

# Supporting Information

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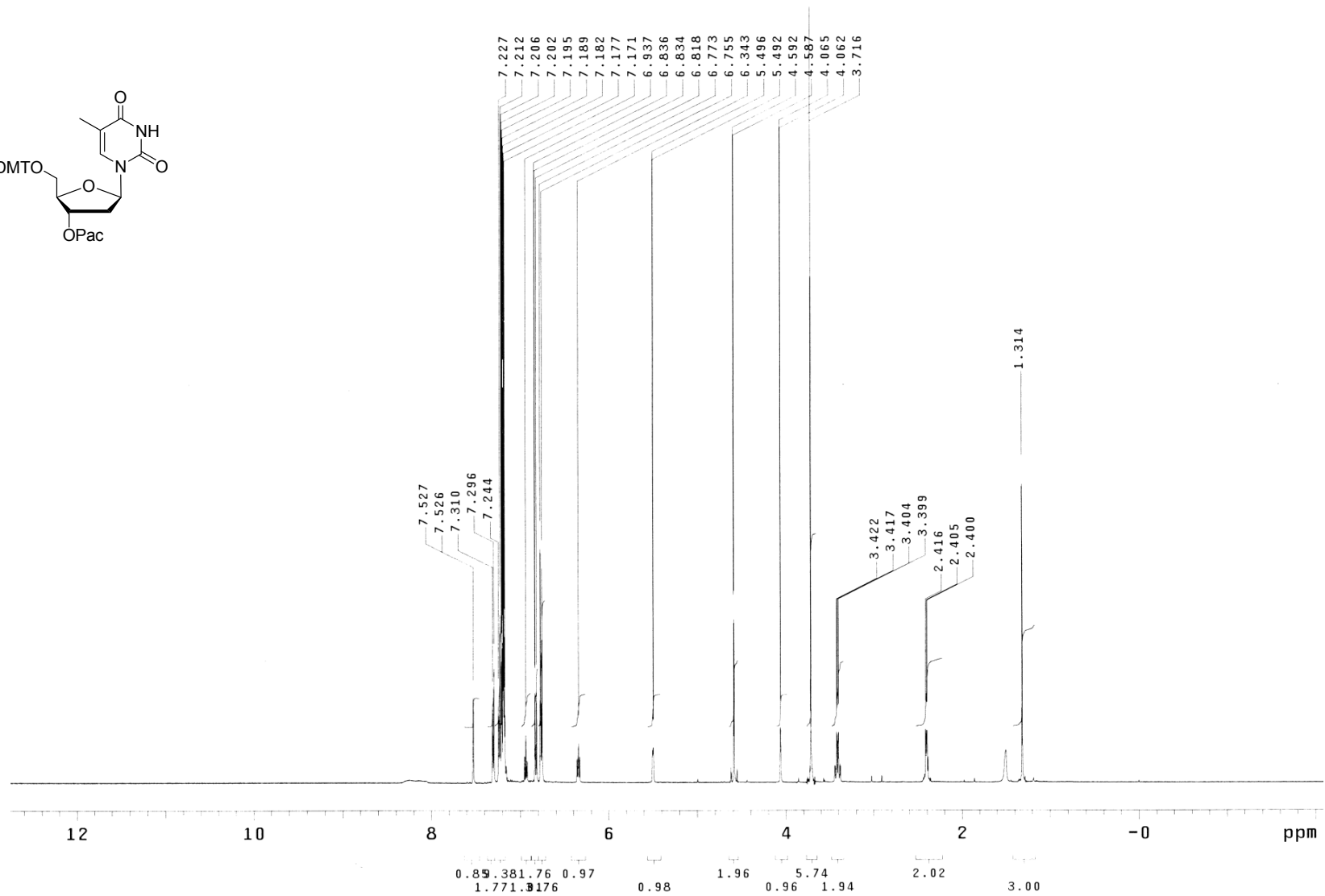
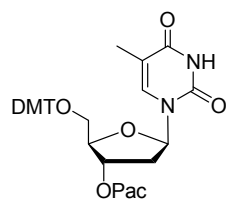


Figure S1. <sup>1</sup>H NMR of Compound 3-1

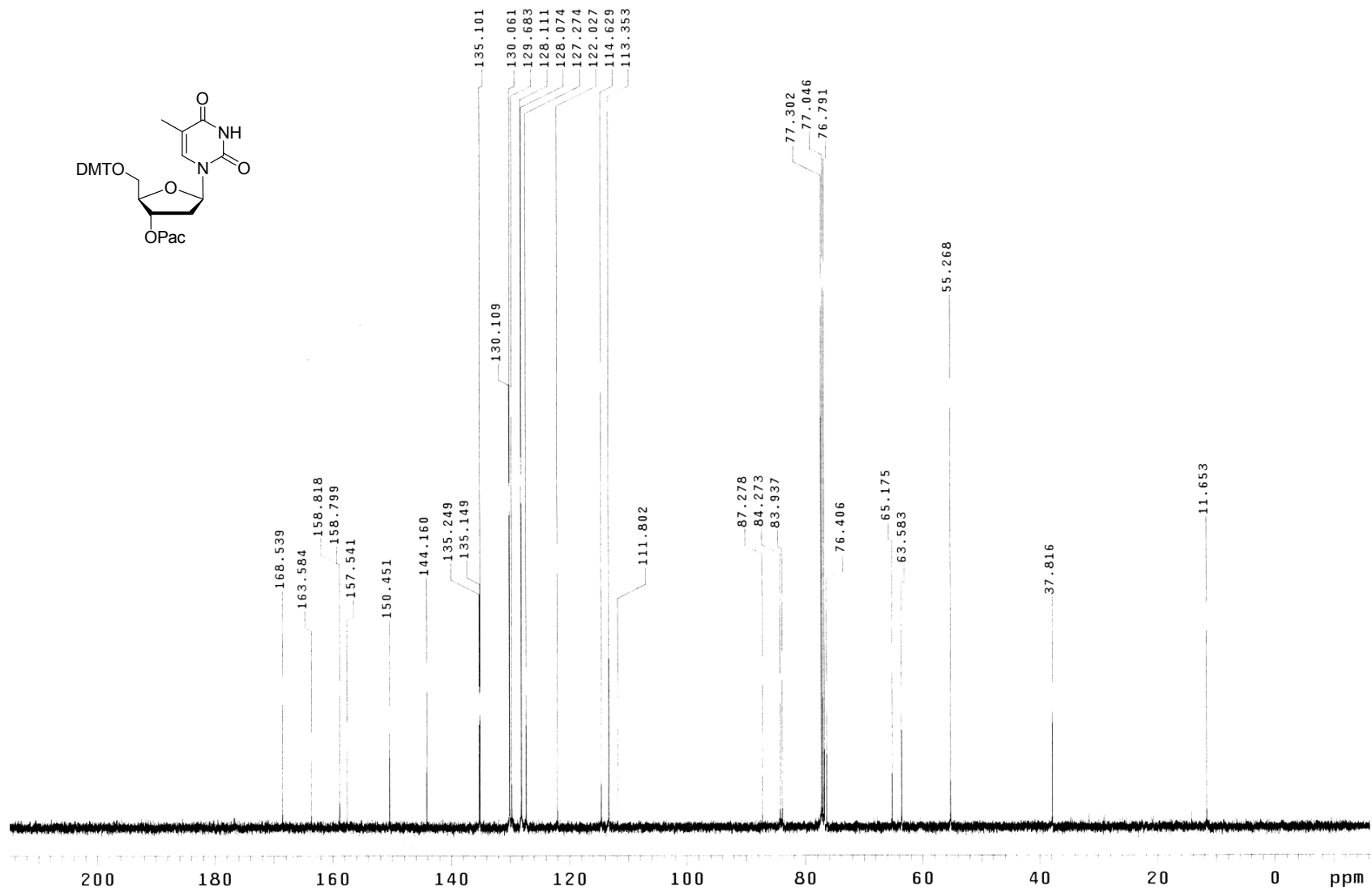


Figure S2. <sup>13</sup>C NMR of Compound 3-1

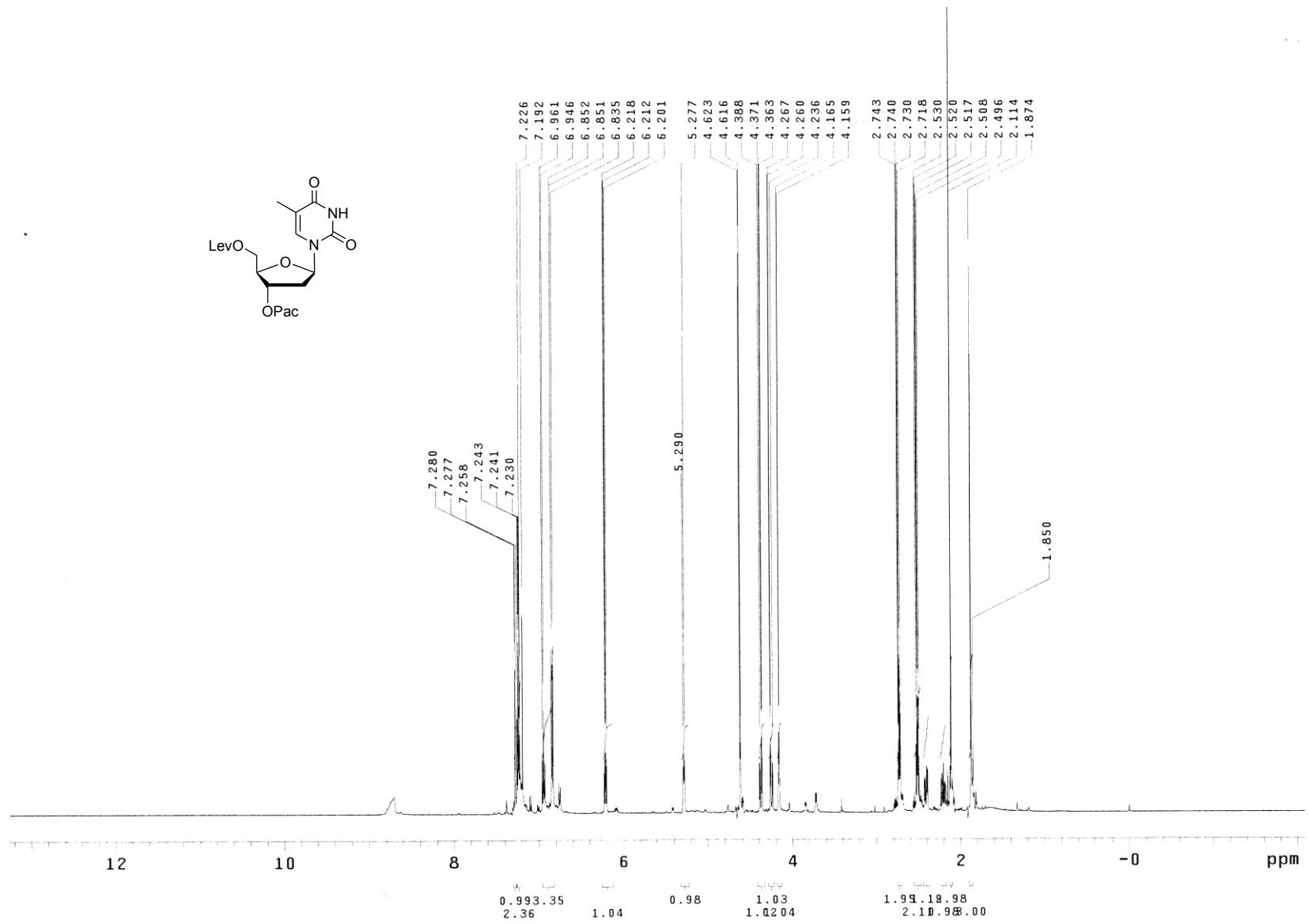


Figure S3. <sup>1</sup>H NMR of Compound 3-2

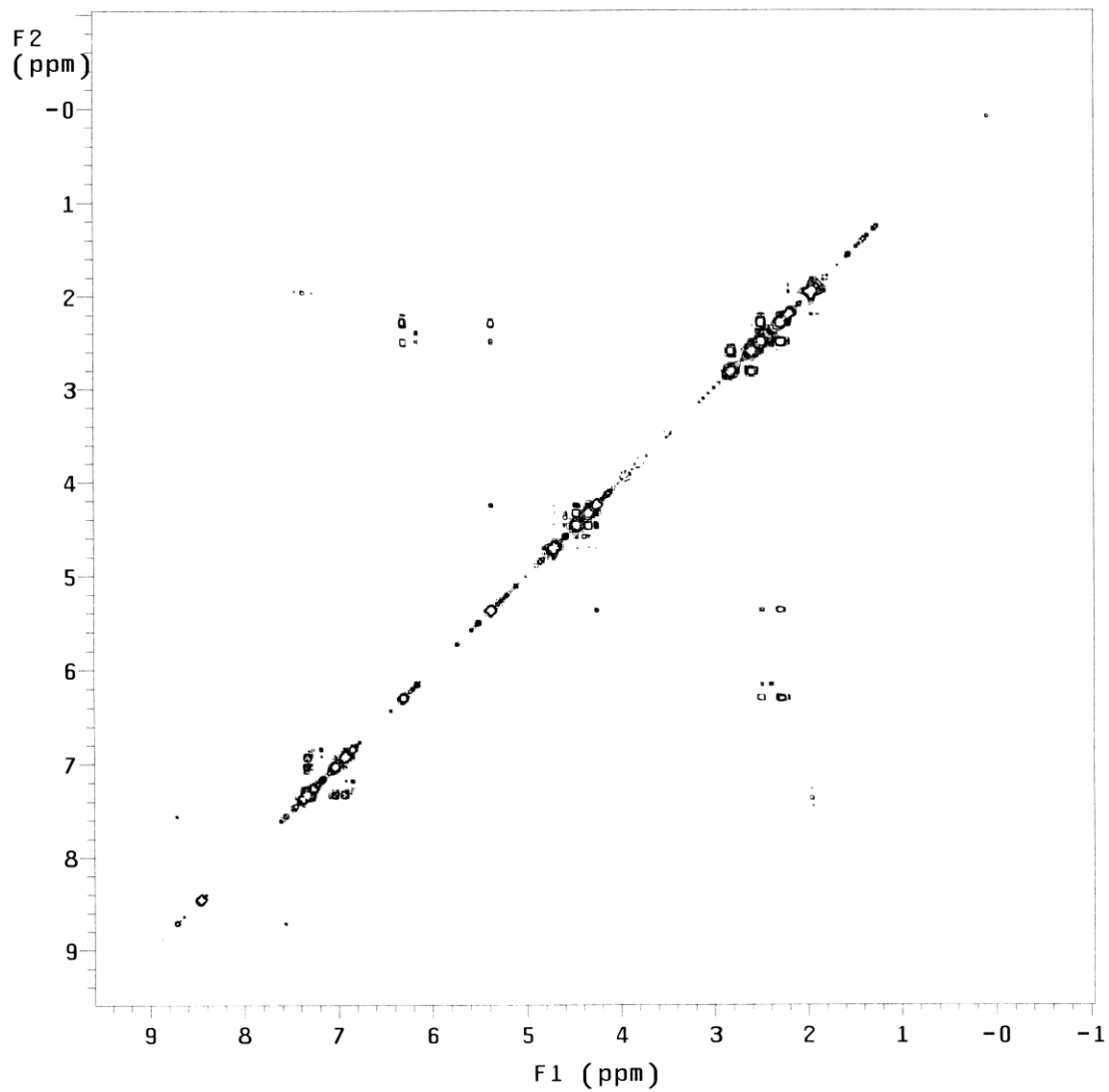
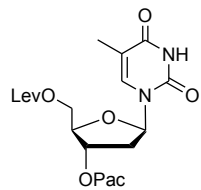


Figure S4. COSY of Compound 3-2

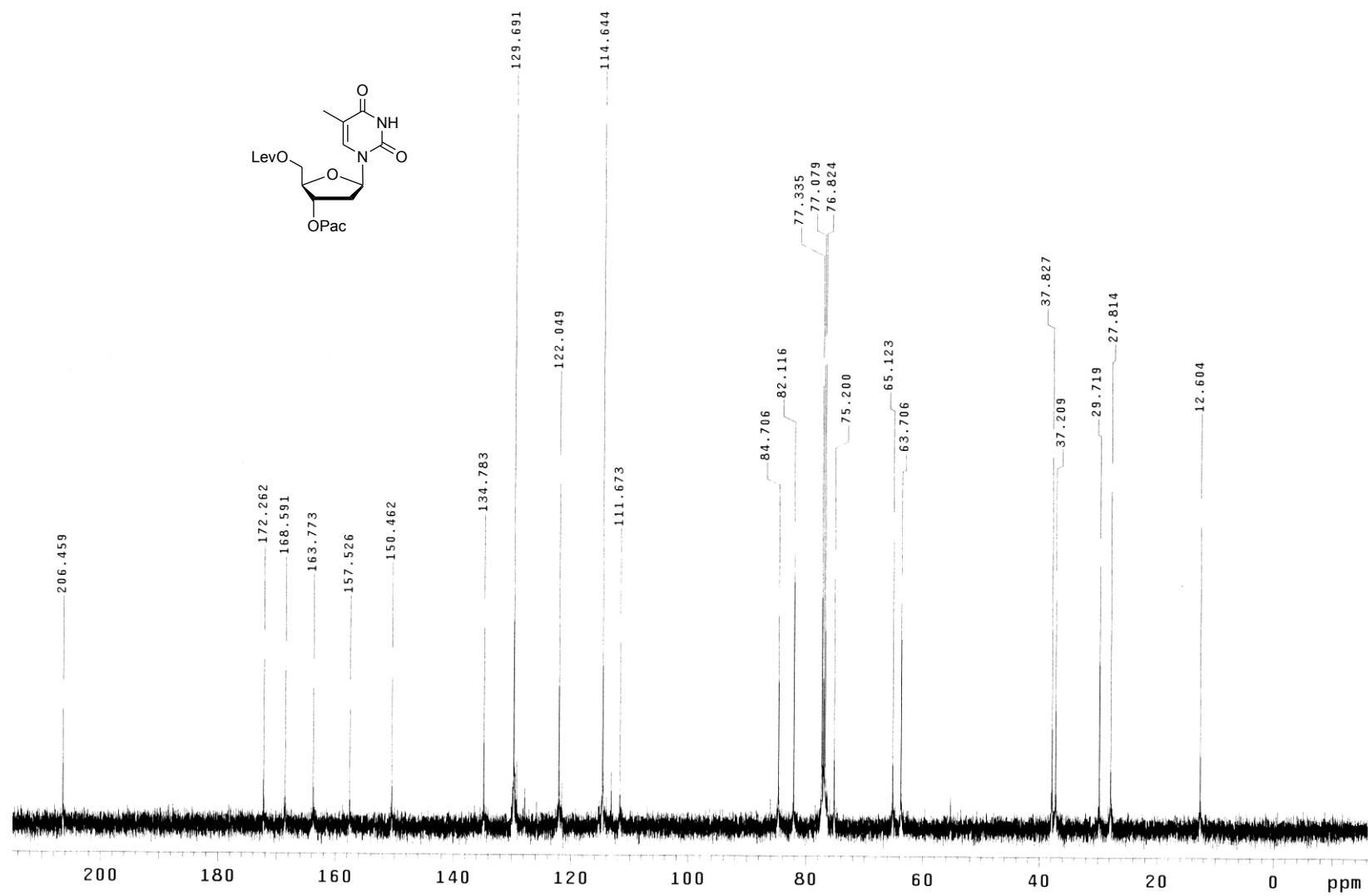
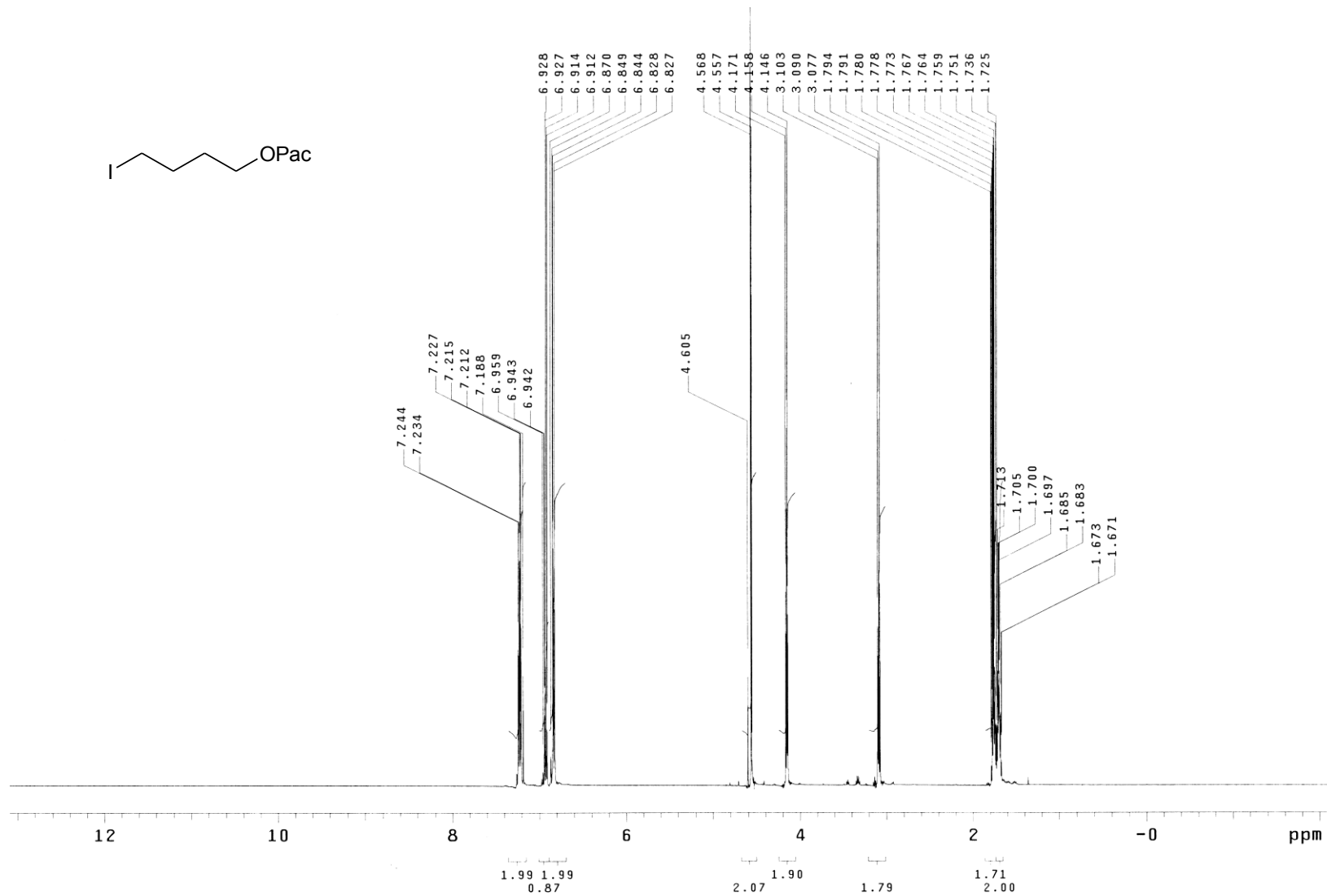


Figure S5. <sup>13</sup>CNMR of Compound 3-2



**Figure S6.**  $^1\text{H}$ NMR of 4-Iodobutyl 2-phenoxyacetate (3-3)



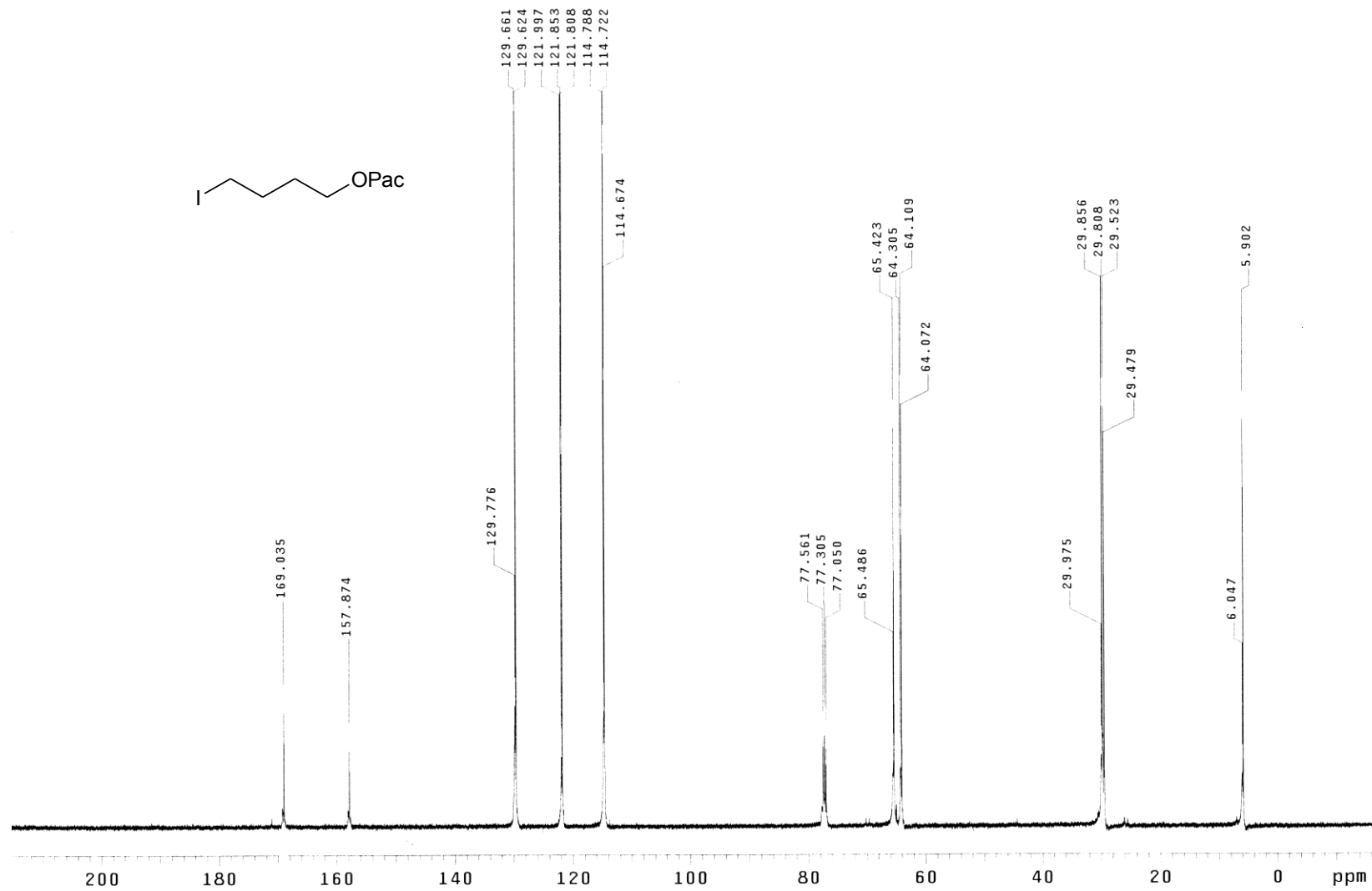


Figure S7.  $^{13}\text{C}$  NMR of 4-Iodobutyl 2-phenoxyacetate (3-3)

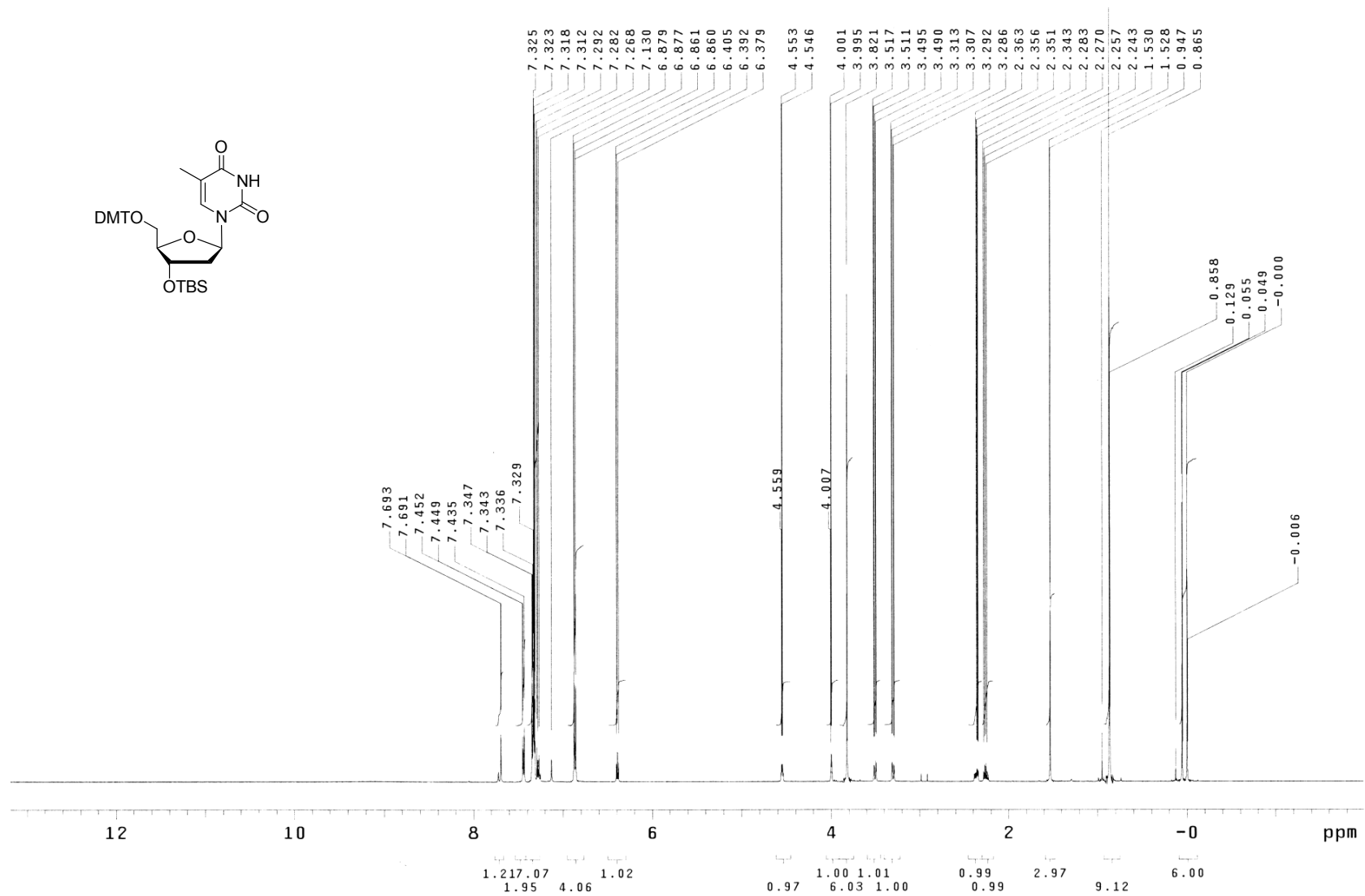


Figure S8. <sup>1</sup>H NMR of Compound 3-4

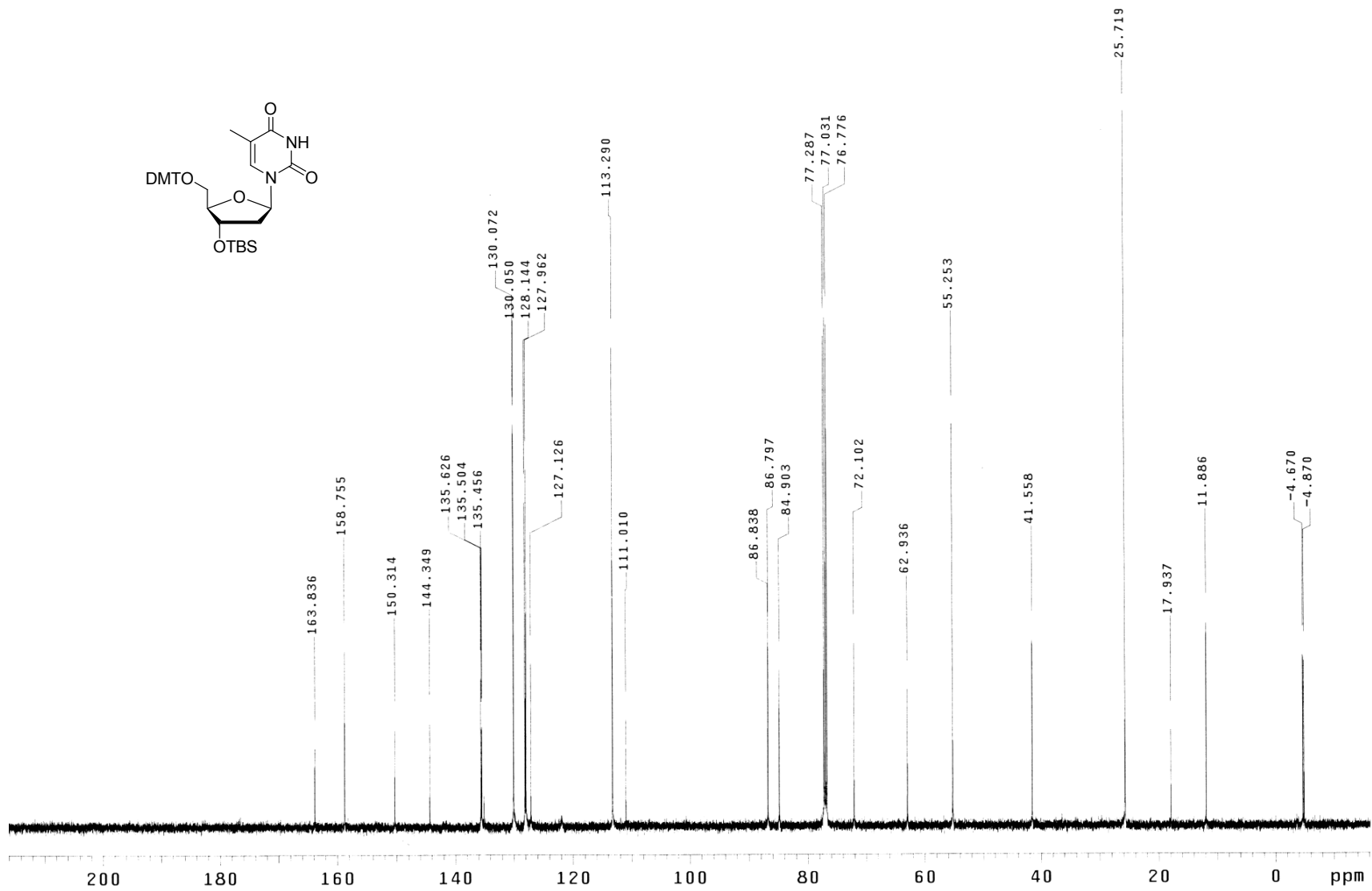
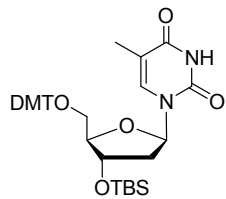


Figure S9. <sup>13</sup>C NMR of Compound 3-4

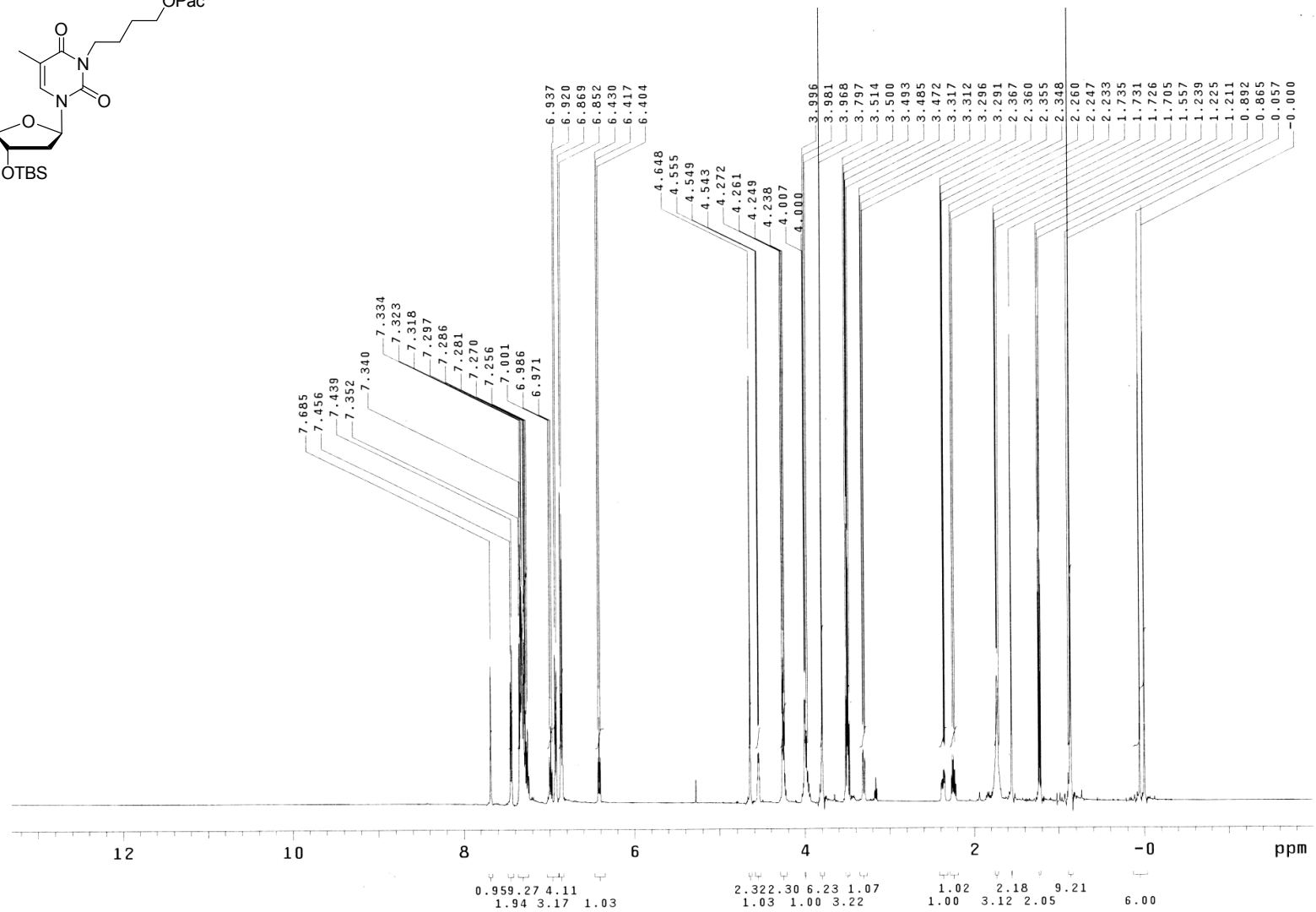
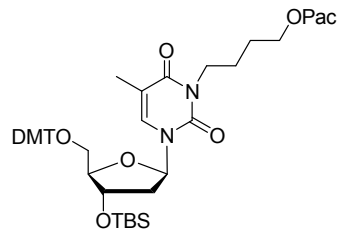


Figure S10. <sup>1</sup>H NMR of Compound 3-5

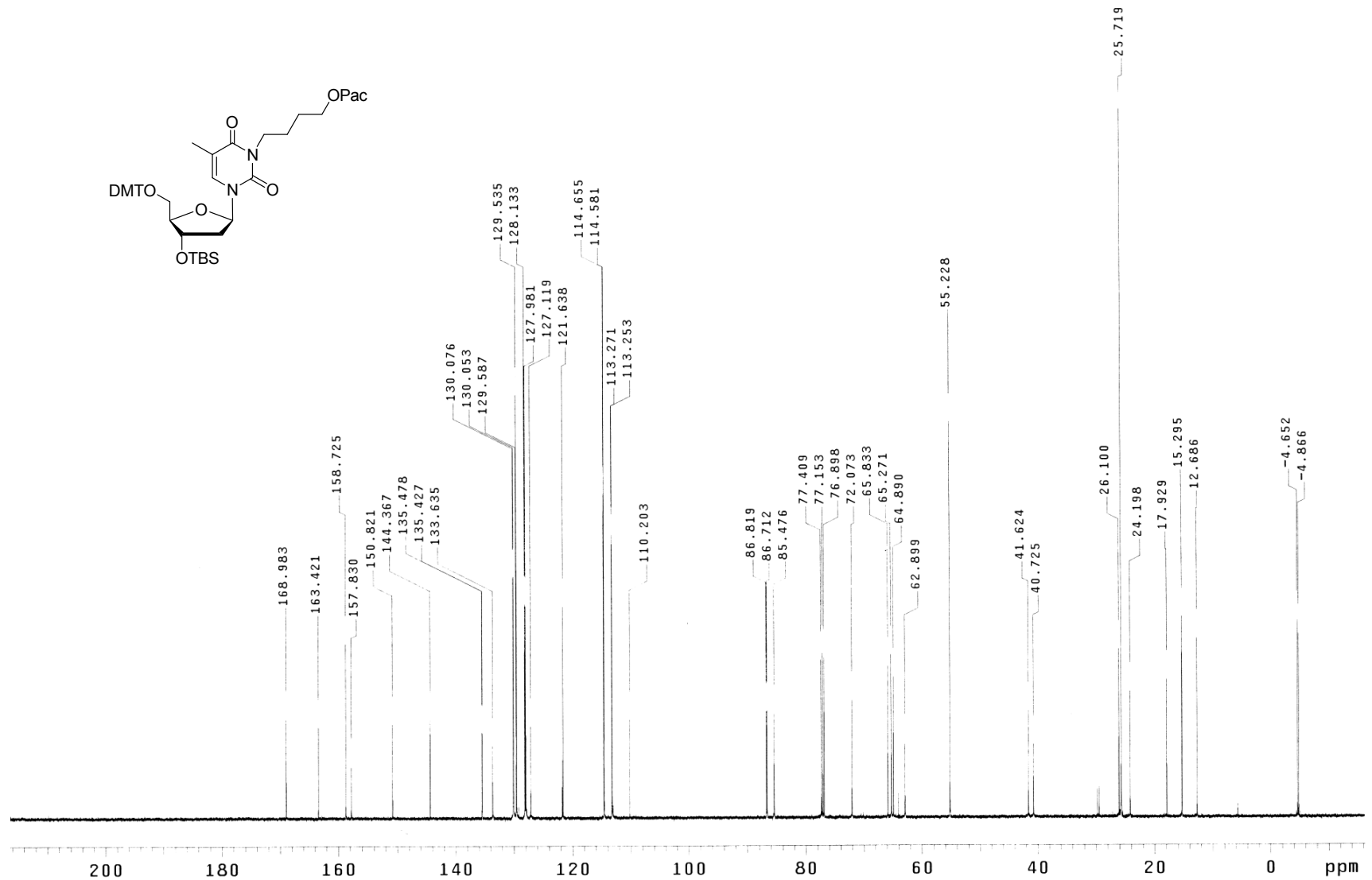


Figure S11. <sup>13</sup>C NMR of Compound 3-5

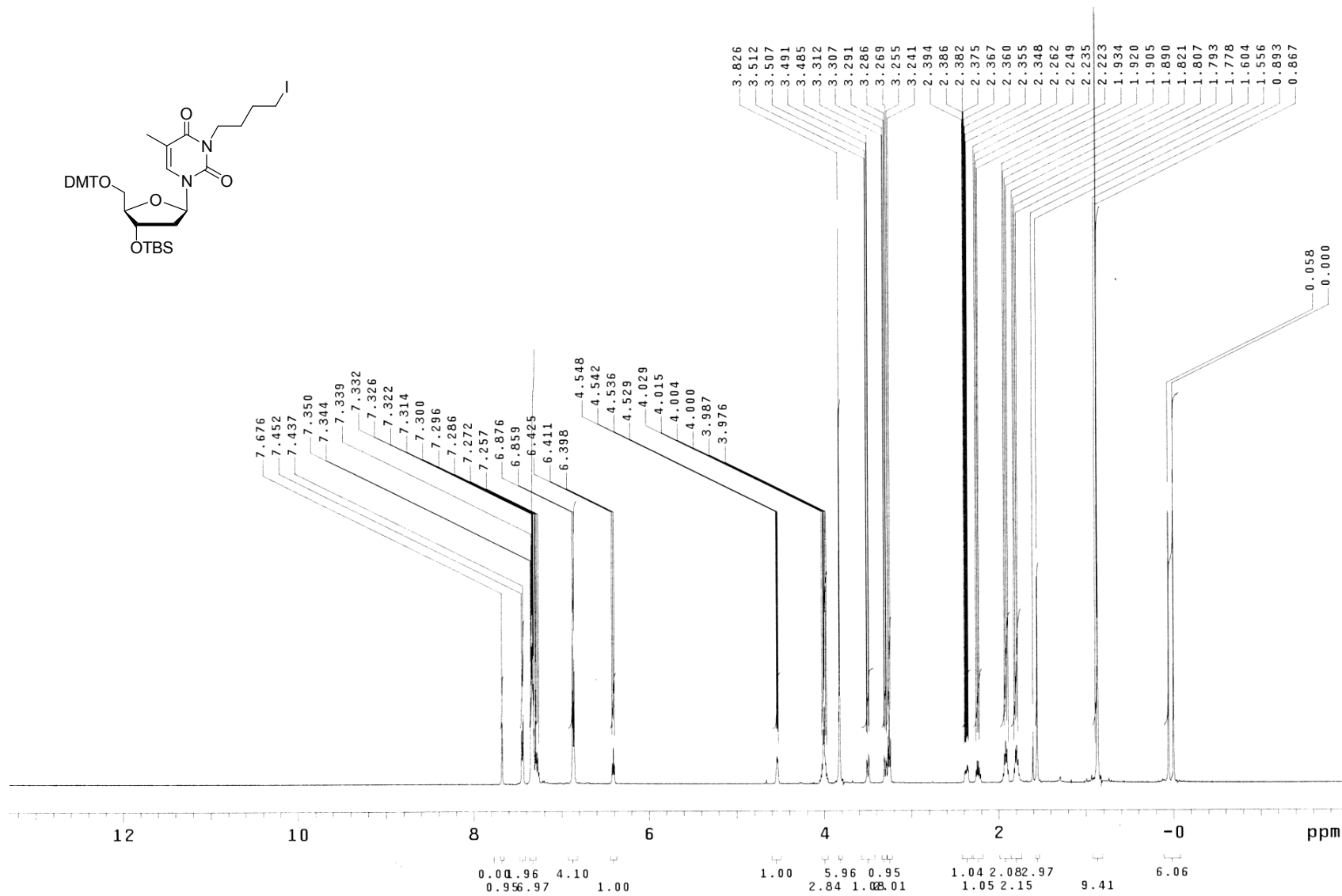


Figure S12. <sup>1</sup>H NMR of Compound 3-6

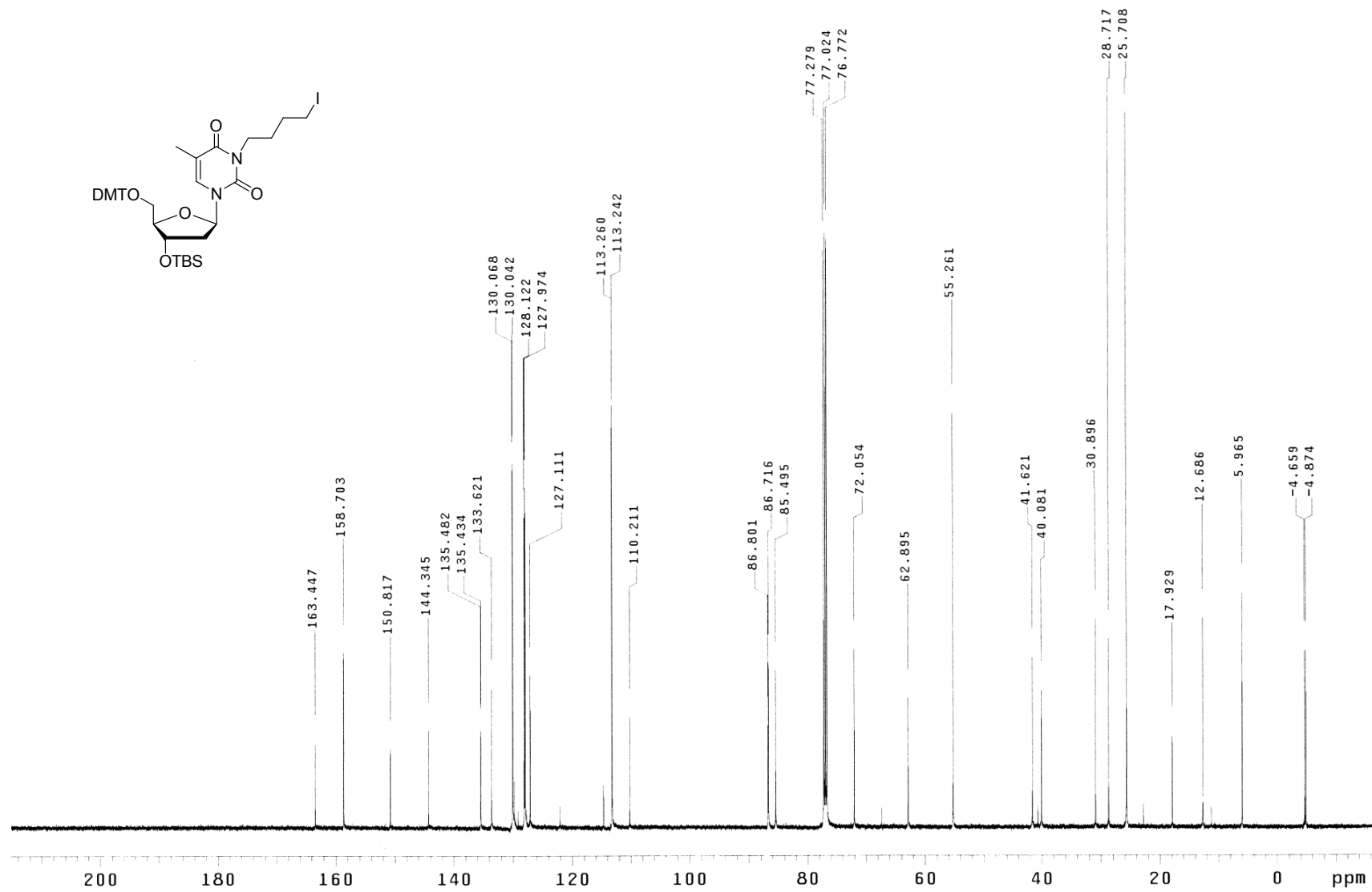
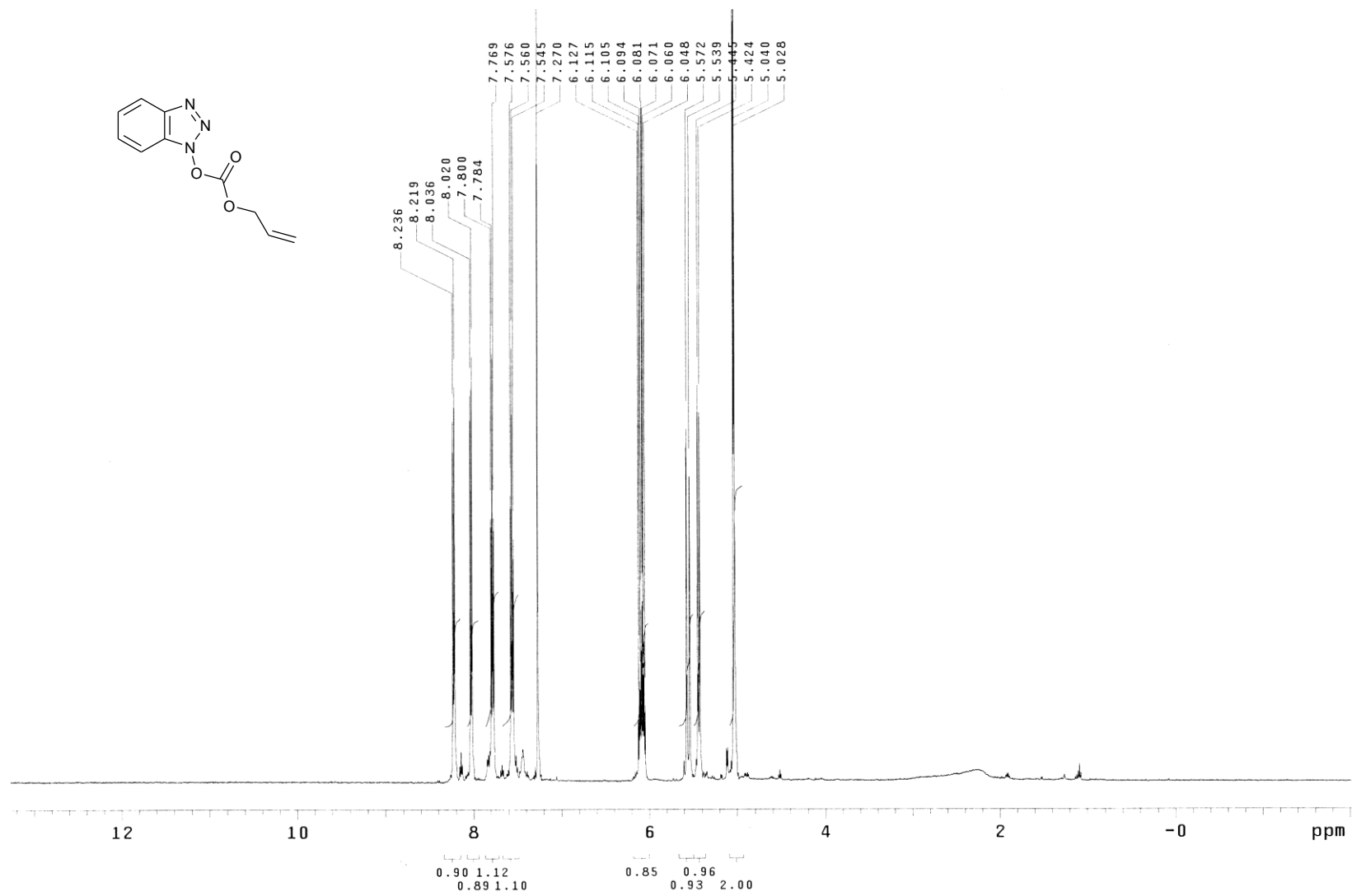


Figure S13. <sup>13</sup>CNMR of Compound 3-6



**Figure S14.** <sup>1</sup>H NMR of Allyl 1-hydroxybenzotriazole carbonate (3-7)



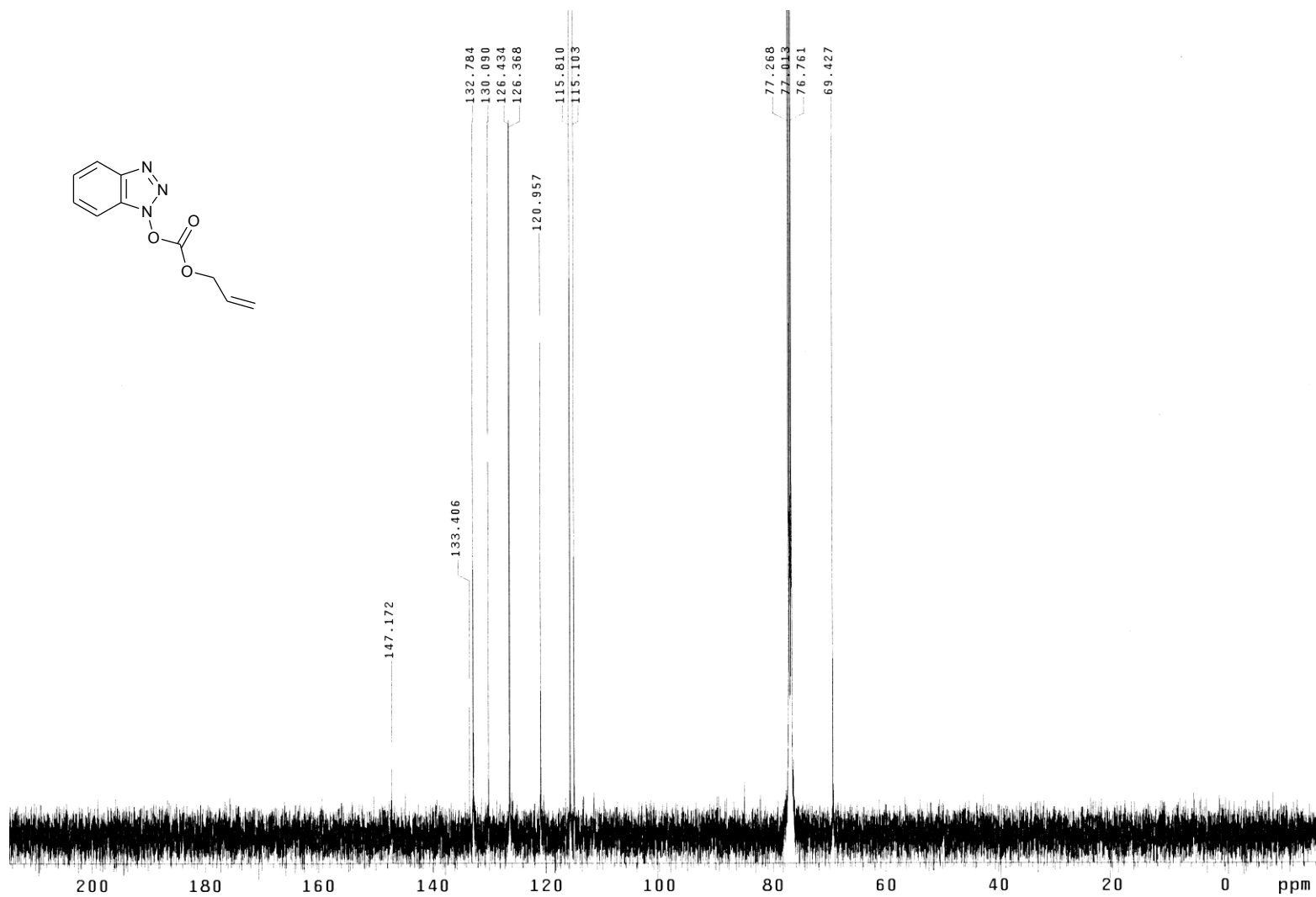


Figure S15. <sup>13</sup>CNMR of Allyl 1-hydroxybenzotriazole carbonate (3-7)

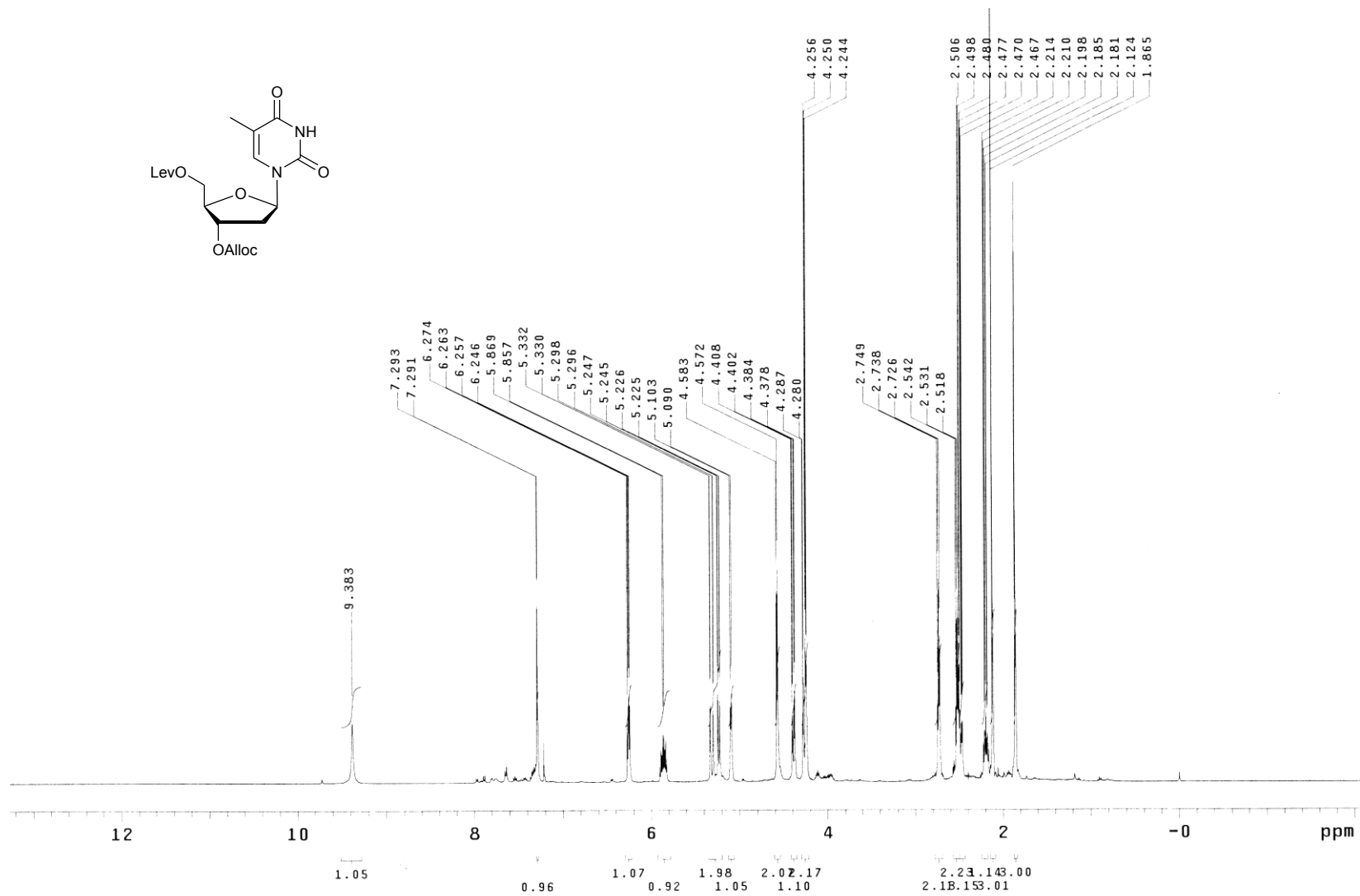


Figure S16. <sup>1</sup>H NMR of Compound 3-8

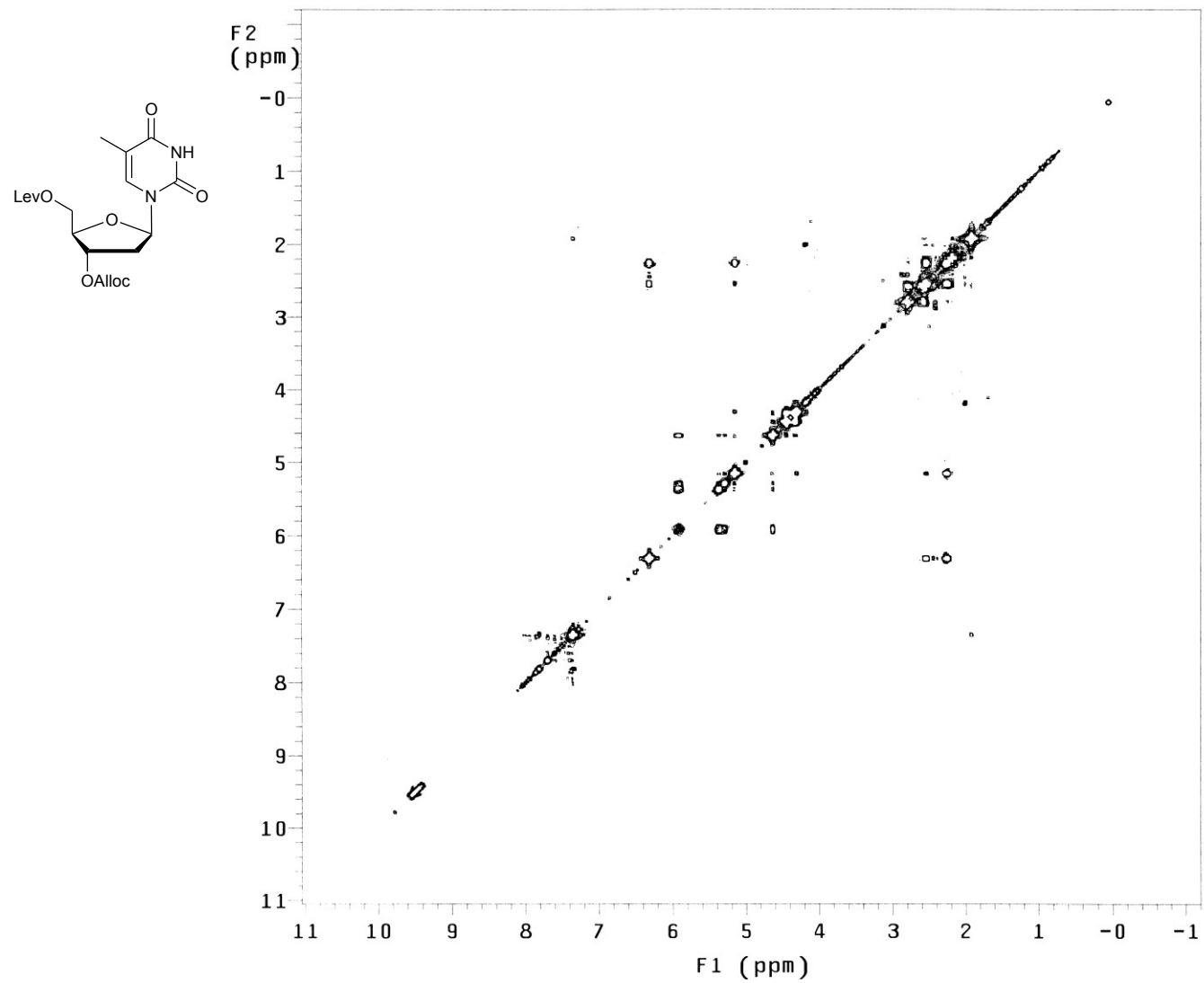


Figure S17. COSY of Compound 3-8

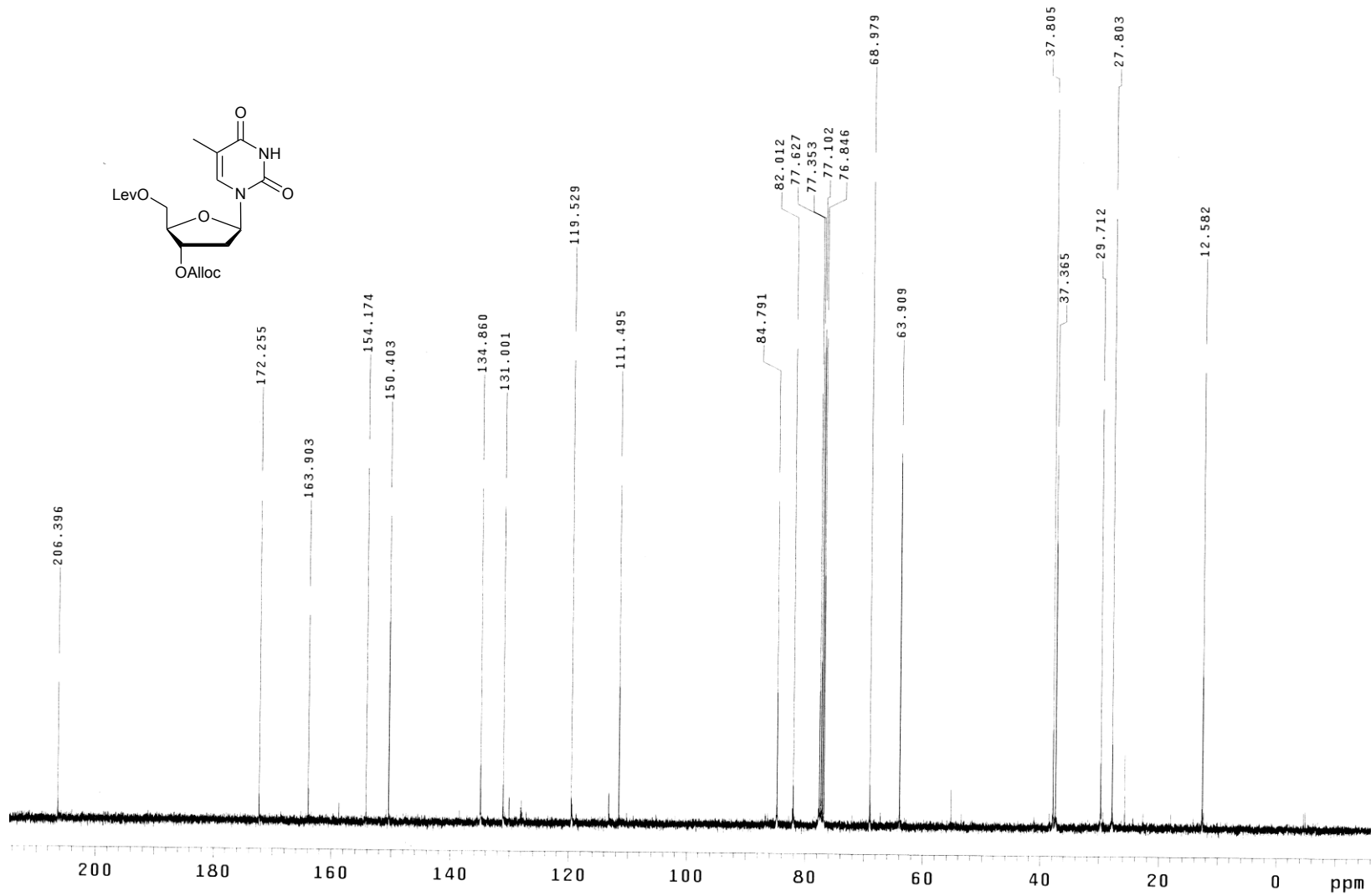


Figure S18. <sup>13</sup>CNMR of Compound 3-8

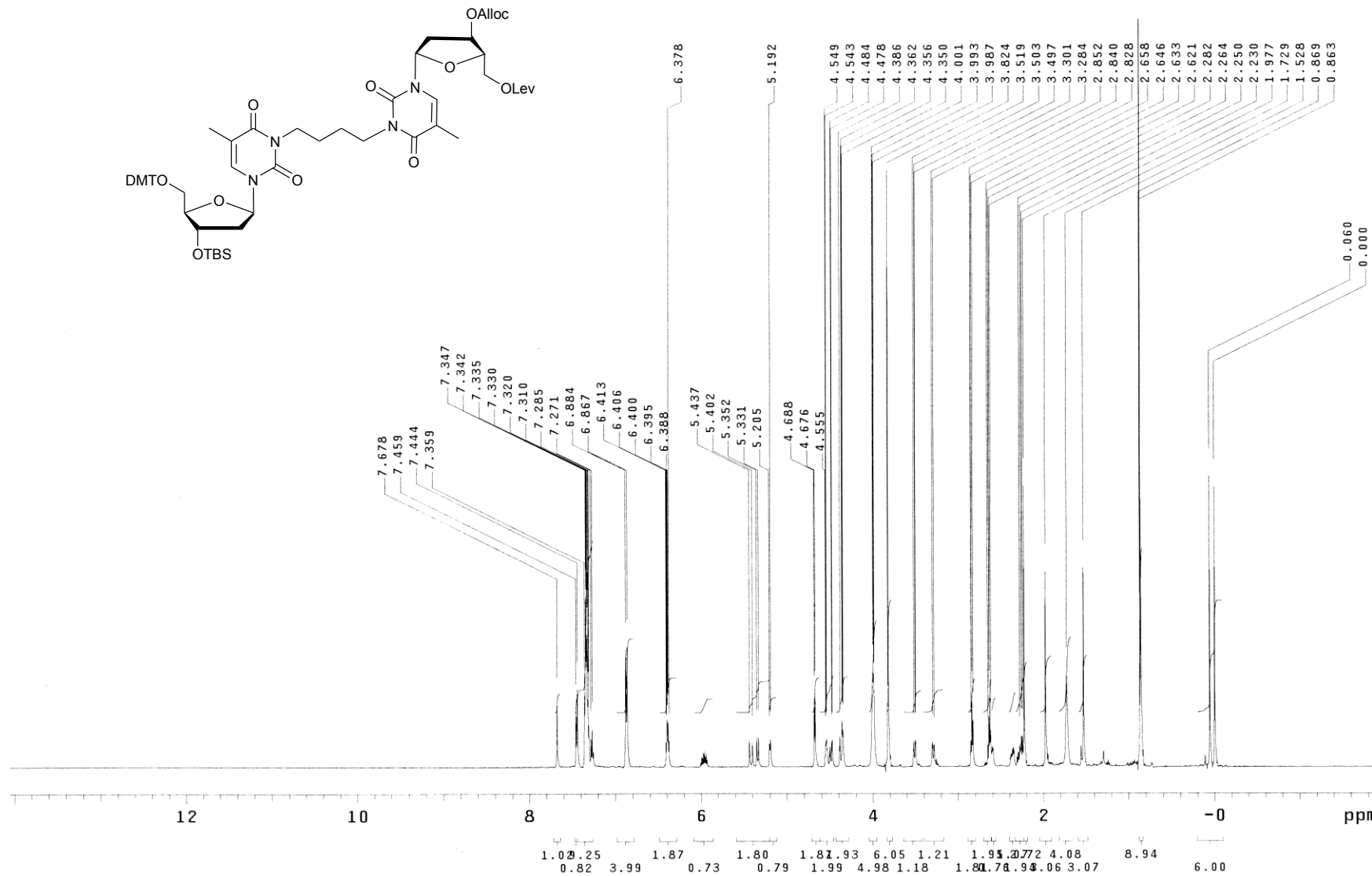


Figure S19. <sup>1</sup>H NMR of Compound 3-9

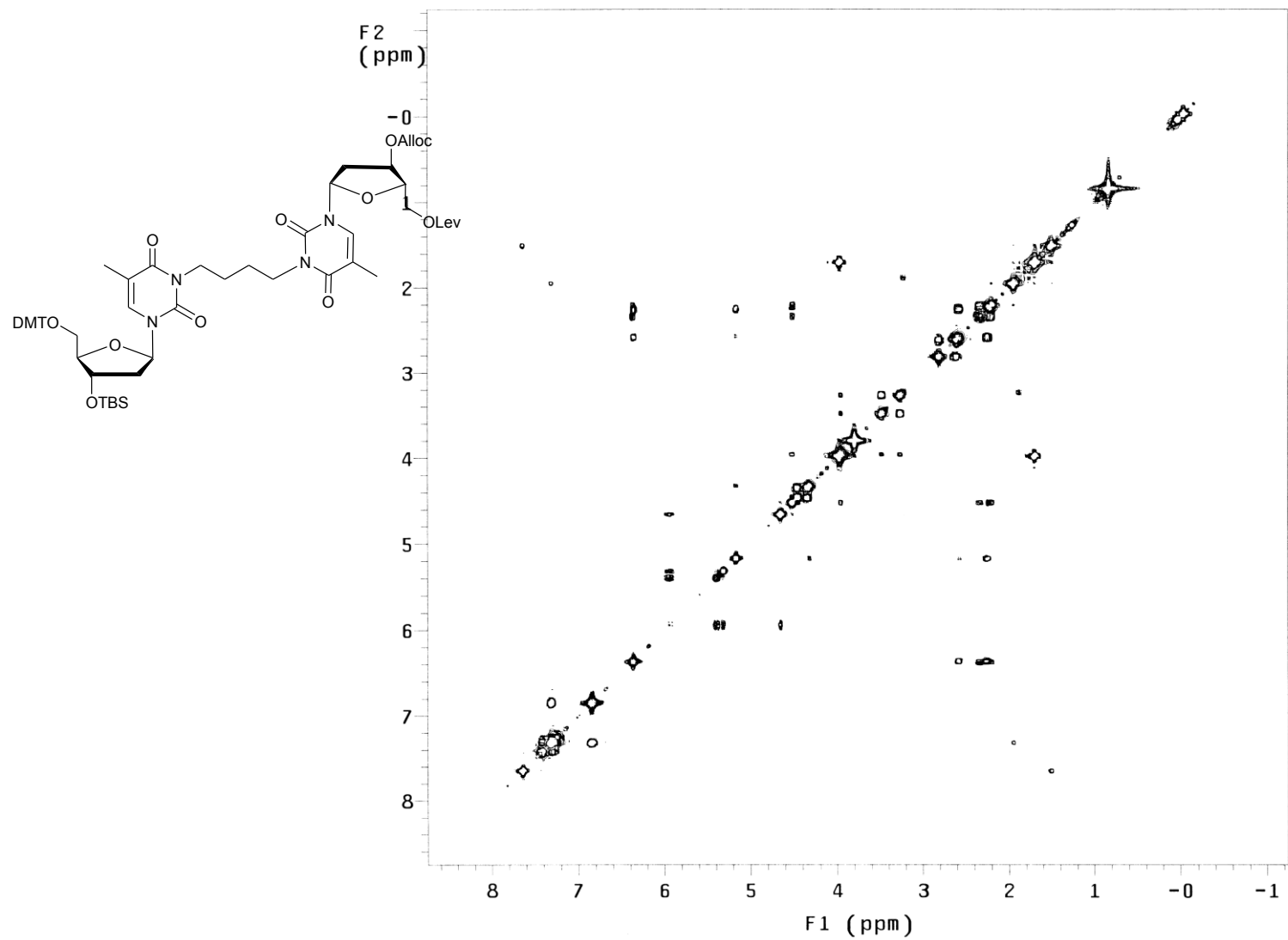


Figure S20. COSY of Compound 3-9

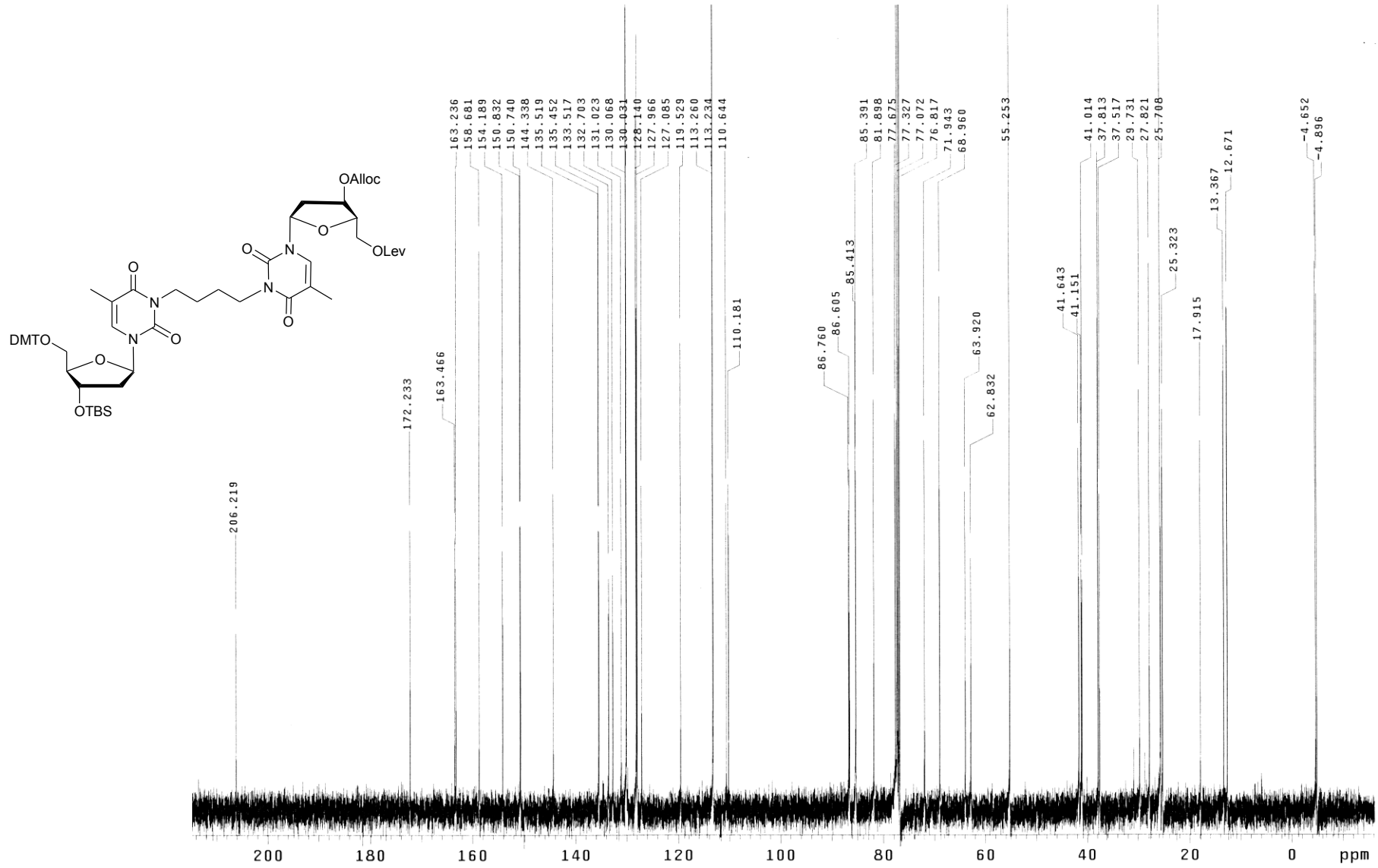


Figure S21. <sup>13</sup>CNMR of Compound 3-9

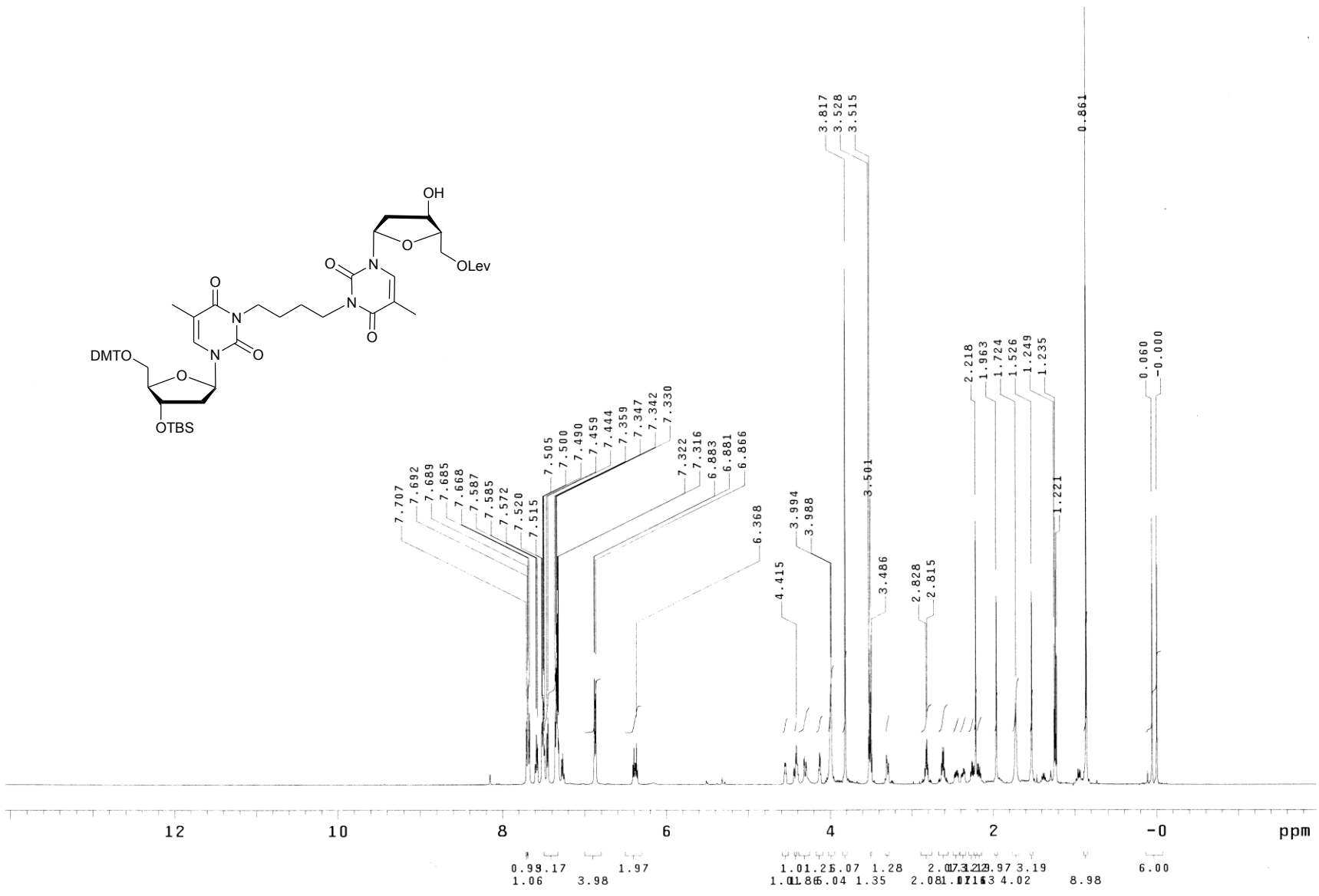


Figure S22. <sup>1</sup>H NMR of Compound 3-10



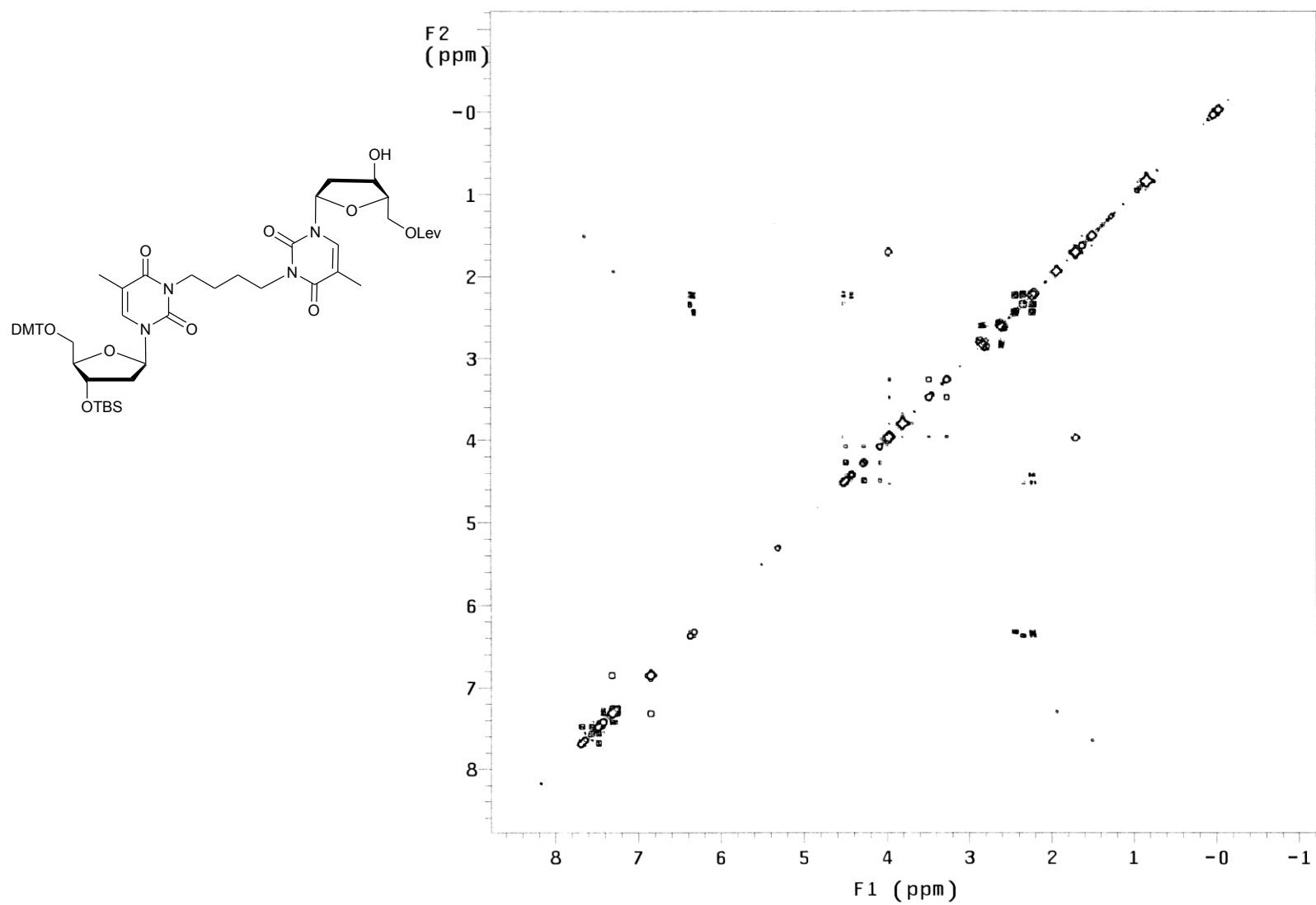


Figure S23. COSY of Compound 3-10

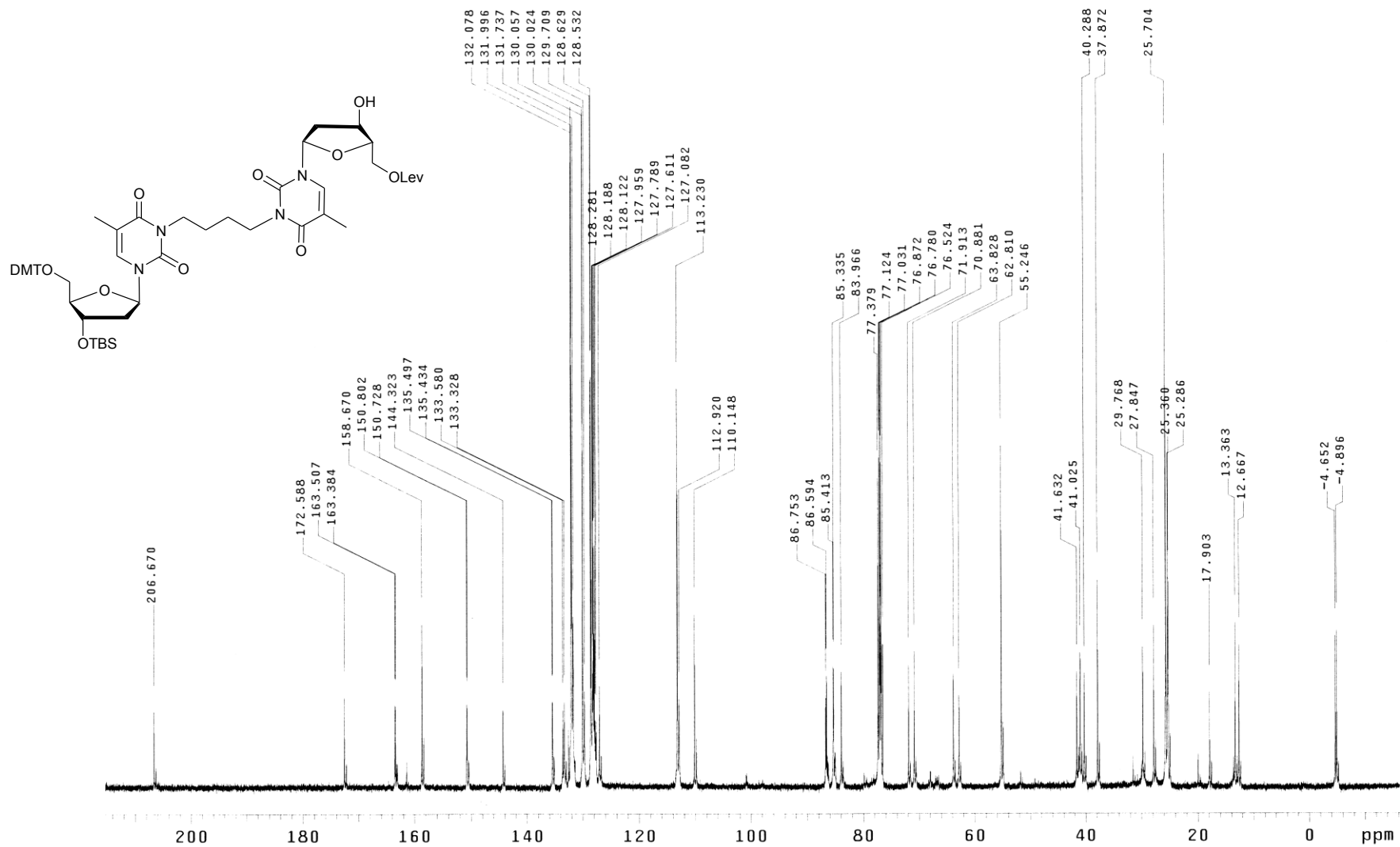
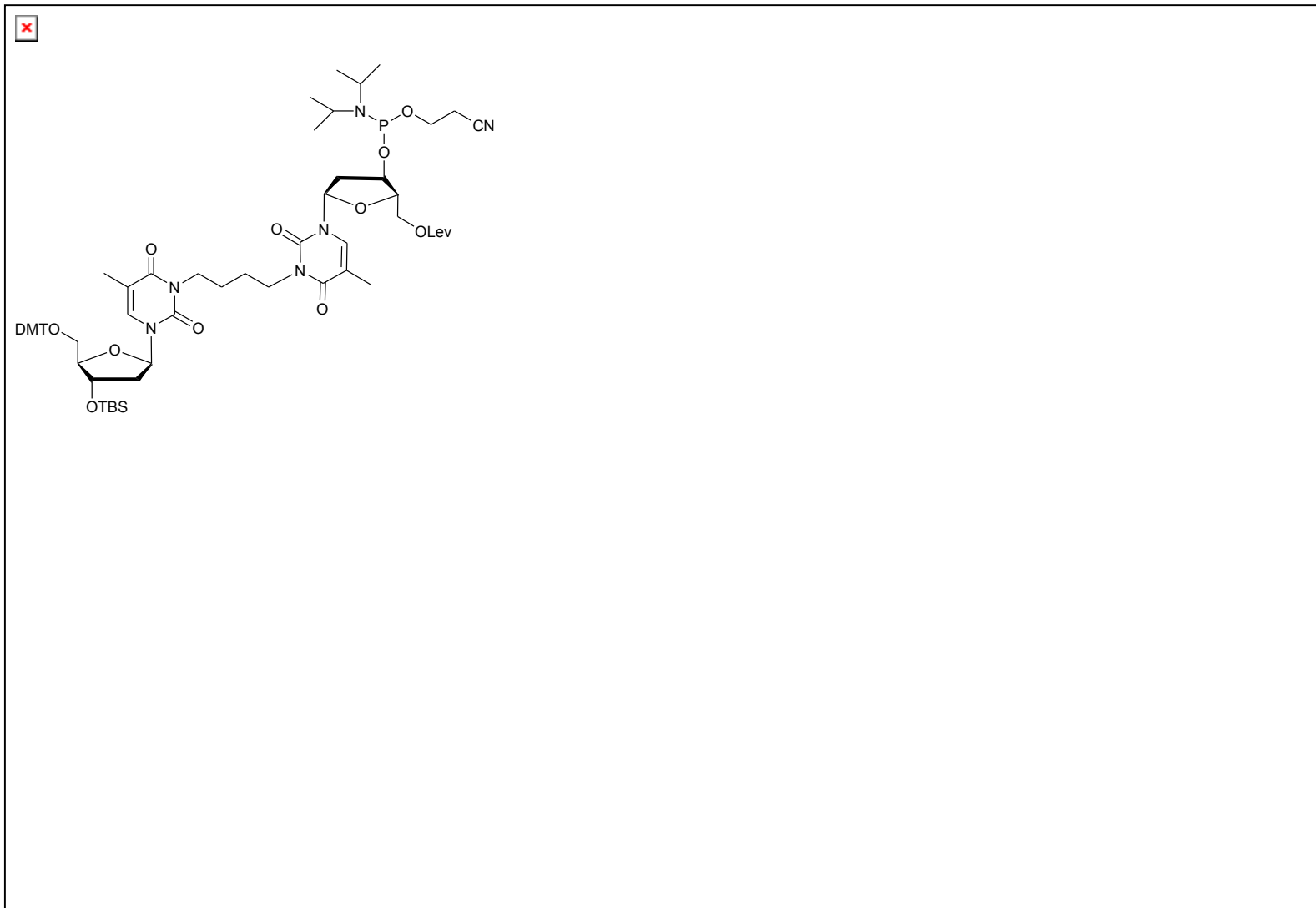


Figure S24. <sup>13</sup>C NMR of Compound 3-10



**Figure S25.** <sup>31</sup>P NMR of Phosphoramidite 3-11

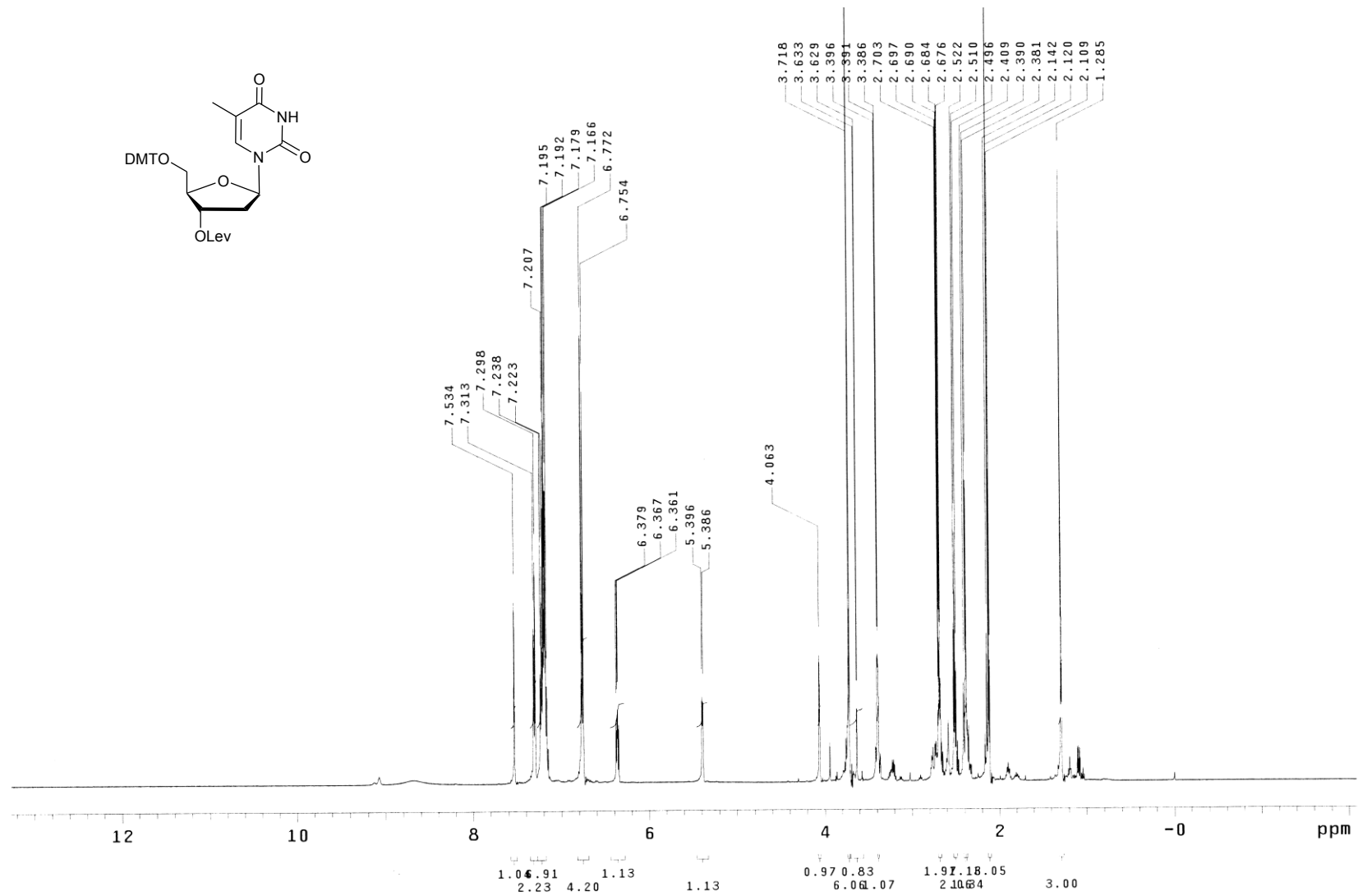


Figure S26. <sup>1</sup>H NMR of Compound 3-12

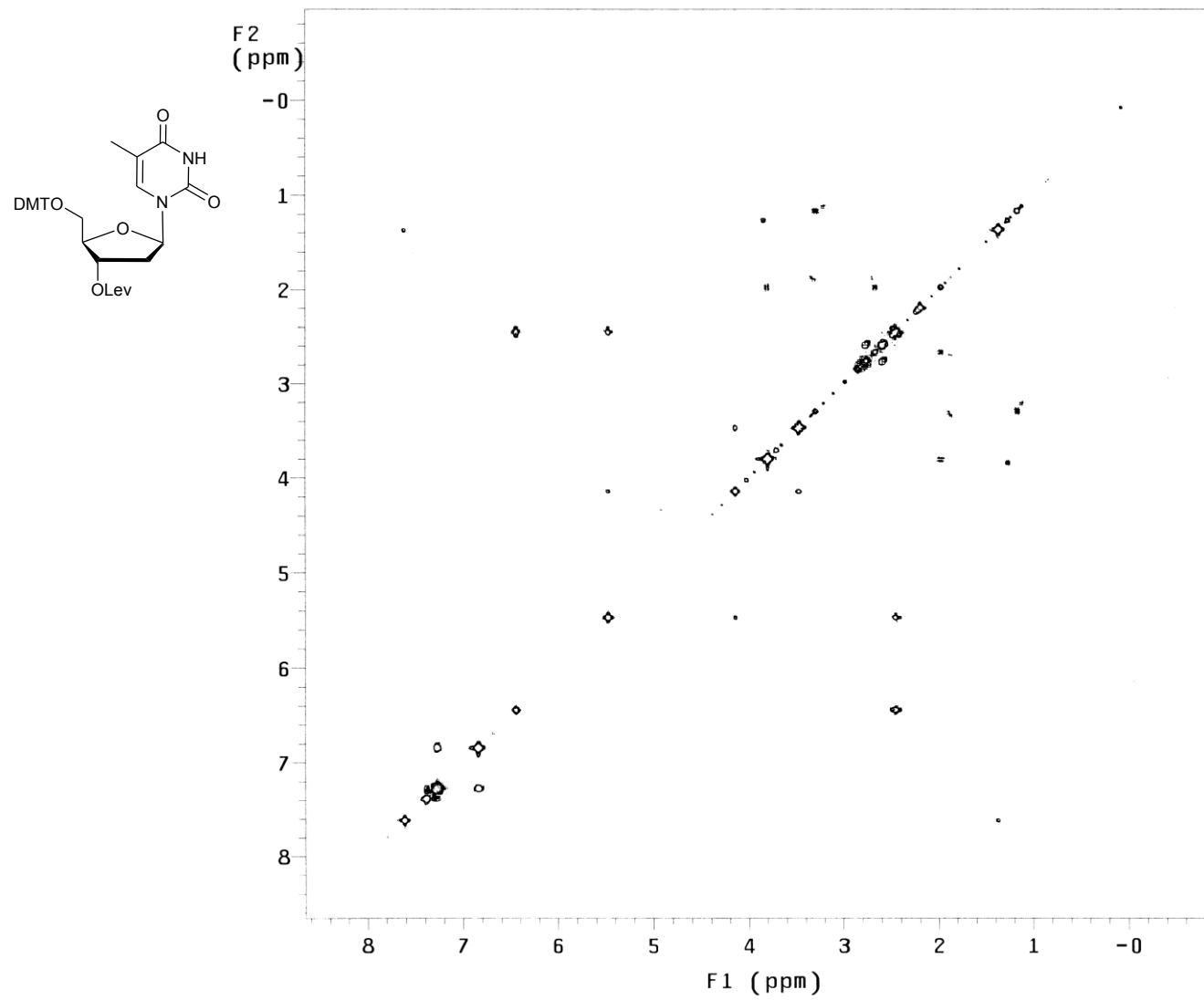


Figure S27. COSY of Compound 3-12

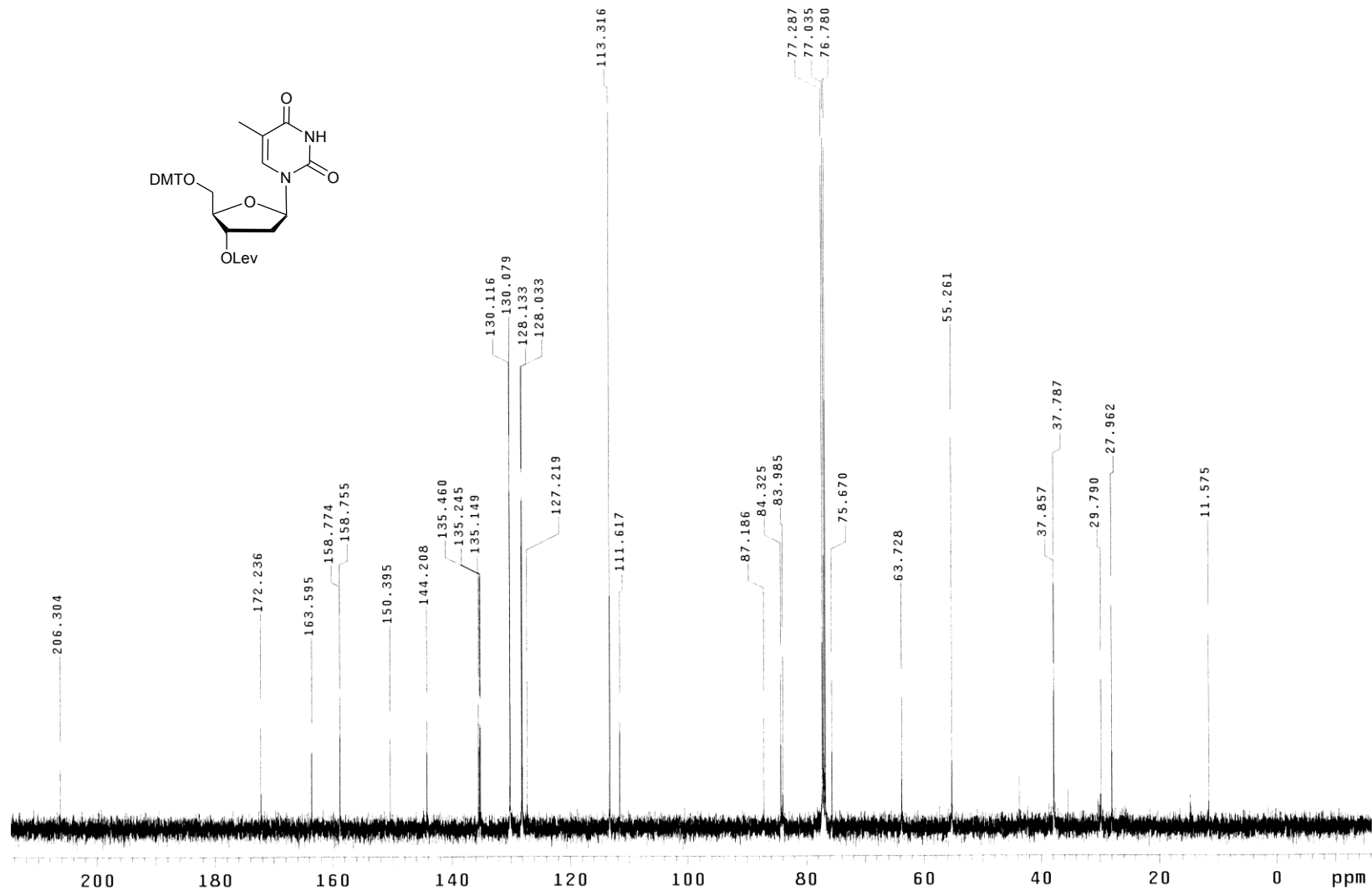


Figure S28. <sup>13</sup>C NMR of Compound 3-12

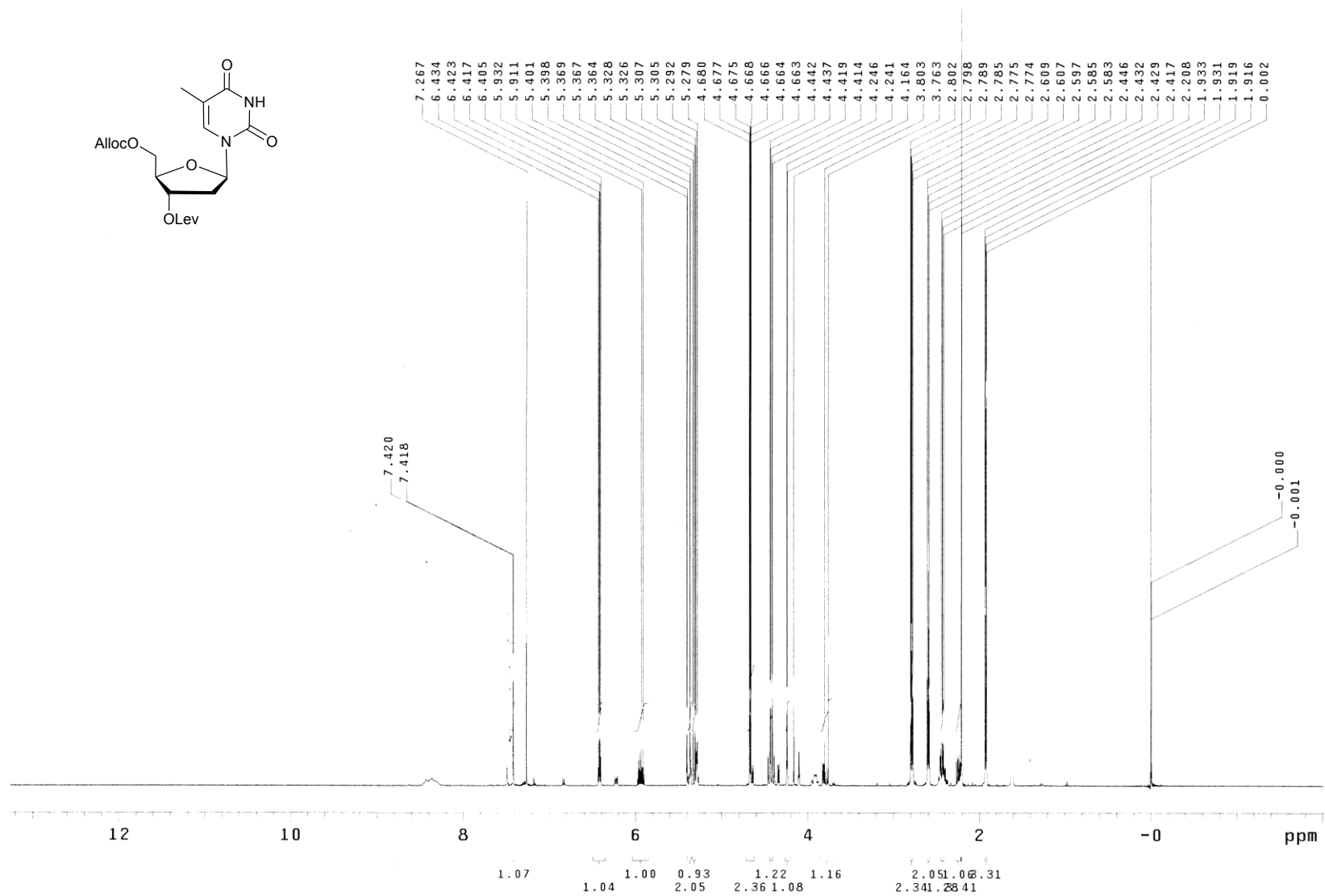


Figure S29. <sup>1</sup>H NMR of Compound 3-13

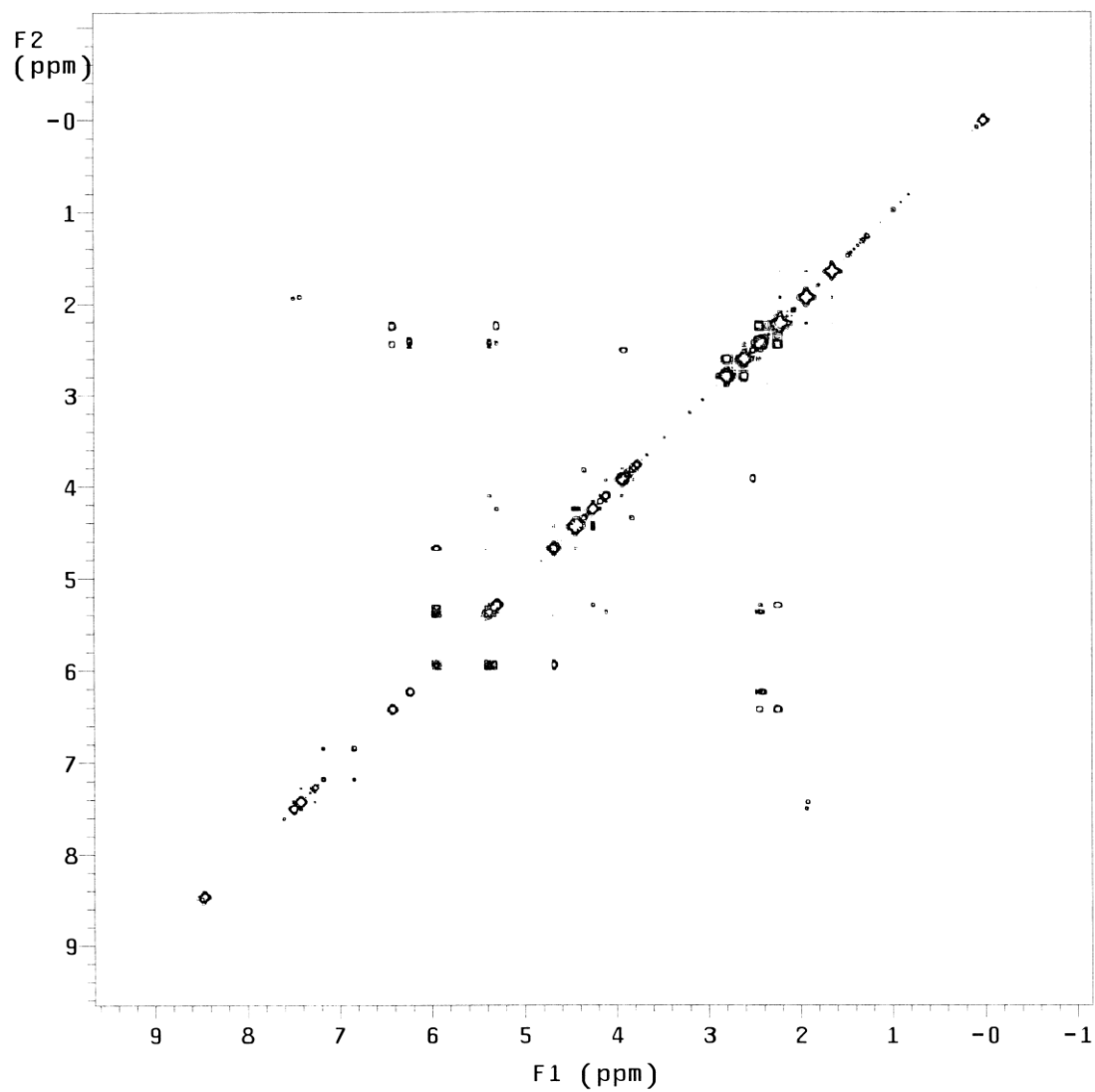
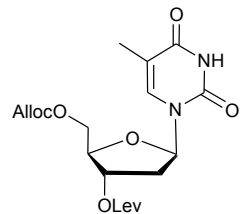


Figure S30. COSY of Compound 3-13



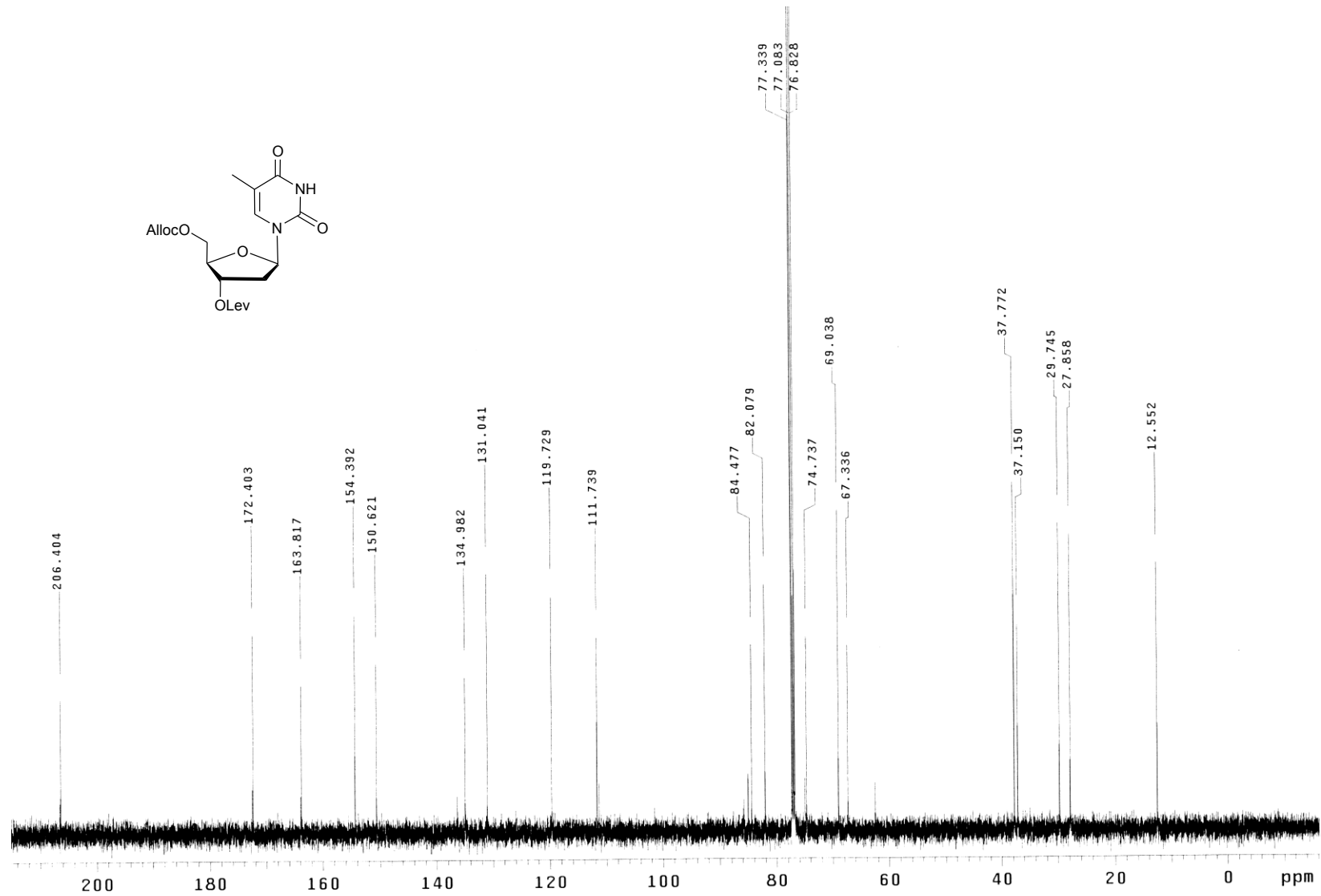


Figure S31. <sup>13</sup>CNMR of Compound 3-13

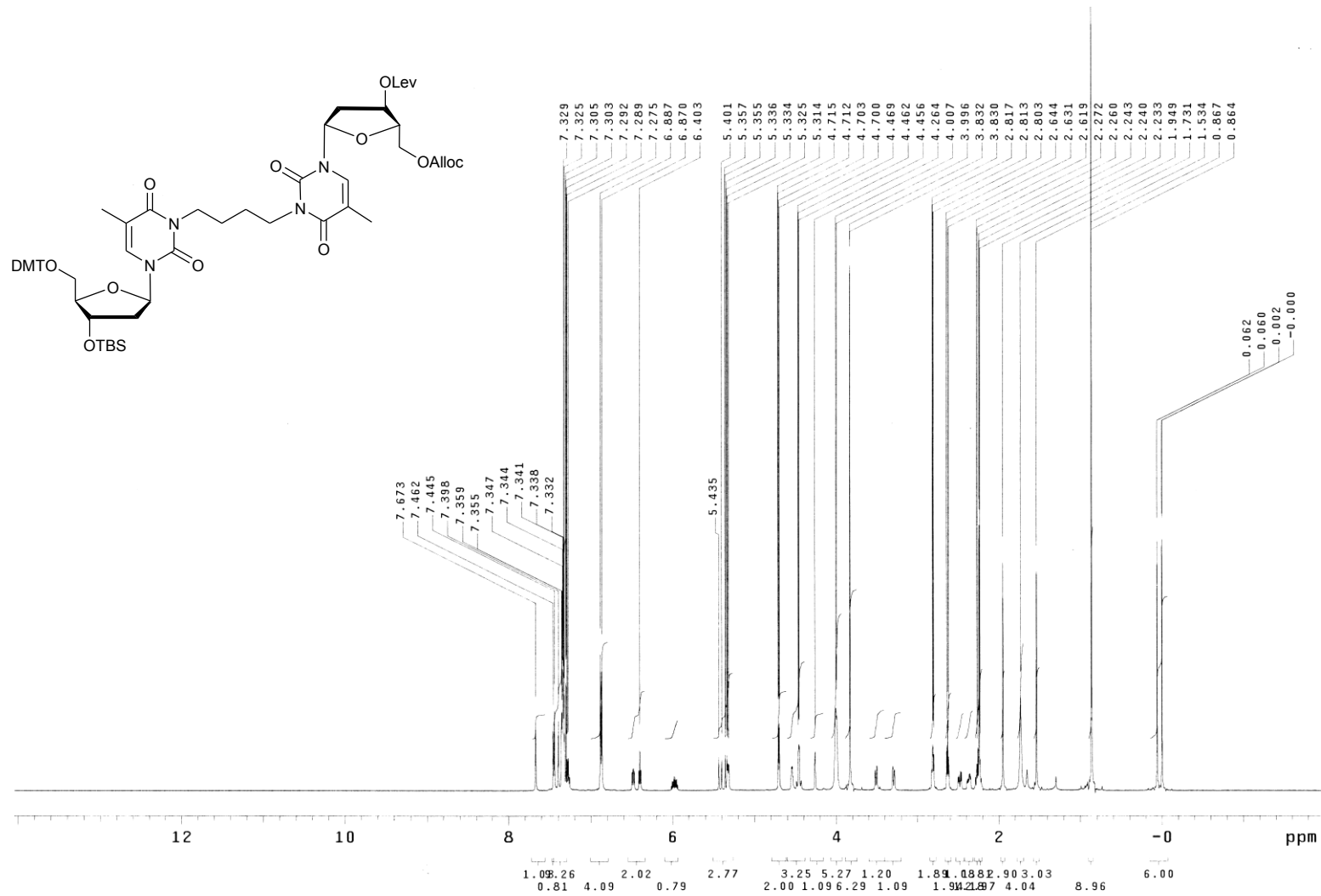


Figure S32. <sup>1</sup>H NMR of Compound 3-14

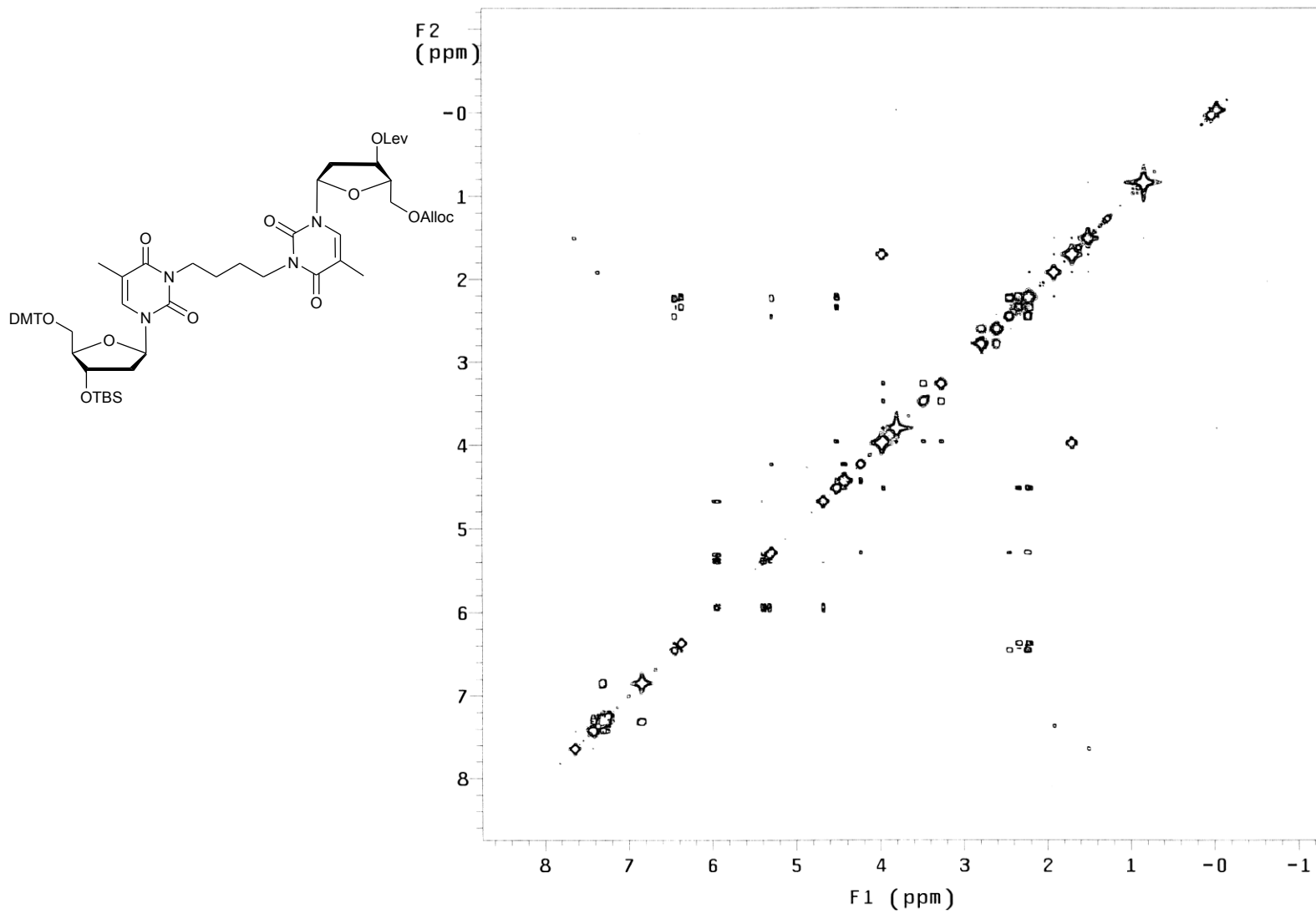


Figure S33. COSY of Compound 3-14

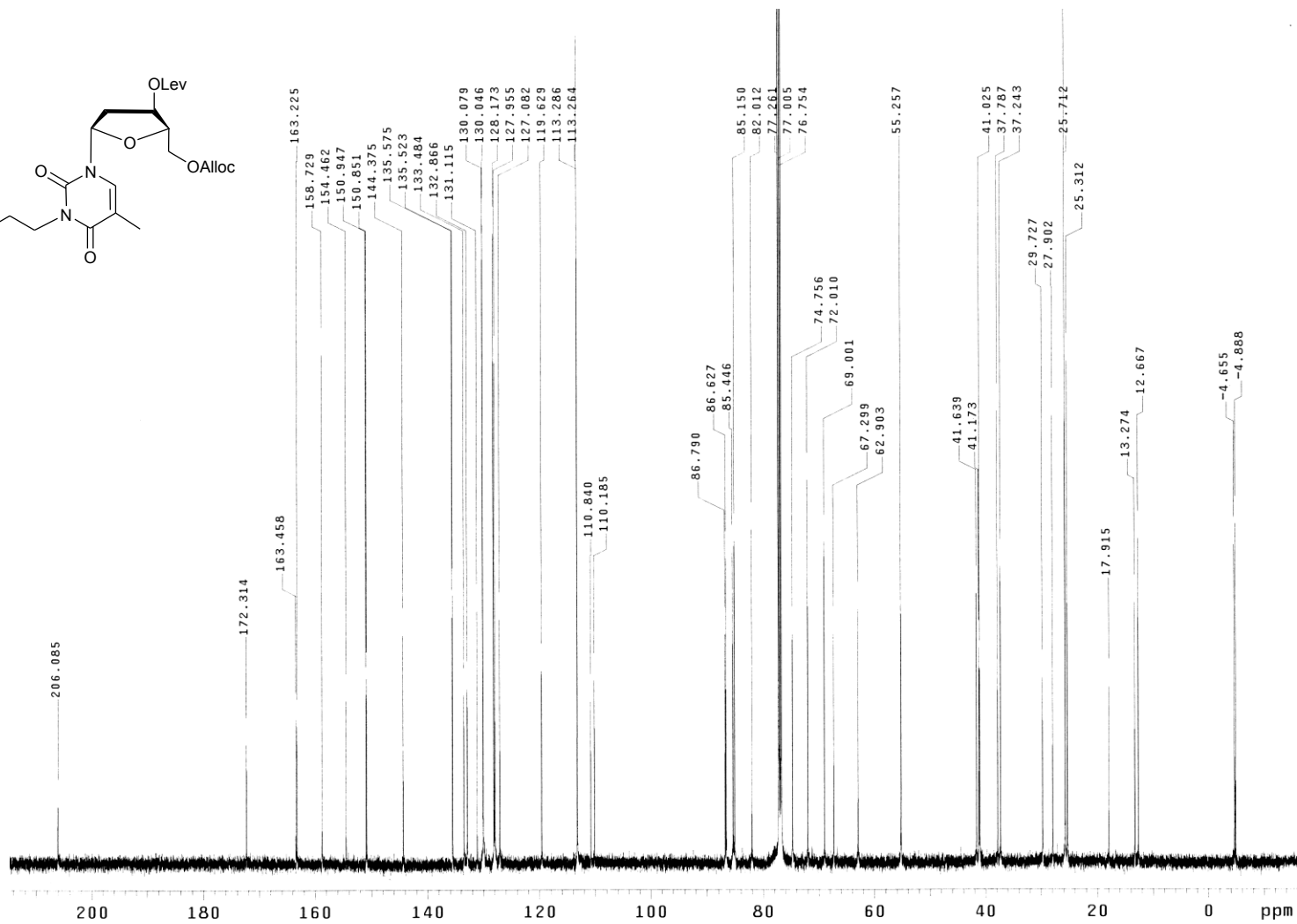
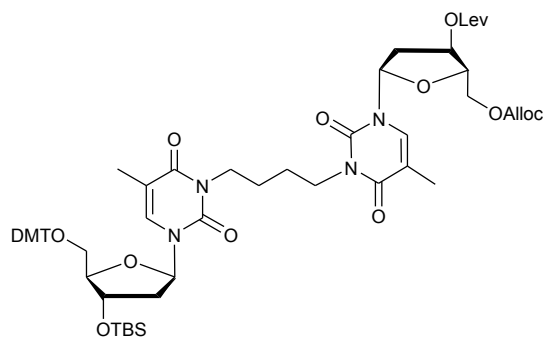


Figure S34. <sup>13</sup>C NMR of Compound 3-14

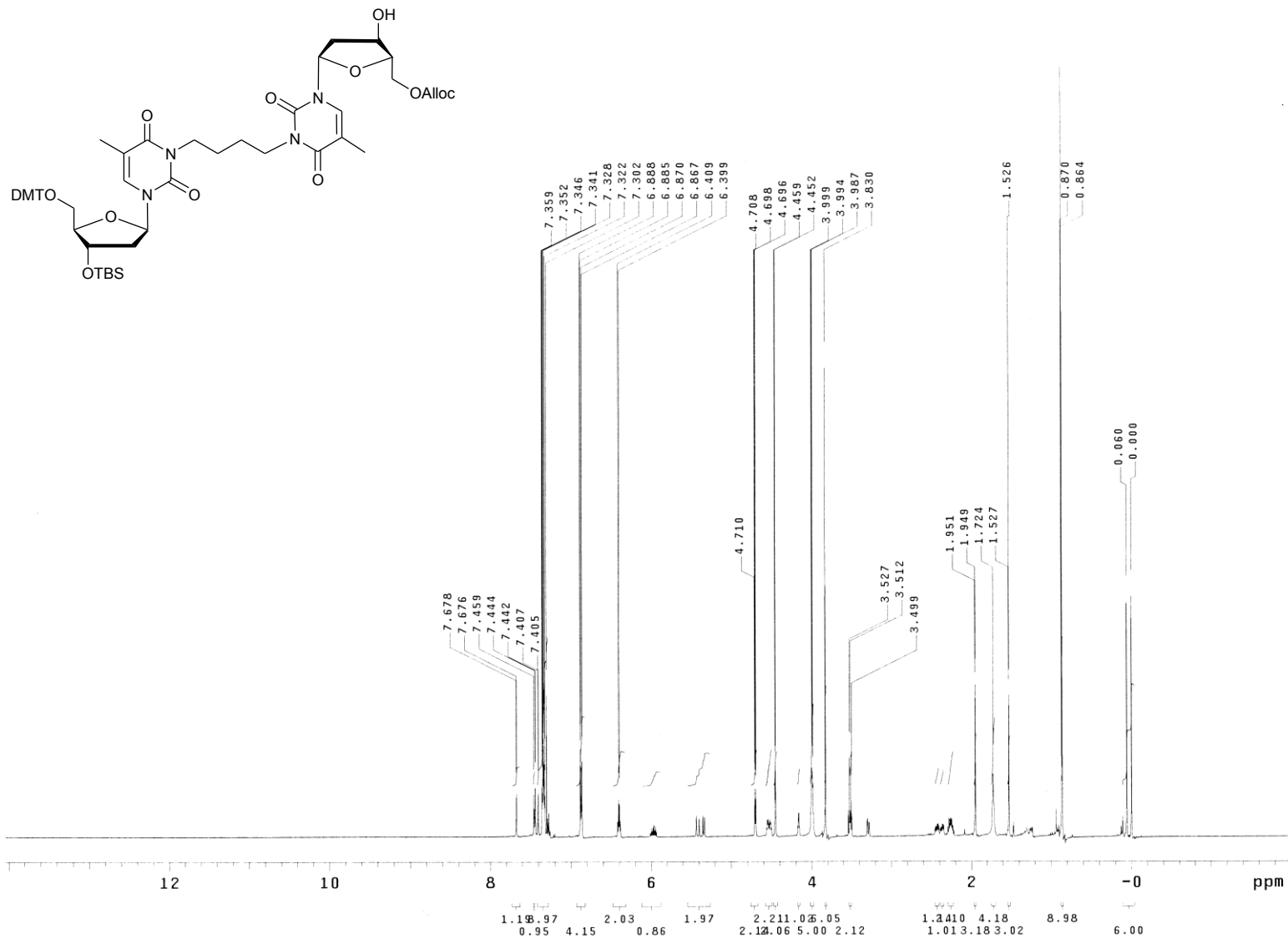


Figure S35. <sup>1</sup>H NMR of Compound 3-15

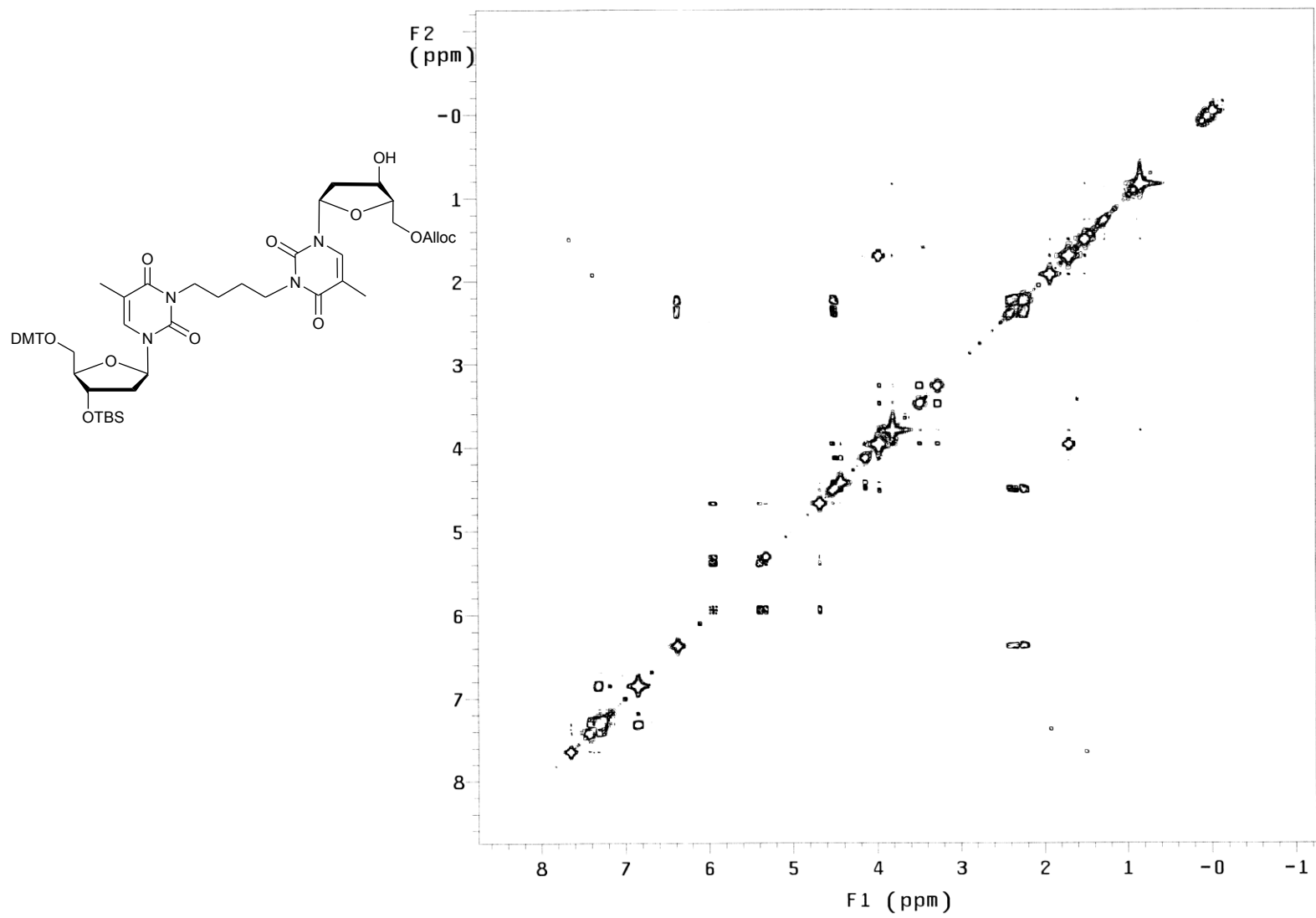


Figure S36. COSY of Compound 3-15

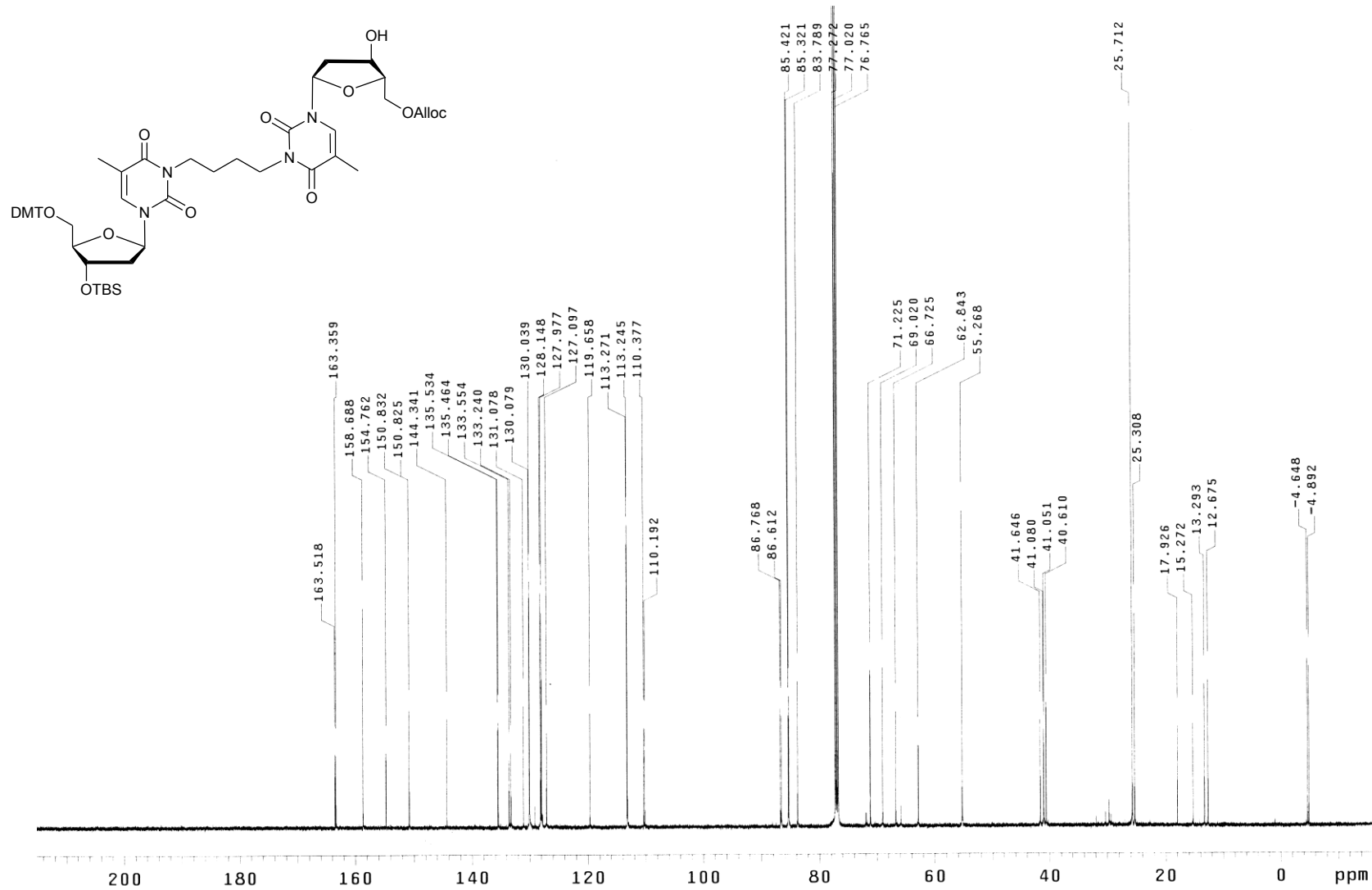


Figure S37. <sup>13</sup>CNMR of Compound 3-15

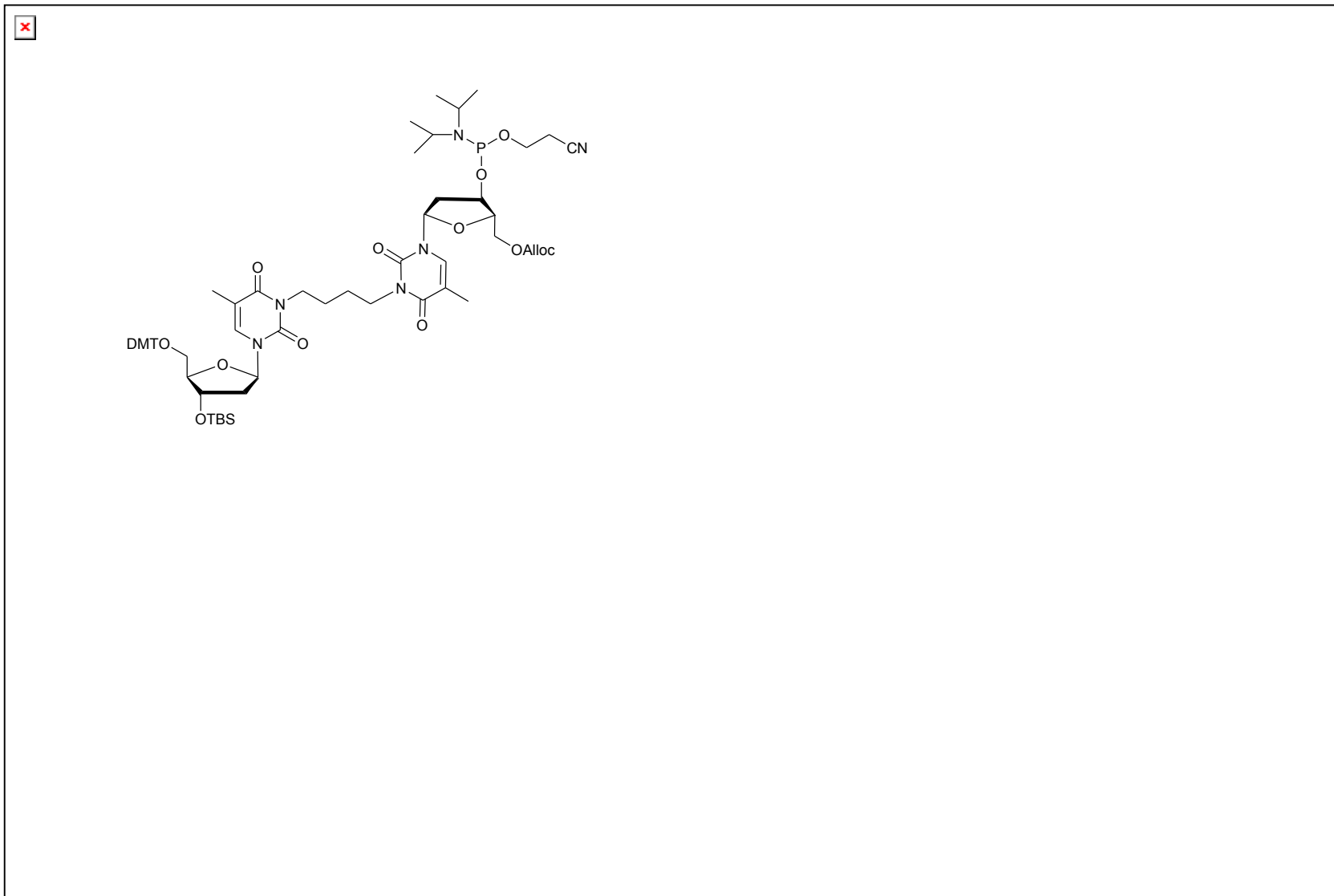
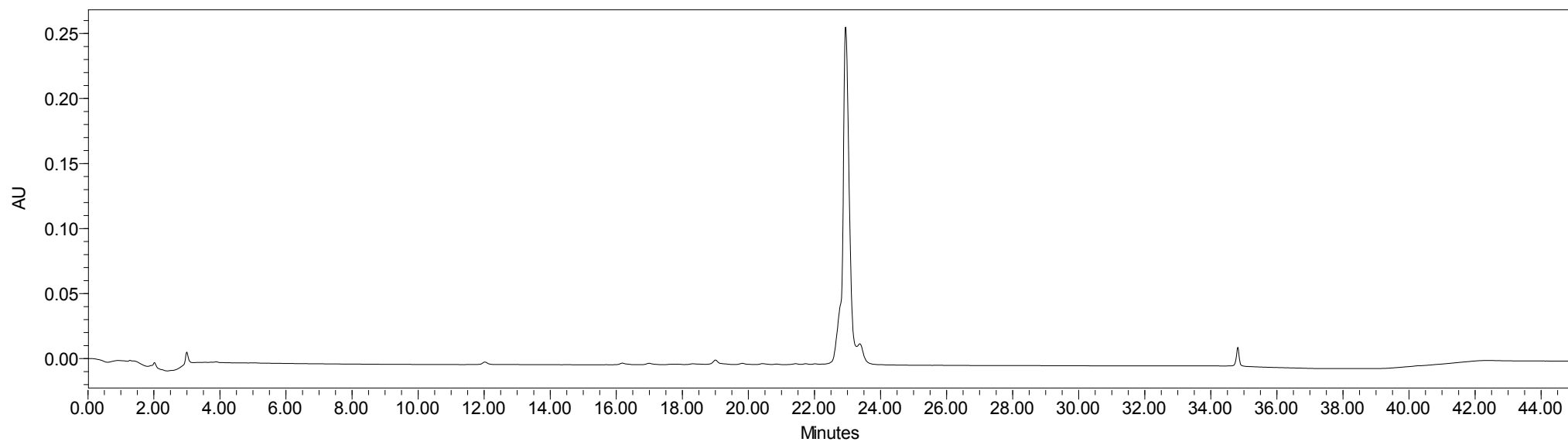
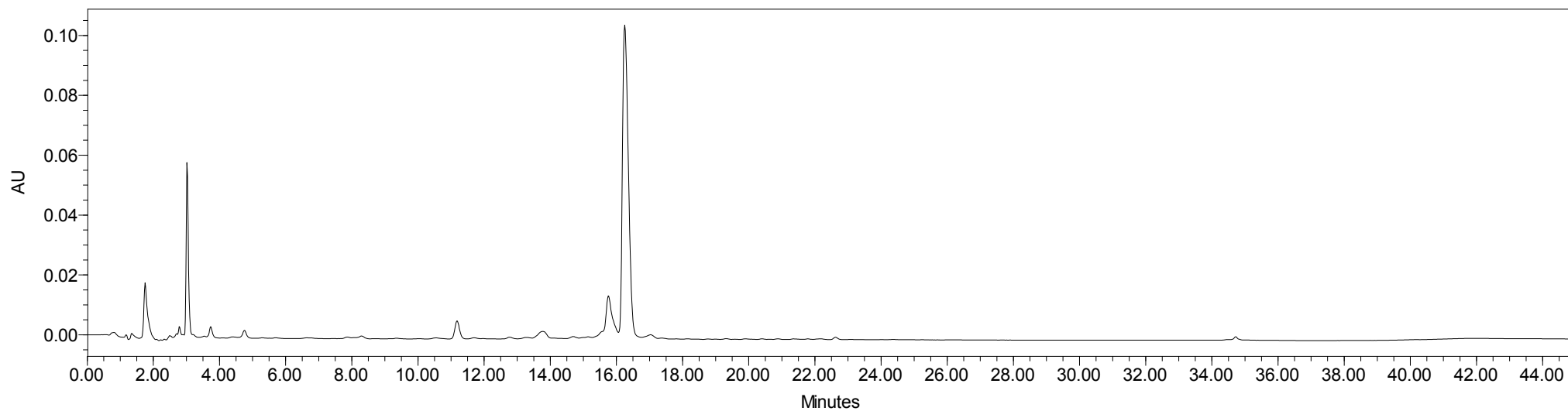


Figure S38.  $^{31}\text{P}$ NMR of Phosphoramidite 3-16

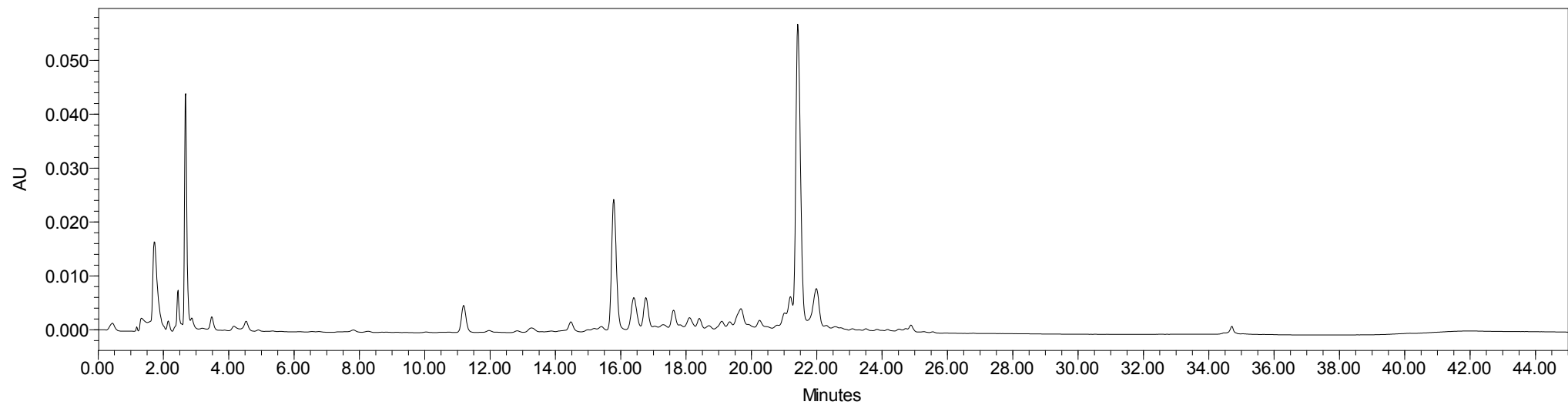




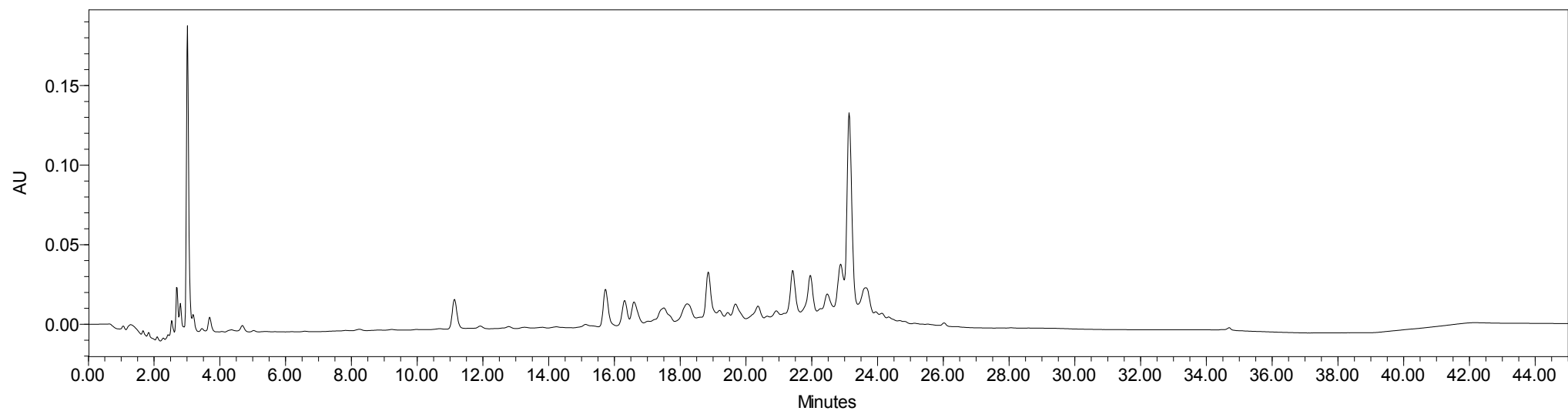
**Figure S39.** IEX HPLC chromatograph of cross-linked duplexes CJW201 with phosphoramidite 14. HPLC conditions are as described in the Figure 6 legend.



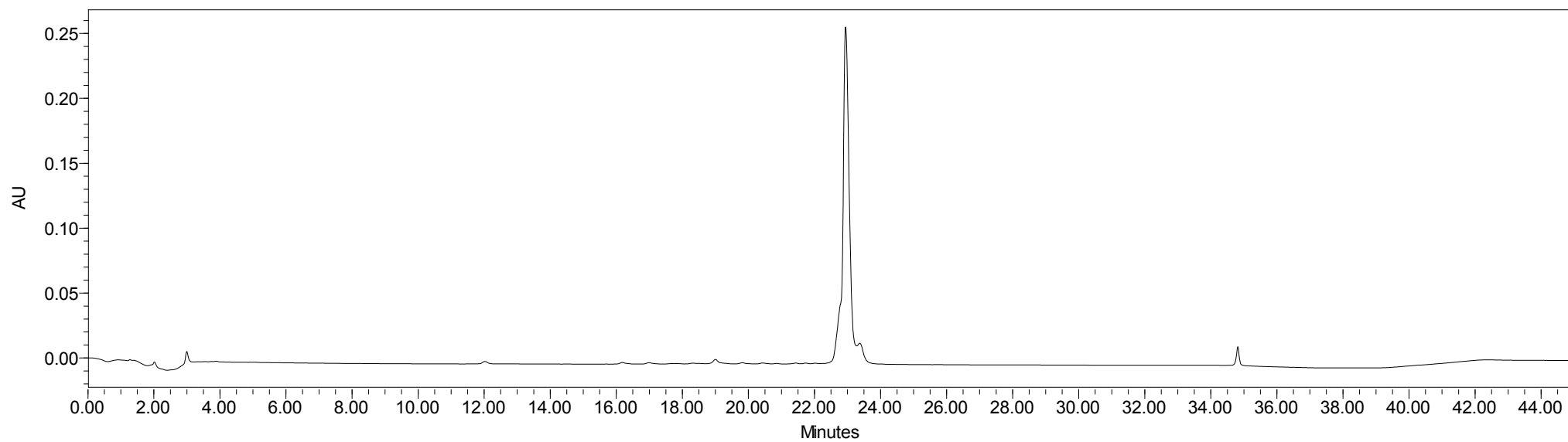
**Figure S40.** IEX HPLC chromatograph of CJW202-U (after the cleavage of Alloc) with phosphoramidite 10. HPLC conditions are as described in the Figure 6 legend.



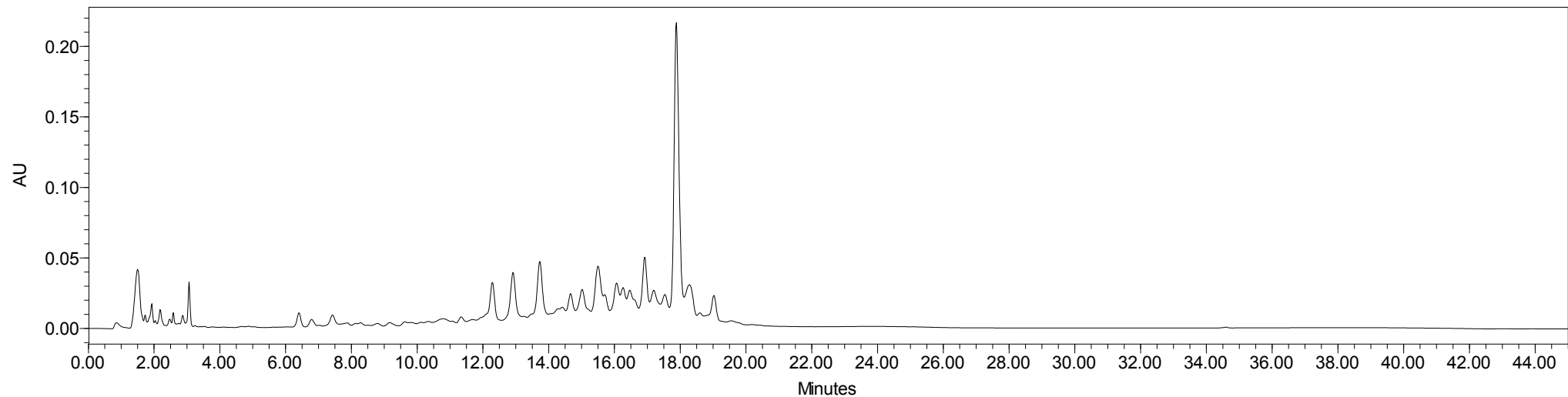
**Figure S41.** IEX HPLC chromatograph of CJW202-Y (after the cleavage of TBS) with phosphoramidite 10. HPLC conditions are as described in the Figure 6 legend.



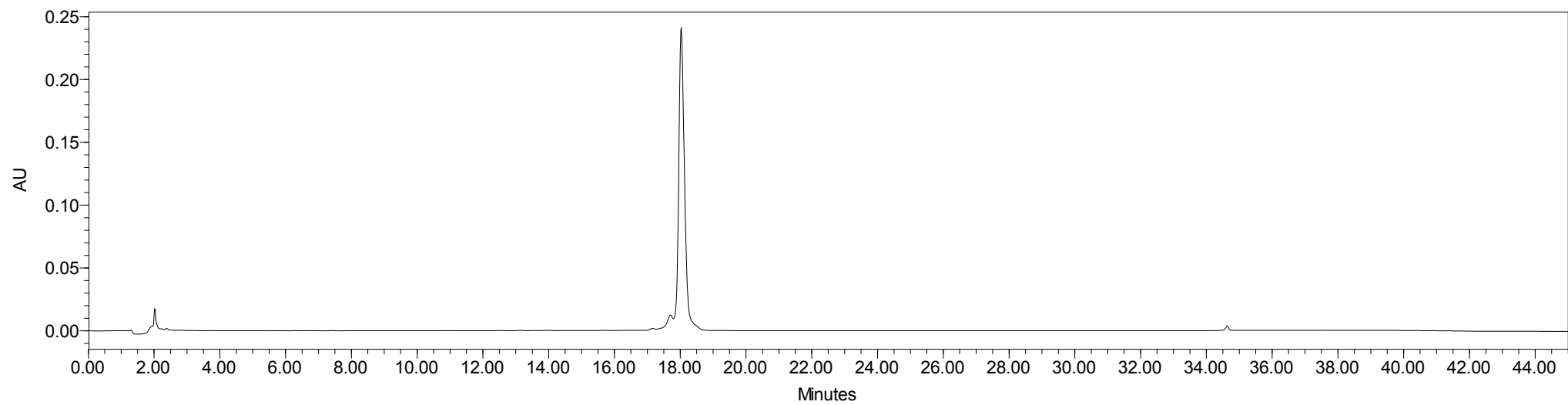
**Figure S42.** IEX HPLC chromatograph of CJW202-H with phosphoramidite 10. HPLC conditions are as described in the Figure 6 legend.



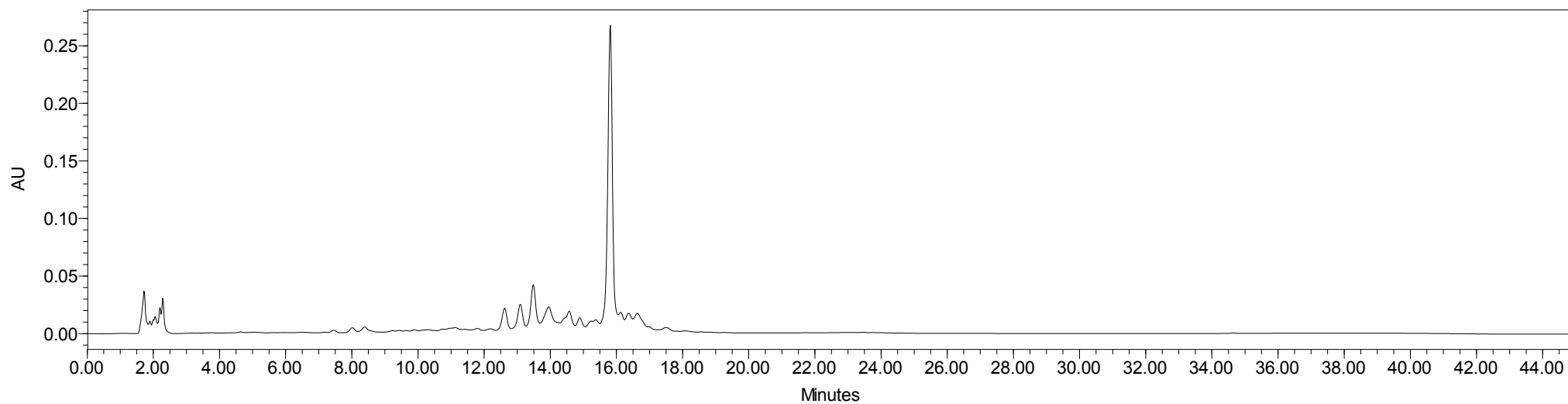
**Figure S43.** IEX HPLC chromatograph of cross-linked duplexes CJW202 with phosphoramidite 10. HPLC conditions are as described in the Figure 6 legend.



**Figure S44.** IEX HPLC chromatograph of CJW216-H with phosphoramidite 10. HPLC conditions are as described in the Figure 3 legend except a gradient of buffer B from 0.2 to 0.55 in 30 minutes.

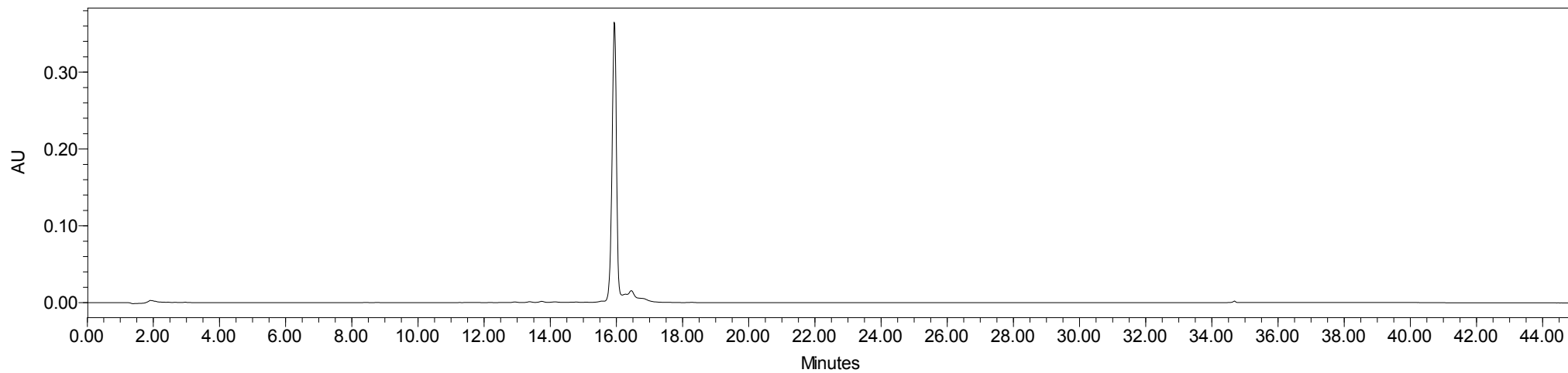


**Figure S45.** IEX HPLC chromatograph of cross-linked duplexes CJW216 with phosphoramidite 10. HPLC conditions are as described in the Figure 3 legend except a gradient of buffer B from 0.2 to 0.55 in 30 minutes.

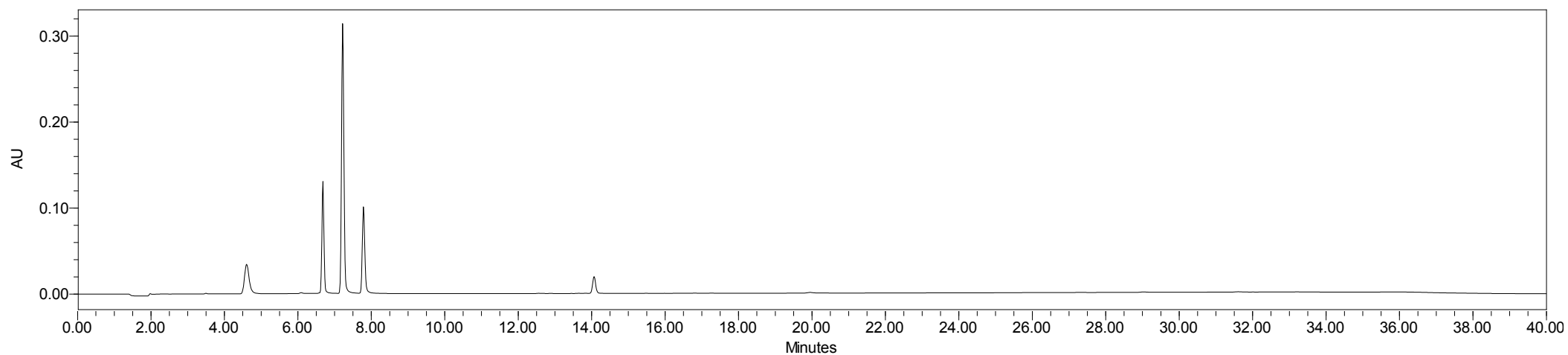


**Figure S46.** IEX HPLC chromatograph of CJW217-H with phosphoramidite 10. HPLC conditions are as described in the Figure 3 legend except a gradient of buffer B from 0.2 to 0.55 in 30 minutes.

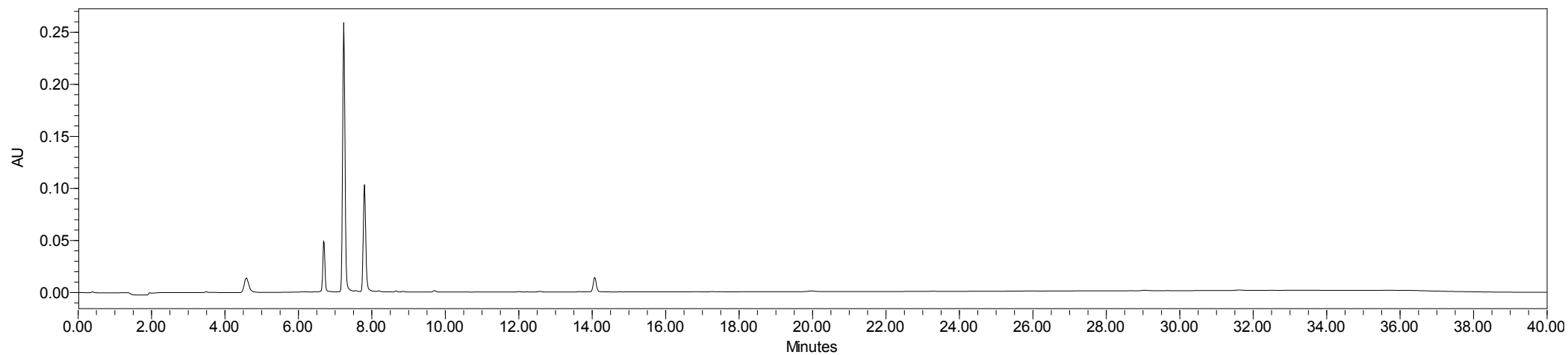




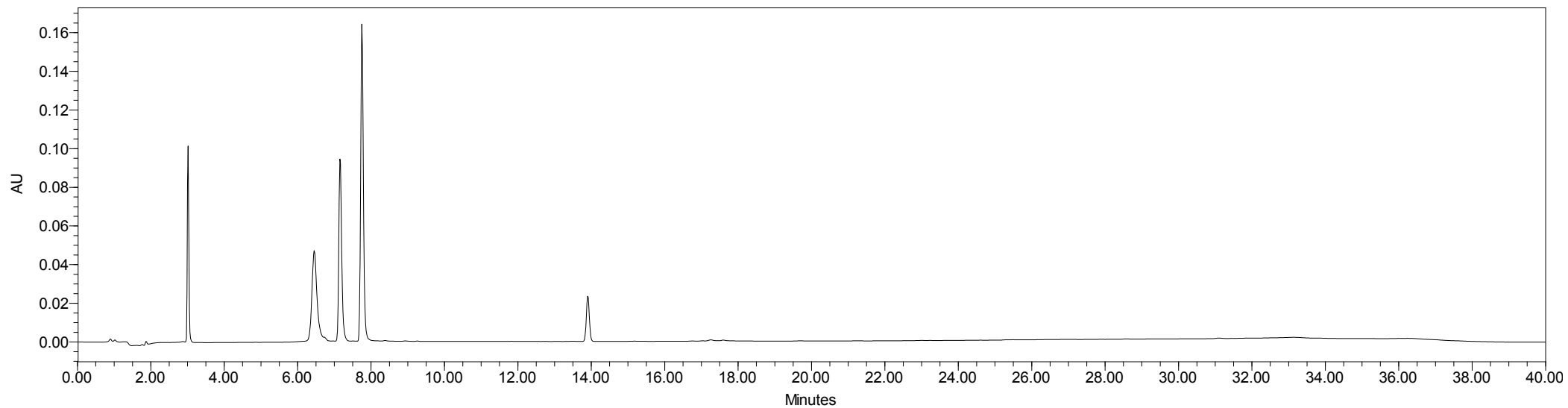
**Figure S47.** IEX HPLC chromatograph of cross-linked duplexes CJW217 with phosphoramidite 10. HPLC conditions are as described in the Figure 3 legend except a gradient of buffer B from 0.2 to 0.55 in 30 minutes.



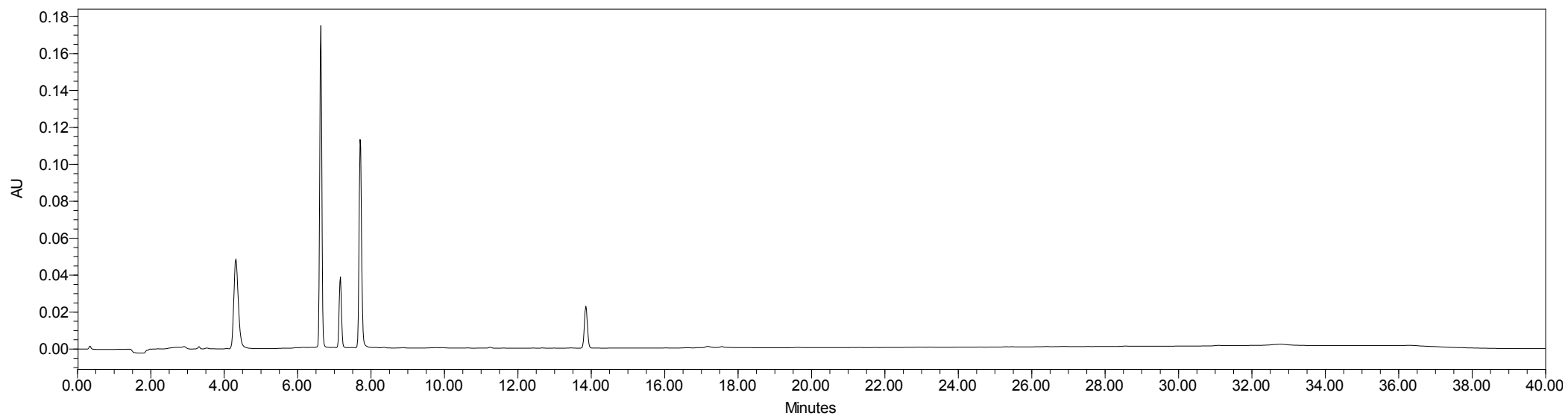
**Figure S48.** Enzymatic digest of cross-linked duplex CJW201. Nucleotide ratios analysis was run with 0 to 60% of mobile buffer B in 30 minutes on RPLC. Buffer A: 2% acetonitrile, 50 mM sodium phosphate, pH 5.8; Buffer B: 50% acetonitrile, 50 mM sodium phosphate, pH 5.8.



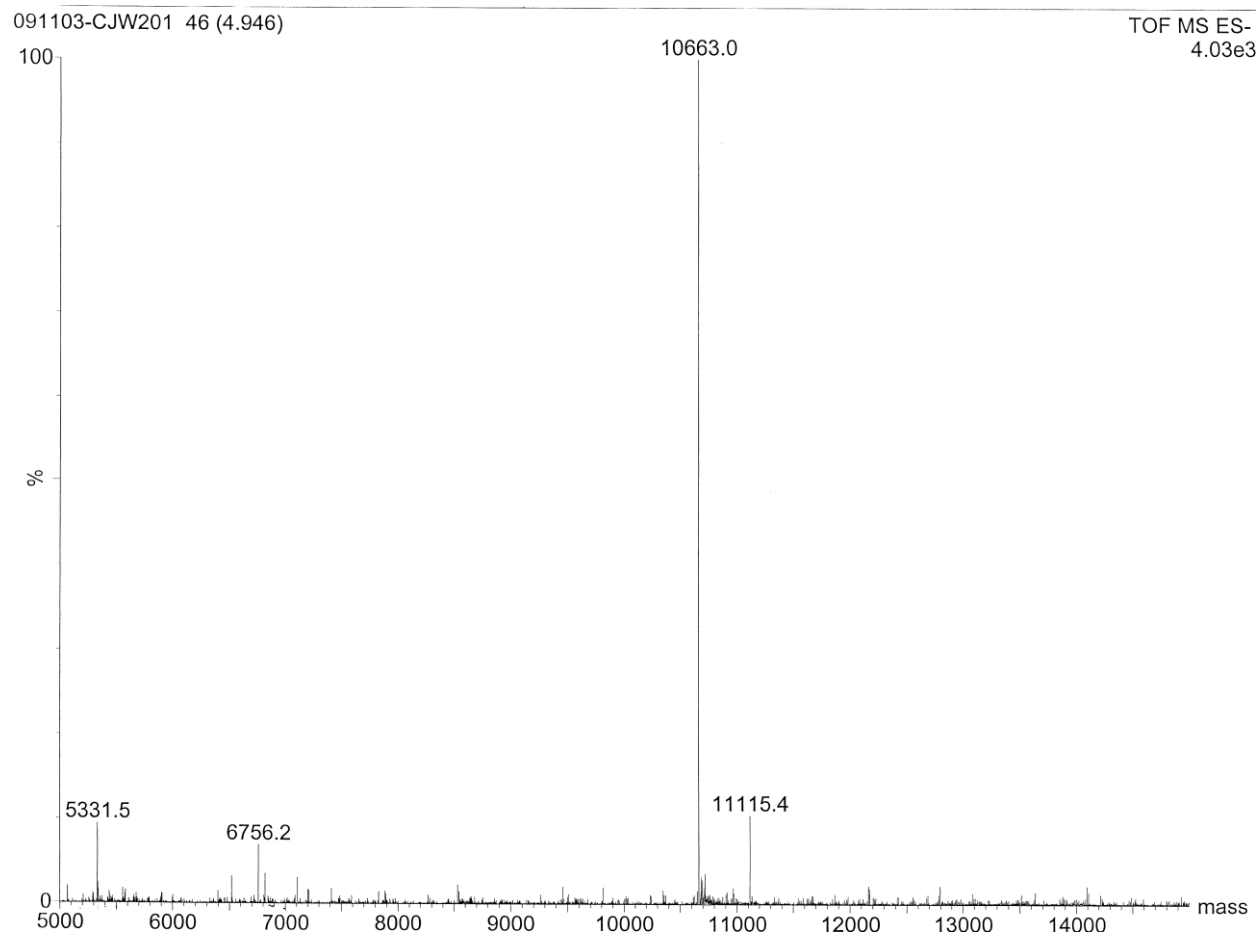
**Figure S49.** Enzymatic digest of cross-linked duplex CJW202. Nucleotide ratios analysis was run with 0 to 60% of mobile buffer B in 30 minutes on RPLC. Buffer A: 2% acetonitrile, 50 mM sodium phosphate, pH 5.8; Buffer B: 50% acetonitrile, 50 mM sodium phosphate, pH 5.8.



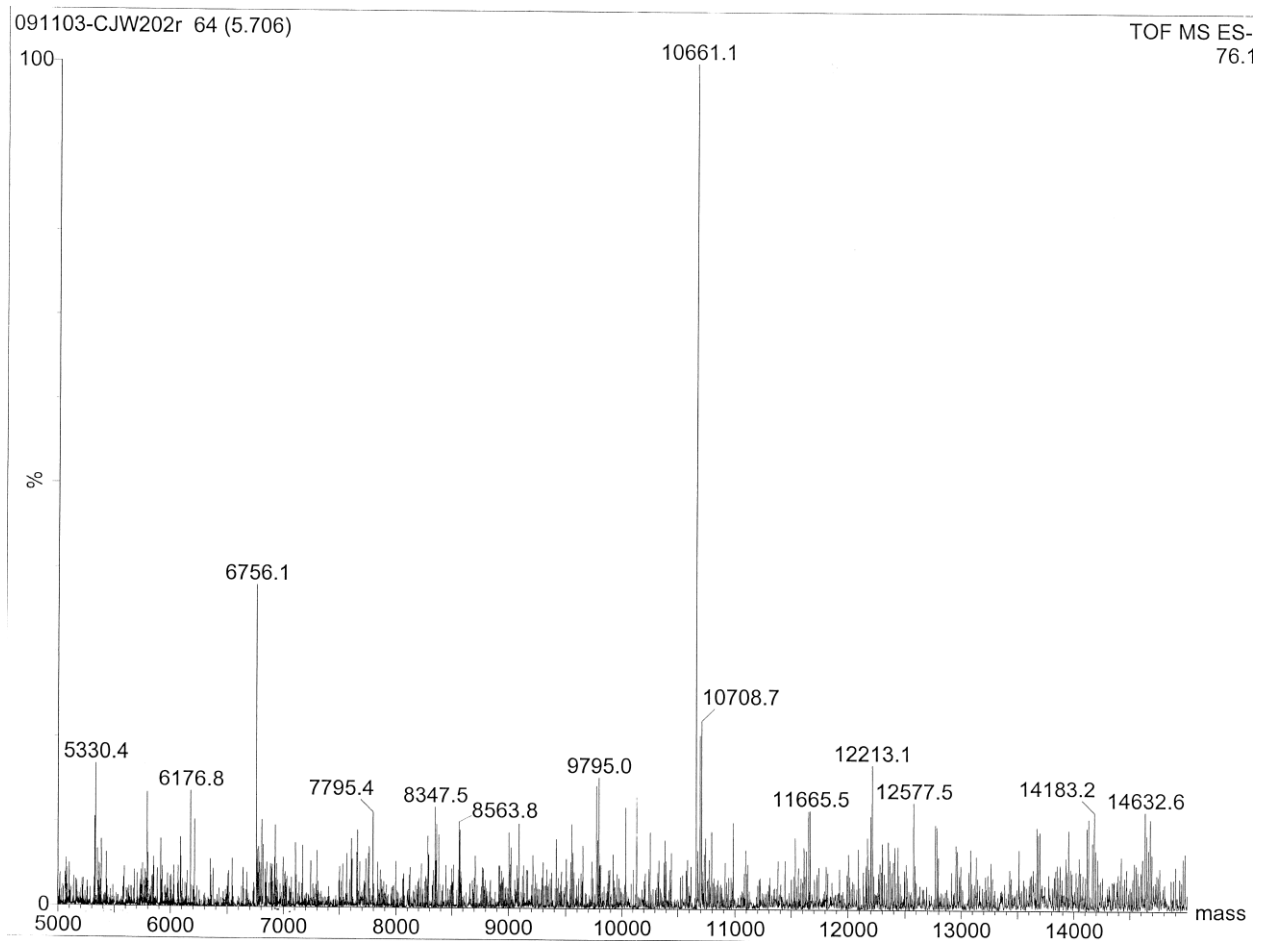
**Figure S50.** Enzymatic digest of cross-linked duplex CJW216. Nucleotide ratios analysis was run with 0 to 60% of mobile buffer B in 30 minutes on RPLC. Buffer A: 2% acetonitrile, 50 mM sodium phosphate, pH 5.8; Buffer B: 50% acetonitrile, 50 mM sodium phosphate, pH 5.8.



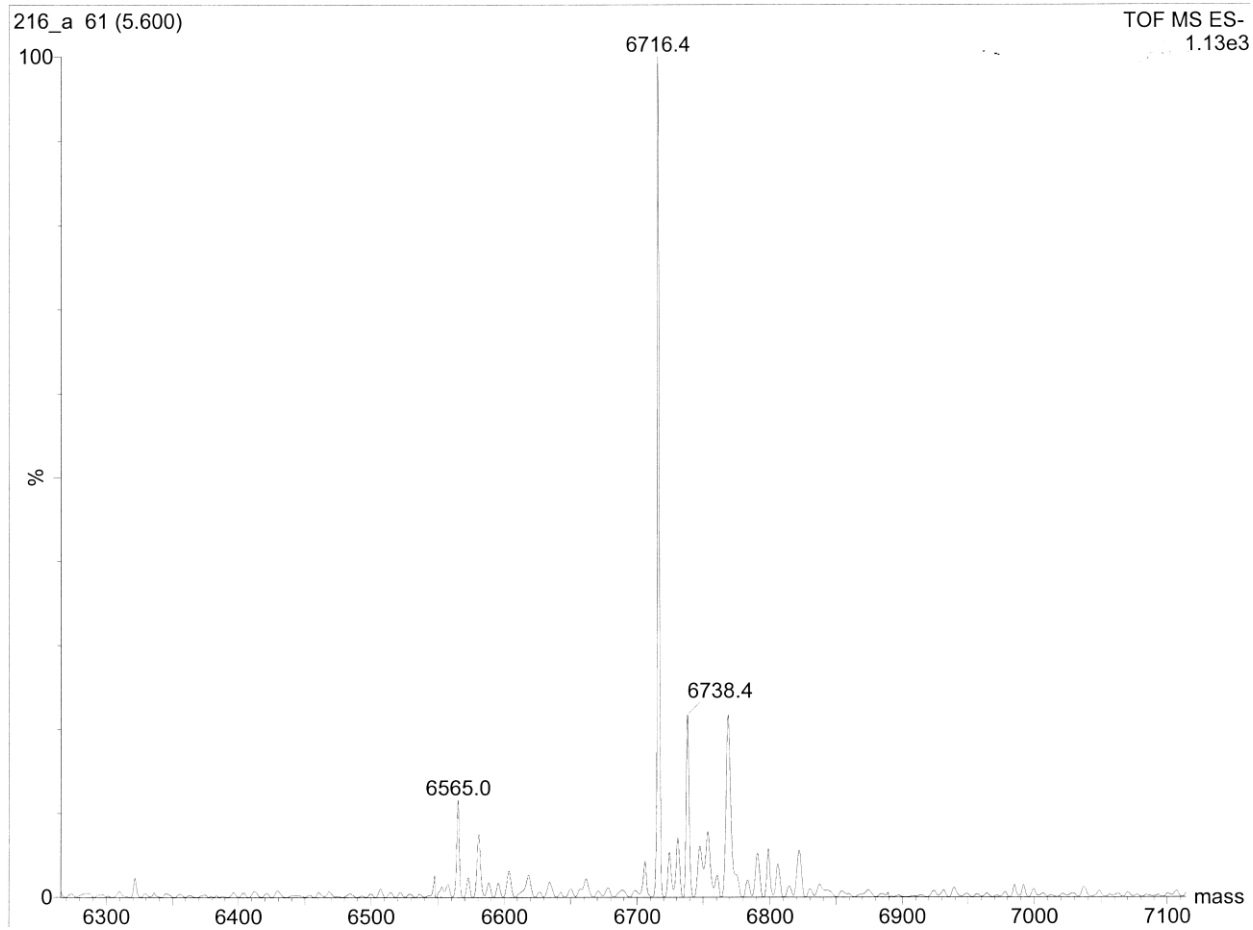
**Figure S51.** Enzymatic digest of cross-linked duplex CJW217. Nucleotide ratios analysis was run with 0 to 60% of mobile buffer B in 30 minutes on RPLC. Buffer A: 2% acetonitrile, 50 mM sodium phosphate, pH 5.8; Buffer B: 50% acetonitrile, 50 mM sodium phosphate, pH 5.



**Figure S52.** Molecular weight of cross-linked duplex CJW201 with ESI-TOF

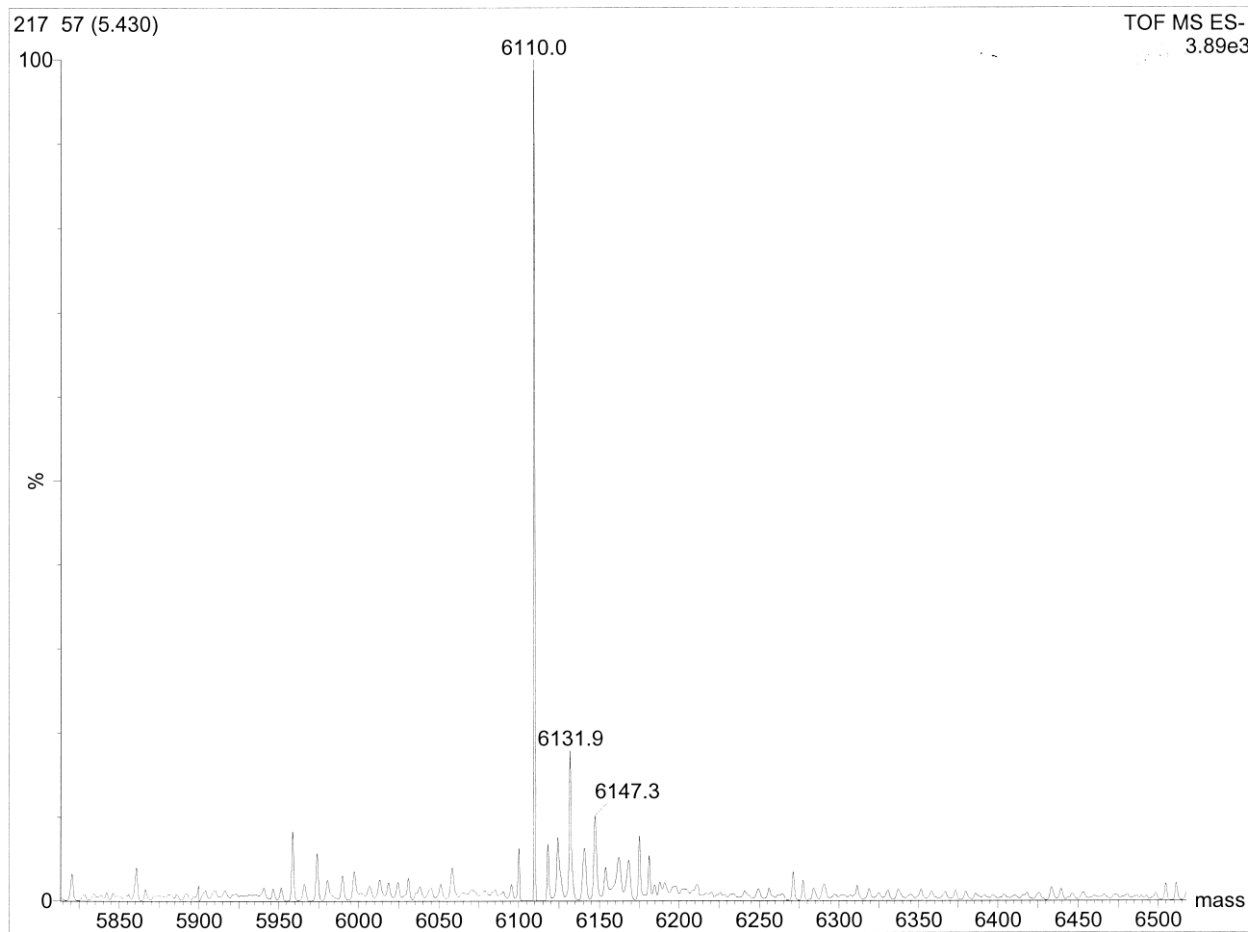


**Figure S53.** Molecular weight of cross-linked duplex CJW202 with ESI-TOF



**Figure S54.** Molecular weight of cross-linked duplex CJW216 with ESI-TOF





**Figure S55.** Molecular weight of cross-linked duplex CJW217 with ESI-TOF

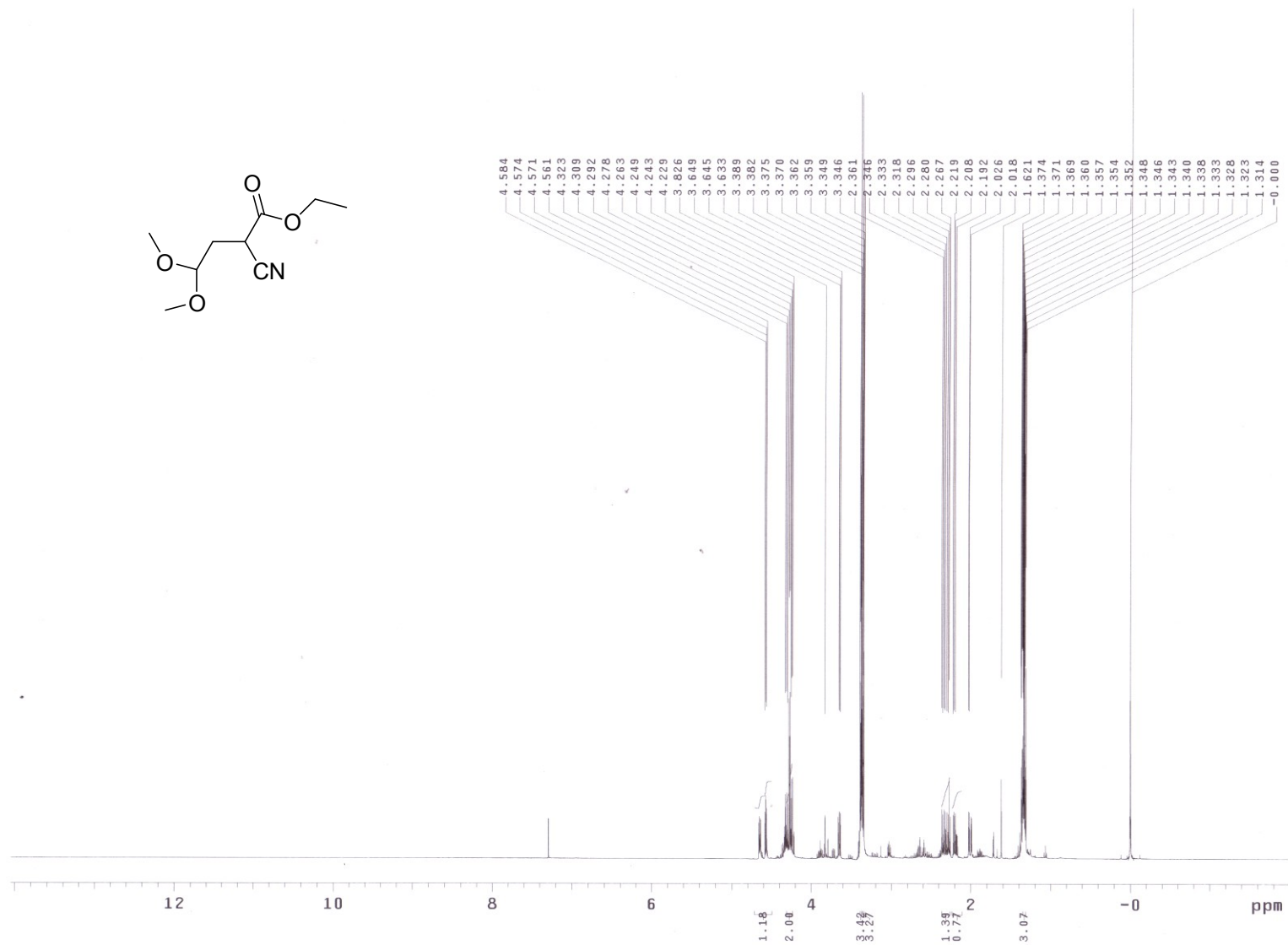


Figure S56. <sup>1</sup>H NMR of compound 4-1

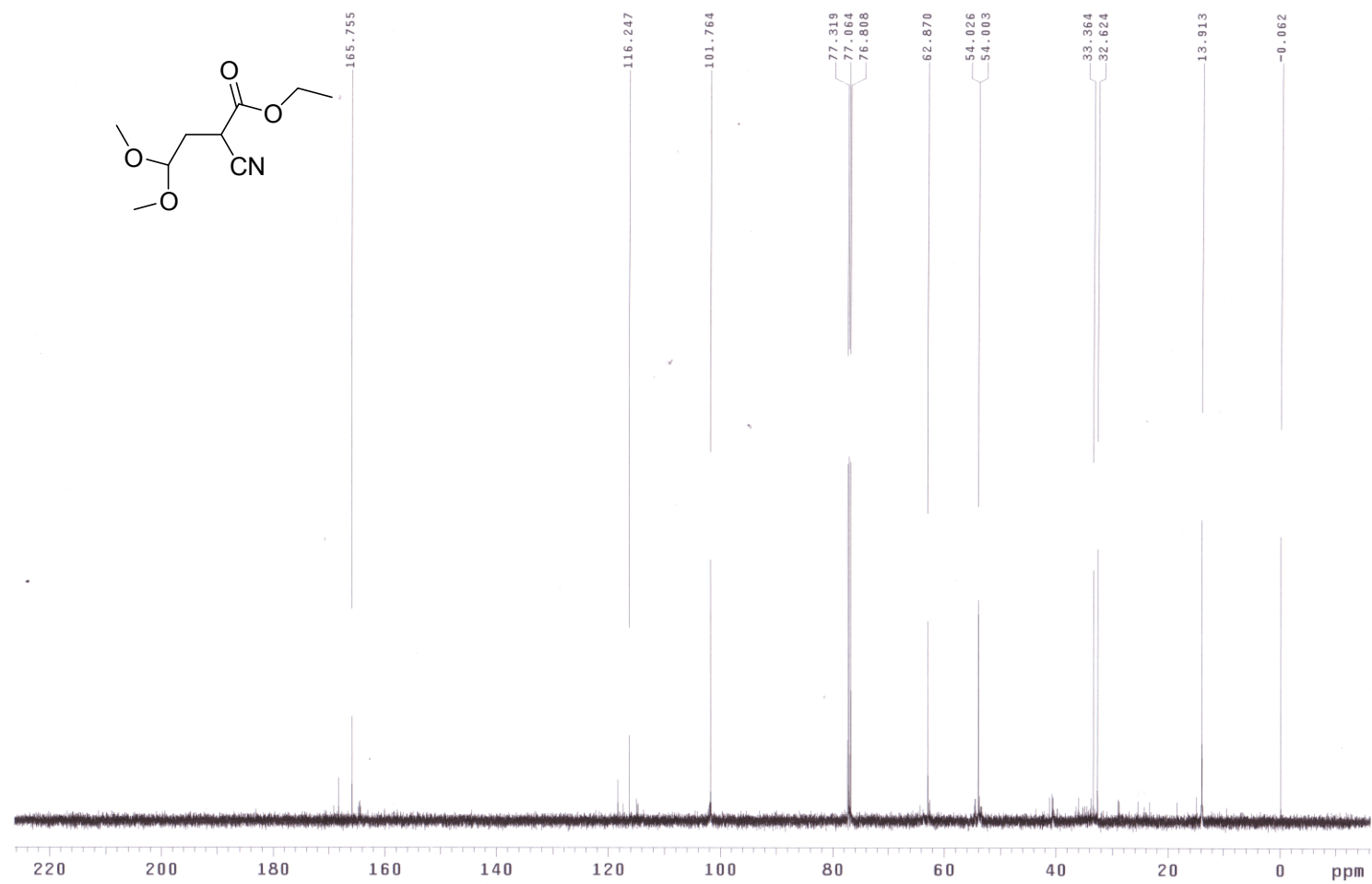


Figure S57. <sup>13</sup>CNMR of compound 4-1

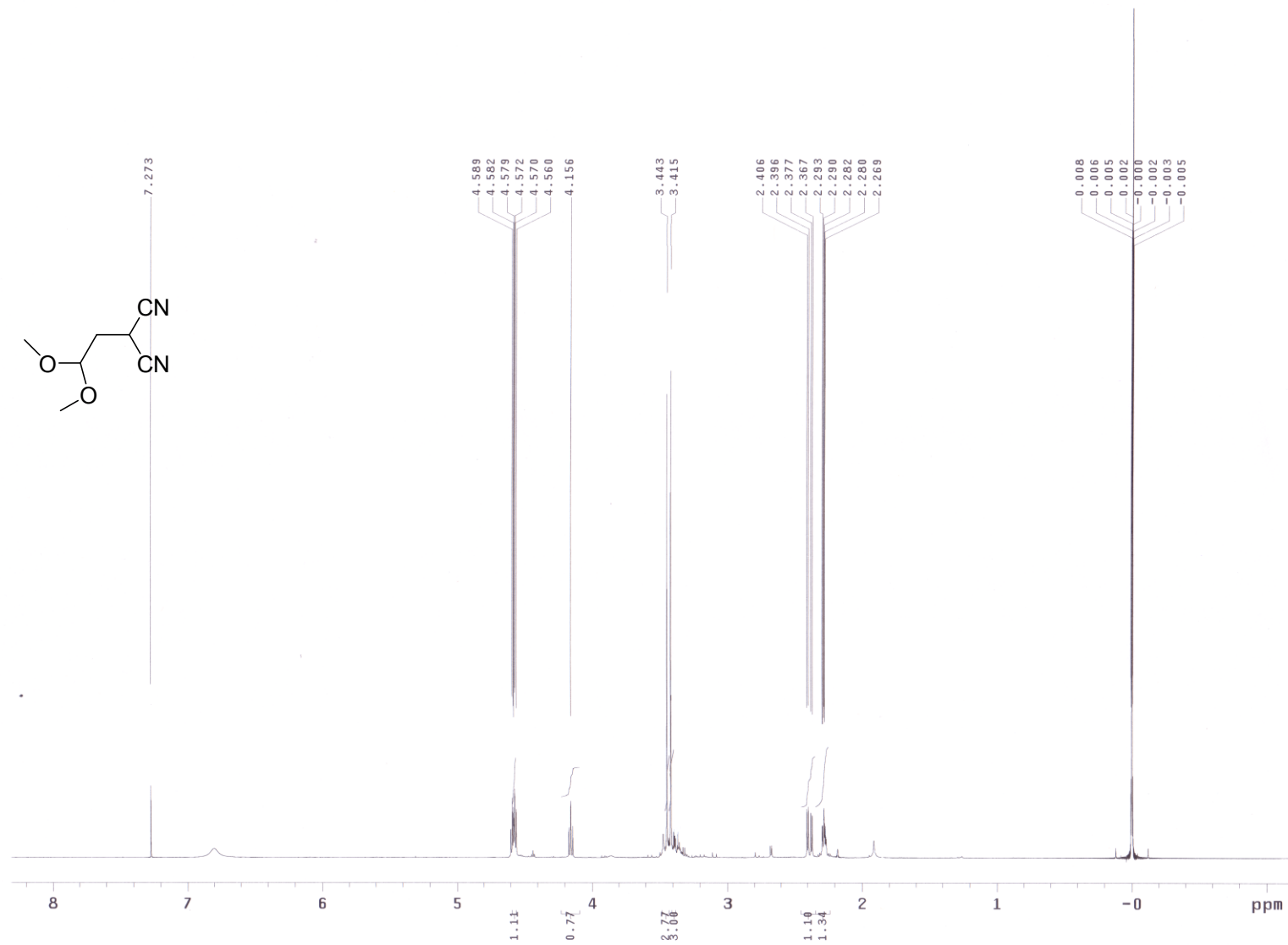


Figure S58. <sup>1</sup>H NMR of compound 4-2

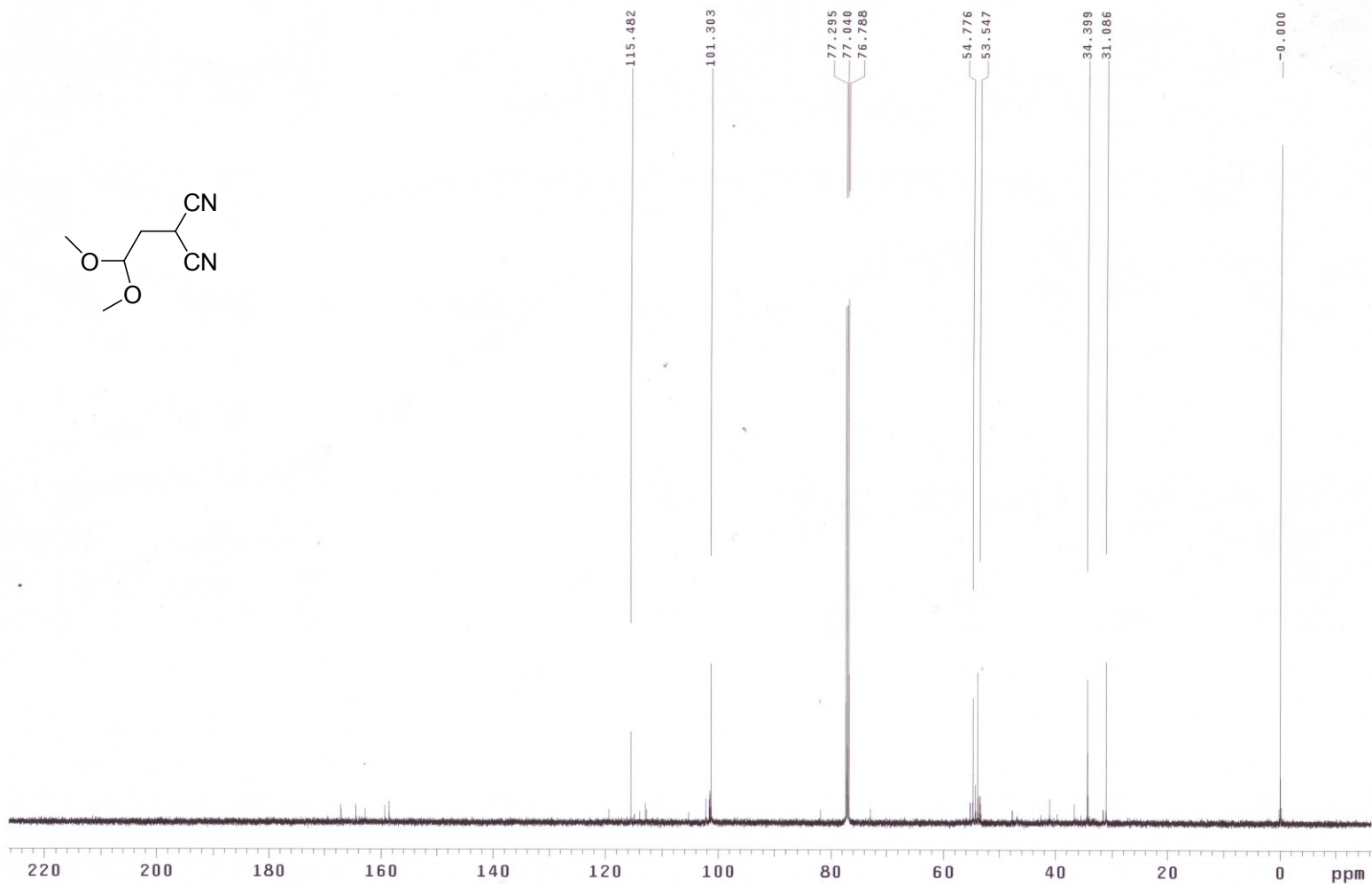


Figure S59.  $^{13}\text{C}$ NMR of compound 4-2

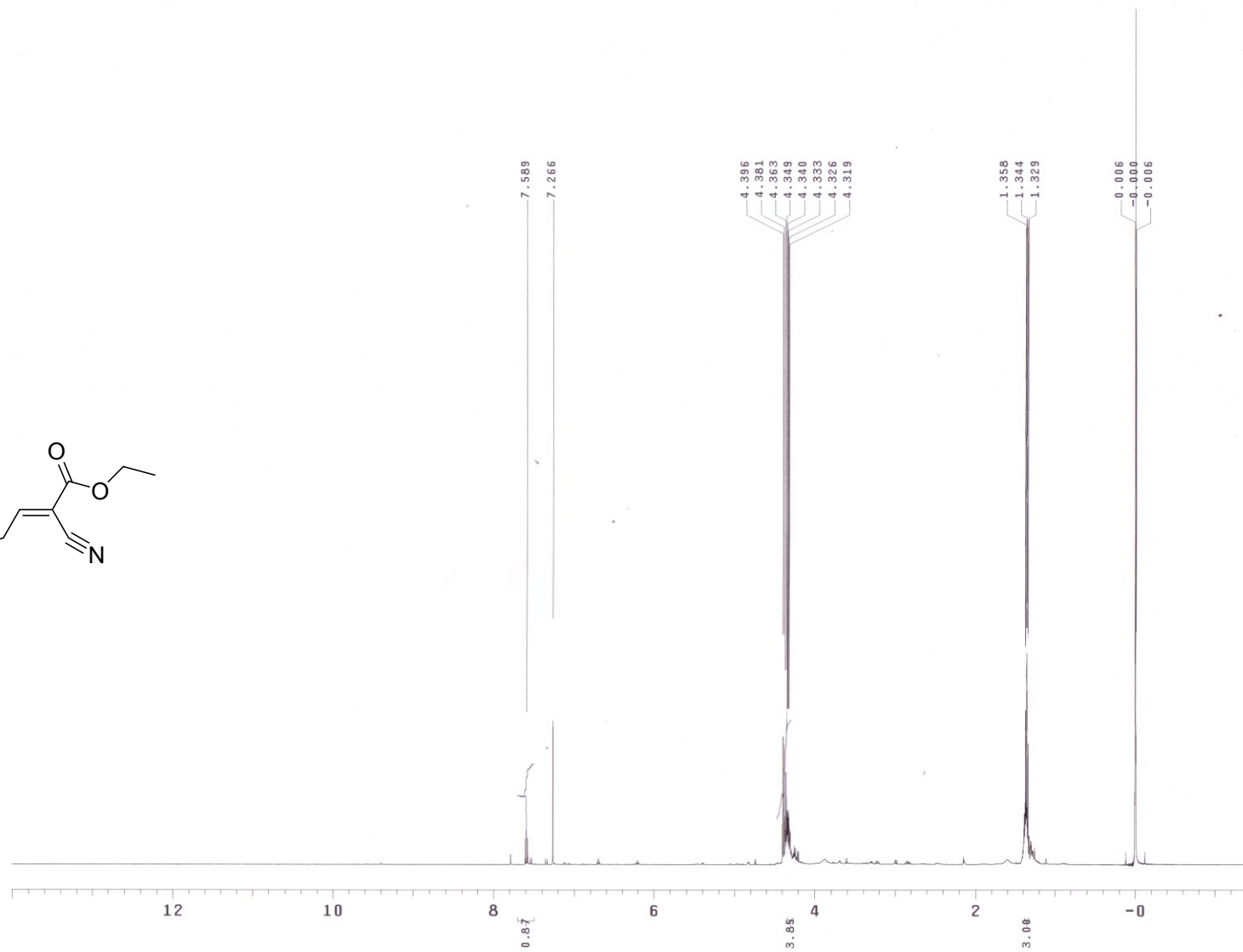
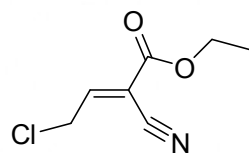


Figure S60. <sup>1</sup>H NMR of compound 4-3

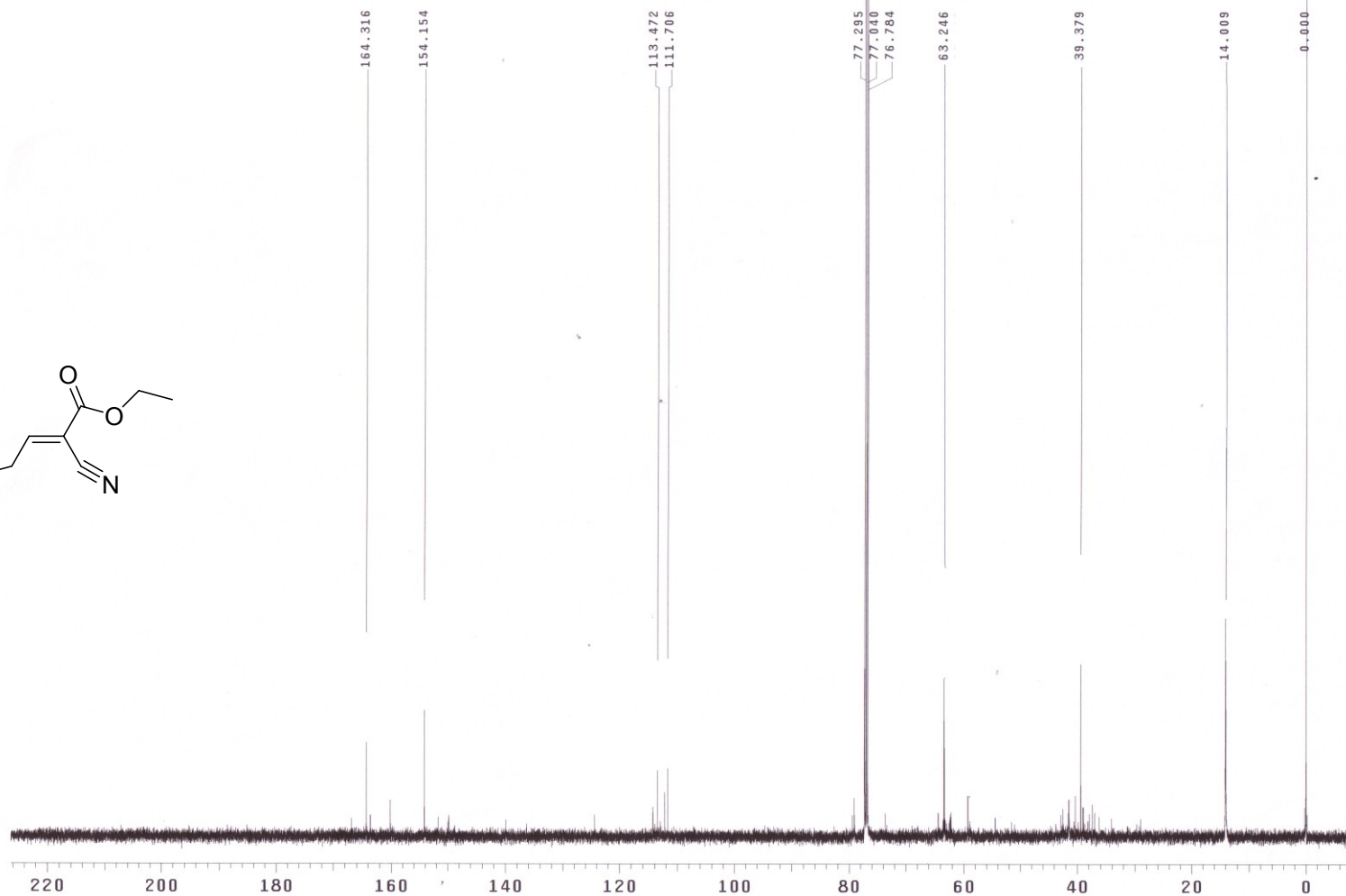
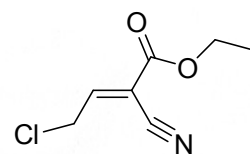


Figure S61.  $^{13}\text{C}$ NMR of compound 4-3

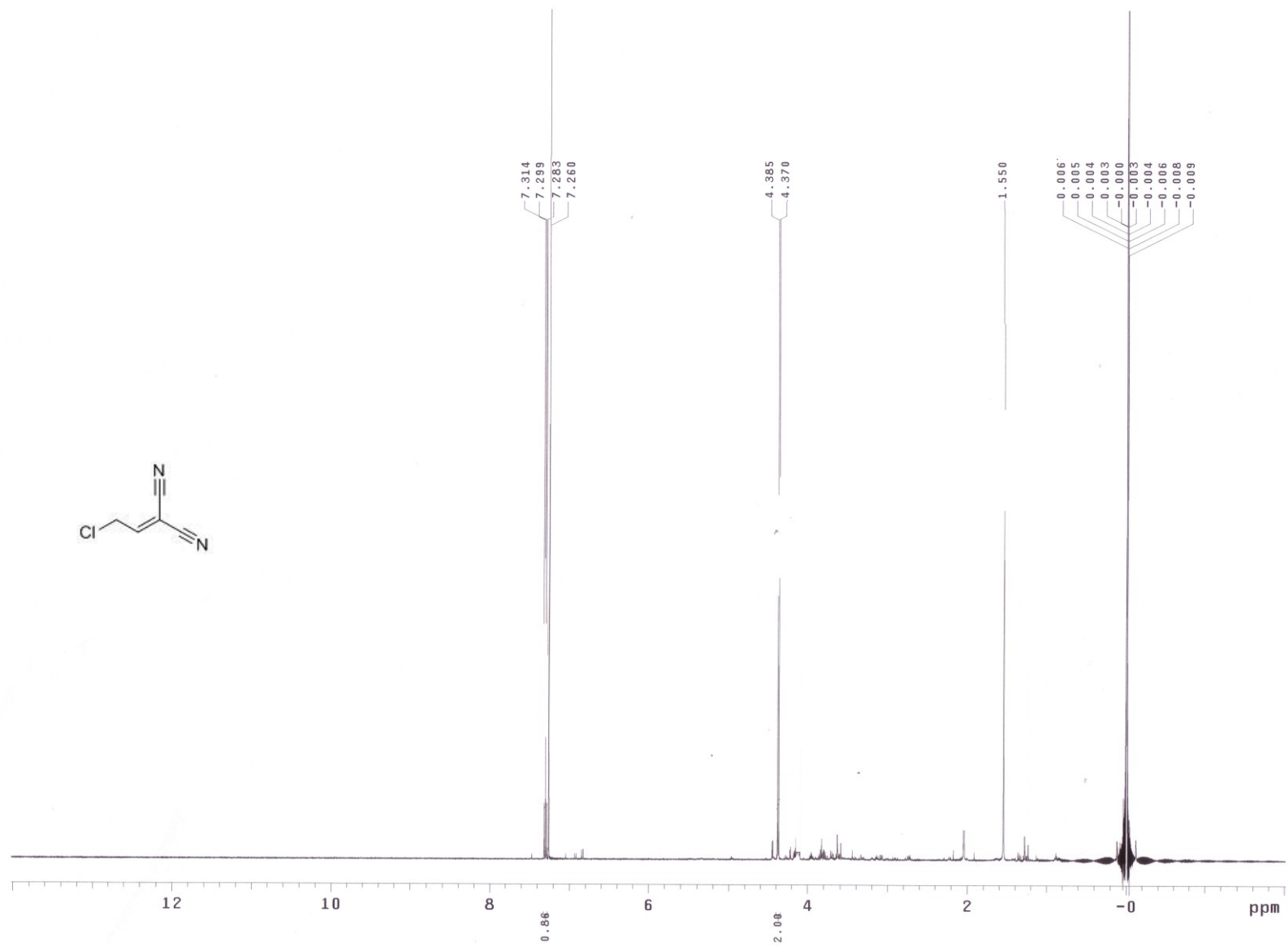


Figure S62. <sup>1</sup>H NMR of compound 4-4



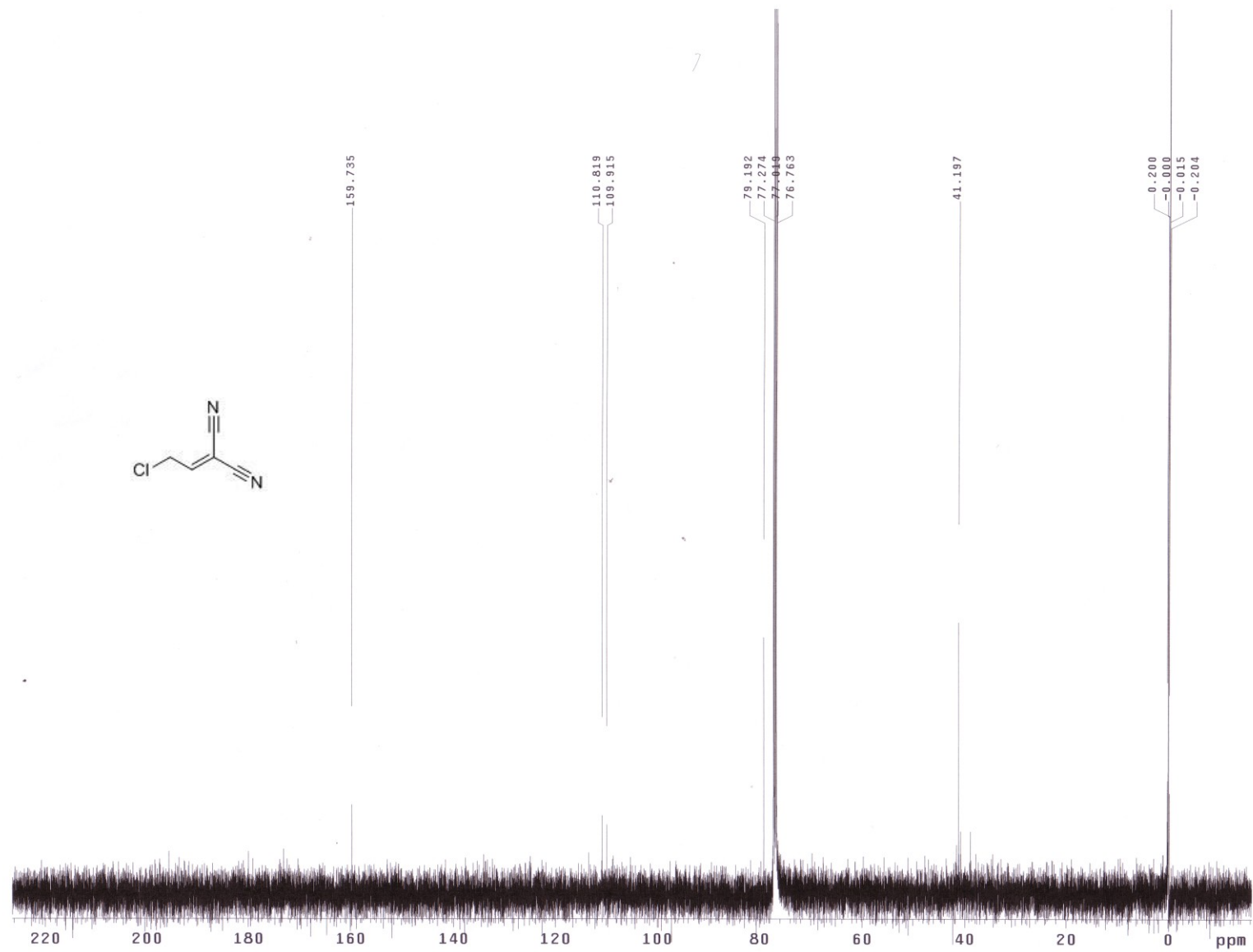
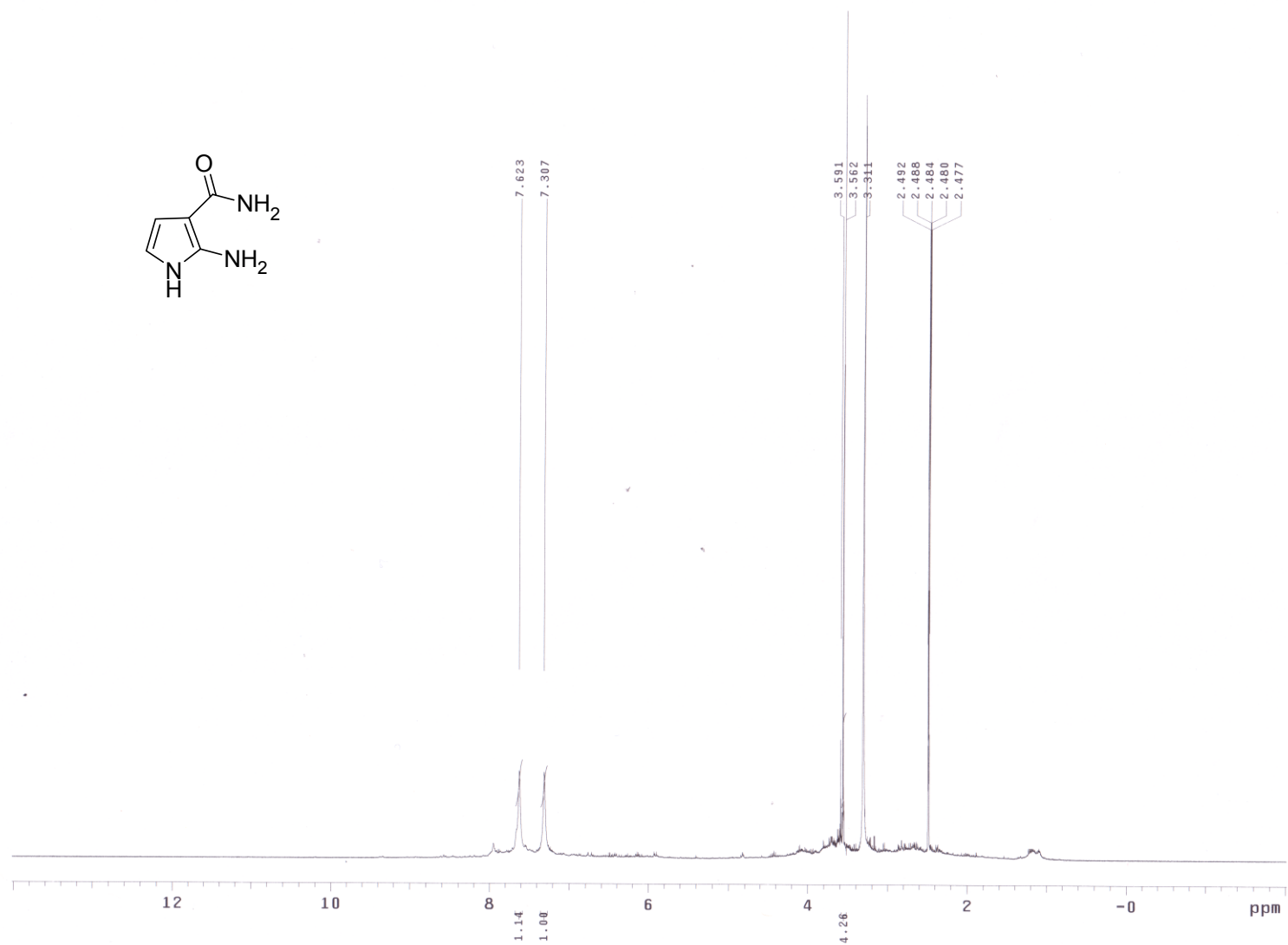


Figure S63.  $^{13}\text{C}$ NMR of compound 4-4



**Figure S64.** <sup>1</sup>H NMR of compound 4-5

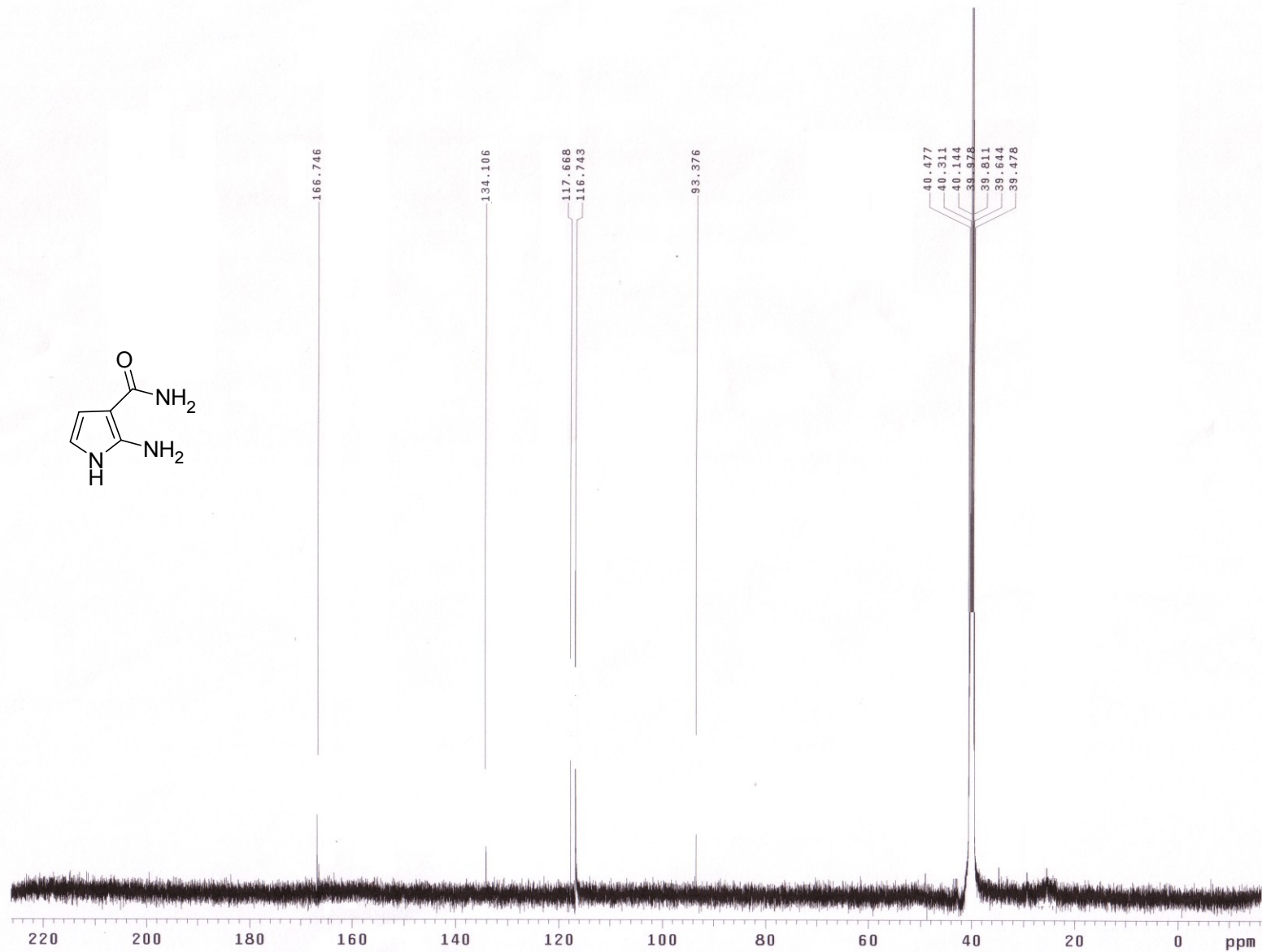


Figure S65.  $^{13}\text{C}$ NMR of compound 4-5

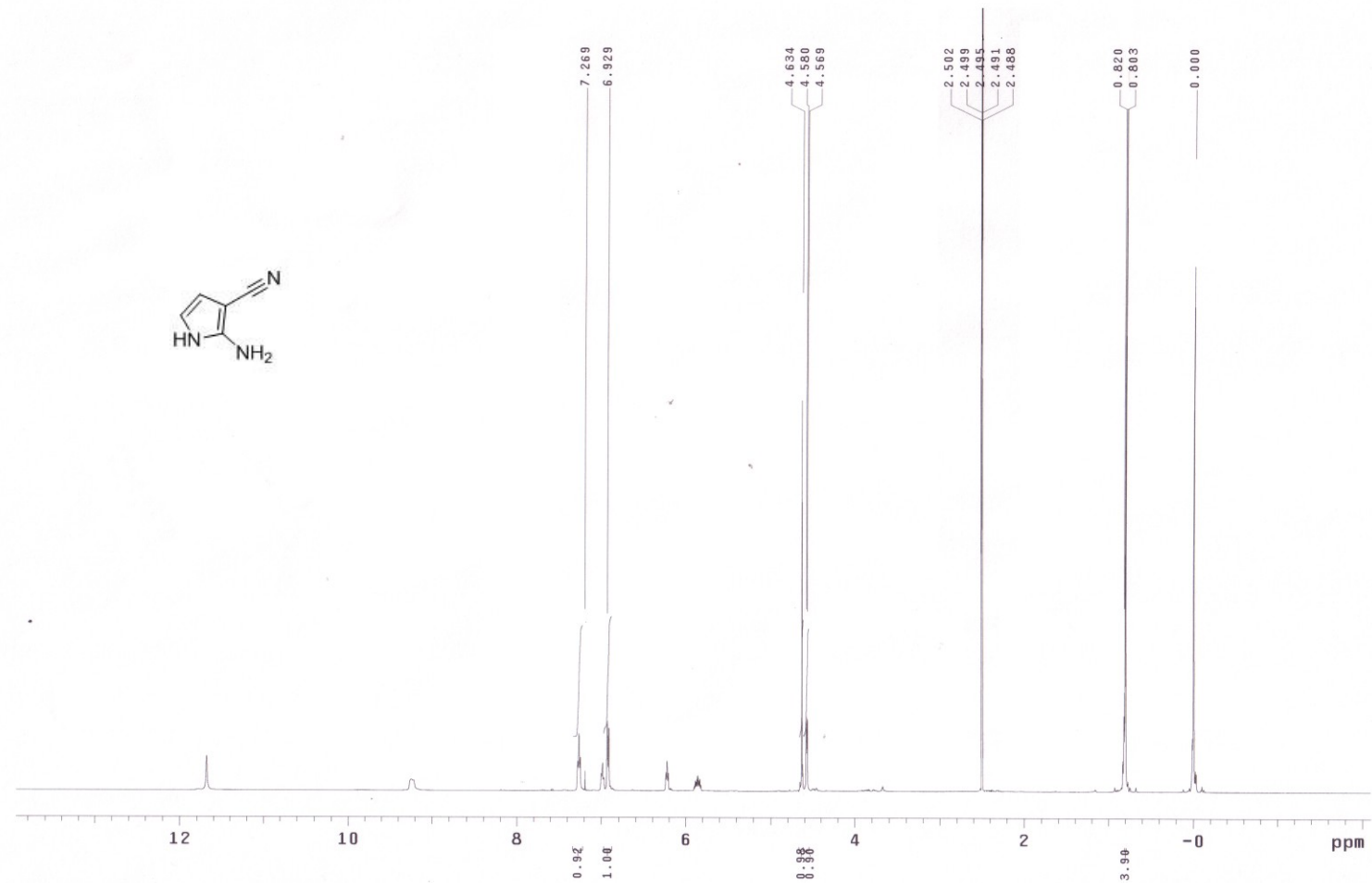


Figure S66. <sup>1</sup>H NMR of compound 4-6

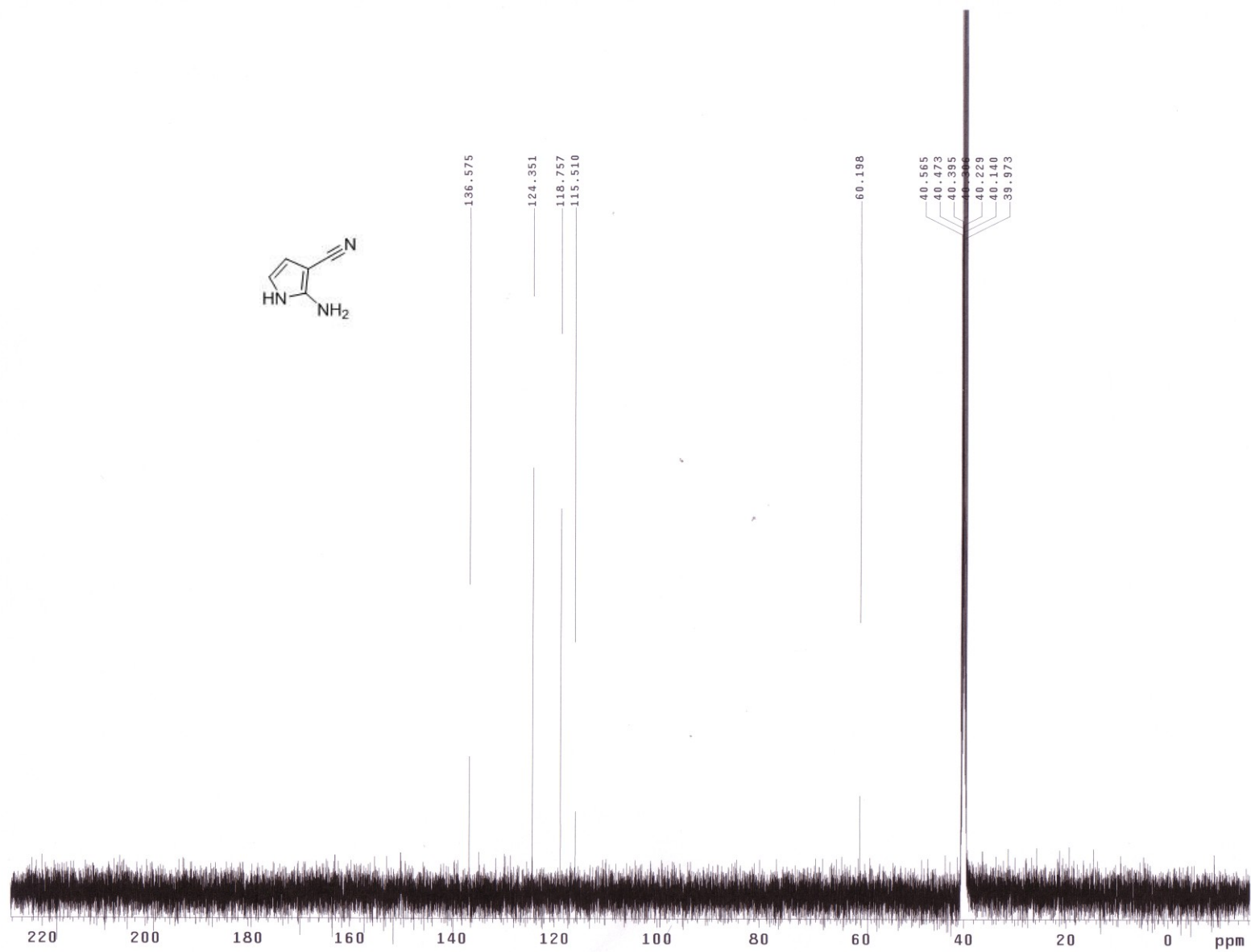


Figure S67.  $^{13}\text{C}$  NMR of compound 4-6

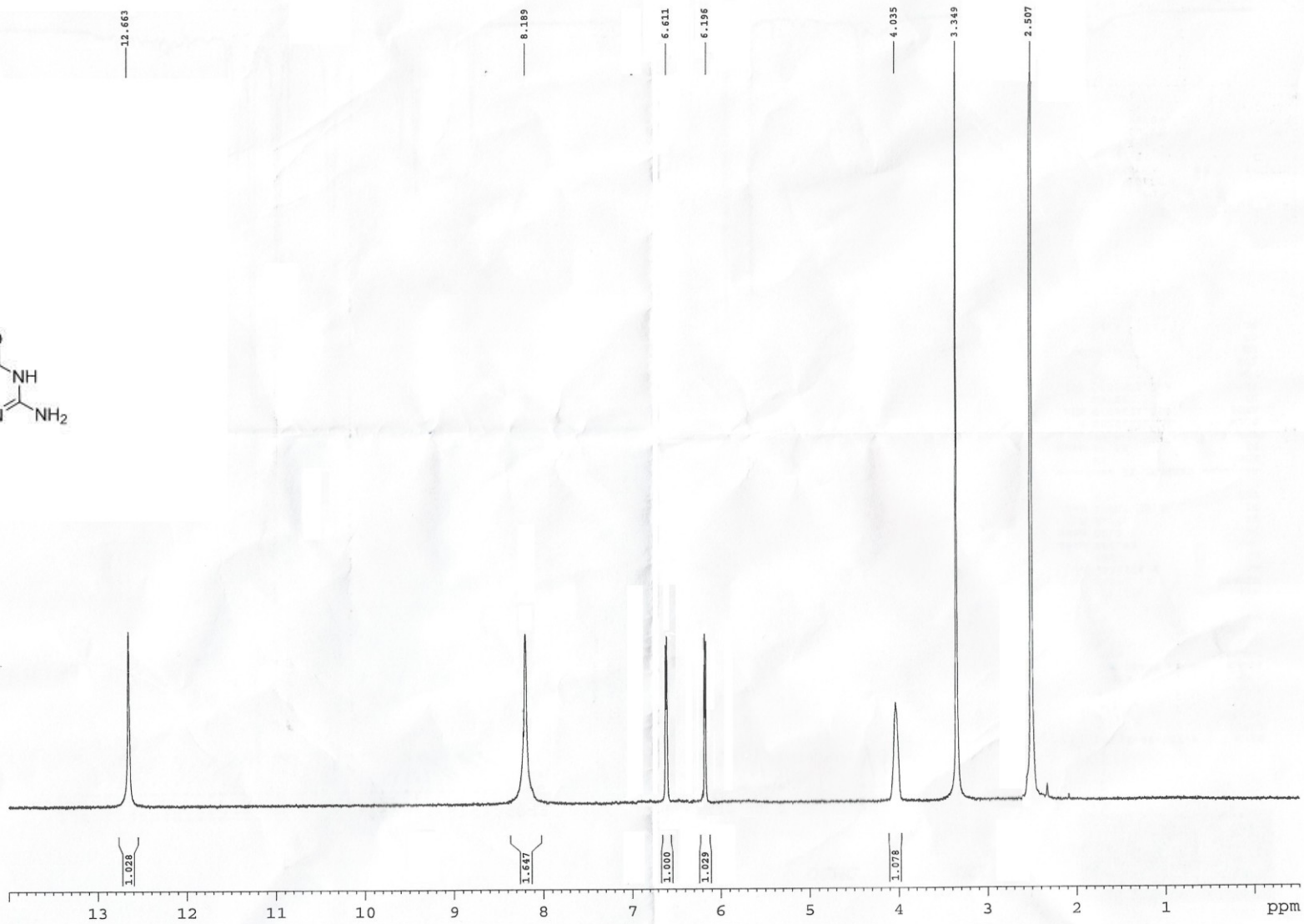
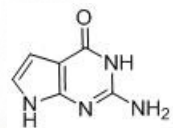


Figure S68.  $^1\text{H}$ NMR of compound 4-7

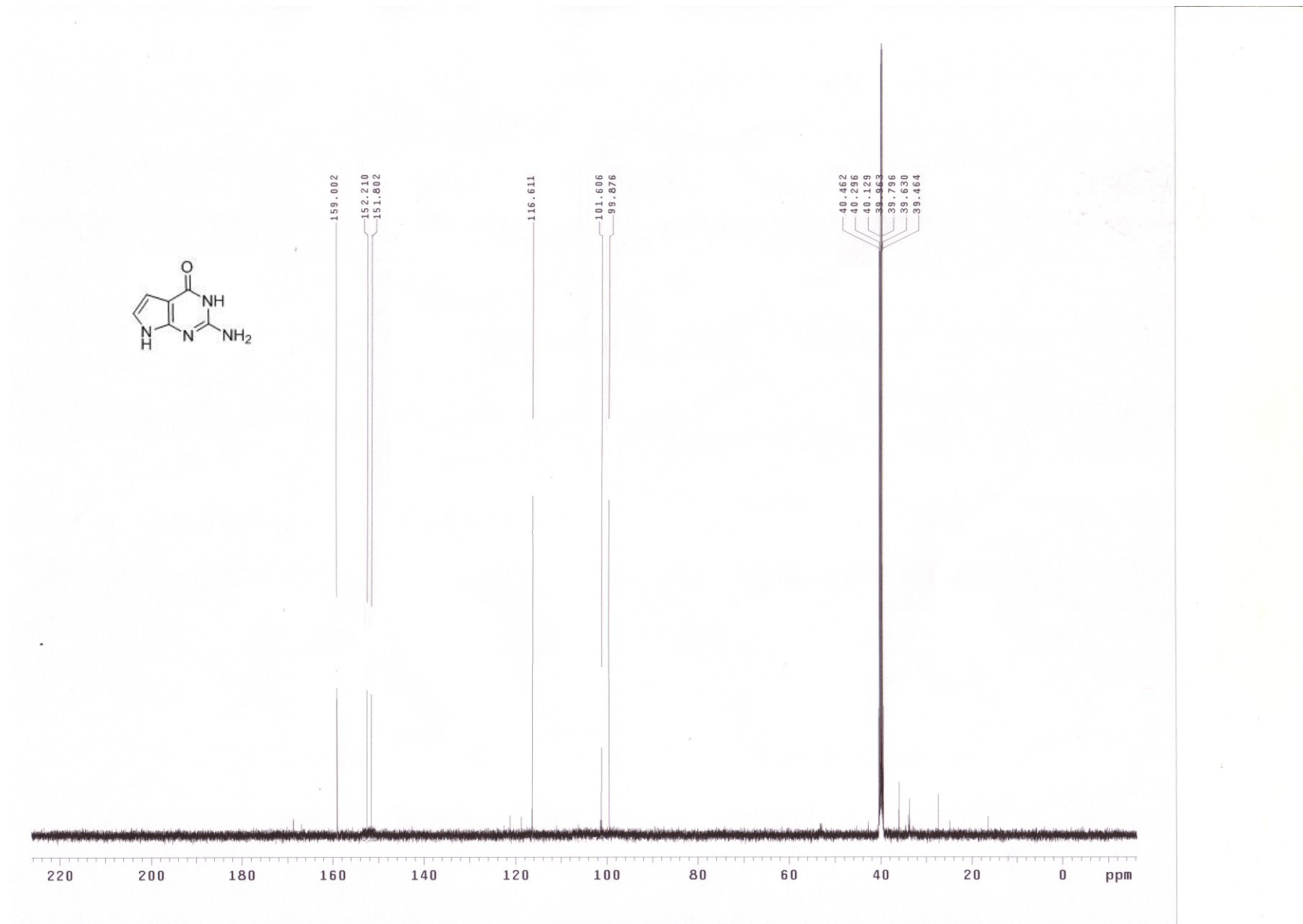


Figure S69.  $^{13}\text{C}$  NMR of compound 4-7



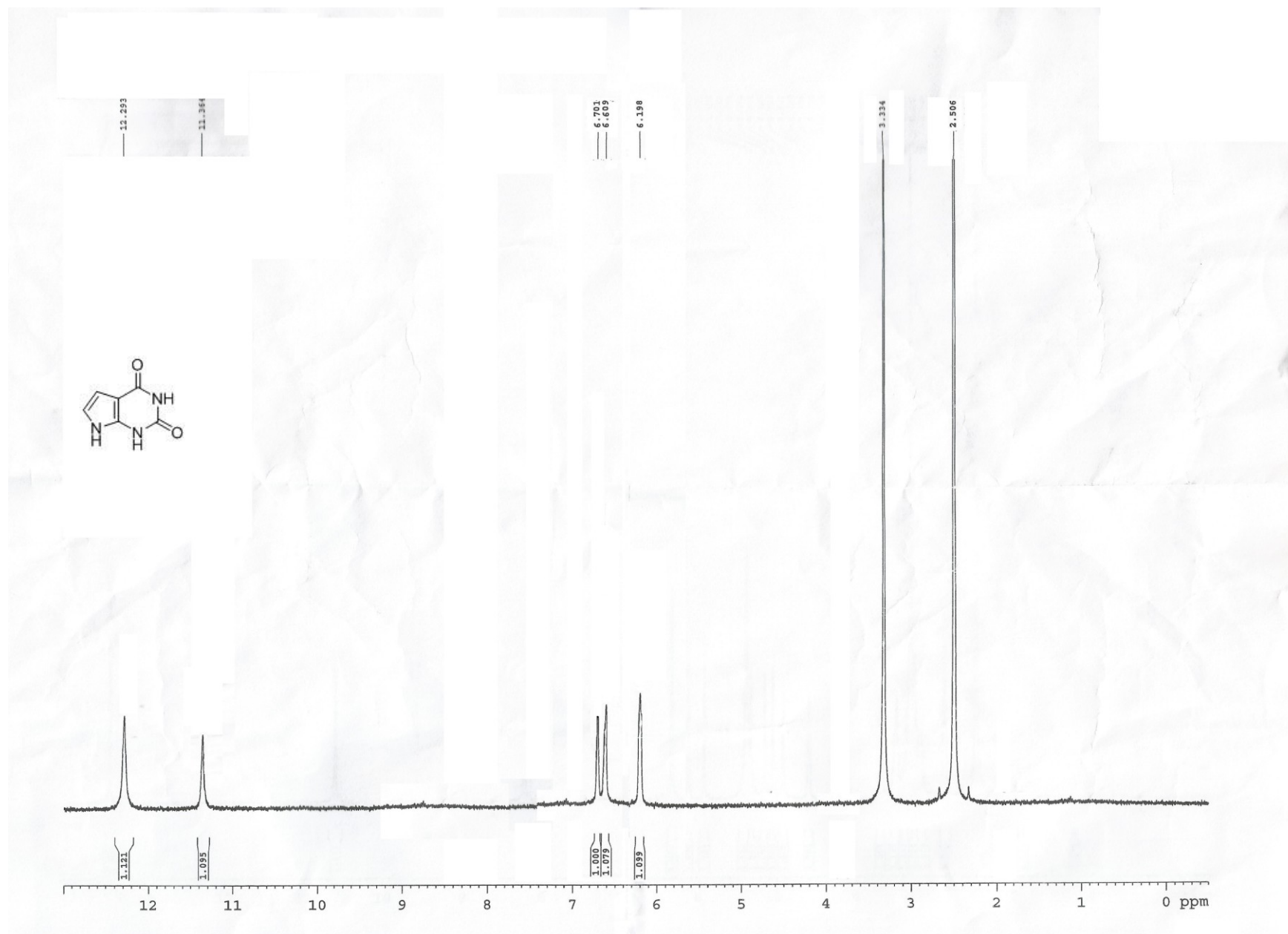


Figure S70. <sup>1</sup>H NMR of compound 4-8



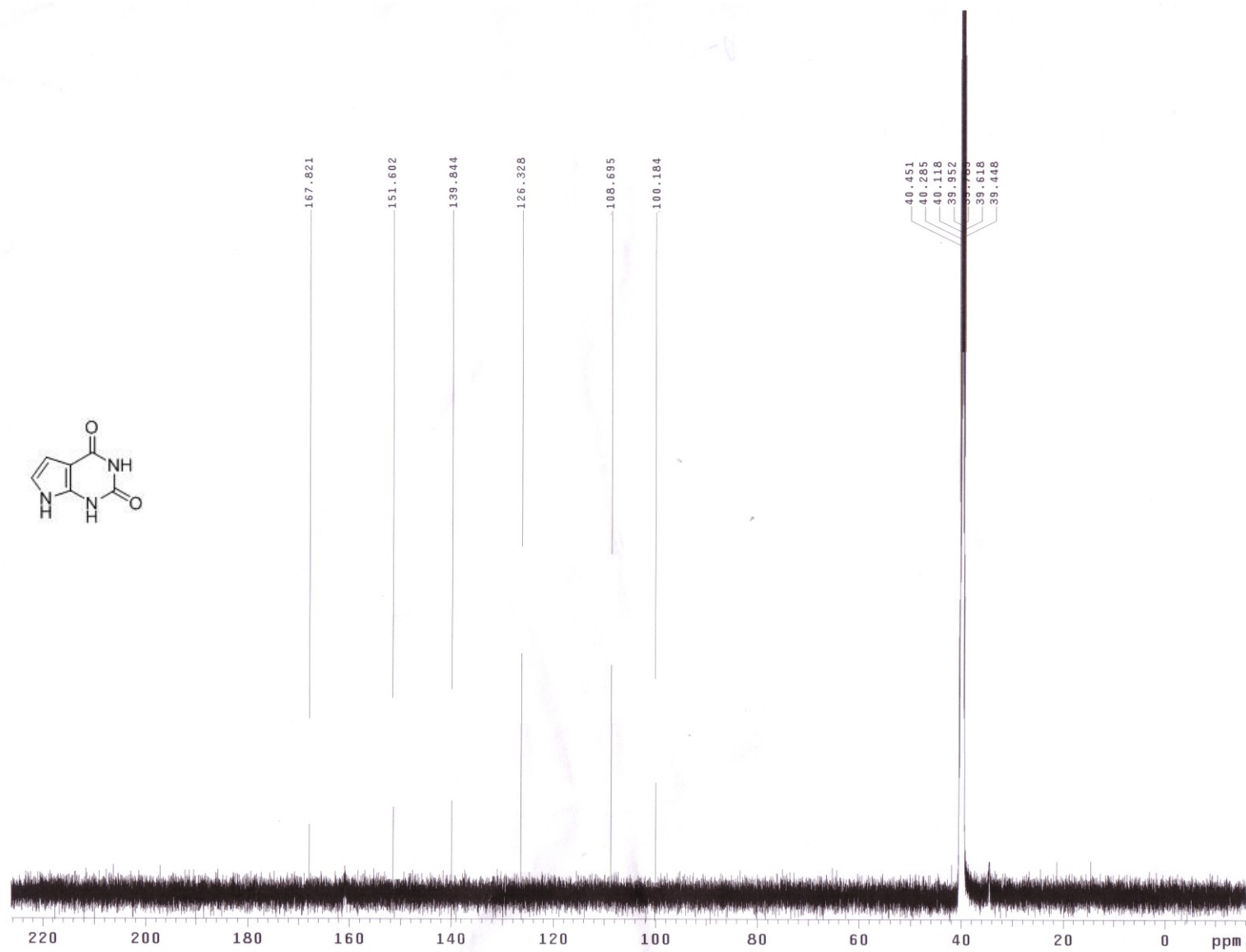


Figure S71.  $^{13}\text{C}$ NMR of compound 4-8

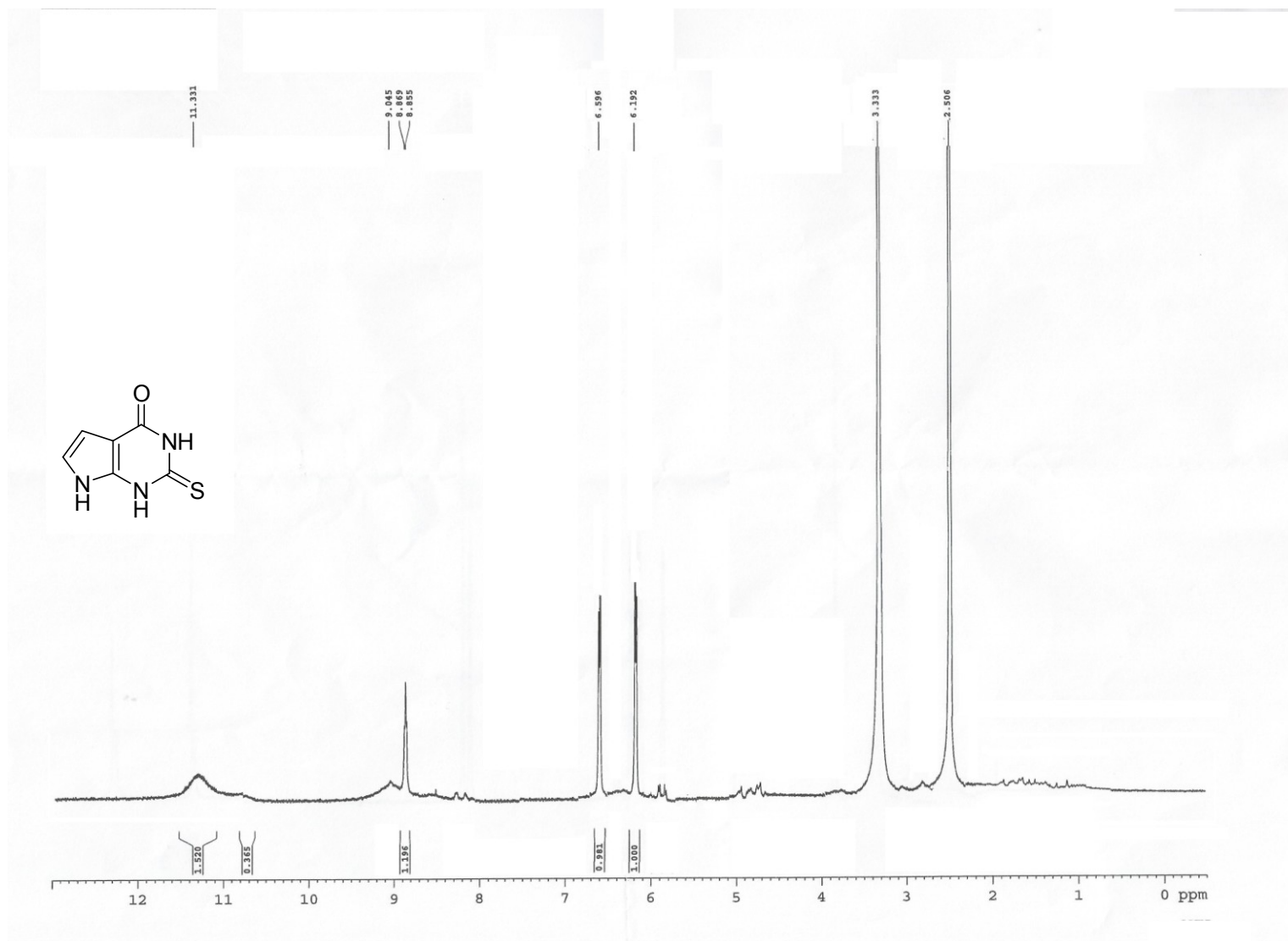


Figure S72. <sup>1</sup>H NMR of compound 4-9

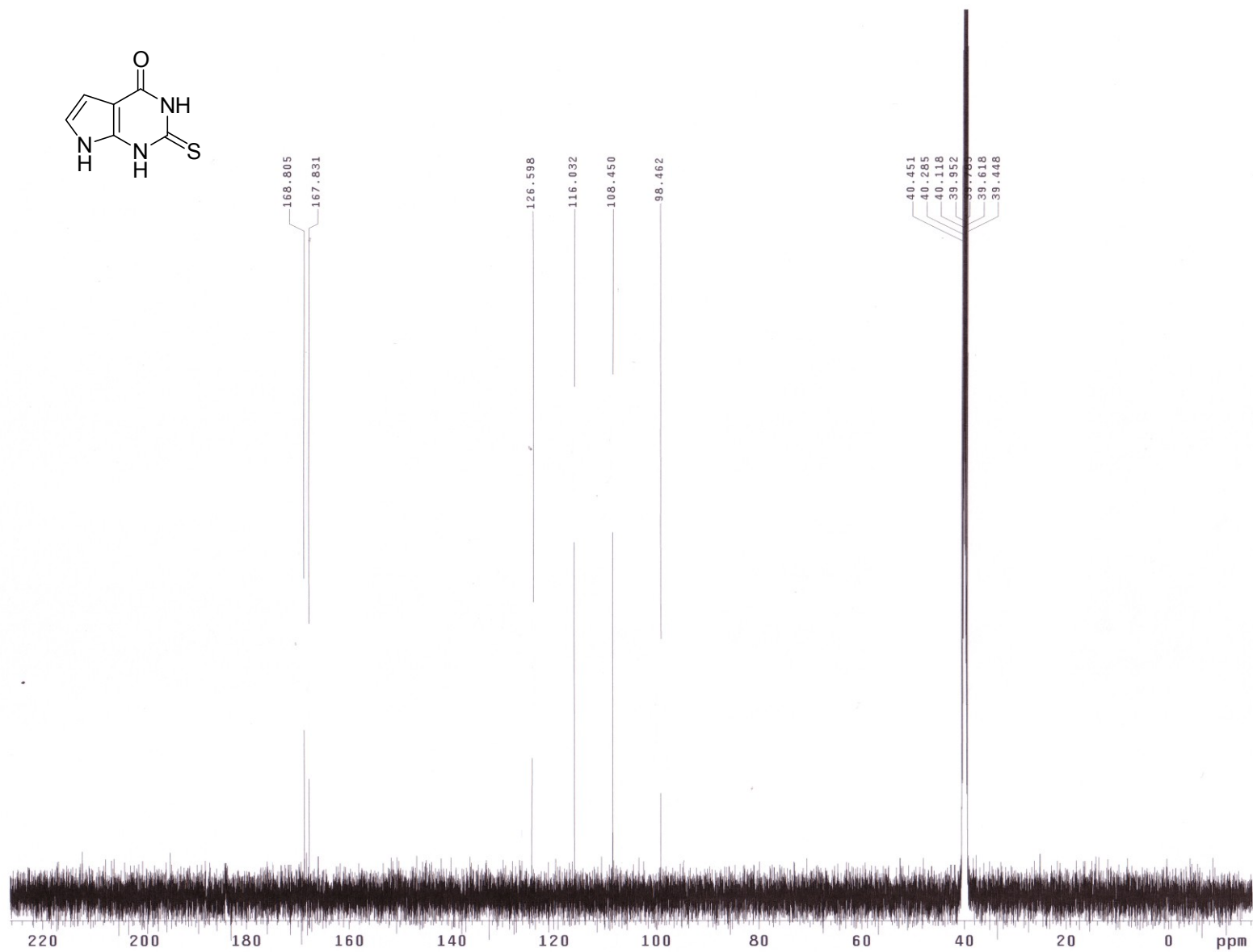
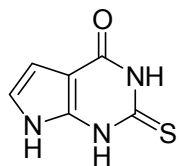


Figure S73.  $^{13}\text{C}$  NMR of compound 4-9

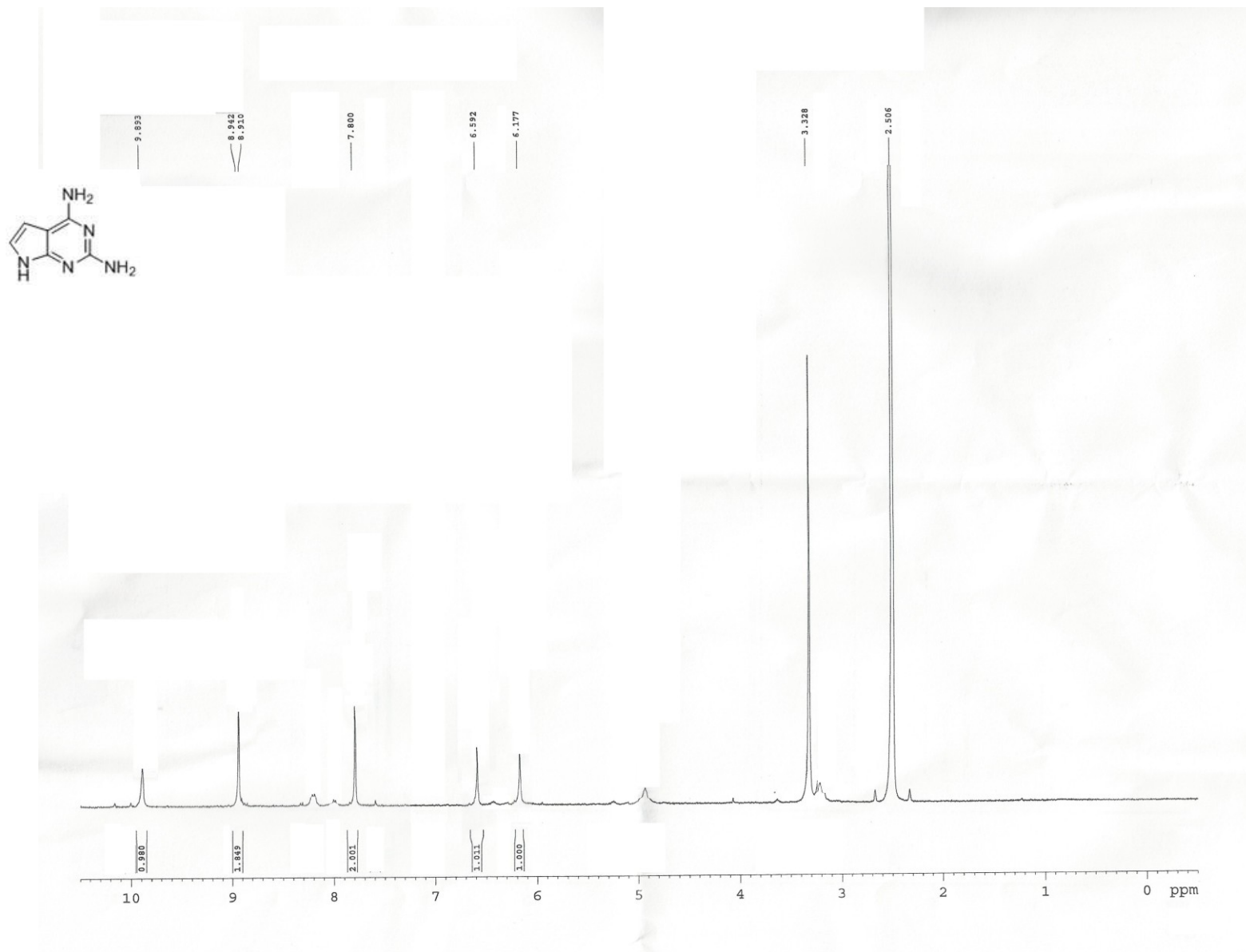


Figure S74. <sup>1</sup>H NMR of compound 4-10

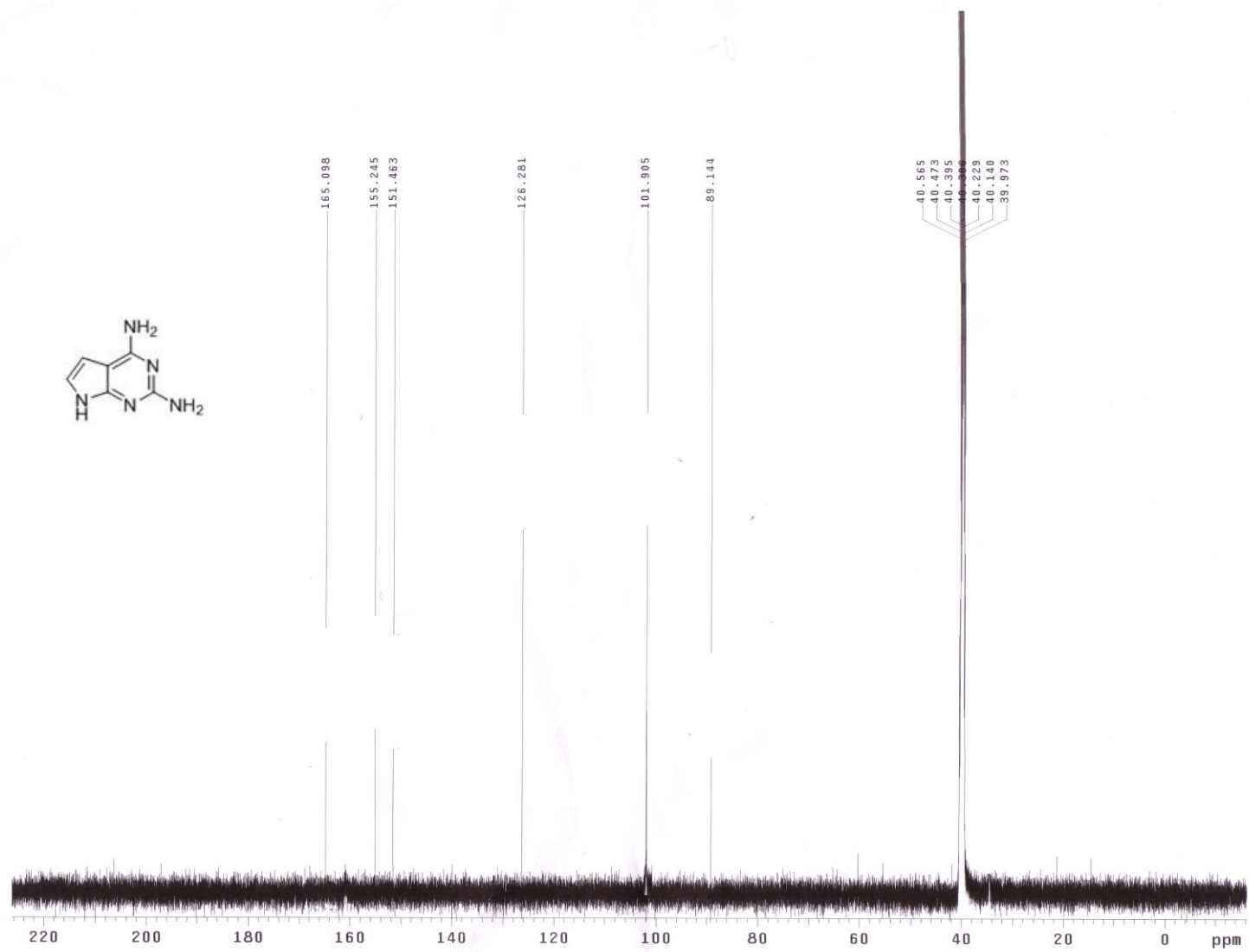


Figure S75. <sup>13</sup>CNMR of compound 4-10

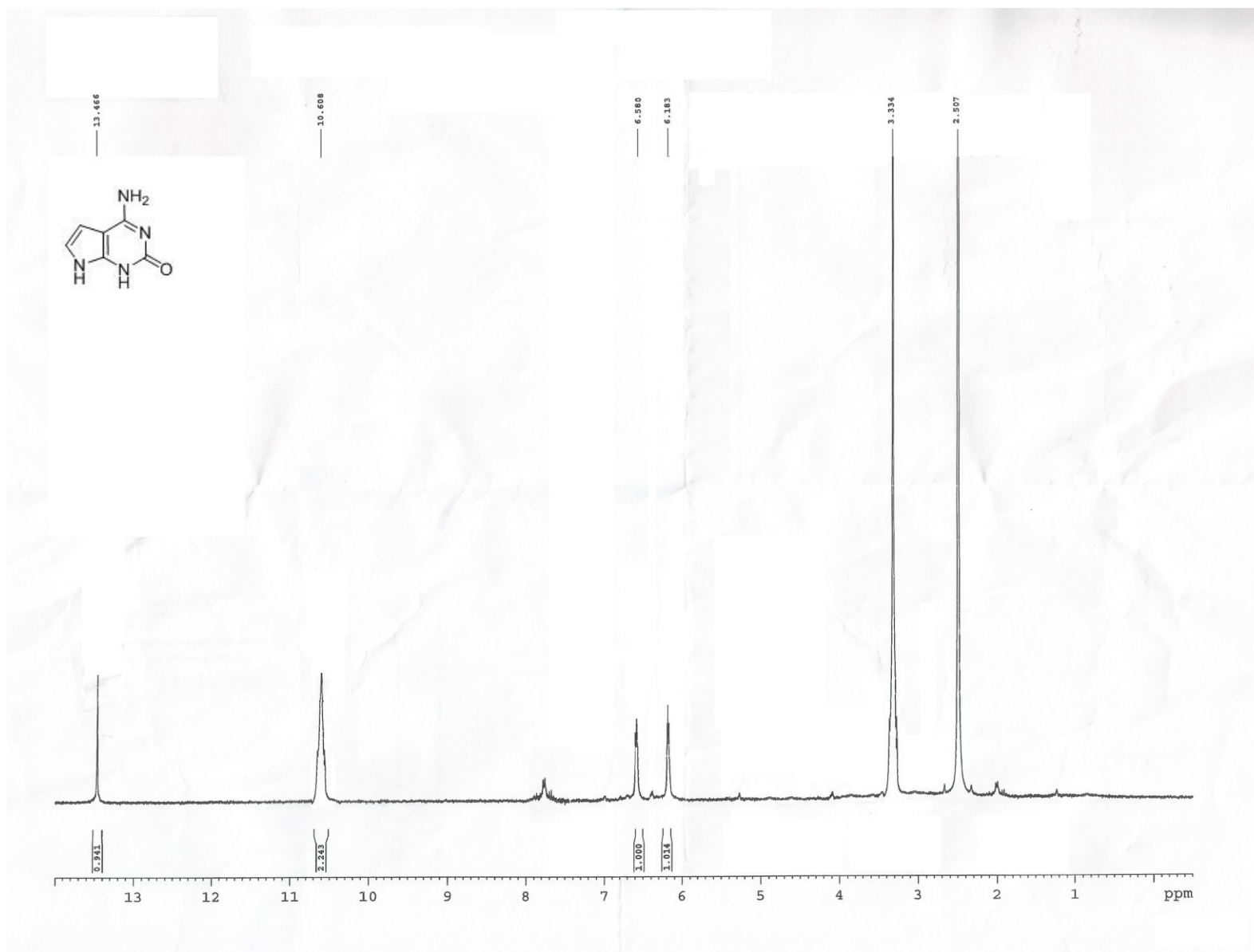


Figure S76. <sup>1</sup>H NMR of compound 4-11

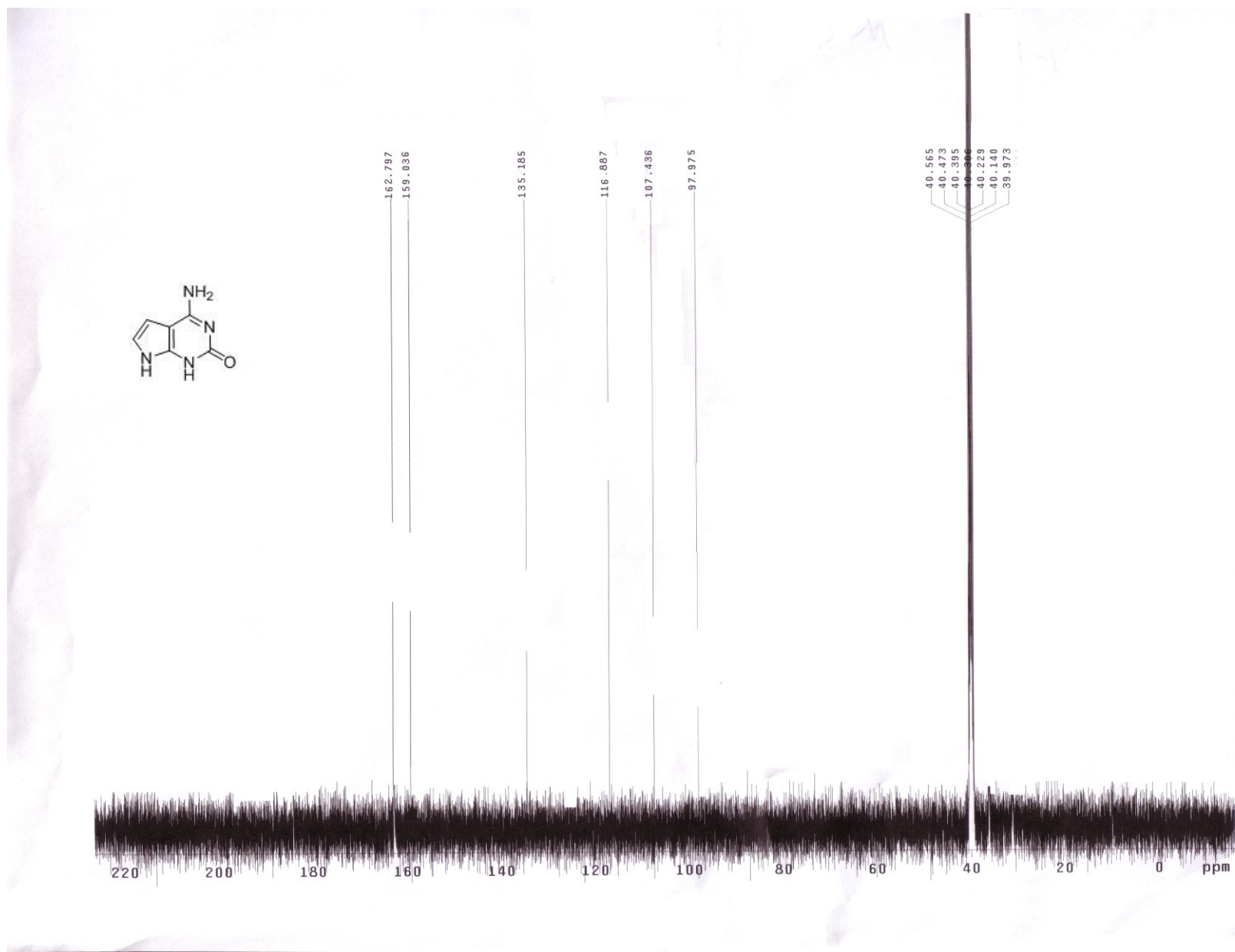


Figure S77.  $^{13}\text{C}$ NMR of compound 4-11

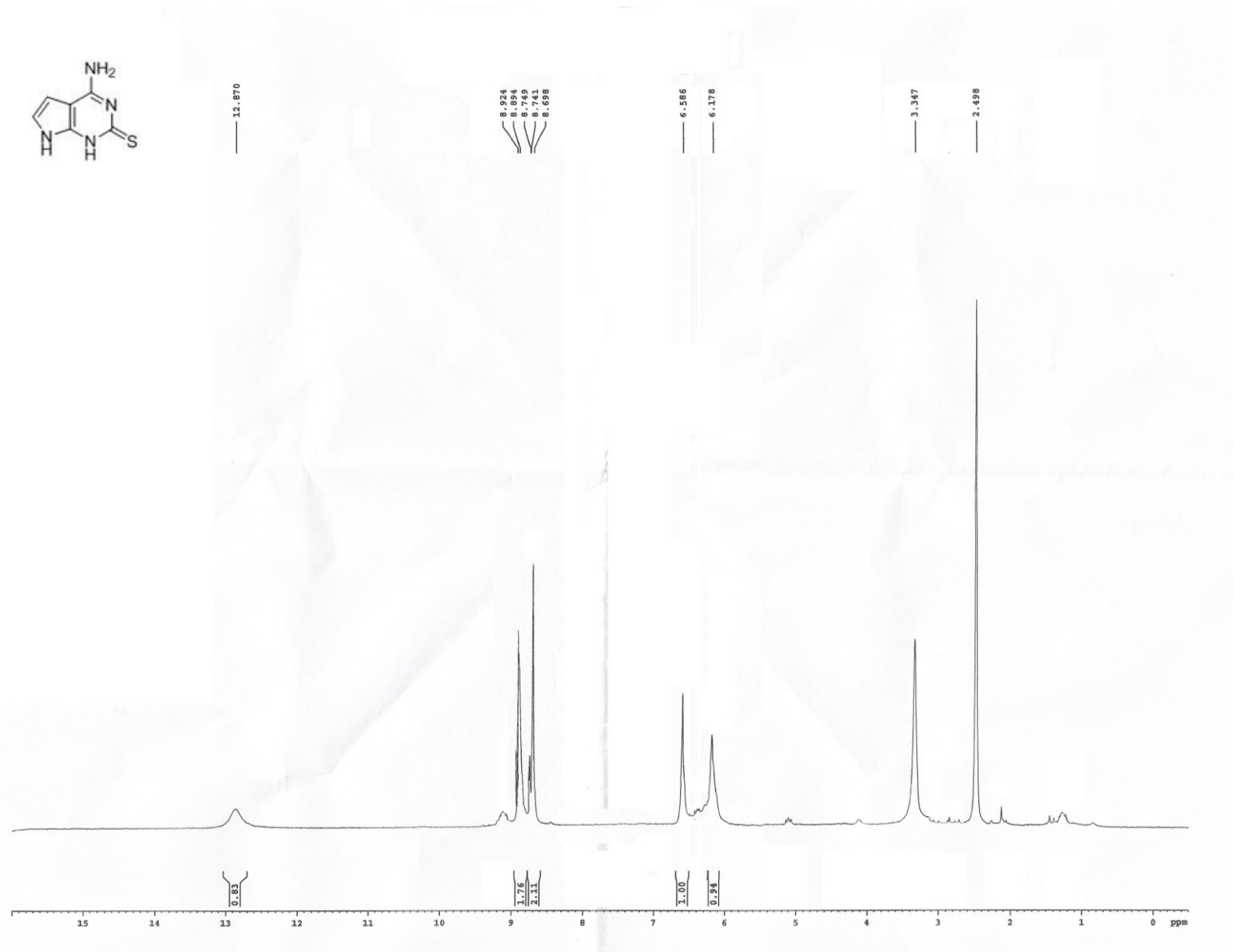


Figure S78. <sup>1</sup>H NMR of compound 4-12



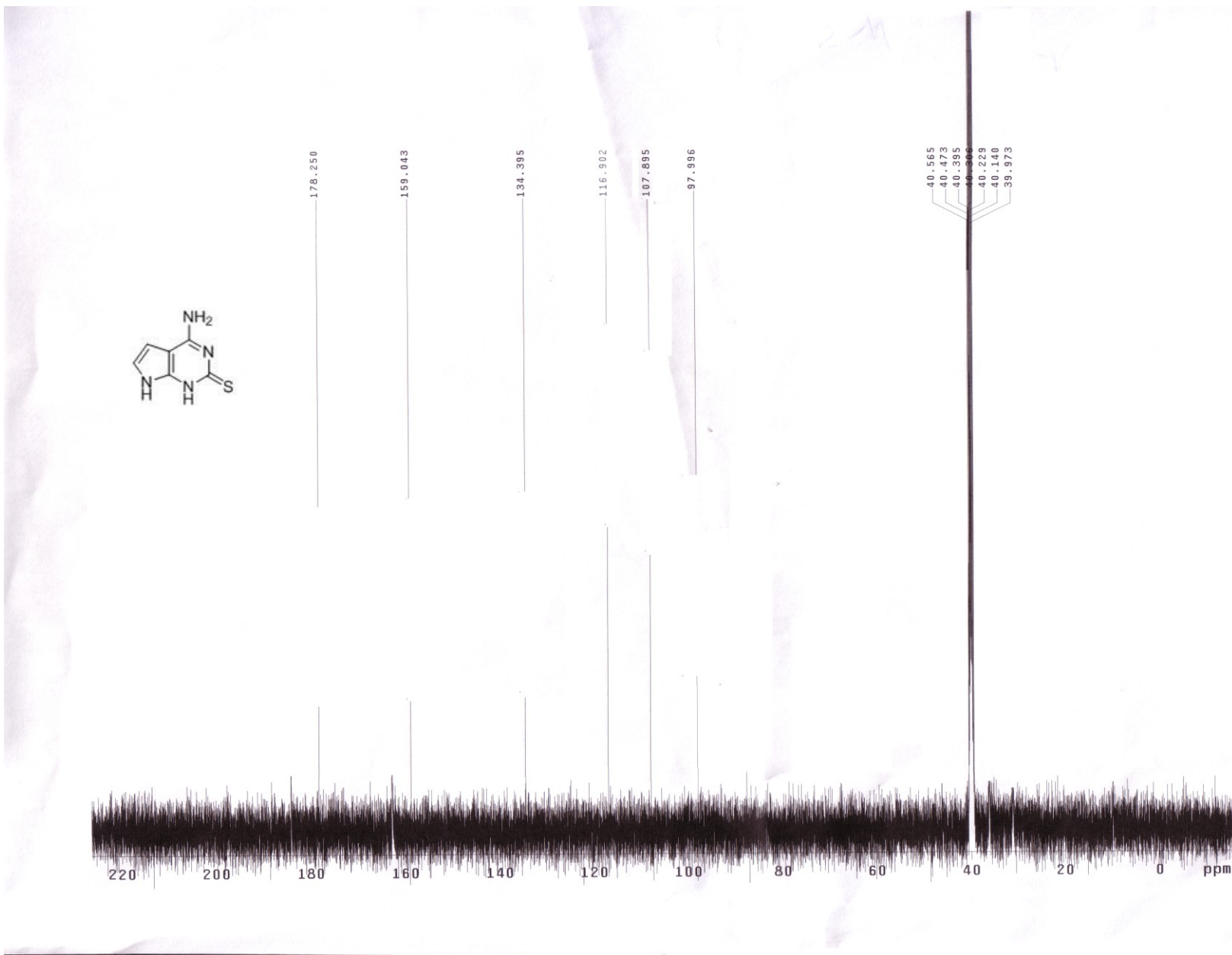


Figure S79.  $^{13}\text{C}$ NMR of compound 4-12

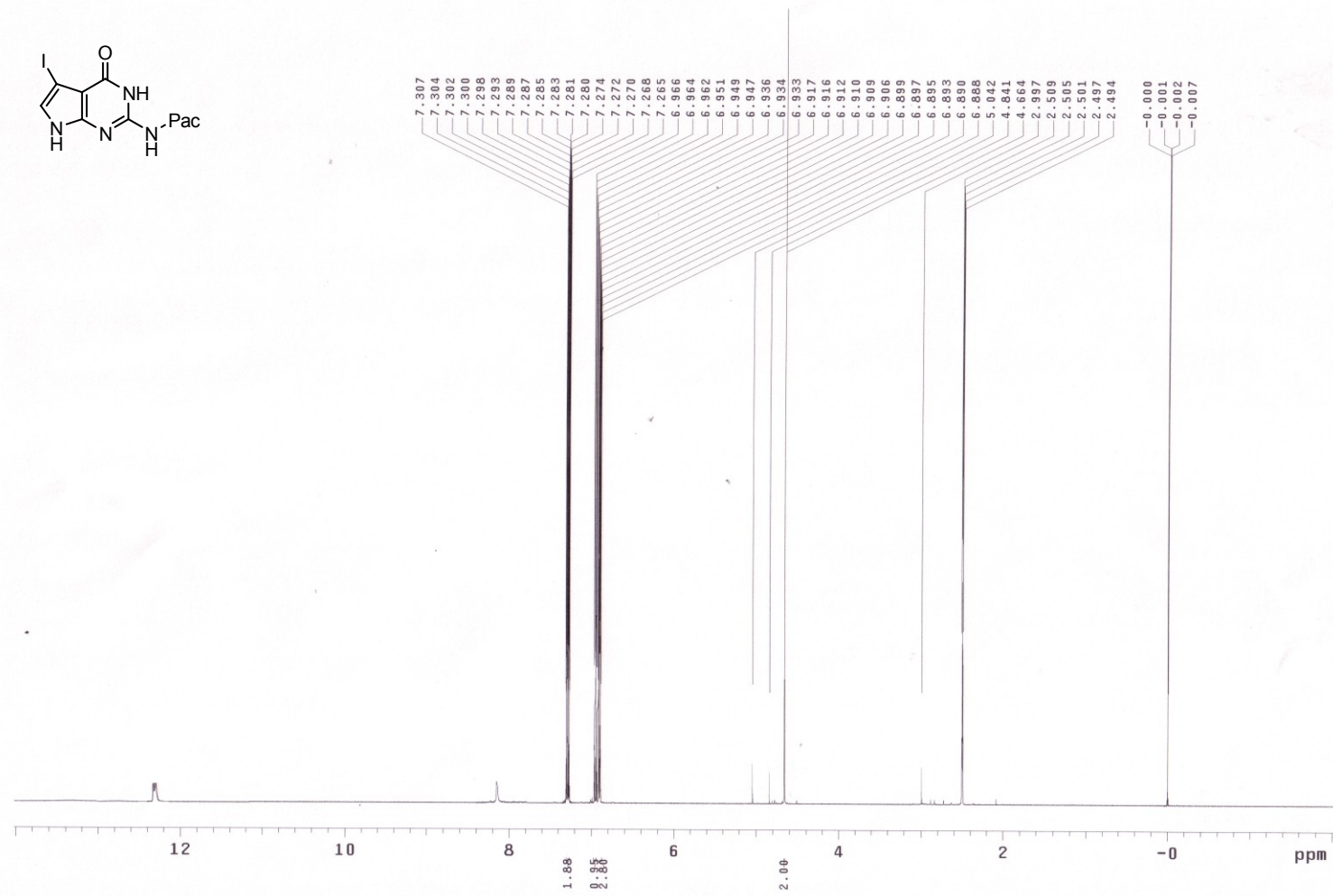


Figure S80. <sup>1</sup>H NMR of compound 5-2

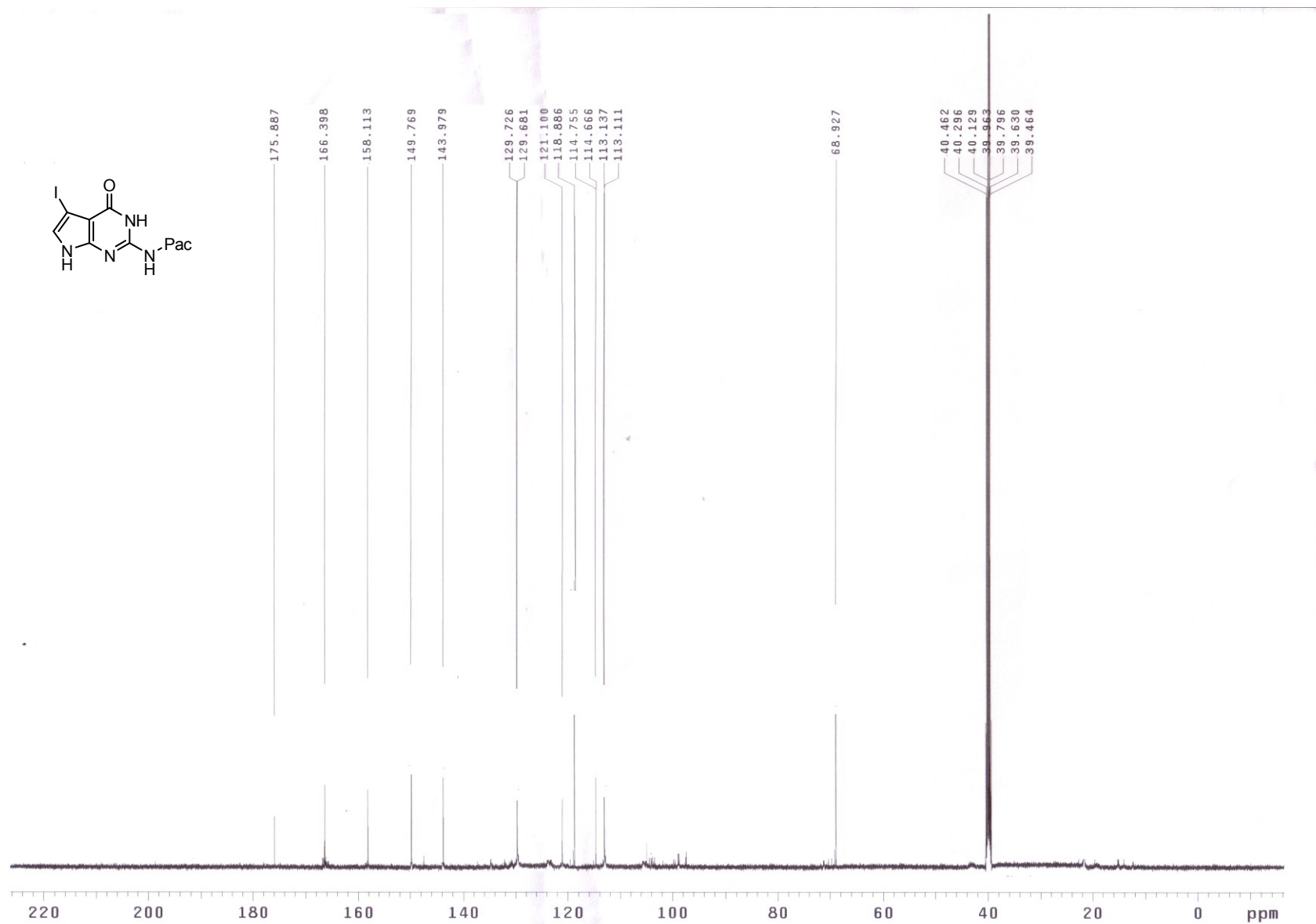


Figure S81. <sup>13</sup>CNMR of compound 5-2

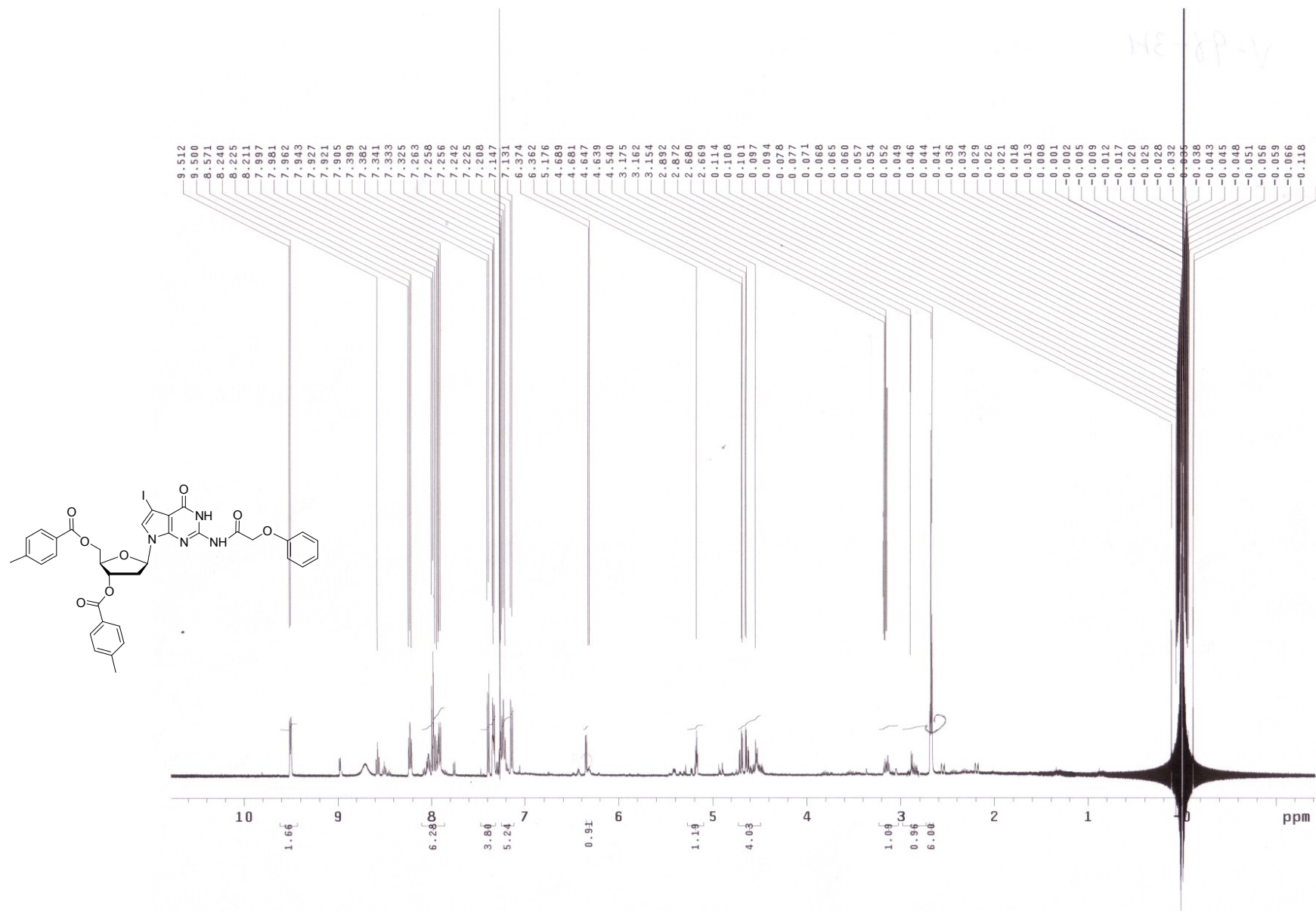


Figure S82. <sup>1</sup>H NMR of compound 5-3

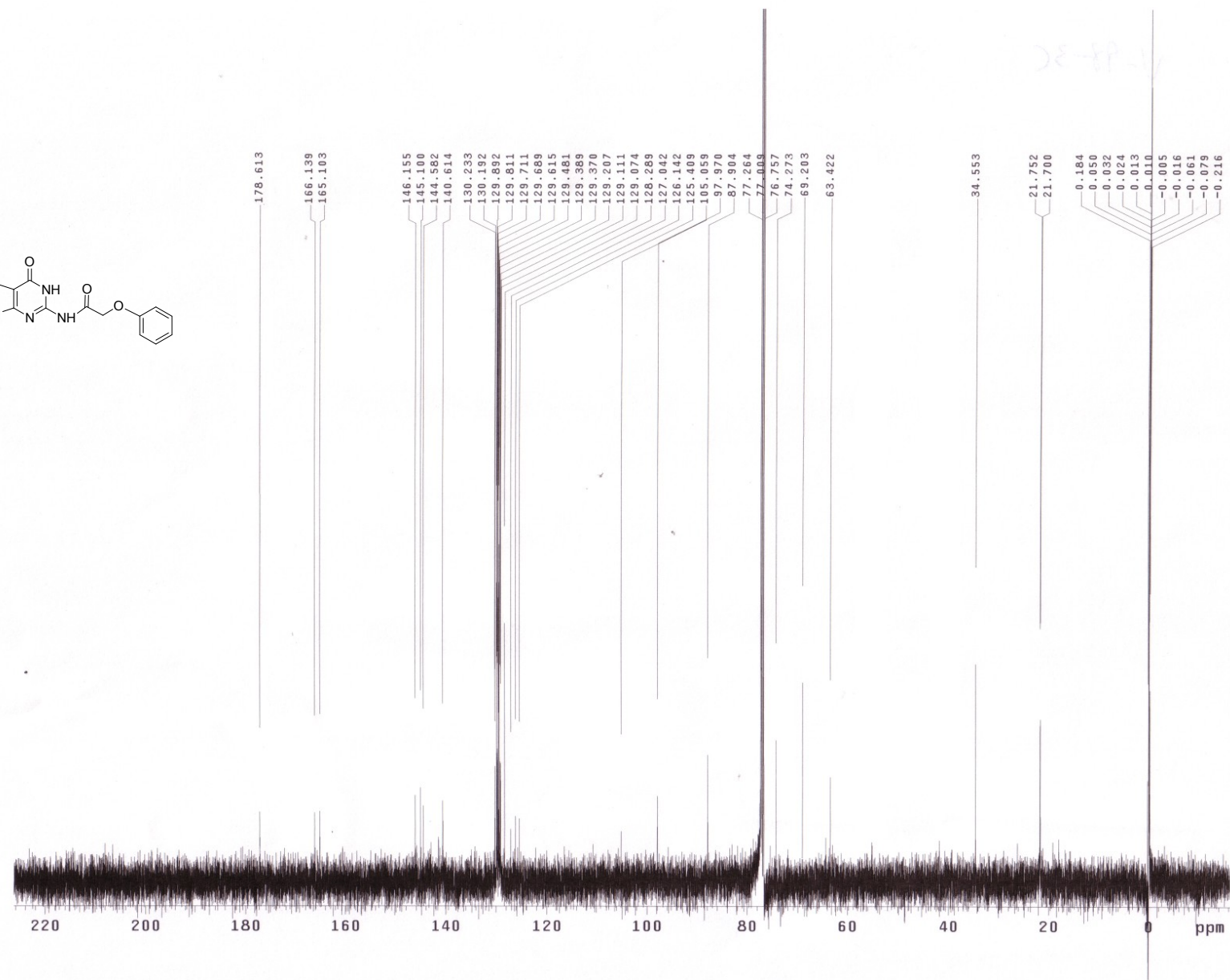
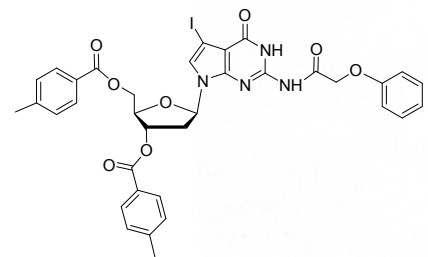


Figure S83.  $^{13}\text{C}$ NMR of compound 5-3

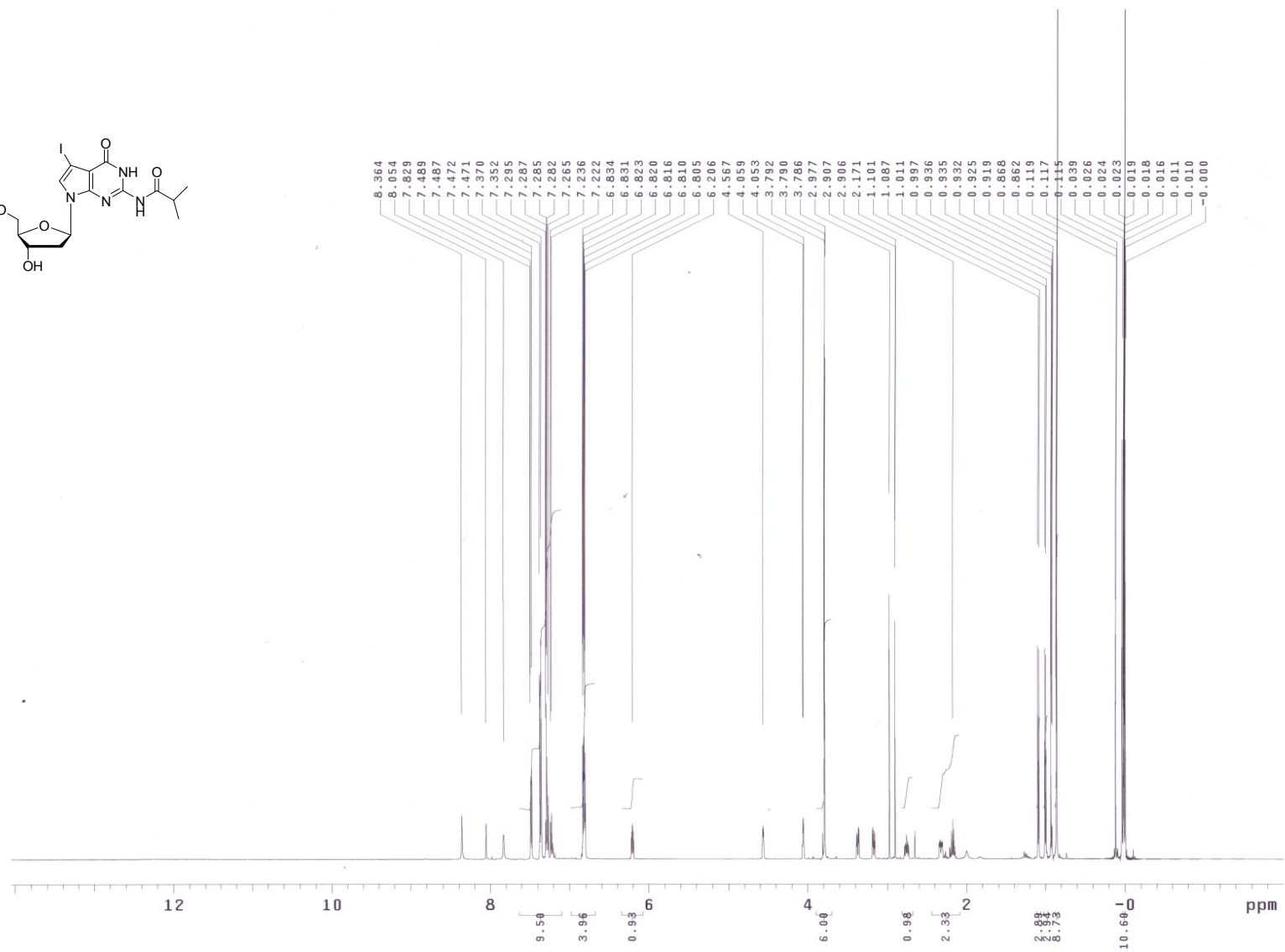
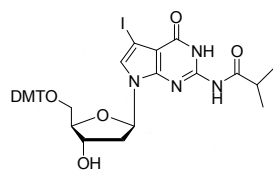


Figure S84. <sup>1</sup>H NMR of compound 5-6



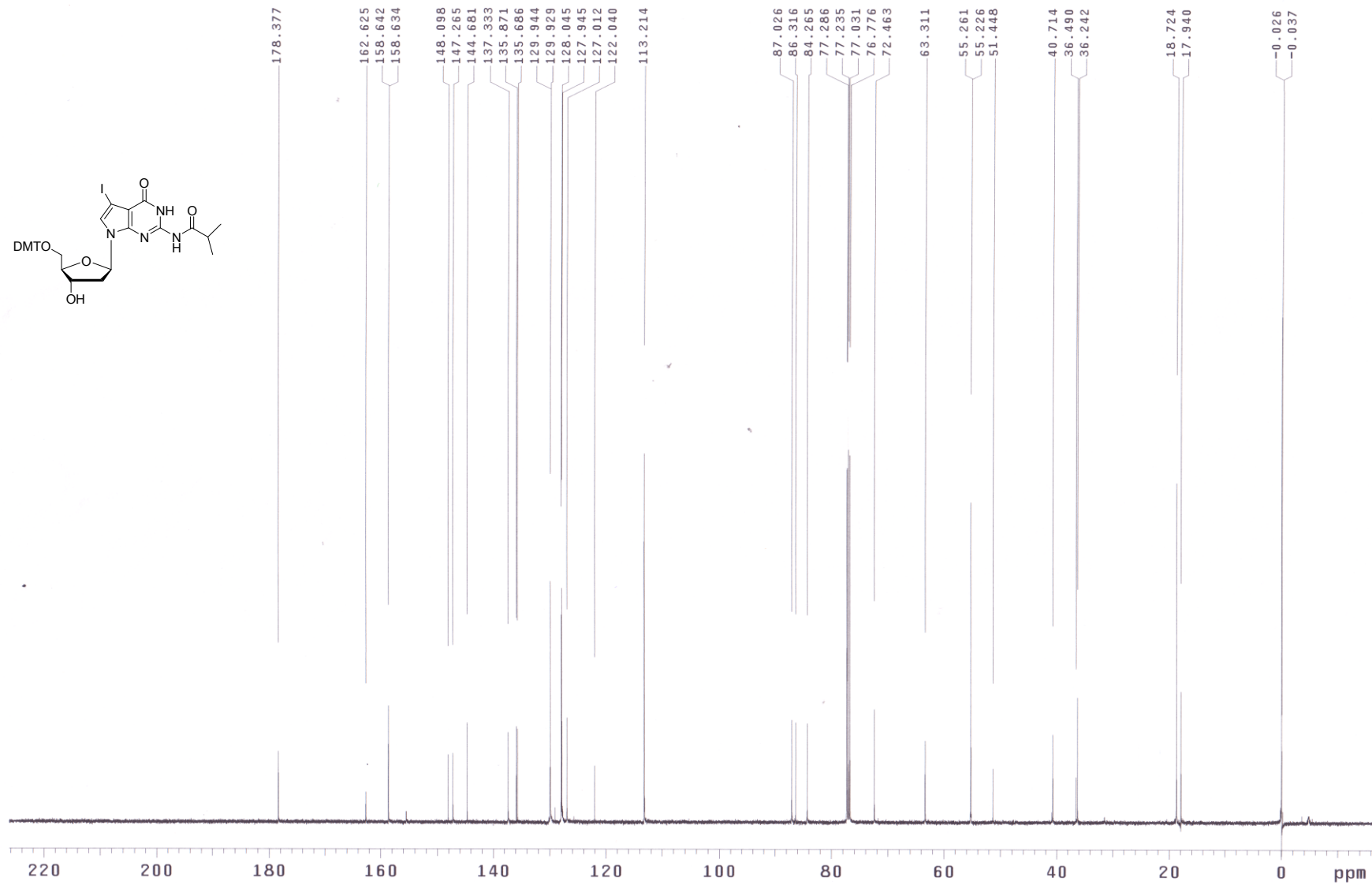


Figure S85. <sup>13</sup>CNMR of compound 5-6

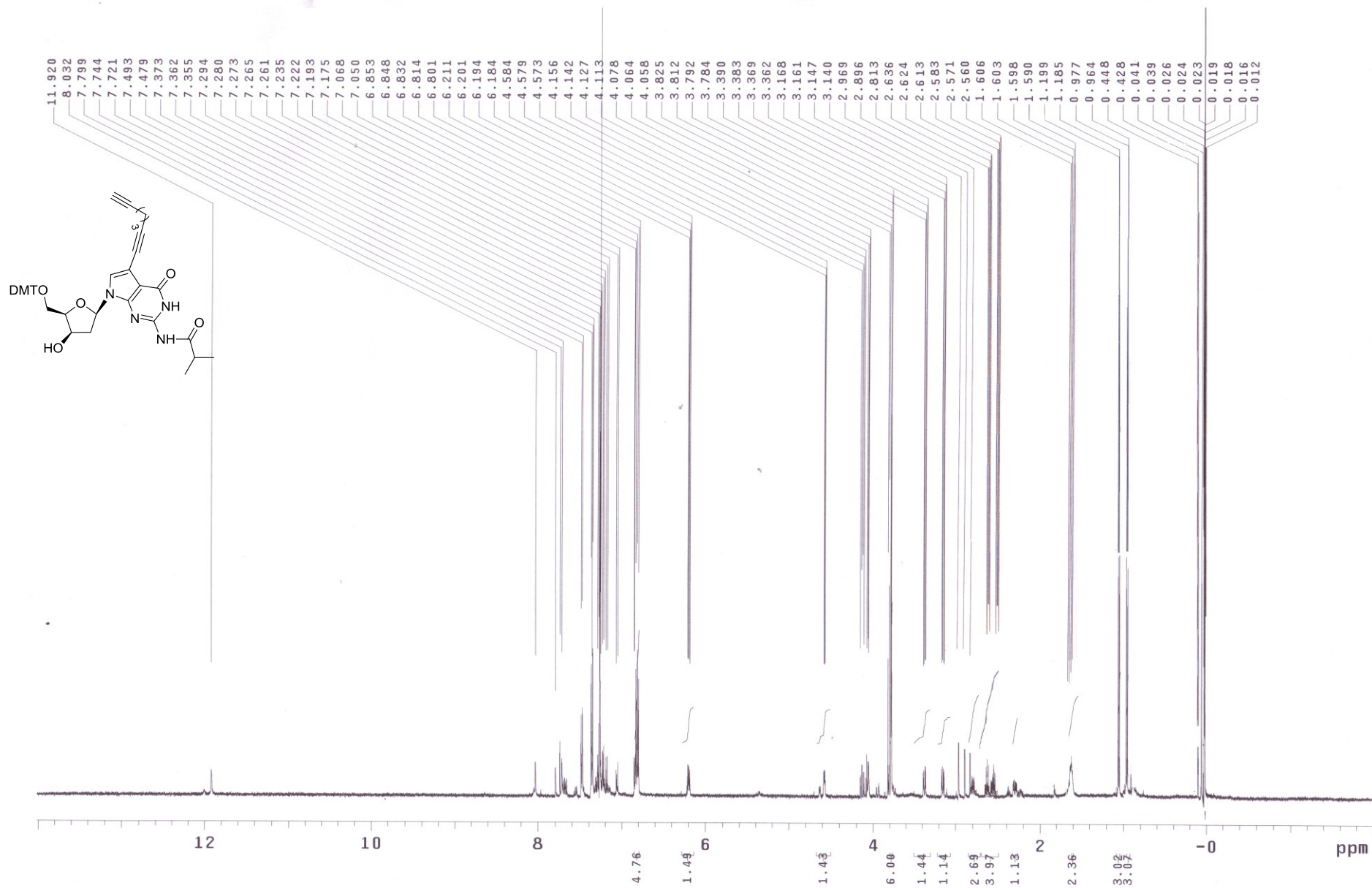


Figure S86. <sup>1</sup>H NMR of compound 5-7



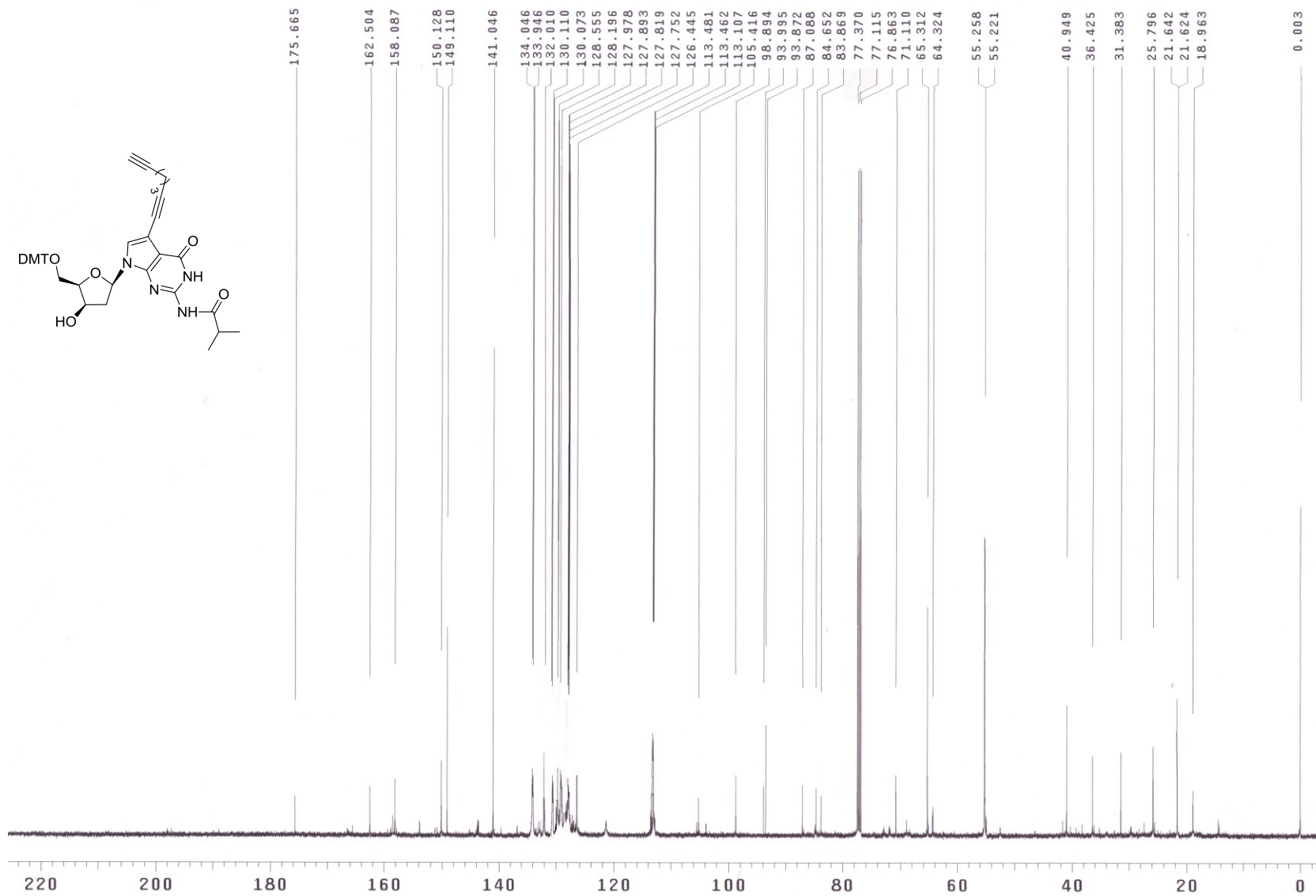


Figure S87. <sup>13</sup>CNMR of compound 5-7