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A Three-Component [3+2]-Cycloaddition/Elimination Cascade for the Synthesis of Spirooxindole-pyrrolizines

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Supporting Information

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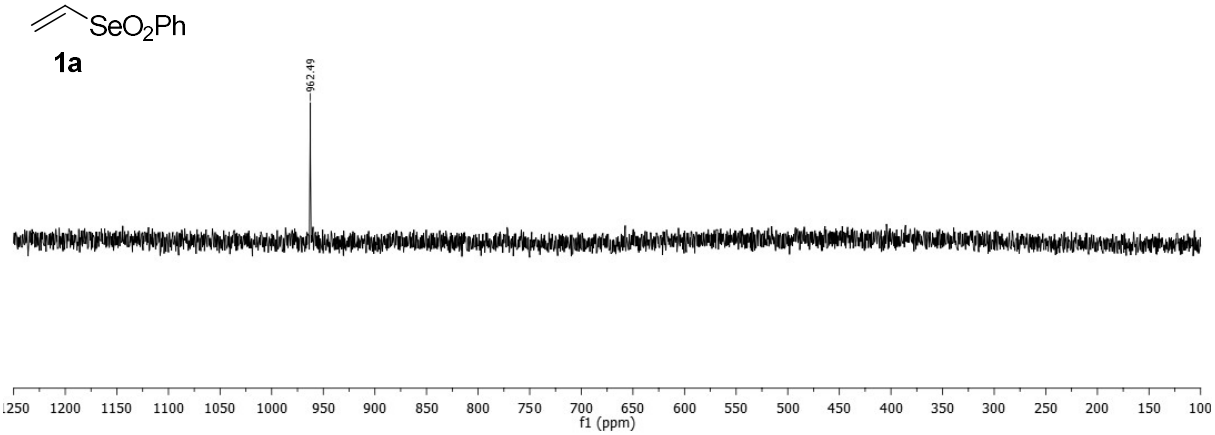
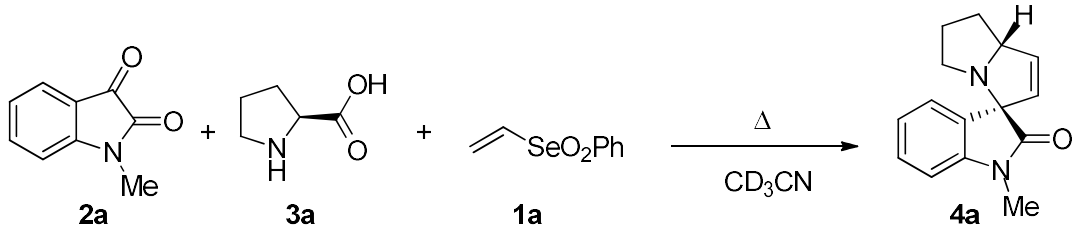




The vinylselenone**1a** (0.10 mmol, 21.6 mg, 1.0 eq.), the *N*-methyl isatin**2a** (0.15 mmol, 24.17 mg, 1.5 eq.) and the *L*-Proline (0.18 mmol, 20.72 mg, 1.8 eq.) were dissolved in 1 ml of CD_3CN. The reaction mixture was vigorously stirred at reflux for 5 minutes. Another experiment was also performed at room temperature for 2 hours.

Figure 2. ^{1}H-NMR of the reaction mixture after 5 minutes (CD_3CN, 400 MHz)

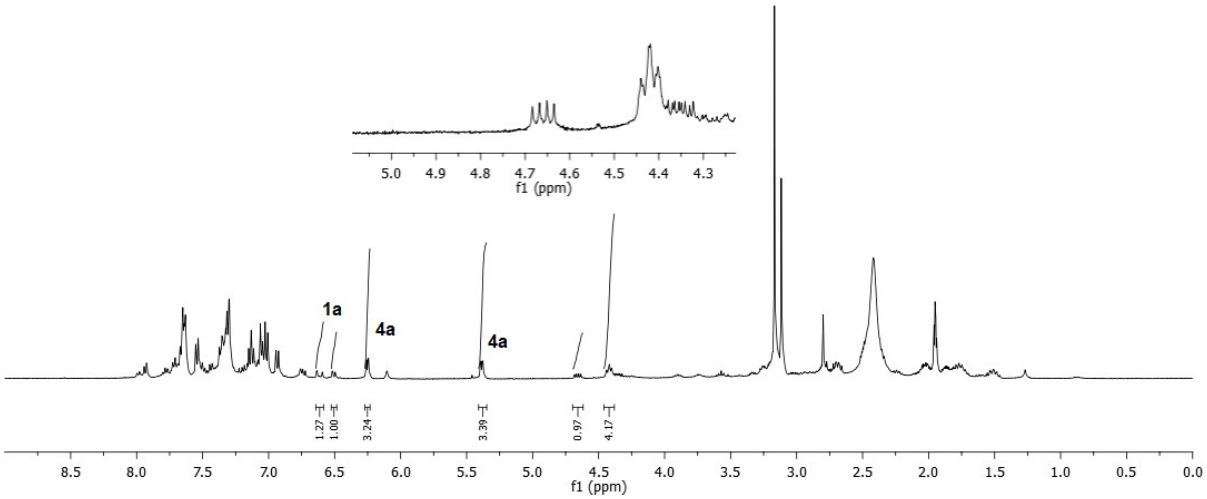


Figure 3. ^{77}Se spectrum of the reaction mixture after 5 minutes (CD_3CN, 76.27 MHz)

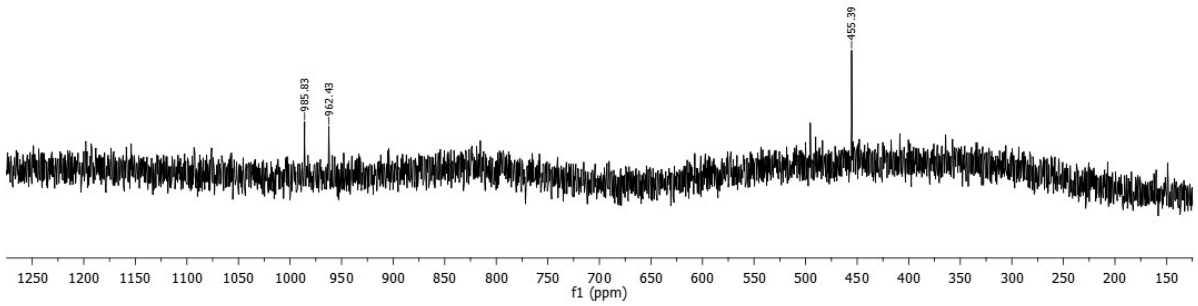


Figure 4. ^{1}H-NMR of the reaction mixture after 2 hours at room temperature (CD_3CN, 400 MHz)

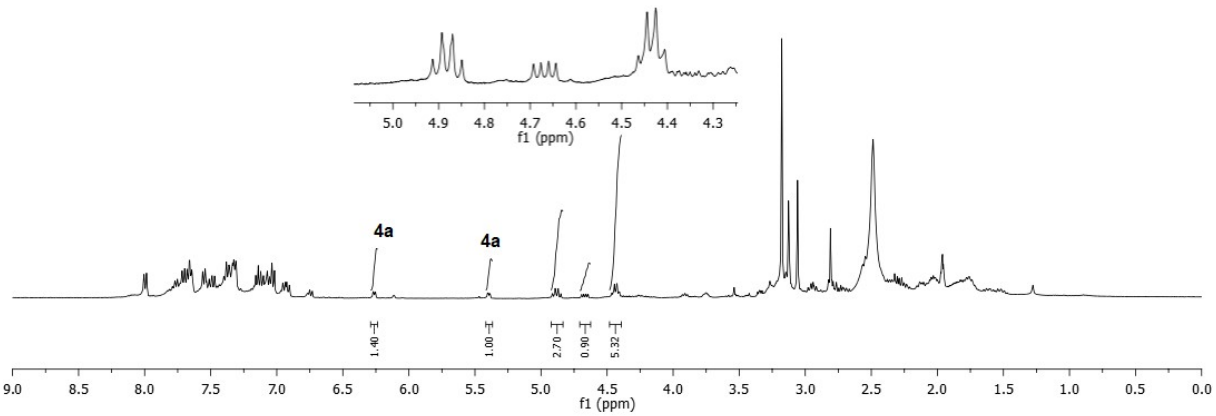
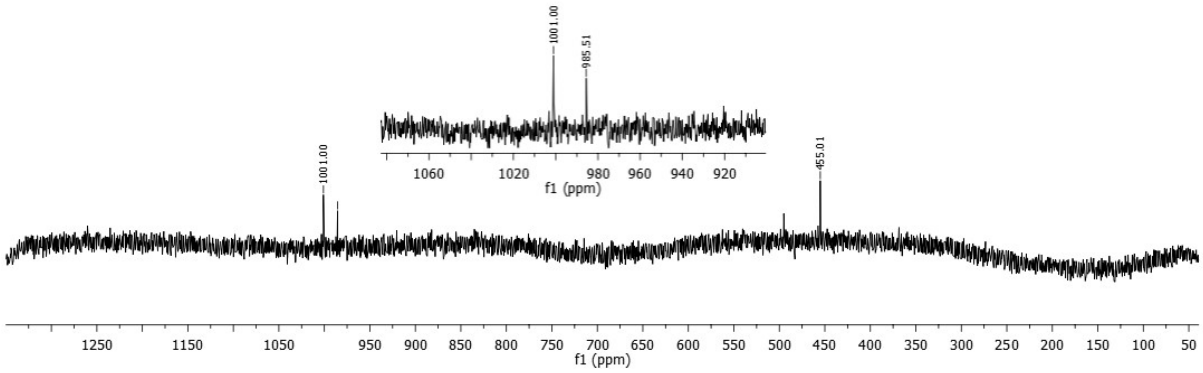
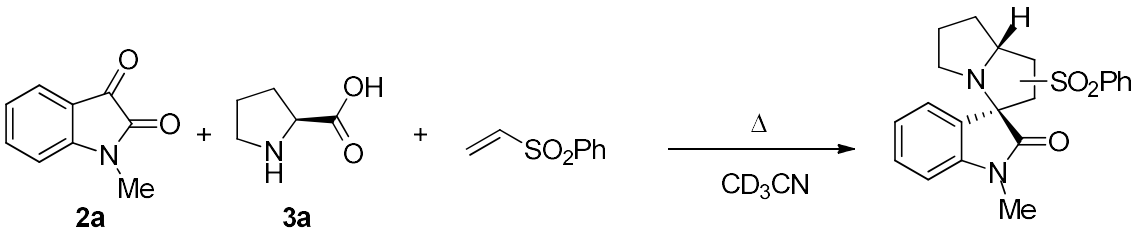


Figure 5. ^{77}Se-NMR spectrum of the reaction mixture 2 hours (CD_3CN, 76.27 MHz)

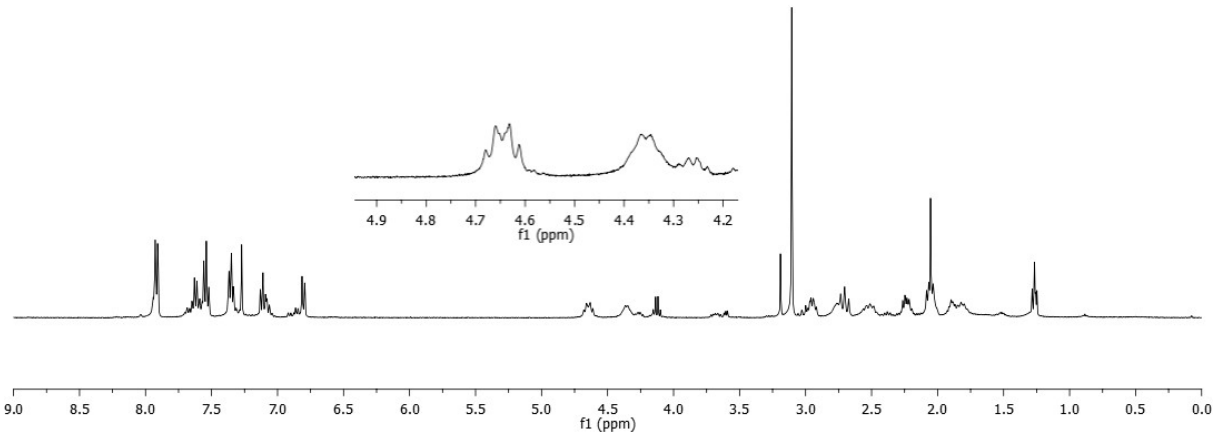




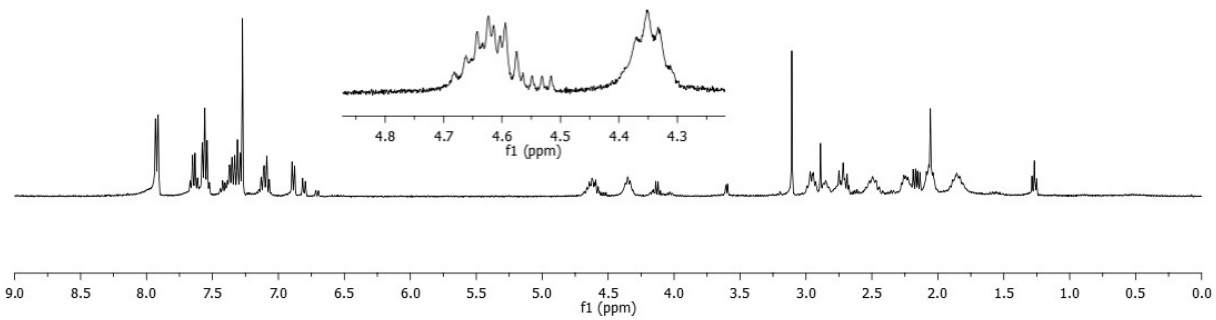
The vinyl sulfone **8**(0.20mmol, 33.64 mg, 1.0 eq.), the *N*-methyl isatin **2a**(0.30 mmol, 48.34 mg, 1.5 eq.) and the *L*-Proline (0.36mmol, 41.45 mg, 1.8 eq.) were dissolved in 4 ml of CH_3CN. The reaction mixture was vigorously stirred at reflux for 3 hours. The purification of the complex mixture was attempt by column chromatography using EtOAc/MeOH/NH_4OHaq. Fractions were reported below.

Figure 6.

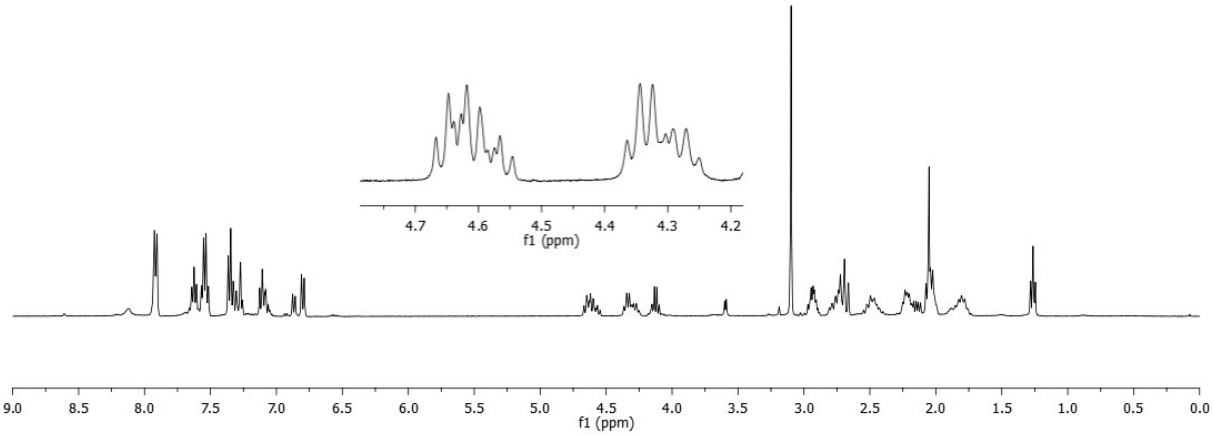
1st fraction



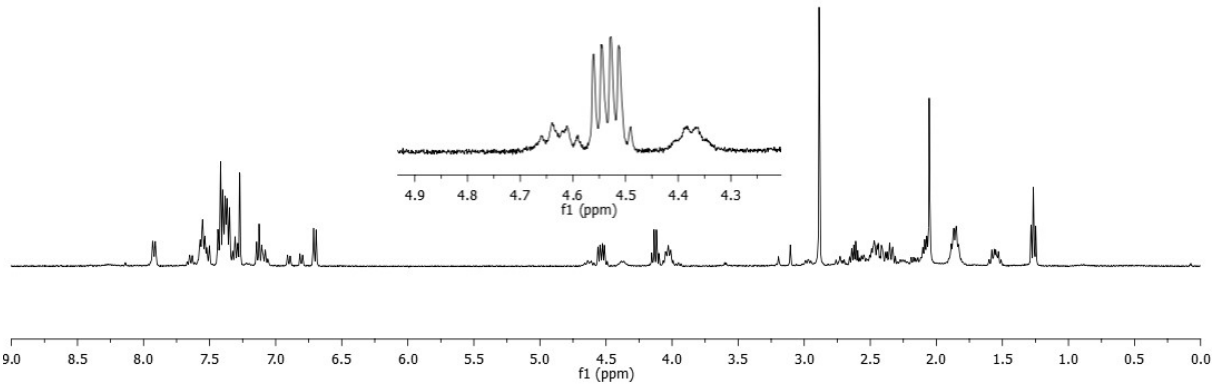
2nd fraction



3rd fraction



4th fraction



5th fraction

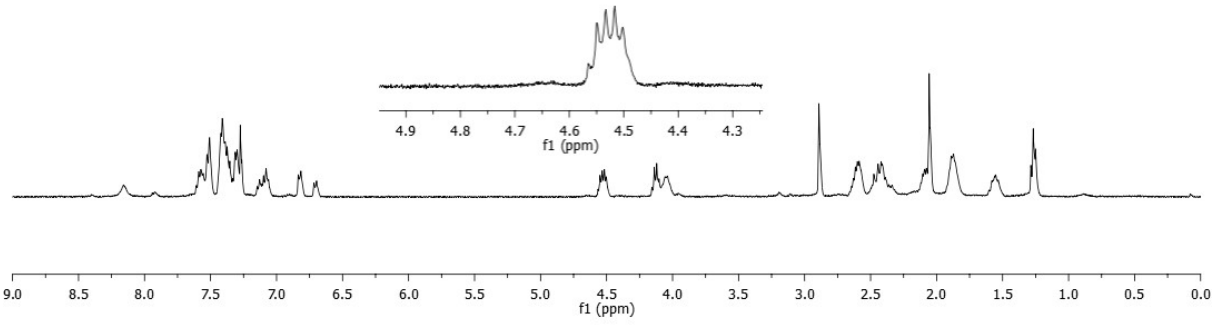


Figure 7. ^{1}H-NMR Spectrum of compound **4a** ($CDCl_3$, 400 MHz)

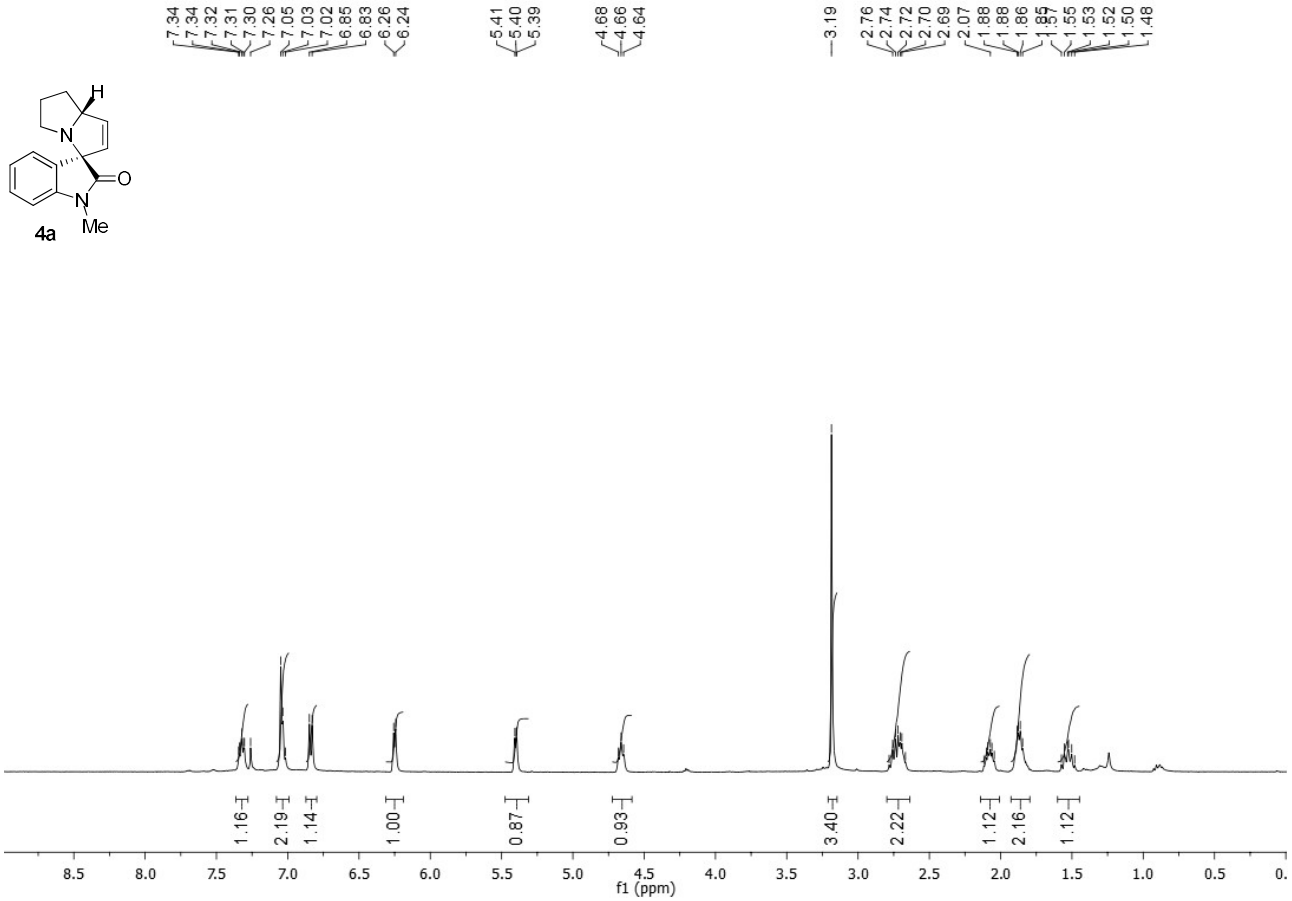


Figure 8. ^{13}C-NMR Spectrum of compound **4a** ($CDCl_3$, 100 MHz)

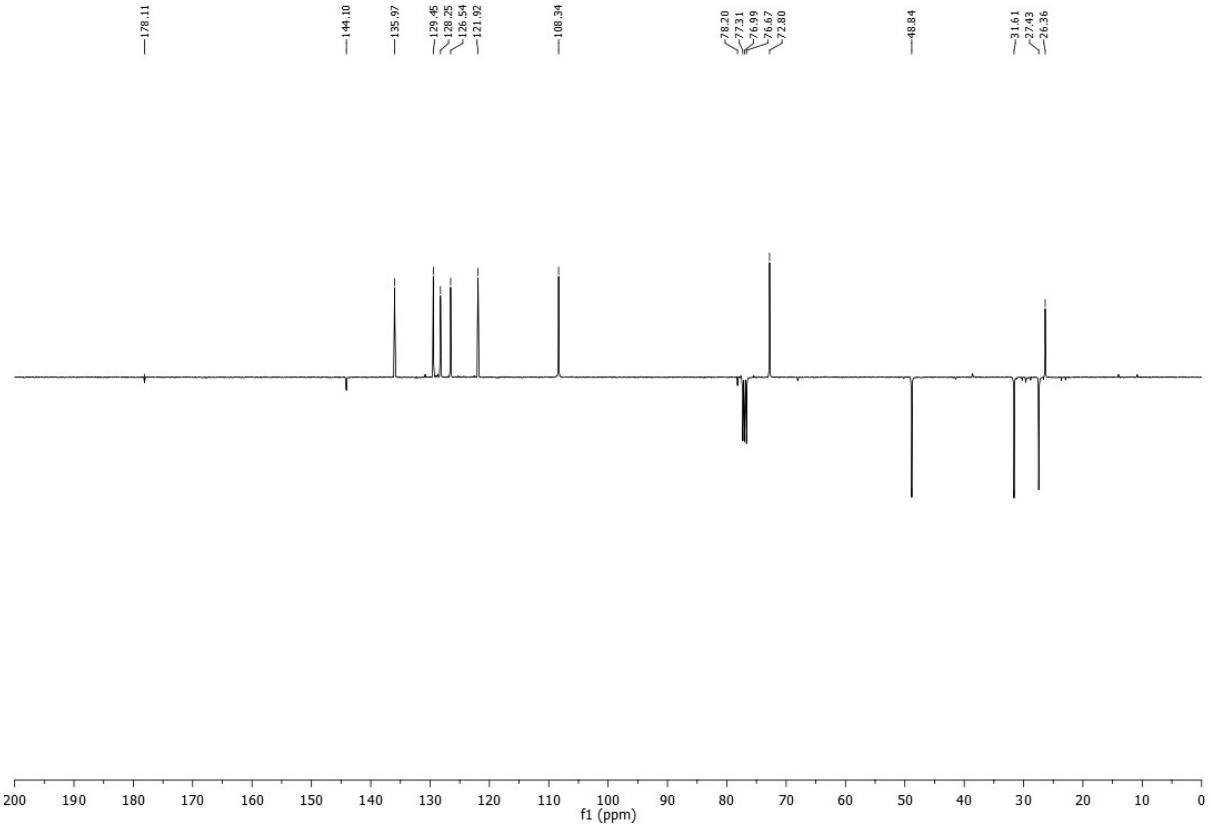


Figure 9. HETCOR (^{1}H-^{13}C) experiment for compound **4a**

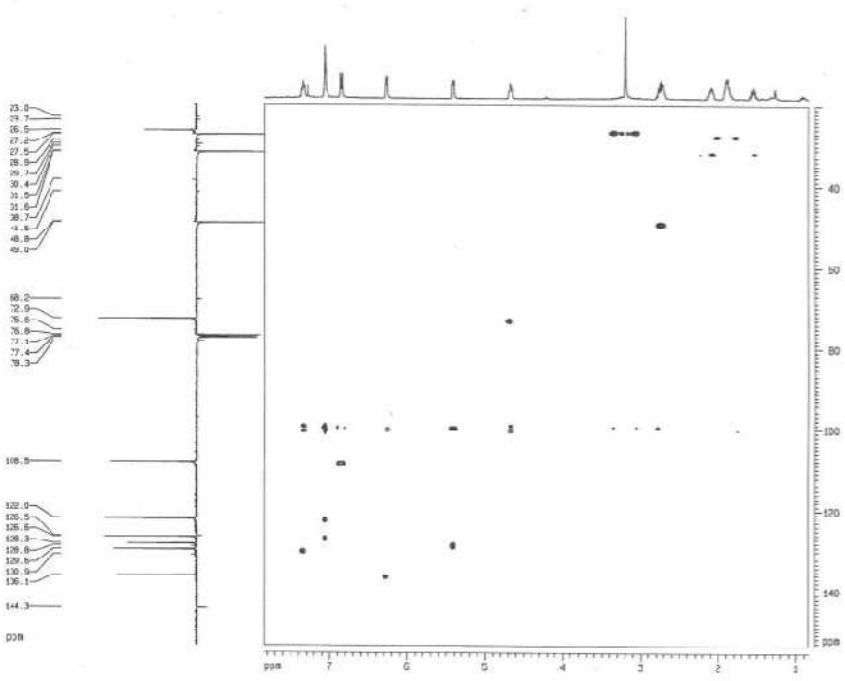
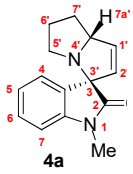


Figure 10. NOESY experiment for compound **4a**



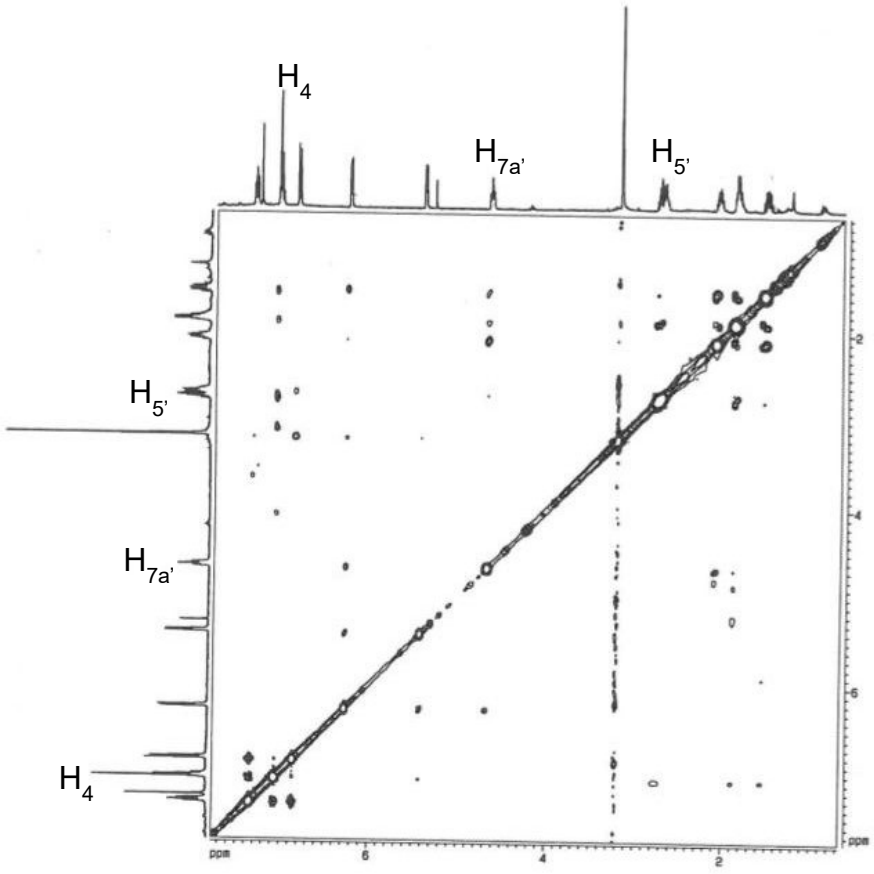


Figure 11. ^{1}H-NMR Spectrum of compound **4b** ($CDCl_3$, 400 MHz)

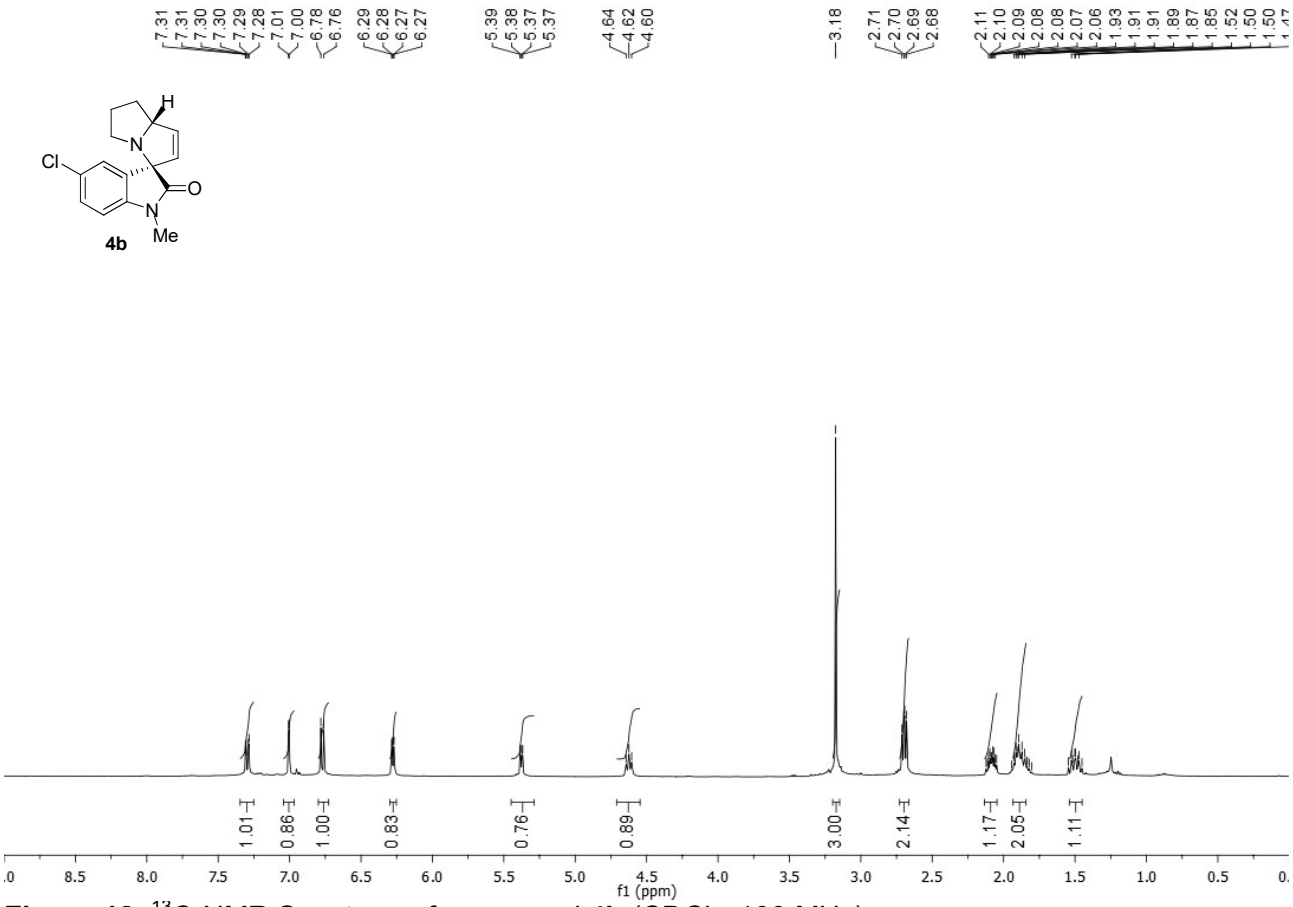


Figure 12. ^{13}C-NMR Spectrum of compound **4b** ($CDCl_3$, 100 MHz)

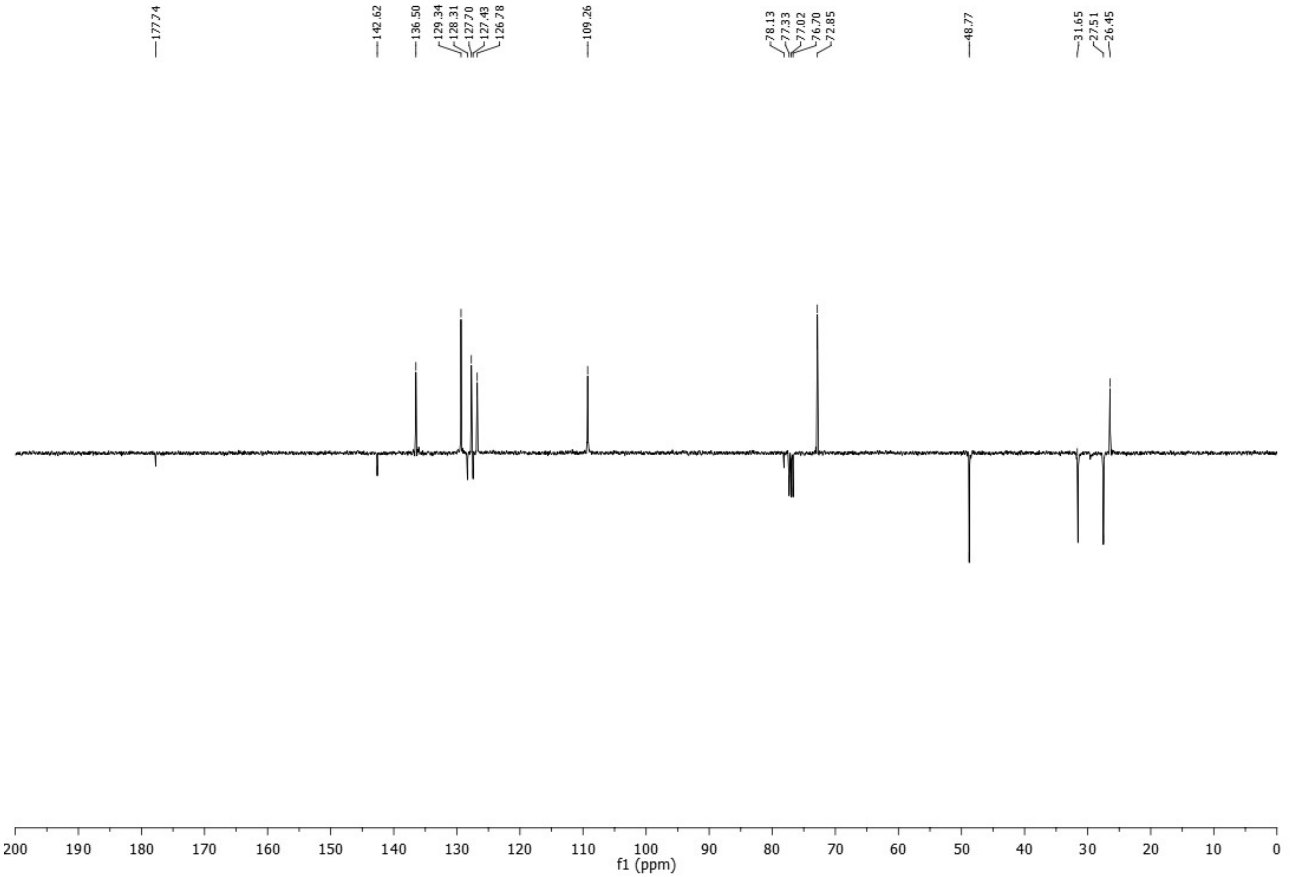


Figure 13. ^{1}H-NMR Spectrum of compound **4c** ($CDCl_3$, 400 MHz)

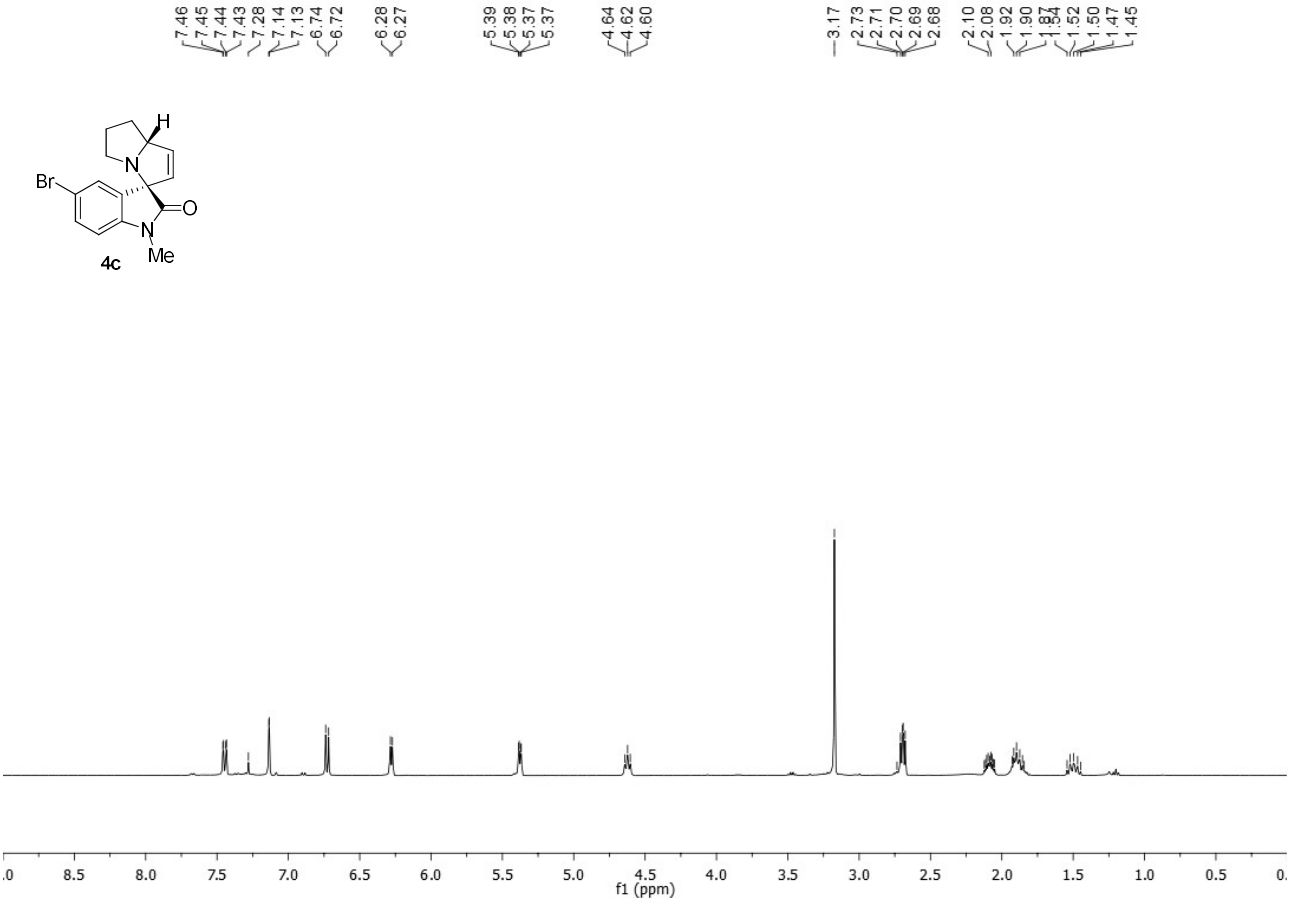


Figure 14. ^{13}C-NMR Spectrum of compound **4c** ($CDCl_3$, 100 MHz)

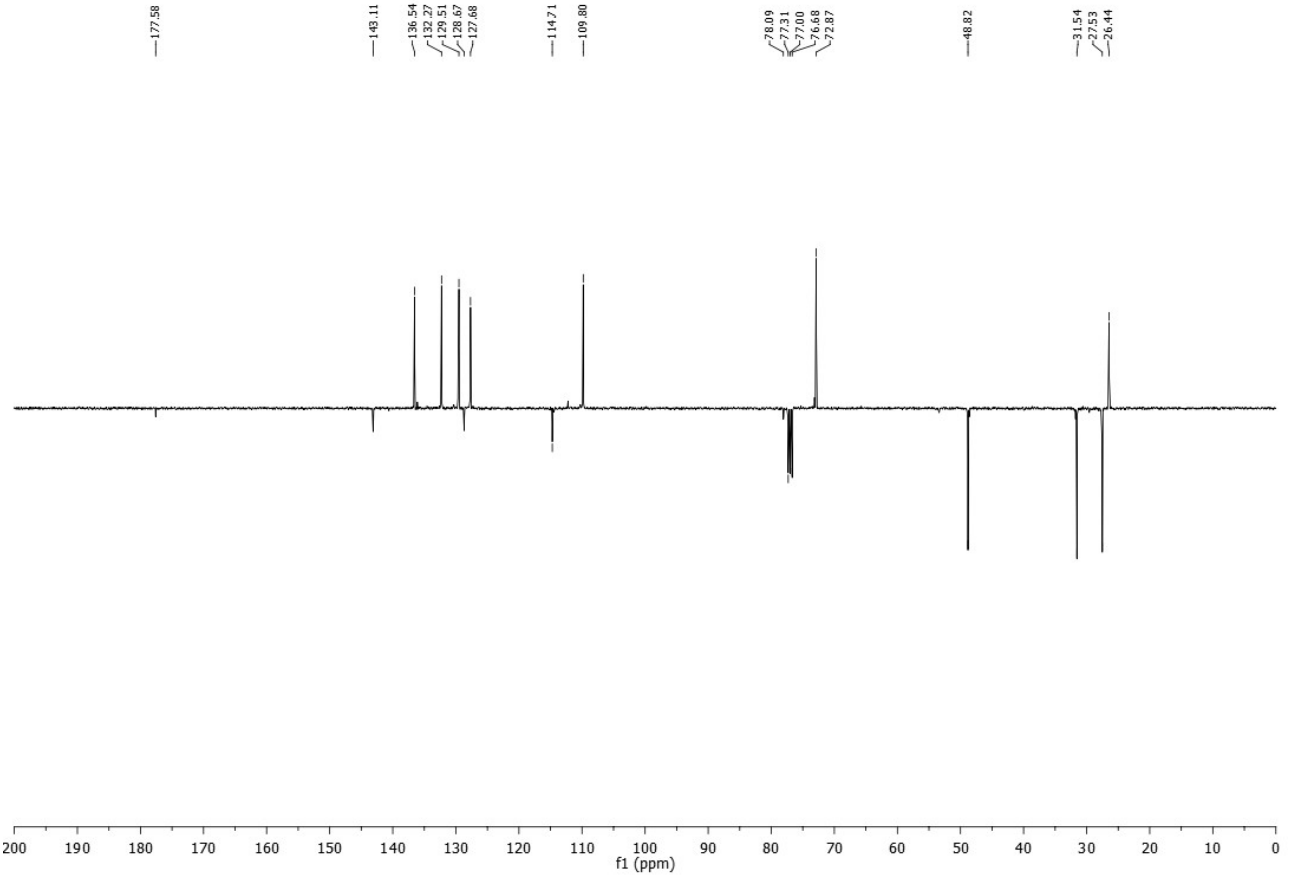


Figure 15. ^{1}H-NMR Spectrum of compound **4d** ($CDCl_3$, 400 MHz)

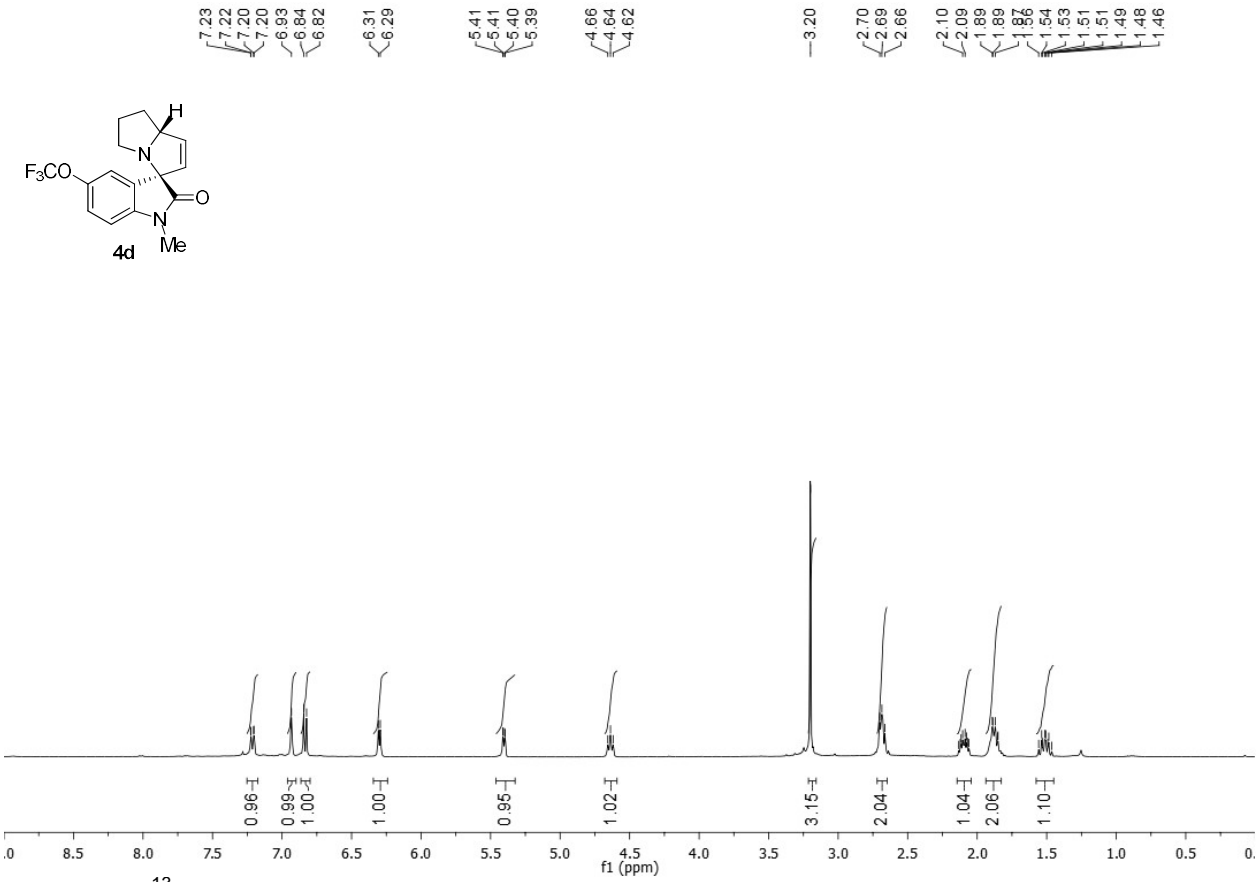


Figure 16. ^{13}C-NMR Spectrum of compound **4d** ($CDCl_3$, 100 MHz)

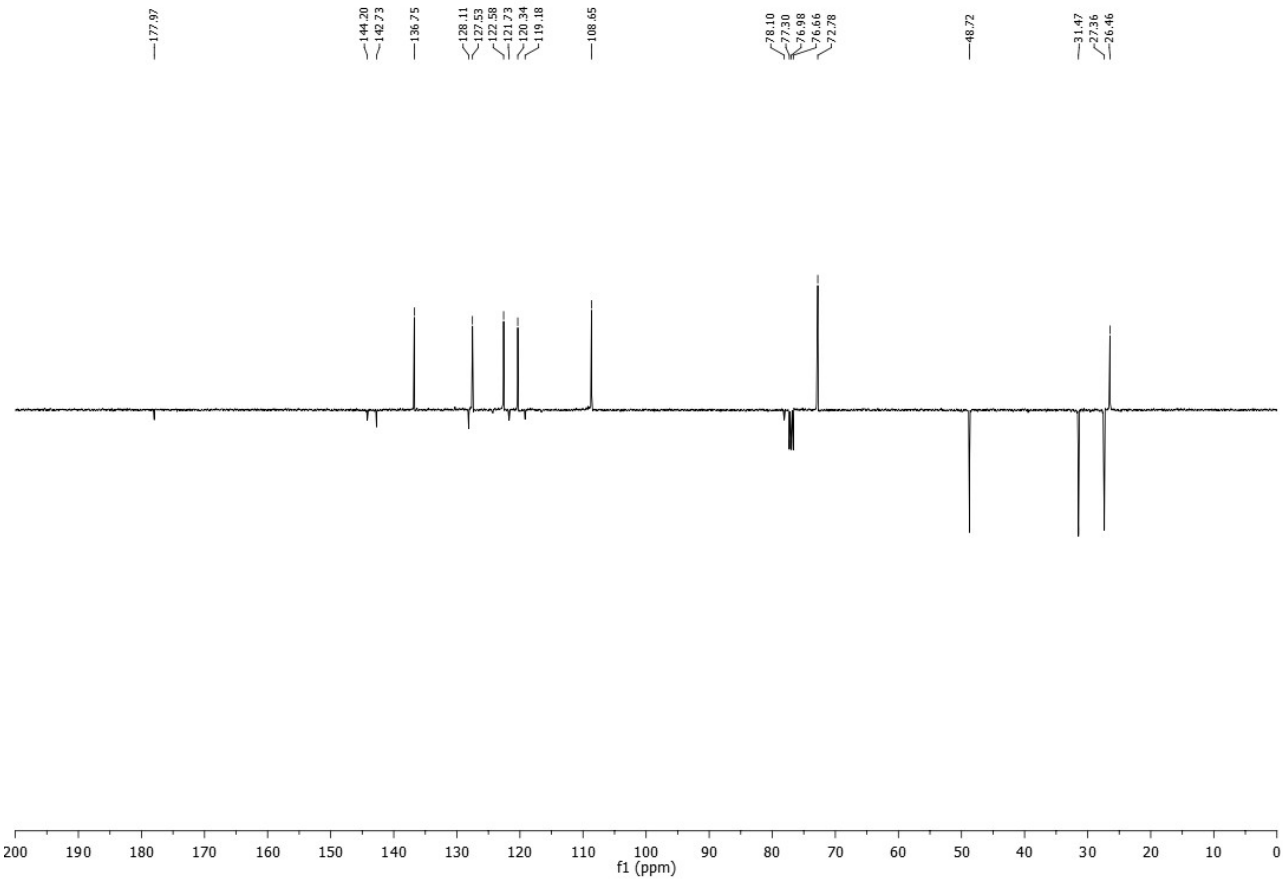


Figure 17. ^{1}H-NMR Spectrum of compound **4e** ($CDCl_3$, 400 MHz)

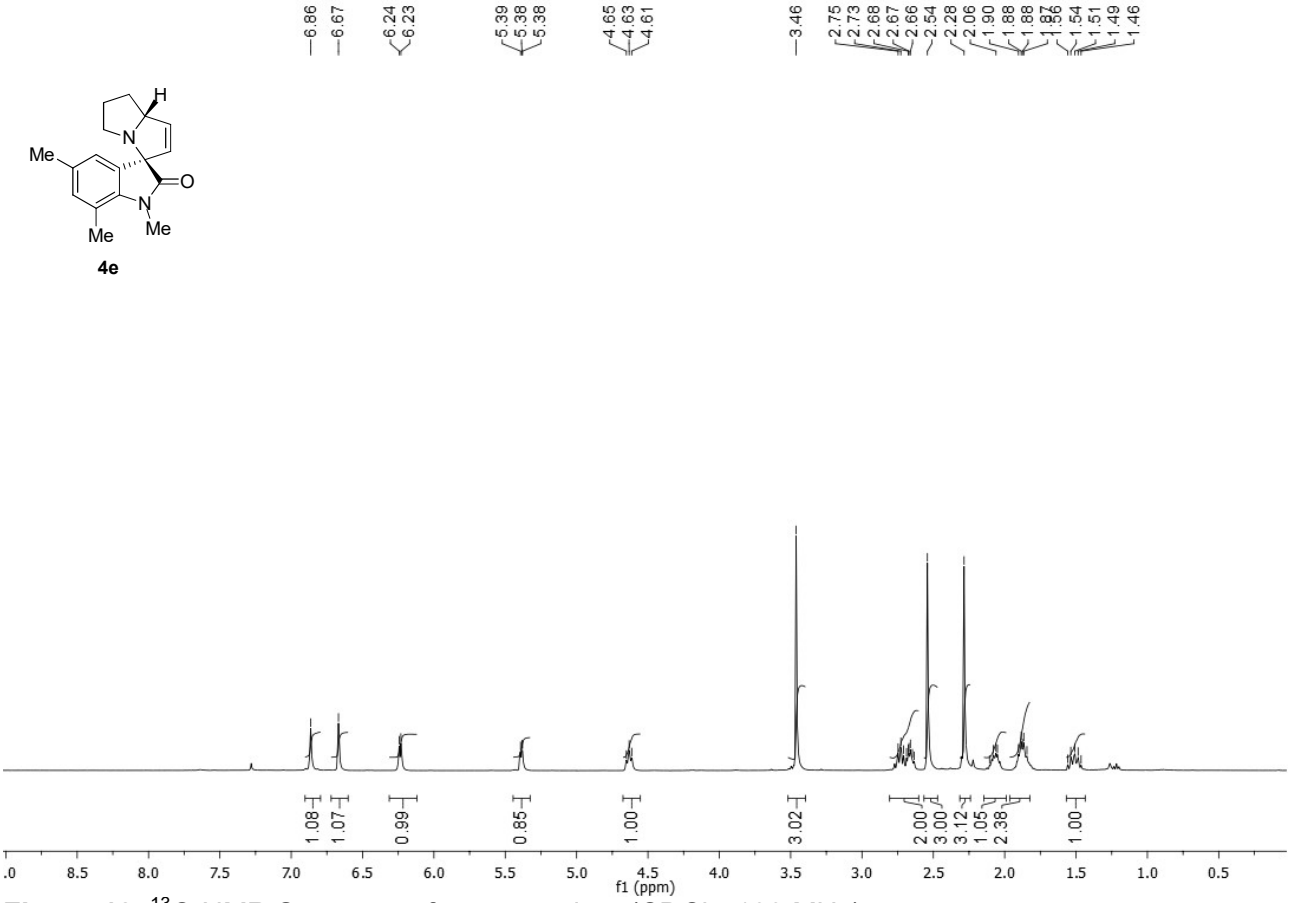


Figure 18. ^{13}C-NMR Spectrum of compound **4e** ($CDCl_3$, 100 MHz)

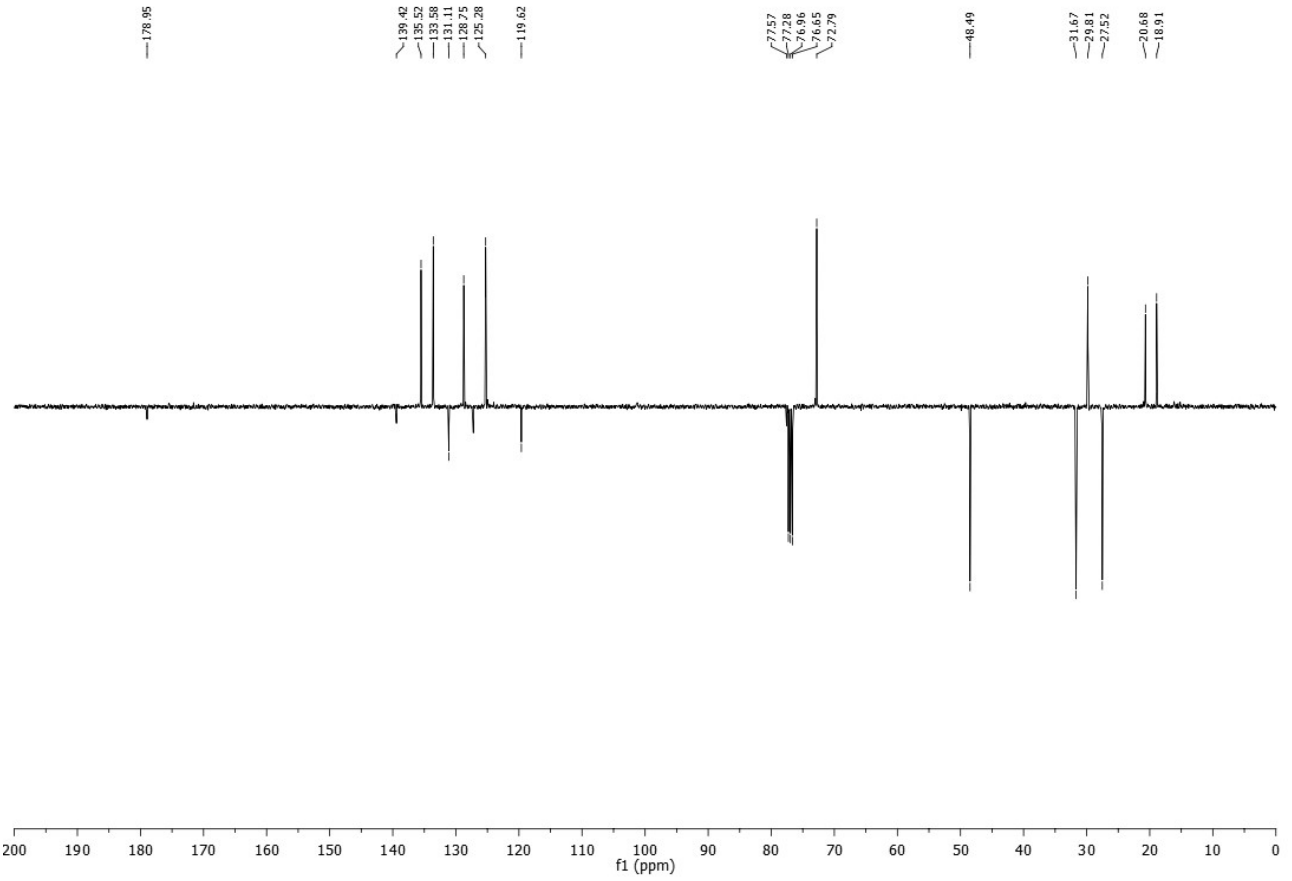


Figure 19. ^{1}H-NMR Spectrum of compound **4f** ($CDCl_3$, 400 MHz)

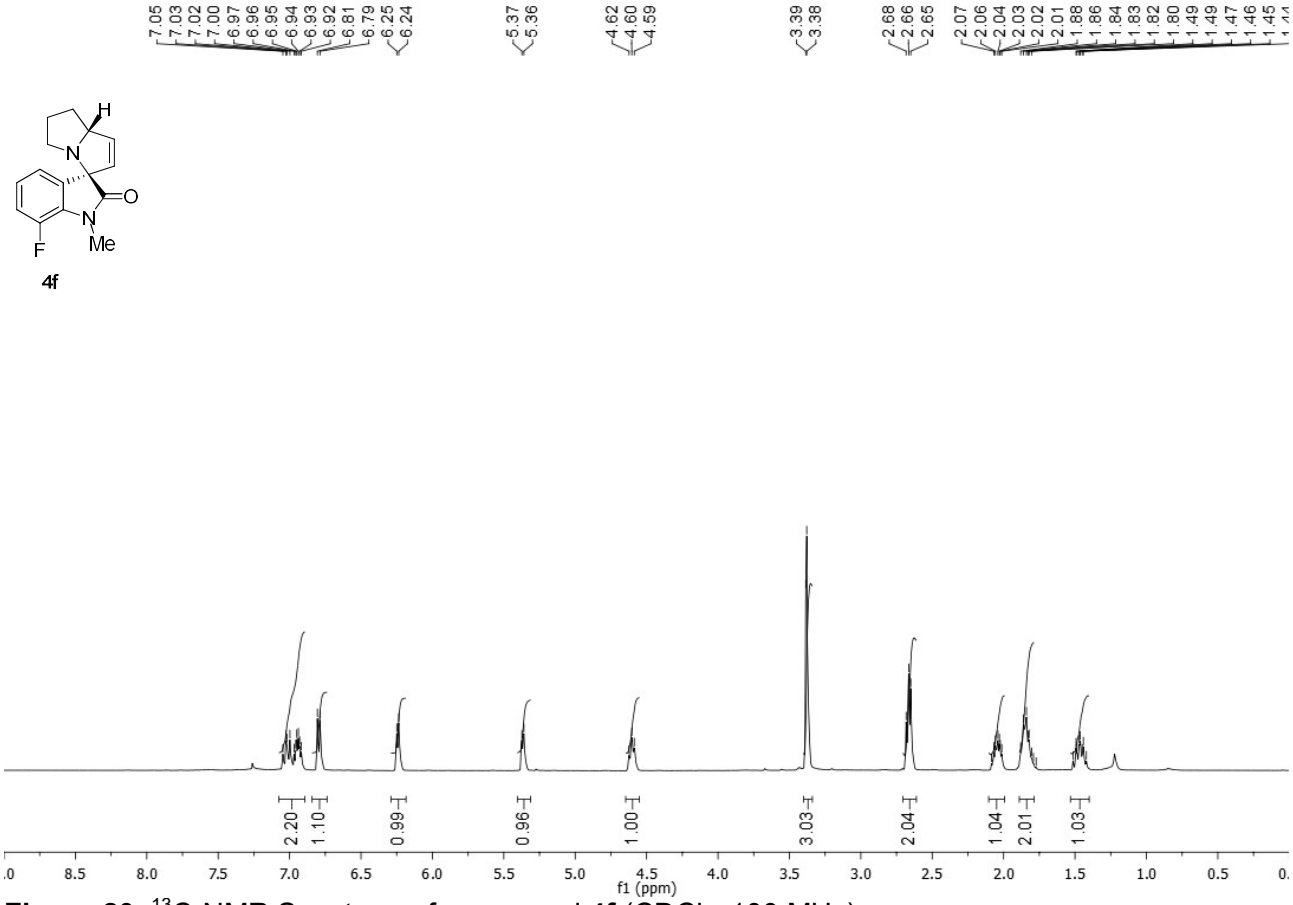


Figure 20. ^{13}C-NMR Spectrum of compound **4f** ($CDCl_3$, 100 MHz)

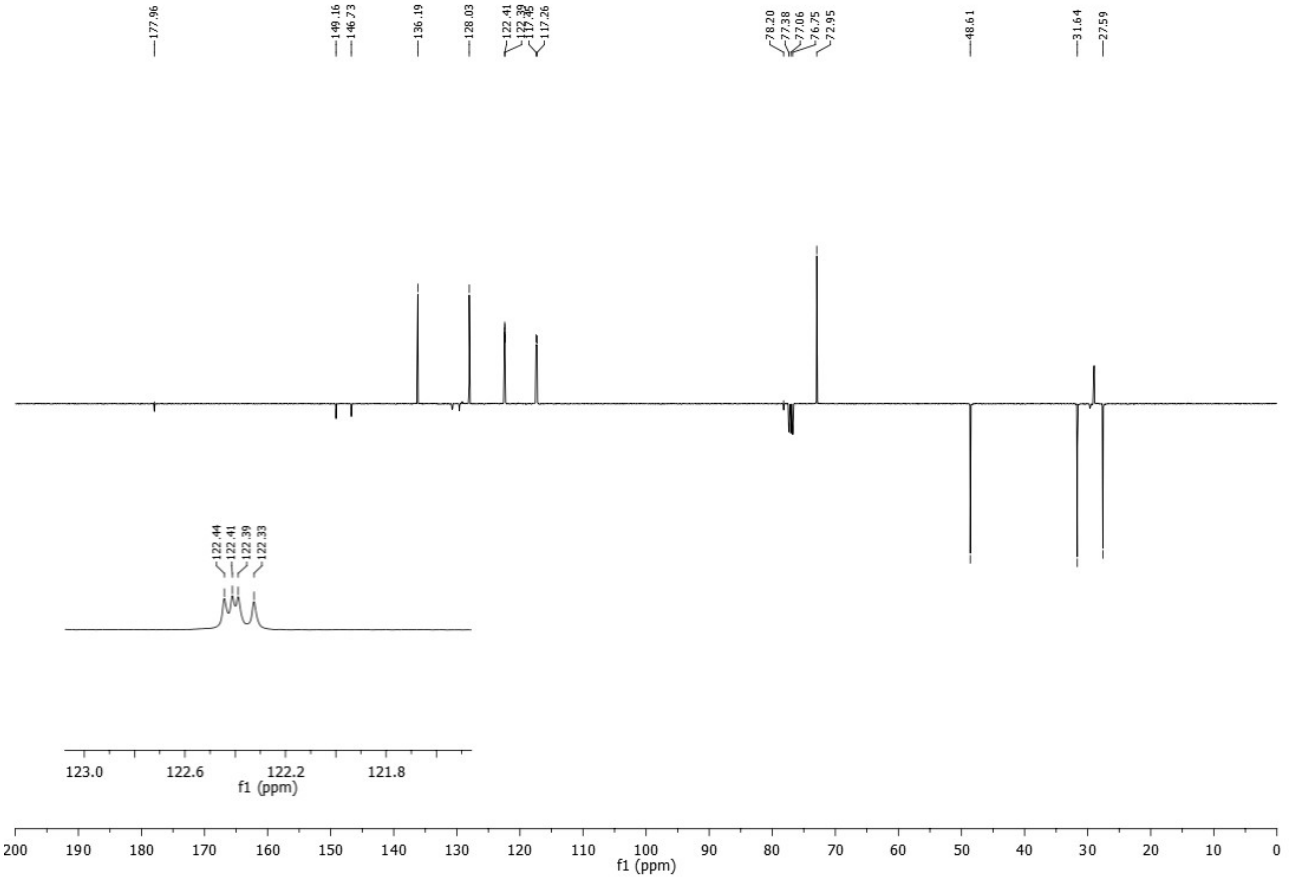


Figure 21. ^{1}H-NMR Spectrum of compound **4g** ($CDCl_3$, 400 MHz)

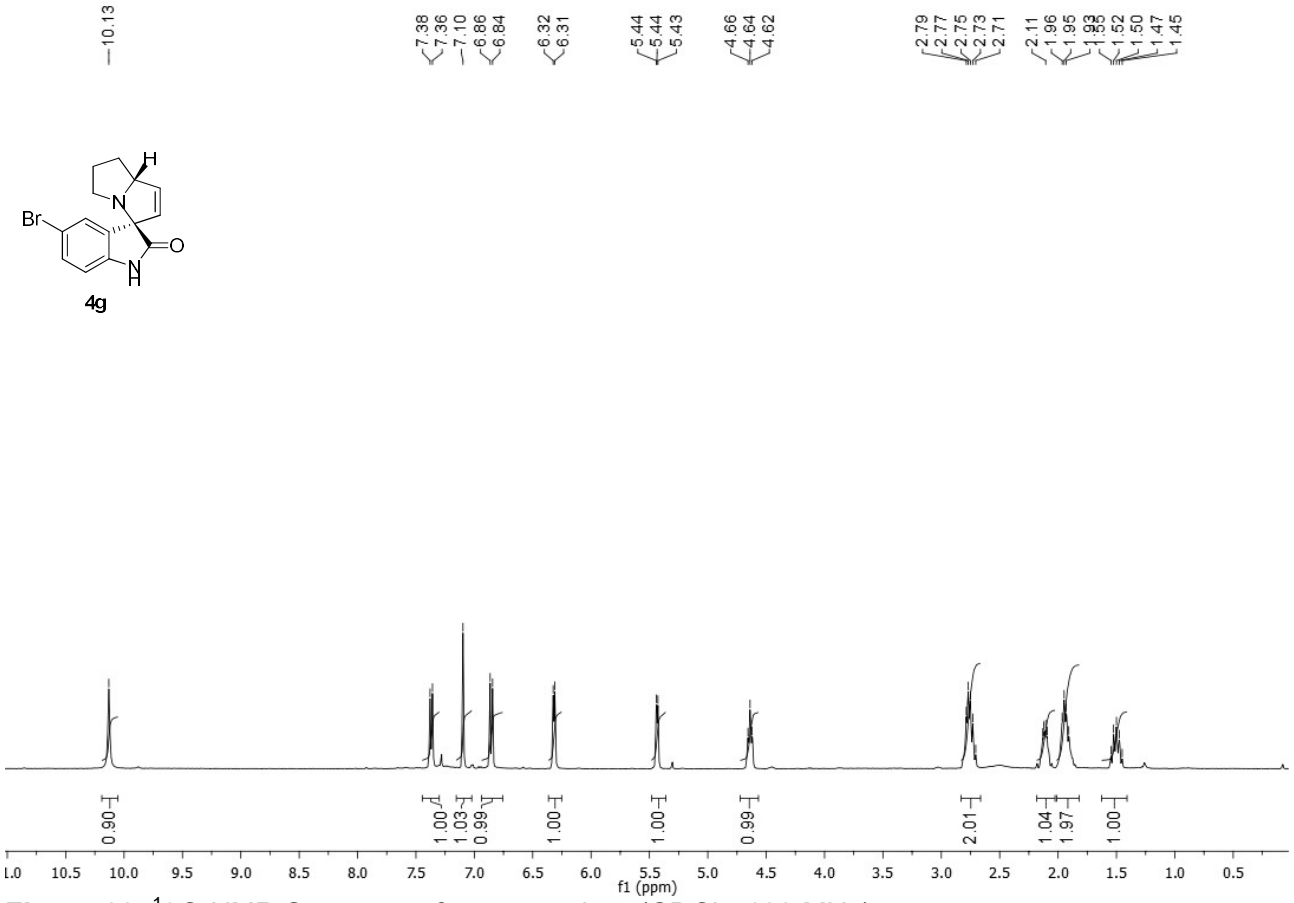


Figure 22. ^{1}3C-NMR Spectrum of compound **4g** ($CDCl_3$, 100 MHz)

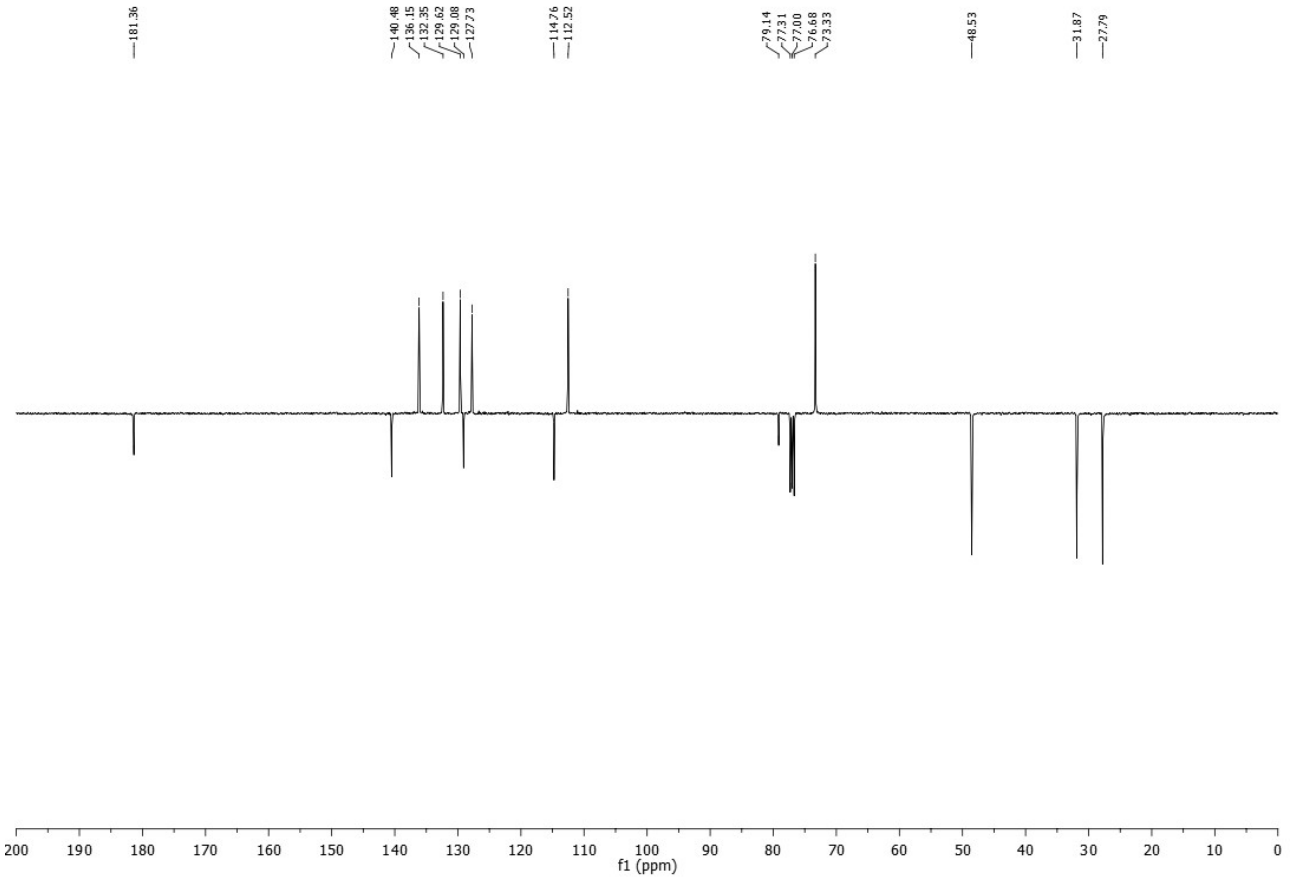


Figure 23. ^{1}H-NMR Spectrum of compound **4h** ($CDCl_3$, 400 MHz)

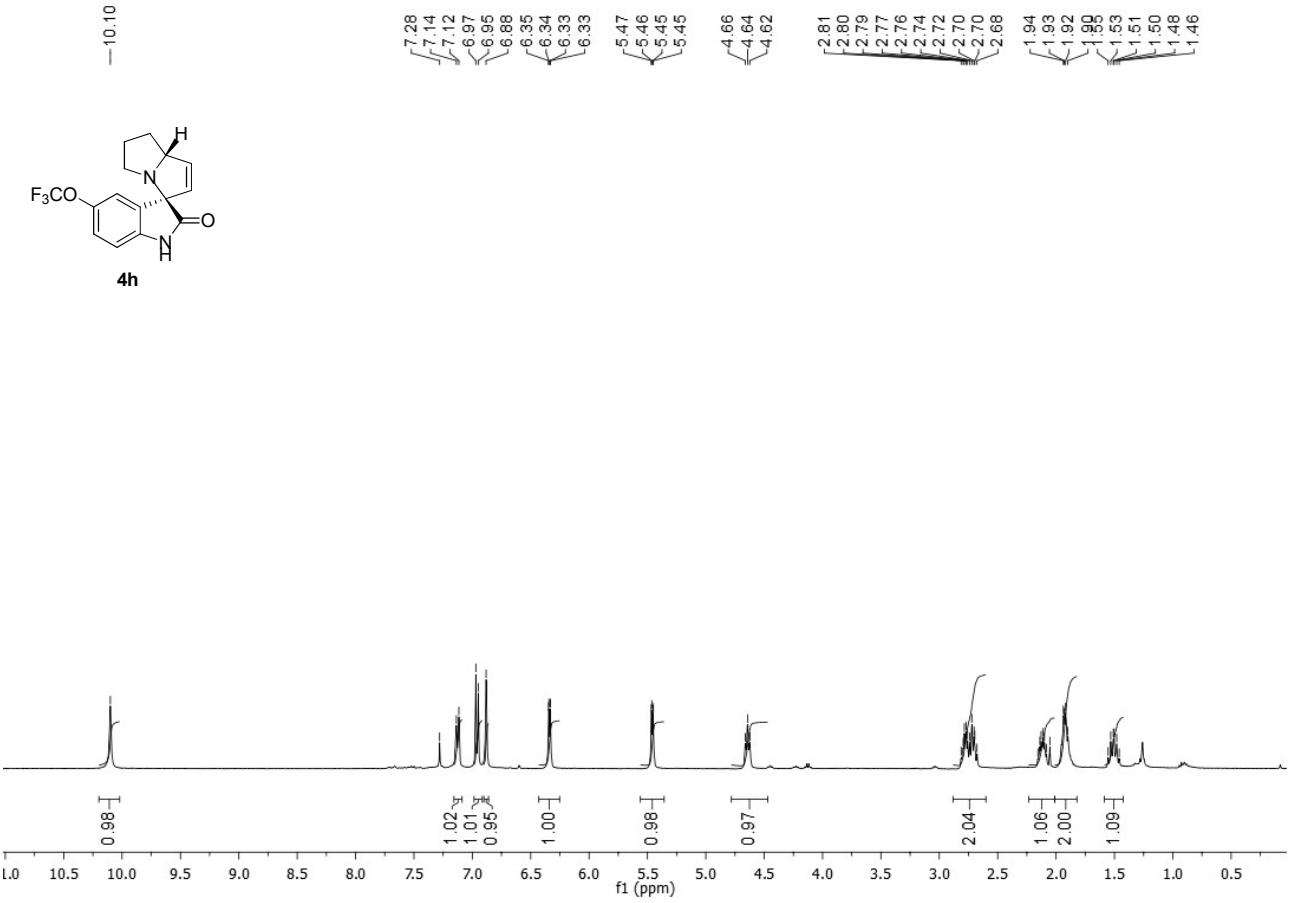


Figure 24. ^{1}3C-NMR Spectrum of compound **4h** ($CDCl_3$, 100 MHz)

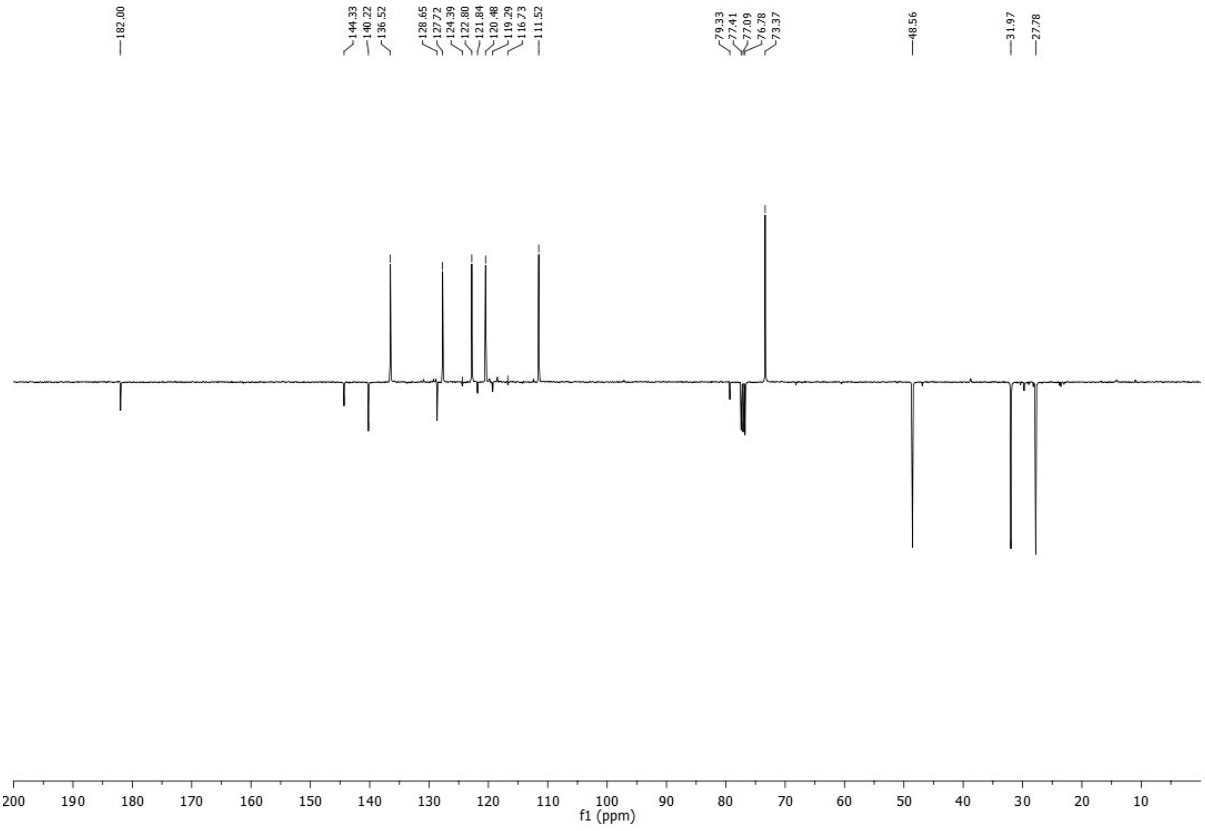


Figure 25. ^{1}H-NMR Spectrum of compound **4i** (DMSO-d_6, 400 MHz)

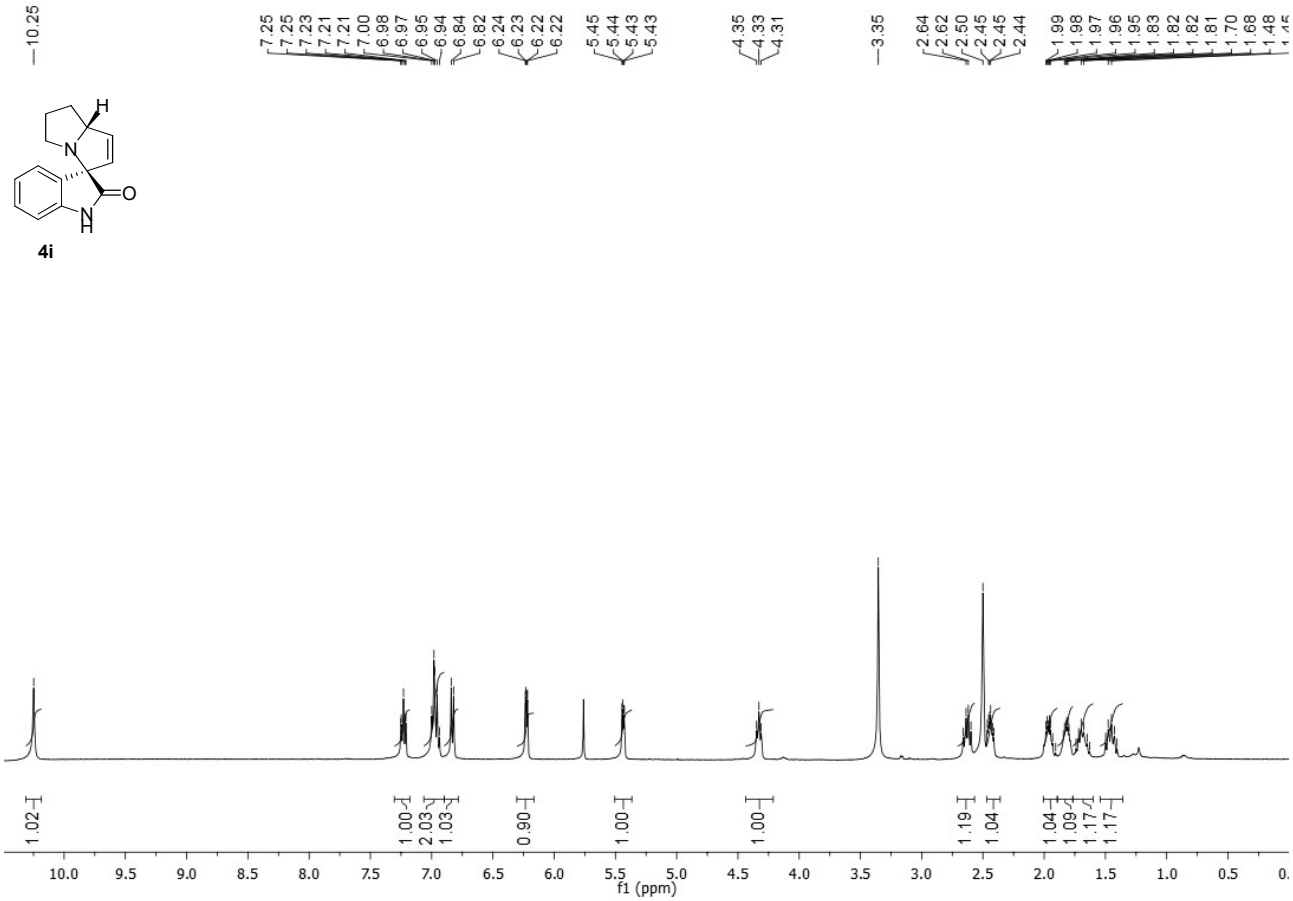


Figure 26. ^{13}C-NMR Spectrum of compound **4i** (DMSO-d_6, 100 MHz)

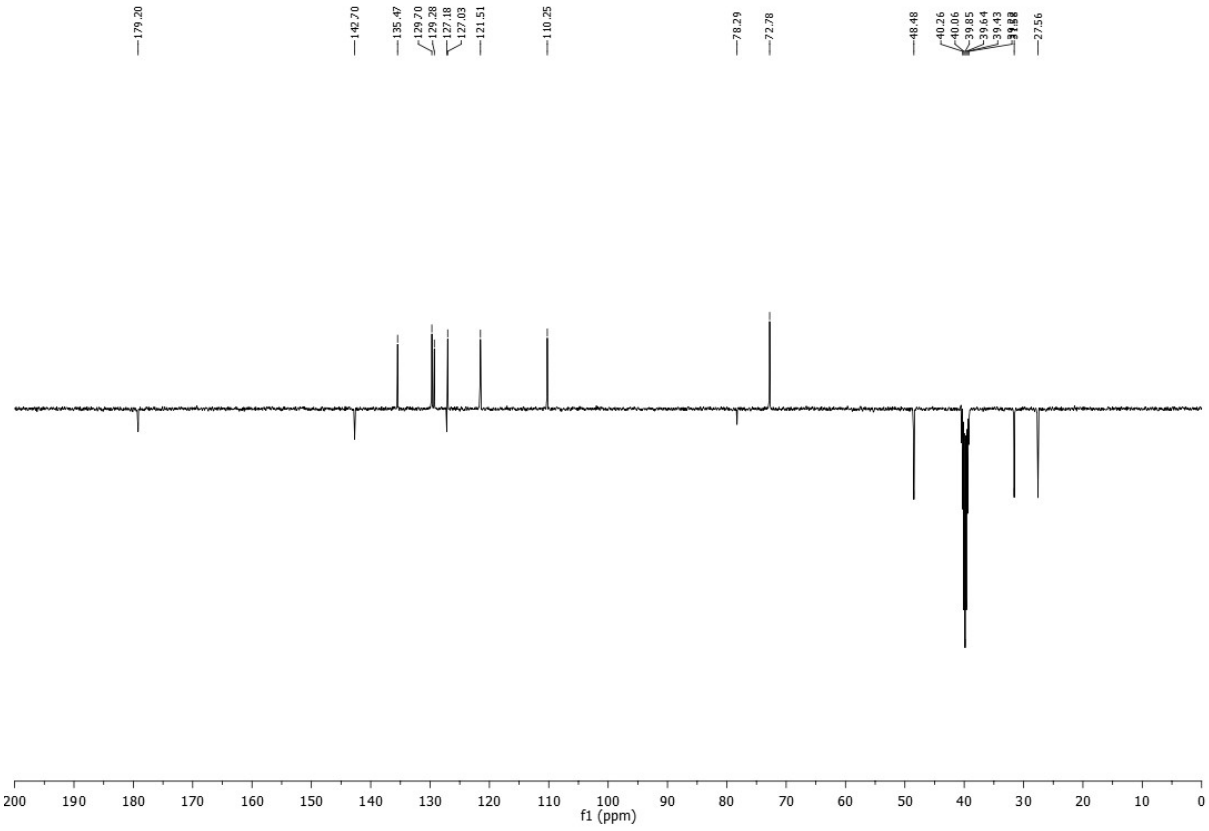


Figure 27. ^{1}H-NMR Spectrum of compound **4j** ($CDCl_3$, 400 MHz)

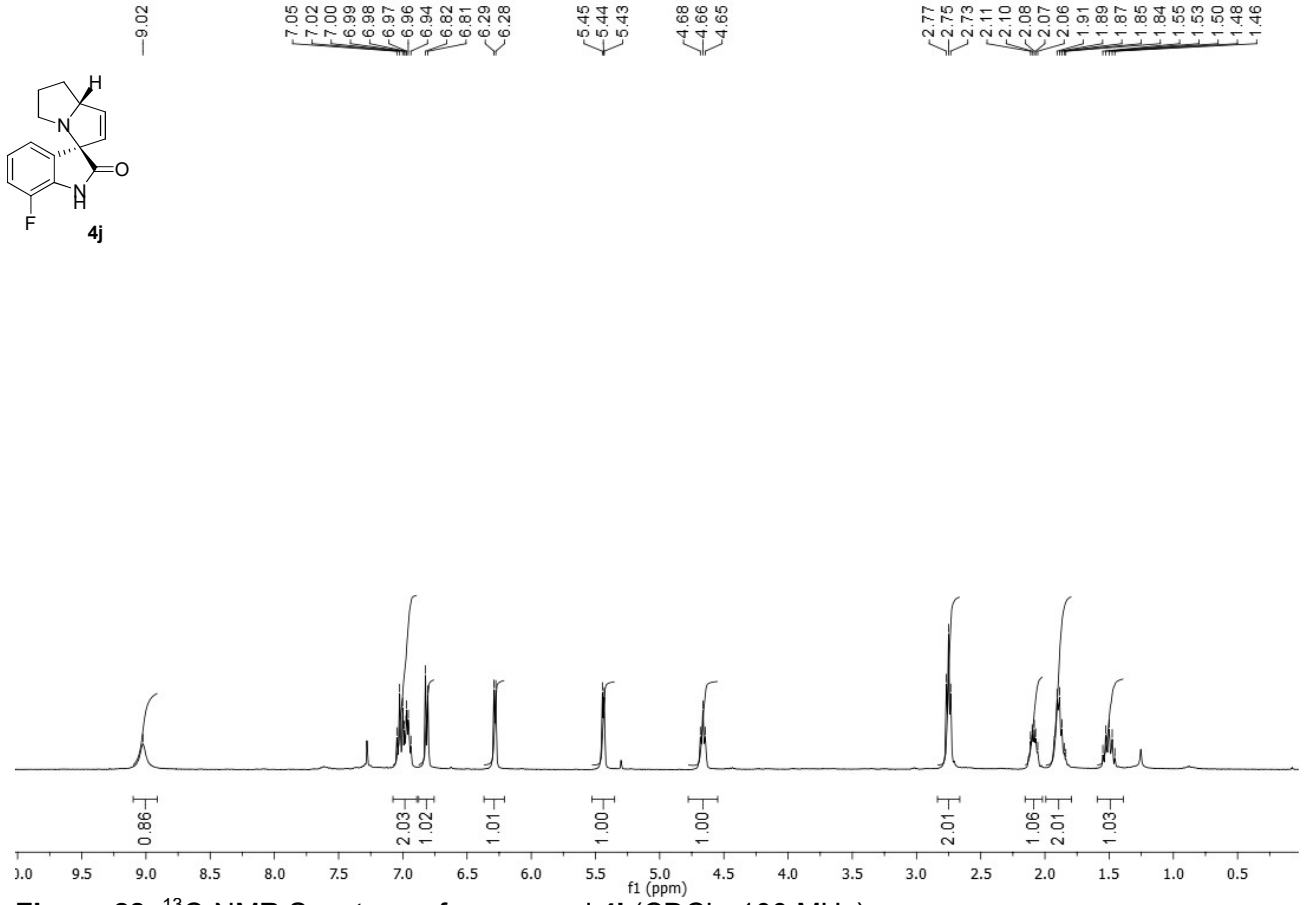


Figure 28. ^{13}C-NMR Spectrum of compound **4j** ($CDCl_3$, 100 MHz)

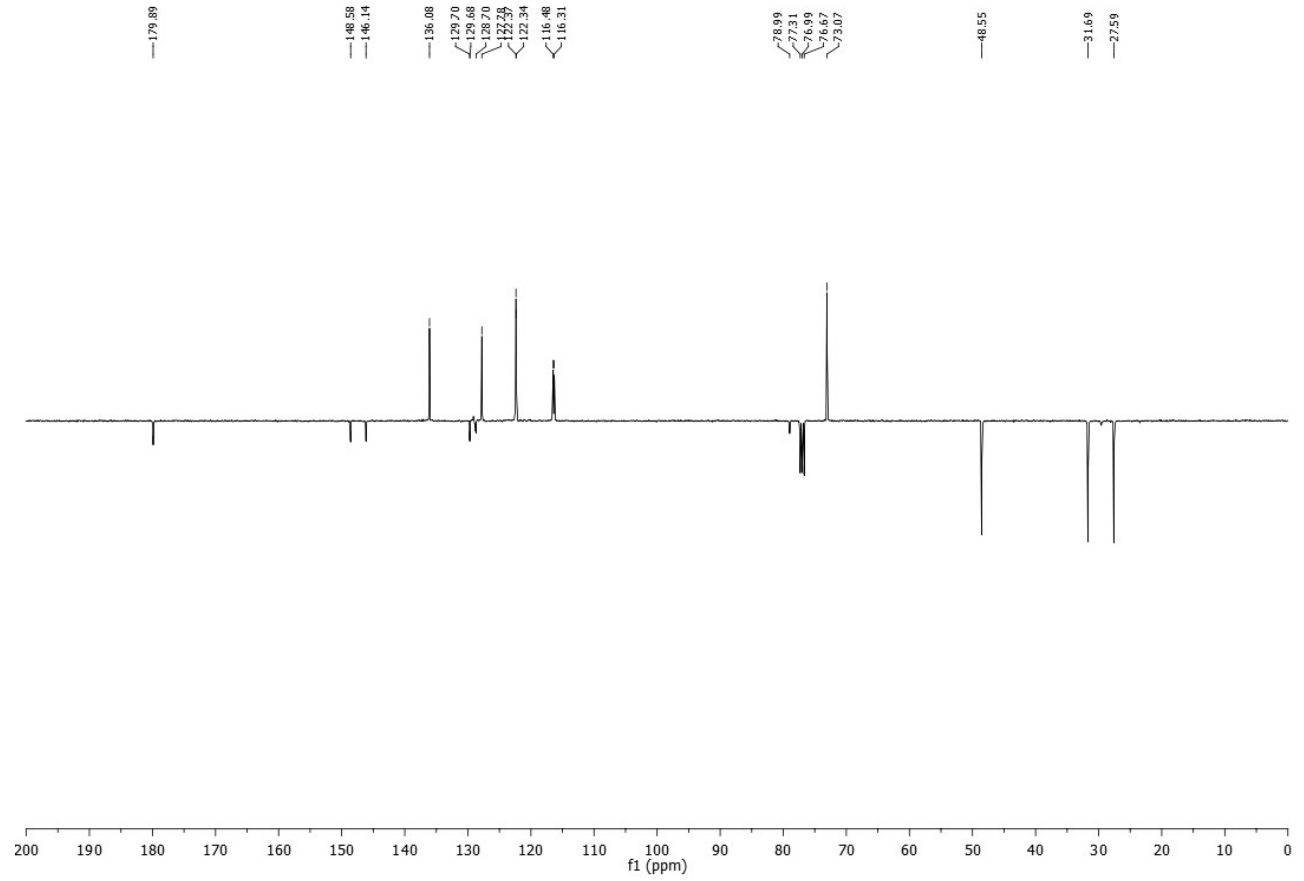


Figure 29. ^{1}H-NMR Spectrum of compound **4k** (DMSO-d_6, 400 MHz)

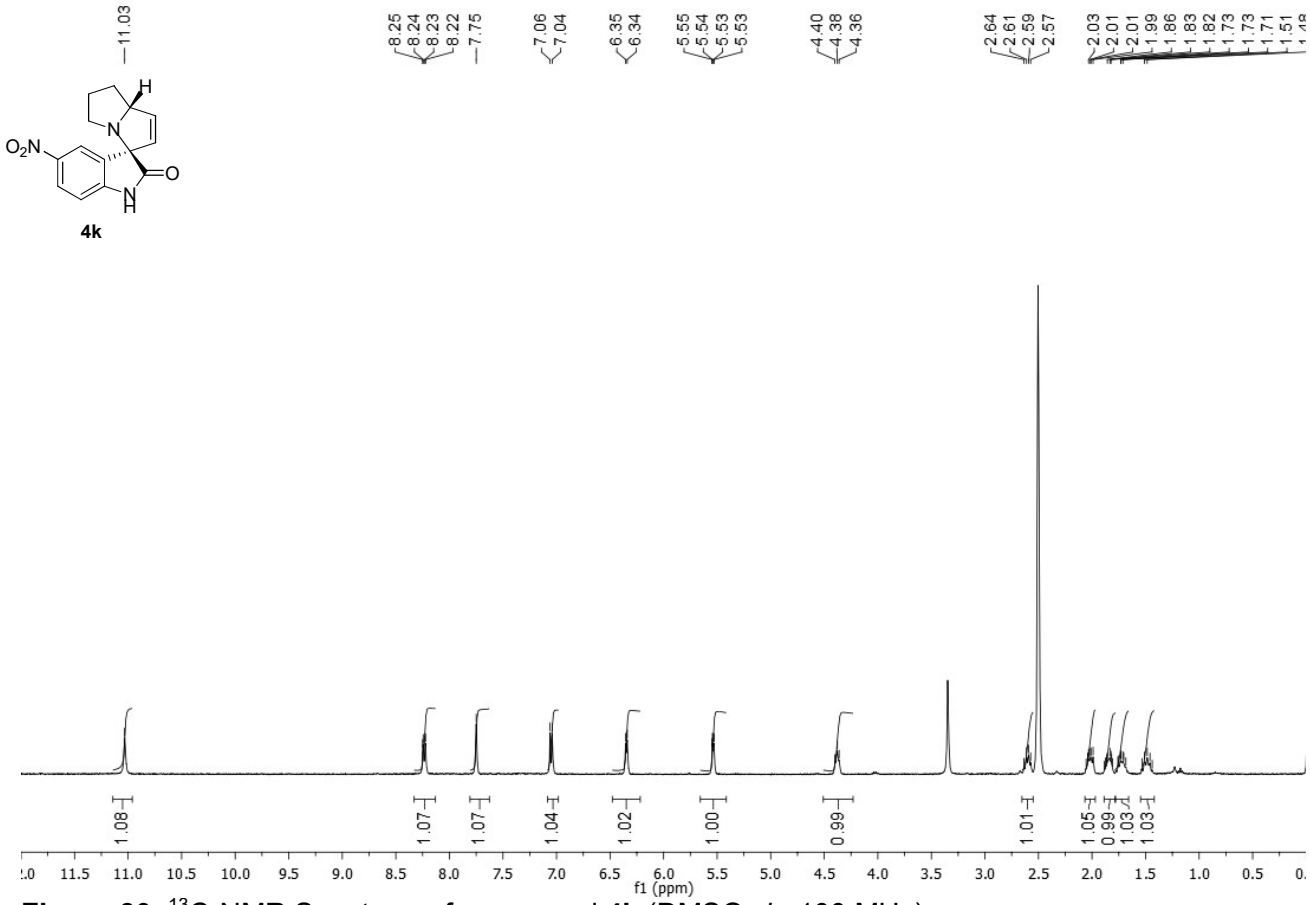


Figure 30. ^{13}C-NMR Spectrum of compound **4k** (DMSO-d_6, 100 MHz)

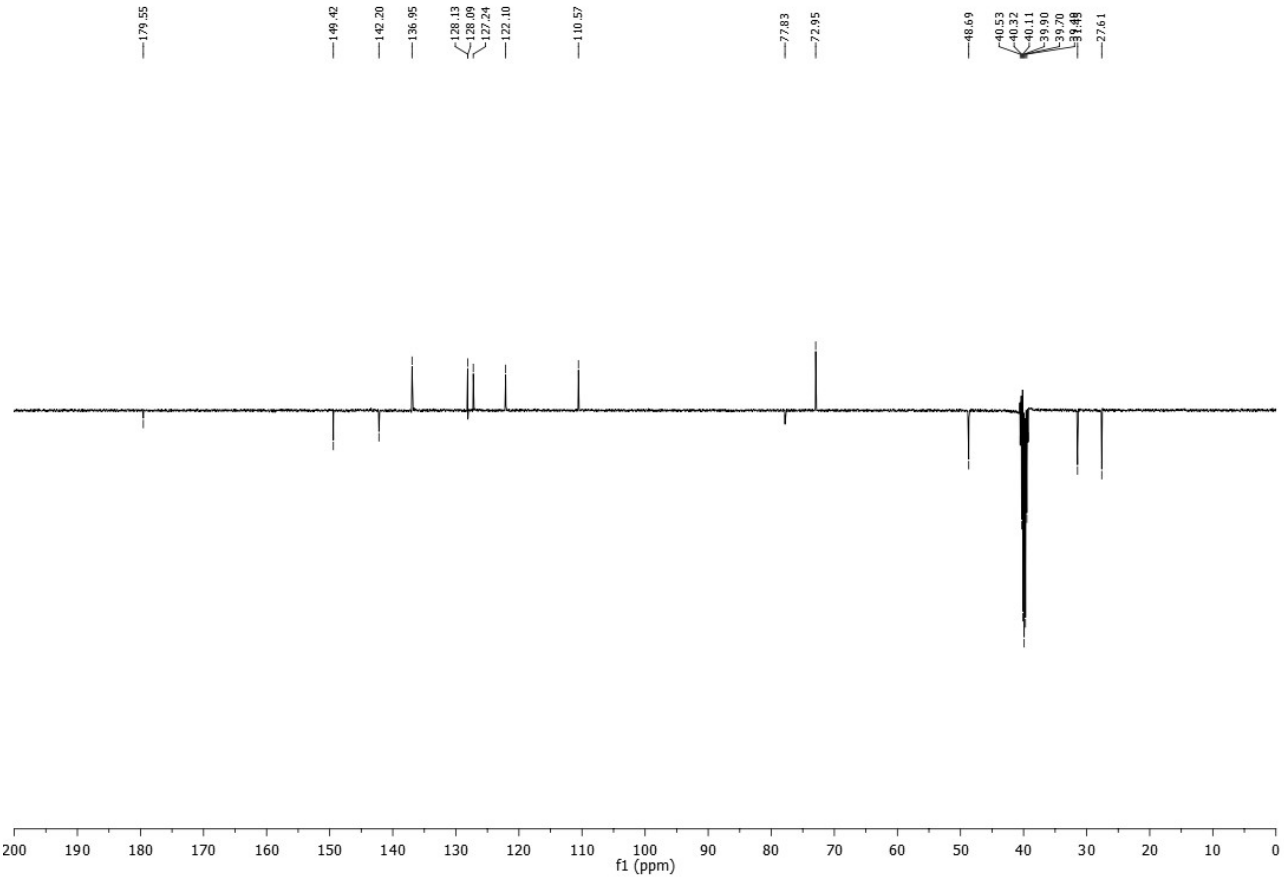


Figure 31. ^{1}H-NMR Spectrum of compound **4l** ($CDCl_3$, 400 MHz)

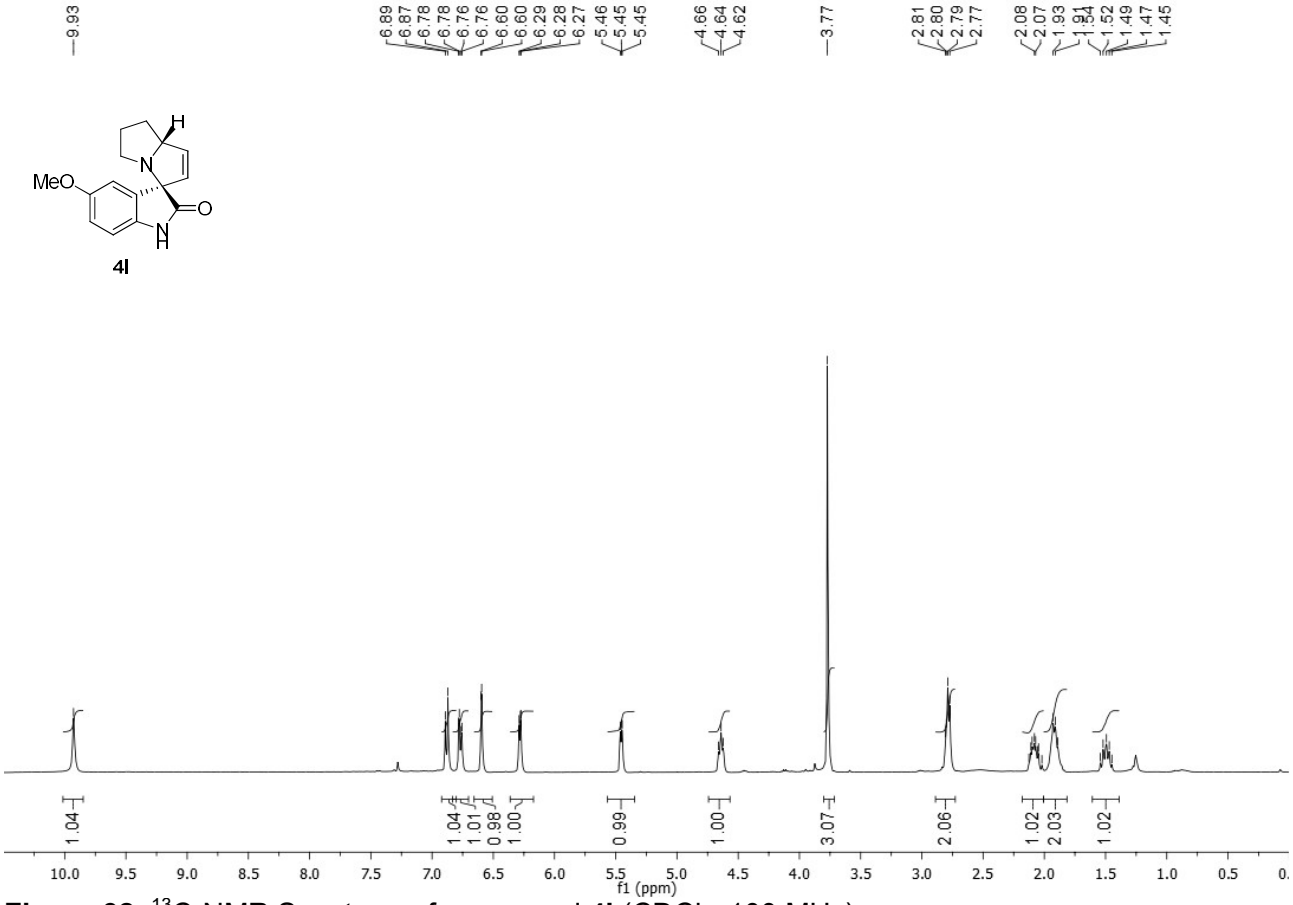


Figure 32. ^{13}C-NMR Spectrum of compound **4l** ($CDCl_3$, 100 MHz)

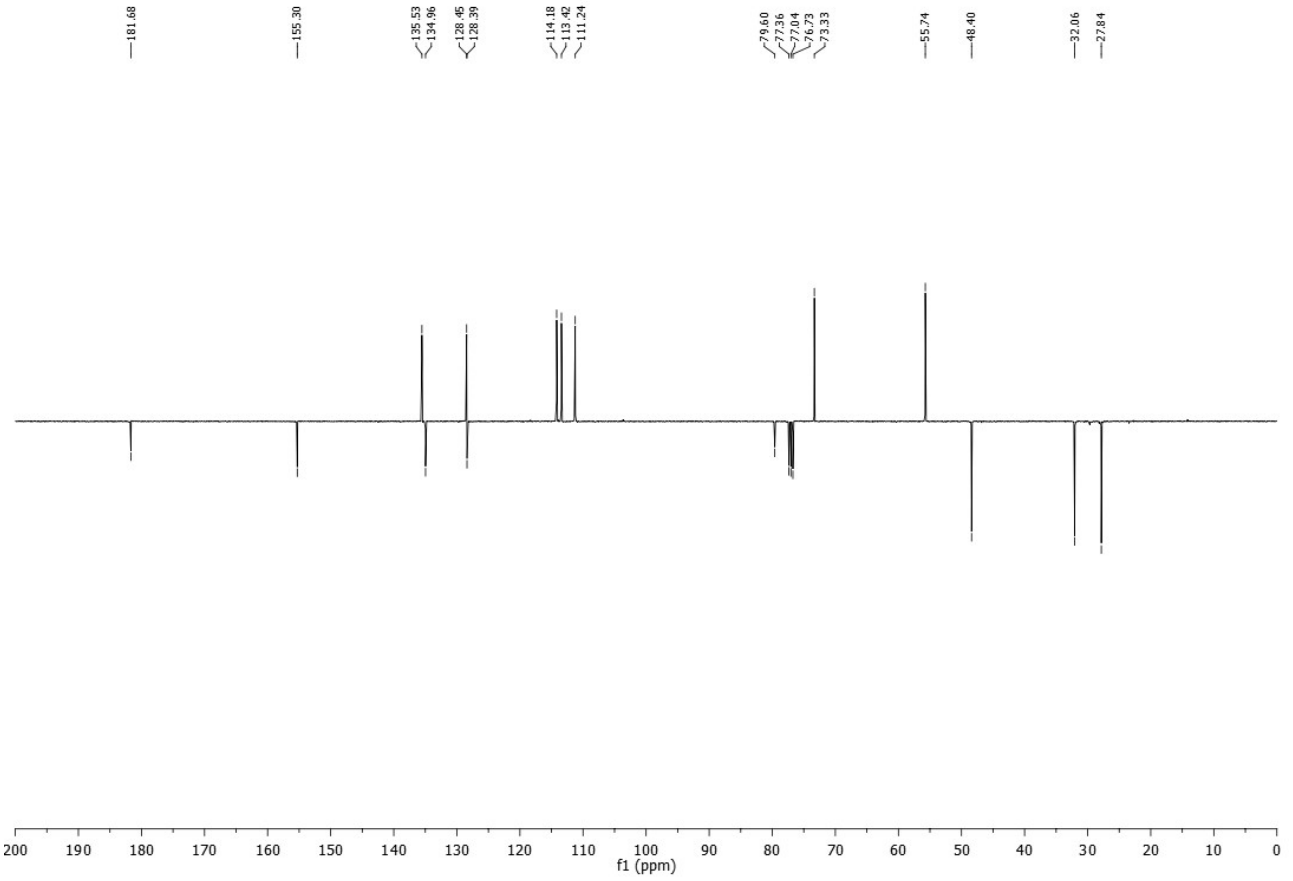


Figure 33. ^{1}H-NMR Spectrum of compound **4m** ($CDCl_3$, 400 MHz)

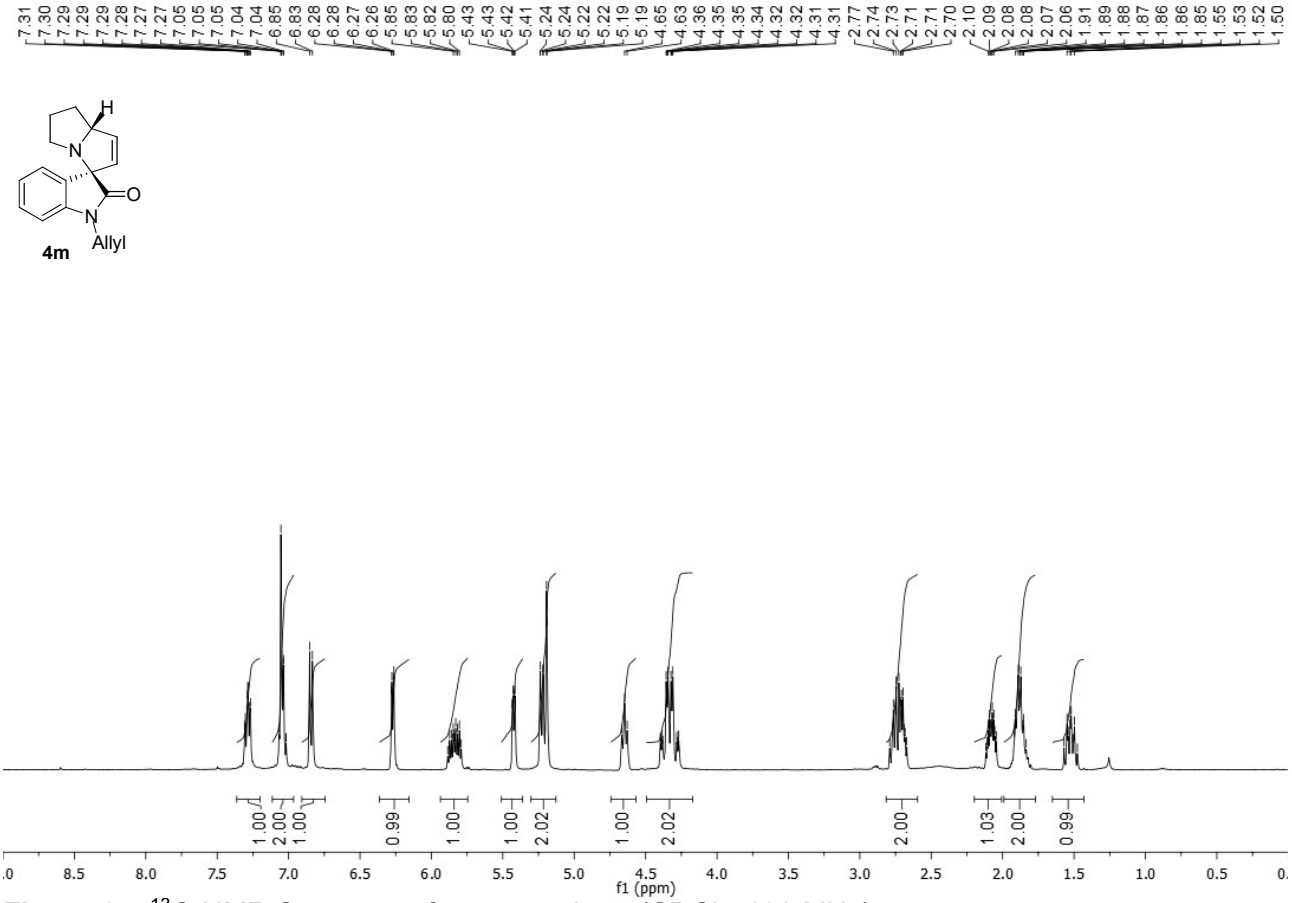


Figure 34. ^{13}C-NMR Spectrum of compound **4m** ($CDCl_3$, 100 MHz)

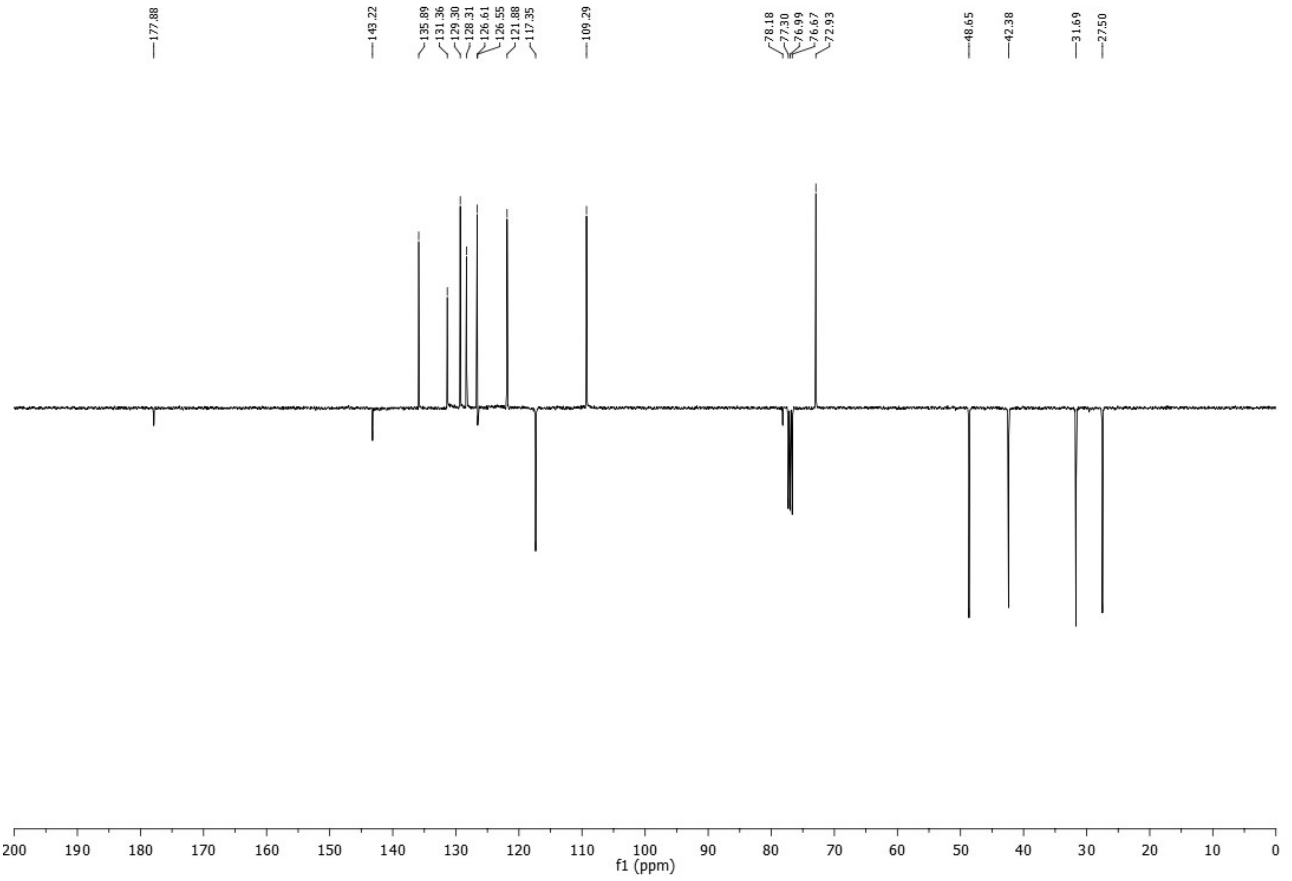


Figure 35. ^{1}H-NMR Spectrum of compound **4n** ($CDCl_3$, 400 MHz)

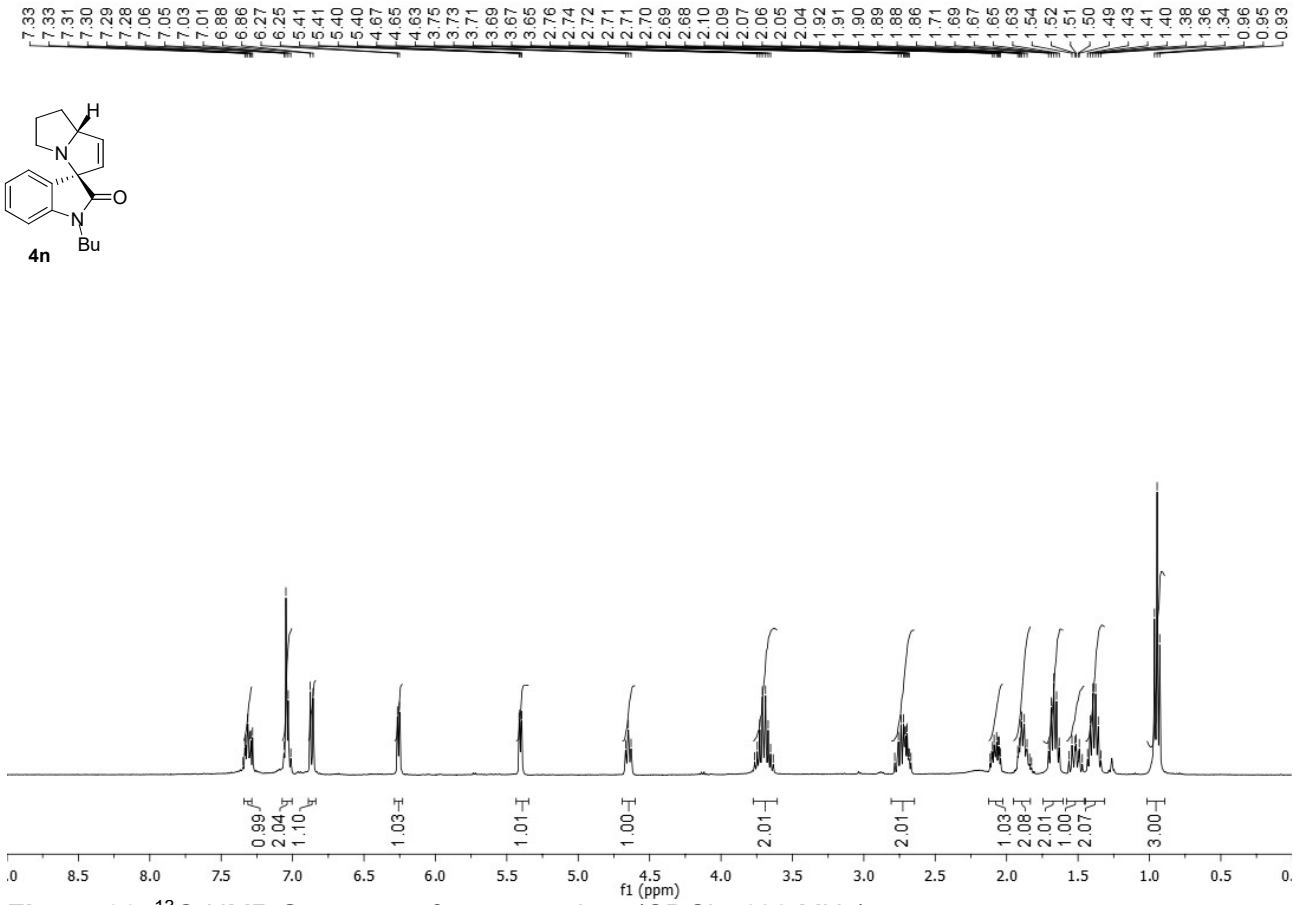


Figure 36. ^{13}C-NMR Spectrum of compound **4n** ($CDCl_3$, 100 MHz)

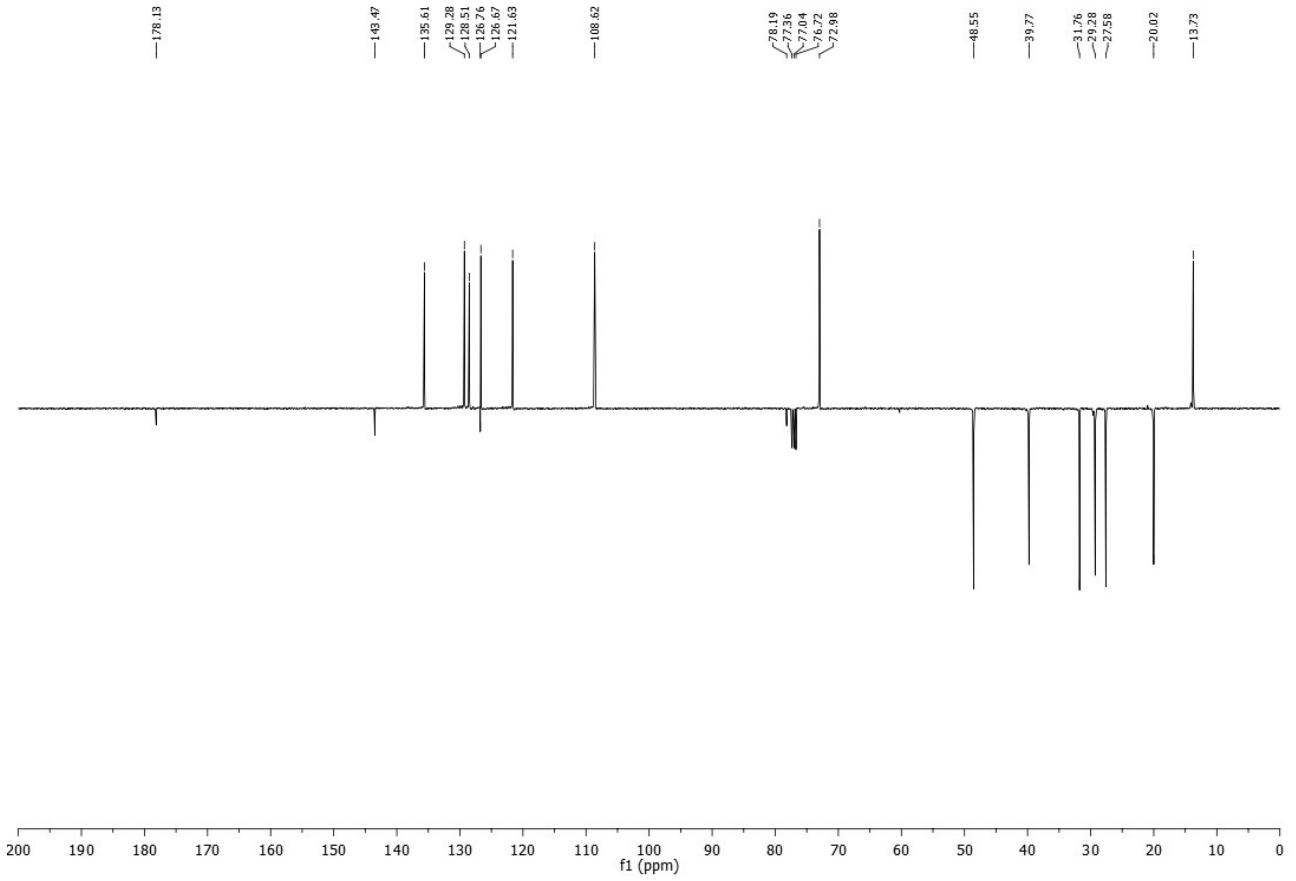


Figure 37. ^{1}H-NMR Spectrum of compound **4o** ($CDCl_3$, 400 MHz)

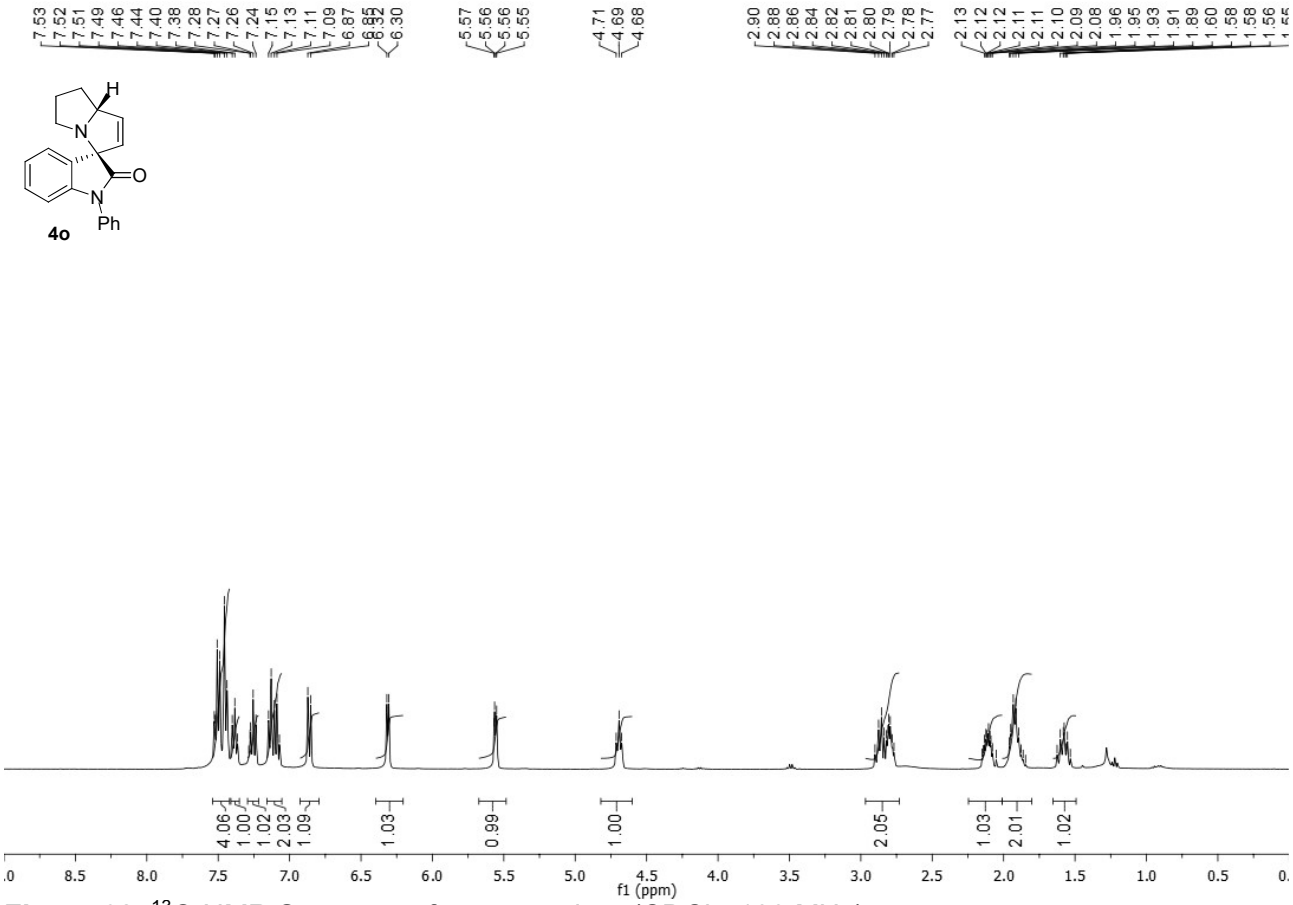


Figure 38. ^{13}C-NMR Spectrum of compound **4o** ($CDCl_3$, 100 MHz)

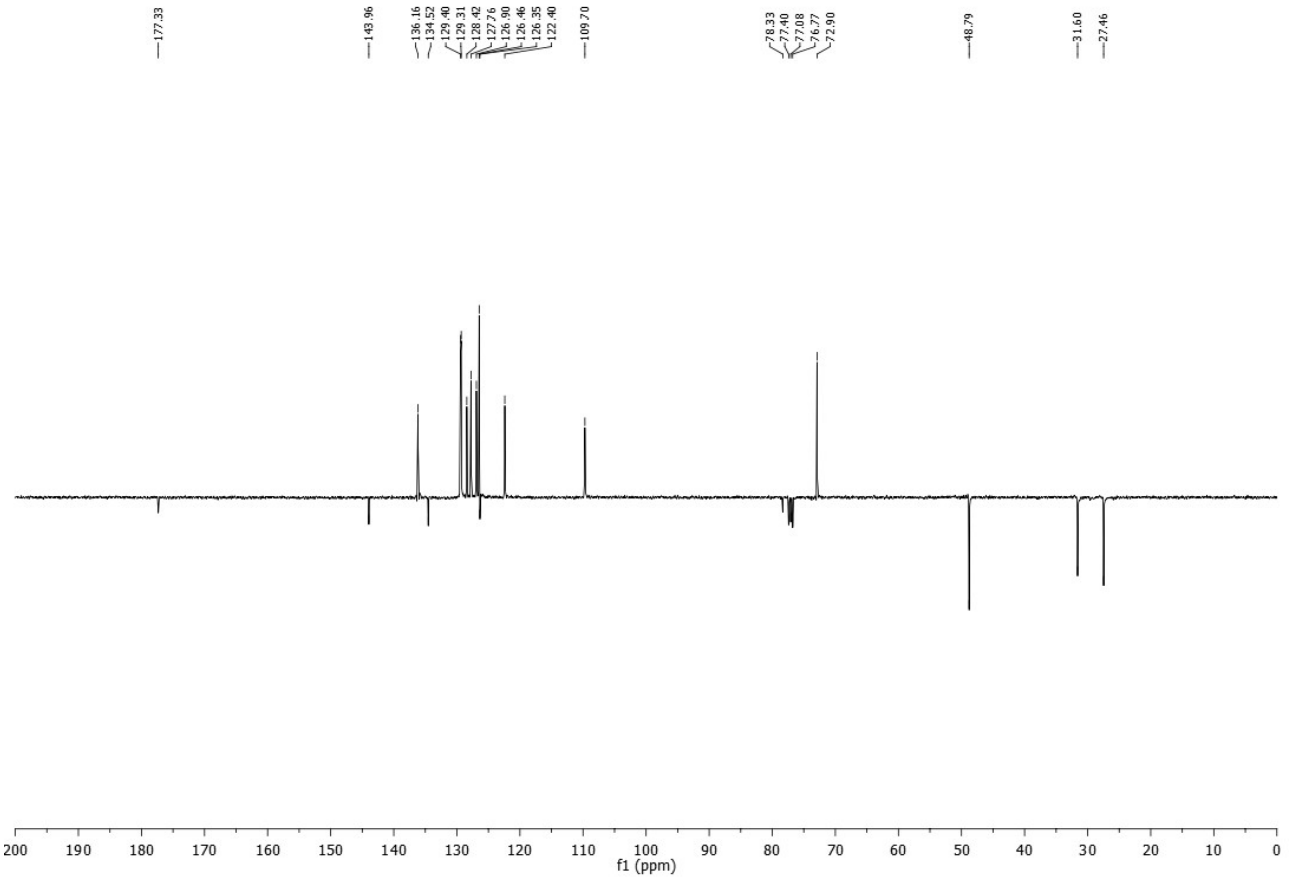


Figure 39. ^{1}H-NMR Spectrum of compound **4p** ($CDCl_3$, 400 MHz)

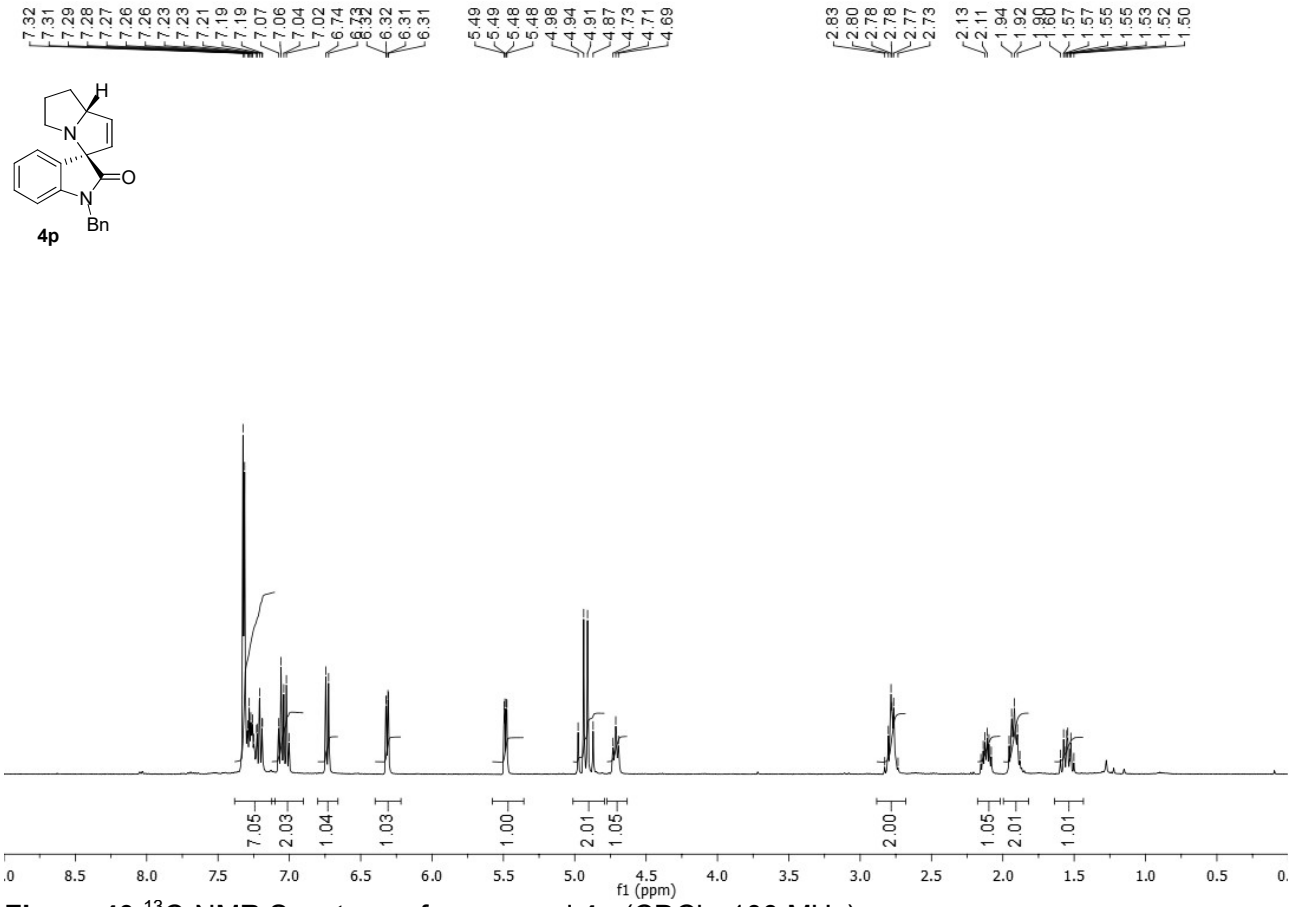


Figure 40. ^{13}C-NMR Spectrum of compound **4p** ($CDCl_3$, 100 MHz)

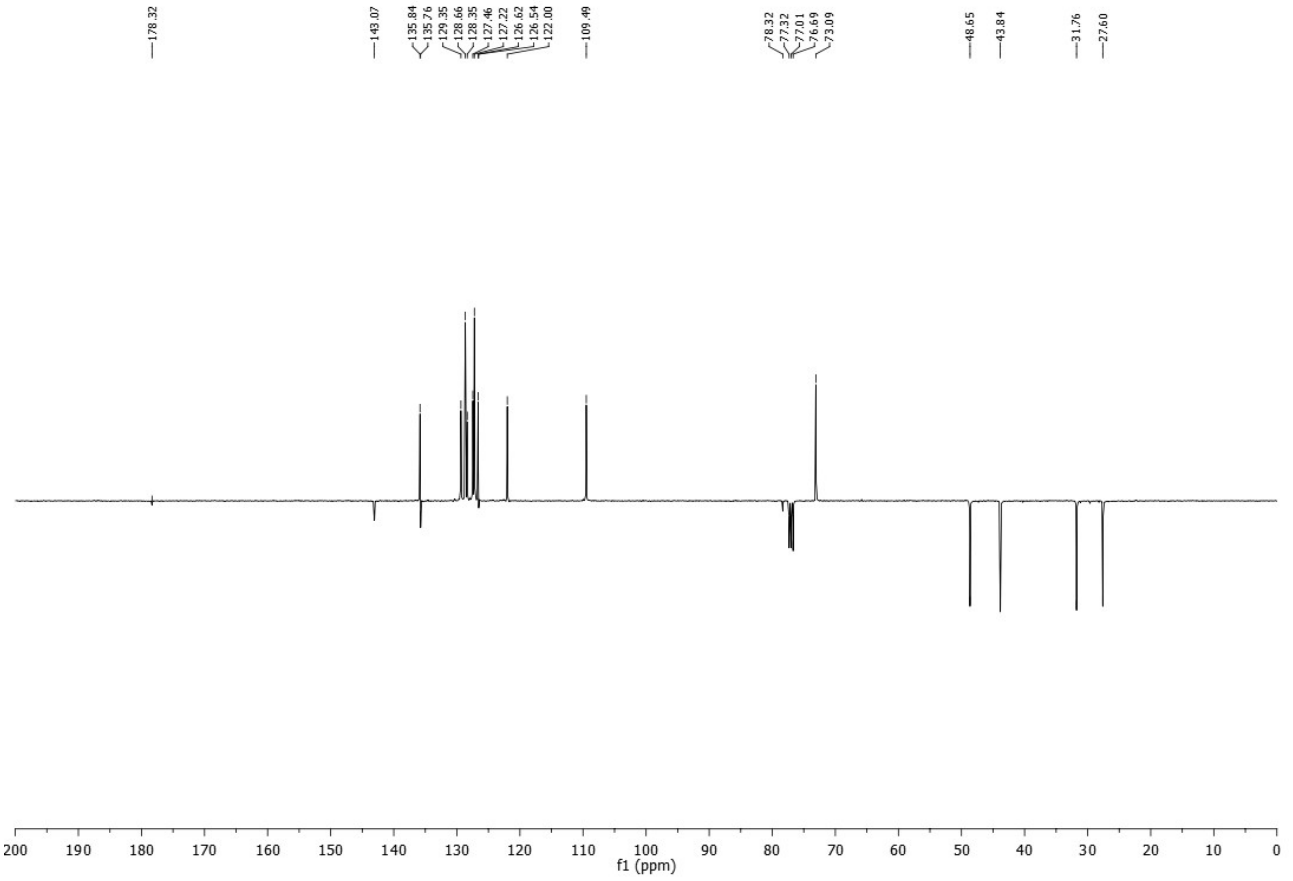


Figure 41. ^{1}H-NMR Spectrum of compound **4q** ($CDCl_3$, 400 MHz)

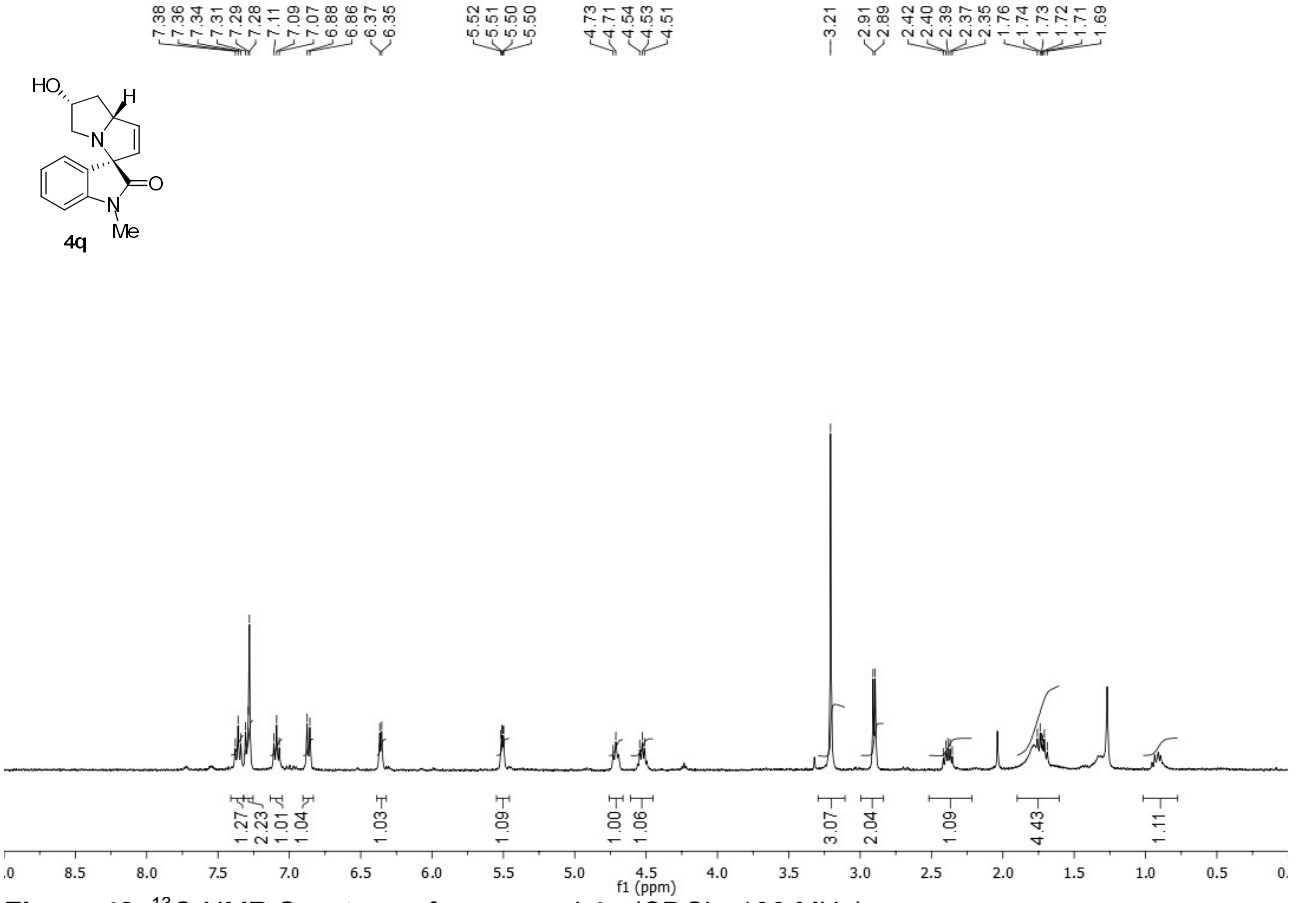


Figure 42. ^{13}C-NMR Spectrum of compound **4q** ($CDCl_3$, 100 MHz)

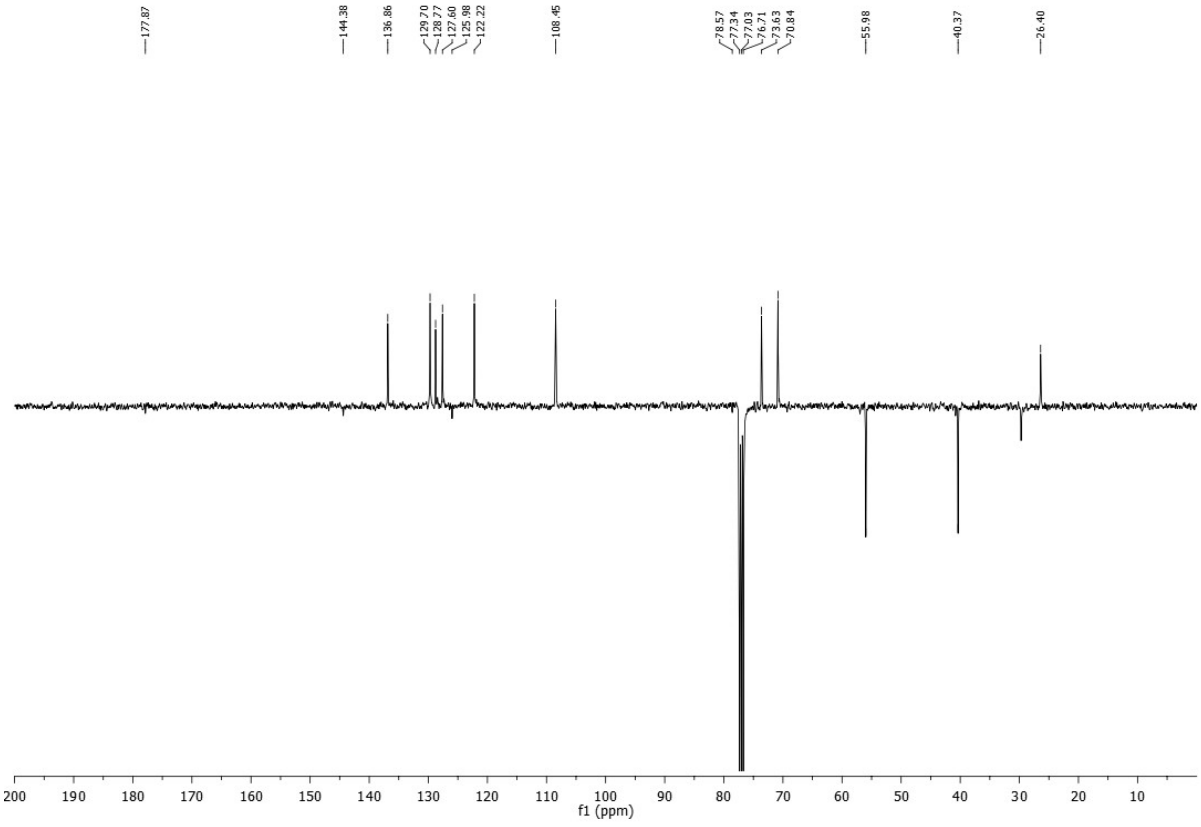
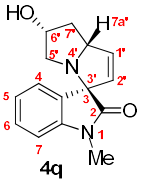
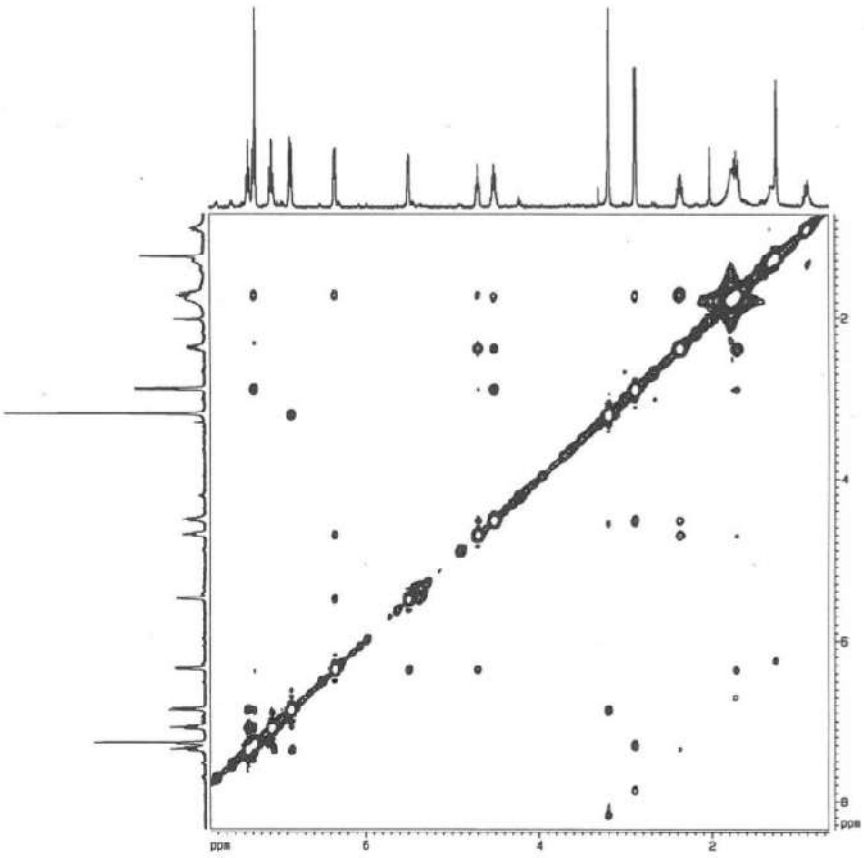
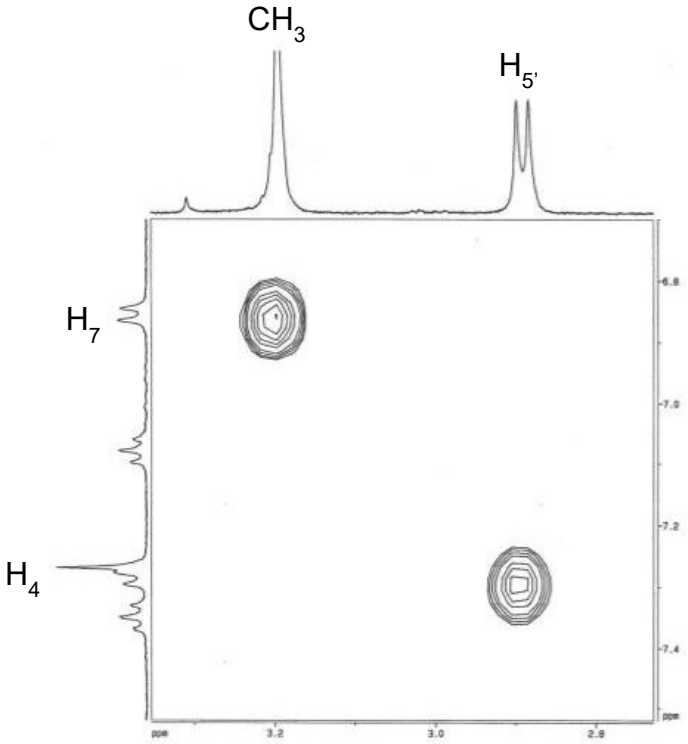


Figure 43. NOESY experiment of compound **4q**



4q





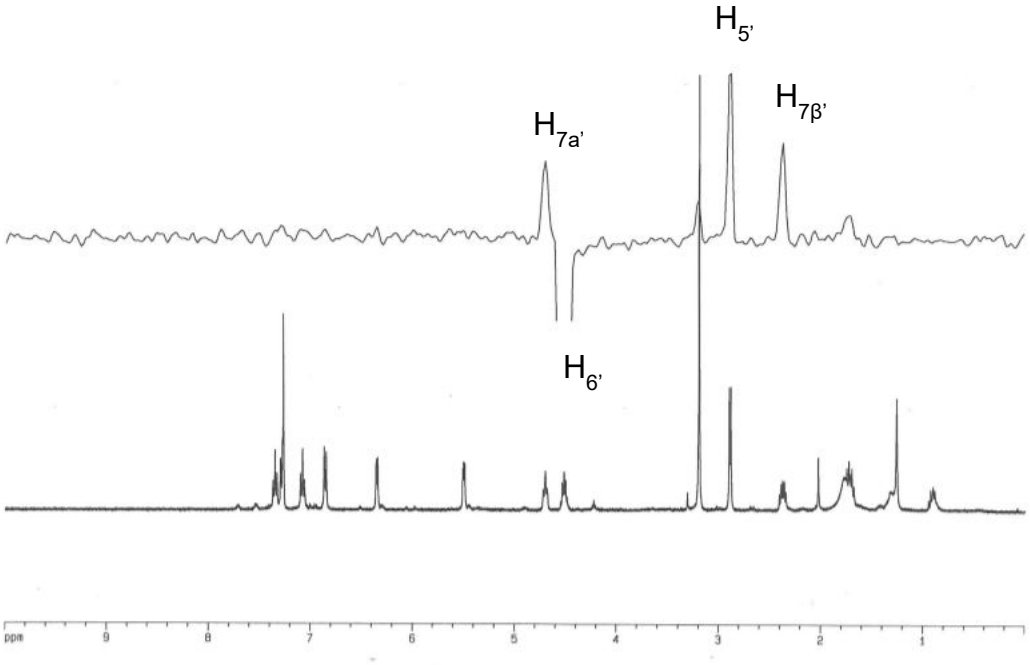

H5'
H7β'
H7a'
H6'
ppm
9
8
7
6
5
4
3
2
1

Figure 44. ^{1}H-NMR Spectrum of compound **4q'**,(CDCl$_3$, 400 MHz)

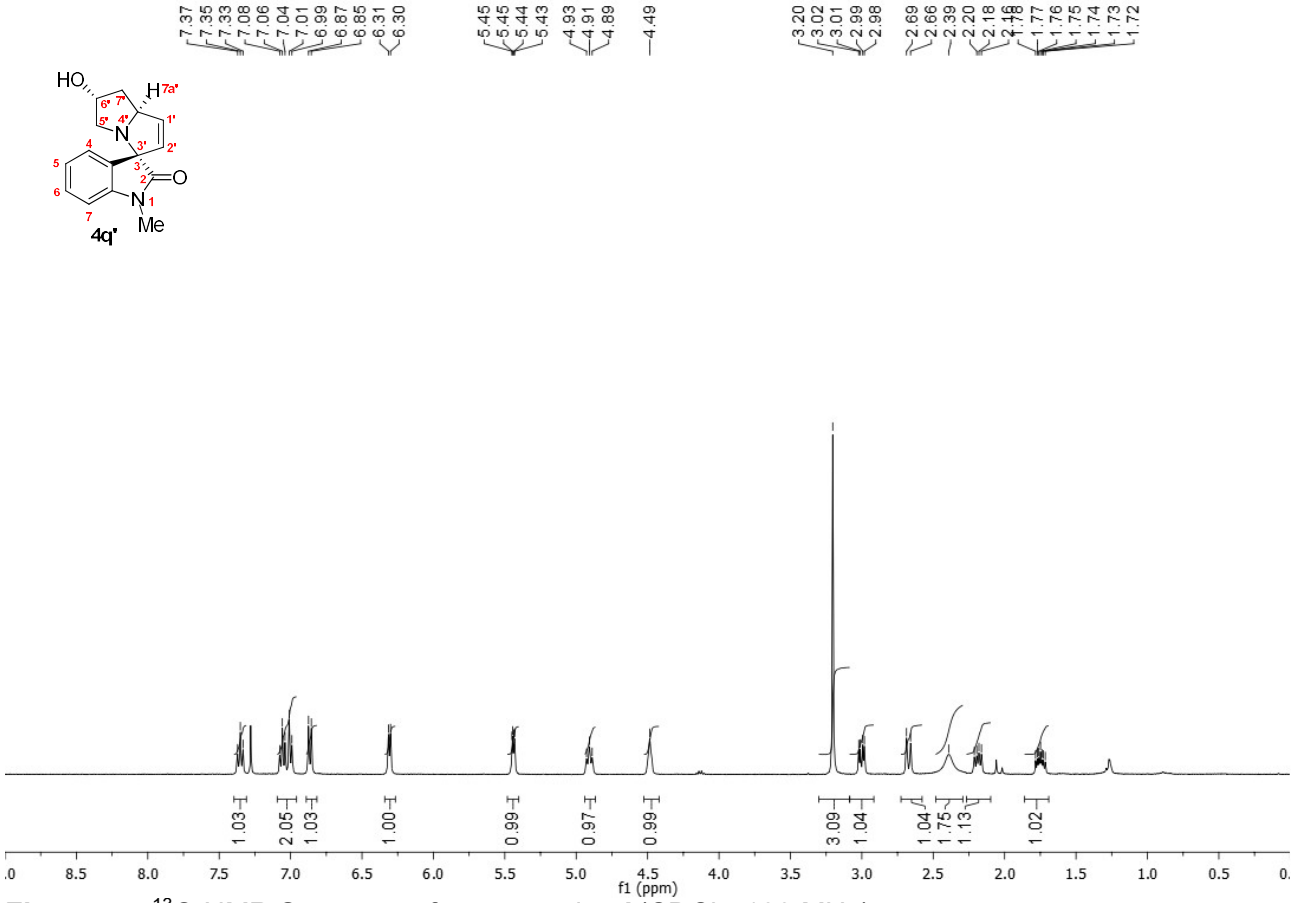


Figure 45. ^{13}C-NMR Spectrum of compound **4q'**,(CDCl$_3$, 100 MHz)

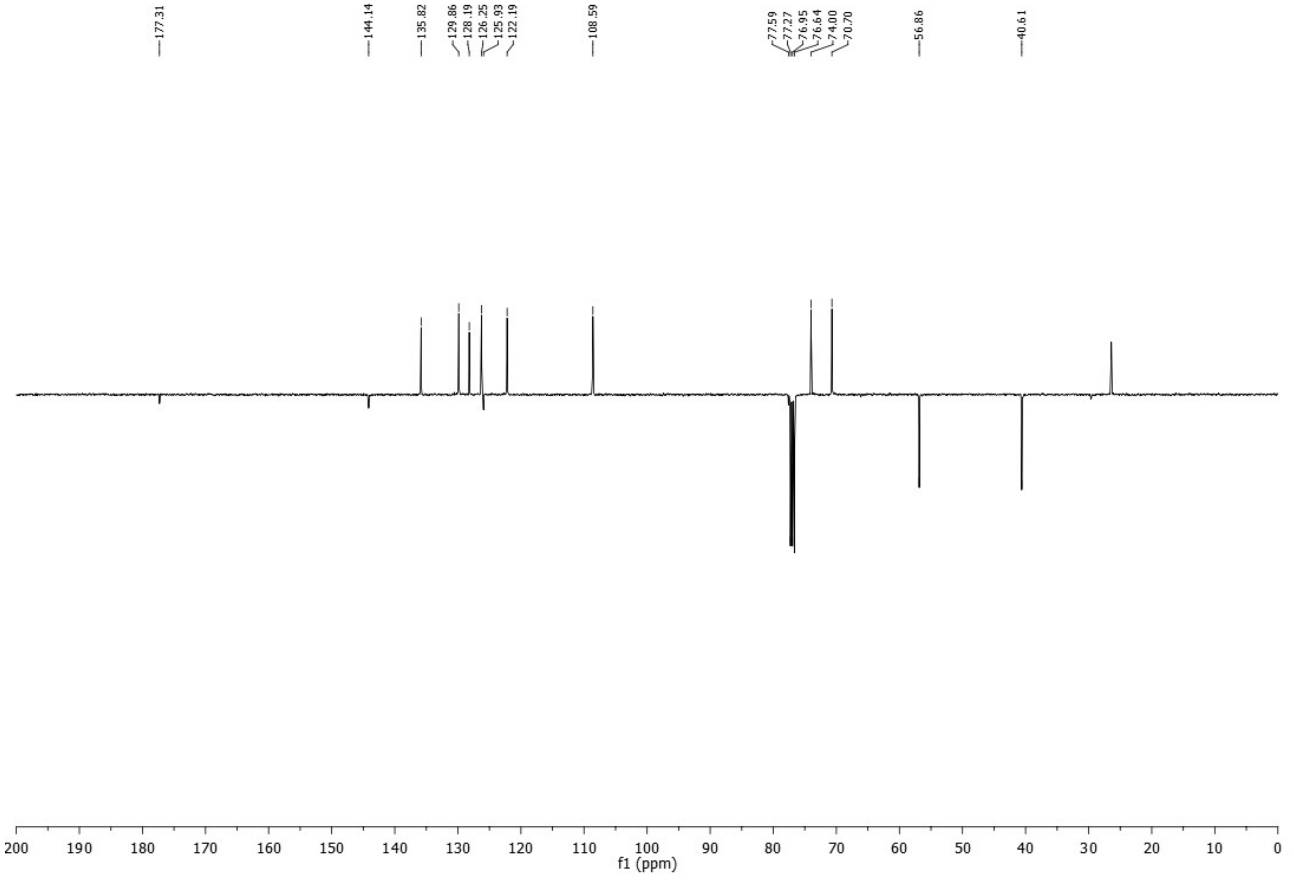
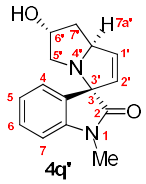
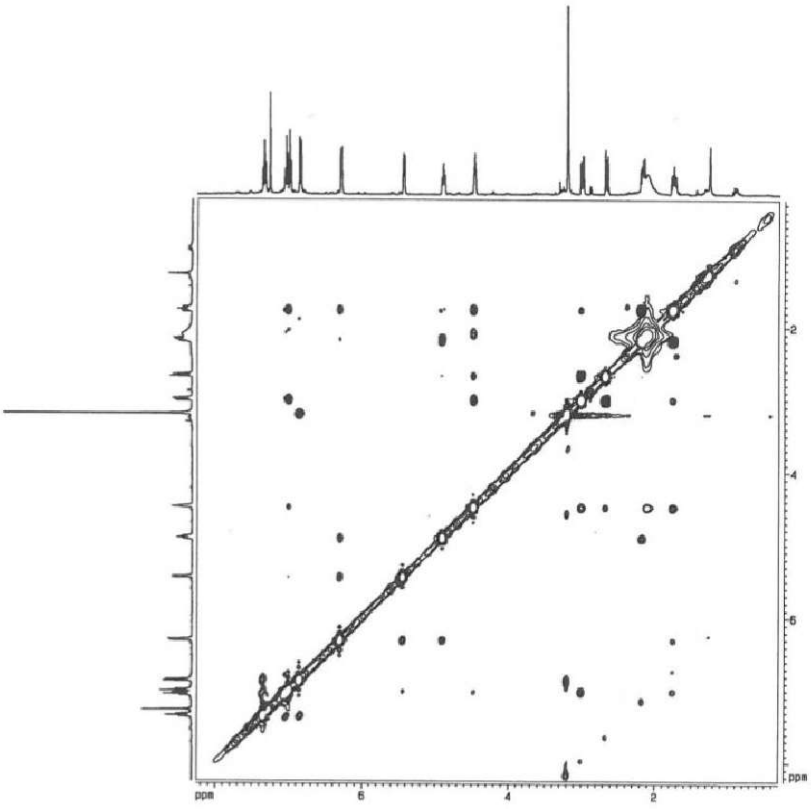


Figure 46. NOESY experiment compound **4q'**





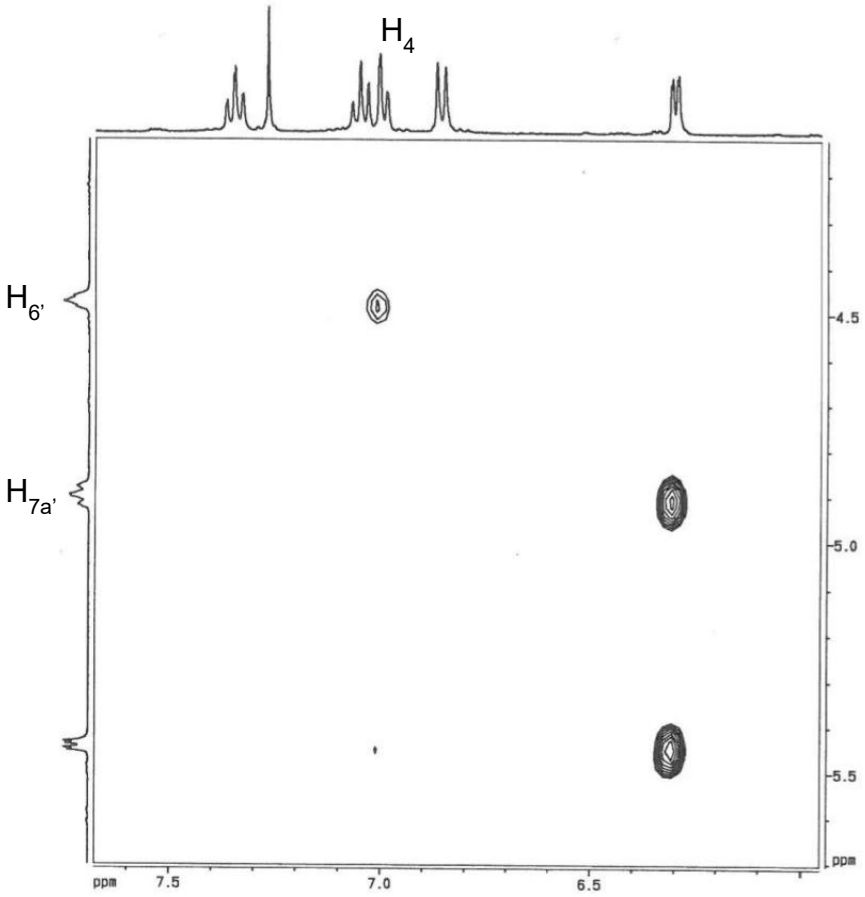


Figure 47. ^{1}H-NMR Spectrum of compound **4r** ($CDCl_3$, 400 MHz)

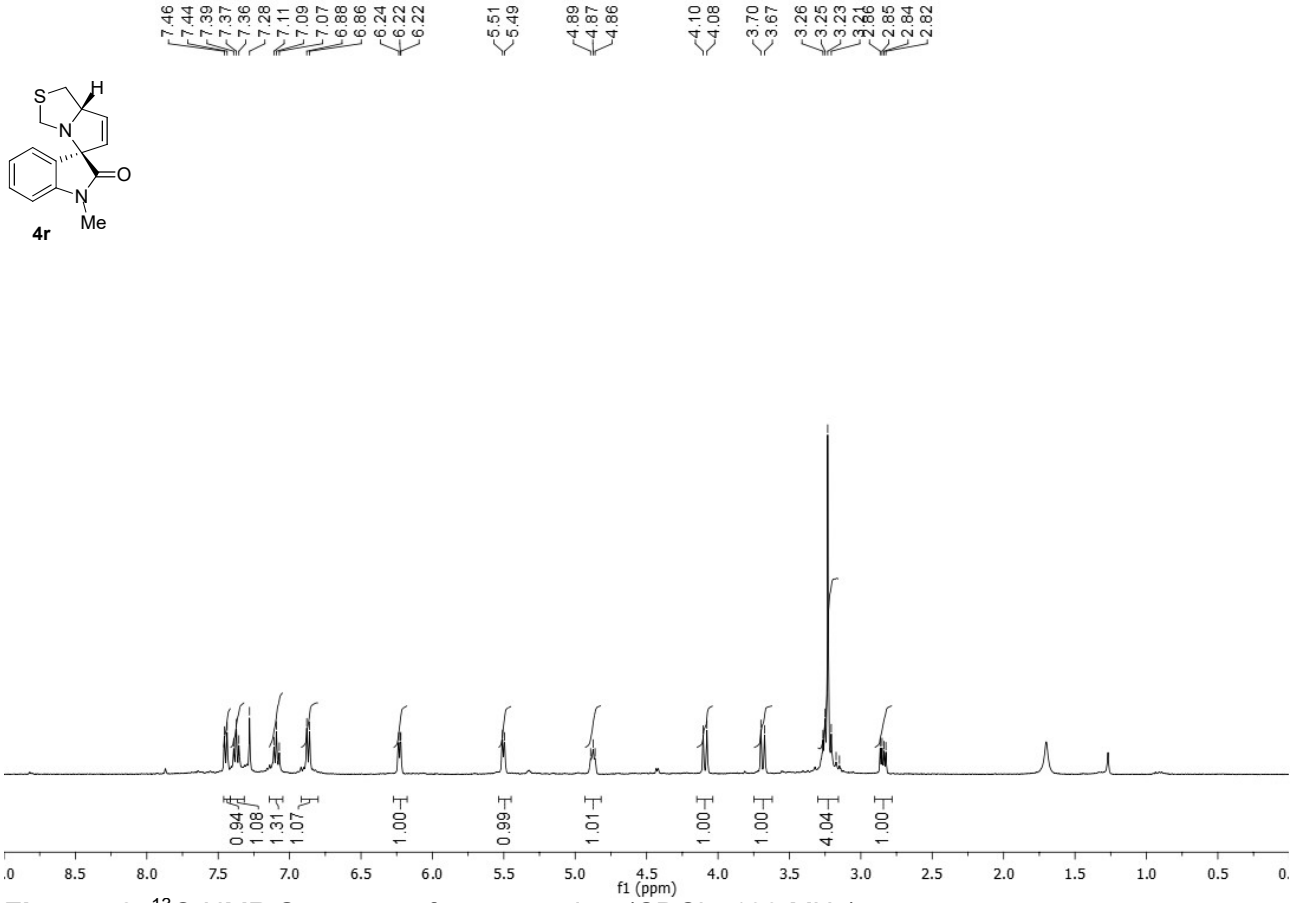


Figure 48. ^{13}C-NMR Spectrum of compound **4r** ($CDCl_3$, 100 MHz)

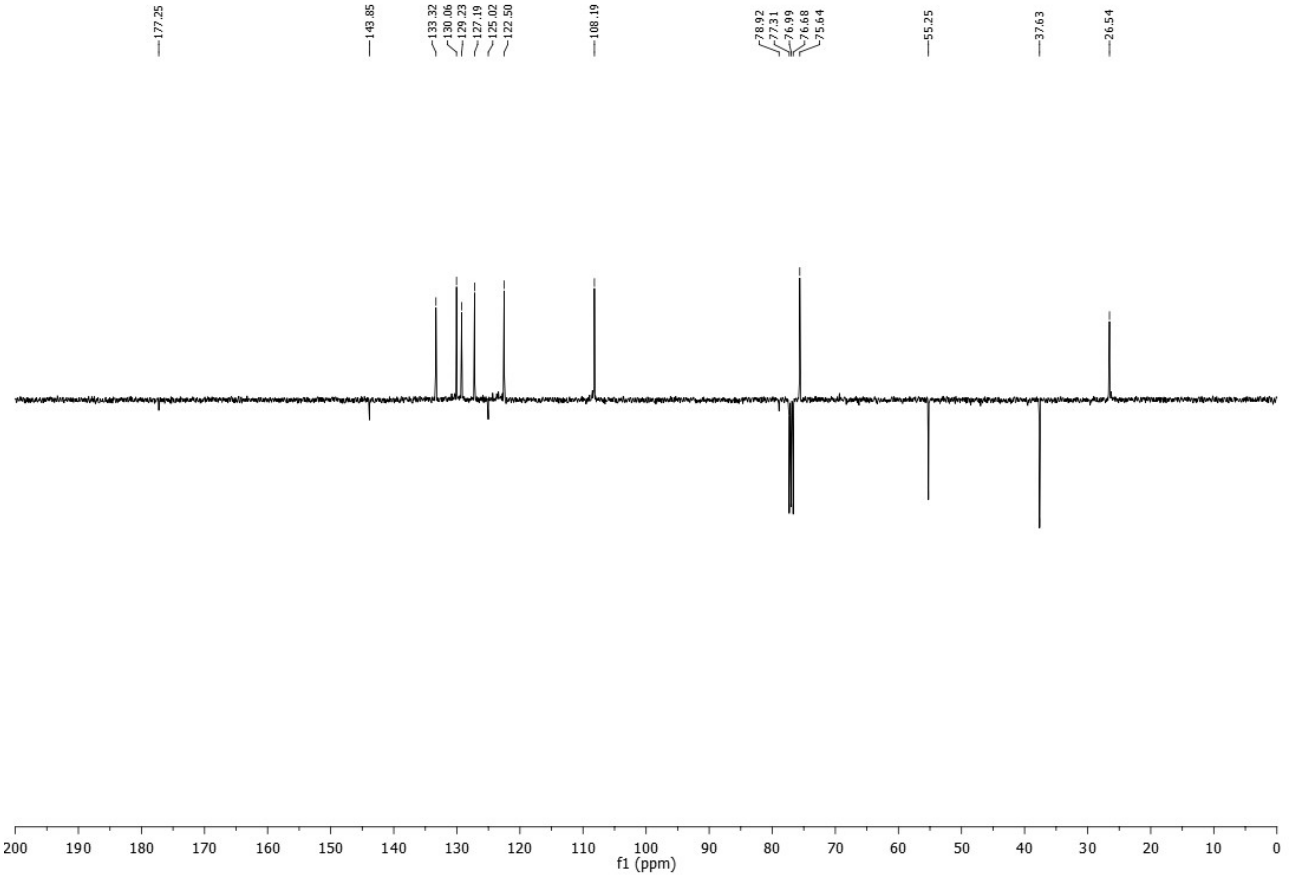


Figure 49. ^{1}H-NMR Spectrum of compound **4s** ($CDCl_3$, 400 MHz)

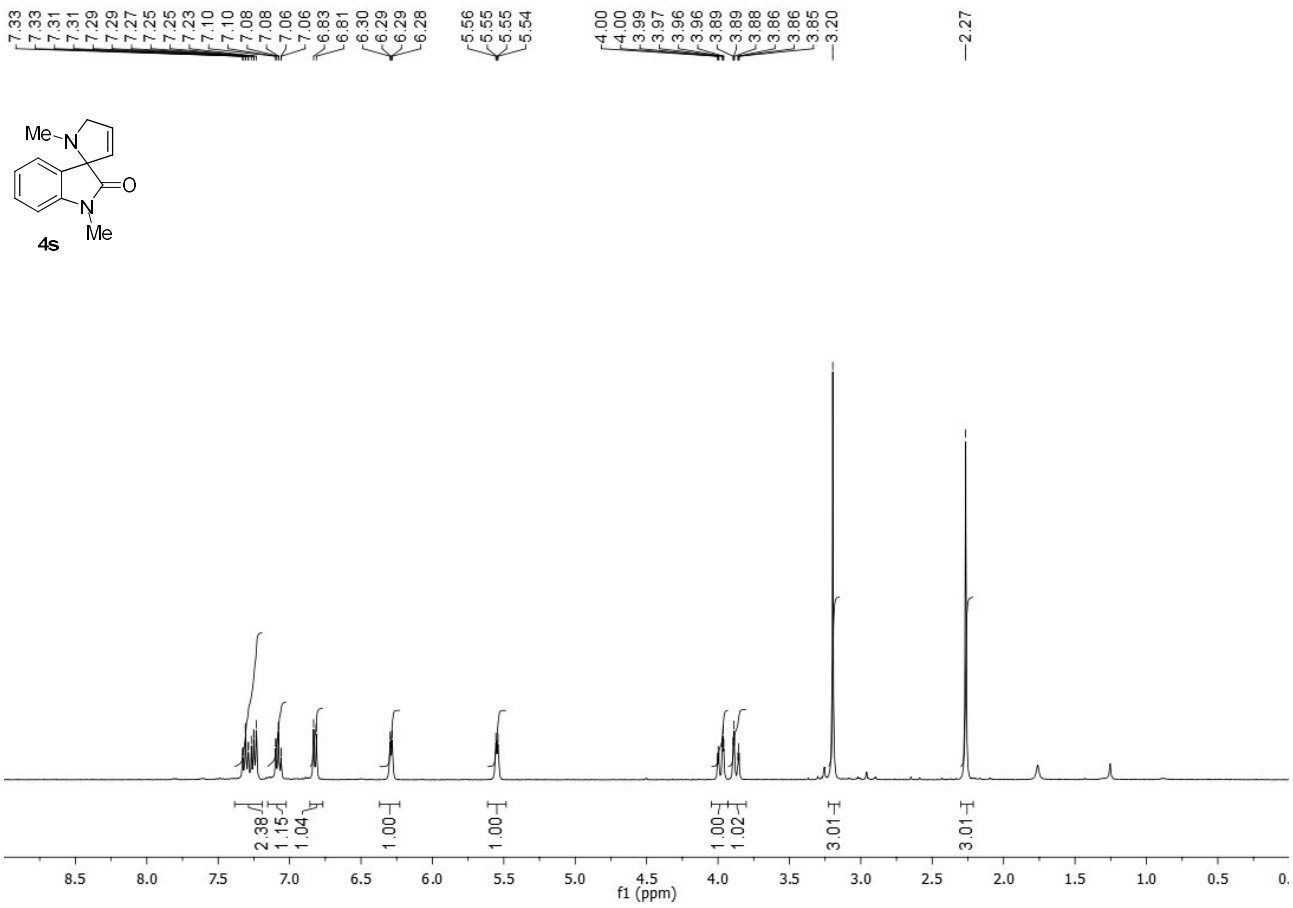


Figure 50. ^{13}C-NMR Spectrum of compound **4t** ($CDCl_3$, 100 MHz)

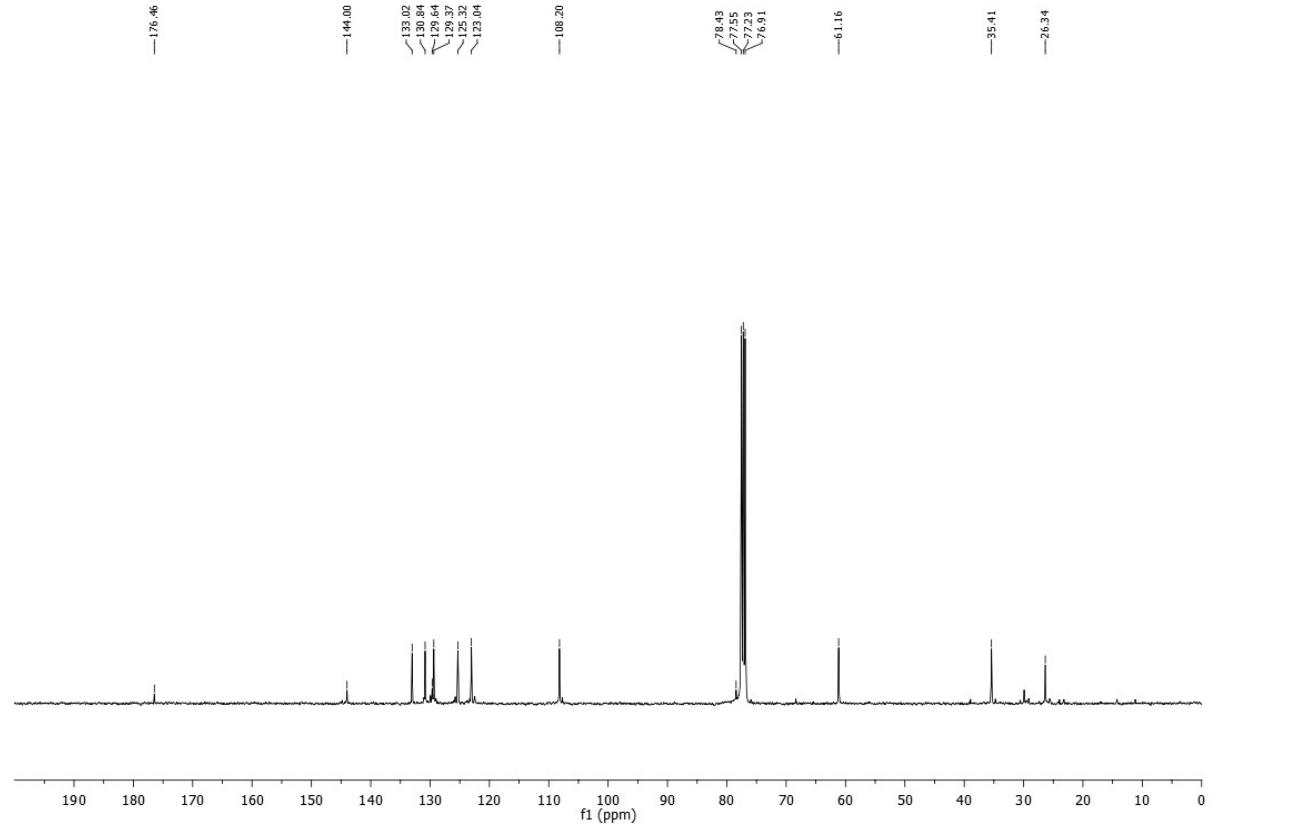


Figure 51. ^{1}H-NMR Spectrum of compound **10a** ($CDCl_3$, 400 MHz)[3]

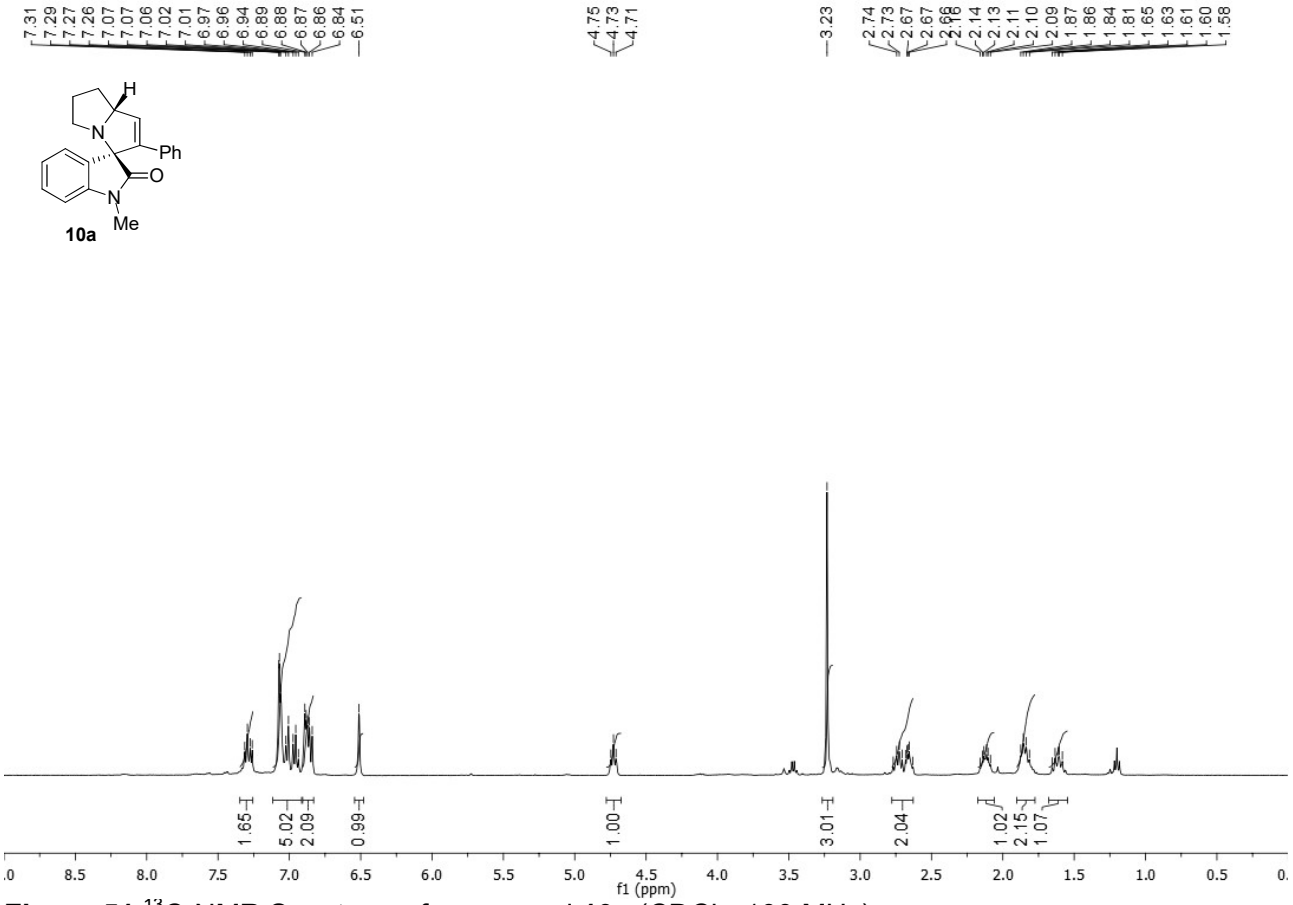


Figure 51. ^{13}C-NMR Spectrum of compound **10a** ($CDCl_3$, 100 MHz)

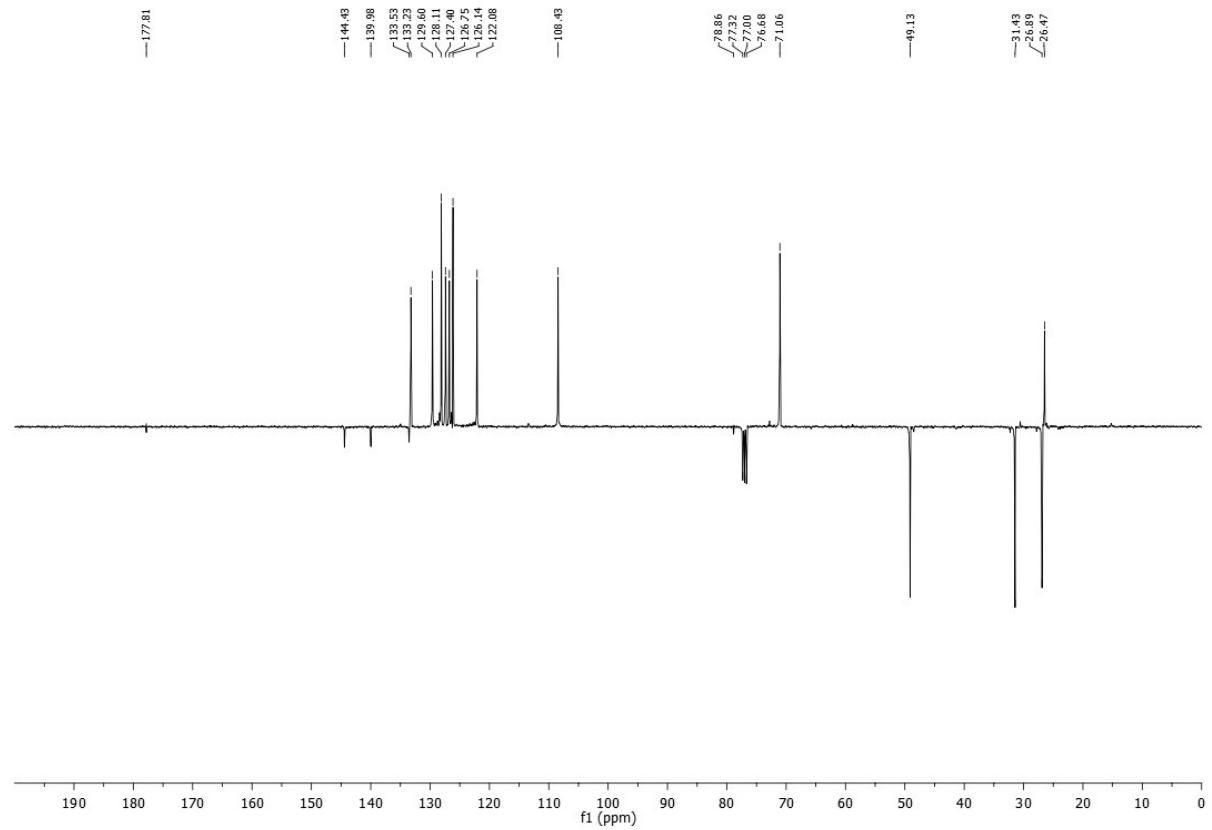


Figure 52. ^{1}H-NMR Spectrum of compound **10b** ($CDCl_3$, 400 MHz)

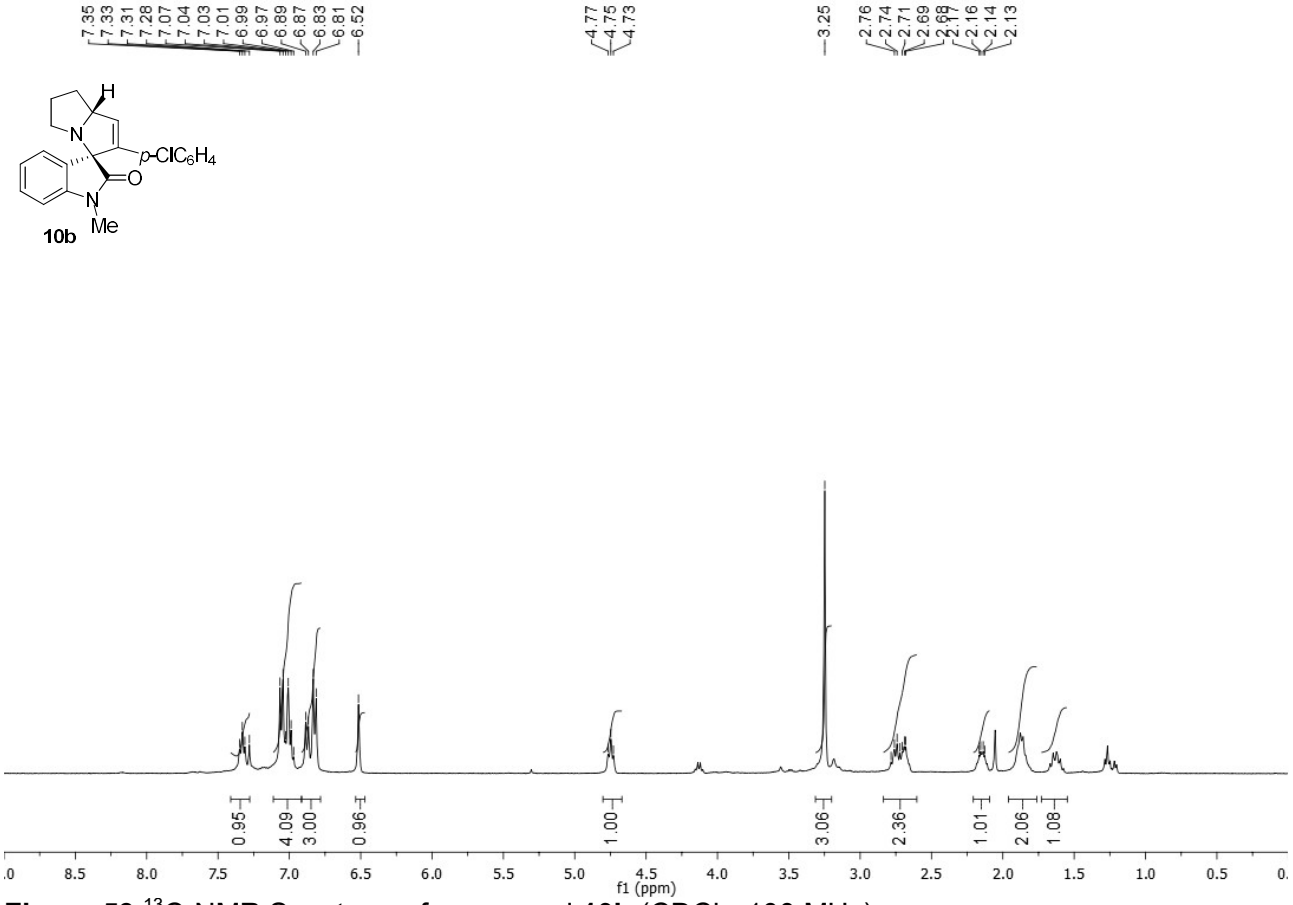


Figure 53. ^{13}C-NMR Spectrum of compound **10b** ($CDCl_3$, 100 MHz)

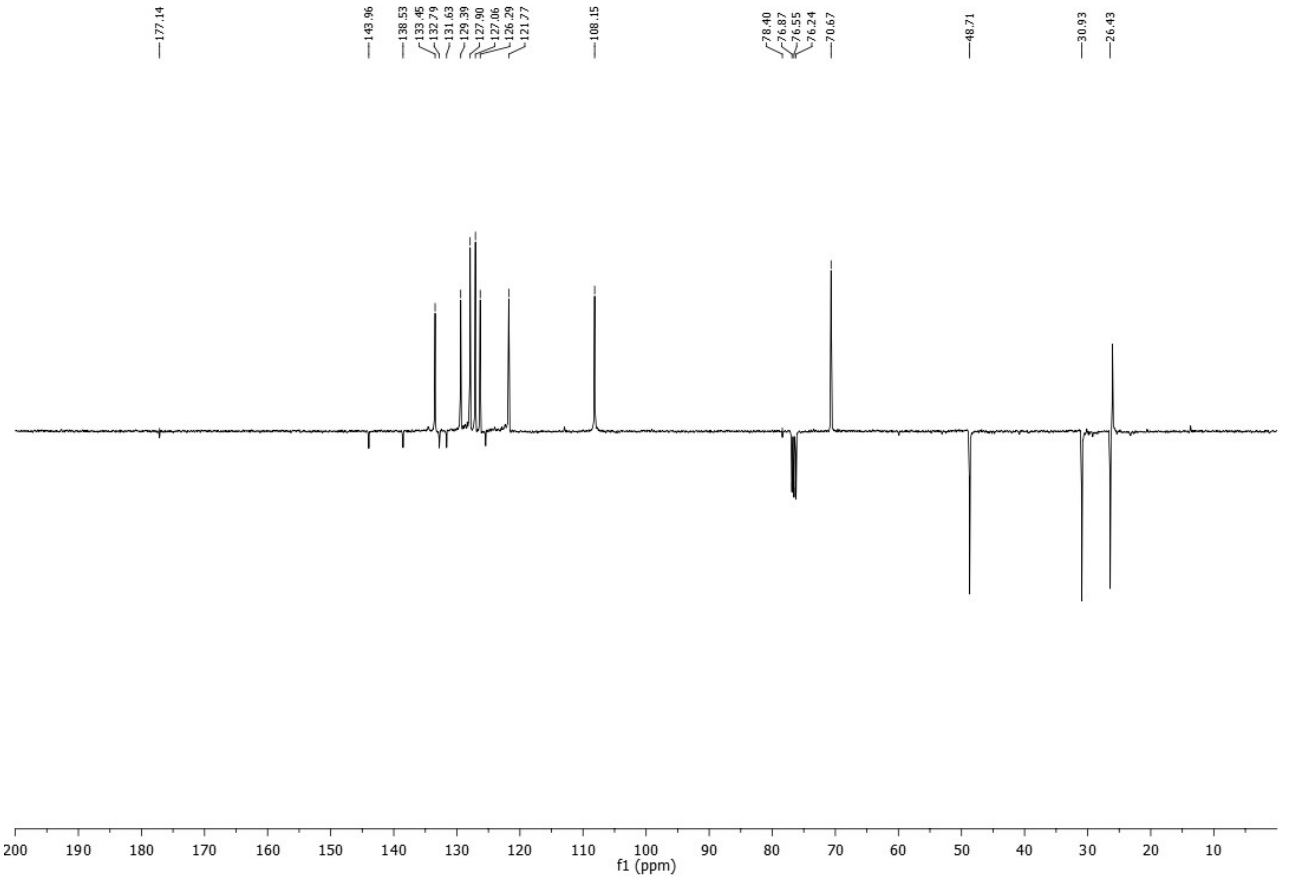
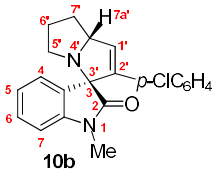
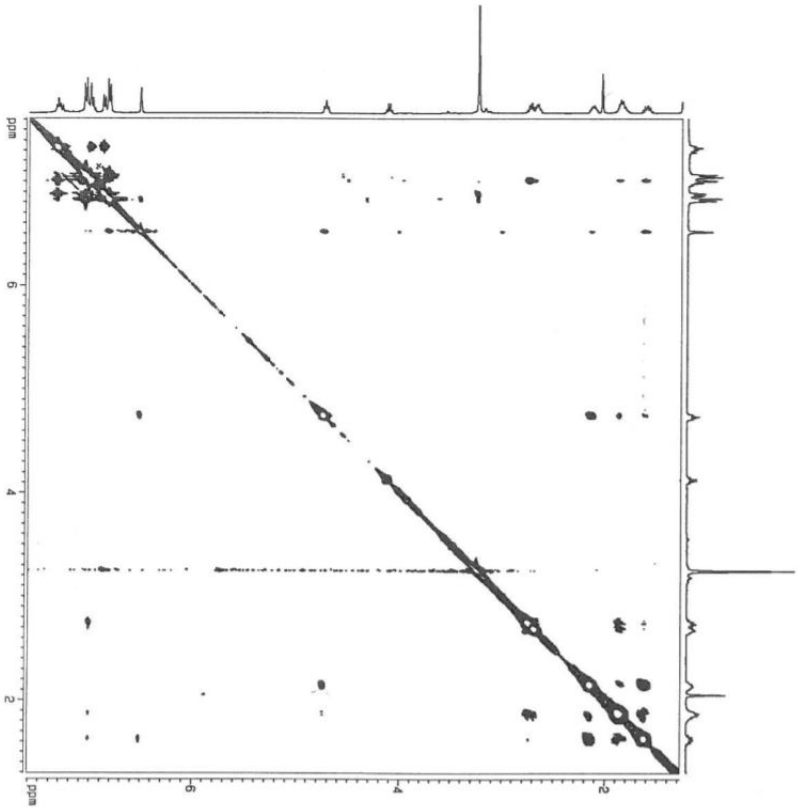
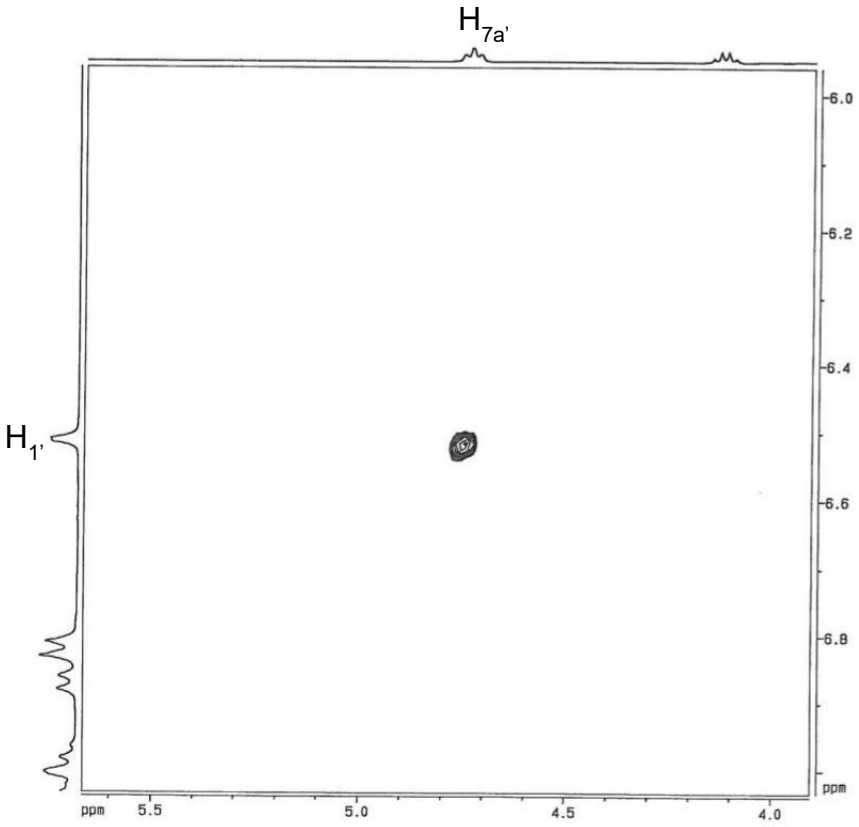


Figure 54. NOESY experiment for compound **10b**







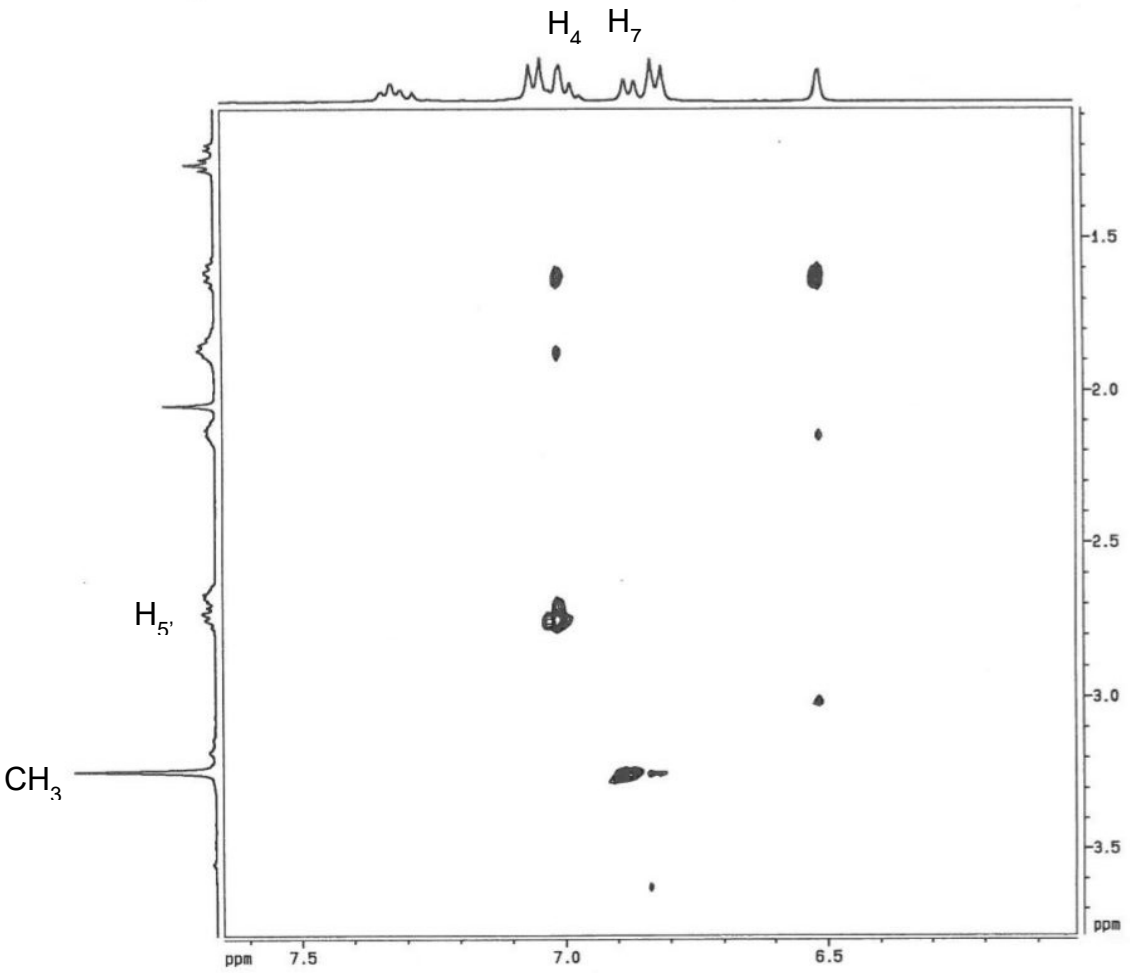

H4 H7
H5'
CH3
1.5
2.0
2.5
3.0
3.5
ppm
ppm 7.5
7.0
6.5

Figure 55. ^{1}H-NMR Spectrum of compound **10c** ($CDCl_3$, 400 MHz)

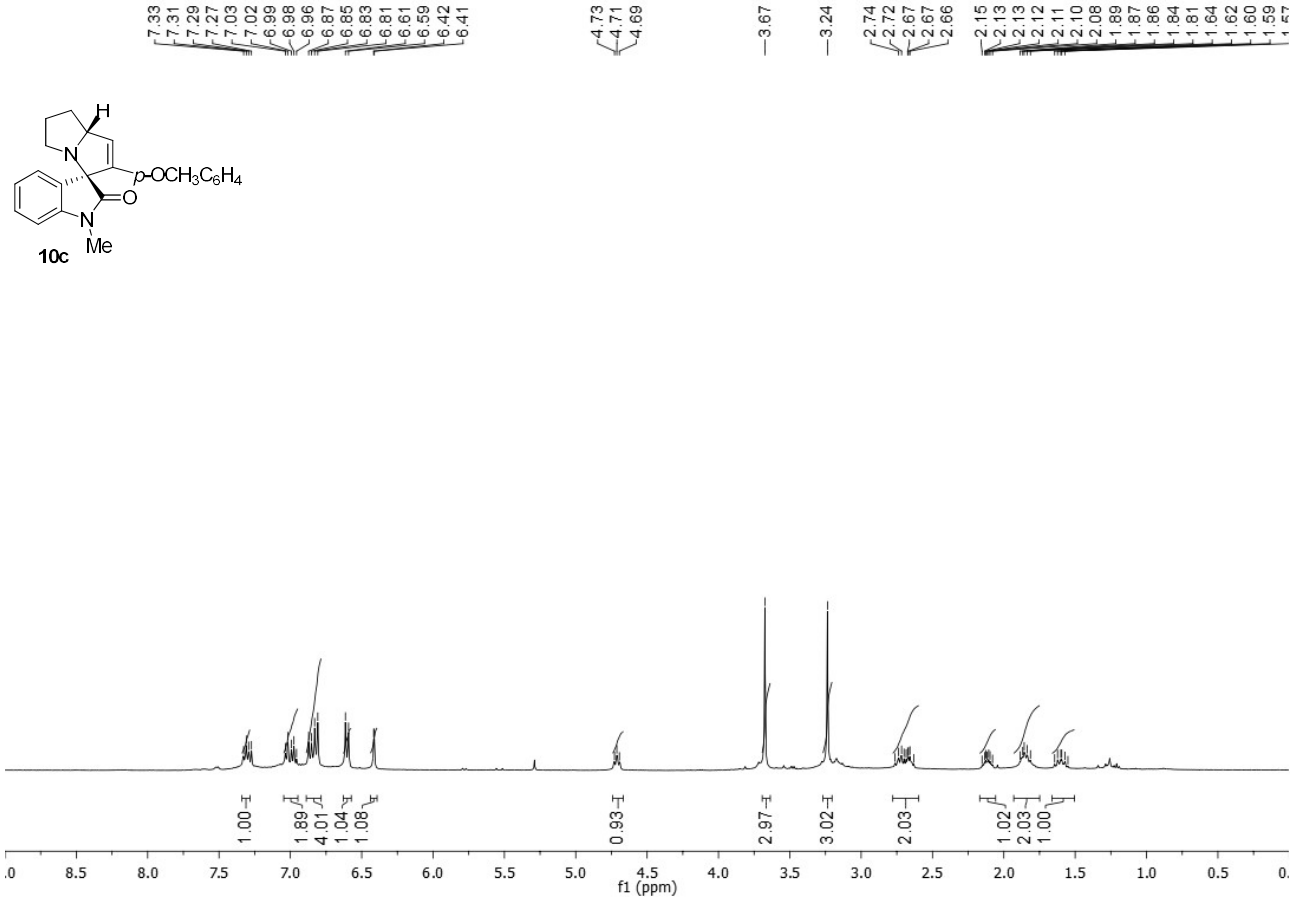


Figure 56. ^{13}C-NMR Spectrum of compound **10c** ($CDCl_3$, 100 MHz)

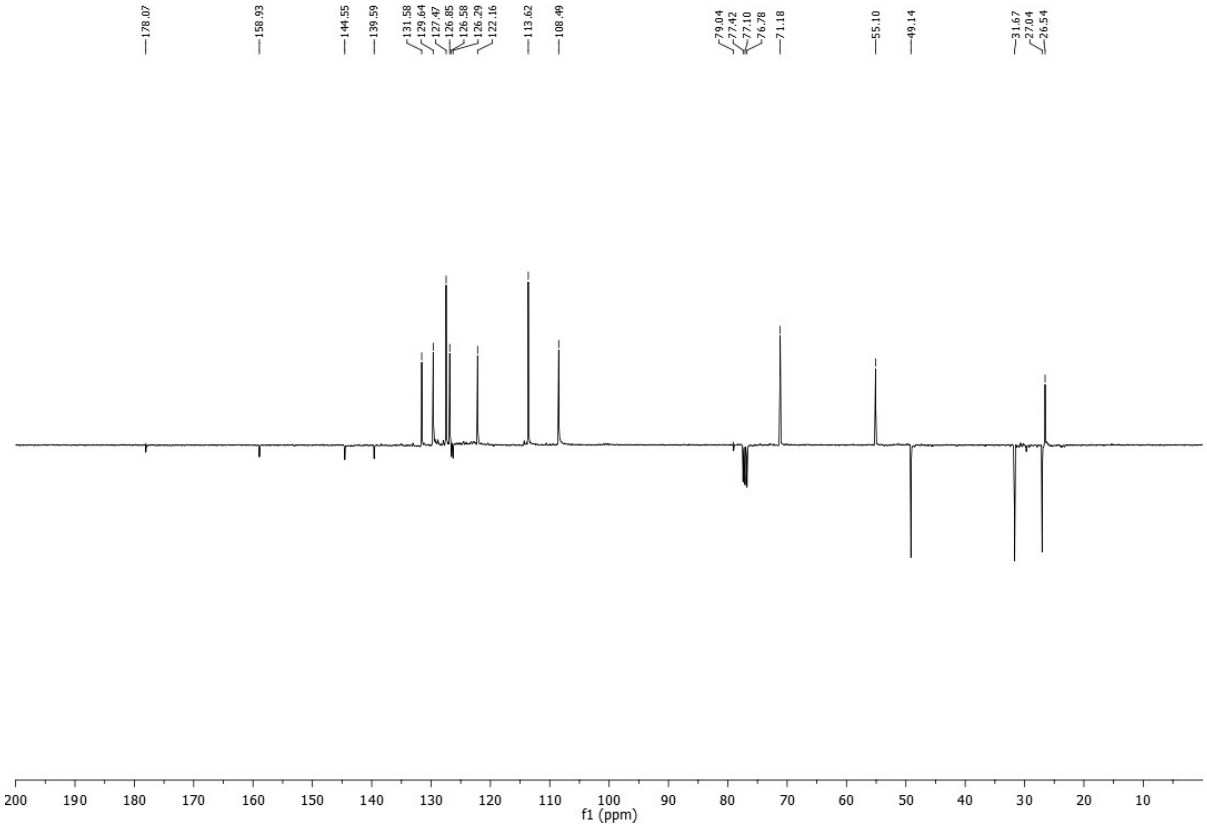


Figure 57. ^{1}H-NMR Spectrum of compound **10d** ($CDCl_3$, 400 MHz)

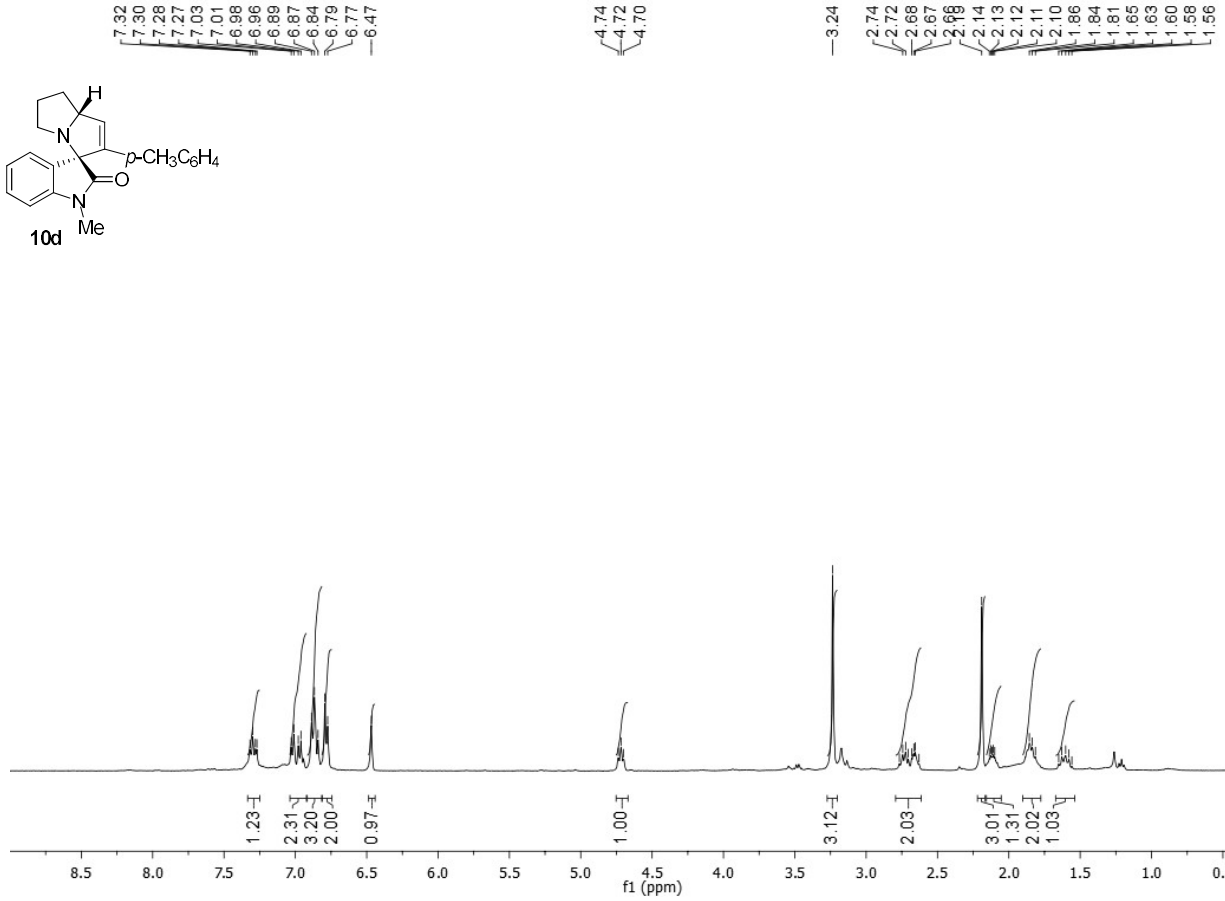


Figure 58. ^{13}C-NMR Spectrum of compound **10d** ($CDCl_3$, 400 MHz)

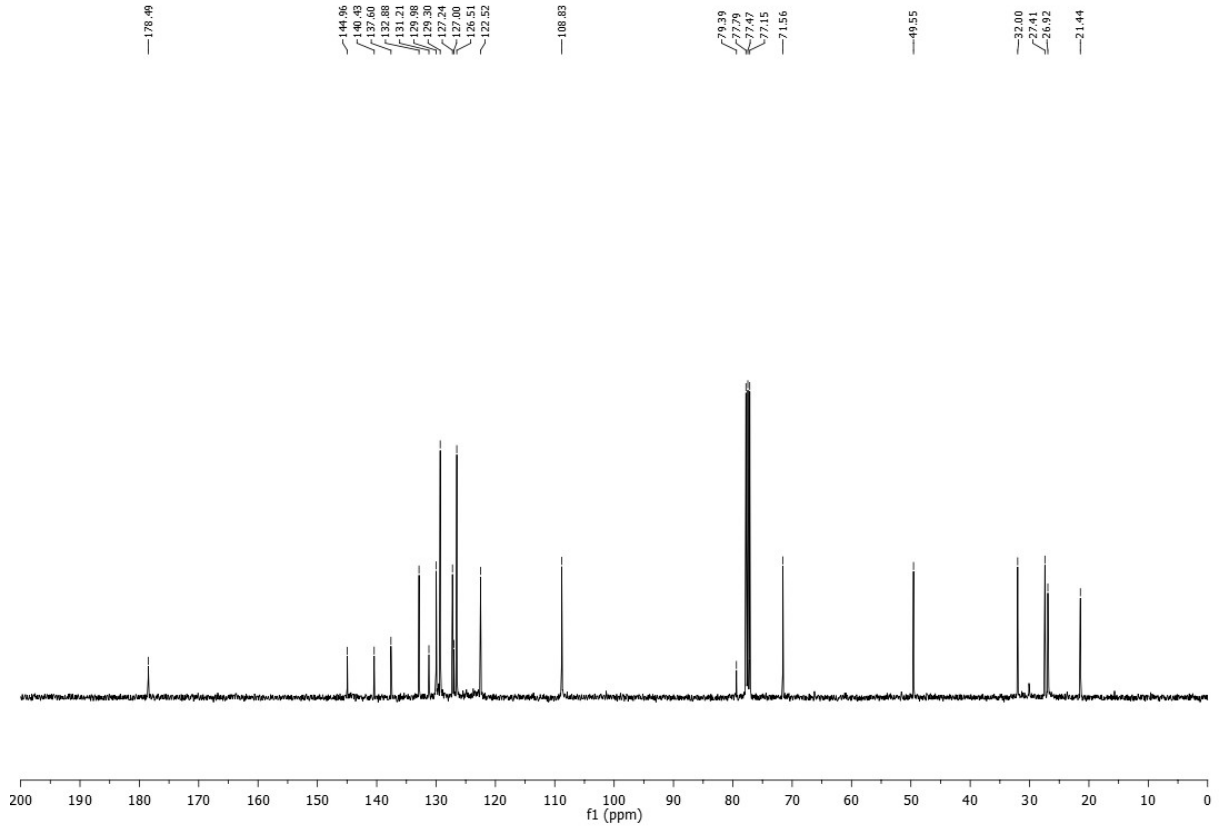


Figure 59. ^{1}H-NMR Spectrum of compound **10e** and **11e** from **1f** ($CDCl_3$, 400 MHz)

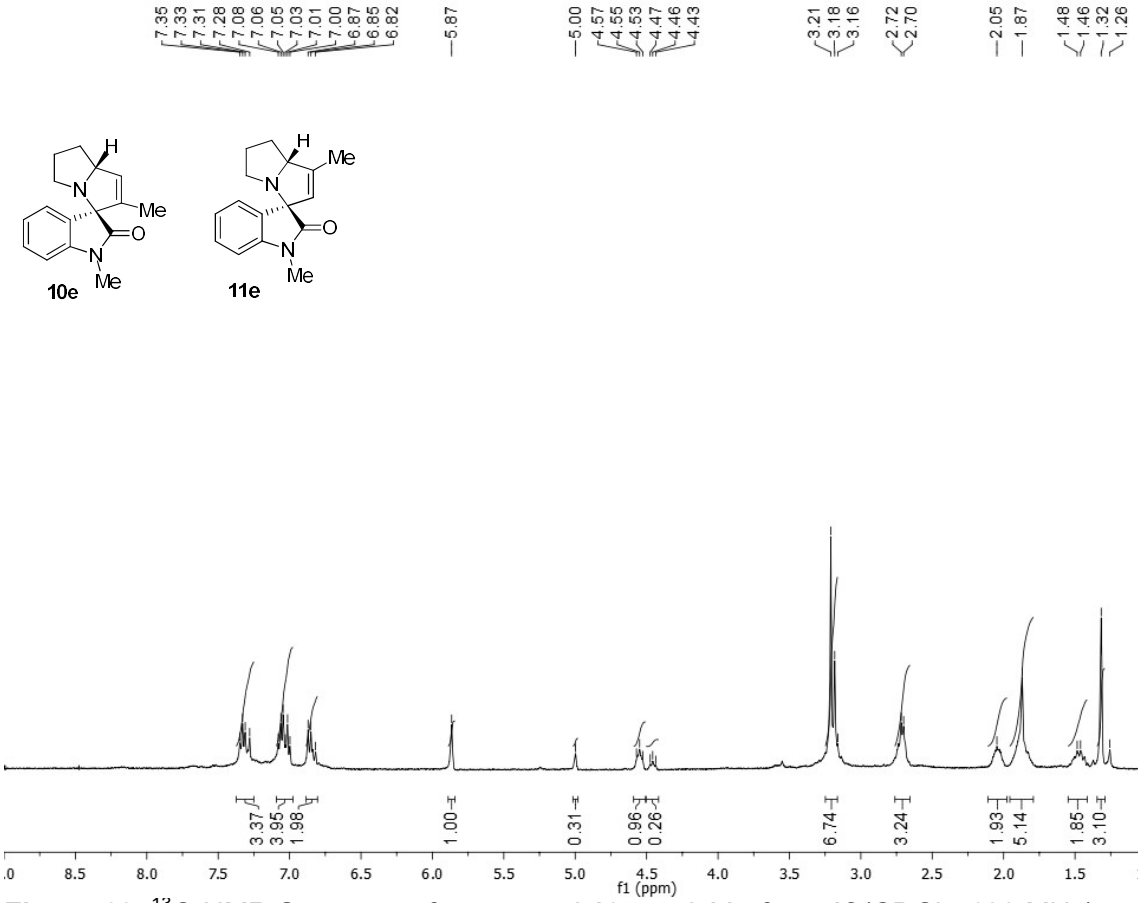


Figure 60. ^{13}C-NMR Spectrum of compound **10e** and **11e** from **1f** ($CDCl_3$, 100 MHz)

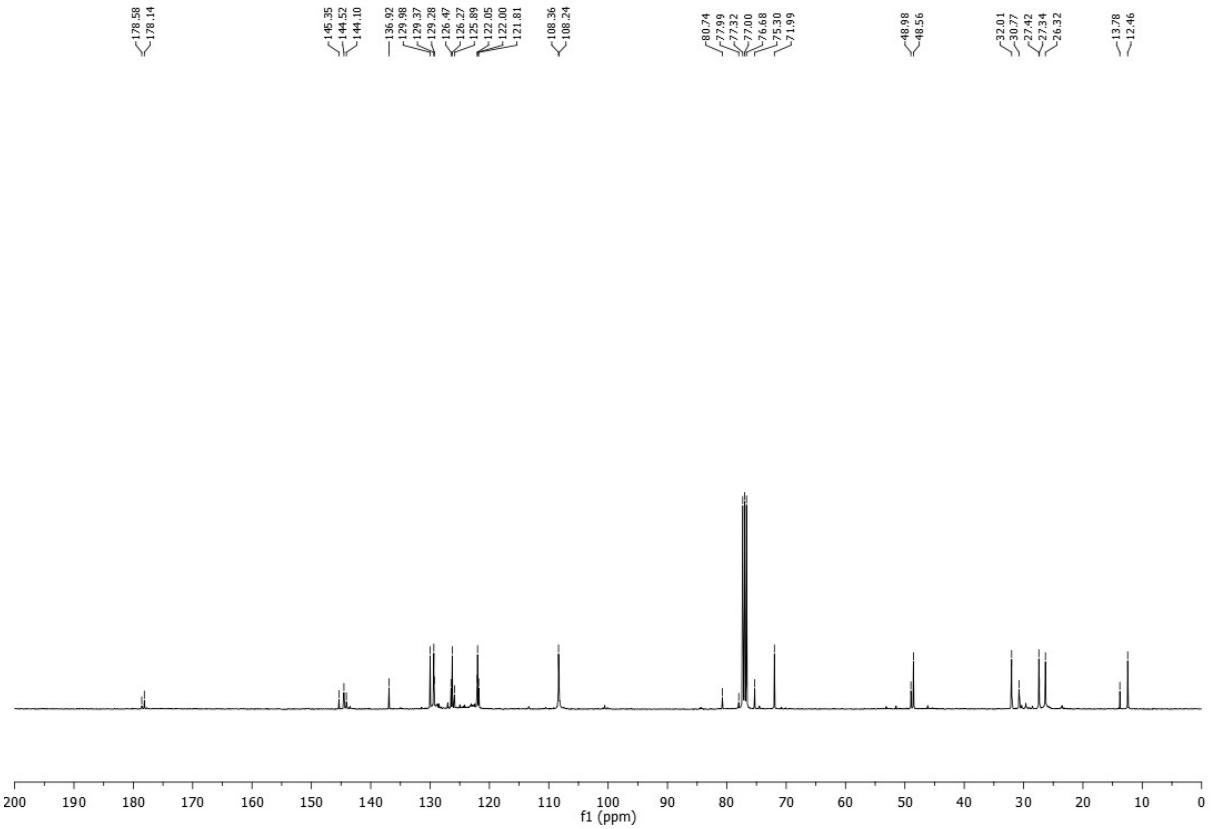
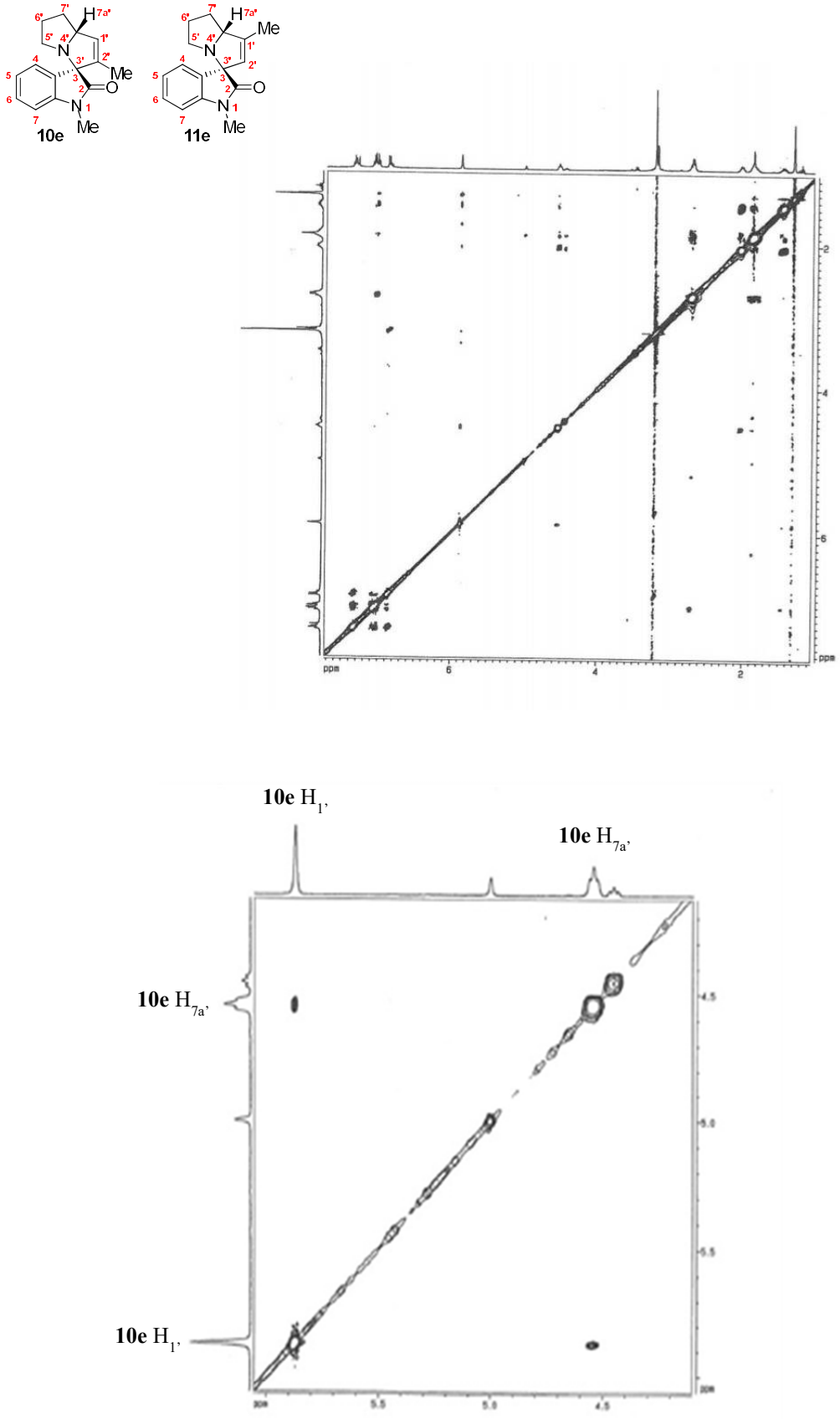


Figure 61. NOESY experiment for compounds **10e** and **11e** from **1f**



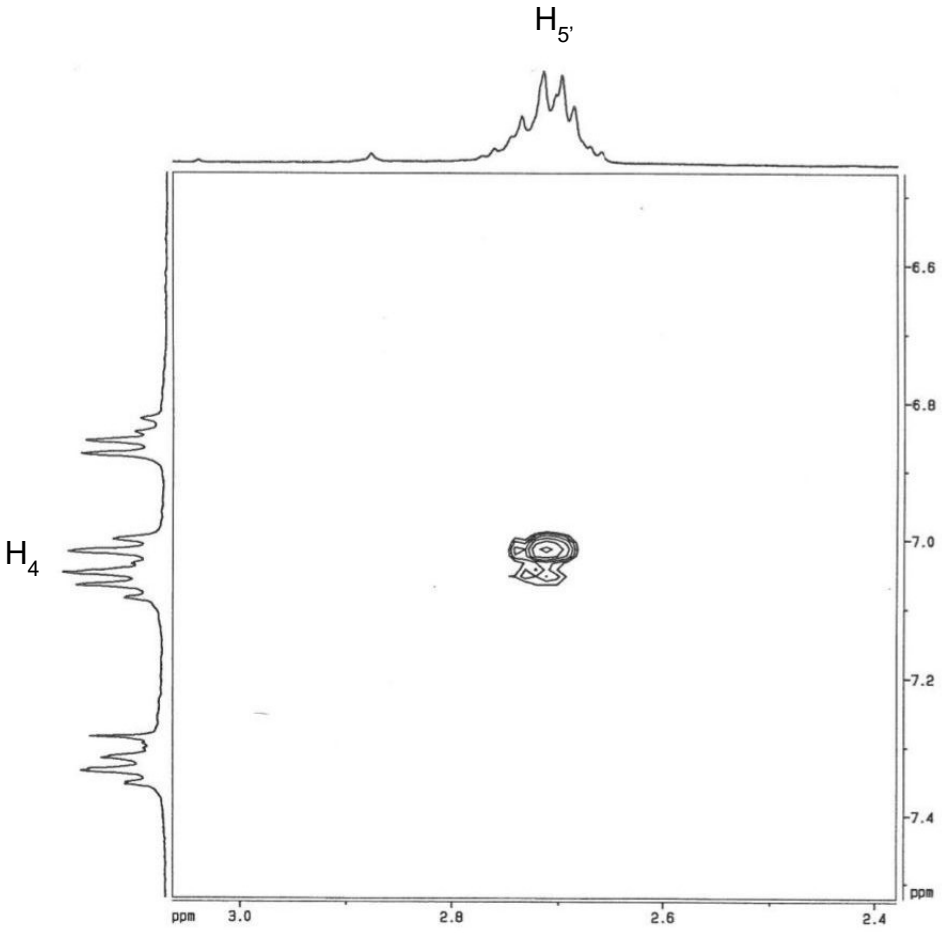
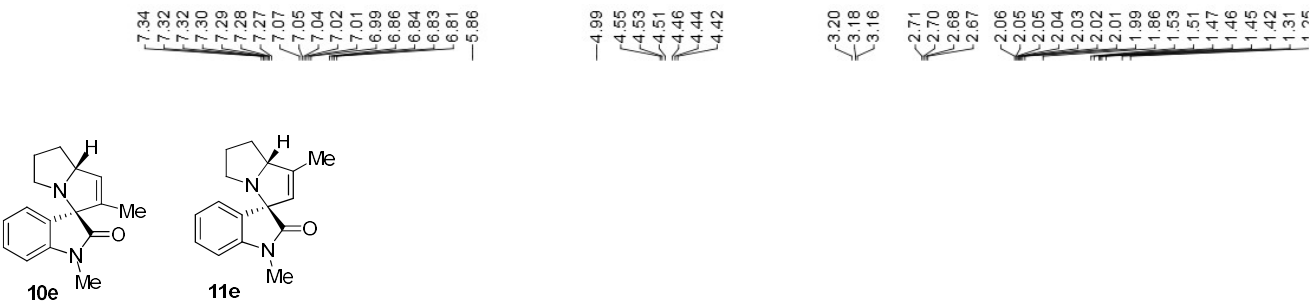

H5'
H4
6.6
6.8
7.0
7.2
7.4
ppm
ppm
3.0
2.8
2.6
2.4

Figure 62. ^{1}H-NMR Spectrum of compound **10e** and **11e** from **1g** ($CDCl_3$, 400 MHz)



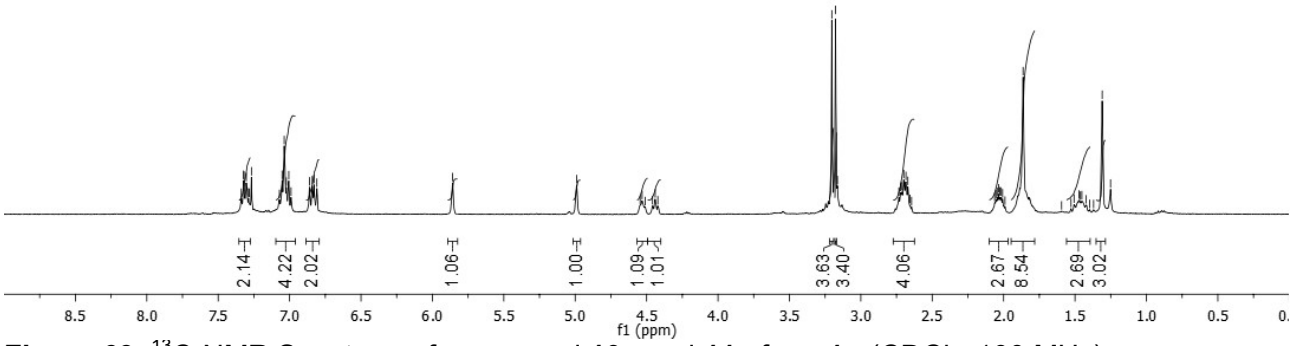


Figure 63. ^{13}C-NMR Spectrum of compound **10e** and **11e** from **1g** ($CDCl_3$, 100 MHz)