

Supporting Information

Total synthesis of Taraxacine A natural product via Ag(I)-catalysed imidate-alkyne cyclization

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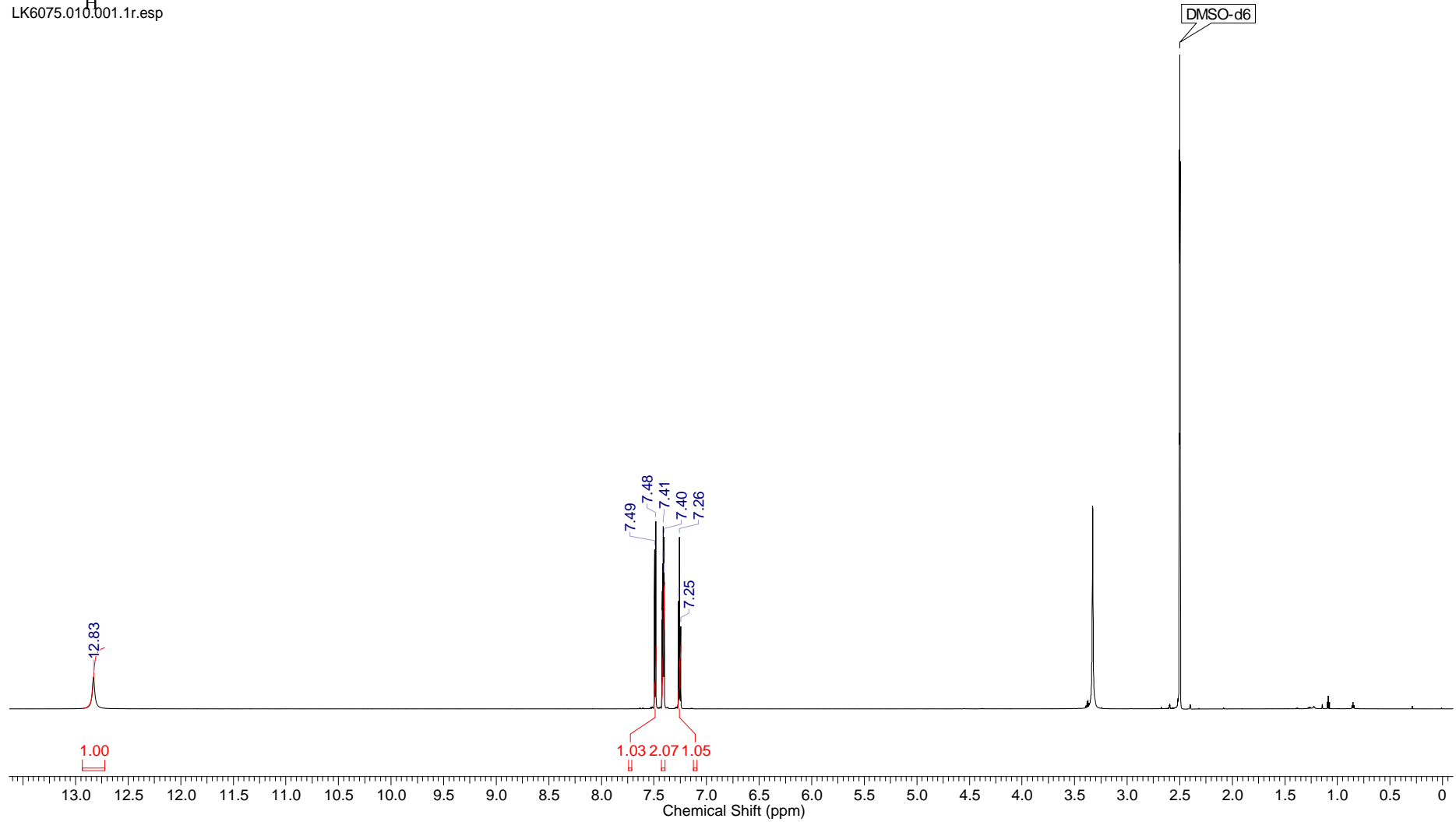
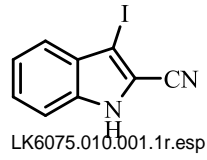
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- b. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russia, Leninsky prosp., 31 Bldg. 4

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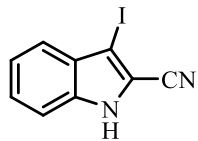
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1. NMR Spectra

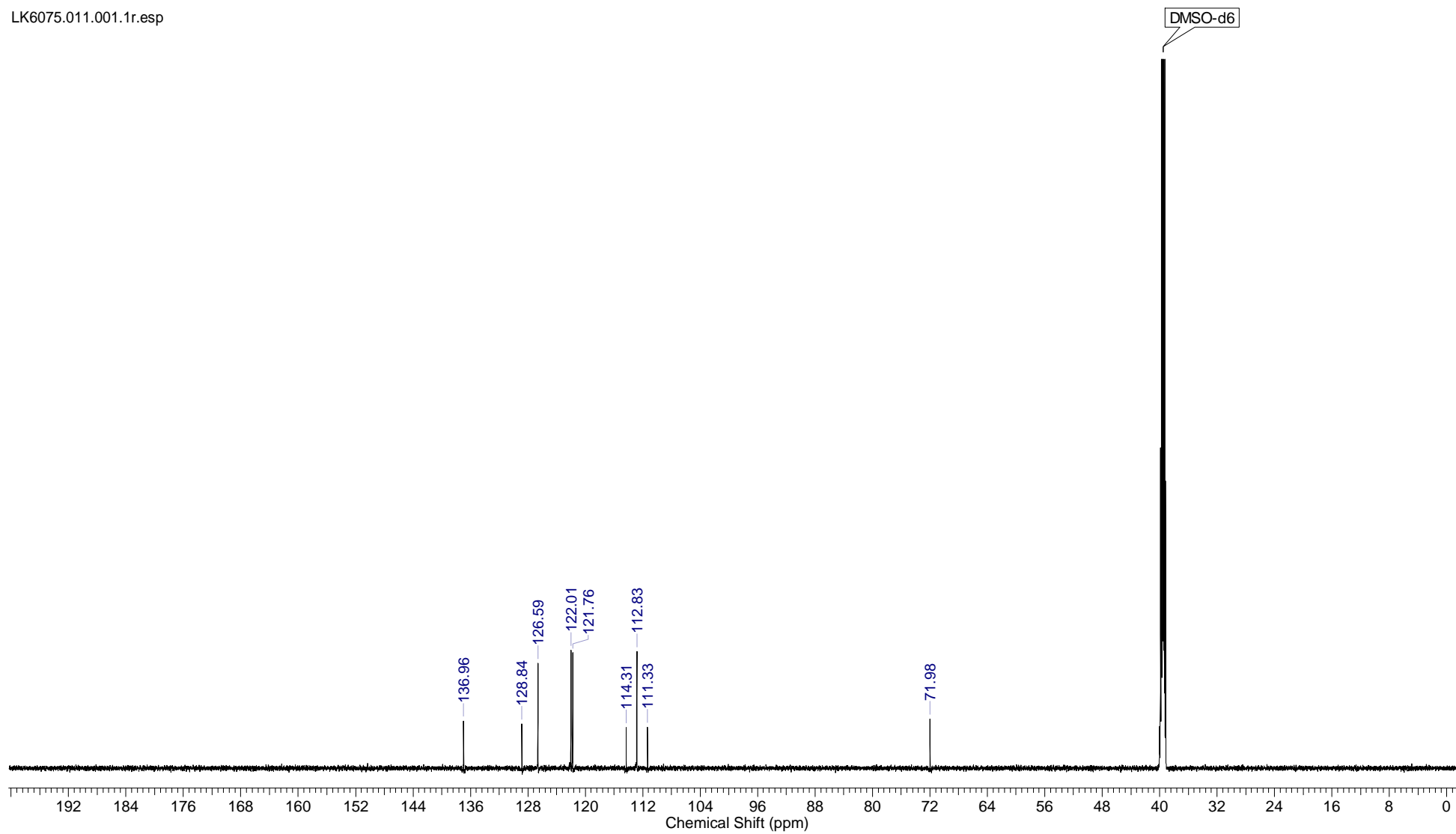
3-iodo-1H-indole-2-carbonitrile (**2**) ¹H NMR (700 MHz, DMSO-d₆)



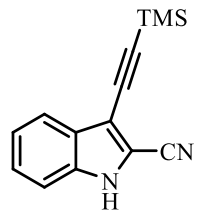
3-iodo-1H-indole-2-carbonitrile (2) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



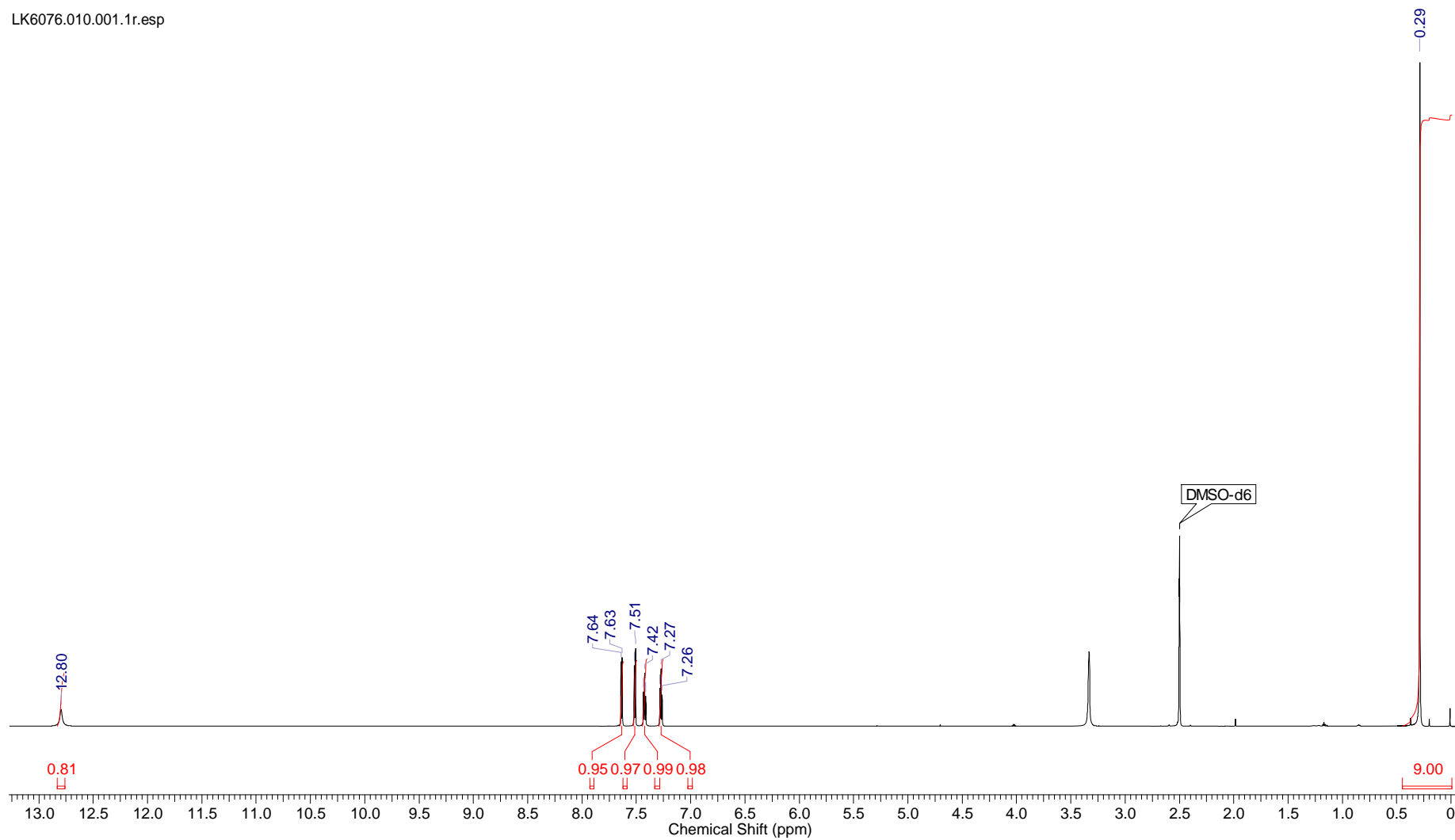
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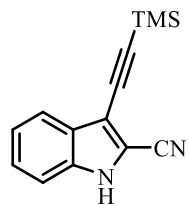
3-((trimethylsilyl)ethynyl)-1H-indole-2-carbonitrile (**3a**) ¹H NMR (700 MHz, DMSO-d₆)



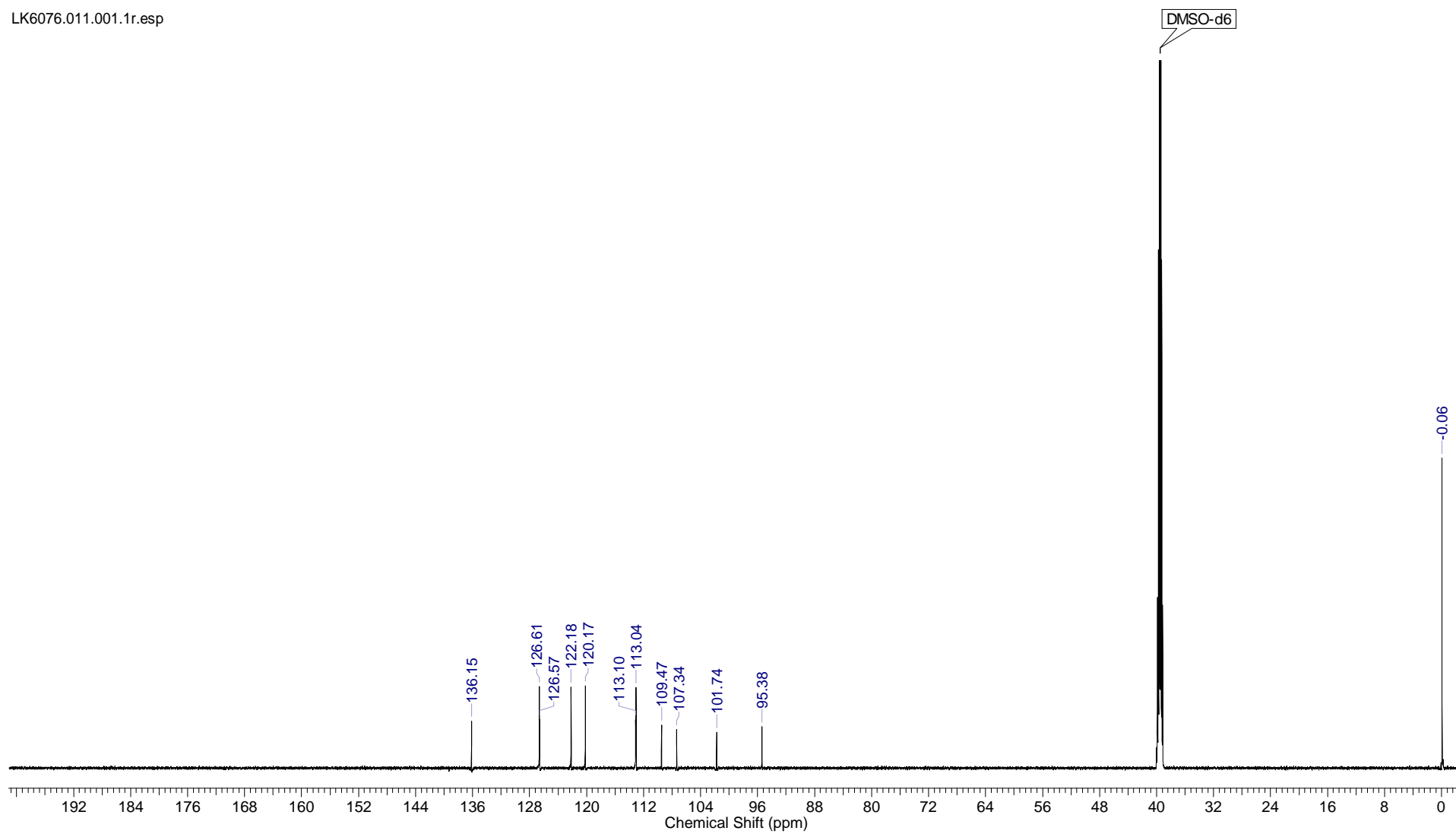
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3-((trimethylsilyl)ethynyl)-1H-indole-2-carbonitrile (**3a**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)

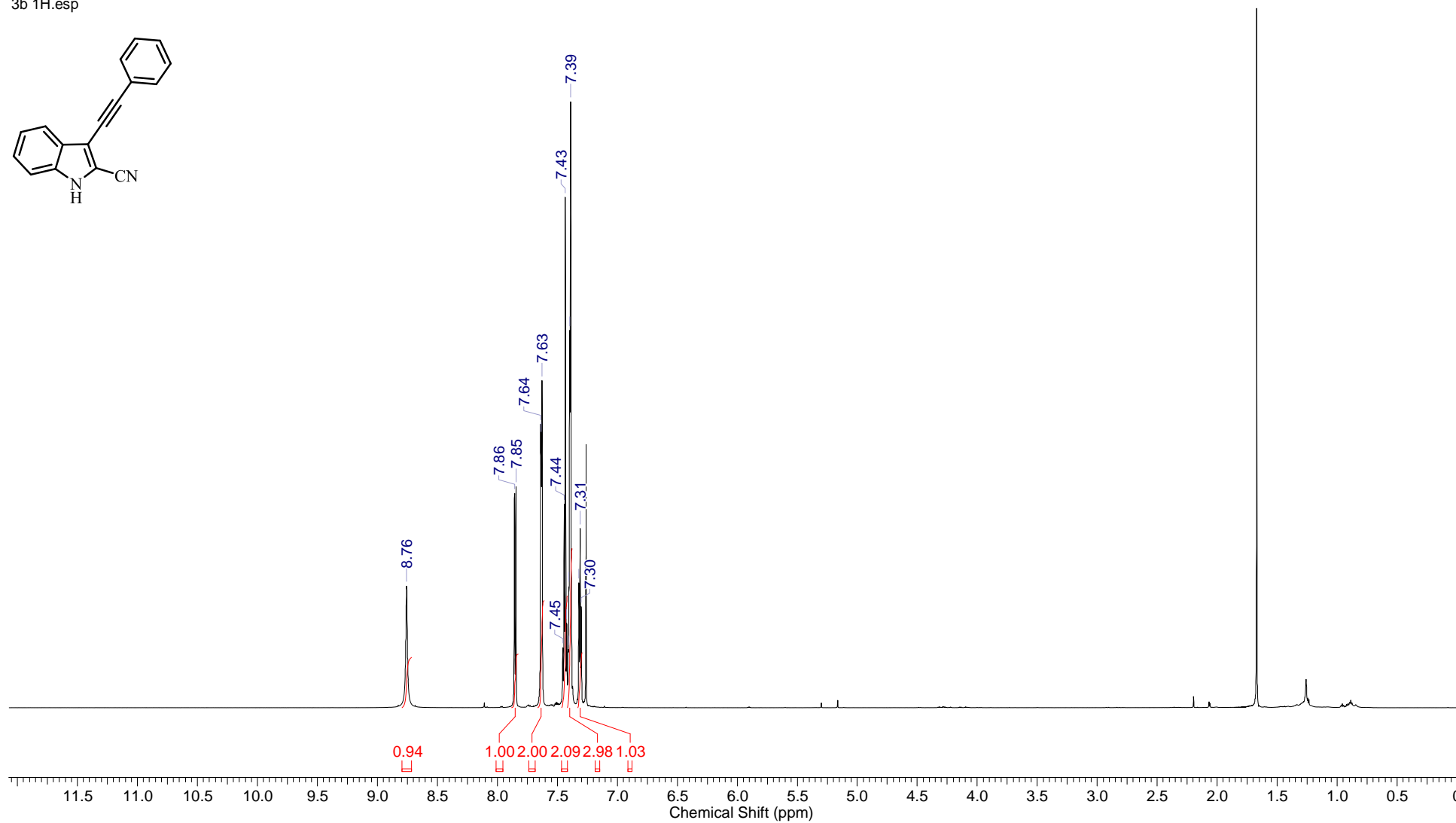
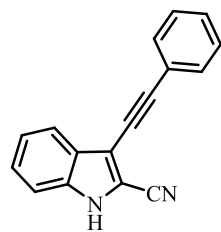


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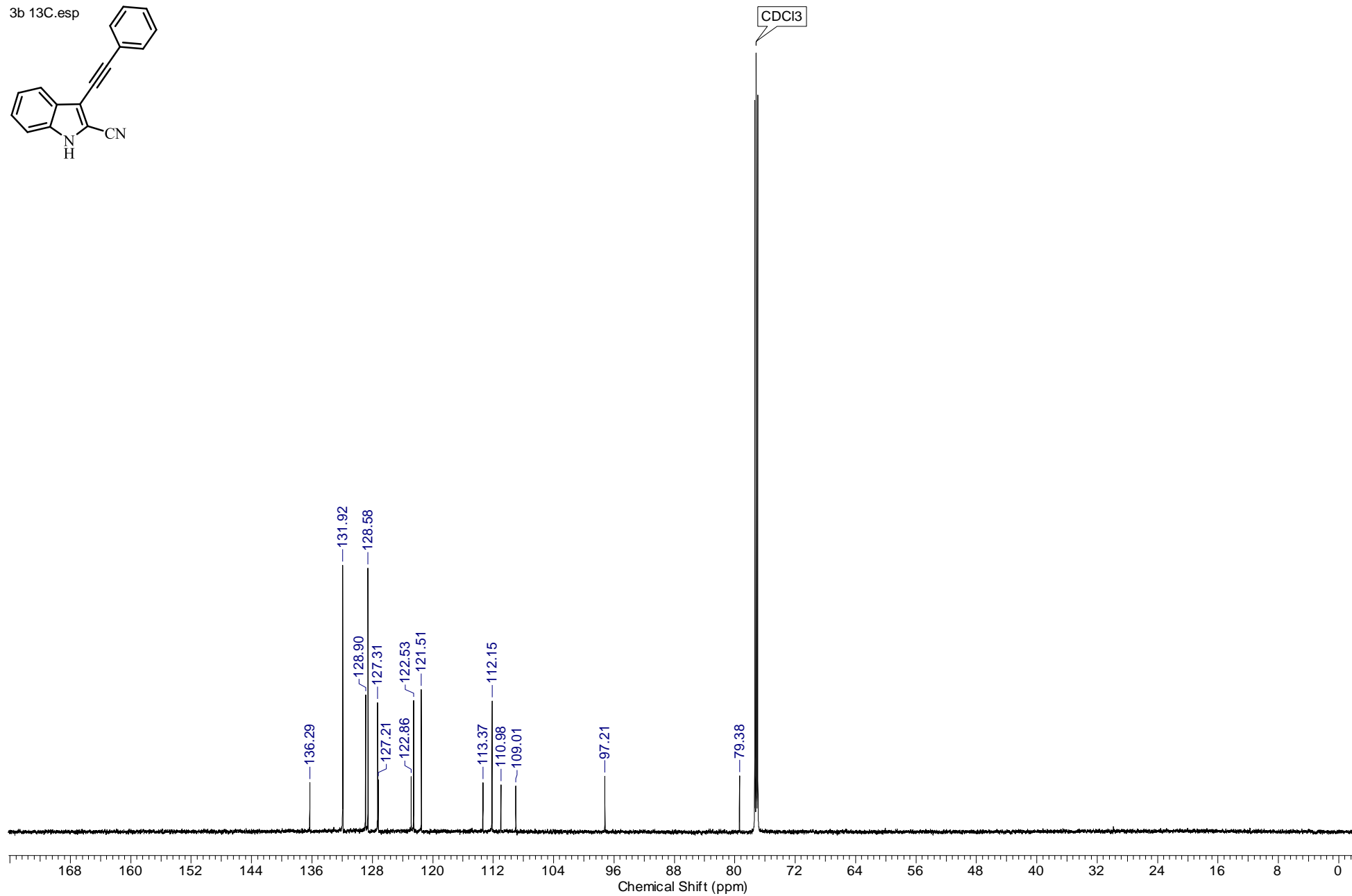
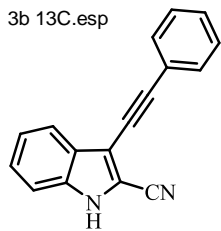
3-(phenylethynyl)-1H-indole-2-carbonitrile (**3b**) ^1H NMR (700 MHz, CDCl_3)

3b 1H.esp



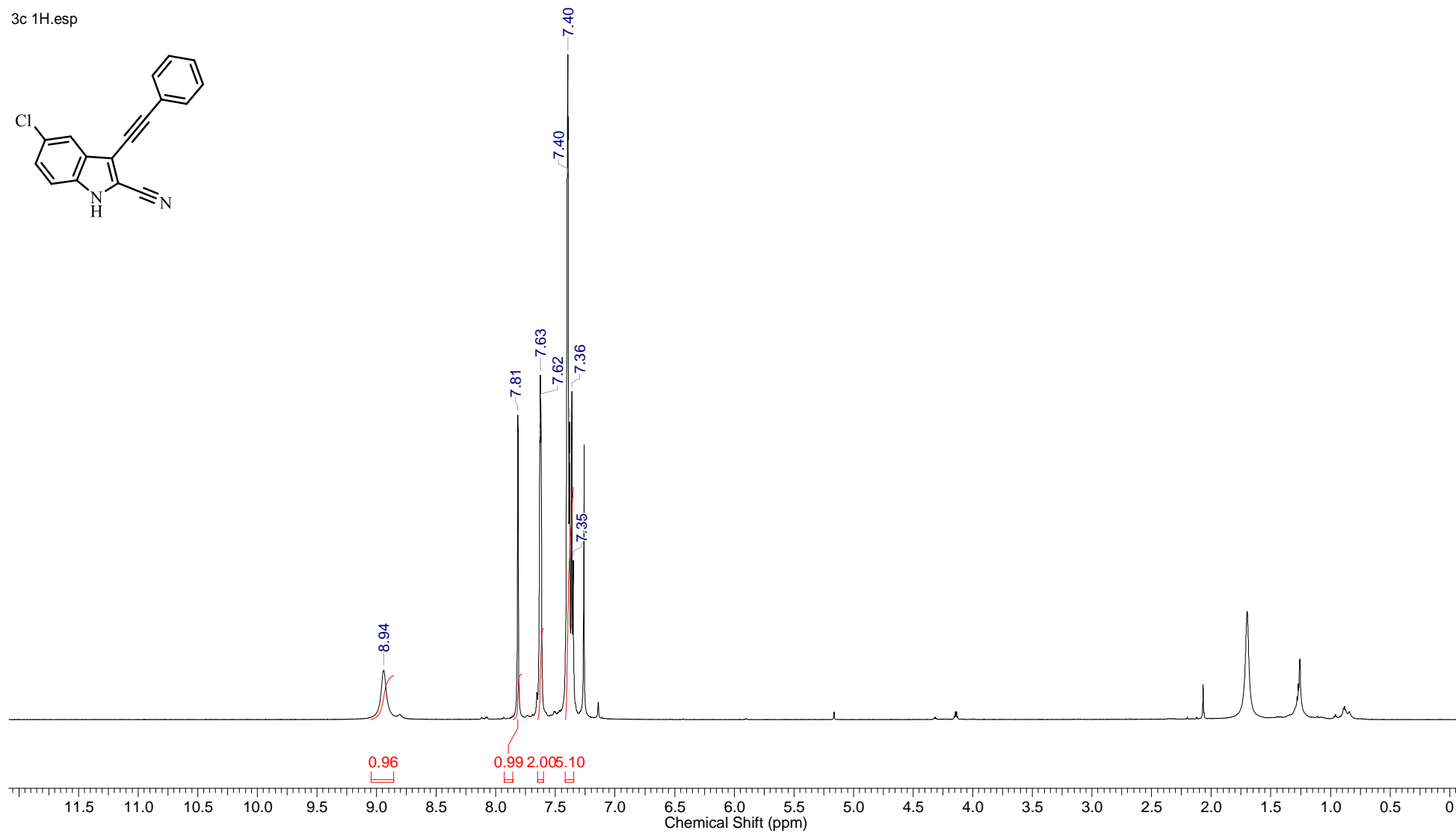
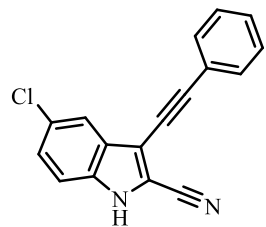
3-(phenylethynyl)-1H-indole-2-carbonitrile (**3b**) ^{13}C {1H} NMR (CDCl_3 , 177 MHz)

3b 13C.esp



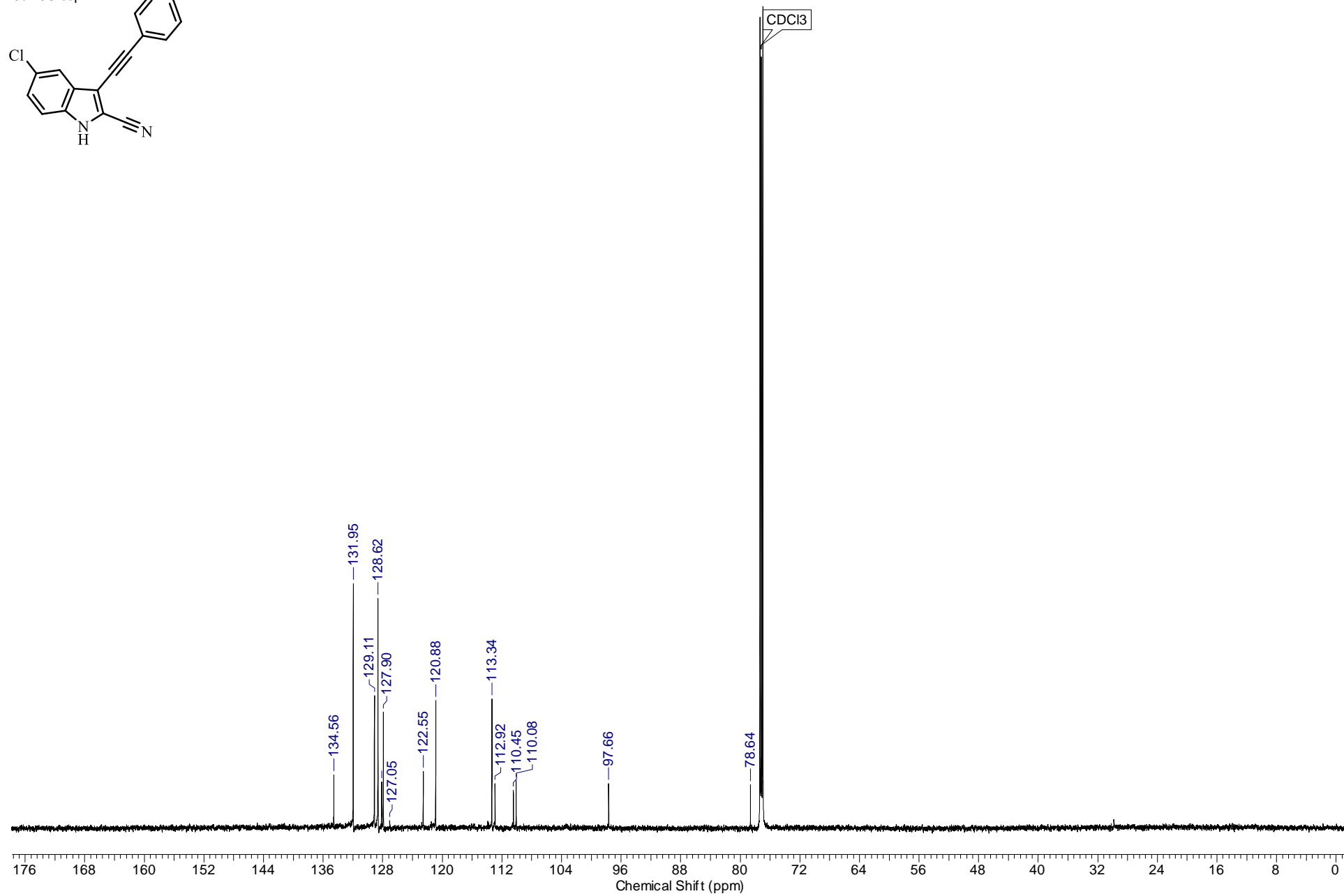
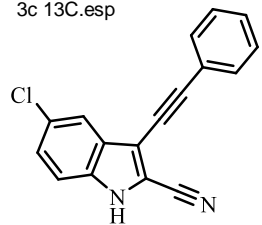
5-chloro-3-(phenylethynyl)-1H-indole-2-carbonitrile (**3c**) ^1H {1H} NMR (700 MHz, CDCl_3)

3c 1H.esp



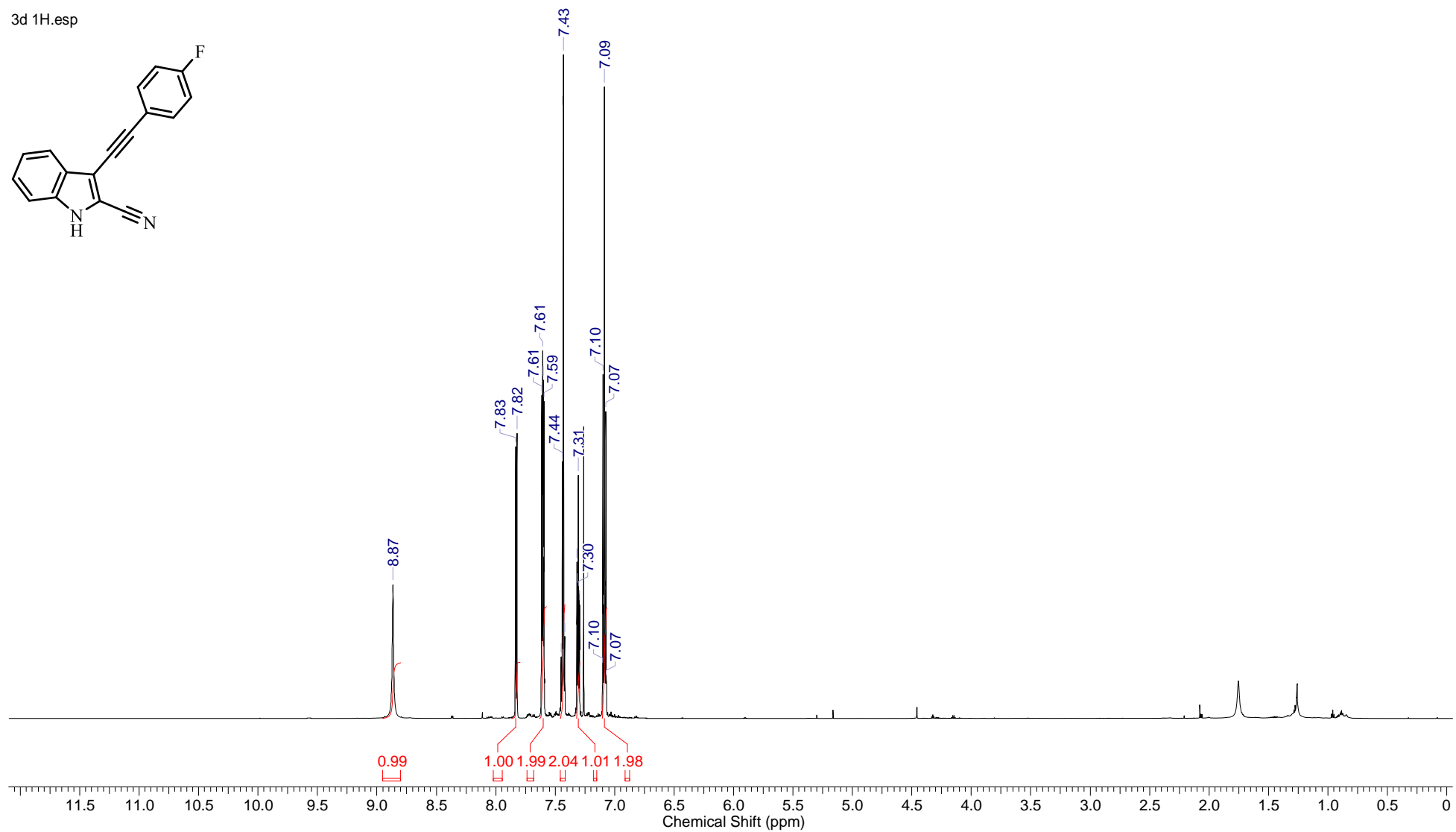
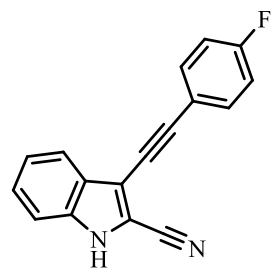
5-chloro-3-(phenylethynyl)-1H-indole-2-carbonitrile (**3c**) ^{13}C {1H} NMR (177 MHz, CDCl_3)

3c 13C.esp



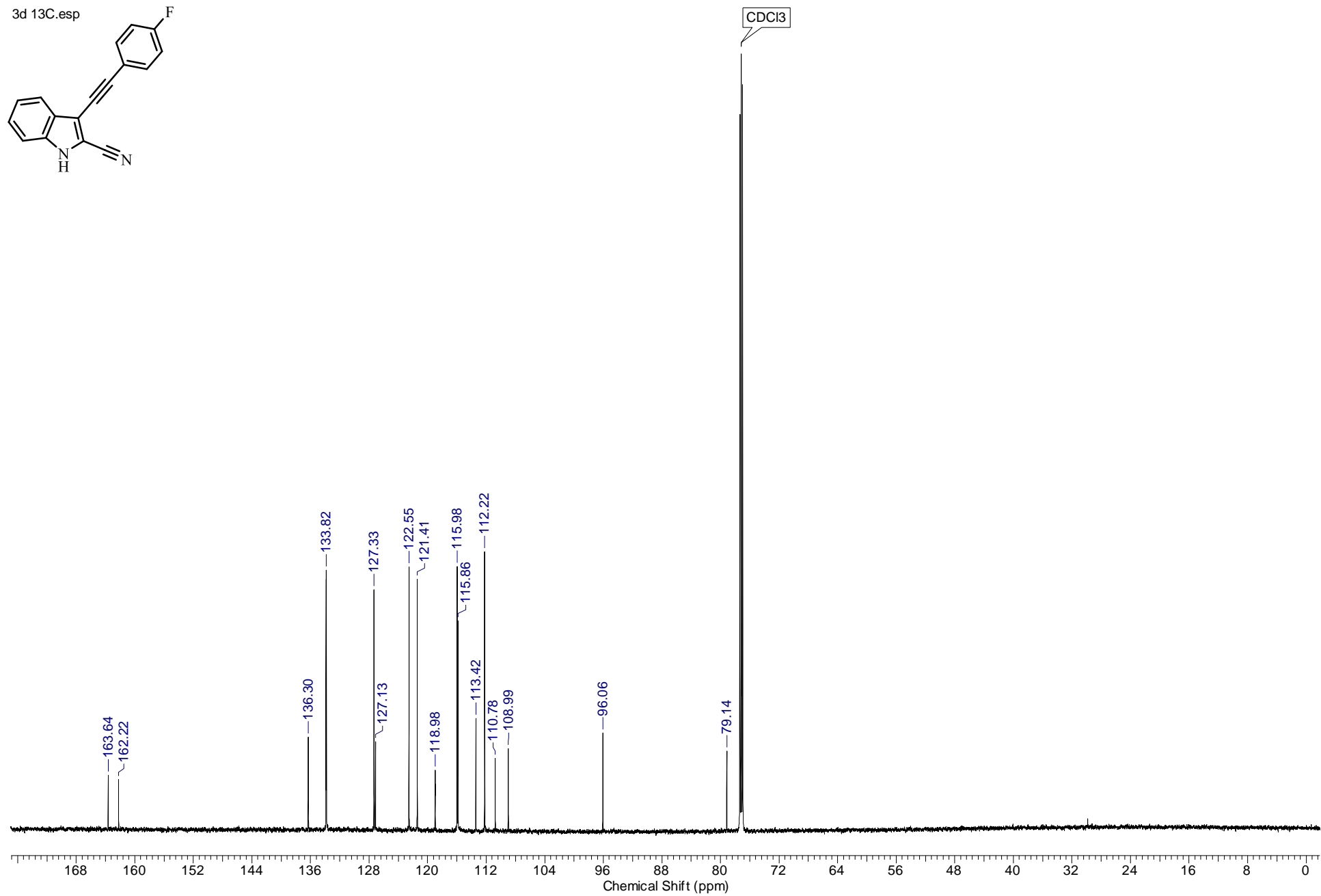
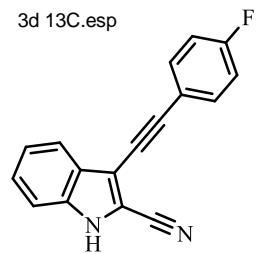
3-((4-fluorophenyl)ethynyl)-1H-indole-2-carbonitrile (**3d**) ¹H NMR (700 MHz, CDCl₃)

3d 1H.esp

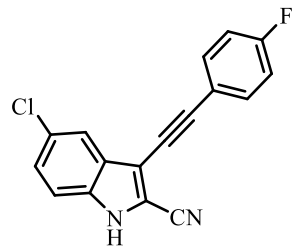


3-((4-fluorophenyl)ethynyl)-1H-indole-2-carbonitrile (**3d**) ^{13}C {1H} NMR (177 MHz, CDCl_3)

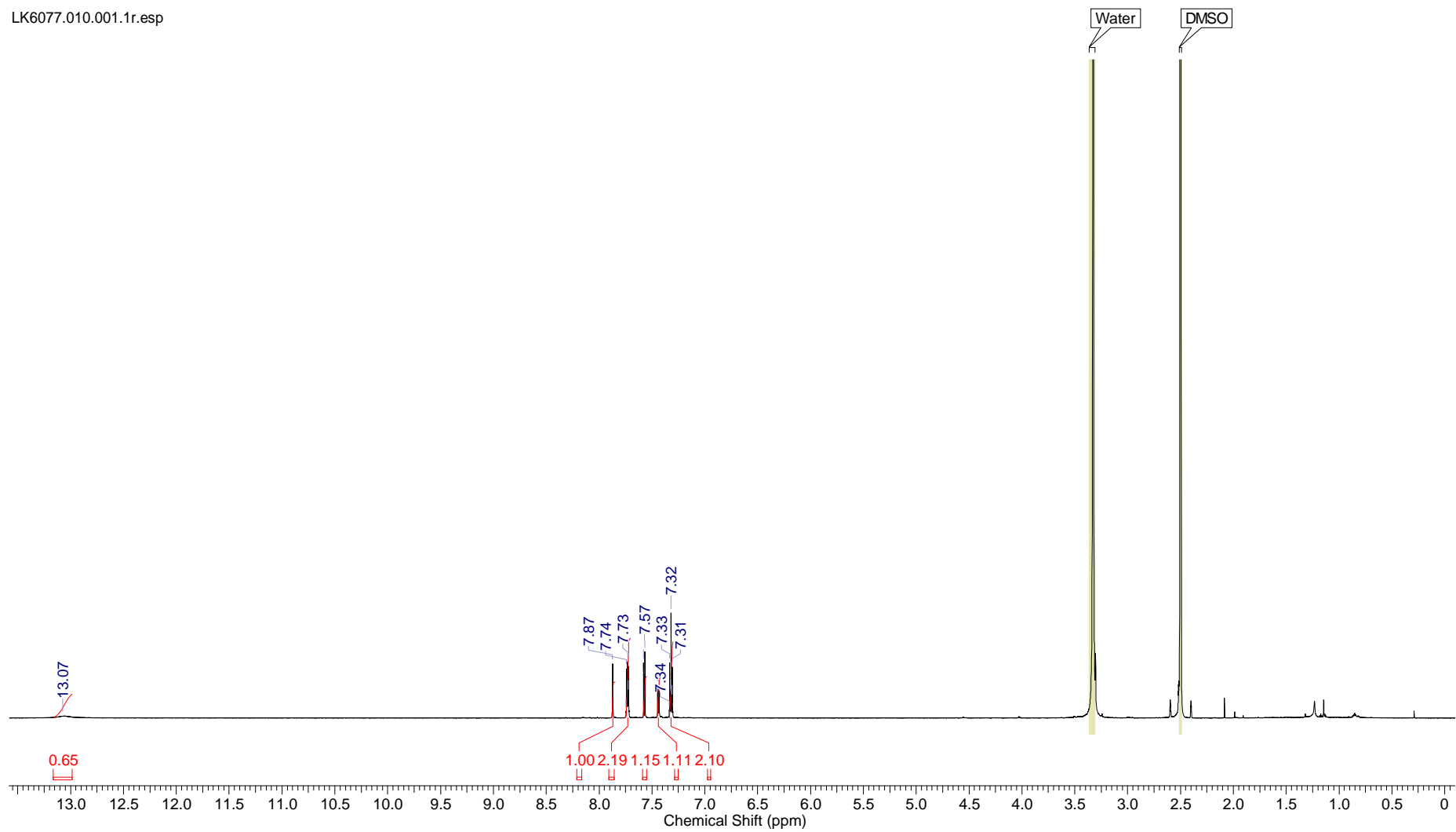
3d 13C.esp



5-chloro-3-((4-fluorophenyl)ethynyl)-1H-indole-2-carbonitrile (**3e**) ^1H NMR (700 MHz, DMSO-d_6)

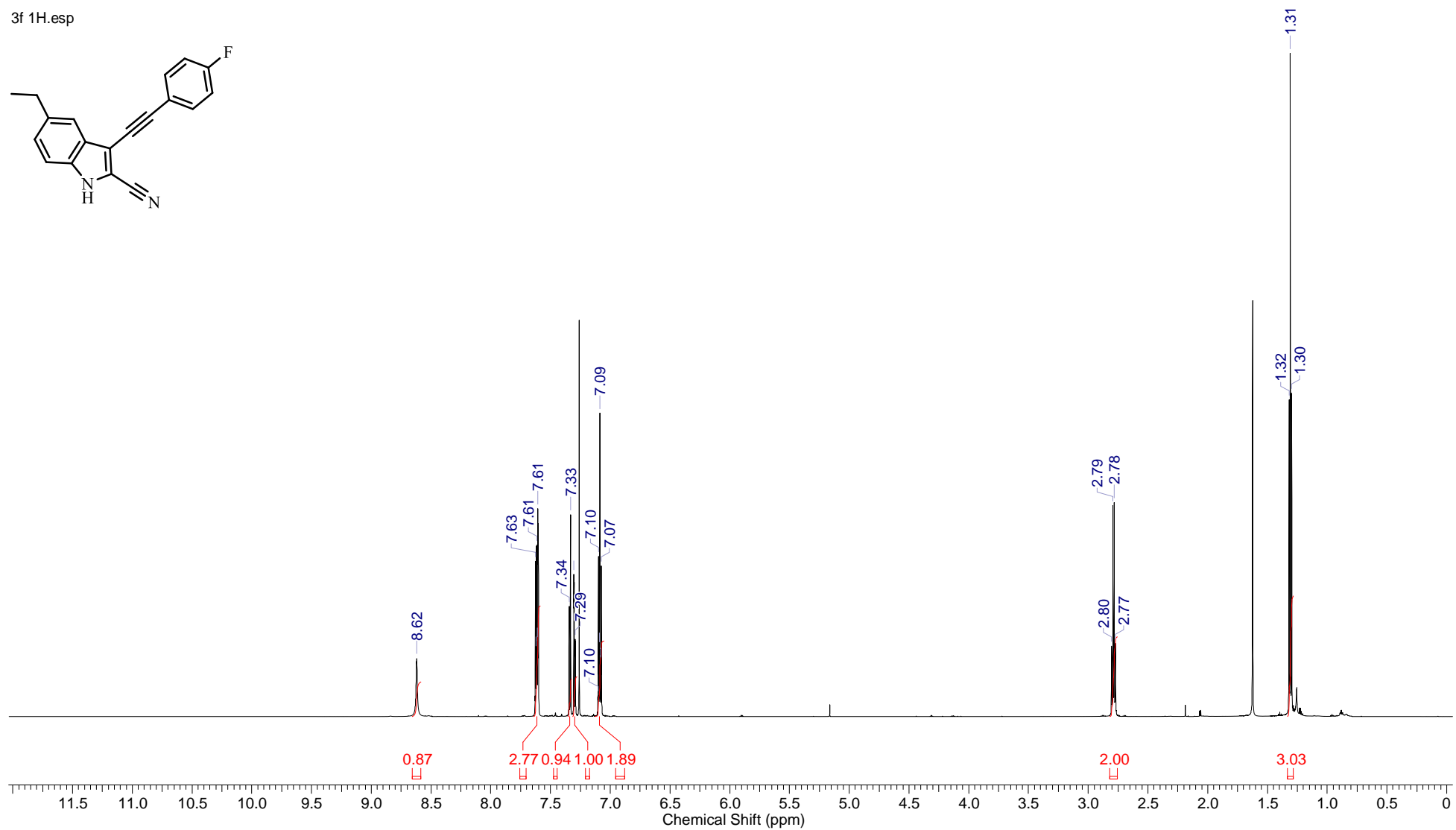
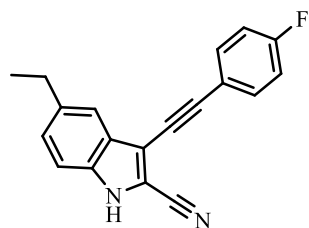


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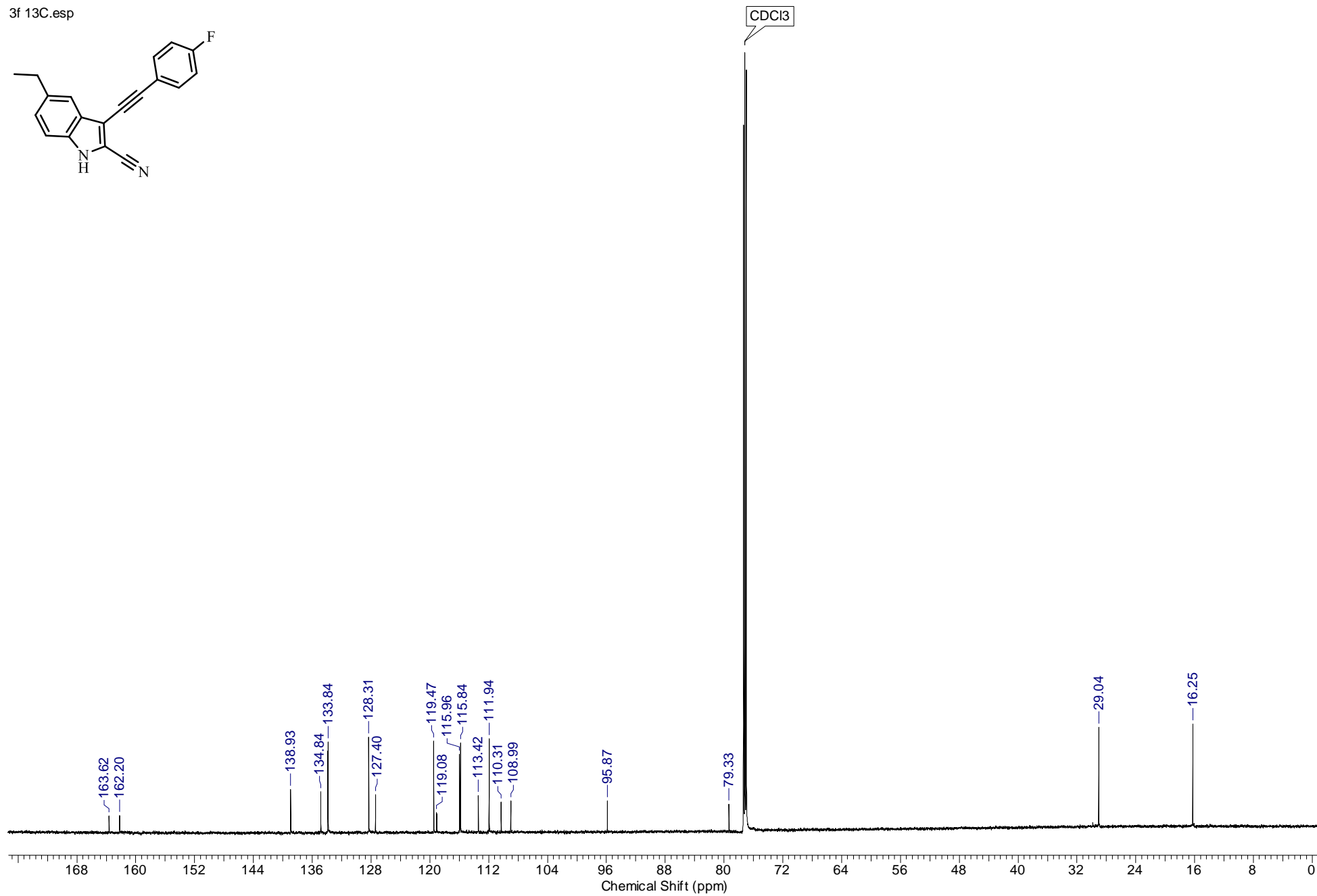
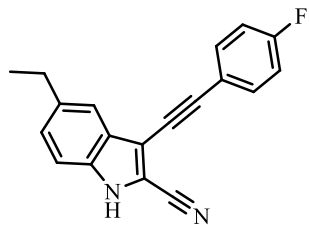
5-ethyl-3-((4-fluorophenyl)ethynyl)-1H-indole-2-carbonitrile (**3f**) ¹H NMR (700 MHz, CDCl₃)

3f 1H.esp

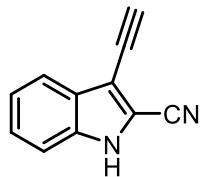


5-ethyl-3-((4-fluorophenyl)ethynyl)-1H-indole-2-carbonitrile (**3f**) ^{13}C {1H} NMR (177 MHz, CDCl_3)

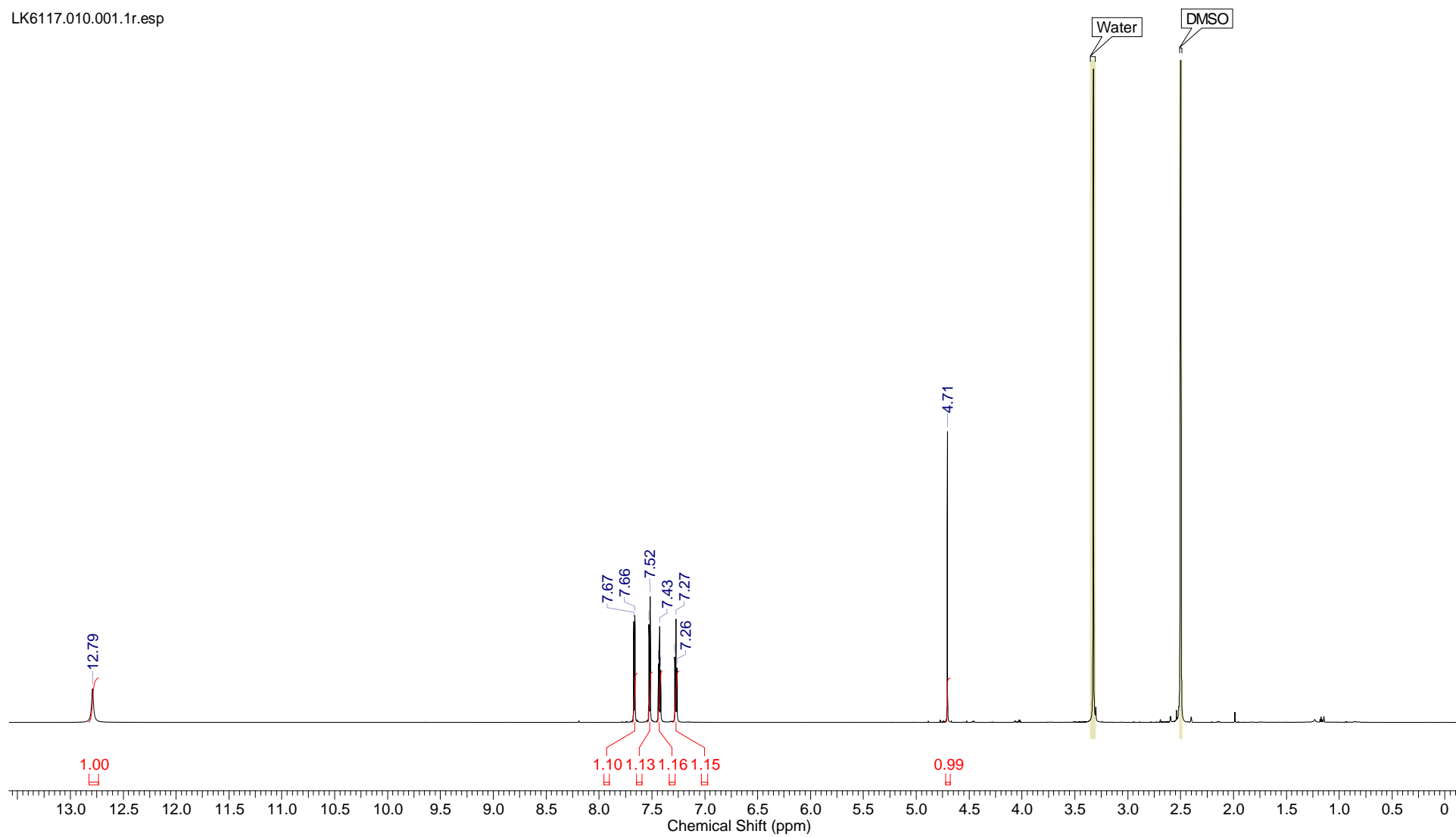
3f 13C.esp



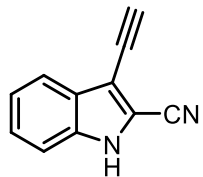
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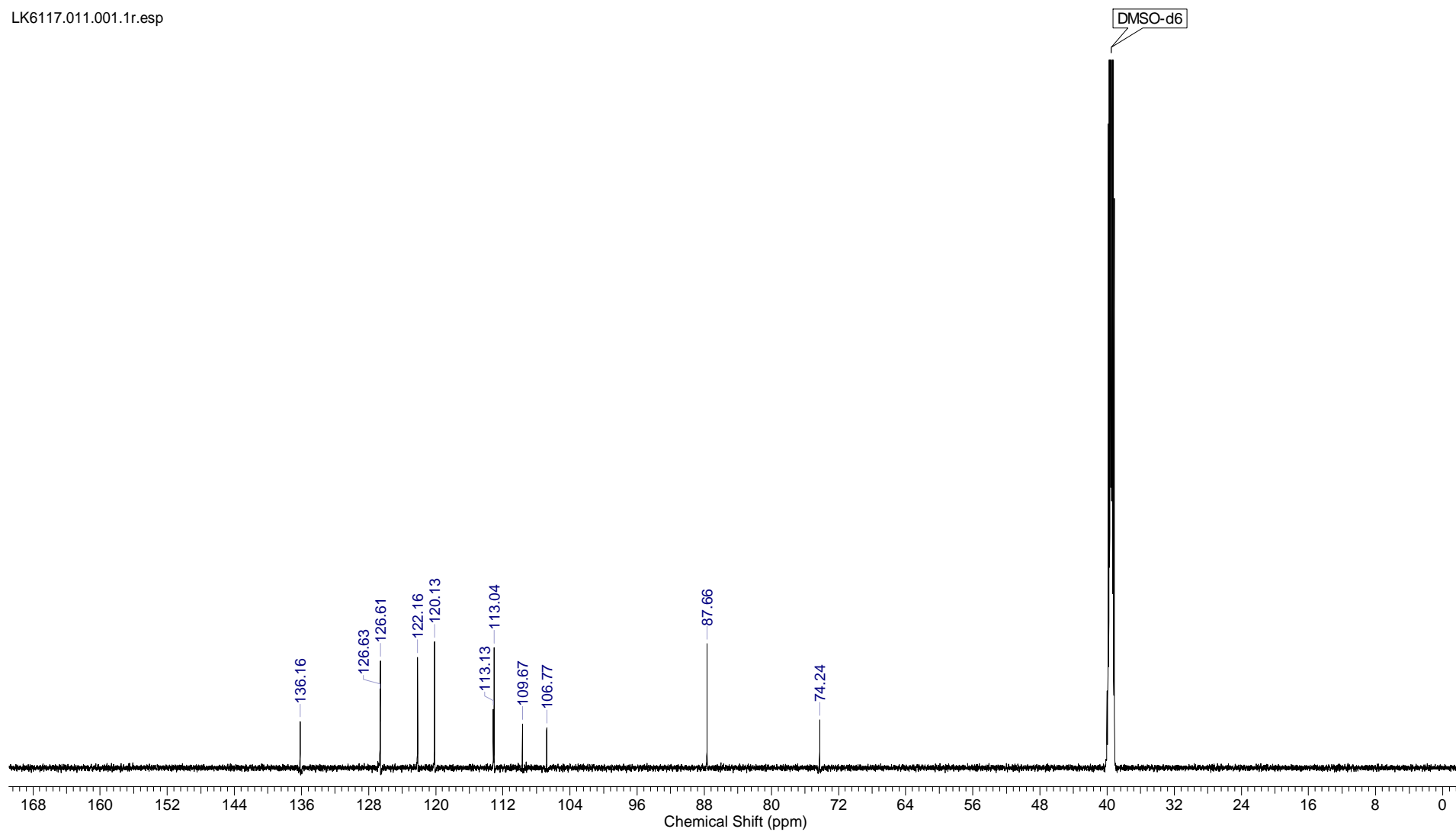
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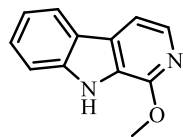
3-ethynyl-1H-indole-2-carbonitrile (**3g**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



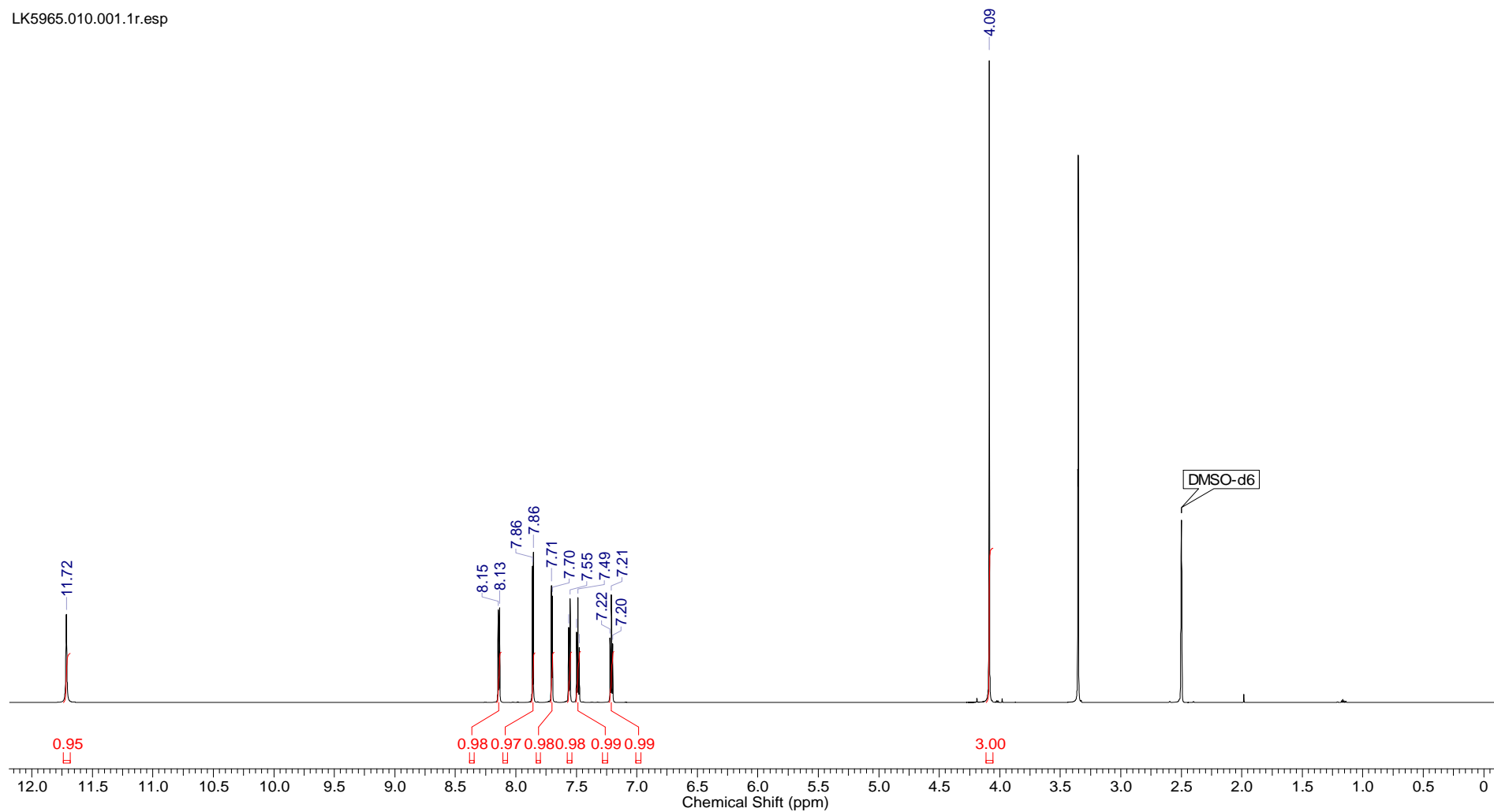
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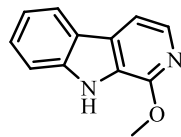
1-methoxy-9H-pyrido[3,4-b]indole (**4a**) ¹H NMR (700 MHz, DMSO-d₆)



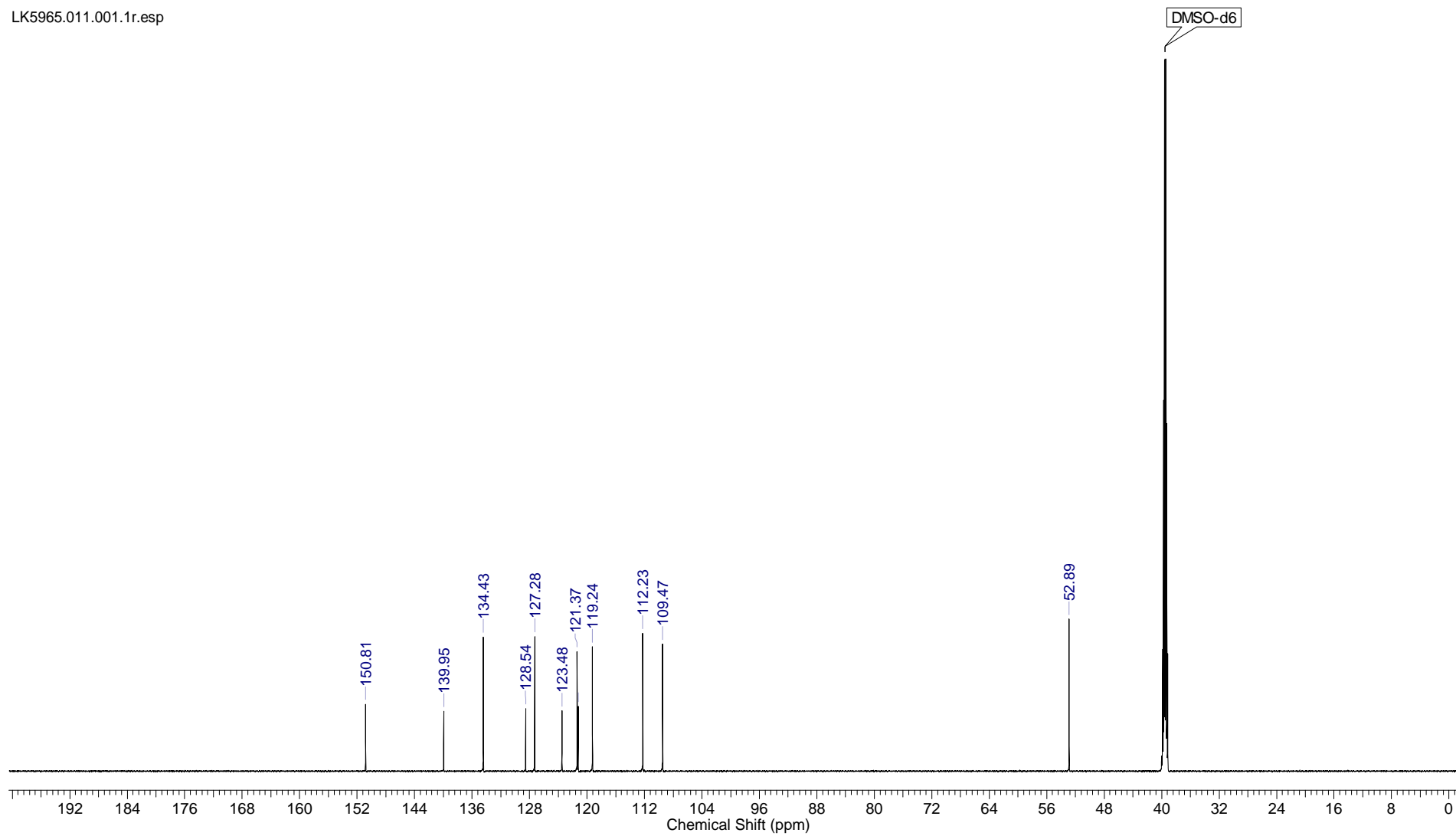
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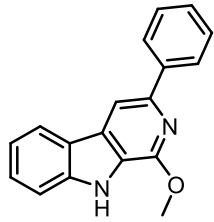
1-methoxy-9H-pyrido[3,4-b]indole (**4a**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



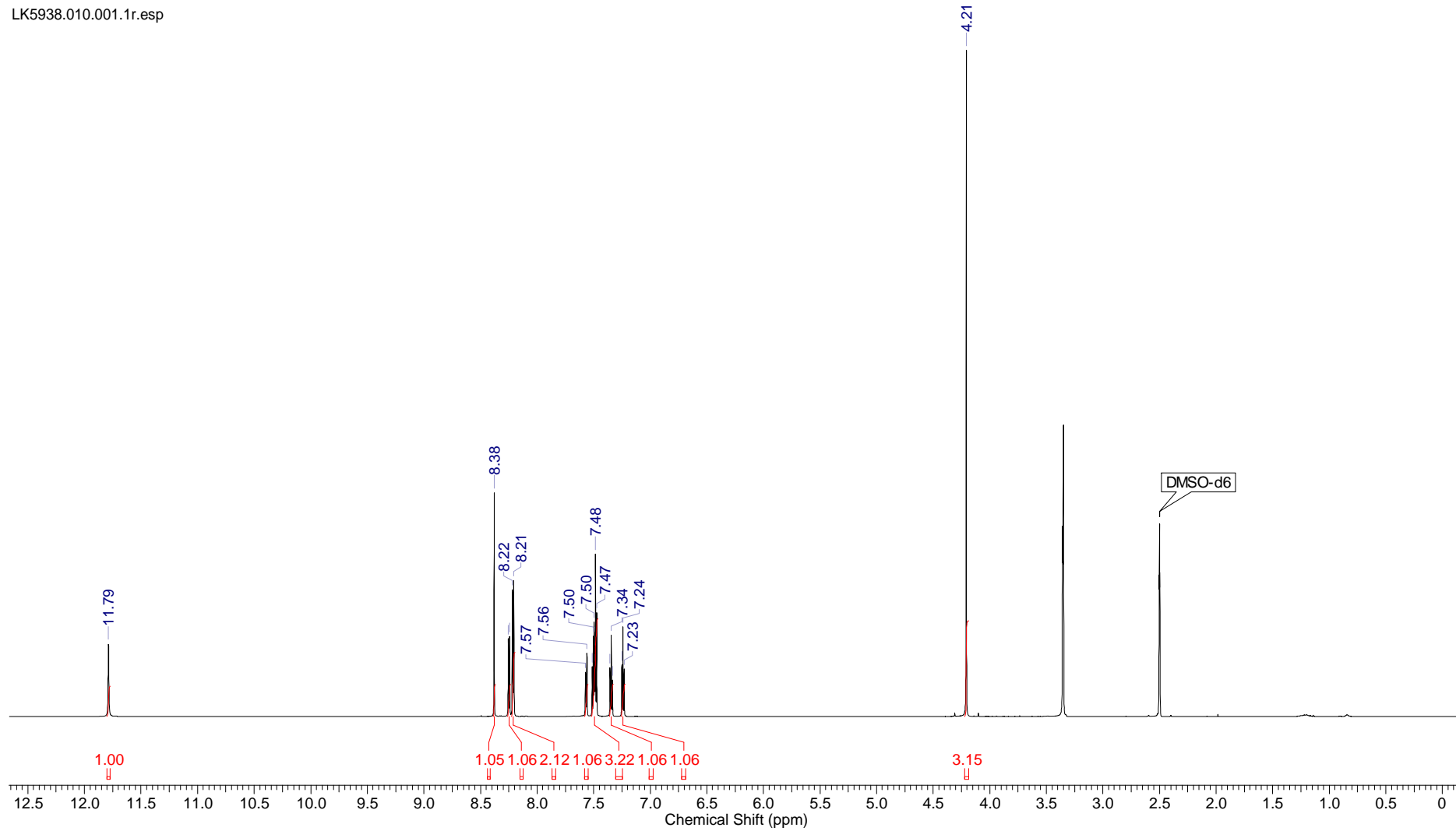
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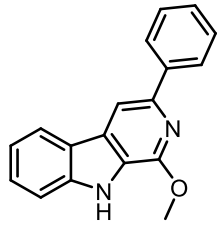
1-methoxy-3-phenyl-9H-pyrido[3,4-b]indole (**4b**) ¹H NMR (700 MHz, DMSO-d₆)



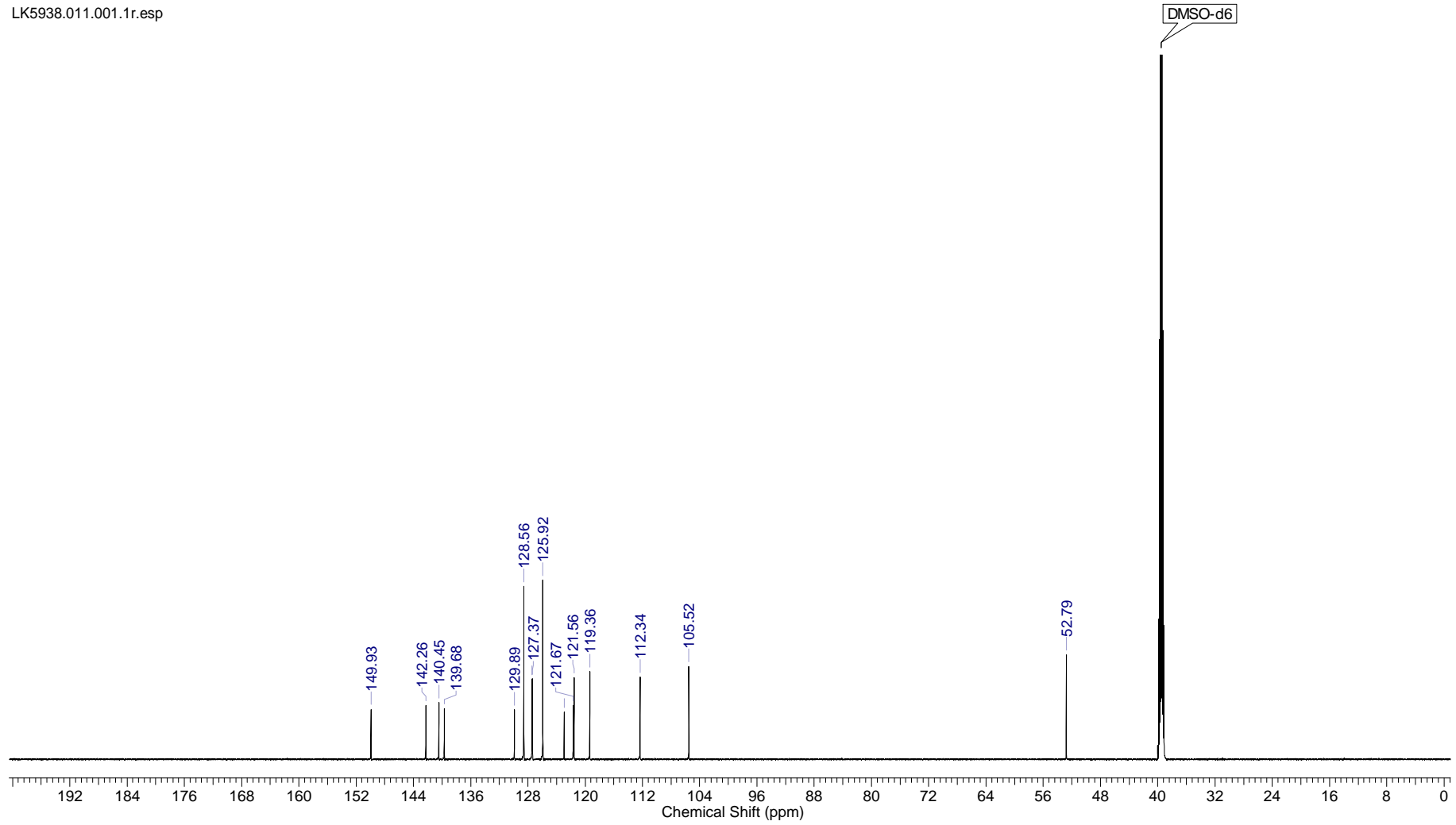
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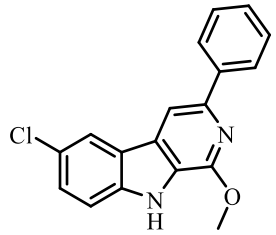
1-methoxy-3-phenyl-9H-pyrido[3,4-b]indole (**4b**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



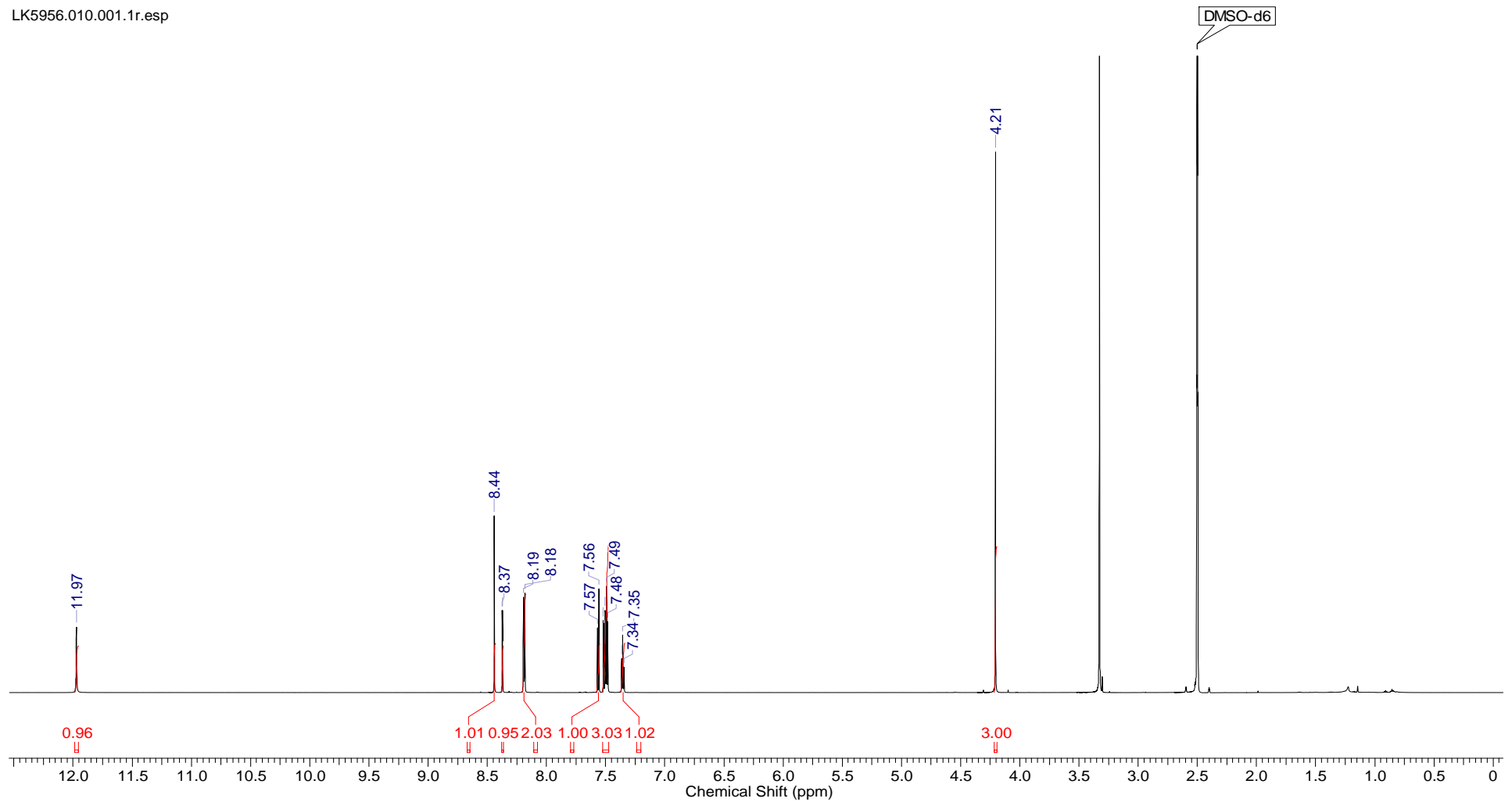
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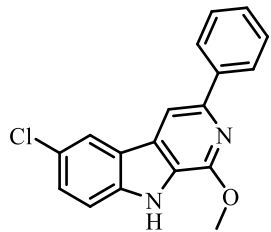
6-chloro-1-methoxy-3-phenyl-9H-pyrido[3,4-b]indole (**4c**) ^1H NMR (700 MHz, DMSO-d_6)



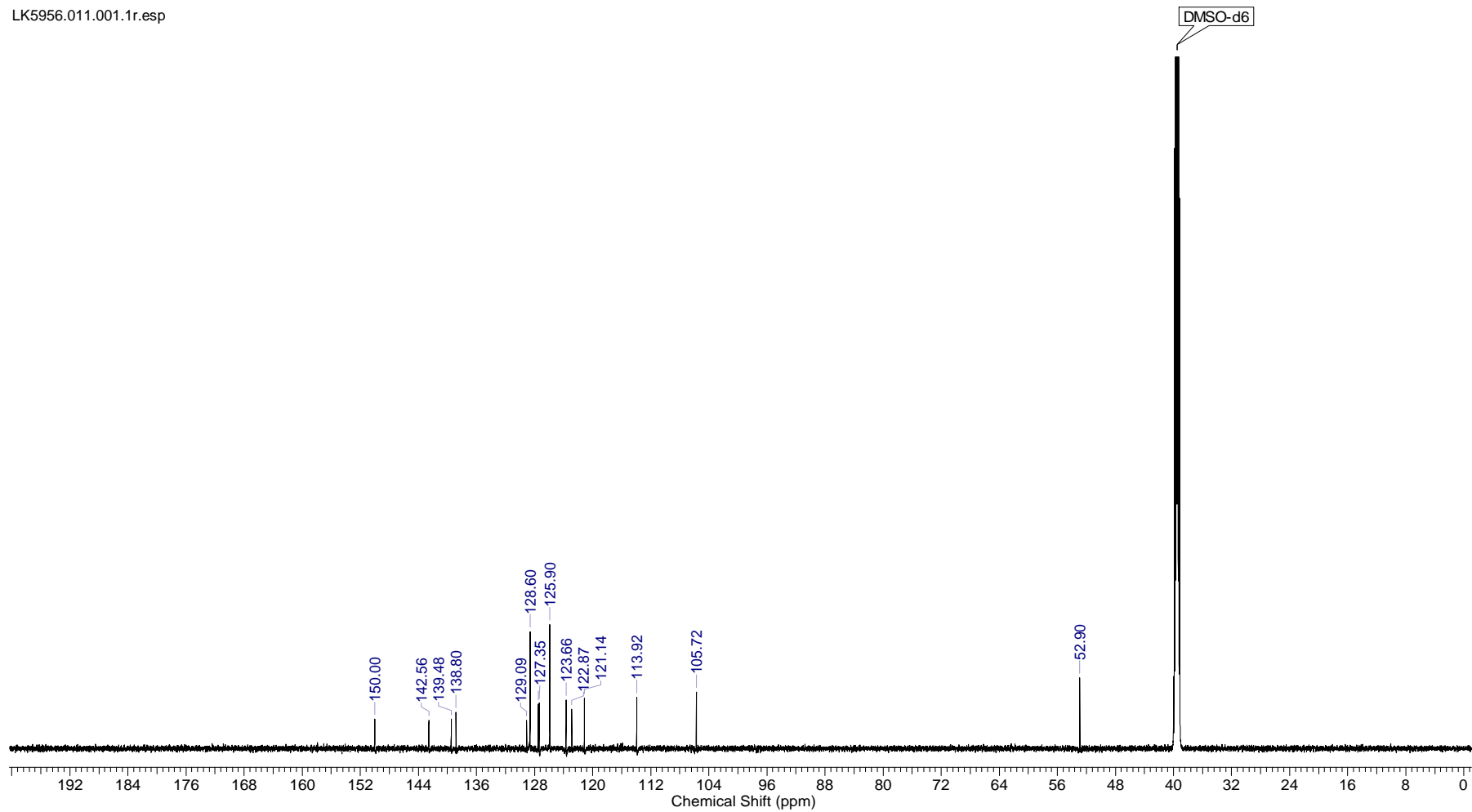
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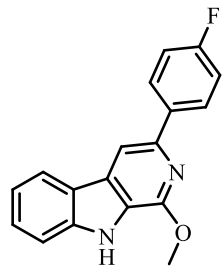
6-chloro-1-methoxy-3-phenyl-9H-pyrido[3,4-b]indole (**4c**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



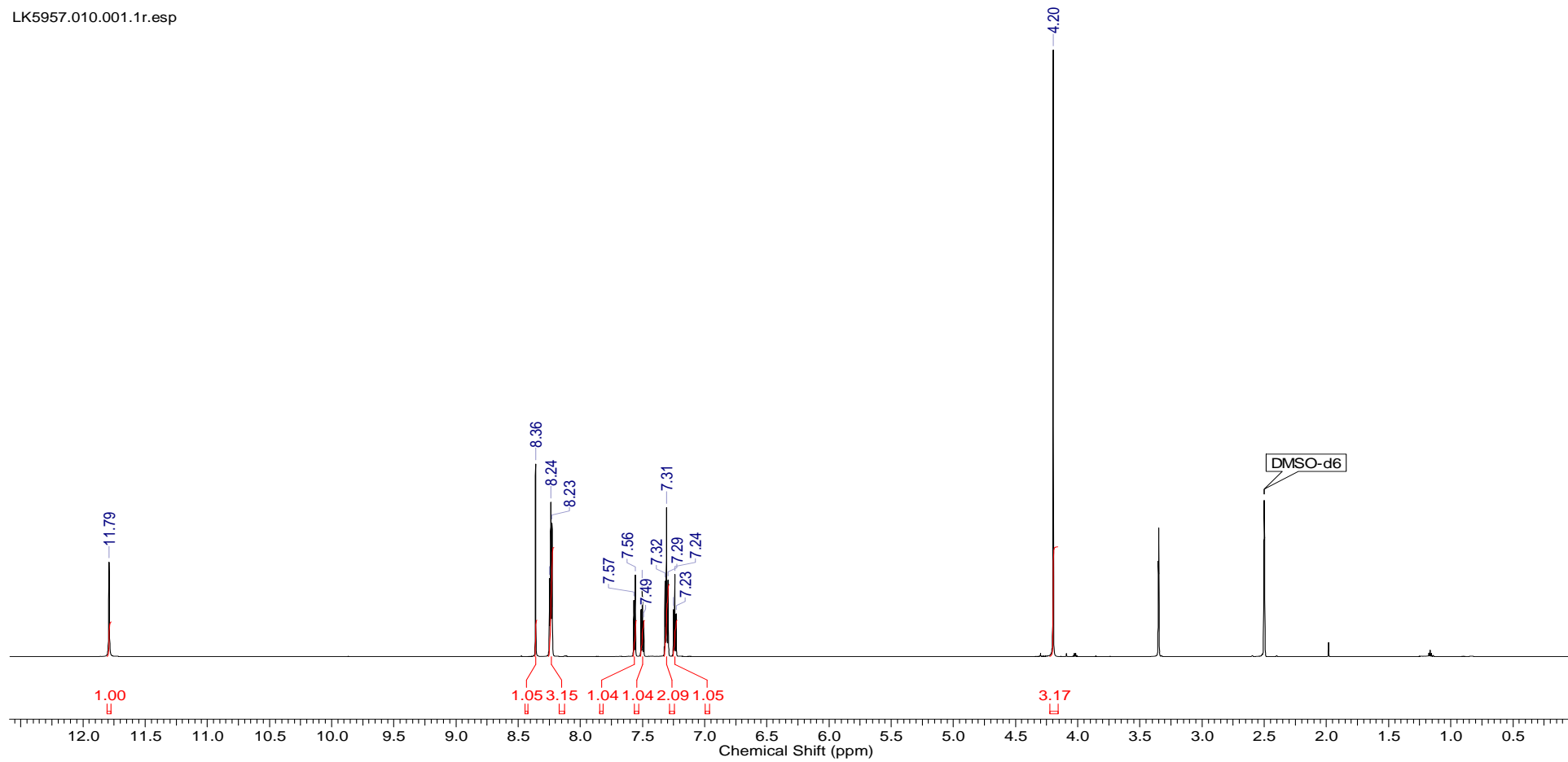
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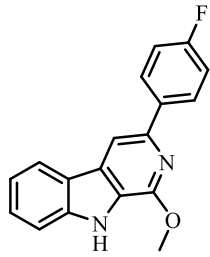
3-(4-fluorophenyl)-1-methoxy-9H-pyrido[3,4-b]indole (**4d**) ^1H NMR (700 MHz, DMSO-d_6)



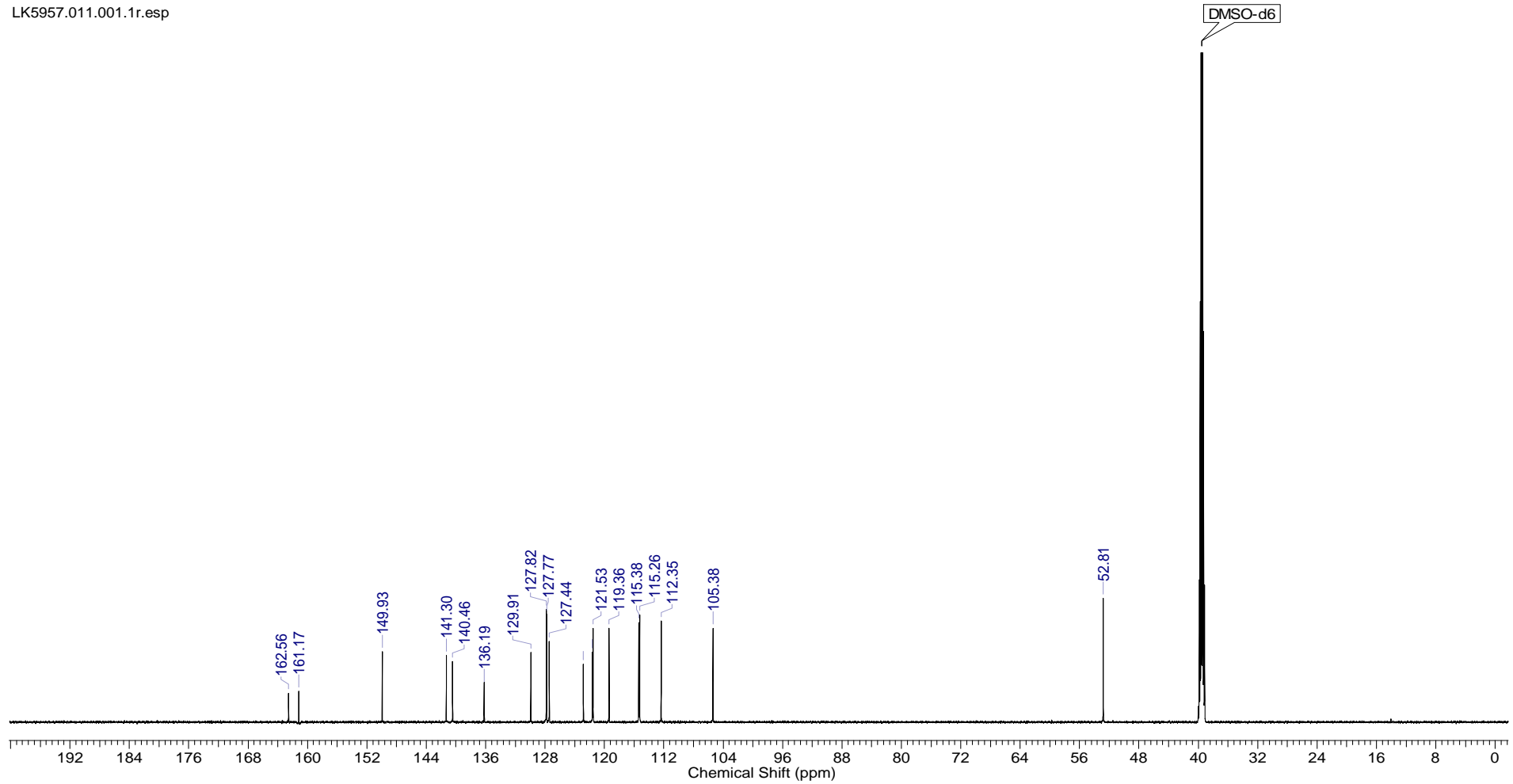
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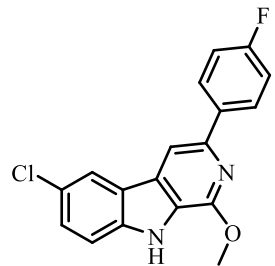
3-(4-fluorophenyl)-1-methoxy-9H-pyrido[3,4-b]indole (**4d**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



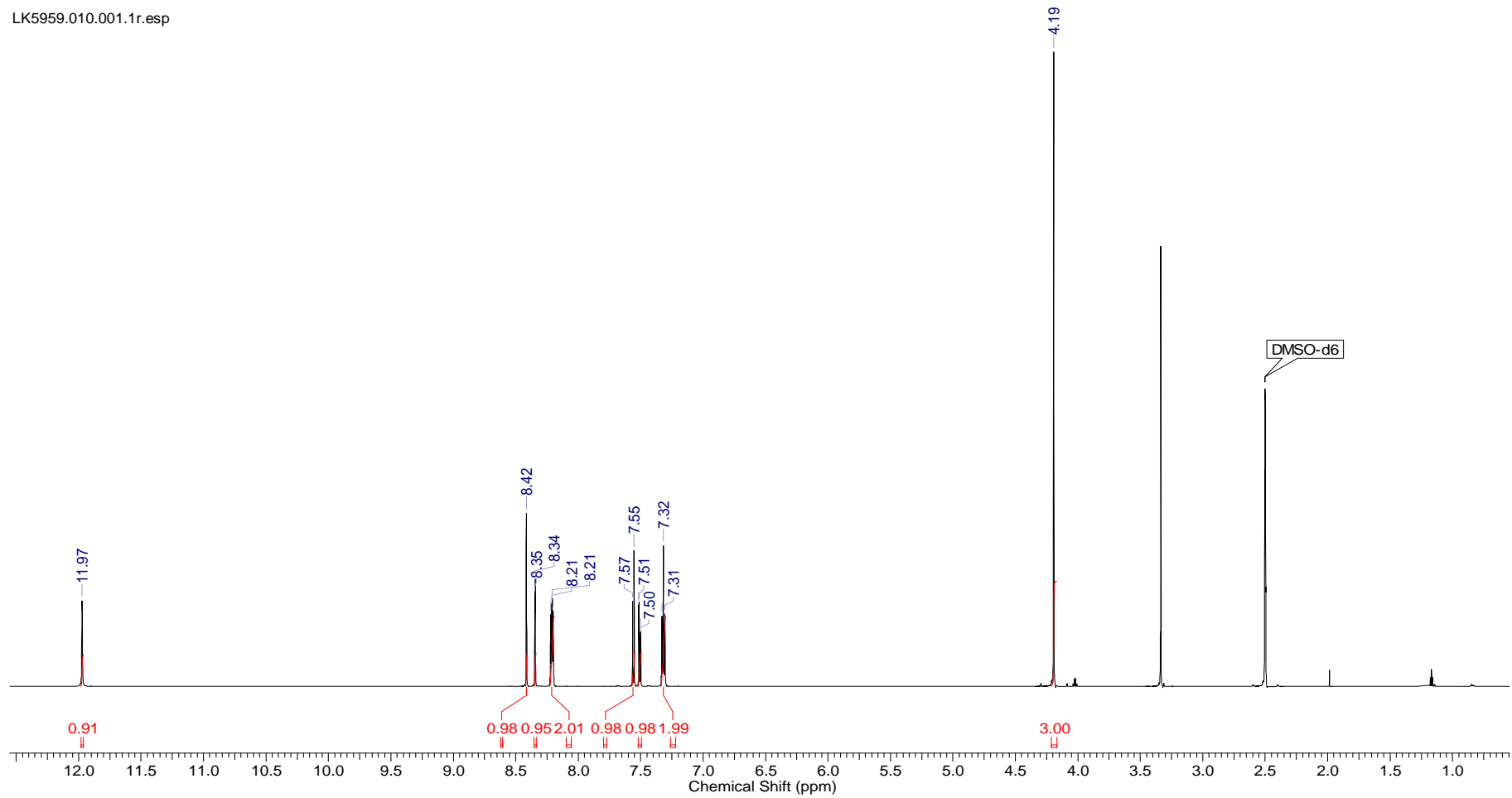
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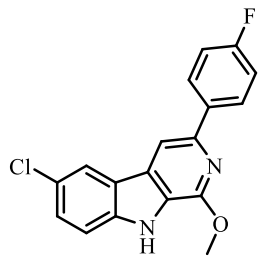
6-chloro-3-(4-fluorophenyl)-1-methoxy-9H-pyrido[3,4-b]indole (**4e**) ¹H NMR (700 MHz, DMSO-d₆)



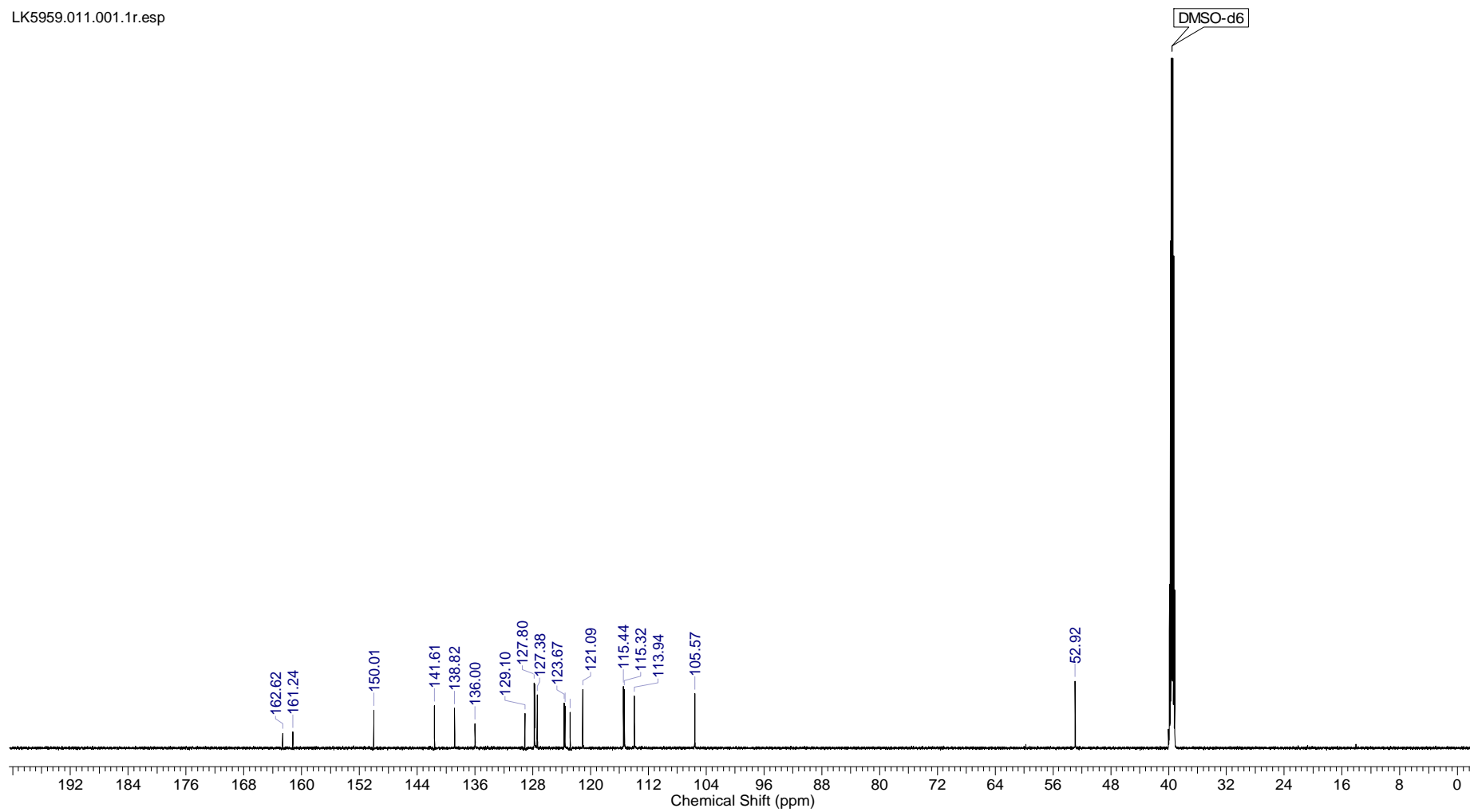
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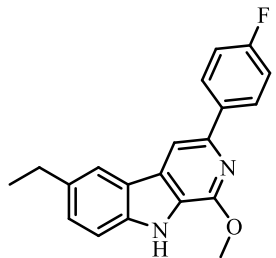
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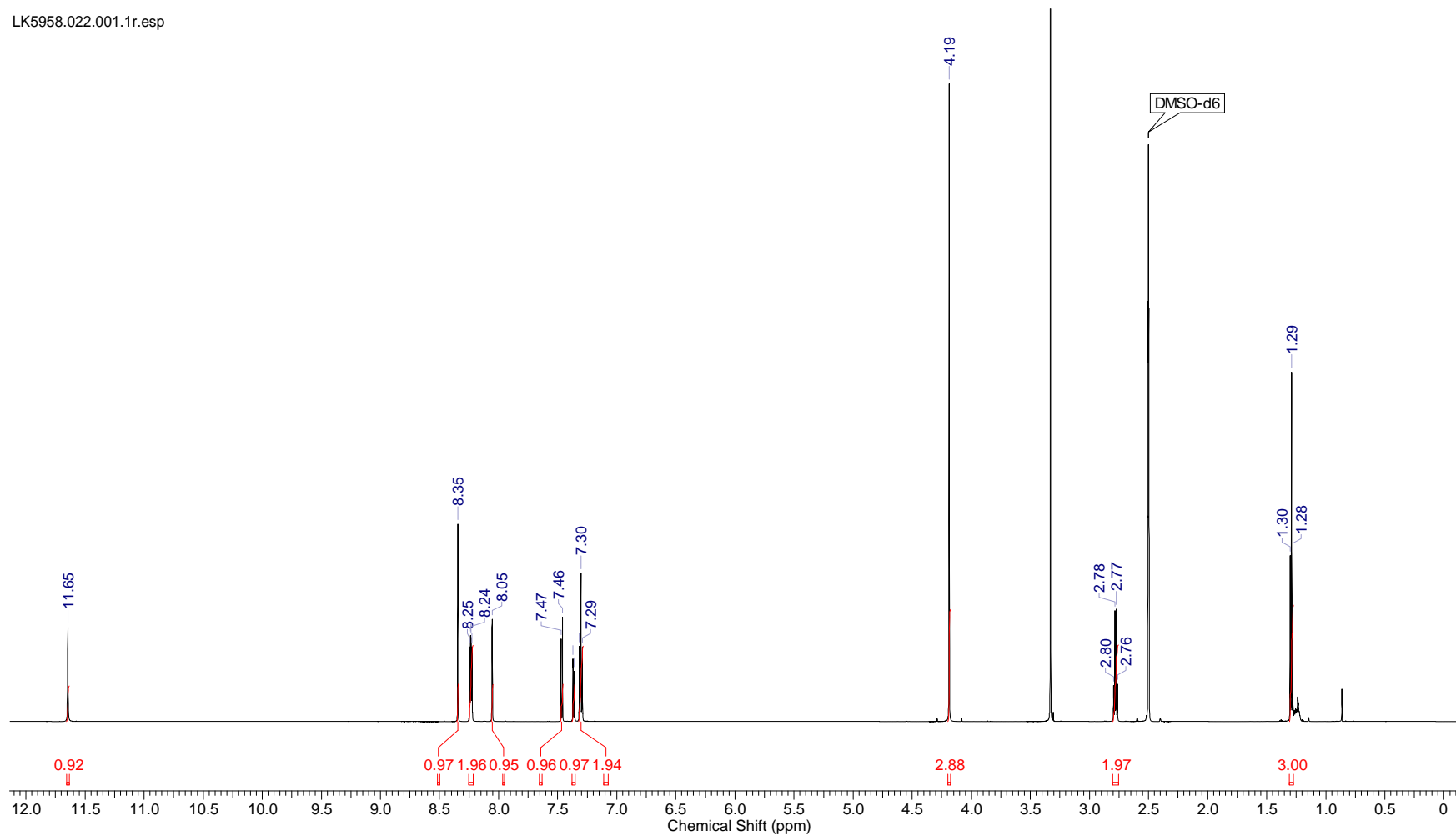
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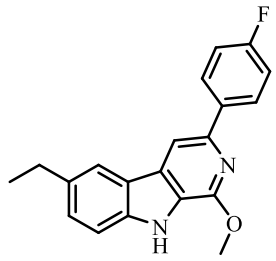
6-ethyl-3-(4-fluorophenyl)-1-methoxy-9H-pyrido[3,4-b]indole (**4f**) ¹H NMR (700 MHz, DMSO-d₆)



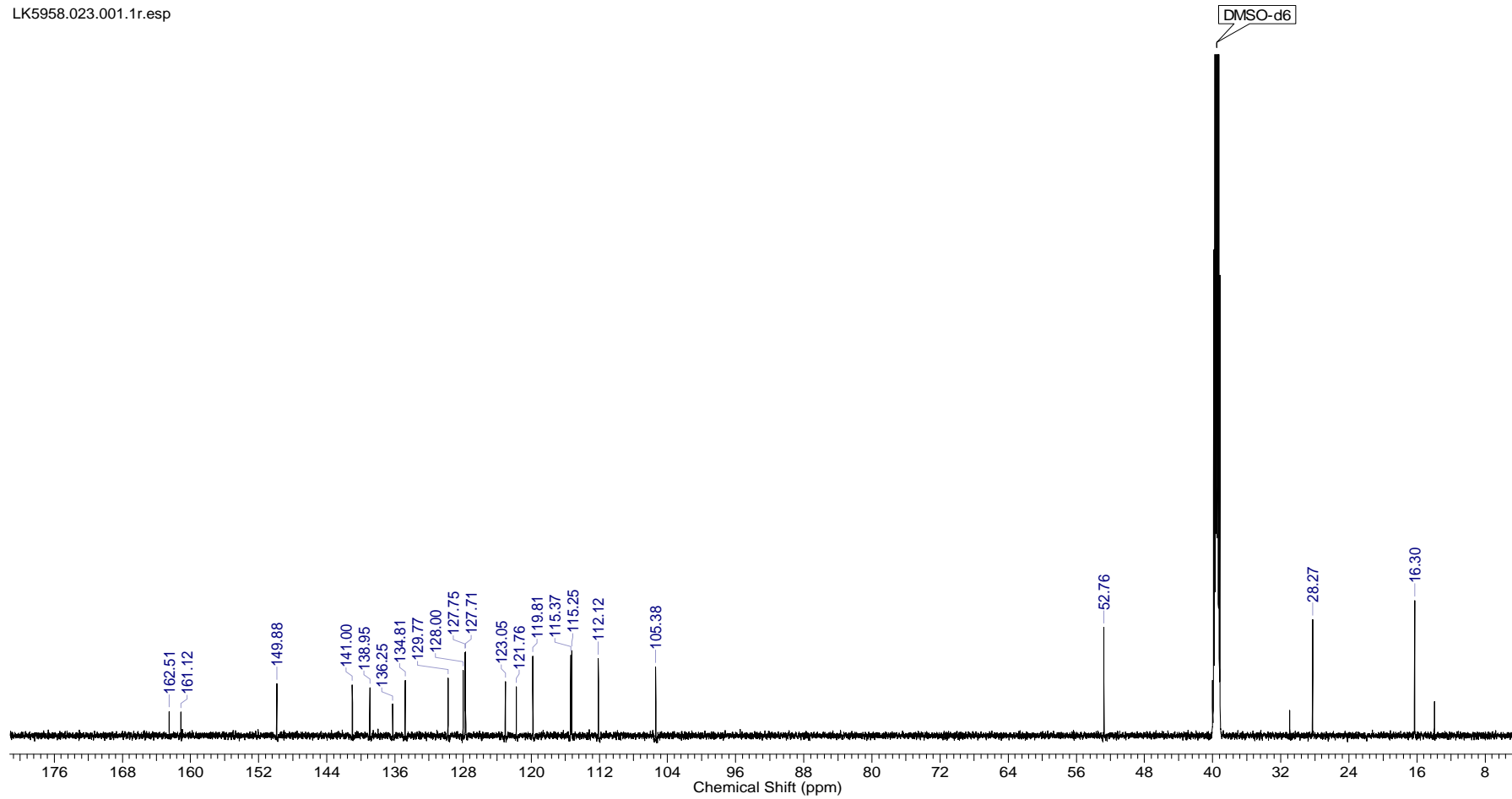
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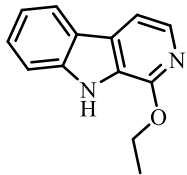
6-ethyl-3-(4-fluorophenyl)-1-methoxy-9H-pyrido[3,4-b]indole (**4f**) ^{13}C { ^1H } NMR (177 MHz, $\text{DMSO-}d_6$)



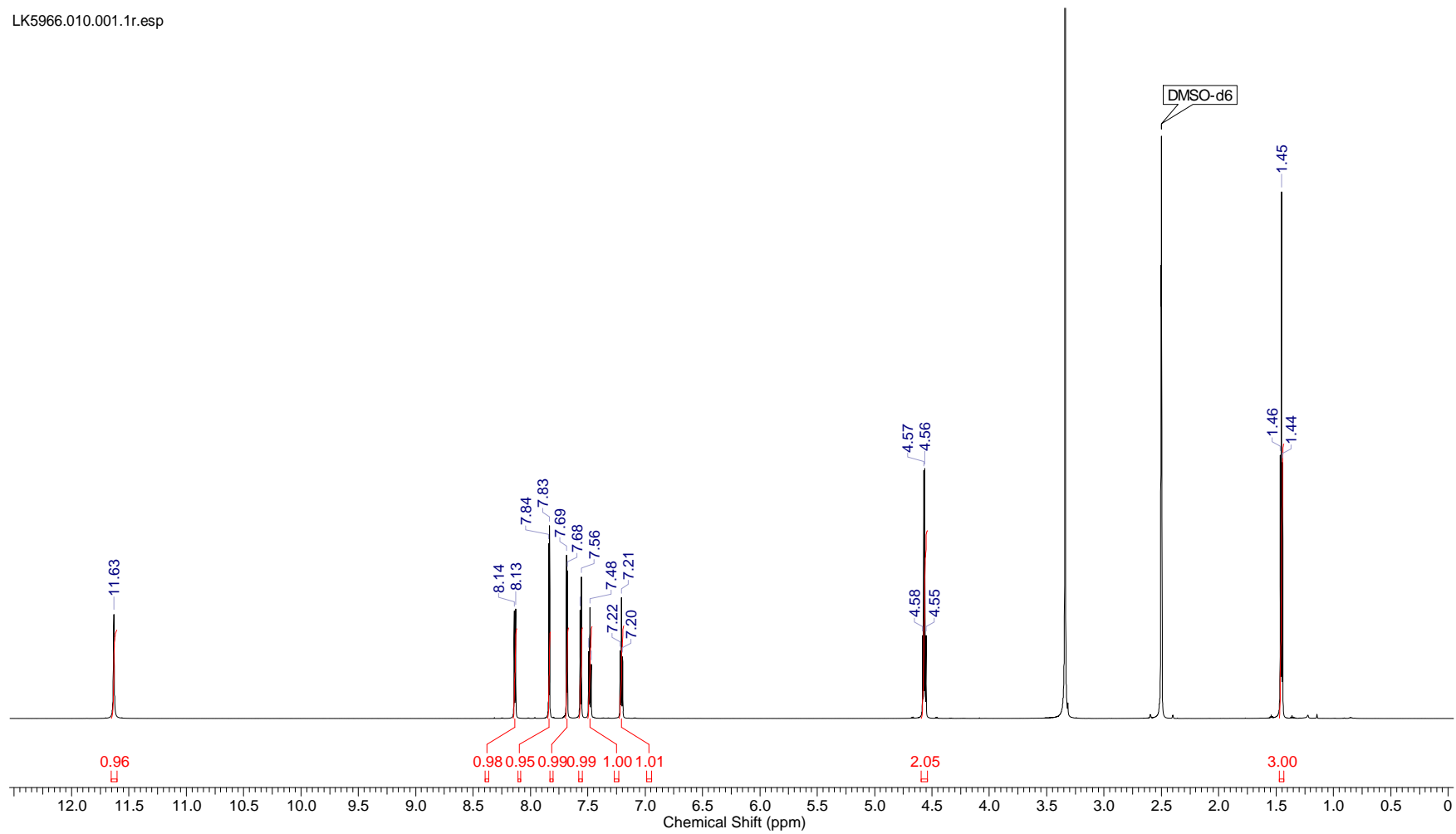
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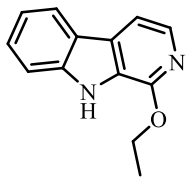
1-ethoxy-9H-pyrido[3,4-b]indole (**4g**) ^1H NMR (700 MHz, DMSO-d_6)



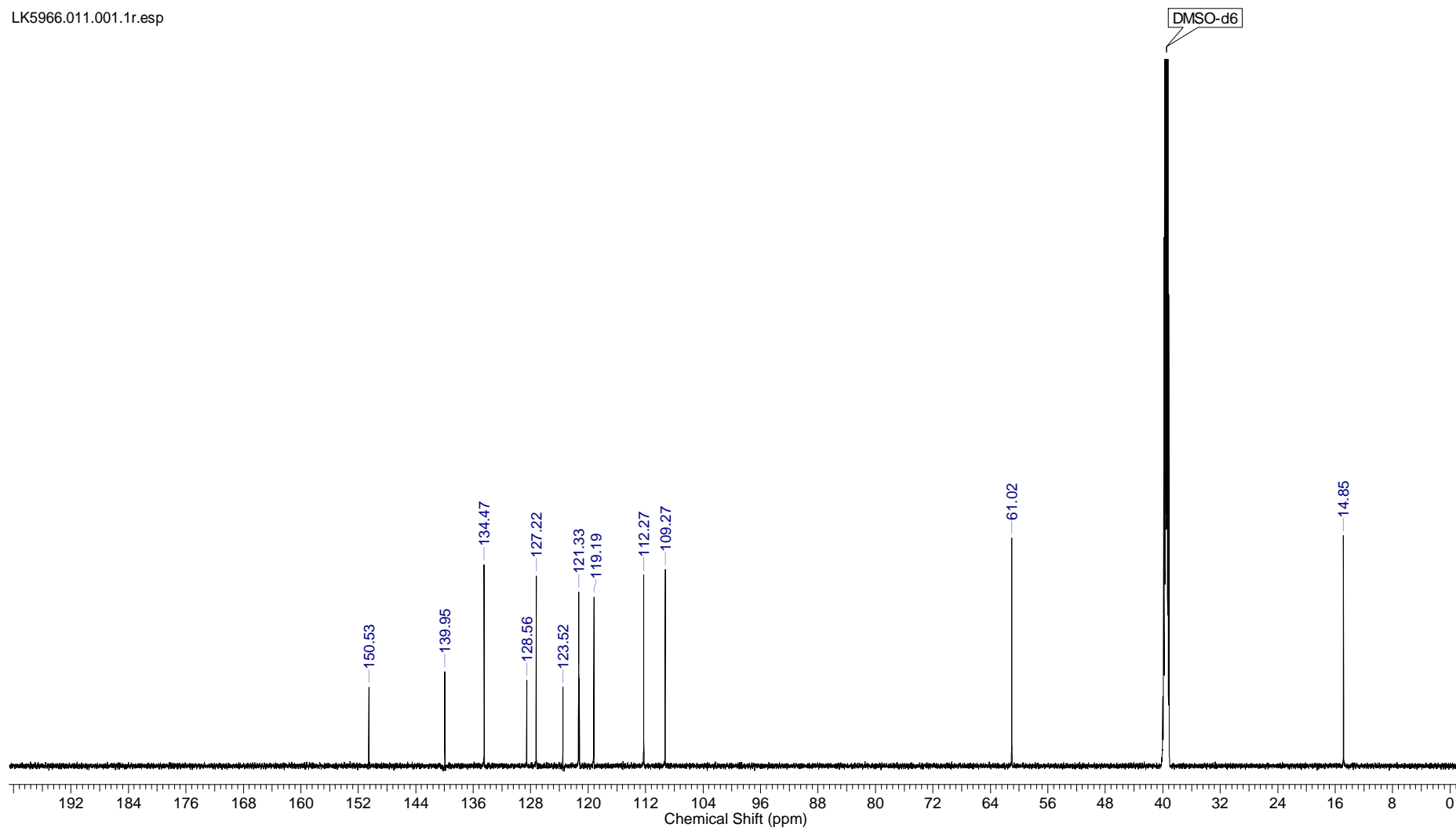
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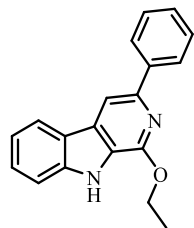
1-ethoxy-9H-pyrido[3,4-b]indole (**4g**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



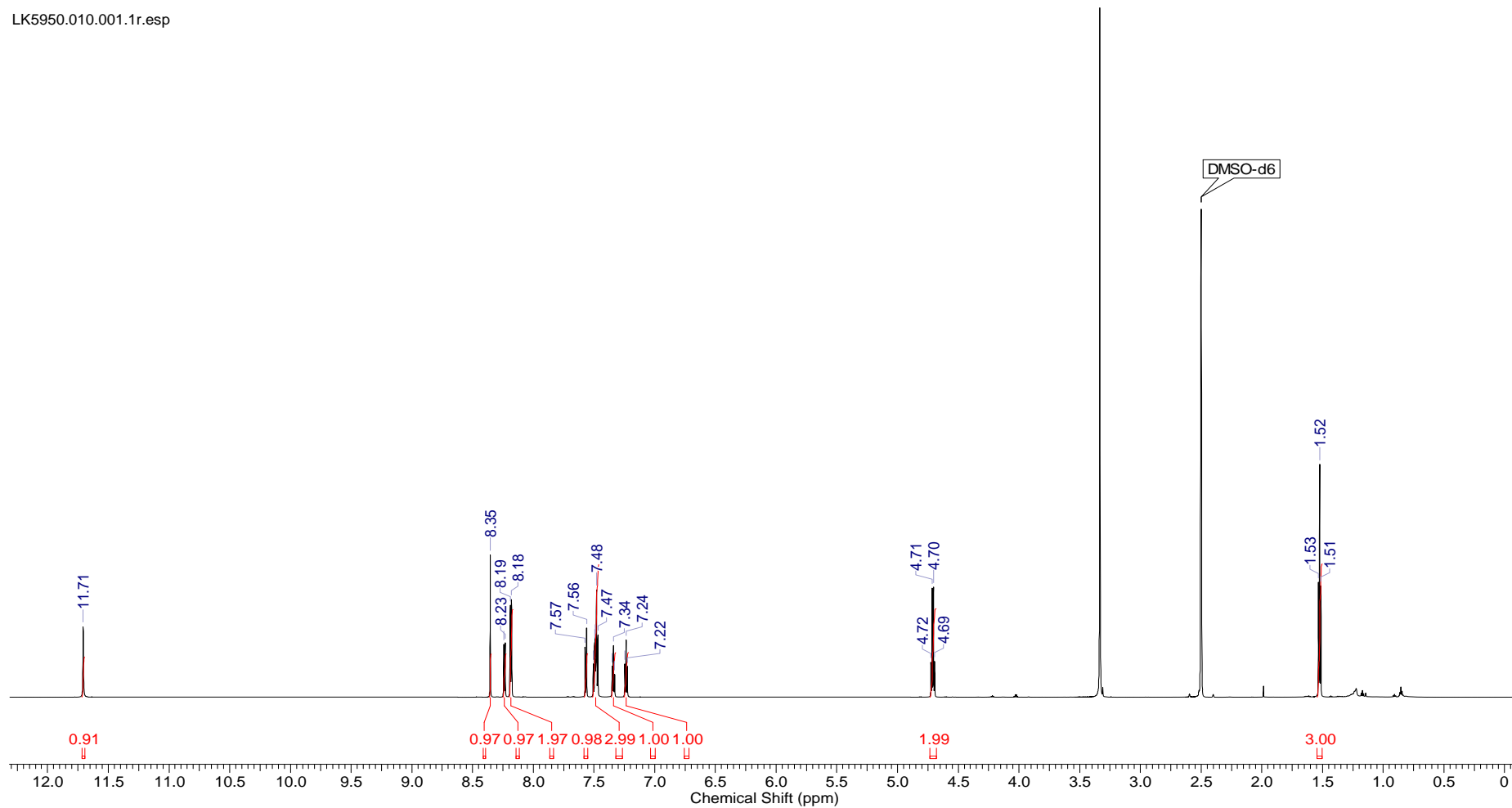
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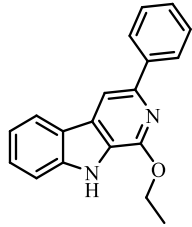
1-ethoxy-3-phenyl-9H-pyrido[3,4-b]indole (**4h**) ¹H NMR (700 MHz, DMSO-d₆)



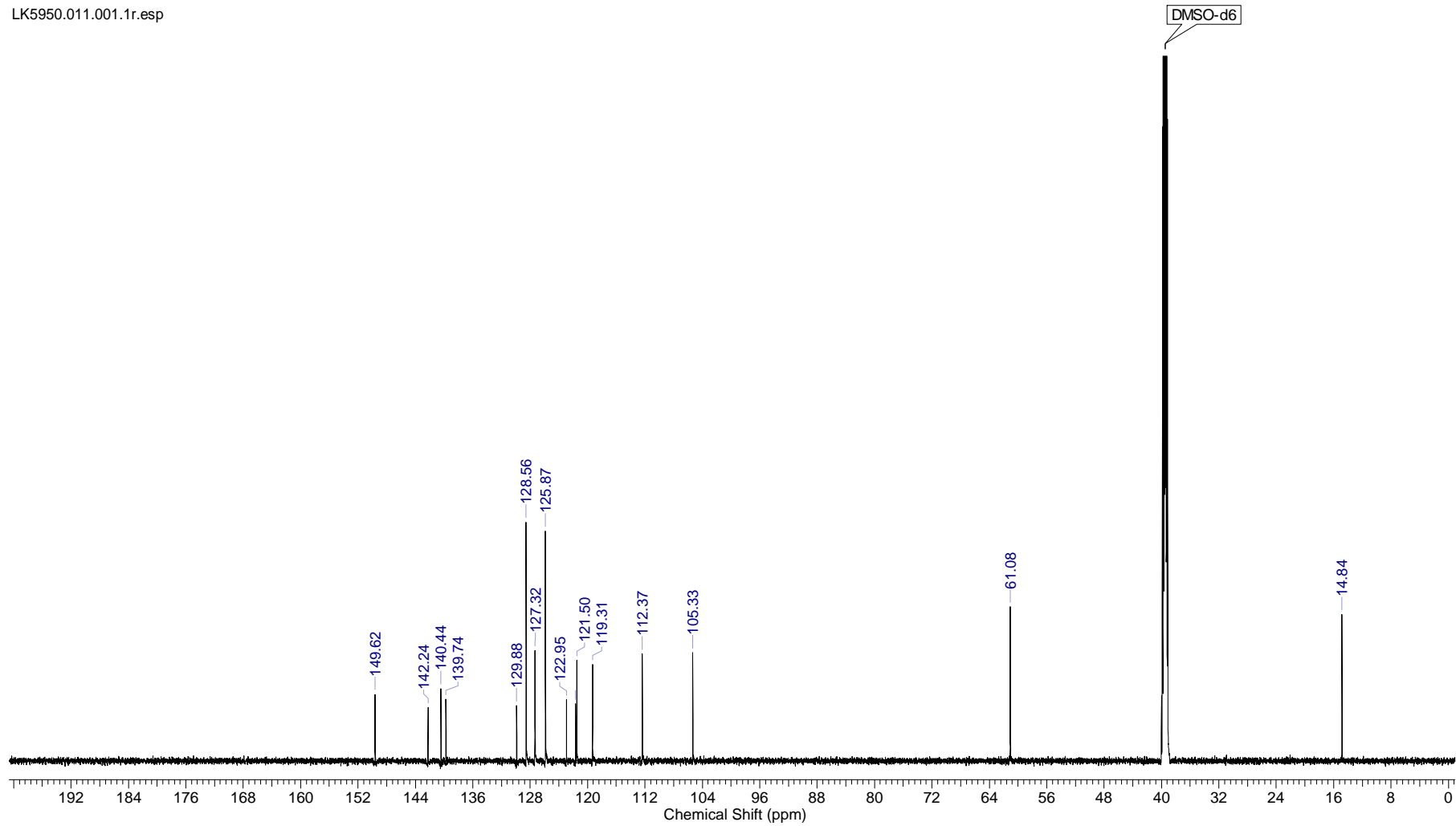
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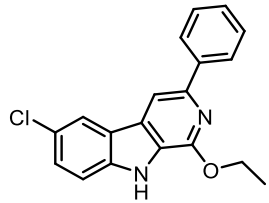
1-ethoxy-3-phenyl-9H-pyrido[3,4-b]indole (**4h**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



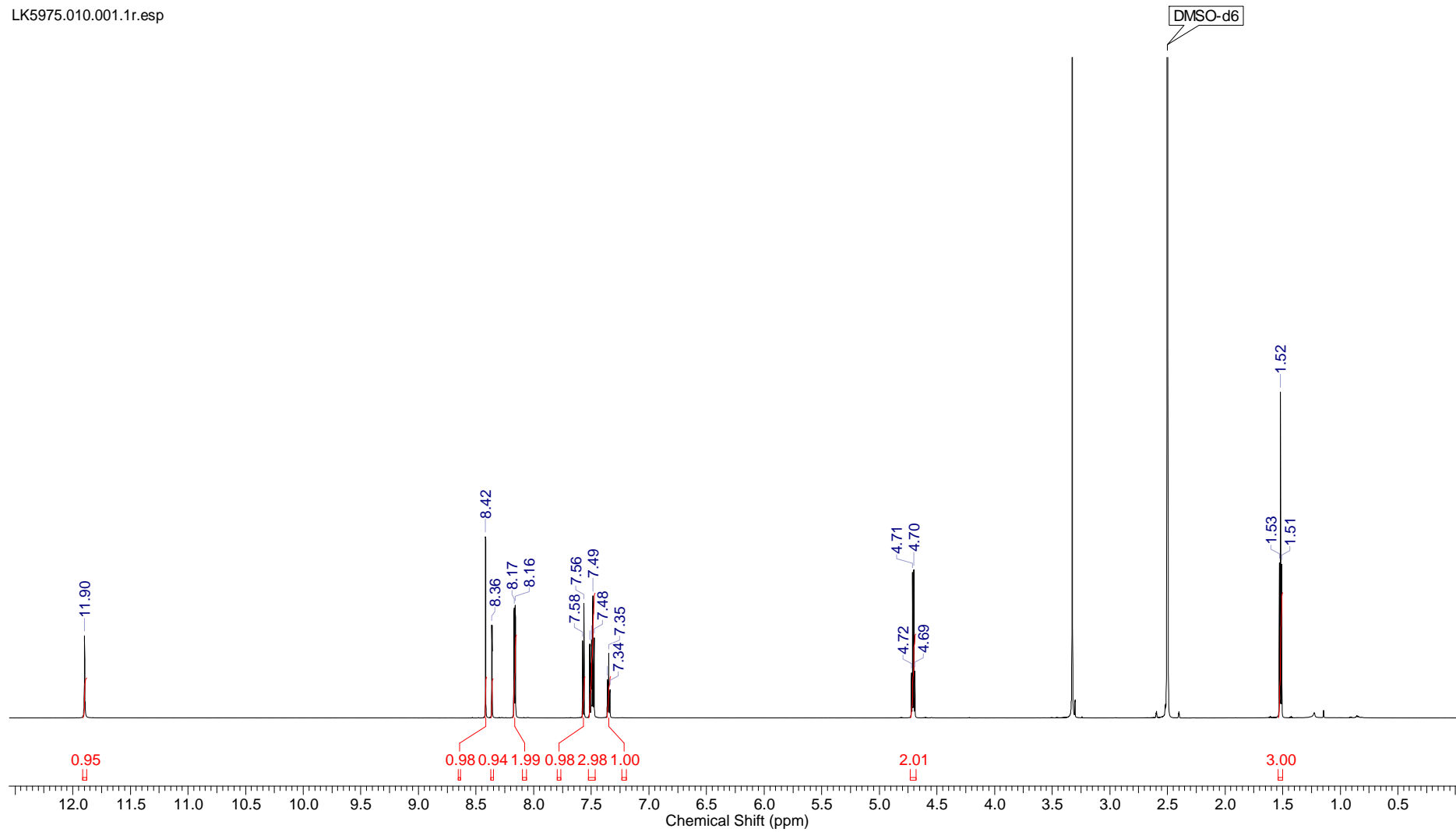
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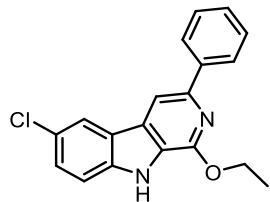
6-chloro-1-ethoxy-3-phenyl-9H-pyrido[3,4-b]indole (**4i**) ¹H NMR (700 MHz, DMSO-d₆)



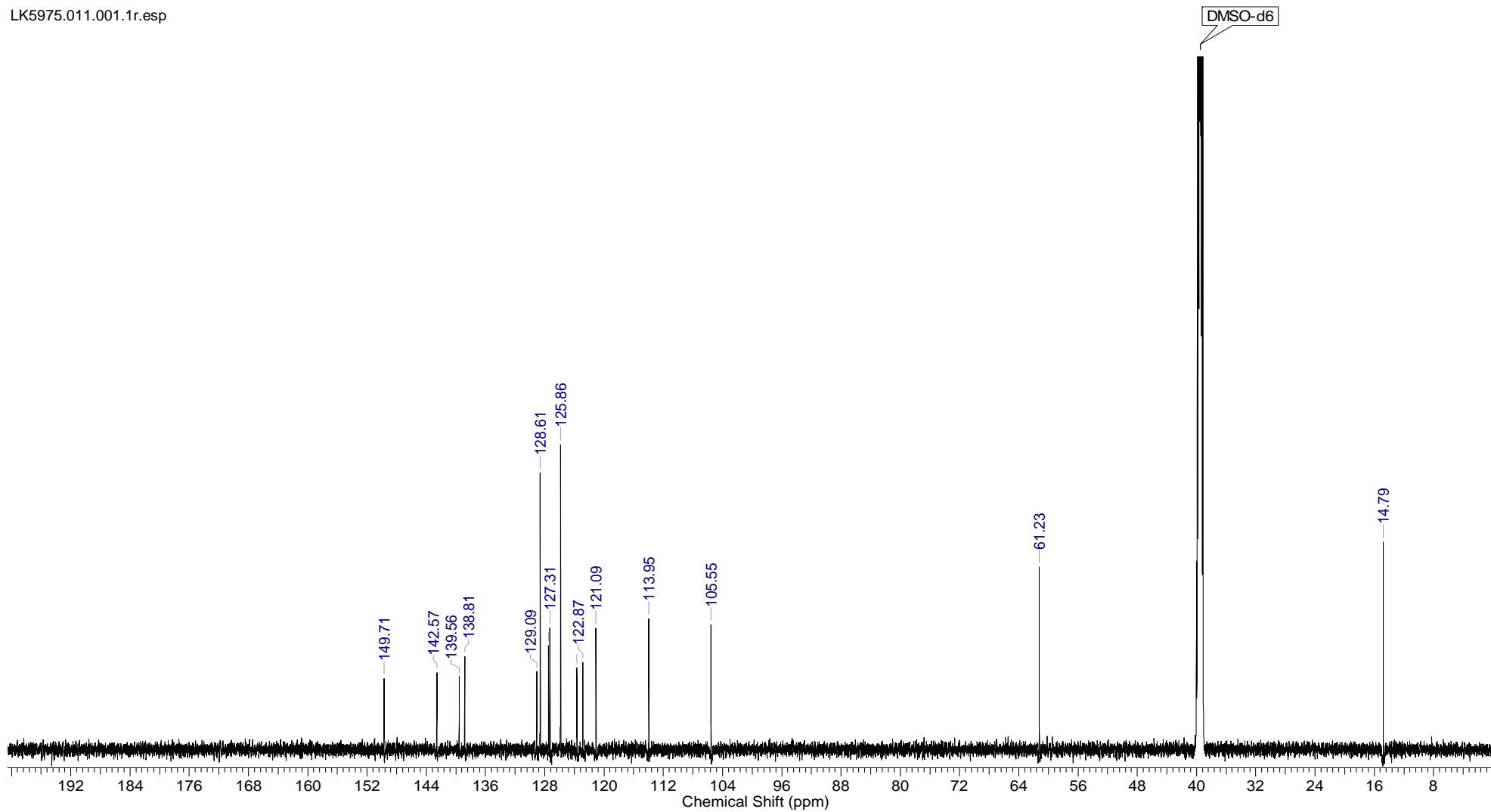
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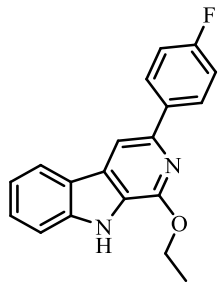
6-chloro-1-ethoxy-3-phenyl-9H-pyrido[3,4-b]indole (**4i**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



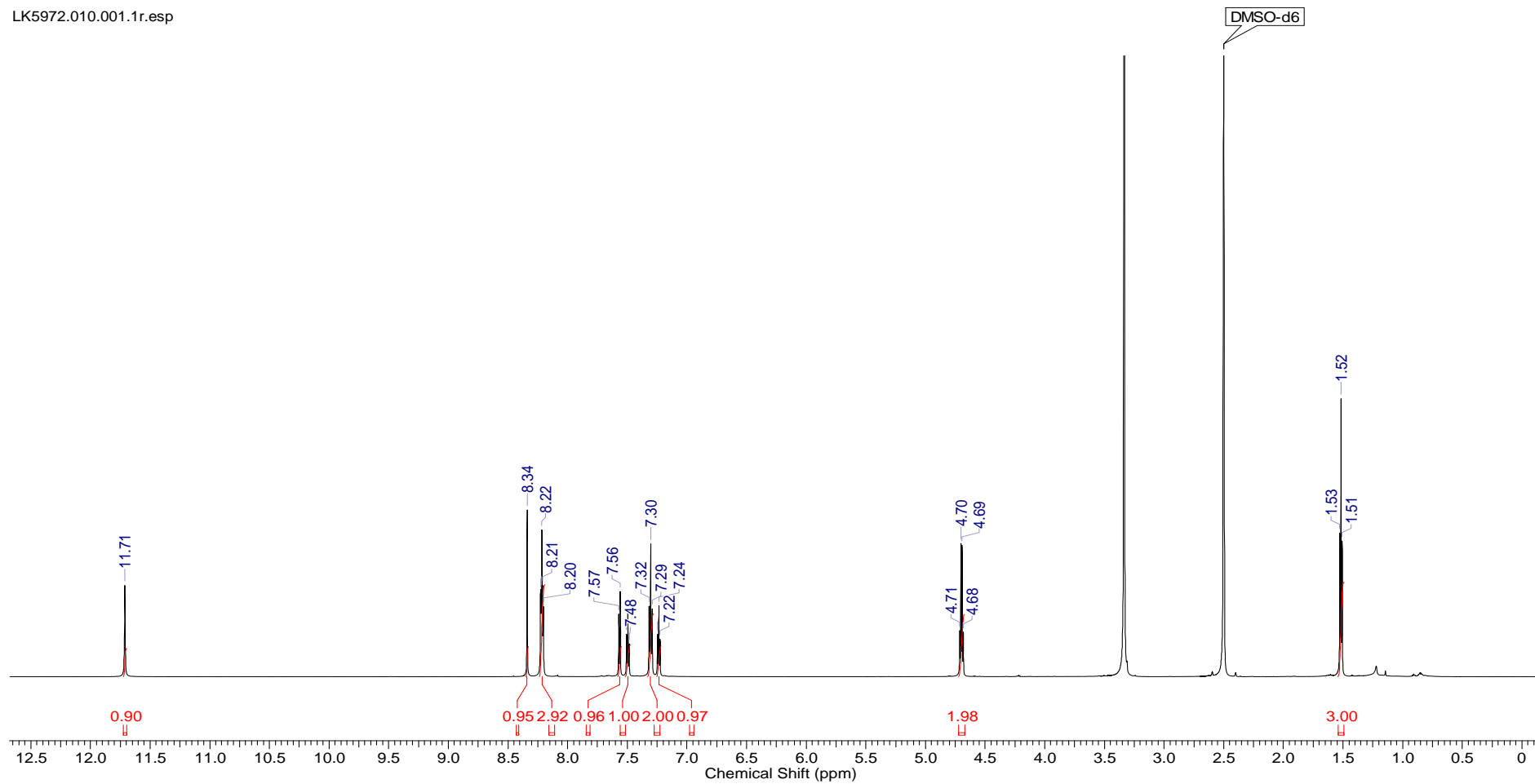
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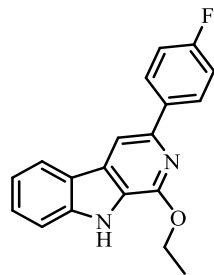
1-ethoxy-3-(4-fluorophenyl)-9H-pyrido[3,4-b]indole (**4j**) ¹H NMR (700 MHz, DMSO-d₆)



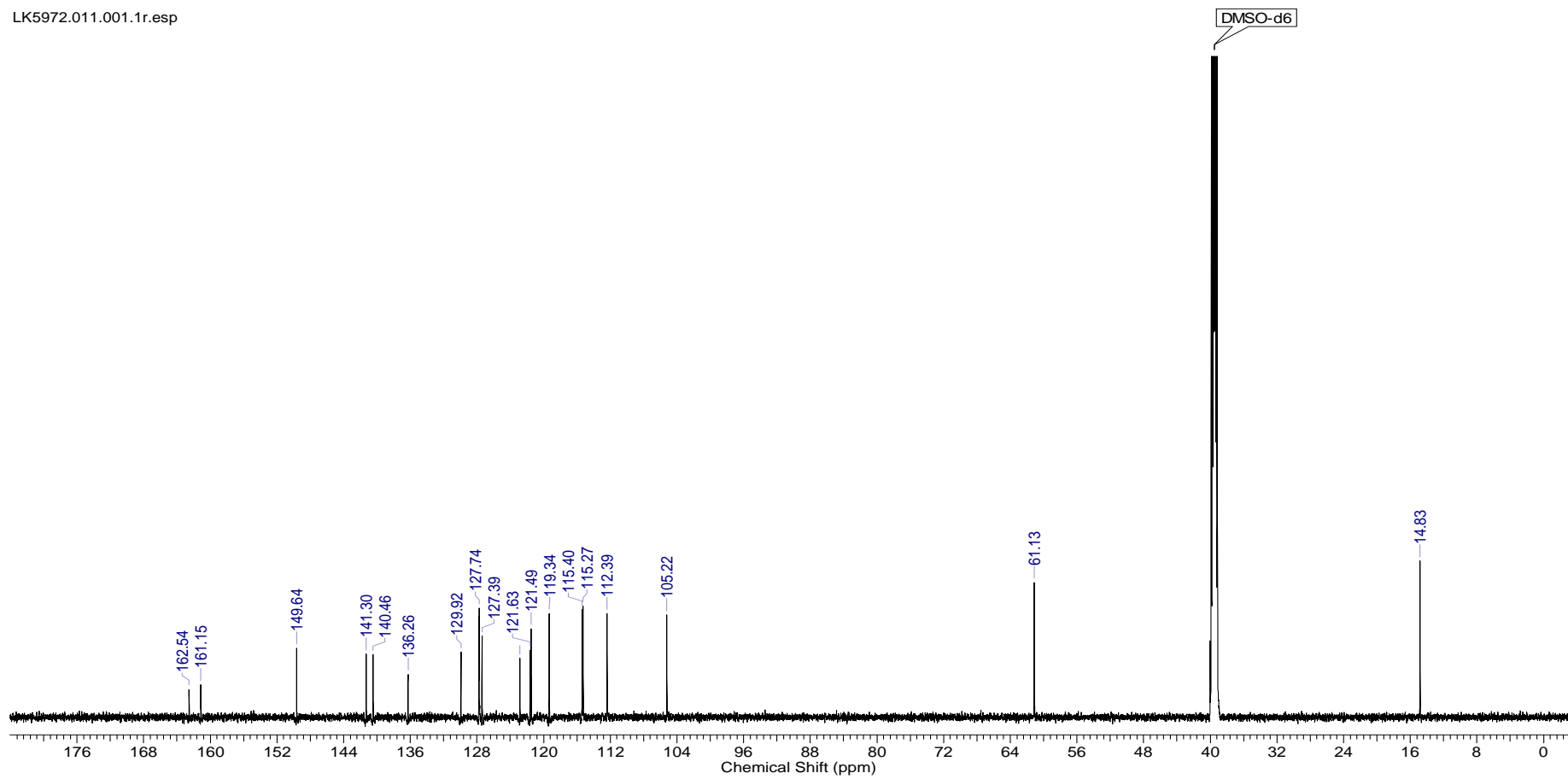
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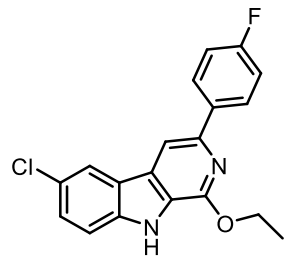
1-ethoxy-3-(4-fluorophenyl)-9H-pyrido[3,4-b]indole (4j) ¹³C {1H} NMR (177 MHz, DMSO-d₆)



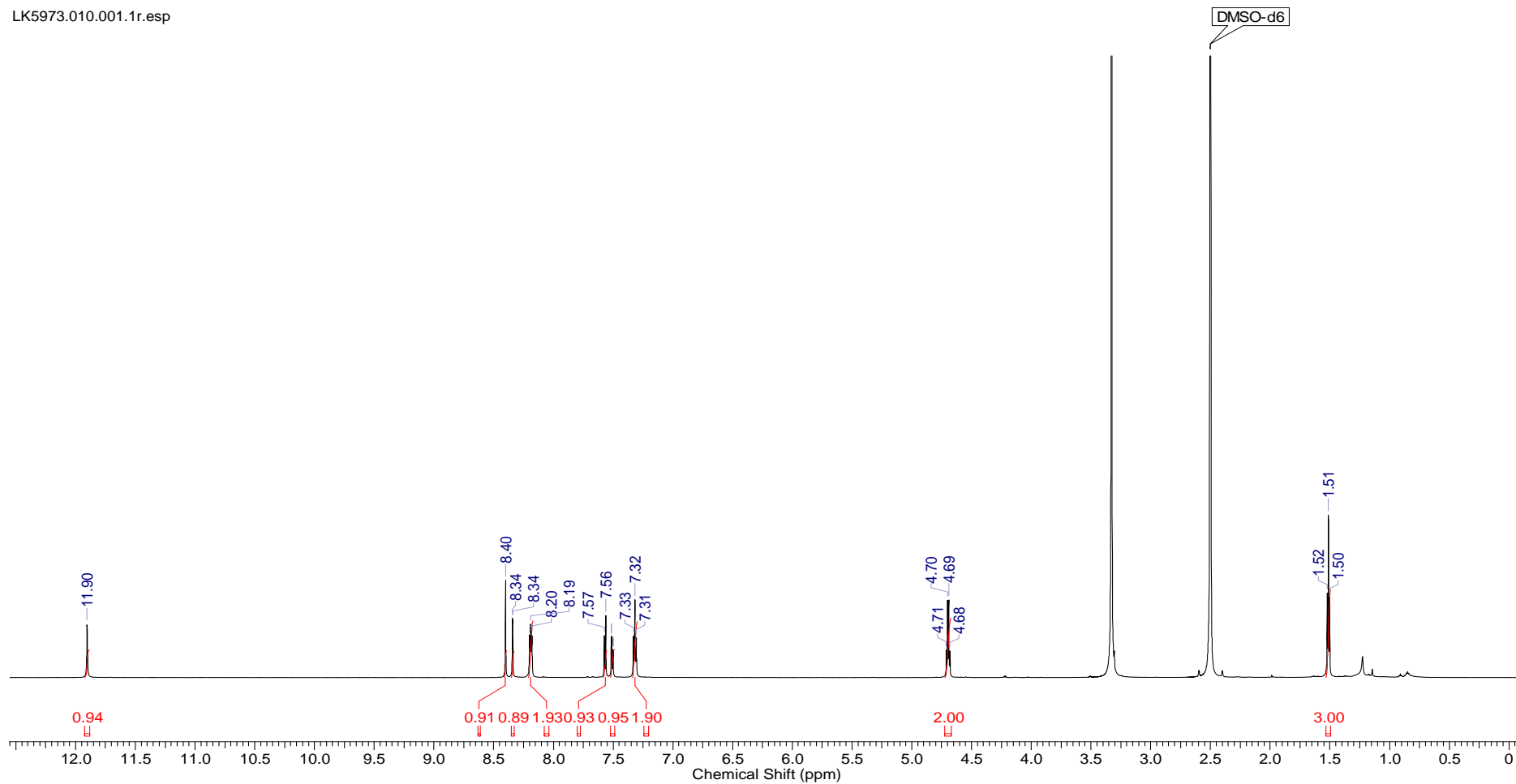
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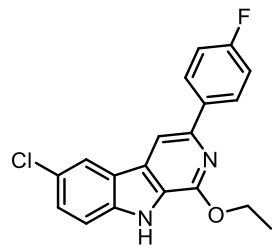
1-ethoxy-3-(4-fluorophenyl)-9H-pyrido[3,4-b]indole (**4k**) ¹H NMR (700 MHz, DMSO-d₆)



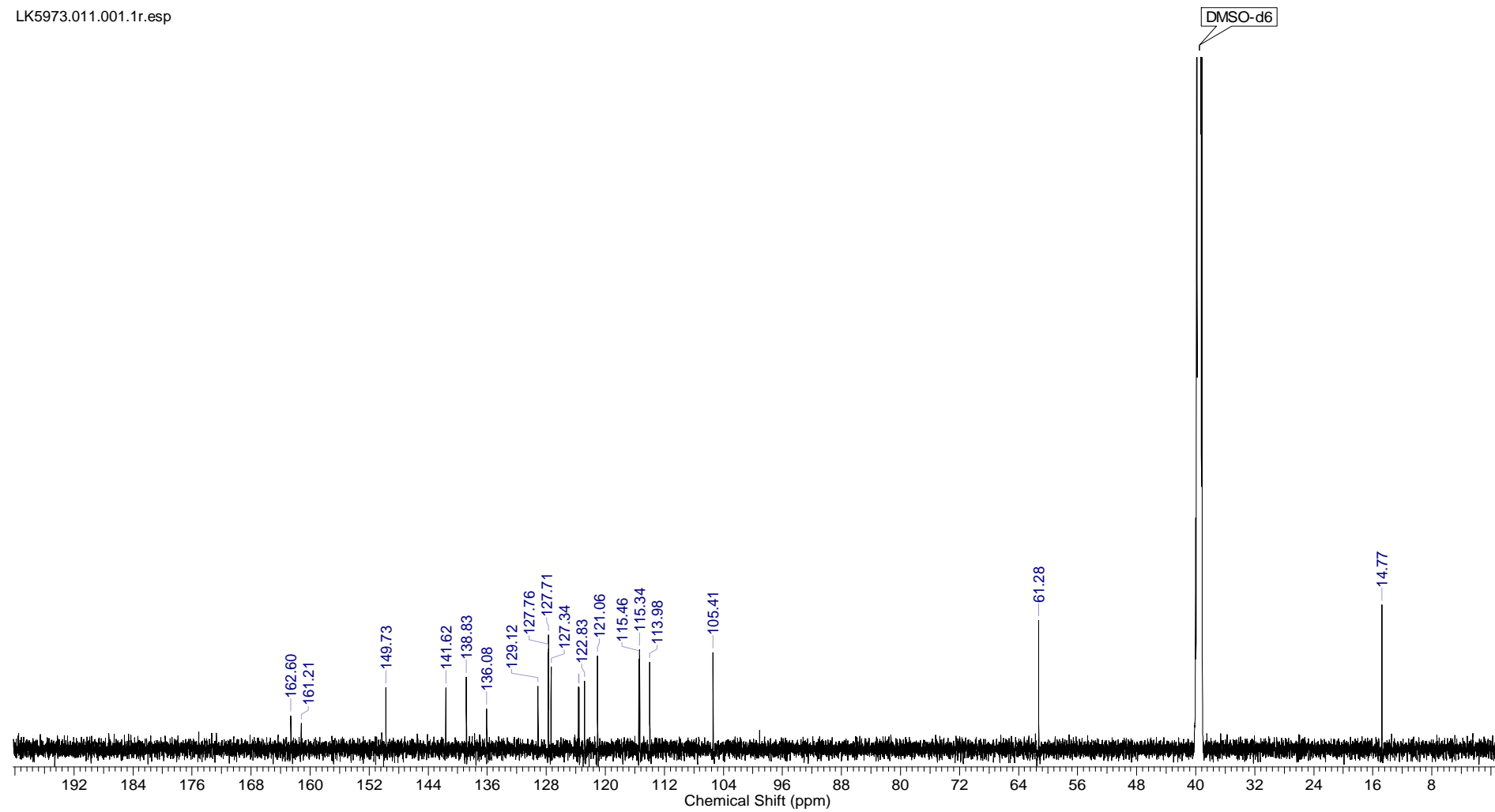
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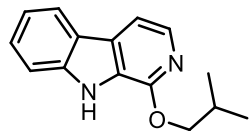
1-ethoxy-3-(4-fluorophenyl)-9H-pyrido[3,4-b]indole (**4k**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



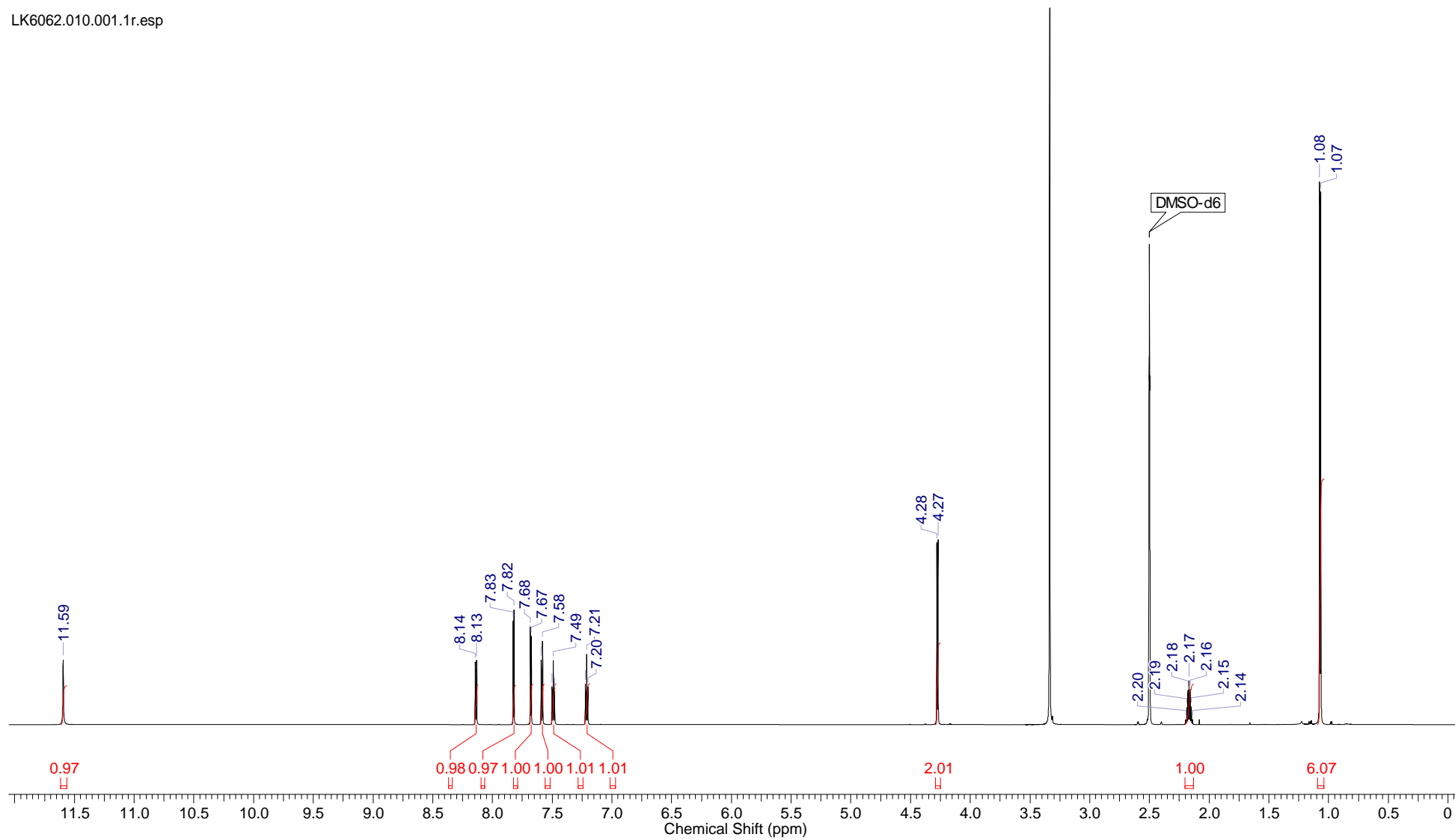
LK5973.011.001.1r.esp



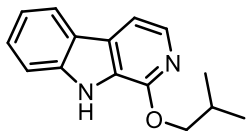
1-isobutoxy-9H-pyrido[3,4-b]indole (**41**) ¹H NMR (700 MHz, DMSO-d₆)



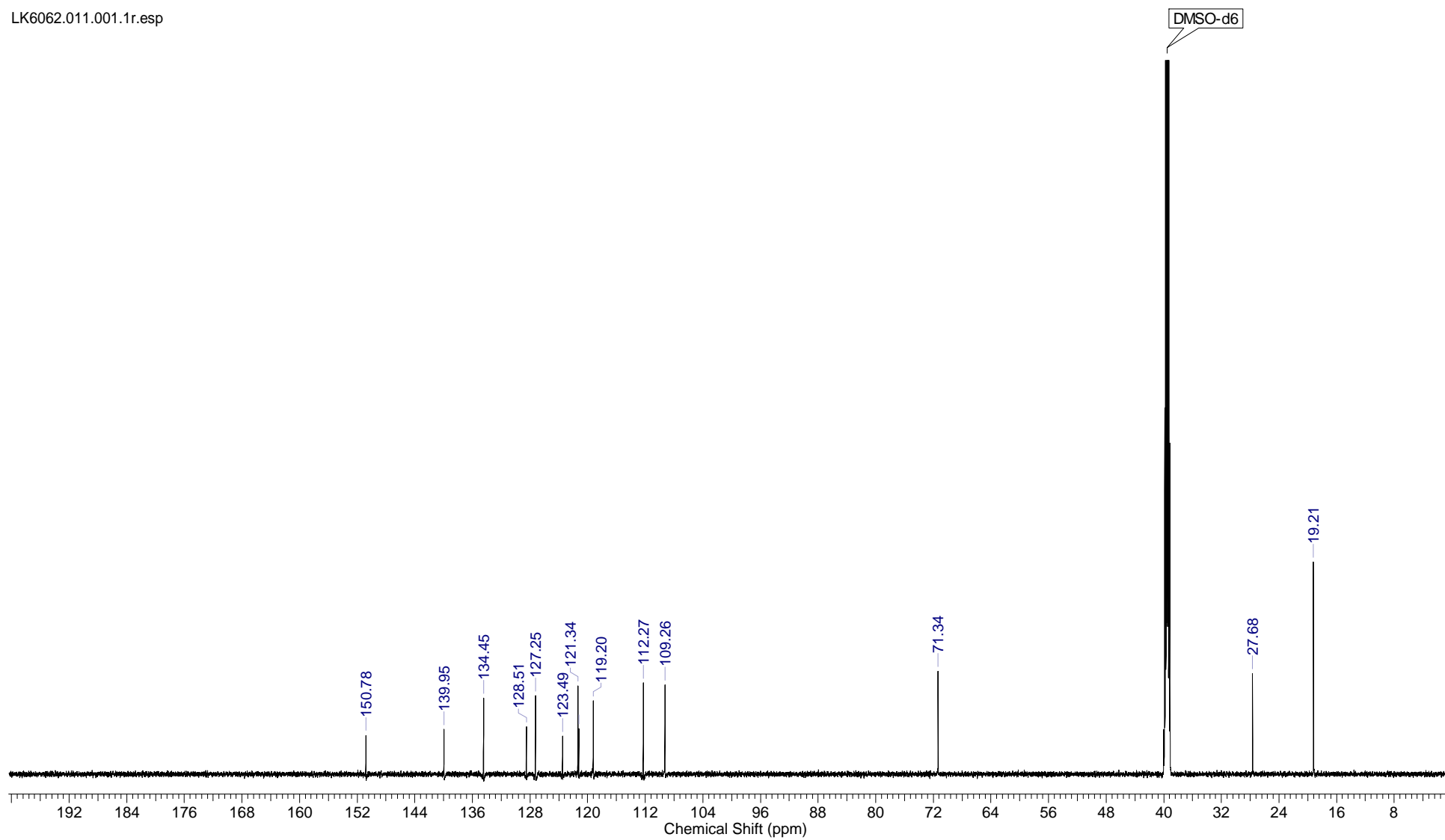
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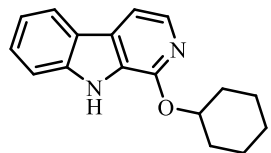
1-isobutoxy-9H-pyrido[3,4-b]indole (4I) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



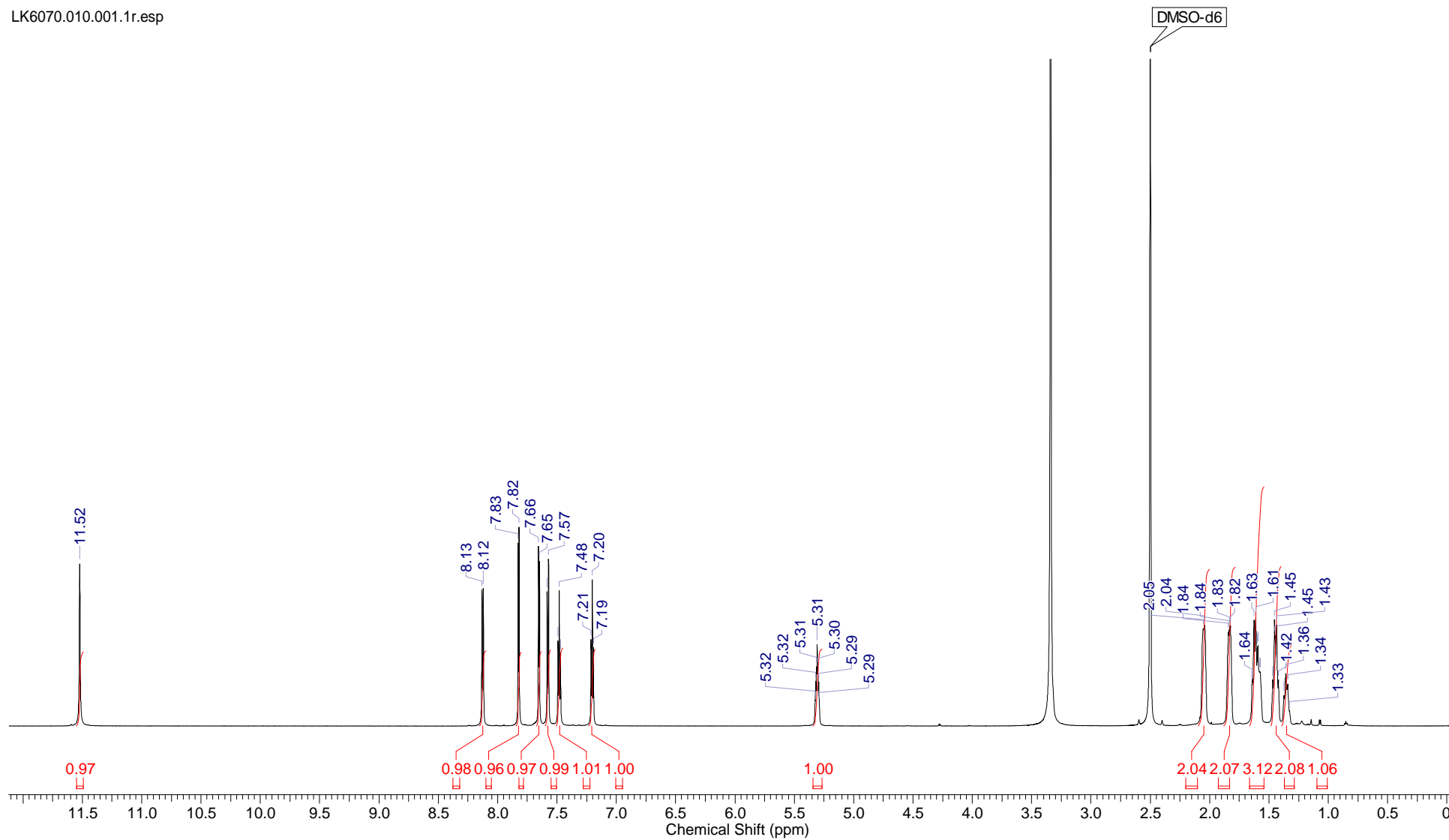
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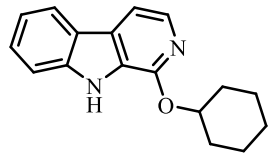
1-(cyclohexyloxy)-9H-pyrido[3,4-b]indole (**4m**) ¹H NMR (700 MHz, DMSO-d₆)



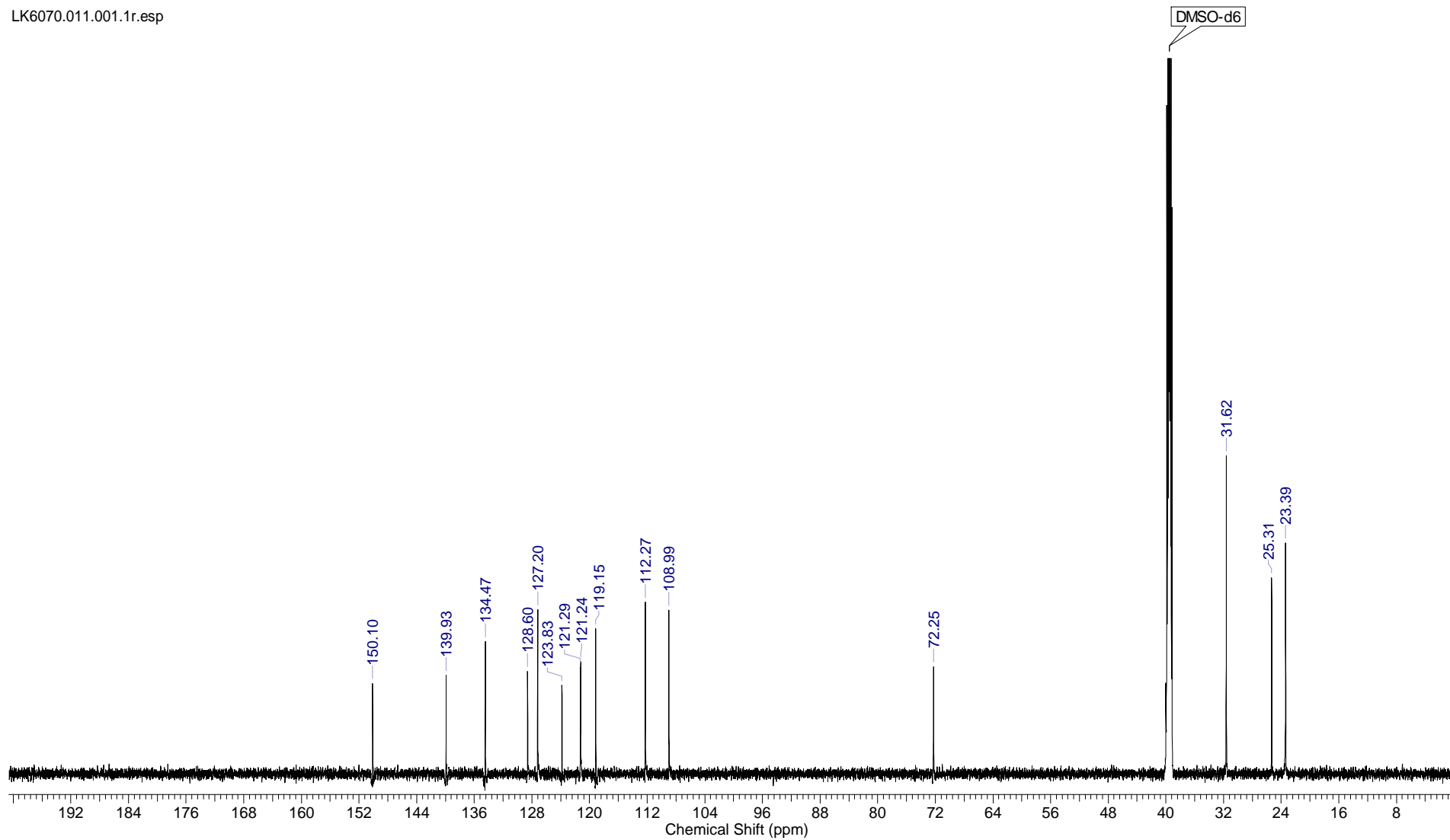
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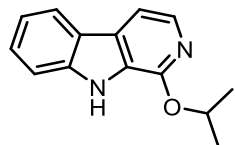
1-(cyclohexyloxy)-9H-pyrido[3,4-b]indole (**4m**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



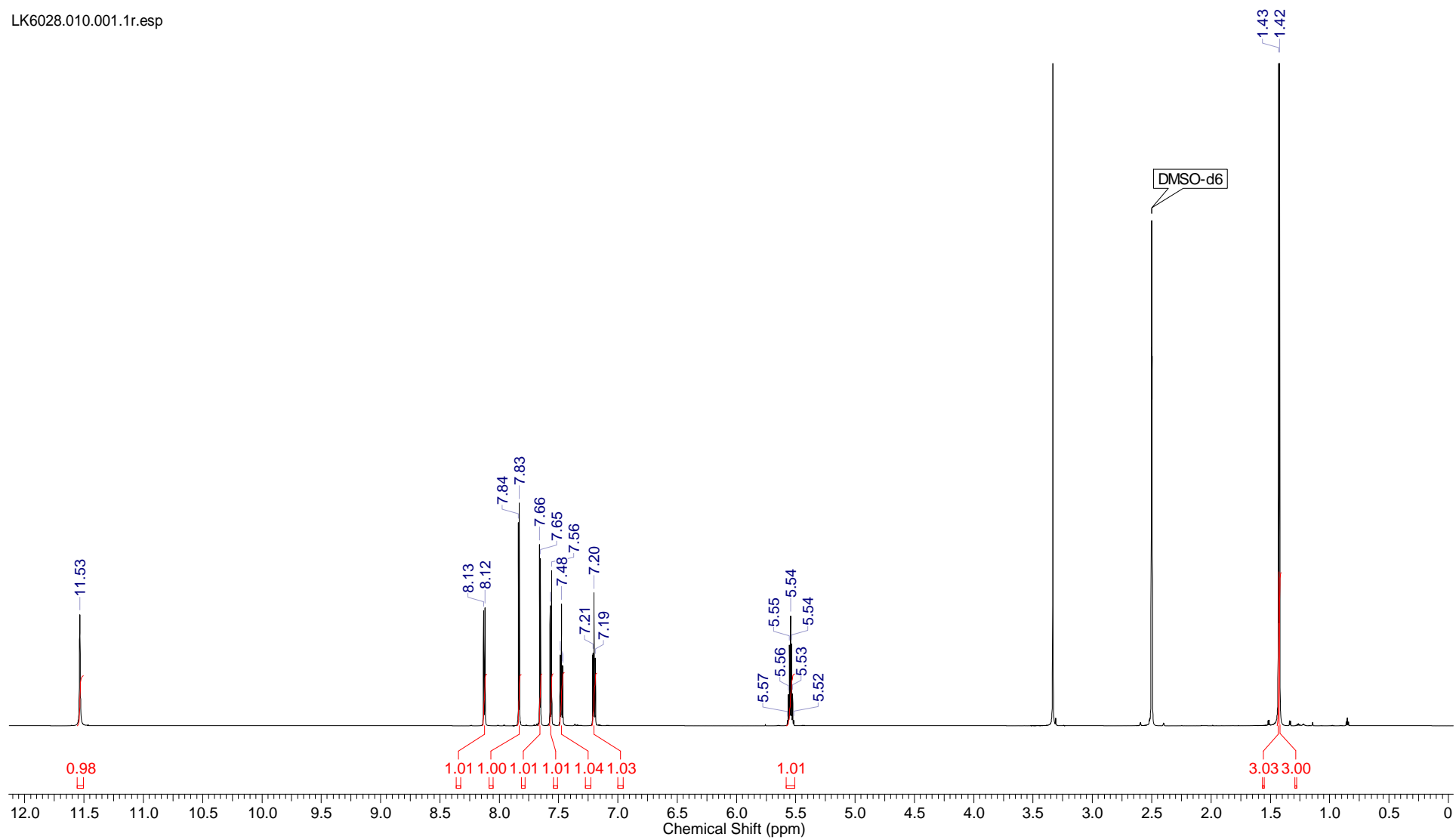
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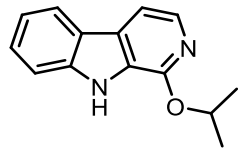
1-isopropoxy-9H-pyrido[3,4-b]indole (**4n**) ¹H NMR (700 MHz, DMSO-d₆)



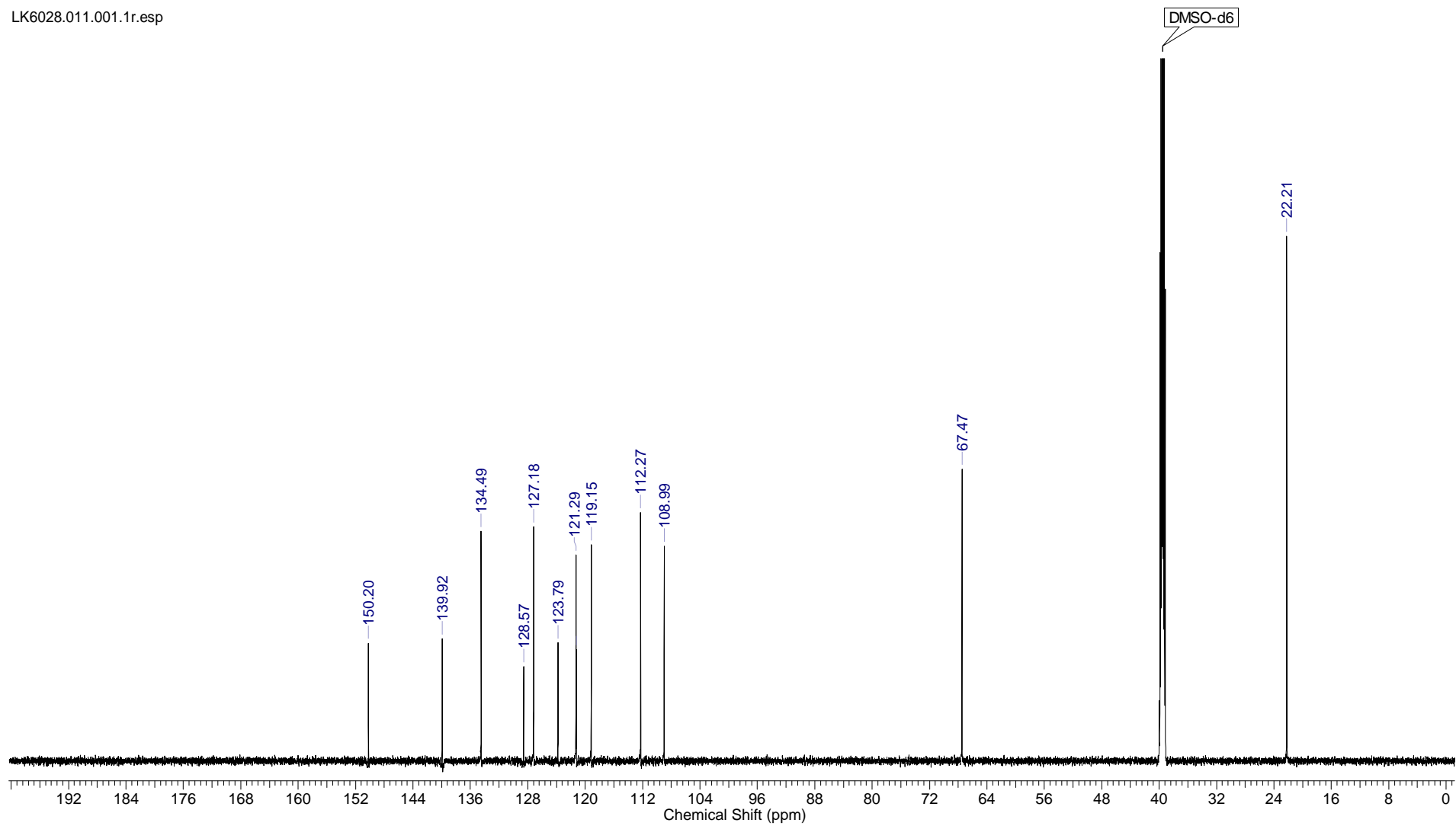
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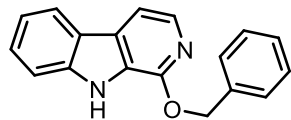
1-isopropoxy-9H-pyrido[3,4-b]indole (4n) ^{13}C {1H} NMR (DMSO, 700 MHz)



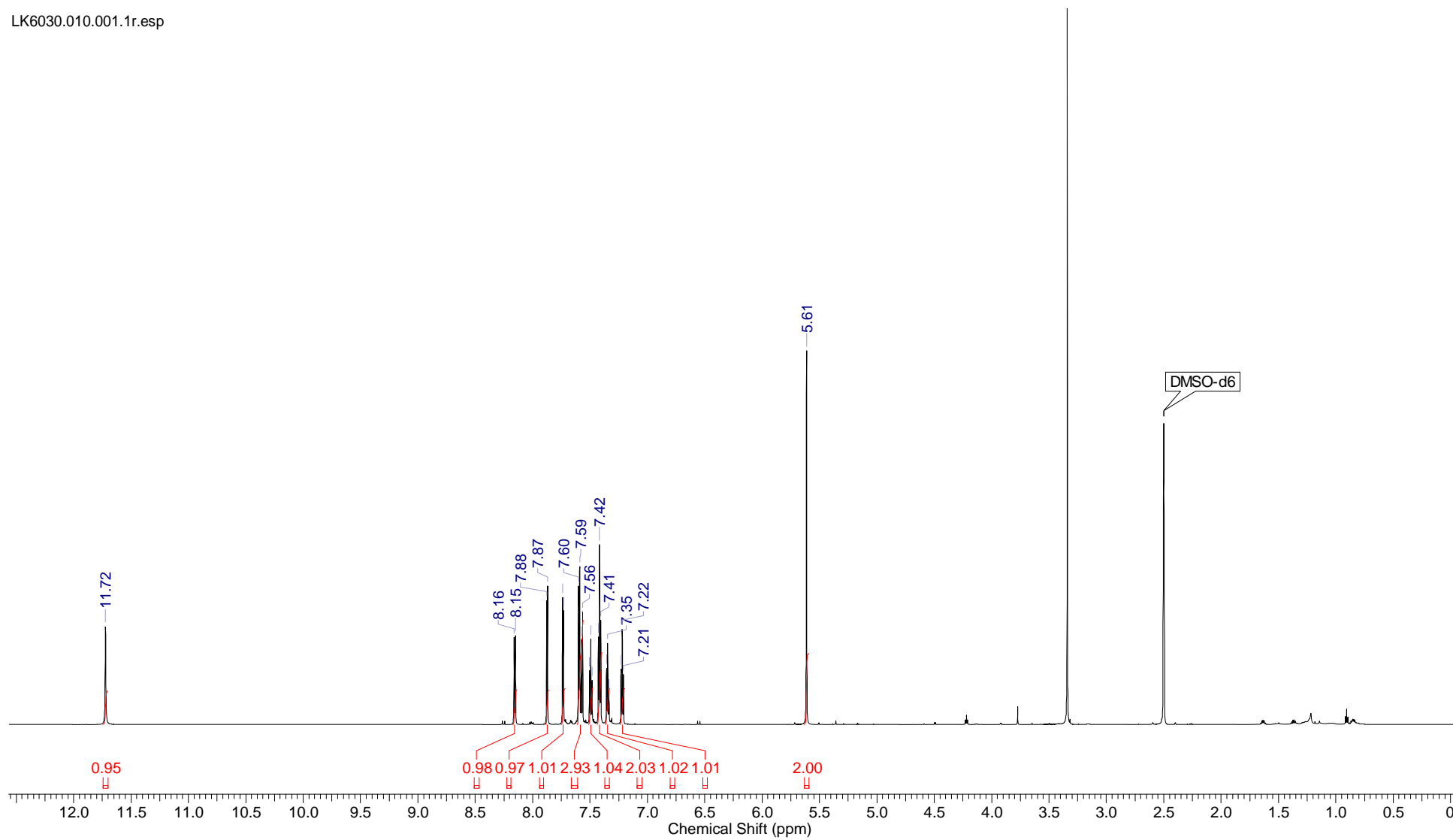
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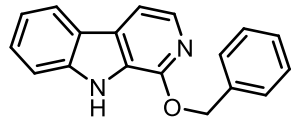
1-(benzyloxy)-9H-pyrido[3,4-b]indole (**4o**) ¹H NMR (700 MHz, DMSO-d₆)



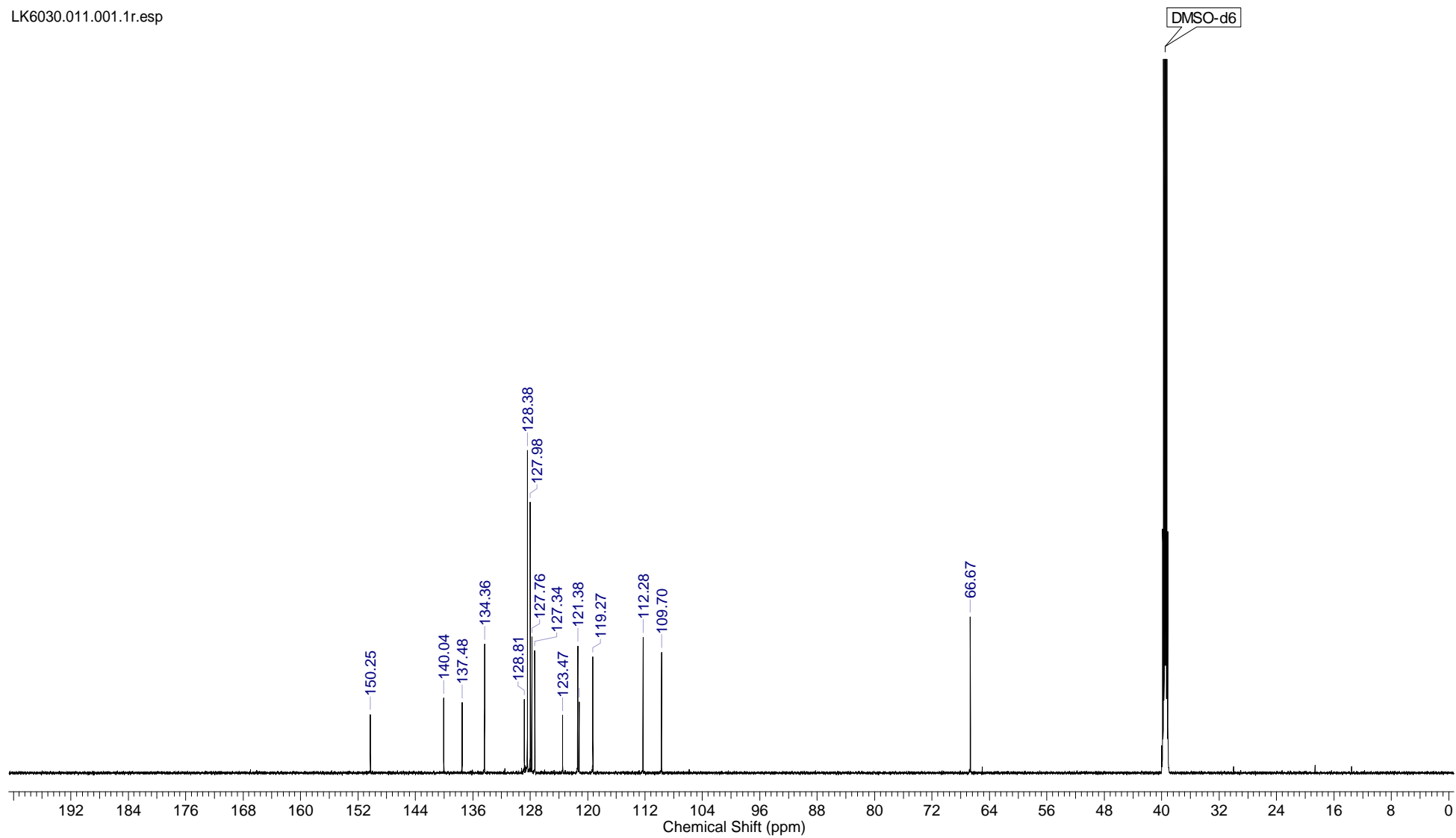
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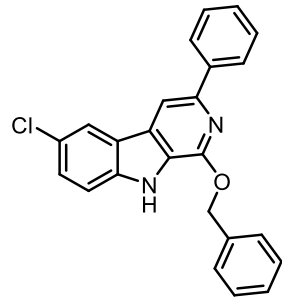
1-(benzyloxy)-9H-pyrido[3,4-b]indole (**4o**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



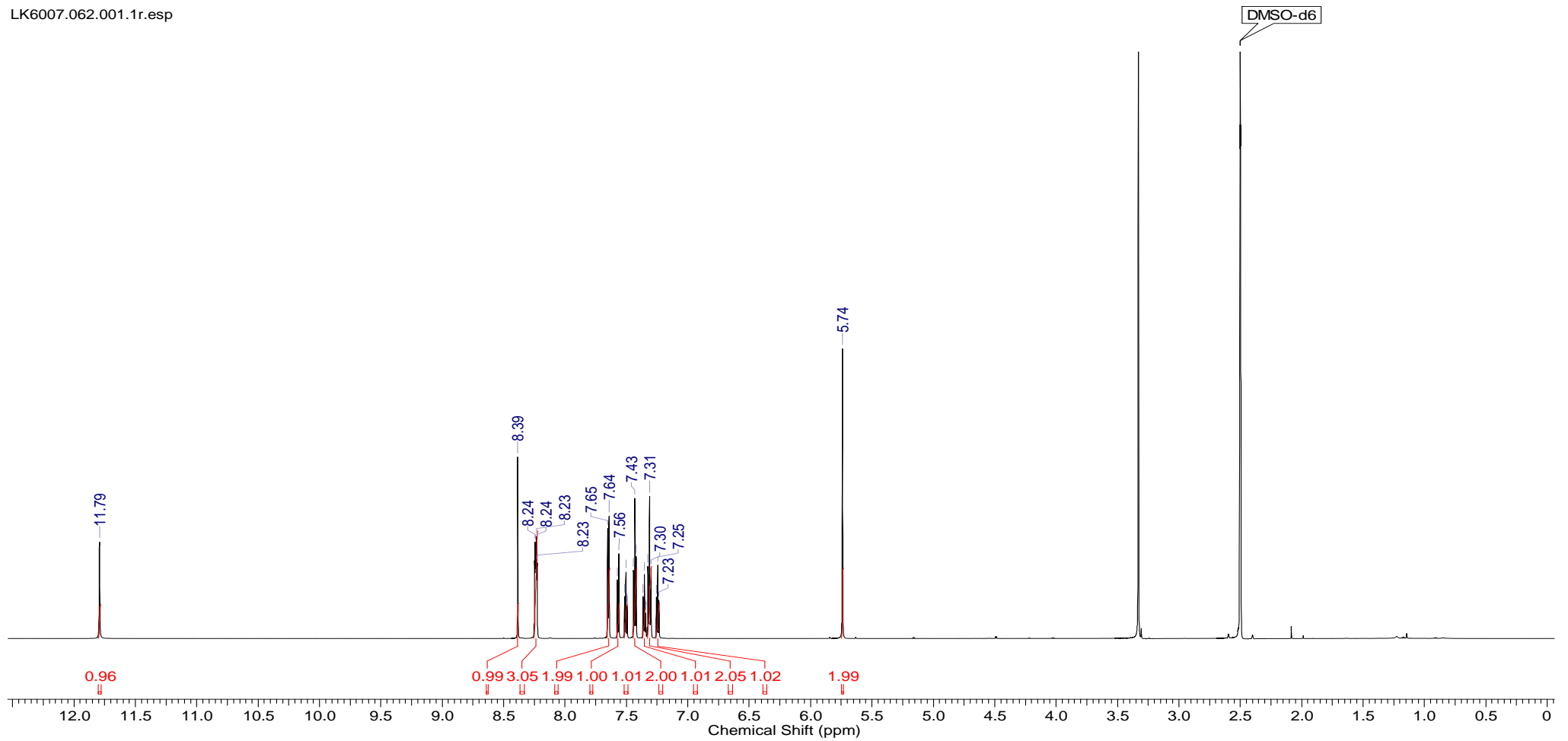
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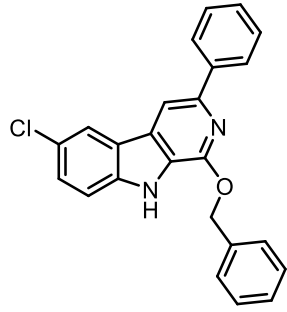
1-(benzyloxy)-6-chloro-3-phenyl-9H-pyrido[3,4-b]indole (**4p**) ¹H NMR (700 MHz, DMSO-d₆)



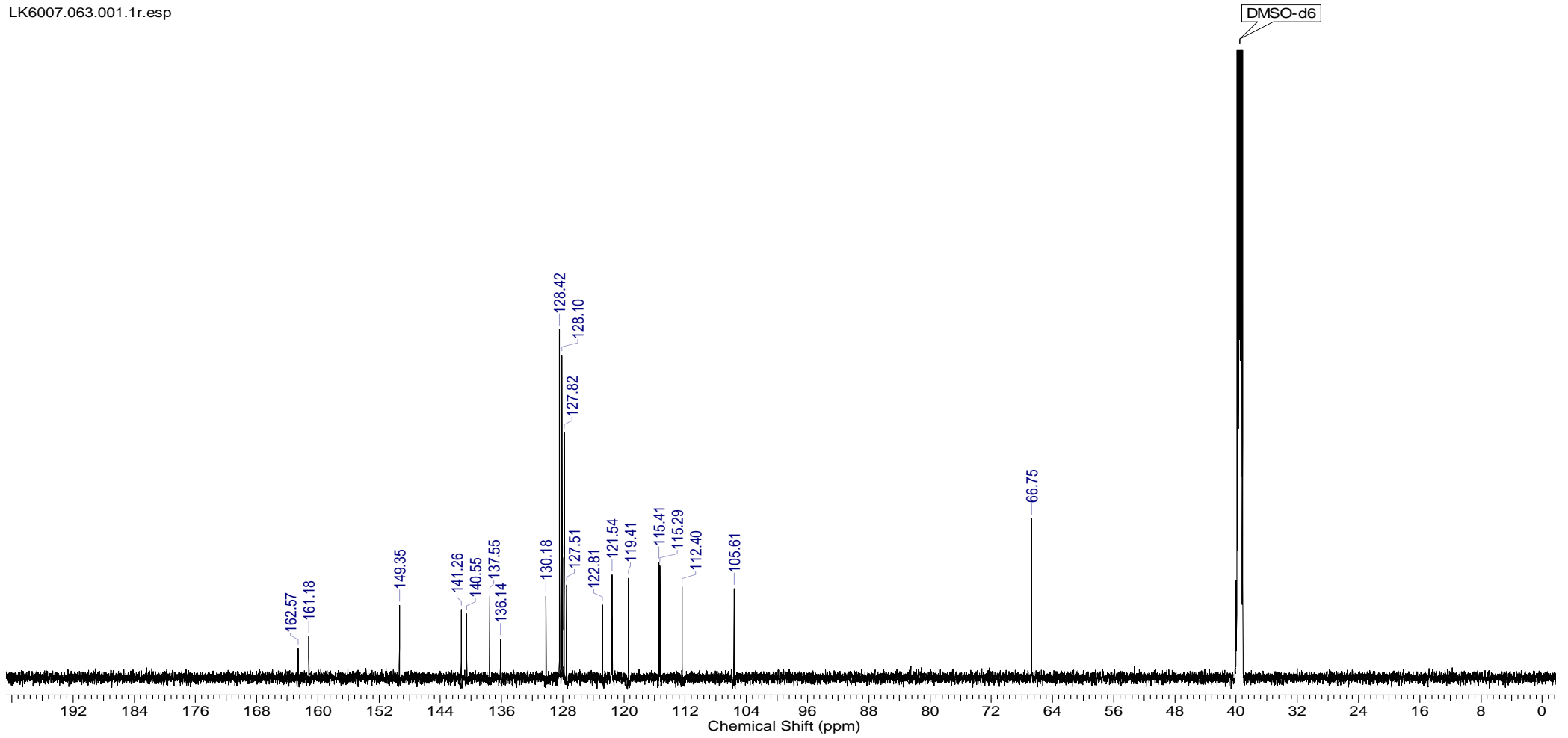
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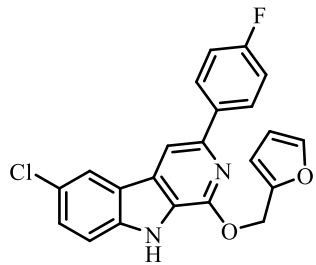
1-(benzyloxy)-6-chloro-3-phenyl-9H-pyrido[3,4-b]indole (**4p**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



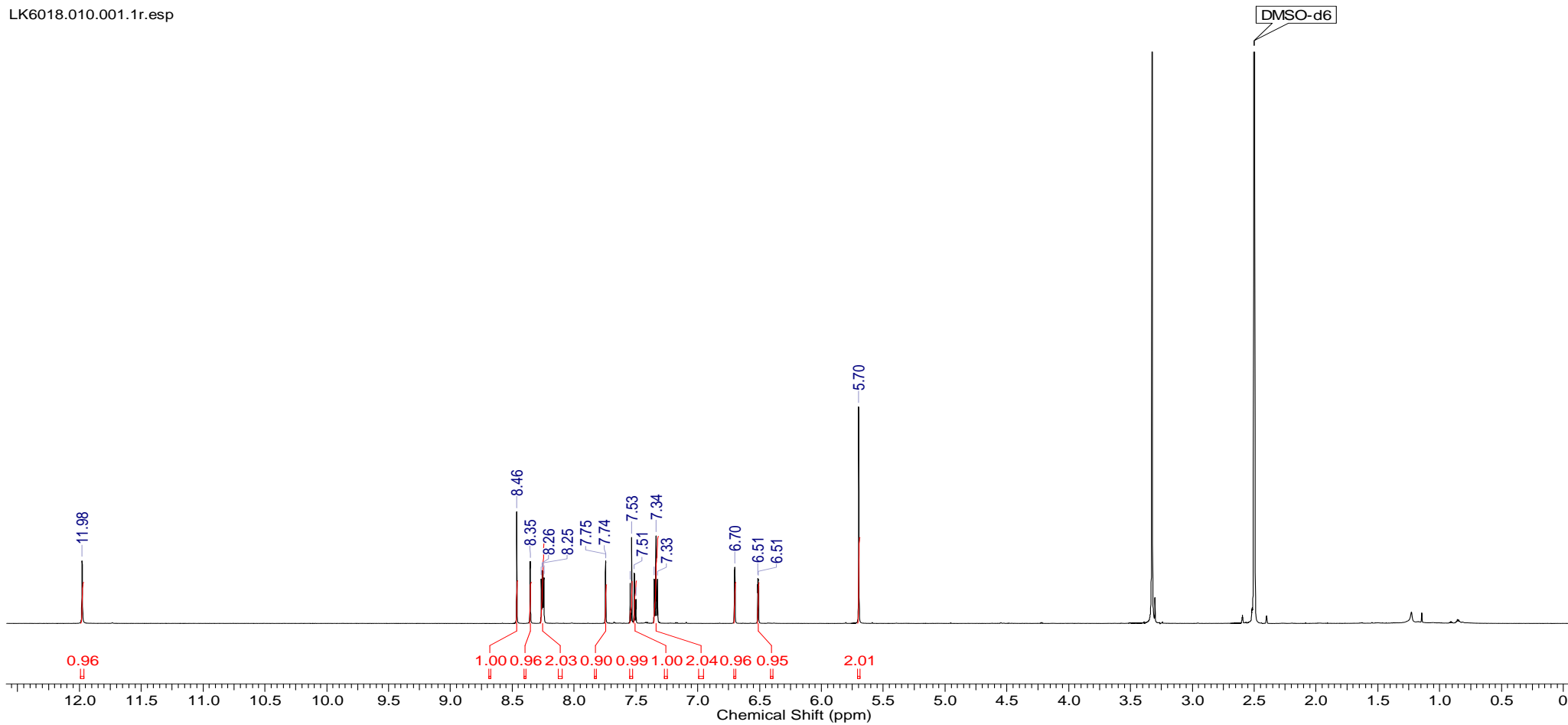
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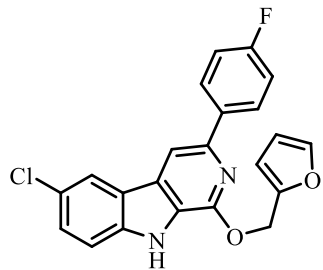
6-chloro-3-(4-fluorophenyl)-1-(furan-2-ylmethoxy)-9H-pyrido[3,4-b]indole (**4q**) ¹H NMR (700 MHz, DMSO-d₆)



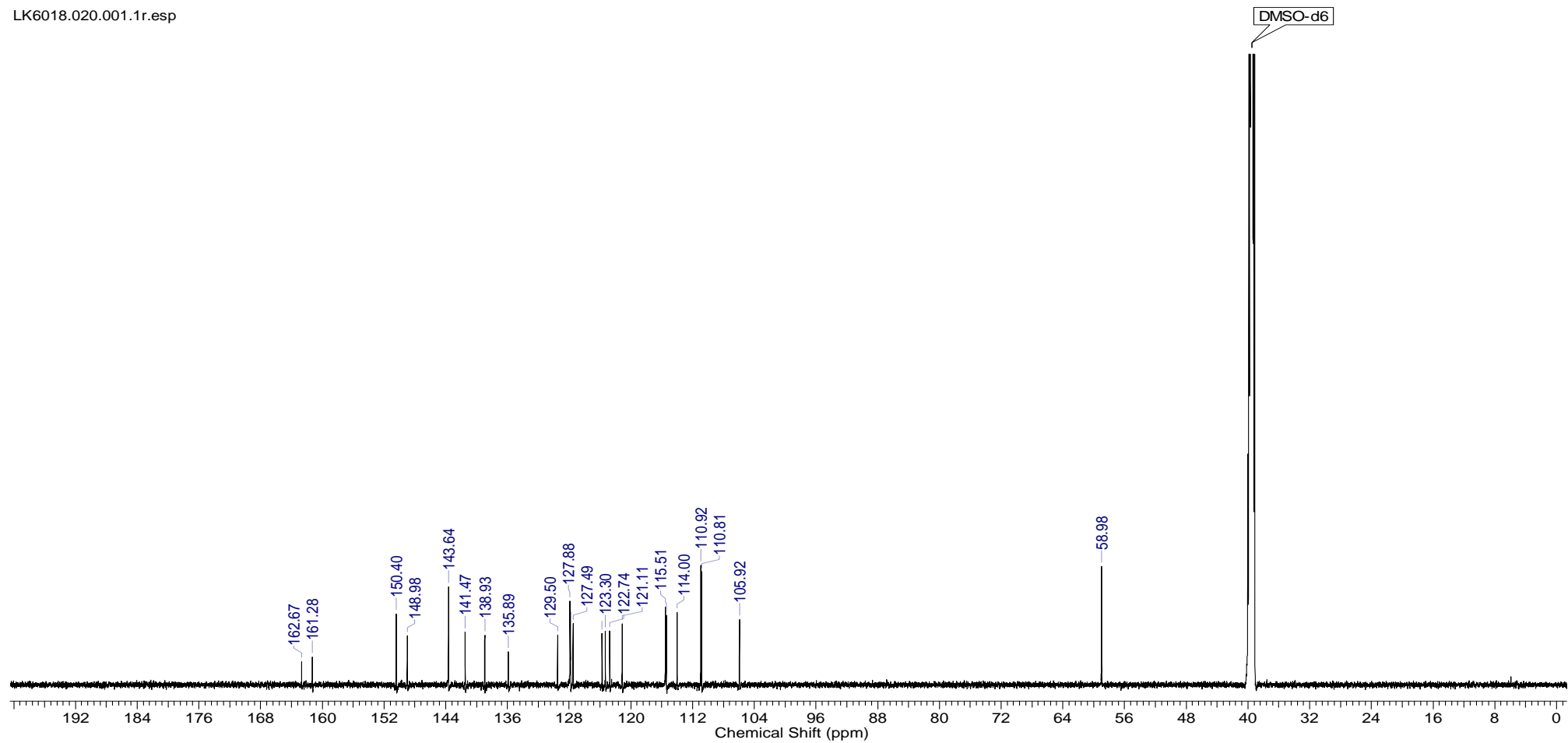
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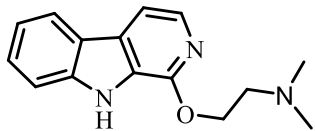
6-chloro-3-(4-fluorophenyl)-1-(furan-2-ylmethoxy)-9H-pyrido[3,4-b]indole (**4q**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



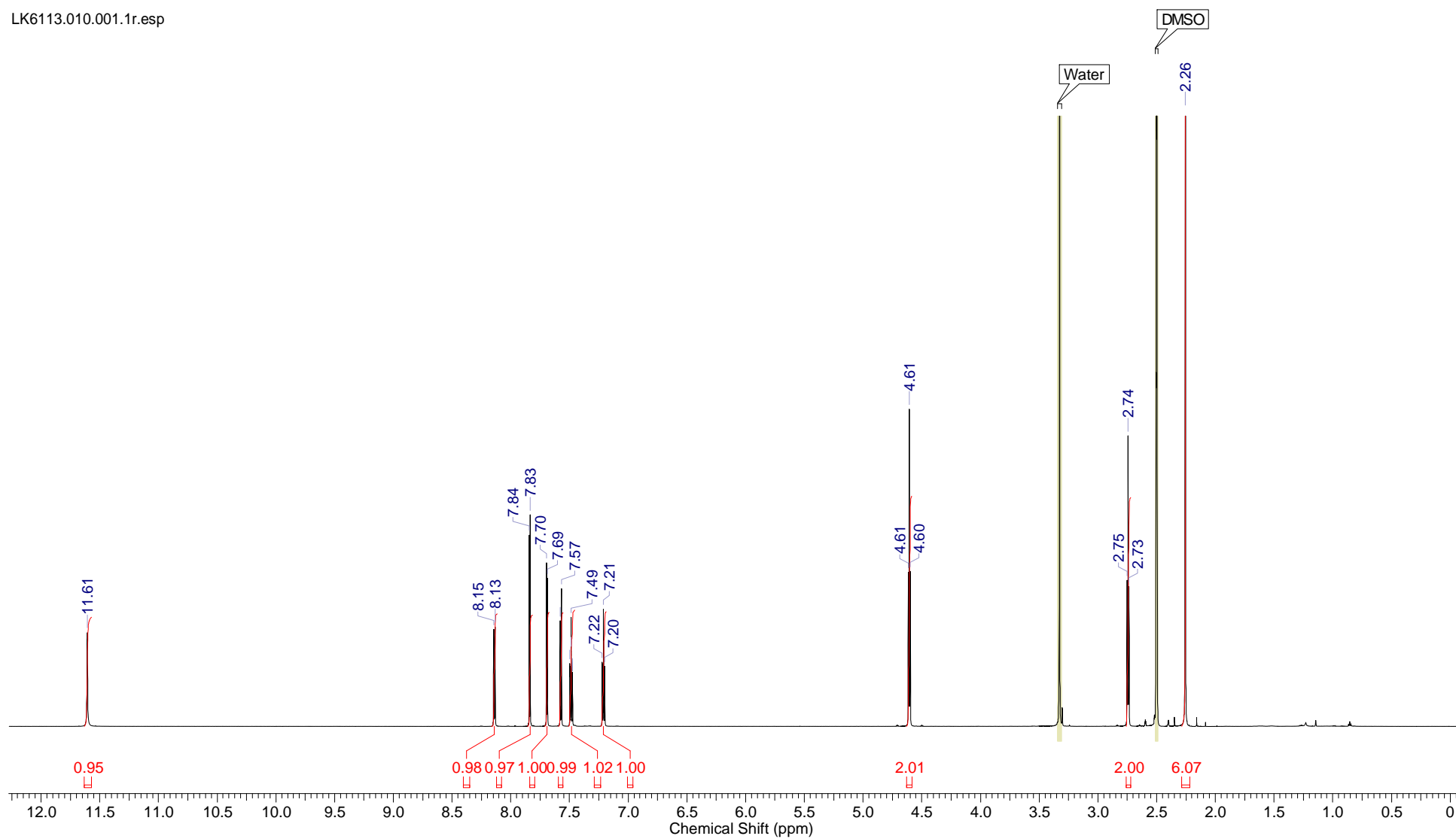
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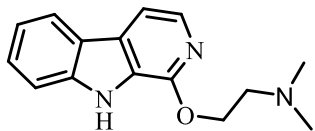
2-((9H-pyrido[3,4-b]indol-1-yl)oxy)-N,N-dimethylethan-1-amine (**4r**) ¹H NMR (700 MHz, DMSO-d₆)



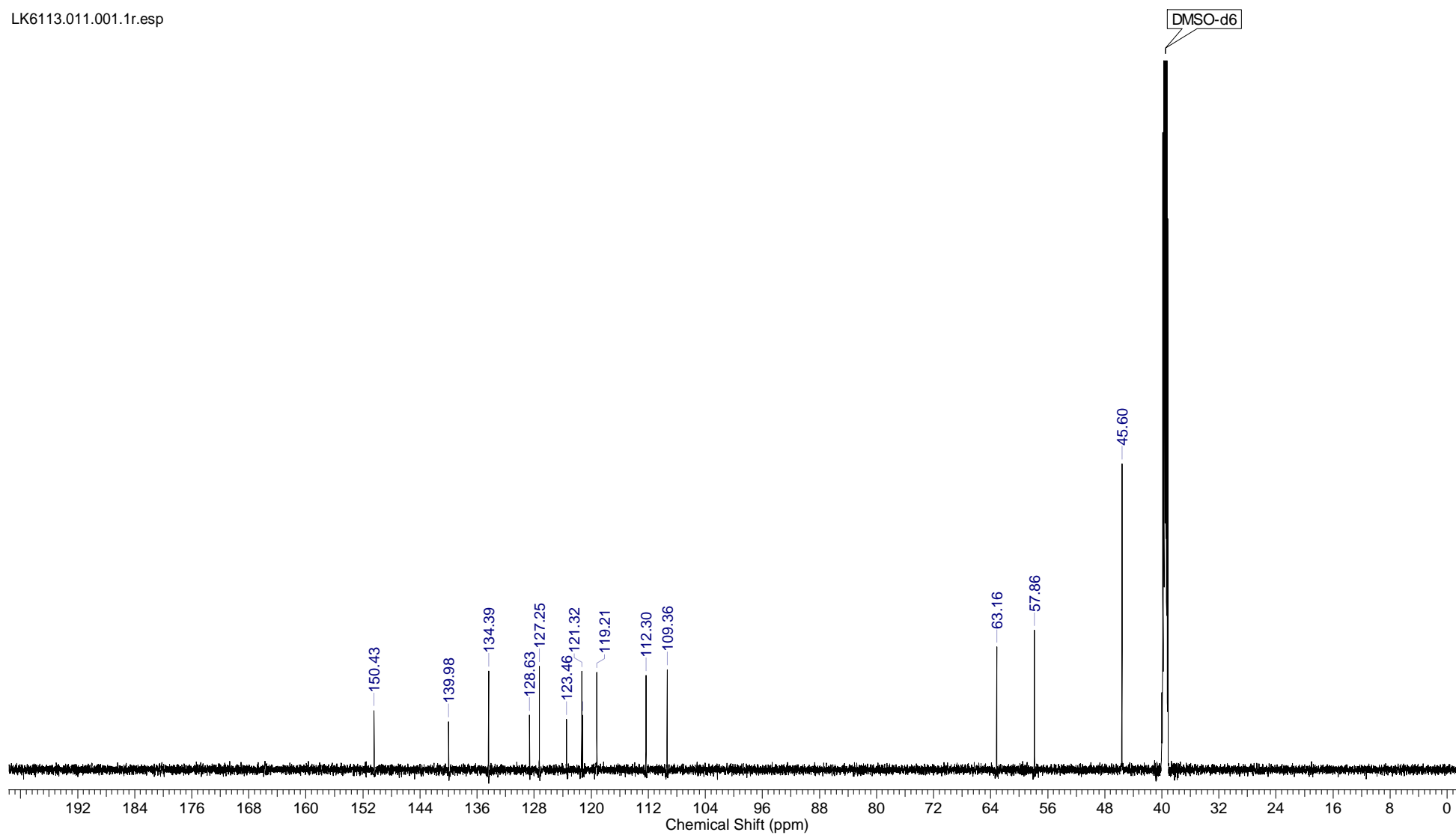
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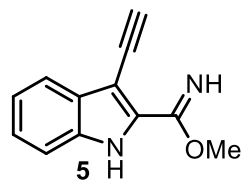
2-((9H-pyrido[3,4-b]indol-1-yl)oxy)-N,N-dimethylethan-1-amine (**4r**) ^{13}C {1H} NMR (177 MHz, DMSO- d_6)



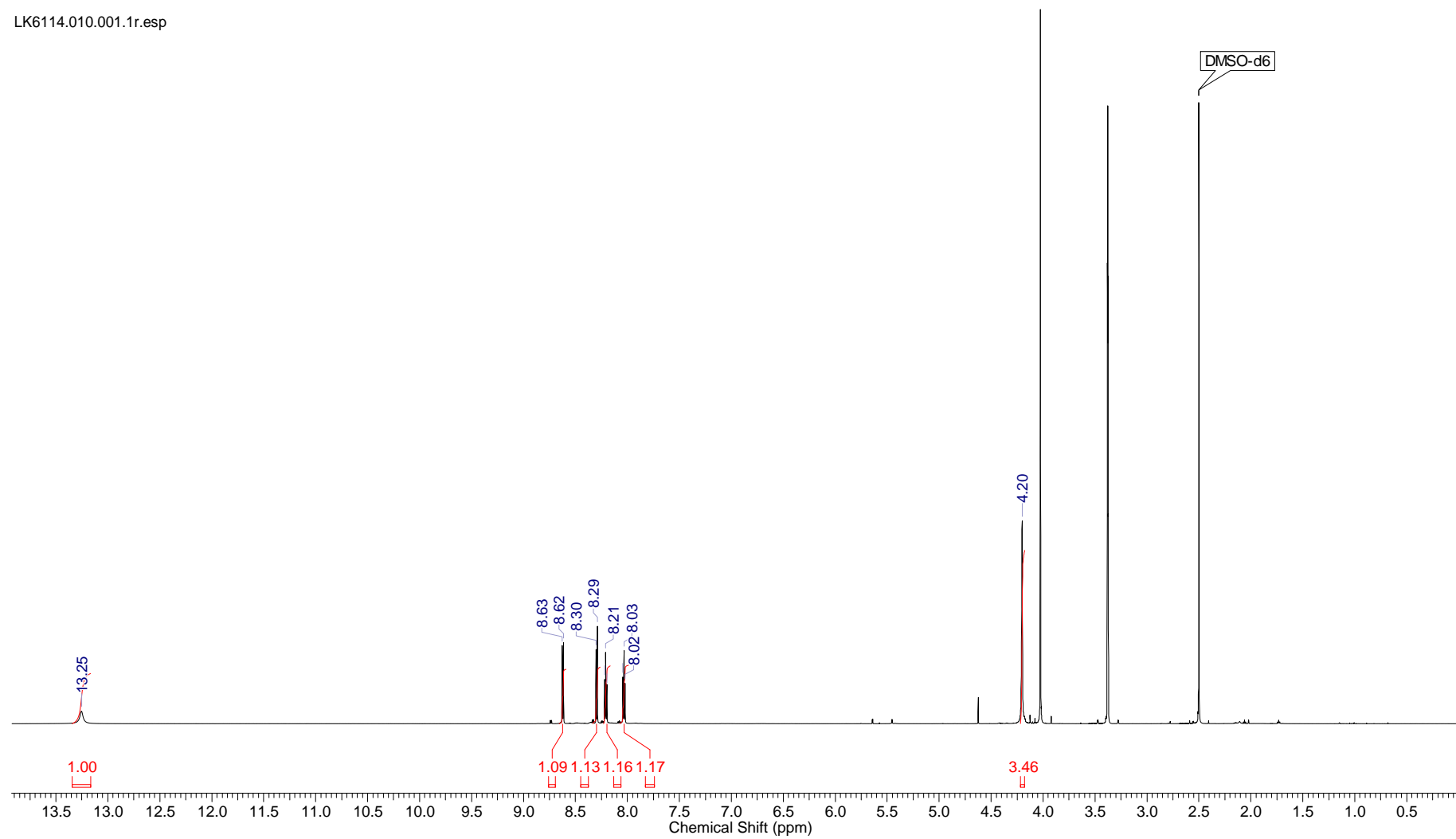
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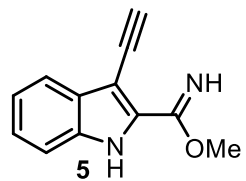
¹H NMR (700 MHz, DMSO-d₆)



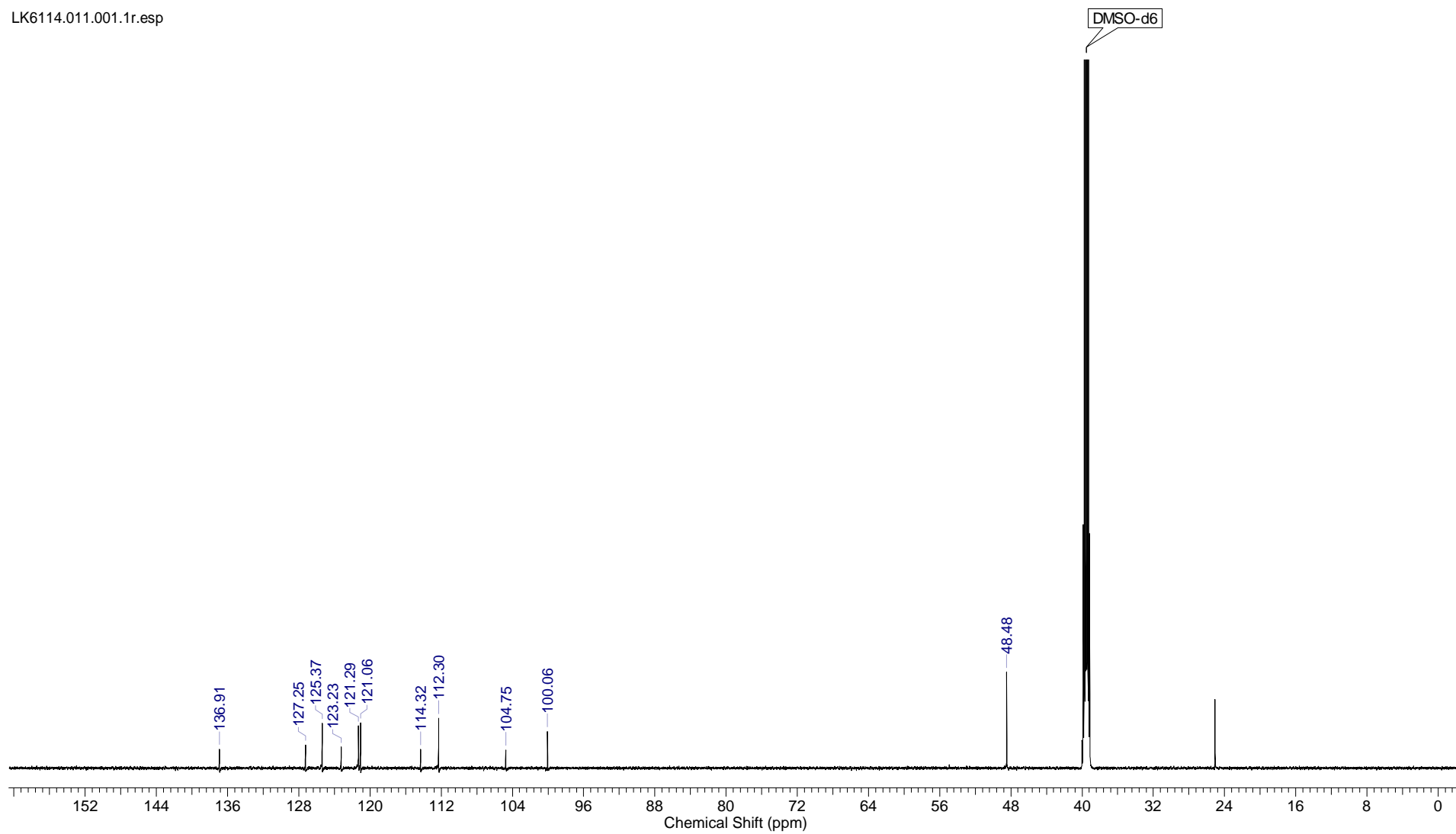
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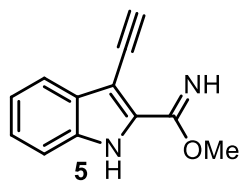


^{13}C {1H} NMR (177 MHz, DMSO- d_6)

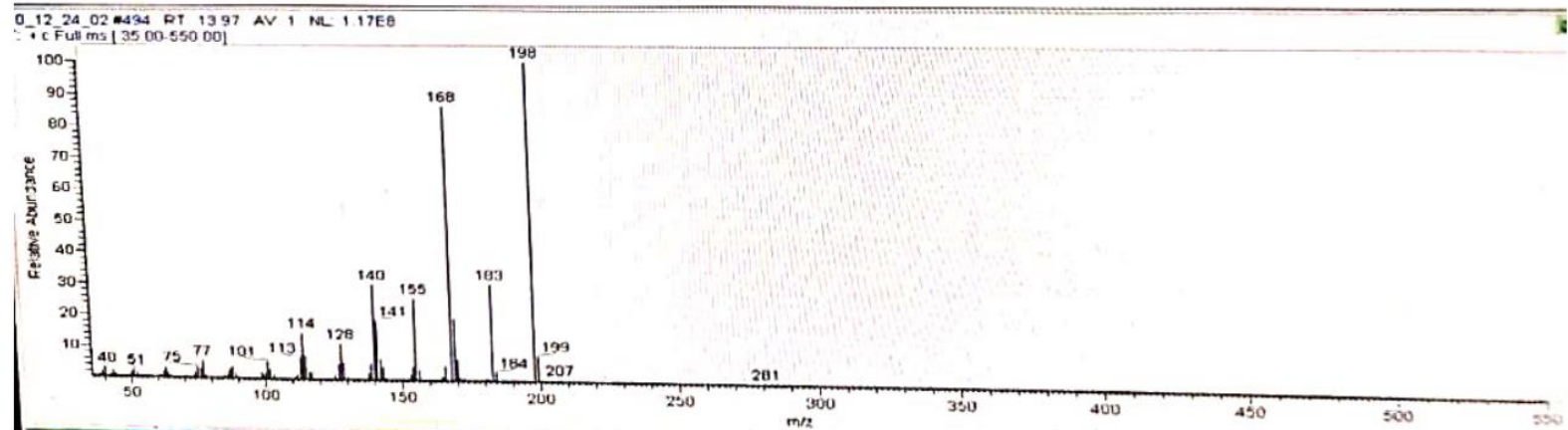
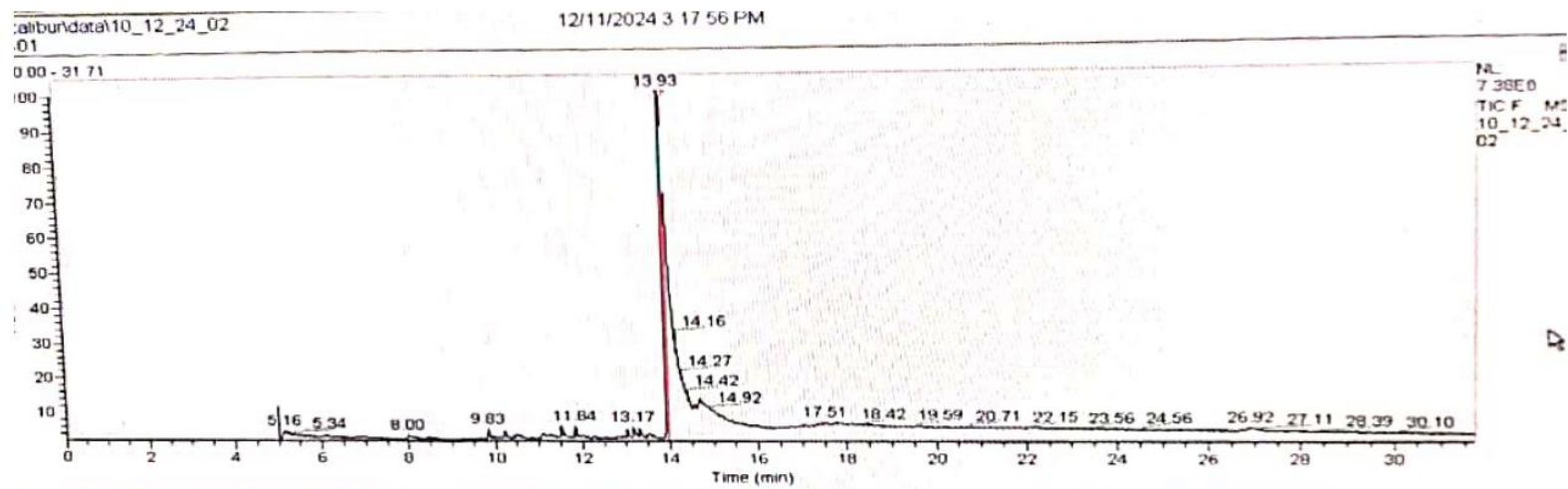


LK6114.011.001.1r.esp





GC-MS data



2. X-Ray crystallographic data for compound **4h**

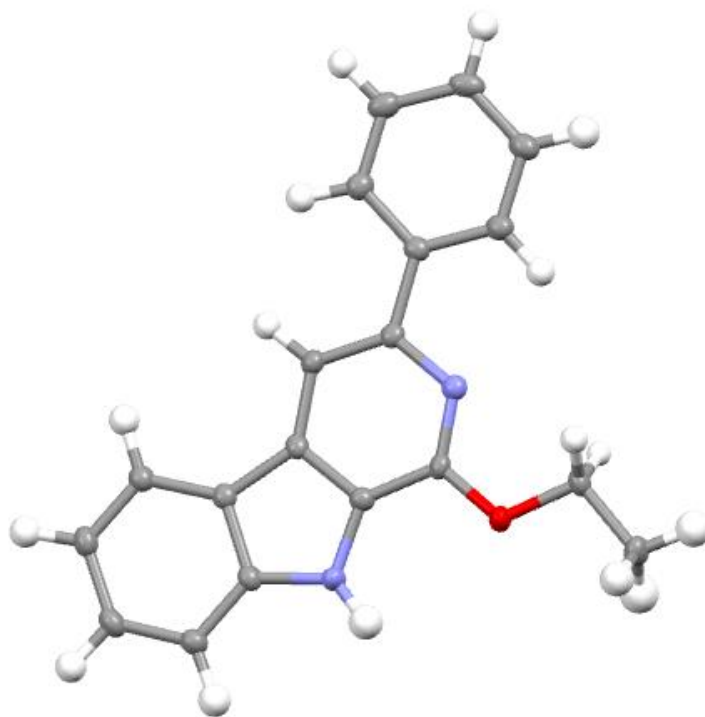


Figure S1. A thermal ellipsoid plot for the crystal structure **4h**. The ellipsoid contour is shown with 50% probability level.

The crystal of **4h** for X-Ray diffraction study has been obtained through the heating of compound in EtOH-EtOAc until complete dissolution, followed by slow cooling to room temperature. X-ray diffraction experiment was performed at the Center for Shared Use of Physical Methods of Investigation at the Frumkin Institute of Physical Chemistry and Electrochemistry, RAS. Colorless crystals of $C_{19}H_{16}N_2O$ are monoclinic, space group $P 2_1/c$, **a** 15.7758 (14) **b** 5.9637 (6) **c** 15.5467 (14) Å, **a** 90 **b** 92.558(4) **g** 90, $V = 1461.21 \text{ \AA}^3$. The R-Factor is 4.76. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC), reference number 2402787.