

## SUPPORTING INFORMATION

### Selective Synthesis of 5-Aryl-10-(Nitromethyl) Substituted 15-azatripyrrane, 15-oxatripyrrane, 15-thiatripyrrane: An Access to Nitromethyl Functionalized A<sub>3</sub>B-Porphyrins

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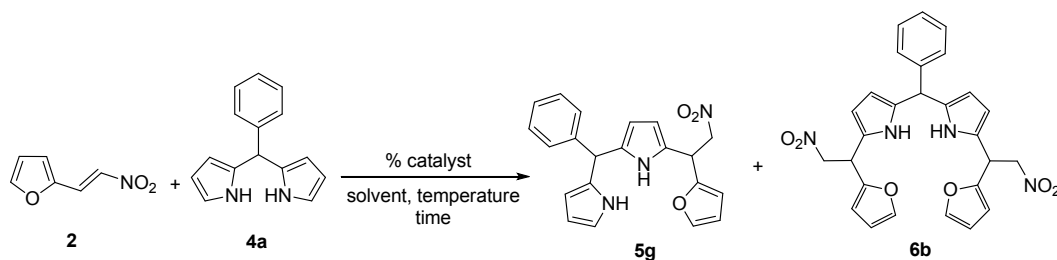
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1. Table S1. Optimization of the reaction conditions for the formation of 5g



Entry	Catalyst (mol %)	Mole ratio (2:4a)	Solvent	Time (h)	Yield (%) <sup>a</sup>	
					5g	6b
1	I <sub>2</sub> (10)	1:4	Ether	24	50	3
2	I <sub>2</sub> (10)	1:6	Ether	24	63	-
3	I <sub>2</sub> (10)	1:6	Ether	48	80	8
<b>4</b>	<b>I<sub>2</sub>(5)</b>	<b>1:6</b>	<b>Ether</b>	<b>48</b>	<b>82</b>	<b>3</b>
5	I <sub>2</sub> (20)	1:6	Ether	48	31	7
6	CAN (5)	1:6	Ether	48	77	trace
7	TsOH (5)	1:6	Ether	48	80	7
8	KHSO <sub>4</sub> (5)	1:6	Ether	48	79	5
9	no cat.	1:6	Ether	48	68	2
10	InCl <sub>3</sub> (5)	16	Ether	48	69	4
11	I <sub>2</sub> (5)	1:6	Ethanol	48	58	5
12	I <sub>2</sub> (5)	1:6	CH <sub>2</sub> Cl <sub>2</sub>	48	29	5
13	I <sub>2</sub> (5)	1:6	THF	48	61	3
14	I <sub>2</sub> (5)	1:6	H <sub>2</sub> O	48	25	26

## 2. NMR Spectra of compounds 5a-l and 6a-e

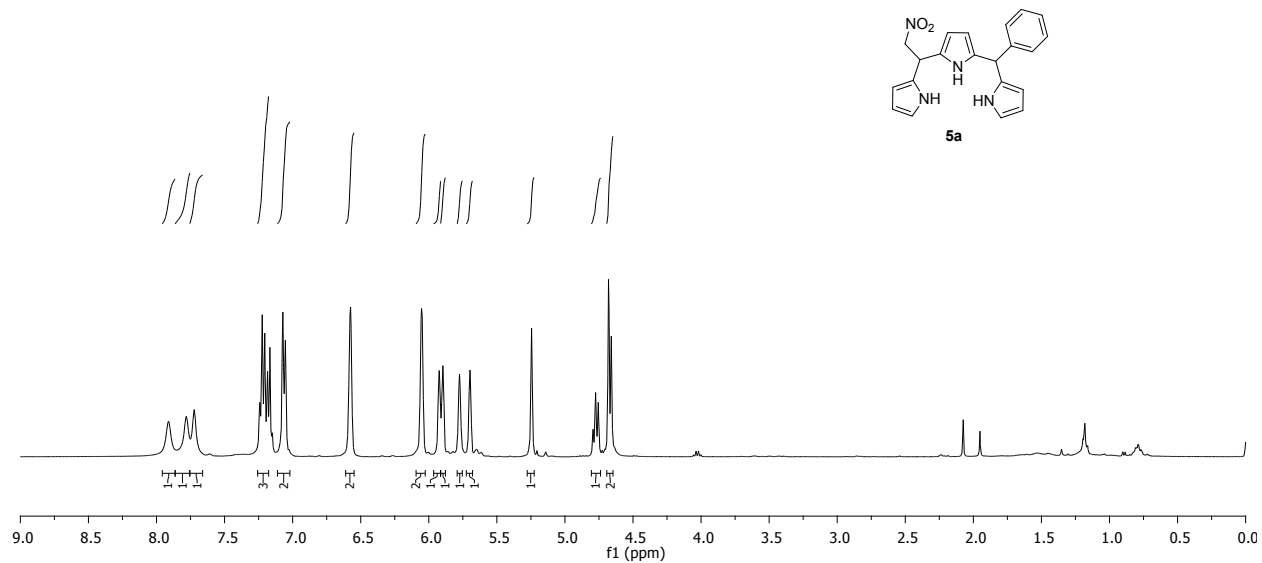


Figure S1. <sup>1</sup>H NMR spectrum of **5a** (Solvent: CDCl<sub>3</sub>)

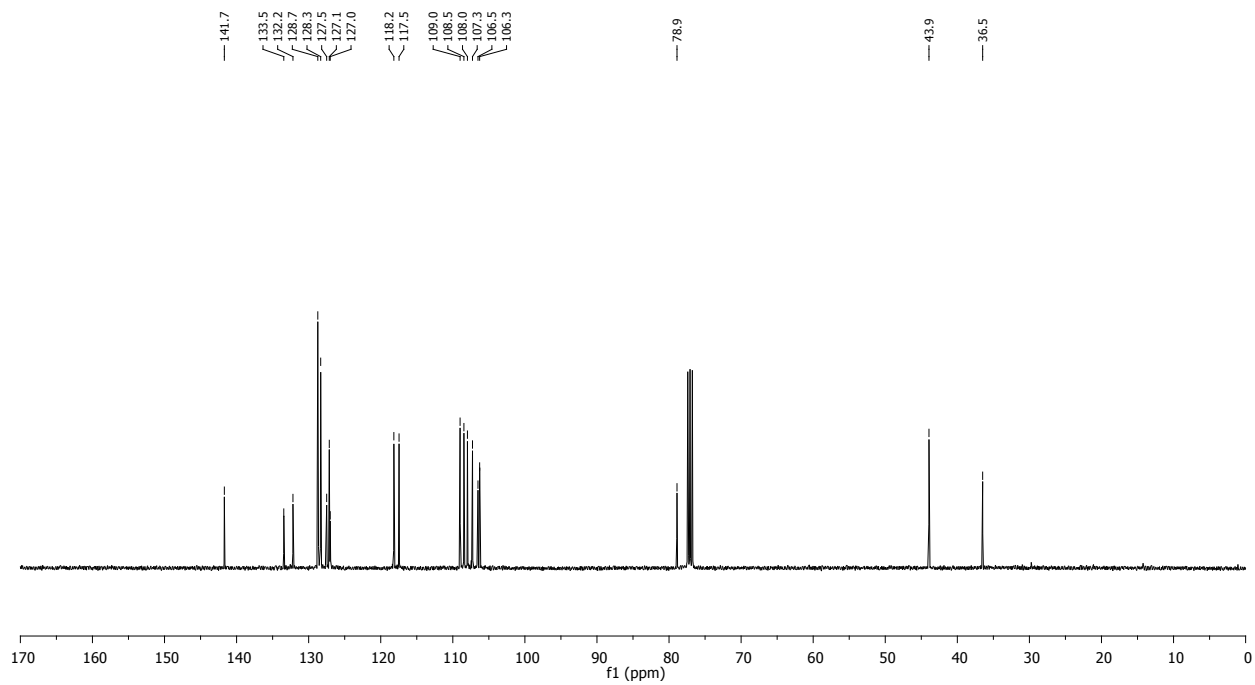


Figure S2. <sup>13</sup>C NMR spectrum of **5a** (Solvent: CDCl<sub>3</sub>)

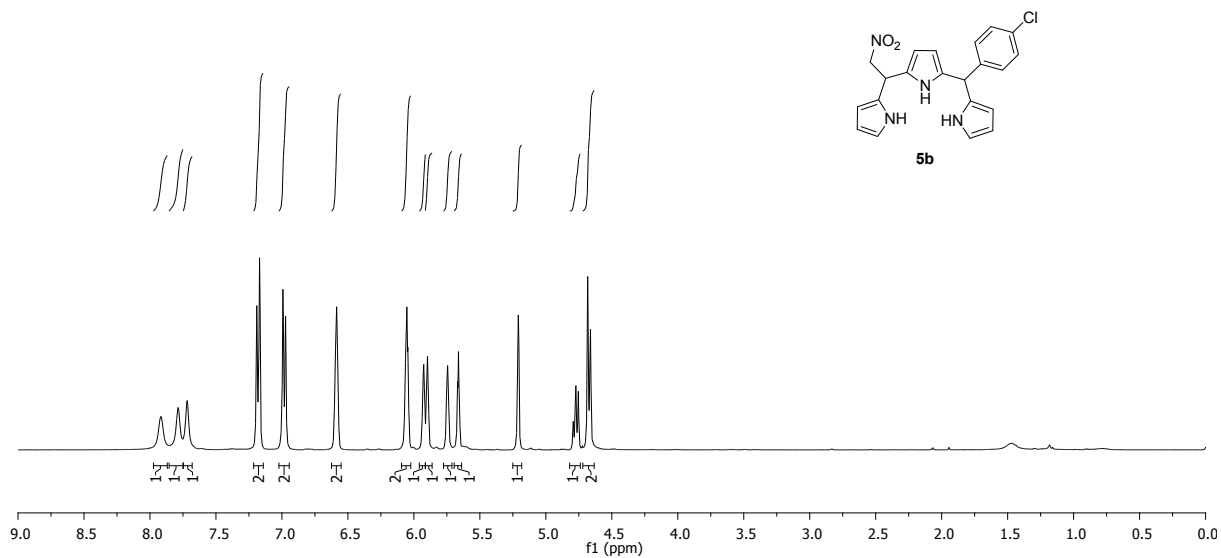


Figure S3. <sup>1</sup>H NMR spectrum of **5b** (Solvent: CDCl<sub>3</sub>)

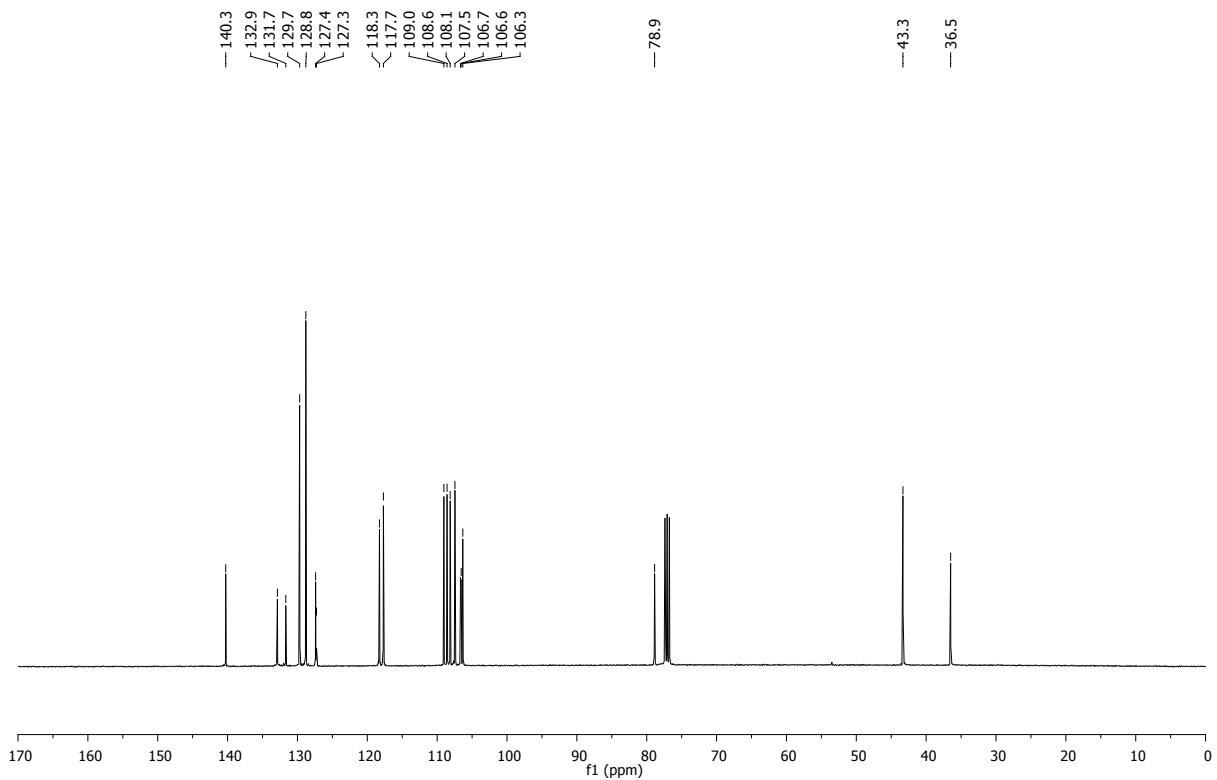


Figure S4. <sup>13</sup>C NMR spectrum of **5b** (Solvent: CDCl<sub>3</sub>)

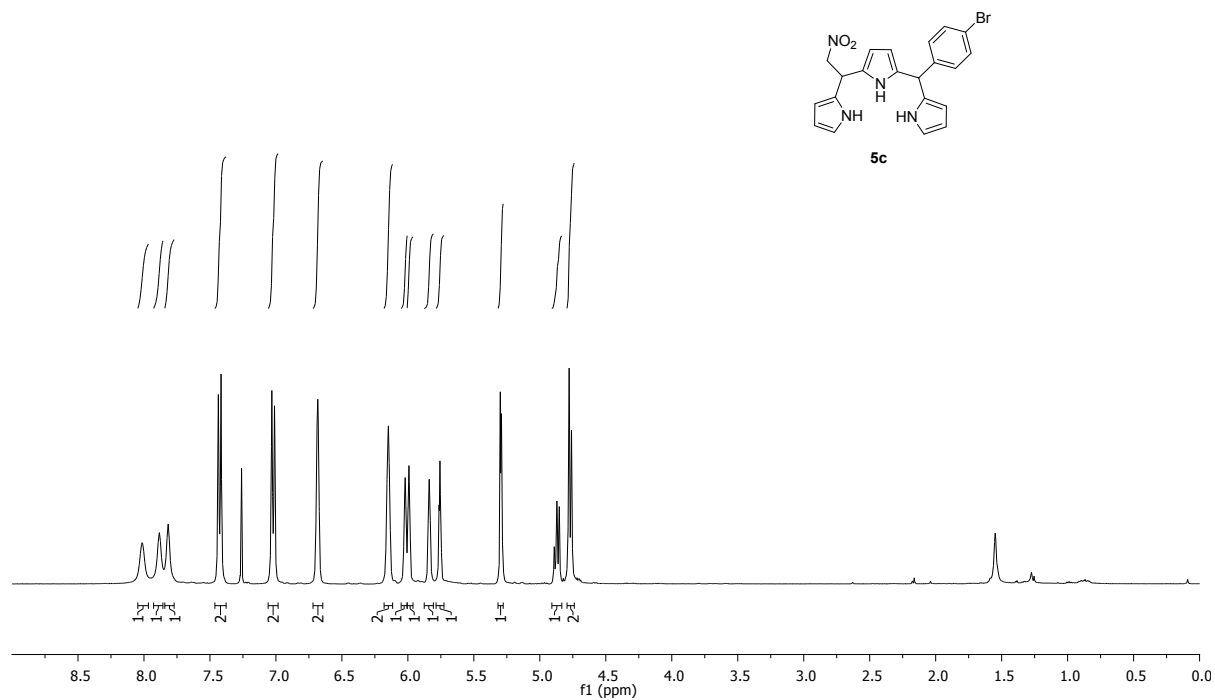


Figure S5. <sup>1</sup>H NMR spectrum of **5c** (Solvent: CDCl<sub>3</sub>)

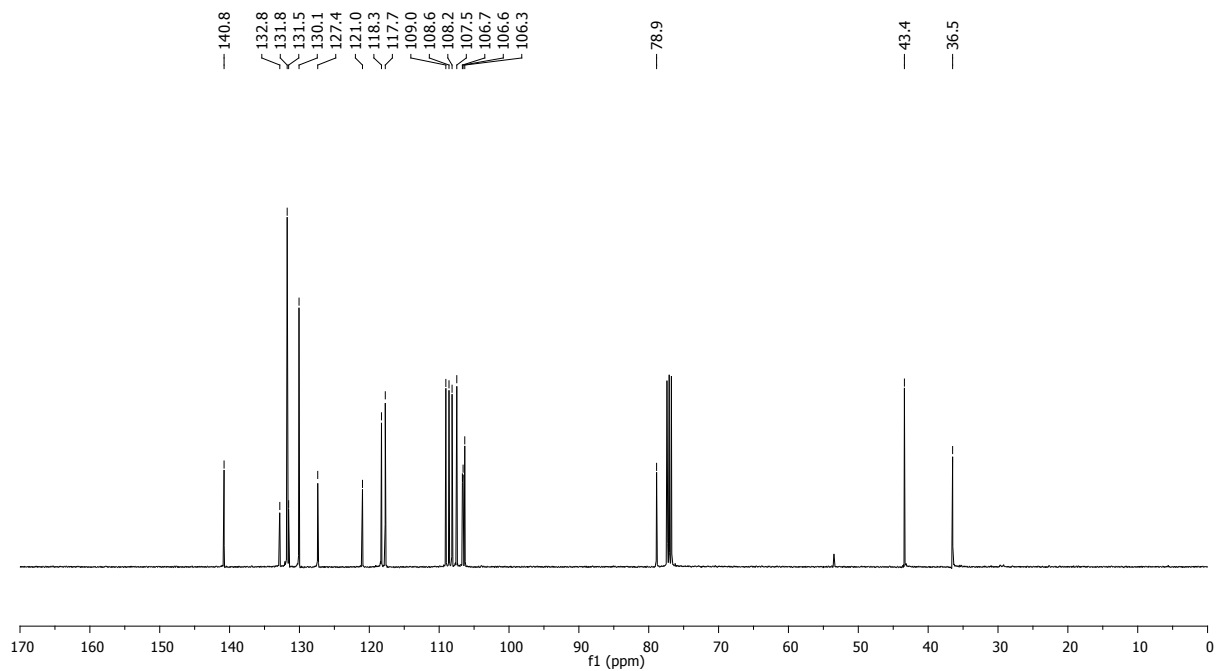


Figure S6. <sup>13</sup>C NMR spectrum of **5c** (Solvent: CDCl<sub>3</sub>)

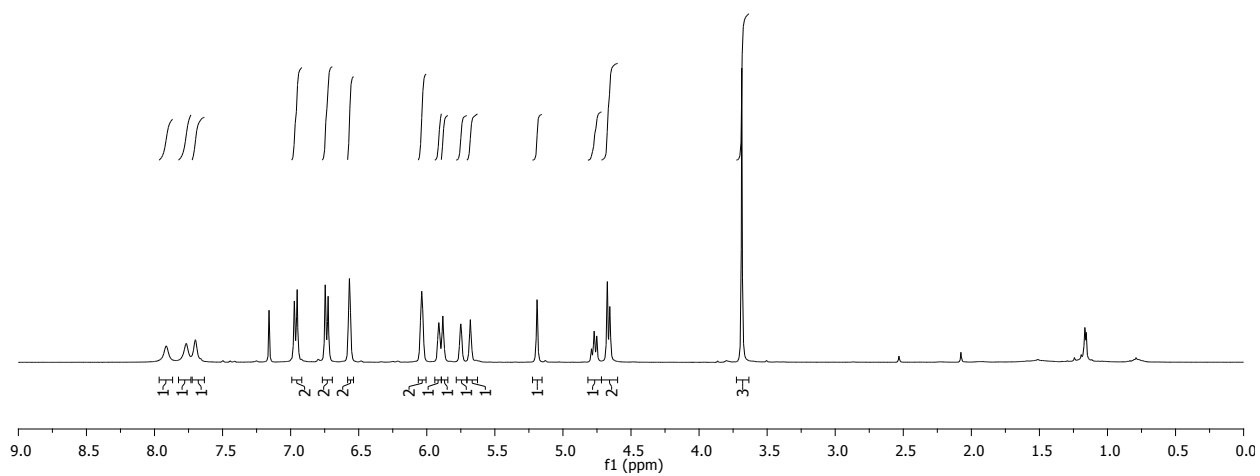
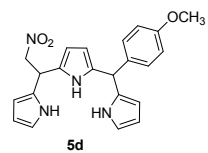


Figure S7. <sup>1</sup>H NMR spectrum of **5d** (Solvent: CDCl<sub>3</sub>)

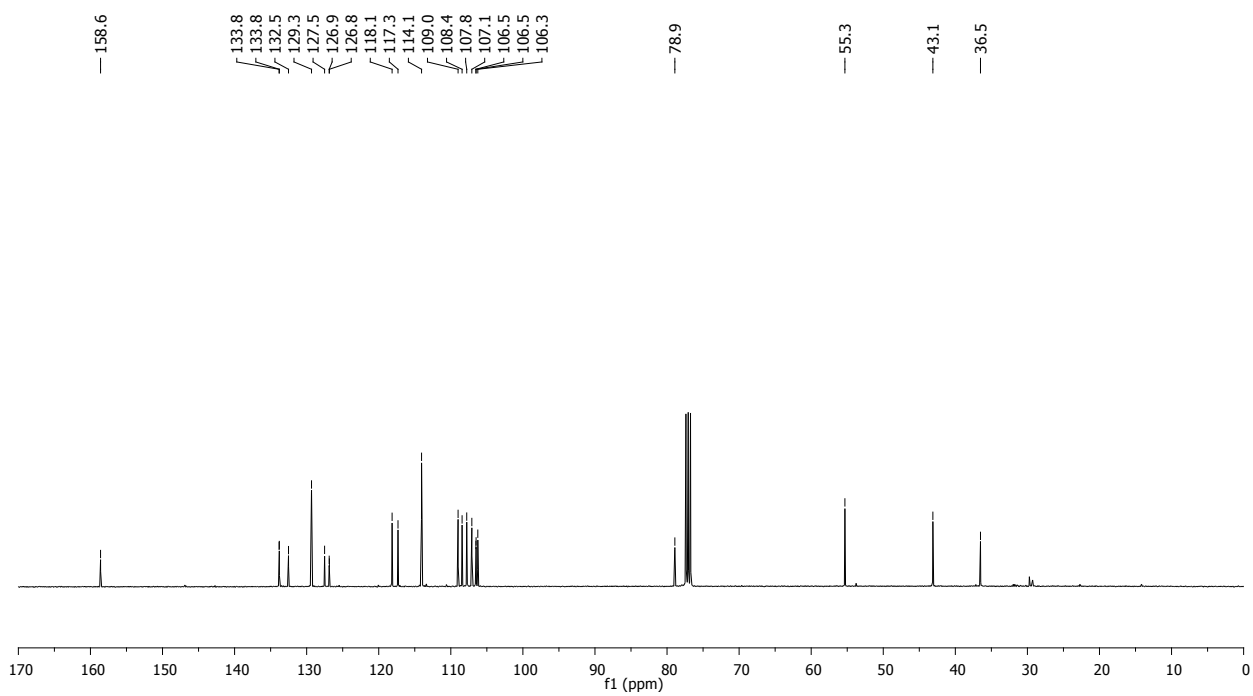


Figure S8. <sup>13</sup>C NMR spectrum of **5d** (Solvent: CDCl<sub>3</sub>)

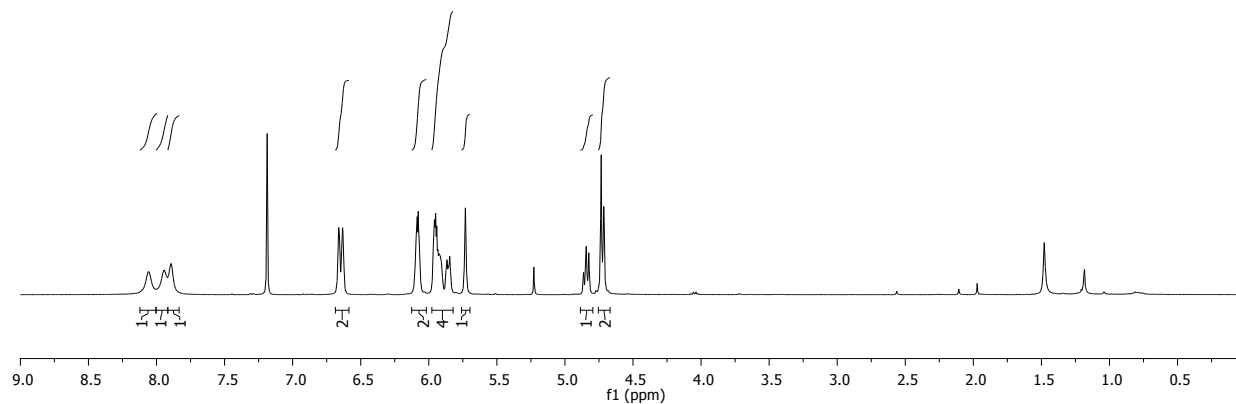
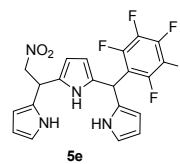


Figure S9. <sup>1</sup>H NMR spectrum of **5e** (Solvent: CDCl<sub>3</sub>)

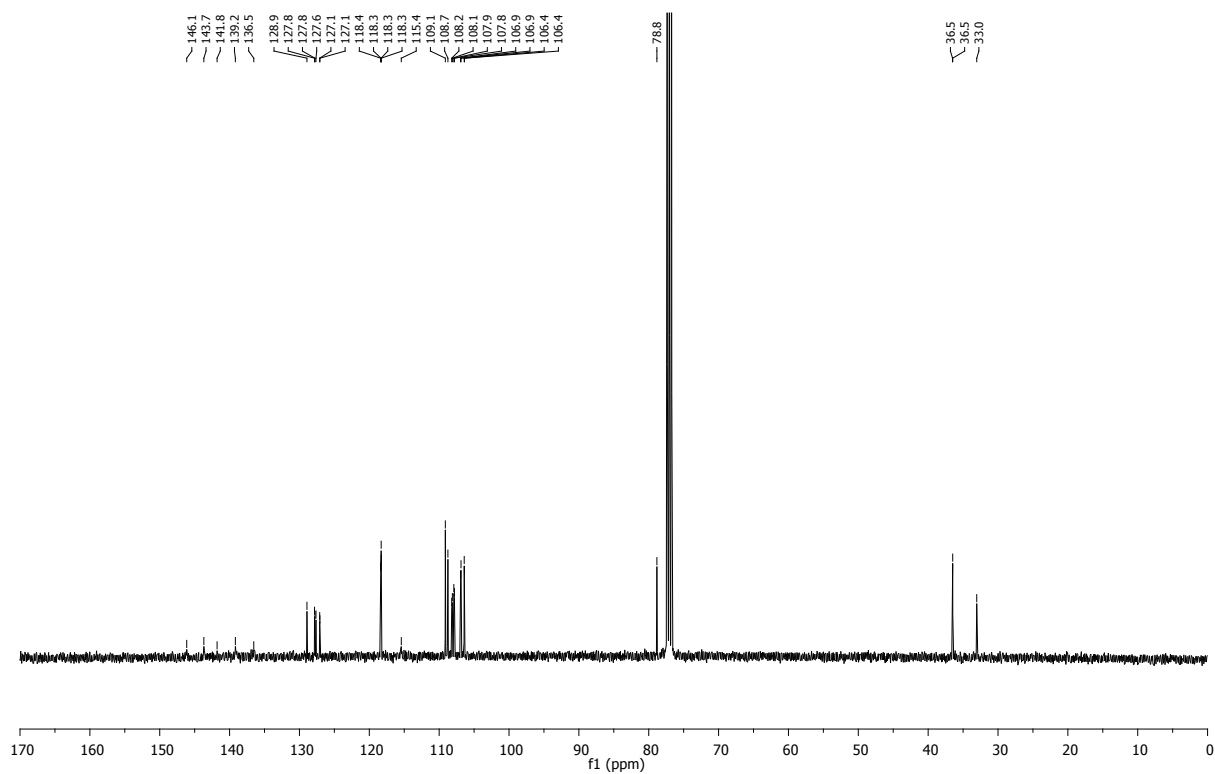


Figure S10. <sup>13</sup>C NMR spectrum of **5e** (Solvent: CDCl<sub>3</sub>)

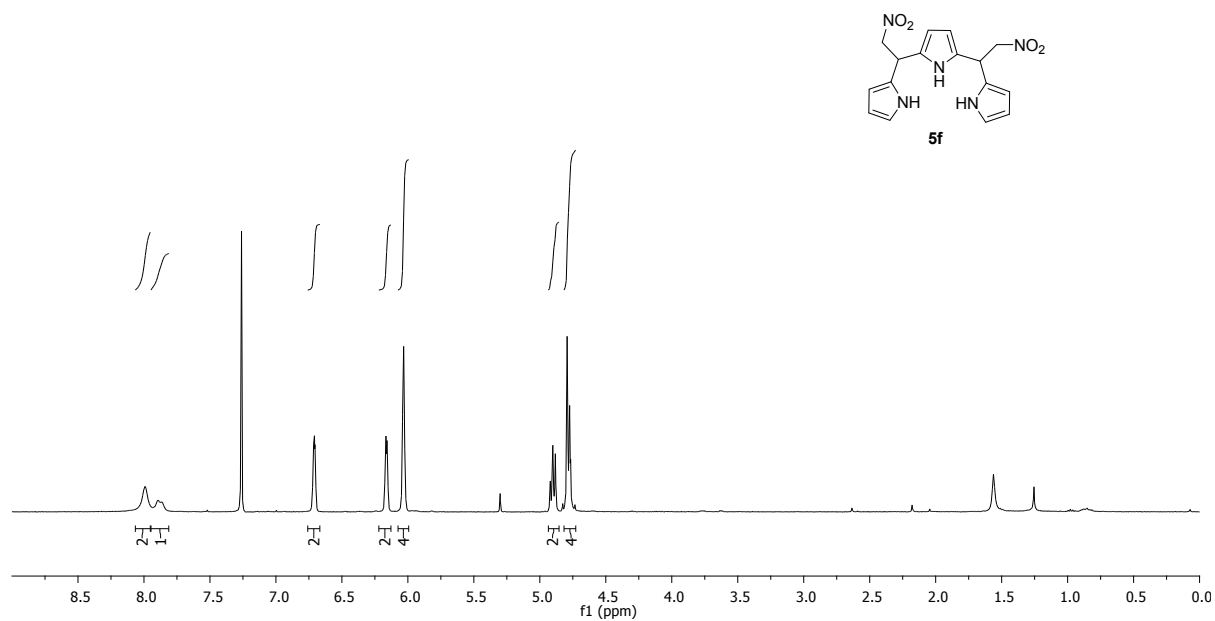


Figure S11.  $^1\text{H}$  NMR spectrum of **5f** (Solvent:  $\text{CDCl}_3$ )

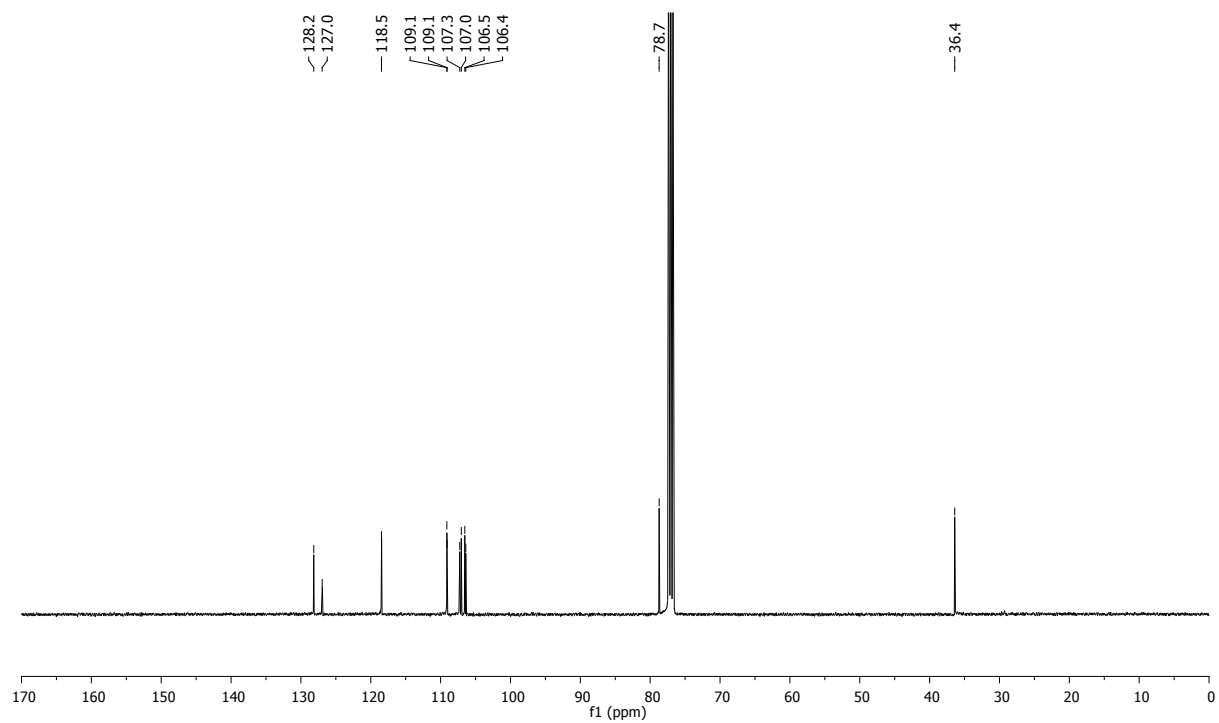


Figure S12.  $^{13}\text{C}$  NMR spectrum of **5f** (Solvent:  $\text{CDCl}_3$ )



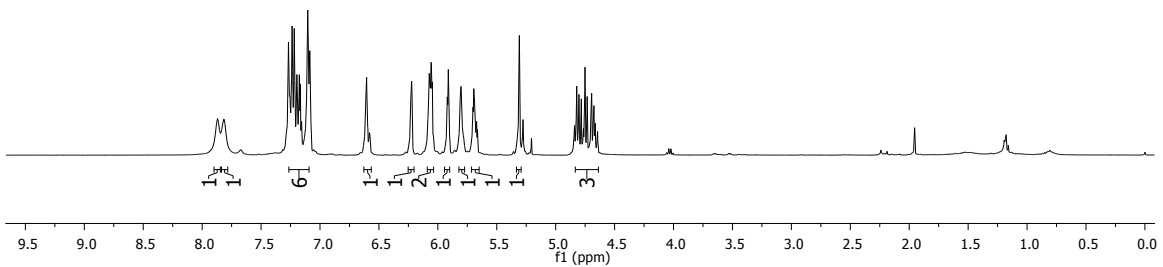
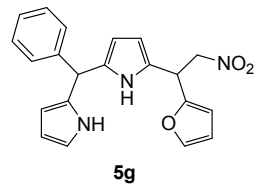
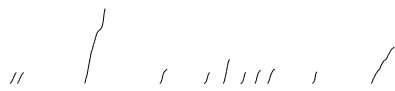


Figure S13. <sup>1</sup>H NMR spectrum of **5g** (Solvent: CDCl<sub>3</sub>)

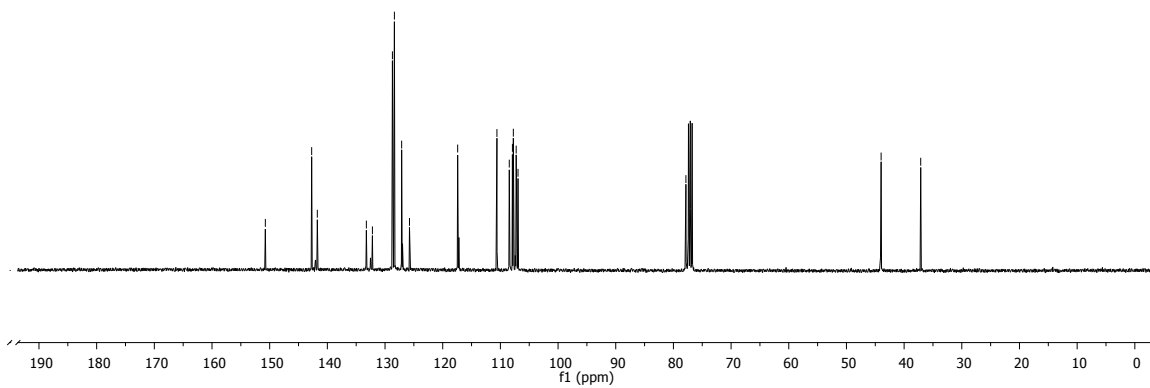
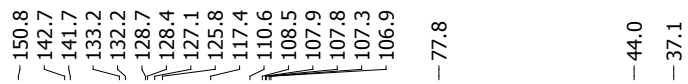


Figure S14. <sup>13</sup>C NMR spectrum of **5g** (Solvent: CDCl<sub>3</sub>)

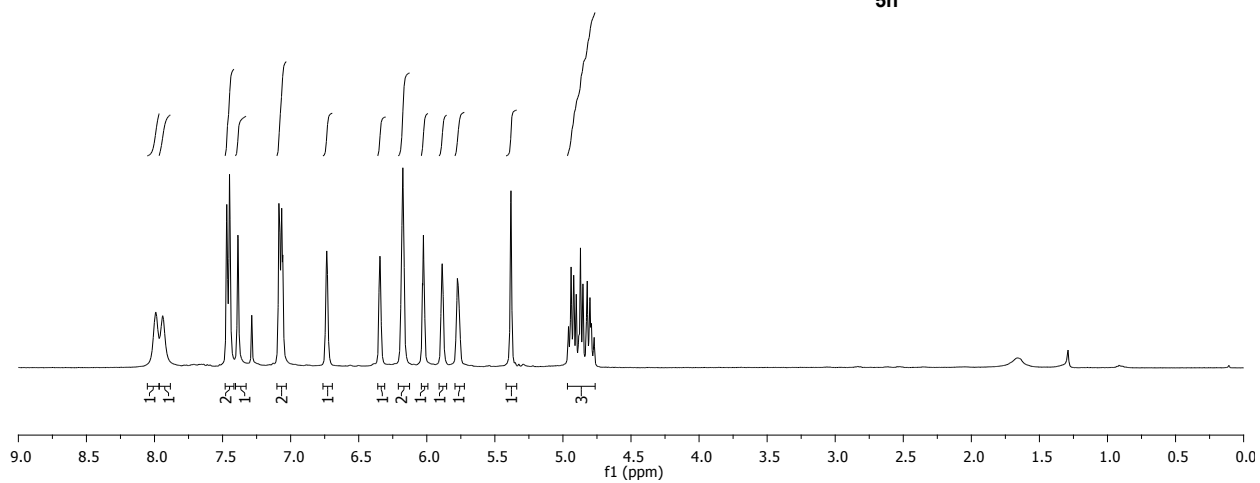
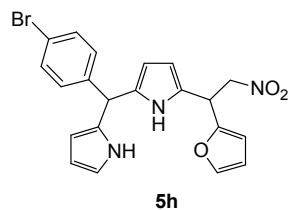


Figure S15. <sup>1</sup>H NMR spectrum of **5h** (Solvent: CDCl<sub>3</sub>)

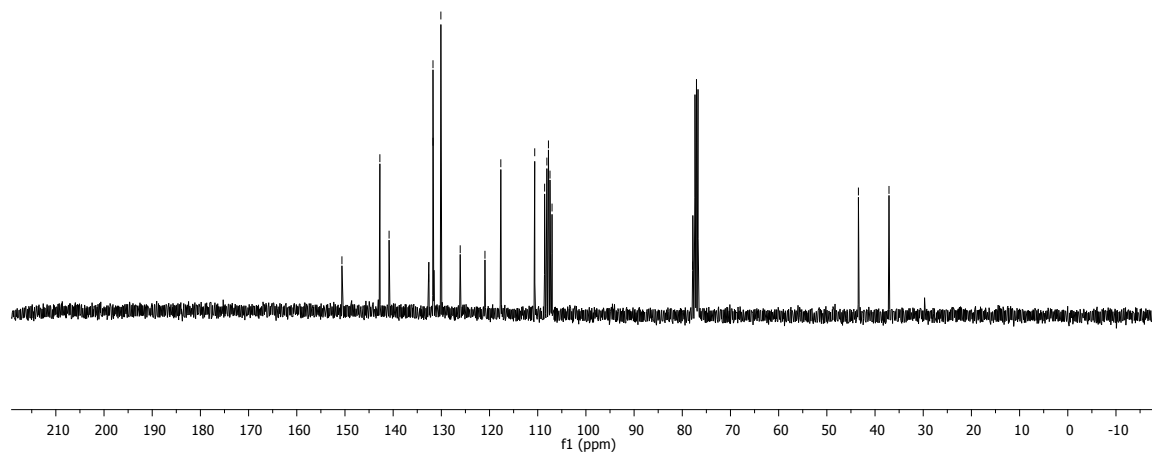
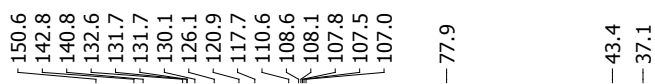


Figure S16. <sup>13</sup>C NMR spectrum of **5h** (Solvent: CDCl<sub>3</sub>)

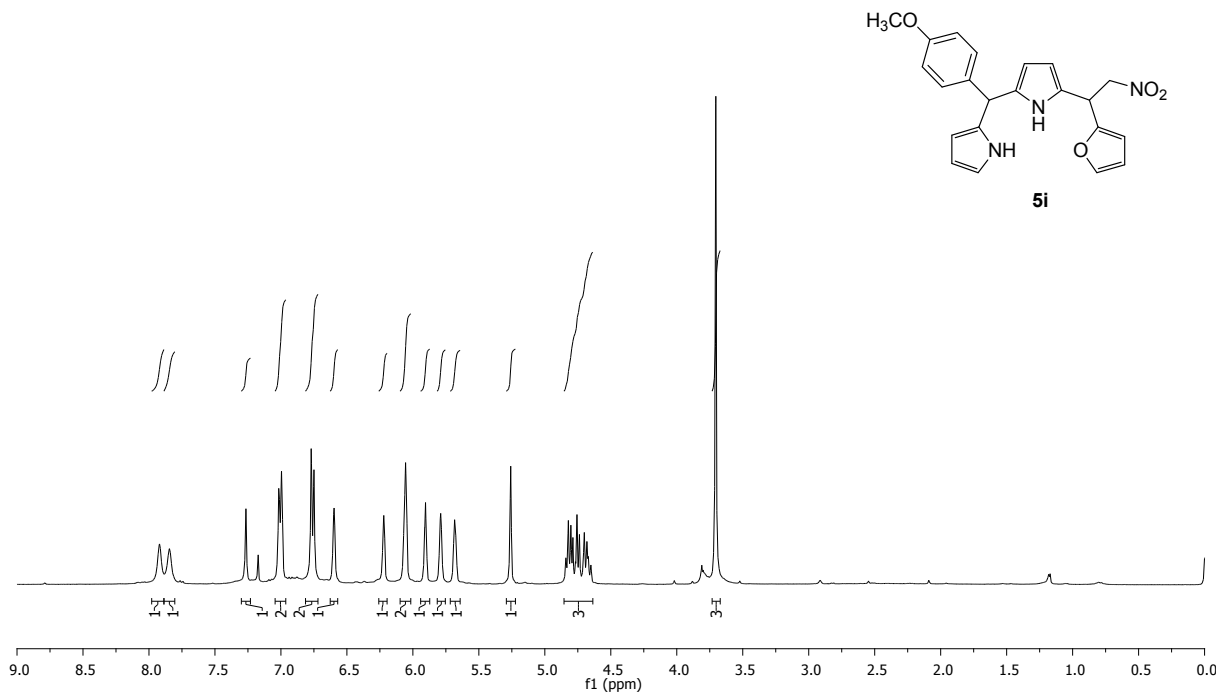


Figure S17. <sup>1</sup>H NMR spectrum of **5i** (Solvent: CDCl<sub>3</sub>)

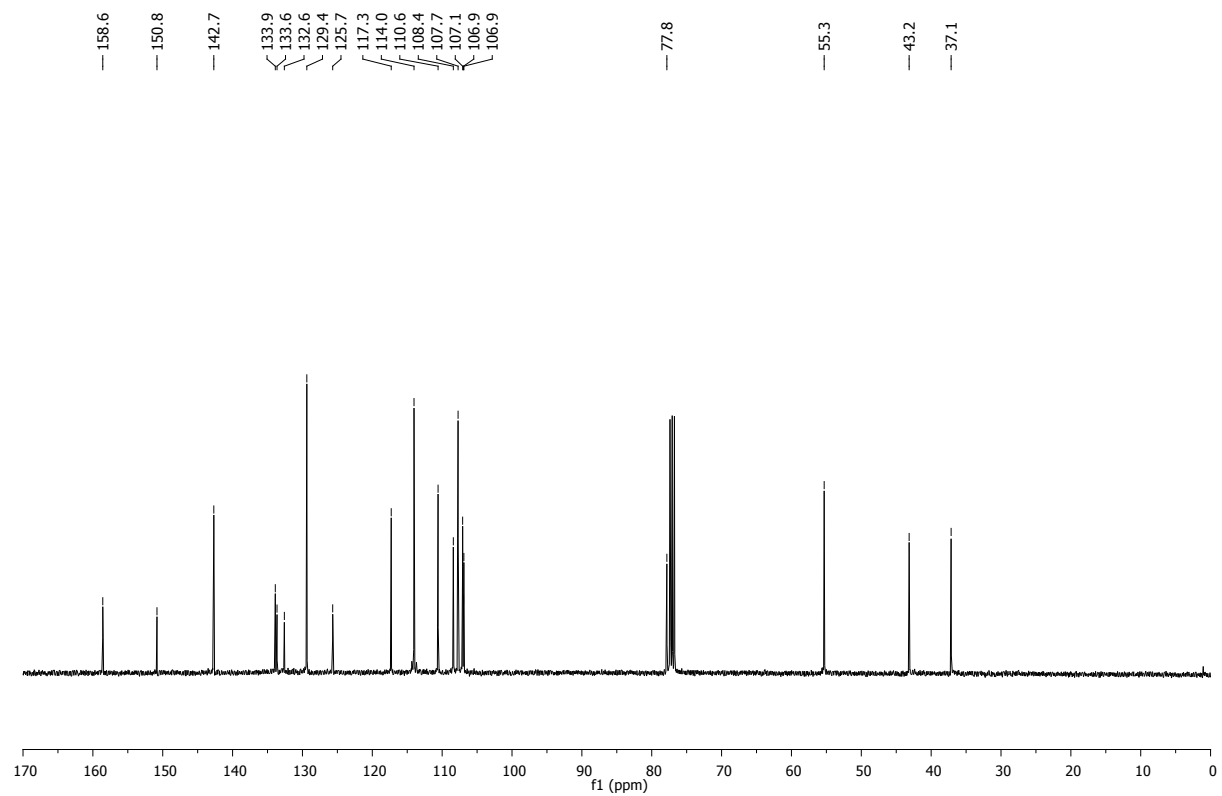
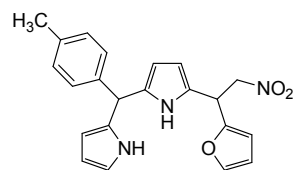


Figure S18. <sup>13</sup>C NMR spectrum of **5i** (Solvent: CDCl<sub>3</sub>)



**5j**

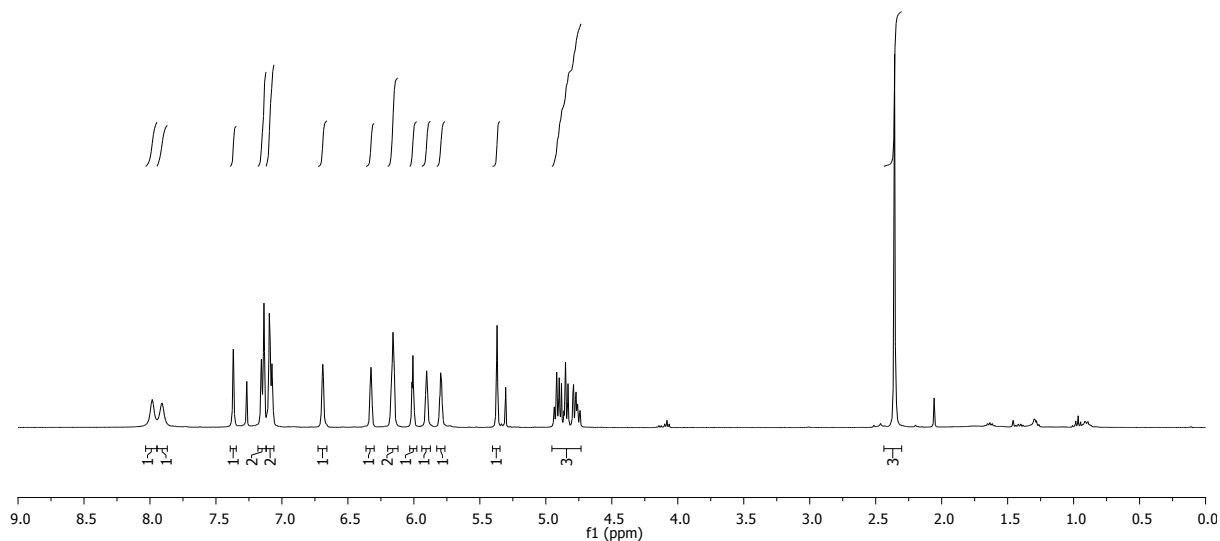


Figure S19. <sup>1</sup>H NMR spectrum of **5j** (Solvent: CDCl<sub>3</sub>)

150.8  
 142.7  
 138.8  
 136.7  
 133.5  
 132.4  
 129.4  
 128.3  
 125.7  
 117.3  
 110.6  
 108.4  
 107.8  
 107.7  
 107.1  
 106.9  
 77.8  
 43.6  
 37.1  
 21.1

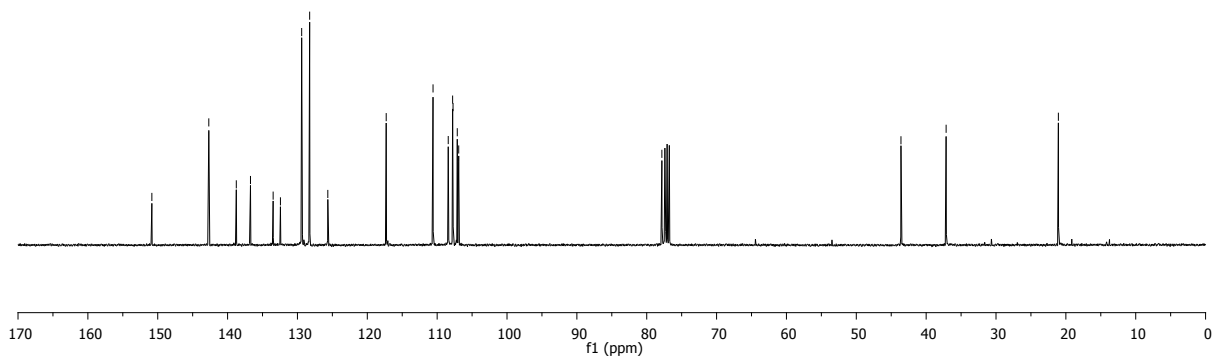


Figure S20. <sup>13</sup>C NMR spectrum of **5j** (Solvent: CDCl<sub>3</sub>)

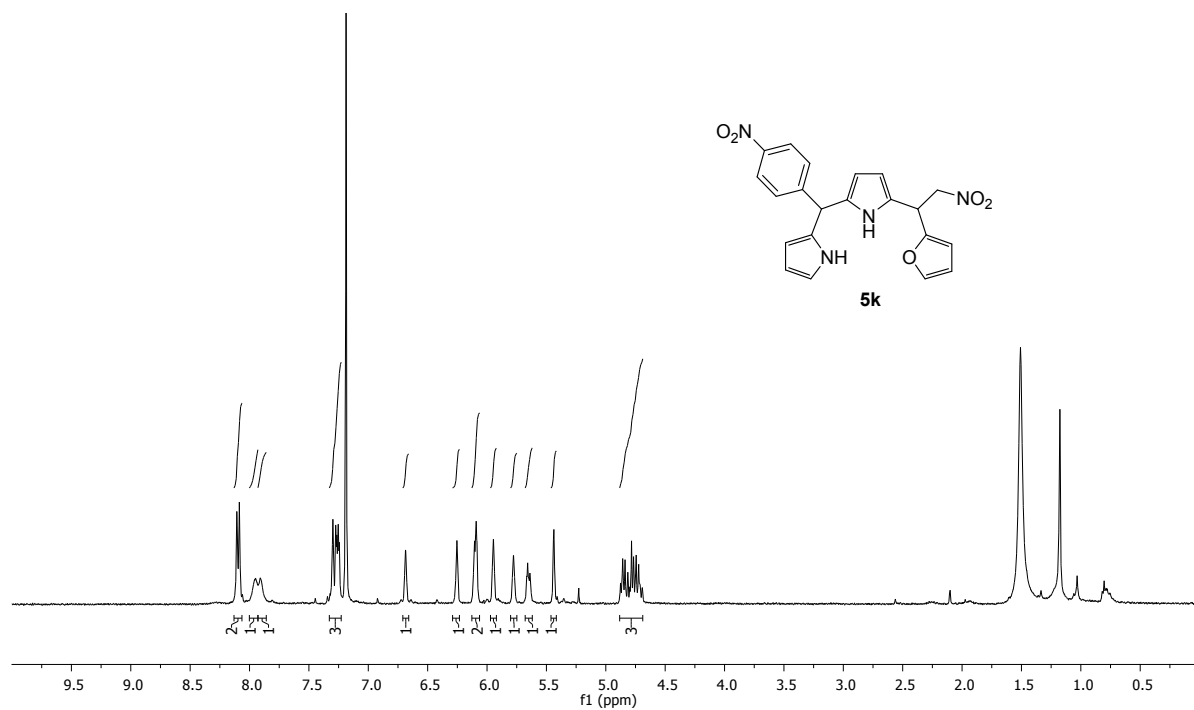


Figure S21. <sup>1</sup>H NMR spectrum of **5k** (Solvent: CDCl<sub>3</sub>)

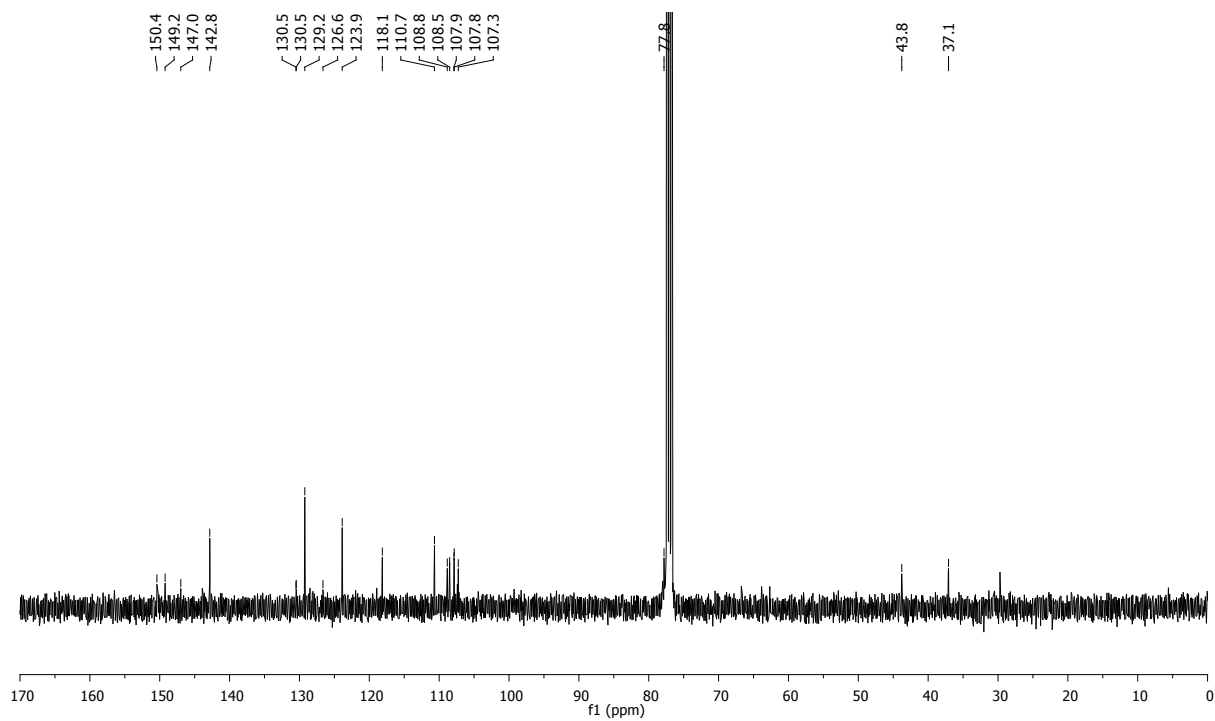
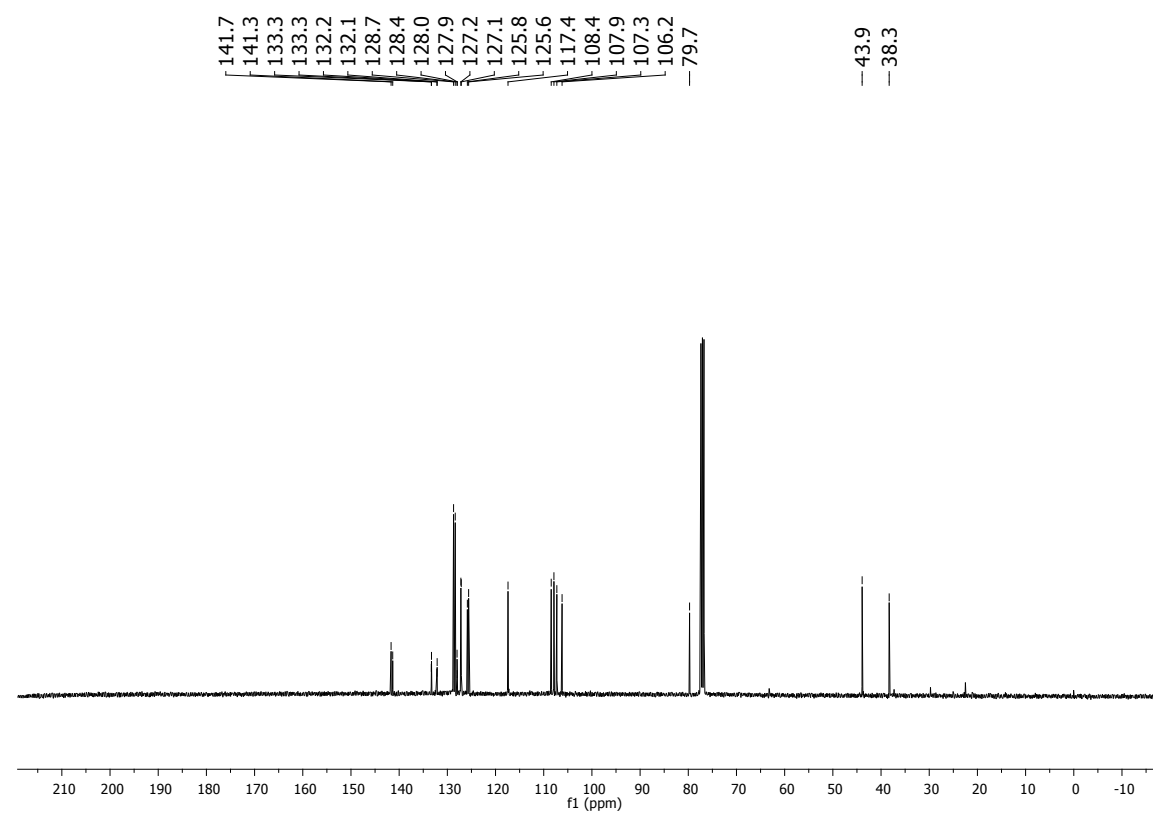
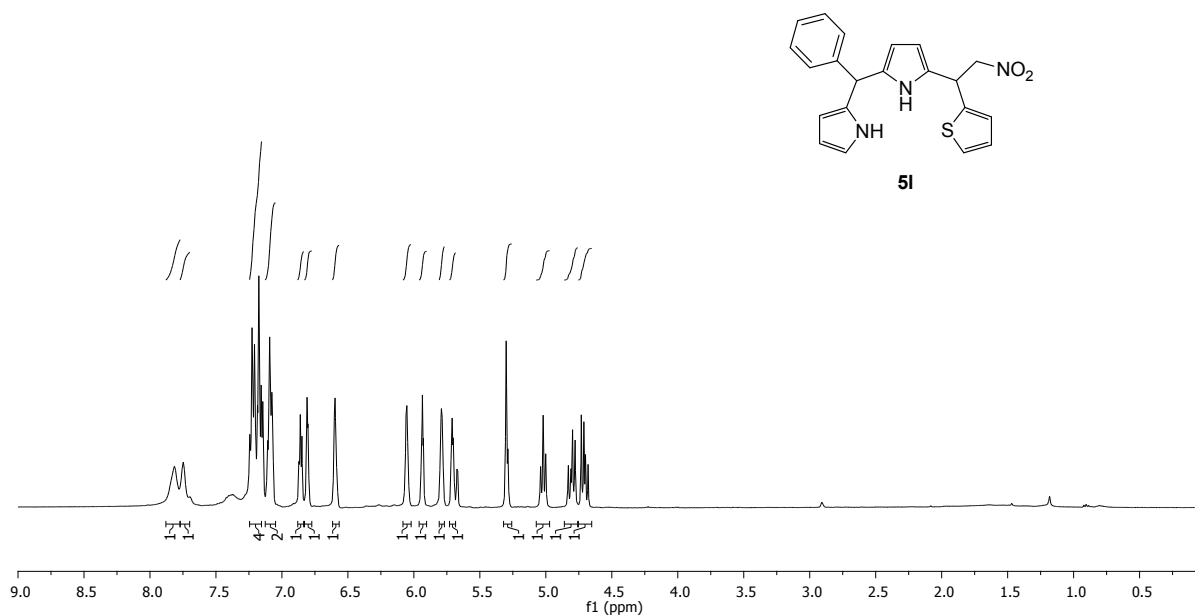


Figure S22. <sup>13</sup>C NMR spectrum of **5k** (Solvent: CDCl<sub>3</sub>)



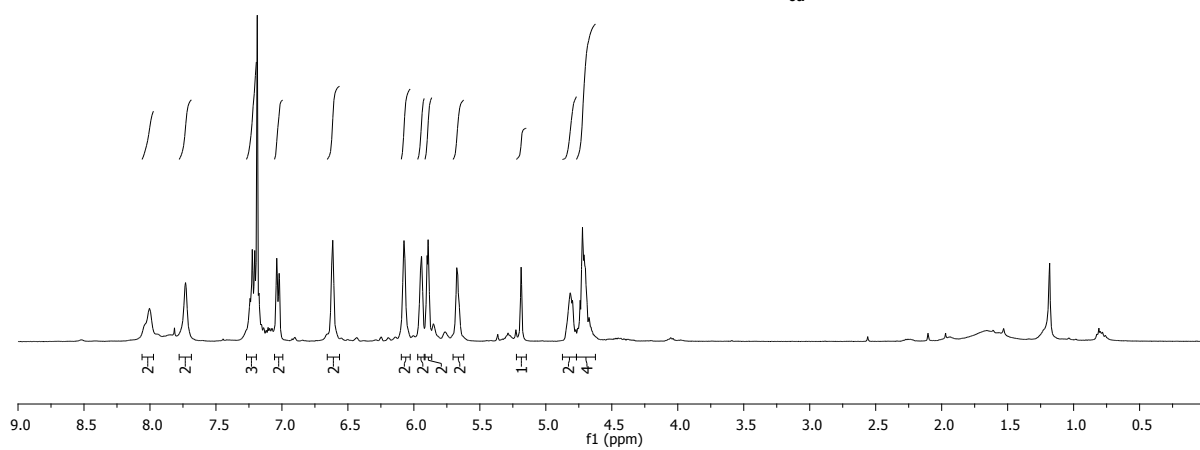
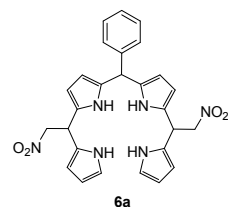


Figure S25.  $^1\text{H}$  NMR spectrum of **6a** (Solvent:  $\text{CDCl}_3$ )

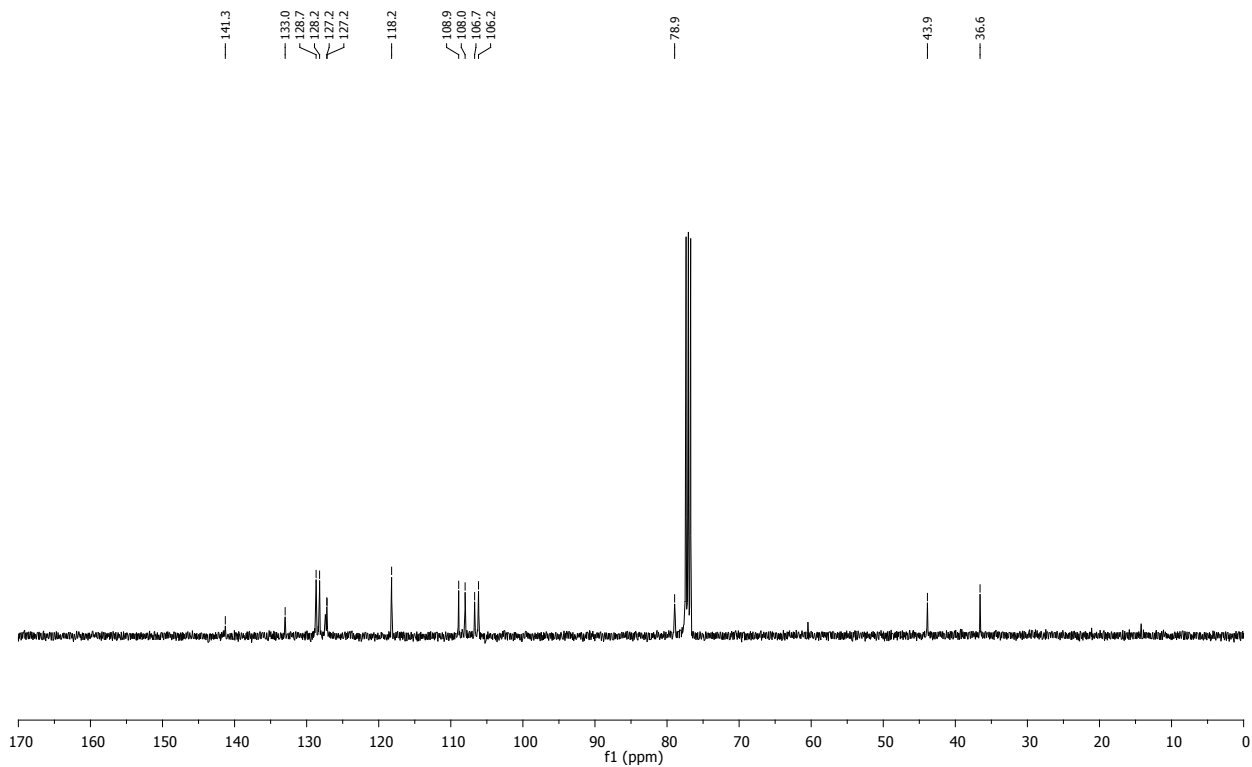


Figure S26.  $^{13}\text{C}$  NMR spectrum of **6a** (Solvent:  $\text{CDCl}_3$ )

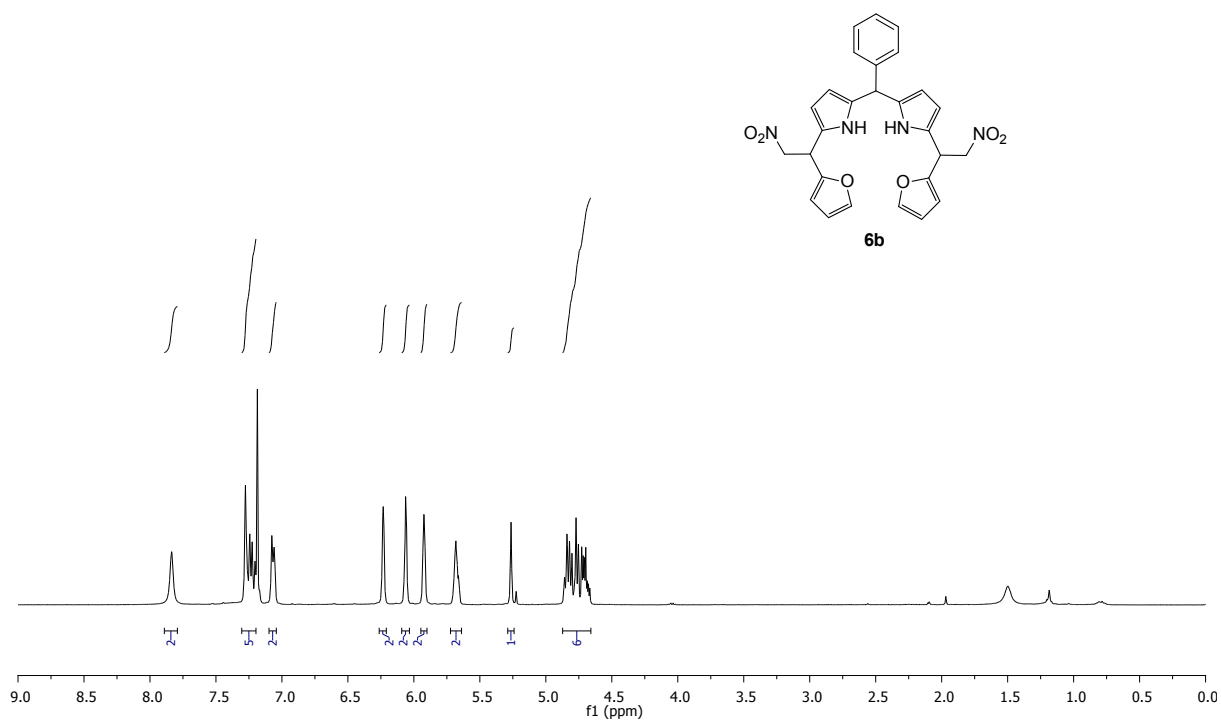


Figure S27. <sup>1</sup>H NMR spectrum of **6b** (Solvent: CDCl<sub>3</sub>)

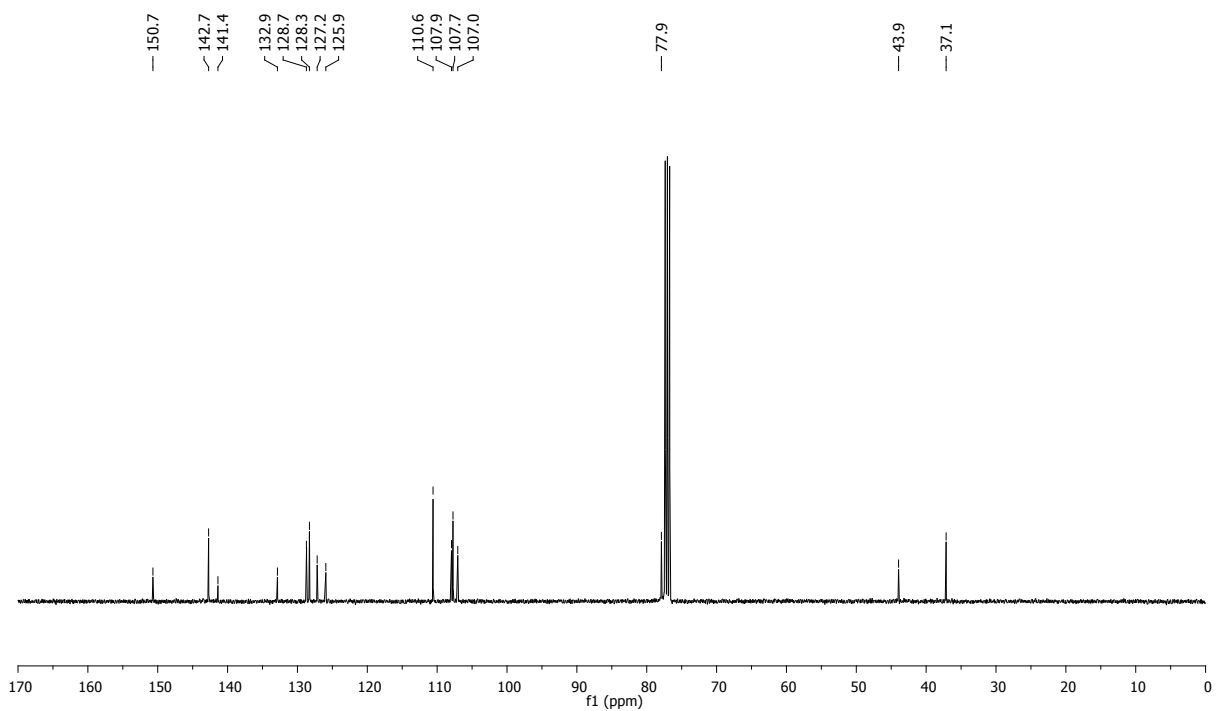


Figure S28. <sup>13</sup>C NMR spectrum of **6b** (Solvent: CDCl<sub>3</sub>)



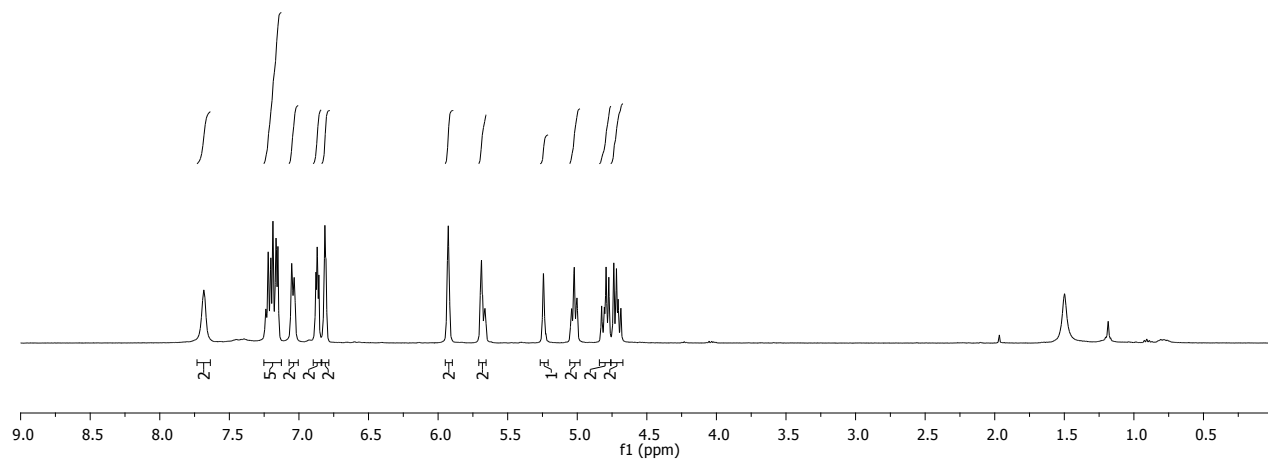
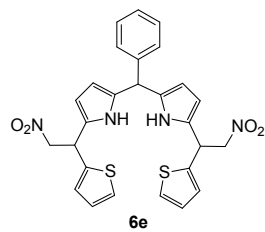


Figure S29. <sup>1</sup>H NMR spectrum of **6e** (Solvent: CDCl<sub>3</sub>)

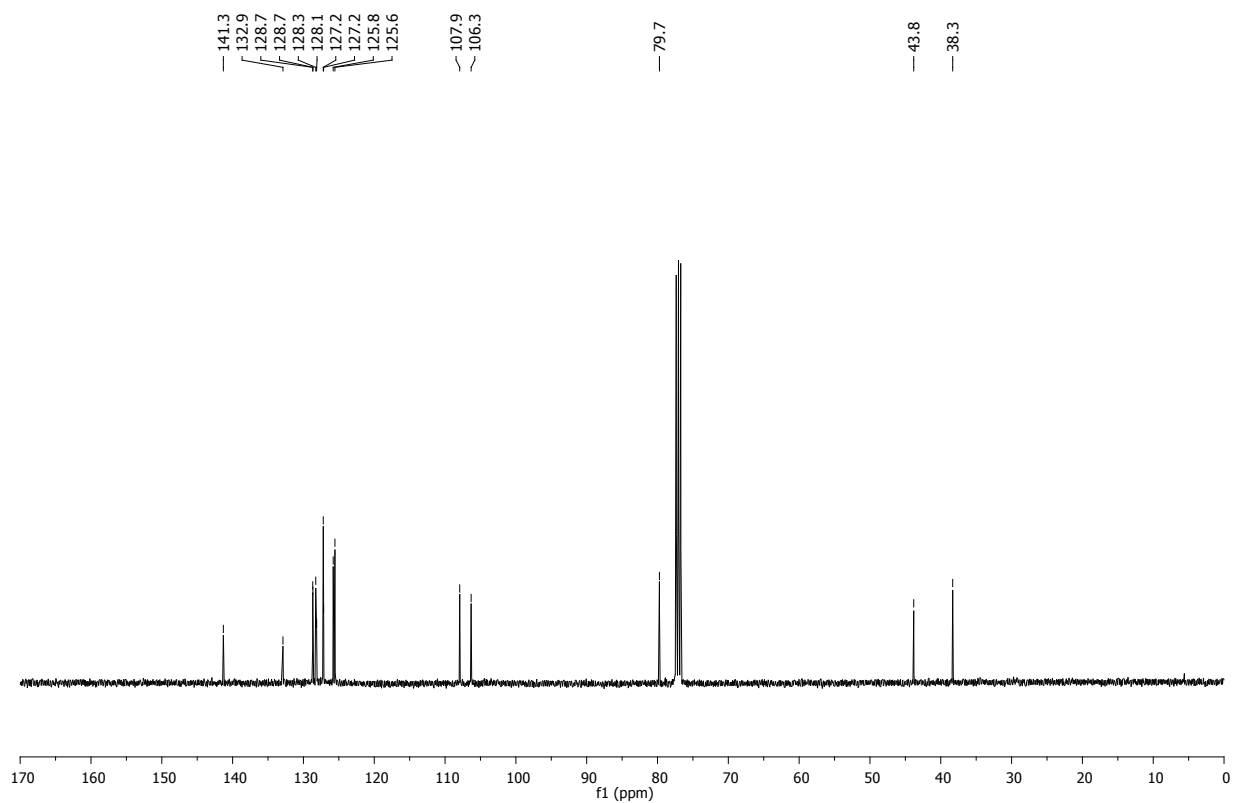


Figure S30.  $^{13}\text{C}$  NMR spectrum of **6e** (Solvent:  $\text{CDCl}_3$ )

### 3. NMR Spectra and Uv-visible spectra of compounds **7a-d**

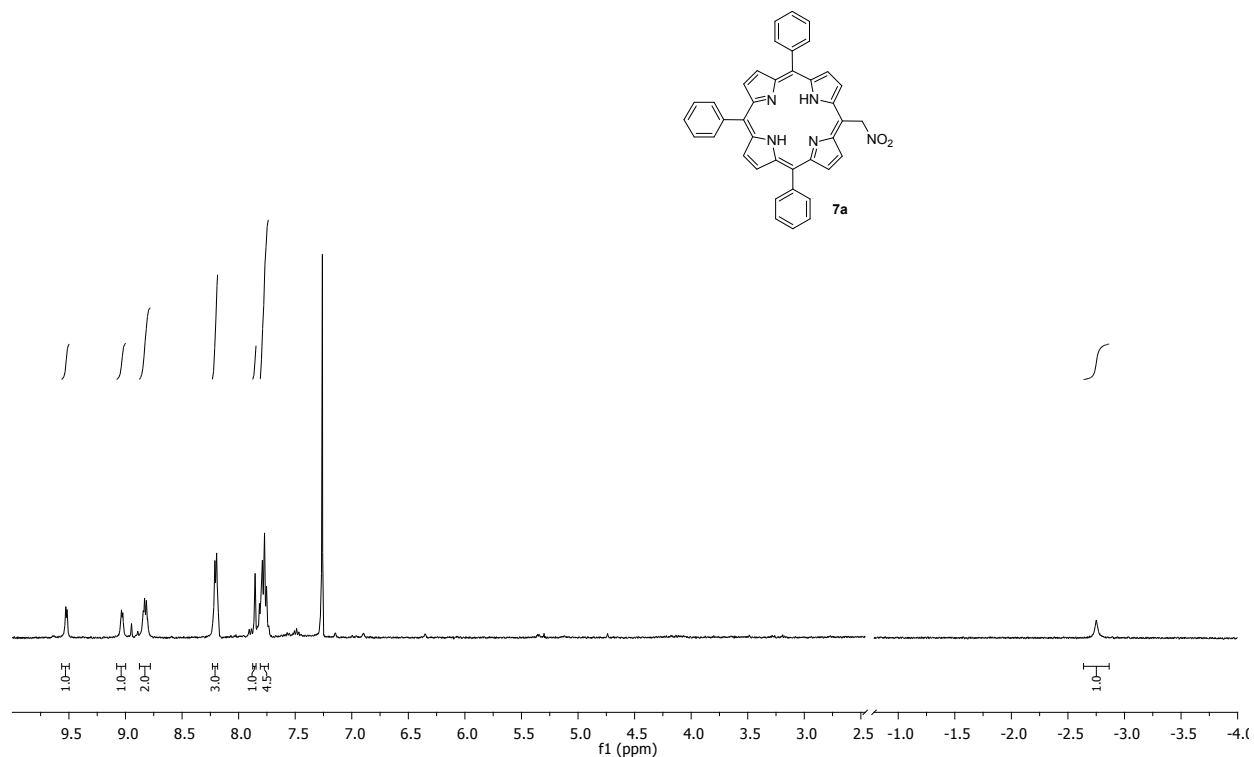


Figure S31.  $^1\text{H}$  NMR spectrum of **7a** (Solvent:  $\text{CDCl}_3$ )

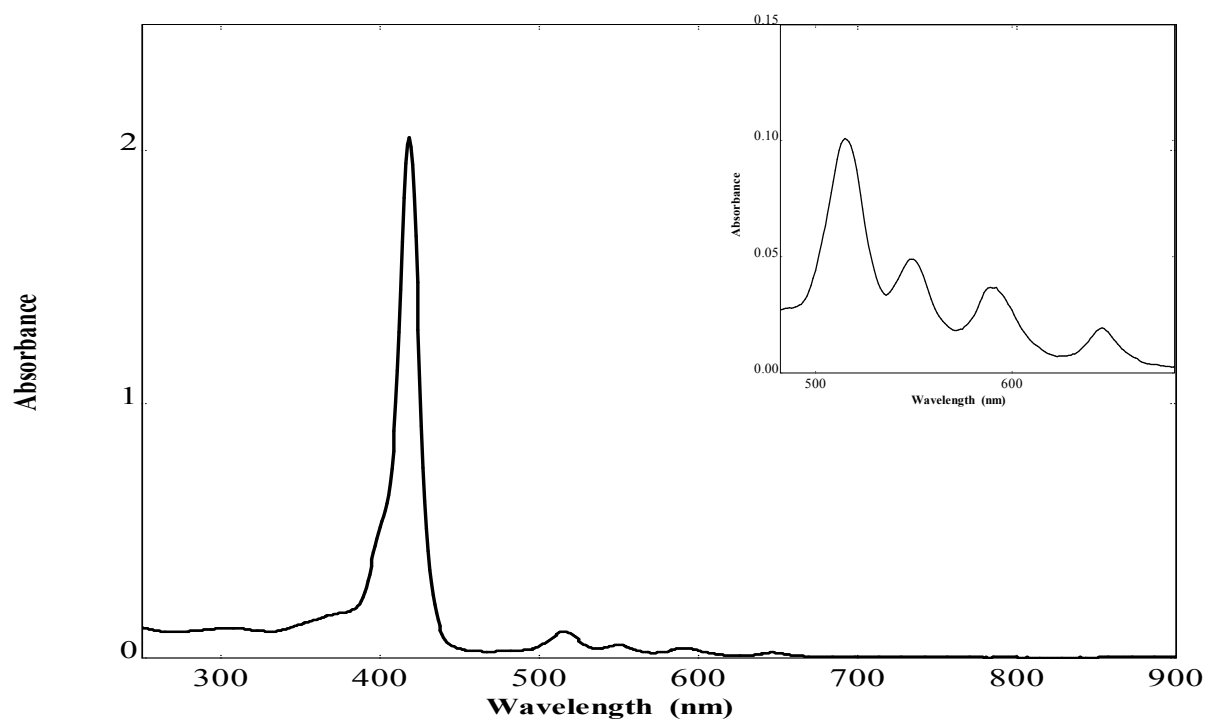


Figure S32. UV-vis spectrum of **7a** (Solvent: CH<sub>2</sub>Cl<sub>2</sub>)

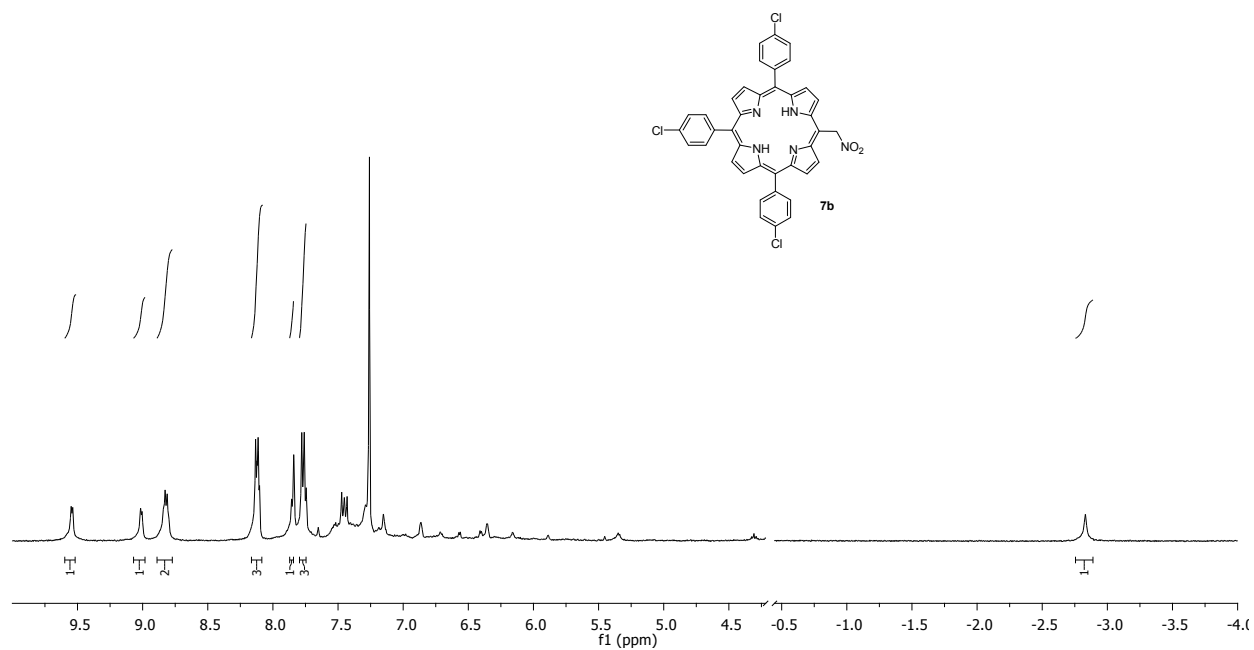


Figure S33. <sup>1</sup>H NMR spectrum of **7b** (Solvent: CDCl<sub>3</sub>)

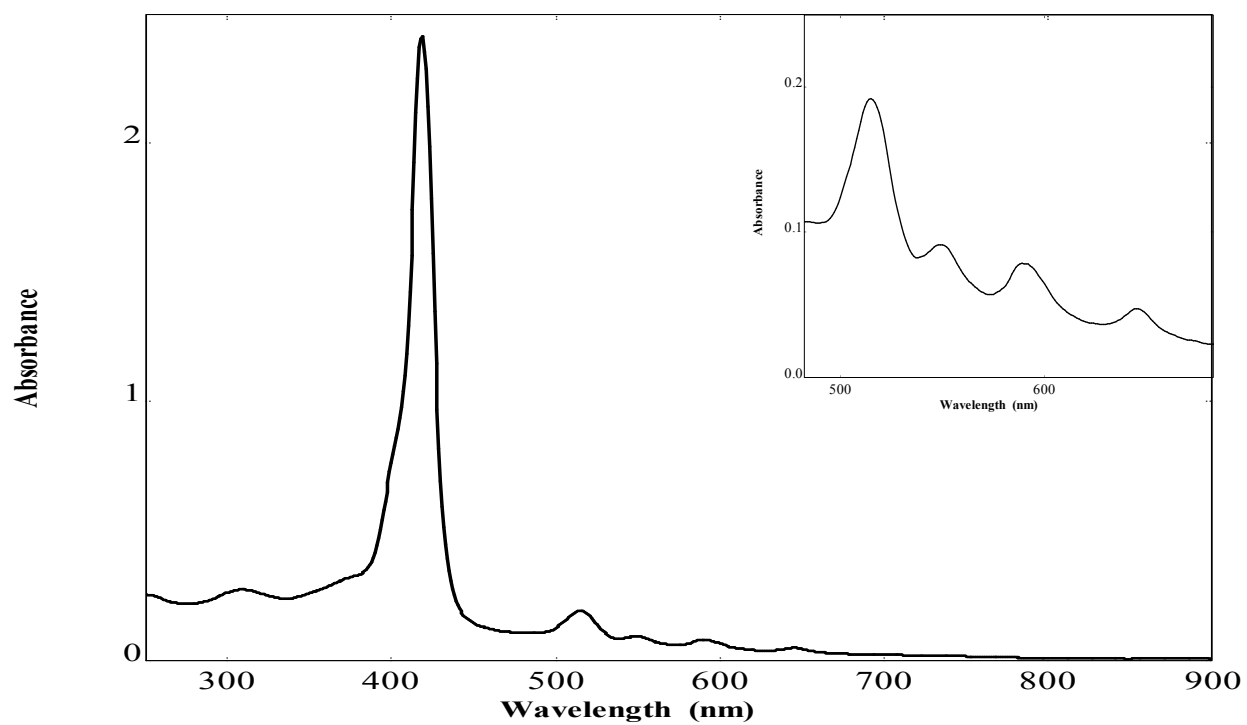
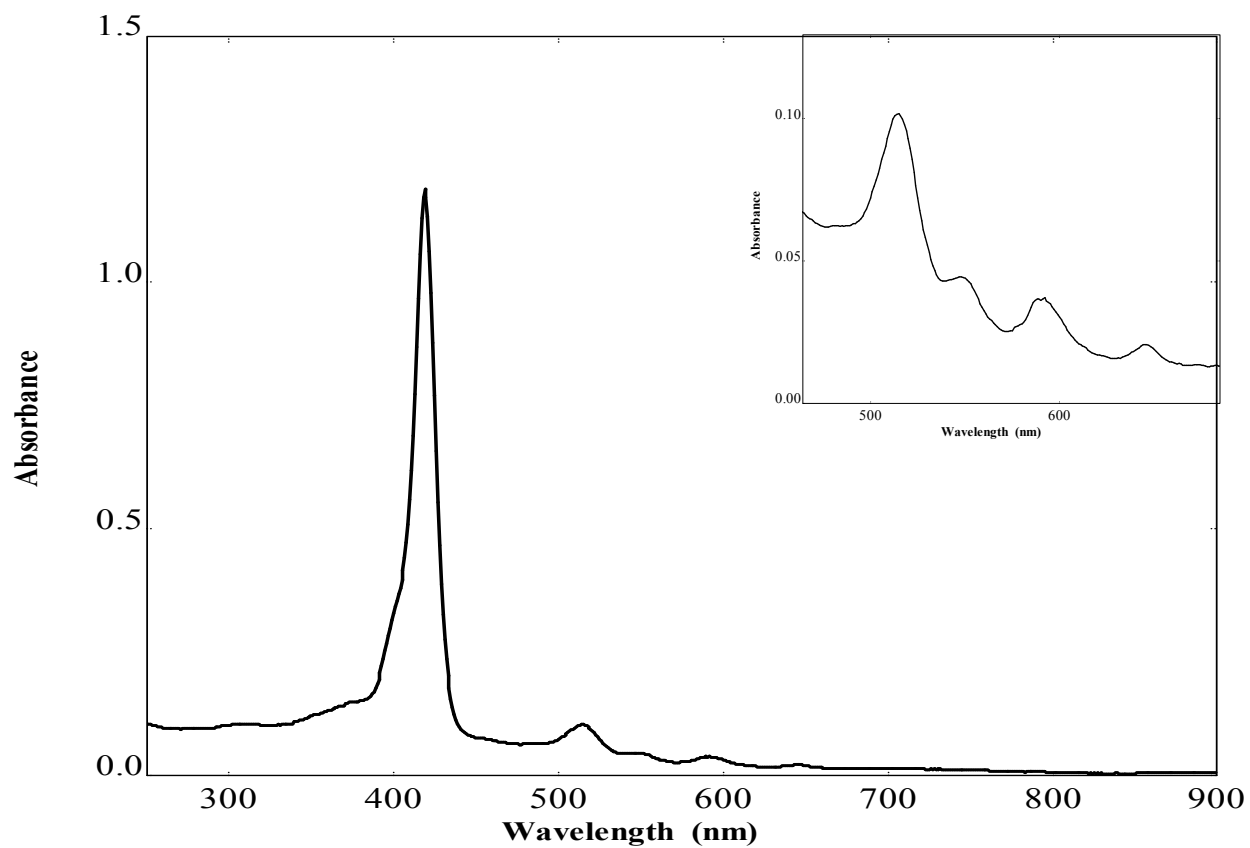
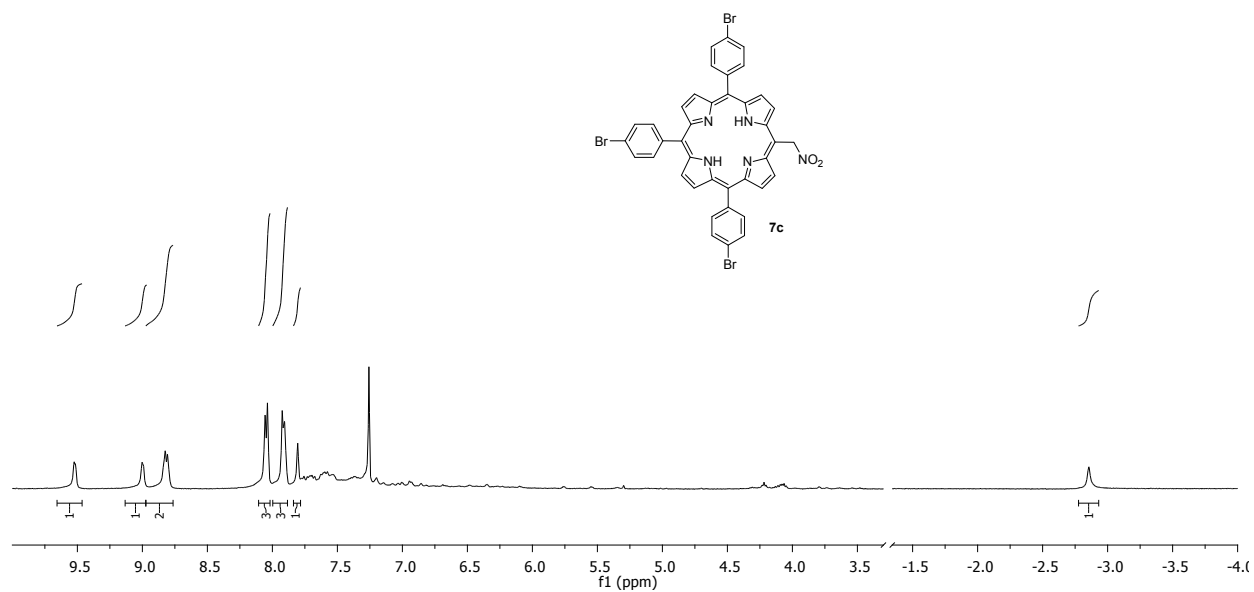


Figure S34. UV-vis spectrum of **7b** (Solvent: CH<sub>2</sub>Cl<sub>2</sub>)



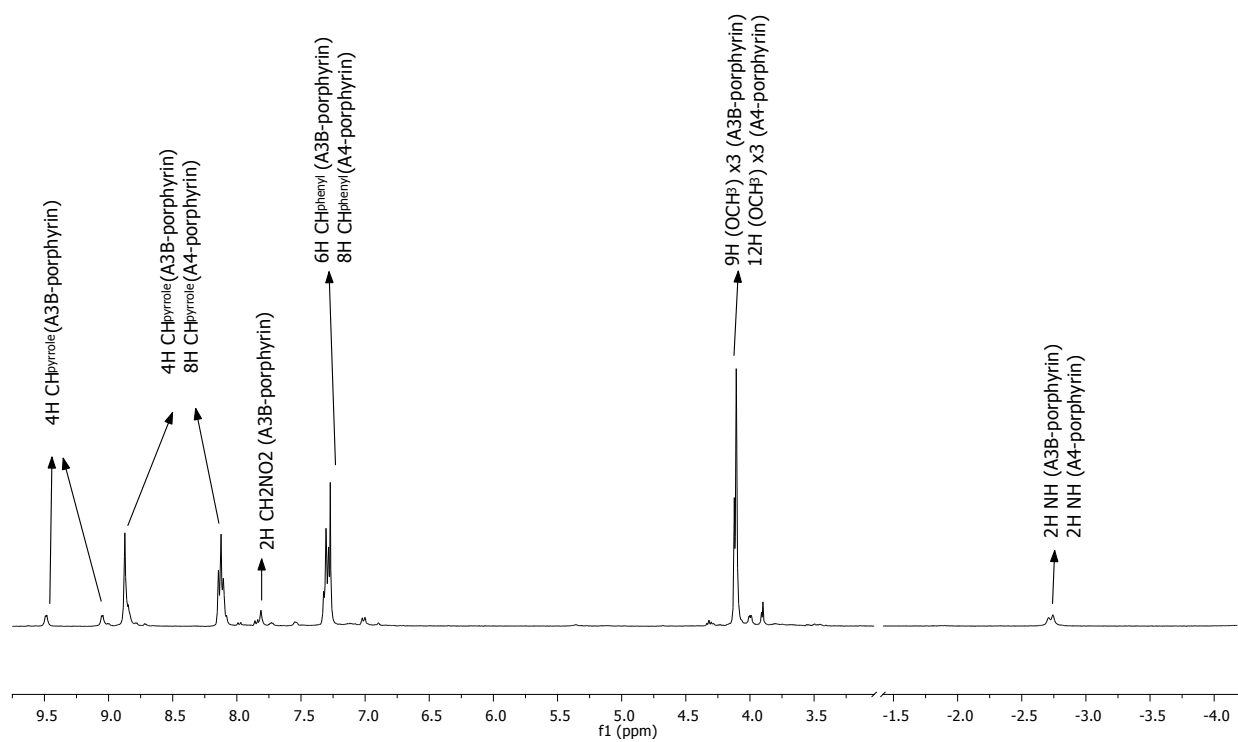


Figure S37. <sup>1</sup>H NMR spectrum of mixture **7d** with corresponding A<sub>4</sub> porphyrin (Solvent: CDCl<sub>3</sub>) (Solvent residual peaks at 0.5-2.5 ppm)