

**Supporting Information**

**Co(III)-Catalyzed C–H Activation: A Site-Selective Conjugate  
Addition of Maleimide to Indole at the C-2 Position**

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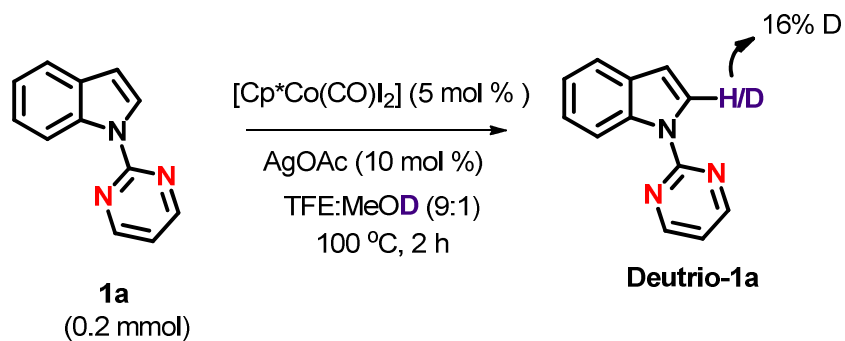
Indian Institute of Science,

Bangalore 560 012, Karnataka, India

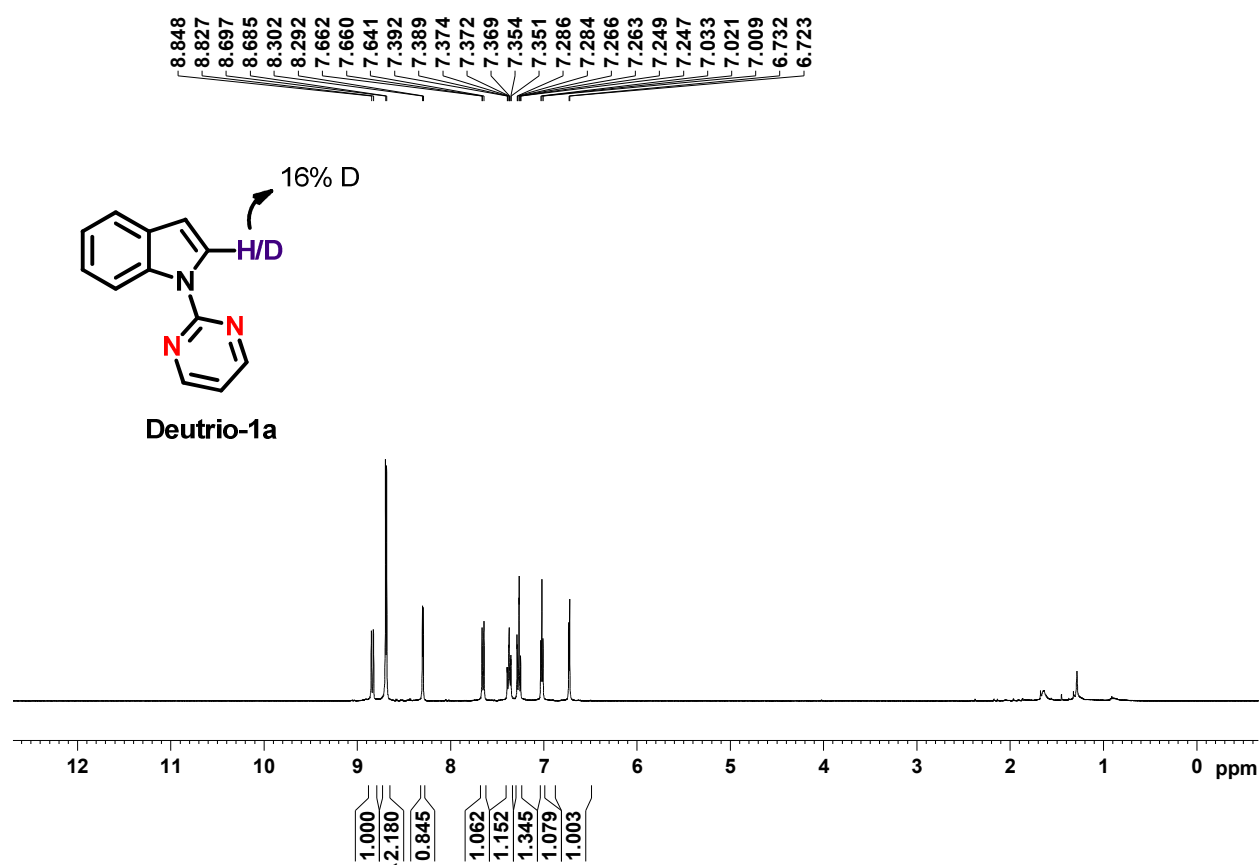
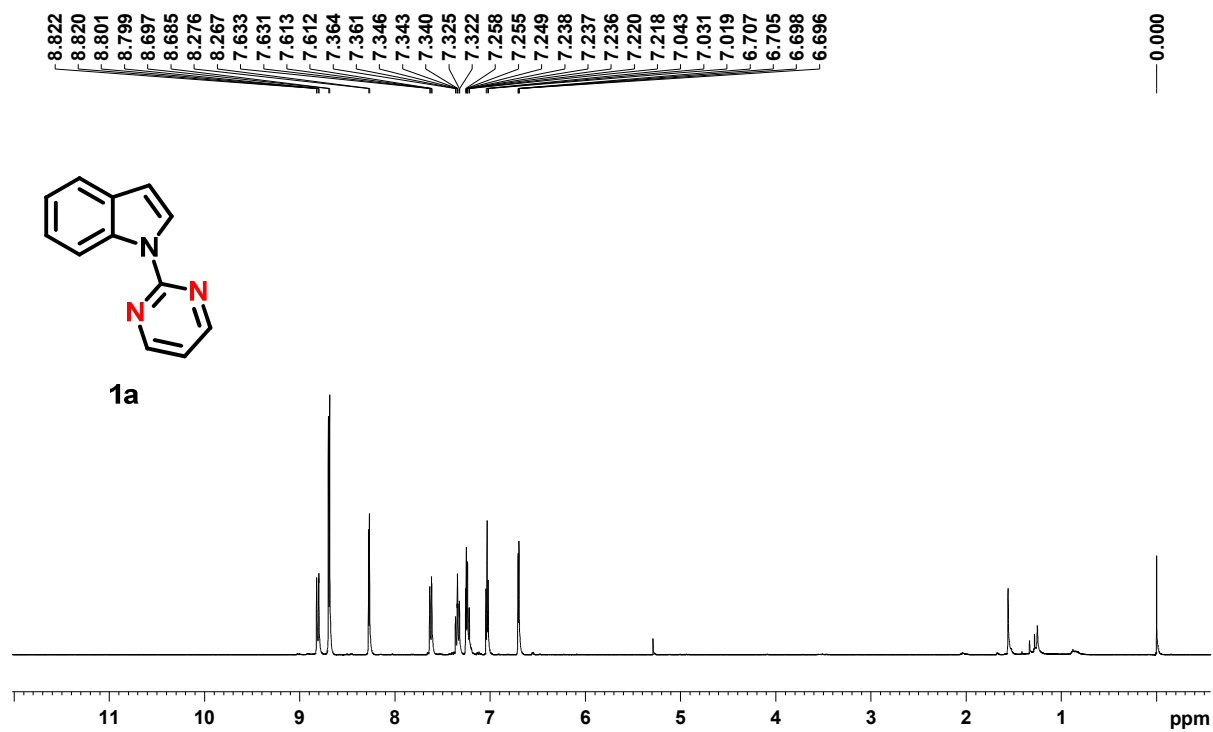
\*E-mail: [prabhu@orgchem.iisc.ernet.in](mailto:prabhu@orgchem.iisc.ernet.in)

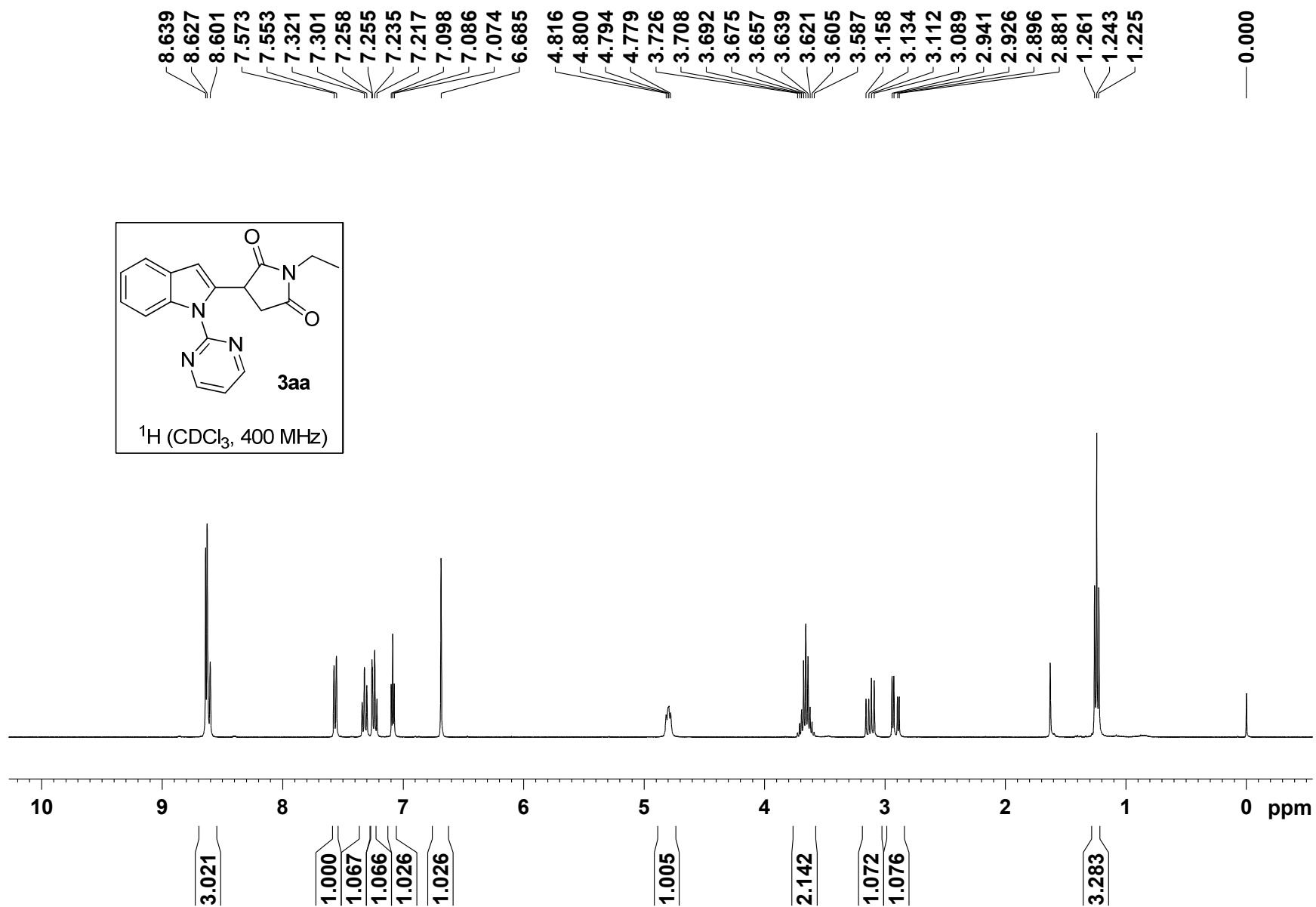
## Contents

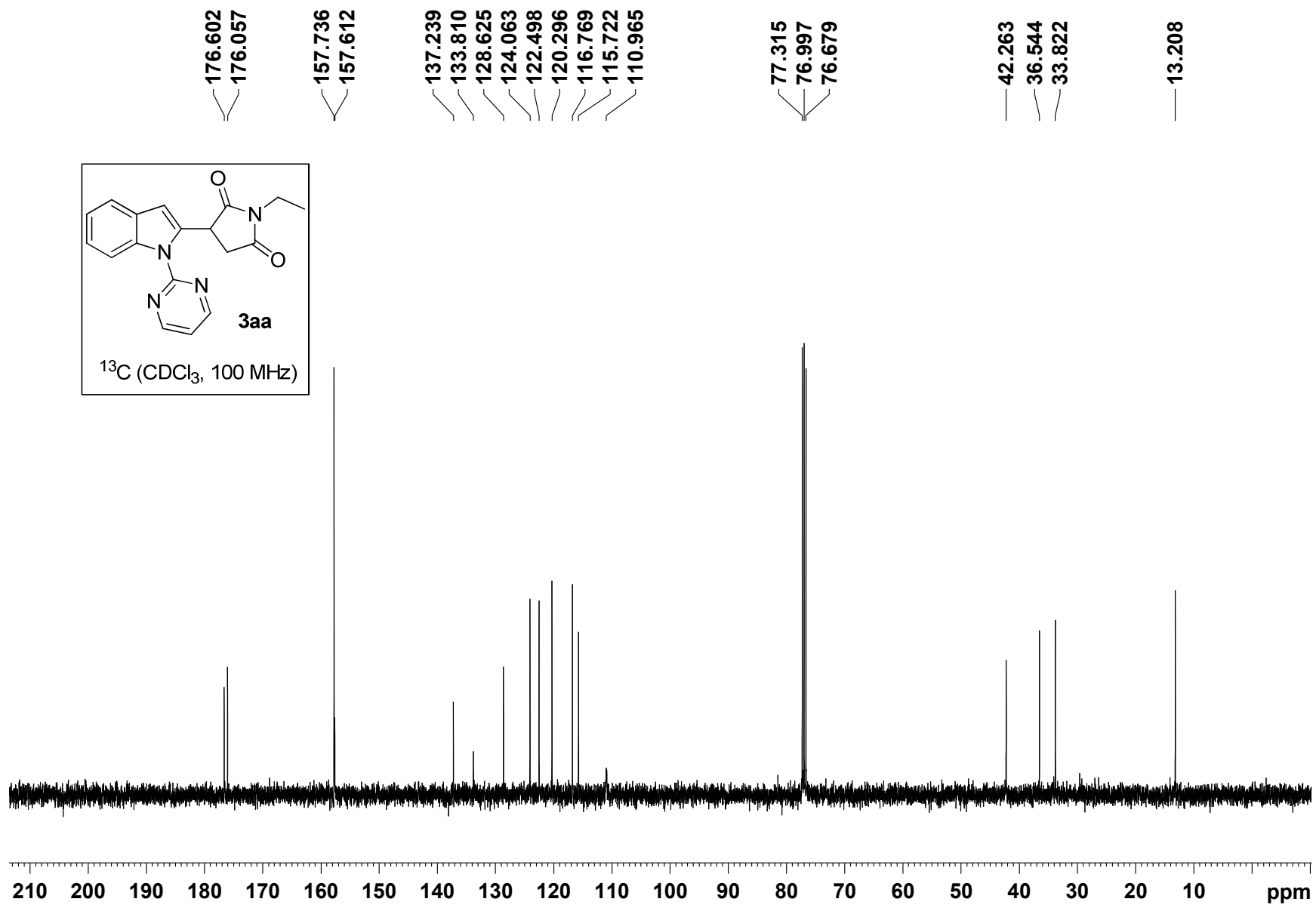
1	Deuterium labelling studies	S-3
2	$^1\text{H}$ and $^{13}\text{C}$ NMR spectra for all the products	S-5

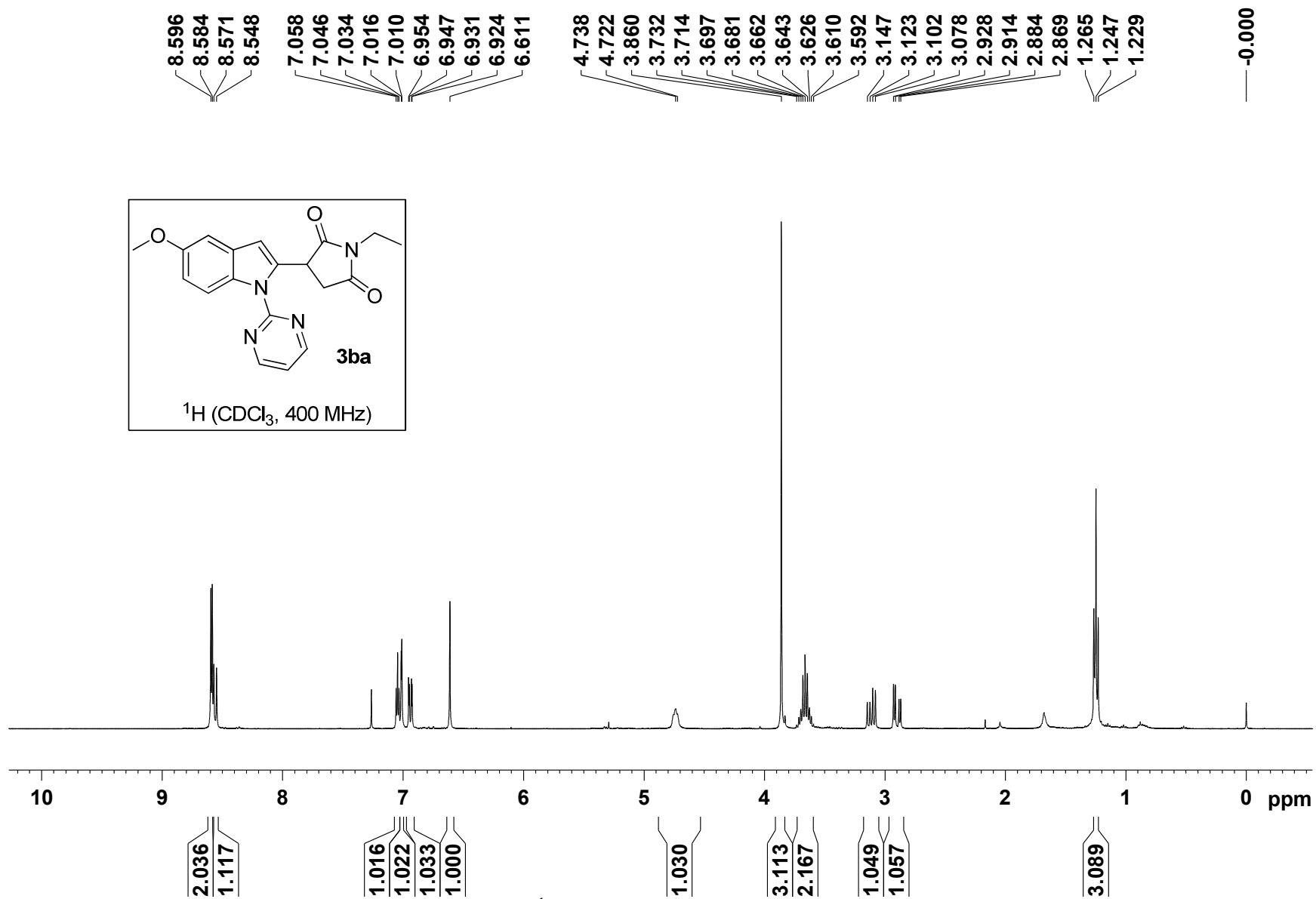
**Deuterium labeling studies:****Scheme S1: Deuterium labeling studies**

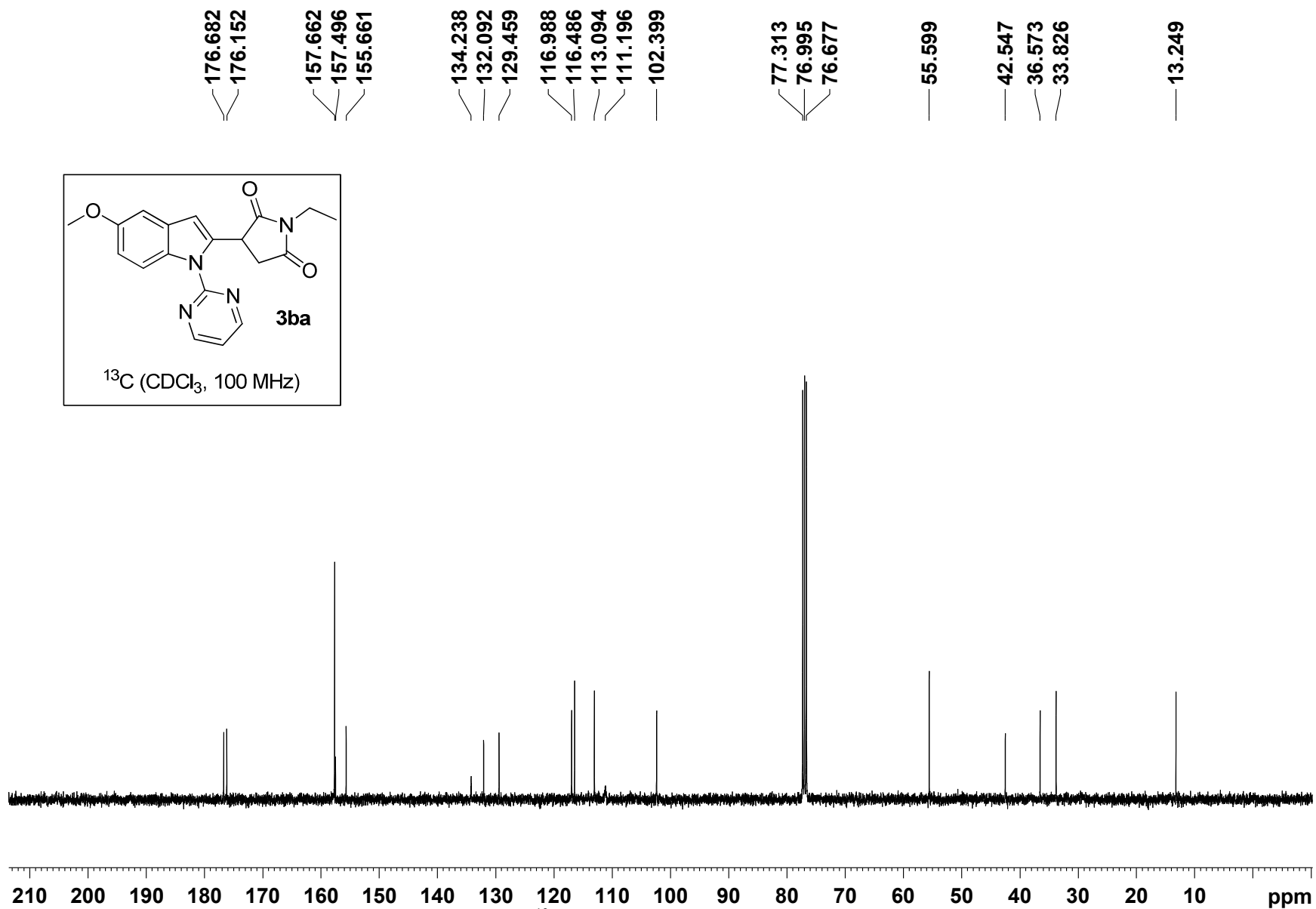
In a 8-mL screw cap reaction vial, *N*-pyrimidinylindole (0.2 mmol), cobalt catalyst (5 mol %) and AgOAc (10 mol %), were added followed by the addition of TFE:MeOD (2 mL, 9:1). This vial was sealed with a screw cap, placed in a pre-heated metal block at 100 °C for 2 h, cooled to room temperature, and concentrated to yield the crude product, which was further purified by flash chromatography to give the desired product **deutrio-1a** in 99% yield. The deuterium incorporation was calculated from <sup>1</sup>H NMR spectroscopy (See the following <sup>1</sup>H NMR spectra).

Figure S1.  $^1\text{H}$  NMR spectra of the compound **1a** and **deutrio-1a**

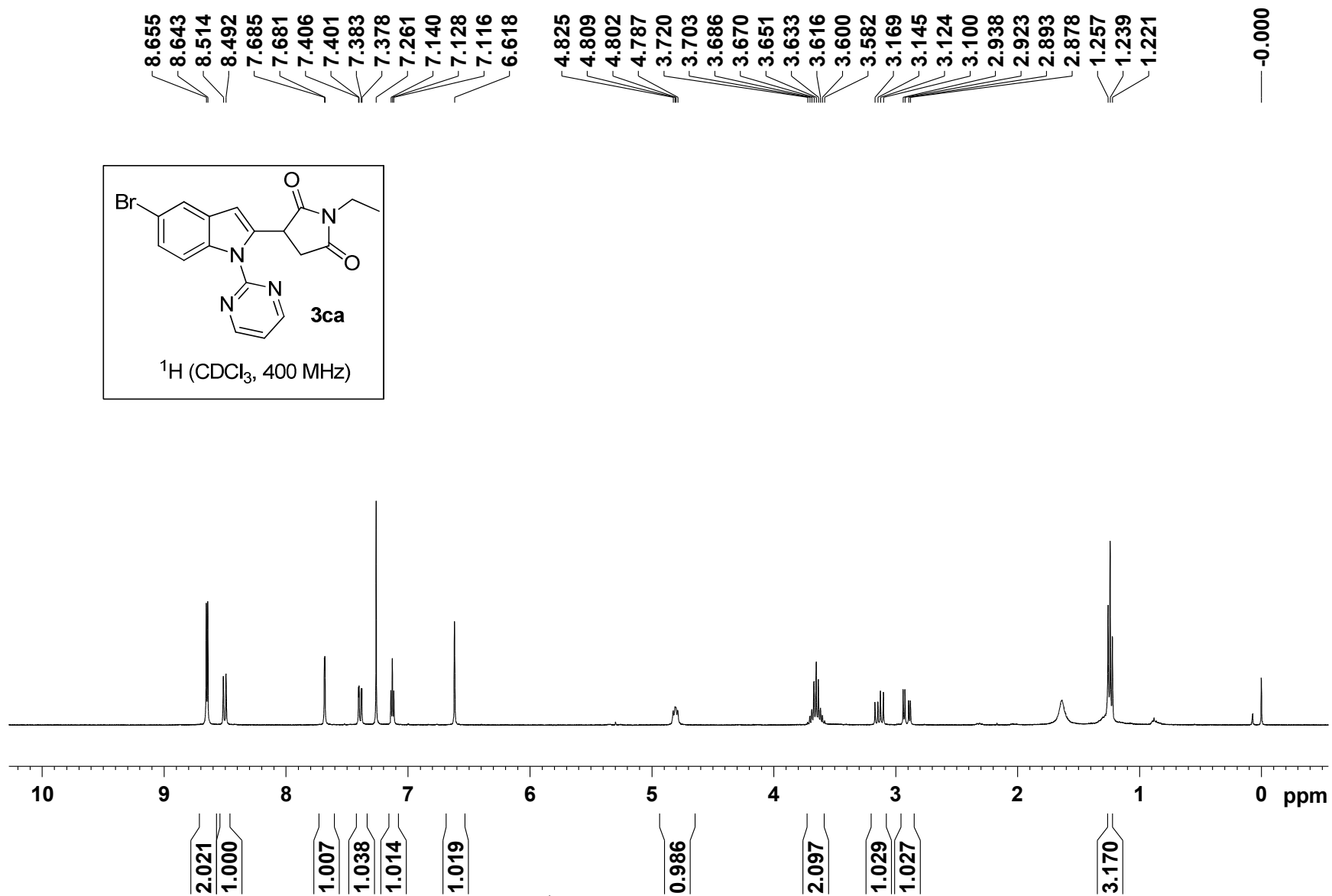
Figure S2.  $^1\text{H}$  NMR spectra of the Compound **3aa**

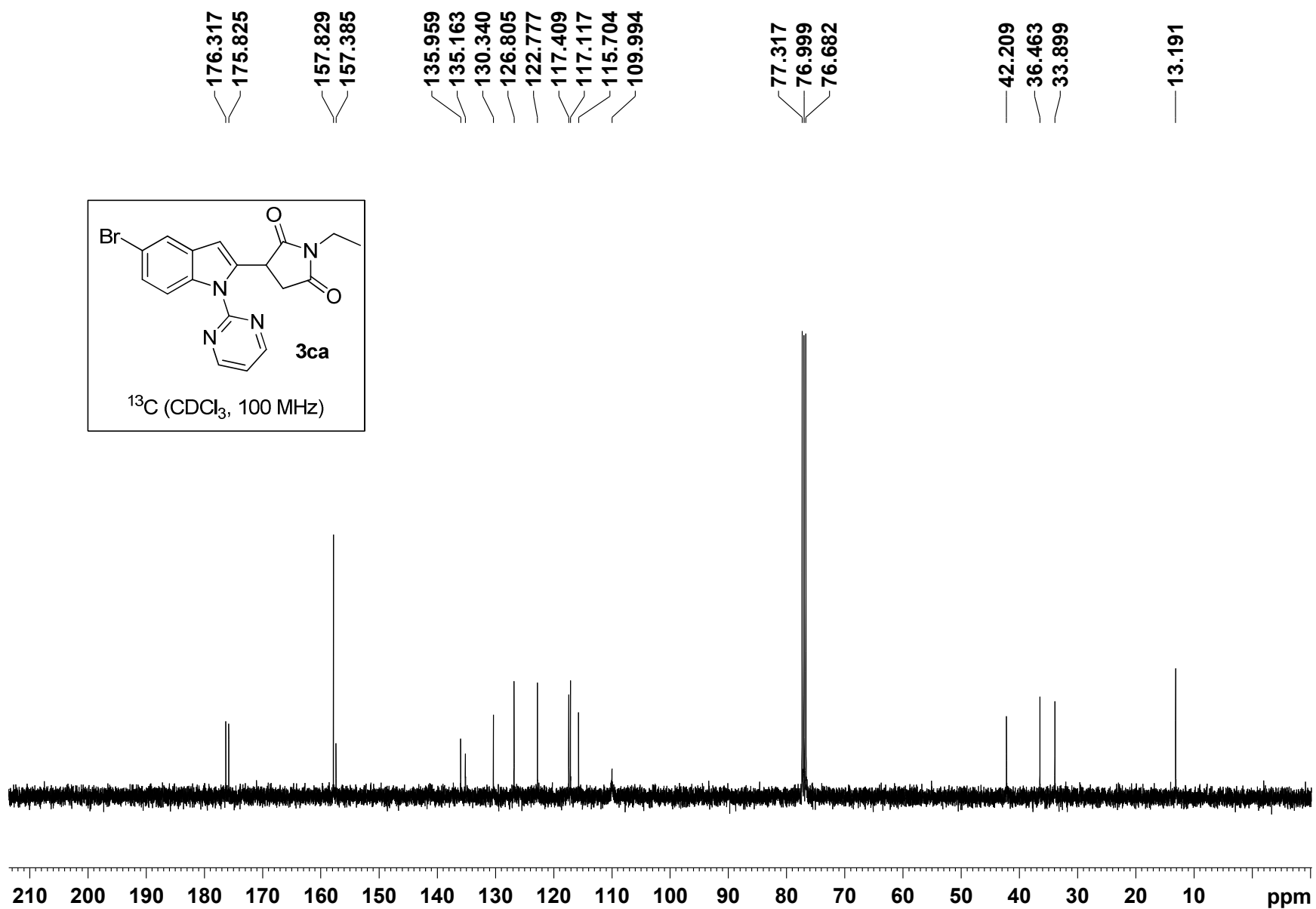
Figure S3.  $^{13}\text{C}$  NMR spectra of the Compound **3aa**

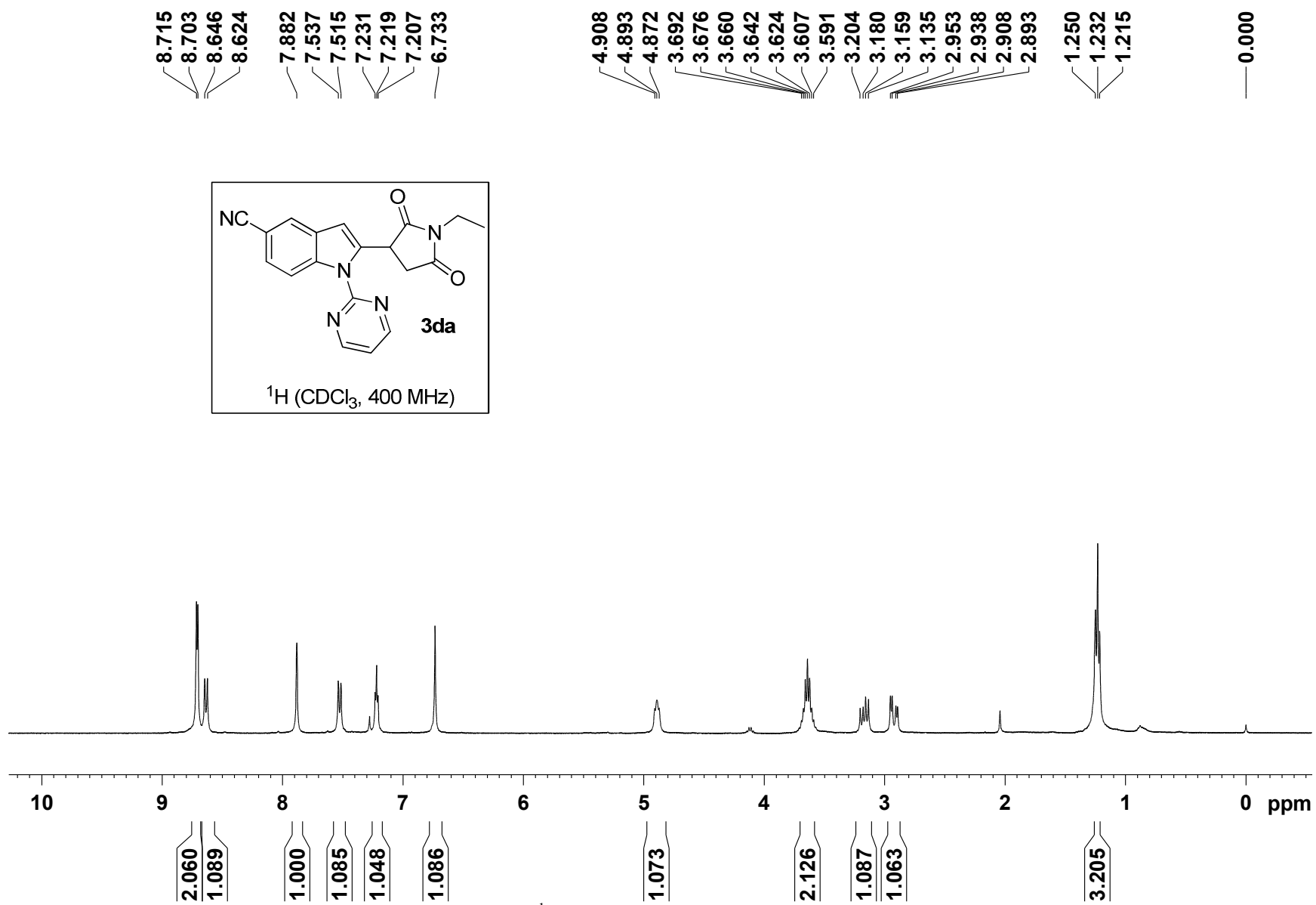
Figure S4. <sup>1</sup>H NMR spectra of the Compound 3ba

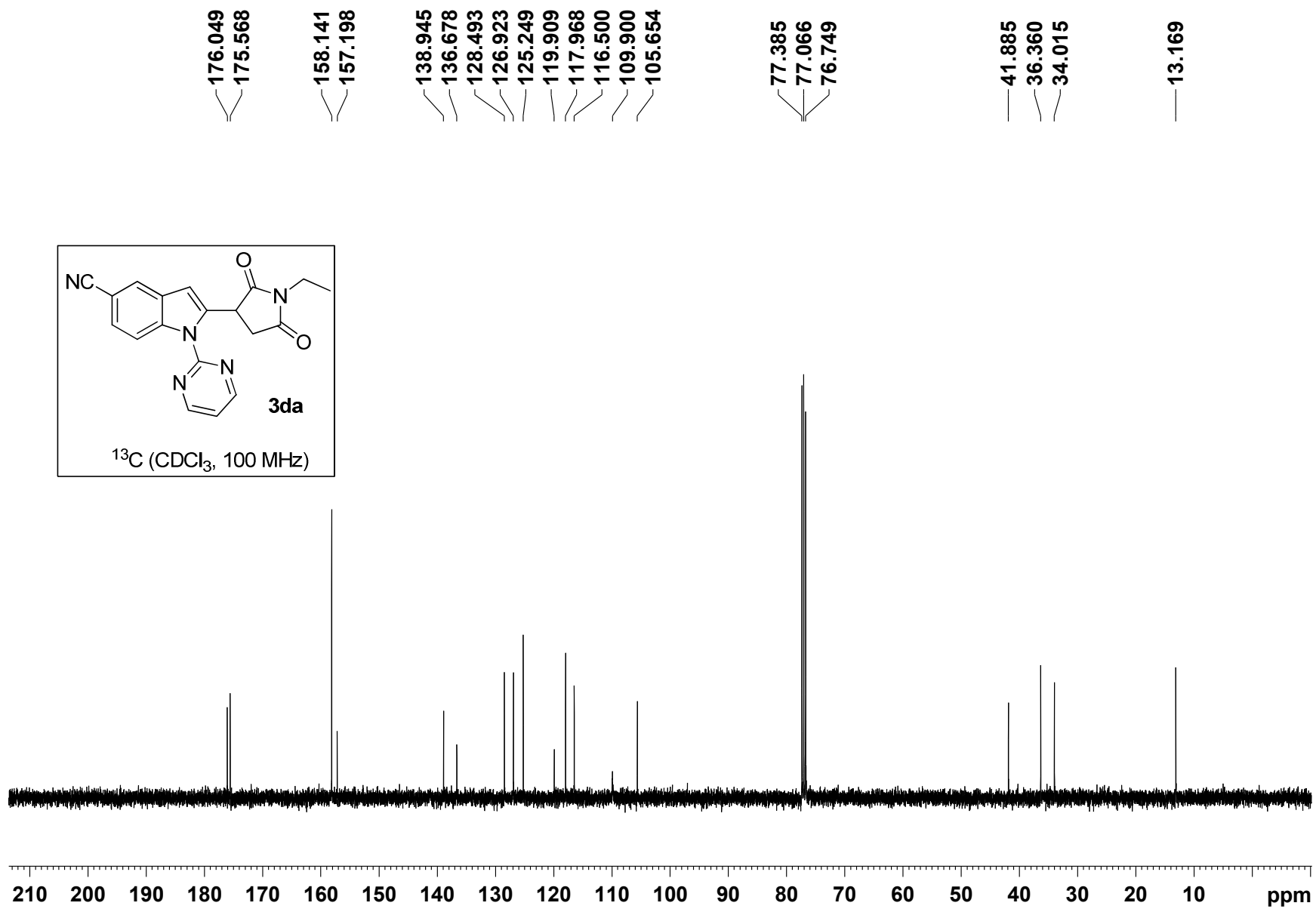
Figure S5.  $^{13}\text{C}$  NMR spectra of the Compound 3ba

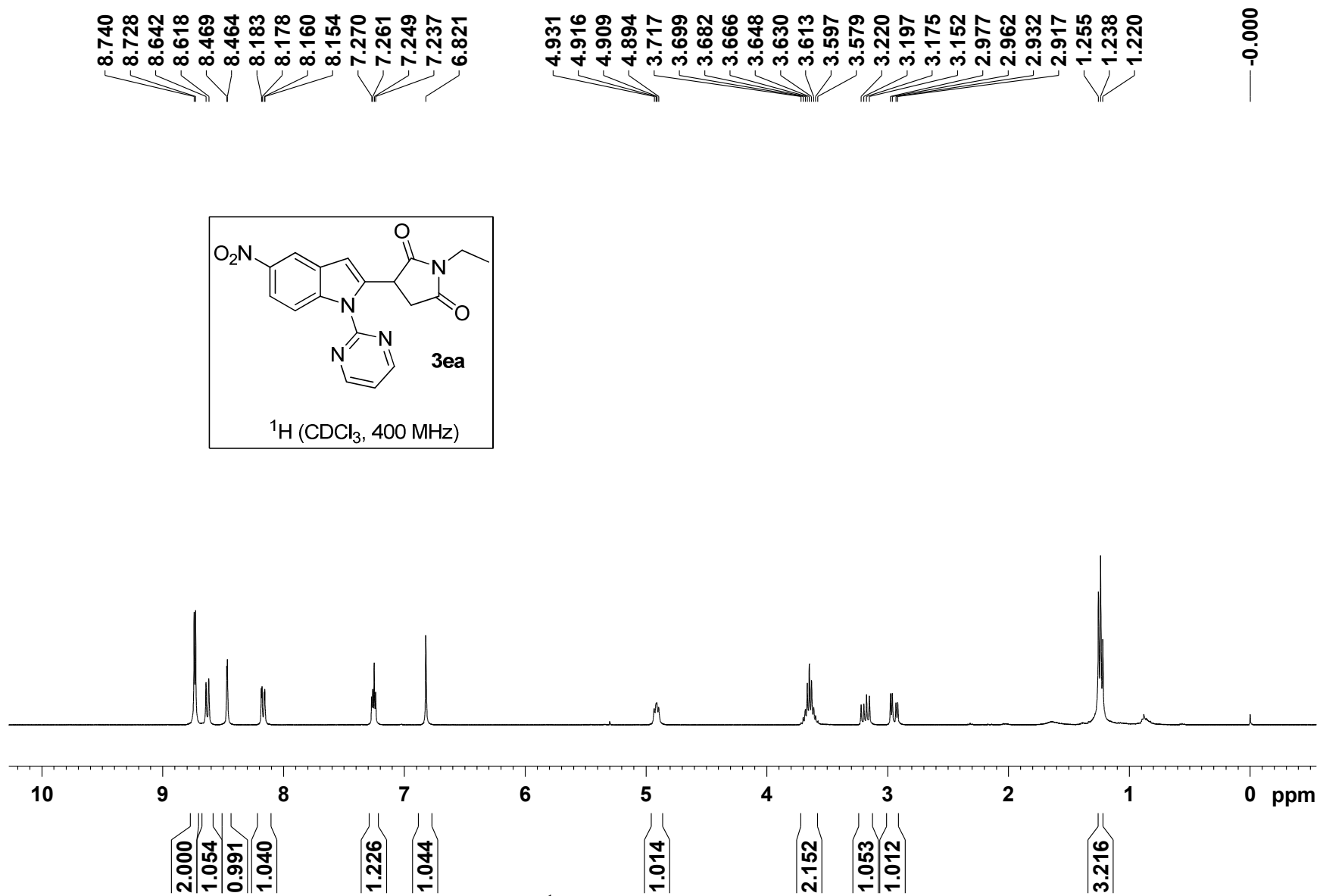


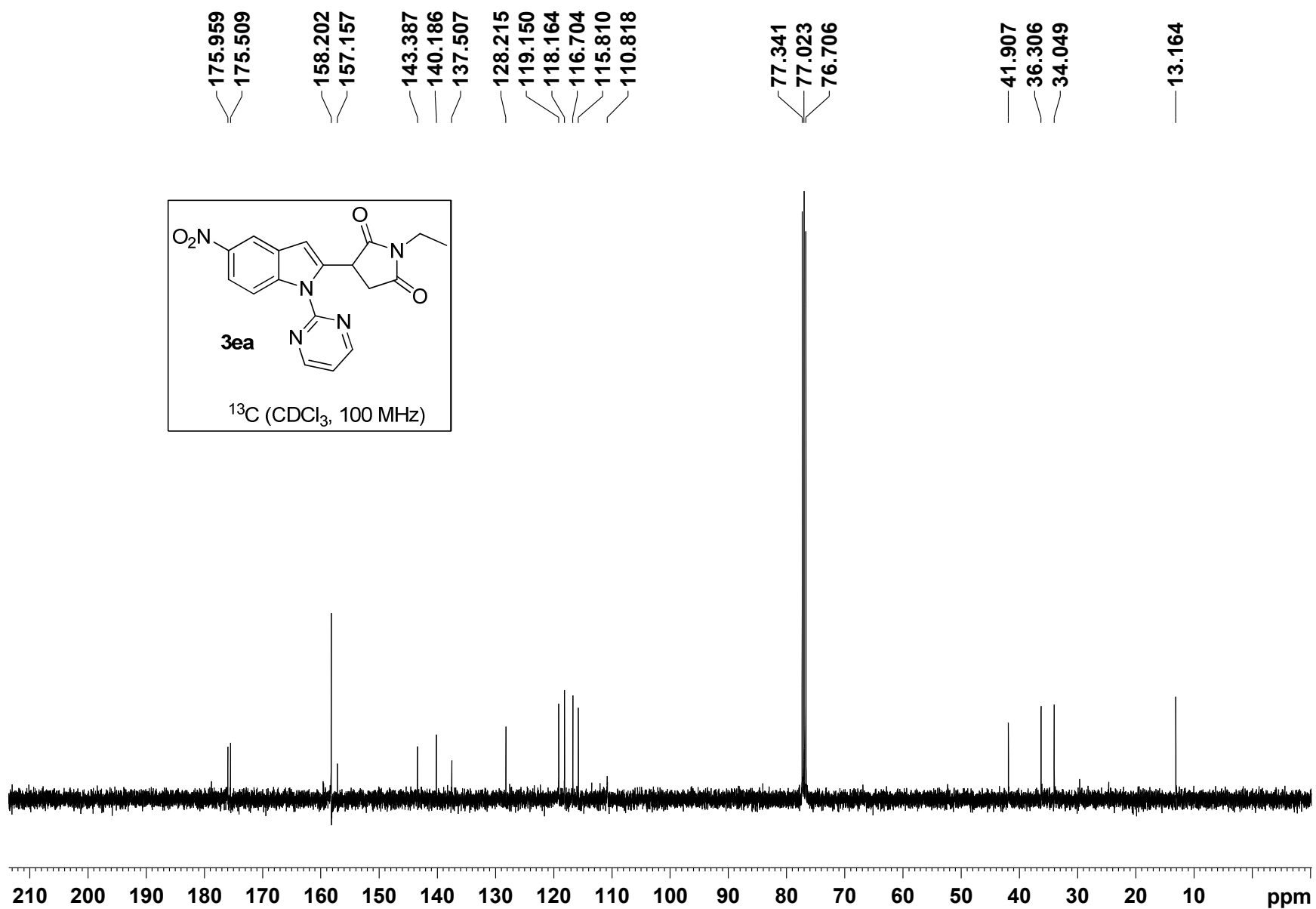
Figure S6.  $^1\text{H}$  NMR spectra of the Compound **3ca**

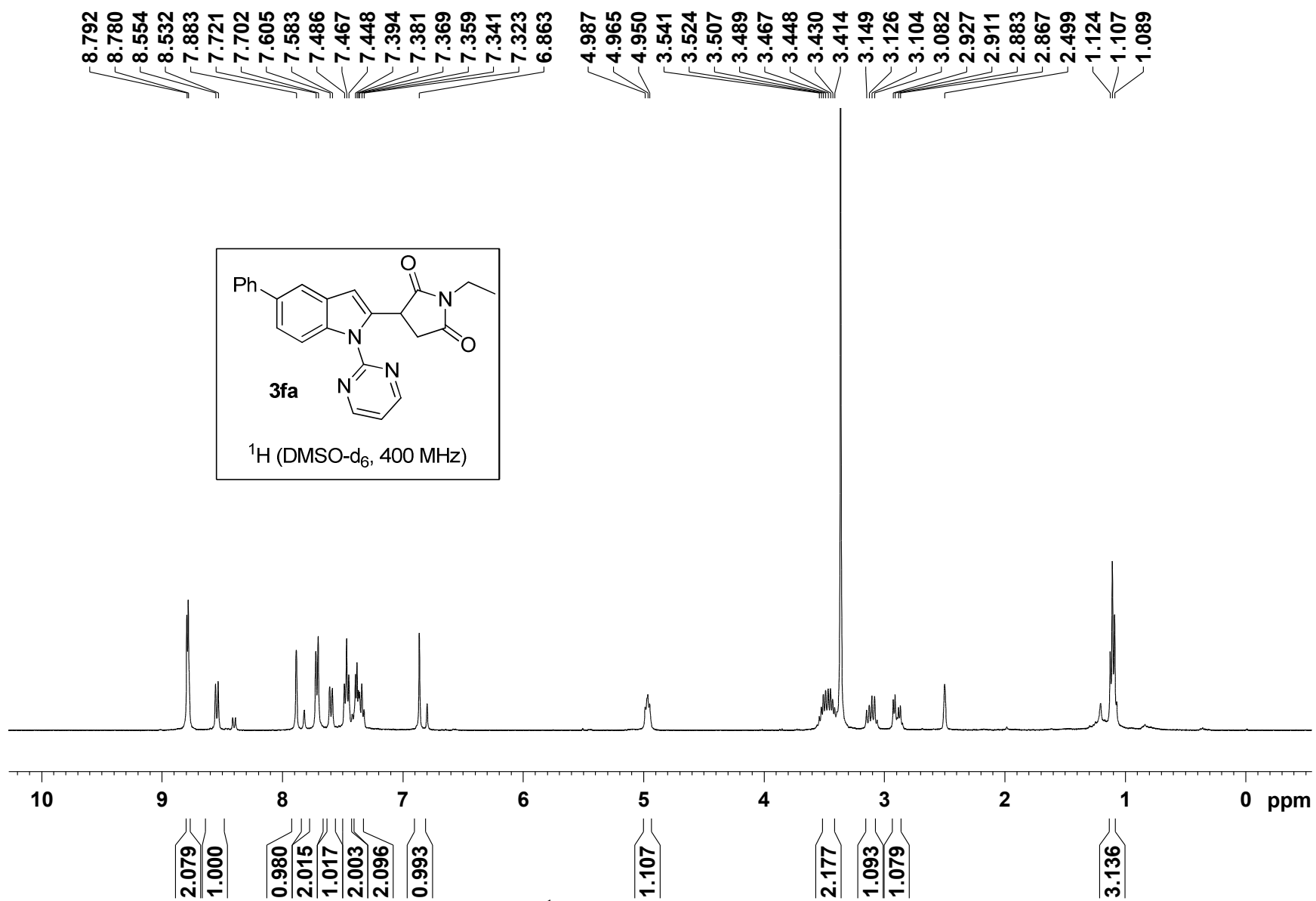
Figure S7.  $^{13}\text{C}$  NMR spectra of the Compound 3ca

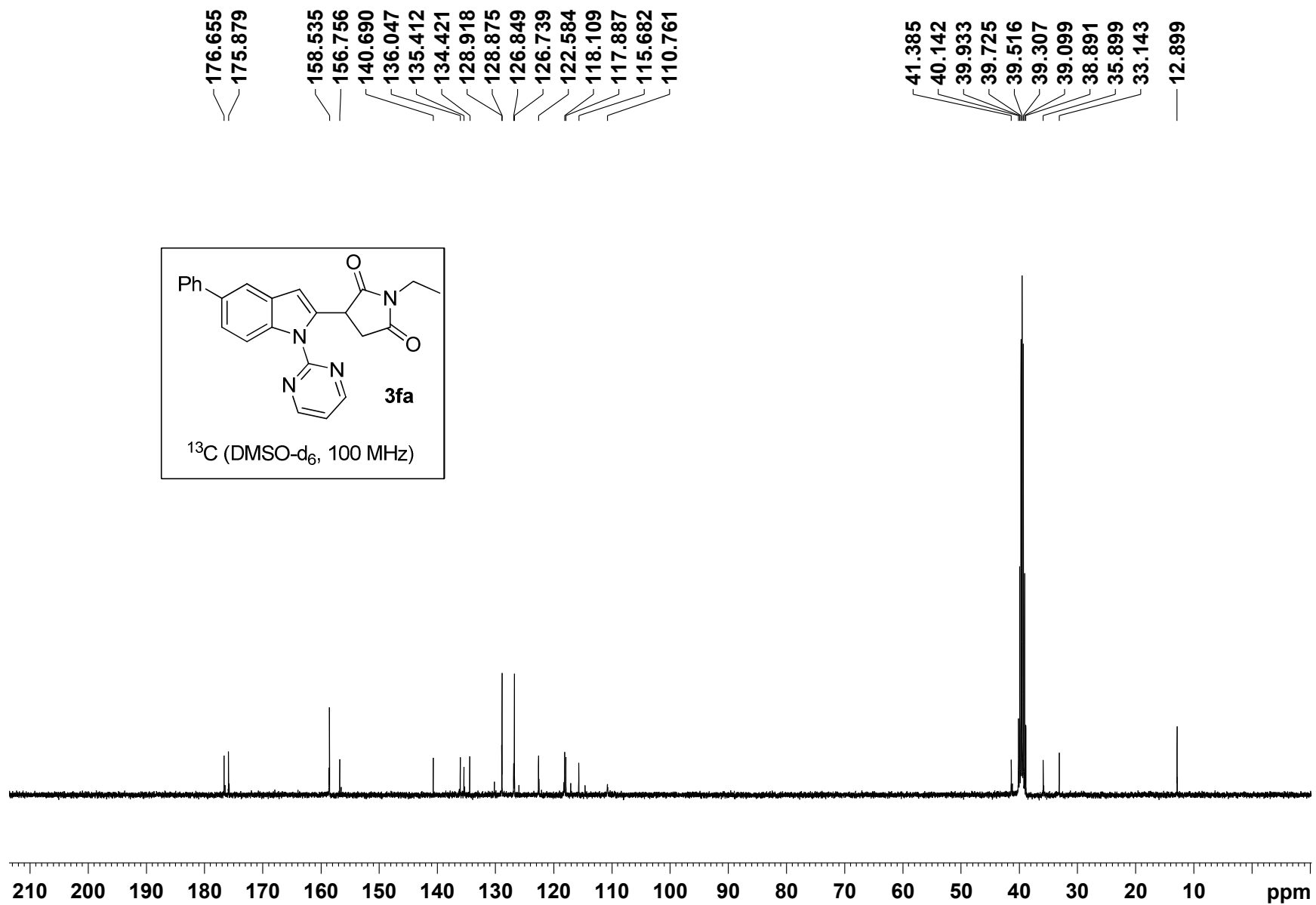
Figure S8.  $^1\text{H}$  NMR spectra of the Compound 3da

Figure S9.  $^{13}\text{C}$  NMR spectra of the Compound 3da

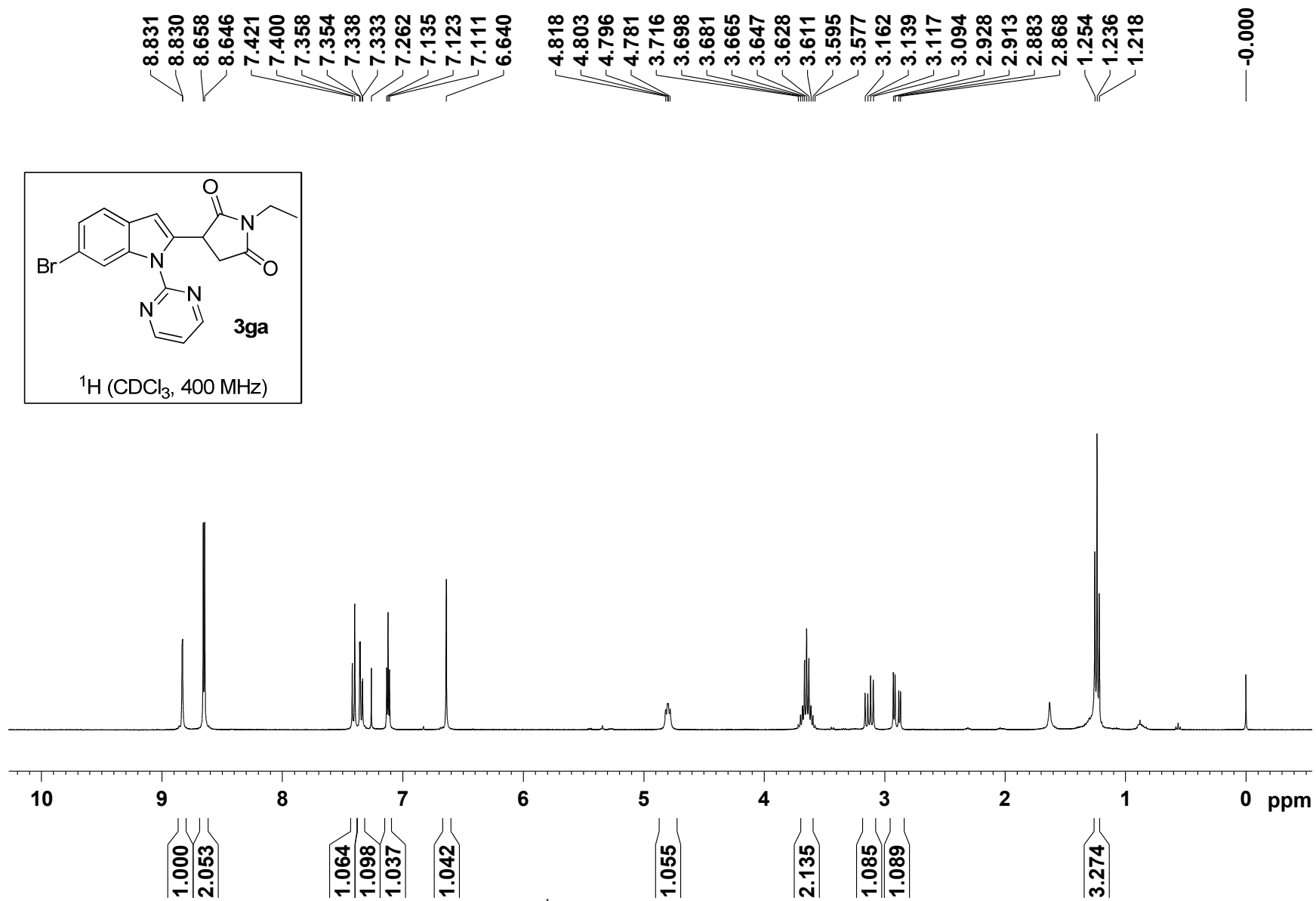
Figure S10.  $^1\text{H}$  NMR spectra of the Compound 3ea

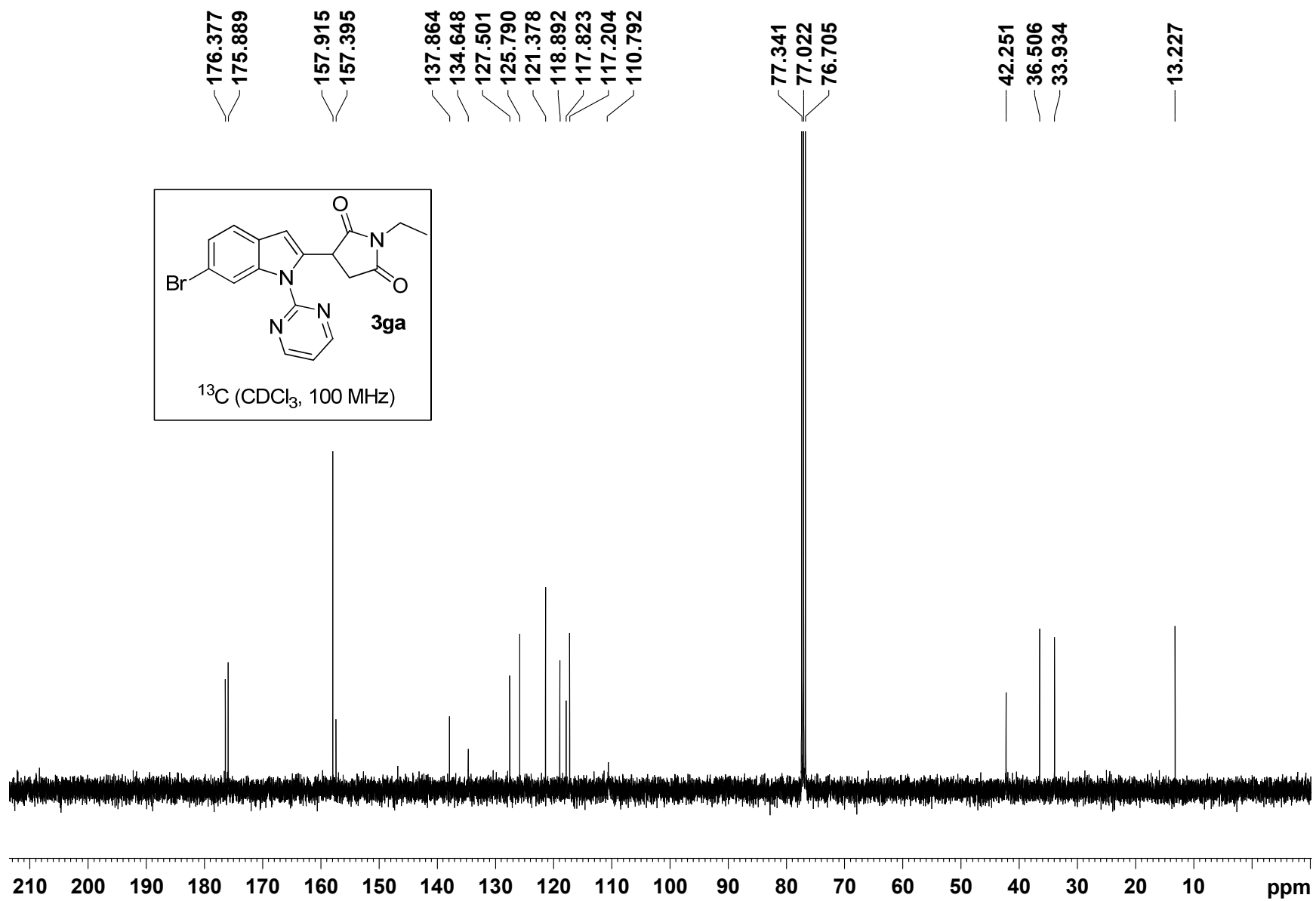
Figure S11.  $^{13}\text{C}$  NMR spectra of the Compound 3ea

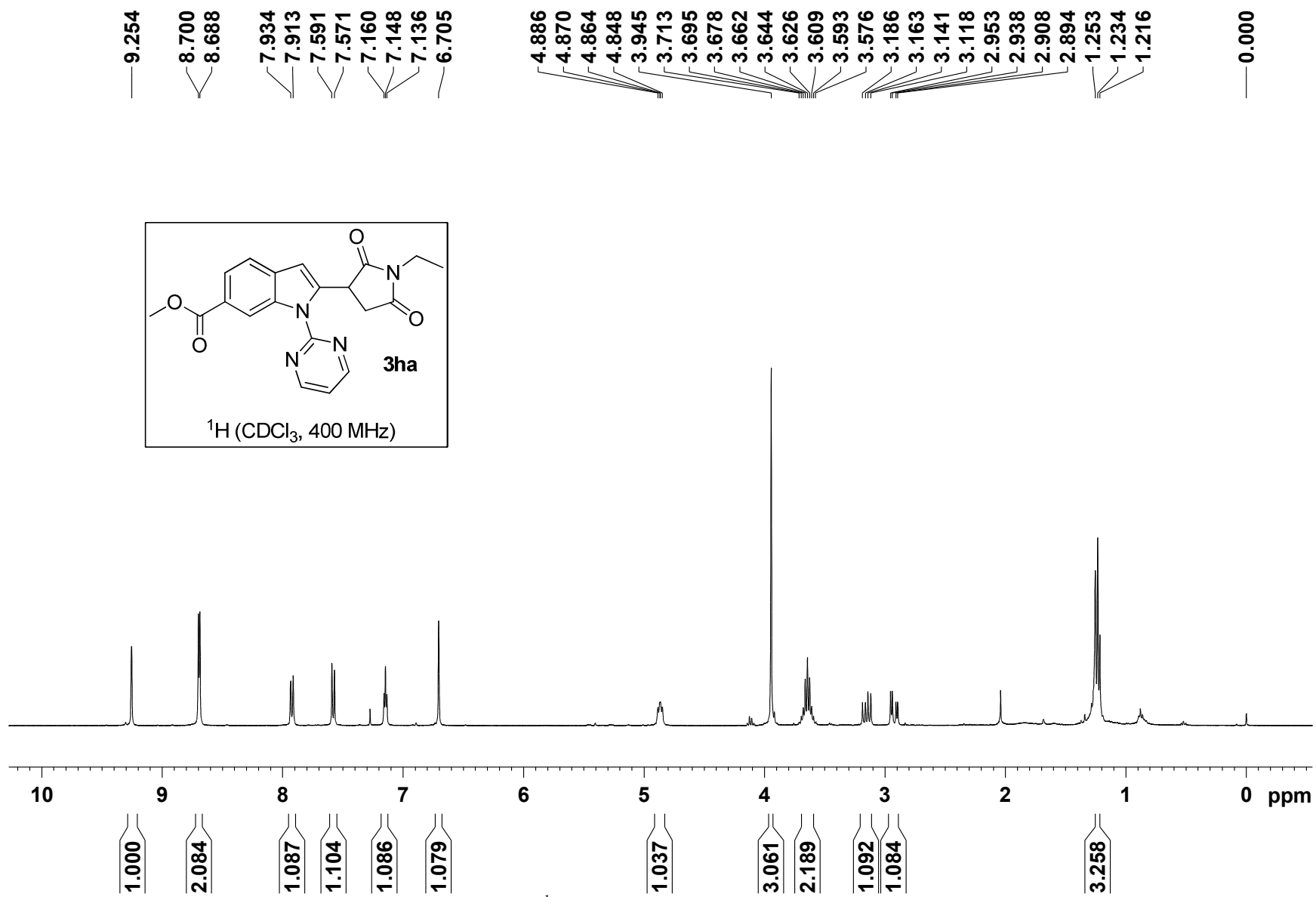
Figure S12. <sup>1</sup>H NMR spectra of the Compound 3fa

Figure S13.  $^{13}\text{C}$  NMR spectra of the Compound 3fa



Figure S14.  $^1\text{H}$  NMR spectra of the Compound 3ga



Figure S16. <sup>1</sup>H NMR spectra of the Compound 3ha

176.224  
175.784  
167.892  
158.080  
157.373  
137.313  
136.682  
132.307  
125.693  
123.608  
120.008  
117.741  
117.428  
110.230

77.378  
77.060  
76.742

52.052

42.148  
36.503  
33.964

13.184

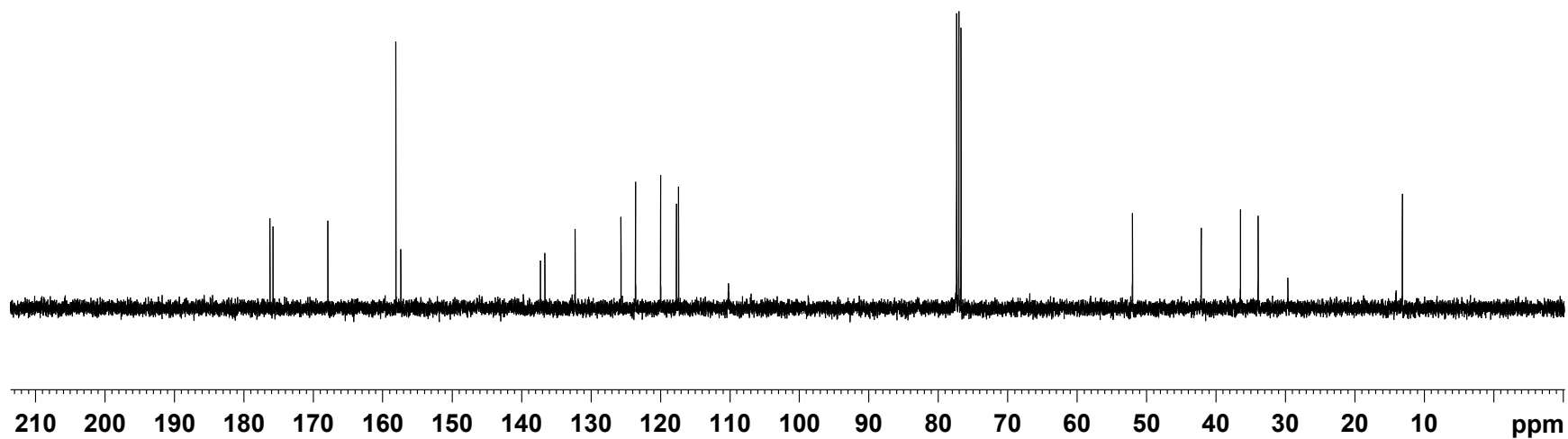
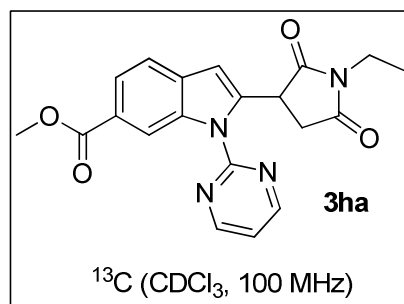
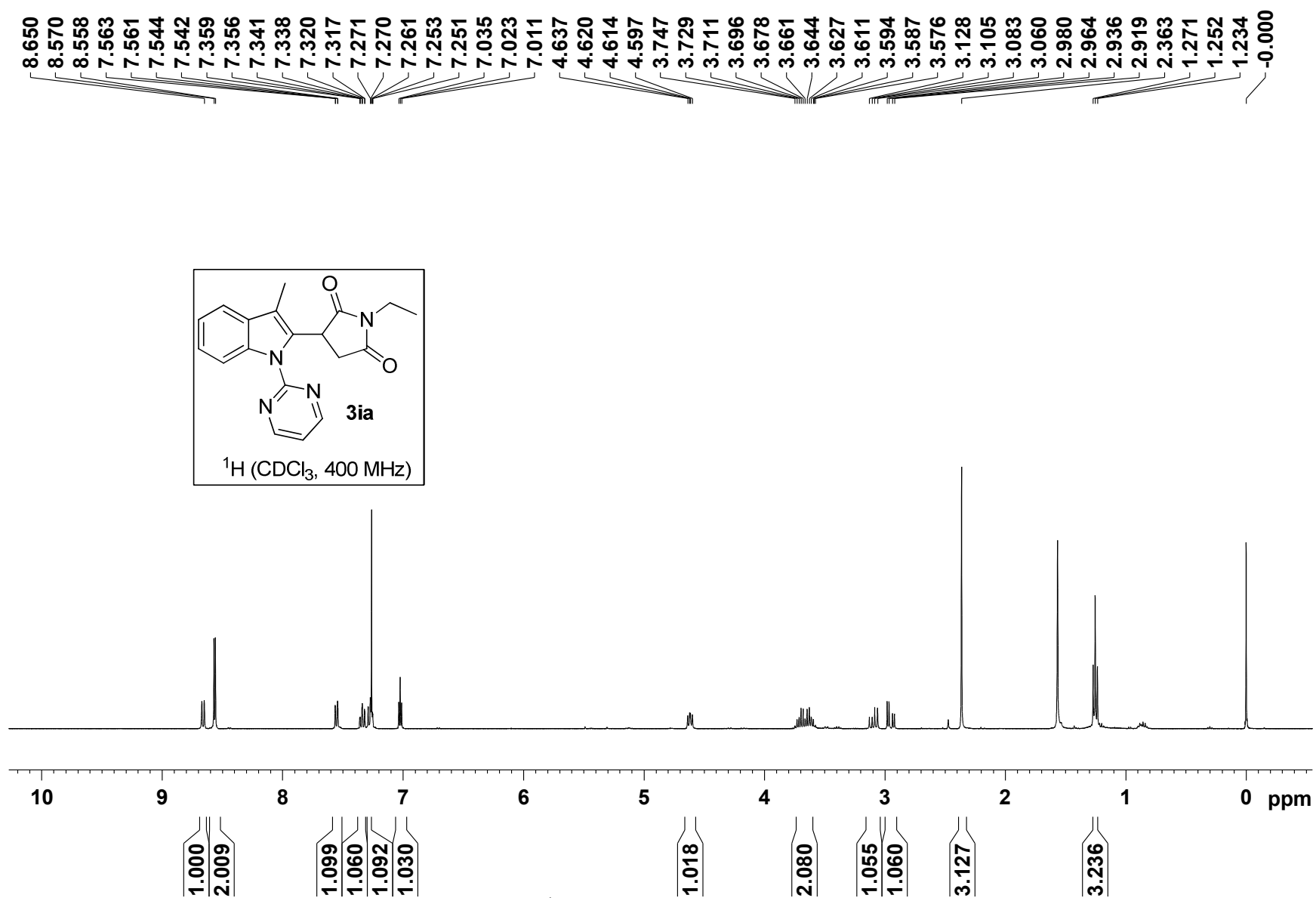
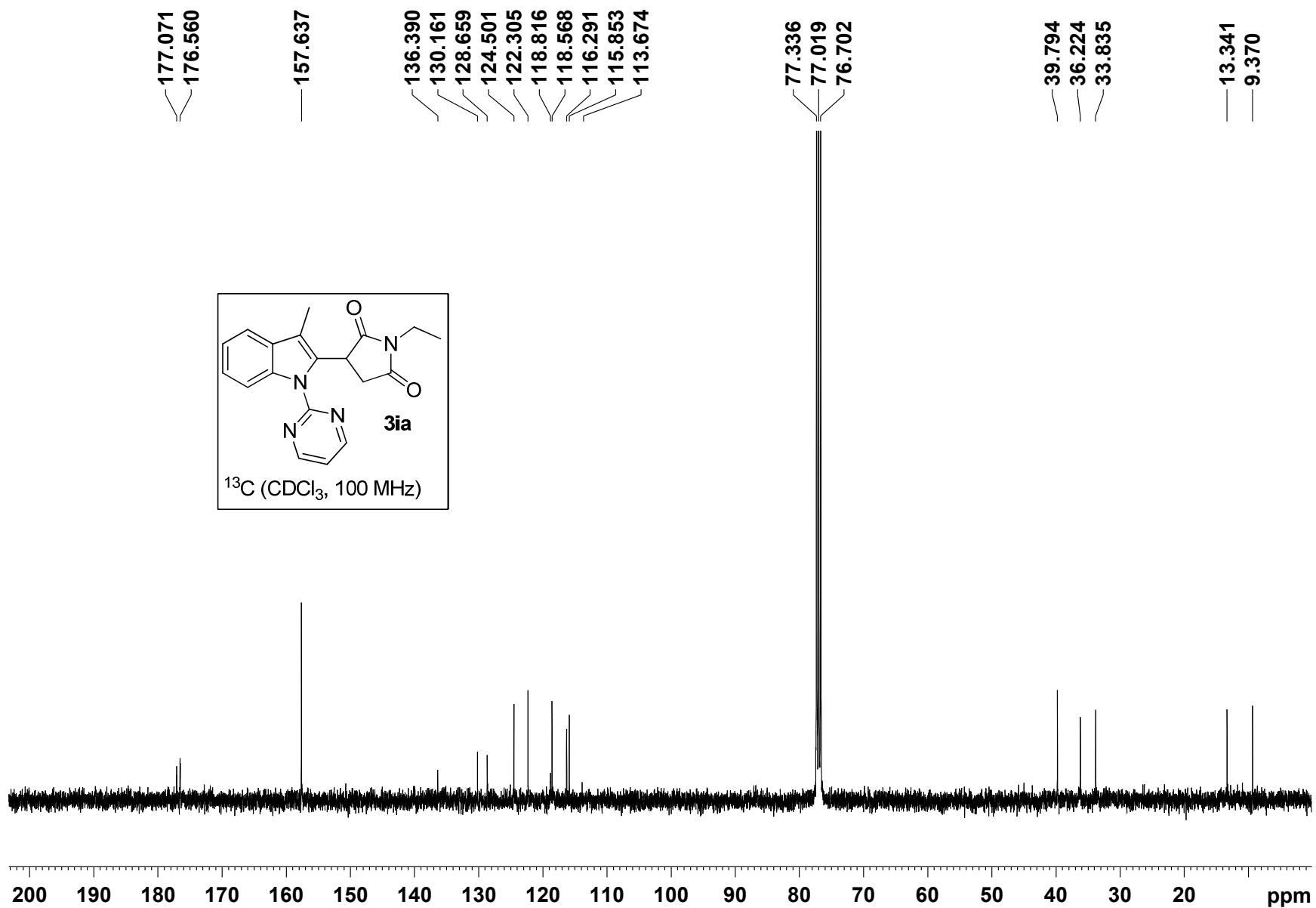
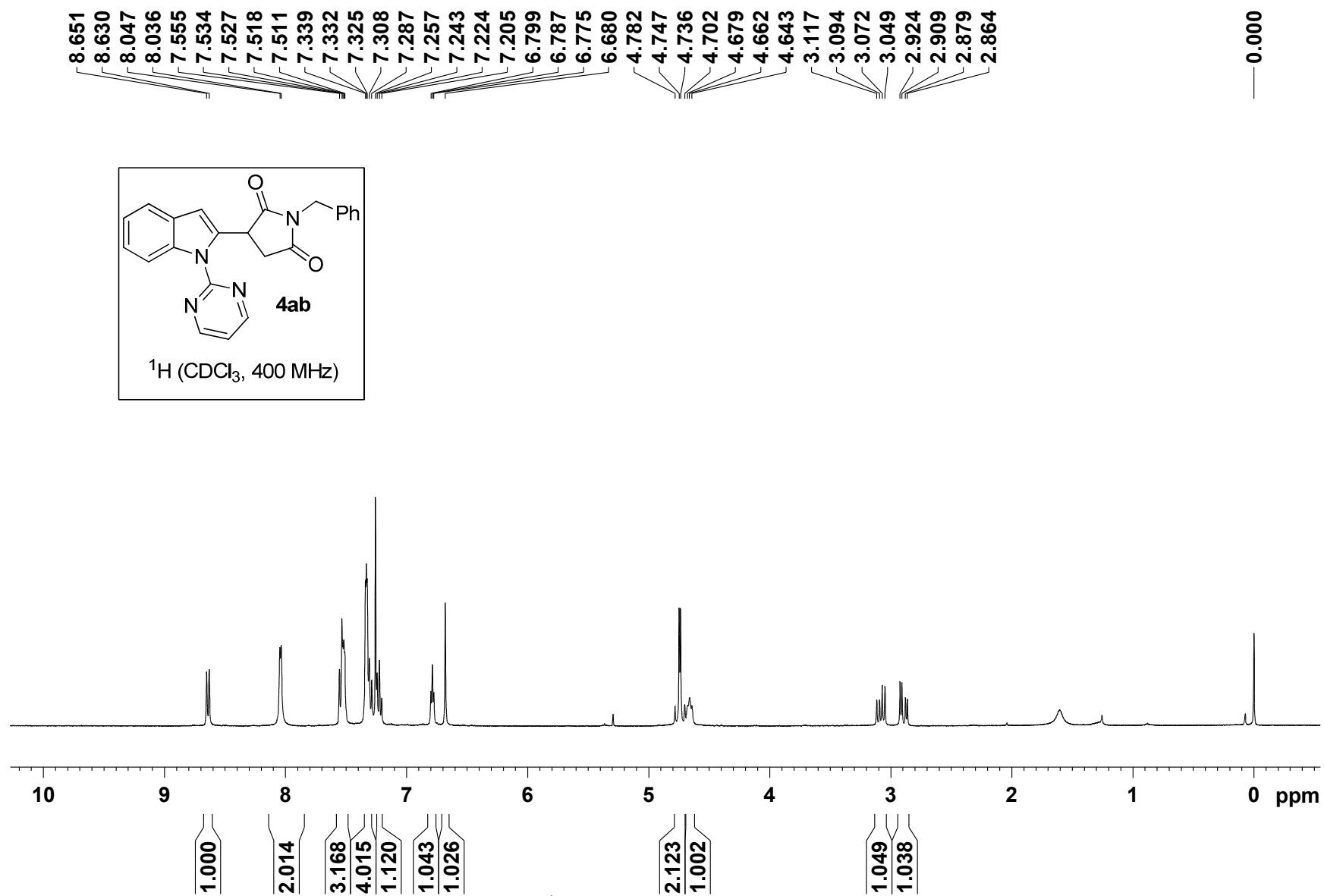
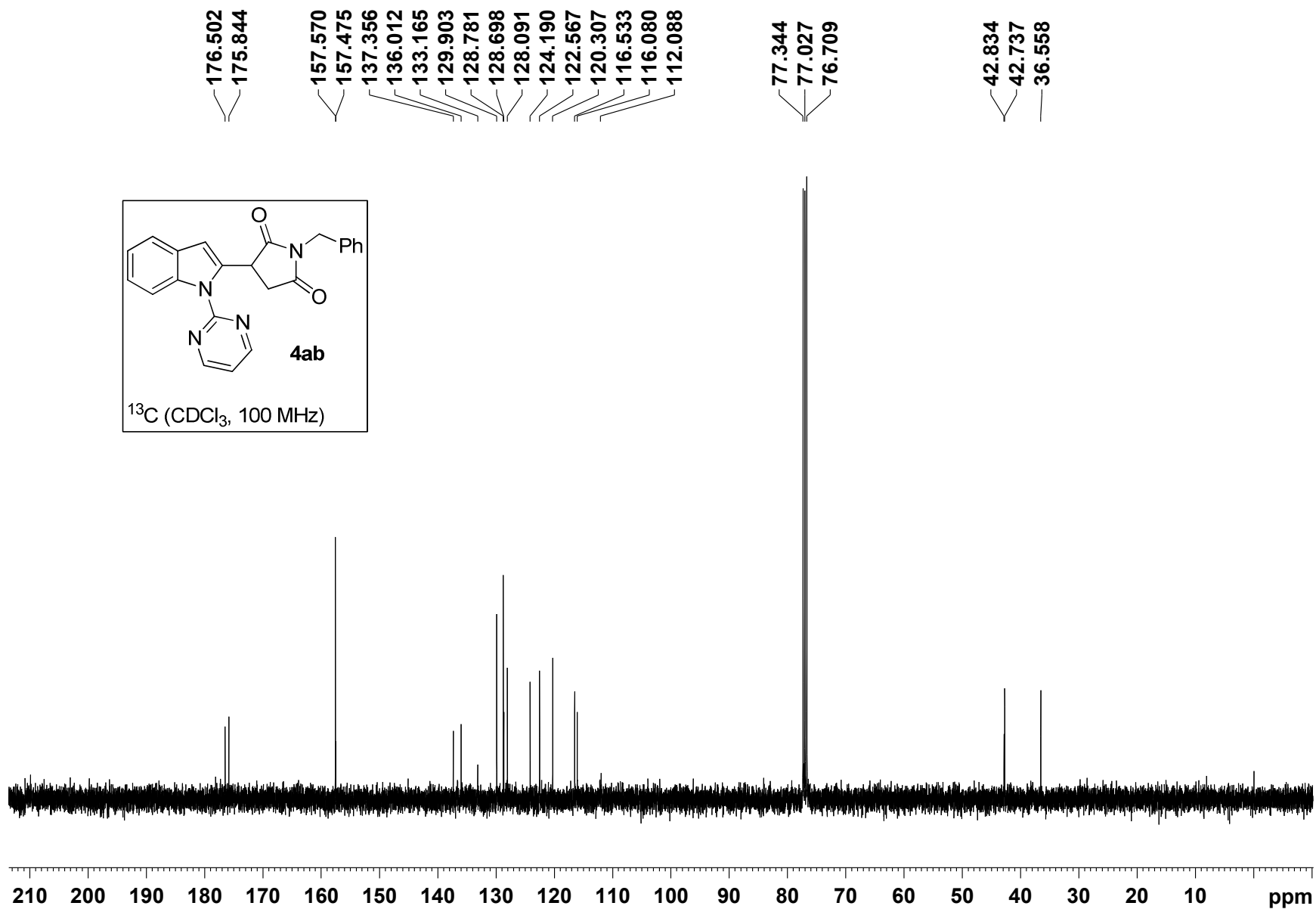


Figure S17.  $^{13}\text{C}$  NMR spectra of the Compound **3ha**

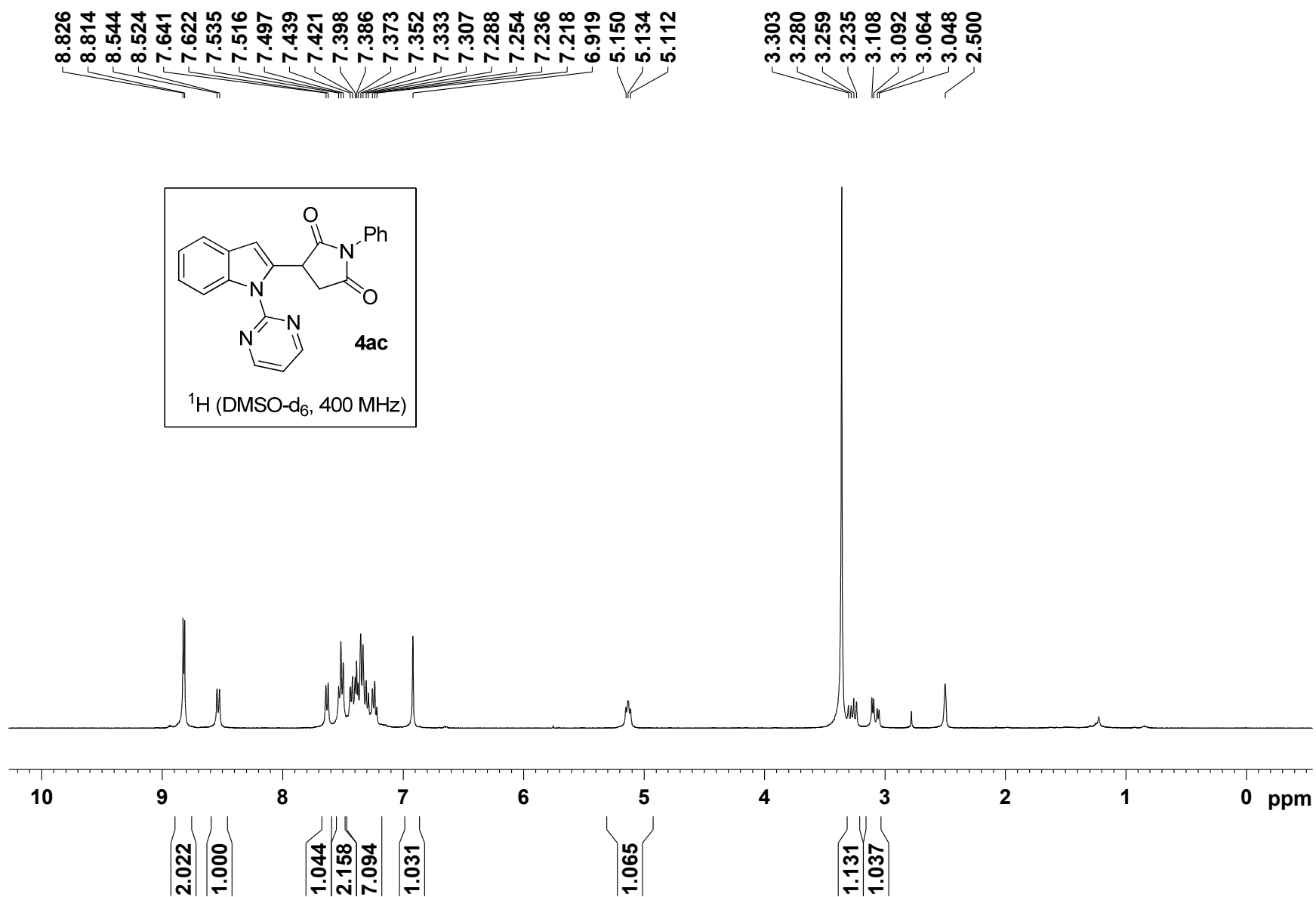
Figure S18. <sup>1</sup>H NMR spectra of the Compound 3ia

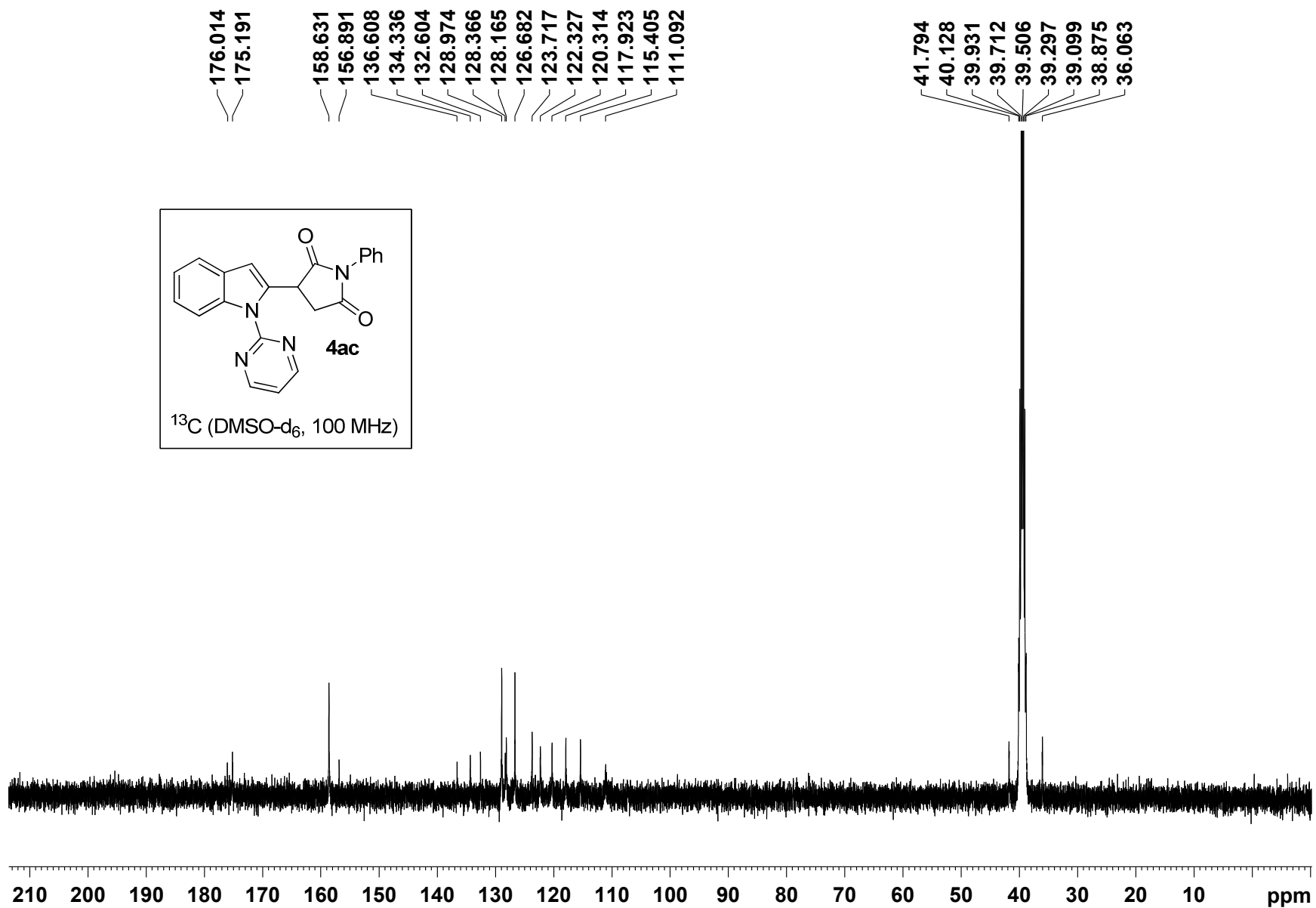
Figure S19. <sup>13</sup>C NMR spectra of the Compound 3ia

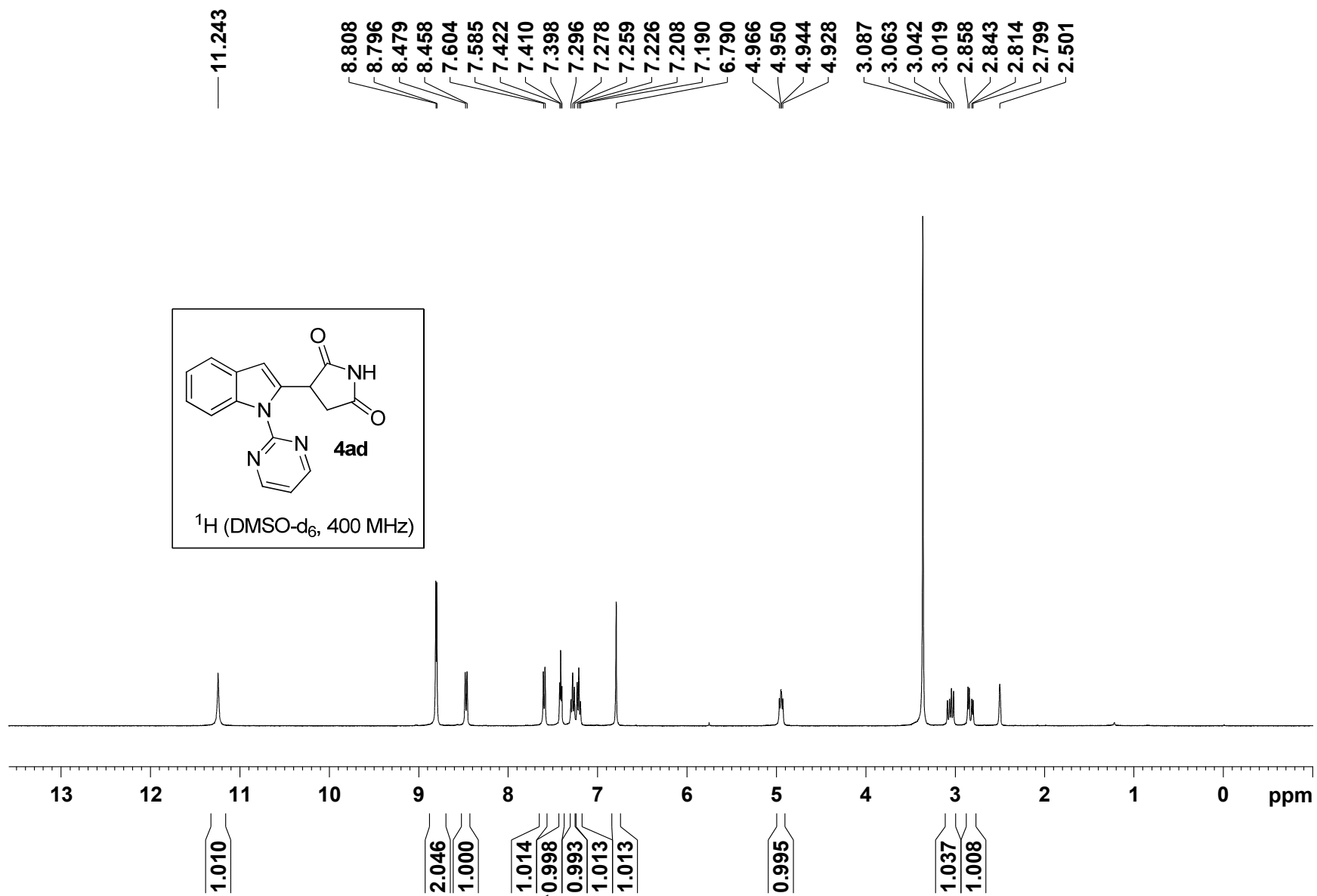
Figure S20. <sup>1</sup>H NMR spectra of the Compound 4ab

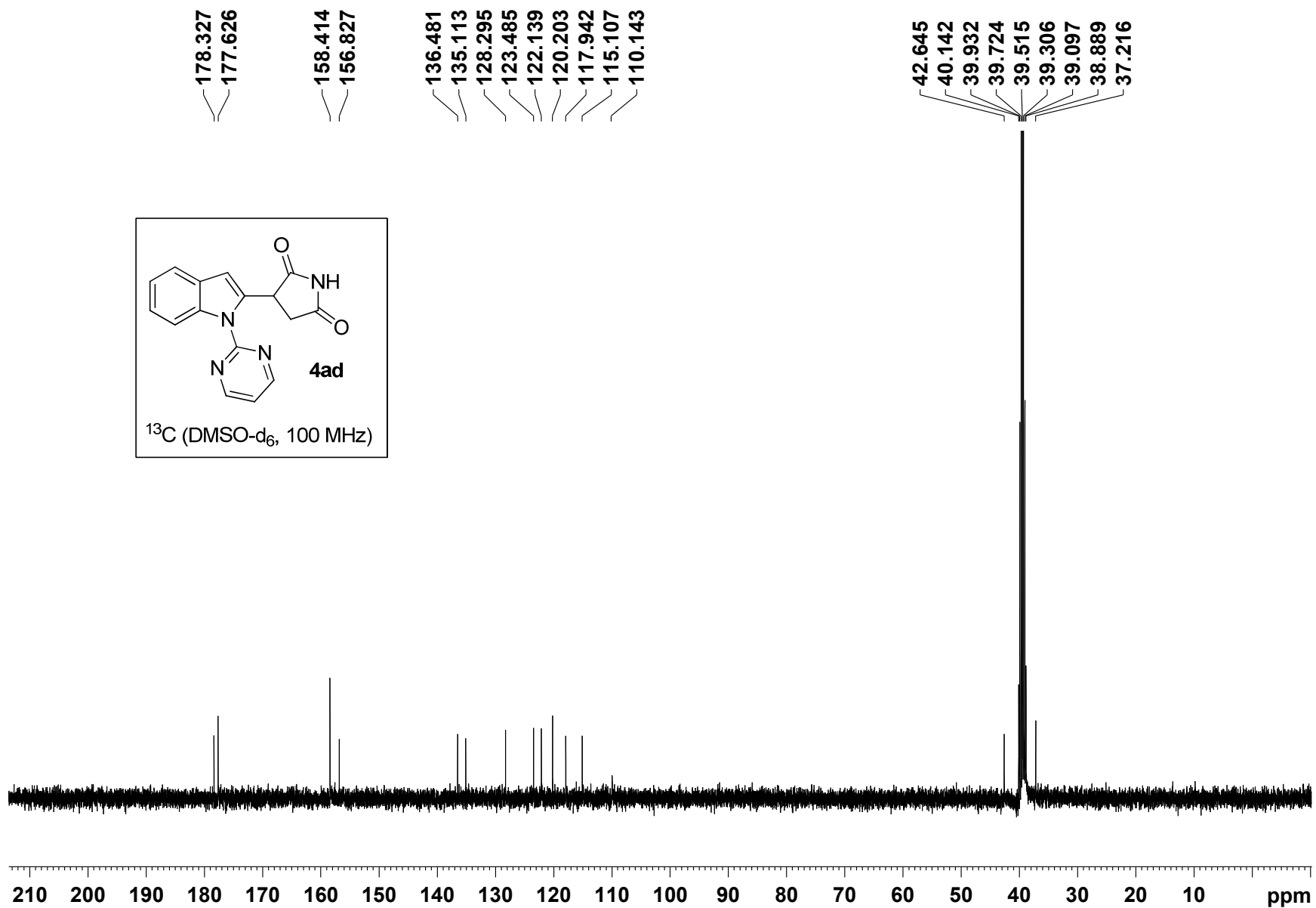
Figure S21.  $^{13}\text{C}$  NMR spectra of the Compound **4ab**

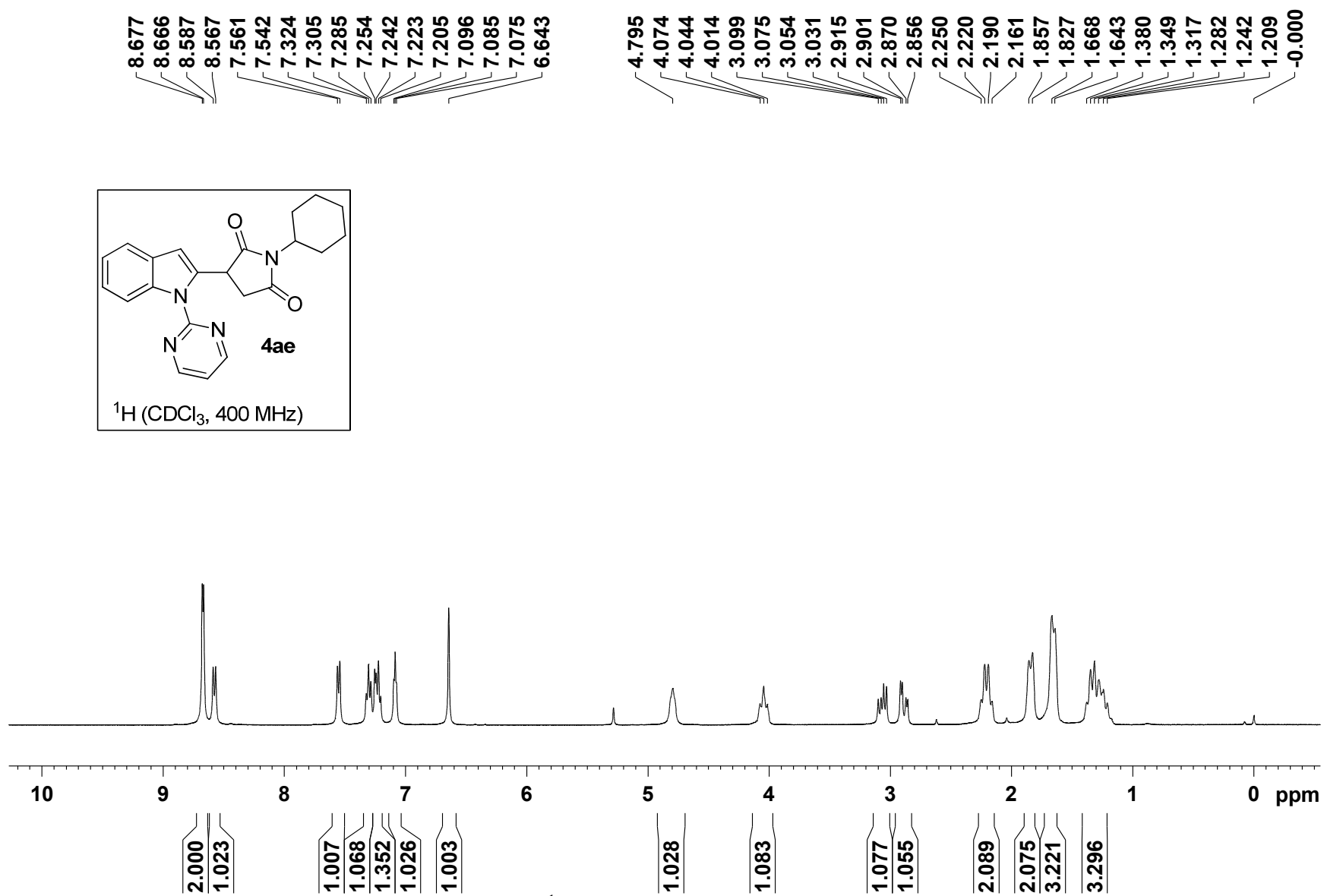


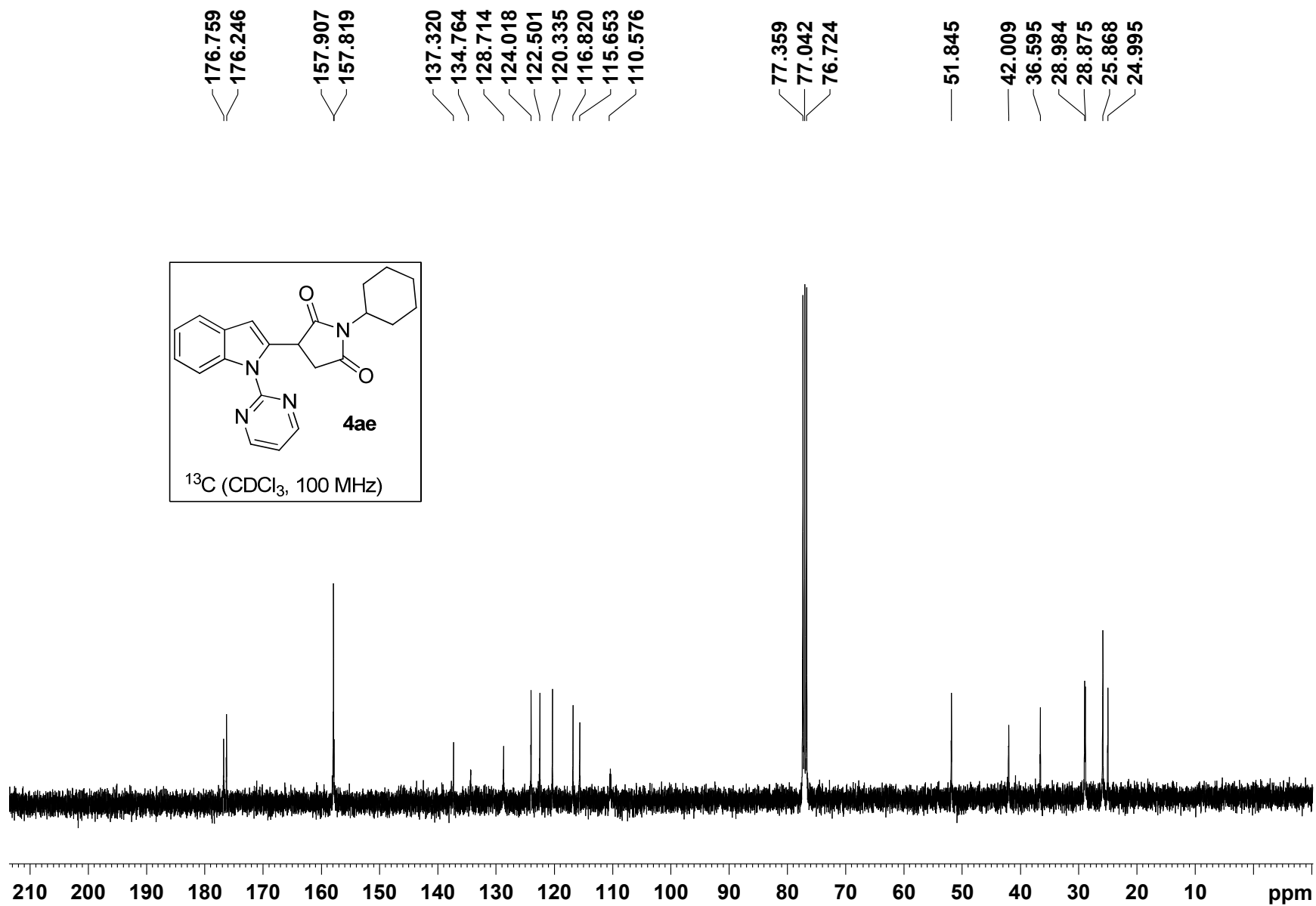
Figure S22. <sup>1</sup>H NMR spectra of the Compound 4ac

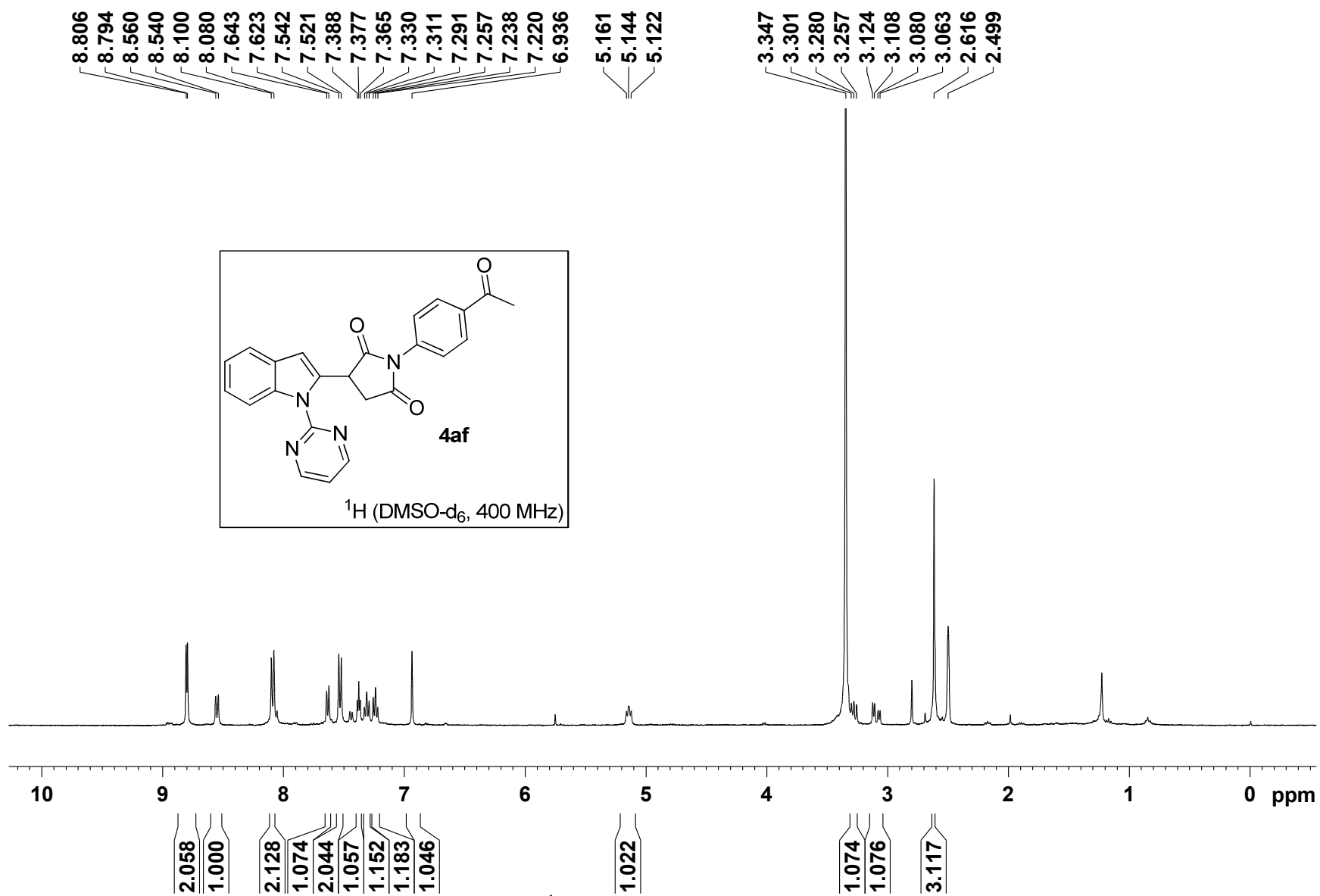
Figure S23. <sup>13</sup>C NMR spectra of the Compound 4ac

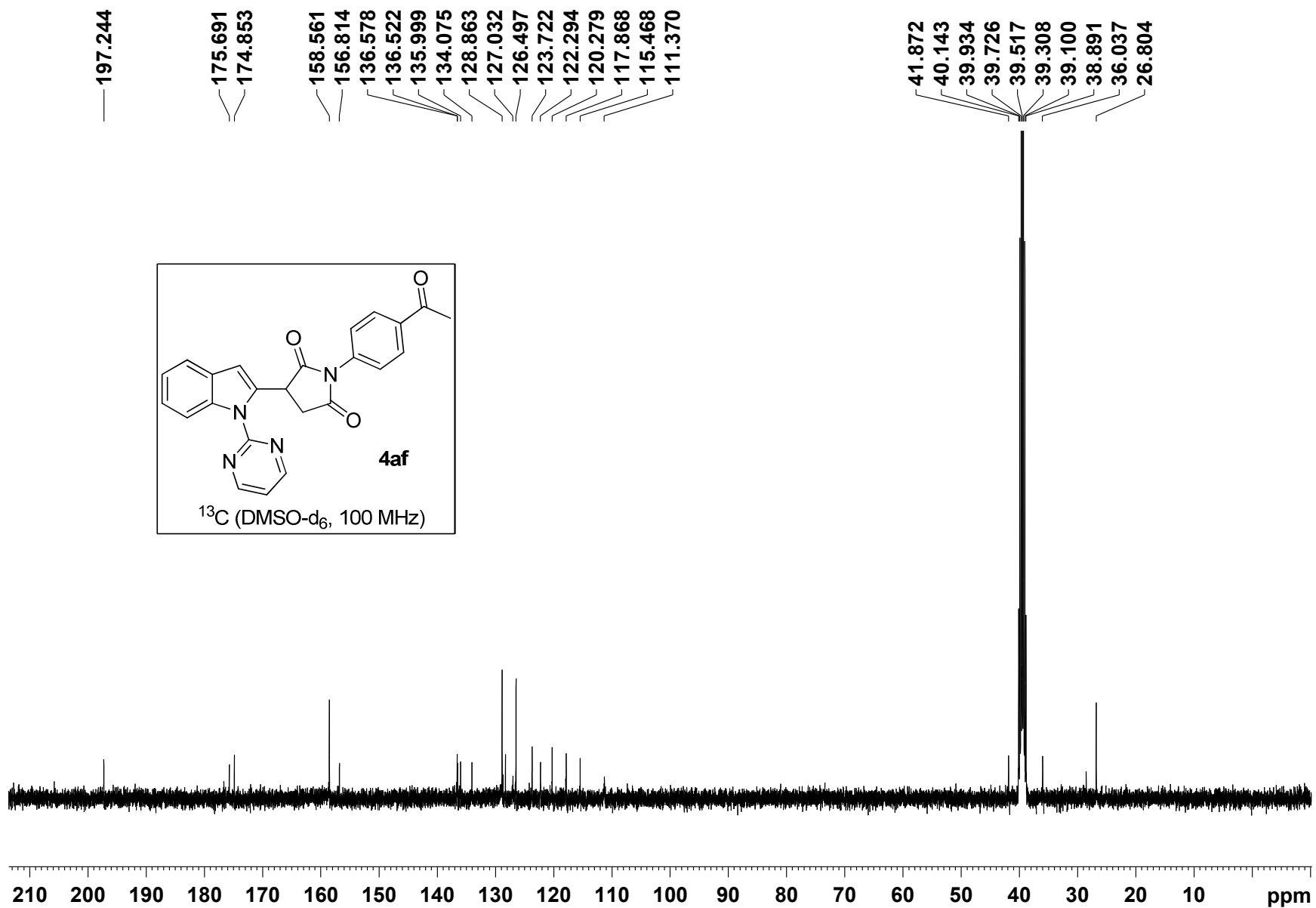
Figure S24. <sup>1</sup>H NMR spectra of the Compound 4ad



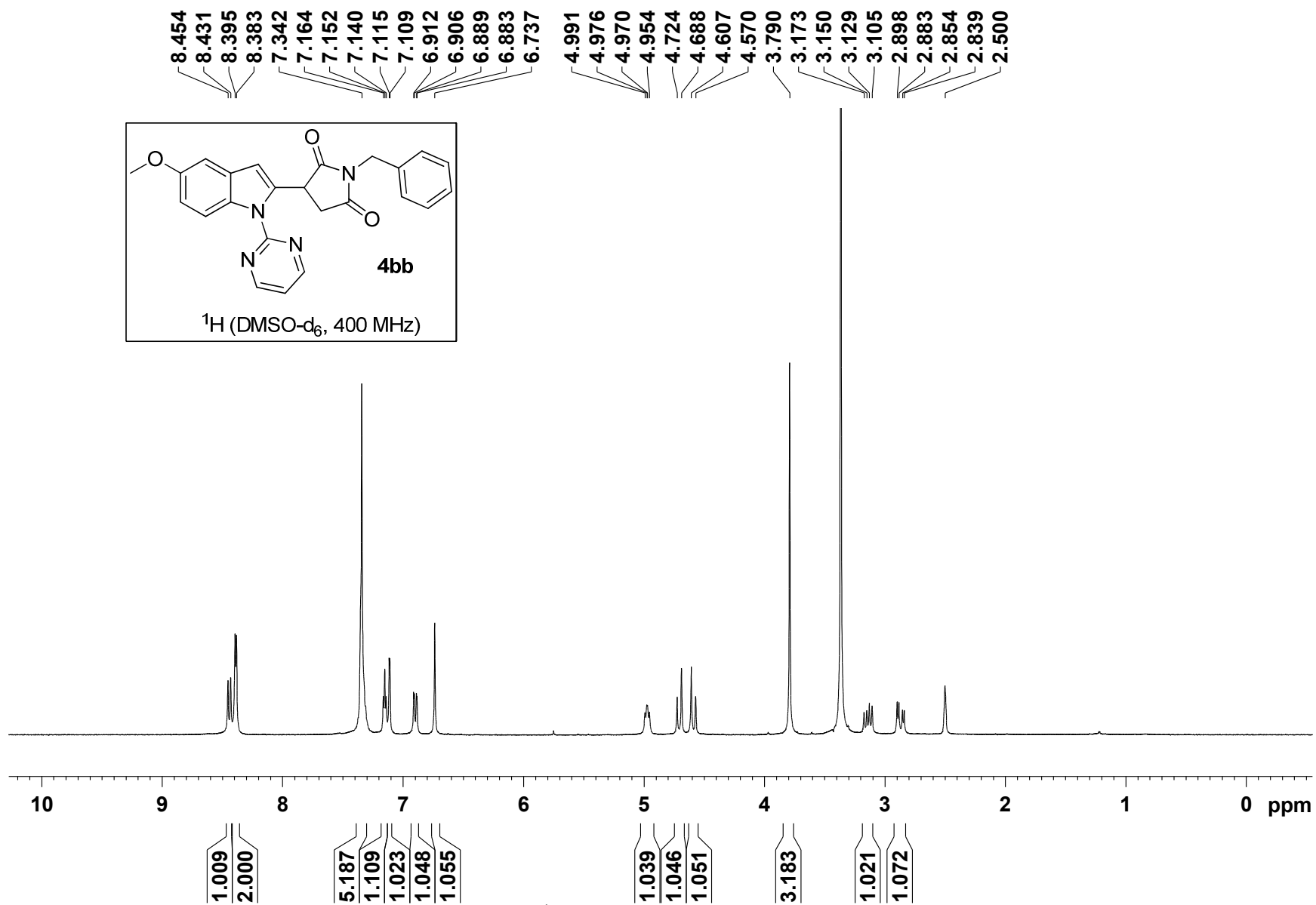


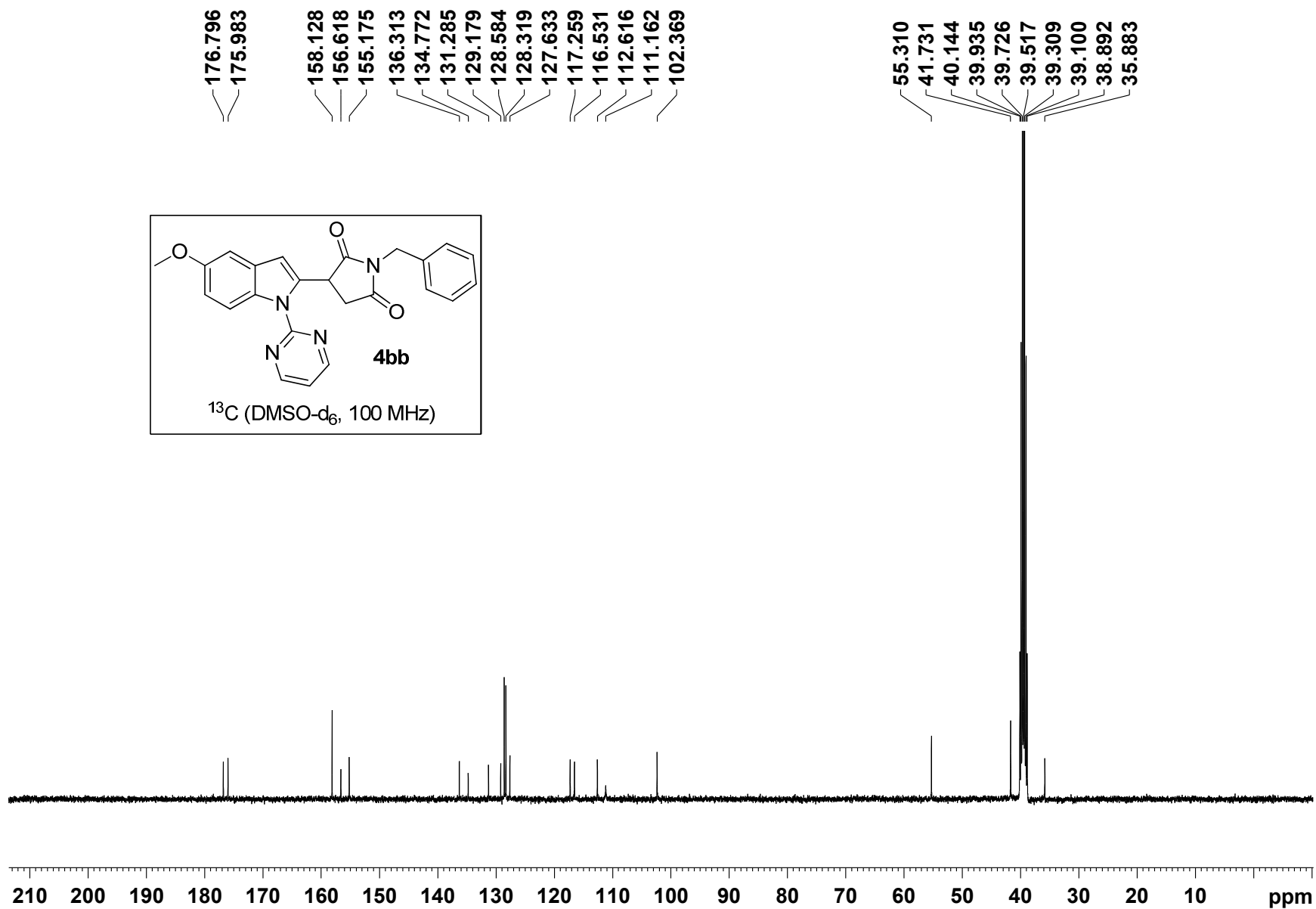
Figure S27. <sup>13</sup>C NMR spectra of the Compound 4ae

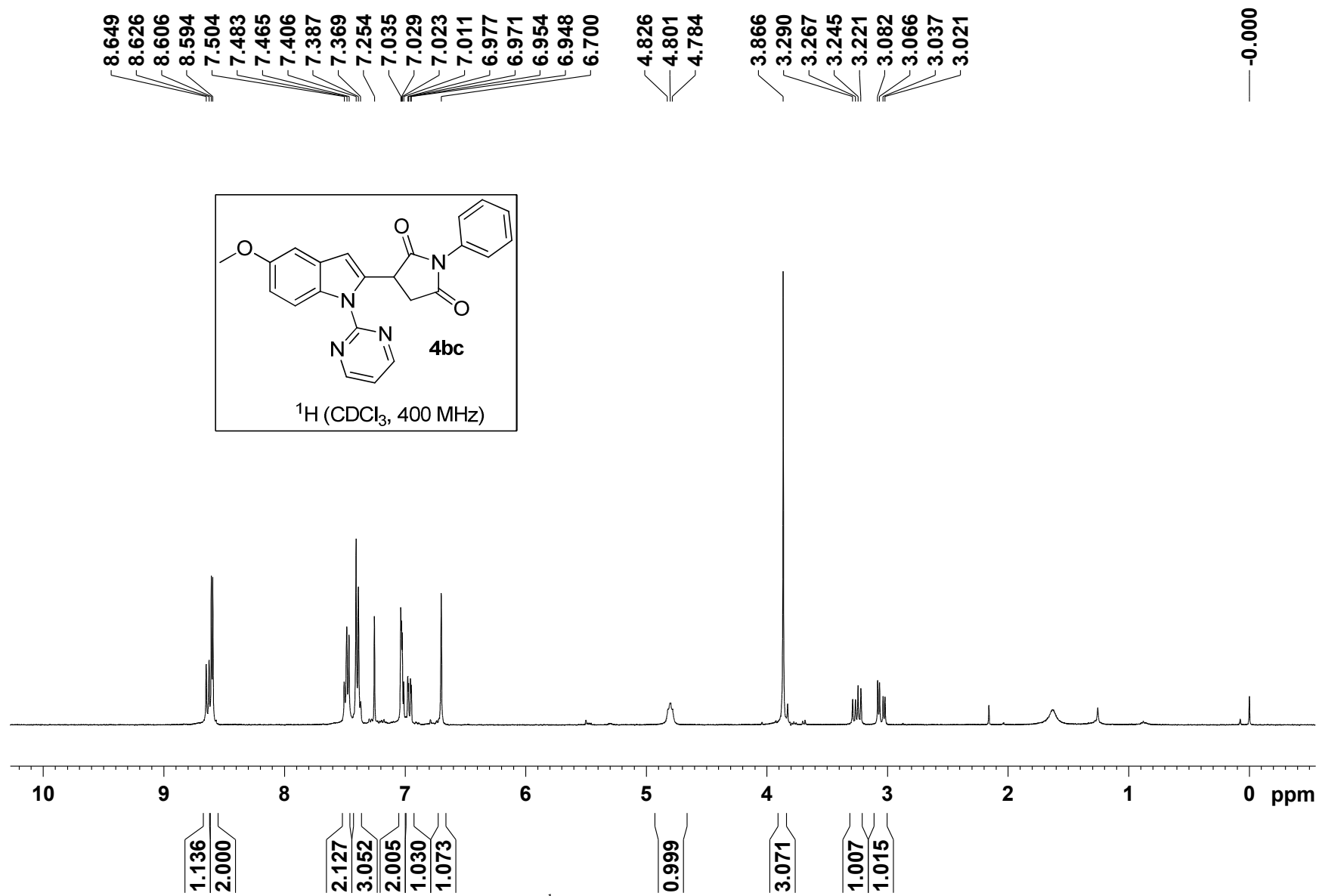
Figure S28. <sup>1</sup>H NMR spectra of the Compound 4af

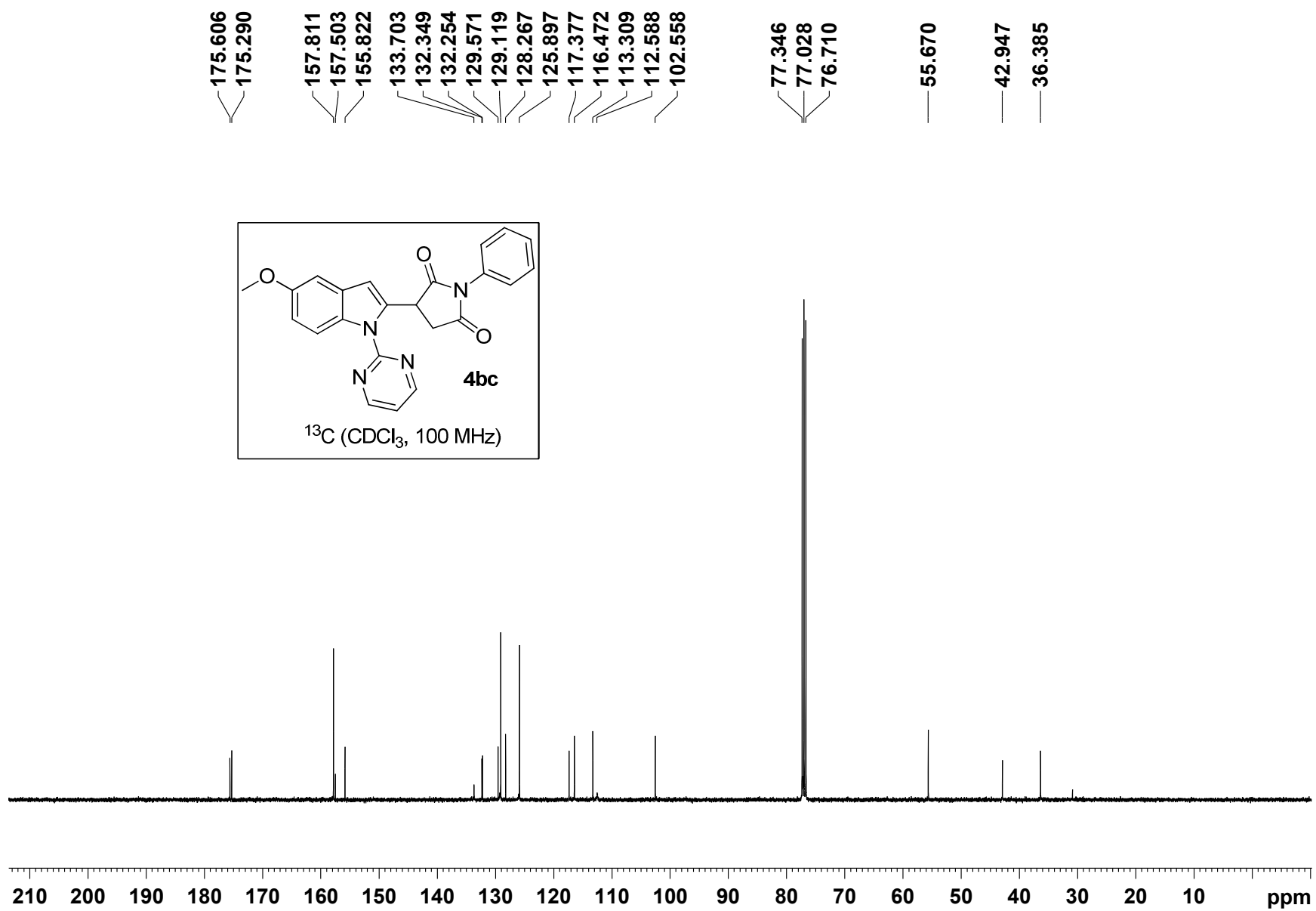
Figure S29. <sup>13</sup>C NMR spectra of the Compound 4af

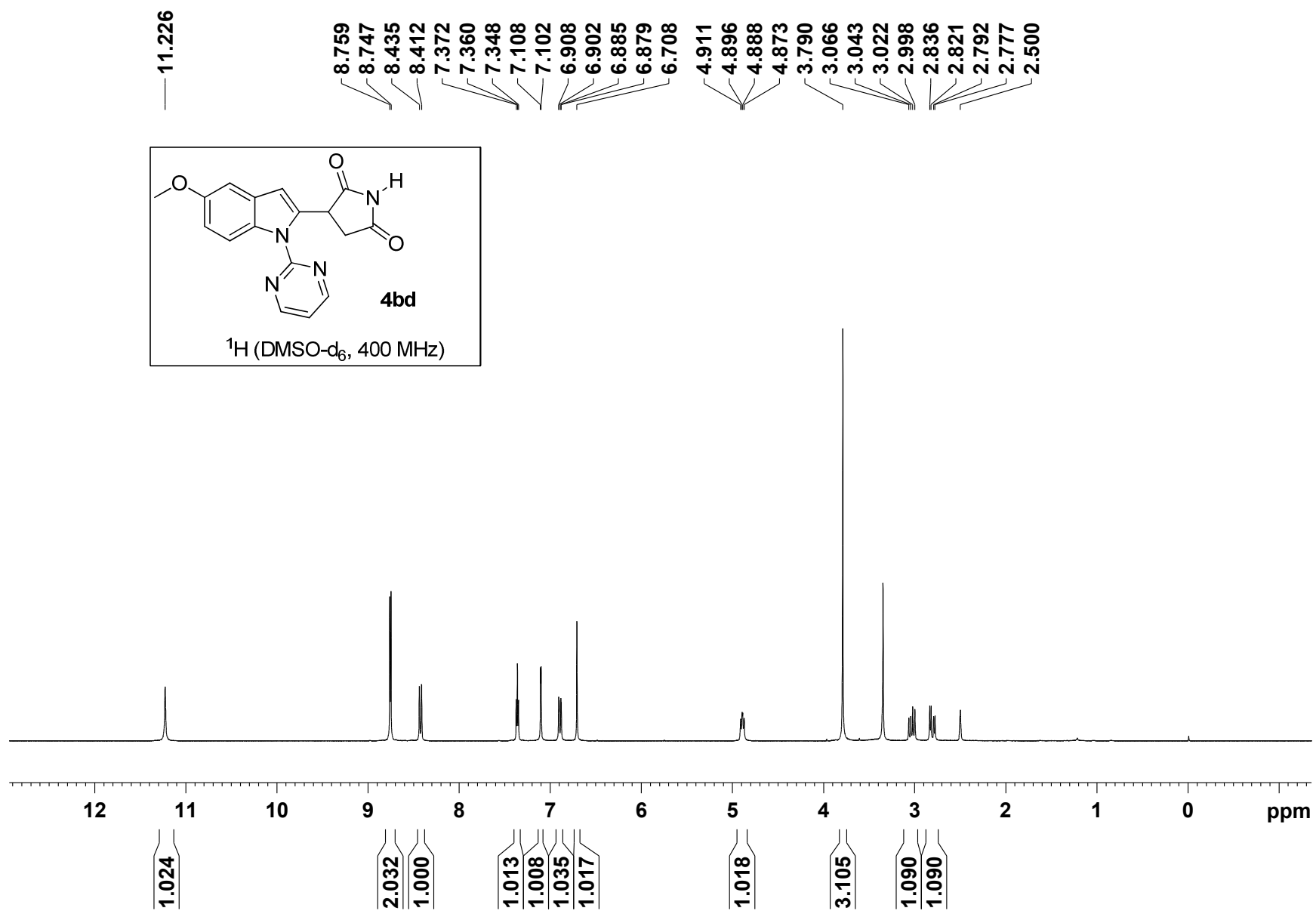


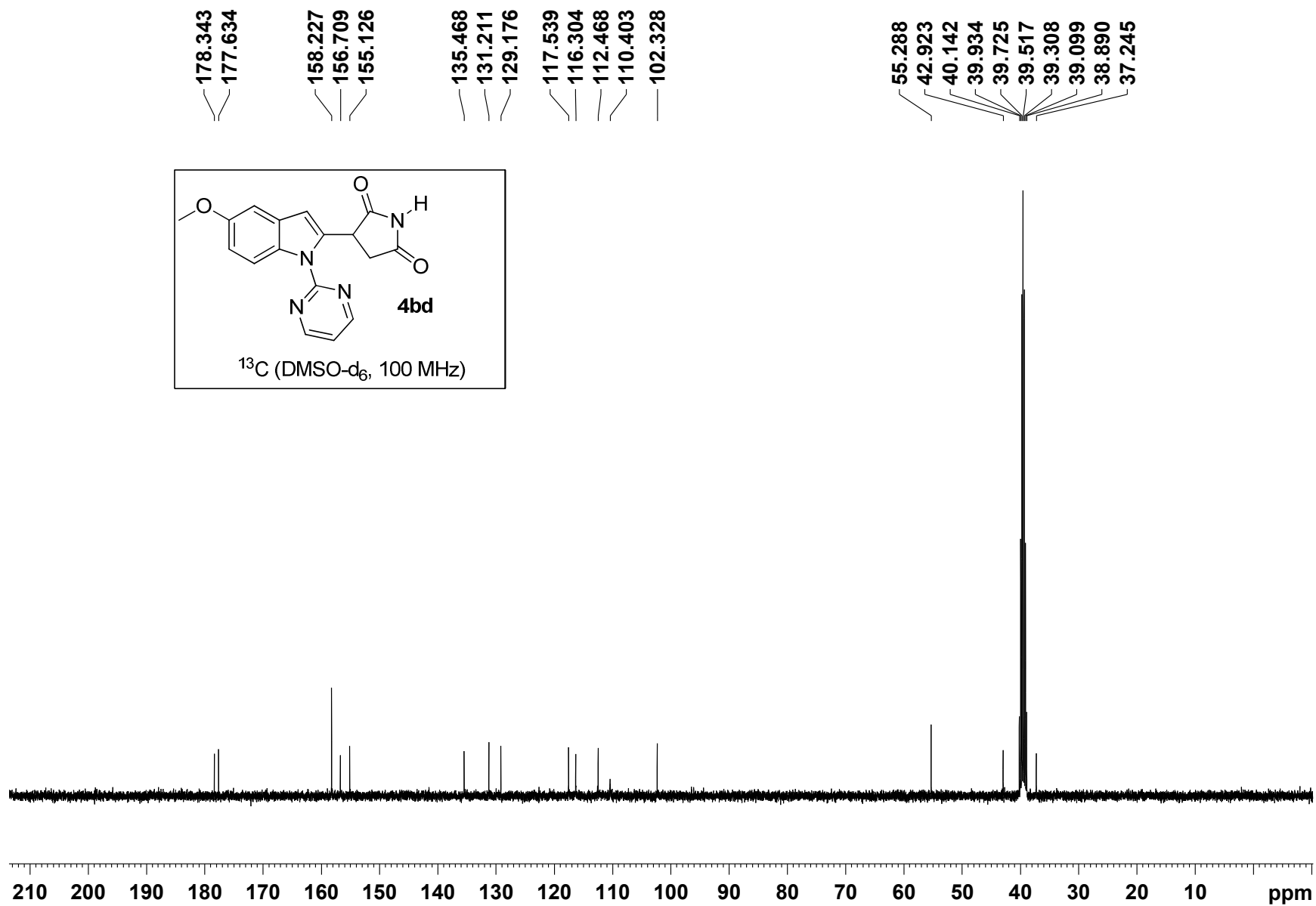
Figure S30. <sup>1</sup>H NMR spectra of the Compound 4bb

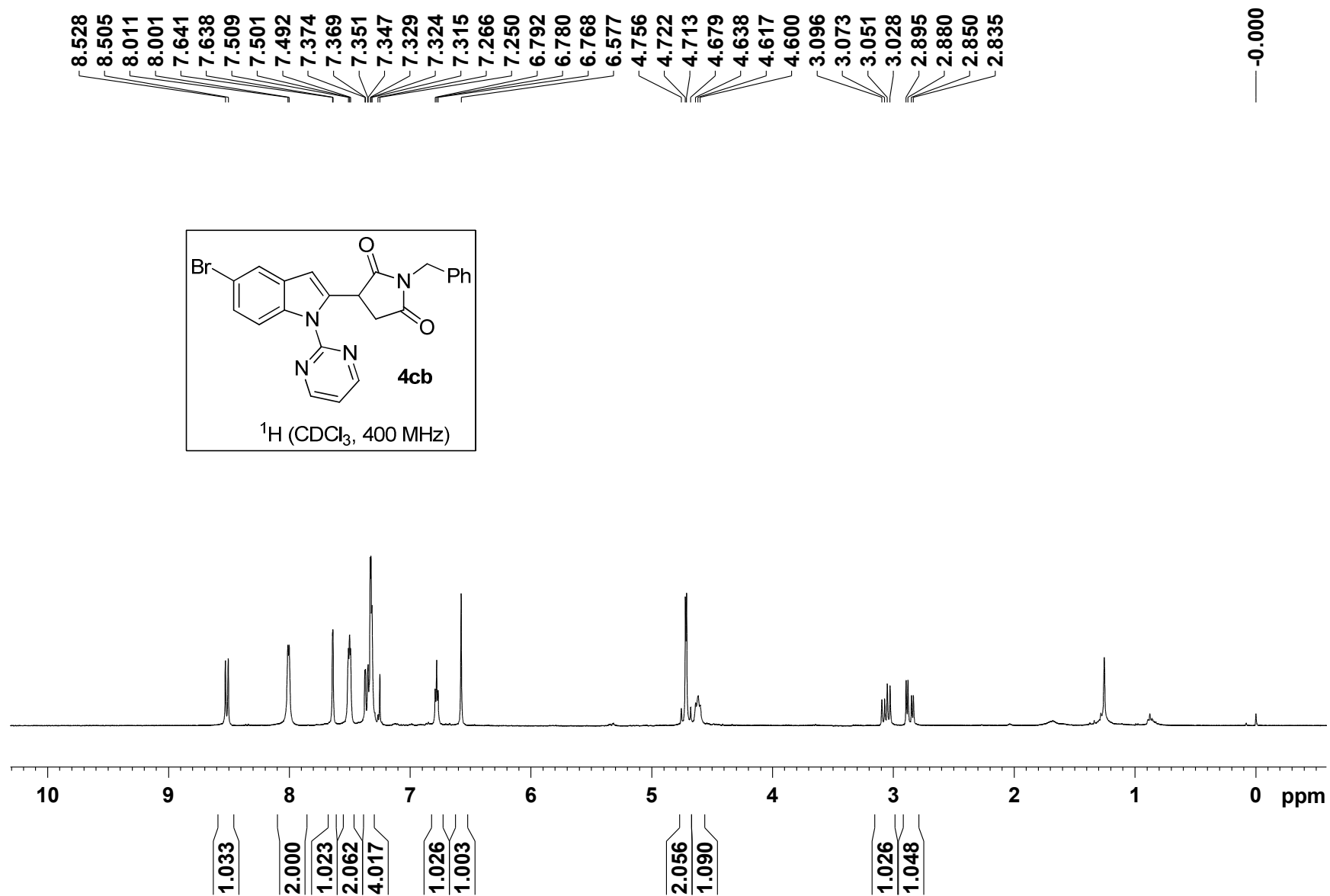
Figure S31.  $^{13}\text{C}$  NMR spectra of the Compound **4bb**

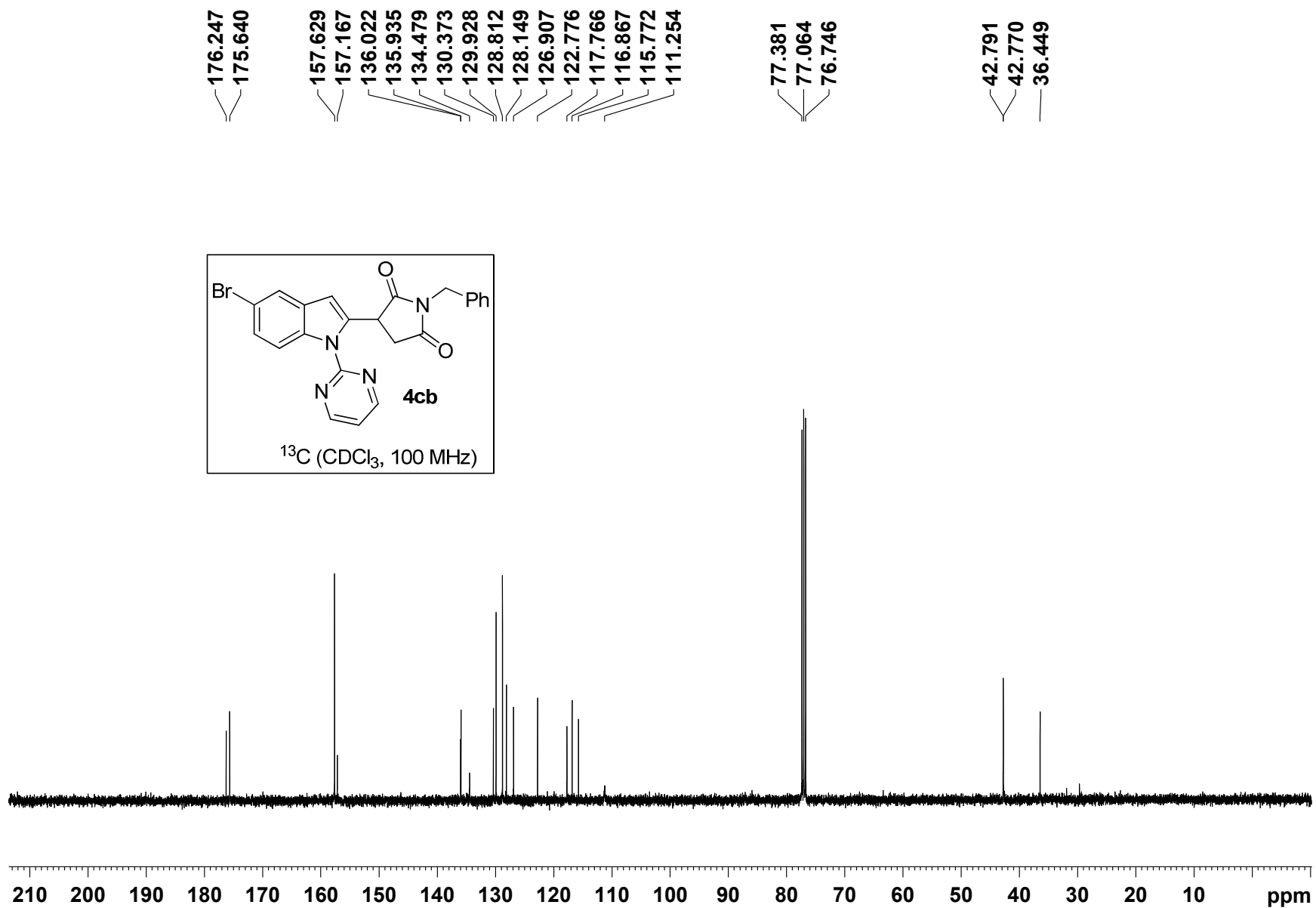
Figure S32.  $^1\text{H}$  NMR spectra of the Compound **4bc**

Figure S33.  $^{13}\text{C}$  NMR spectra of the Compound 4bc

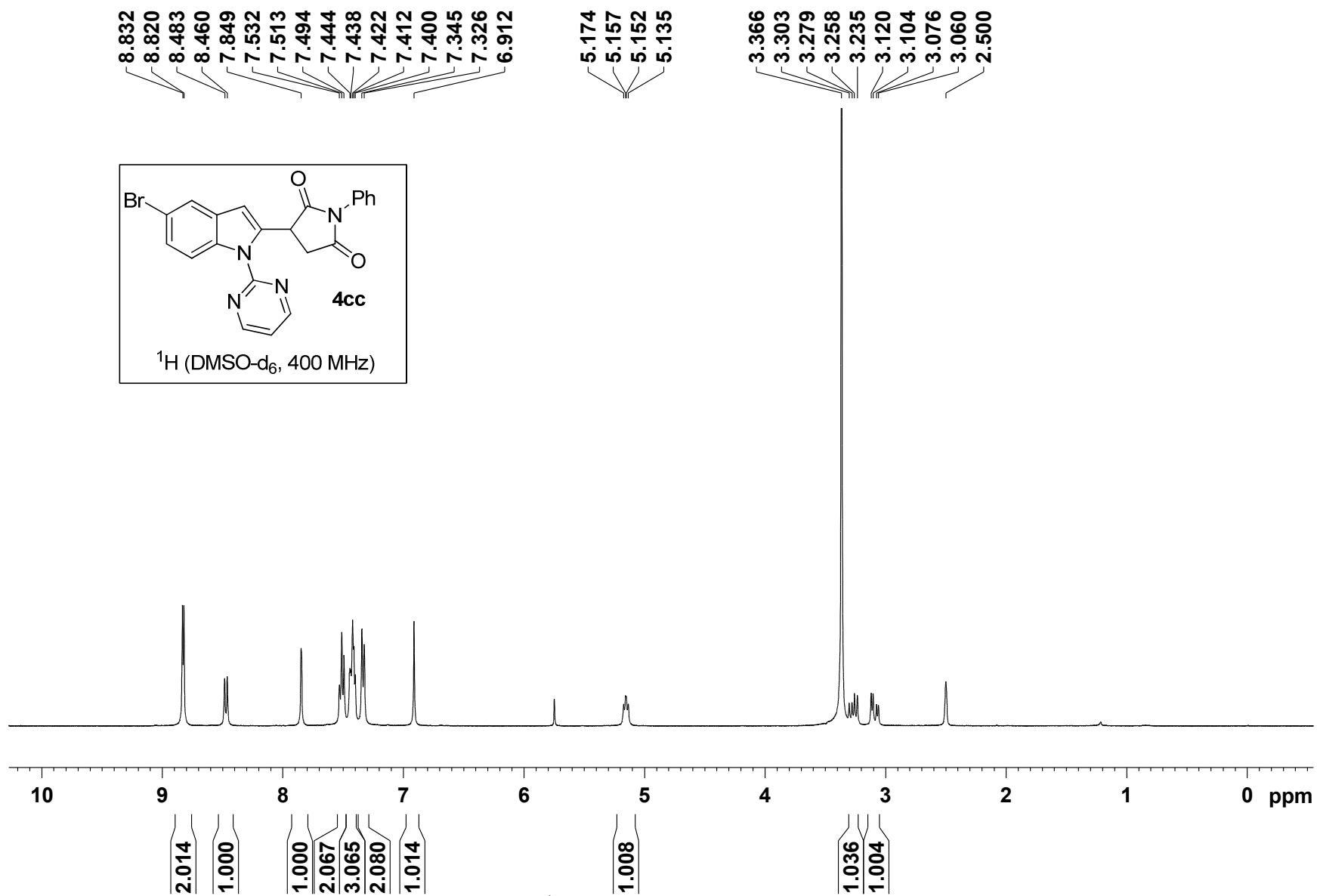
Figure S34. <sup>1</sup>H NMR spectra of the Compound 4bd

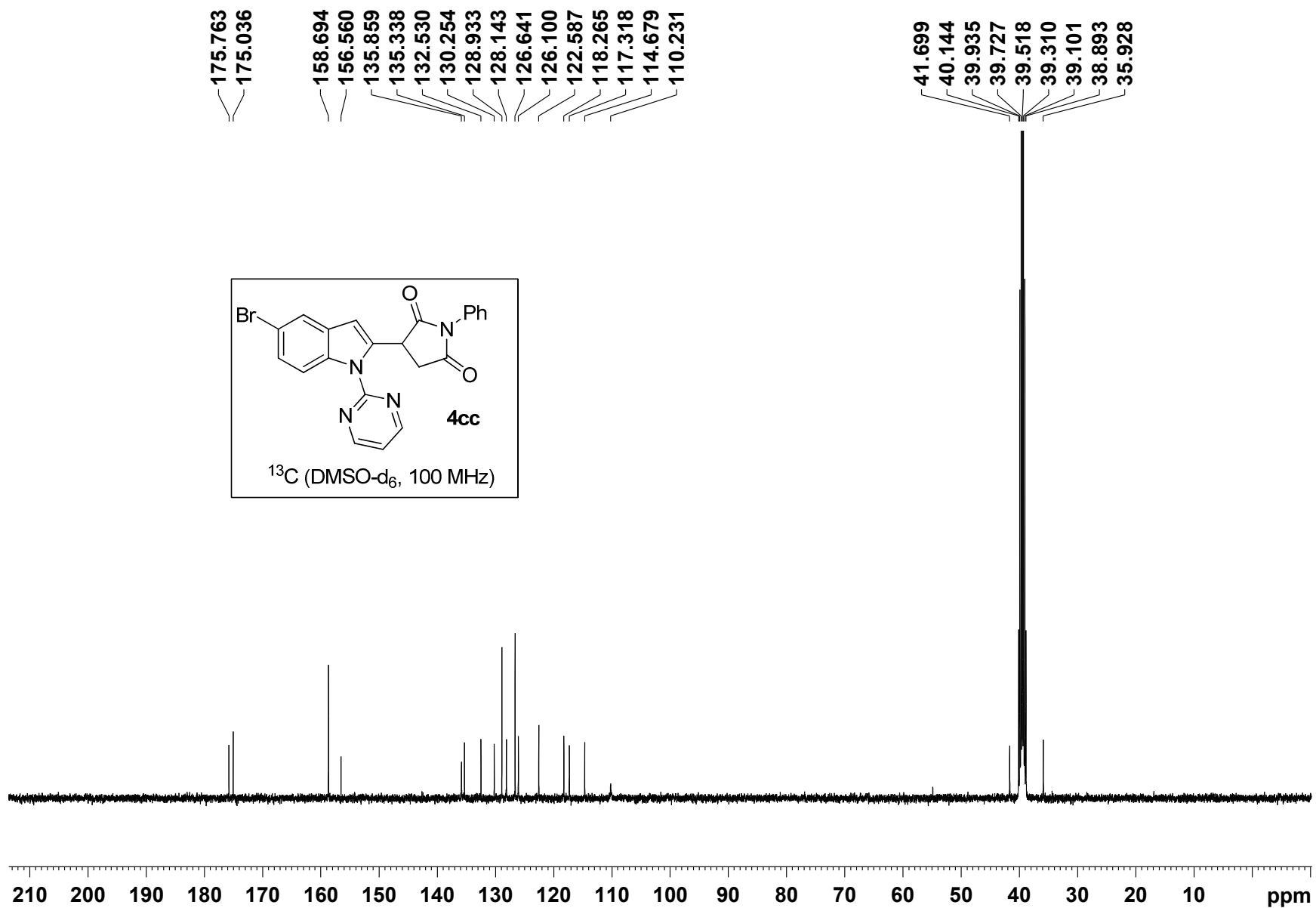
Figure S35. <sup>13</sup>C NMR spectra of the Compound 4bd

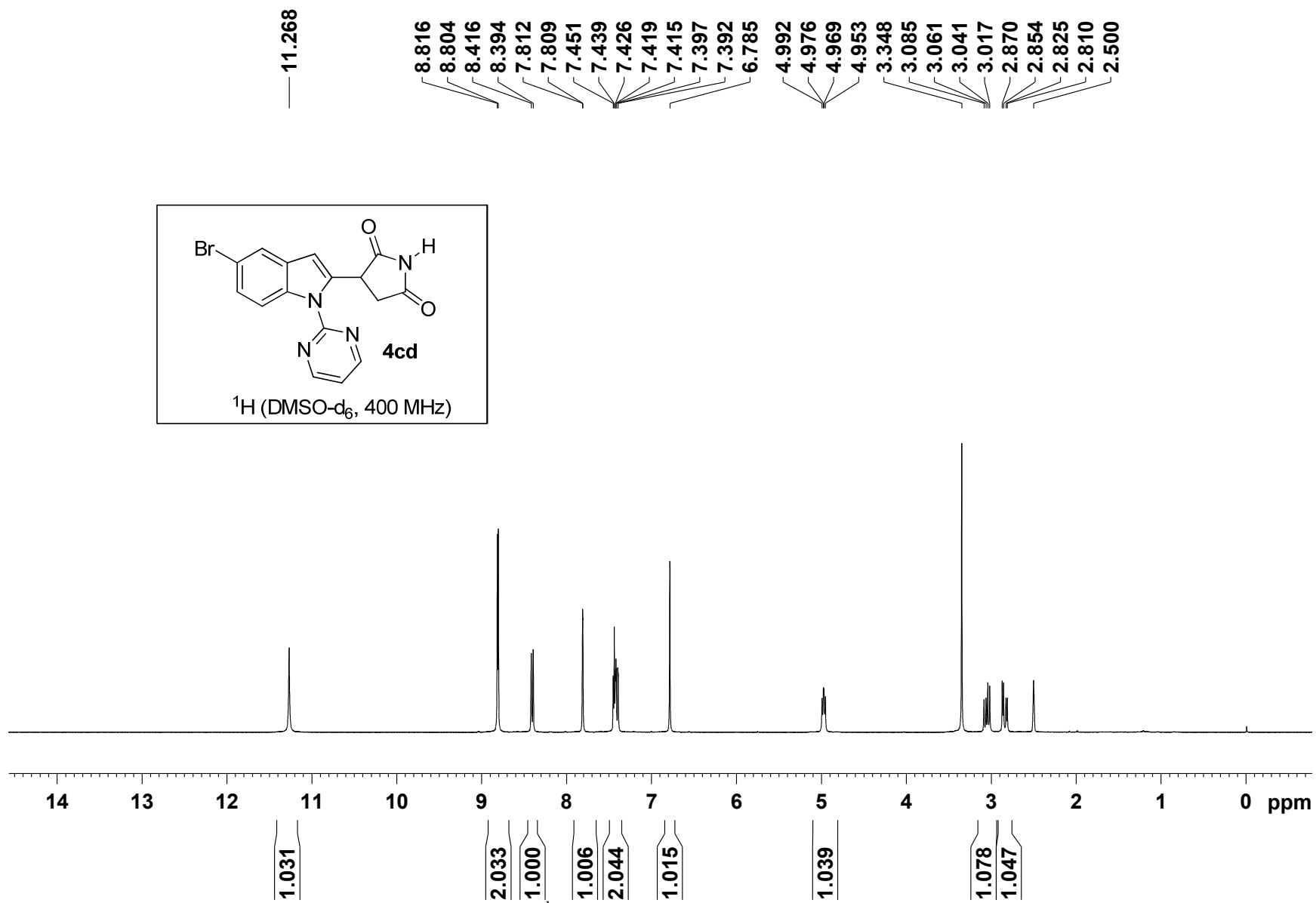
Figure S36. <sup>1</sup>H NMR spectra of the Compound 4cb

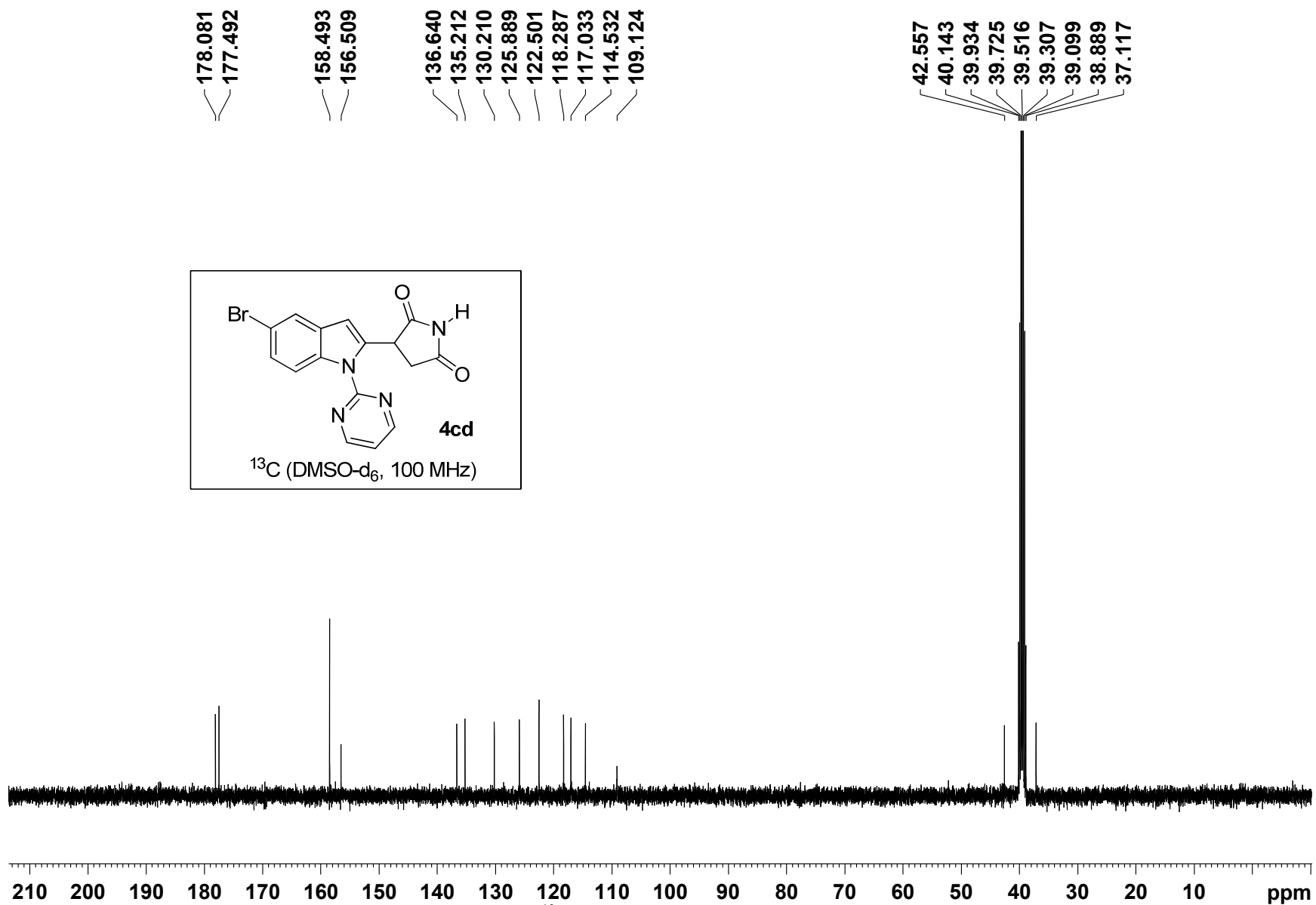
Figure S37. <sup>13</sup>C NMR spectra of the Compound 4cb

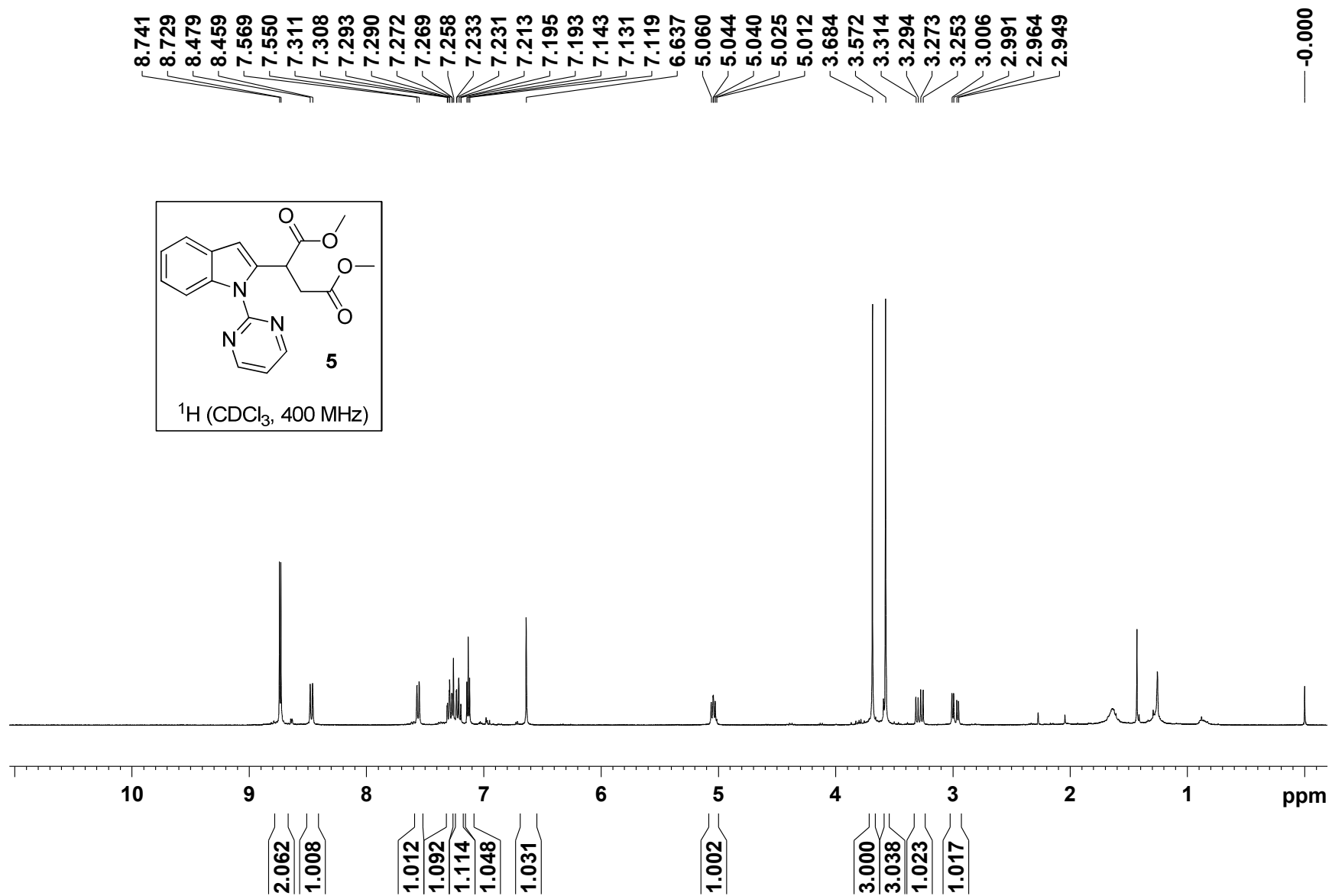


Figure S38. <sup>1</sup>H NMR spectra of the Compound 4cc



Figure S40. <sup>1</sup>H NMR spectra of the Compound 4cd

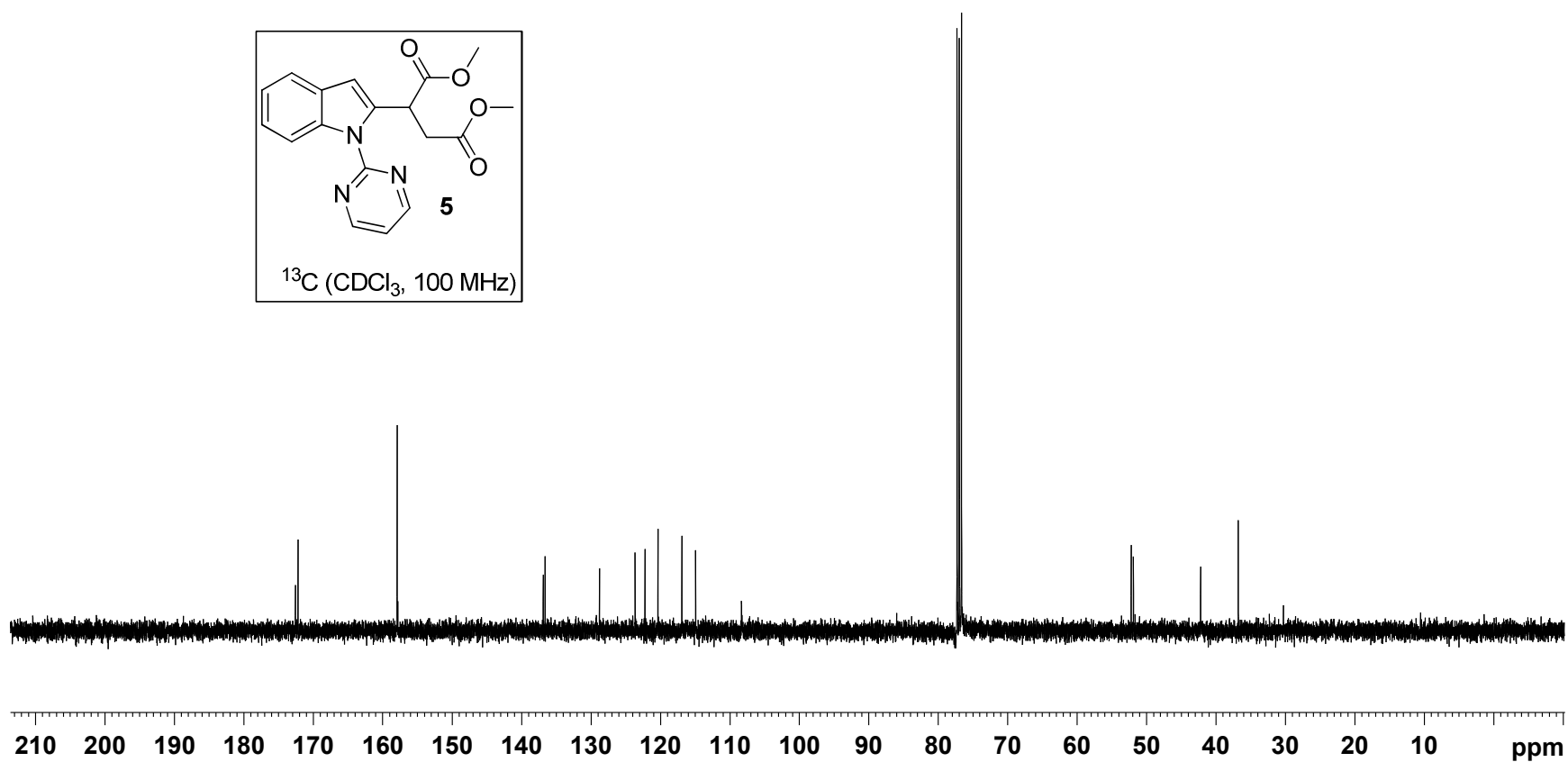
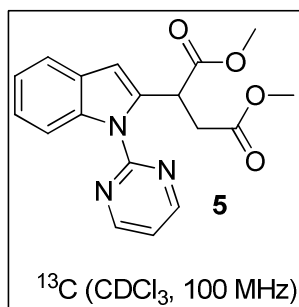
Figure S41.  $^{13}\text{C}$  NMR spectra of the Compound 4cd

Figure S42. <sup>1</sup>H NMR spectra of the Compound 5

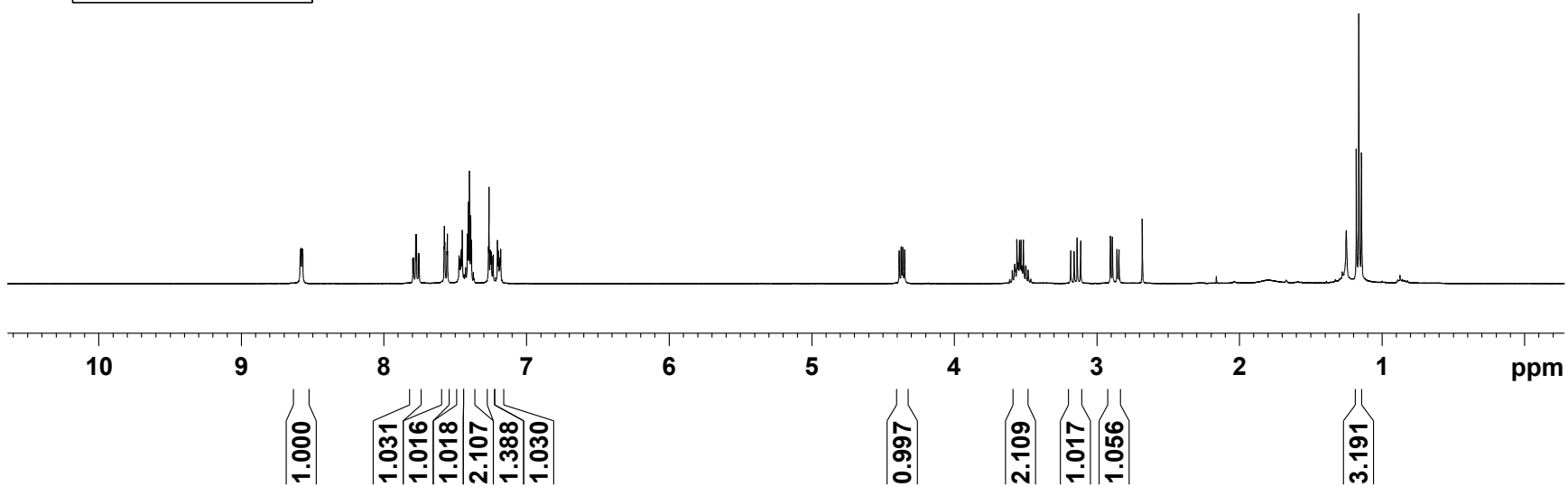
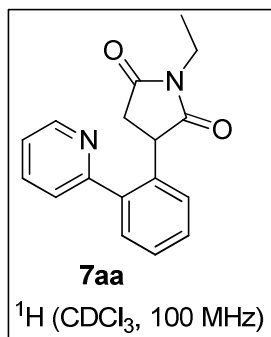
172.576  
172.171  
157.912  
157.812  
136.898  
136.635  
128.805  
123.685  
122.264  
120.393  
116.938  
114.968  
108.344

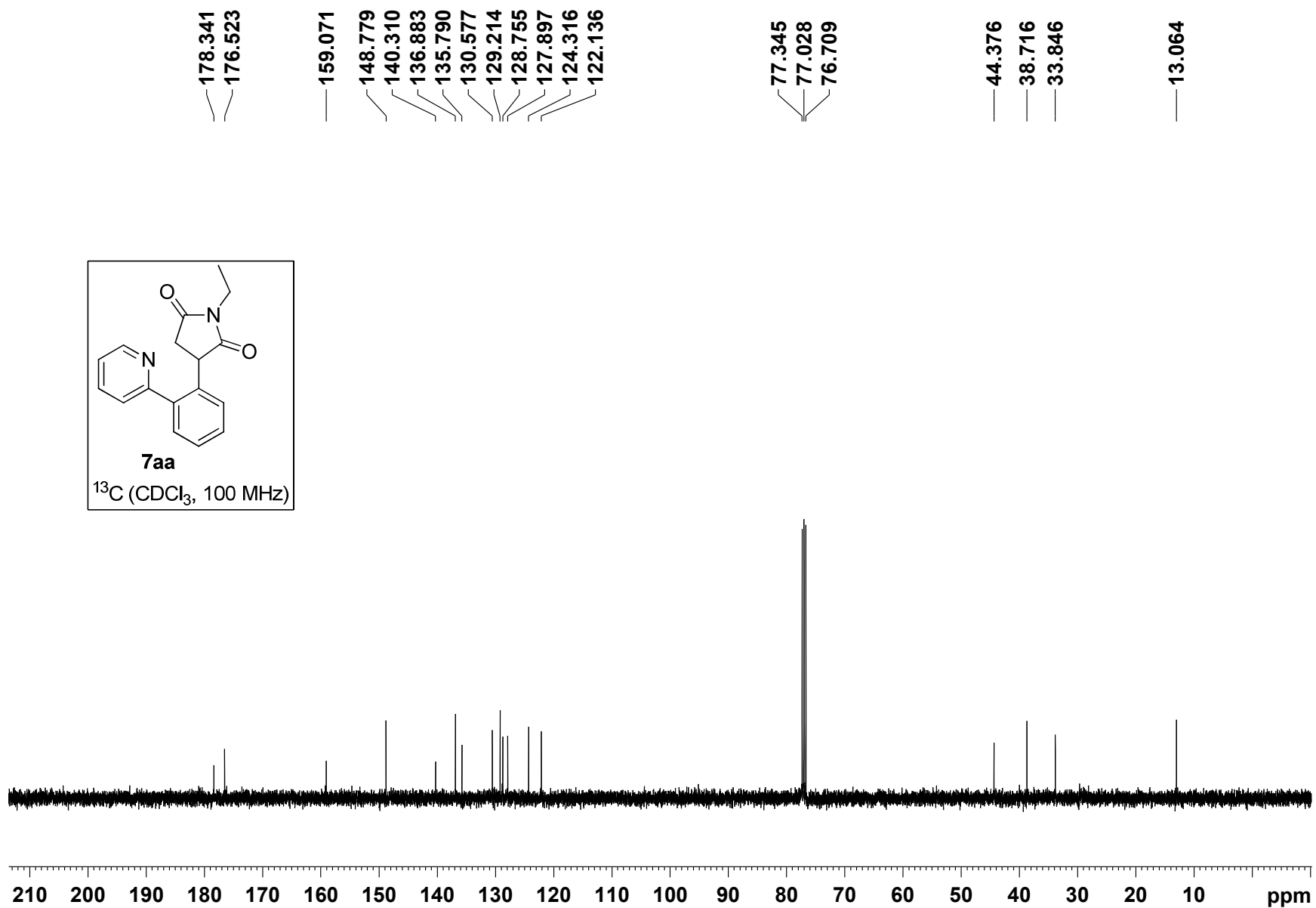
77.328  
77.011  
76.693

52.251  
51.933  
42.220  
36.814

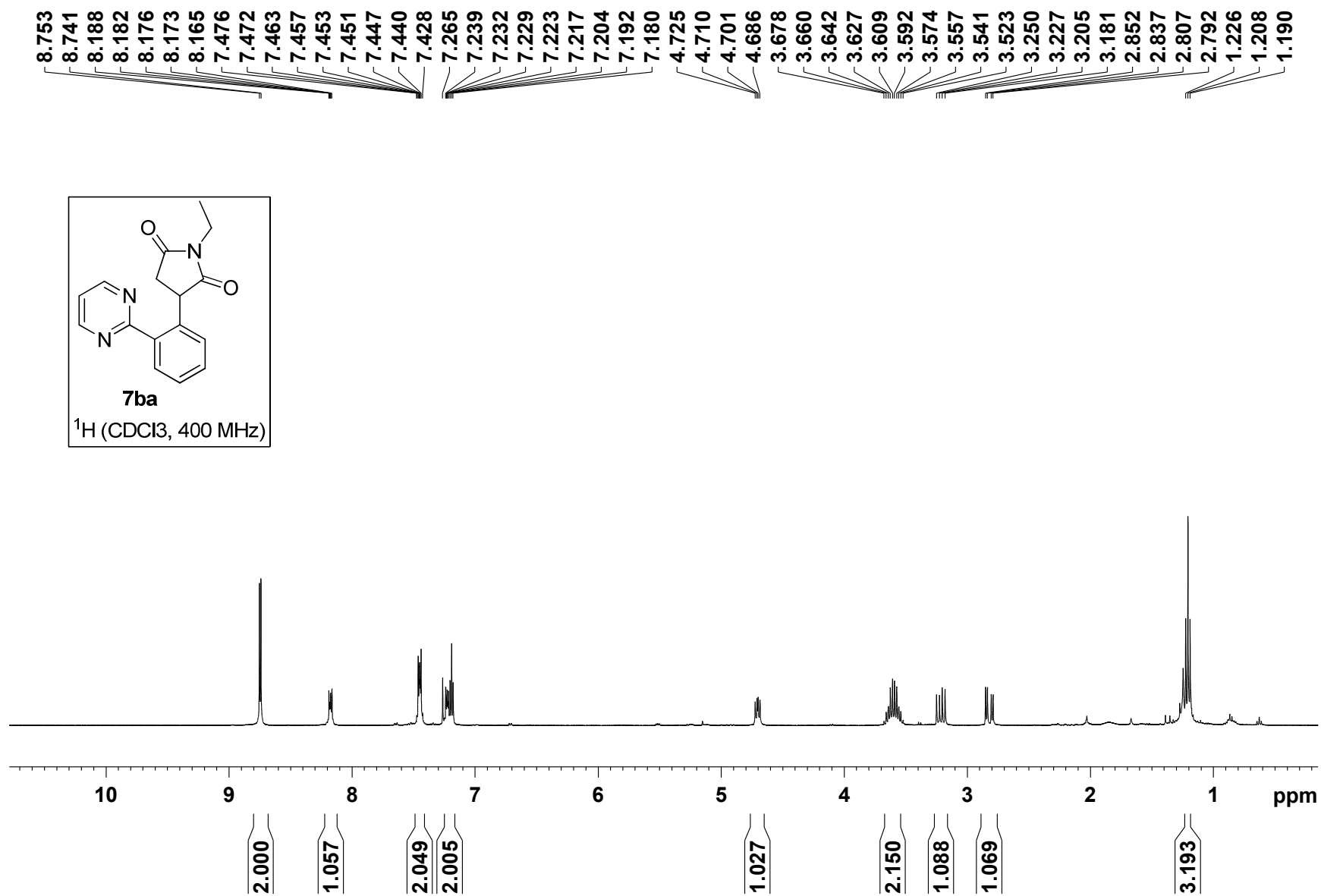
Figure S43.  $^{13}\text{C}$  NMR spectra of the Compound 5

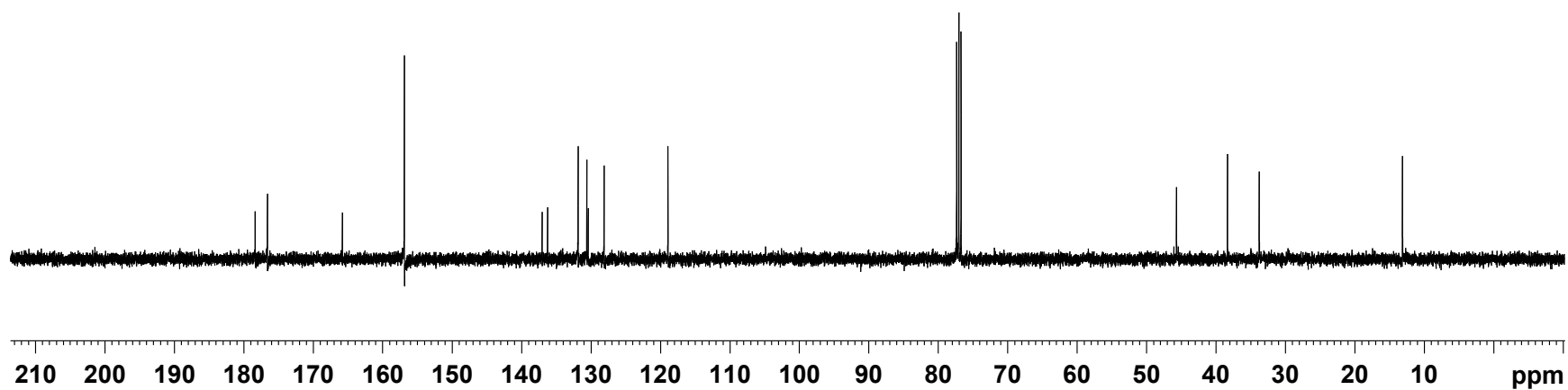
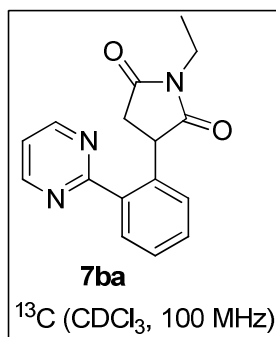
8.585  
8.583  
8.581  
8.575  
8.573  
8.571  
7.777  
7.773  
7.758  
7.578  
7.576  
7.573  
7.558  
7.556  
7.553  
7.458  
7.457  
7.450  
7.415  
7.408  
7.400  
7.391  
7.386  
7.263  
7.255  
7.252  
7.248  
7.246  
7.204  
7.198  
7.181  
4.386  
4.372  
4.362  
4.348  
3.560  
3.542  
3.532  
3.514  
3.183  
3.159  
3.137  
3.113  
2.904  
2.890  
2.858  
2.844  
2.681  
1.182  
1.164  
1.146

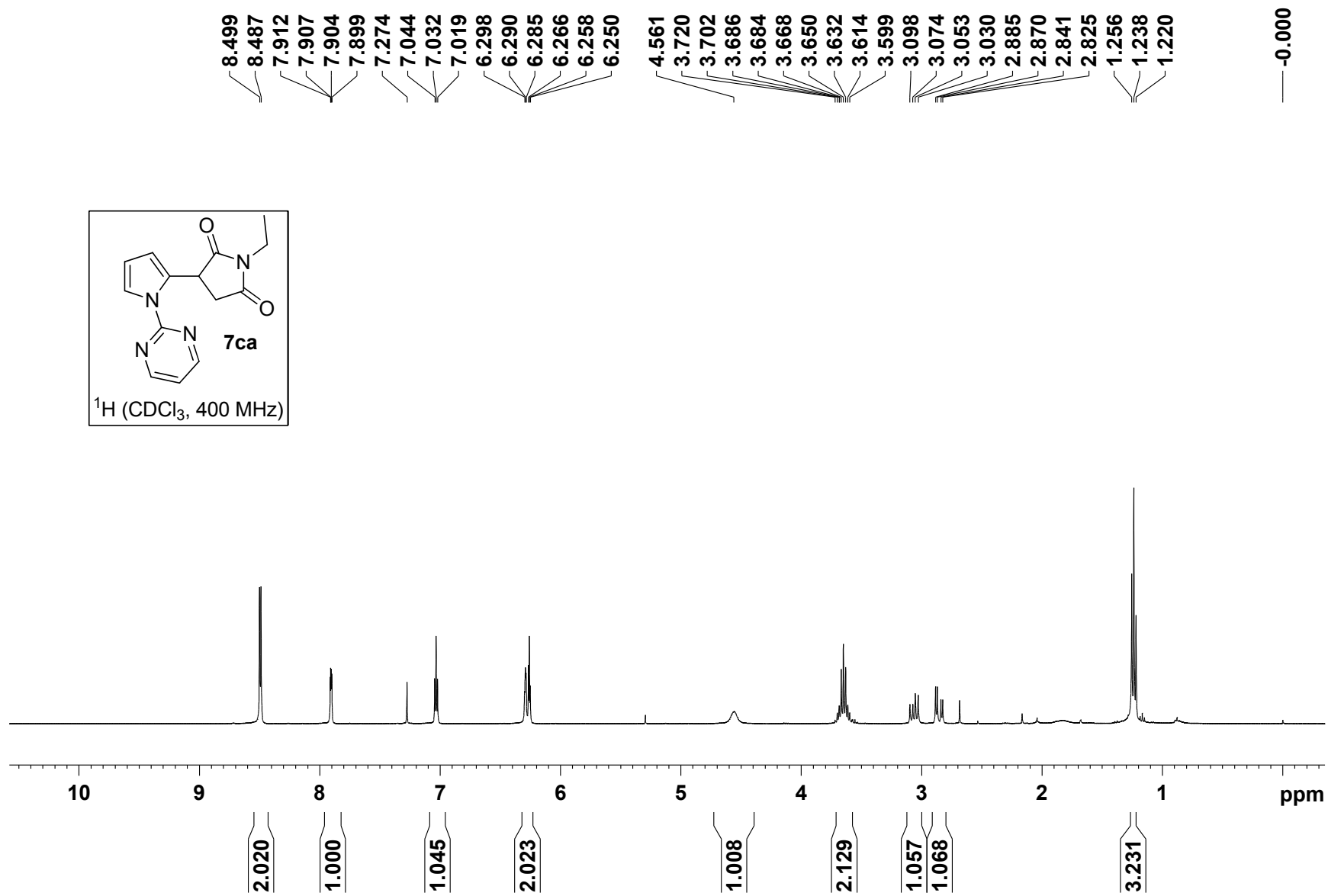
Figure S44.  $^1\text{H}$  NMR spectra of the Compound 7aa

Figure S45.  $^{13}\text{C}$  NMR spectra of the Compound 7aa



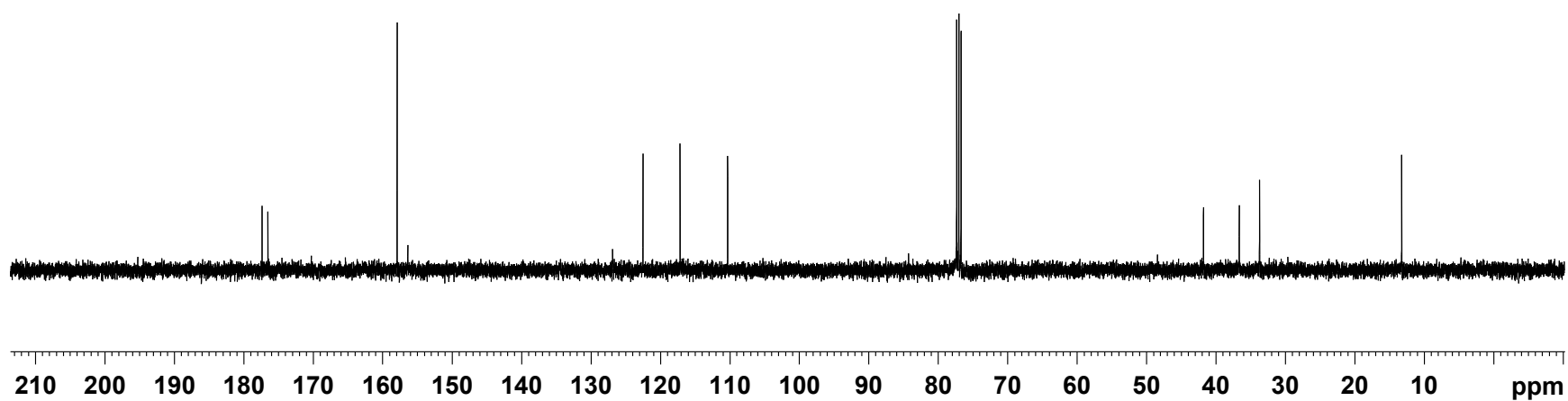
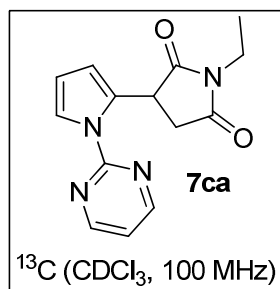
Figure S46. <sup>1</sup>H NMR spectra of the Compound 7ba

Figure S47.  $^{13}\text{C}$  NMR spectra of the Compound 7ba

Figure S48. <sup>1</sup>H NMR spectra of the Compound 7ca

177.354  
176.534157.919  
156.360126.918  
122.551  
117.202  
110.36277.370  
77.052  
76.73441.815  
36.660  
33.745

13.276

Figure S49.  $^{13}\text{C}$  NMR spectra of the Compound 7ca

8.563  
8.551  
7.286  
7.165  
7.161  
7.153  
7.149  
7.141  
7.136  
6.202  
6.199  
4.734  
4.720  
4.711  
4.696  
4.679  
4.670  
3.573  
3.567  
3.558  
3.553  
3.549  
3.540  
3.535  
3.530  
3.521  
3.517  
3.512  
3.496  
3.112  
3.088  
3.076  
3.066  
3.053  
3.043  
3.031  
3.008  
2.944  
2.930  
2.906  
2.899  
2.891  
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2.861  
2.846  
1.180  
1.169  
1.162  
1.151  
1.144  
1.133

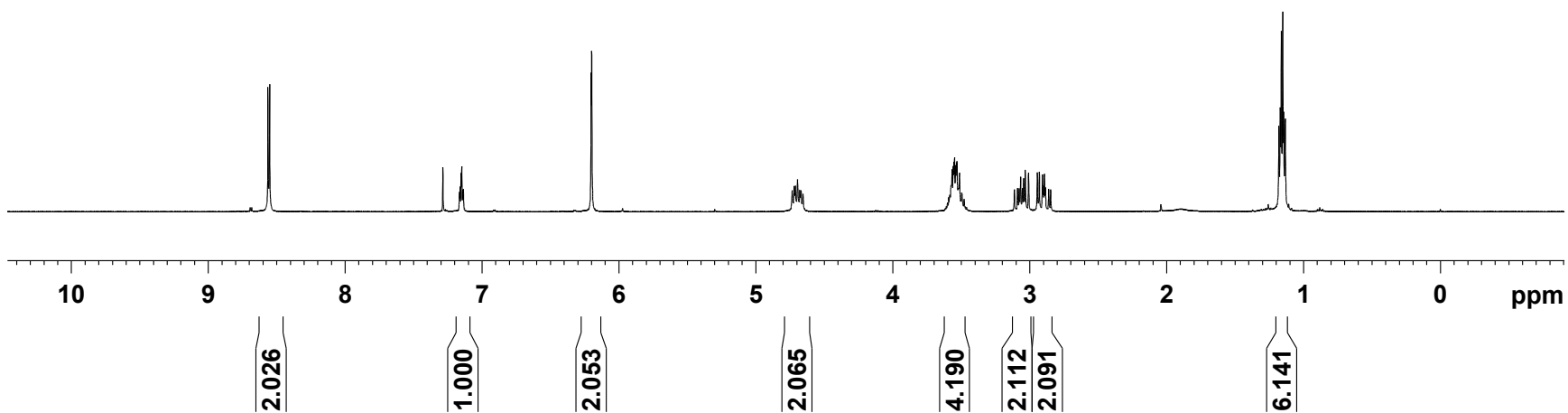
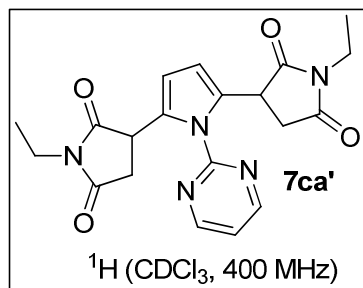
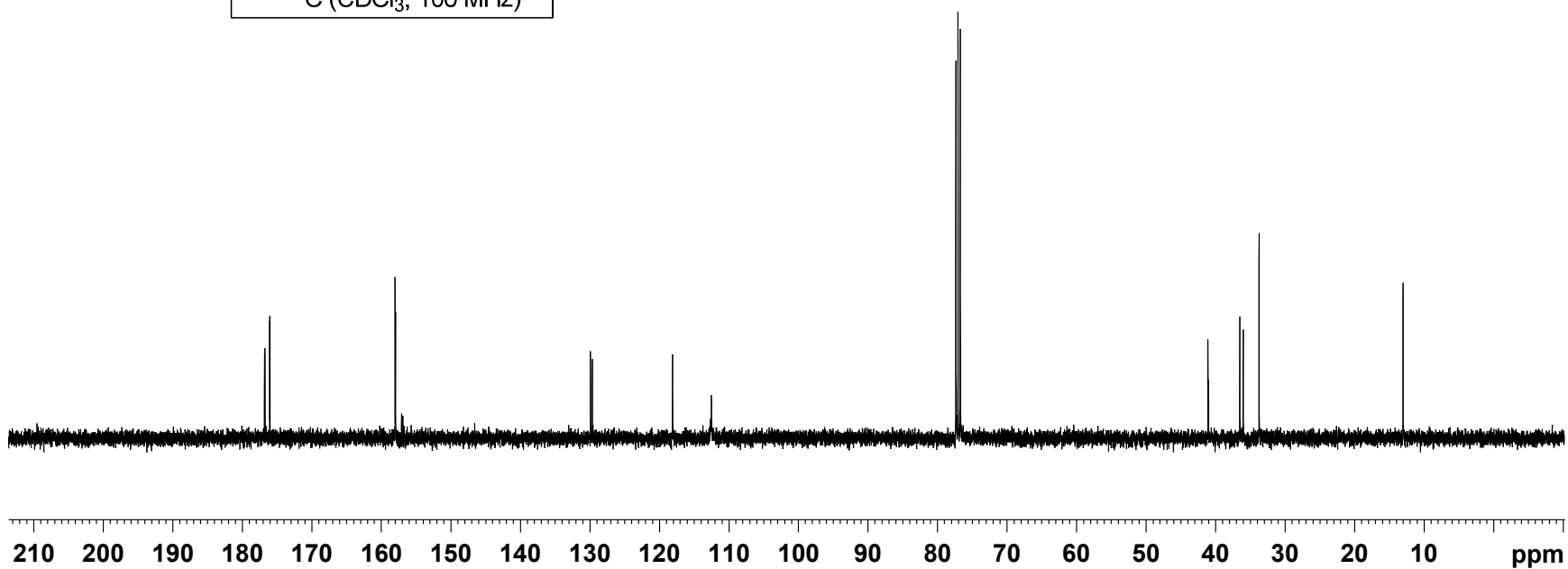
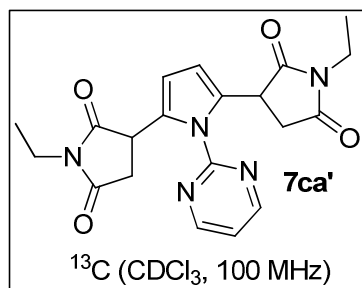
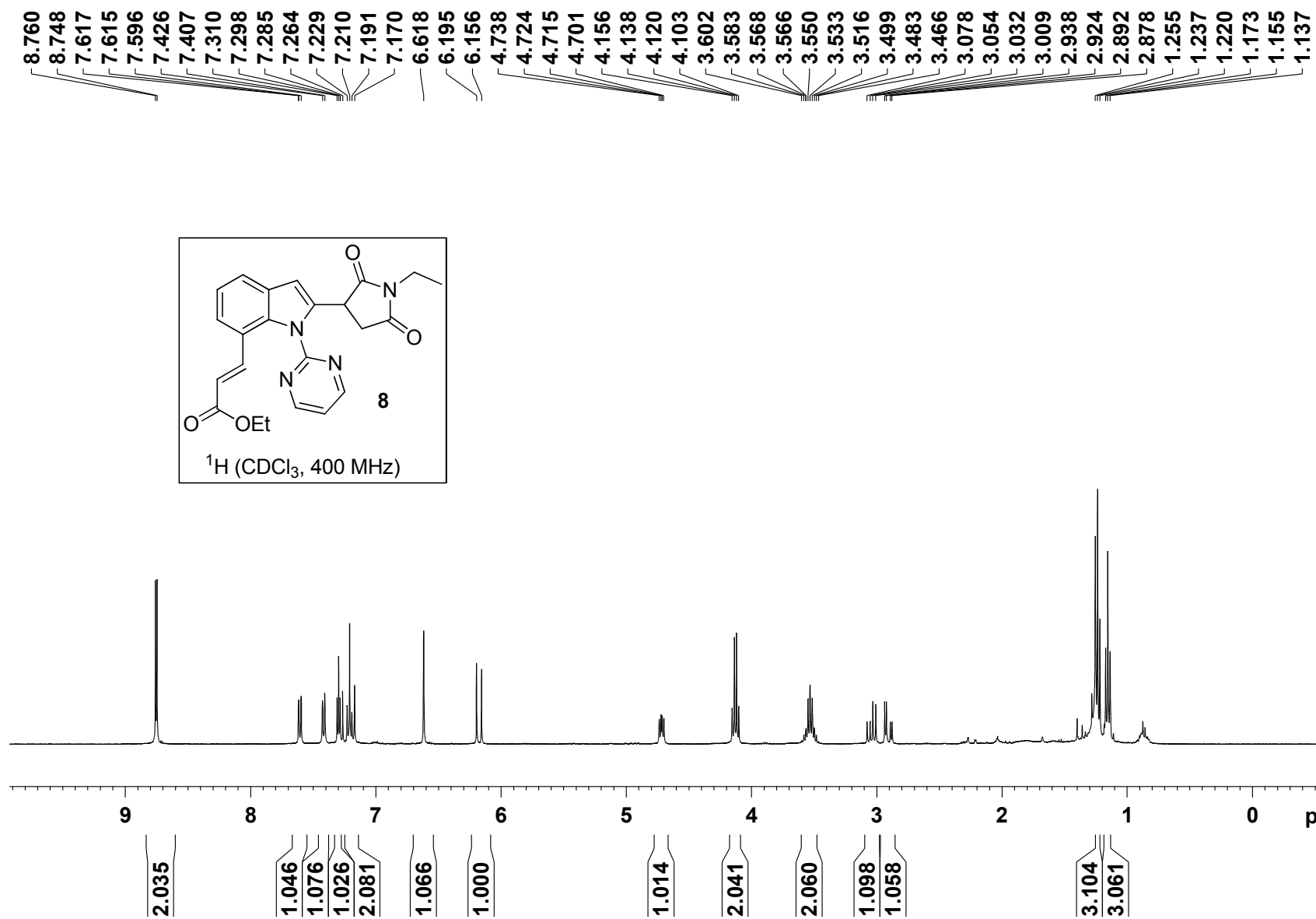


Figure S50.  $^1\text{H}$  NMR spectra of the Compound 7ca'

Figure S51.  $^{13}\text{C}$  NMR spectra of the Compound **7ca'**

Figure S52.  $^1\text{H}$  NMR spectra of the Compound 8

175.745  
175.450  
166.733  
158.789  
158.160  
142.676  
136.460  
135.689  
129.604  
123.549  
122.595  
122.201  
120.922  
119.303  
117.273  
106.294

77.385  
77.067  
76.749

60.183

39.828  
36.412  
34.006

14.316  
12.991

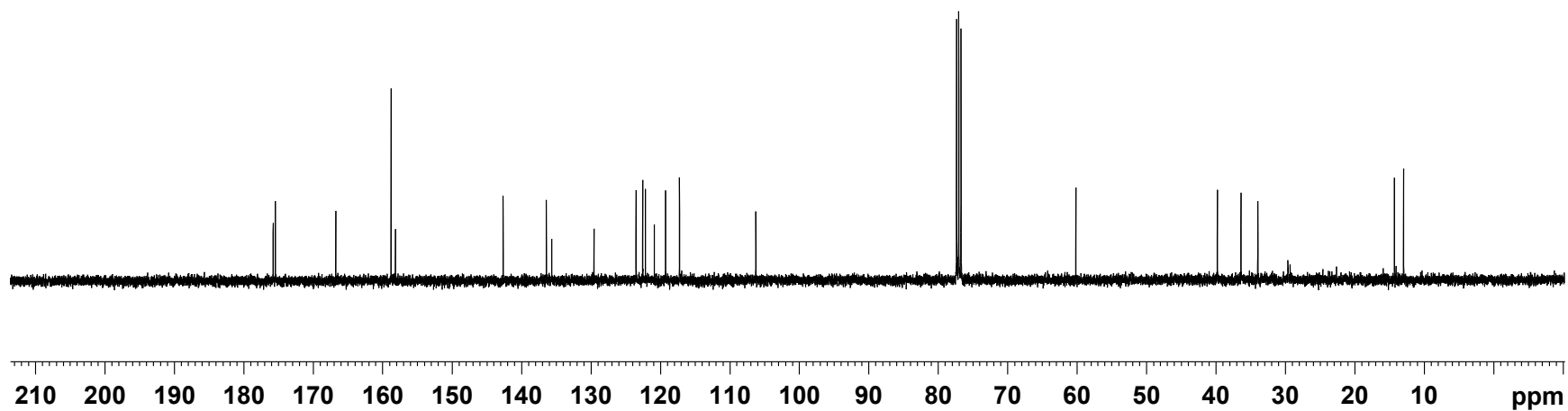
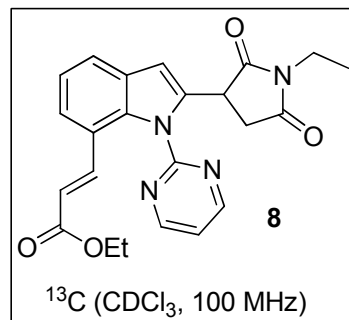


Figure S53.  $^{13}\text{C}$  NMR spectra of the Compound 8