

## Supplementary Information

### Unsubstituted Quinoidal Pyrrole and its Reaction with Oxygen, Charge Transfer and Palladium(II) Complexes via DDQ Oxidation

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## 2. NMR, IR UV-Vis and Emission Spectra

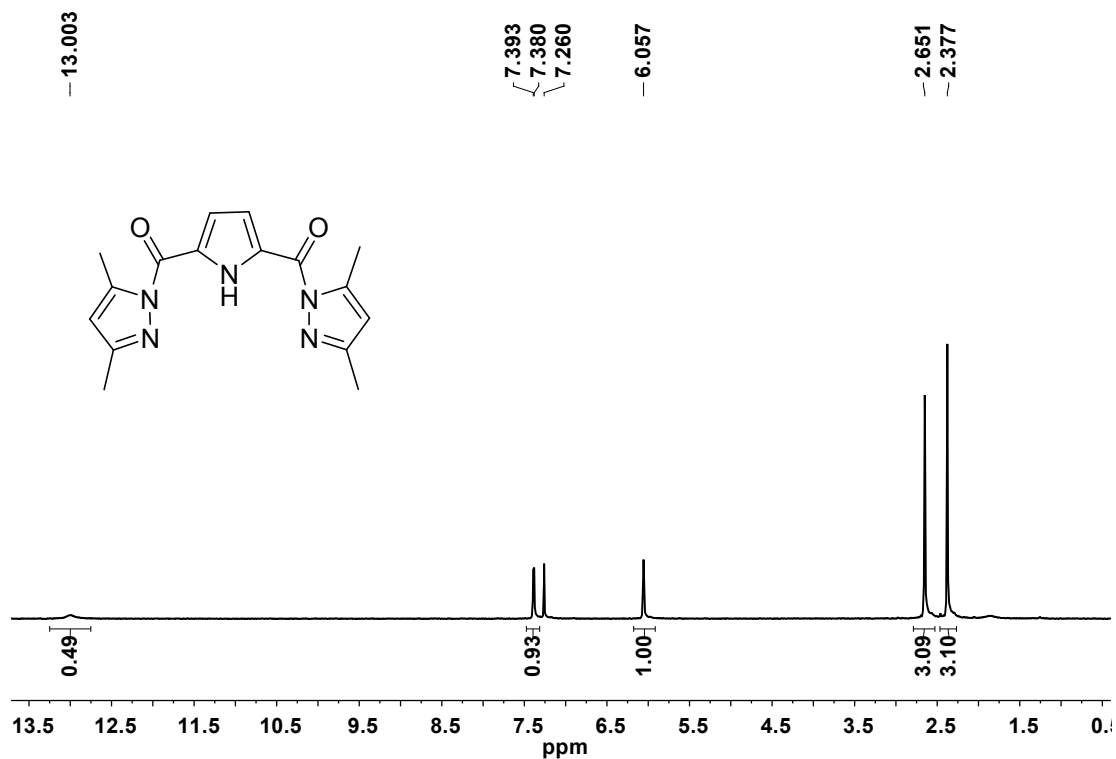


Figure S1.  $^1\text{H}$  NMR spectrum of 2,5-bis(3,5-dimethylpyrazolylcarbonyl)pyrrole 2 in  $\text{CDCl}_3$ .

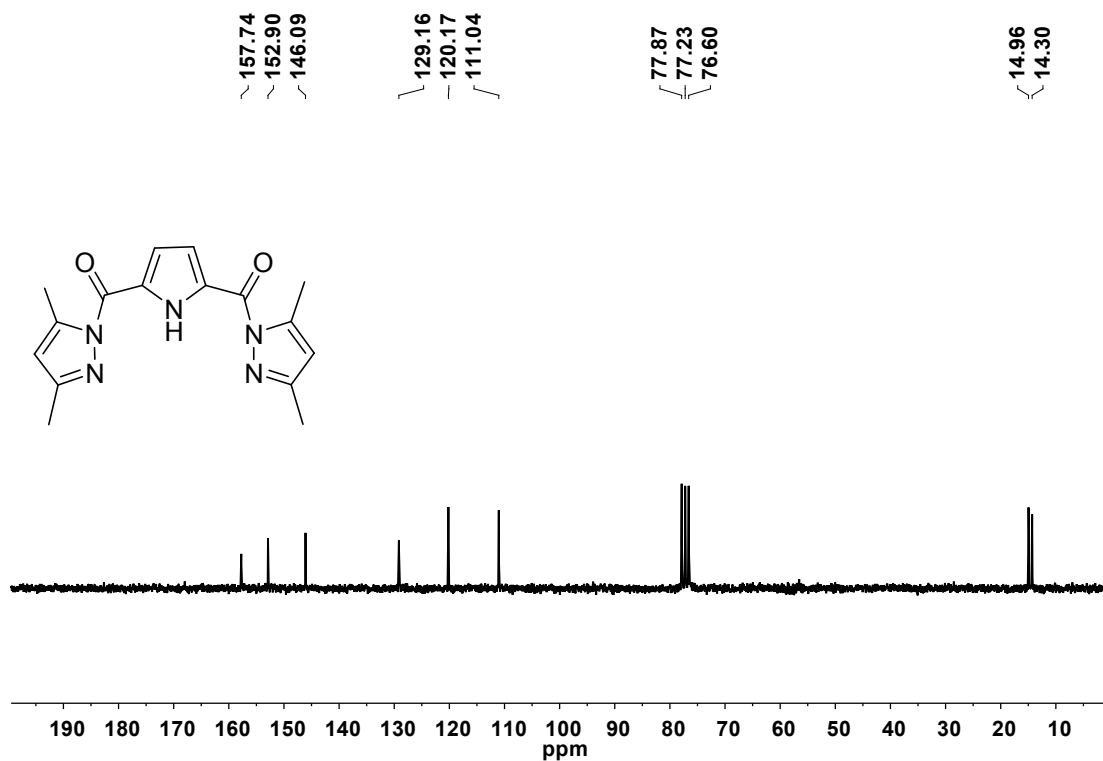
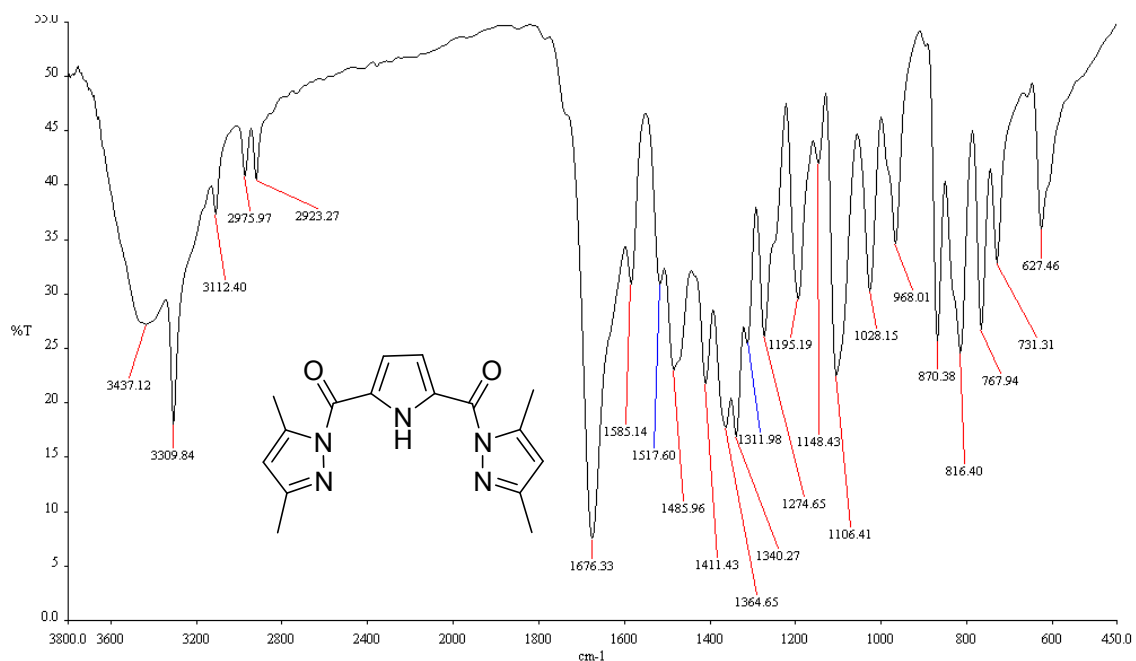
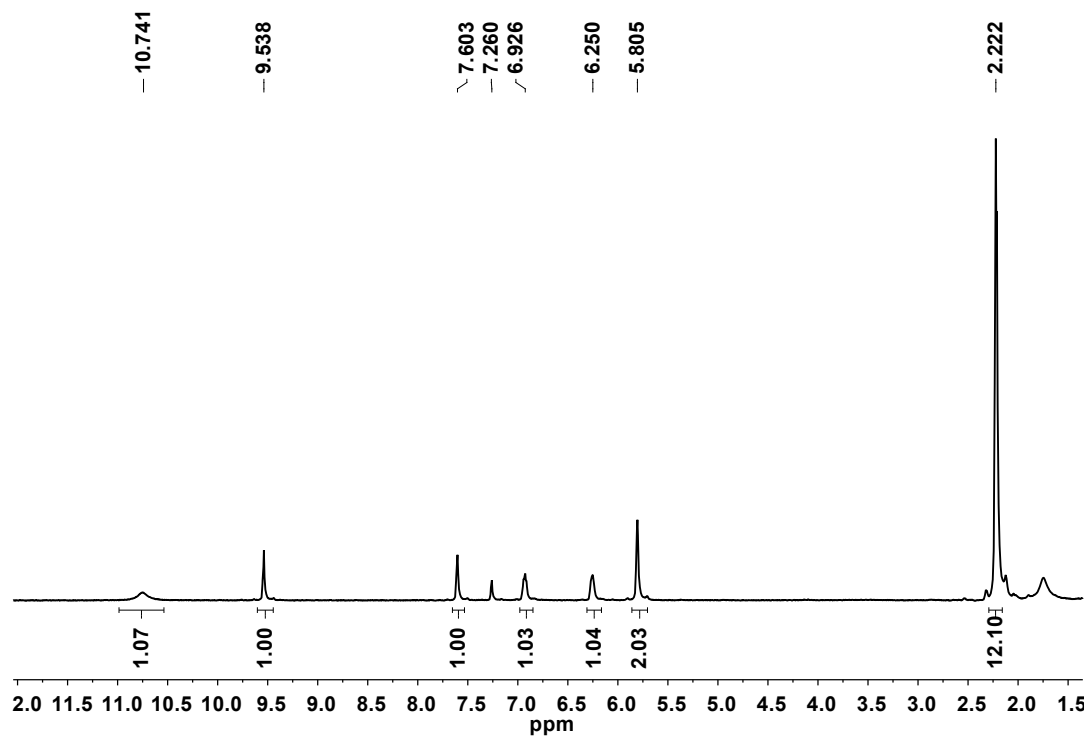


Figure S2.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 2,5-bis(3,5-dimethylpyrazolylcarbonyl)pyrrole 2 in  $\text{CDCl}_3$ .



**Figure S3.** IR spectrum of 2,5-bis(3,5-dimethylpyrazolylcarbonyl)pyrrole **2** recorded as a KBr disc.



**Figure S4.**  $^1\text{H}$  NMR spectrum of 5-{bis(3,5-dimethylpyrazolyl)methyl}pyrrole-2-carbaldehyde **3** in  $\text{CDCl}_3$ .

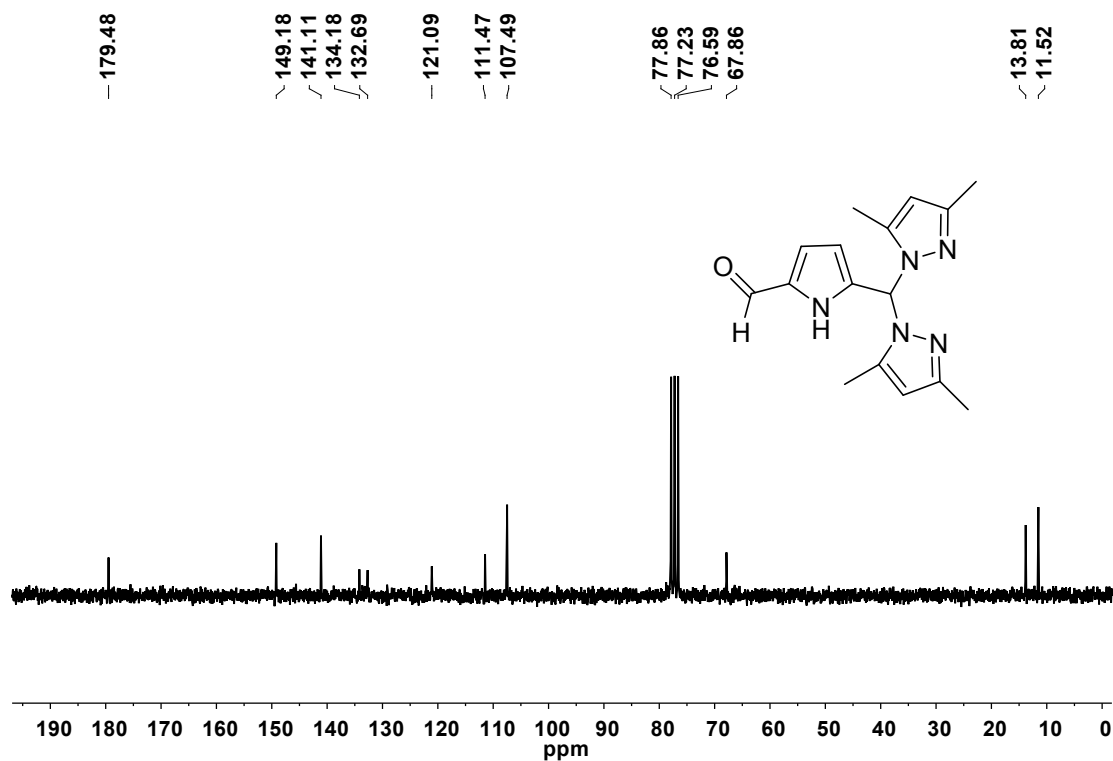


Figure S5.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 5-bis-(3,5-dimethylpyrazolyl)methylpyrrole-2-carbaldehyde **3** in  $\text{CDCl}_3$ .

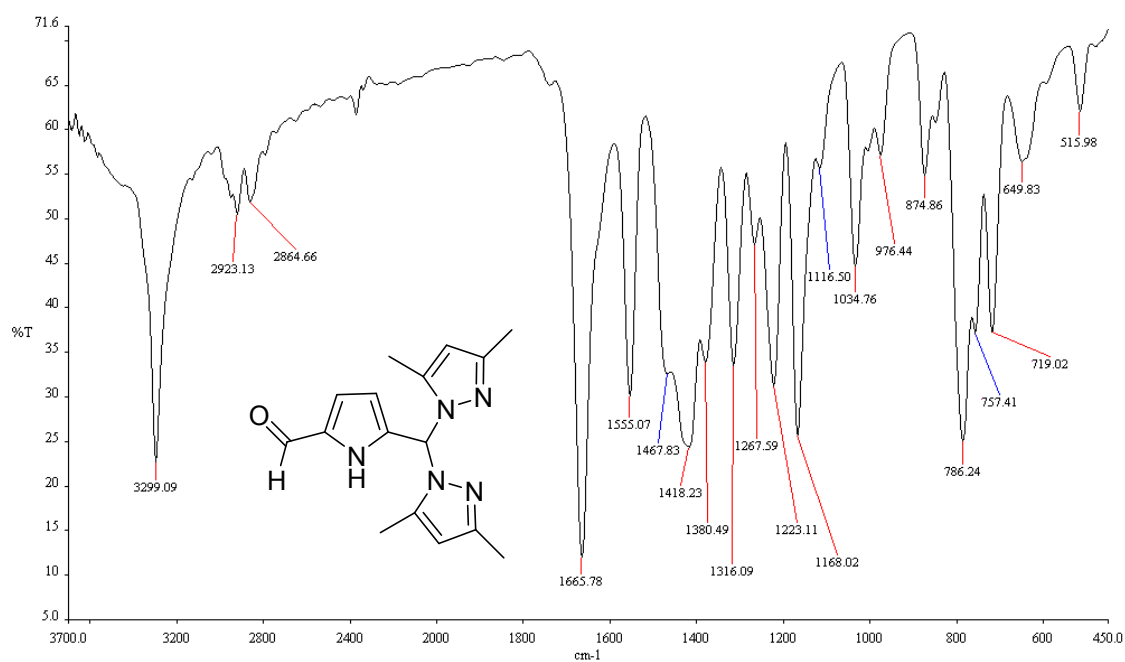
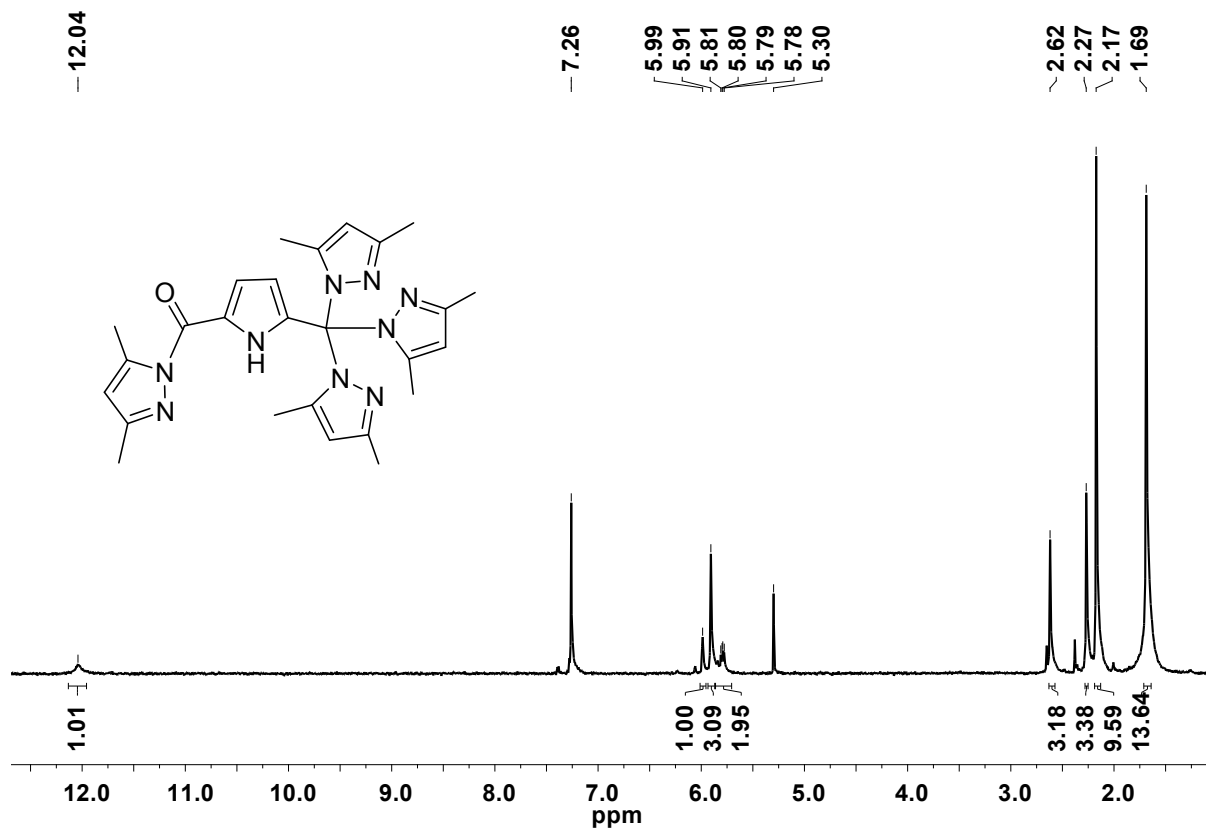


Figure S6. IR spectrum of 5-bis-(3,5-dimethylpyrazolyl)methylpyrrole-2-carbaldehyde **3** recorded as a KBr disc.



**Figure S7.** <sup>1</sup>H NMR spectrum of 2-tris(3,5-dimethylpyrazolylmethyl)-5-(3,5-dimethylpyrazolylcarbonyl)pyrrole **4** in CDCl<sub>3</sub>.

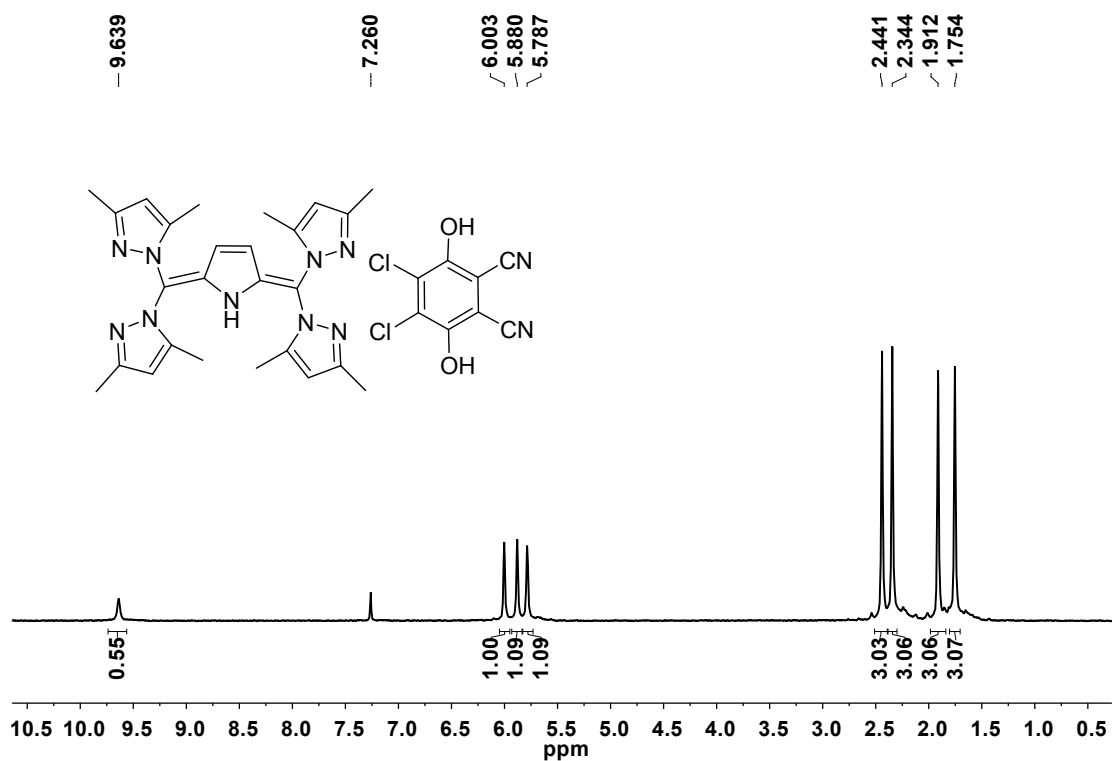


Figure S8.  $^1\text{H}$  NMR spectrum of DDQH<sub>2</sub> adduct **5** in CDCl<sub>3</sub>.

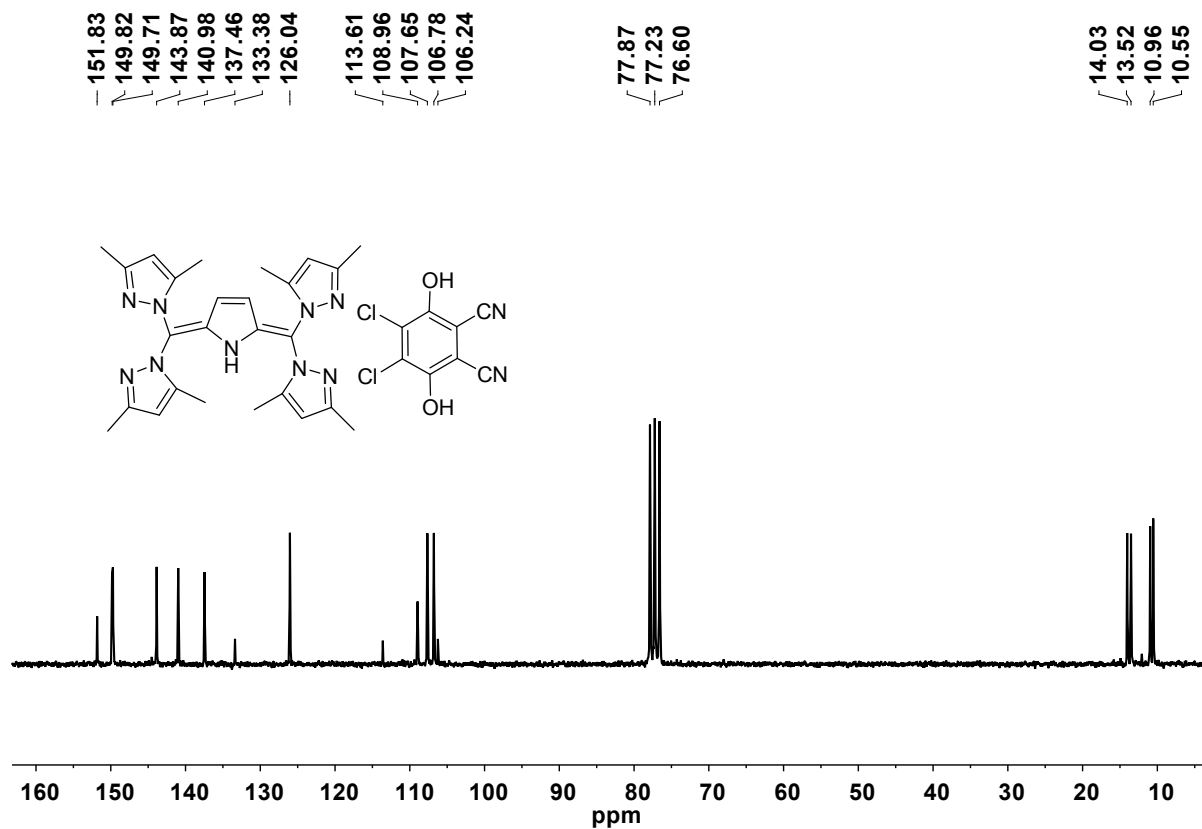


Figure S9.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of DDQH<sub>2</sub> adduct **5** in CDCl<sub>3</sub>.

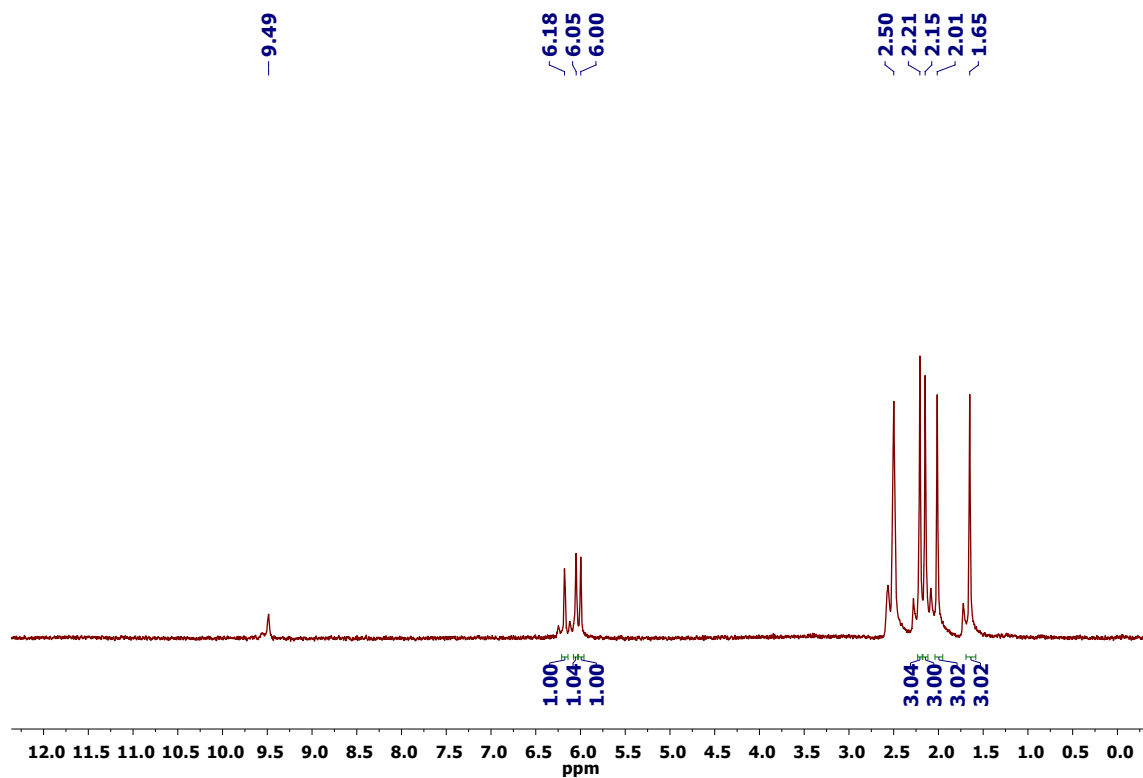


Figure S10.  $^1\text{H}$  NMR spectrum of the DDQH<sub>2</sub> adduct **5** in DMSO-*d*<sub>6</sub>.

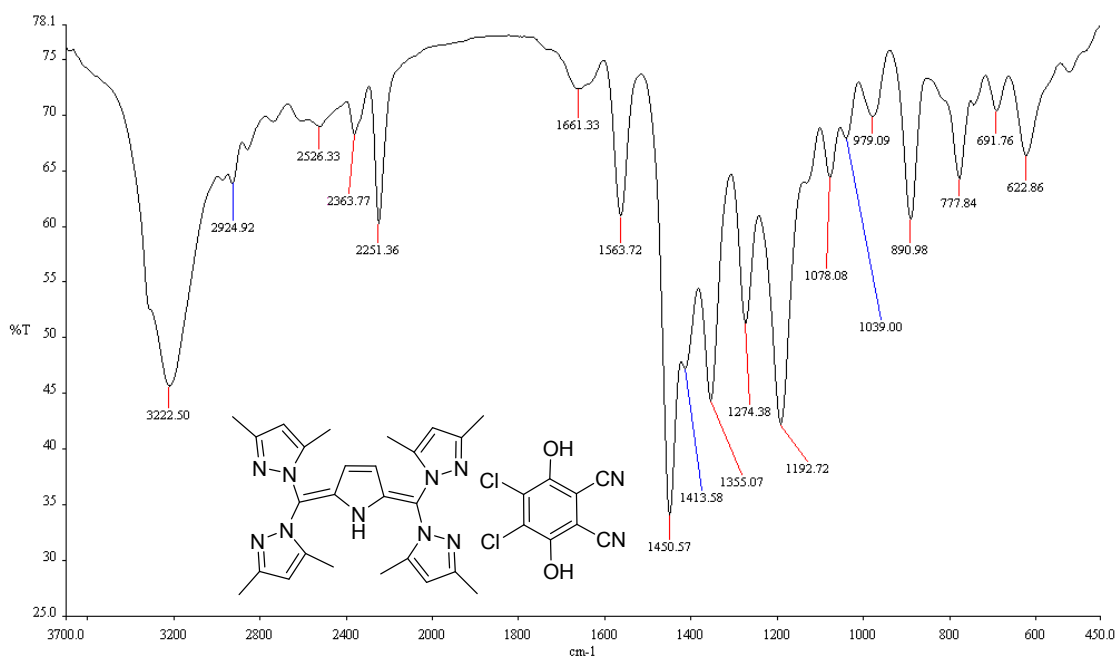
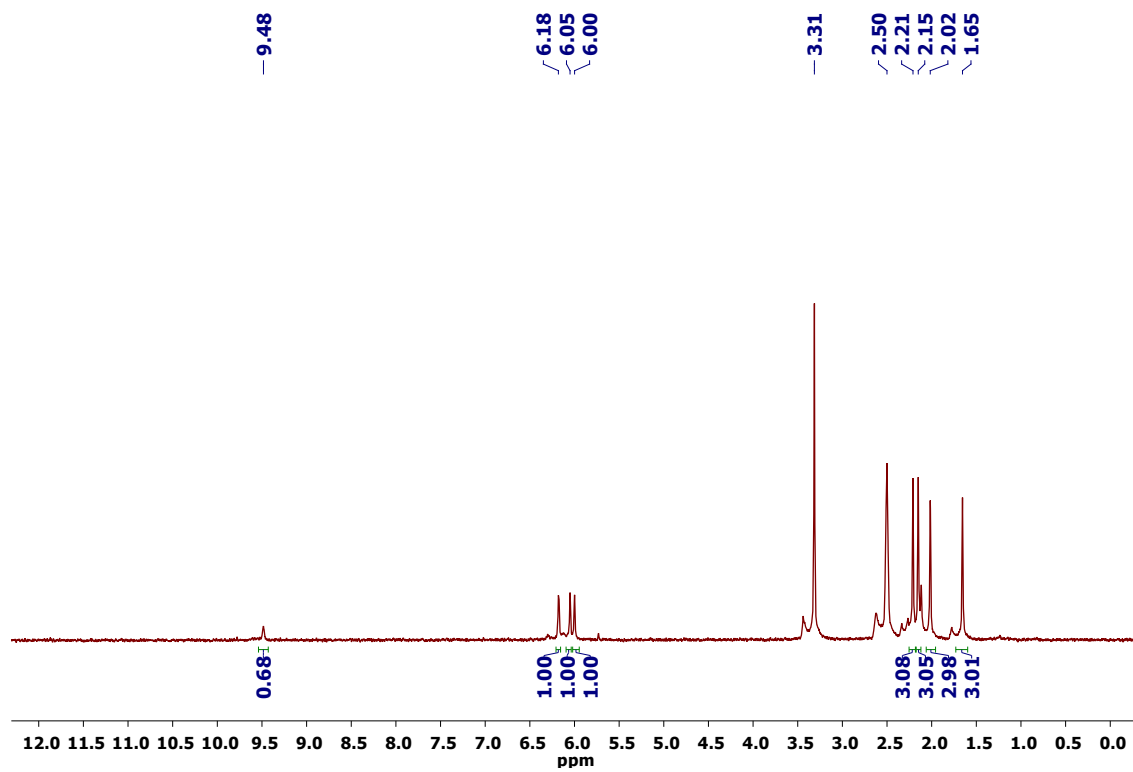
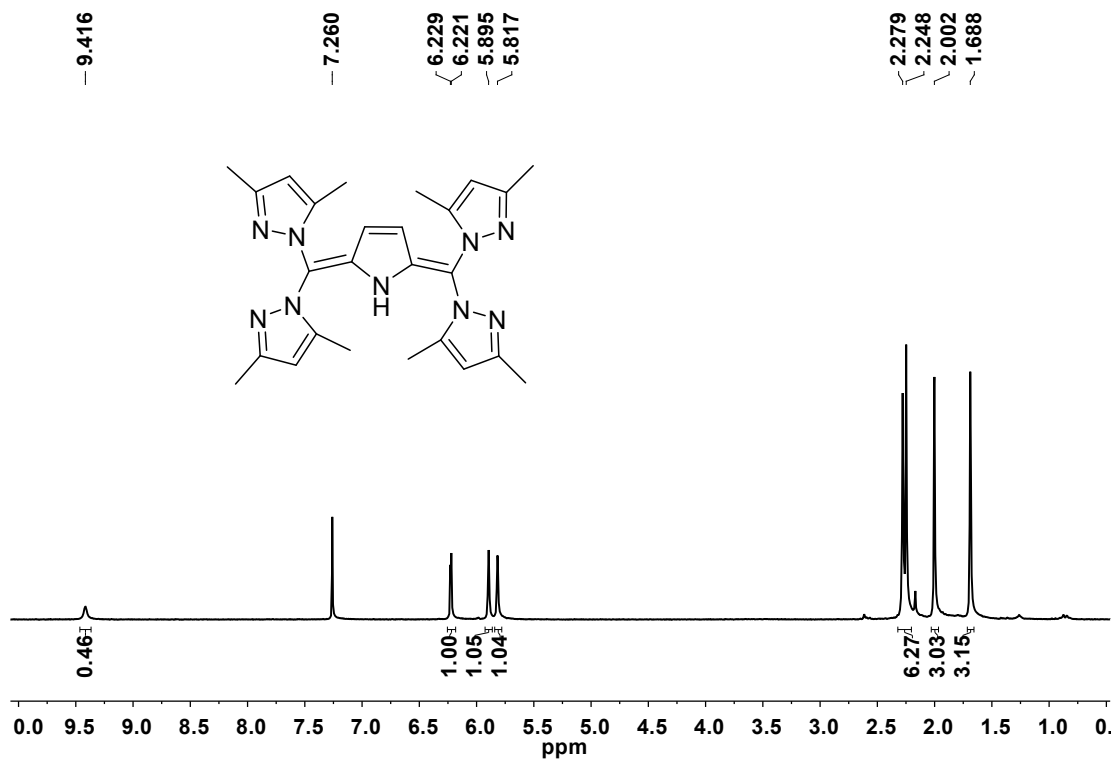


Figure S11. IR spectrum of DDQH<sub>2</sub> adduct **5** recorded as a KBr disc.

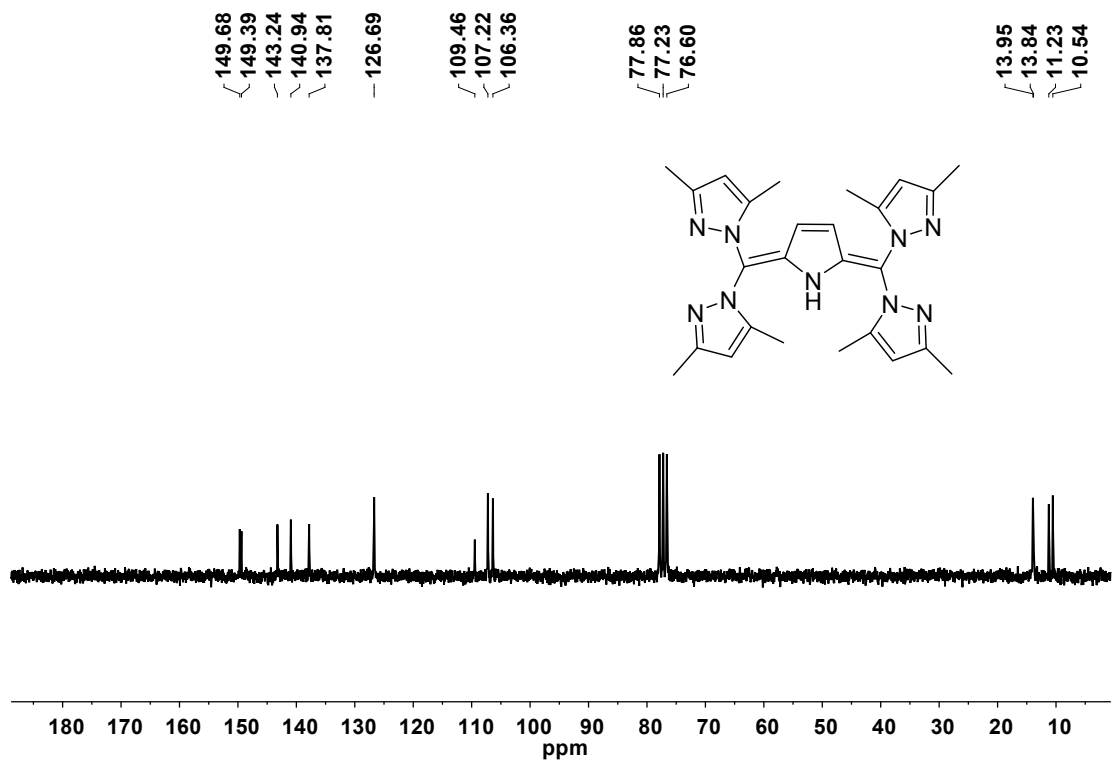


**Figure S12.**  $^1\text{H}$  NMR spectrum of 2,5-bis{di(3,5-dimethylpyrazolyl)methene}-2,5-dihydropyrrole **6** in  $\text{DMSO-}d_6$ .

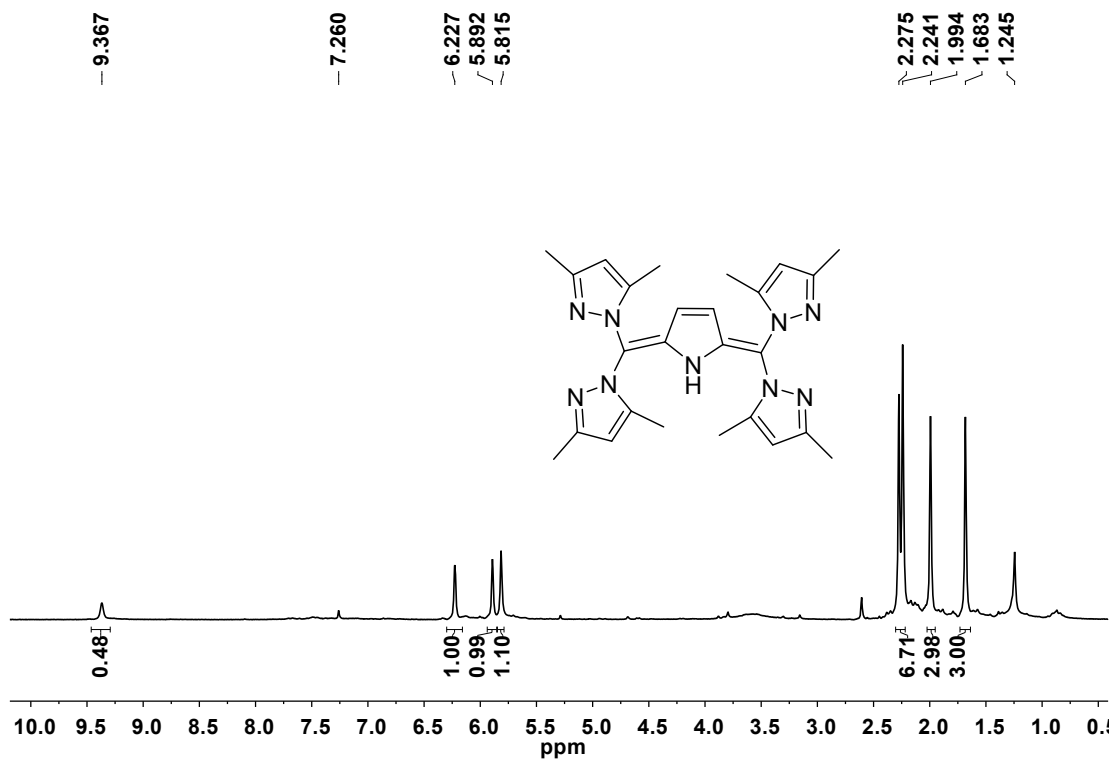




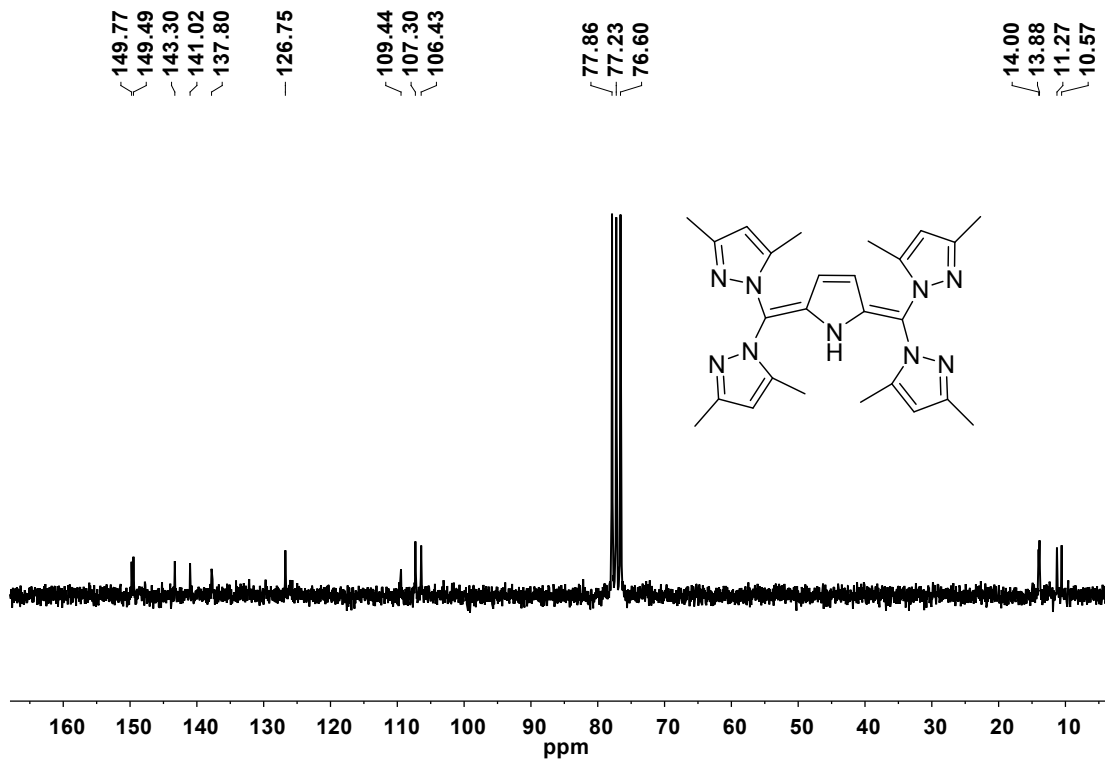
**Figure S13.** <sup>1</sup>H NMR spectrum of 2,5-bis{di(3,5-dimethylpyrazolyl)methene}-2,5-dihydropyrrole **6** in CDCl<sub>3</sub>, obtained by basic Al<sub>2</sub>O<sub>3</sub> method.



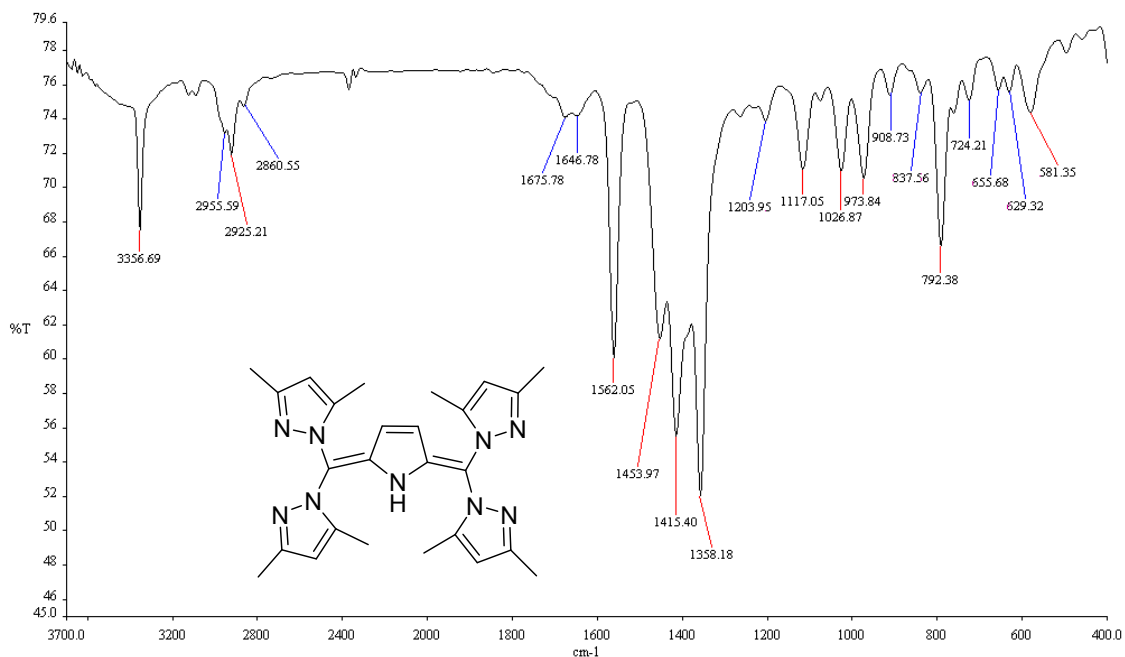
**Figure S14.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 2,5-bis{di(3,5-dimethylpyrazolyl)methene}-2,5-dihydropyrrole **6** in CDCl<sub>3</sub>, obtained by basic Al<sub>2</sub>O<sub>3</sub> method.



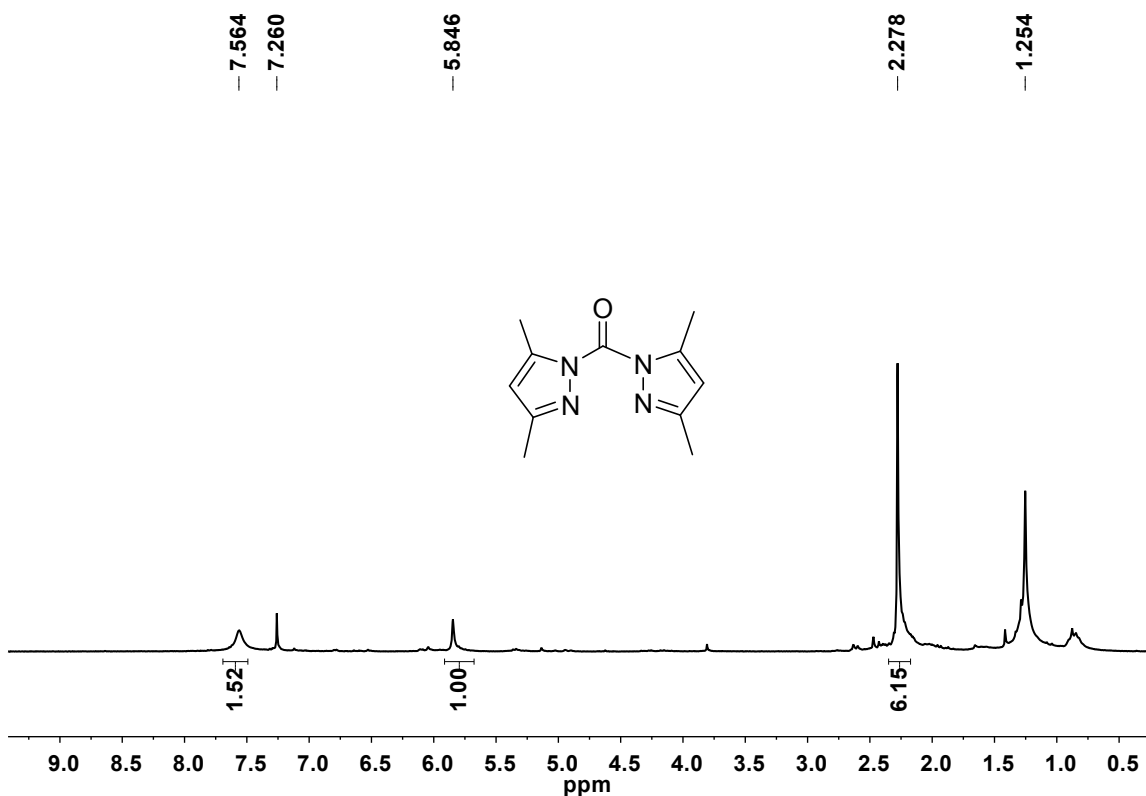
**Figure S15.**  $^1\text{H}$  NMR spectrum of 2,5-bis{di(3,5-dimethylpyrazolyl)methene}-2,5-dihydropyrrole **6** in  $\text{CDCl}_3$ , obtained by  $\text{NaBH}_4$  method.



**Figure S16.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 2,5-bis{di(3,5-dimethylpyrazolyl)methene}-2,5-dihydropyrrole **6** in  $\text{CDCl}_3$ , obtained by  $\text{NaBH}_4$  method.



**Figure S17.** IR spectrum of 2,5-bis{di(3,5-dimethylpyrazolyl)methene}-2,5-dihydropyrrole **6** recorded as a KBr disc.



**Figure S18.** <sup>1</sup>H NMR spectrum of bis-(3,5-dimethylpyrazolyl)methanone **7** in CDCl<sub>3</sub>.

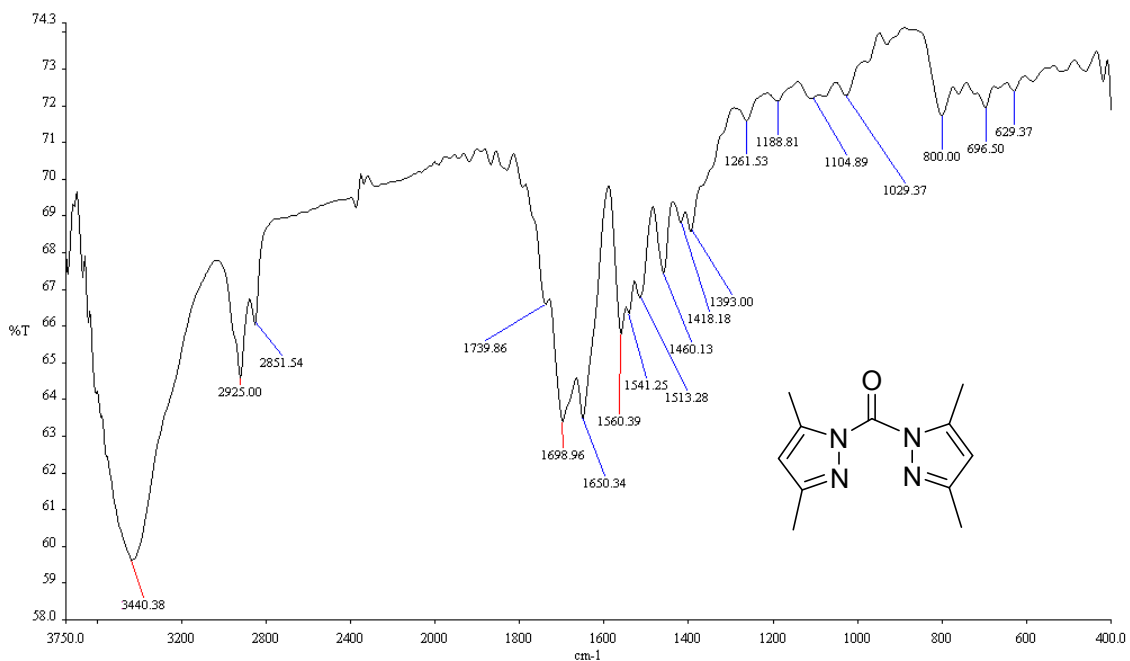


Figure S19. IR spectrum of bis-(3,5-dimethylpyrazolyl)methanone **7** recorded as a KBr disc.

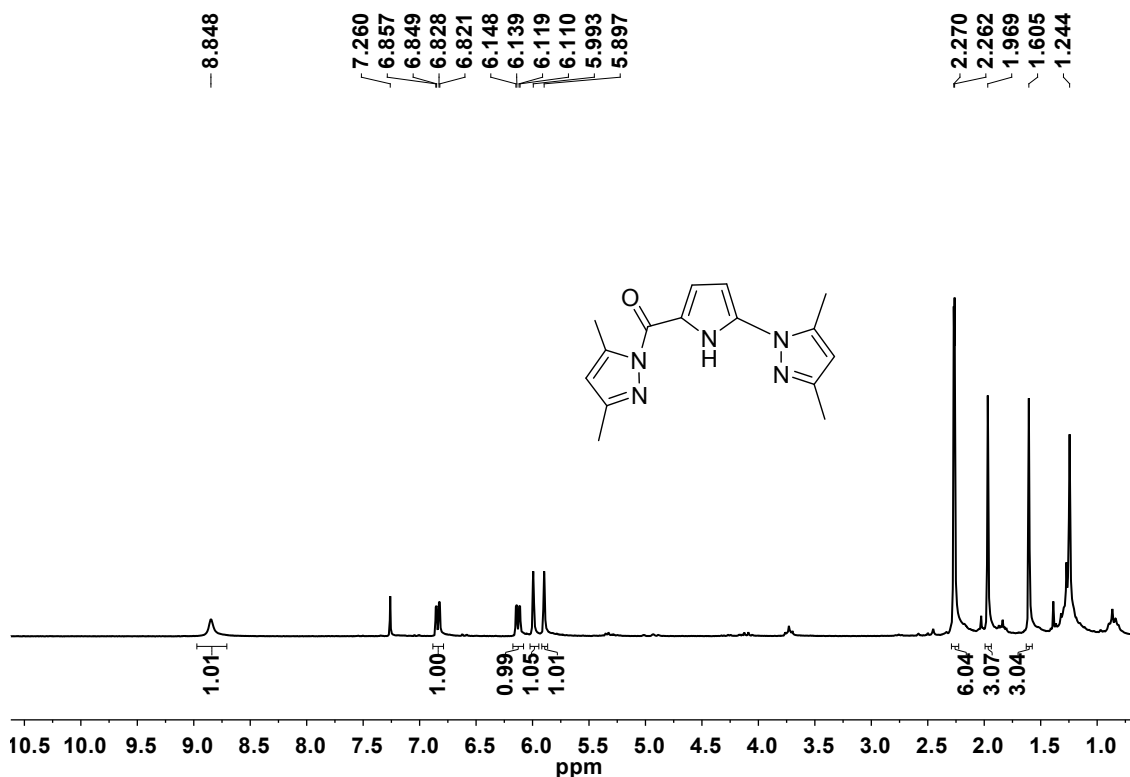
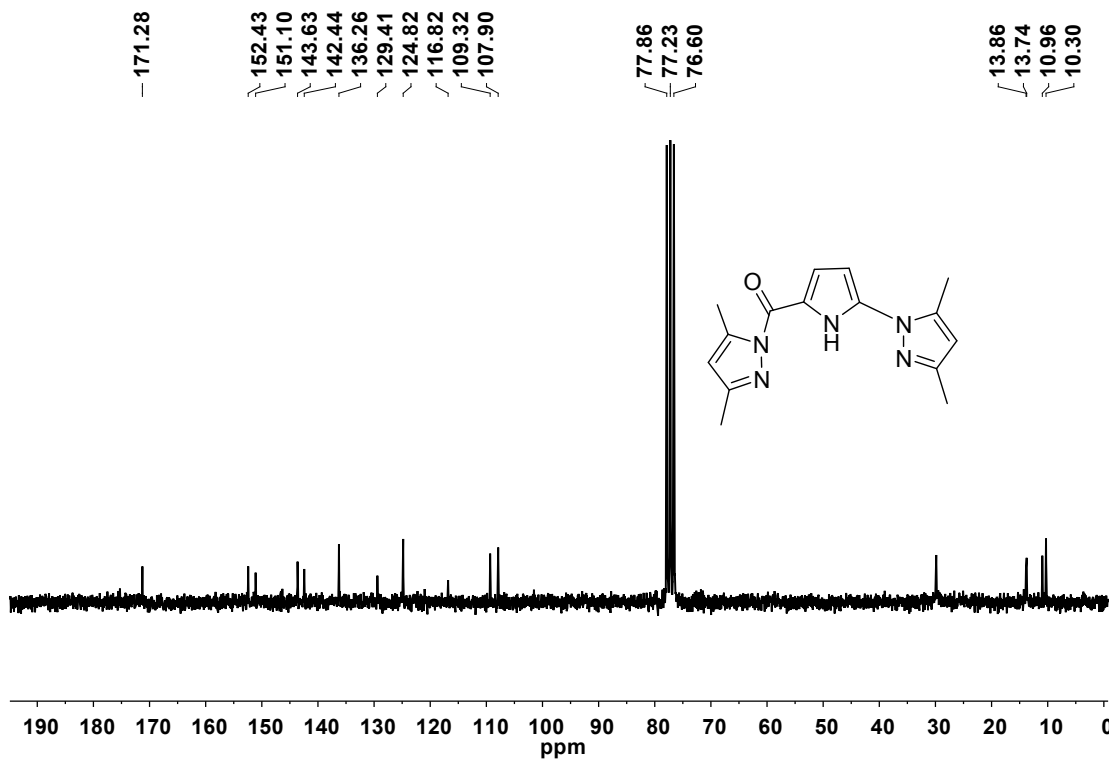
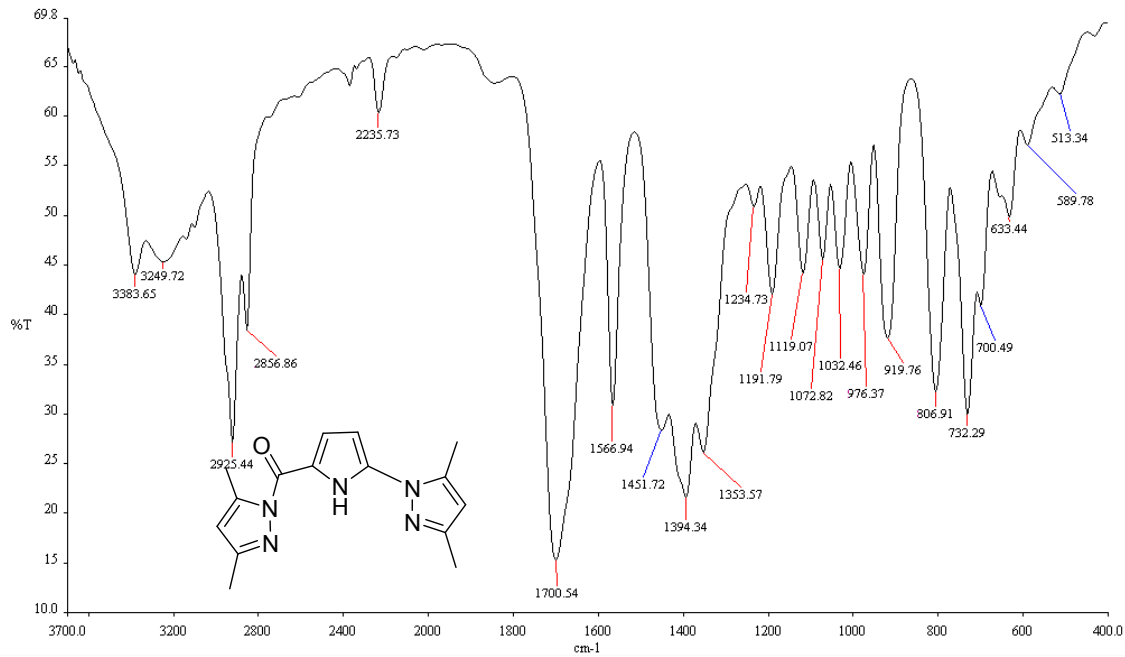


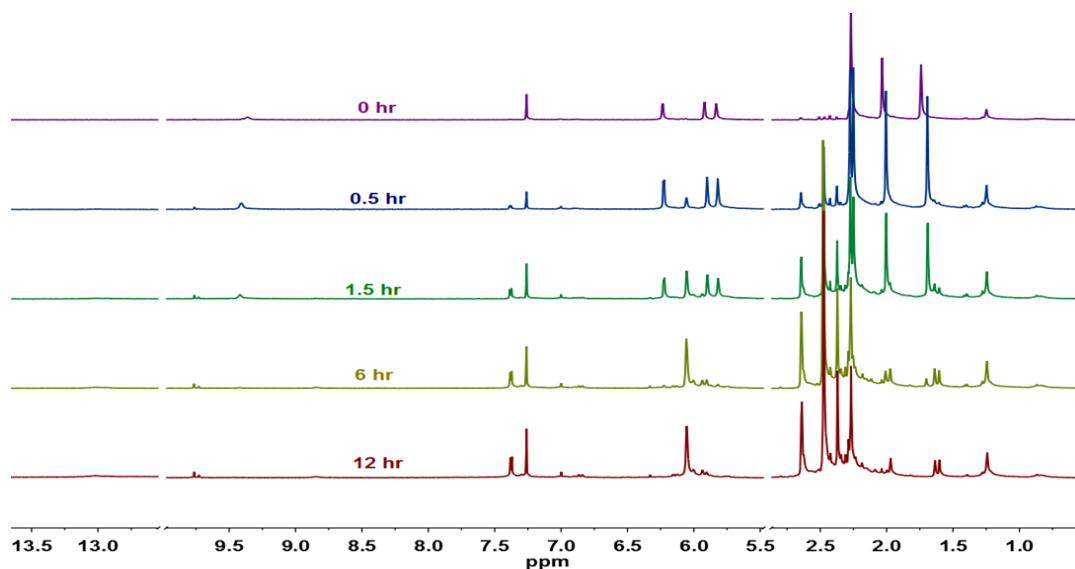
Figure S20. <sup>1</sup>H NMR spectrum of 2-(3,5-dimethylpyrazolylcarbonyl)-5-(3,5-dimethylpyrazolyl)pyrrole **8** in CDCl<sub>3</sub>.



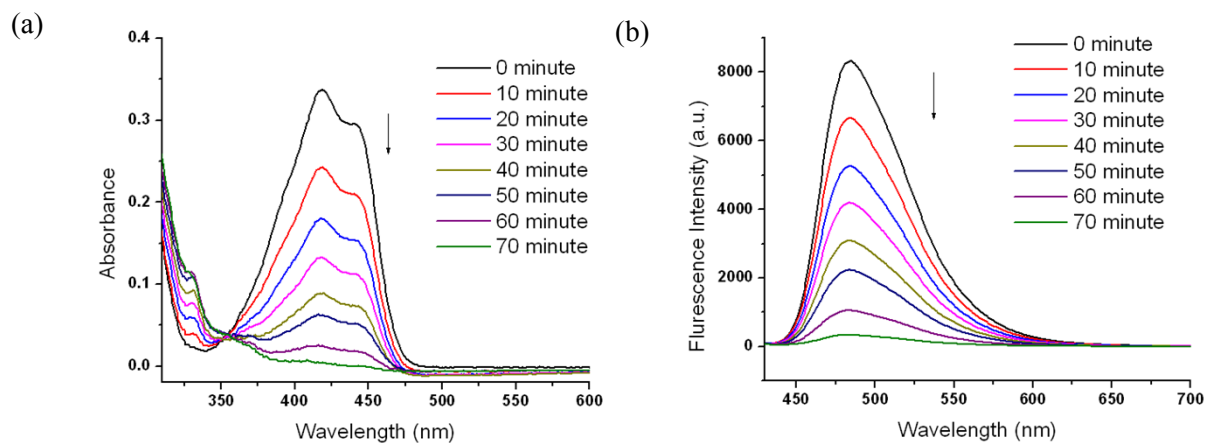
**Figure S21.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 2-(3,5-dimethylpyrazolylcarbonyl)-5-(3,5-dimethylpyrazolyl) pyrrole, **8** in  $\text{CDCl}_3$ .



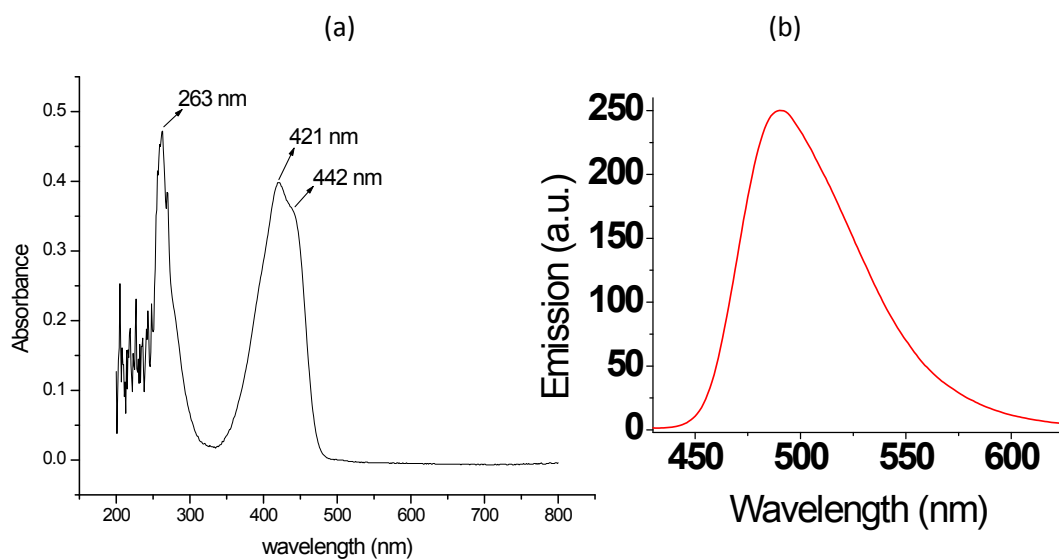
**Figure S22.** IR spectrum of 2-(3,5-dimethylpyrazolylcarbonyl)-5-(3,5-dimethylpyrazolyl)pyrrole, **8** recorded as a KBr disc.



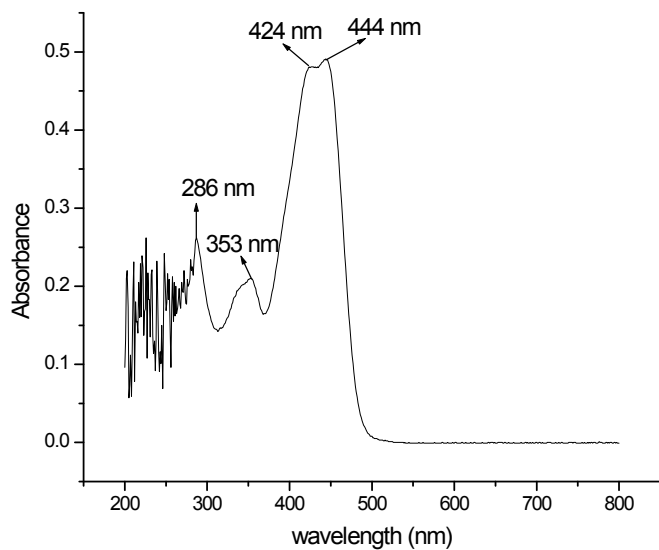
**Figure S23.** The  $^1\text{H}$  NMR spectra of **6** in  $\text{CDCl}_3$  recorded at different time intervals, showing the formation of compound **2** which has the characteristic peaks at  $\delta$  6.06 ppm and  $\delta$  7.38 ppm as the major compound along with other resonances due to the other products.



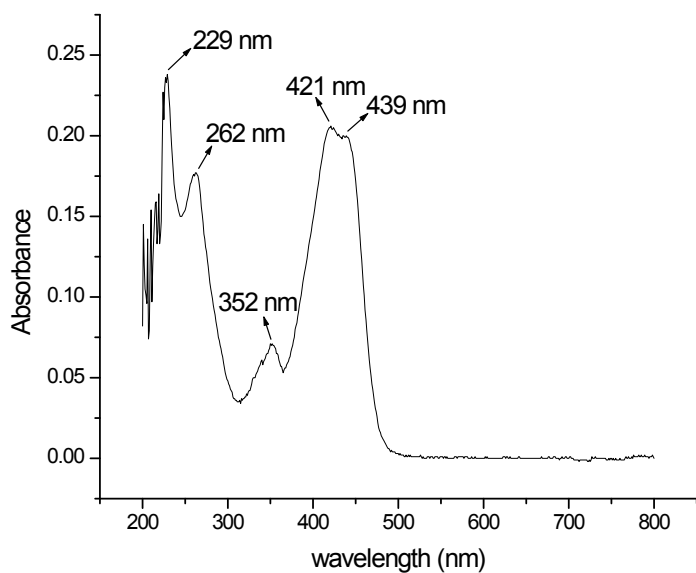
**Figure S24.** The change in the UV-Vis (a) and the fluorescence (b) spectra of **6** in toluene solution ( $1 \times 10^{-5}$  M) upon reaction with oxygen at different time intervals under sunlight irradiation.



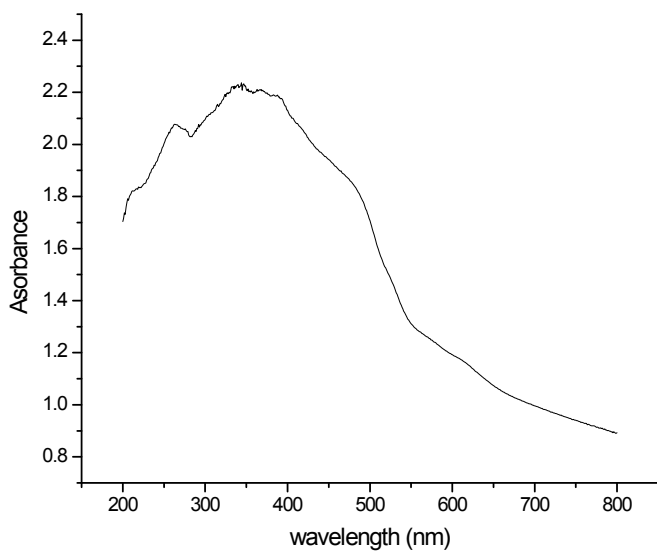
**Figure S25.** (a) The UV-vis spectrum of the adduct **5** in DMSO ( $1 \times 10^{-5}$  M); (b) the emission spectrum of **5** in DMSO solution ( $1 \times 10^{-5}$  M) (excitation at 420 nm).



**Figure S26.** The UV-vis spectrum of the adduct **5** in toluene ( $1 \times 10^{-4}$  M).

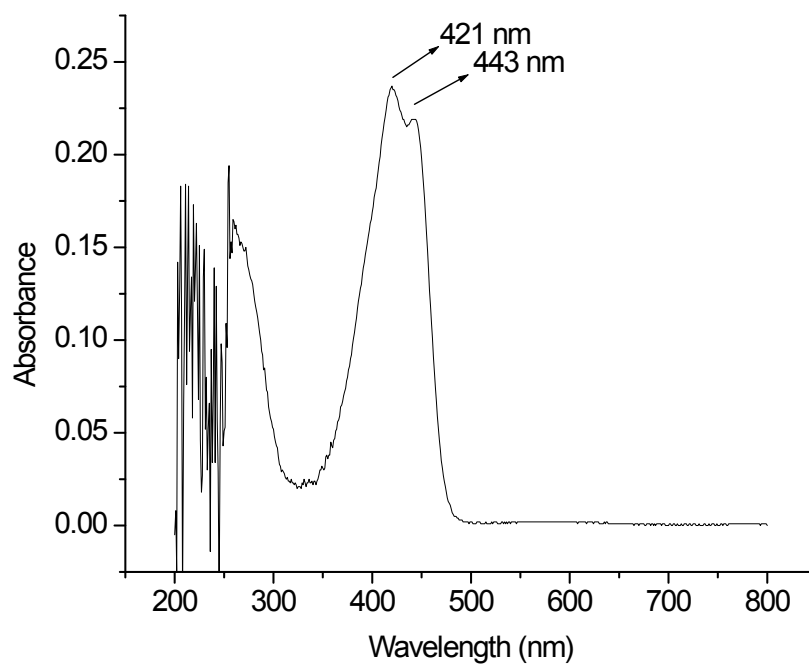


**Figure S27.** The UV-vis spectrum of the adduct **5** in dichloromethane ( $1 \times 10^{-5}$  M).

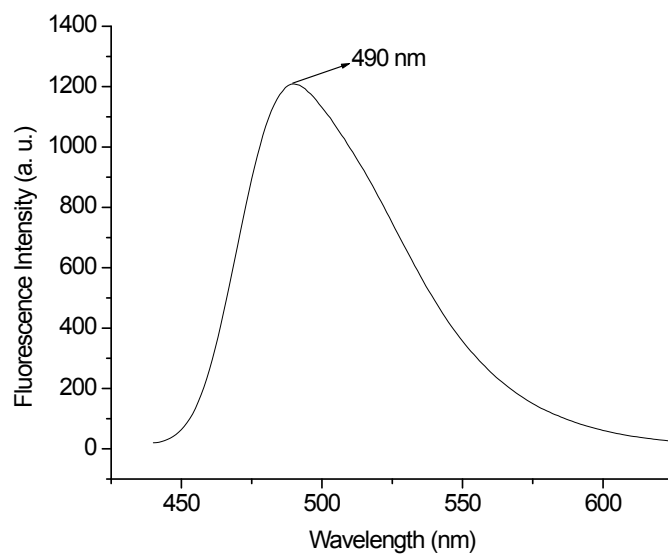


**Figure S28.** The solid state UV-vis spectrum of the adduct **5**.

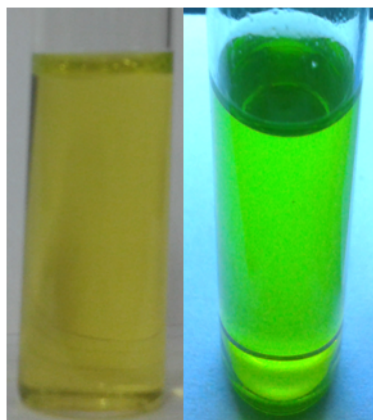




**Figure S29.** The UV-vis spectrum of the free base **6** in DMSO ( $1 \times 10^{-5}$  M).

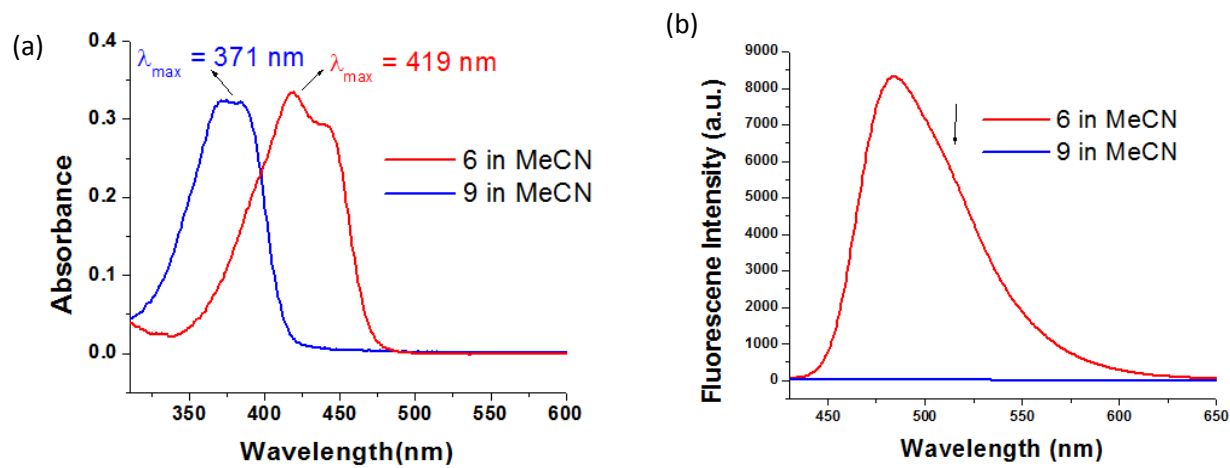


**Figure S30.** The emission spectrum of the free base **6** in DMSO solution ( $1 \times 10^{-5}$  M) (excitation at 420 nm).

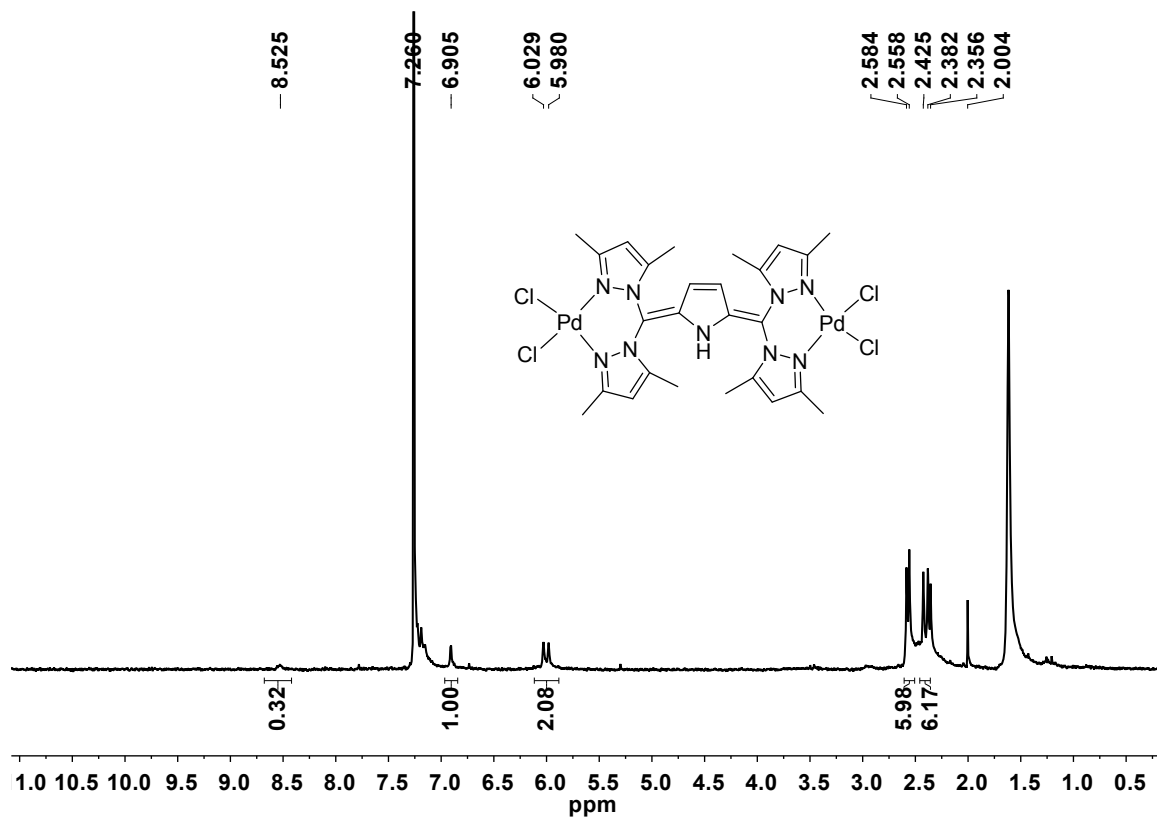


a b

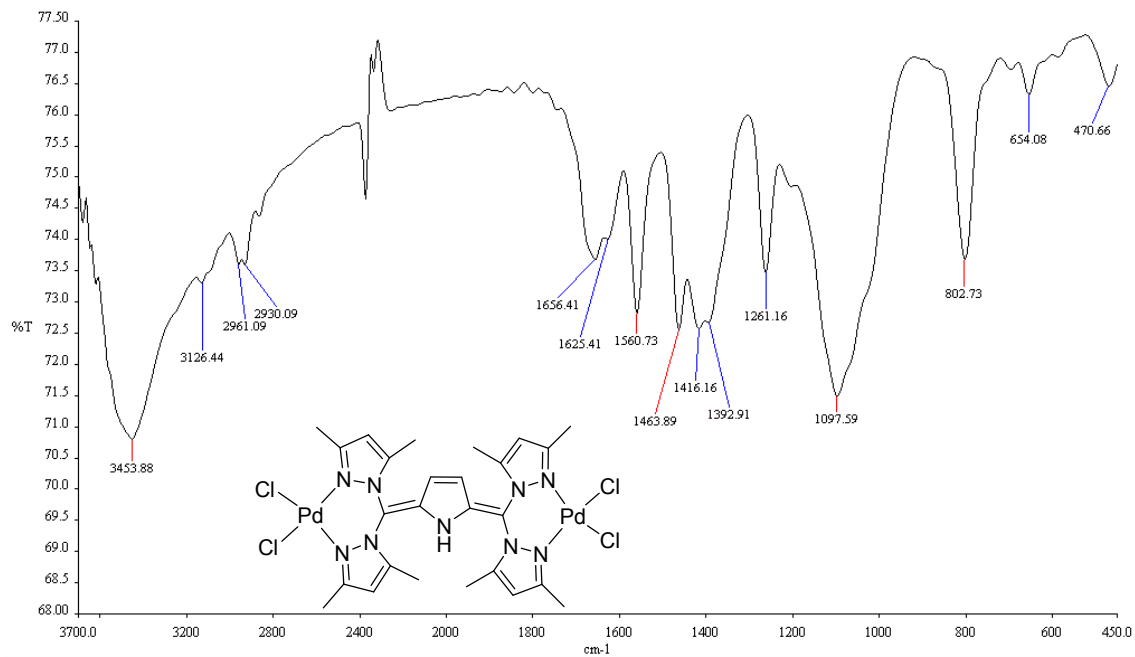
**Figure S31.** The DMSO solution of the quinoidal pyrrole molecule **6** under irradiation of (a) ordinary and (b) UV light.



**Figure S32.** (a) The UV-vis spectra of **6** and **9** in MeCN, showing the blue shifted  $\lambda_{\max}$  for **9** and (b) the emission spectra of **9** showing the disappearance of fluorescence.



**Figure S33.**  $^1\text{H}$  NMR spectrum of  $[\text{Pd}_2\text{Cl}_4\{\mu\text{-C}_4\text{H}_3\text{N-2,5-(C(Me}_2\text{pz})_2)_2\text{-N,N,N,N}\}]$ , **9** in  $\text{CDCl}_3$ .



**Figure S34.** IR spectrum of  $[\text{Pd}_2\text{Cl}_4\{\mu\text{-C}_4\text{H}_3\text{N-2,5-(C(Me}_2\text{pz})_2)_2\text{-N,N,N,N}\}]$ , **9** recorded as a KBr disc.