Supplementary Material

Malic acid as an effective and valuable bioorganocatalyst for one-pot, three-component synthesis of pyrrolidinone derivatives

Hamideh Ahankar,*[a] Ali Ramazani,*[b,c] Katarzyna Ślepokura,[d] and Vasyl Kinzhybalo[e]

[a] *Department of Chemistry, Abhar Branch, Islamic Azad University P O Box 22, Abhar, Iran*
[b] *Department of Chemistry, University of Zanjan, 45371-38791, Zanjan, Iran*
[c] *Department of Biotechnology, Research Institute of Modern Biological Techniques (RIMBT), University of Zanjan, Zanjan 45371-38791, Iran*
[d] *Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie St., 50-383 Wrocław, Poland*
[e] *Institute of Low Temperature and Structure Research, PAS, 2 Okólna St., 50-422 Wrocław, Poland*
Email: hahankar@gmail.com, aliramazani@gmail.com

Table of Contents

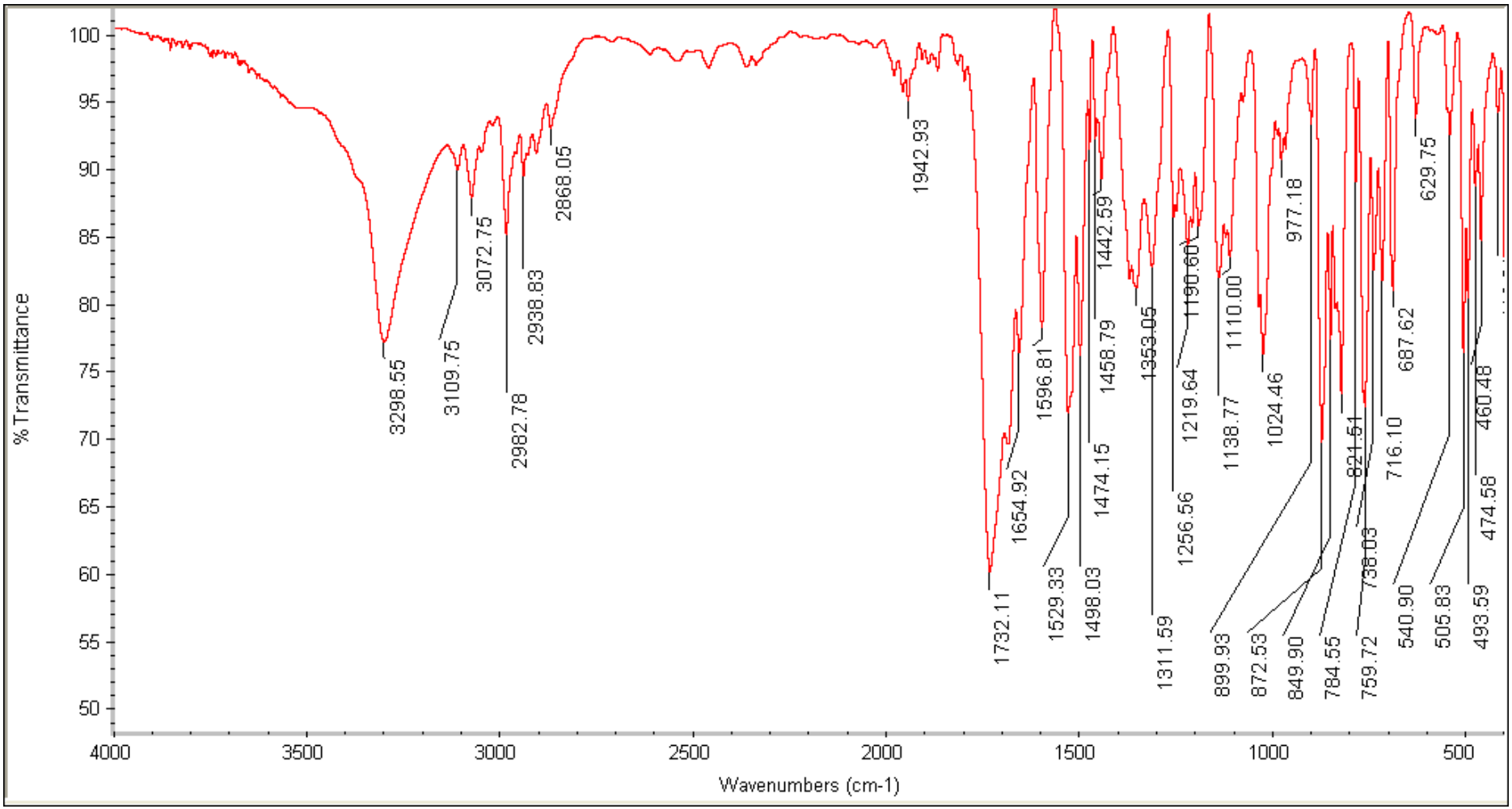


Figure 1. FT-IR spectrum of Ethyl 2-(4-nitrophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4a**).

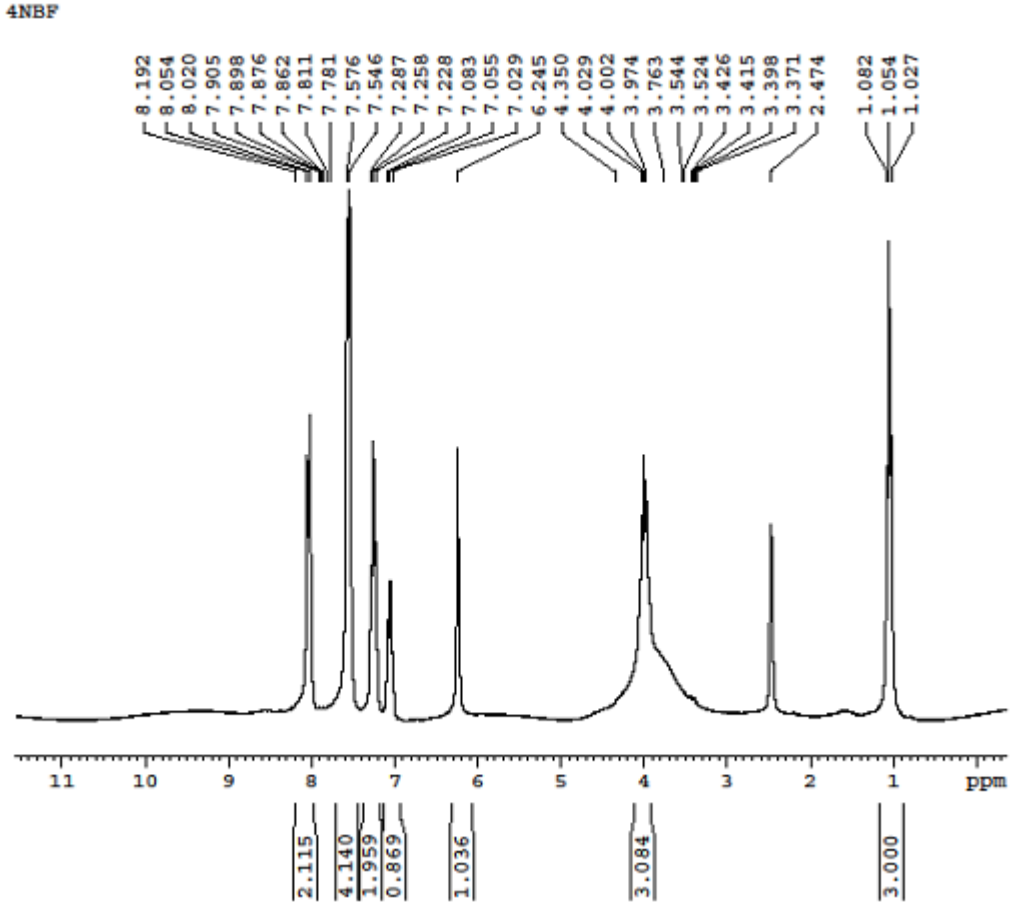


Figure 2. ^{1}H NMR (250.13 MHz, DMSO-d_6) of Ethyl 2-(4-nitrophenyl)-4-hydroxy-5-oxo-1-phenyl-2, 5-dihydro-1H-pyrrole-3-carboxylate **(4a).**

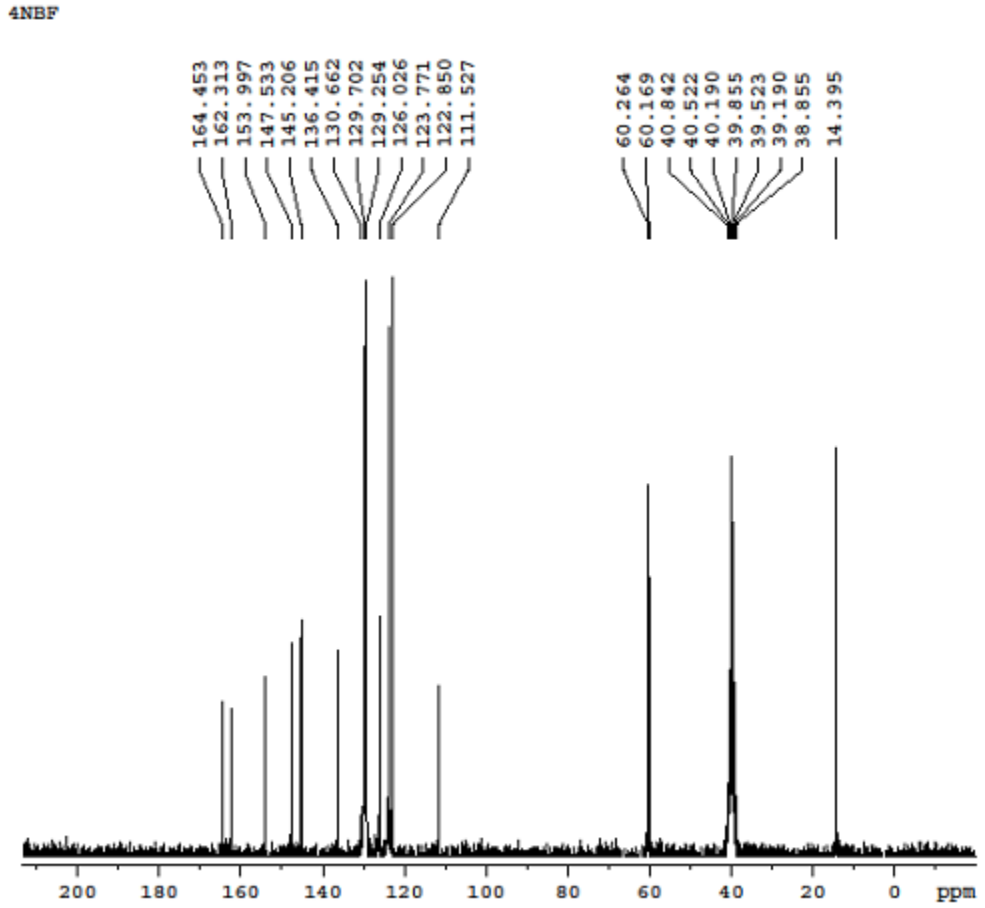


Figure 3. ^{13}C NMR (62.90 MHz, DMSO-d6) of Ethyl 2-(4-nitrophenyl)-4-hydroxy-5-oxo-1-phenyl-2, 5-dihydro-1H-pyrrole-3-carboxylate **(4a).**

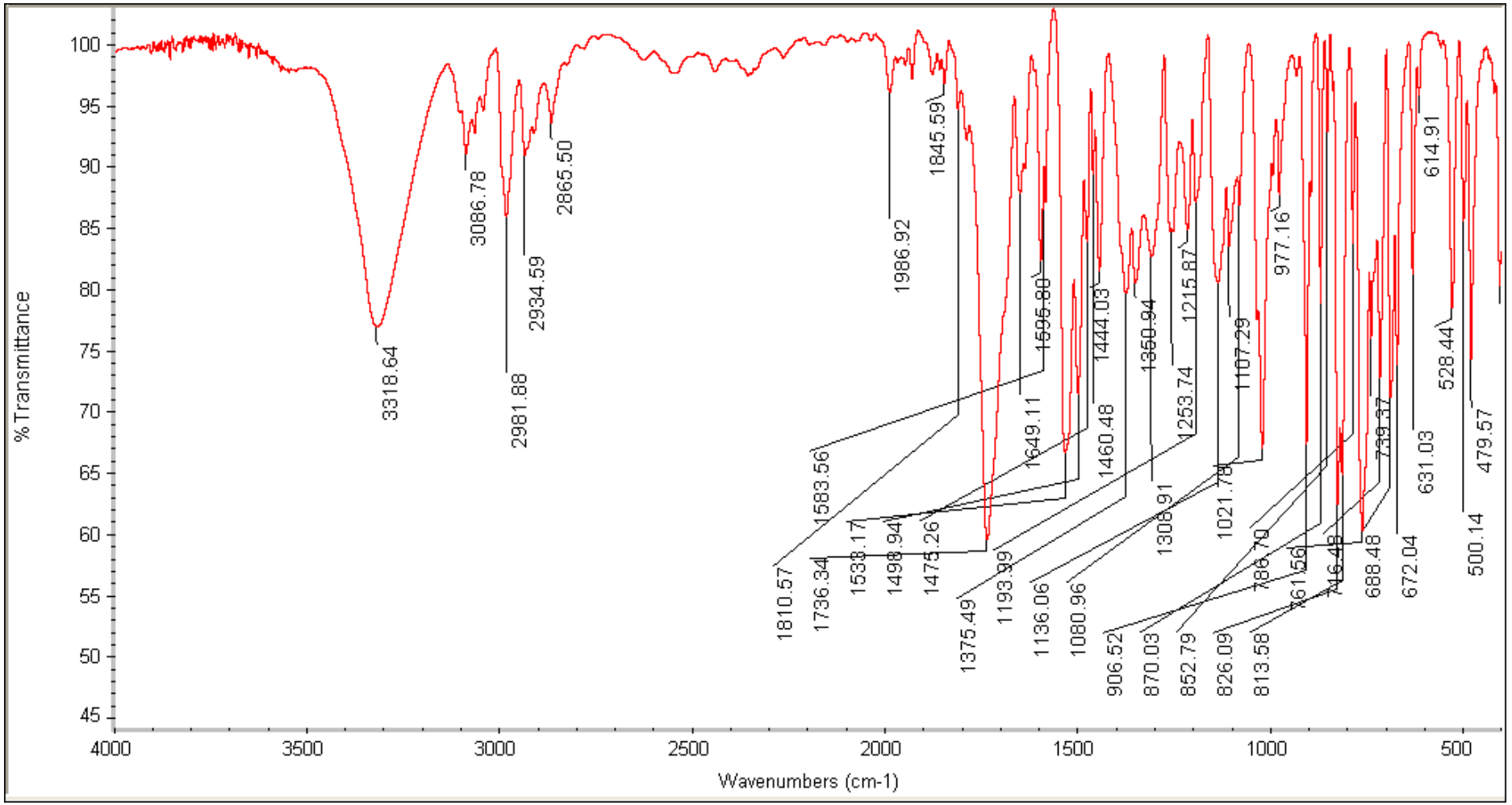


Figure 4. FT-IR spectrum of Ethyl 2-(3-nitrophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate **(4b).**

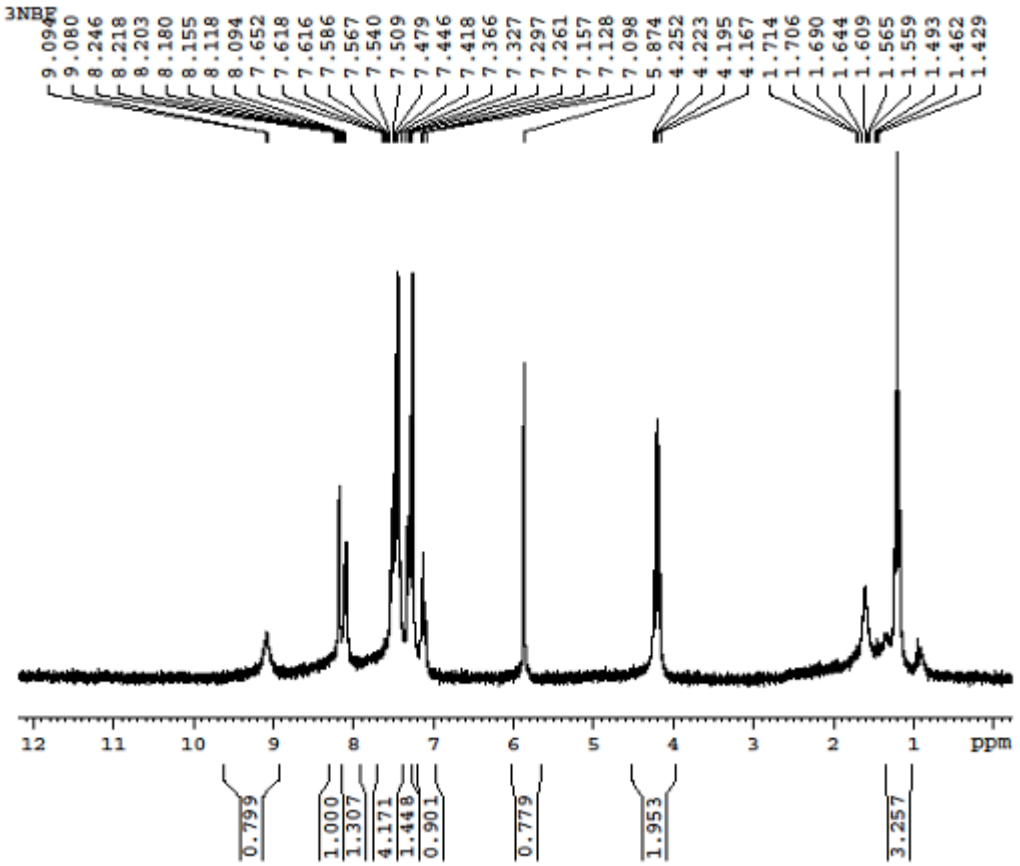


Figure 5. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 2-(3-nitrophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate **(4b).**

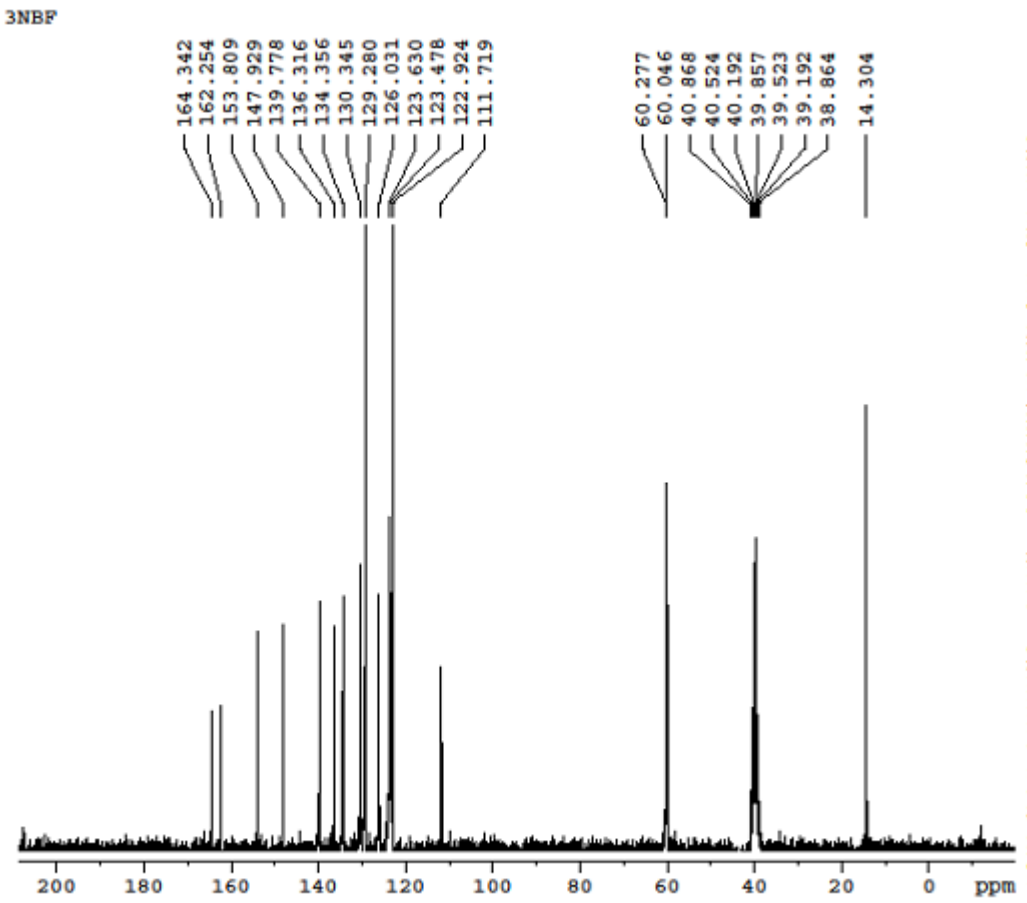


Figure 6. ^{13}C NMR (62.90 MHz, DMSO-d_6) spectrum of Ethyl 2-(3-nitrophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate **(4b).**

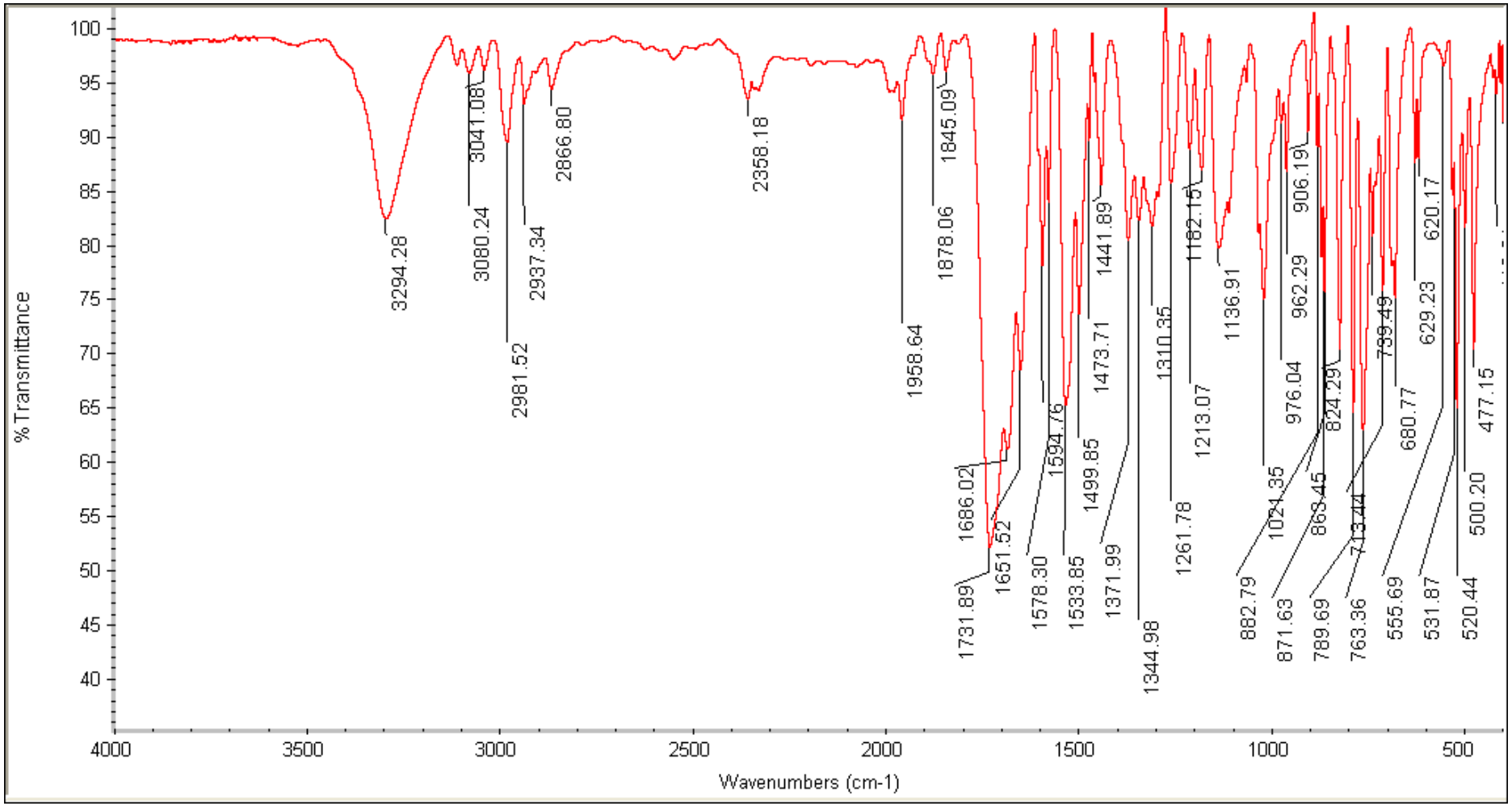


Figure 7. FT-IR spectrum of Ethyl 2-(2-nitrophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate **(4c).**

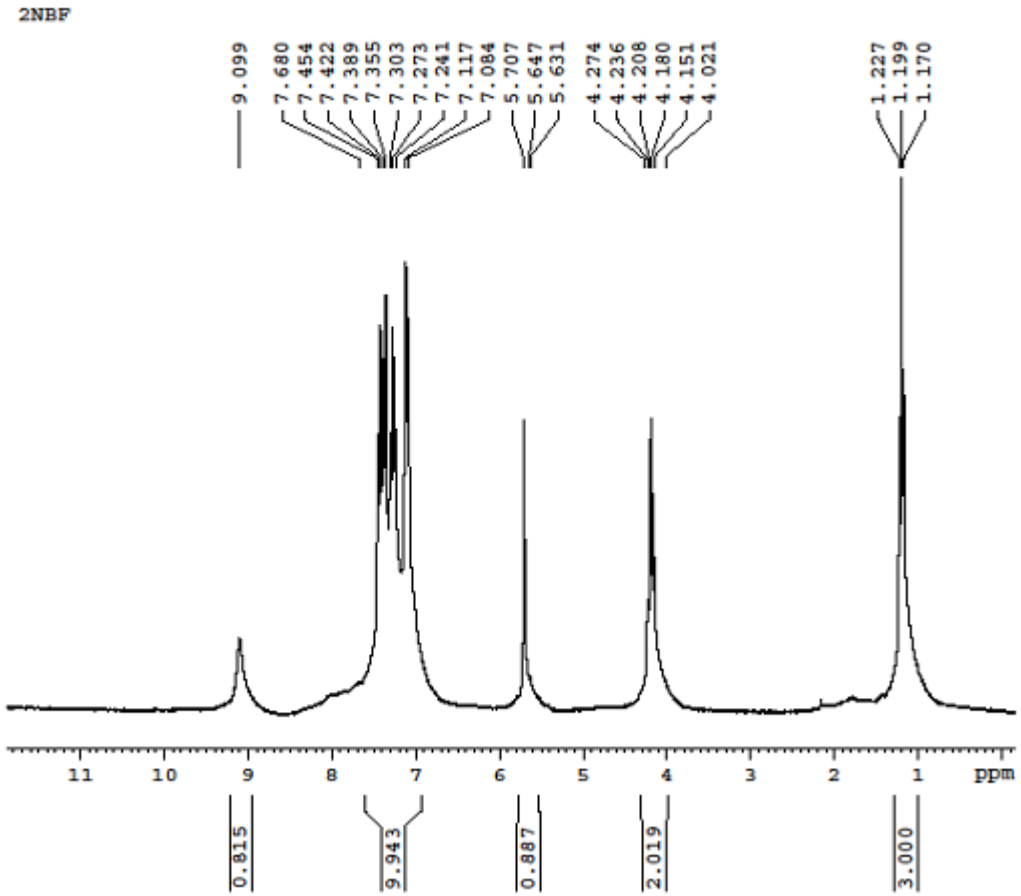


Figure 8. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 2-(2-nitrophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate **(4c).**

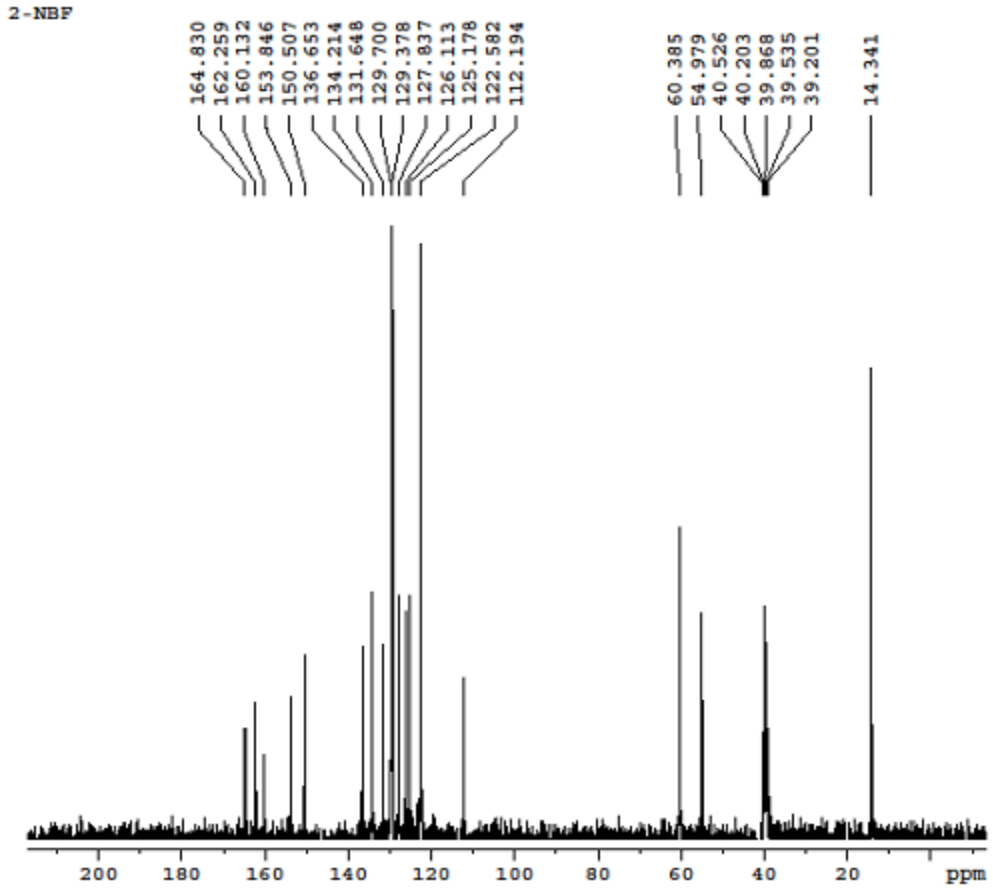


Figure 9. ^{13}C NMR (62.90 MHz, DMSO-d_6) spectrum of Ethyl 2-(2-nitrophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate **(4c).**

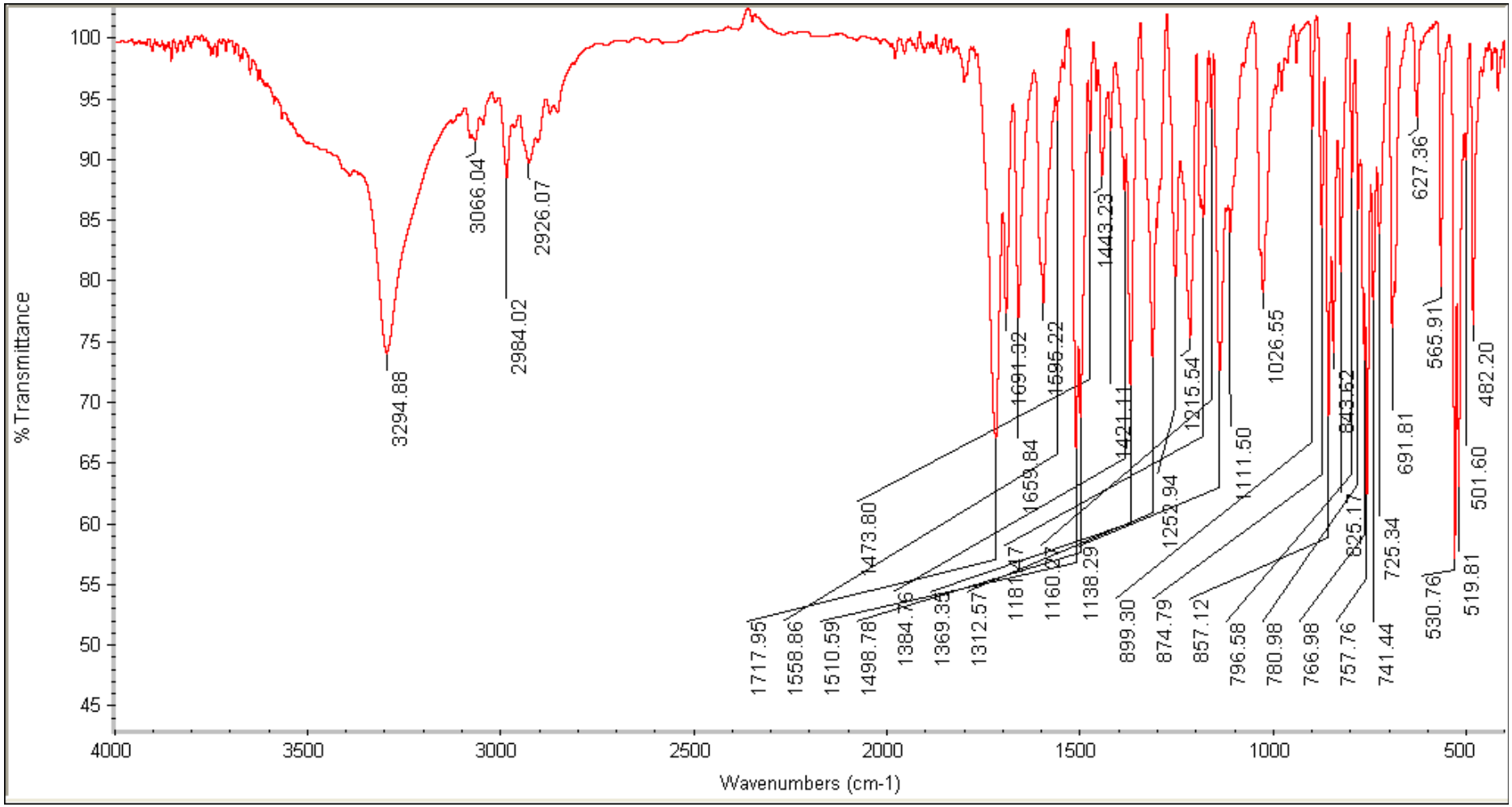


Figure 10. FT-IR spectrum of Ethyl 2-(4-fluorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate **(4d).**

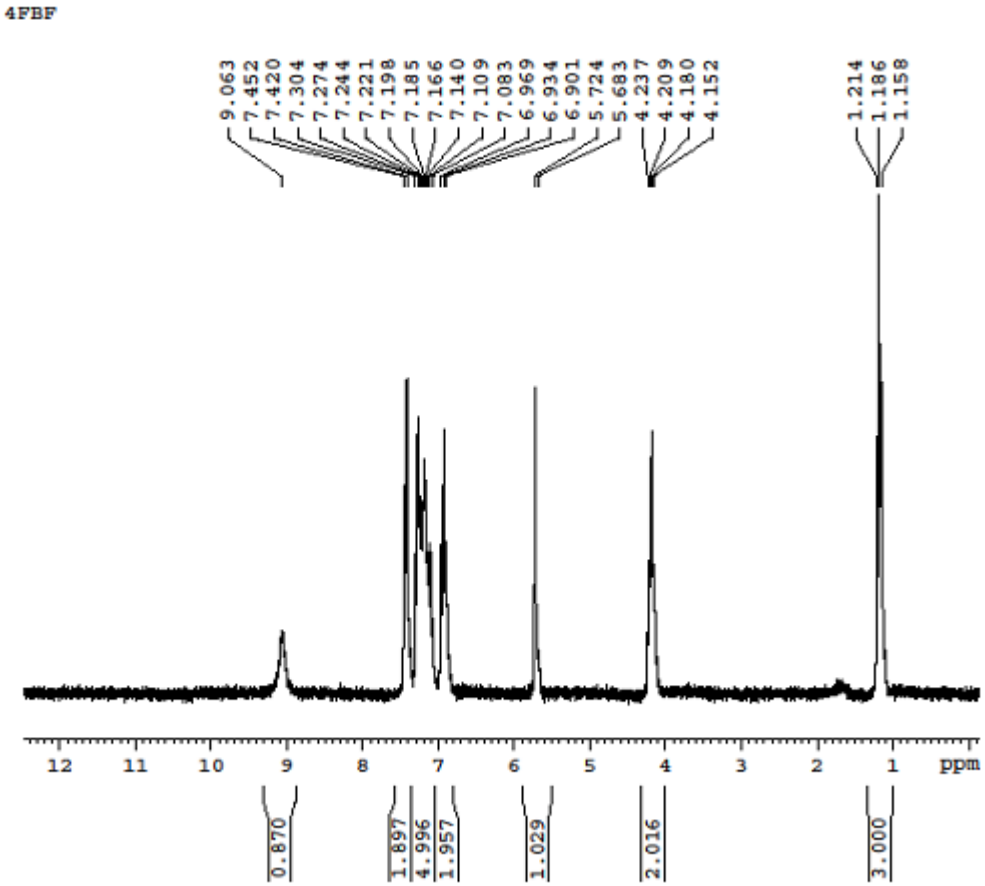


Figure 11. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 2-(4-fluorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate **(4d).**

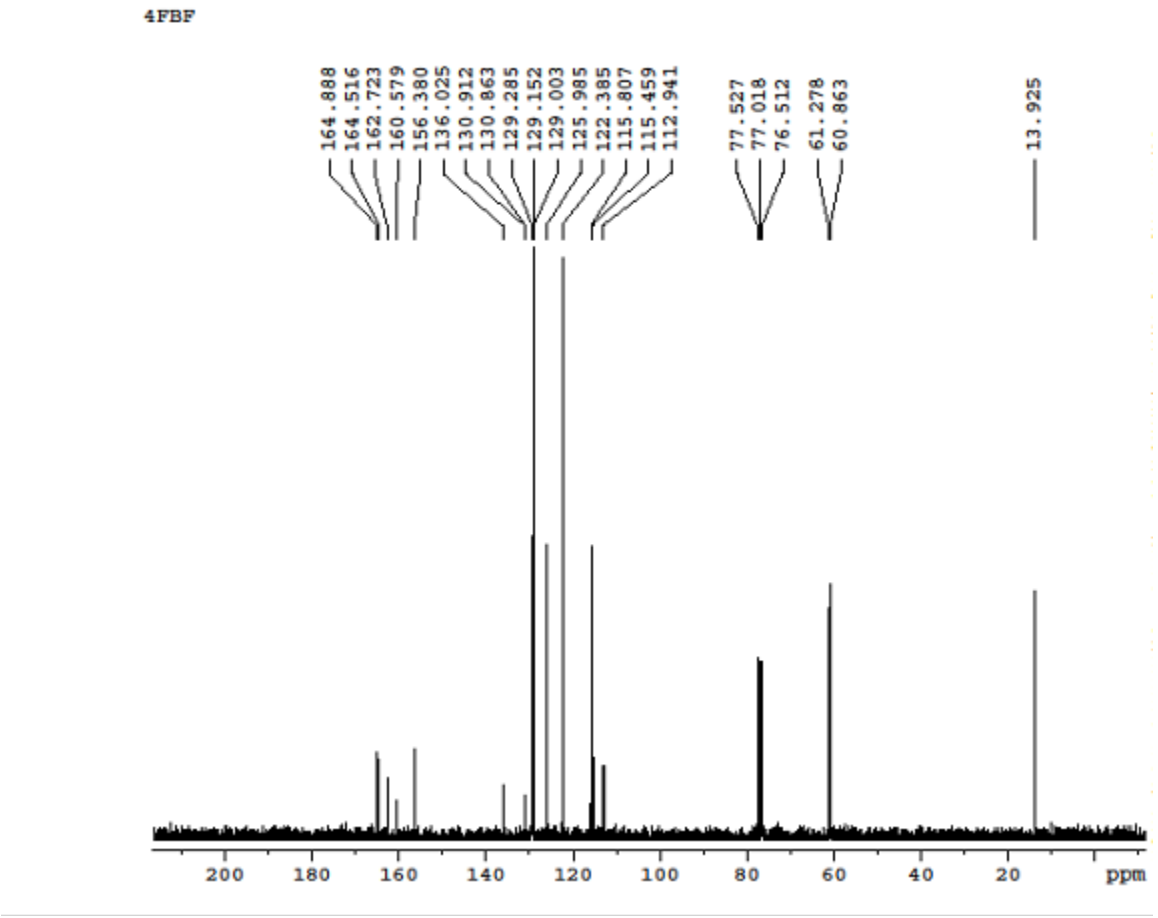


Figure 12. ^{13}C NMR (62.90 MHz, $CDCl_3$) spectrum of Ethyl 2-(4-fluorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate **(4d).**

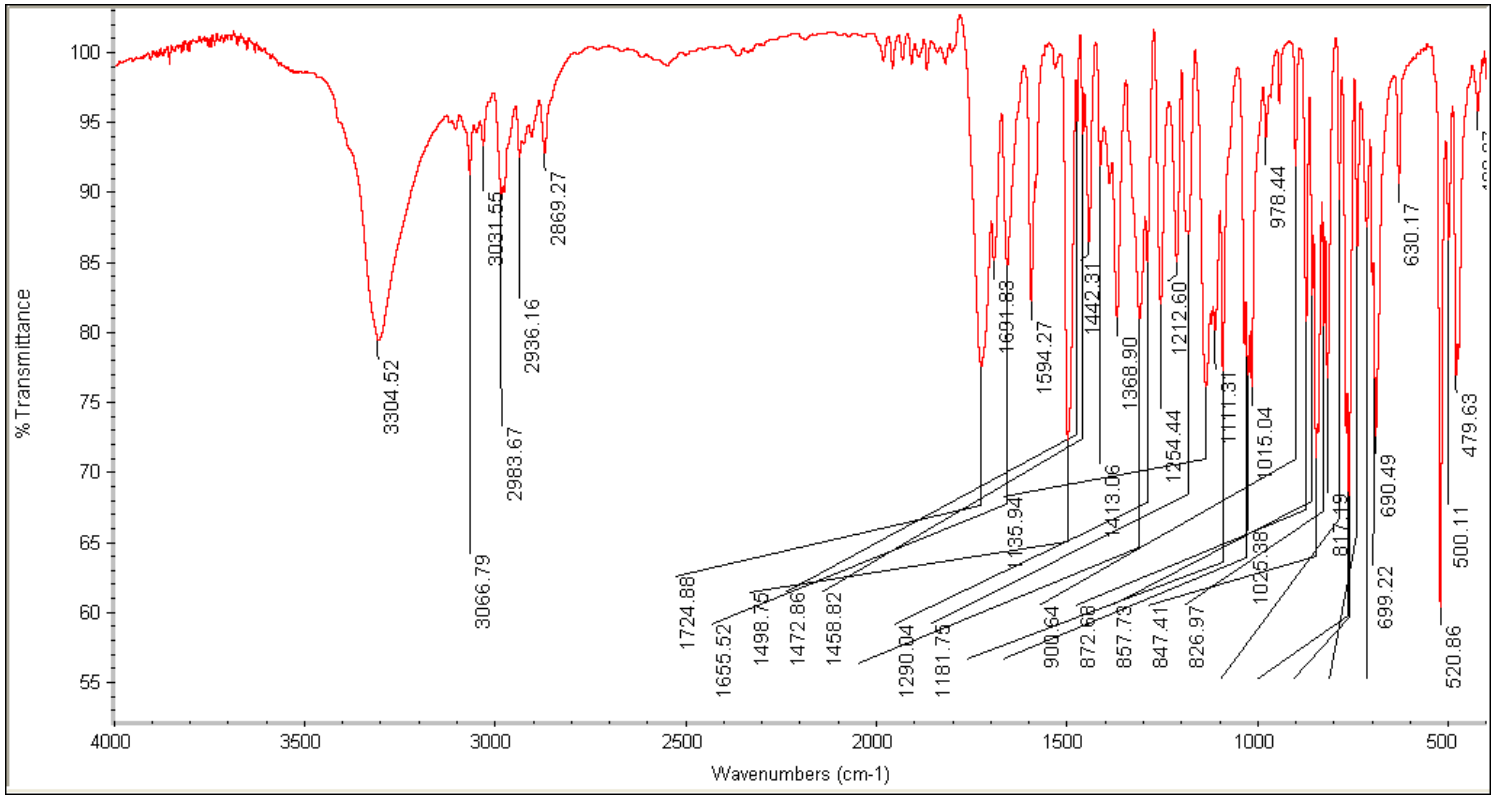


Figure 13. FT-IR spectrum of Ethyl 2-(4-chlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate **(4e).**

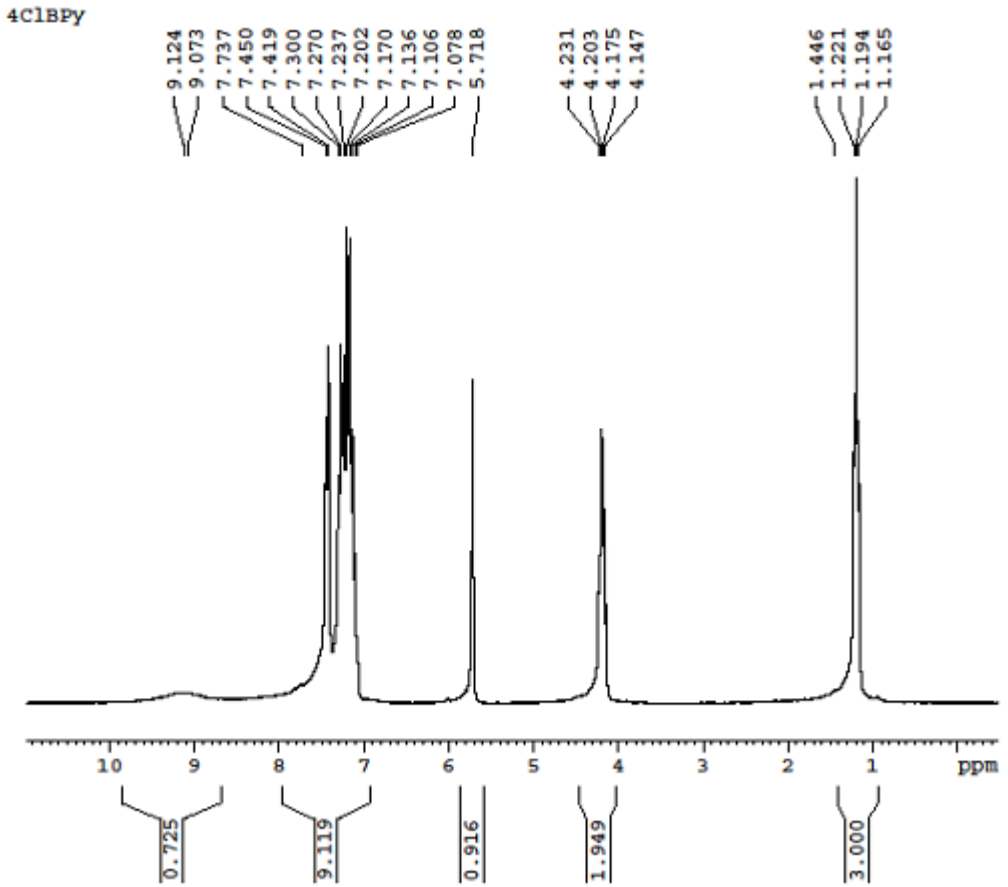


Figure 14. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 2-(4-chlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate **(4e).**

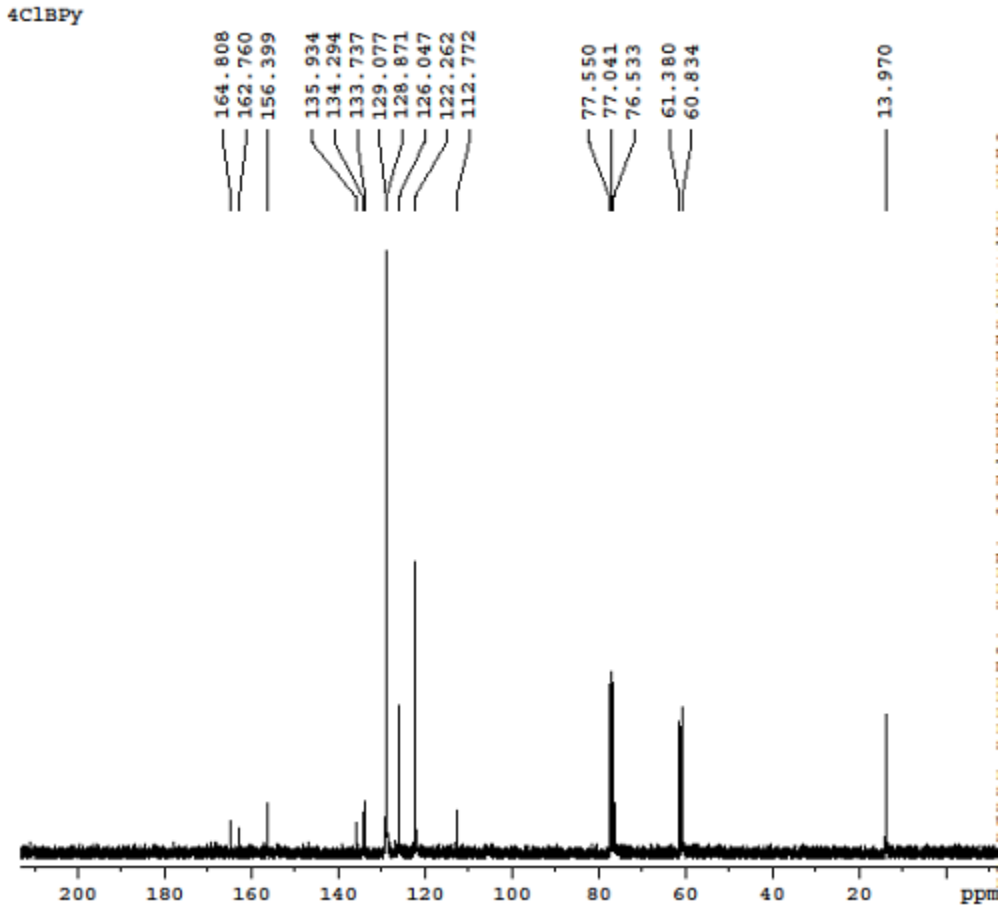


Figure 15. ^{13}C NMR (62.90 MHz, $CDCl_3$) spectrum of Ethyl 2-(4-chlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate **(4e).**

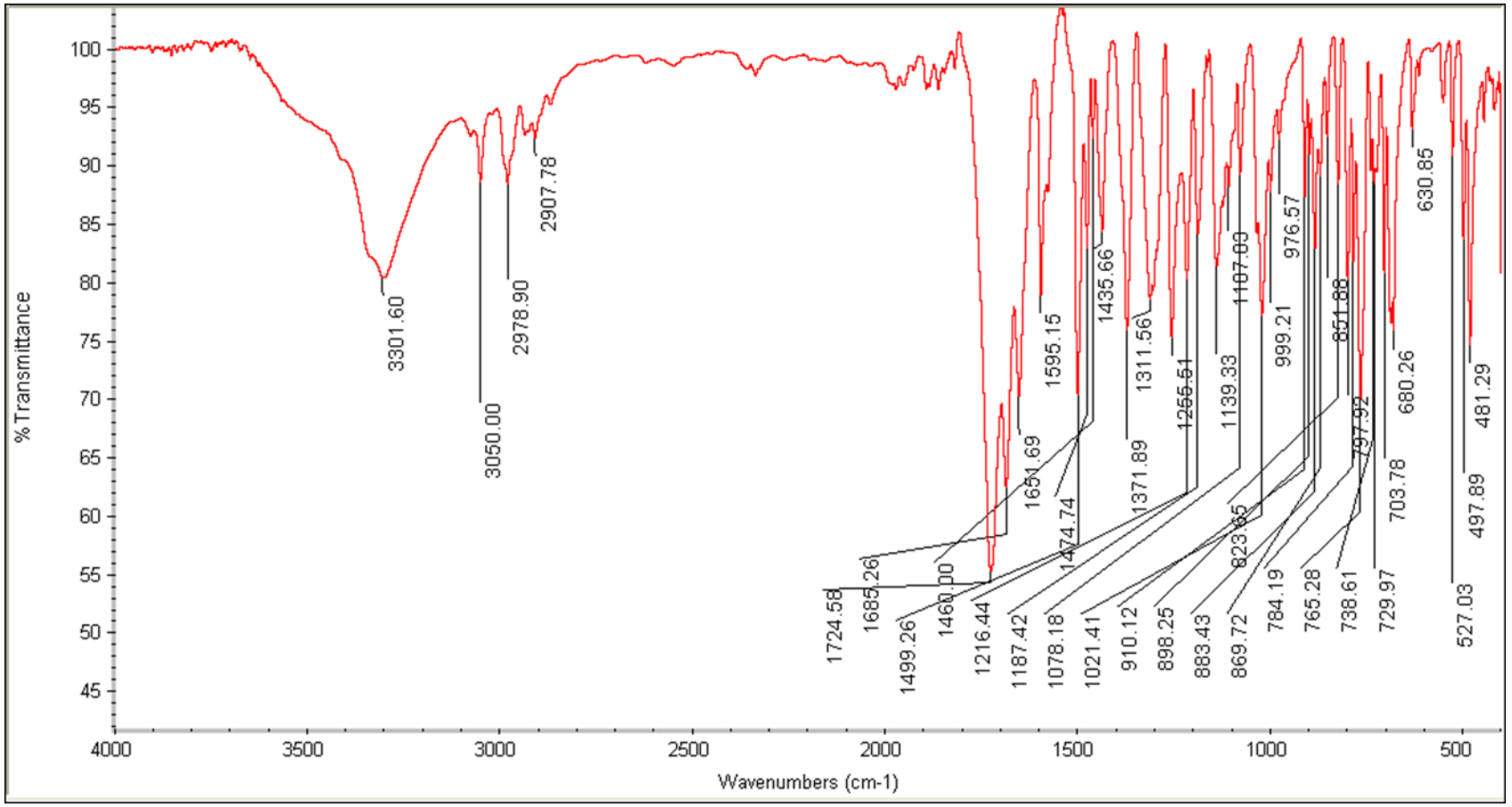
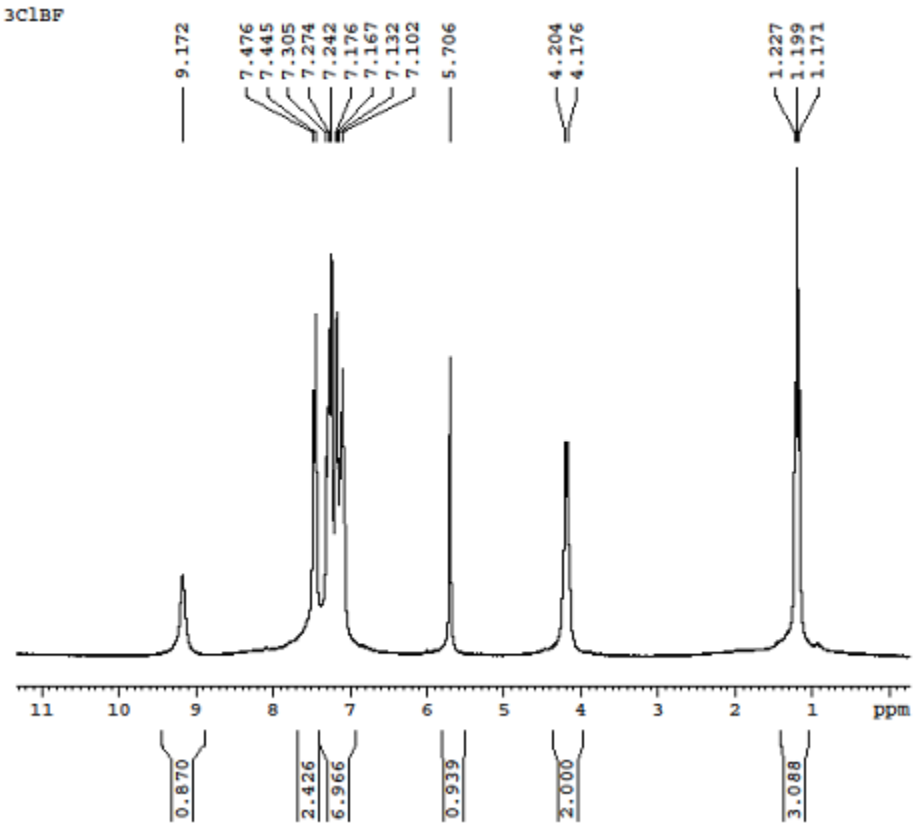


Figure 16. FT-IR spectrum of Ethyl 2-(3-chlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4f**)



Figur 17. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 2-(3-chlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4f**).

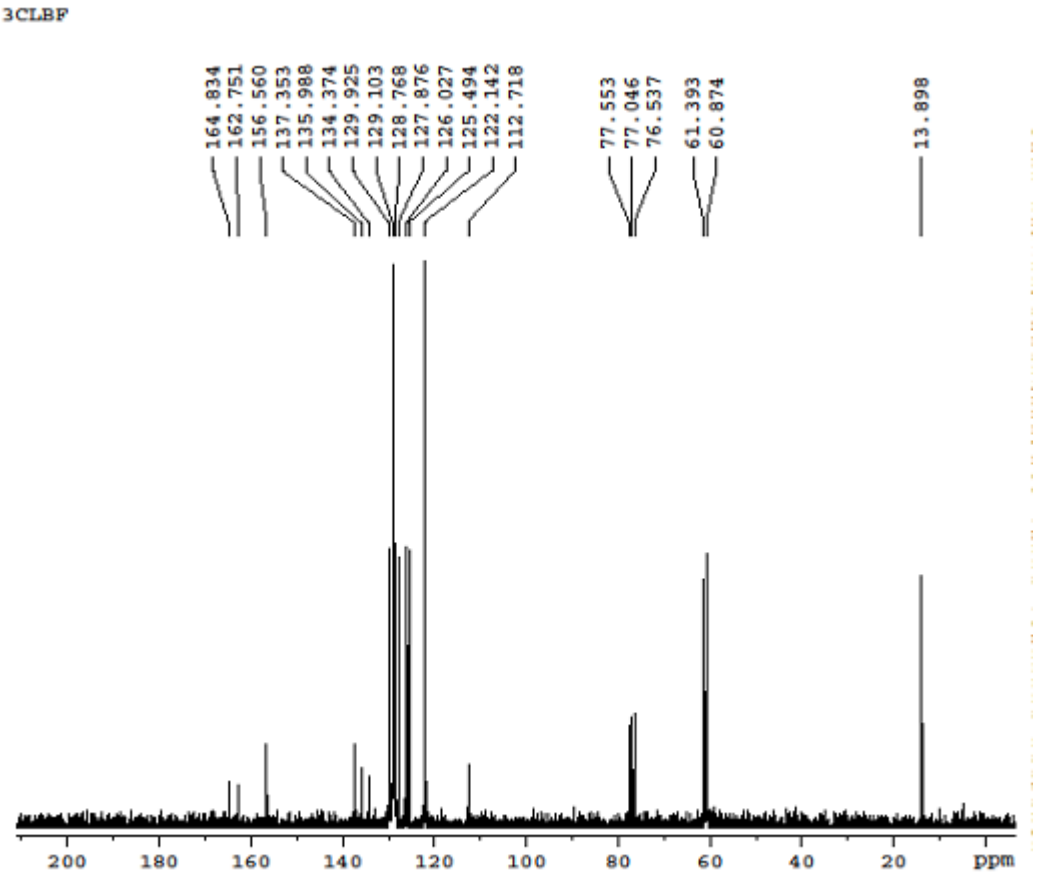


Figure 18. ^{13}C NMR (62.90 MHz, $CDCl_3$) spectrum of Ethyl 2-(3-chlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4f**).

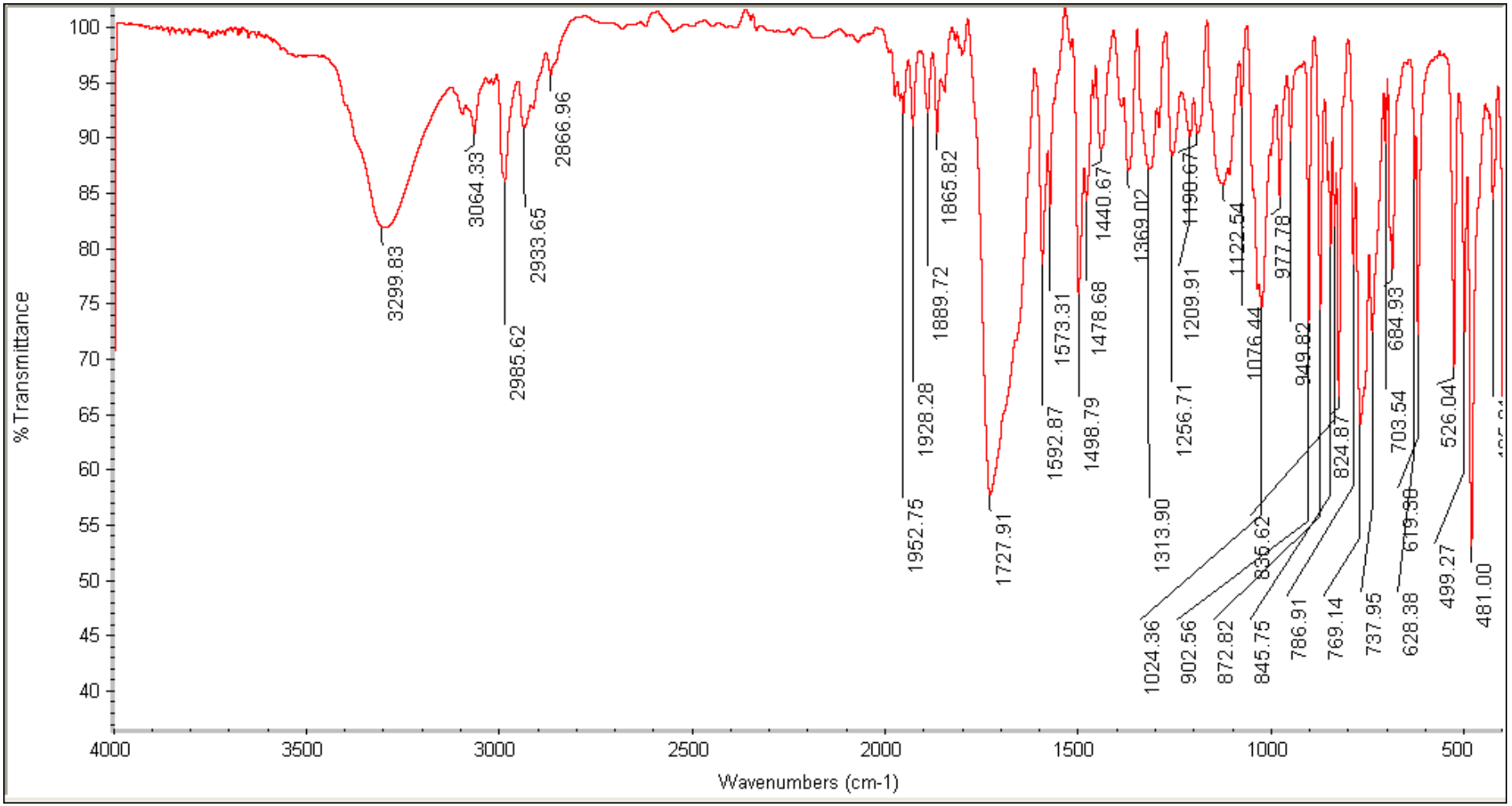


Figure 19. FT-IR spectrum of Ethyl 2-(2-chlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4g**)

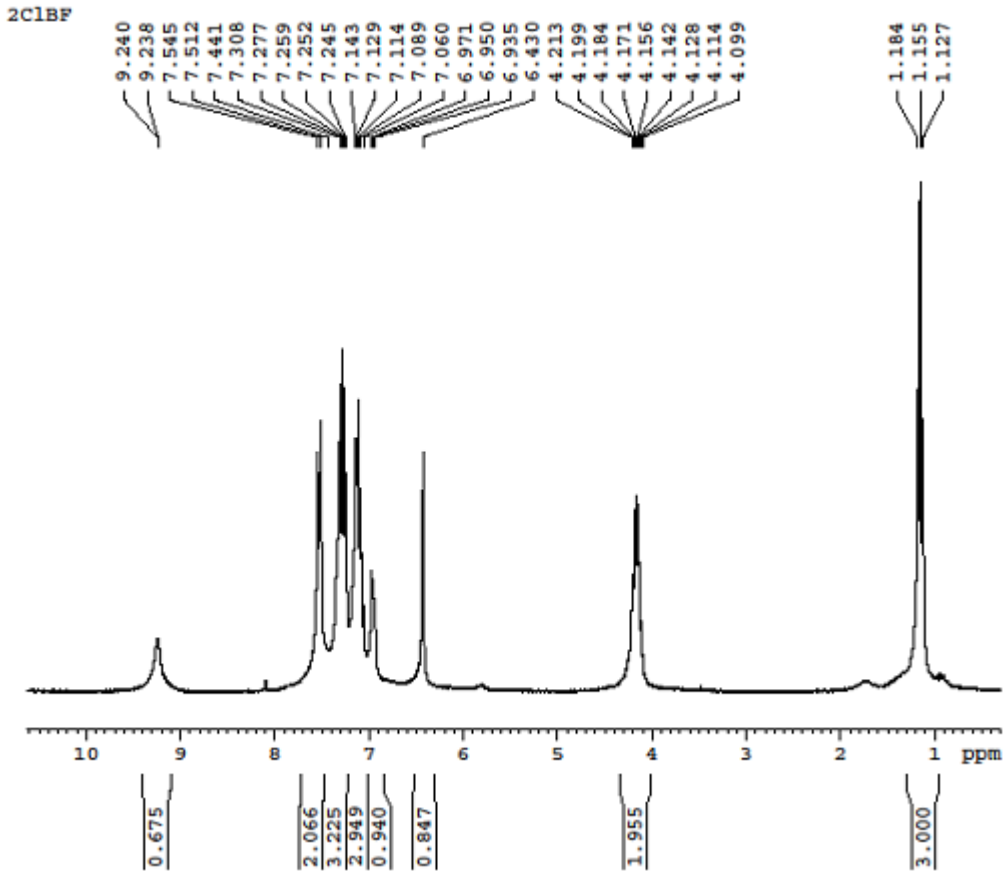


Figure 20. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 2-(2-chlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4g**)

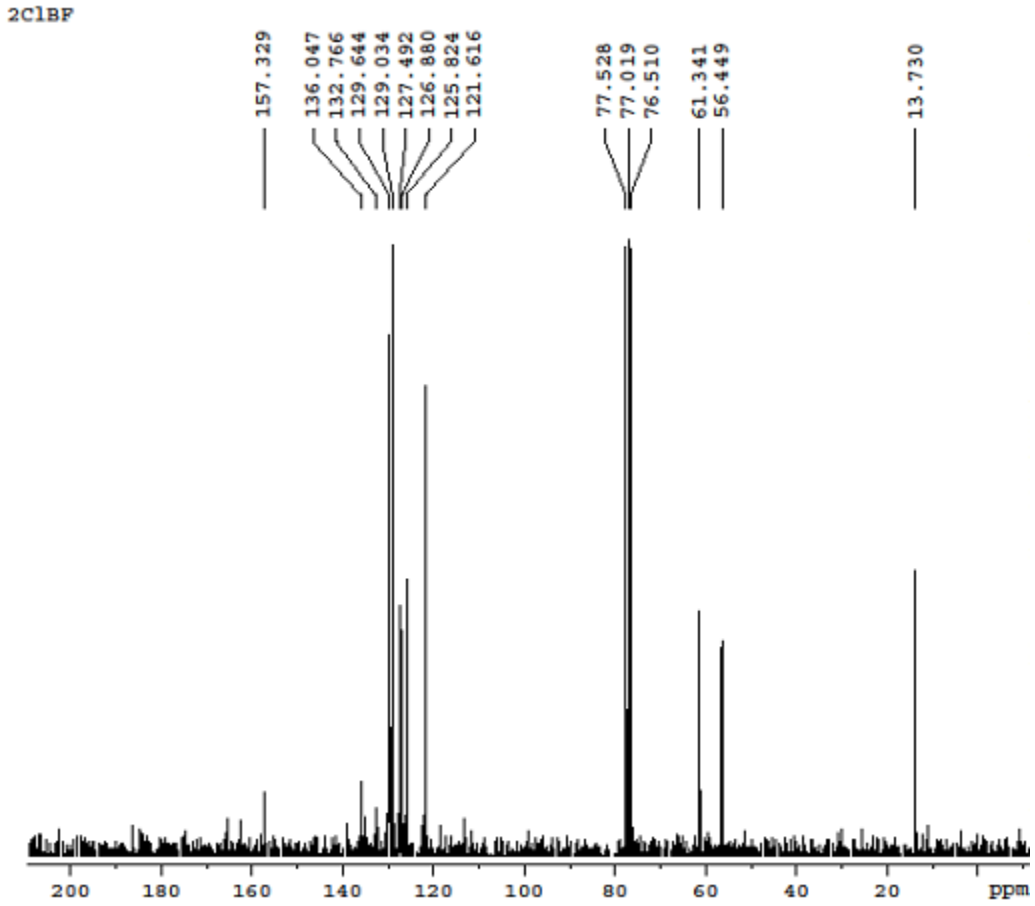


Figure 21. ^{13}C NMR (62.90 MHz, $CDCl_3$) spectrum of Ethyl 2-(2-chlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4g**)

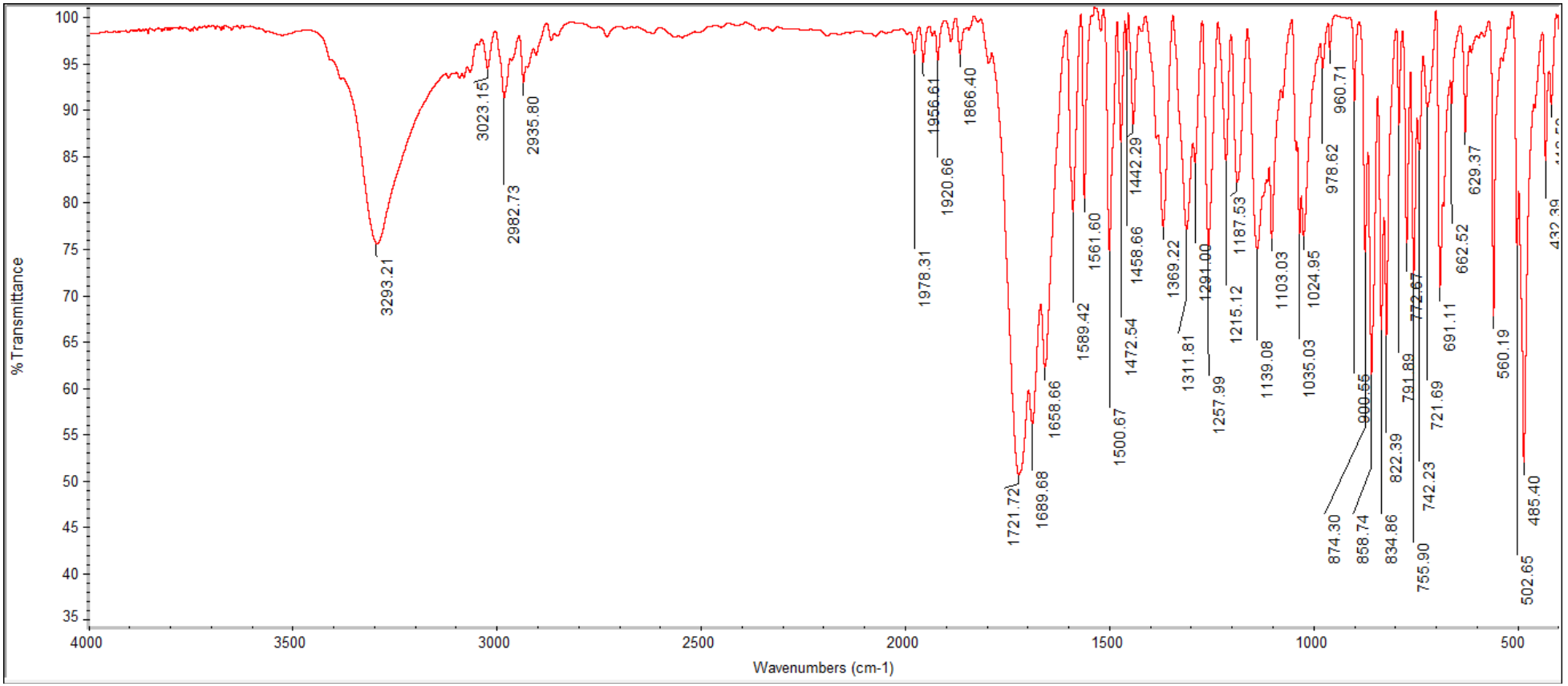


Figure 22. FT-IR spectrum of Ethyl 2-(2,4-dichlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4h**)

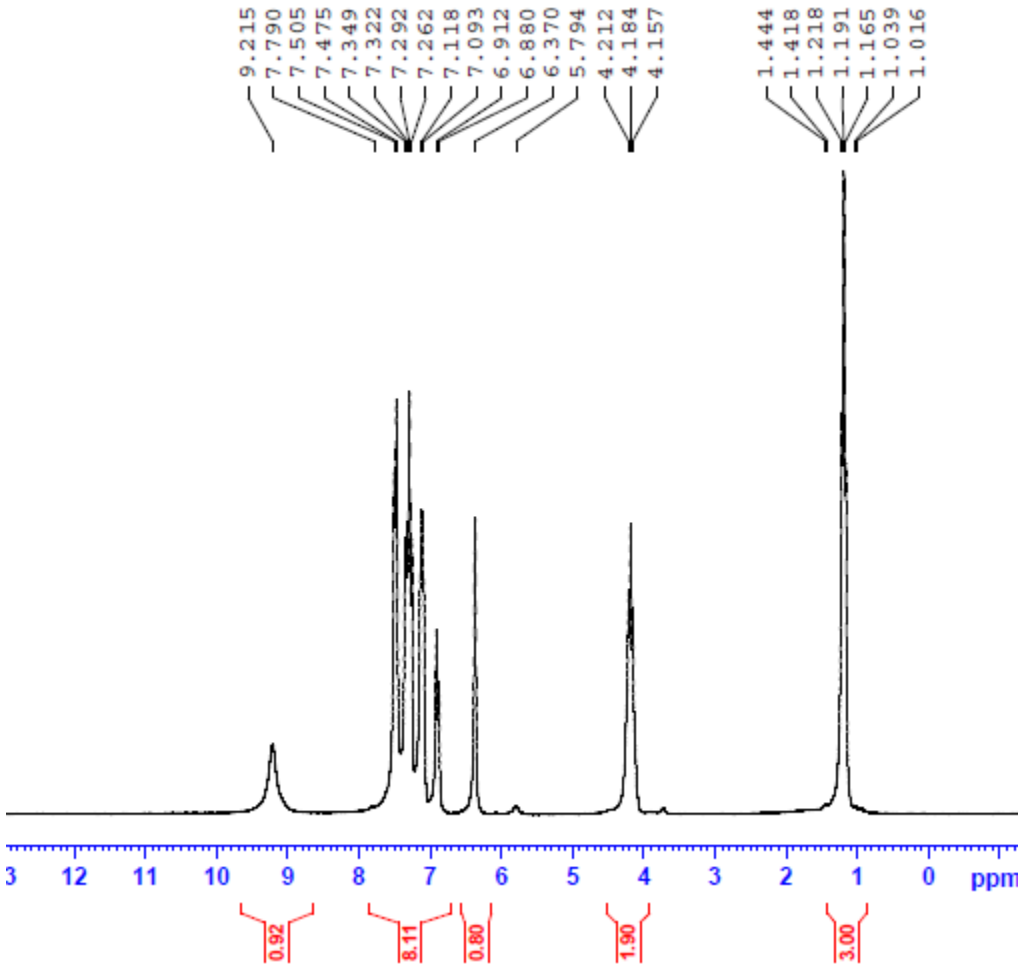


Figure 23. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 2-(2,4-dichlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4h**)

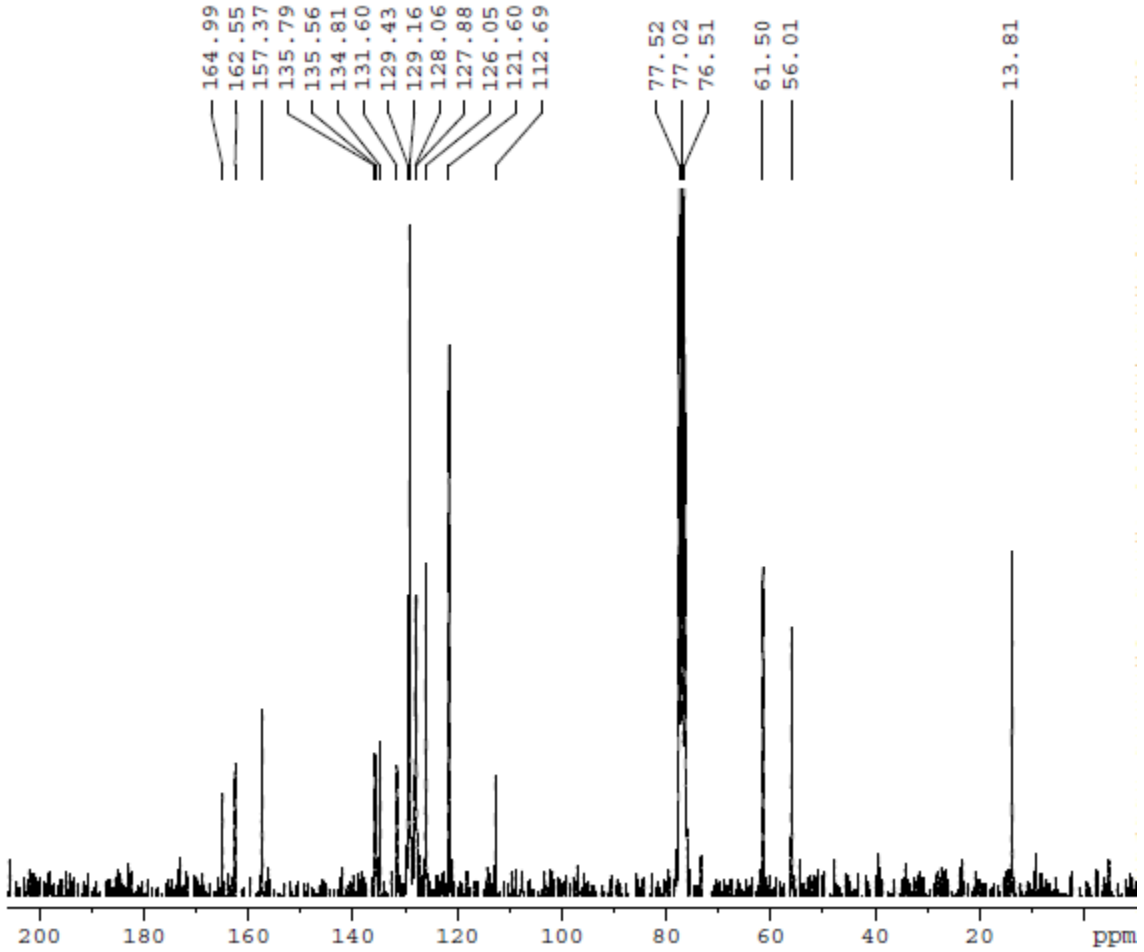


Figure 24. ^{13}C NMR (62.90 MHz, $CDCl_3$) spectrum of Ethyl 2-(2,4-dichlorophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4h**)

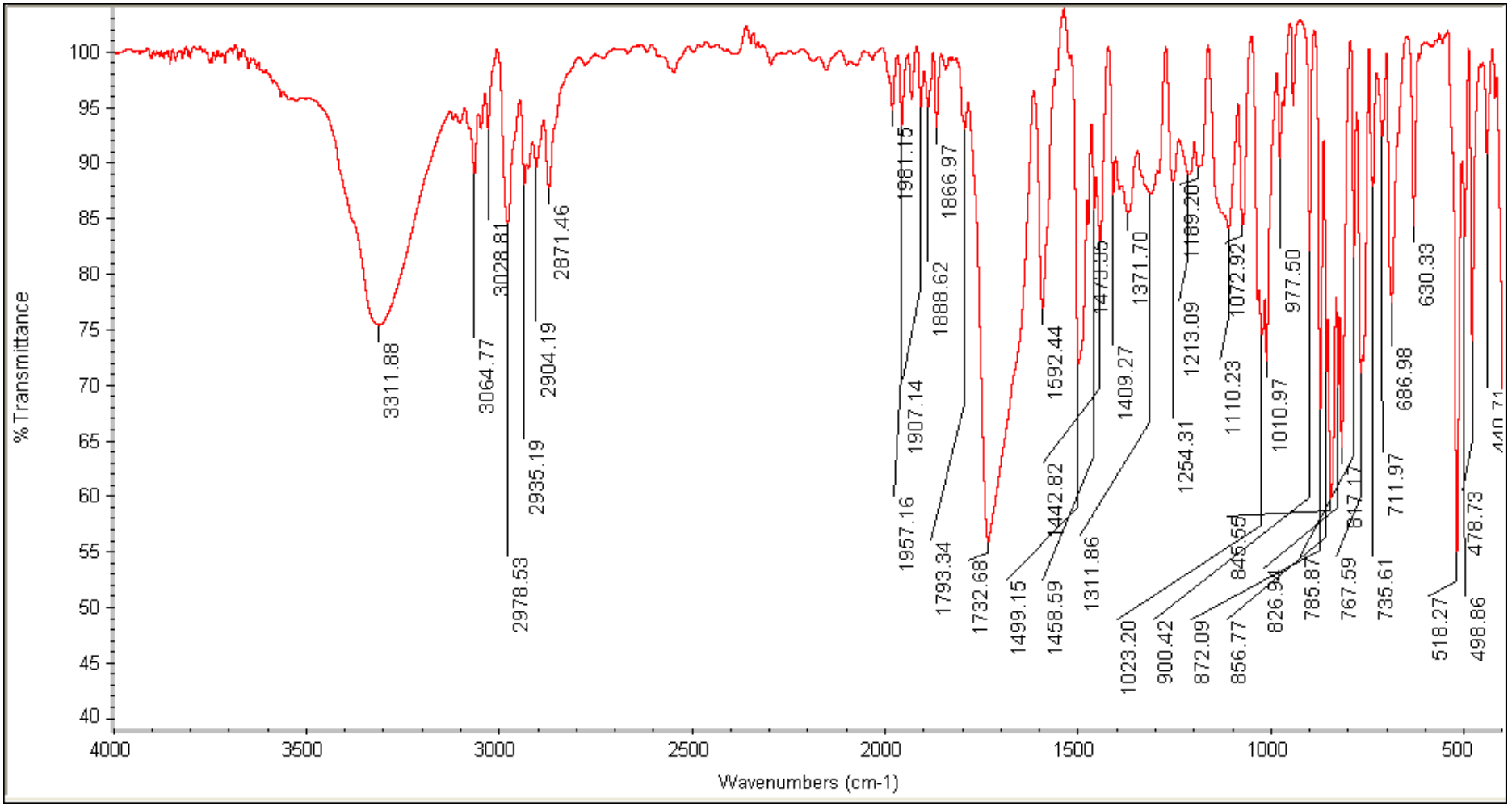


Figure 25. FT-IR spectrum of Ethyl 2-(4-bromophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4i**)

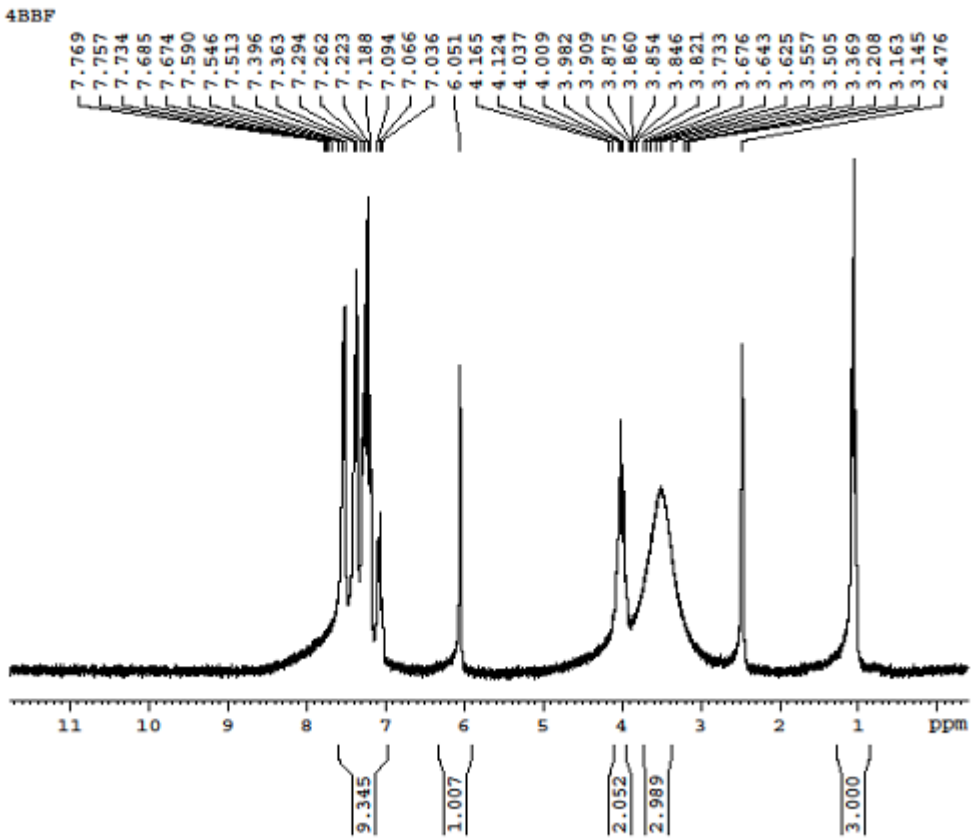


Figure 26. ^{1}H NMR (250.13 MHz, DMSO-d_6) spectrum of Ethyl 2-(4-bromophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4i**)

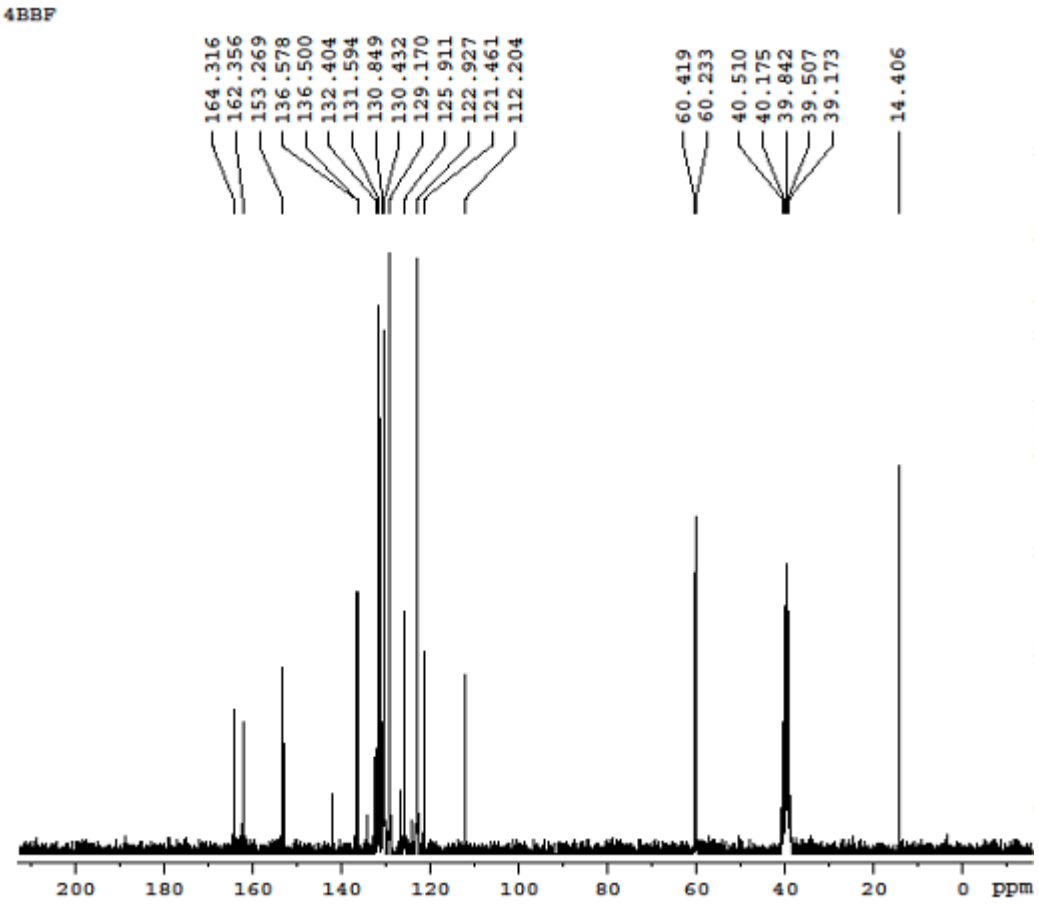


Figure 27. ^{13}C NMR (62.90 MHz, DMSO-d_6) spectrum of Ethyl 2-(4-bromophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4e**)

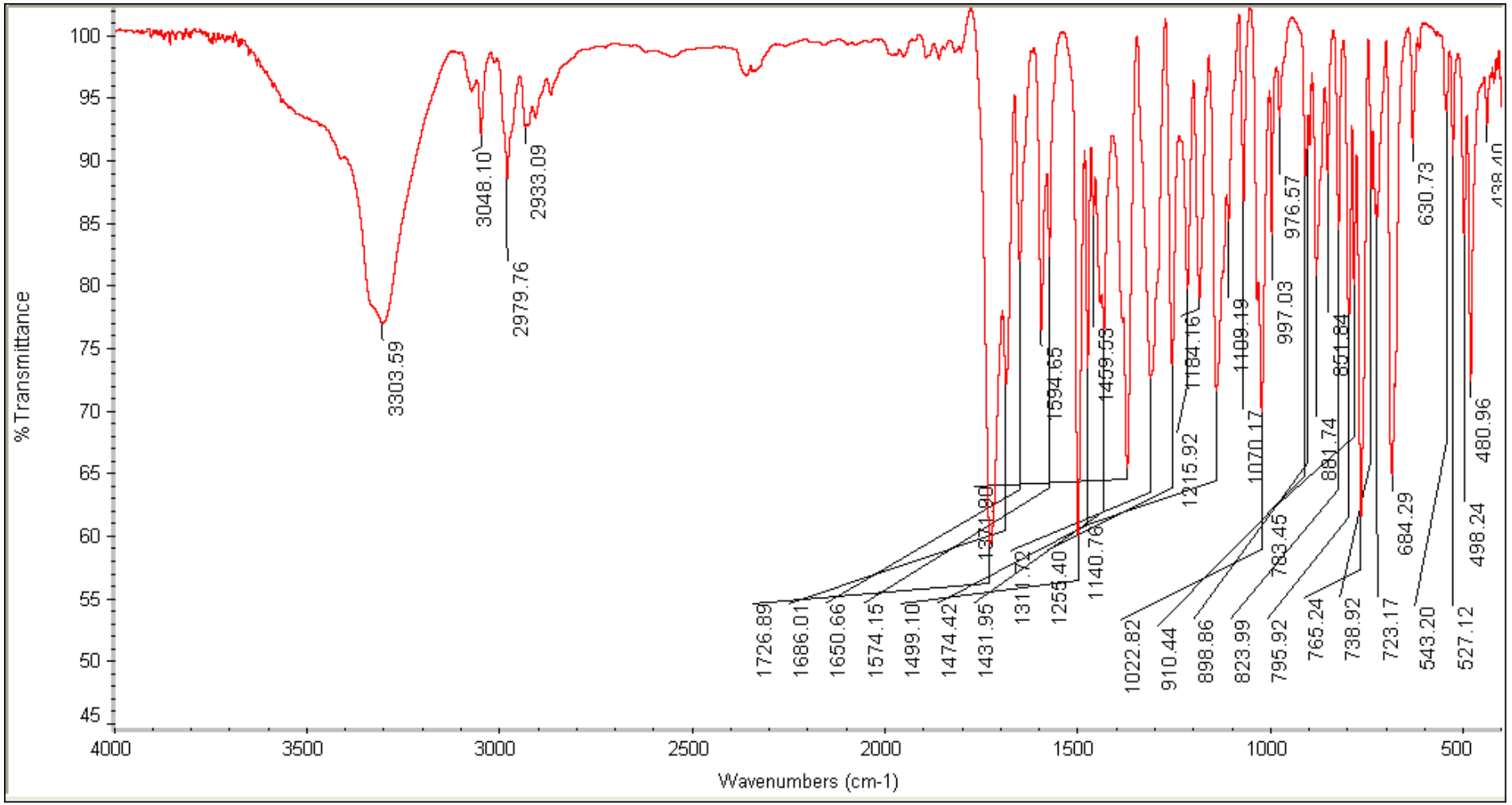


Figure 28. FT-IR spectrum of Ethyl 2-(3-bromophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4j**)

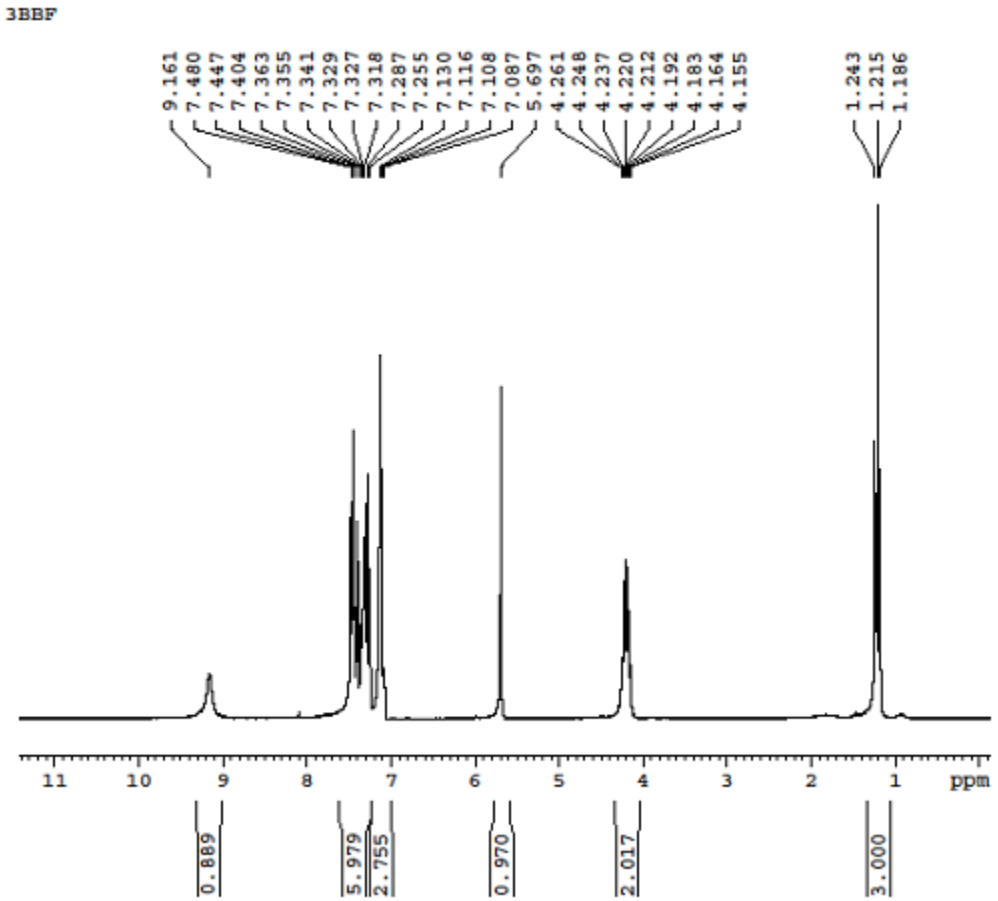


Figure 29. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 2-(3-bromophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4j**)

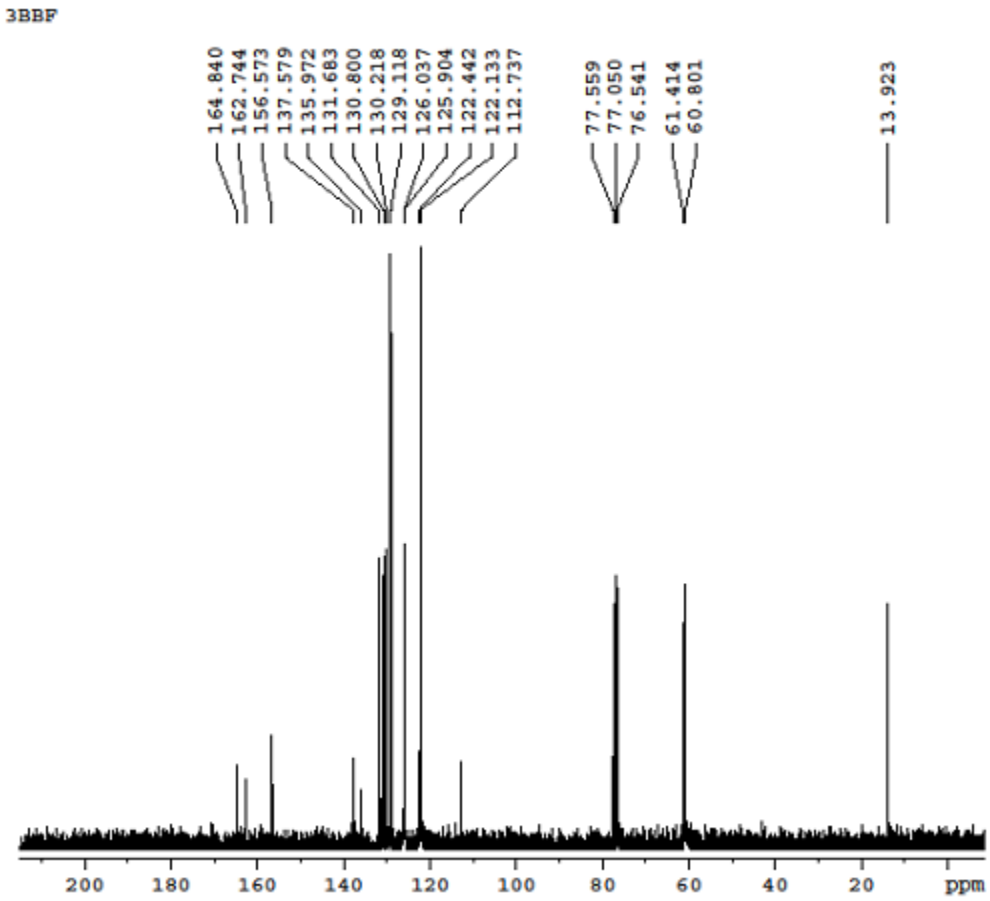


Figure 30. ^{13}C NMR (62.90 MHz, $CDCl_3$) spectrum of Ethyl 2-(4-bromophenyl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate **(4j**)

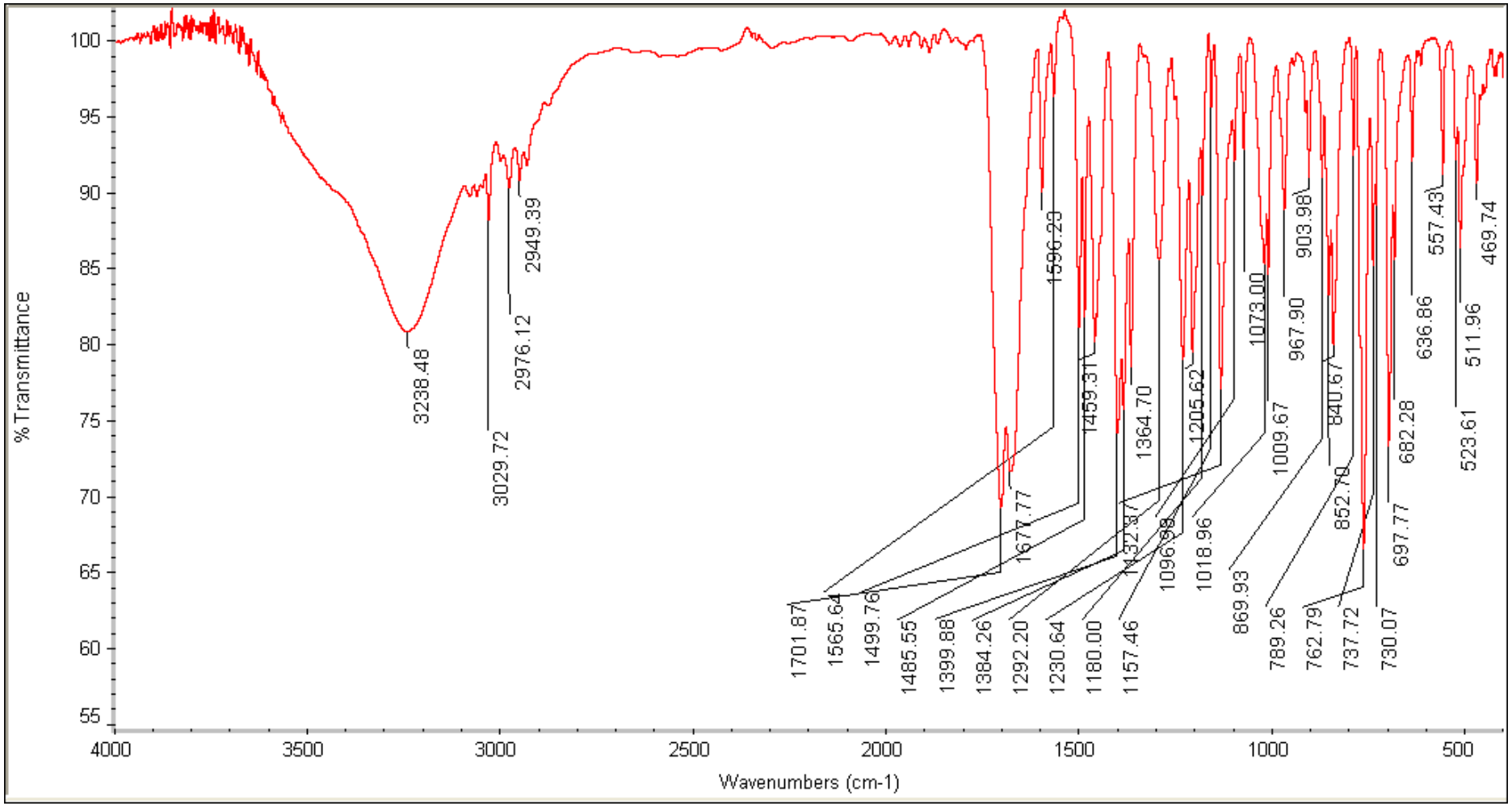


Figure 31. FT-IR spectrum of Ethyl 2-([1, 1'-biphenyl]-4-yl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4k**).

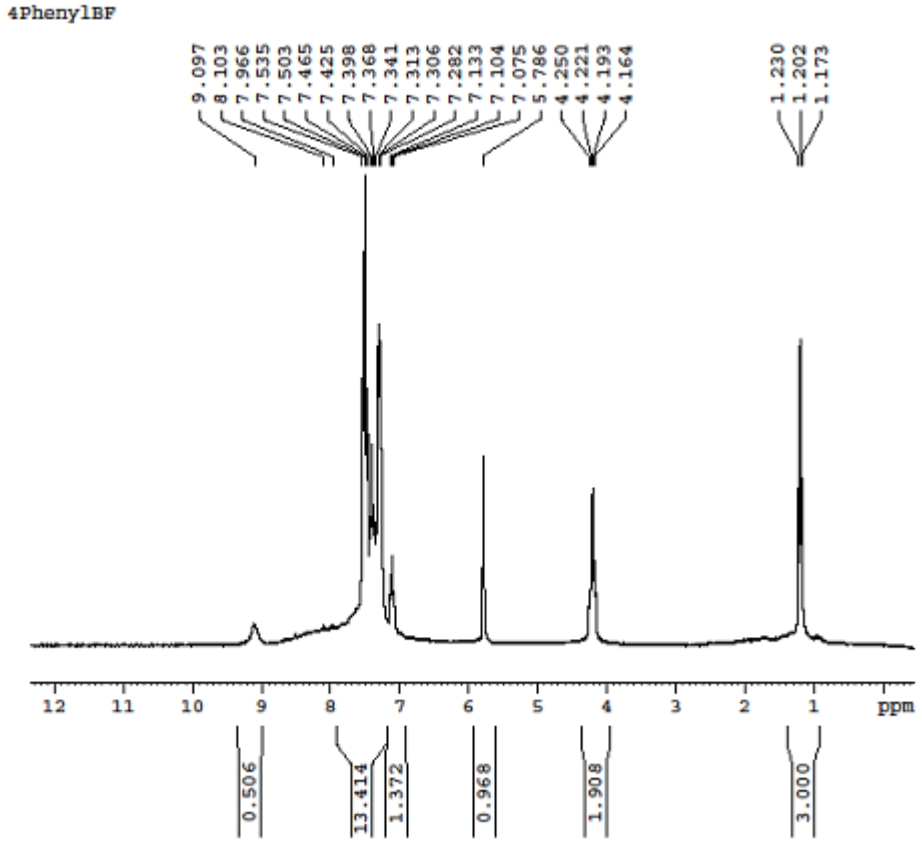


Figure 32. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 2-([1,1'-biphenyl]-4-yl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4k**)

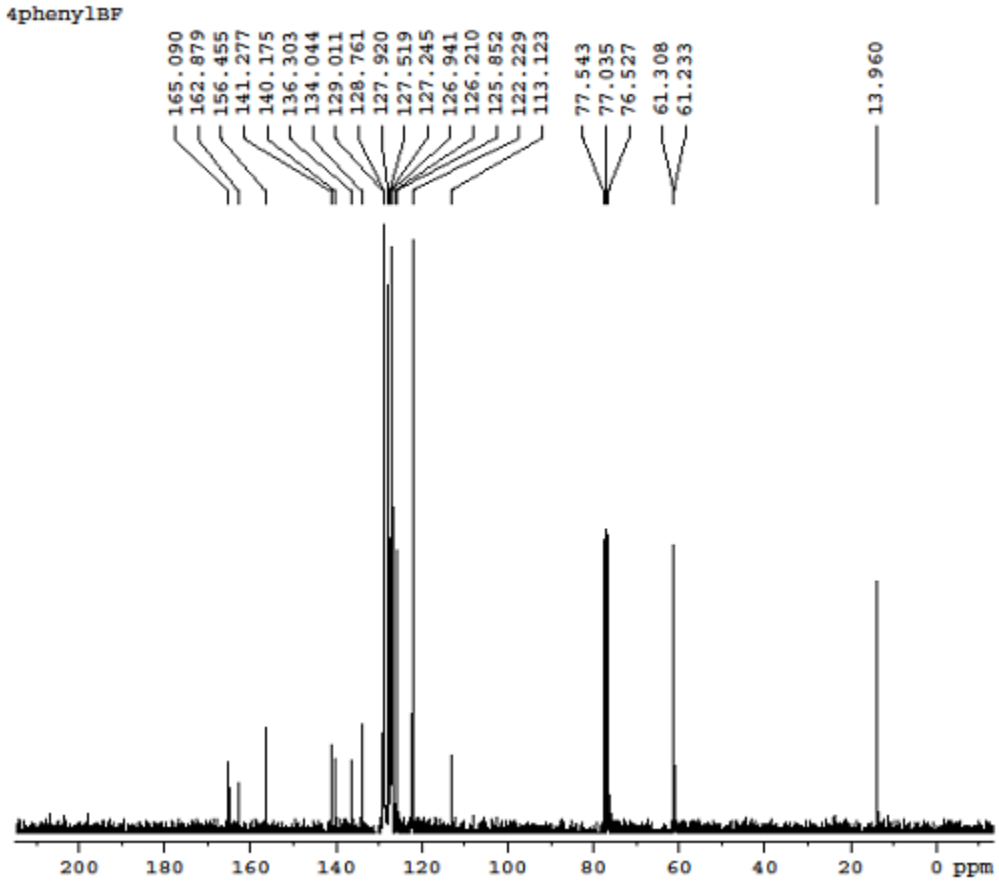


Figure 33. ^{13}C NMR (62.90 MHz, $CDCl_3$) spectrum of Ethyl 2-([1,1'-biphenyl]-4-yl)-4-hydroxy-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4k**)

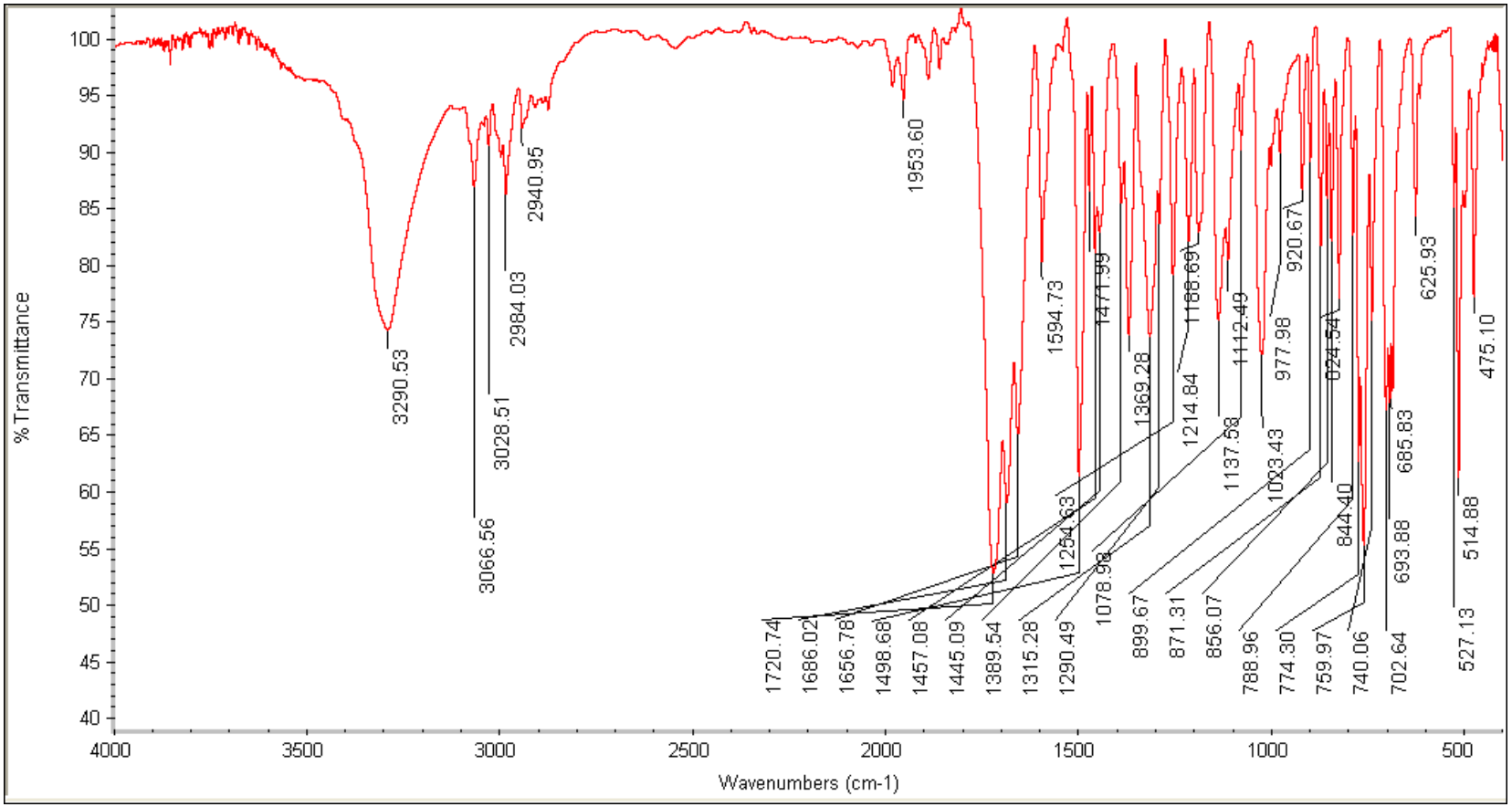


Figure 34. FT-IR spectrum of Ethyl 4-hydroxy-5-oxo-1,2-diphenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4l**)

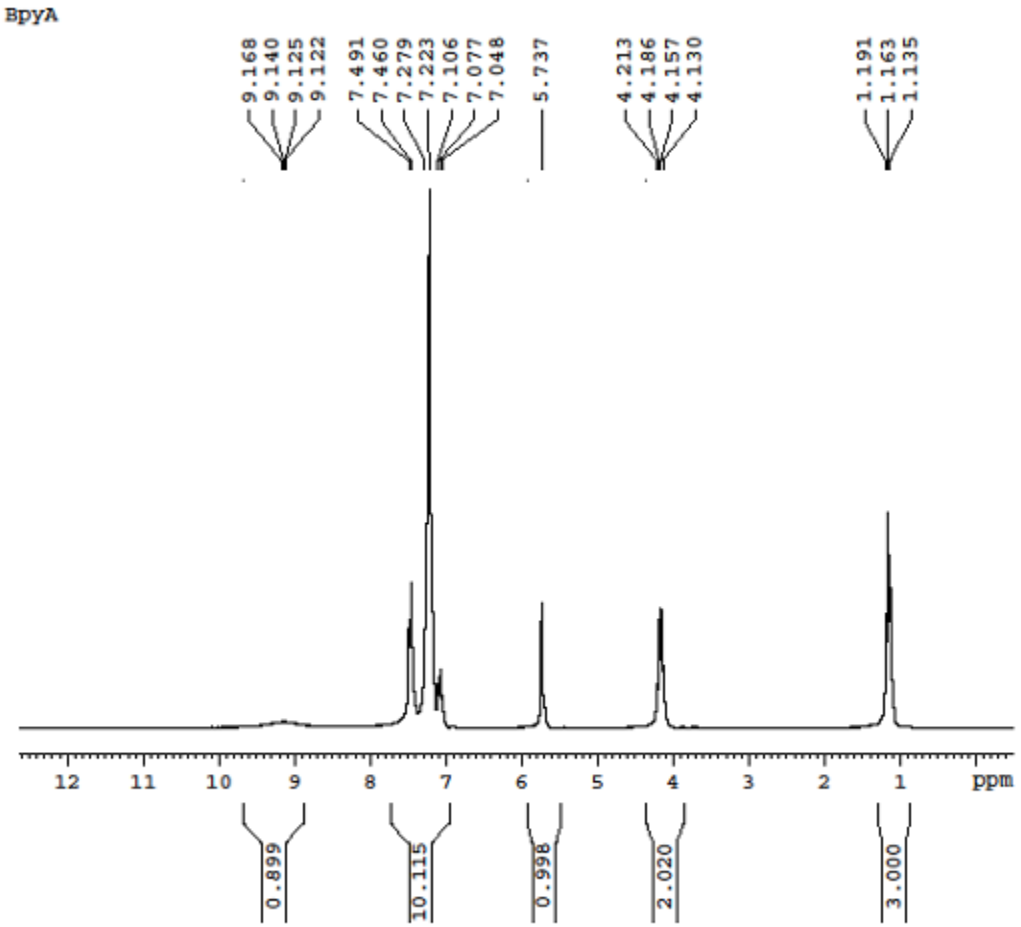


Figure 35. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 4-hydroxy-5-oxo-1,2-diphenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4l**)

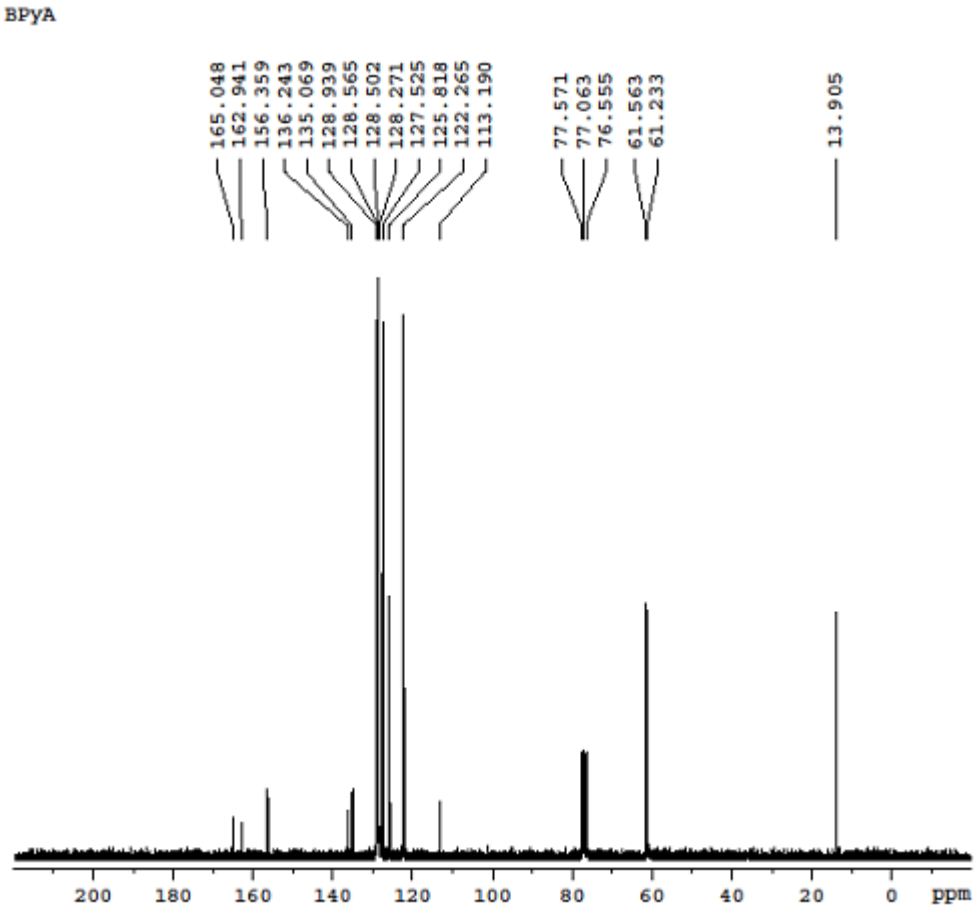


Figure 36. ^{13}C NMR (62.90 MHz, $CDCl_3$) spectrum of Ethyl 4-hydroxy-5-oxo-1,2-diphenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4l**)

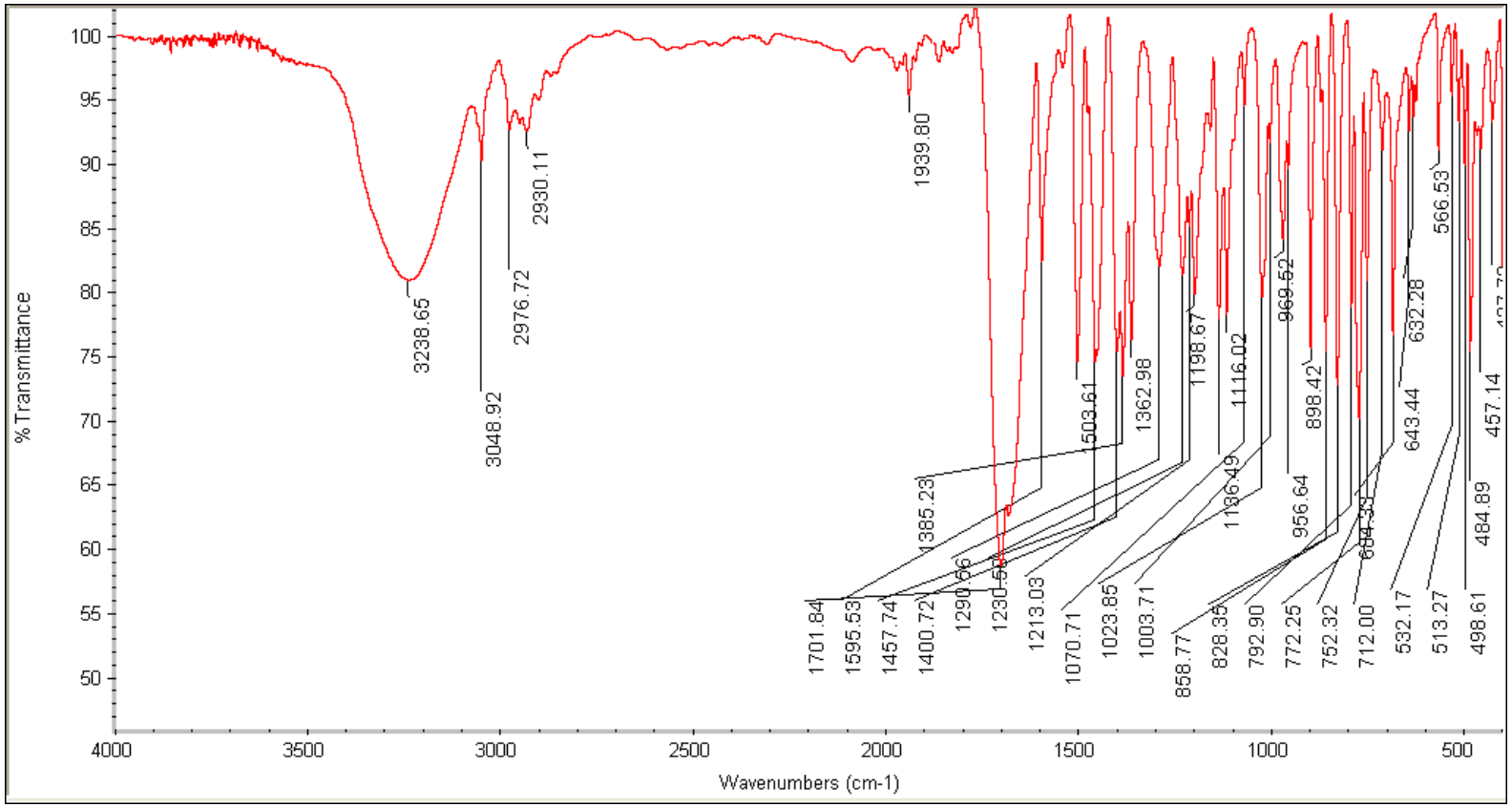


Figure 37. FT-IR spectrum of Ethyl 4-hydroxy-2-(naphthalen-2-yl)-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4m**)

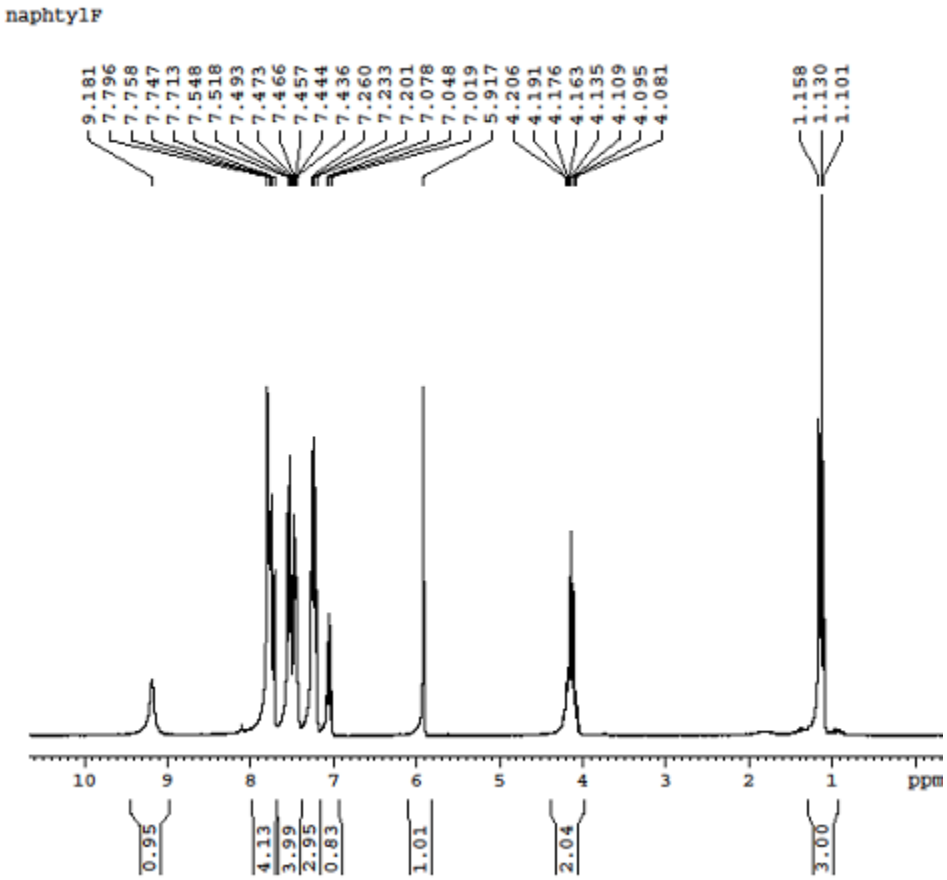


Figure 38. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 4-hydroxy-2-(naphthalen-2-yl)-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4m**)

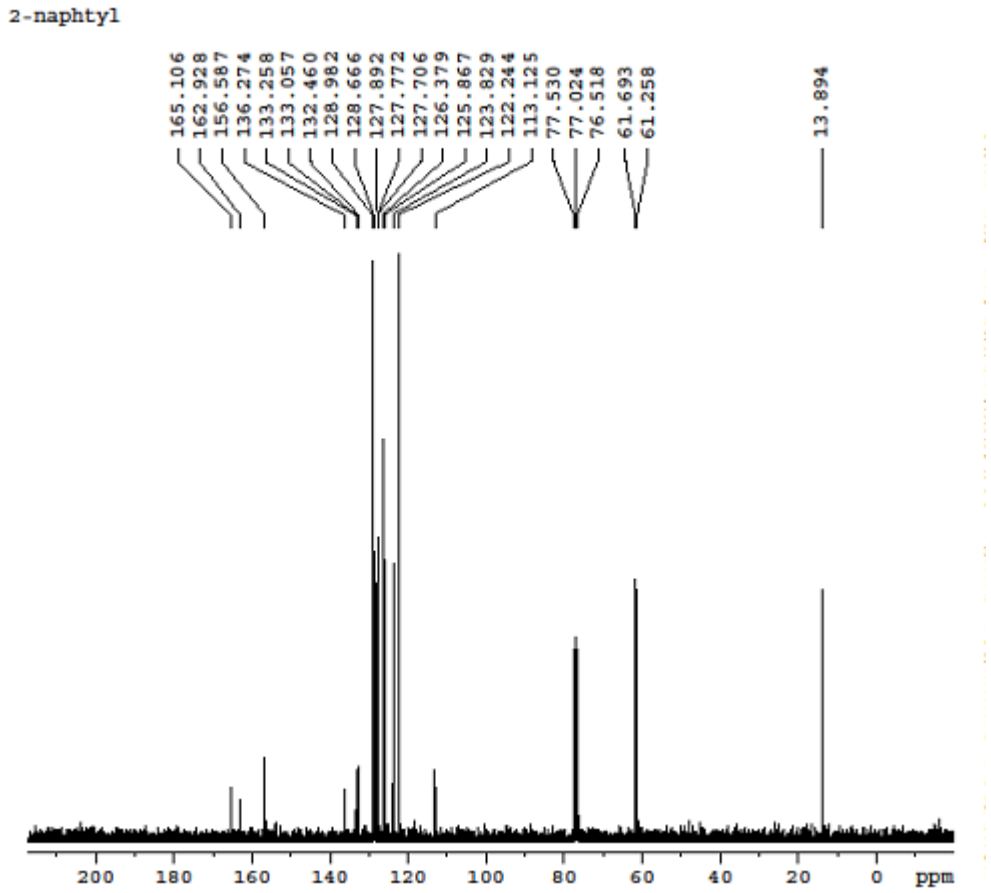


Figure 39. ^{13}C NMR (62.90 MHz, $CDCl_3$) spectrum of Ethyl 4-hydroxy-2-(naphthalen-2-yl)-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4m**)

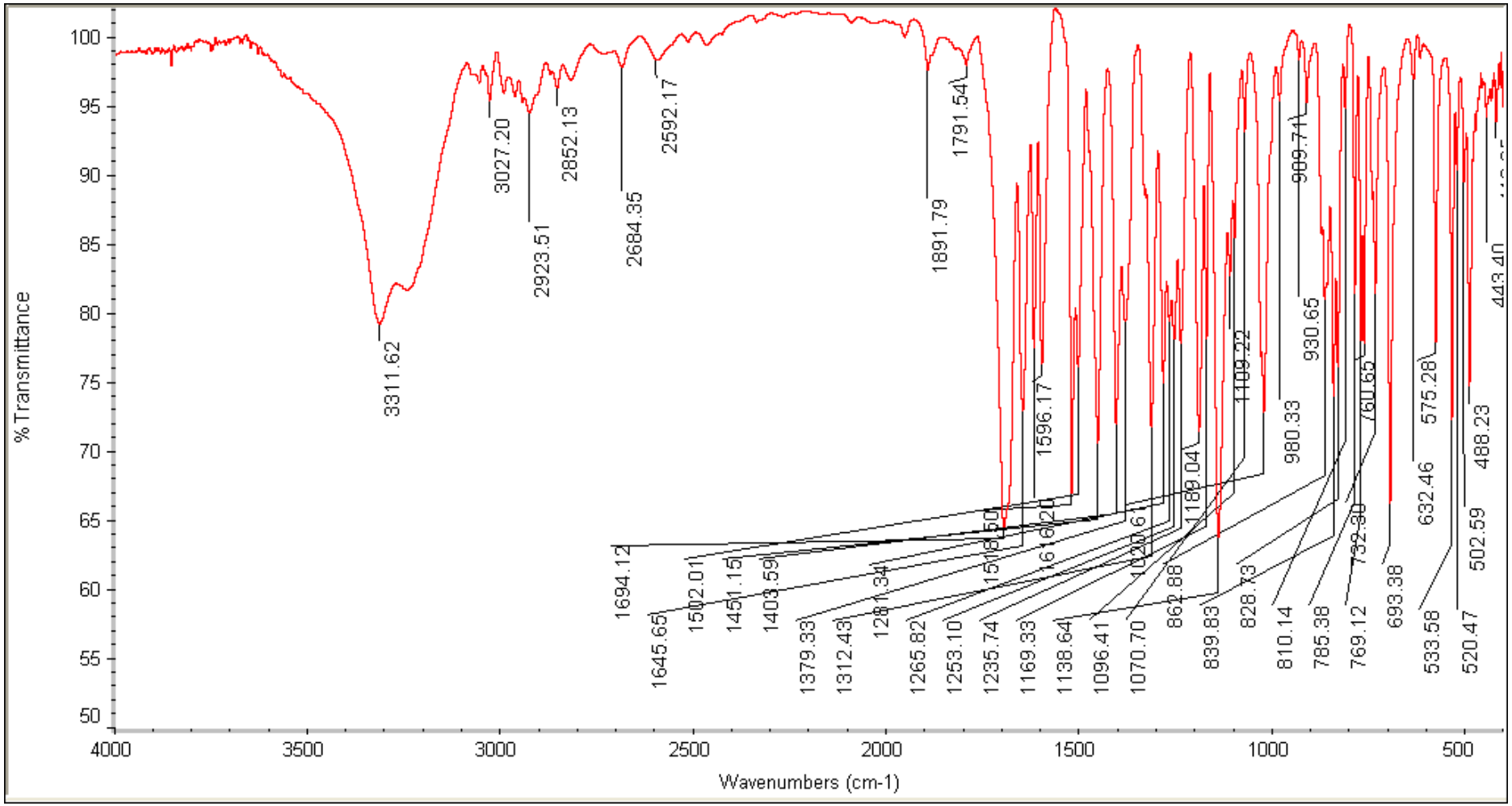


Figure 40. FT-IR spectrum of Ethyl 4-hydroxy-2-(4-hydroxyphenyl)-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4n**)

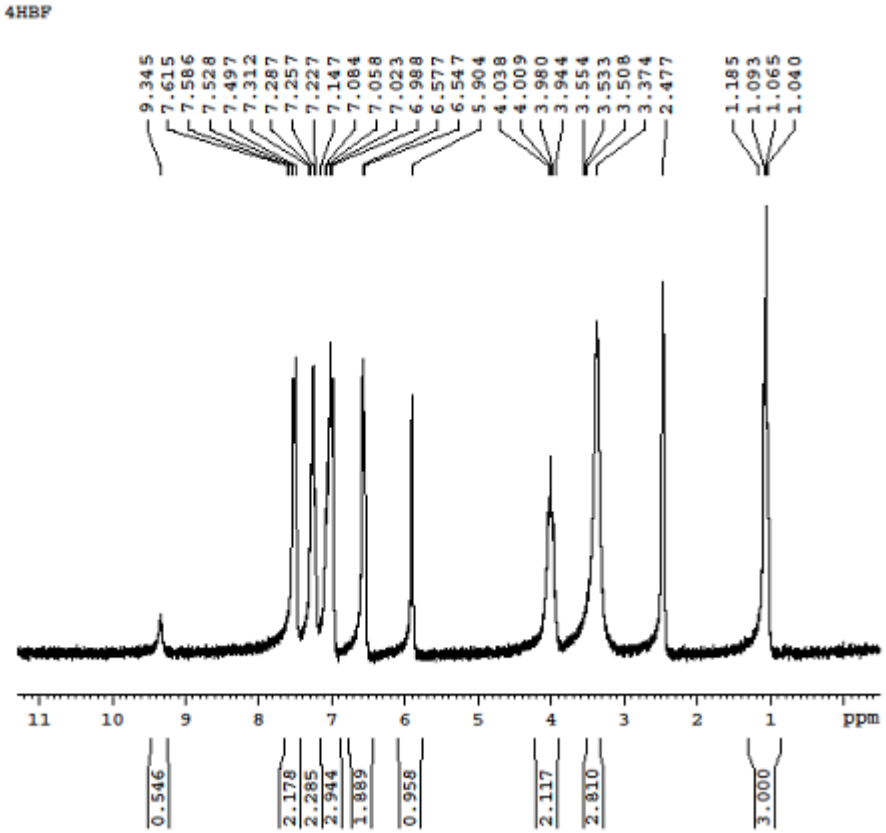


Figure 41. ^{1}H NMR (250.13 MHz, DMSO-d_6) spectrum of Ethyl 4-hydroxy-2-(4-hydroxyphenyl)-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4n**)

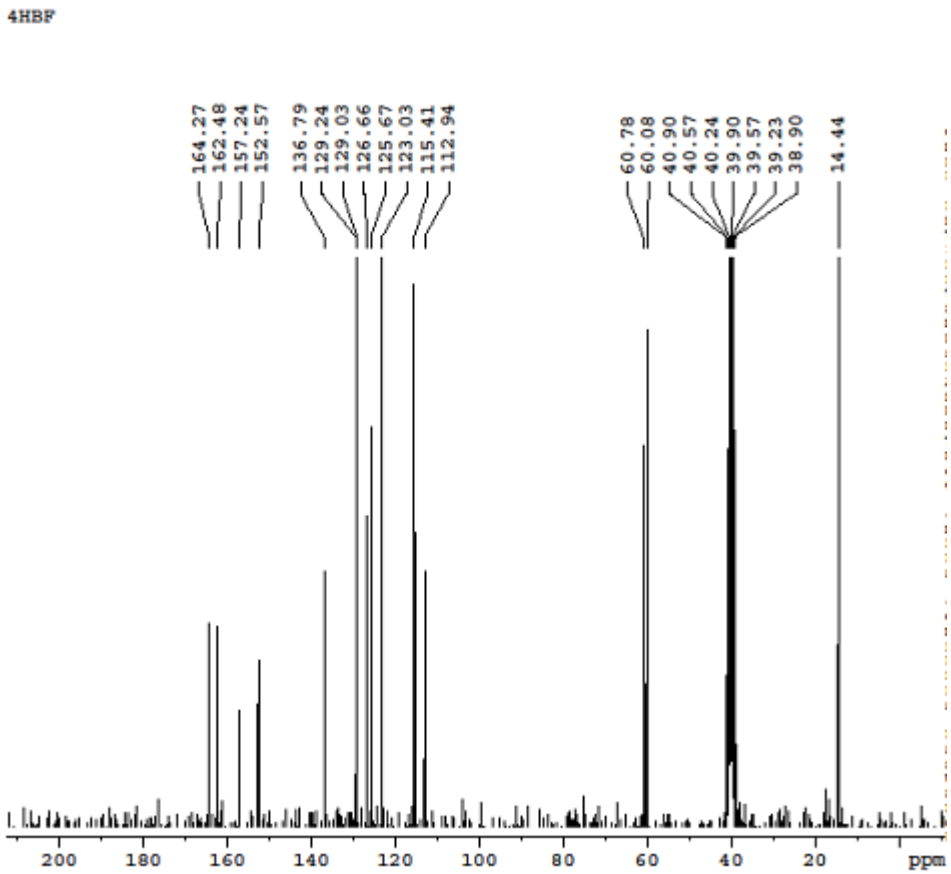


Figure 42. ^{1}H NMR (62.90 MHz, DMSO-d_6) spectrum of Ethyl 4-hydroxy-2-(4-hydroxyphenyl)-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4n**)

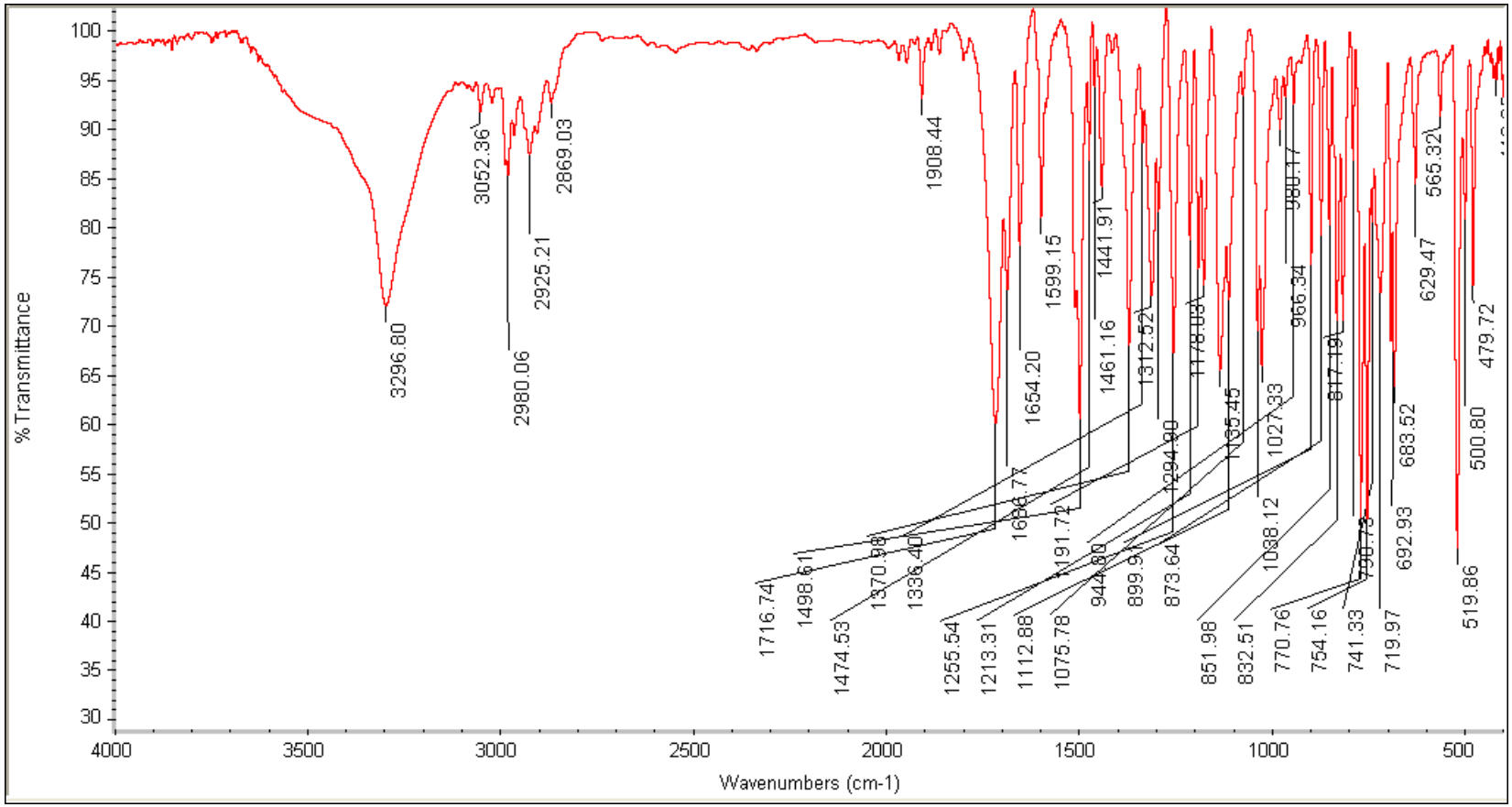


Figure 43. FT-IR spectrum of Ethyl 4-hydroxy-5-oxo-1-phenyl-2-(p-tolyl)-2,5-dihydro-1H-pyrrole-3-carboxylate (**4o**)

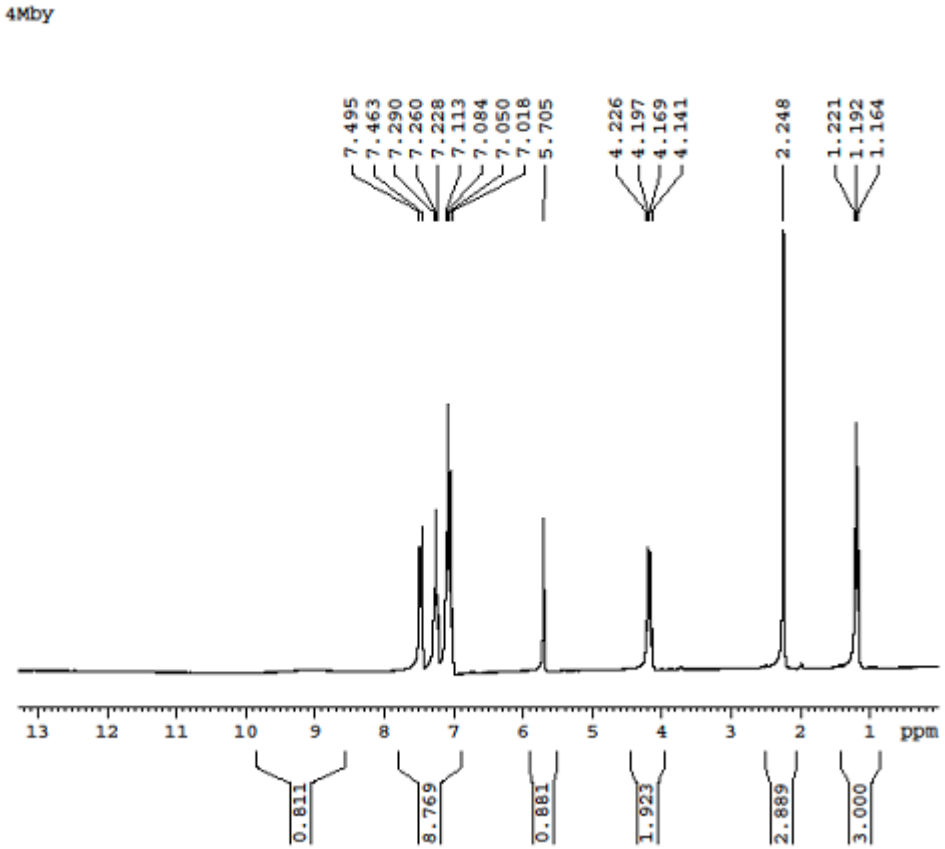


Figure 44. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 4-hydroxy-5-oxo-1-phenyl-2-(p-tolyl)-2, 5-dihydro-1H-pyrrole-3-carboxylate (**4o**)

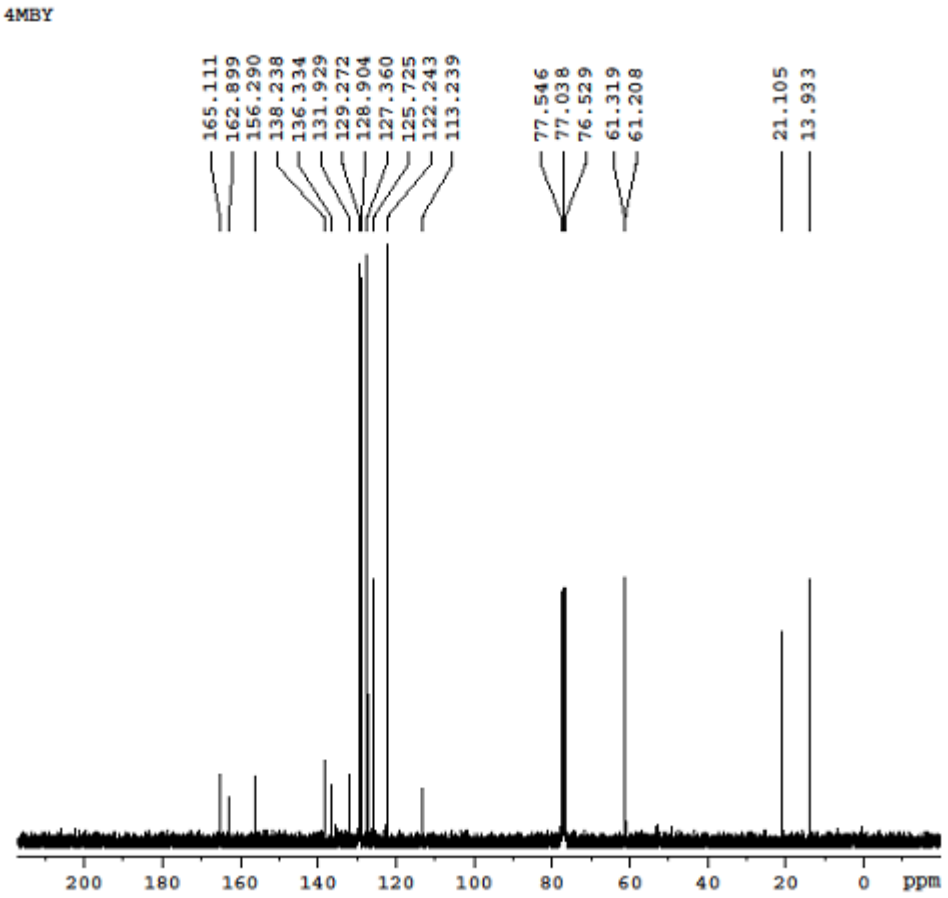


Figure 45. ^{13}C NMR (62.90 MHz, $CDCl_3$) spectrum of Ethyl 4-hydroxy-5-oxo-1-phenyl-2-(p-tolyl)-2,5-dihydro-1H-pyrrole-3-carboxylate (**4o**).

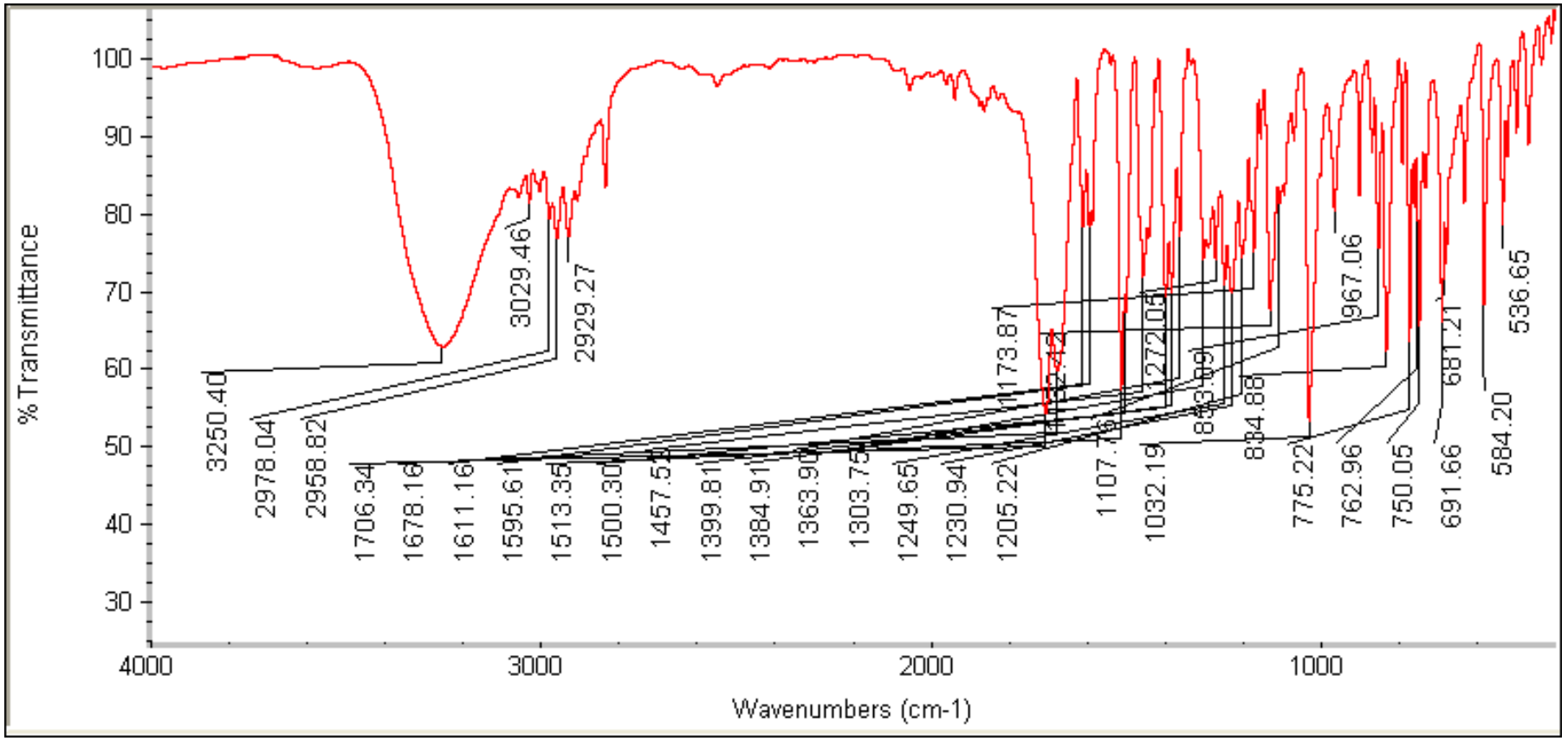


Figure 46. FT-IR spectrum of Ethyl 4-hydroxy-2-(4-methoxyphenyl)-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4p**).

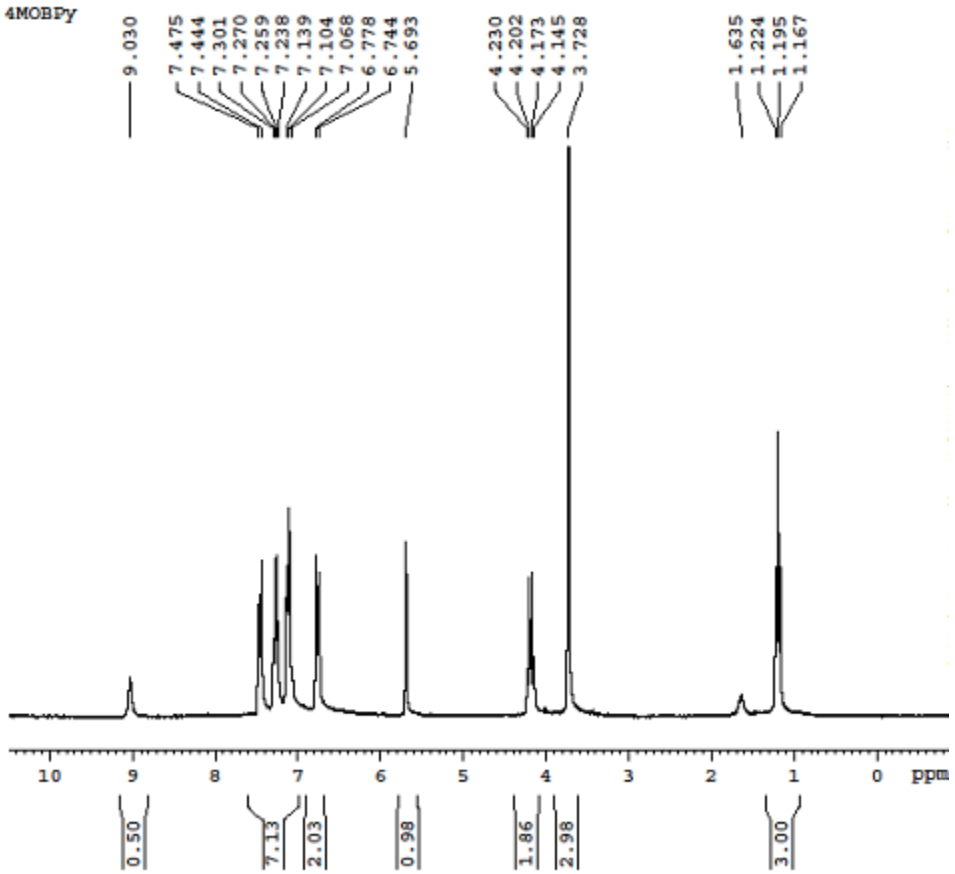


Figure 47. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 4-hydroxy-2-(4-methoxyphenyl)-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4p**)

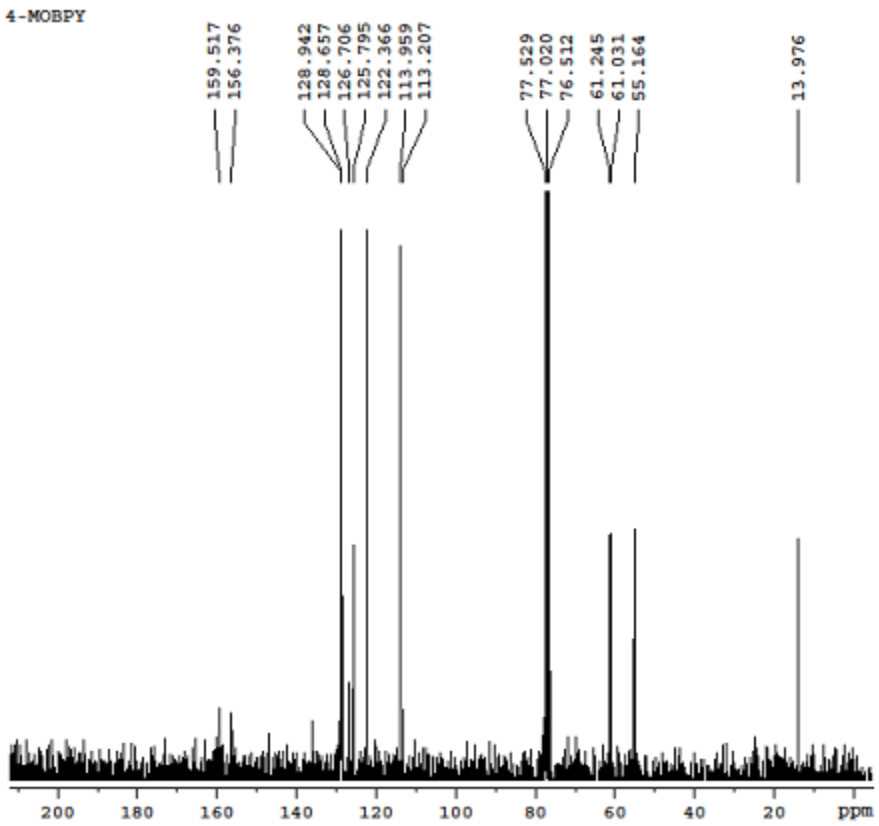


Figure 48. ^{13}C NMR (62.90 MHz, $CDCl_3$) spectrum of Ethyl 4-hydroxy-2-(4-methoxyphenyl)-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4p**)

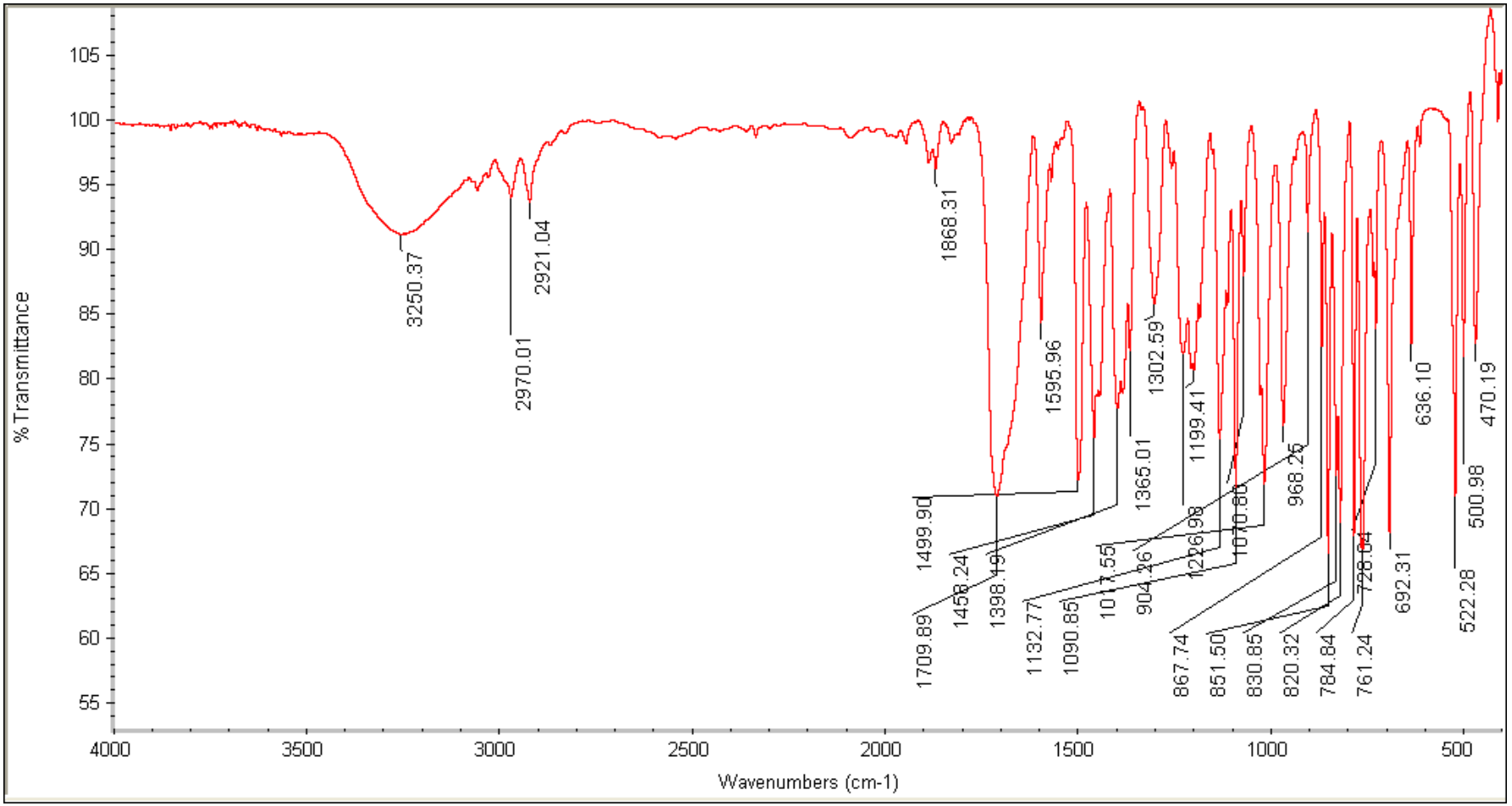


Figure 49. FT-IR spectrum of Ethyl 4-hydroxy-2-(4-(methylthio)phenyl)-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4q**)

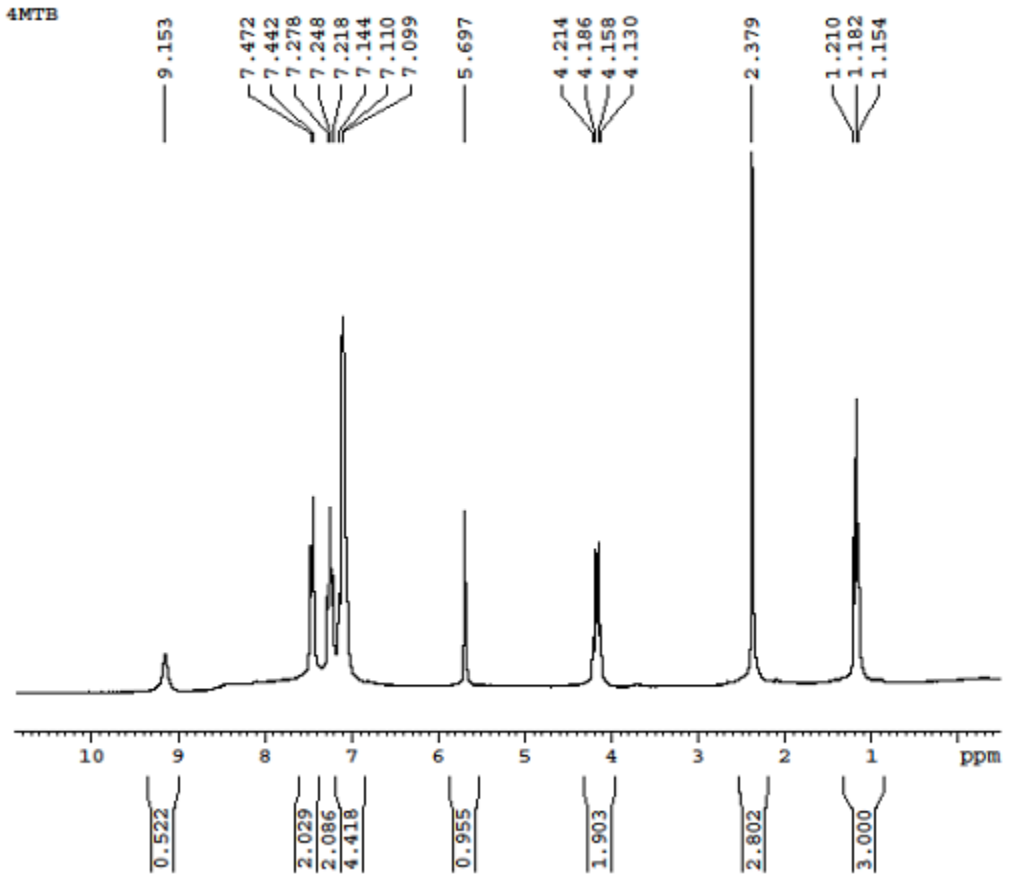


Figure 50. ^{1}H NMR (250.13 MHz, $CDCl_3$) spectrum of Ethyl 4-hydroxy-2-(4-(methylthio)phenyl)-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4q**)

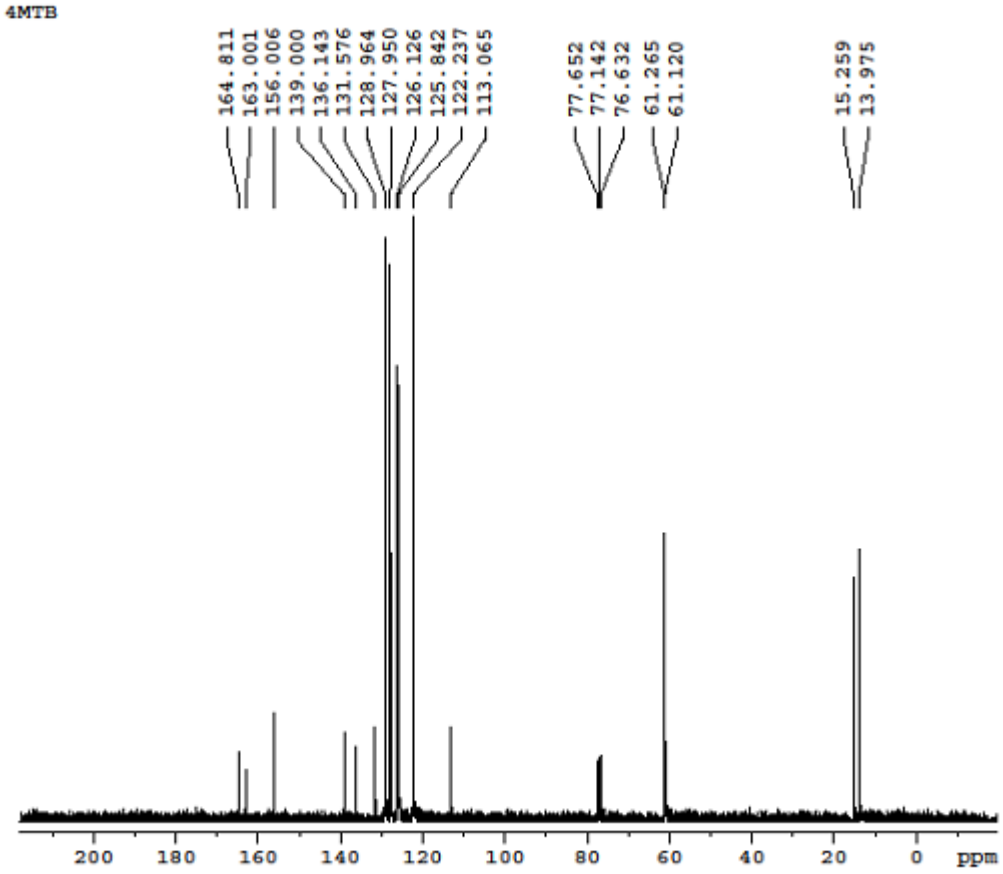


Figure 51. ^{13}C NMR (62.90 MHz, $CDCl_3$) spectrum of Ethyl 4-hydroxy-2-(4-(methylthio)phenyl)-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4q**)

Table1. X-ray diffraction study details for Ethyl 4-hydroxy-2-(4-(methylthio)phenyl)-5-oxo-1-phenyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4q**)

CCDC No.	2021152
Chemical formula	$C_{20}H_{19}NO_4S$
M_r	369.42
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	9.922 (3), 6.156 (2), 28.905 (9)
β (°)	92.68 (3)
V (Å^3)	1763.6 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.21
Crystal size (mm)	0.43 × 0.22 × 0.11
Diffractometer	Agilent Technologies Xcalibur R diffractometer
Absorption correction	Multi-scan
T_{min}, T_{max}	0.991, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10885, 5008, 4131
R_{int}	0.025
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.720
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.099, 1.03
No. of reflections	5008
No. of parameters	241
No. of restraints	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.45, −0.31