Supplementary Information (SI) for Organic & Biomolecular Chemistry.
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Experimental Supporting Information

Atom-Efficient Chlorinative Dearomatization of Naphthol, Quinolinol, and Isoquinolinol Derivatives using Trichloroisocyanuric Acid (TCCA)

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Substrates that failed or gave complex mixtures:

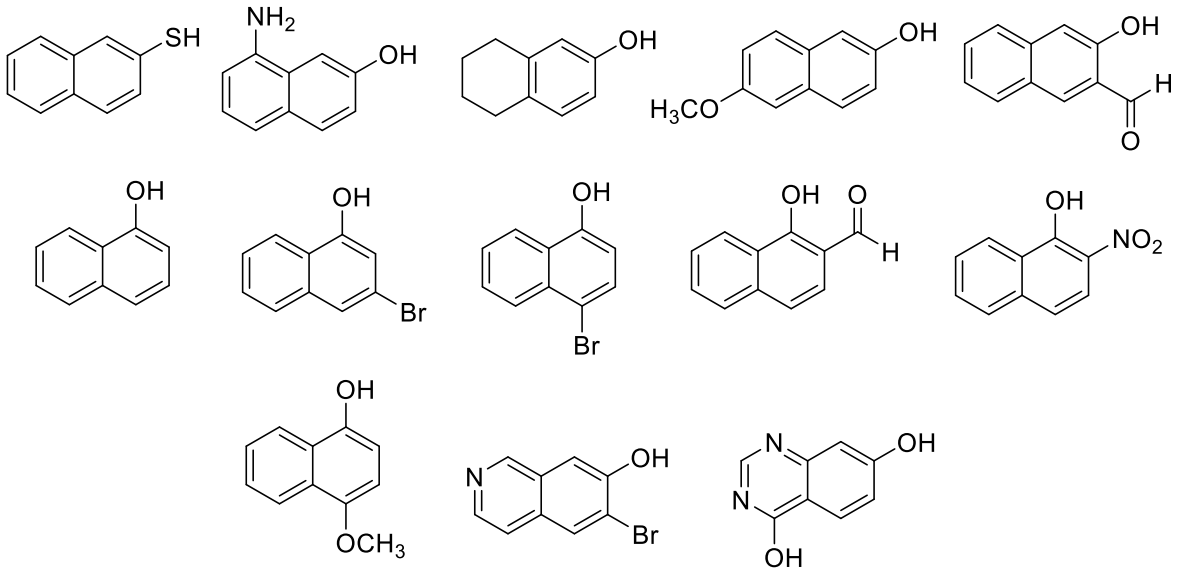


Figure S1. Substrates that failed or gave complex mixtures.

The interaction between 1-chloro-2-naphthol and DCCA was examined (HF-DFT SCF/ωB97X-D/6-31G*/C-PCM: acetonitrile as solvent).

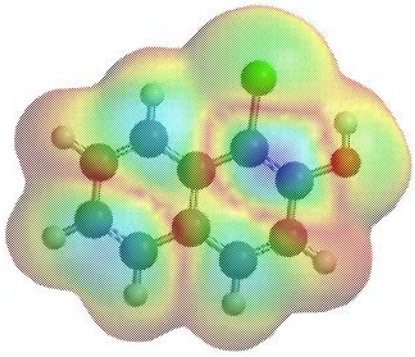


Figure S2. The availability of the HOMO for 1-chloro-2-naphthol is shown in blue.

This model suggests strongly that there are four possible sites for electrophilic attack (shown with blue tint) with the maximum HOMO availability at the 1-position. Attack at this position is enhanced by the potential hydrogen bonding between the OH functionality at the 2-position and DCCA.

The potential energy surface for the intermolecular interactions between the 1-chloro-2-naphthol and DCCA shows three types of potential energy wells: hydrogen bonding (shown in the article results and discussion), DCCA chlorine atom to π-cloud interactions, and π-stacking interactions. The deepest of these wells involve hydrogen bonding interactions in which the oxygen atom of the naphthol can act as either a hydrogen bond donor or acceptor with the DCCA molecule.

Shallower wells that do not involve hydrogen bonding also exist. Those interactions show weaker intermolecular interaction between the chlorine atom of the DCCA and the π system of the substituted naphthalene ring (shown below).

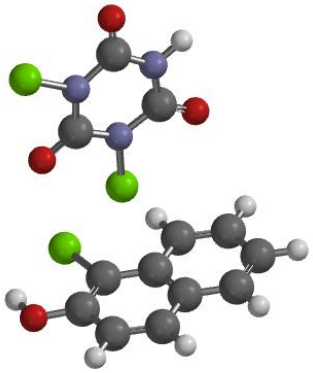


Figure S3. DCCA chlorine atom to π-cloud interaction

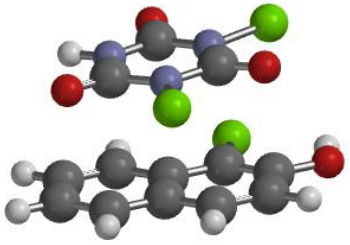


Figure S4. π-stacking interaction

In the case of the hydrogen bonding interactions, the attraction draws the DCCA close to the 1-position of the naphthalene. This attraction catalyzes the chlorination at the 1-position relative to either chlorination of the 4-position or chlorination of the unsubstituted ring. As a result, the kinetic product of 1,1-dichloro-2-naphthone is favored over the thermodynamic product of 1,4-dichloro-2-naphthol which is about 54 $kJ \cdot mol^{-1}$ more stable.

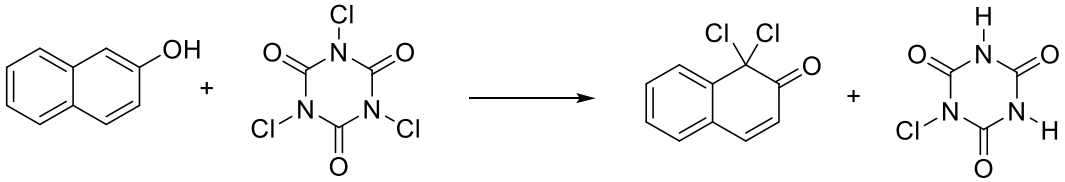
Determination of reaction mechanism:

Restricted hybrid HF-DFT SCF calculations were performed using Pulay DIIS + geometric direct minimization and a ωB97X-D/6-31G* model. A polarizable continuum solvation model (C-PCM) was applied using a dielectric of 37.50 simulating acetonitrile. Calculations were conducted using Spartan'24 version 1.0 (by Wavefunction Inc.). TCCA = trichloroisocyanuric acid; DCCA = dichloroisocyanuric acid; MCCA = monochloroisocyanuric acid.

Species	G^o (in au)	H^o (in au)
2-Naphthol	-460.851009	-460.809492
TCCA	-1884.53404	-1884.48756
TCCA_2Naphthol_TS_acetonitrile	-2345.34751	-2345.28436
1-chloro-2-naphthonium	-920.836057	-920.791949
DCCA- ion	-1424.55563	-1424.51138
1-chloro-2-naphthol	-920.441096	-920.396931
DCCA_N-H	-1425.00845	-1424.9639
DCCA_NH__1chloro2Naphthol_TS	-2345.39388	-2345.33077
1-1-dichloro_2naphthonium+	-1380.40829	-1380.36157
MCCA-_ion	-965.018821	-964.977318
1,1-dichloro_2_naphthone	-1380.00968	-1379.96315
1,4-dichloro-2-naphthol	-1380.03012	-1379.98323
MCCA	-965.479357	-965.43817

Table S1. Enthalpic values calculated using a HF-DFT SCF model.

The overall energy profile is shown below and consists of the following steps (1-6).



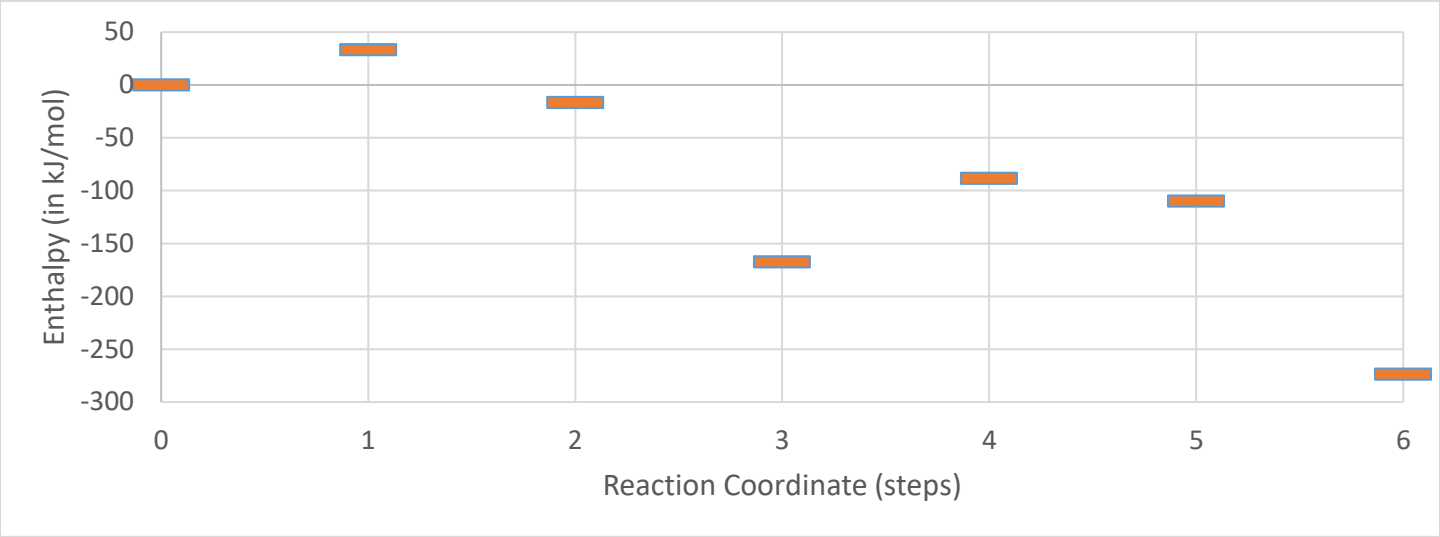
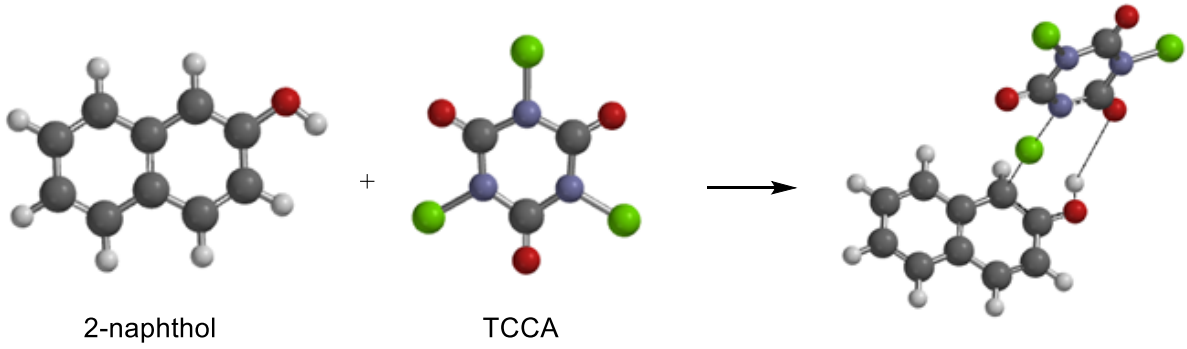


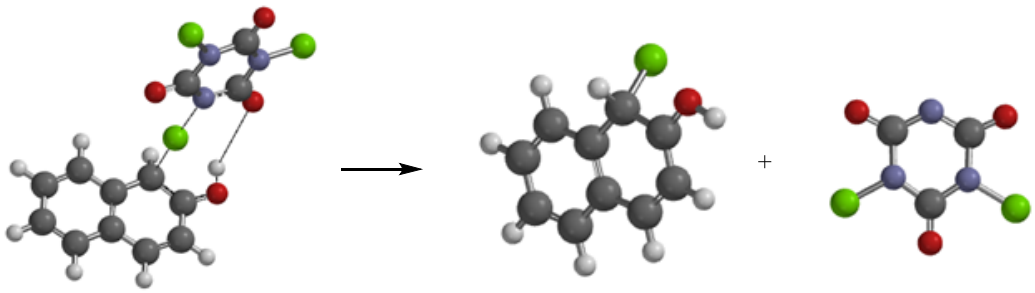
Figure S5. Mechanistic energy profile of the conversion of 2-naphthol to 1,1-dichloronaphtalen-2-one.

The enthalpy profile was produced along the reaction coordinate defined by the following steps:

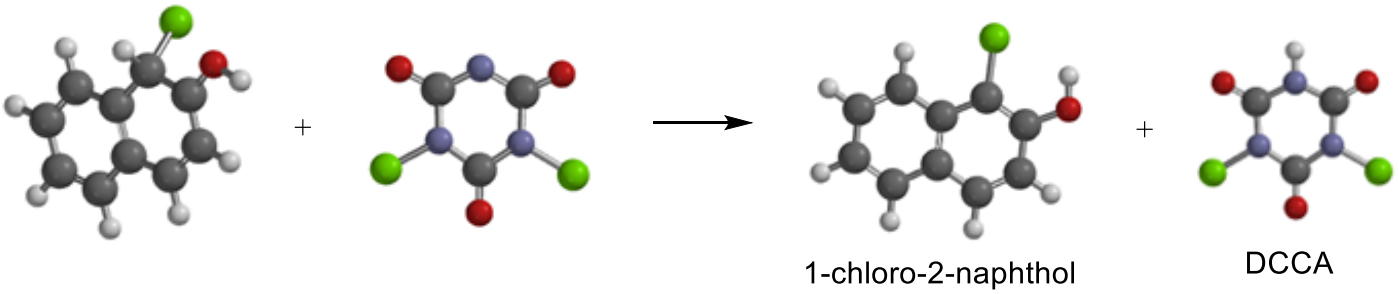
Step 1: Formation of the chlorination transition state



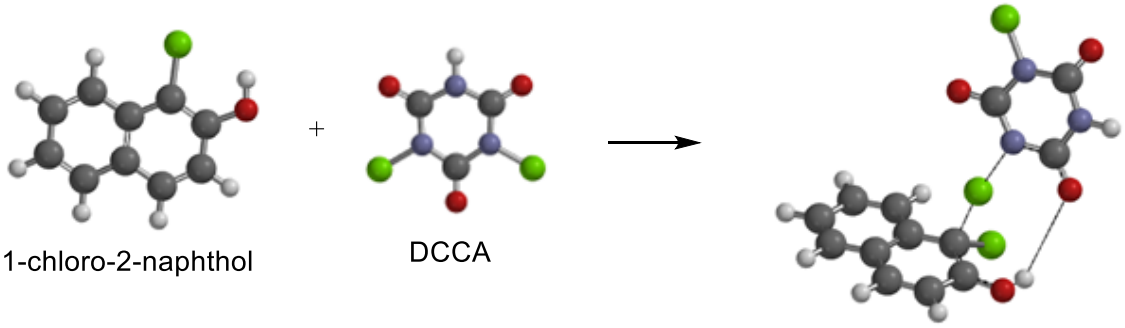
Step 2: Formation of the 1-chloro-2-naphthonium ion



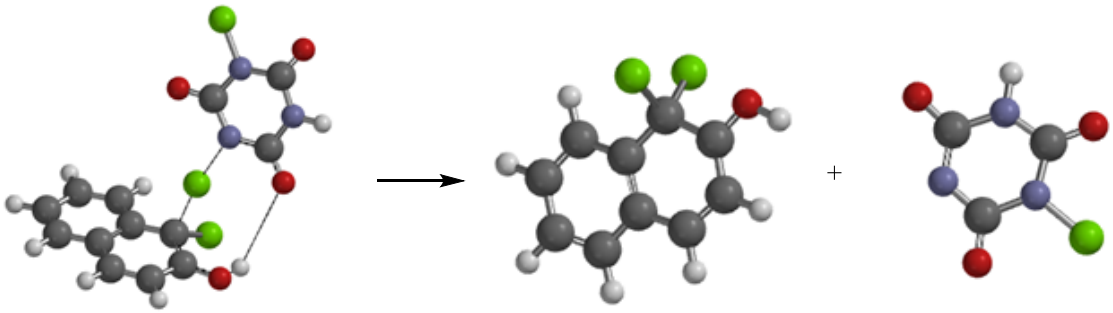
Step 3: Deprotonation of C-1 of the 1-chloro-2-naphthonium ion to produce the 1-chloro-2-naphthol



Step 4: Formation of the transition state during the chlorination of 1-chloro-2-naphthol



Step 5: Formation of the 1,1-dichloro-2-naphthonium cation



Step 6: Deprotonation of the 1,1-dichloro-2-naphthonium ion to produce the 1,1-dichloronaphthalen-2-one

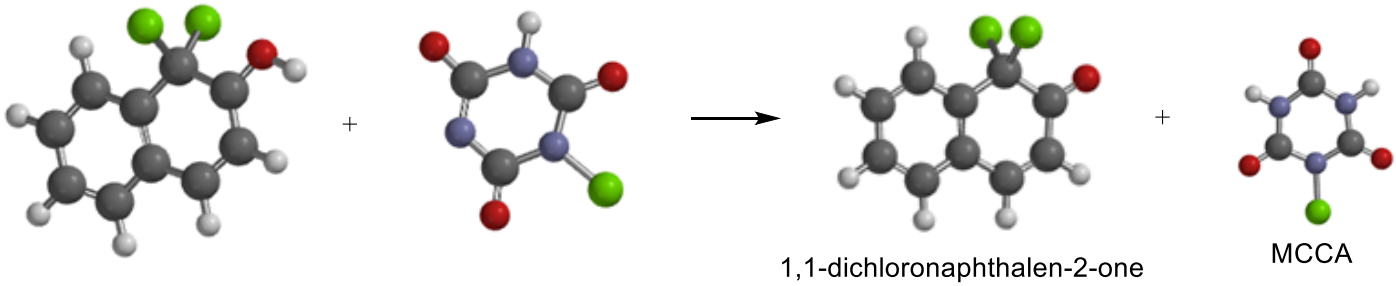


Figure S6. Ball and stick models of mechanistic steps 1-6.

The transition states in Step 1 and Step 4 yield a single imaginary corresponding to the chlorine atom transfer at 352 cm^{-1} and 311 cm^{-1} respectively. The transition state searches allowed for a concerted mechanism in which the chlorine atom and the proton on the oxygen atom could be transferred; however, the modeling suggested that these two processes occur consecutively.

The activation enthalpy of Step 1 is +33 $kJ{\cdot}mol^{-1}$ and that of Step 4 is +79 $kJ{\cdot}mol^{-1}$, suggesting that the second chlorination step is rate determining. The overall process is highly exergonic, downhill by about 270 $kJ{\cdot}mol^{-1}$.

The relative stability of the N-H DCCA and the O-H DCCA was also modeled employing an HF-DFT SCF calculation (ωB97X-D/6-31G*/C-PCM: acetonitrile).

Species	G^o (in au)
DCCA_N-H	-1425.00845
DCCA_O-H	-1424.97717

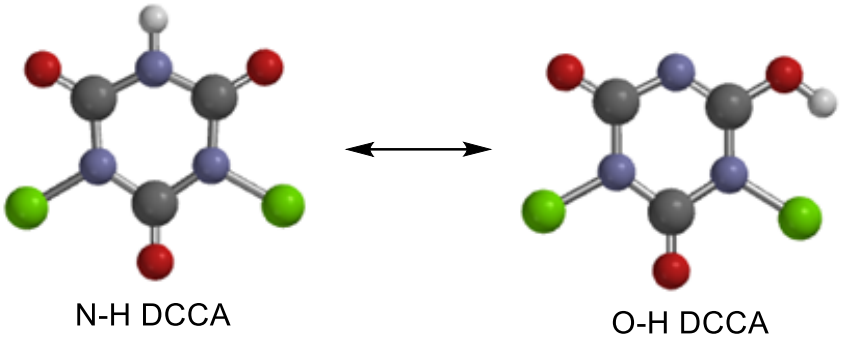


Figure S7. Depictions of the N-H DCCA and O-H DCCA molecules.

From the implicit acetonitrile solvation model, the free energy of N-H DCCA molecule is about 82 $kJ{\cdot}mol^{-1}$ *lower* than that of the O-H DCCA molecule. Thus N-H DCCA is used in the mechanistic model above.

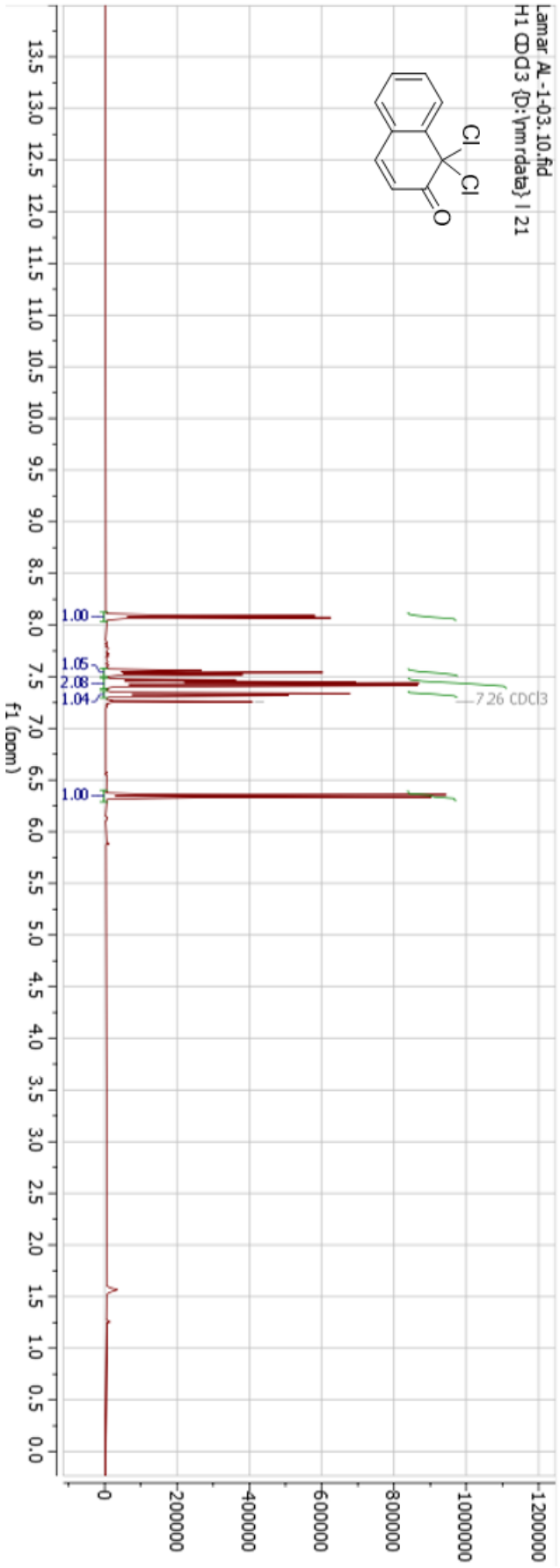


Figure S8. ^{1}H NMR of Product **2**.

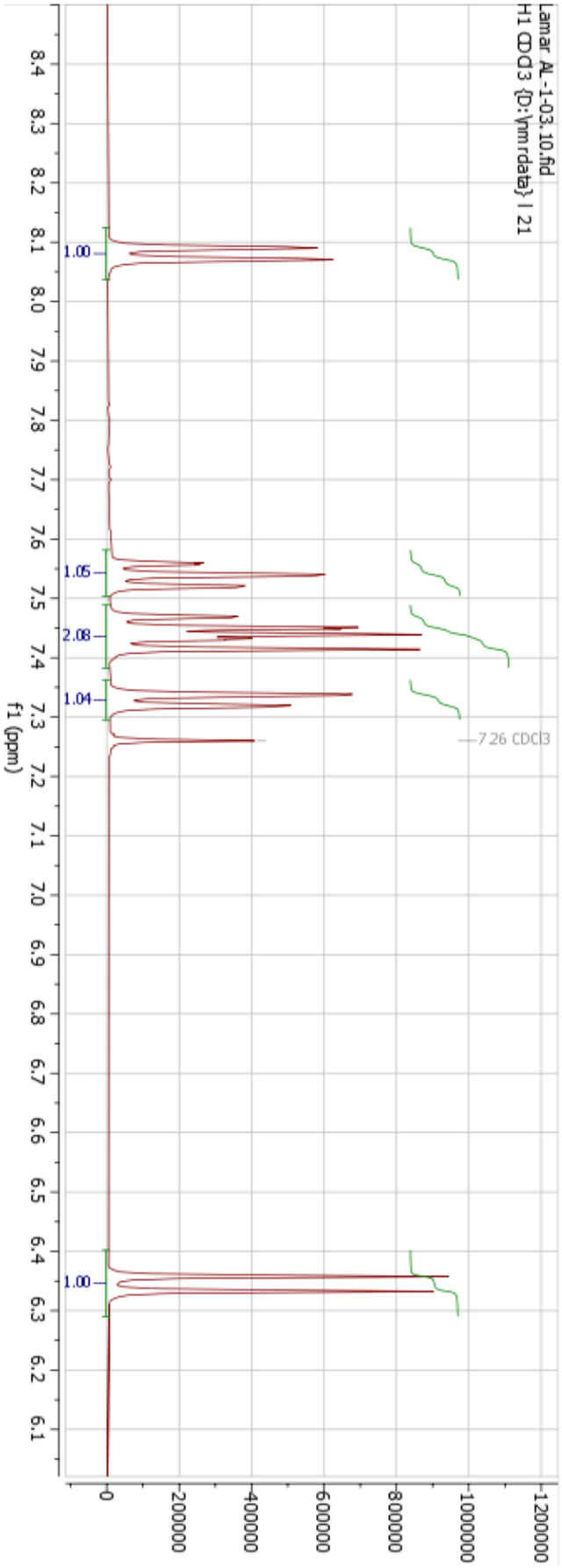


Figure S9. Zoomed in aromatic region ^{1}H NMR of Product **2**.

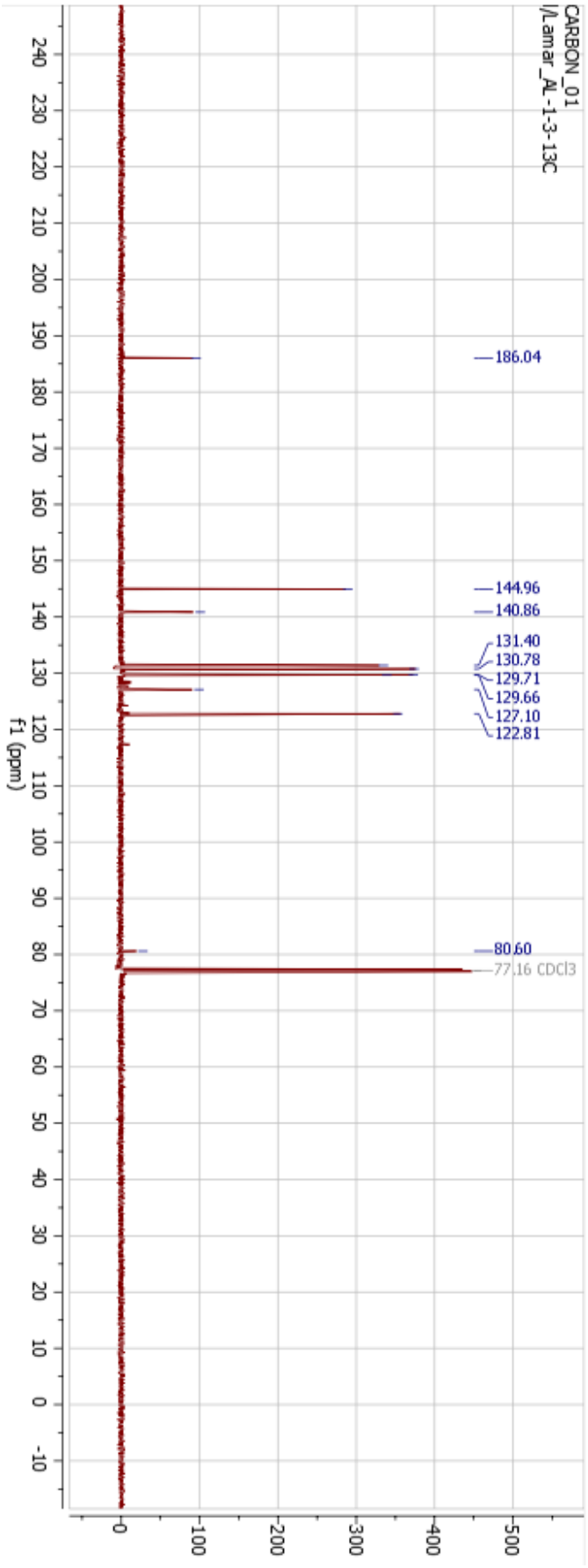


Figure S10. ^{13}C NMR of Product **2**.

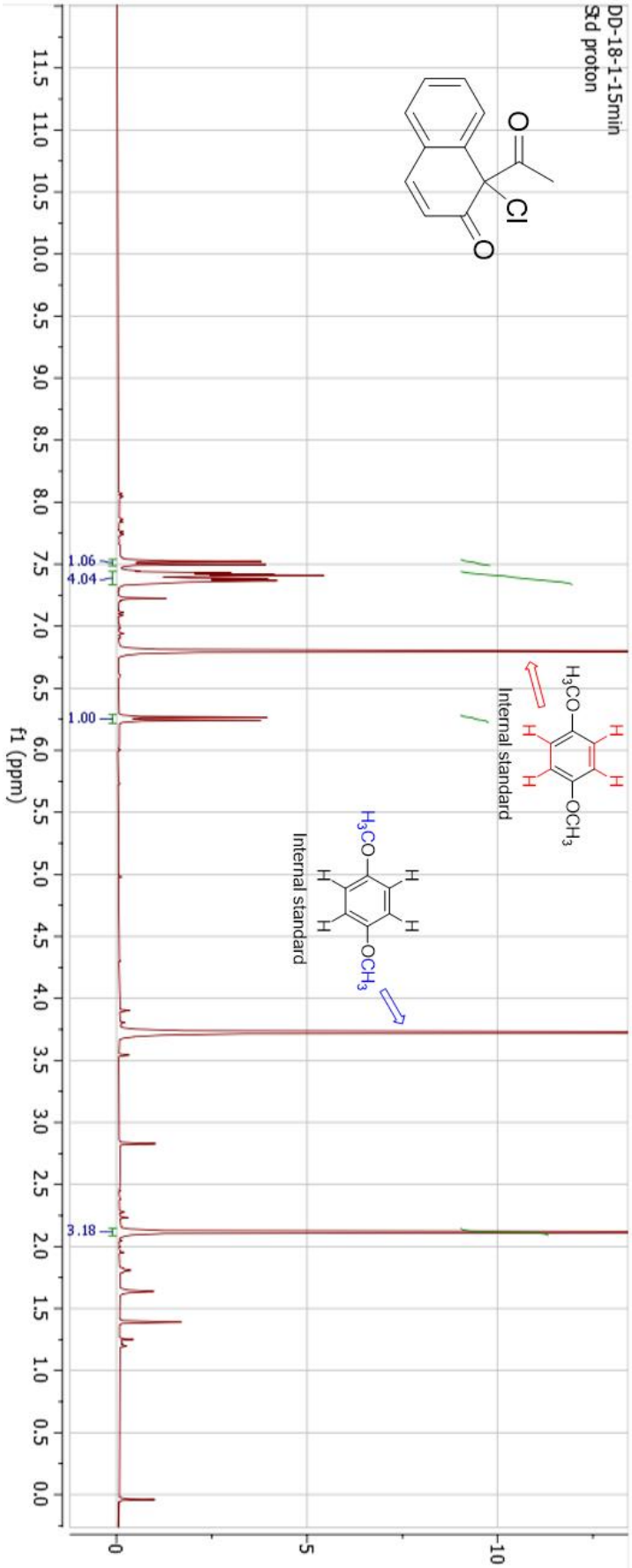


Figure S11. [1]H of Product **3** with 1,4-dimethoxybenzene added as internal standard.

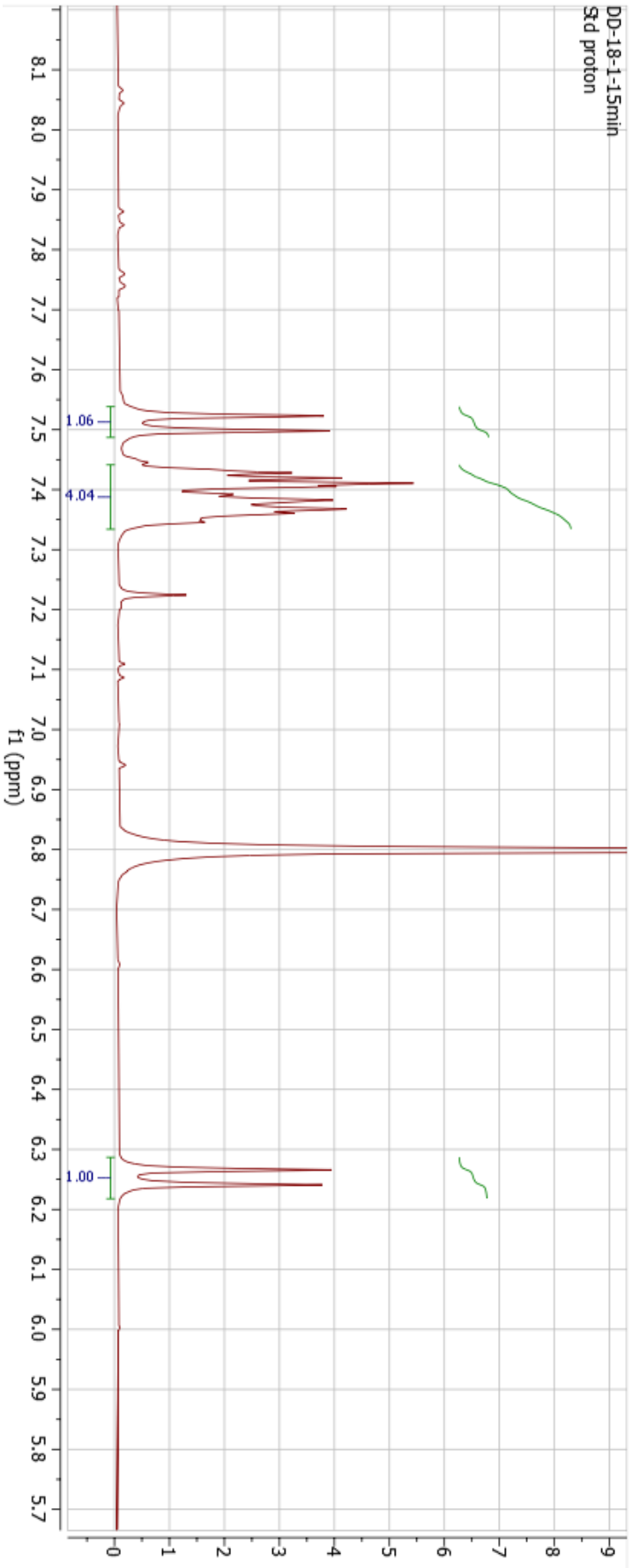


Figure S12. Zoomed in aromatic region of ^{1}H of Product **3** with 1,4-dimethoxybenzene added as internal standard.

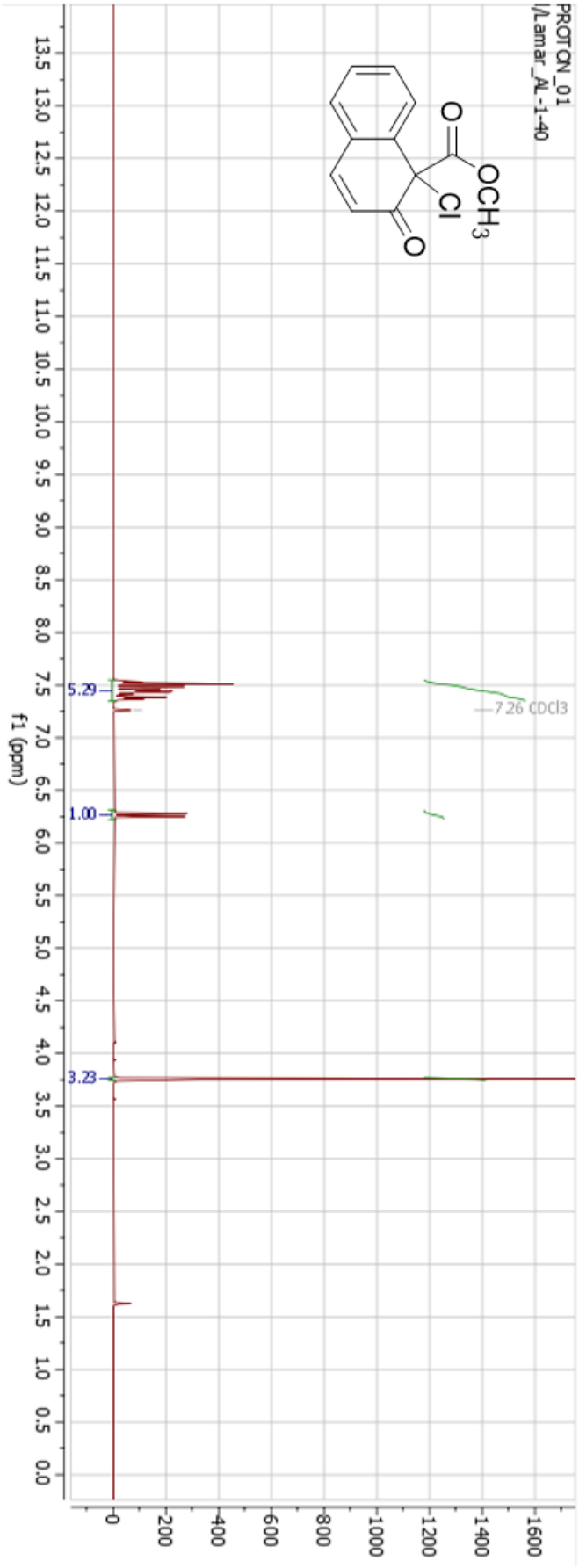


Figure S13. ^{1}H of Product **4**.

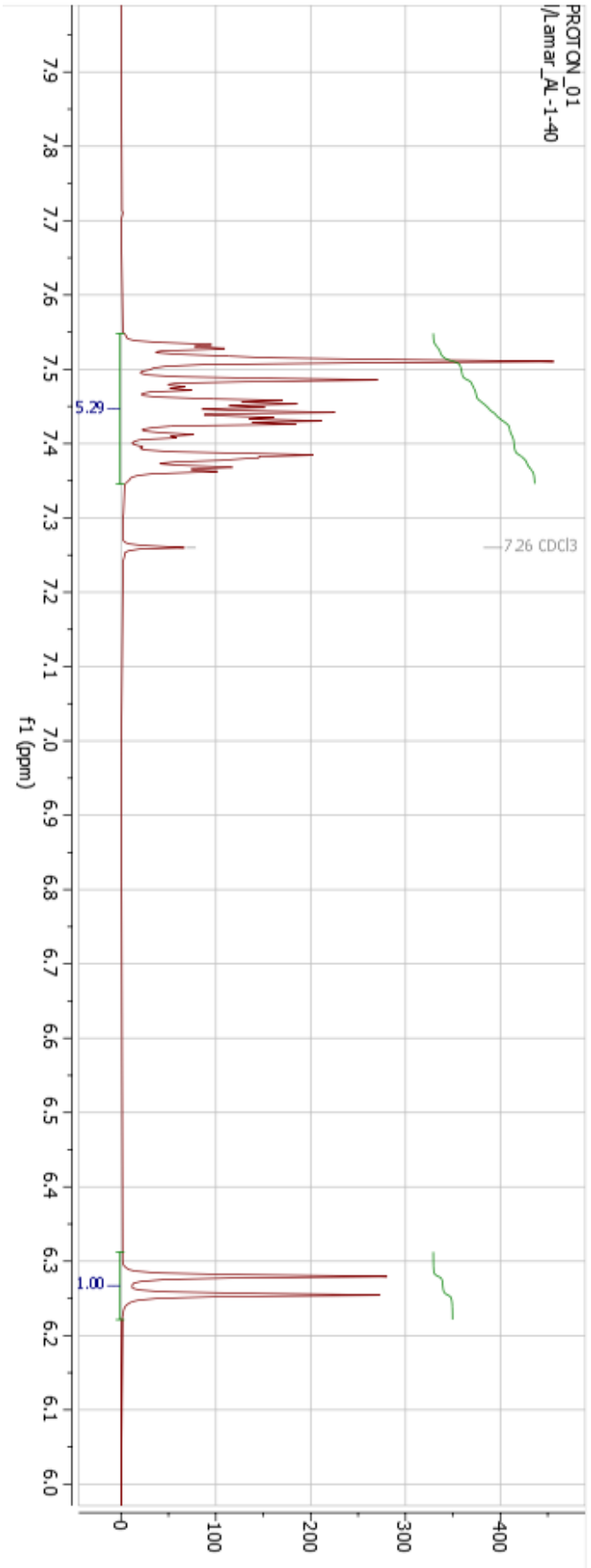


Figure S14. Zoomed in aromatic region of ^{1}H NMR of Product **4**.

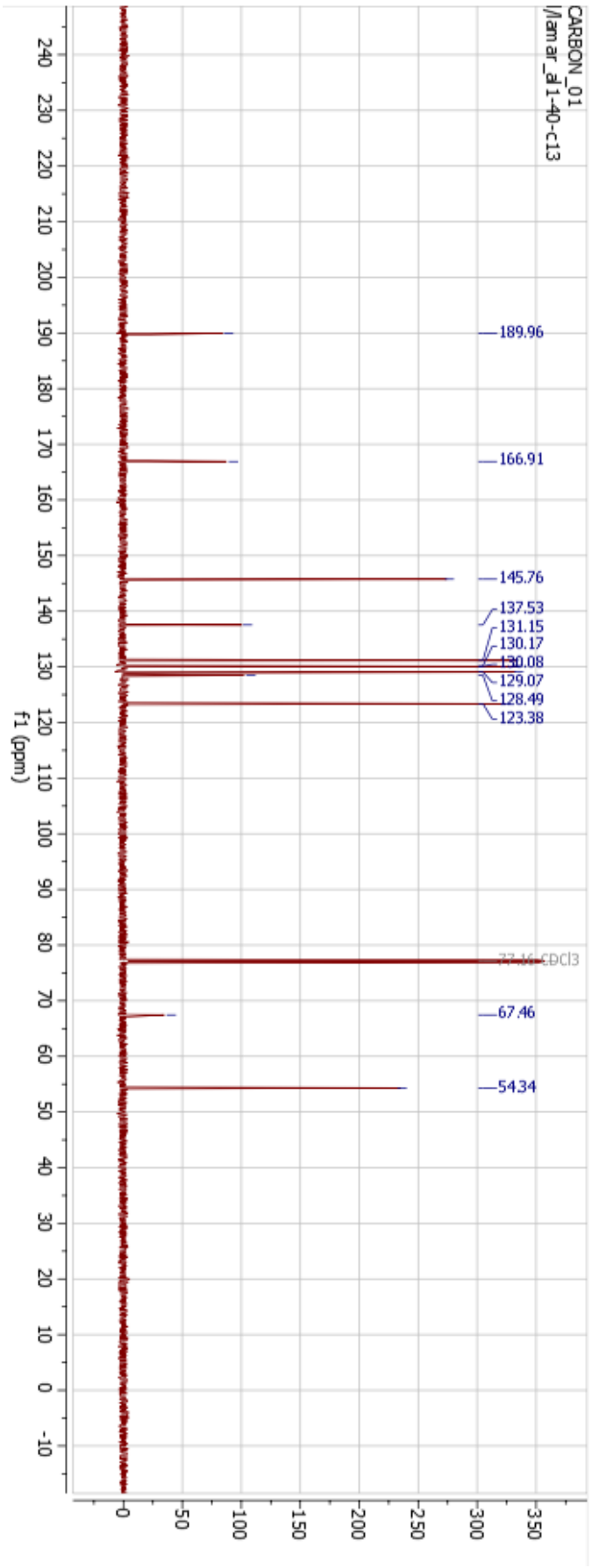


Figure S15. ^{13}C NMR of Product **4**.

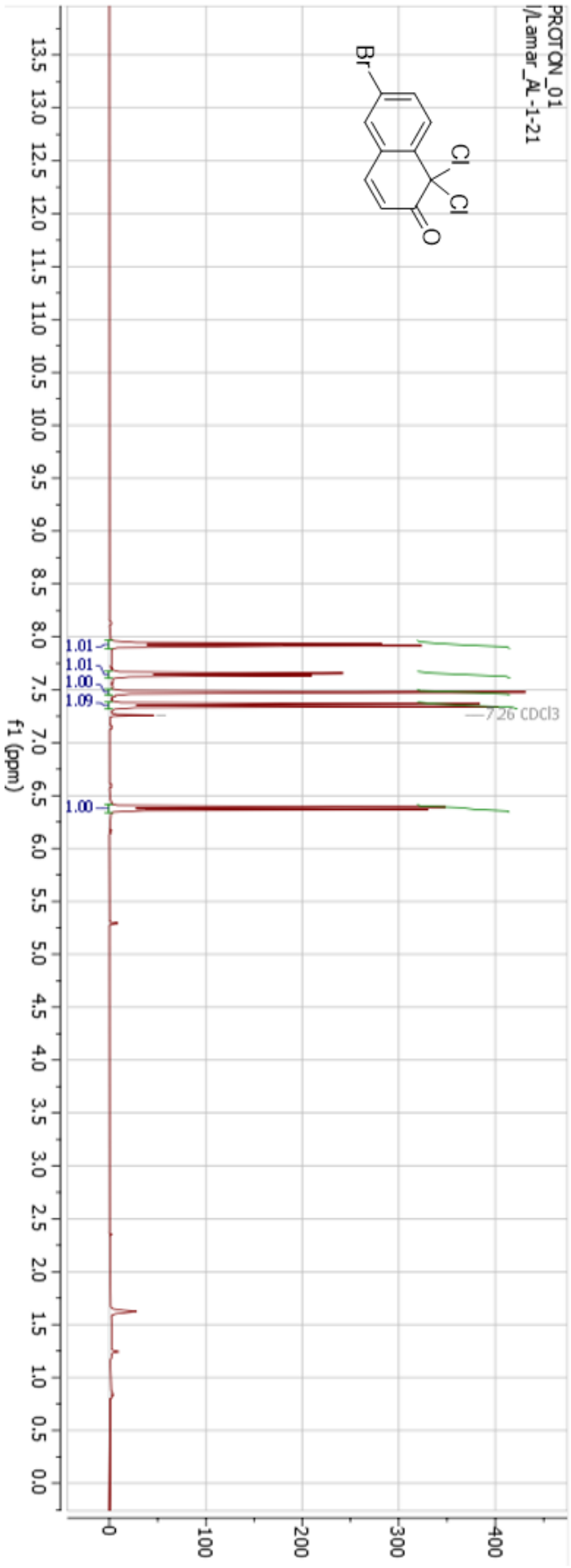


Figure S16. ^{1}H of Product **5**.

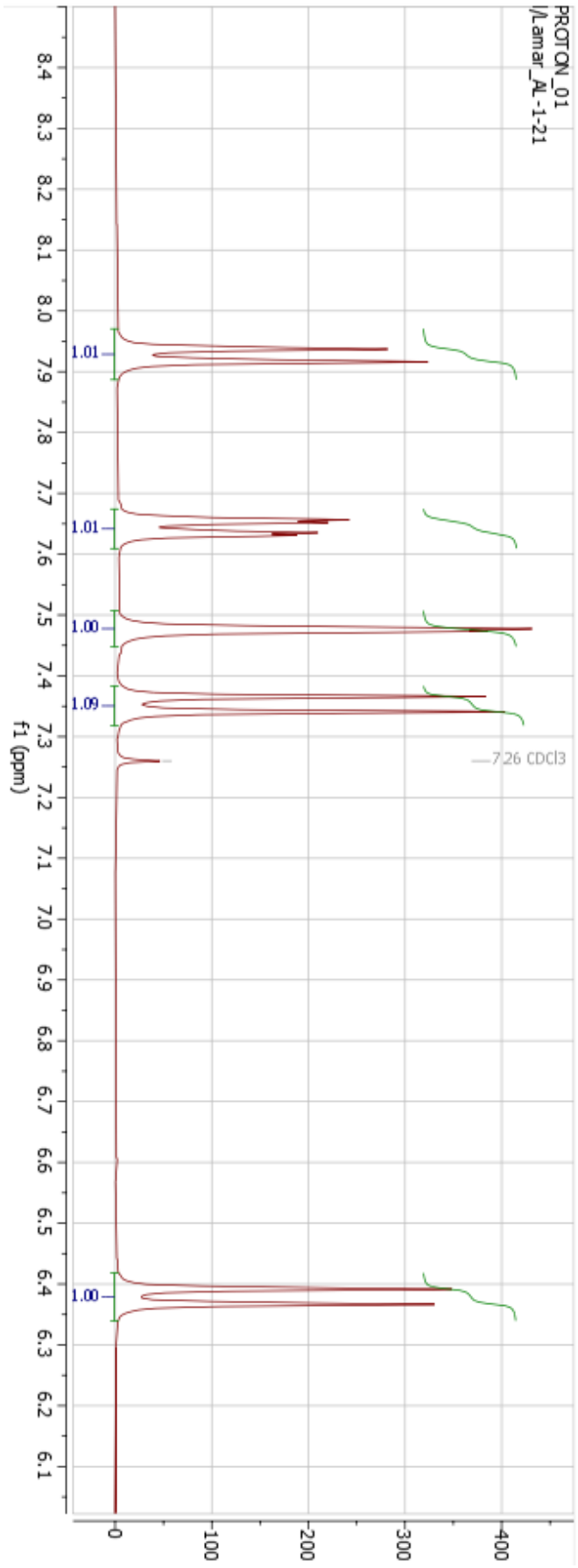


Figure S17. Zoomed in aromatic region of ^{1}H NMR of Product **5**.

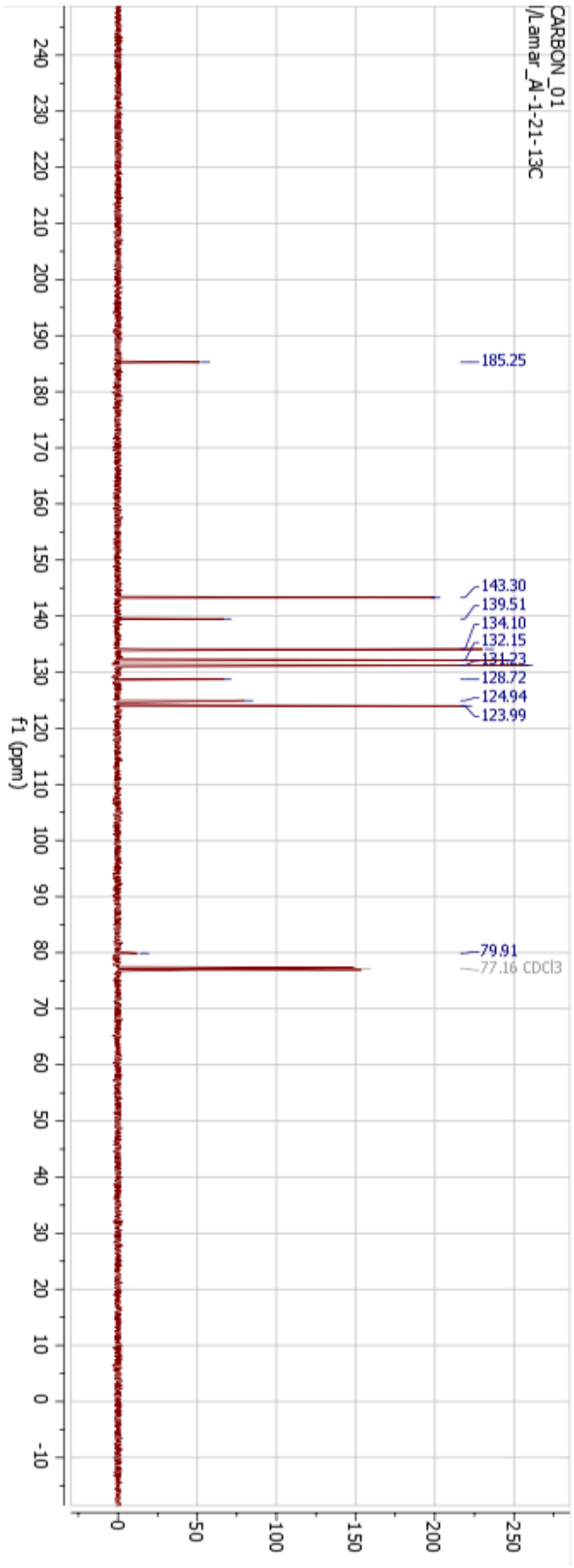


Figure S18. ^{13}C NMR of Product **5**.

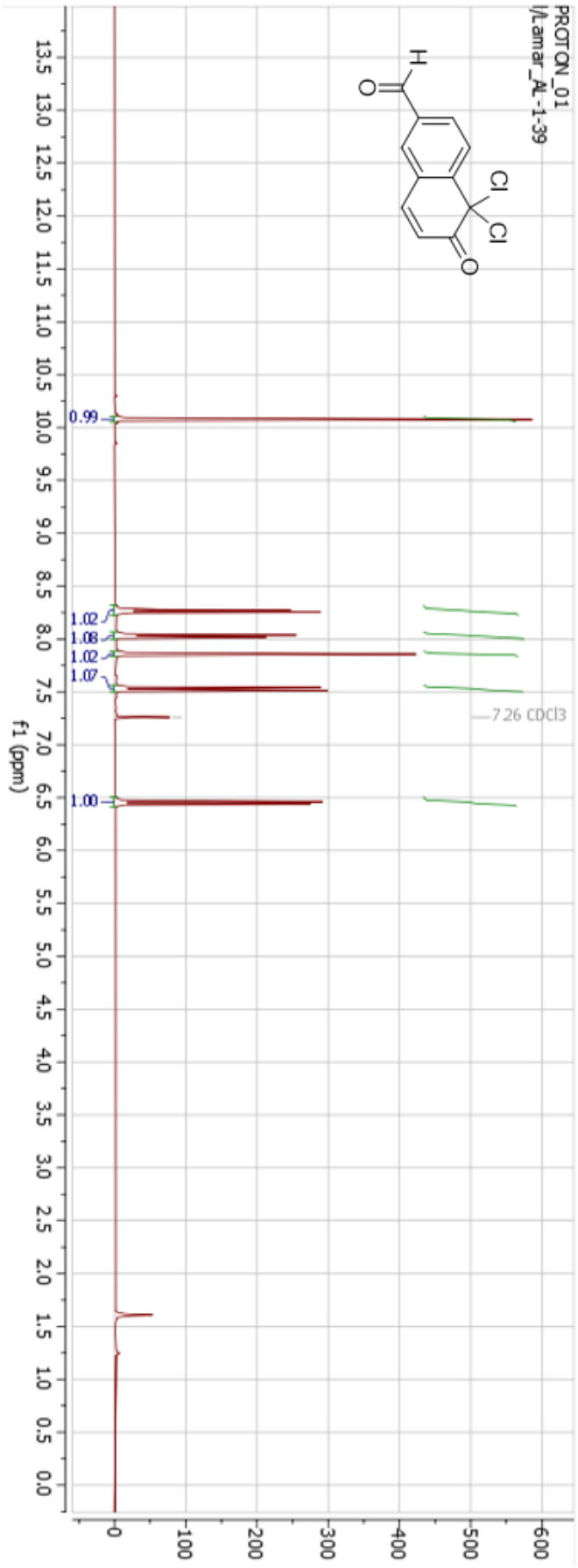


Figure S19. ^{1}H of Product **6**.

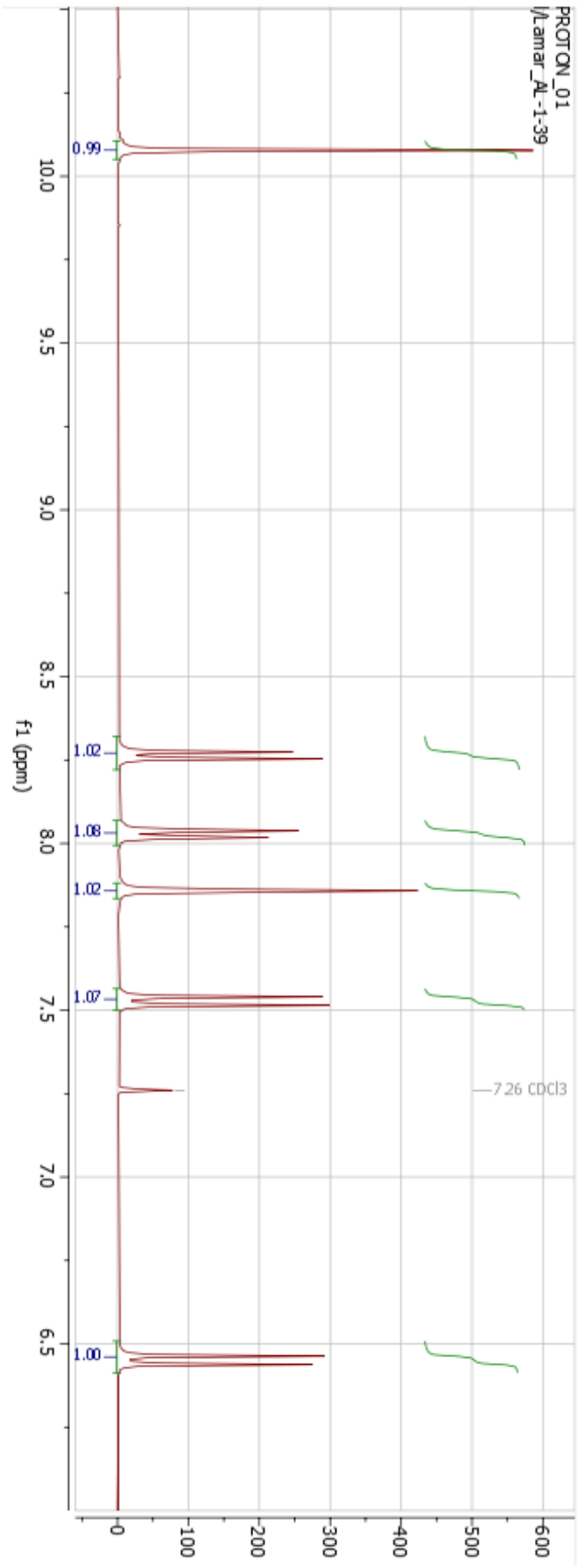


Figure S20. Zoomed in aromatic region of ^{1}H NMR of Product **6**.

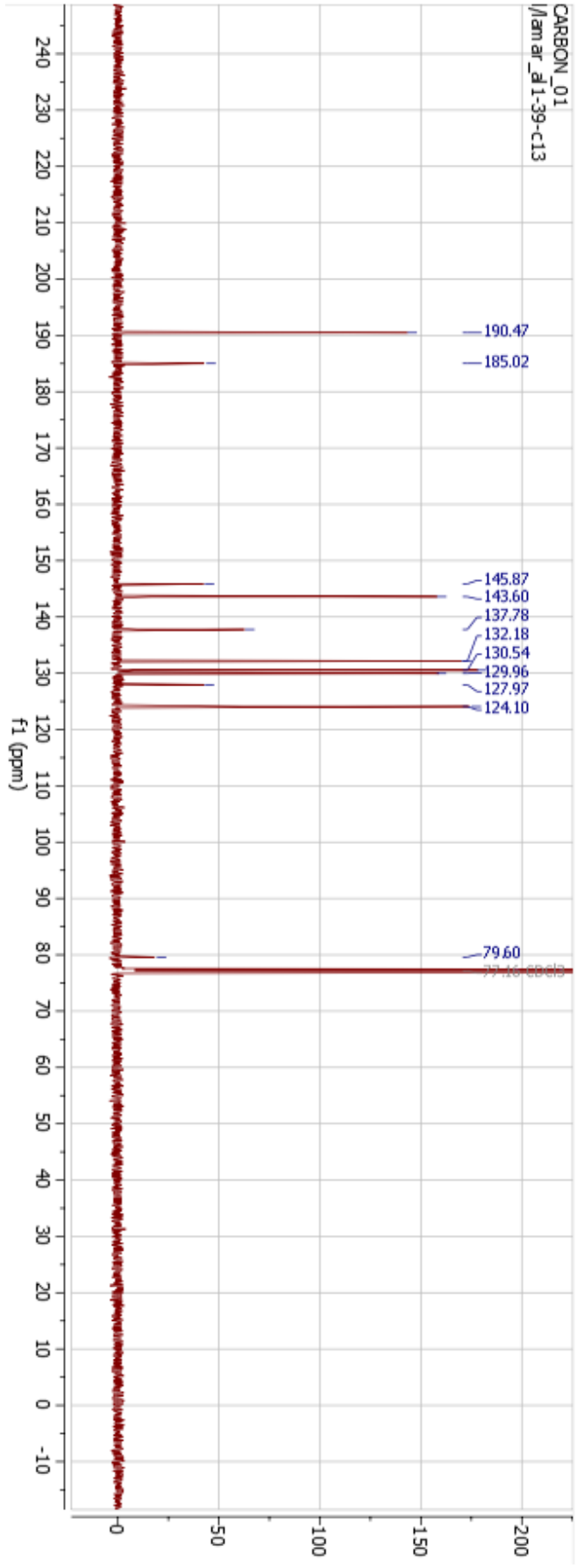


Figure S21. ^{13}C NMR of Product **6**.

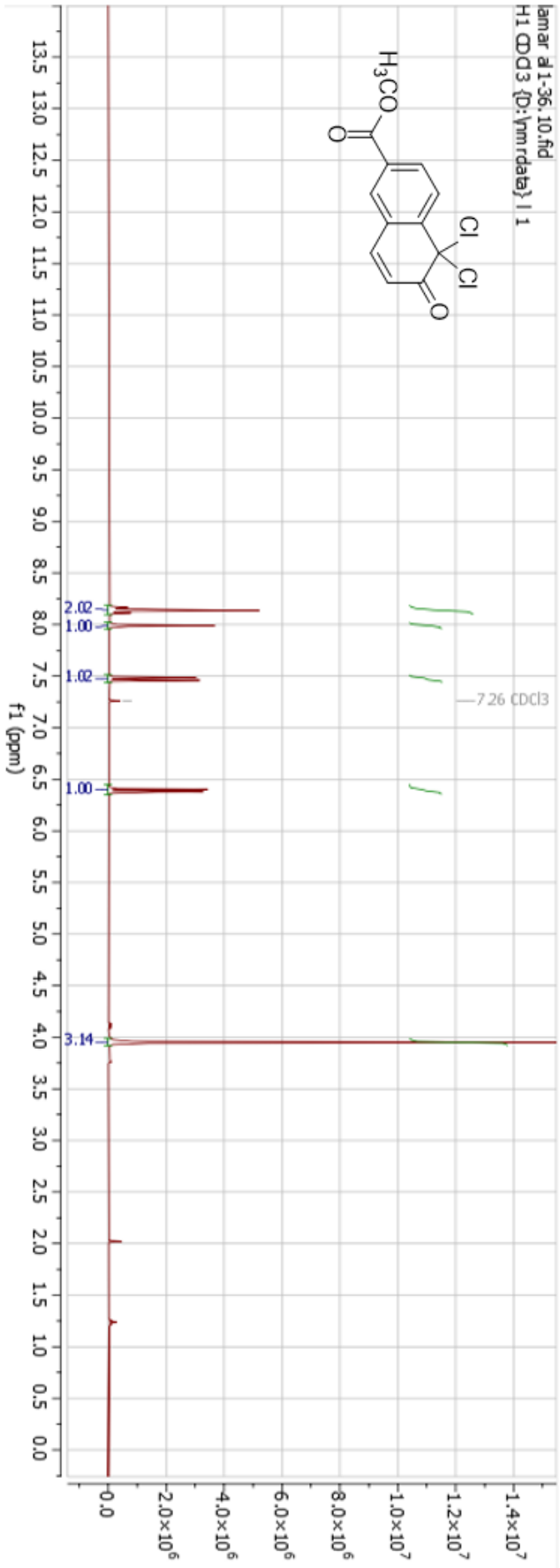


Figure S22. [1]H NMR of Product **7**.

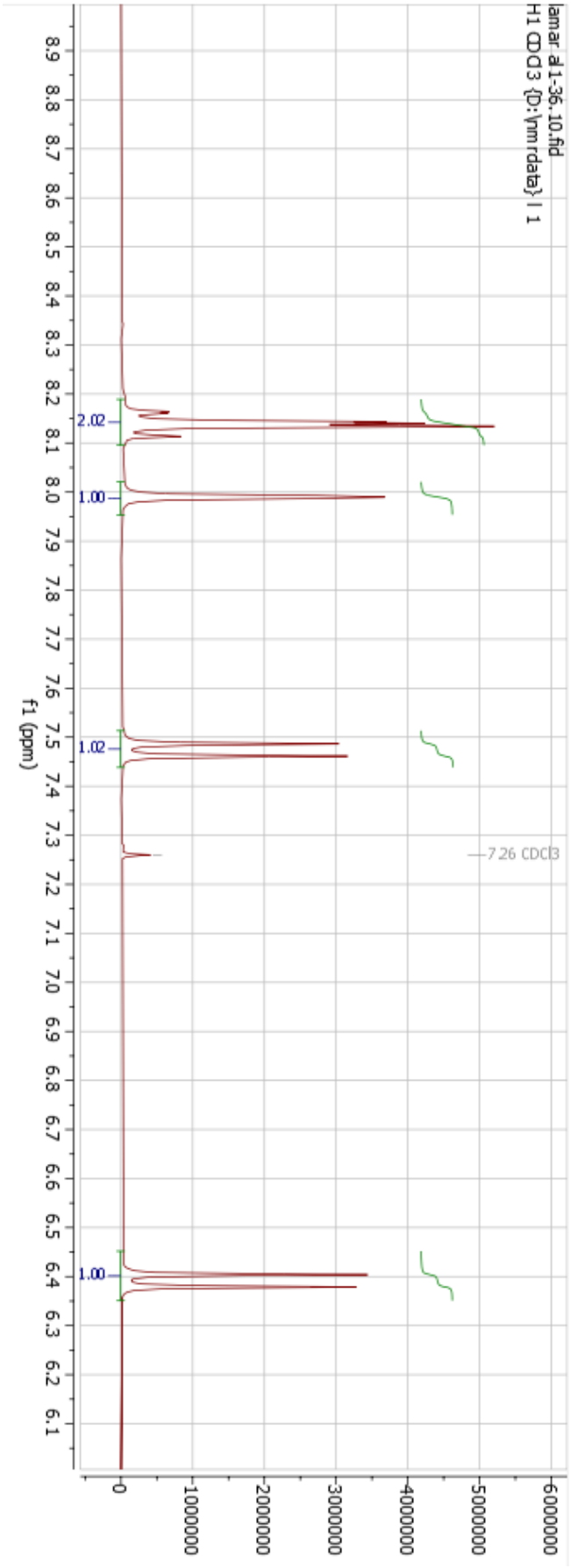


Figure S23. Zoomed in aromatic region of ^{1}H NMR of Product **7**.

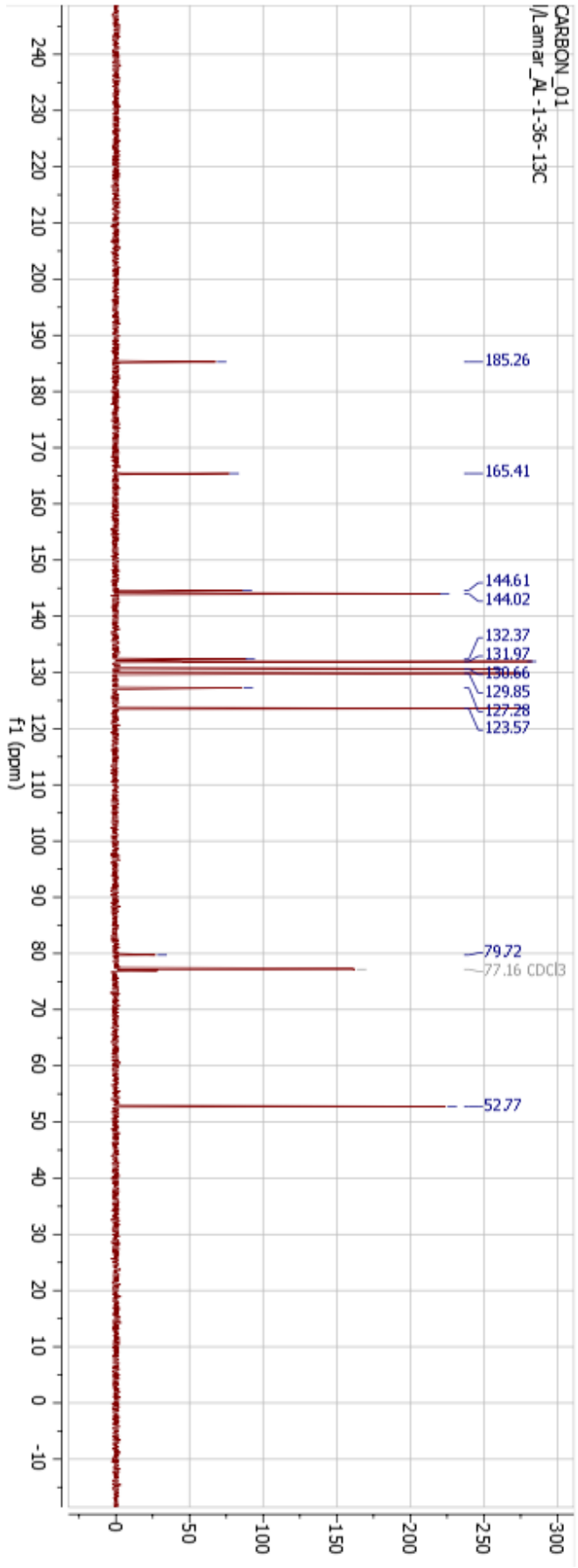


Figure S24. ^{13}C NMR of Product **7**.

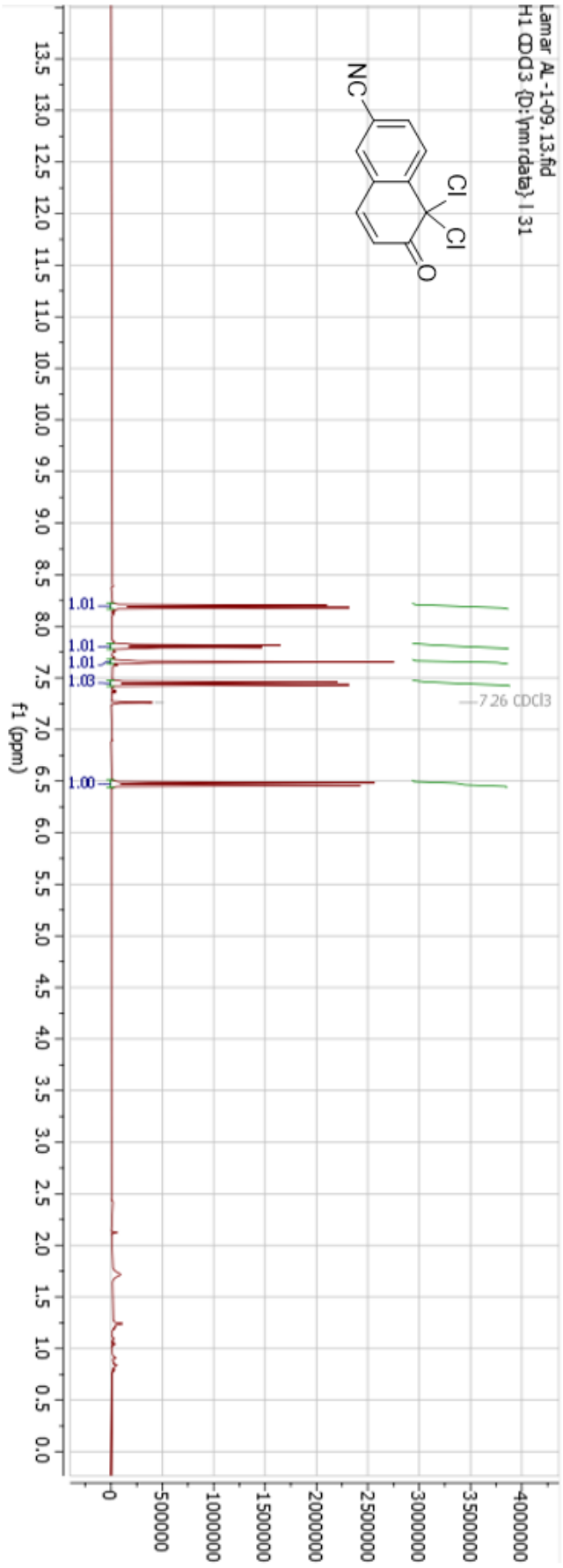


Figure S25. ^{1}H NMR of Product **8**.

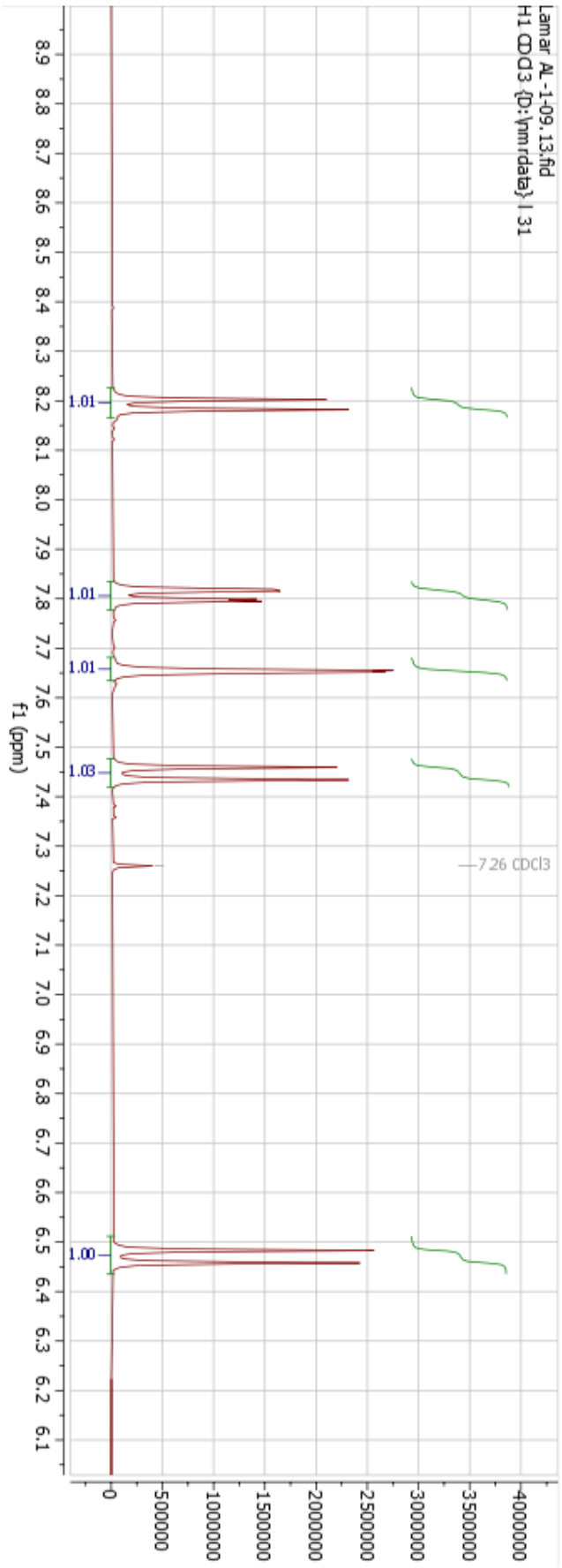


Figure S26. Zoomed in aromatic region of ^{1}H NMR of Product **8**.

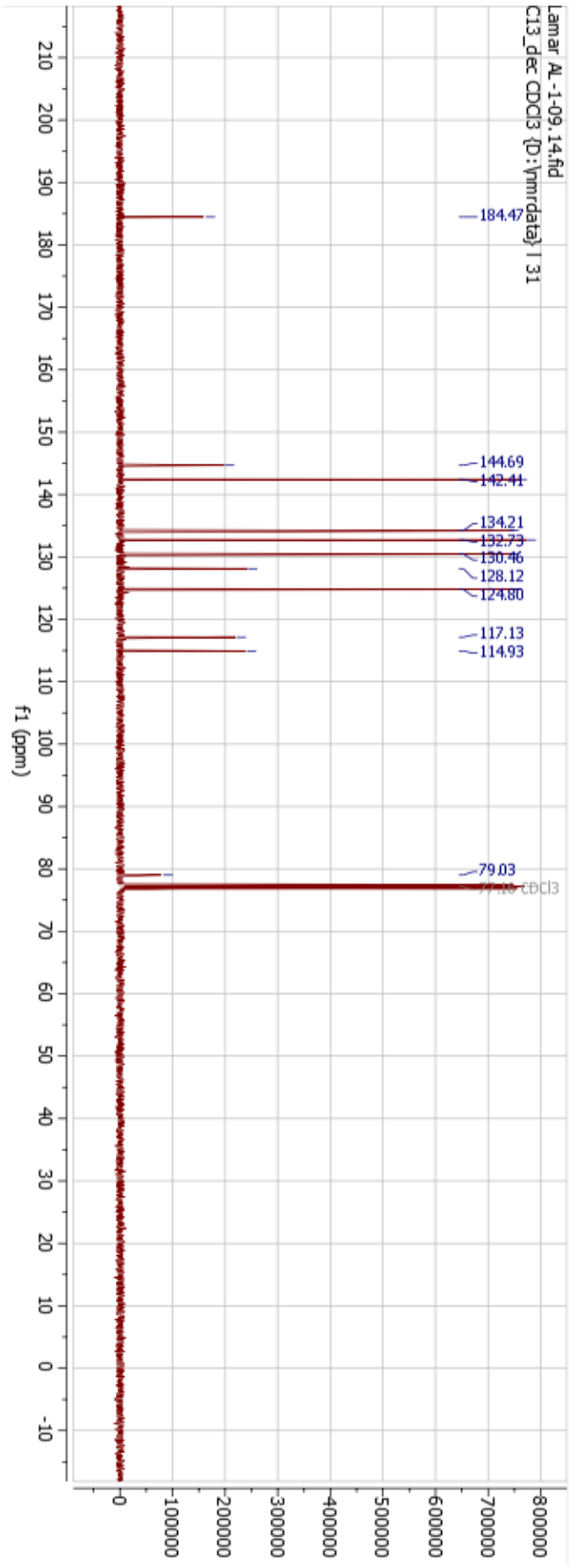


Figure S27. ^{13}C NMR of Product **8**.

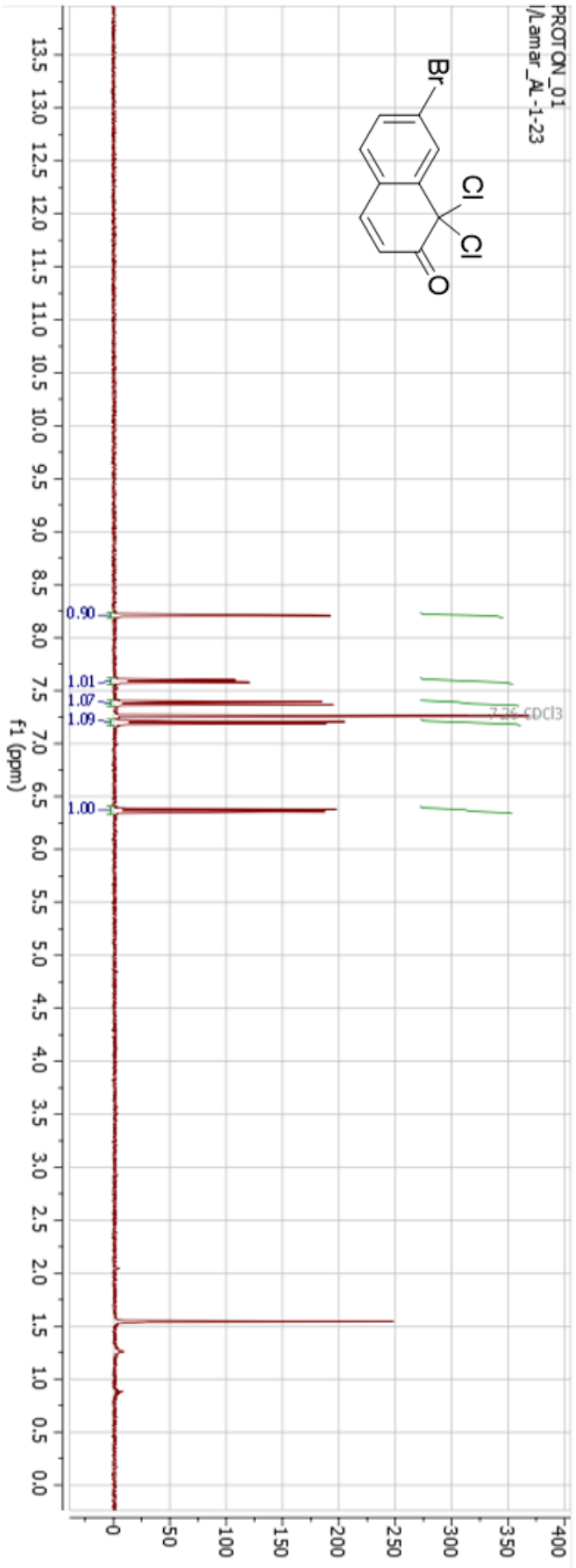


Figure S28. ^{1}H NMR of Product **9**.

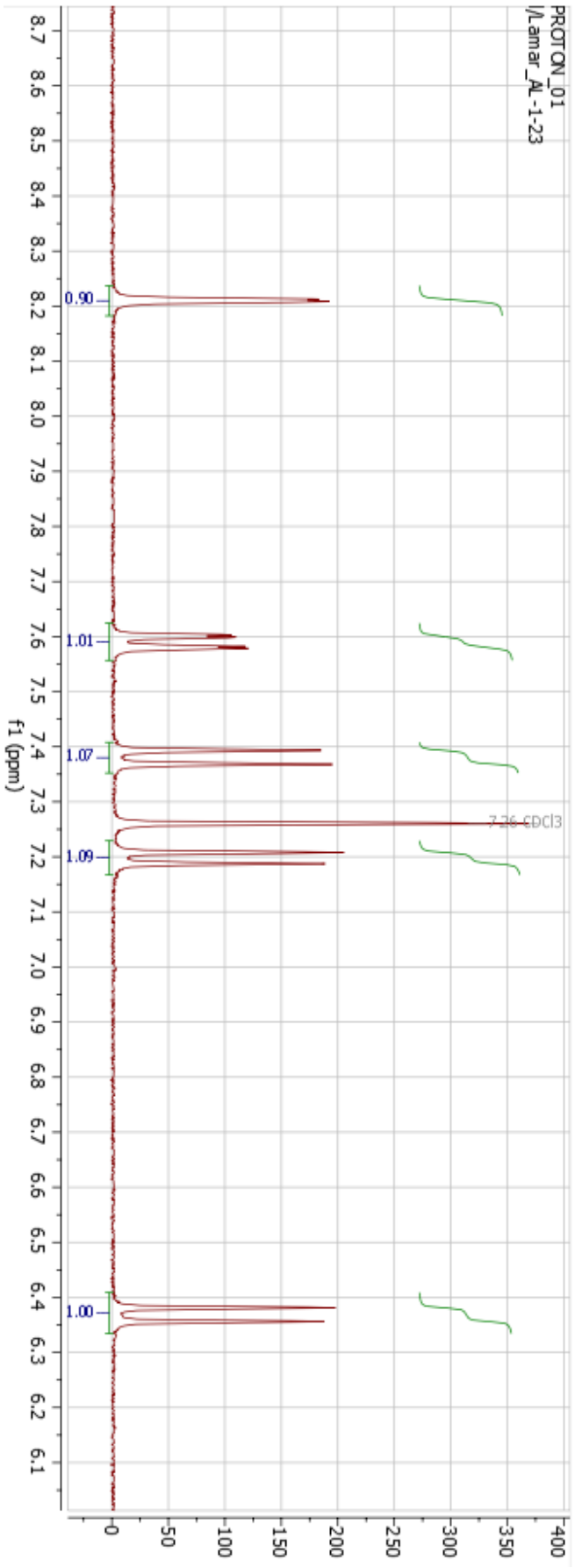


Figure S29. Zoomed in aromatic region of ^{1}H NMR of Product **9**.

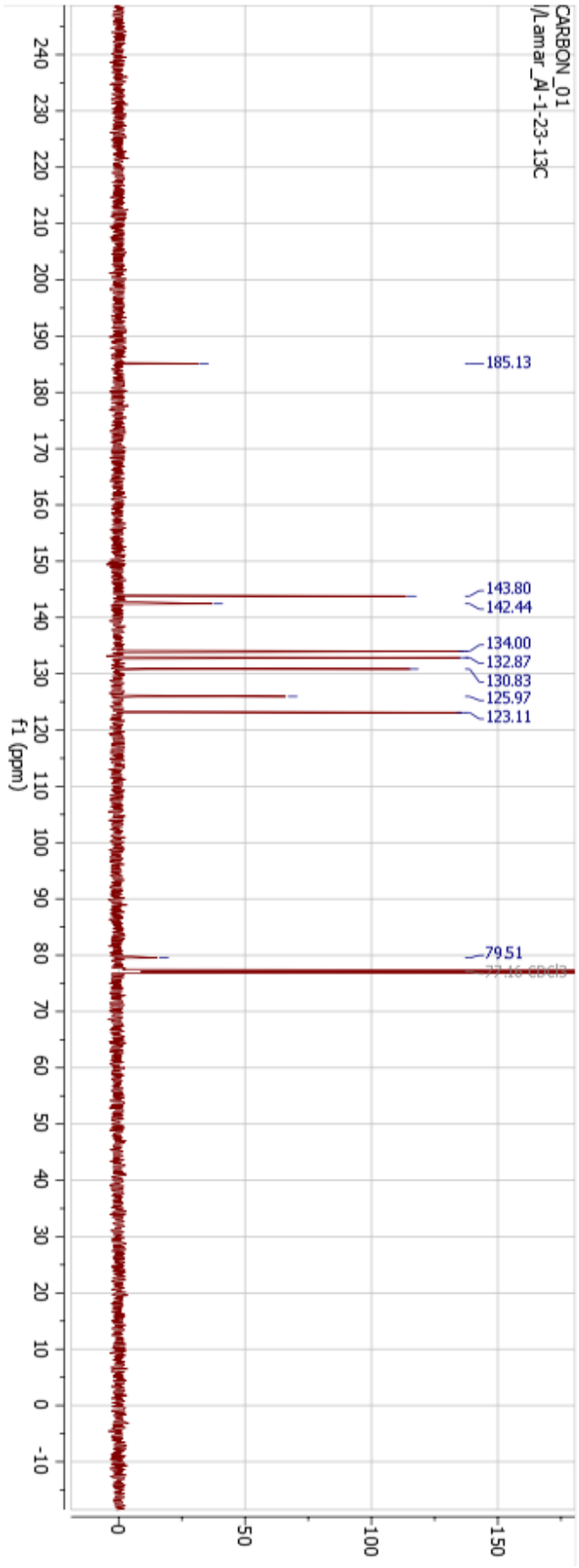


Figure S30. ^{13}C NMR of Product **9**.

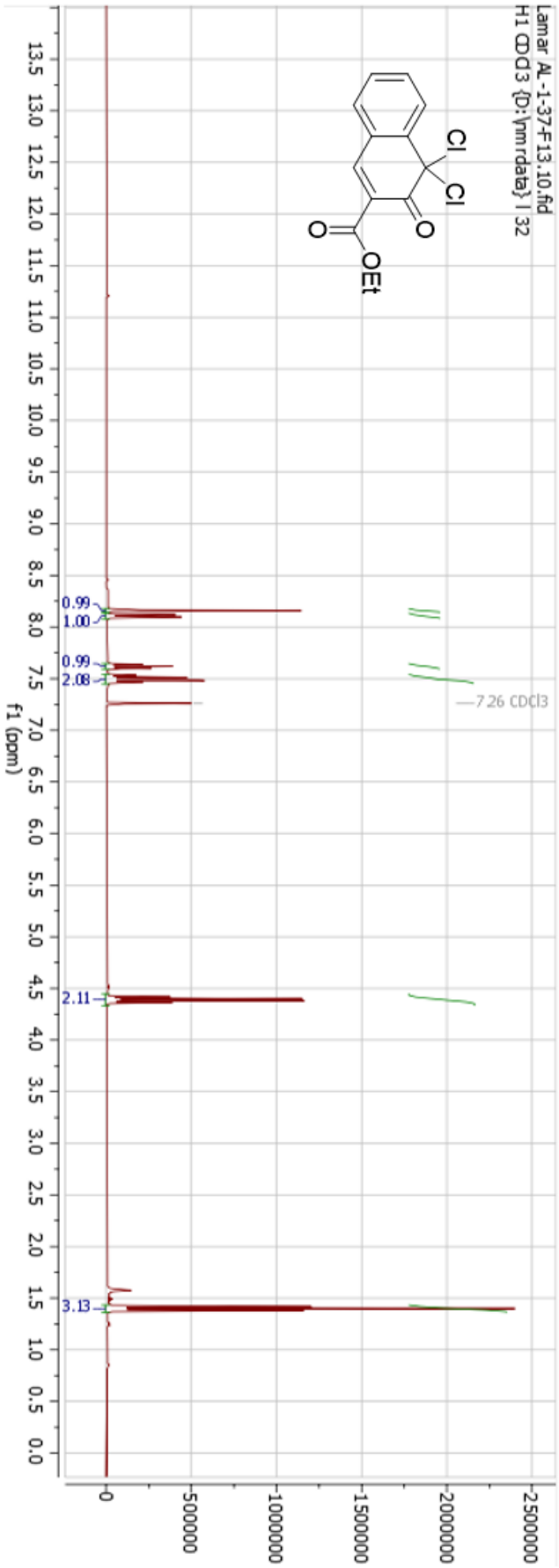


Figure S31. ^{1}H NMR of Product **10**.

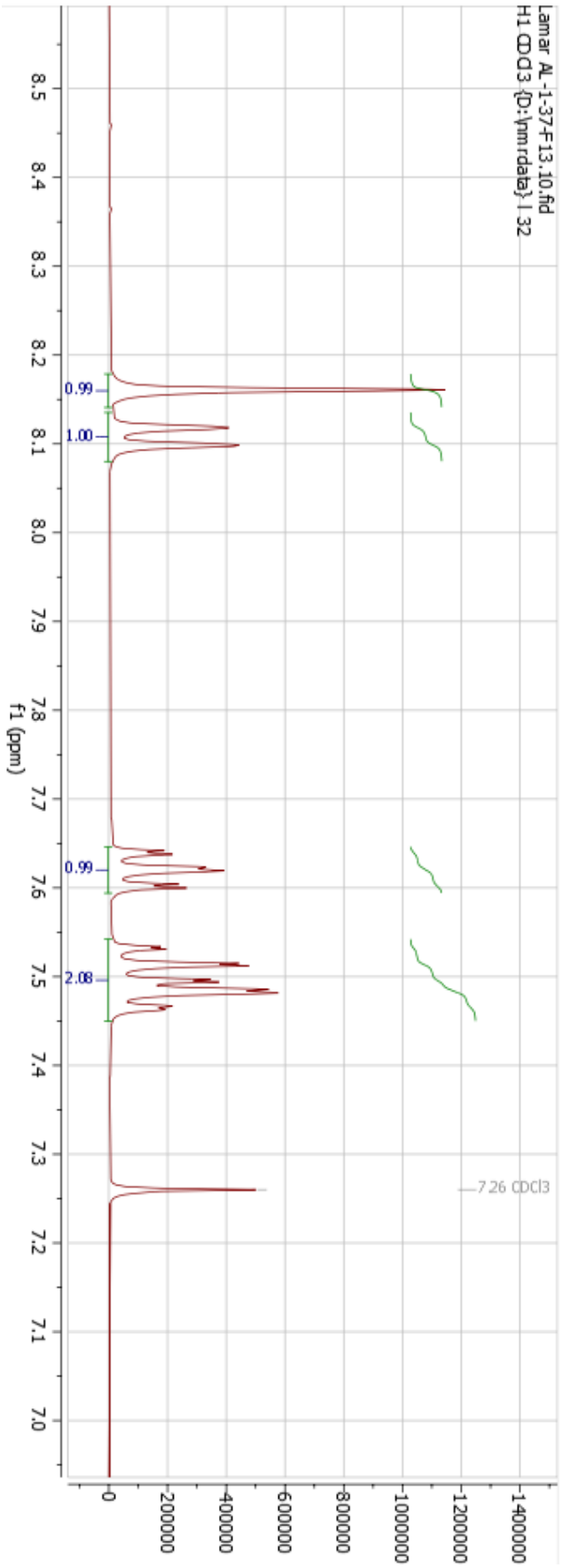


Figure S32. Zoomed in aromatic region of ^{1}H NMR of Product **10**.

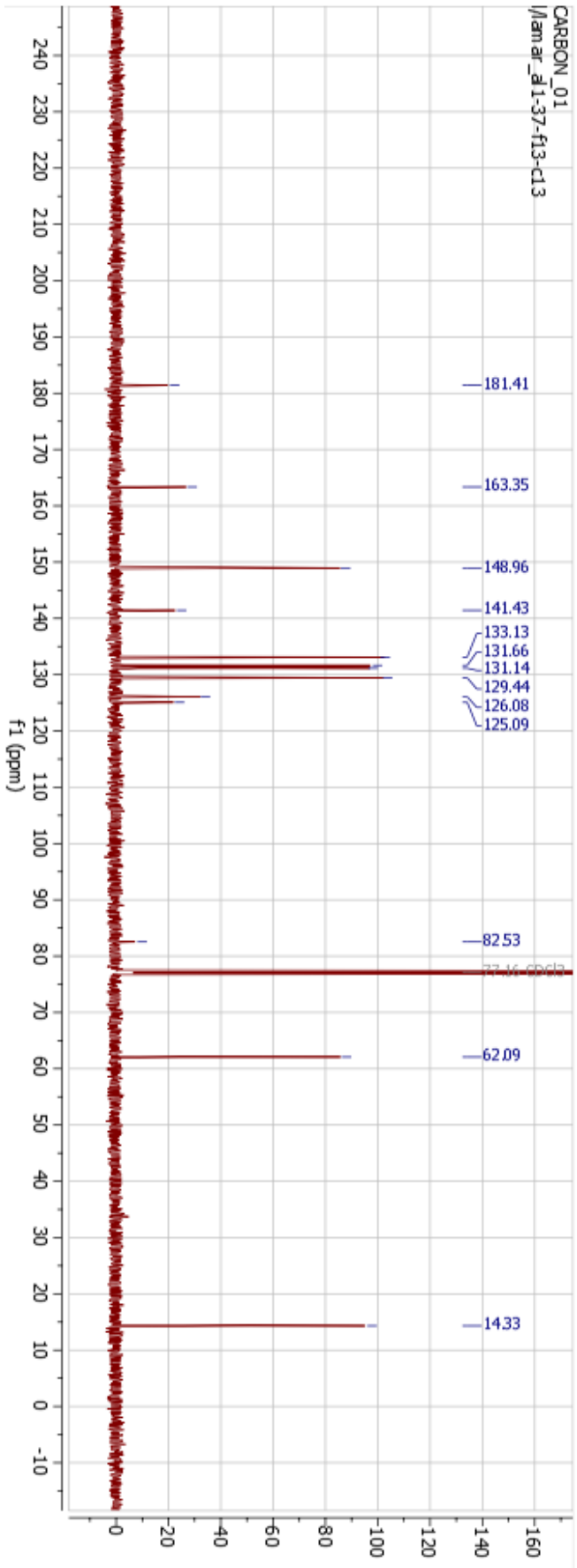


Figure S33. ^{13}C NMR of Product **10**.

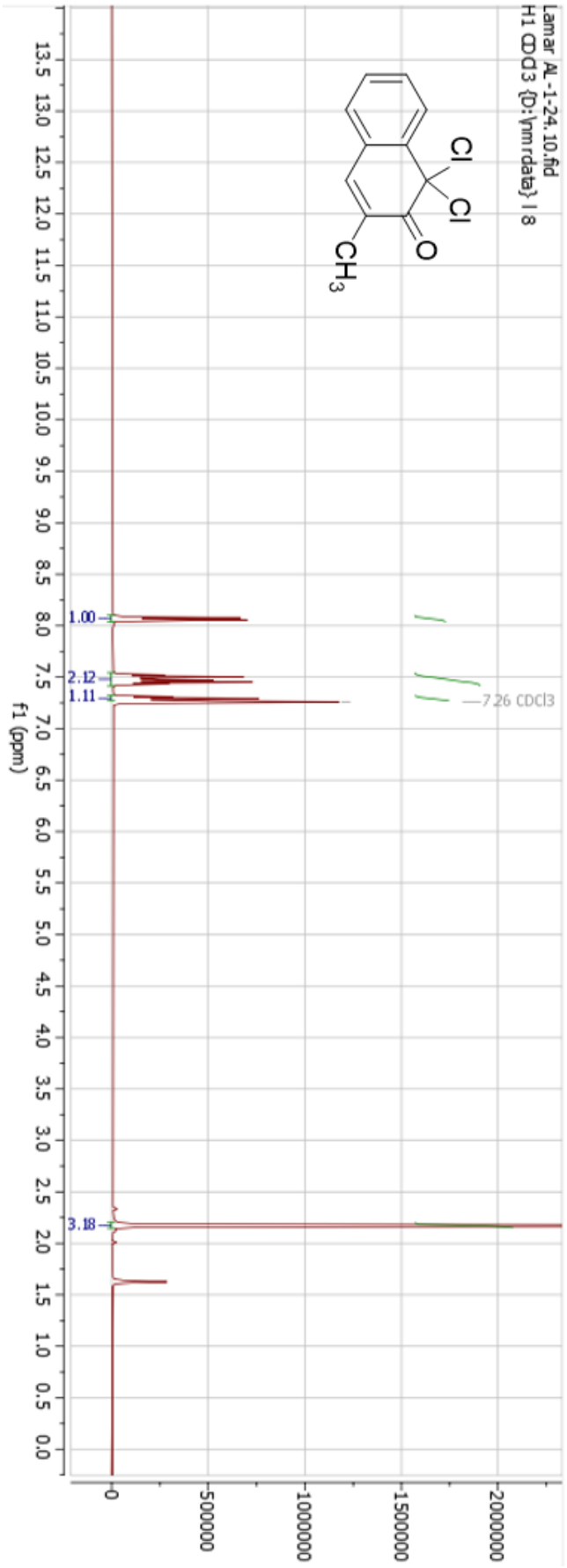


Figure S34. ^{1}H NMR of Product **11**.

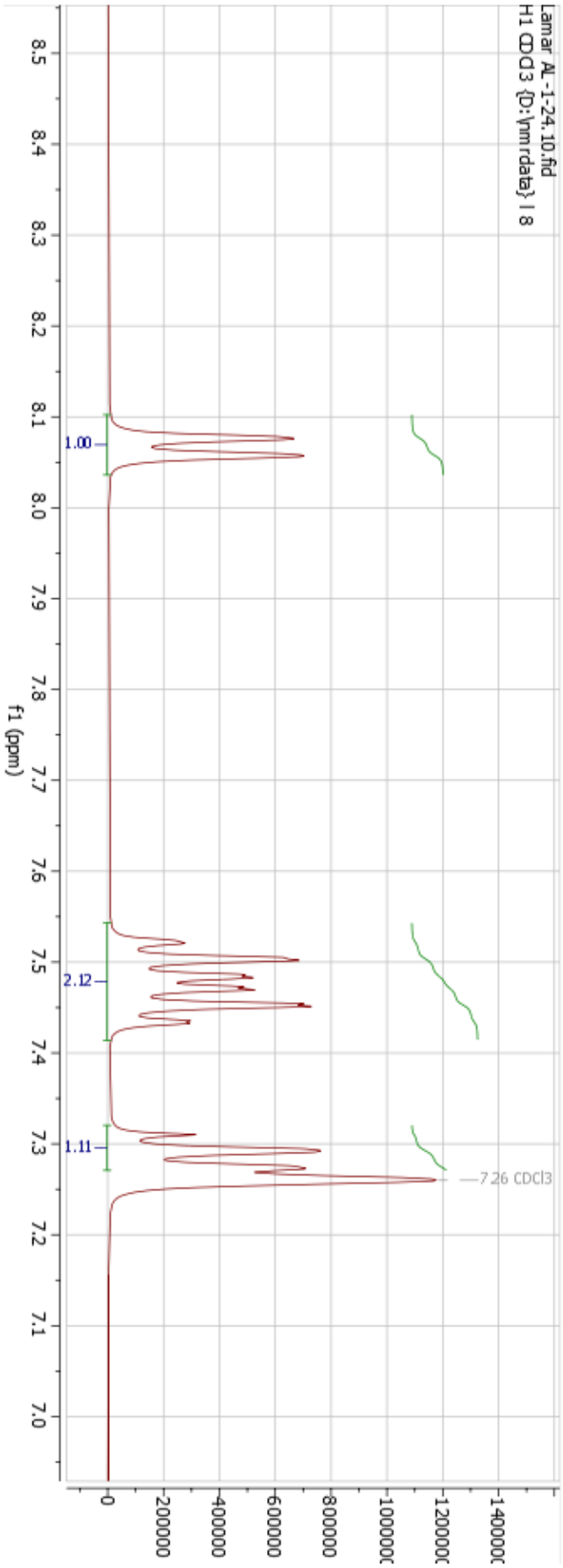


Figure S35. Zoomed in aromatic region of ^{1}H NMR of Product **11**.

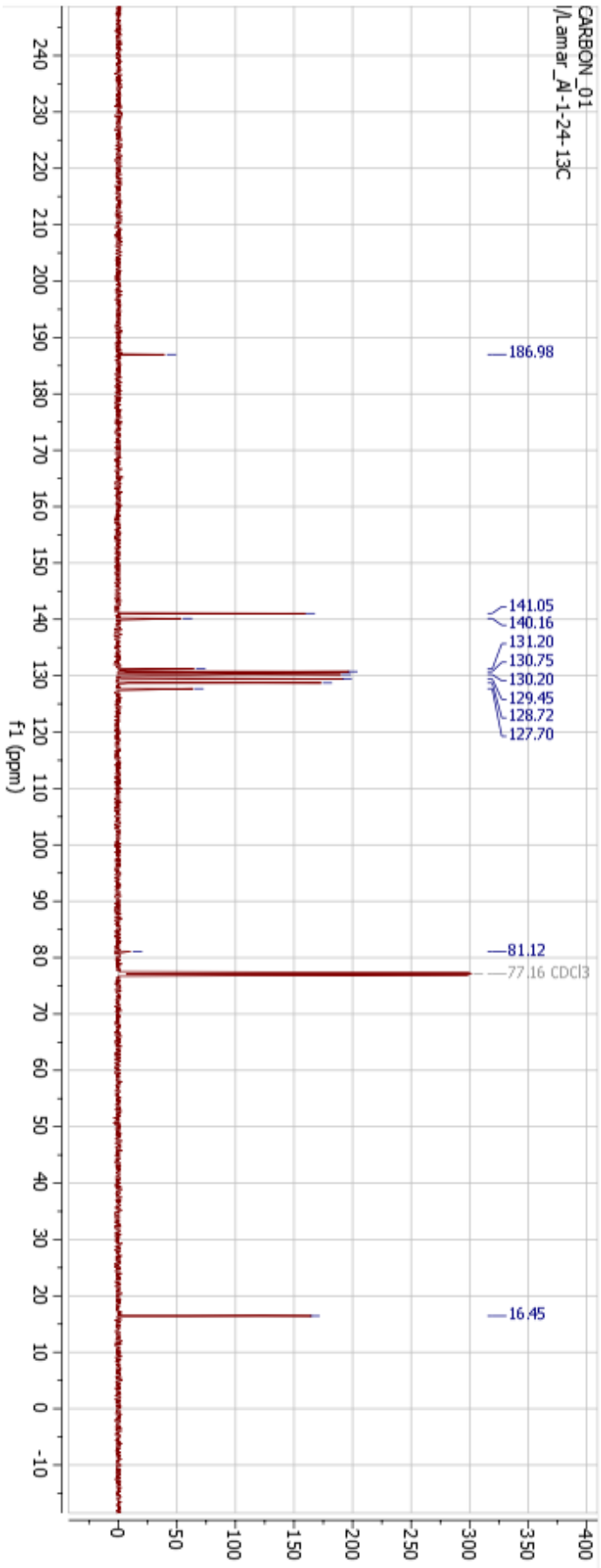


Figure S36. ^{13}C NMR of Product **11**.

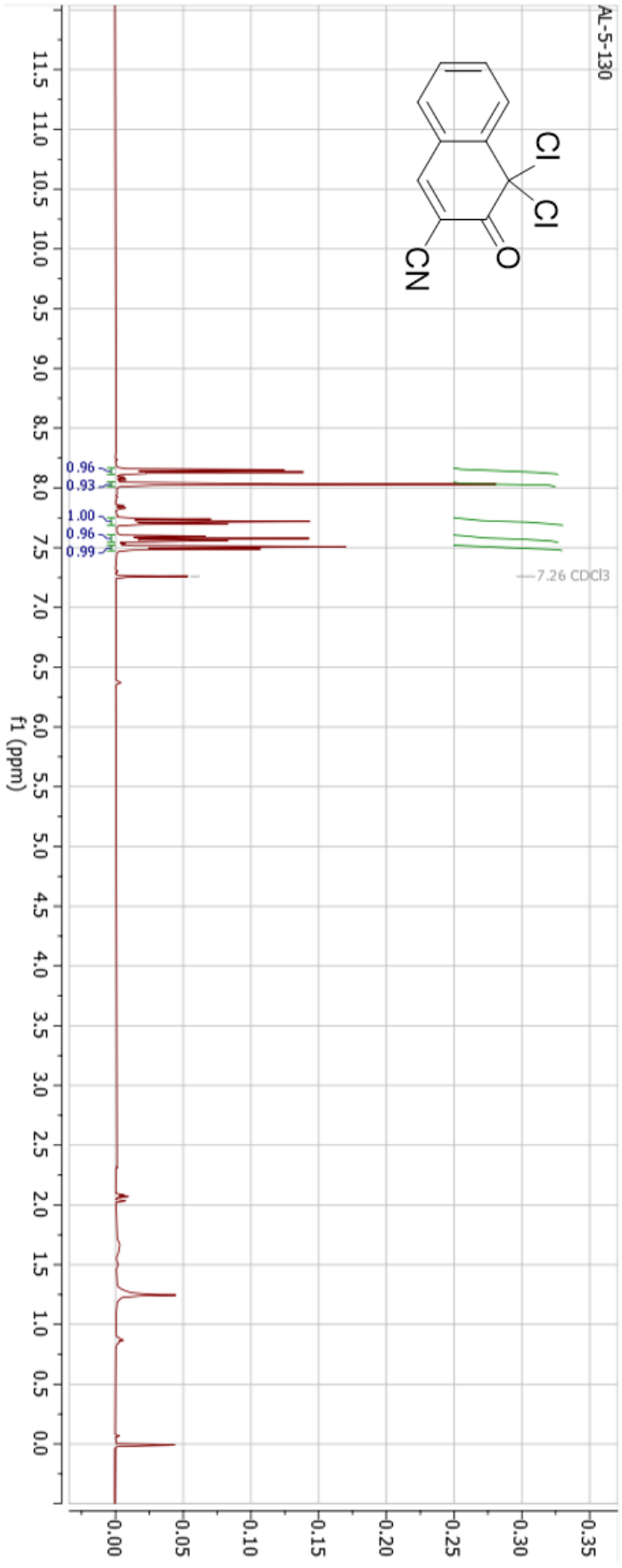


Figure S37. ^{1}H NMR of Product **12**.

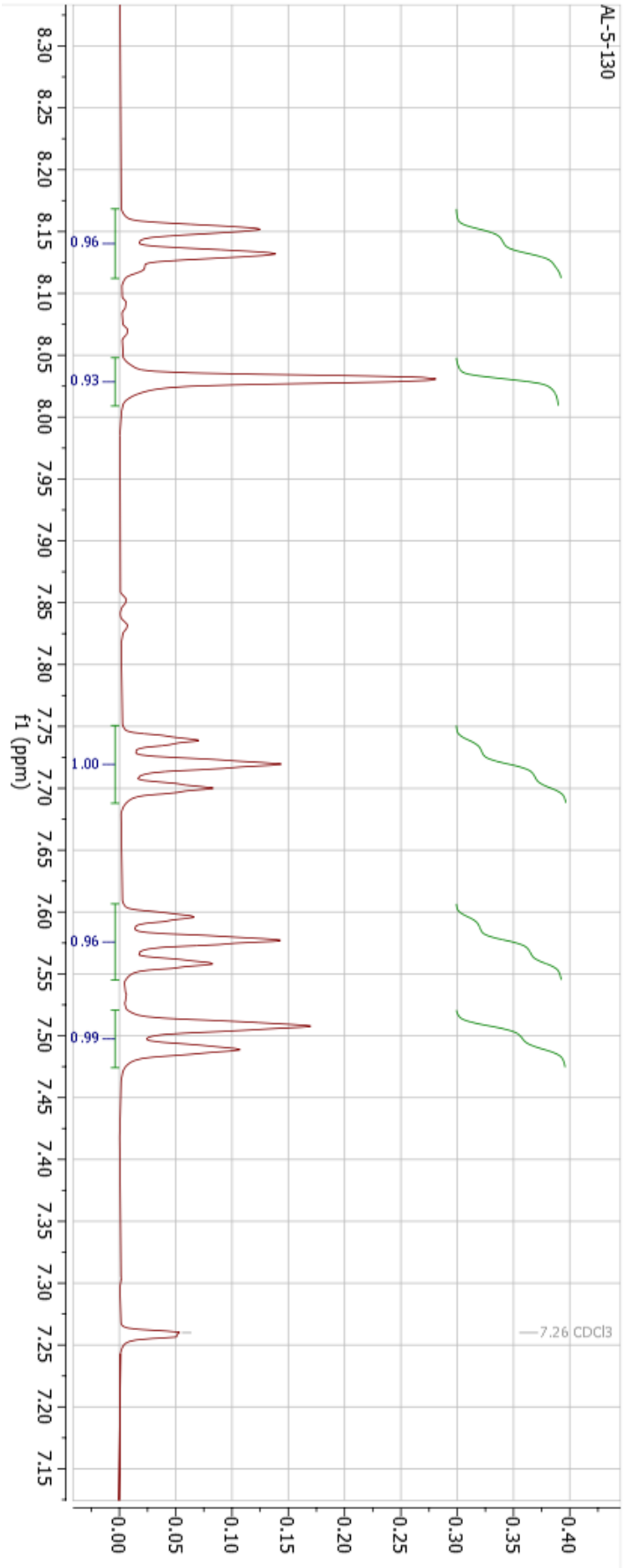


Figure S38. Zoomed in aromatic region of ^{1}H NMR of Product **12**.

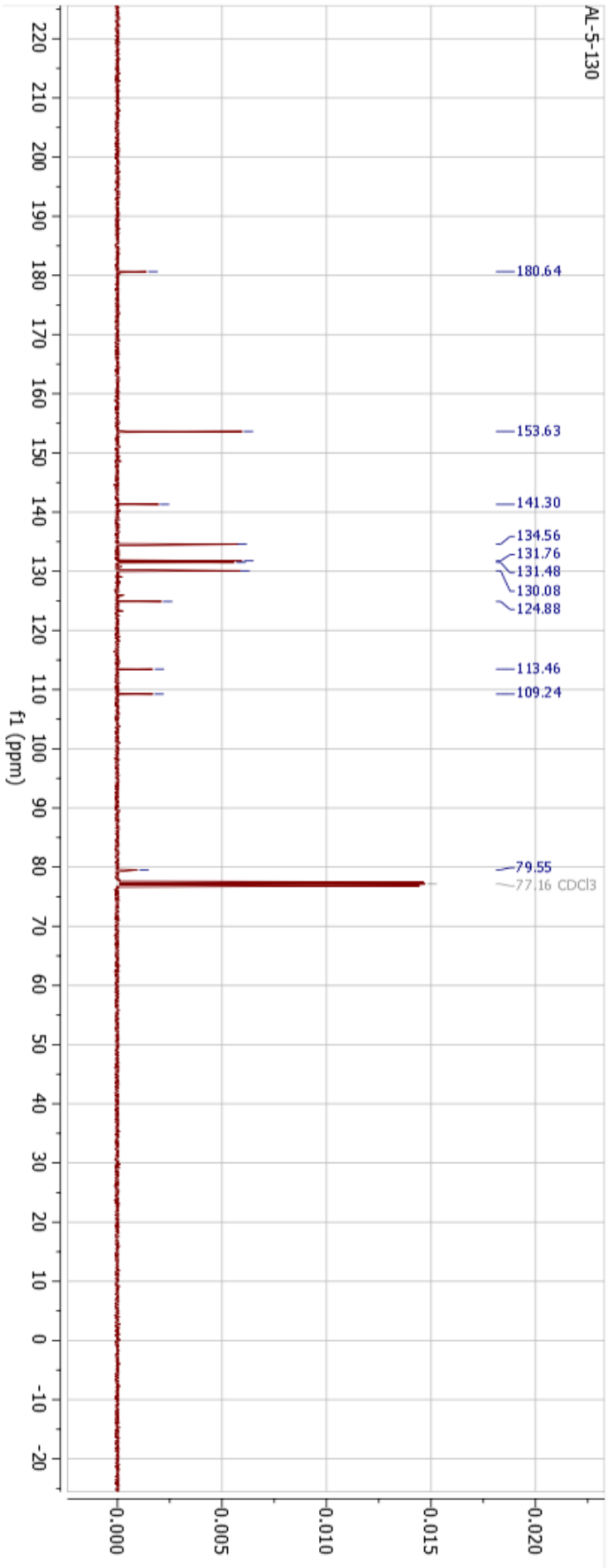


Figure S39. ^{13}C NMR of Product **12**.

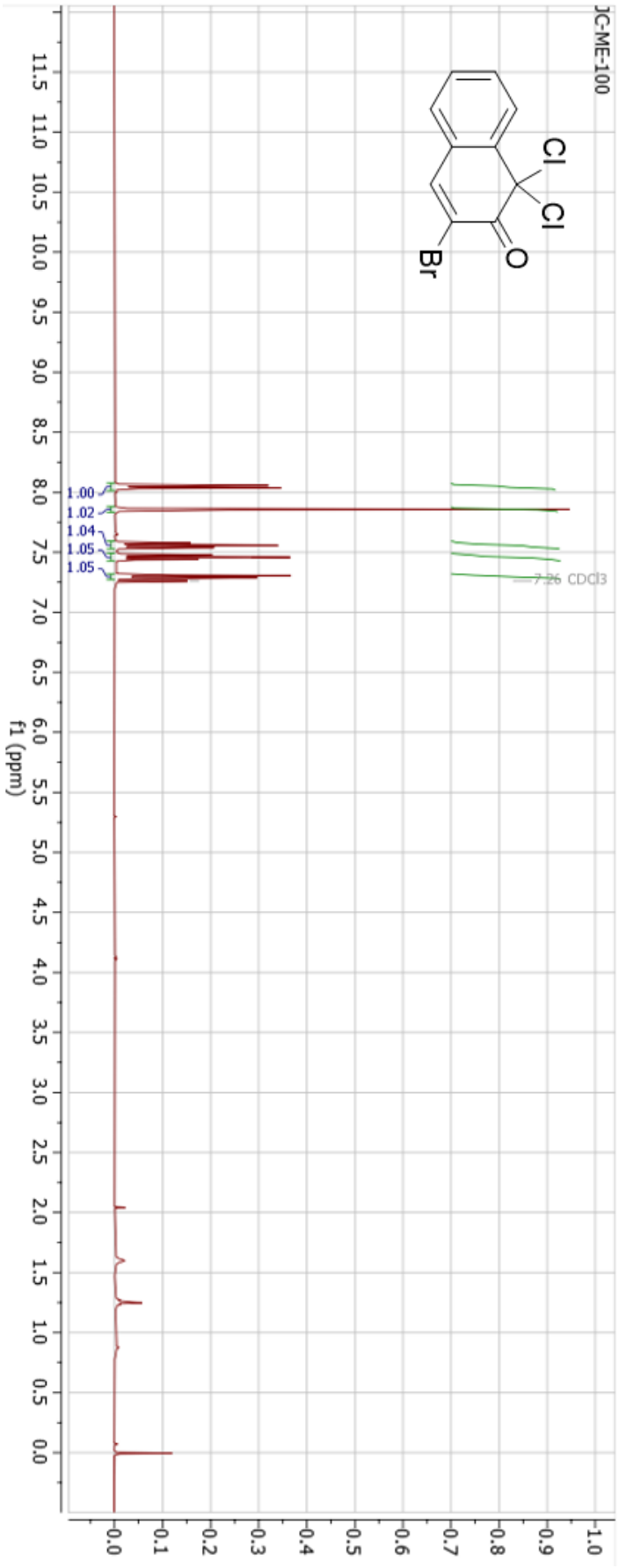


Figure S40. ^{1}H NMR of Product **13**.

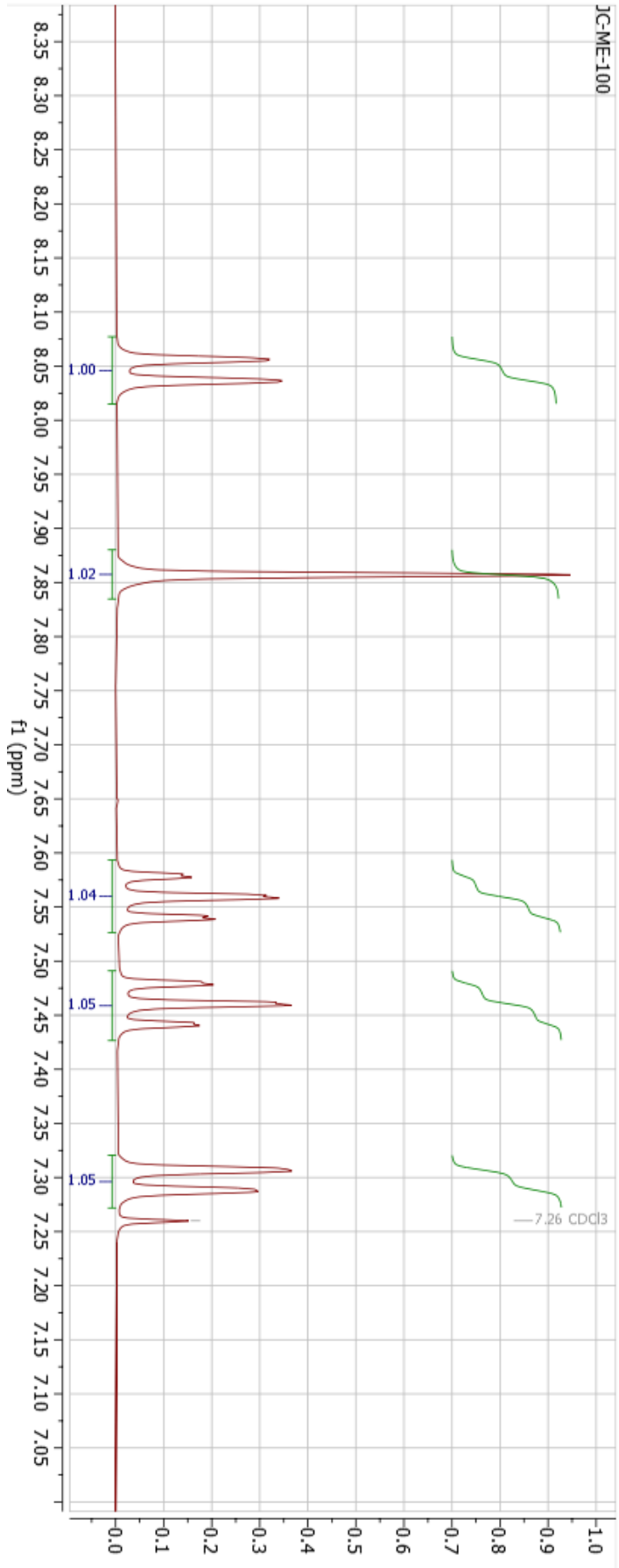


Figure S41. Zoomed in aromatic region of ^{1}H NMR of Product **13**.

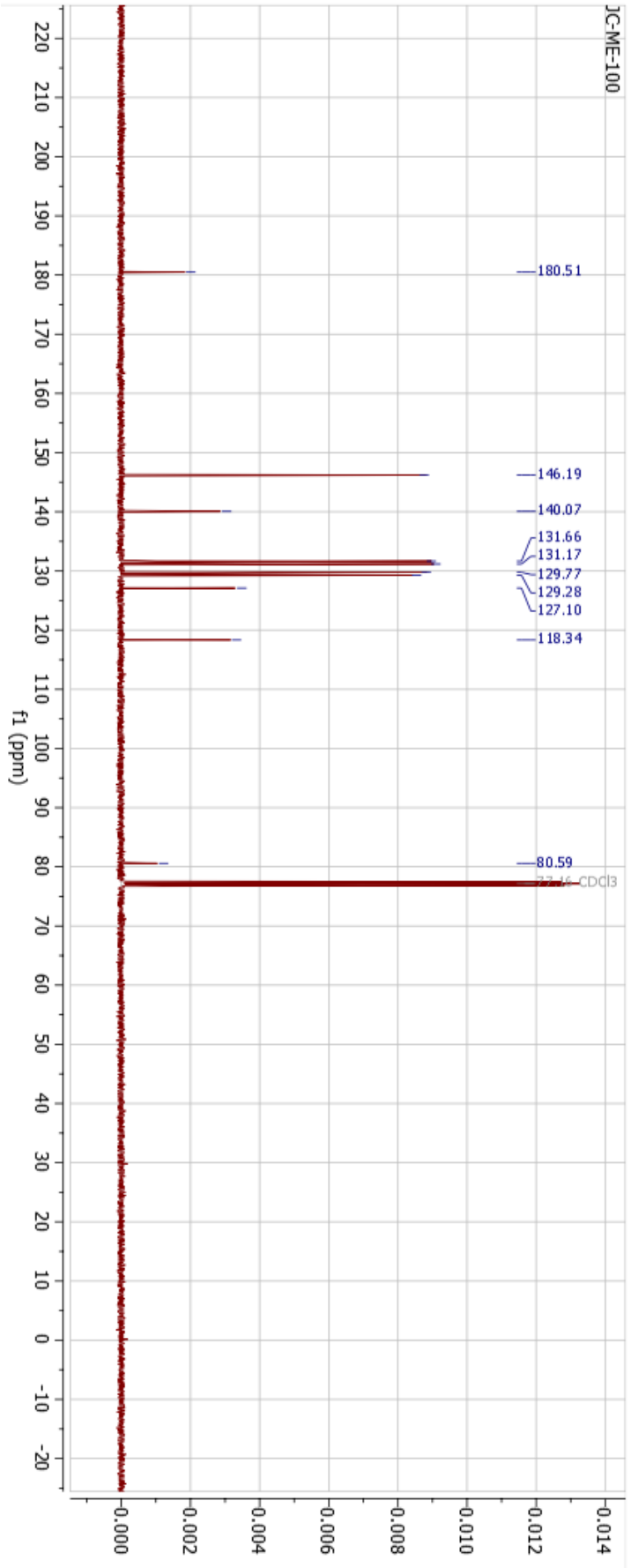


Figure S42. ^{13}C NMR of Product **13**.

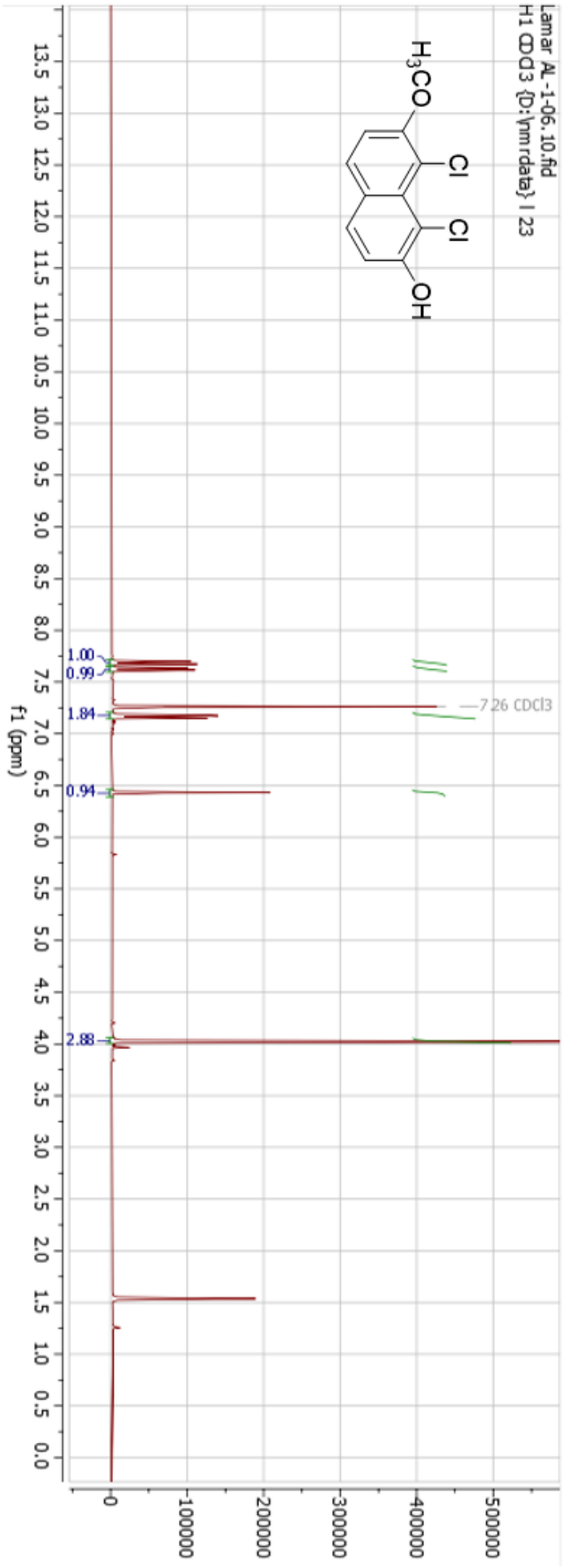


Figure S43. [1]H NMR of Product **14**.

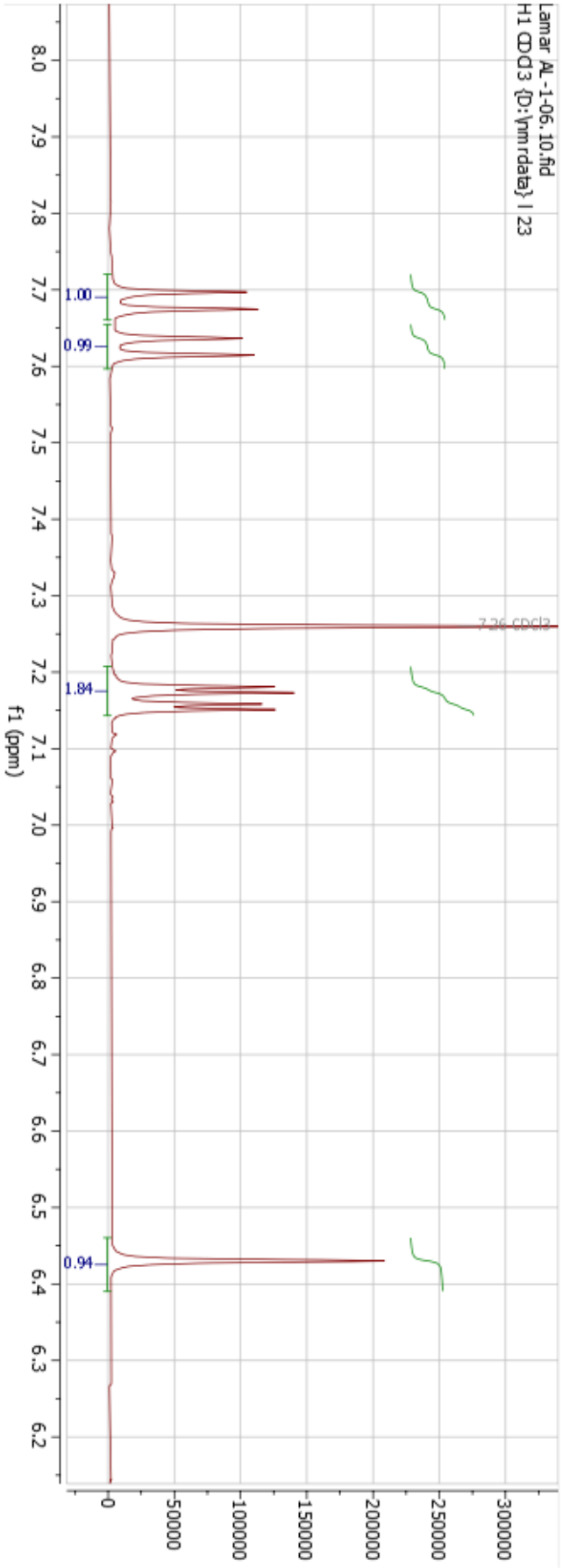


Figure S44. Zoomed in aromatic region of ^{1}H NMR of Product **14**.

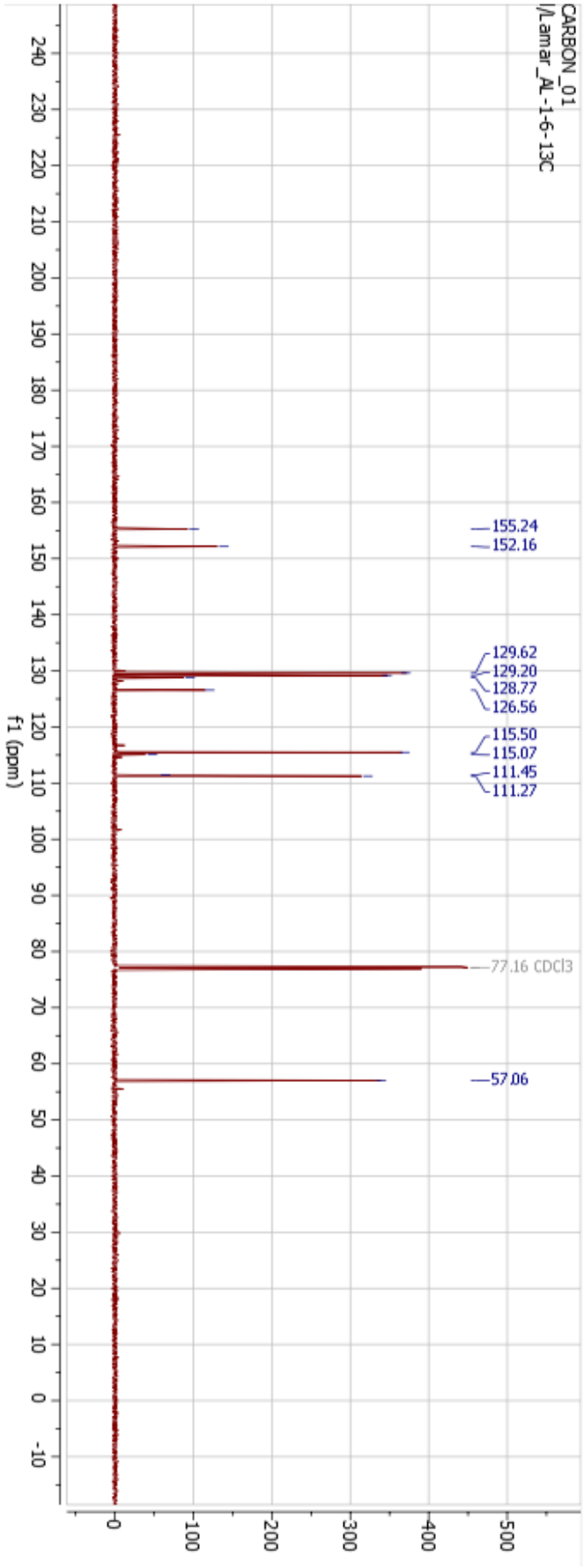


Figure S45. ^{13}C NMR of Product **14**.

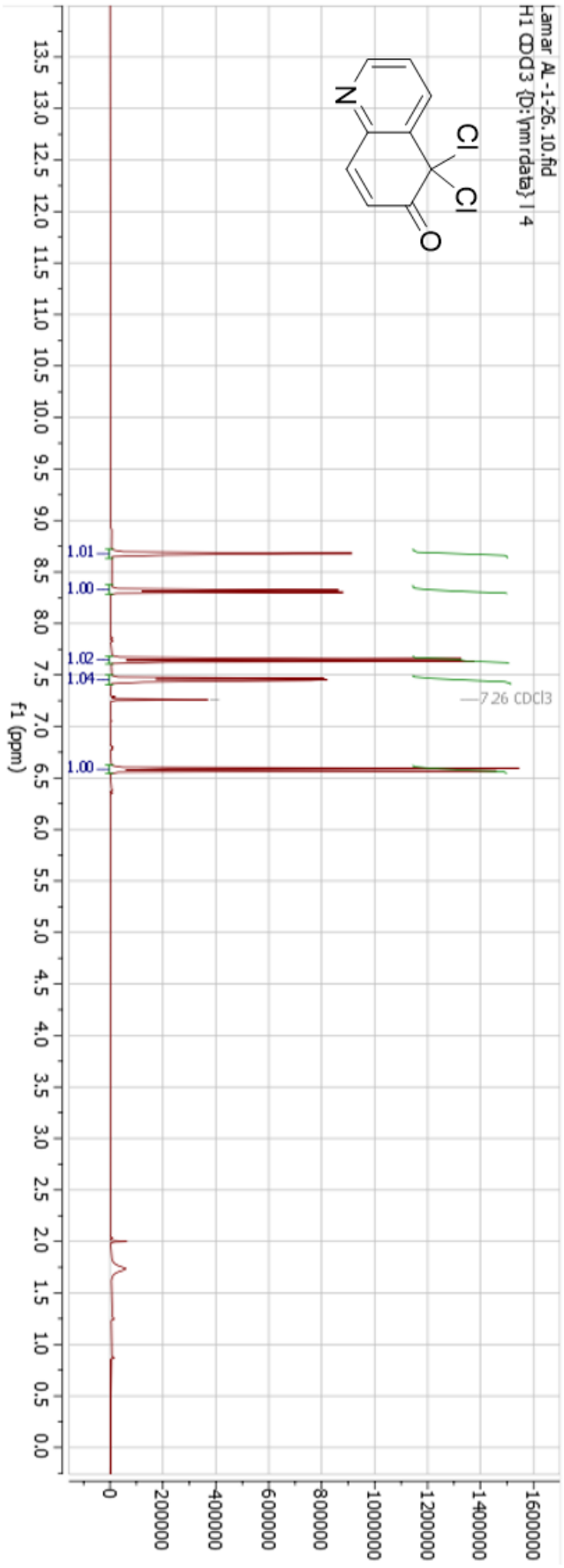


Figure S46. ^{1}H NMR of Product **15**.

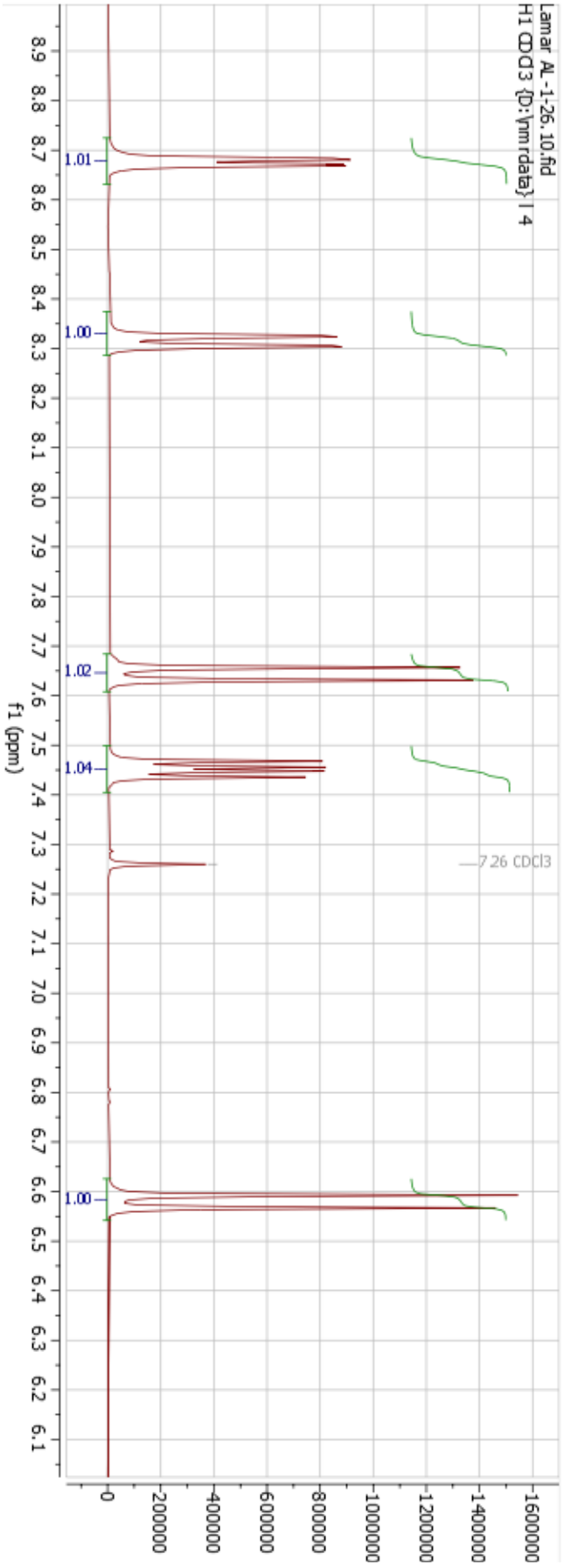


Figure S47. Zoomed in aromatic region of ^{1}H NMR of Product **15**.

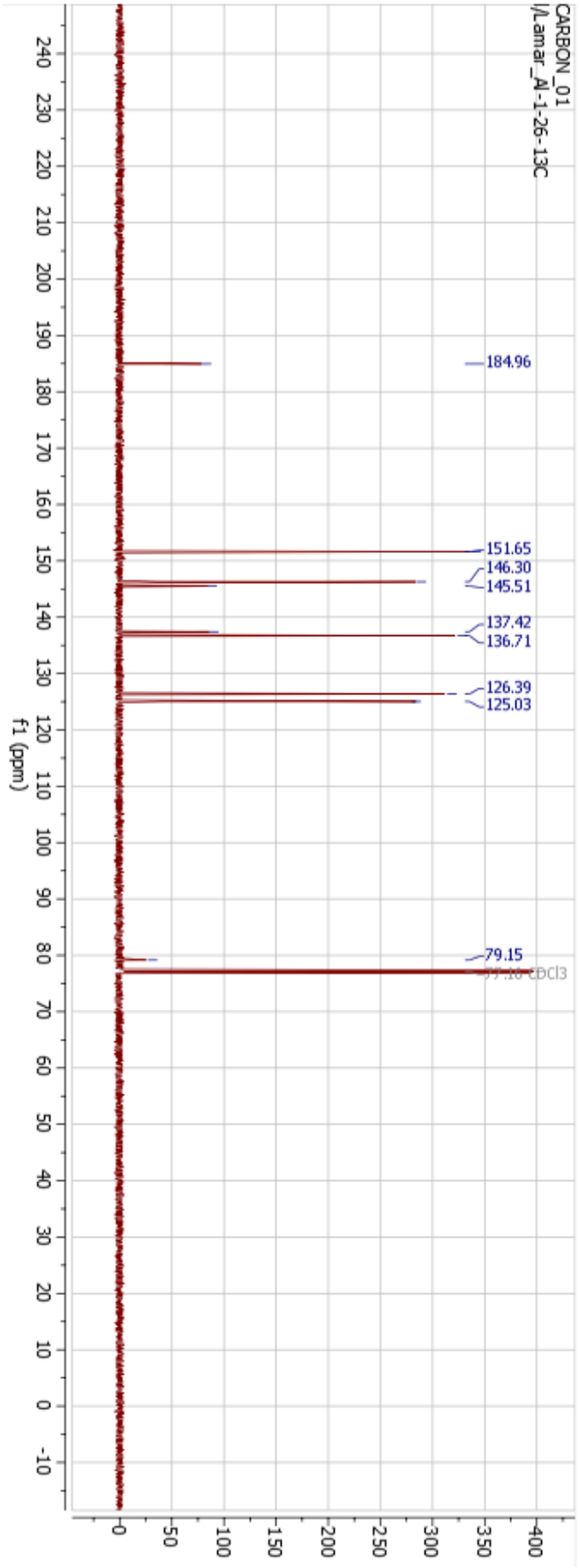


Figure S48. ^{13}C NMR of Product **15**.

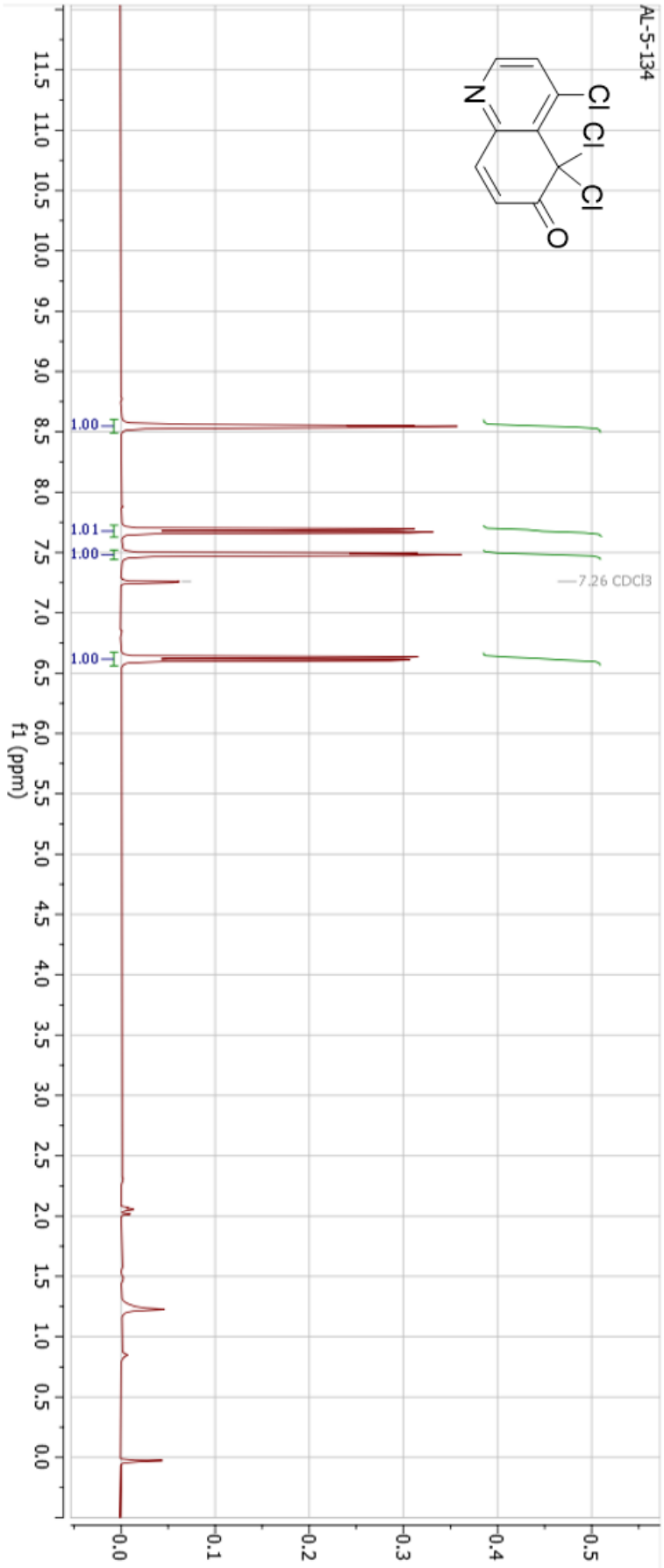


Figure S49. ^{1}H NMR of Product **16**.

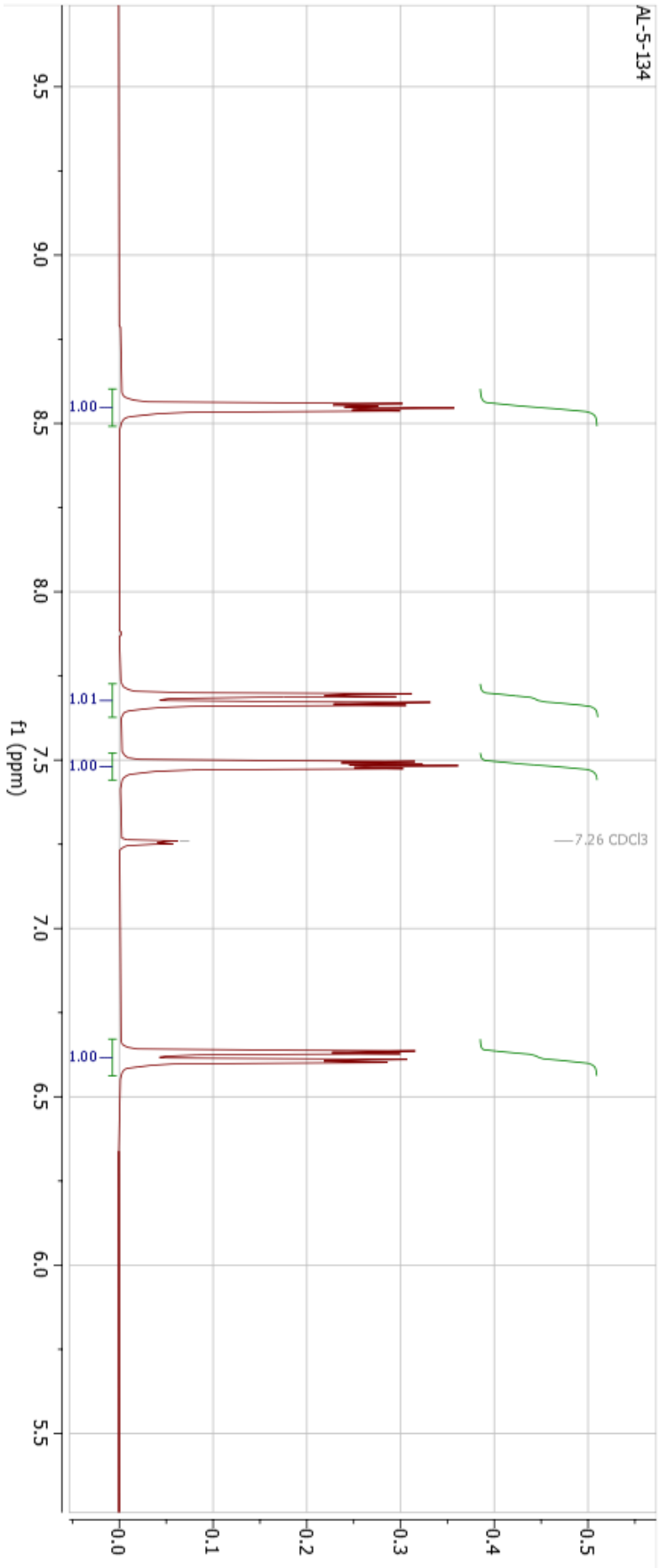


Figure S50. Zoomed in aromatic region of ^{1}H NMR of Product **16**.

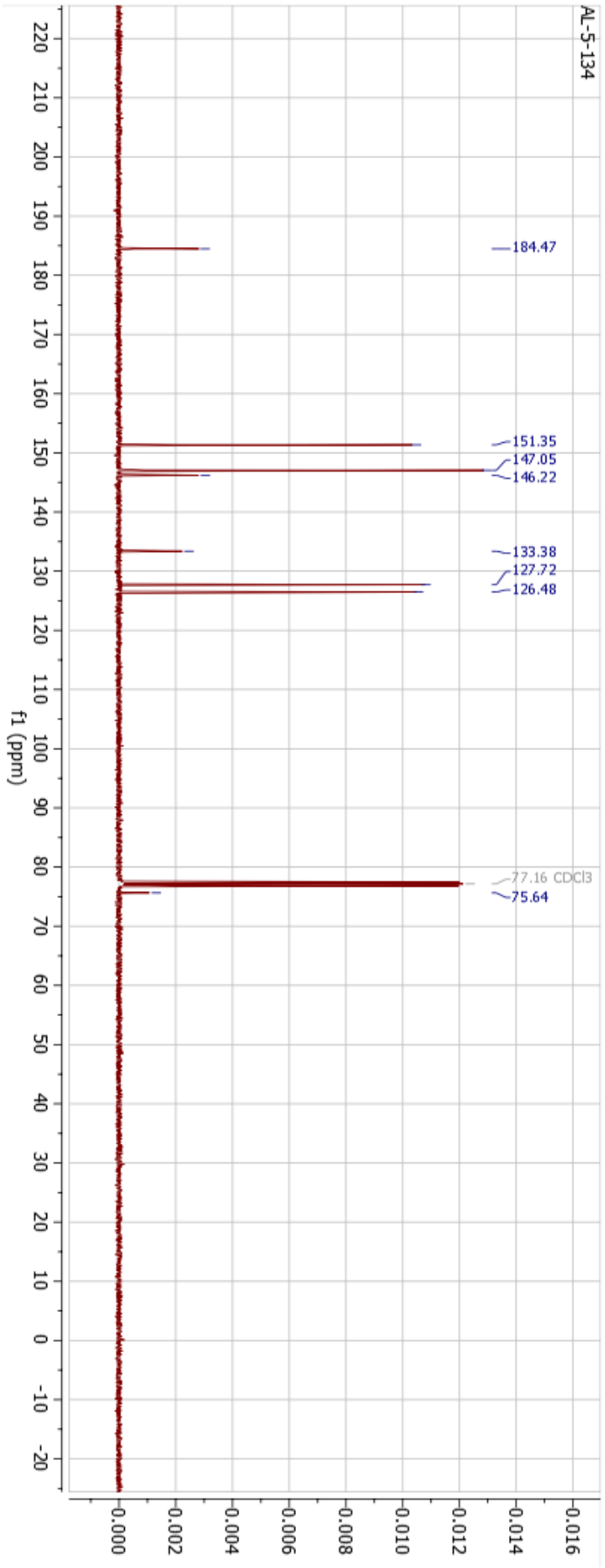


Figure S51. ^{13}C NMR of Product **16**.

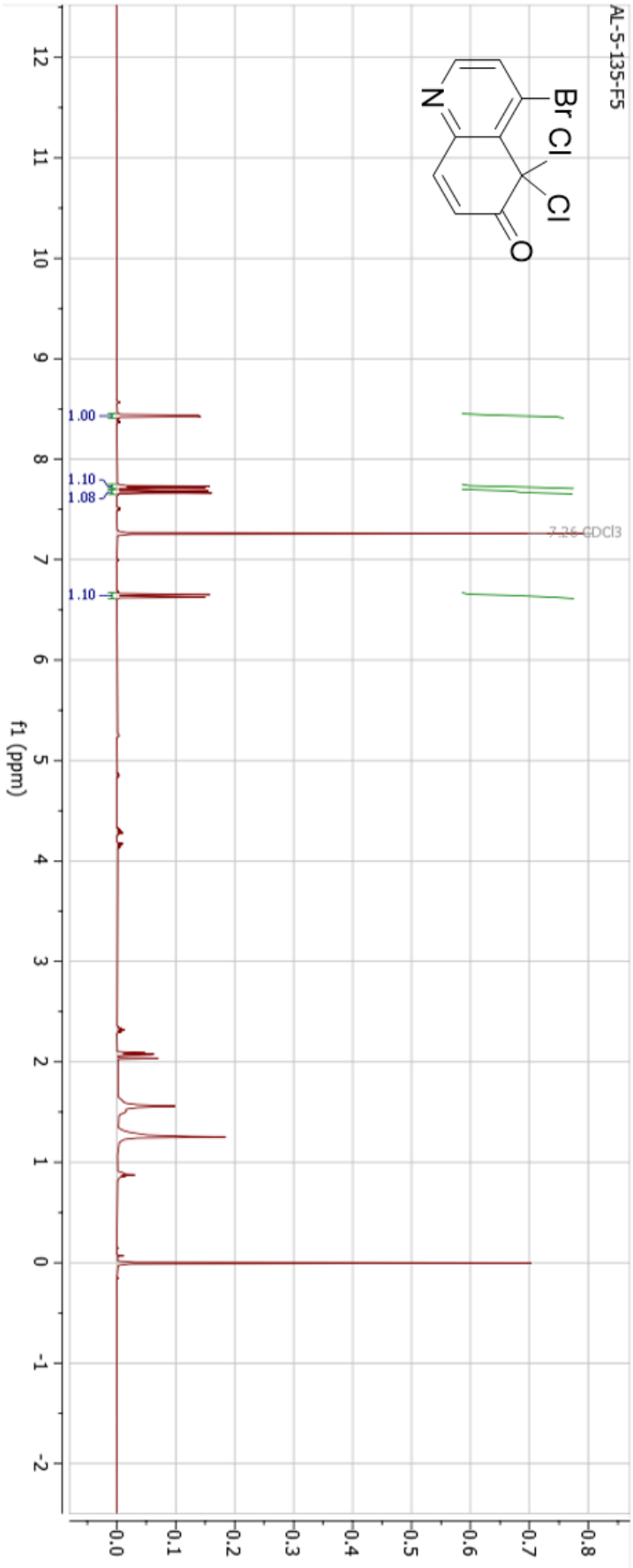


Figure S52. ^{1}H NMR of Product **17**.

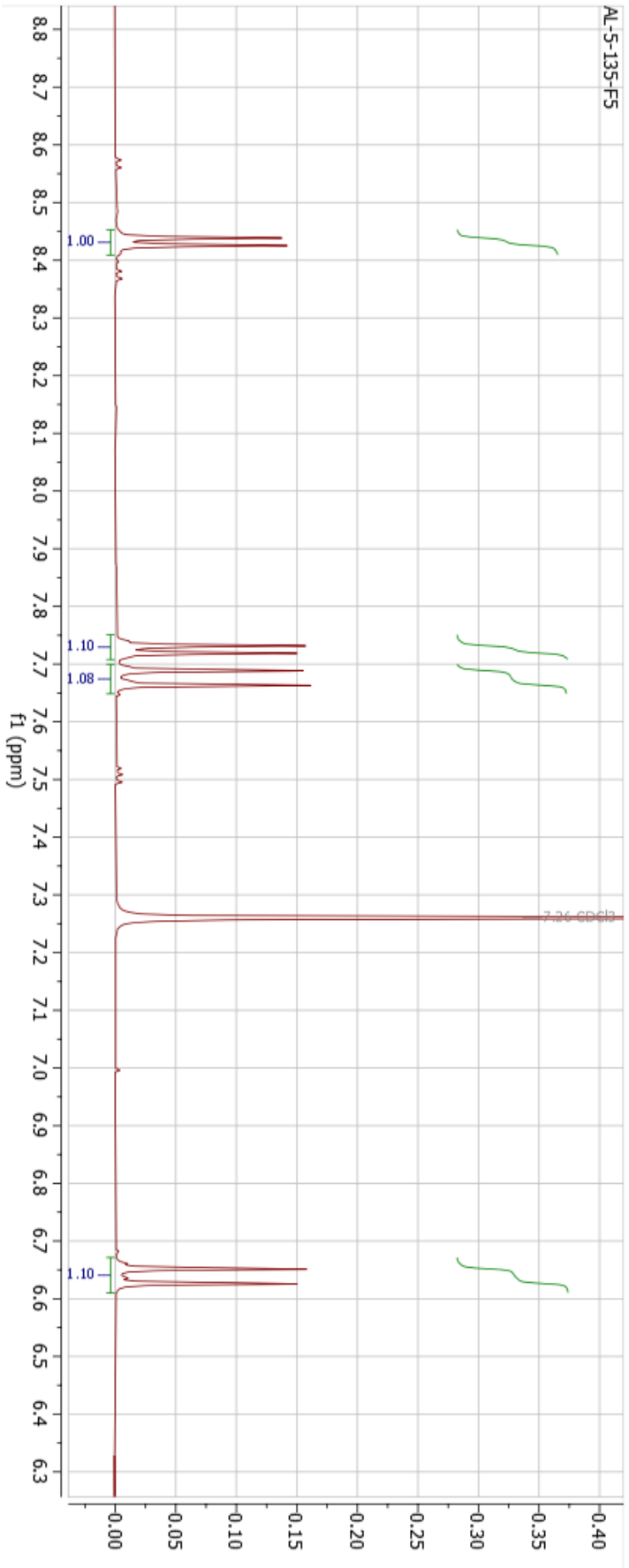


Figure S53. Zoomed in aromatic region of ^{1}H NMR of Product **17**.

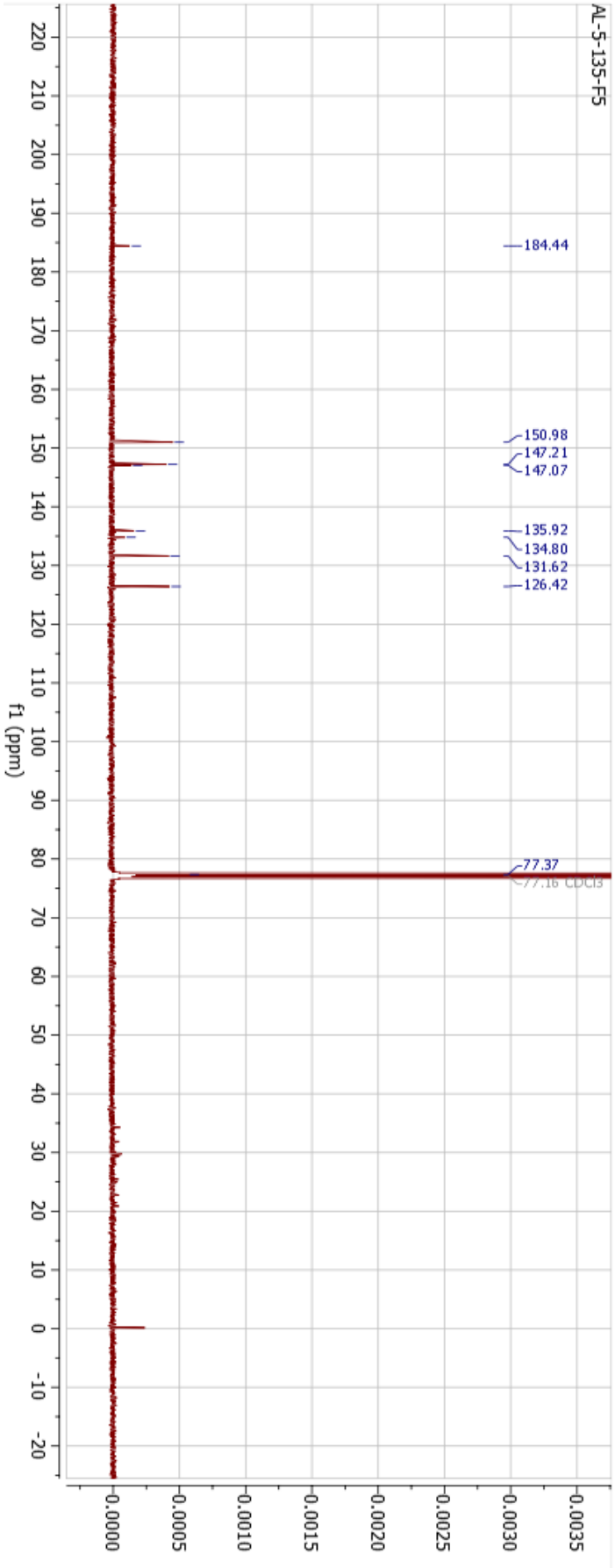


Figure S54. ^{13}C NMR of Product **17**.

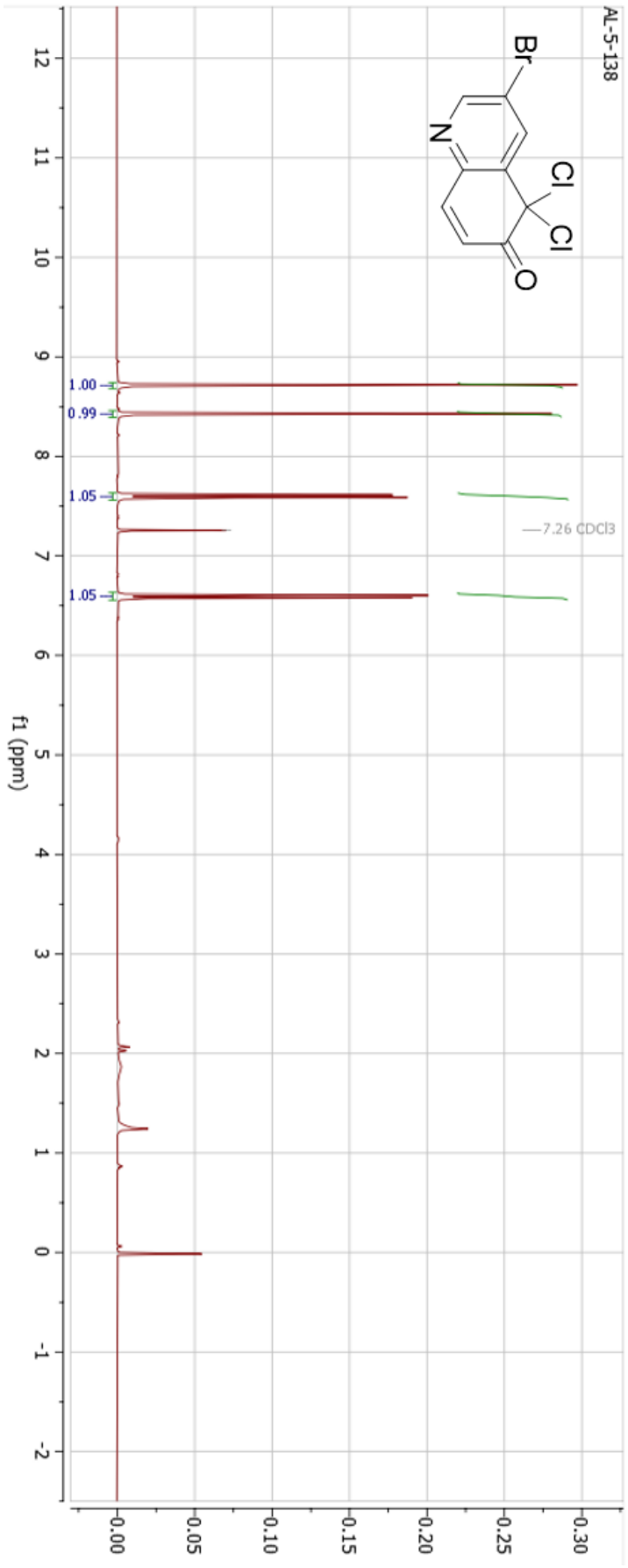


Figure S55. ^{1}H NMR of Product **18**.

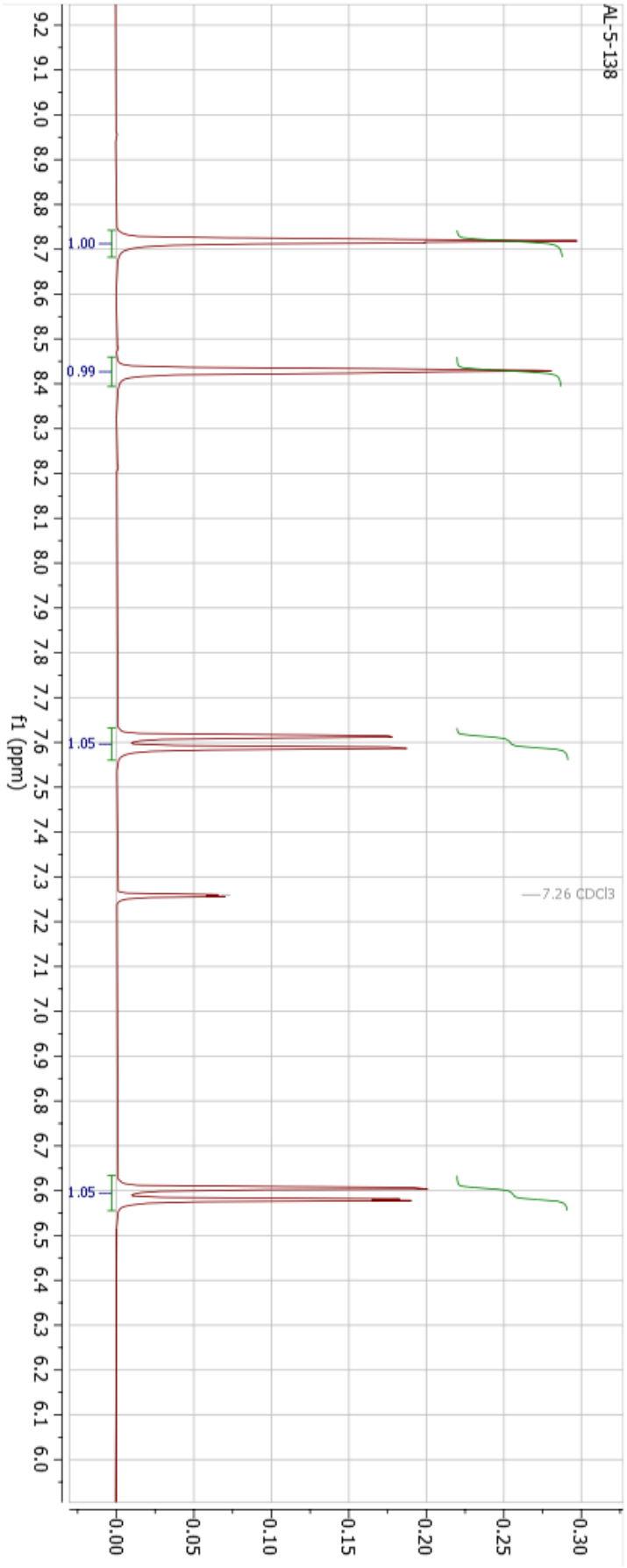


Figure S56. Zoomed in aromatic region of ^{1}H NMR of Product **18**.

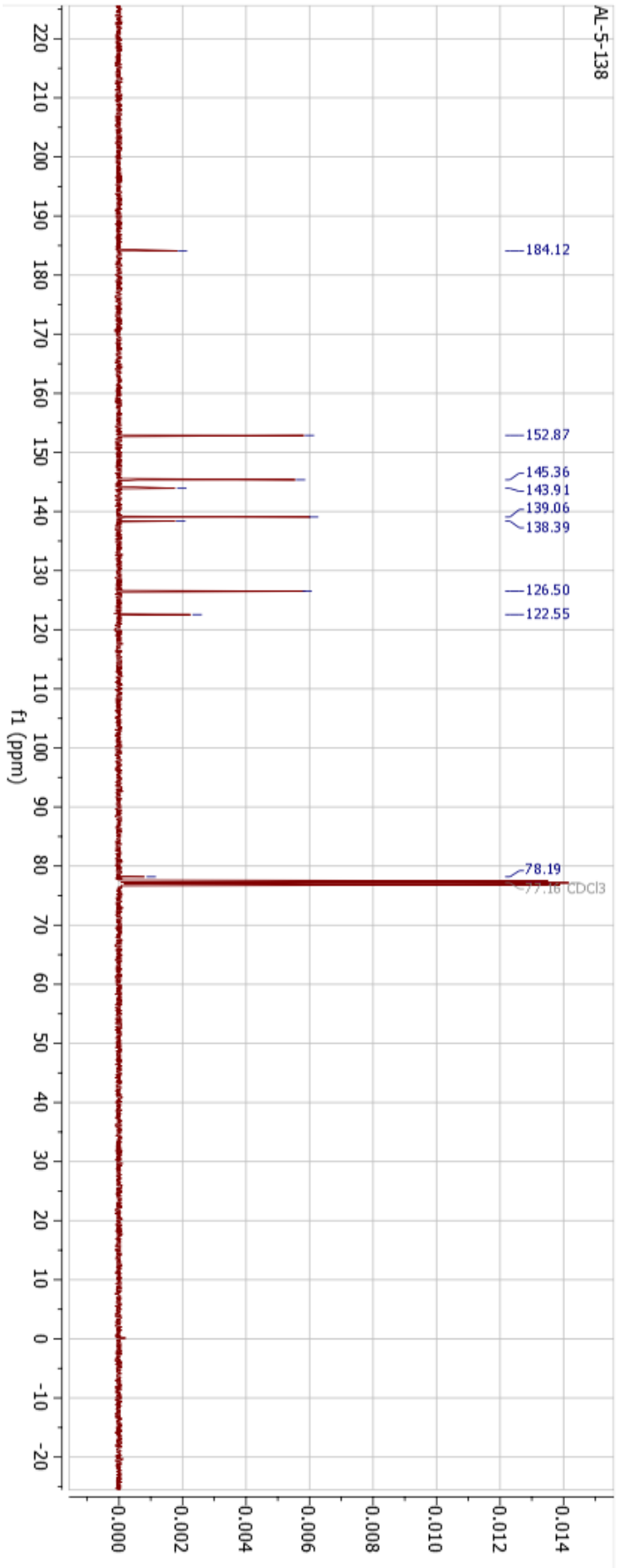


Figure S57. ^{13}C NMR of Product **18**.

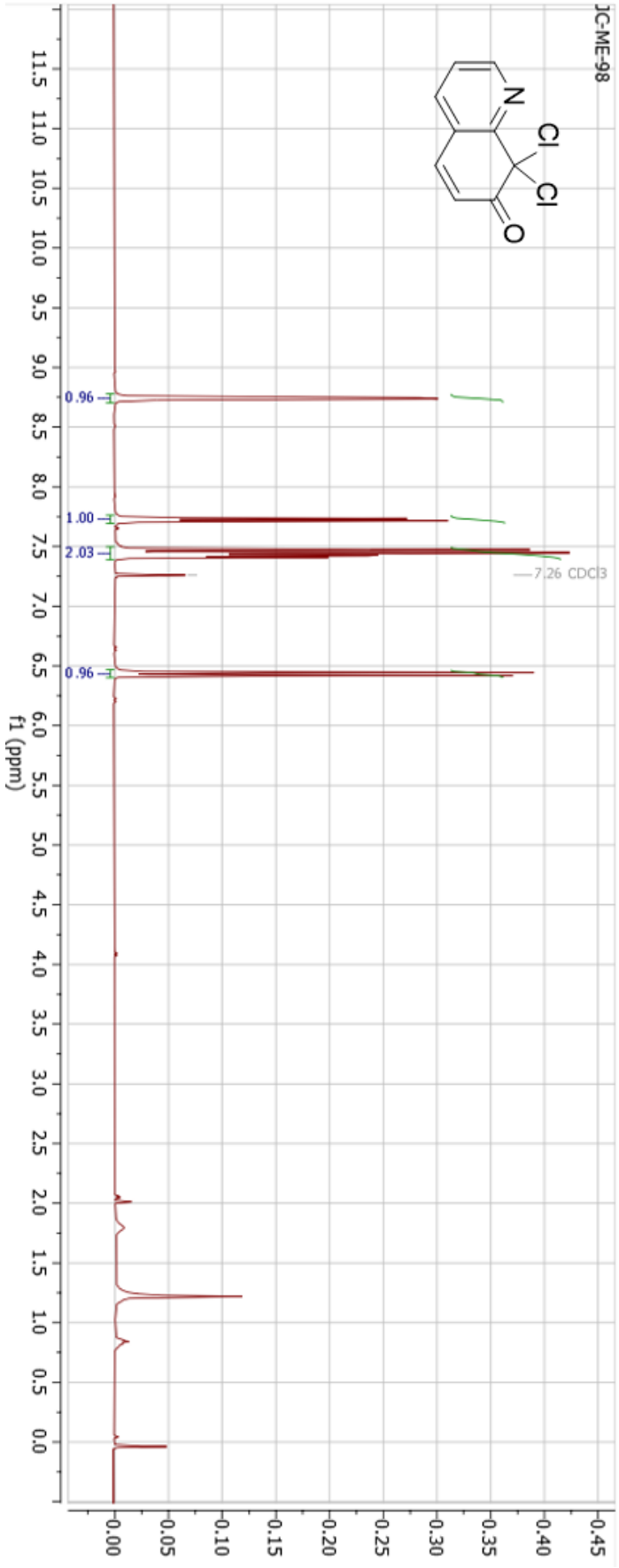


Figure S58. ^{1}H NMR of Product **19**.

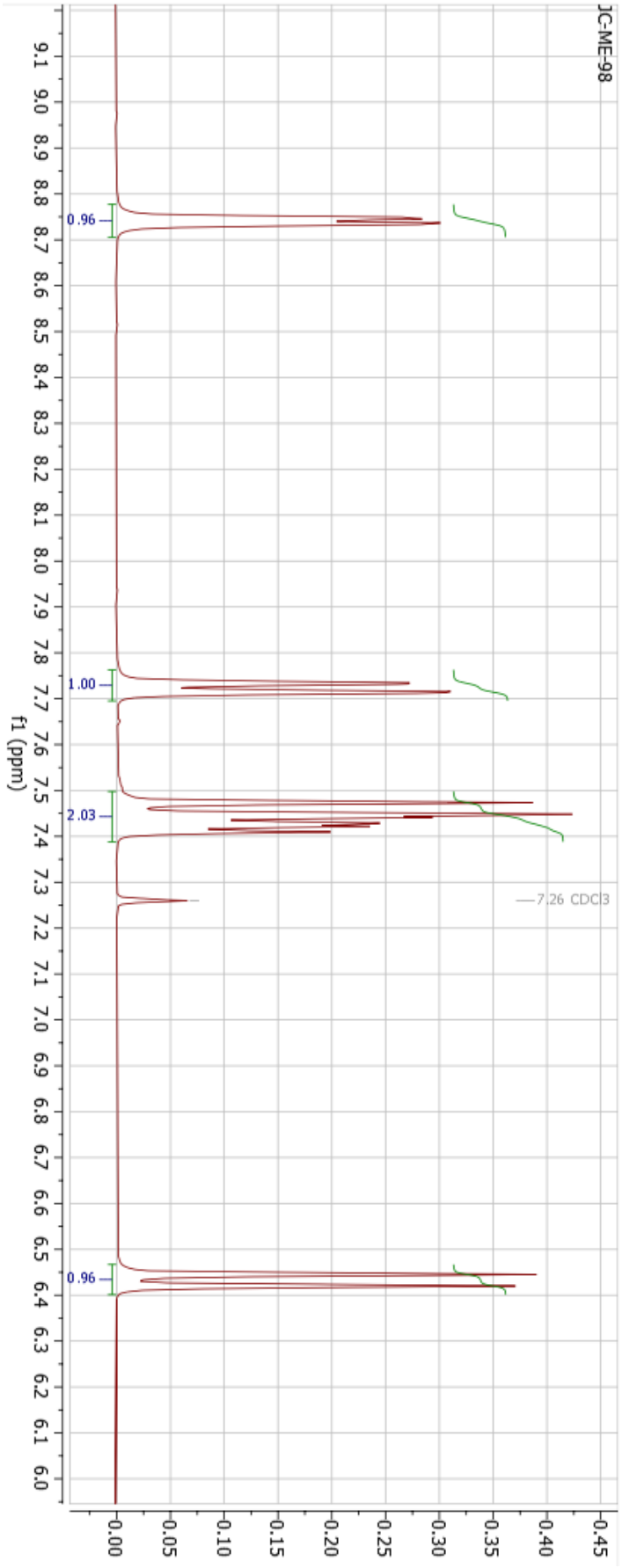


Figure S59. Zoomed in aromatic region of ^{1}H NMR of Product **19**.

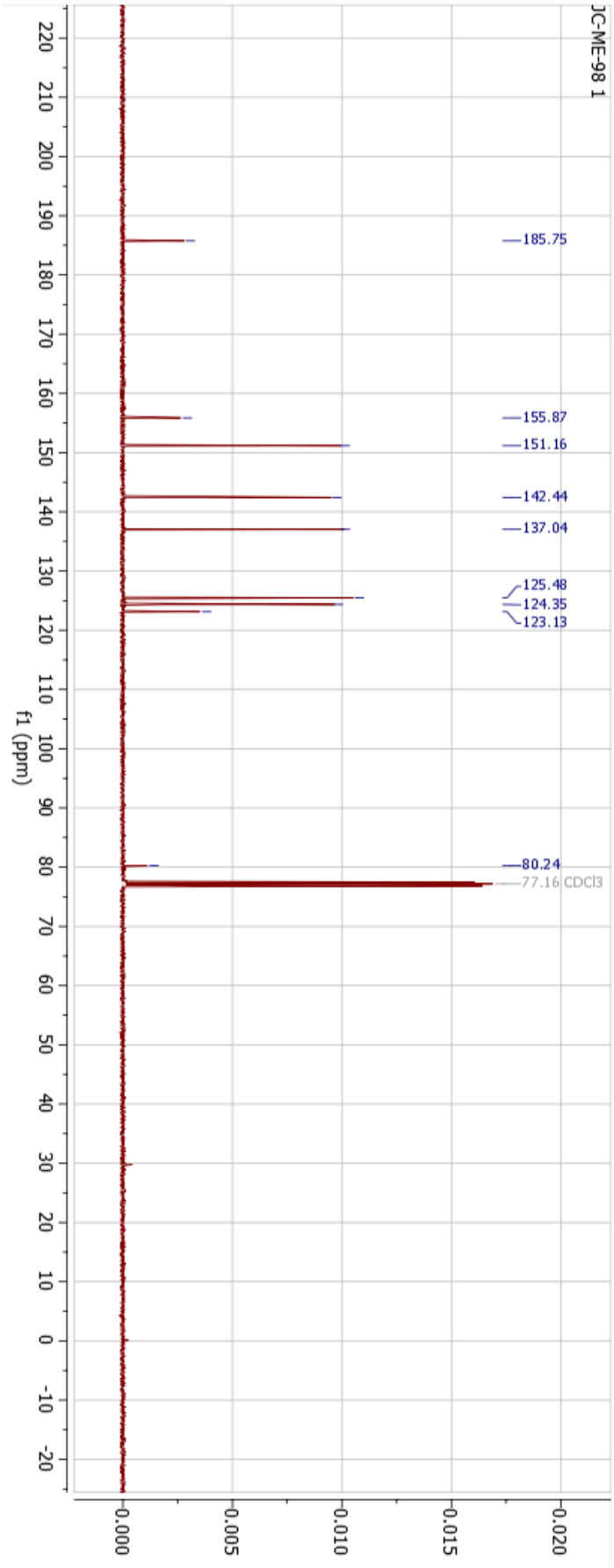


Figure S60. ^{13}C NMR of Product **19**.

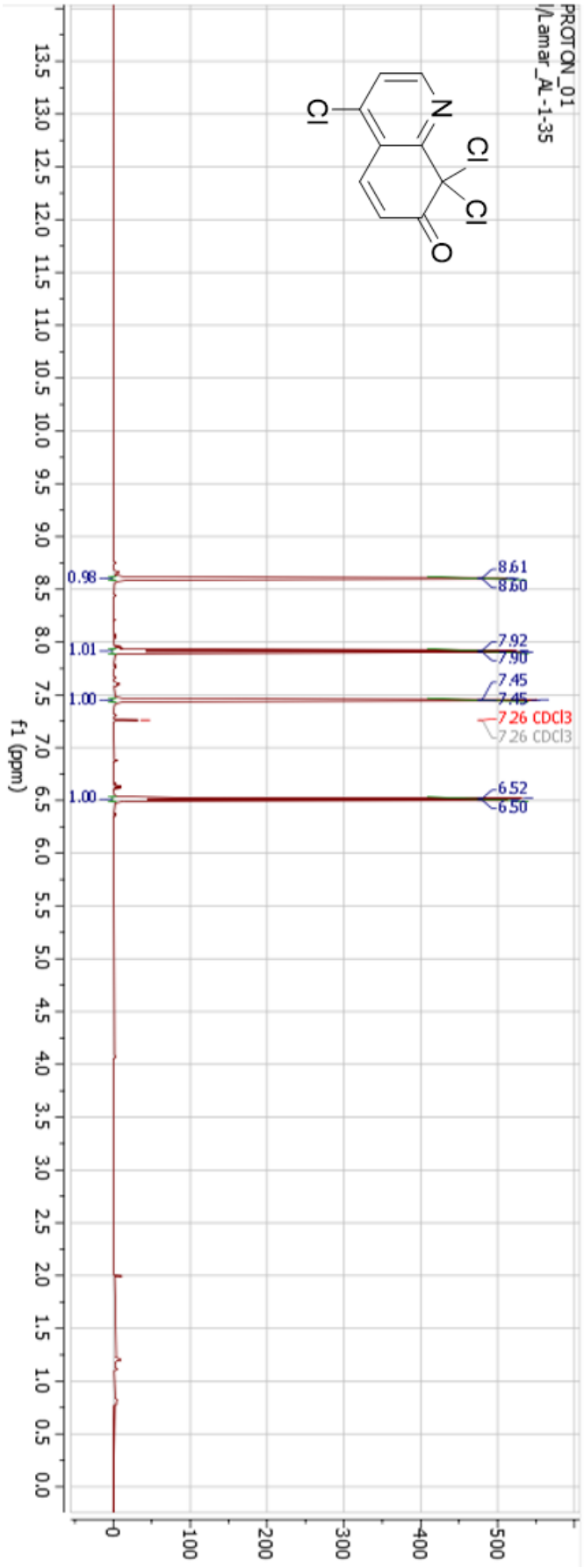


Figure S61. ^{1}H NMR of Product **20**.

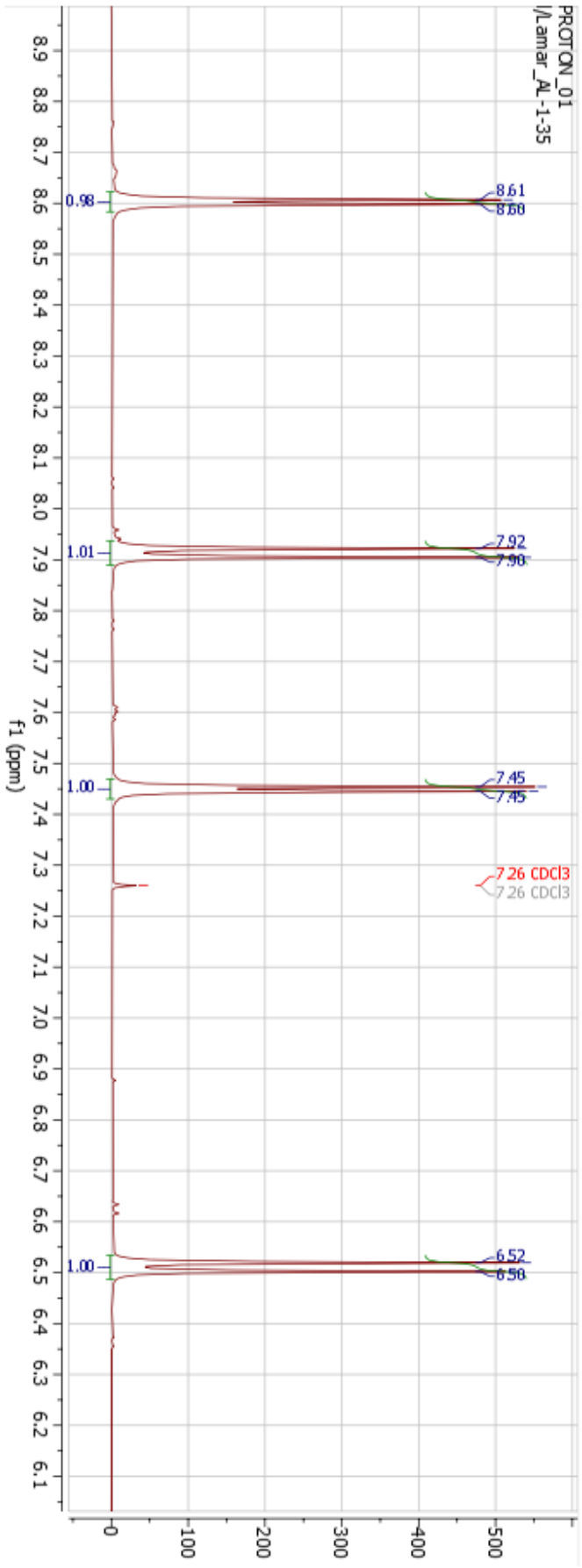


Figure S62. Zoomed in aromatic region of ^{1}H NMR of Product **20**.

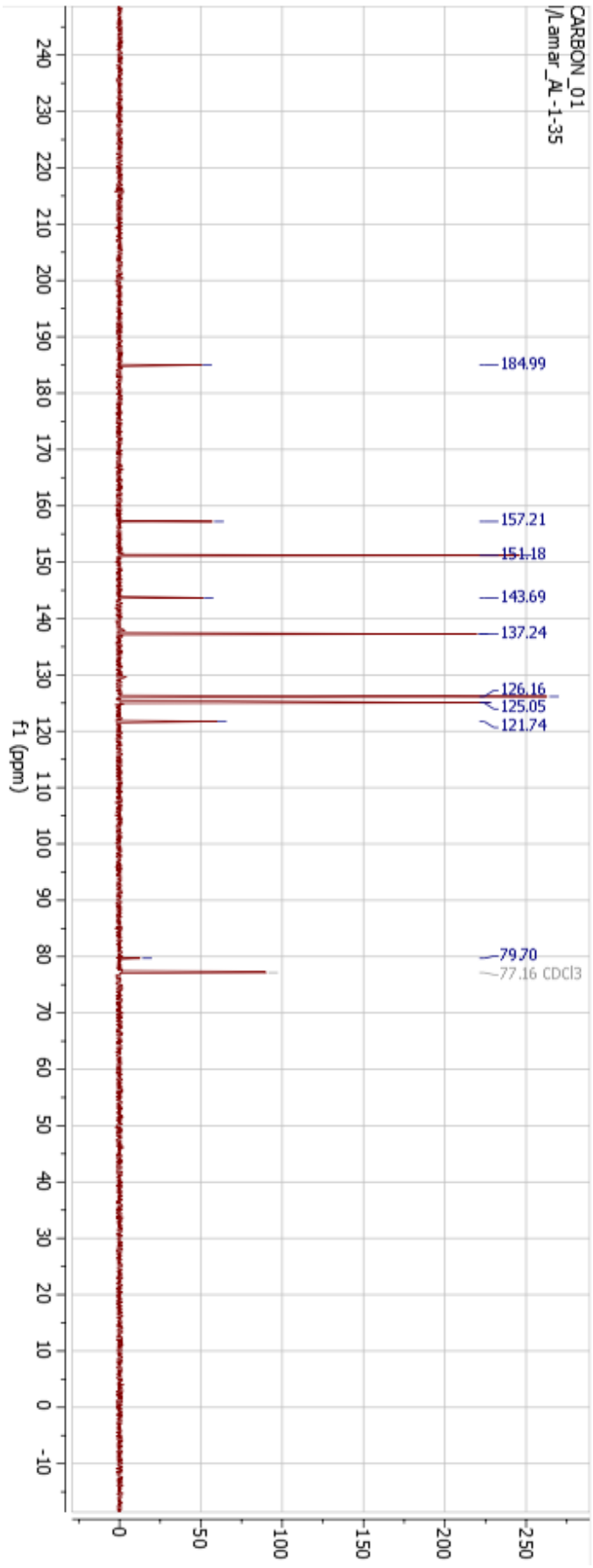


Figure S63. ^{13}C NMR of Product **20**.

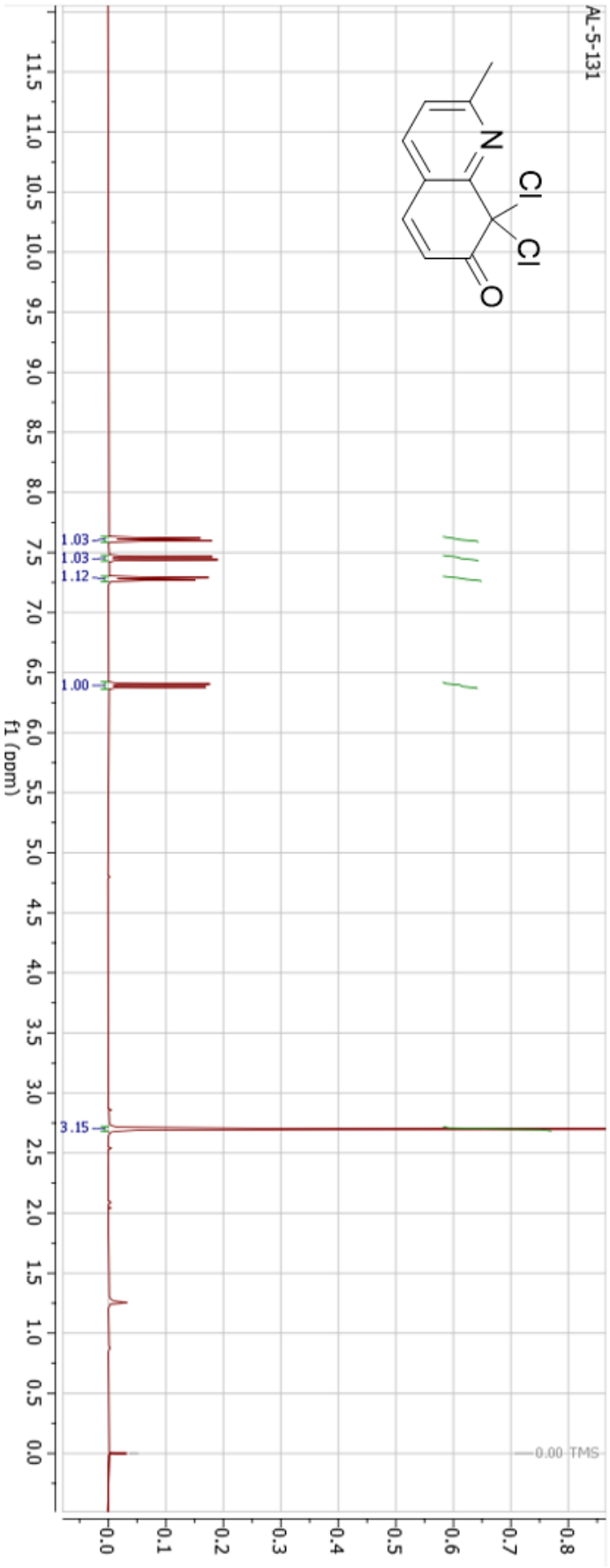


Figure S64. [1]H NMR of Product **21**.

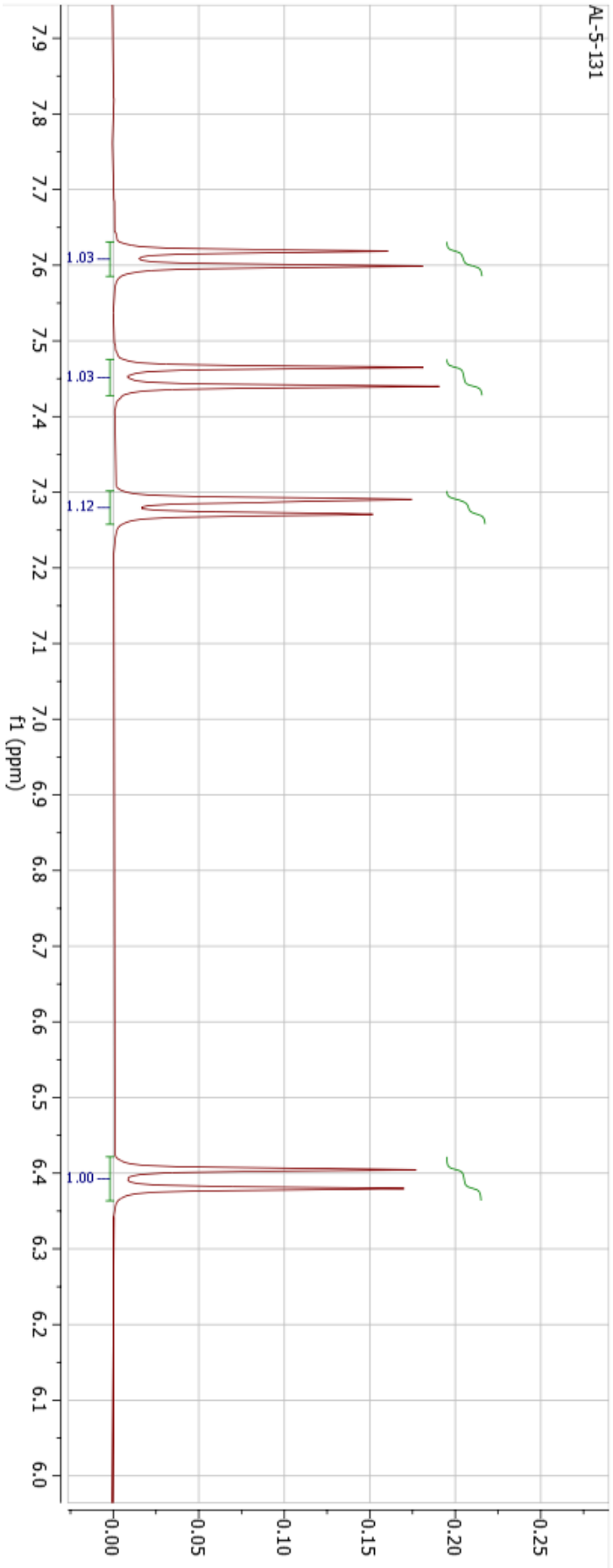


Figure S65. Zoomed in aromatic region of ^{1}H NMR of Product **21**.

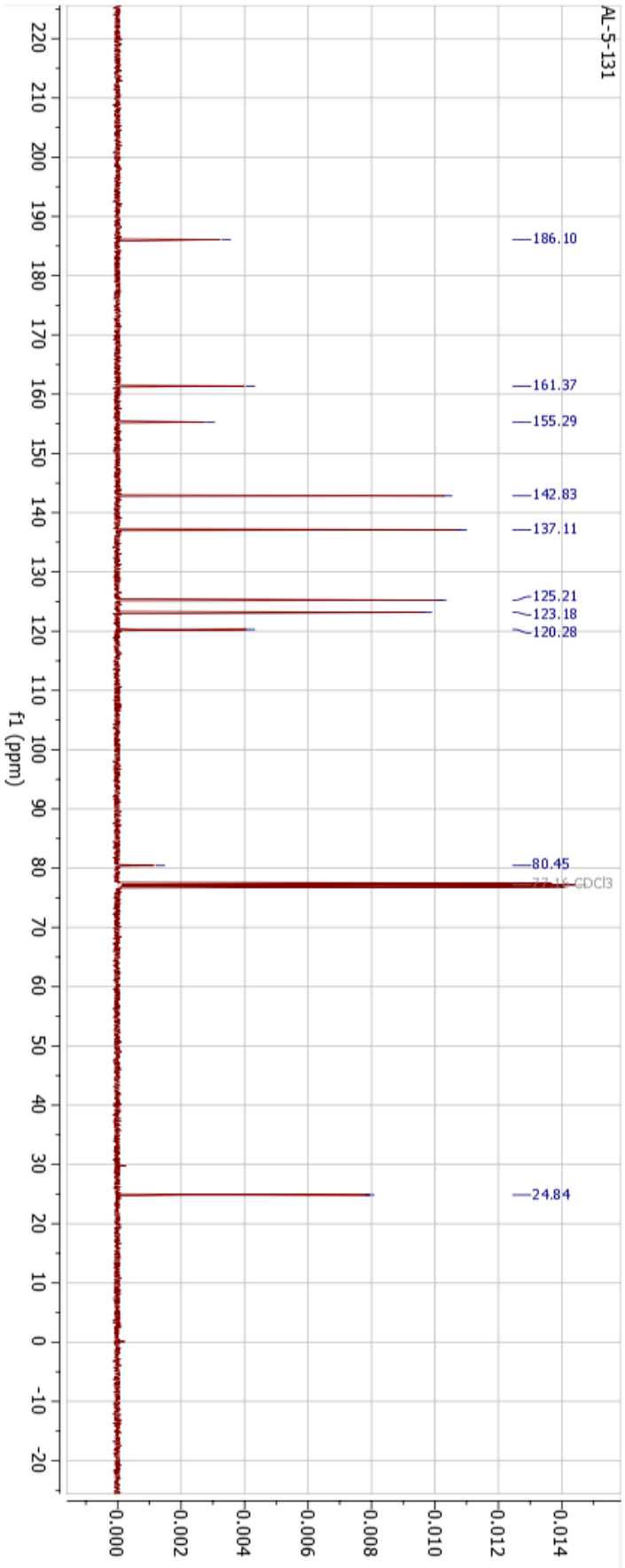


Figure S66. ^{13}C NMR of Product **21**.

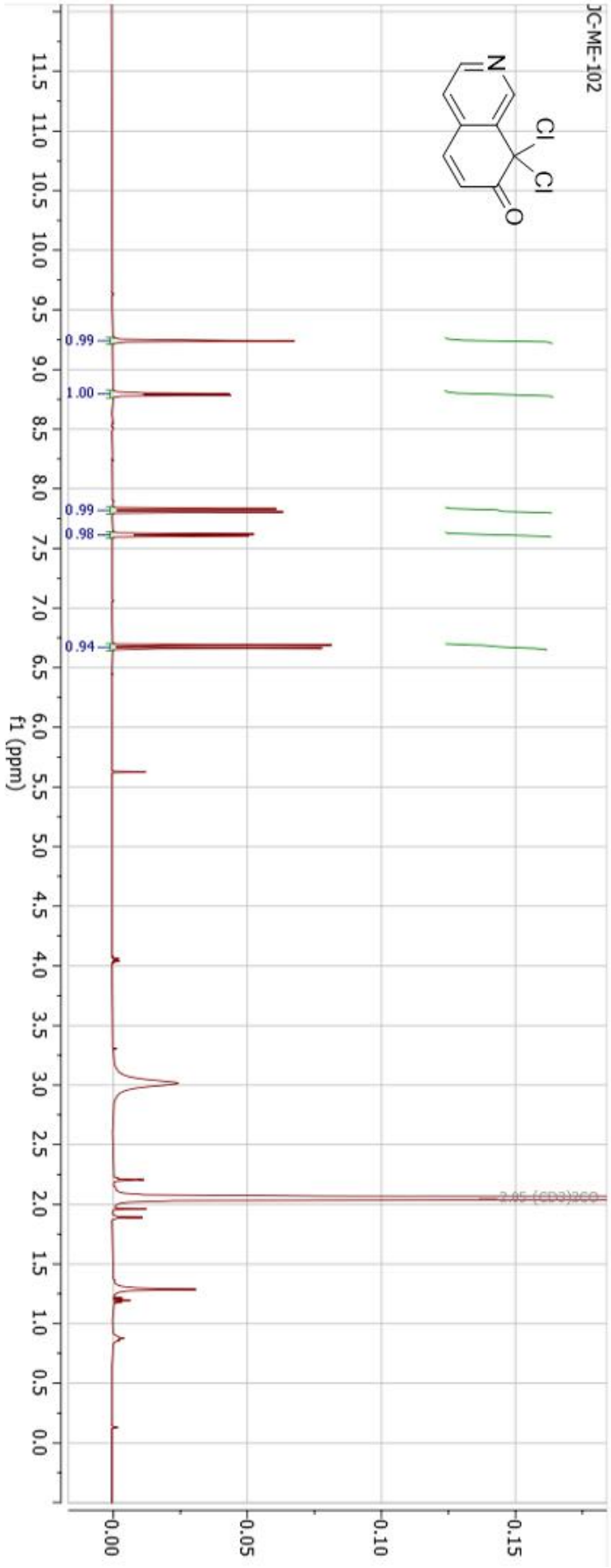


Figure S67. ^{1}H NMR of Product **22**.

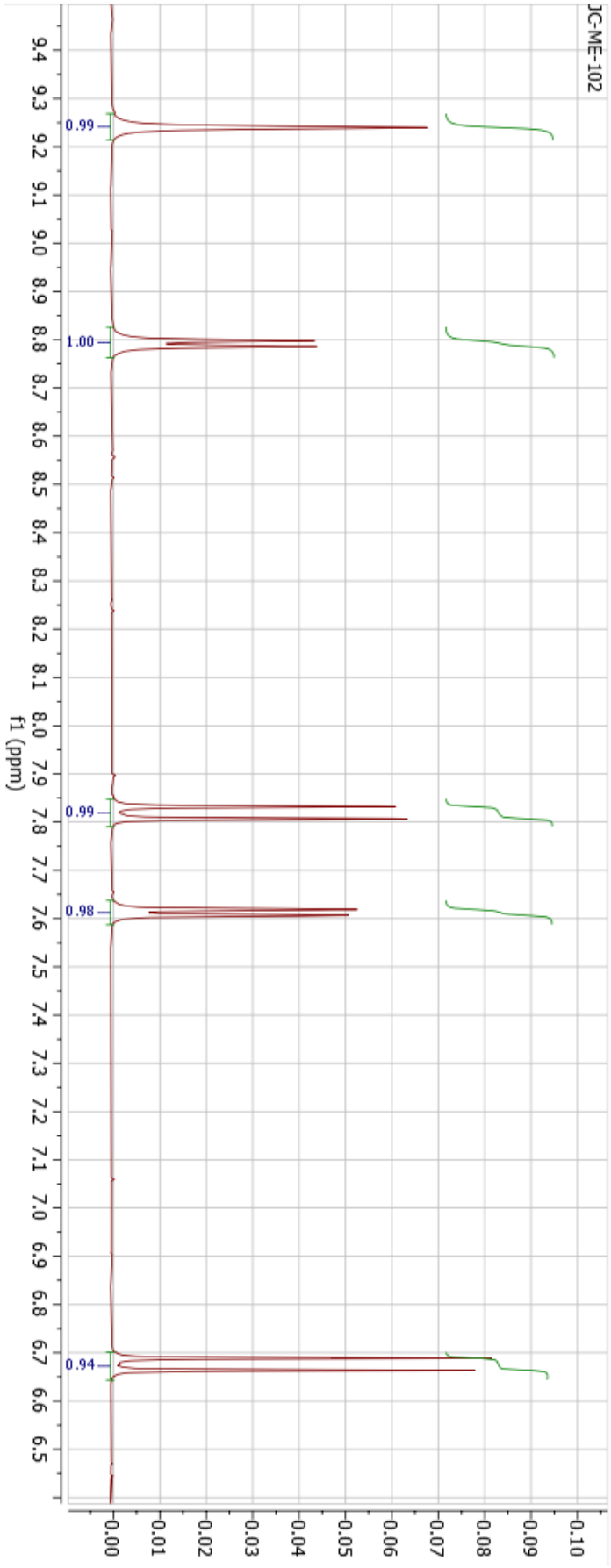


Figure S68. Zoomed in aromatic region of ^{1}H NMR of Product **22**.

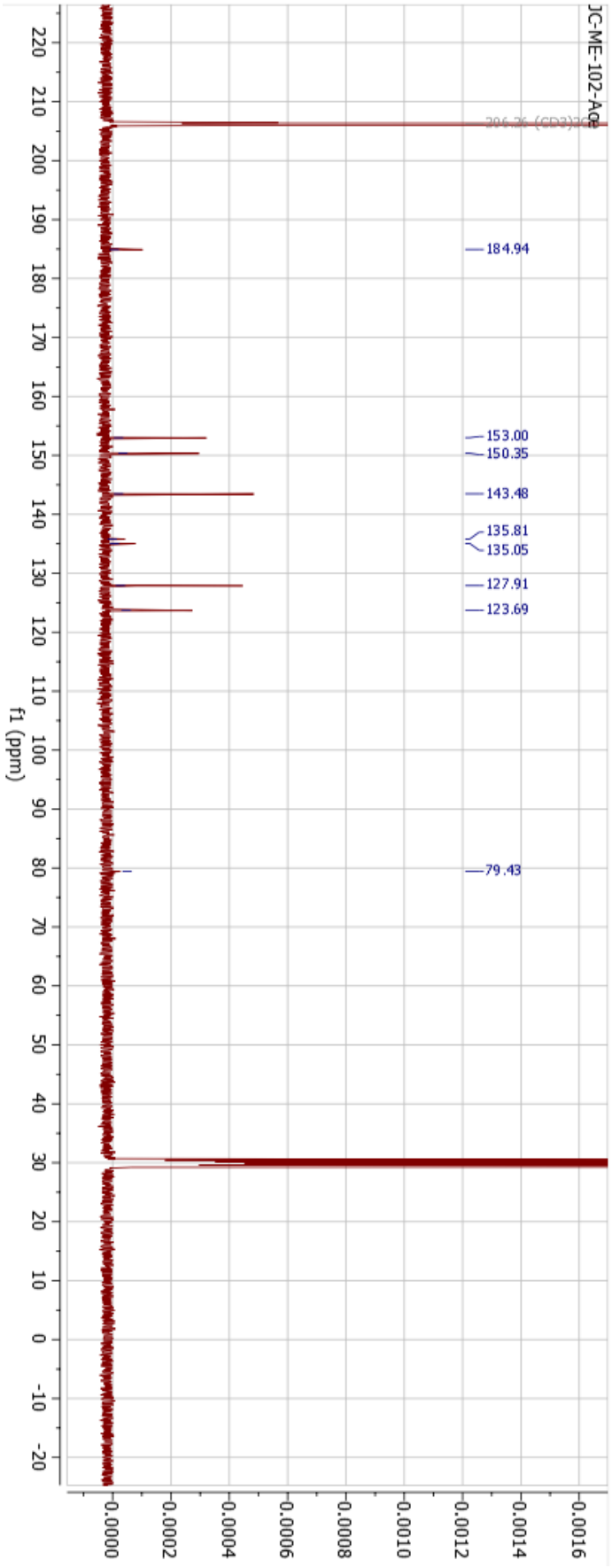


Figure S69. ^{13}C NMR of Product **22**.

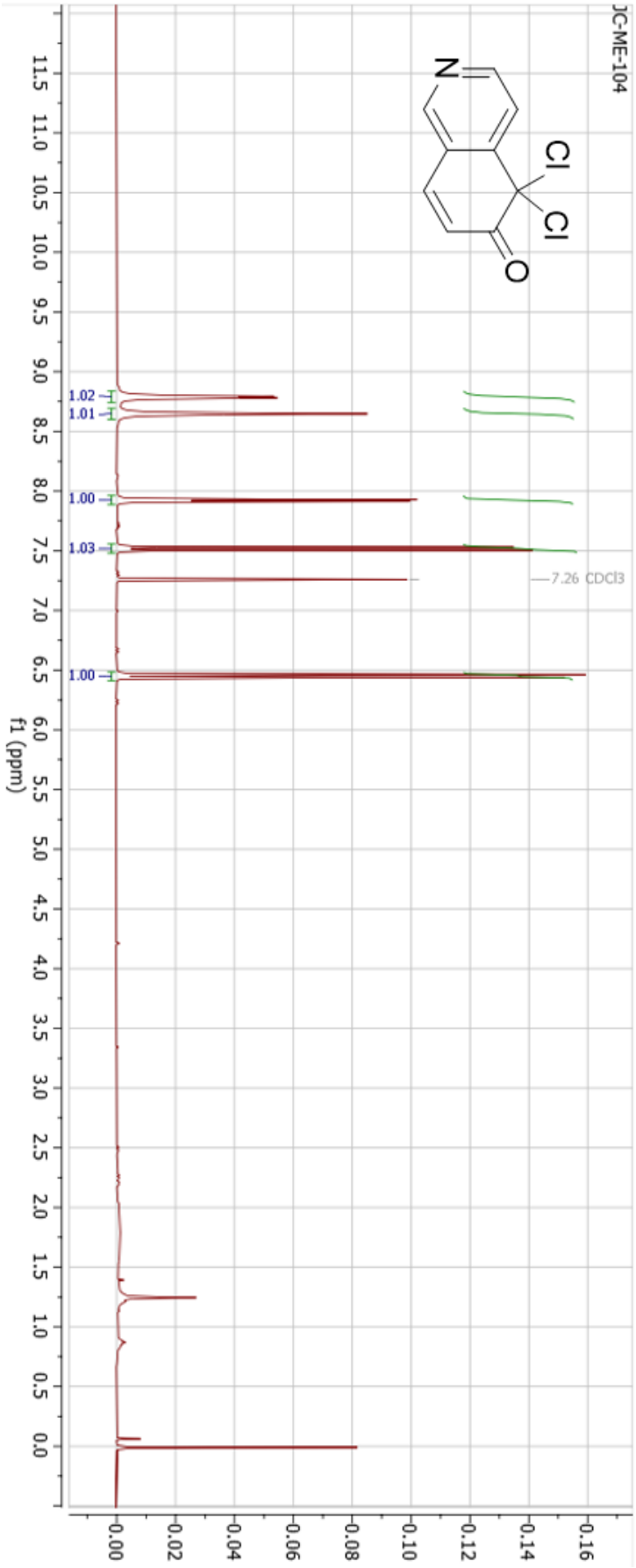


Figure S70. ^{1}H NMR of Product **23**.

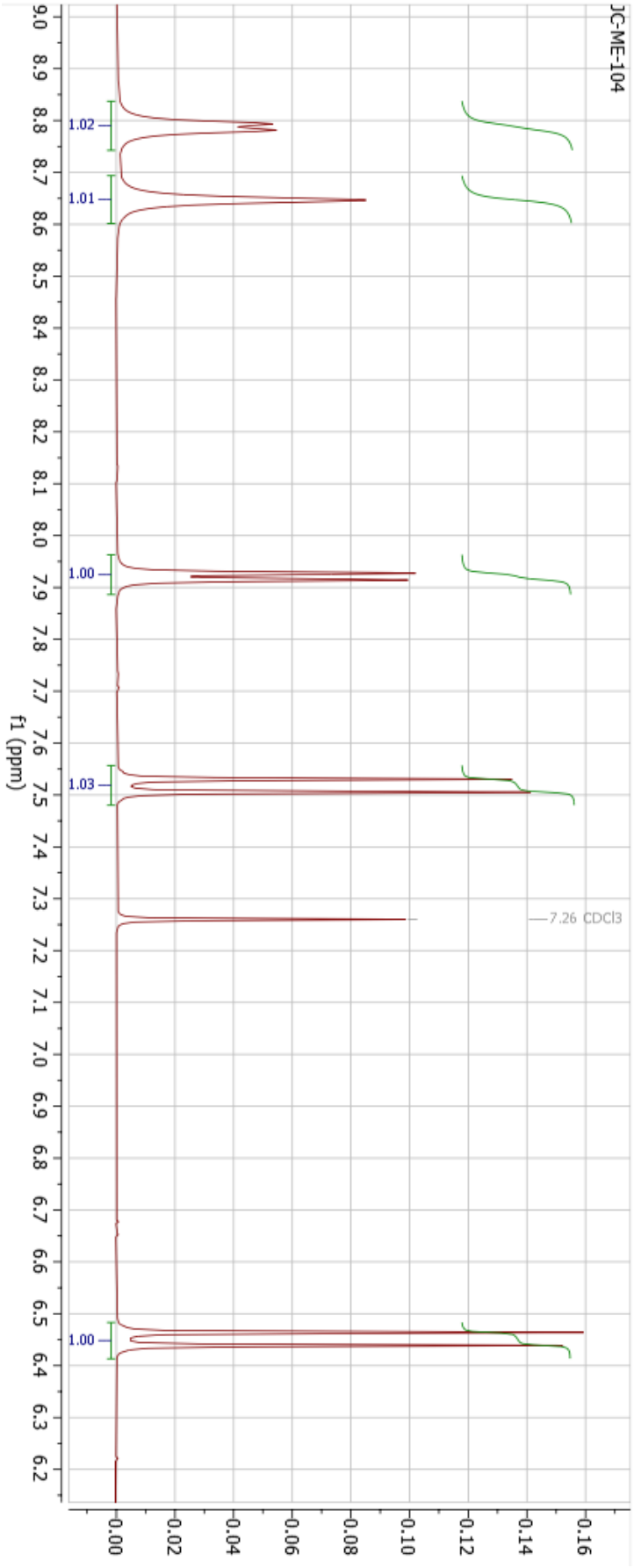


Figure S71. Zoomed in aromatic region of ^{1}H NMR of Product **23**.

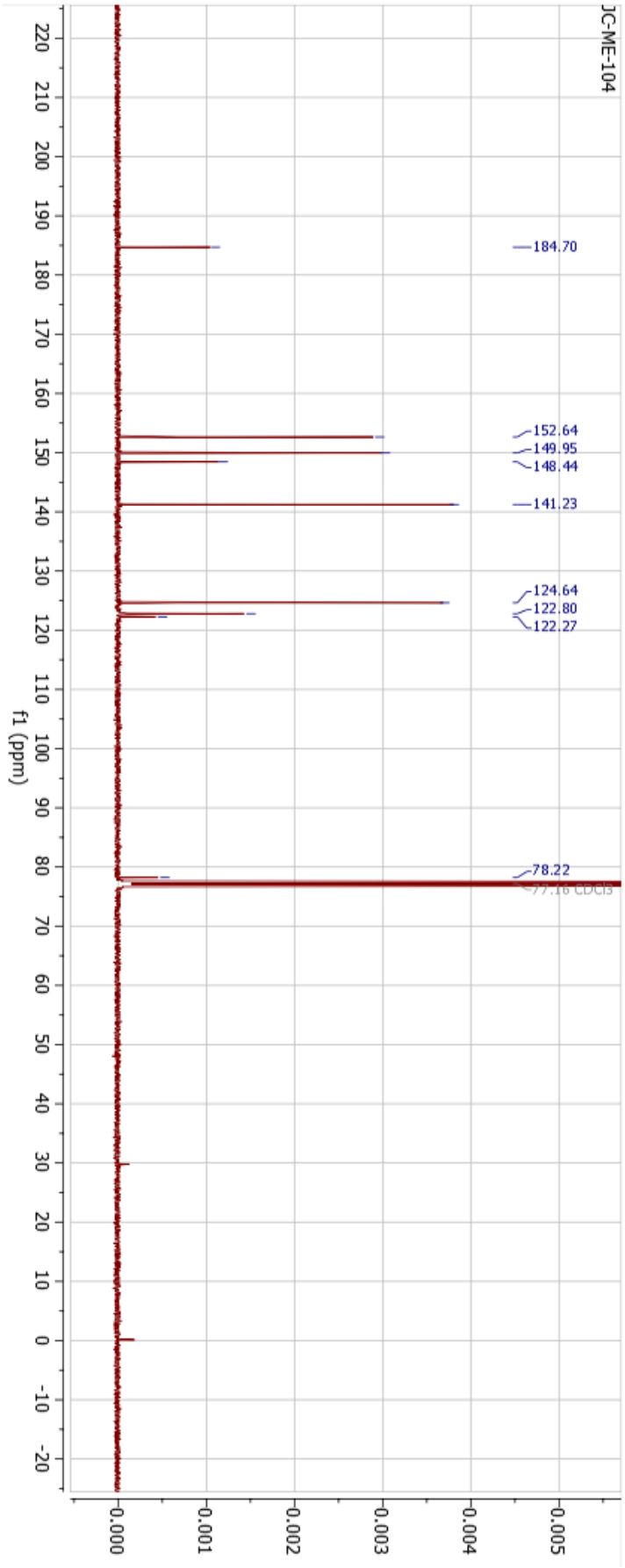


Figure S72. ^{13}C NMR of Product **23**.

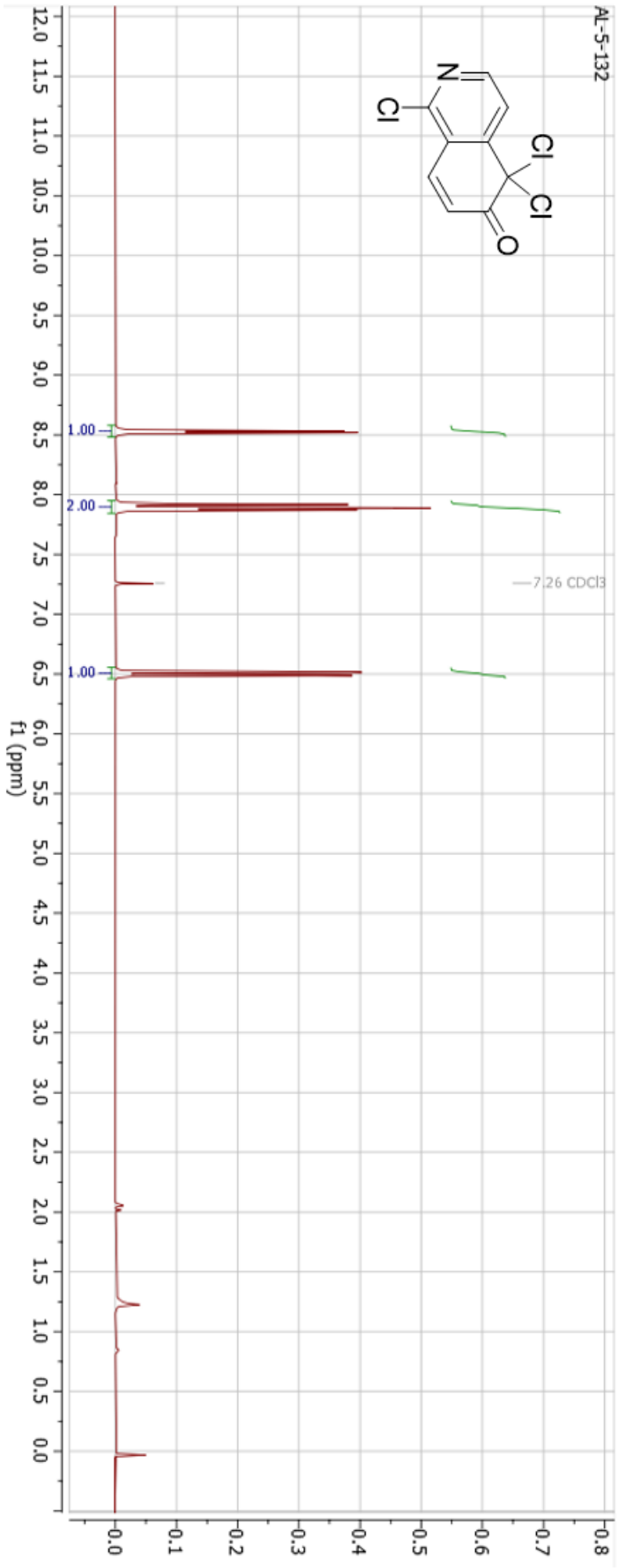


Figure S73. ^{1}H NMR of Product **24**.

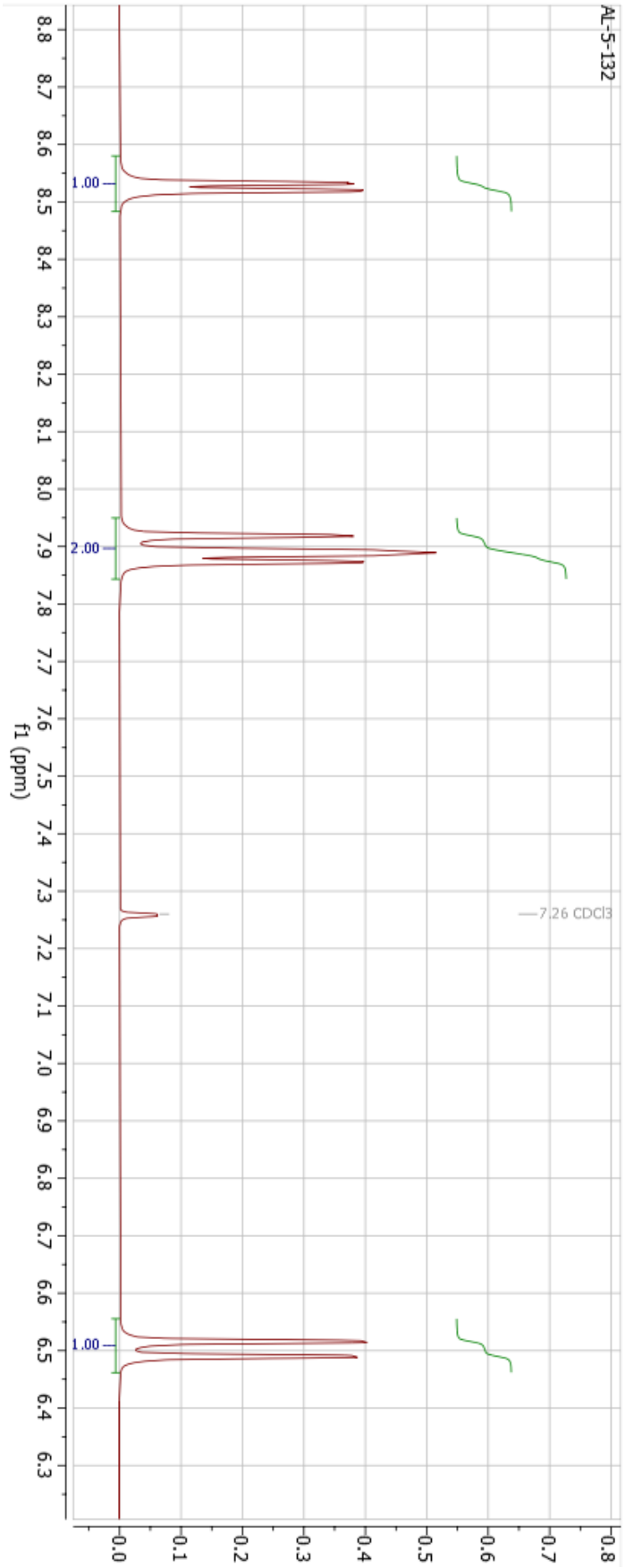


Figure S74. Zoomed in aromatic region of ^{1}H NMR of Product **24**.

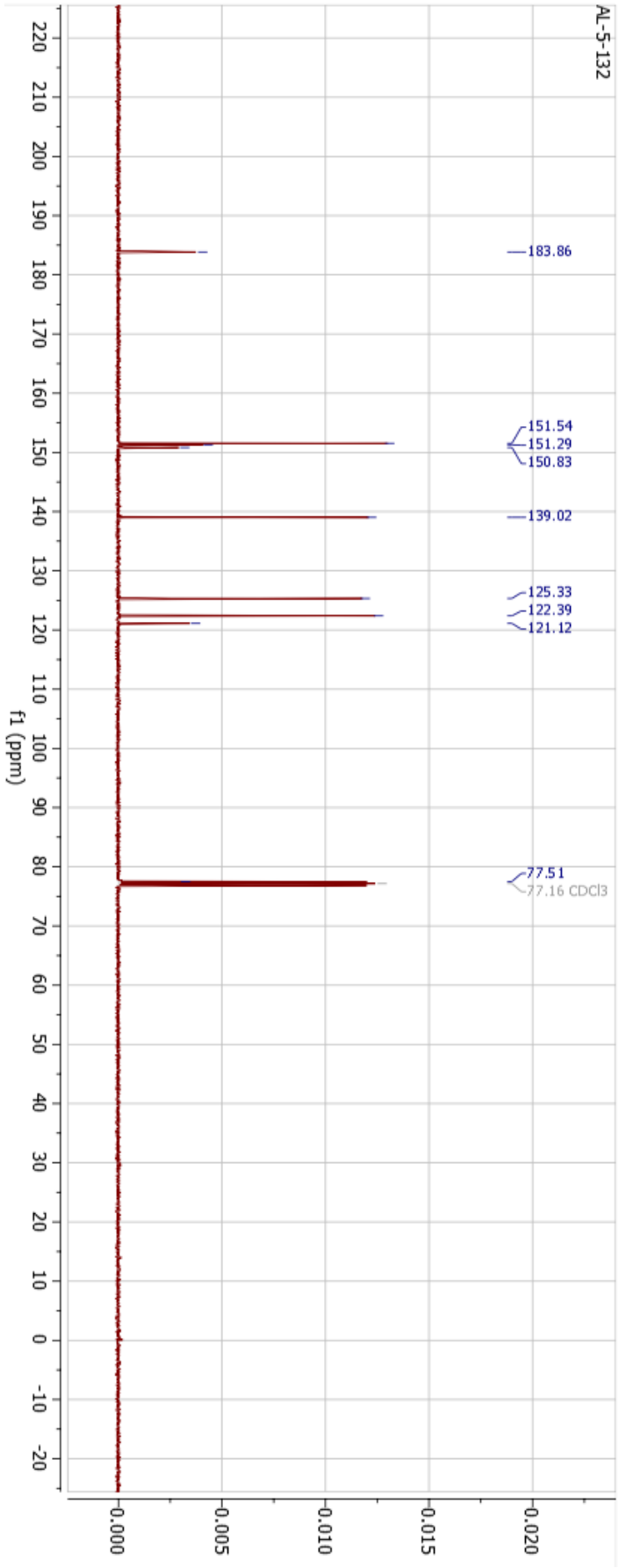


Figure S75. ^{13}C NMR of Product **24**.

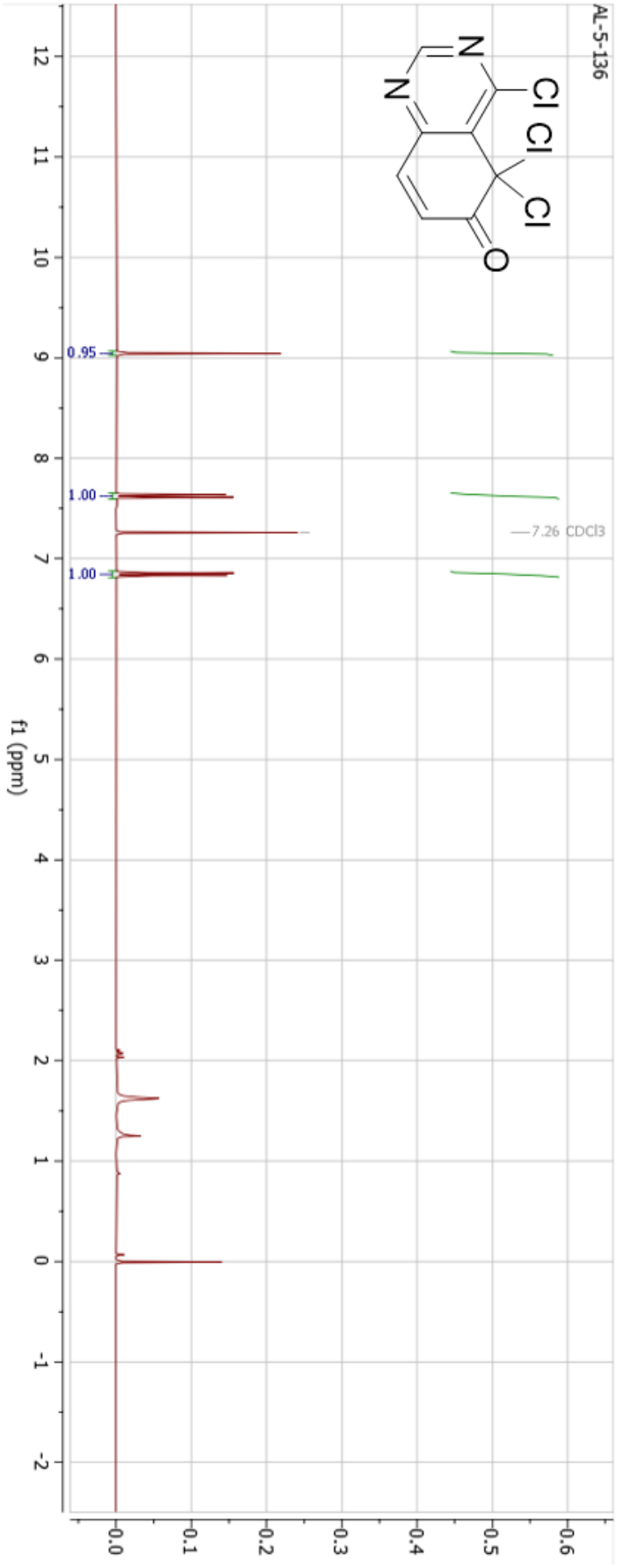


Figure S76. ^{1}H NMR of Product **25**.

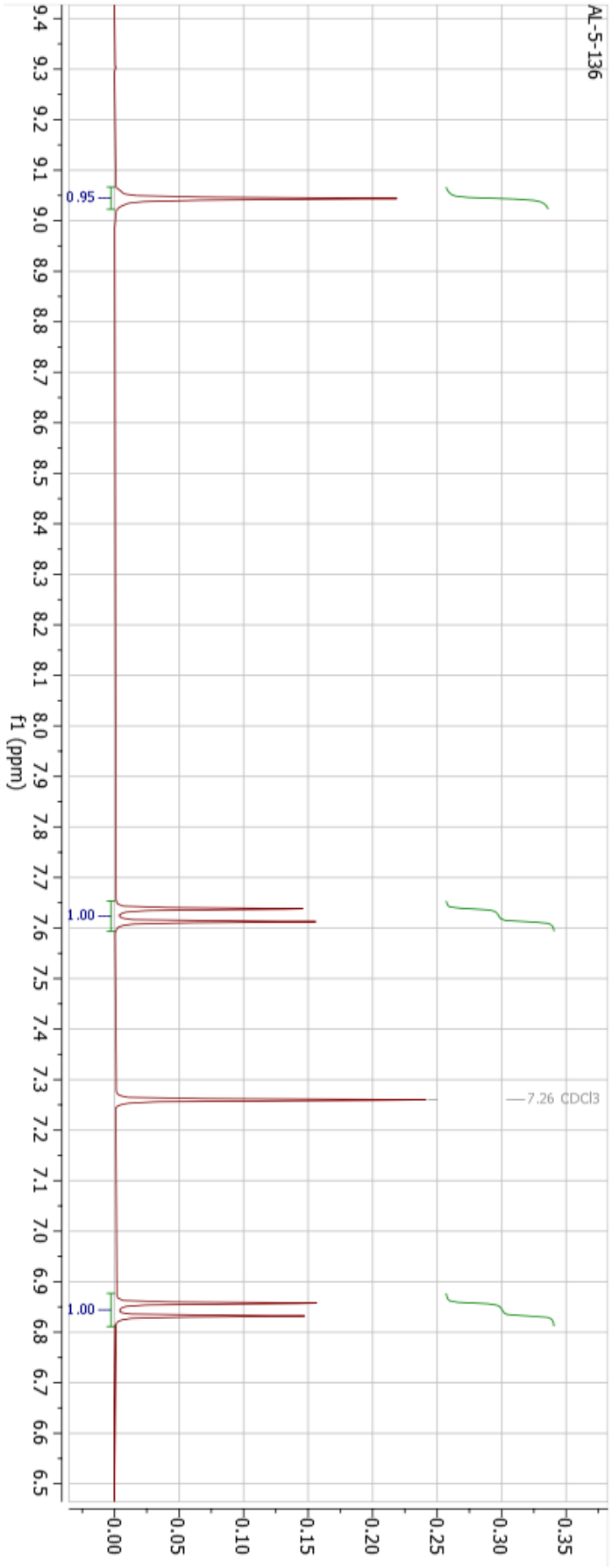


Figure S77. Zoomed in aromatic region of ^{1}H NMR of Product **25**.

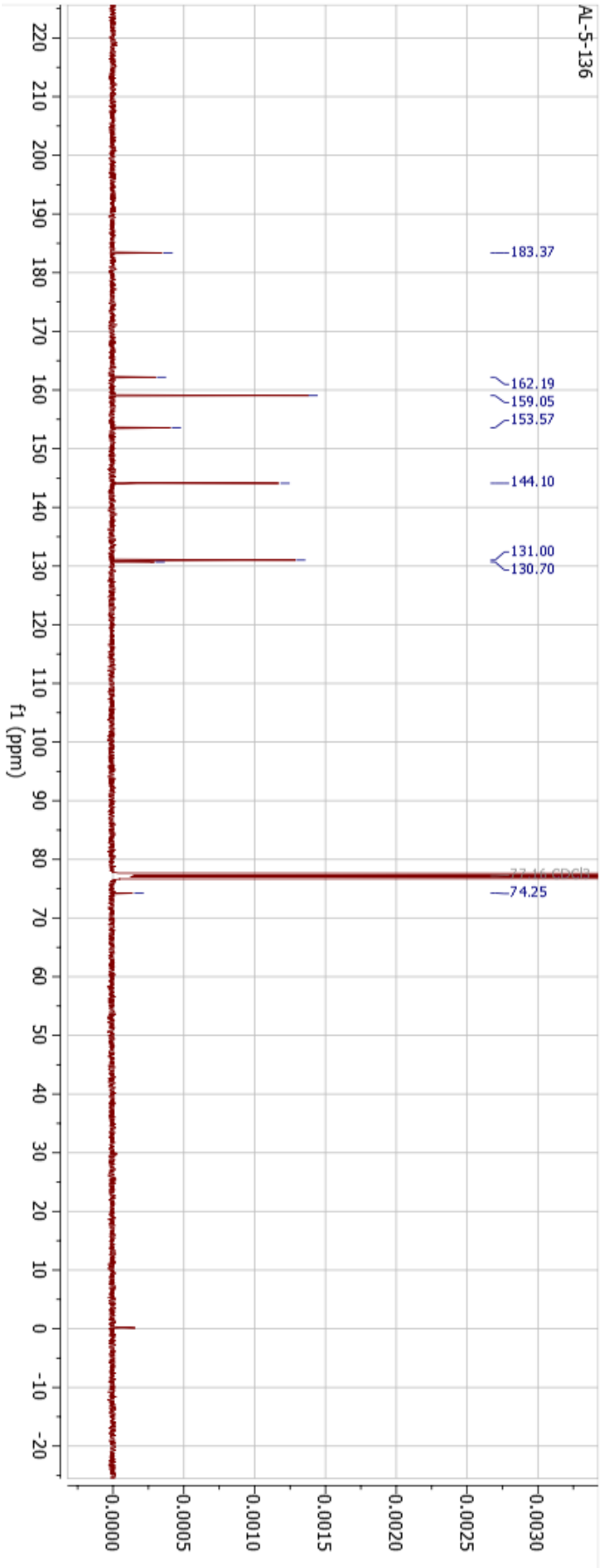


Figure S78. ^{13}C NMR of Product **25**.

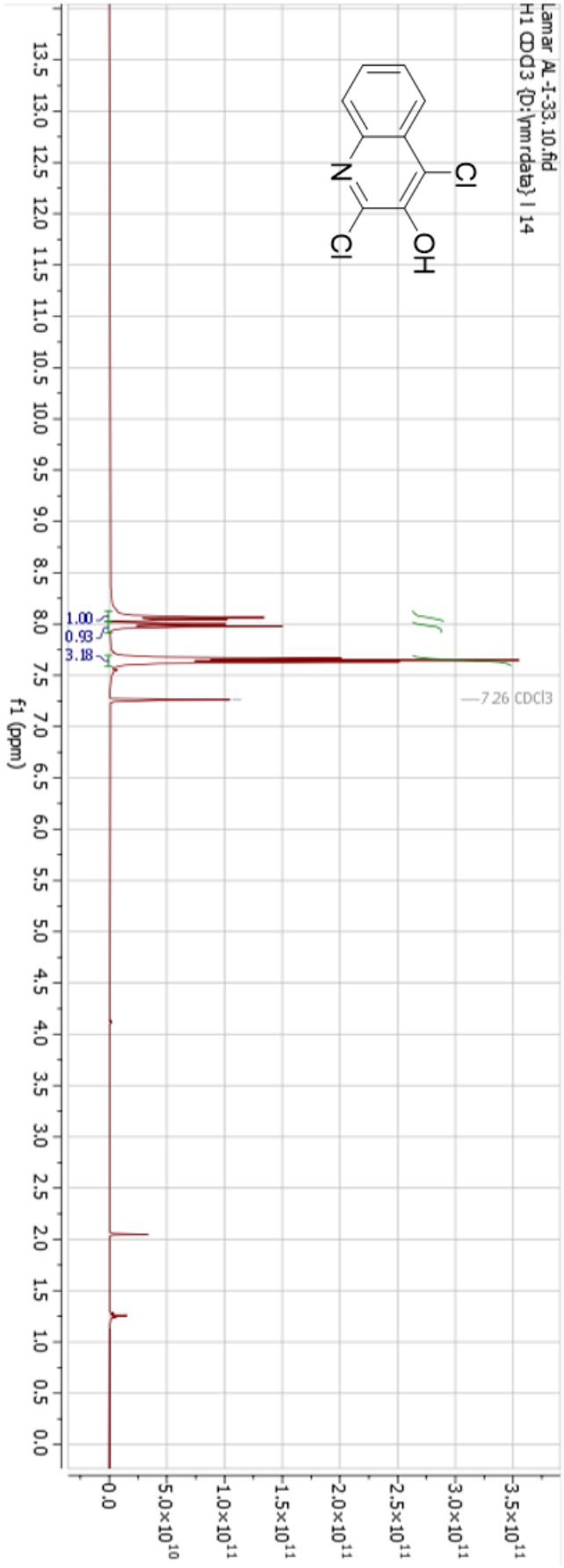


Figure S79. ^{1}H NMR of Product **26**.

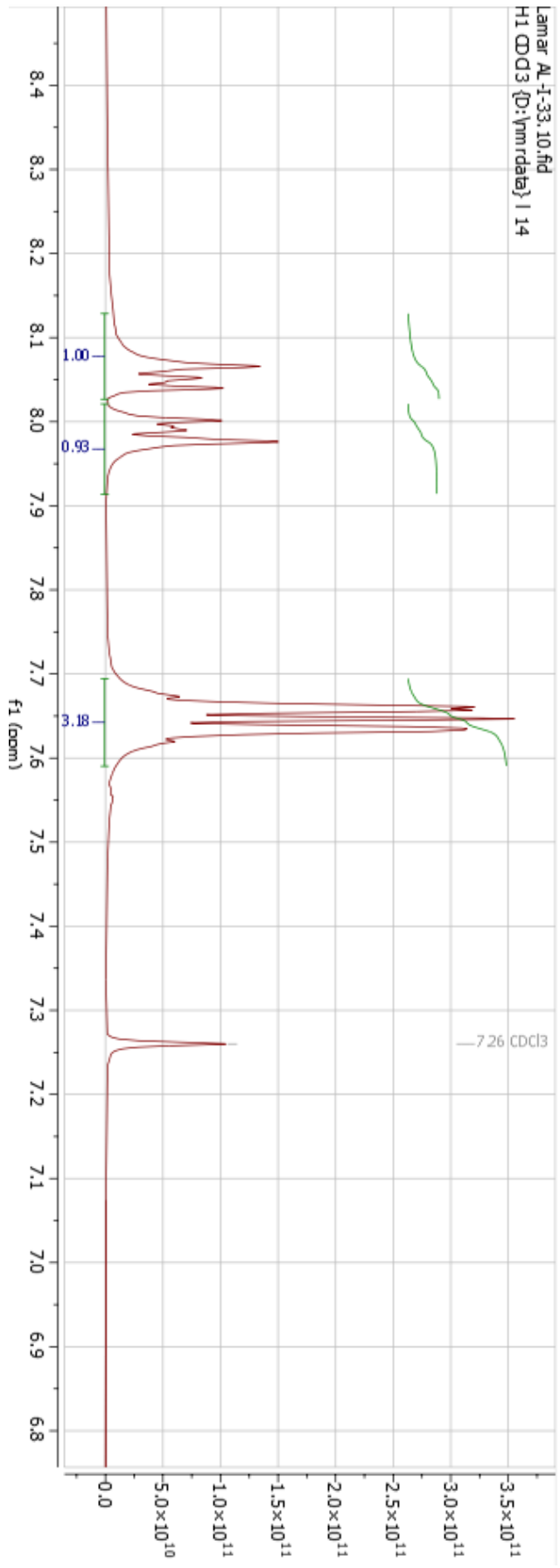


Figure S80. Zoomed in aromatic region of ^{1}H NMR of Product **26**.

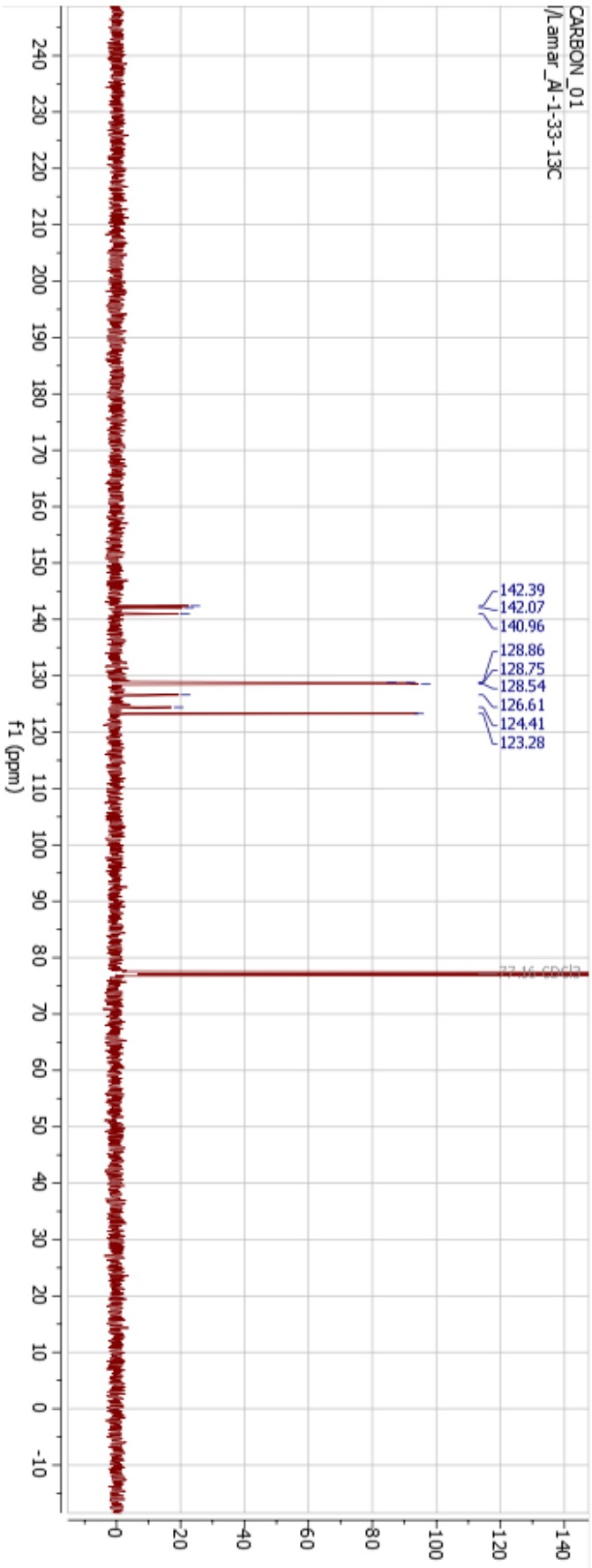


Figure S81. ^{13}C NMR of Product **26**.

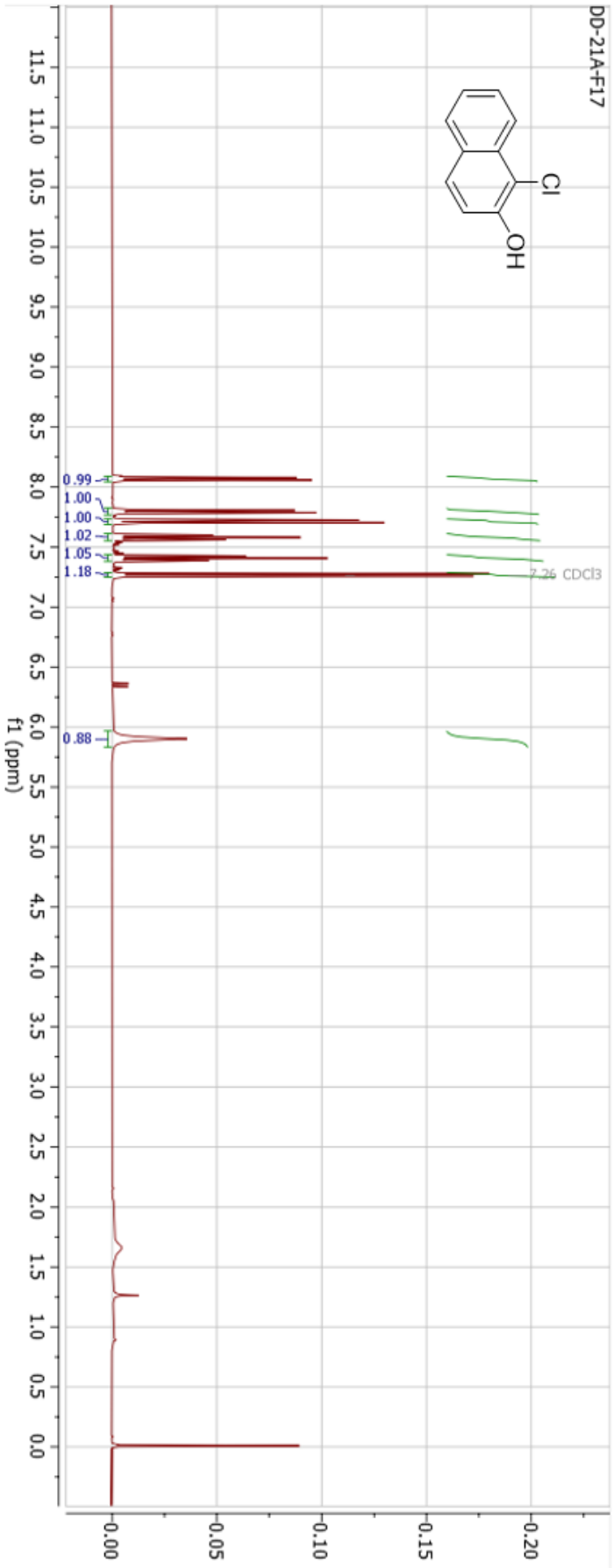


Figure S82. [1]H NMR of Product **27**.

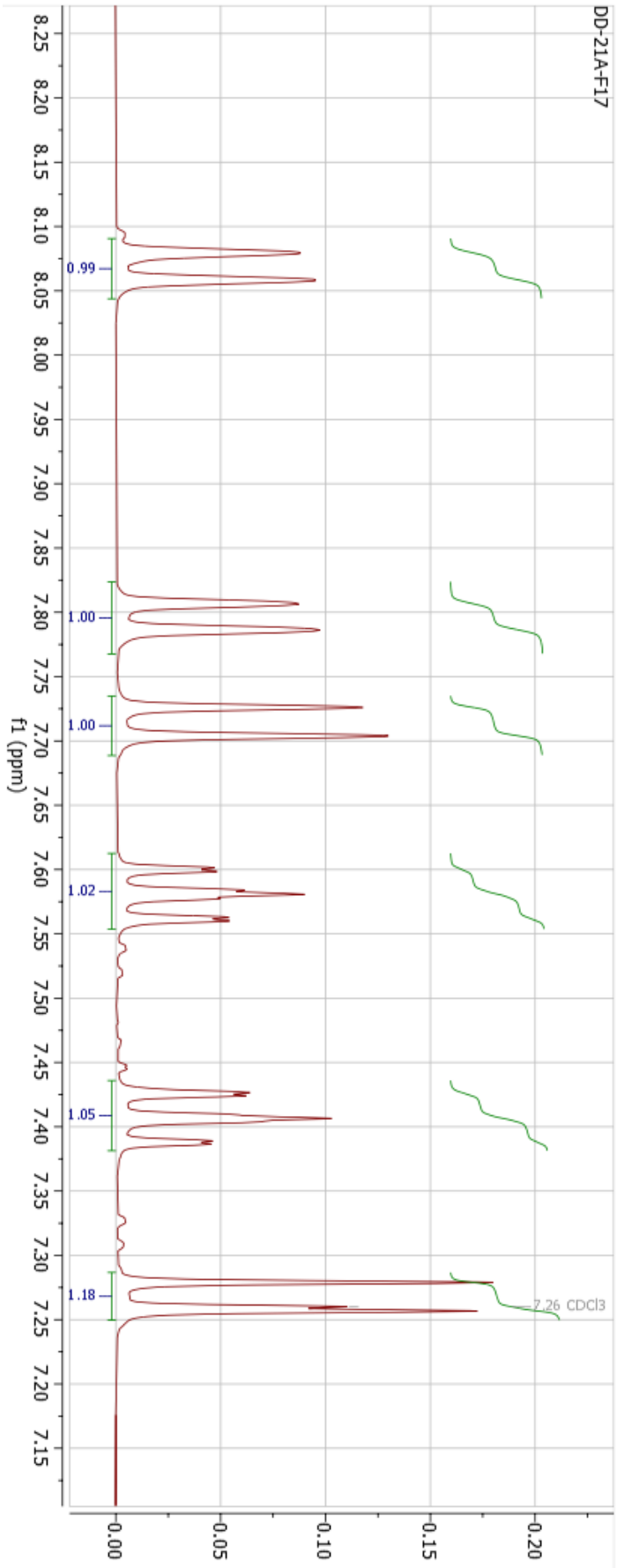


Figure S83. Zoomed in aromatic region of ^{1}H NMR of Product **27**.

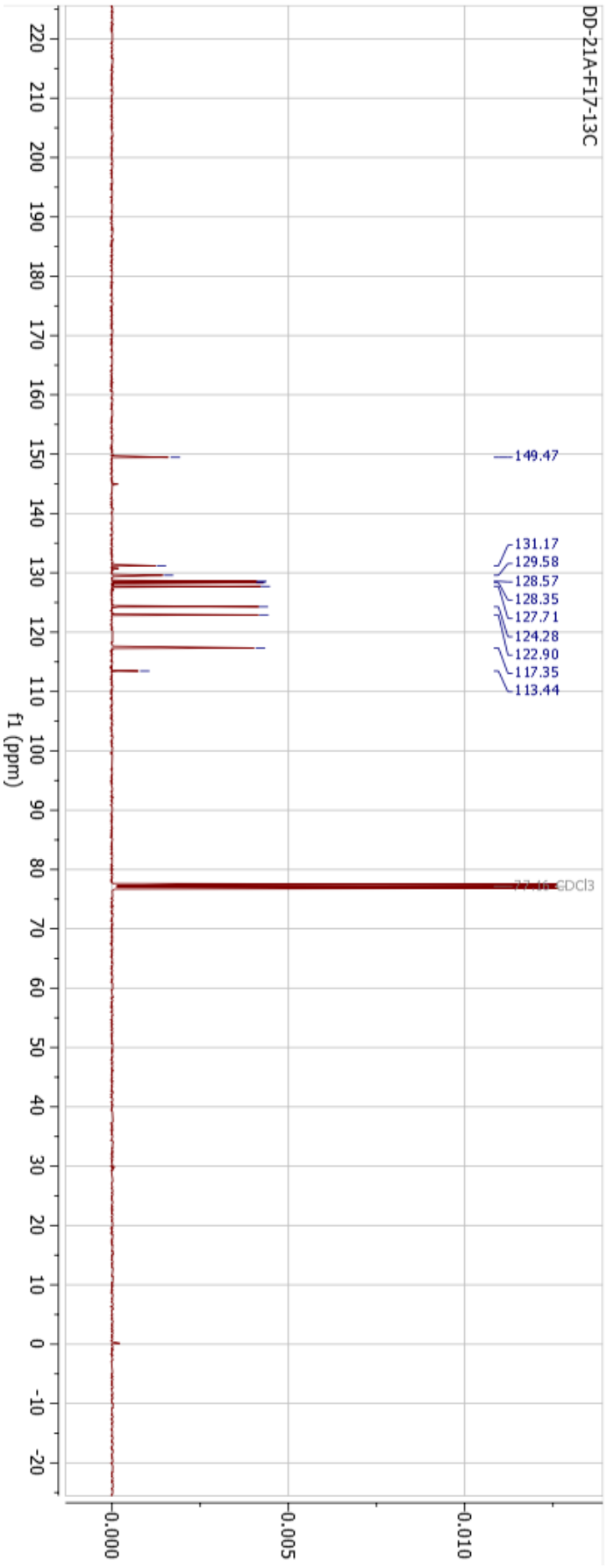


Figure S84. ^{13}C NMR of Product **27**.

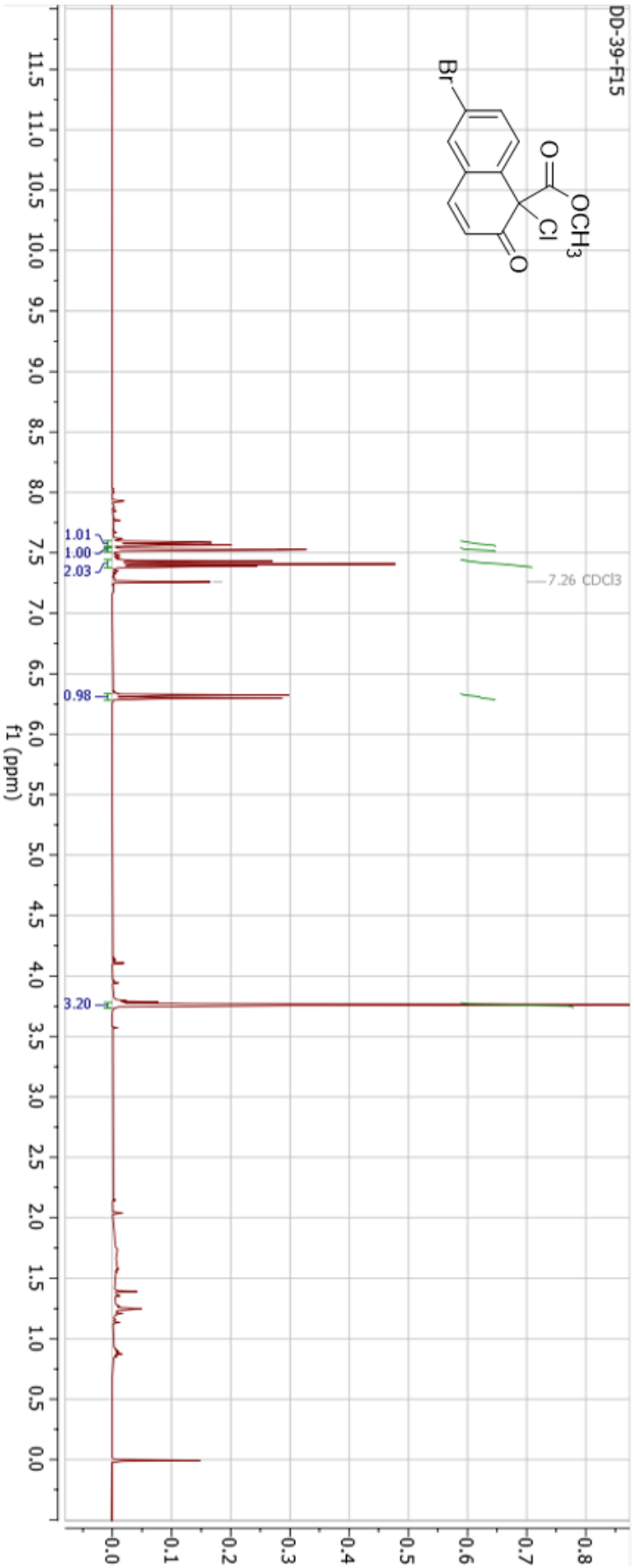


Figure S85. ^{1}H NMR of Product **28**.

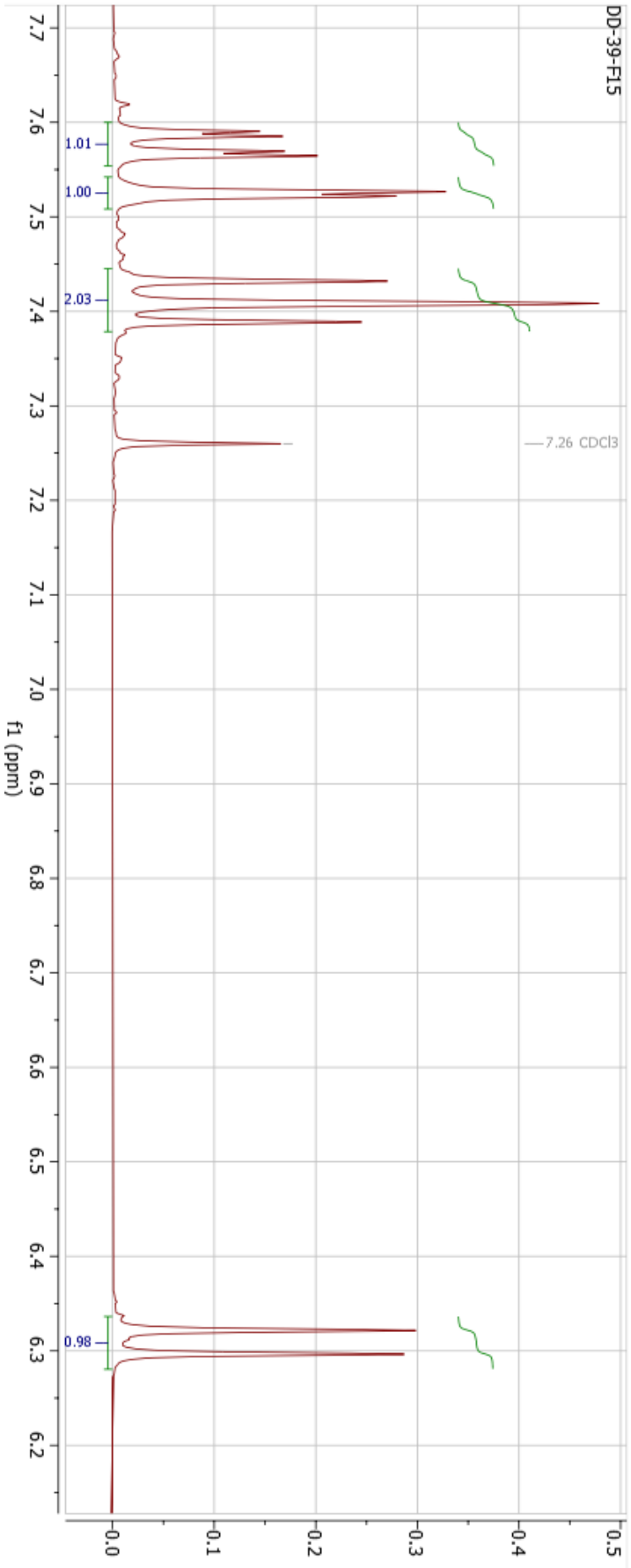


Figure S86. Zoomed in aromatic region of ^{1}H NMR of Product **28**.

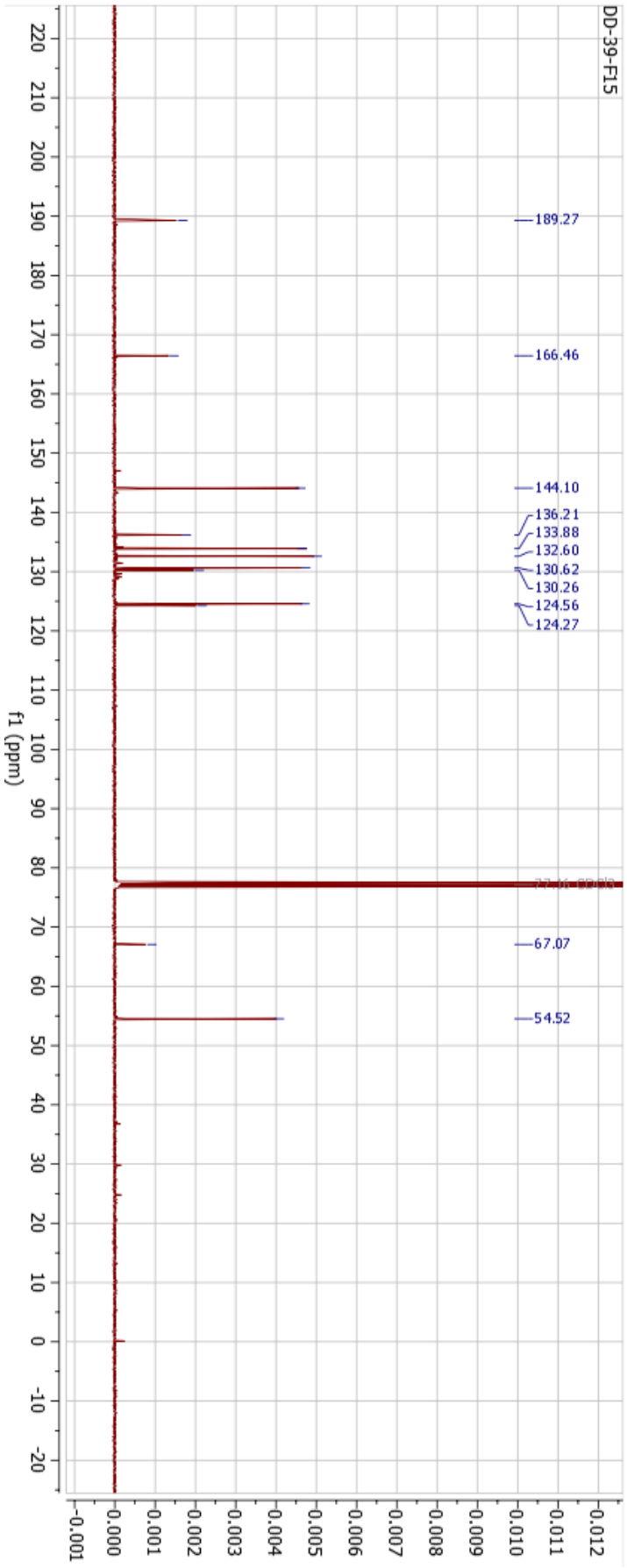


Figure S87. ^{13}C NMR of Product **28**.

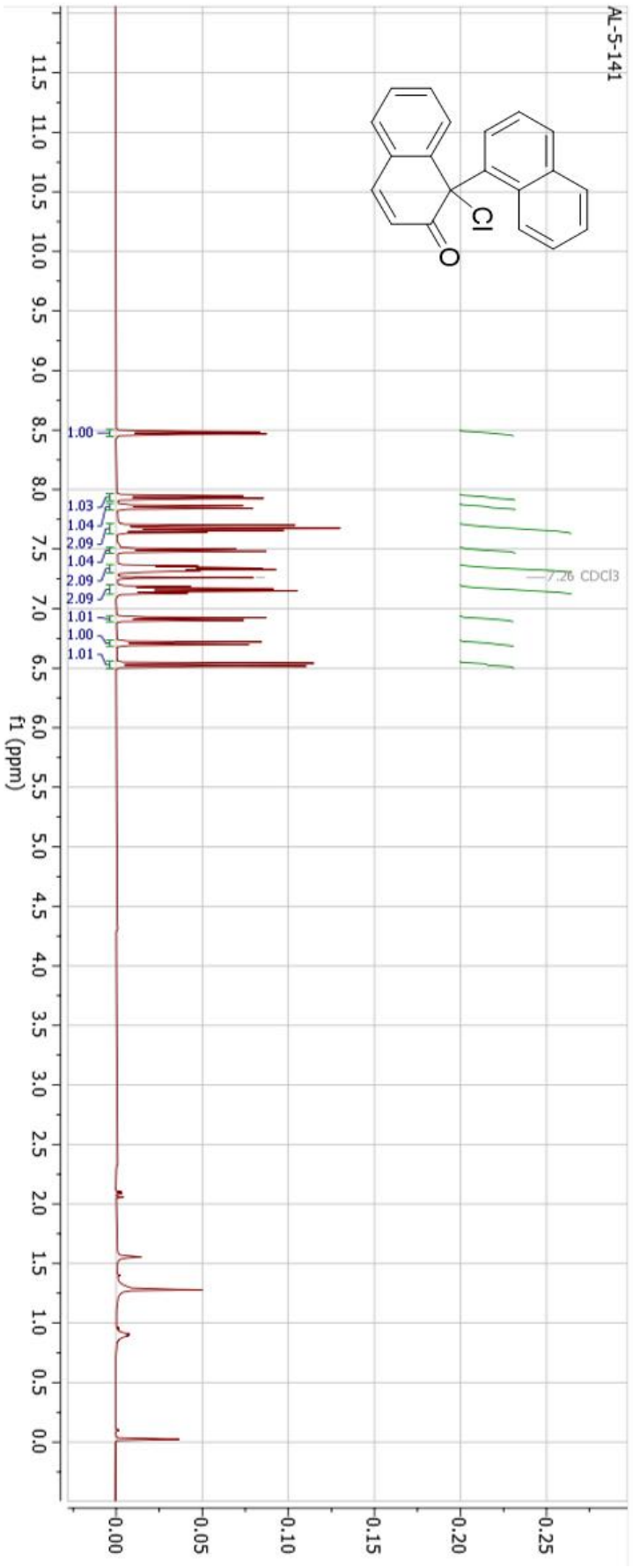


Figure S88. [1]H NMR of Product **29**.

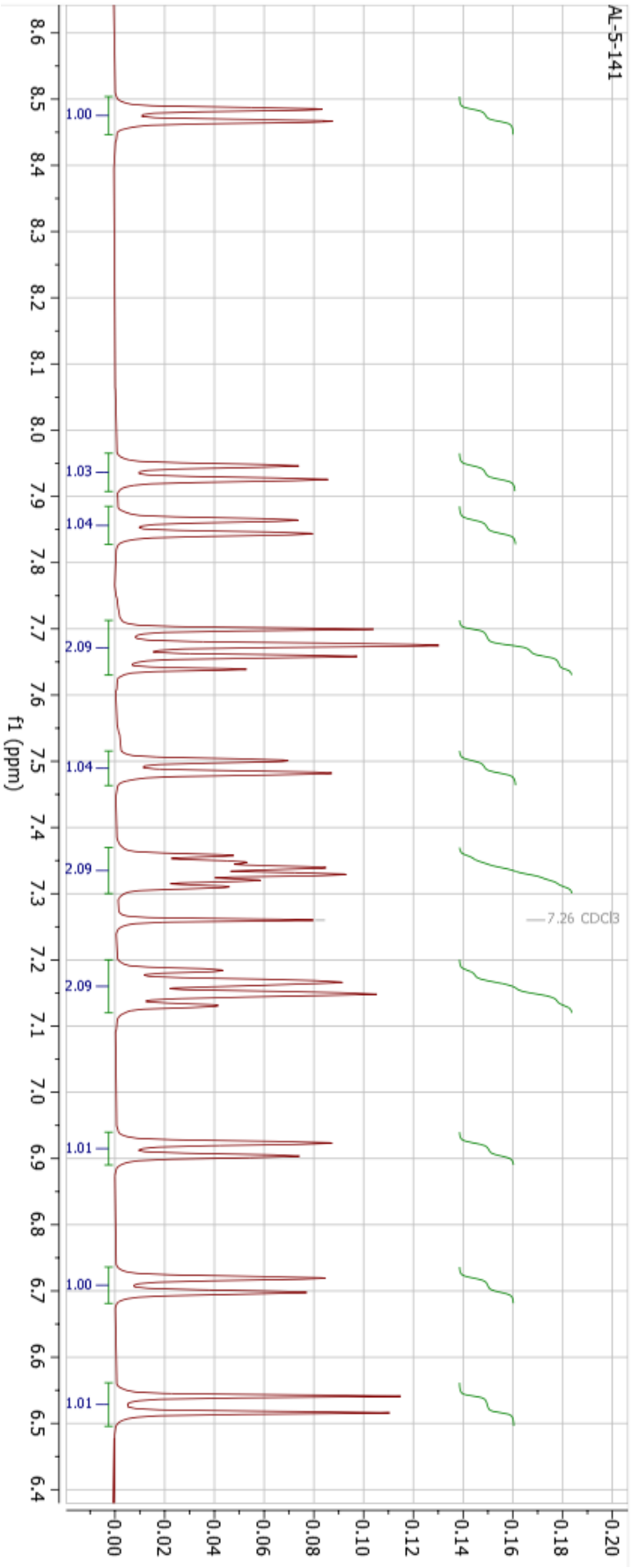


Figure S89. Zoomed in aromatic region of ^{1}H NMR of Product **29**.

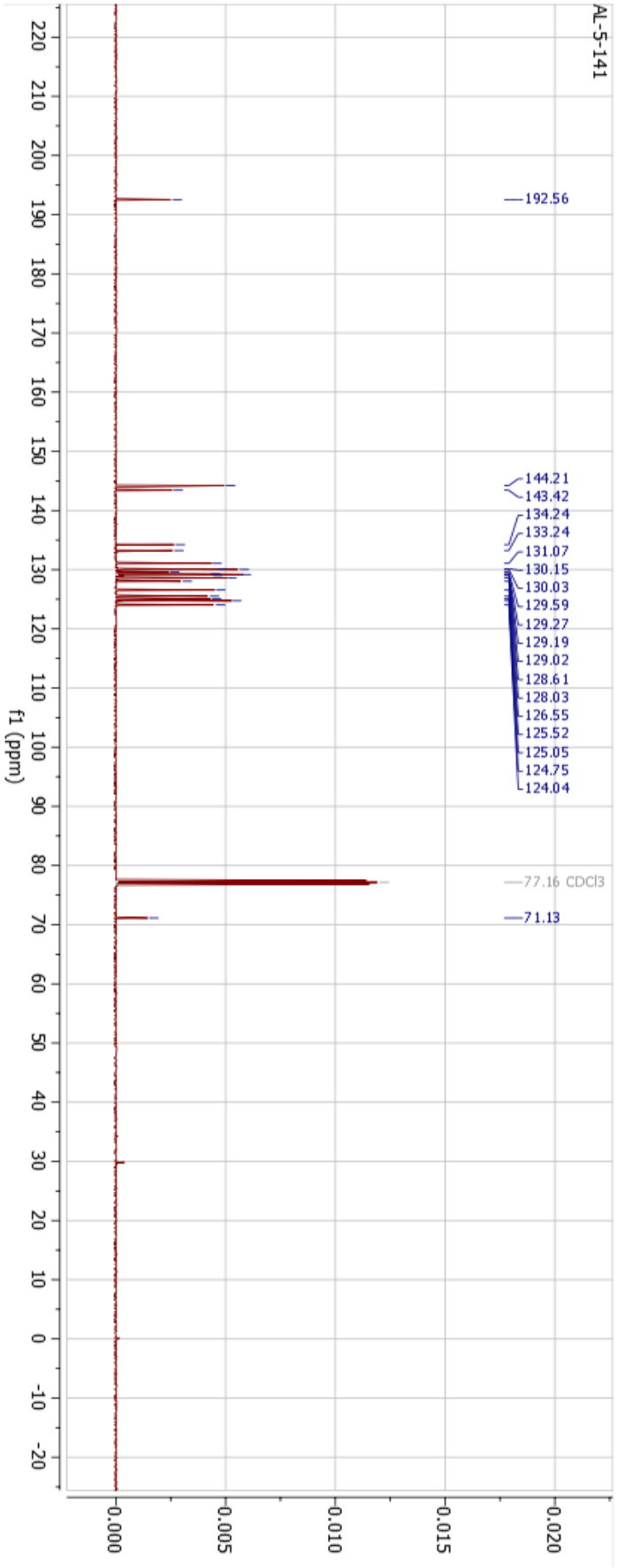


Figure S90. ^{13}C NMR of Product **29**.

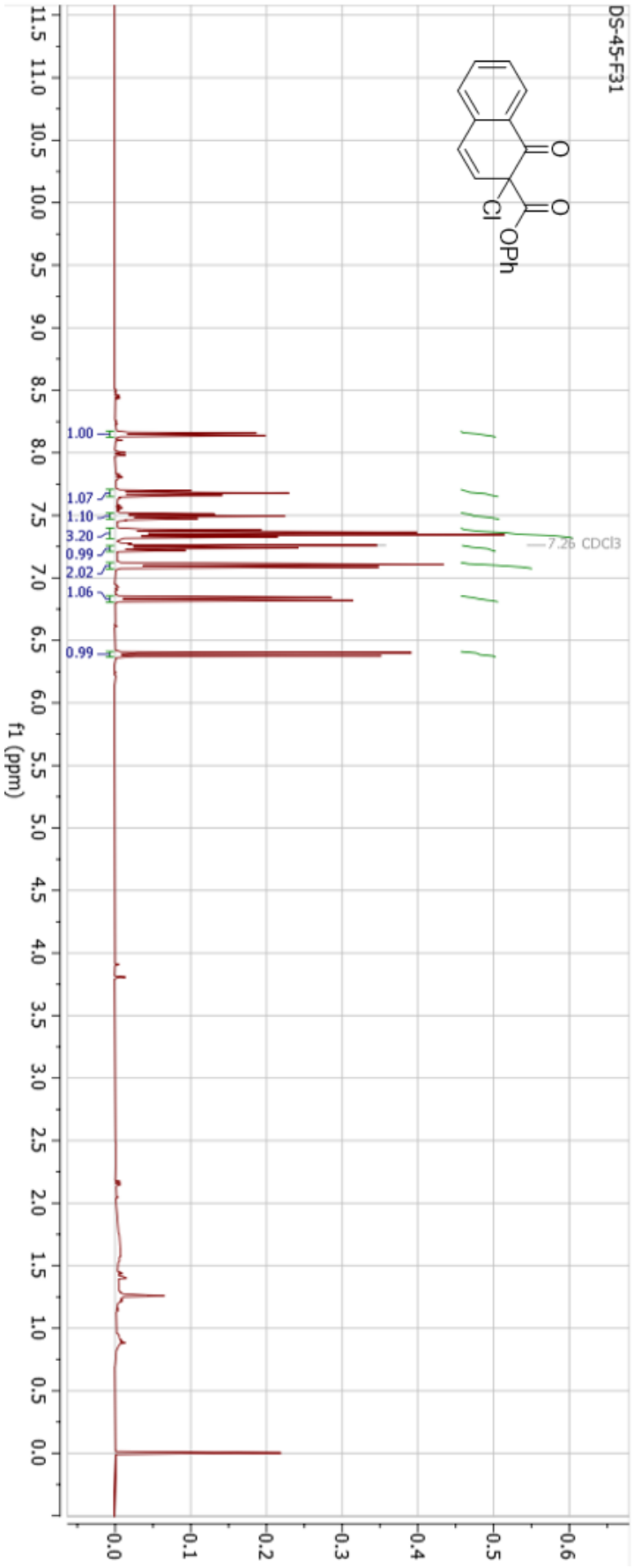


Figure S91. ^{1}H NMR of Product **30**.

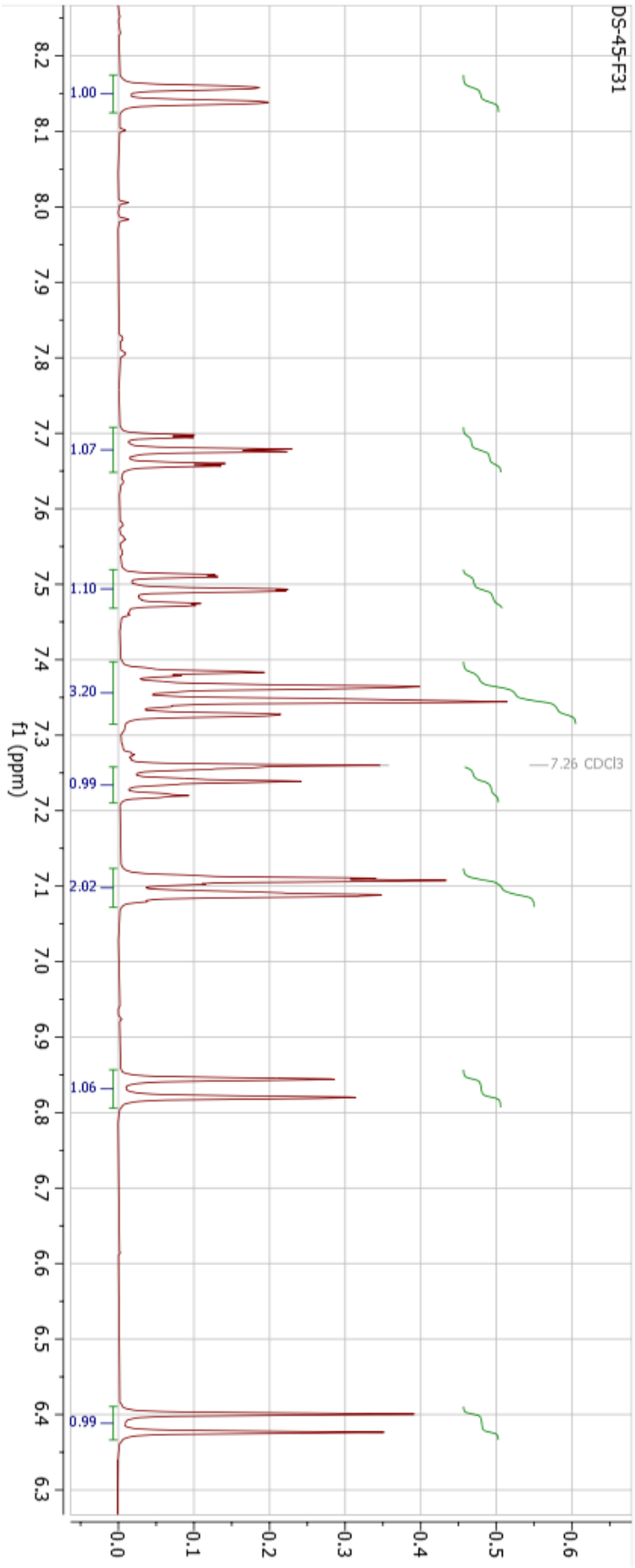


Figure S92. Zoomed in aromatic region of ^{1}H NMR of Product **30**.

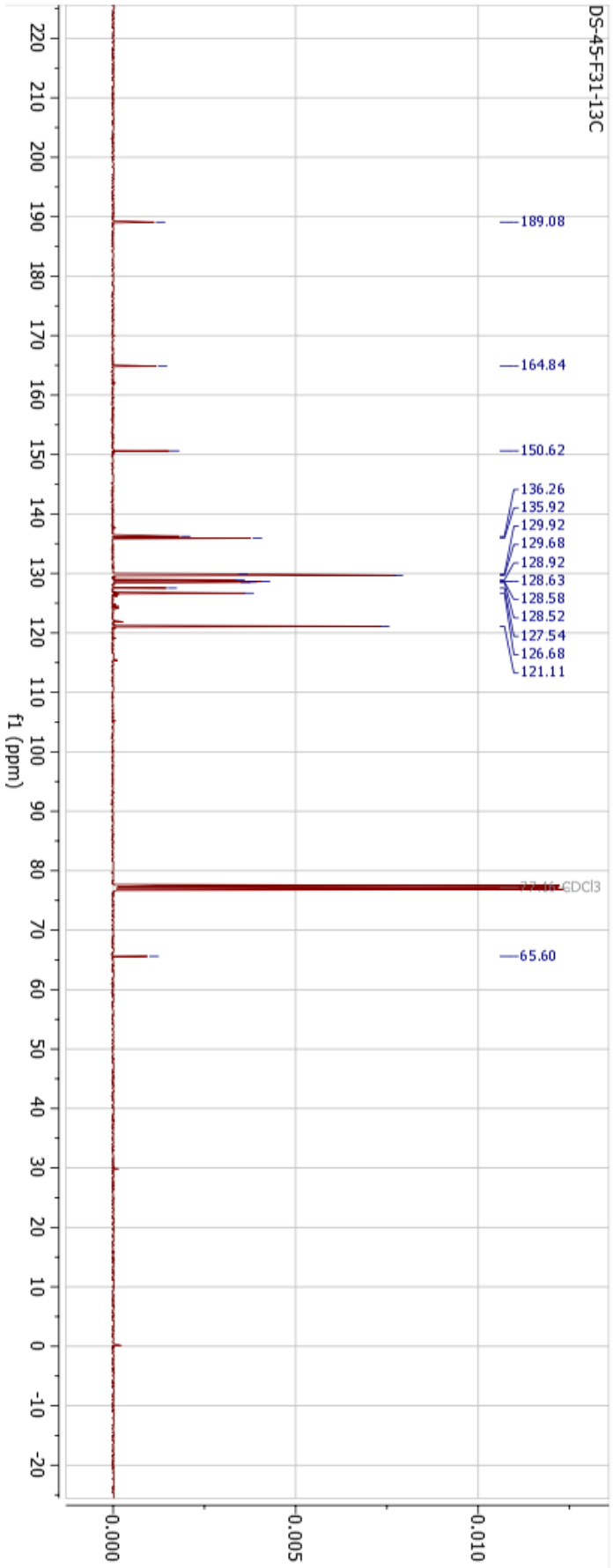


Figure S93. ^{13}C NMR of Product **30**.

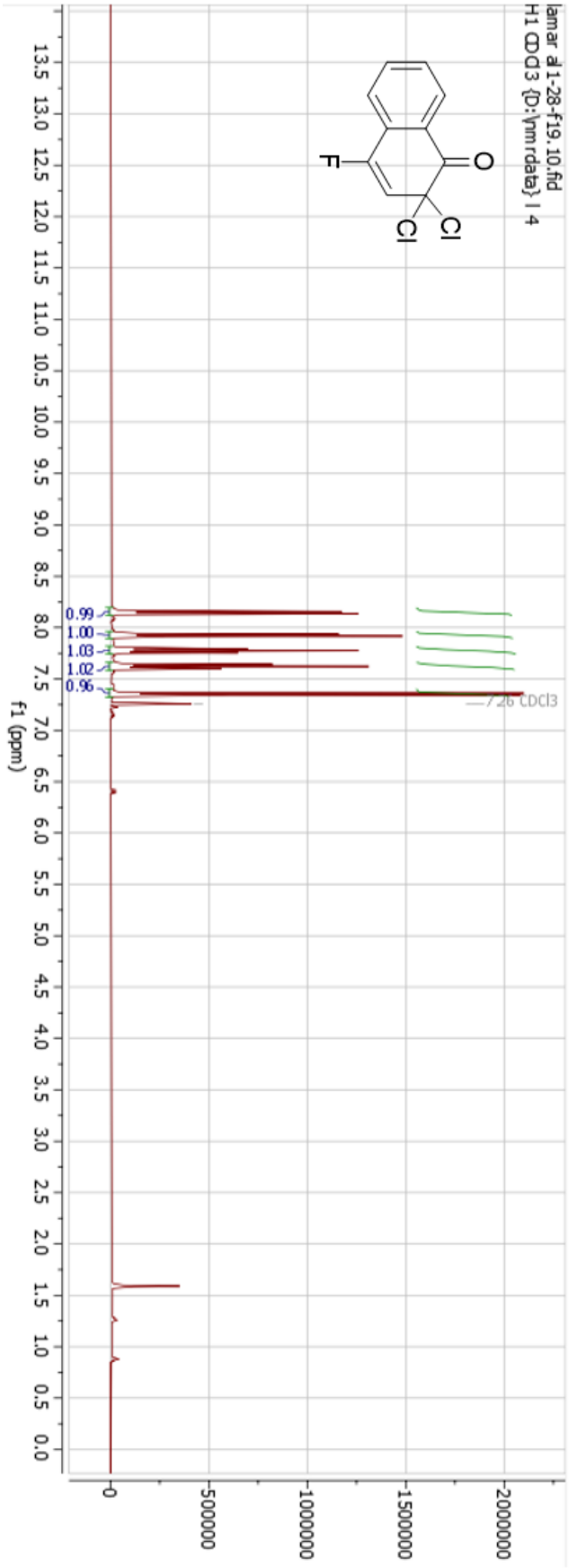


Figure S94. ^{1}H NMR of Product **31**.

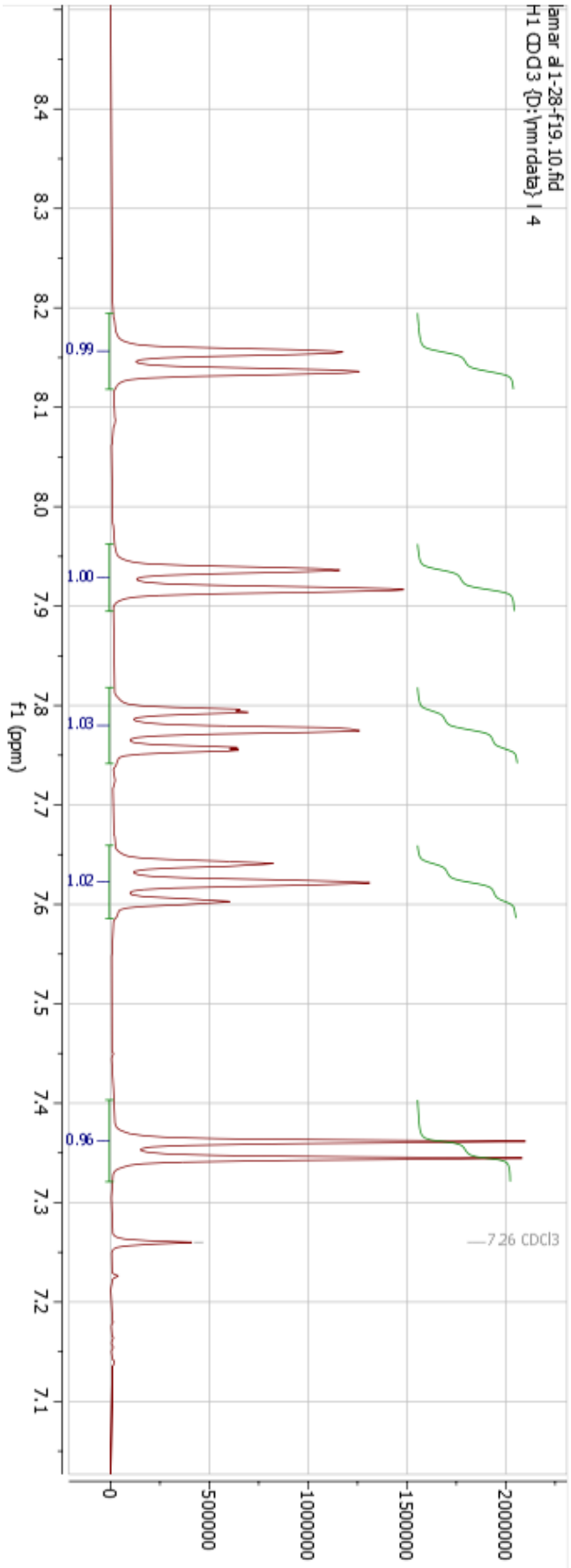


Figure S95. Zoomed in aromatic region of ^{1}H NMR of Product **31**.

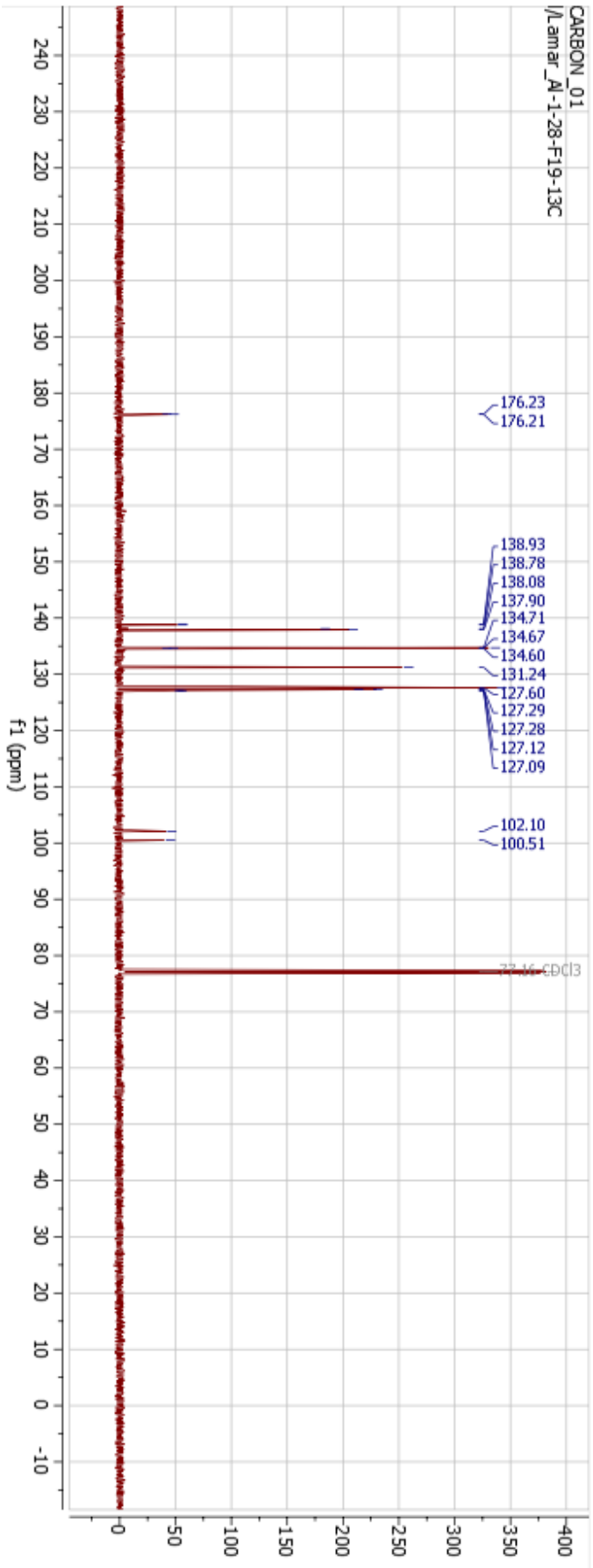


Figure S96. ^{13}C NMR of Product **31**.

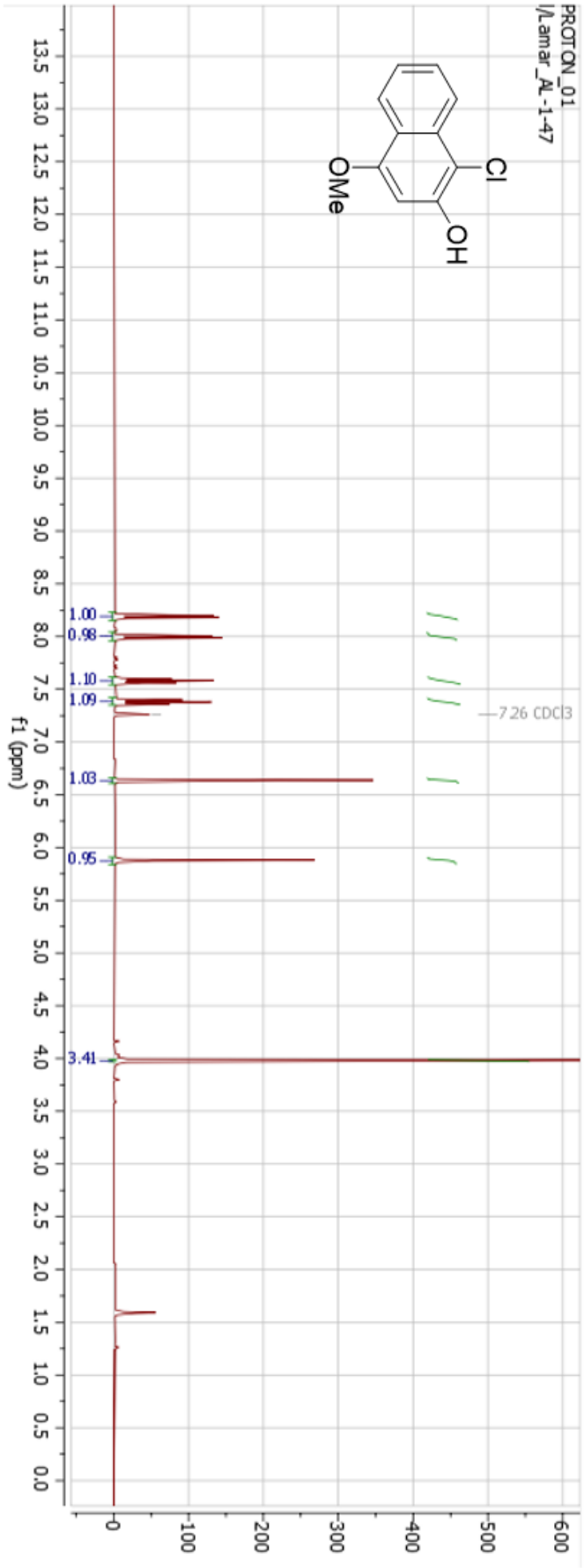


Figure S97. ^{1}H NMR of Product **32**.

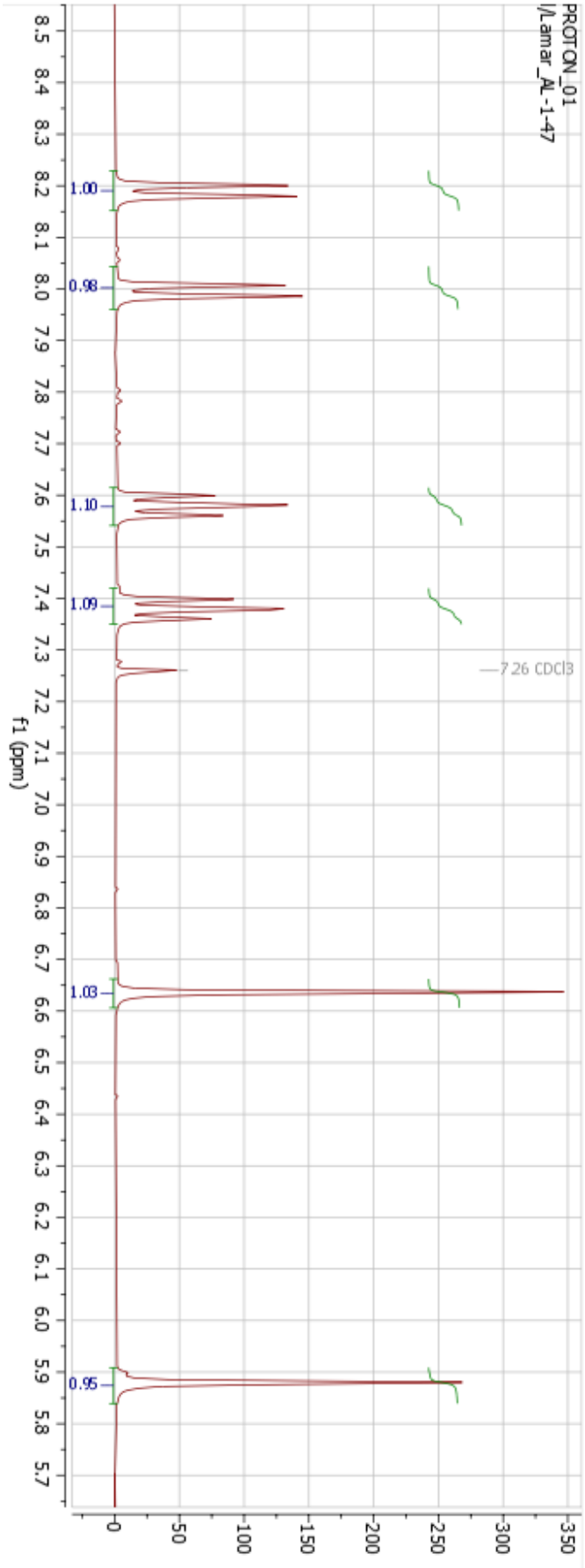


Figure S98. Zoomed in aromatic region of ^{1}H NMR of Product **32**.

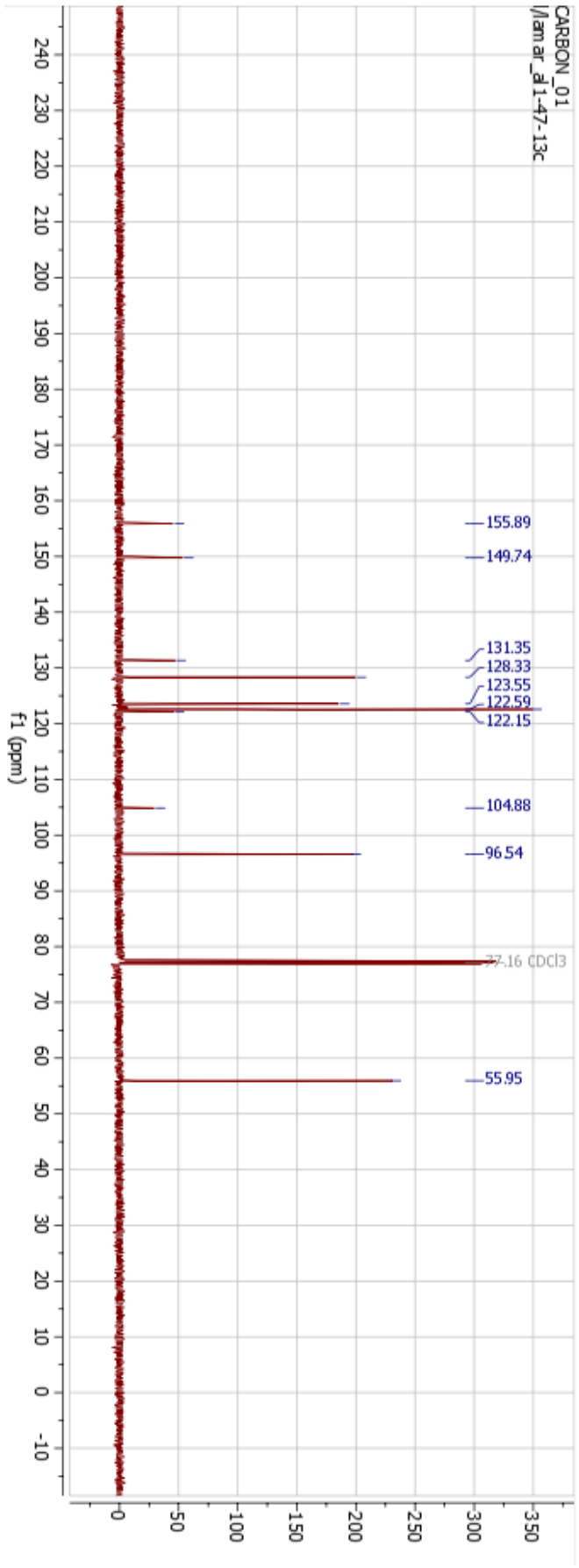


Figure S99. ^{13}C NMR of Product **32**.

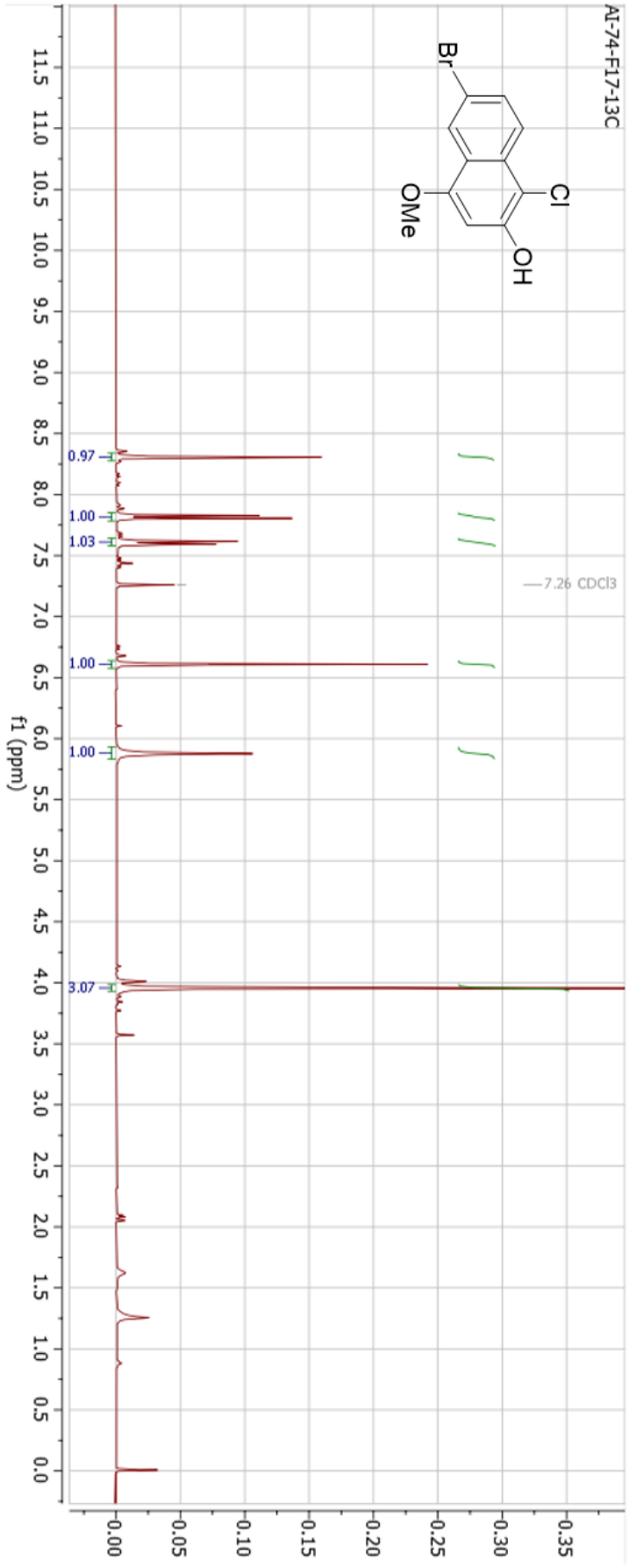


Figure S100. ^{1}H NMR of Product **33**.

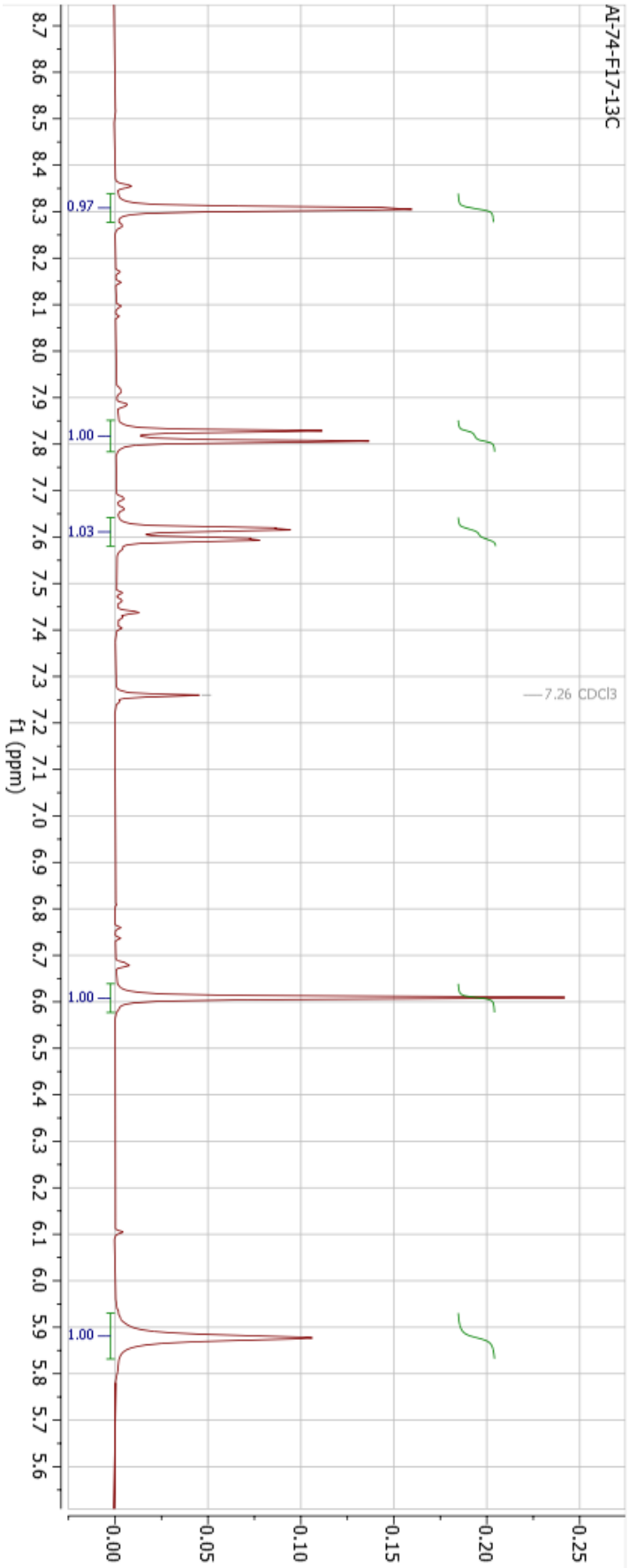


Figure S101. Zoomed in aromatic region of ^{1}H NMR of Product **33**.

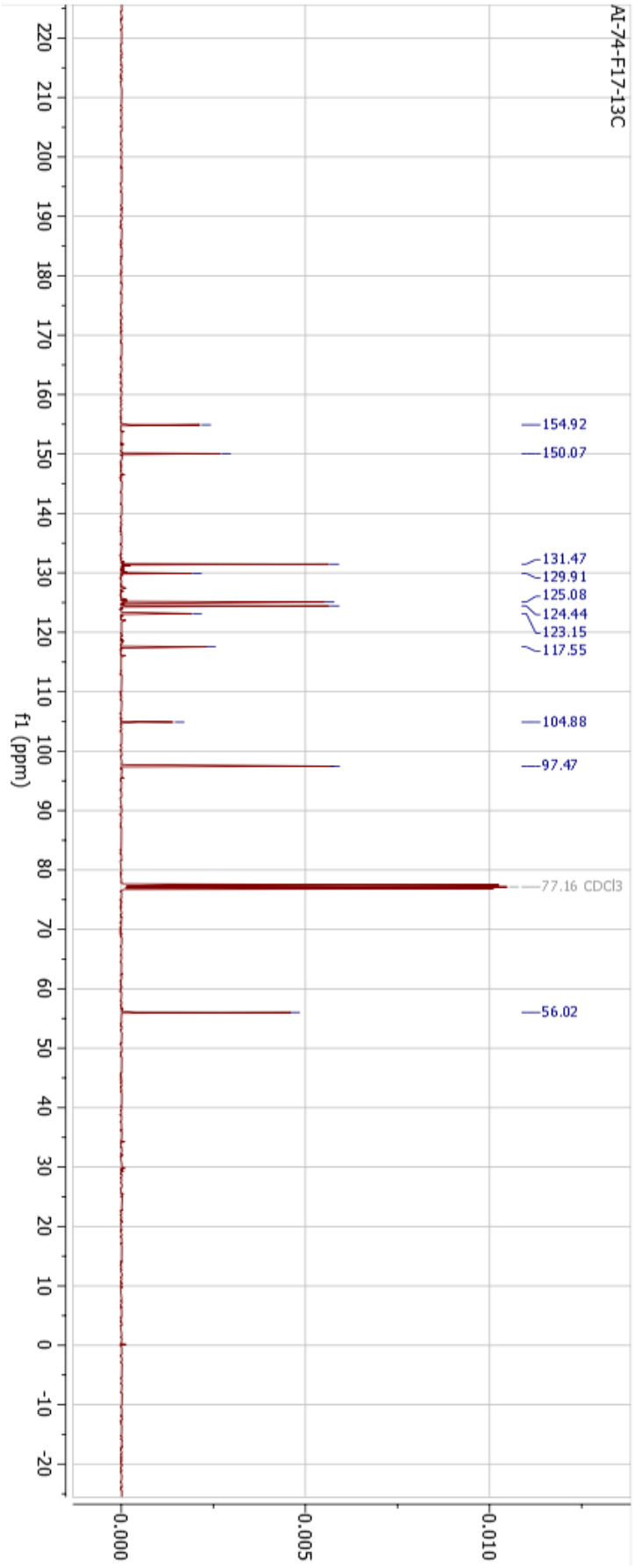


Figure S102. ^{13}C NMR of Product **33**.

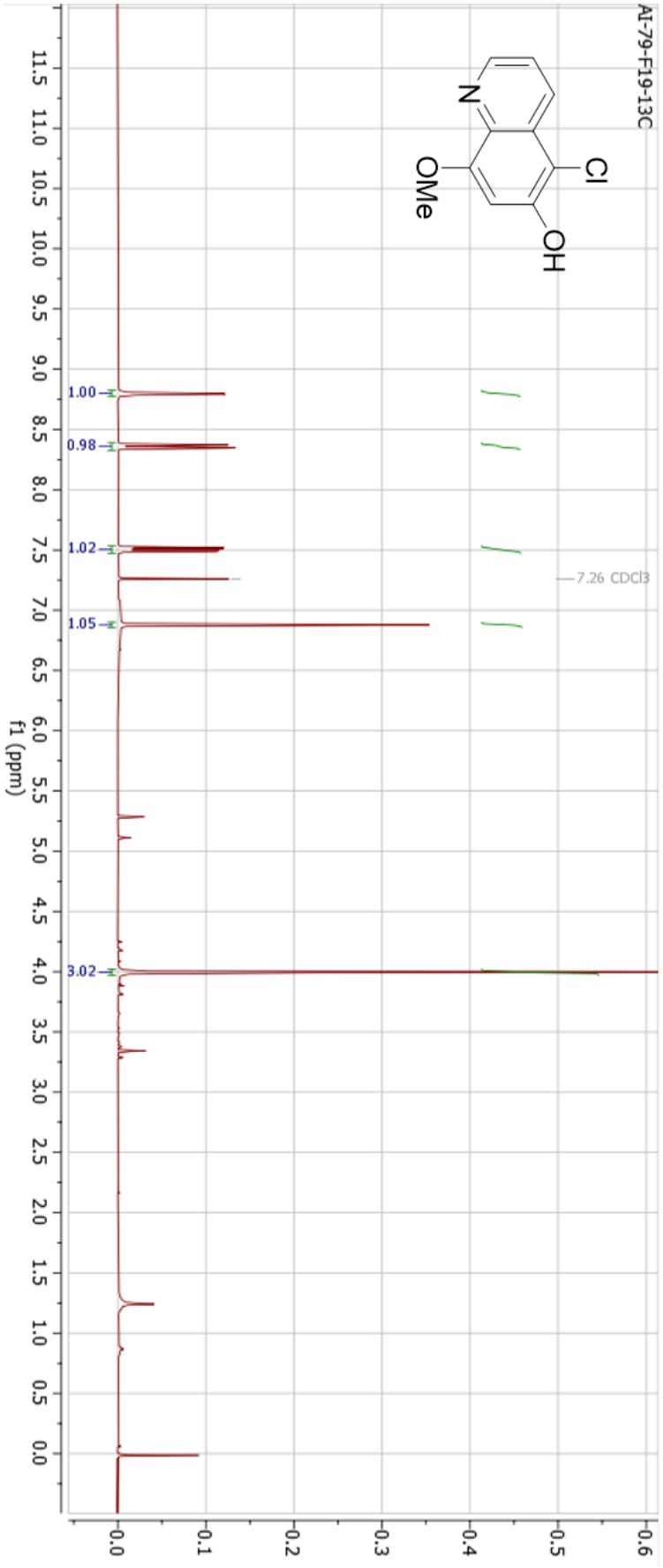


Figure S103. ^{1}H NMR of Product **34**.

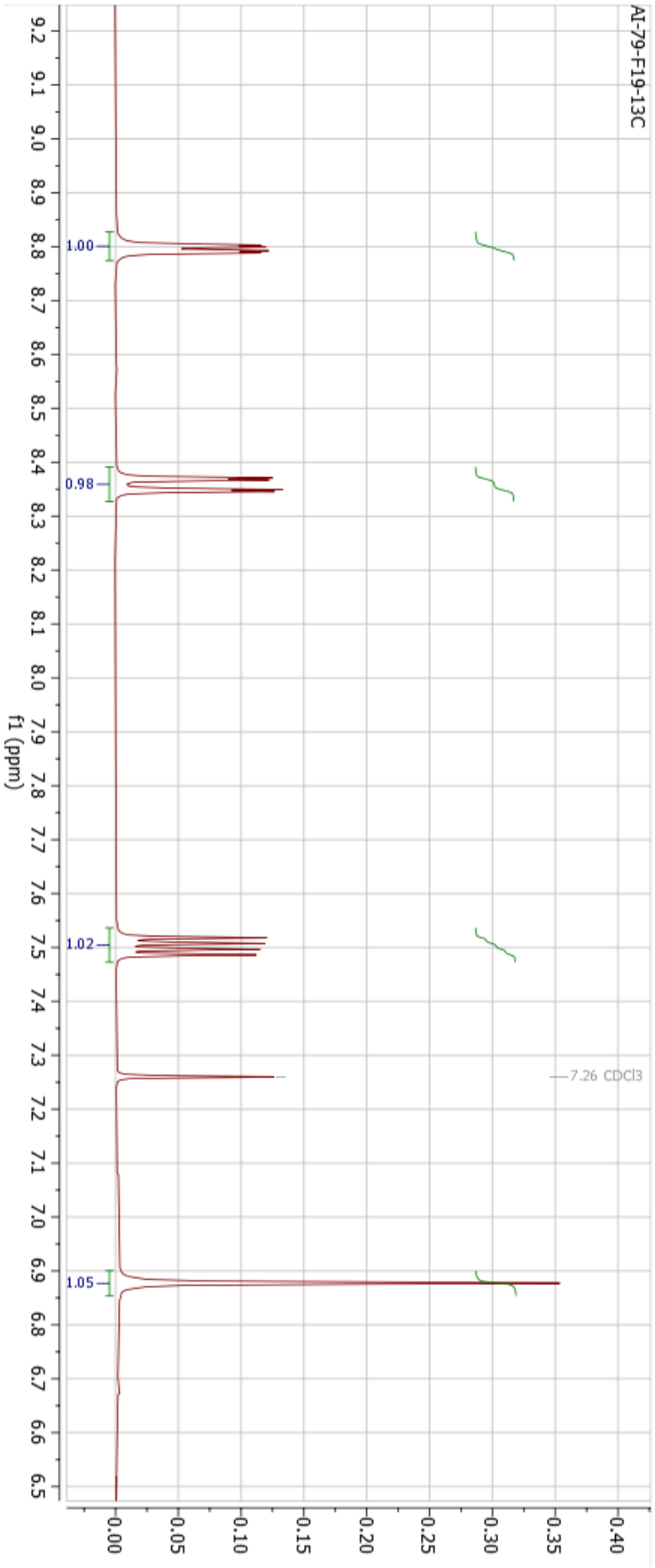


Figure S104. Zoomed in aromatic region of ^{1}H NMR of Product **34**.

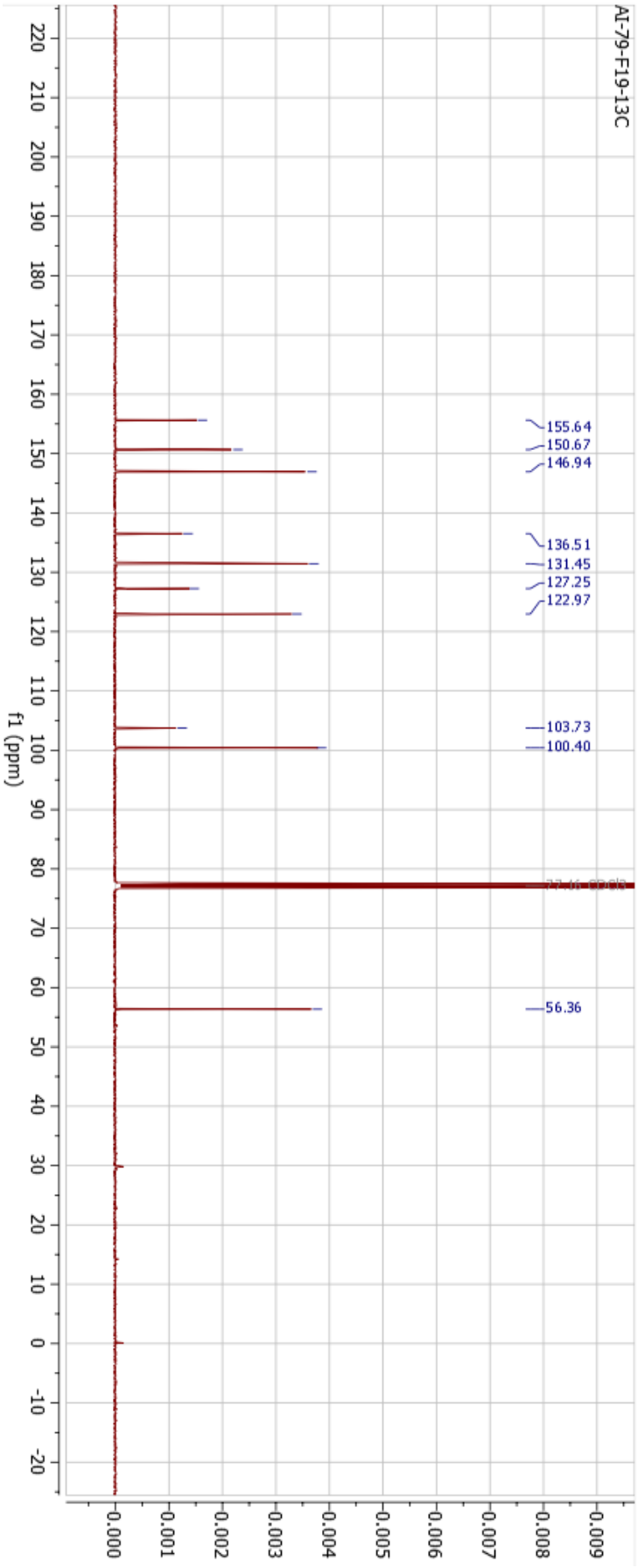


Figure S105. ^{13}C NMR of Product **34**.