

Rhenium-Imido Corroles

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Contents	Page
A. ¹ H NMR spectra	S2
B. HR-ESI mass spectra	S8
C. Photophysical studies	S14

A. NMR spectra.

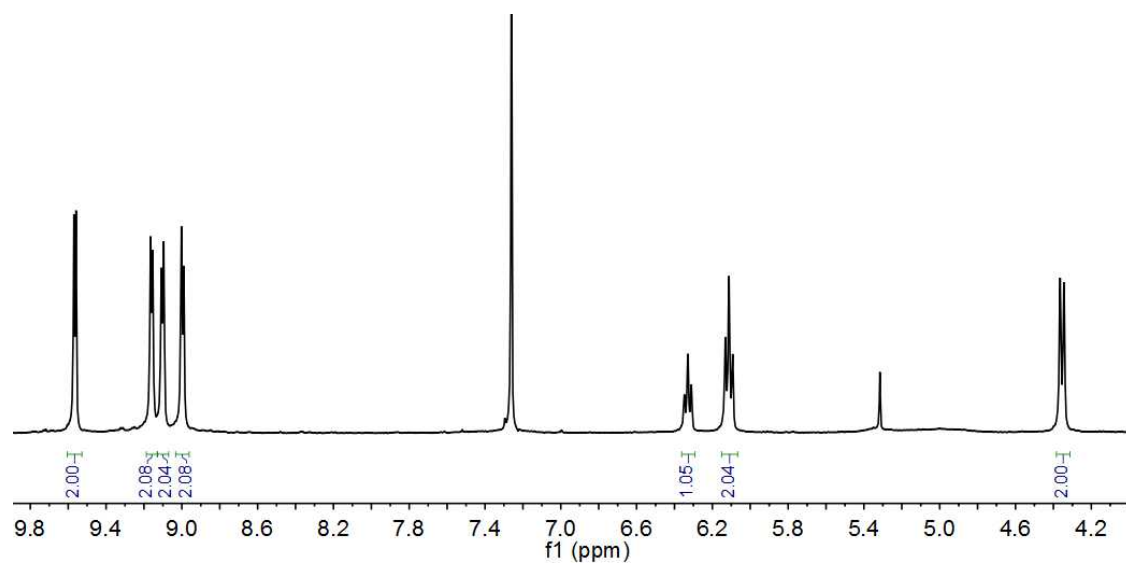


Figure S1. ^1H NMR spectrum of $\text{Re}[\text{TPFPC}](\text{NPh})$ in CDCl_3 at 253 K.

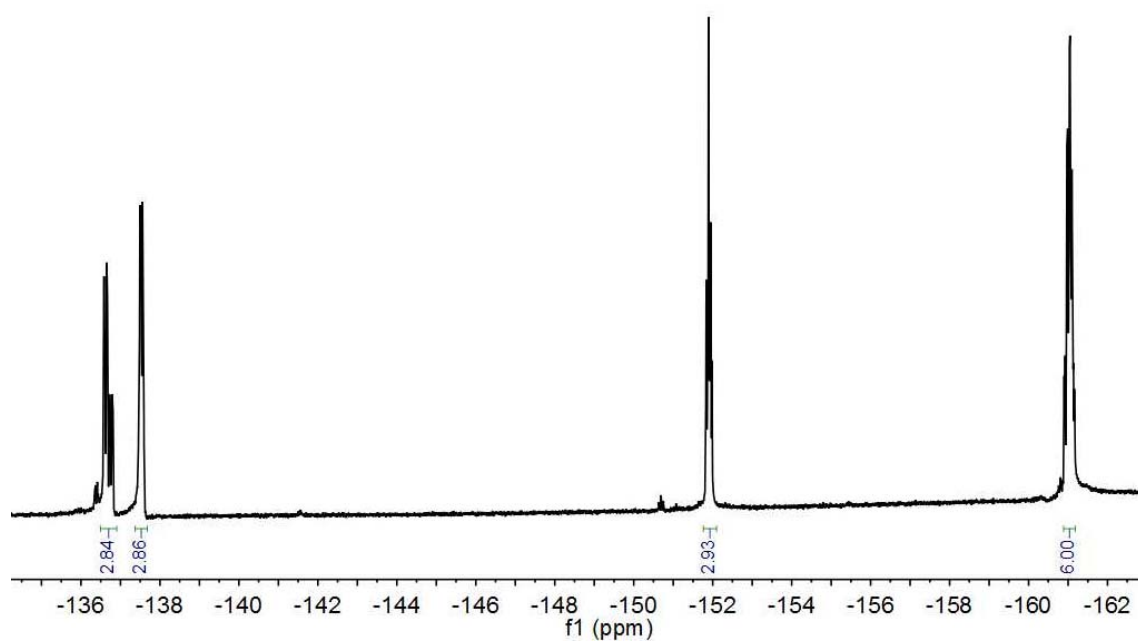


Figure S2. ^{19}F NMR spectrum of $\text{Re}[\text{TPFPC}](\text{NPh})$ in CDCl_3 at 253 K.

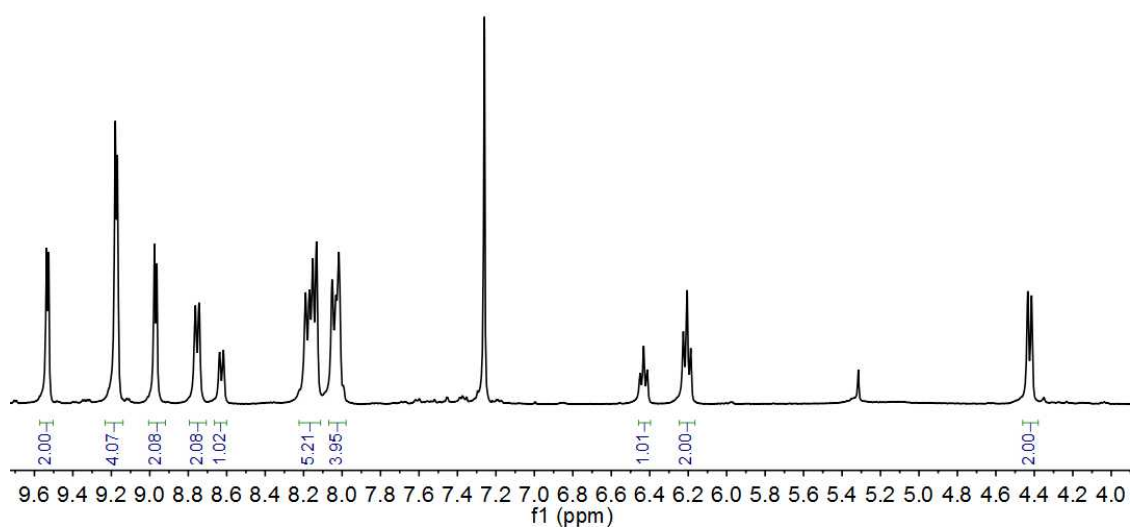


Figure S3. ^1H NMR spectrum of $\text{Re}[\text{TpCF}_3\text{PC}](\text{NPh})$ in CDCl_3 at 253 K.

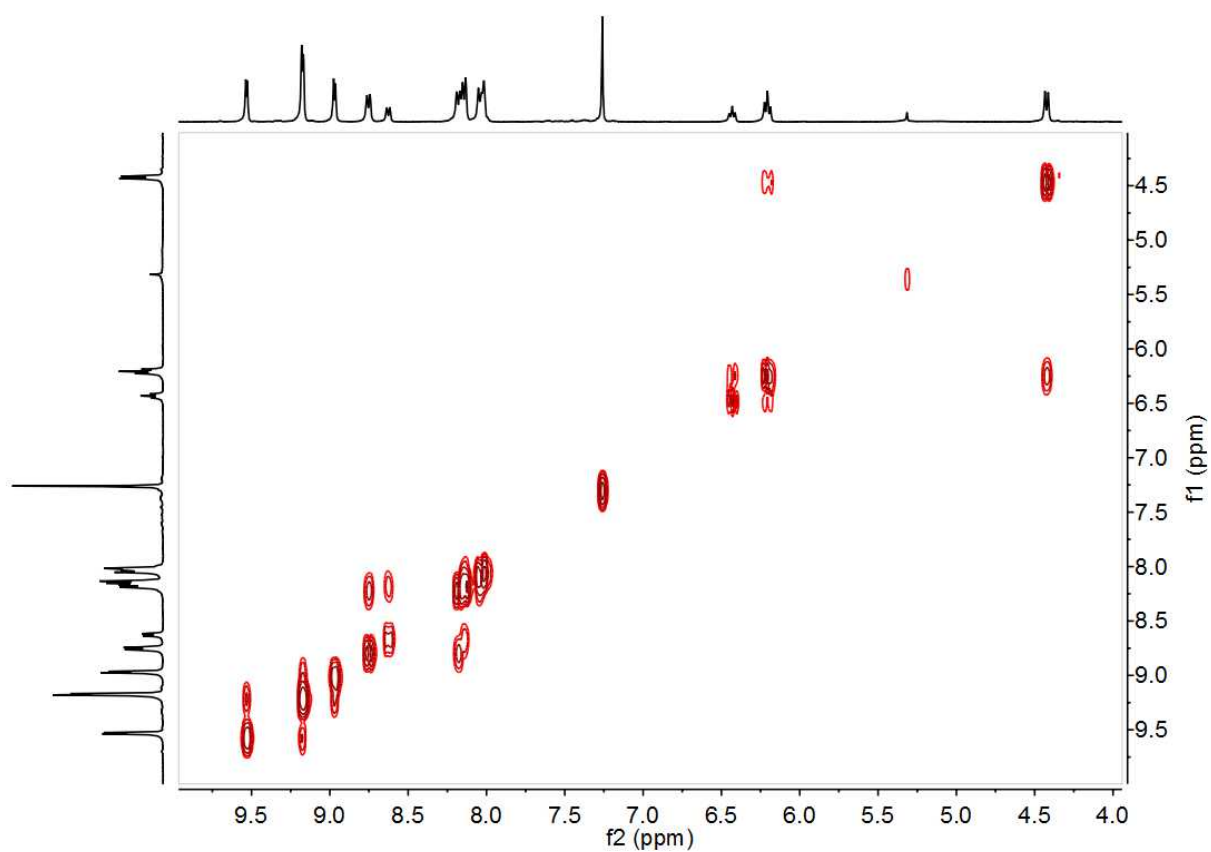


Figure S4. ^1H - ^1H COSY of $\text{Re}[\text{TpCF}_3\text{PC}](\text{NPh})$ in CDCl_3 at 253 K.

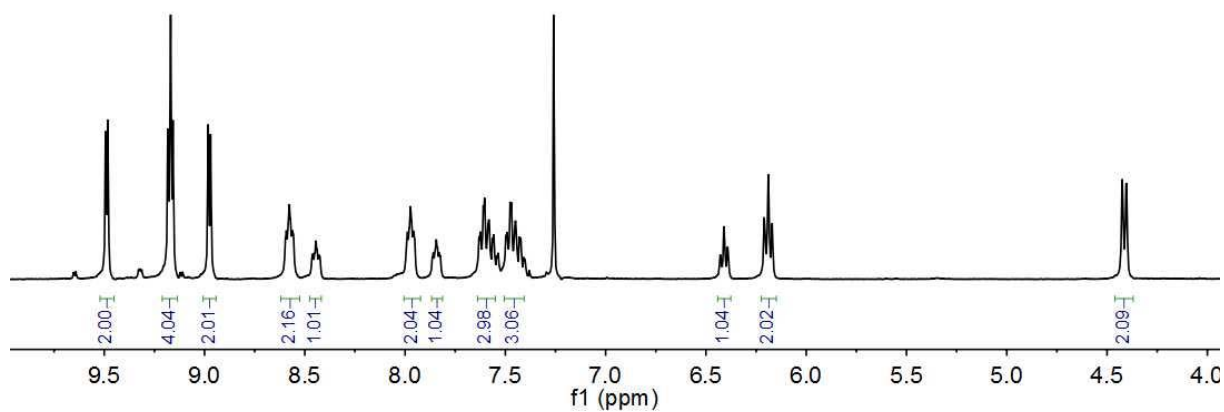


Figure S5. ^1H NMR spectrum of $\text{Re}[\text{TpFPC}](\text{NPh})$ in CDCl_3 at 253 K.

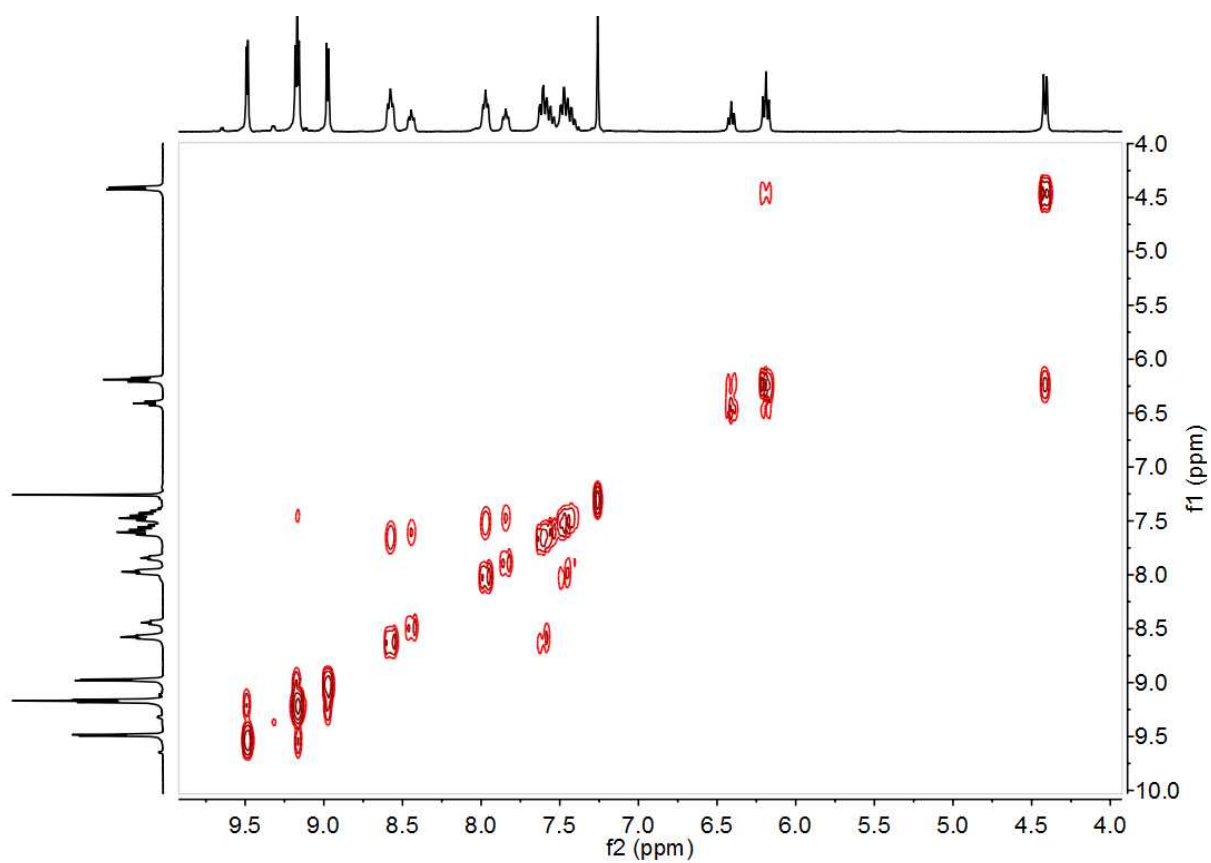


Figure S6. ^1H - ^1H COSY of $\text{Re}[\text{TpFPC}](\text{NPh})$ in CDCl_3 at 253 K

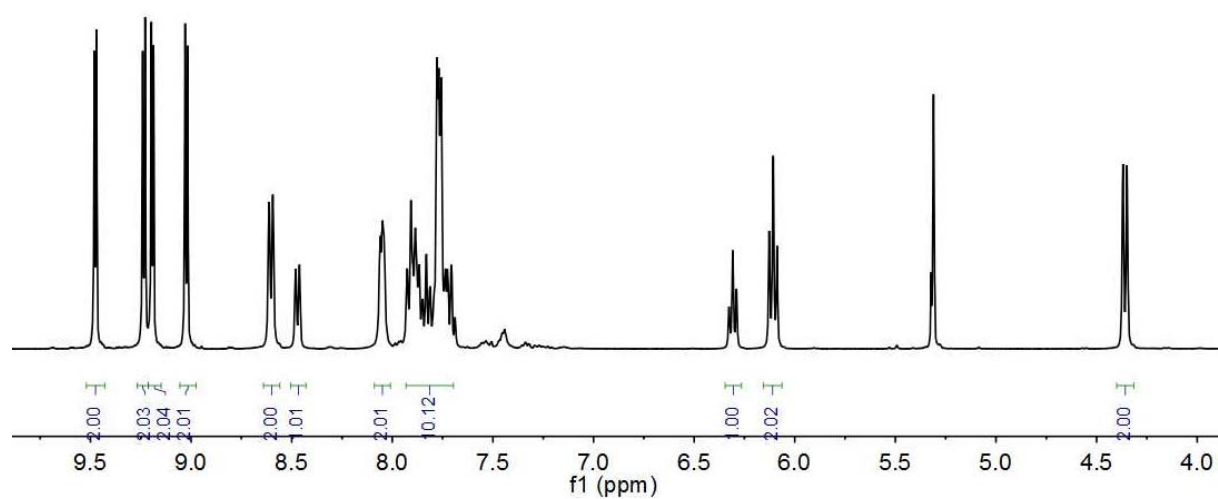


Figure S7. ^1H NMR spectrum of $\text{Re}[\text{TPC}](\text{NPh})$ in CD_2Cl_2 at 253 K.

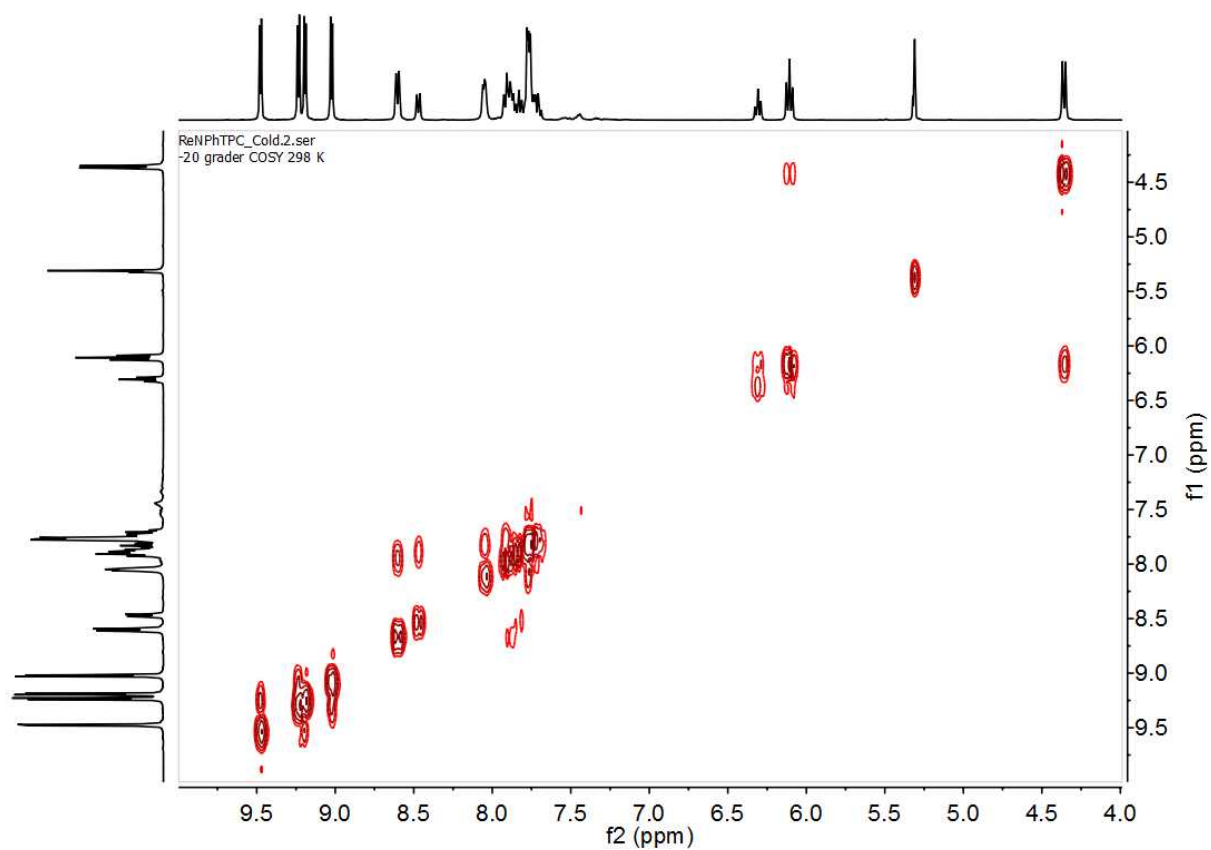


Figure S8. ^1H - ^1H COSY of $\text{Re}[\text{TPC}](\text{NPh})$ in CD_2Cl_2 at 253 K.

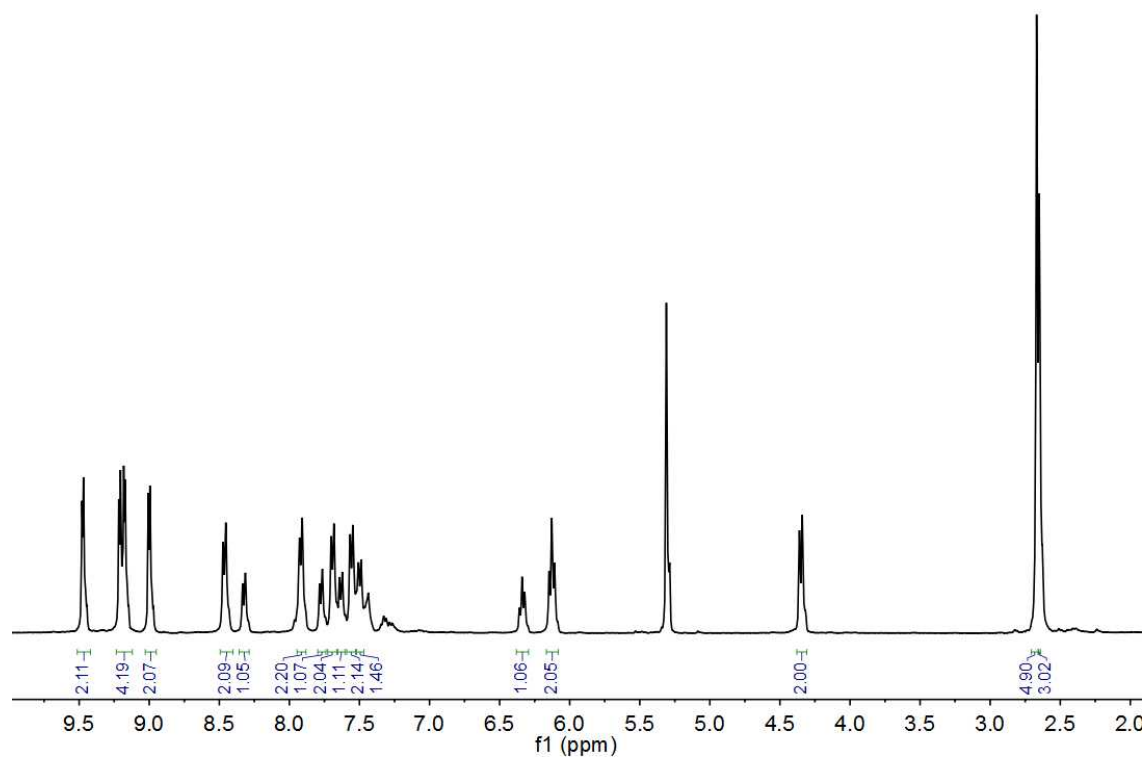


Figure S9. ^1H NMR spectrum of $\text{Re}[\text{TpCH}_3\text{PC}](\text{NPh})$ in CD_2Cl_2 at 253 K.

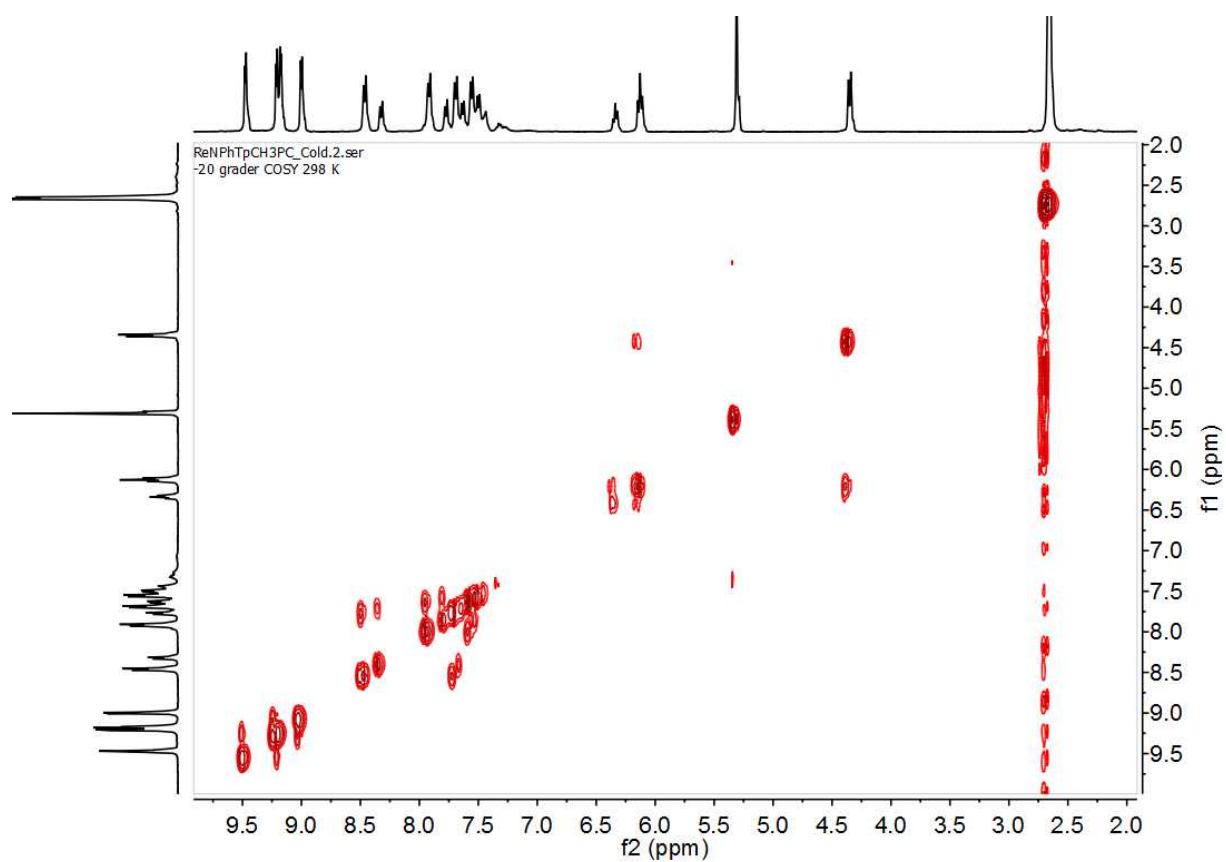


Figure S10. ^1H - ^1H COSY of $\text{Re}[\text{TpCH}_3\text{PC}](\text{NPh})$ in CD_2Cl_2 at 253 K.

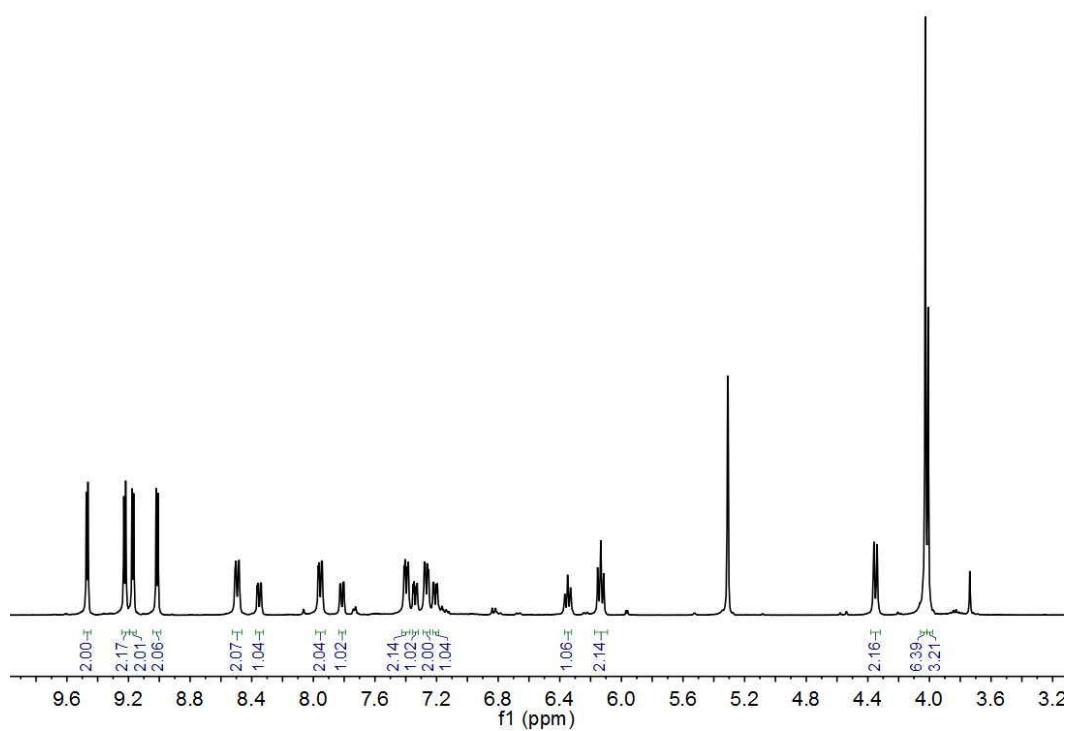


Figure S11. ^1H NMR spectrum of $\text{Re}[\text{TpOCH}_3\text{PC}](\text{NPh})$ in CD_2Cl_2 at 253 K.

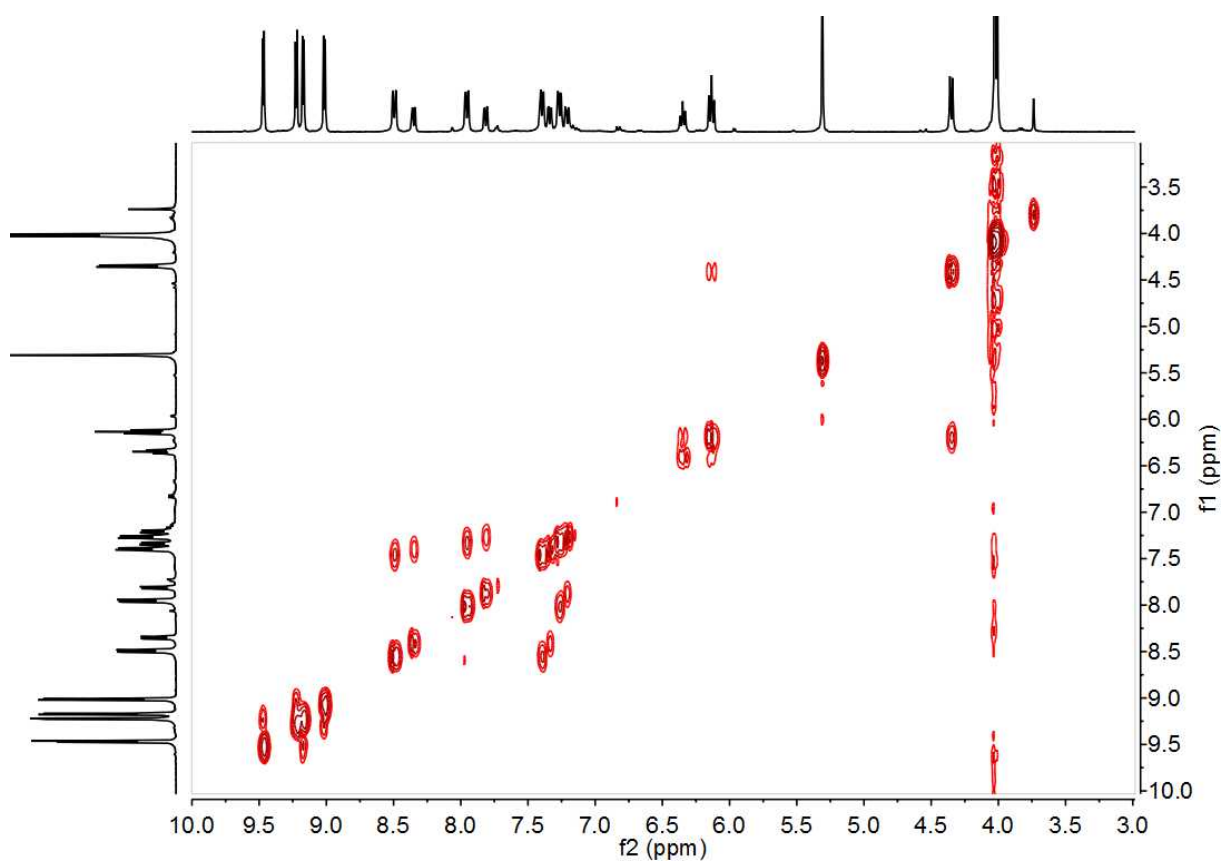
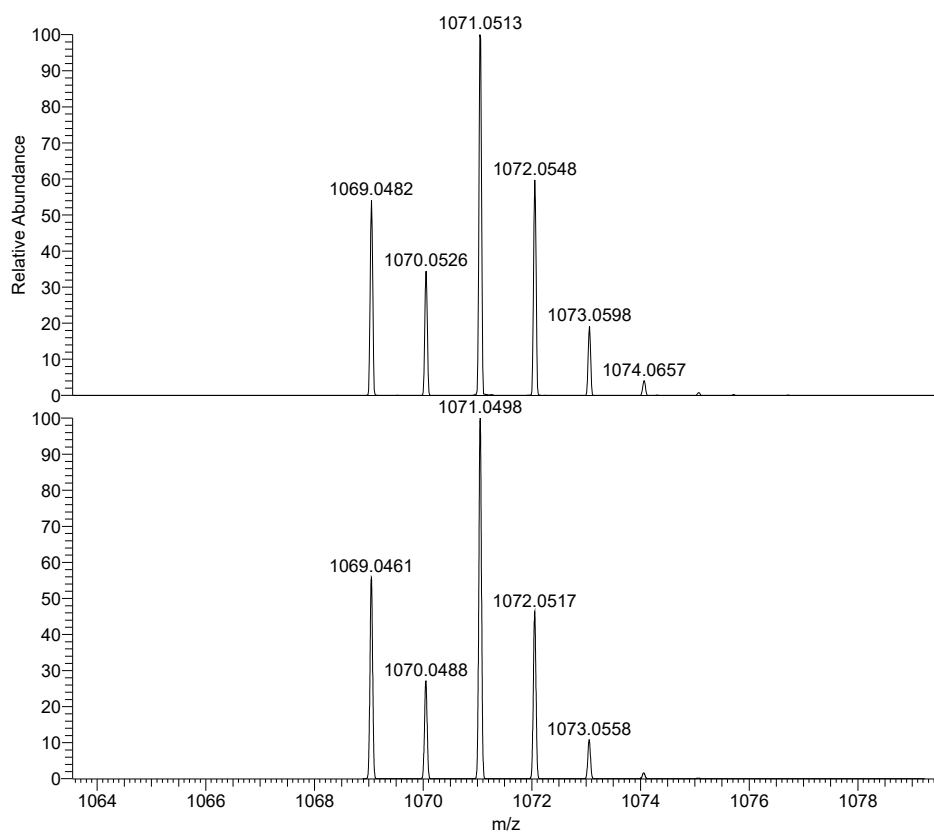
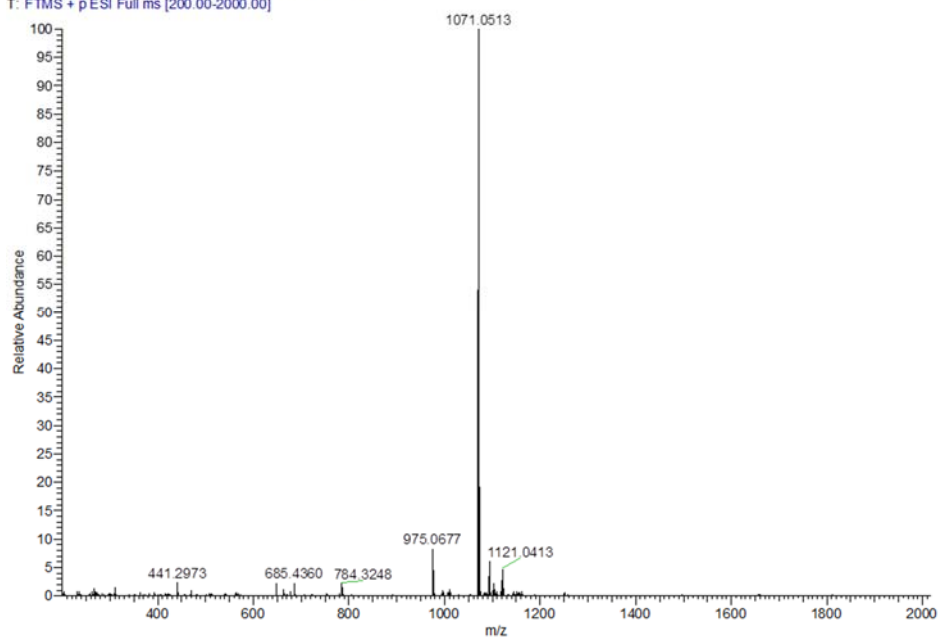


Figure S12. ^1H - ^1H COSY of $\text{Re}[\text{TpOCH}_3\text{PC}](\text{NPh})$ in CD_2Cl_2 at 253 K.

B. ESI mass spectra

ReNPhTPFPC-1_pos #2-5 RT: 0.01-0.04 AV: 4 NL: 2.02E7
T: FTMS + p ESI Full ms [200.00-2000.00]



NL:
2.02E7
ReNPhTPFPC-1_pos#2-5
RT: 0.01-0.04 AV: 4 T: FTMS
+ p ESI Full ms
[200.00-2000.00]

NL:
9.68E3
C₄₃ H₁₃ F₁₅ N₅ Re:
C₄₃ H₁₃ F₁₅ N₅ Re₁
p (gss, s /p:40) Chrg 0
R: 20000 Res .Pwr . @FWHM

Figure S13. Positive mode ESI-MS of Re[TPFPC](NPh): experimental spectrum (top) and simulation (bottom).

ReNPhTpCF3PC-1_pos #2-5 RT: 0.01-0.03 AV: 4 NL: 6.62E7
T: FTMS + p ESI Full ms [200.00-2000.00]

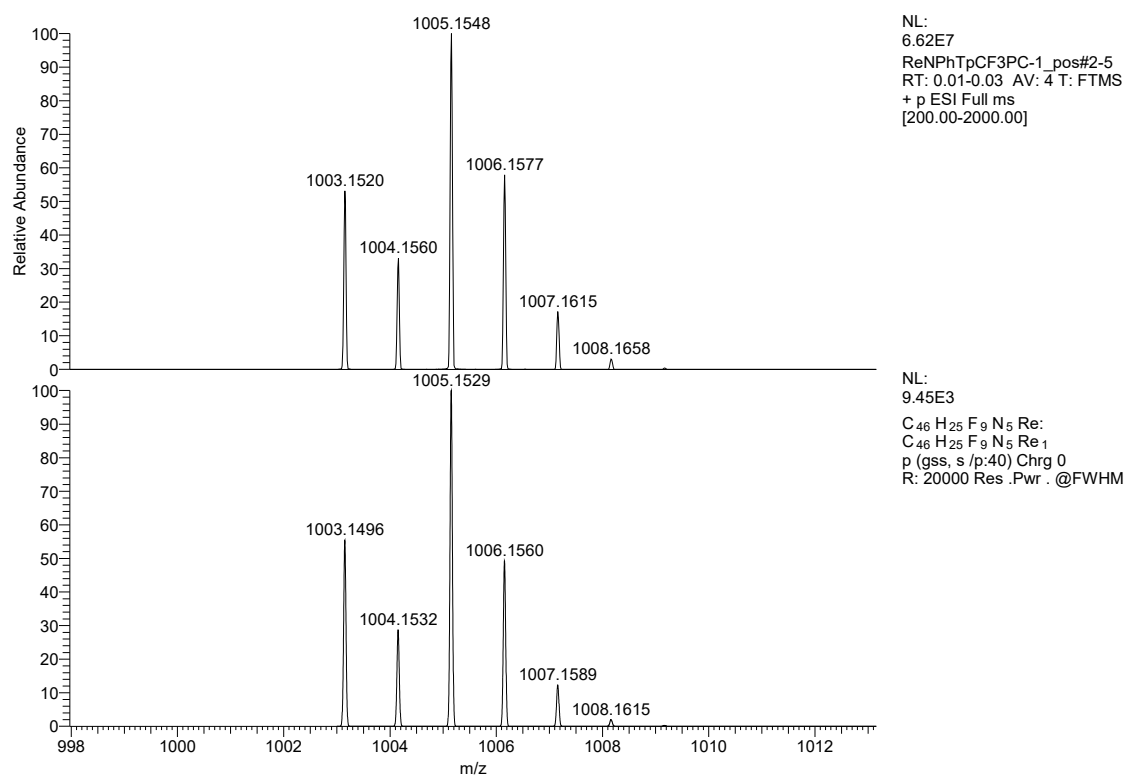
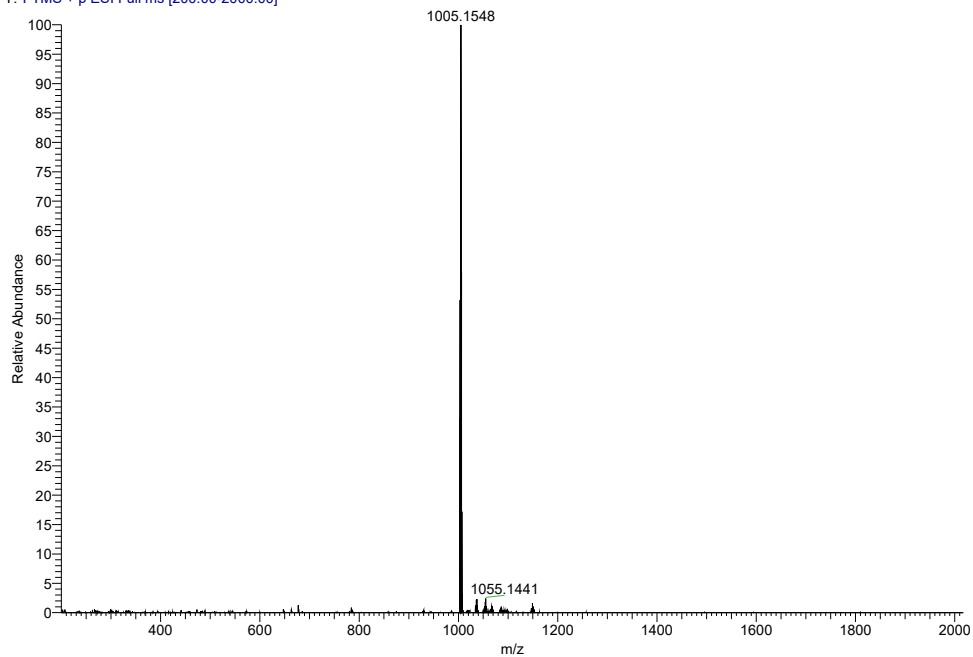
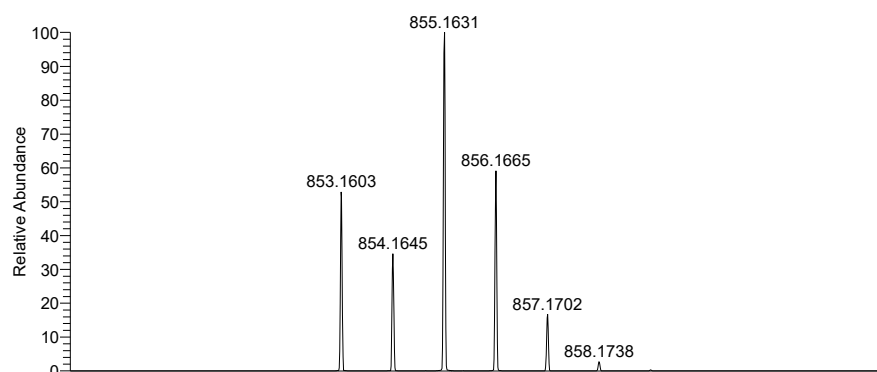
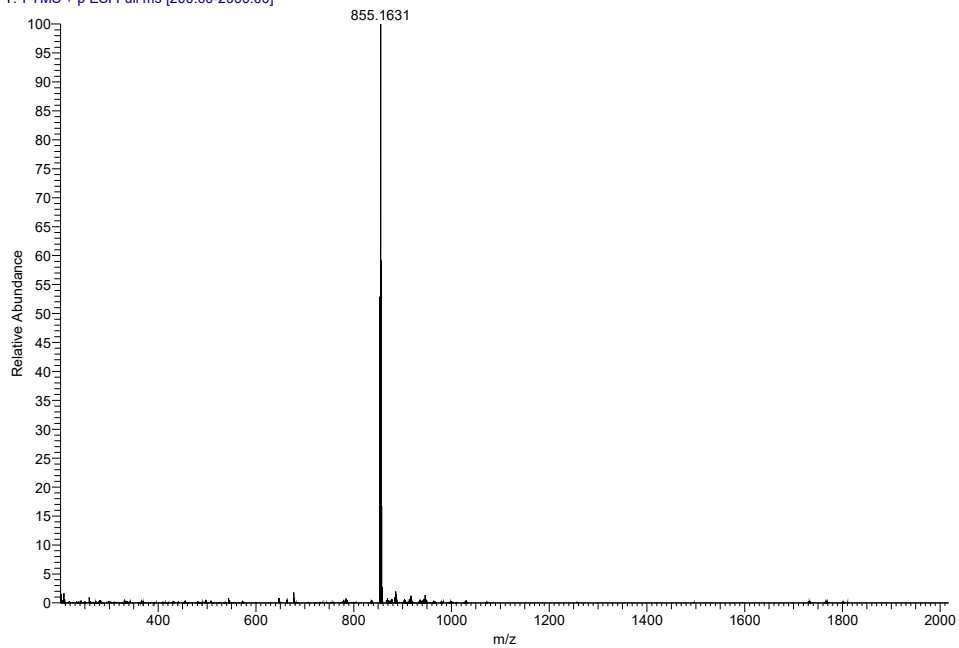
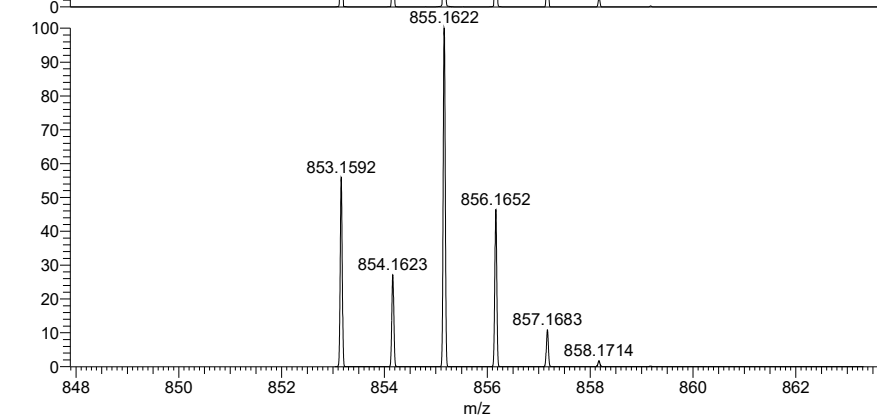


Figure S14. Positive mode ESI-MS of Re[*Tp*CF₃PC](NPh): experimental spectrum (top) and simulation (bottom).

ReNPhTpFPC-1_191004140524 #2-5 RT: 0.01-0.03 AV: 4 NL: 5.38E7
T: FTMS + p ESI Full ms [200.00-2000.00]



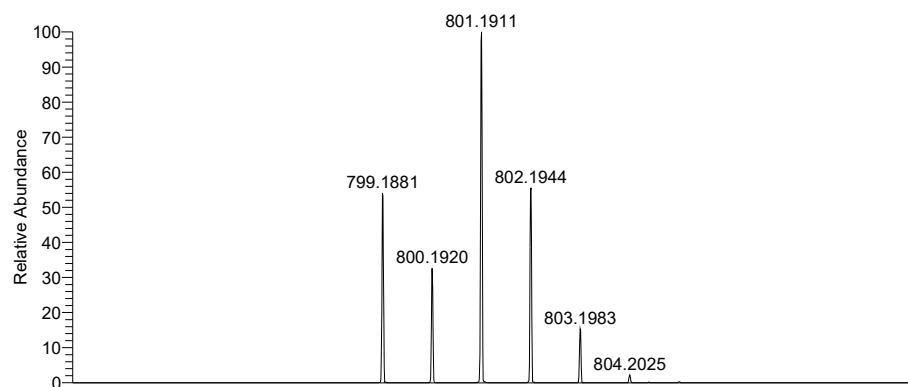
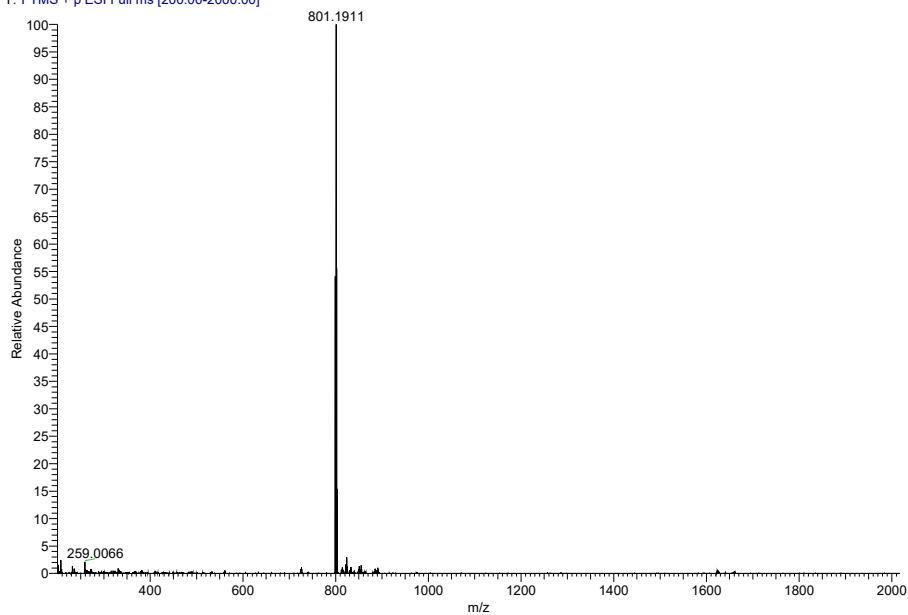
NL:
5.38E7
ReNPhTpFPC-
1_191004140524#2-5 RT:
0.01-0.03 AV: 4 T: FTMS + p
ESI Full ms [200.00-2000.00]



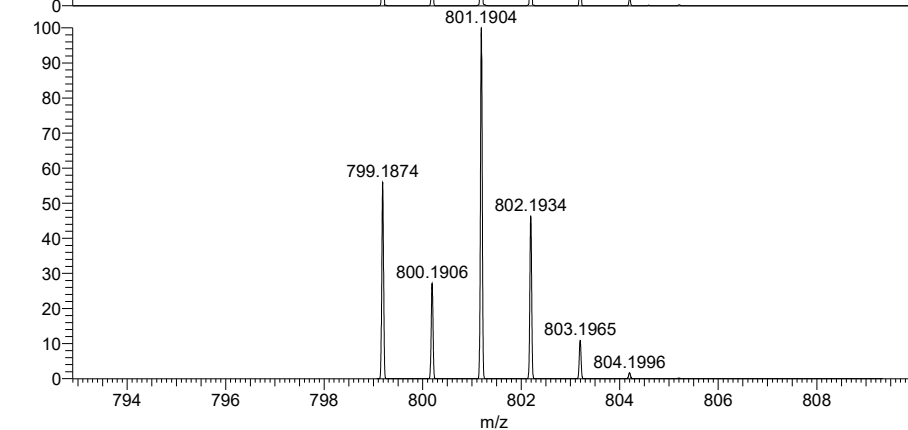
NL:
9.67E3
C₄₃ H₂₅ F₃ N₅ Re:
C₄₃ H₂₅ F₃ N₅ Re₁
p (gss, s /p:40) Chrg 0
R: 20000 Res .Pwr .@FWHM

Figure S15. Positive mode ESI-MS of Re[*Tp*FPC](NPh): experimental spectrum (top) and simulation (bottom).

ReNPhTPC-1_191004140524 #2-5 RT: 0.01-0.05 AV: 4 NL: 2.80E7
T: FTMS + p ESI Full ms [200.00-2000.00]



NL:
2.80E7
ReNPhTPC-
1_191004140524#2-5 RT:
0.01-0.05 AV: 4 T: FTMS + p
ESI Full ms [200.00-2000.00]



NL:
9.66E3
C₄₃ H₂₈ N₅ Re:
C₄₃ H₂₈ N₅ Re₁
p (gss, s /p:40) Chrg 0
R: 20000 Res .Pwr . @FWHM

Figure S16. Positive mode ESI-MS of Re[TPC](NPh): experimental spectrum (top) and simulation (bottom).

ReNPhTpCH3PC-1_191004140524 #1-5 RT: 0.01-0.05 AV: 5 NL: 5.99E7
T: FTMS + p ESI Full ms [200.00-2000.00]

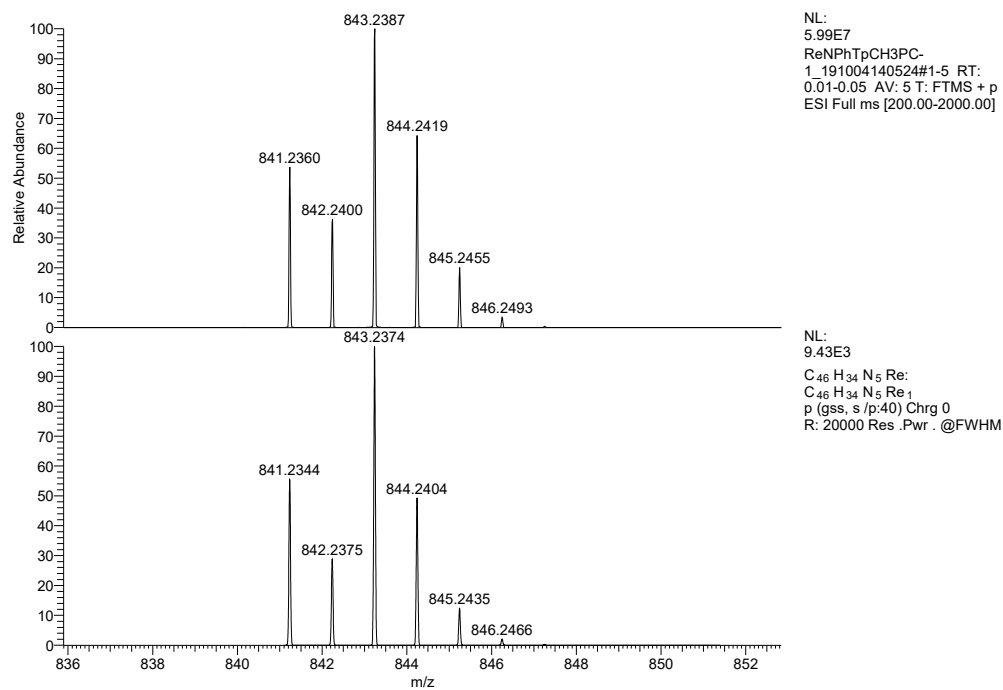
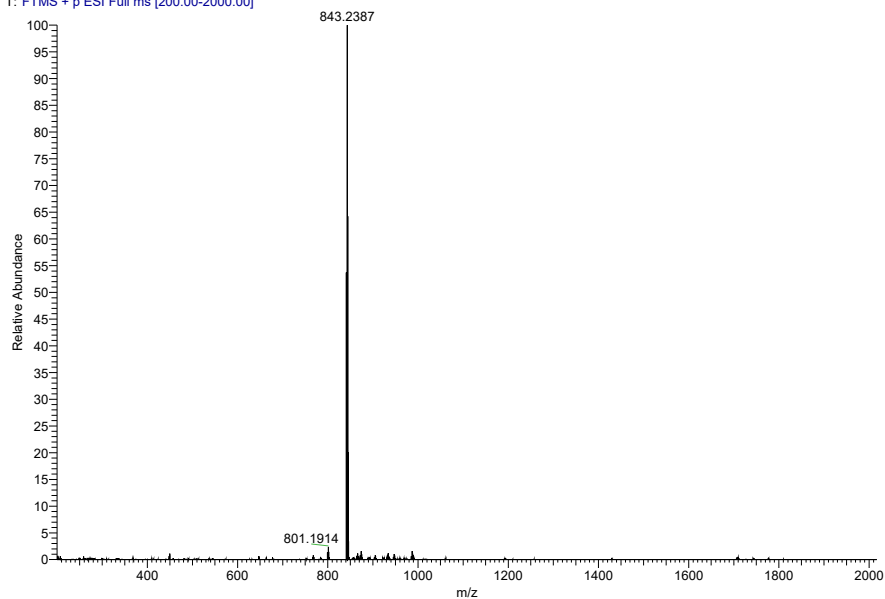


Figure S17. Positive mode ESI-MS of Re[*Tp*CH₃PC](NPh): experimental spectrum (top) and simulation (bottom).

ReNPhTpOCH3PC-1 191004140524 #2-6 RT: 0.01-0.04 AV: 5 NL: 4.47E7
T: FTMS + p ESI Full ms [200.00-2000.00]

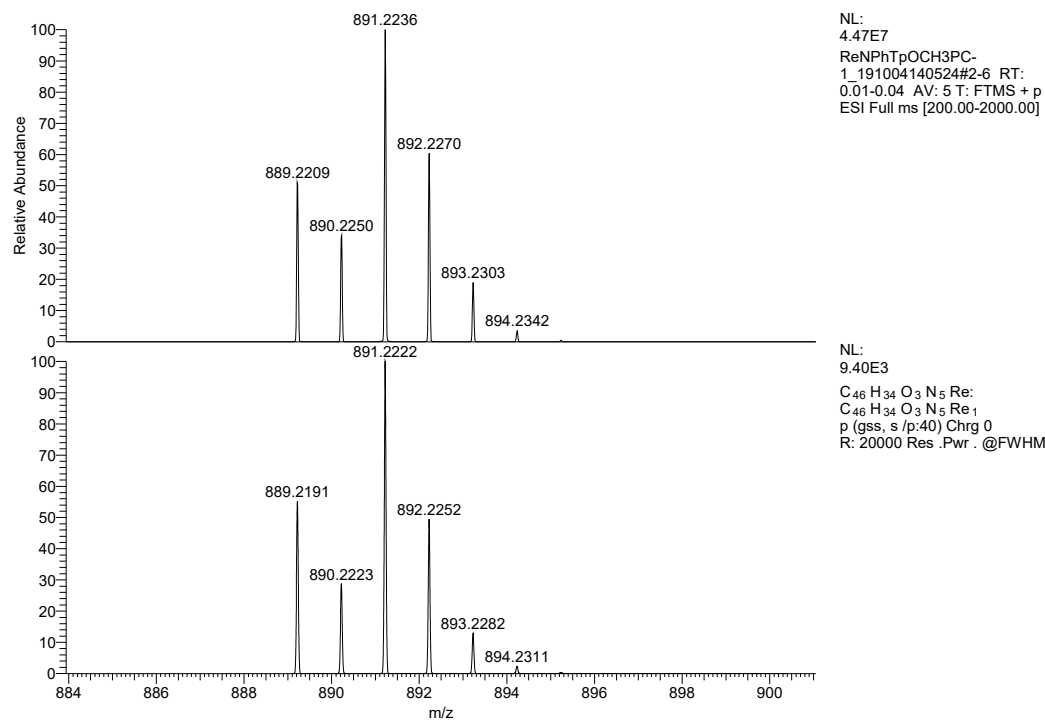
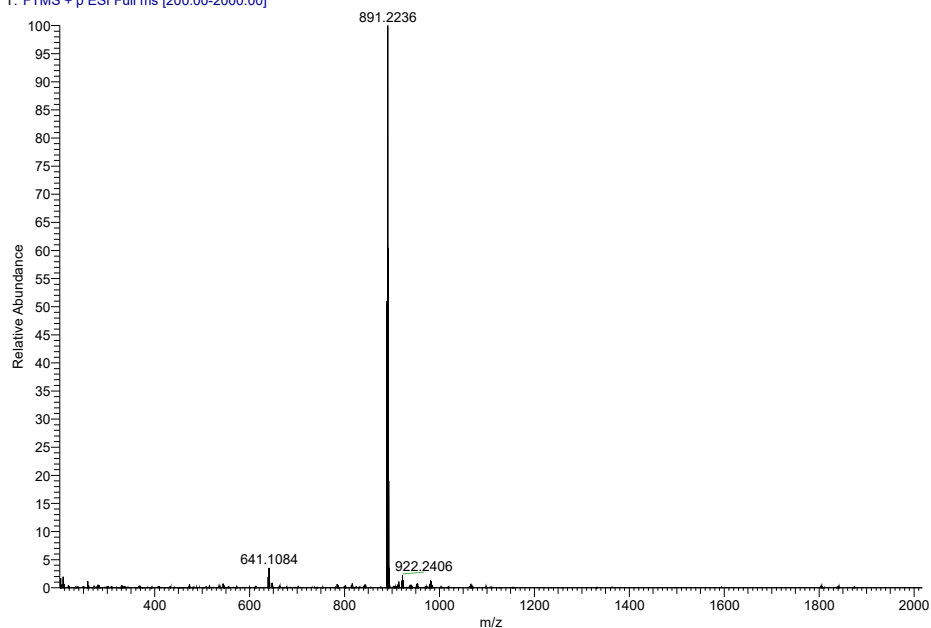


Figure S18. Positive mode ESI-MS of Re[*Tp*OCH₃PC](NPh): experimental spectrum (top) and simulation (bottom).

C. Photophysical Studies

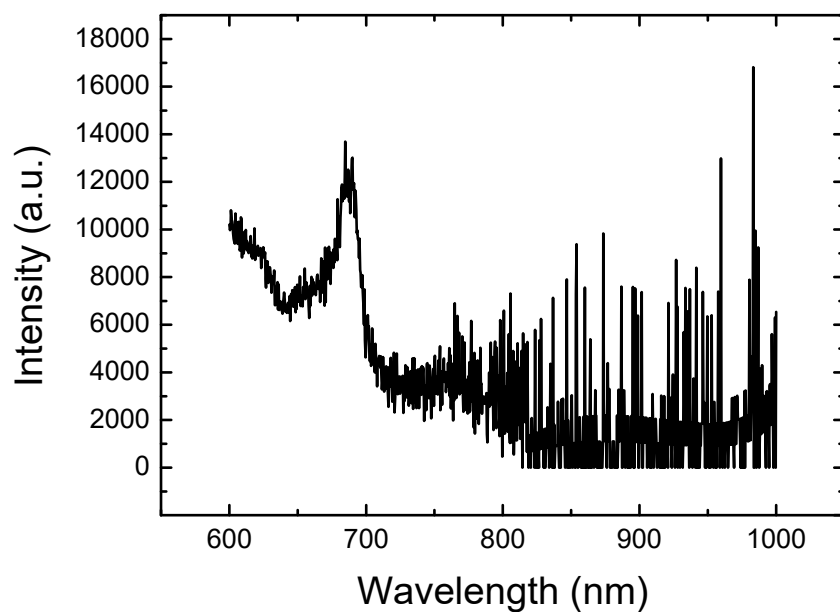


Figure S19. Emission spectrum of Re[TPC](NPh) in anoxic toluene at RT upon 570 nm excitation. An RG 610 filter was used to eliminate the second order artefact. No phosphorescence from the corrole is visible.

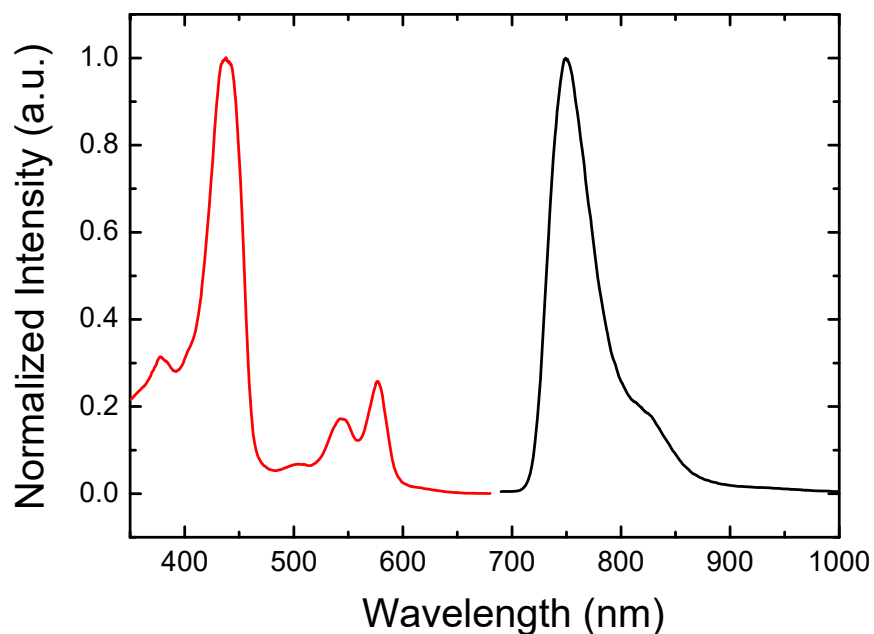


Figure S20. Excitation (red line, $\lambda_{em} = 765$ nm) and emission spectra (black line, $\lambda_{exc} = 440$ nm) of Re[TpCF₃PC](NPh) in a 4:6 v/v toluene:THF frozen glass at 77K.

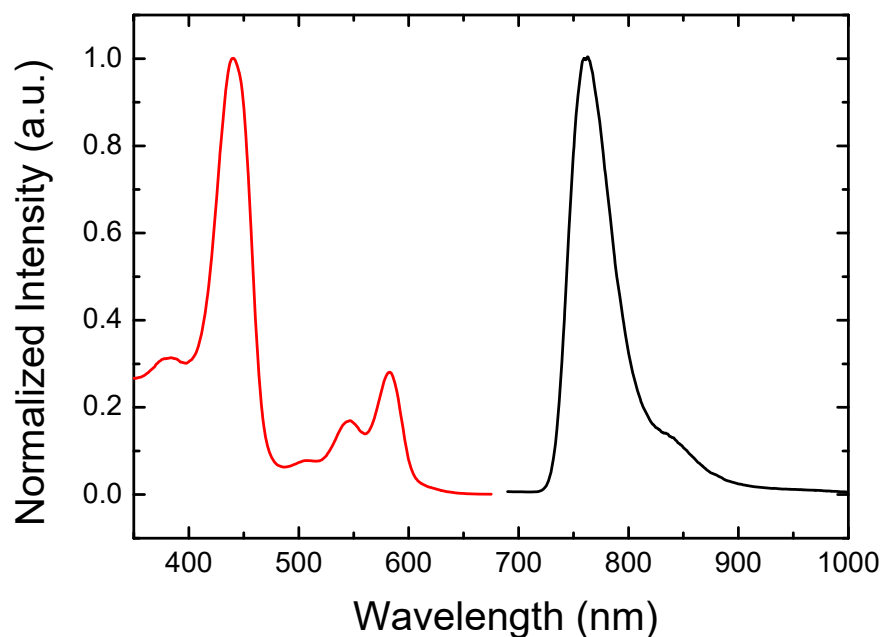


Figure S21. Excitation (red line, $\lambda_{em} = 765$ nm) and emission spectra (black line, $\lambda_{exc} = 440$ nm) of Re[TpOCH₃PC](NPh) in toluene:THF 4:6 v/v frozen glass at 77K.

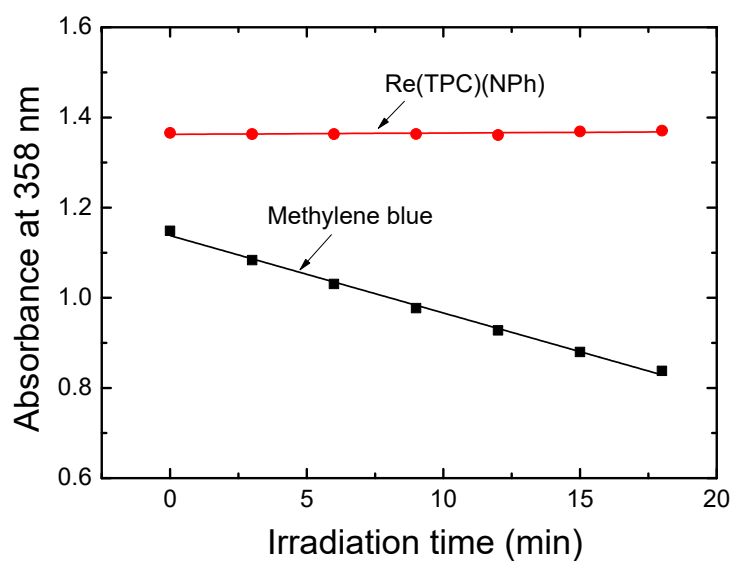


Figure S22. Investigation of singlet oxygen generation by Re(TPC)(NPh) in ethanol using 9,10-dimethylantracene as a singlet oxygen acceptor and methylene blue as a standard ($\Phi(^1O_2) = 0.48$). Excitation of both sensitizers is performed at 575 nm. No generation of 1O_2 by Re(TPC)(NPh) is visible.

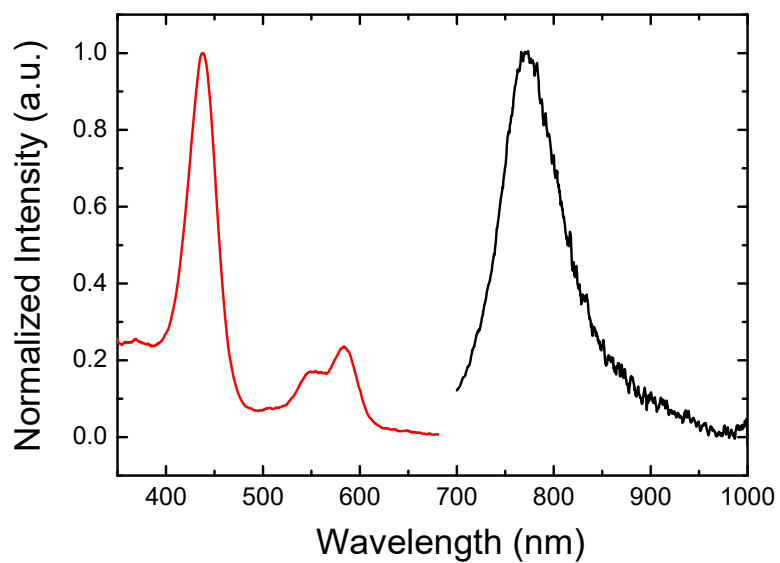


Figure S23. Excitation (red line, $\lambda_{em} = 775$ nm) and emission spectrum (black line, $\lambda_{exc} = 580$ nm) of Re(TPC)(NPh) in polystyrene (anoxic conditions, room temperature).