

Supporting Information

PhI(OAc)₂-Mediated one-pot oxidative decarboxylation and aromatization of tetrahydro- β -carbolines: synthesis of norharmine, harmine, eudistomin U and eudistomin I

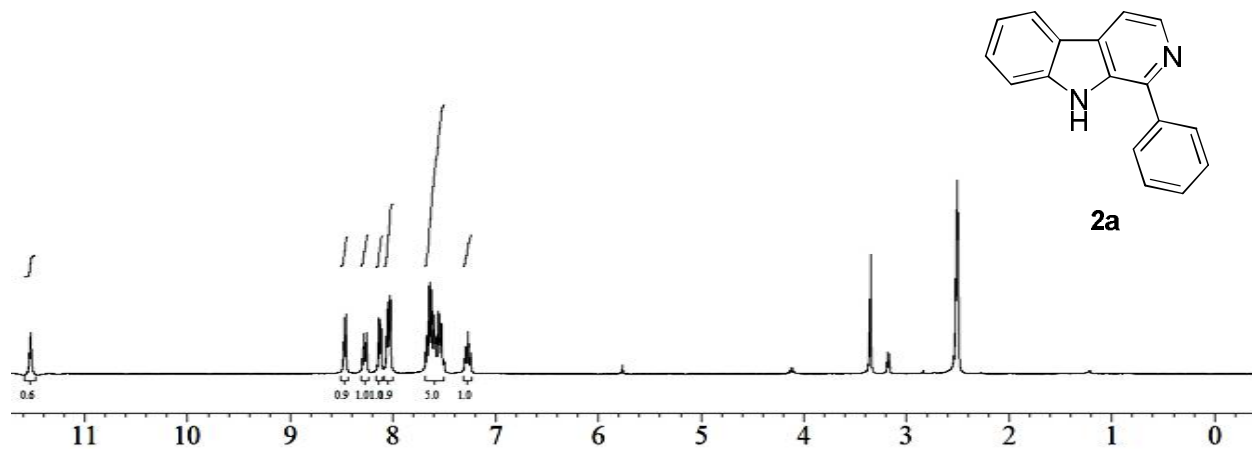
Ahmed Kamal*, Yellaiah Tangella, Kesari Lakshmi Manasa, Manda Sathish,
Vunnam Srinivasulu Jadala Chetna and Abdullah Alarifi

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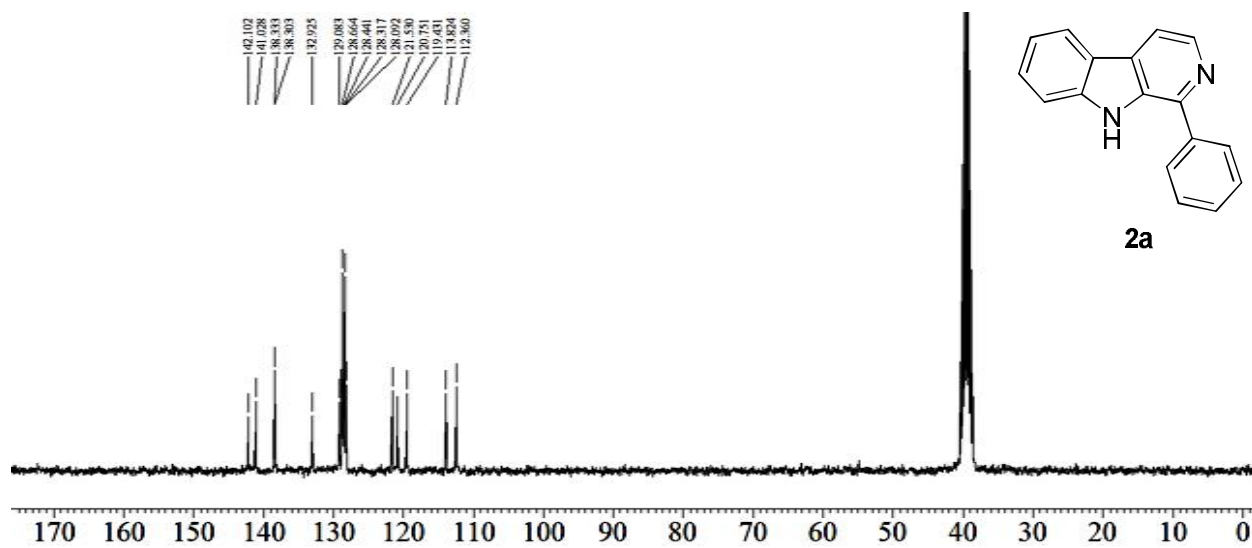
¹ H and ¹³ C NMR spectra of compounds 2a-p and 4a-p.....	2-39
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1-Phenyl-9H-pyrido[3,4-*b*]indole (2a)

^1H NMR (300 MHz, DMSO- d_6)

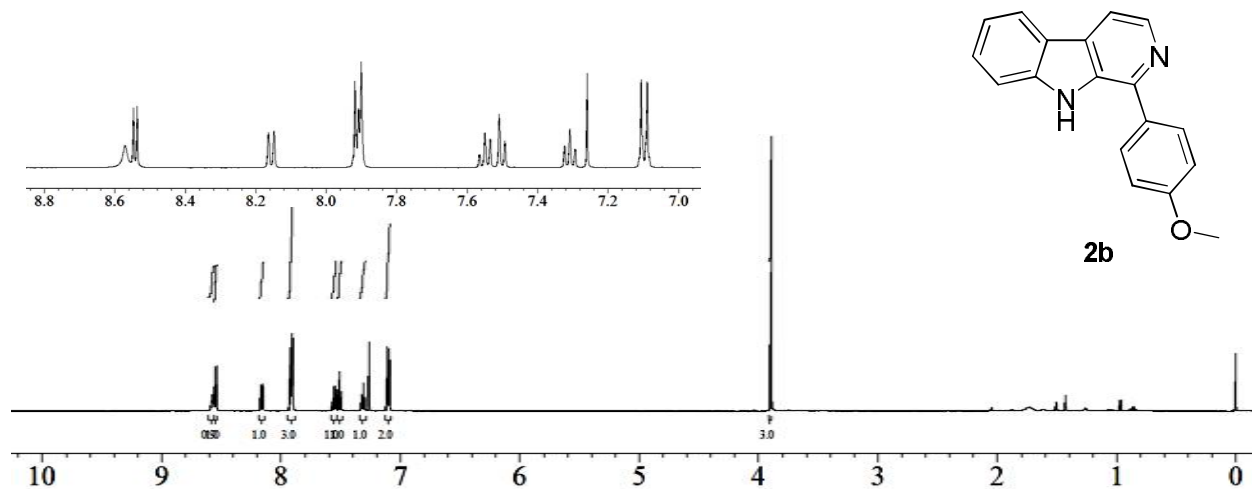


^{13}C NMR (75 MHz, DMSO- d_6)

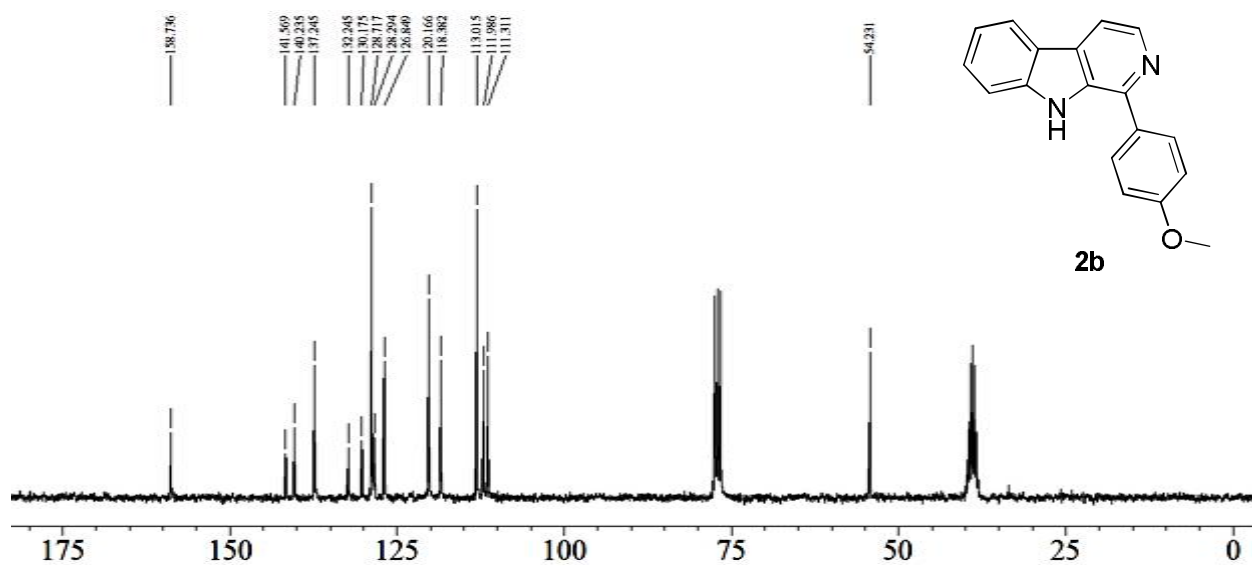


1-(4-Methoxyphenyl)-9H-pyrido[3,4-*b*]indole (2b)

¹H NMR (500 MHz, CDCl₃)

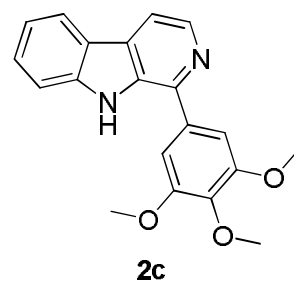
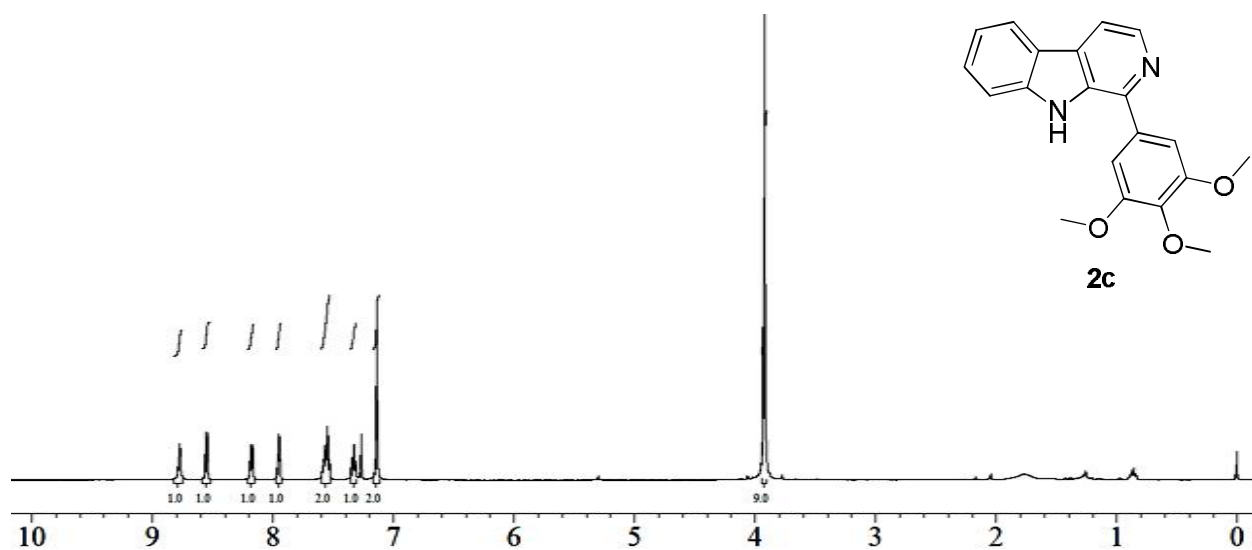


¹³C NMR (75 MHz, CDCl₃ + DMSO-*d*₆)

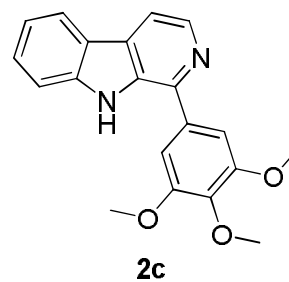
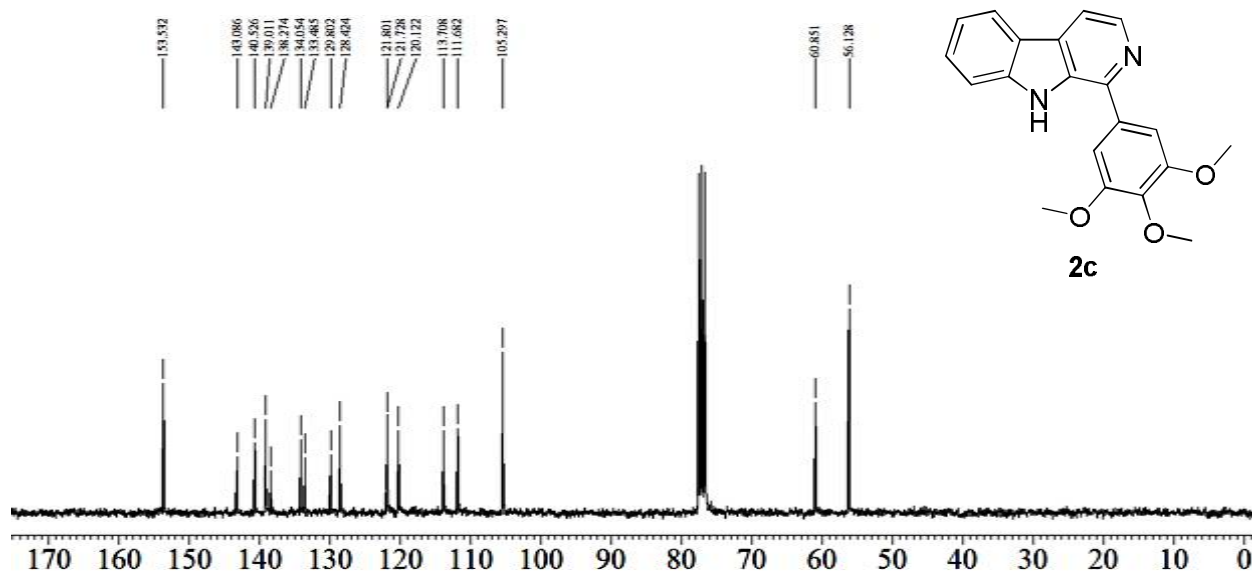


1-(3,4,5-Trimethoxyphenyl)-9H-pyrido[3,4-*b*]indole (2c)

^1H NMR (500 MHz, CDCl_3)

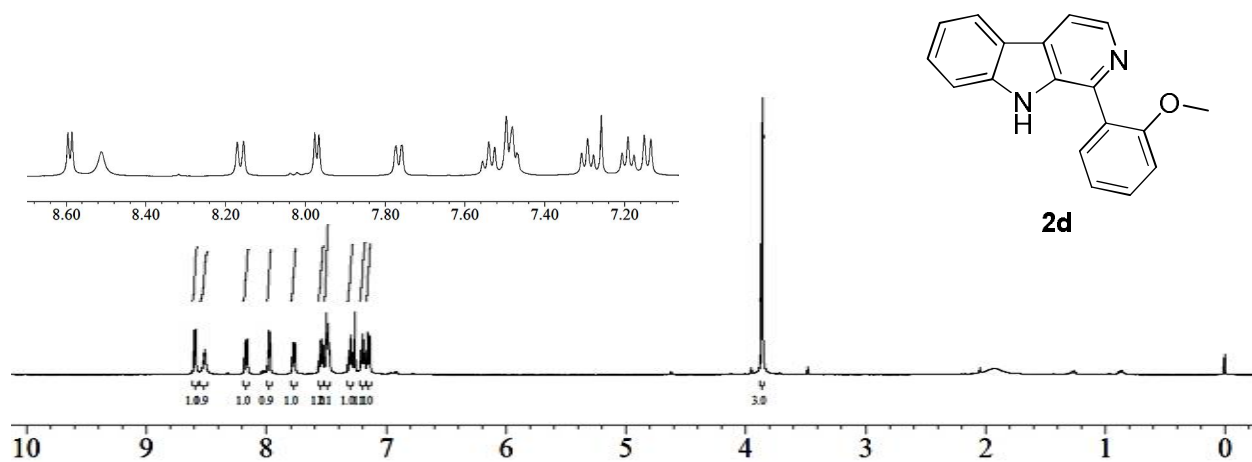


^{13}C NMR (75 MHz, CDCl_3)

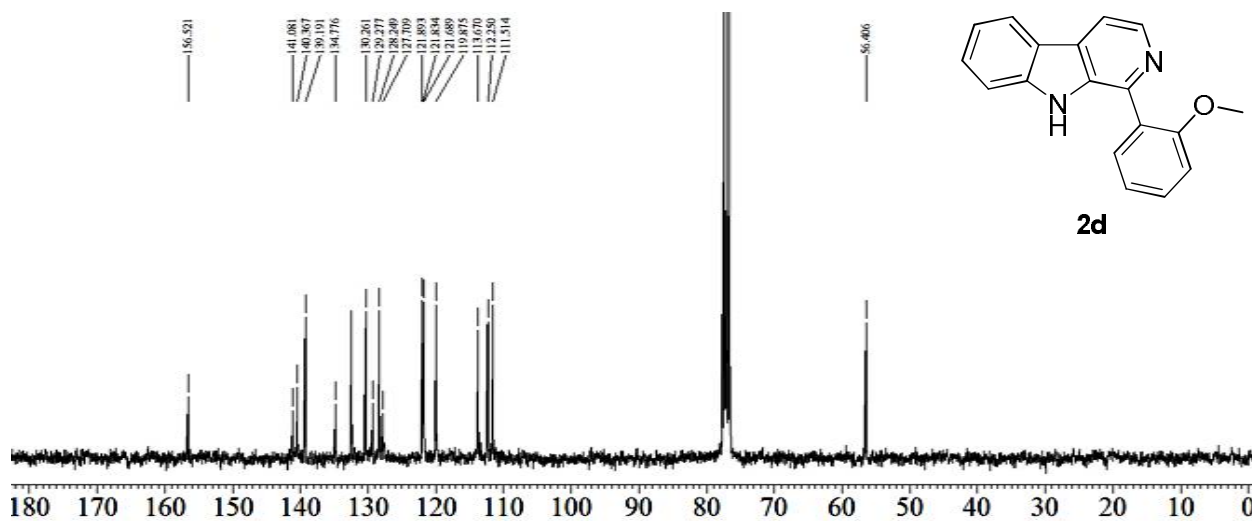


1-(2-Methoxyphenyl)-9H-pyrido[3,4-*b*]indole (2d)

¹H NMR (500 MHz, CDCl₃)

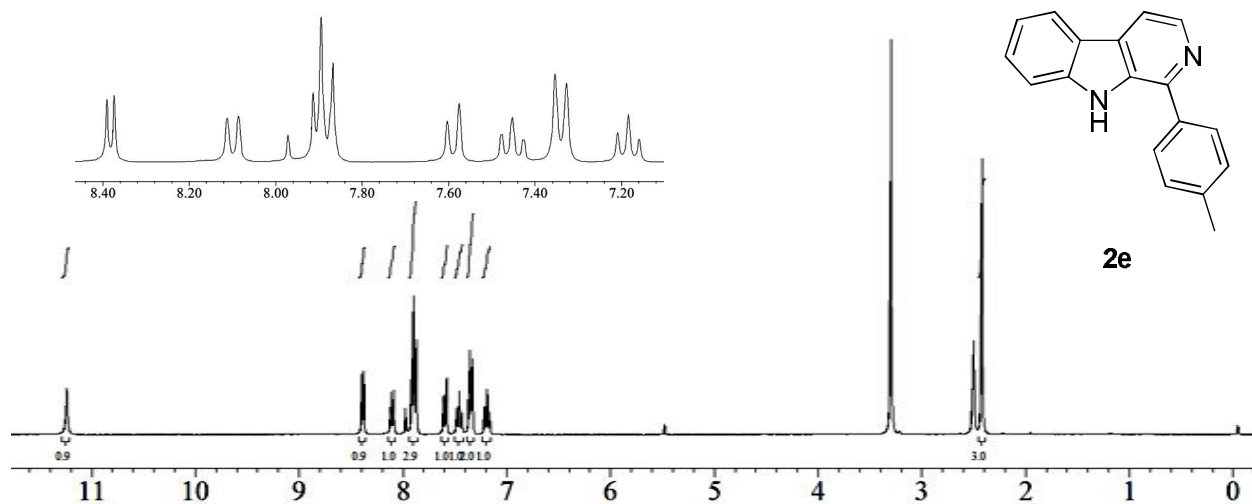


¹³C NMR (75 MHz, CDCl₃)

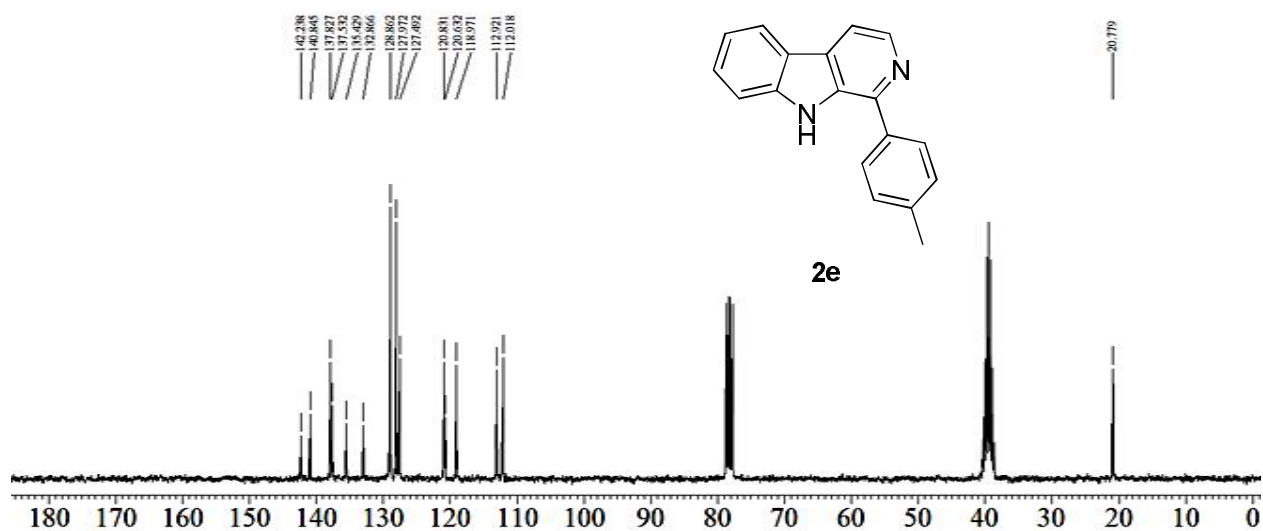


1-(*p*-Tolyl)-9*H*-pyrido[3,4-*b*]indole (2e)

¹H NMR (300 MHz, CDCl₃ + DMSO-*d*₆)

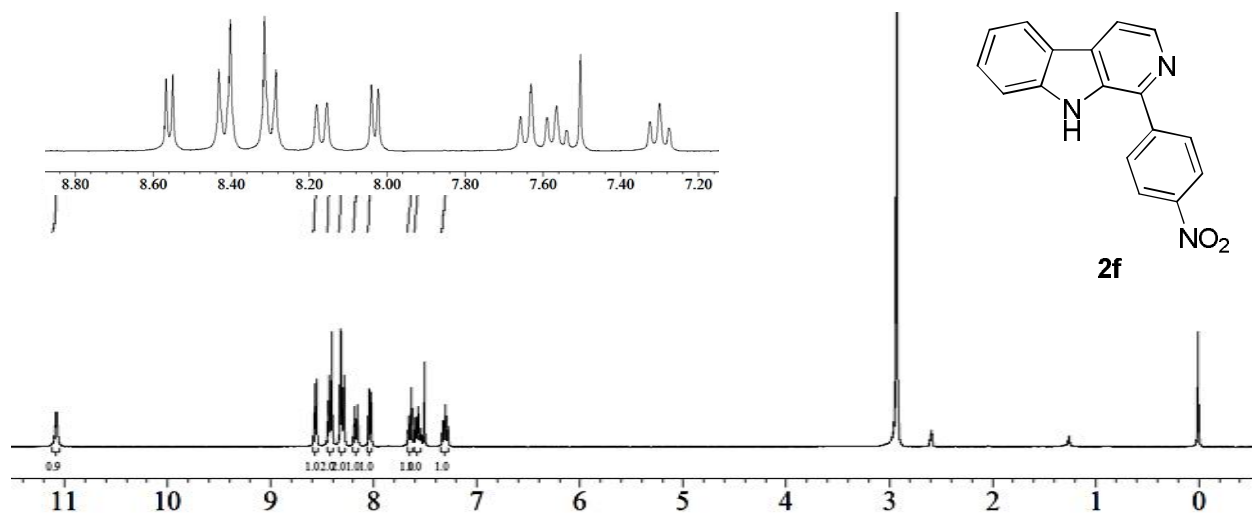


¹³C NMR (75 MHz, CDCl₃ + DMSO-*d*₆)

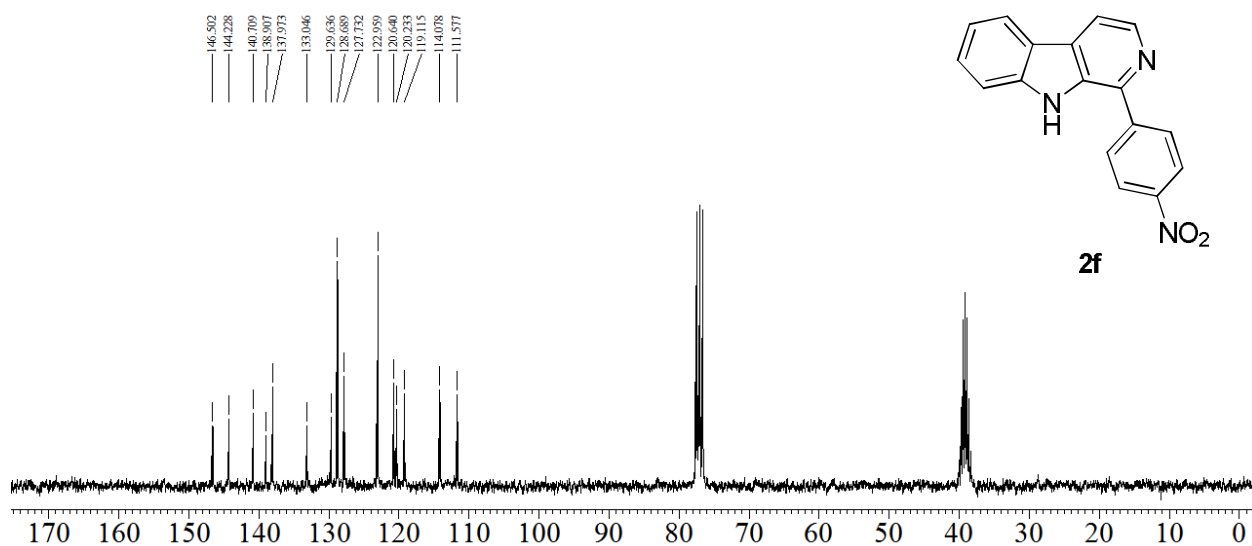


1-(4-Nitrophenyl)-9H-pyrido[3,4-*b*]indole (2f)

^1H NMR (300 MHz, CDCl_3 + $\text{DMSO}-d_6$)

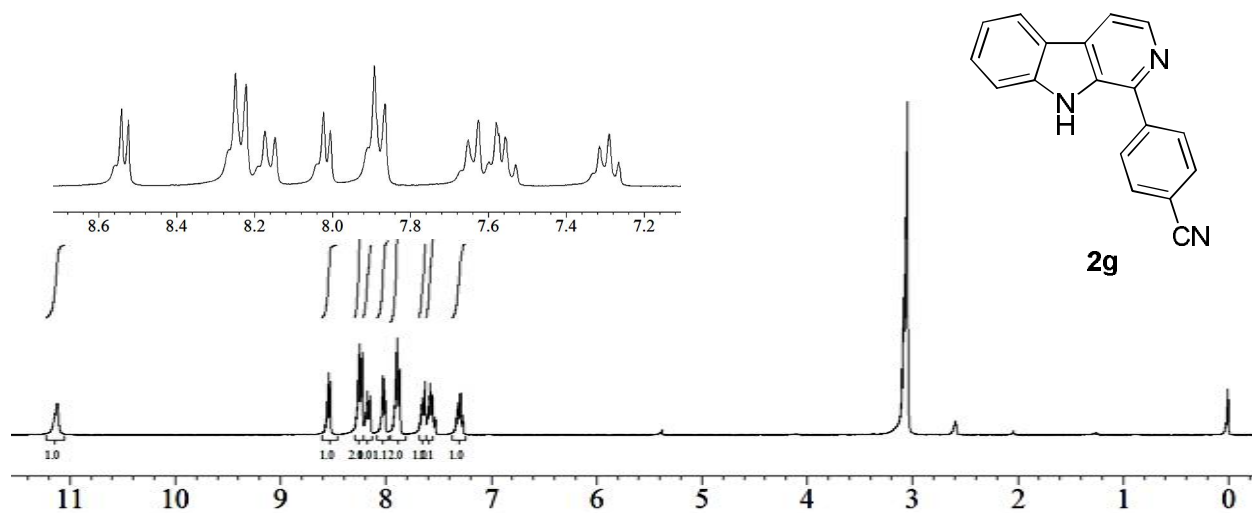


^{13}C NMR (75 MHz, CDCl_3 + $\text{DMSO}-d_6$)

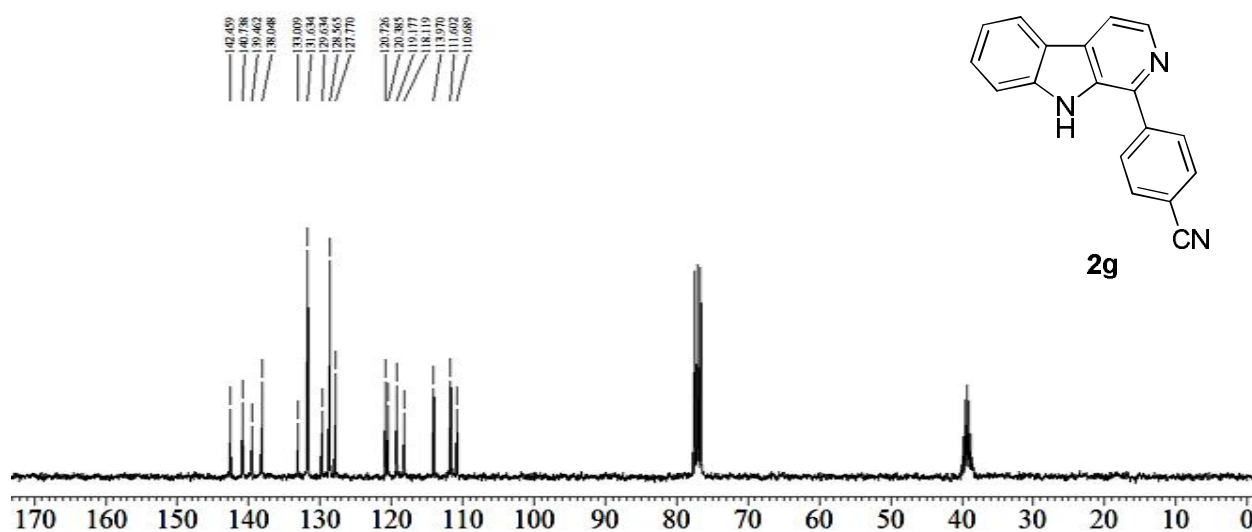


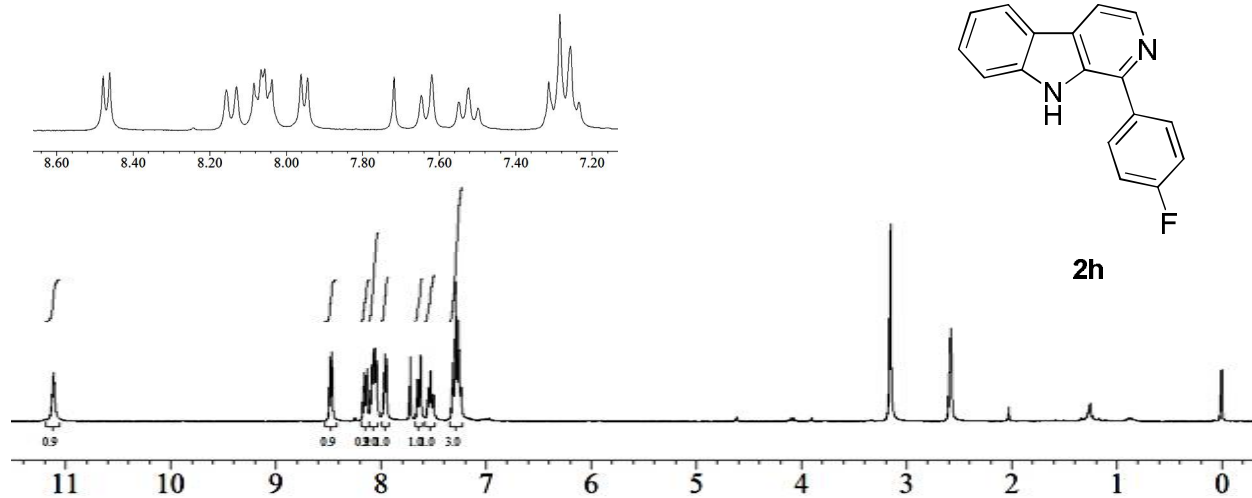
4-(9*H*-Pyrido[3,4-*b*]indol-1-yl)benzonitrile (2g)

¹H NMR (300 MHz, CDCl₃ + DMSO-*d*₆)



¹³C NMR (75 MHz, CDCl₃ + DMSO-*d*₆)



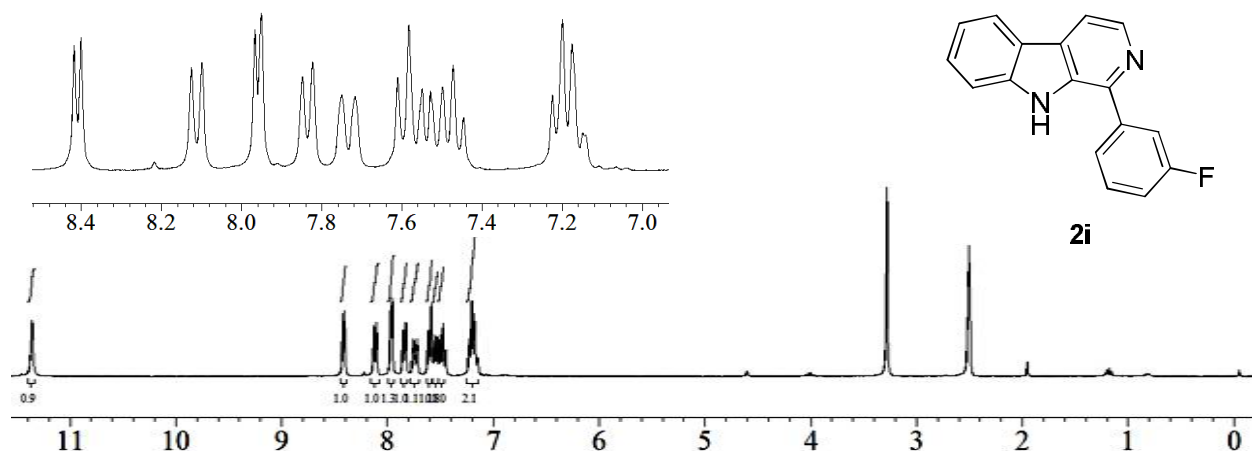
^1H NMR (300 MHz, $\text{CDCl}_3 + \text{DMSO}-d_6$)

Chemical structure of **2h** is shown in the top right corner: Fc1ccc(cc1)-c2nc3ccccc3[nH]2.

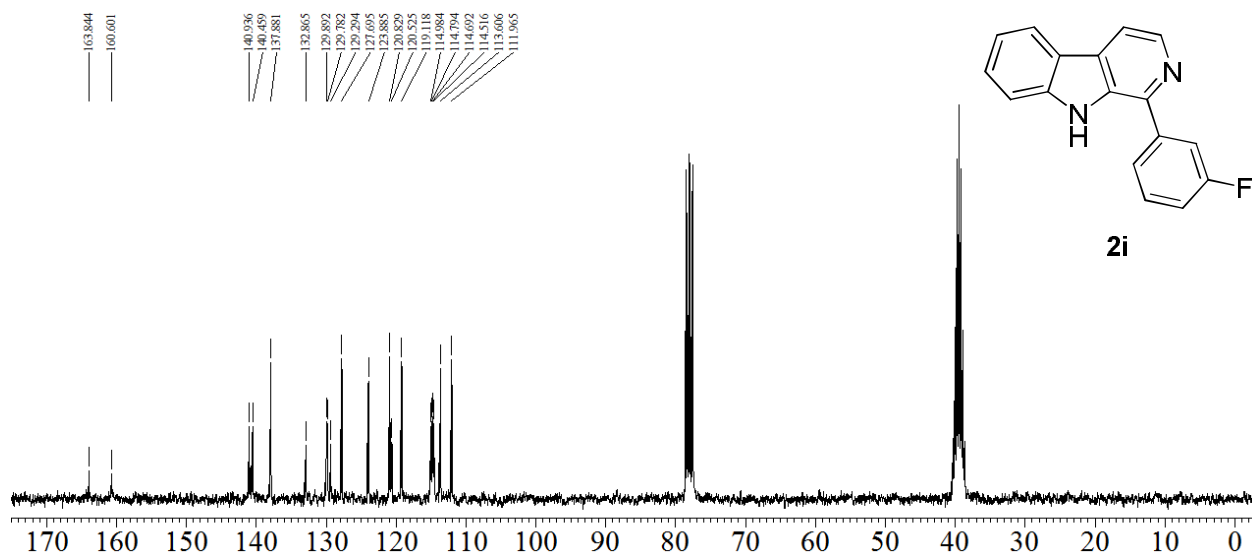
¹³C NMR spectrum (CDCl₃) of compound **2h**. The spectrum displays peaks corresponding to the aromatic and heterocyclic carbons of the molecule. Key peaks are labeled with their chemical shifts (ppm): 163.242, 159.959, 140.593, 140.307, 137.540, 133.029, 132.333, 132.333, 129.437, 129.335, 128.565, 127.027, 120.231, 118.406, 114.559, 114.282, 112.538, 111.286, and 39.000 (triplet, solvent CDCl₃).

1-(3-Fluorophenyl)-9H-pyrido[3,4-b]indole (2i)

^1H NMR (300 MHz, CDCl_3 + $\text{DMSO}-d_6$)

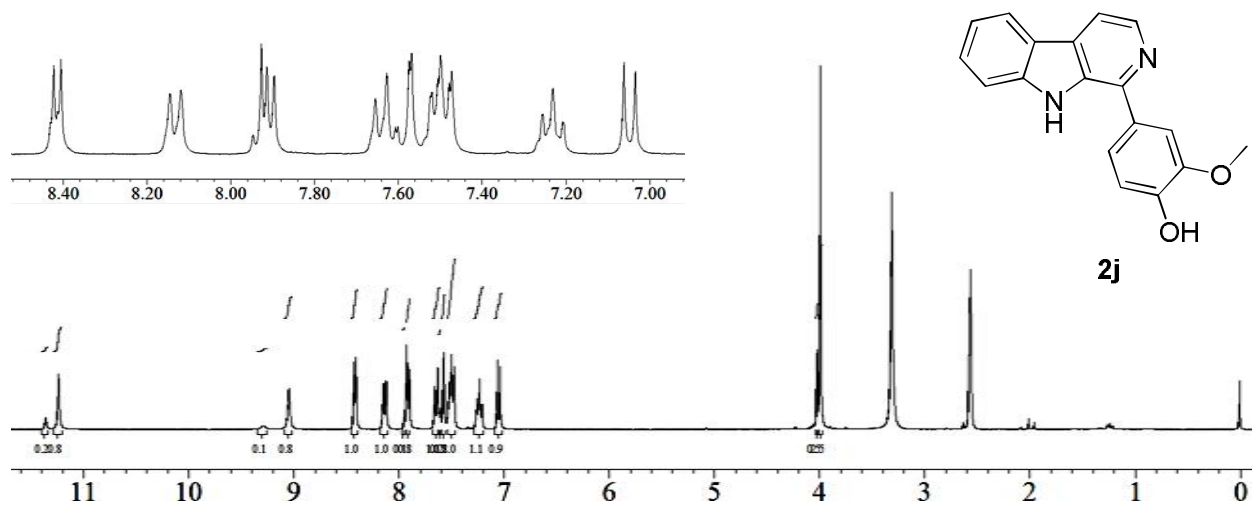


^{13}C NMR (75 MHz, CDCl_3 + $\text{DMSO}-d_6$)

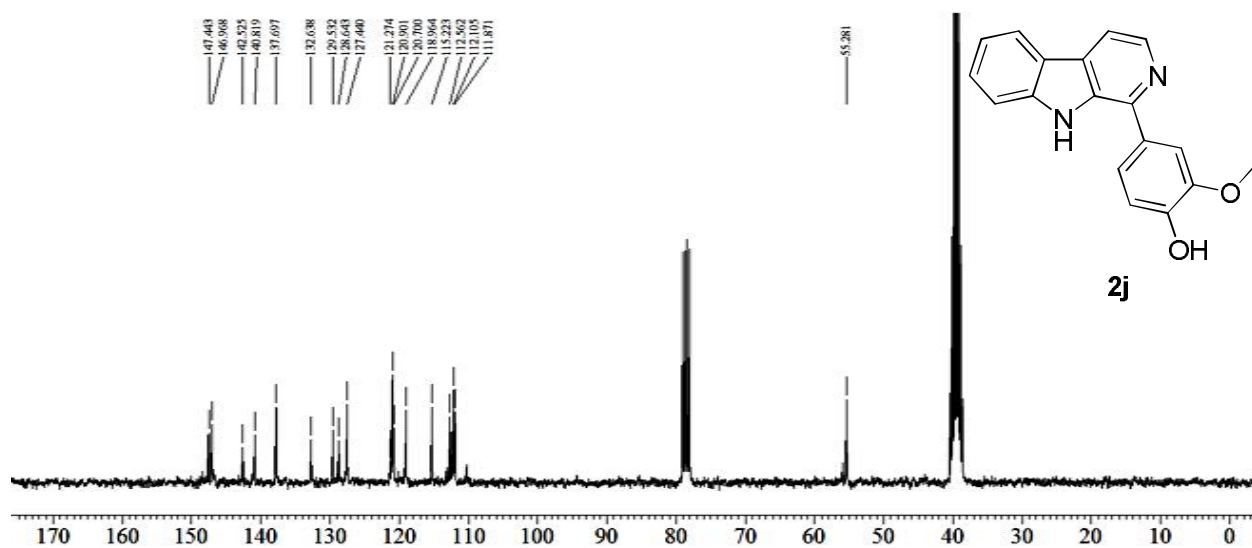


2-Methoxy-4-(9*H*-pyrido[3,4-*b*]indol-1-yl)phenol (2j)

¹H NMR (300 MHz, CDCl₃ + DMSO-*d*₆)

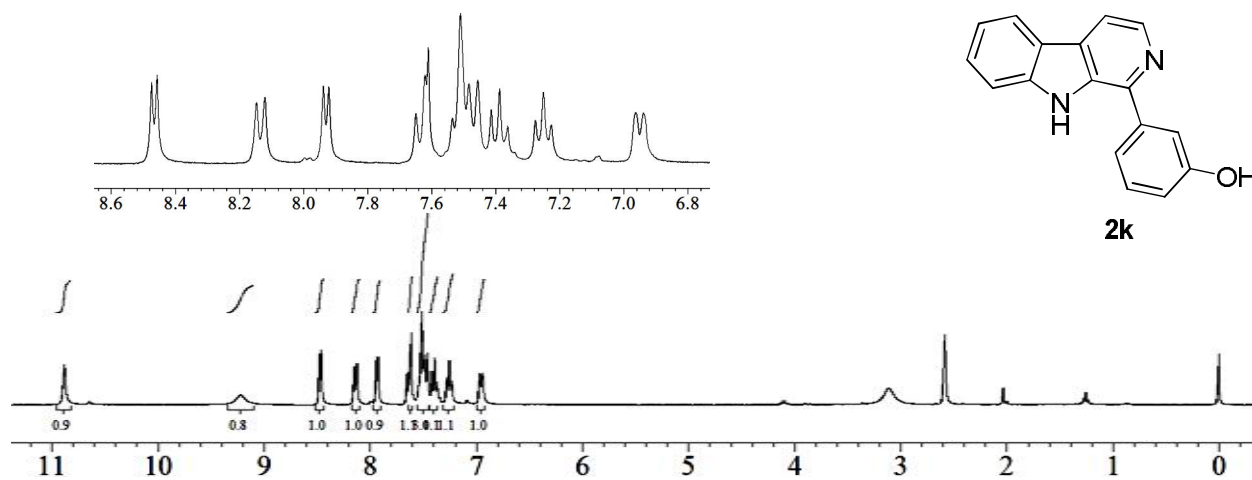


¹³C NMR (75 MHz, CDCl₃ + DMSO-*d*₆)

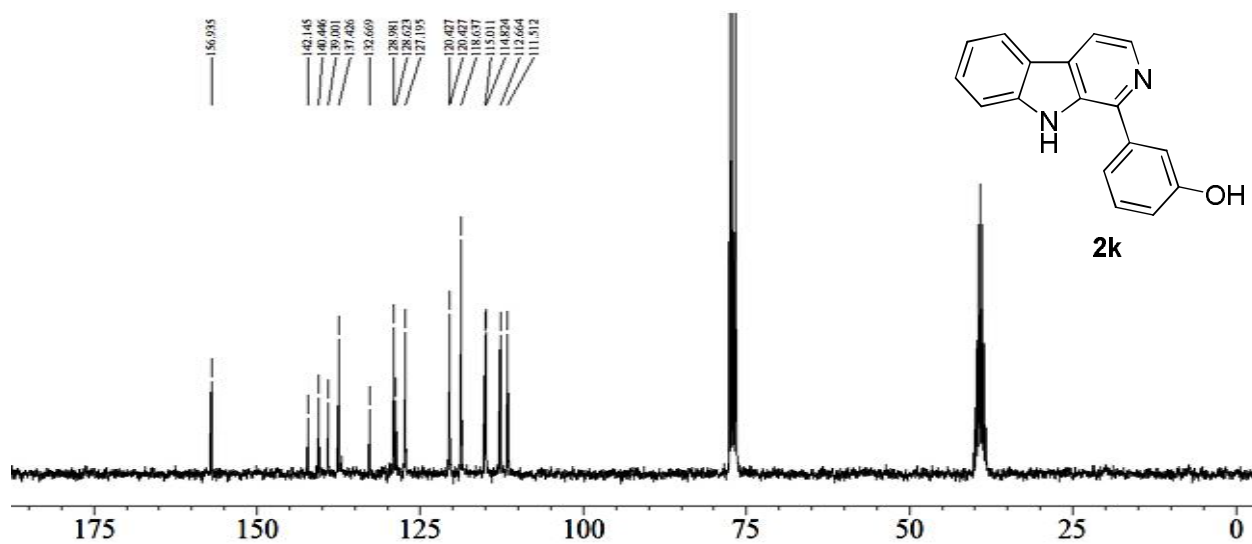


3-(9H-Pyrido[3,4-*b*]indol-1-yl)phenol (2k)

^1H NMR (300 MHz, CDCl_3 + $\text{DMSO}-d_6$)

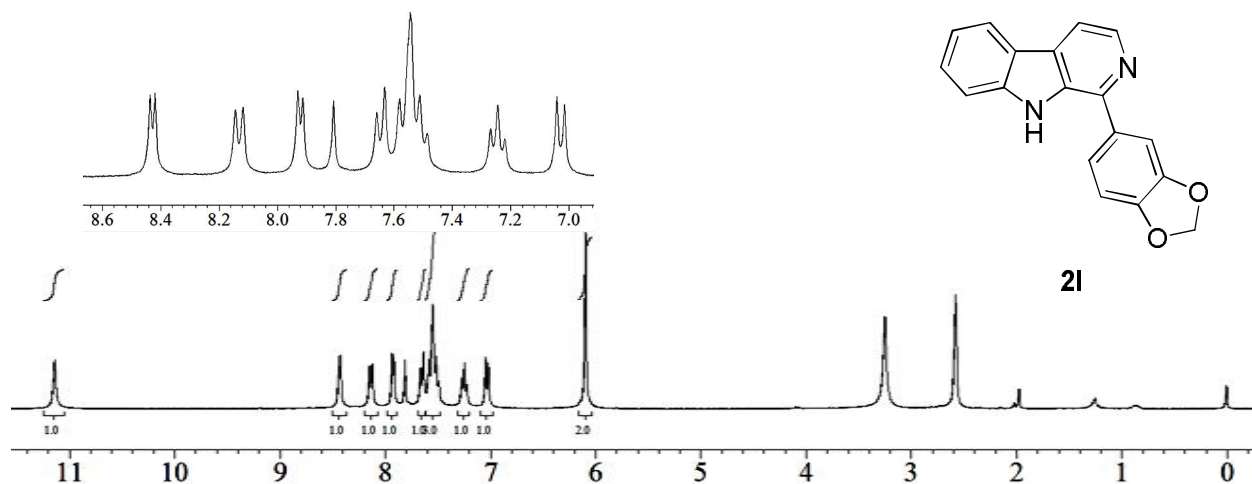


^{13}C NMR (75 MHz, CDCl_3 + $\text{DMSO}-d_6$)

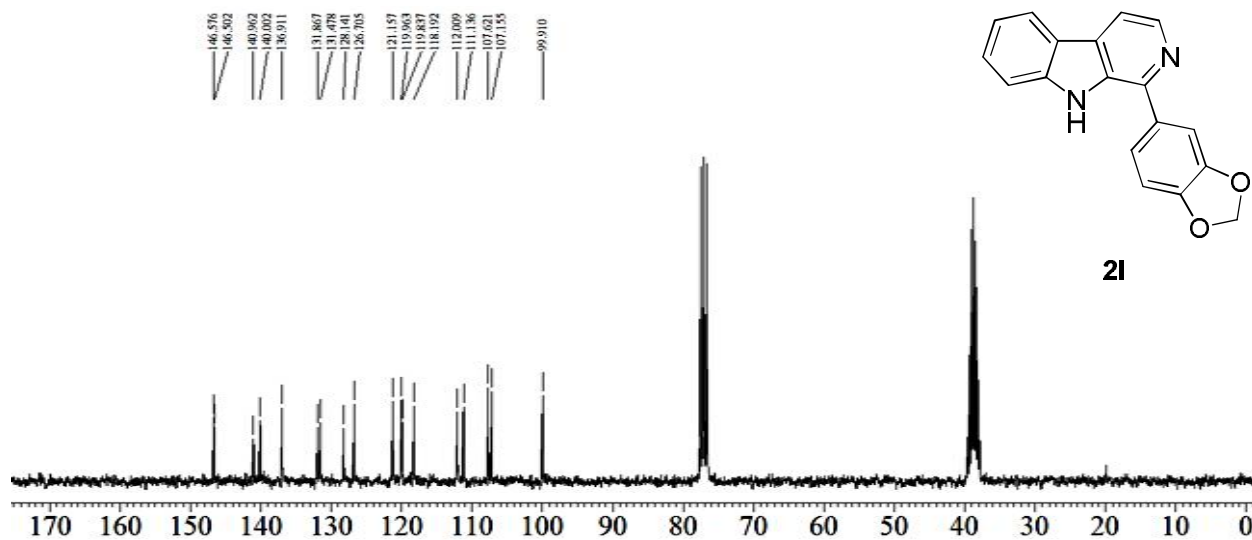


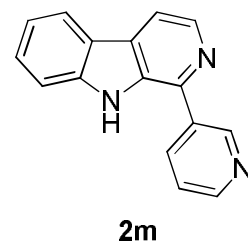
1-(Benzo[d][1,3]dioxol-5-yl)-9H-pyrido[3,4-b]indole (2l)

¹H NMR (500 MHz, CDCl₃ + DMSO-d₆)



¹³C NMR (75 MHz, CDCl₃ + DMSO-d₆)



^1H NMR (300 MHz, $\text{CDCl}_3 + \text{DMSO}-d_6$)

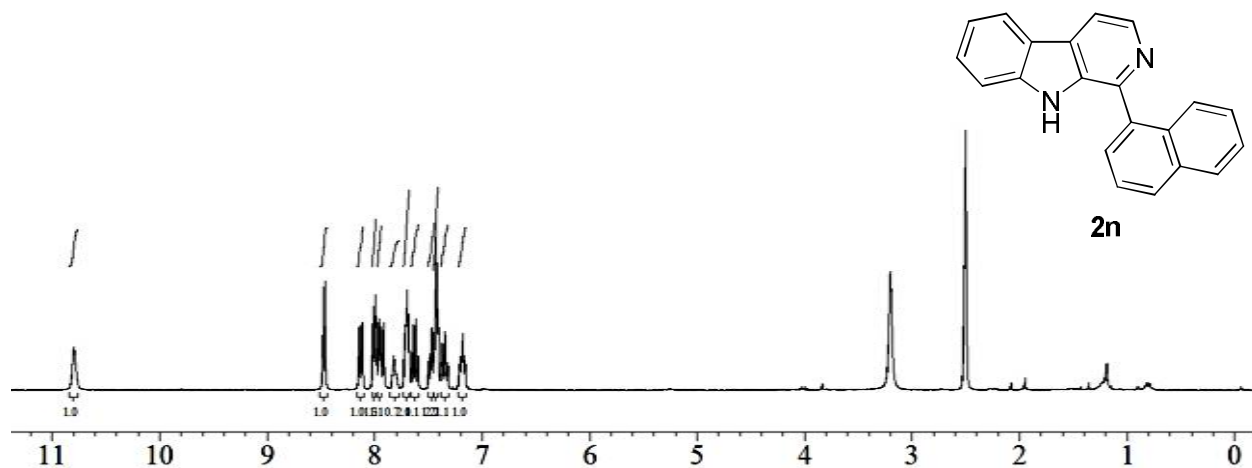
Chemical structure of **2m** (2-(1H-indol-3-yl)pyridine) is shown in the top right corner.

The ¹³C NMR spectrum displays the following chemical shifts (ppm):

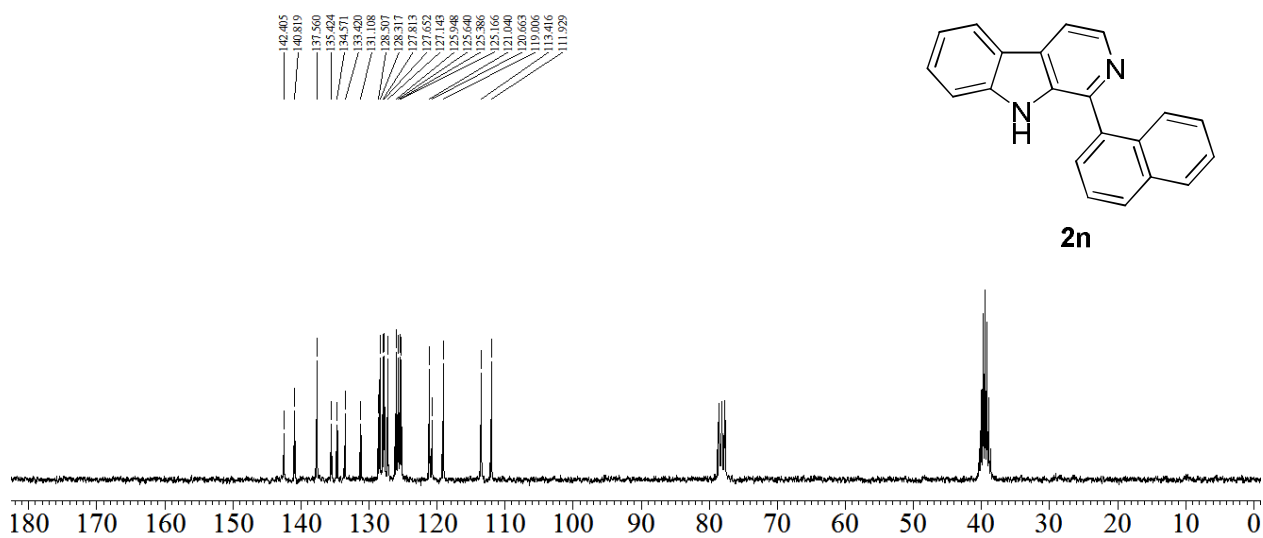
- 149.303
- 148.959
- 141.111
- 139.266
- 138.549
- 137.599
- 133.073
- 133.186
- 129.329
- 128.729
- 123.803
- 121.646
- 120.639
- 119.597
- 114.415
- 112.351

1-(Naphthalen-1-yl)-9H-pyrido[3,4-*b*]indole (2n)

¹H NMR (300 MHz, CDCl₃ + DMSO-*d*₆)

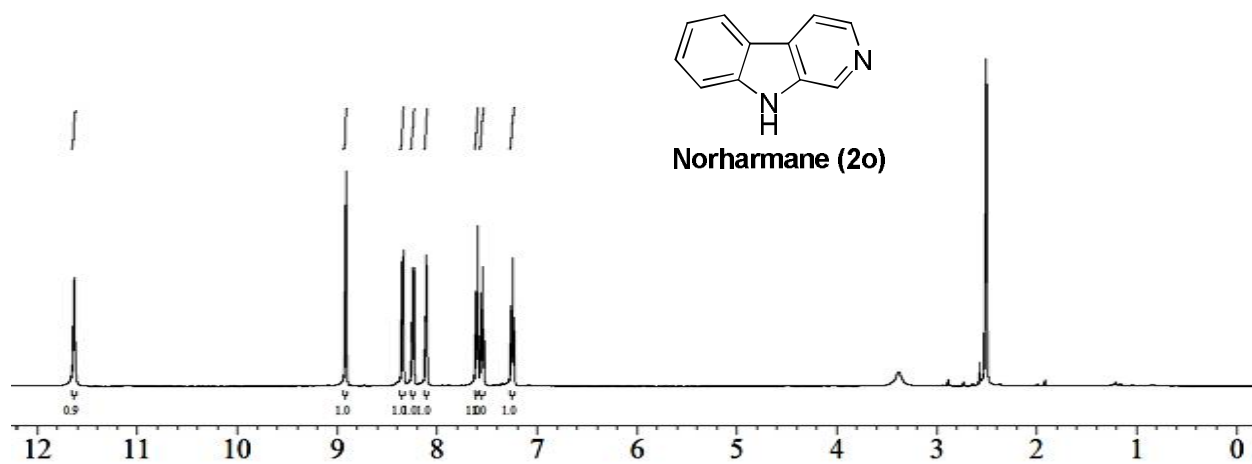


¹³C NMR (75 MHz, CDCl₃ + DMSO-*d*₆)

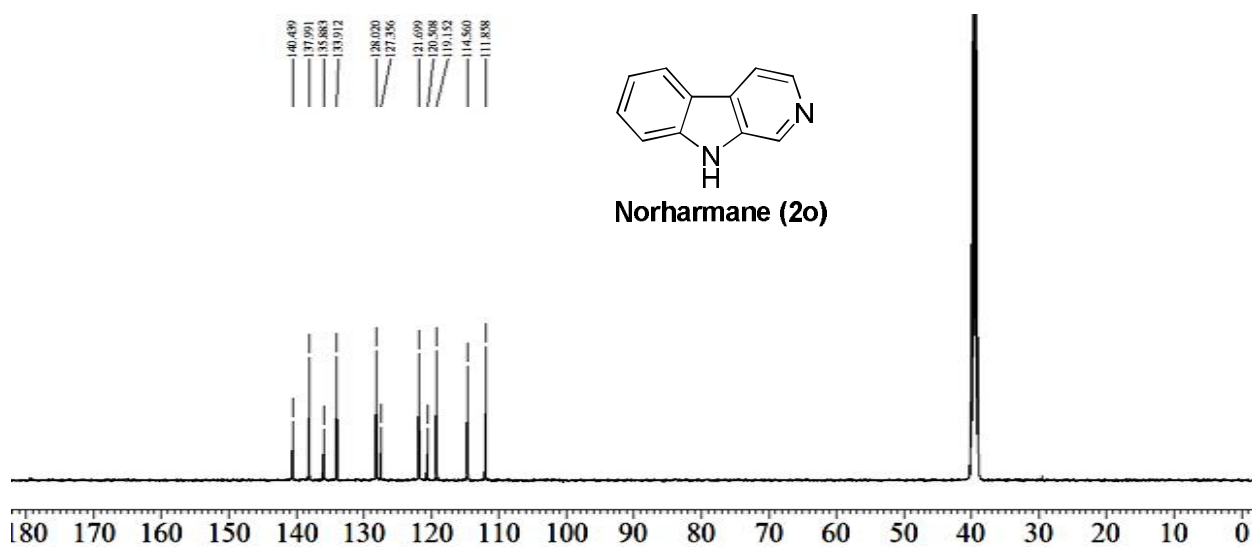


Norharmaline (2o)

^1H NMR (500 MHz, $\text{DMSO}-d_6$)

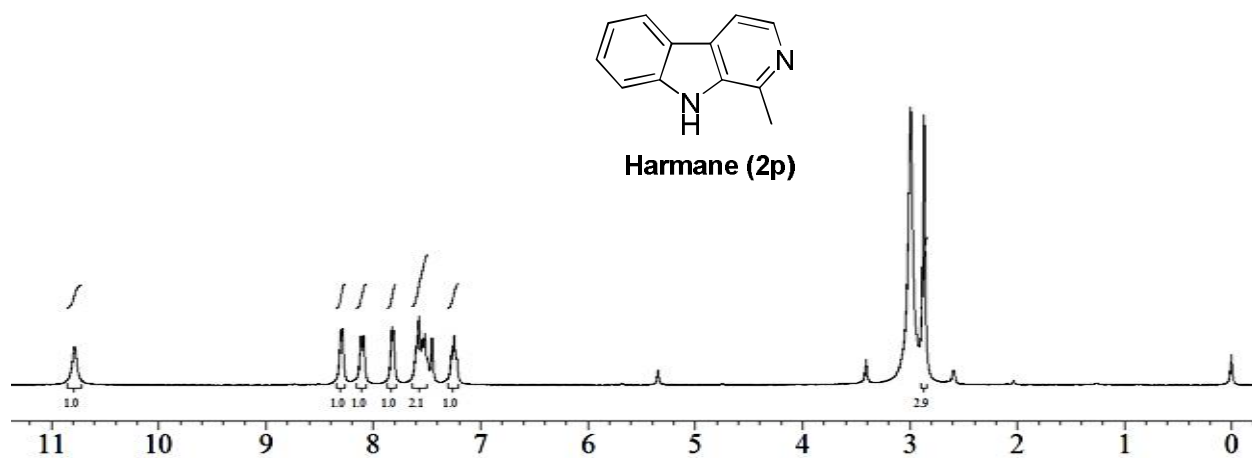


^{13}C NMR (125 MHz, $\text{DMSO}-d_6$)

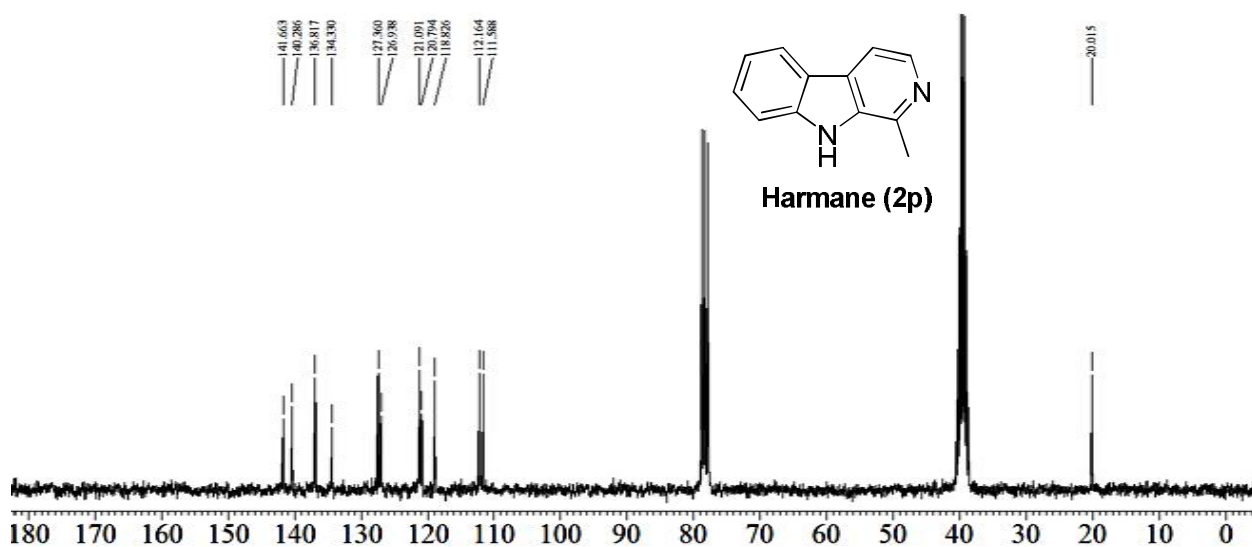


Harmaline (2p):

^1H NMR (300 MHz, CDCl_3 + $\text{DMSO}-d_6$)

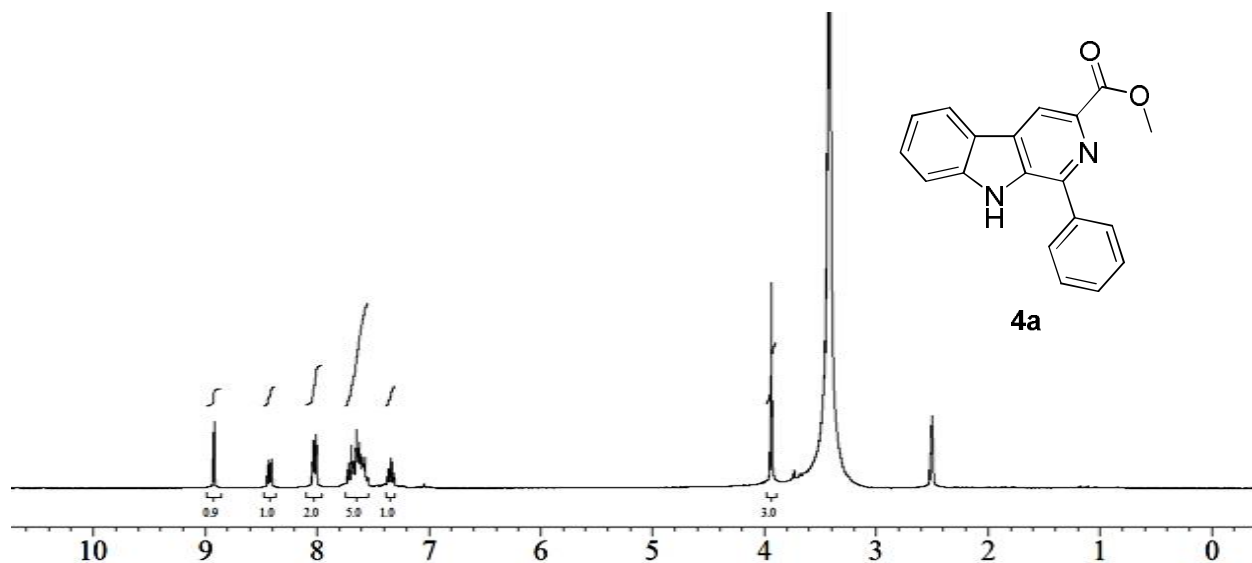


^{13}C NMR (75 MHz, CDCl_3 + $\text{DMSO}-d_6$)

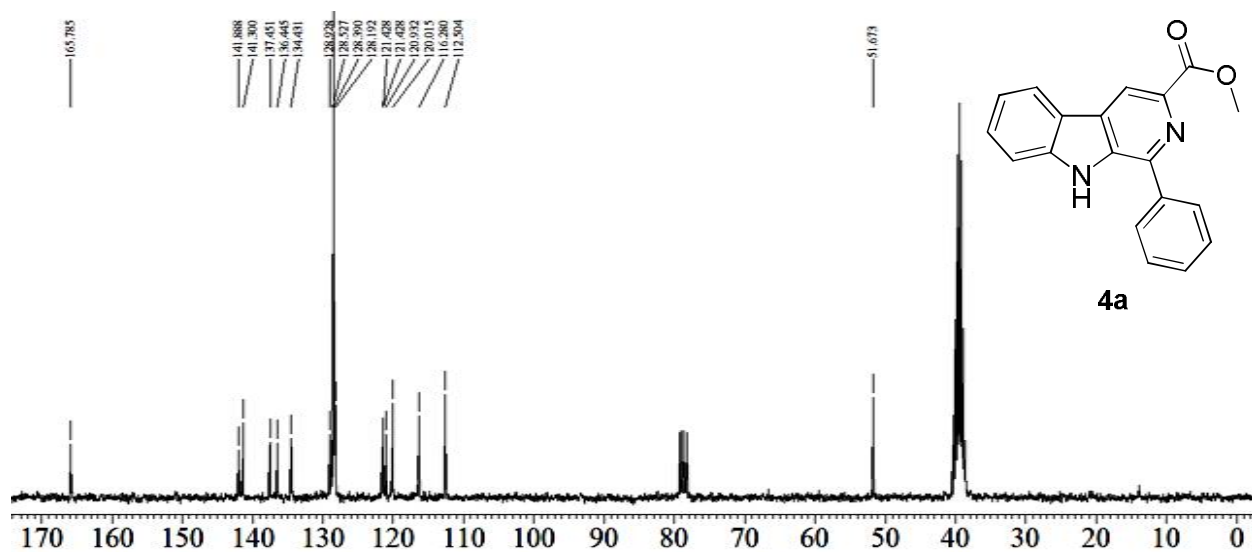


Methyl 1-phenyl-9H-pyrido [3, 4-*b*] indole-3-carboxylate (4a)

¹H NMR (300 MHz, DMSO-*d*₆)

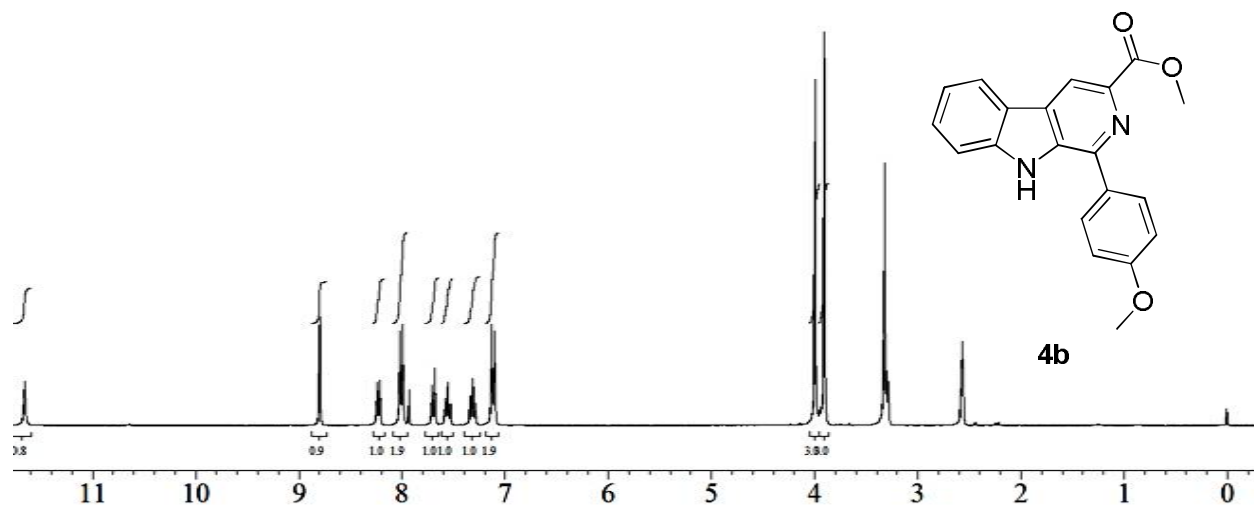


¹³C NMR (75 MHz, CDCl₃ + DMSO-*d*₆)

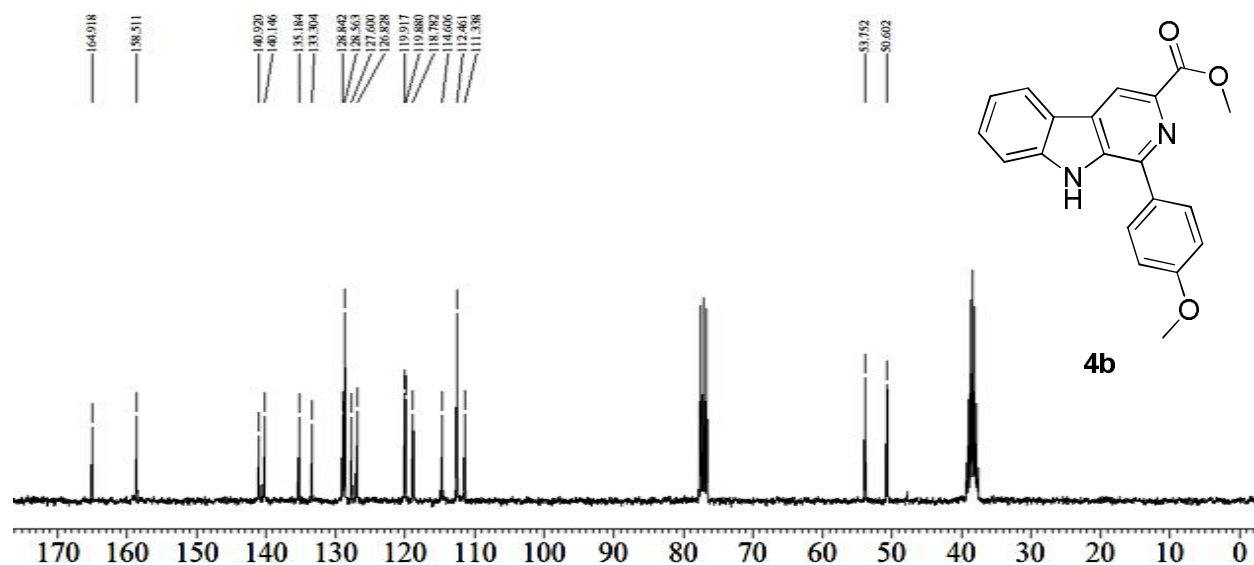


Methyl 1-(4-methoxyphenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (4b)

^1H NMR (300 MHz, CDCl_3 + $\text{DMSO}-d_6$)

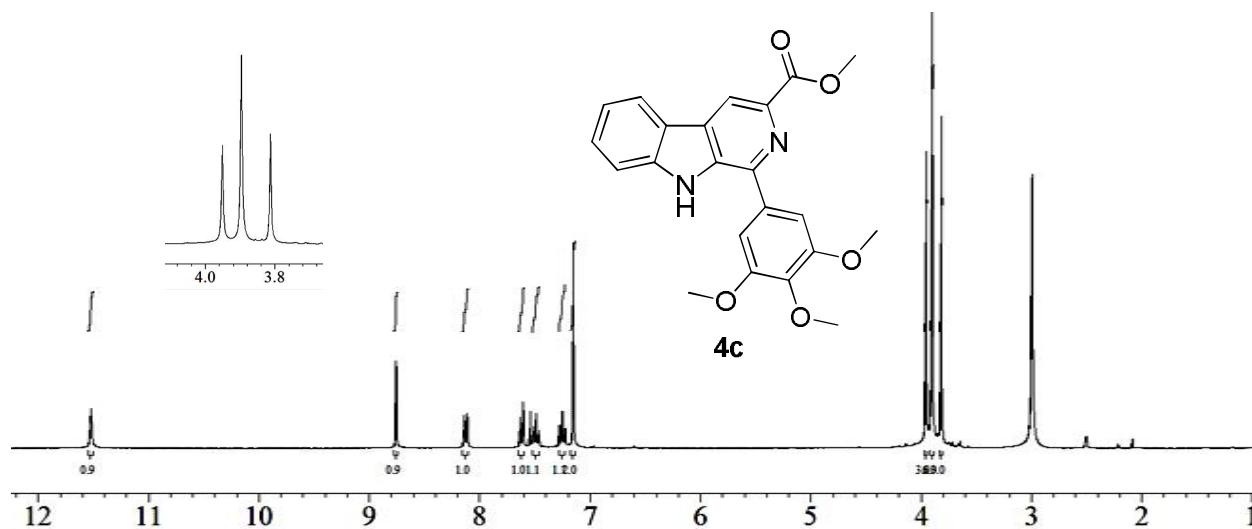


^{13}C NMR (75 MHz, CDCl_3 + $\text{DMSO}-d_6$)

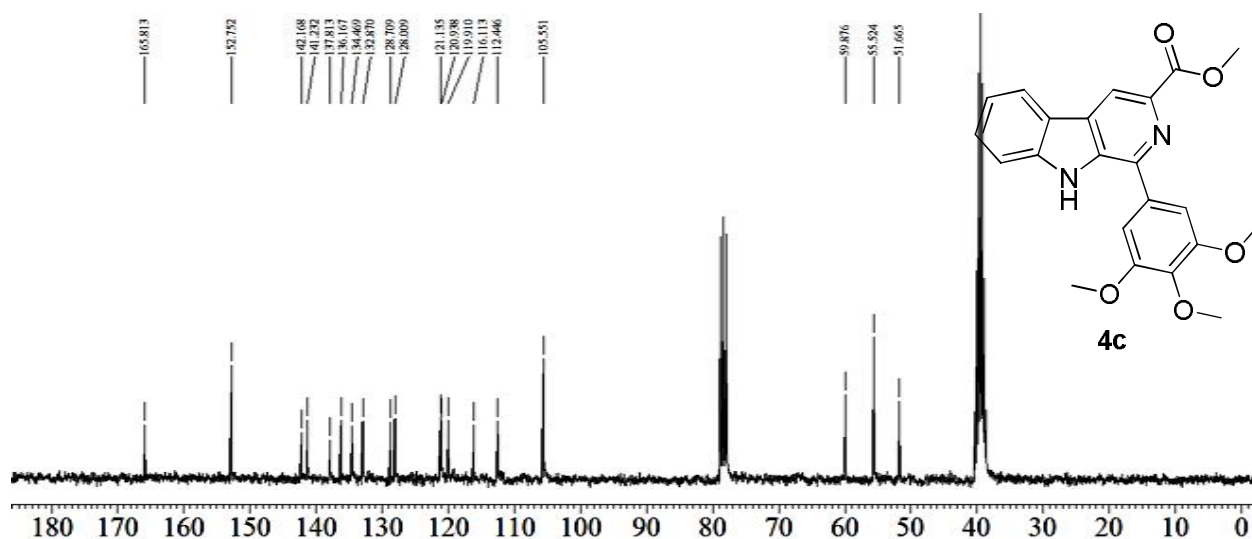


Methyl 1-(3,4,5-trimethoxyphenyl)-9H-pyrido[3,4-*b*]indole-3-carboxylate (4c)

^1H NMR (300 MHz, CDCl_3 + $\text{DMSO}-d_6$)

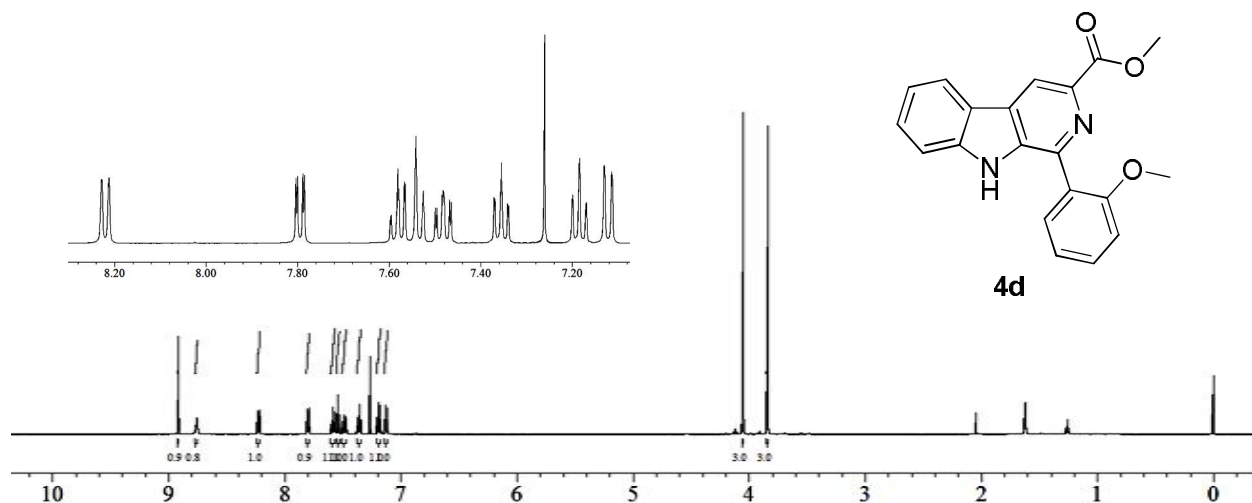


^{13}C NMR (75 MHz, CDCl_3 + $\text{DMSO}-d_6$)

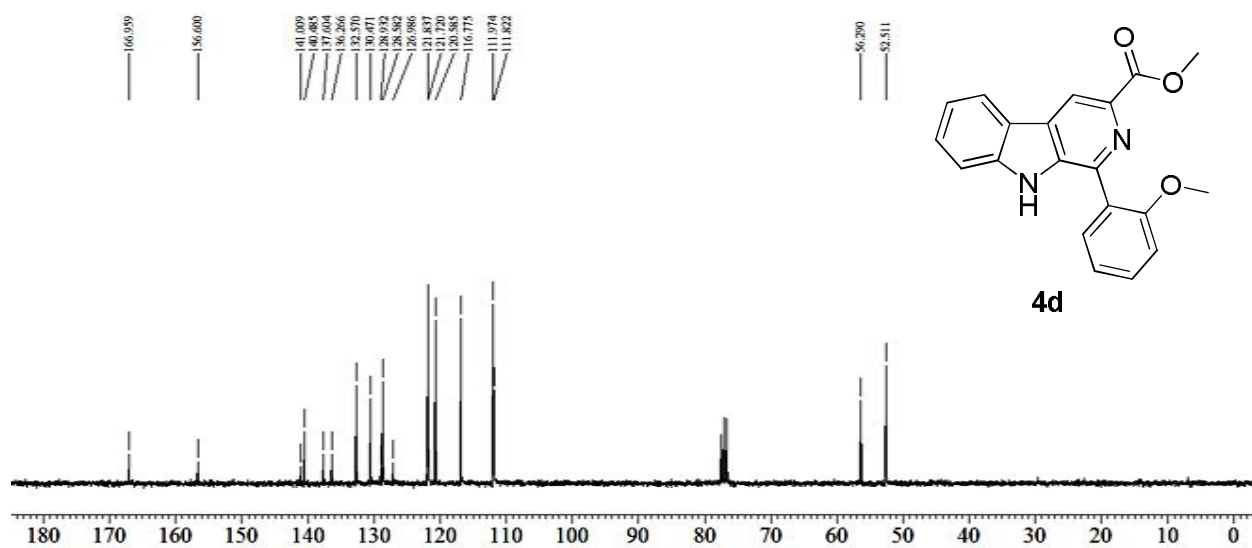


Methyl 1-(2-methoxyphenyl)-9H-pyrido[3,4-b]indole-3-carboxylate (4d)

^1H NMR (500 MHz, CDCl_3)

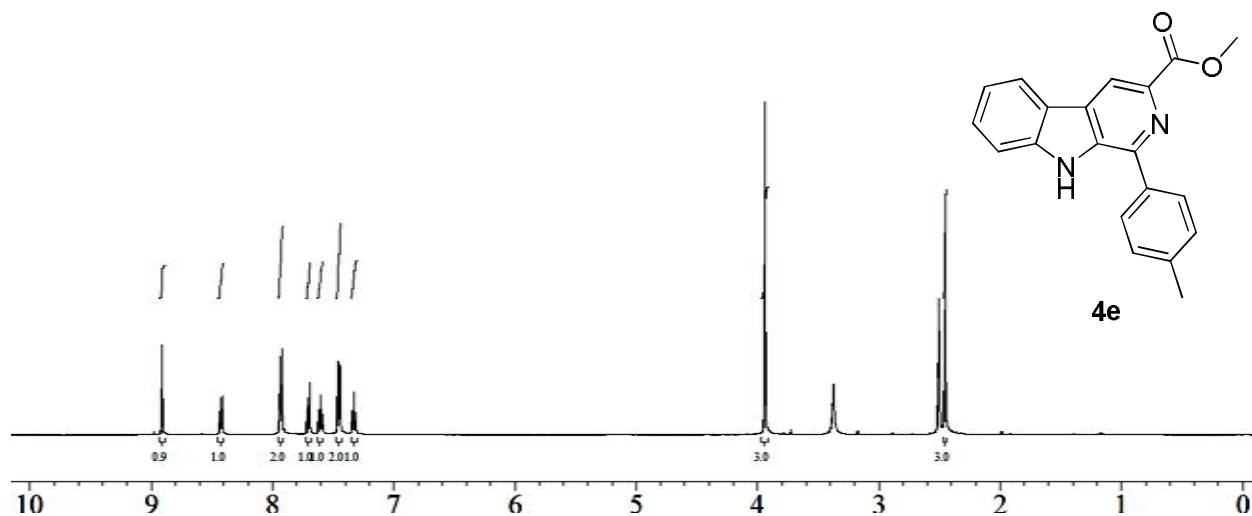


^{13}C NMR (75 MHz, CDCl_3)

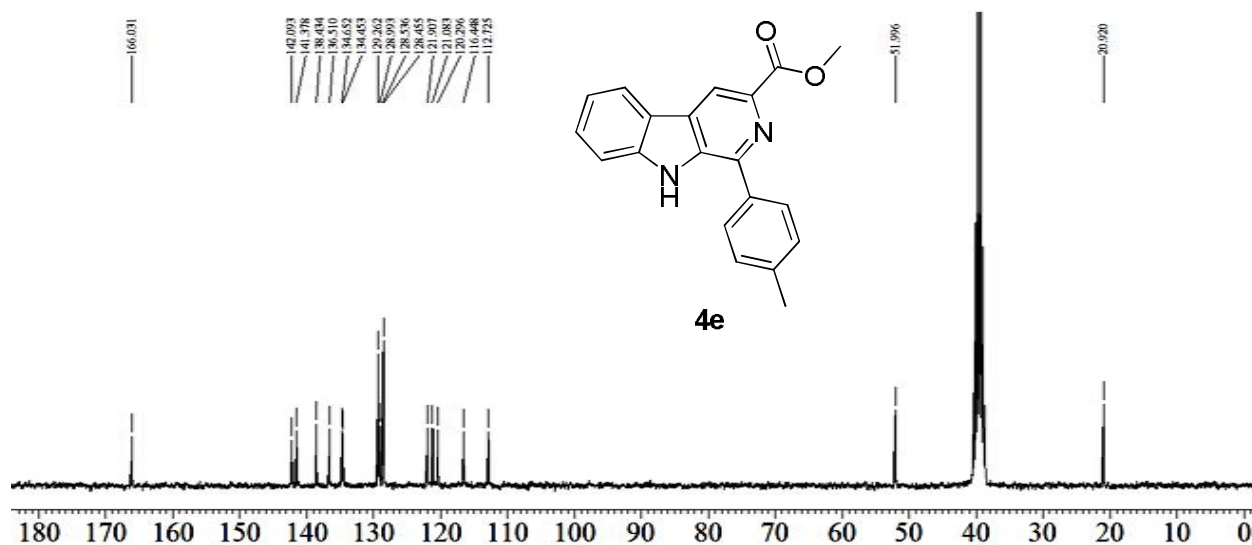


Methyl 1-(p-tolyl)-9H-pyrido[3,4-b]indole-3-carboxylate (4e)

^1H NMR (500 MHz, $\text{DMSO}-d_6$)

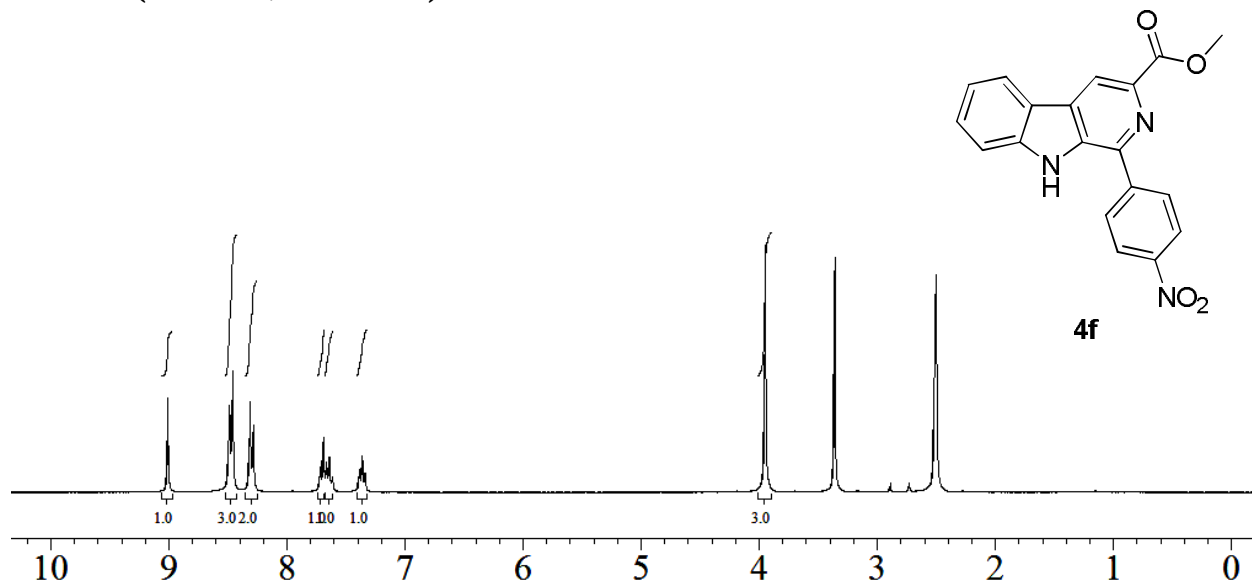


^{13}C NMR (500 MHz, $\text{DMSO}-d_6$)

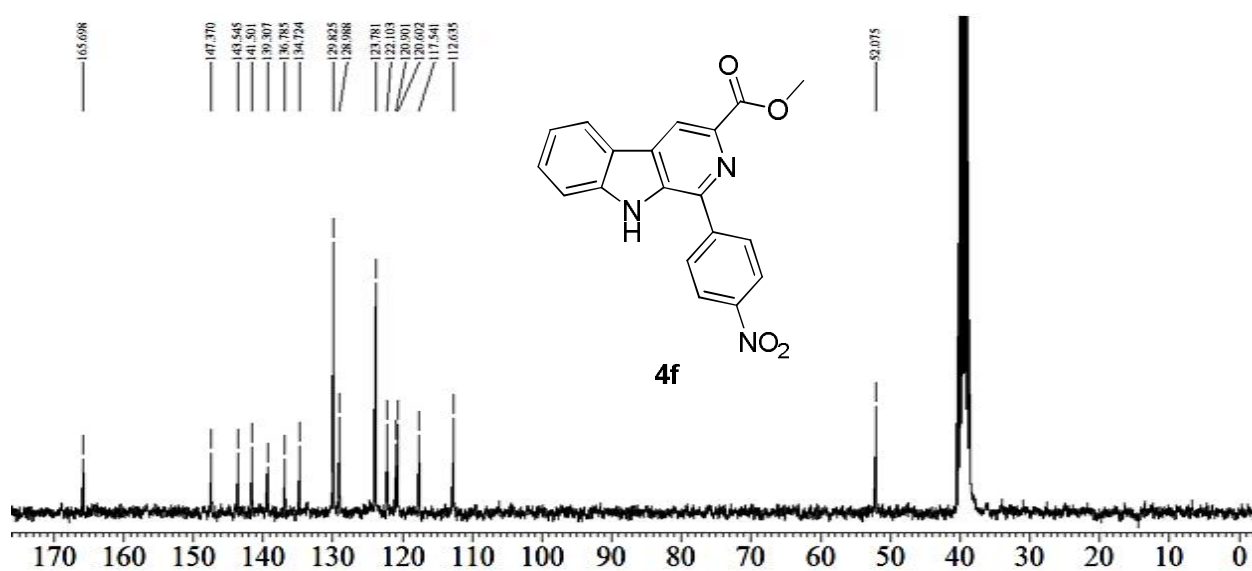


Methyl 1-(4-nitrophenyl)-9H-pyrido[3,4-*b*]indole-3-carboxylate (4f)

¹H NMR (300 MHz, DMSO-*d*₆)

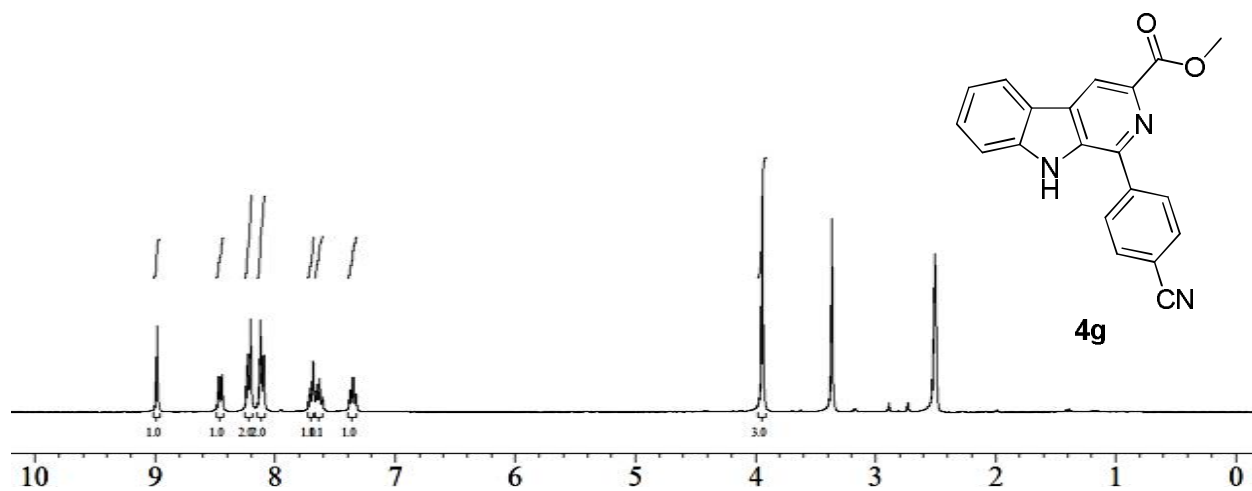


¹³C NMR (75 MHz, DMSO-*d*₆)

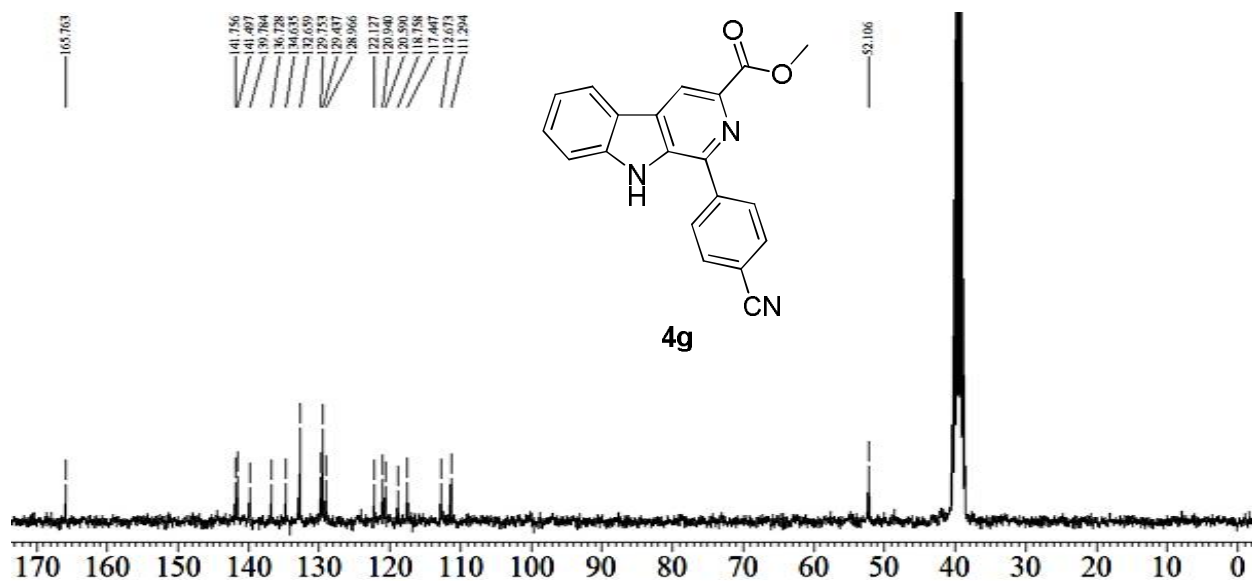


Methyl 1-(4-cyanophenyl)-9H-pyrido[3,4-*b*]indole-3-carboxylate (4g)

¹H NMR (300 MHz, DMSO-*d*₆)

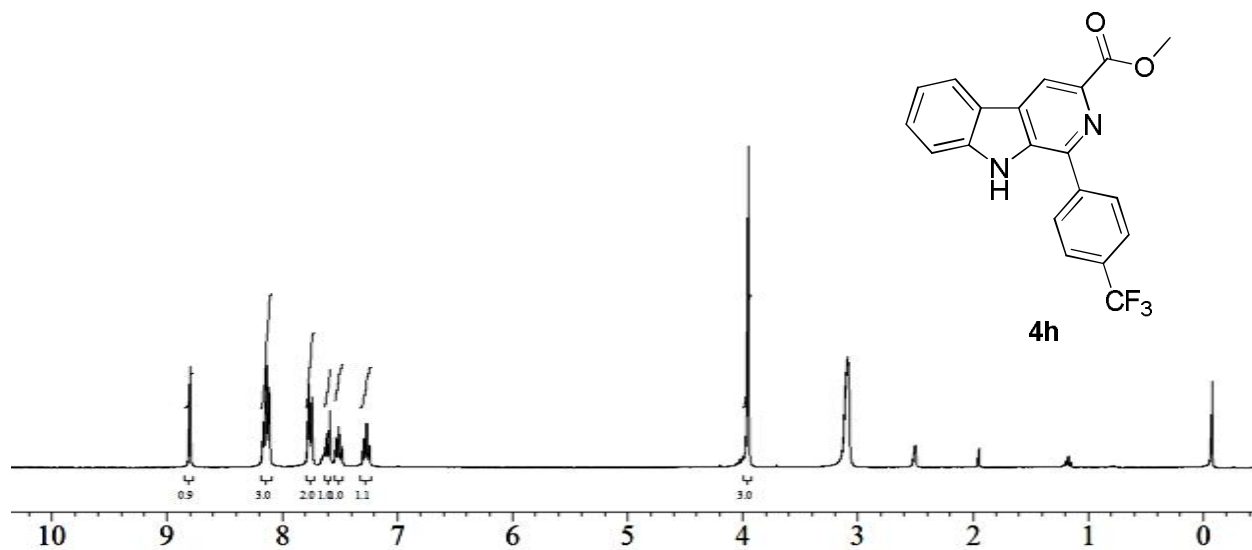


¹³C NMR (75 MHz, DMSO-*d*₆)

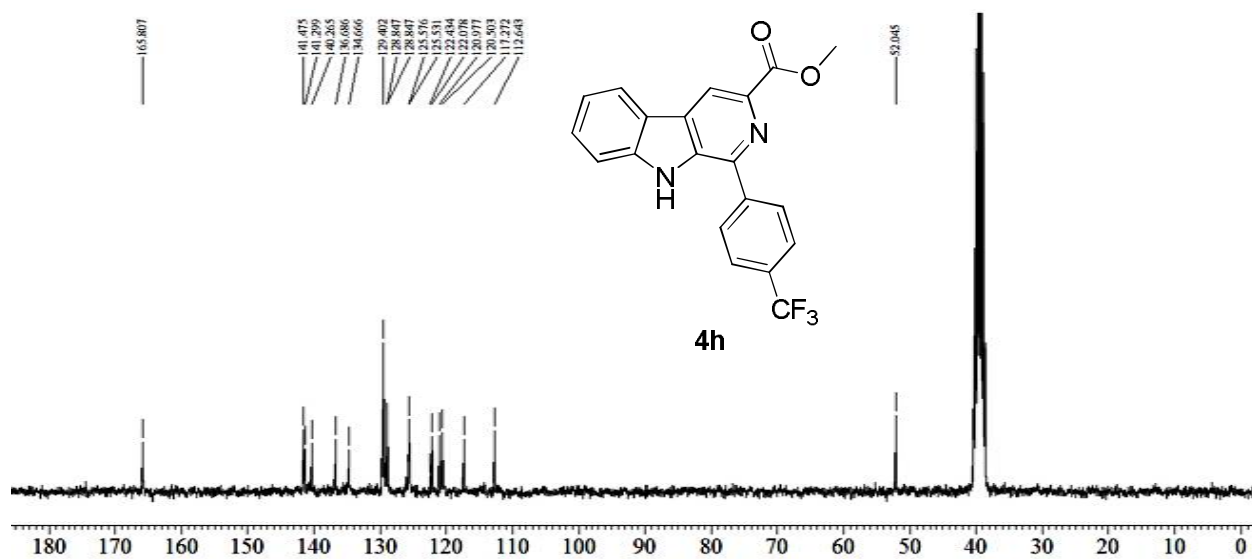


Methyl 1-(4-(trifluoromethyl)phenyl)-9H-pyrido[3,4-*b*]indole-3-carboxylate (4h)

¹H NMR (300 MHz, DMSO-*d*₆)

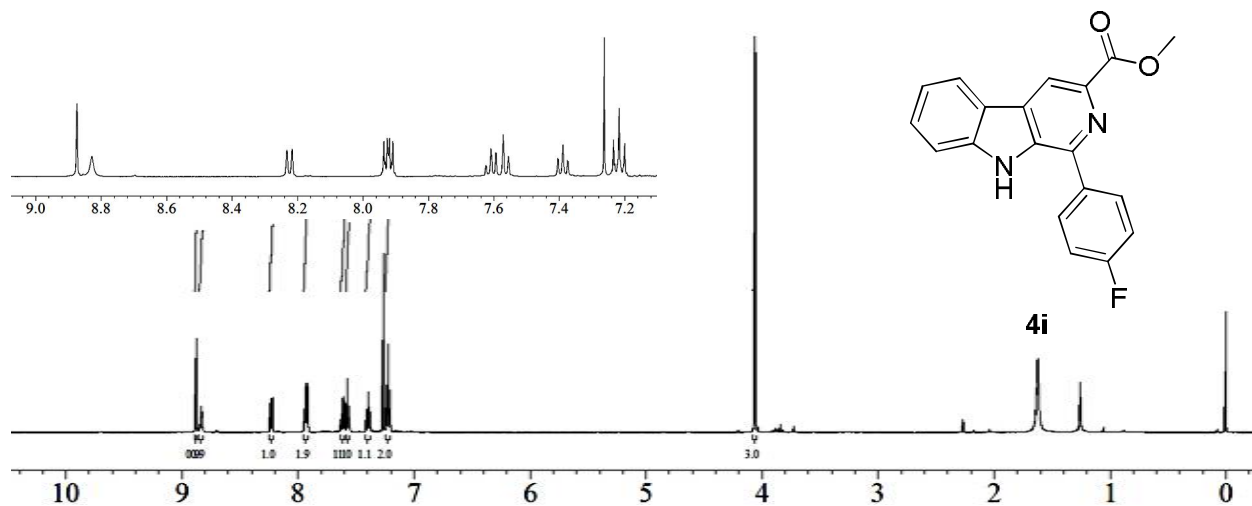


¹³C NMR (75 MHz, DMSO-*d*₆)

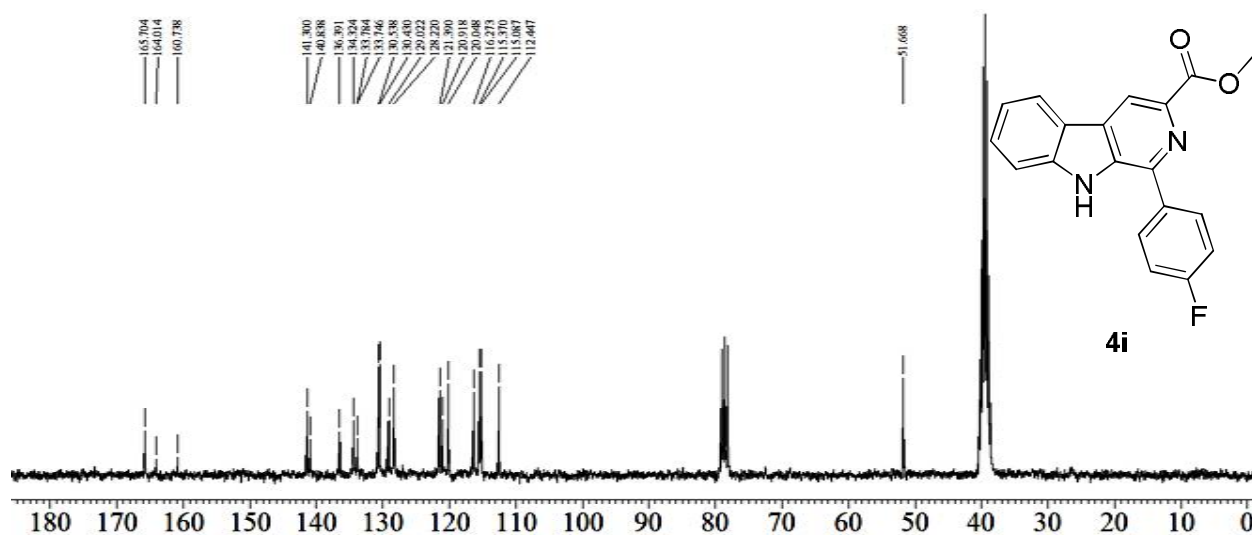


Methyl 1-(4-fluorophenyl)-9H-pyrido[3,4-*b*]indole-3-carboxylate (4i)

^1H NMR (500 MHz, CDCl_3 + $\text{DMSO-}d_6$)

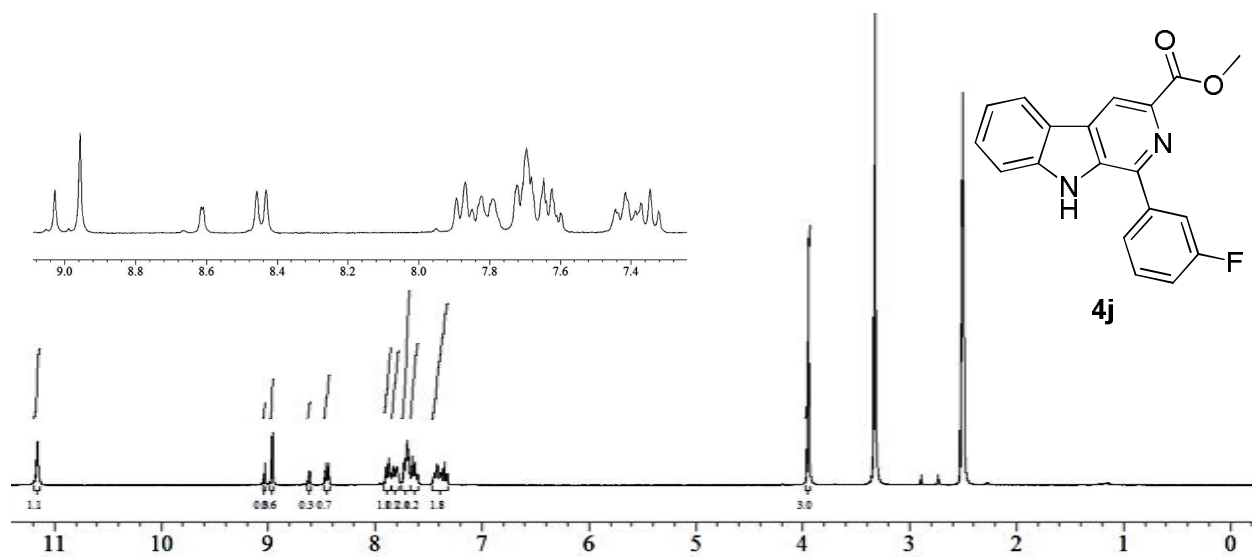


^{13}C NMR (75 MHz, CDCl_3 + $\text{DMSO-}d_6$)

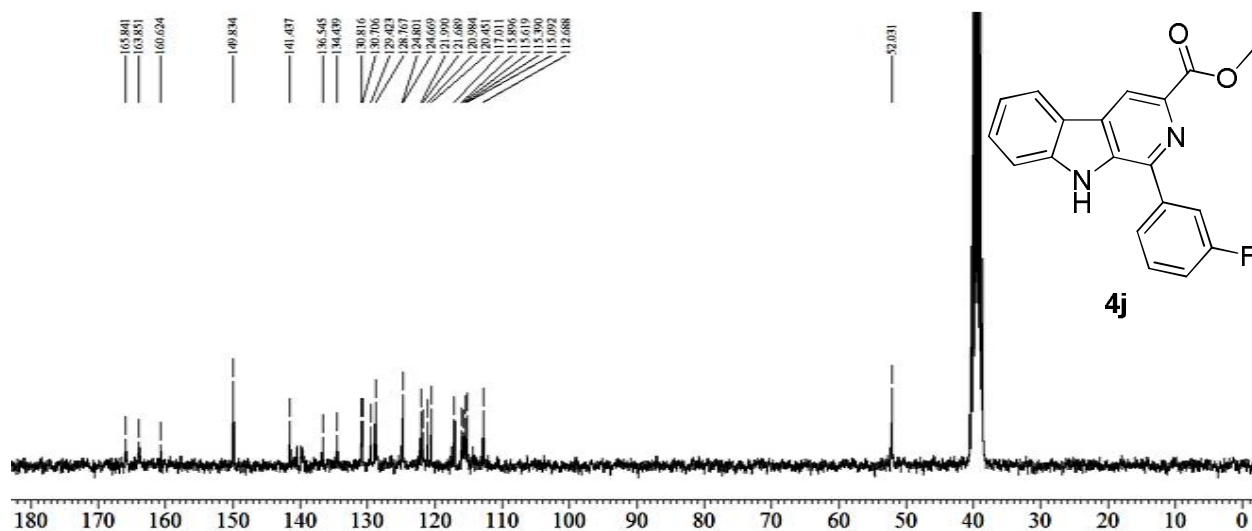


Methyl 1-(3-fluorophenyl)-9H-pyrido[3,4-*b*]indole-3-carboxylate (4j)

^1H NMR (300 MHz, $\text{DMSO}-d_6$)

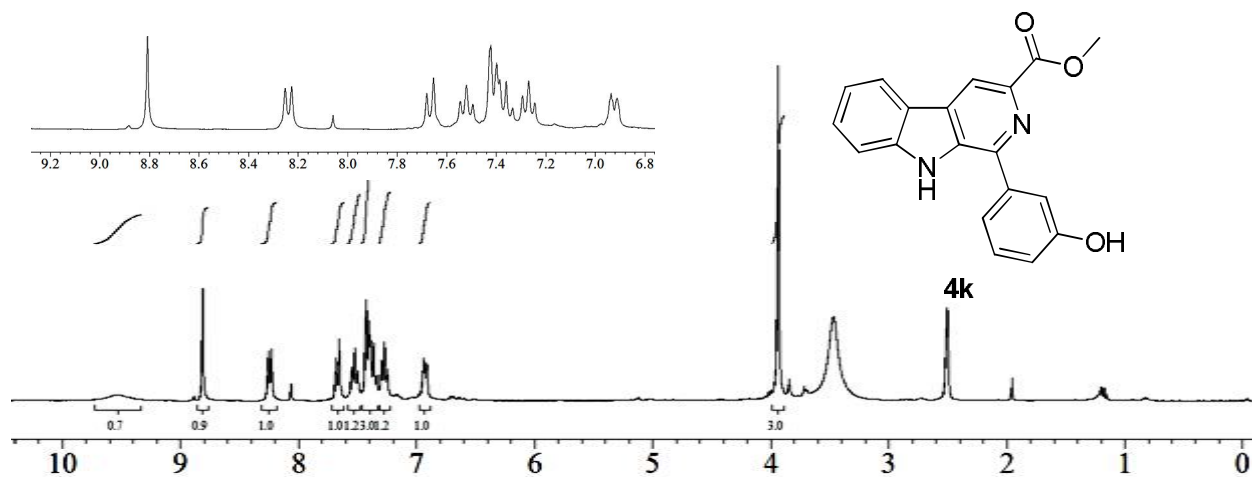


^{13}C NMR (75 MHz, $\text{DMSO}-d_6$)

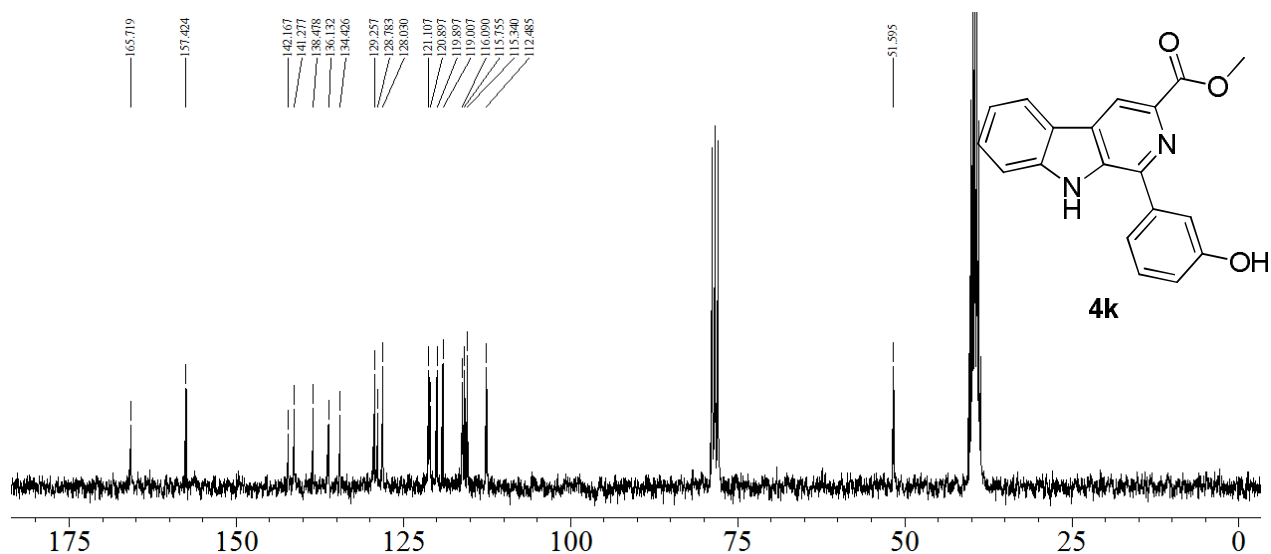


Methyl 1-(3-hydroxyphenyl)-9H-pyrido[3,4-*b*]indole-3-carboxylate (4k)

^1H NMR (300 MHz, CDCl_3 + $\text{DMSO}-d_6$)

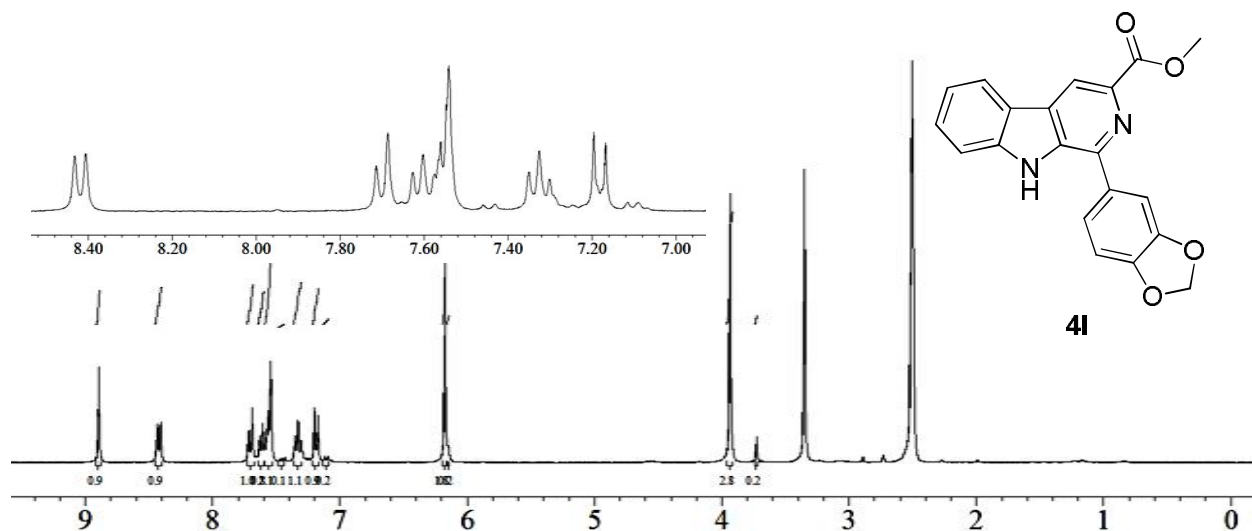


^{13}C NMR (75 MHz, CDCl_3 + $\text{DMSO}-d_6$)

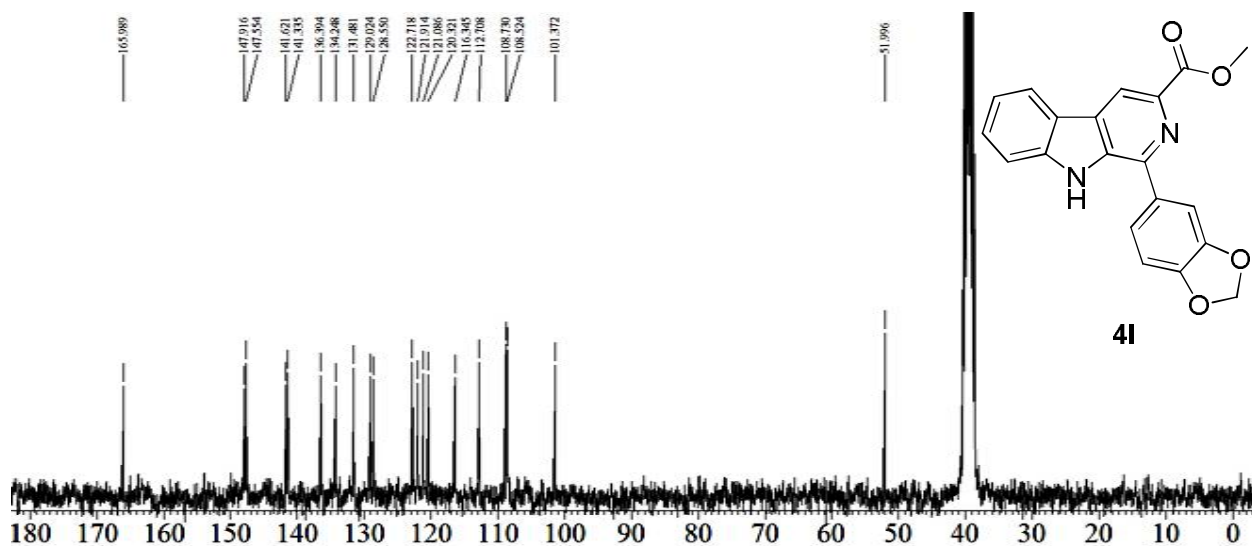


Methyl 1-(benzo[d][1,3]dioxol-5-yl)-9H-pyrido[3,4-*b*]indole-3-carboxylate (4I)

^1H NMR (300 MHz, DMSO- d_6)

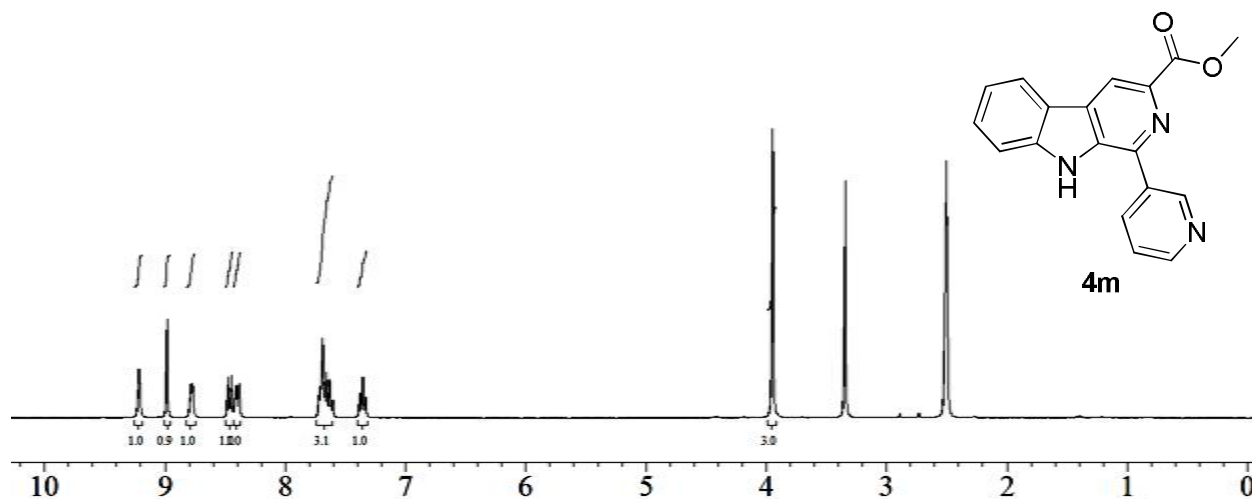


^{13}C NMR (75 MHz, DMSO- d_6)

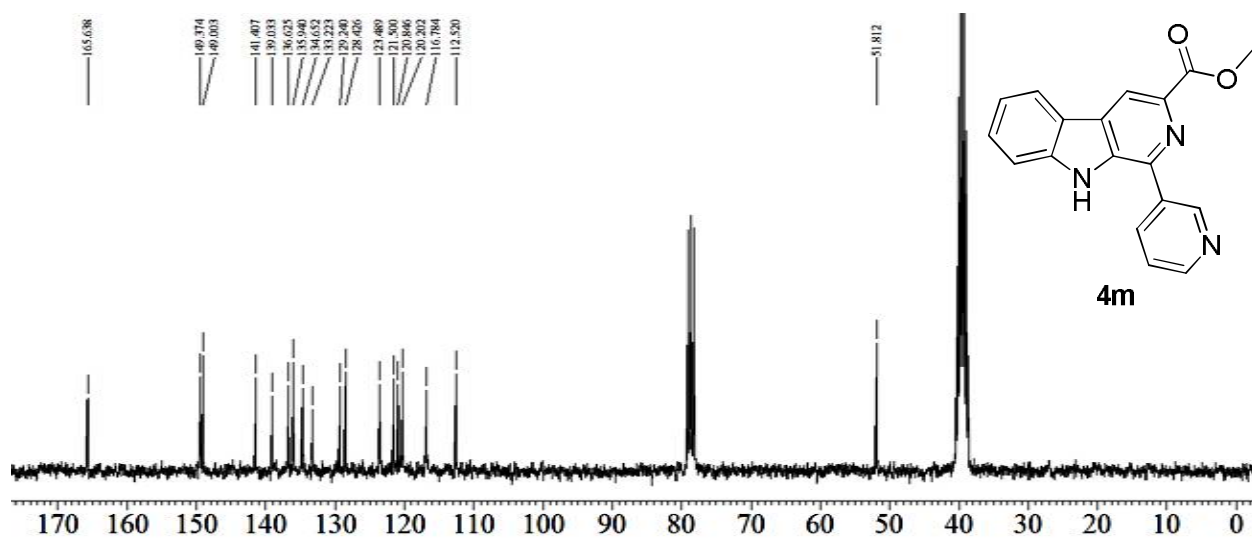


Methyl 1-(pyridin-3-yl)-9H-pyrido [3, 4-*b*] indole-3-carboxylate (4m)

^1H NMR (300 MHz, DMSO- d_6)

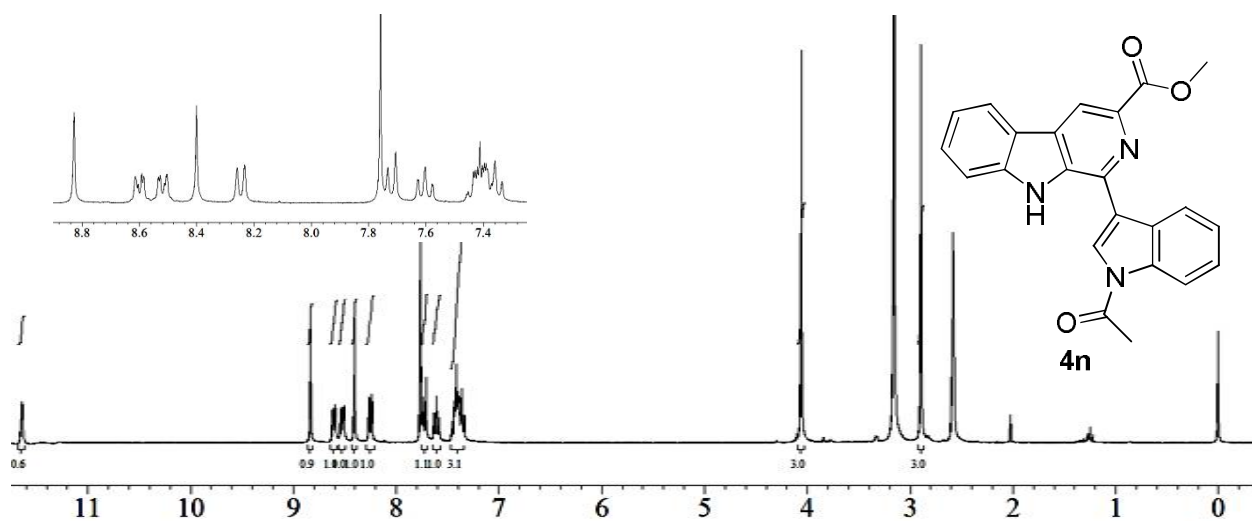


^{13}C NMR (75 MHz, CDCl_3 + DMSO- d_6)

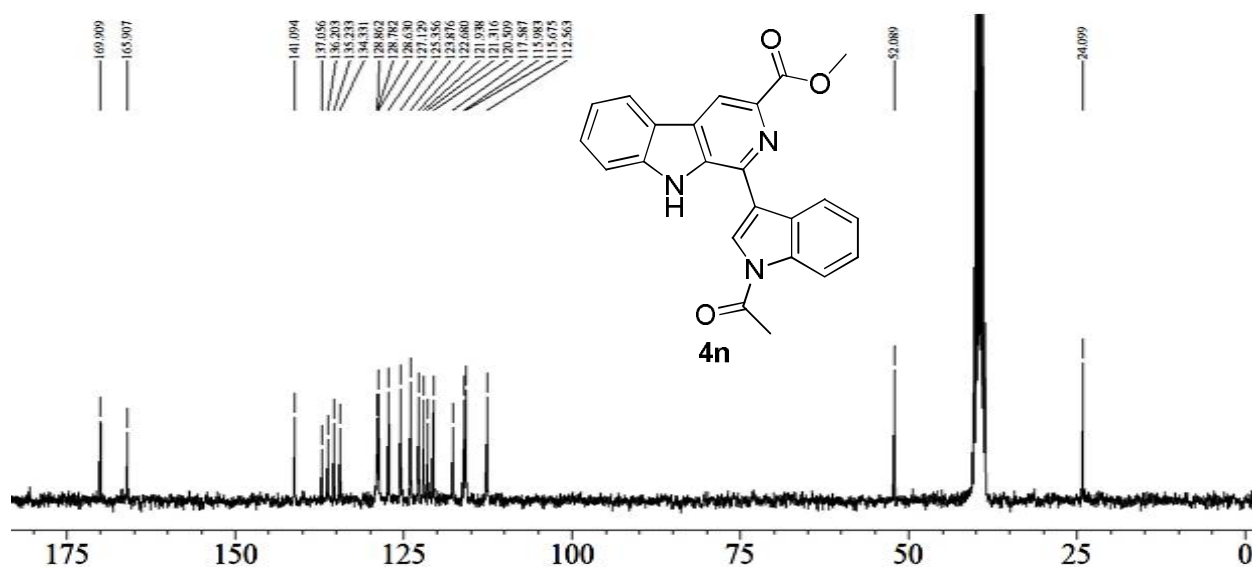


Methyl 1-(1-acetyl-1*H*-indol-3-yl)-9*H*-pyrido[3,4-*b*]indole-3-carboxylate (4n)

¹H NMR (300 MHz, CDCl₃ + DMSO-*d*₆)

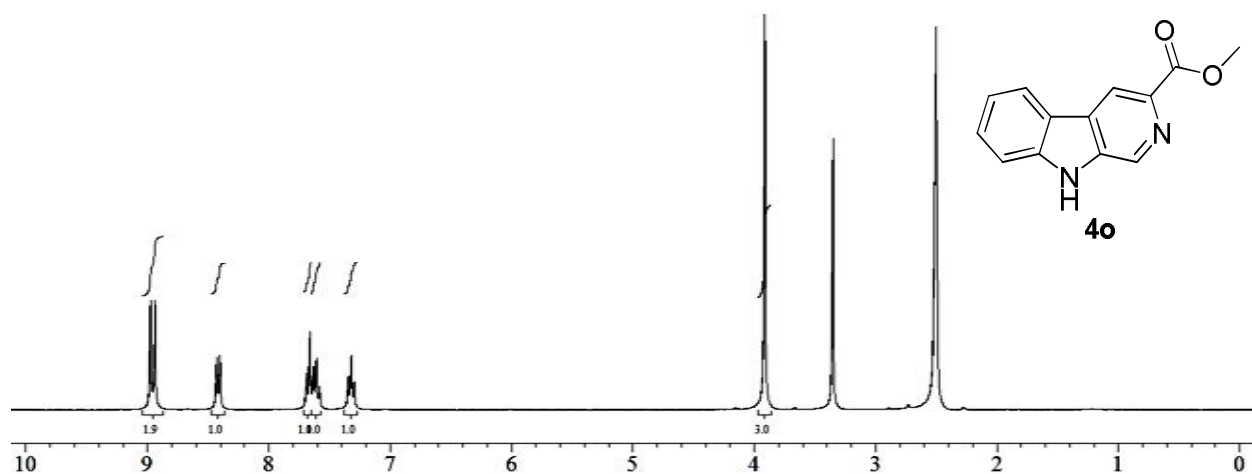


¹³C NMR (75 MHz, DMSO-*d*₆)

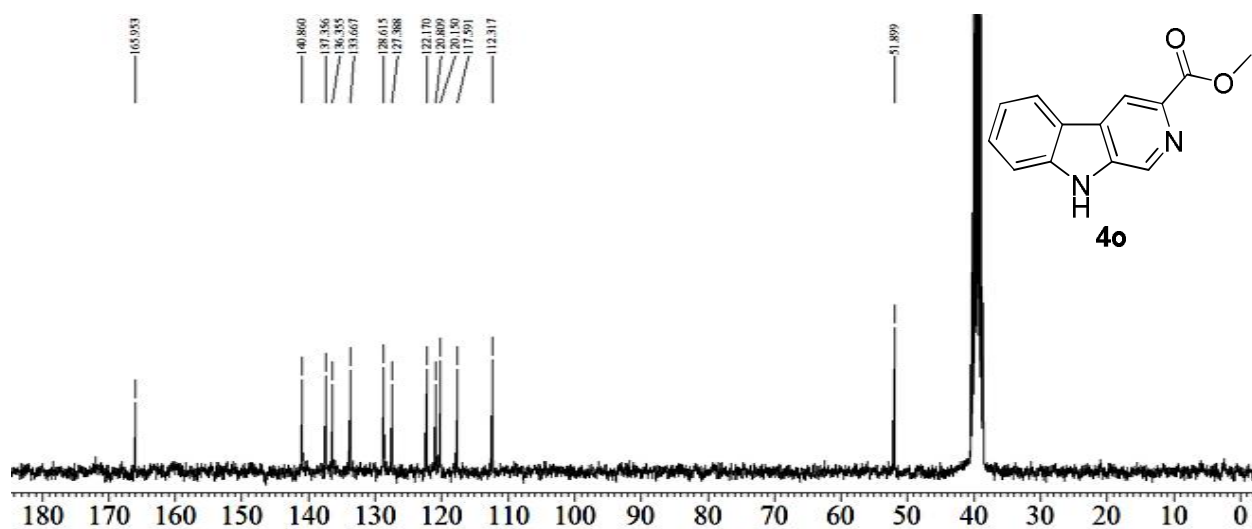


Methyl 9H-pyrido [3, 4-b] indole-3-carboxylate (4o)

NMR (300 MHz, DMSO-*d*₆)

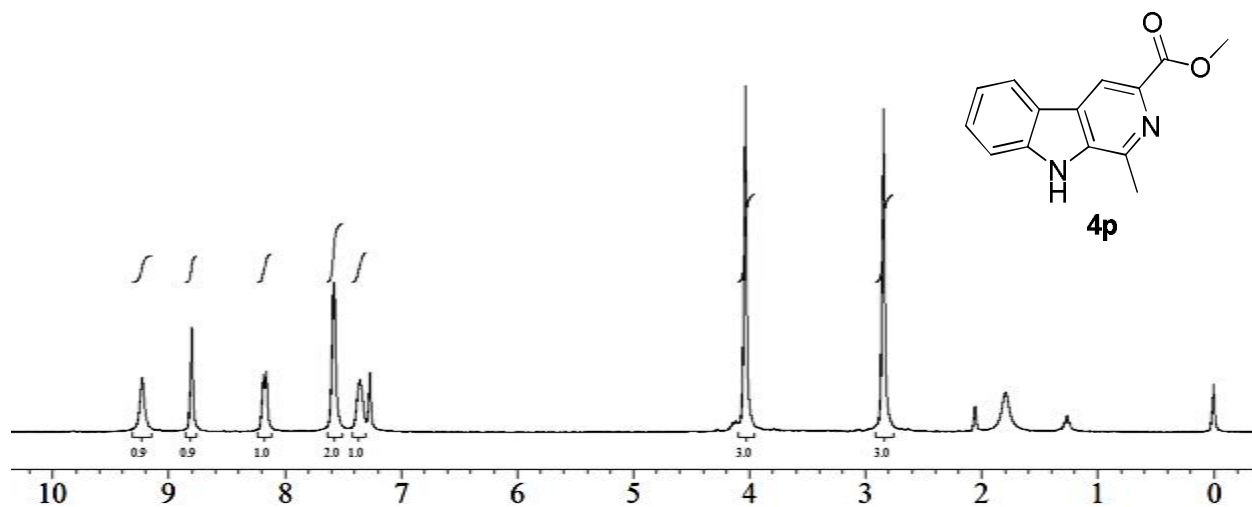


¹³C NMR (75 MHz, DMSO-*d*₆)

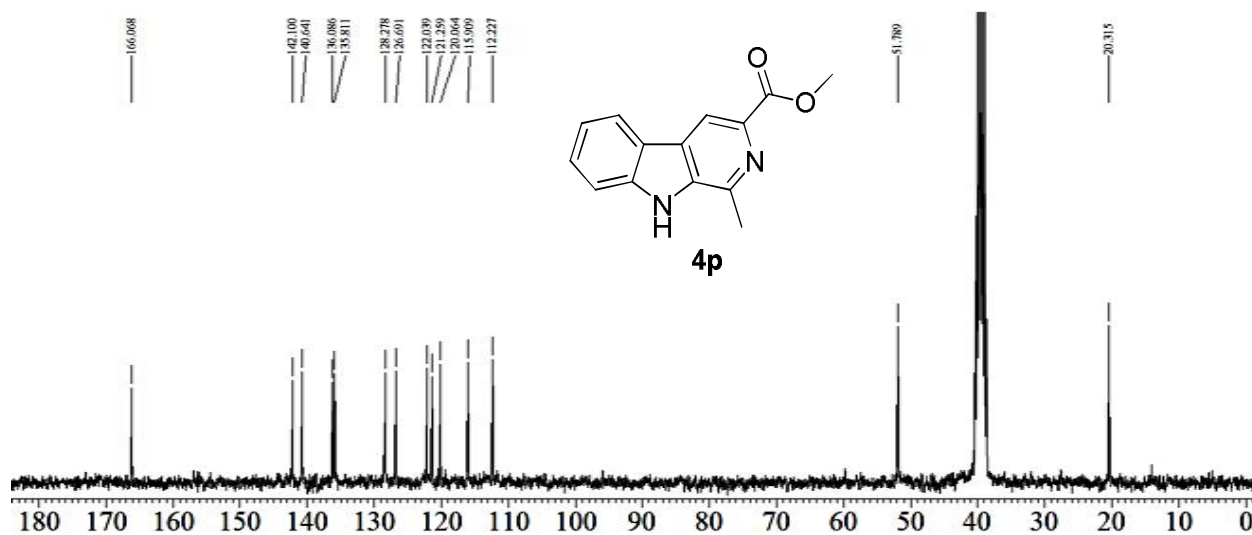


Methyl 1-methyl-9H-pyrido[3,4-*b*]indole-3-carboxylate (4p)

^1H NMR (300 MHz, CDCl_3)

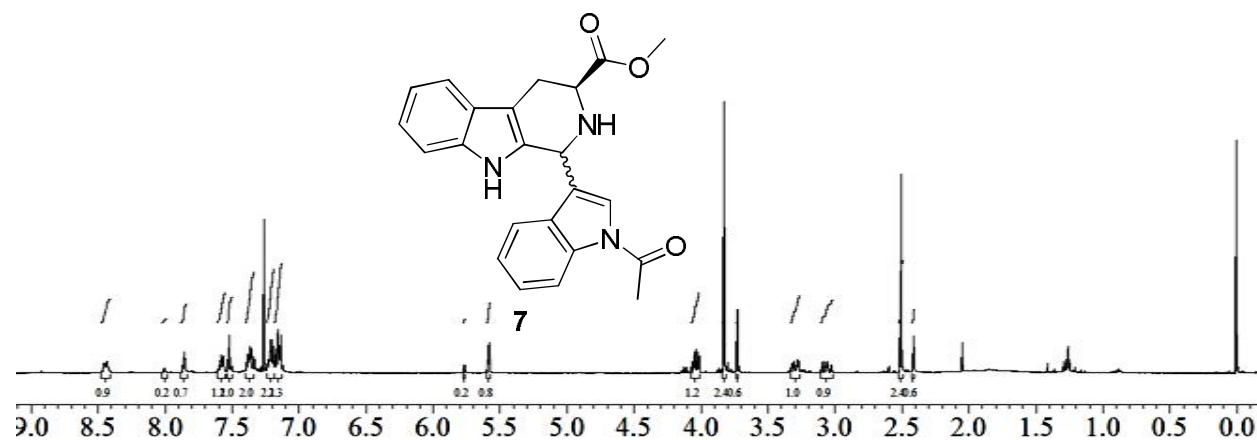


^{13}C NMR (75 MHz, $\text{DMSO}-d_6$)

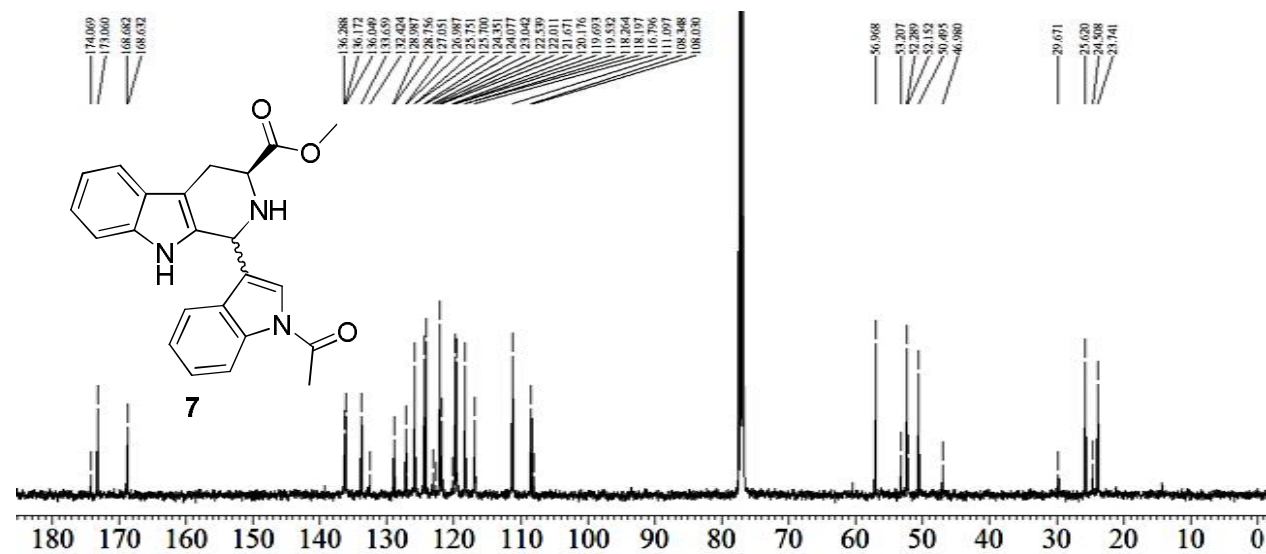


Methyl 1-(1-acetyl-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole-3-carboxylate (7)

¹H NMR (400 MHz, CDCl₃)

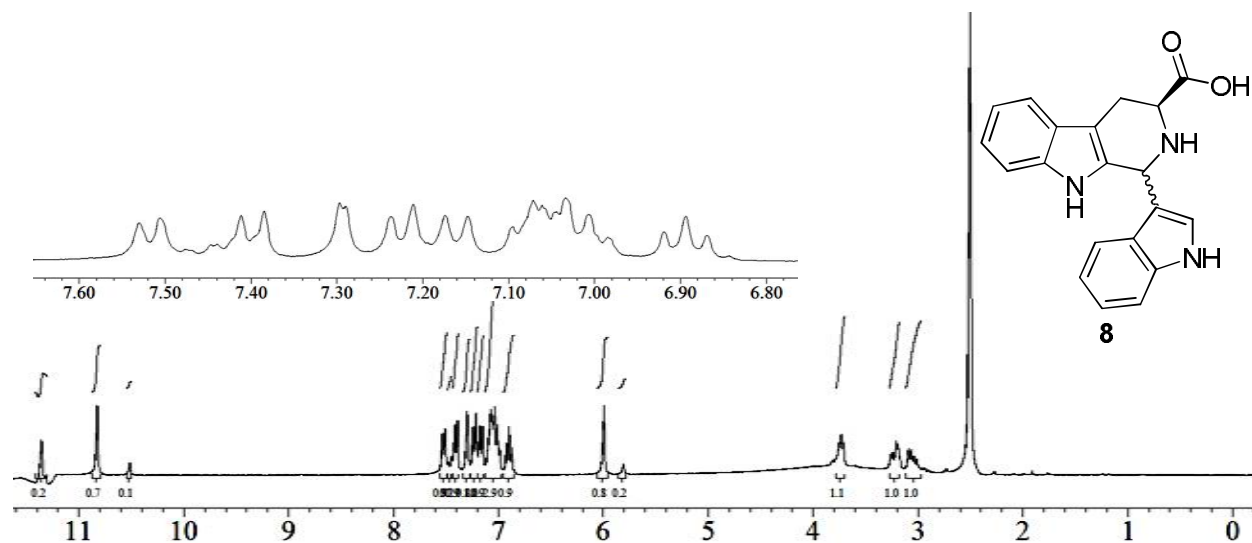


¹³C NMR (125 MHz, CDCl₃)

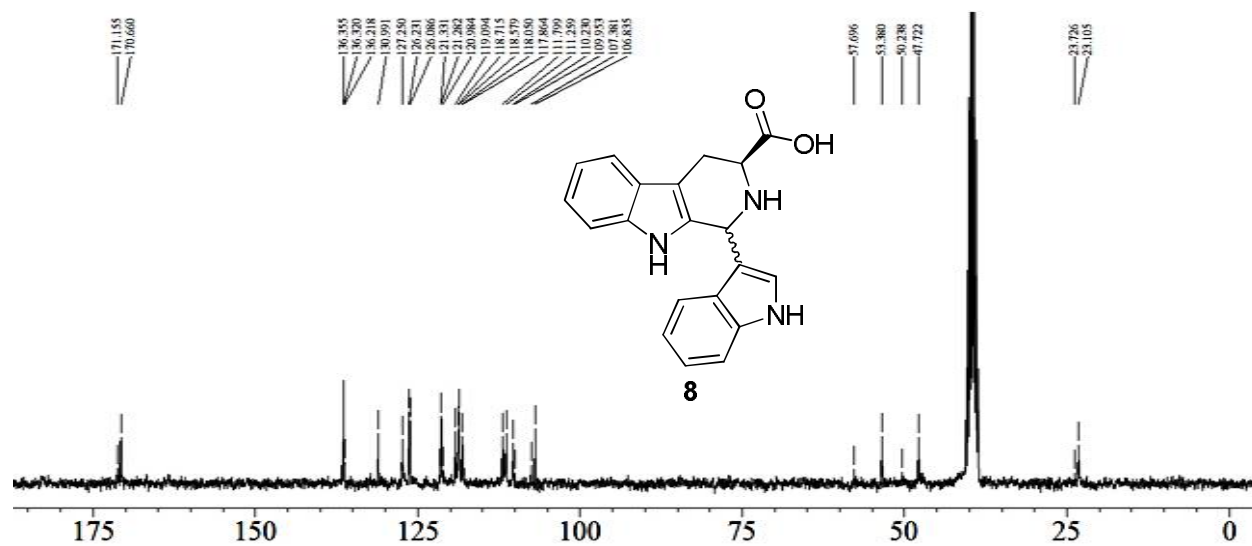


1-(1*H*-Indol-3-yl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole-3-carboxylic acid (8)

¹H NMR (300 MHz, DMSO-*d*₆)

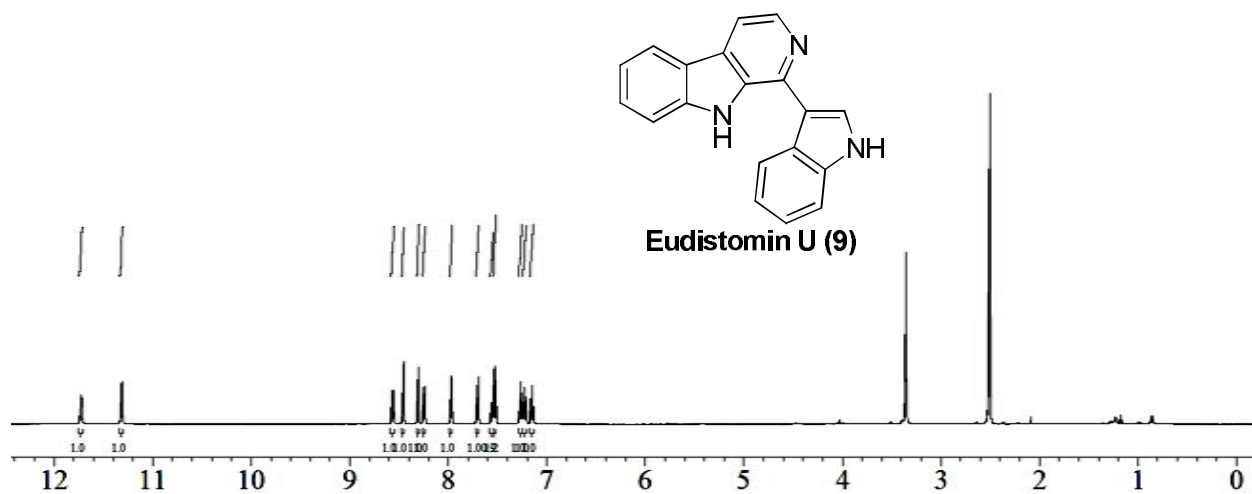


¹³C NMR (75 MHz, DMSO-*d*₆)

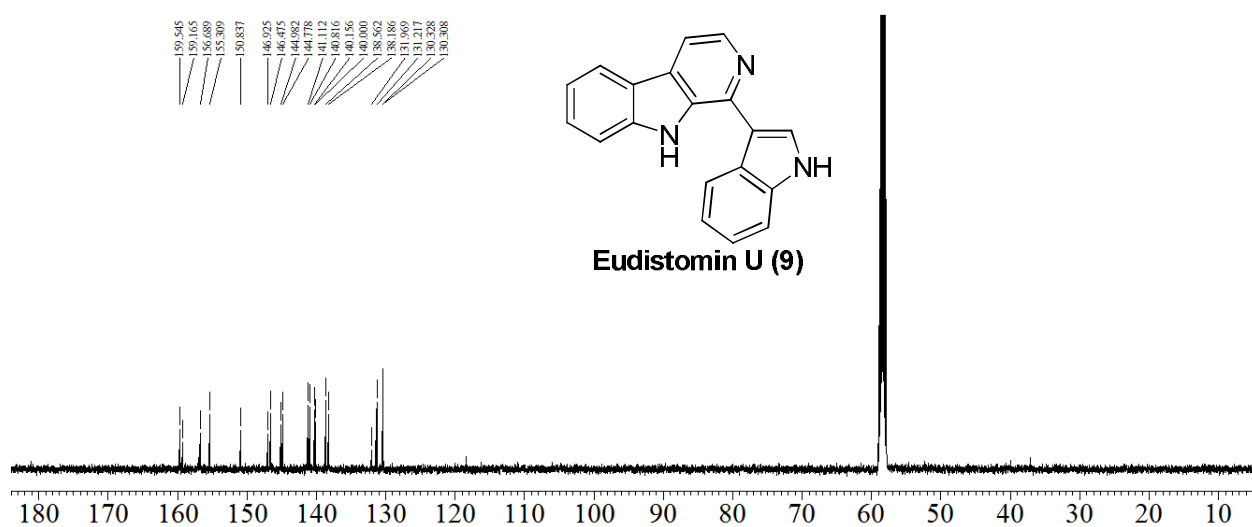


Eudistomin U (9):

^1H NMR (500 MHz, $\text{DMSO}-d_6$)

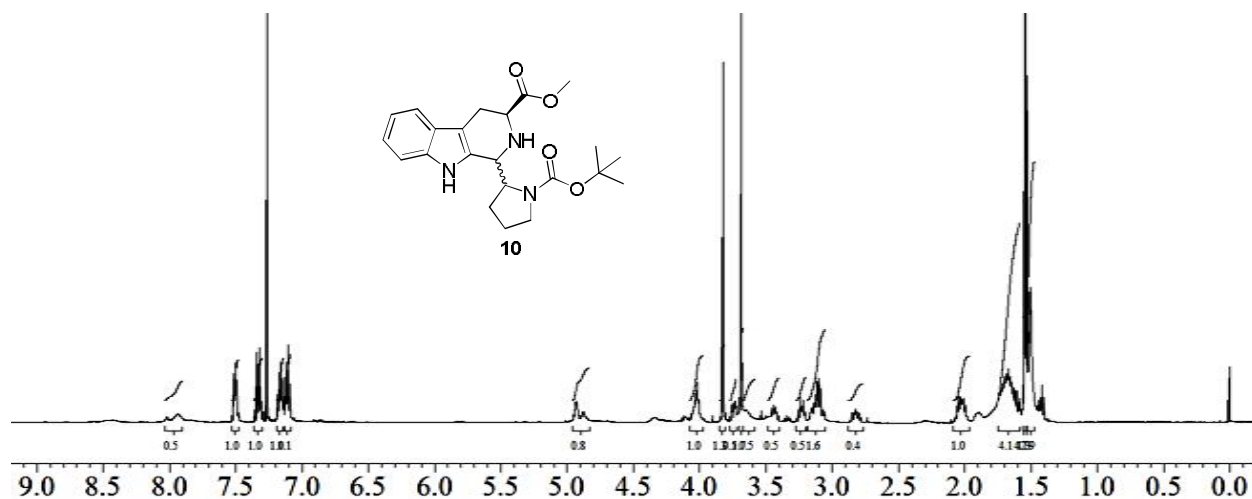


^{13}C NMR (125 MHz, $\text{DMSO}-d_6$)

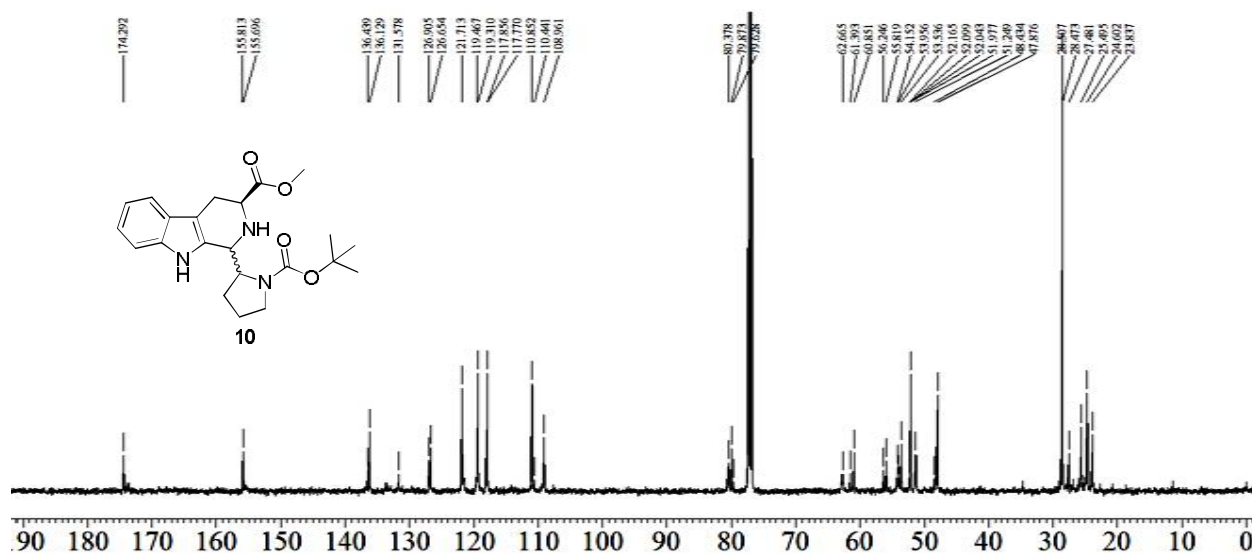


Methyl 1-(1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole-3-carboxylate (10)

¹H NMR (500 MHz, CDCl₃)

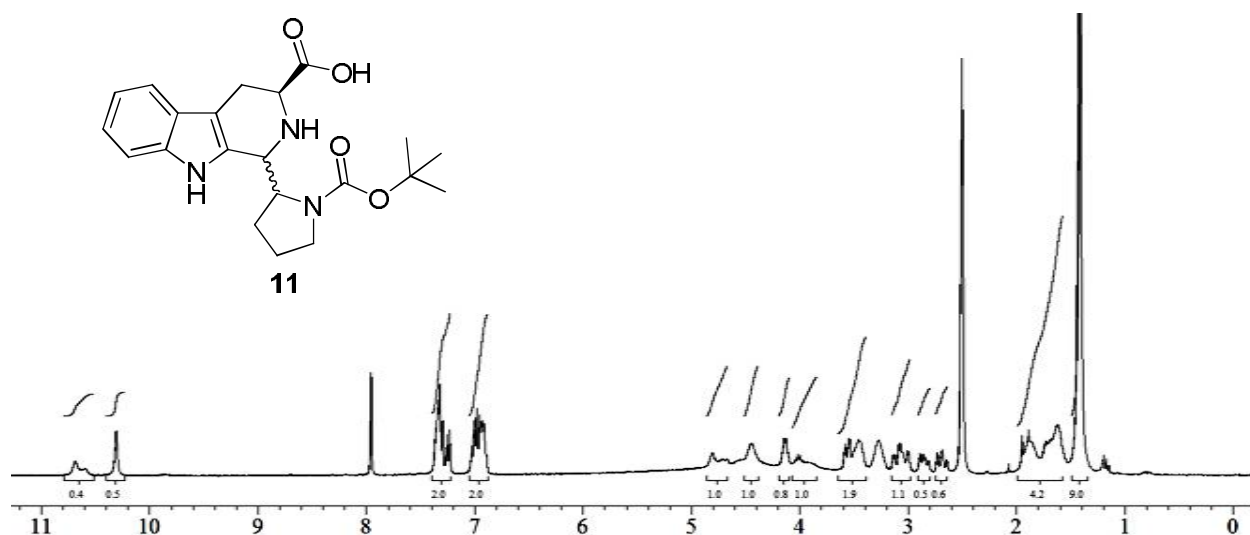


¹³C NMR (125 MHz, CDCl₃)

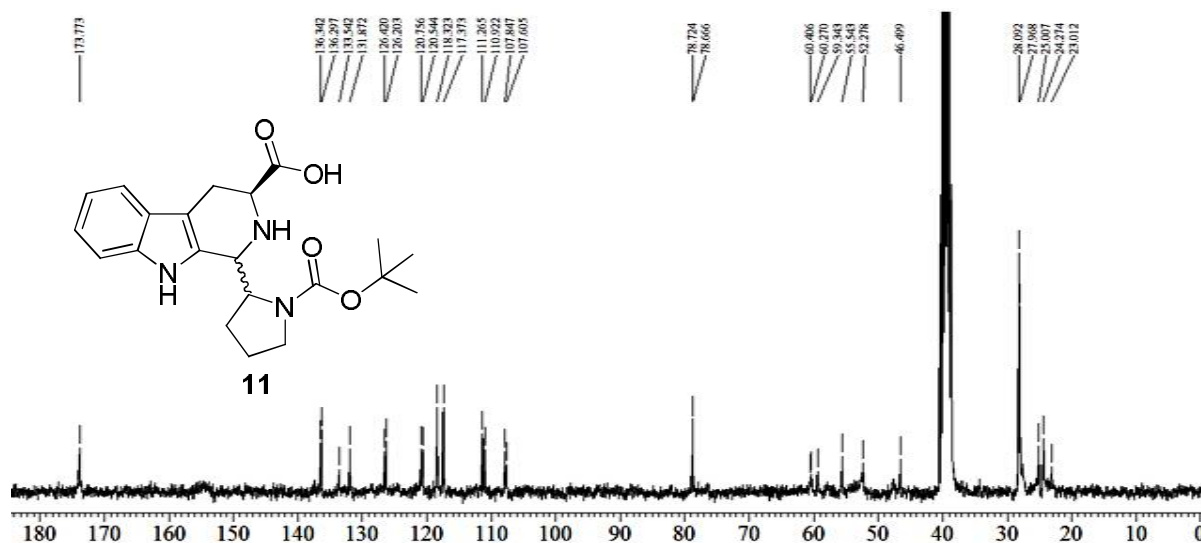


1-(1-(*tert*-butoxycarbonyl)pyrrolidin-2-yl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole-3-carboxylic acid (11)

^1H NMR (300 MHz, CDCl_3 + $\text{DMSO}-d_6$)

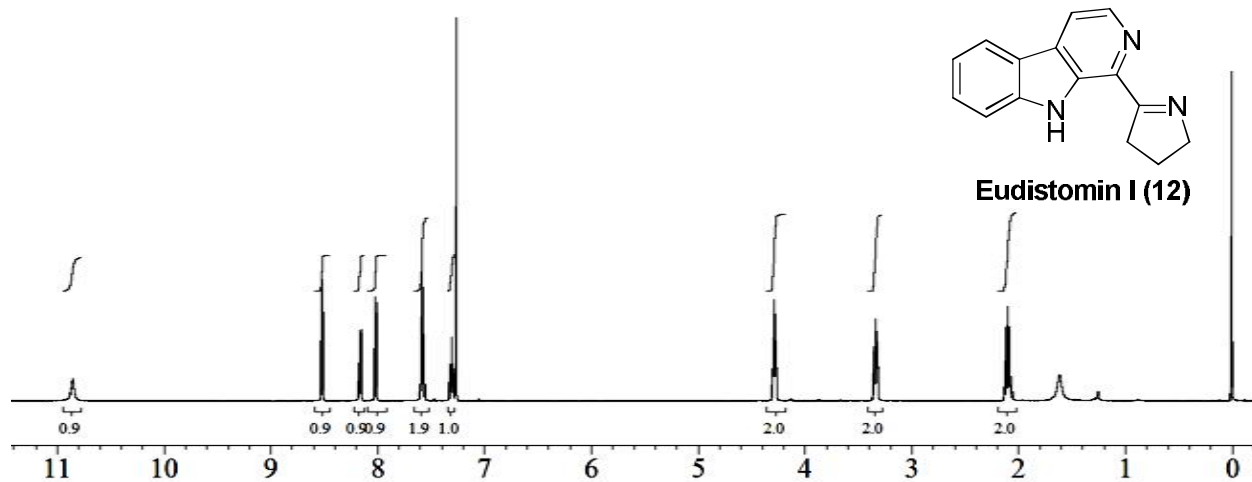


^{13}C NMR (75 MHz, $\text{DMSO}-d_6$)



Eudistomin I (12):

^1H NMR (500 MHz, CDCl_3)



^{13}C NMR (125 MHz, CDCl_3)

