



## Supporting Information

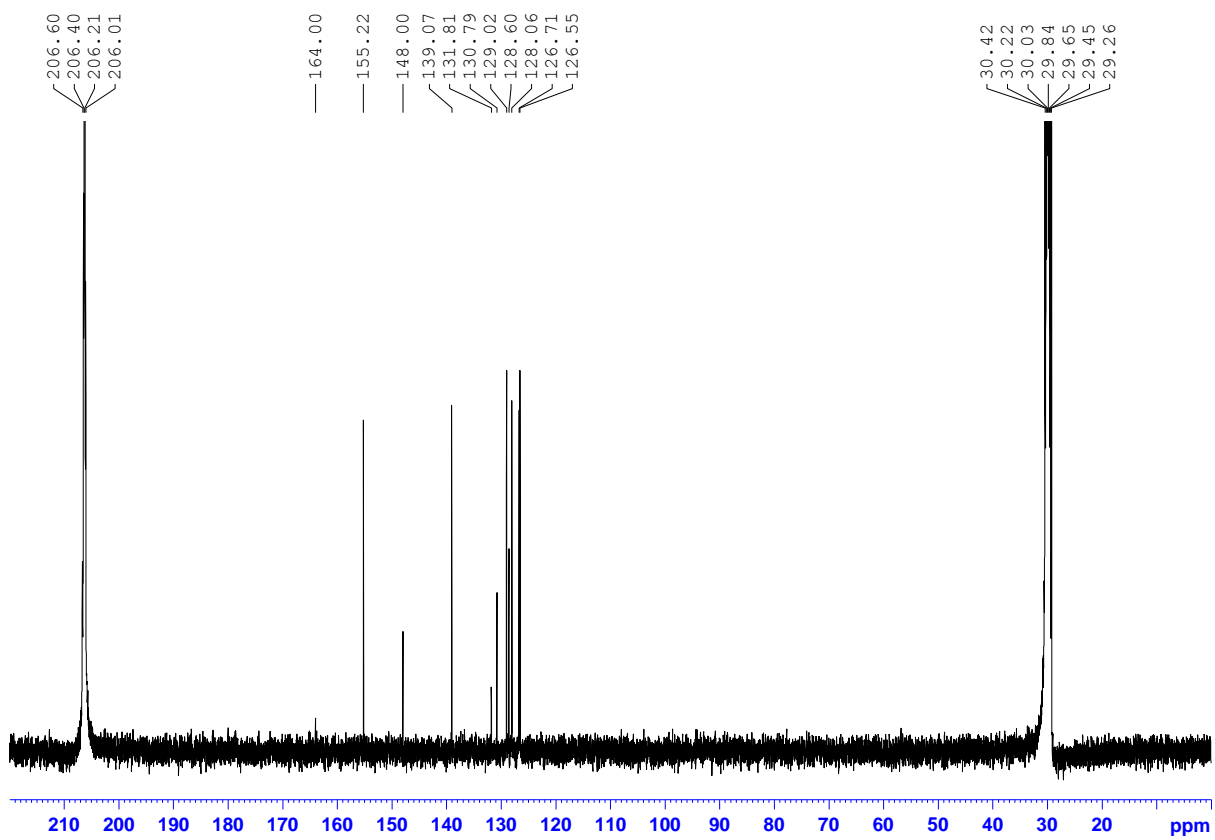
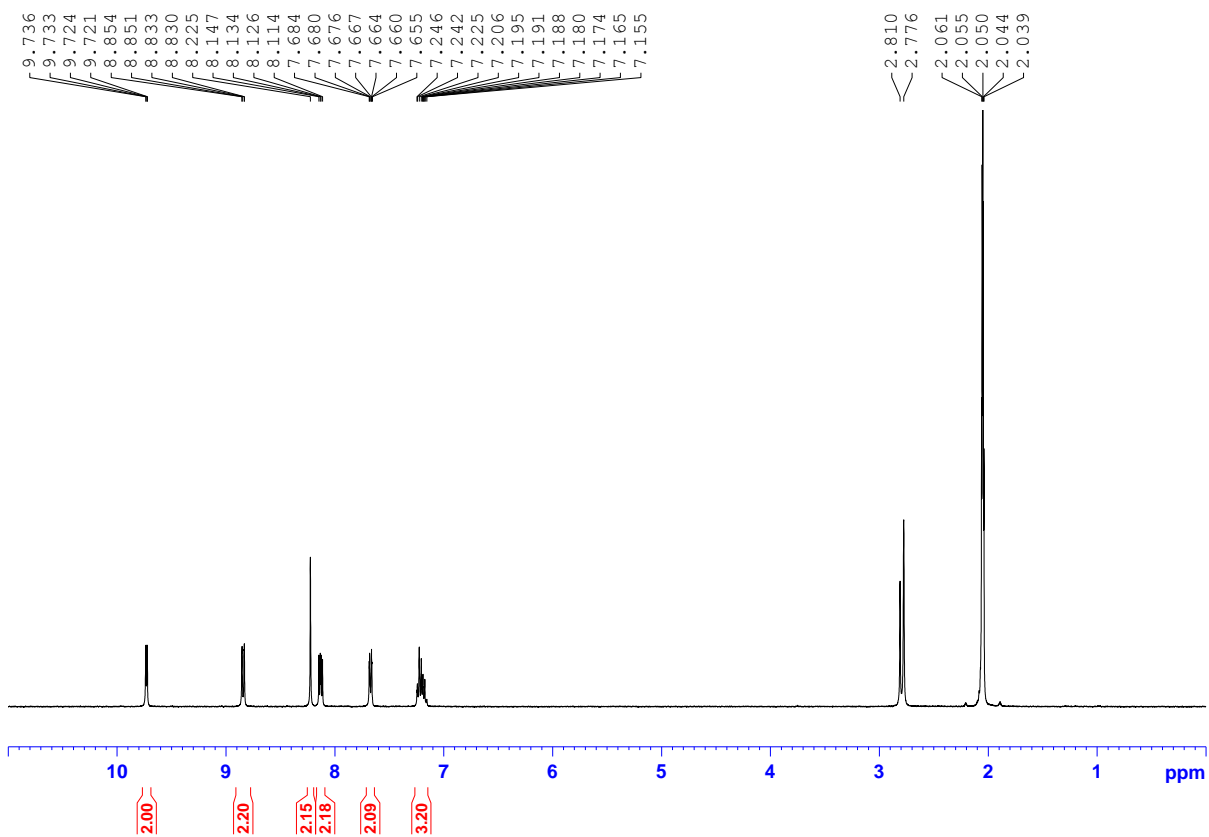
### **Synthesis and Photochemical Properties of Manganese(I) Tricarbonyl Diimine Complexes Bound to Tetrazolato Ligands**

Matthew J. Stout, Alessandra Stefan, Brian W. Skelton,  
Alexandre N. Sobolev, Massimiliano Massi,\* Alejandro Hochkoepler,  
Stefano Stagni, and Peter V. Simpson\*

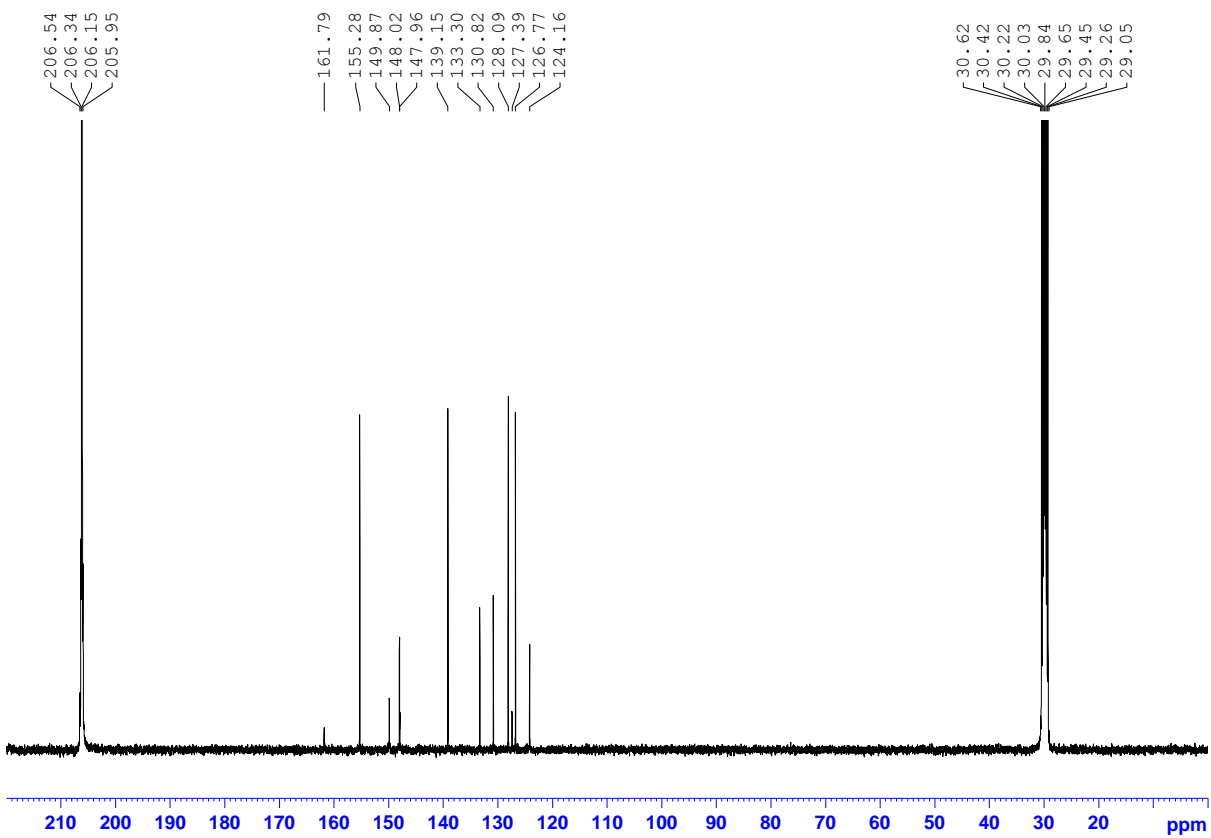
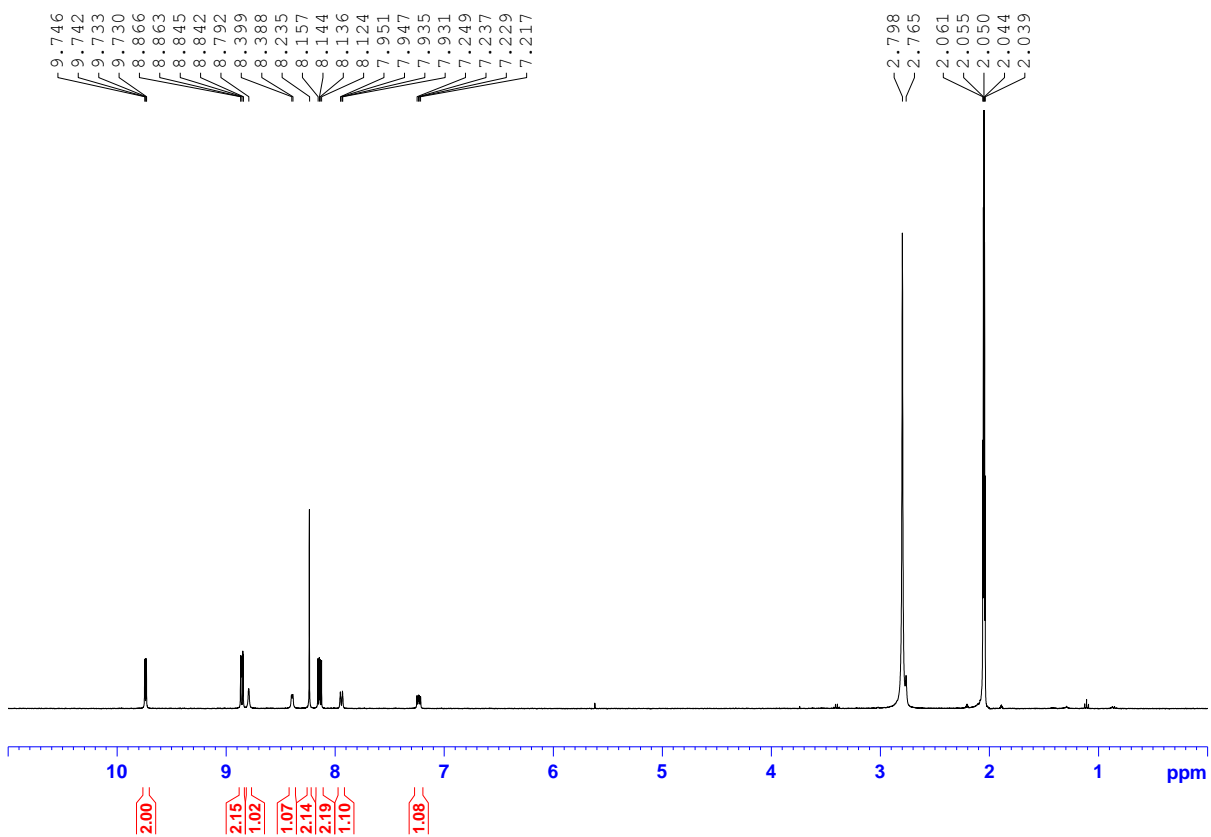
[ejic201900987-sup-0001-SupMat.pdf](#)

## **Index:**

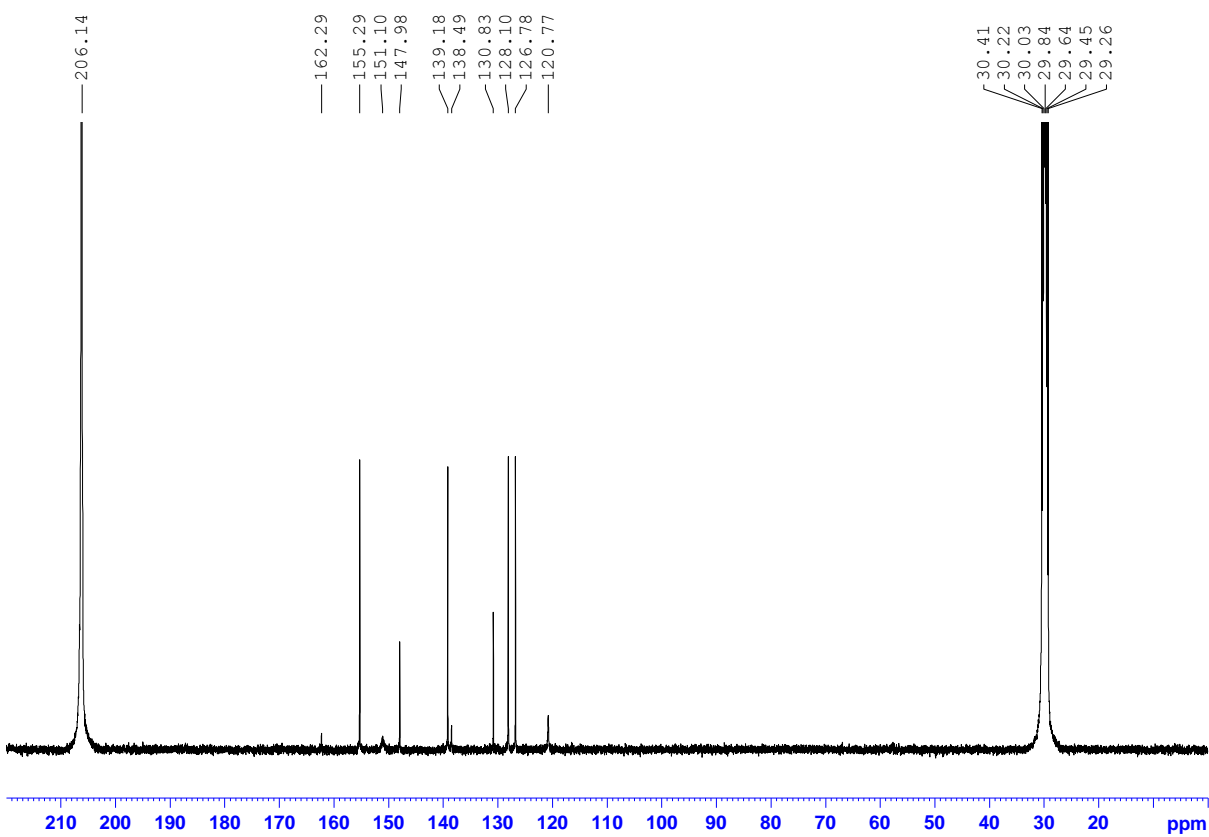
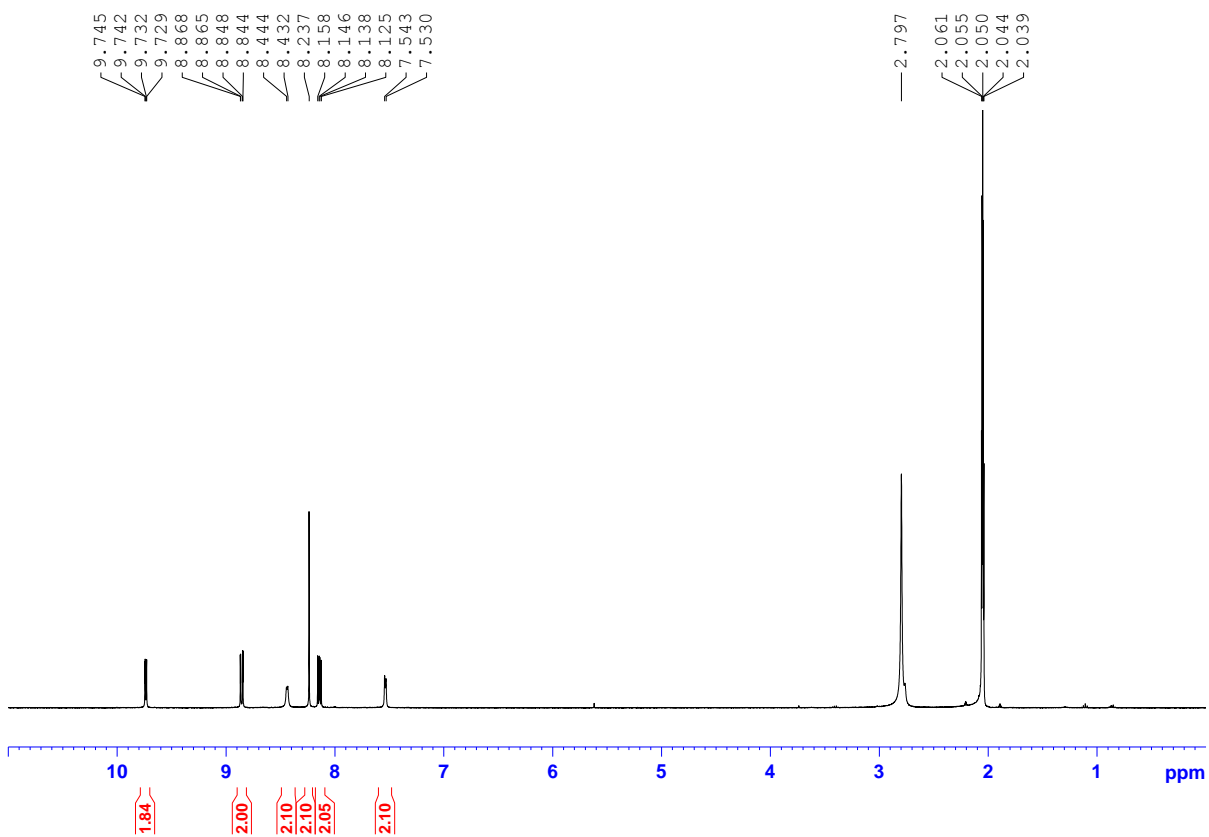
- S1-20:**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra for the complexes
- S21-22:** UV-Vis spectra for the complexes
- S23-32:** Progressive IR spectra during photolysis for the complexes
- S33-34:** PoliLight photolysis
- S35-37:** Growth curves for *E. coli* cultures
- S38-39:** Progressive UV-Vis spectra during photolysis for the complexes
- TS-5:** Tables of crystallographic data



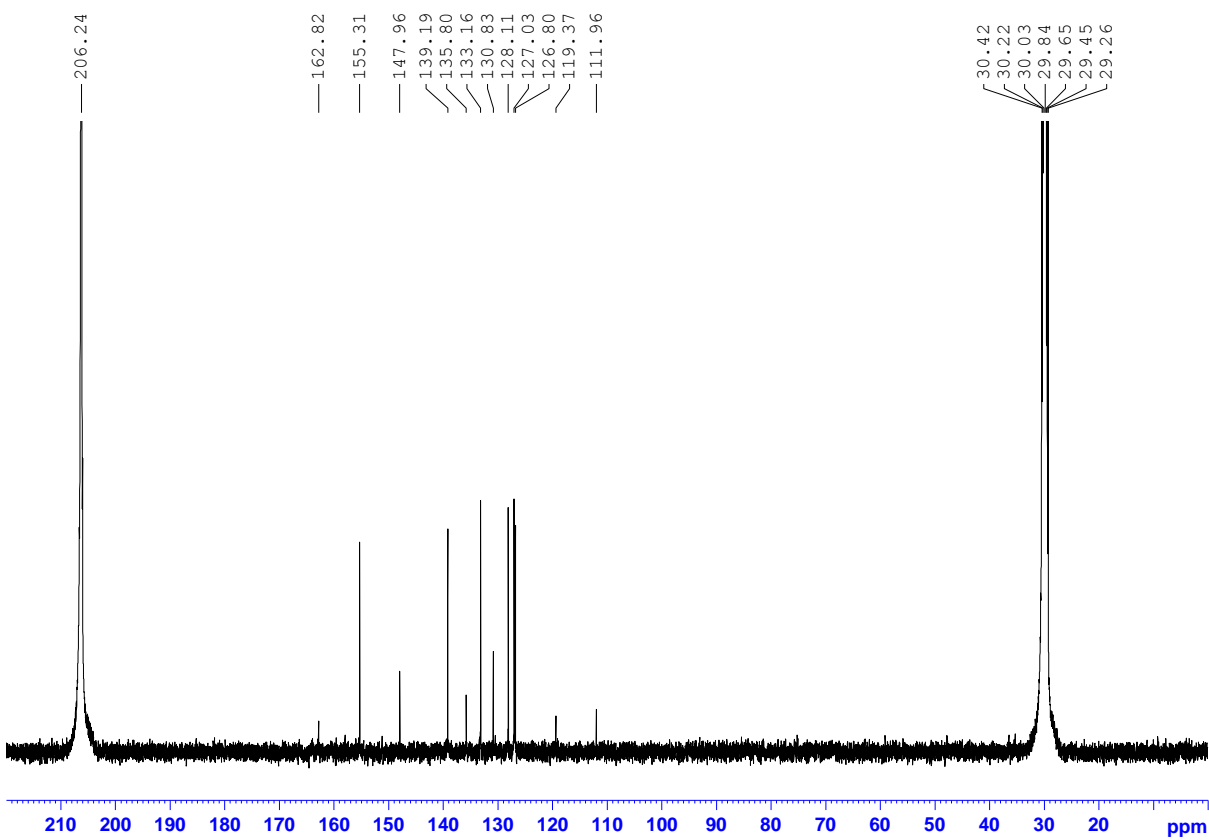
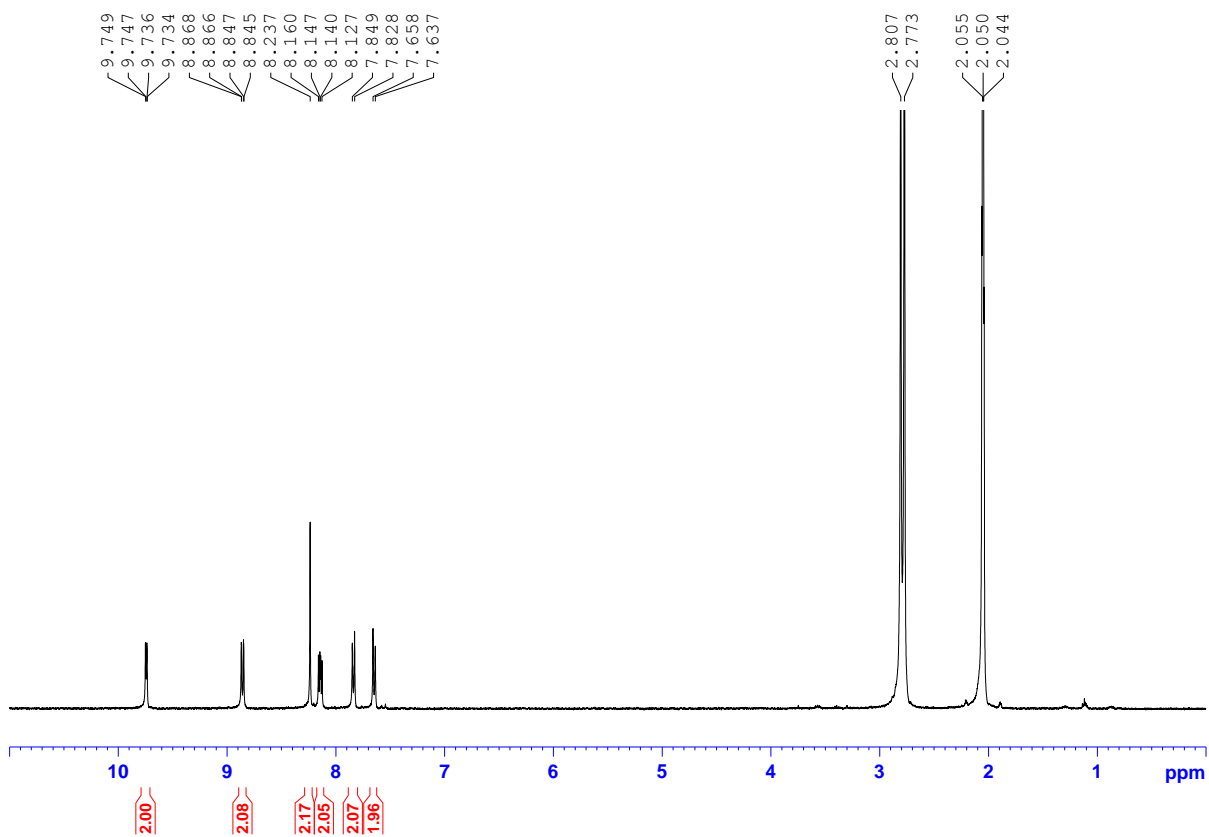
Figures S1 and S2: <sup>1</sup>H and <sup>13</sup>C-NMR of Mn(phen)(CO)<sub>3</sub>1 in acetone-d<sub>6</sub>



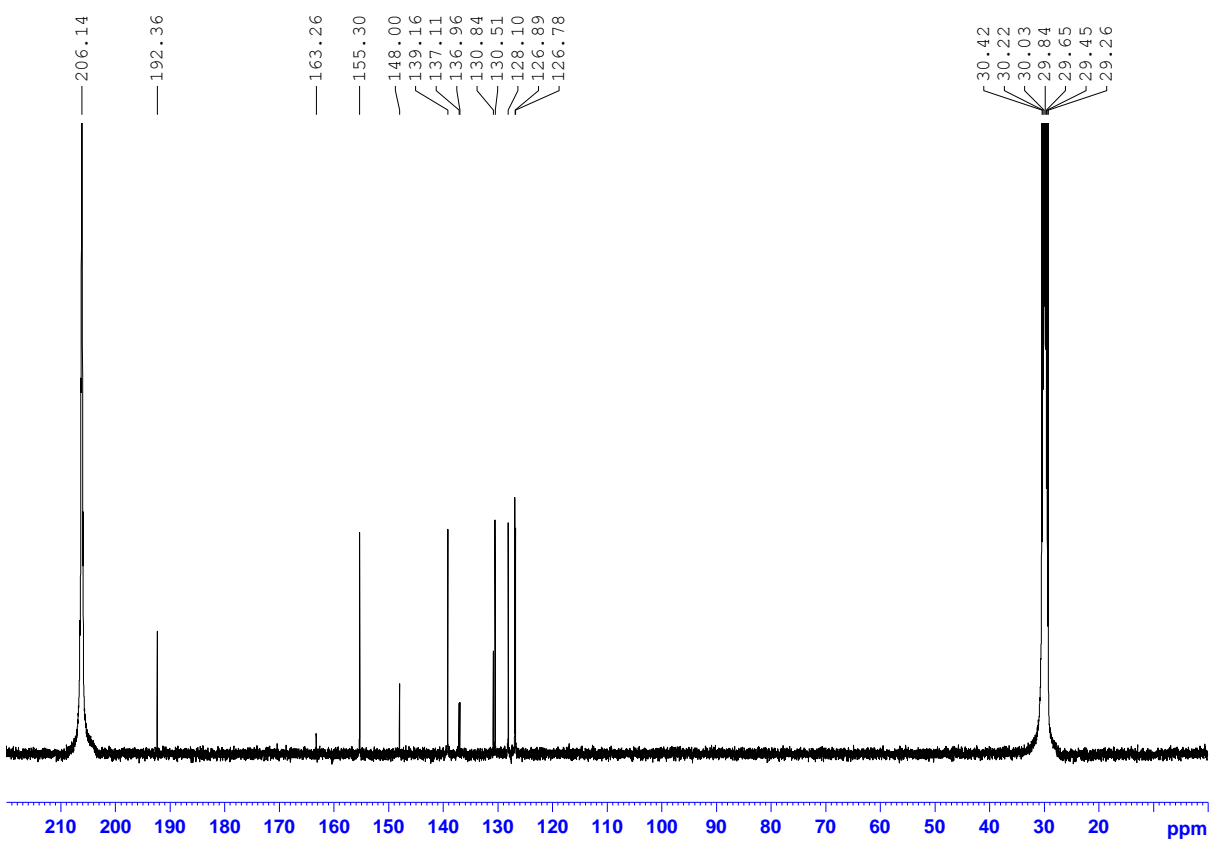
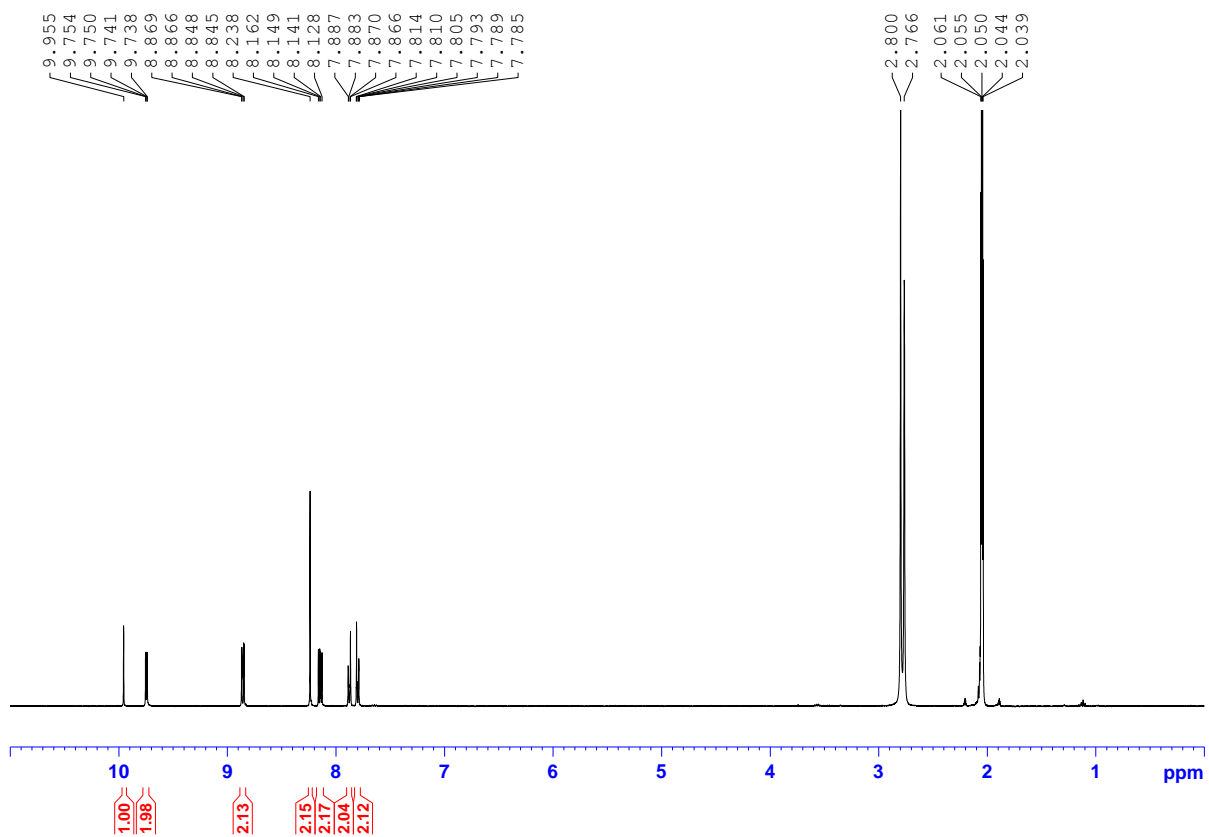
Figures S3 and S4: <sup>1</sup>H and <sup>13</sup>C-NMR of Mn(phen)(CO)<sub>3</sub>2 in acetone-d<sub>6</sub>



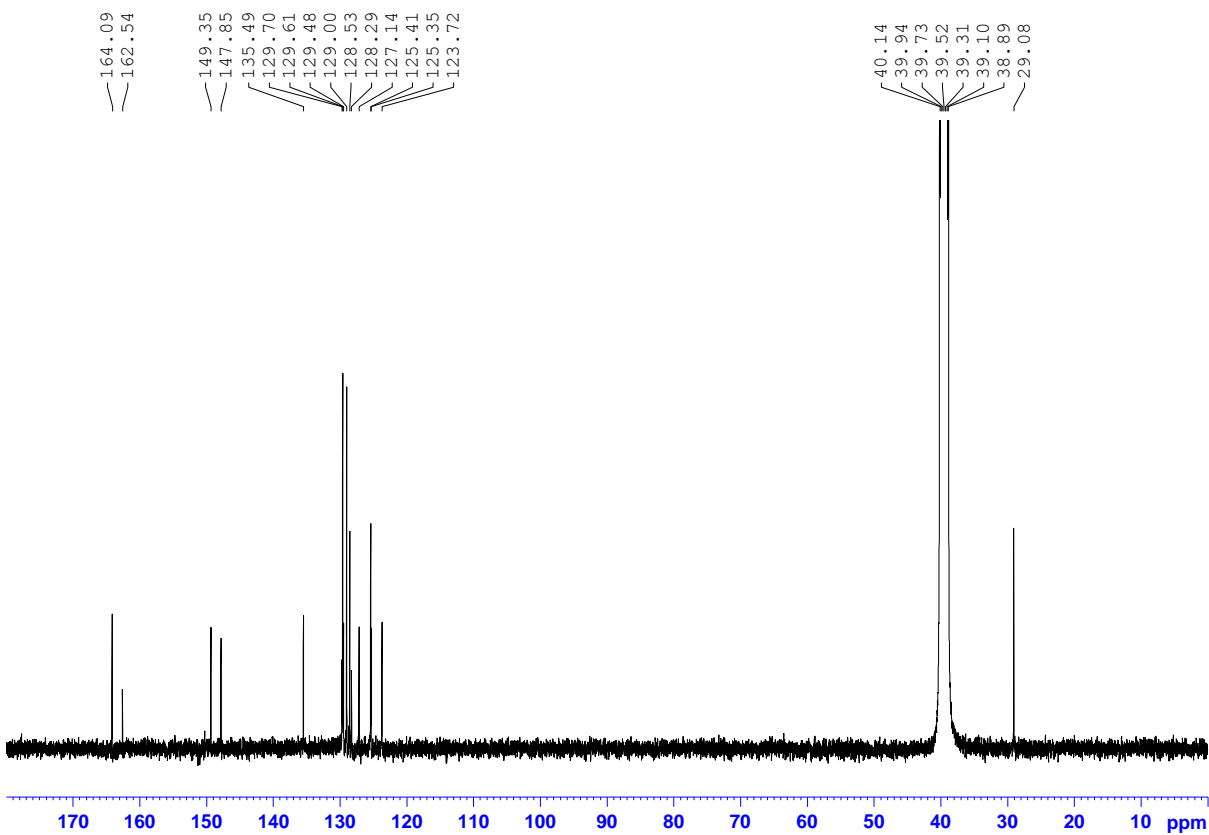
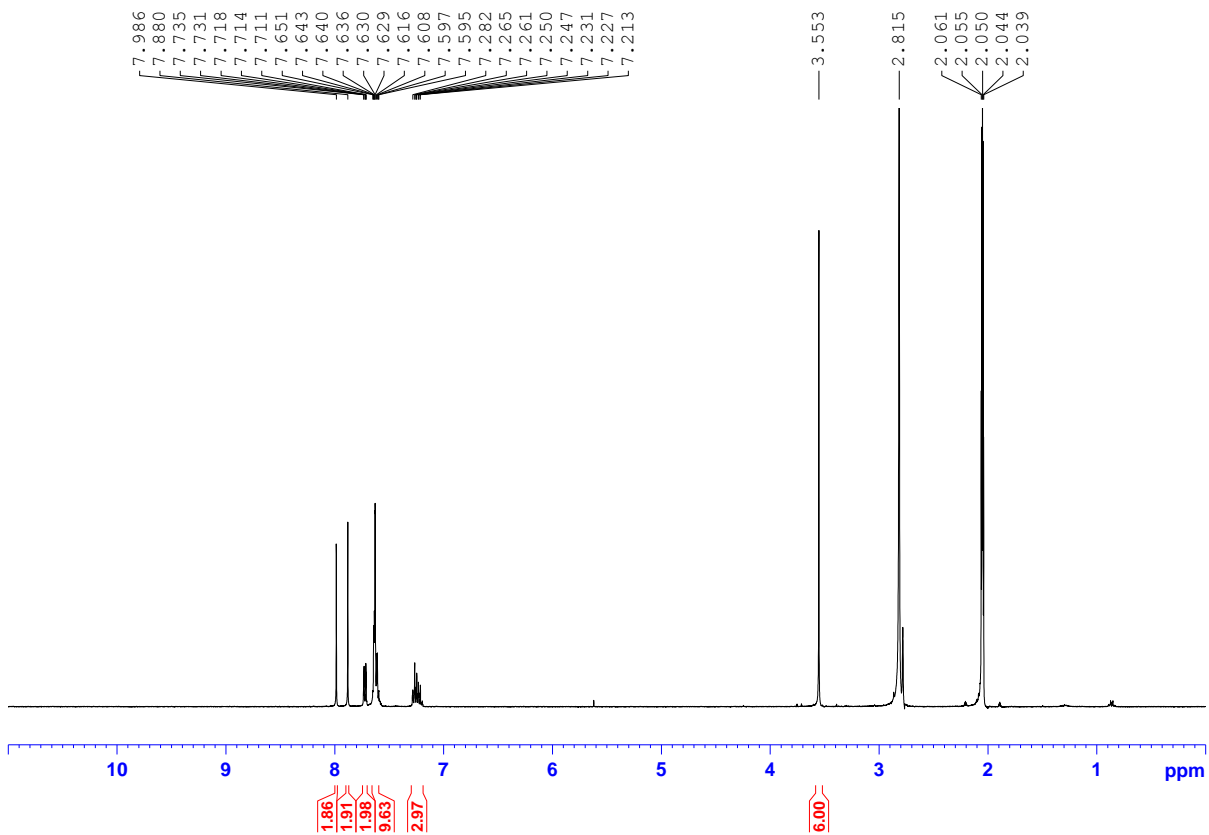
Figures S5 and S6:  $^1\text{H}$  and  $^{13}\text{C}$ -NMR of  $\text{Mn}(\text{phen})(\text{CO})_3$  in acetone- $\text{d}_6$



Figures S7 and S8  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR of  $\text{Mn}(\text{phen})(\text{CO})_3$  in acetone- $d_6$

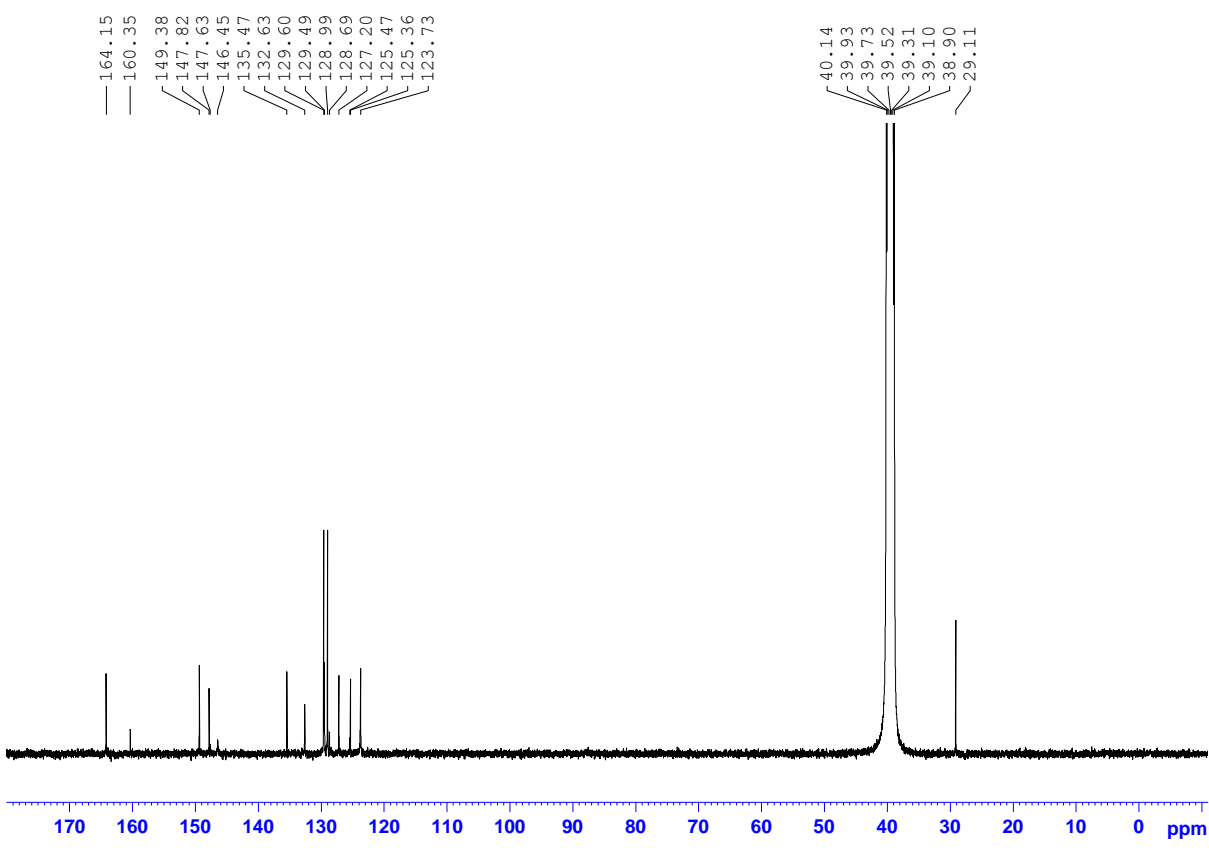
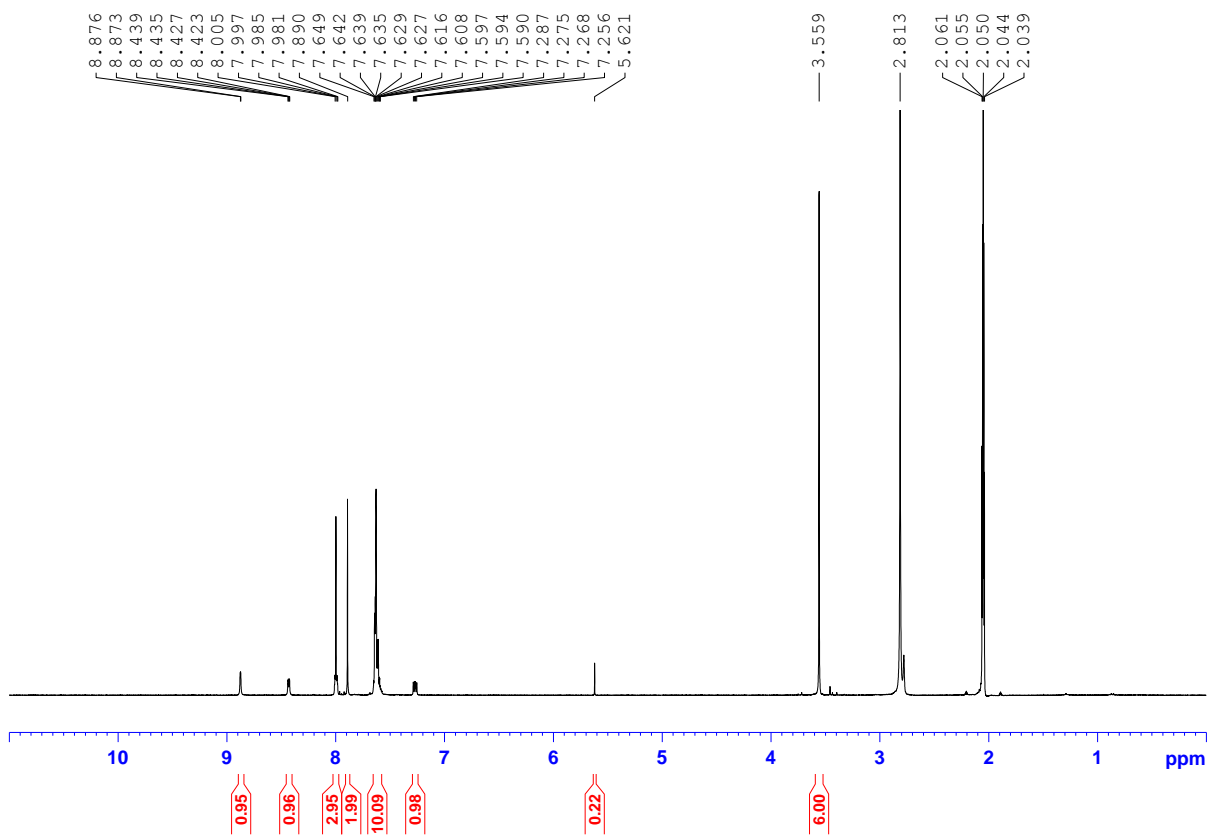


Figures S9 and S10: <sup>1</sup>H and <sup>13</sup>C-NMR of Mn(phen)(CO)<sub>3</sub>5 in acetone-d<sub>6</sub>

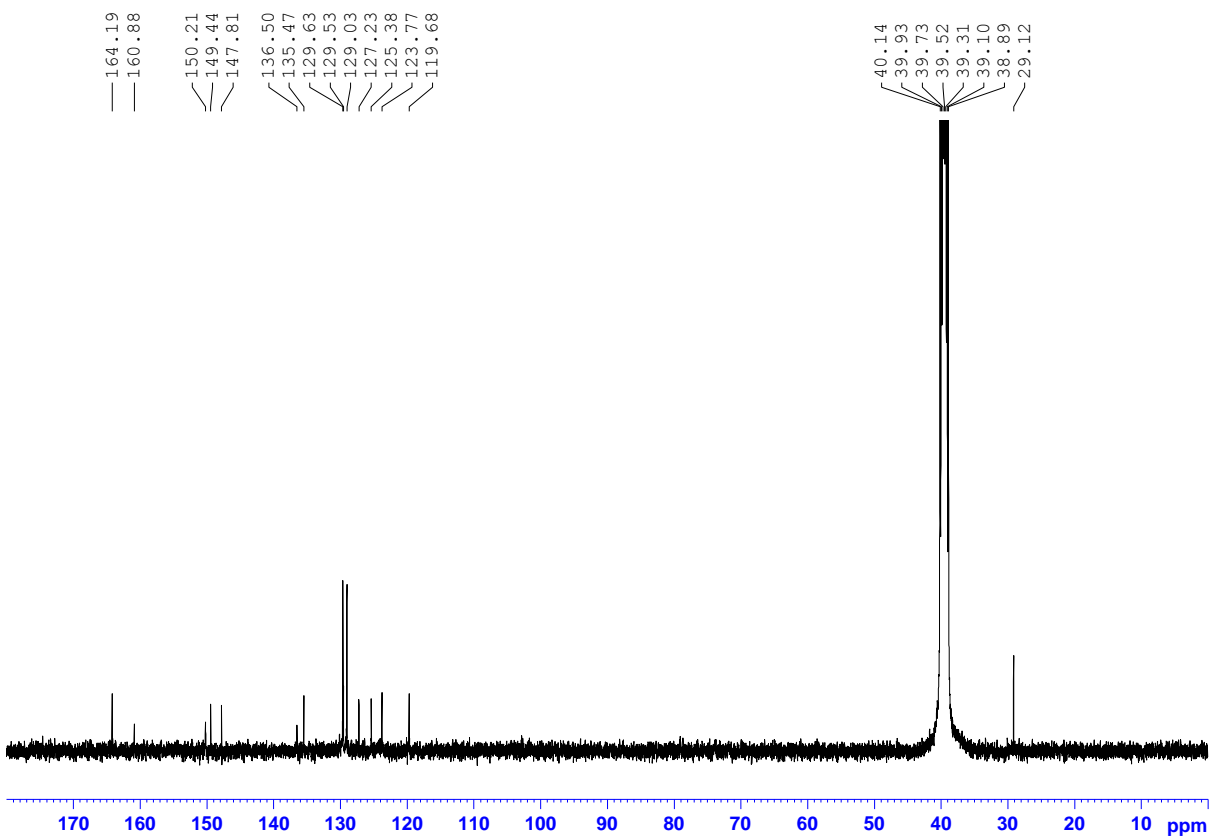
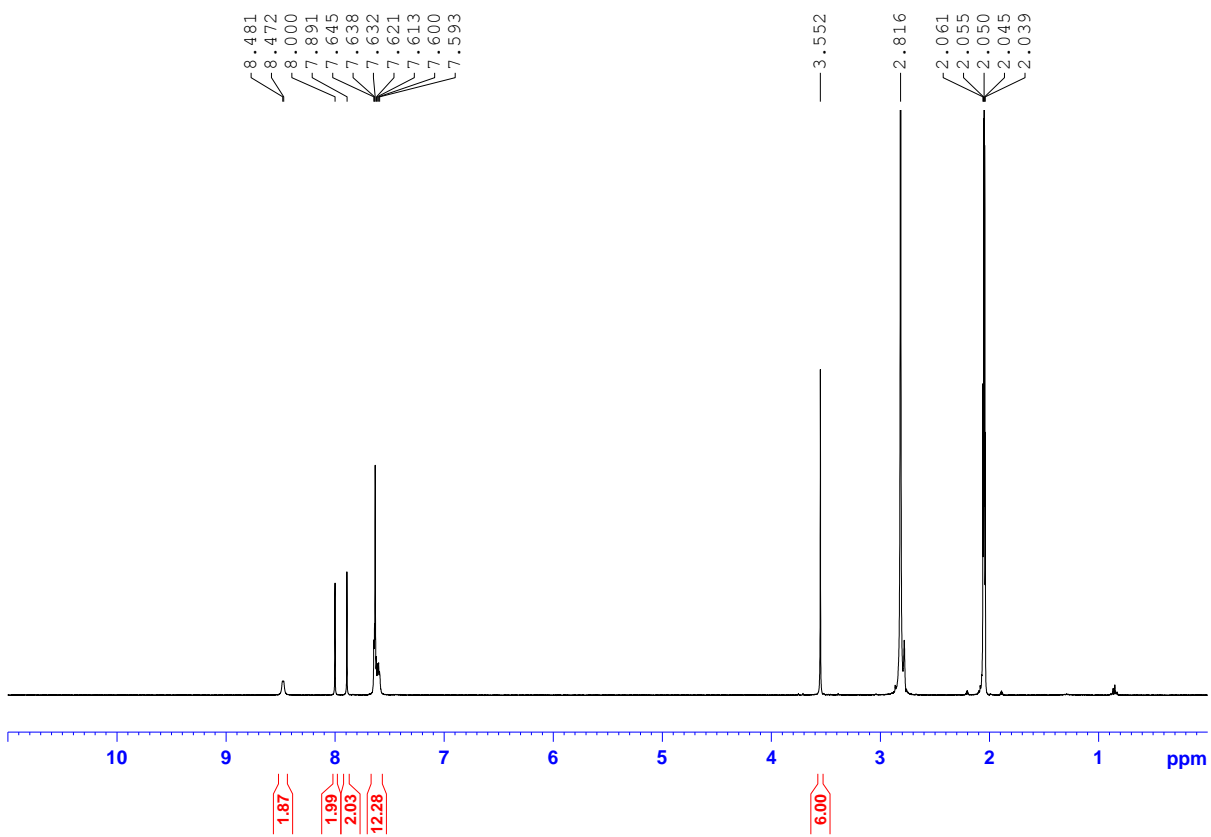


Figures S11 and S12: <sup>1</sup>H-NMR in acetone-d<sub>6</sub> and <sup>13</sup>C-NMR of Mn(batho)(CO)<sub>3</sub> in DMSO-d<sub>6</sub>

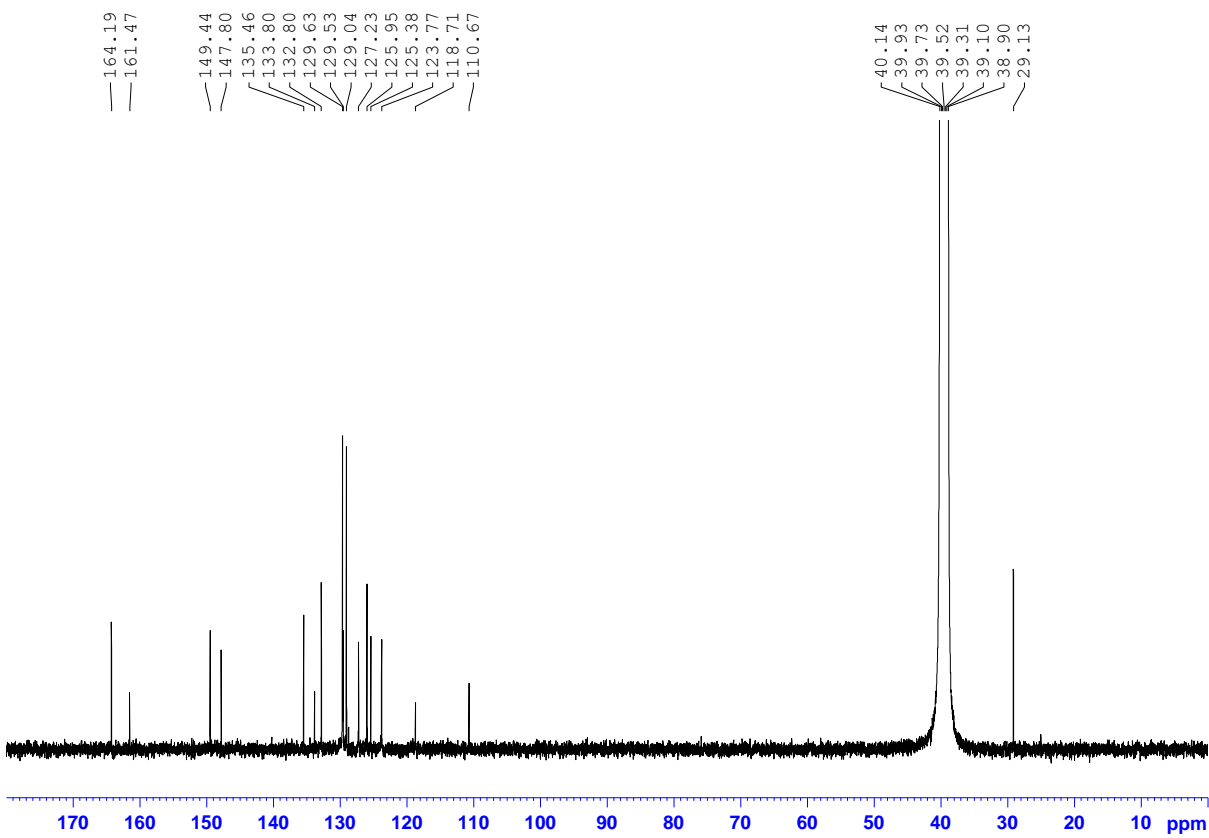
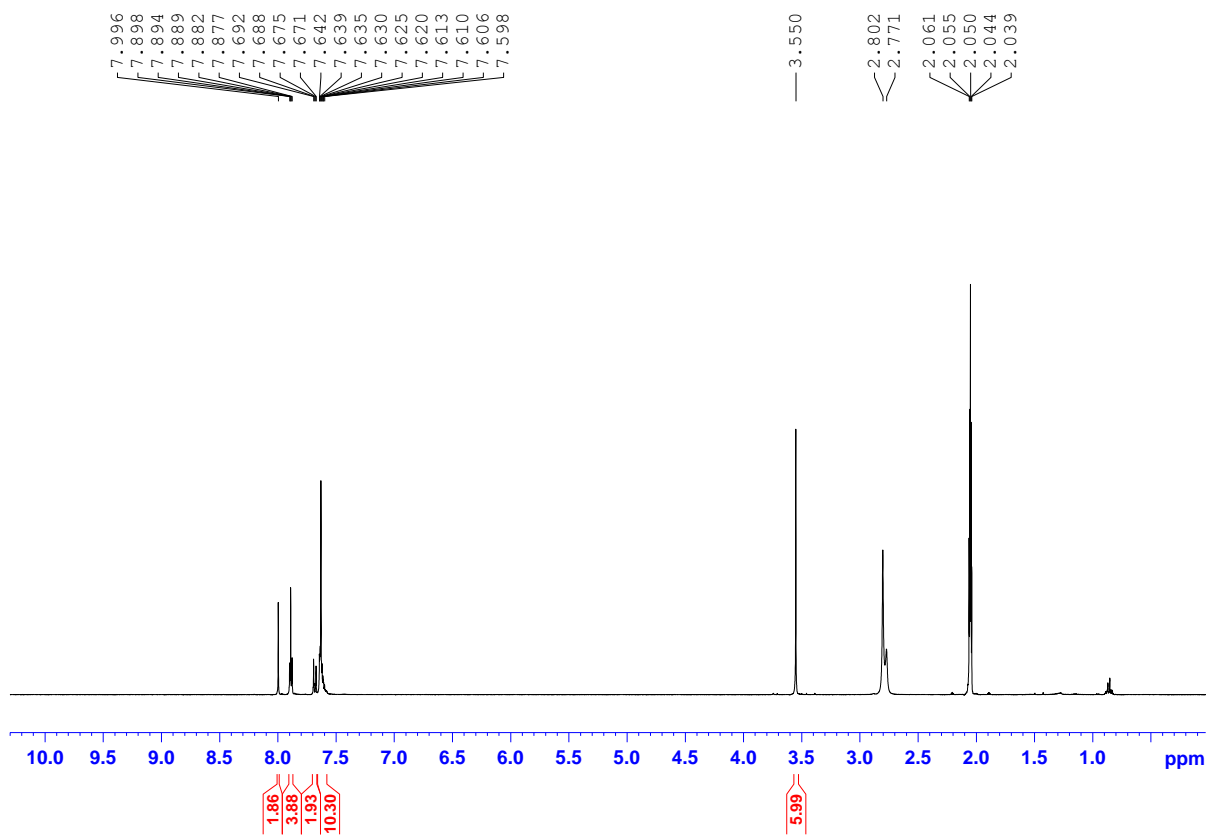




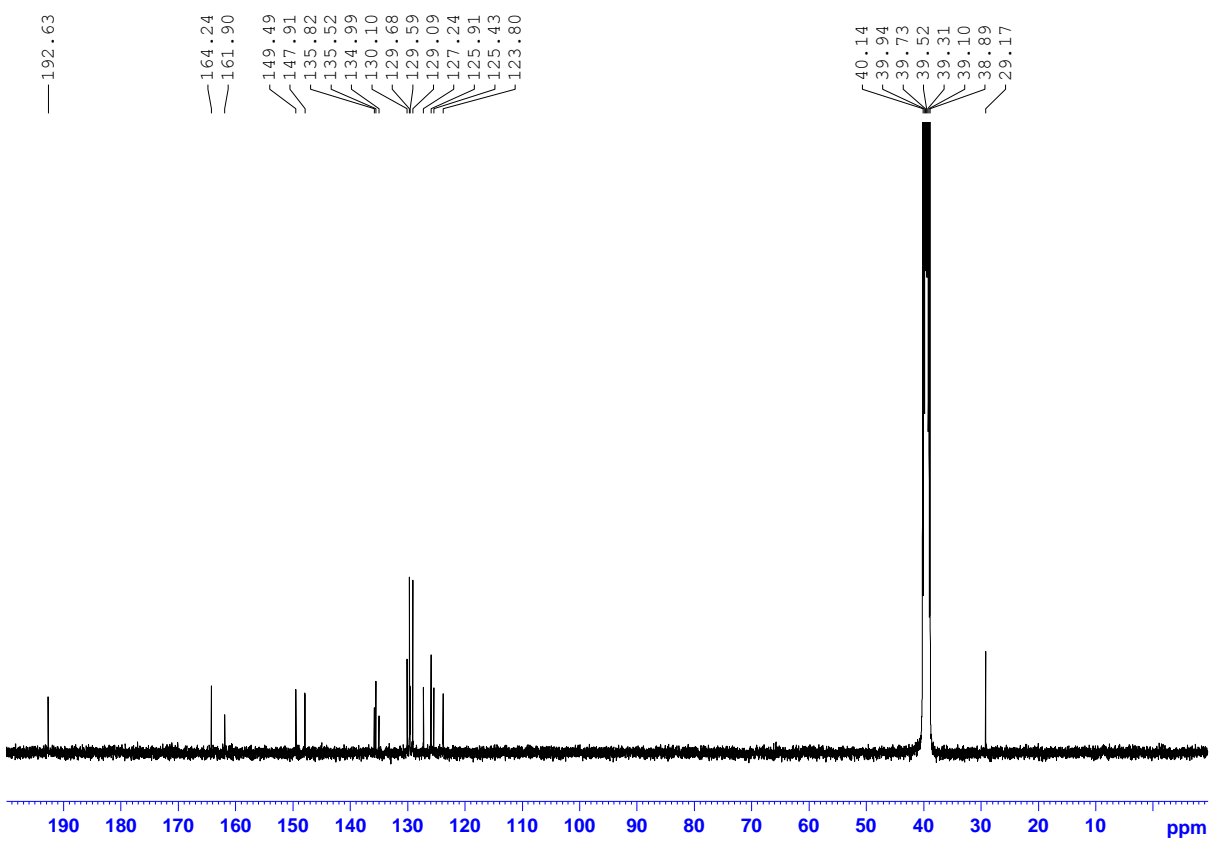
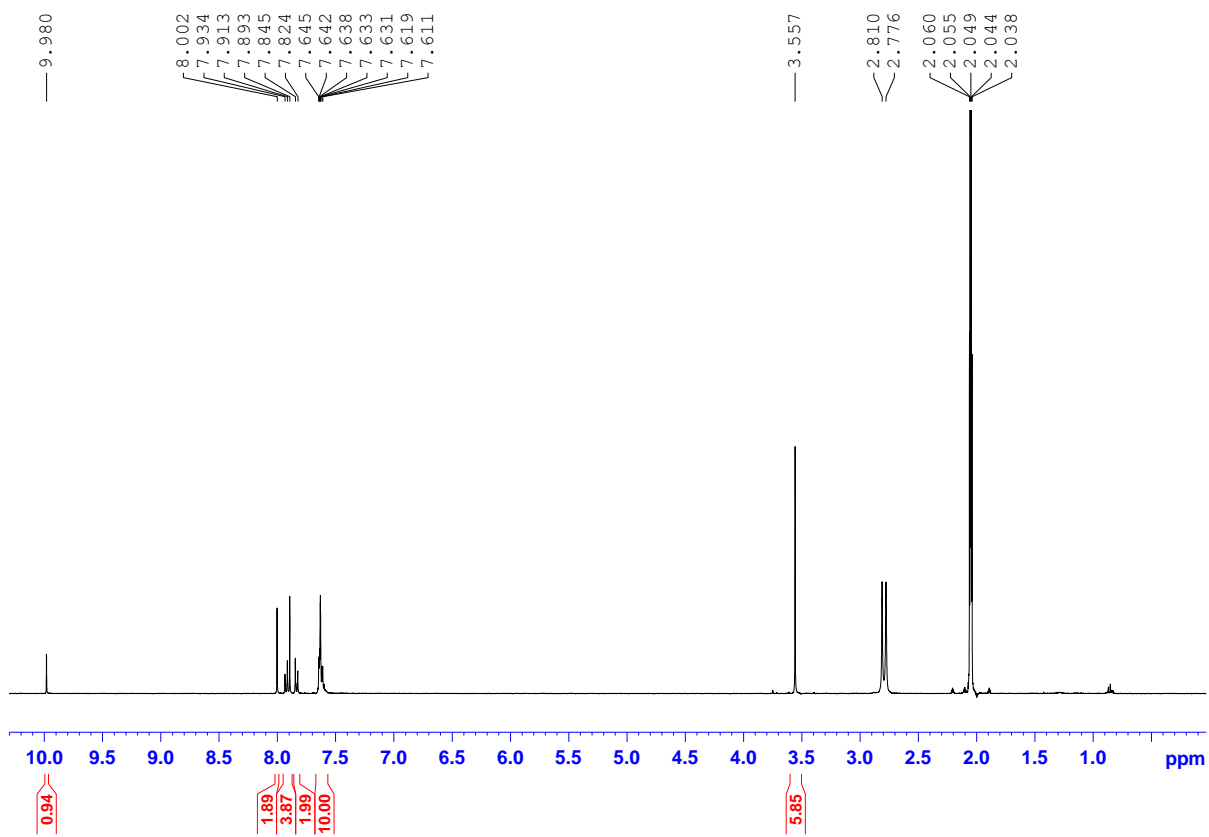
Figures S13 and S14: <sup>1</sup>H-NMR in acetone-d<sub>6</sub> and <sup>13</sup>C-NMR of Mn(batho)(CO)<sub>3</sub> in DMSO-d<sub>6</sub>



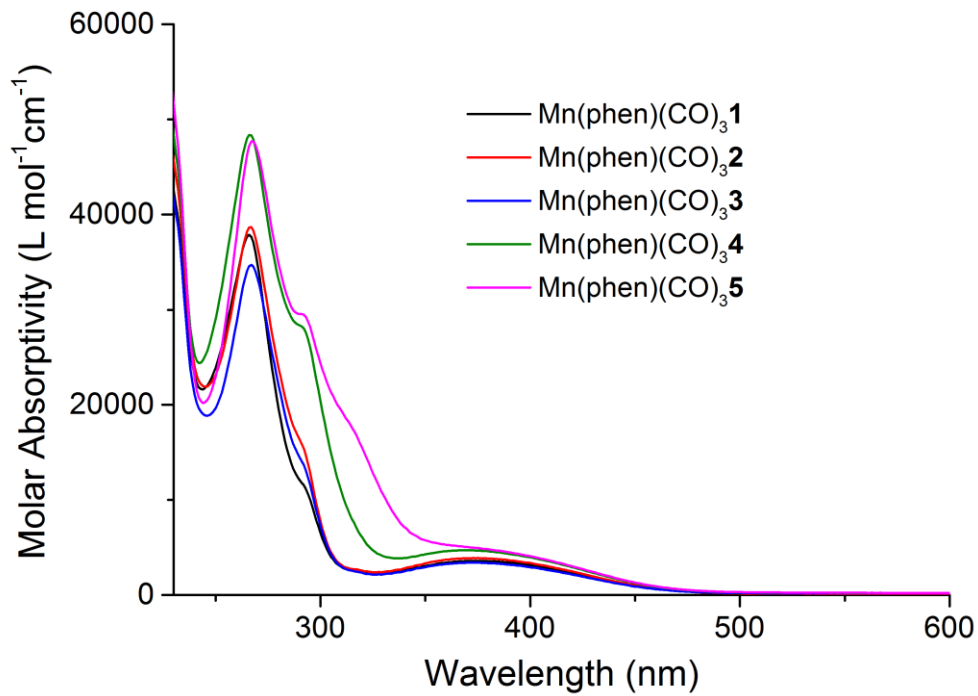
Figures S15 and S16:  $^1\text{H}$ -NMR in acetone- $d_6$  and  $^{13}\text{C}$ -NMR of  $\text{Mn}(\text{batho})(\text{CO})_3$  in  $\text{DMSO}-d_6$



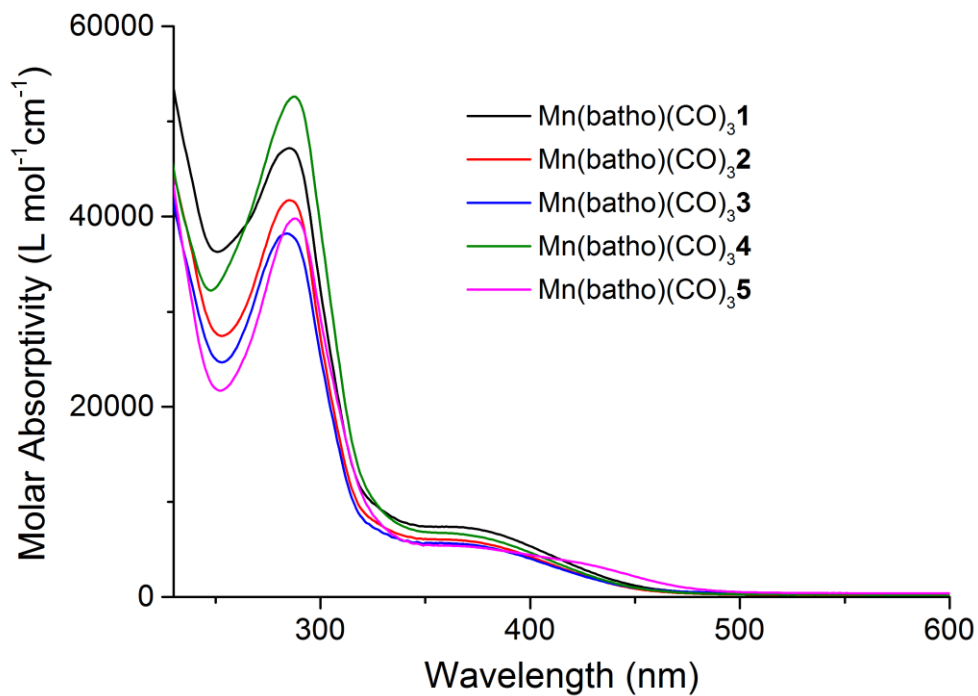
Figures S17 and S18: <sup>1</sup>H-NMR in acetone-d<sub>6</sub> and <sup>13</sup>C-NMR of Mn(batho)(CO)<sub>3</sub>4 in DMSO-d<sub>6</sub>



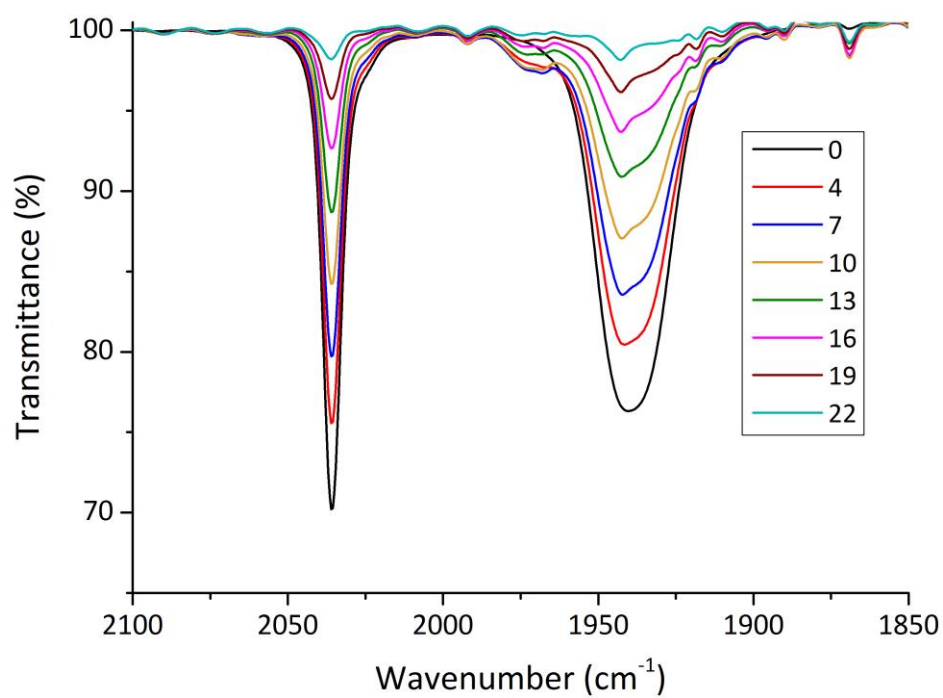
Figures S19 and S20:  $^1\text{H-NMR}$  in acetone- $d_6$  and  $^{13}\text{C-NMR}$  of  $\text{Mn}(\text{batho})(\text{CO})_3$  in  $\text{DMSO-d}_6$



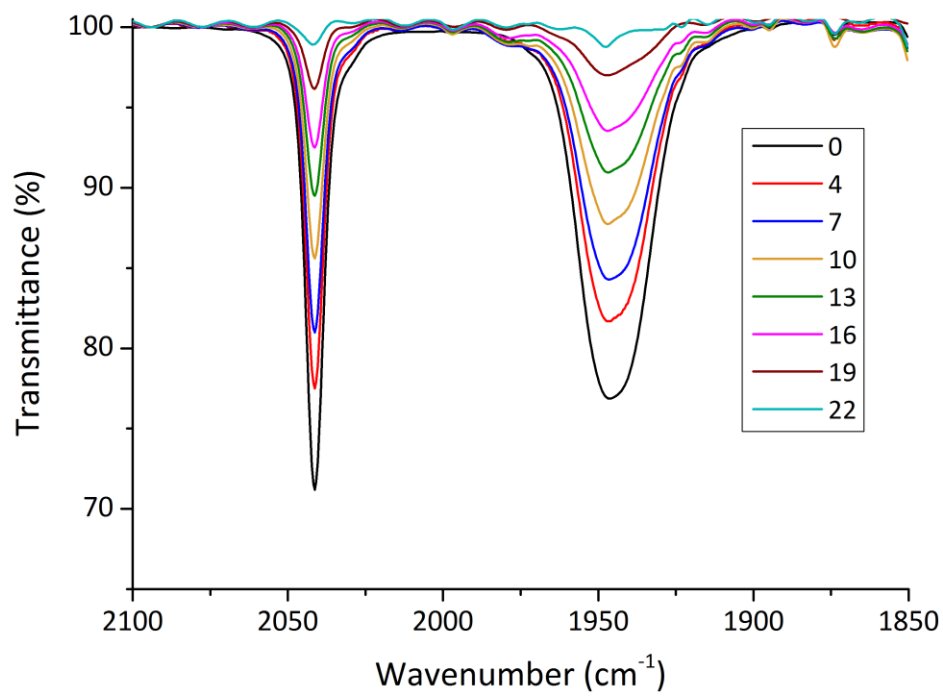
**Figure S21:** UV-Vis absorption spectra of Mn(phen)(CO)<sub>3</sub>(1-5) from diluted DCM solutions



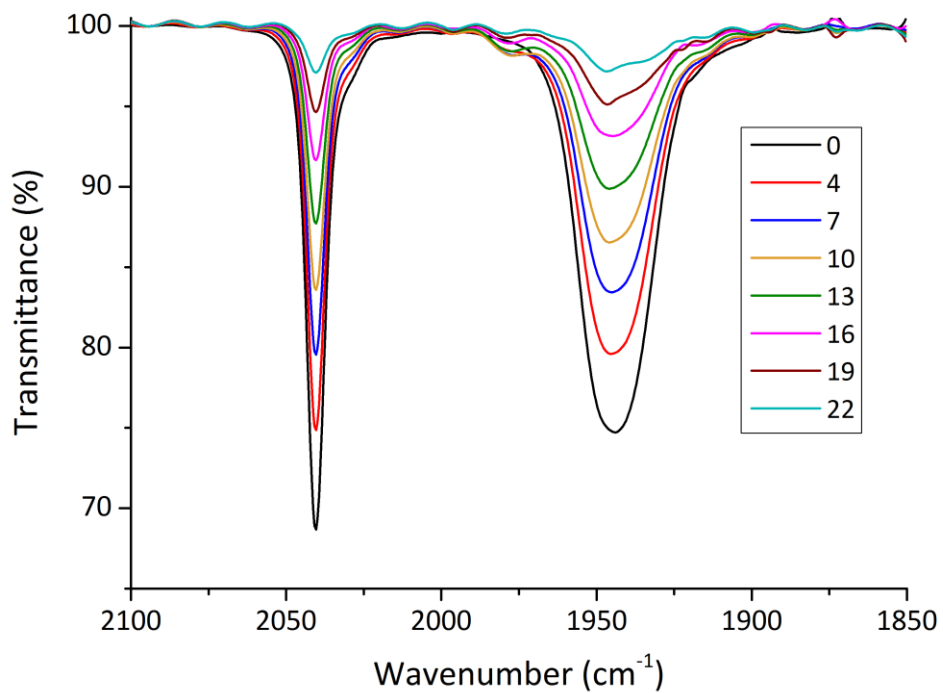
**Figure S22:** UV-Vis absorption spectra of Mn(batho)(CO)<sub>3</sub>(1-5) from diluted DCM solutions



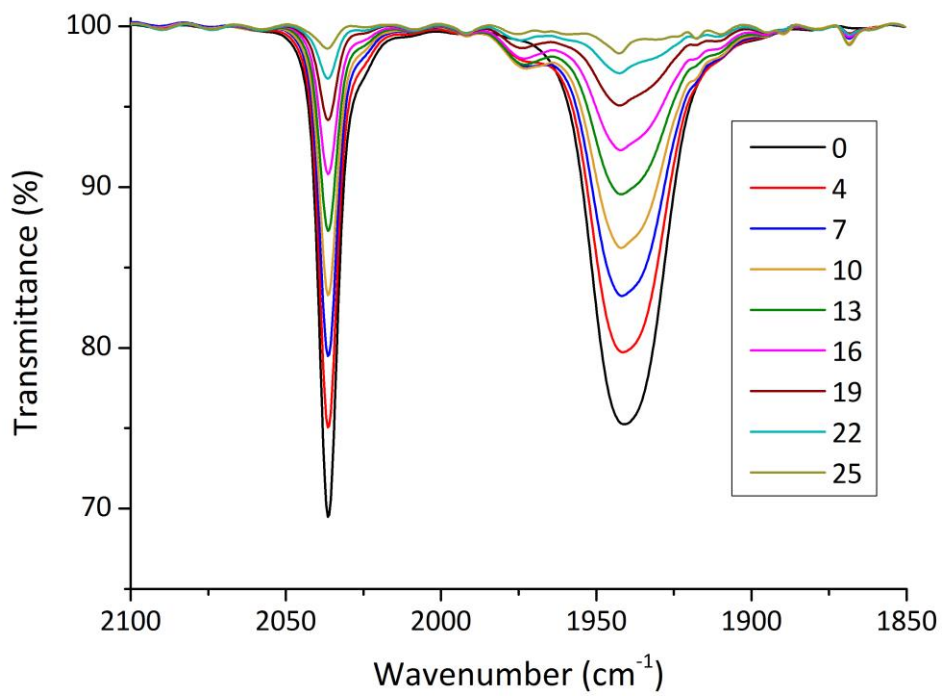
**Figure S23:** IR photolysis spectra of Mn(phen)(CO)<sub>3</sub>1



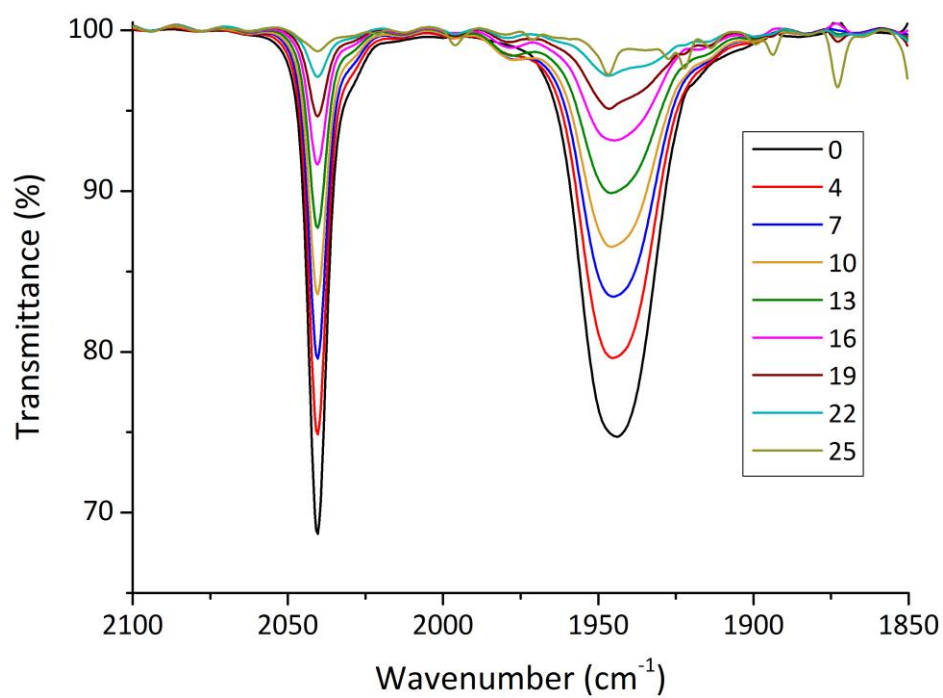
**Figure S24:** IR photolysis spectra of Mn(phen)(CO)<sub>3</sub>2



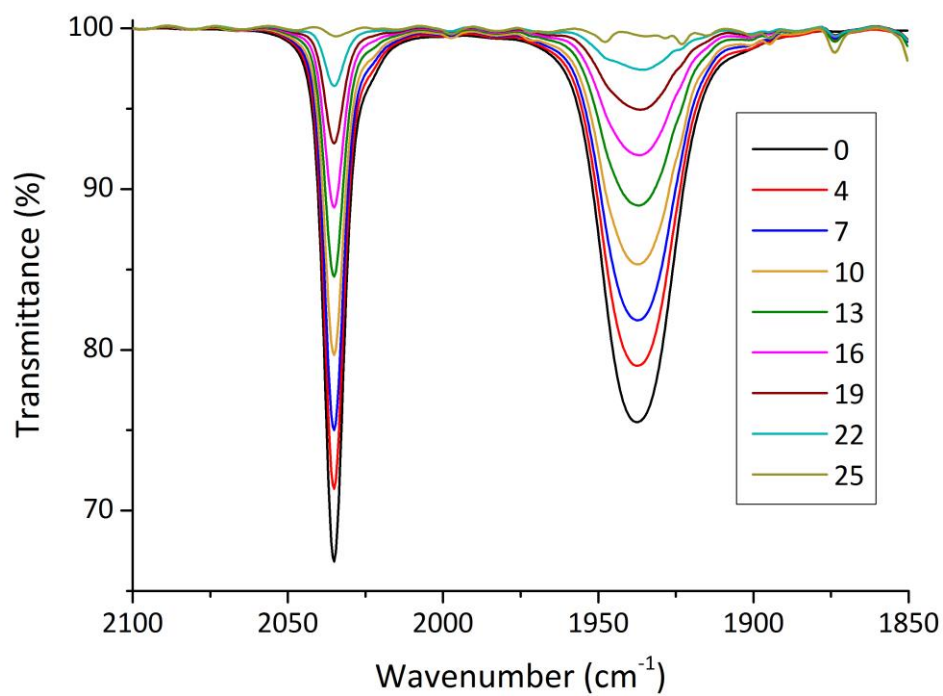
**Figure S25:** IR photolysis spectra of Mn(phen)(CO)<sub>3</sub>3



**Figure S26:** IR photolysis spectra of Mn(phen)(CO)<sub>3</sub>4

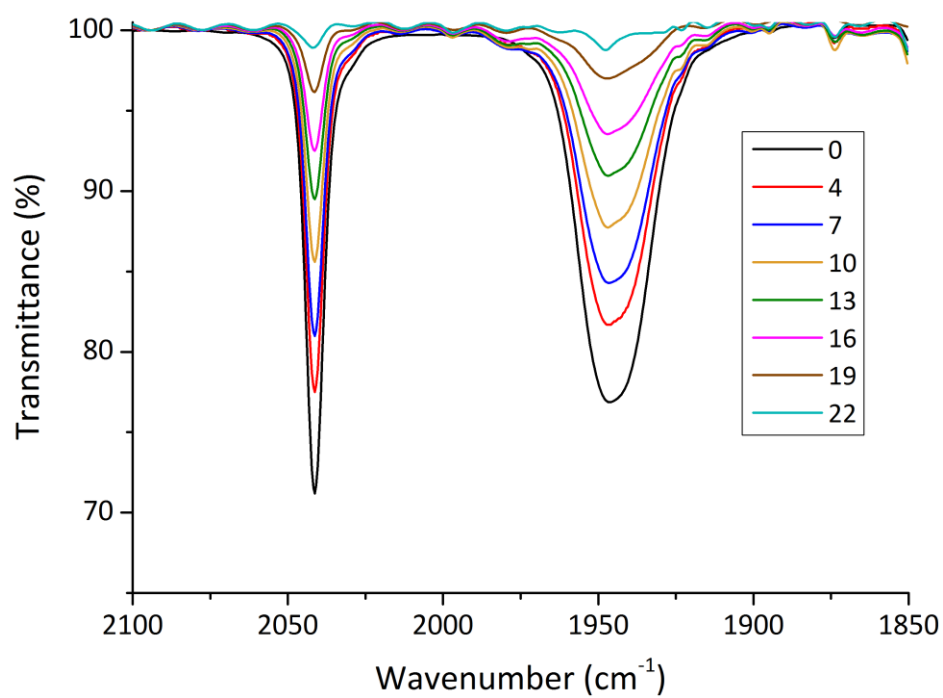


**Figure S27:** IR photolysis spectra of Mn(phen)(CO)<sub>35</sub>

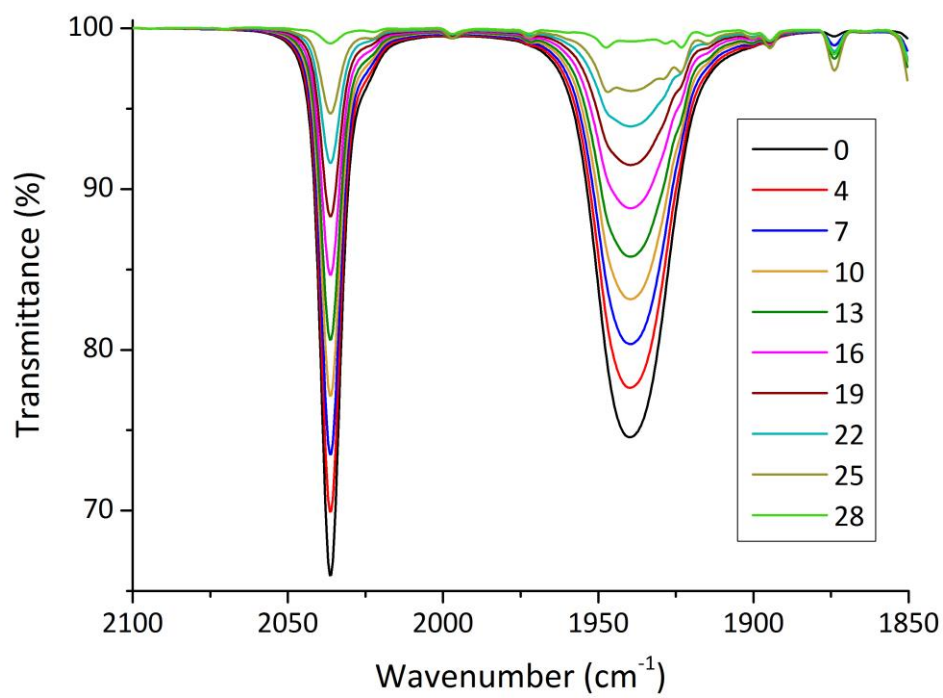


**Figure S28:** IR photolysis spectra of Mn(batho)(CO)<sub>31</sub>

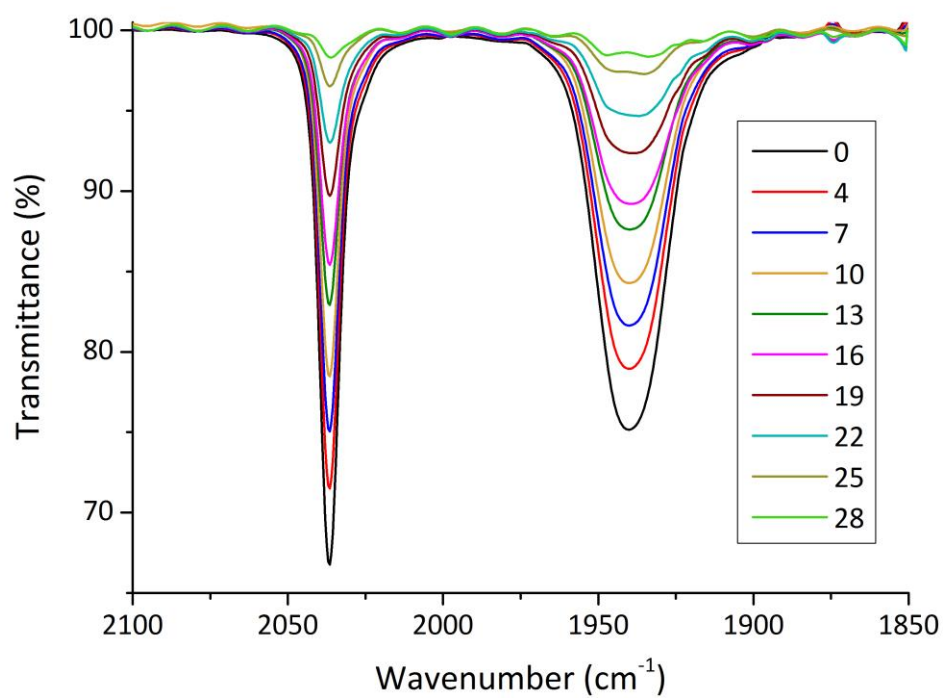




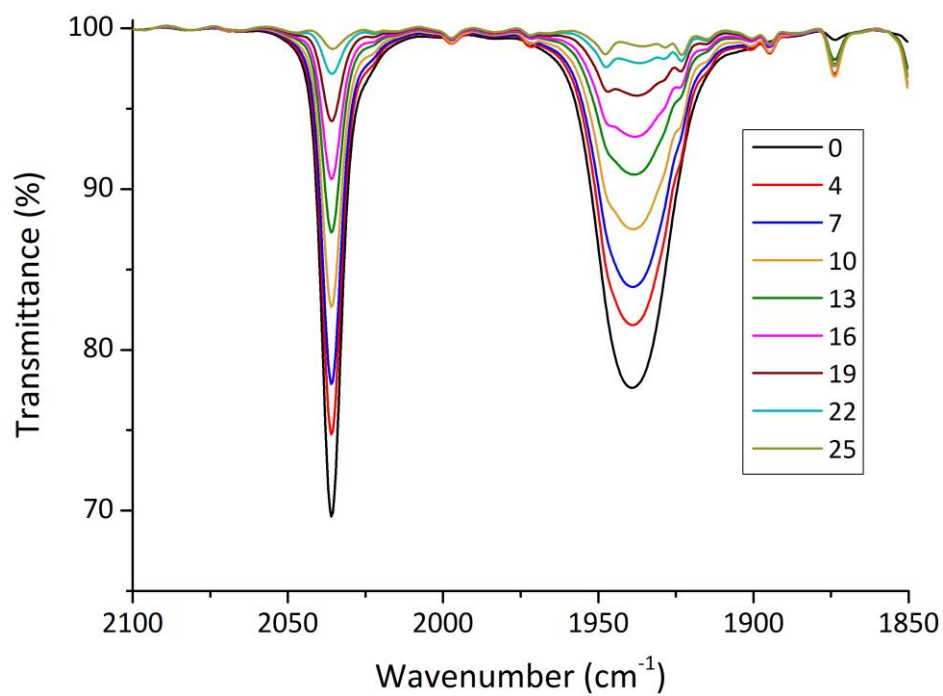
**Figure S29:** IR photolysis spectra of Mn(batho)(CO)<sub>3</sub>2



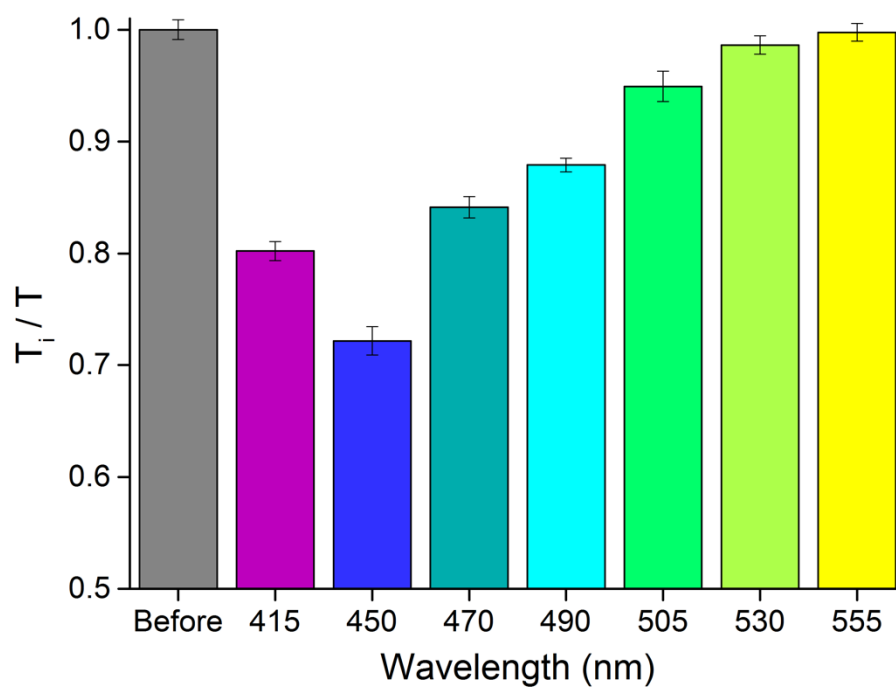
**Figure S30:** IR photolysis spectra of Mn(batho)(CO)<sub>3</sub>3



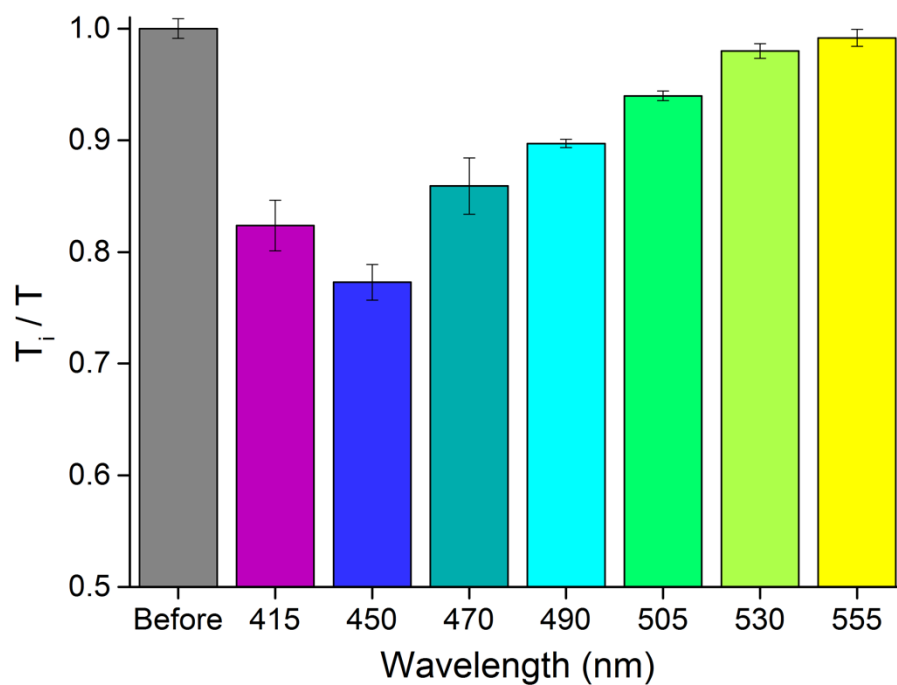
**Figure S31:** IR photolysis spectra of Mn(batho)(CO)<sub>34</sub>



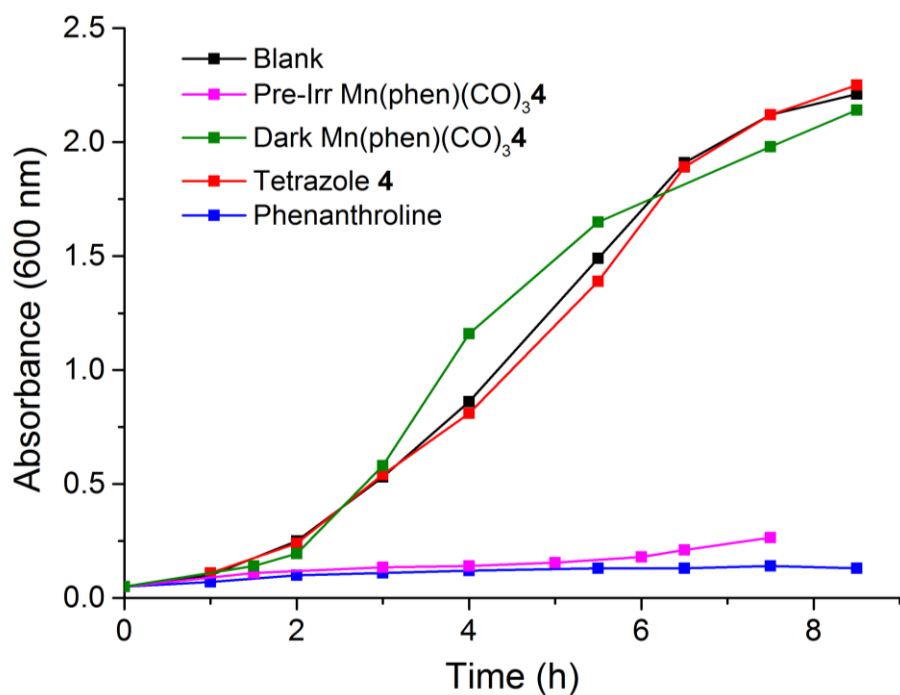
**Figure S32:** IR photolysis spectra of Mn(batho)(CO)<sub>35</sub>



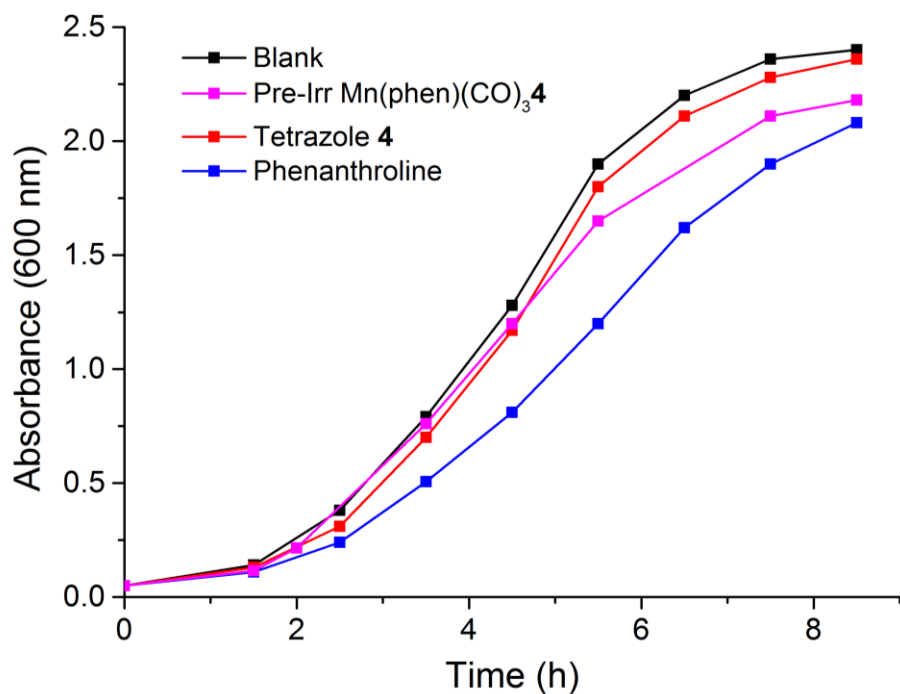
**Figure S33:** Polilight photolysis spectra of  $\text{Mn(phen)(CO)}_34$



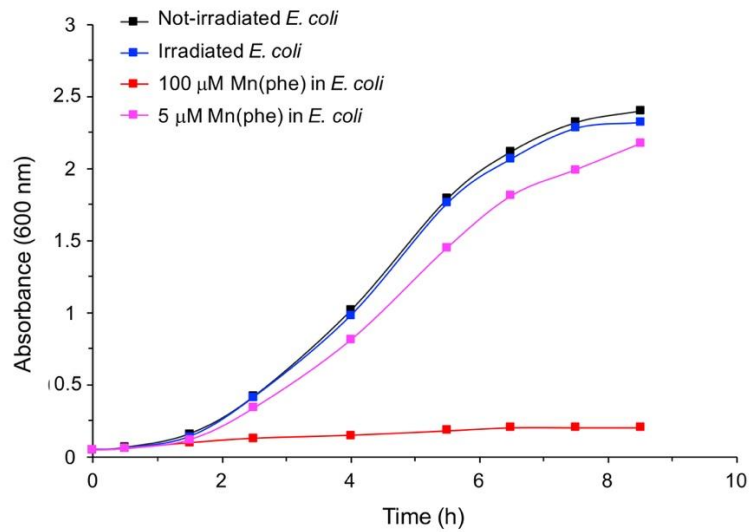
**Figure S34:** Polilight photolysis spectra of  $\text{Mn(batho)(CO)}_34$



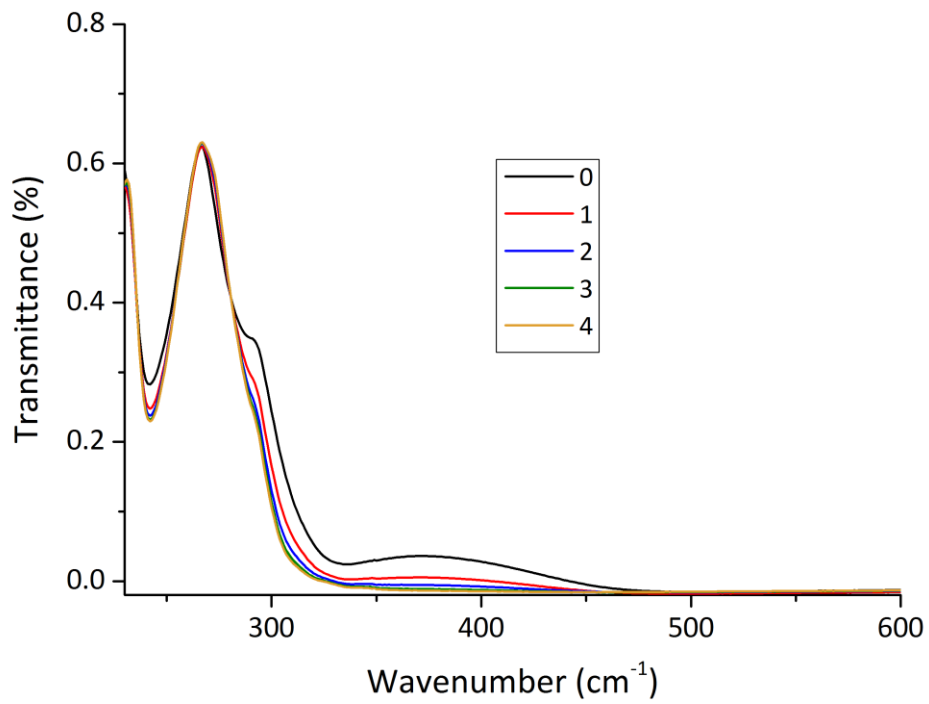
**Figure S35:** *E. coli* growth curves at 37 °C in the presence of 100 μM Mn(phen)(CO)<sub>3</sub>4 pre-photolysed or maintained in the dark (pink and green lines, respectively), phenanthroline (blue line) and 4 tetrazole (red line). A control culture containing DMSO alone (1.2%) was prepared (dark line)



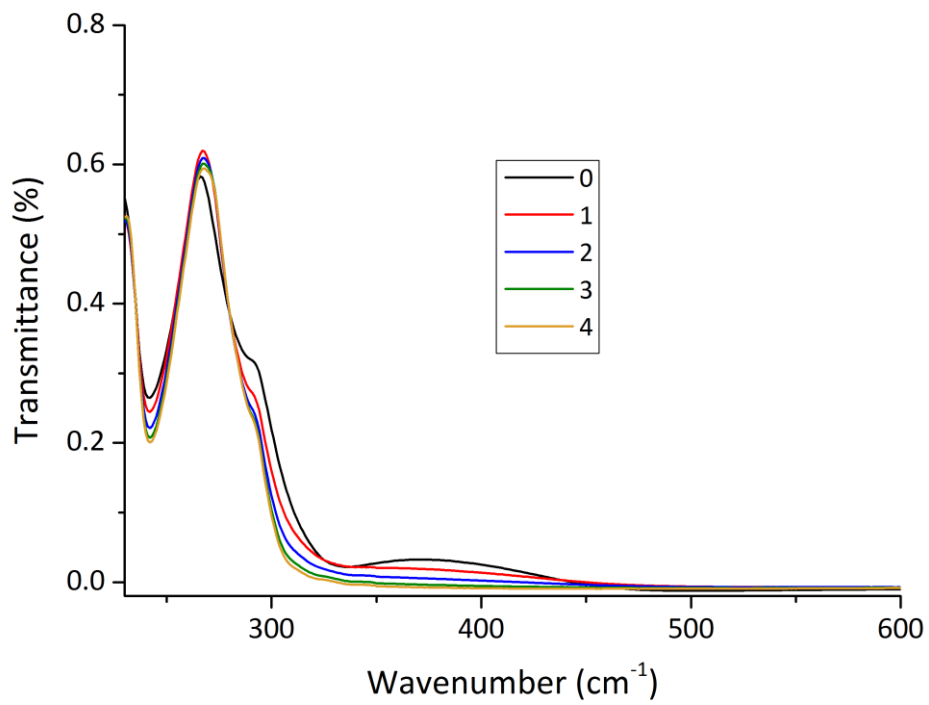
**Figure S36:** *E. coli* growth curves at 37 °C in LB medium supplemented with 5 μM of pre-irradiated Mn(phen)(CO)<sub>3</sub>4 (pink line), 4 tetrazole (red line) and phenanthroline (blue line). A control culture containing 0.5% DMSO was prepared (dark line)



**Figure S37:** *E. coli* growth curves at 37 °C in LB medium incubated with Mn(phen)(CO)<sub>3</sub>4 and irradiated post-incubation at 365 nm (red and pink lines), along with non-irradiated sample (black line) and irradiated sample without any complex (blue line)



**Figure S38:** UV-Vis absorption spectra of Mn(phen)(CO)<sub>3</sub>4 exposed to 365 nm light (time minutes)



**Figure S39:** UV-Vis absorption spectra of degassed Mn(phen)(CO)<sub>3</sub>4 exposed to 365 nm light (time minutes)

**Table S1:** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $\text{Mn(phen)(CO)}_3\mathbf{1}$ 

---

Mn(1)-C(2)	1.8121 (18)
Mn(1)-C(3)	1.8156 (17)
Mn(1)-C(1)	1.8191 (18)
Mn(1)-N(2)	2.0425 (15)
Mn(1)-N(21)	2.0500 (13)
Mn(1)-N(11)	2.0526 (14)
C(2)-Mn(1)-C(3)	90.18 (8)
C(2)-Mn(1)-C(1)	89.77 (8)
C(3)-Mn(1)-C(1)	89.12 (8)
C(2)-Mn(1)-N(2)	175.14 (7)
C(3)-Mn(1)-N(2)	91.15 (7)
C(1)-Mn(1)-N(2)	94.92 (7)
C(2)-Mn(1)-N(21)	91.52 (6)
C(3)-Mn(1)-N(21)	175.03 (7)
C(1)-Mn(1)-N(21)	95.56 (6)
N(2)-Mn(1)-N(21)	86.78 (6)
C(2)-Mn(1)-N(11)	93.36(6)
C(3)-Mn(1)-N(11)	95.24 (7)
C(1)-Mn(1)-N(11)	174.62 (7)
N(2)-Mn(1)-N(11)	81.86 (6)
N(21)-Mn(1)-N(11)	79.99 (5)

---

**Table S2:** Selected bond lengths [Å] and angles [°] for Mn(phen)(CO)<sub>3</sub>2

---

Mn(1)-C(2)	1.8034(16)
Mn(1)-C(3)	1.8133(16)
Mn(1)-C(1)	1.8289(15)
Mn(1)-N(2)	2.0413(13)
Mn(1)-N(21)	2.0482(12)
Mn(1)-N(11)	2.0526(12)
C(2)-Mn(1)-C(3)	90.06(7)
C(2)-Mn(1)-C(1)	88.89(7)
C(3)-Mn(1)-C(1)	87.97(7)
C(2)-Mn(1)-N(2)	174.36(5)
C(3)-Mn(1)-N(2)	91.36(6)
C(1)-Mn(1)-N(2)	96.61(6)
C(2)-Mn(1)-N(21)	91.75(6)
C(3)-Mn(1)-N(21)	175.94(6)
C(1)-Mn(1)-N(21)	95.70(6)
N(2)-Mn(1)-N(21)	86.50(5)
C(2)-Mn(1)-N(11)	92.78(6)
C(3)-Mn(1)-N(11)	96.32(6)
C(1)-Mn(1)-N(11)	175.39(6)
N(2)-Mn(1)-N(11)	81.64(5)
N(21)-Mn(1)-N(11)	79.96(5)

---



**Table S3:** Selected bond lengths [Å] and angles [°] for Mn(phen)(CO)<sub>3</sub>3

---

Mn(1)-C(1)	1.802(3)
Mn(1)-C(2)	1.808(3)
Mn(1)-C(3)	1.817(3)
Mn(1)-N(2)	2.044(2)
Mn(1)-N(21)	2.047(2)
Mn(1)-N(11)	2.055(2)
C(1)-Mn(1)-C(2)	87.64(13)
C(1)-Mn(1)-C(3)	91.09(13)
C(2)-Mn(1)-C(3)	91.22(13)
C(1)-Mn(1)-N(2)	89.58(12)
C(2)-Mn(1)-N(2)	177.10(11)
C(3)-Mn(1)-N(2)	89.65(11)
C(1)-Mn(1)-N(21)	94.69(12)
C(2)-Mn(1)-N(21)	93.21(11)
C(3)-Mn(1)-N(21)	172.85(11)
N(2)-Mn(1)-N(21)	86.19(9)
C(1)-Mn(1)-N(11)	174.58(12)
C(2)-Mn(1)-N(11)	93.84(11)
C(3)-Mn(1)-N(11)	94.08(11)
N(2)-Mn(1)-N(11)	88.85(9)
N(21)-Mn(1)-N(11)	80.03(9)

---

**Table S4:** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $\text{Mn(phen)(CO)}_3$ 

---

Mn(1)-C(1)	1.806(2)
Mn(1)-C(3)	1.807(2)
Mn(1)-C(2)	1.829(3)
Mn(1)-N(11)	2.0461(18)
Mn(1)-N(2)	2.0465(19)
Mn(1)-N(21)	2.0572(17)
C(1)-Mn(1)-C(3)	85.33(10)
C(1)-Mn(1)-C(2)	90.02(11)
C(3)-Mn(1)-C(2)	90.14(10)
C(1)-Mn(1)-N(11)	176.42(8)
C(3)-Mn(1)-N(11)	98.02(8)
C(2)-Mn(1)-N(11)	91.23(10)
C(1)-Mn(1)-N(2)	92.11(9)
C(3)-Mn(1)-N(2)	89.56(8)
C(2)-Mn(1)-N(2)	177.82(10)
N(11)-Mn(1)-N(2)	86.67(7)
C(1)-Mn(1)-N(21)	96.58(8)
C(3)-Mn(1)-N(21)	176.62(9)
C(2)-Mn(1)-N(21)	92.64(9)
N(11)-Mn(1)-N(21)	80.01(7)
N(2)-Mn(1)-N(21)	87.59(7)

---

**Table S5:** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $\text{Mn(phen)(CO)}_3\mathbf{5}$ 

---

Mn(1)-C(3)	1.8104 (14)
Mn(1)-C(1)	1.8160 (13)
Mn(1)-C(2)	1.8175 (13)
Mn(1)-N(21)	2.0505 (10)
Mn(1)-N(32)	2.0541 (11)
Mn(1)-N(11)	2.0632 (11)
C(3)-Mn(1)-C(1)	87.78 (6)
C(3)-Mn(1)-C(2)	89.73 (6)
C(1)-Mn(1)-C(2)	91.32 (6)
C(3)-Mn(1)-N(21)	93.98 (5)
C(1)-Mn(1)-N(21)	172.74 (5)
C(2)-Mn(1)-N(21)	95.73 (5)
C(3)-Mn(1)-N(32)	177.11 (5)
C(1)-Mn(1)-N(32)	92.57 (5)
C(2)-Mn(1)-N(32)	87.39 (5)
N(21)-Mn(1)-N(32)	86.03 (4)
C(3)-Mn(1)-N(11)	95.47 (5)
C(1)-Mn(1)-N(11)	92.95 (5)
C(2)-Mn(1)-N(11)	173.39 (5)
N(21)-Mn(1)-N(11)	79.87 (4)
N(32)-Mn(1)-N(11)	87.38 (4)

---