

## Transition Metal-free Approach towards Regioselective Synthesis of $\beta$ -Carboline C-1 Tethered 2, 3-dihydro-1*H*-pyrroles & Pyrroles

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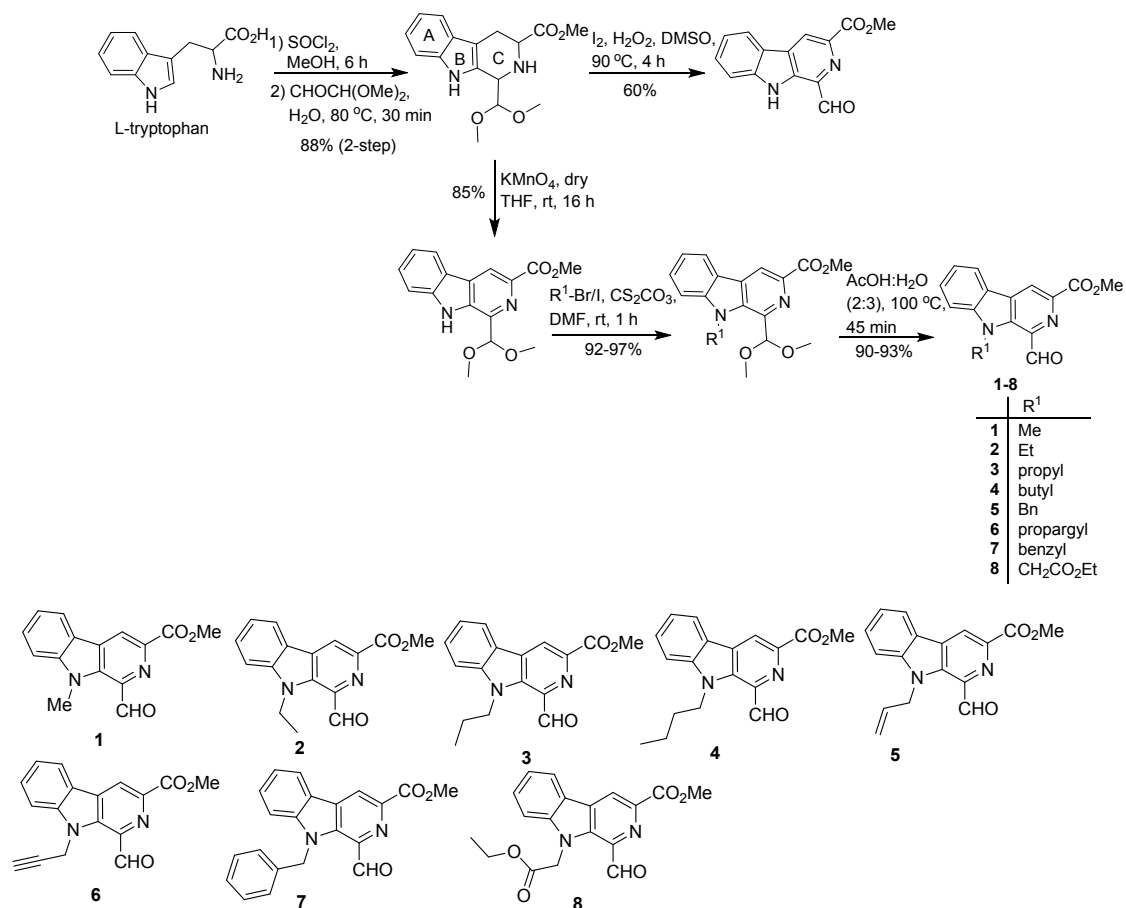
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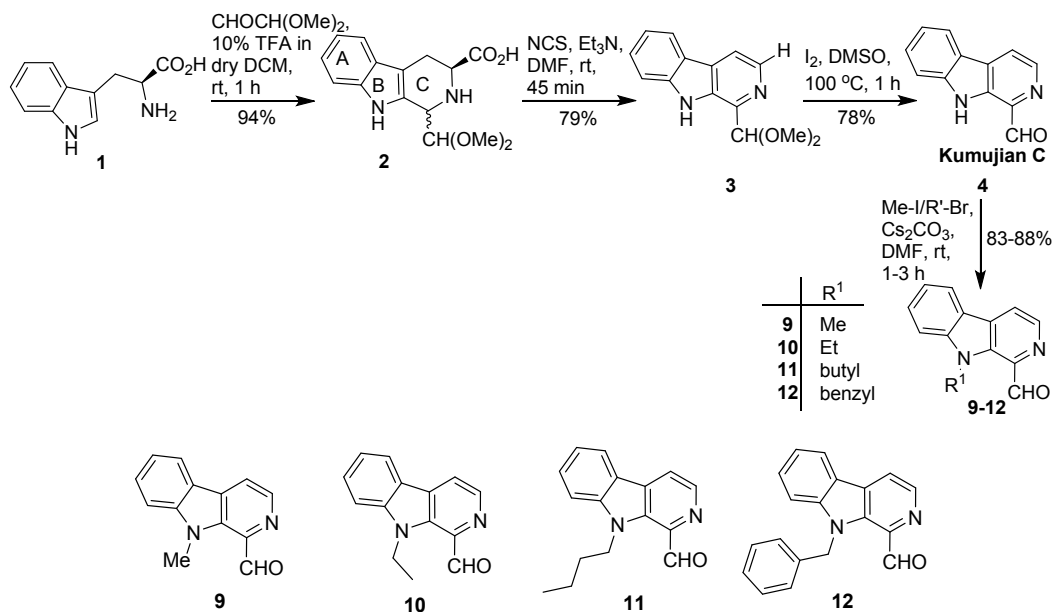
### Supporting Information

#### Table of Contents

<b>1.</b>	<b>Synthesis of 1-formyl-<math>\beta</math>-carboline derivatives</b>	<b>2</b>
<b>2.</b>	<b>X-ray Crystallographic Data of 1aA</b>	<b>3-5</b>
<b>3.</b>	<b><sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of new products</b>	<b>6-39</b>



**Scheme S1.** Synthesis of 1-formyl-9H-pyrido[3,4-b]indole derivatives<sup>21</sup>



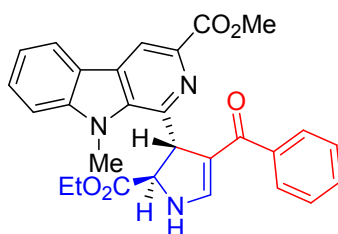
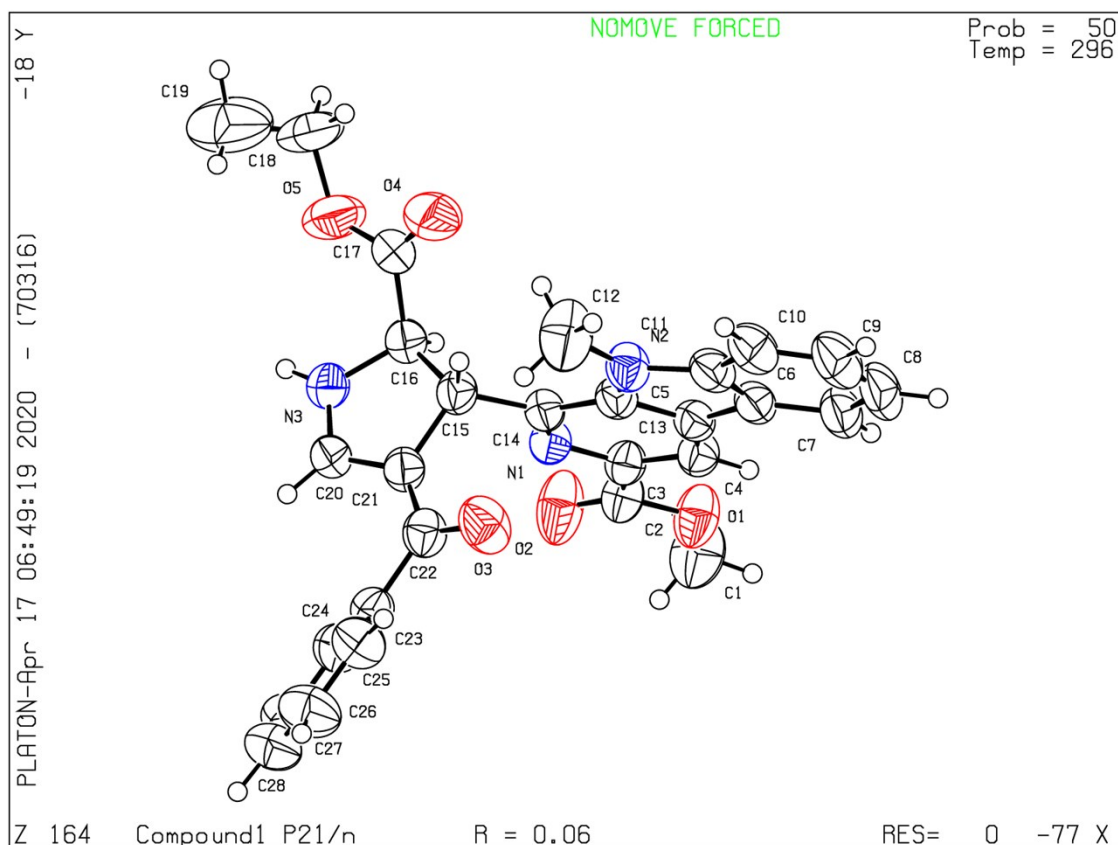
**Scheme S2.** Synthesis of Kumujian C and its derivative<sup>21</sup>

**Reference:**

(21) M. Singh, P. Awasthi and V. Singh, *Eur. J. Org. Chem.*, 2020, **2020**, 1023-1041.

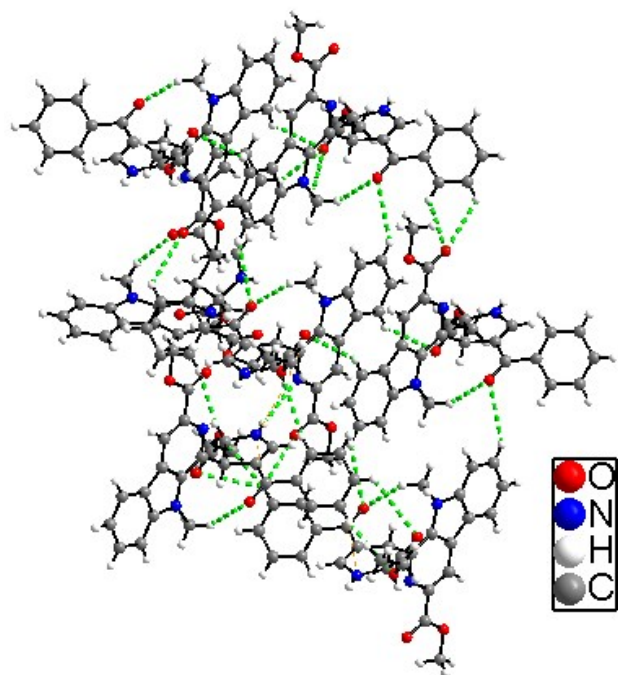
**Table 1:** Description of crystal data and structure refinement parameters

Parameters	1aA
Empirical formula	C <sub>28</sub> H <sub>25</sub> N <sub>3</sub> O <sub>5</sub>
Formula mass	483.51
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
a (Å)	12.9292(12)
b (Å)	10.5655(10)
c (Å)	17.6719(16)
α (°)	90.000
β (°)	92.537(2)
γ (°)	90.000
V (Å <sup>3</sup> )	2411.7(4)
Z	4
T/K	296(2)
ρ (g cm <sup>-3</sup> )	1.332
μ(mm <sup>-1</sup> )	0.093
λ (Mo Kα) (Å)	0.71073
θ min (°)	3.01
θ max (°)	25.00
Total data	23039
Unique data	4205
Rint	0.0739
R indexes [ <i>I</i> >2σ( <i>I</i> )]	R <sub>1</sub> = 0.0608 wR <sub>2</sub> = 0.1475
R indexes (all data)	R <sub>1</sub> = 0.1294 wR <sub>2</sub> = 0.1746
CCDC numbers	1996773
F(000)	1016
GOF on F <sup>2</sup>	0.925
<sup>a</sup> R <sub>1</sub> = $\sum   F_o  -  F_c   / \sum  F_o $ ; <sup>b</sup> wR <sub>2</sub> = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ , $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ . $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$ ;	



**Figure S3. X-ray crystallographic analysis of 1aA.**

Recrystallized from DCM/MeOH/THF (V/V/V = 1/1/1). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1996773.



**Figure S4.** Packing diagram of **1aA** Green dotted lines correspond to intra- and inter-molecular hydrogen bonds (CCDC 1996773)

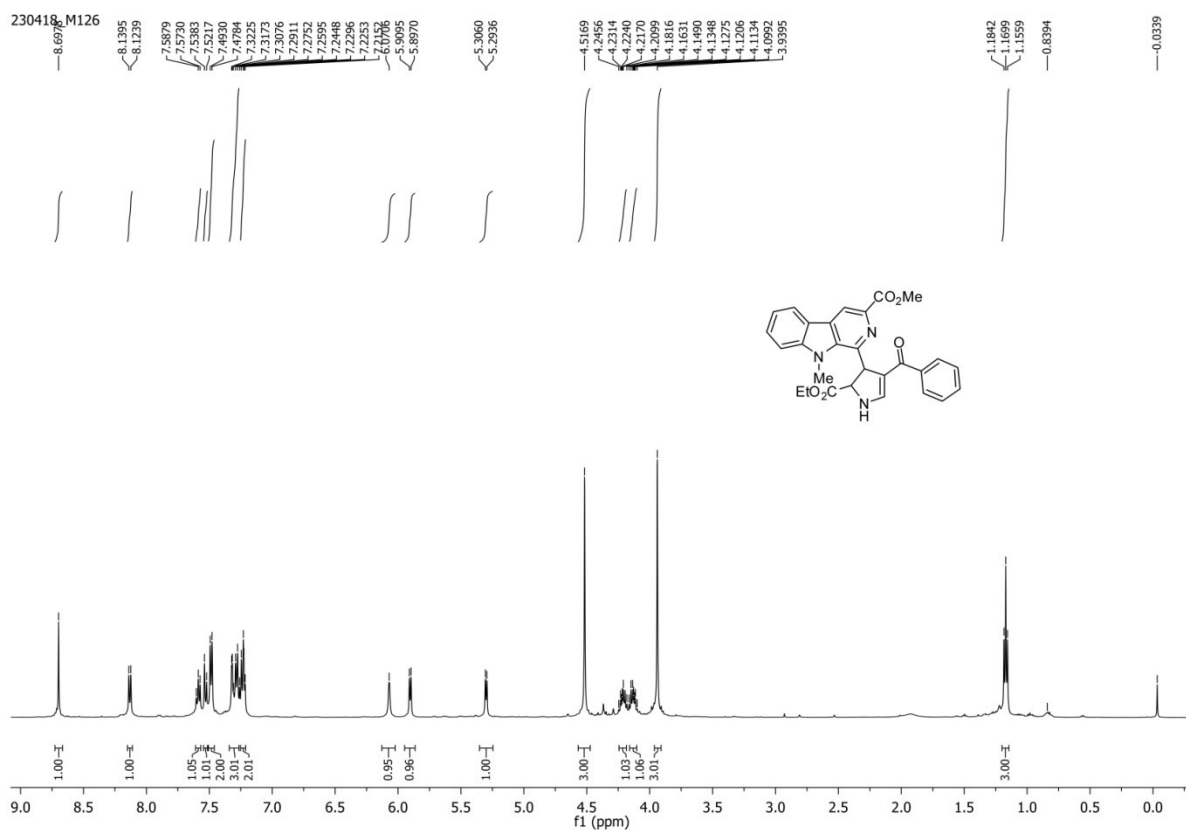


Figure S5. <sup>1</sup>H-NMR spectrum of **1aA** in CDCl<sub>3</sub>.

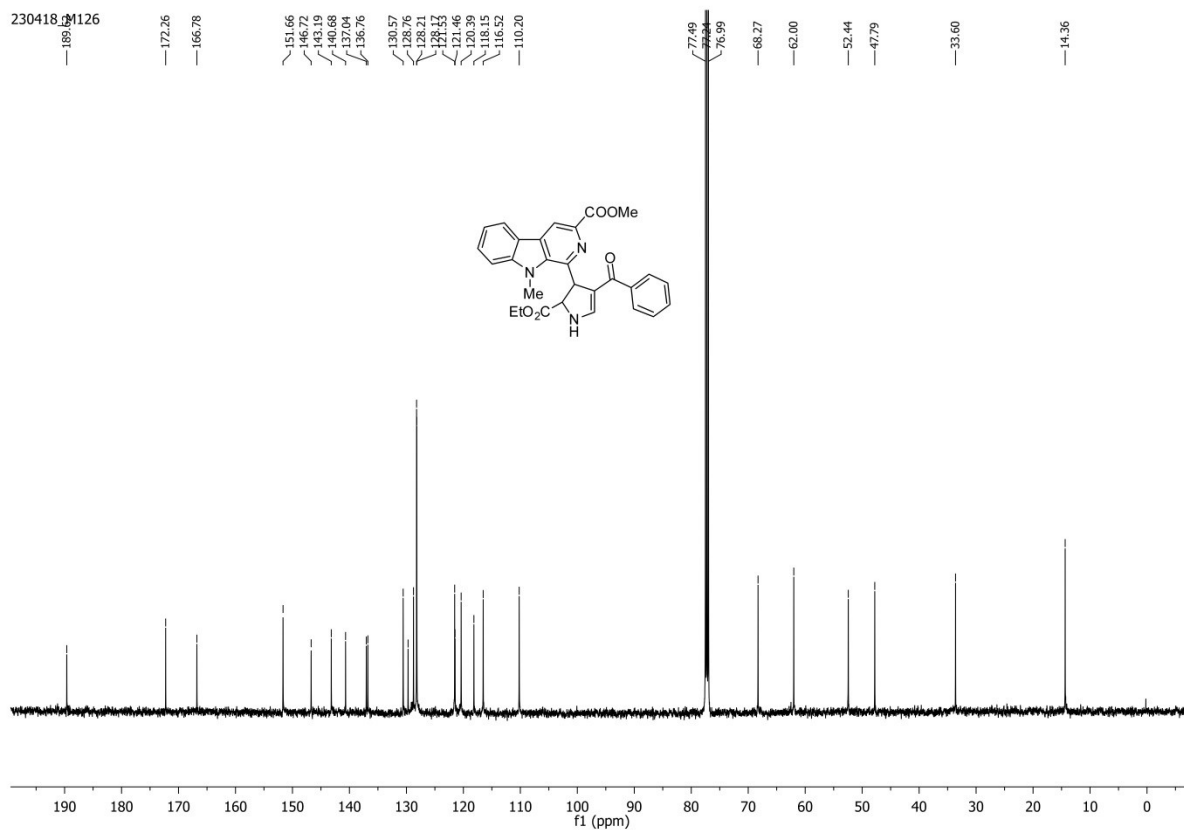


Figure S6. <sup>13</sup>C-NMR spectrum of **1aA** in CDCl<sub>3</sub>.

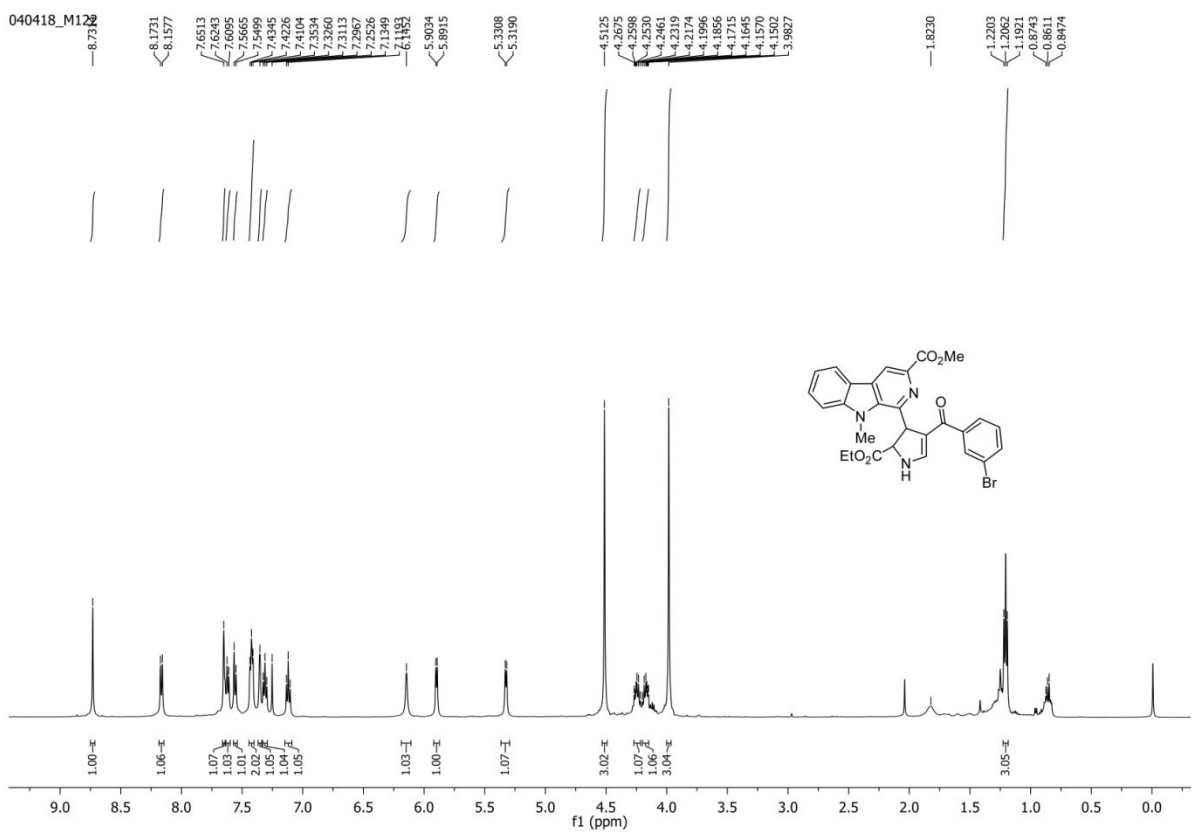


Figure S7. <sup>1</sup>H-NMR spectrum of **1aB** in CDCl<sub>3</sub>.

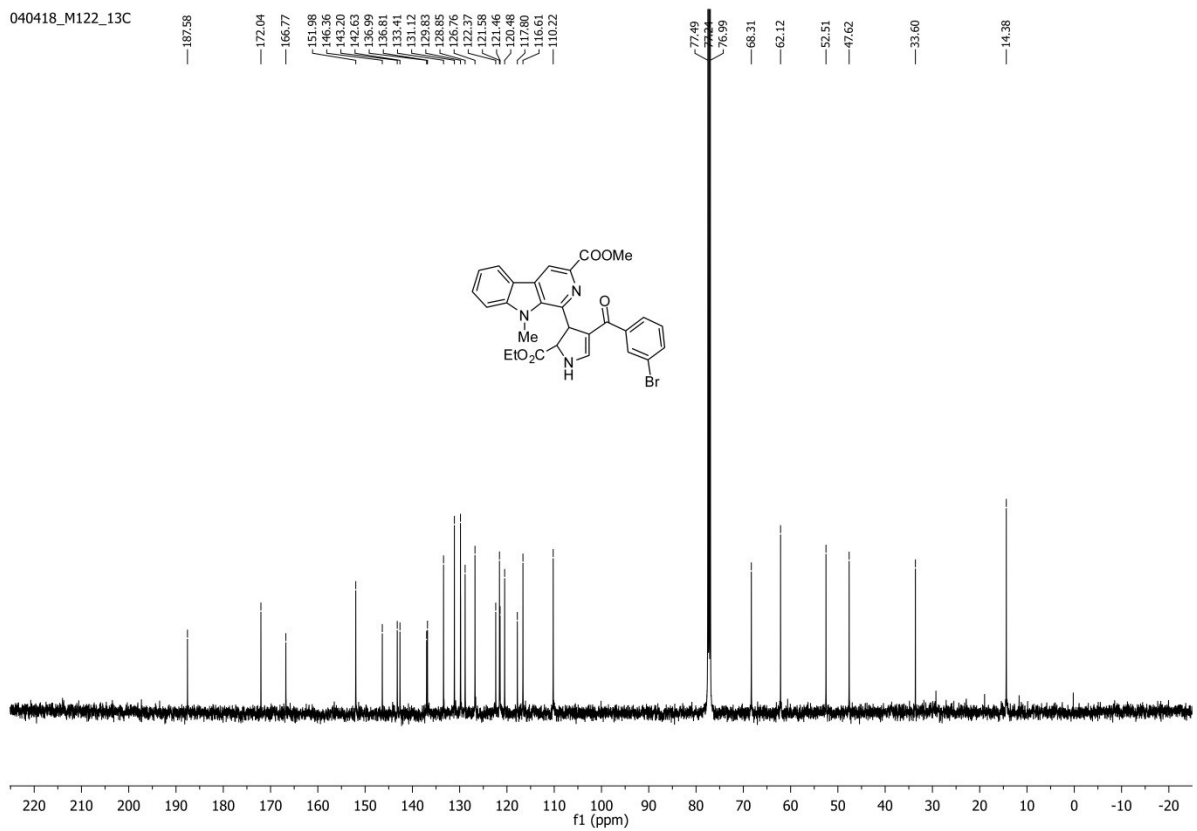


Figure S8. <sup>13</sup>C-NMR spectrum of **1aB** in CDCl<sub>3</sub>.

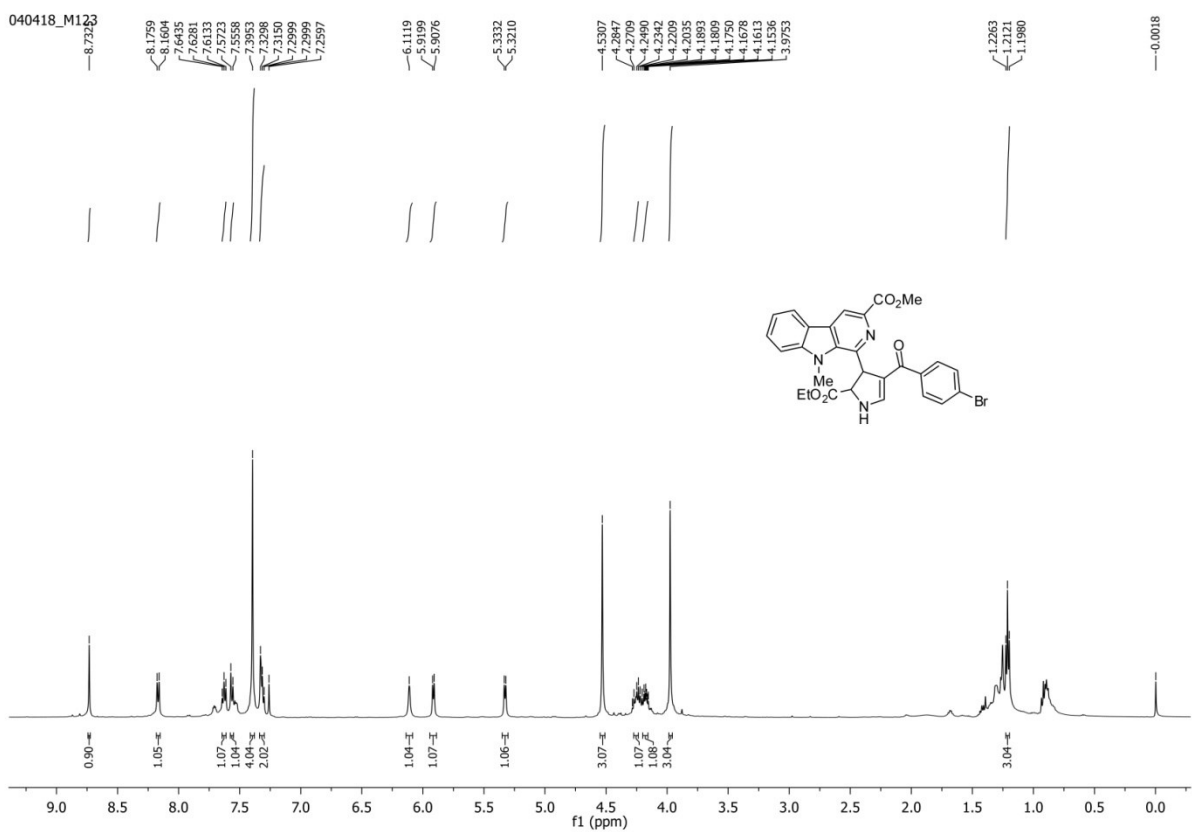


Figure S9.  $^1\text{H-NMR}$  spectrum of **1aC** in  $\text{CDCl}_3$ .

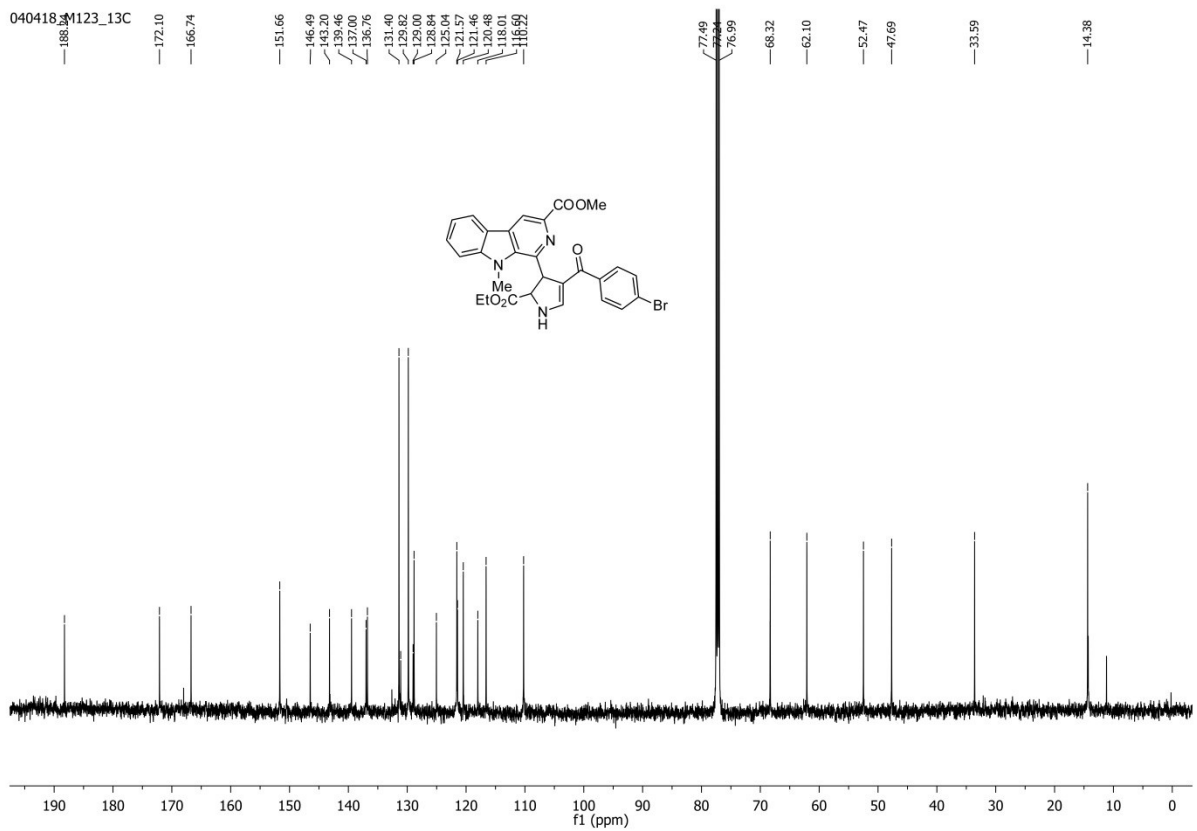


Figure S10.  $^{13}\text{C-NMR}$  spectrum of **1aC** in  $\text{CDCl}_3$ .



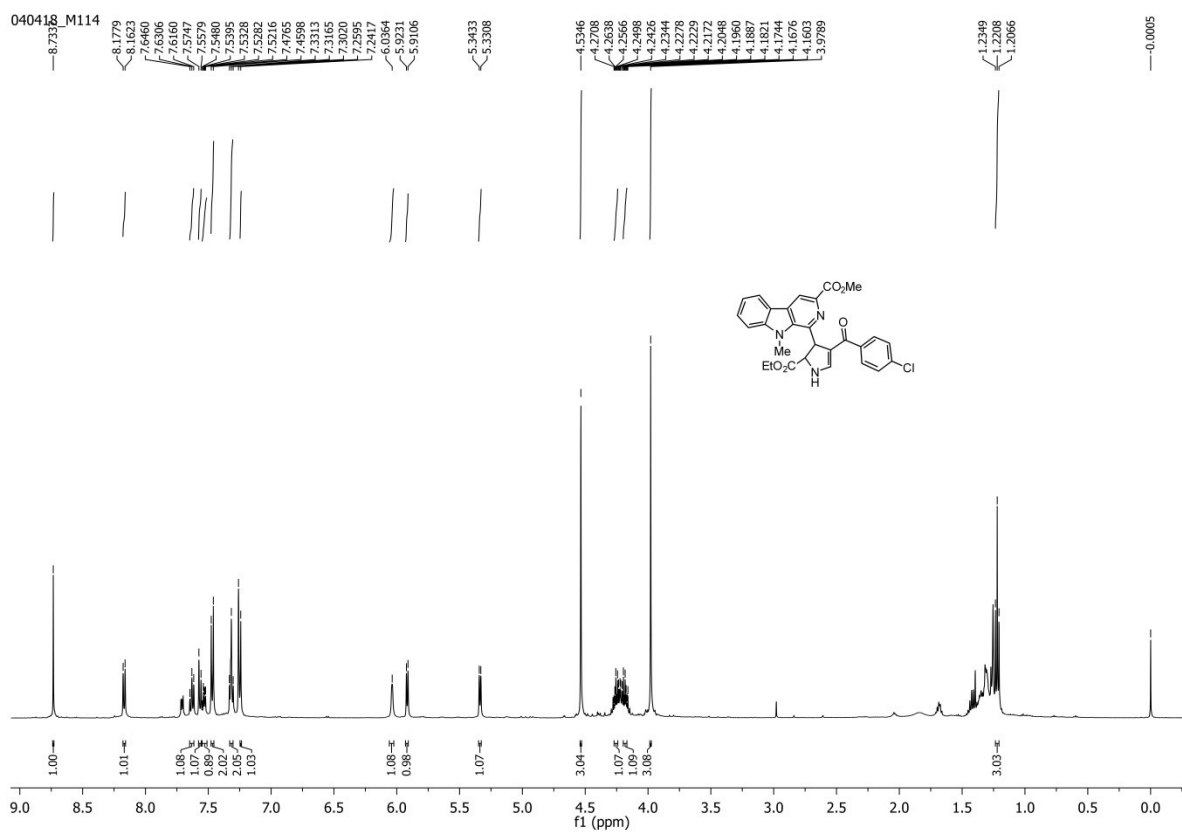


Figure S11.  $^1\text{H-NMR}$  spectrum of **1aD** in  $\text{CDCl}_3$ .

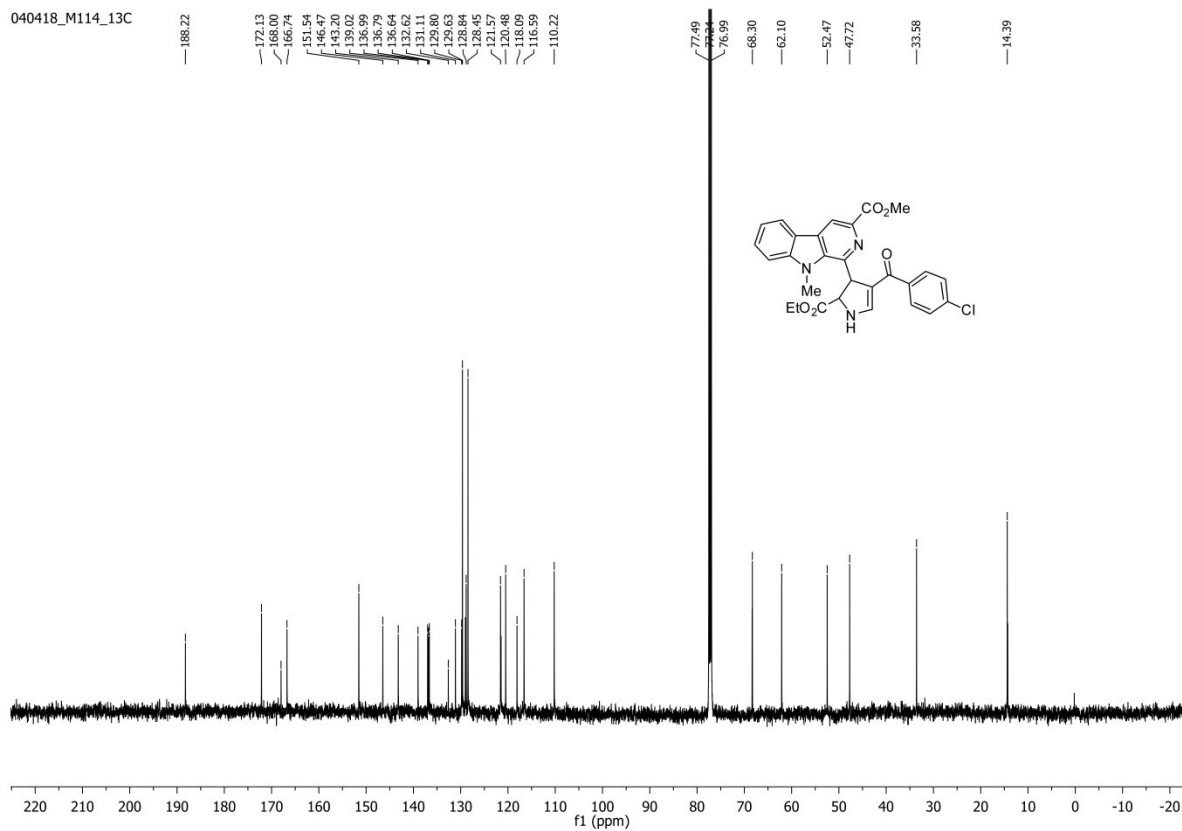


Figure S12.  $^{13}\text{C-NMR}$  spectrum of **1aD** in  $\text{CDCl}_3$ .

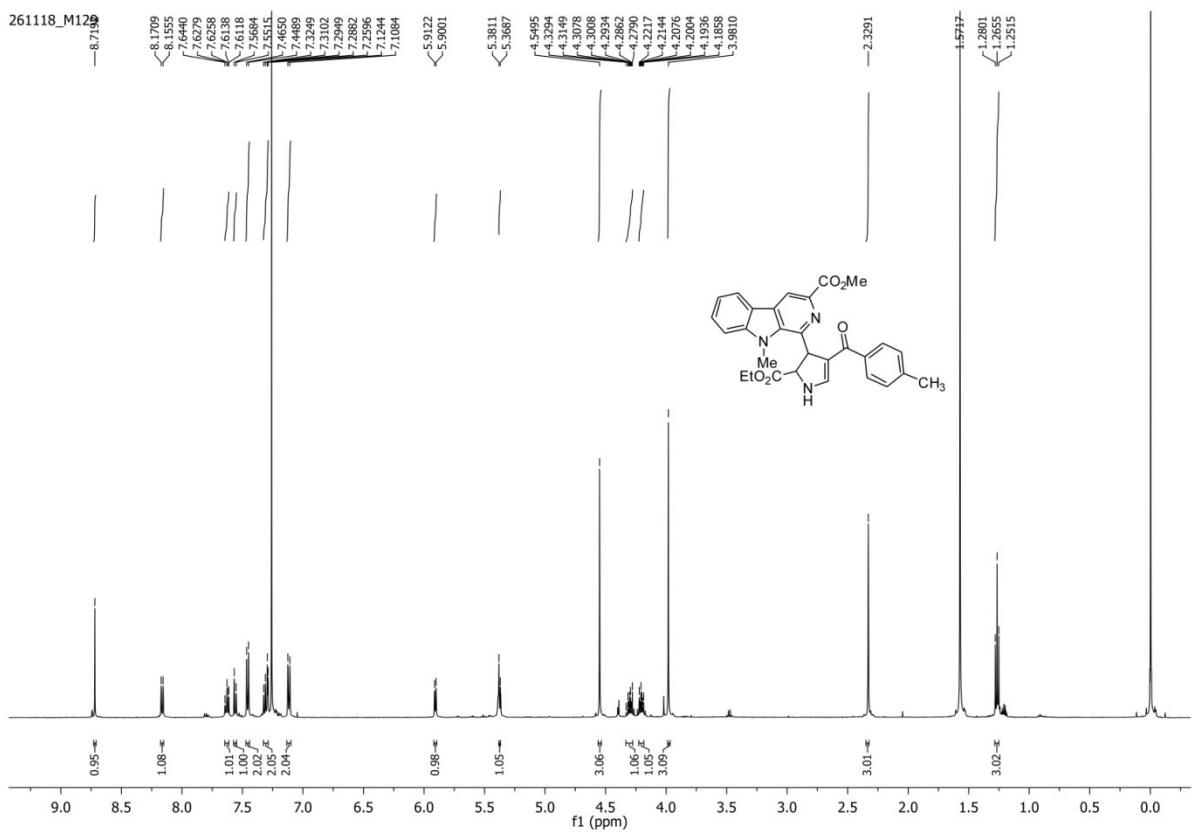


Figure S13. <sup>1</sup>H-NMR spectrum of **1aE** in CDCl<sub>3</sub>.

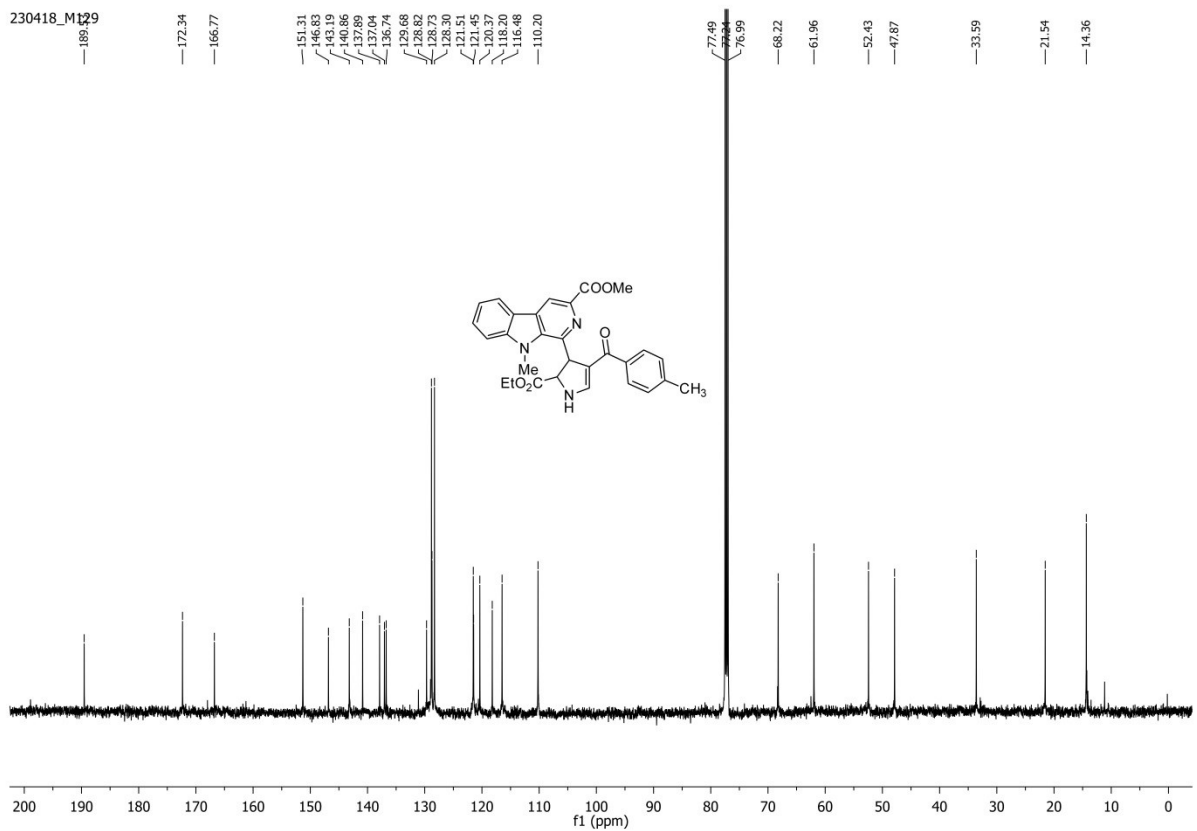


Figure S14. <sup>13</sup>C-NMR spectrum of **1aE** in CDCl<sub>3</sub>.

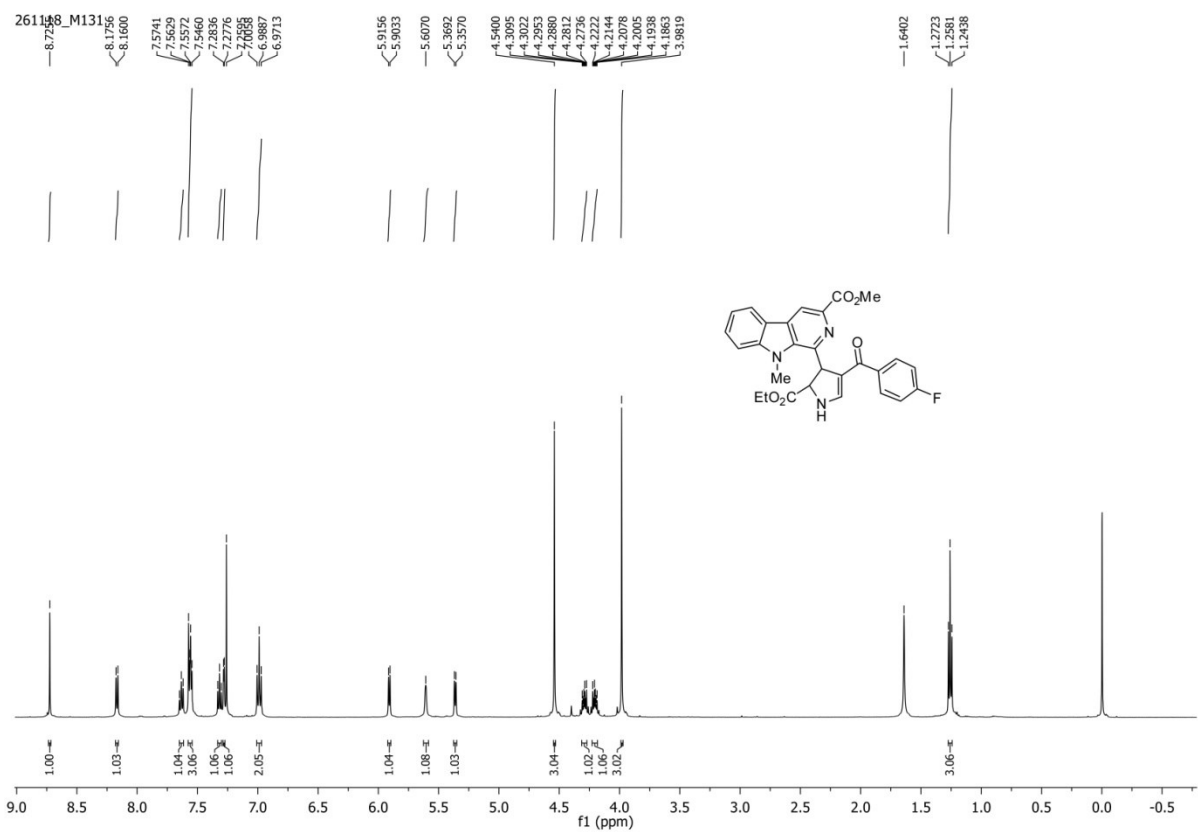


Figure S15. <sup>1</sup>H-NMR spectrum of **1aF** in CDCl<sub>3</sub>.

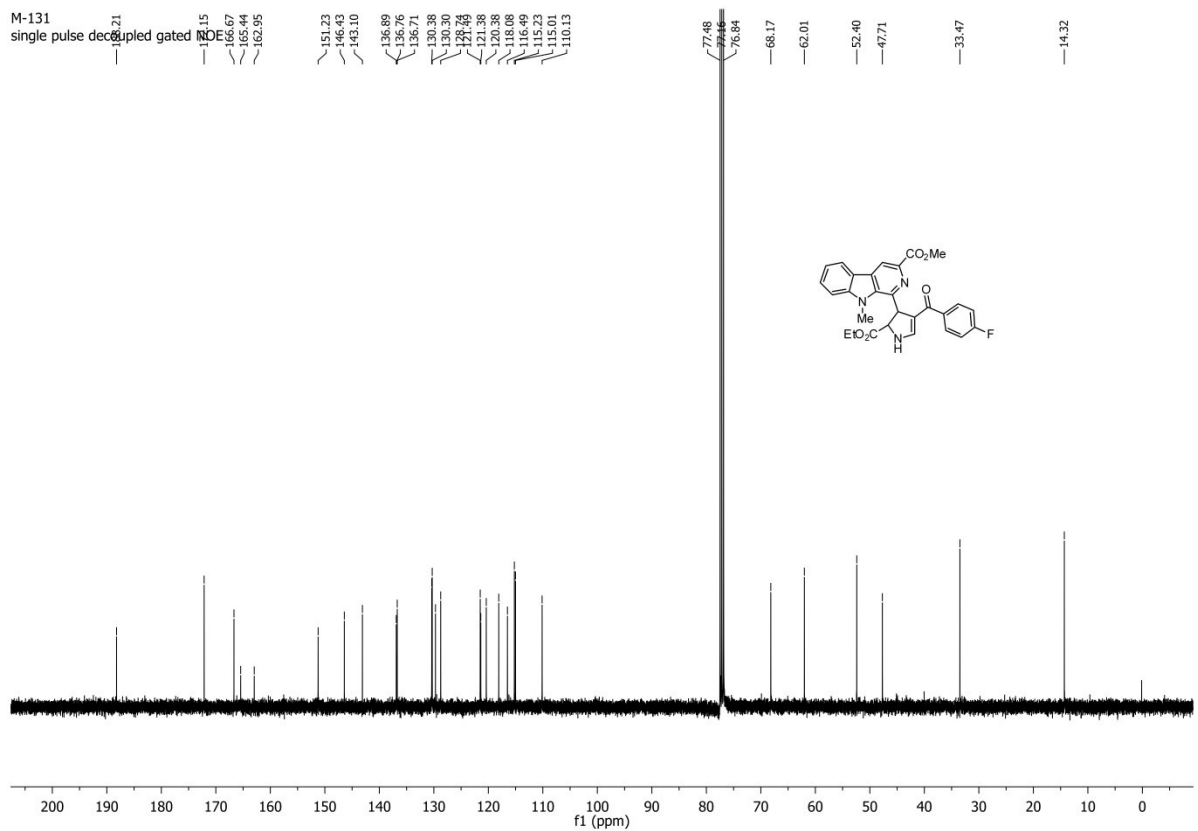


Figure S16. <sup>13</sup>C-NMR spectrum of **1aF** in CDCl<sub>3</sub>.

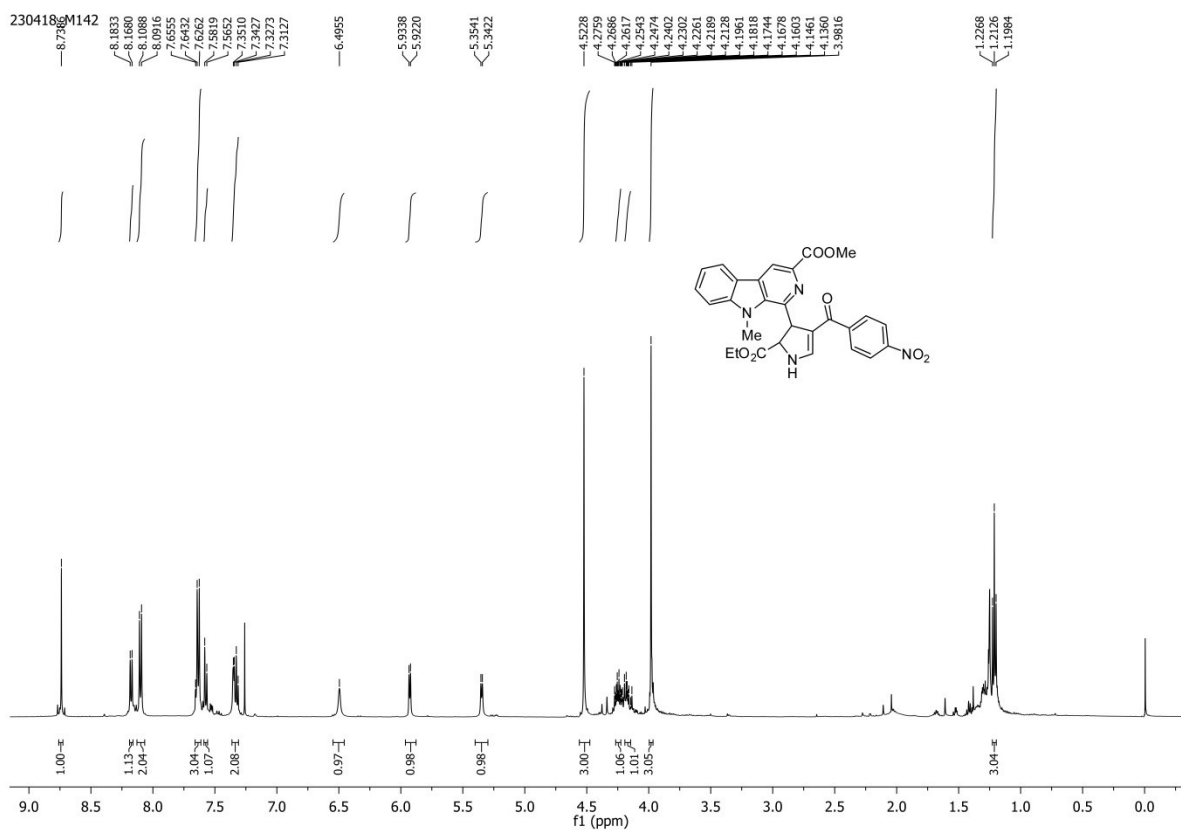


Figure S17. <sup>1</sup>H-NMR spectrum of **1aG** in CDCl<sub>3</sub>.

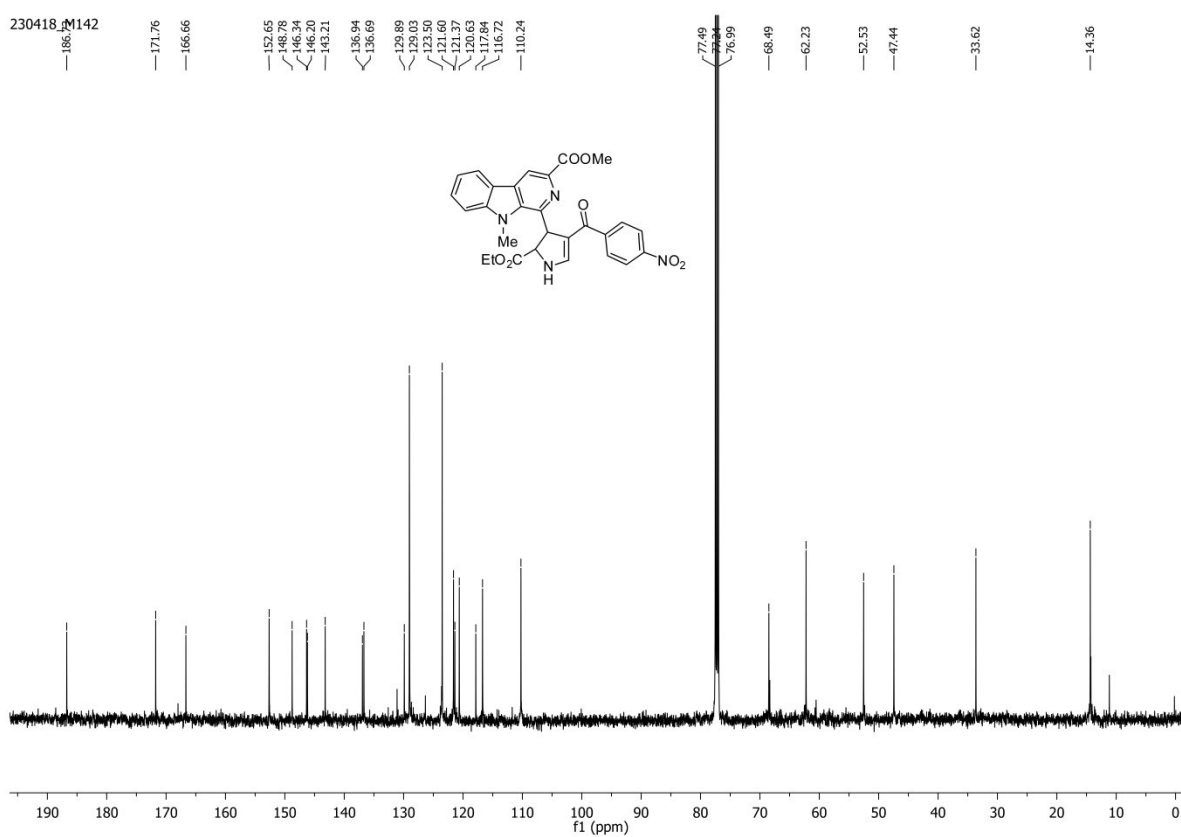


Figure S18. <sup>13</sup>C-NMR spectrum of **1aG** in CDCl<sub>3</sub>.

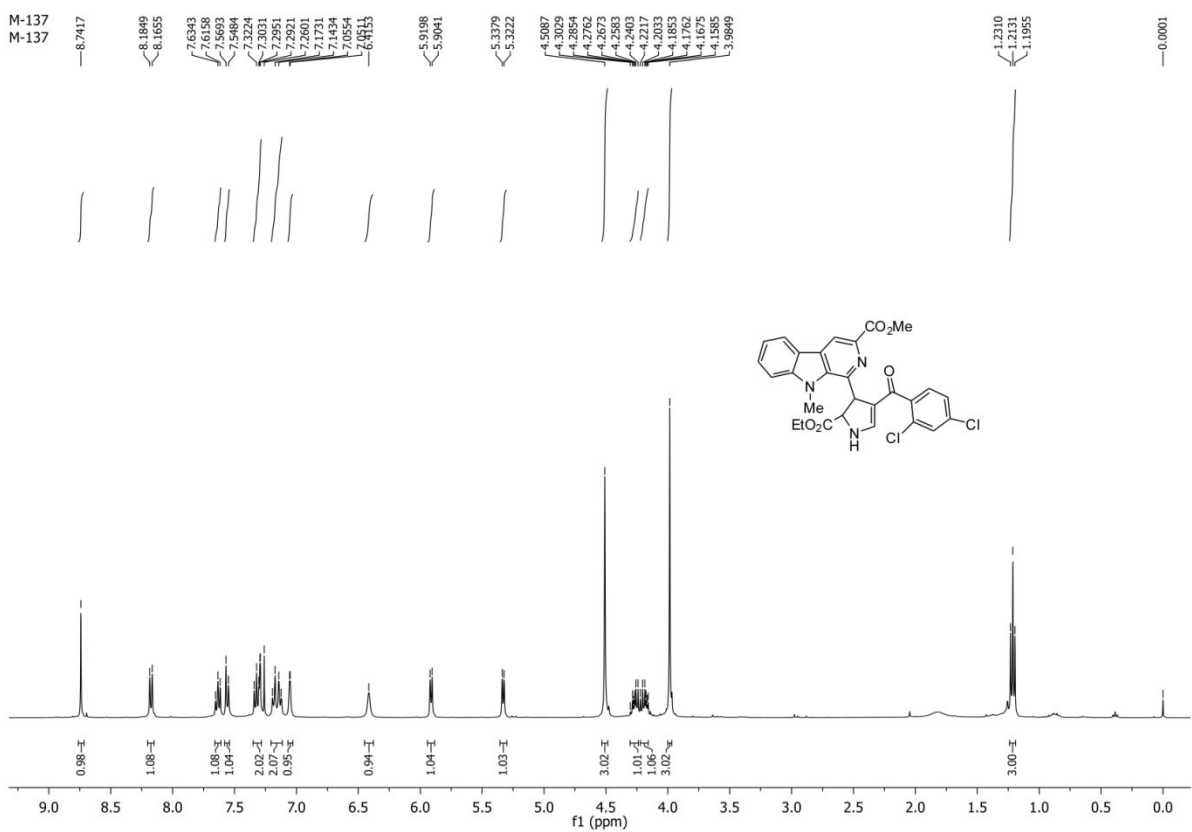


Figure S19.  $^1\text{H-NMR}$  spectrum of **1aH** in  $\text{CDCl}_3$ .

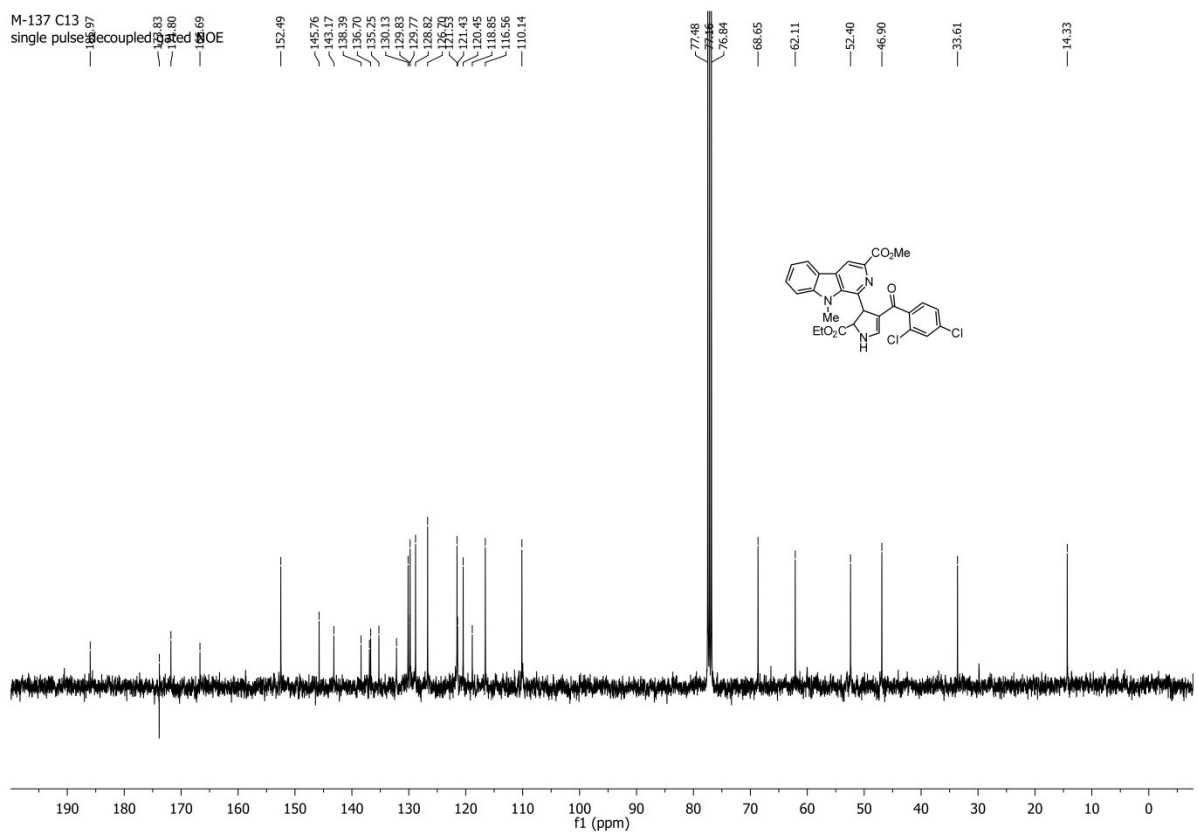


Figure S20.  $^{13}\text{C-NMR}$  spectrum of **1aH** in  $\text{CDCl}_3$ .

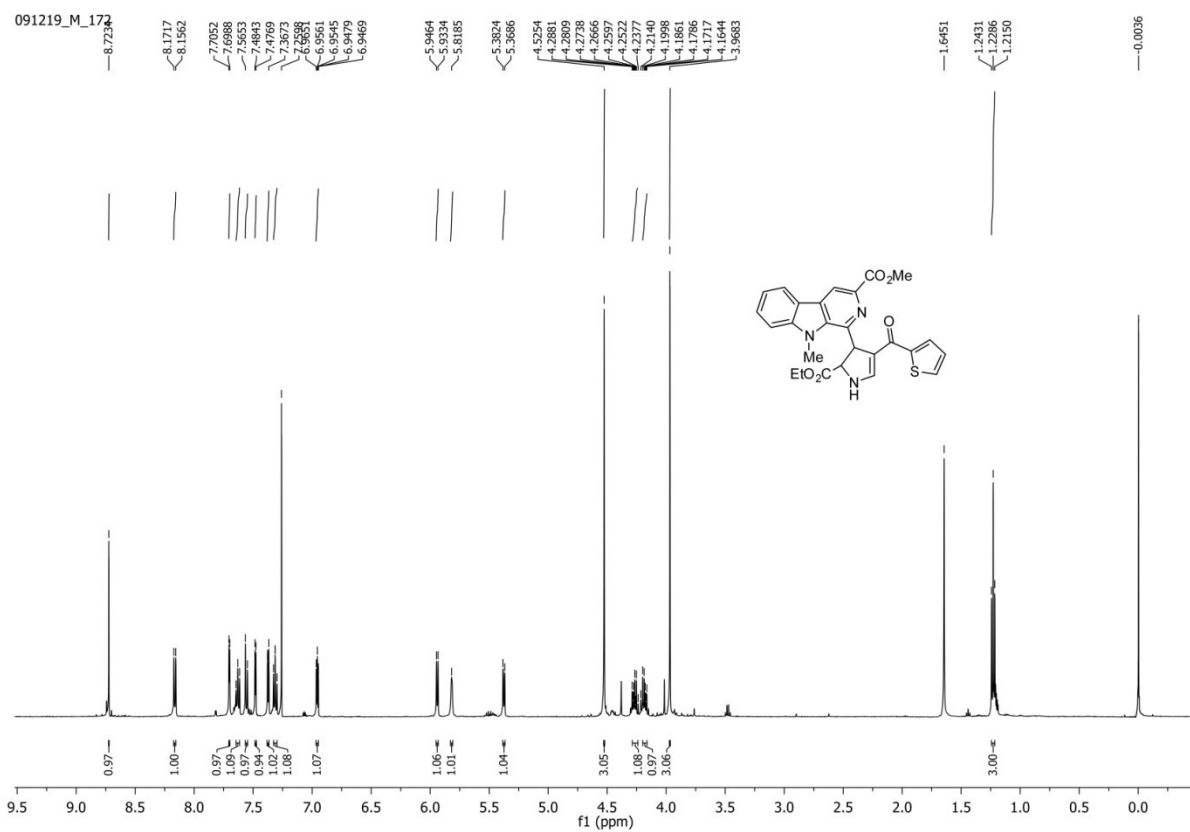


Figure S21. <sup>1</sup>H-NMR spectrum of **1aI** in CDCl<sub>3</sub>.

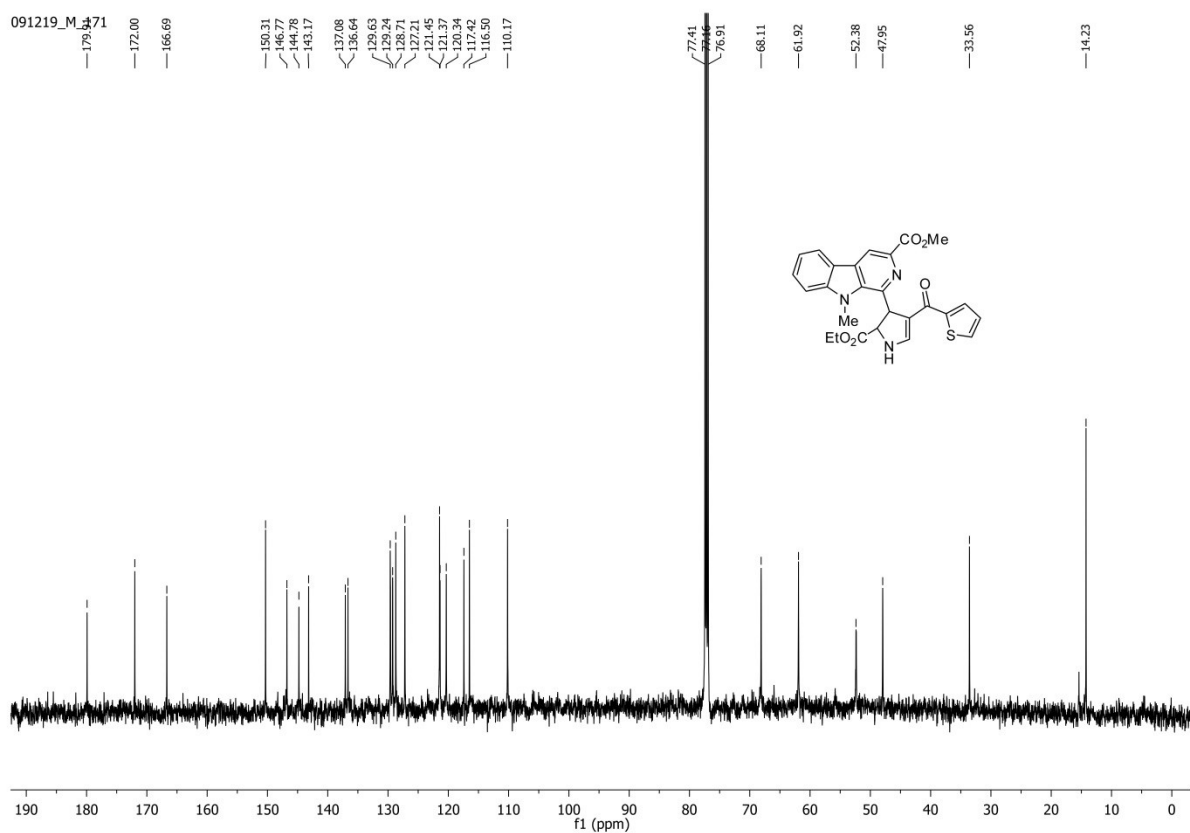


Figure S22. <sup>13</sup>C-NMR spectrum of **1aI** in CDCl<sub>3</sub>.

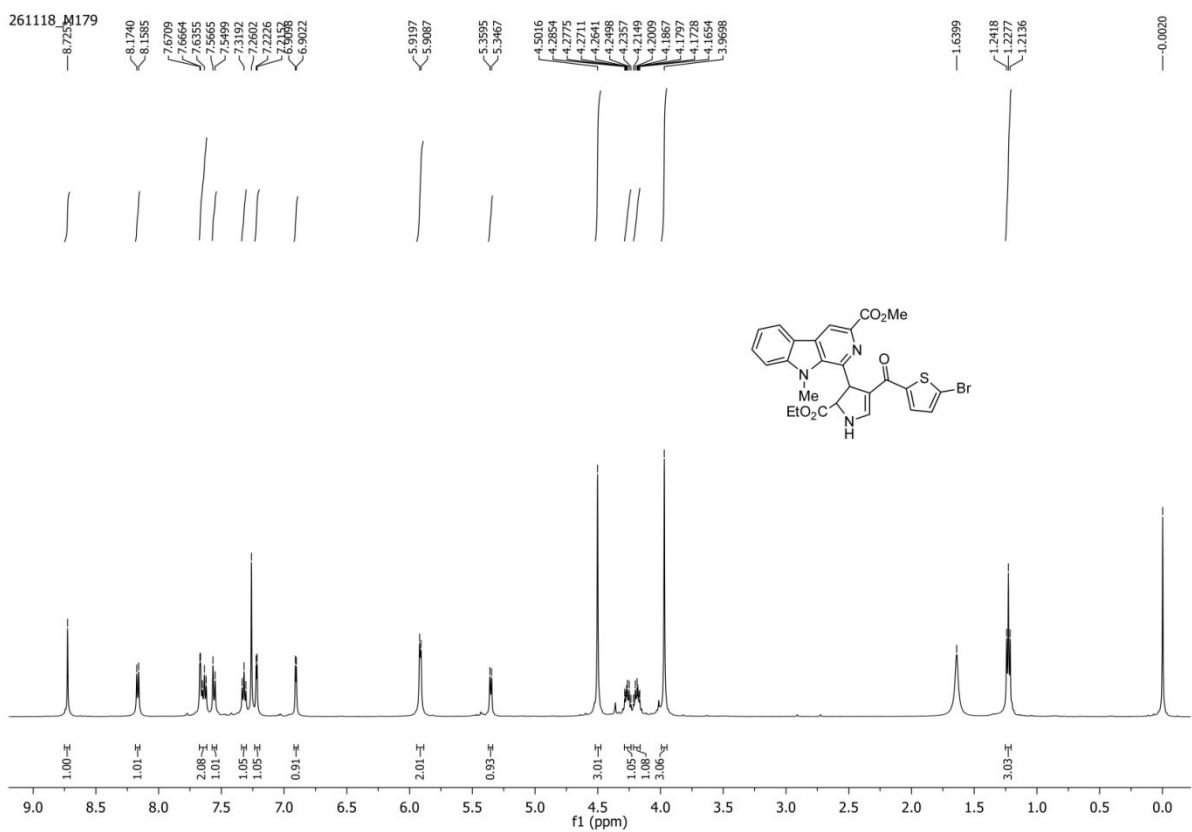


Figure S23.  $^1\text{H-NMR}$  spectrum of **1aJ** in  $\text{CDCl}_3$ .

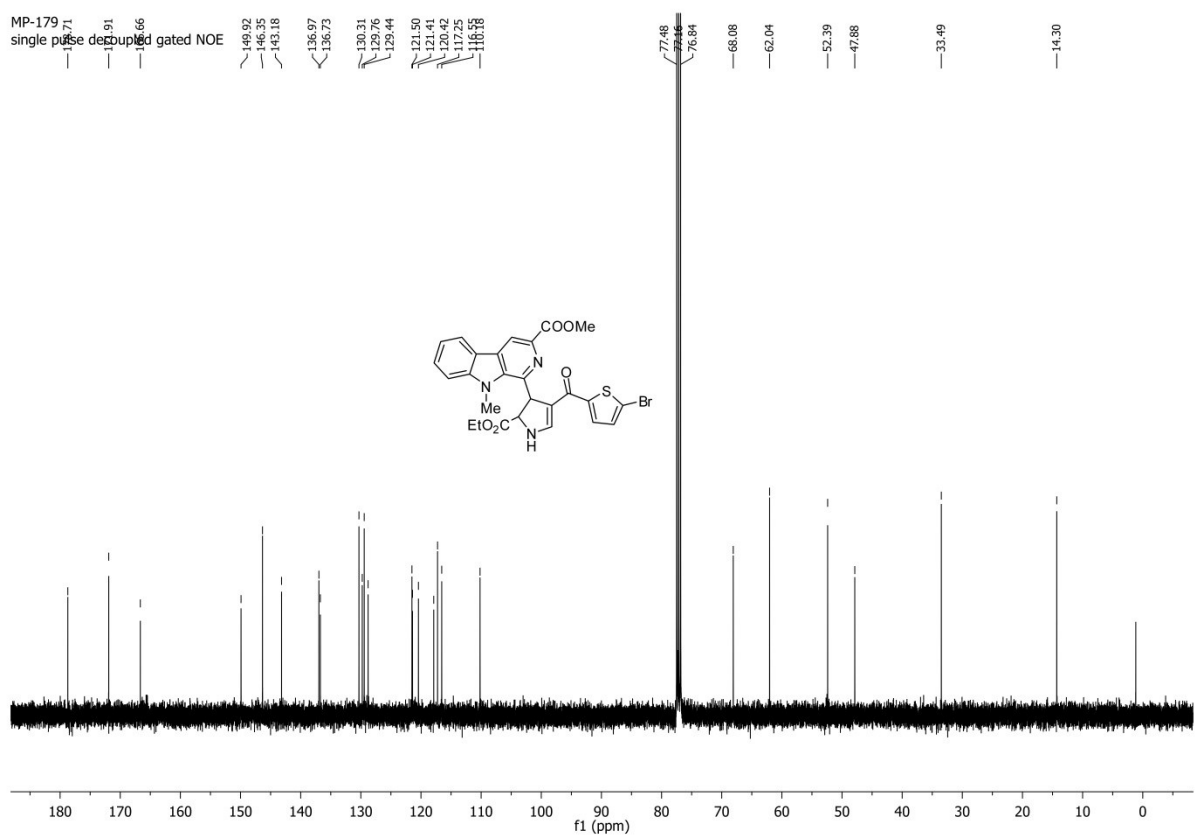


Figure S24.  $^{13}\text{C-NMR}$  spectrum of **1aJ** in  $\text{CDCl}_3$ .

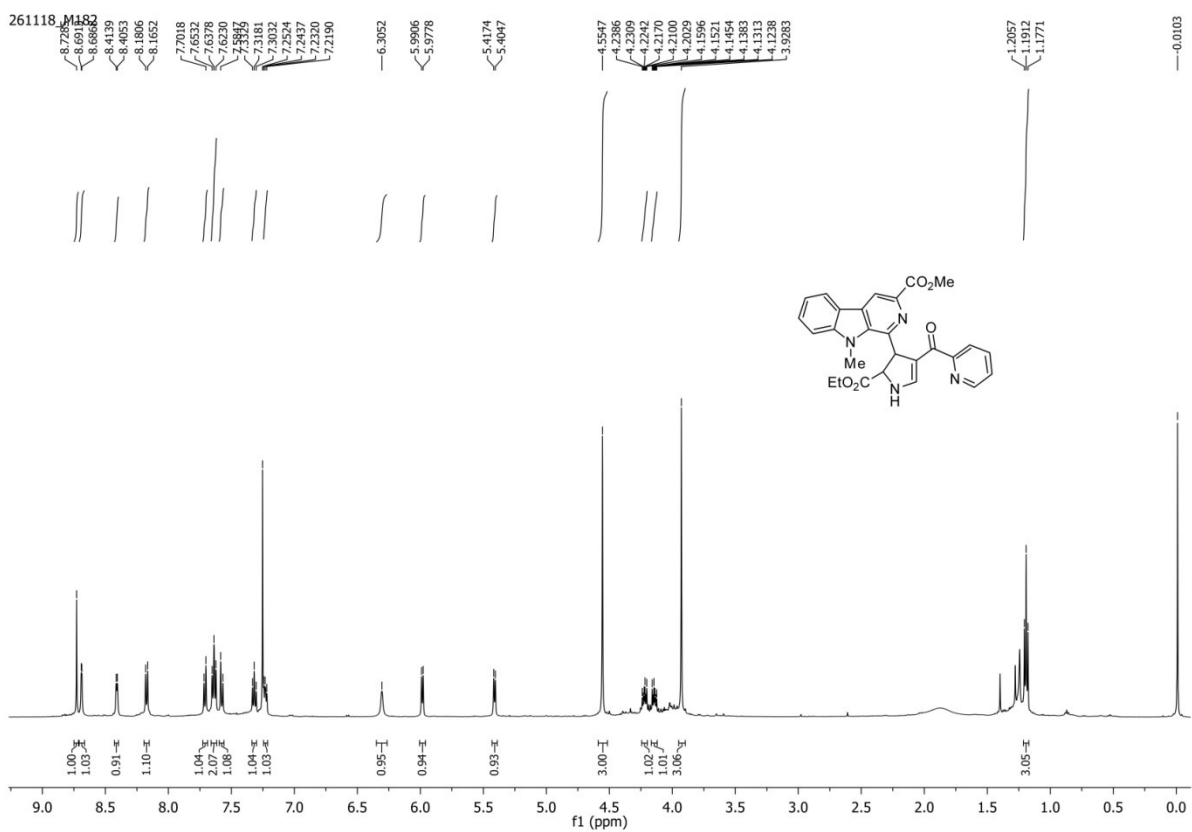


Figure S25. <sup>1</sup>H-NMR spectrum of **1aK** in CDCl<sub>3</sub>.

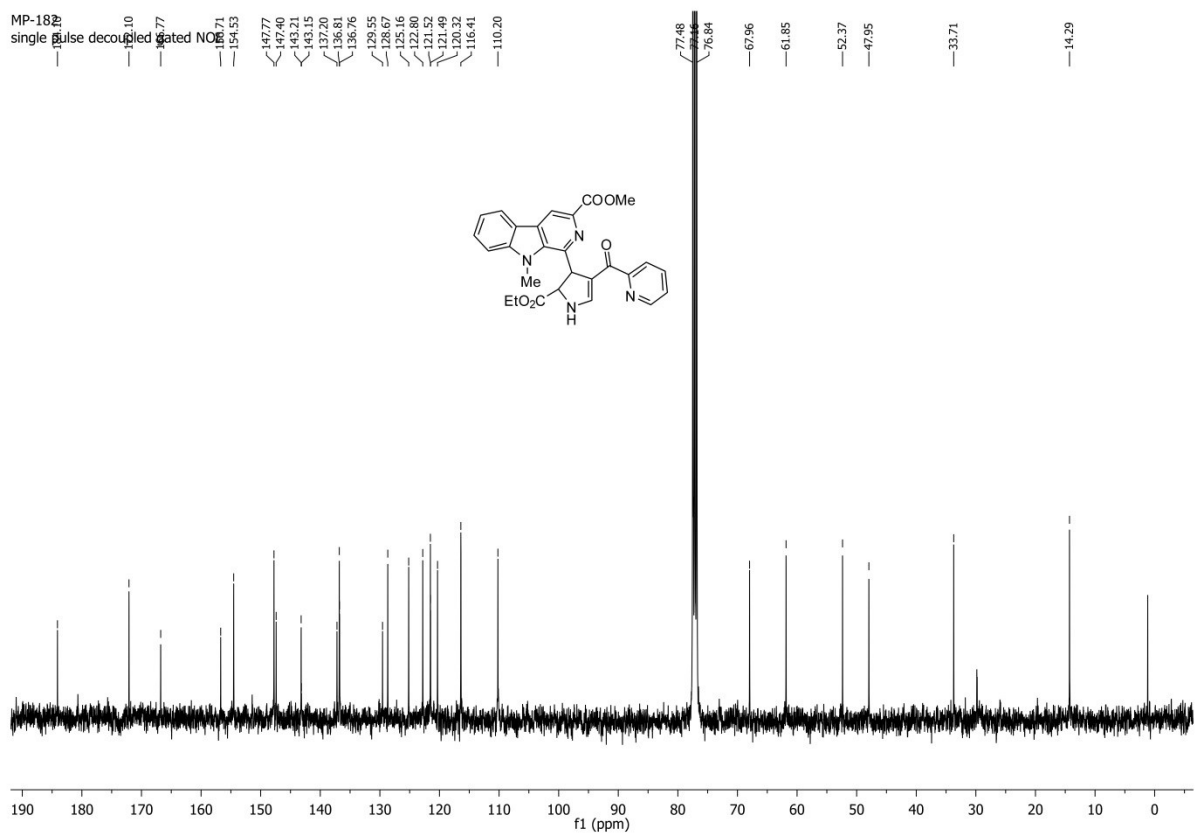


Figure S26. <sup>13</sup>C-NMR spectrum of **1aK** in CDCl<sub>3</sub>.



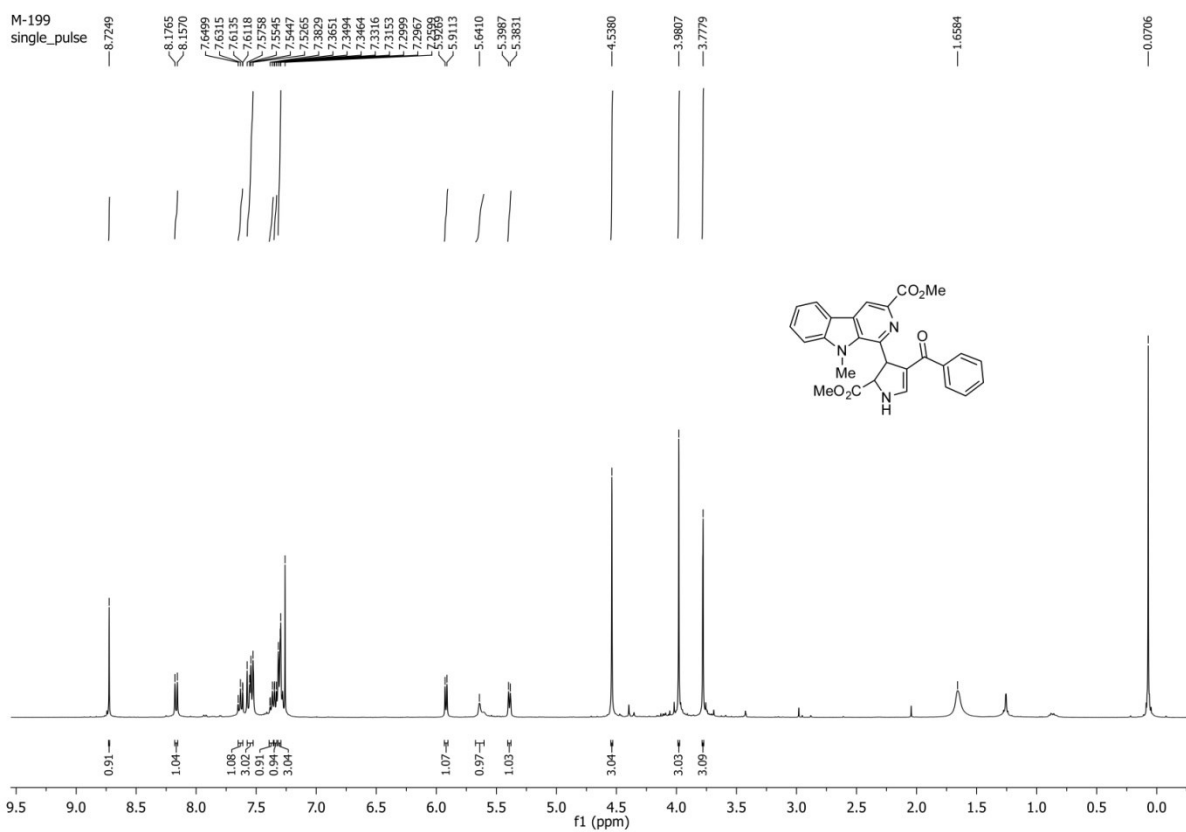


Figure S27.  $^1\text{H-NMR}$  spectrum of **1bA** in  $\text{CDCl}_3$ .

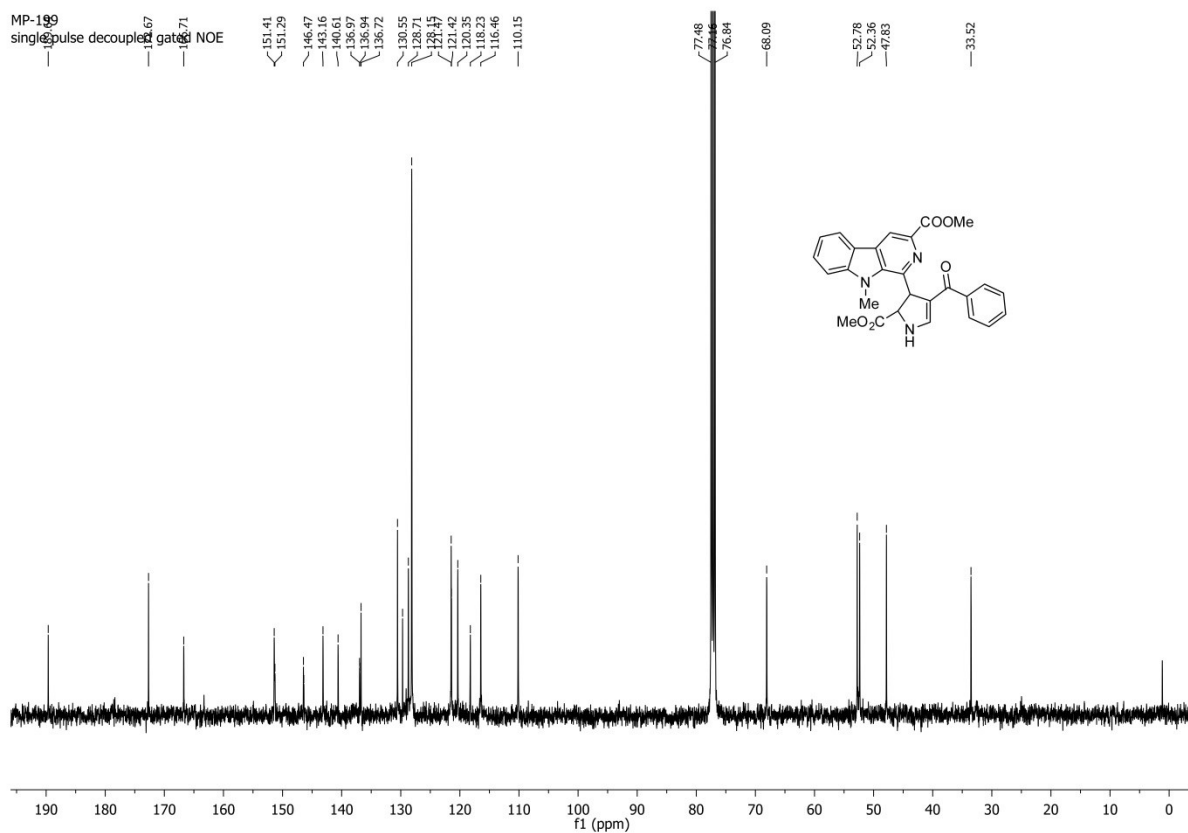


Figure S28.  $^{13}\text{C-NMR}$  spectrum of **1bA** in  $\text{CDCl}_3$ .

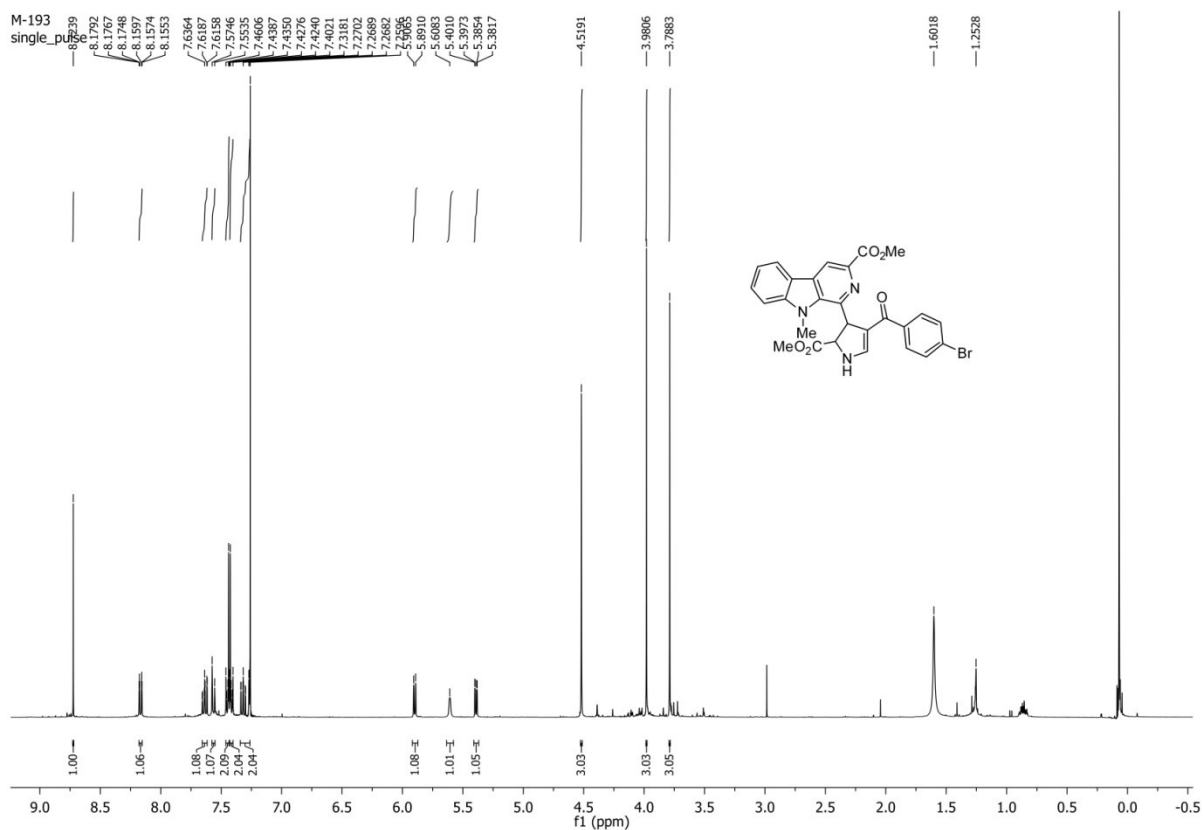


Figure S29. <sup>1</sup>H-NMR spectrum of **1bC** in CDCl<sub>3</sub>.

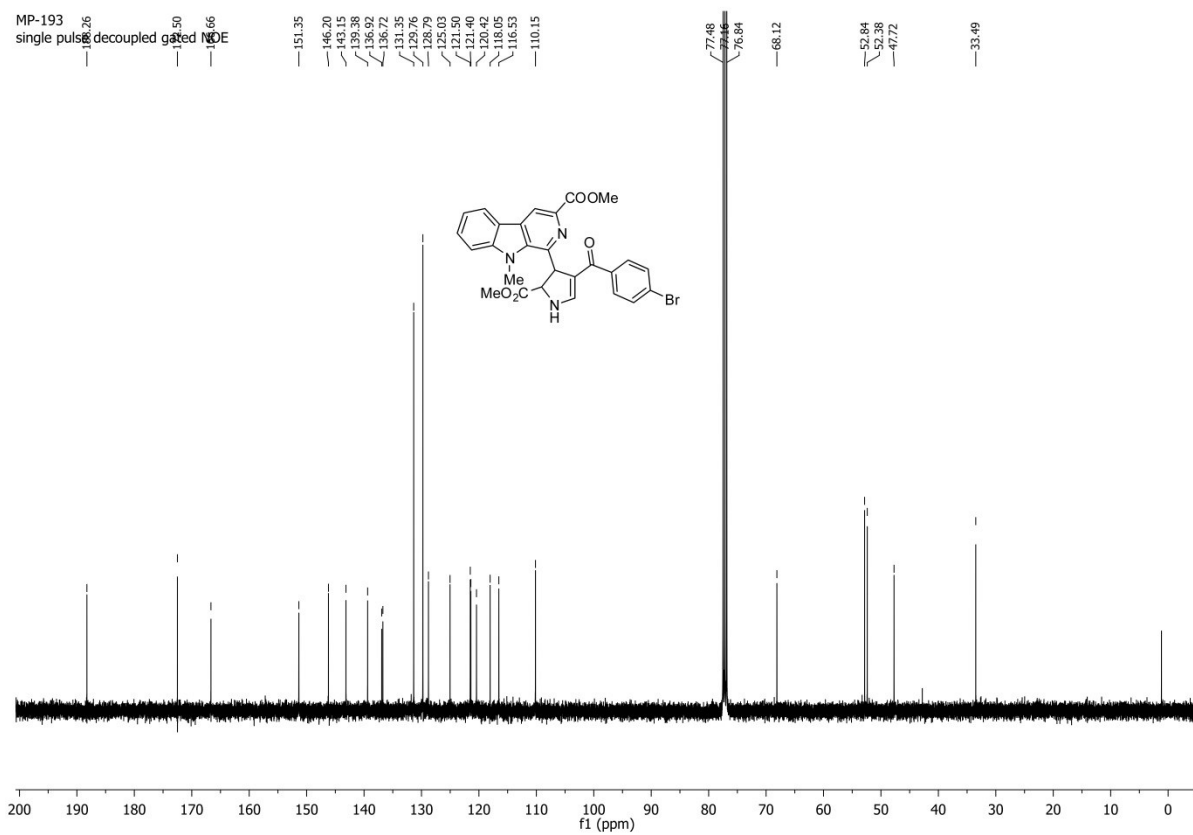


Figure S30. <sup>13</sup>C-NMR spectrum of **1bC** in CDCl<sub>3</sub>.

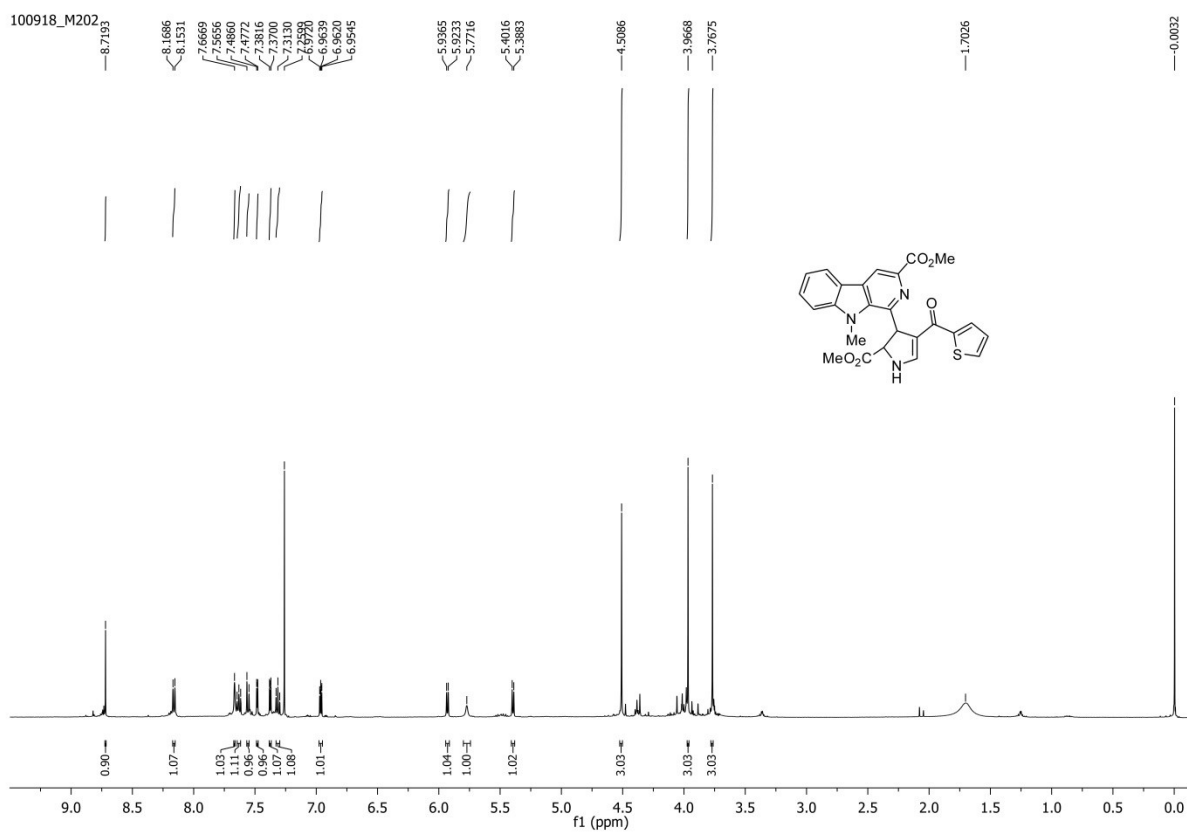


Figure S31.  $^1\text{H-NMR}$  spectrum of **1bI** in  $\text{CDCl}_3$ .

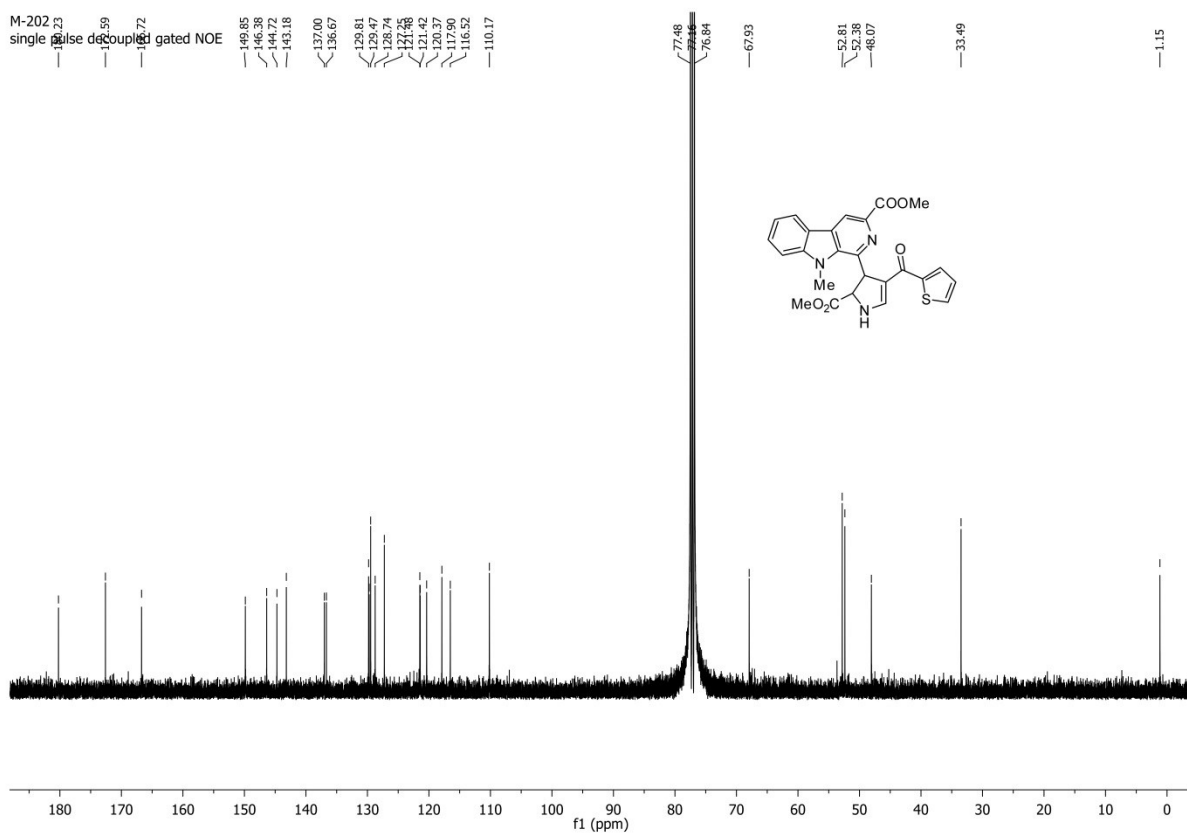


Figure S32.  $^{13}\text{C-NMR}$  spectrum of **1bI** in  $\text{CDCl}_3$ .

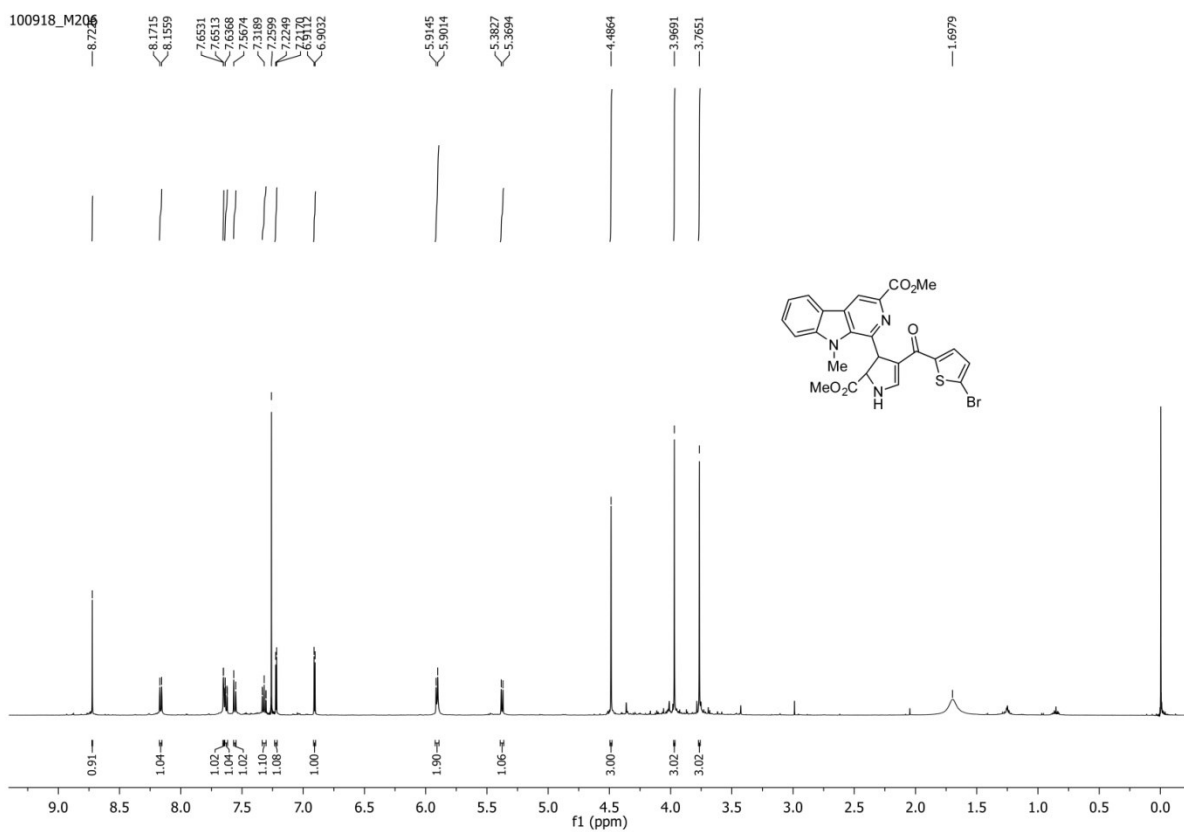


Figure S33.  $^1\text{H-NMR}$  spectrum of **1bJ** in  $\text{CDCl}_3$ .

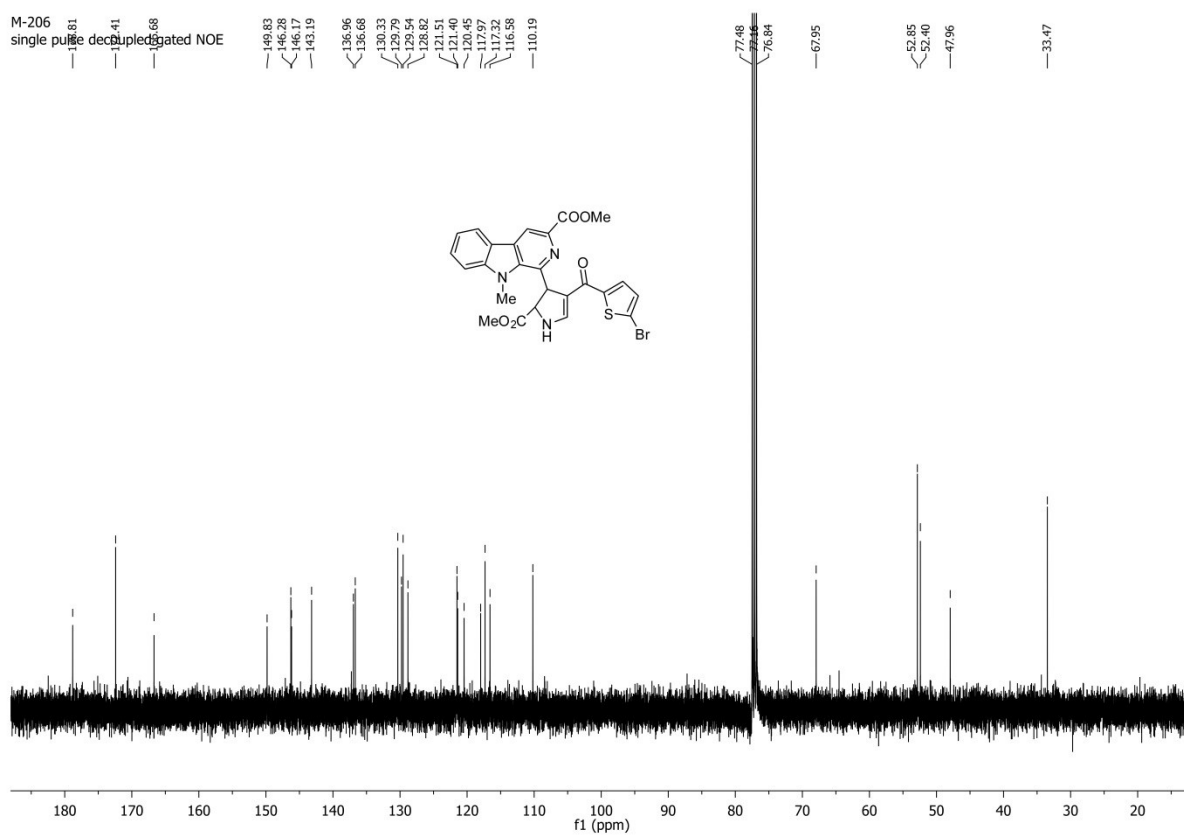


Figure S34.  $^{13}\text{C-NMR}$  spectrum of **1bJ** in  $\text{CDCl}_3$ .

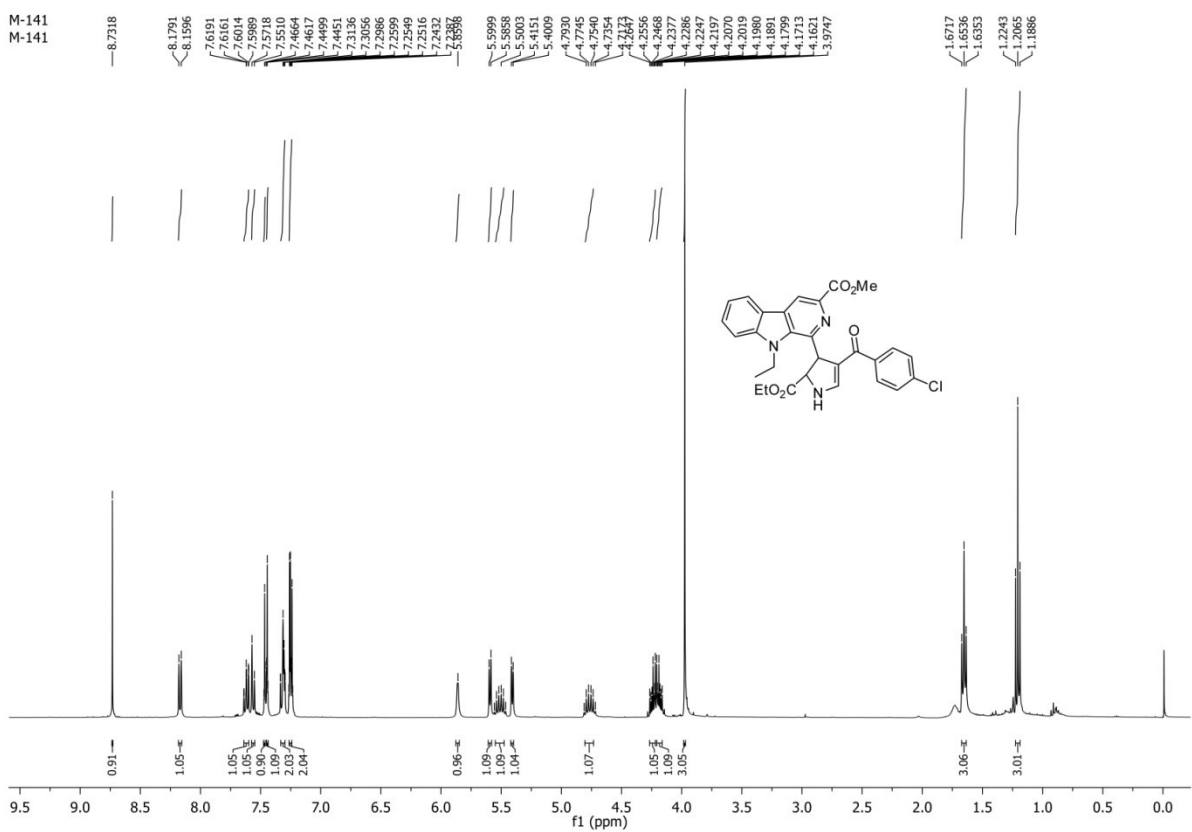


Figure S35.  $^1\text{H-NMR}$  spectrum of **2aD** in  $\text{CDCl}_3$ .

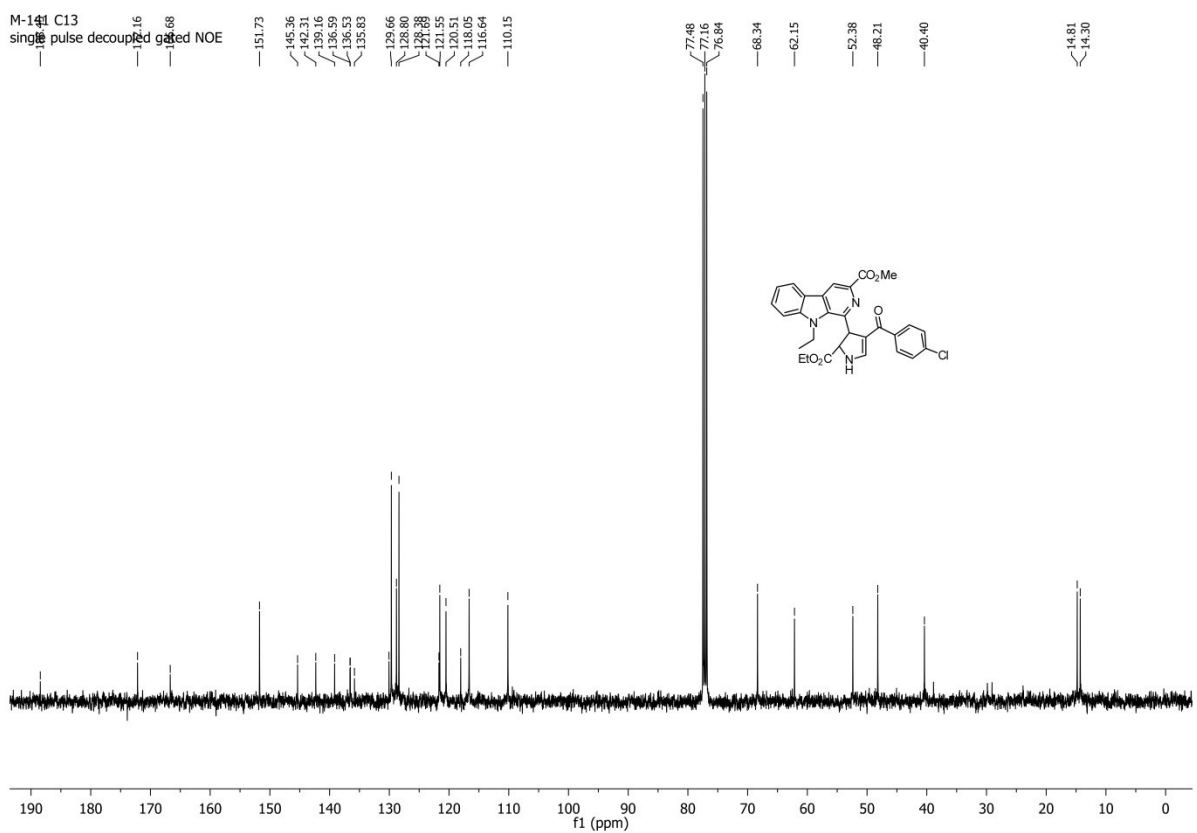


Figure S36.  $^{13}\text{C-NMR}$  spectrum of **2aD** in  $\text{CDCl}_3$ .

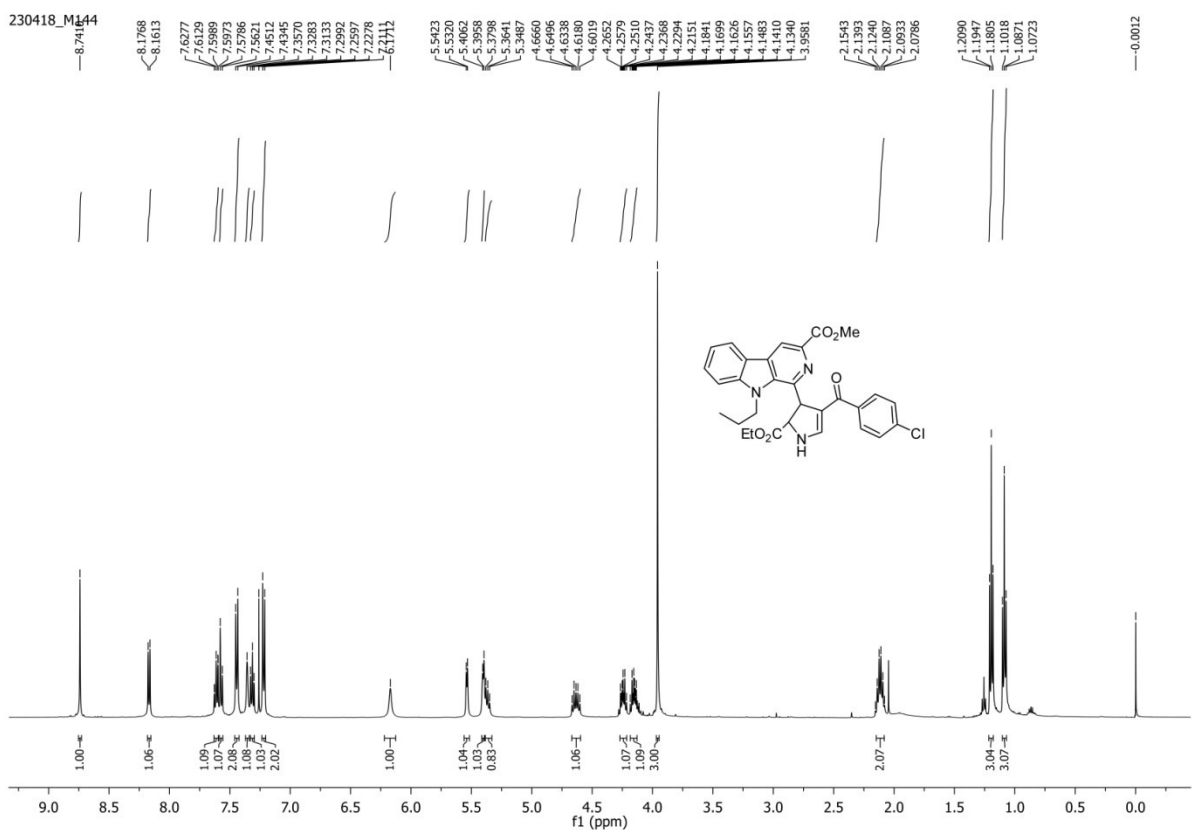


Figure S37.  $^1\text{H-NMR}$  spectrum of **3aD** in  $\text{CDCl}_3$ .

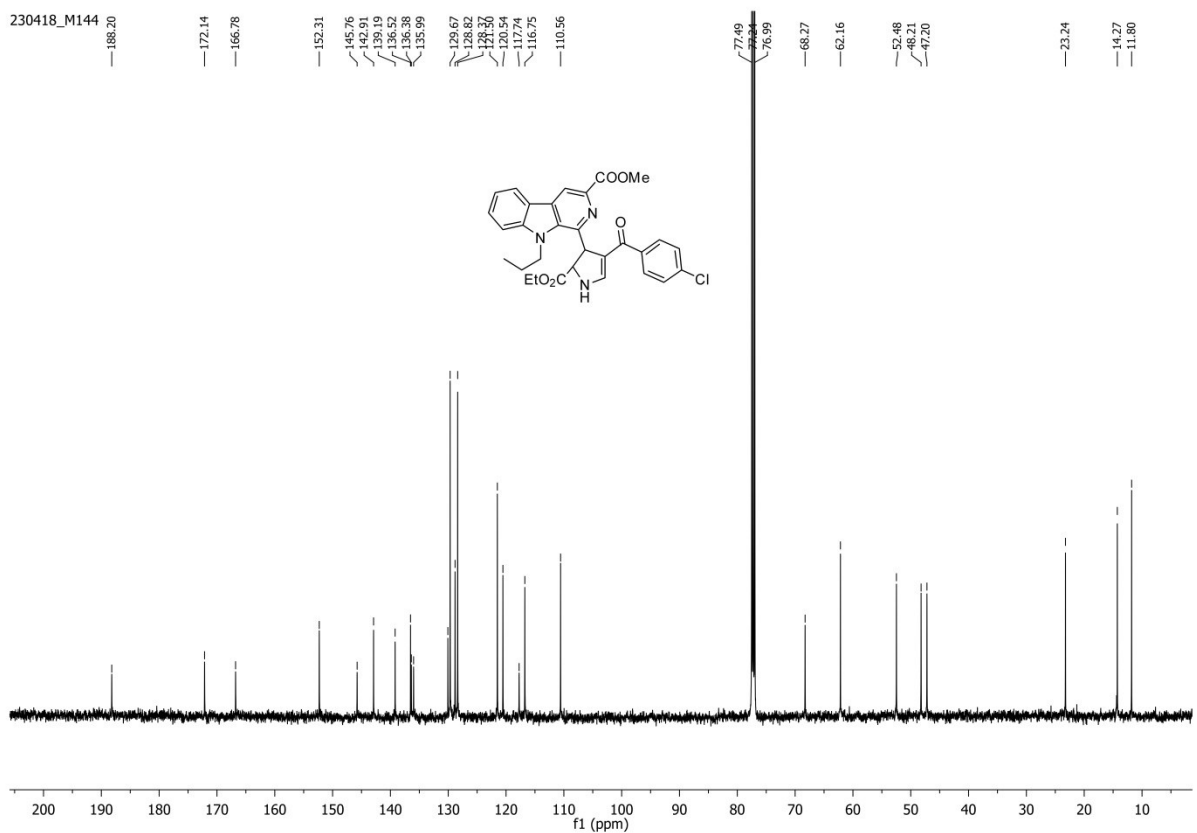


Figure S38.  $^{13}\text{C-NMR}$  spectrum of **3aD** in  $\text{CDCl}_3$ .

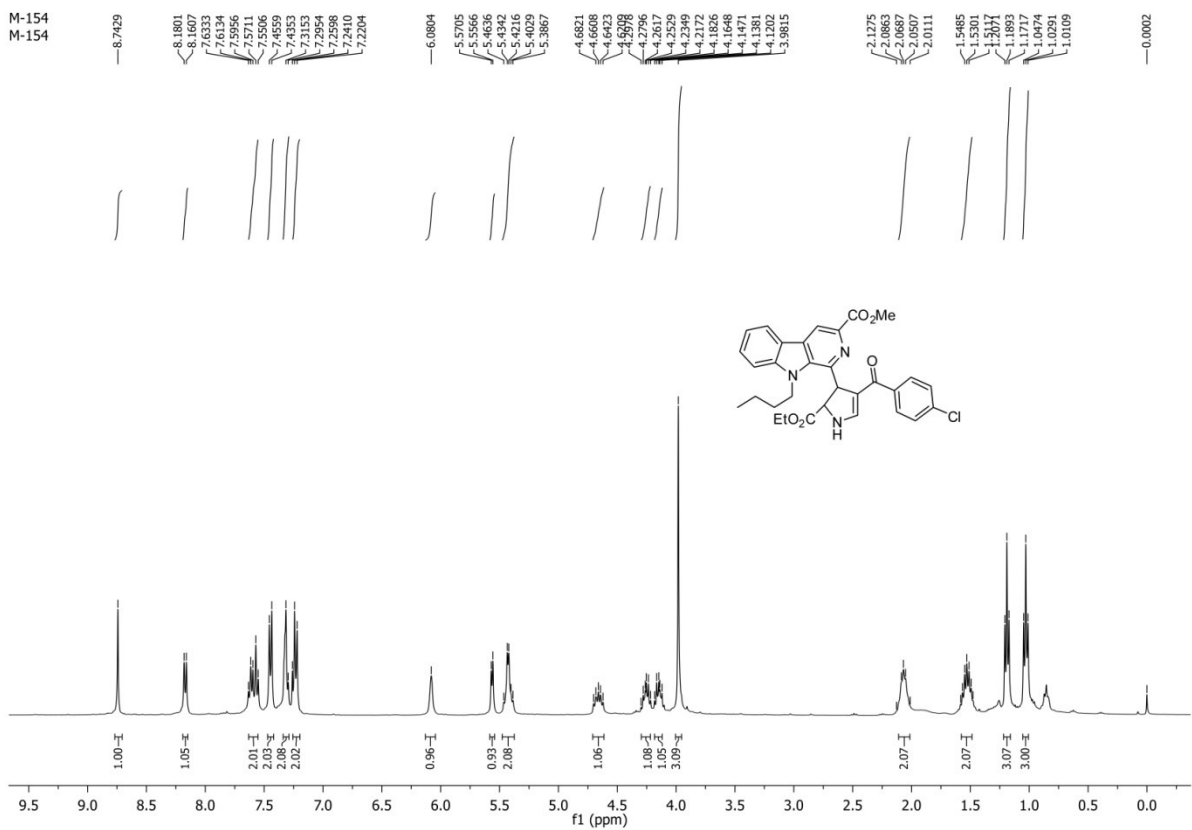


Figure S39.  $^1\text{H-NMR}$  spectrum of **4aD** in  $\text{CDCl}_3$ .

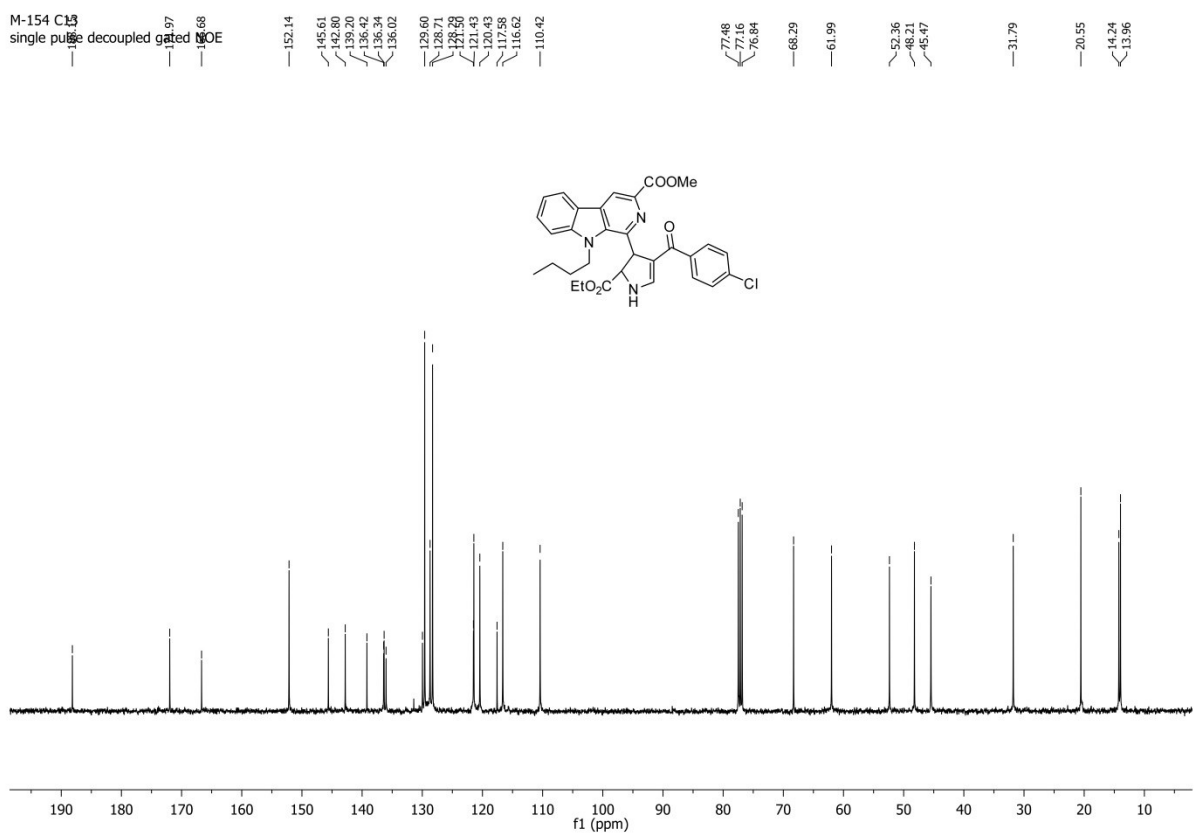


Figure S40.  $^{13}\text{C-NMR}$  spectrum of **4aD** in  $\text{CDCl}_3$ .

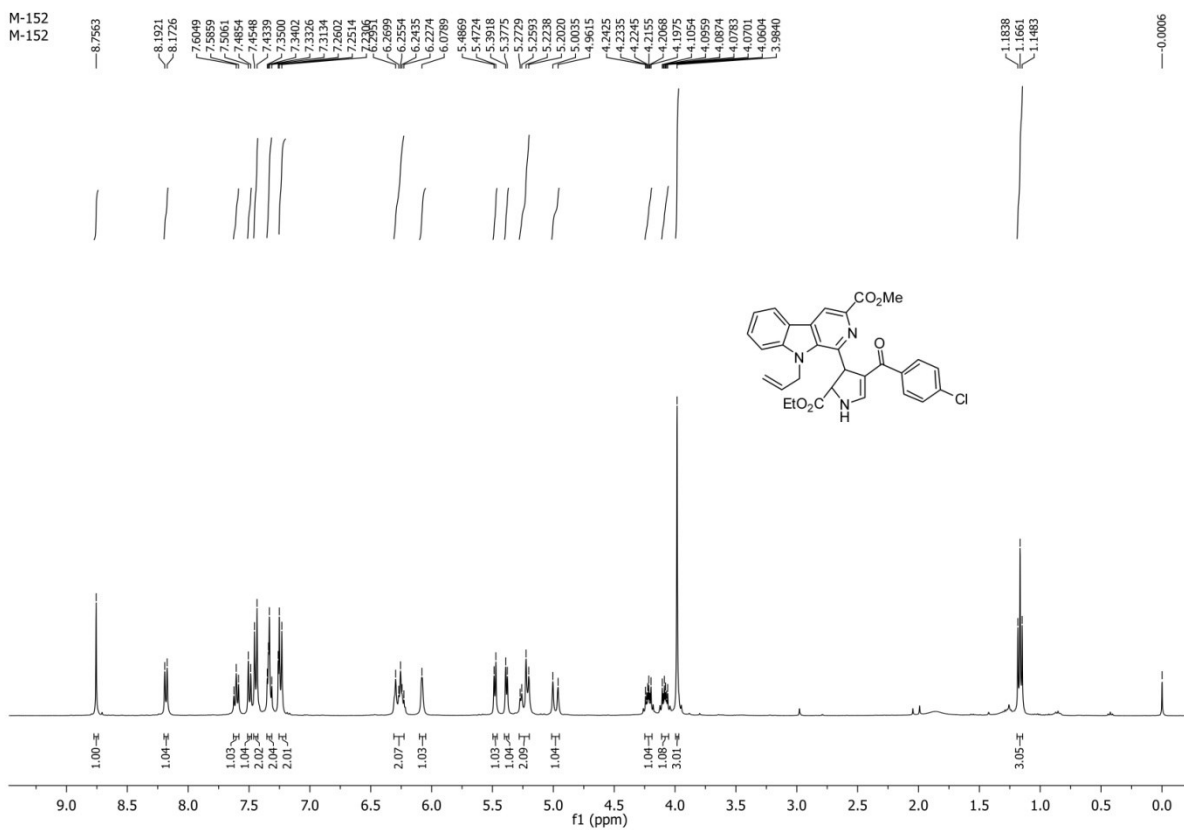


Figure S41.  $^1\text{H-NMR}$  spectrum of **5aD** in  $\text{CDCl}_3$ .

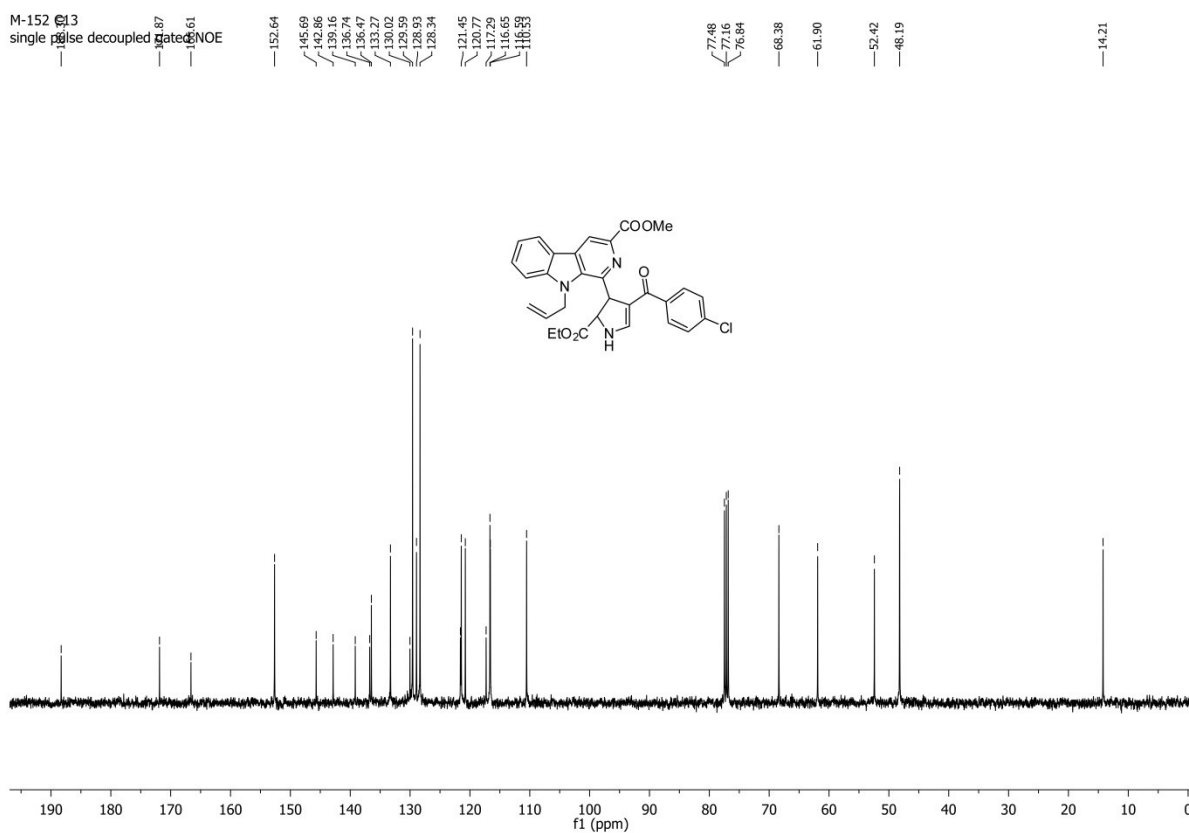


Figure S42.  $^{13}\text{C-NMR}$  spectrum of **5aD** in  $\text{CDCl}_3$ .



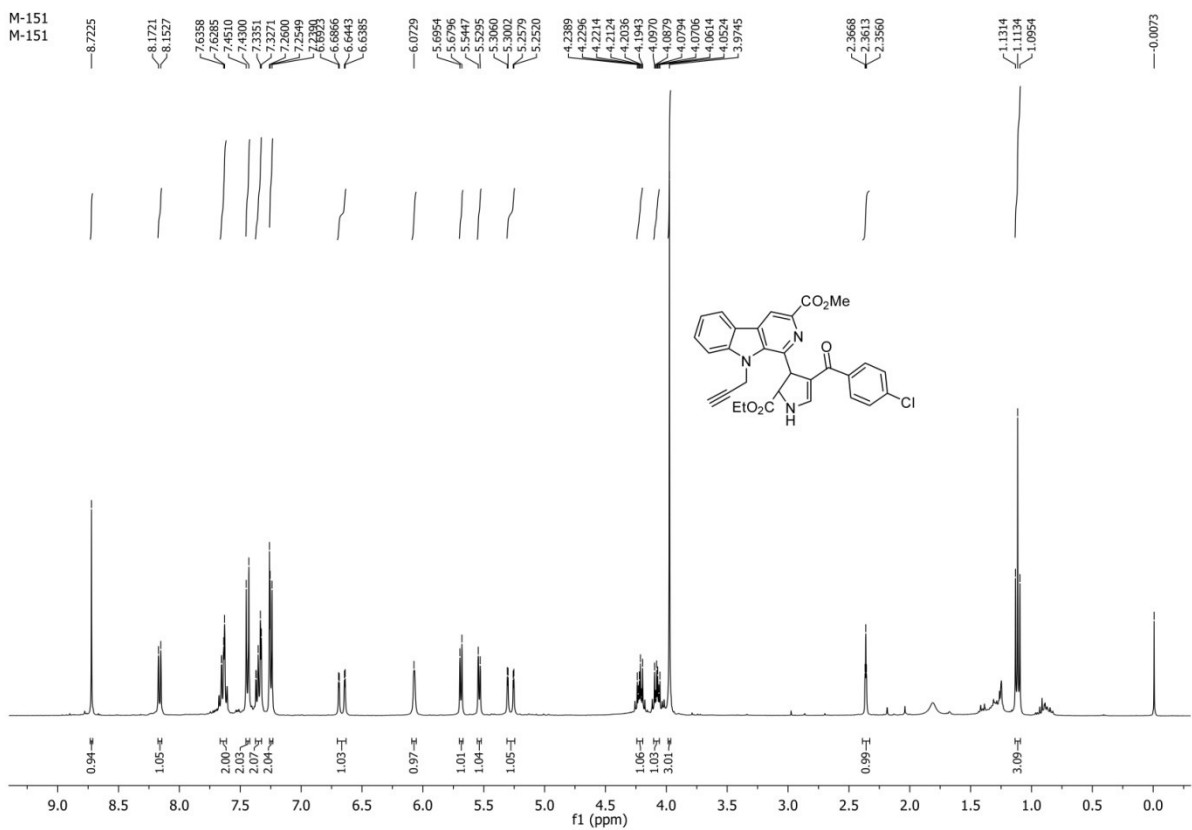


Figure S43.  $^1\text{H-NMR}$  spectrum of **6aD** in  $\text{CDCl}_3$ .

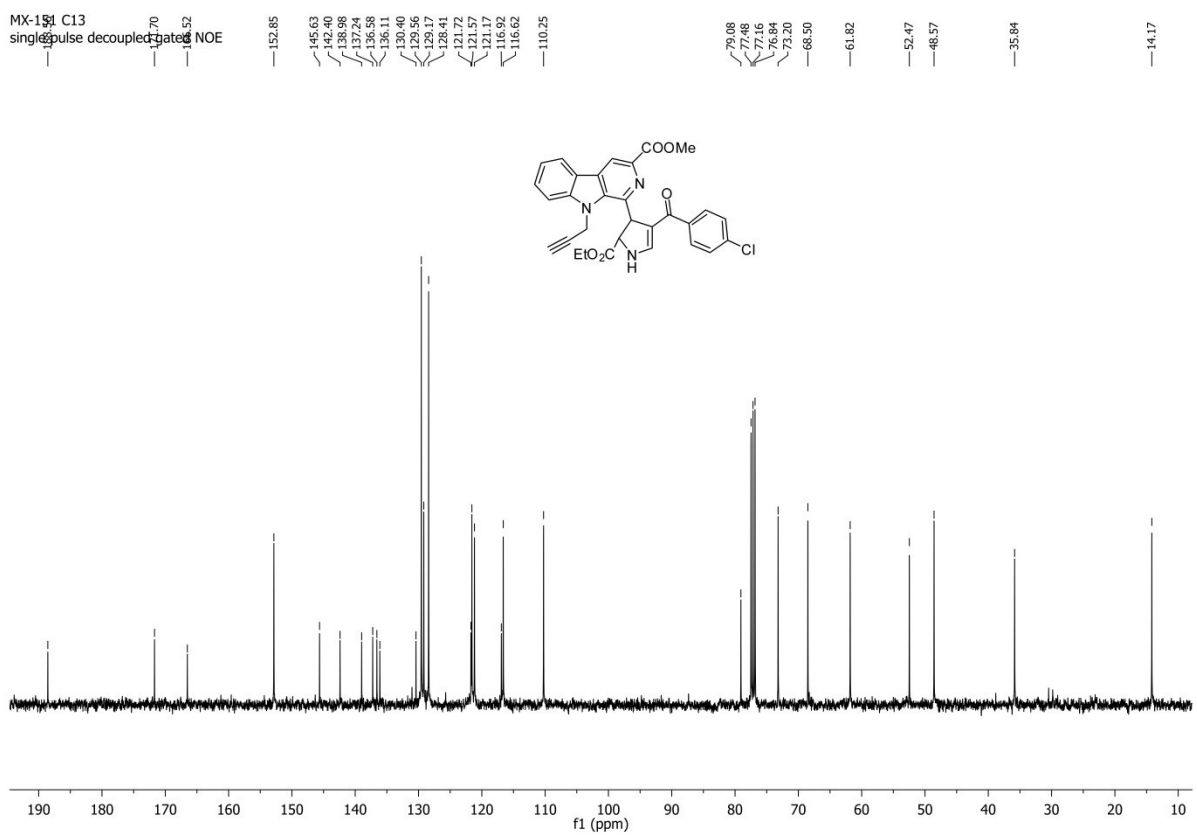


Figure S44.  $^{13}\text{C-NMR}$  spectrum of **6aD** in  $\text{CDCl}_3$ .

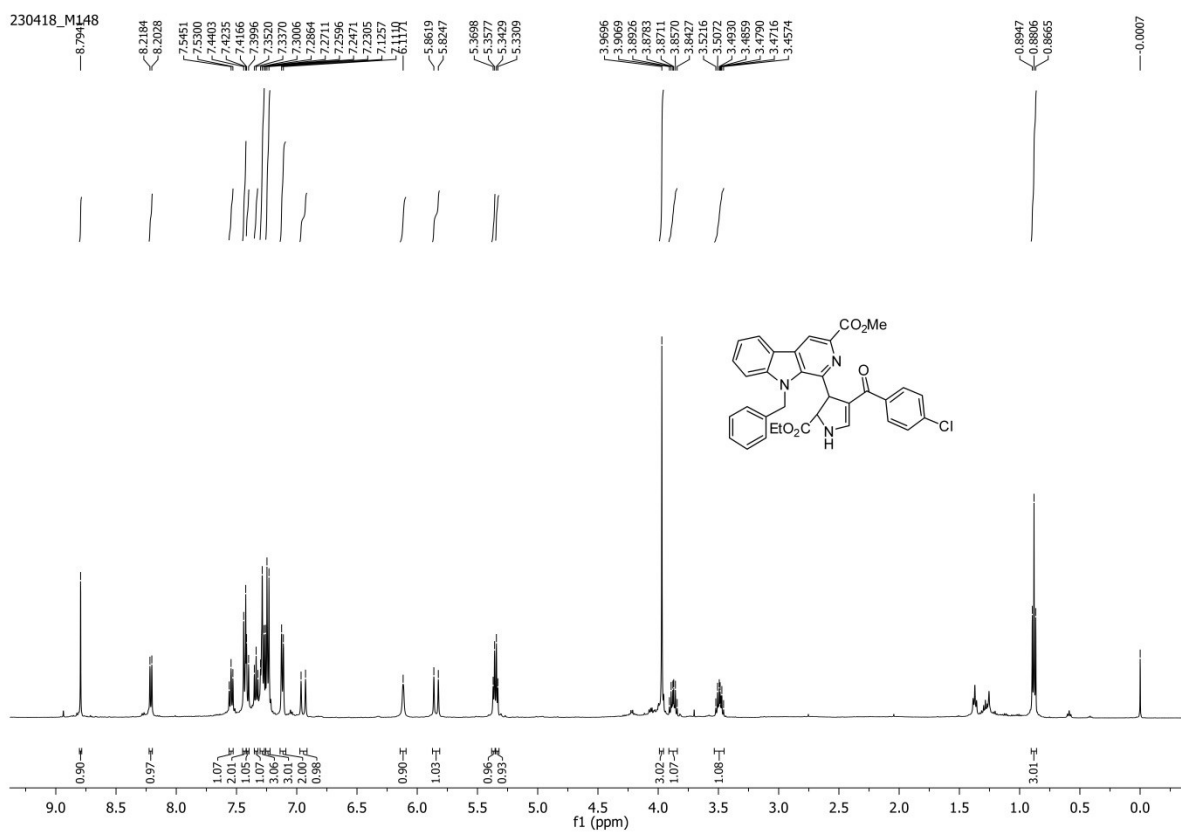


Figure S45. <sup>1</sup>H-NMR spectrum of **7aD** in CDCl<sub>3</sub>.

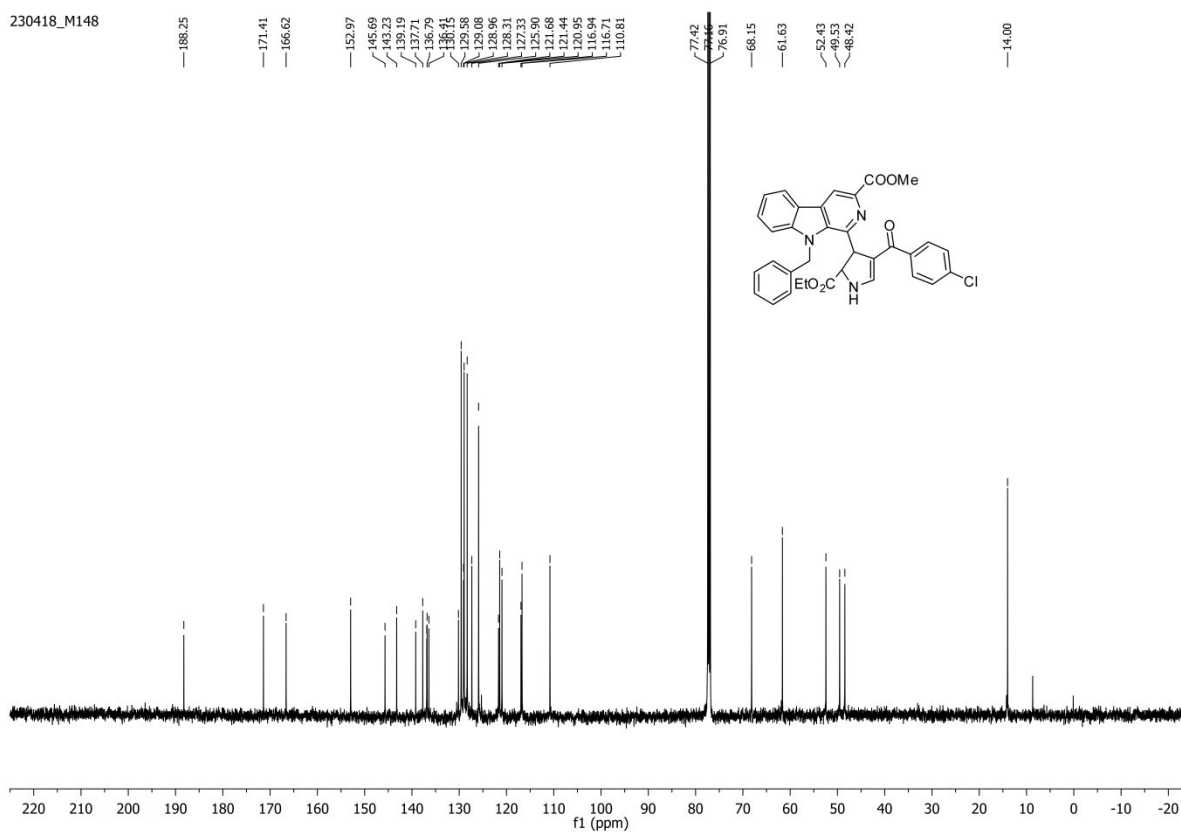


Figure S46. <sup>13</sup>C-NMR spectrum of **7aD** in CDCl<sub>3</sub>.

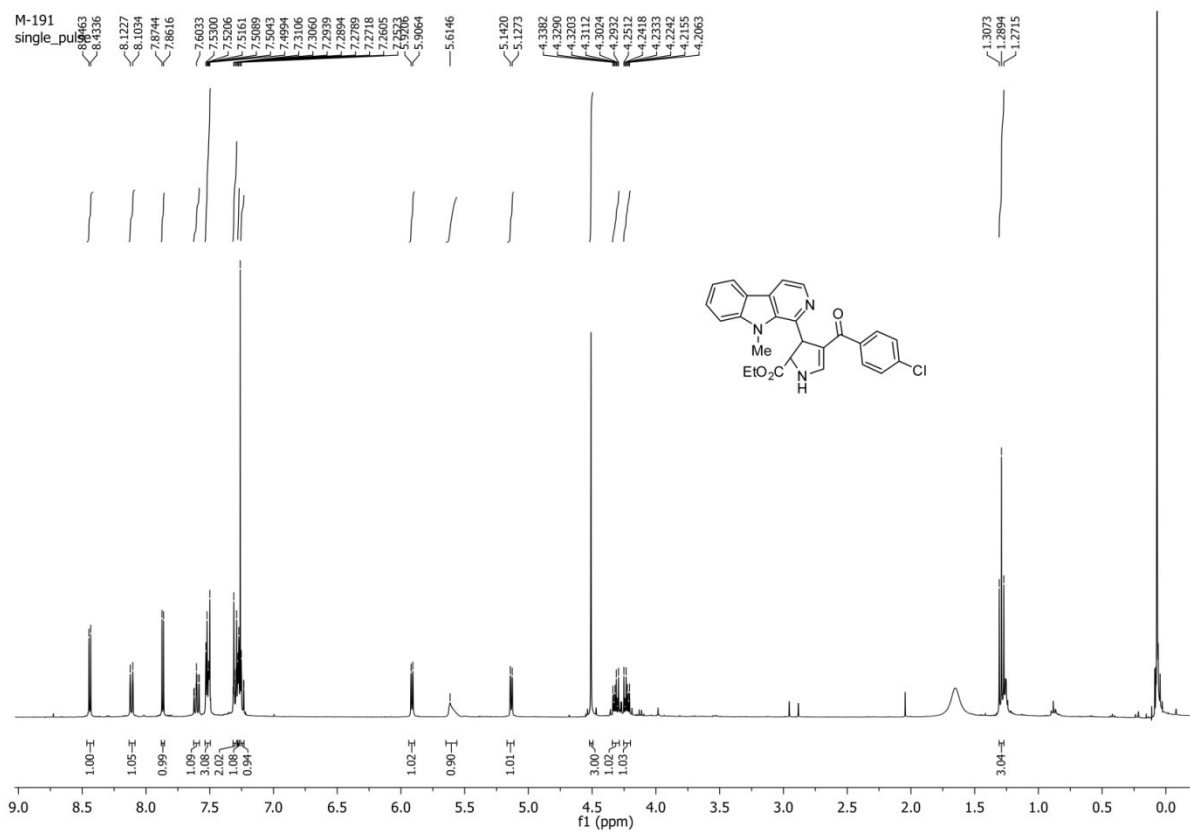


Figure S47.  $^1\text{H-NMR}$  spectrum of **9aD** in  $\text{CDCl}_3$ .

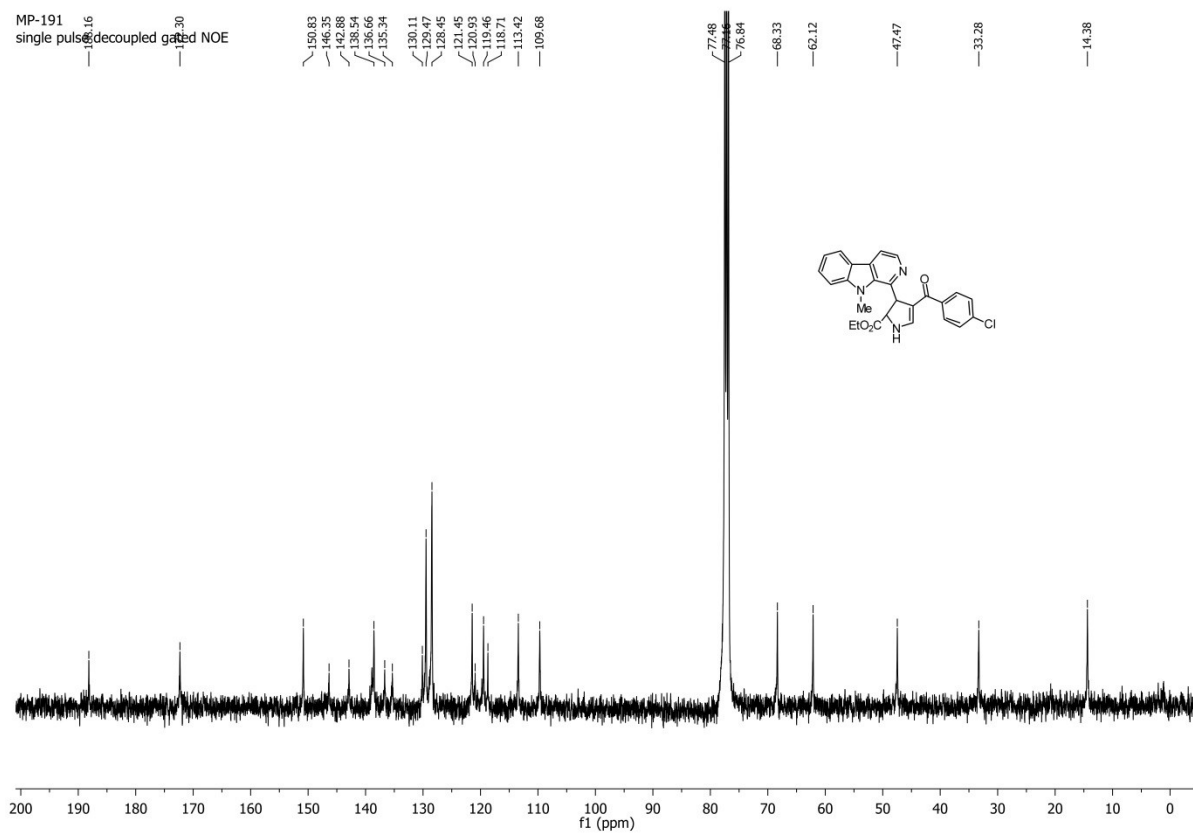


Figure S48.  $^{13}\text{C-NMR}$  spectrum of **9aD** in  $\text{CDCl}_3$ .

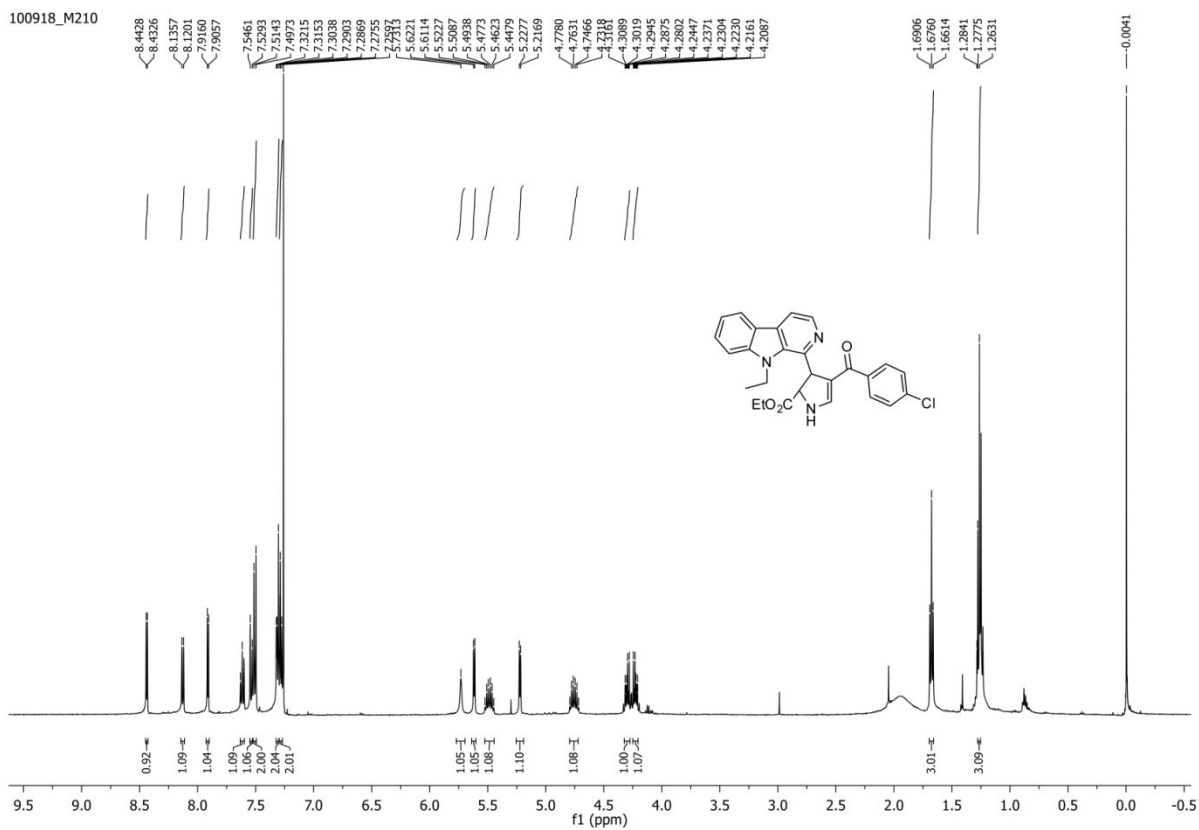


Figure S49.  $^1\text{H-NMR}$  spectrum of **10aD** in  $\text{CDCl}_3$ .

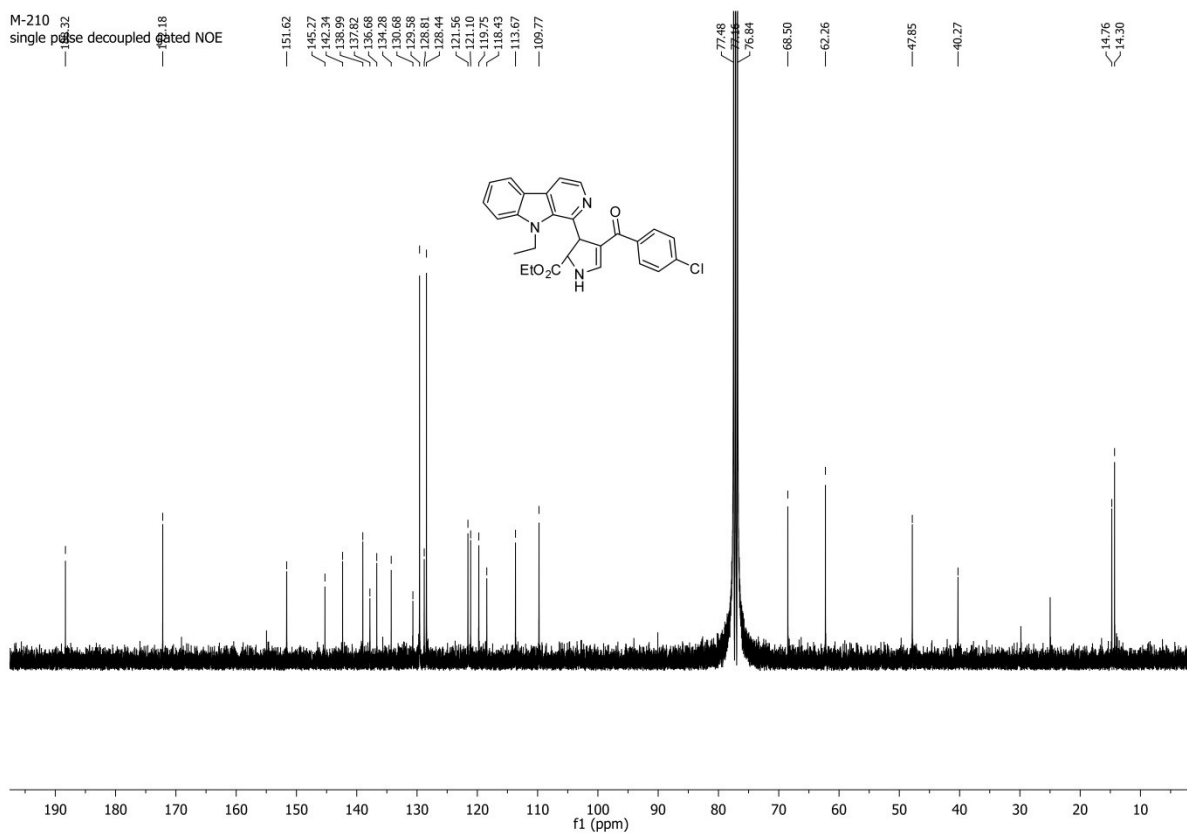


Figure S50.  $^{13}\text{C-NMR}$  spectrum of **10aD** in  $\text{CDCl}_3$ .

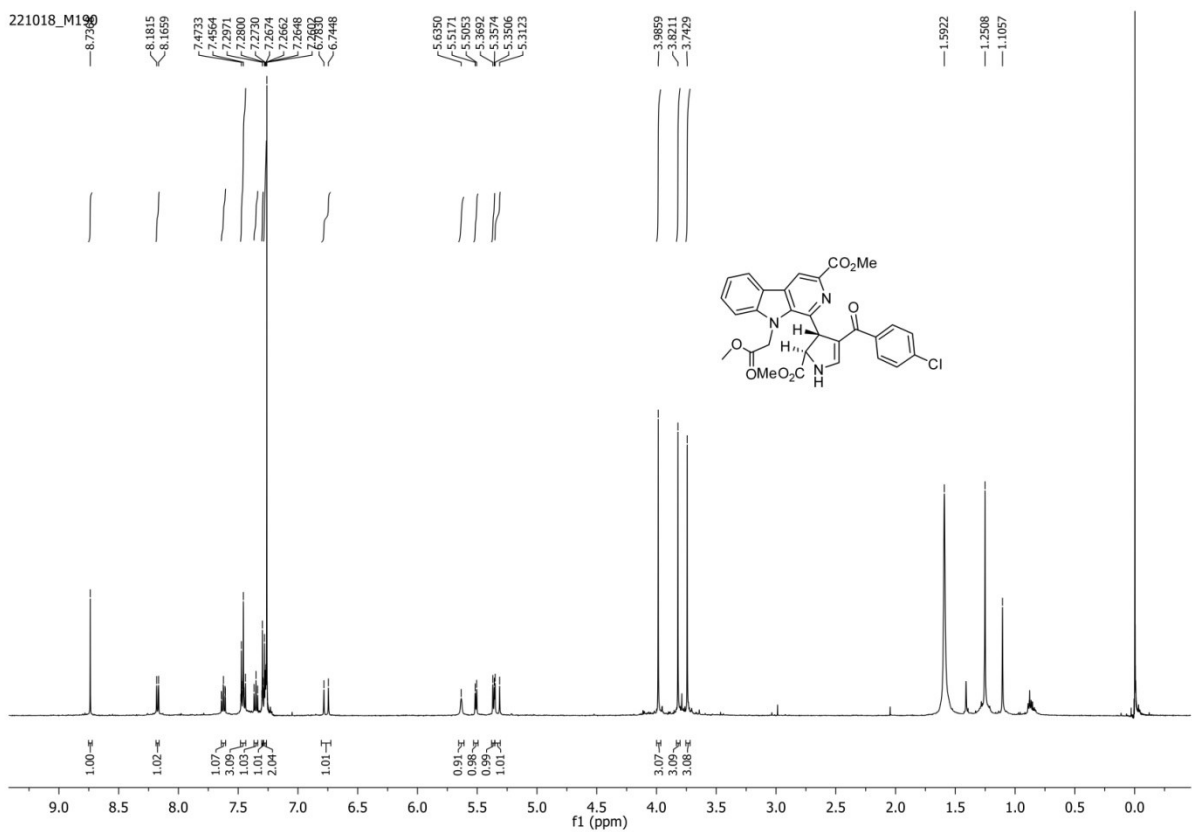


Figure S51.  $^1\text{H-NMR}$  spectrum of **8bD** in  $\text{CDCl}_3$ .

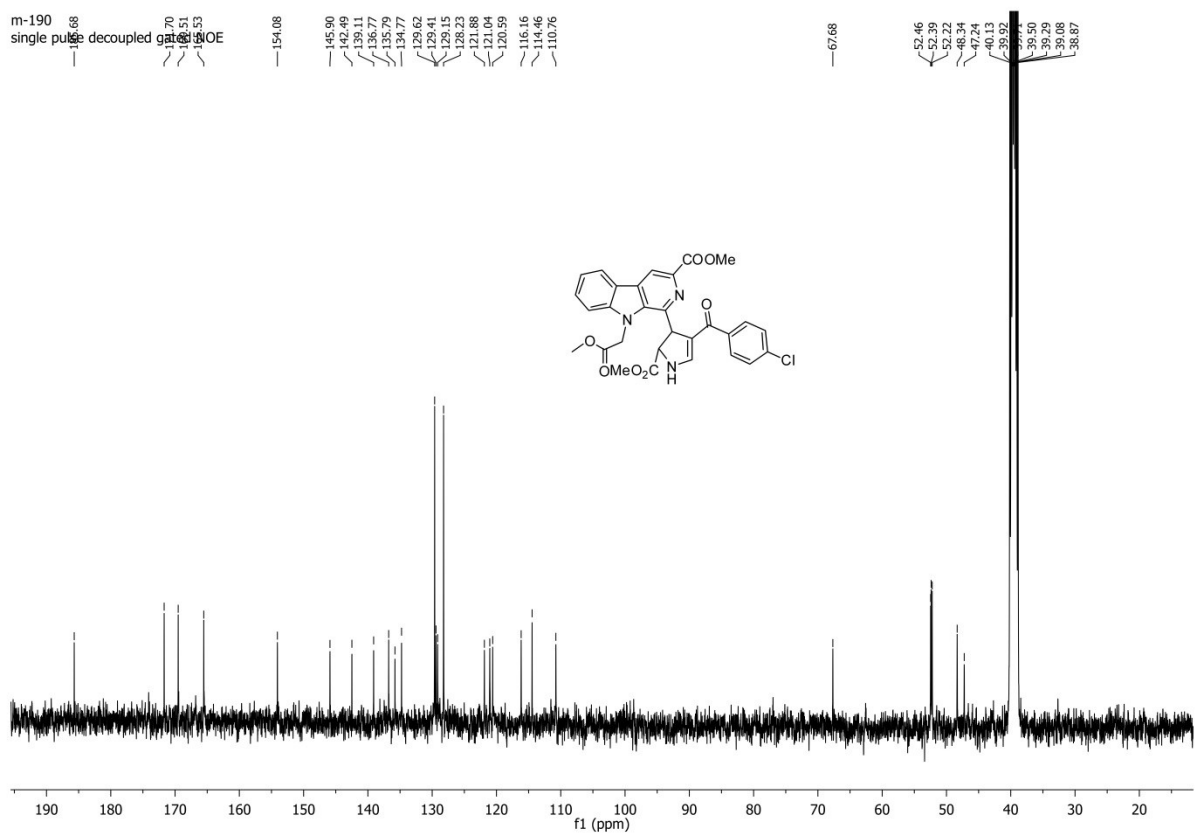
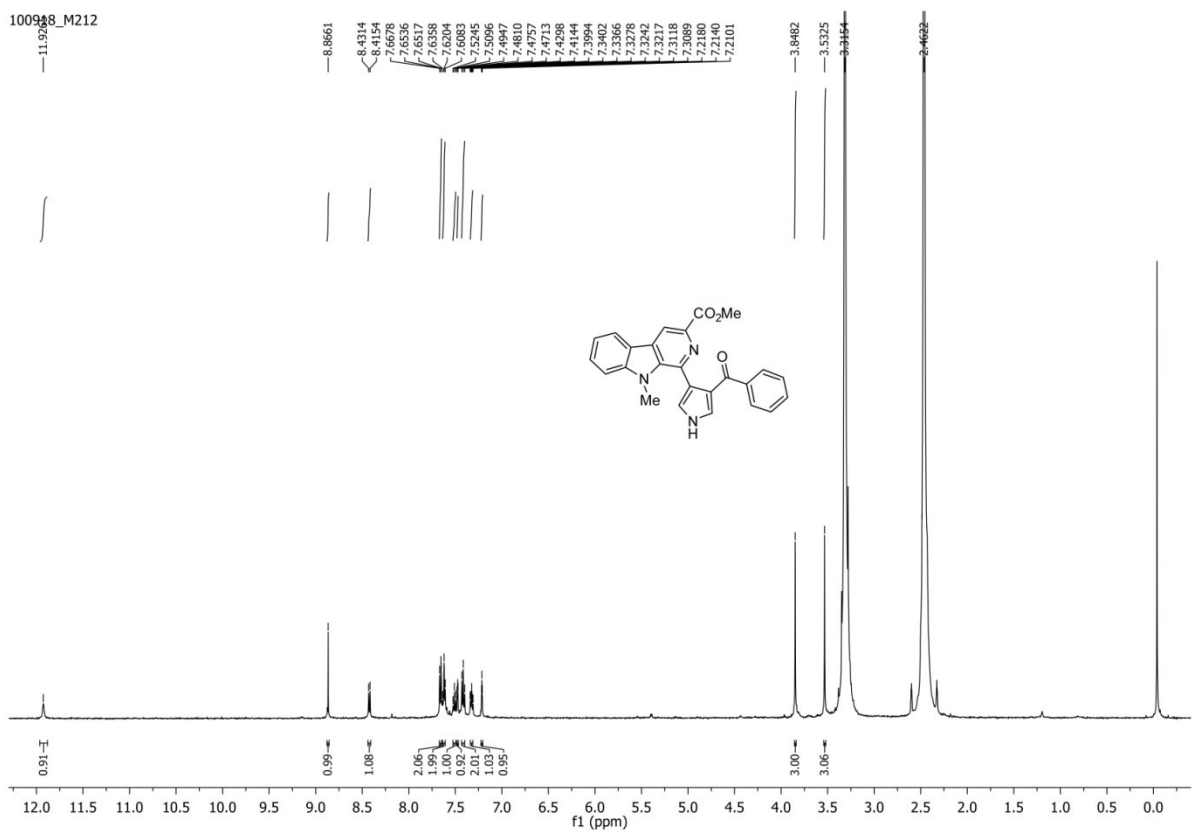
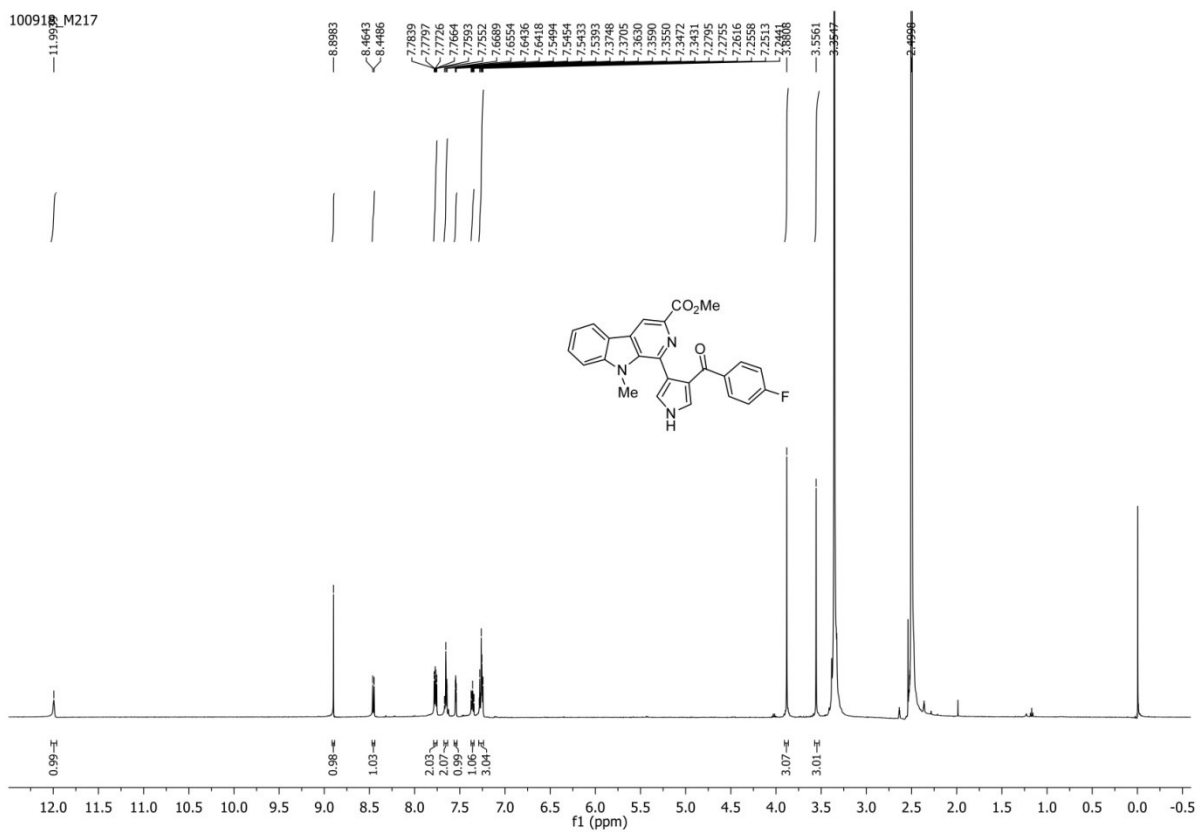


Figure S52.  $^{13}\text{C-NMR}$  spectrum of **8bD** in  $\text{DMSO-d}_6$ .



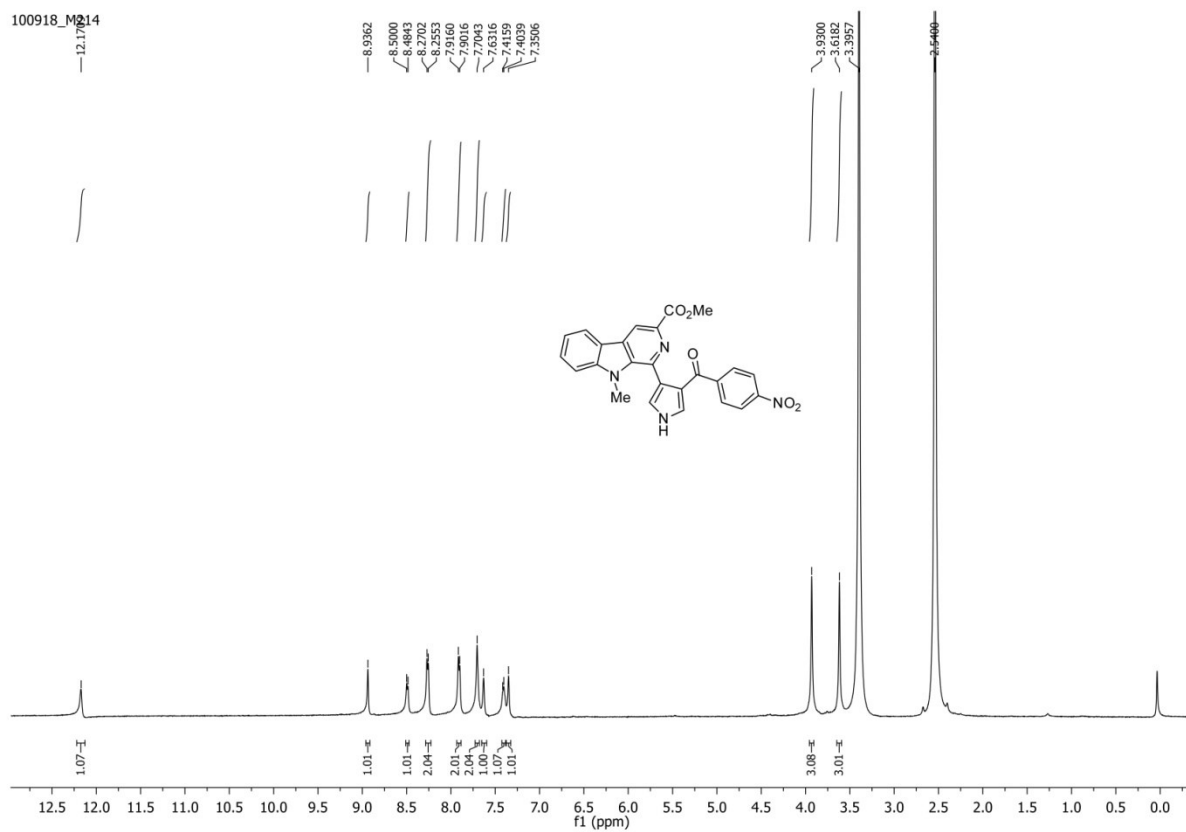
**Figure S53.** <sup>1</sup>H-NMR spectrum of **1cA** in DMSO-*d*<sub>6</sub>.

It is mentioned that the <sup>13</sup>C-NMR spectrum of **1cA** could not be recorded due to solubility problem in CDCl<sub>3</sub> as well as DMSO-*d*<sub>6</sub>.



**Figure S54.** <sup>1</sup>H-NMR spectrum of **1cF** in DMSO-*d*<sub>6</sub>.

It is mentioned that the <sup>13</sup>C-NMR spectrum of **1cF** could not be recorded due to solubility problem in CDCl<sub>3</sub> as well as DMSO-*d*<sub>6</sub>.



**Figure S55.** <sup>1</sup>H-NMR spectrum of **1cG** in DMSO-*d*<sub>6</sub>.

It is mentioned that the <sup>13</sup>C-NMR spectrum of **1cG** could not be recorded due to solubility problem in CDCl<sub>3</sub> as well as DMSO-*d*<sub>6</sub>.



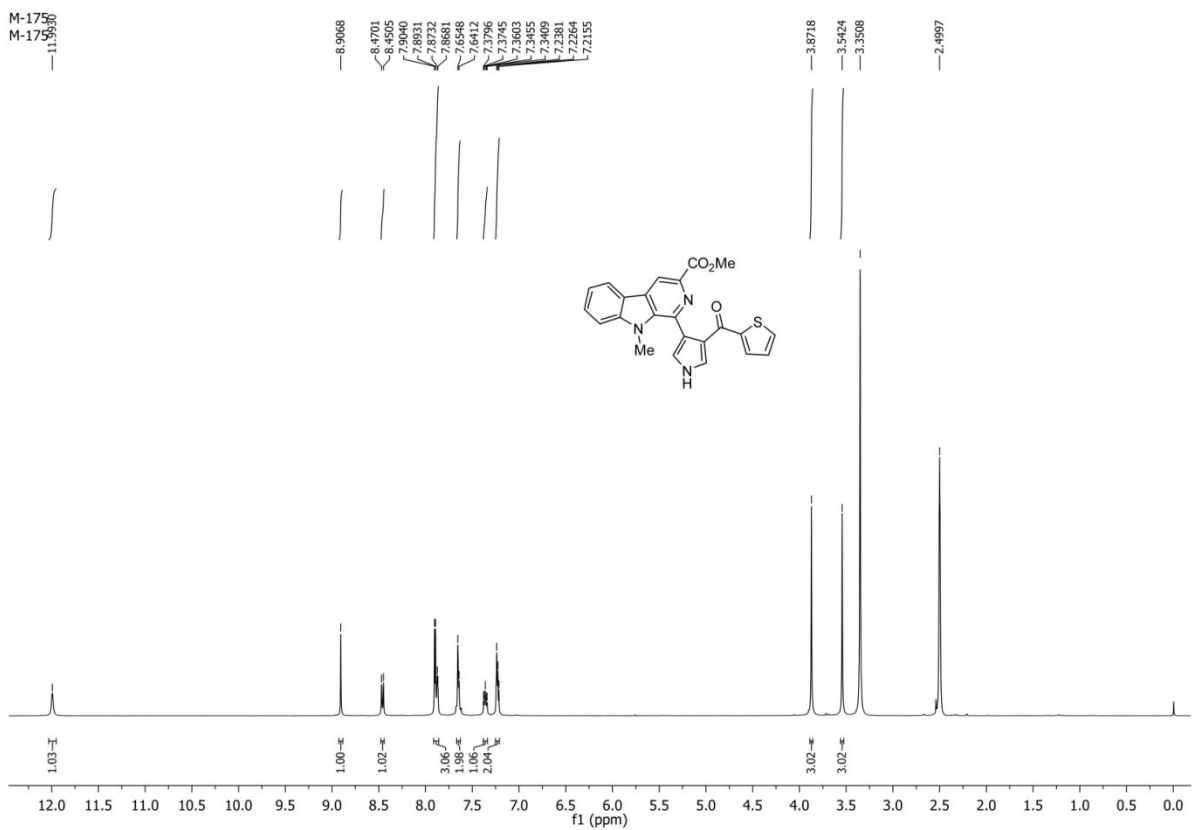


Figure S56.  $^1\text{H-NMR}$  spectrum of **1cI** in  $\text{DMSO-d}_6$ .

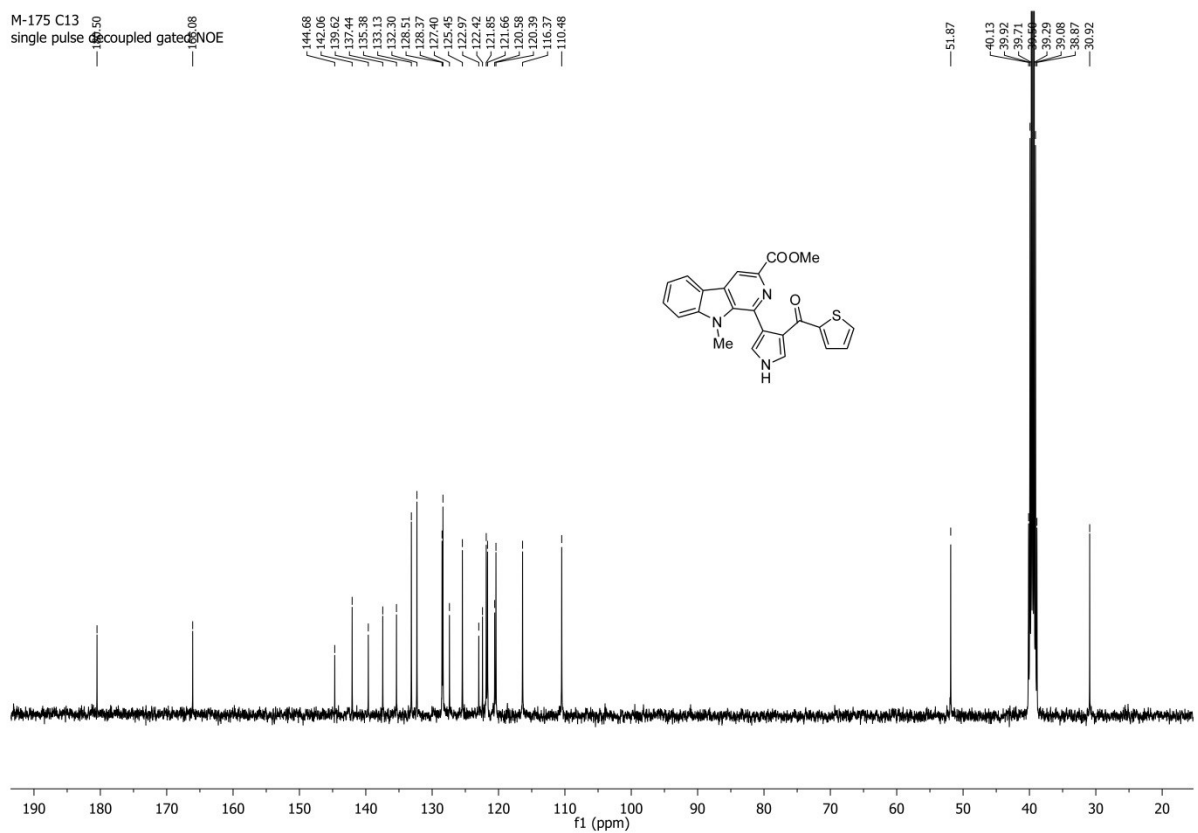
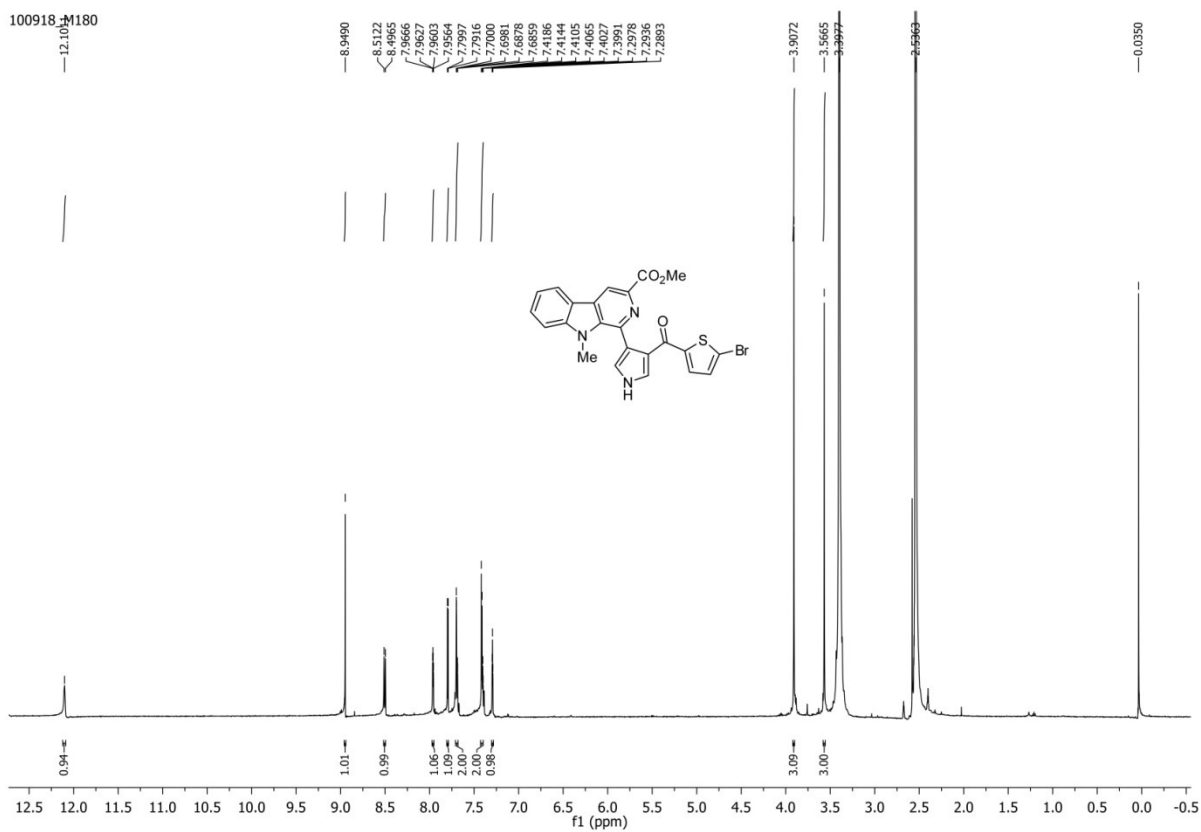


Figure S57.  $^{13}\text{C-NMR}$  spectrum of **1cI** in  $\text{DMSO-d}_6$ .



**Figure S58.**  $^1\text{H}$ -NMR spectrum of **1cJ** in  $\text{DMSO-}d_6$ .

It is mentioned that the  $^{13}\text{C}$ -NMR spectrum of **1cJ** could not be recorded due to solubility problem in  $\text{CDCl}_3$  as well as  $\text{DMSO-}d_6$ .

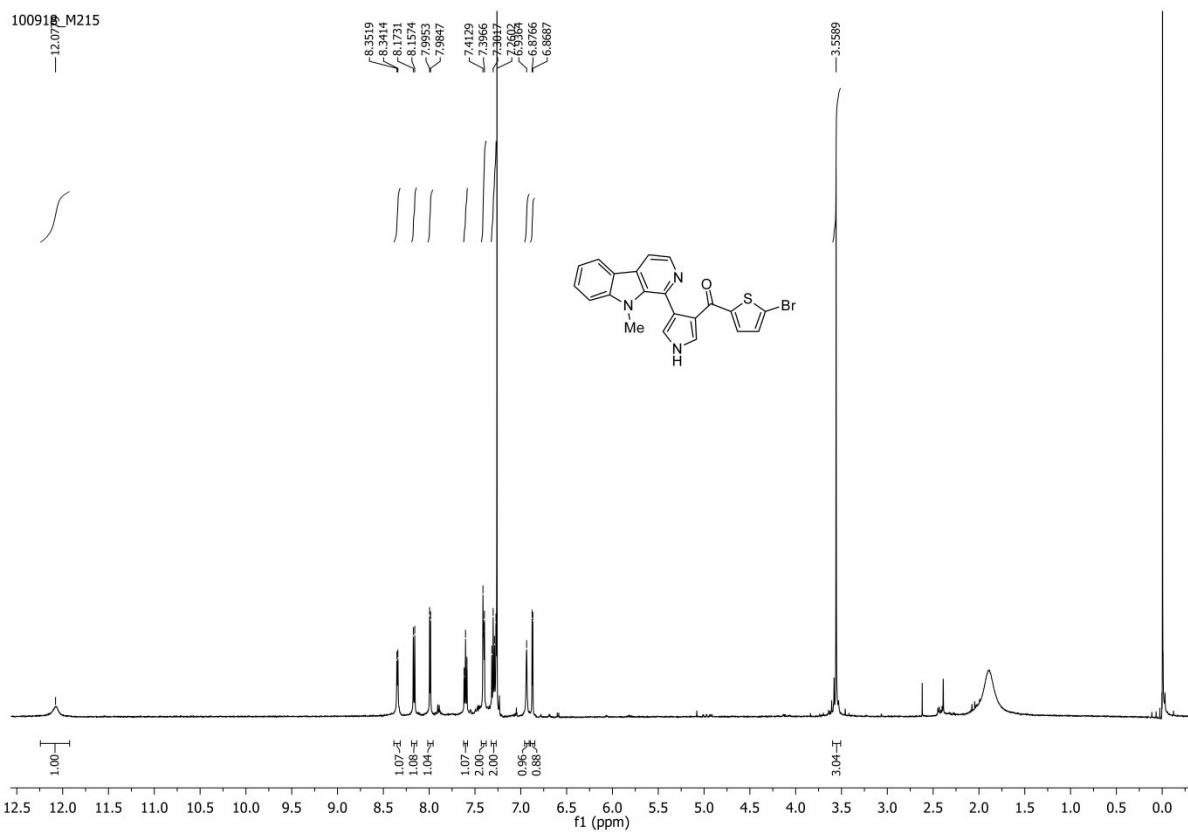


Figure S59.  $^1\text{H-NMR}$  spectrum of **9cJ** in  $\text{CDCl}_3$ .

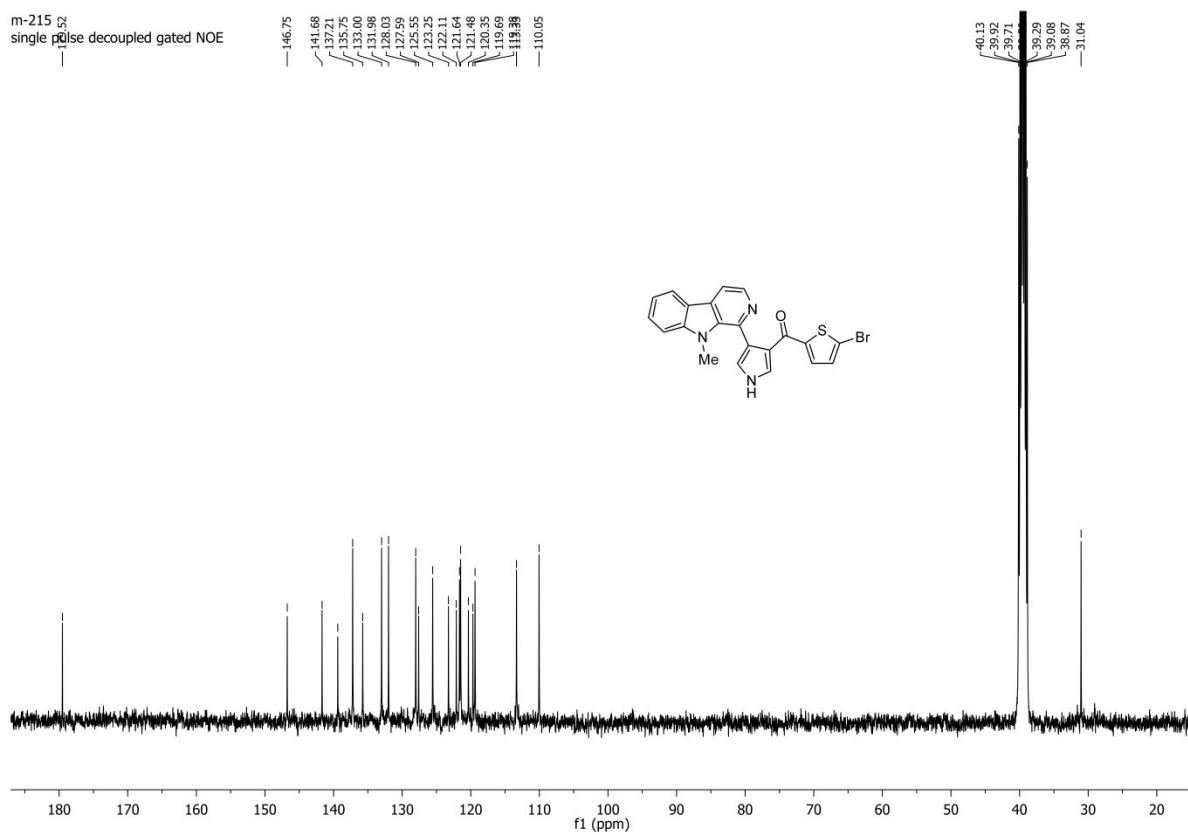


Figure S60.  $^{13}\text{C-NMR}$  spectrum of **9cJ** in  $\text{DMSO-d}_6$ .

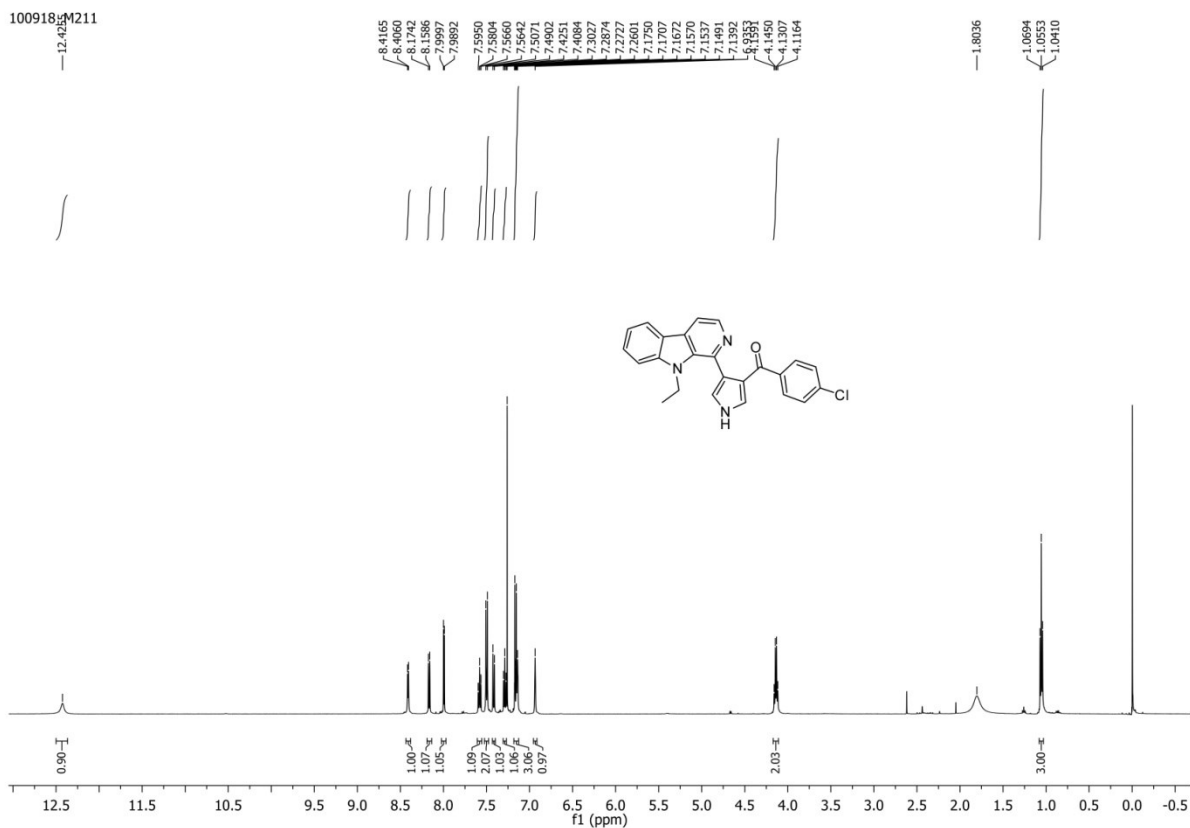


Figure S61.  $^1\text{H-NMR}$  spectrum of **10cD** in  $\text{CDCl}_3$ .

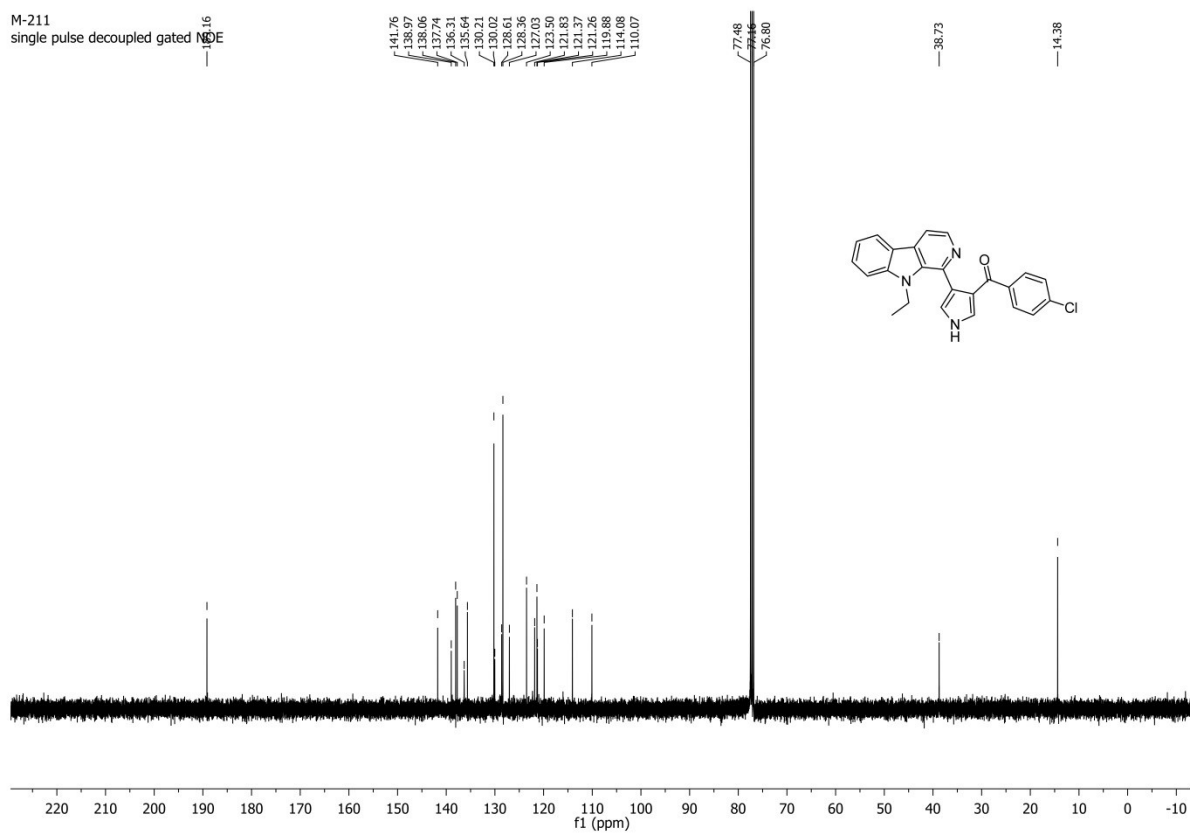


Figure S62.  $^{13}\text{C-NMR}$  spectrum of **10cD** in  $\text{CDCl}_3$ .

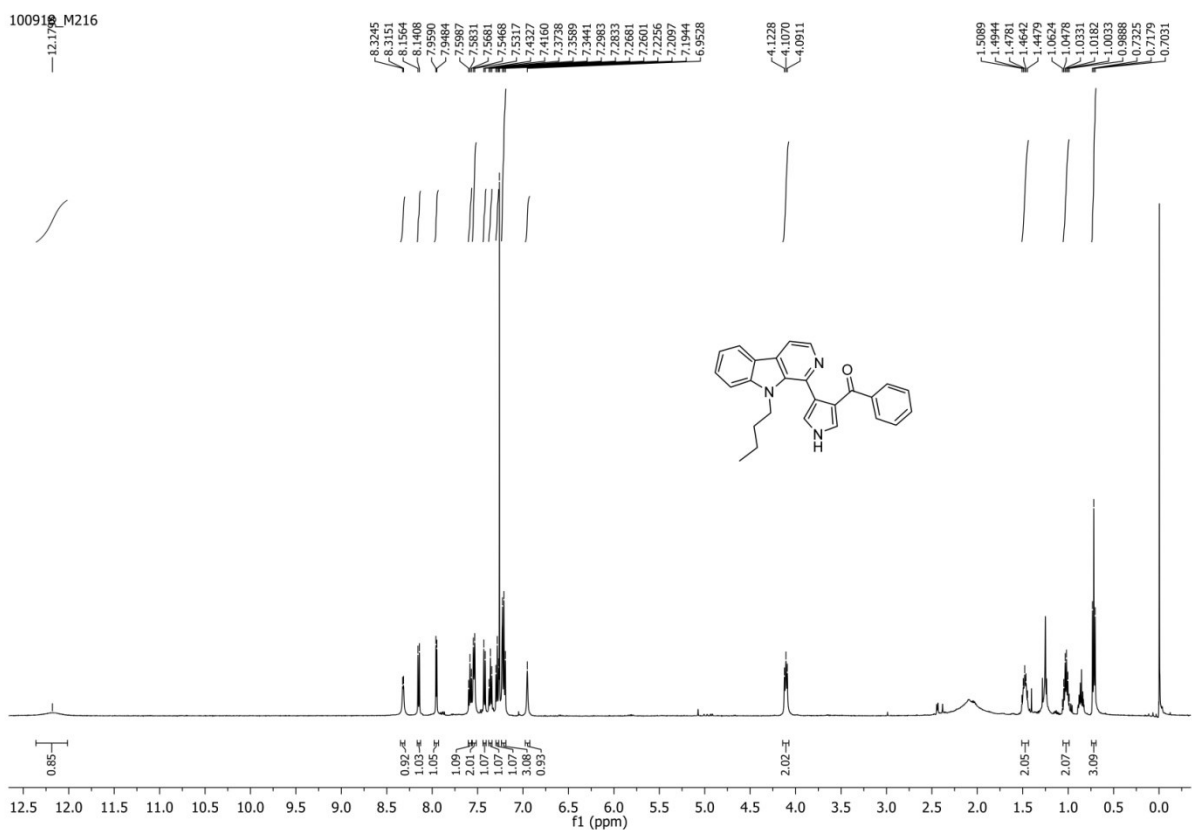


Figure S63.  $^1\text{H-NMR}$  spectrum of **11cA** in  $\text{CDCl}_3$ .

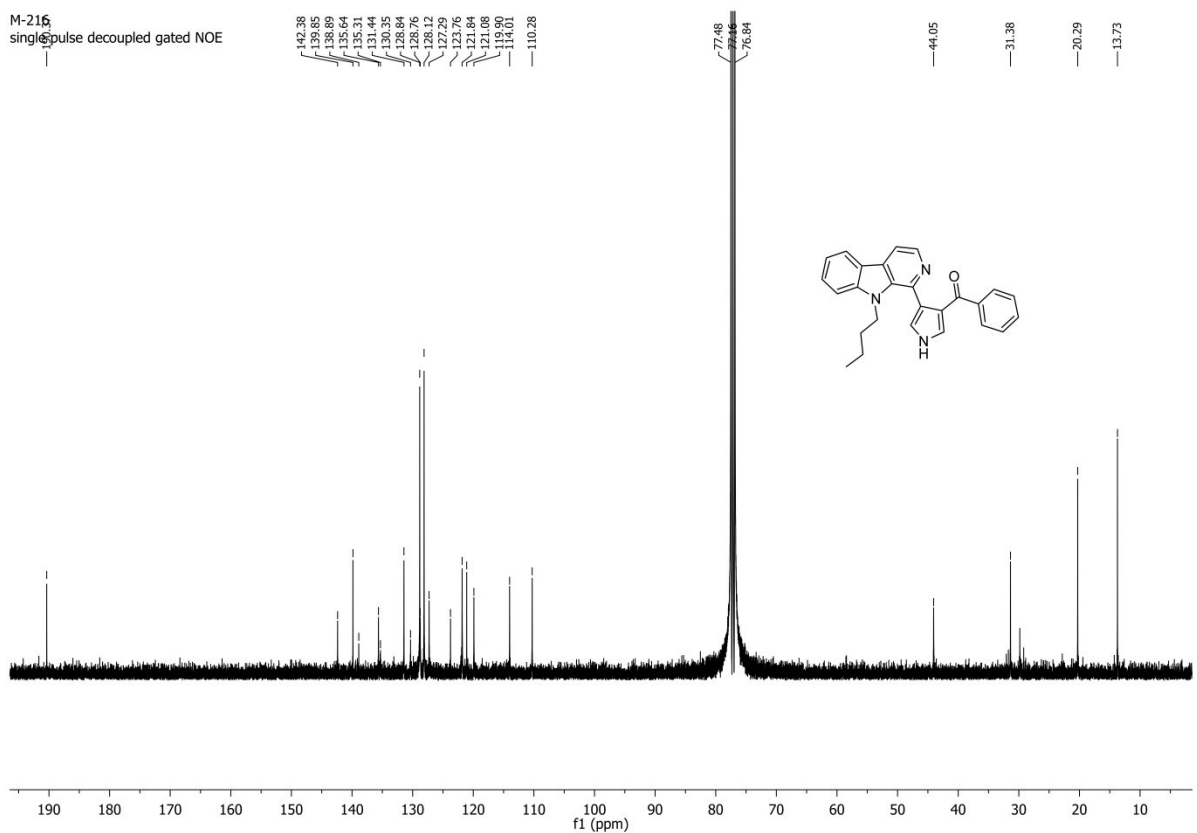


Figure S64.  $^{13}\text{C-NMR}$  spectrum of **11cA** in  $\text{CDCl}_3$ .

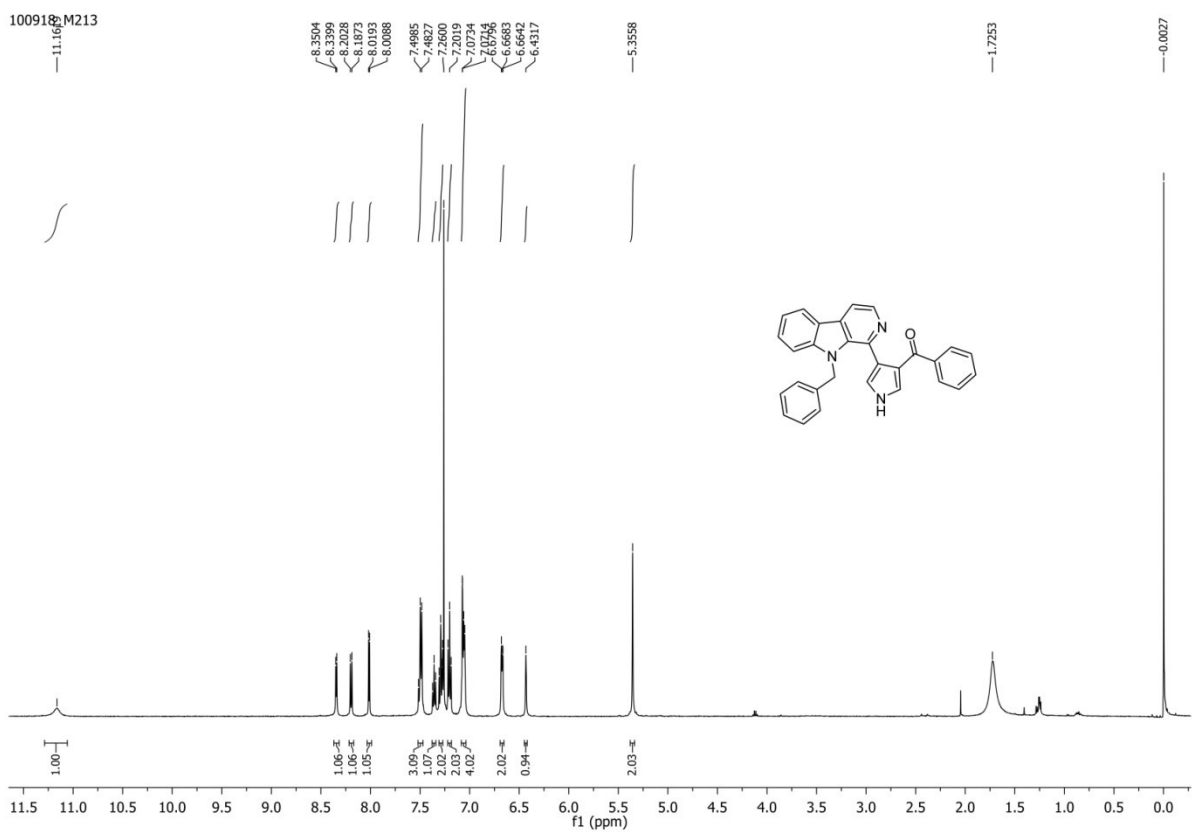


Figure S65.  $^1\text{H-NMR}$  spectrum of **12cA** in  $\text{CDCl}_3$ .

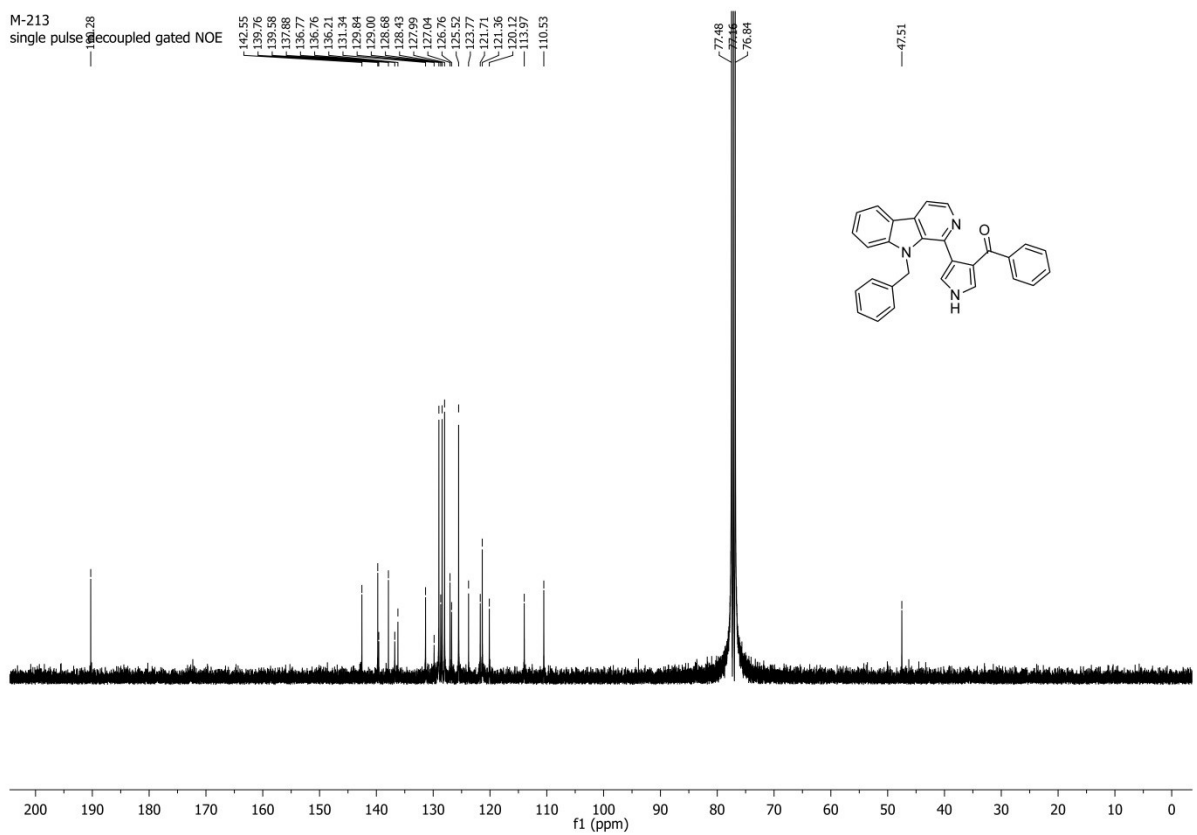


Figure S66.  $^{13}\text{C-NMR}$  spectrum of **12cA** in  $\text{CDCl}_3$ .

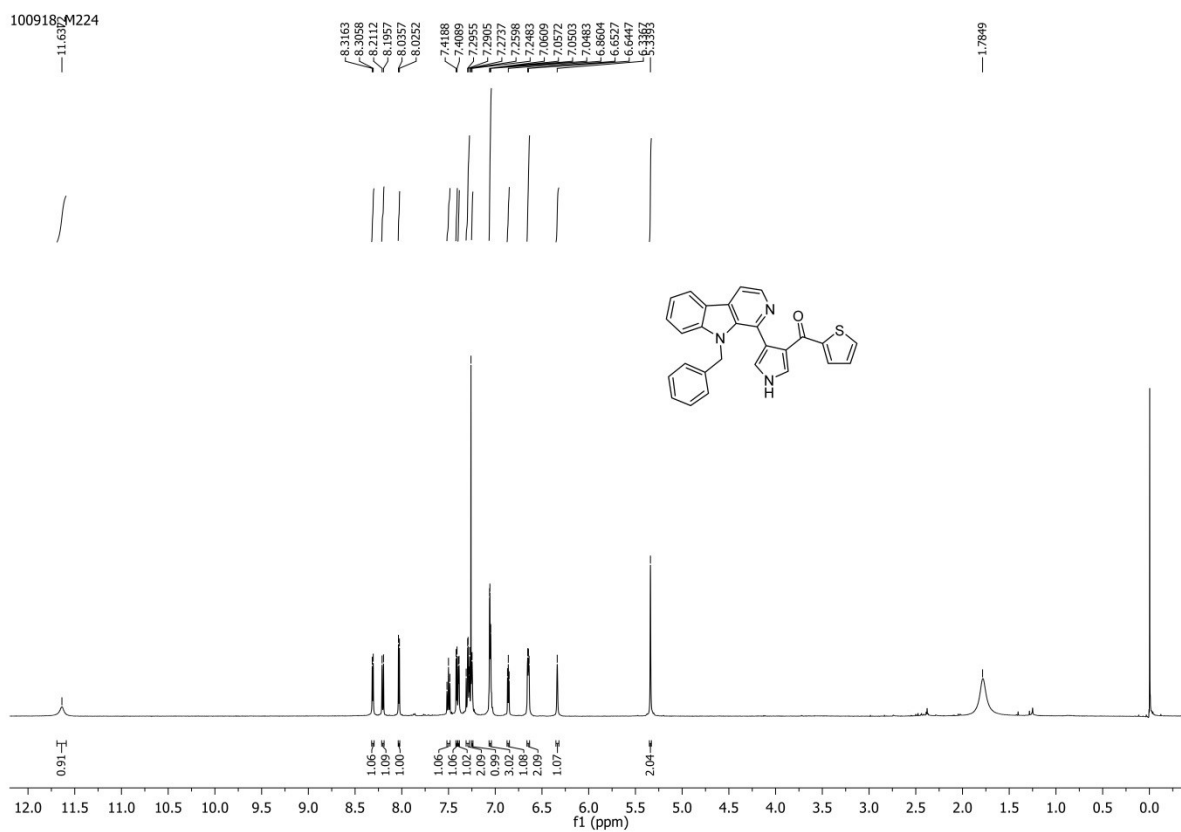


Figure S67.  $^1\text{H-NMR}$  spectrum of **12cI** in  $\text{CDCl}_3$ .

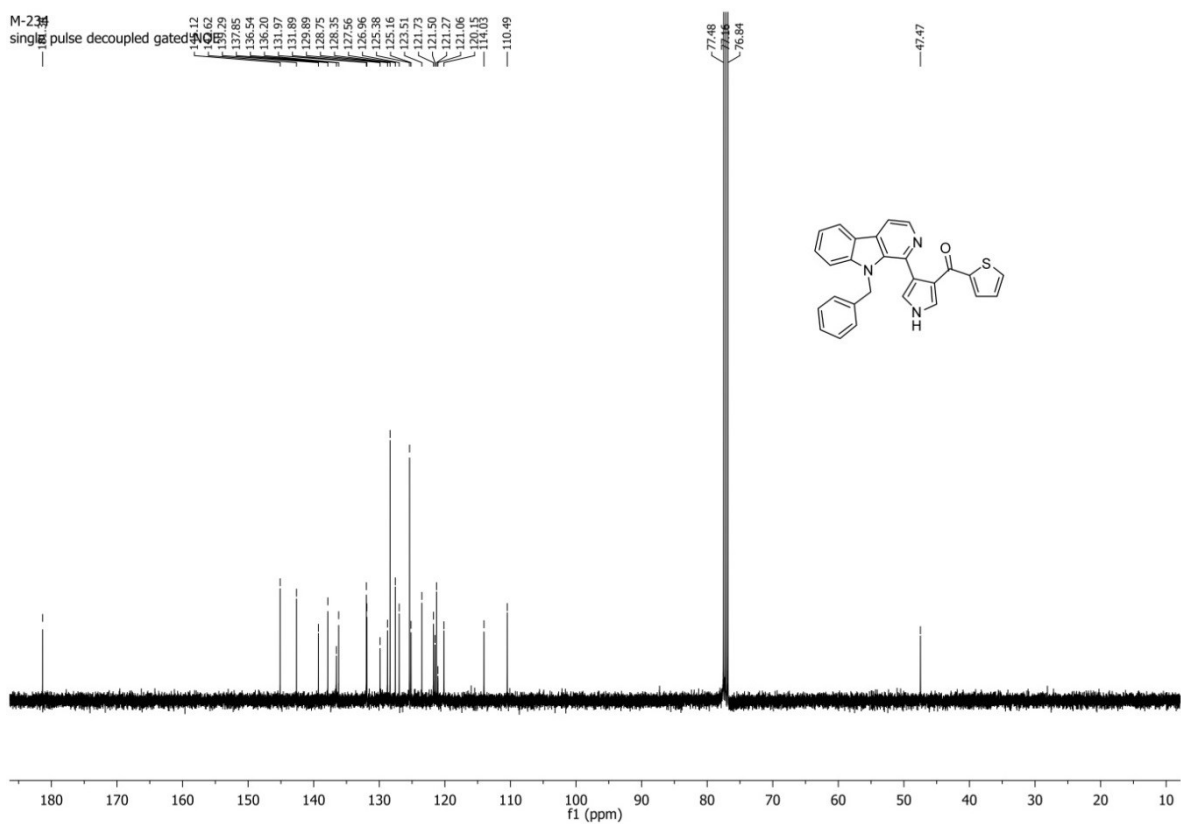


Figure S68.  $^{13}\text{C-NMR}$  spectrum of **12cI** in  $\text{CDCl}_3$ .