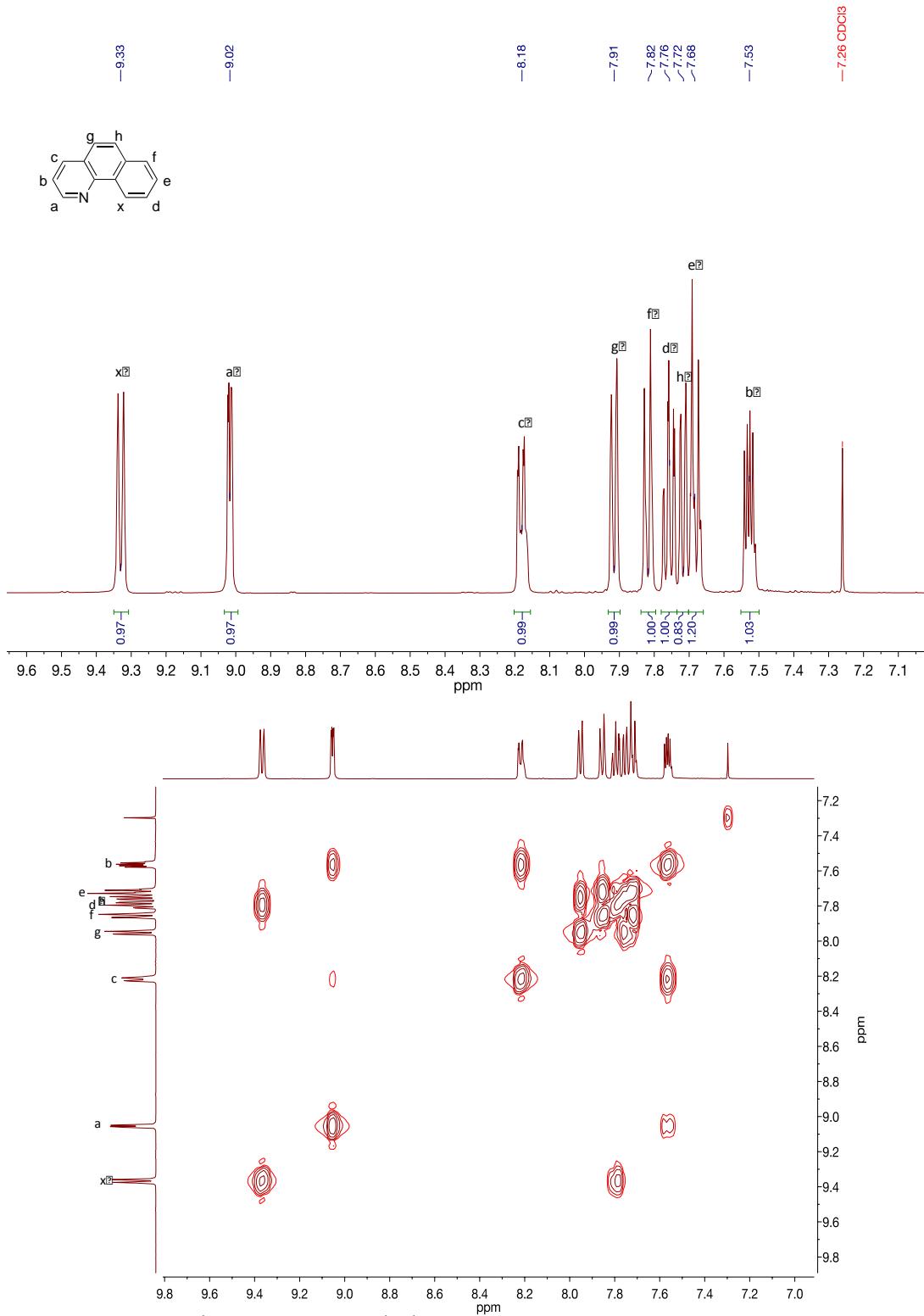


# Organometallic Ru(II) Photosensitizers Derived from $\pi$ -Expansive Cyclometalating Ligands: Surprising Theranostic PDT Effects

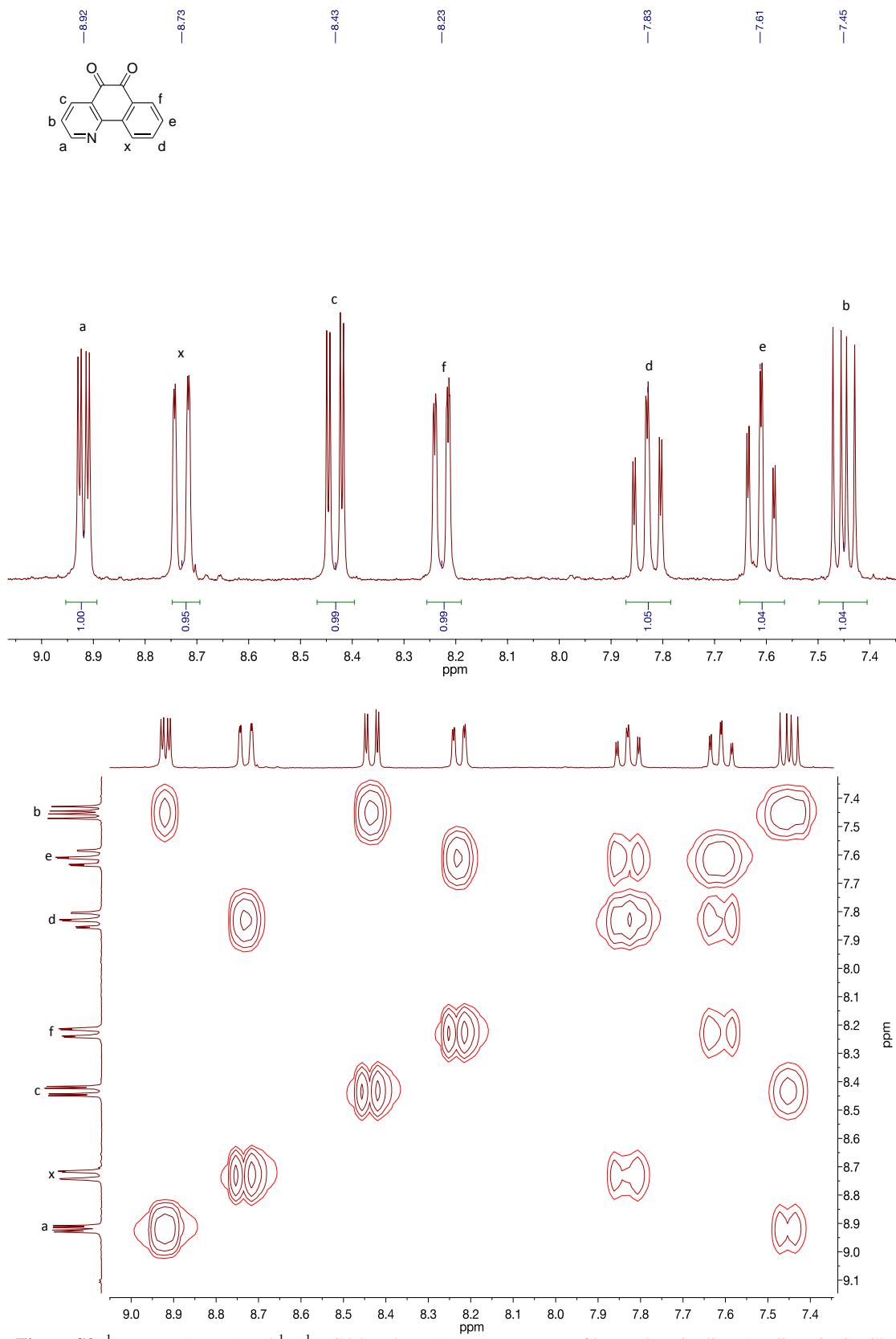
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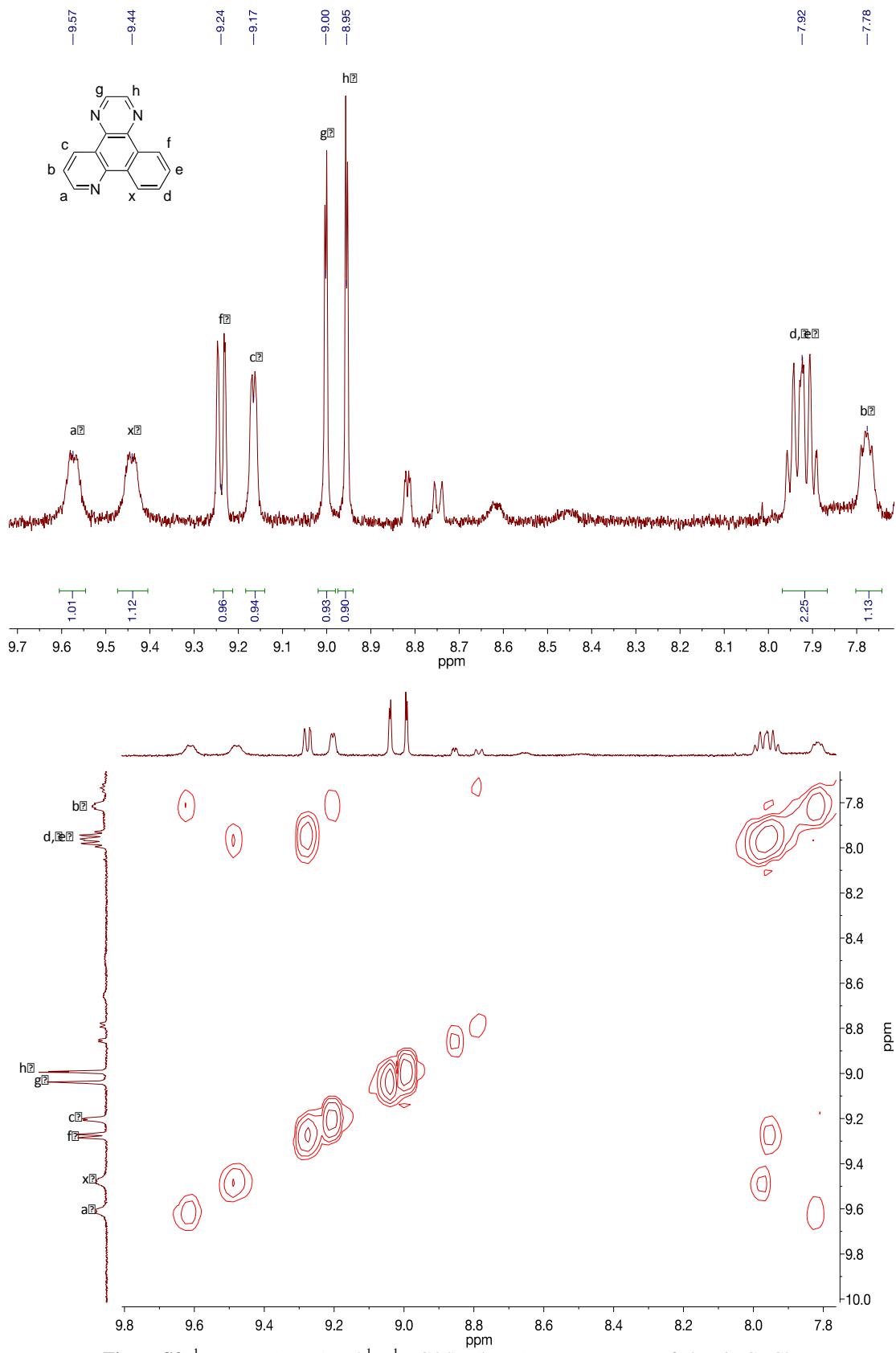
Supporting Information	Page
Figure S1. $^1\text{H}$ NMR (upper) and $^1\text{H}$ - $^1\text{H}$ COSY (lower) NMR spectrum of bhq in $\text{CDCl}_3$ .....	2
Figure S2. $^1\text{H}$ NMR (upper) and $^1\text{H}$ - $^1\text{H}$ COSY (lower) NMR spectrum of benzo[h]quinoline-5,6-dione in $\text{CDCl}_3$ .....	3
Figure S3. $^1\text{H}$ NMR (upper) and $^1\text{H}$ - $^1\text{H}$ COSY (lower) NMR spectrum of pbpq in $\text{CDCl}_3$ .....	4
Figure S4. $^1\text{H}$ NMR (upper) and $^1\text{H}$ - $^1\text{H}$ COSY (lower) NMR spectrum of pbpz in $\text{CDCl}_3$ .....	5
Figure S5. $^1\text{H}$ NMR (upper) and $^1\text{H}$ - $^1\text{H}$ COSY (lower) NMR spectrum of pbpn in $\text{CDCl}_3$ .....	6
Figure S6. $^1\text{H}$ NMR (upper) and $^1\text{H}$ - $^1\text{H}$ COSY (lower) NMR spectrum of compound 1 in $\text{MeCN-}d_3$ .....	7
Figure S7. $^1\text{H}$ NMR (upper) and $^1\text{H}$ - $^1\text{H}$ COSY (lower) NMR spectrum of compound 2 in $\text{MeCN-}d_3$ .....	8
Figure S8. $^{13}\text{C}$ NMR full spectrum (upper) and its aromatic region (lower) of compound 2 in $\text{MeCN-}d_3$ .....	9
Figure S9. $^1\text{H}$ NMR (upper) and $^1\text{H}$ - $^1\text{H}$ COSY (lower) NMR spectrum of compound 3 in $\text{MeCN-}d_3$ .....	10
Figure S10. $^{13}\text{C}$ NMR full spectrum (upper) and its aromatic region (lower) of compound 3 in $\text{MeCN-}d_3$ .....	11
Figure S11. $^1\text{H}$ NMR (upper) and $^1\text{H}$ - $^1\text{H}$ COSY (lower) NMR spectrum of compound 4 in $\text{MeCN-}d_3$ .....	12
Figure S12. $^{13}\text{C}$ NMR full spectrum (upper) and its aromatic region (lower) of compound 4 in $\text{MeCN-}d_3$ .....	13
Figure S13. DNA photocleavage of pUC19 DNA dosed with metal complex 3 and visible light. ....	14
Figure S14. DNA photocleavage of pUC19 DNA dosed with metal complex 4 and visible light.....	15
Figure S15. Microscopic images of MC-DNA samples used for gel electrophoresis experiments. ....	16



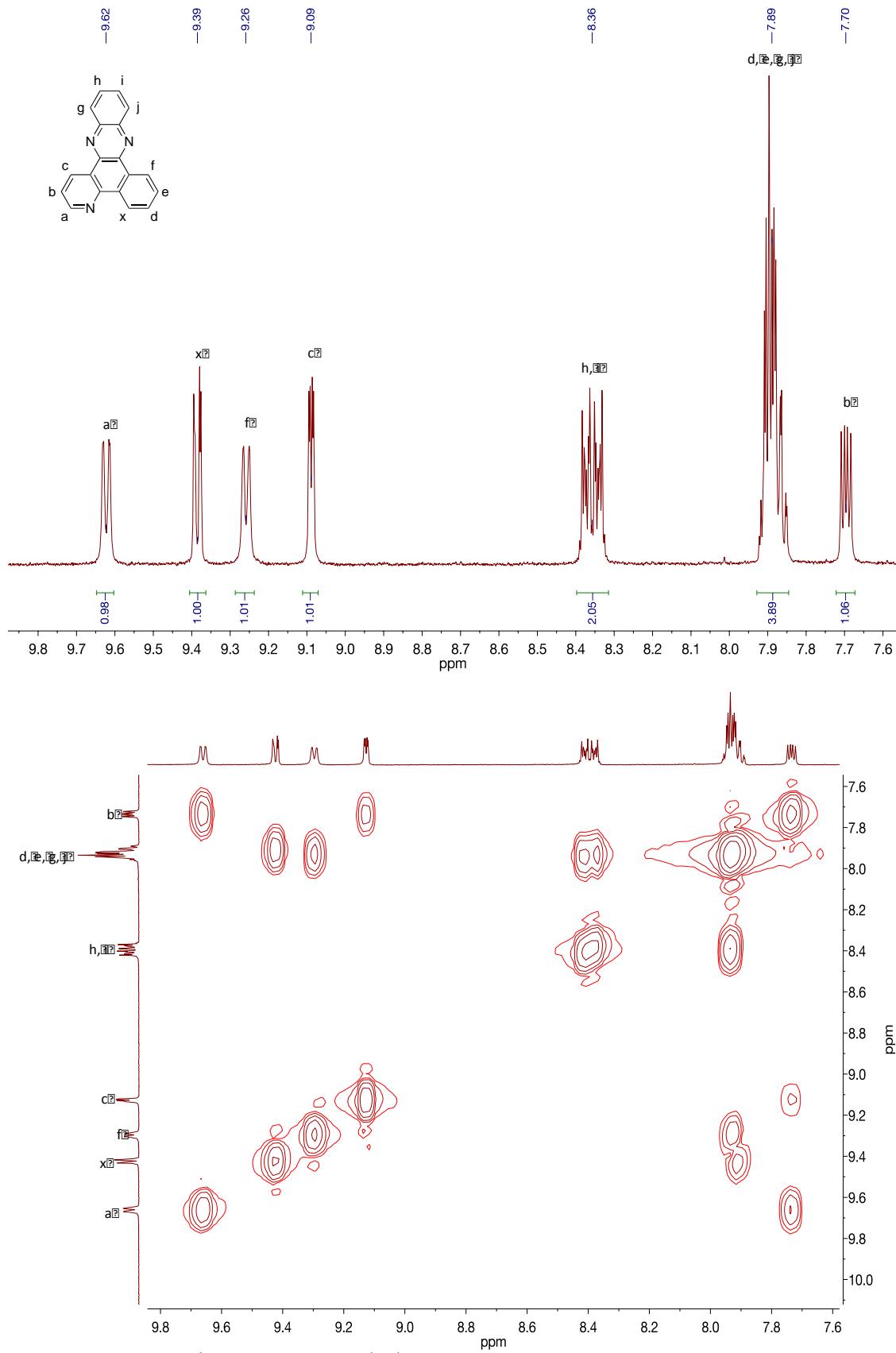
**Figure S1.** <sup>1</sup>H NMR (upper) and <sup>1</sup>H-<sup>1</sup>H COSY (lower) NMR spectrum of bhq in CDCl<sub>3</sub>.



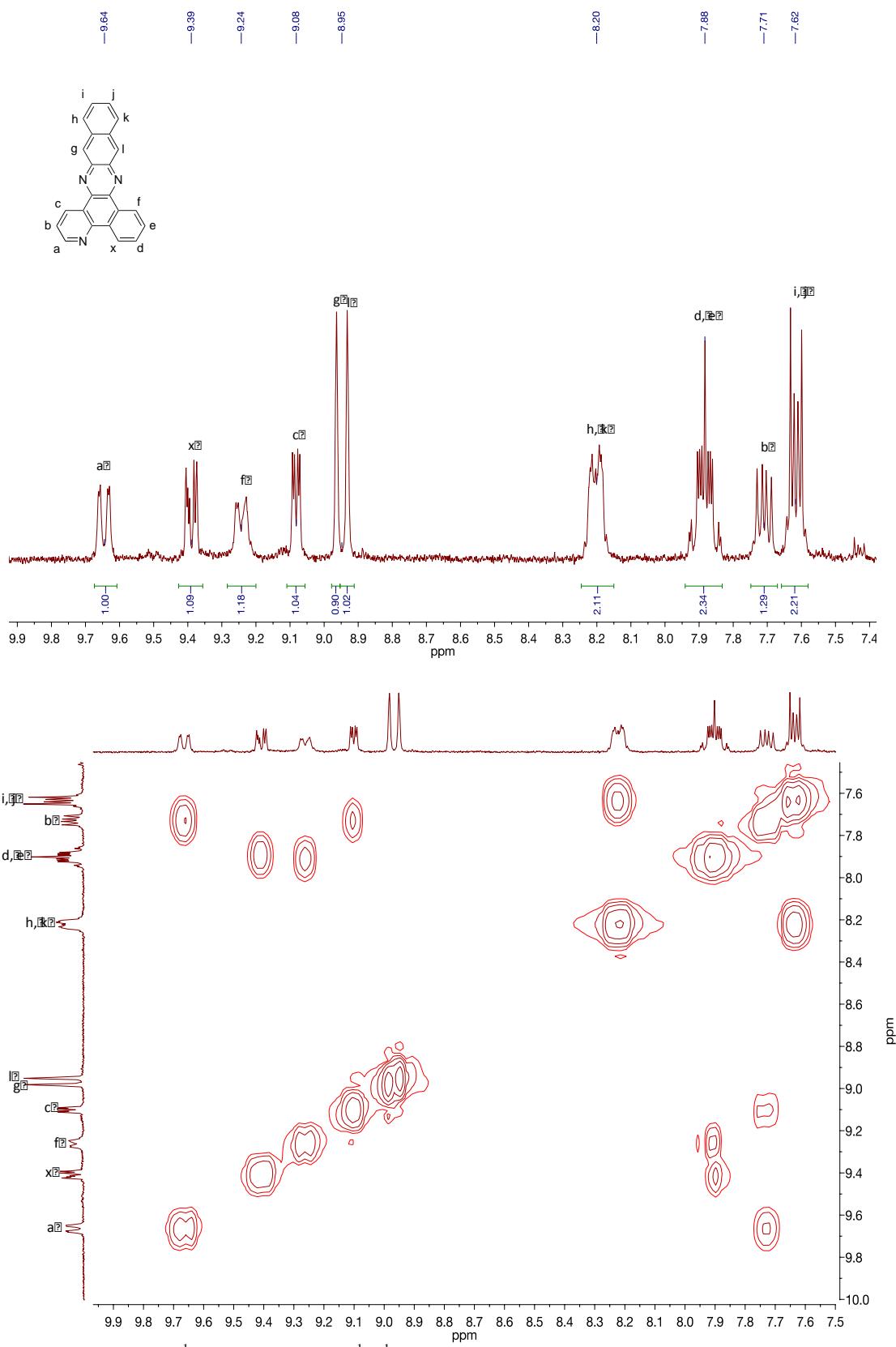
**Figure S2.**  $^1\text{H}$  NMR (upper) and  $^1\text{H}-^1\text{H}$  COSY (lower) NMR spectrum of benzo[h]quinoline-5,6-dione in  $\text{CDCl}_3$ .



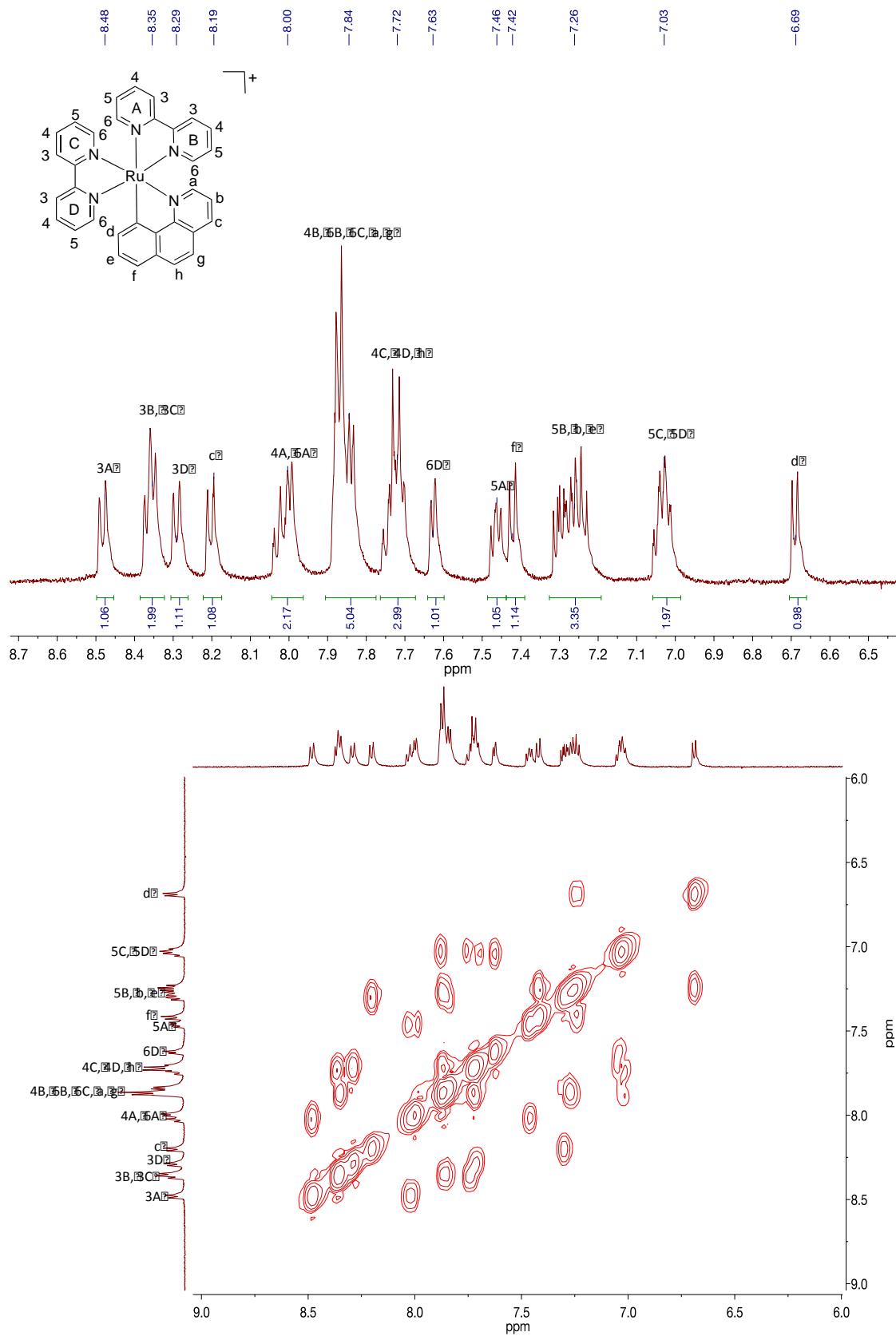
**Figure S3.**  $^1\text{H}$  NMR (upper) and  $^1\text{H}-^1\text{H}$  COSY (lower) NMR spectrum of pbpq in  $\text{CDCl}_3$ .



**Figure S4.**  $^1\text{H}$  NMR (upper) and  $^1\text{H}-^1\text{H}$  COSY (lower) NMR spectrum of pbpz in  $\text{CDCl}_3$ .



**Figure S5.** <sup>1</sup>H NMR (upper) and <sup>1</sup>H-<sup>1</sup>H COSY (lower) NMR spectrum of pbpn in CDCl<sub>3</sub>.



**Figure S6.**  $^1\text{H}$  NMR (upper) and  $^1\text{H}-^1\text{H}$  COSY (lower) spectrum of compound **1** in  $\text{MeCN}-d_3$ .

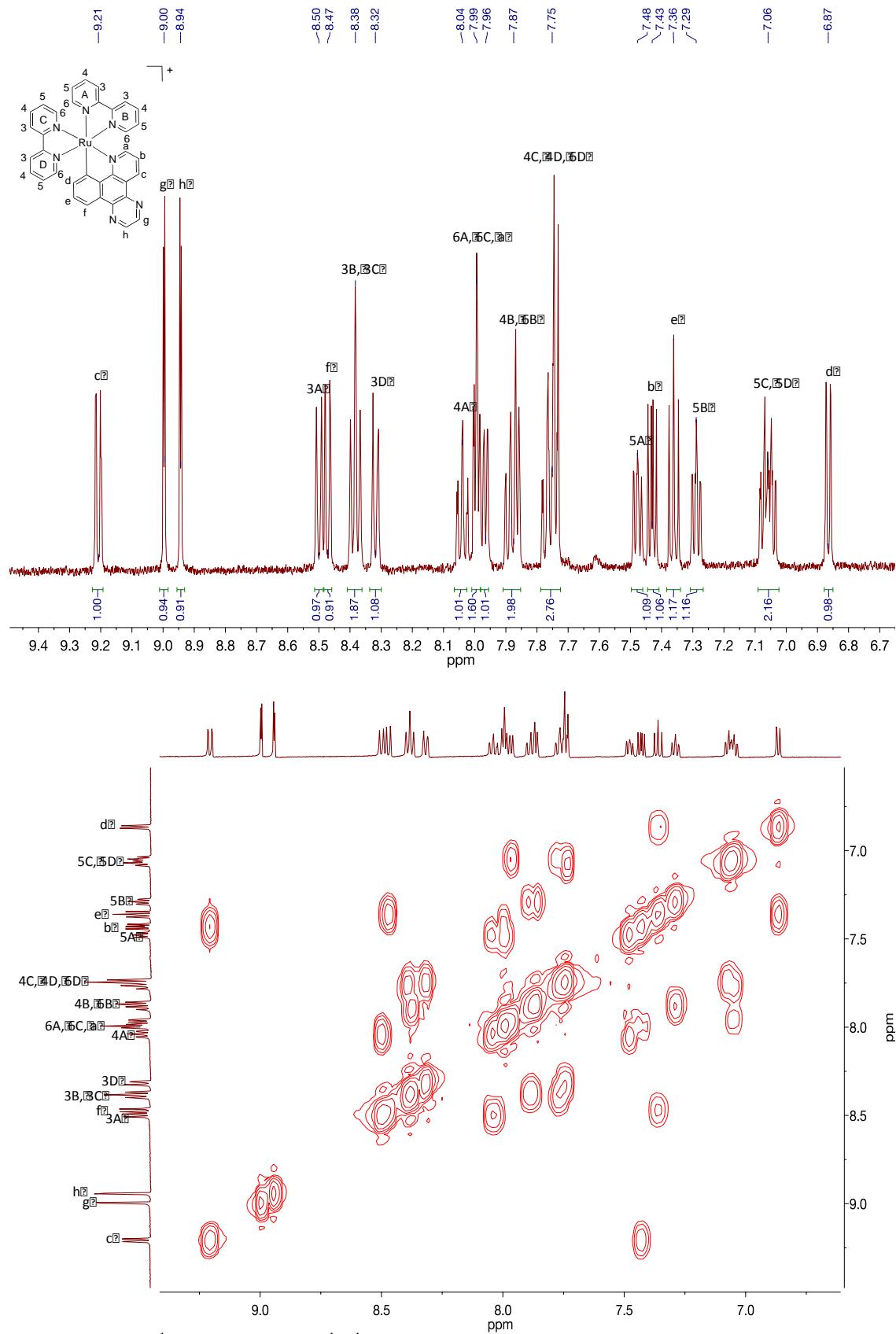
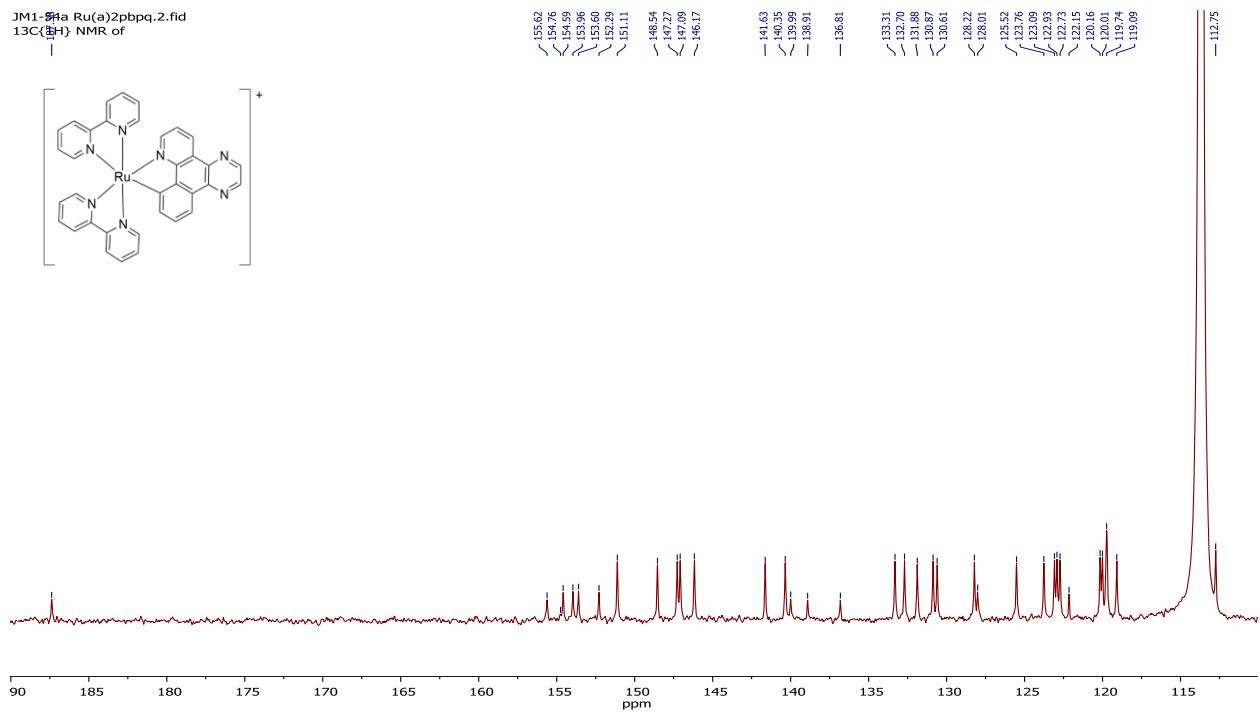
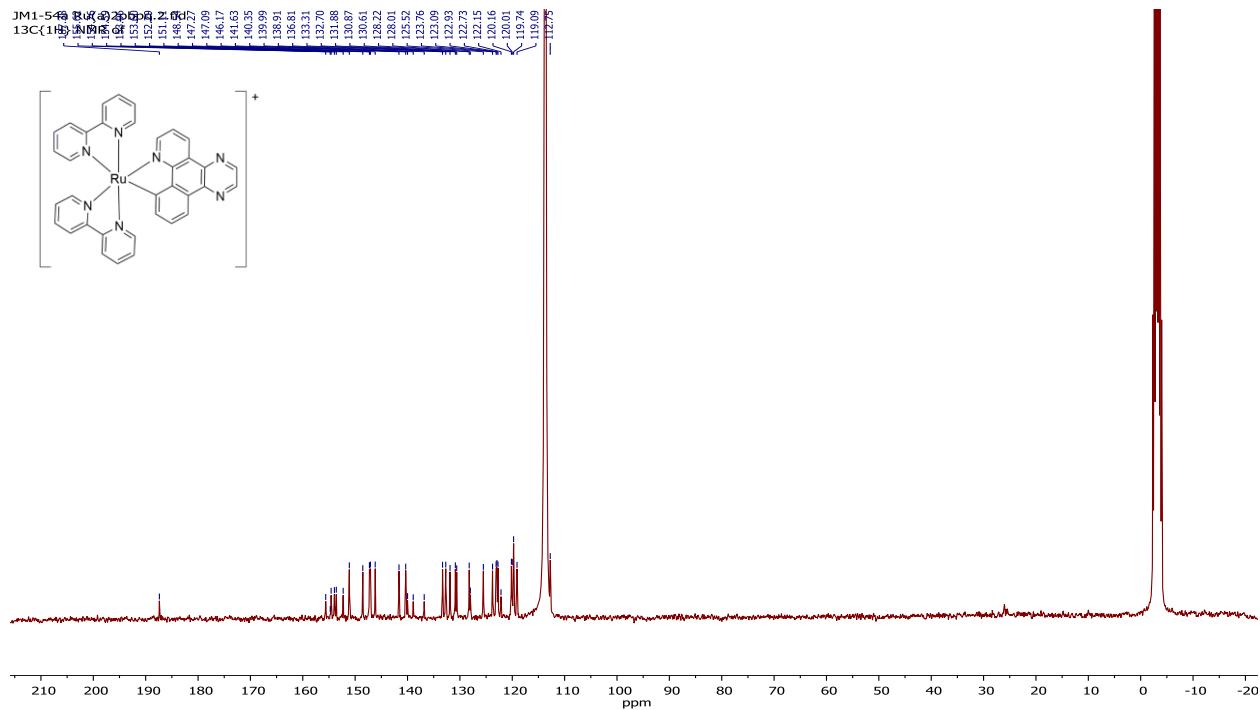
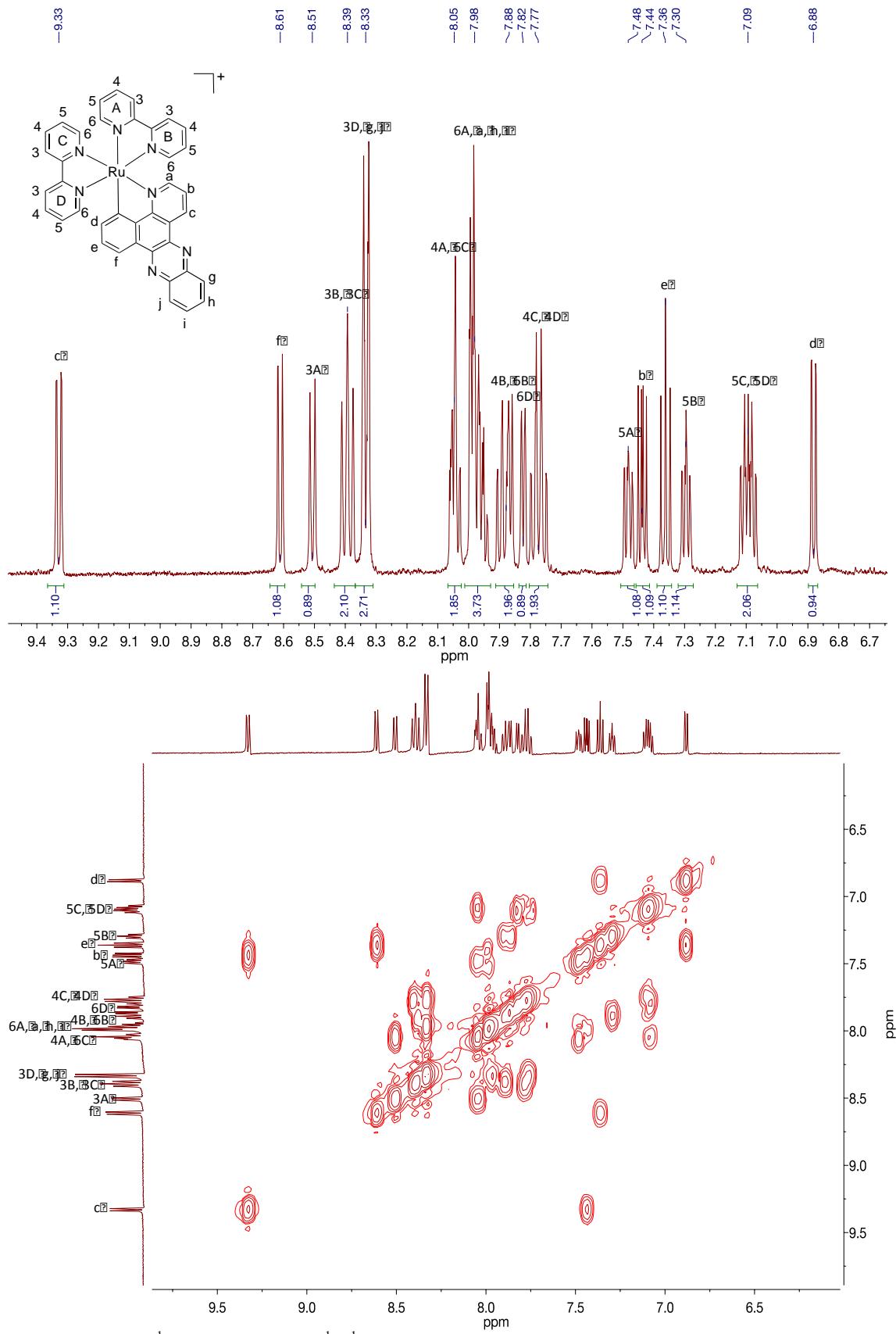


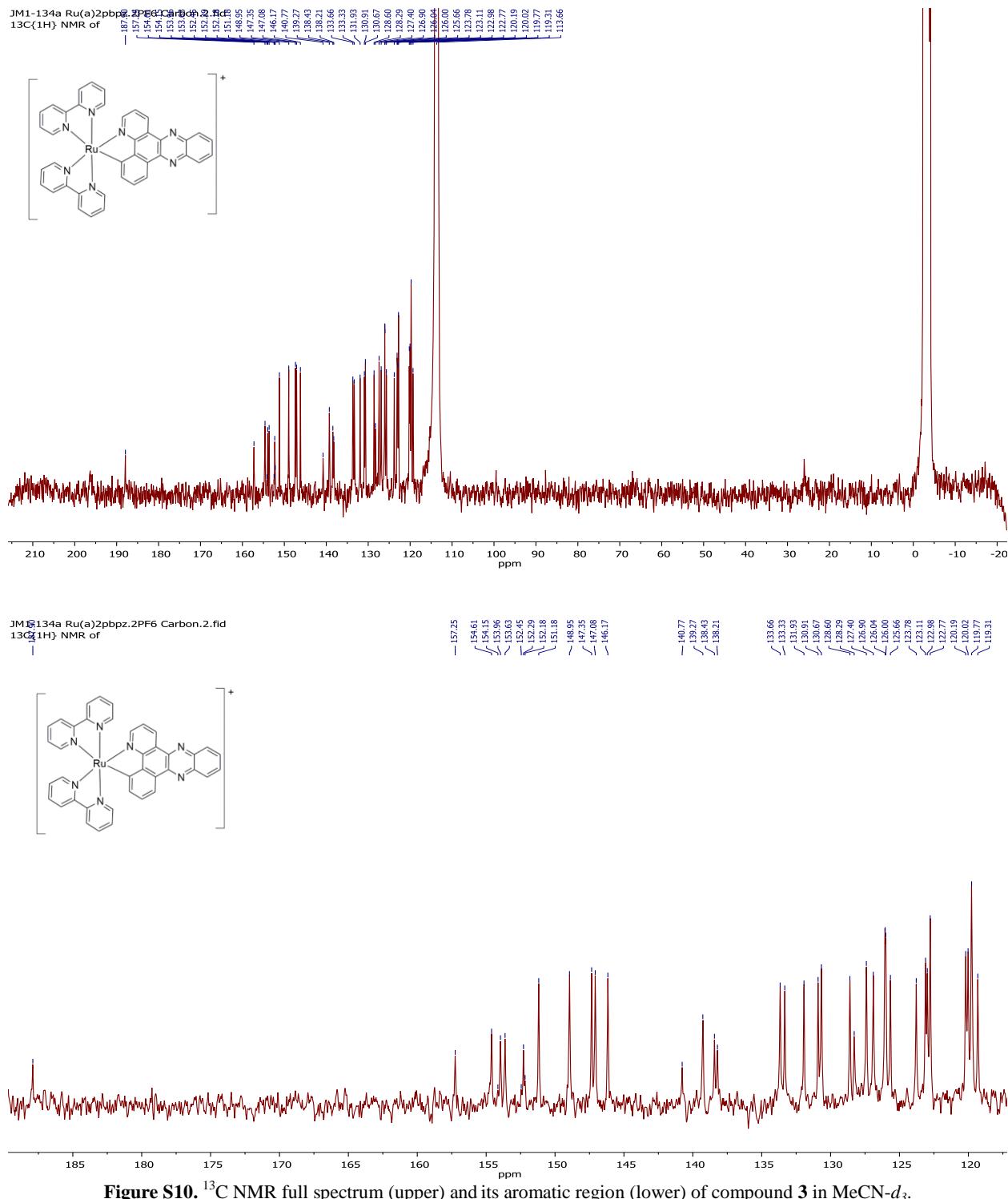
Figure S7. <sup>1</sup>H NMR (upper) and <sup>1</sup>H-<sup>1</sup>H COSY (lower) NMR spectrum of compound 2 in MeCN-*d*<sub>3</sub>.



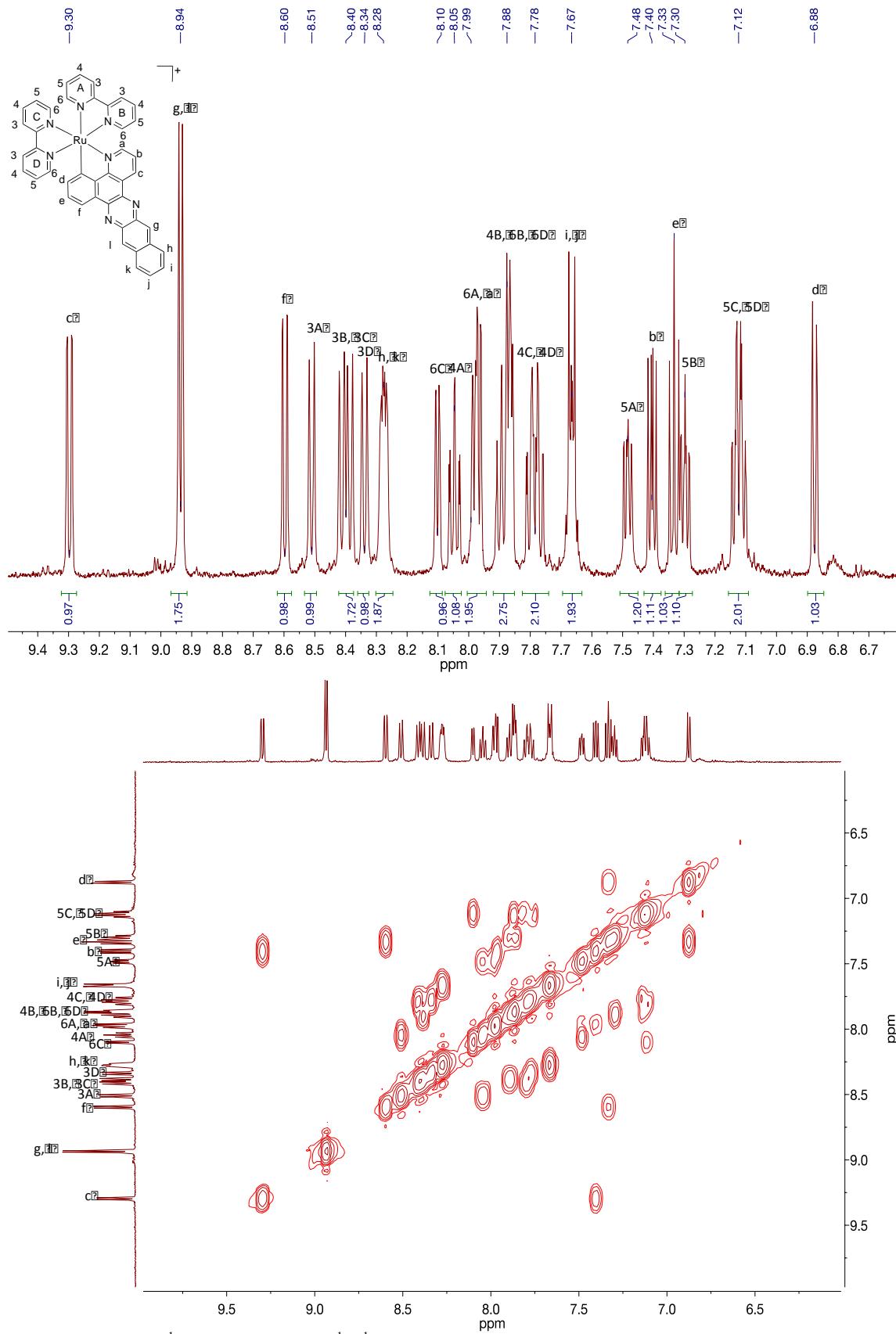
**Figure S8.**  $^{13}\text{C}$  NMR full spectrum (upper) and its aromatic region (lower) of compound **2** in  $\text{MeCN}-d_3$ .



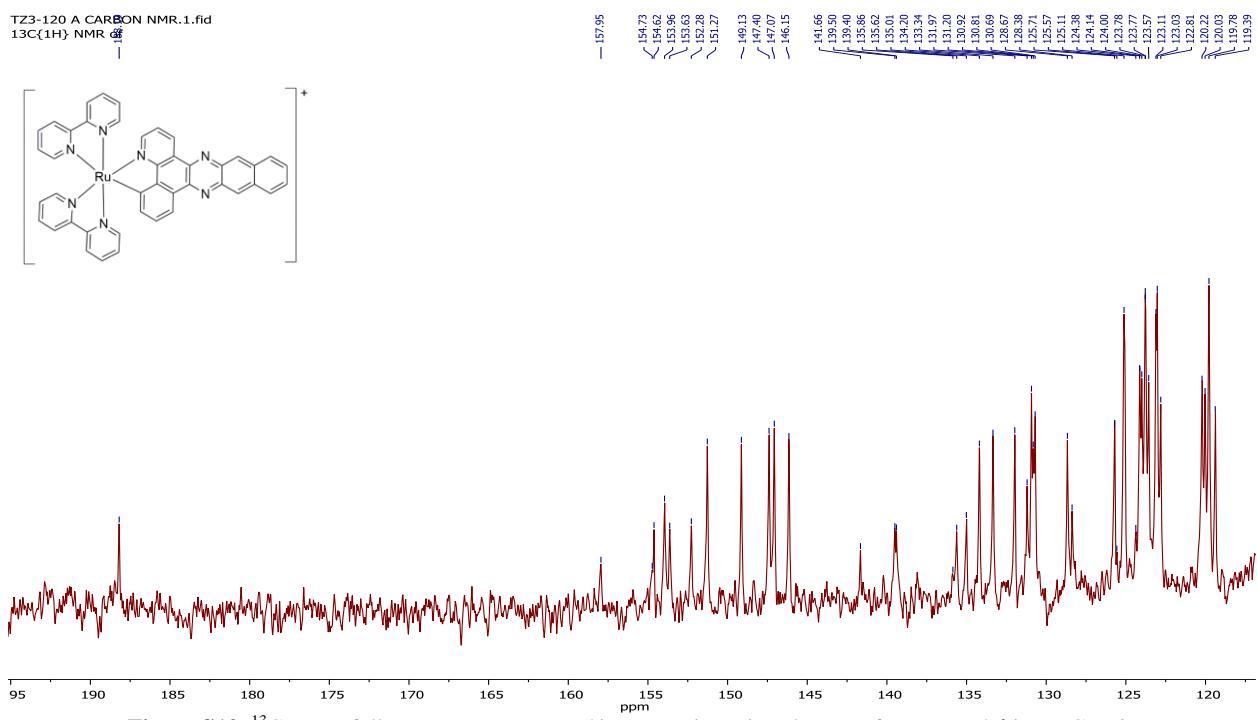
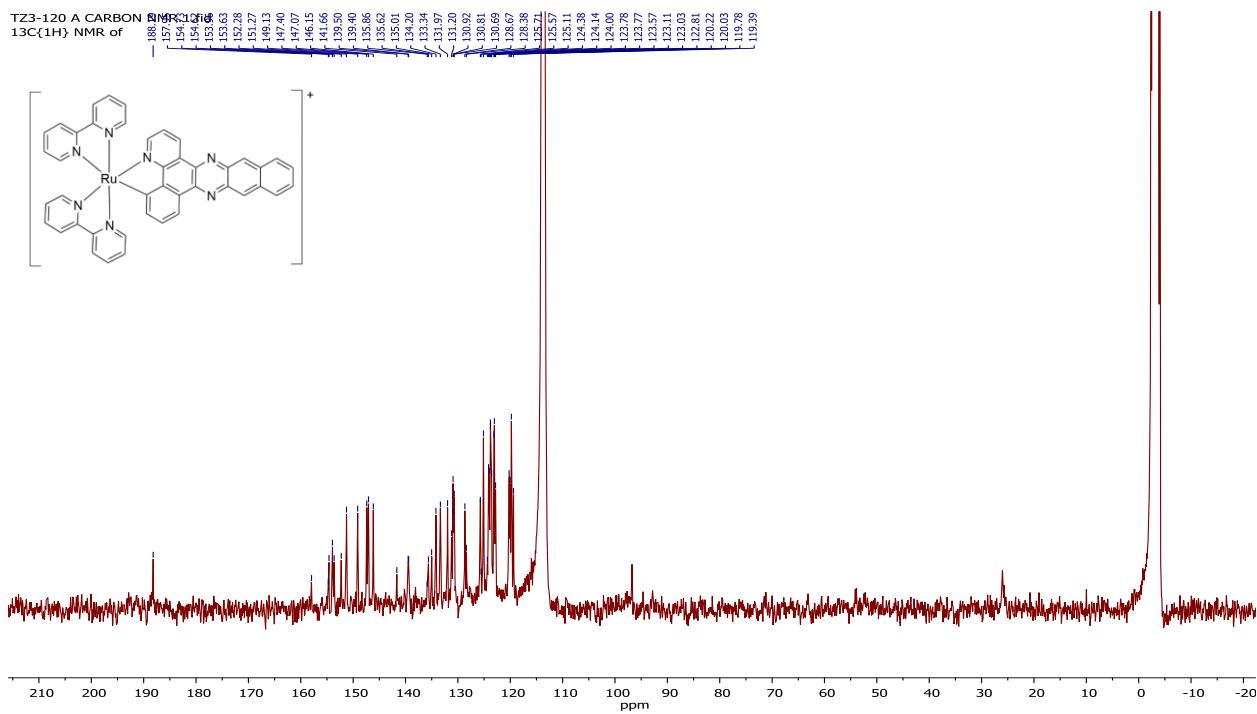
**Figure S9.**  $^1\text{H}$  NMR (upper) and  $^1\text{H}$ - $^1\text{H}$  COSY (lower) NMR spectrum of compound 3 in  $\text{MeCN}-d_3$ .



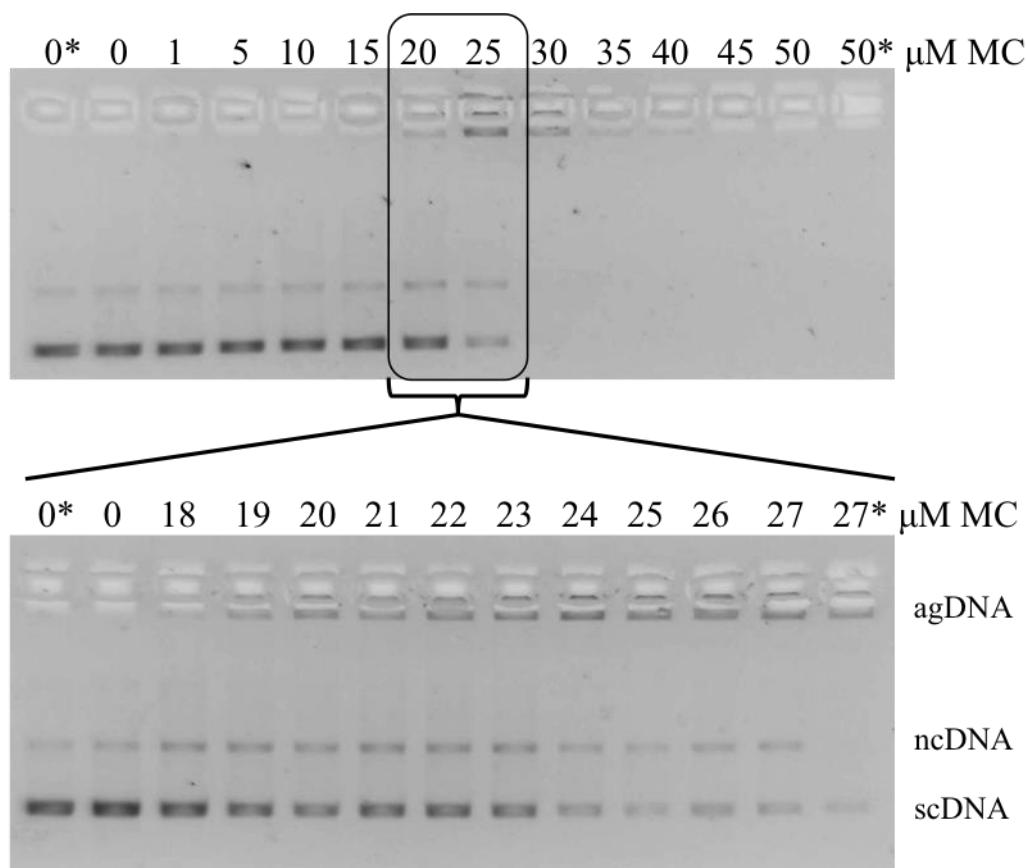
**Figure S10.** <sup>13</sup>C NMR full spectrum (upper) and its aromatic region (lower) of compound **3** in MeCN-*d*<sub>3</sub>.



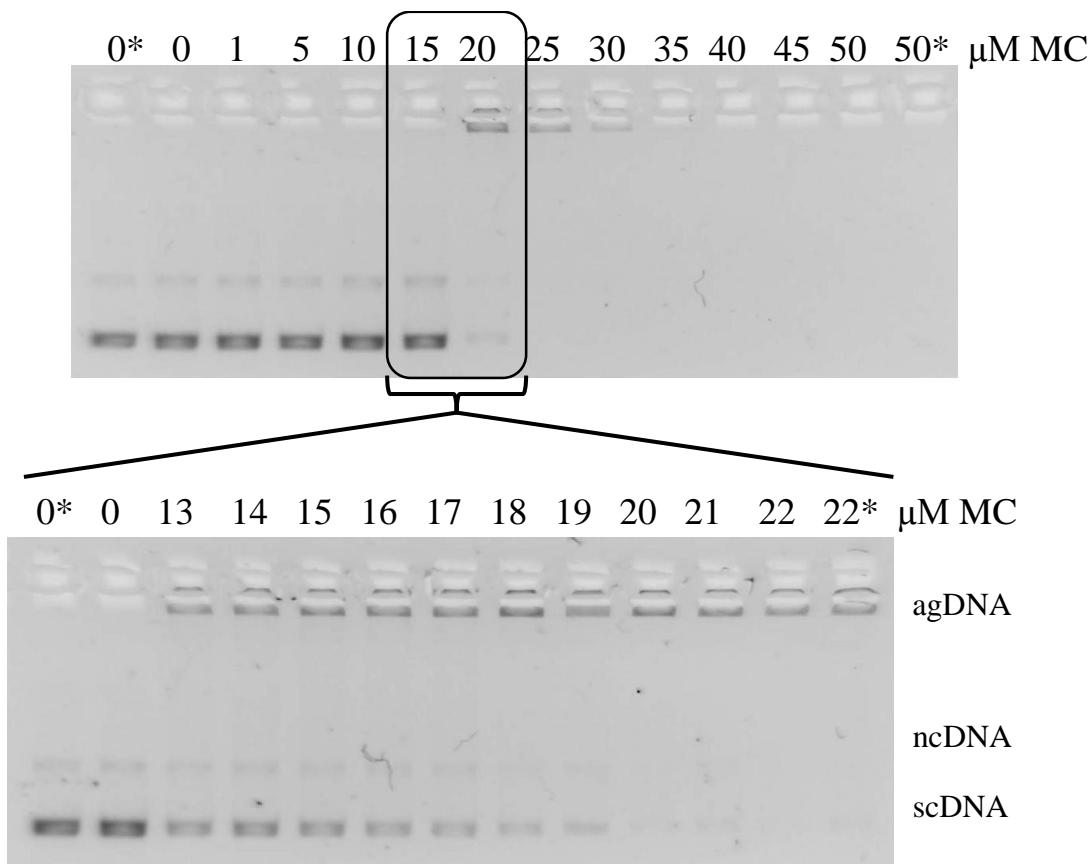
**Figure S11.** <sup>1</sup>H NMR (upper) and <sup>1</sup>H-<sup>1</sup>H COSY (lower) NMR spectrum of compound 4 in MeCN-*d*<sub>3</sub>.



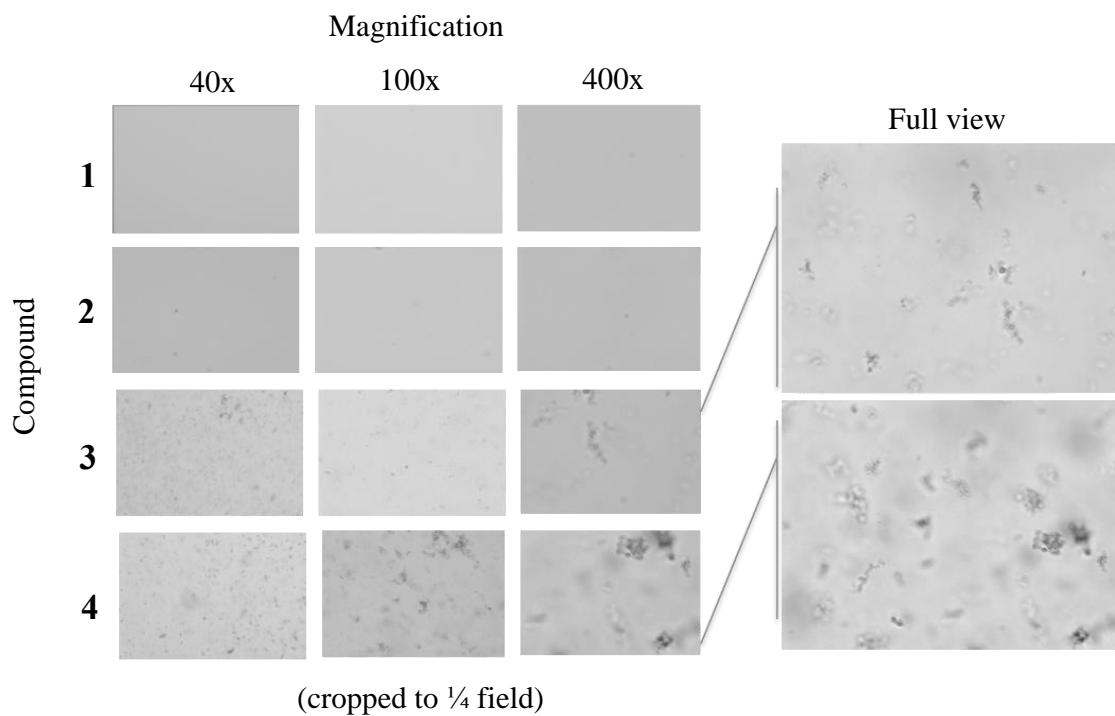
**Figure S12.**  $^{13}\text{C}$  NMR full spectrum (upper) and its aromatic region (lower) of compound **4** in  $\text{MeCN}-d_3$ .



**Figure S13.** DNA photocleavage of pUC19 DNA ( $28.6 \mu\text{M}$  bases) dosed with metal complex **3** and visible light ( $14 \text{ J}\cdot\text{cm}^{-2}$ ). Gel mobility shift assays employed 1% agarose gels ( $0.75 \mu\text{g mL}^{-1}$  ethidium bromide) electrophoresed in 1X TAE at  $80 \text{ V cm}^{-1}$  for 30 min. \*Samples not irradiated. Upper gel: 0-50  $\mu\text{M}$  MC; lower gel: 0-27  $\mu\text{M}$  MC.



**Figure S14.** DNA photocleavage of pUC19 DNA (28.6  $\mu\text{M}$  bases) dosed with metal complex **4** and visible light ( $14 \text{ J}\cdot\text{cm}^{-2}$ ). Gel mobility shift assays employed 1% agarose gels ( $0.75 \text{ }\mu\text{g mL}^{-1}$  ethidium bromide) electrophoresed in 1X TAE at  $80 \text{ V cm}^{-1}$  for 30 min. \*Samples not irradiated. Upper gel: 0-50  $\mu\text{M}$  MC; lower gel: 0-22  $\mu\text{M}$  MC.



**Figure S15.** Microscopic images (Nikon Eclipse TE2000-U inverted light microscope, phase-contrast mode) of MC-DNA mixtures ( $[MC]=40 \mu\text{M}$ ,  $[DNA]=28.6 \mu\text{M}$ ) used for gel electrophoresis experiments (lane 5 in Figure 7).