Supporting Information

Of

A FACILE PREPARATION OF IMIDAZO[1,2-*a*]PYRIDIN-3-AMINE DERIVATIVES VIA A THREE COMPONENT REACTION WITH β-CYCLODEXTRIN–SO_3H AS CATALYST

Jian Wu,* Fang-Zhou Xu,[#] She-Lei Feng, Wei Xue, and Zhen-Zhen Wang

Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Guizhou University; Research and Development Center for Fine Chemicals, Guizhou University, Huaxi District, Guiyang 550025, P.R. China. E-mail: jianwu2691@126.com

[#] Co-first author for the manuscript

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1. GENERAL INFORMATION

The substituted pyridin-2-amines were obtained from TCI (Shanghai, China), isocyanides aromatic aldehydes were purchased from Accela ChemBio Co., Ltd (Shanghai, China). melting points were uncorrected and determined on a WRX-4 monocular microscope (Shanghai Yice Apparatus & Equipment Co., Ltd, China). The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL ECX 500 NMR spectrometer (JEOL Ltd, Japan) at room temperature operating at 500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR by using $CDCl_3$ or CD_3OD as solvents and TMS as an internal standard; infrared spectra were recorded in KBr on a IR Pristige-21 spectrometer (Shimadzu corporation, Japan), absorbencies are reported in cm^{-1}; HR-MS were recorded on a Orbitrap LC-MS instrument (Q-Exative, Thermo Scientific™, American). The course of the reactions was monitored by TLC; analytical TLC was performed on silica gel GF 254.

2. EXPERIMENTAL PROCEDURES

2.1. Preparation of sulfonated β-cyclodextrin.[1]

To a well stirred mixture of *β*-cyclodextrin (10.0 g, 4.5 mmol) in CH_2Cl_2 (50 mL), chlorosulfonic acid (2.00 g, 10 mmol) was added slowly at 0 °C during 3 h. The resulting mixture was stirred for another 2 h to remove HCl from the reaction vessel. Then, the mixture was filtered and washed with methanol and dried at room temperature to obtain *β*-cyclodextrin-SO_3H as a white powder.

2.2. General procedure for the preparation of imidazo[1,2-*a*]pyridin-3-amines

To a mixture of 2-aminopyridines (1 mmol), aromatic aldehydes (1 mmol) and isocyanides in ethanol (or acetonitrile) was added β-cyclodextrin-SO_3H (10 mol %). The reaction mixture was then allowed to stir for 1 hour under 80 ^{o}C. after complication of this reaction, the resulting mixture was cooled and theβ-cyclodextrin-SO_3H was removed by filtration, the organic phase was evaporated in vacuum. Afterwards the residue were washed with ethyl acetate and cyclohexane (1 : 3) and dried to give the product.

3. Notes and References

1. Wu, J.; Du, X.; Ma, J.; Zhang, Y.; Shi, Q.; Luo, L.; Song, B.; Yang, S.; Hu, D. *Green Chem.* 2014, **16**, 3210.

4. NMR and HR-MS Spectras of the Products

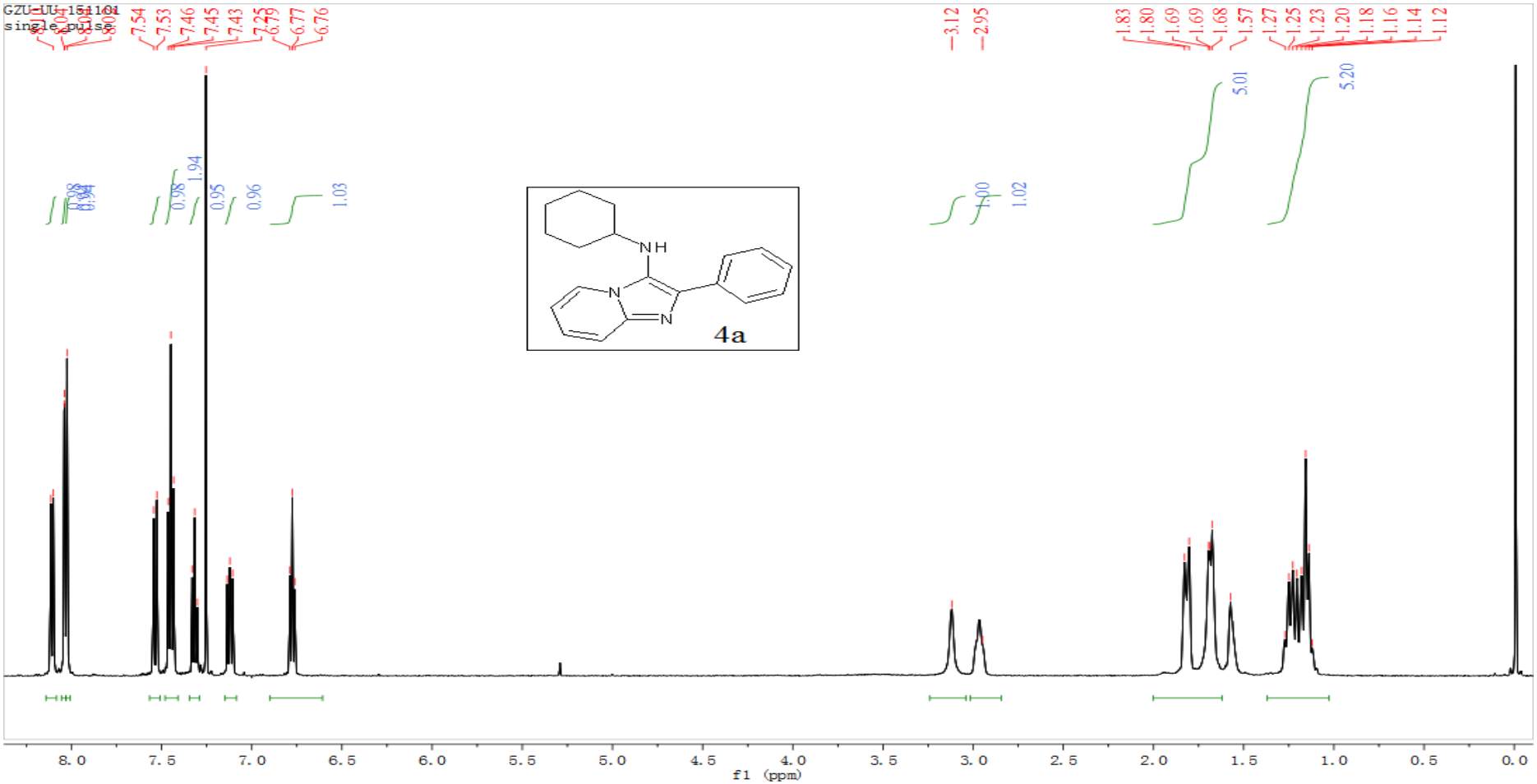

Figure 1. ^{1}H NMR (500 MHz) spectrum of compound **4a** in $CDCl_3$.

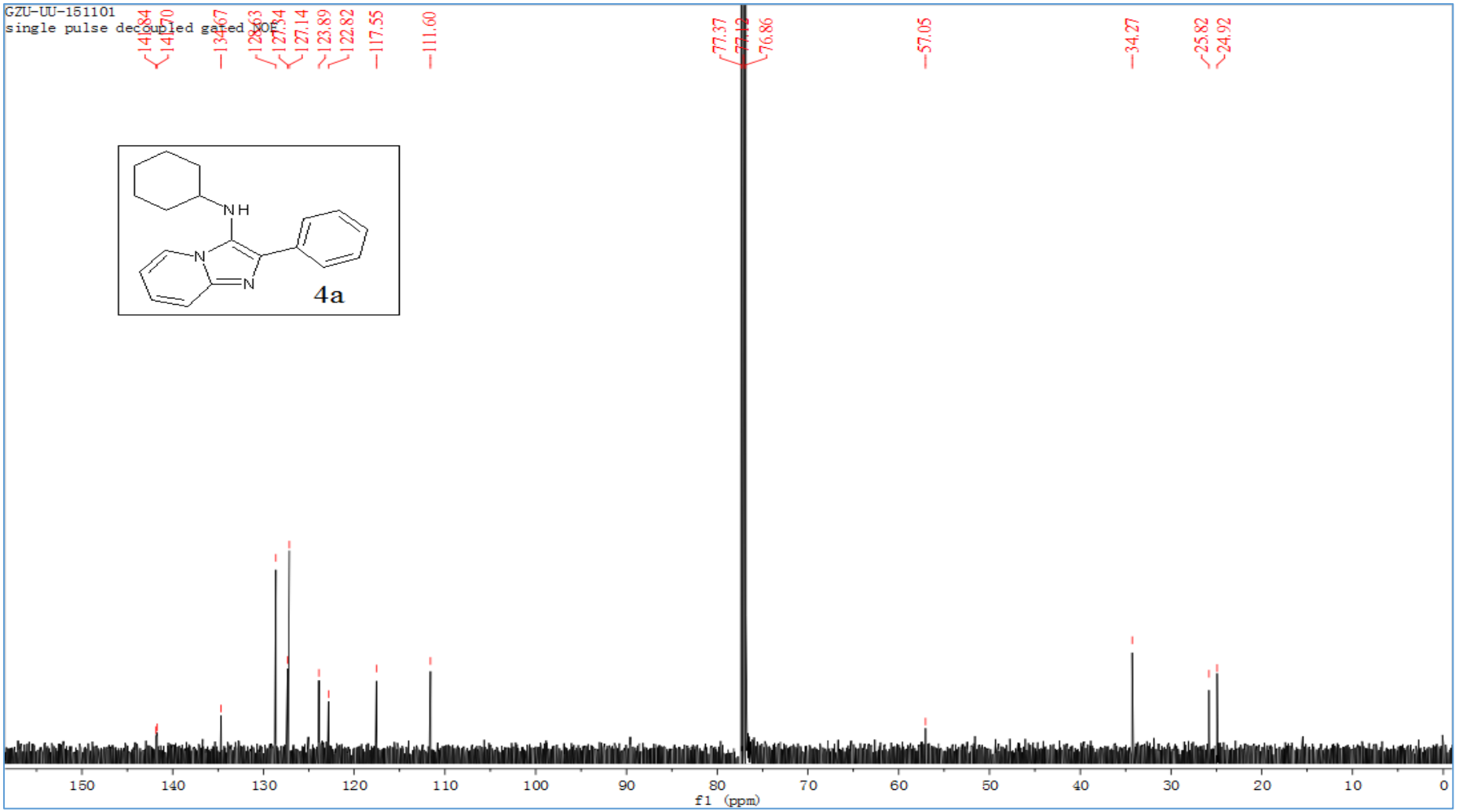

Figure 2. ^{13}C NMR (125 MHz) spectrum of compound **4a** in $CDCl_3$.

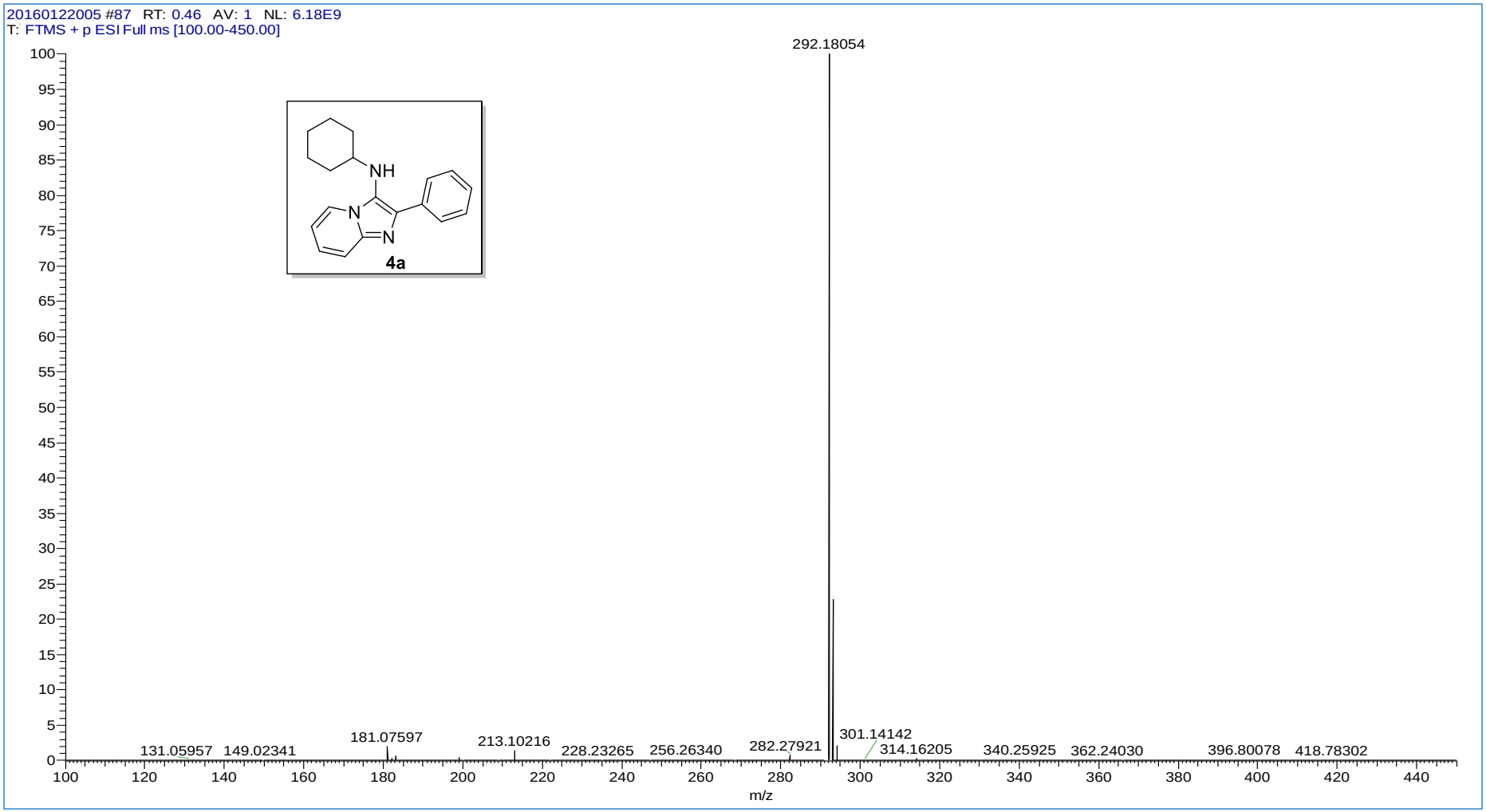

Figure 3. HRMS spectrum of compound **4a**.

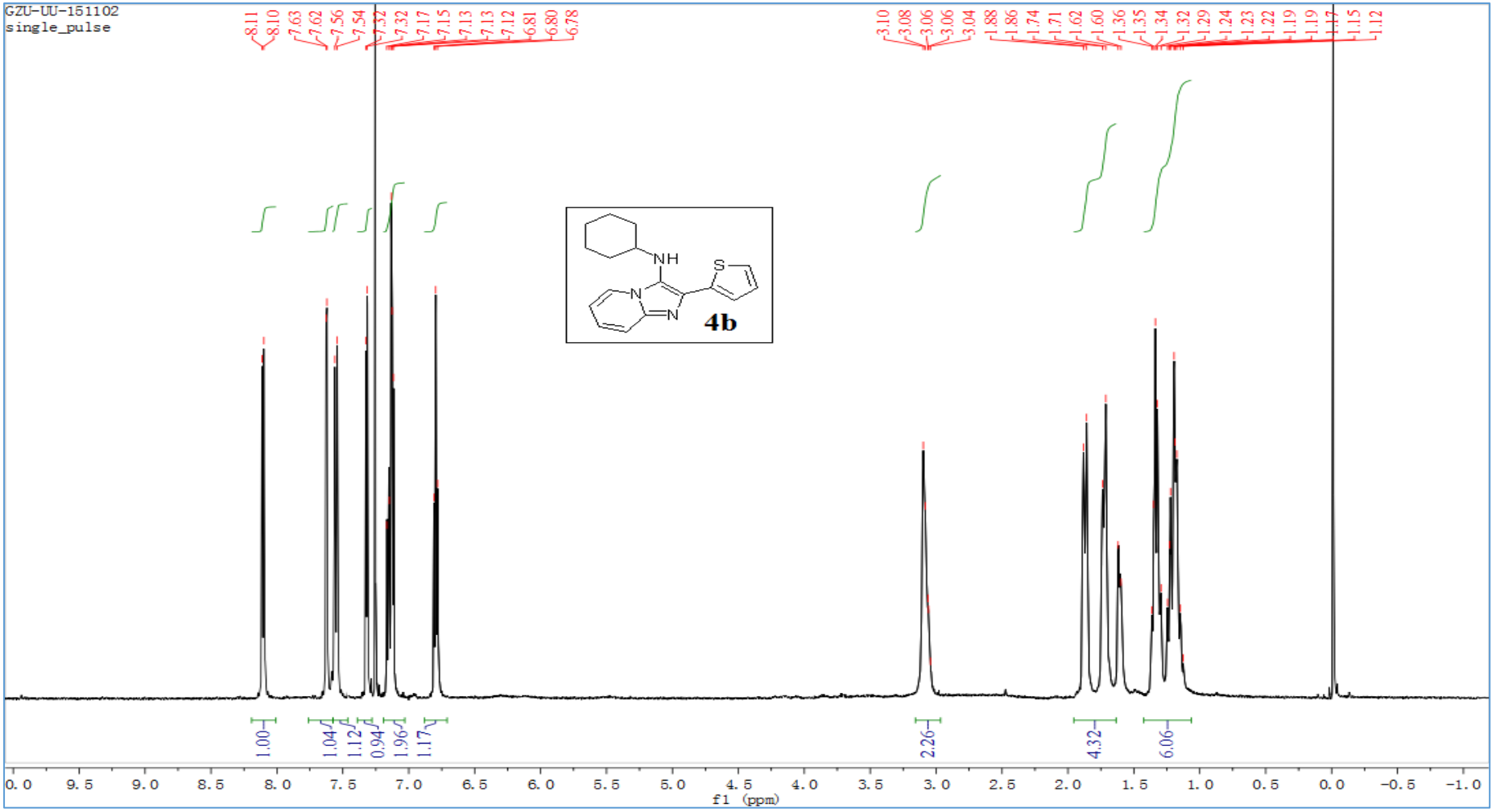

Figure 4. ^{1}H NMR (500 MHz) spectrum of compound **4b** in $CDCl_3$.

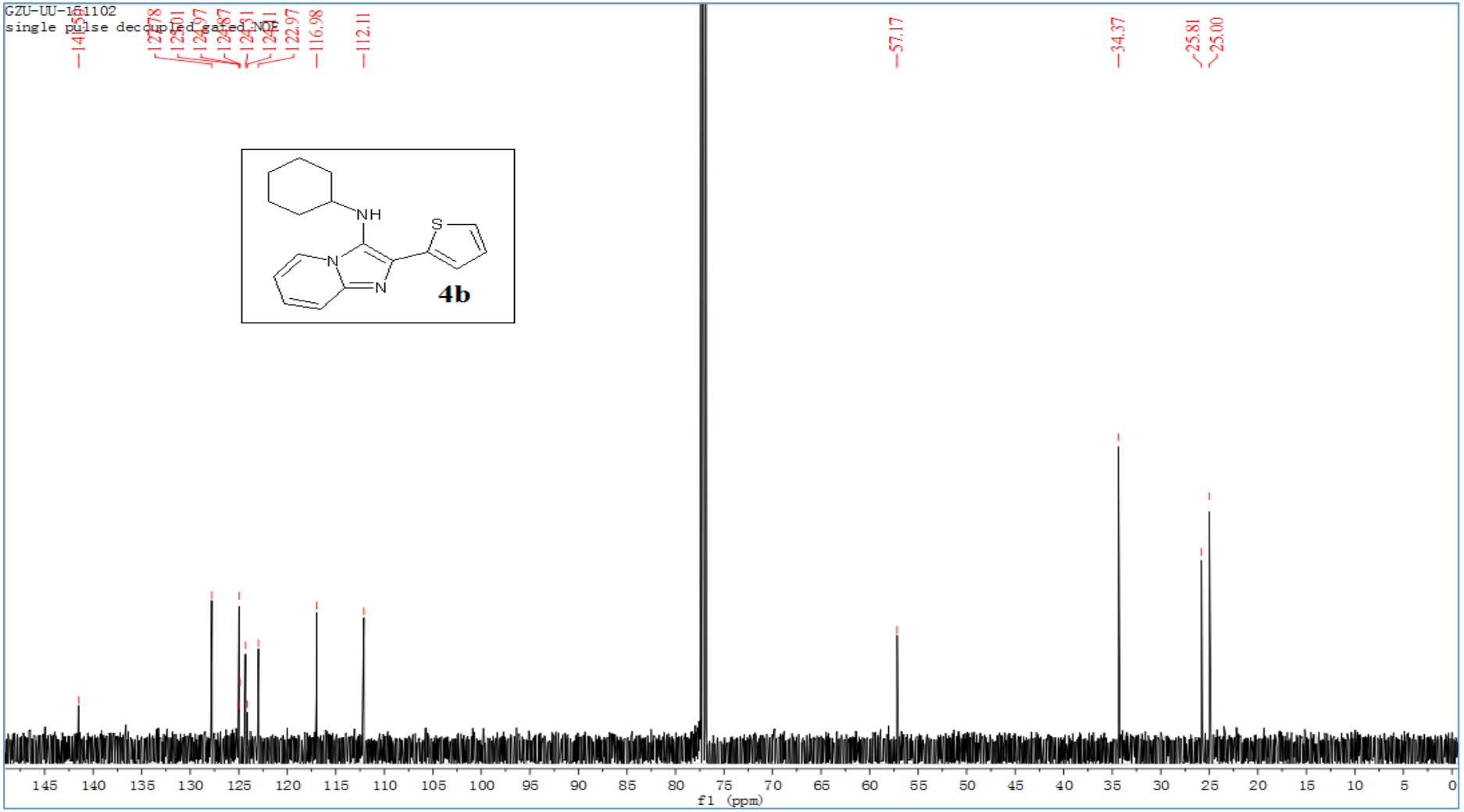

Figure 5: ^{13}C NMR (125 MHz) spectrum of compound **4b** in $CDCl_3$.

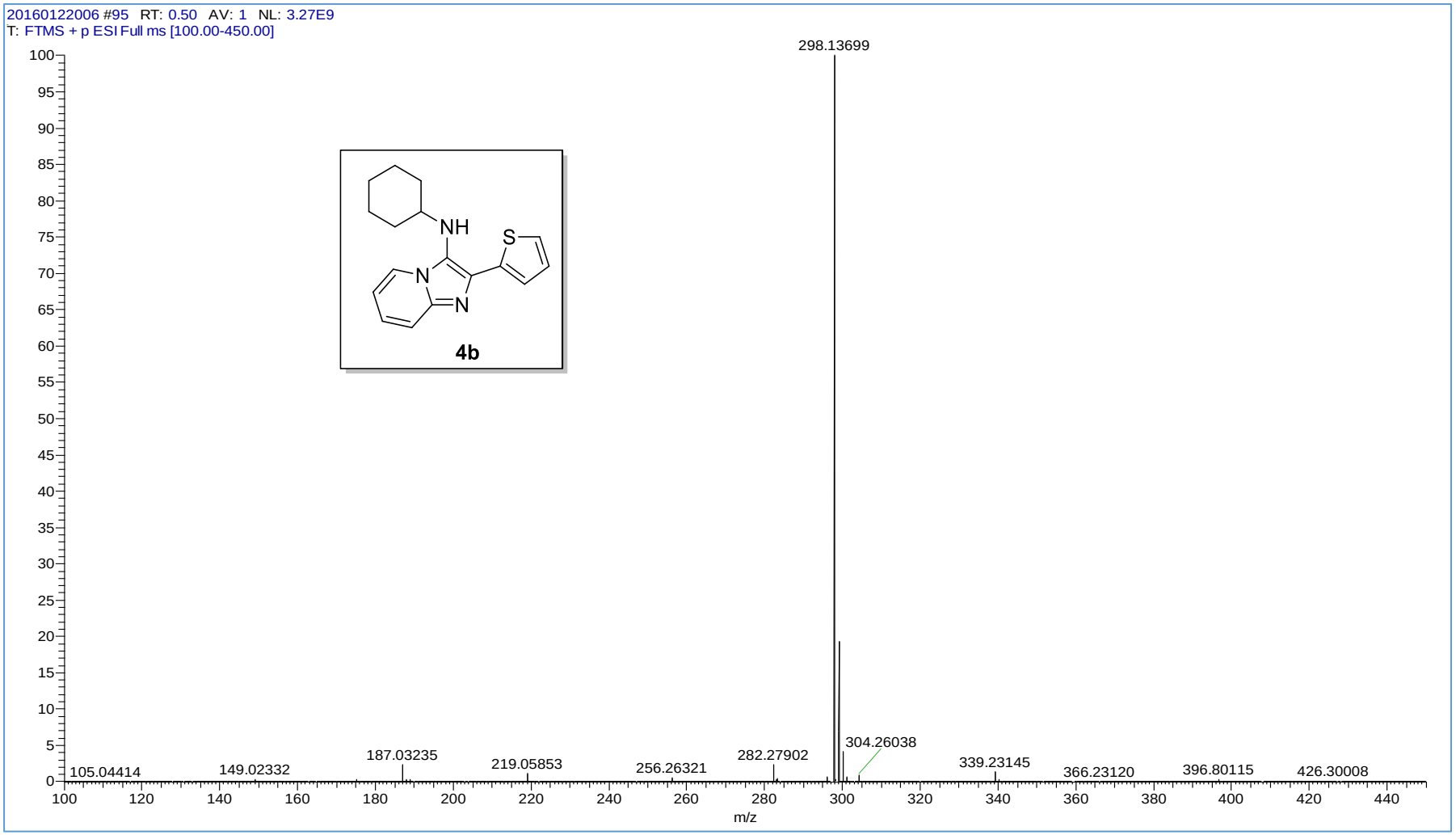

Figure 6. HRMS spectrum of compound **4b**.

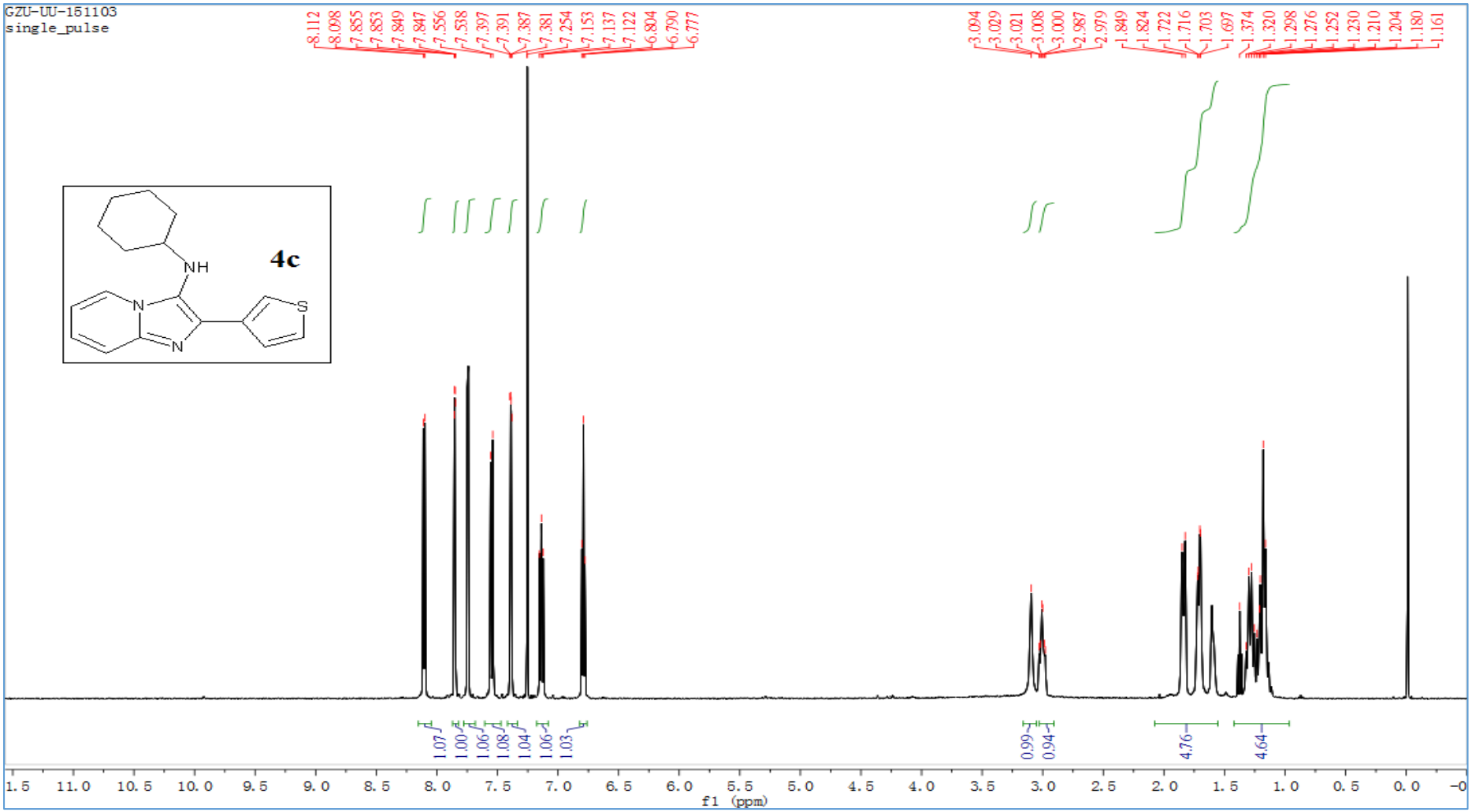

Figure 7. ^{1}H NMR (500 MHz) spectrum of compound **4c** in $CDCl_3$.

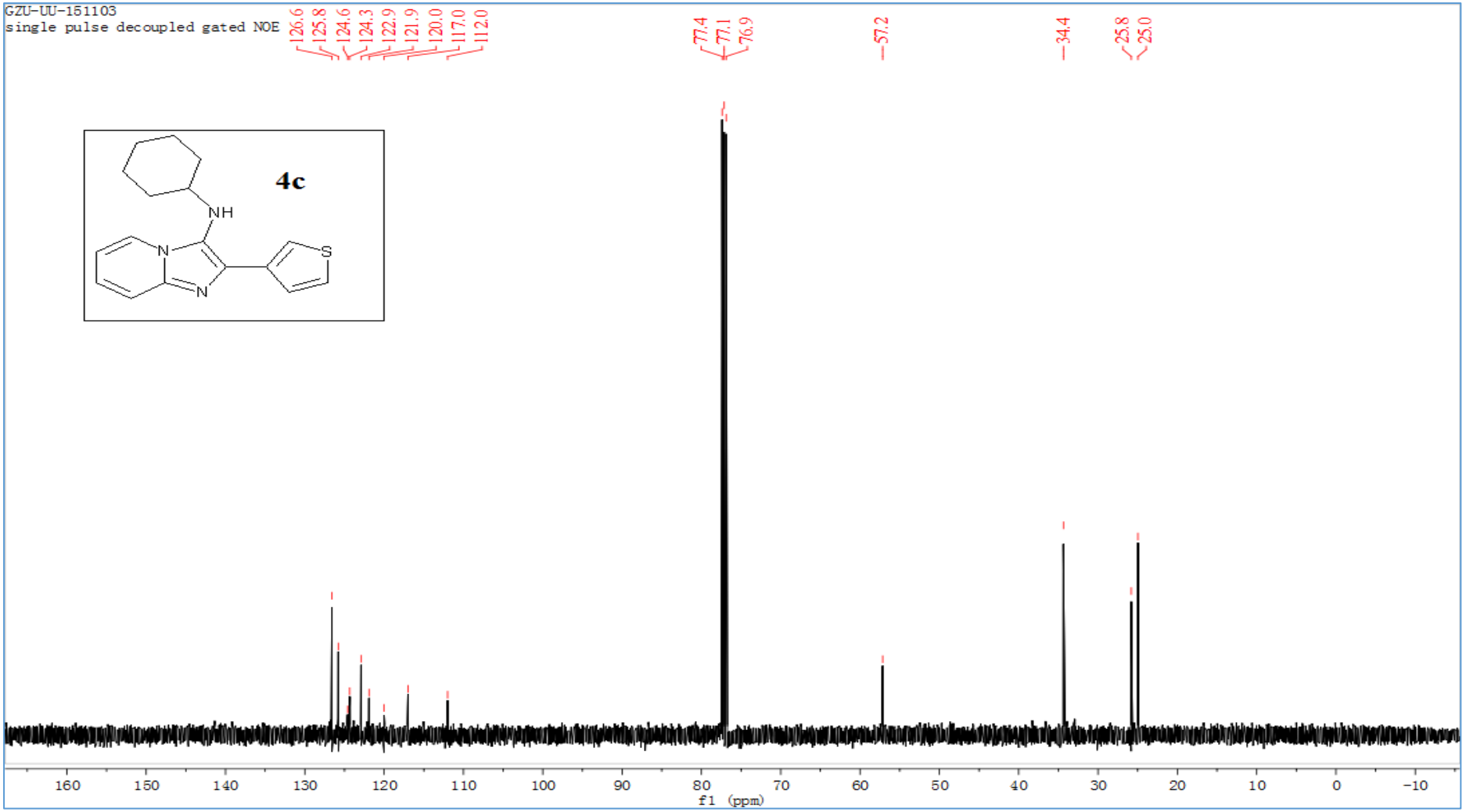

Figure 8. ^{13}C NMR (125 MHz) spectrum of compound **4c** in $CDCl_3$.

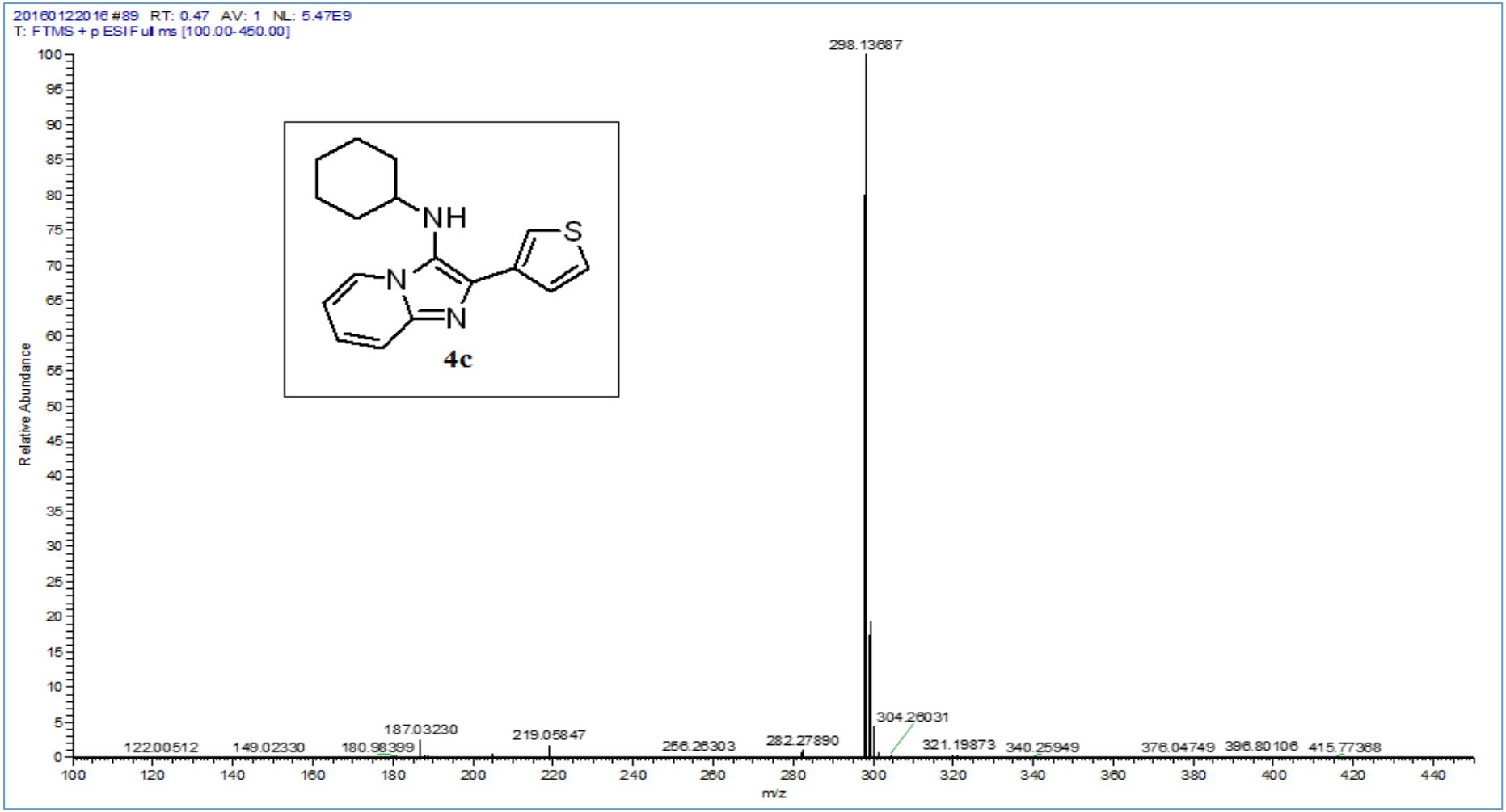

Figure 9. HRMS spectrum of compound **4c**.

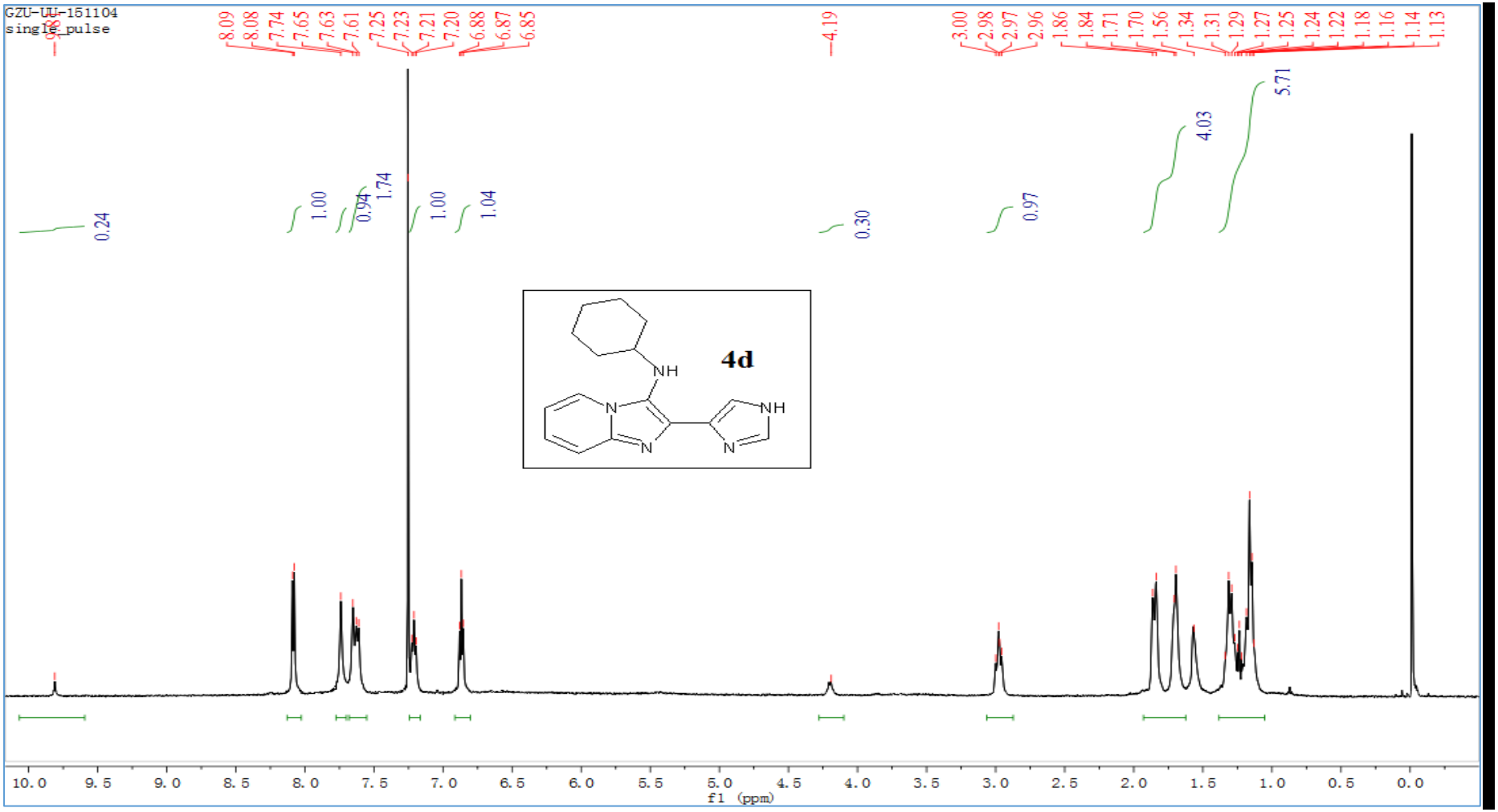

Figure 10. ^{1}H NMR (500 MHz) spectrum of compound **4d** in $CDCl_3$.

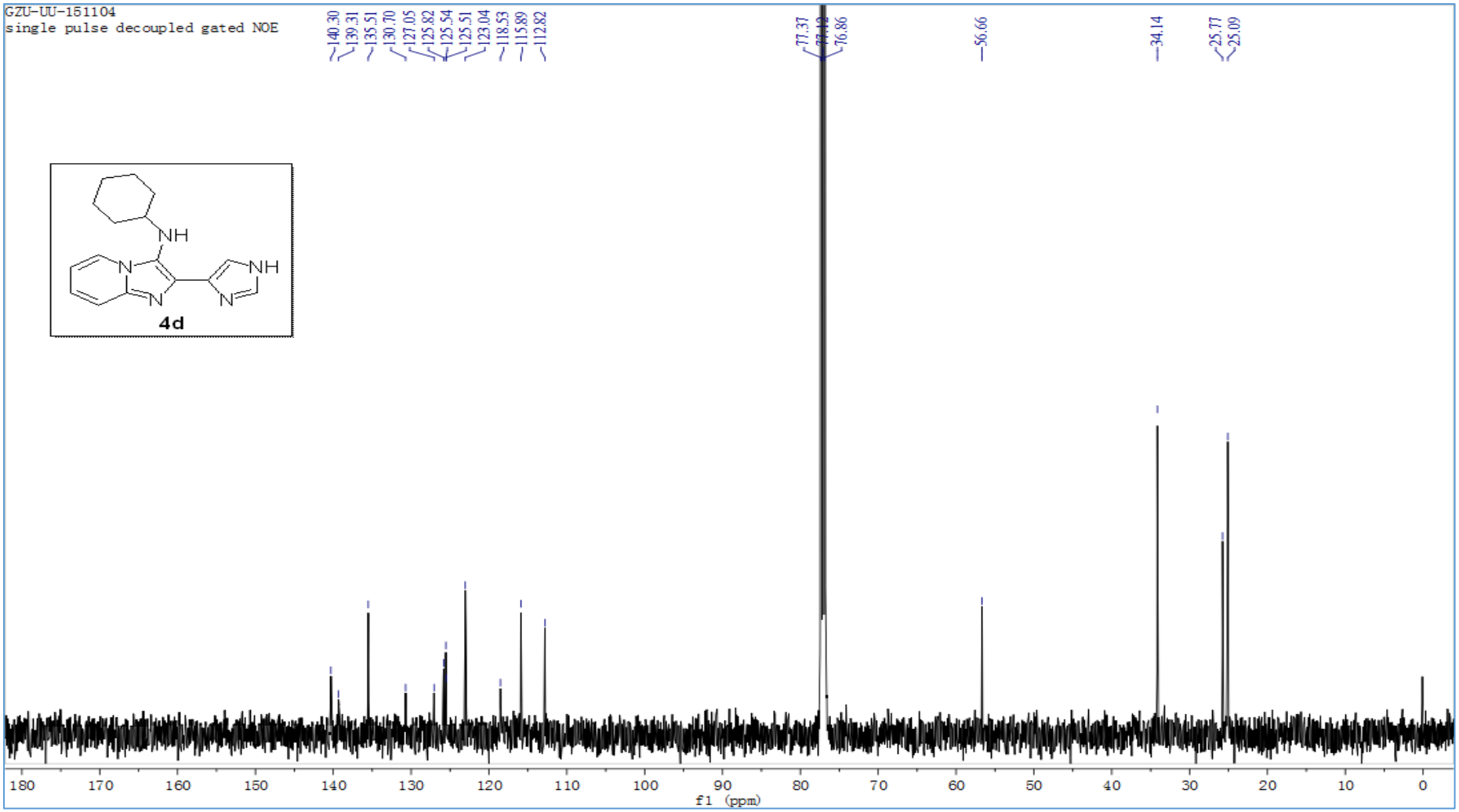

Figure 11. ^{13}C NMR (125 MHz) spectrum of compound **4d** in $CDCl_3$.

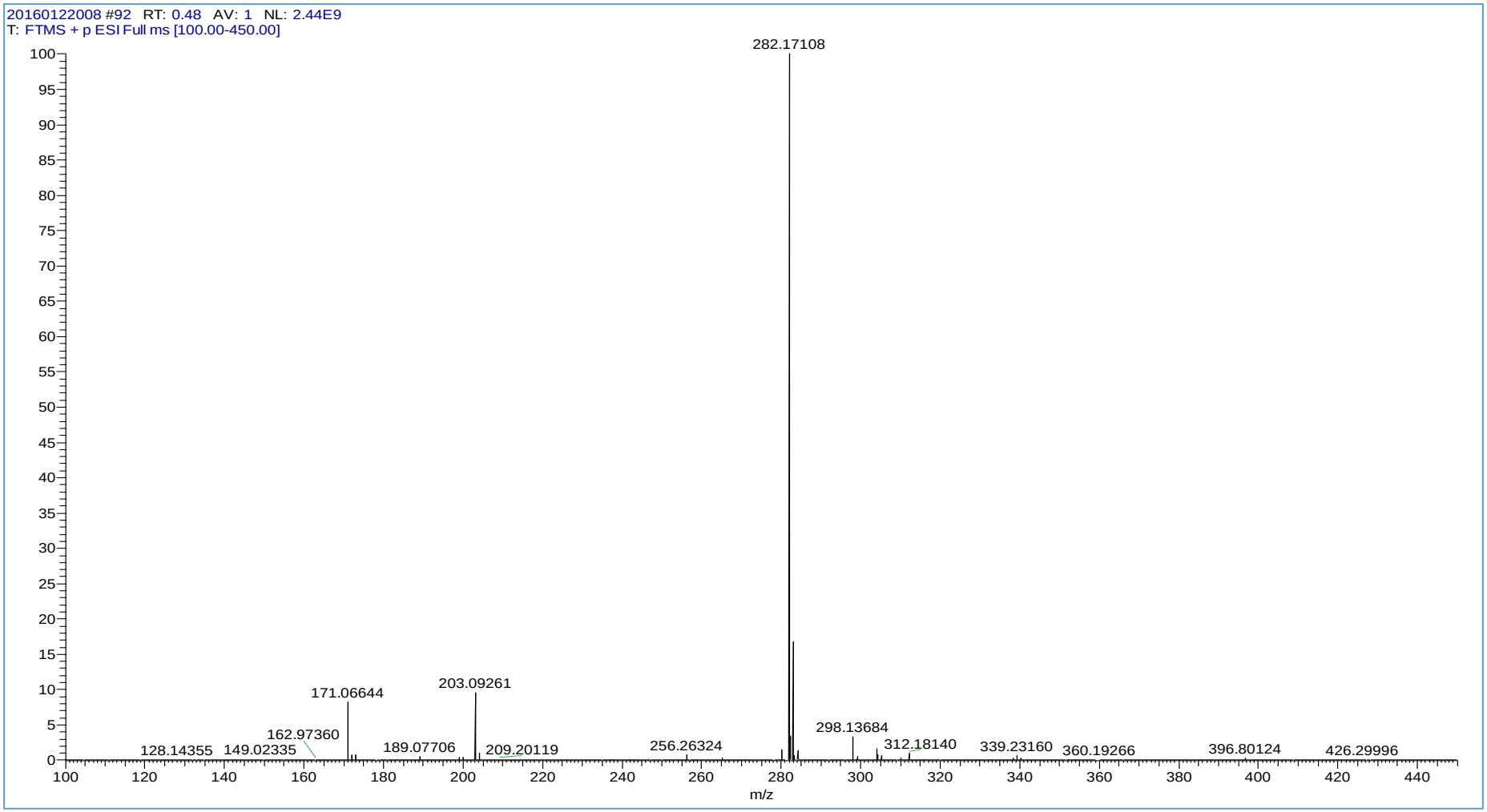

Figure 12. HRMS spectrum of compound **4d**.

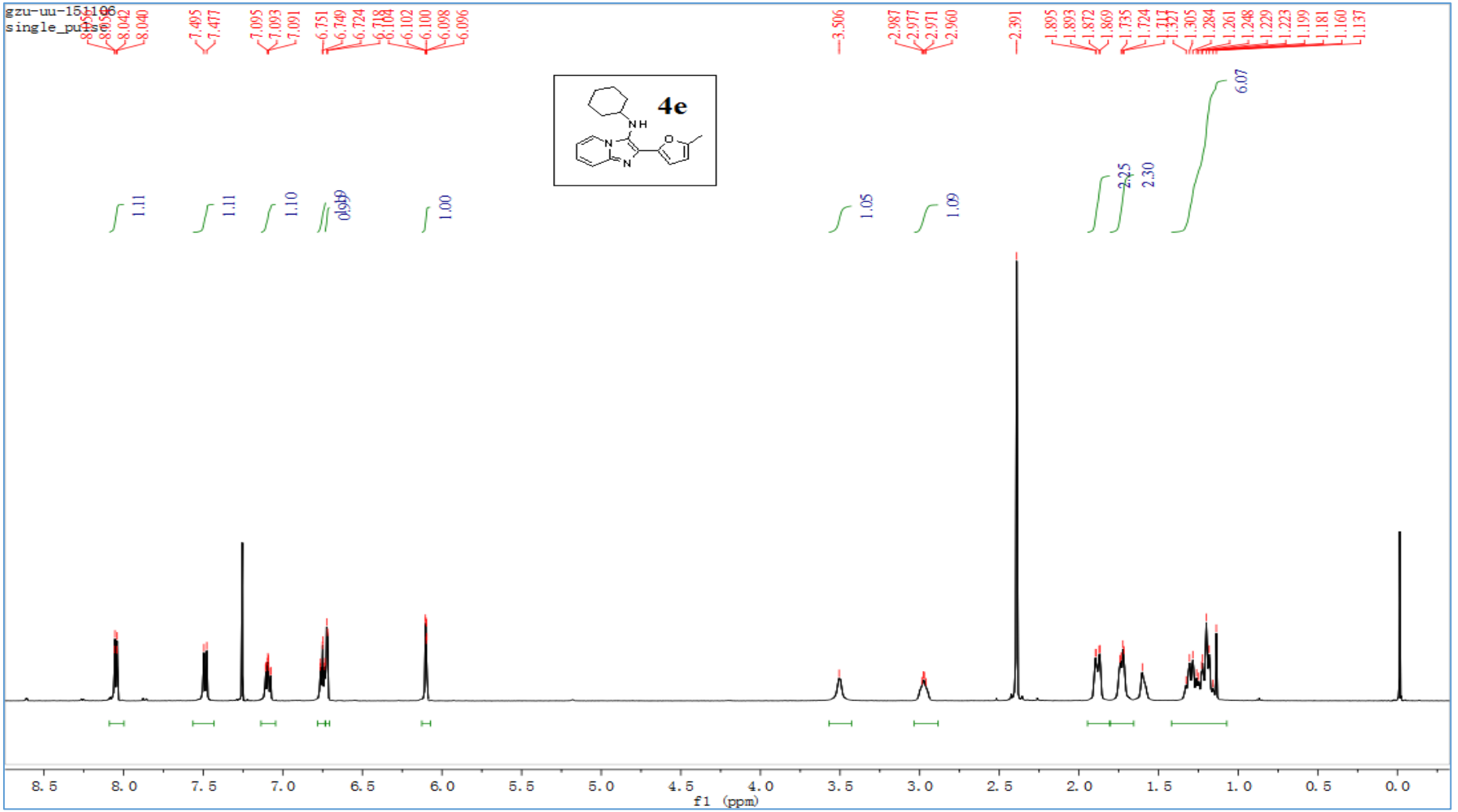

Figure 13. ^{1}H NMR (500 MHz) spectrum of compound **4e** in $CDCl_3$.

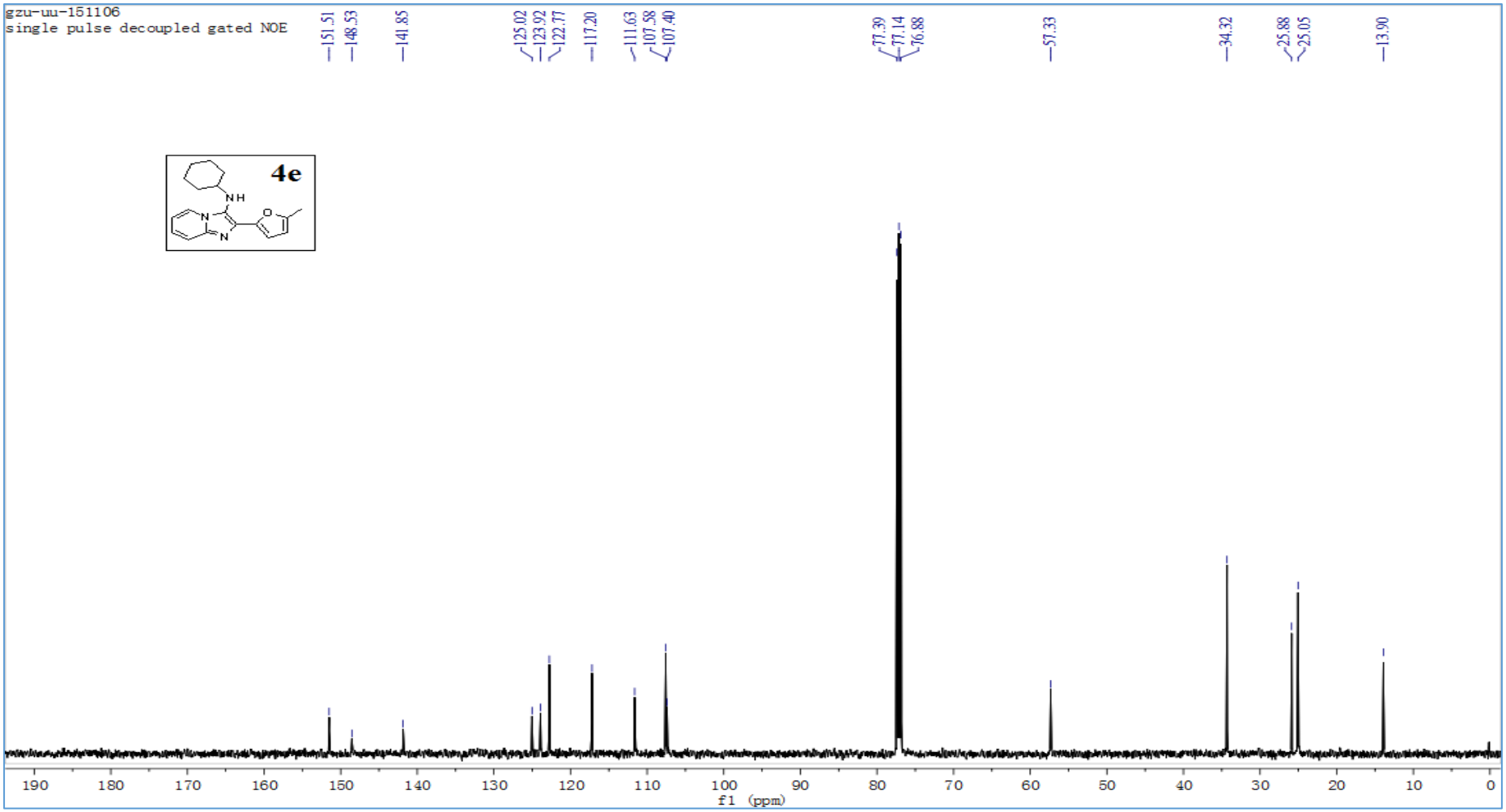

Figure 14. ^{13}C NMR (125 MHz) spectrum of compound **4e** in $CDCl_3$.

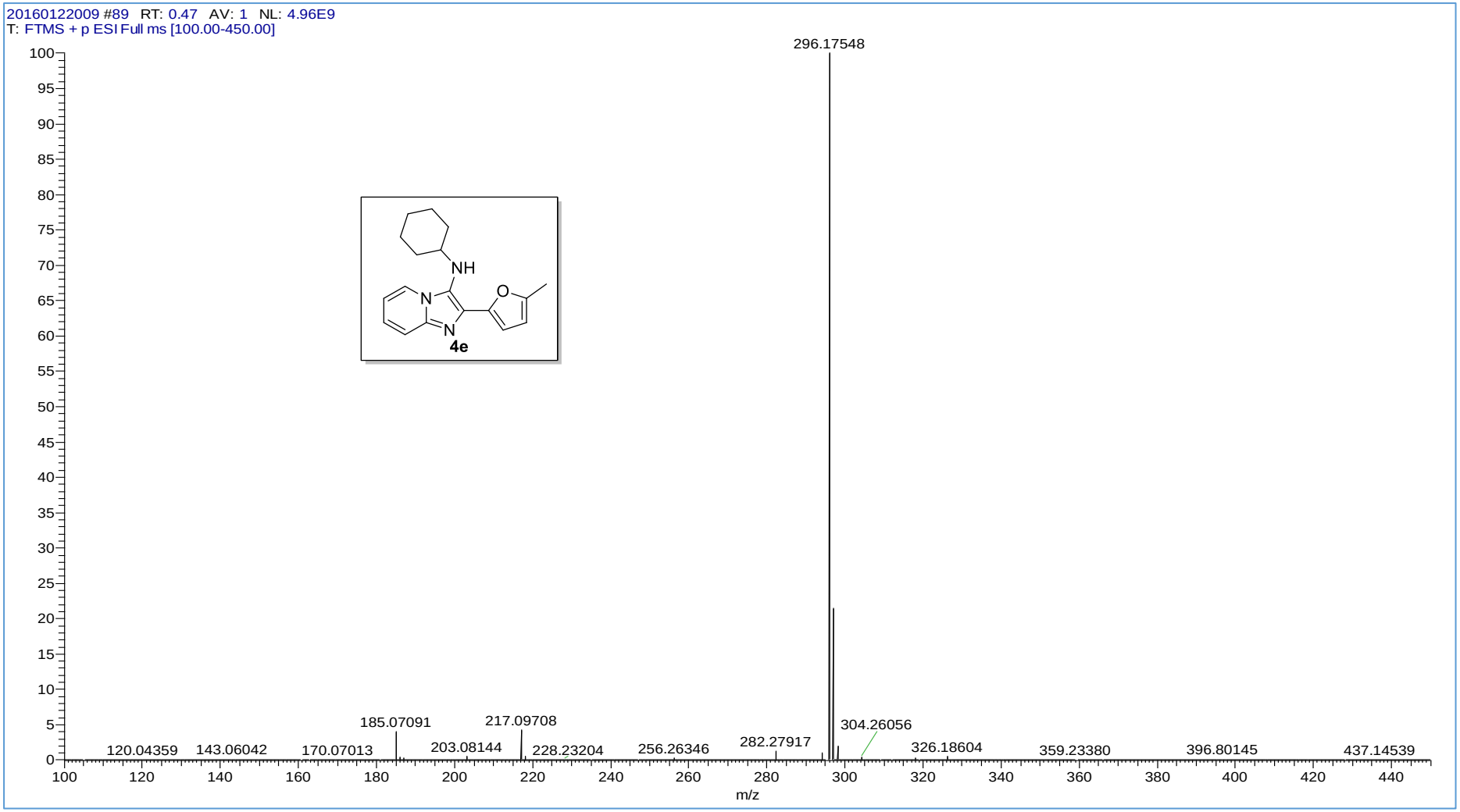

Figure 15. HRMS spectrum of compound **4e**.

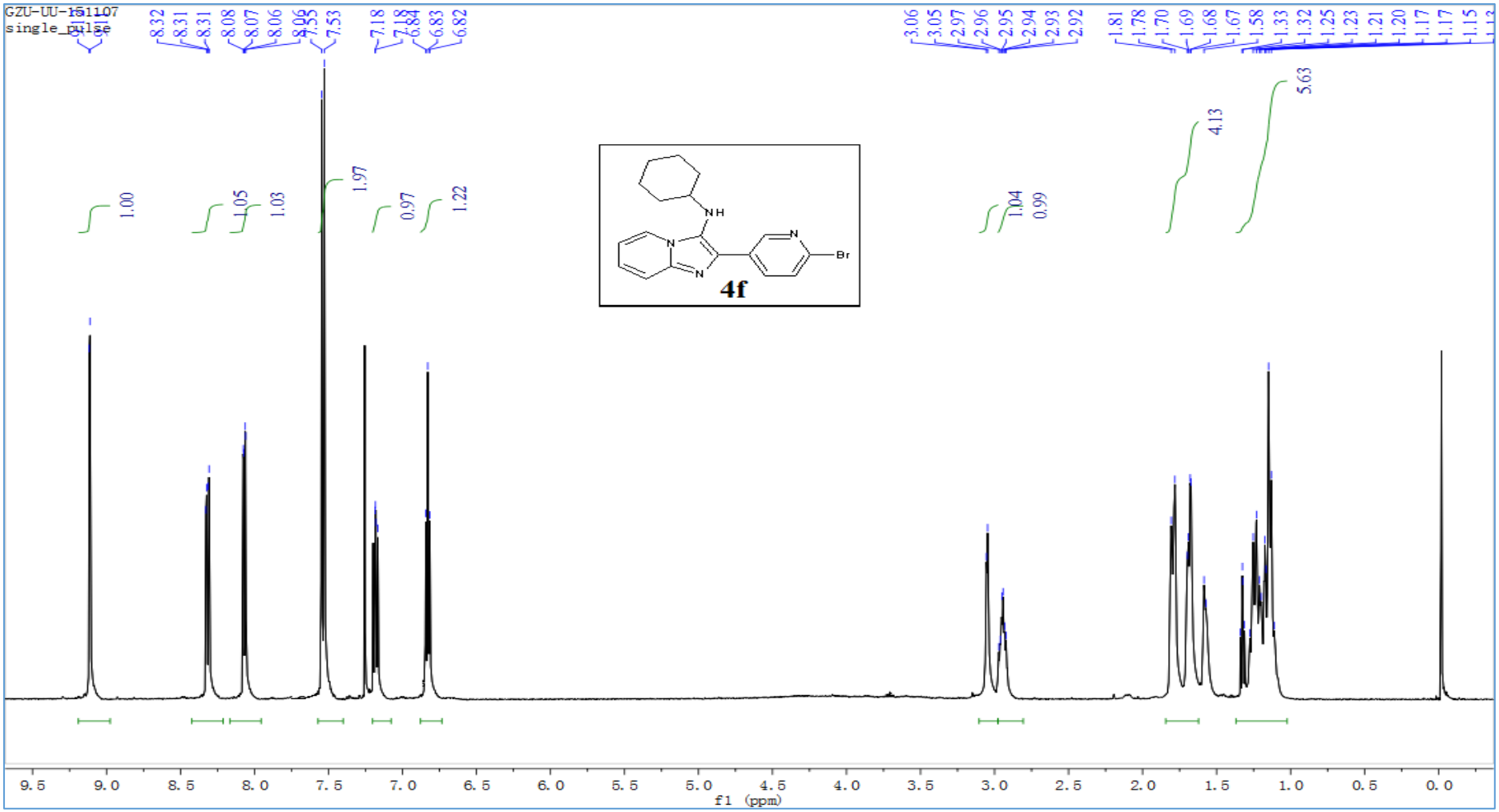

Figure 16. ^{1}H NMR (500 MHz) spectrum of compound **4f** in $CDCl_3$.

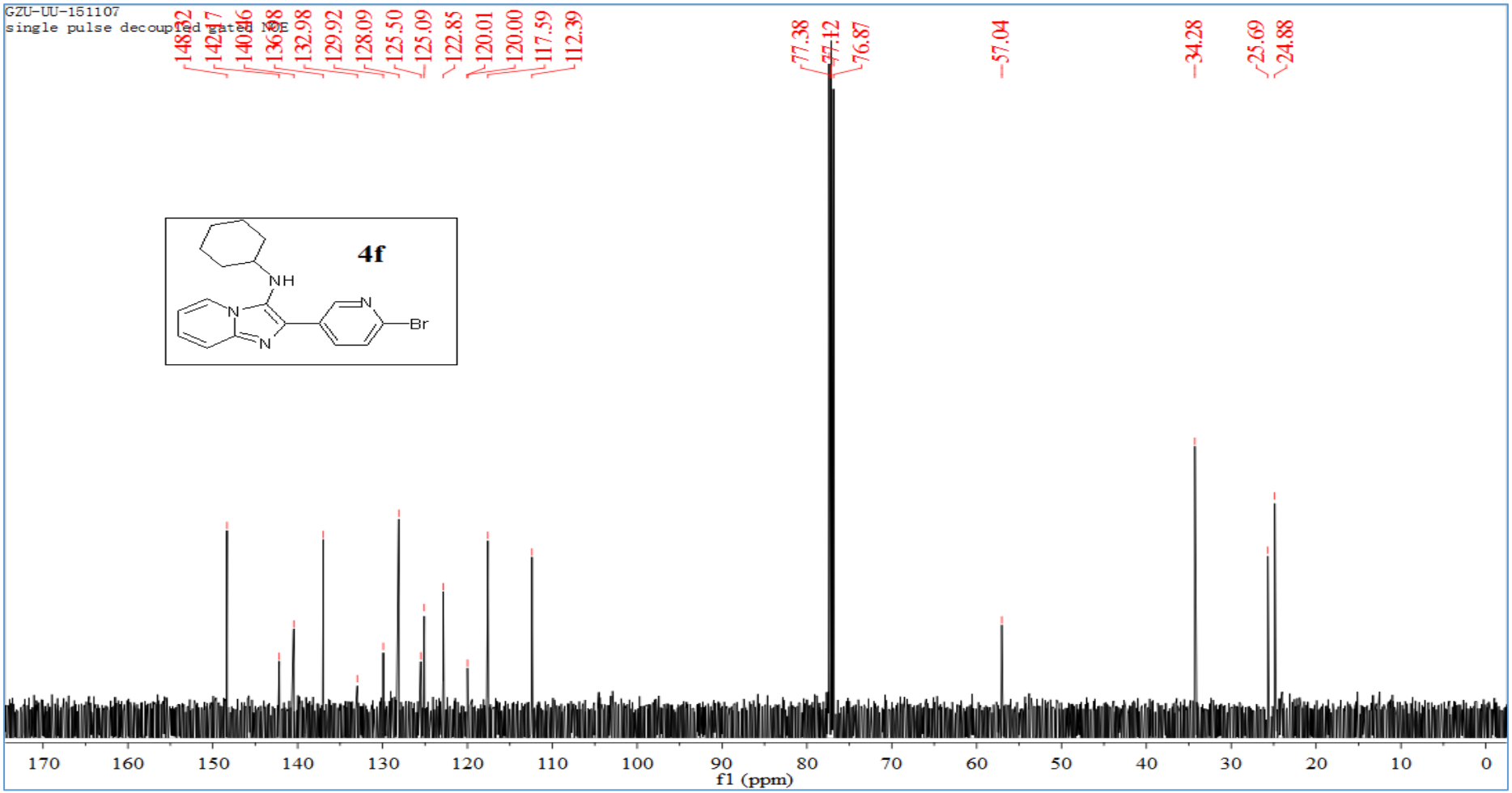

Figure 17. ^{13}C NMR (125 MHz) spectrum of compound **4f** in $CDCl_3$.

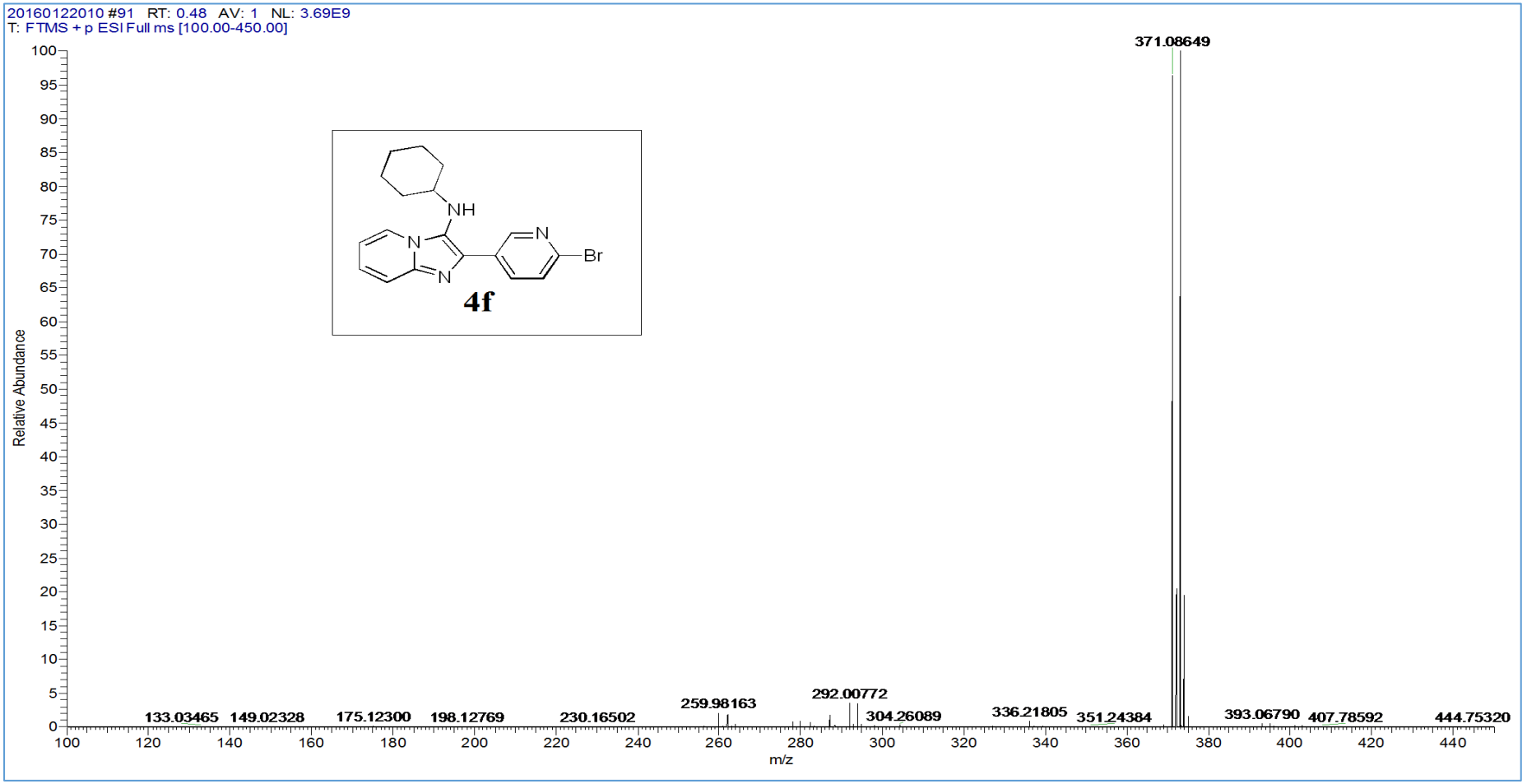

Figure 18. HRMS spectrum of compound **4f**.

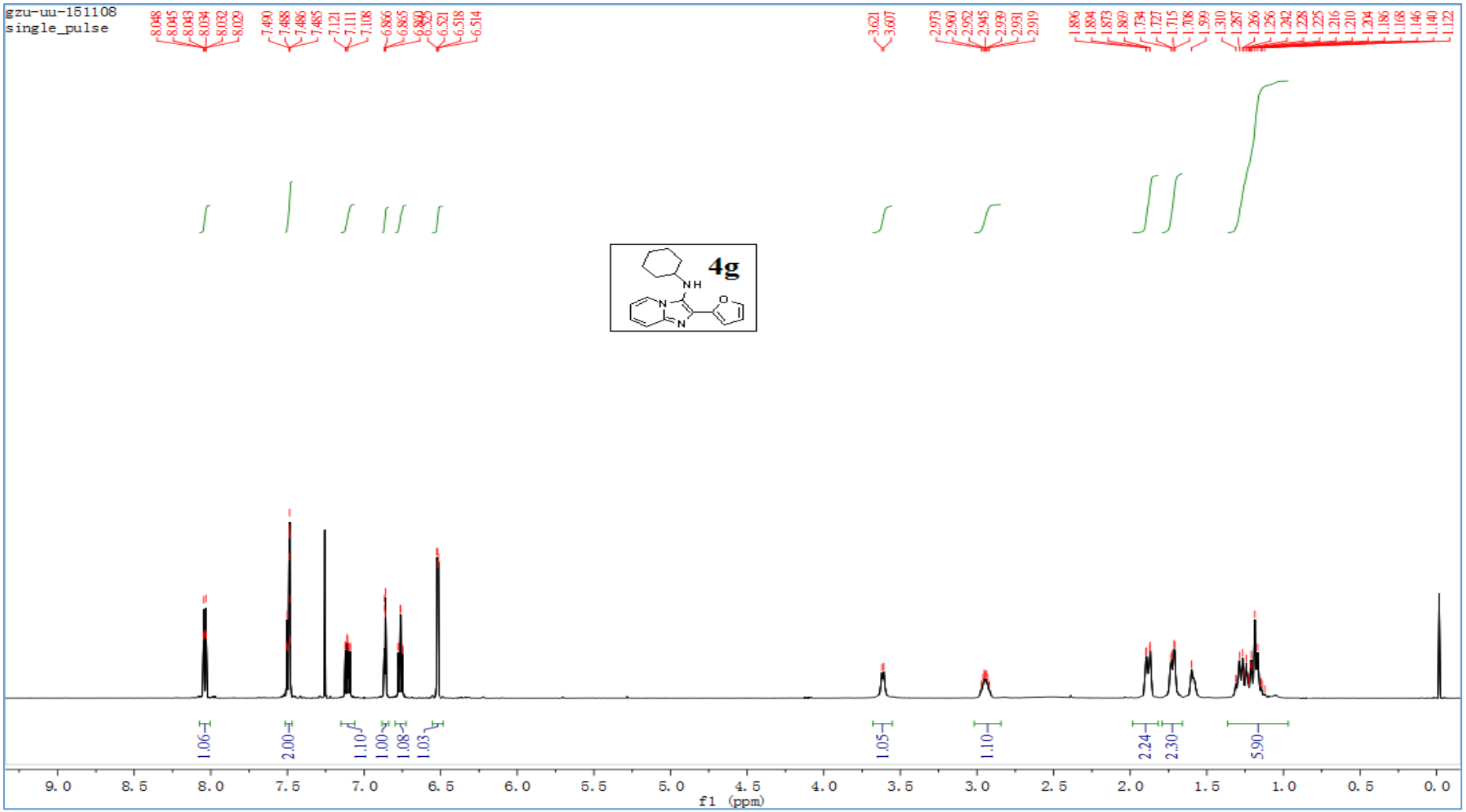

Figure 19. ^{1}H NMR (500 MHz) spectrum of compound **4g** in $CDCl_3$.

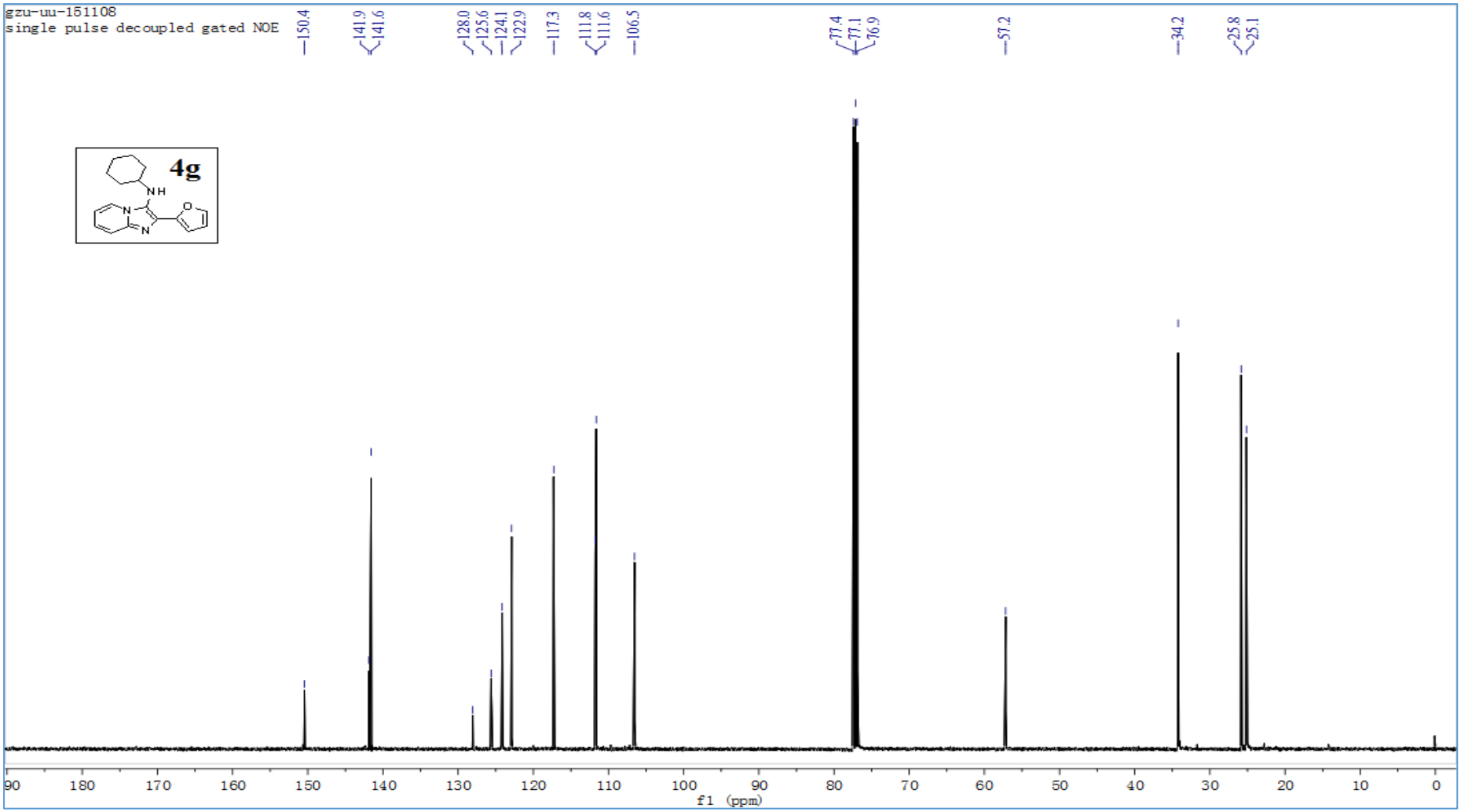

Figure 20. ^{13}C NMR (125 MHz) spectrum of compound **4g** in $CDCl_3$.

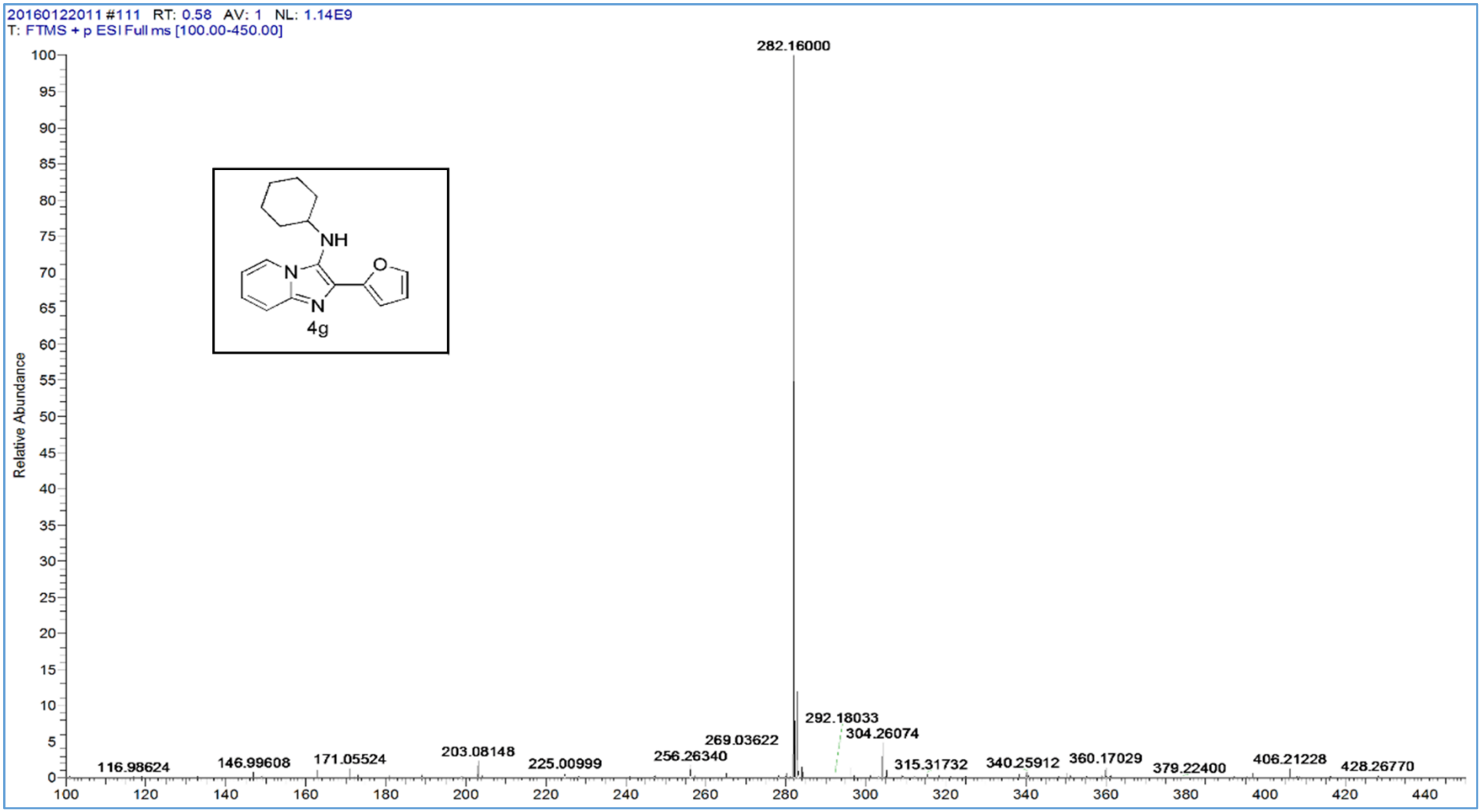

Figure 21. HRMS spectrum of compound **4g**.

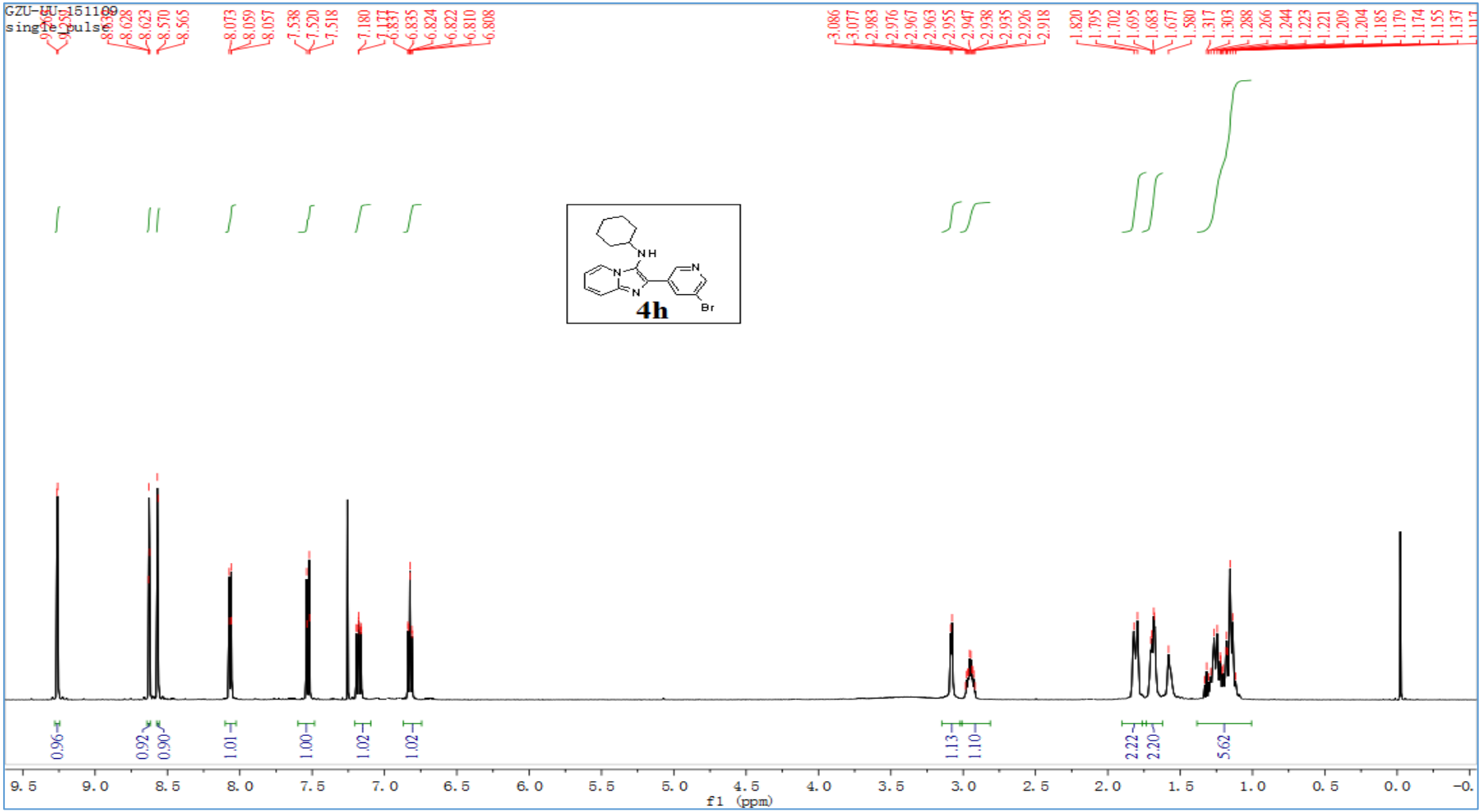

Figure 22. ^{1}H NMR (500 MHz) spectrum of compound **4h** in $CDCl_3$.

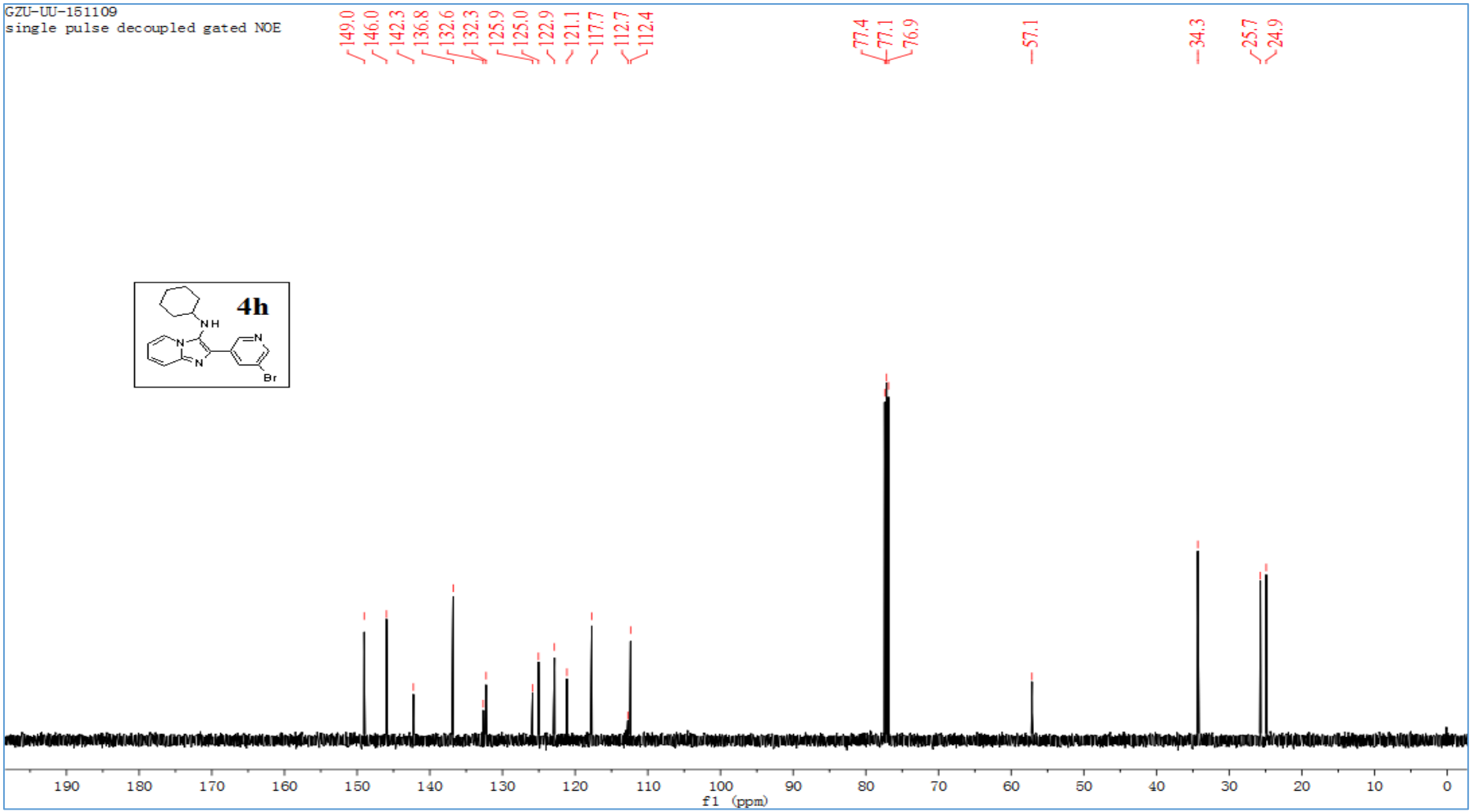

Figure 23. ^{1}H NMR (500 MHz) spectrum of compound **4h** in $CDCl_3$.

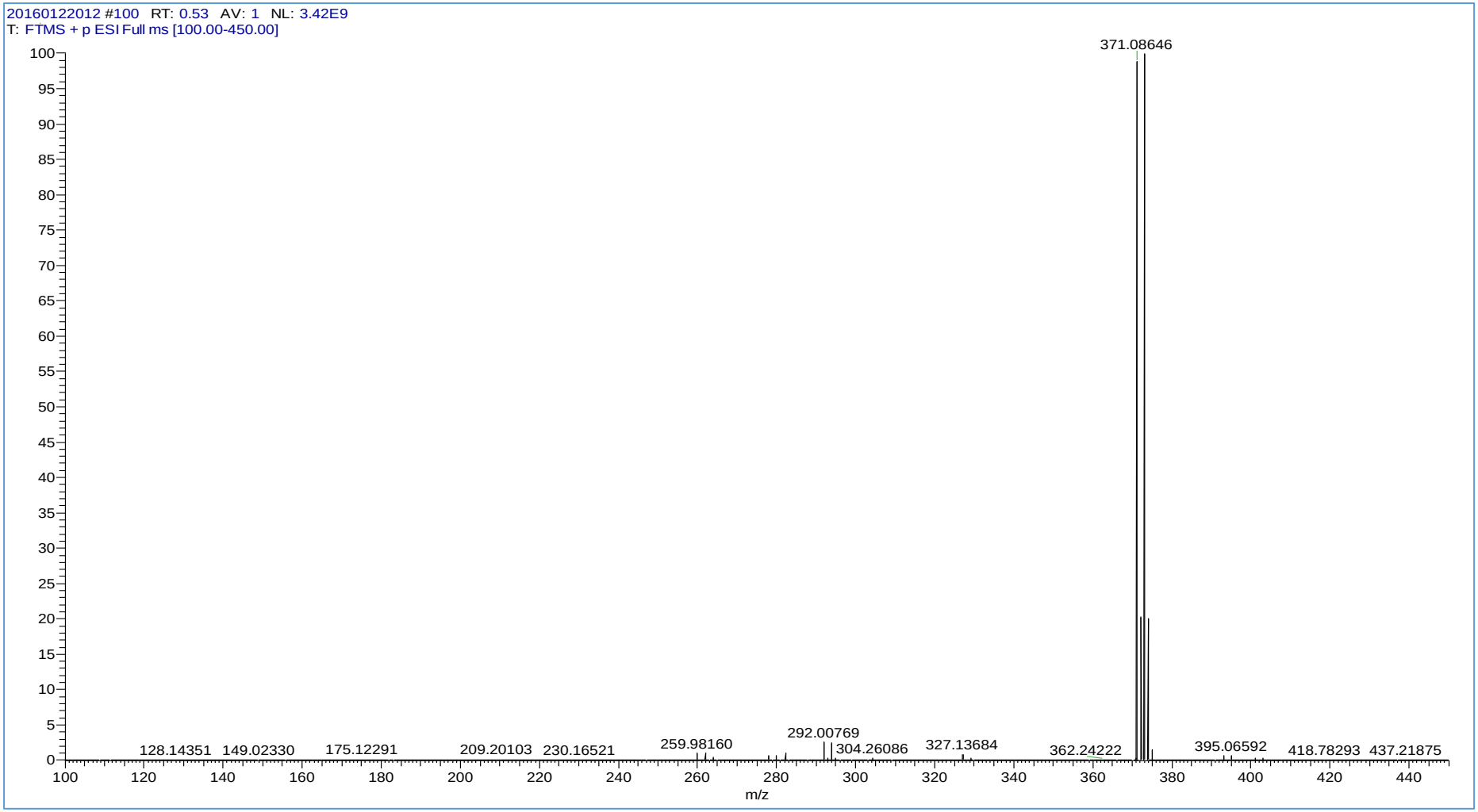

Figure24. HRMS spectrum of compound **4h**.

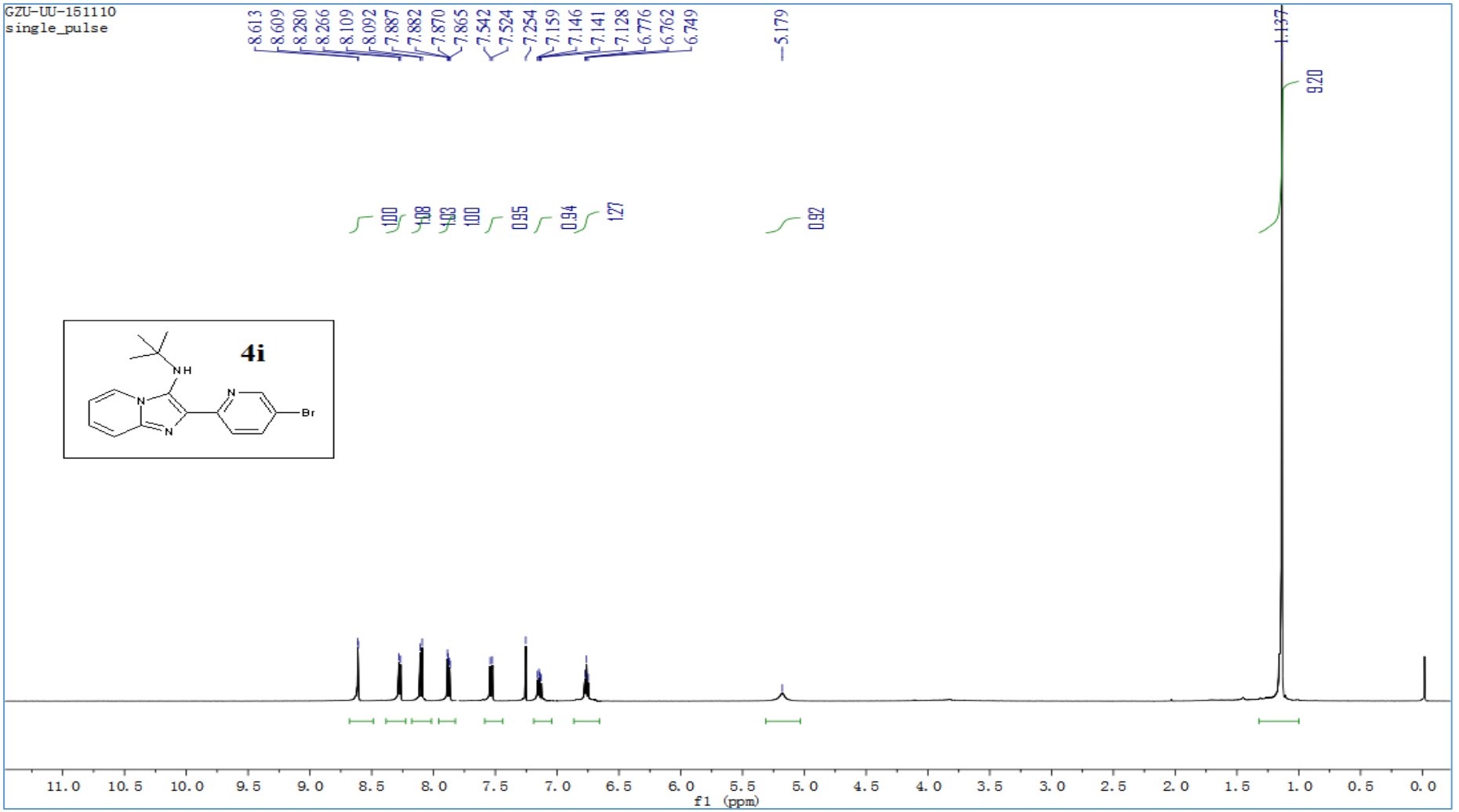

Figure 25. ^{1}H NMR (500 MHz) spectrum of compound **4i** in $CDCl_3$.

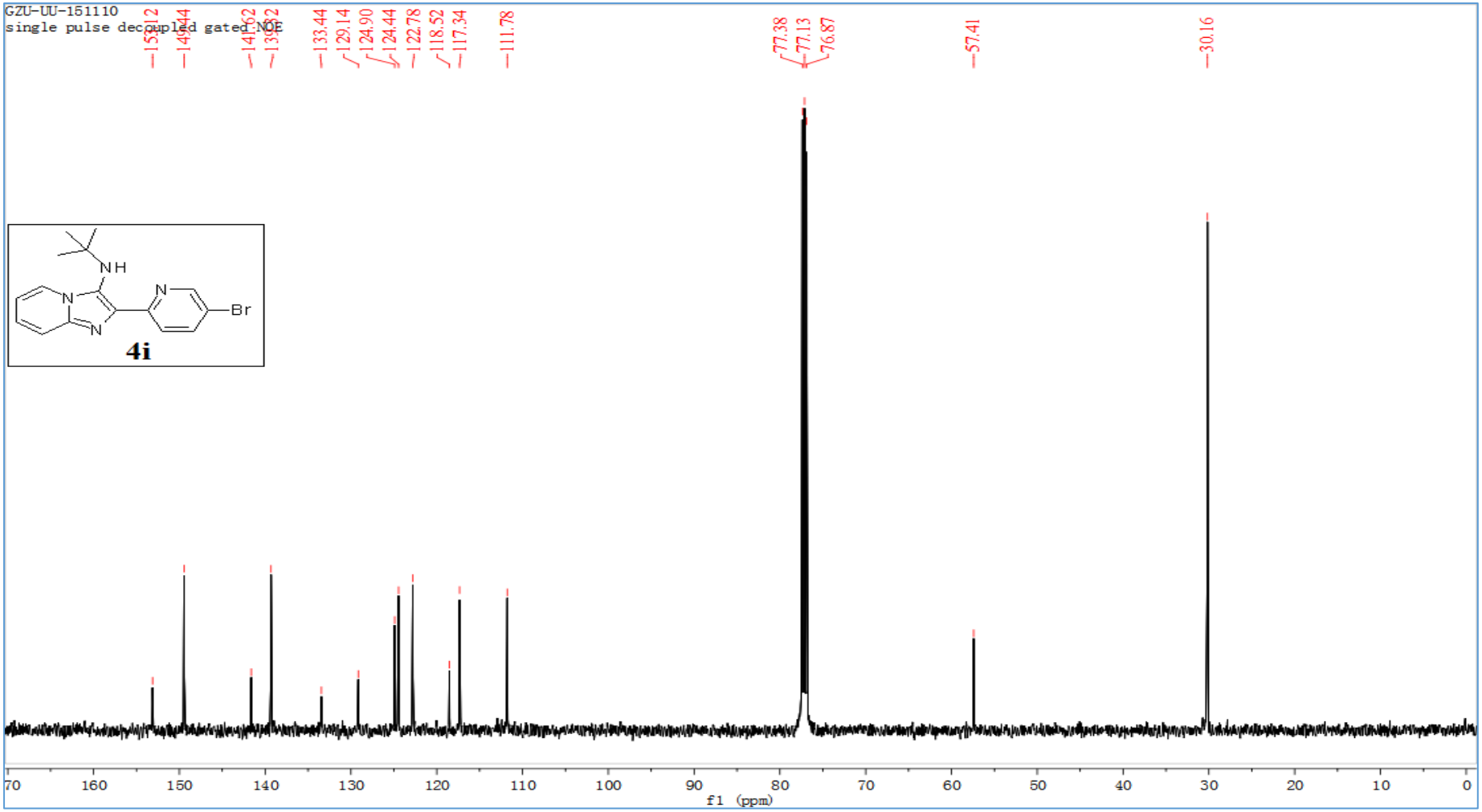

Figure 26. ^{13}C NMR (125 MHz) spectrum of compound **4i** in $CDCl_3$.

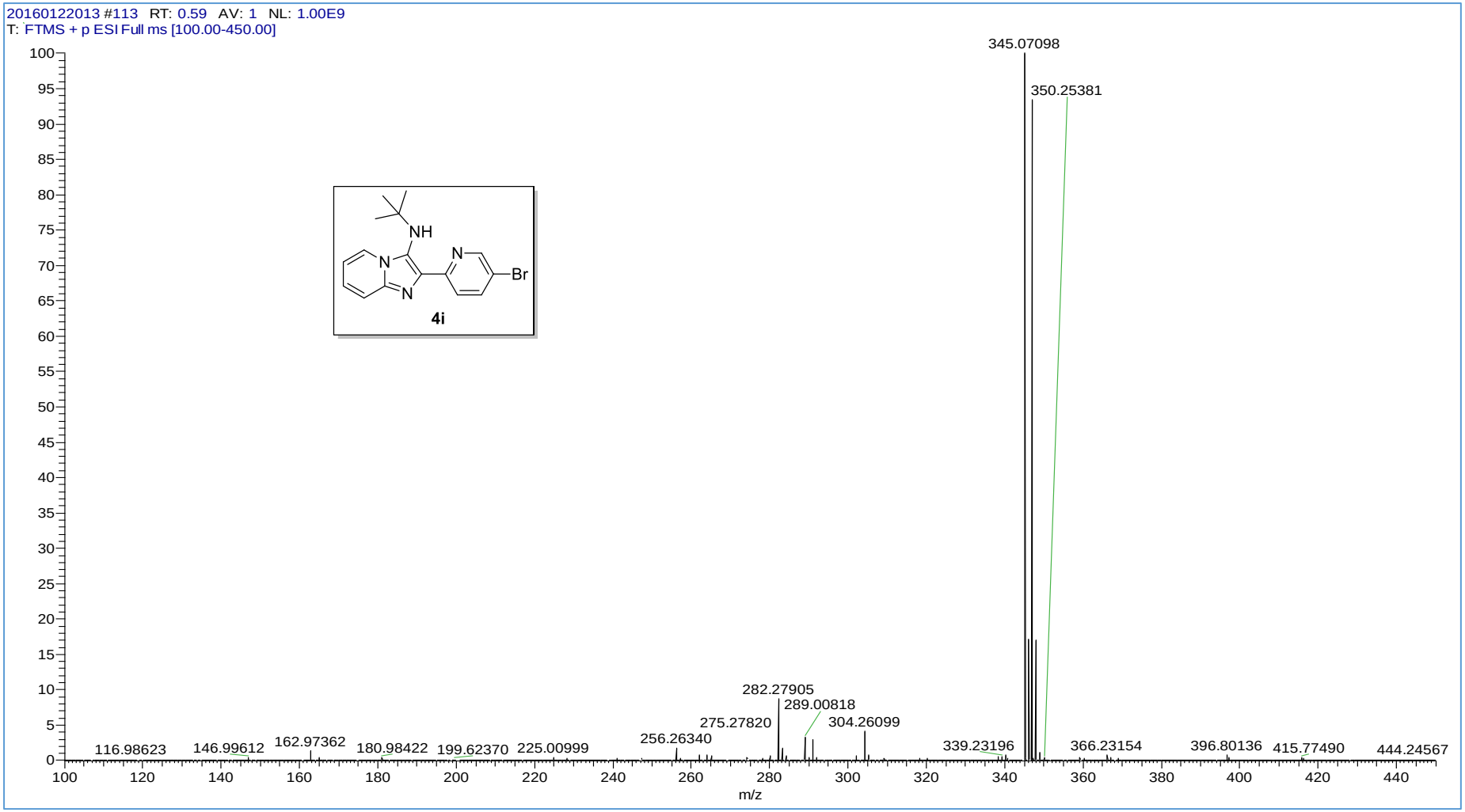

Figure 27. HRMS spectrum of compound **4i**.

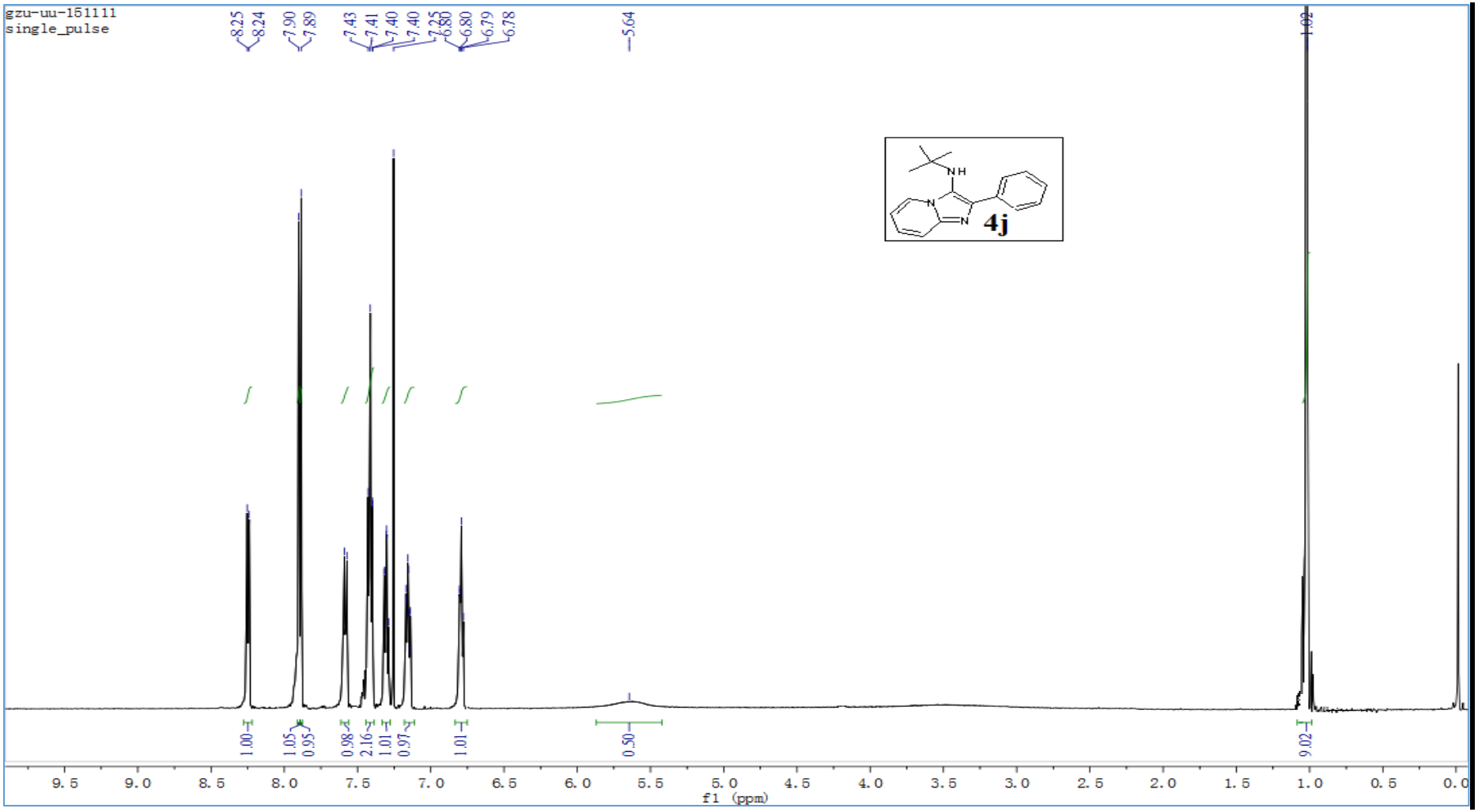

Figure 28. ^{1}H NMR (500 MHz) spectrum of compound **4j** in $CDCl_3$.

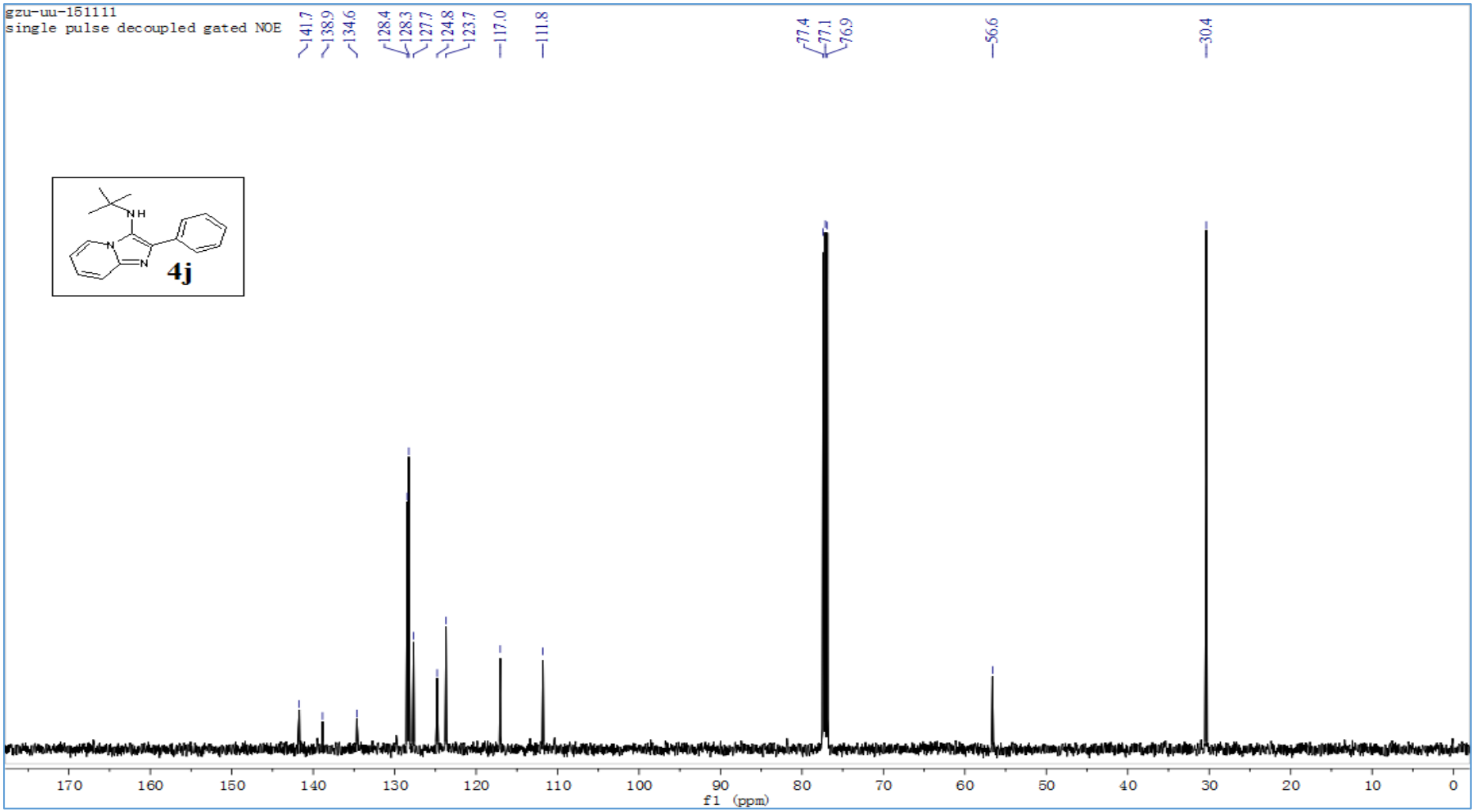

Figure 29. ^{13}C NMR (125 MHz) spectrum of compound **4j** in $CDCl_3$.

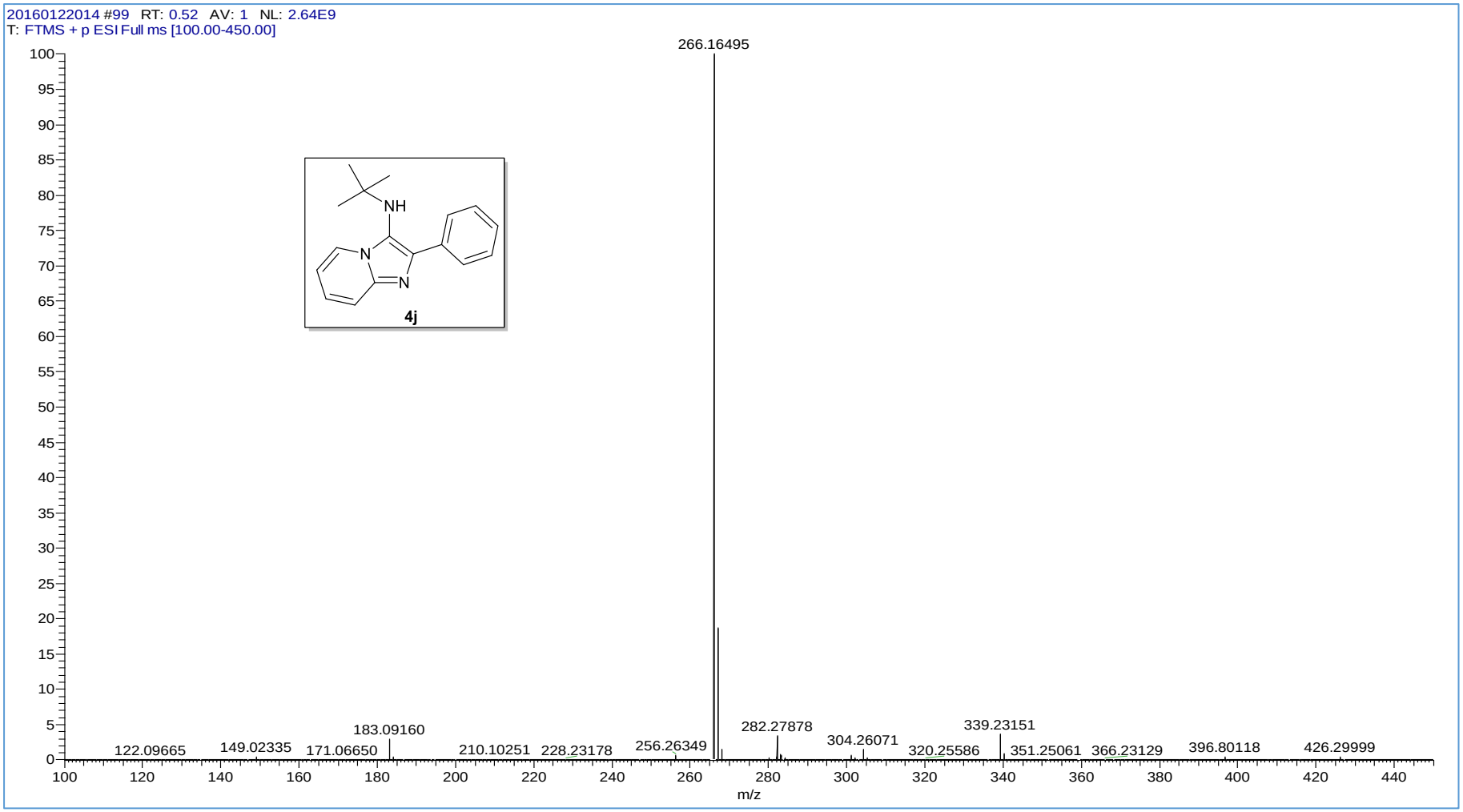

Figure 30. HRMS spectrum of compound **4j**.

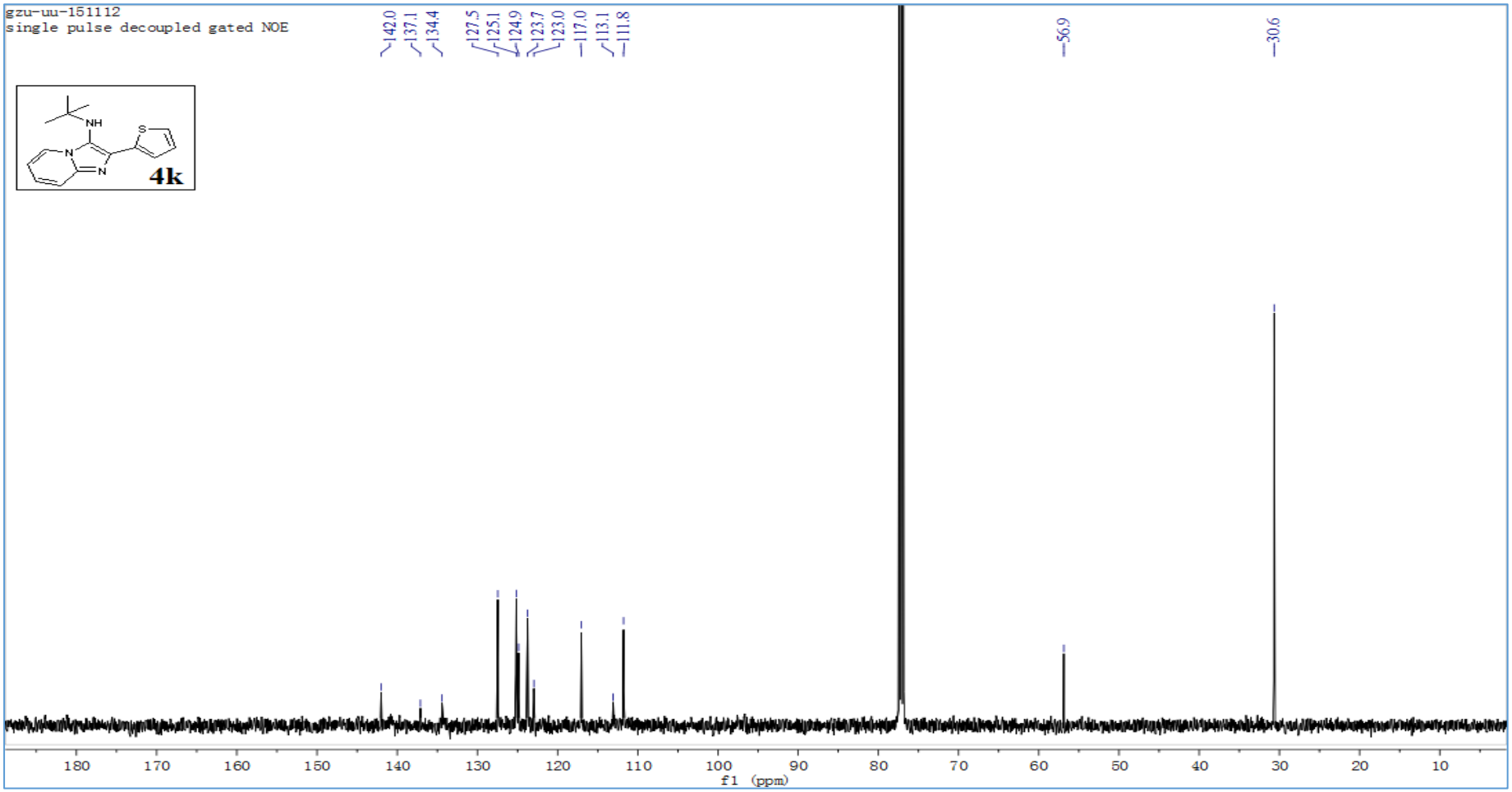

Figure 31. ^{1}H NMR (500 MHz) spectrum of compound **4k** in $CDCl_3$.

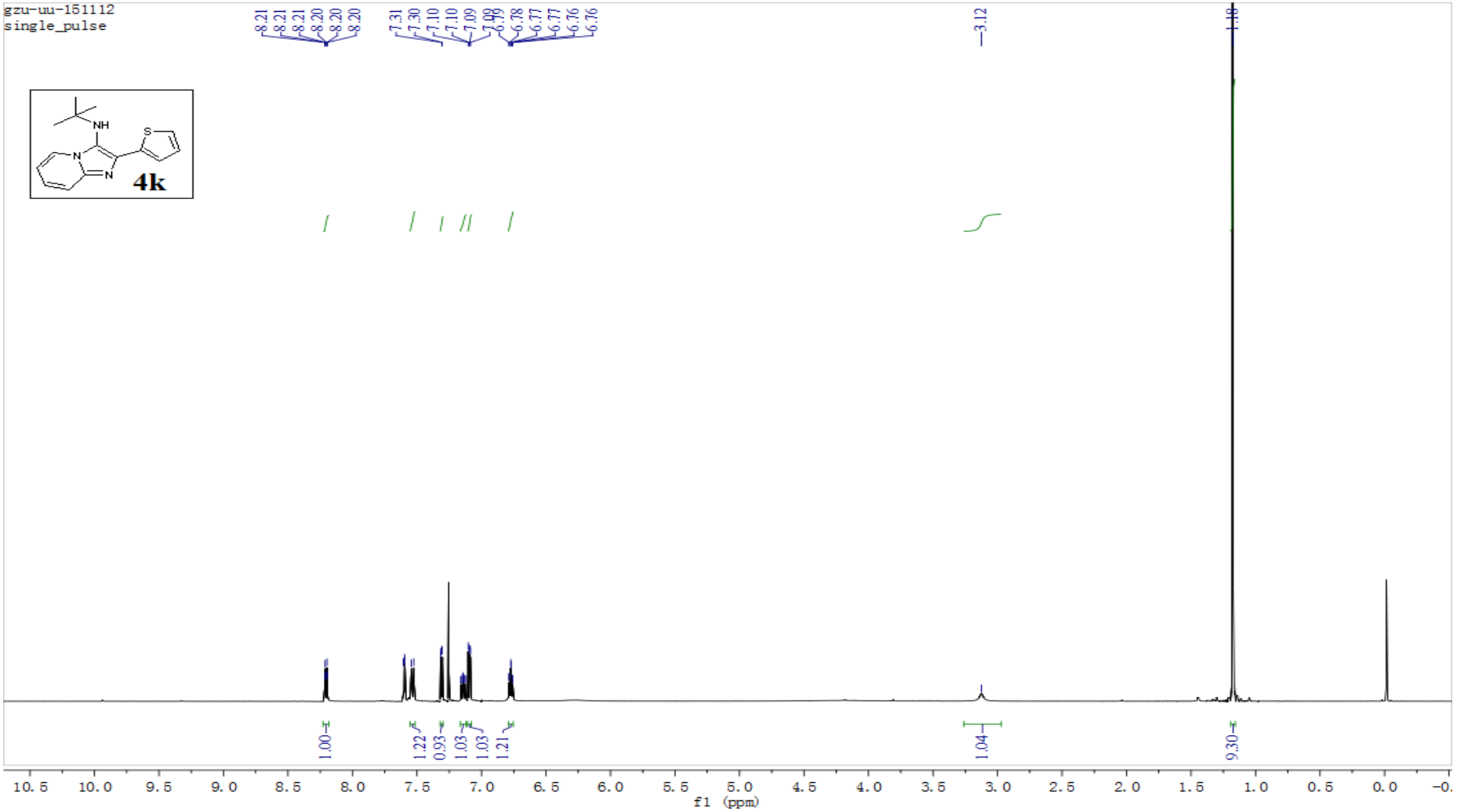

Figure 32. ^{1}H NMR (500 MHz) spectrum of compound **4k** in $CDCl_3$.

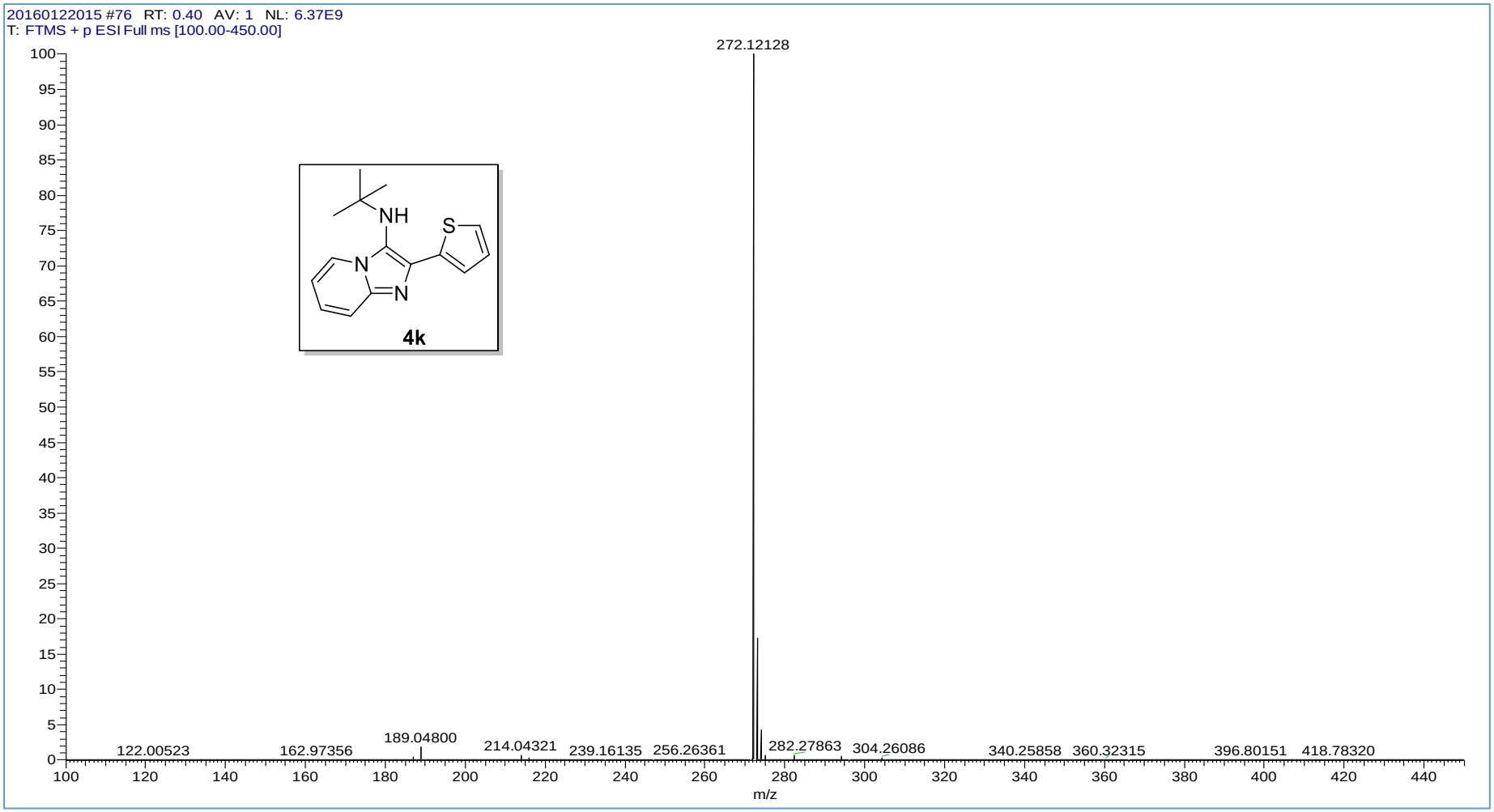

Figure 33. HRMS spectrum of compound **4k**.

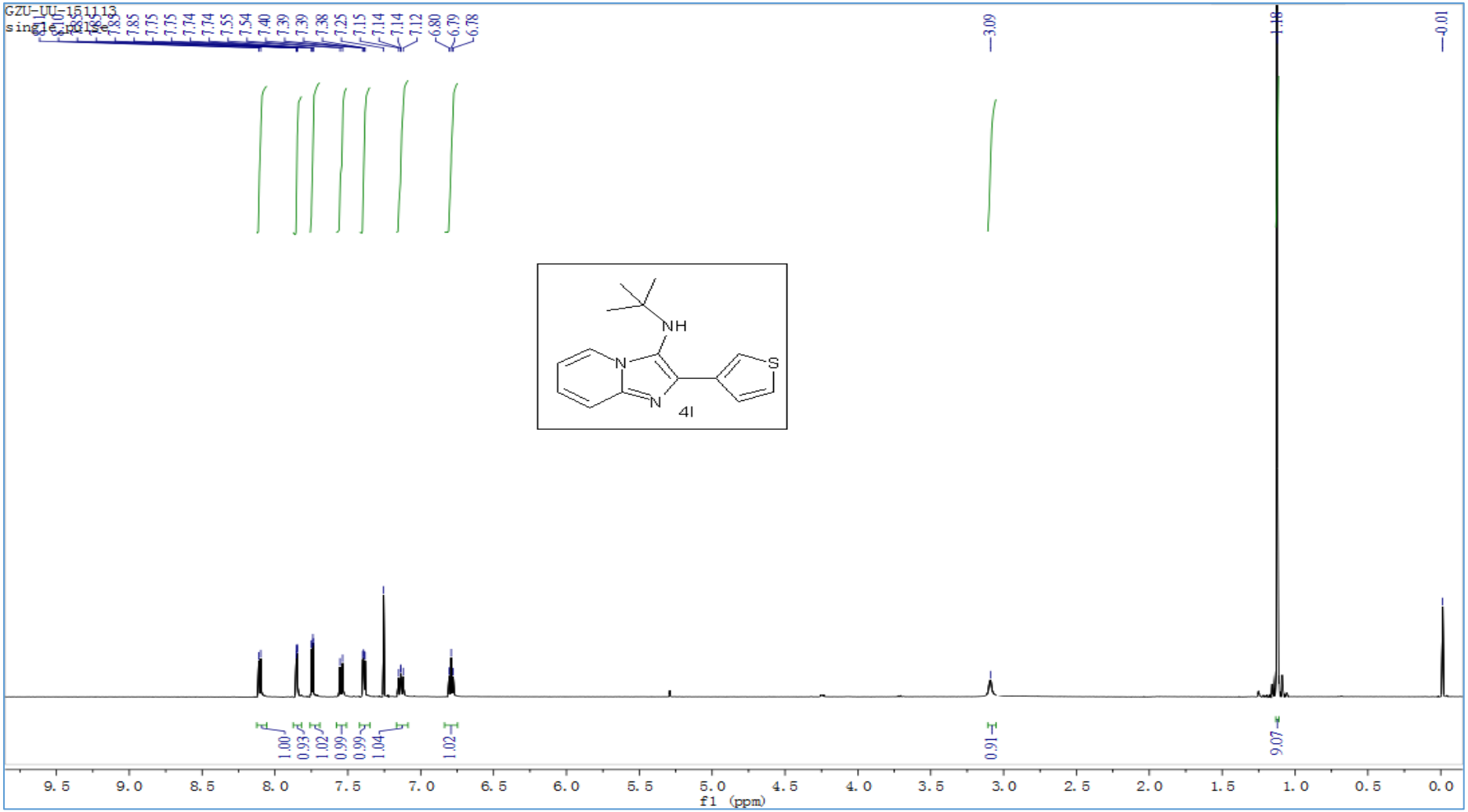

Figure 34. ^{1}H NMR (500 MHz) spectrum of compound **4l** in $CDCl_3$.

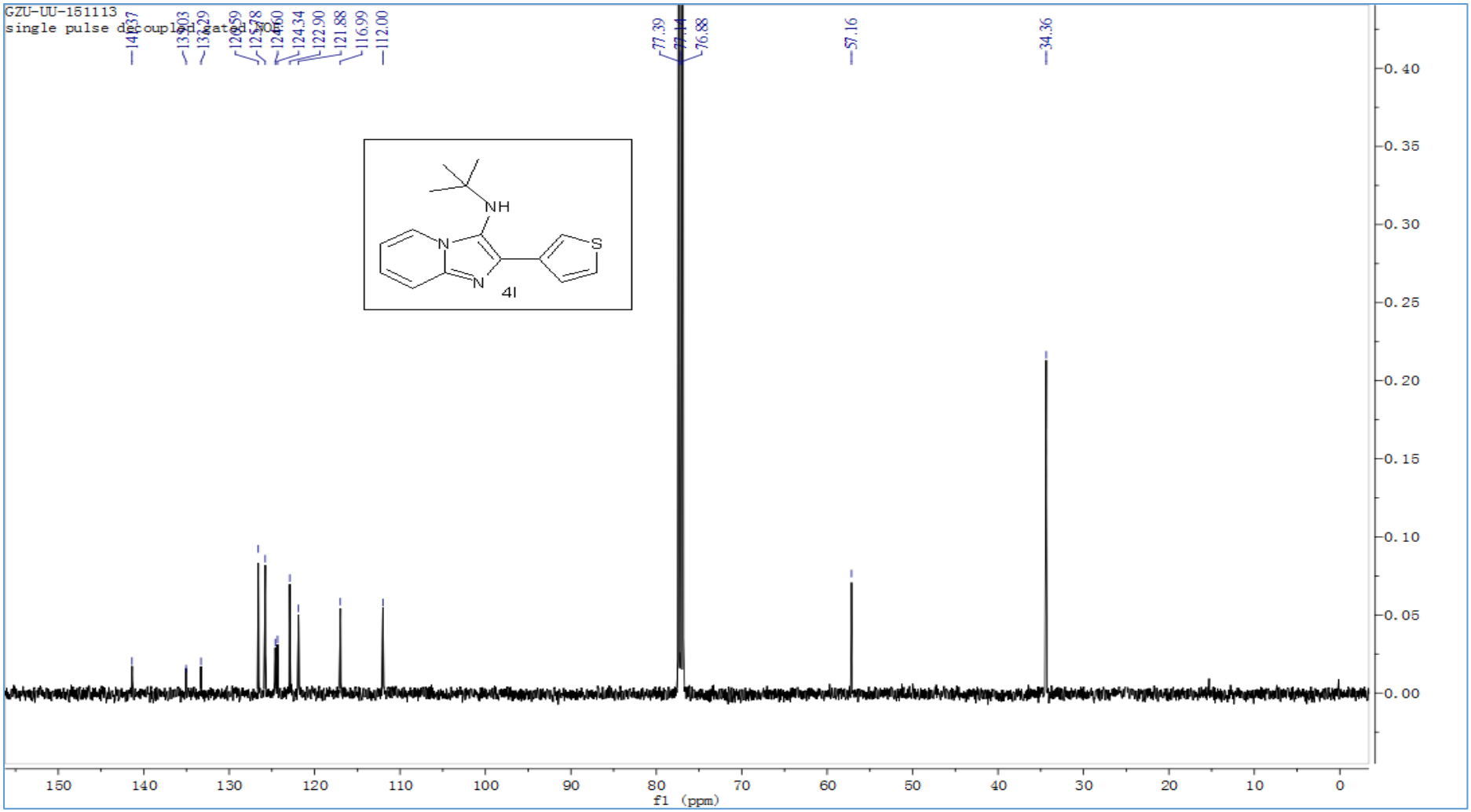

Figure 35. ^{13}C NMR 125 MHz) spectrum of compound **4l** in $CDCl_3$.

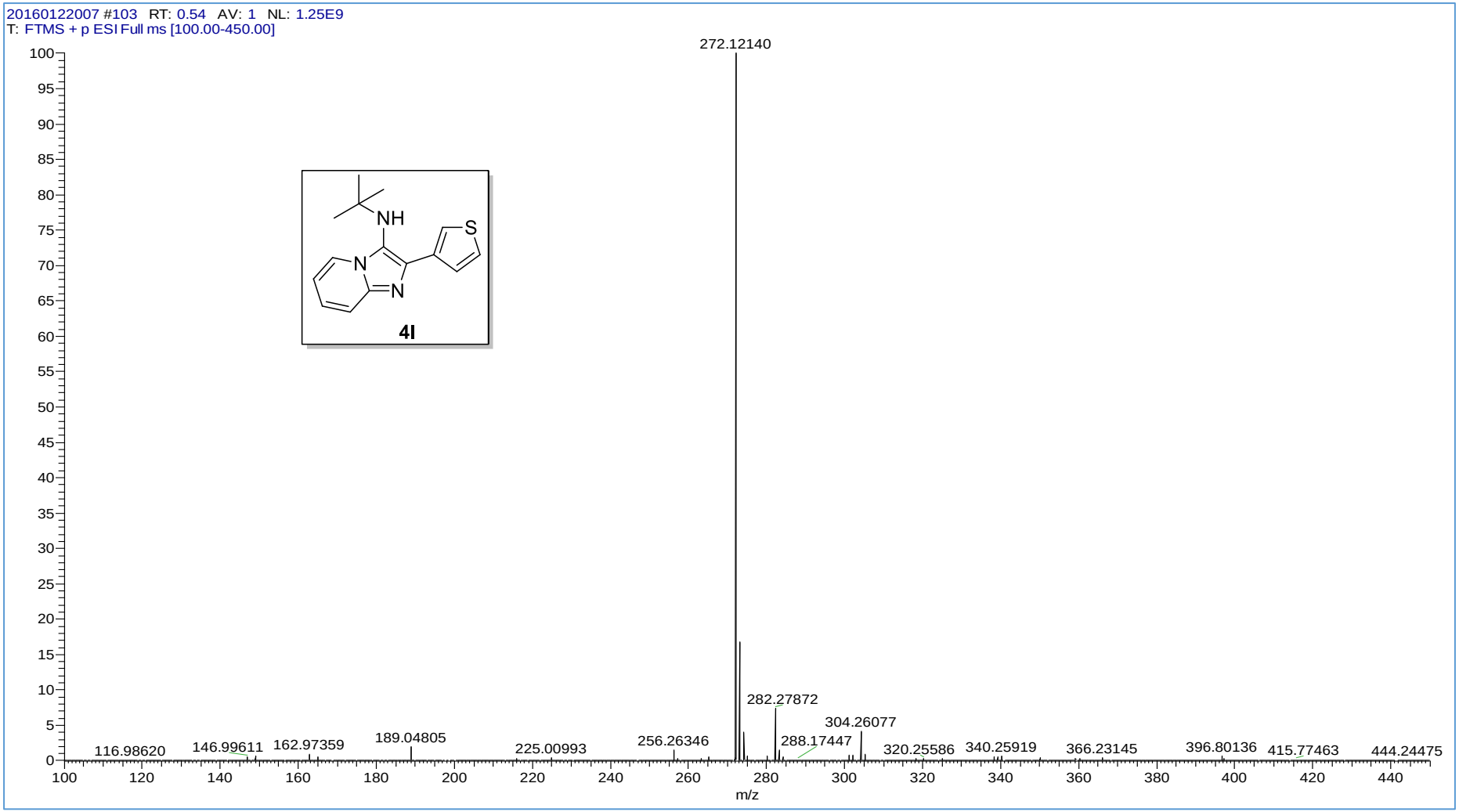

Figure 36. HRMS spectrum of compound **4l**.

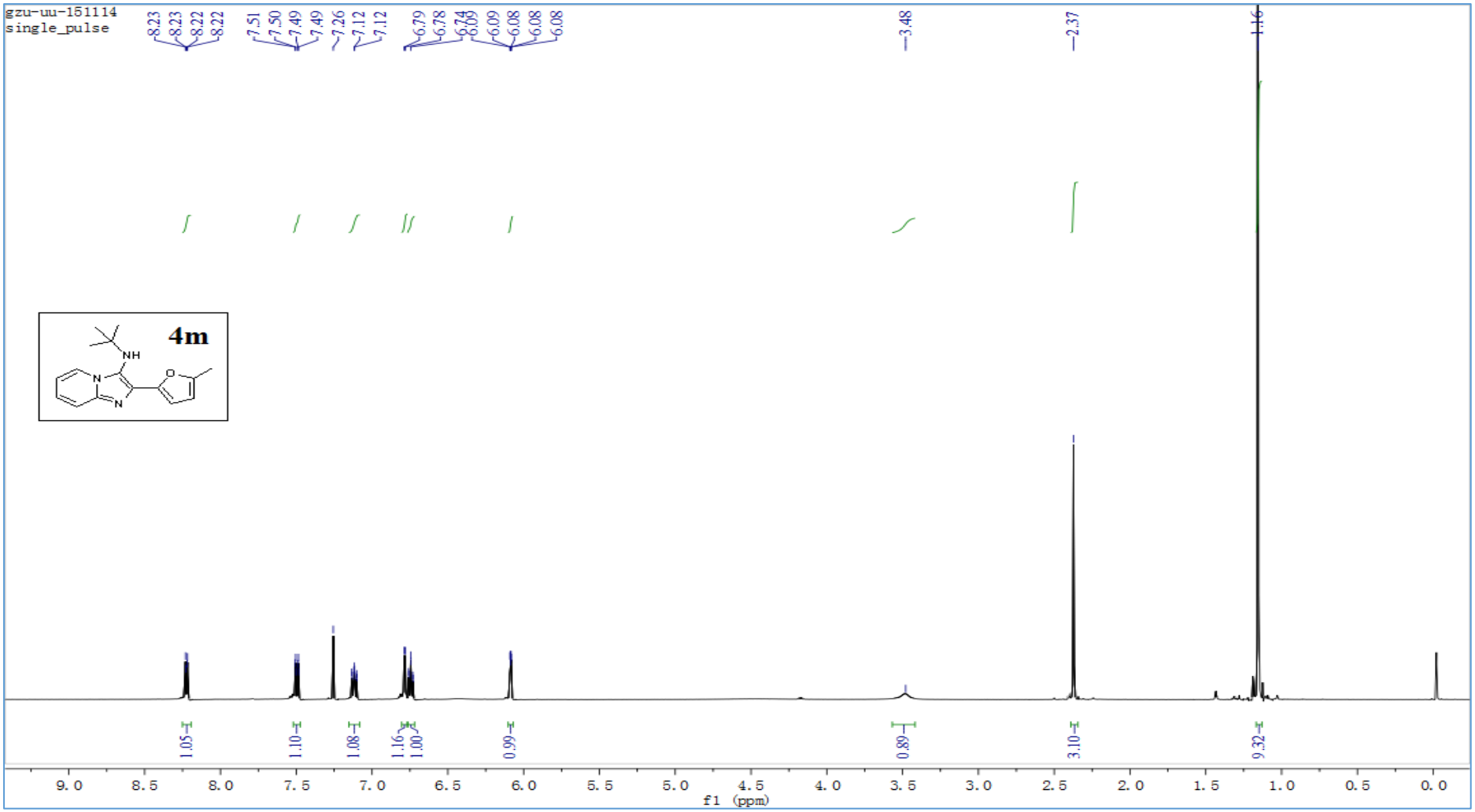

Figure 37. ^{1}H NMR (500 MHz) spectrum of compound **4m** in $CDCl_3$.

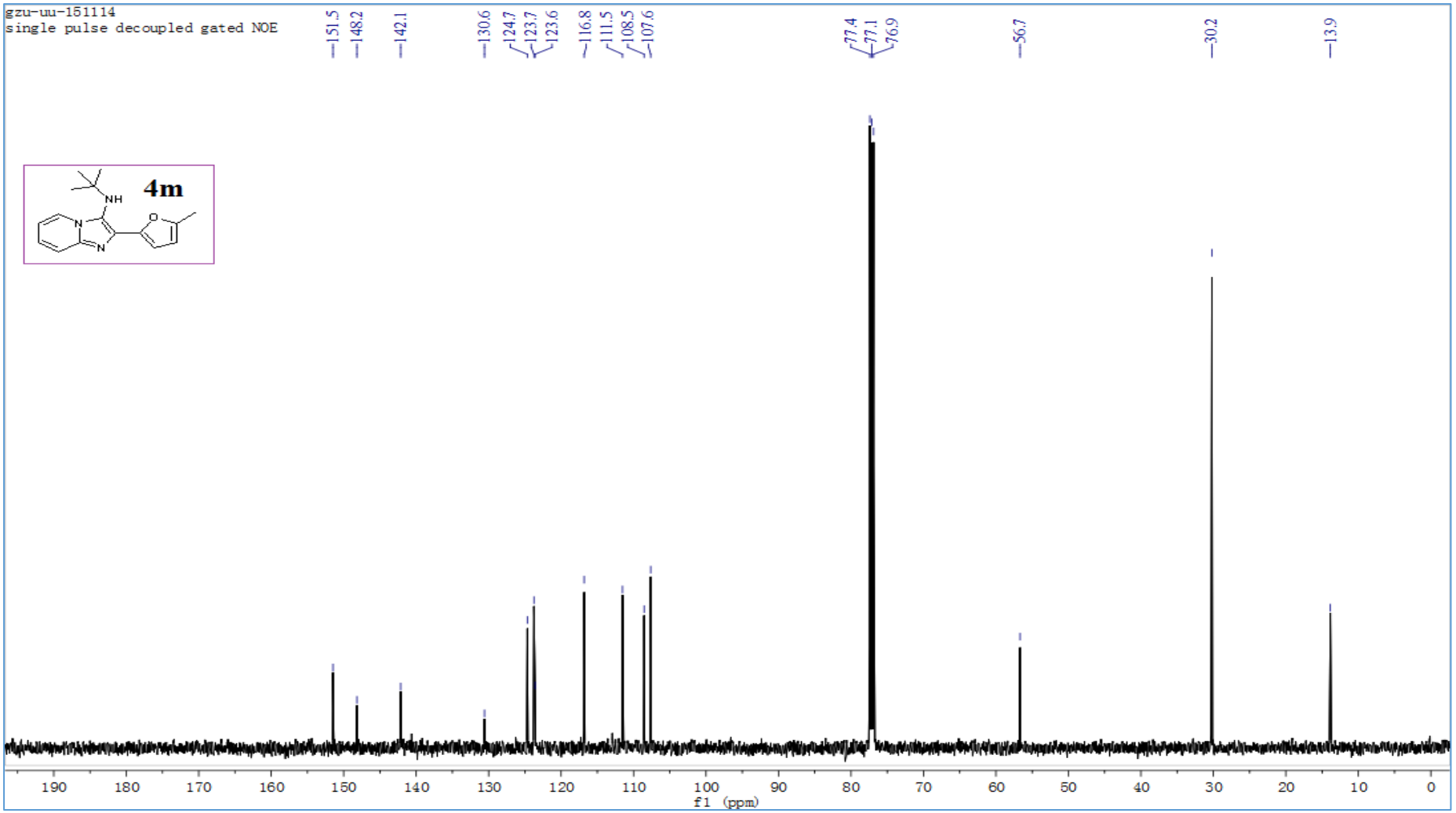

Figure 38. ^{13}C NMR (125 MHz) spectrum of compound **4m** in $CDCl_3$.

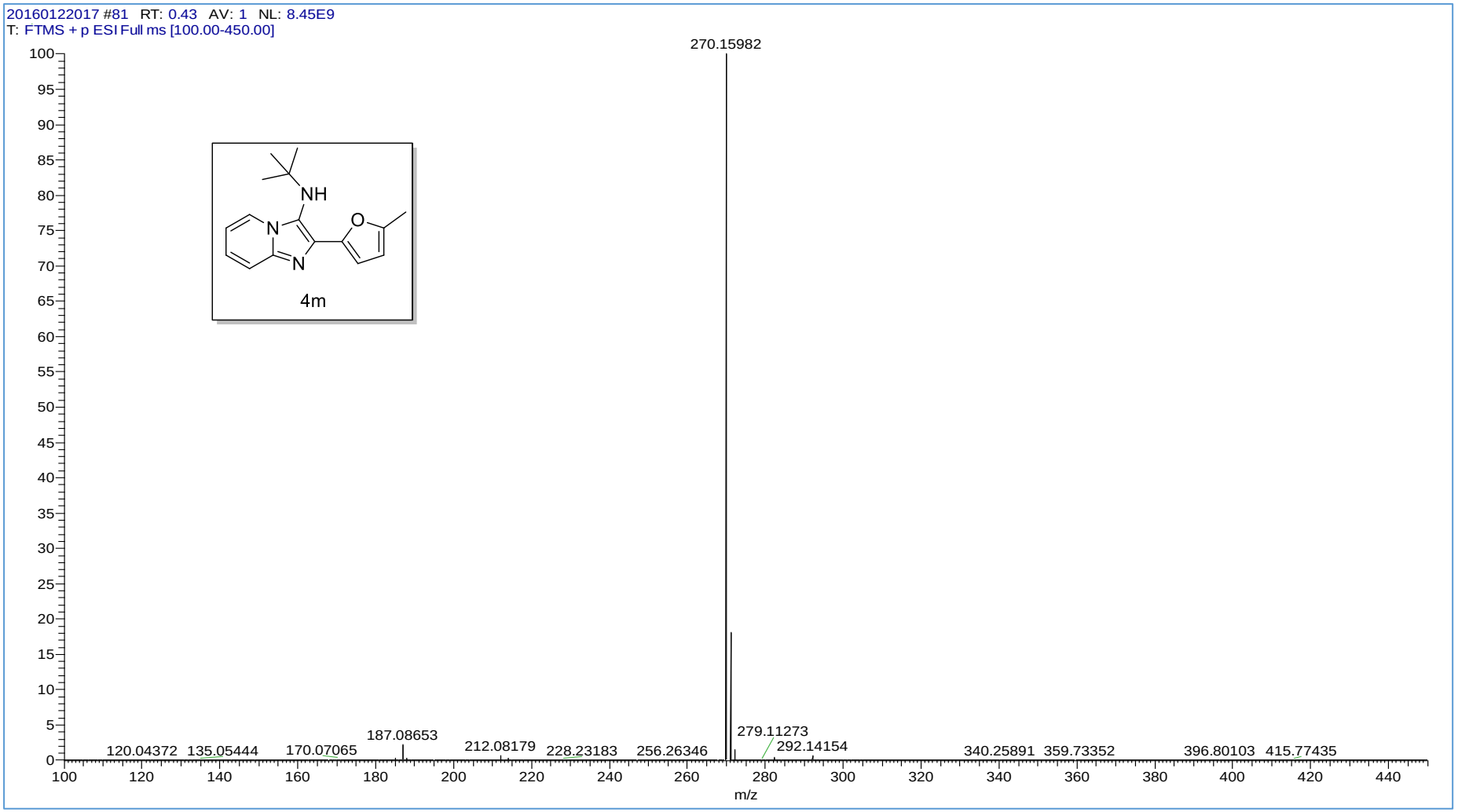

Figure 39. HRMS spectrum of compound **4m**.

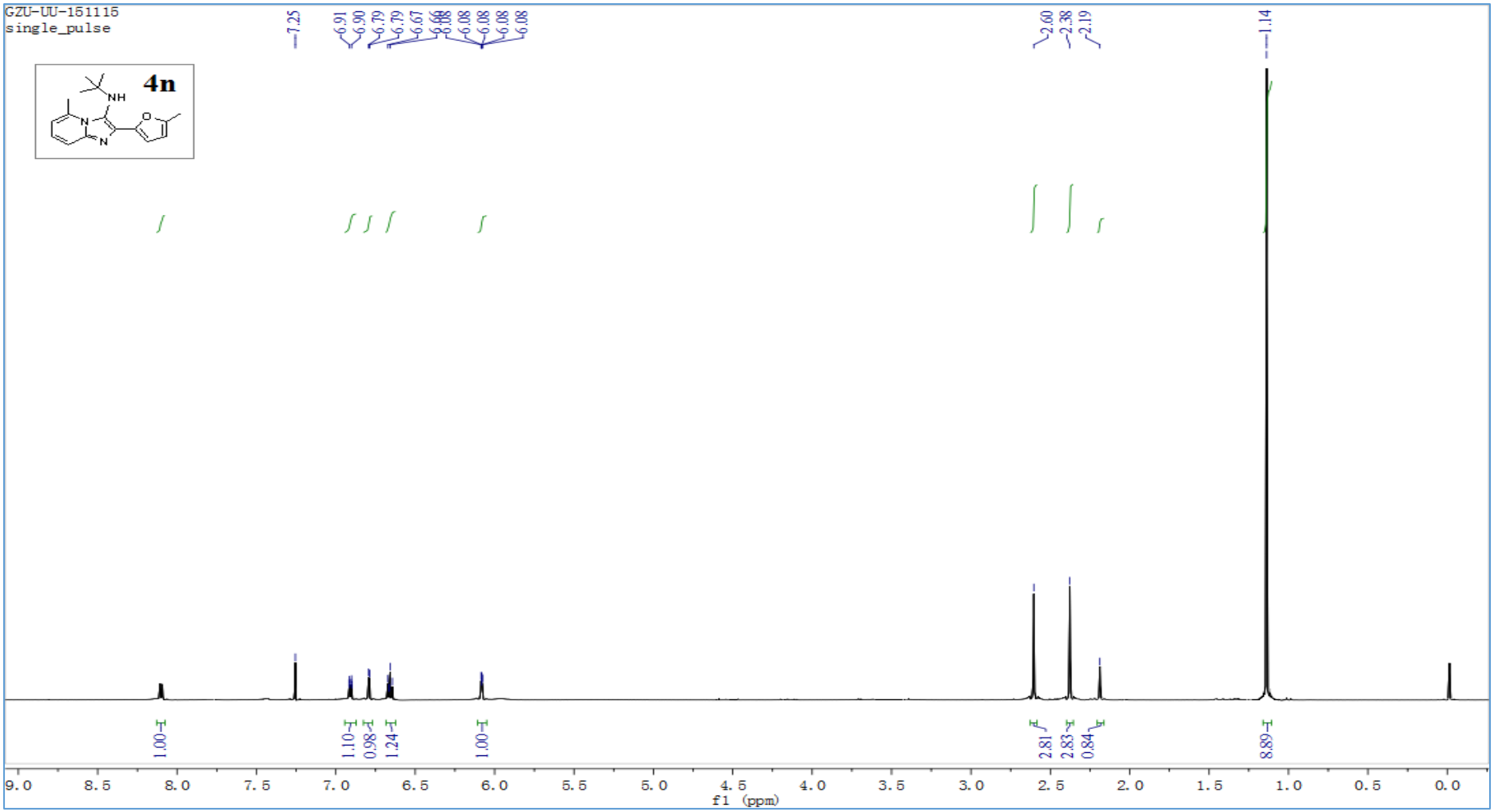

Figure 40. ^{1}H NMR (500 MHz) spectrum of compound **4n** in $CDCl_3$.

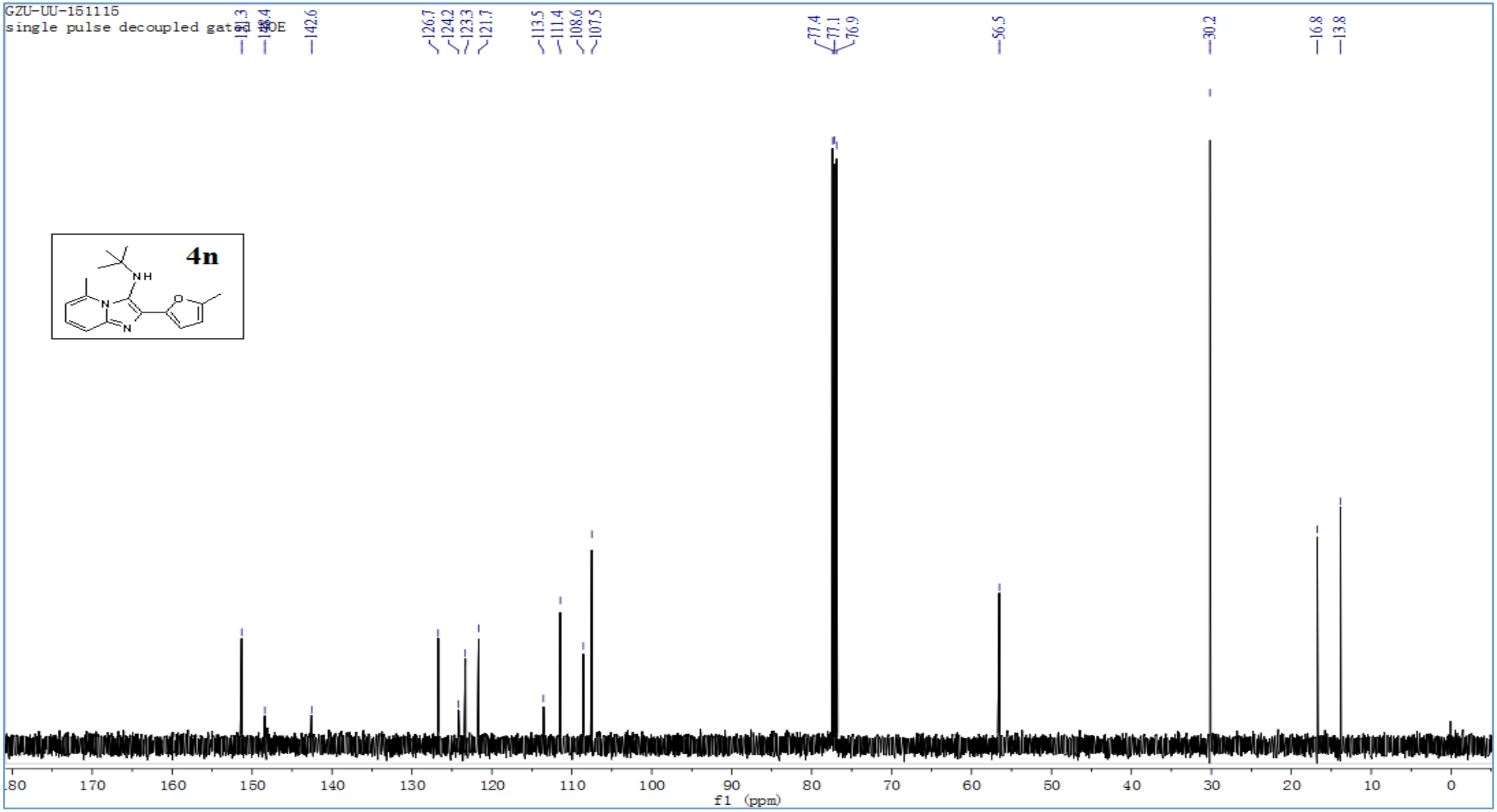

Figure 41. ^{13}C NMR (125 MHz) spectrum of compound **4n** in $CDCl_3$.

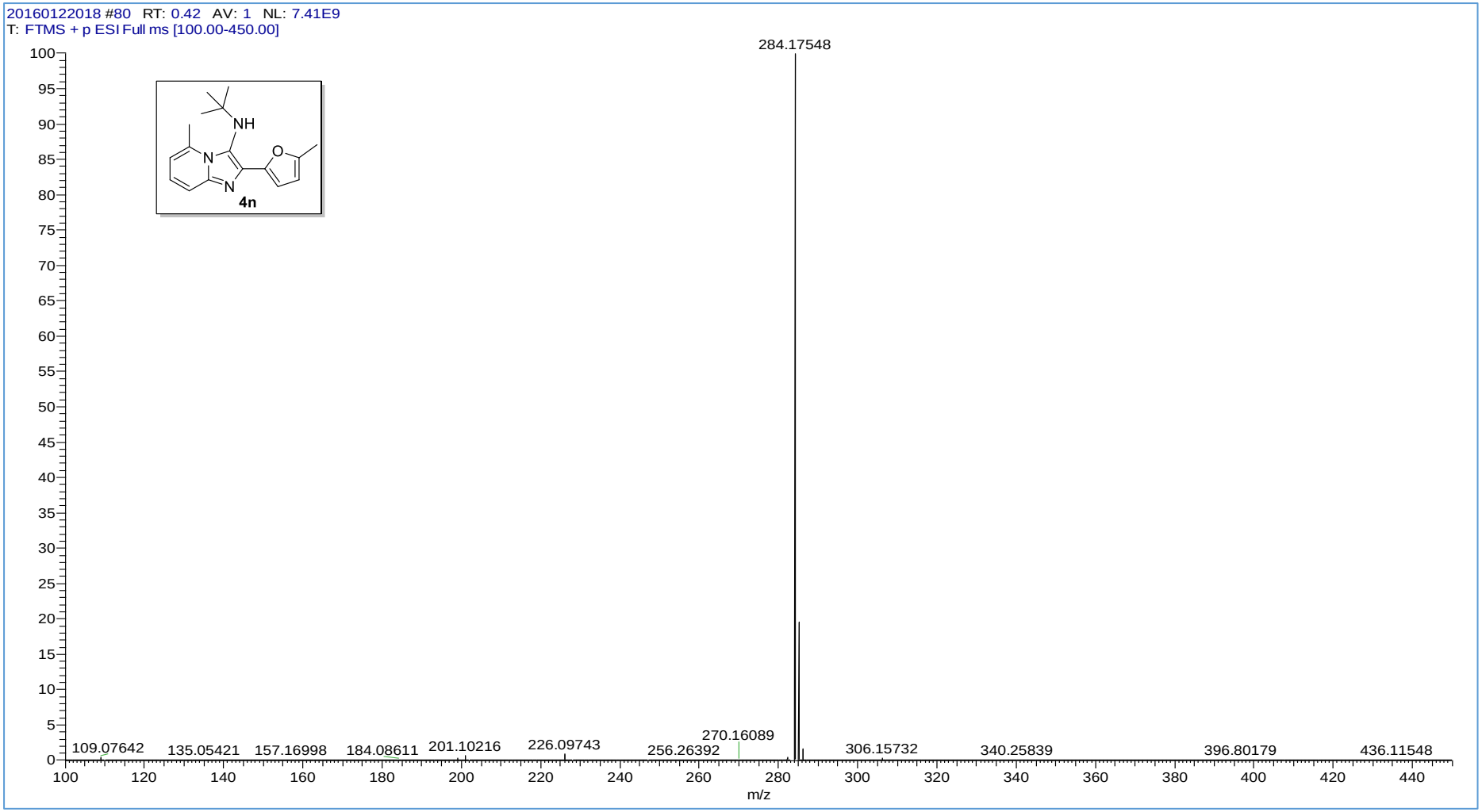

Figure 42. HRMS spectrum of compound **4n**.

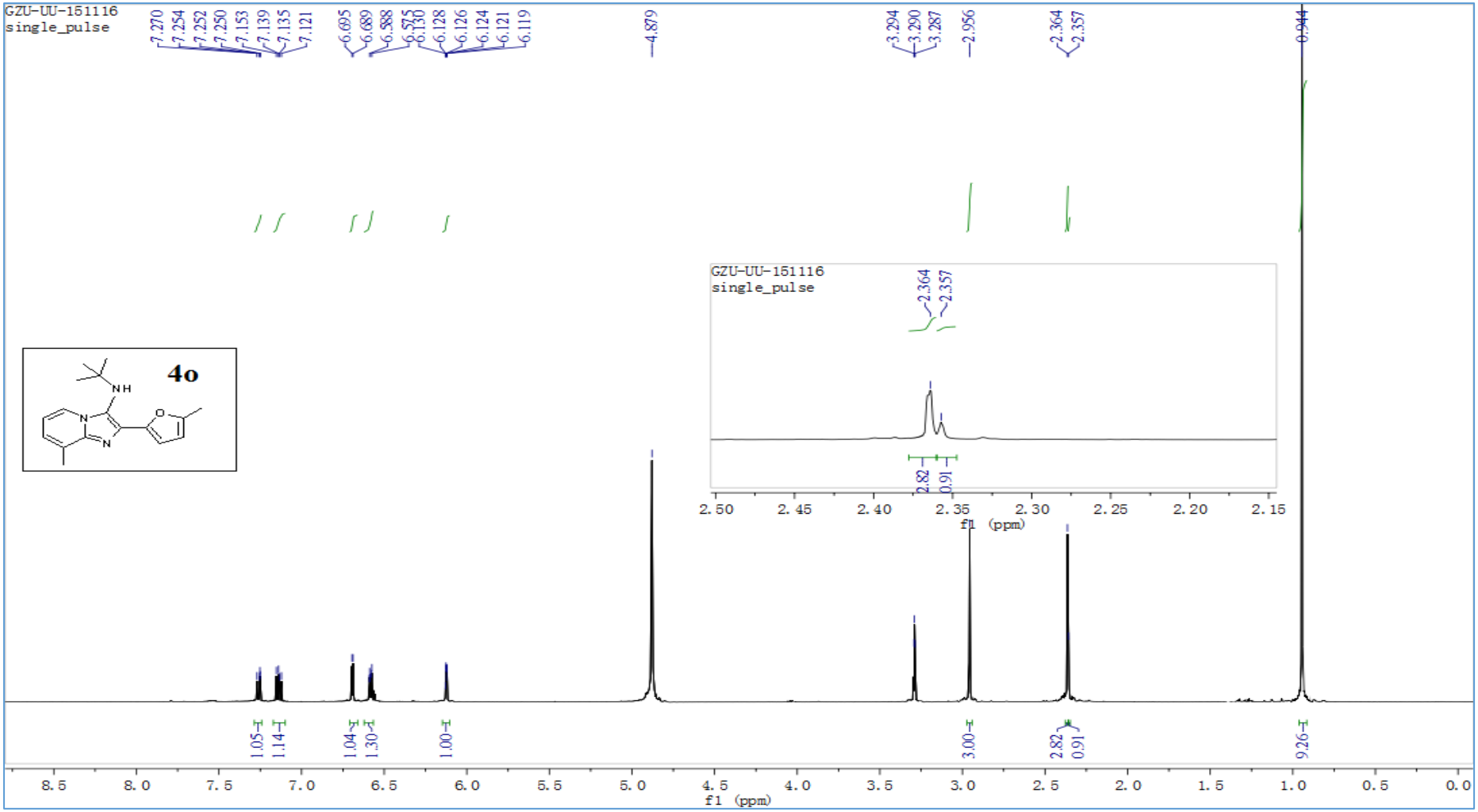

Figure 43. ^{1}H NMR (500 MHz) spectrum of compound **4o** in D_3COD.

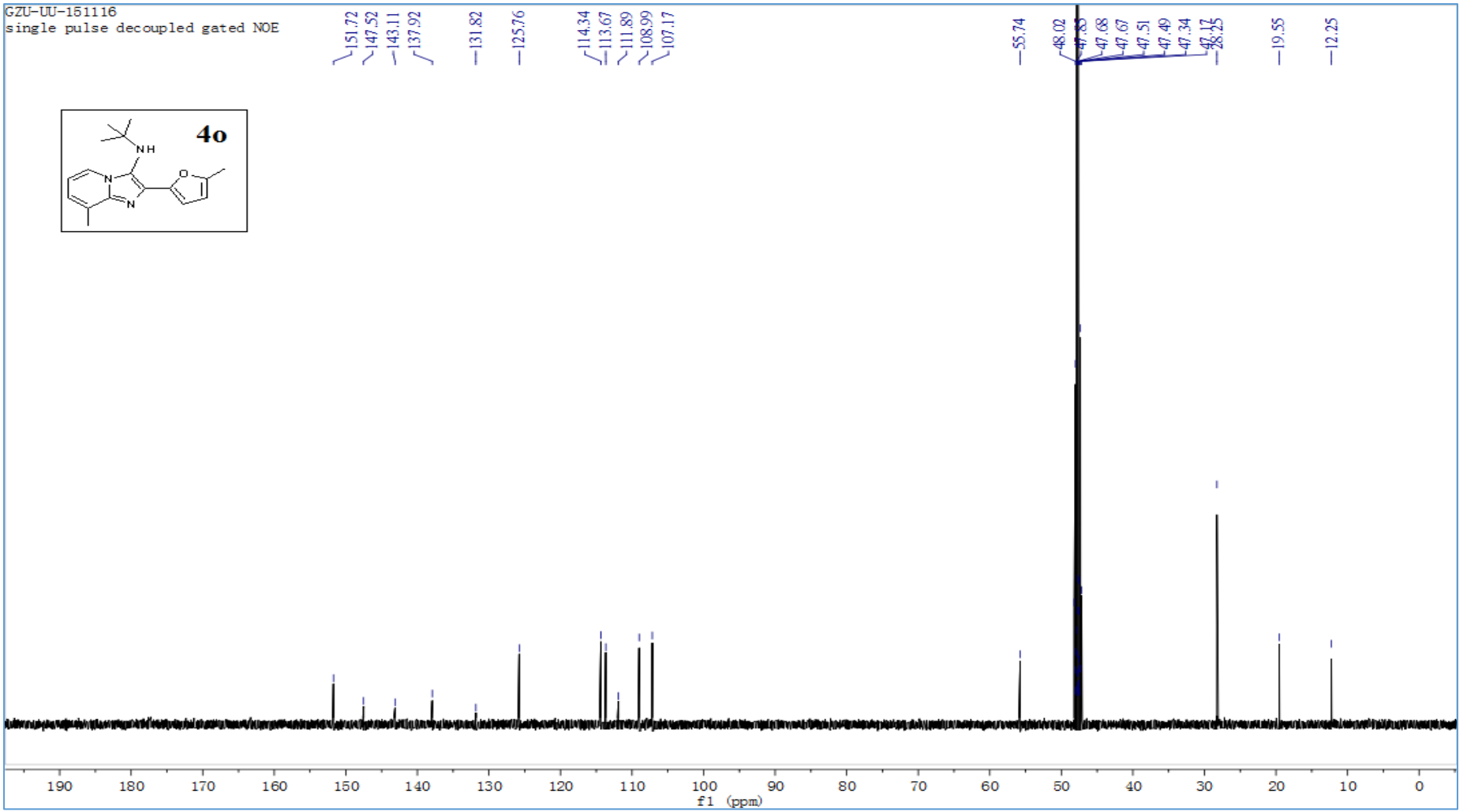

Figure 44. ^{13}C NMR (125 MHz) spectrum of compound **4o** in D_3COD.

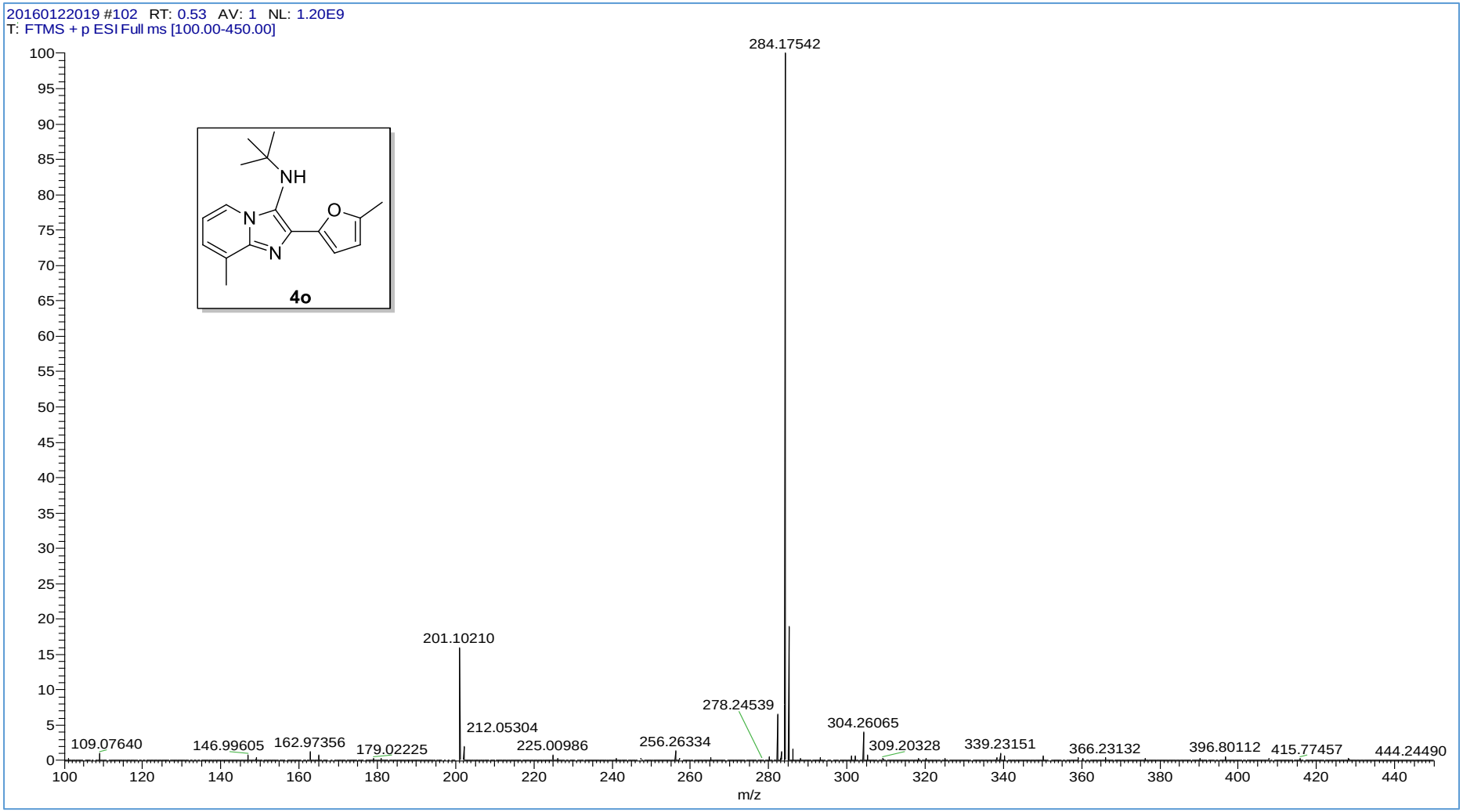

Figure 45. HRMS spectrum of compound **4o**.

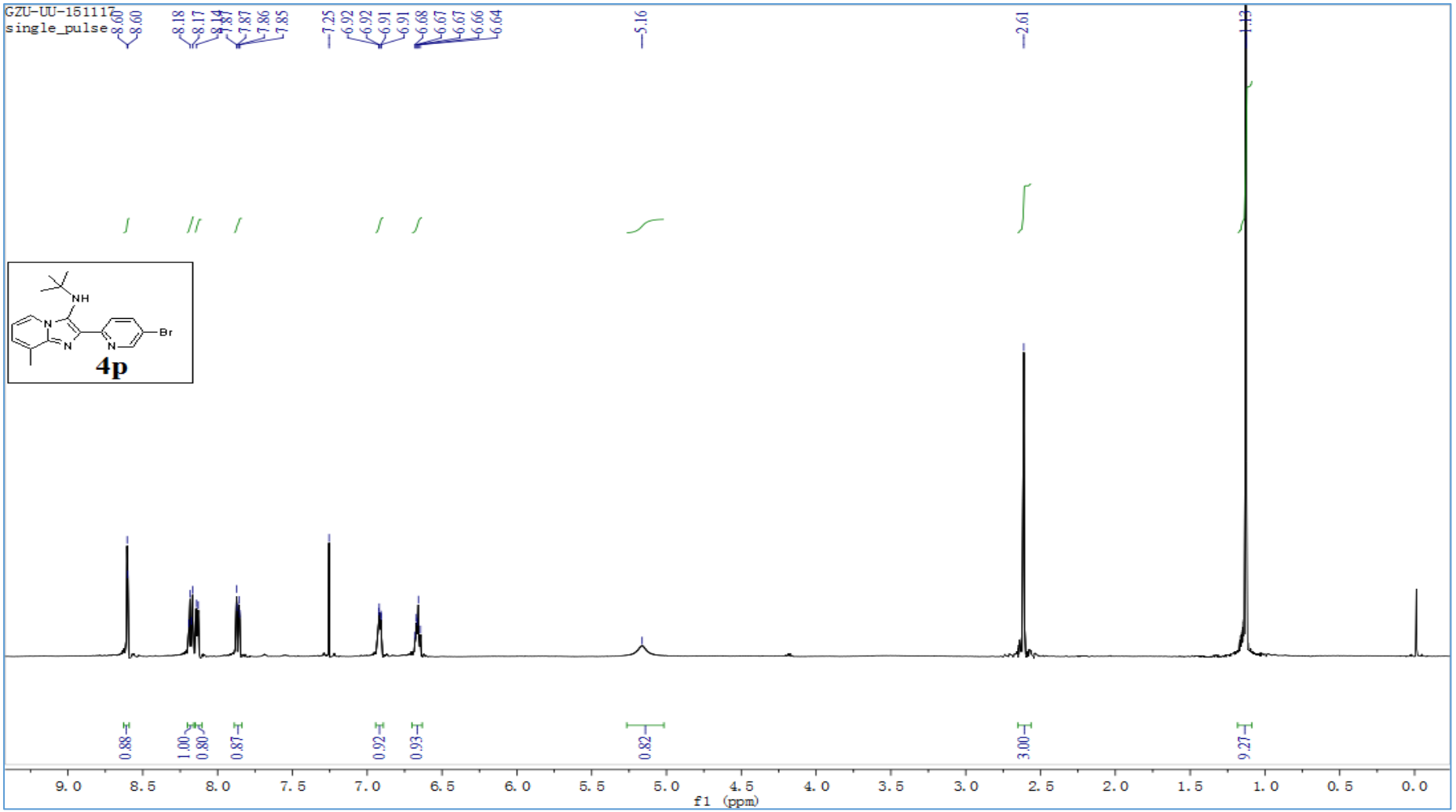

Figure 46. ^{1}H NMR (500 MHz) spectrum of compound **4p** in $CDCl_3$.

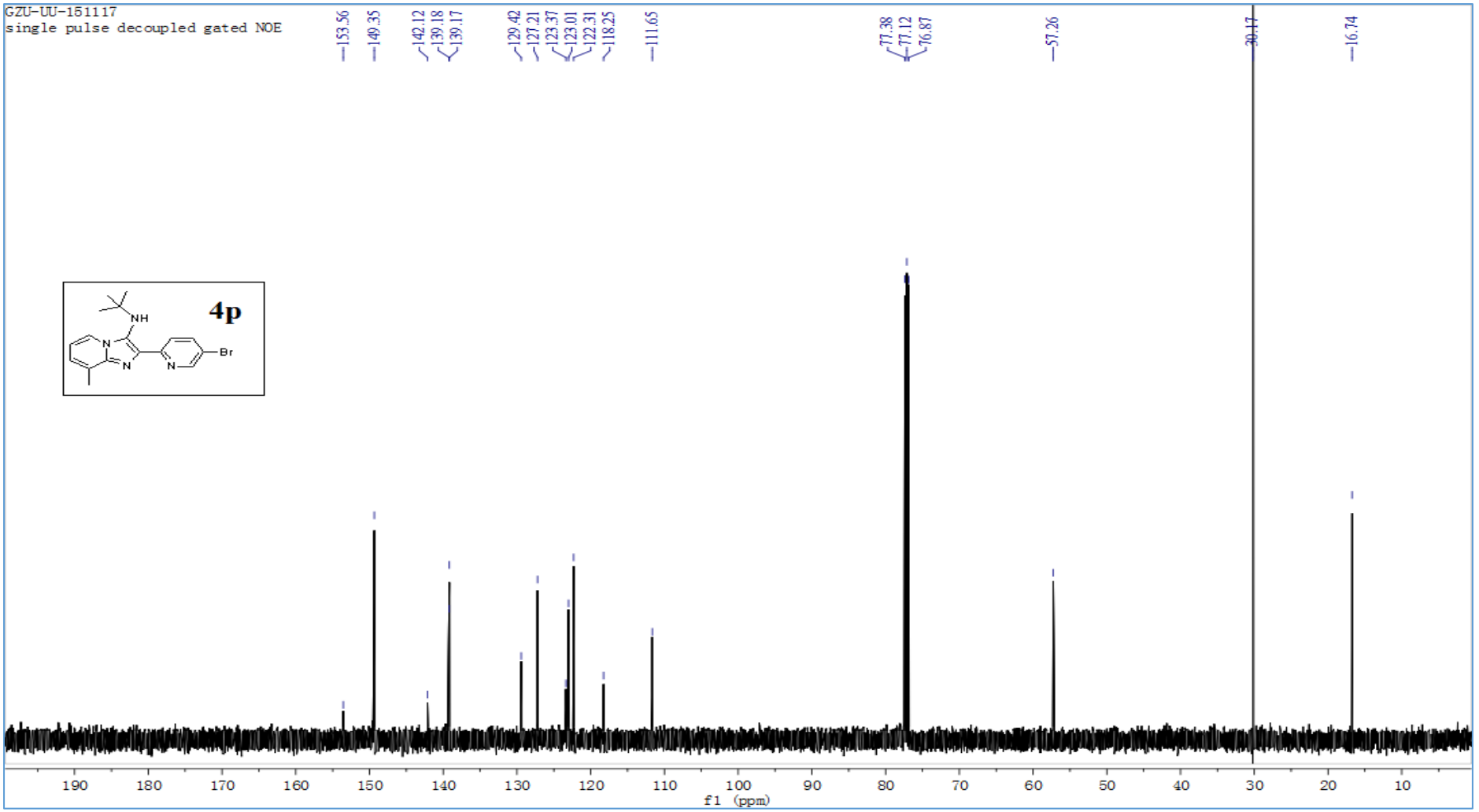

Figure 47. ^{13}C NMR (125 MHz) spectrum of compound **4p** in $CDCl_3$.

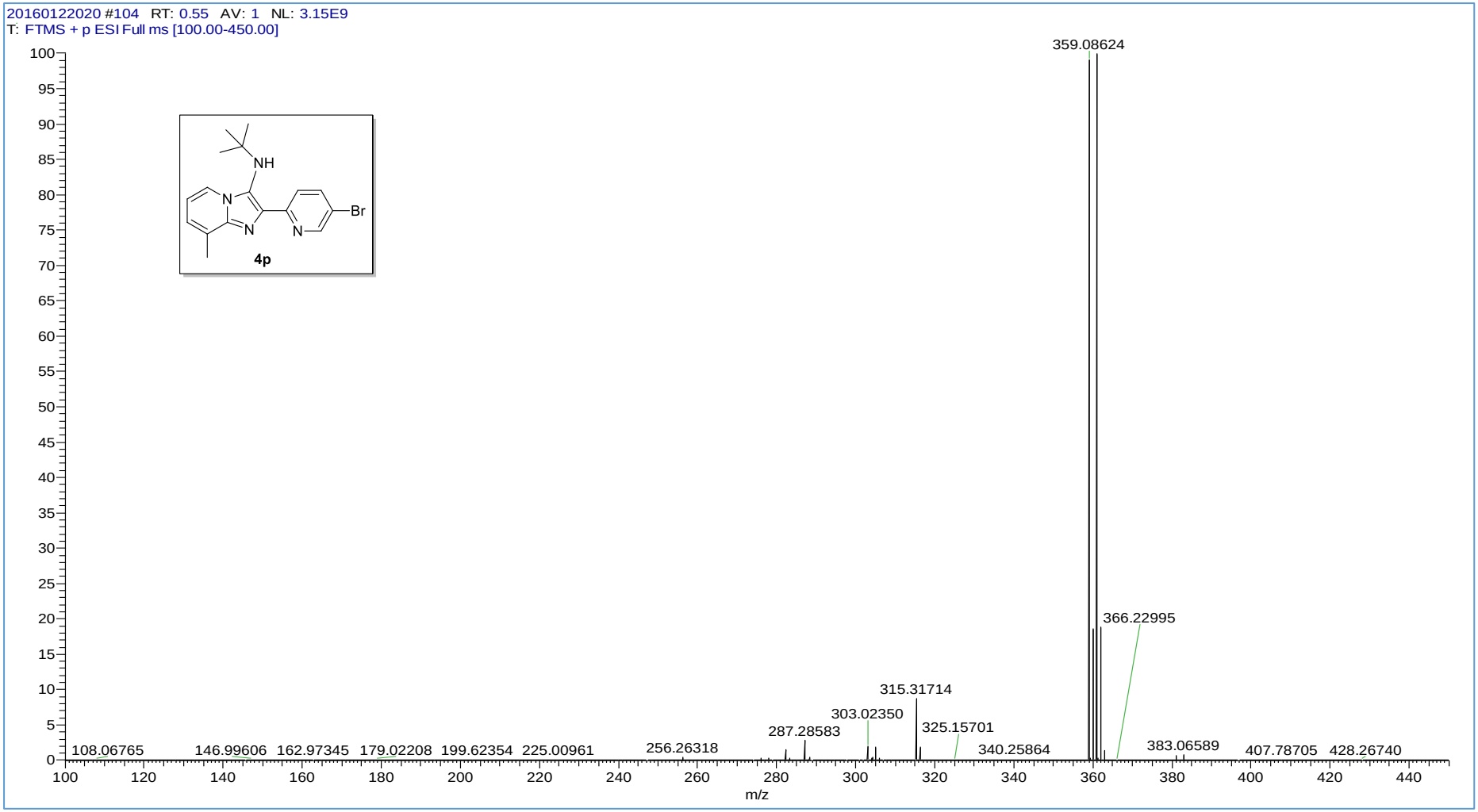

Figure 48. HRMS spectrum of compound **4p**.

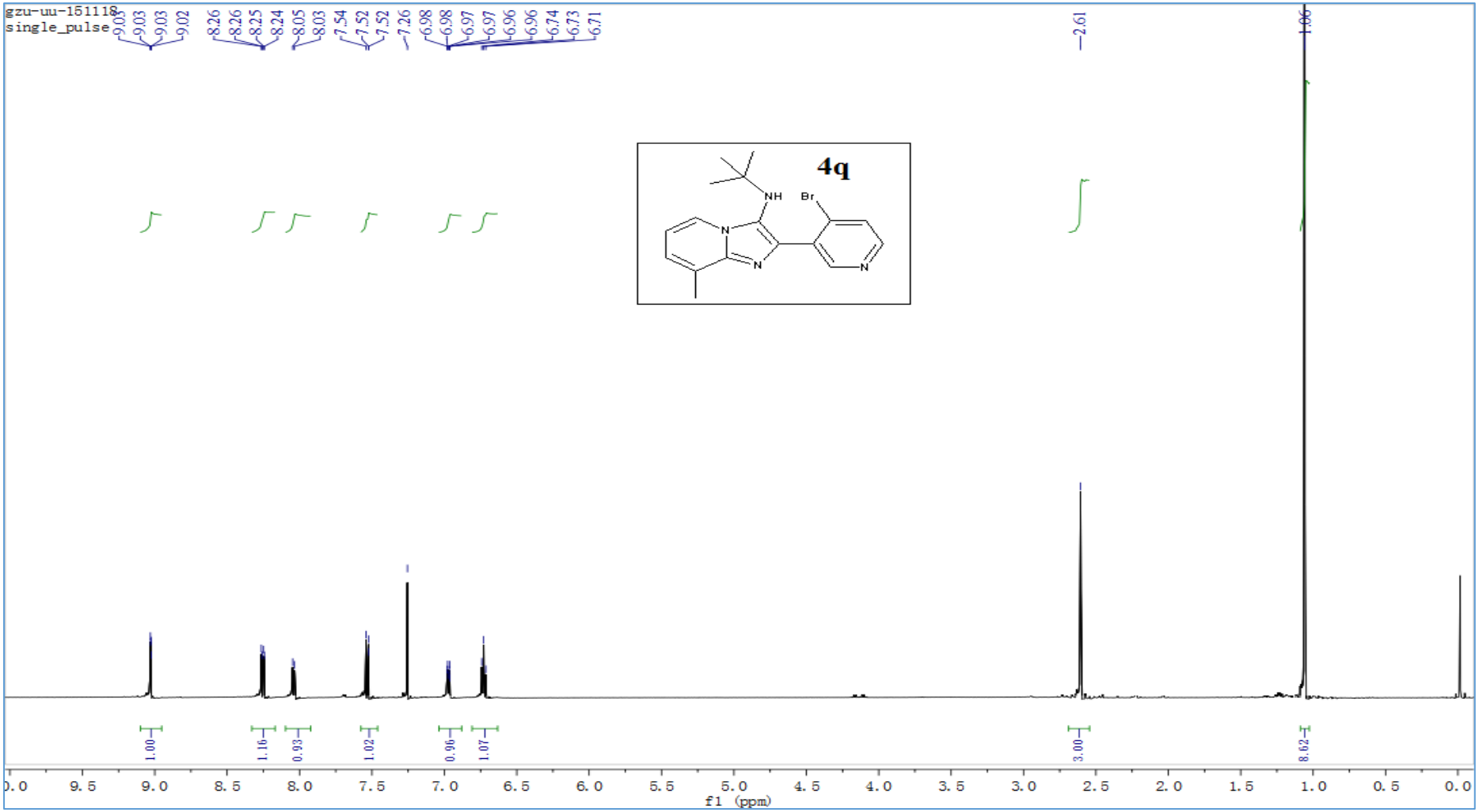

Figure 49. ^{1}H NMR (500 MHz) spectrum of compound **4q** in $CDCl_3$.

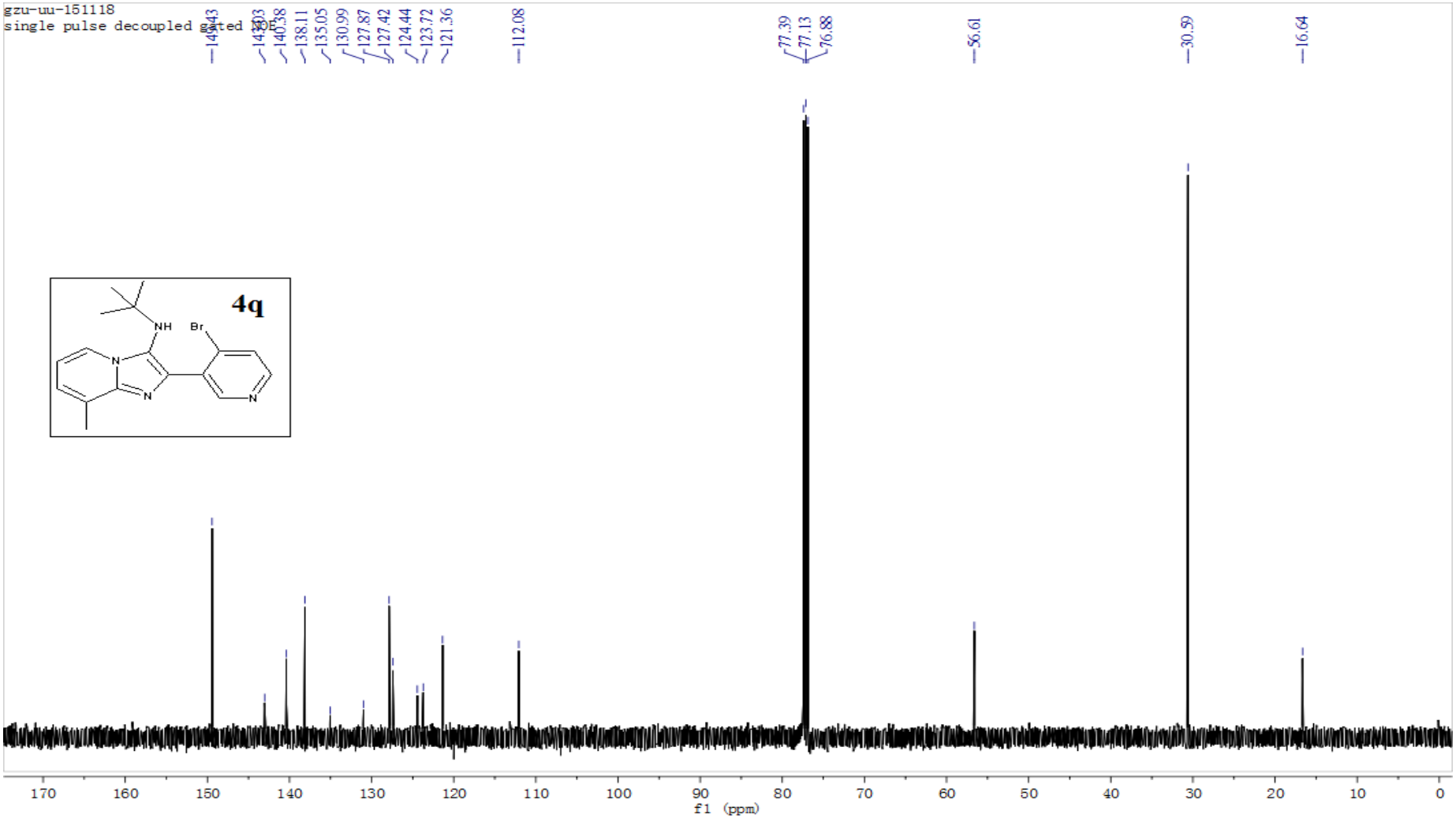

Figure 50. ^{13}C NMR (125 MHz) spectrum of compound **4q** in $CDCl_3$.

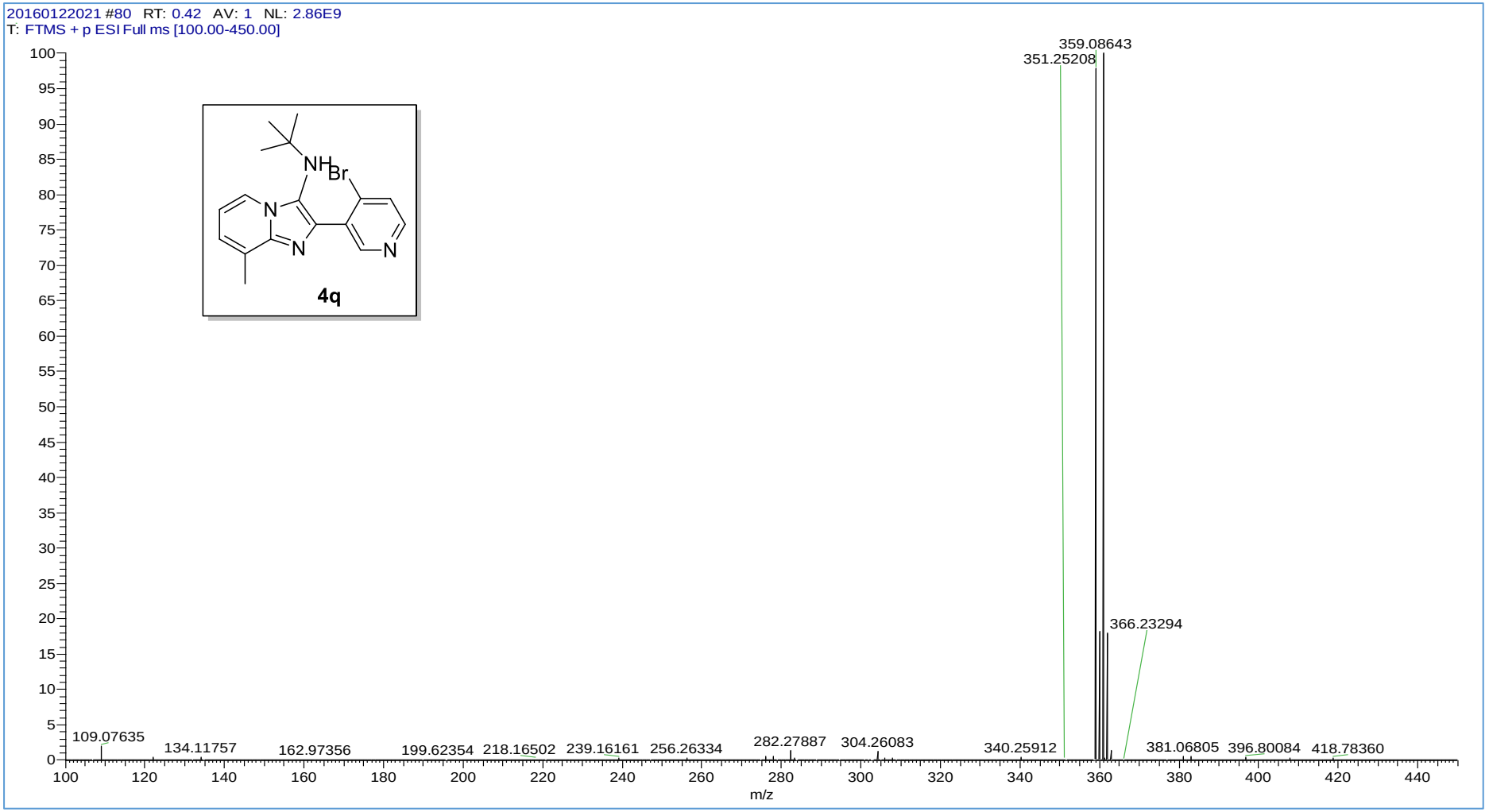

Figure 51. HRMS spectrum of compound **4q**.

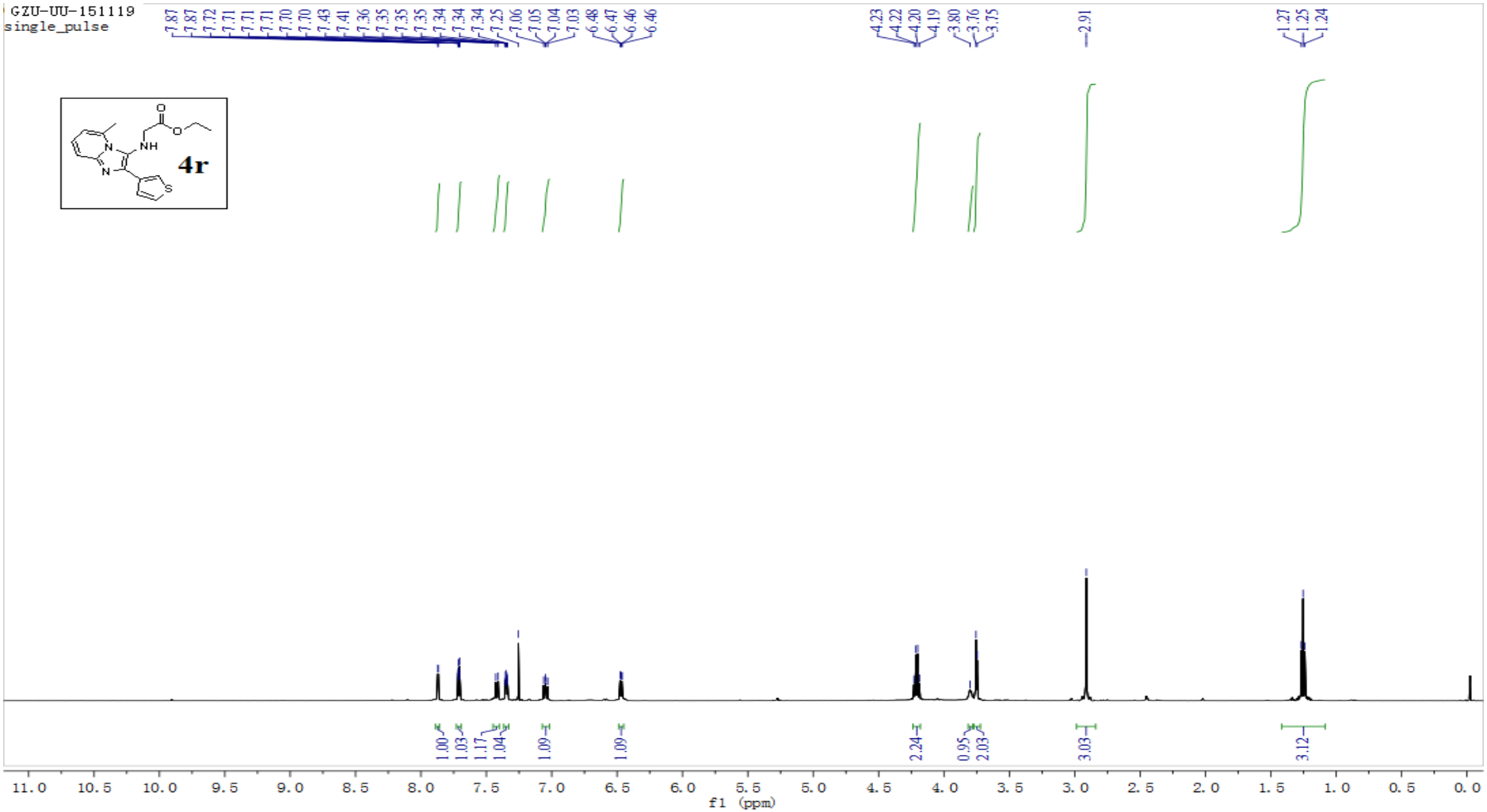

Figure 52. ^{1}H NMR (500 MHz) spectrum of compound **4r** in $CDCl_3$.

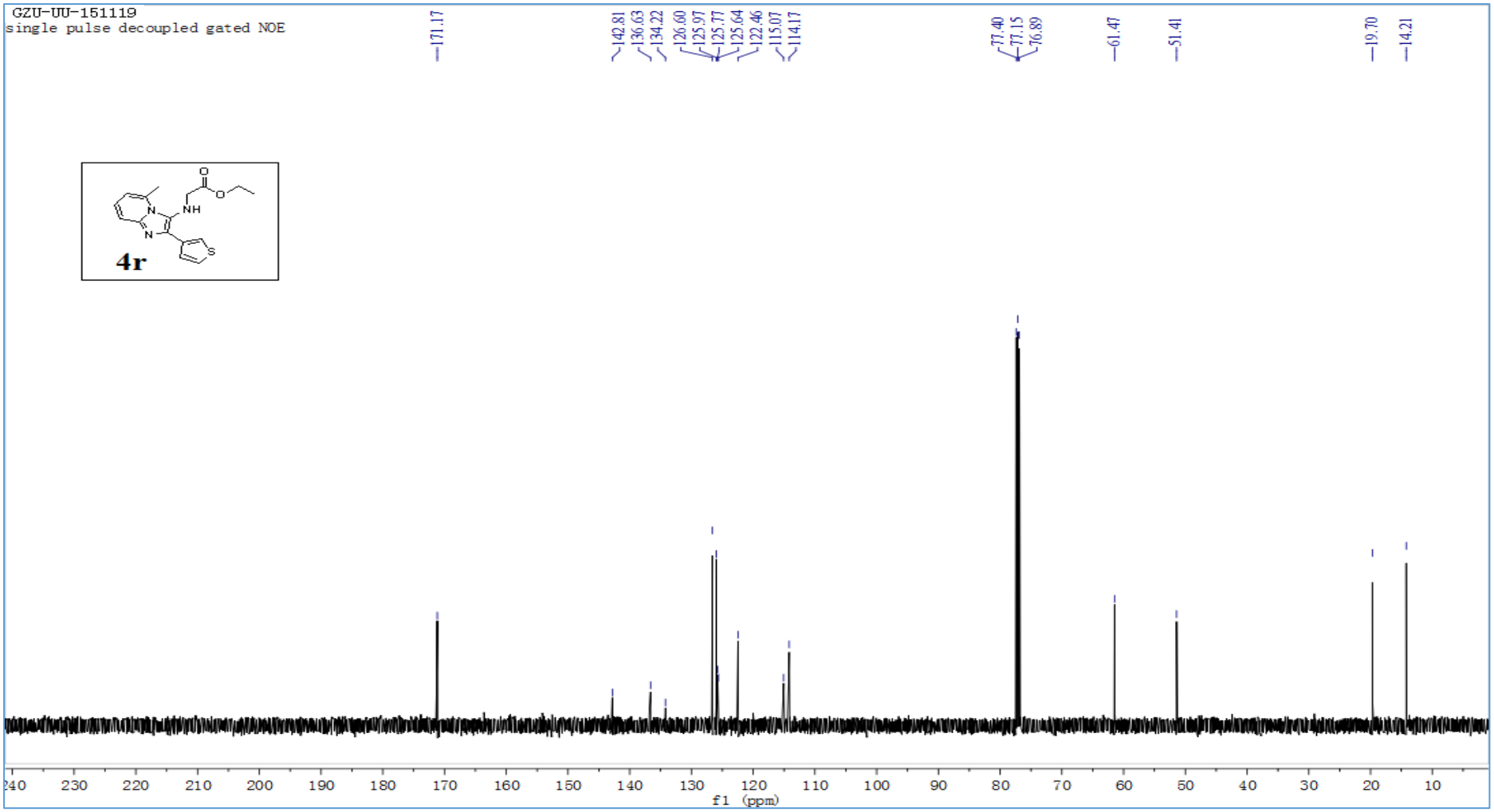

Figure 53. ^{13}C NMR (125 MHz) spectrum of compound **4r** in $CDCl_3$.

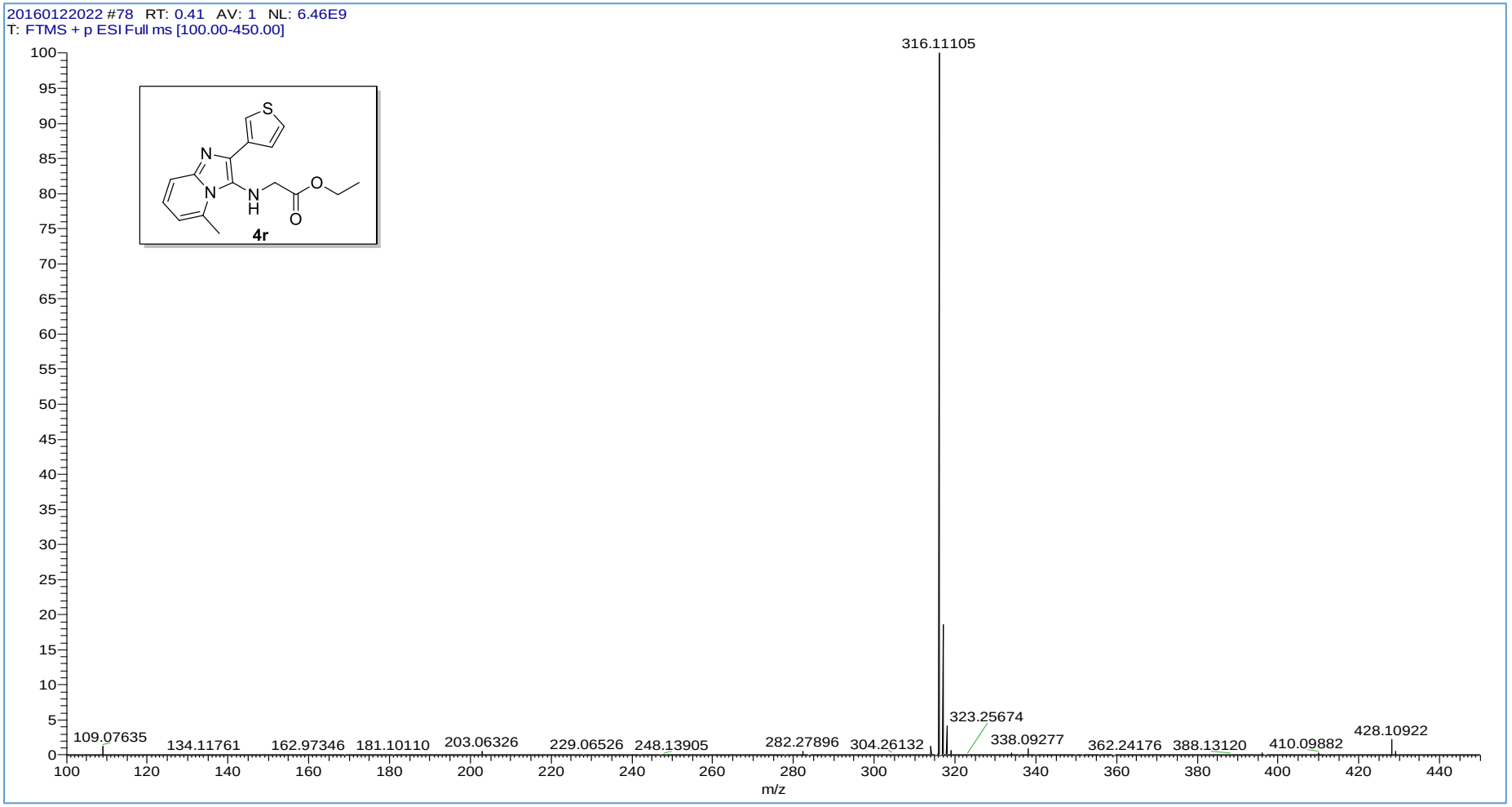

Figure 54. HRMS spectrum of compound **4r**.

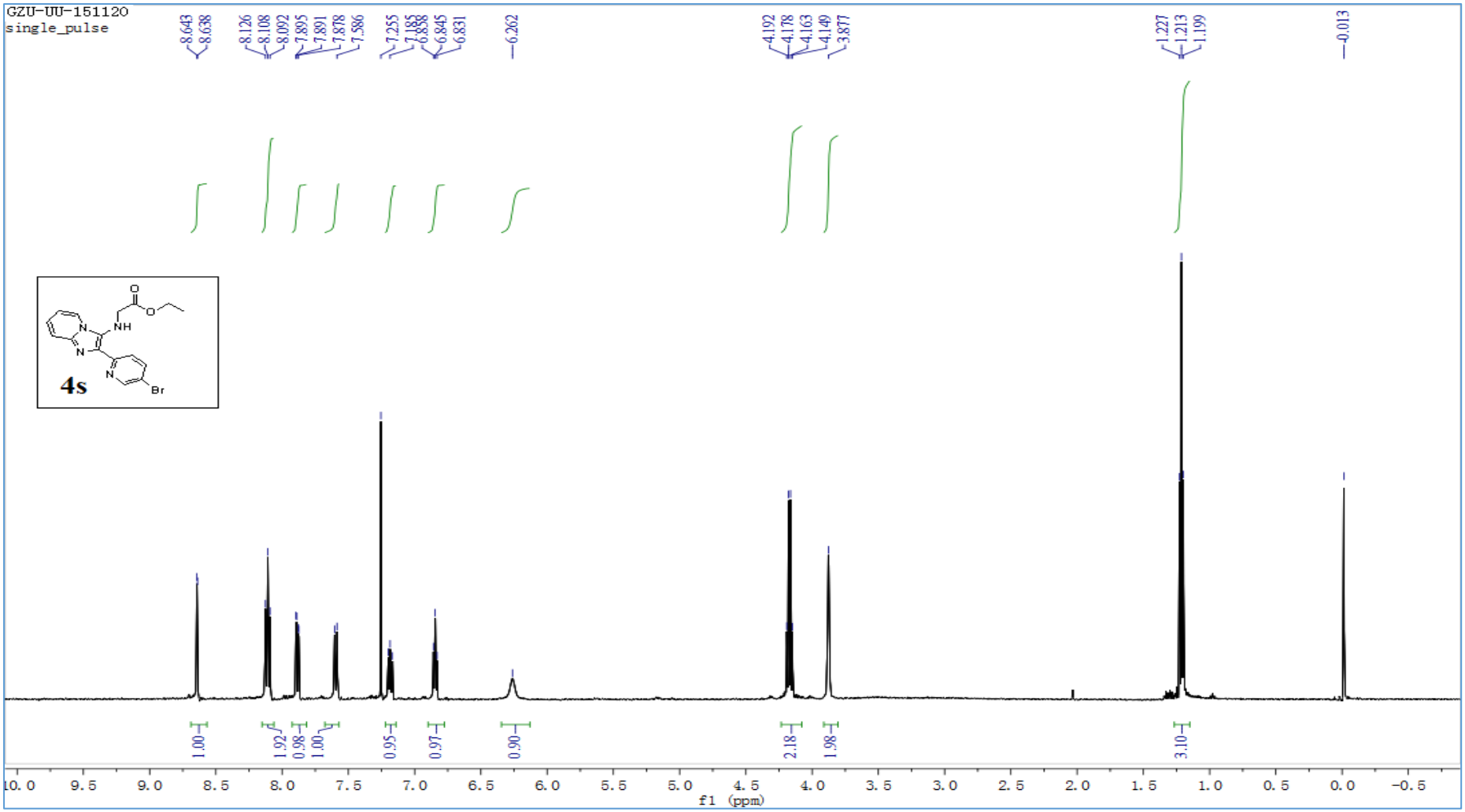

Figure 55. ^{1}H NMR (500 MHz) spectrum of compound **4s** in $CDCl_3$.

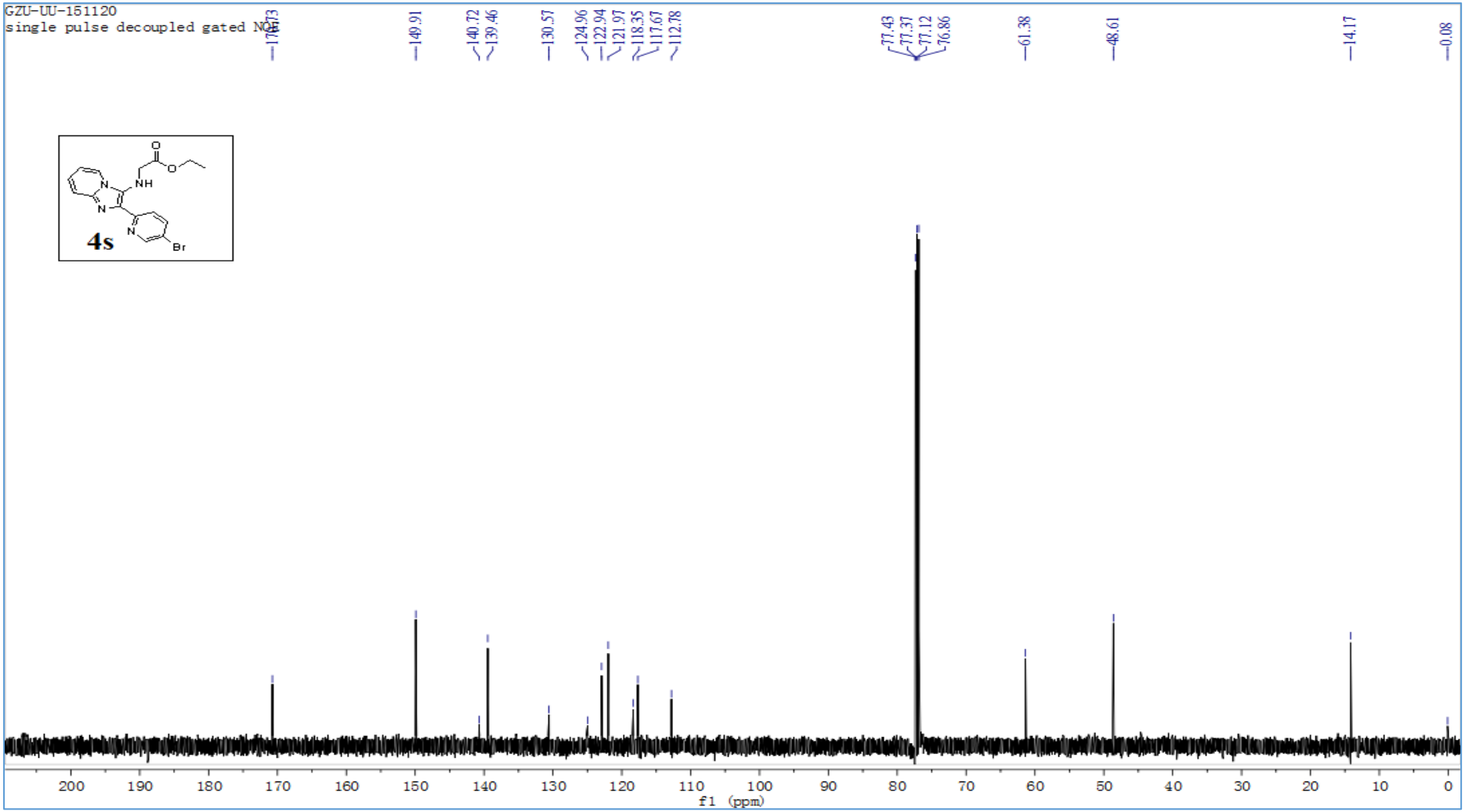

Figure 56. ^{13}C NMR (125 MHz) spectrum of compound **4s** in $CDCl_3$.

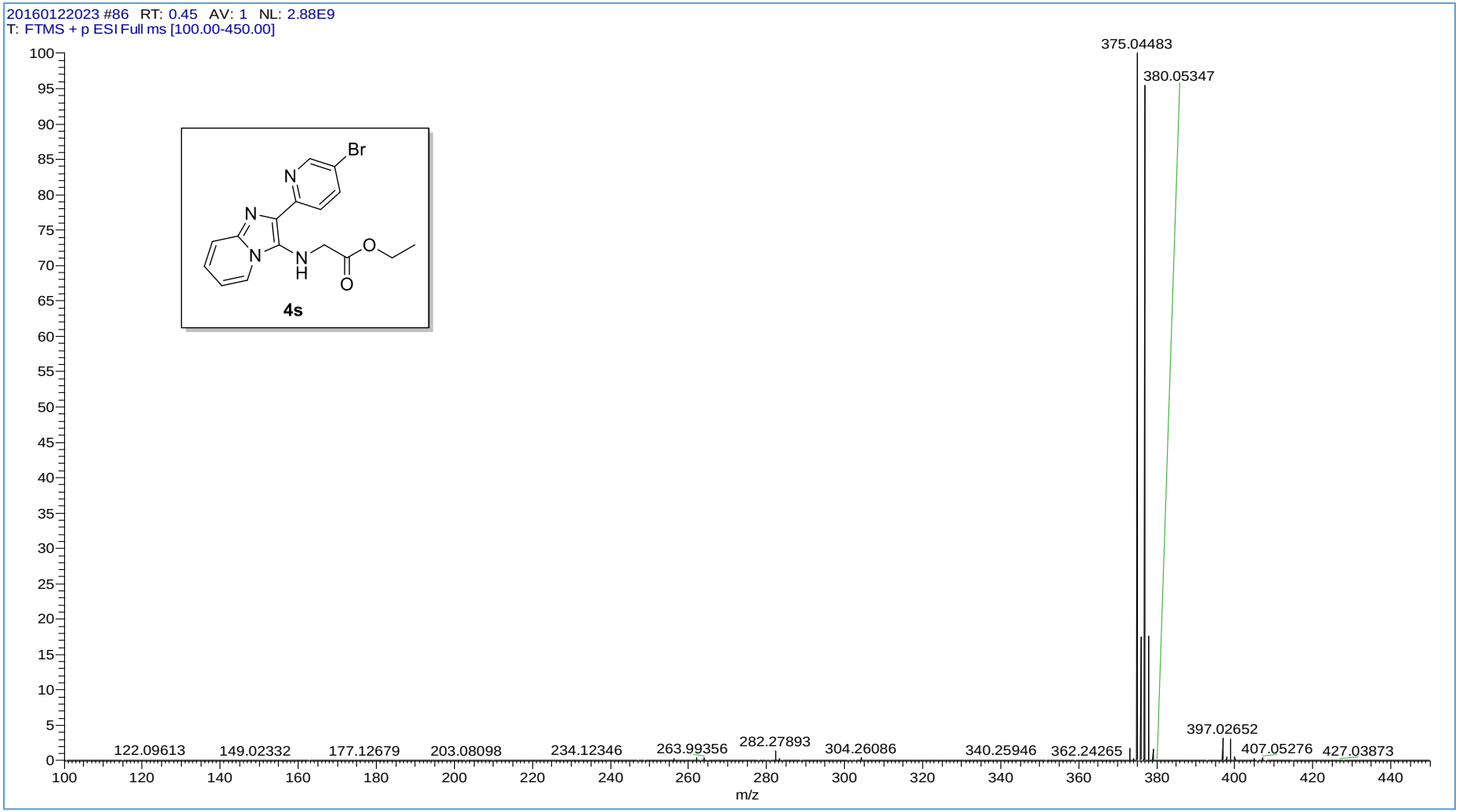

Figure 57. HRMS spectrum of compound **4s**.

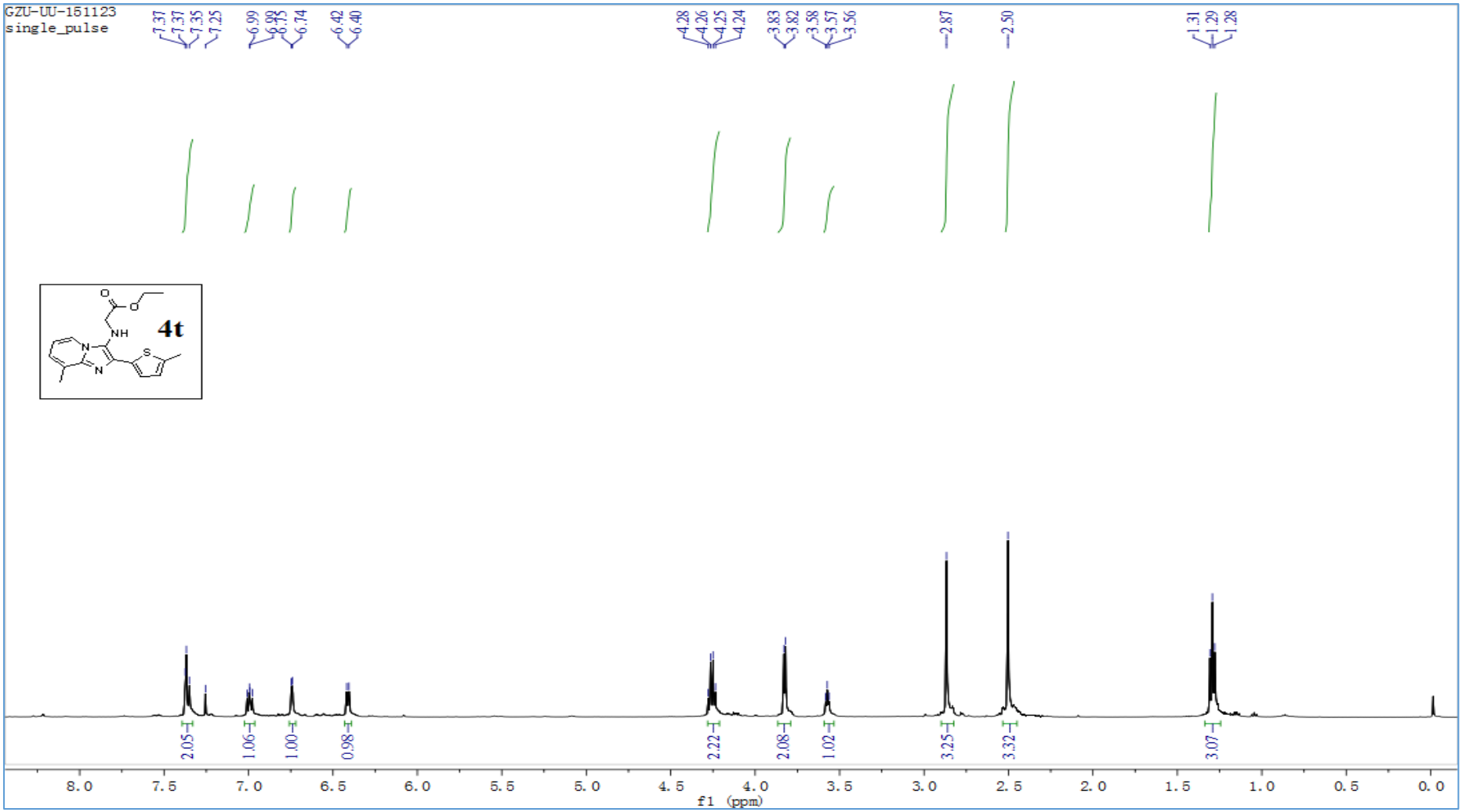

Figure 58. ^{1}H NMR (500 MHz) spectrum of compound **4t** in $CDCl_3$.

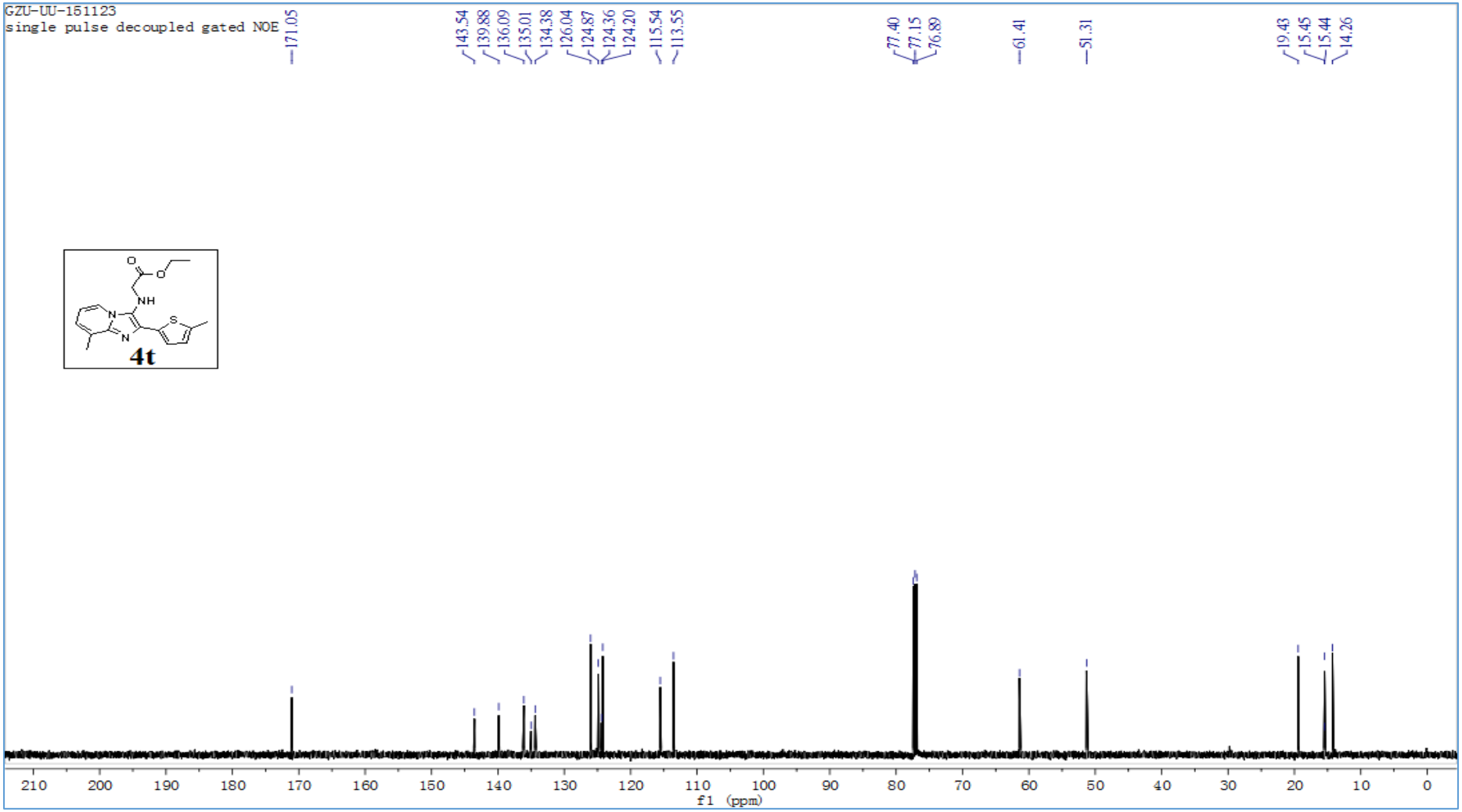

Figure 59. ^{13}C NMR (125 MHz) spectrum of compound **4t** in $CDCl_3$.

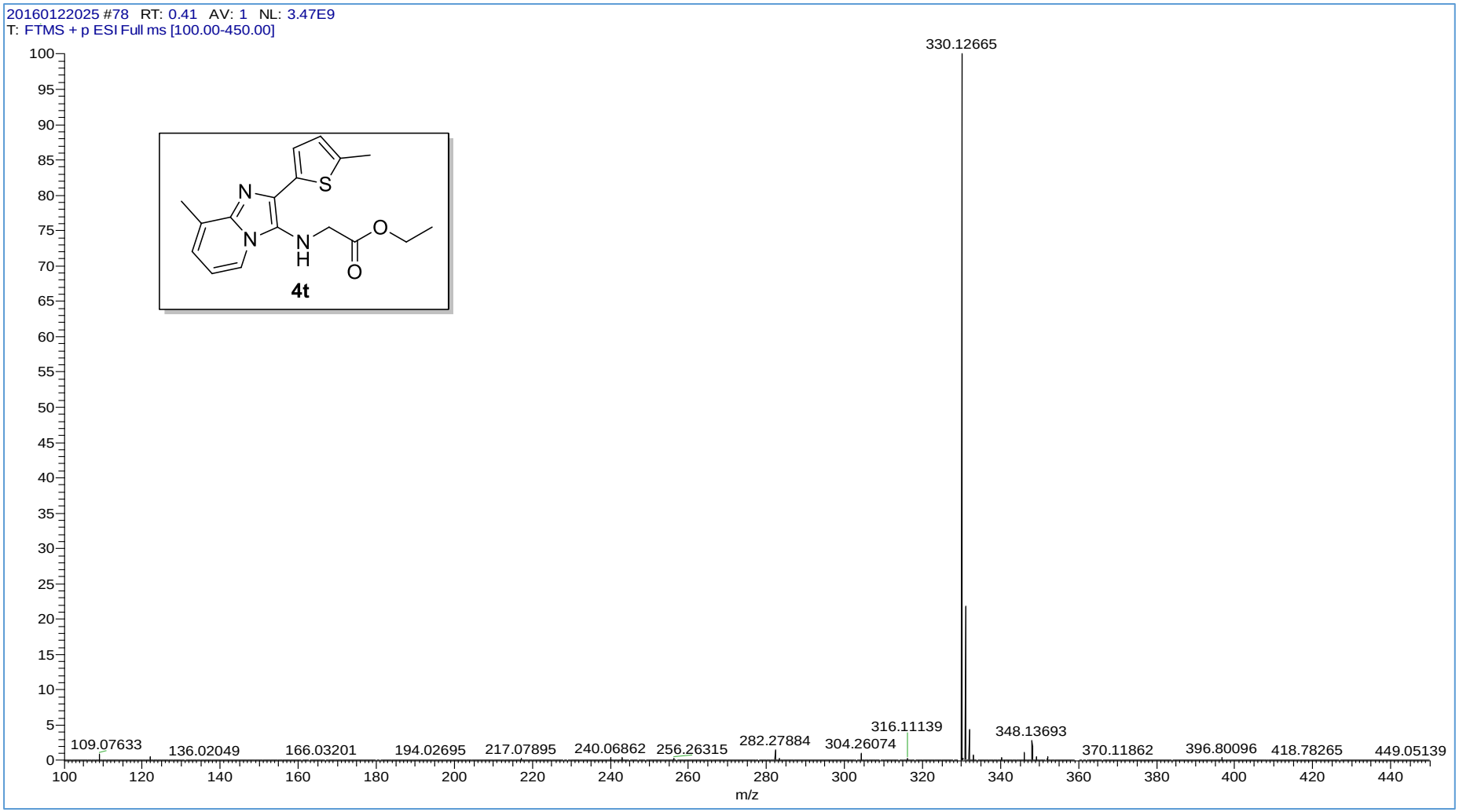

Figure 60. HRMS spectrum of compound **4t**.

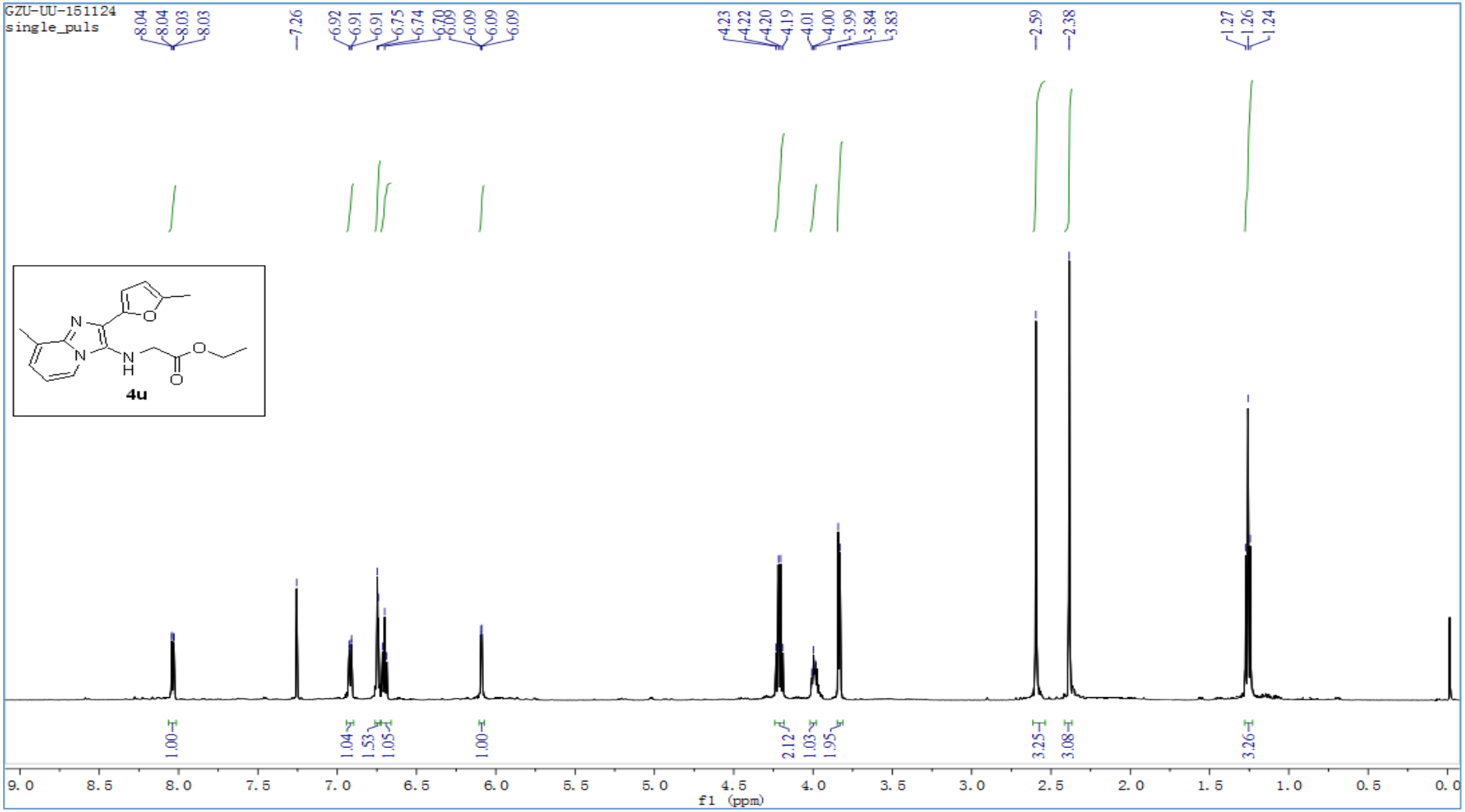

Figure 61. ^{13}H NMR (500 MHz) spectrum of compound **4u** in $CDCl_3$.

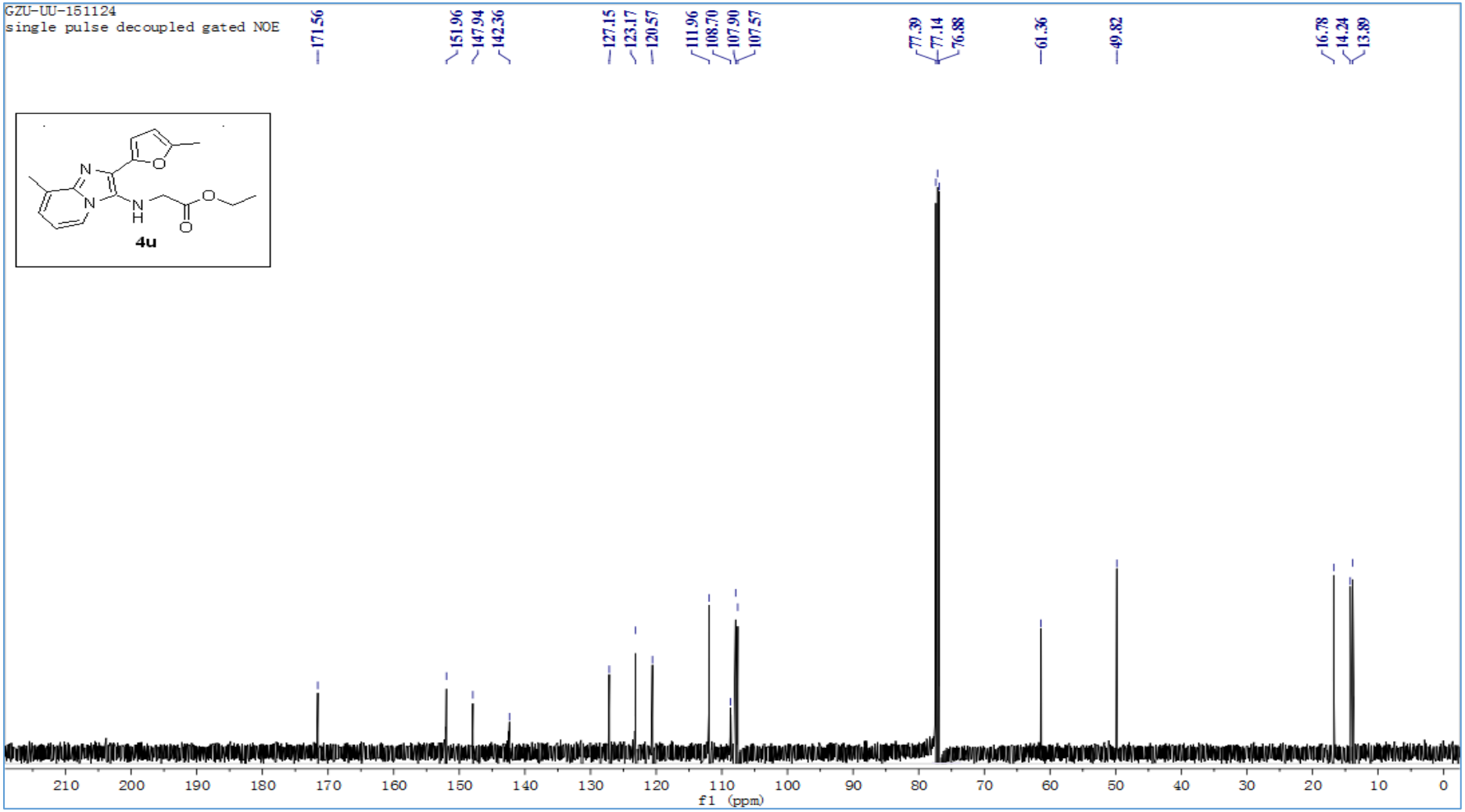

Figure 62. ^{13}C NMR (125 MHz) spectrum of compound **4u** in $CDCl_3$.

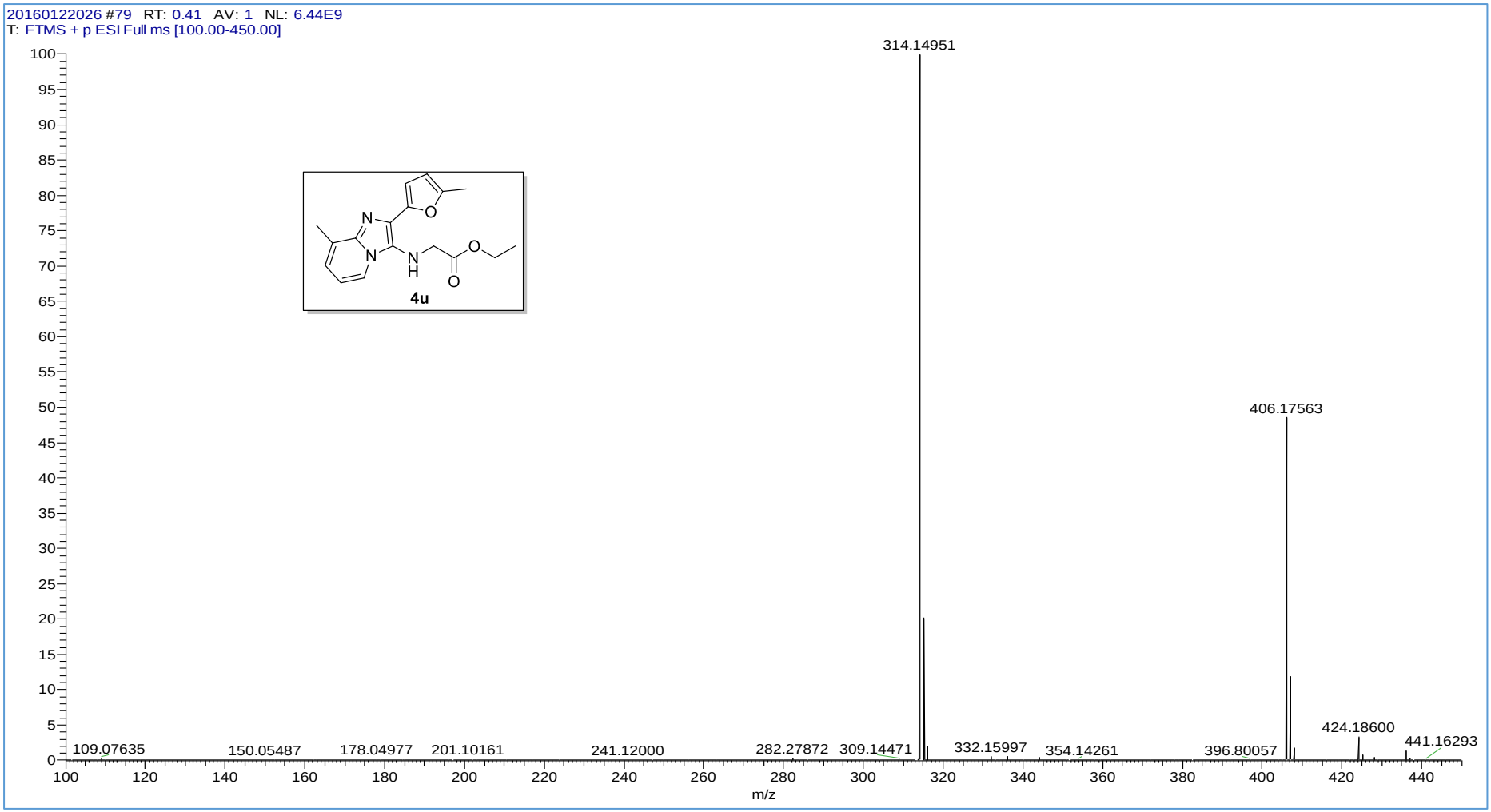

Figure 63. HRMS spectrum of compound **4u**.

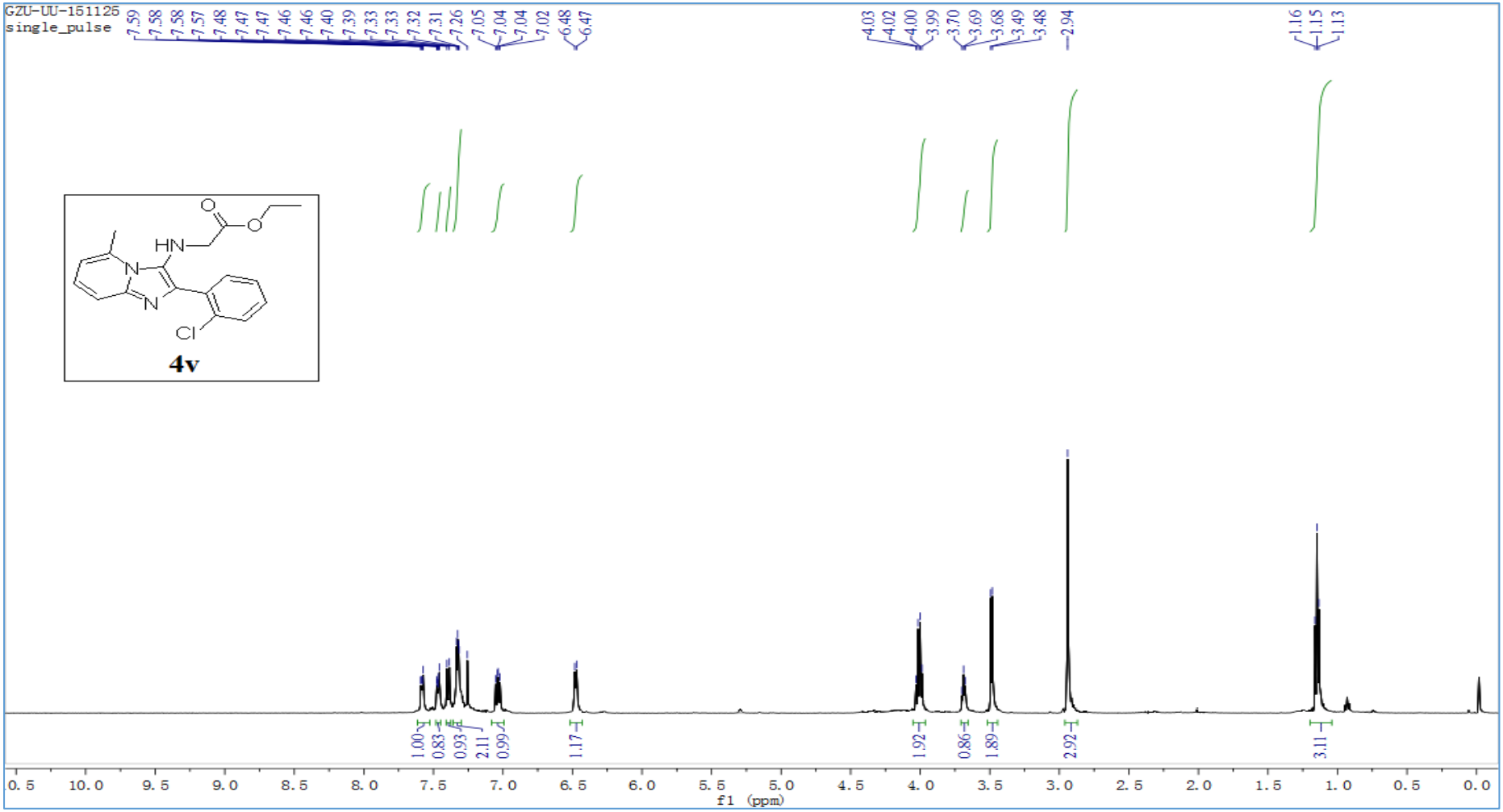

Figure 64. ^{1}H NMR (500 MHz) spectrum of compound **4v** in $CDCl_3$.

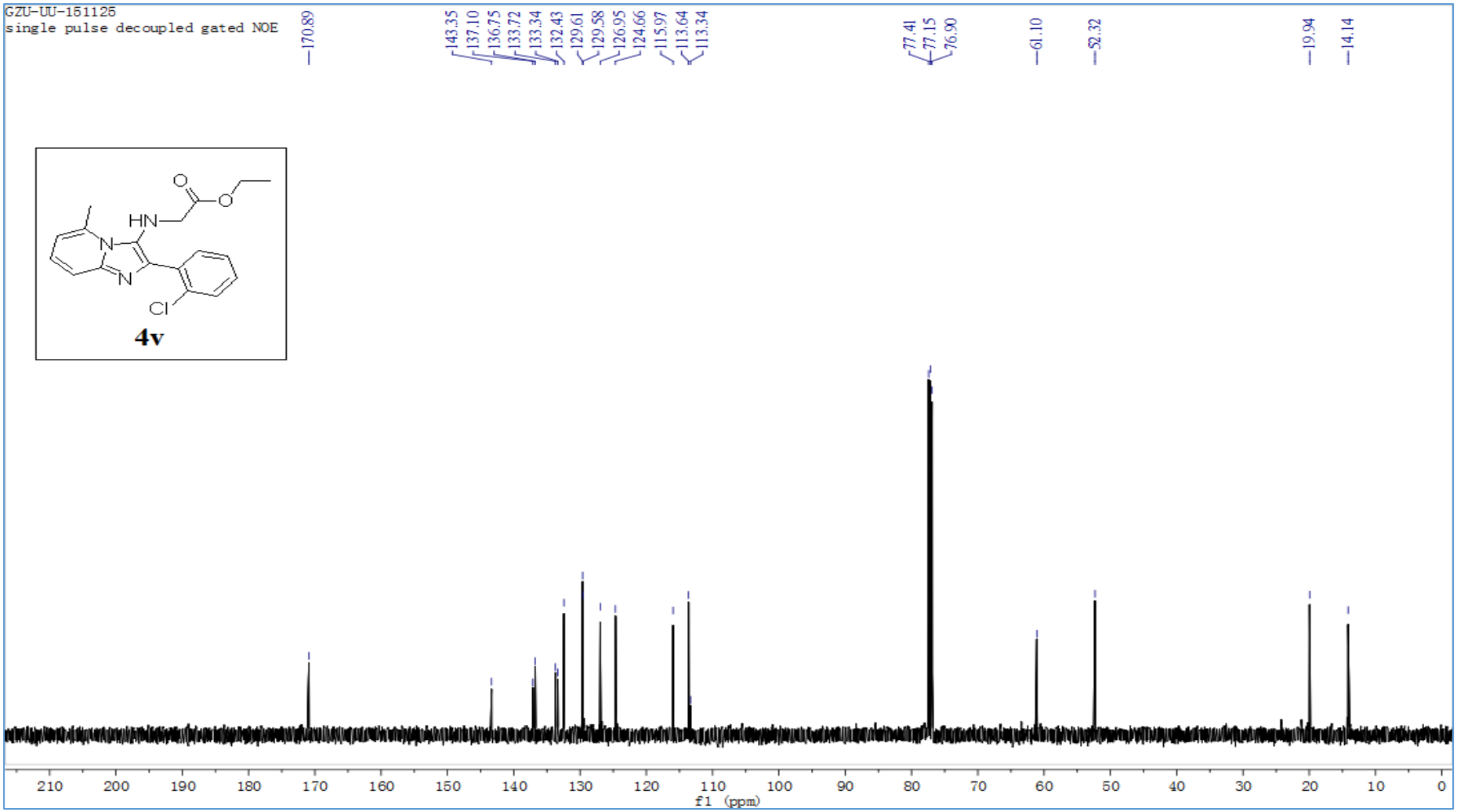

Figure 65. ^{13}C NMR (125 MHz) spectrum of compound **4v** in $CDCl_3$.

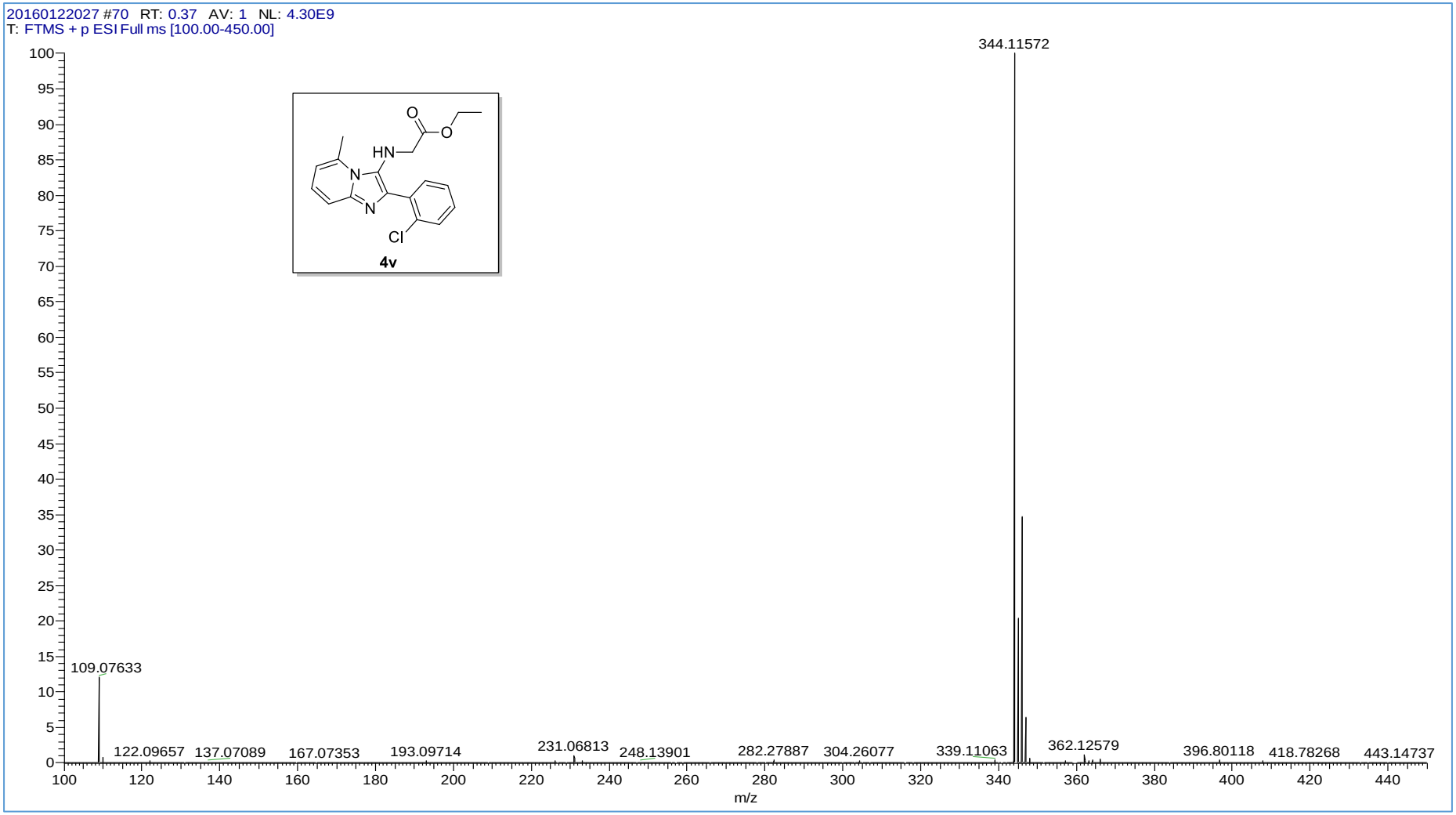

Figure 66. HRMS spectrum of compound **4v**.

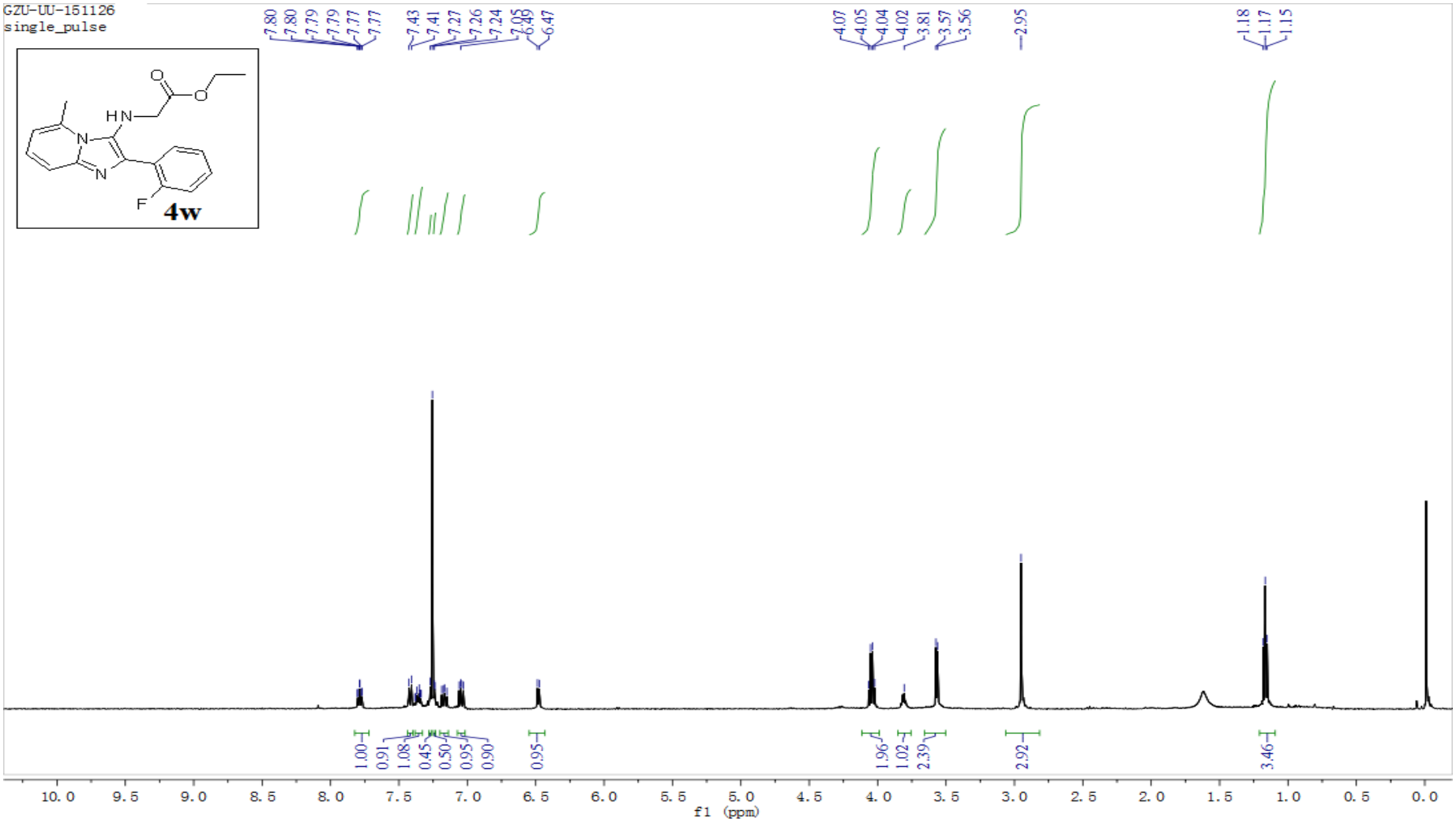

Figure 67. ^{1}H NMR (500 MHz) spectrum of compound **4w** in $CDCl_3$.

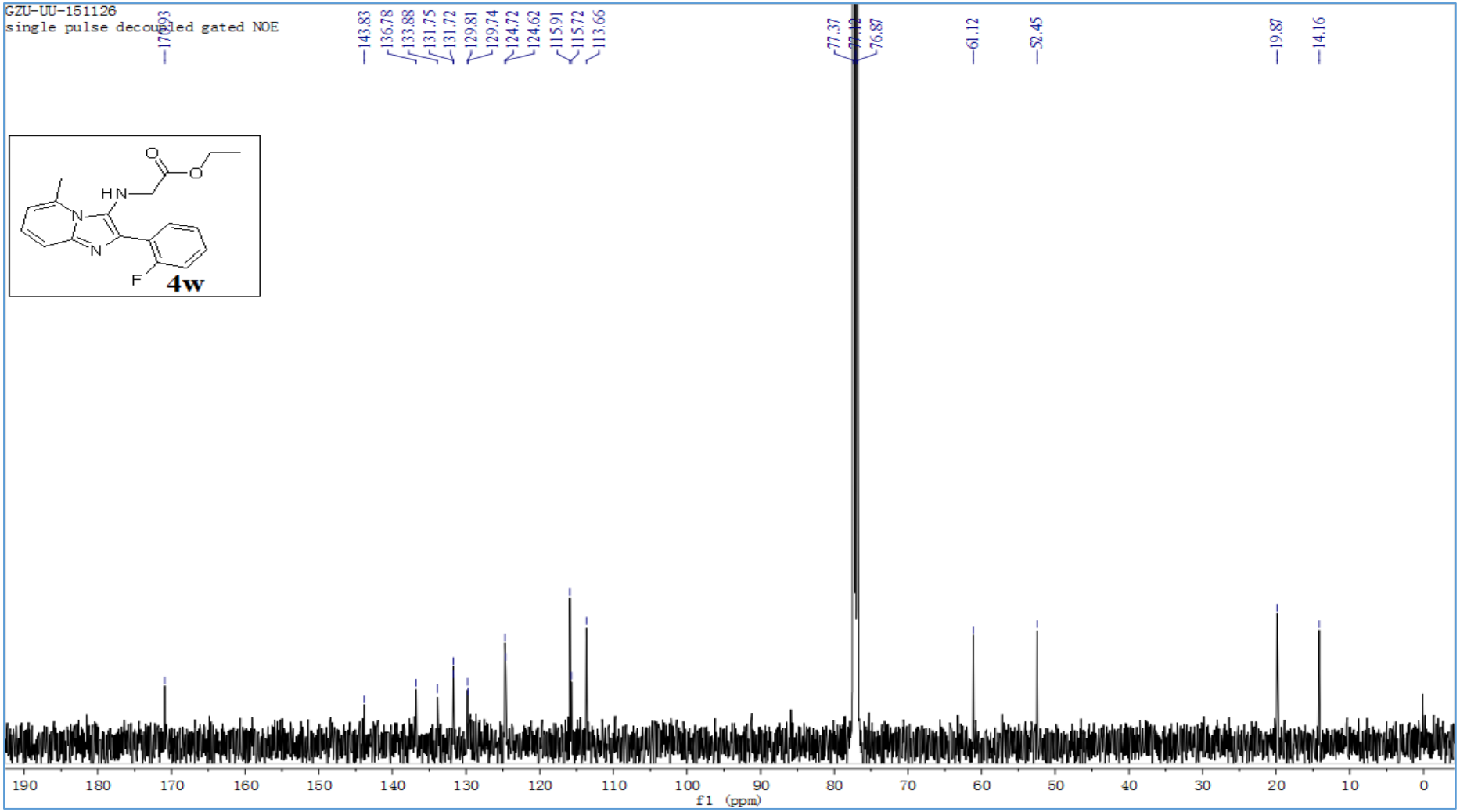

Figure 68. ^{13}C NMR (125 MHz) spectrum of compound **4w** in $CDCl_3$.

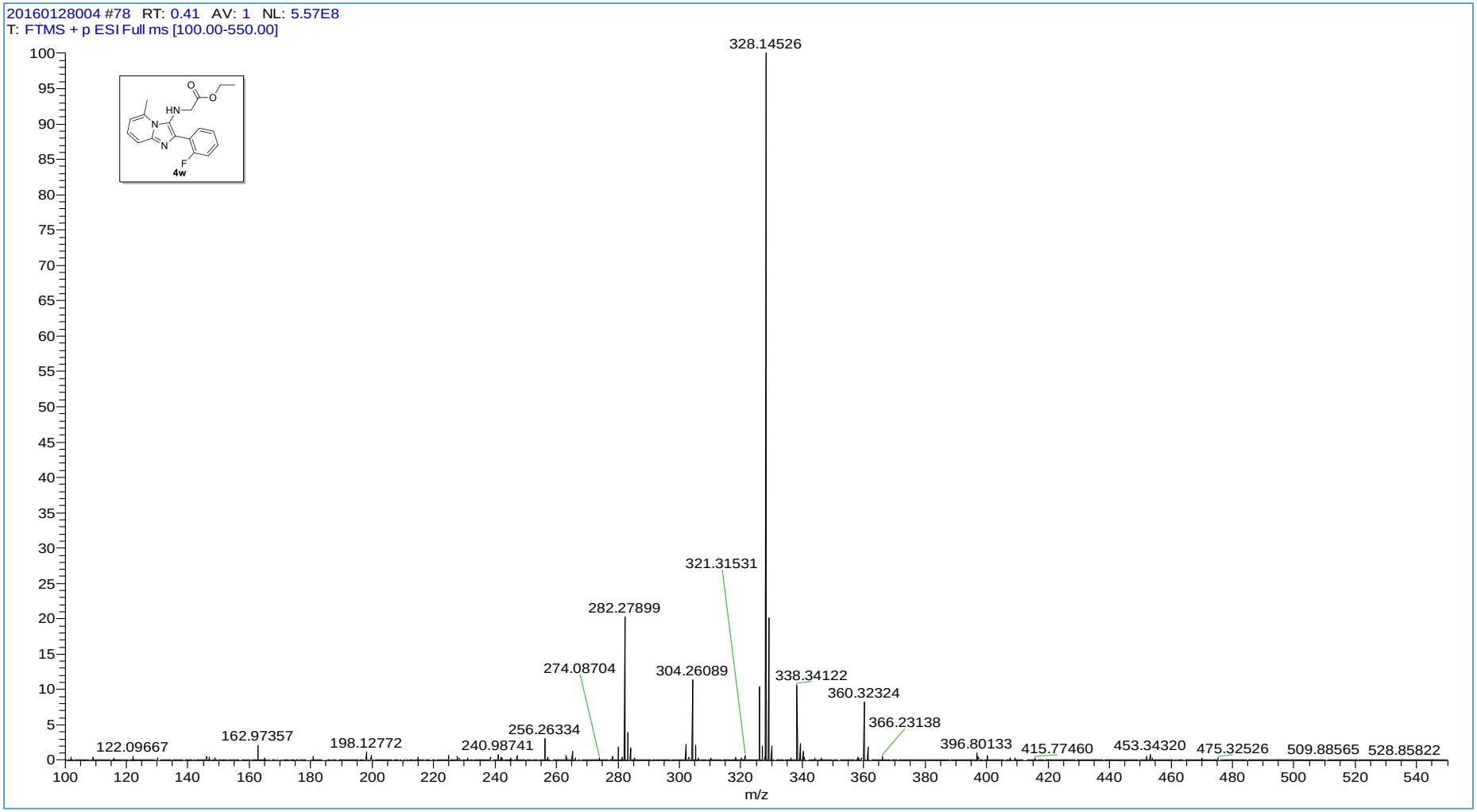

Figure 69. HRMS spectrum of compound **4w**.