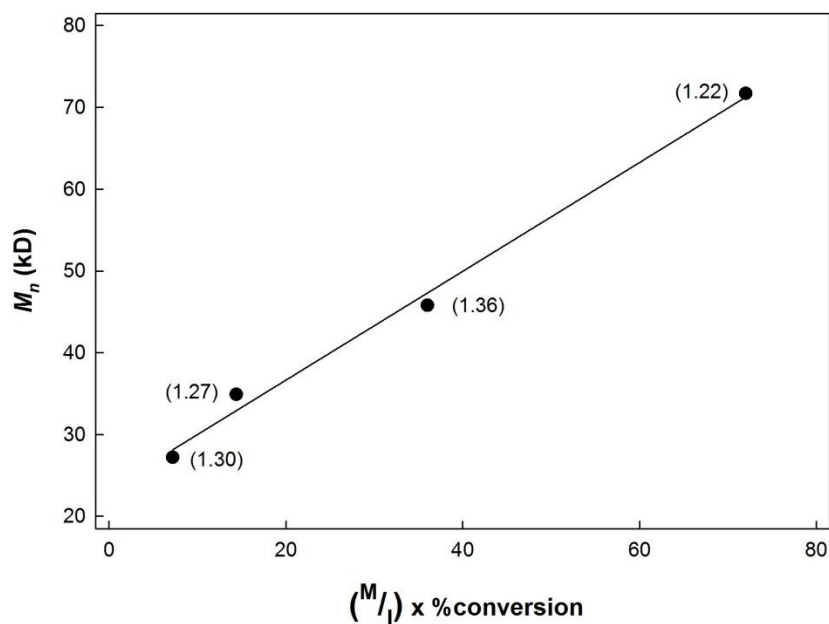
SI Figure 20. $\{^1\text{H}\}^1\text{H}$ NMR spectrum of isolated PLLA from [L-lac]:[**1a**]=500 to 1, Table 4 entry 4



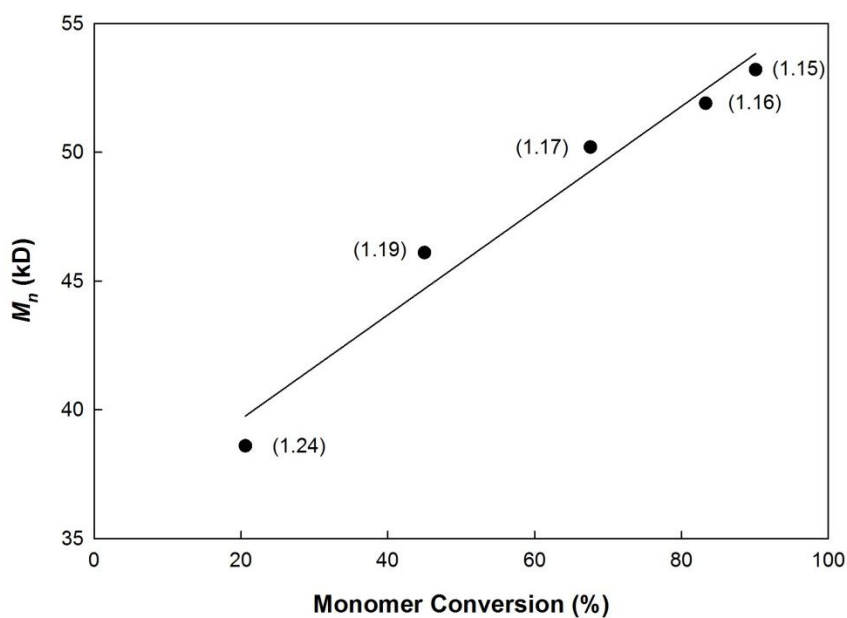
Inset from above $\{^1\text{H}\}^1\text{H}$ NMR spectrum



SI Figure 21. Linear relationship observed between M_n and monomer/initiator ratio of PLA produced from the ROP of L-lactide by **1a** in CH_2Cl_2 .



SI Figure 22. PLA M_n versus percentage conversion for the ring opening polymerization of L-Lactide by **1a**; $[\text{L-lactide}]/[\mathbf{1a}]_0 = 100$, CDCl_3 , ambient temperature. PDI values are provided in parentheses.



SI Figure 23. Chromatograms of polymeric materials isolated in double feed experiment with **1a**. Chromatogram of isolated PLLA after treatment of **1a** with 250 mg of L-lactide and 3 h of reaction time (solid line, M_n = 17.9 kDa, PDI = 1.27) and chromatogram of isolated PLLA after second addition of 250 mg of L-lactide and 3 additional hours of reaction time (dashed line, M_n = 30.1 kDa, PDI = 1.24).

