Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

A General Strategy for the Synthesis of Indoloquinolizine Alkaloids via Cyanide-Catalyzed Imino-Stetter Reaction

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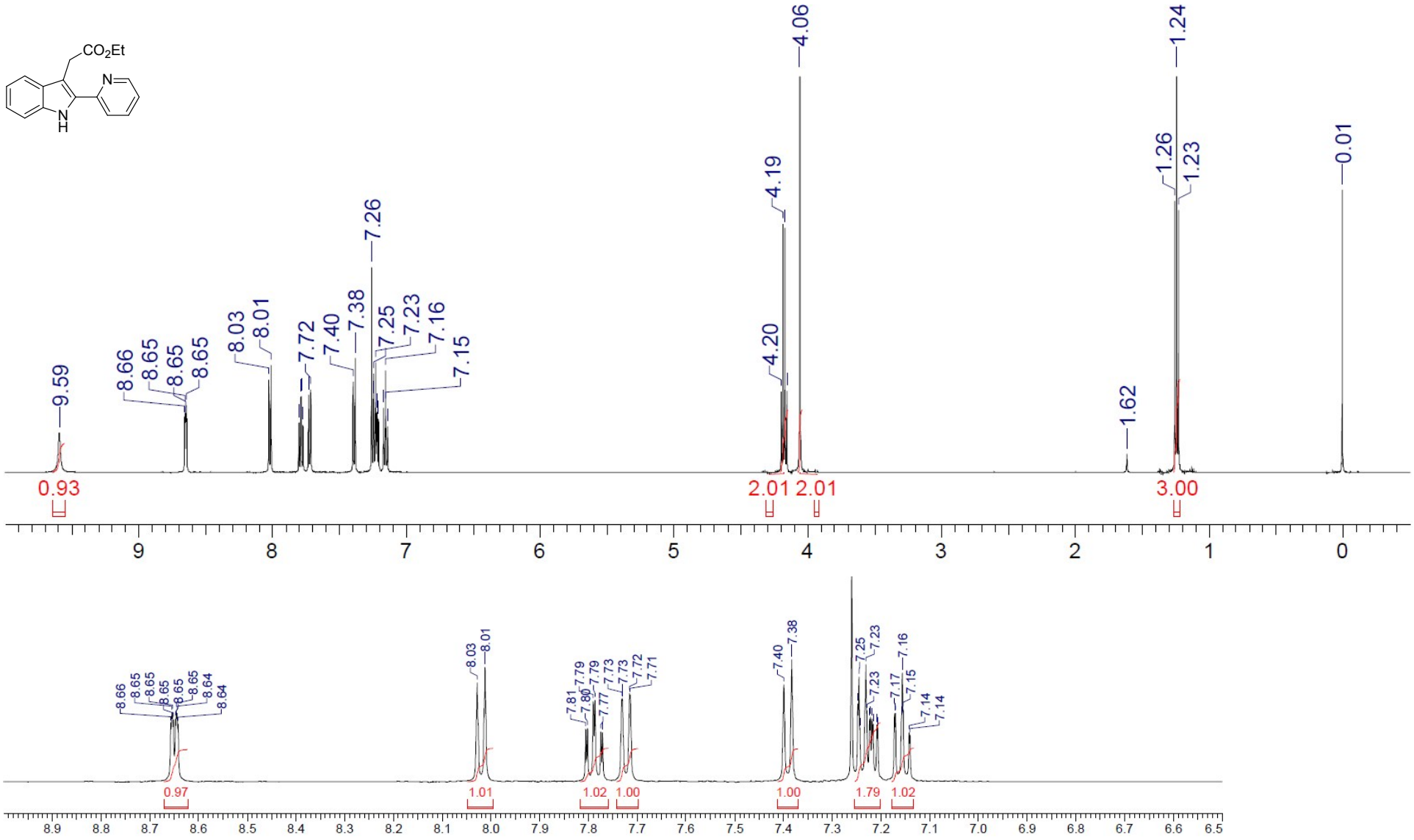
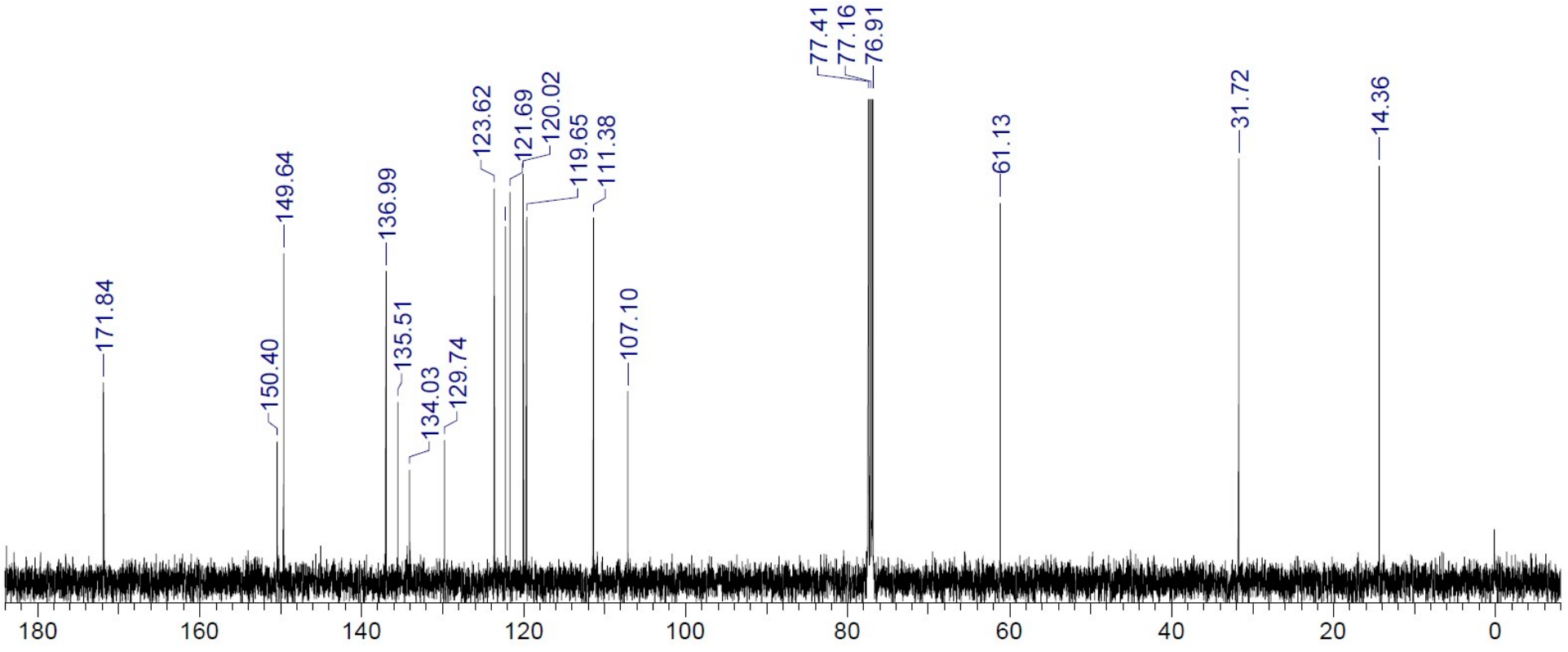
Spectroscopic Data

1. NMR Spectra of Ethyl 2-(2-(pyridin-2-yl)-1*H*-indol-3-yl)acetate (**4aa**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

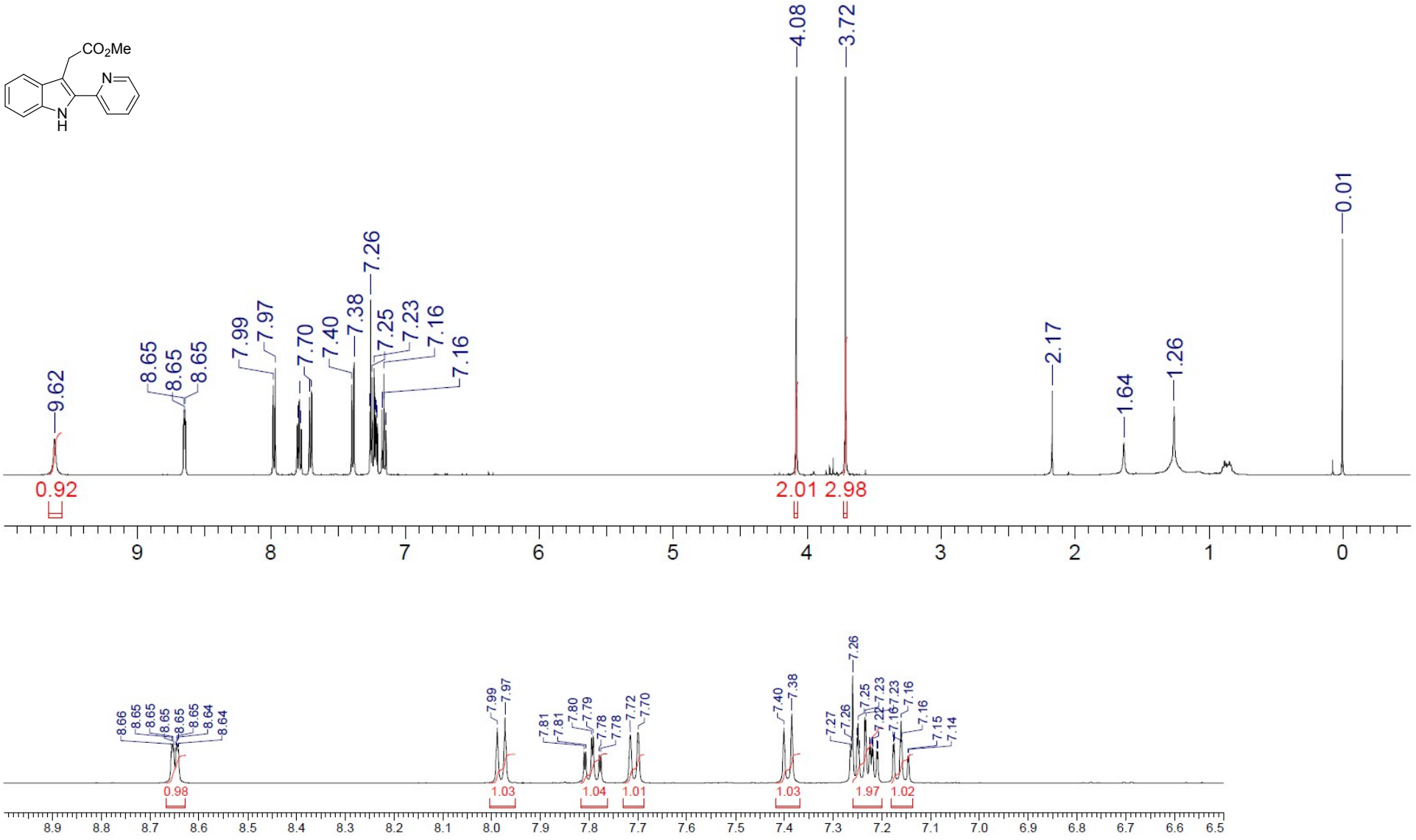


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

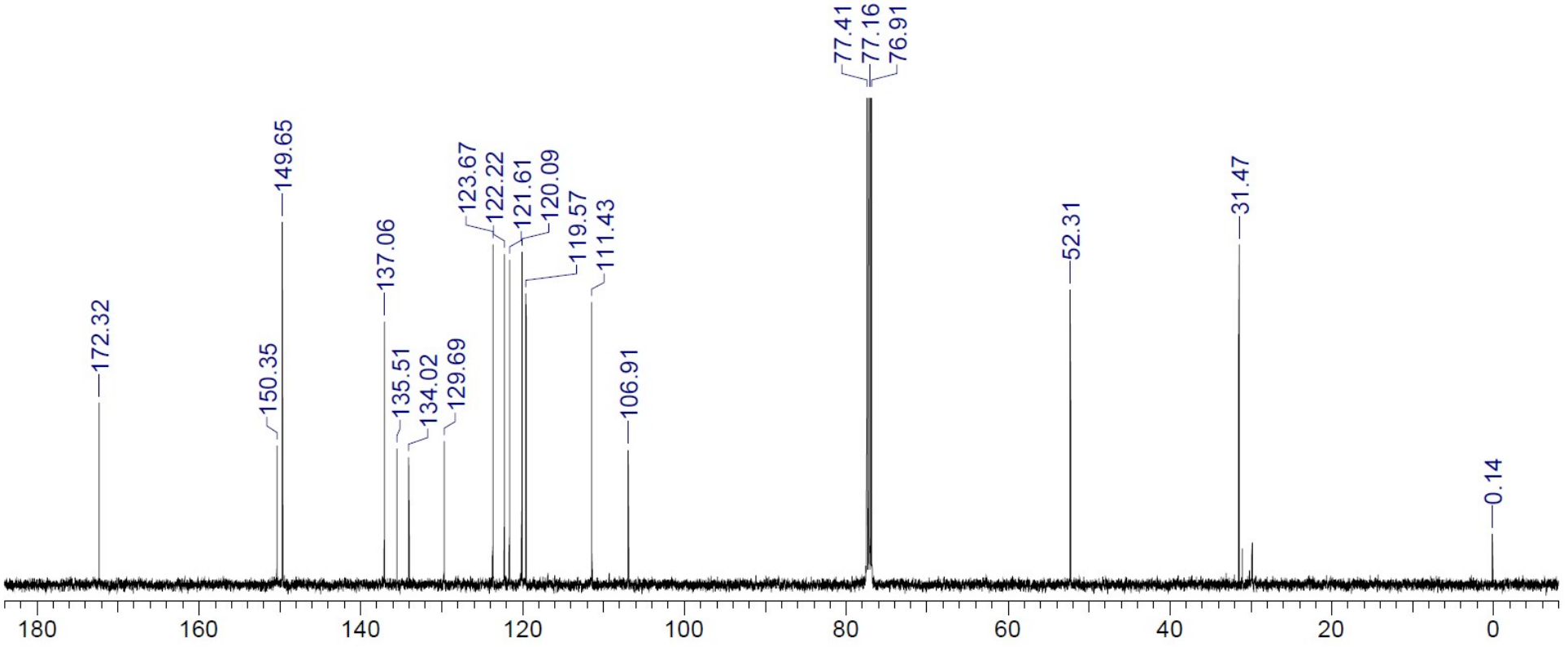


2. NMR Spectra of Methyl 2-(2-(pyridin-2-yl)-1*H*-indol-3-yl)acetate (**4ba**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

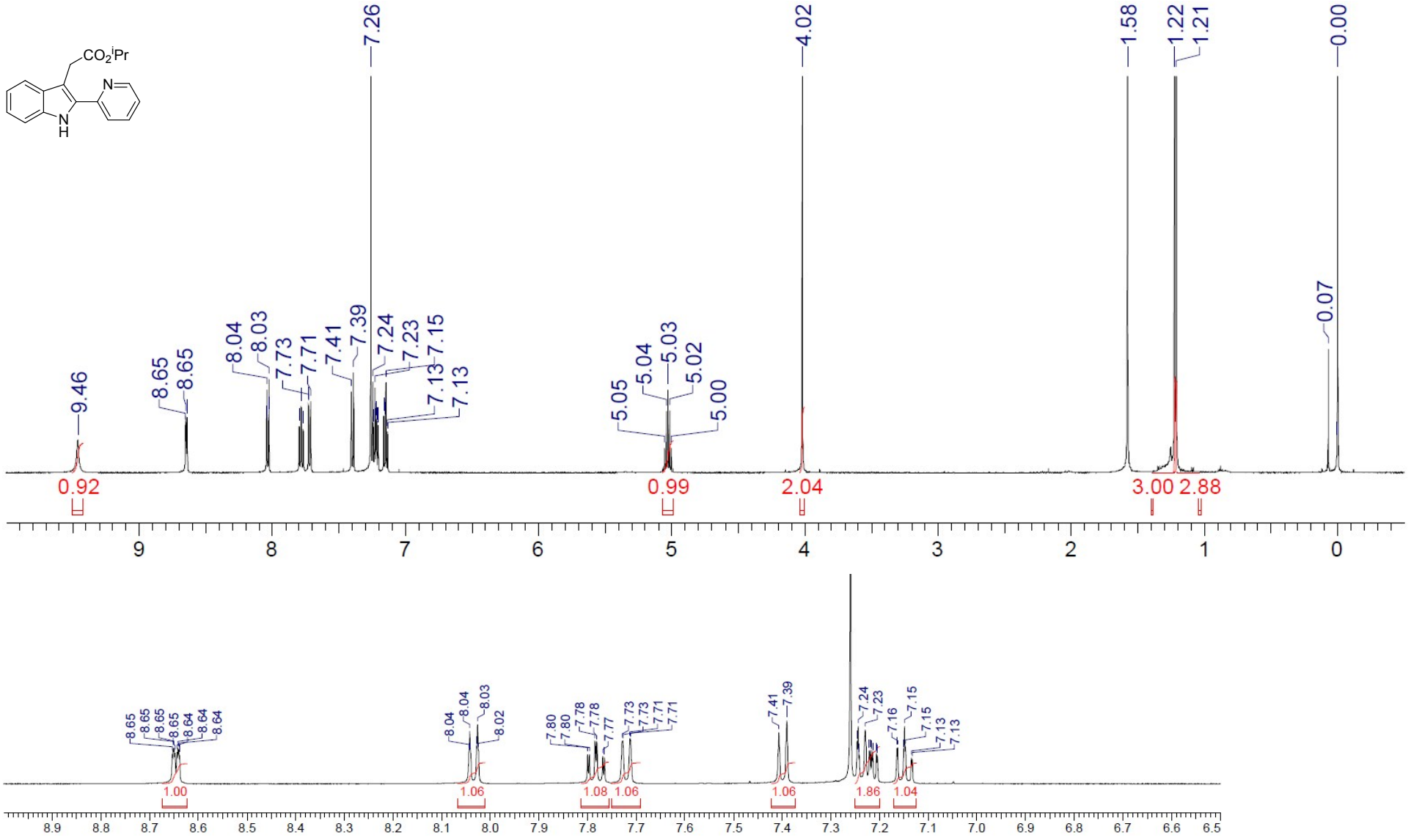


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

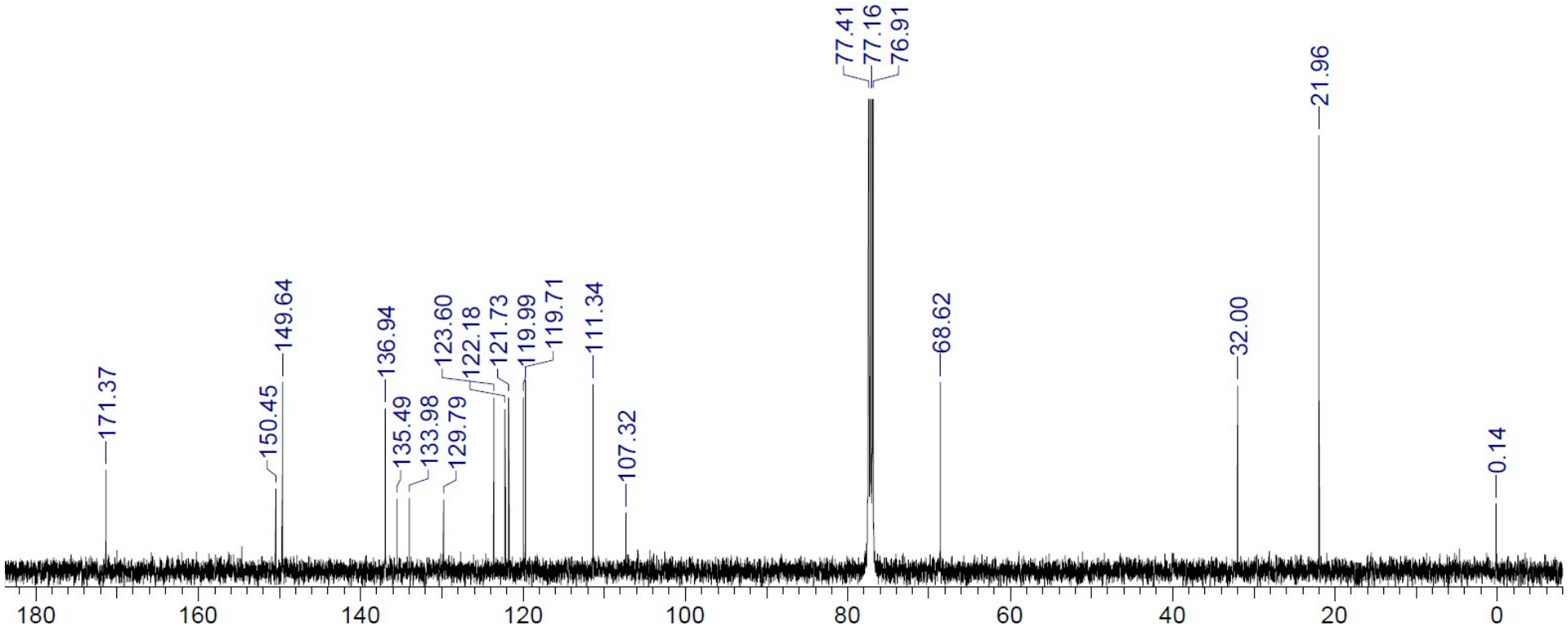


3. NMR Spectra of Isopropyl 2-(2-(pyridin-2-yl)-1*H*-indol-3-yl)acetate (**4ca**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

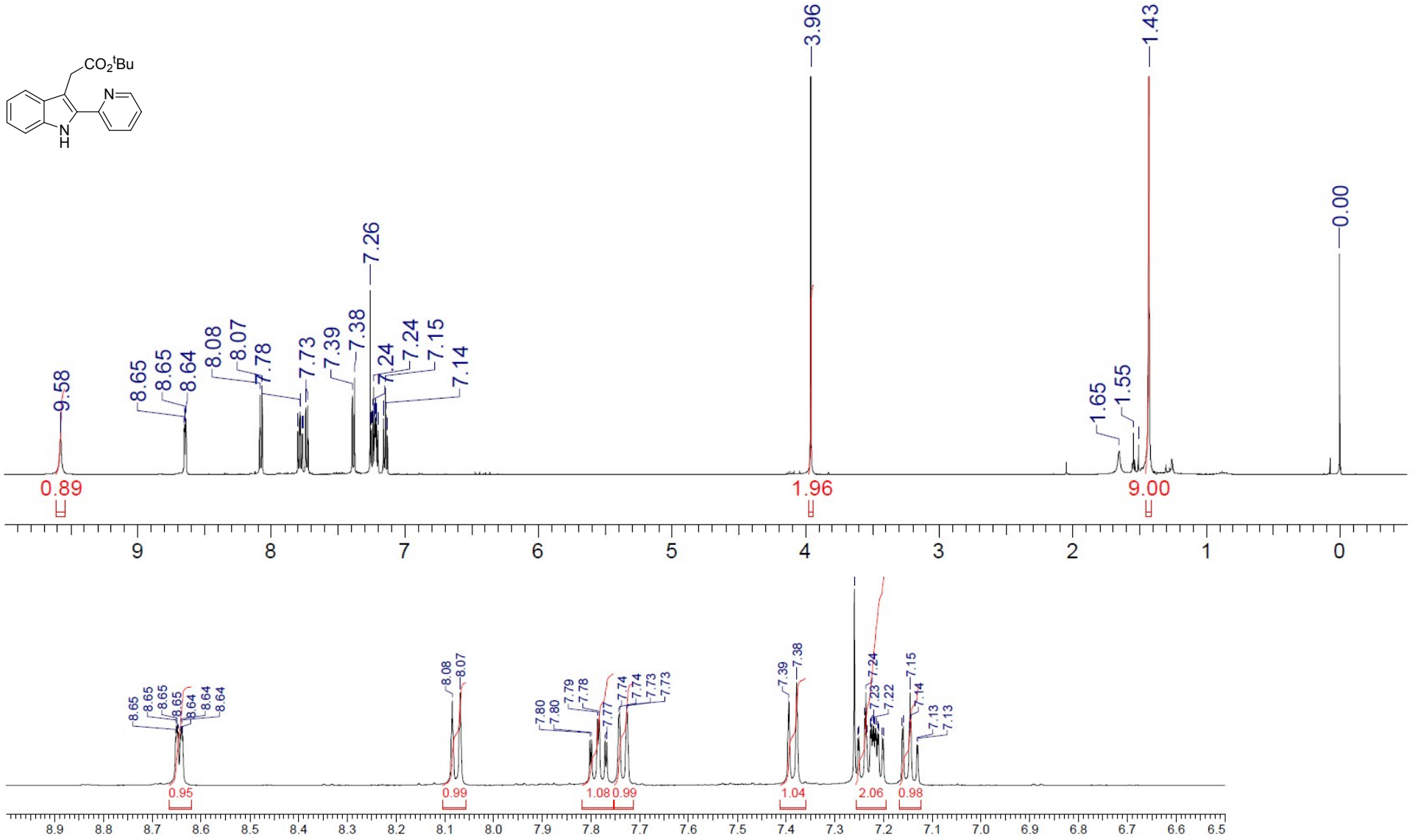


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

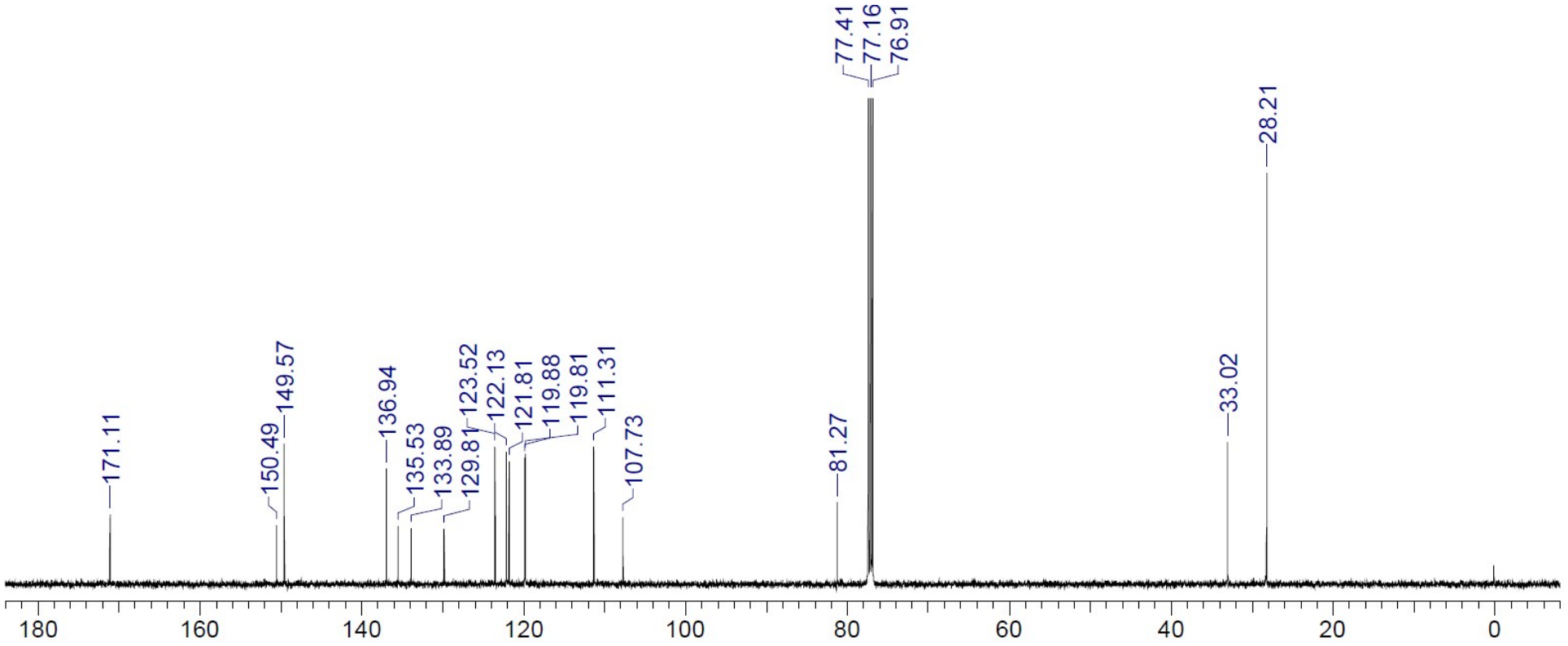


4. NMR Spectra of *tert*-Butyl-2-(2-(pyridin-2-yl)-1*H*-indol-3-yl)acetate (**4da**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

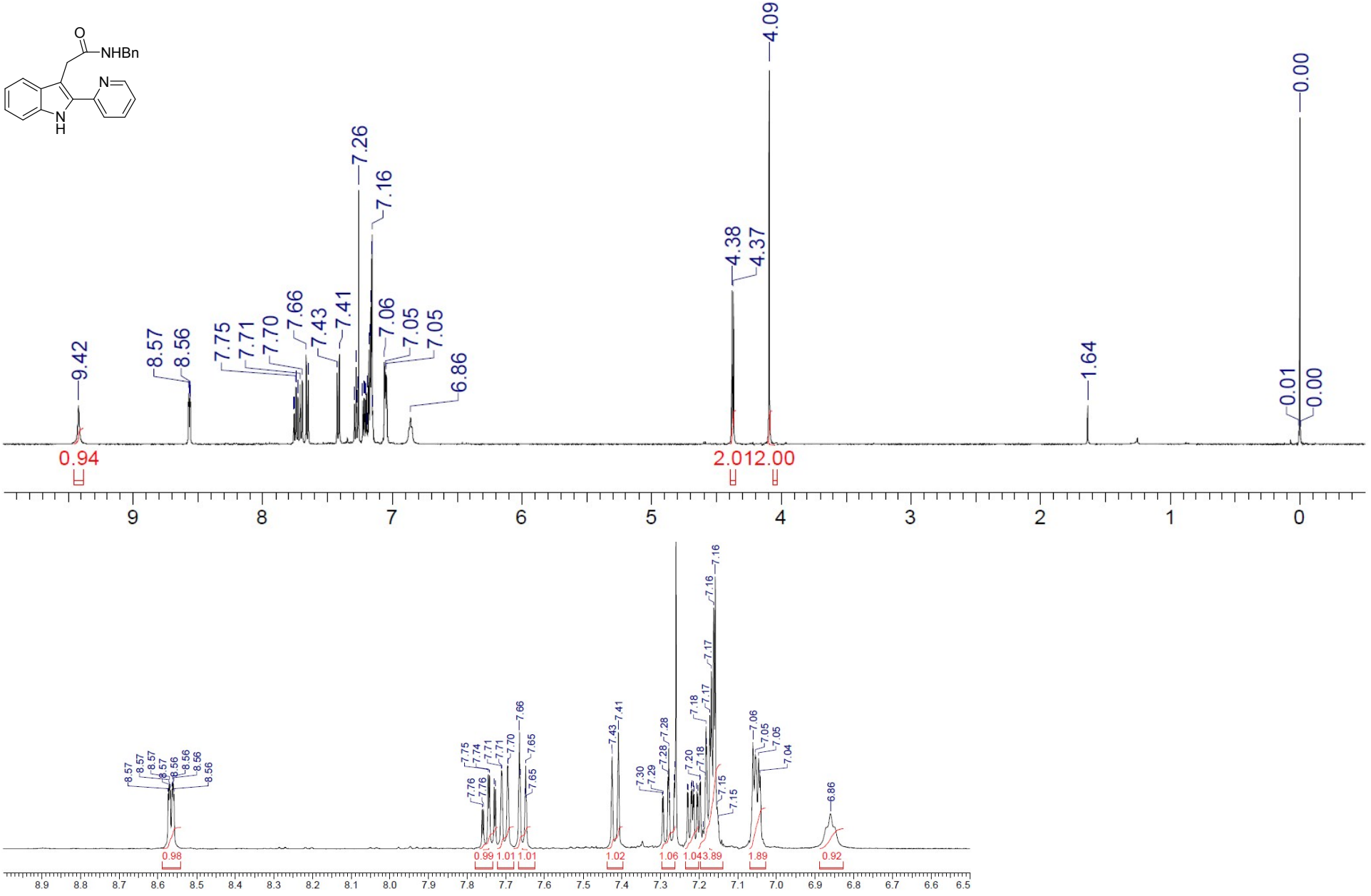


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

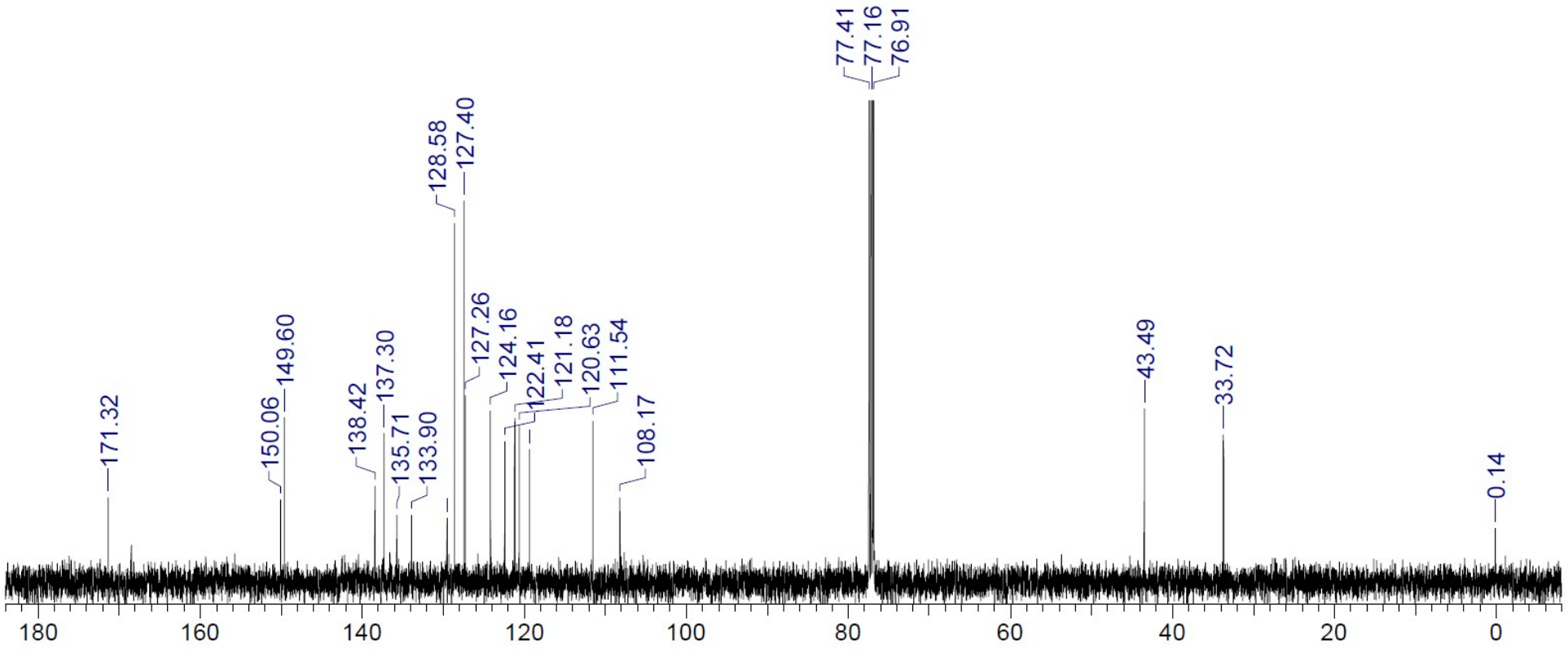


5. NMR Spectra of N-Benzyl-2-(2-(pyridin-2-yl)-1*H*-indol-3-yl)acetamide (**4ea**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

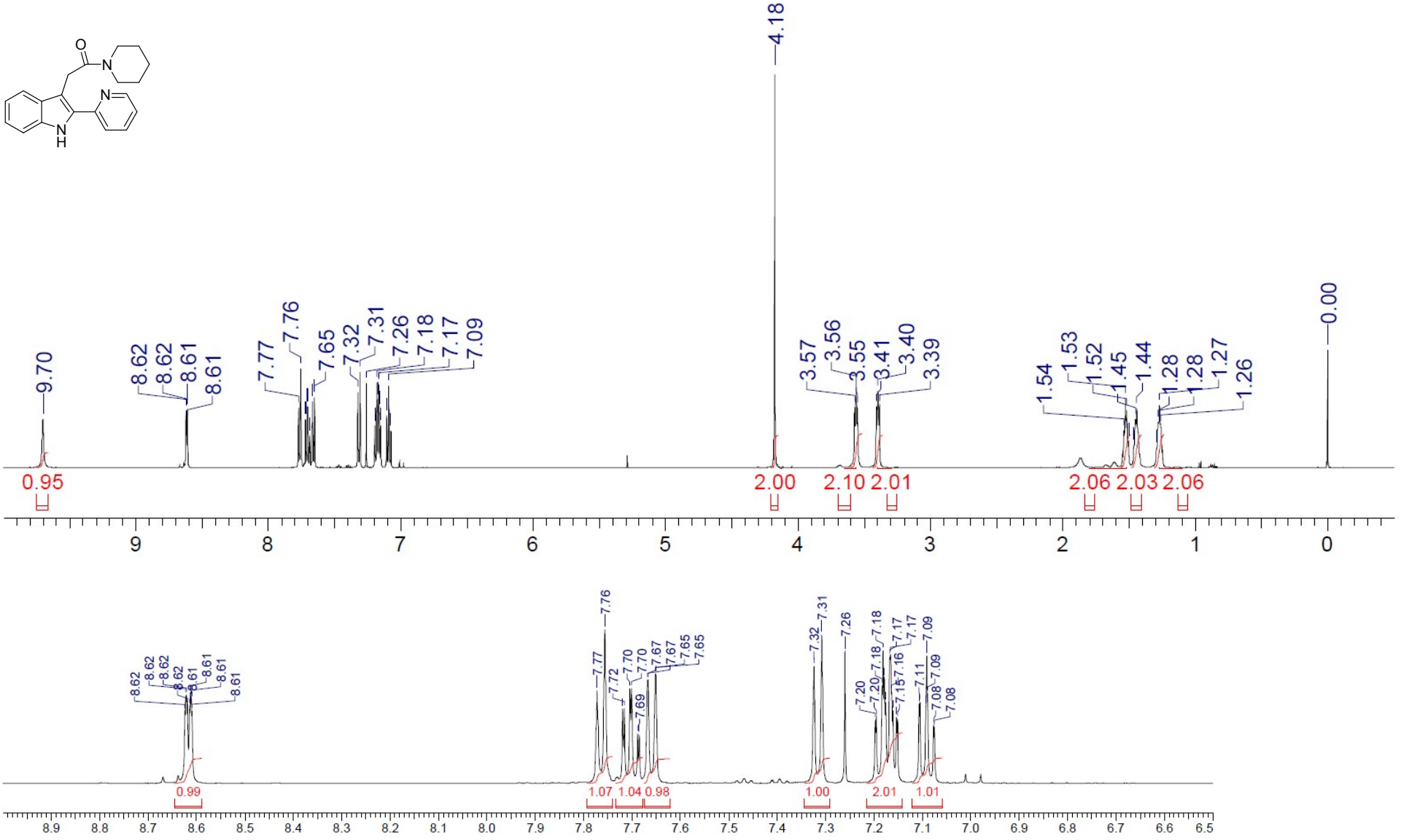


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

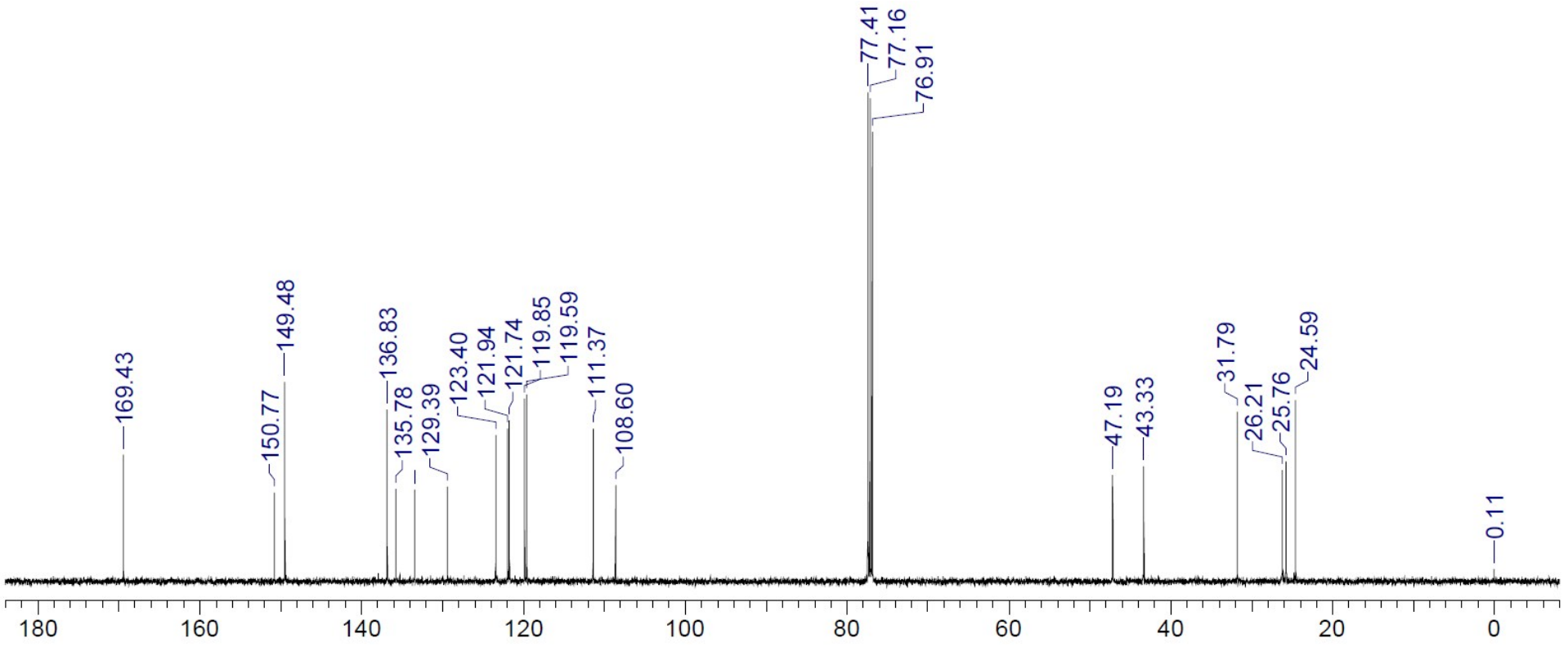


6. NMR Spectra of 2-(2-(Pyridin-2-yl)-1*H*-indol-3-yl)-piperidyl amide (**4fa**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

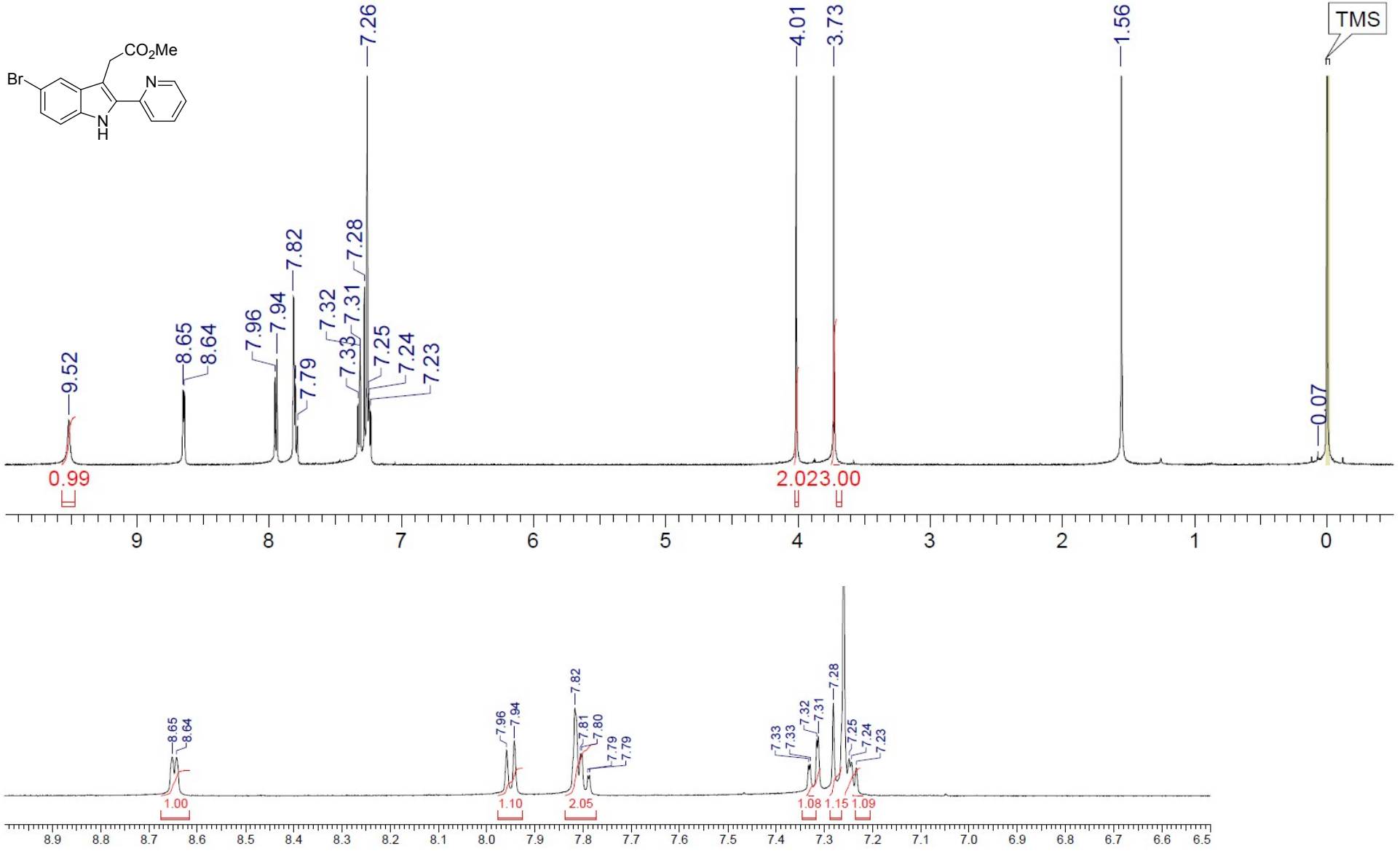


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

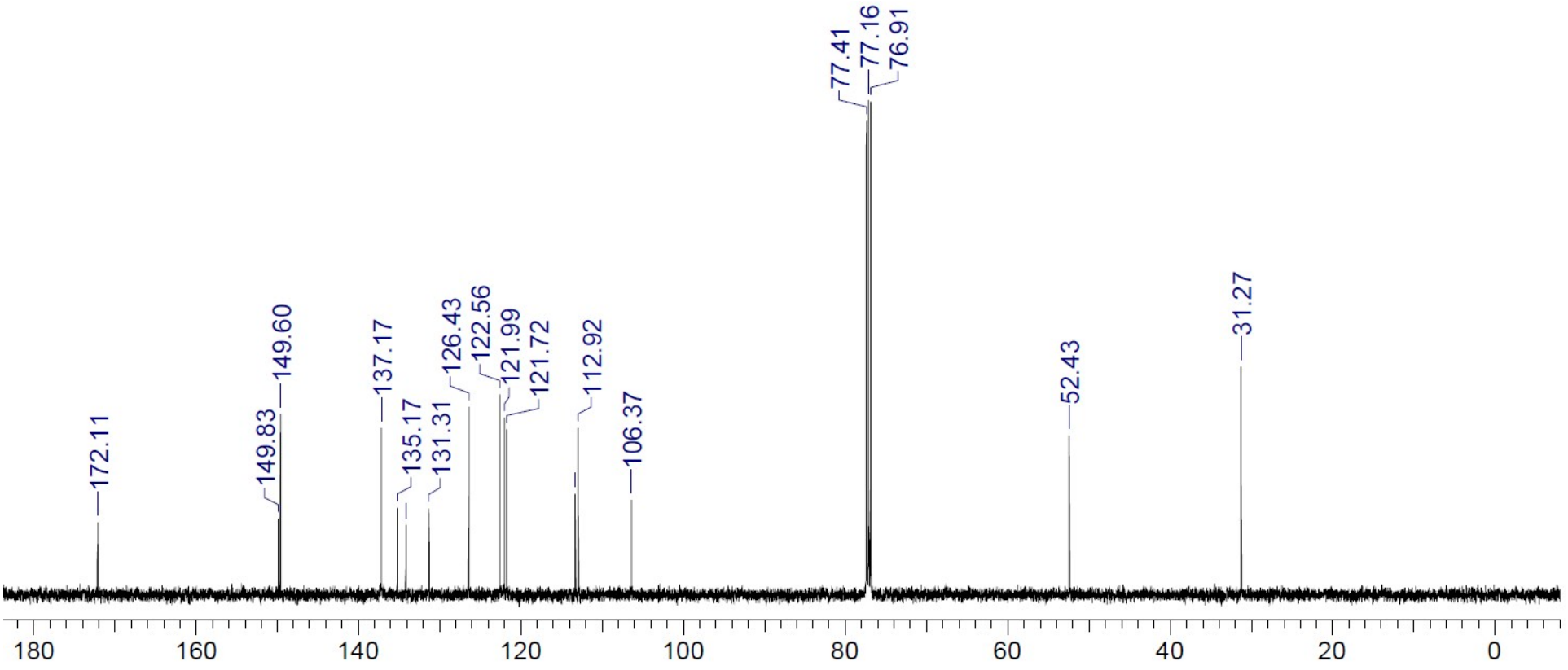


7. NMR Spectra of Methyl 2-(5-bromo-2-(pyridin-2-yl)-1*H*-indol-3-yl)acetate (**4ga**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

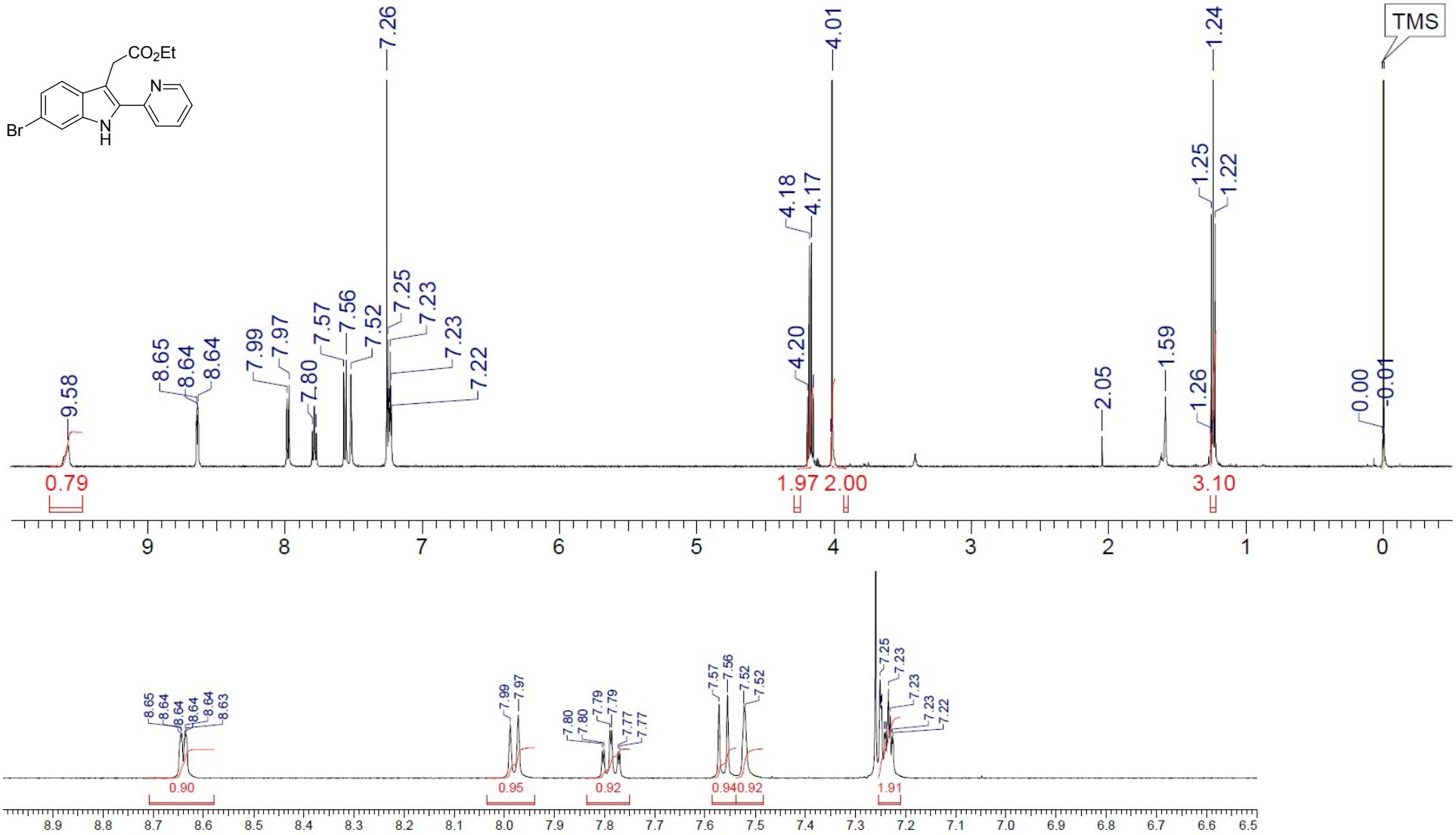


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

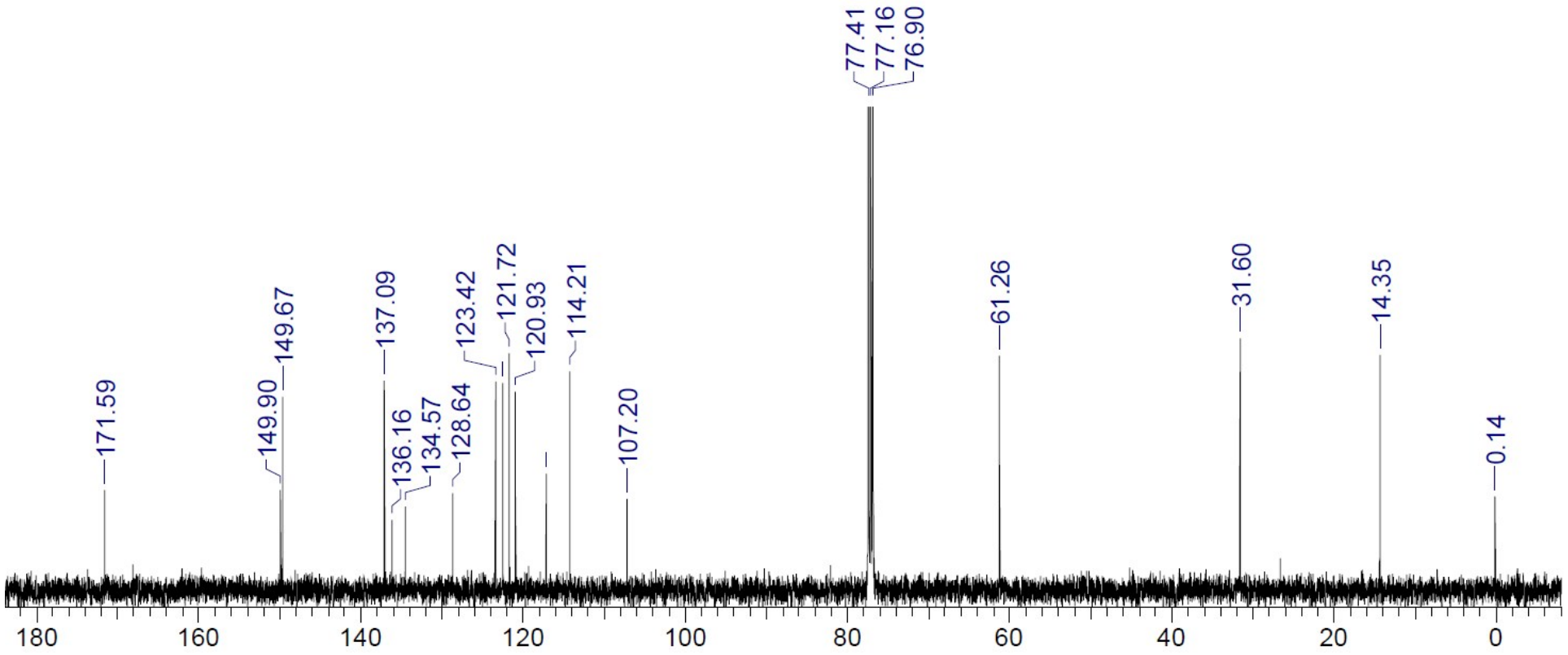


8. NMR Spectra of Ethyl 2-(6-bromo-2-(pyridin-2-yl)-1*H*-indol-3-yl)acetate (**4ha**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

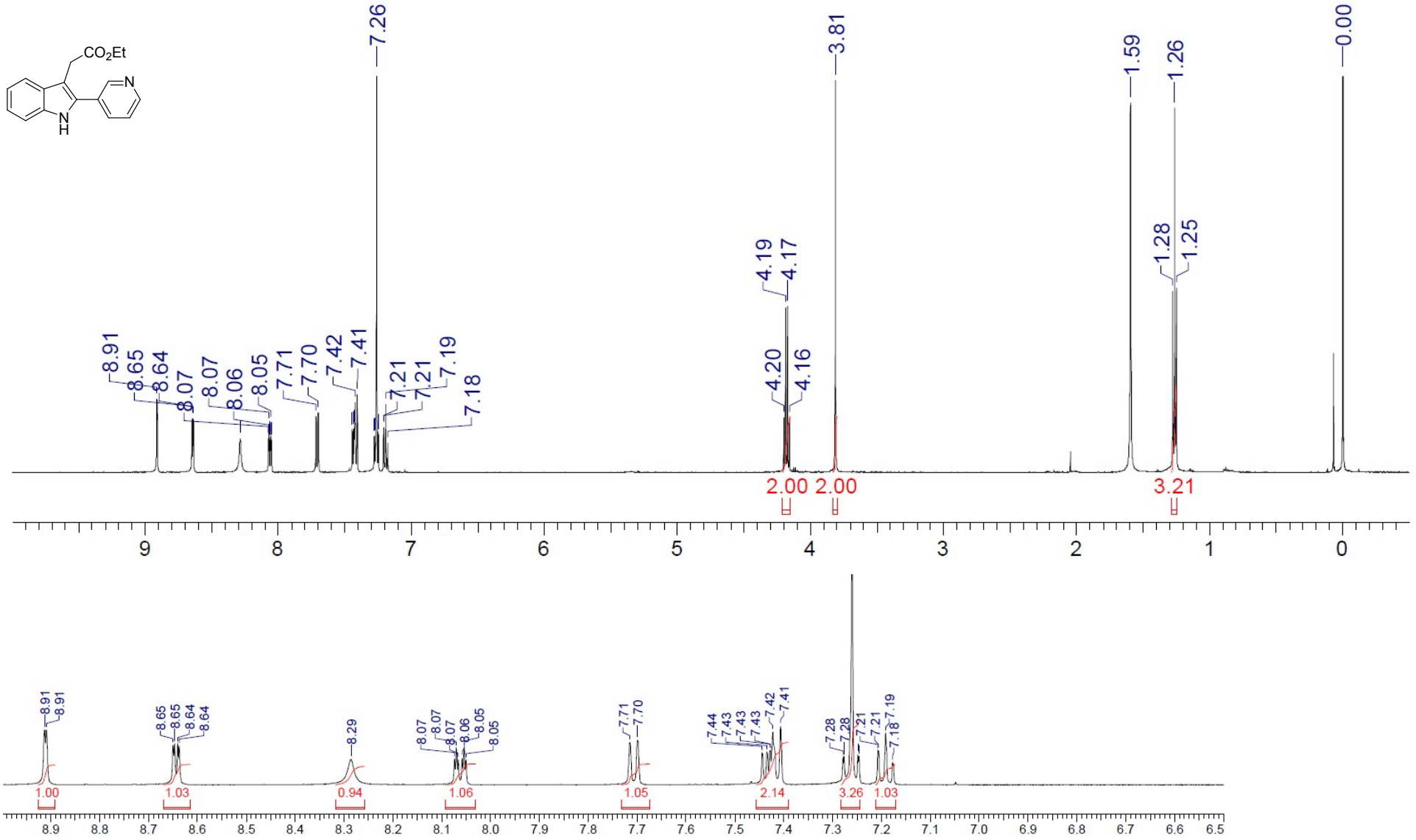


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

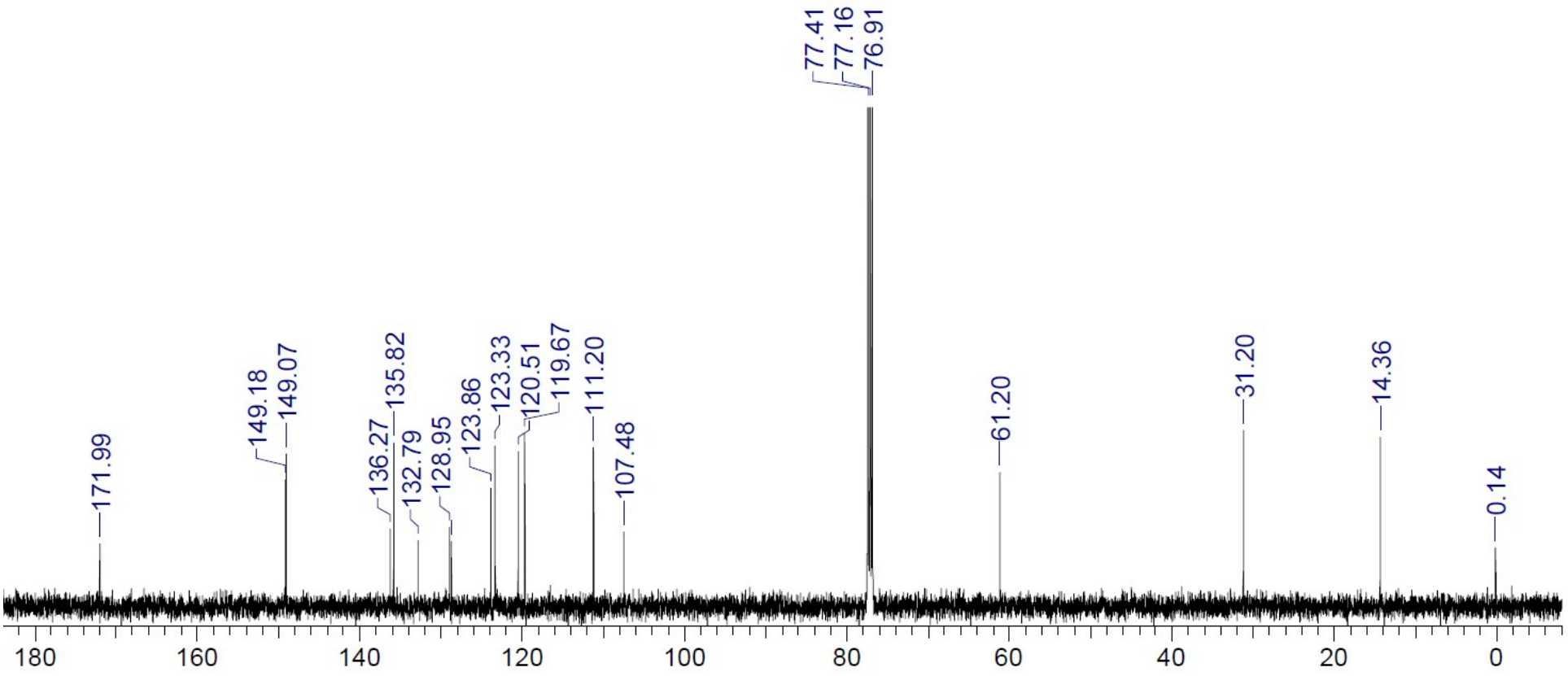


9. NMR Spectra of Ethyl 2-(2-(pyridin-3-yl)-1*H*-indol-3-yl)acetate (**4ab**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

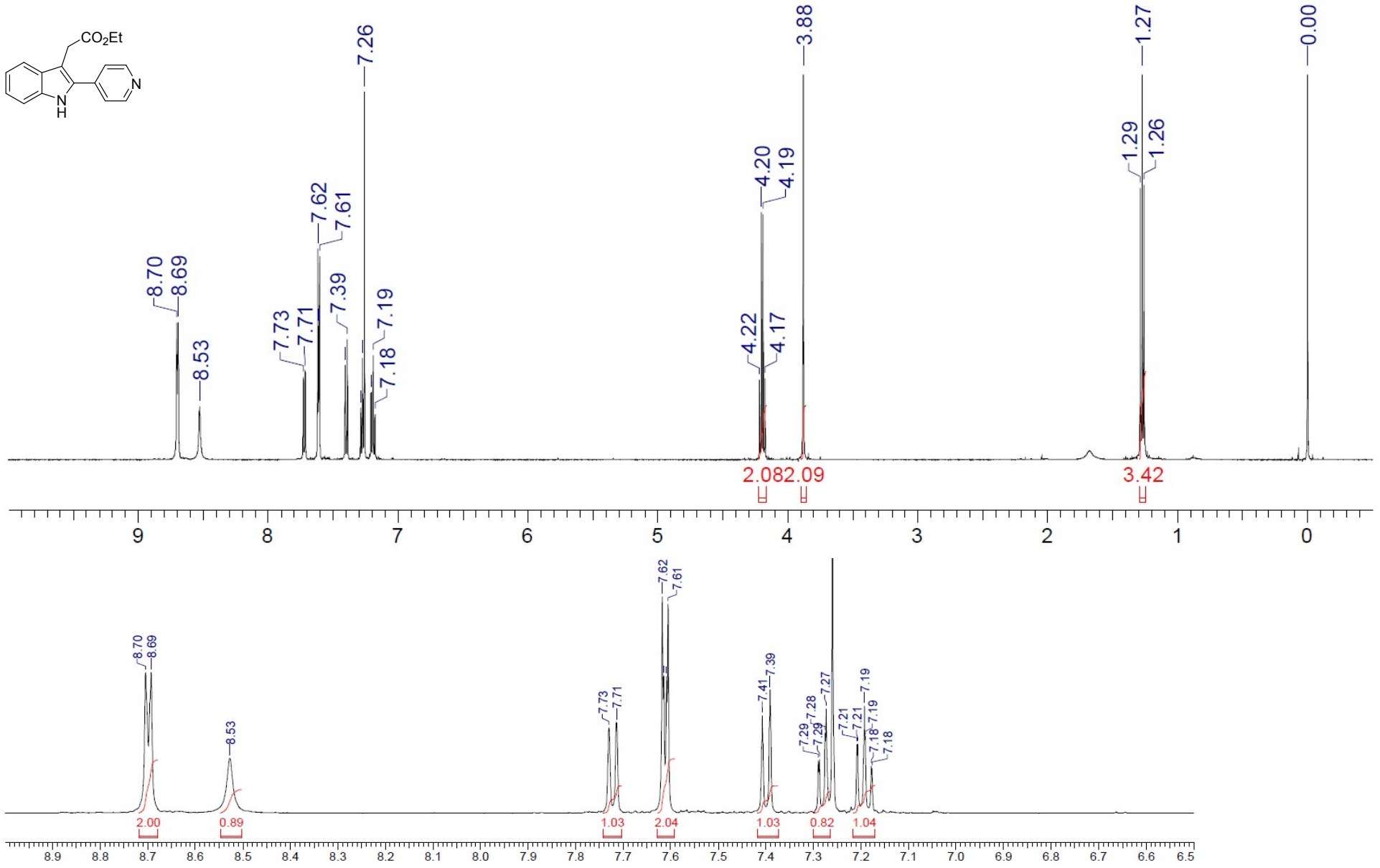


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)



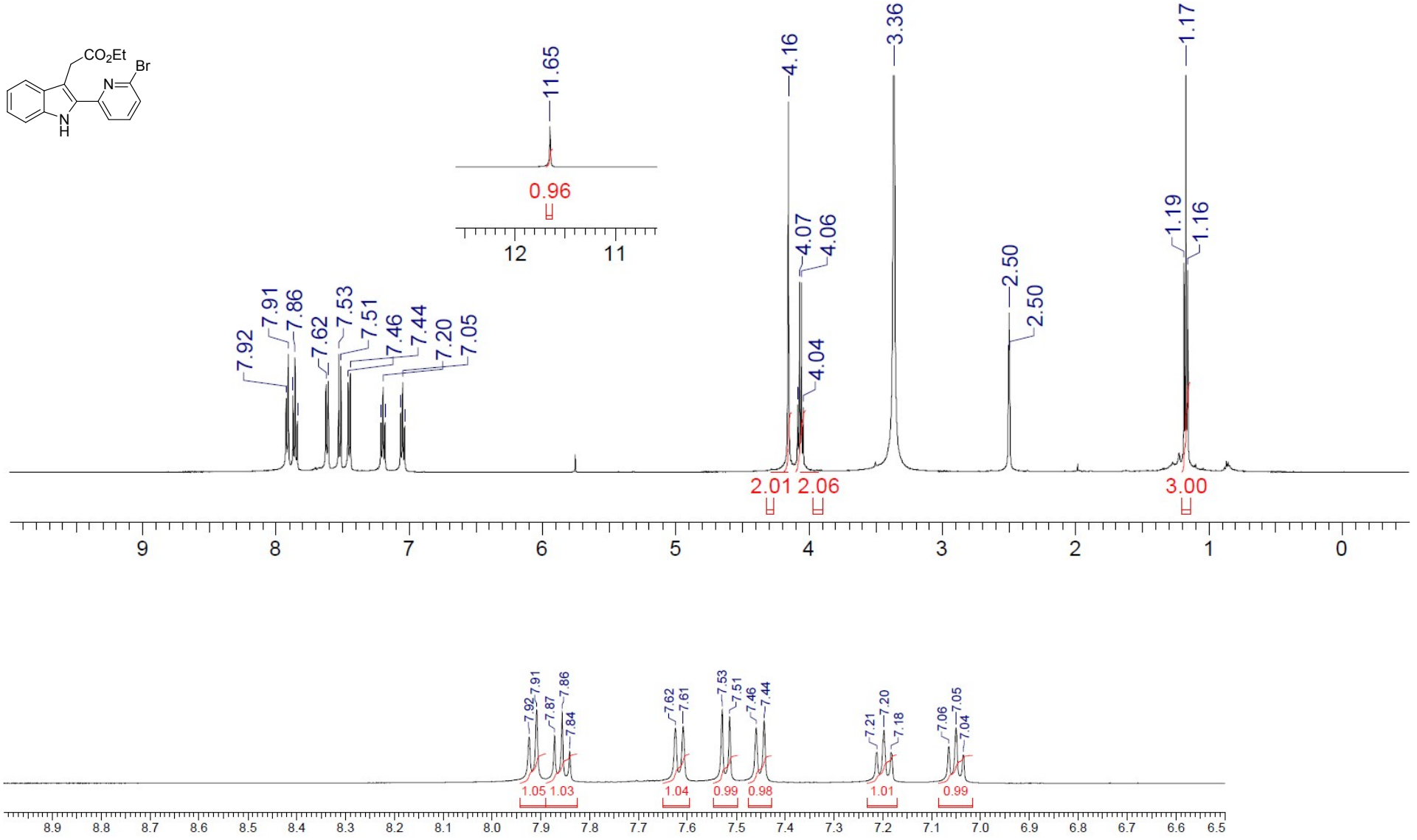
10. NMR Spectra of Ethyl 2-(2-(pyridin-4-yl)-1*H*-indol-3-yl)acetate (**4ac**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

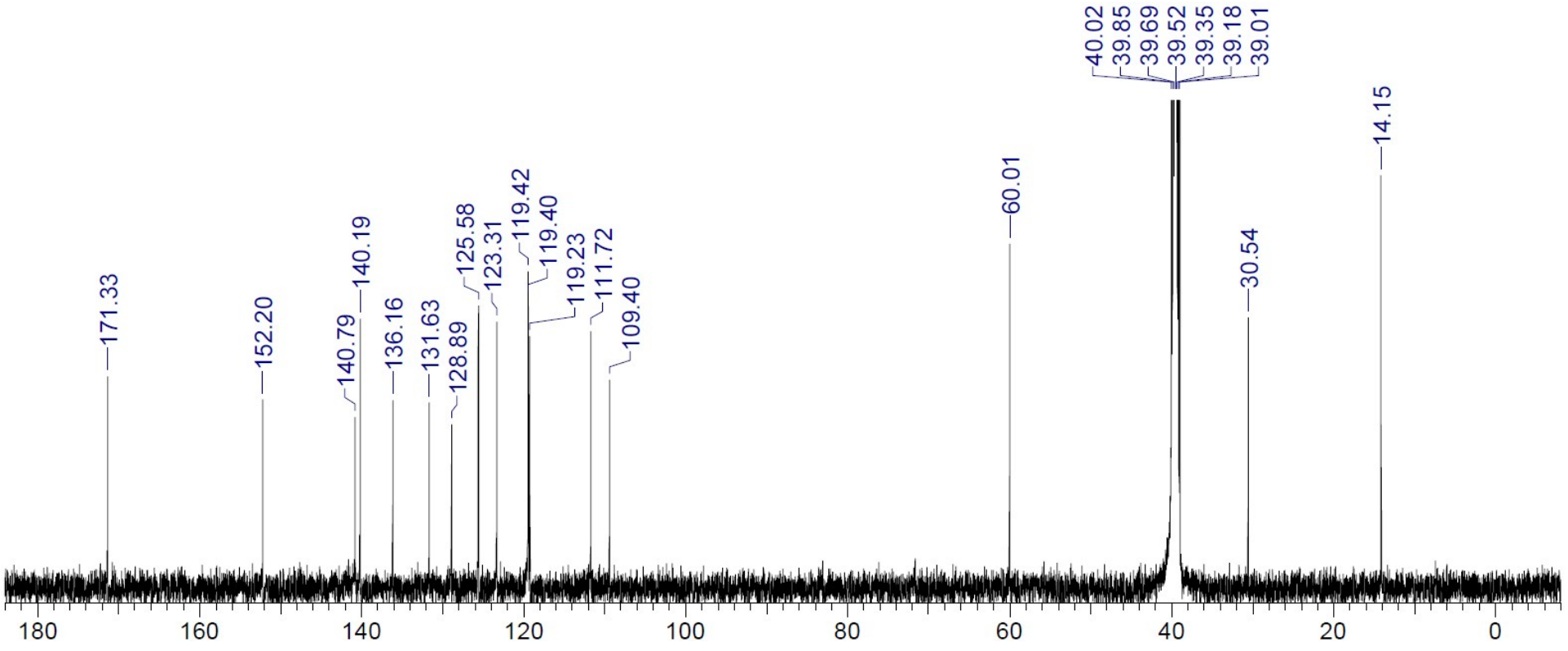


11. NMR Spectra of Ethyl 2-(2-(6-bromopyridin-2-yl)-1*H*-indol-3-yl)acetate (**4ad**)

a) ^{1}H NMR Spectrum (in DMSO-d_6, 500 MHz)

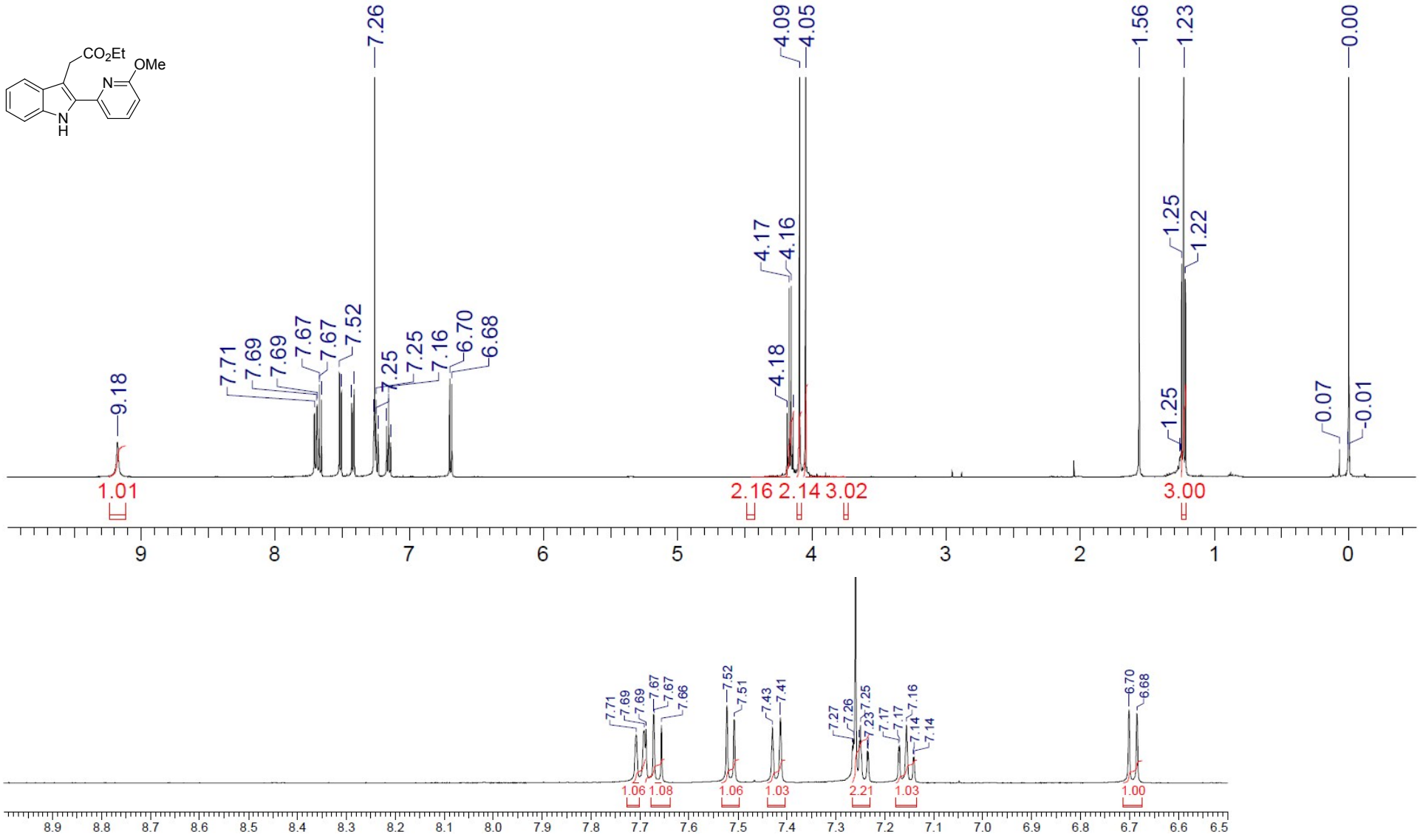


b) ^{13}C NMR Spectrum (in DMSO-d_6, 125 MHz)

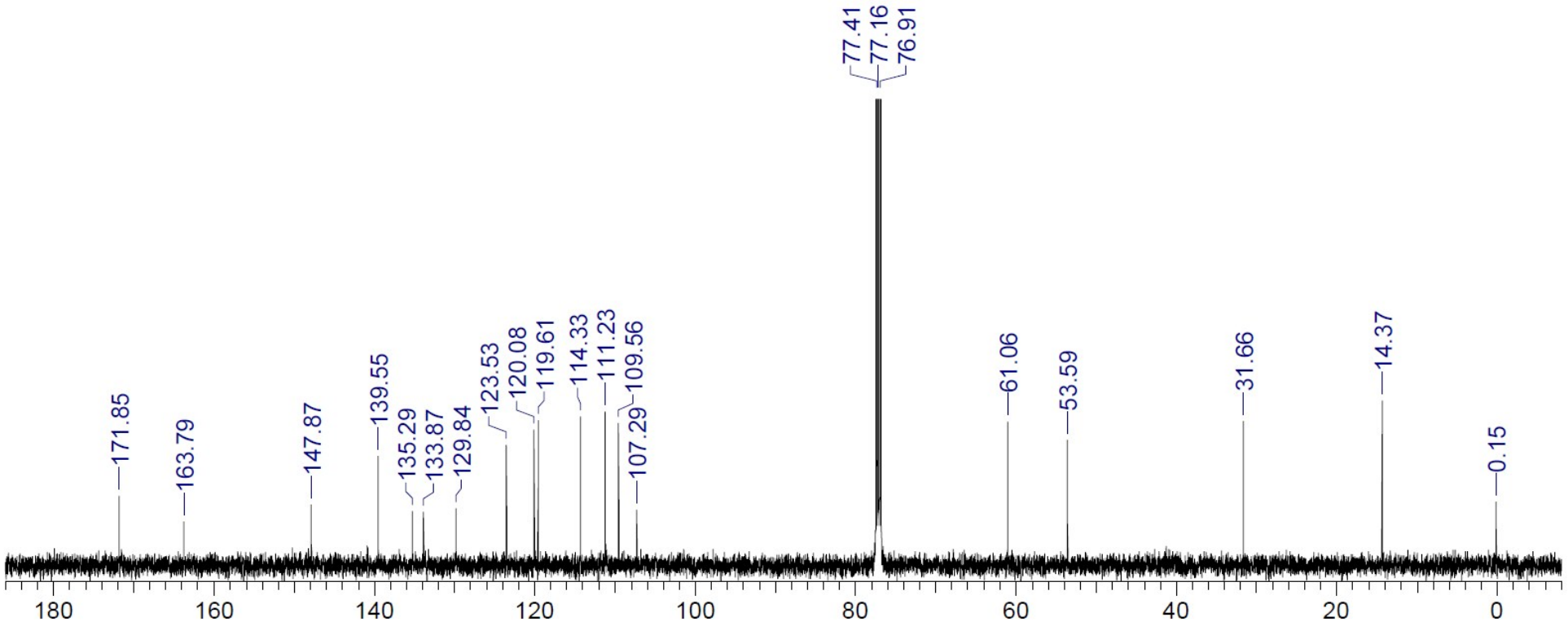


12. NMR Spectra of Ethyl 2-(2-(6-methoxypyridin-2-yl)-1*H*-indol-3-yl)acetate (**4ae**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

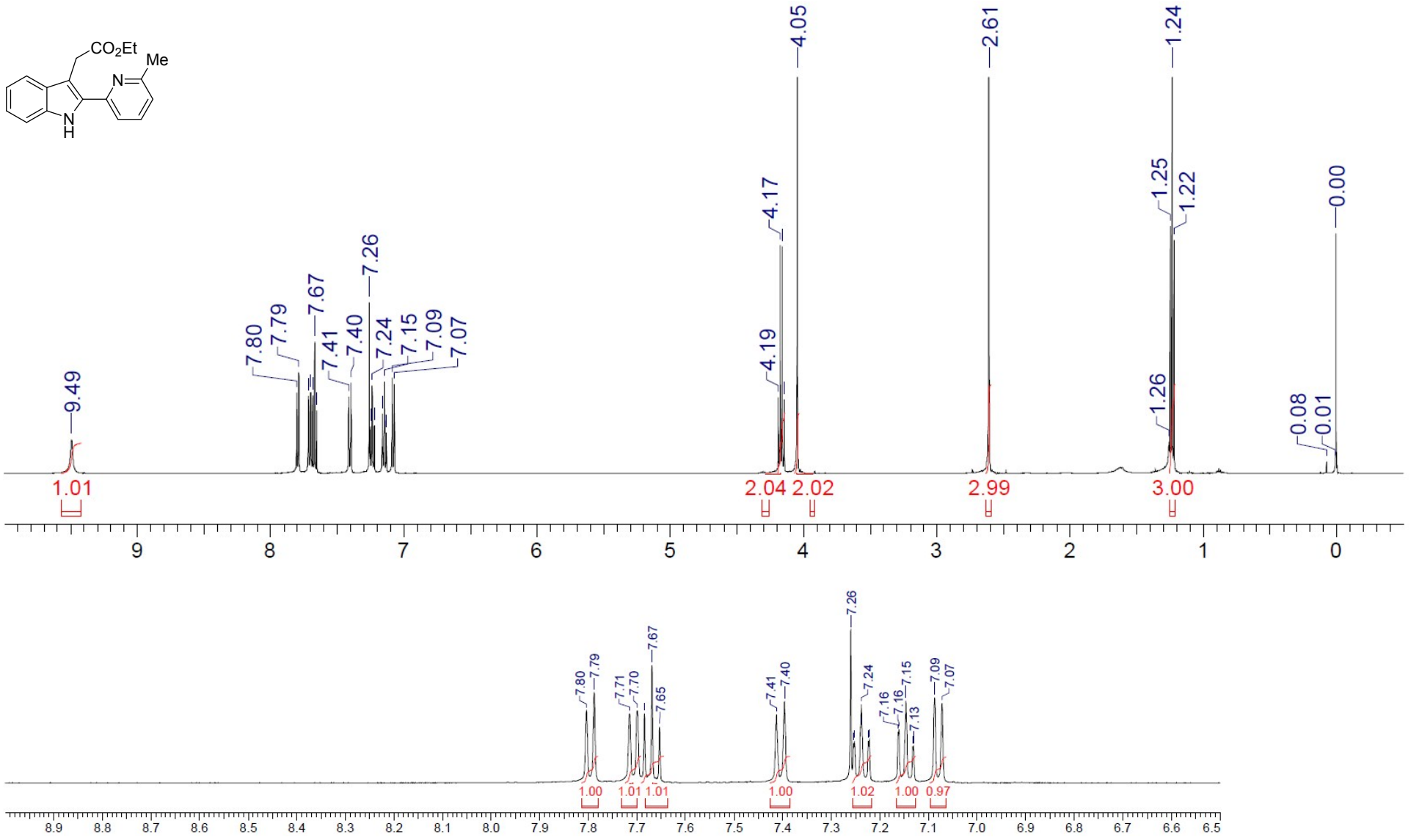


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

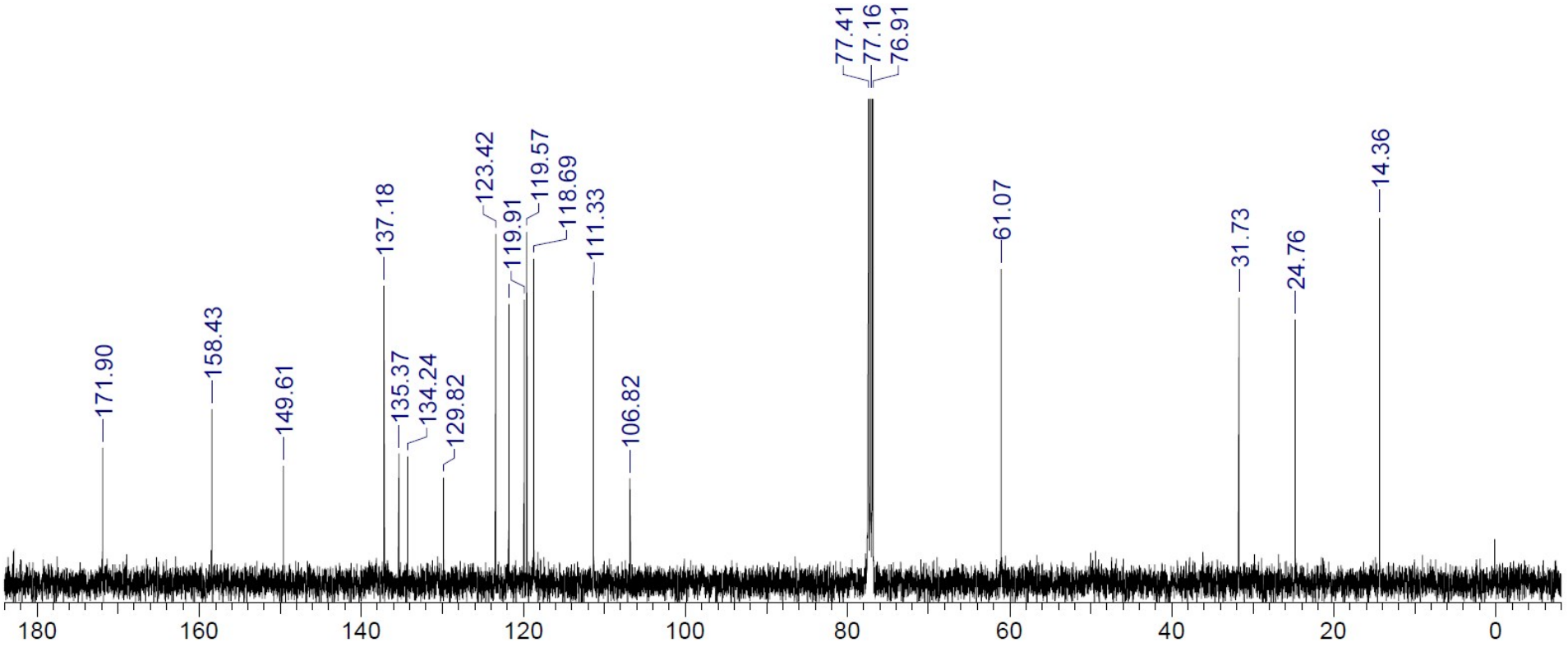


13. NMR Spectra of Ethyl 2-(2-(6-methylpyridin-2-yl)-1*H*-indol-3-yl)acetate (**4af**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

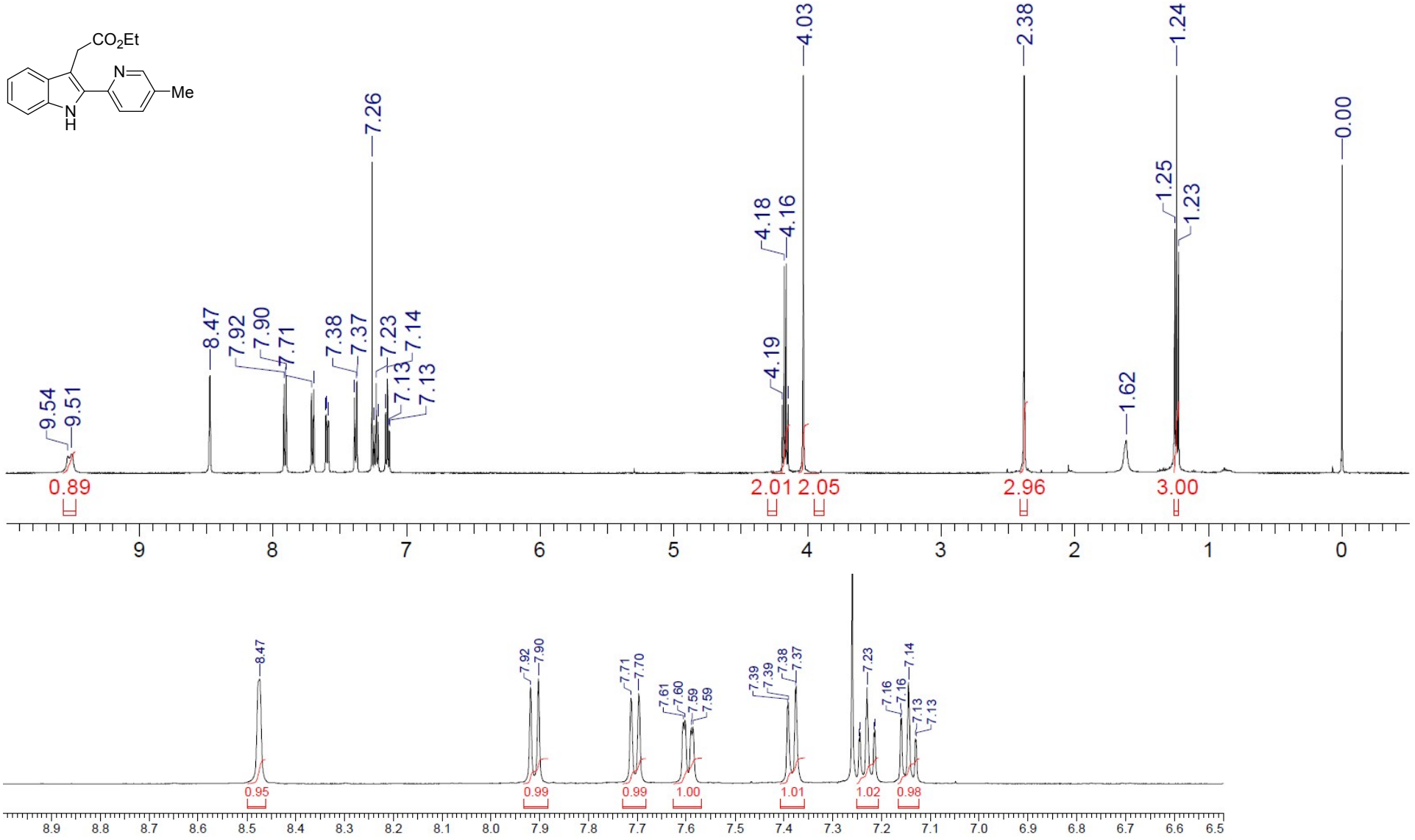


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

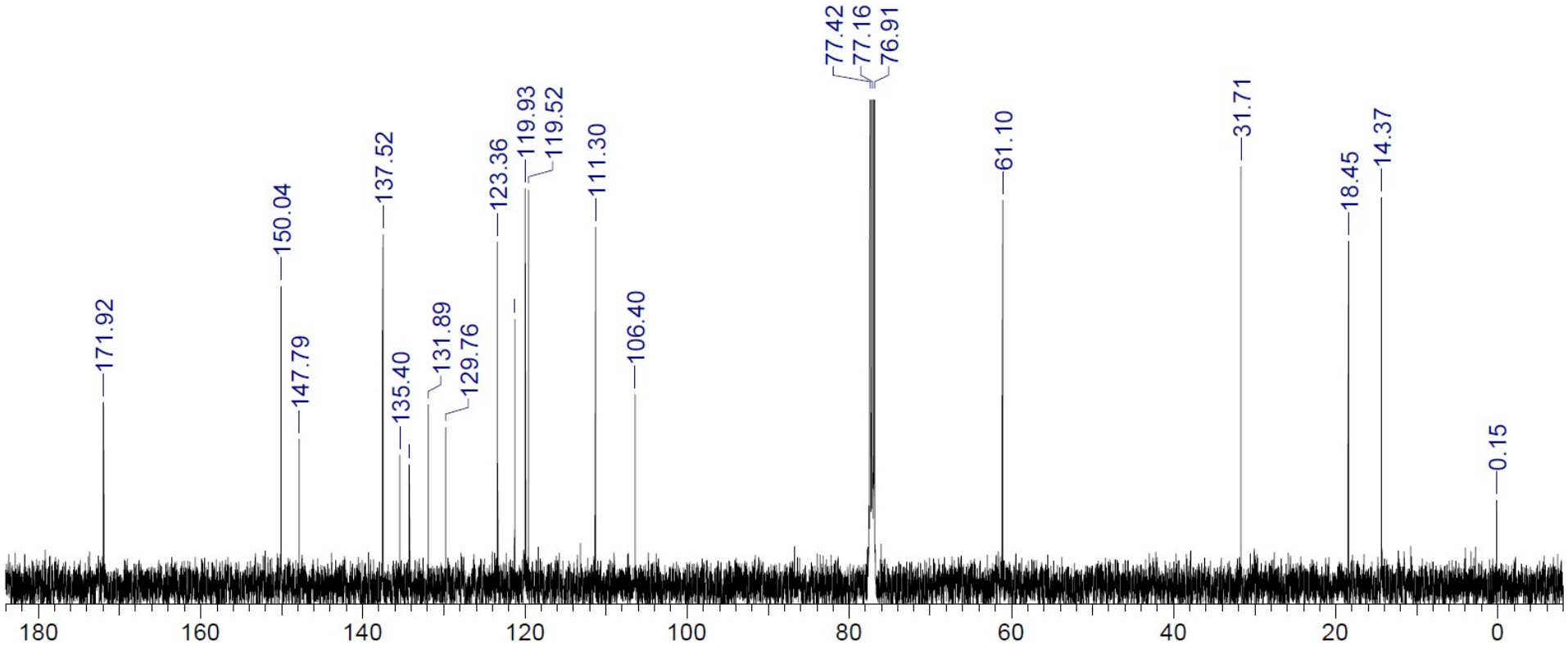


14. NMR Spectra of Ethyl 2-(2-(5-methylpyridin-2-yl)-1*H*-indol-3-yl)acetate (**4ag**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

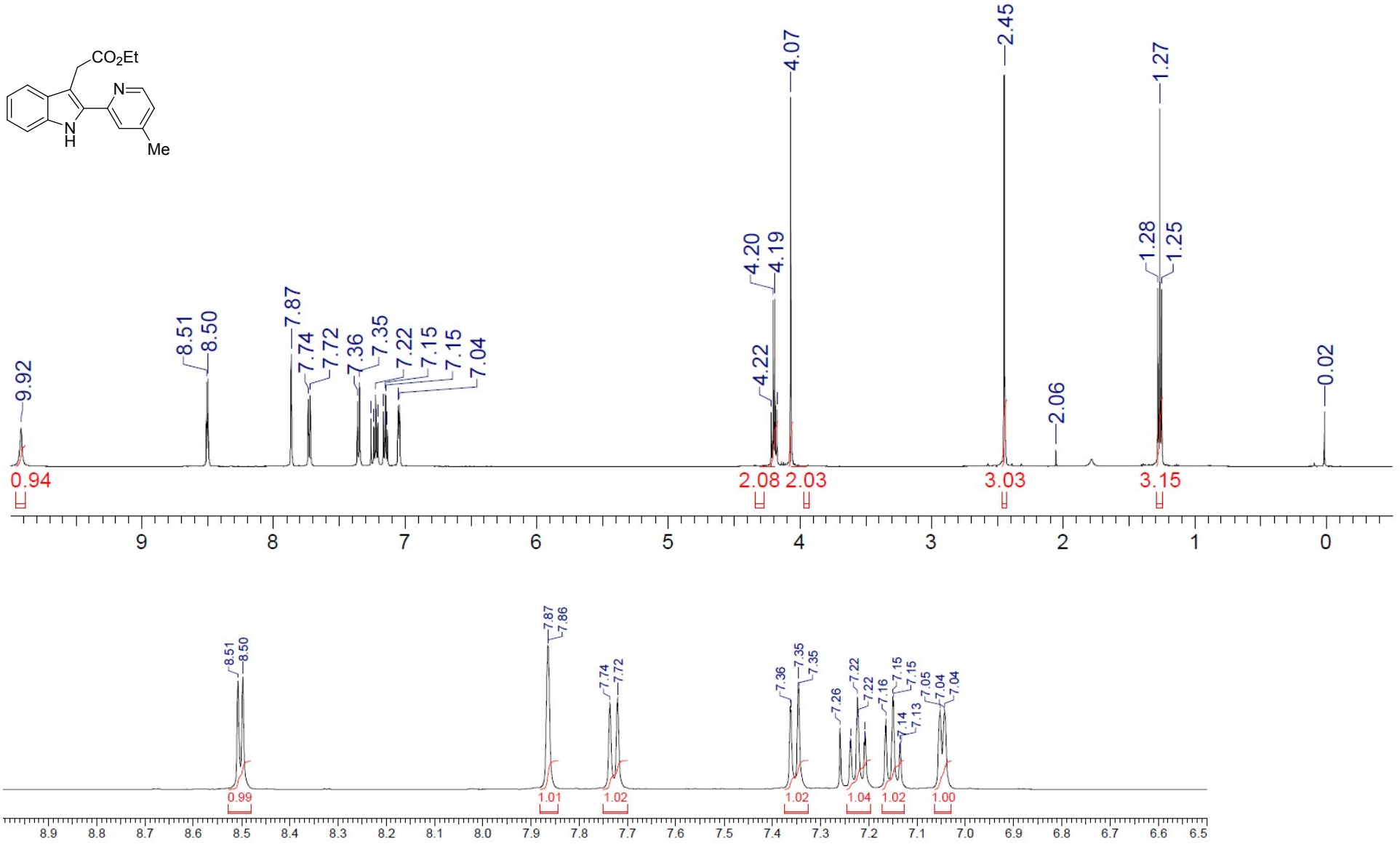


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

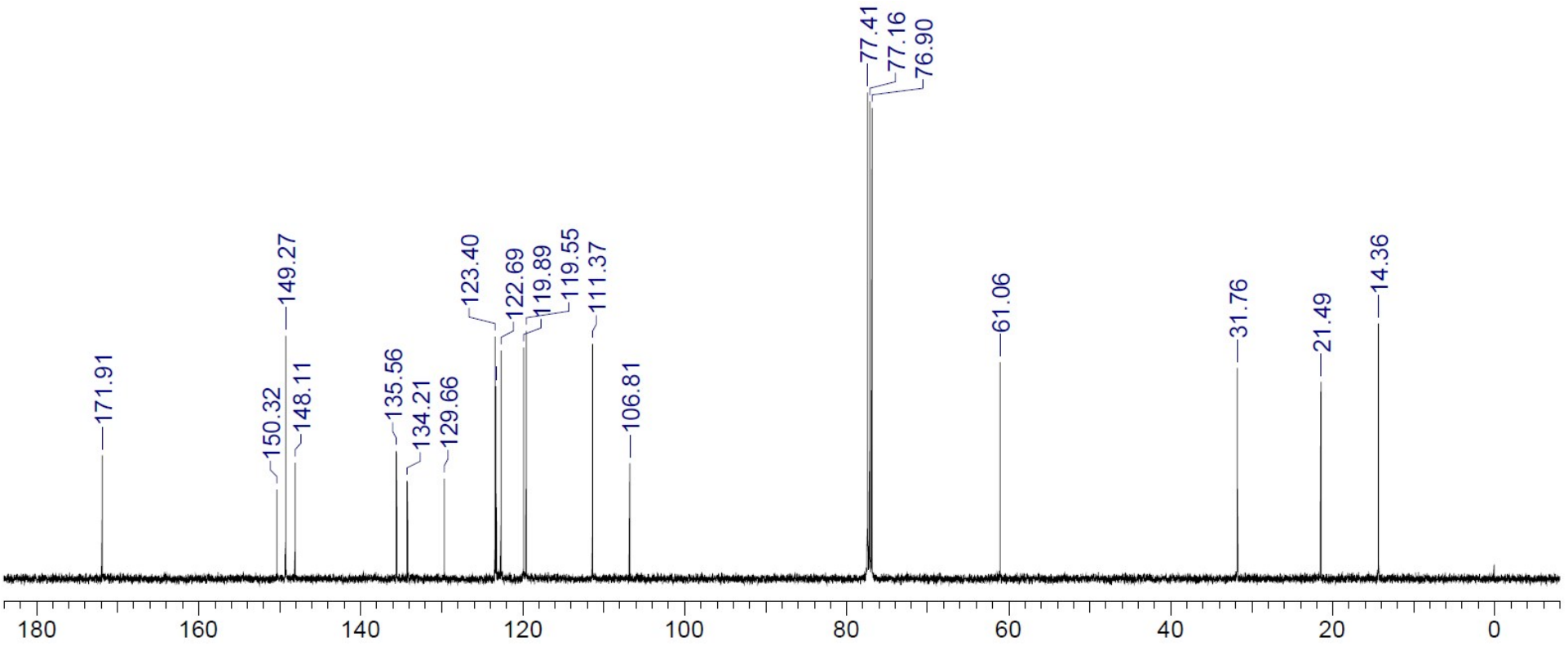


15. NMR Spectra of Ethyl 2-(2-(4-methylpyridin-2-yl)-1*H*-indol-3-yl)acetate (**4ah**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

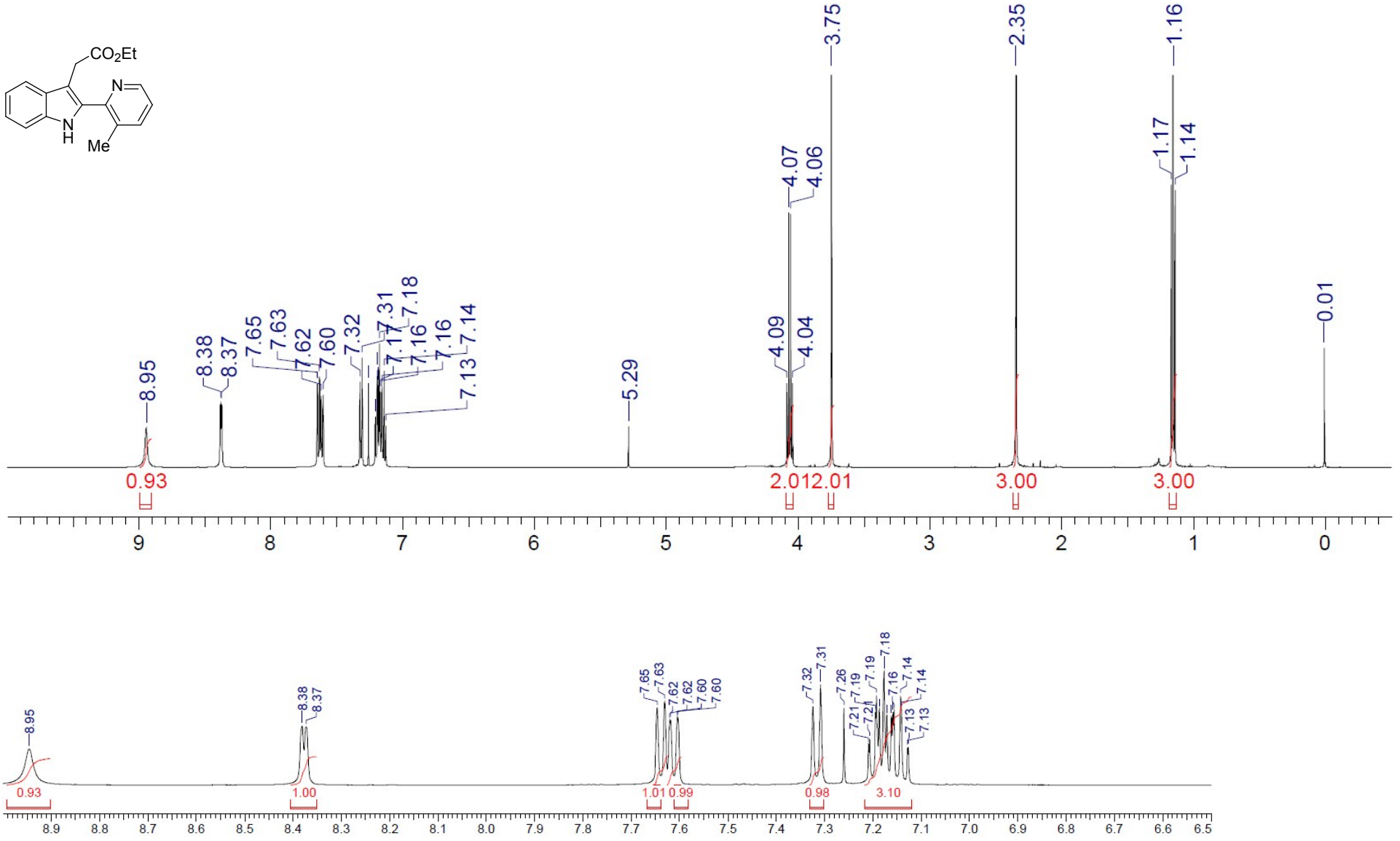


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

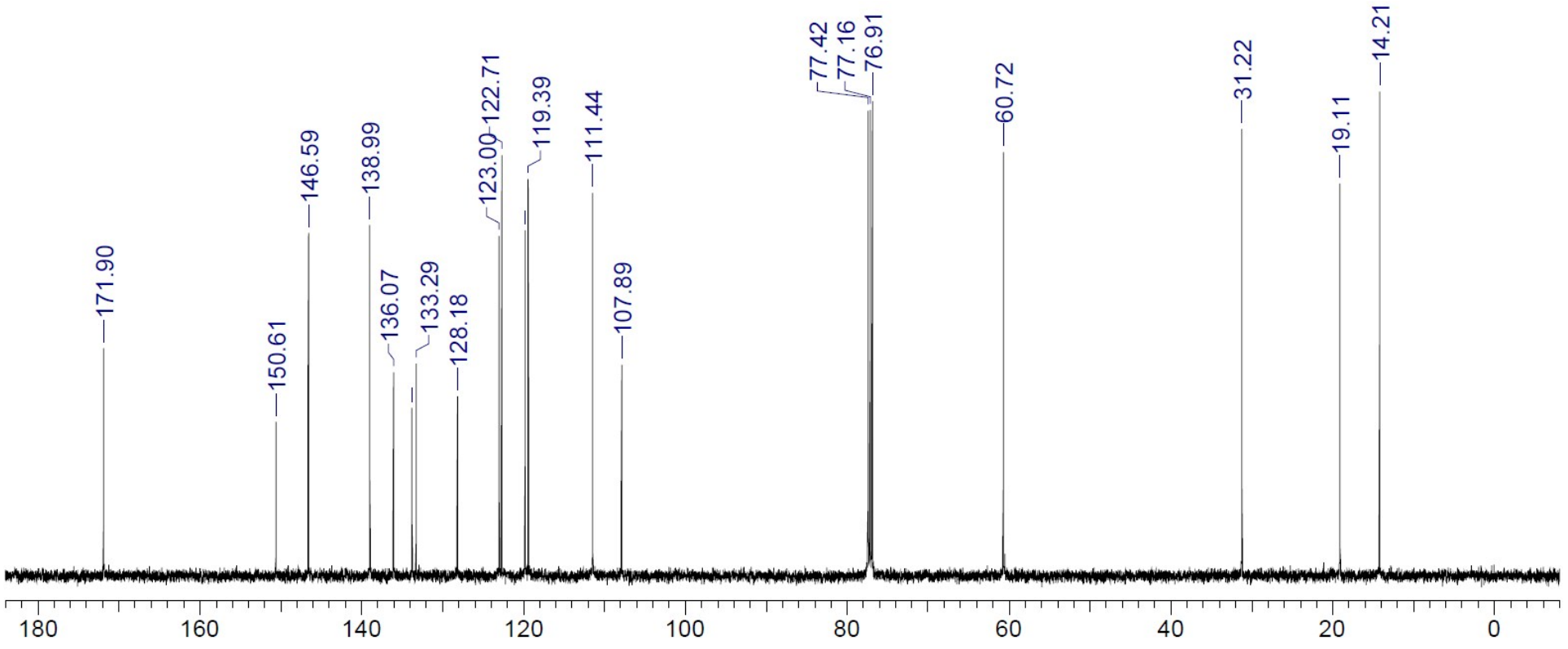


16. NMR Spectra of Ethyl 2-(2-(3-methylpyridin-2-yl)-1*H*-indol-3-yl)acetate (**4ai**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

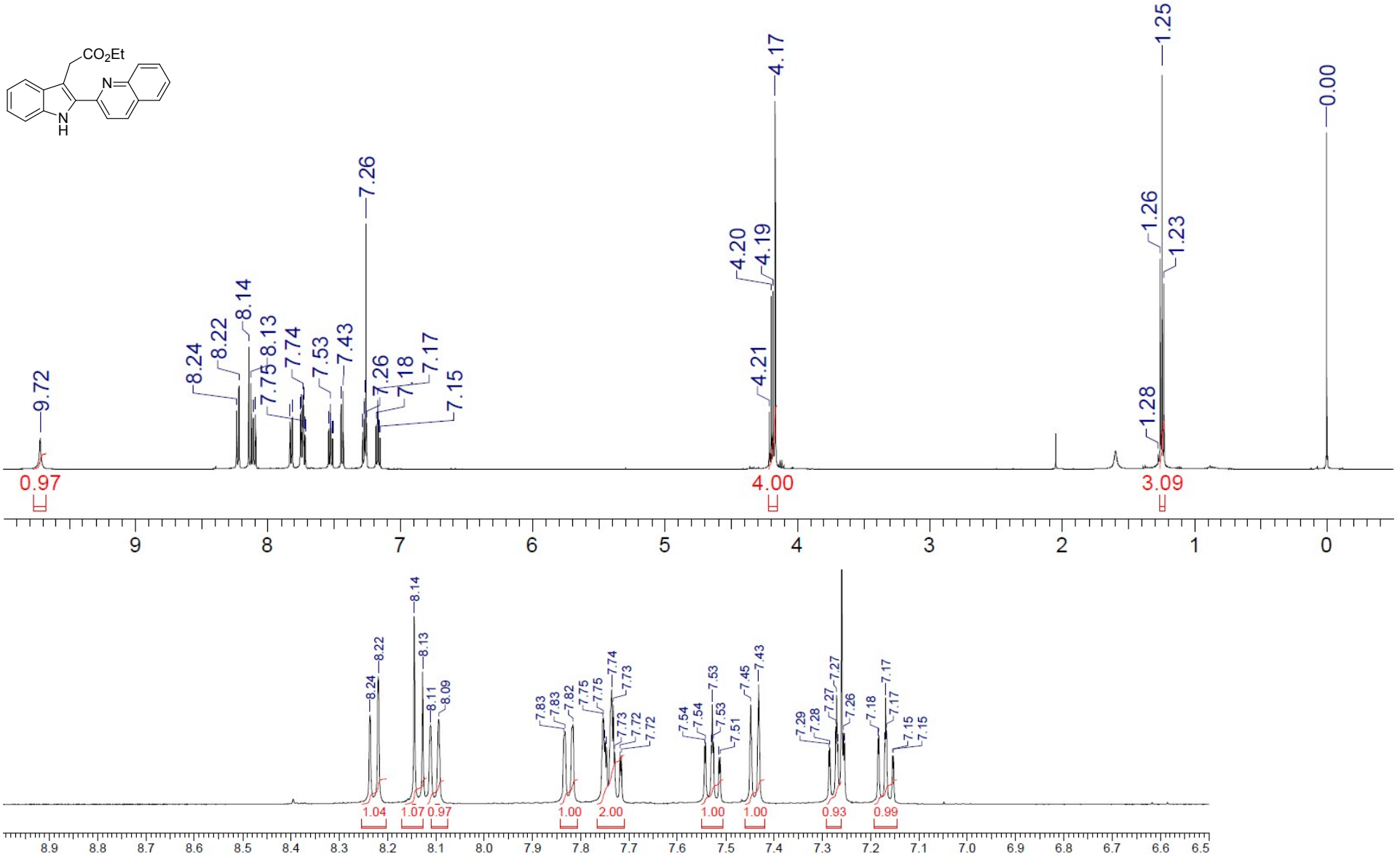


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

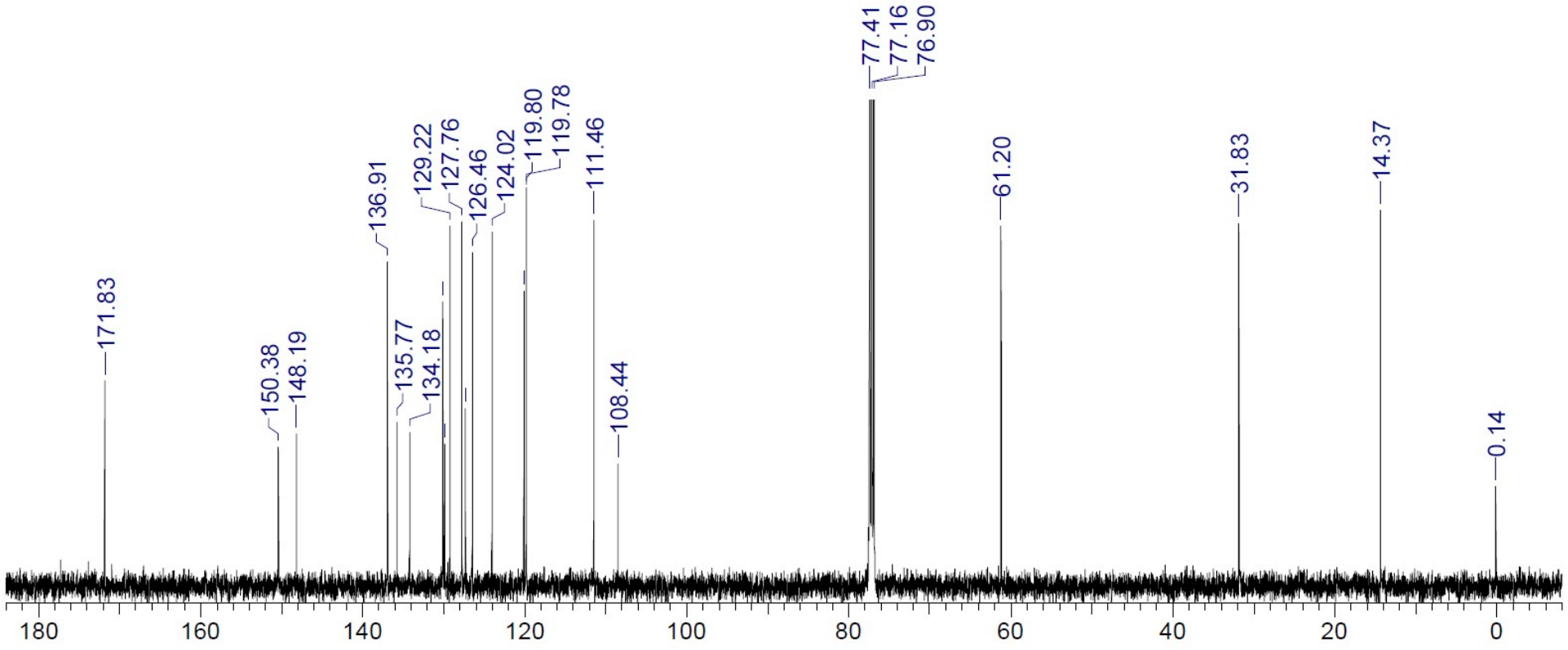


17. NMR Spectra of Ethyl 2-(2-(quinolin-2-yl)-1*H*-indol-3-yl)acetate (**4aj**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

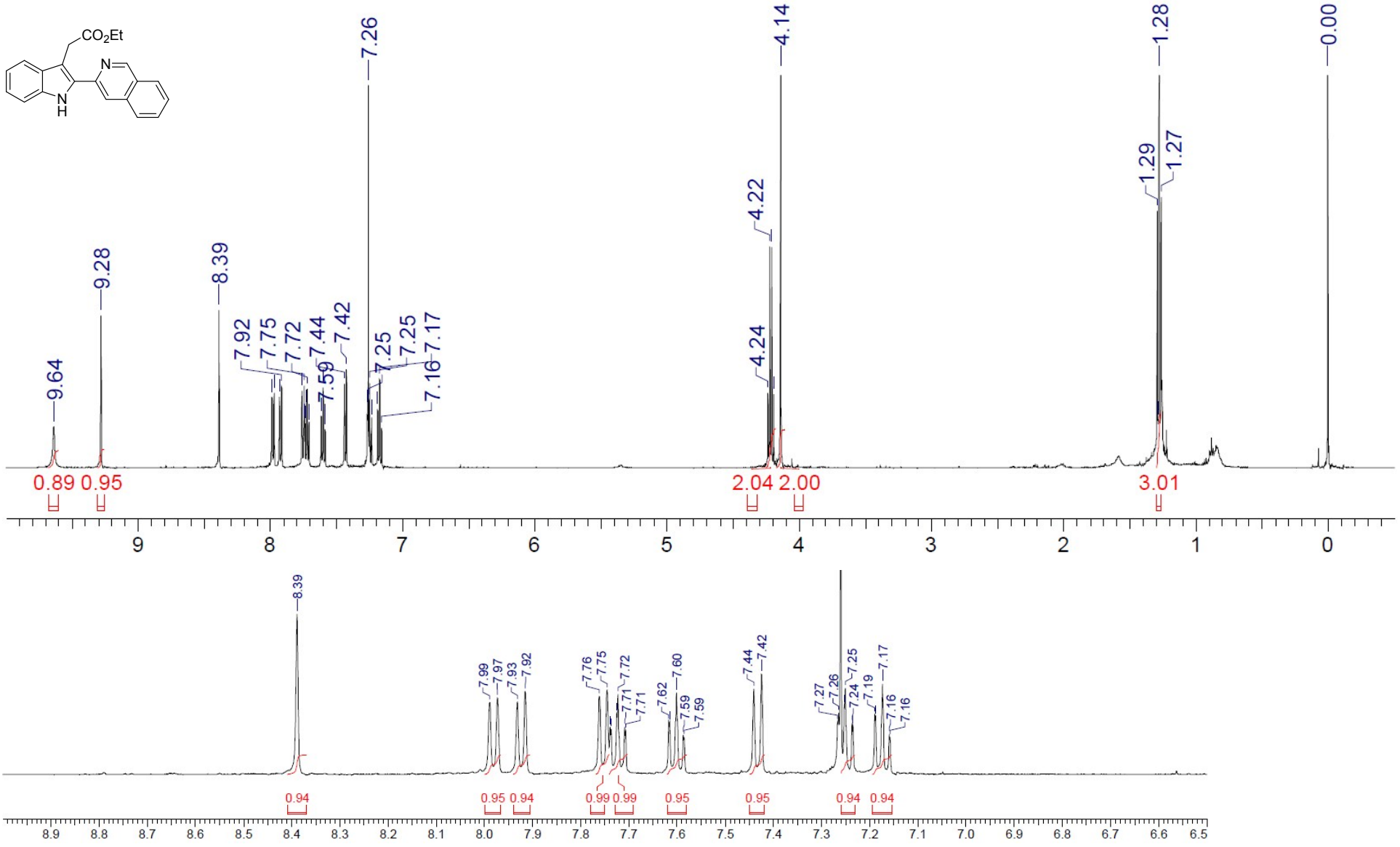


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

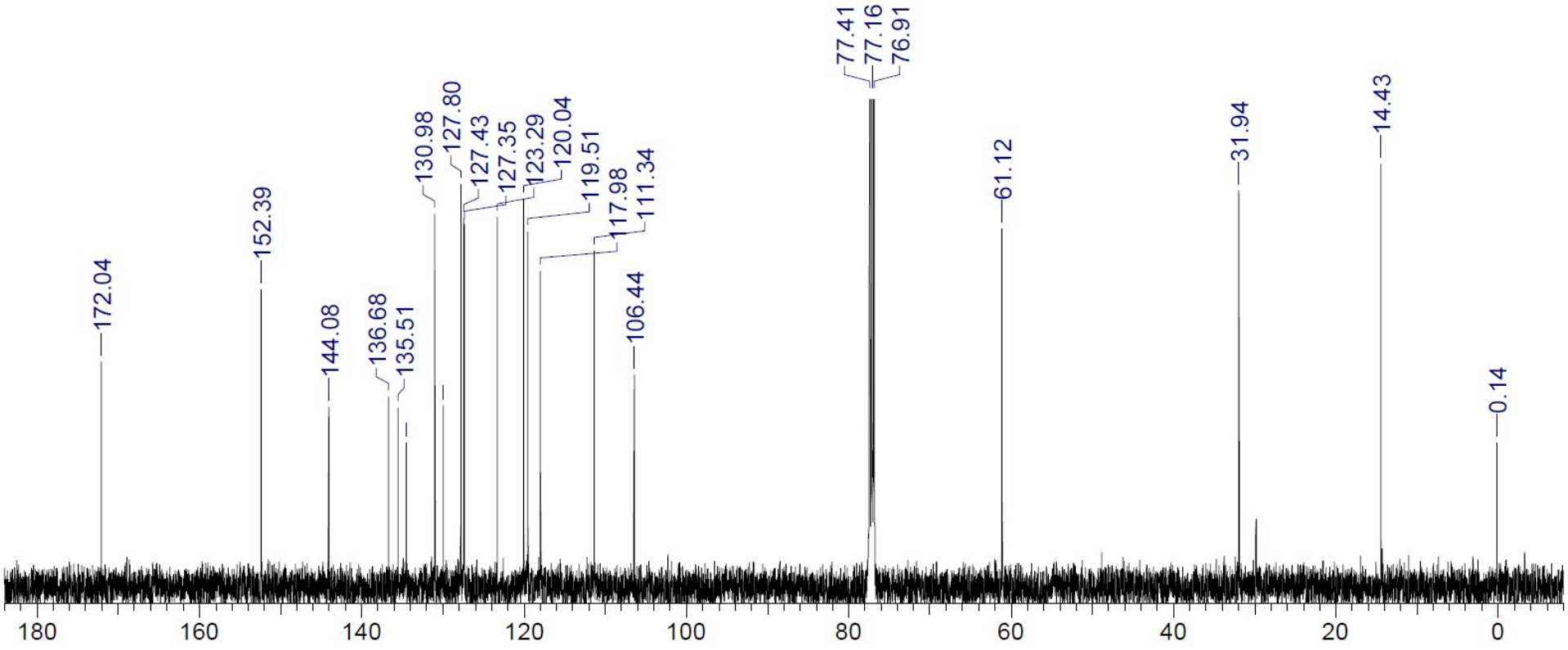


18. NMR Spectra of Ethyl 2-(2-(isoquinolin-3-yl)-1*H*-indol-3-yl)acetate (**4ak**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

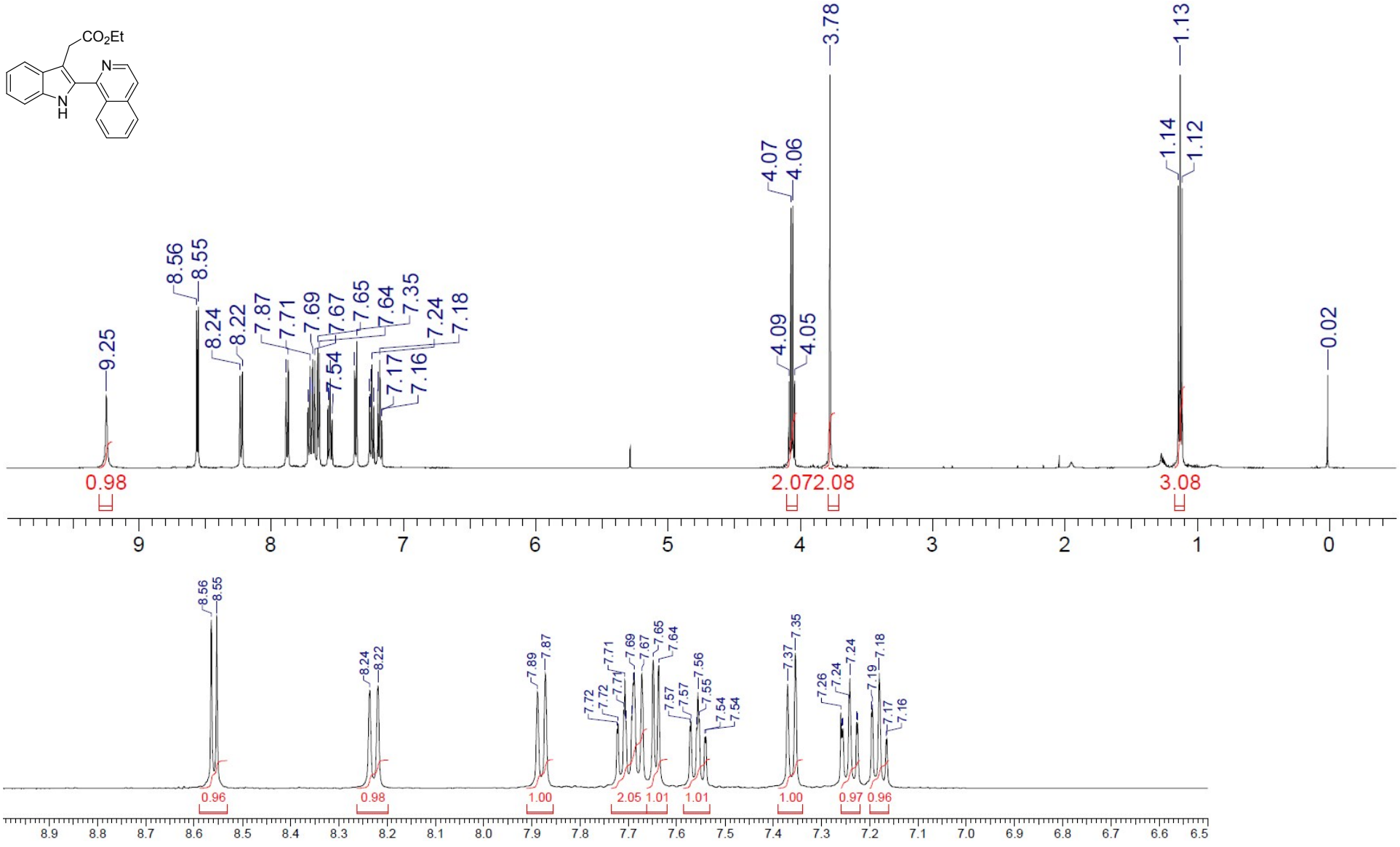


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

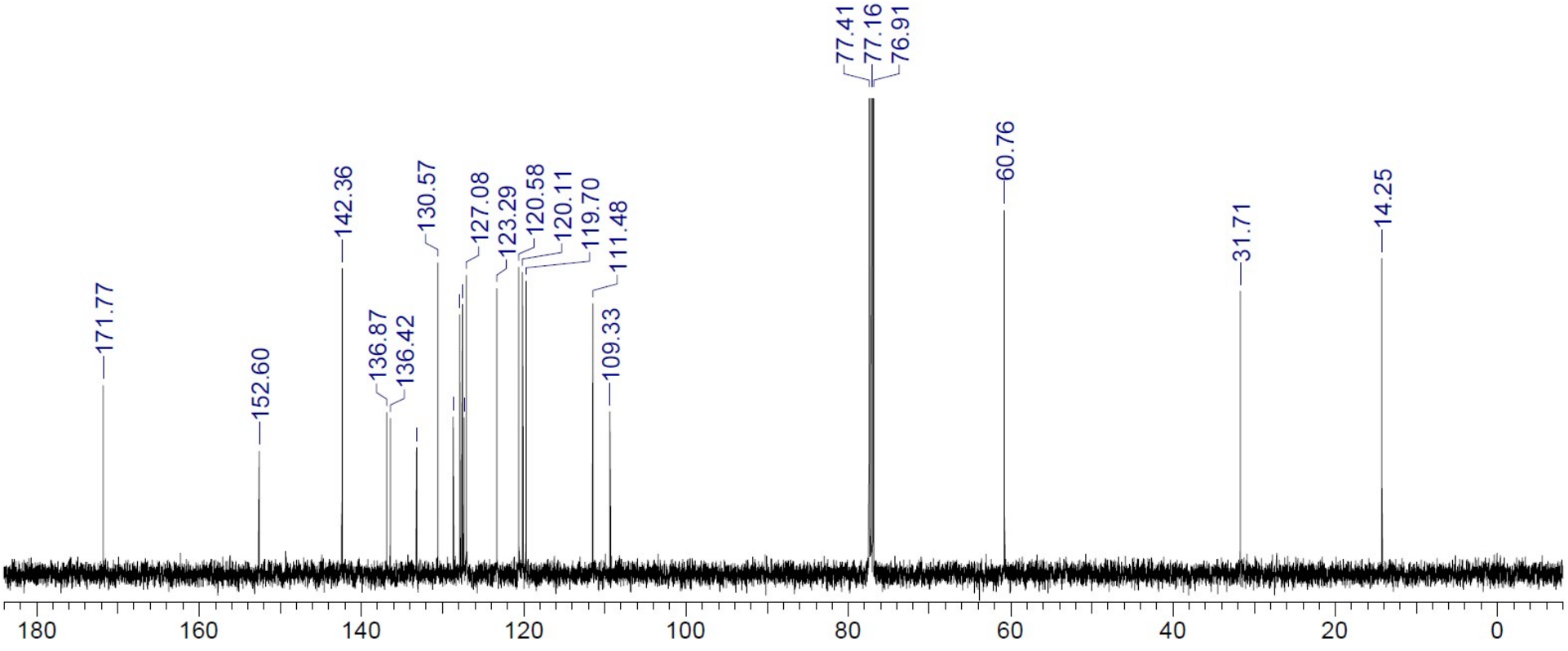


19. NMR Spectra of Ethyl 2-(2-(isoquinolin-1-yl)-1*H*-indol-3-yl)acetate (**4al**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

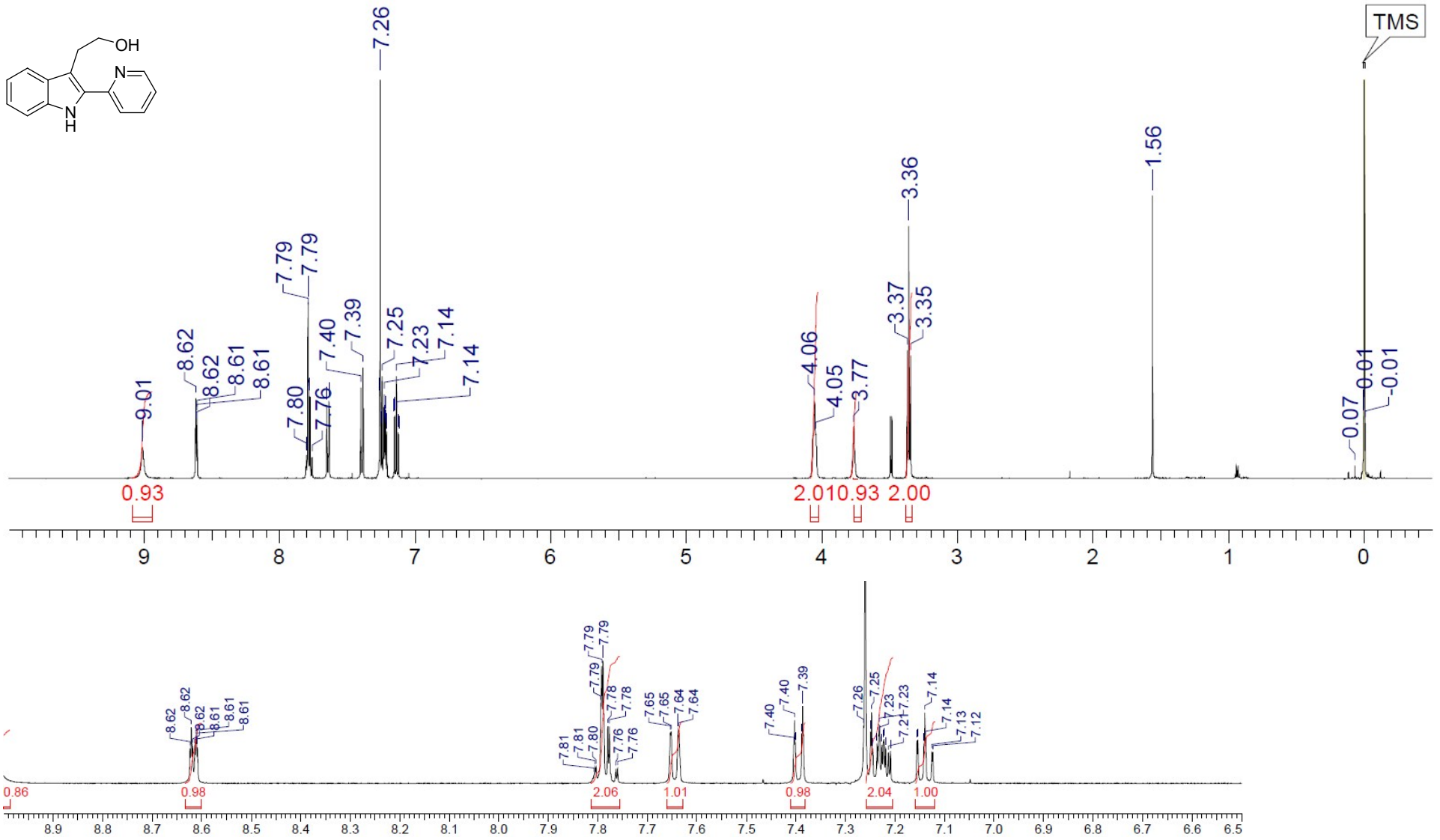


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)



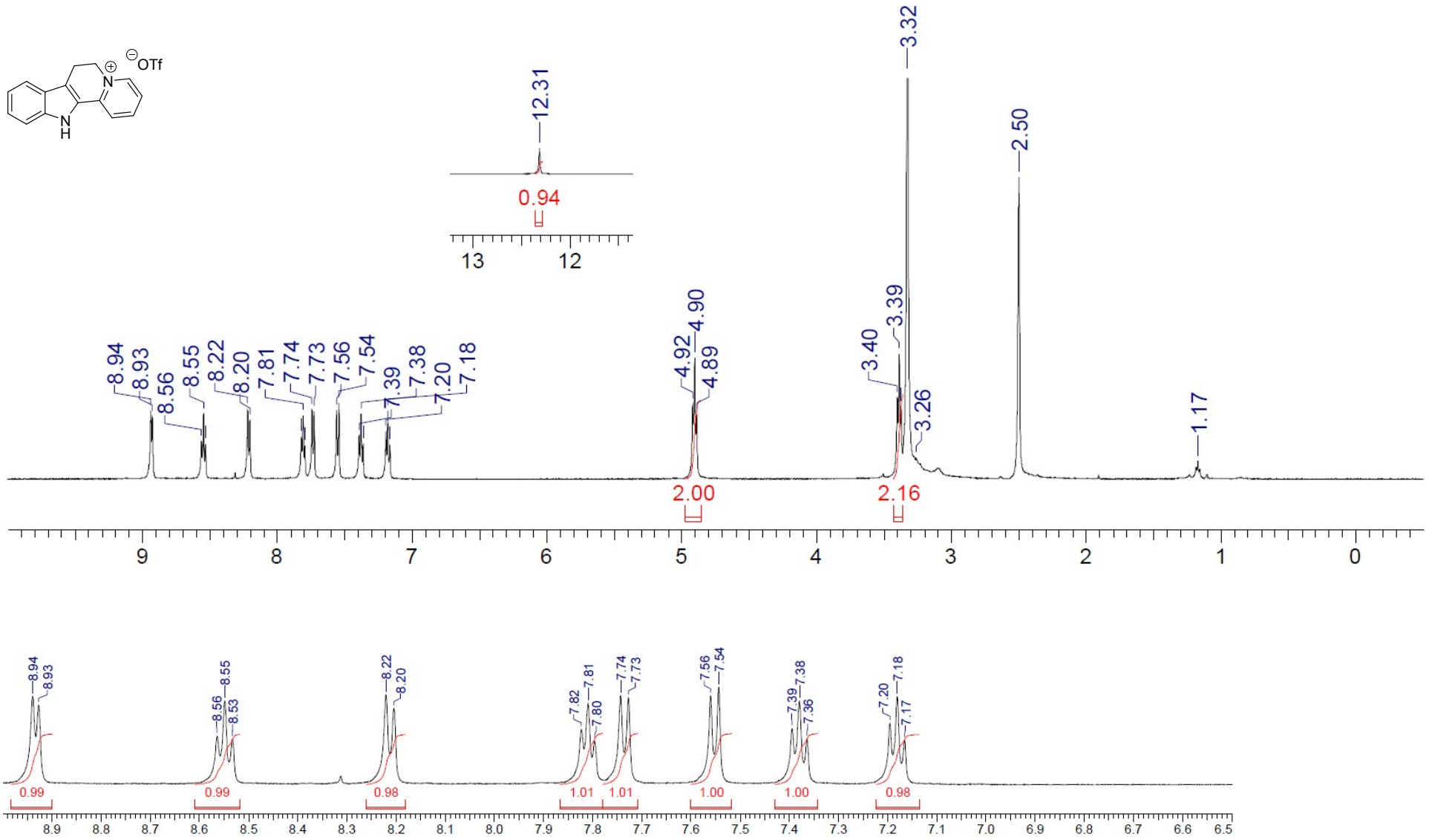
20. NMR Spectra of 2-(2-(Pyridin-2-yl)-1*H*-indol-3-yl)ethan-1-ol (**8**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)



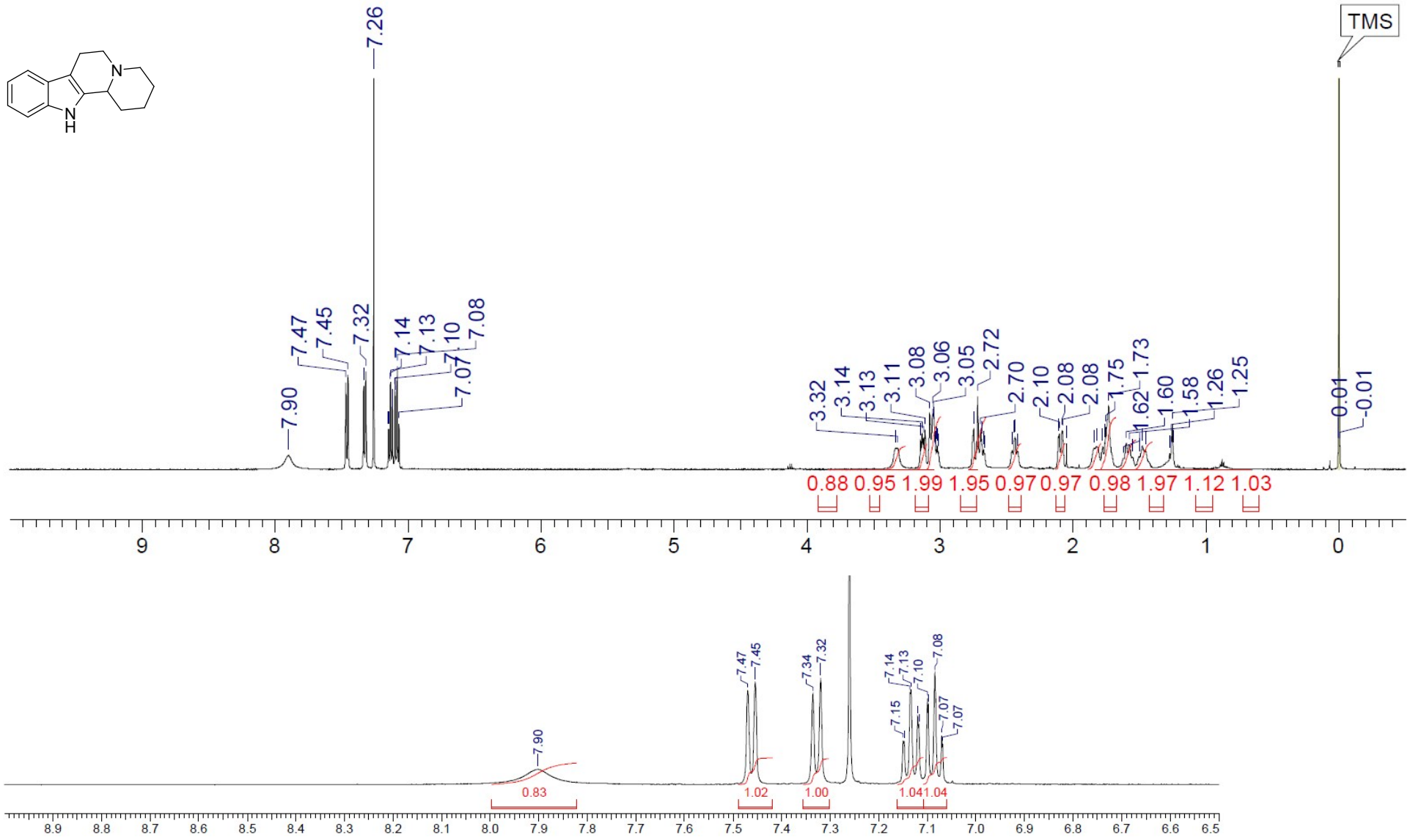
21. NMR Spectra of 7,12-Dihydro-6*H*-indolo[2,3-*a*]quinolizin-5-ium Trifluoromethanesulfonate (**10**)

a) ^{1}H NMR Spectrum (in DMSO-d_6, 500 MHz)

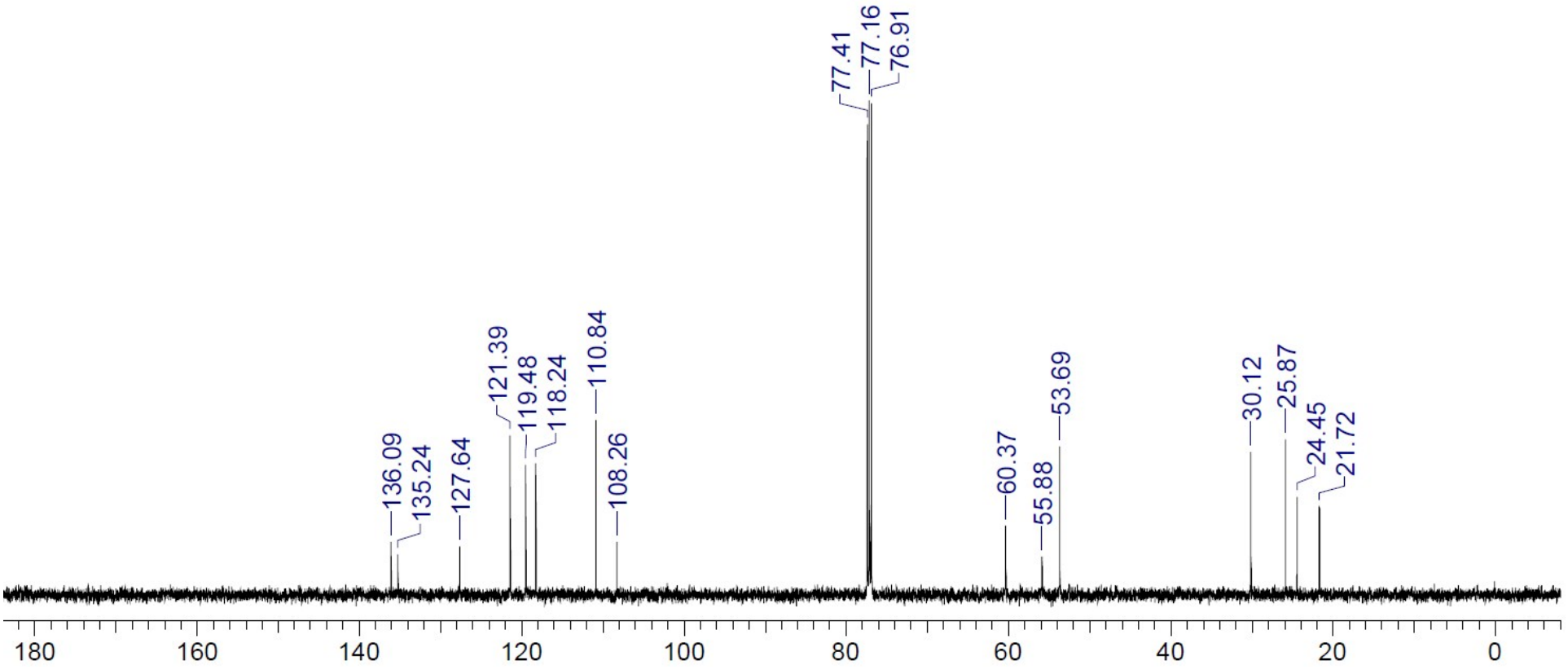


22. NMR Spectra of 10-Desbromoarborescidine A (**11**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

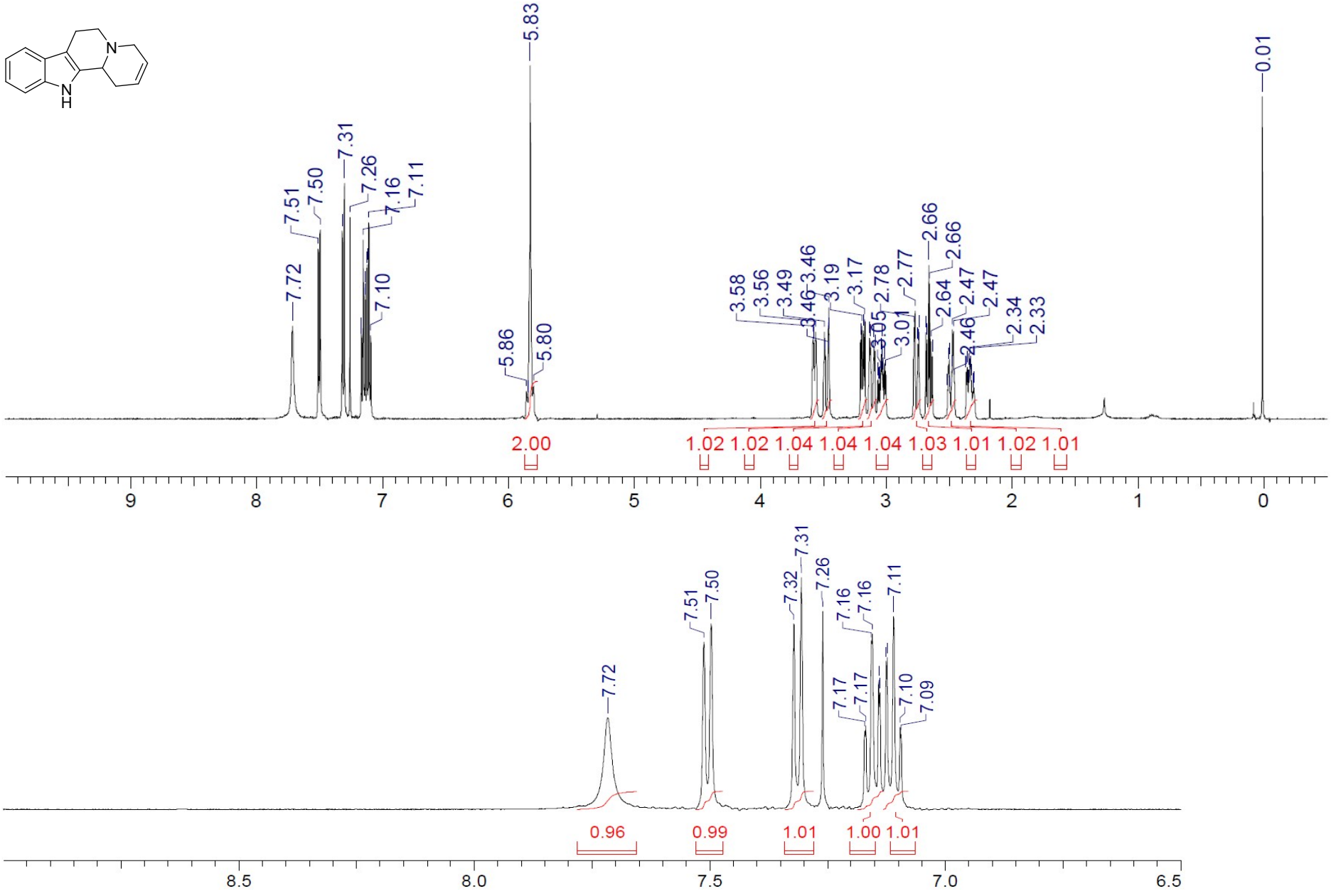


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

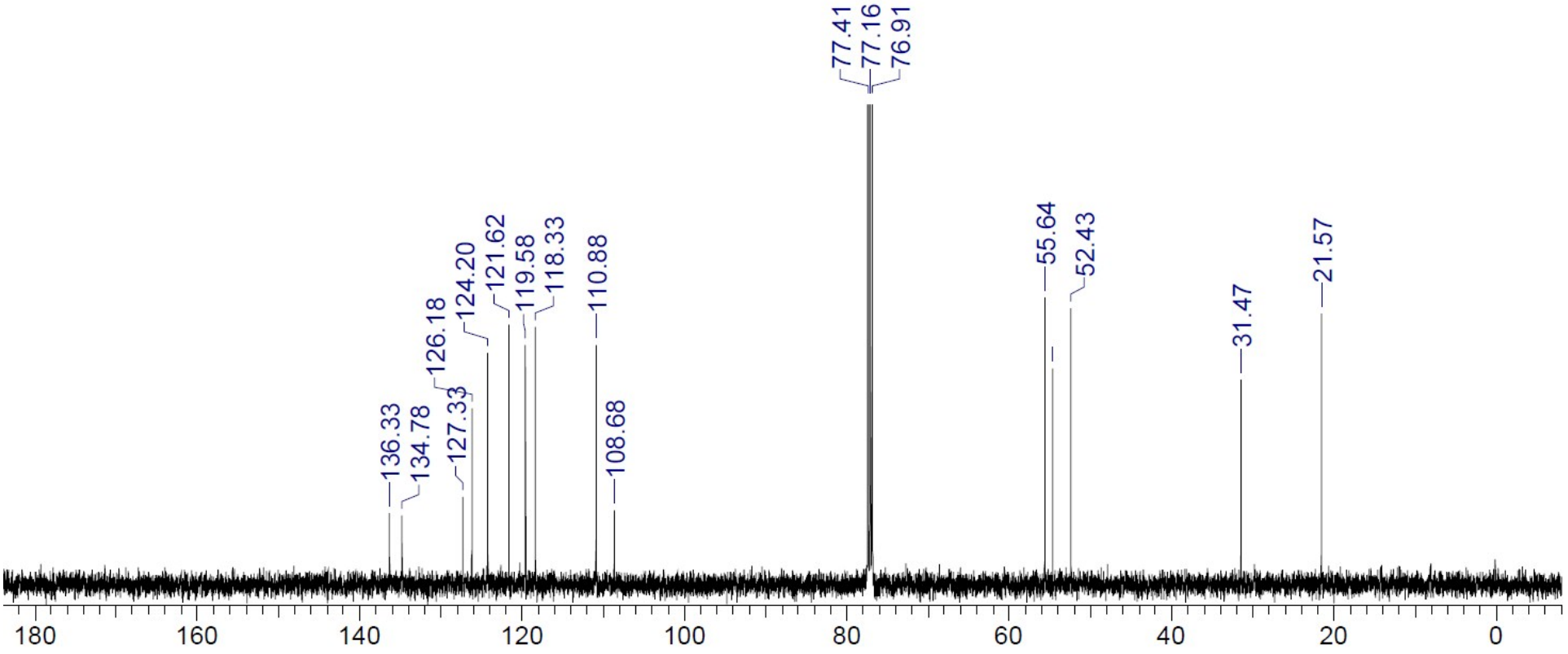


23. NMR Spectra of 1,4,6,7,12,12*b*-Hexahydroindolo[2,3-*a*]quinolizine (**12**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

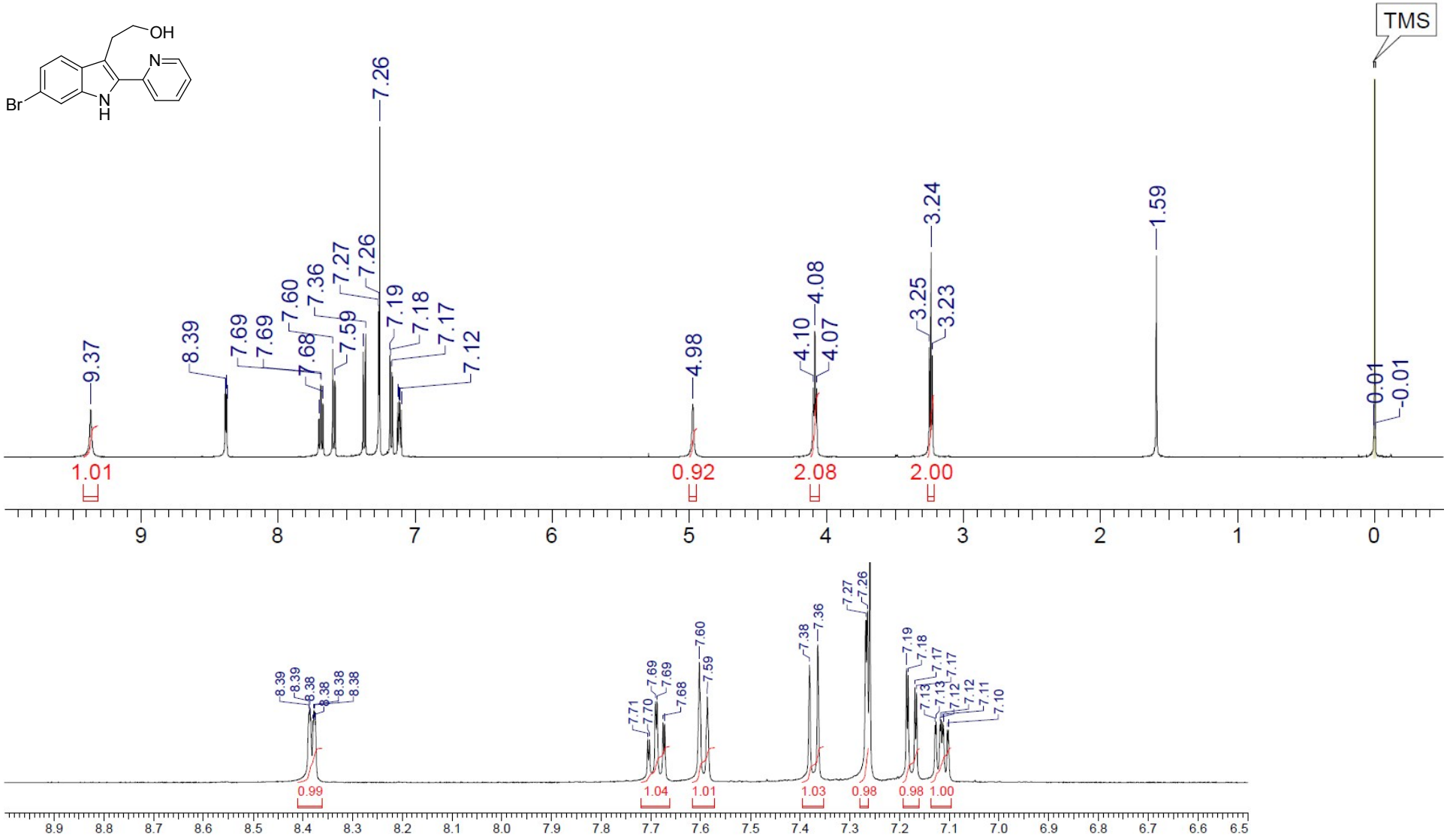


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

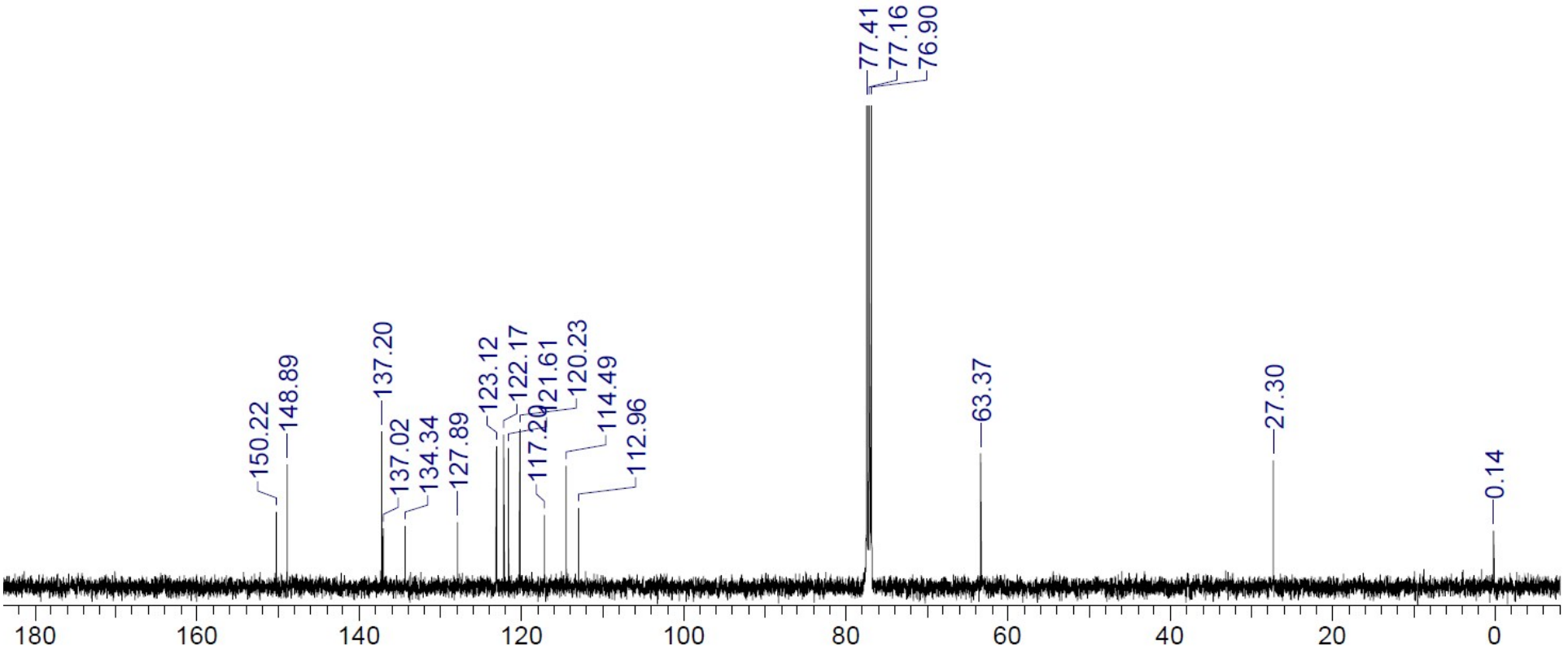


24. NMR Spectra of 2-(6-Bromo-2-(pyridin-2-yl)-1*H*-indol-3-yl)ethan-1-ol (**13**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

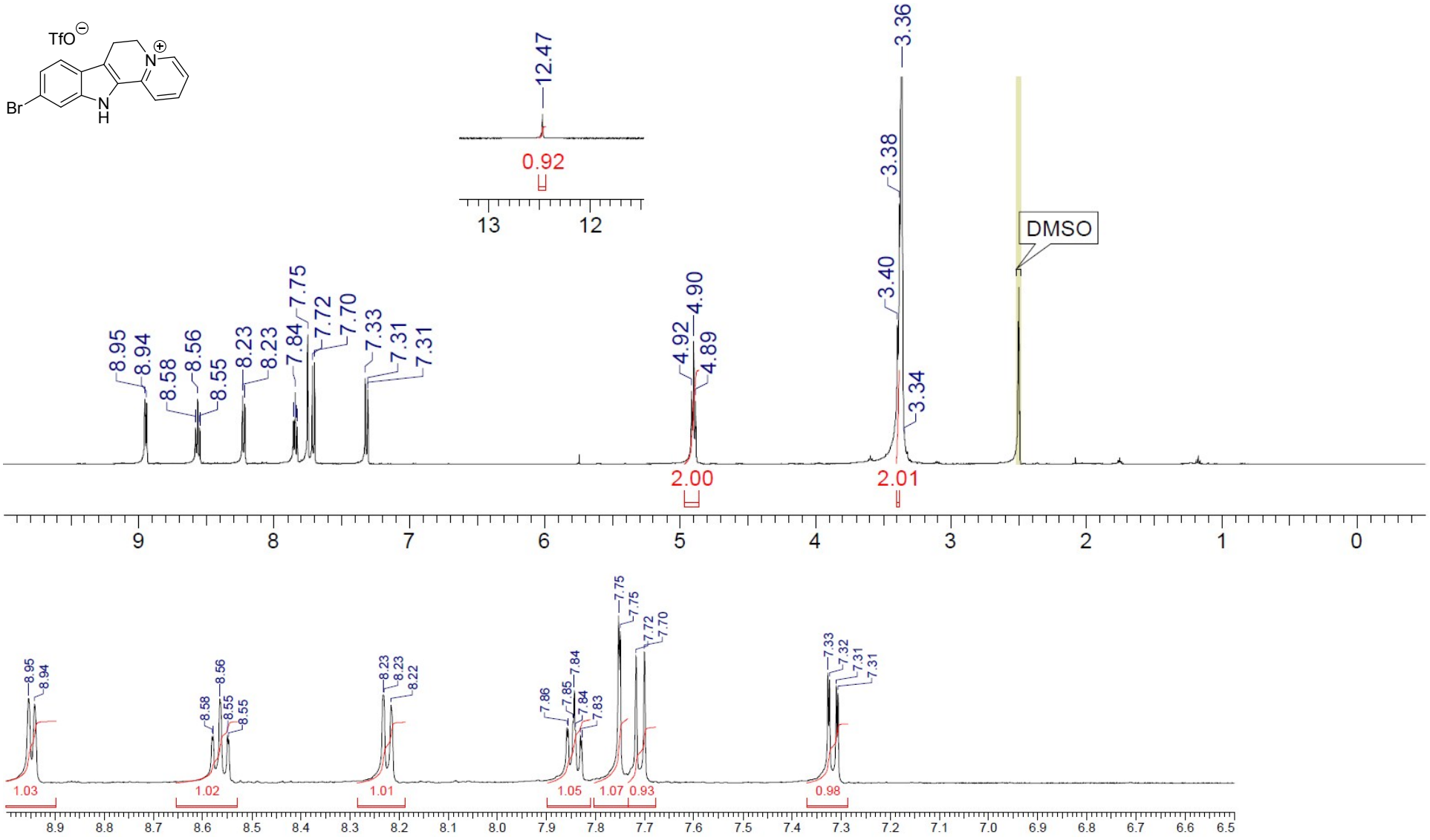


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

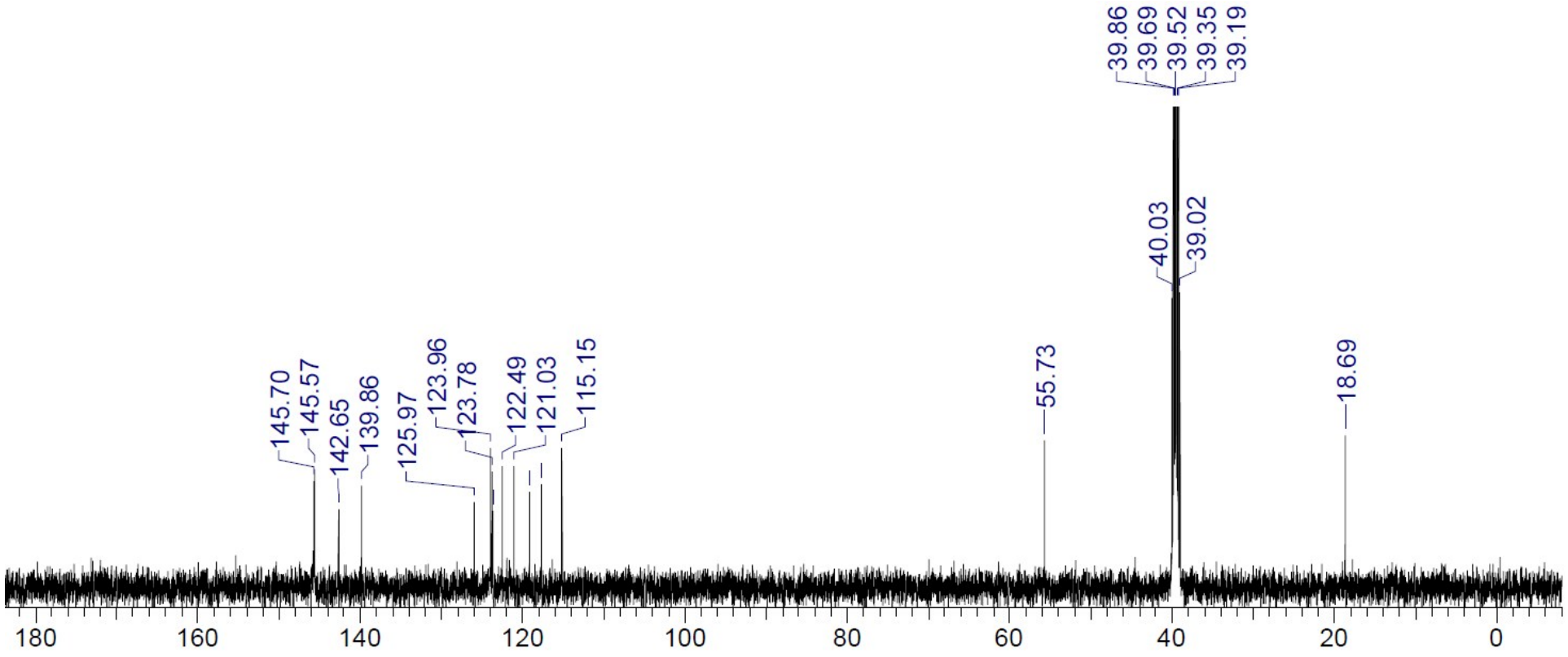


25. NMR Spectra of 10-Bromo-7,12-dihydro-6*H*-indolo[2,3-*a*]quinolizin-5-ium Trifluoromethanesulfonate (**14**)

a) ^{1}H NMR Spectrum (in DMSO-d_6, 500 MHz)

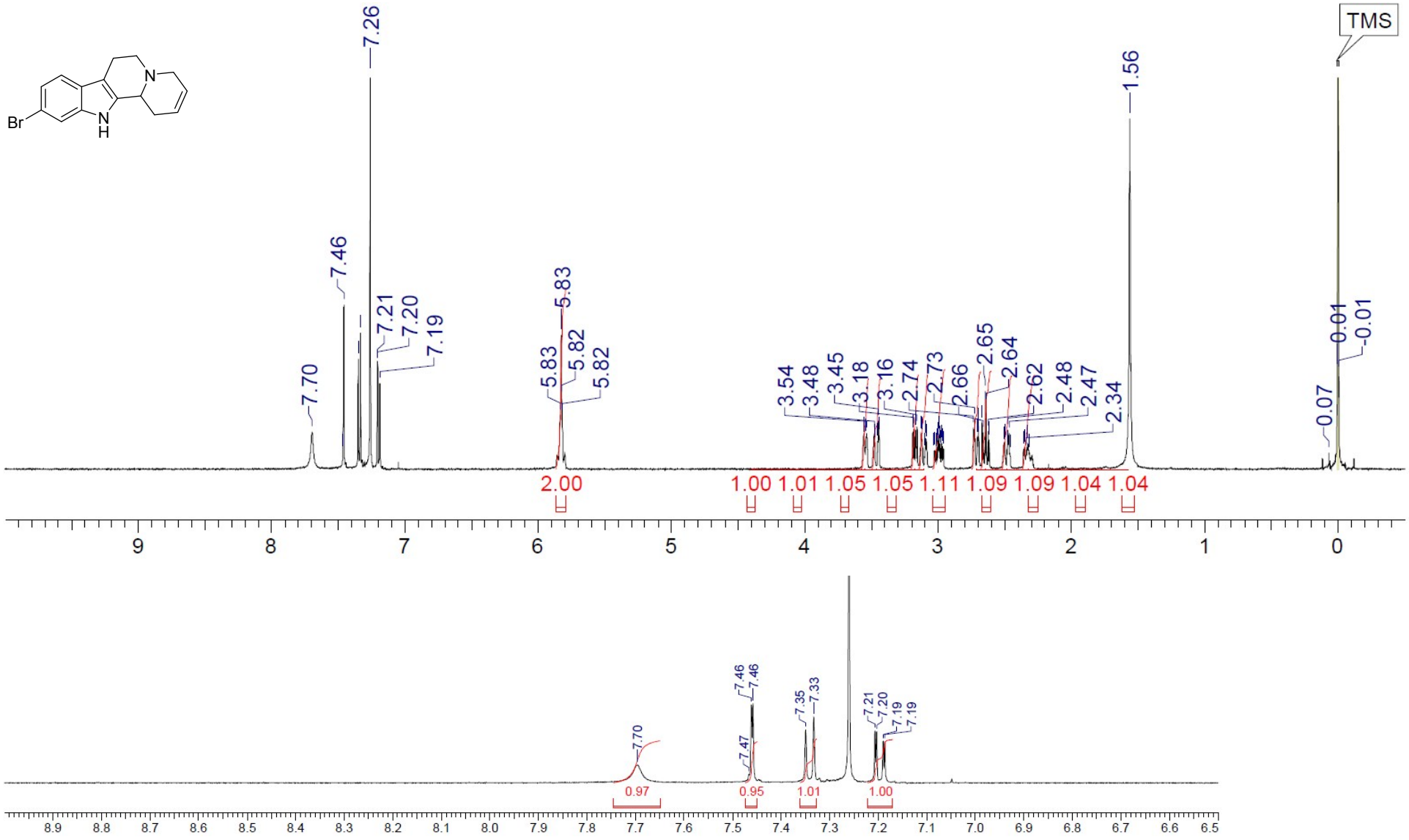


b) ^{13}C NMR Spectrum (in DMSO-d_6, 125 MHz)

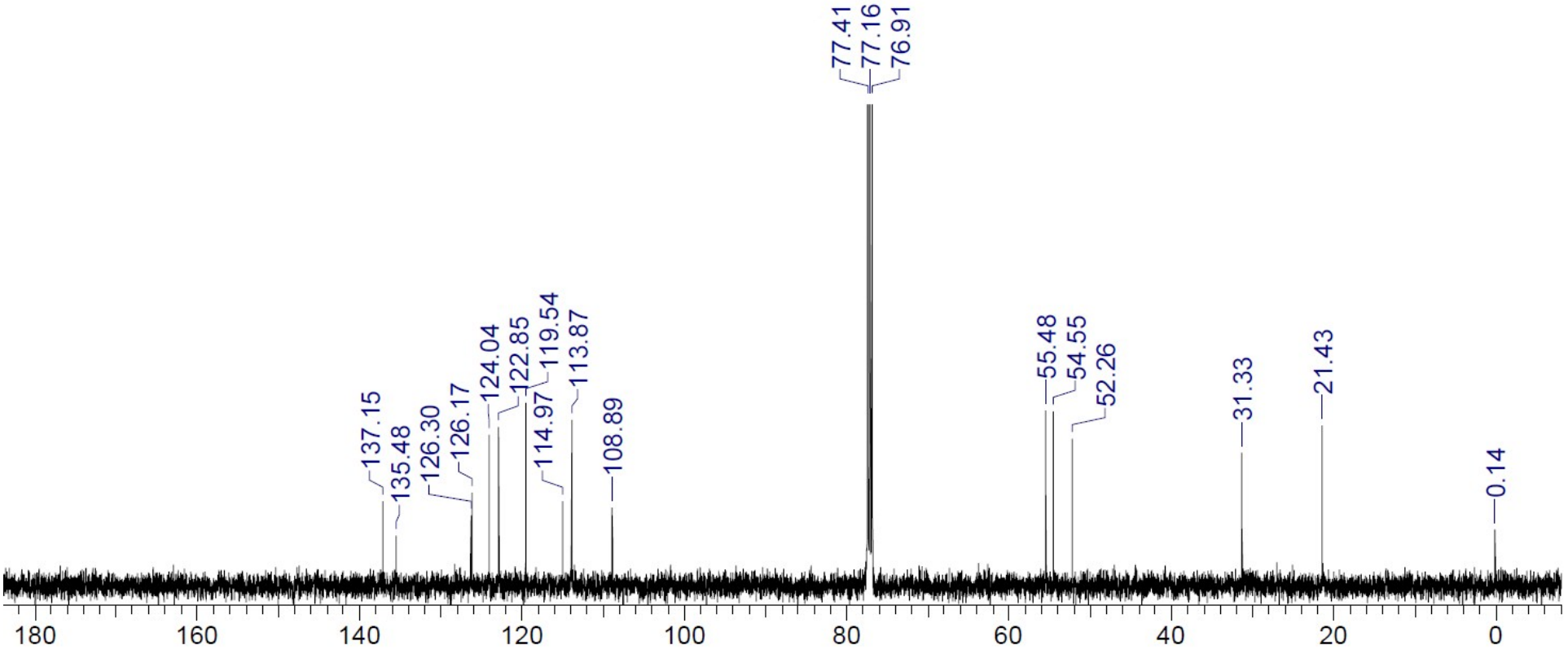


26. NMR Spectra of 10-Bromo-1,4,6,7,12,12*b*-hexahydroindolo[2,3-*a*]quinolizine (**15**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

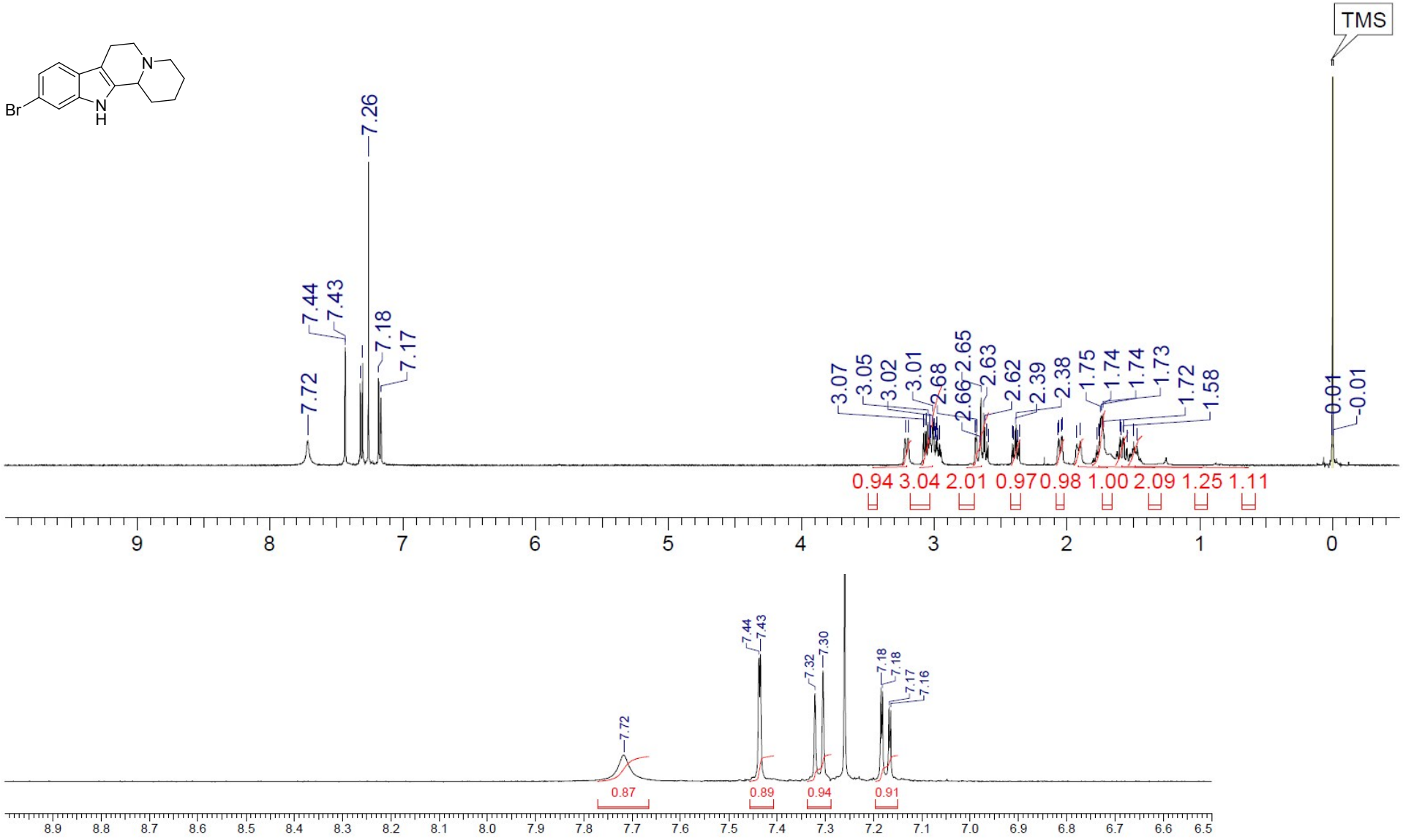


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

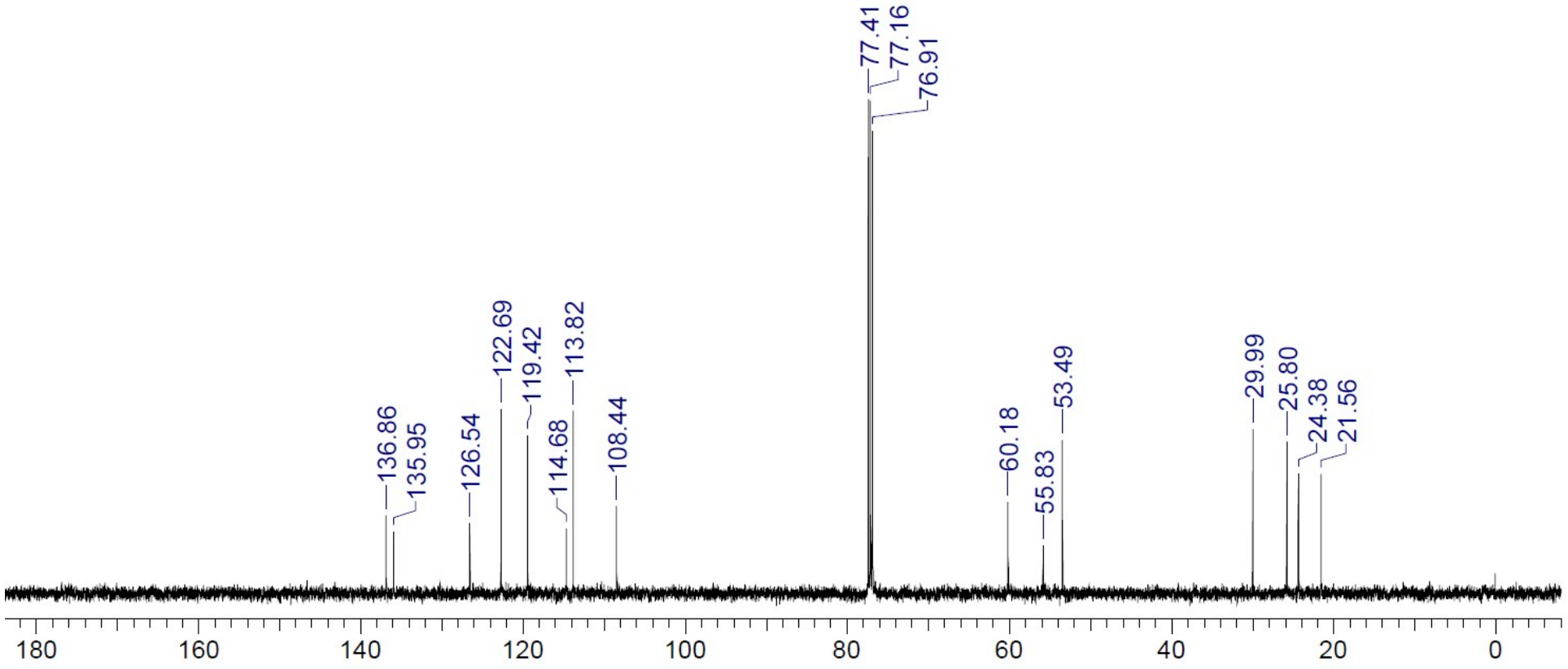


27. NMR Spectra of Arborescidine A (**6**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)



b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)



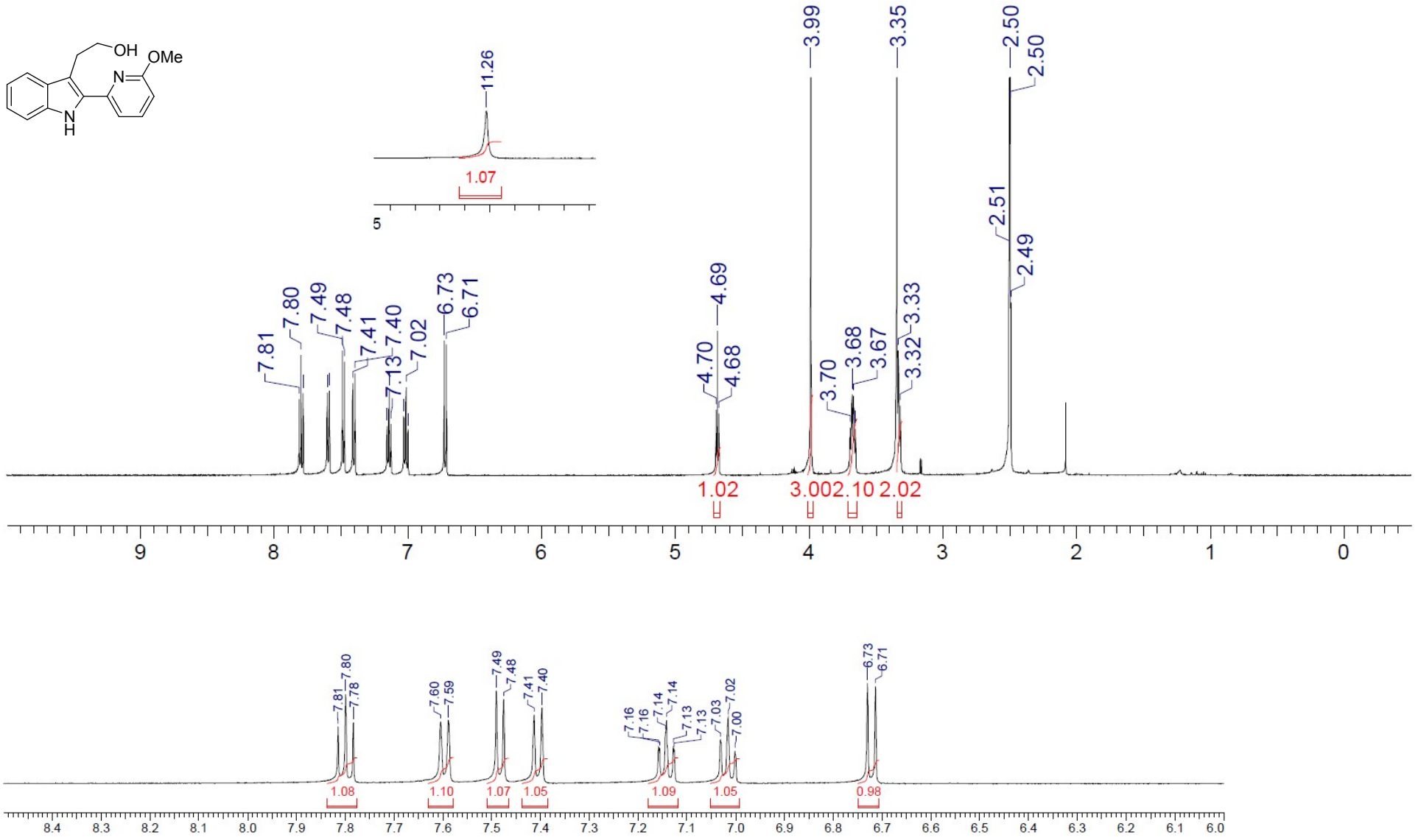
c) Comparison Table of the NMR Data of Arborescidine A (**6**) with Previous Literature Data

	Our work (500 MHz spectrometers)				Previous work (300 MHz spectrometers)[a]			
	chemical shift	multiplicity	coupling constant	integration	chemical shift	multiplicity	coupling constant	integration
^{1}H NMR	7.72 ppm	br s		1H	7.75 ppm	s		1H
	7.44 ppm	d	1.7 Hz	1H	7.42 ppm	d	1.5 Hz	1H
	7.31 ppm	d	8.4 Hz	1H	7.30 ppm	d	8.4 Hz	1H
	7.17 ppm	dd	8.4, 1.7 Hz	1H	7.16 ppm	dd	8.4, 1.5 Hz	1H
	3.21 ppm	d	10.1 Hz	1H	3.19 ppm	d	8.8 Hz	1H
	3.11 – 2.94 ppm	m		3H	3.09 – 2.92 ppm	m		3H
	2.71 – 2.58 ppm	m		2H	2.69 – 2.57 ppm	m		2H
	2.39 ppm	td	4.1, 11.1 Hz	1H	2.42 – 2.34 ppm	m		1H
	2.05 ppm	dd	12.4, 2.8 Hz	1H	2.09 – 2.03 ppm	m		1H
	1.91 ppm	d	13.0 Hz	1H	1.97 – 1.86 ppm	m		1H
	1.82 – 1.72 ppm	m		2H	1.79 – 1.70 ppm	m		2H
	1.64 – 1.54 ppm	m		1H	1.65 – 1.49 ppm	m		1H
	1.49 ppm	d	12.7 Hz	1H	1.48 – 1.44 ppm	m		1H
^{13}C NMR	136.9 ppm				136.7 ppm			
	135.9 ppm				135.8 ppm			
	126.5 ppm				126.4 ppm			
	122.7 ppm				122.7 ppm			
	119.4 ppm				119.3 ppm			
	114.7 ppm				114.5 ppm			
	113.8 ppm				113.7 ppm			
	108.4 ppm				108.3 ppm			
	60.2 ppm				60.0 ppm			
	55.8 ppm				55.7 ppm			
	53.5 ppm				53.4 ppm			
	30.0 ppm				29.9 ppm			
	25.8 ppm				25.7 ppm			
	24.4 ppm				24.3 ppm			
	21.6 ppm				21.4ppm			

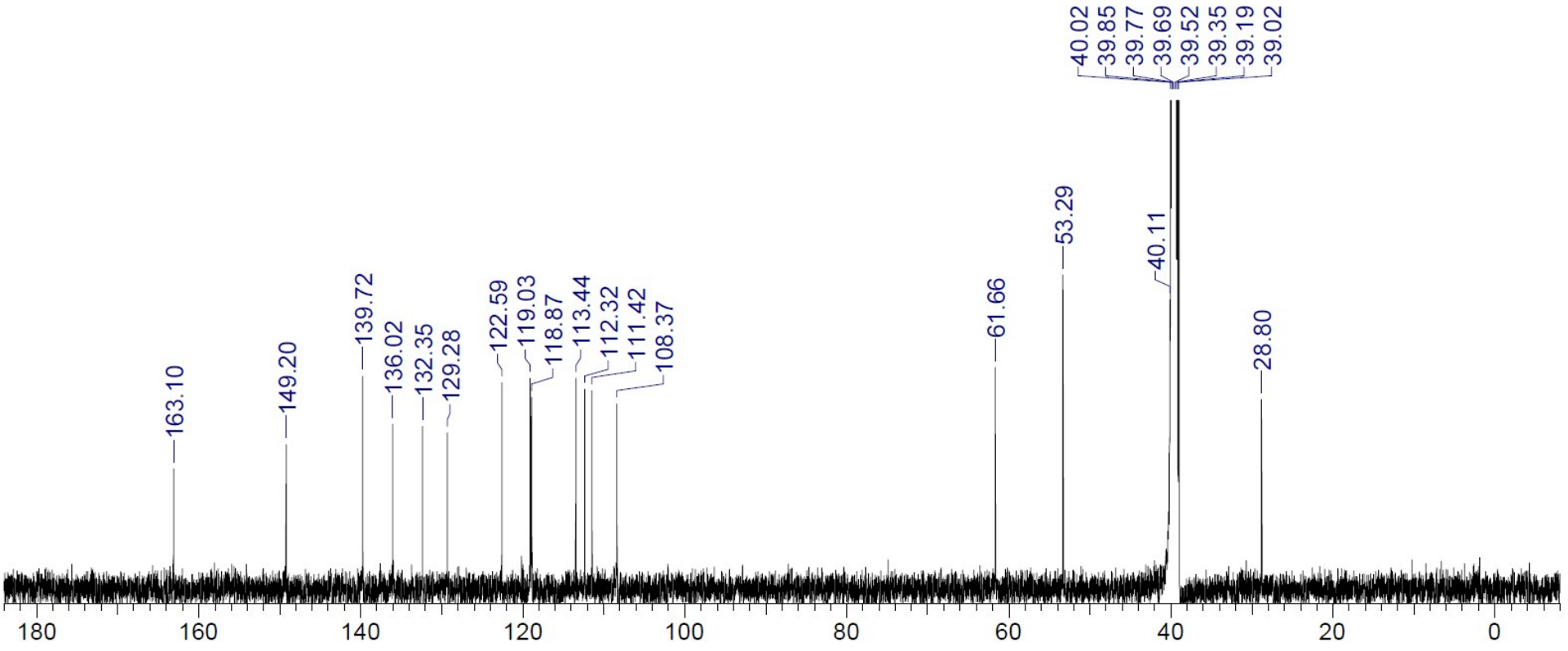
[a] Previous report: L. S. Santos, R. A. Pilli and V. H. Rawal, *J. Org. Chem.*, 2004, **69**, 1283.

28. NMR Spectra of 2-(2-(6-Methoxypyridin-2-yl)-1*H*-indol-3-yl)ethan-1-ol (**16**)

a) ^{1}H NMR Spectrum (in DMSO-d_6, 500 MHz)

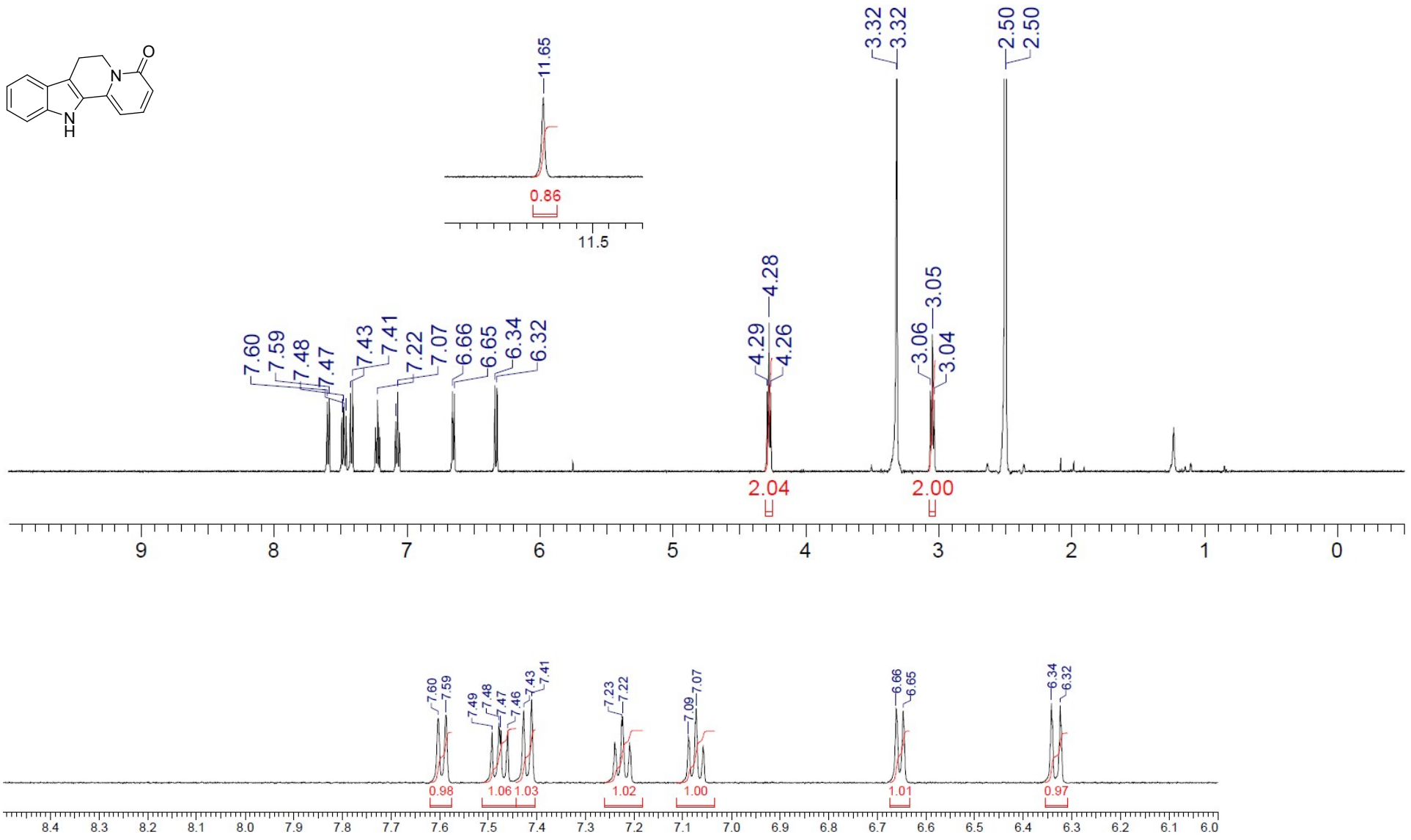


b) ^{13}C NMR Spectrum (in DMSO-d_6, 125 MHz)

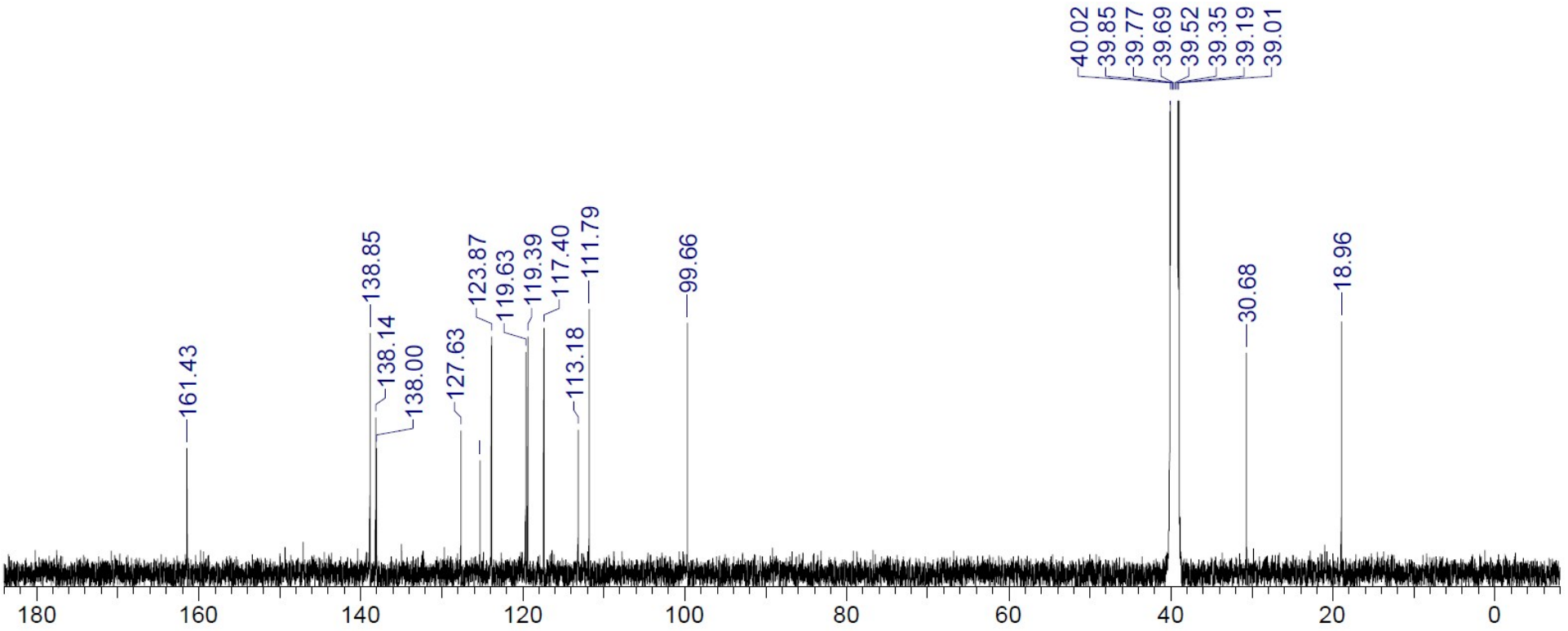


29. NMR Spectra of 7,12-Dihydroindolo[2,3-*a*]quinolizin-4(6*H*)-one (**17**)

a) ^{1}H NMR Spectrum (in DMSO-d_6, 500 MHz)

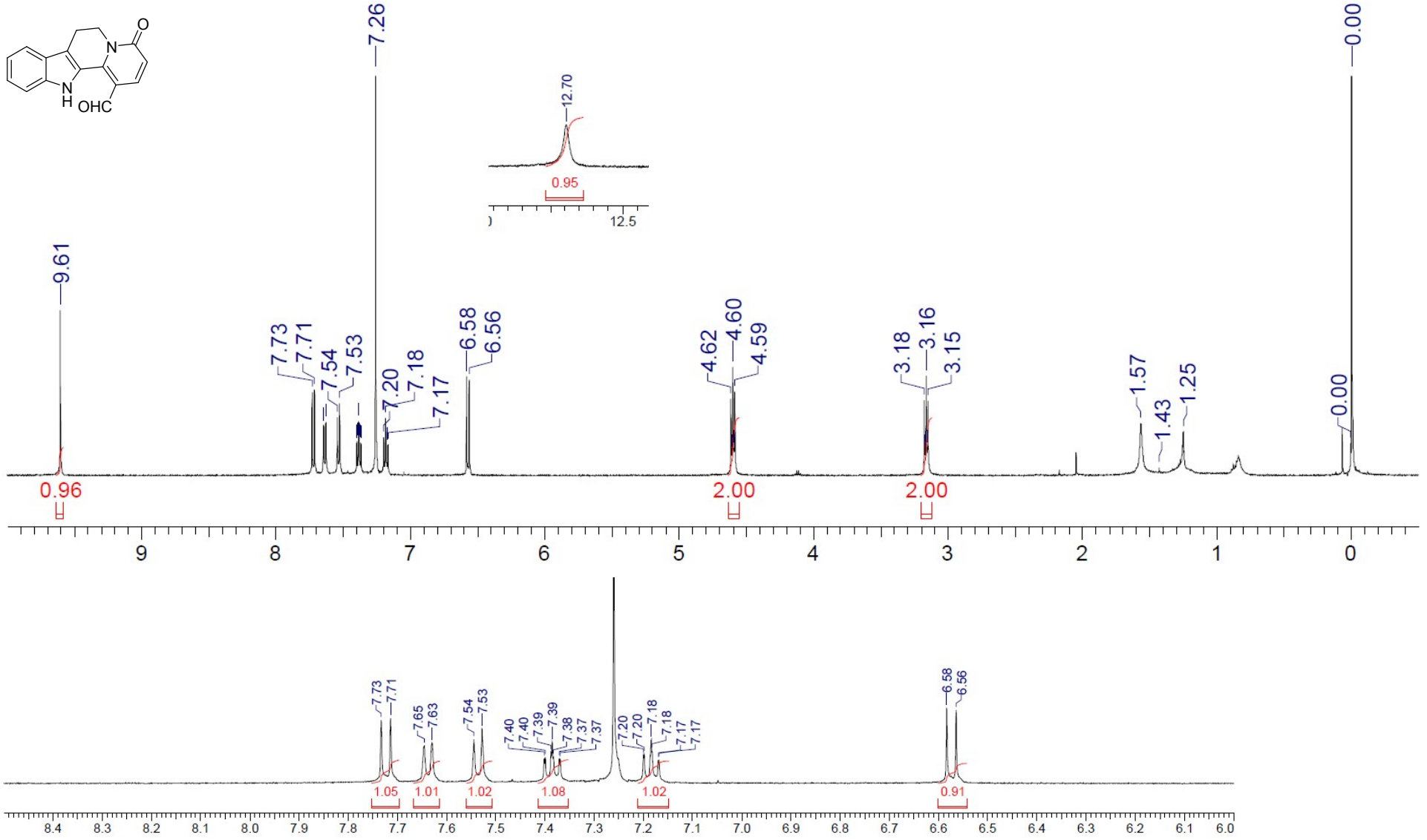


b) ^{13}C NMR Spectrum (in DMSO-d_6, 125 MHz)



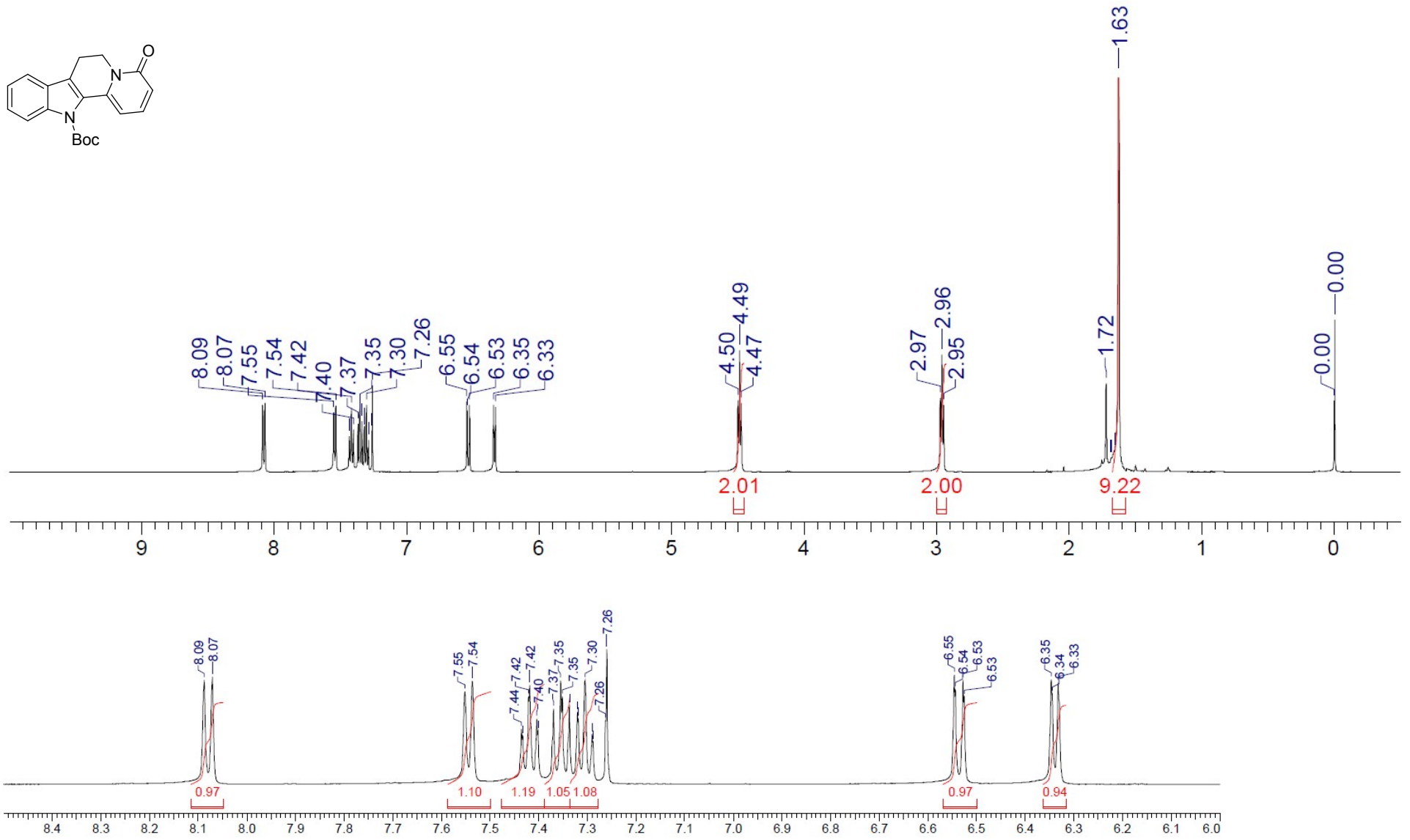
30. NMR Spectra of 4-Oxo-4,6,7,12-tetrahydroindolo[2,3-a]quinolizine-1-carbaldehyde (**18**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

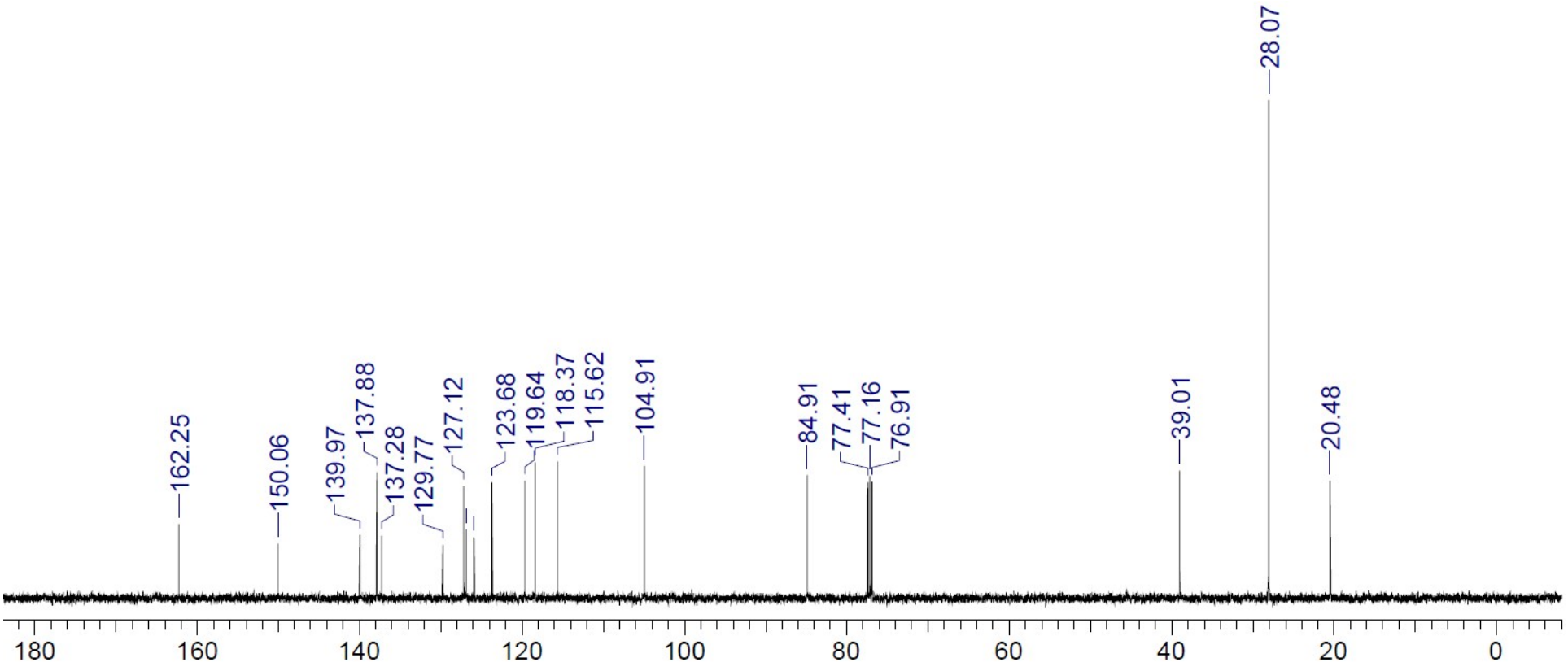


31. NMR Spectra of *tert*-Butyl 4-oxo-6,dihydroindolo[2,3-*a*]quinolizine-12(4*H*)-carboxylate (**19**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

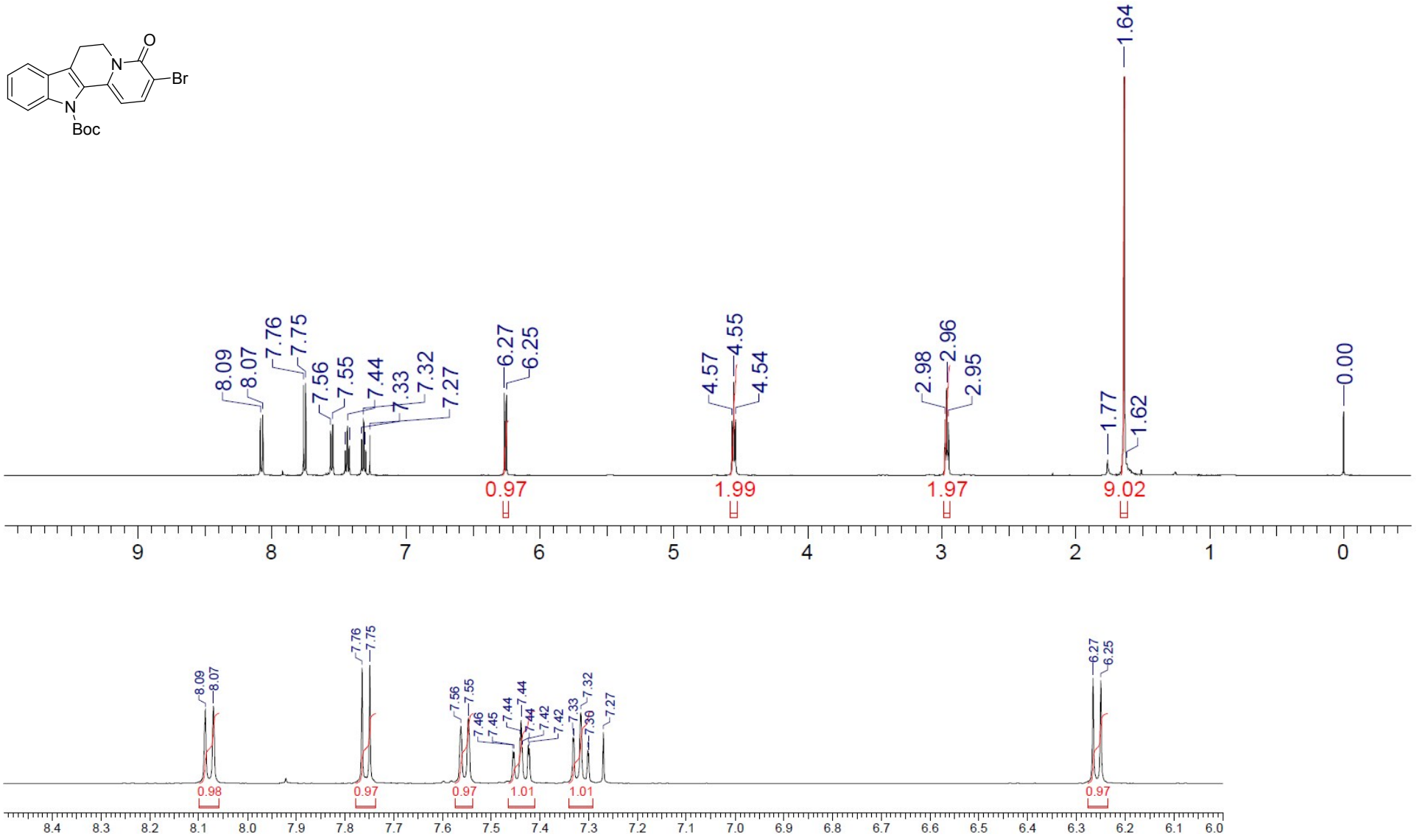


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

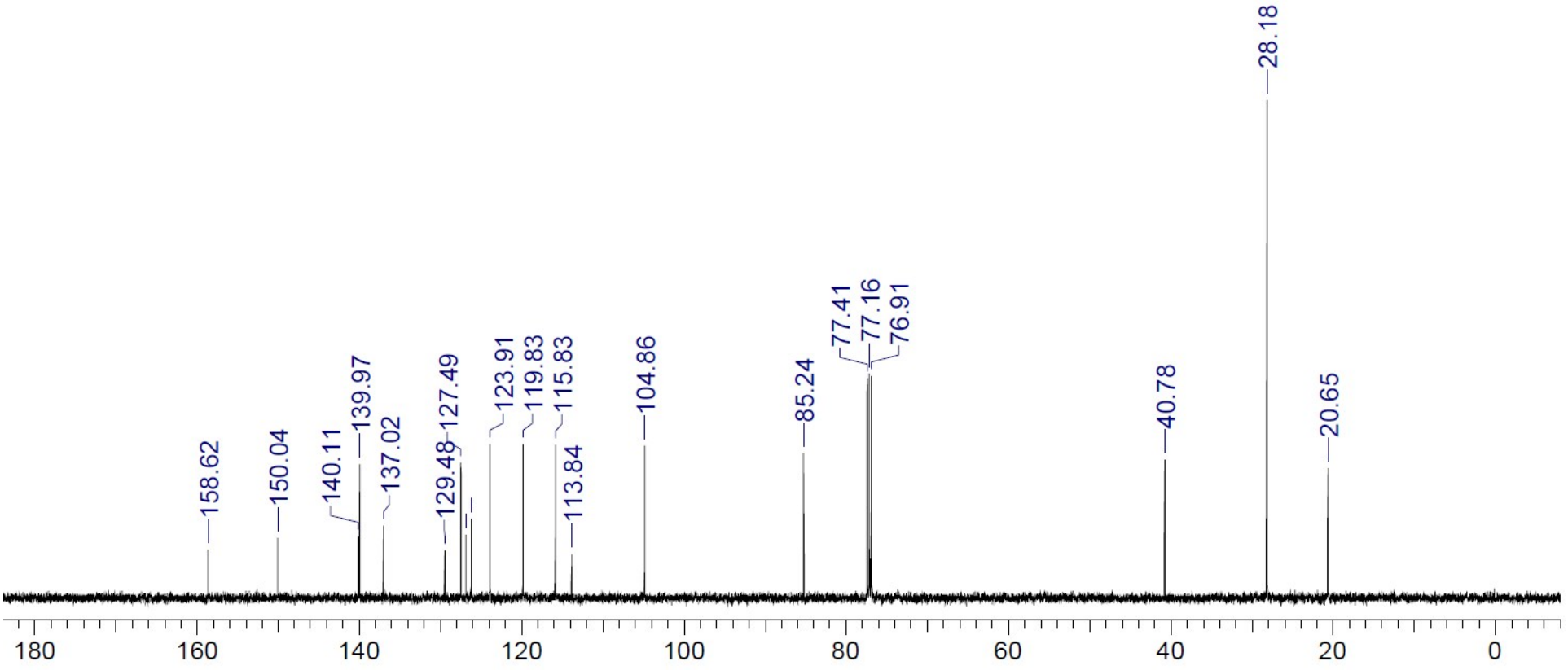


32. NMR Spectra of *tert*-Butyl 3-bromo-4-oxo-6,dihydroindolo[2,3-*a*]quinolizine-12(4*H*)-carboxylate (**20**)

a) ^{1}H NMR Spectrum (in $CDCl_3$, 500 MHz)

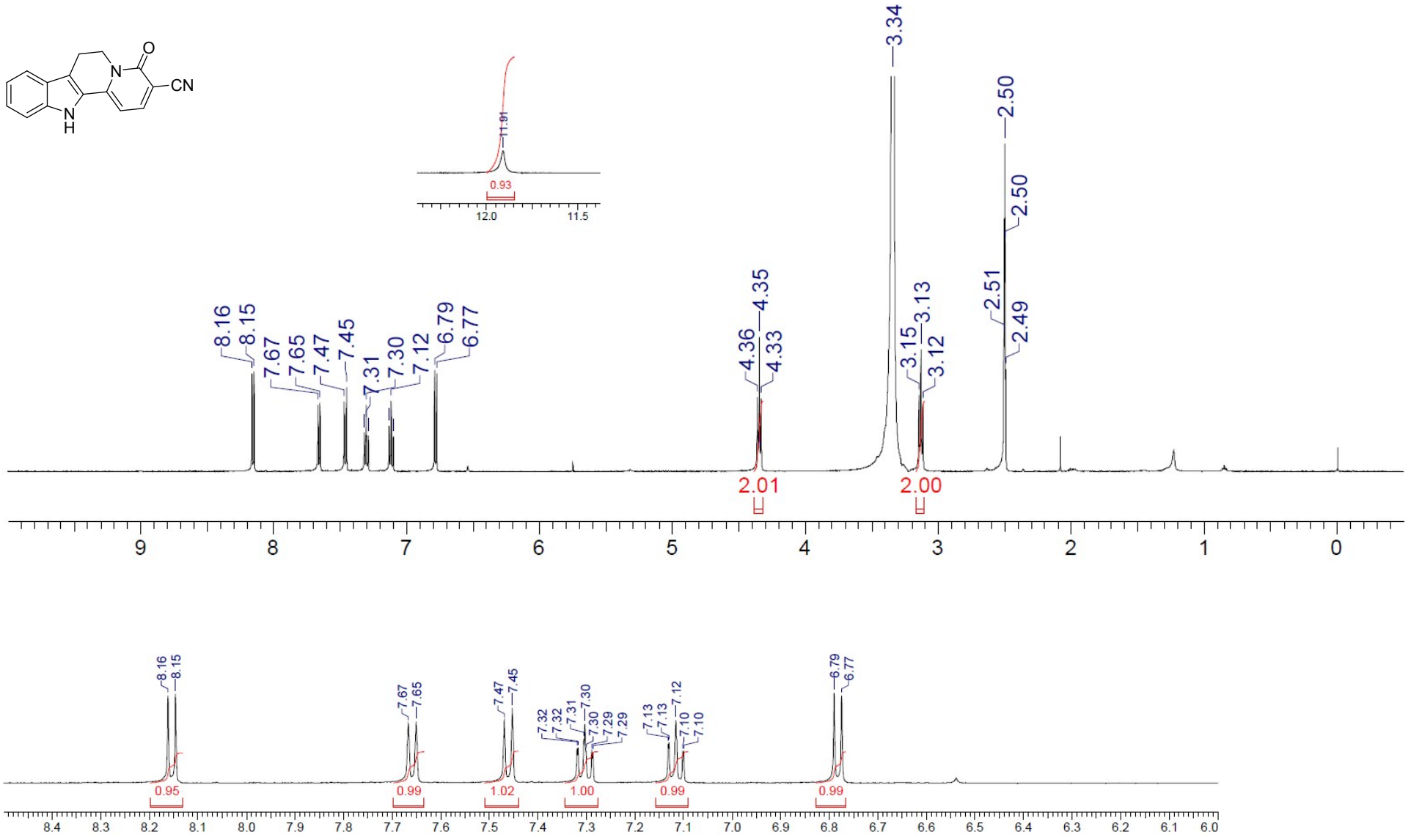


b) ^{13}C NMR Spectrum (in $CDCl_3$, 125 MHz)

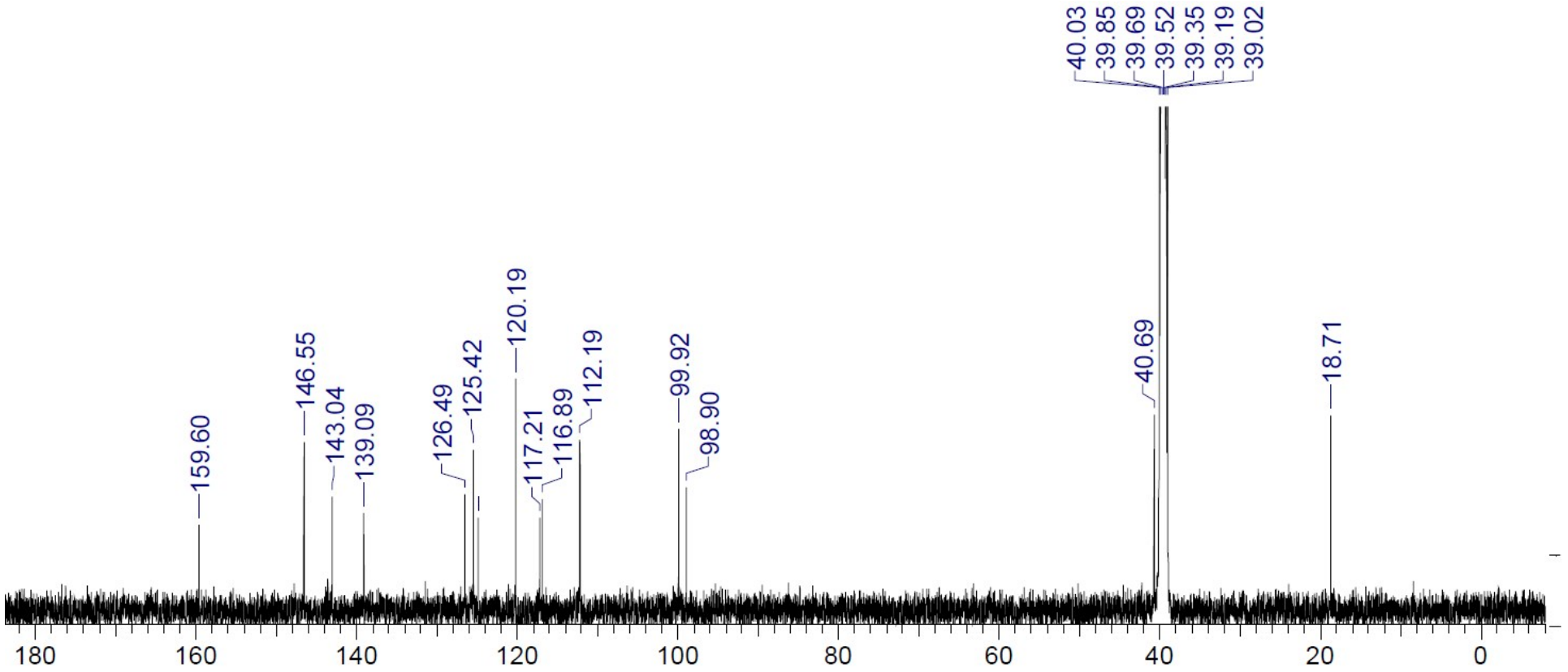


33. NMR Spectra of 4-Oxo-4,6,7,12-tetrahydroindolo[2,3-*a*]quinolizine-3-carbonitrile (**21**)

a) ^{1}H NMR Spectrum (in DMSO-d_6, 500 MHz)

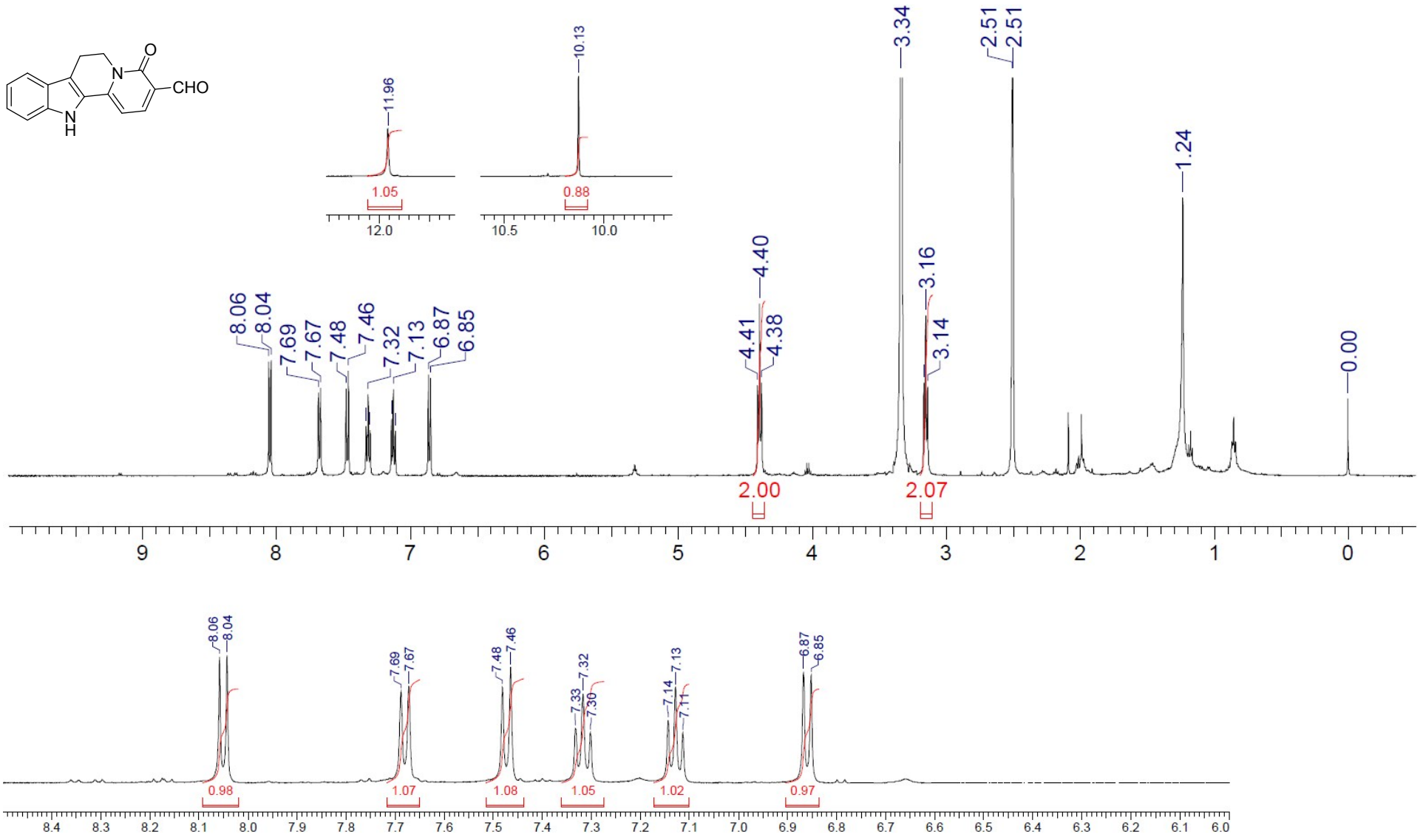


b) ^{13}C NMR Spectrum (in DMSO-d_6, 125 MHz)

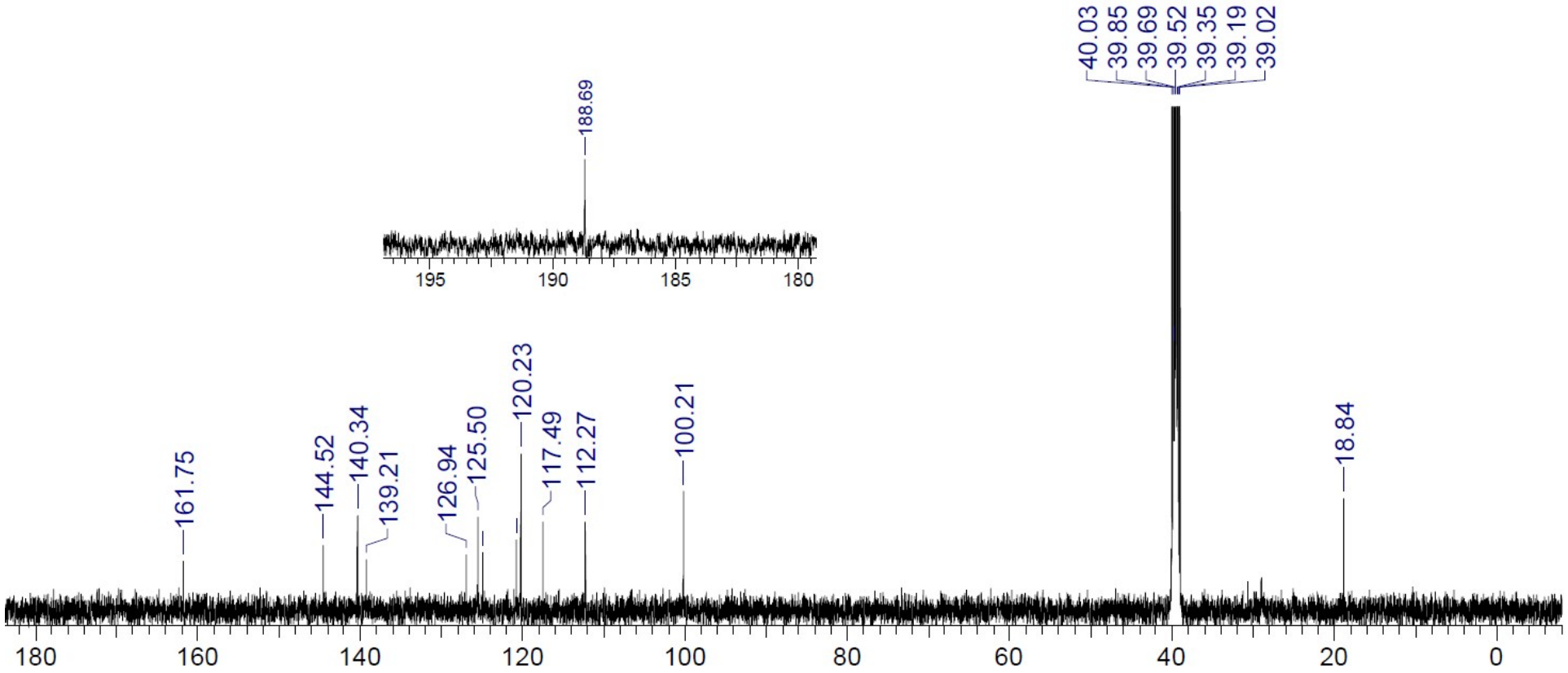


34. NMR Spectra of Nauclefidine (**7**)

a) ^{1}H NMR Spectrum (in DMSO-d_6, 500 MHz)



b) ^{13}C NMR Spectrum (in DMSO-d_6, 125 MHz)



c) Comparison Table of the NMR Data of Nauclefidine (**7**) with Previous Literature Data

	Our work (500 MHz spectrometers)				Previous work (200 MHz spectrometers)[a,b]			
	chemical shift	multiplicity	coupling constant	integration	chemical shift	multiplicity	coupling constant	integration
^{1}H NMR	11.96 ppm	s		1H	11.80 ppm	s		1H
	10.13 ppm	s		1H	10.10 ppm	s		1H
	8.05 ppm	d	7.6 Hz	1H	7.95 ppm	d	7.7 Hz	1H
	7.68 ppm	d	7.9 Hz	1H	7.60 ppm	d	8.1 Hz	1H
	7.47 ppm	d	8.2 Hz	1H	7.40 ppm	d	8.1 Hz	1H
	7.32 ppm	t	7.6 Hz	1H	7.25 ppm	t	7.5 Hz	1H
	7.13 ppm	t	7.4 Hz	1H	7.05 ppm	t	7.5 Hz	1H
	6.86 ppm	d	7.6 Hz	1H	6.80 ppm	d	7.7 Hz	1H
	4.40 ppm	t	7.2 Hz	2H	4.35 ppm	t	7.2 Hz	2H
	3.16 ppm	t	7.2 Hz	2H	3.10 ppm	t	7.2 Hz	2H
^{13}C NMR	188.7 ppm				188.6 ppm			
	161.7 ppm				161.7 ppm			
	144.5 ppm				144.5 ppm			
	140.3 ppm				140.3 ppm			
	139.2 ppm				139.2 ppm			
	126.9 ppm				126.9 ppm			
	125.5 ppm				125.4 ppm			
	124.9 ppm				124.9 ppm			
	120.7 ppm				120.7 ppm			
	120.2 ppm				120.17 ppm			
	120.2 ppm				120.16 ppm			
	117.5 ppm				117.4 ppm			
	112.3 ppm				112.2 ppm			
	100.2 ppm				100.1 ppm			
	18.8 ppm				18.8ppm			

Previous reports: [a] ^{1}H NMR: R. K. Manna, P. Jaisankar and V. S. Giri, *Synth. Commun.*, 1998, **28**, 9.

[b] ^{13}C NMR: H. Takayama, R. Yamamoto, M. Kurihara, M. Kitajima, N. L. Mao and S.-I. Sakai, *Tetrahedron Lett.*, 1994, **35**, 8813.