

## Supporting Information

### TCCA-mediated oxidative rearrangement of tetrahydro- $\beta$ -carbolines: Facile access to spirooxindoles and total synthesis of ( $\pm$ )-coerulescine and ( $\pm$ )-horsfiline

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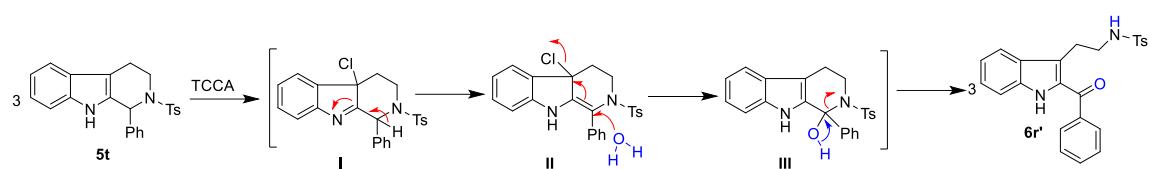
<sup>d</sup>*Laboratory of Asymmetric Synthesis, Instituto de Química de Recursos Naturales, Universidad de Talca, Campus Lircay, Talca 3460000, Chile*

<sup>!</sup>M. Sathish and A. P. Sakla contributed equally.

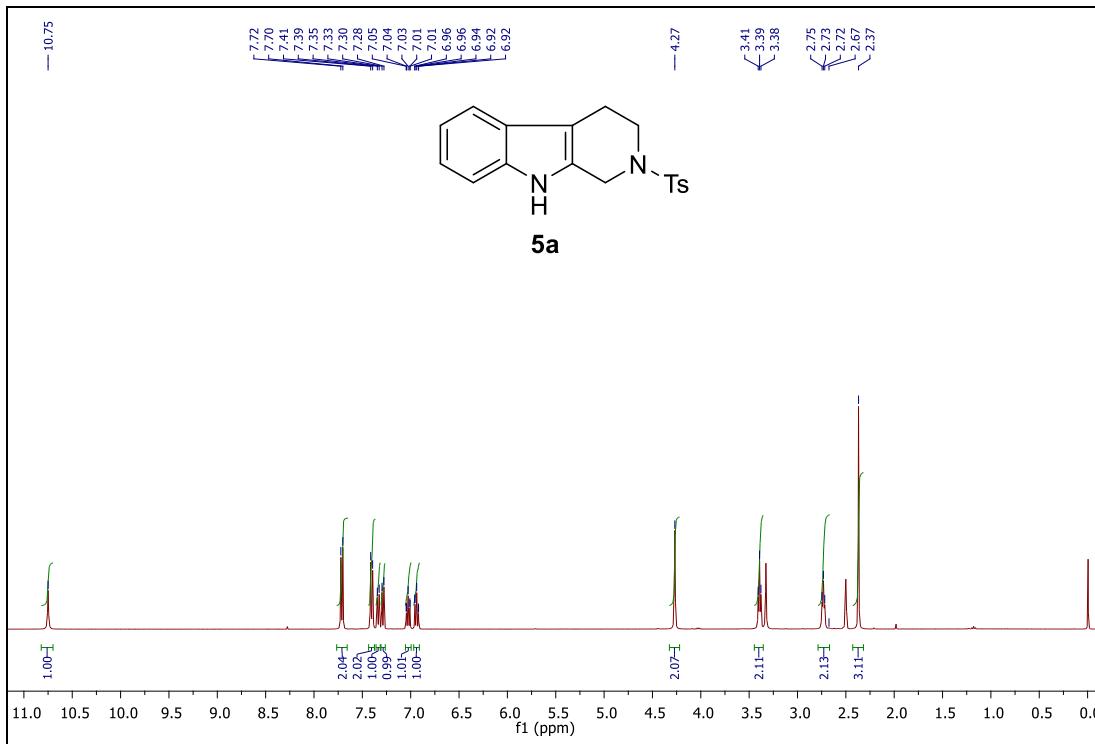
\*Corresponding author: Email: [issantos@utalca.cl](mailto:issantos@utalca.cl); [shankar@niperhyd.ac.in](mailto:shankar@niperhyd.ac.in)

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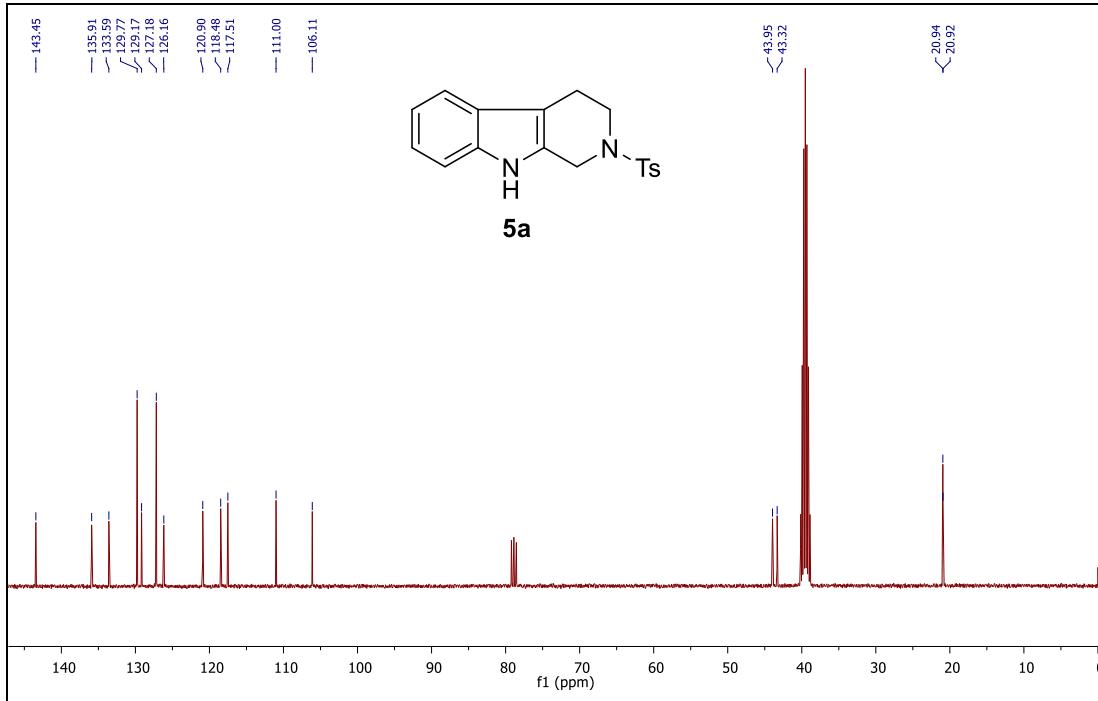
1. Plausible reaction mechanism for the formation of <b>6r'</b> .....	S2
2. Copies of <sup>1</sup> H and <sup>13</sup> C NMR Spectrum.....	S3 – S49.



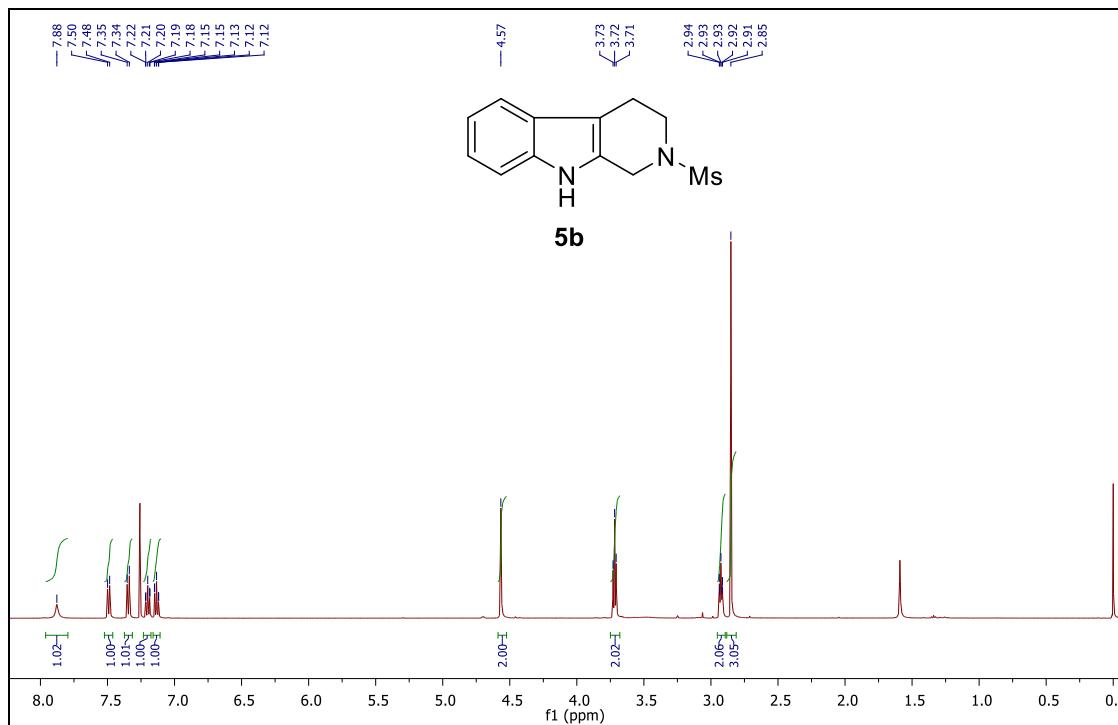
**Scheme 1.** Plausible reaction mechanism for the formation of **6r'**



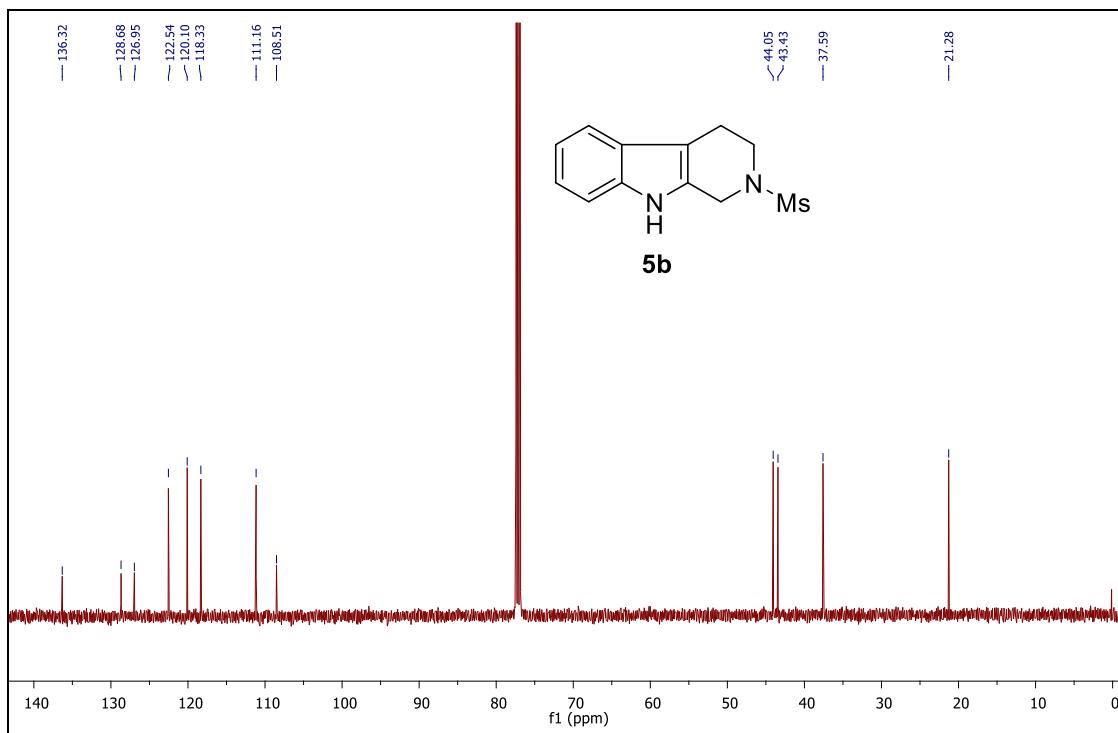
$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) for compound **5a**.



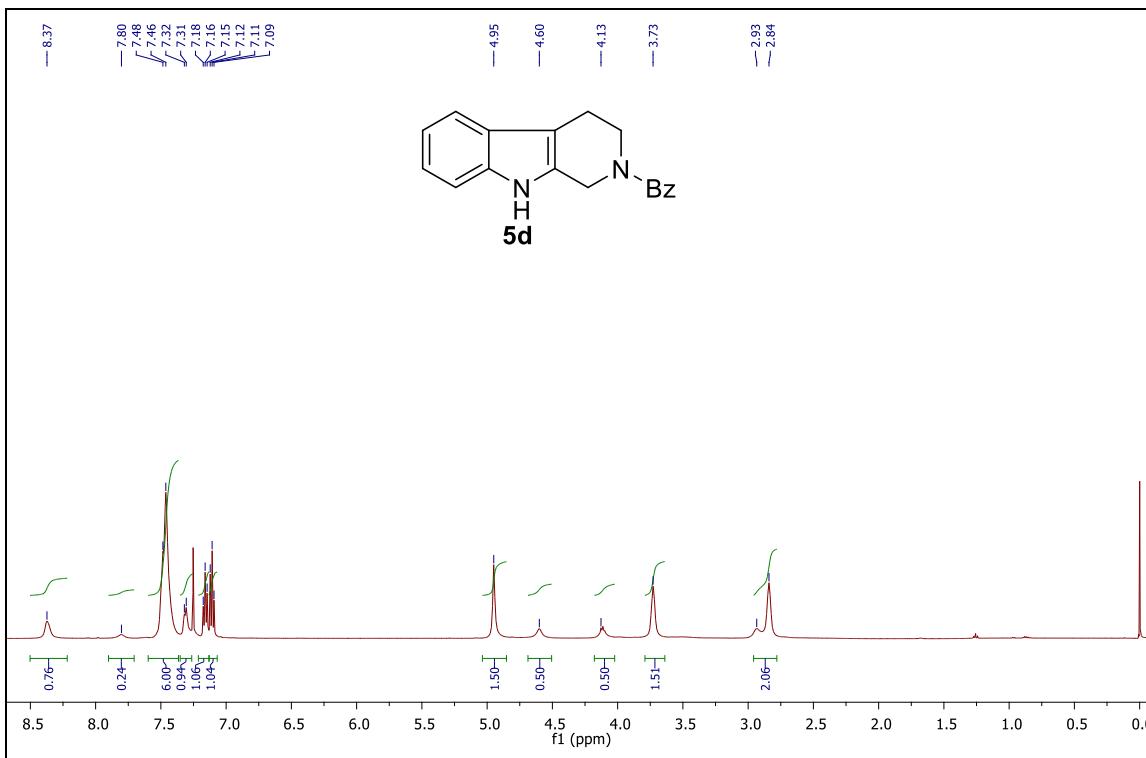
$^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ) for compound **5a**.



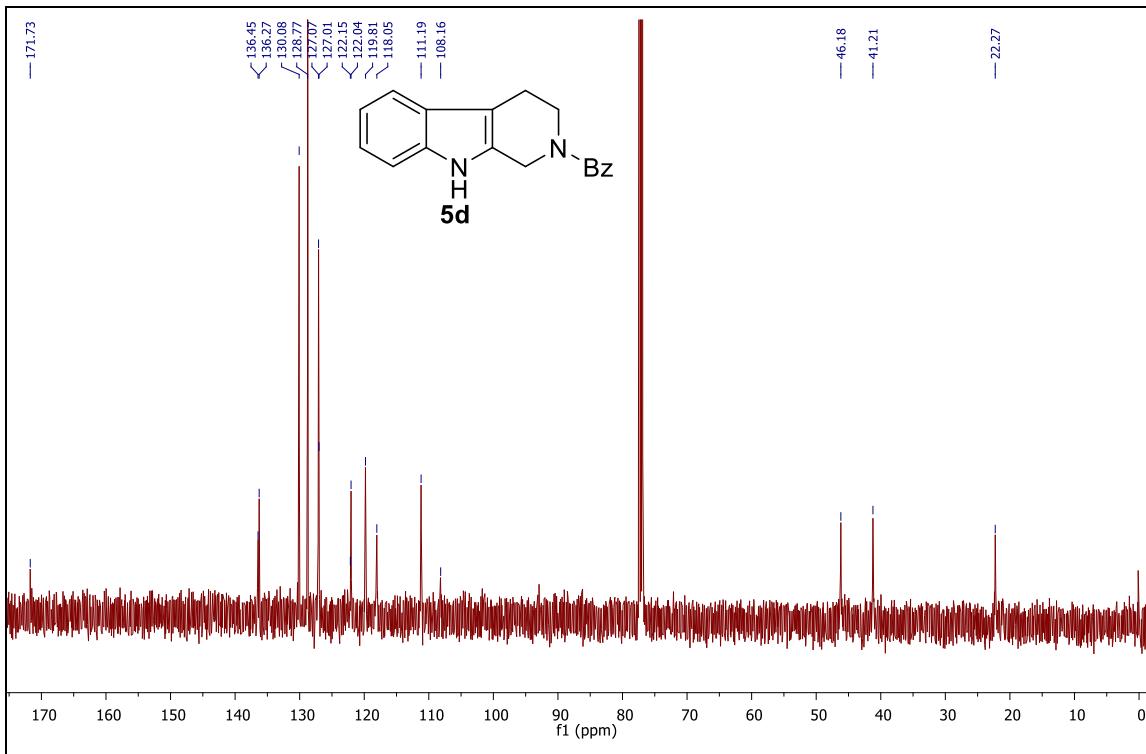
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) for compound **5b**.



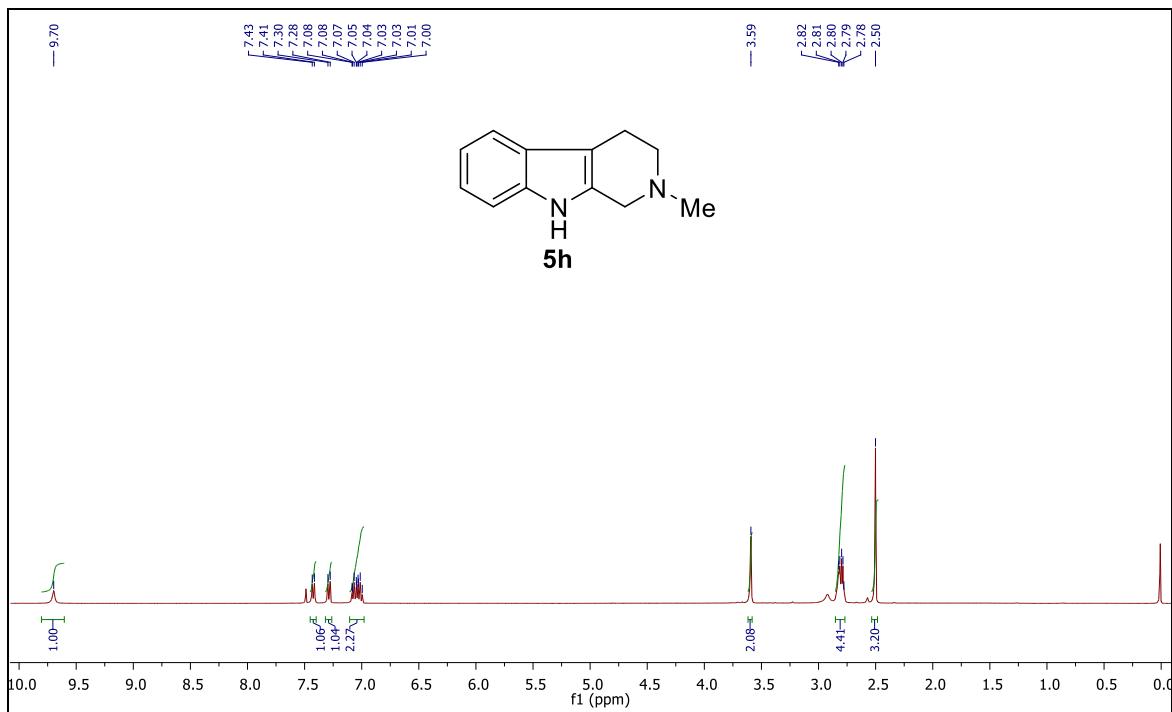
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) for compound **5b**.



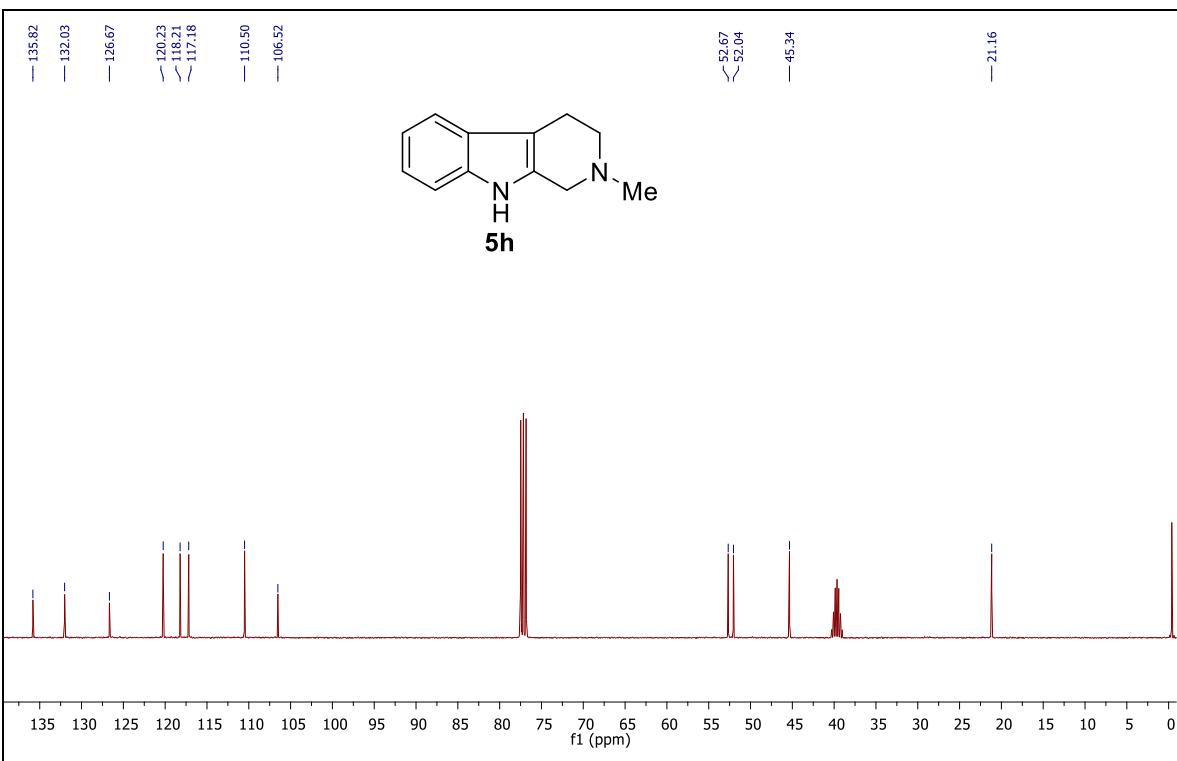
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **5d**.



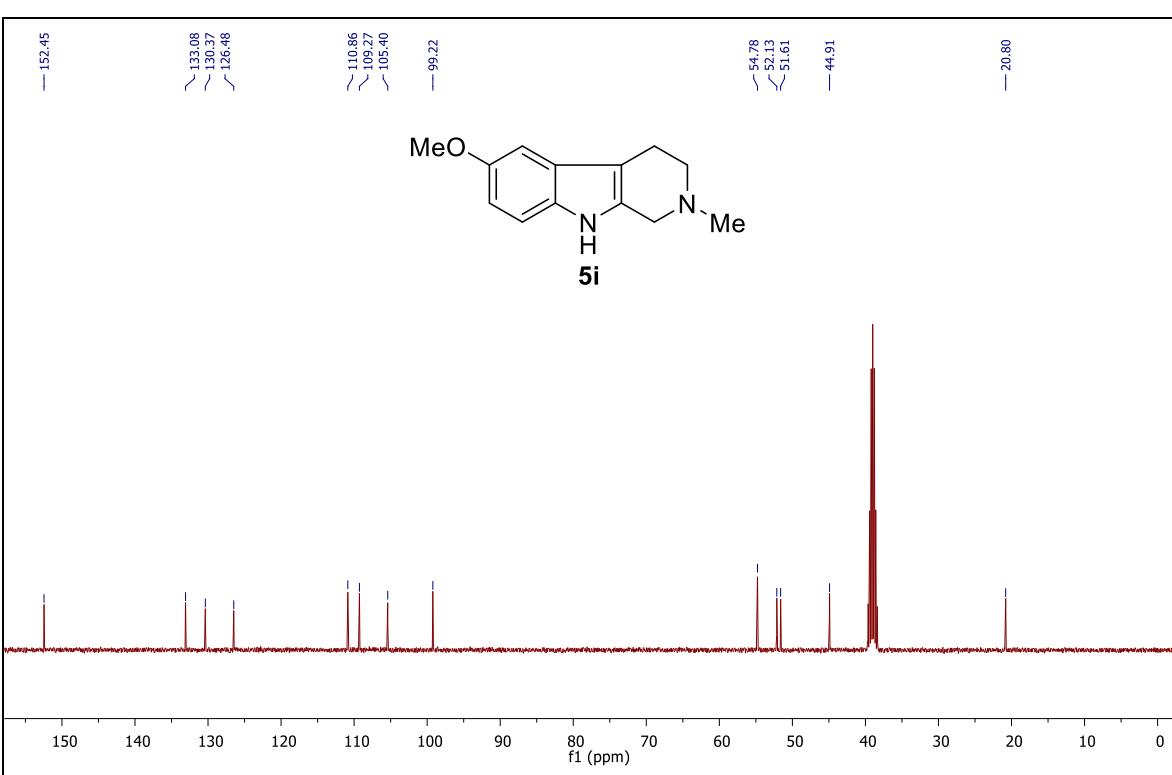
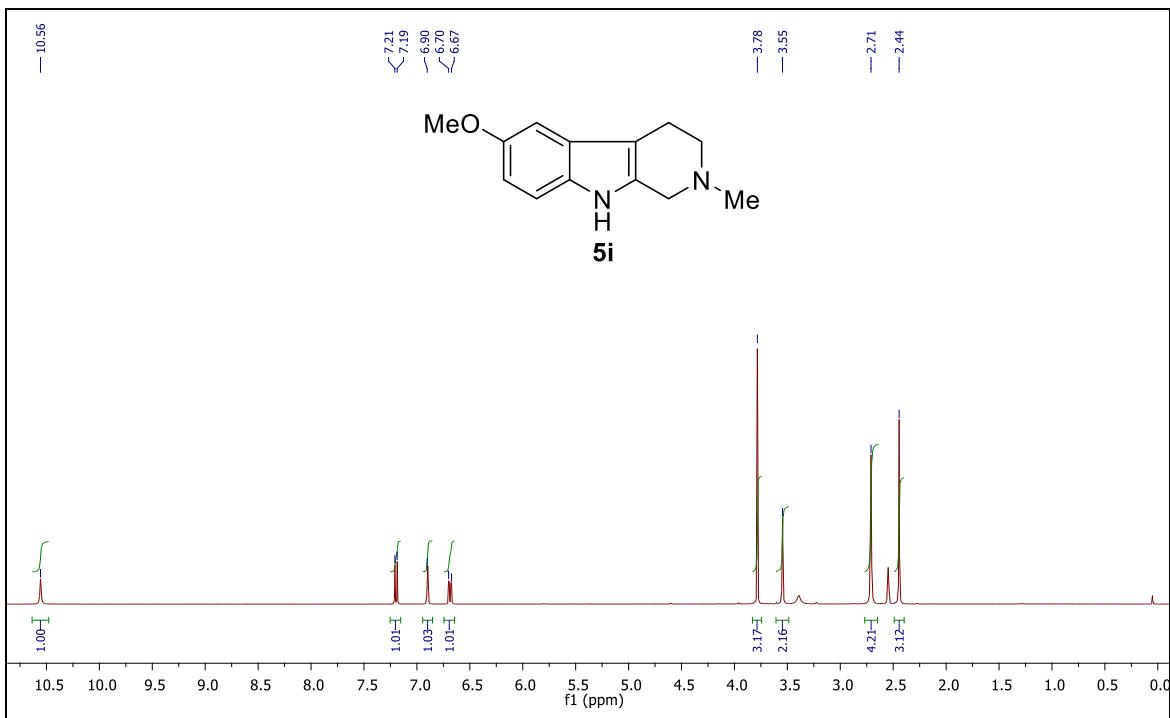
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) for compound **5d**.

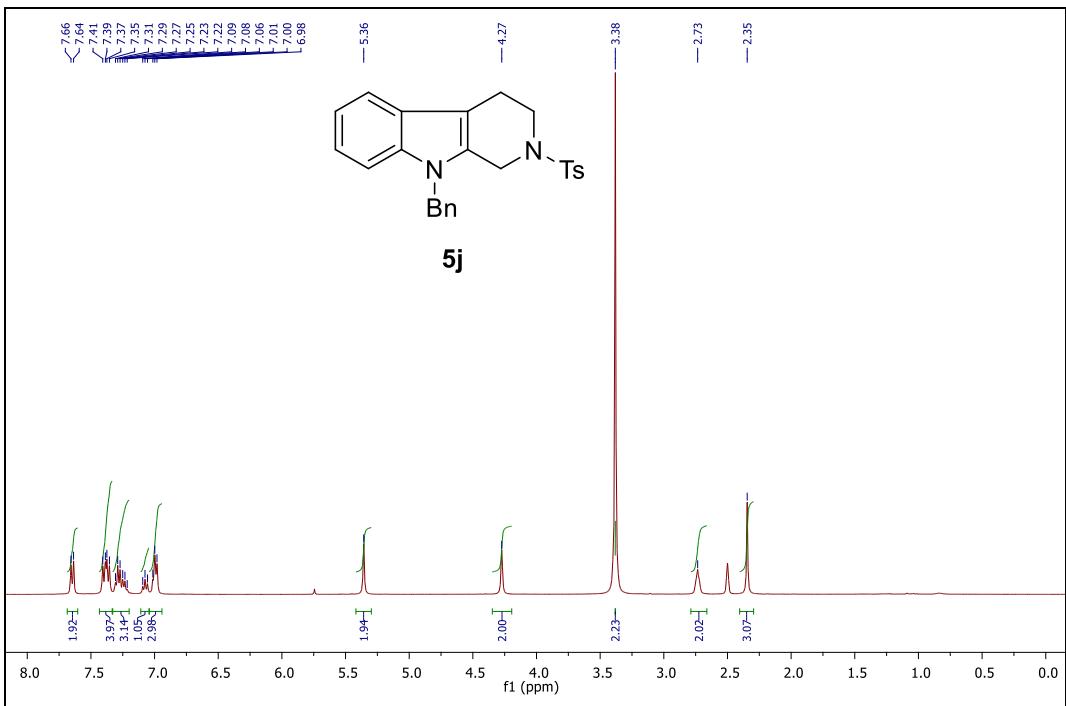


$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$  + CDCl<sub>3</sub>) for compound **5h**.

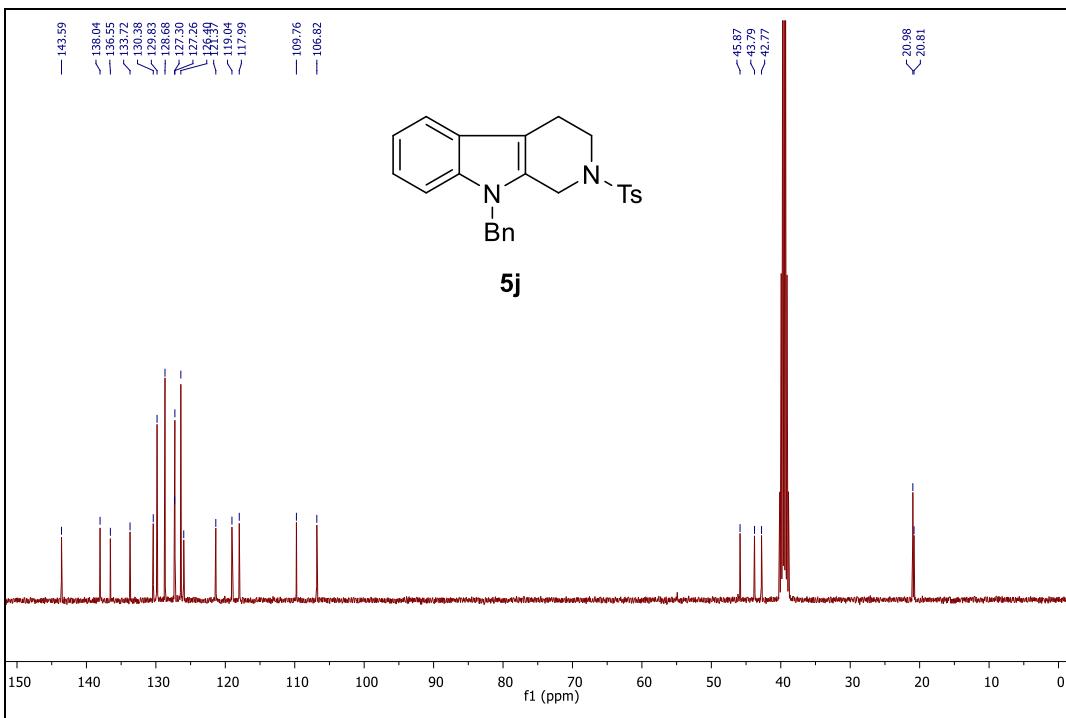


$^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$  + CDCl<sub>3</sub>) for compound **5h**.

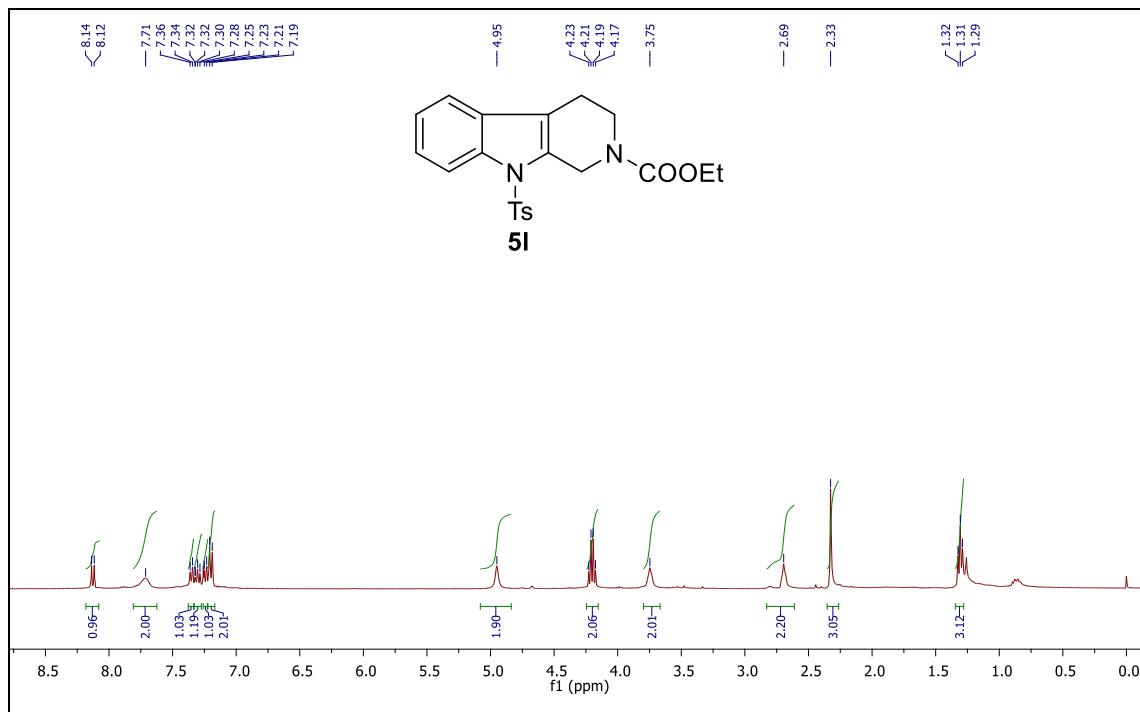




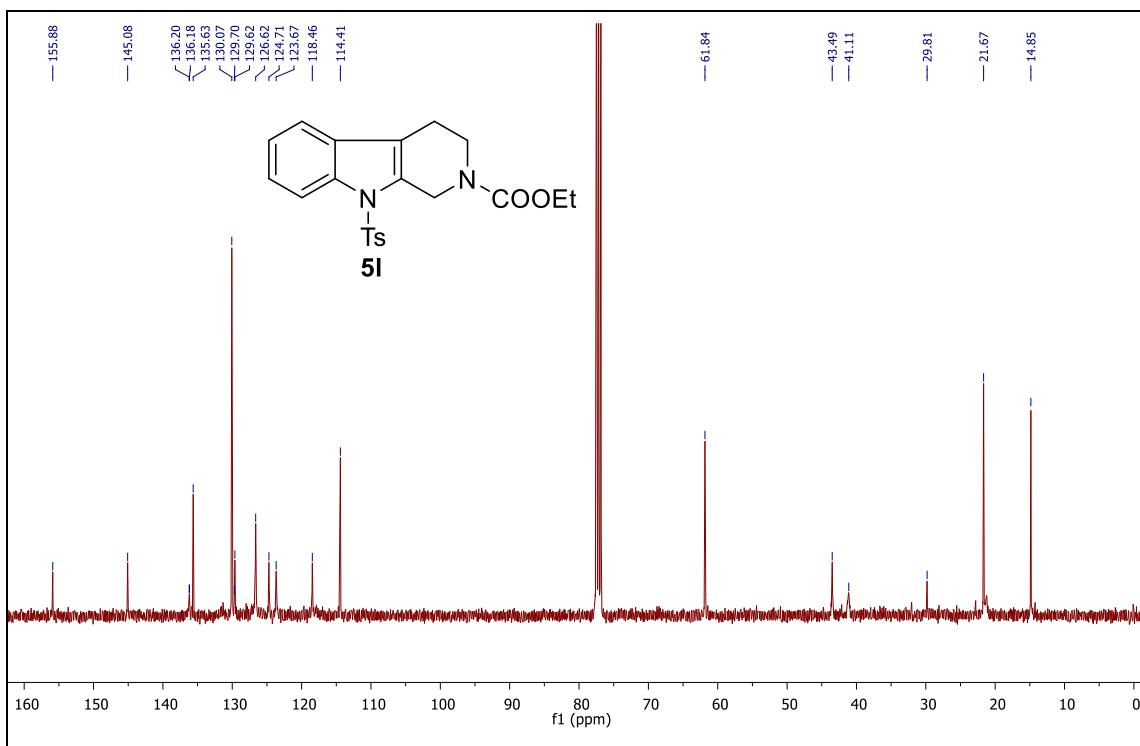
$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) for compound **5j**.



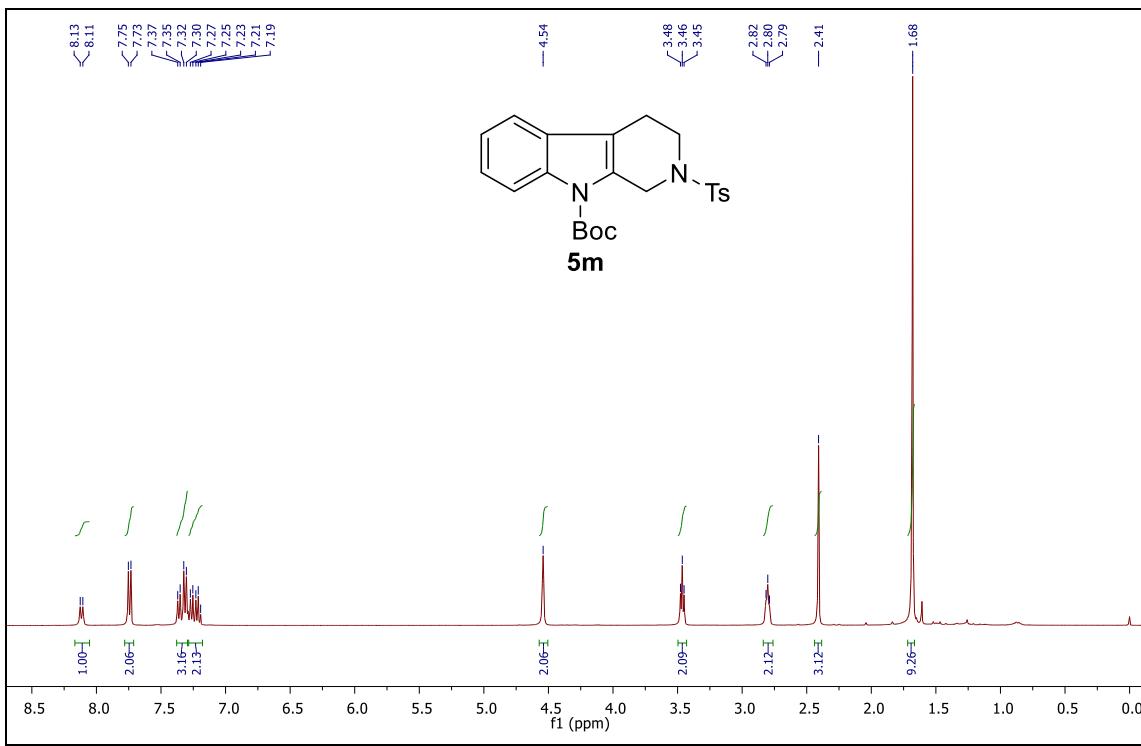
$^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ) for compound **5j**.



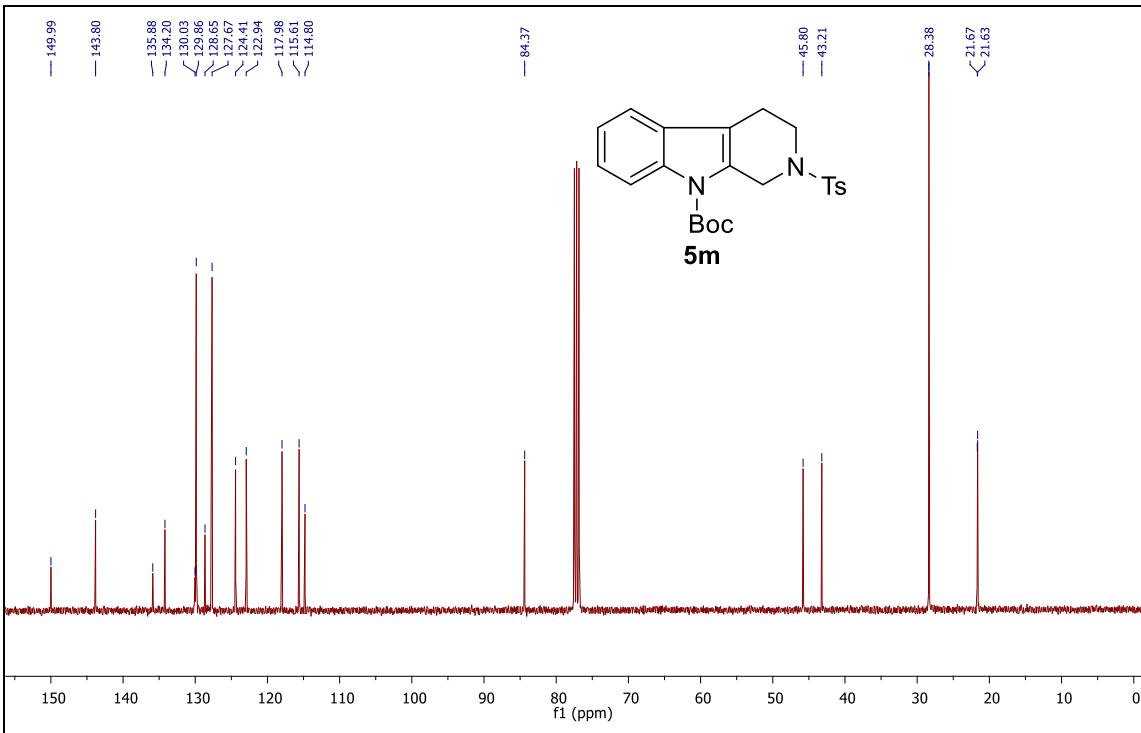
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound **5l**.



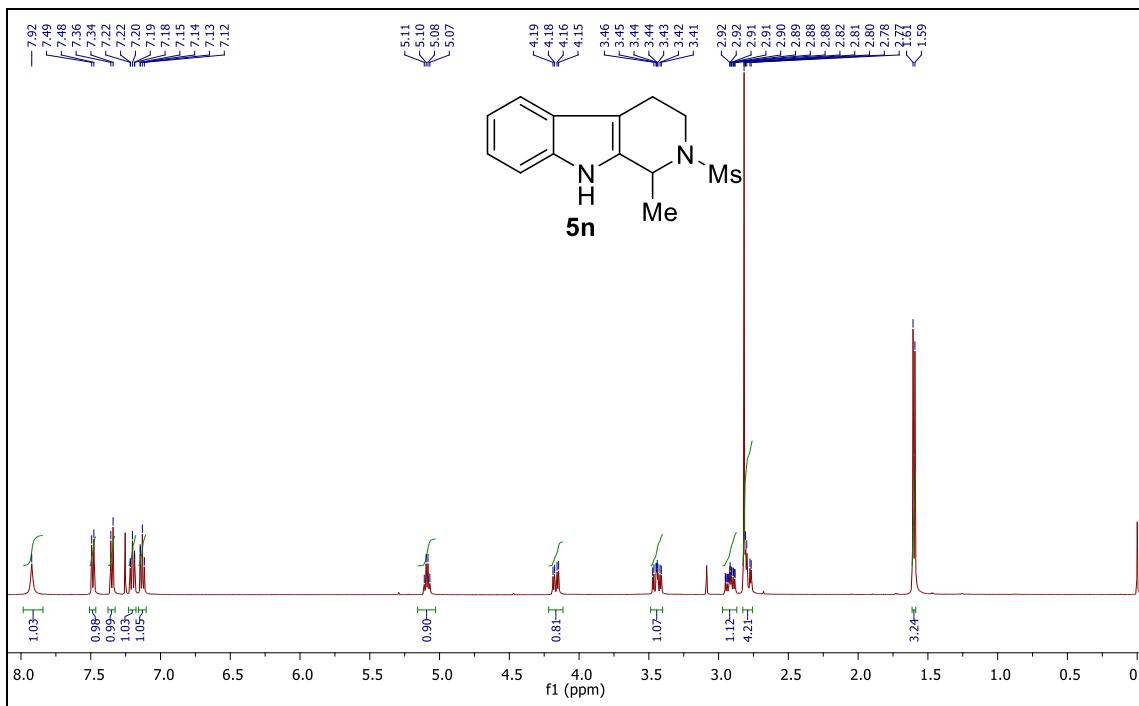
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for compound **5l**.



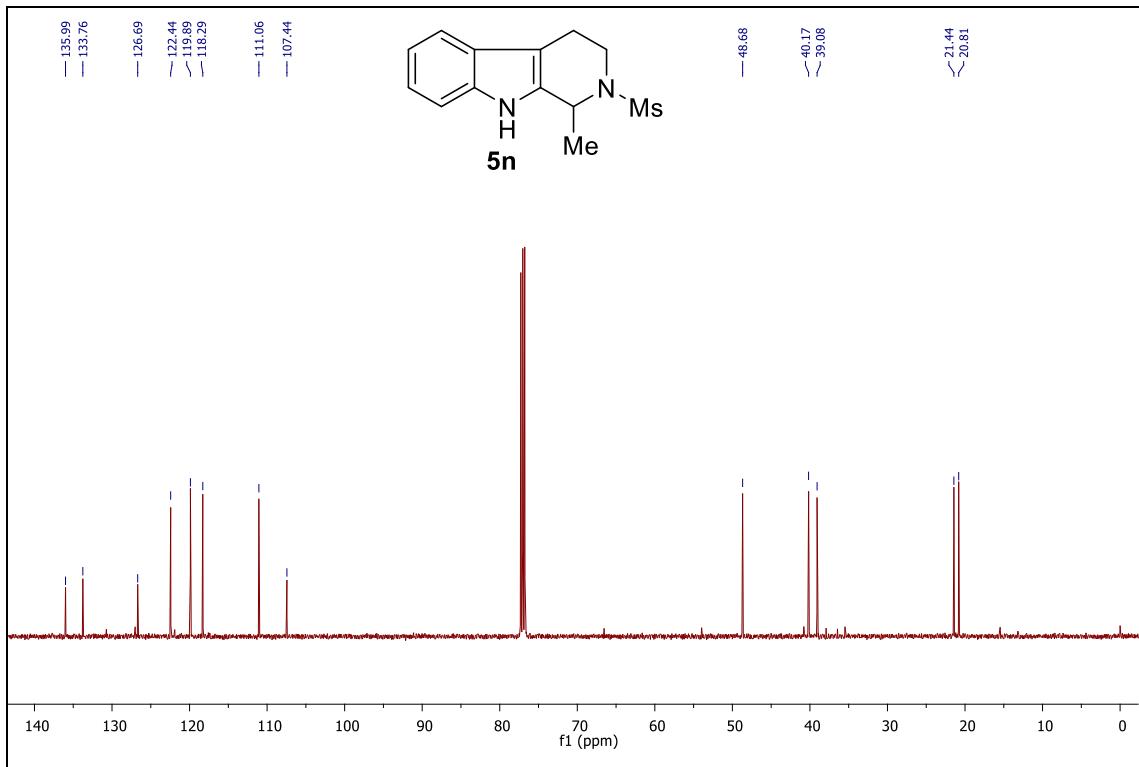
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **5m**.



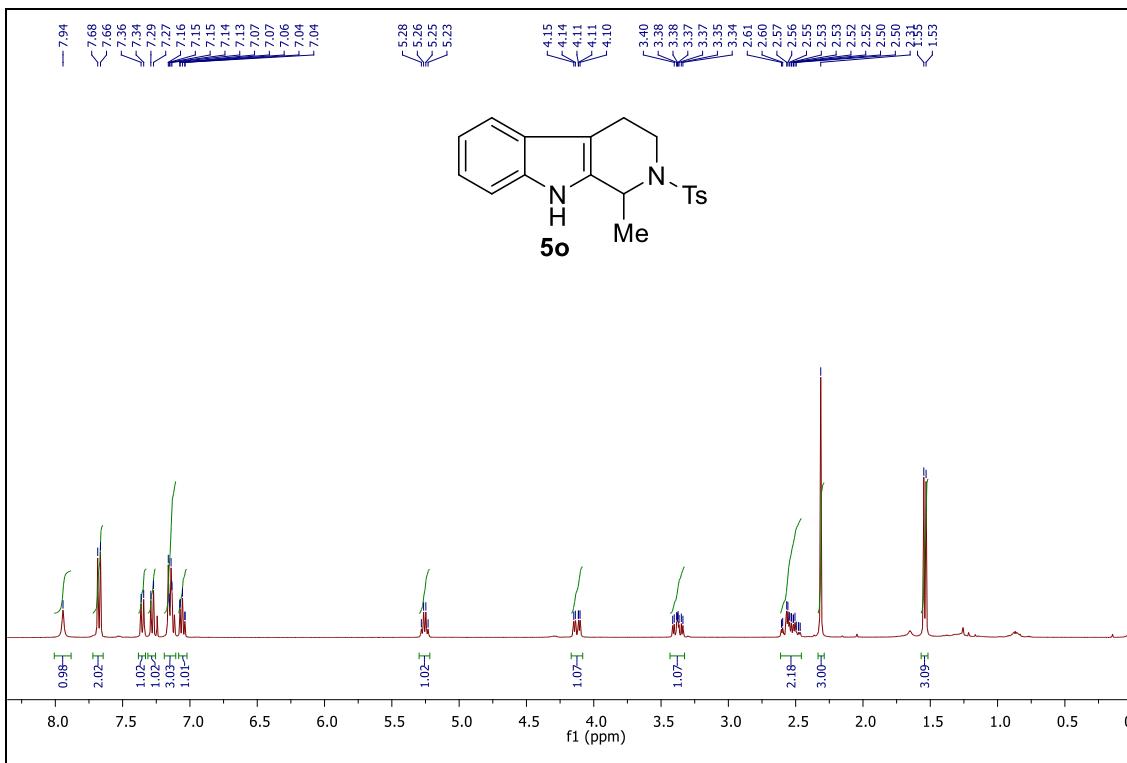
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) for compound **5m**.



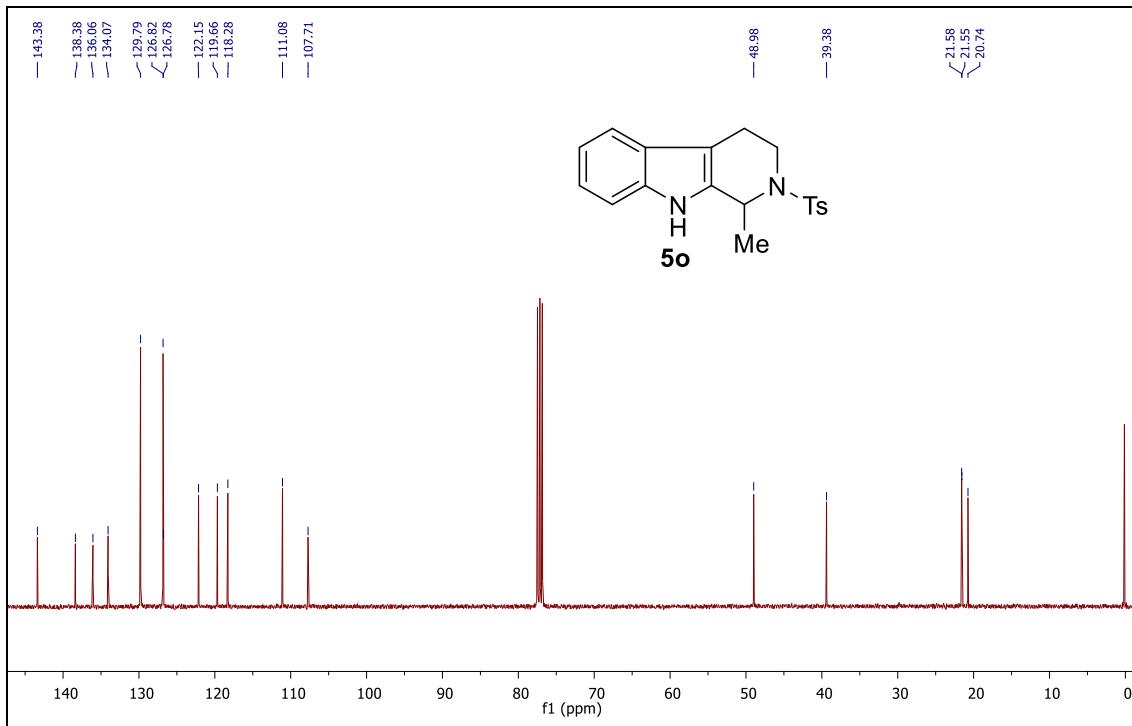
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) for compound **5n**.



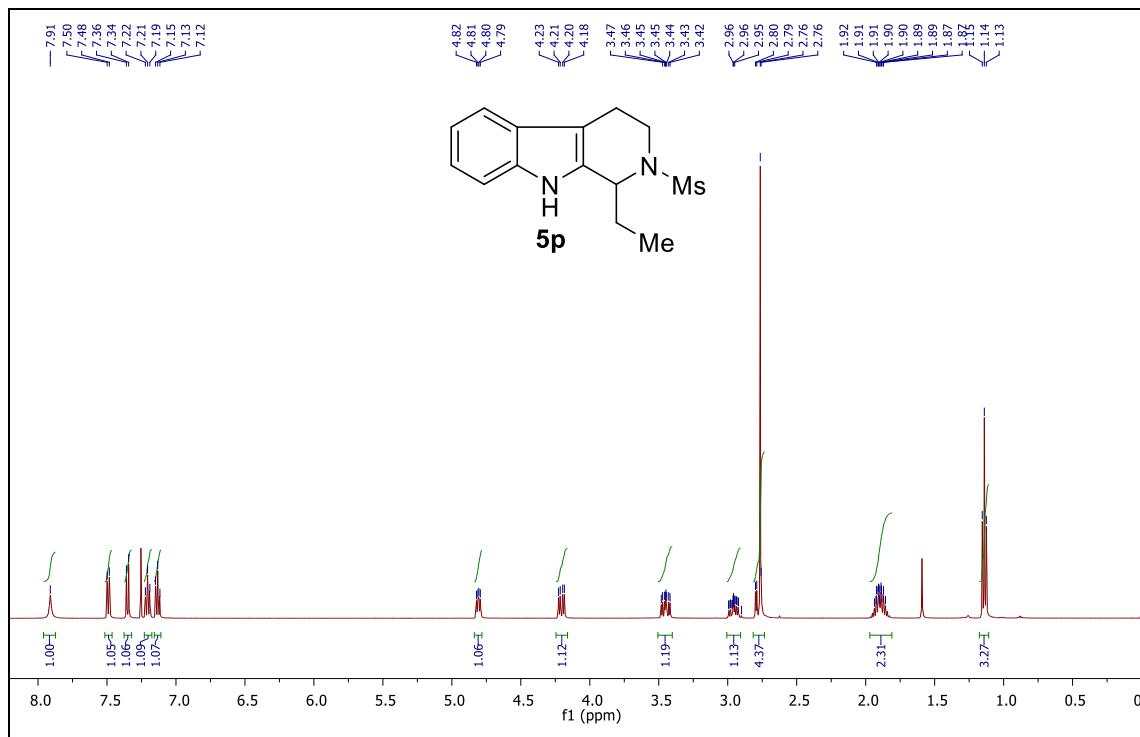
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) for compound **5n**.



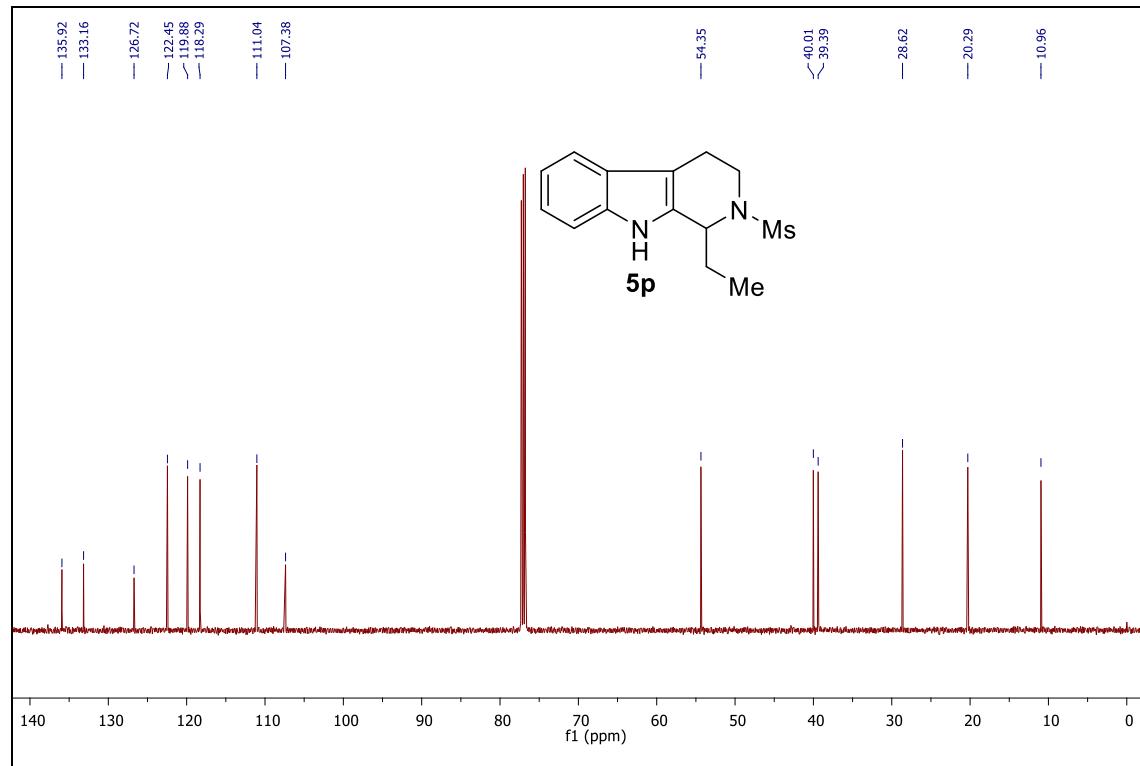
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound **5o**.



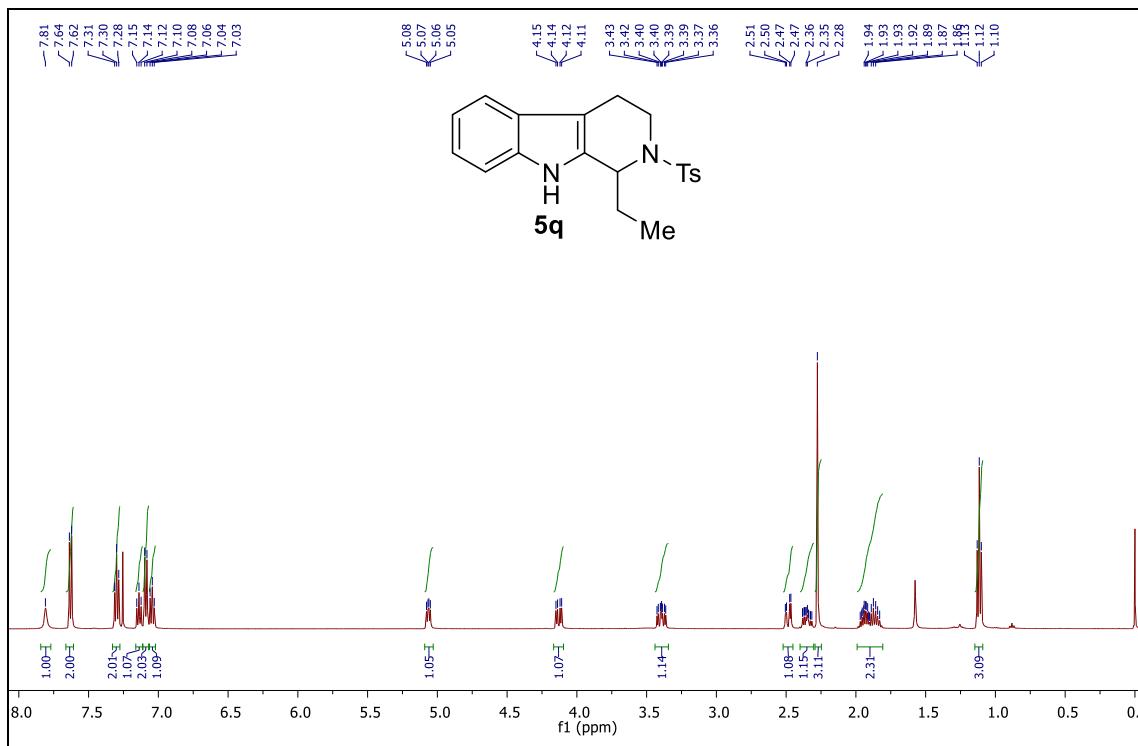
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for compound **5o**.



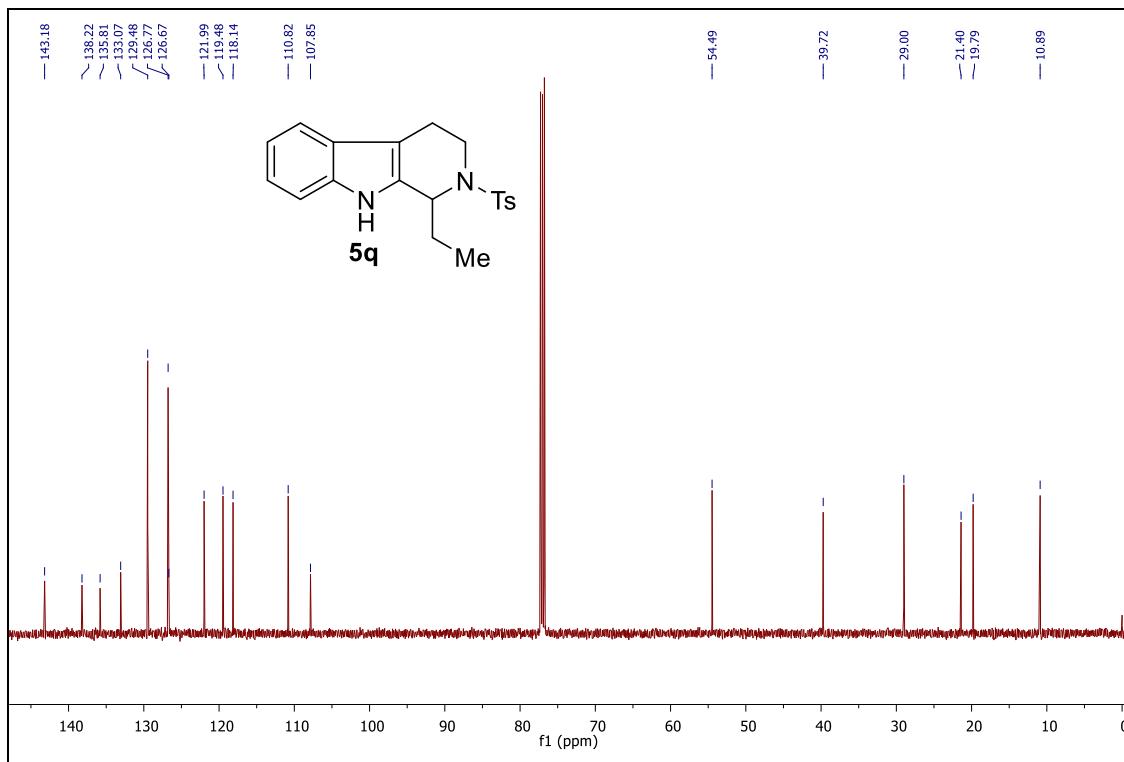
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) for compound **5p**.



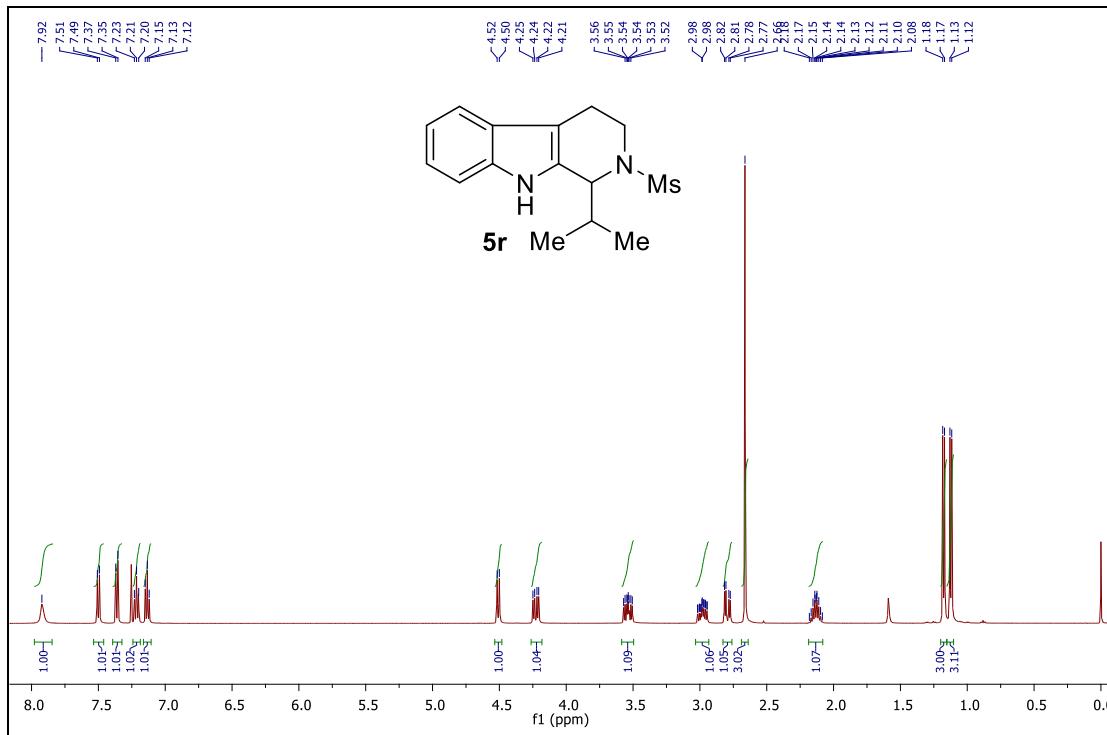
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) for compound **5p**.



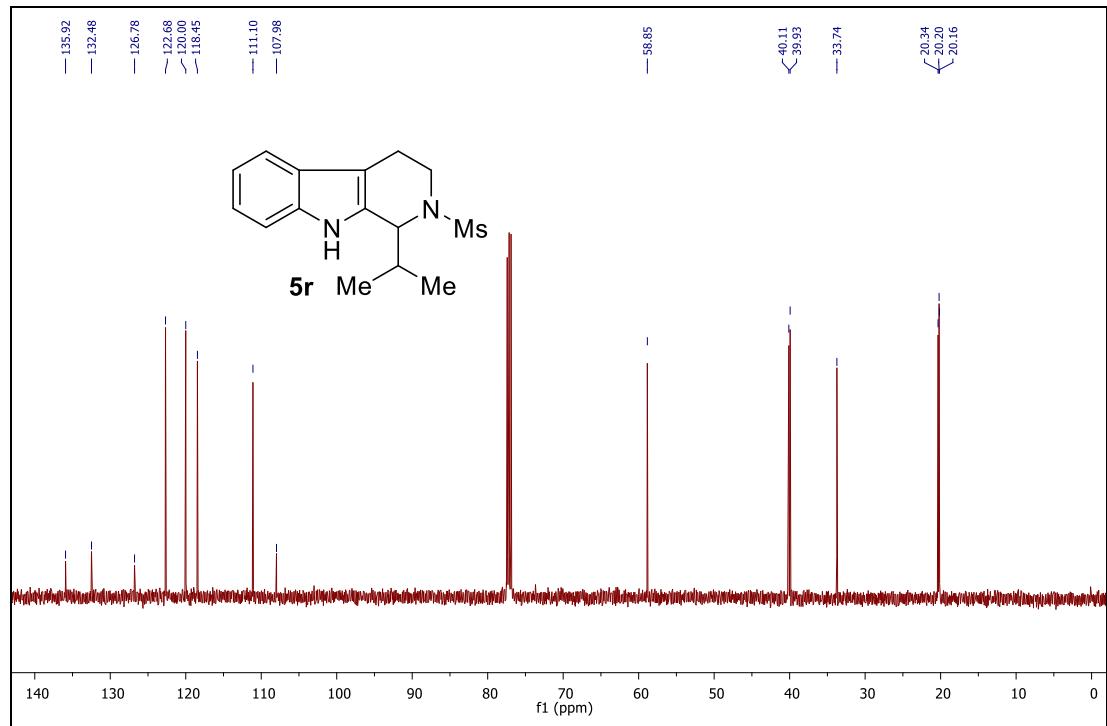
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) for compound **5q**.



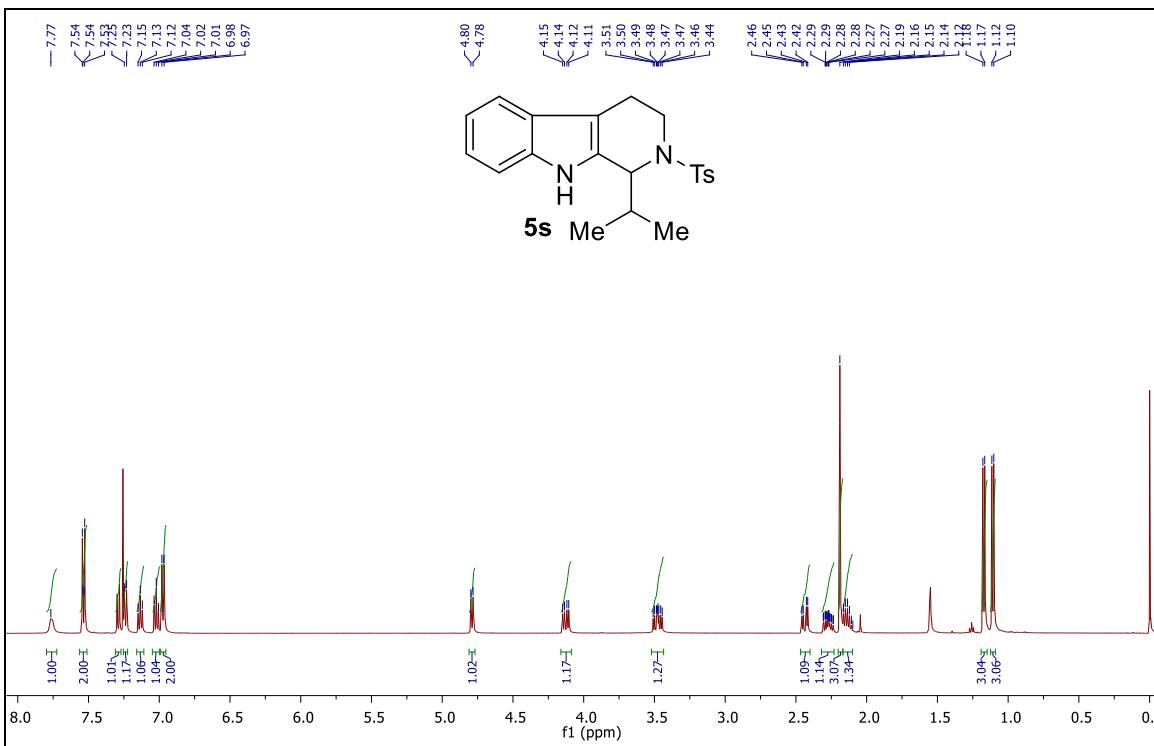
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) for compound **5q**.



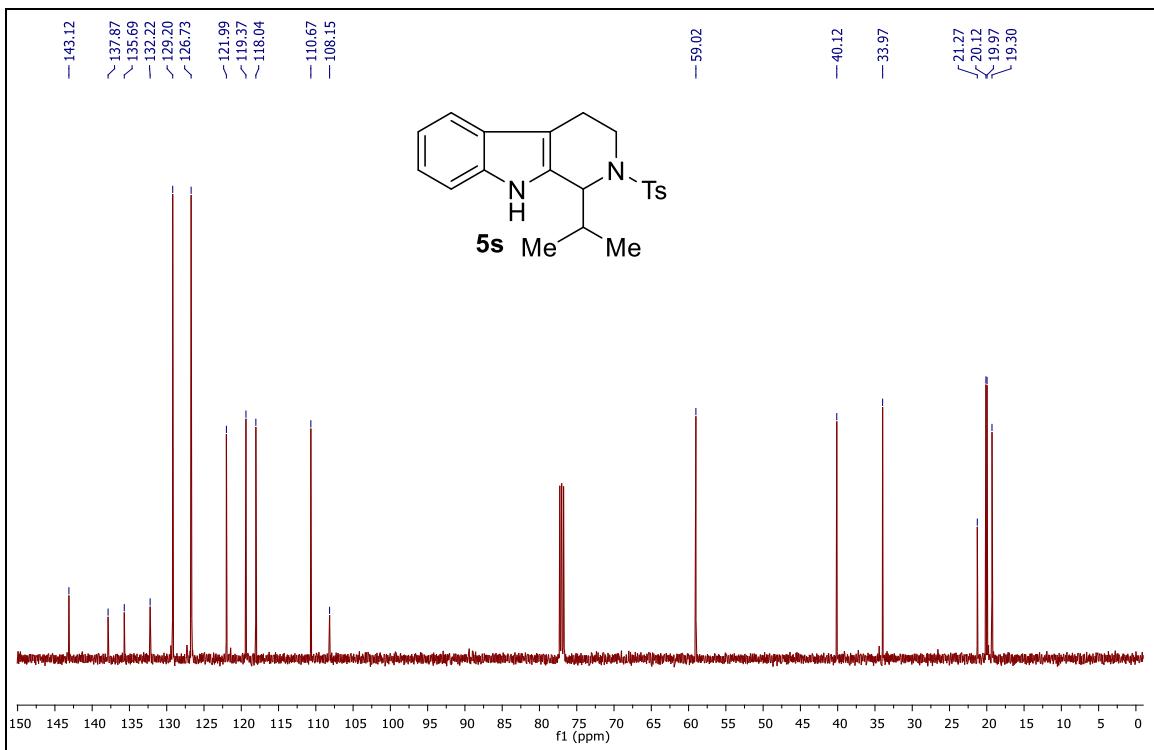
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) for compound **5r**.



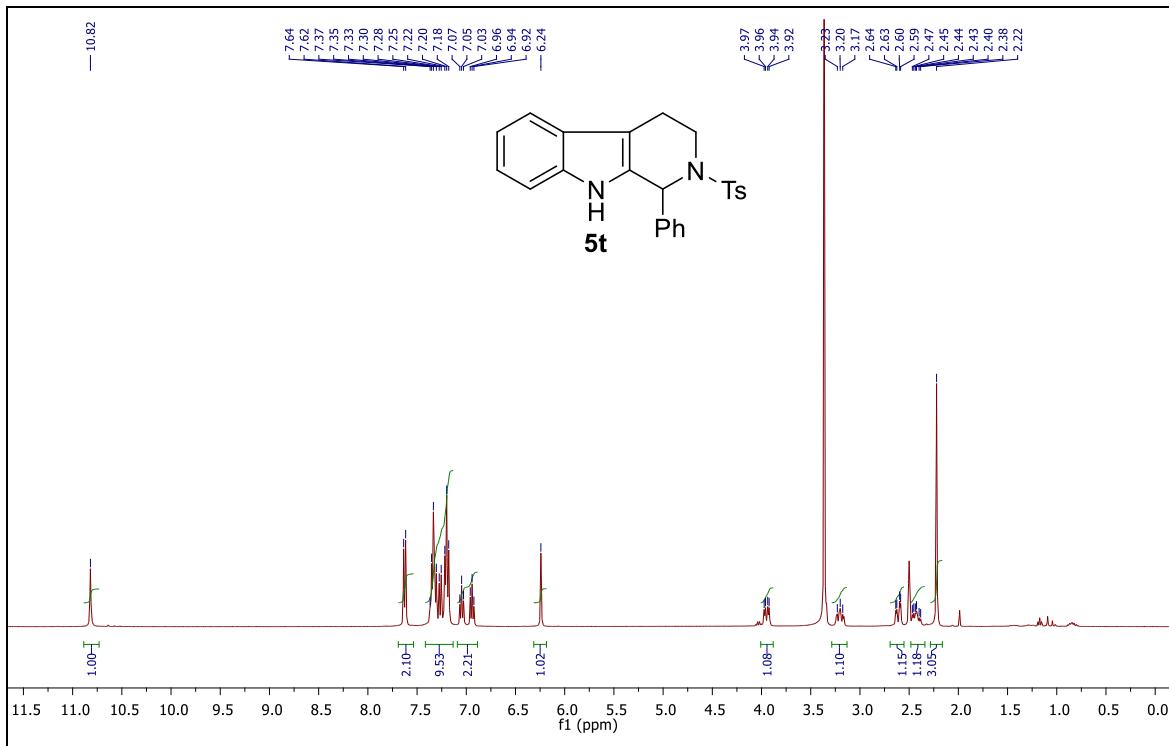
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) for compound **5r**.



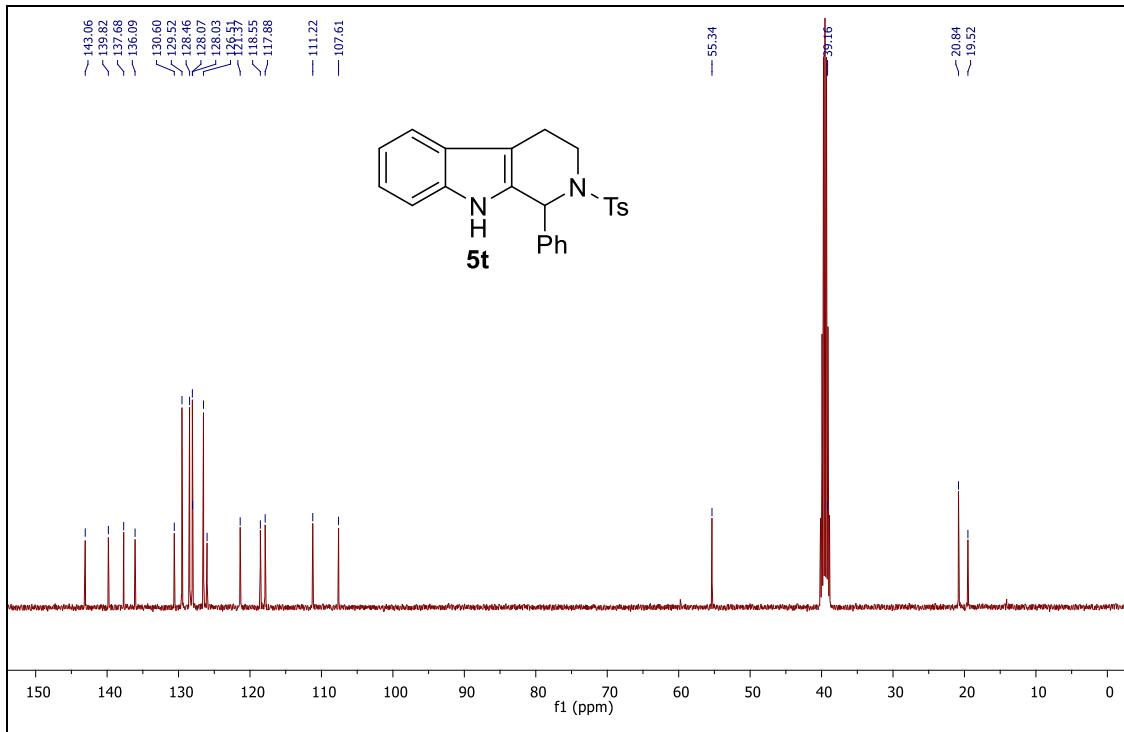
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) for compound **5s**.



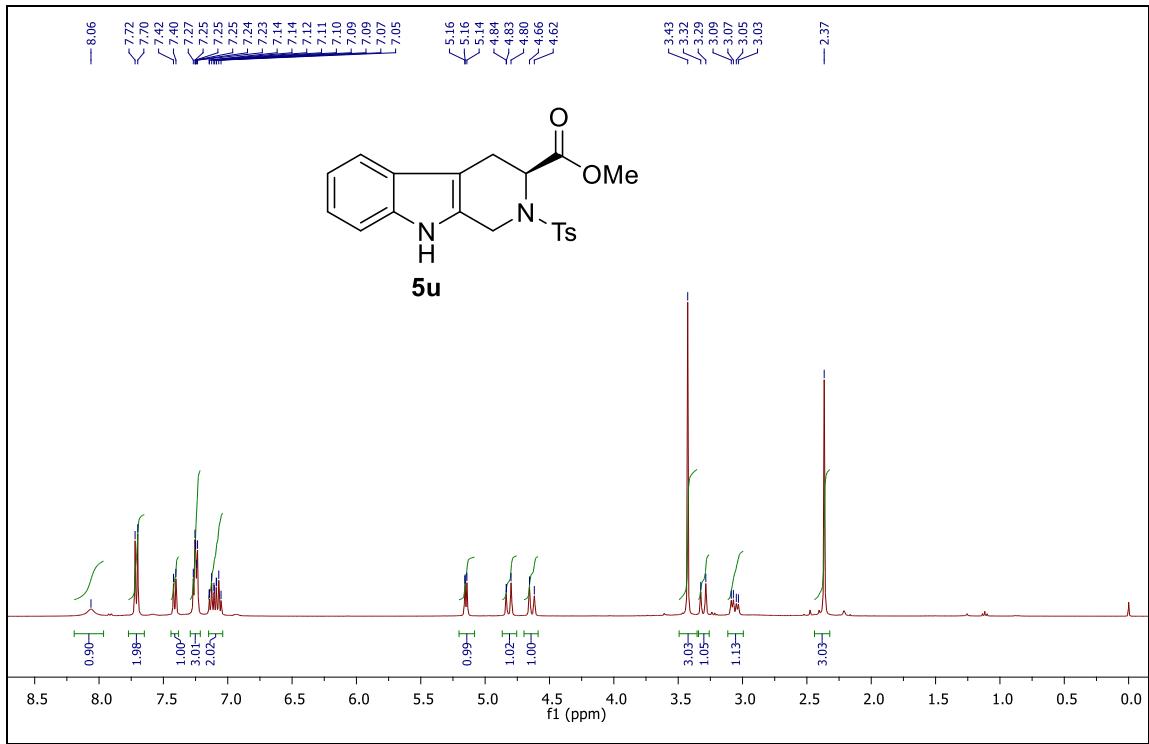
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) for compound **5s**.



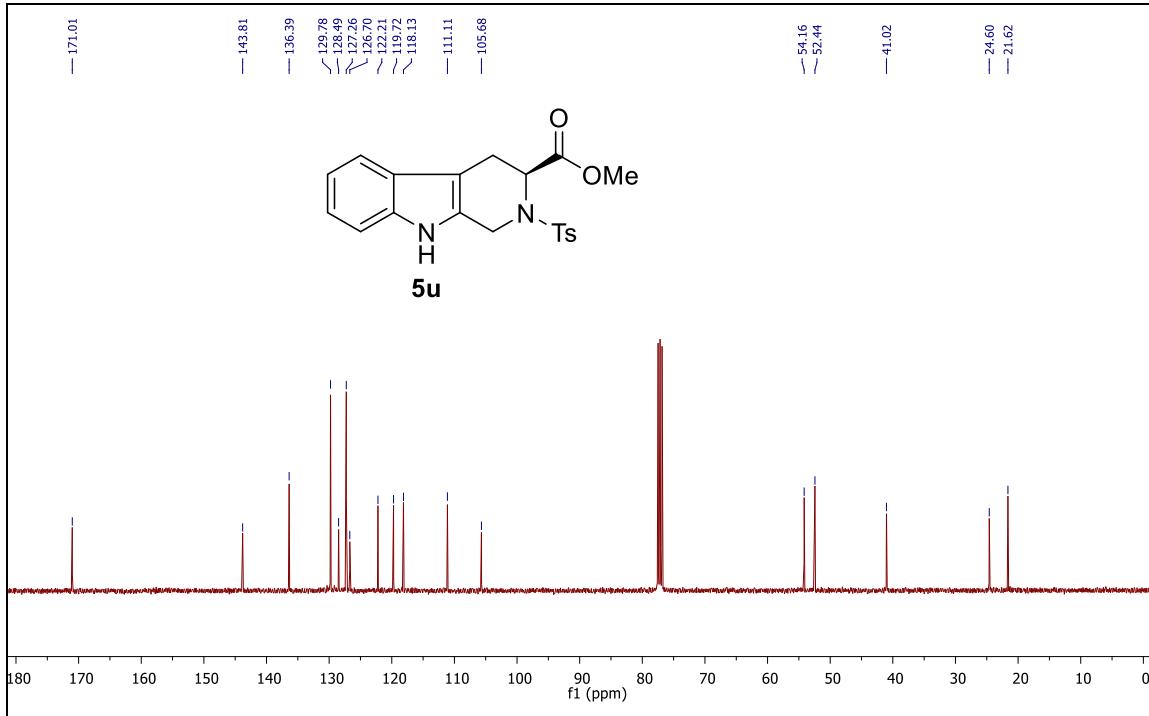
$^1\text{H}$  NMR (400 MHz, DMSO-*d*<sub>6</sub>) for compound **5t**.



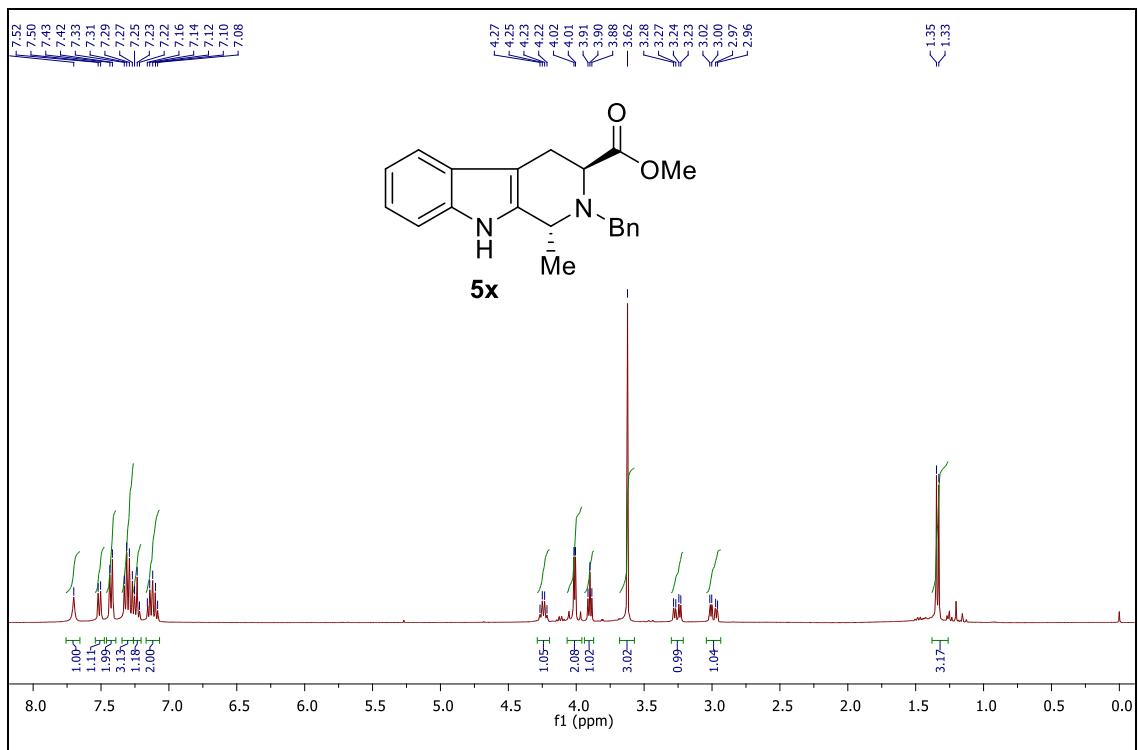
$^{13}\text{C}$  NMR (100 MHz, DMSO-*d*<sub>6</sub>) for compound **5t**.



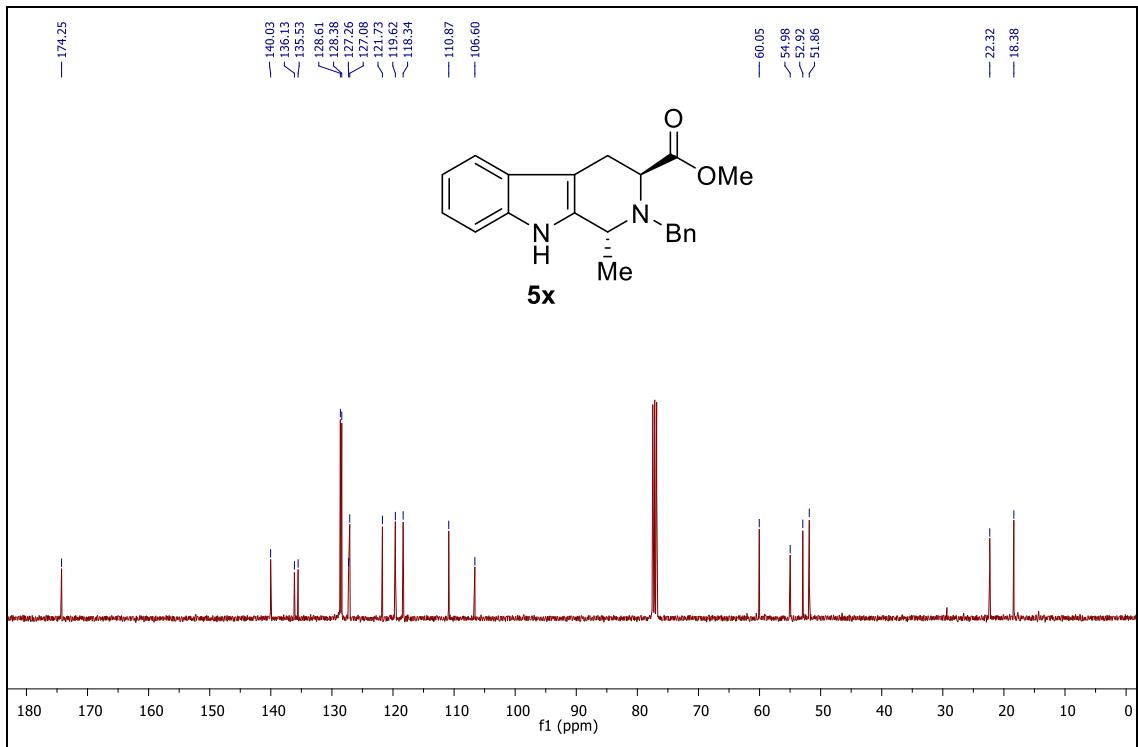
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **5u**.



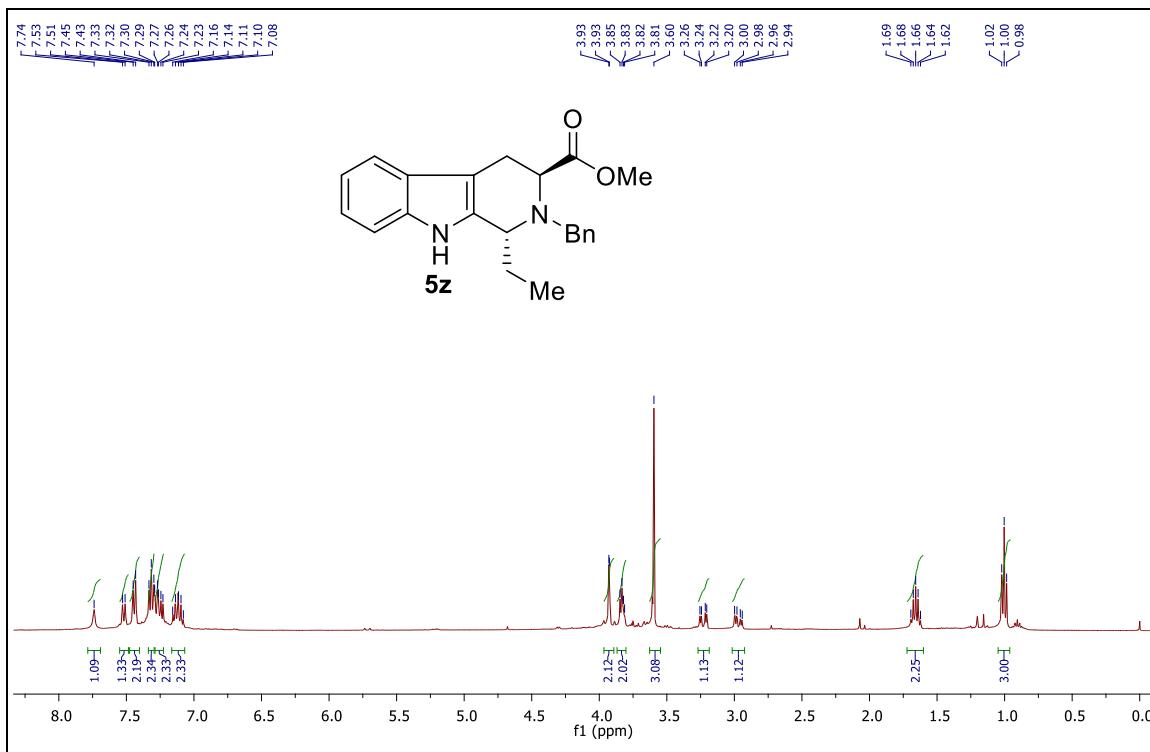
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) for compound **5u**.



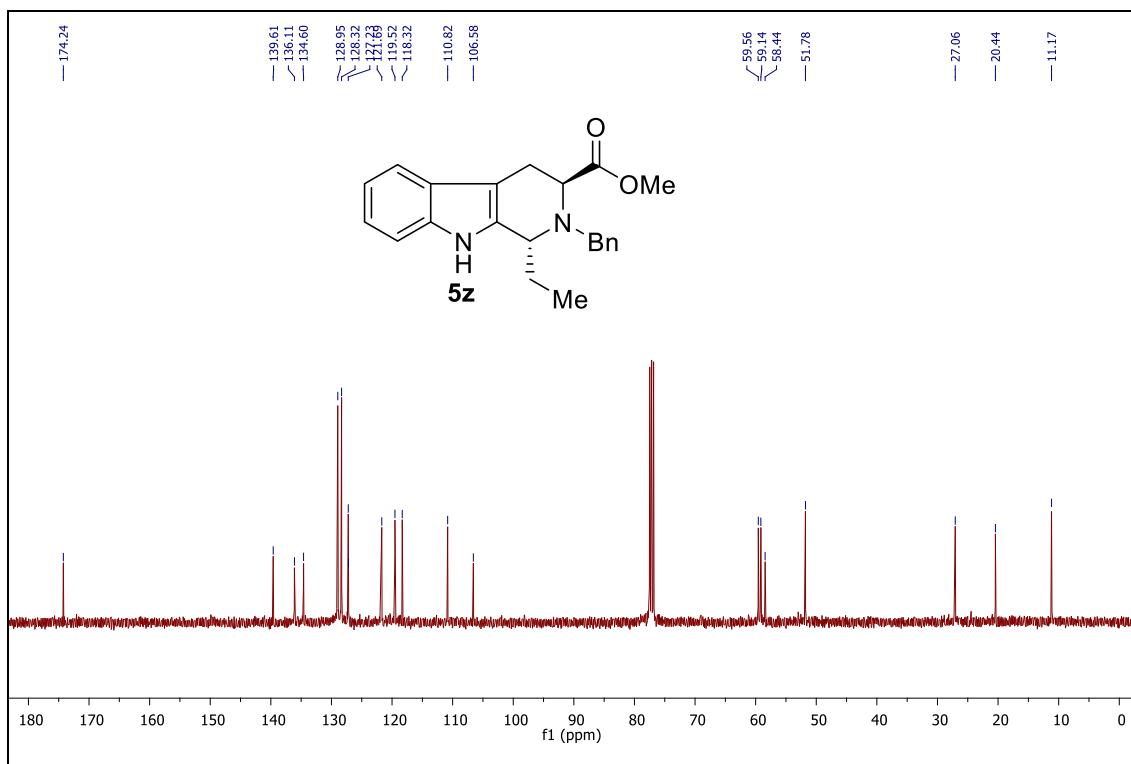
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **5x**.



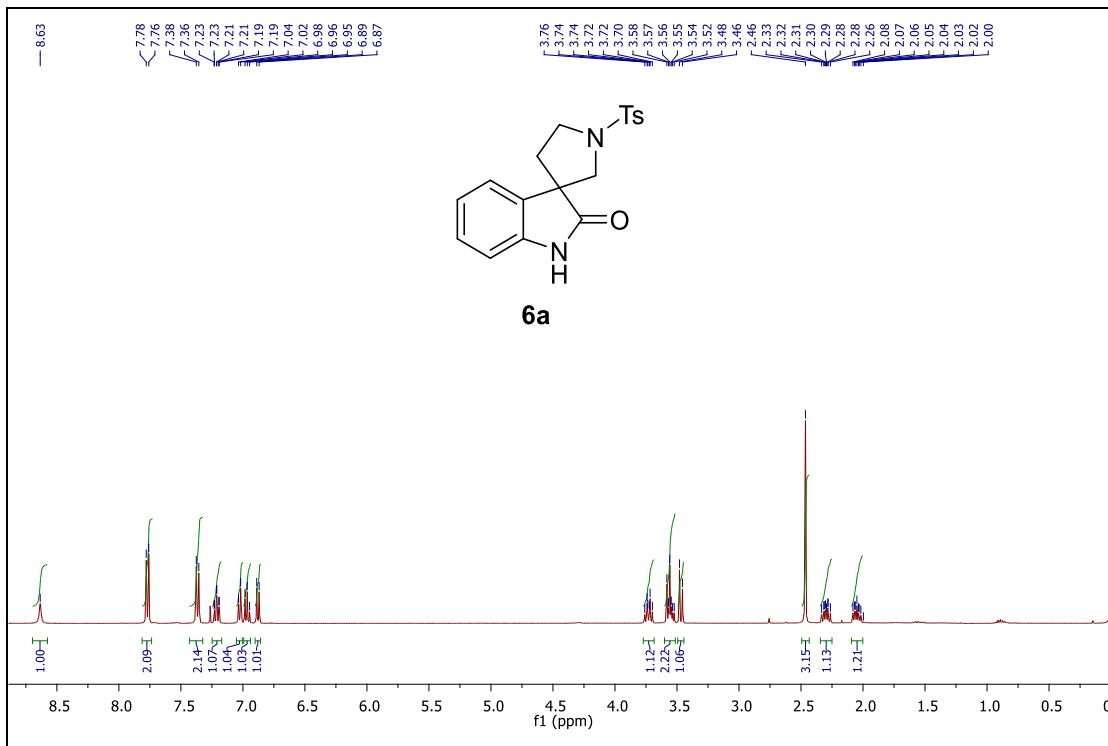
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) for compound **5x**.



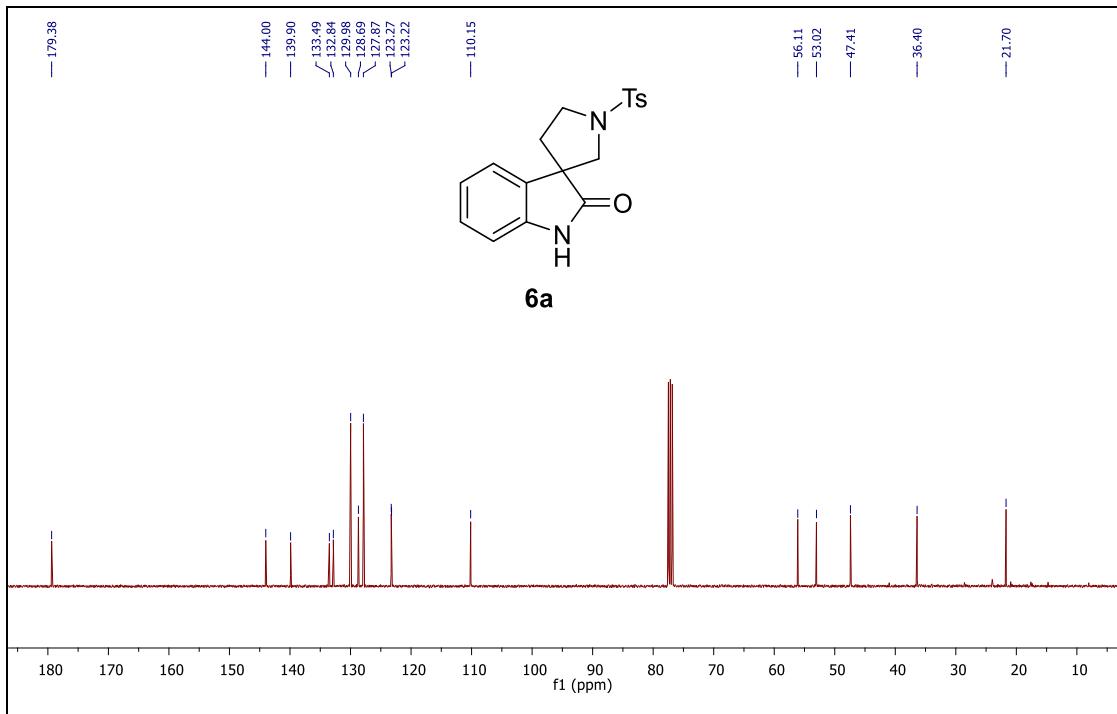
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **5z**.



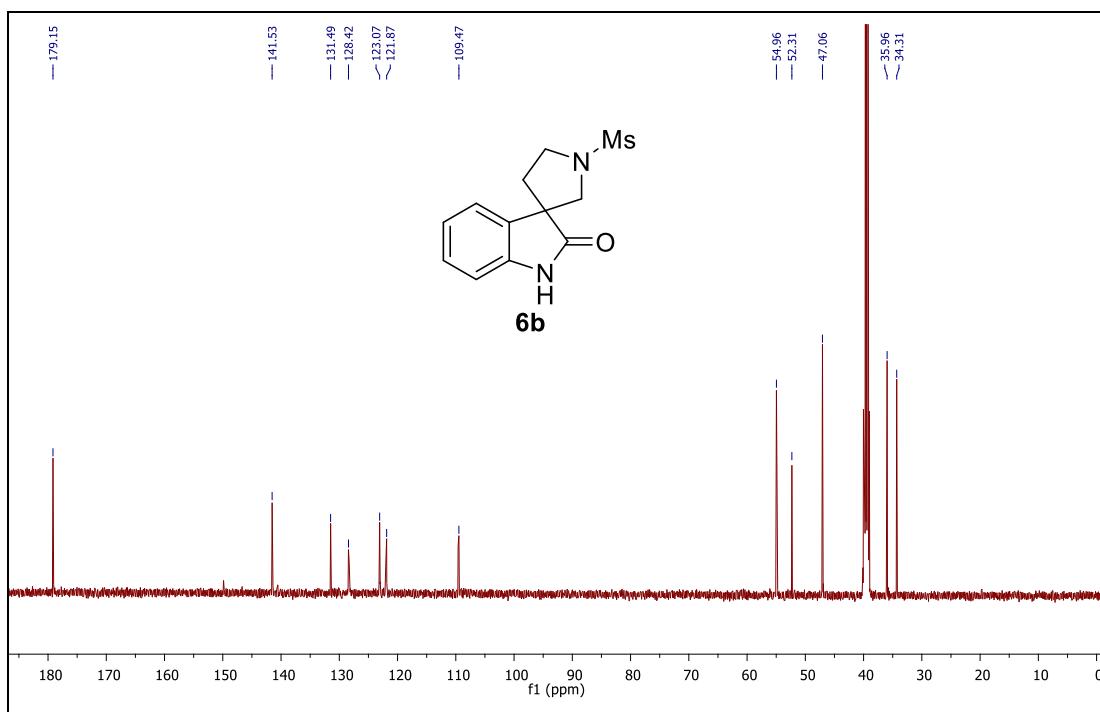
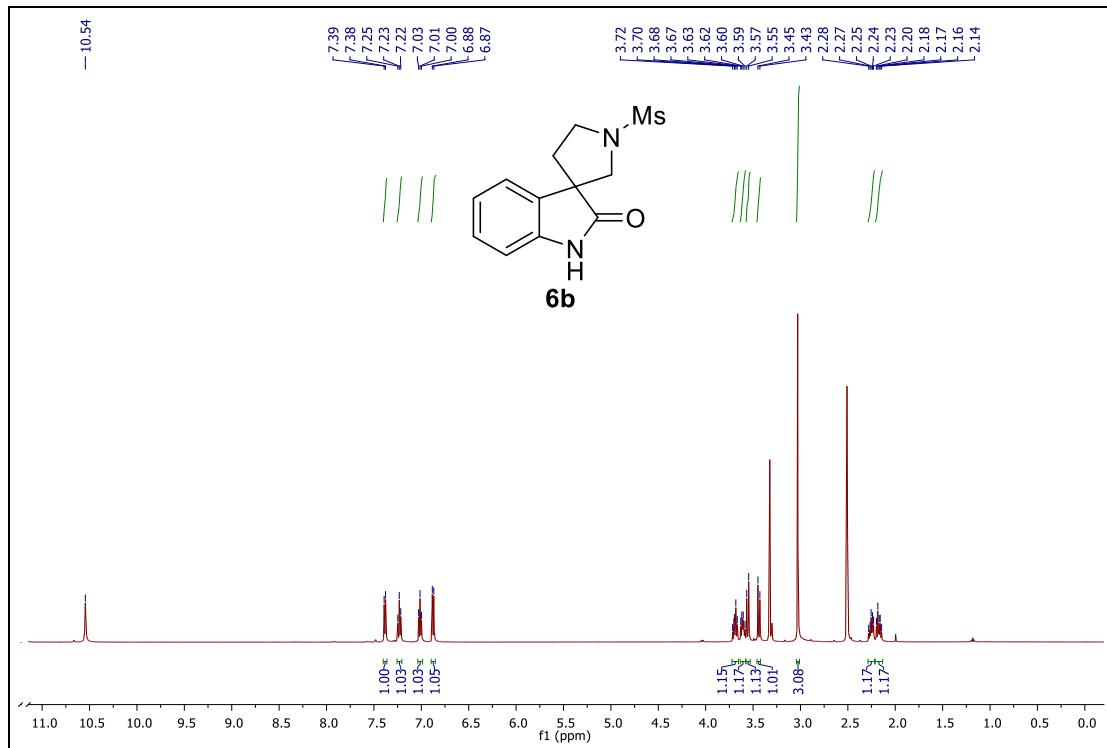
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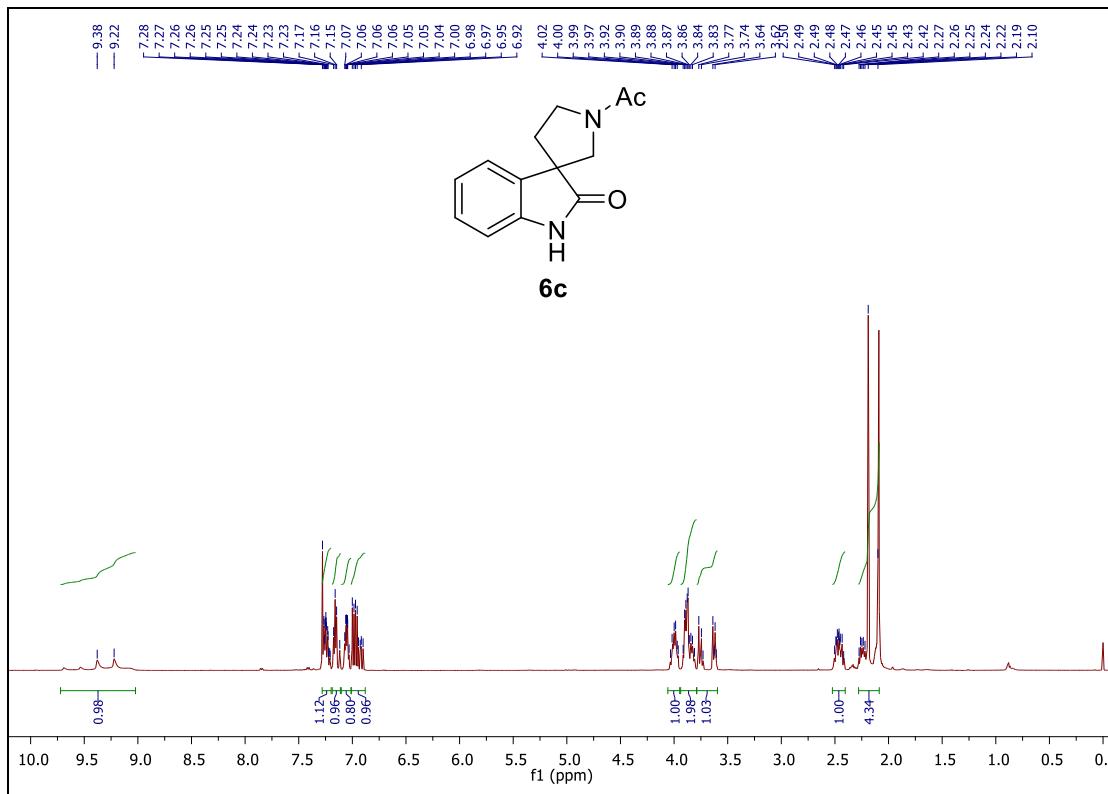


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **6a**.

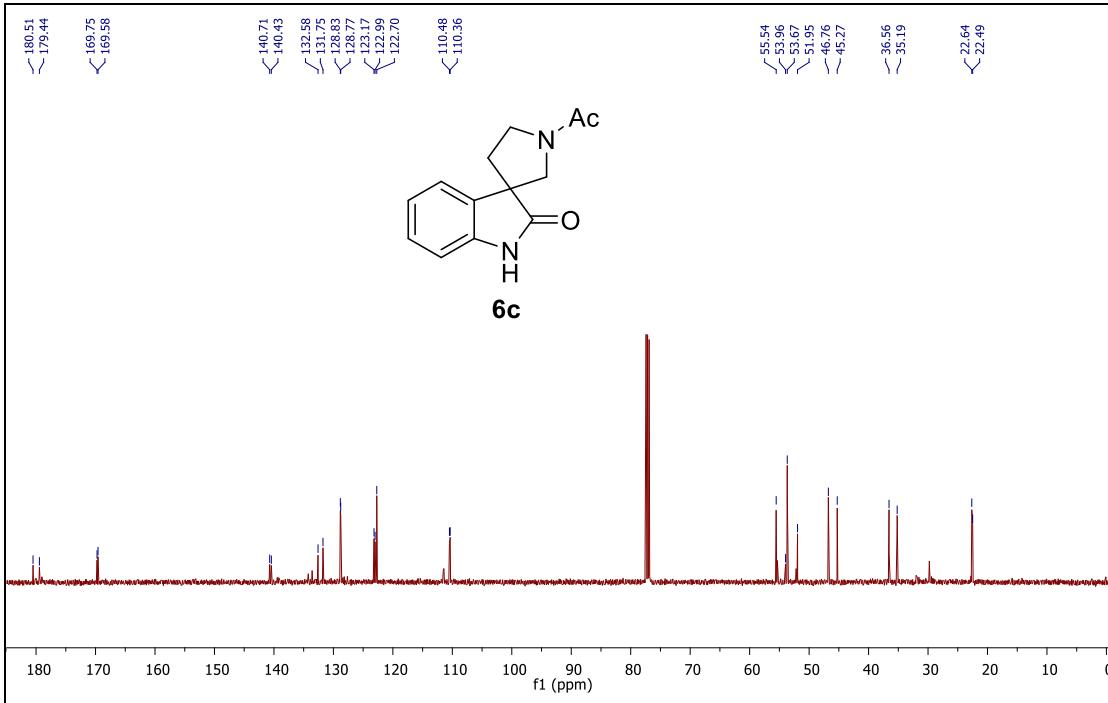


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) for compound **6a**.

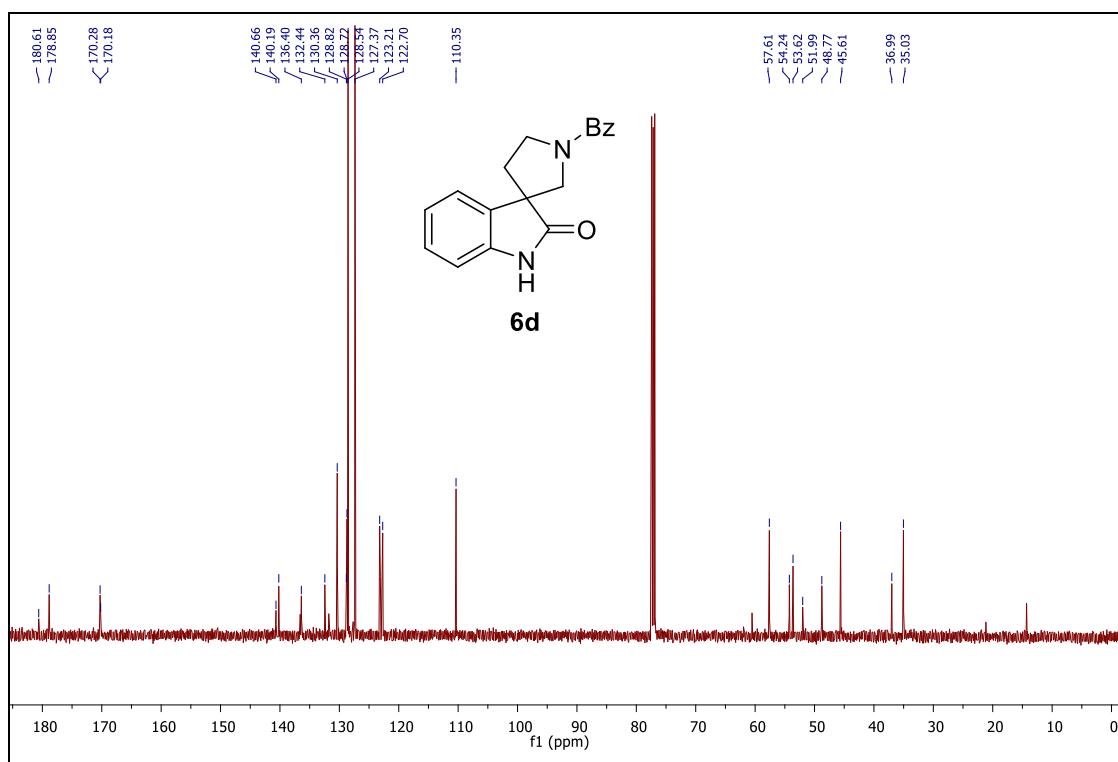
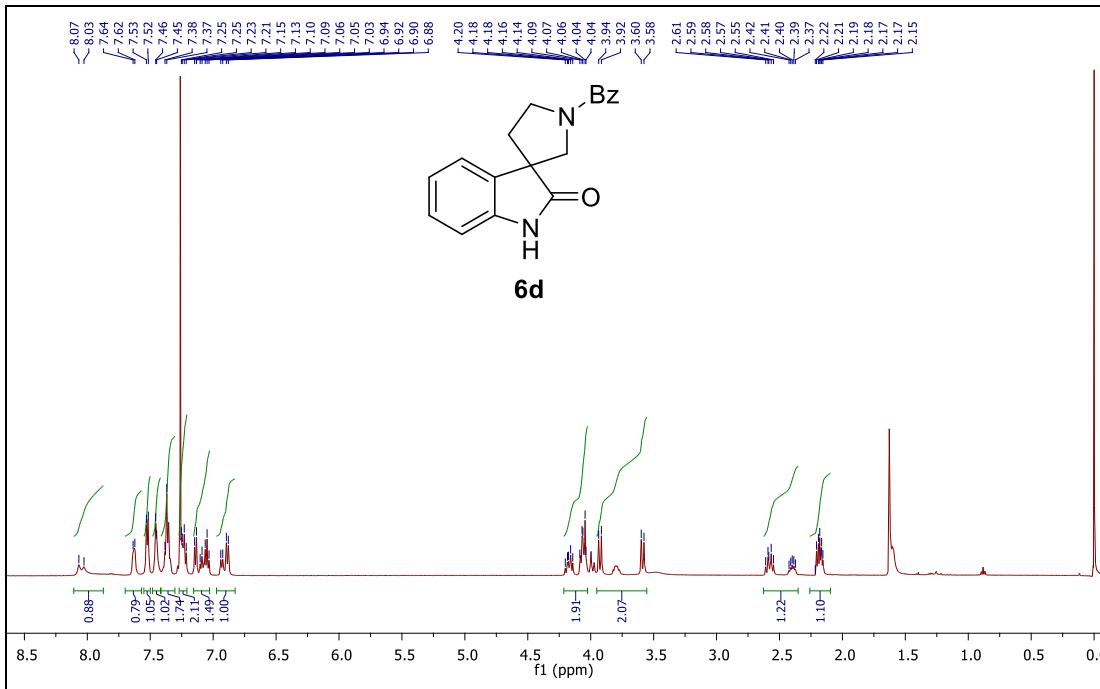


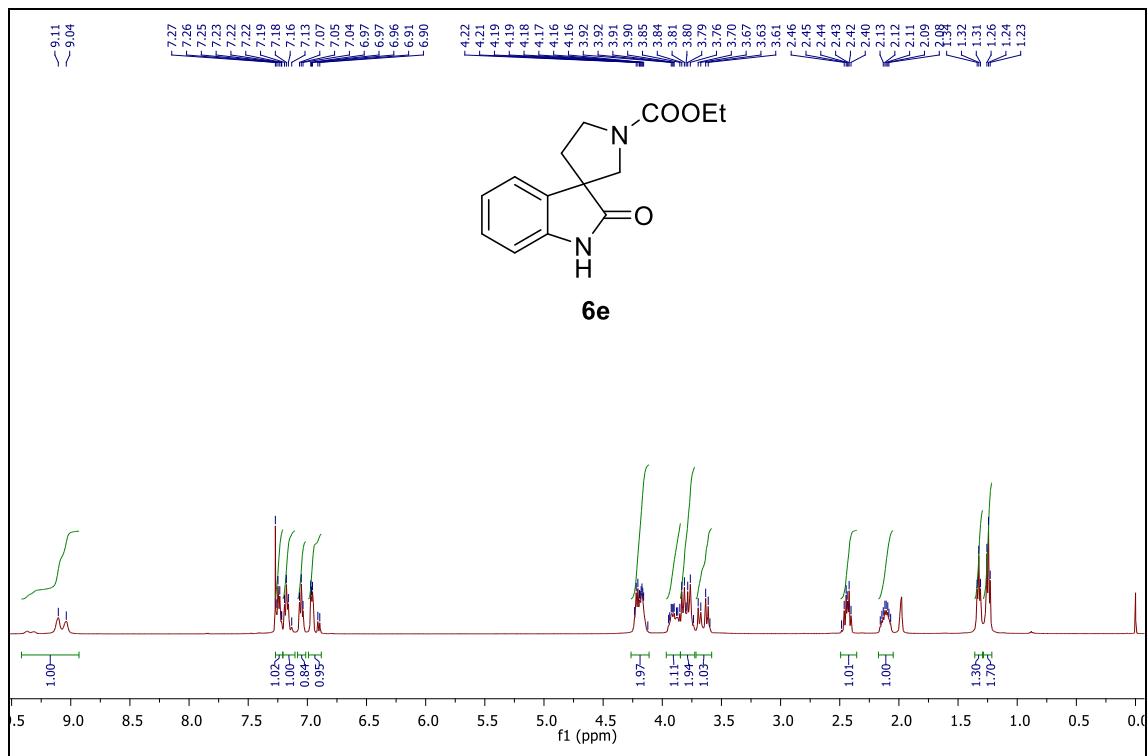


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) for compound **6c**.

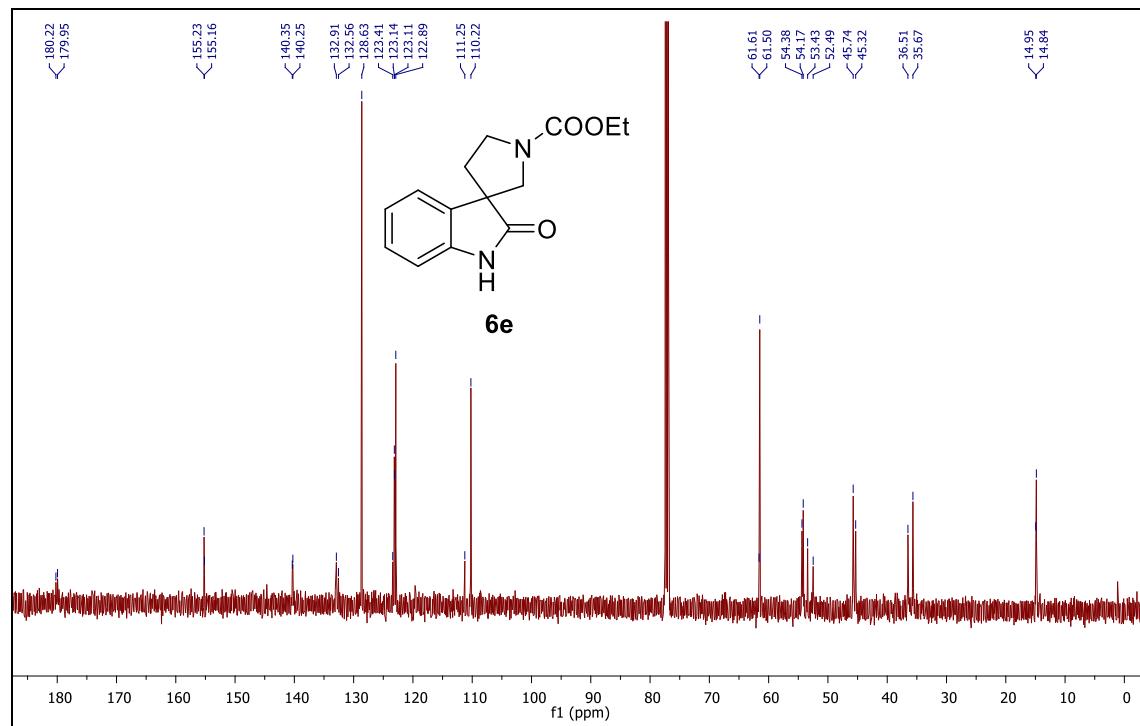


$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) for compound **6c**.

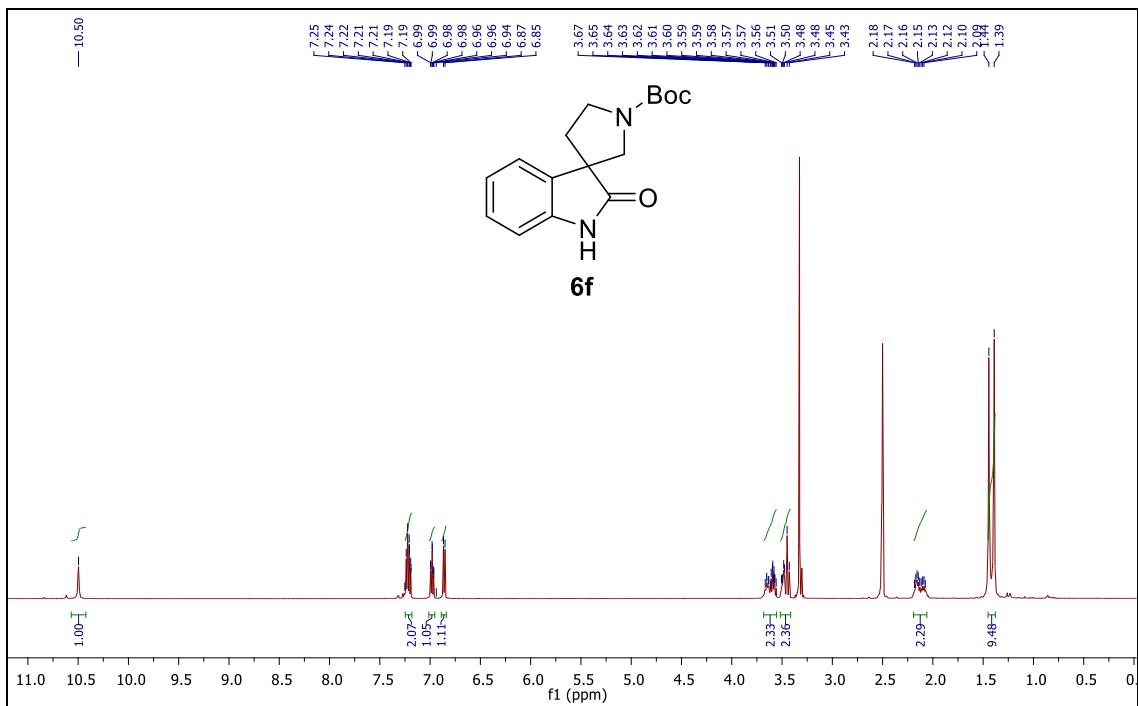




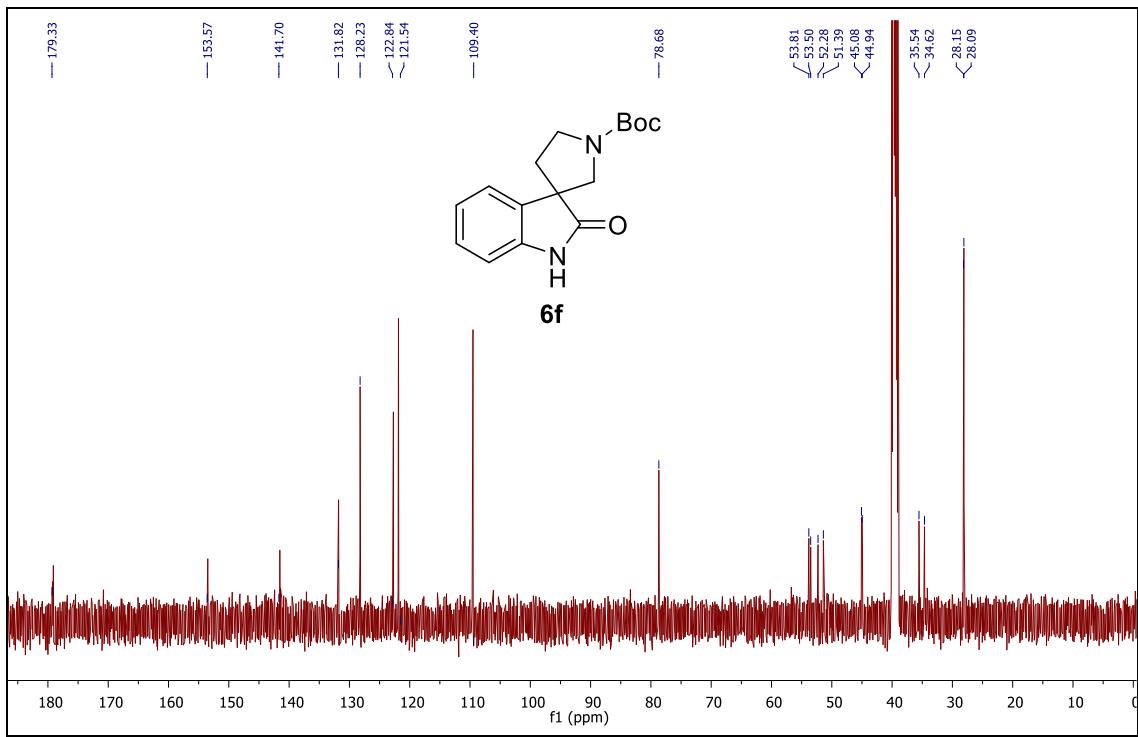
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) for compound **6e**.



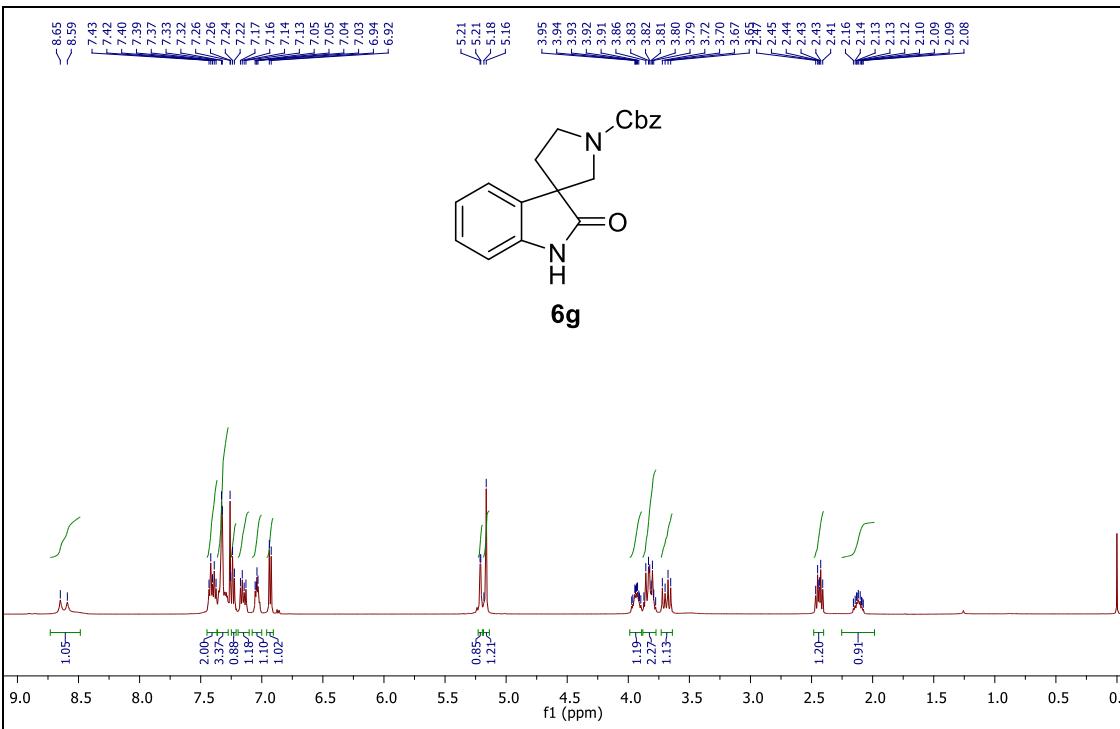
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) for compound **6e**.



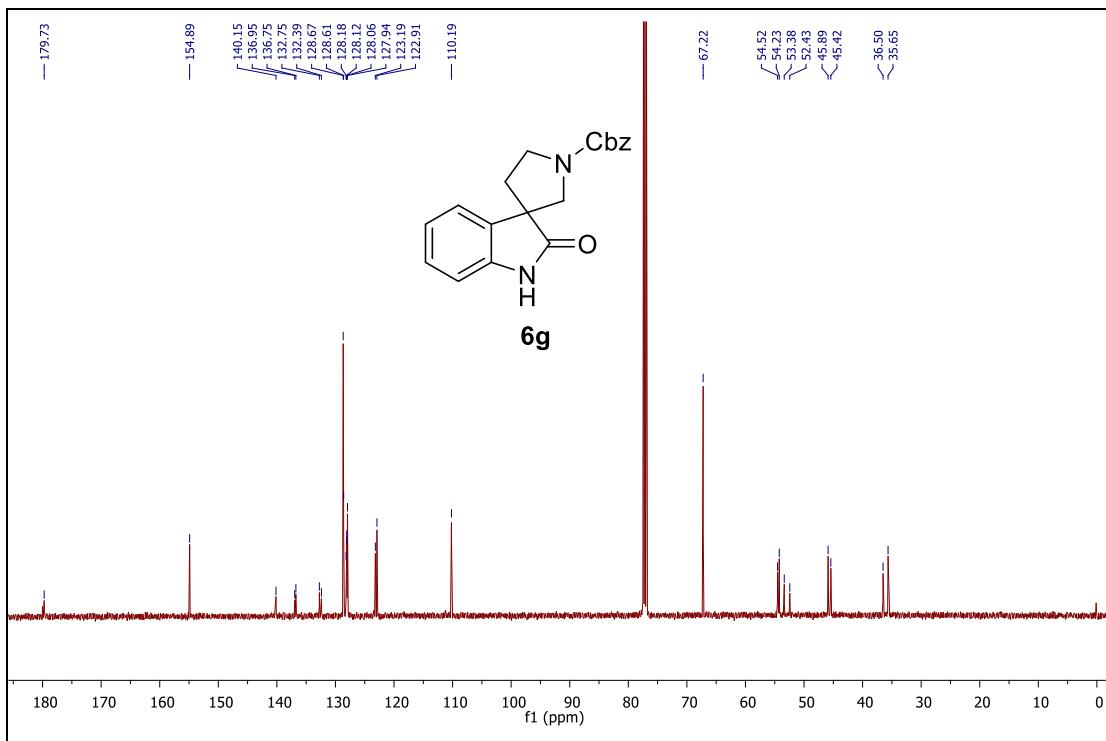
<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) for compound **6f**.



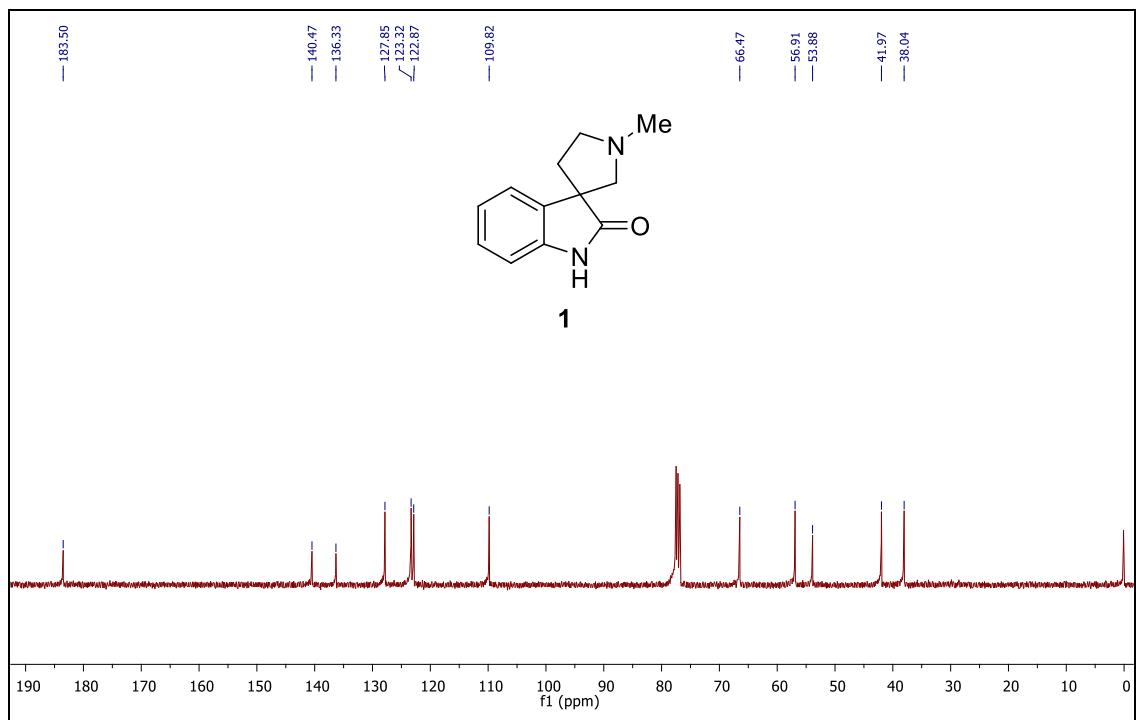
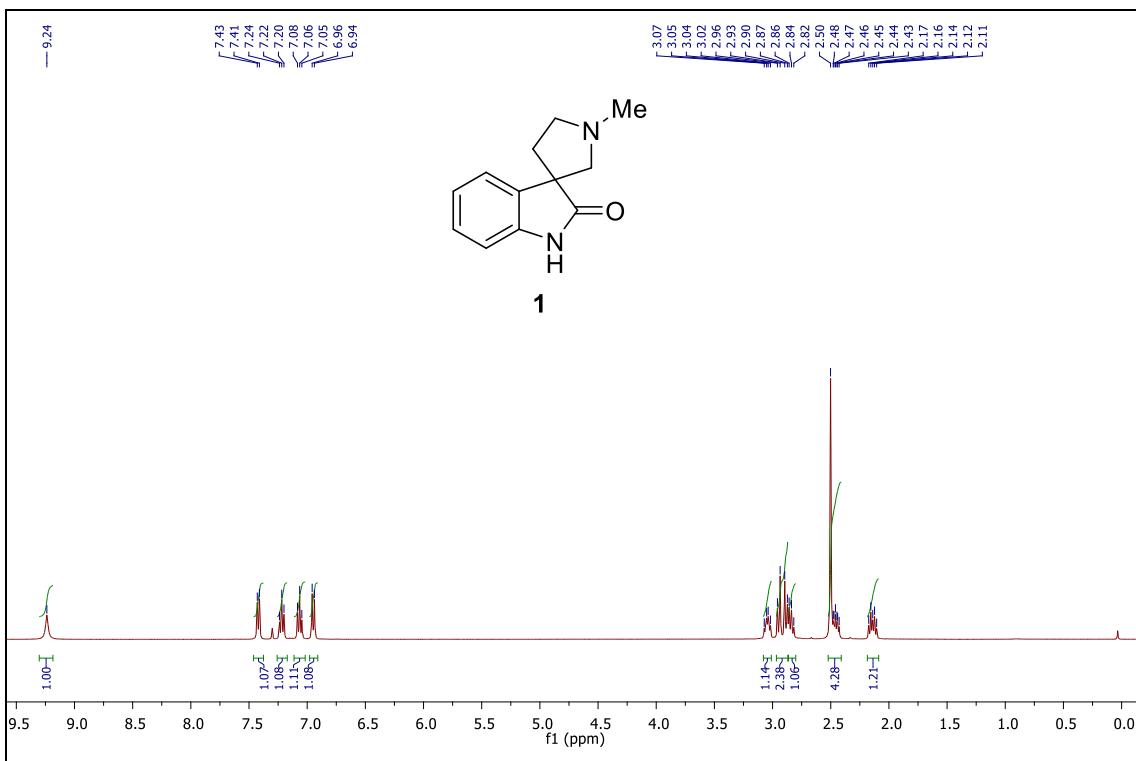
<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) for compound **6f**.



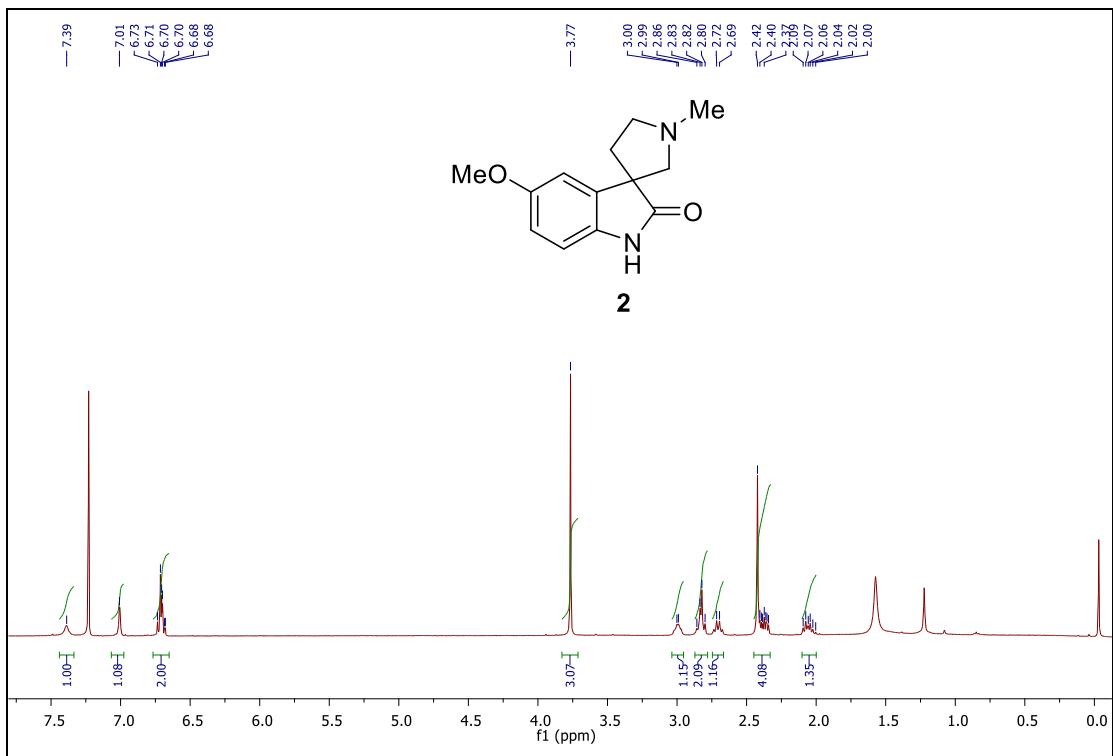
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) for compound **6g**.



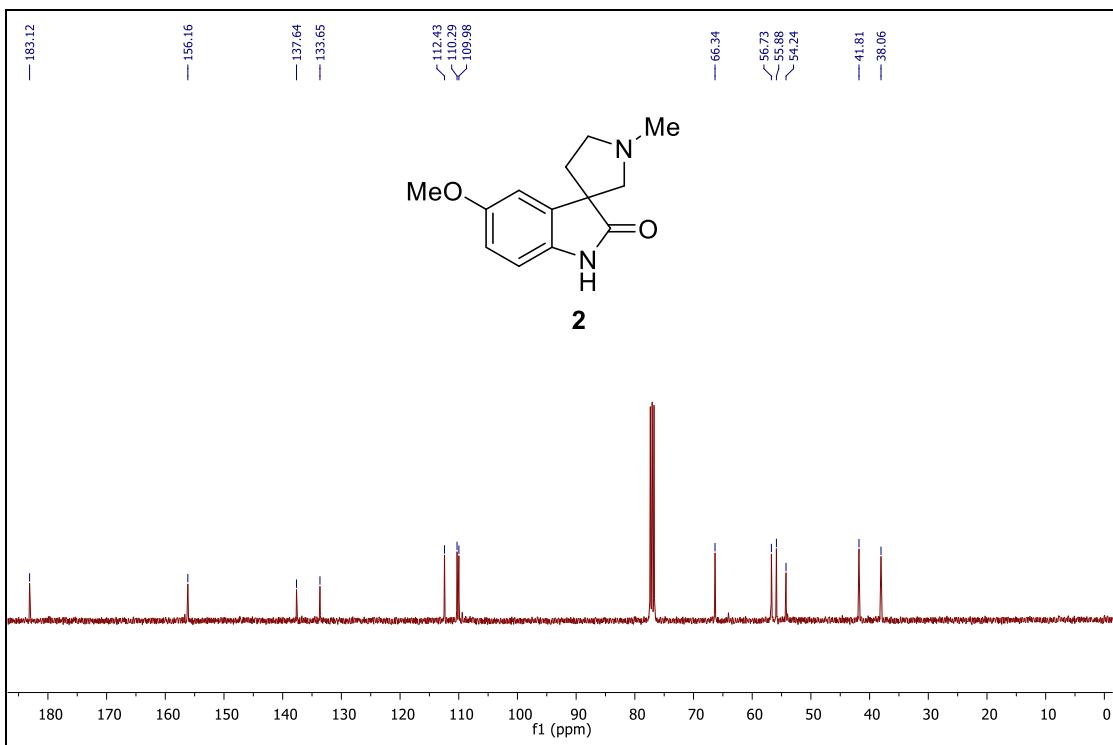
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) for compound **6g**.



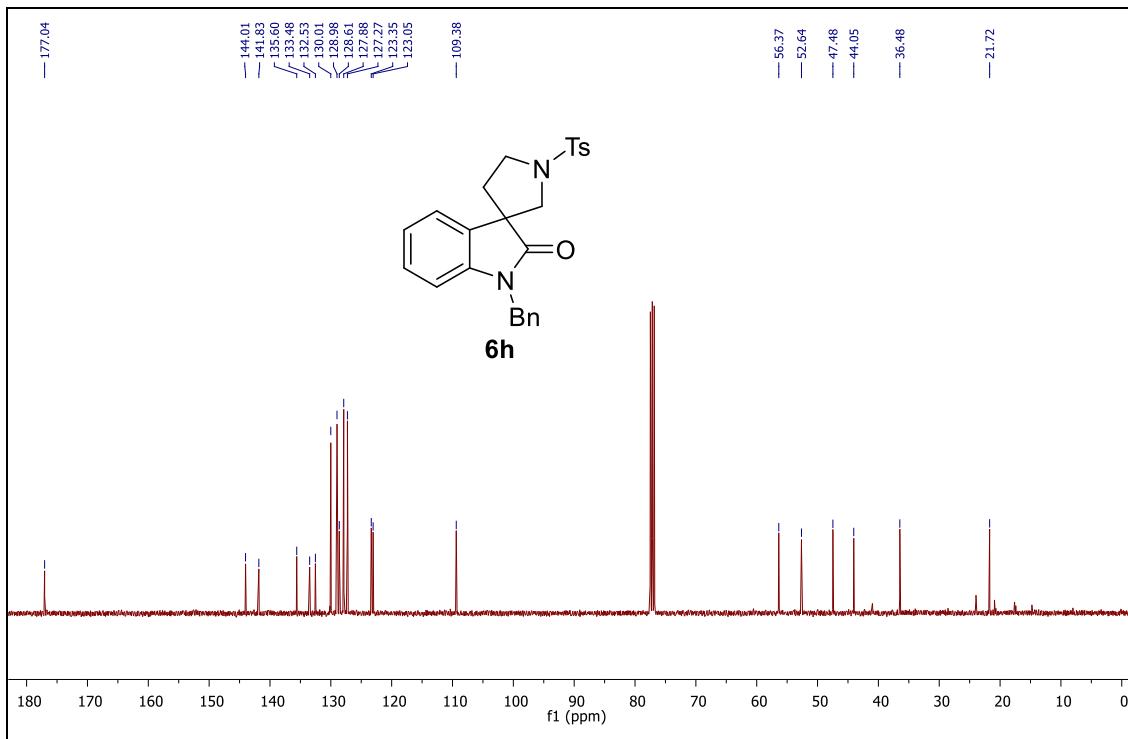
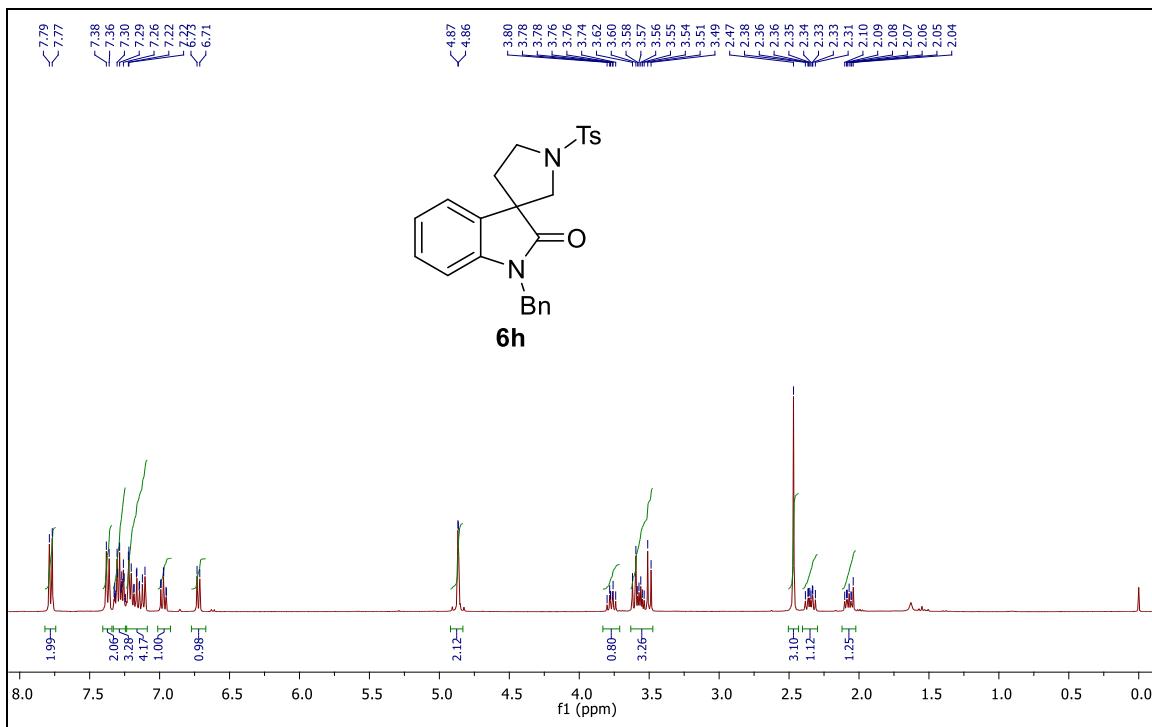
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for compound **1**.



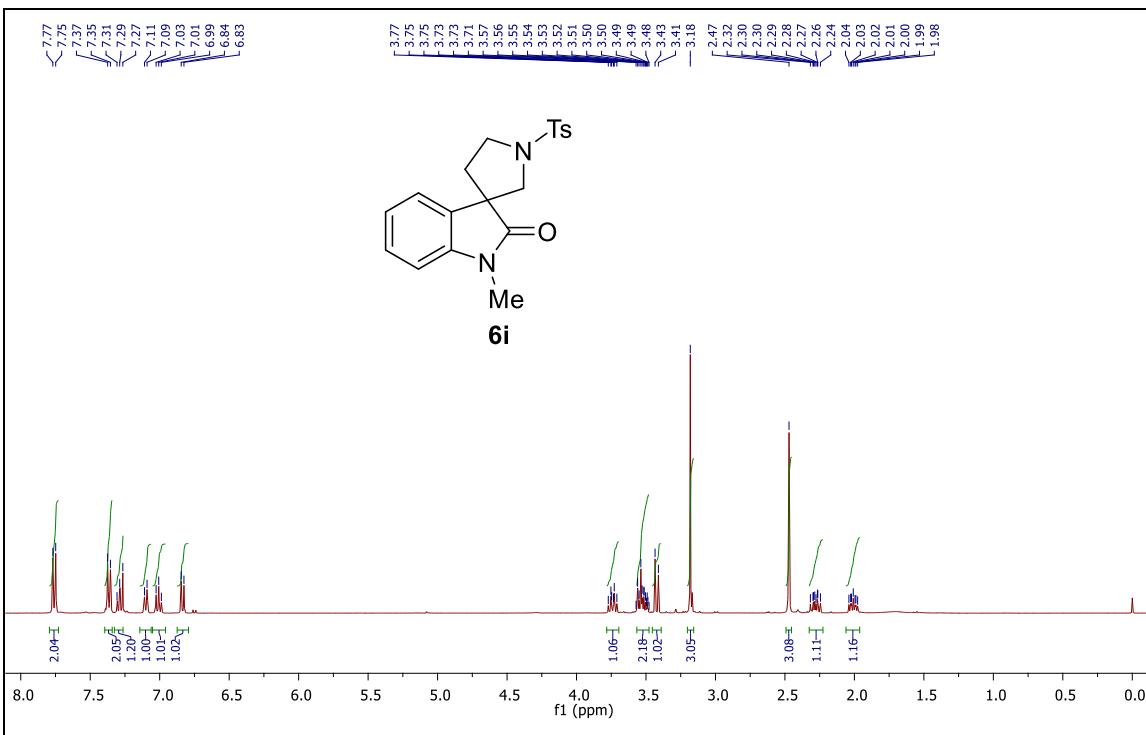
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **2**.



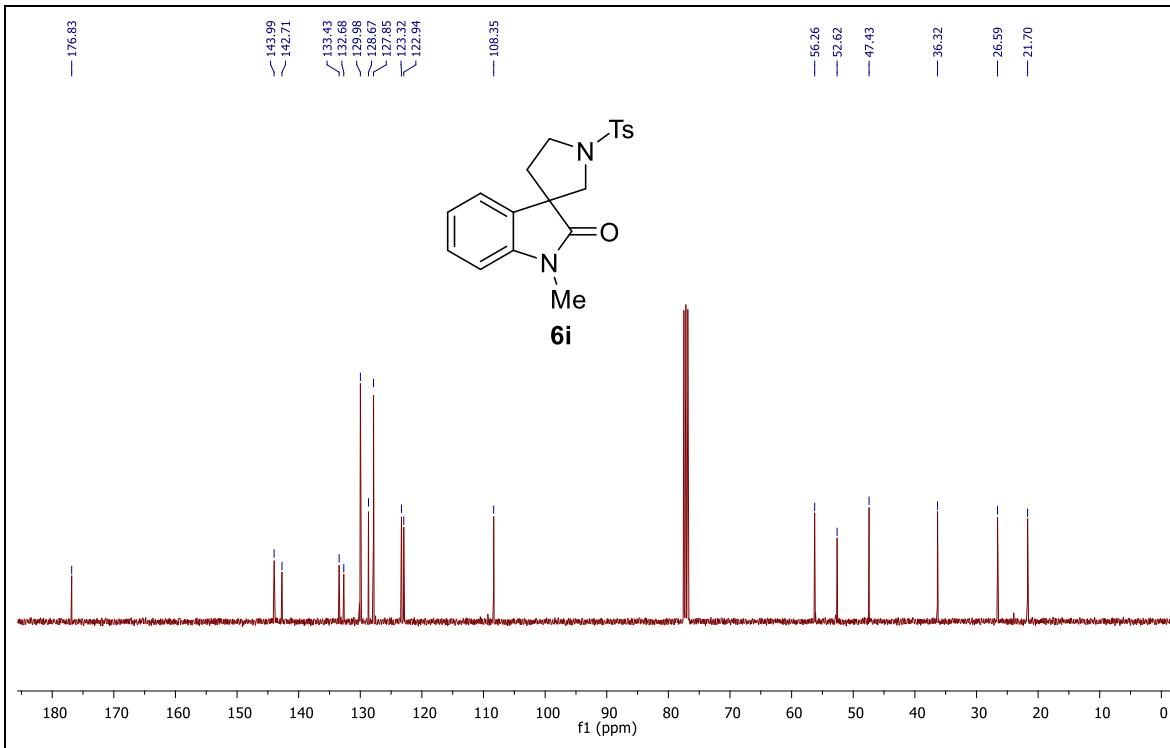
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) for compound **2**.



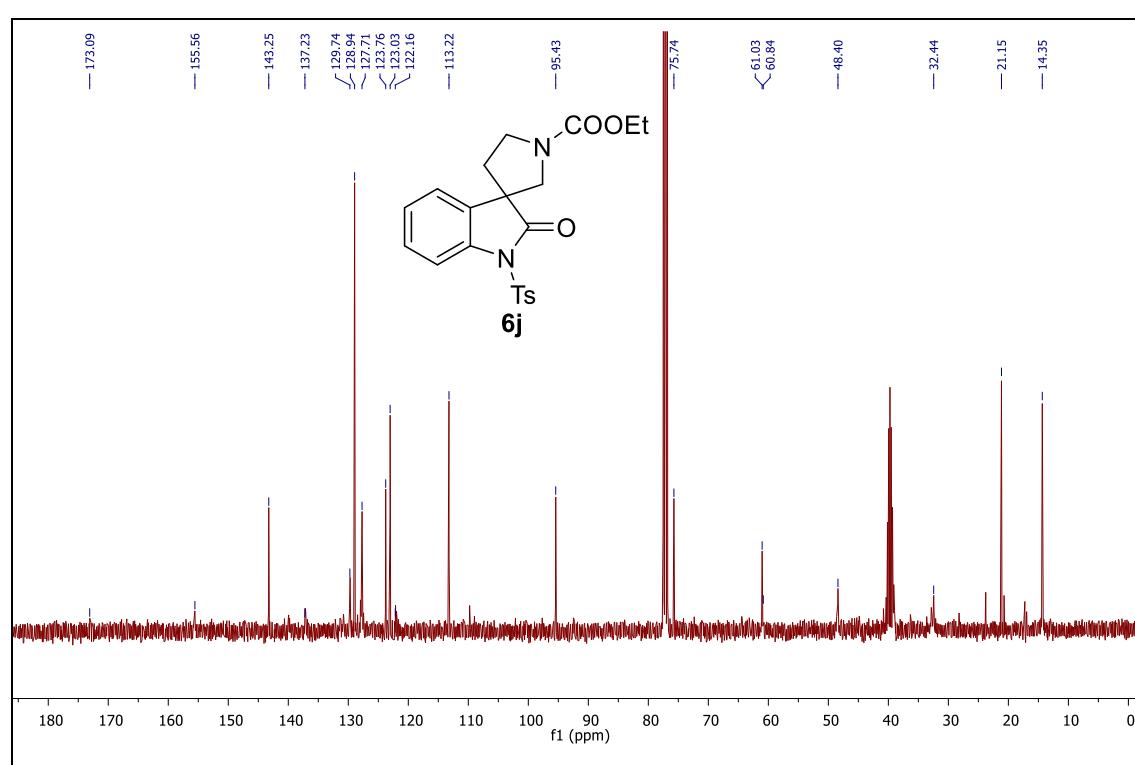
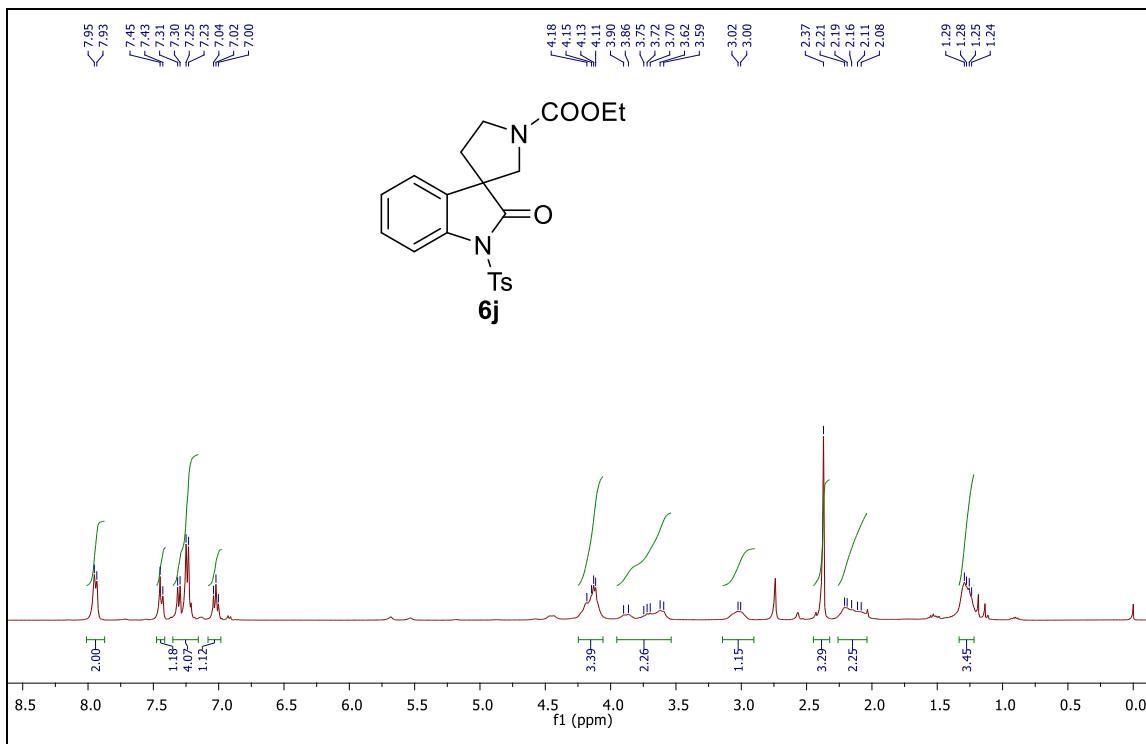
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for compound **6h**.

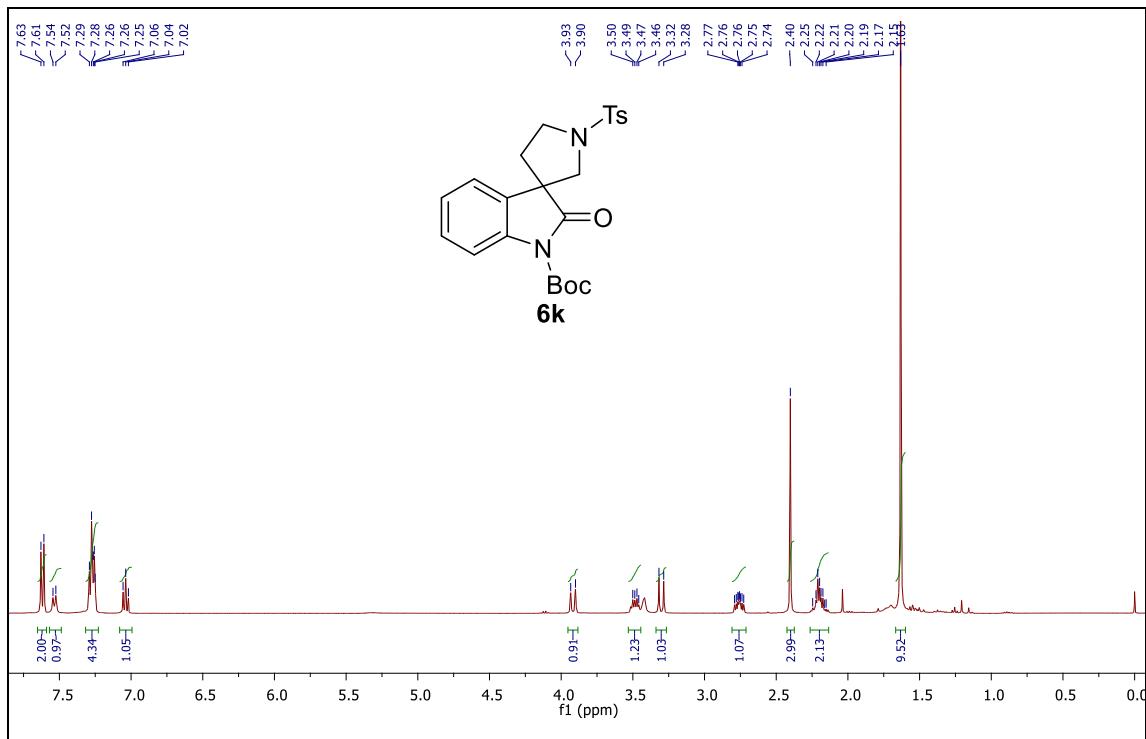


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **6i**.

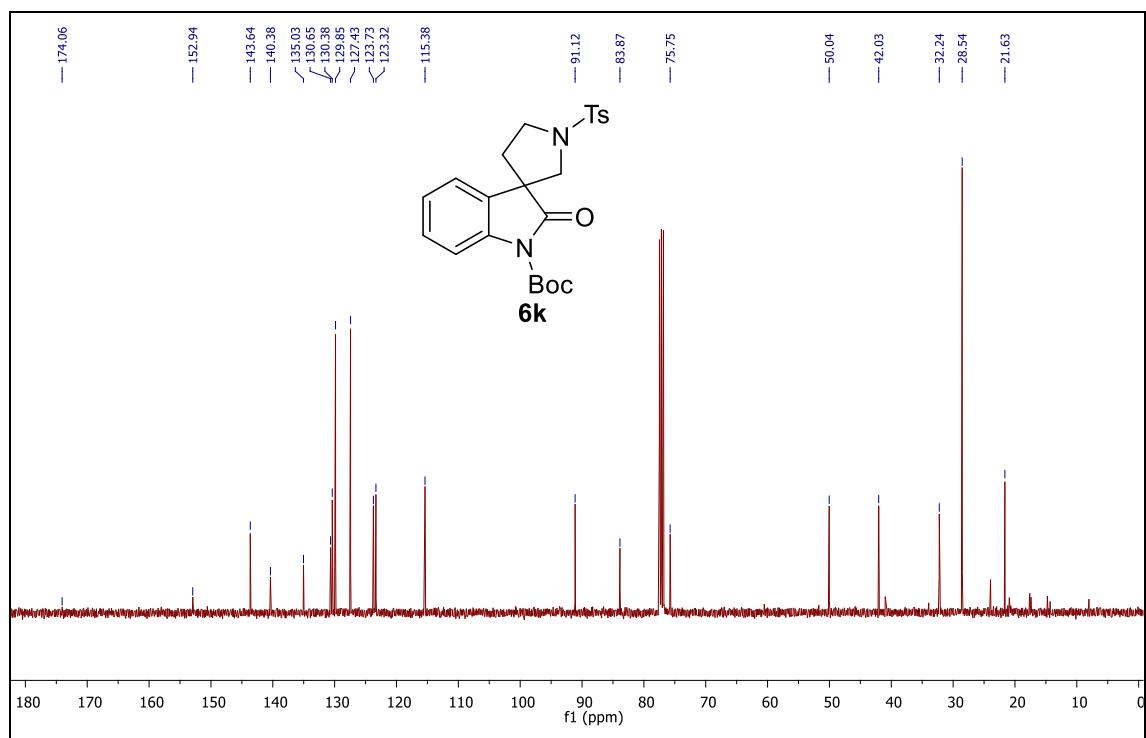


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) for compound **6i**.

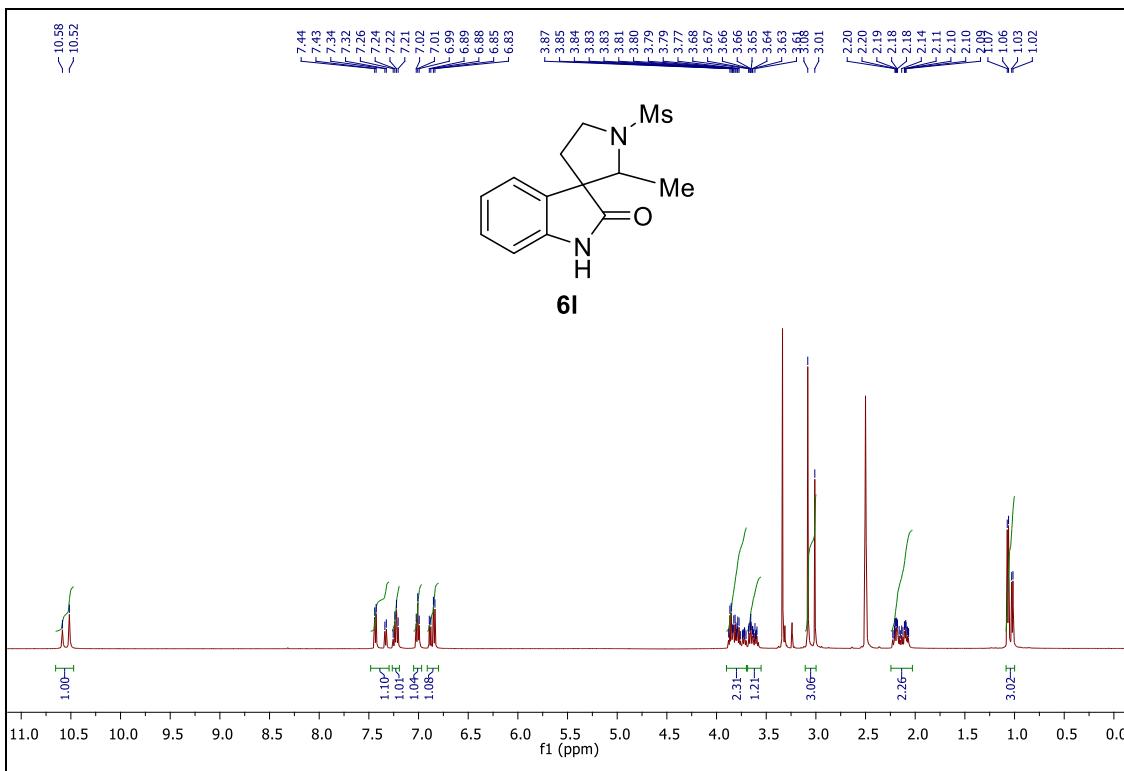




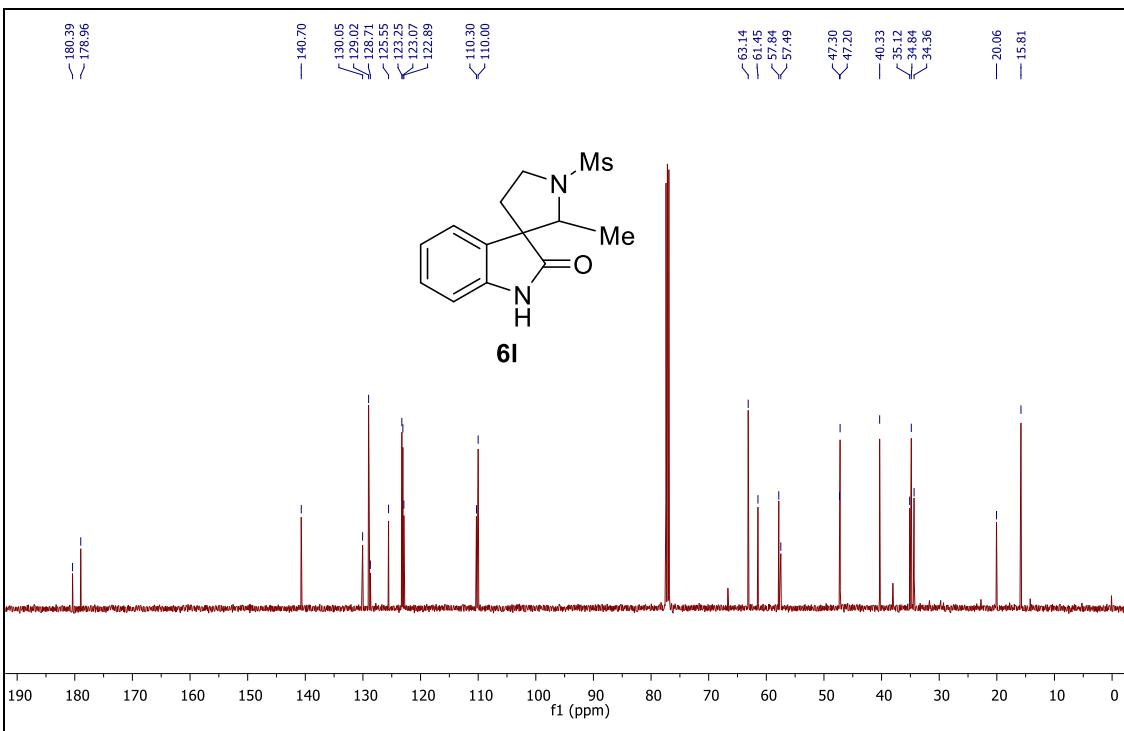
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound **6k**.



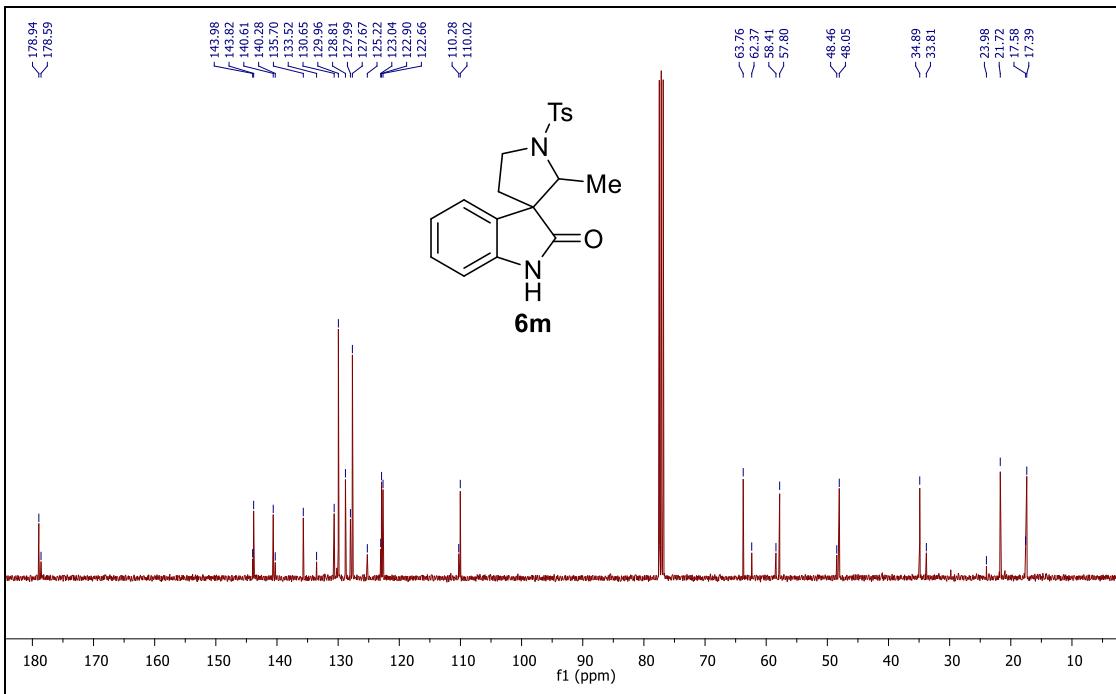
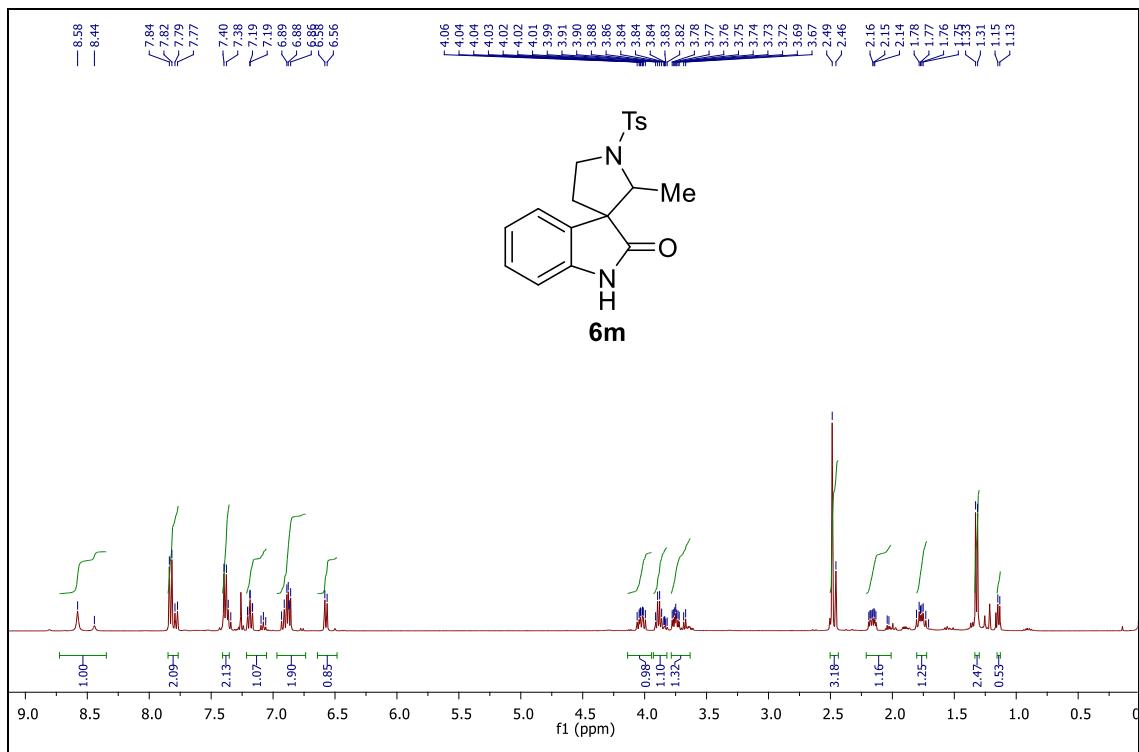
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for compound **6k**.

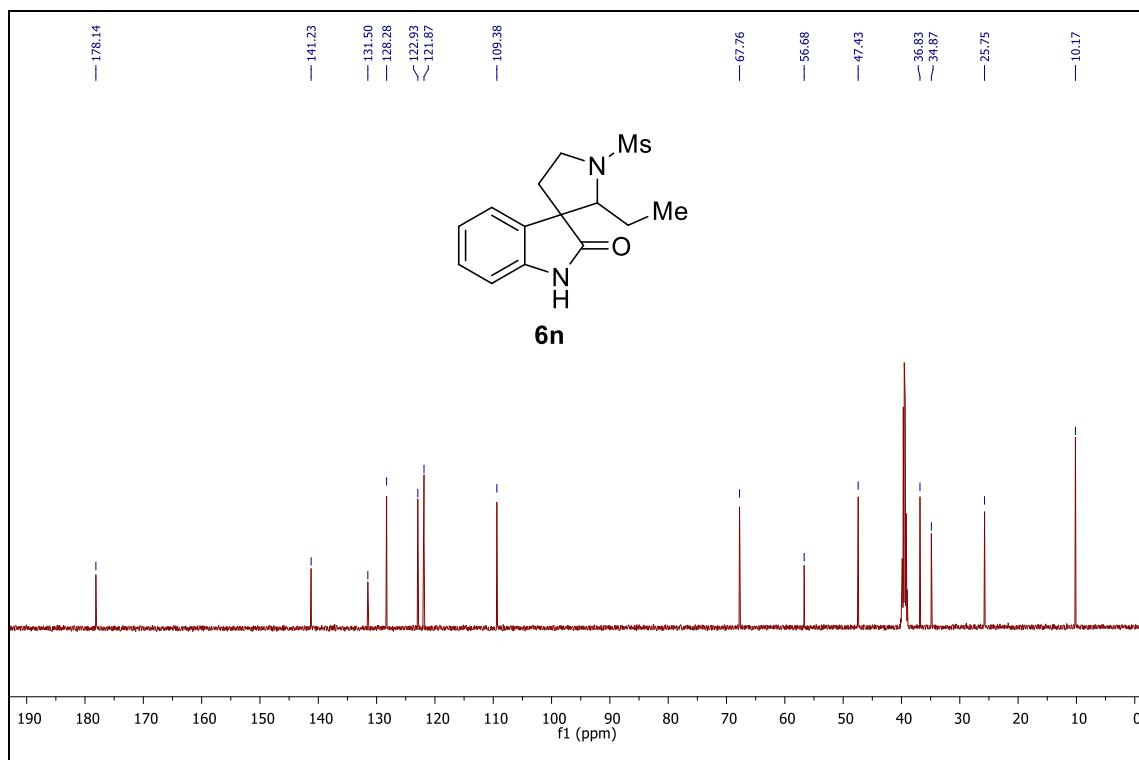
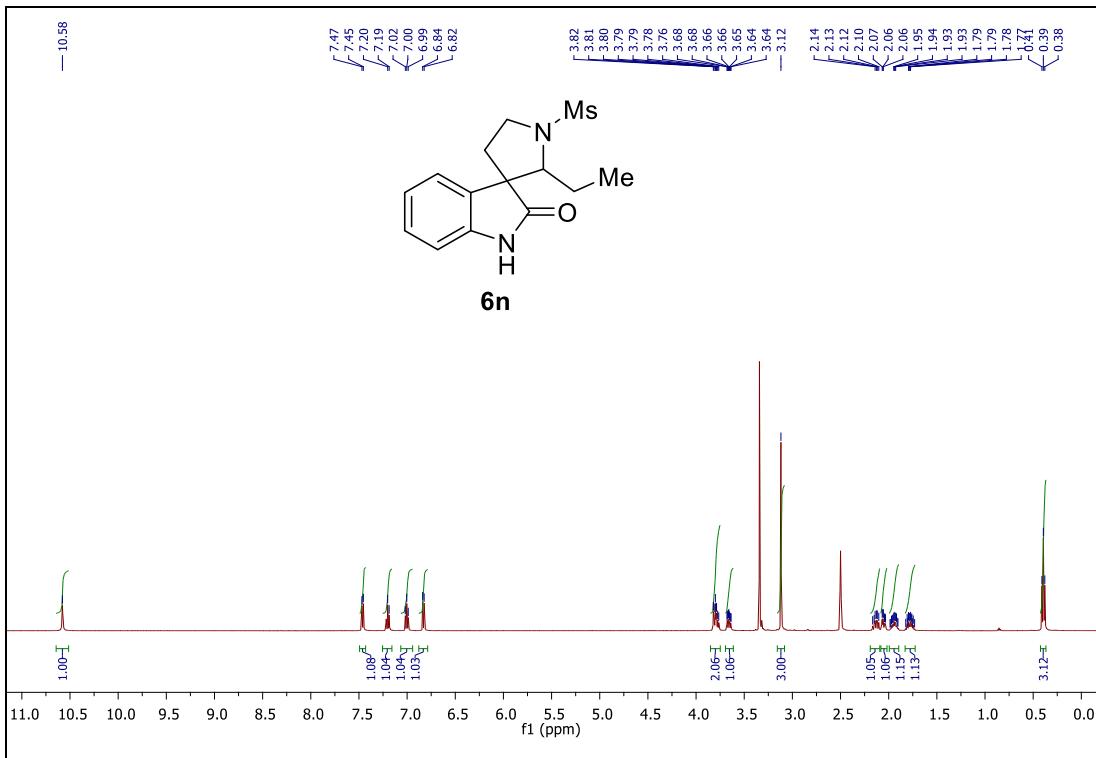


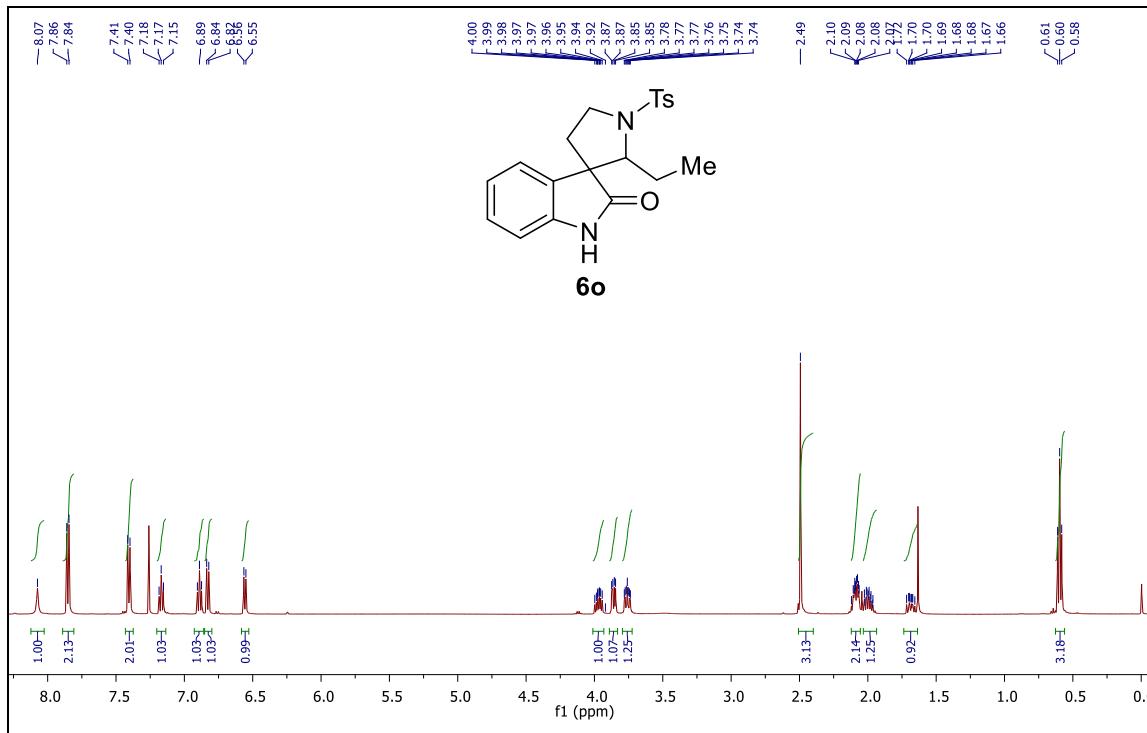
$^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ) for compound **6l**.



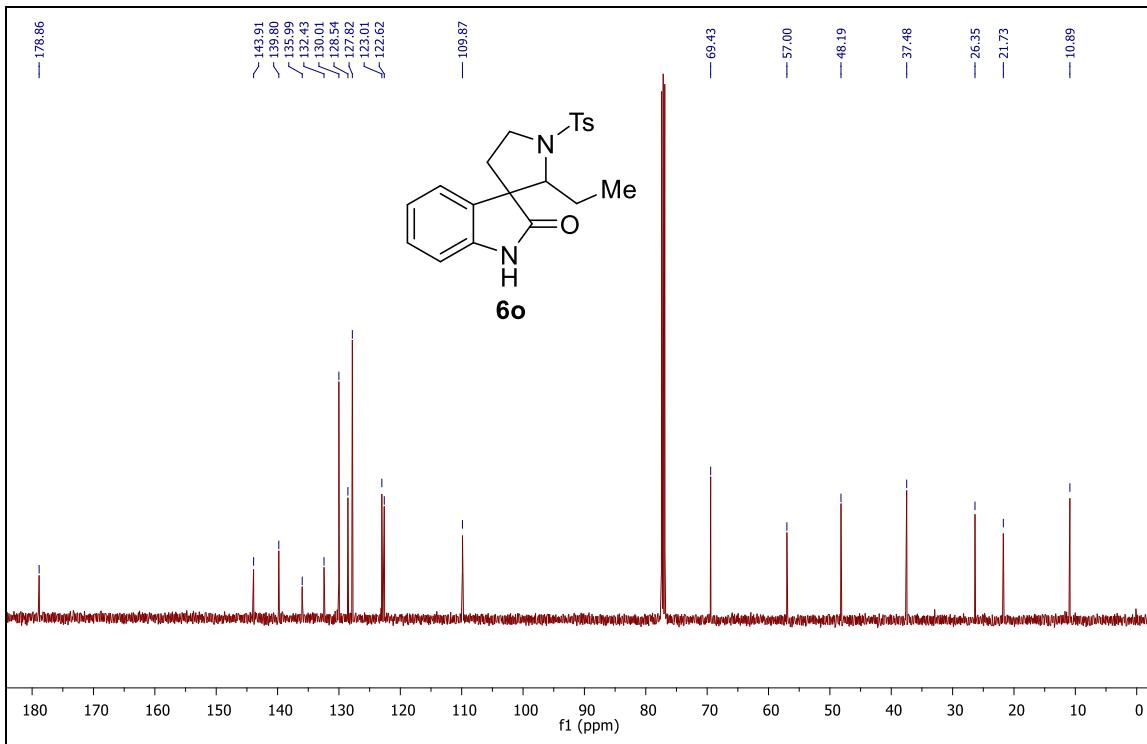
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) for compound **6l**.



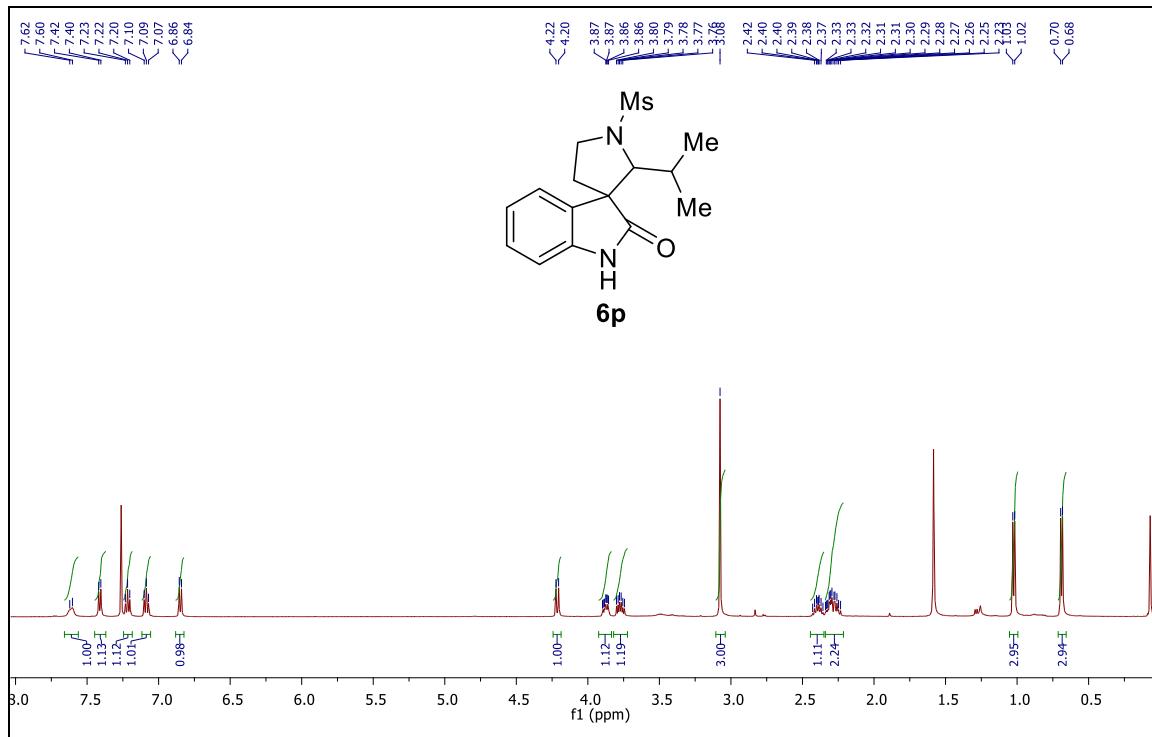




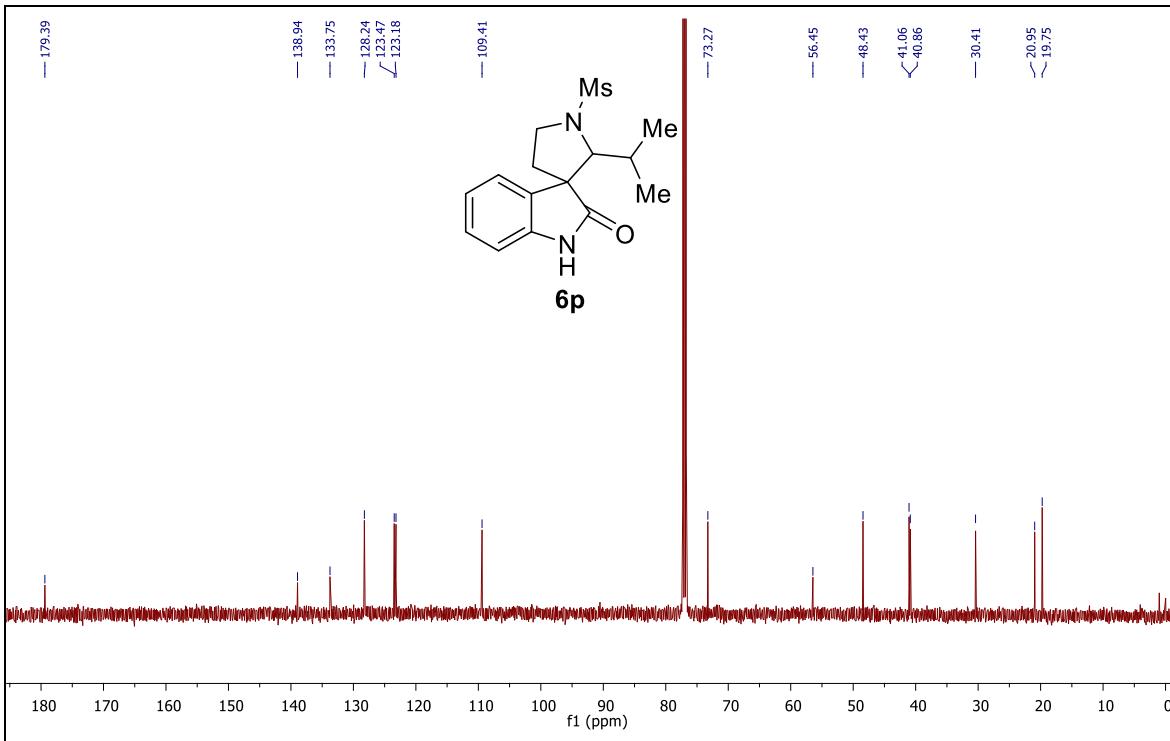
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) for compound **6o**.



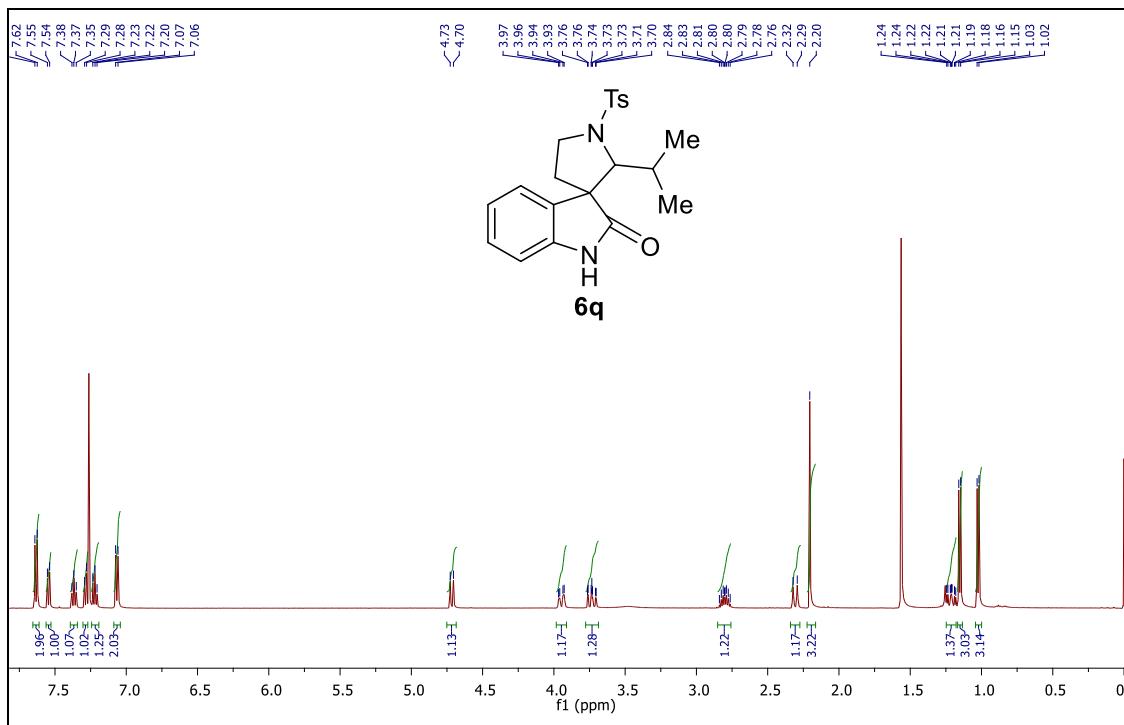
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) for compound **6o**.



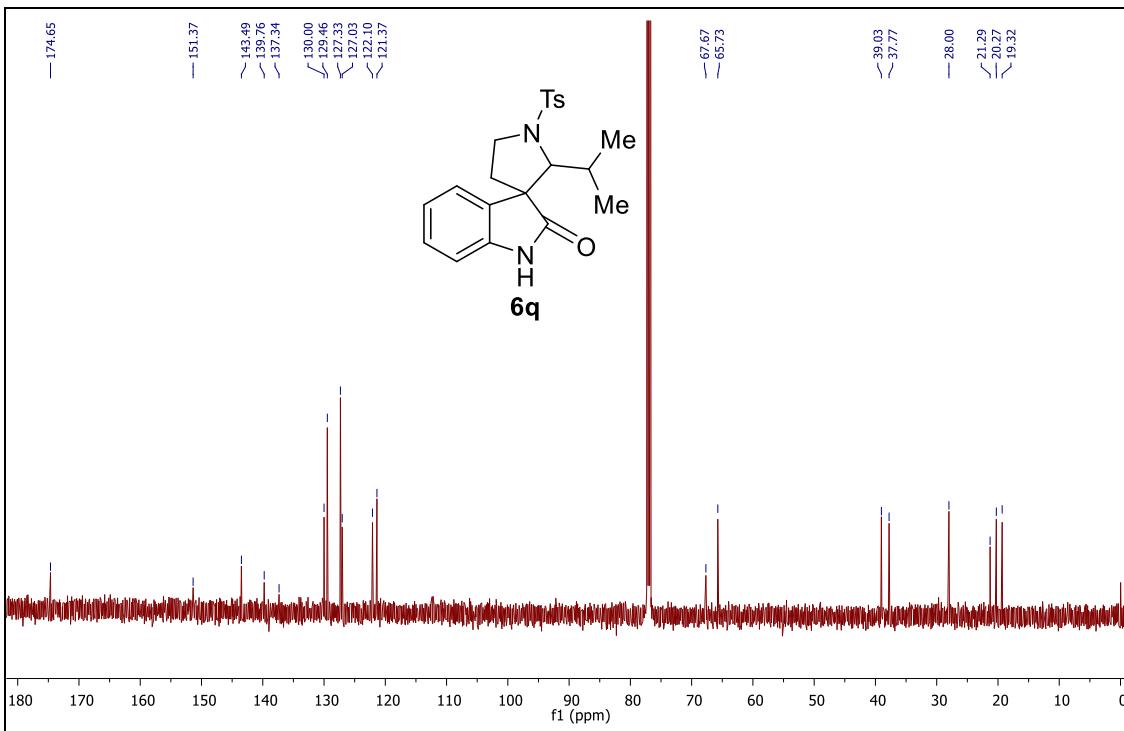
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) for compound **6p**.



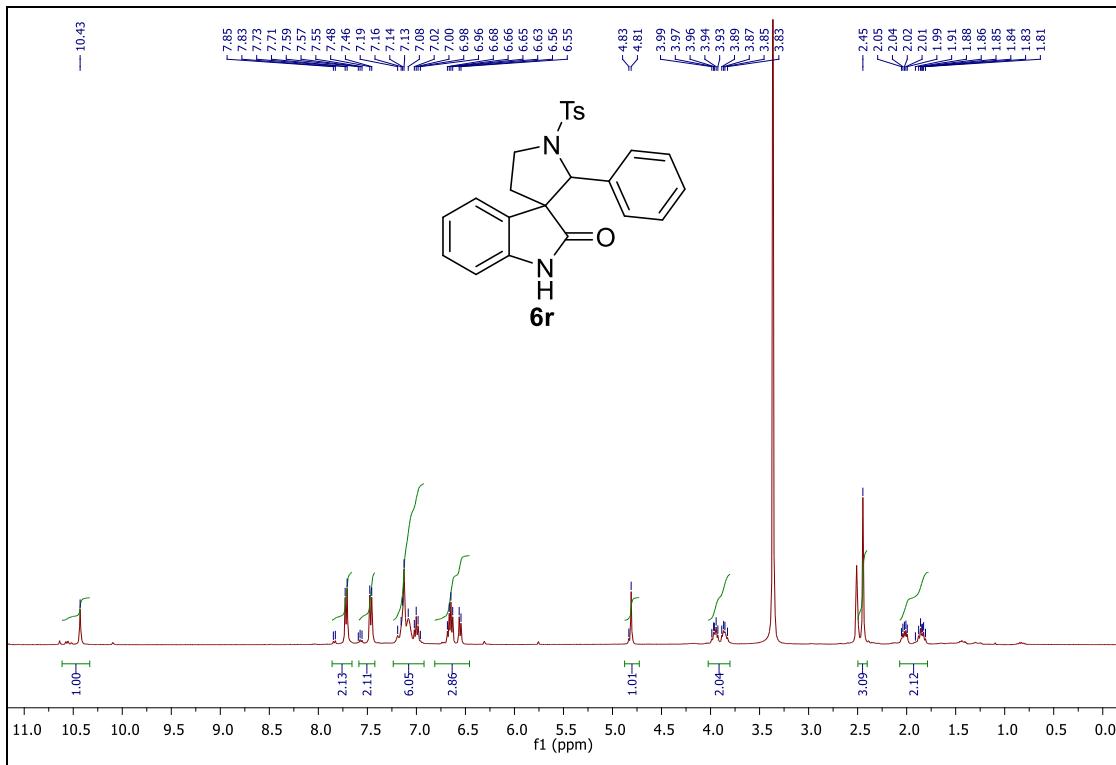
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) for compound **6p**.



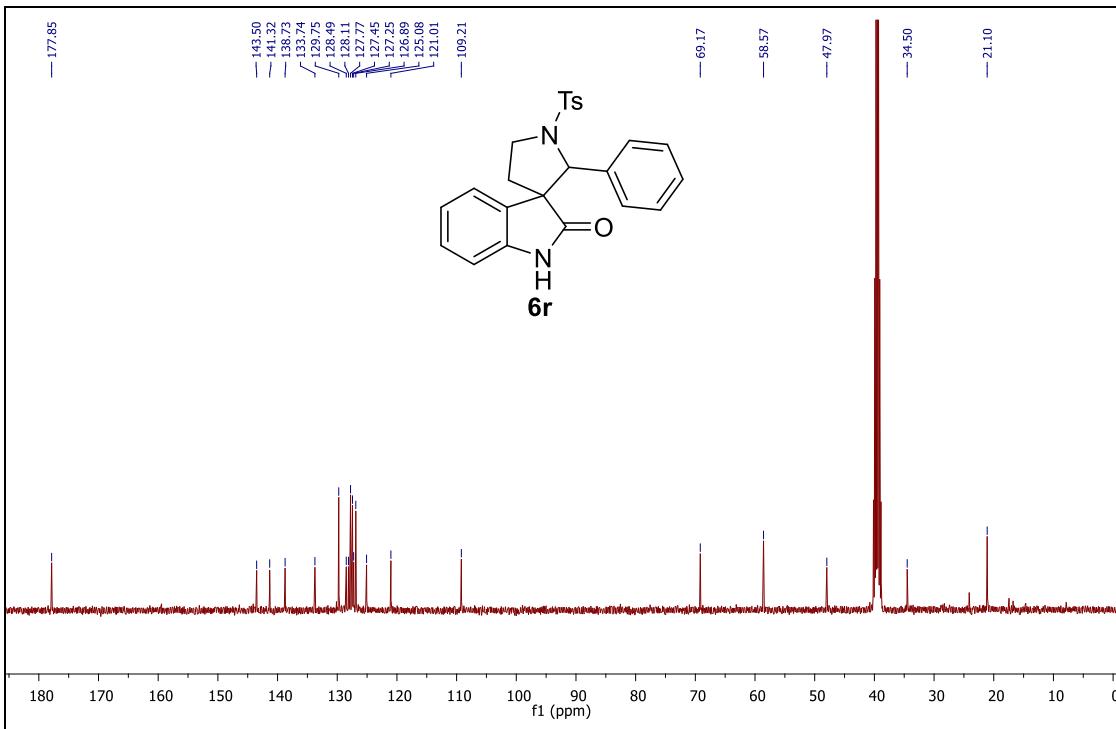
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) for compound **6q**.



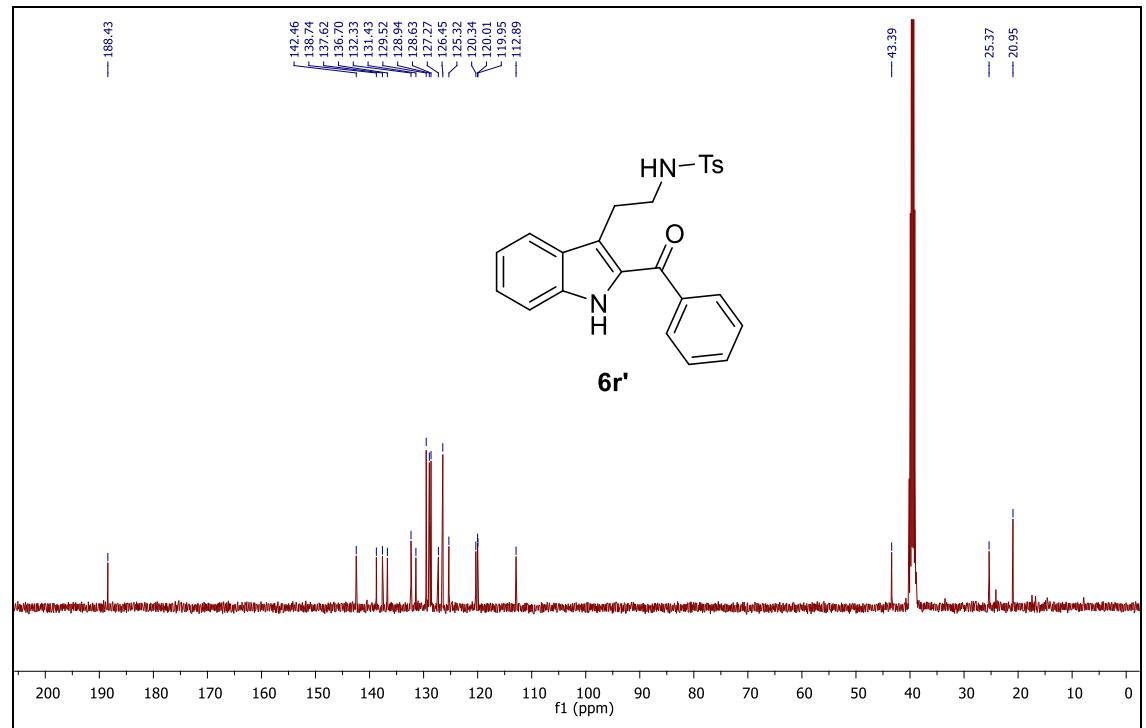
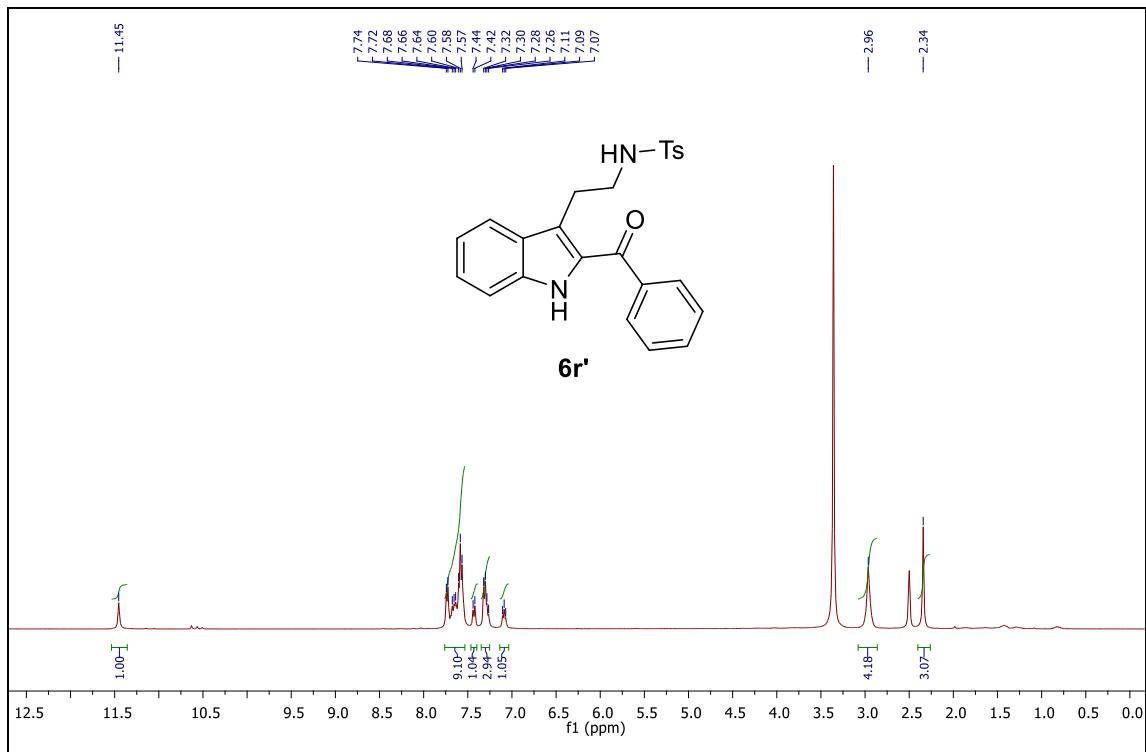
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) for compound **6q**.



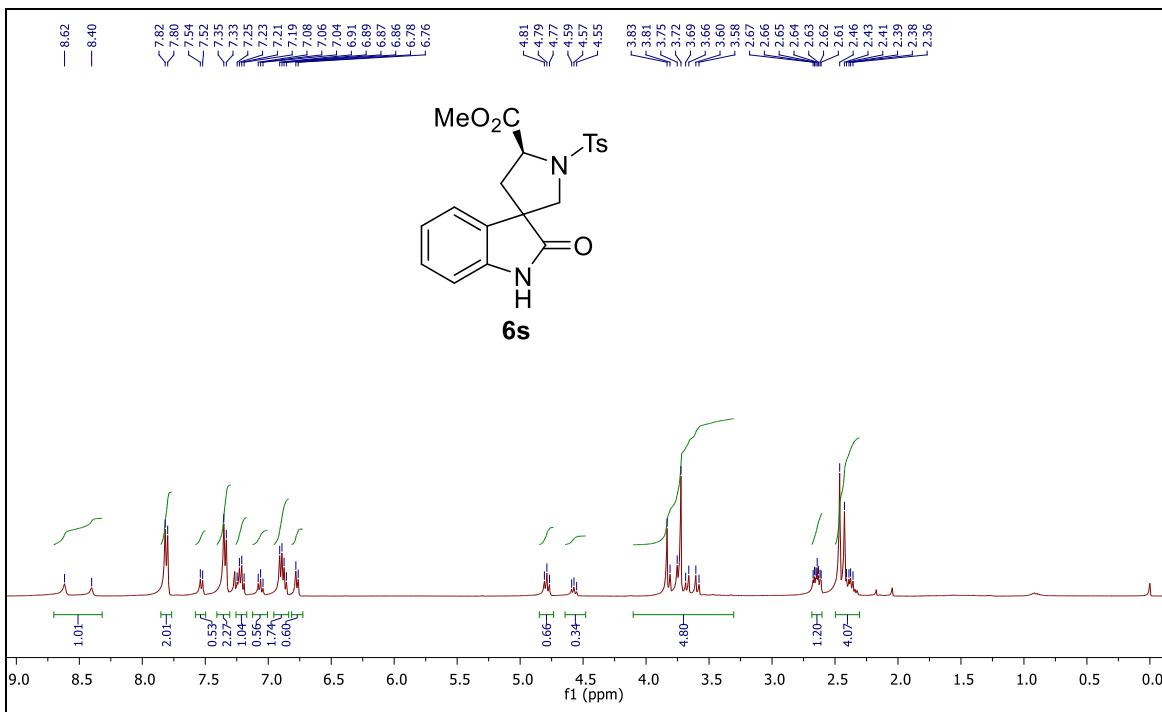
$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) for compound **6r**.



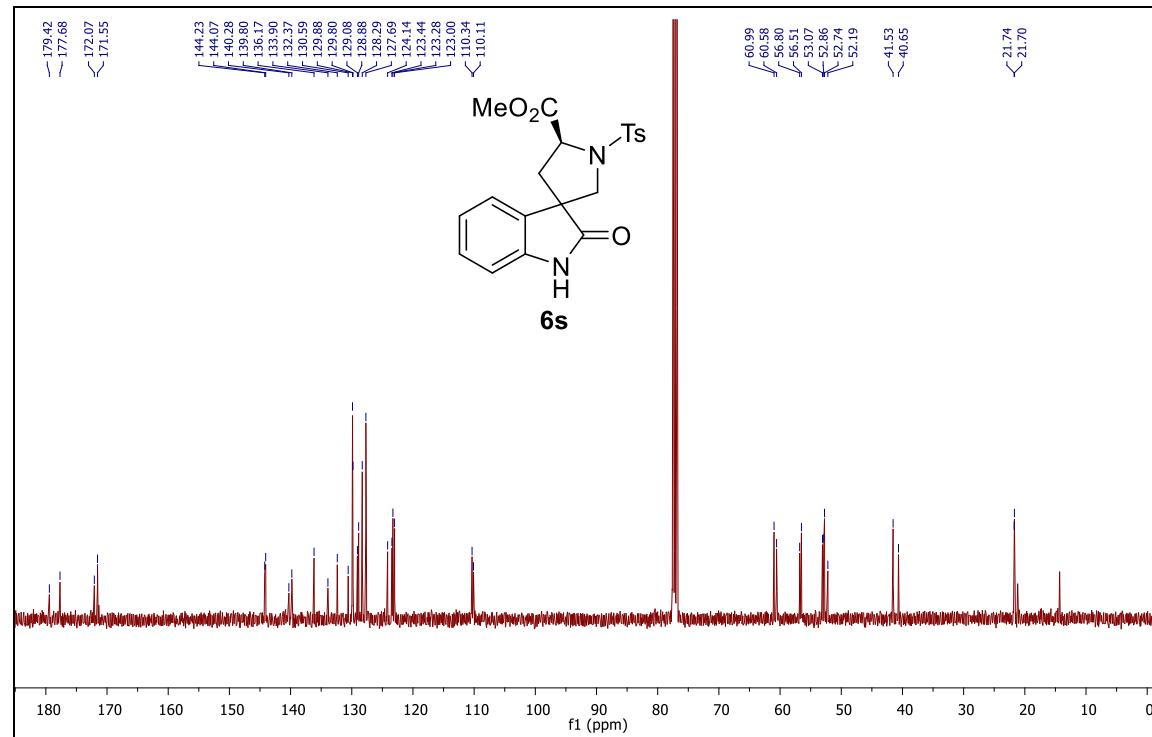
$^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ) for compound **6r**.



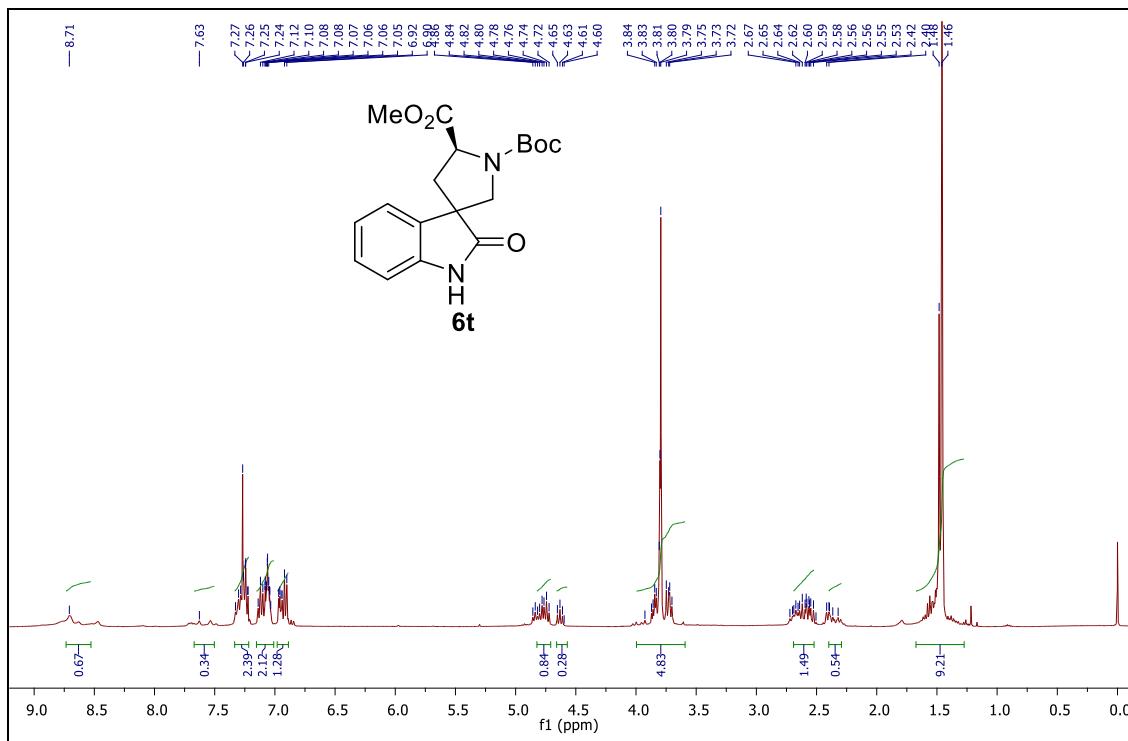
<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) for compound **6r'**.



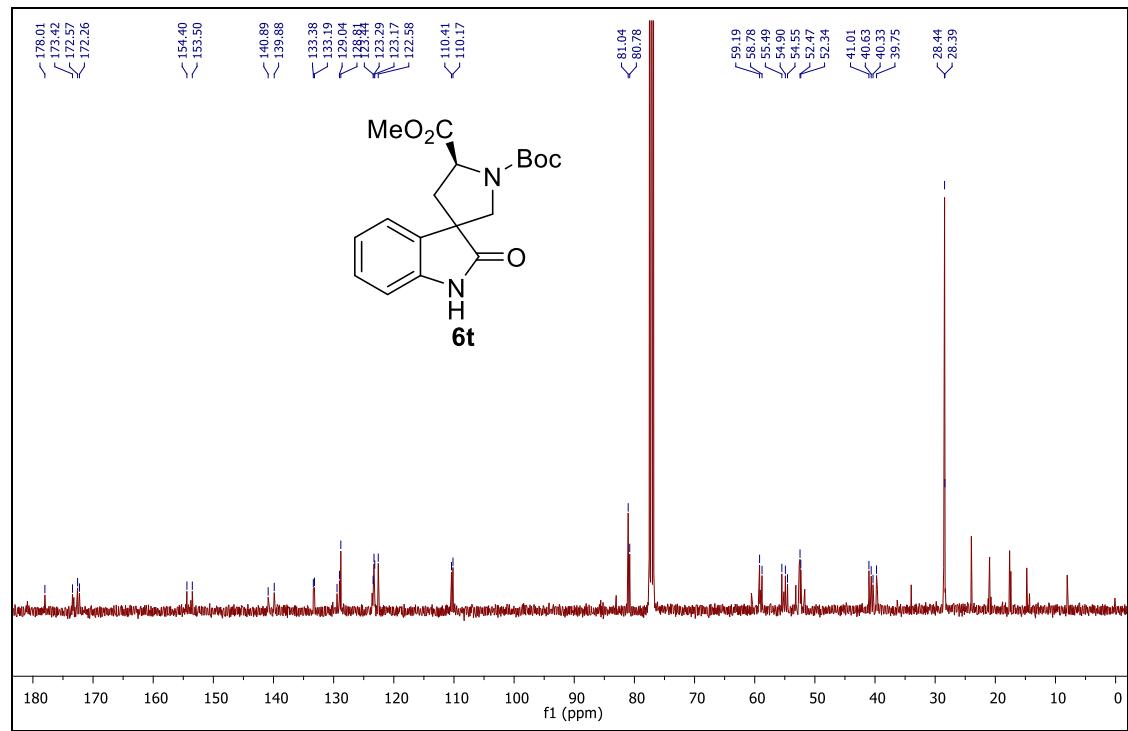
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound **6s**.



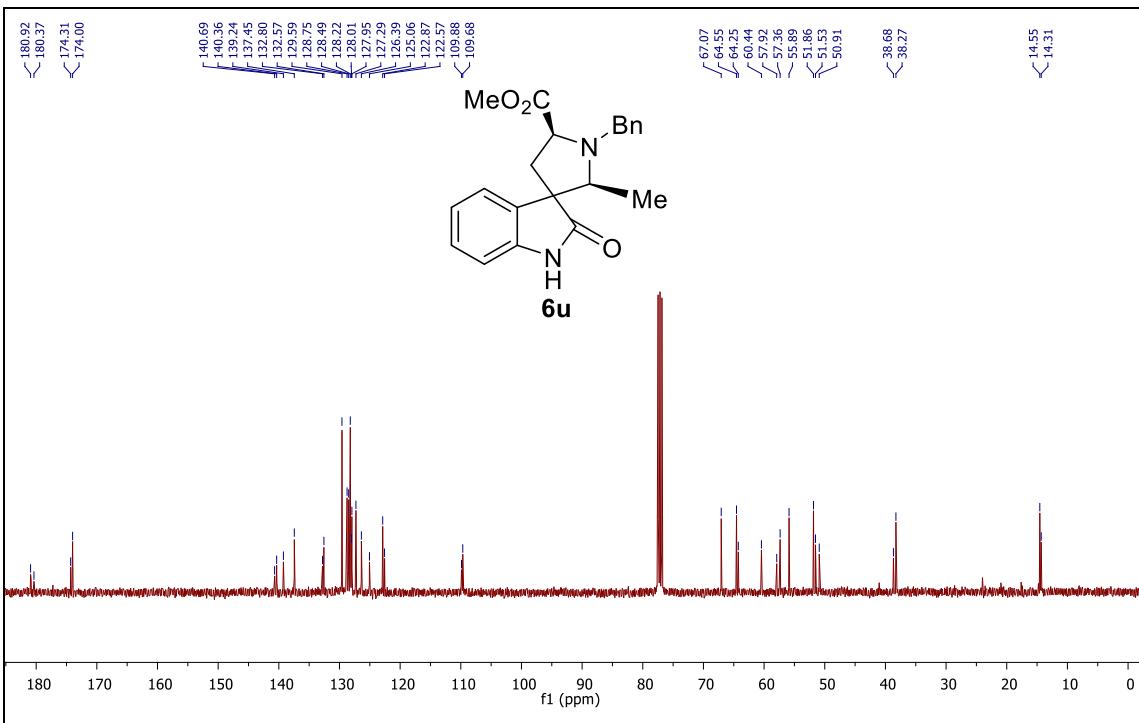
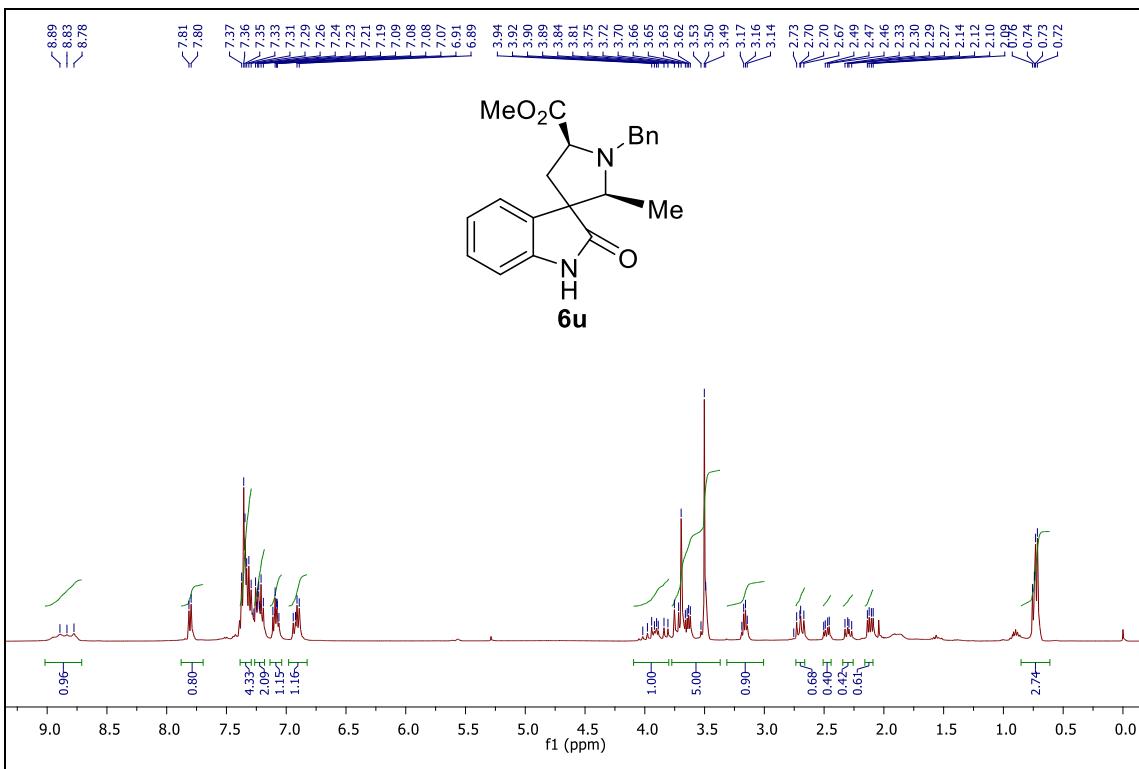
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for compound **6s**.

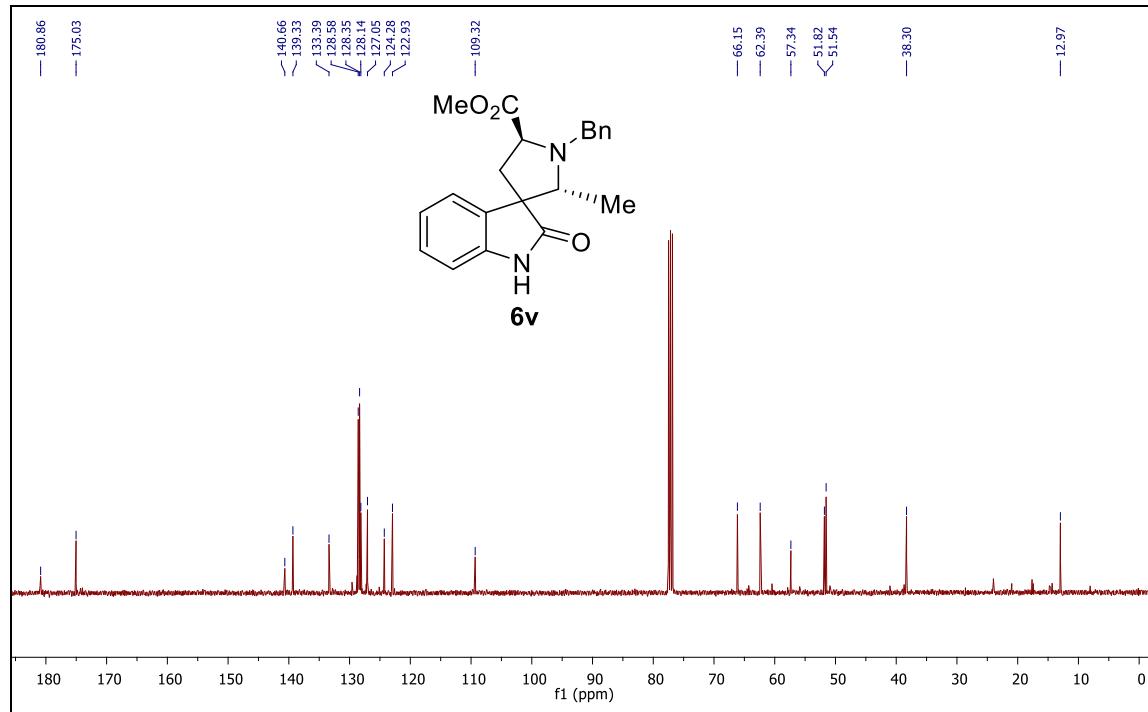
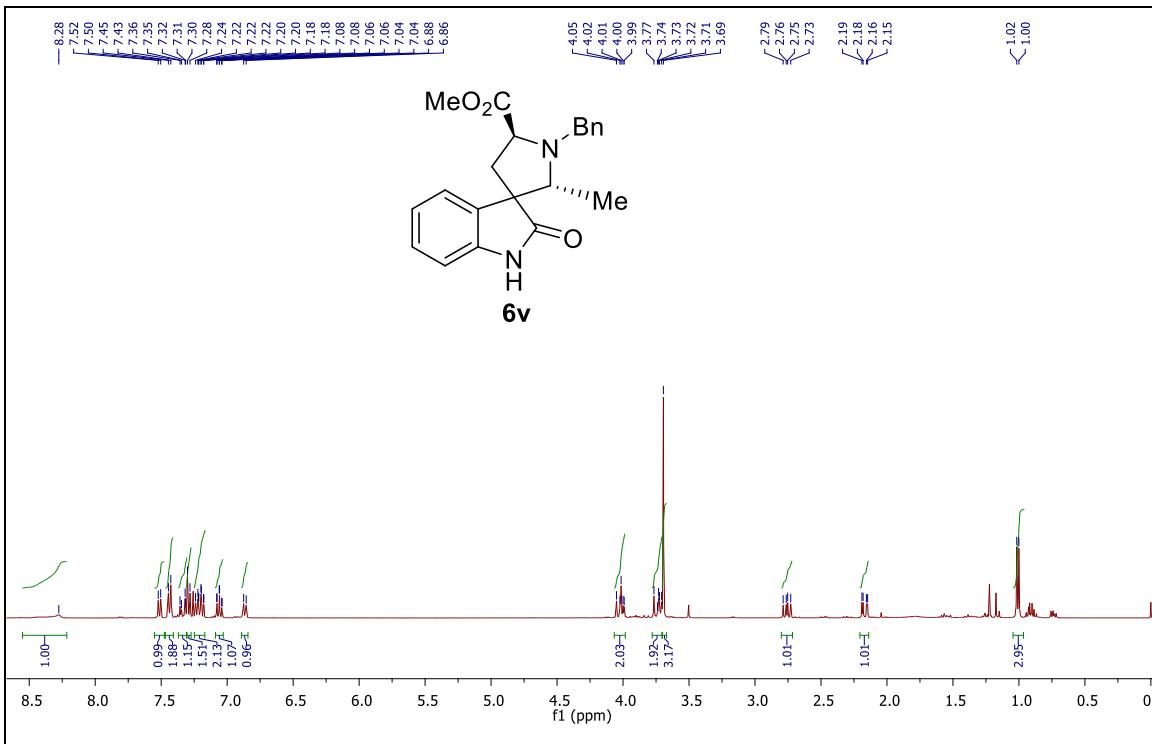


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound **6t**.

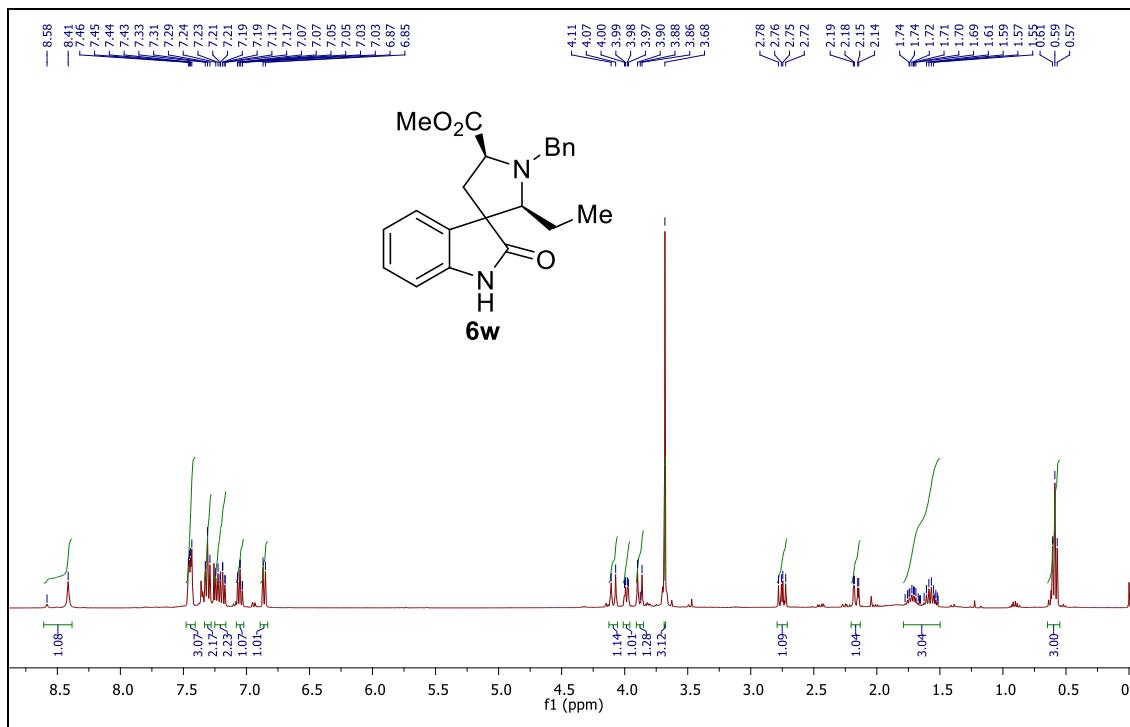


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for compound **6t**.

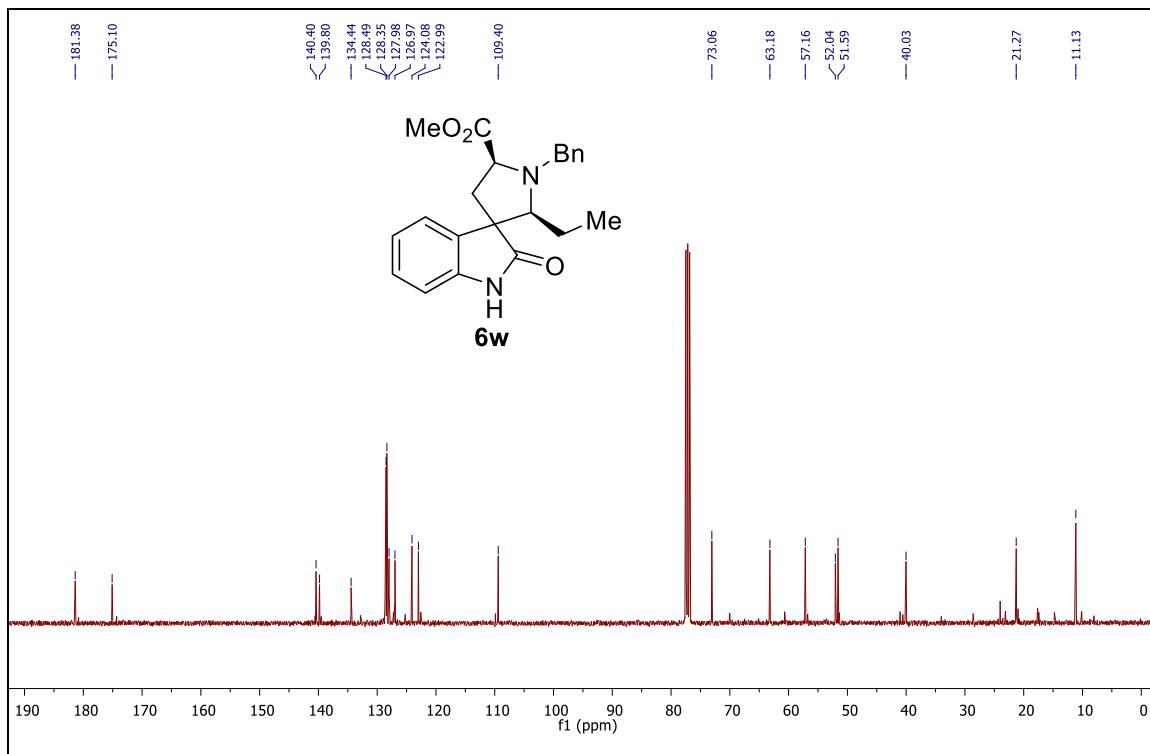




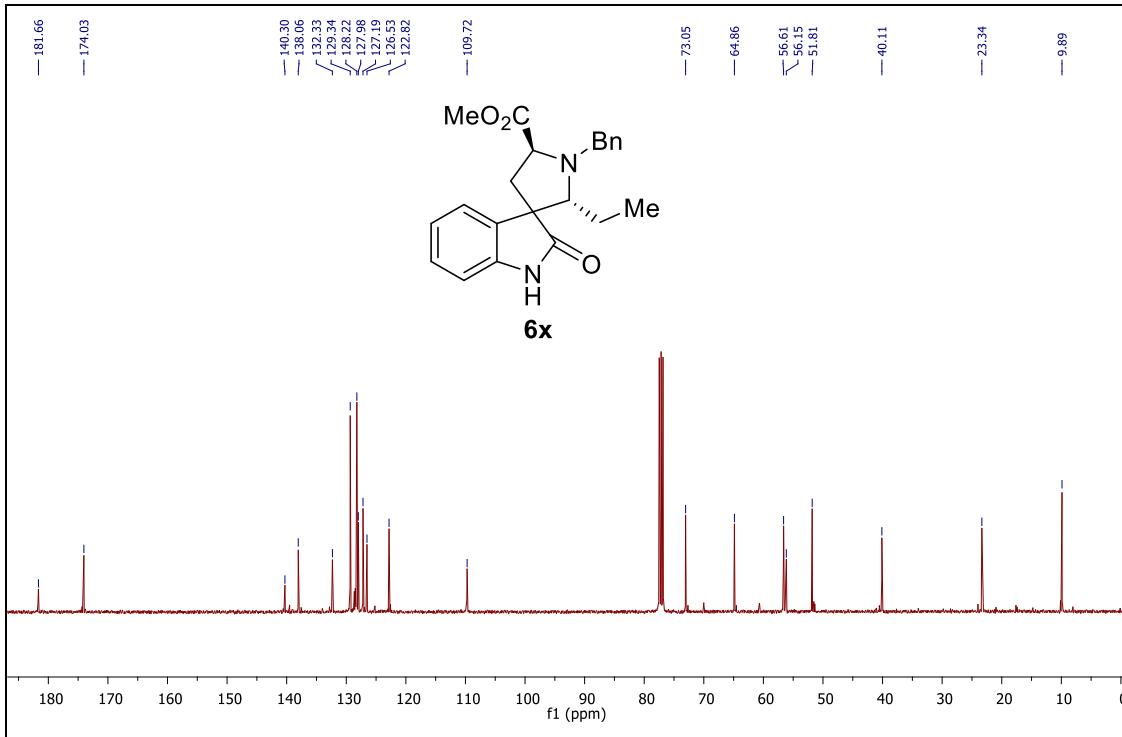
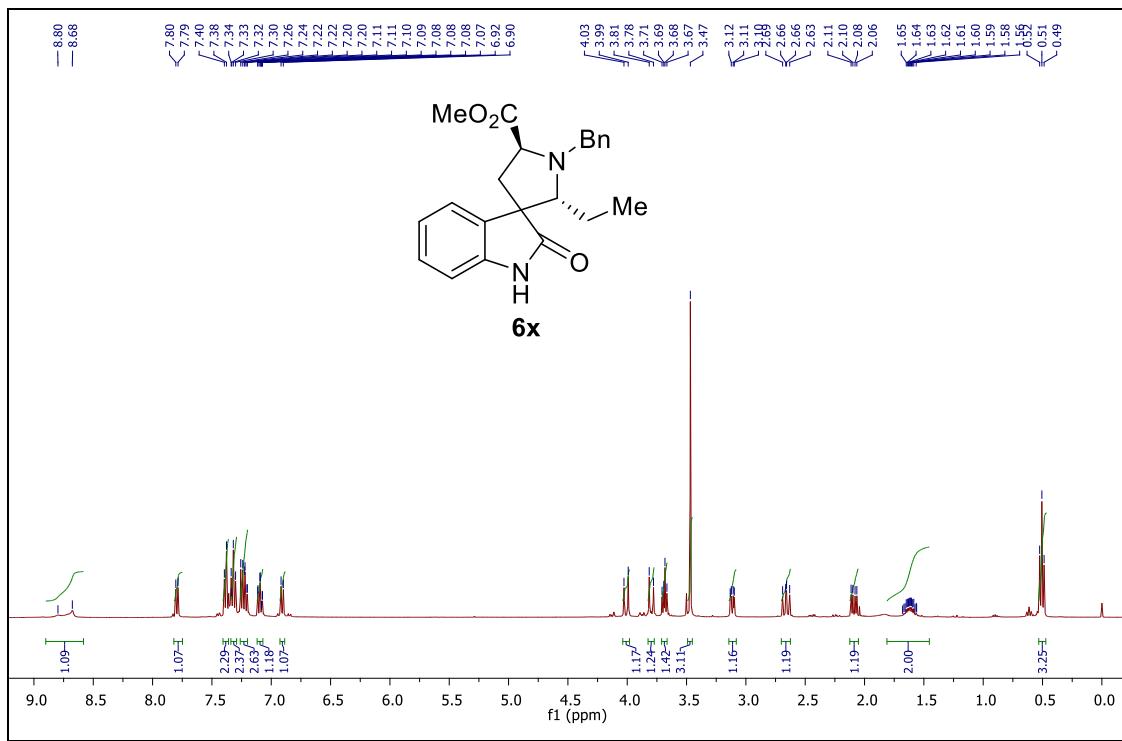
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for compound **6v**.**

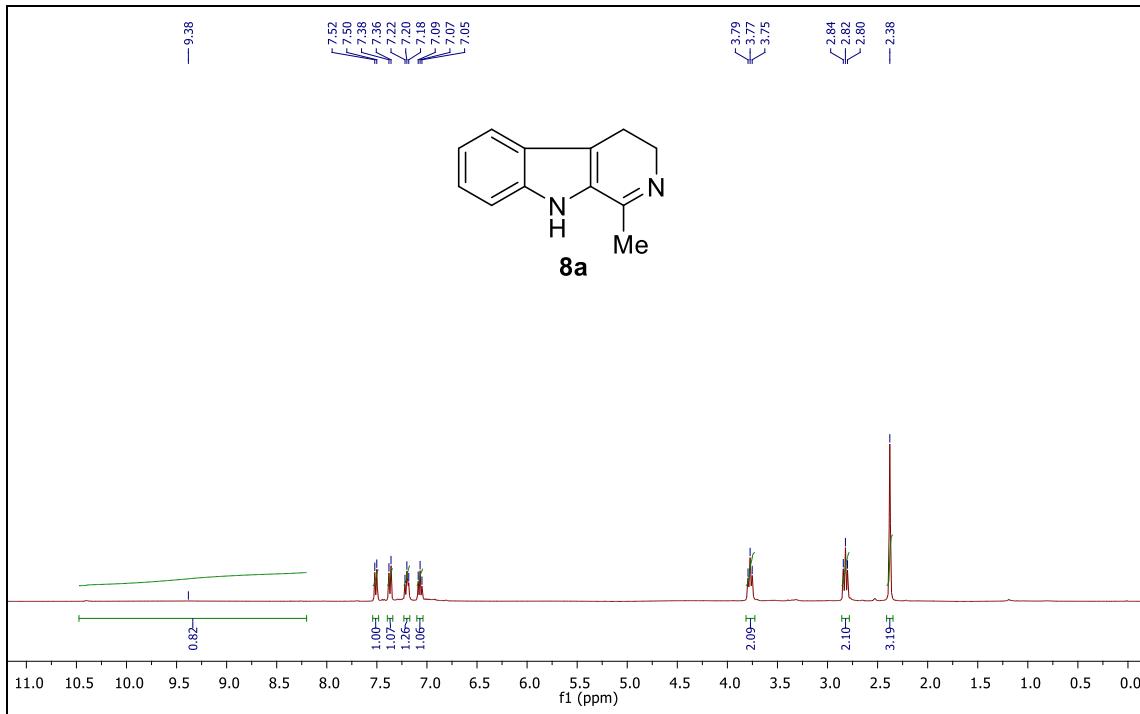


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound **6w**.

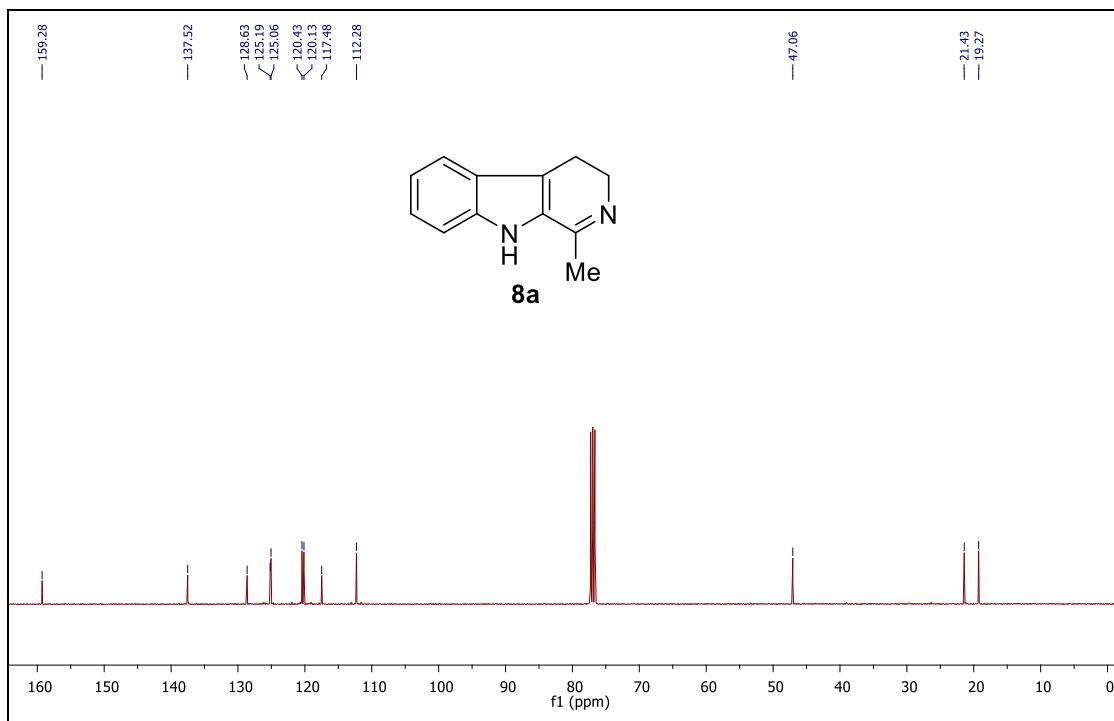


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for compound **6w**.

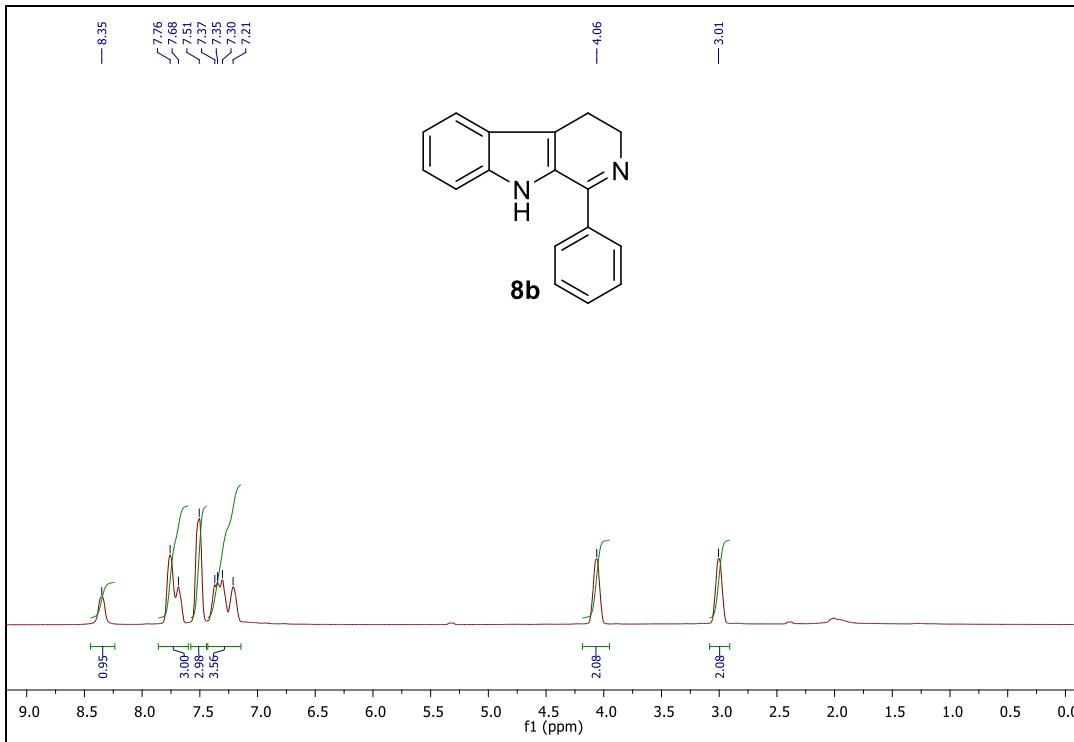




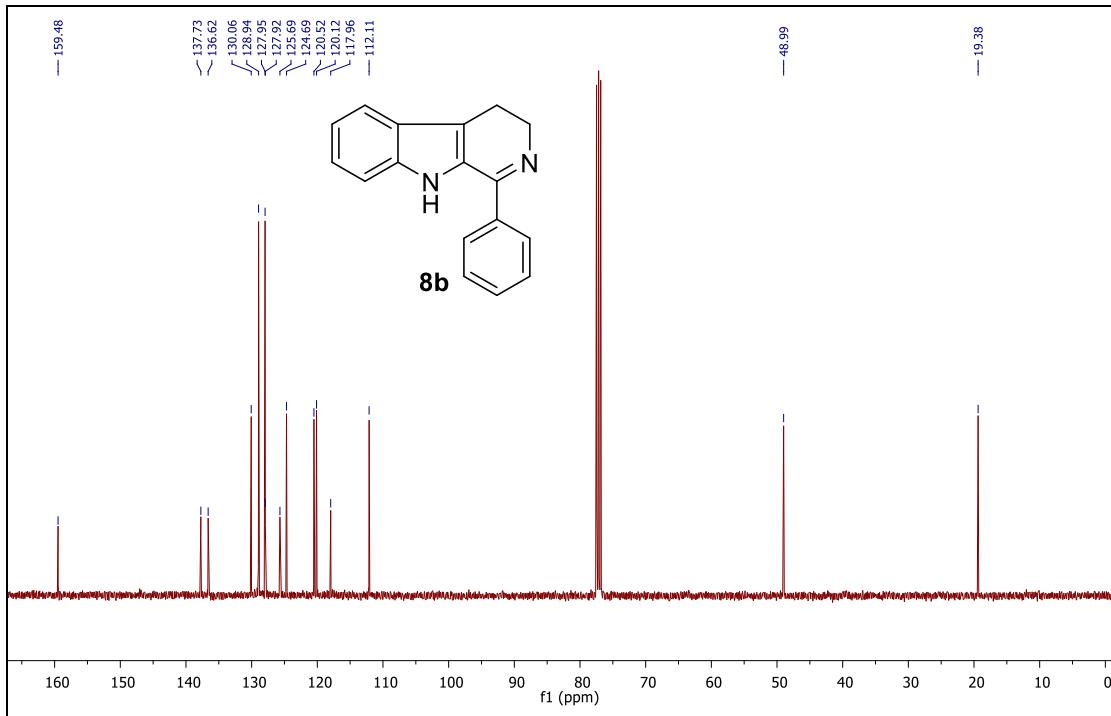
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for compound **8a**.



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) for compound **8a**.



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for compound **8b**.



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) for compound **8b**.