An environmentally benign multi-component reaction: Regioselective synthesis of fluorinated 2-aminopyridines using diverse properties of nitro group

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Supporting Information

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X-ray Structure and Data of 4a & 5s

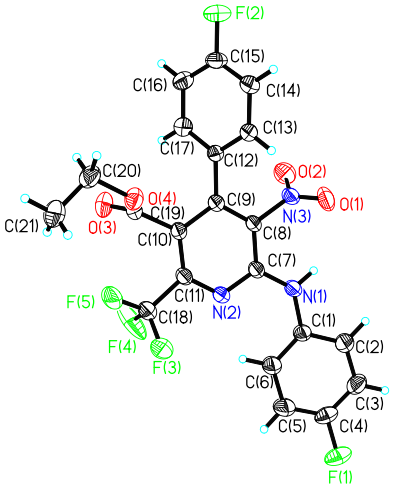

Figure S1. X-Ray crystal structure of **4a**; ellipsoids are drawn at the 30% probability level.

Table S1. Crystal data and structure refinement for **4a**

Identification code	1
Empirical formula	$C_{21}H_{14}F_5N_3O_4$
Formula weight	467.35
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.2387(14) A alpha = 78.884(2) deg. b = 9.1226(15) A beta = 77.335(2) deg. c = 15.647(3) A gamma = 63.875(2) deg.
Volume	1023.9(3) A^3
Z, Calculated density	2, 1.516 Mg/m^3
Absorption coefficient	0.136 mm^-1
F(000)	476
Crystal size	0.300 x 0.250 x 0.230 mm
Theta range for data collection	2.502 to 24.995 deg.
Limiting indices	-9<=h<=9, -10<=k<=10, -18<=l<=18
Reflections collected / unique	7987 / 3571 [R(int) = 0.0226]
Completeness to theta = 25.242	96.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.969 and 0.960
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3571 / 0 / 300
Goodness-of-fit on F^2	1.094
Final R indices [I>2sigma(I)]	R1 = 0.0501, wR2 = 0.1497
R indices (all data)	R1 = 0.0658, wR2 = 0.1619
Extinction coefficient	0.023(5)
Largest diff. peak and hole	0.432 and -0.275eA^-3

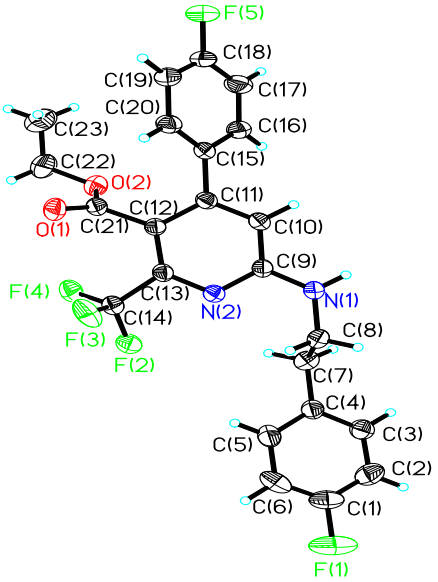

Figure S2. X-Ray crystal structure of **5s**; ellipsoids are drawn at the 30% probability level.

Table S2. Crystal data and structure refinement for **5s**

Identification code	1
Empirical formula	$C_{23}H_{19}F_5N_2O_2$
Formula weight	450.40
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.6308(16) A alpha = 78.895(2) deg. b = 9.4049(18) A beta = 81.887(2) deg. c = 13.955(3) A gamma = 74.726(2) deg.
Volume	1067.4(3) A^3
Z, Calculated density	2, 1.401 Mg/m^3
Absorption coefficient	0.120 mm^-1
F(000)	464
Crystal size	0.350 x 0.300 x 0.200 mm
Theta range for data collection	1.494 to 25.150 deg.
Limiting indices	-10<=h<=10, -11<=k<=11, -16<=l<=16
Reflections collected / unique	8534 / 3809 [R(int) = 0.0261]
Completeness to theta = 25.242	98.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.976 and 0.959
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3809 / 0 / 290
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0512, wR2 = 0.1386
R indices (all data)	R1 = 0.0861, wR2 = 0.1679
Extinction coefficient	n/a
Largest diff. peak and hole	0.383 and -0.235 e.A^-3

Symmetry transformations used to generate equivalent atoms:

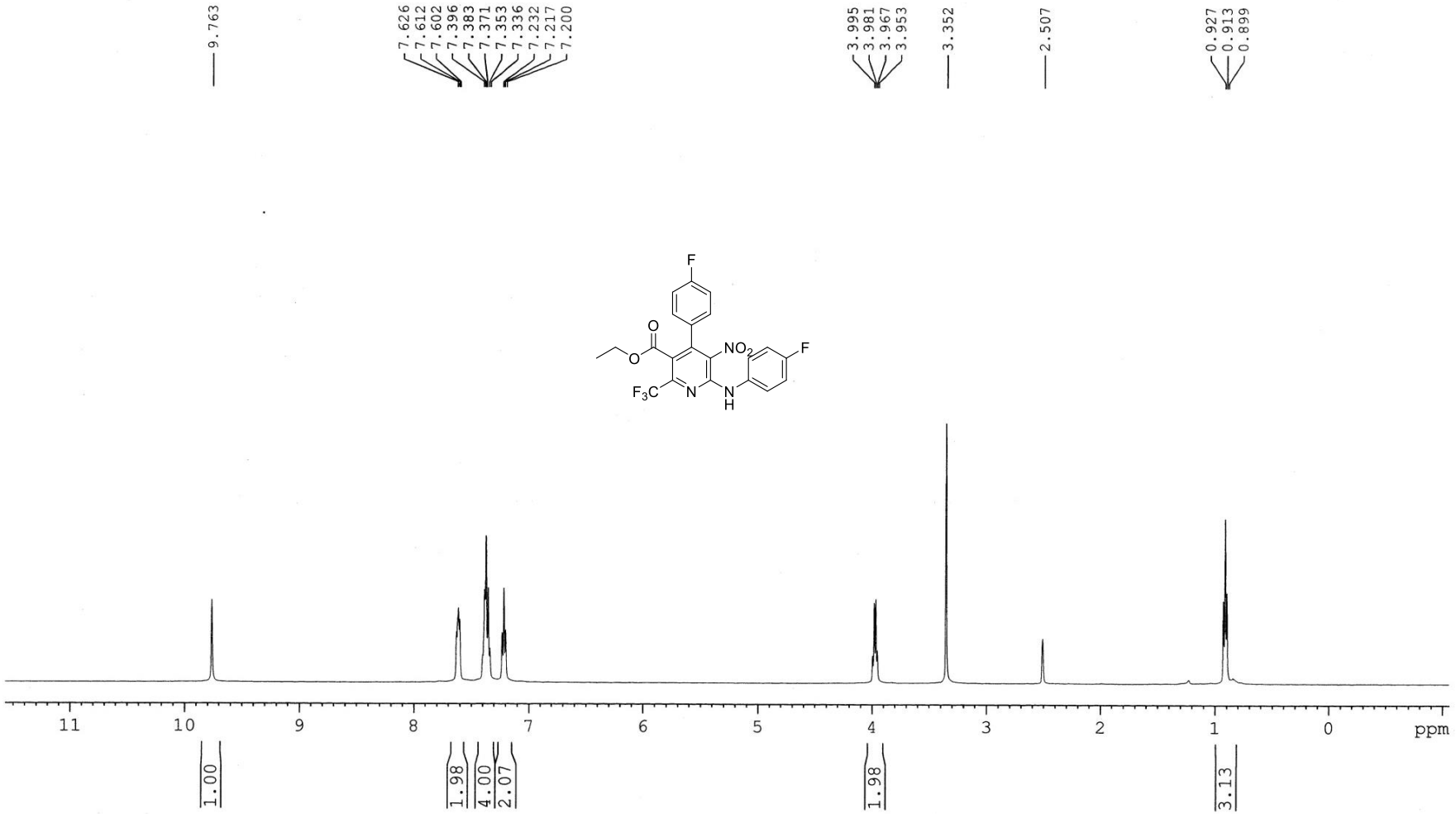

Figure S3. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4a**

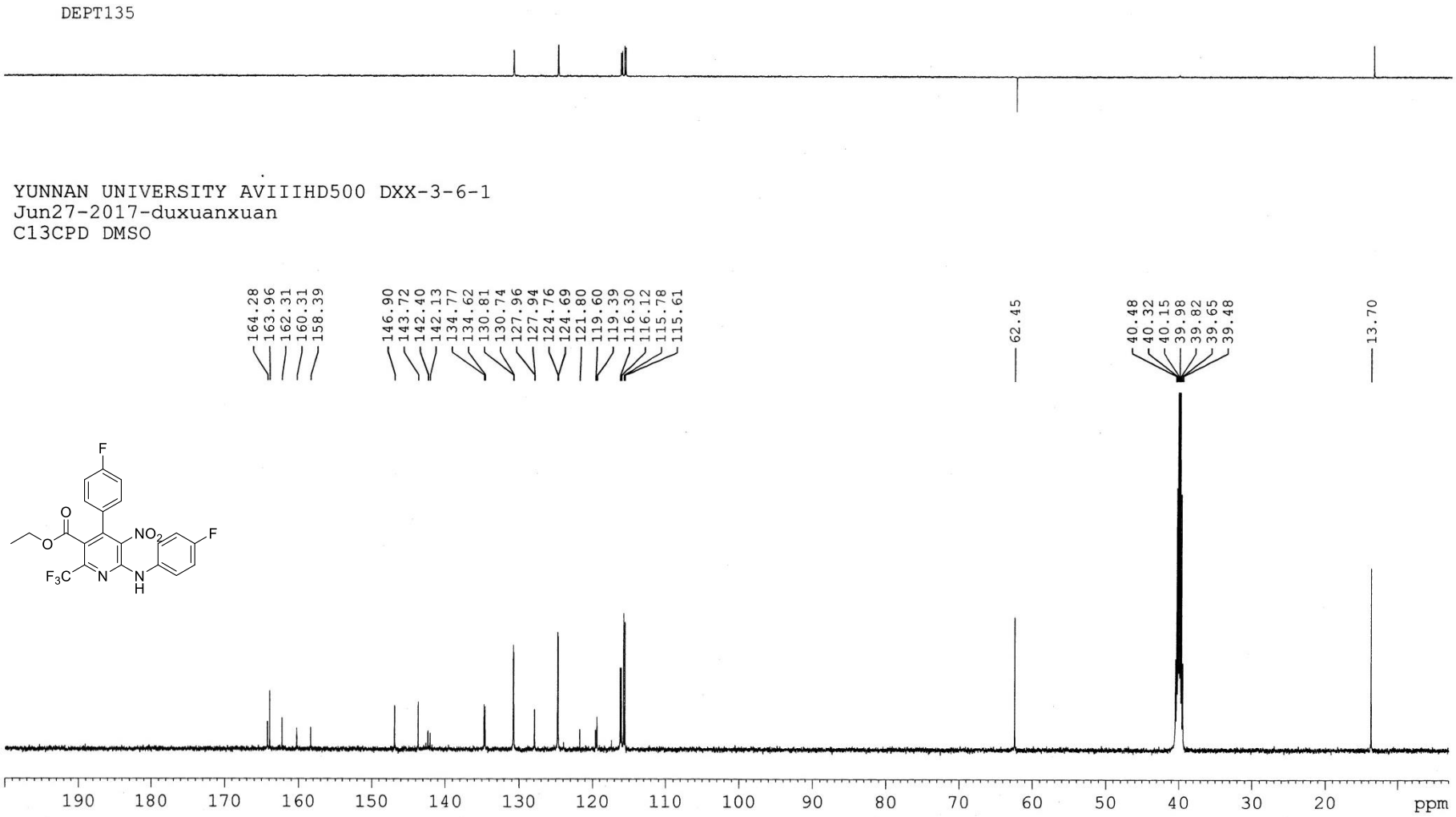

Figure S4. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4a**

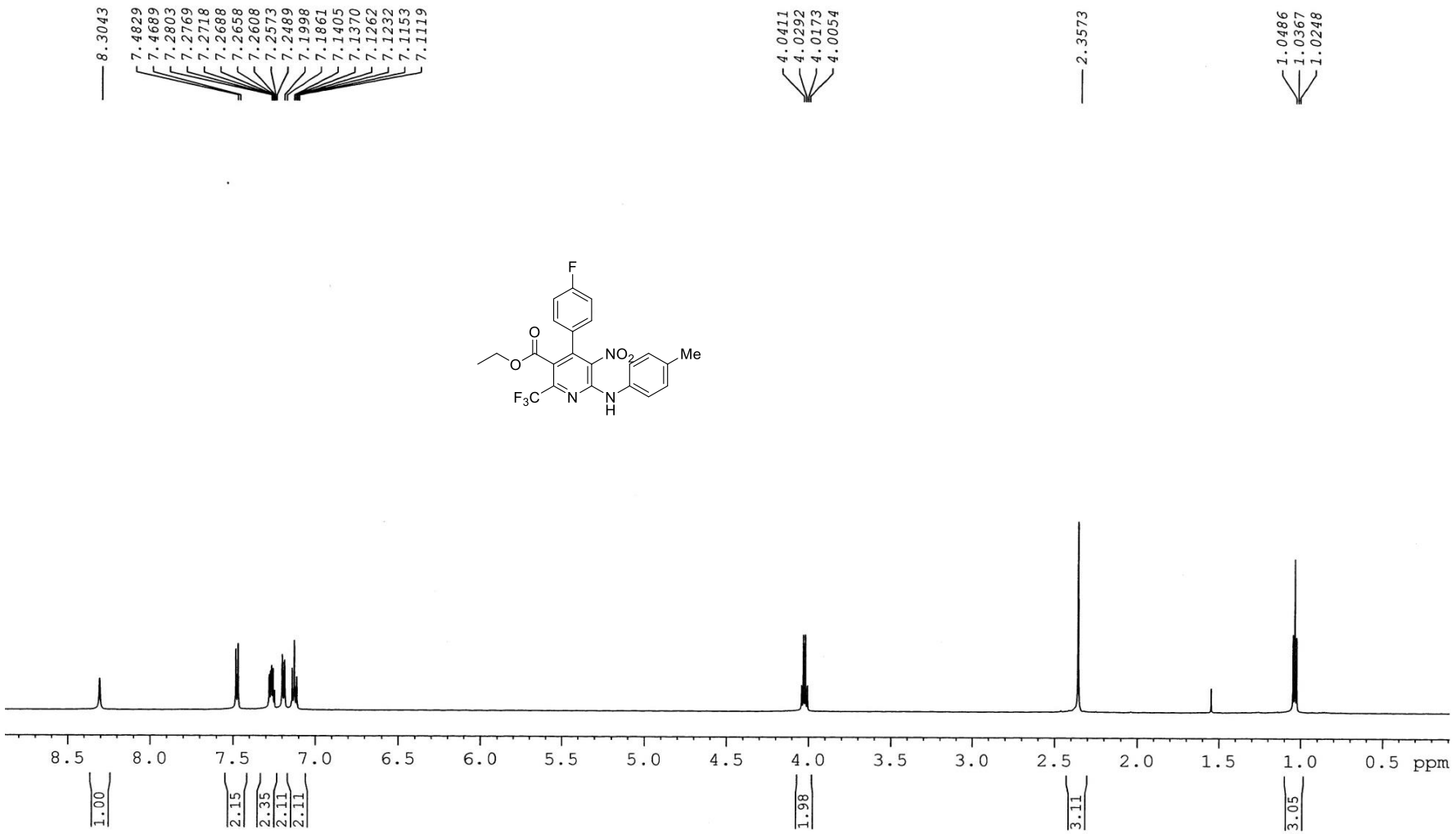

Figure S5. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **4b**

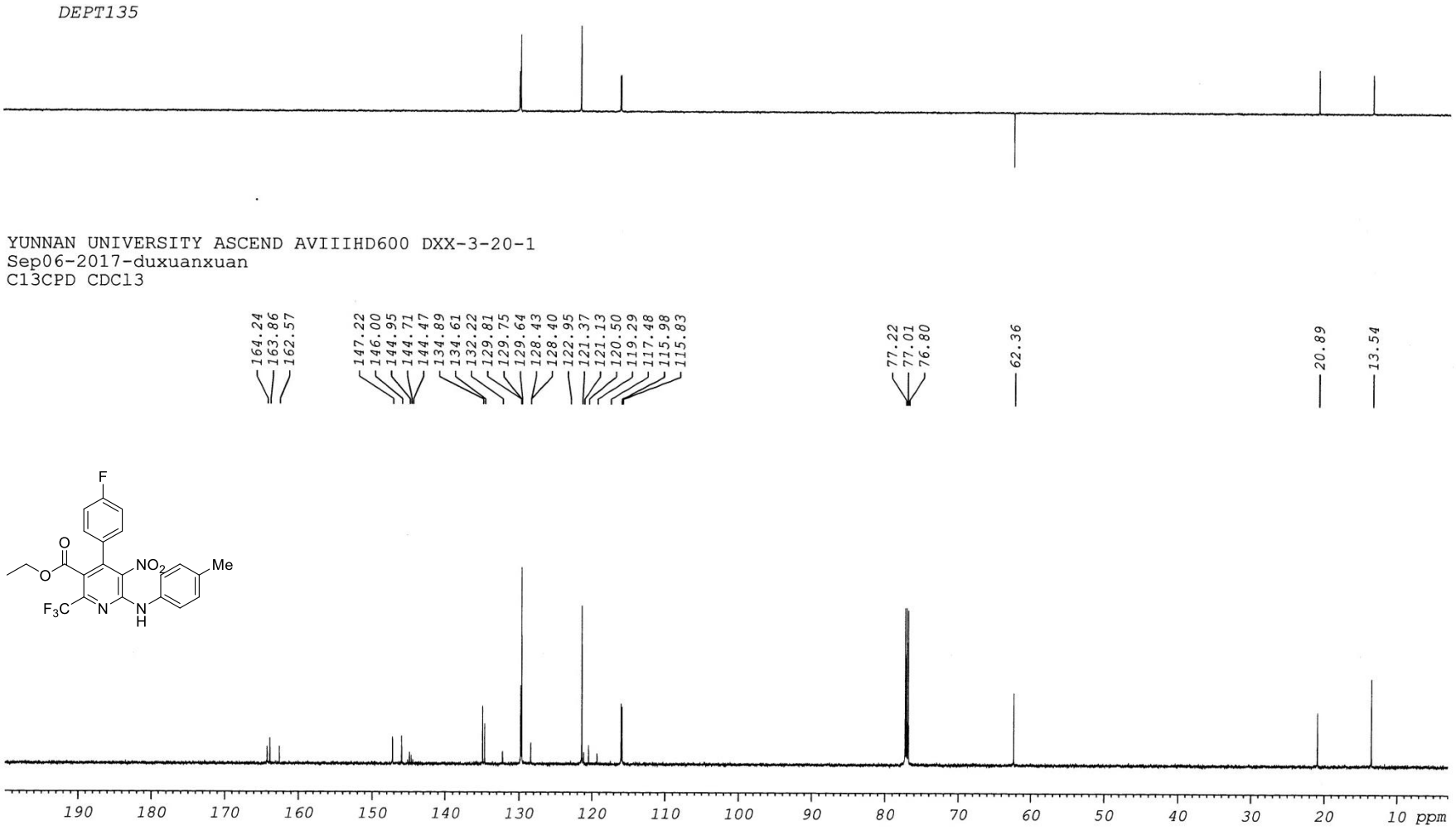

Figure S6. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **4b**

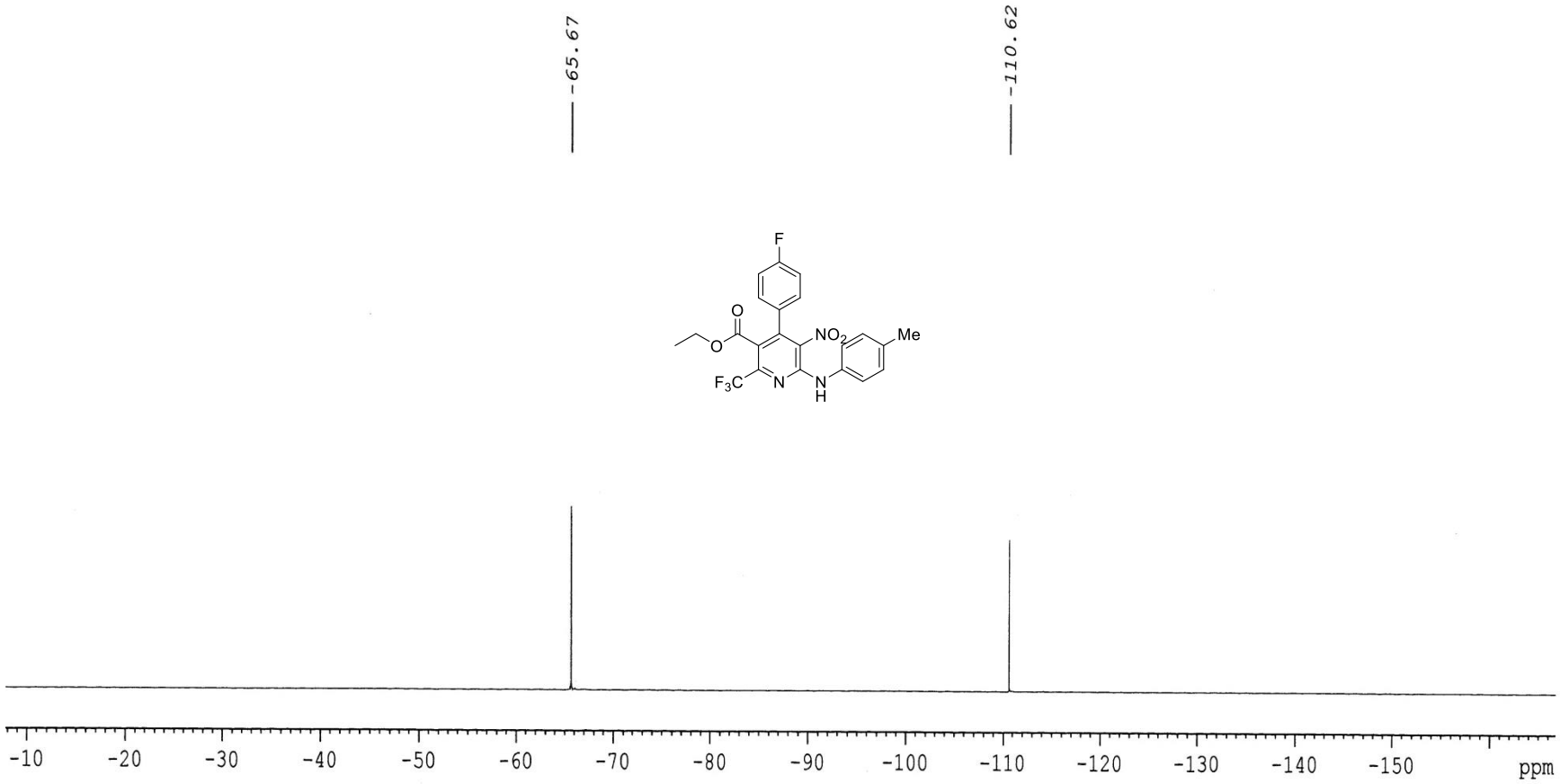

Figure S7. ^{19}F NMR (564 MHz, $CDCl_3$) spectra of compound **4b**

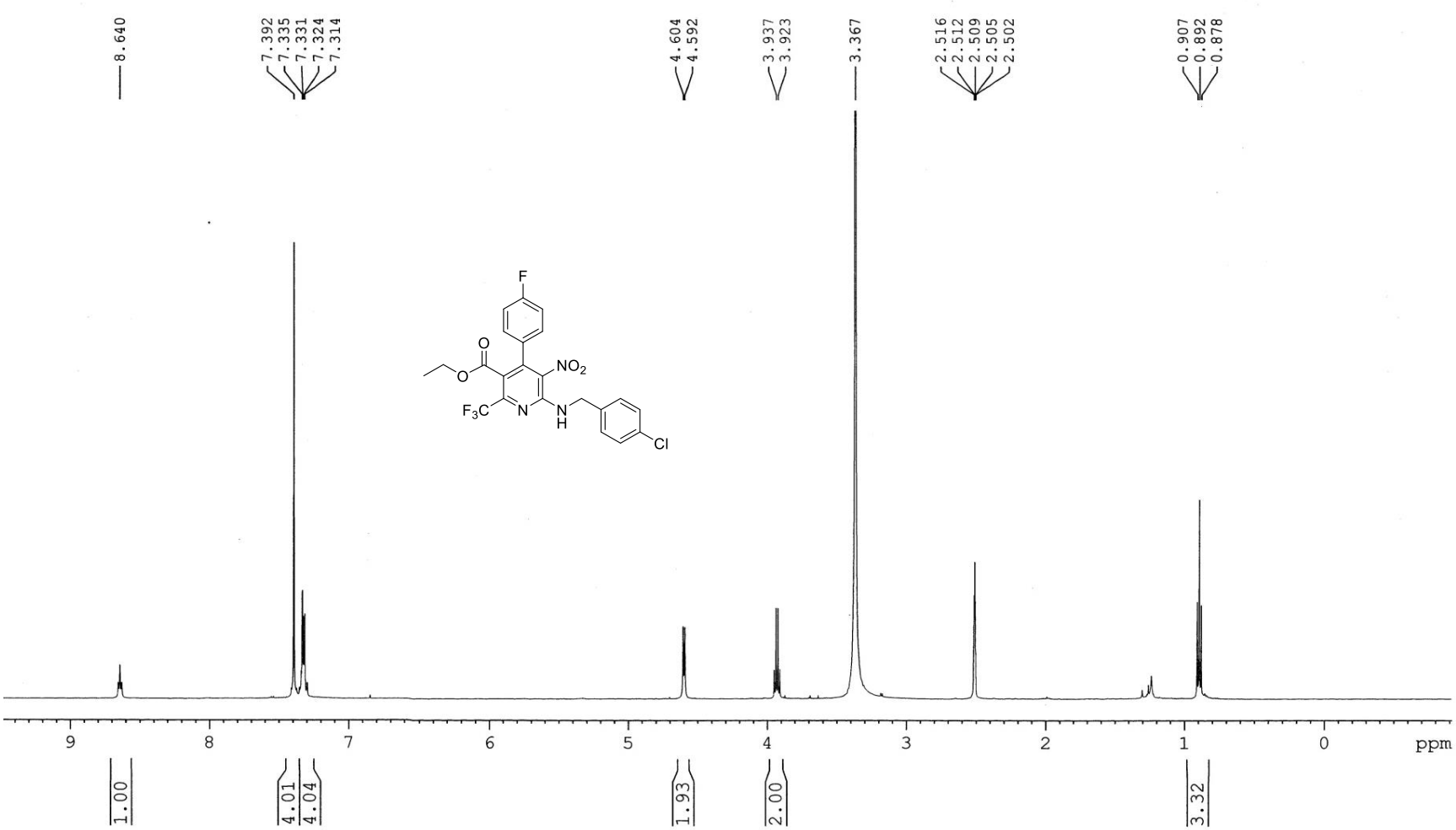

Figure S8. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4c**

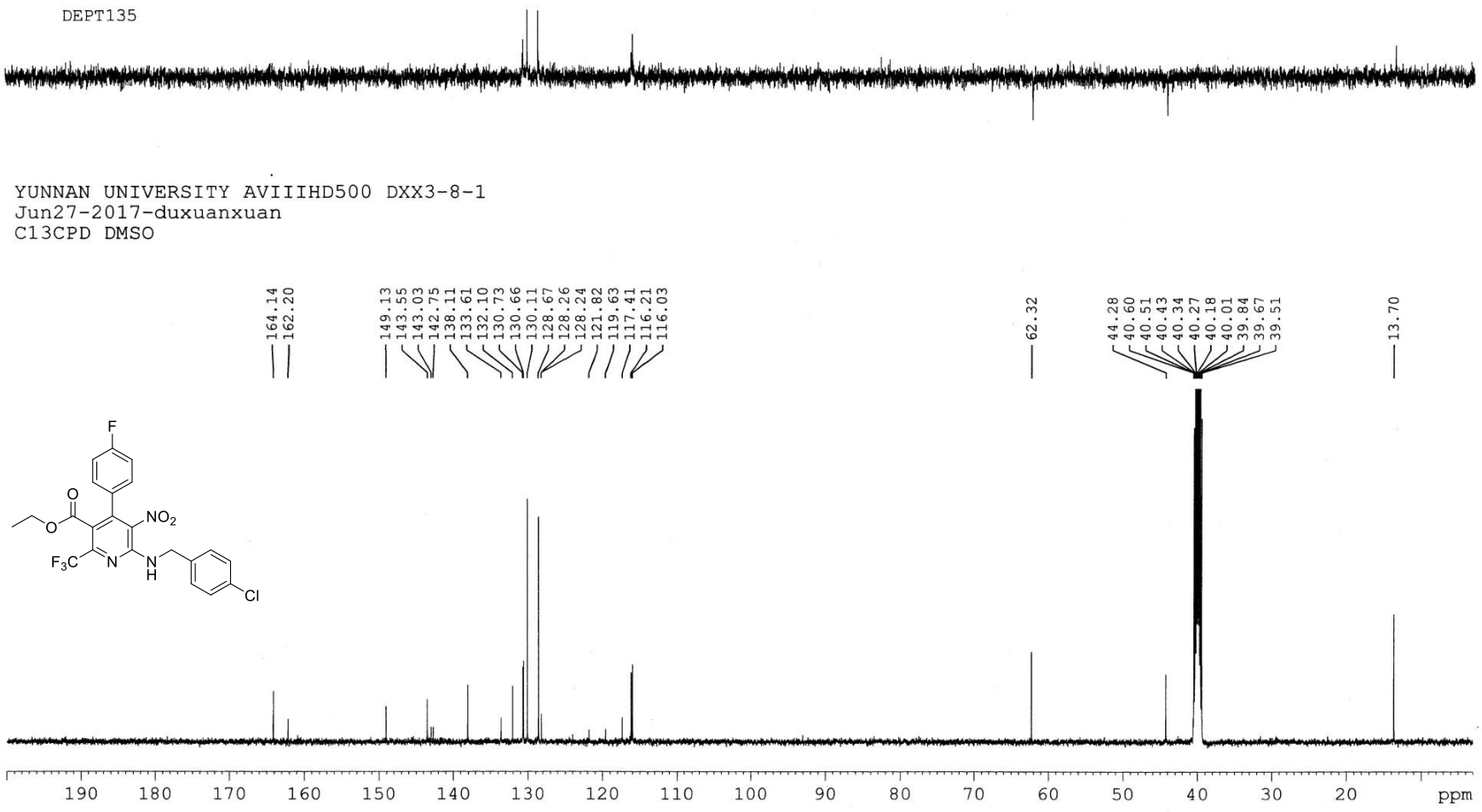

Figure S9. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4c**

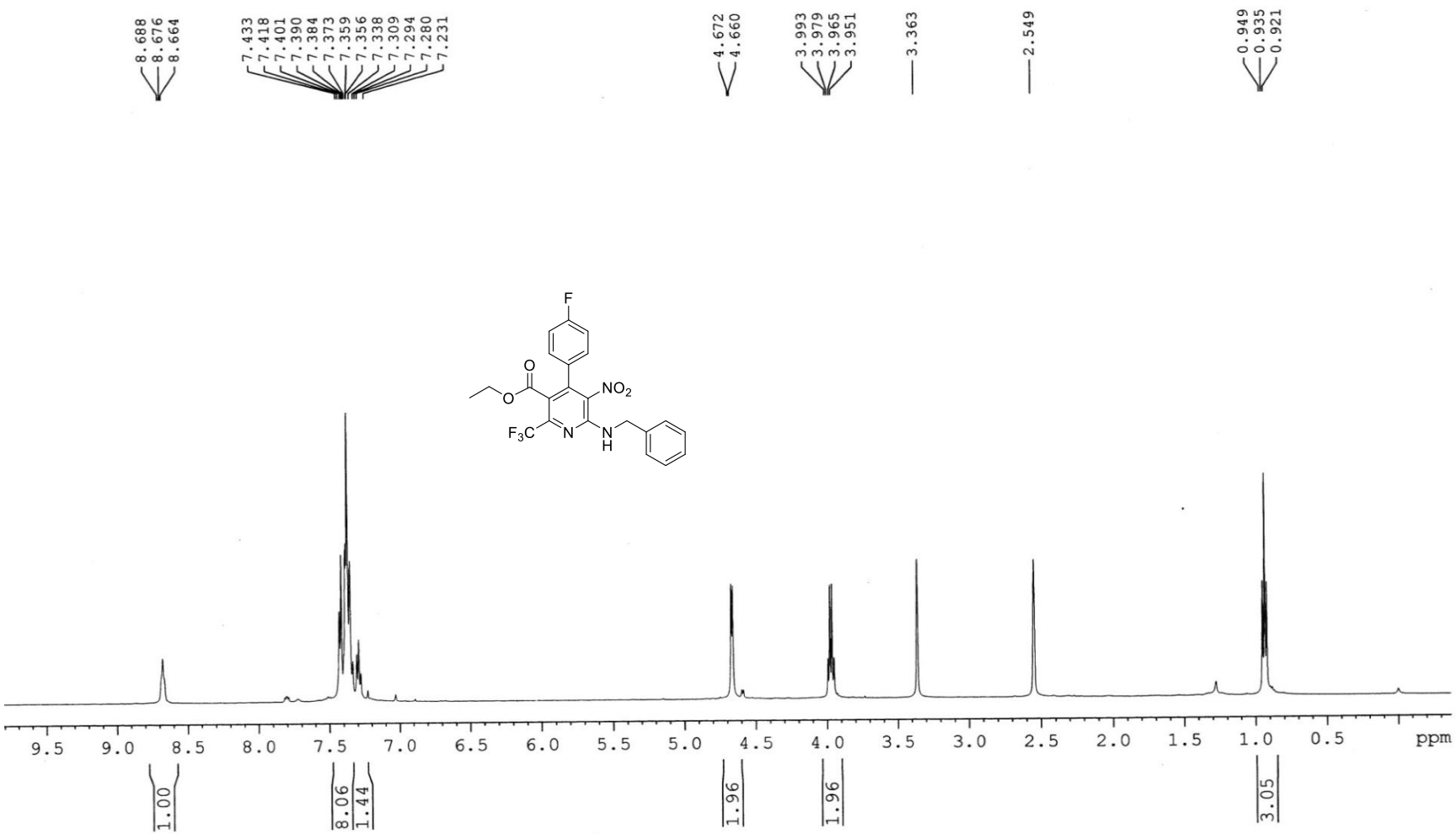

Figure S10. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4d**

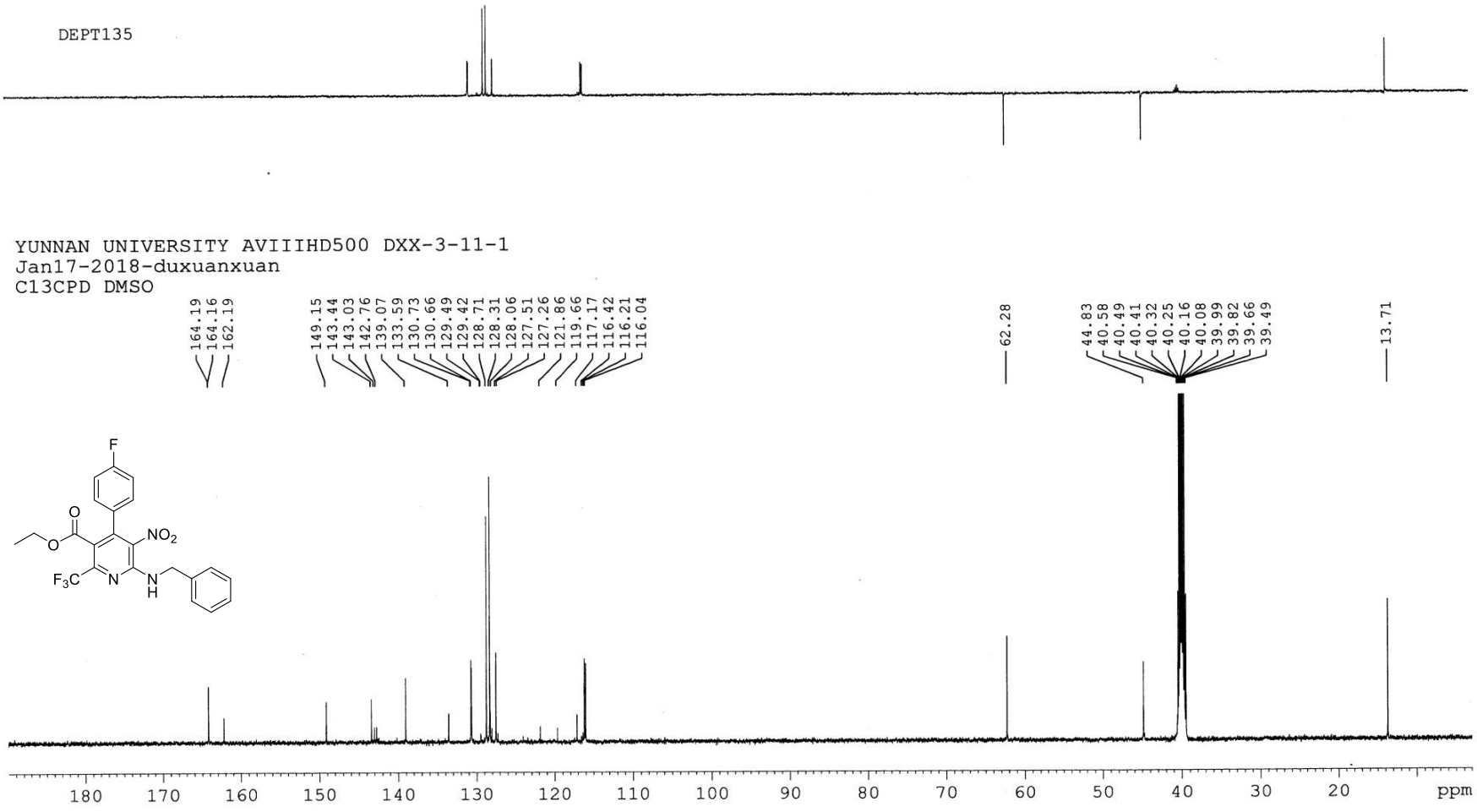

Figure S11. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4d**

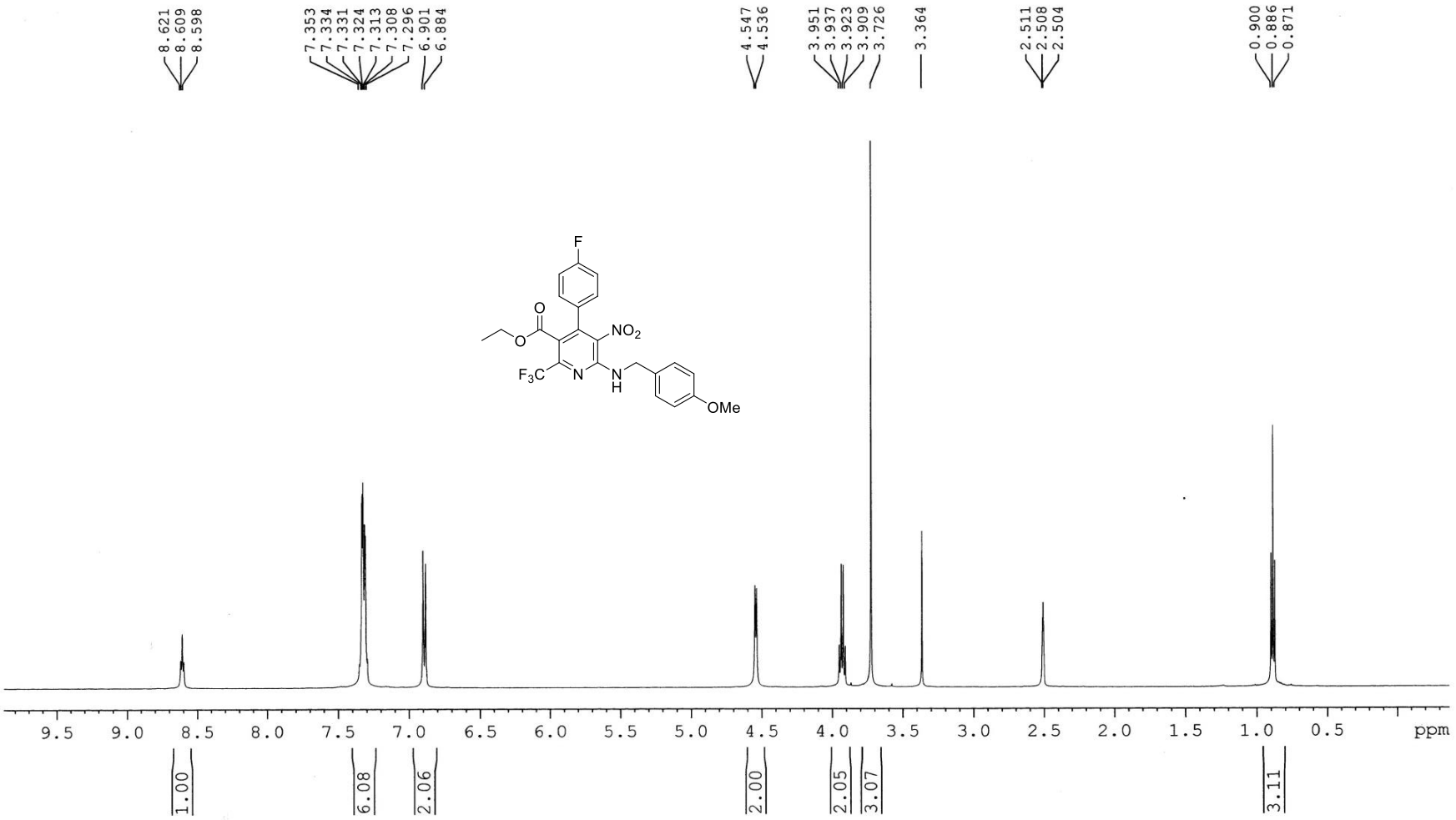

Figure S12. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4e**

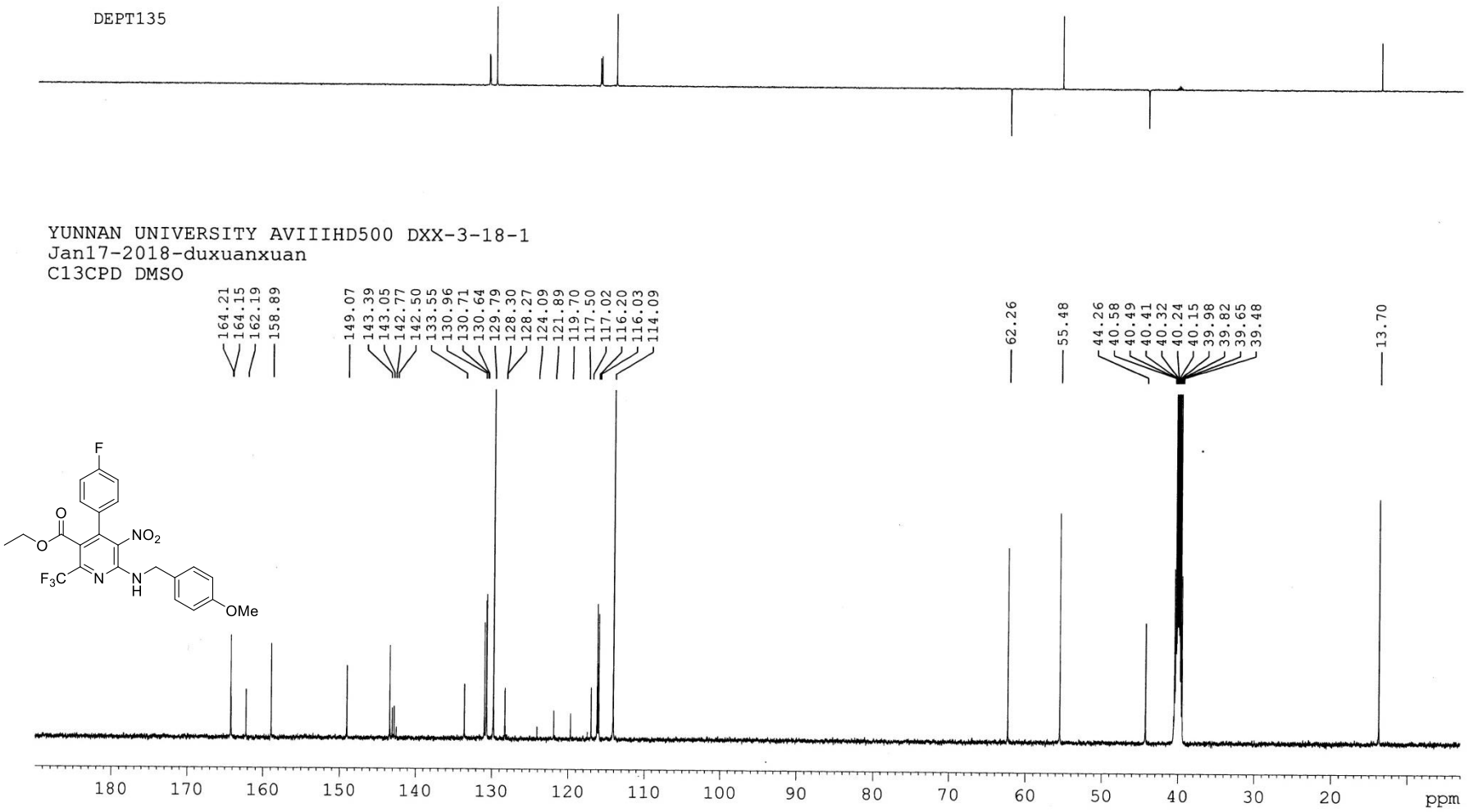

Figure S13. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4e**

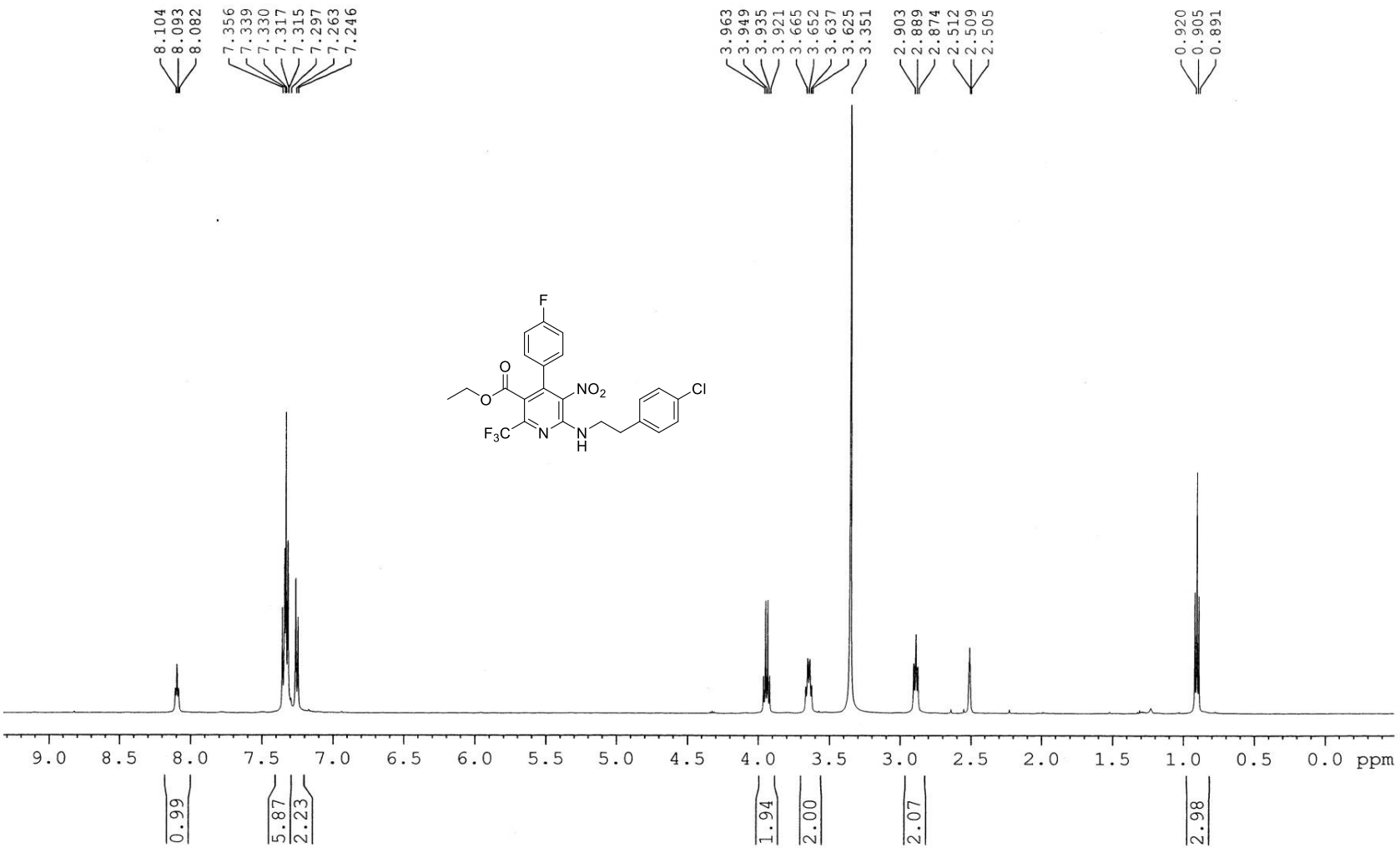

Figure S14. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4f**

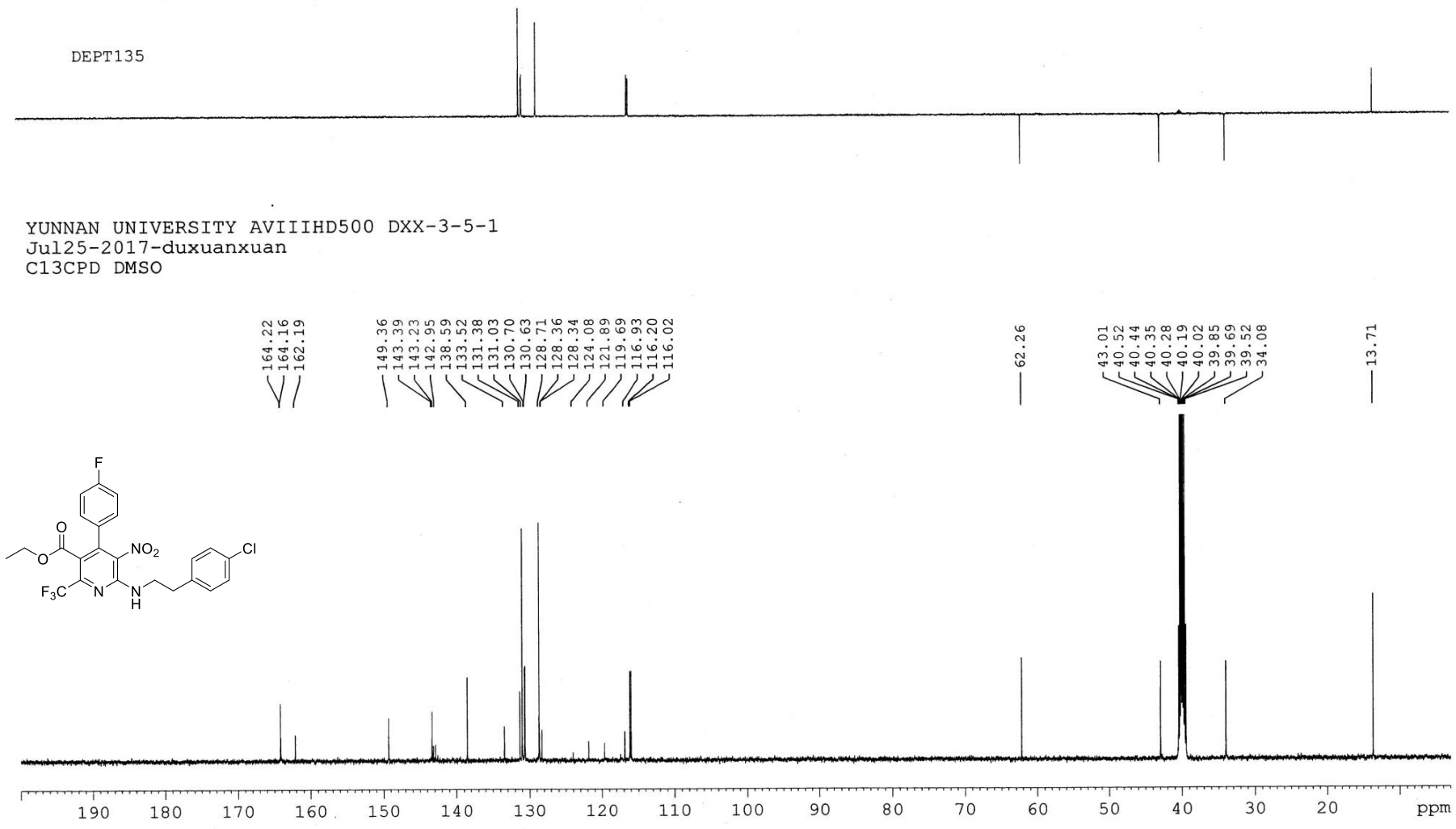

Figure S15. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4f**

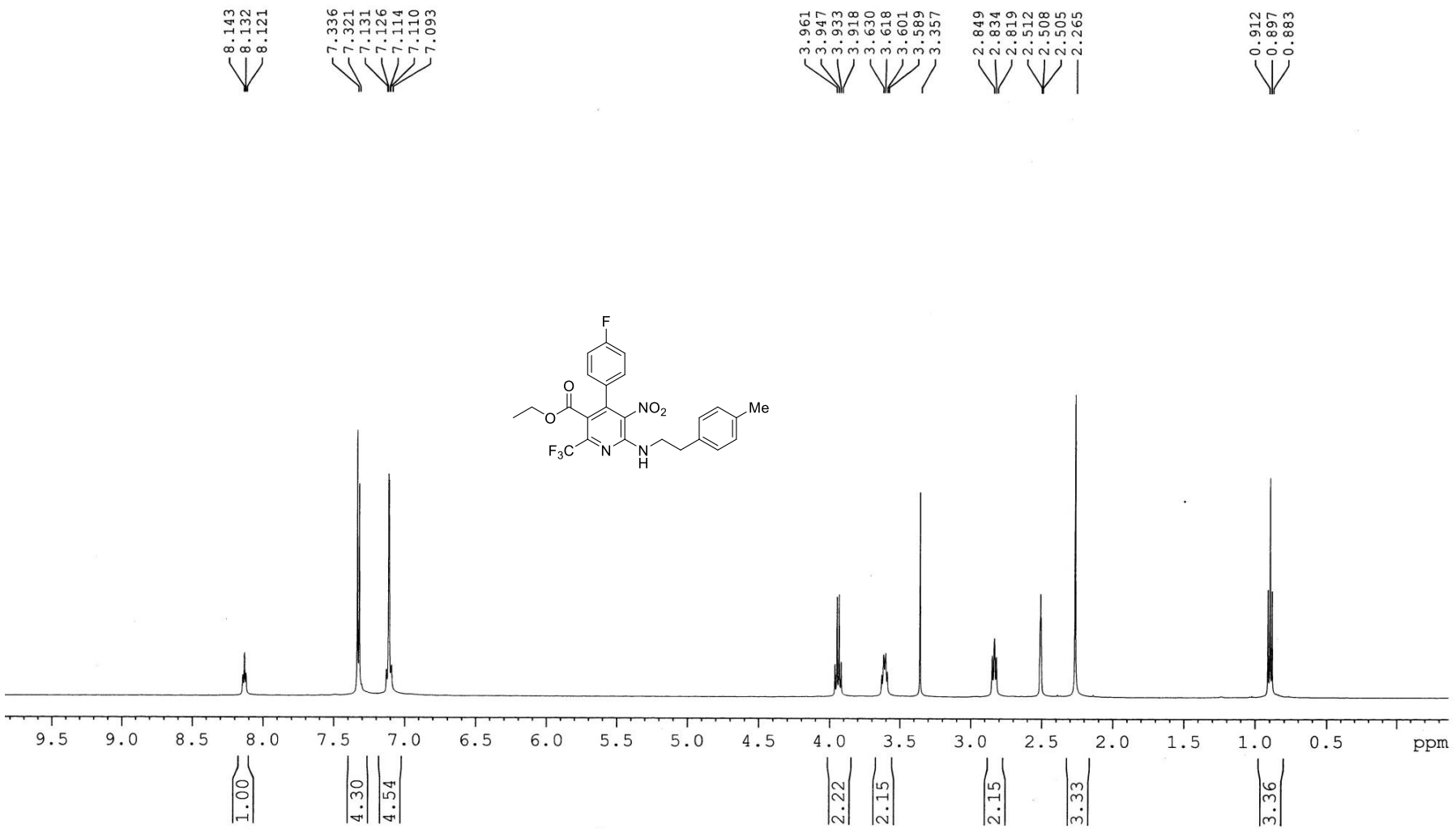

Figure S16. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4g**

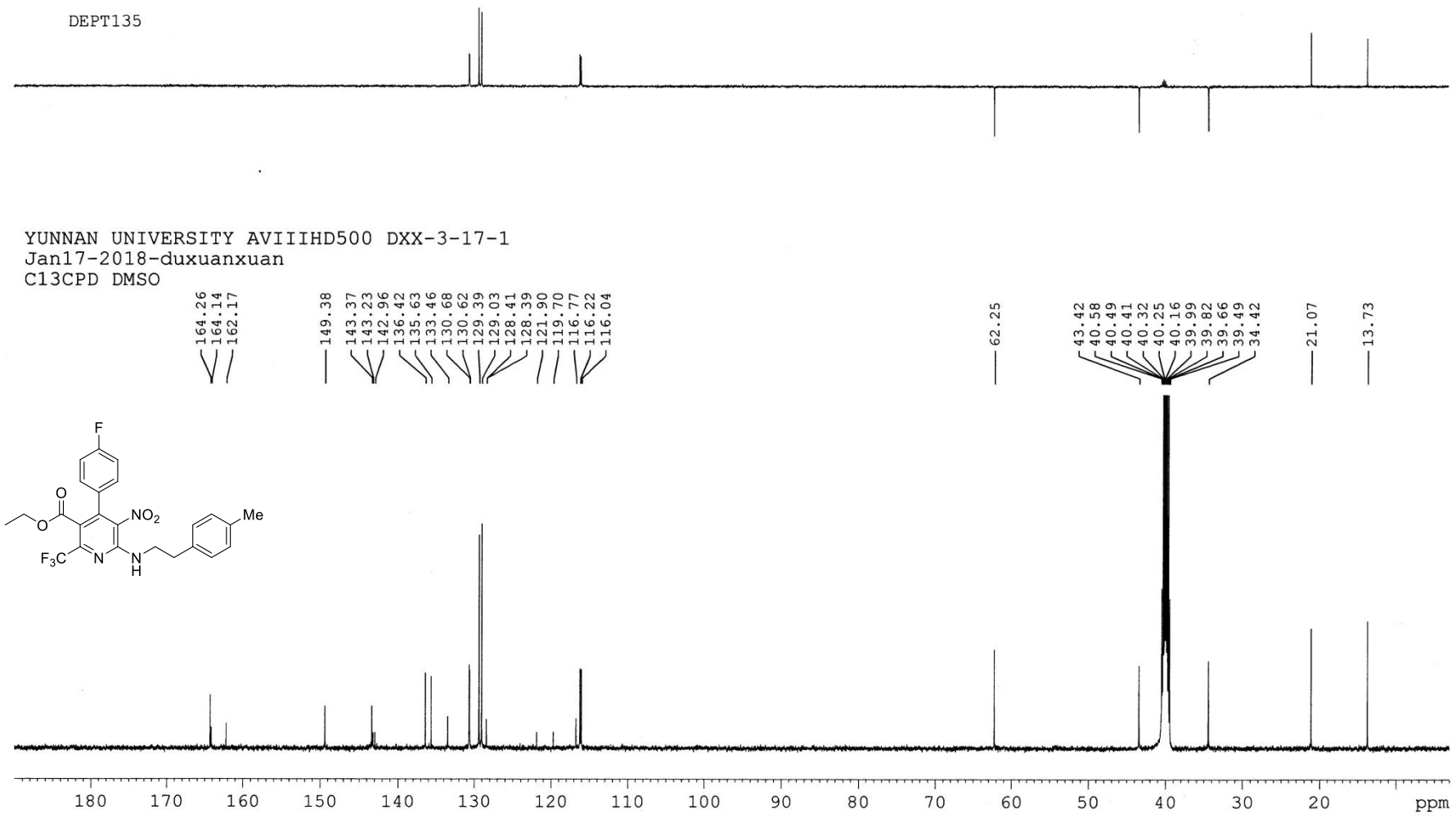

Figure S17. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4g**

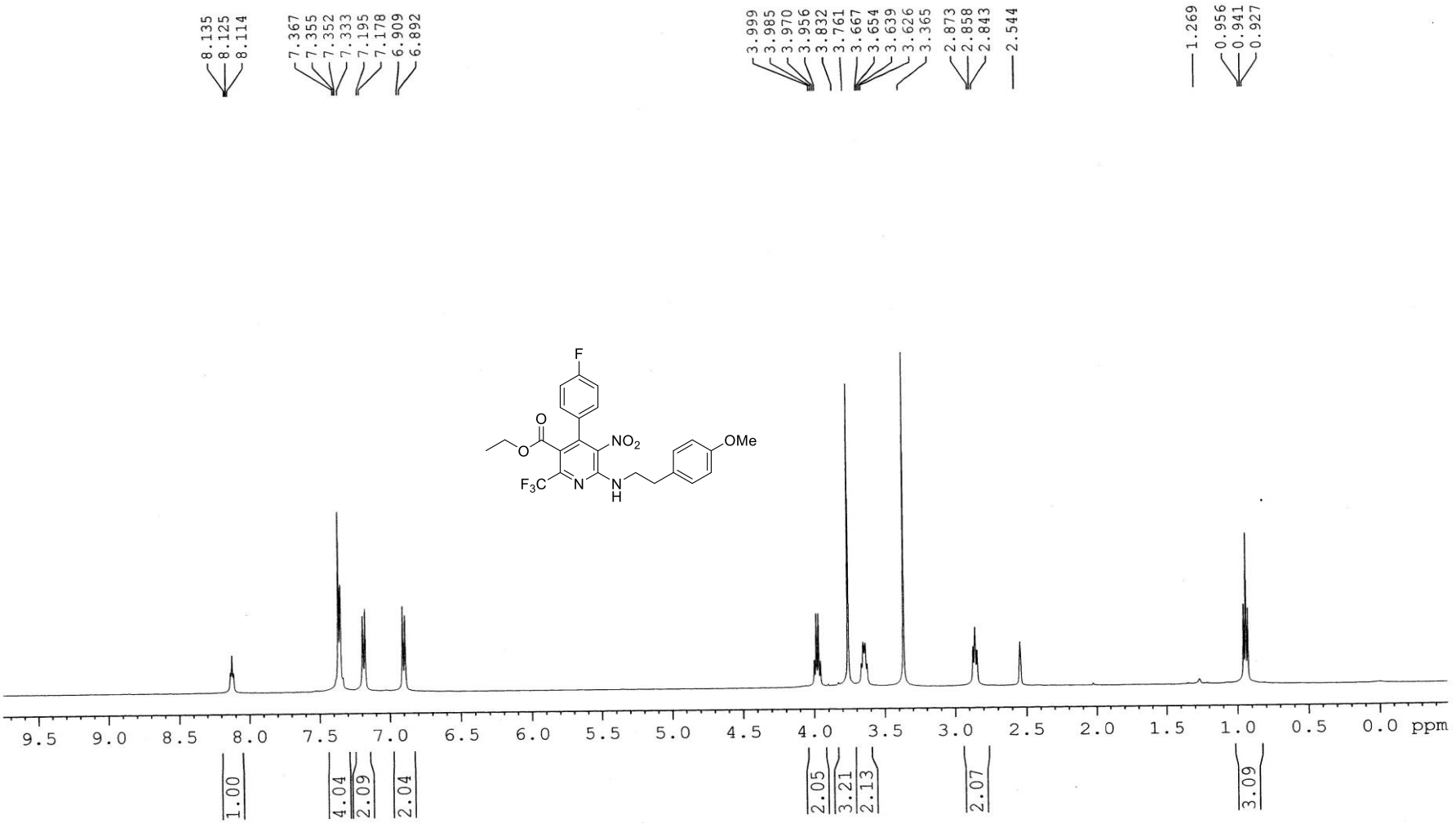

Figure S18. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4h**

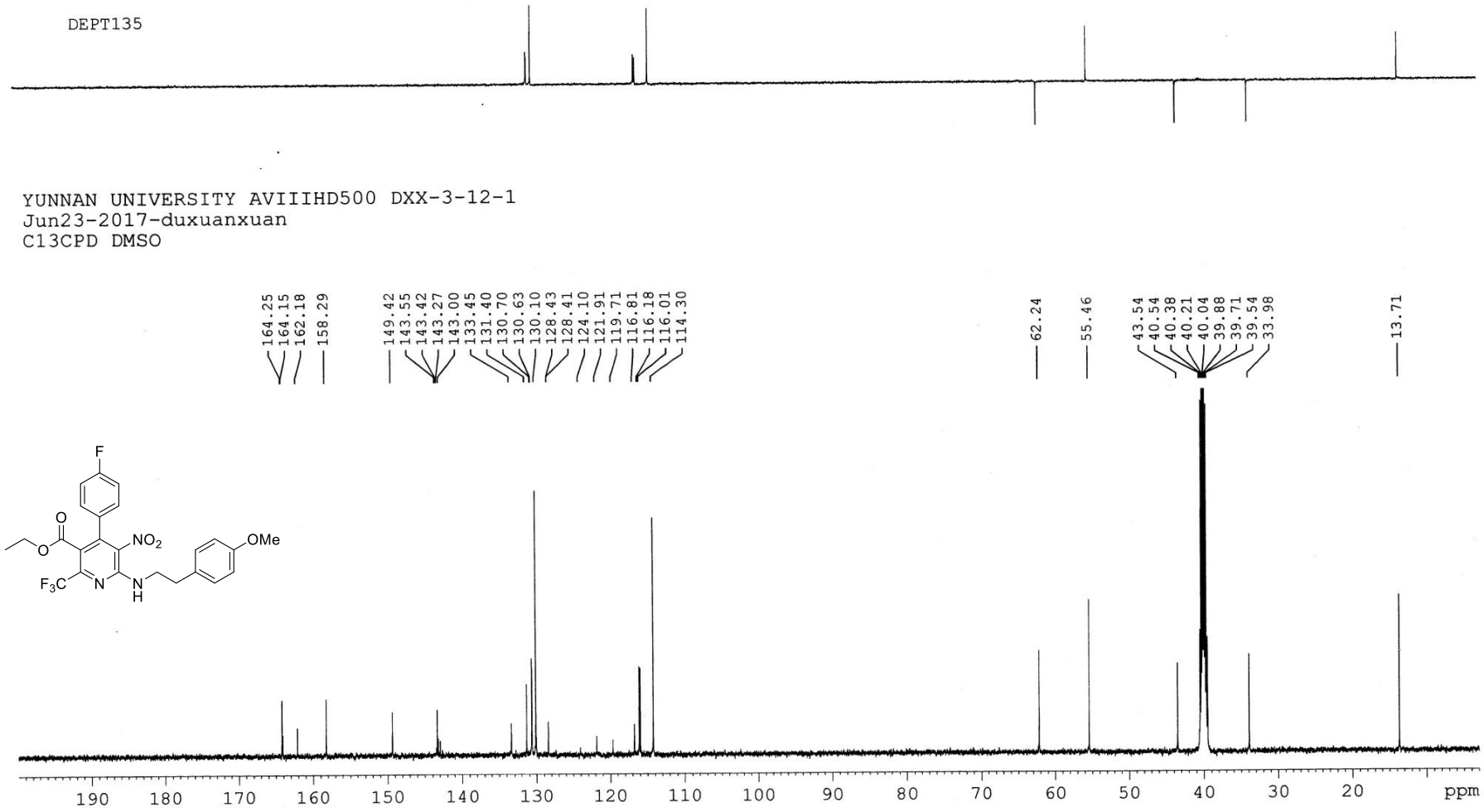

Figure S19. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4h**

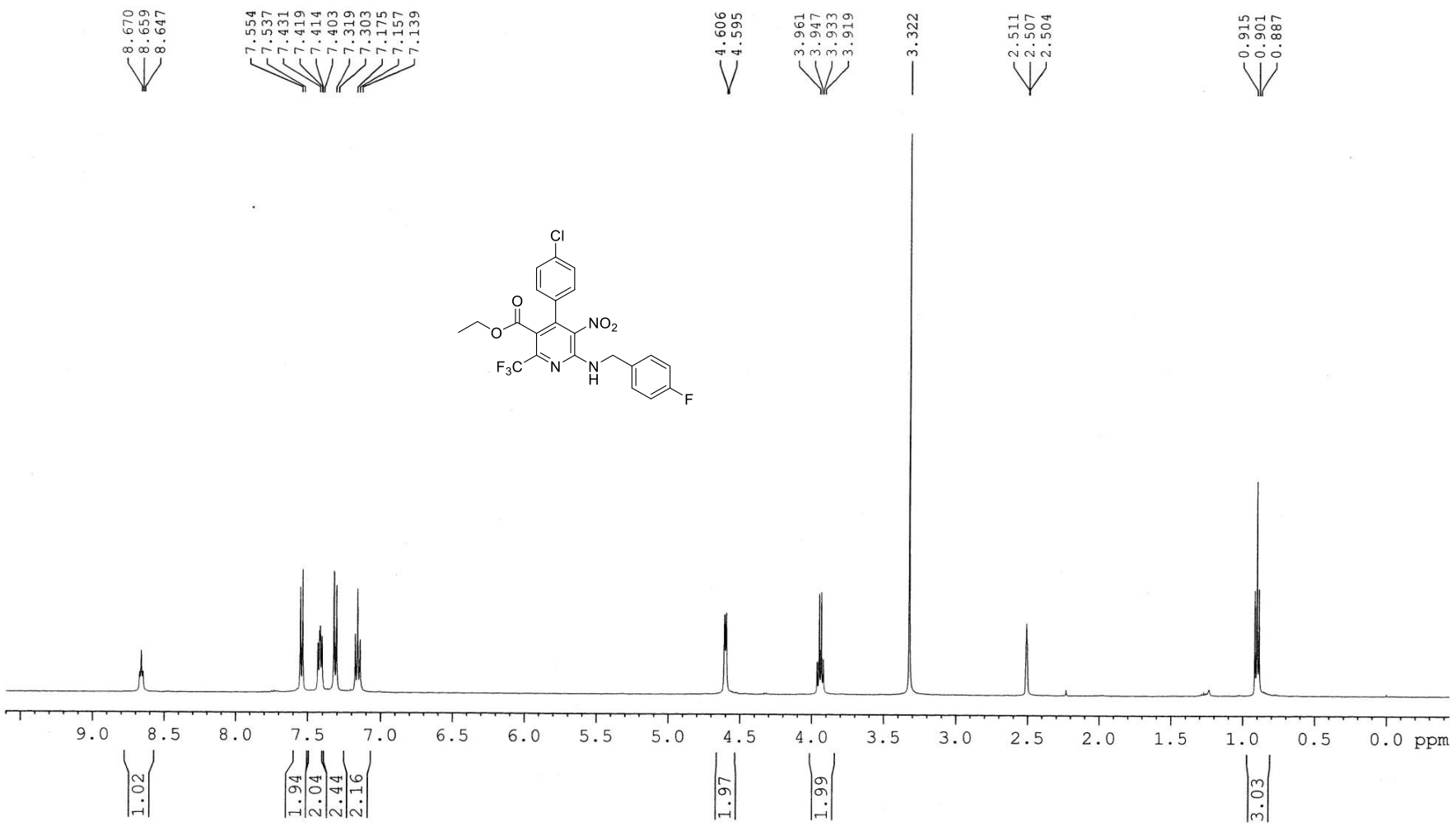

Figure S20. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4i**

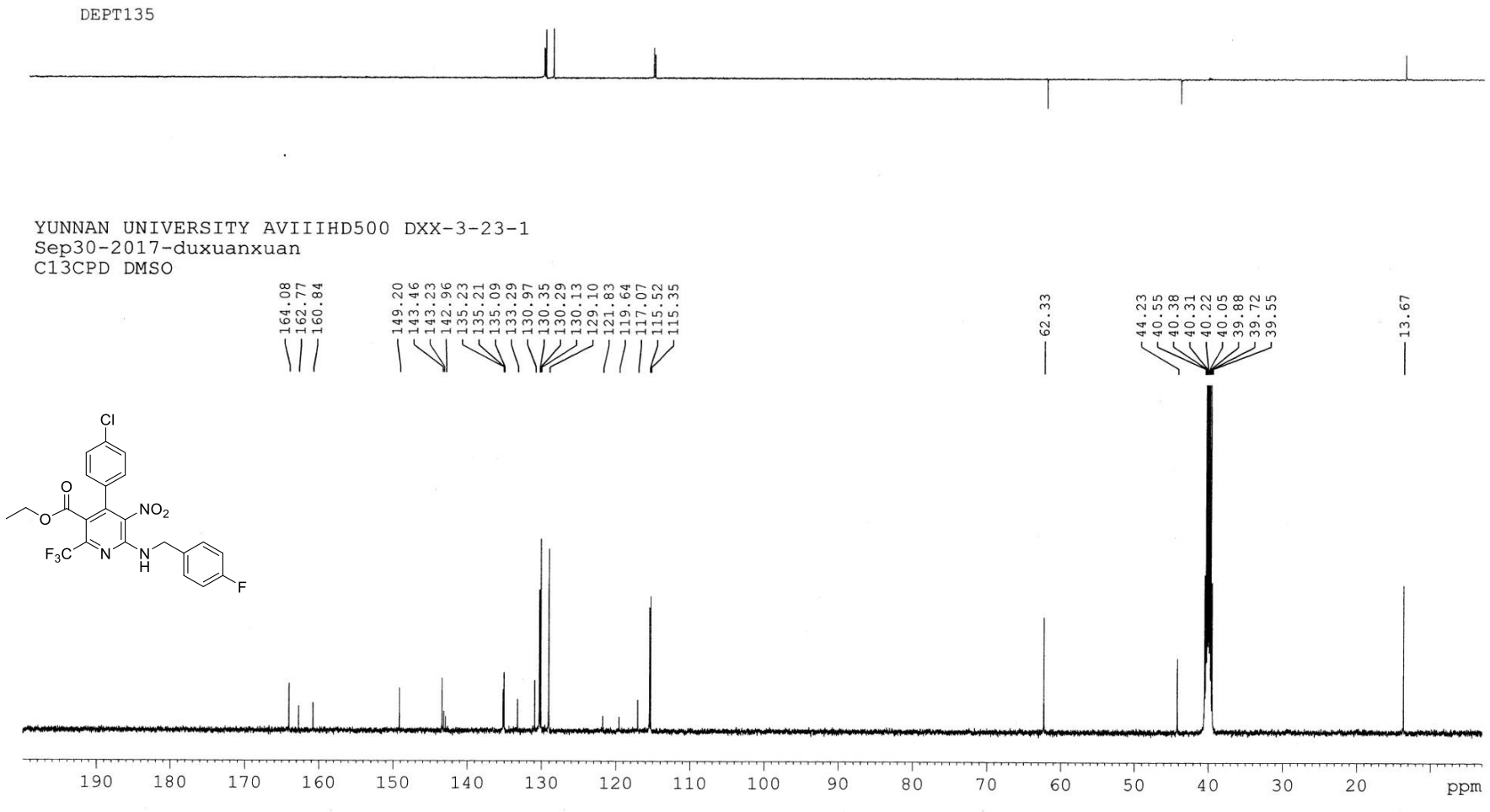

Figure S21. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4i**

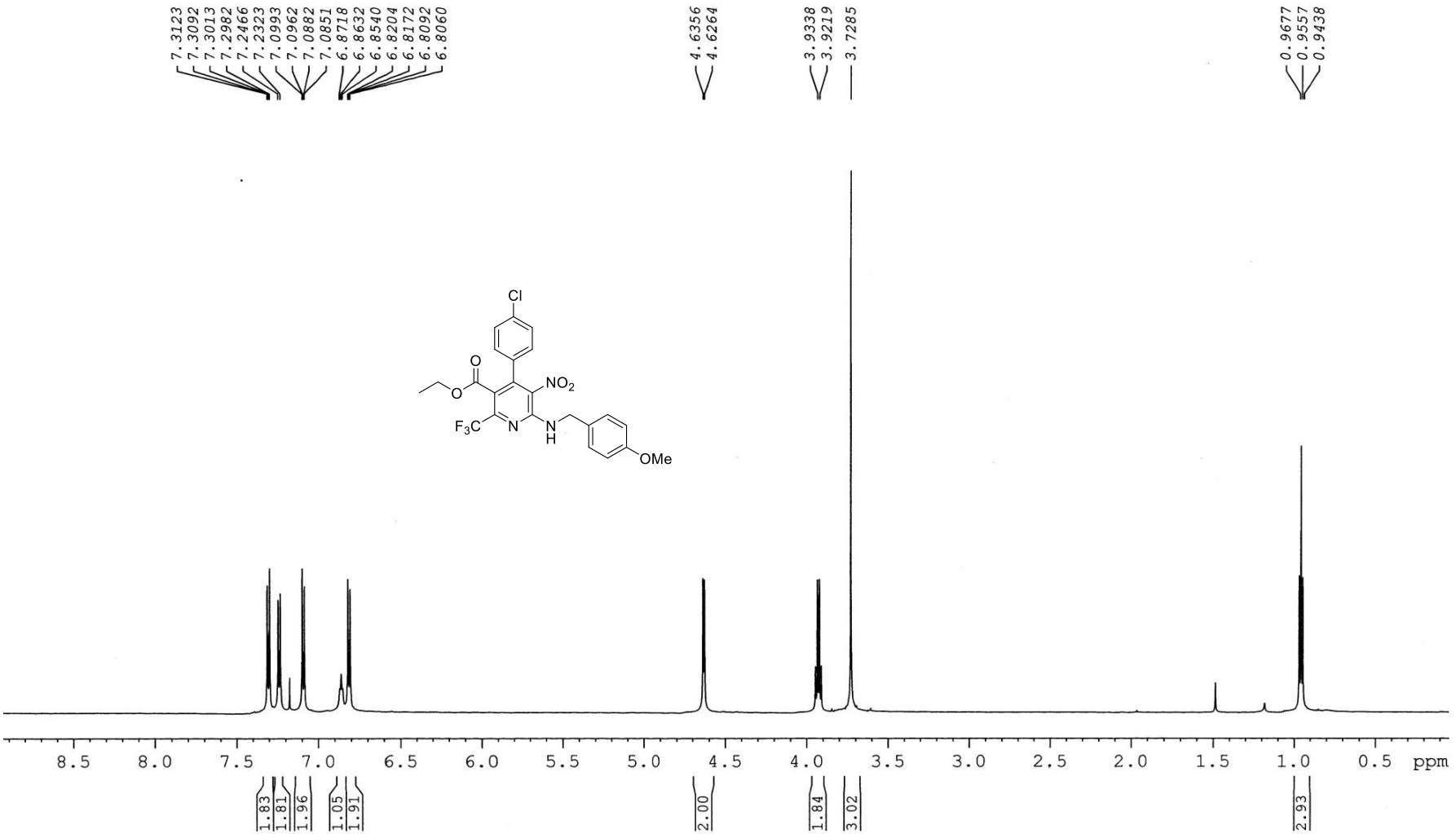

Figure S22. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **4j**

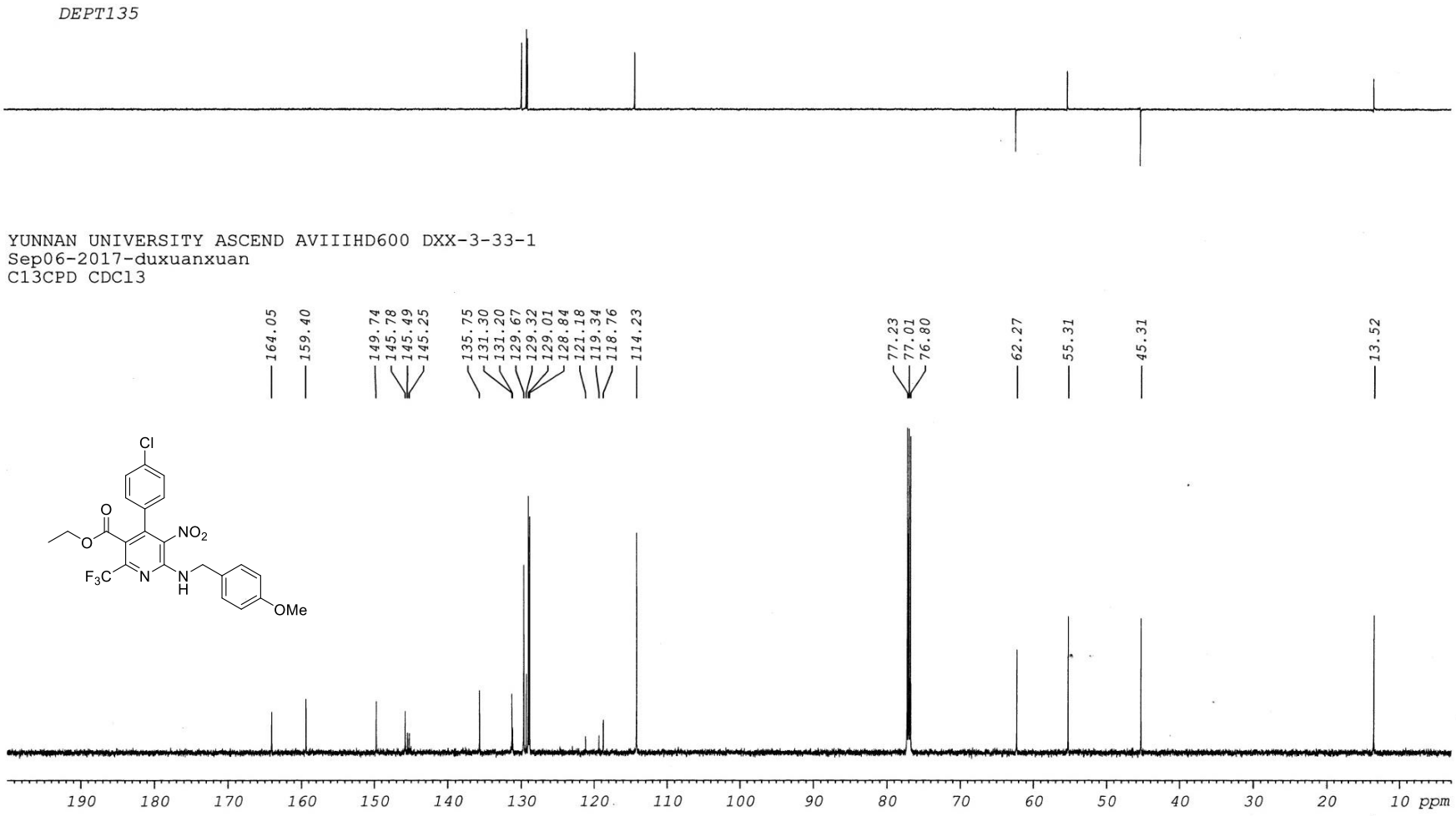

Figure S23. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **4j**

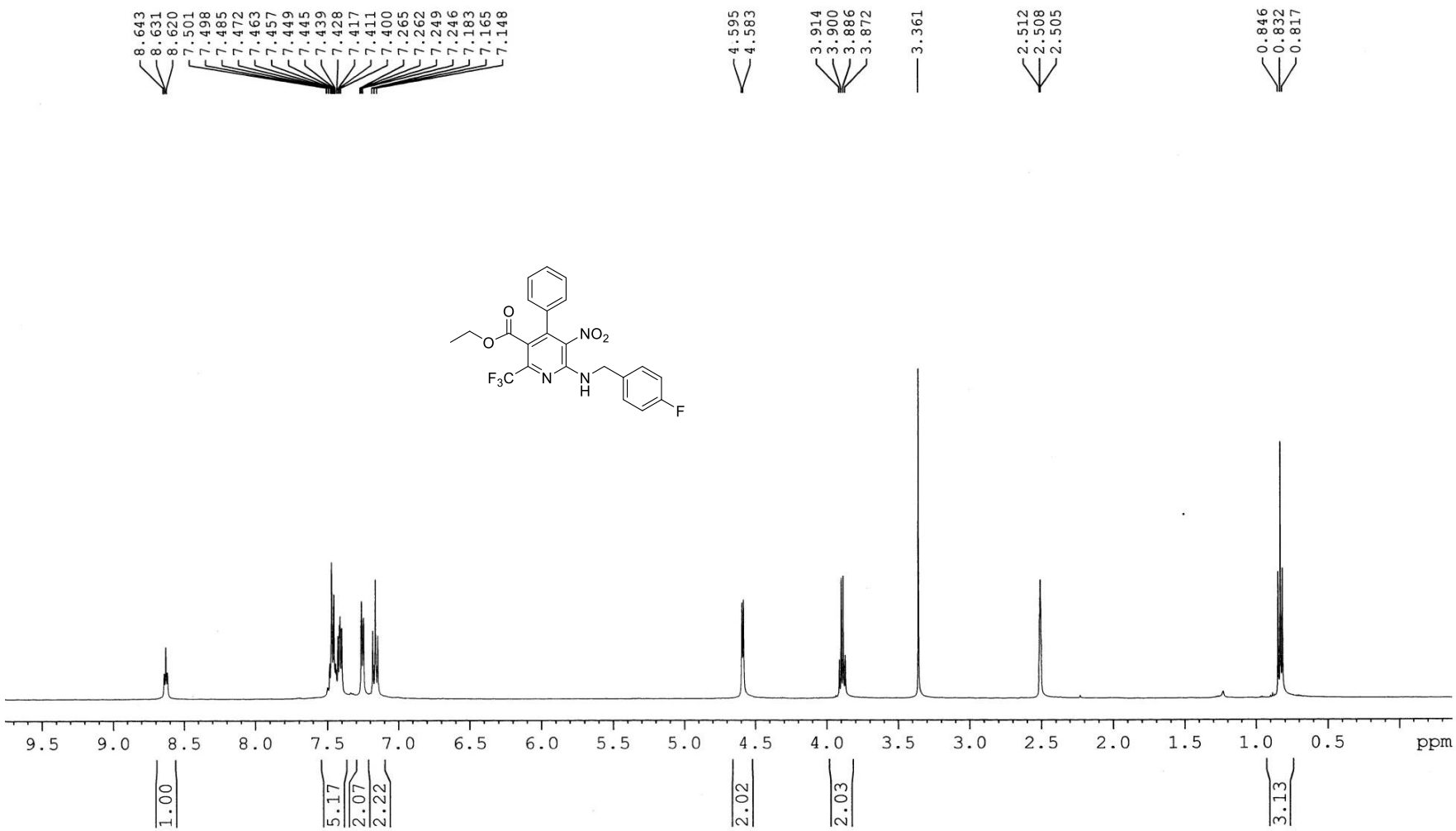

Figure S24. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4k**

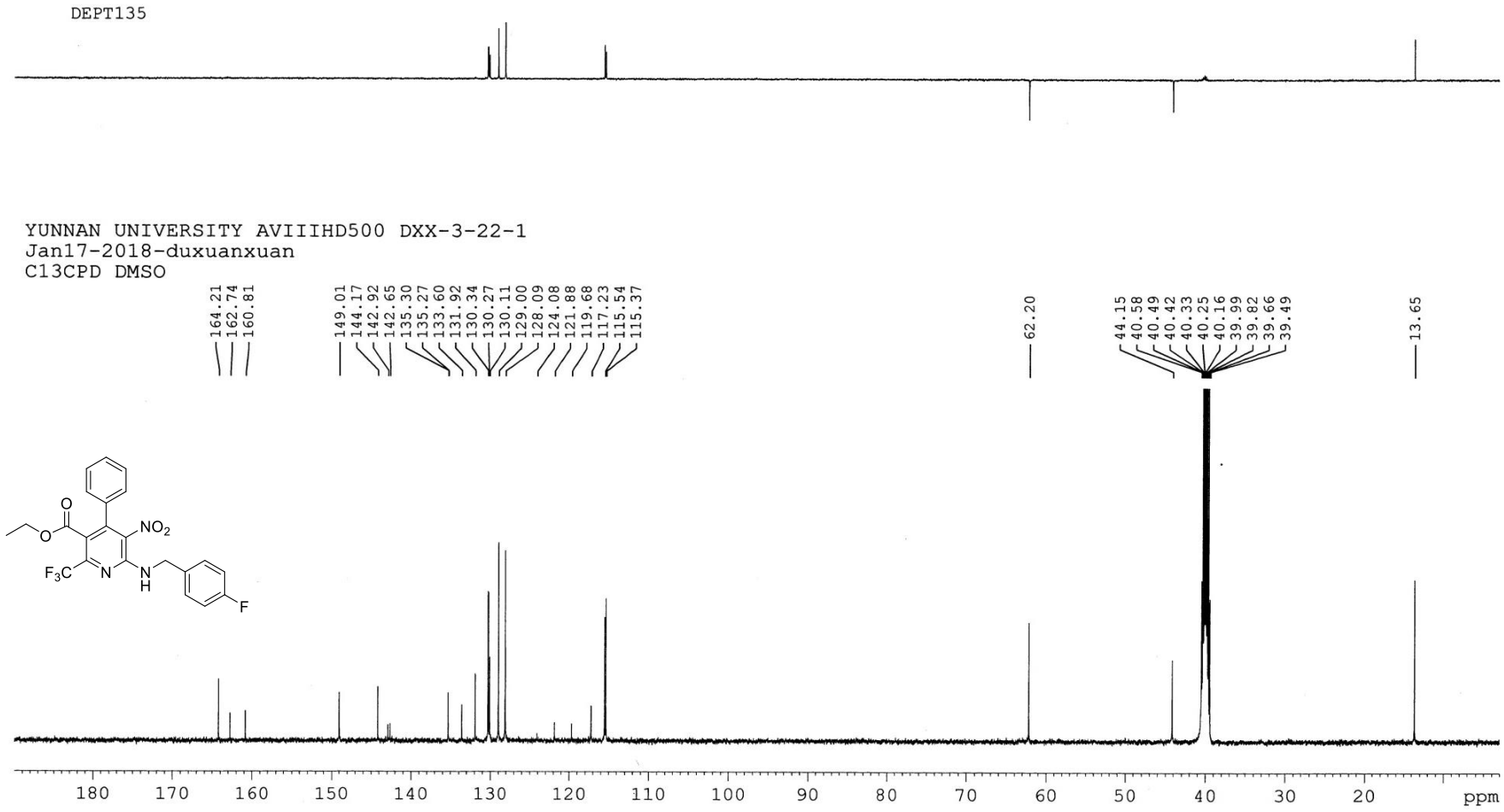

Figure S25. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4k**

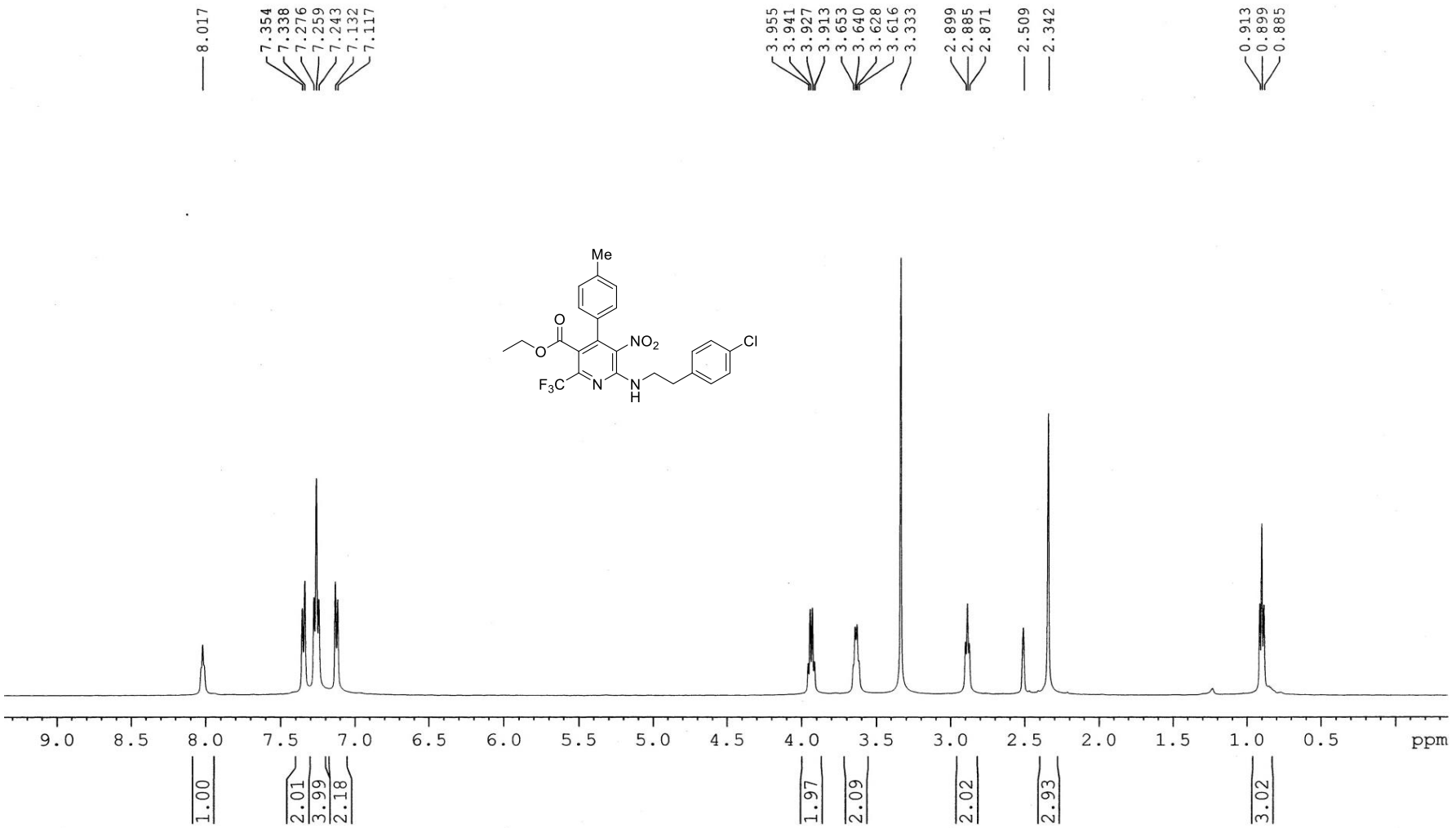

Figure S26. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4l**

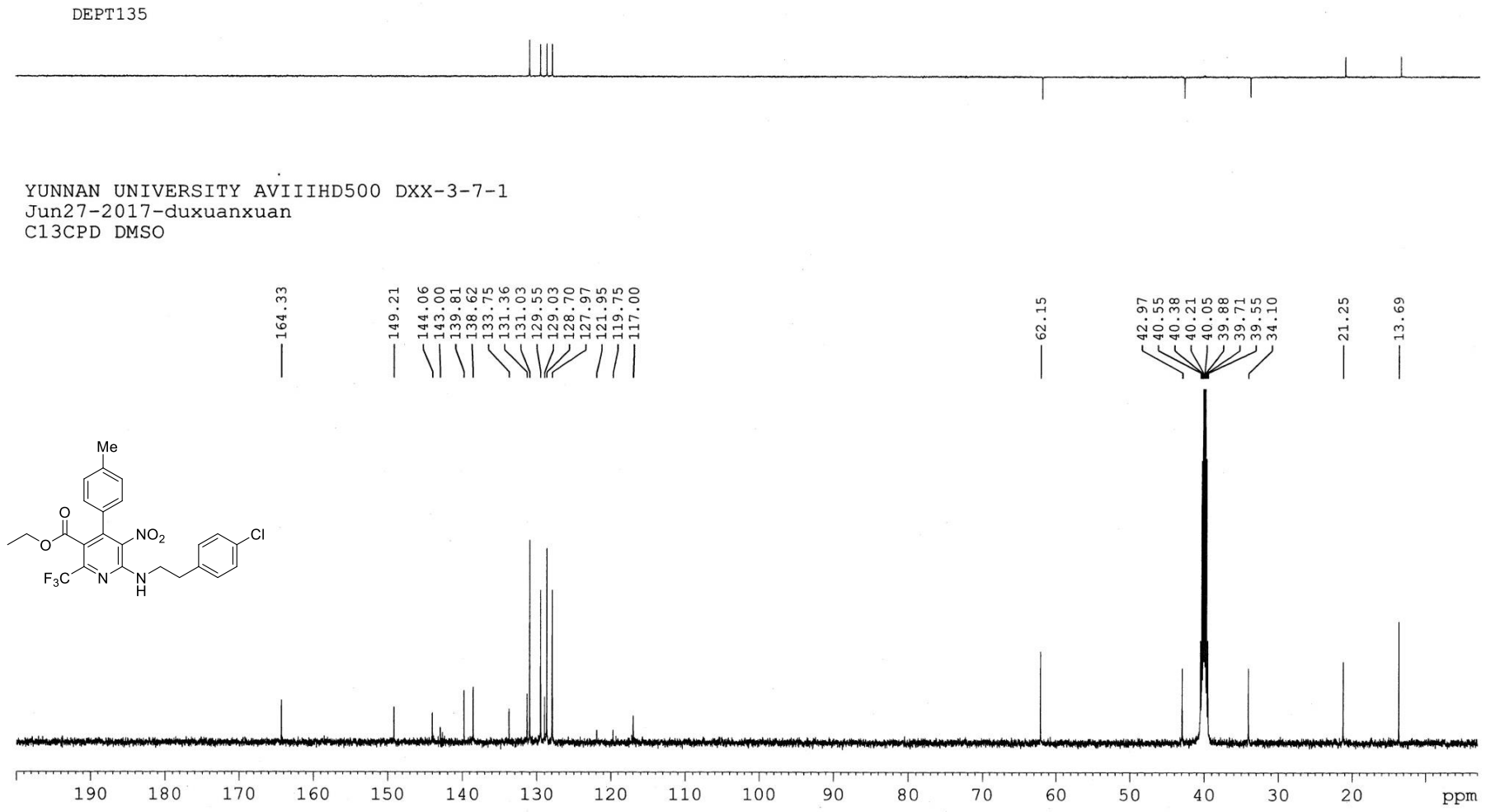

Figure S27. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4l**

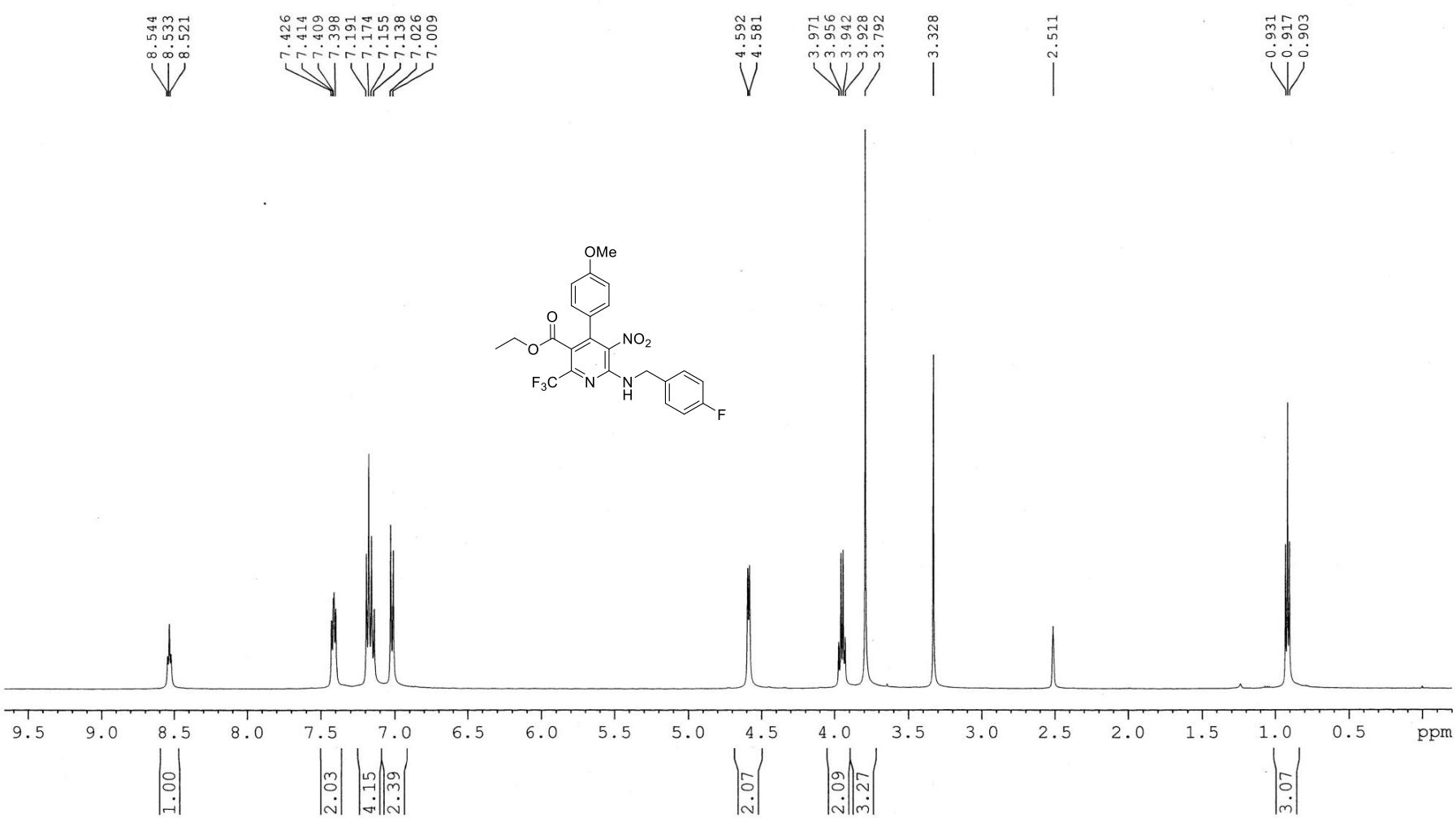

Figure S28. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4m**

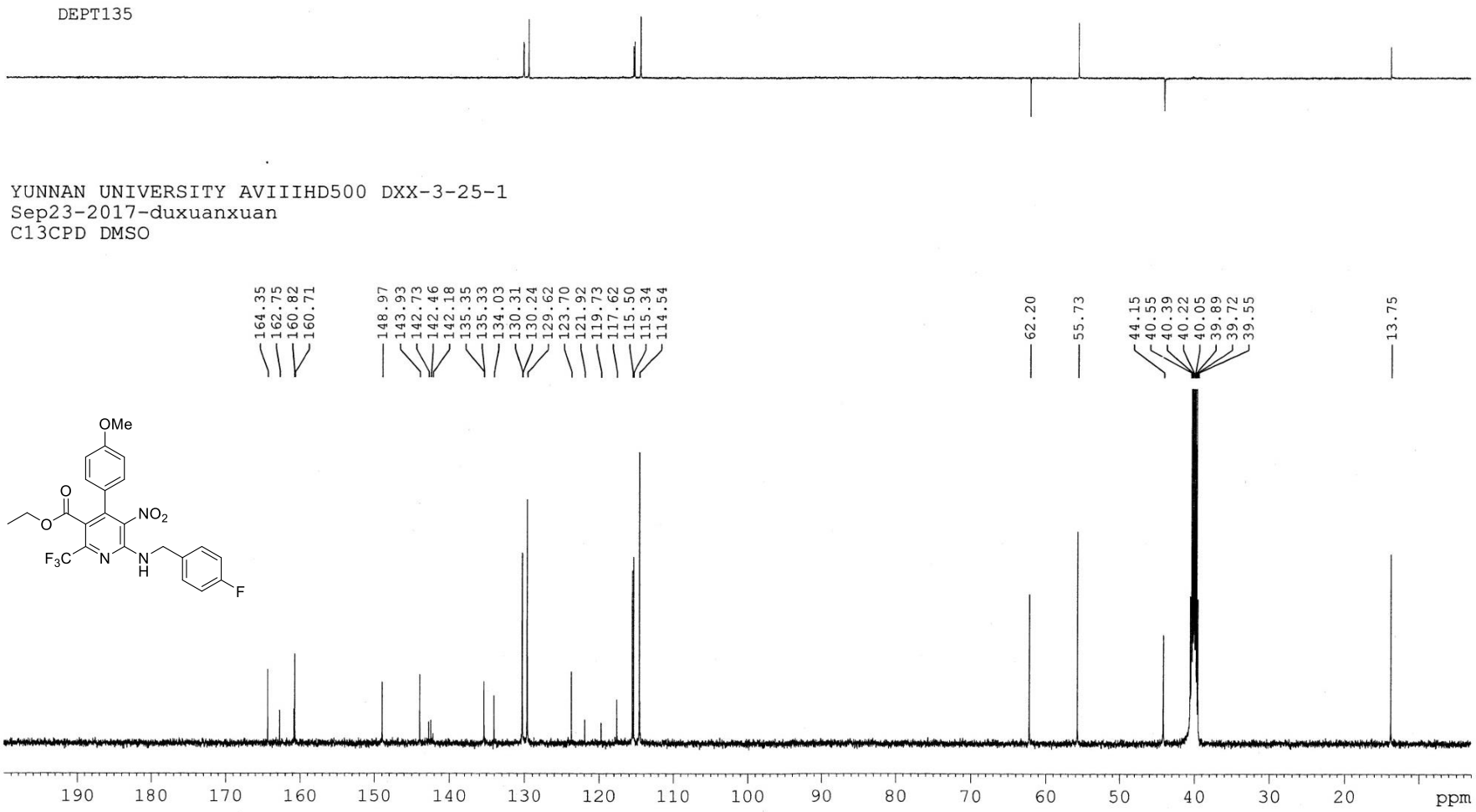

Figure S29. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4m**

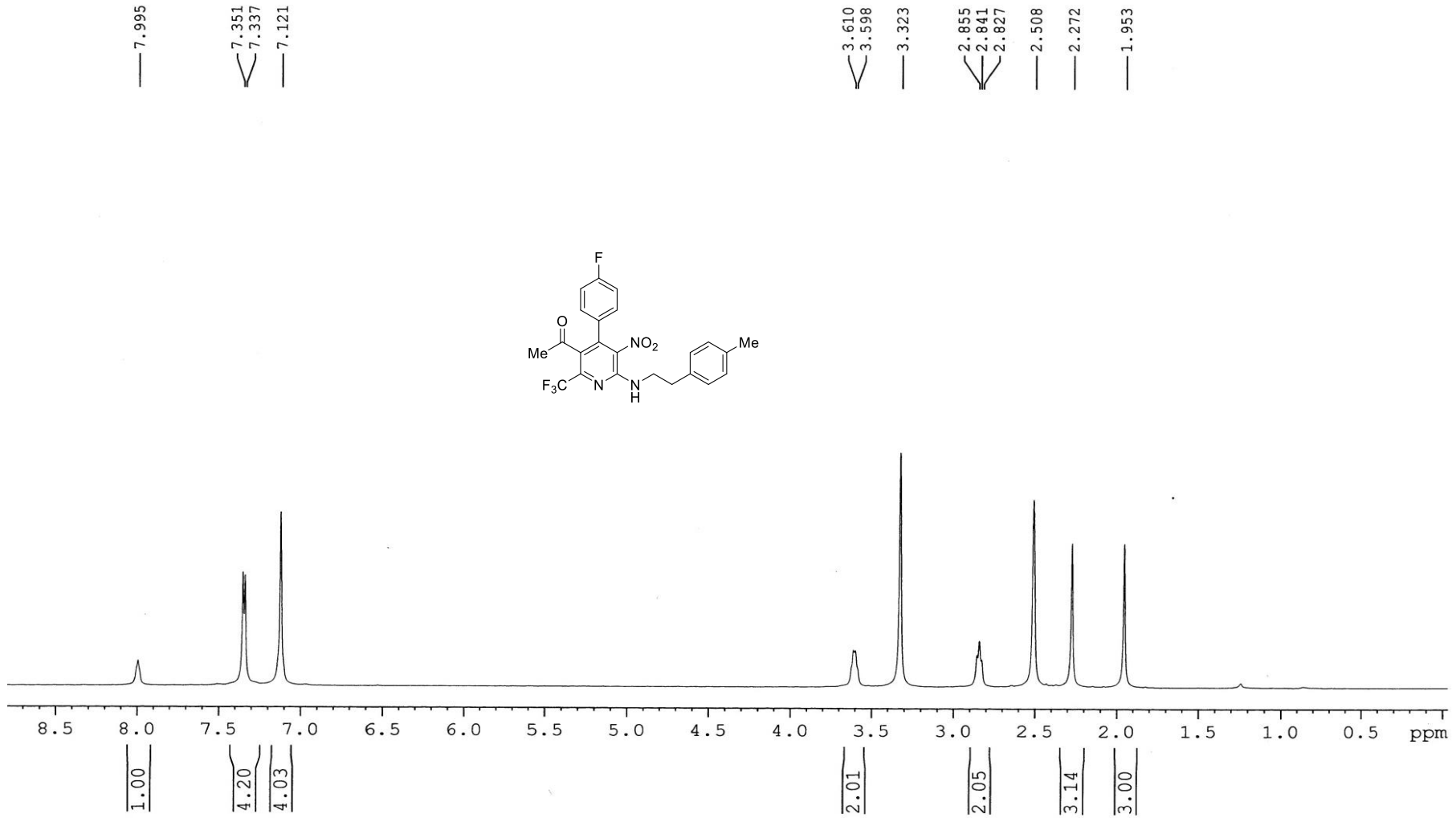

Figure S30. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4n**

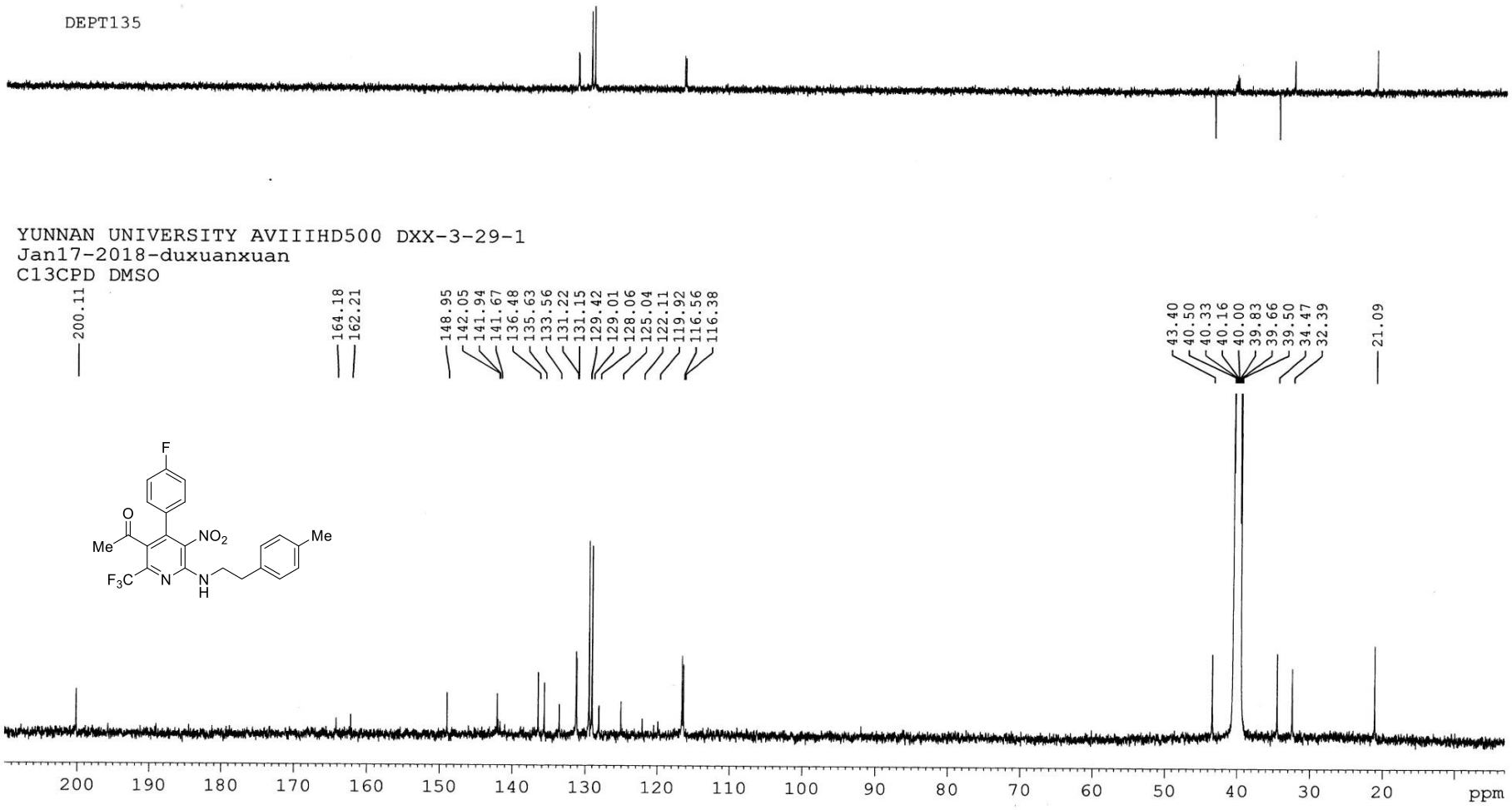

Figure S31. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4n**

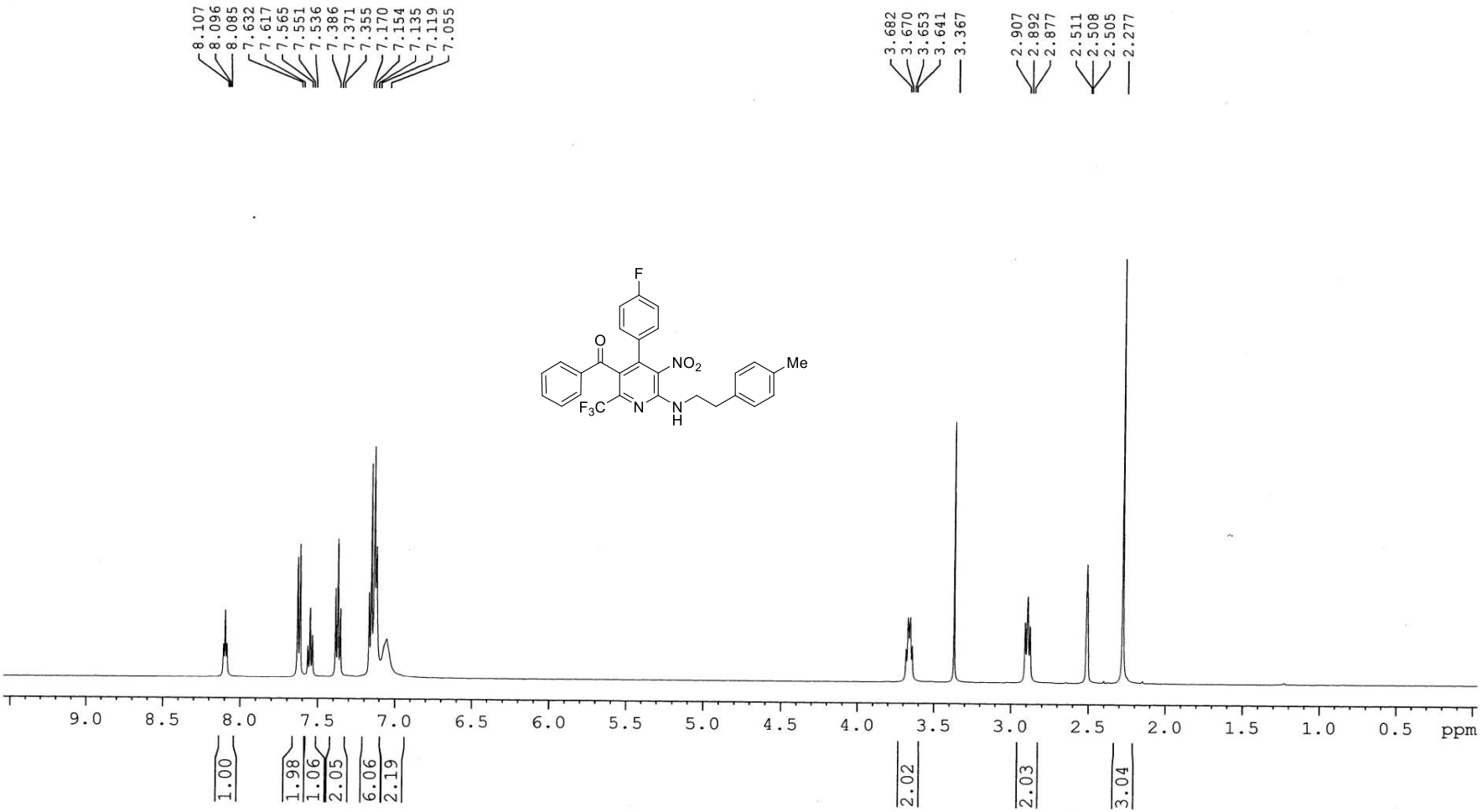

Figure S32. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4o**

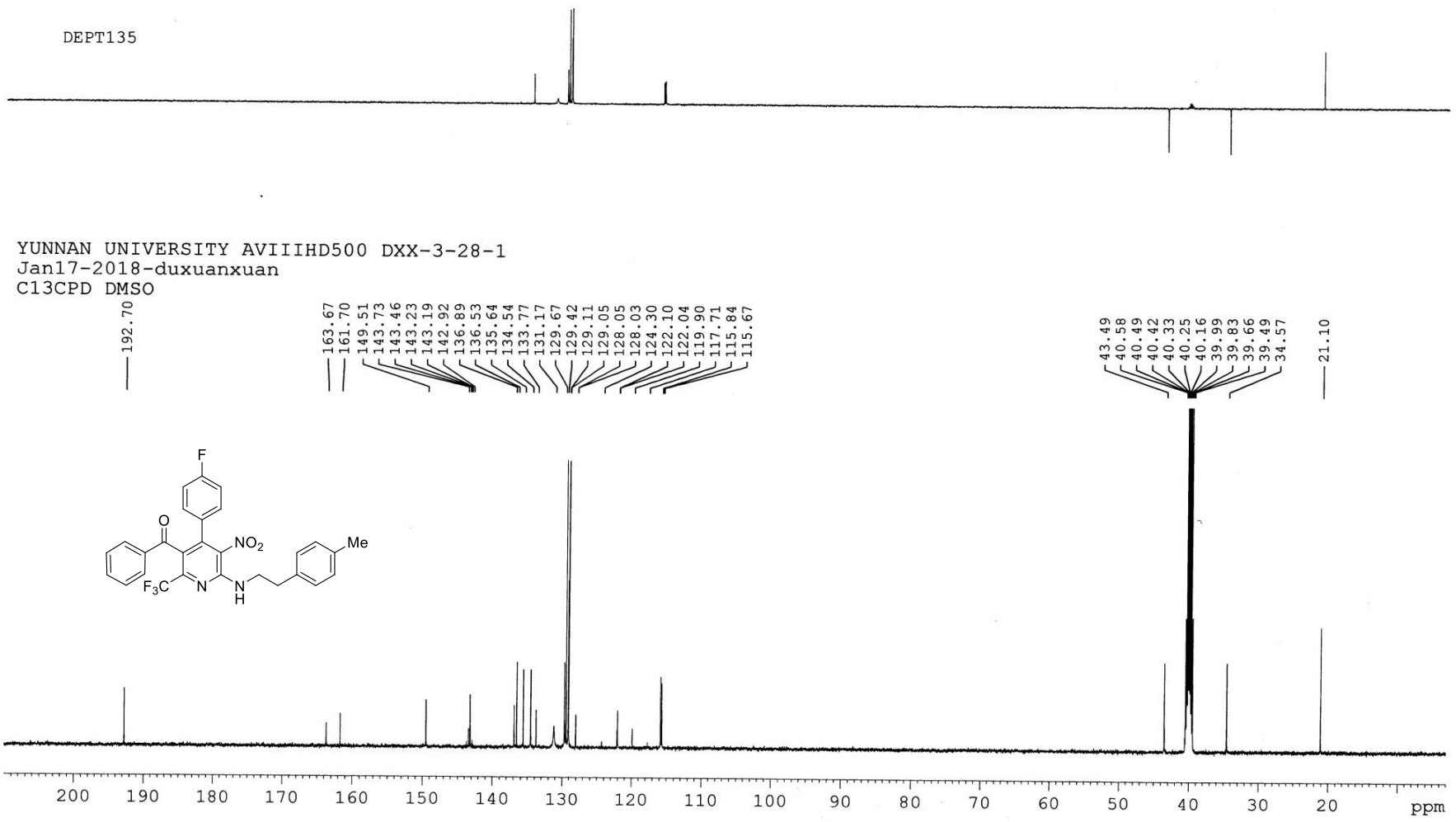

Figure S33. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4o**

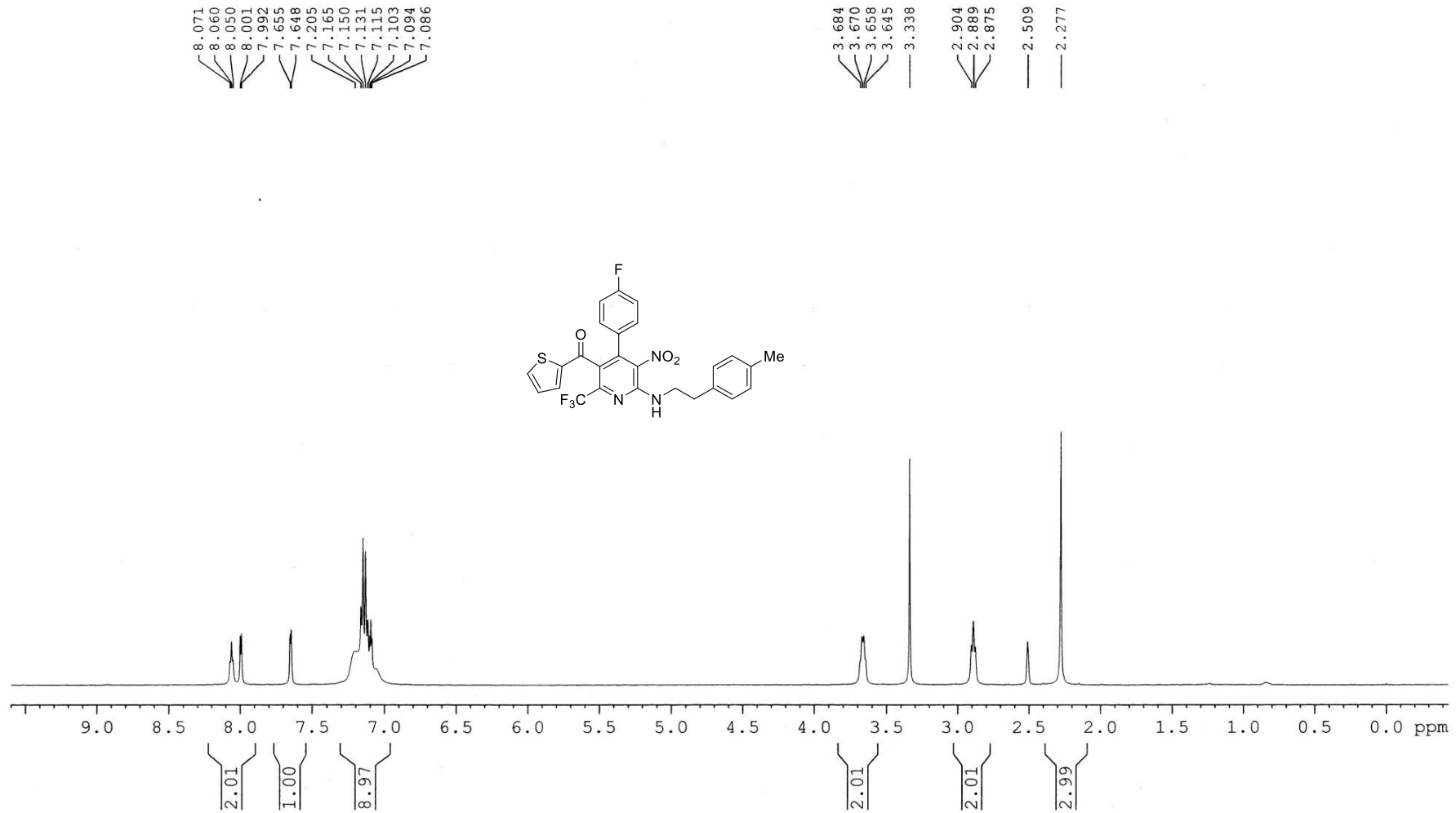

Figure S34. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4p**

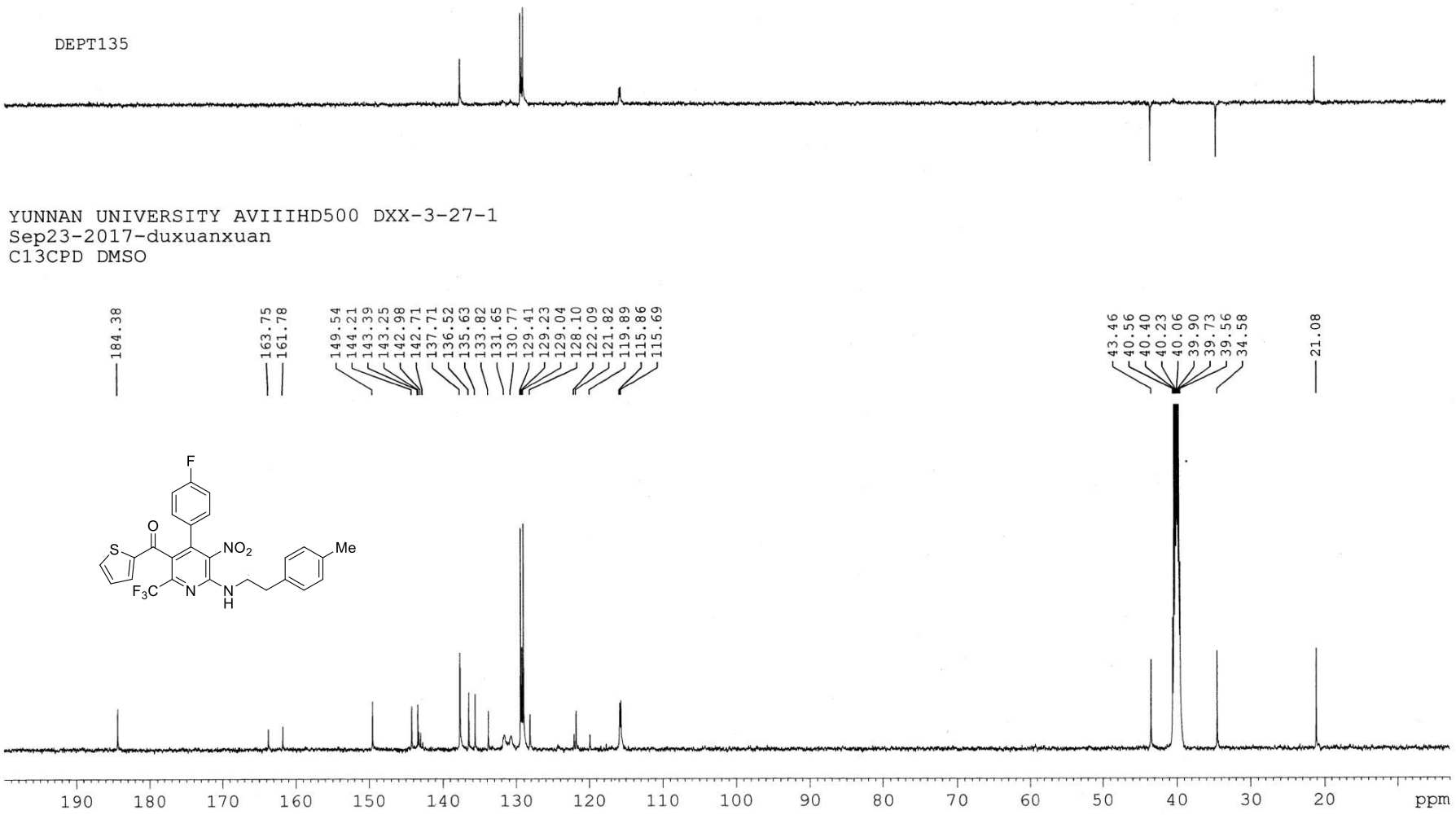

Figure S35. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4p**

Figure S36. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4q**

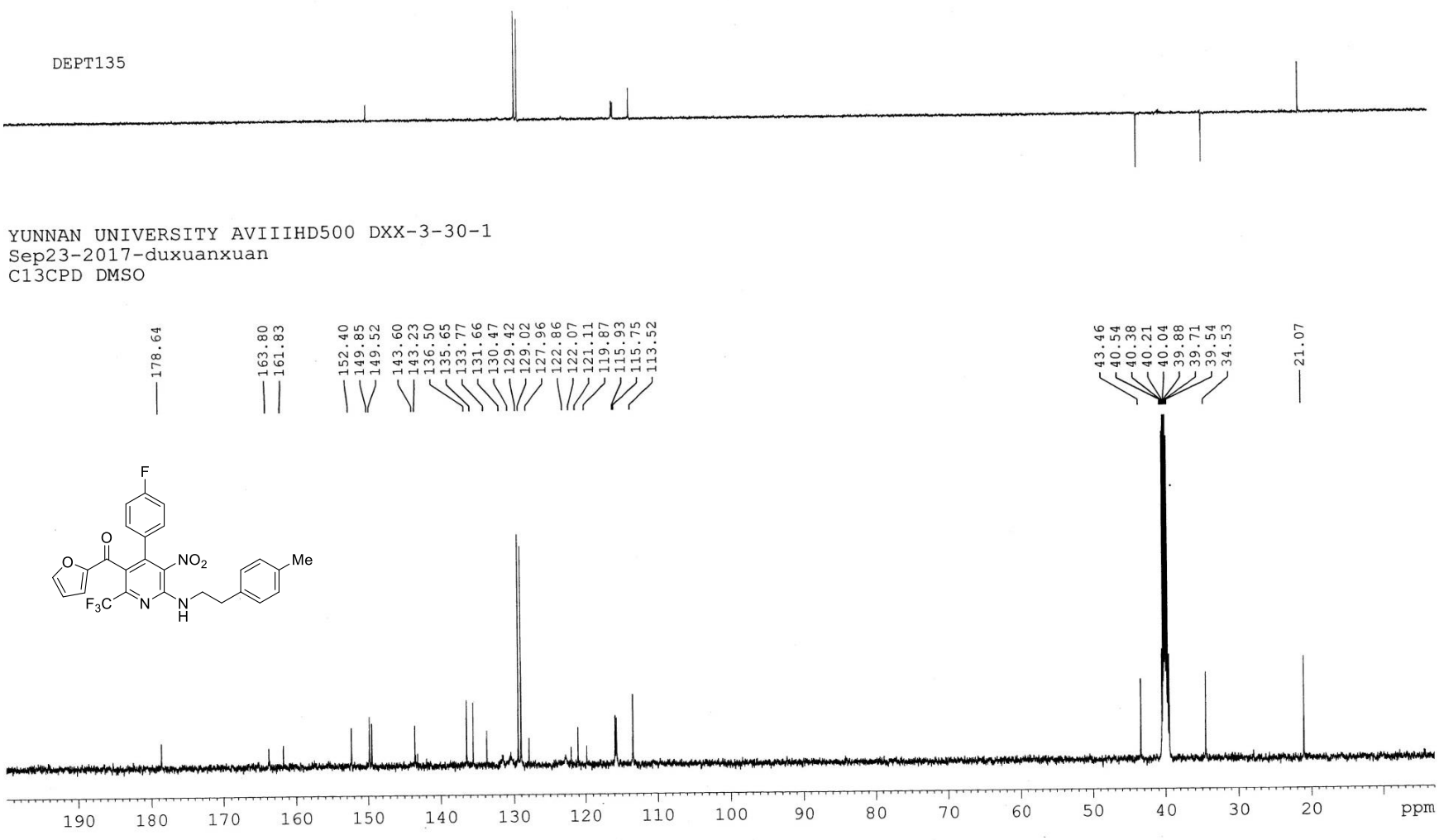

Figure S37. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4q**

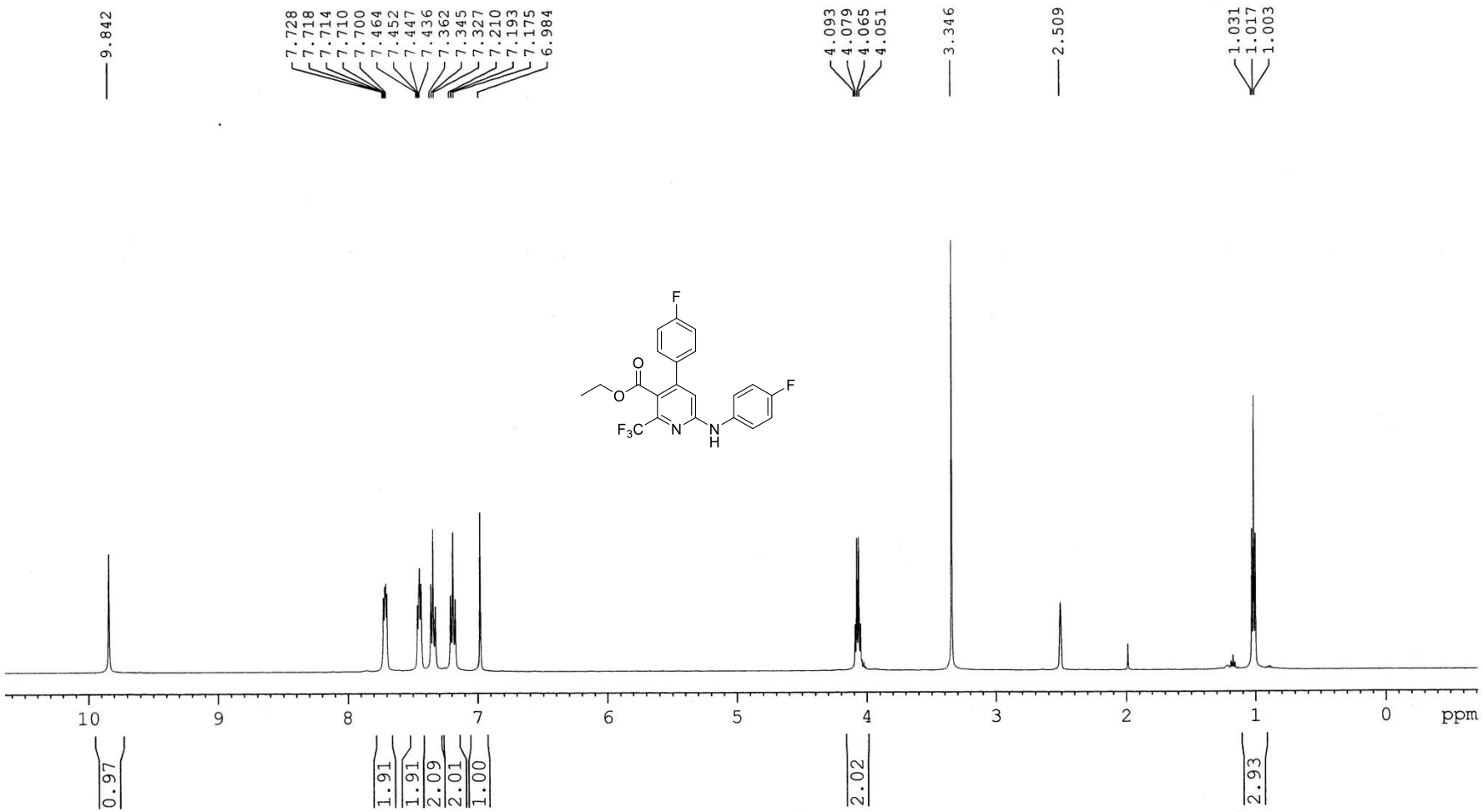

Figure S38. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5a**

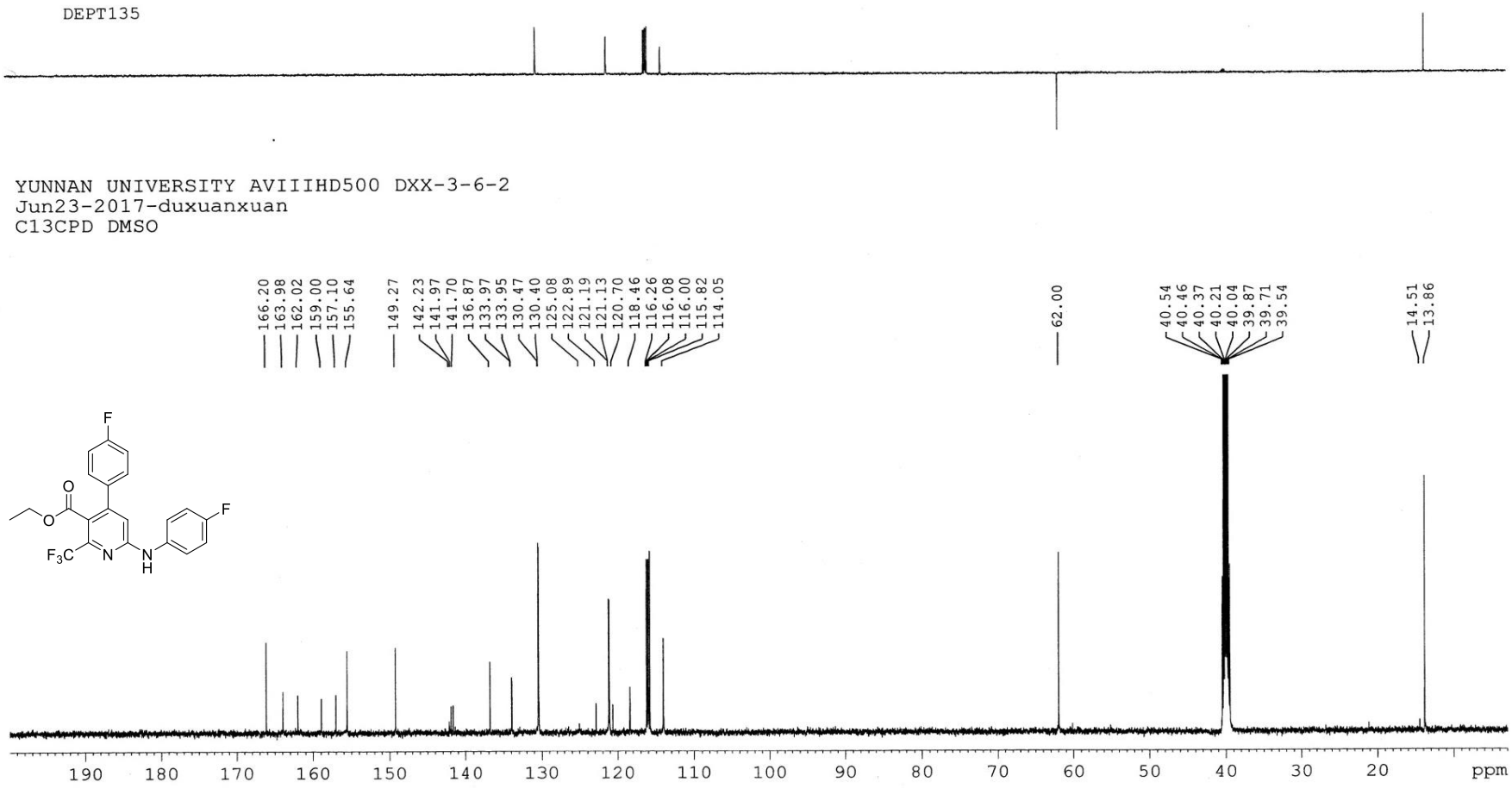

Figure S39. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5a**

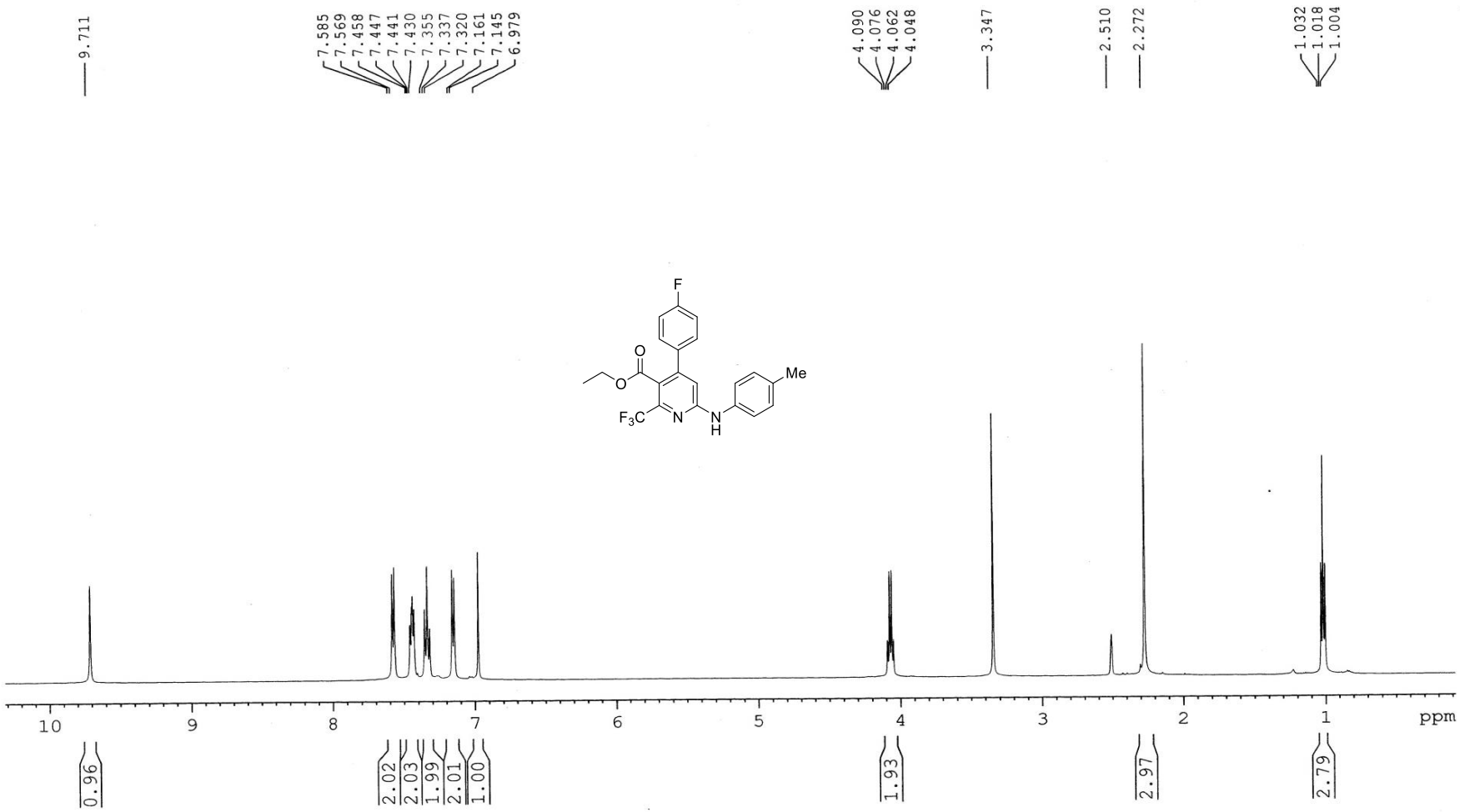

Figure S40. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5b**

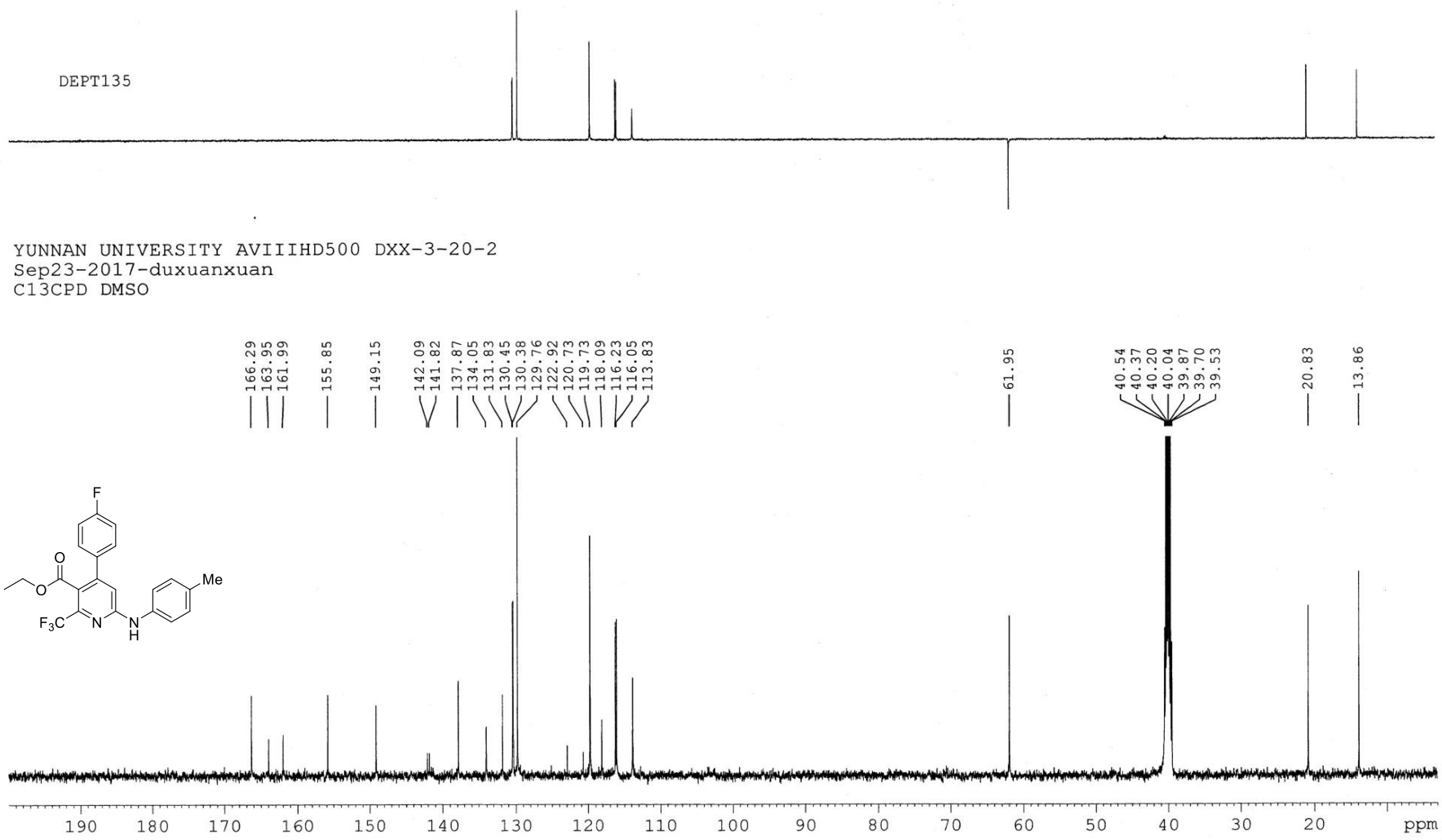

Figure S41. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5b**

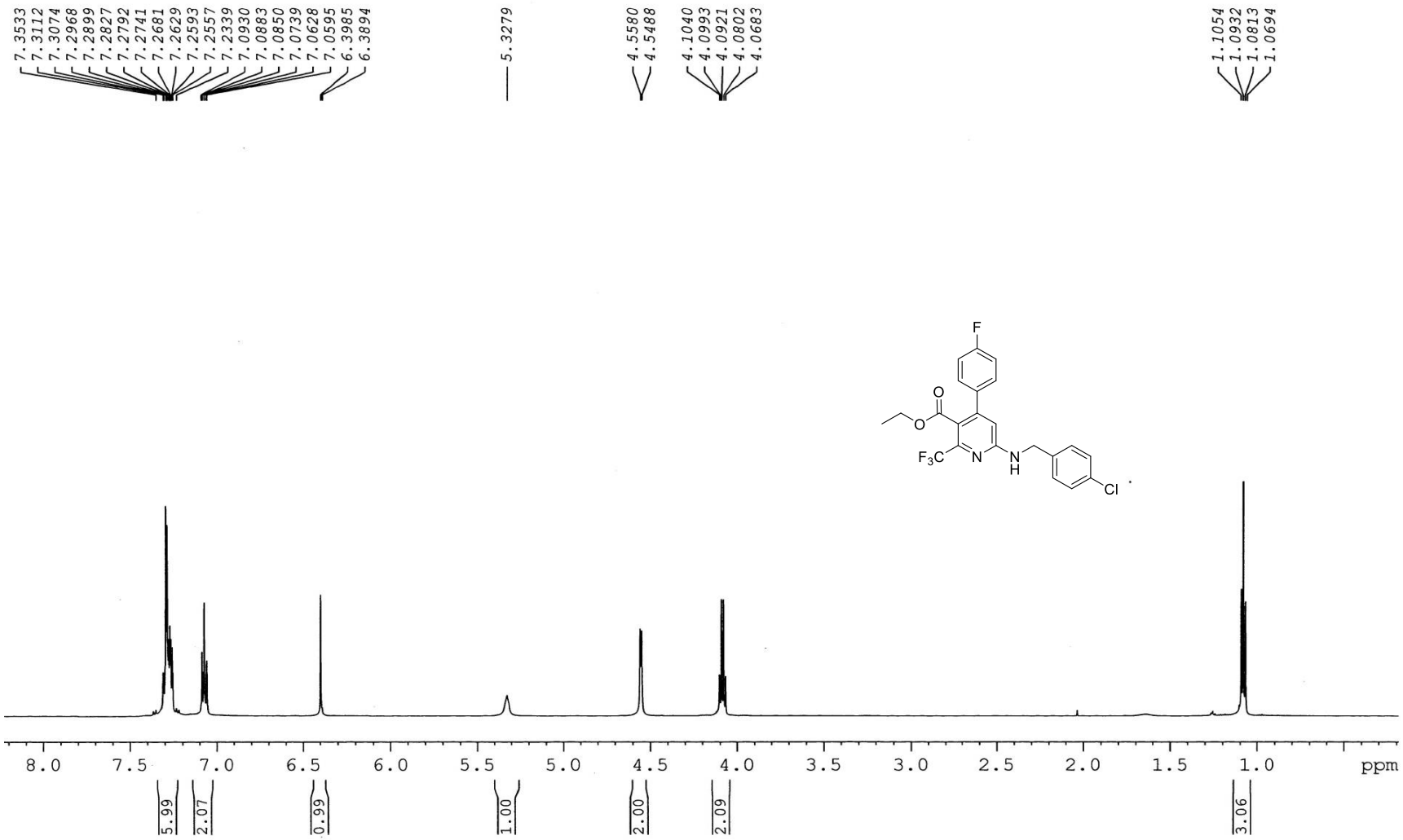

Figure S42. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **5c**

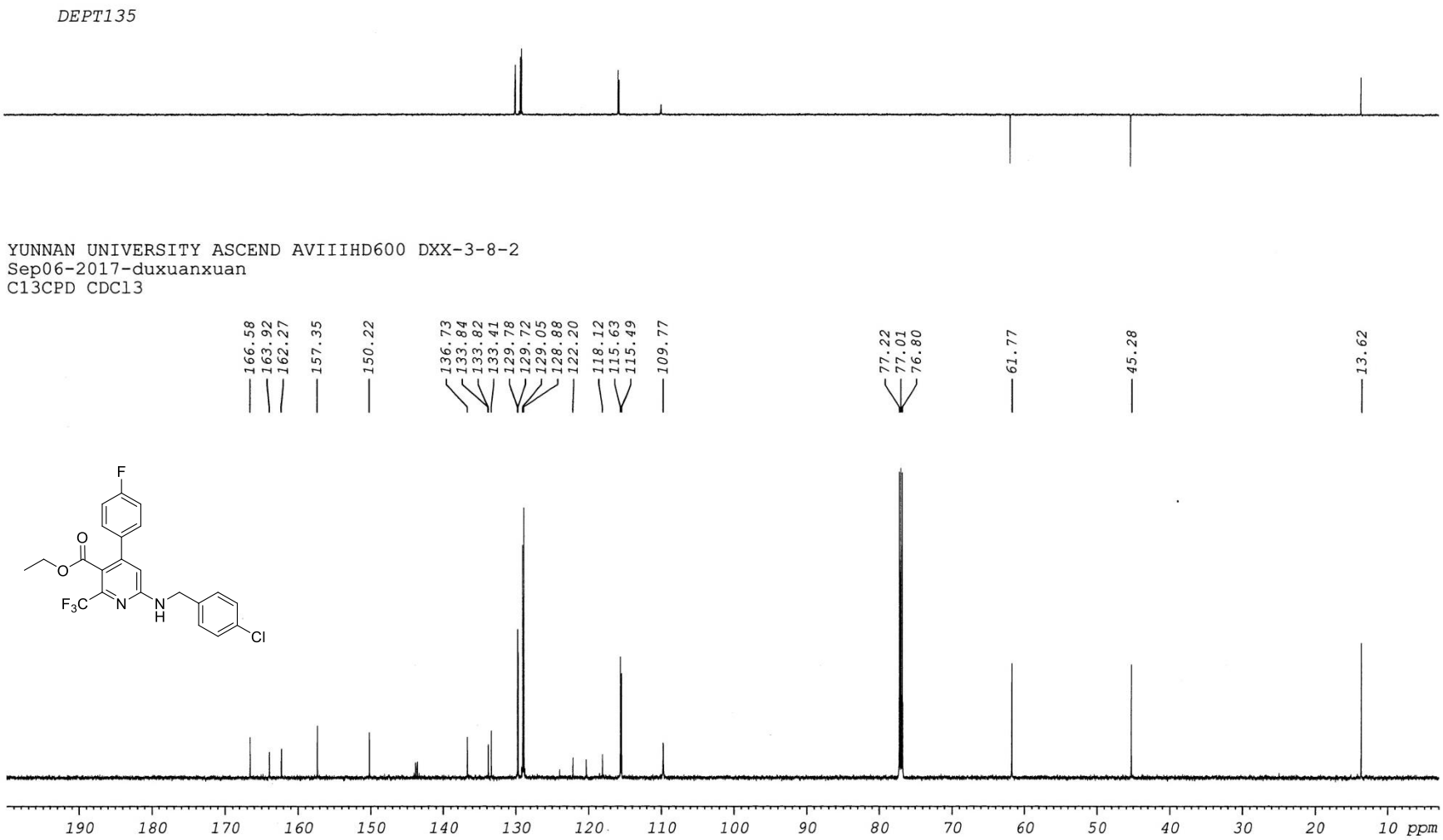

Figure S43. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **5c**

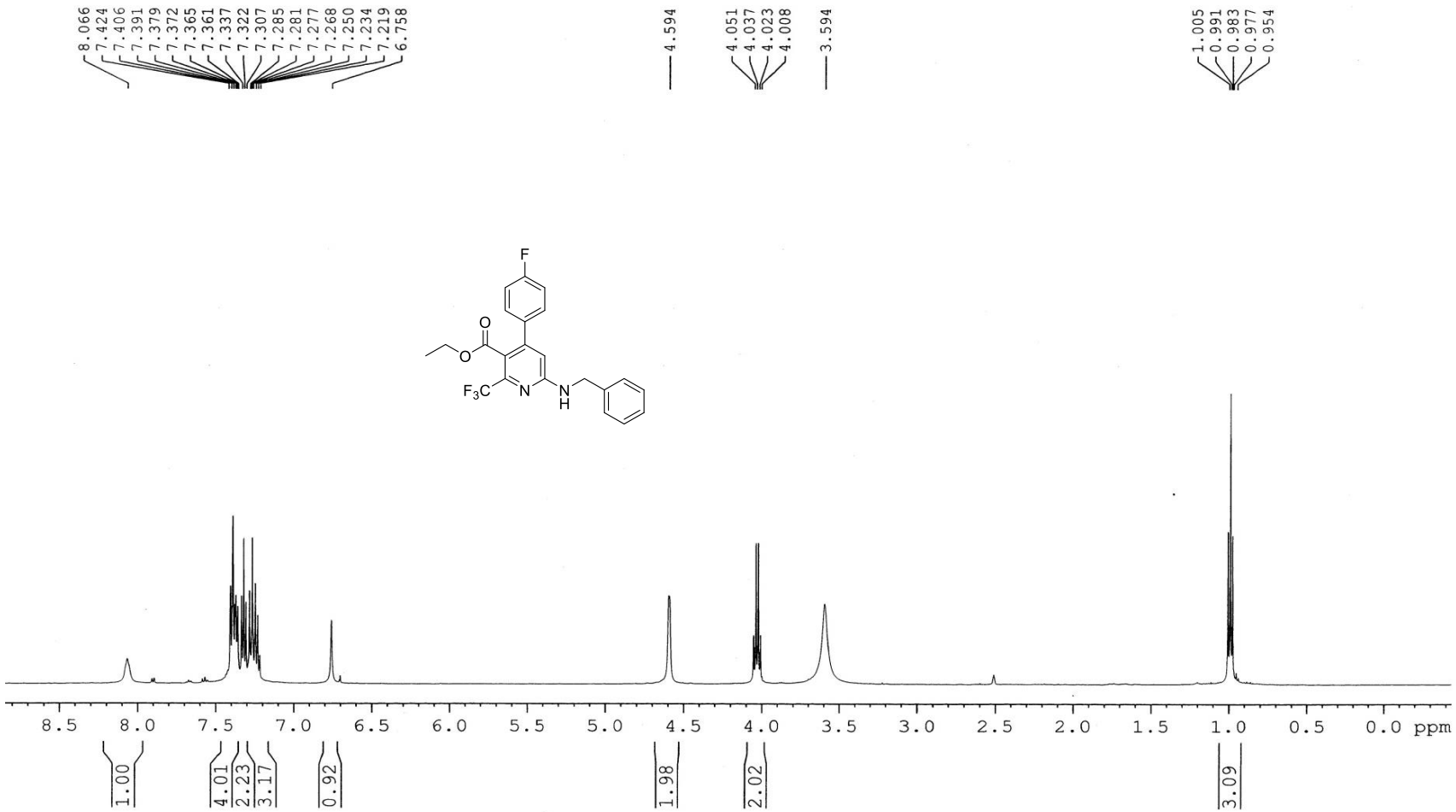

Figure S44. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5d**

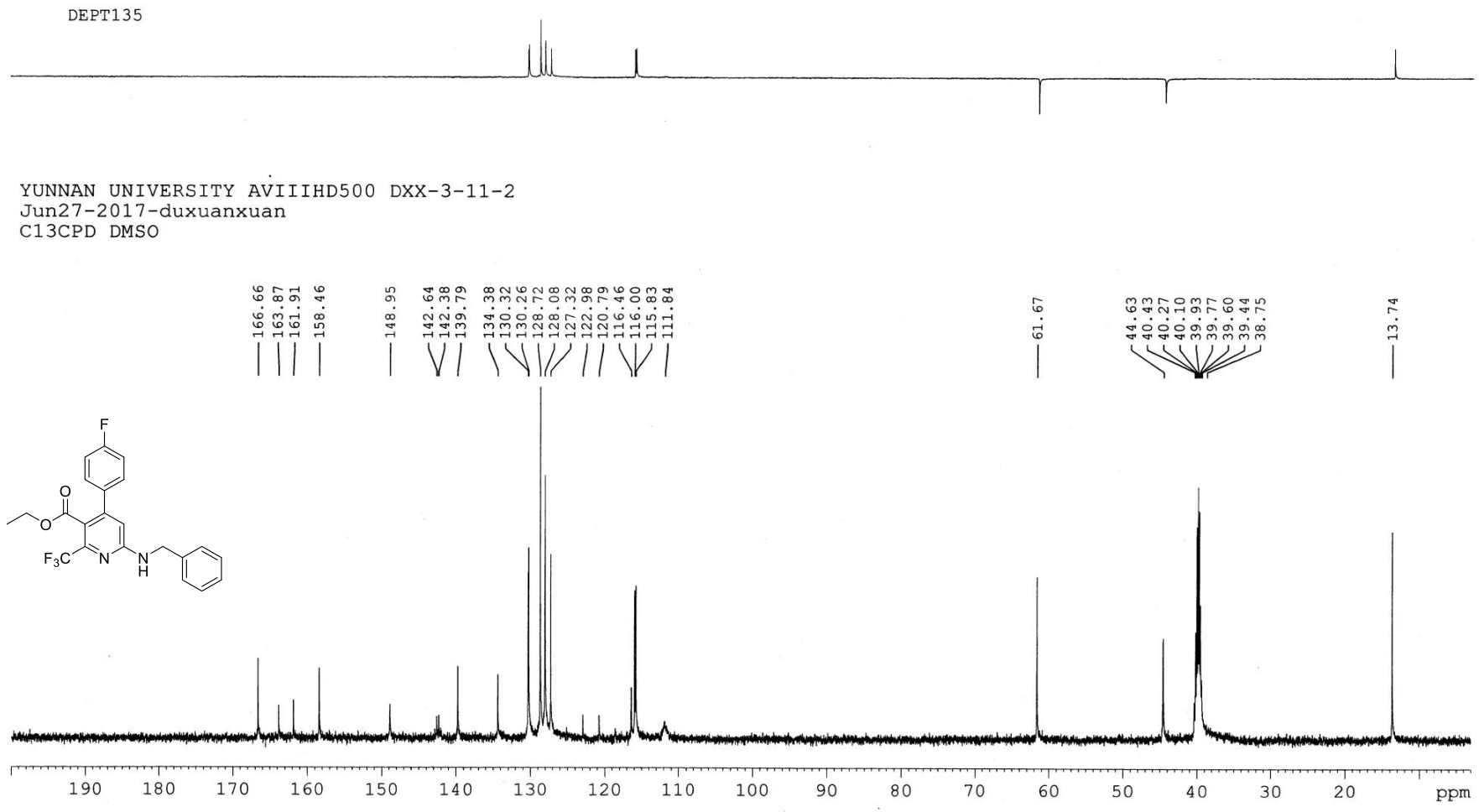

Figure S45. ^{13}C NMR (125MHz, DMSO-d_6) spectra of compound **5d**

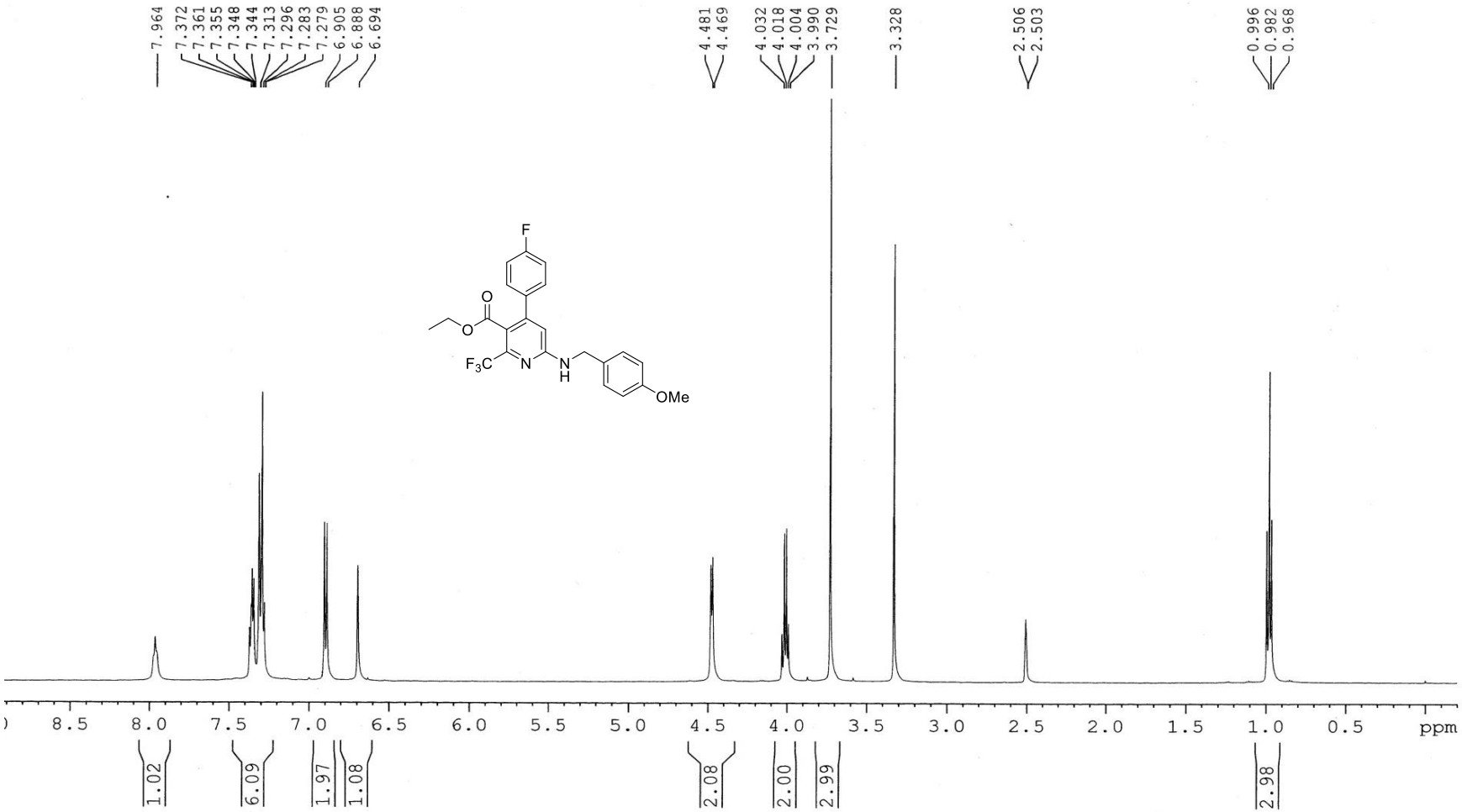

Figure S46. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5e**

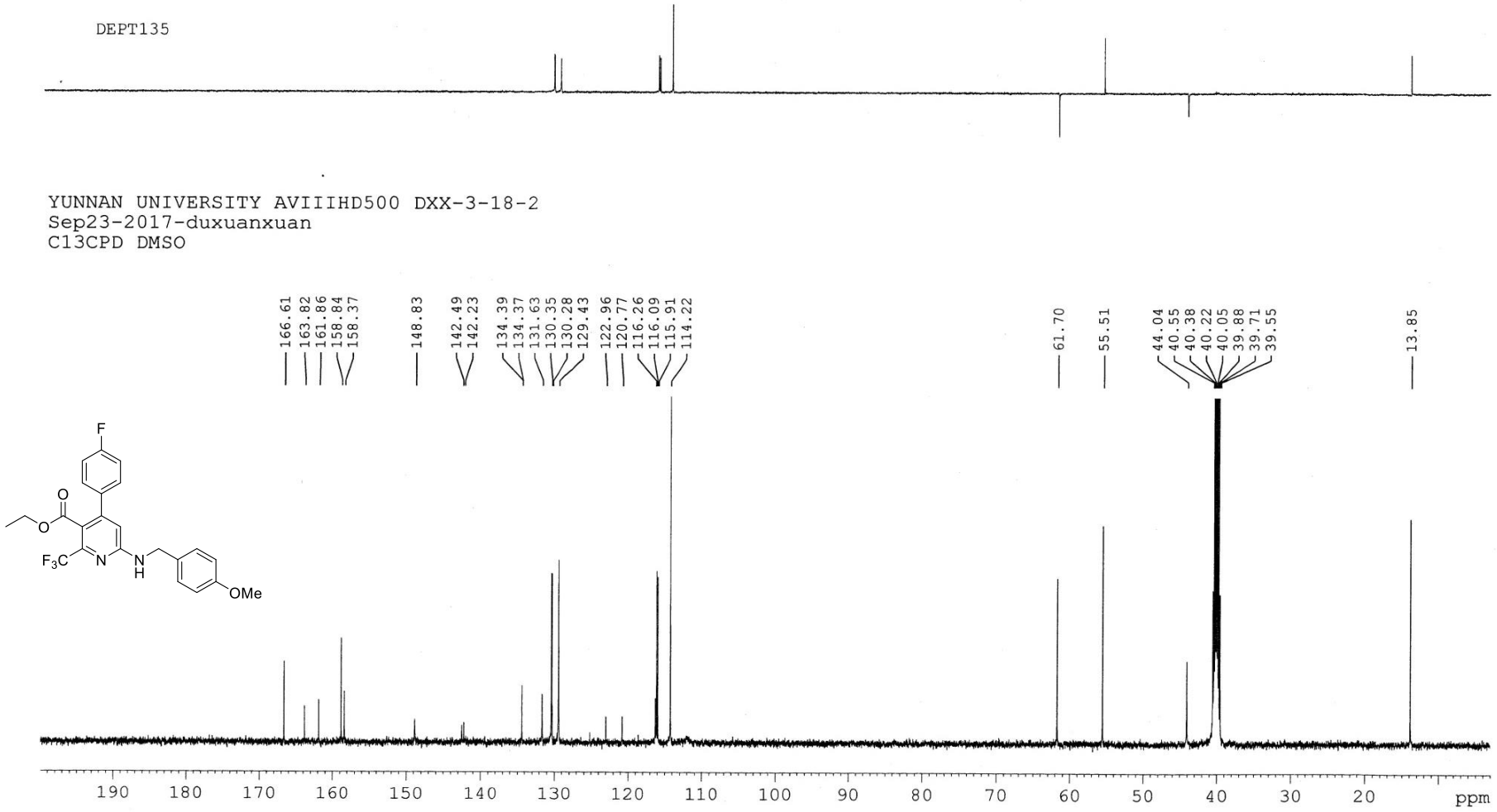

Figure S47. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5e**

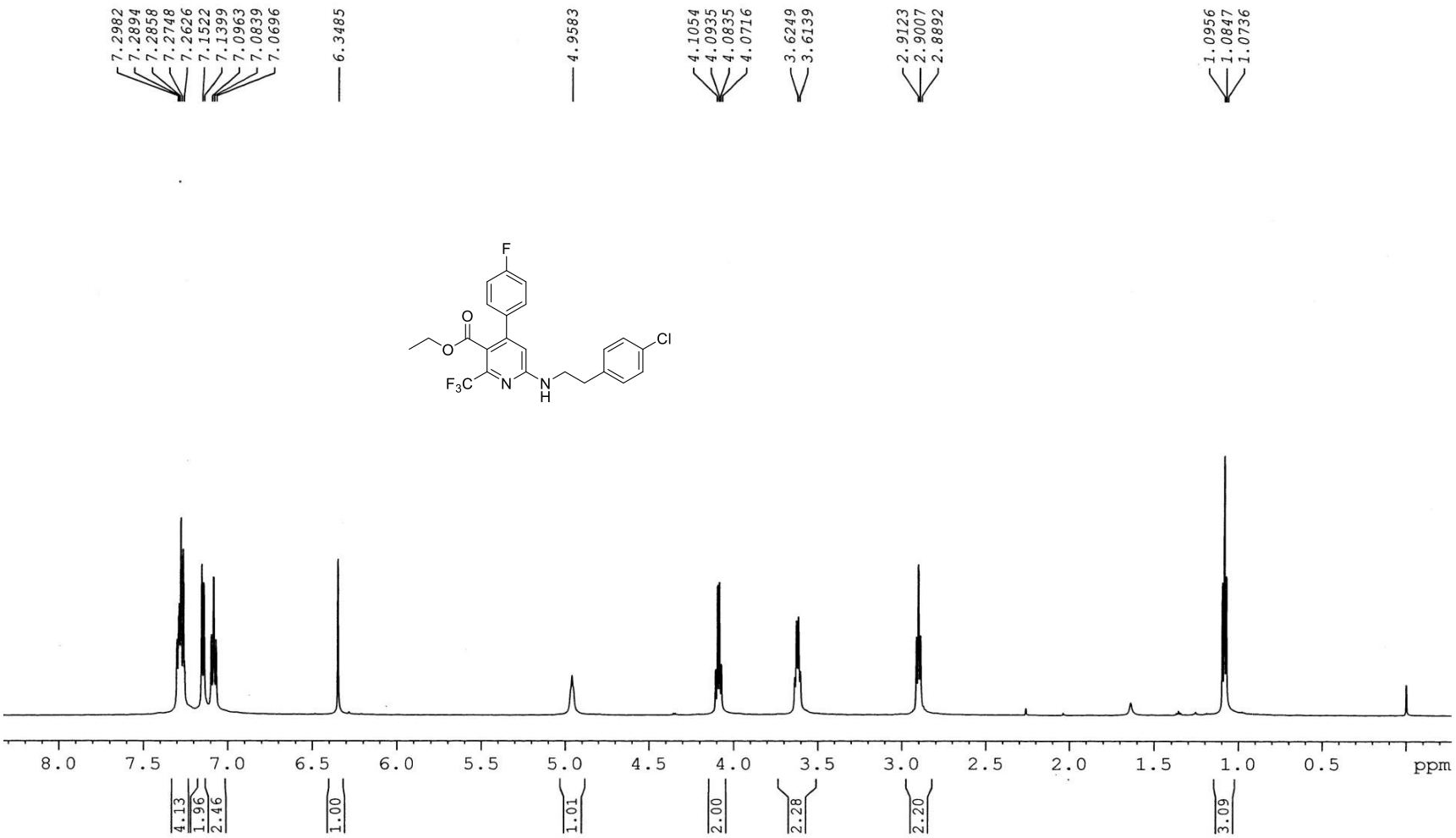

Figure S48. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **5f**

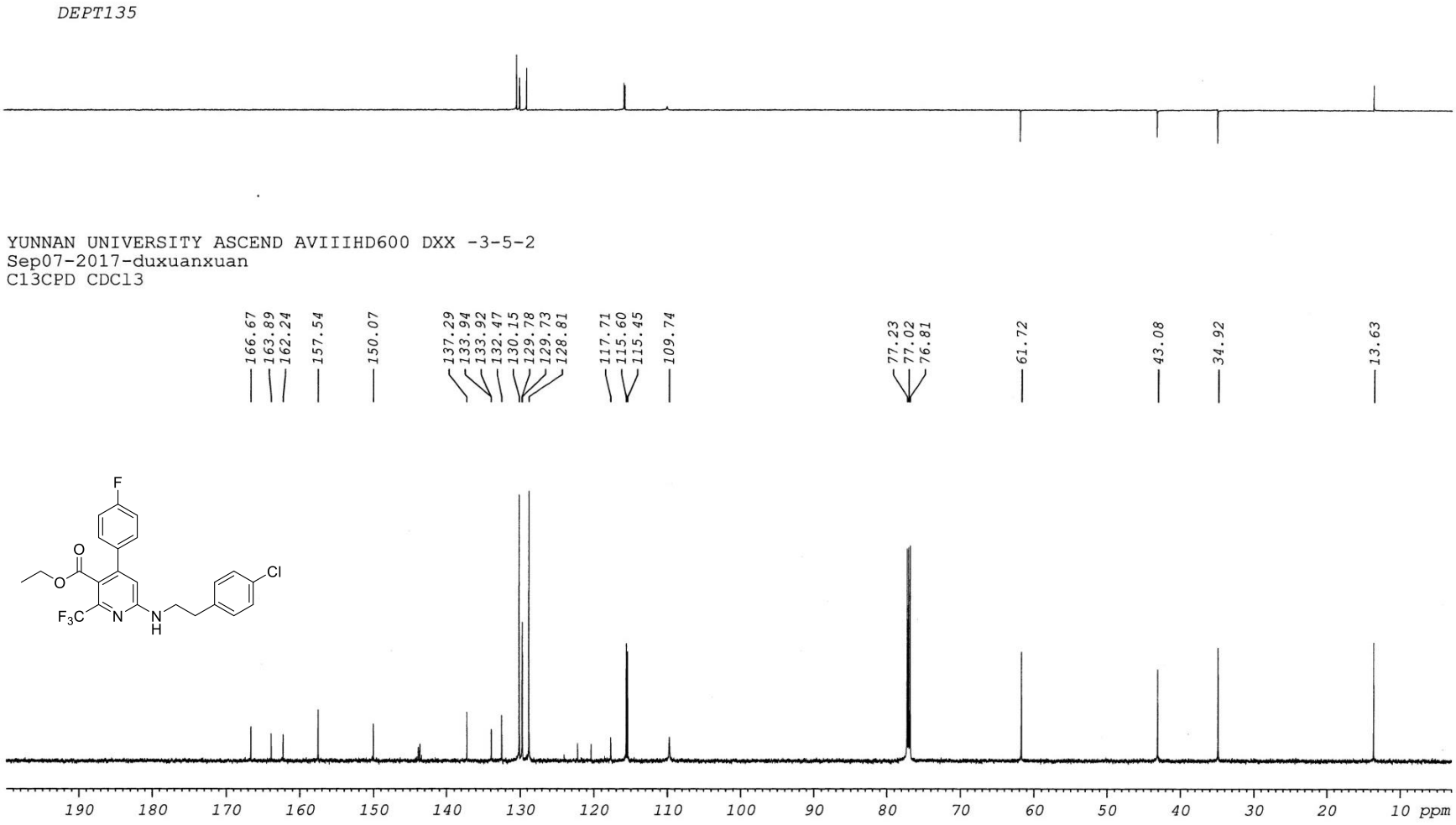

Figure S49. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **5f**

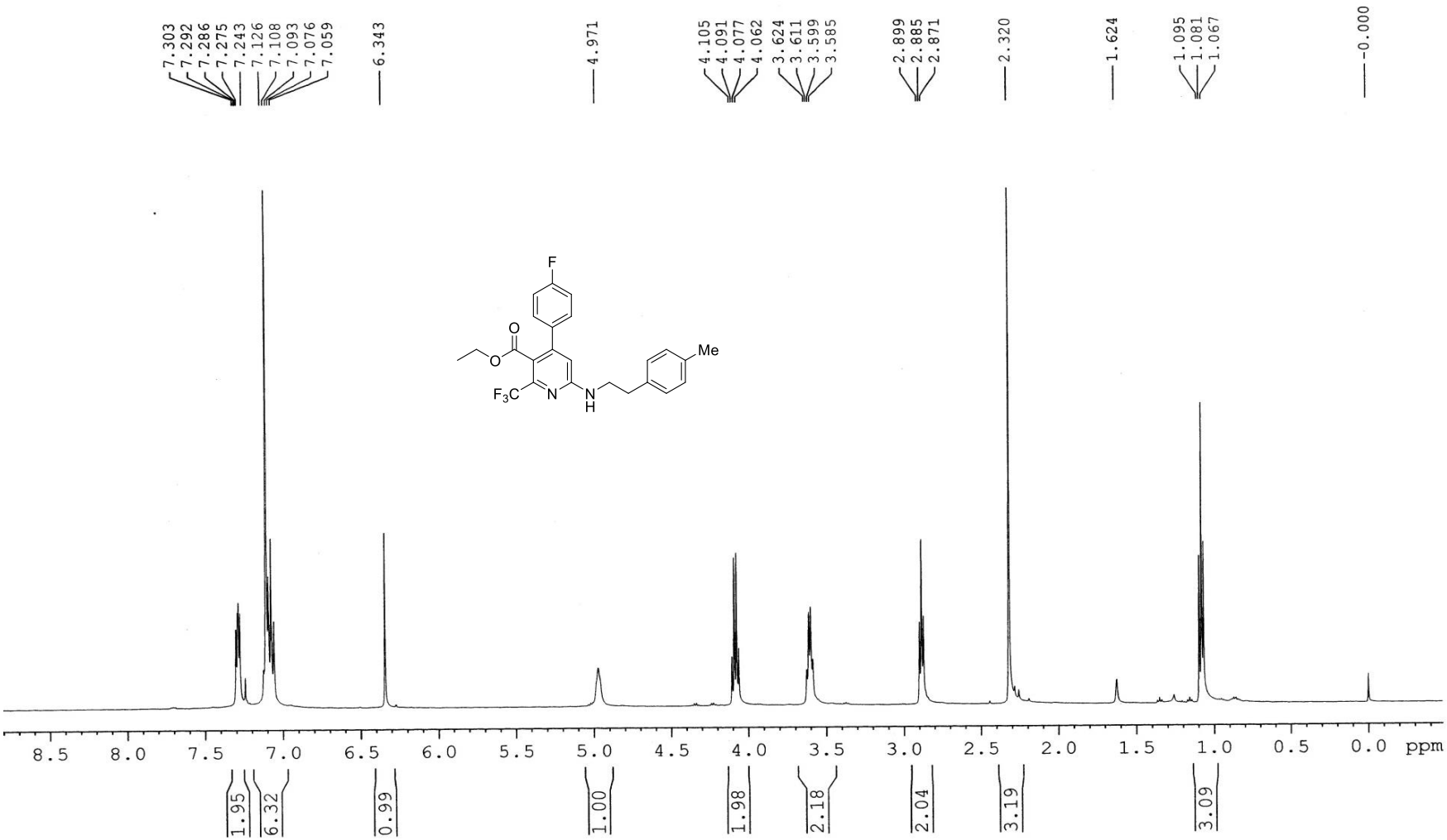

Figure S50. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **5g**

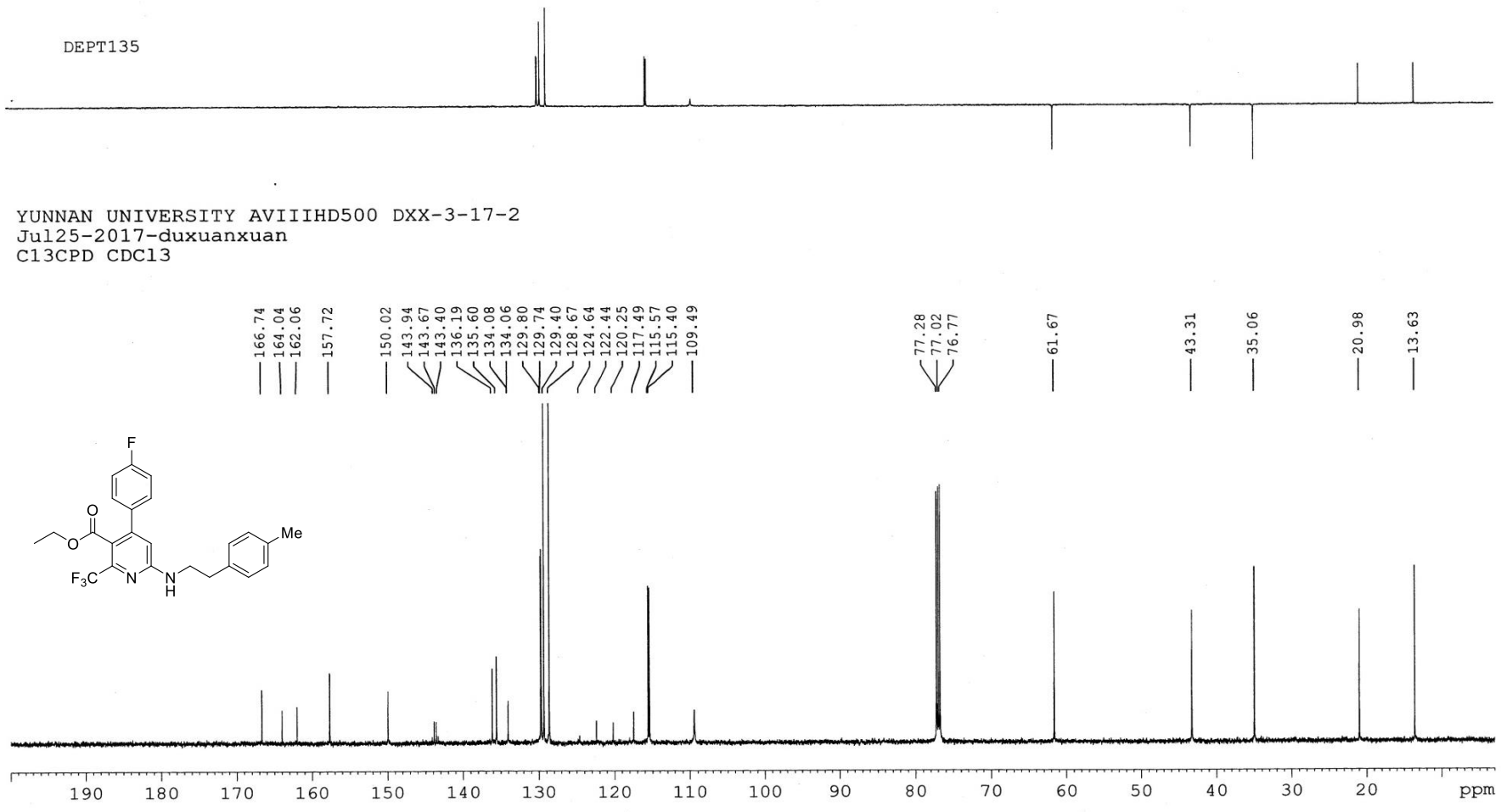

Figure S51. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **5g**

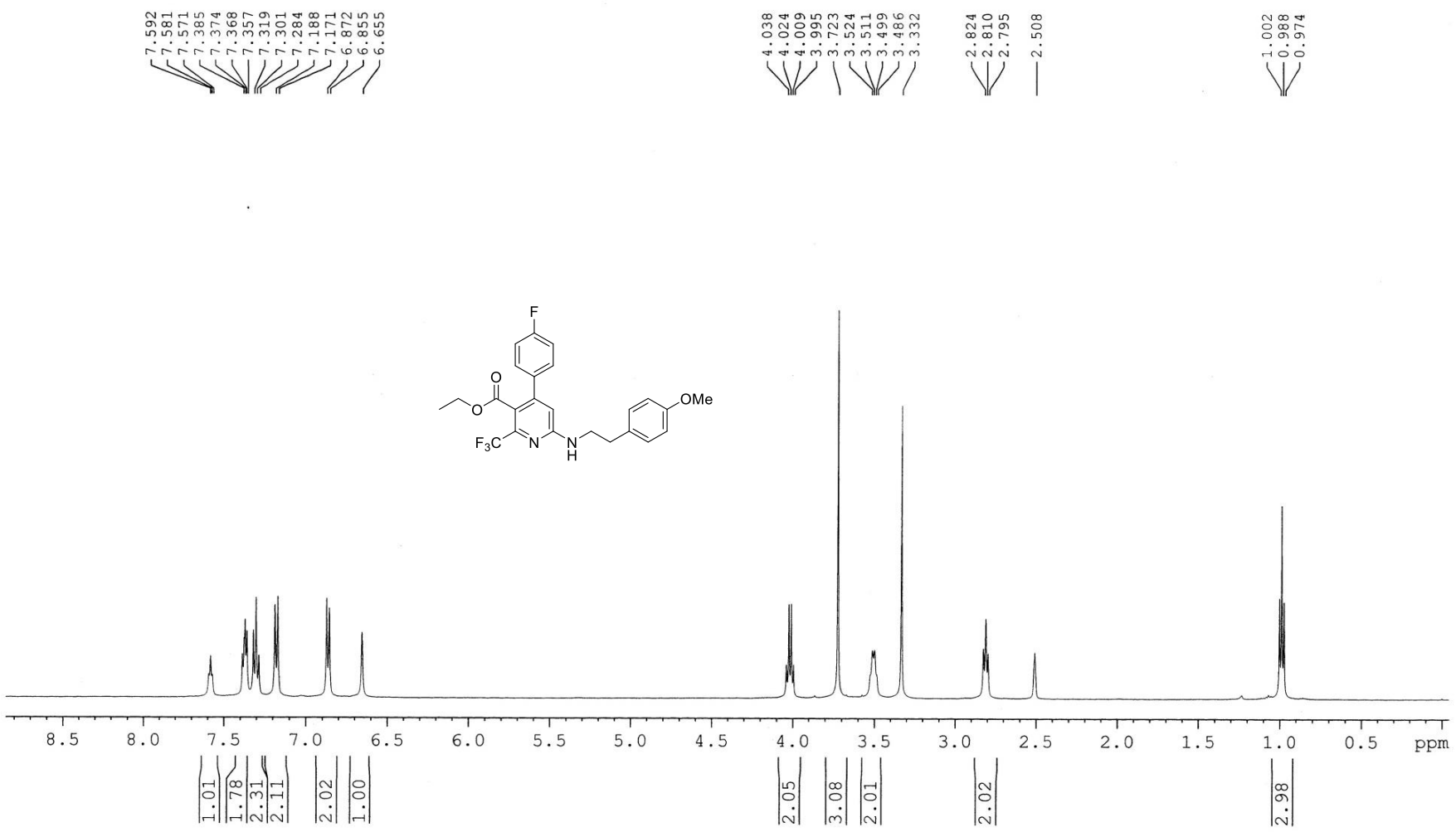

Figure S52. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5h**

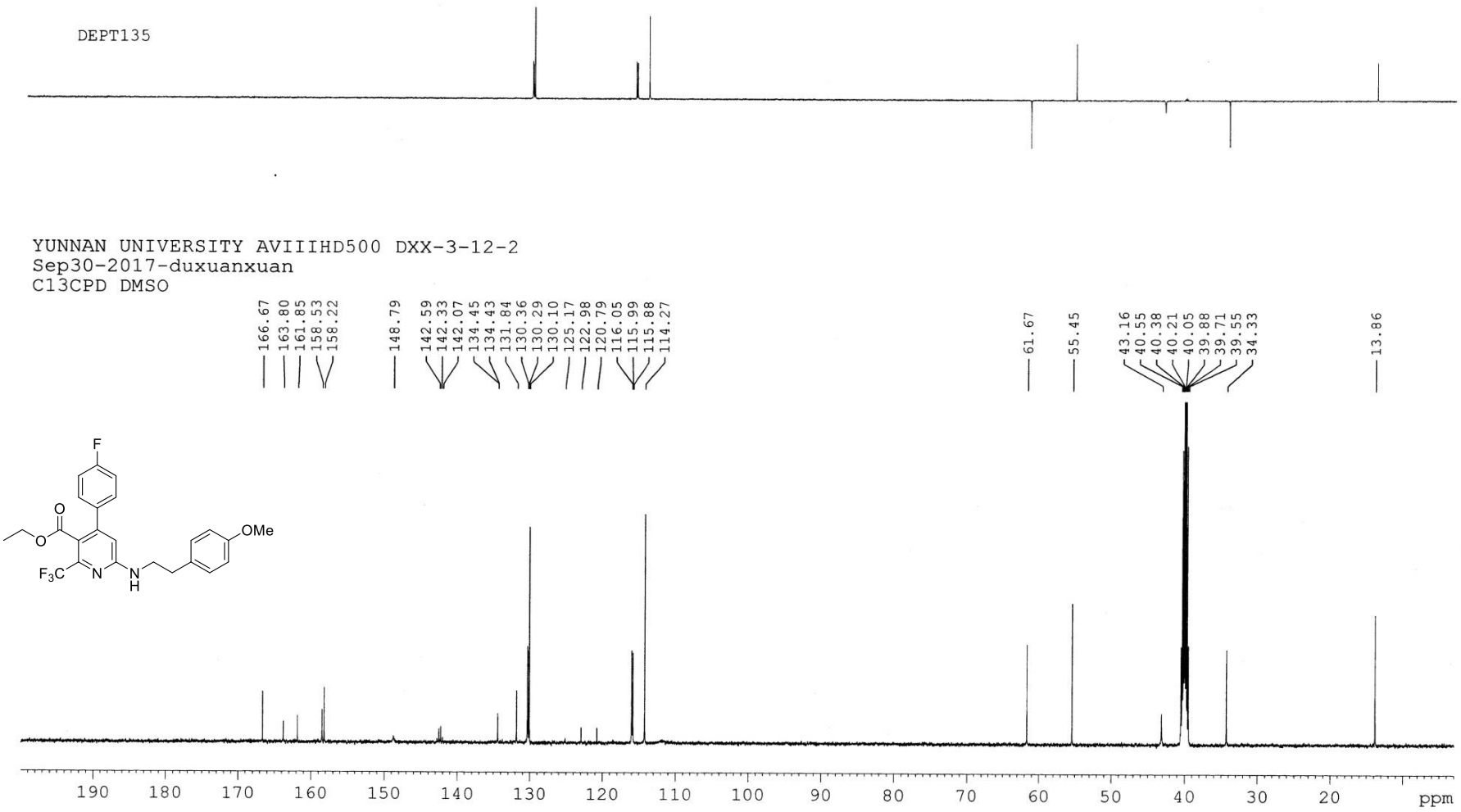

Figure S53. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5h**

Figure S54. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5i**

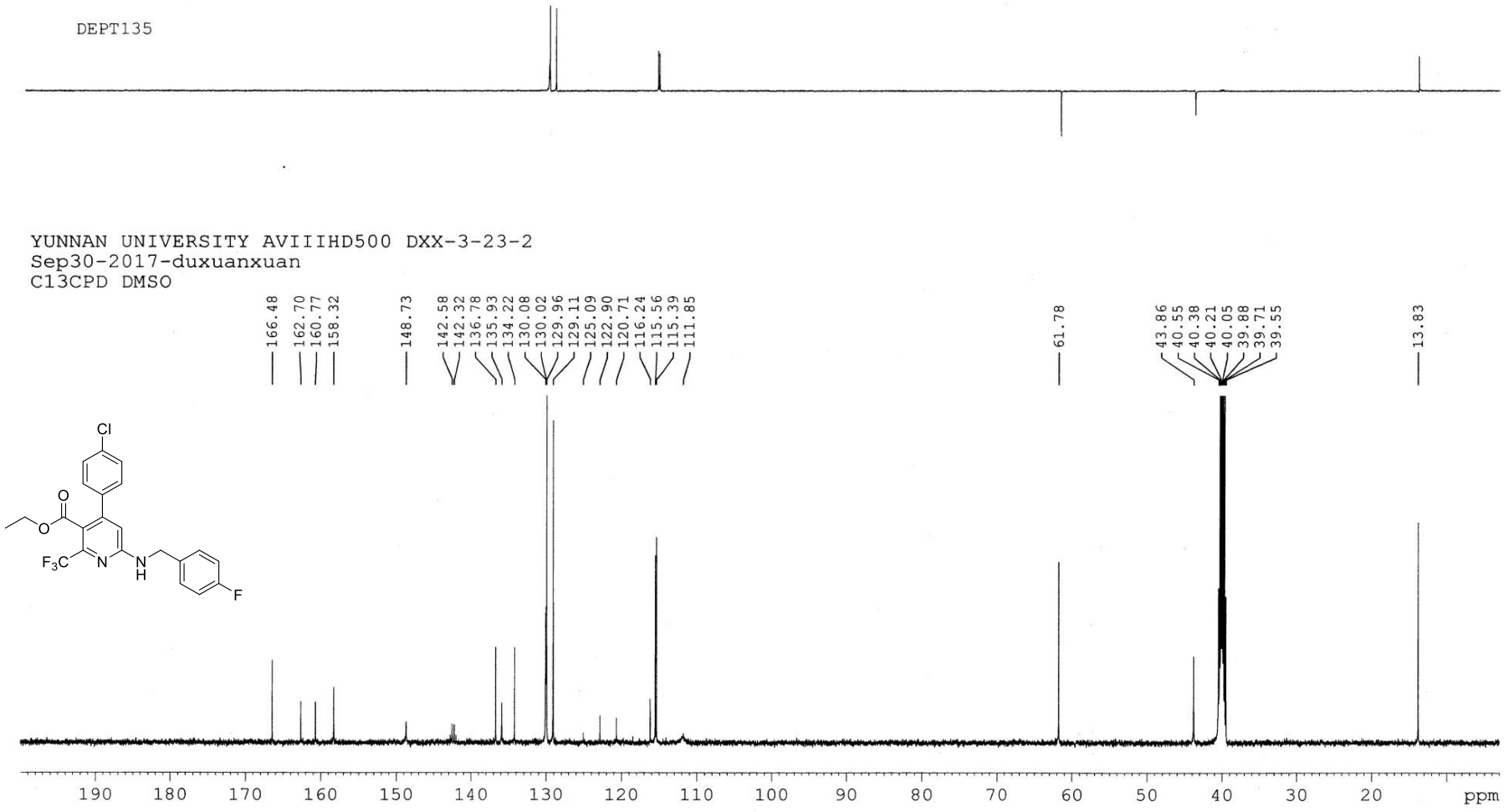

Figure S55. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5i**

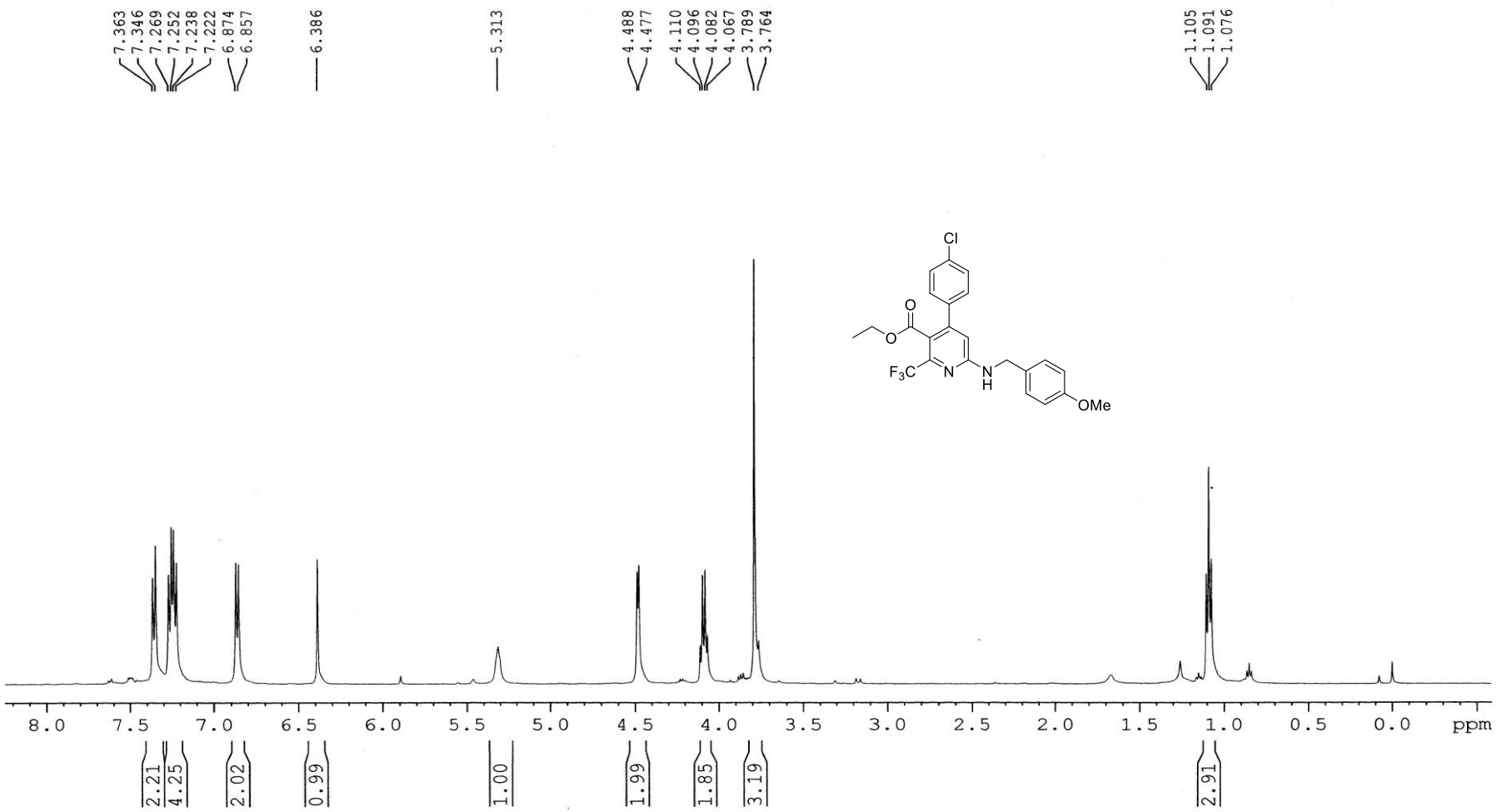

Figure S56. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **5j**

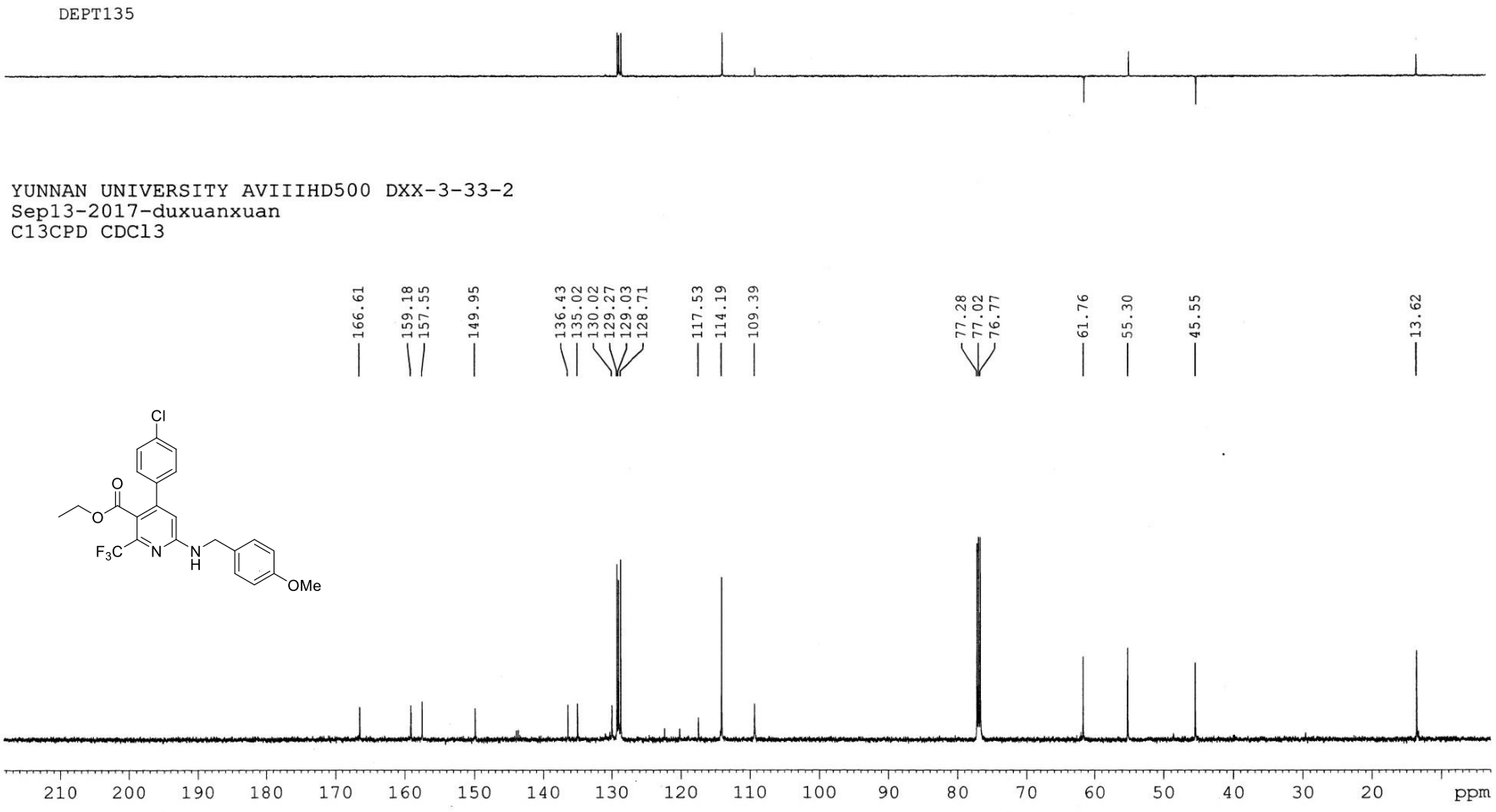

Figure S57. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **5j**

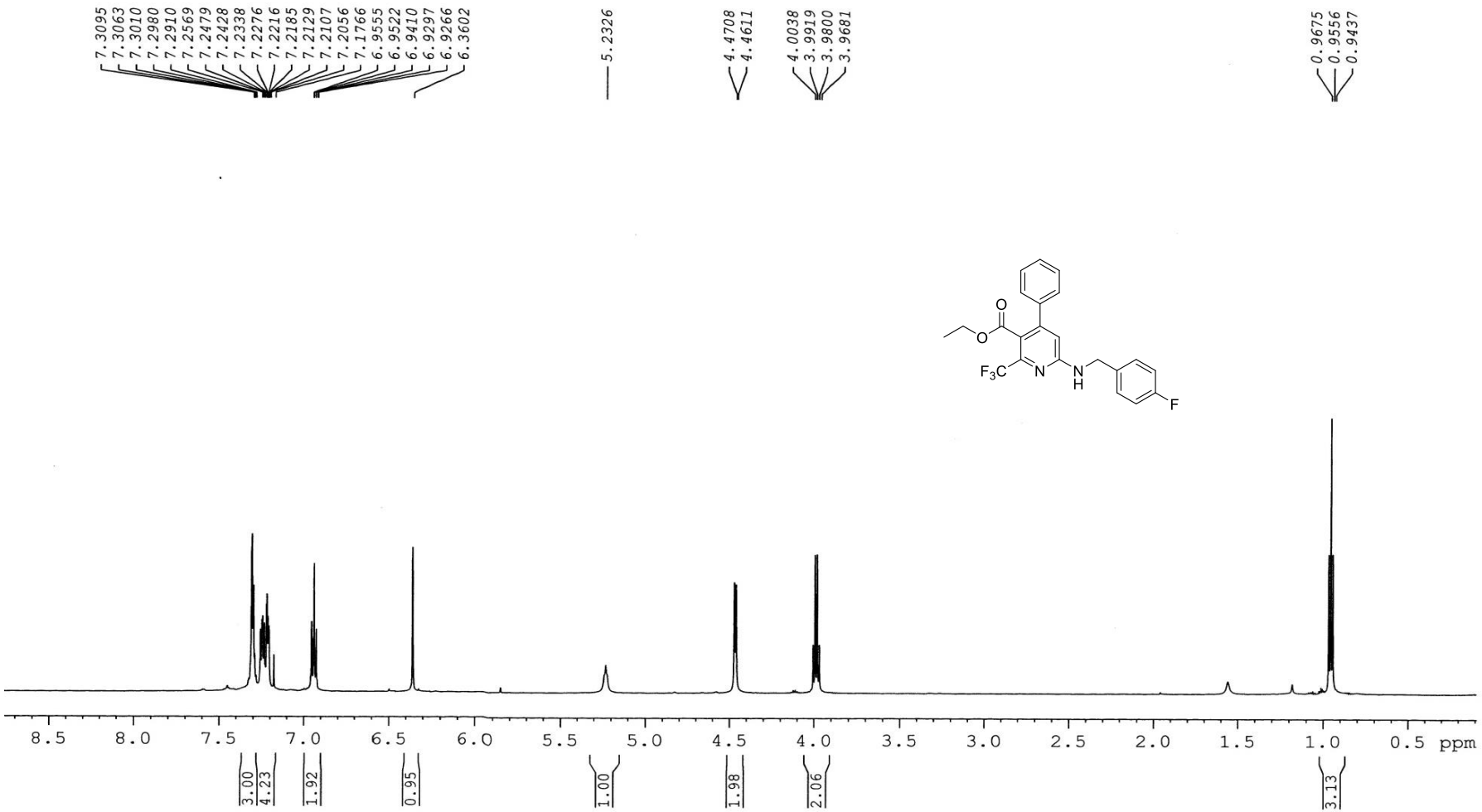

Figure S58. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **5k**

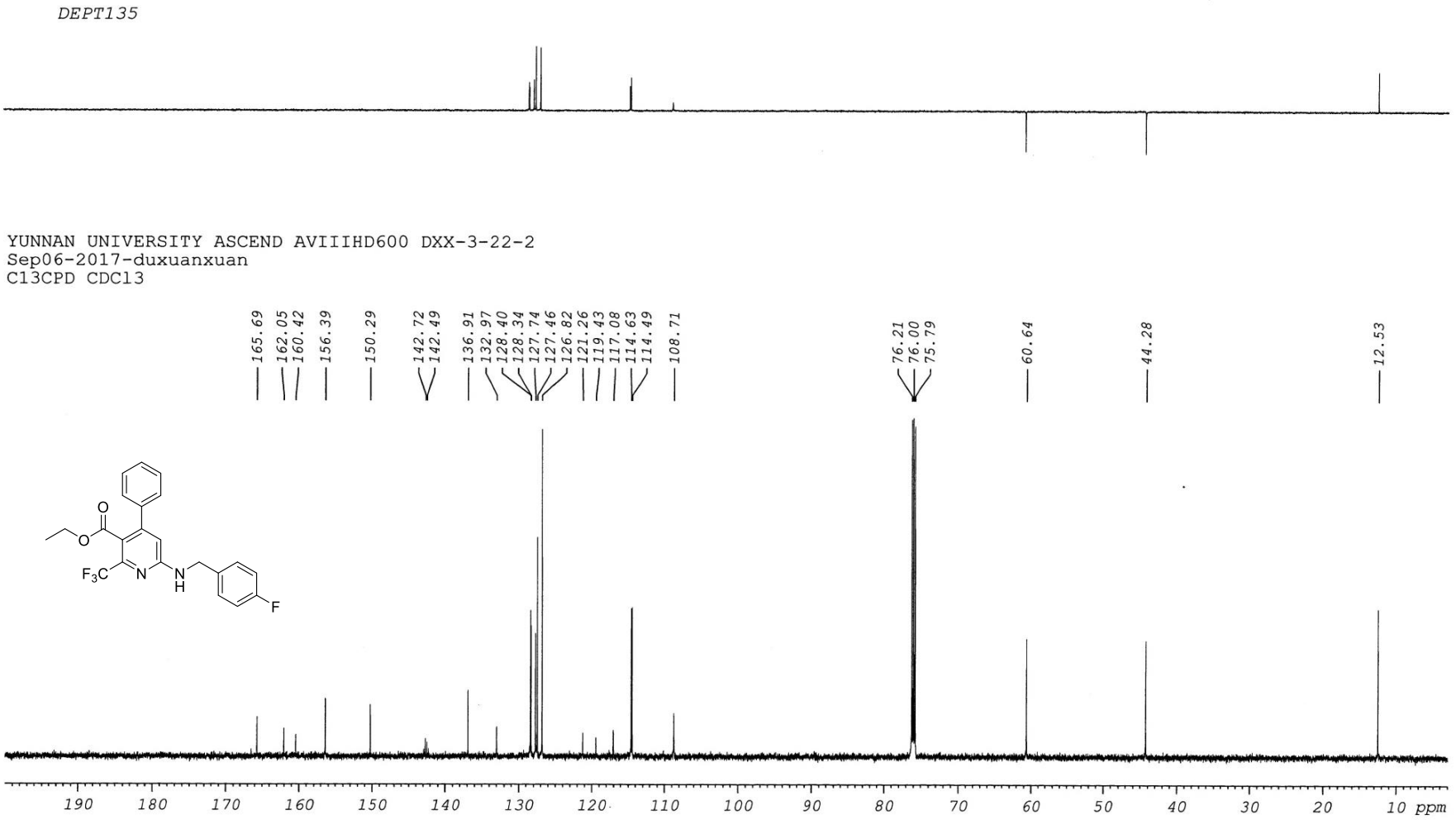

Figure S59. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **5k**

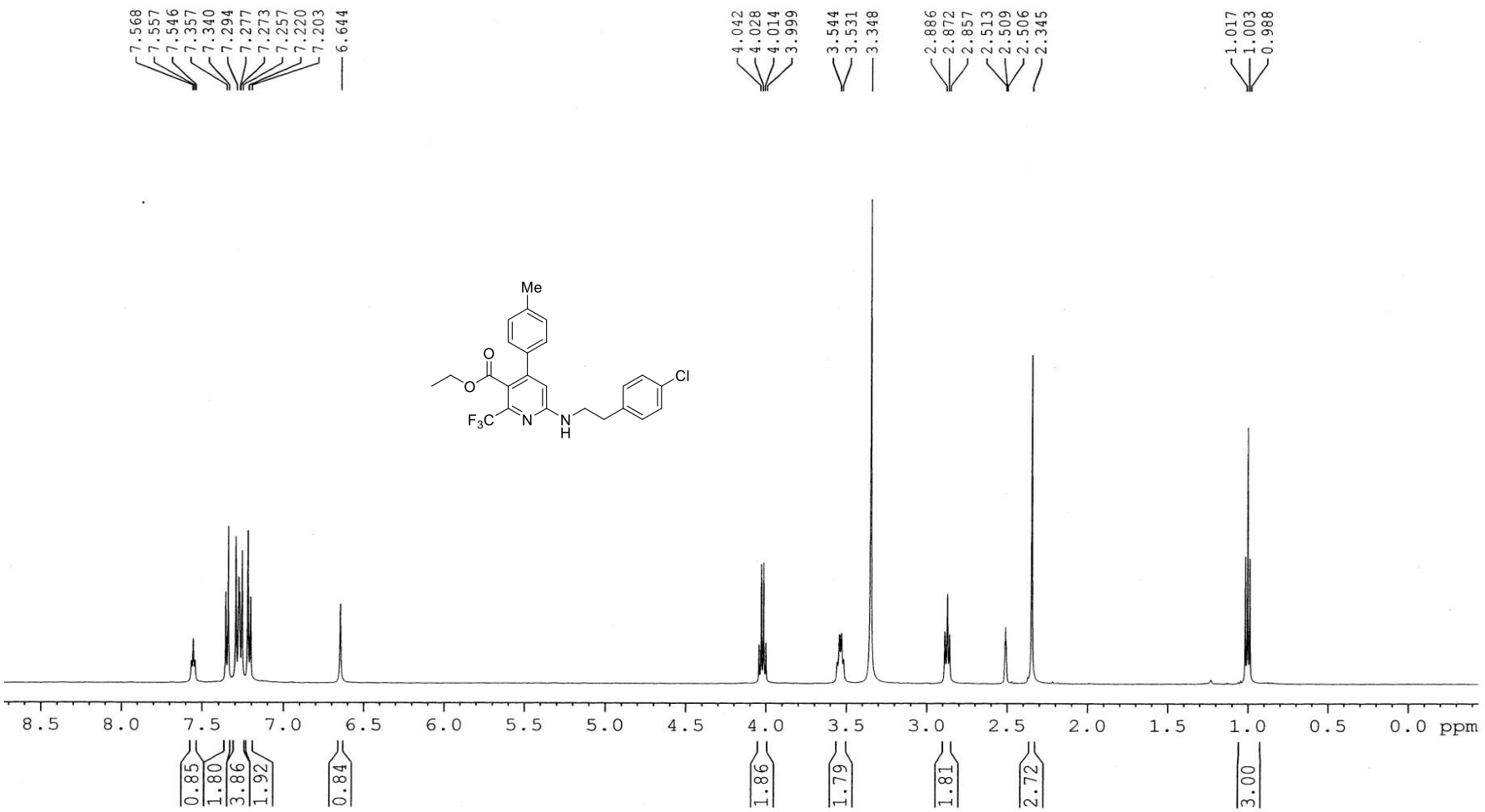

Figure S60. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5l**

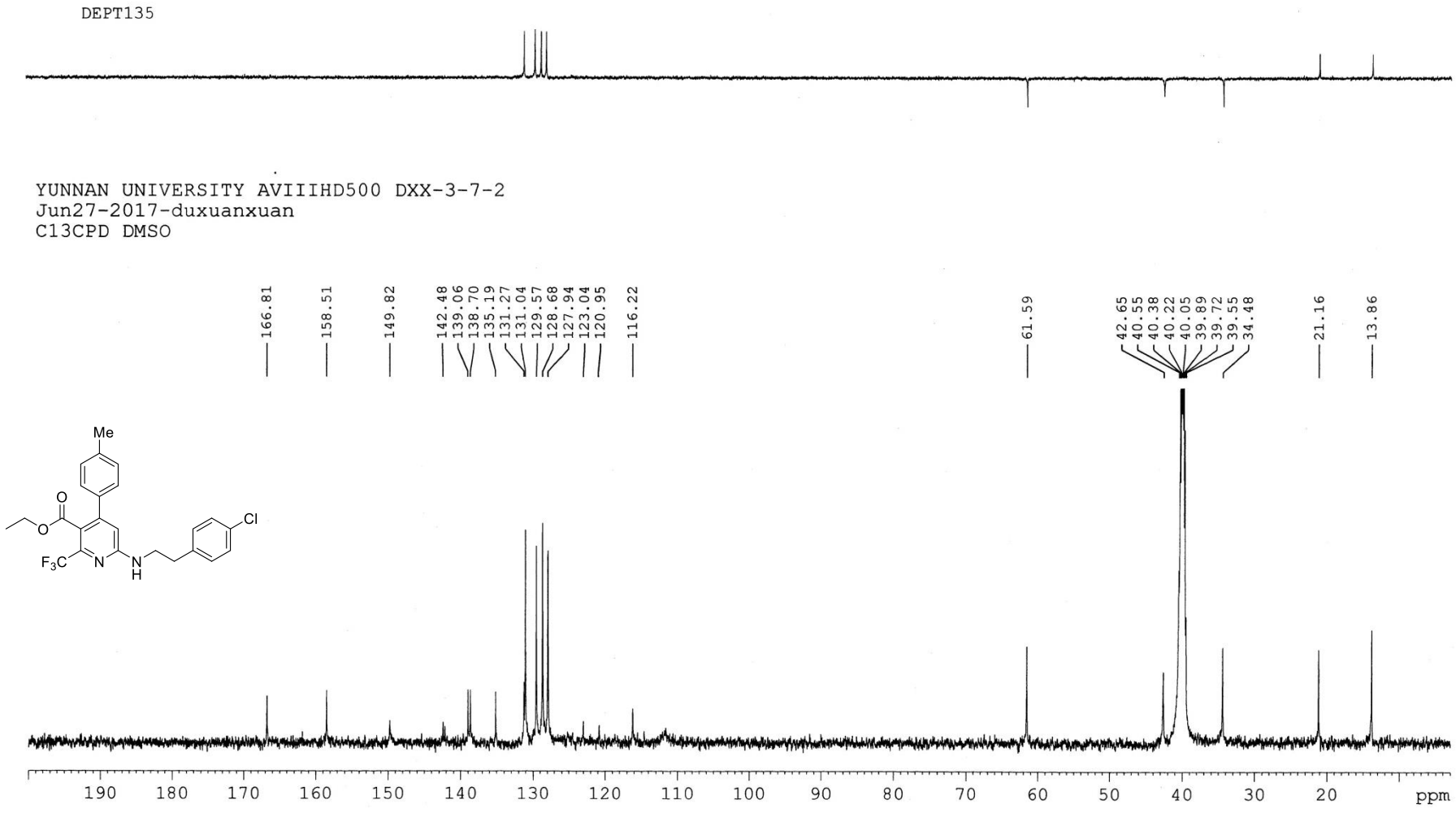

Figure S61. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5l**

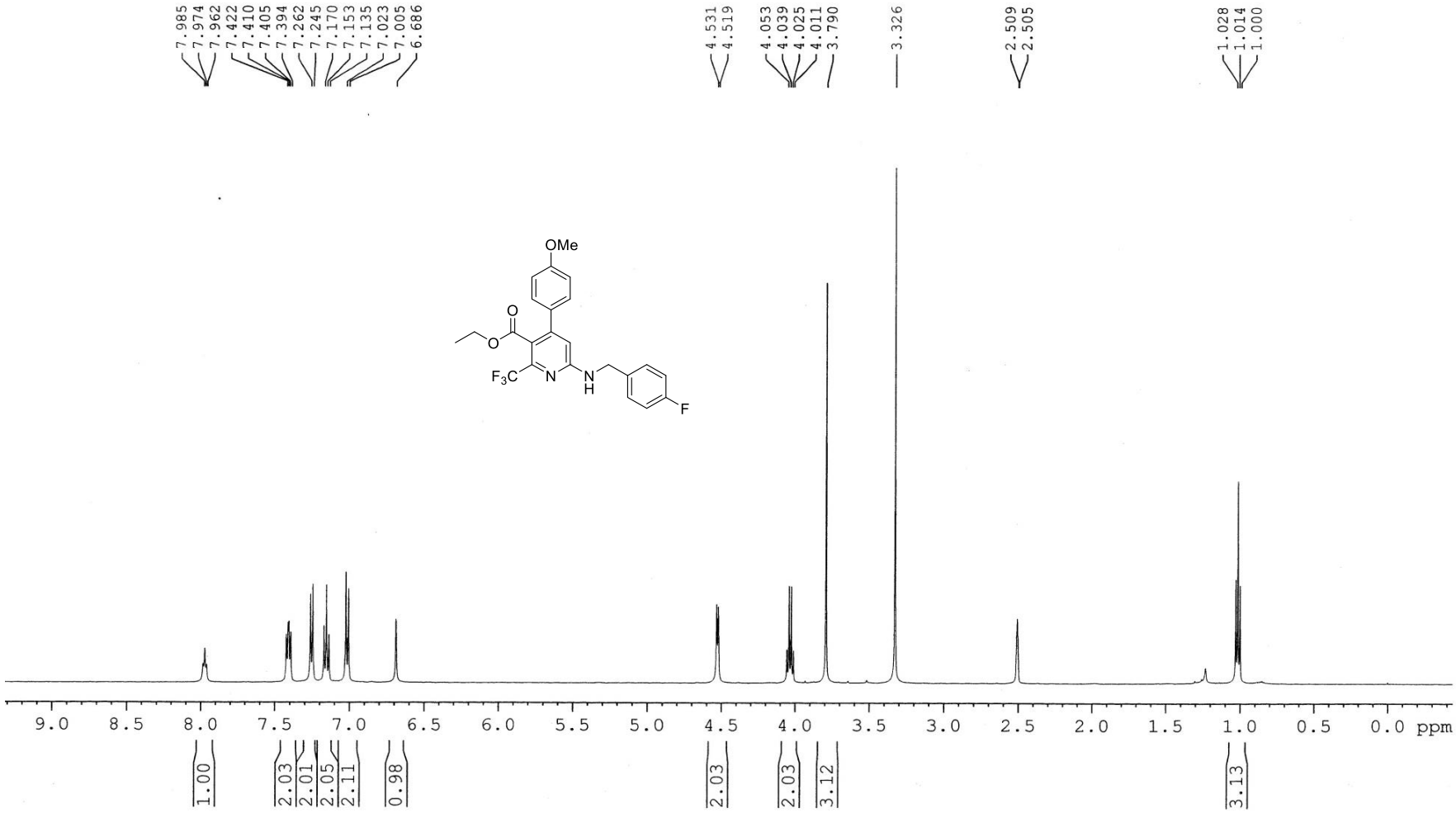

Figure S62. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5m**

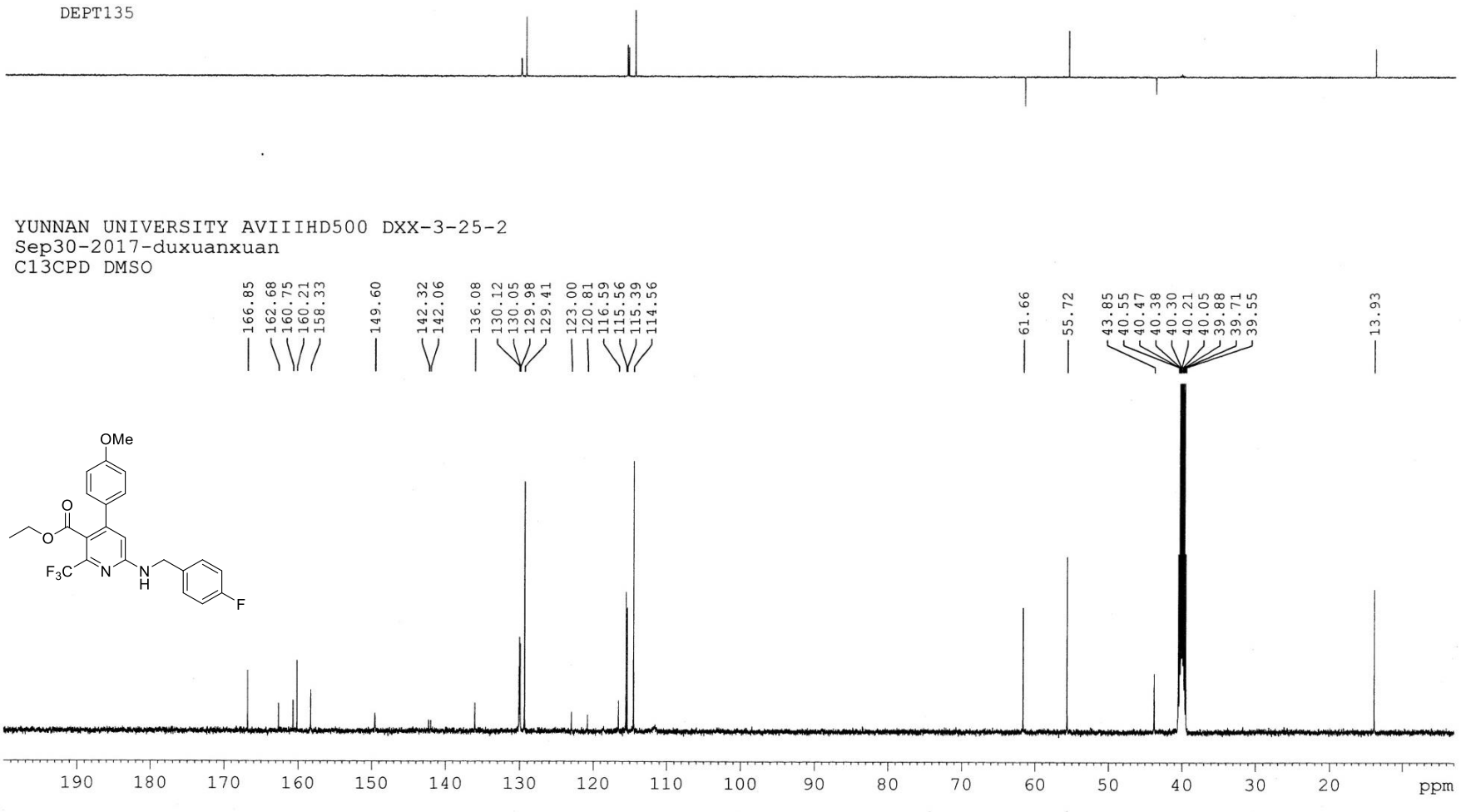

Figure S63. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5m**

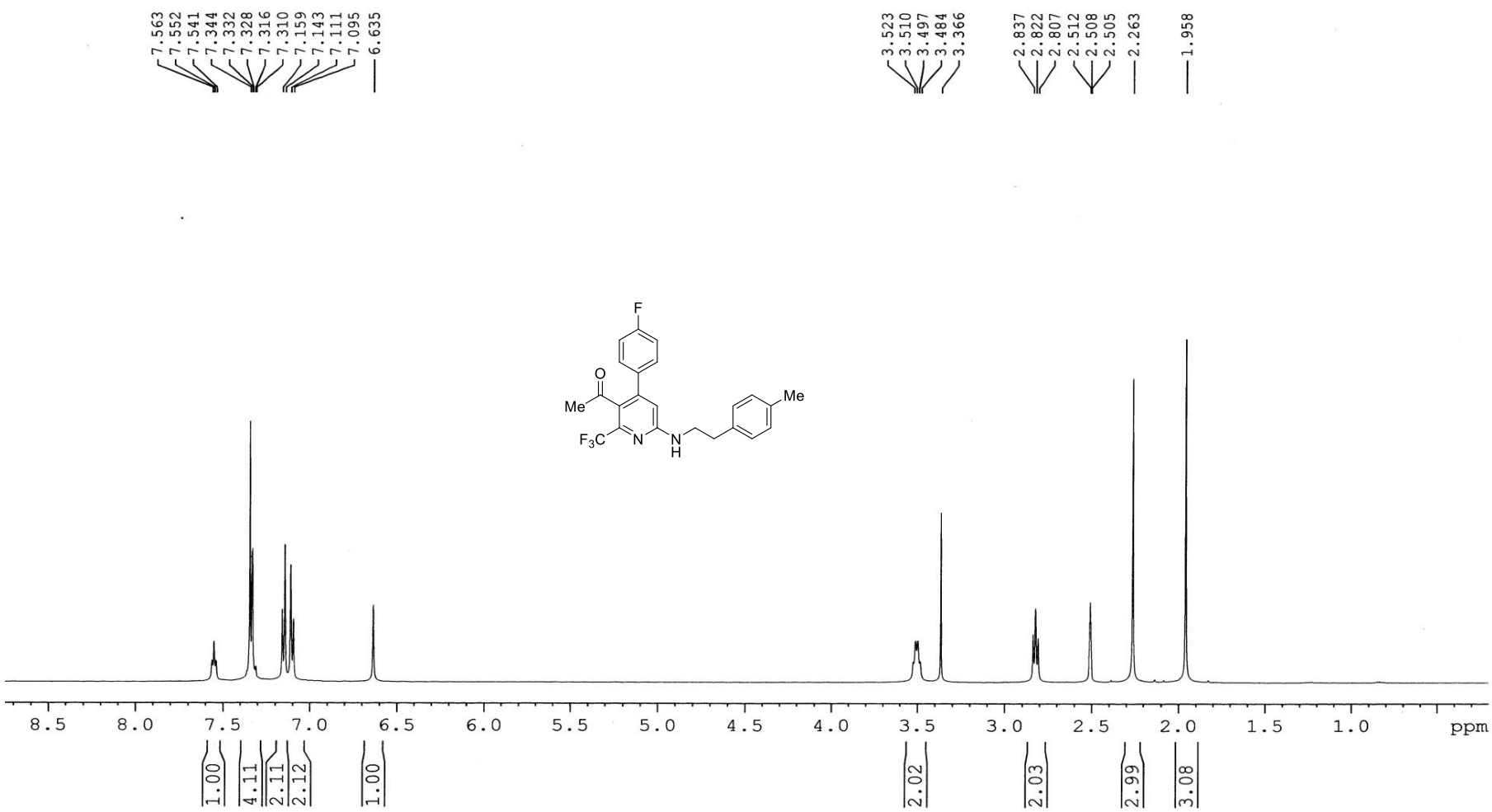

Figure S64. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5n**

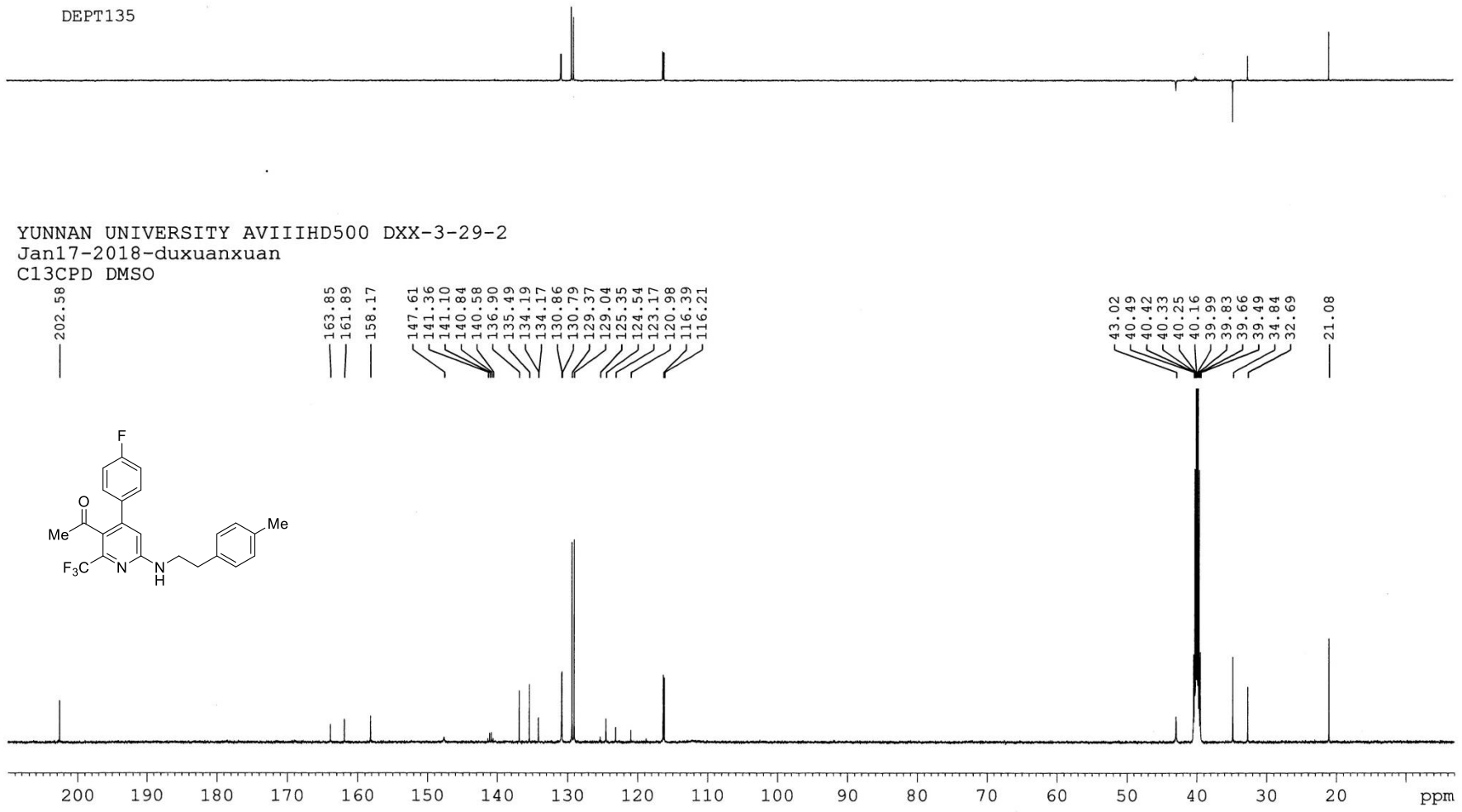

Figure S65. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5n**

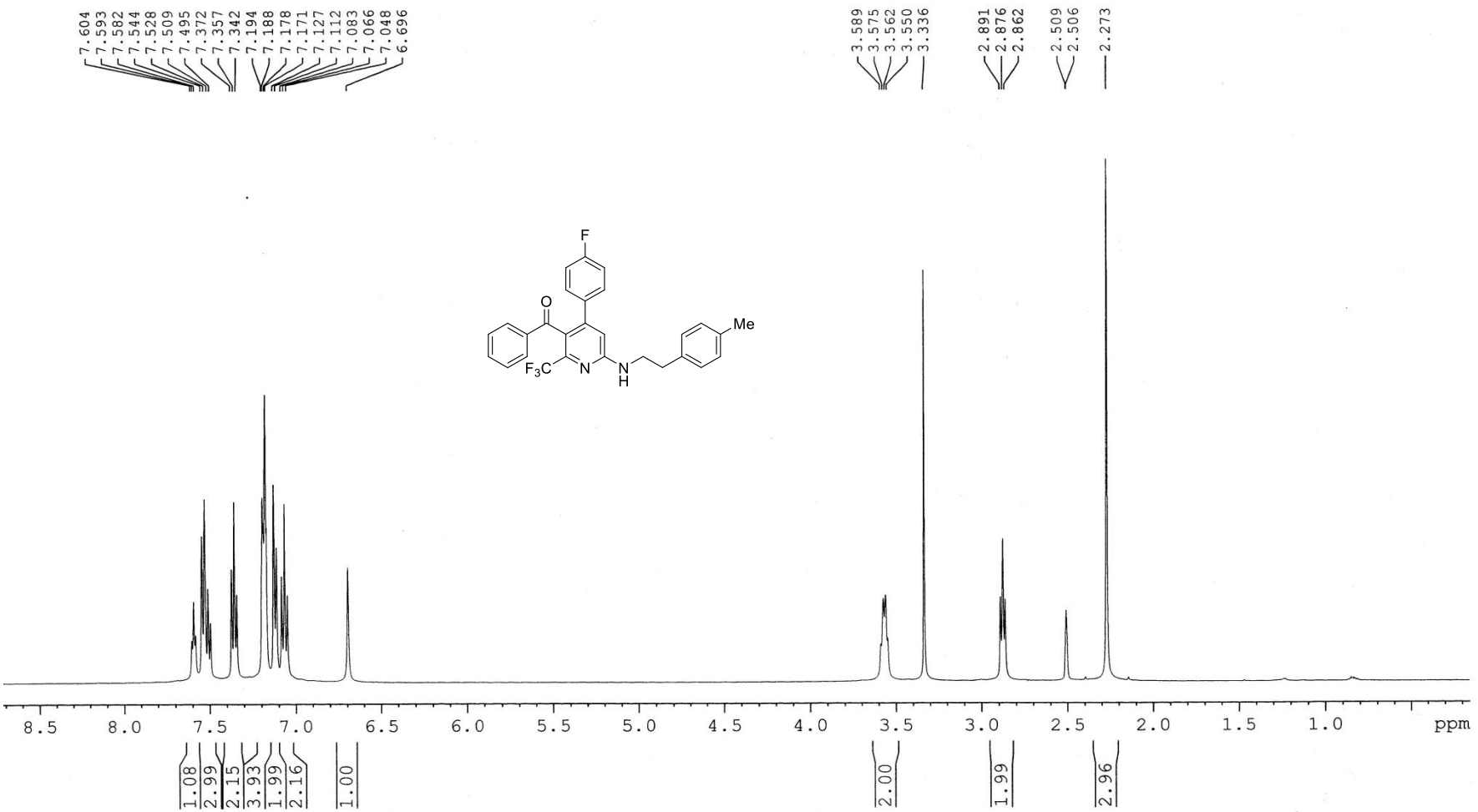

Figure S66. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5o**

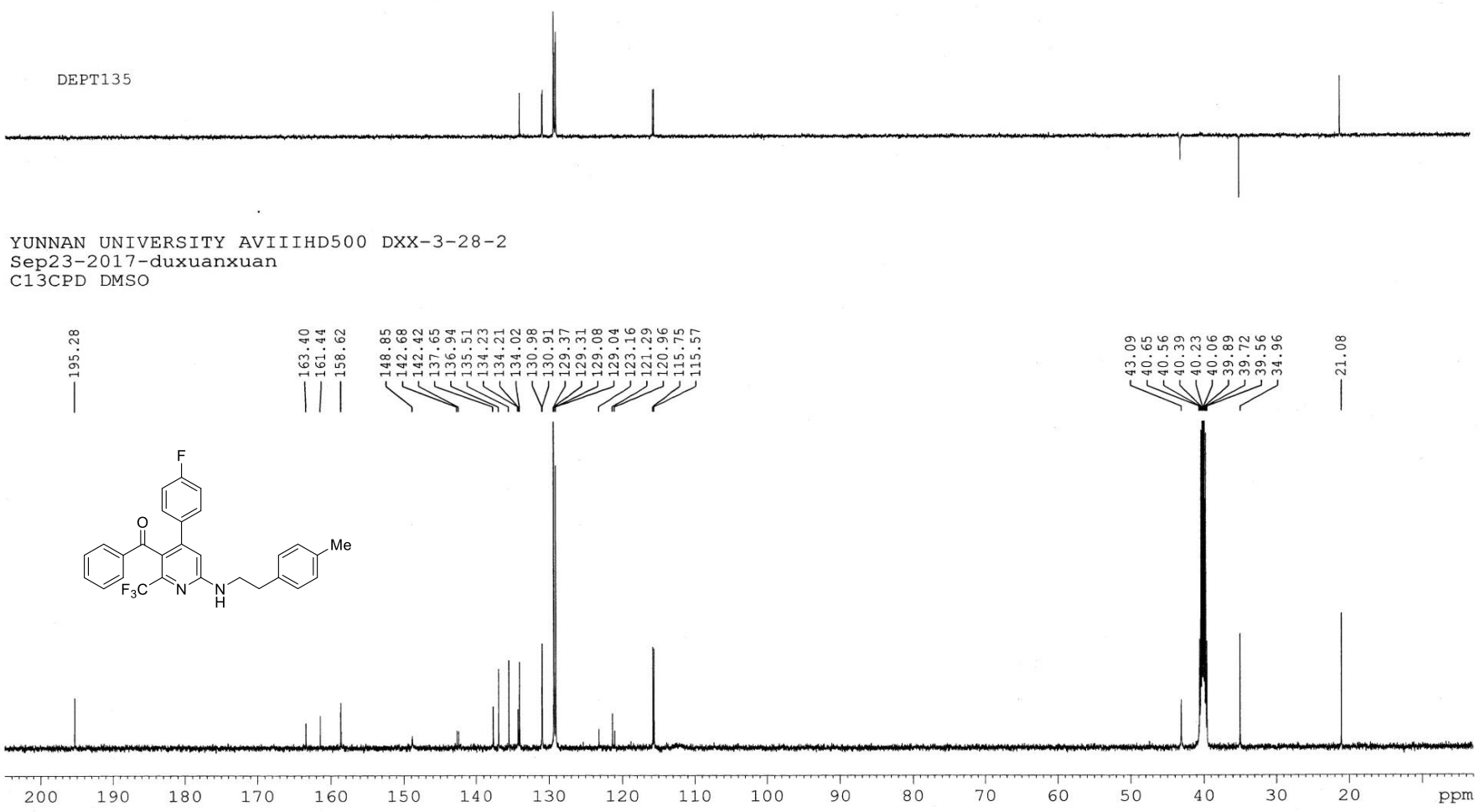

Figure S67. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5o**

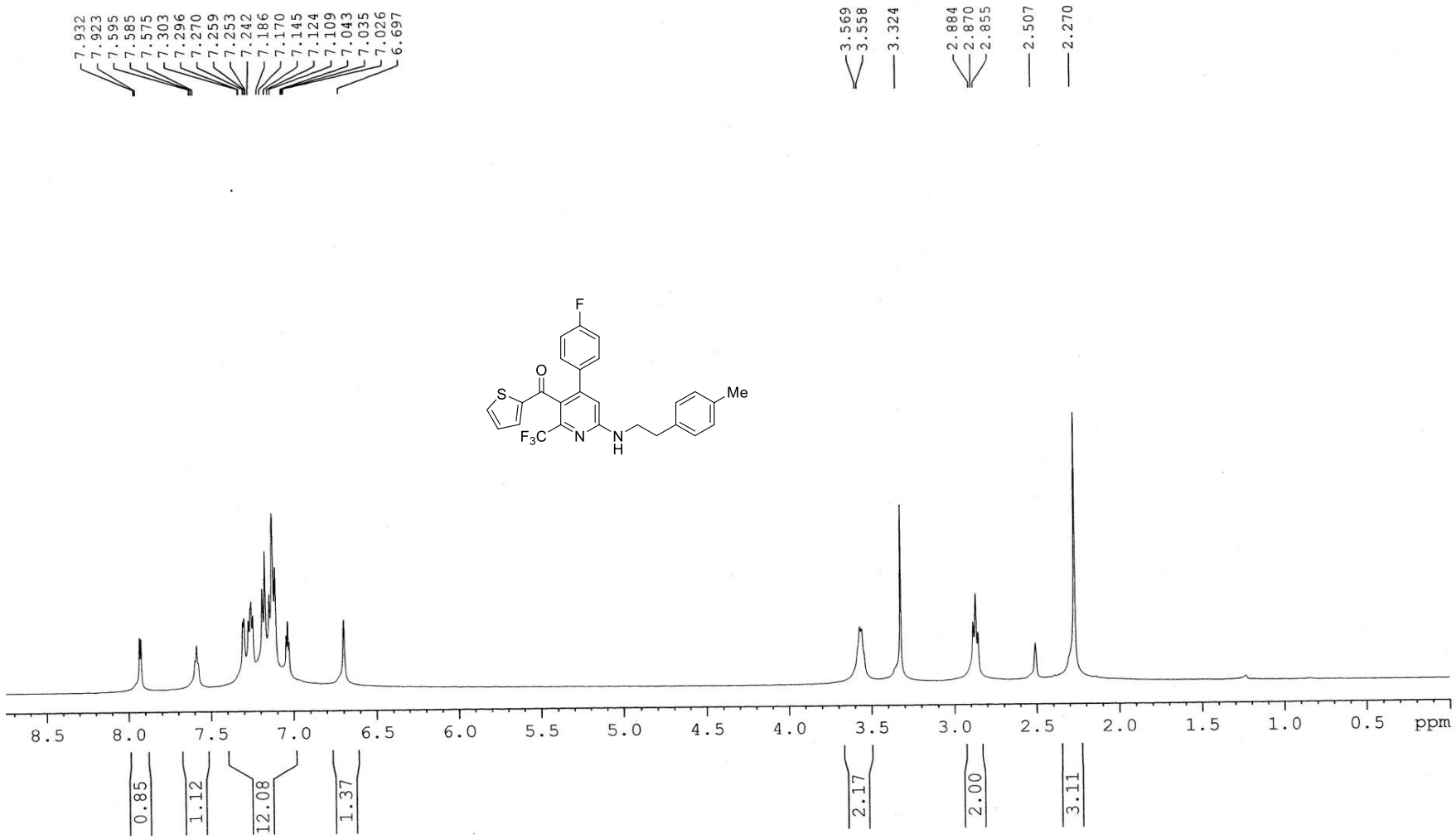

Figure S68. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5p**

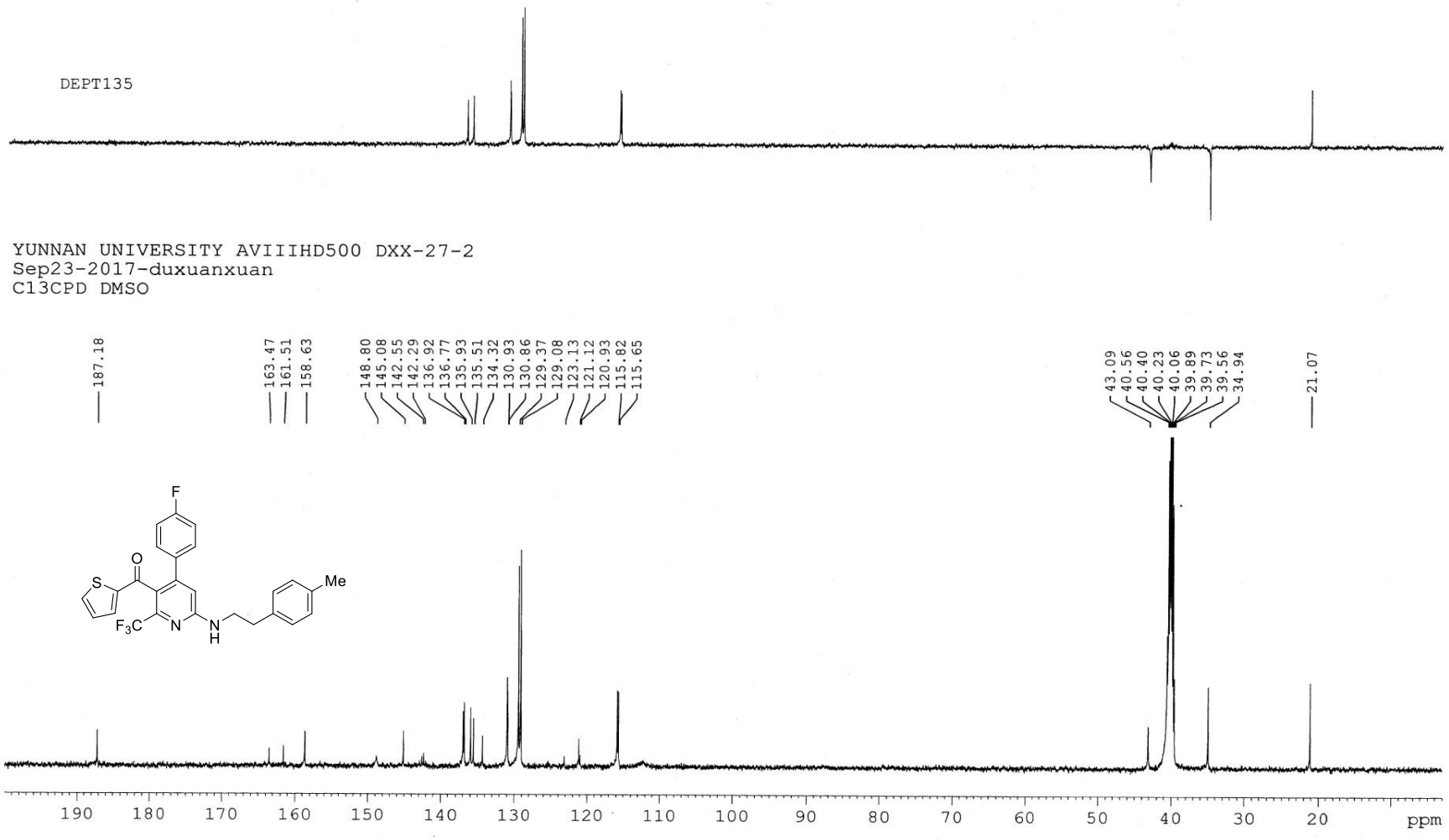

Figure S69. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5p**

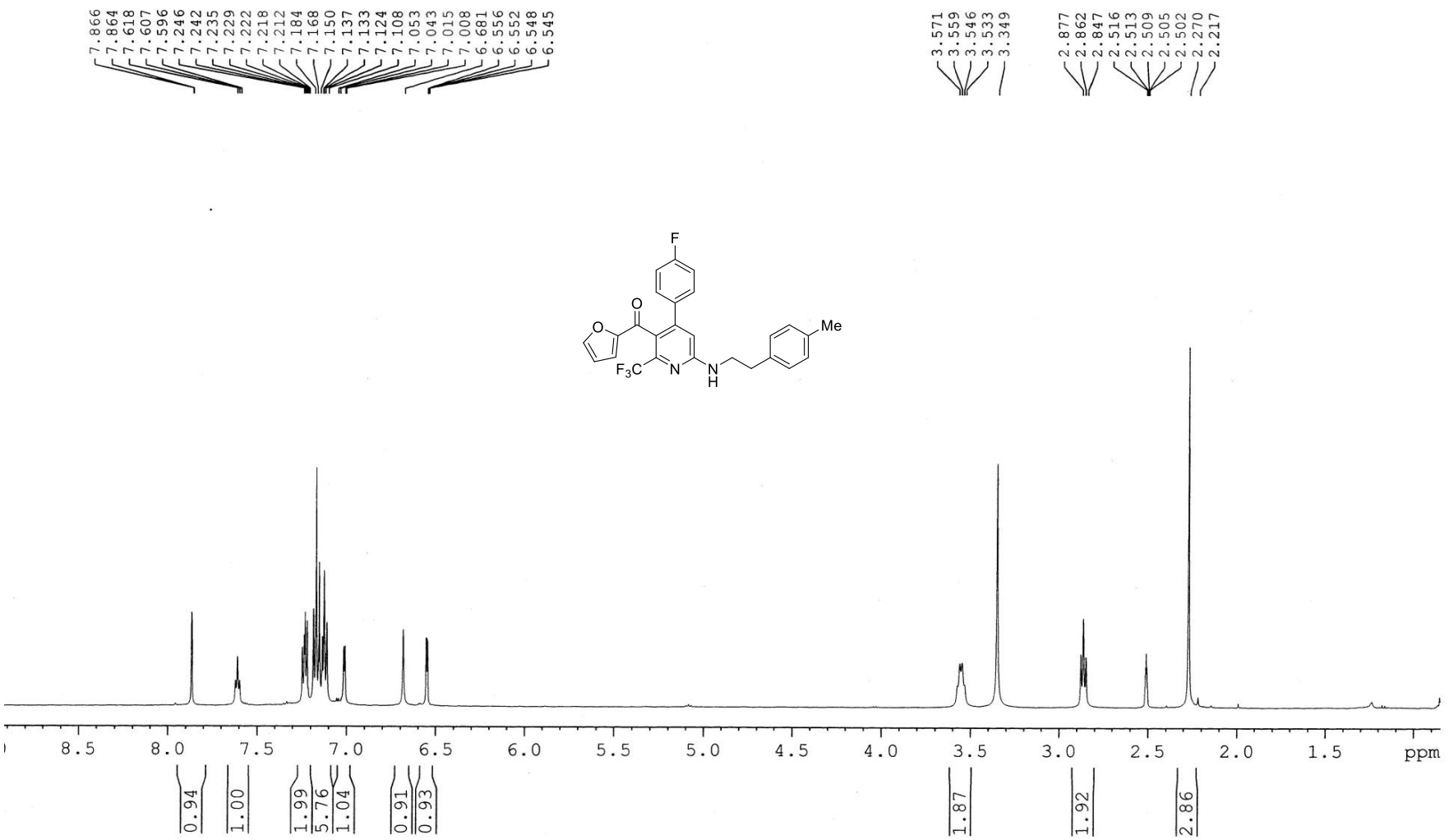

Figure S70. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5q**

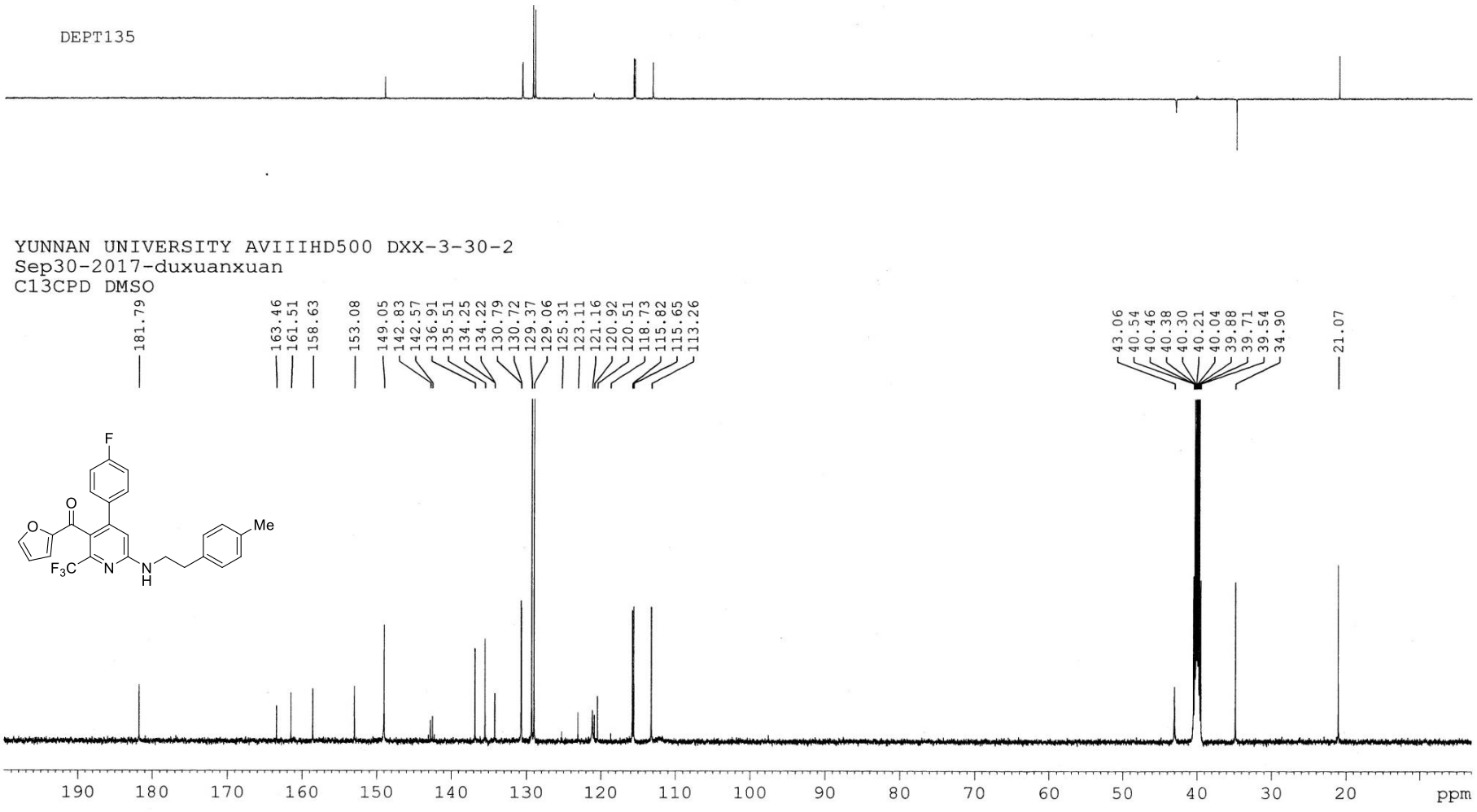

Figure S71. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5q**

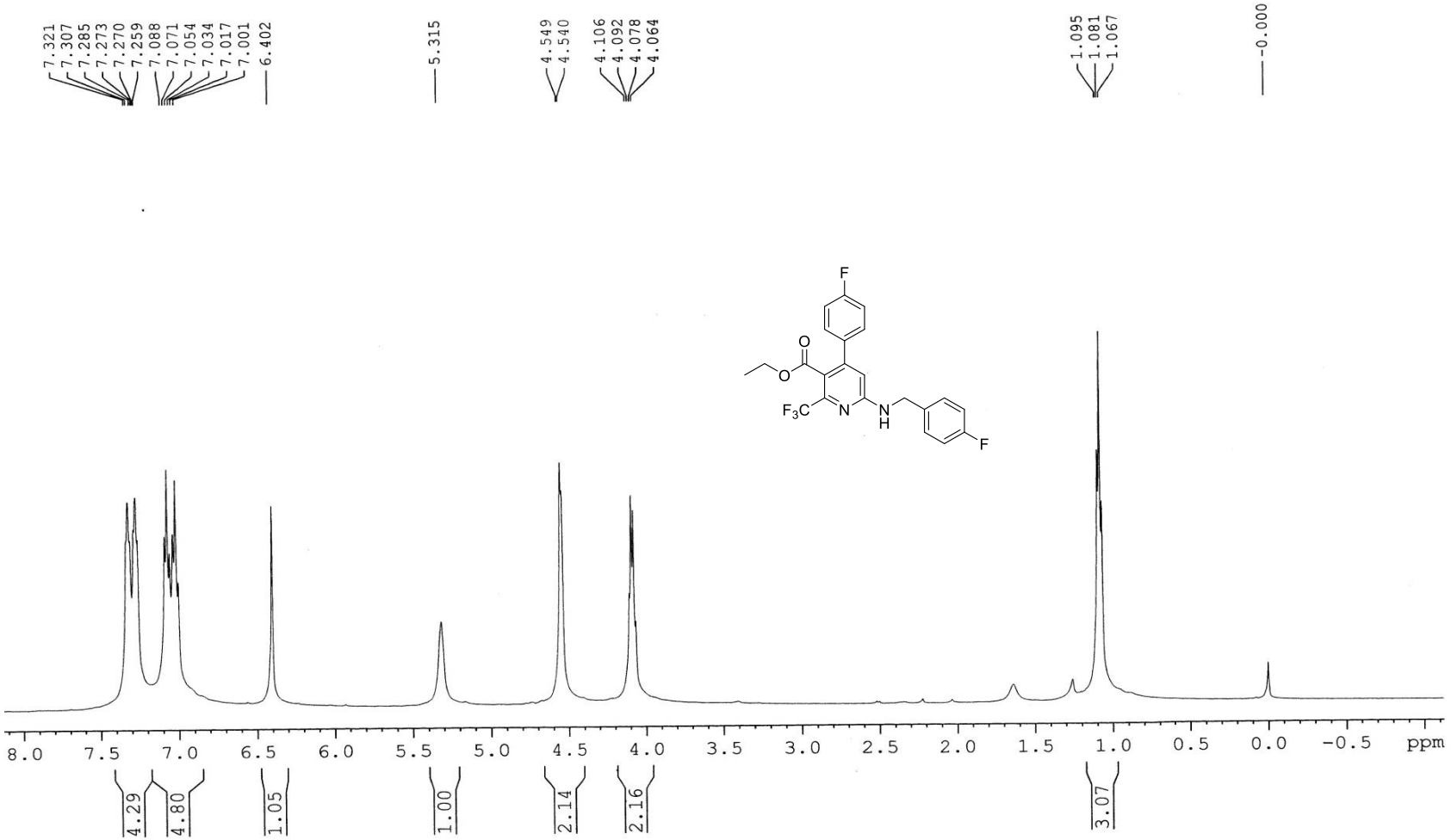

Figure S72. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **5r**

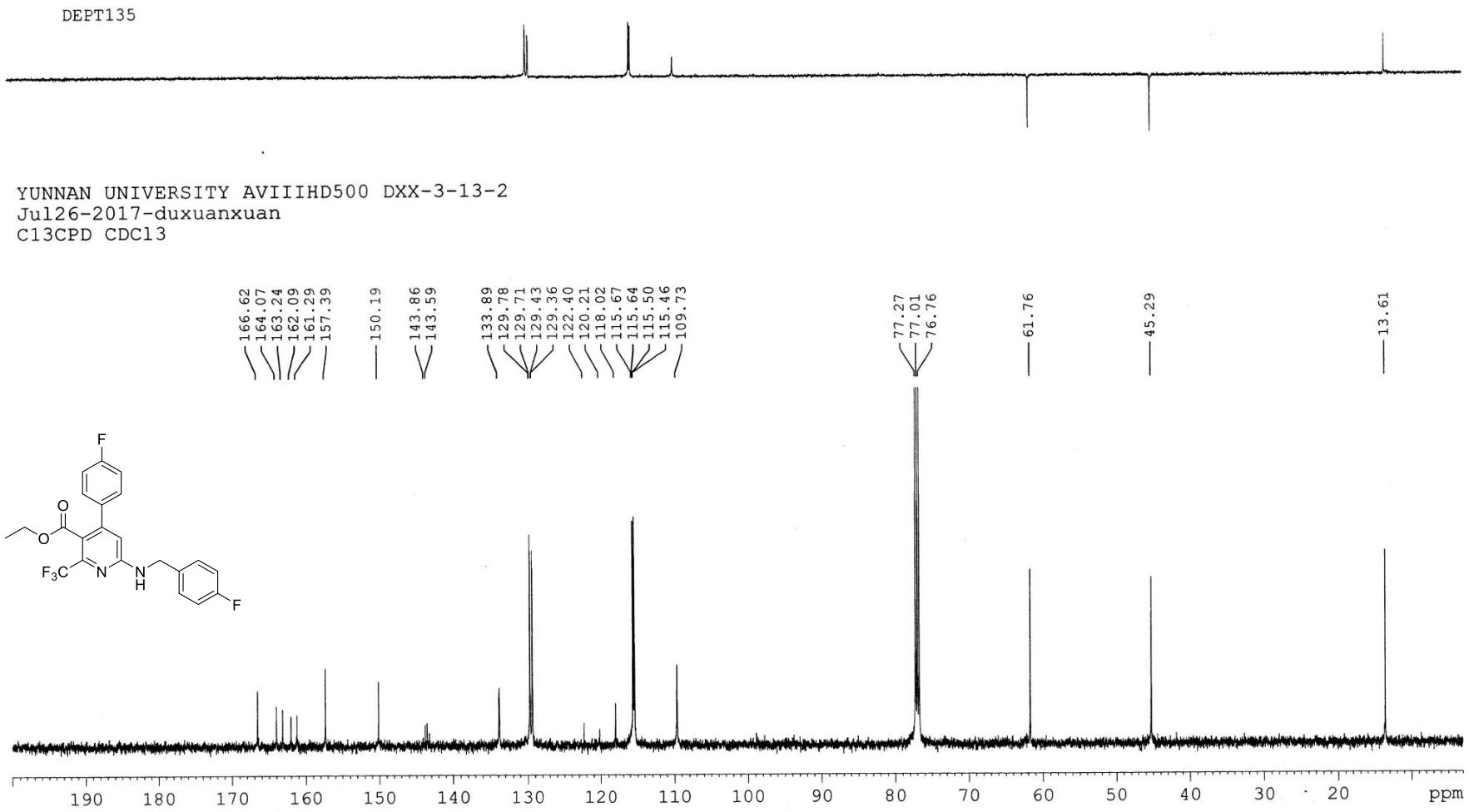

Figure S73. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **5r**

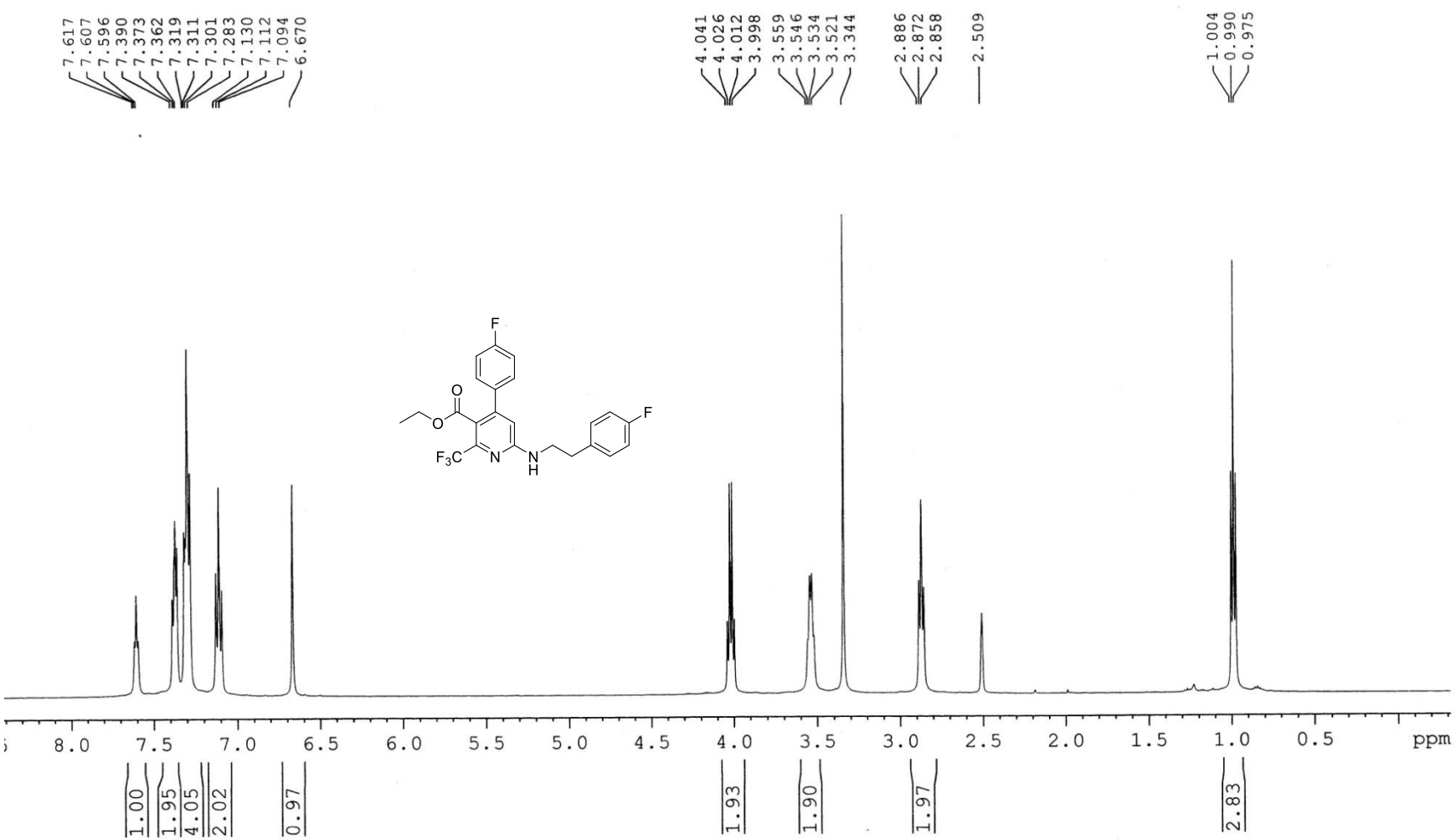

Figure S74. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5s**

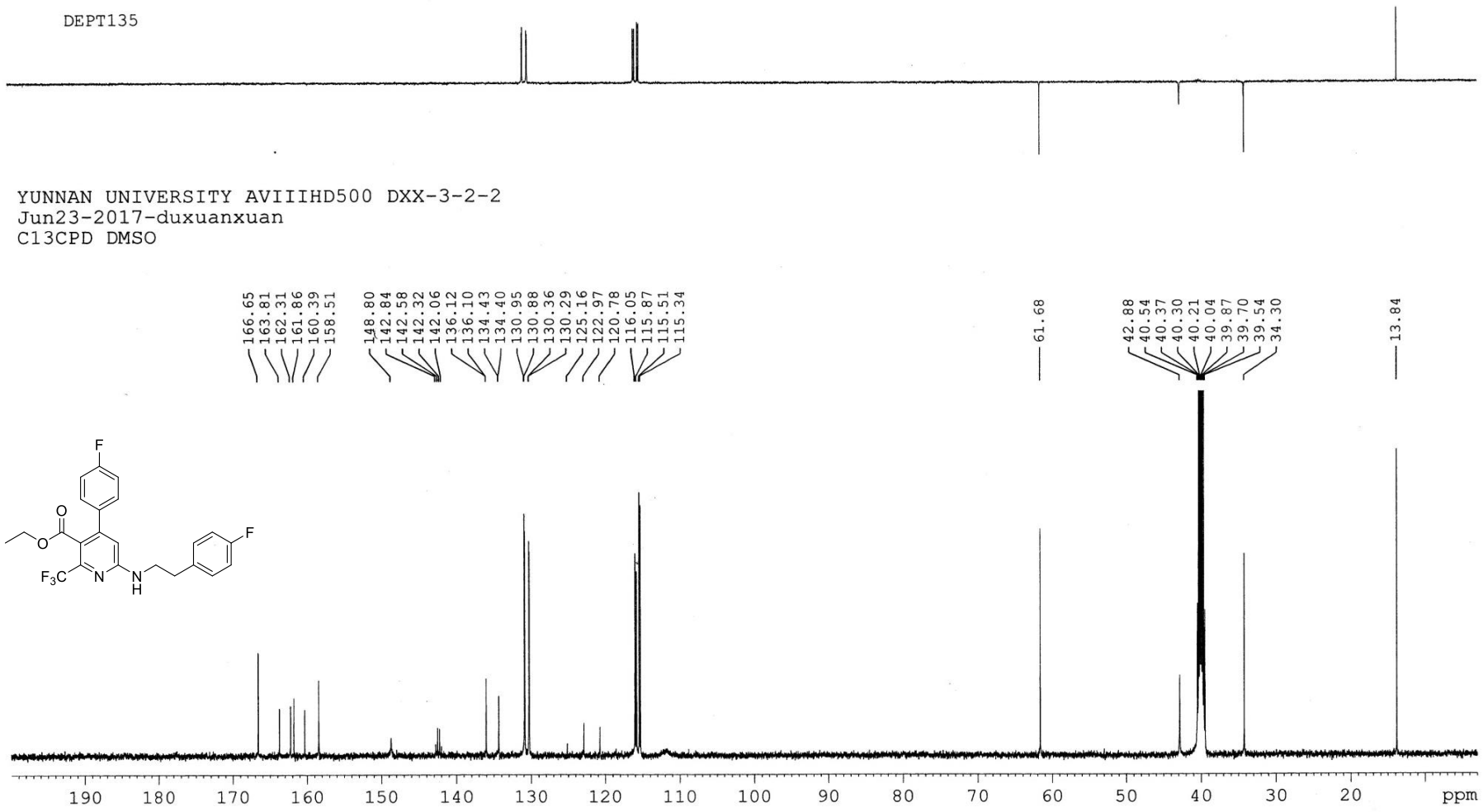

Figure S75. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5s**

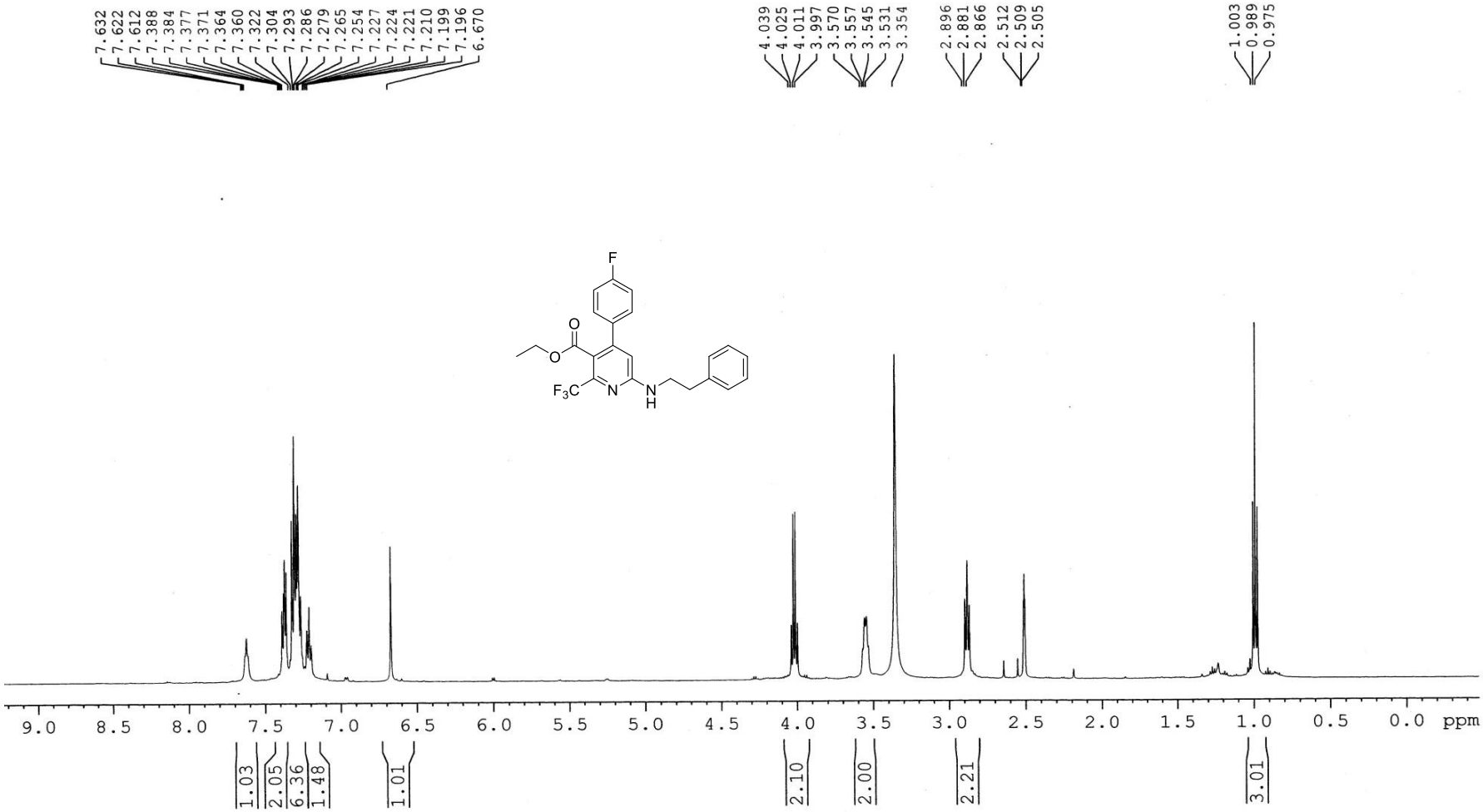

Figure S76. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5t**

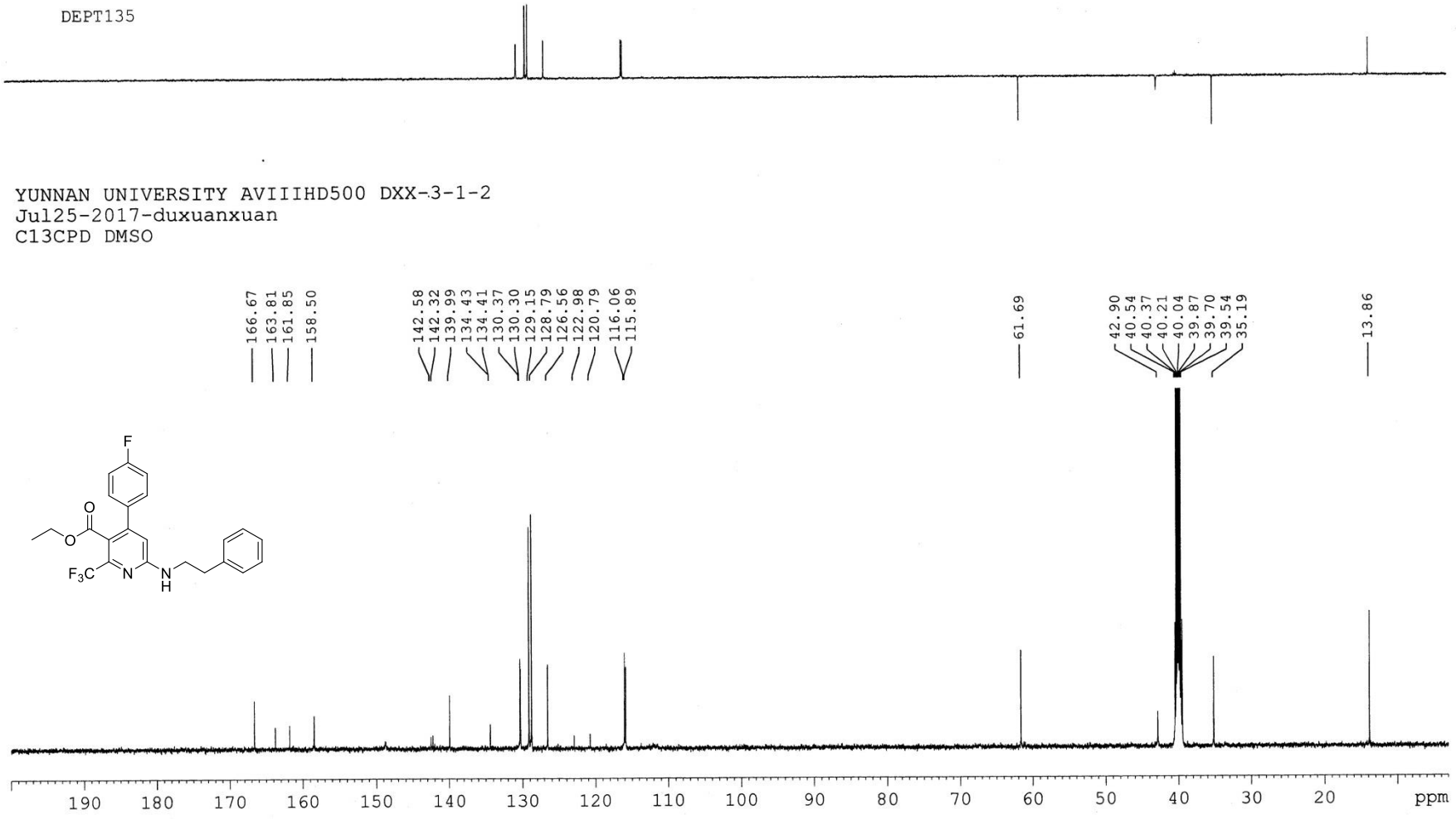

Figure S77. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5t**

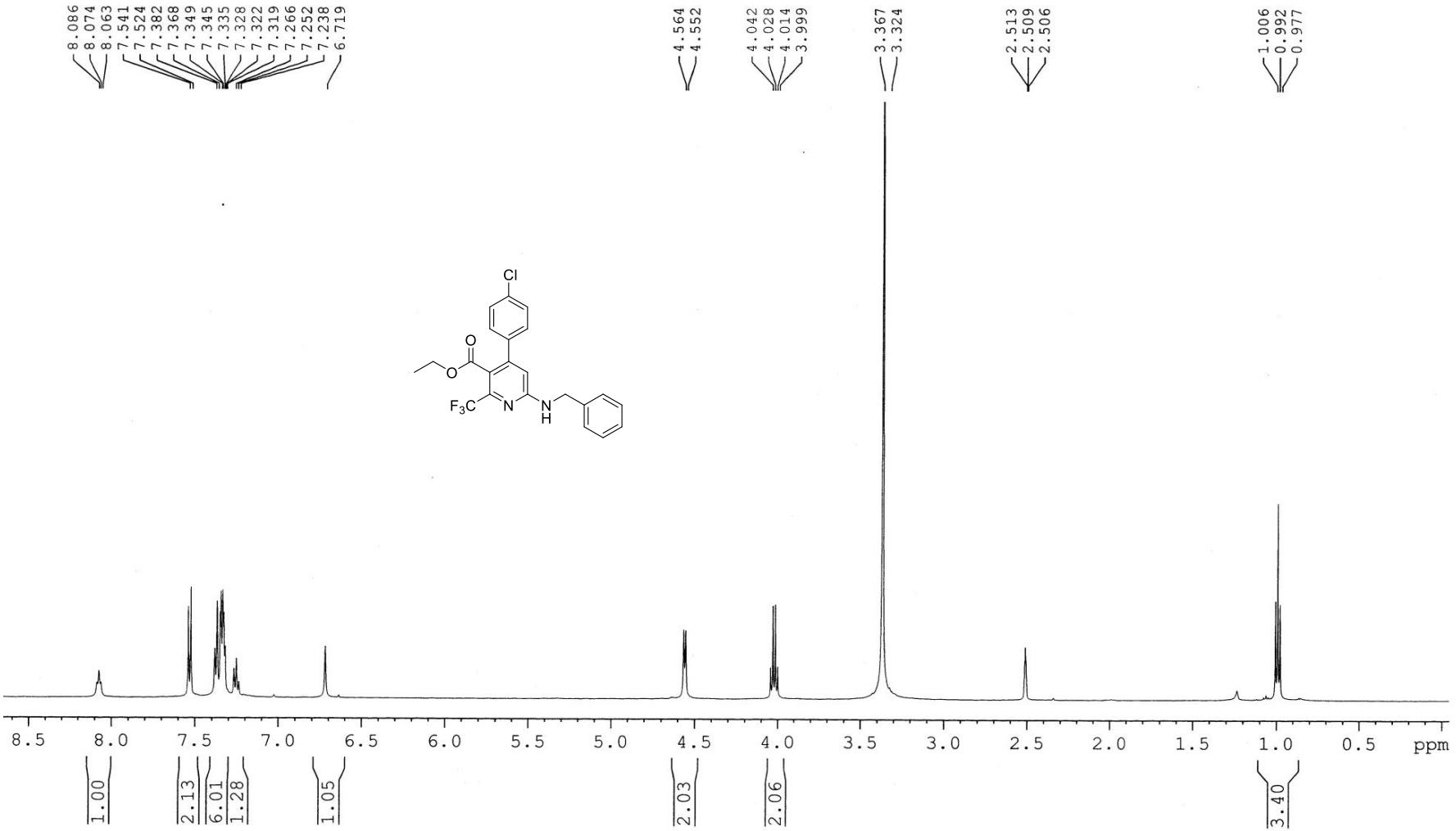

Figure S78. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5u**

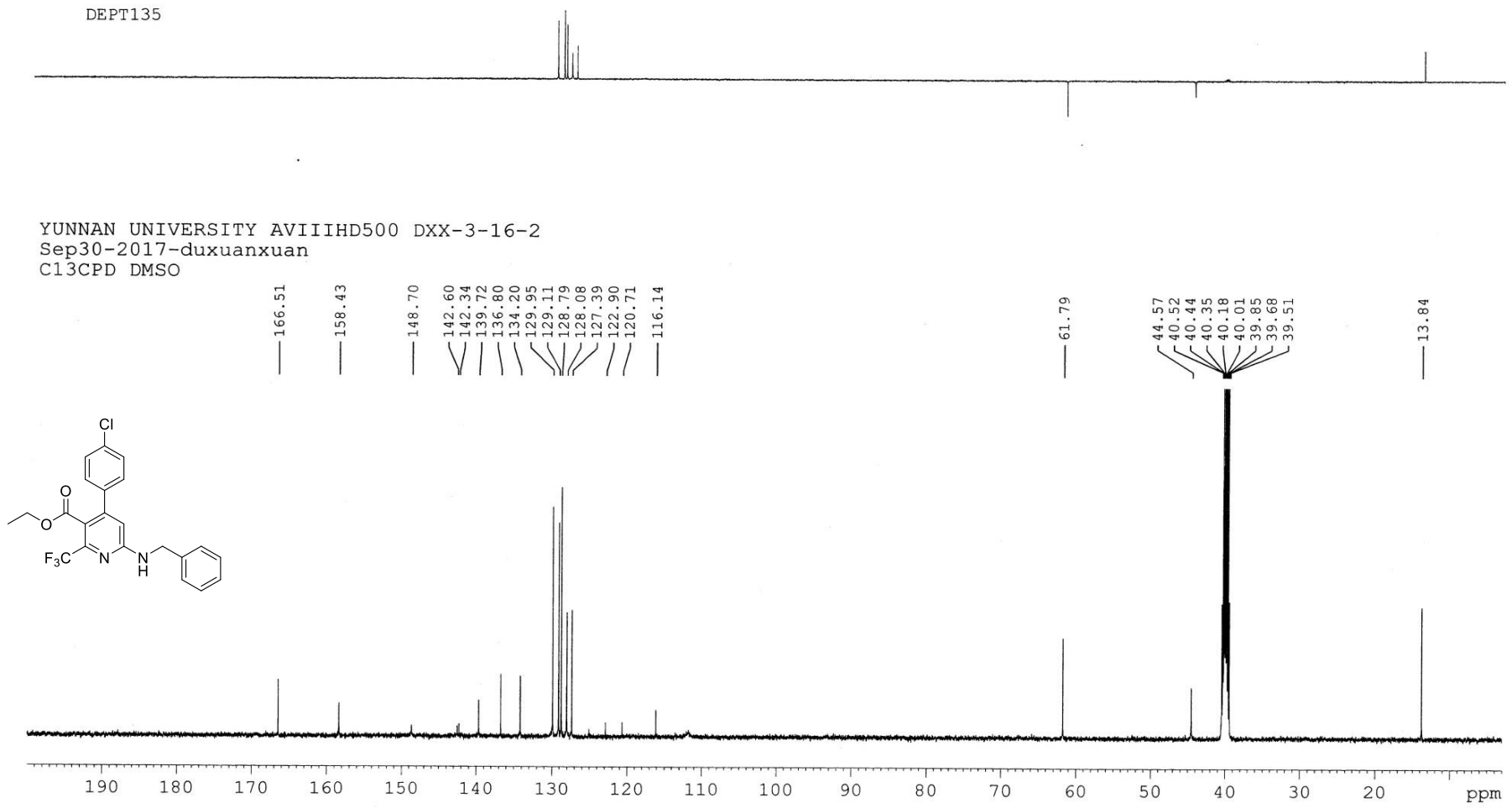

Figure S79. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5u**

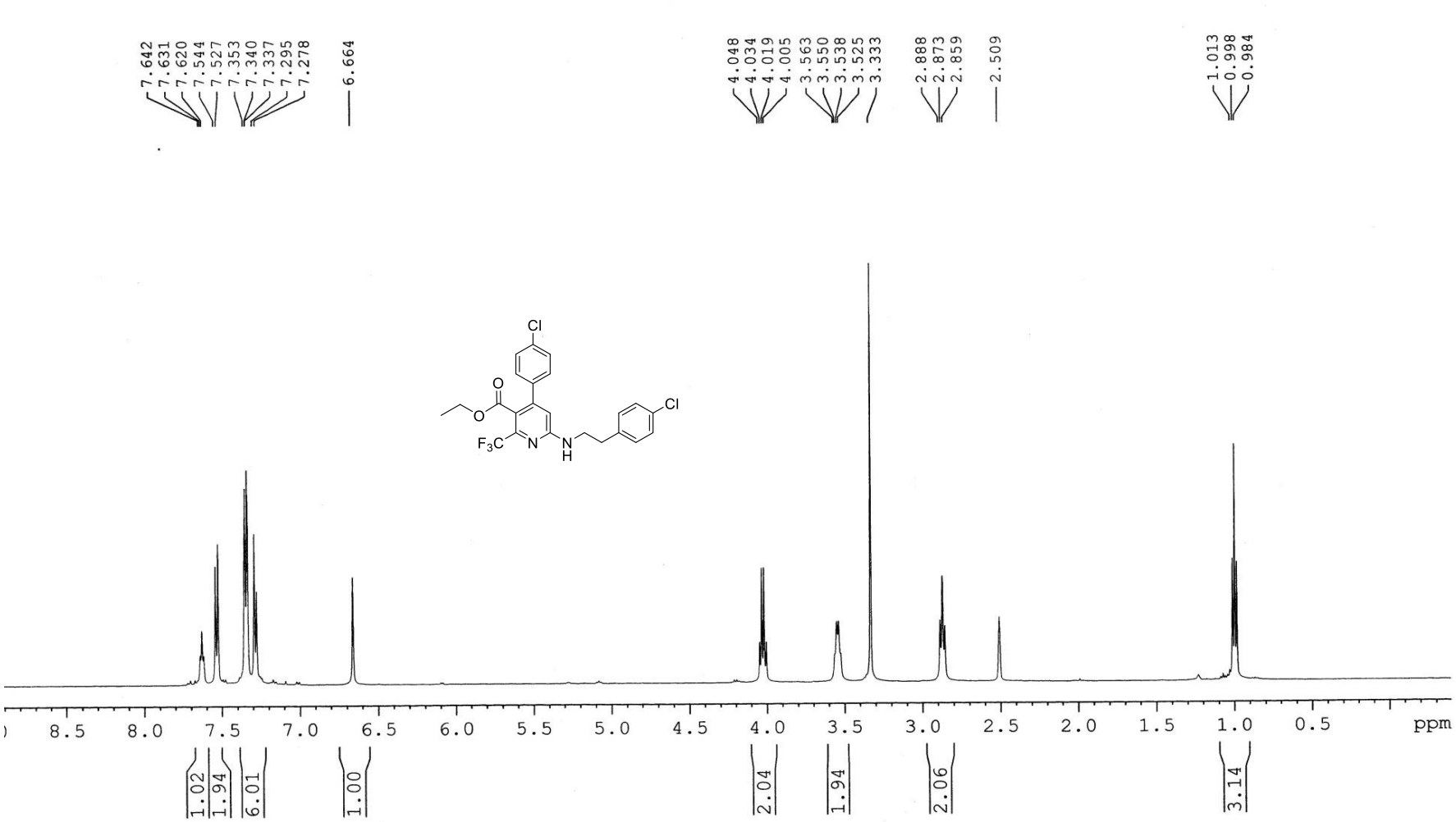

Figure S80. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **5v**

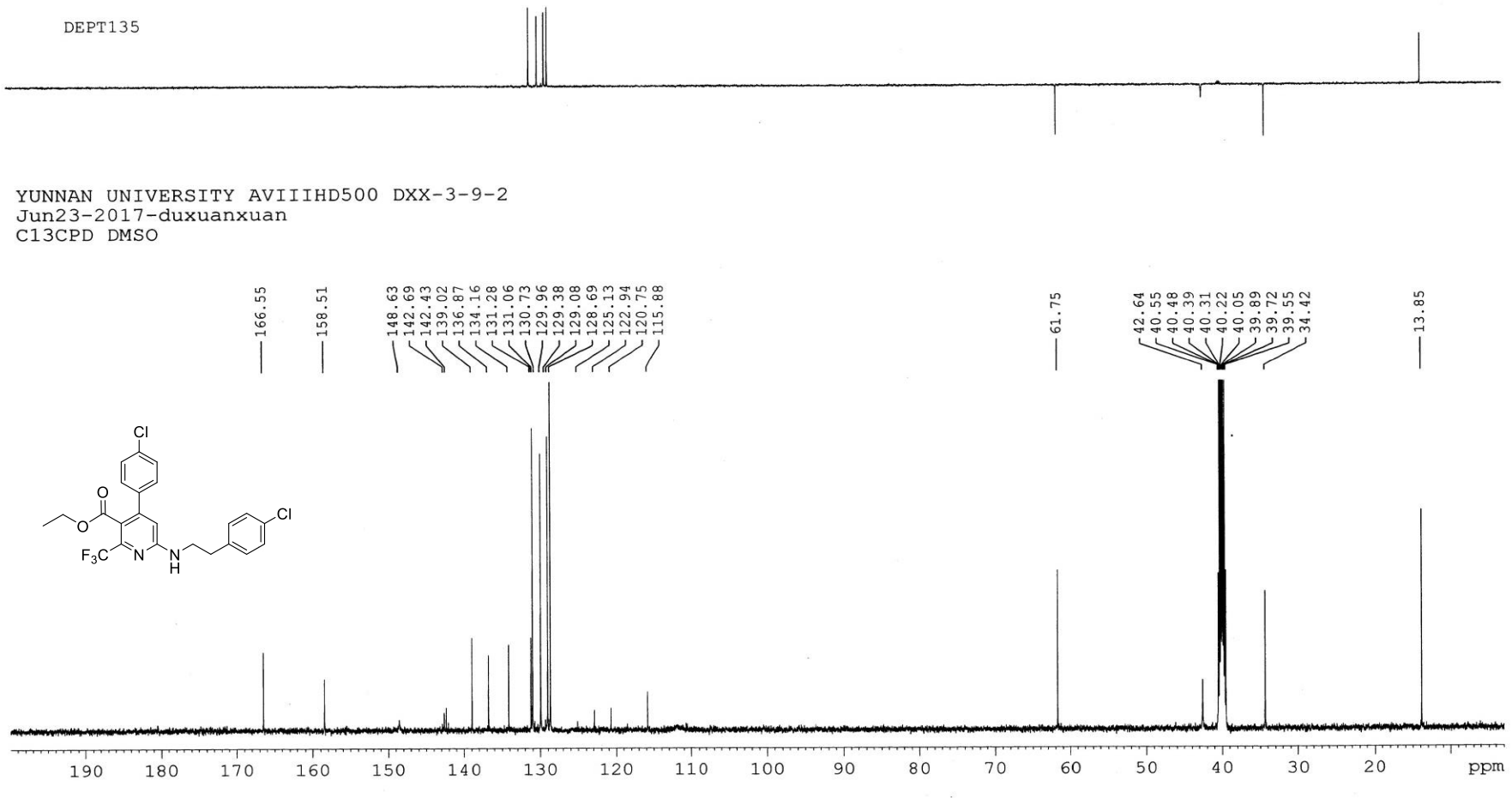

Figure S81. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **5v**

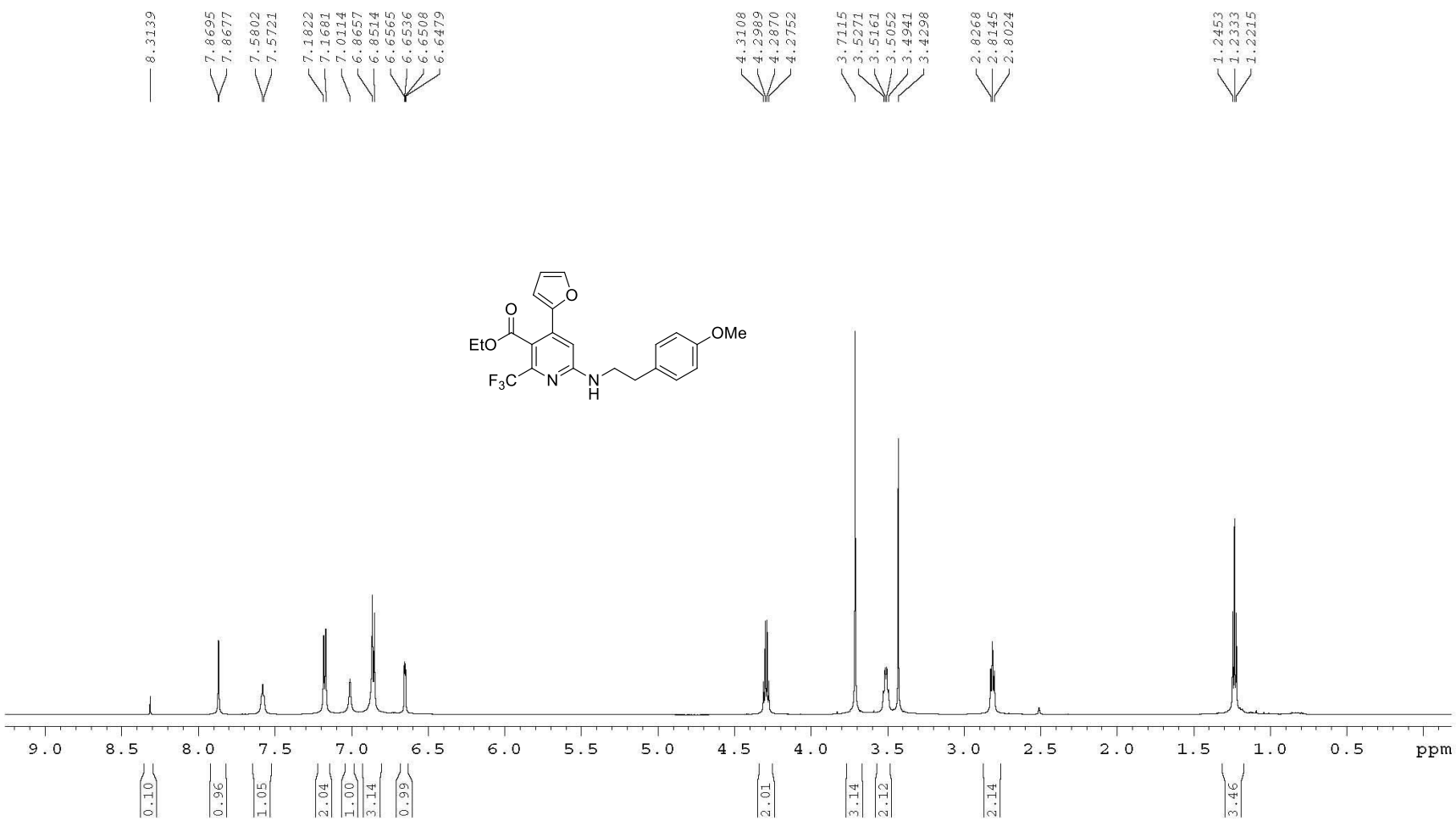

Figure S82. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **5w**

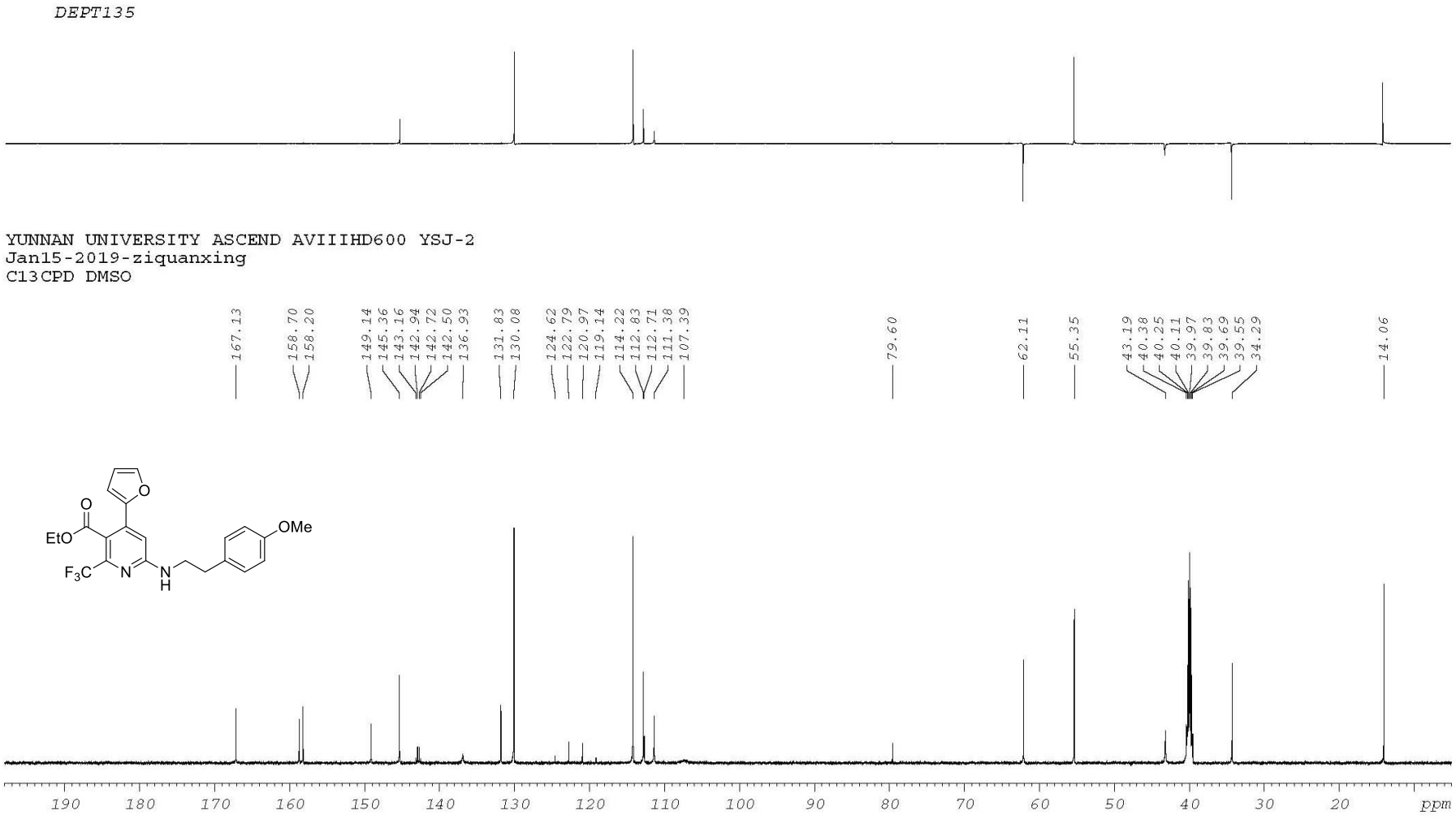

Figure S83. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **5w**

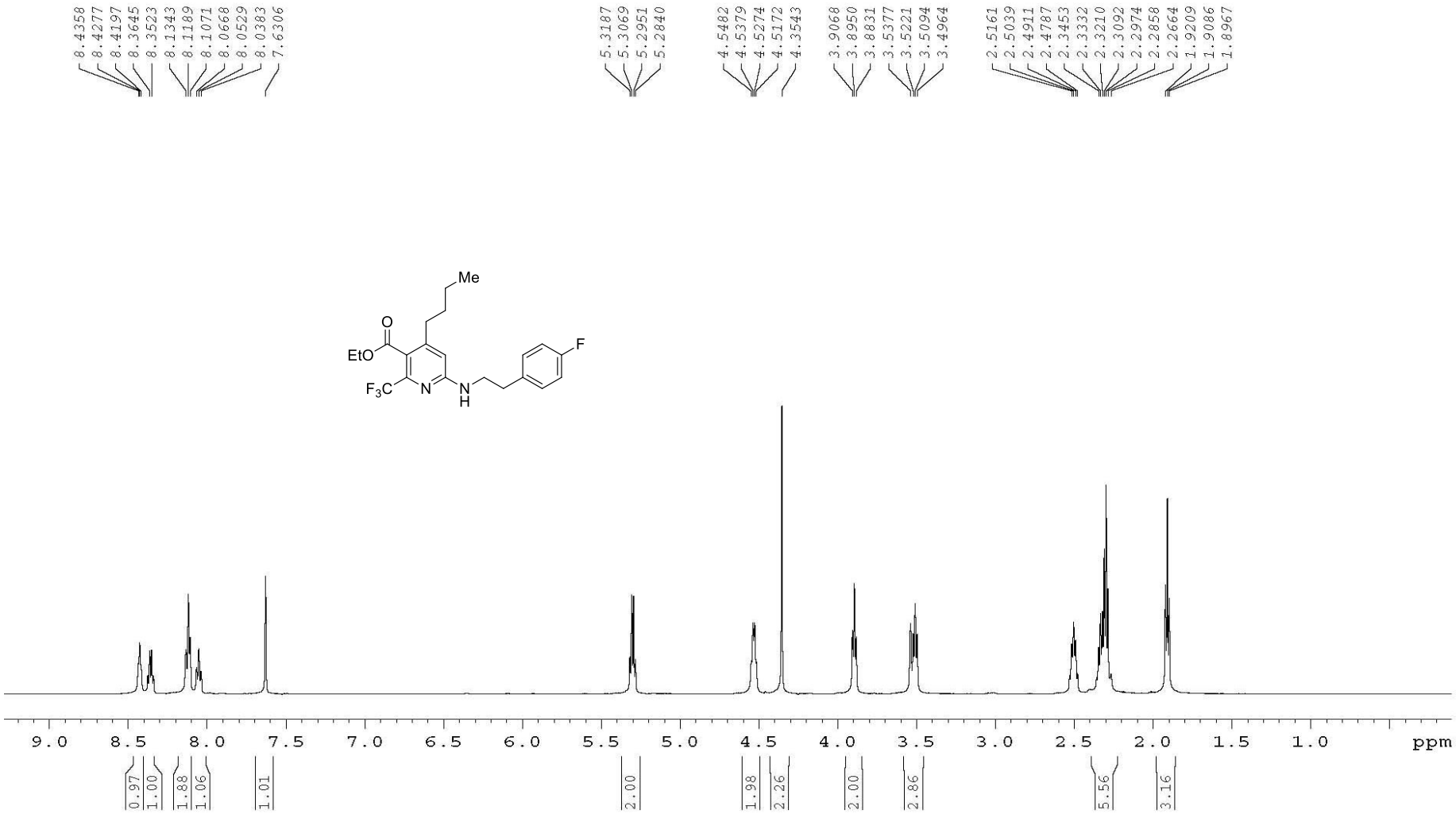

Figure S84. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **5x**

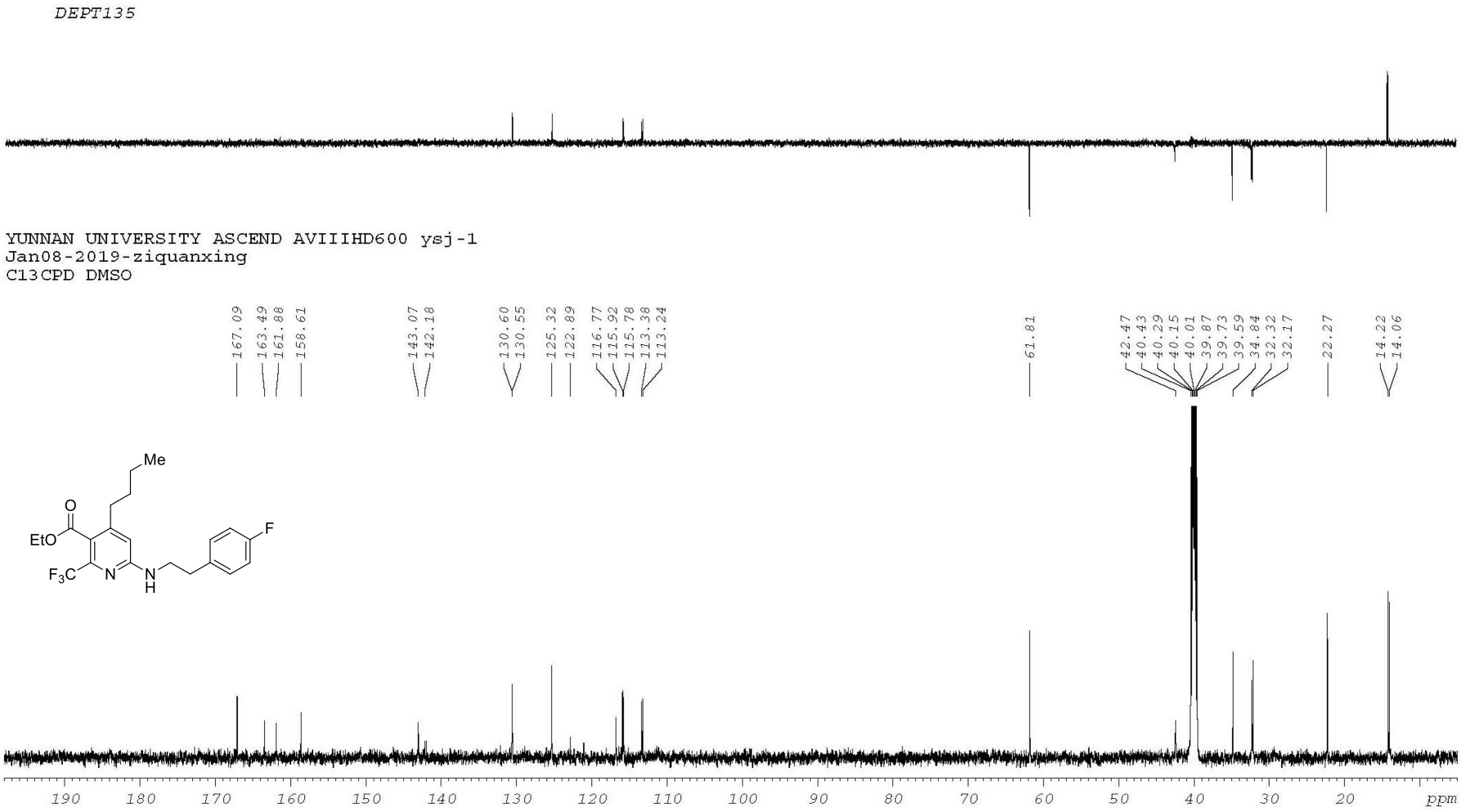

Figure S85. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **5x**

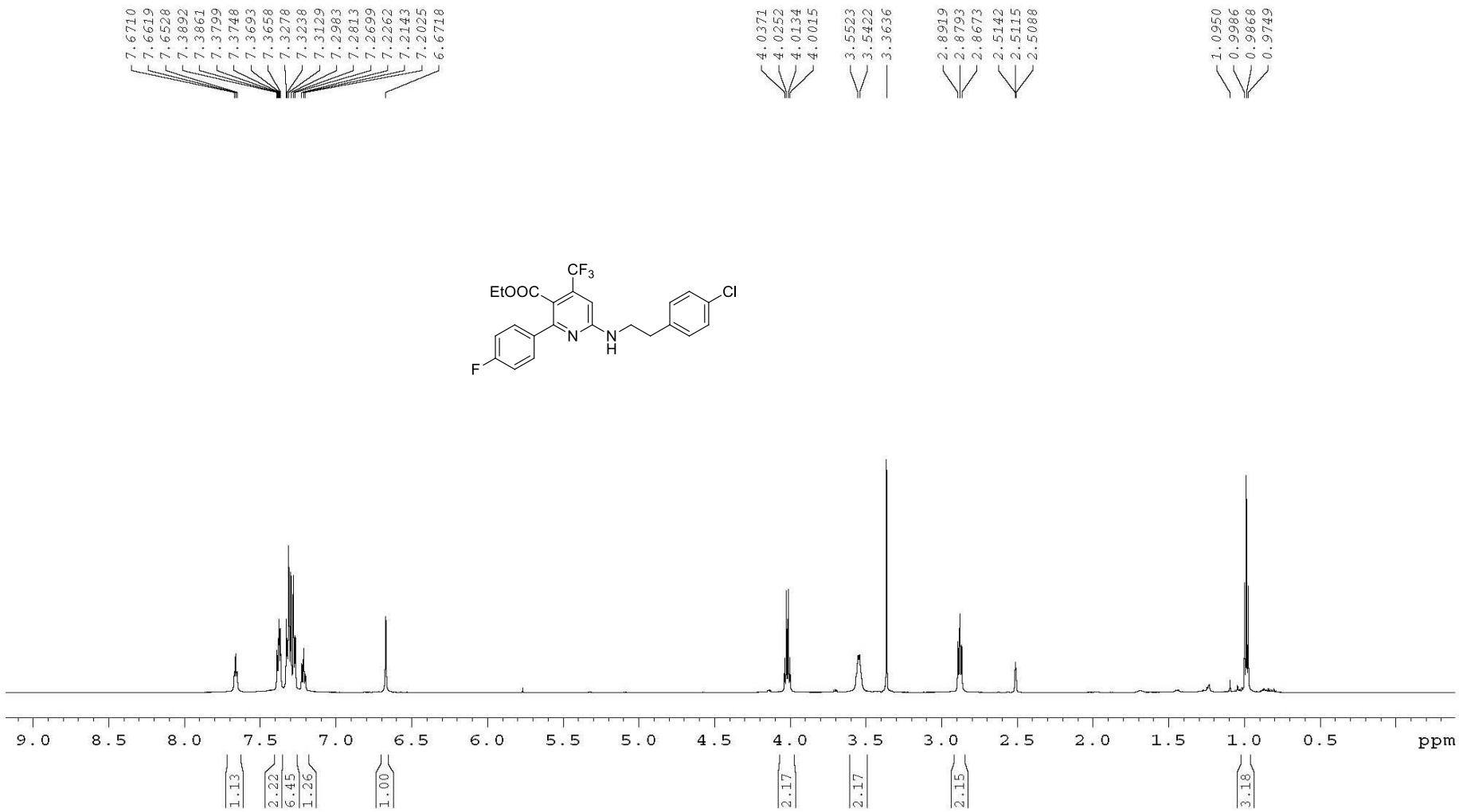

Figure S86. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **5f'**

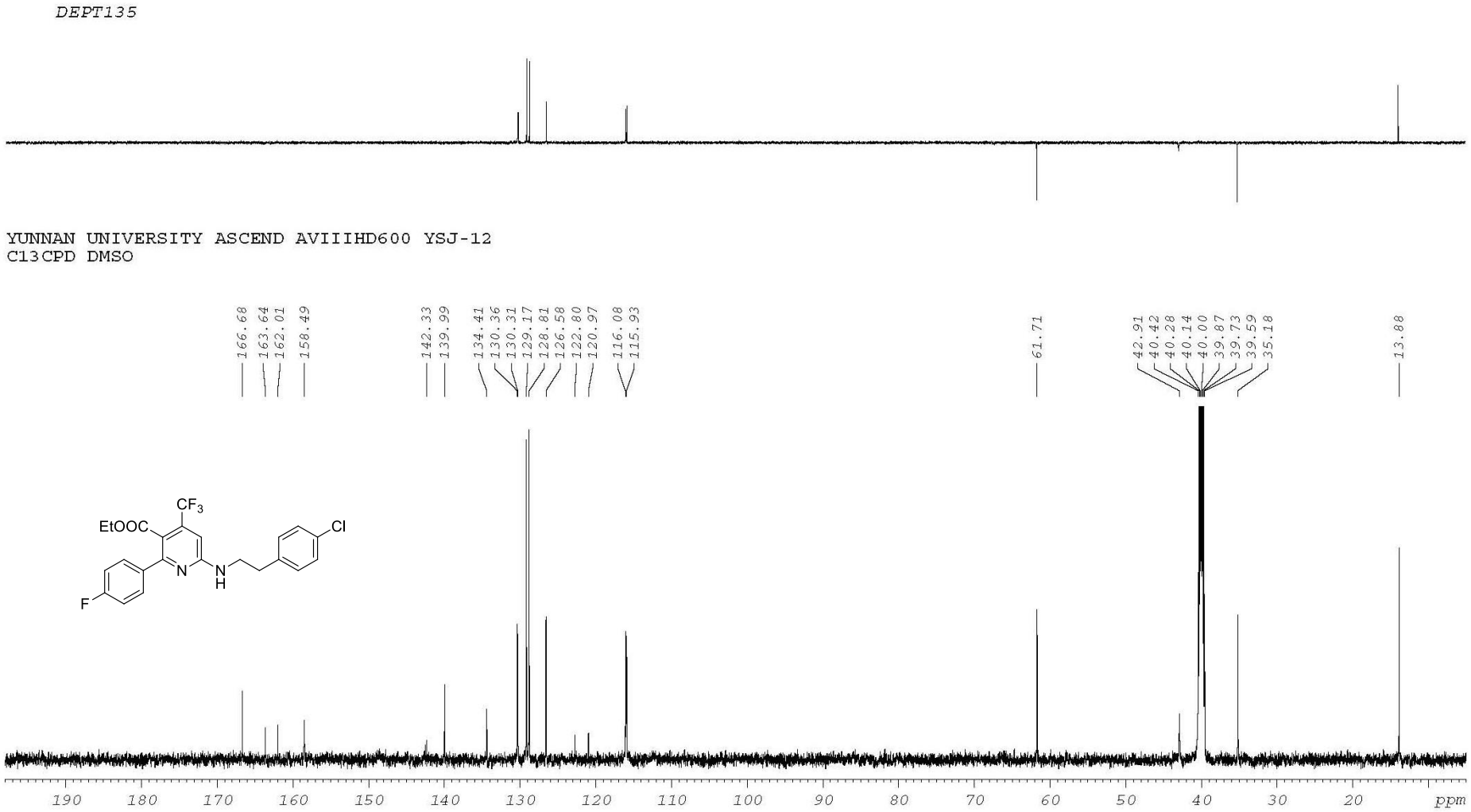

Figure S87. ^{13}C NMR (150MHz, DMSO-d_6) spectra of compound **5f'**

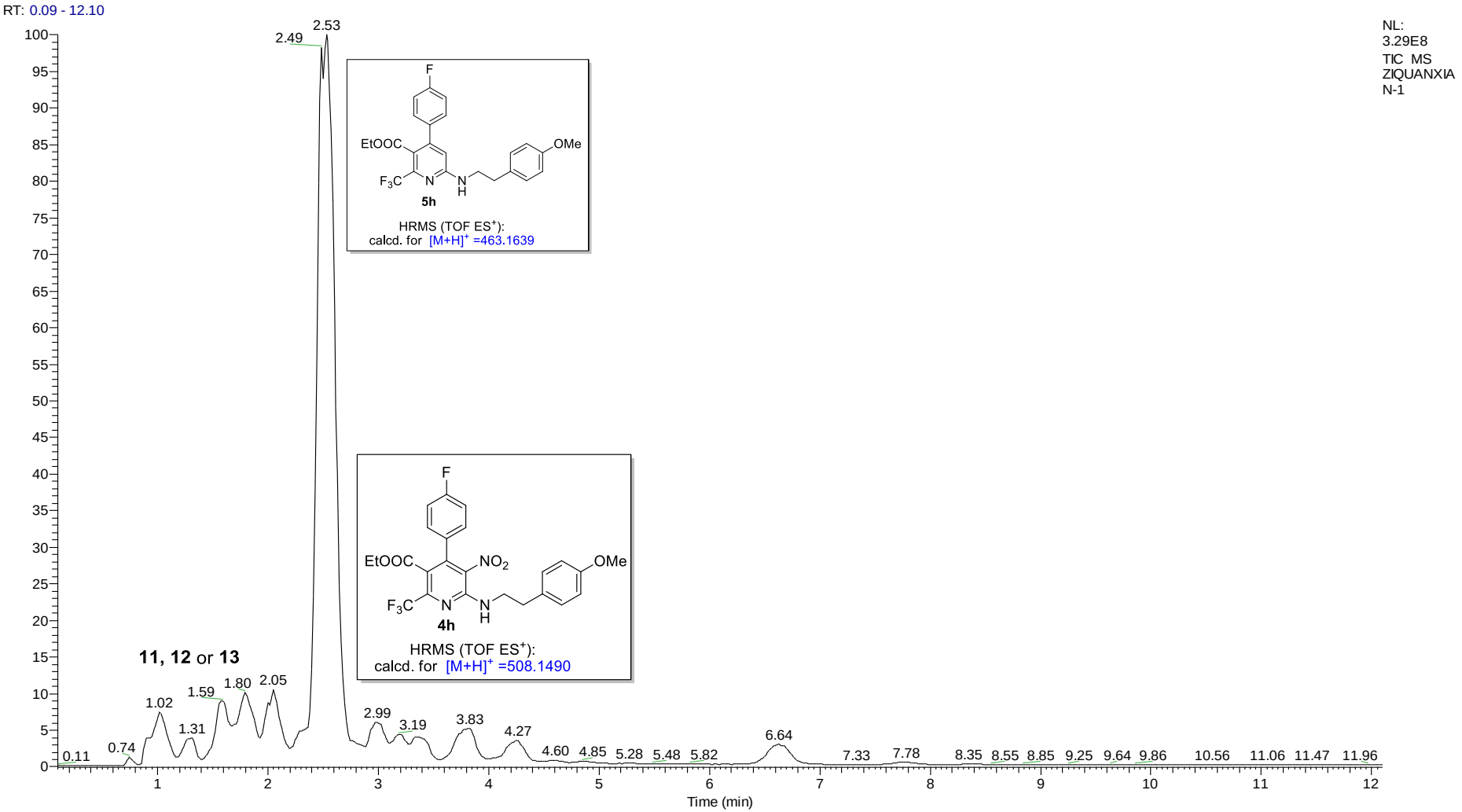

Figure S88. HPLC of the reaction mixture

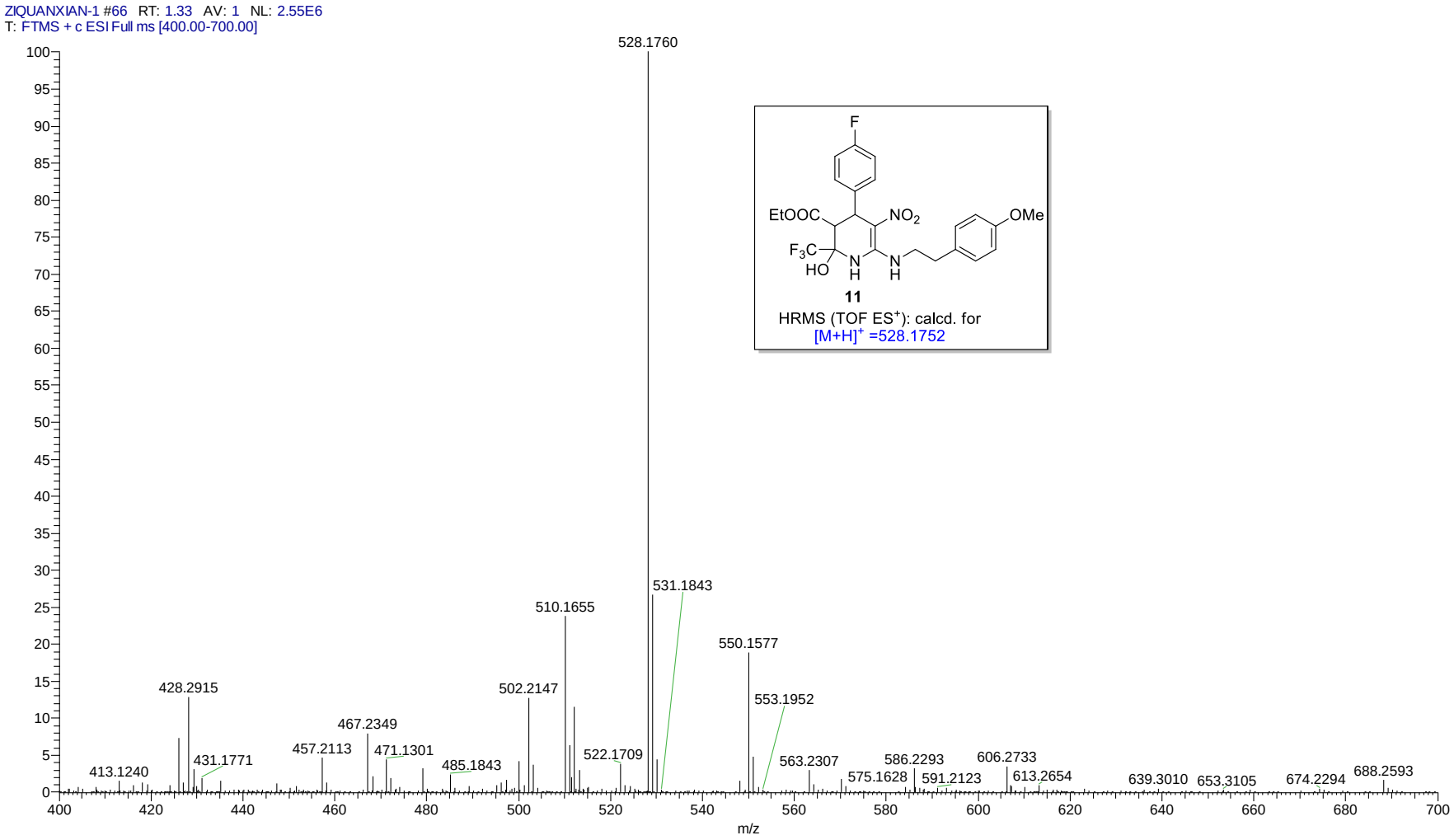

Figure S89. HRMS of intermediate **11**

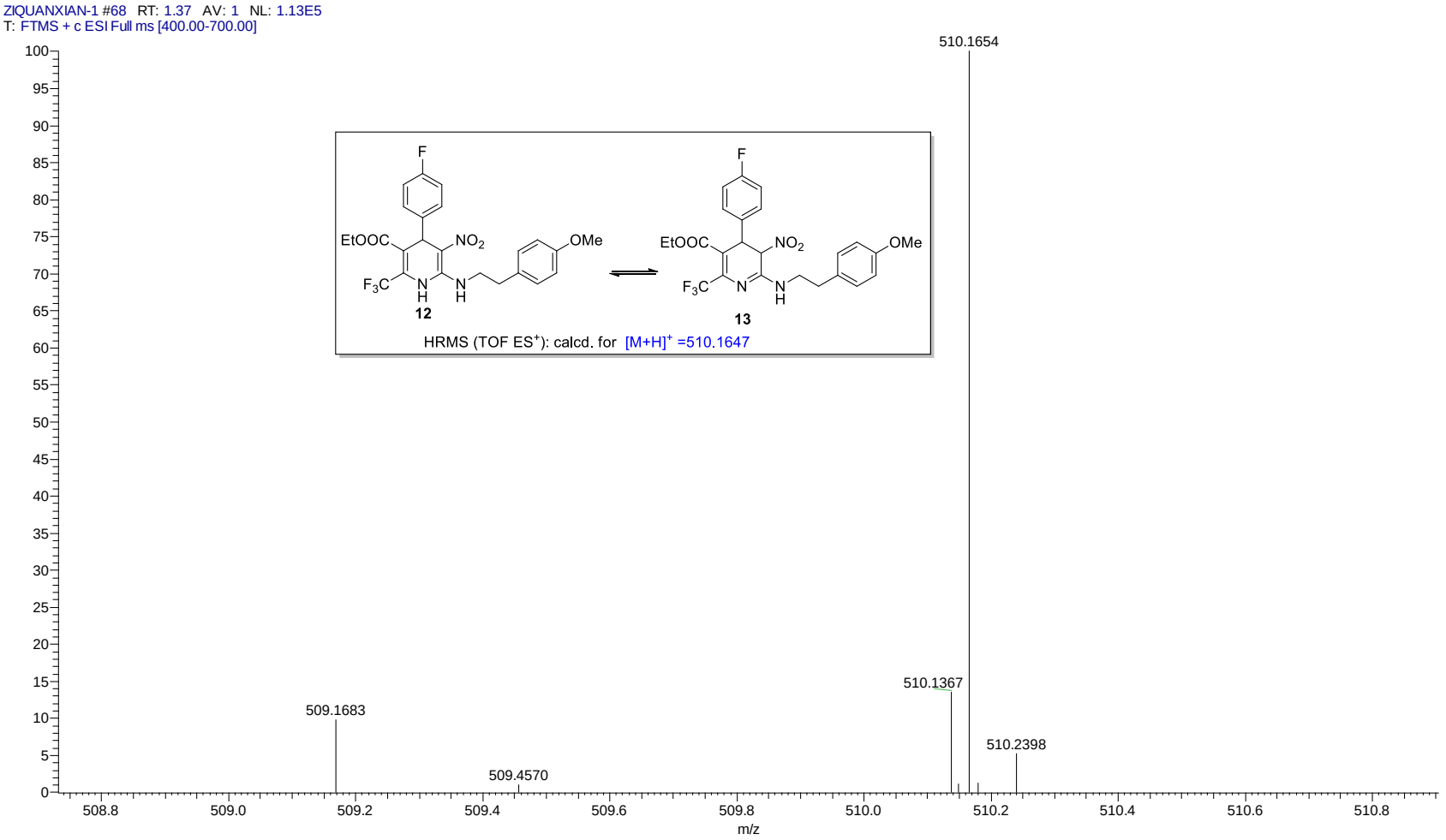

Figure S90. HRMS of intermediate **12/13**

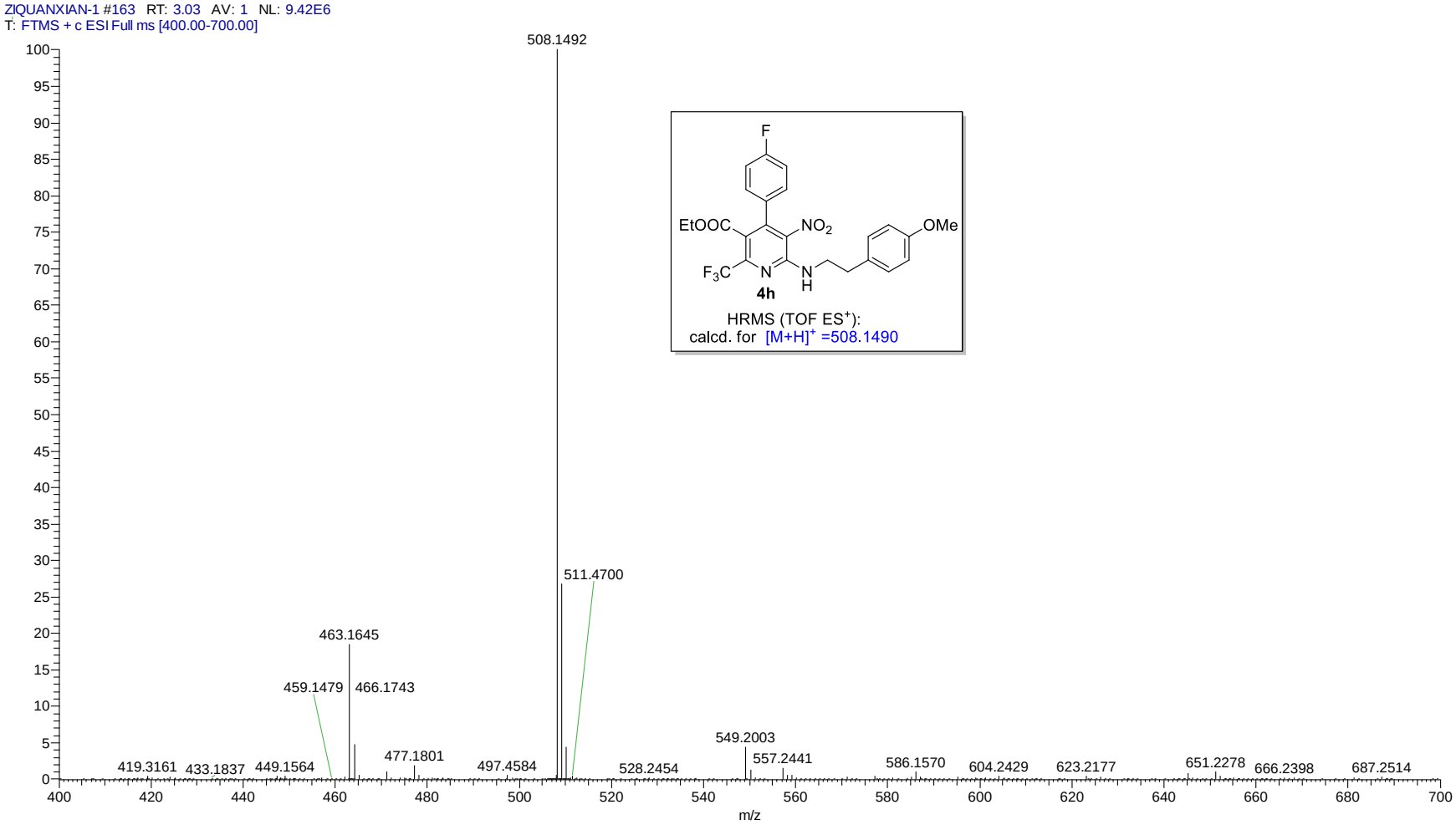

Figure S91. HRMS of compound **4h**

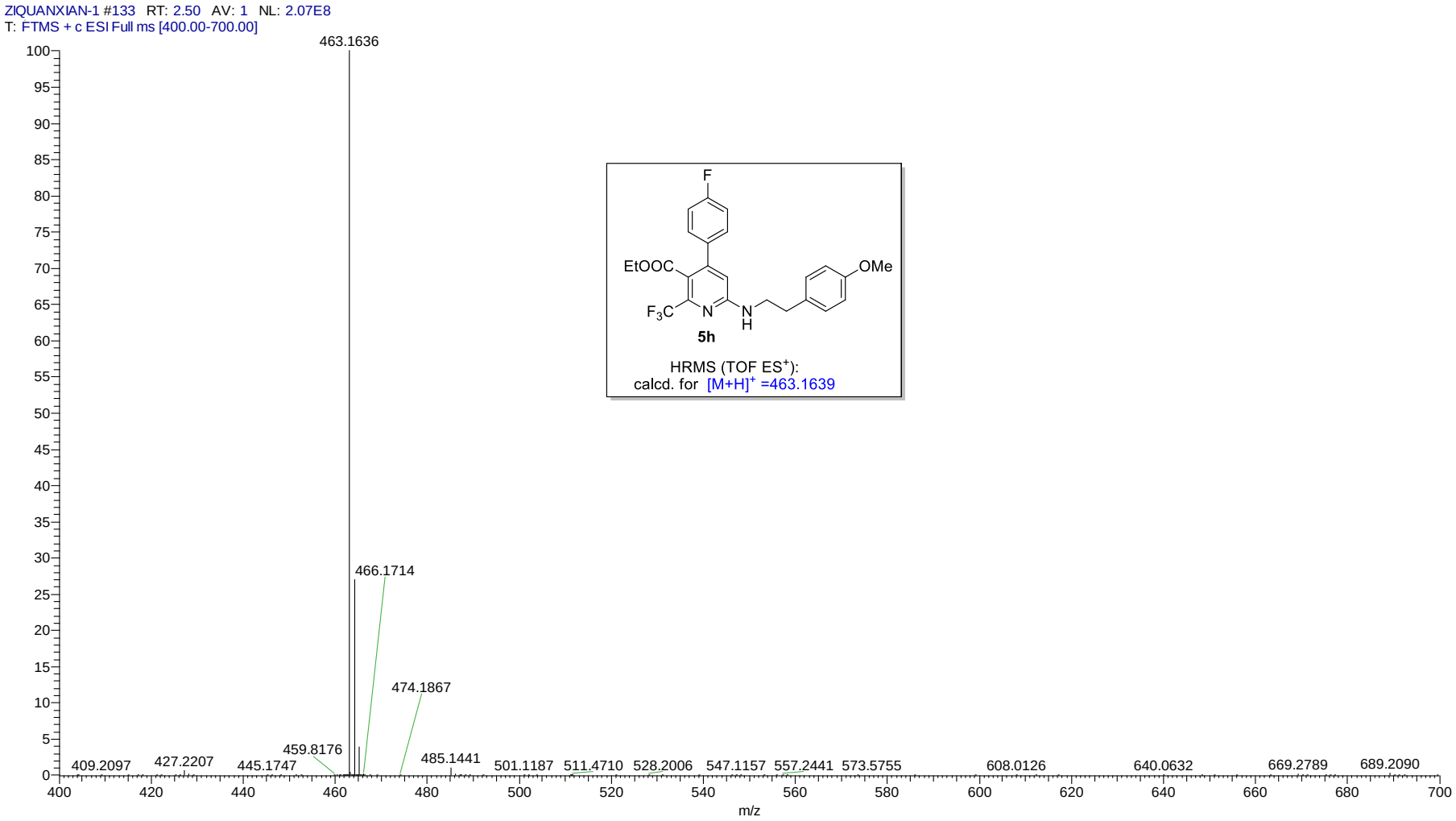

Figure S92. HRMS of compound **5h**