

Supplementary Information

Regioselective Formylation of Rhenium-Oxo and Gold Corroles: Substituent Effects on Optical Spectra and Redox Potentials

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A. UV-vis spectra

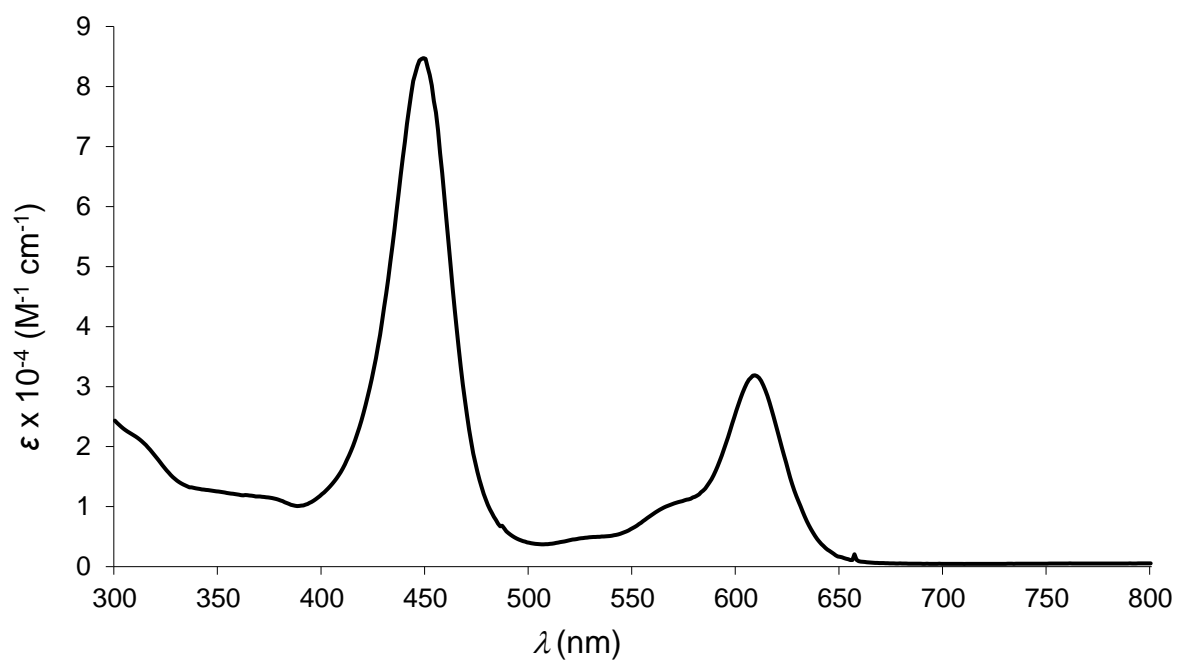


Figure S1. UV-vis spectrum of Re[TPC-3-CHO](O) in dichloromethane.

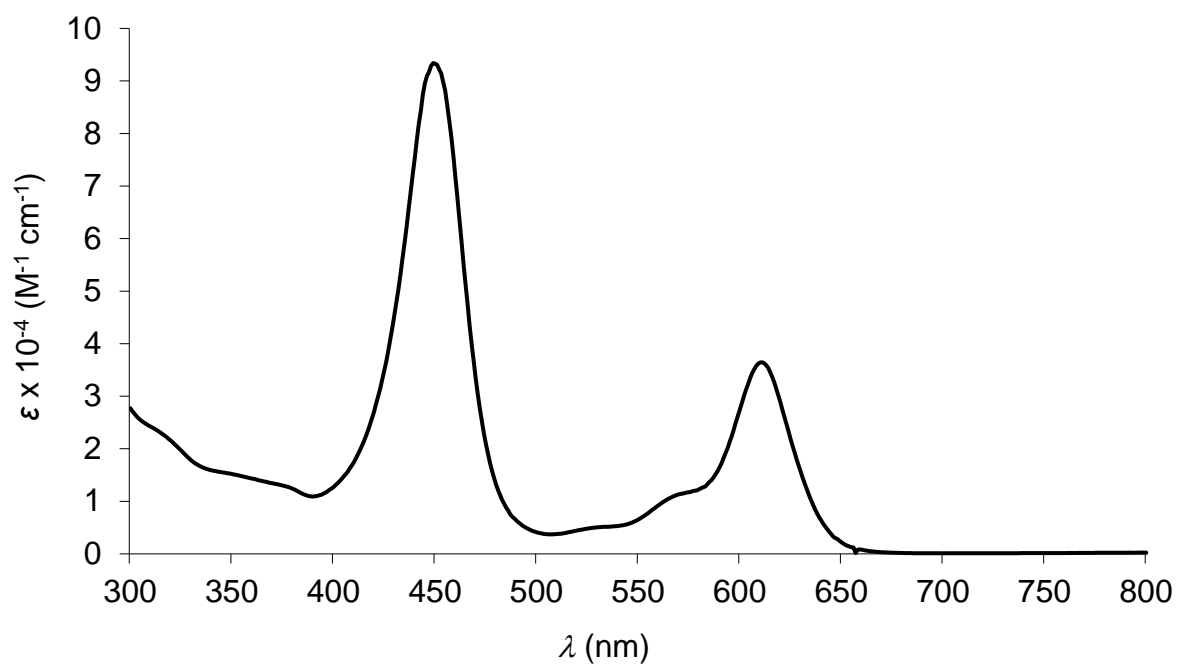


Figure S2. UV-vis spectrum of Re[TpCH₃PC-3-CHO](O) in dichloromethane.

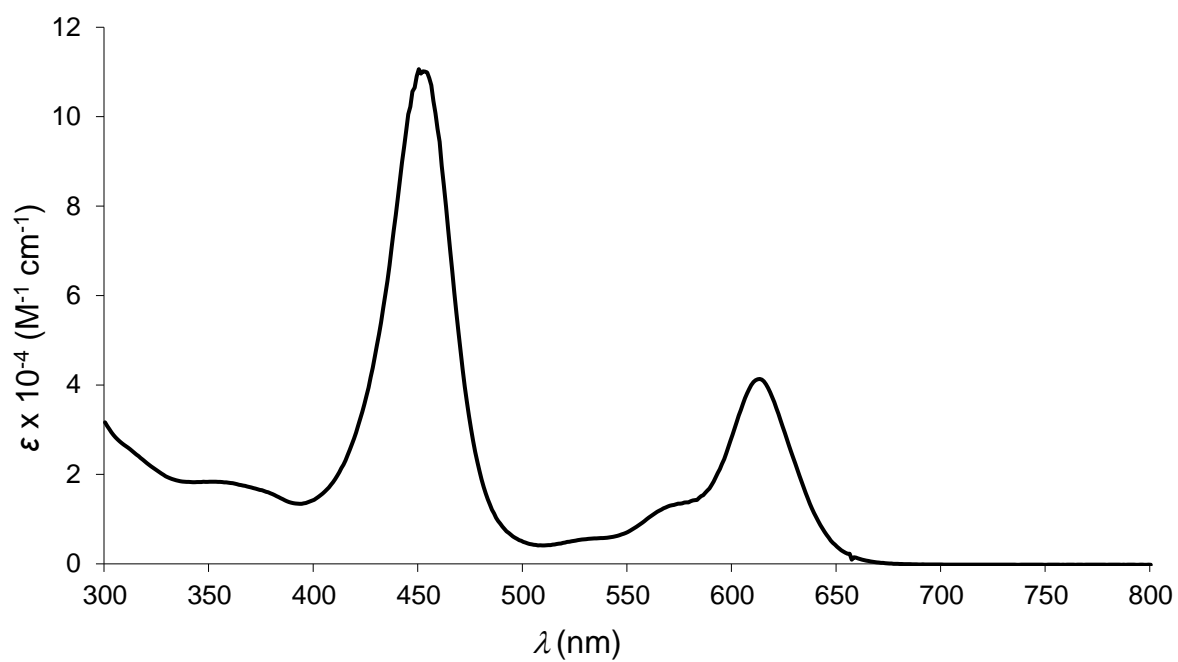


Figure S3. UV-vis spectrum of $\text{Re}[\text{TpOCH}_3\text{PC-3-CHO}](\text{O})$ in dichloromethane.

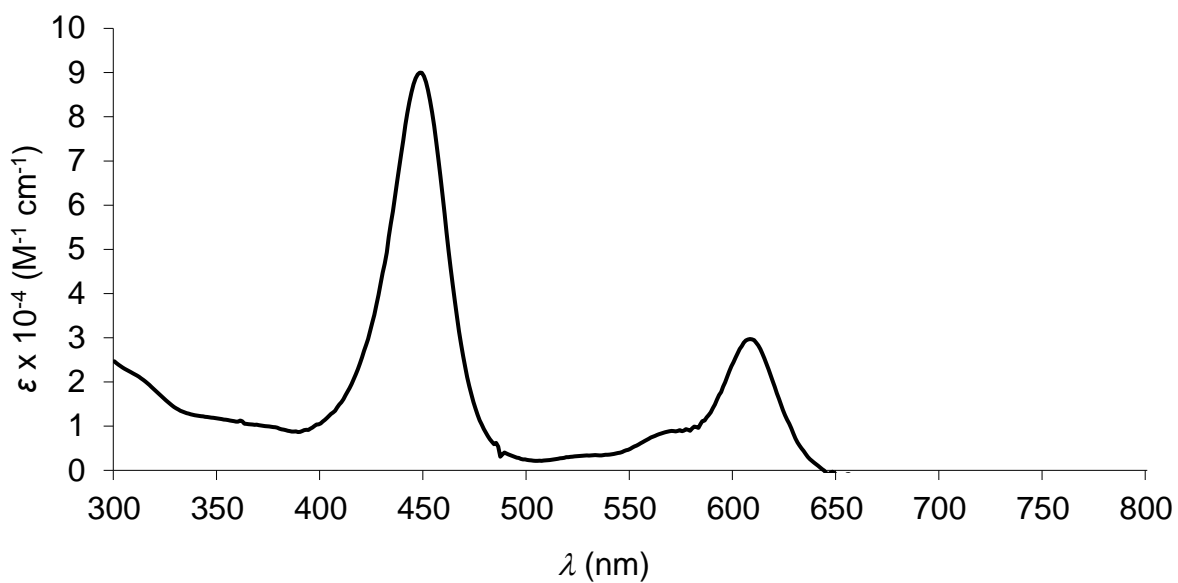


Figure S4. UV-vis spectrum of $\text{Re}[\text{TpFPC-3-CHO}](\text{O})$ in dichloromethane.

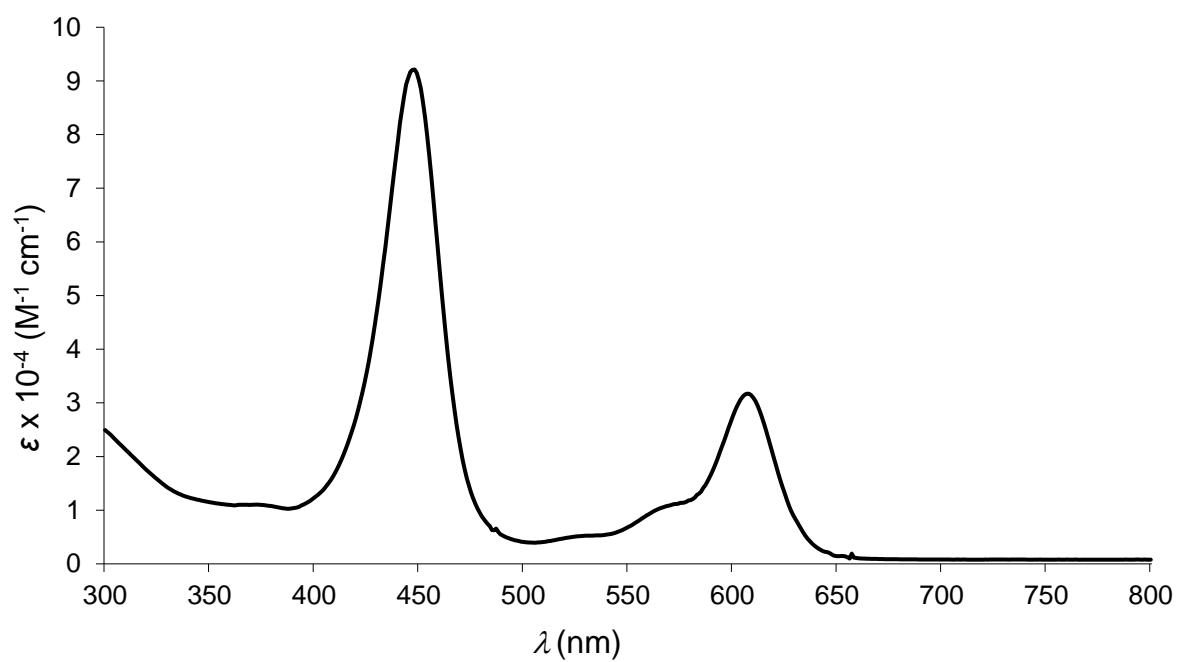


Figure S5. UV-vis spectrum of $\text{Re}[\text{TpCF}_3\text{PC-3-CHO}](\text{O})$ in dichloromethane.

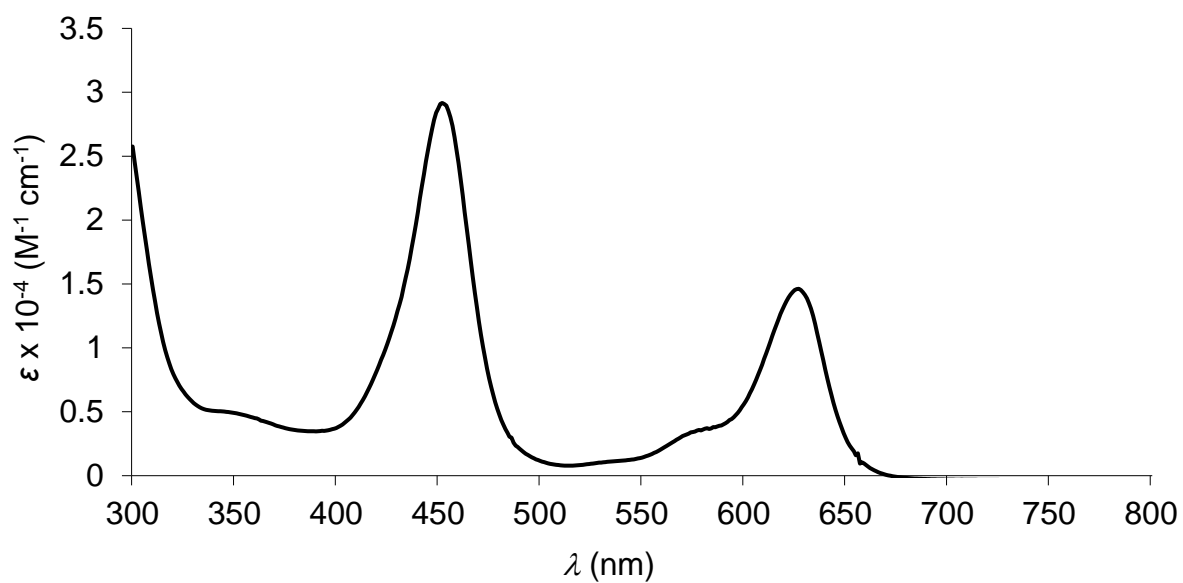


Figure S6. UV-vis spectrum of $\text{Re}[\text{TpFPC-3,17-(CHO)}_2](\text{O})$ in dichloromethane.

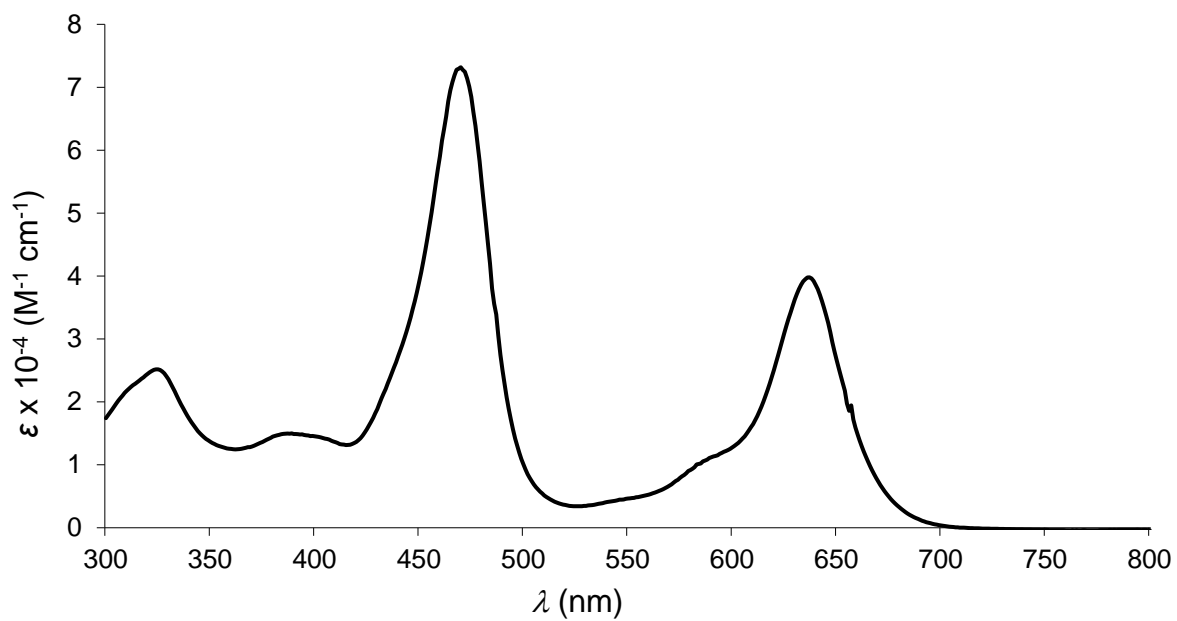


Figure S7. UV-vis spectrum of $\text{Re}[\text{TPC-3-CH}(\text{CN})\text{COOH}](\text{O})$ in dichloromethane.

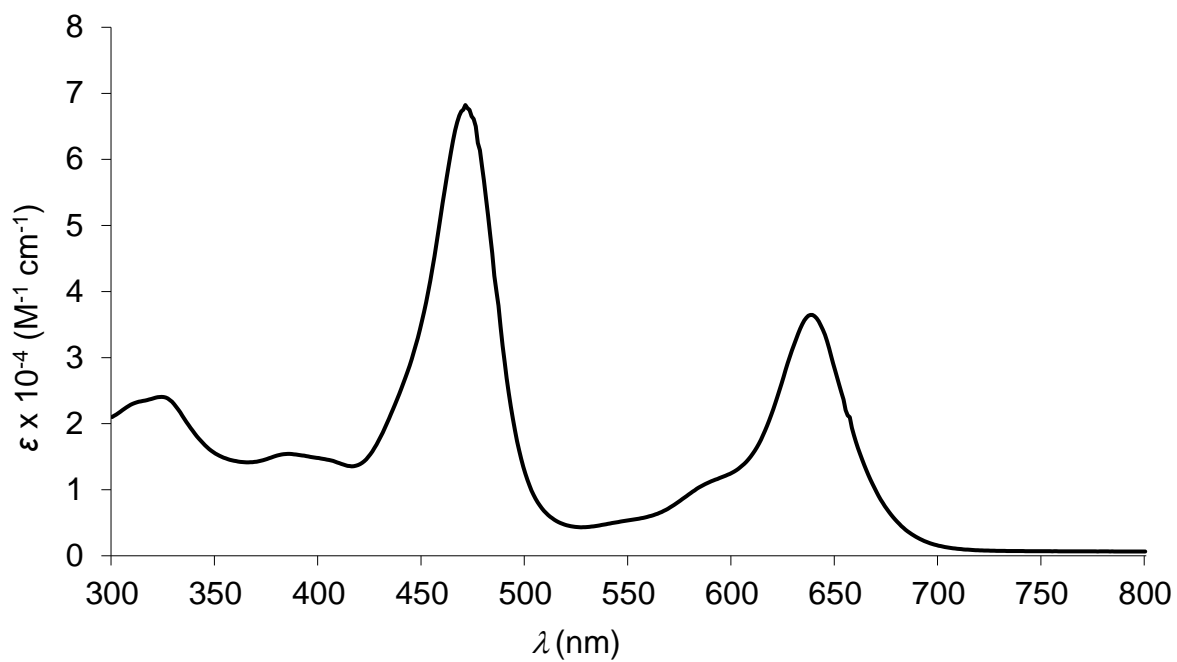


Figure S8. UV-vis spectrum of $\text{Re}[\text{TpCH}_3\text{PC-3-CH}(\text{CN})\text{COOH}](\text{O})$ in dichloromethane.

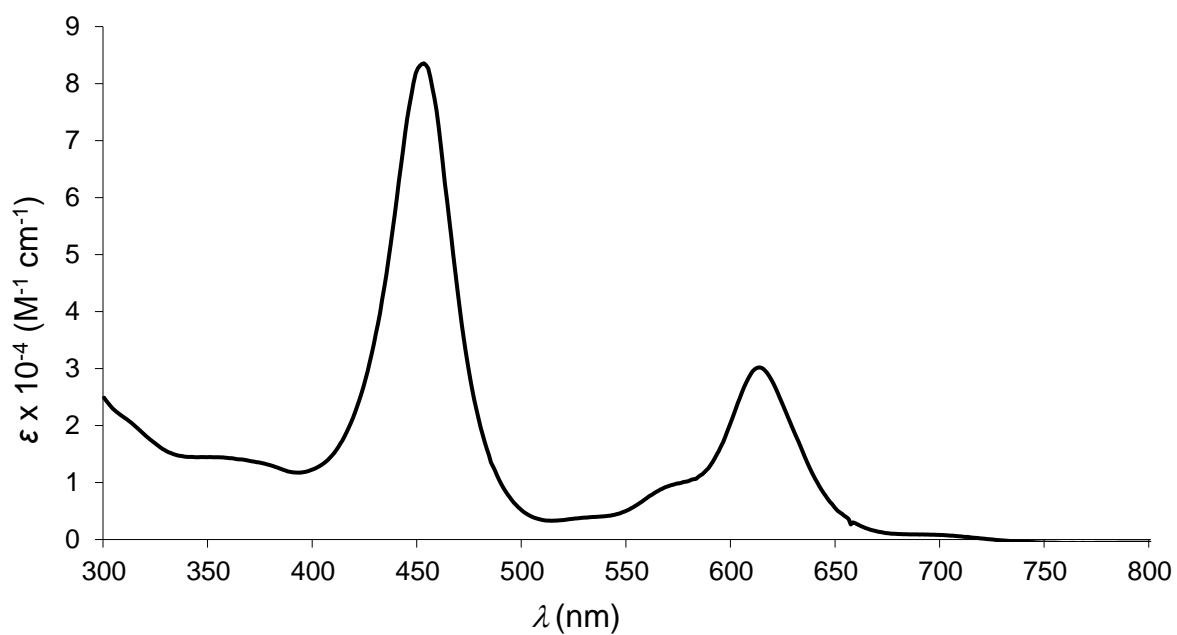


Figure S9. UV-vis spectrum of $\text{Re}[\text{TpOCH}_3\text{PC-3-CH}(\text{CN})\text{COOH}](\text{O})$ in dichloromethane.

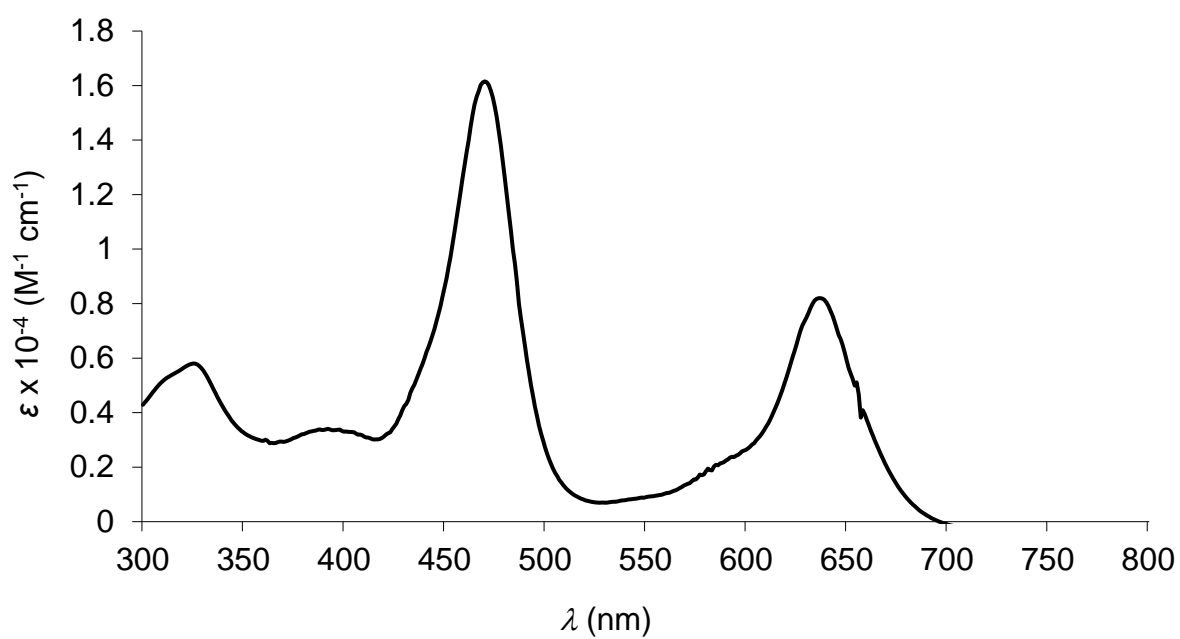


Figure S10. UV-vis spectrum of $\text{Re}[\text{TpFPC-3-CH}(\text{CN})\text{COOH}](\text{O})$ in dichloromethane.

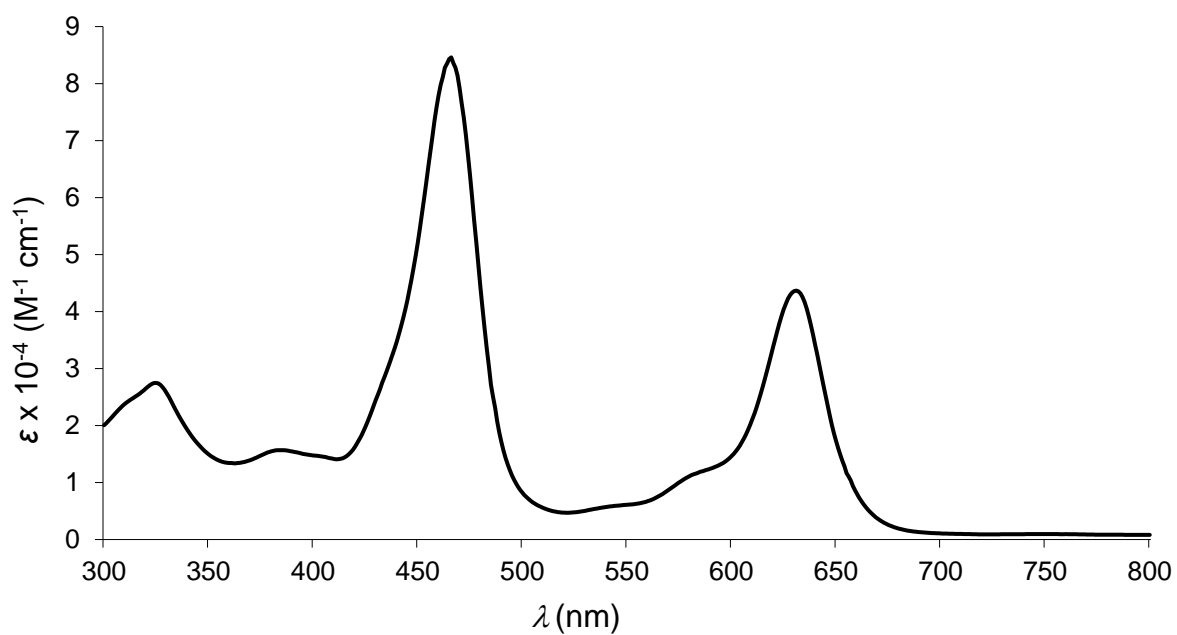


Figure S11. UV-vis spectrum of Re[TpCF₃PC-3-CH(CN)COOH](O) in dichloromethane.

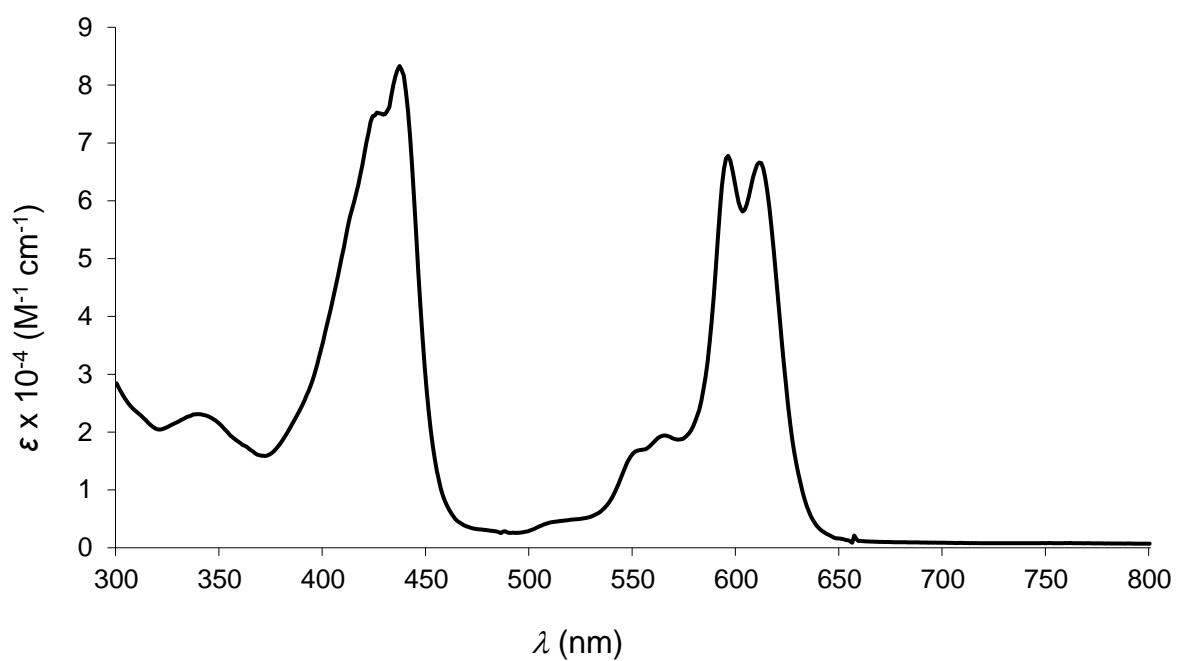


Figure S12. UV-vis spectrum of Au[TPC-3,17-(CHO)₂] in dichloromethane.

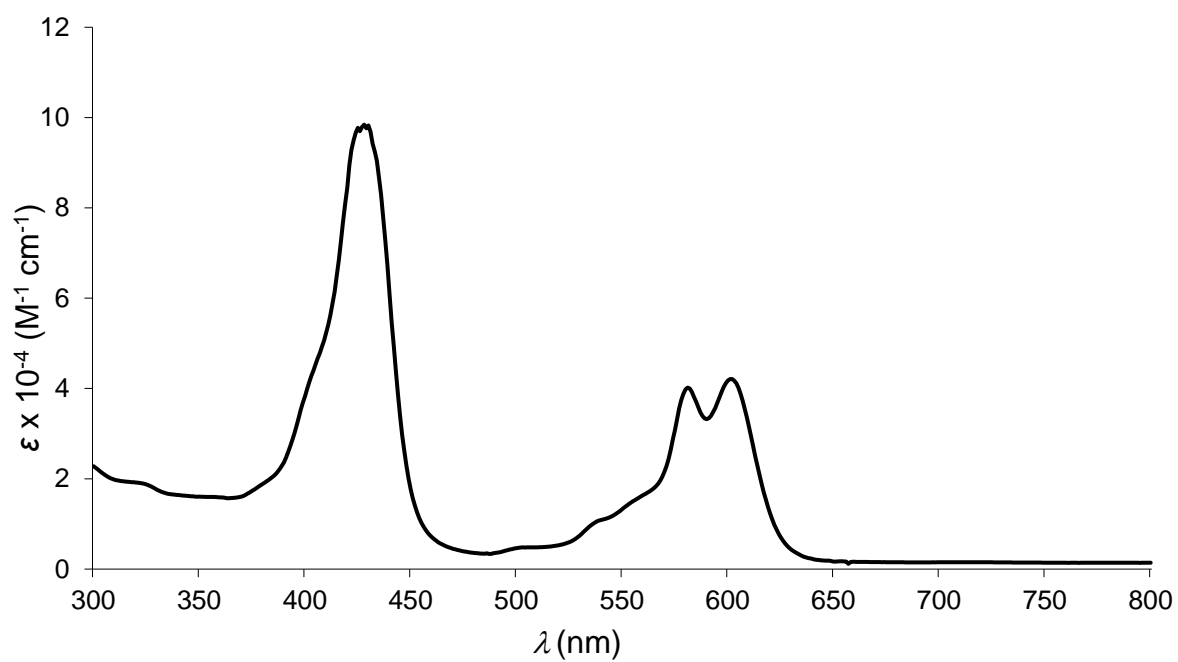


Figure S13. UV-vis spectrum of Au[TpCH₃PC-3-CHO] in dichloromethane.

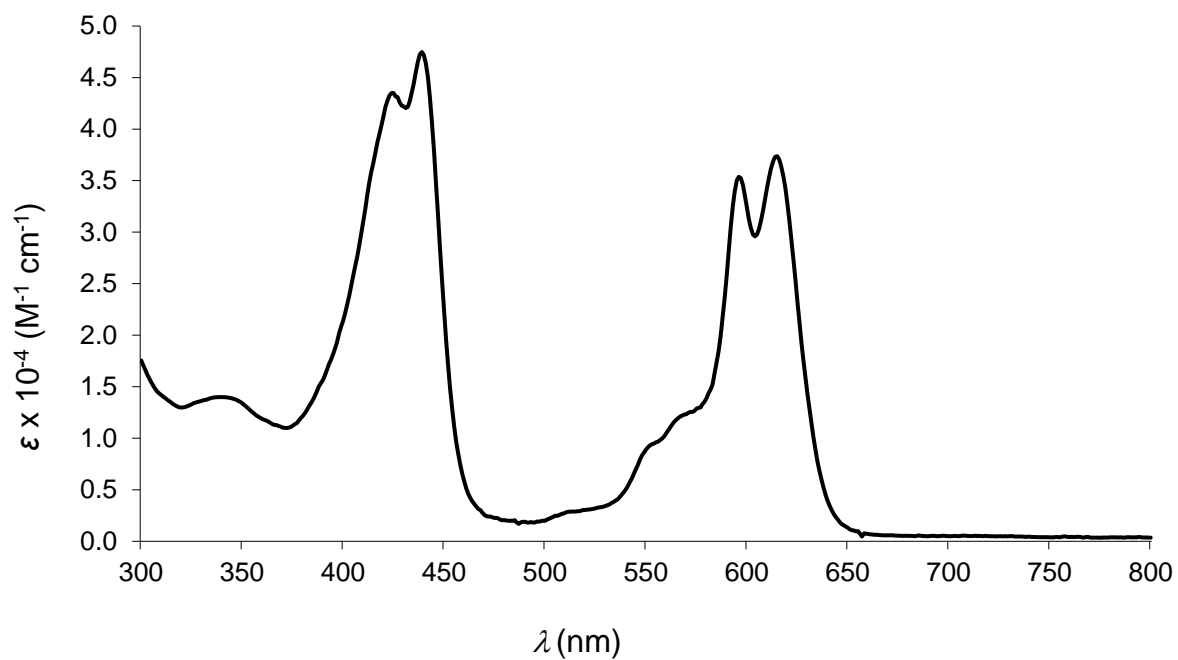


Figure S14. UV-vis spectrum of Au[TpCH₃PC-3,17-(CHO)₂] in dichloromethane.

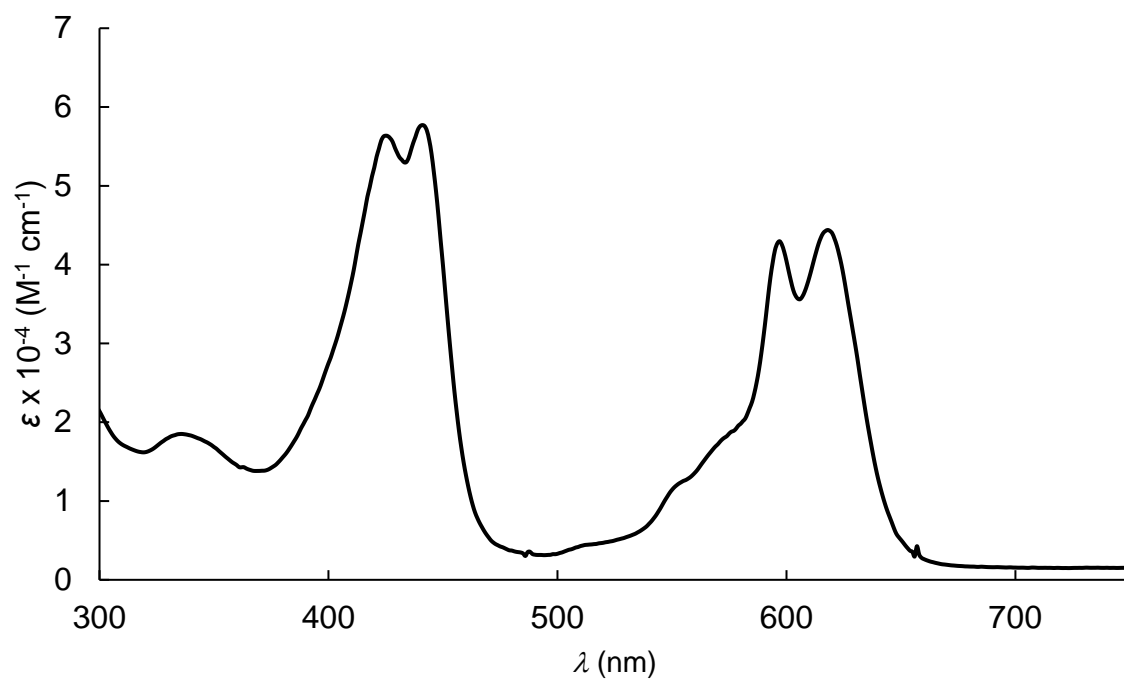


Figure S15. UV-vis spectrum of Au[TpOCH₃PC-3,17-(CHO)₂] in dichloromethane.

B. HRMS-ESI mass spectra

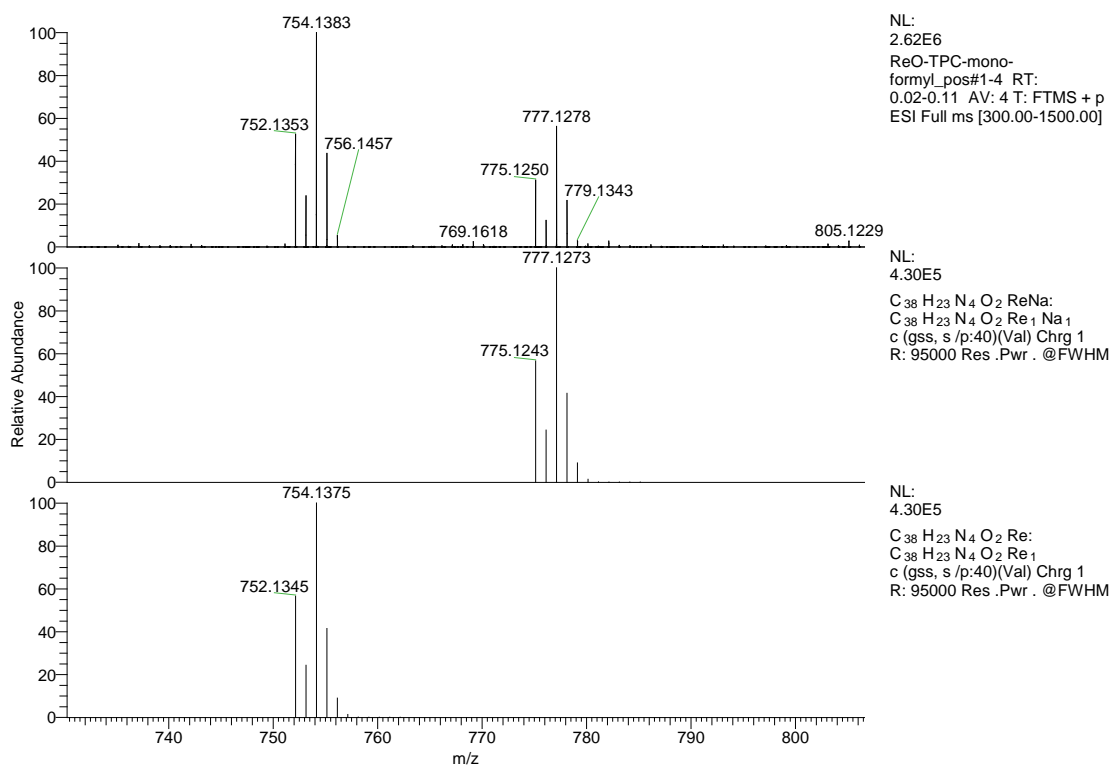


Figure S16. HRMS-ESI mass spectrum of $\text{Re}[\text{TPC-3-CHO}](\text{O})$.

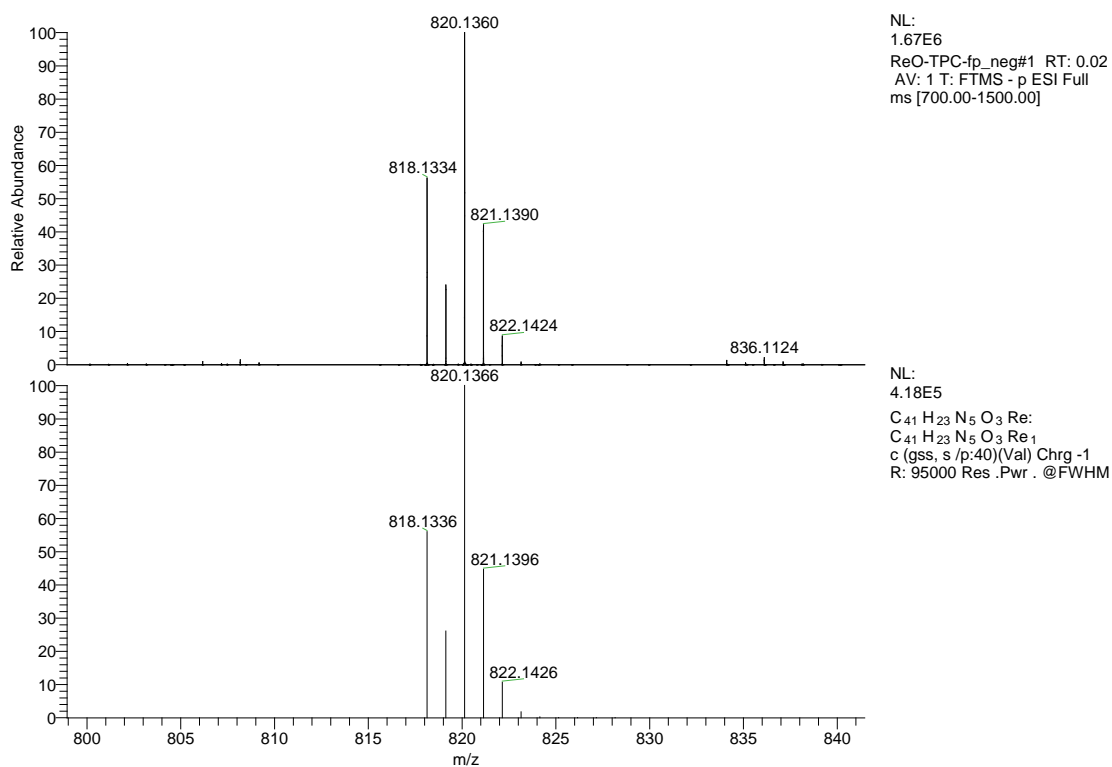
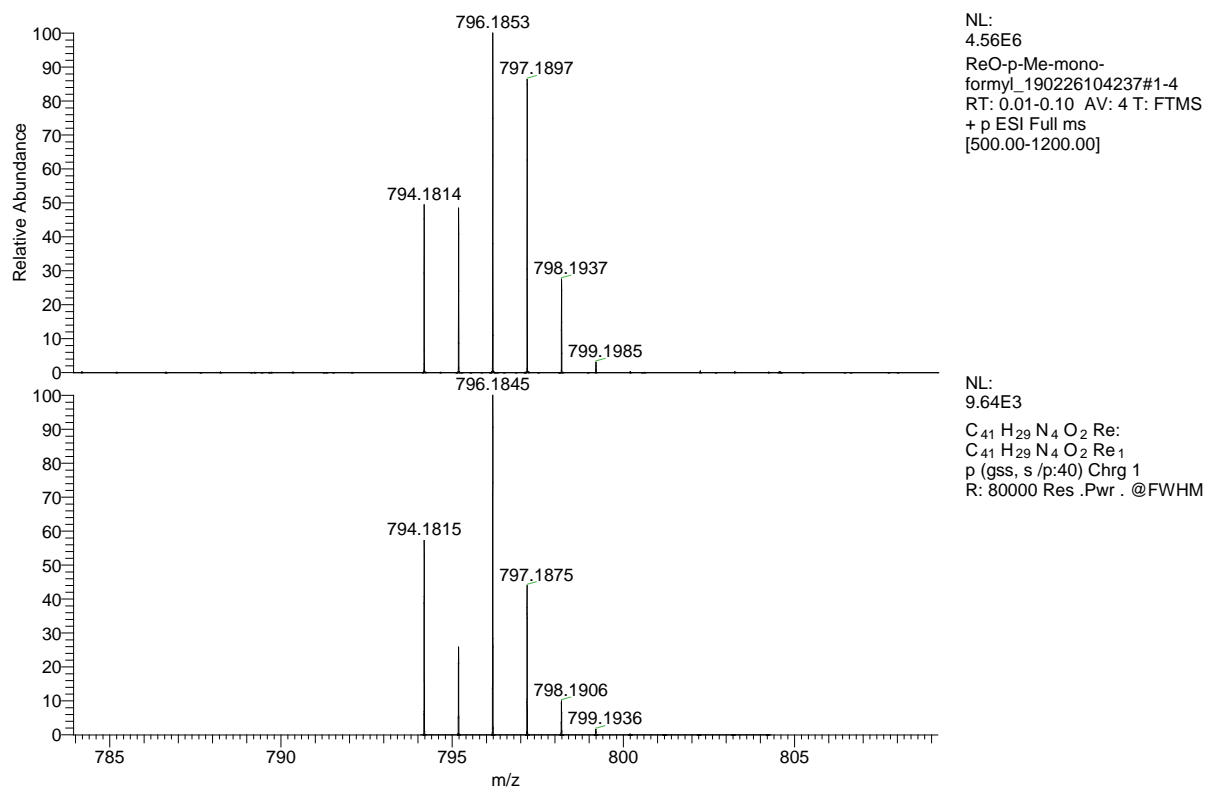


Figure S17. HRMS-ESI mass spectrum of $\text{Re}[\text{TPC-3-CH}(\text{CN})\text{COOH}](\text{O})$.



ReO-p-Me-mono-formyl_190226104237 #1-4 RT: 0.01-0.10 AV: 4 NL: 4.56E6
T: FTMS + p ESI Full ms [500.00-1200.00]

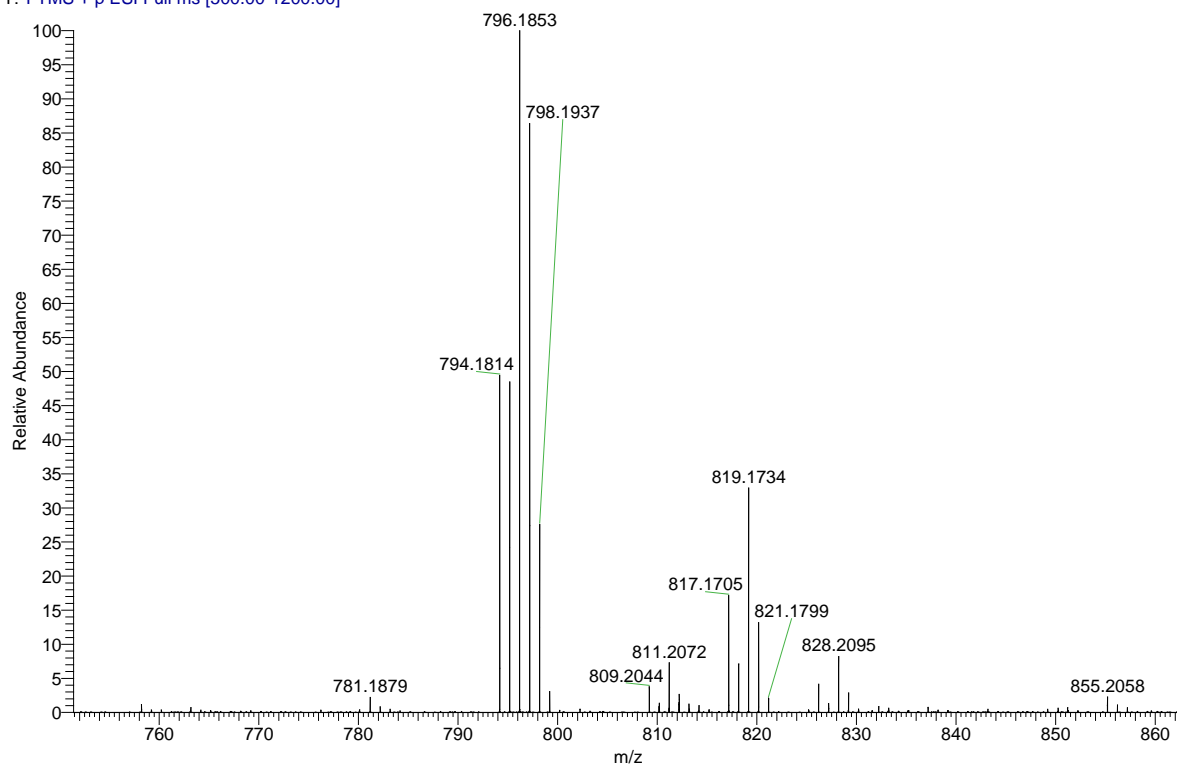


Figure S18. HRMS-ESI mass spectra of Re[*Tp*CH₃PC-3-CHO](O).

ReOTpMePC(CHO)₂_pos #1-5 | RT: 0.01-0.12 | AV: 5 | NL: 3.06E6
T: FTMS + p ESI Full ms [100.00-2000.00]

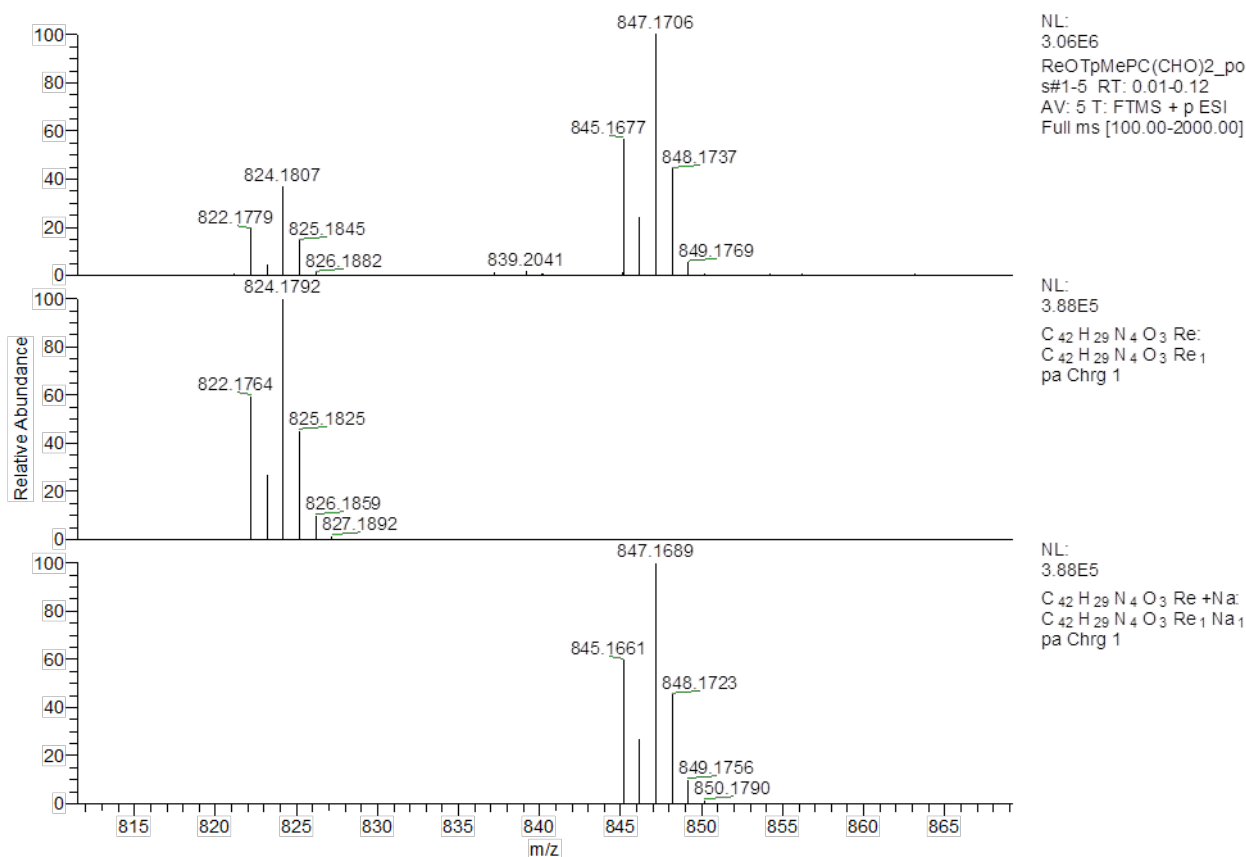
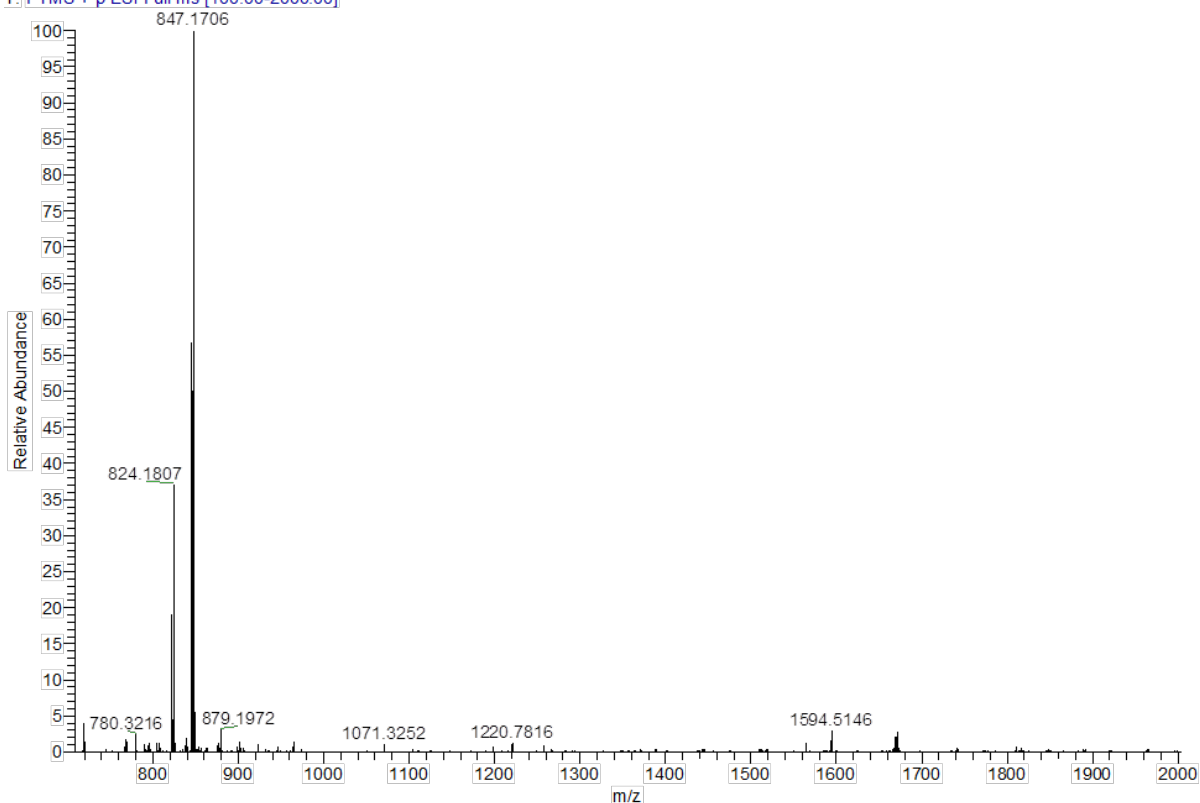
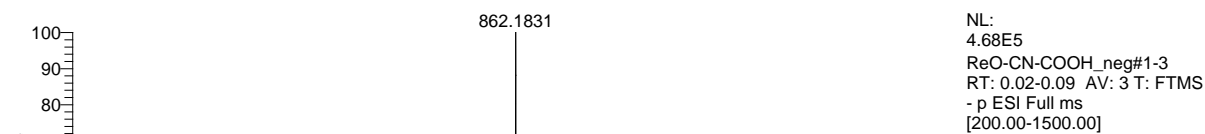
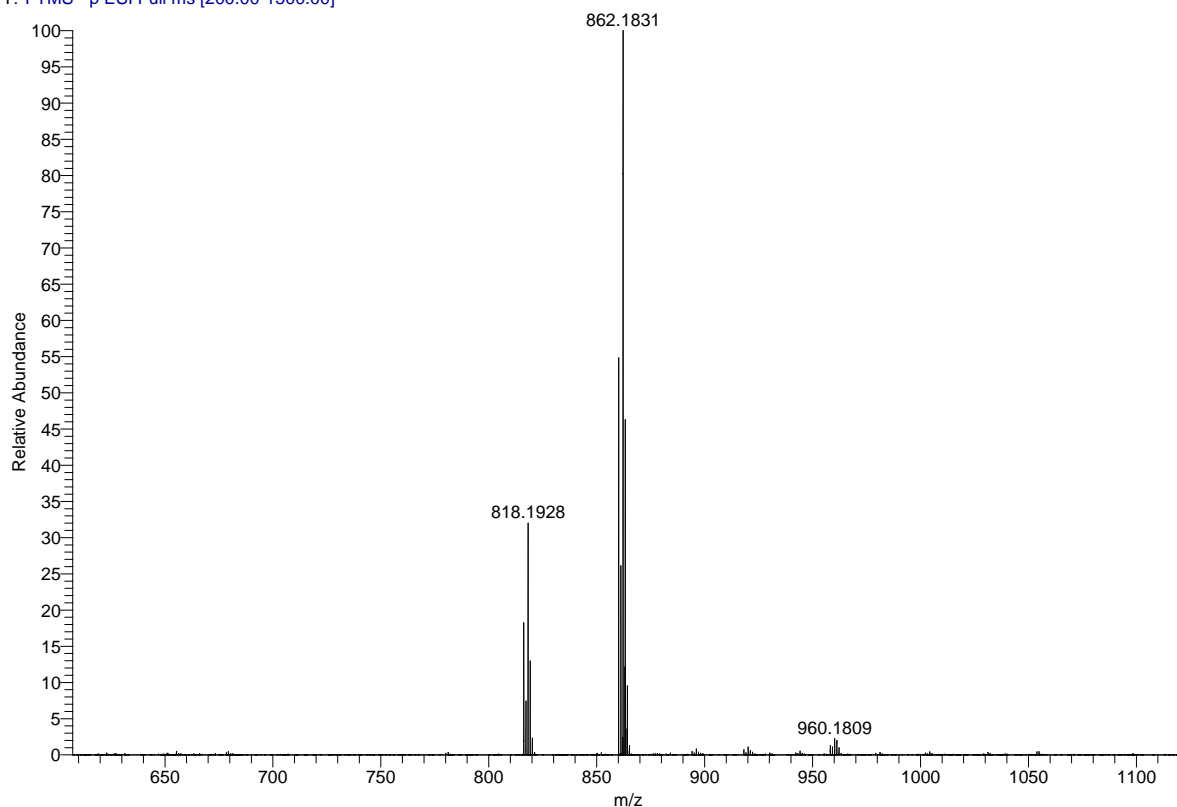
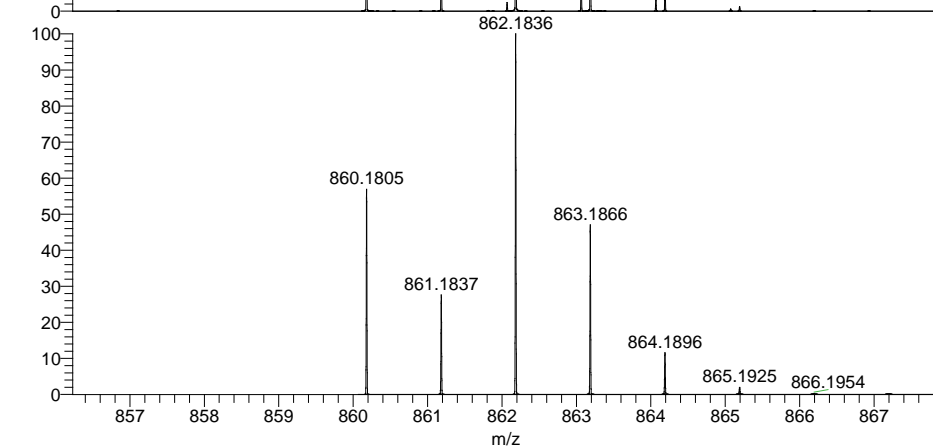


Figure S19. HRMS-ESI mass spectra of Re[*Tp*CH₃PC-3,17-(CHO)₂](O).

ReO-CN-COOH_neg #1-3 RT: 0.02-0.09 AV: 3 NL: 4.68E5
T: FTMS - p ESI Full ms [200.00-1500.00]



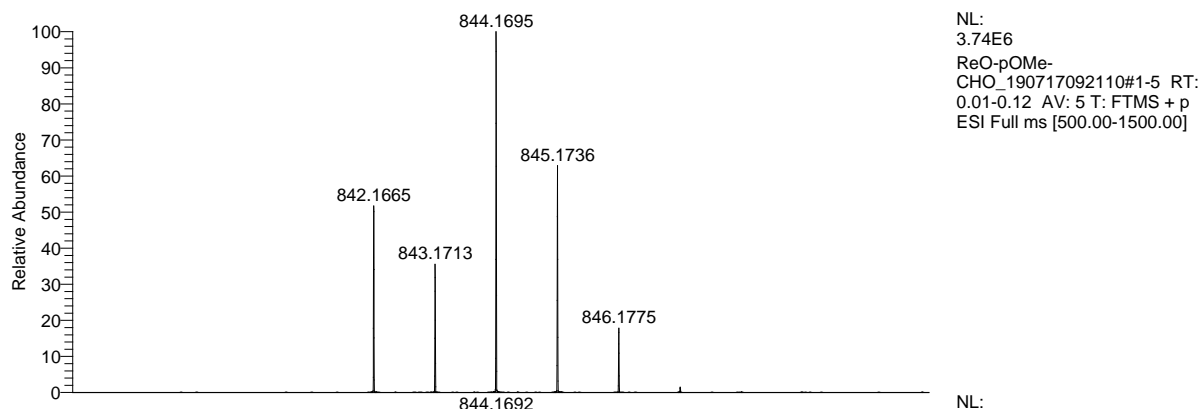
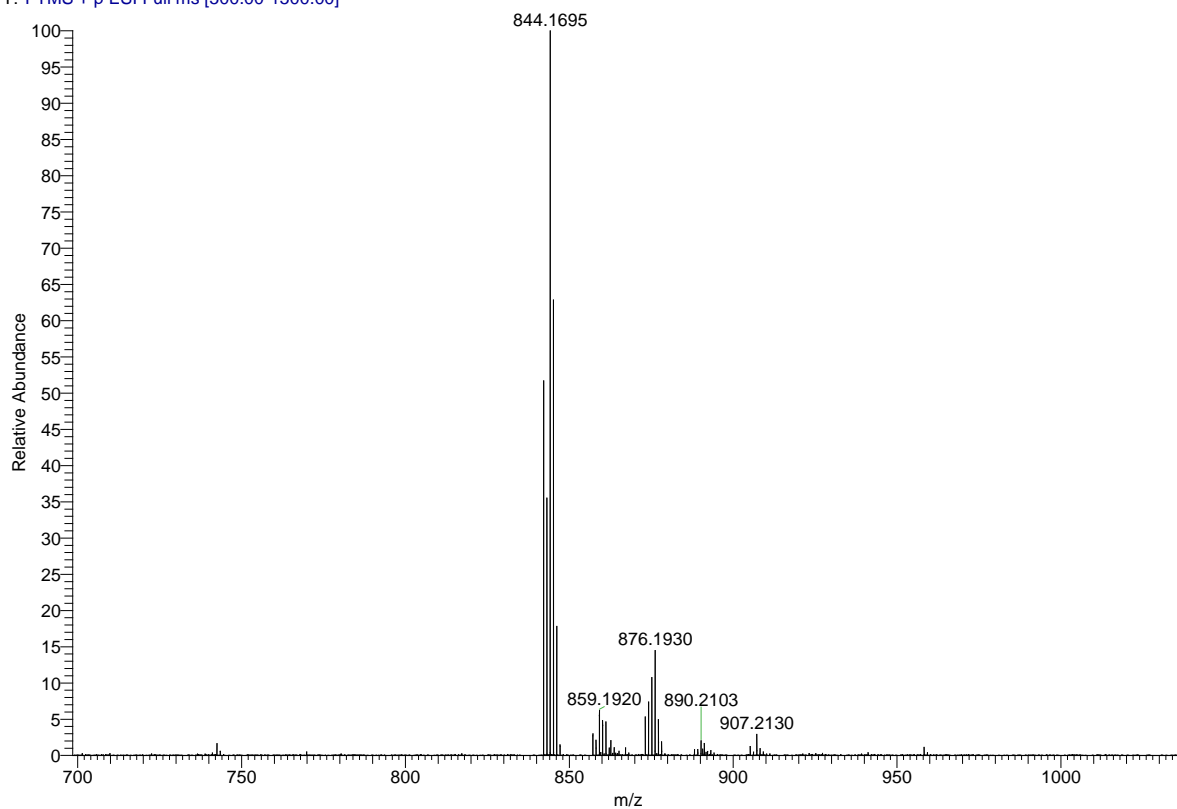
NL:
4.68E5
ReO-CN-COOH_neg#1-3
RT: 0.02-0.09 AV: 3 T: FTMS
- p ESI Full ms
[200.00-1500.00]



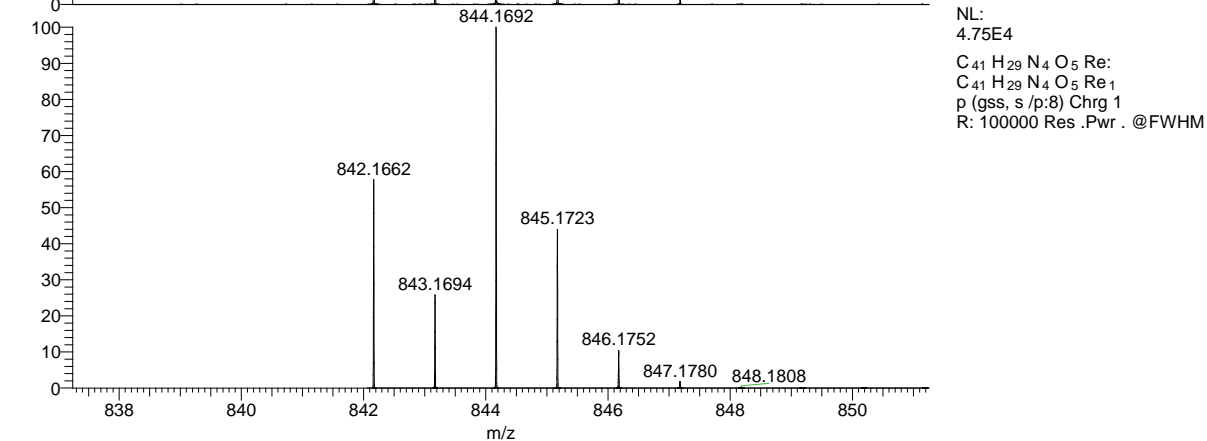
NL:
9.33E3
C₄₄ H₂₉ N₅ O₃ Re:
C₄₄ H₂₉ N₅ O₃ Re₁
p (gss, s /p:40) Chrg -1
R: 91000 Res .Pwr . @FWHM

Figure S20. HRMS-ESI mass spectra of Re[*Tp*CH₃PC-3-CH(CN)COOH](O).

ReO-pOMe-CHO_190717092110 #1-5 RT: 0.01-0.12 AV: 5 NL: 3.74E6
T: FTMS + p ESI Full ms [500.00-1500.00]



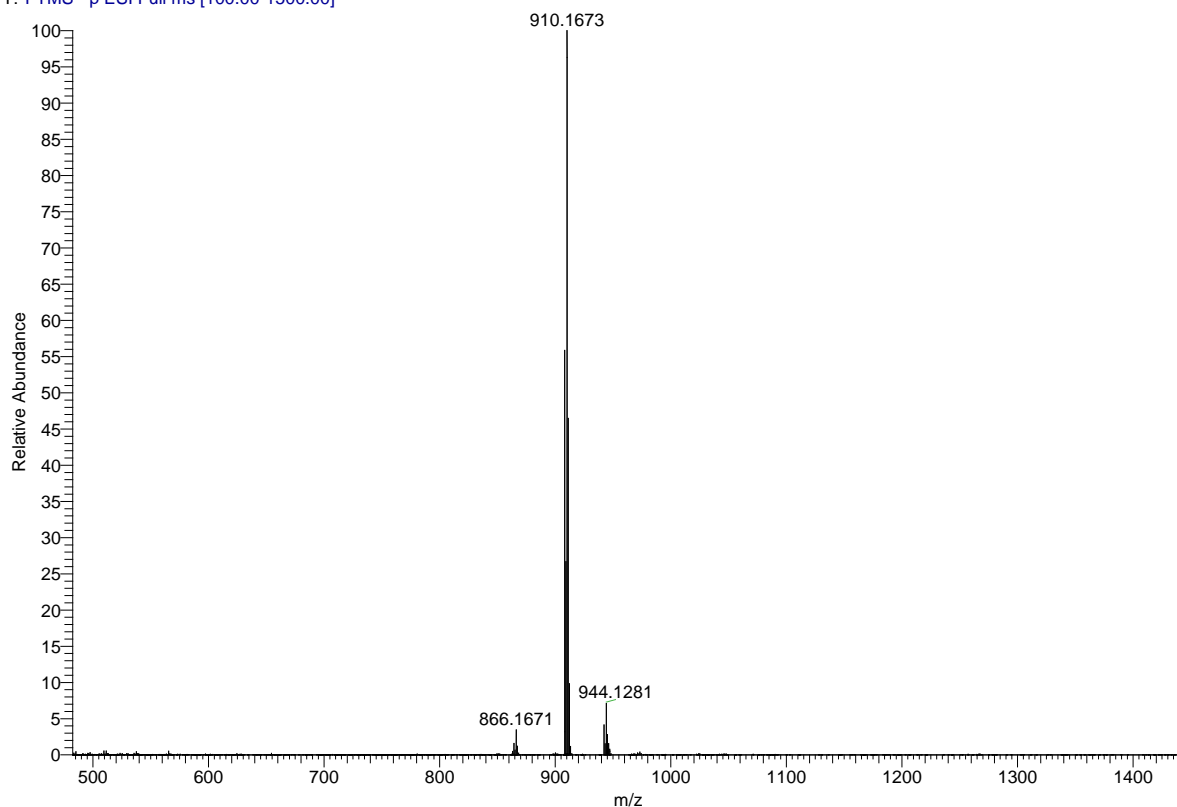
NL:
3.74E6
ReO-pOMe-
CHO_190717092110#1-5 RT:
0.01-0.12 AV: 5 T: FTMS + p
ESI Full ms [500.00-1500.00]



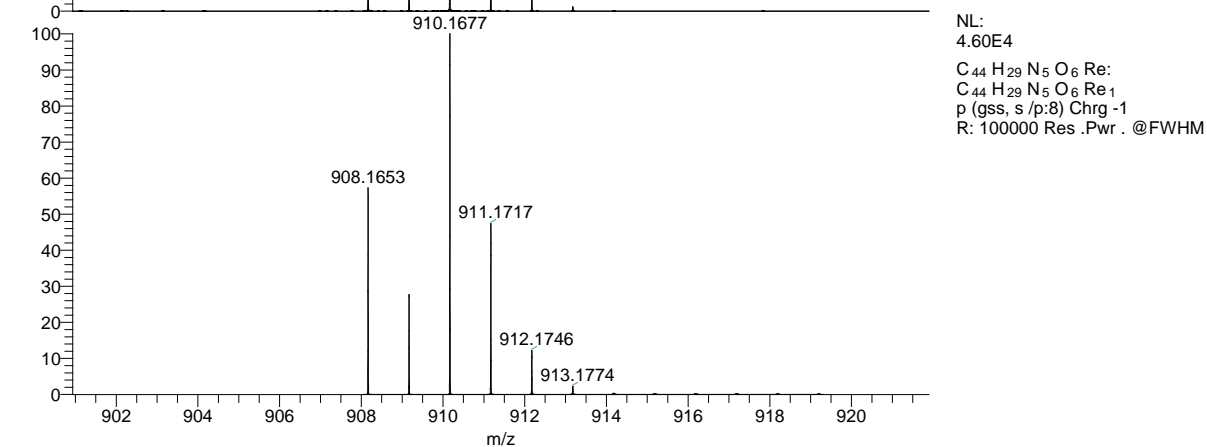
NL:
4.75E4
C₄₁ H₂₉ N₄ O₅ Re:
C₄₁ H₂₉ N₄ O₅ Re₁
p (gss, s /p:8) Chrg 1
R: 100000 Res .Pwr . @FWHM

Figure S21. HRMS-ESI mass spectra of Re[*Tp*OCH₃PC-3-CHO](O).

ReOpOMeCNCOOH_neg #1-3 RT: 0.01-0.07 AV: 3 NL: 1.07E6
T: FTMS - p ESI Full ms [100.00-1500.00]



NL:
1.07E6
ReOpOMeCNCOOH_neg#1-3
RT: 0.01-0.07 AV: 3 T: FTMS -
p ESI Full ms [100.00-1500.00]



NL:
4.60E4
C₄₄ H₂₉ N₅ O₆ Re:
C₄₄ H₂₉ N₅ O₆ Re₁
p (gss, s /p:8) Chrg -1
R: 100000 Res .Pwr . @FWHM

Figure S22. HRMS-ESI mass spectra of Re[*Tp*OCH₃PC-3-CH(CN)COOH](O).

ReO-pCF₃-CHO #1-10 RT: 0.01-0.16 AV: 10 NL: 1.85E6
T: FTMS - p ESI Full ms [300.00-1500.00]

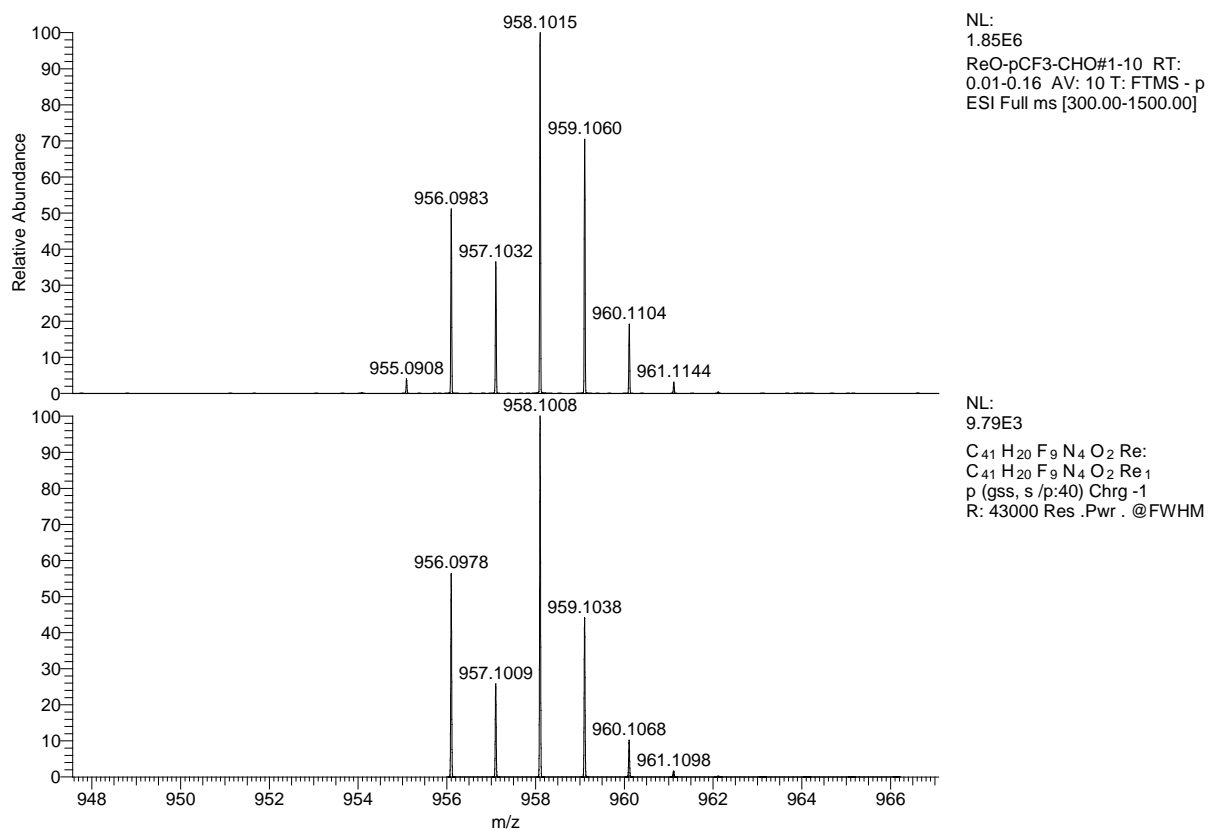
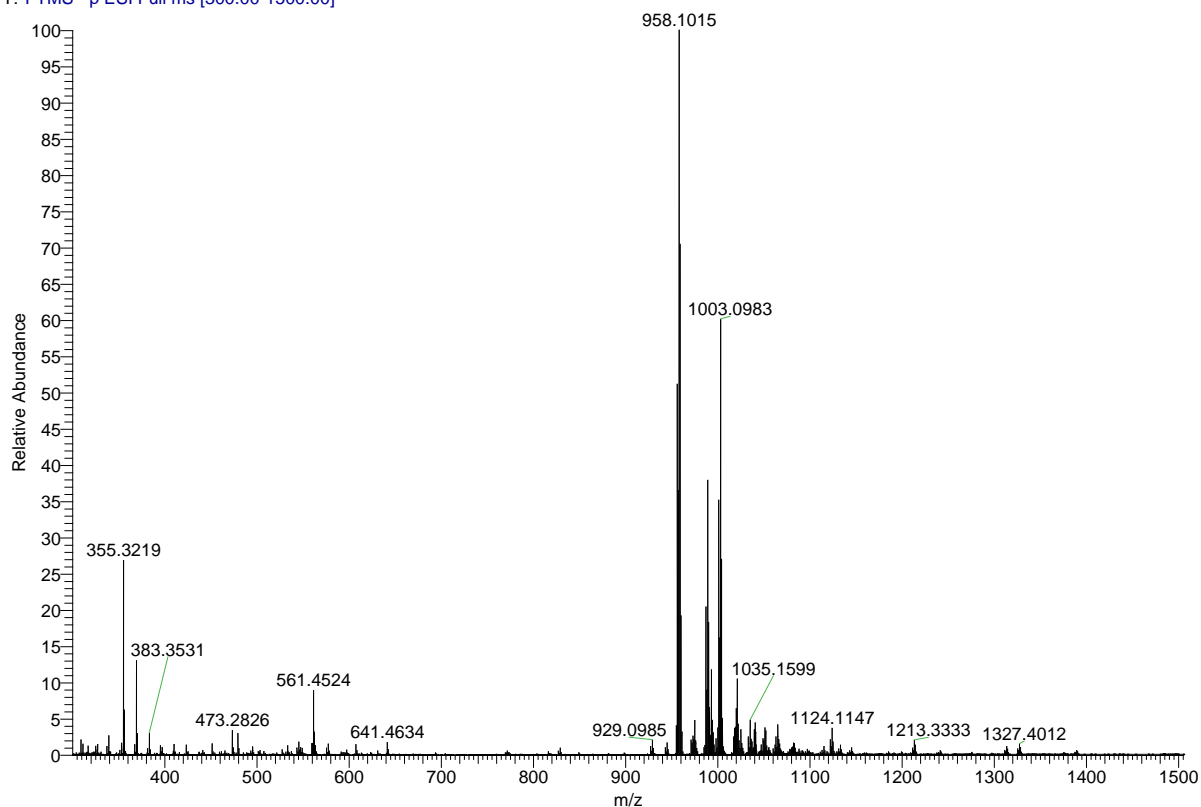


Figure S23. HRMS-ESI mass spectra of Re[*Tp*CF₃PC-3-CHO](O).

Au-TPC-mono-formyl_190409110618 #1-4 RT: 0.02-0.12 AV: 4 NL: 3.54E5
T: FTMS + p ESI Full ms [300.00-1500.00]

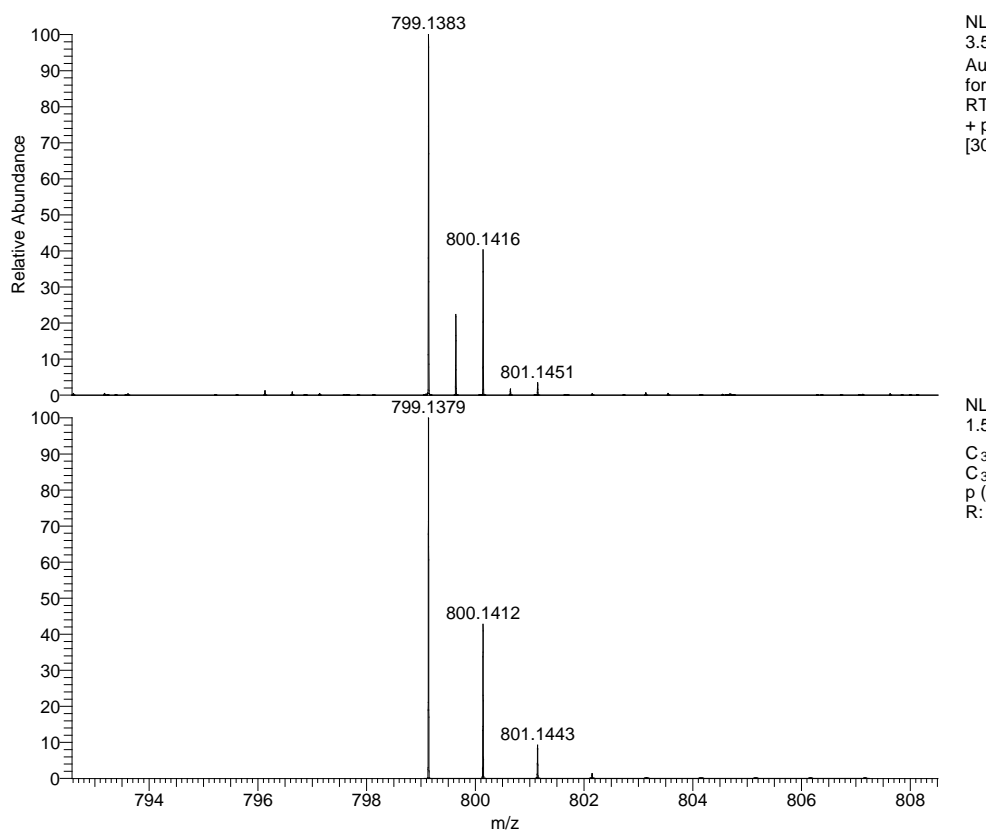
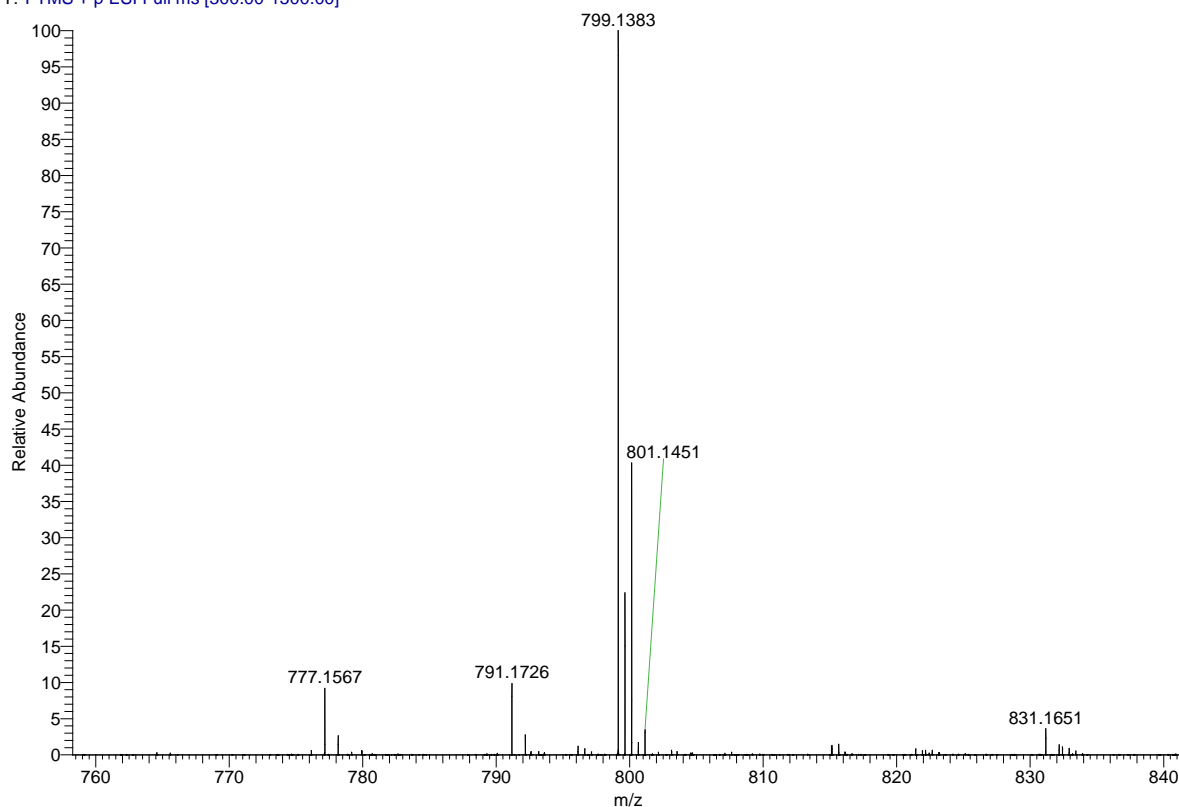


Figure S24. HRMS-ESI mass spectrum of Au[TPC-3,17-(CHO)₂].

Au-p-Me-monoformyl #1-4 RT: 0.02-0.10 AV: 4 NL: 2.58E6
T: FTMS + p ESI Full ms [200.00-1500.00]

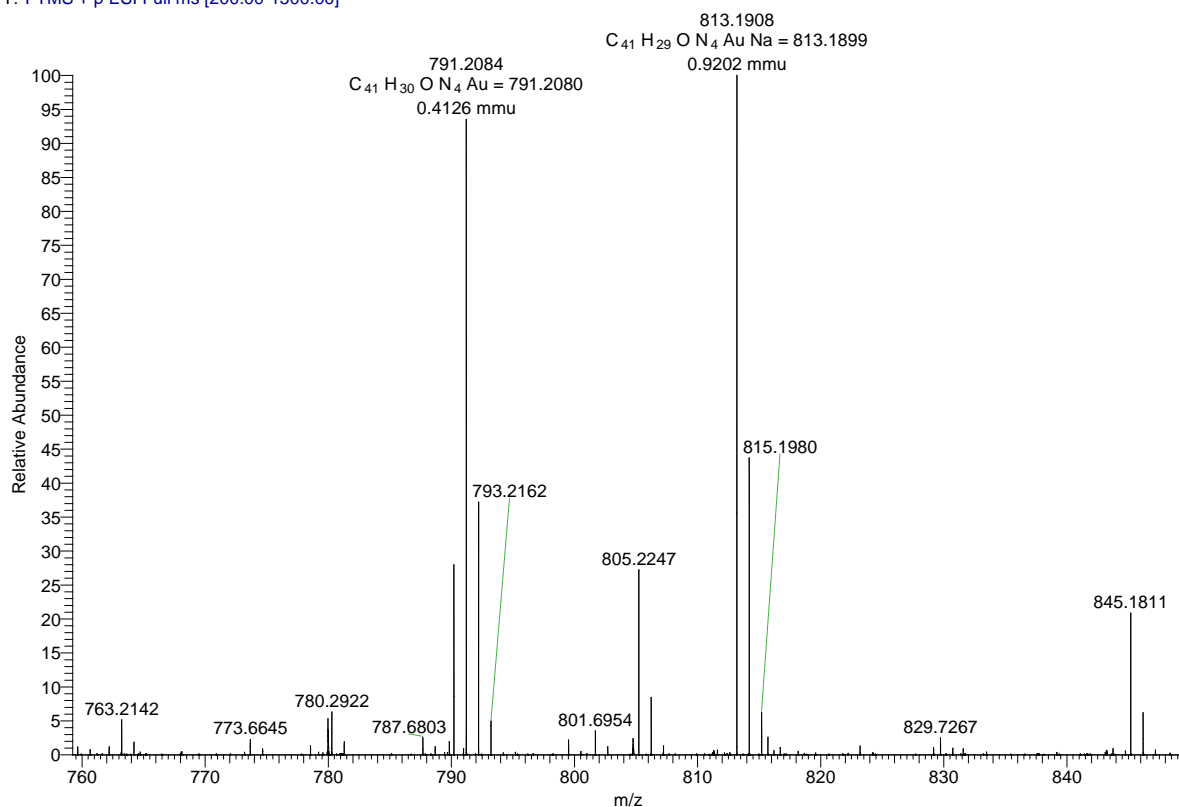


Figure S25. HRMS-ESI mass spectrum of Au[*Tp* CH₃PC-3-CHO].

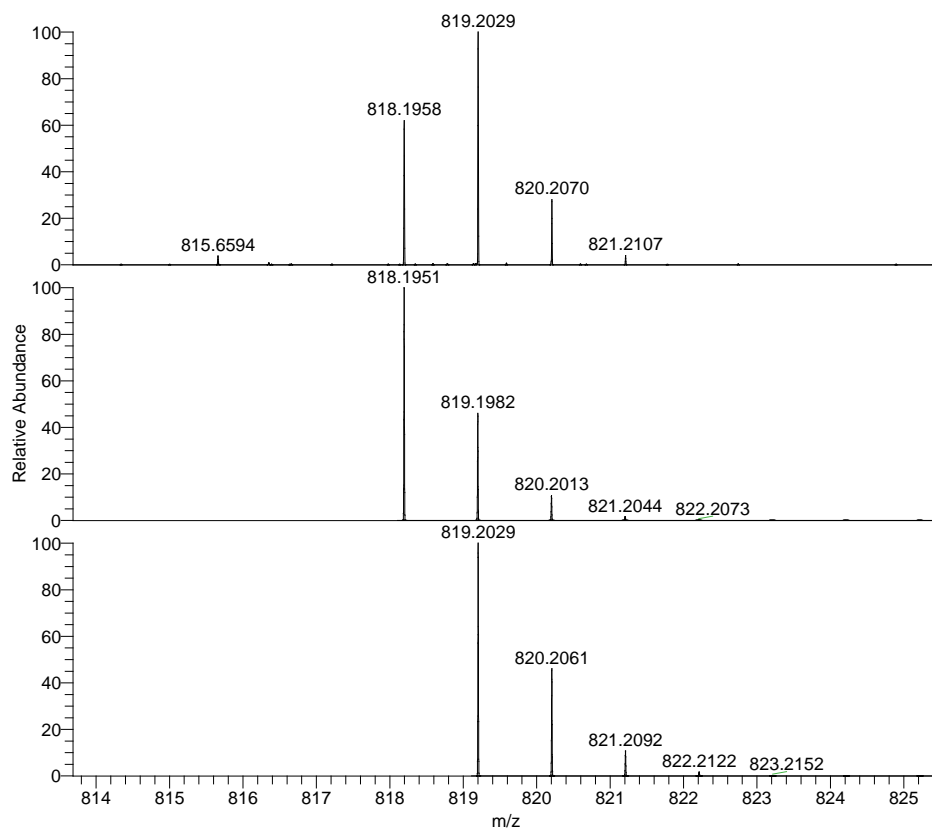


Figure S26. HRMS-ESI mass spectrum of Au[*Tp* CH₃PC-3,17-(CHO)₂].

AupOMeCHO2_Na-b #2 RT: 0.03 AV: 1 NL: 5.21E6
T: FTMS + p ESI Full ms [100.00-1500.00]

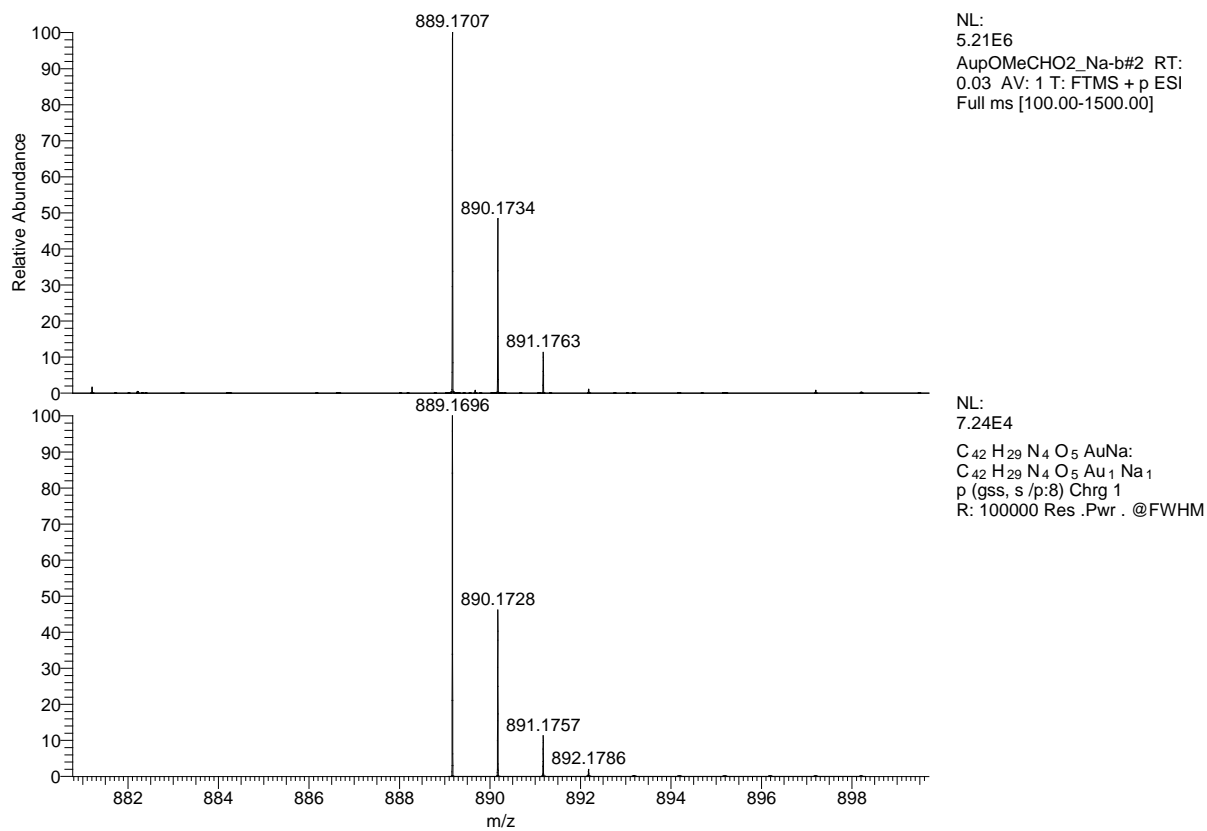
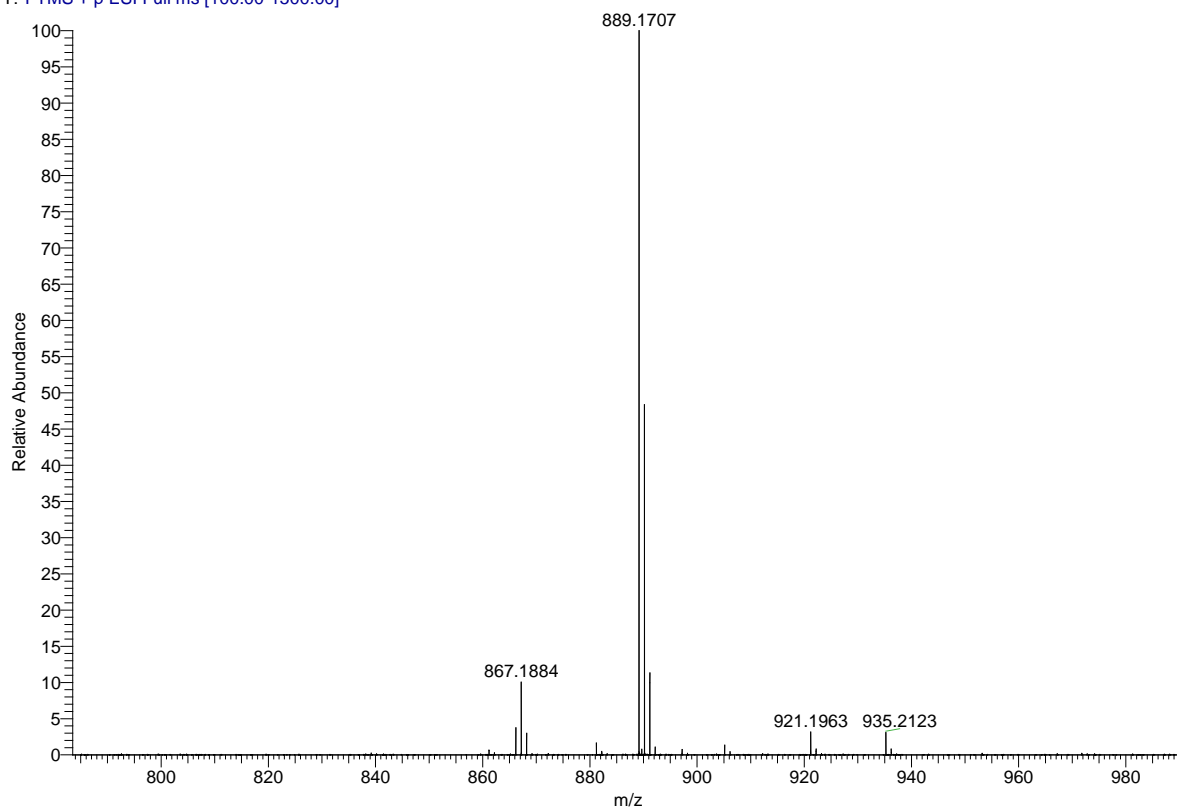


Figure S27. HRMS-ESI mass spectrum of Au[TpOCH₃PC-3,17-(CHO)₂].

C. ^1H NMR spectra

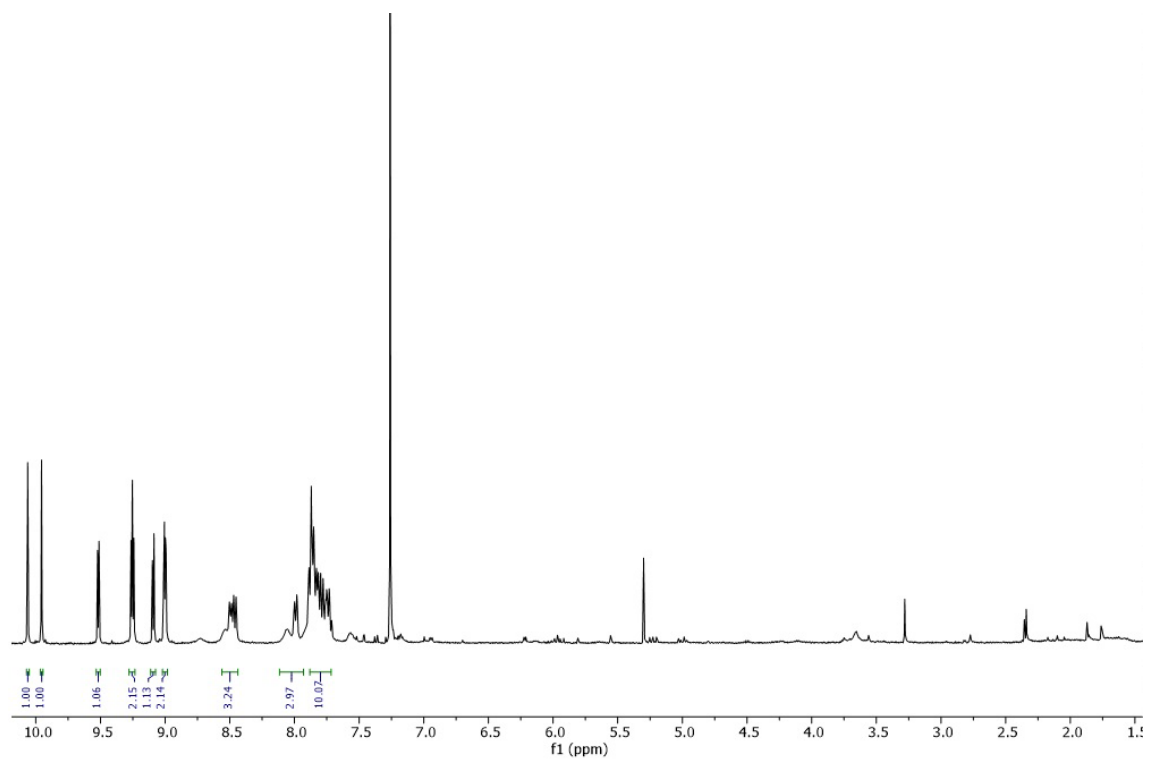
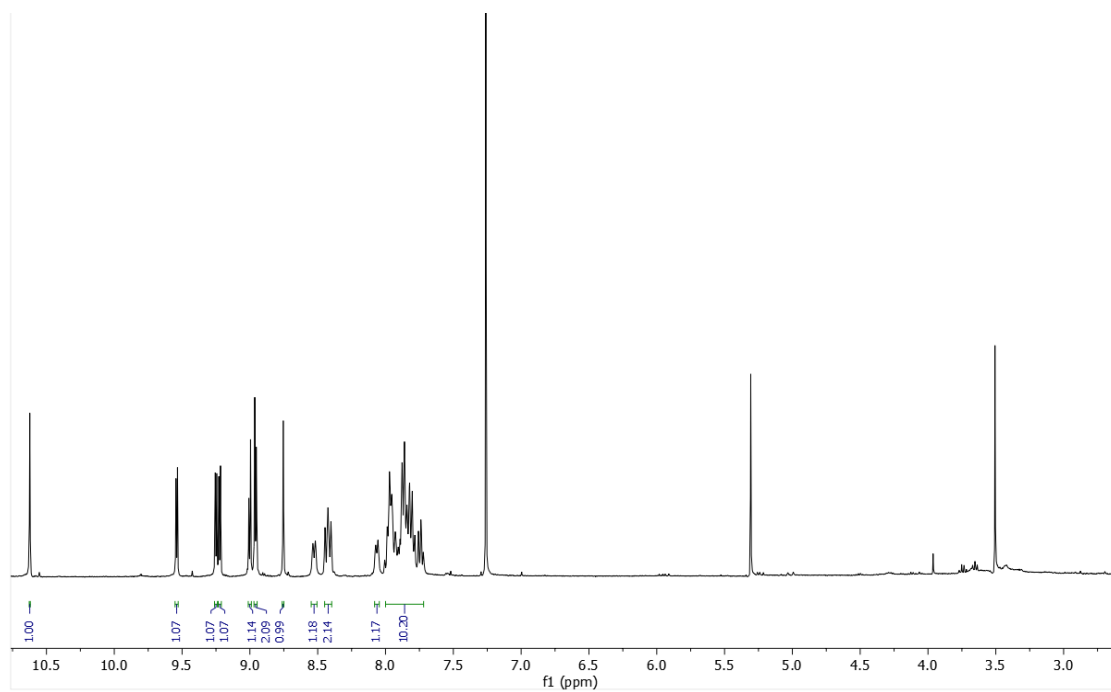


Figure S28. ^1H NMR spectrum of $\text{Re}[\text{TPC-3-CHO}](\text{O})$ at -20°C .



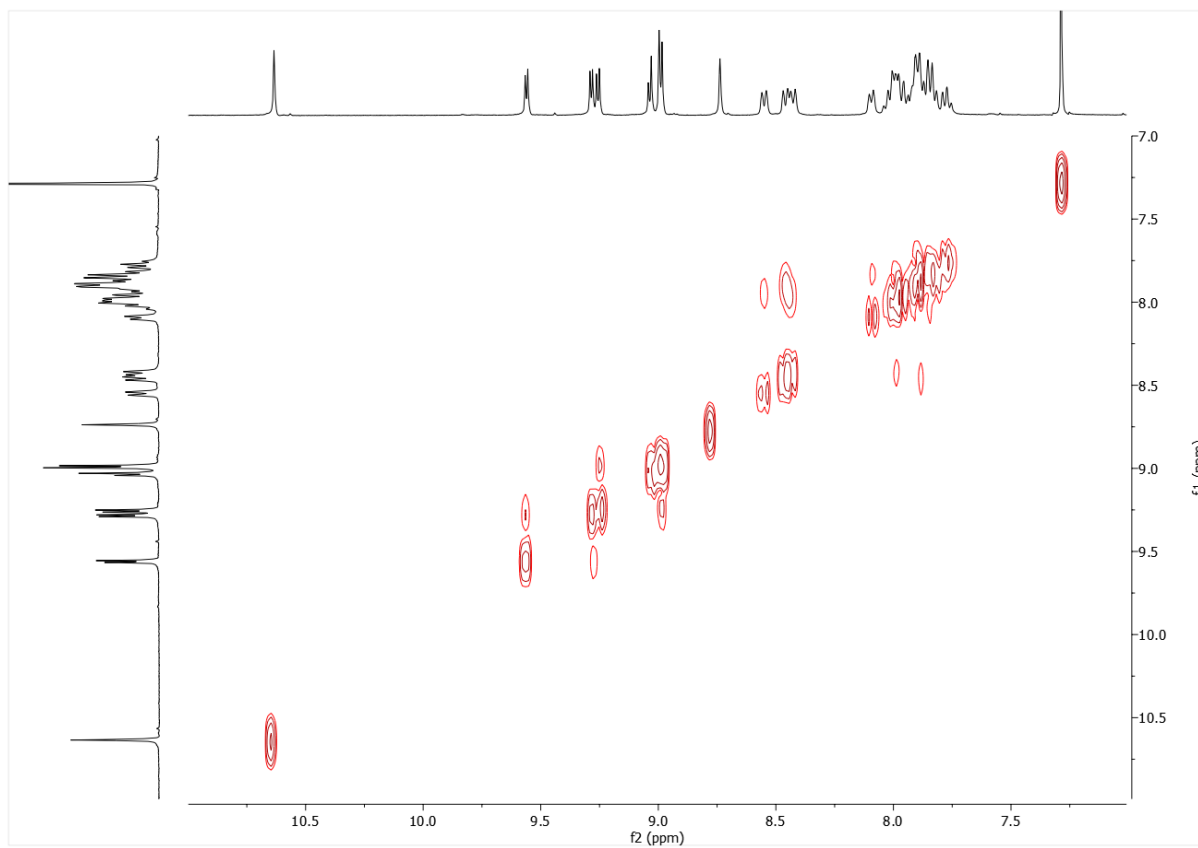


Figure S29. ^1H NMR and ^1H — ^1H COSY spectra of $\text{Re}[\text{TPC-3-CH}(\text{CN})\text{COOH}](\text{O})$ at -20°C .

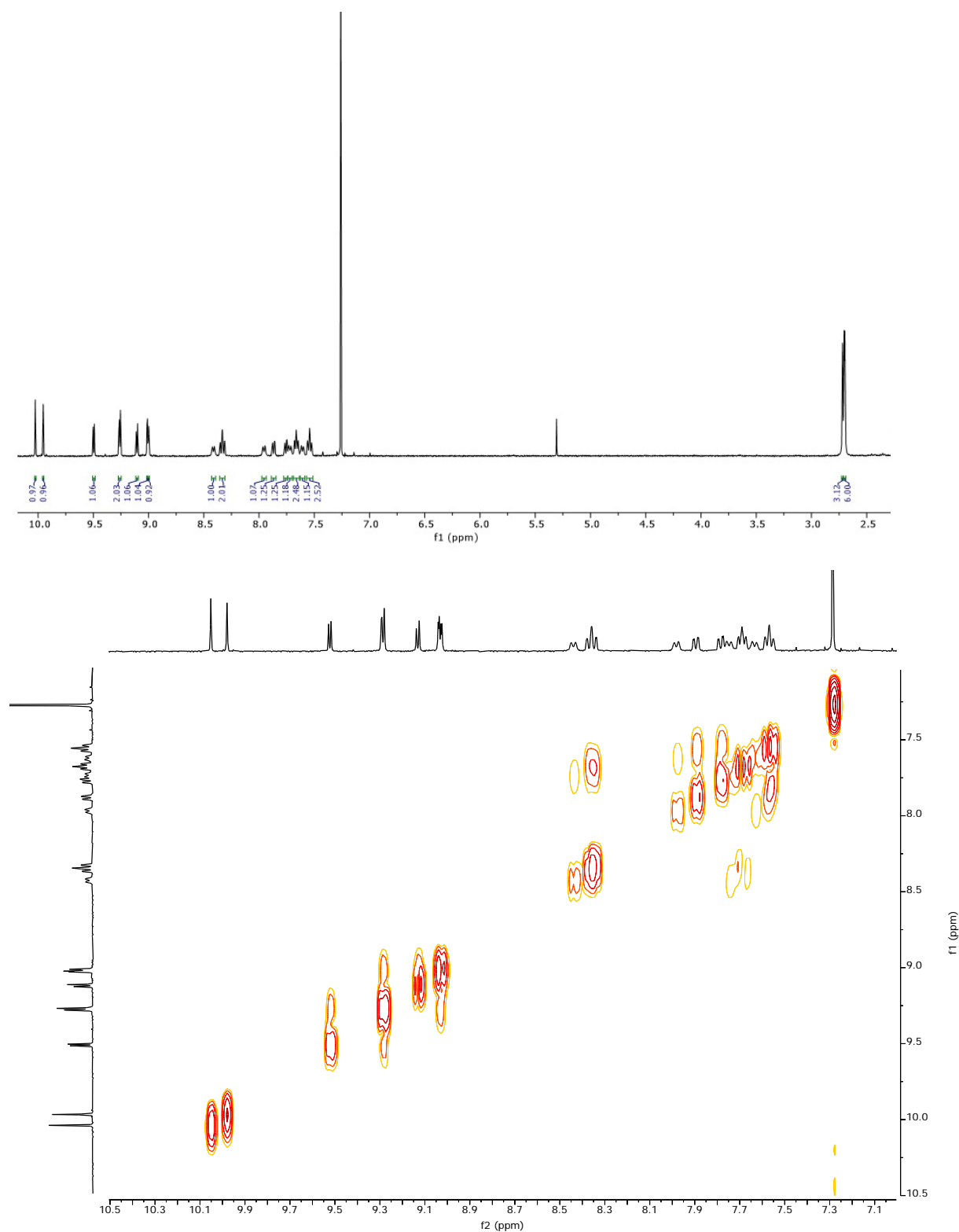


Figure S30. ^1H NMR and ^1H - ^1H COSY spectrum of $\text{Re}[\text{TpCH}_3\text{PC-3-CHO}](\text{O})$ at -20°C .

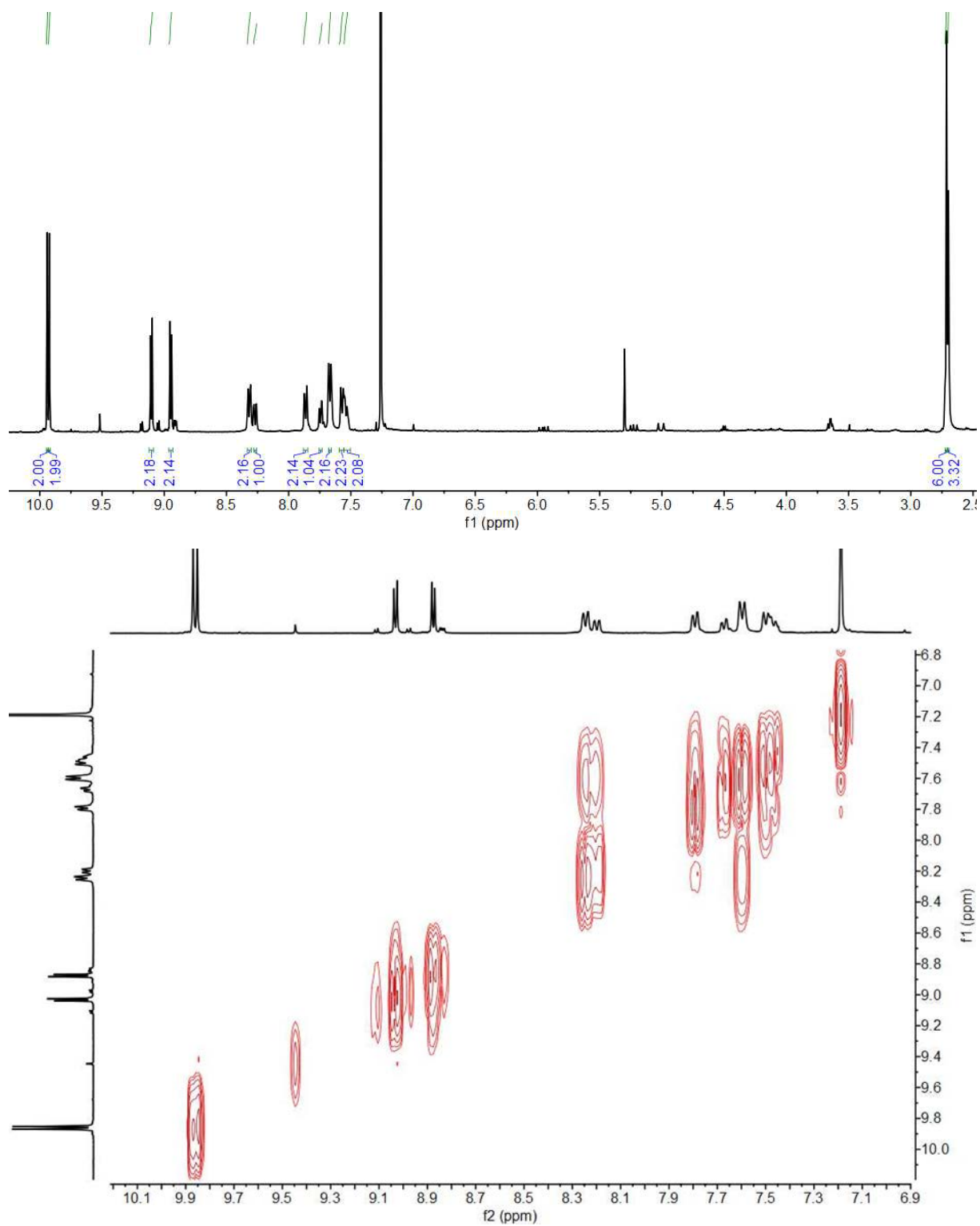


Figure S31. ^1H NMR and ^1H — ^1H COSY spectra of $\text{Re}[\text{TpCH}_3\text{PC-3,17-(CHO)}_2](\text{O})$ at -20°C .

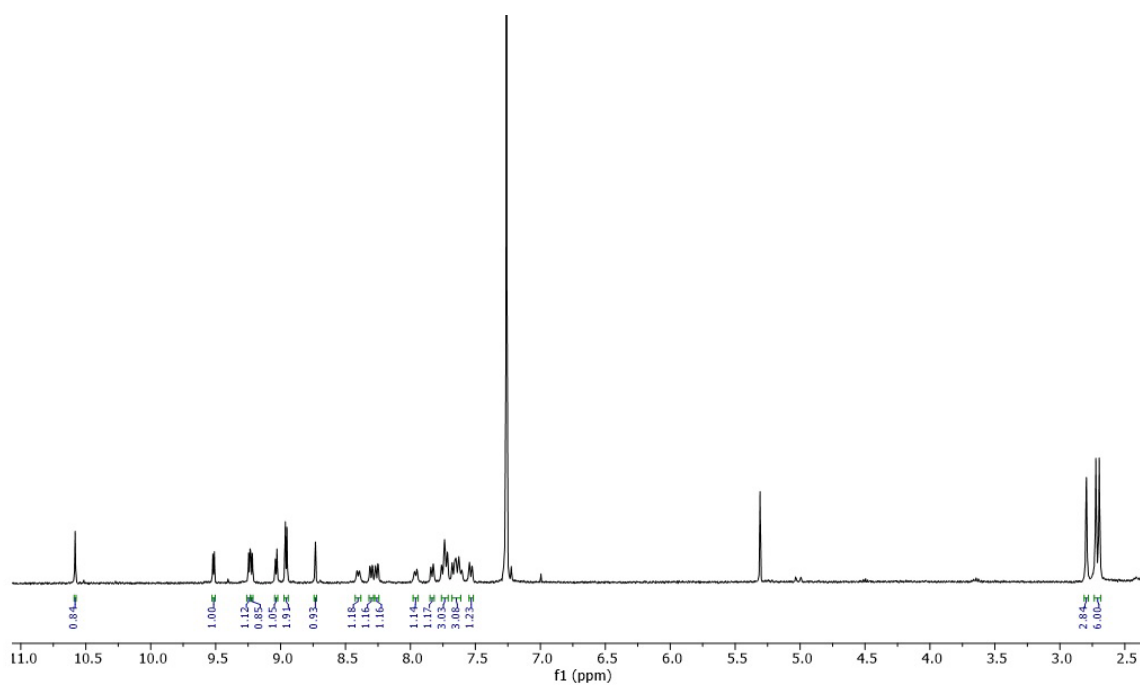


Figure S32. ^1H NMR spectrum of $\text{Re}[\text{TpCH}_3\text{PC-3-CH}(\text{CN})\text{COOH}](\text{O})$ in CDCl_3 at -20°C .

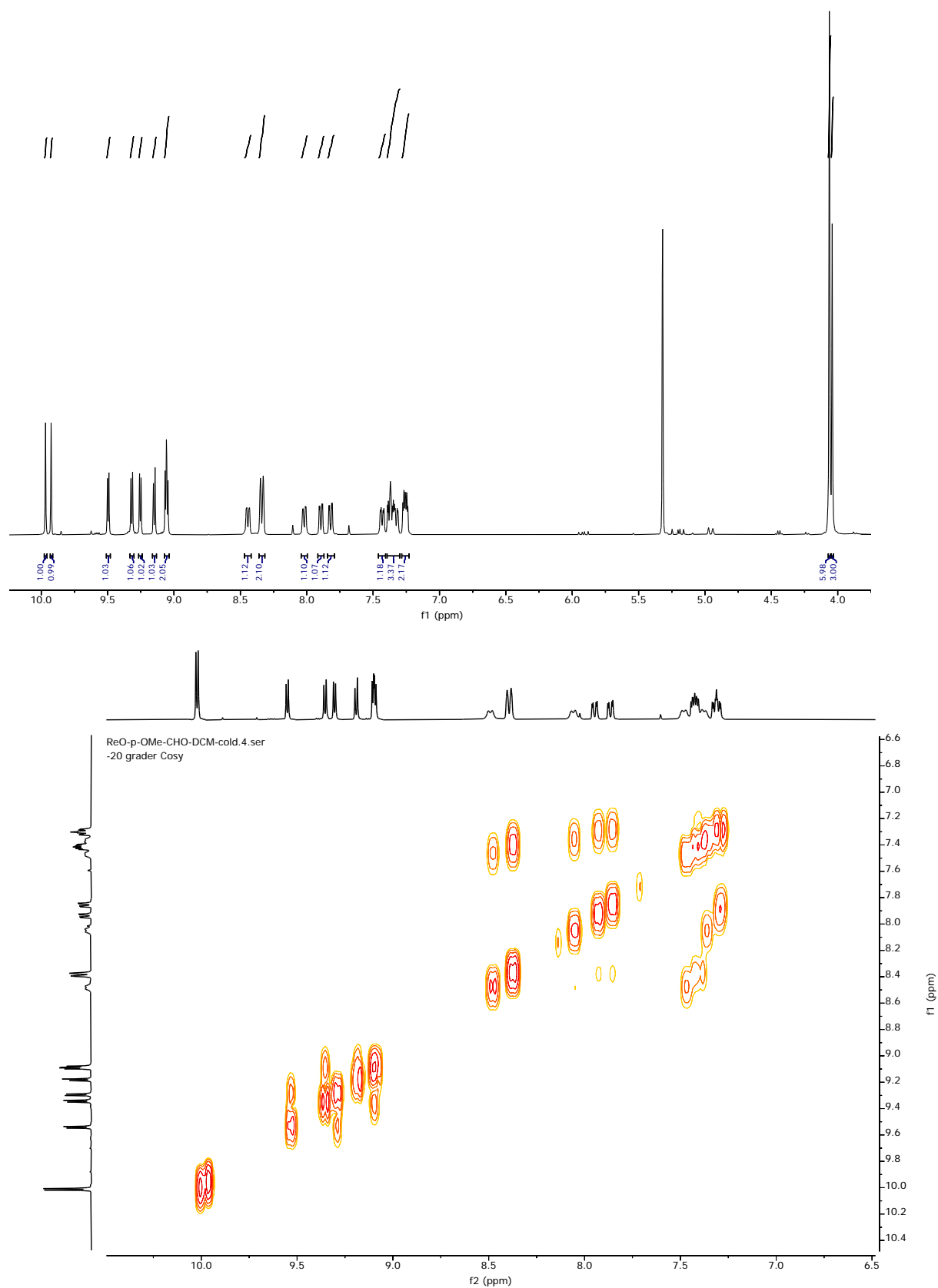


Figure S33. ^1H NMR and ^1H — ^1H COSY spectra of $\text{Re}[\text{TpOCH}_3\text{PC-3-CHO}](\text{O})$ in CDCl_3 at -20°C .

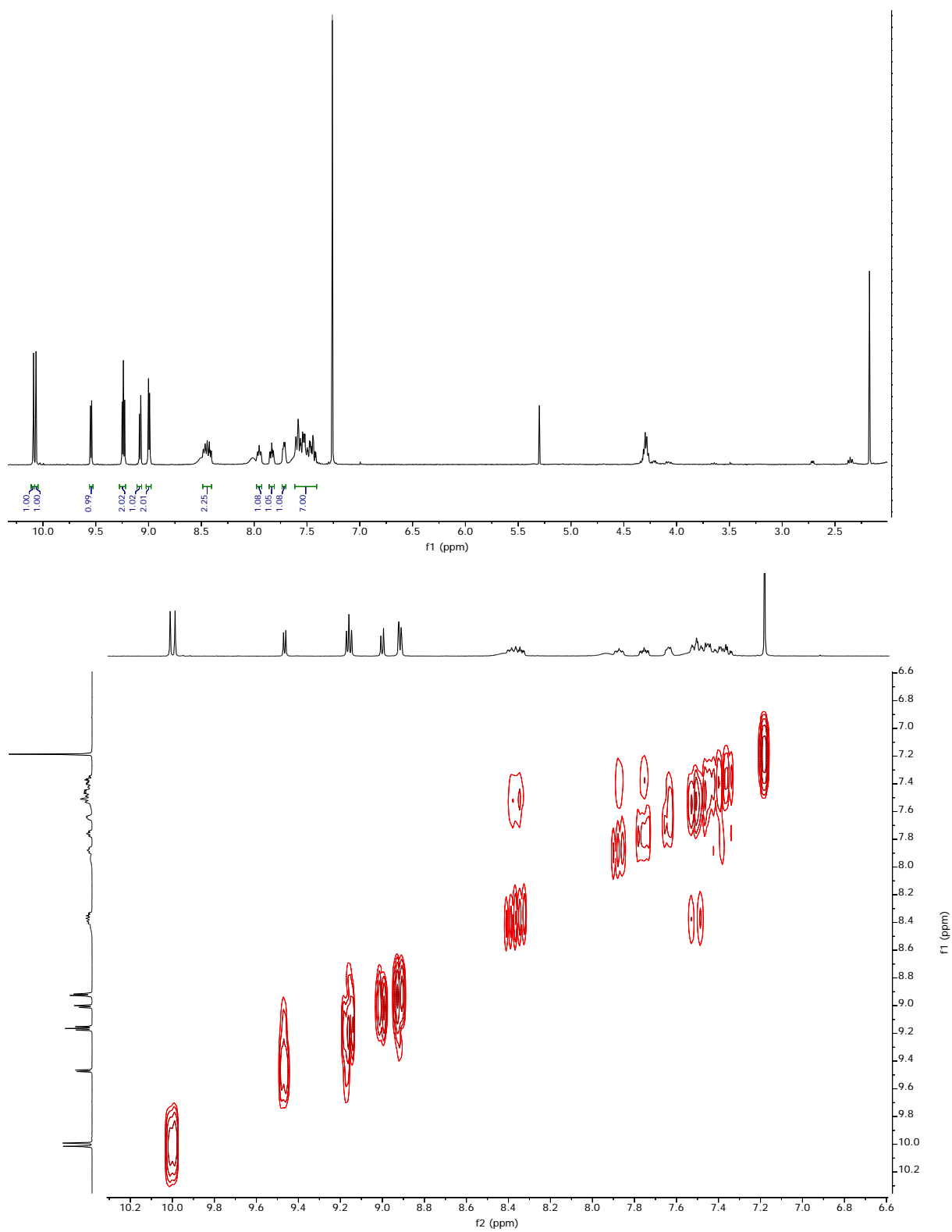


Figure S34. ^1H NMR and ^1H - ^1H COSY spectra of $\text{Re}[\text{TpFPC-3-CHO}]\text{O}$ in CDCl_3 at 20°C .

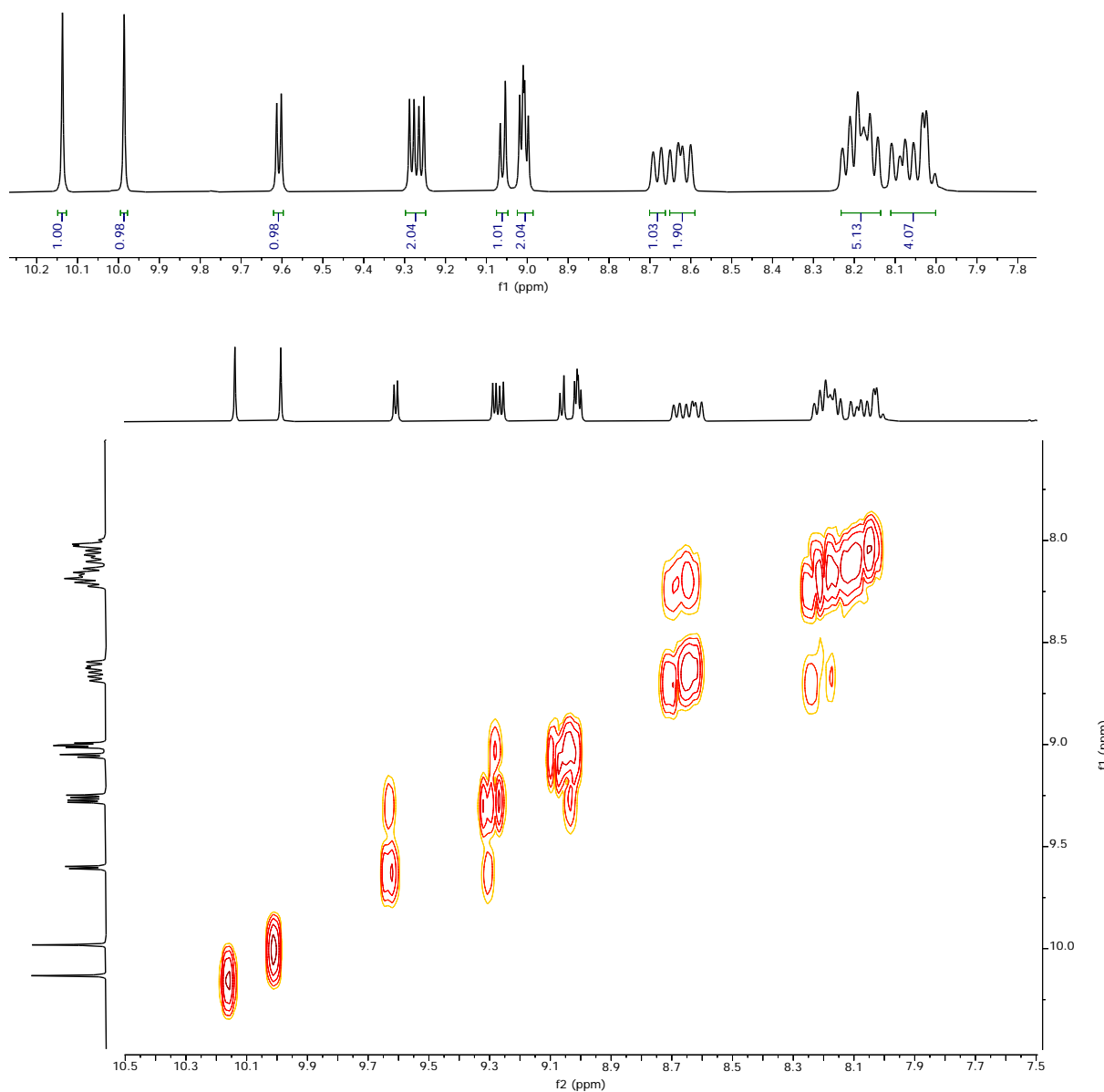


Figure S35. ^1H NMR and ^1H — ^1H COSY spectra of $\text{Re}[\text{TpCF}_3\text{PC-3-CHO}]\text{O}$ in CDCl_3 at -20°C .

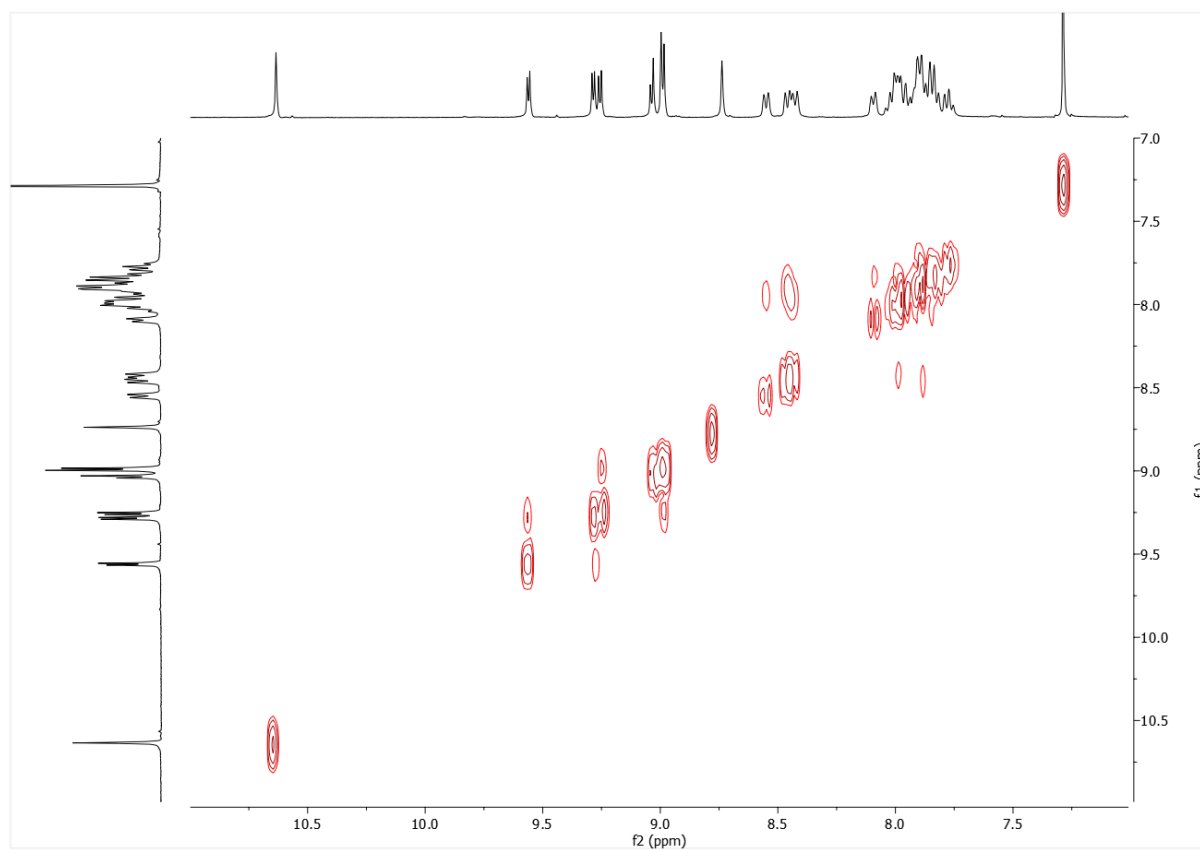
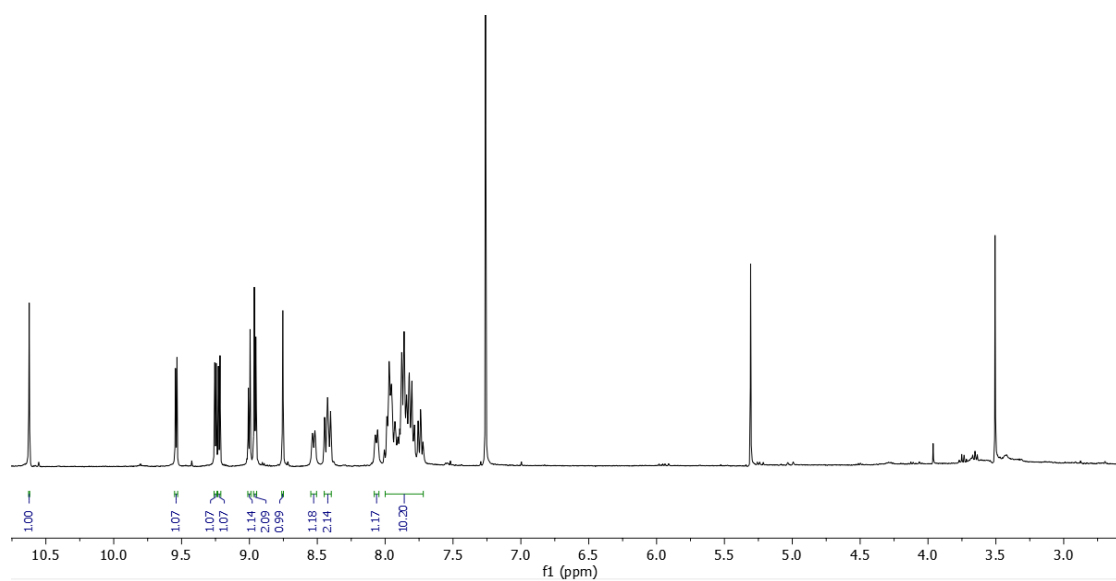


Figure S36. ^1H NMR and ^1H — ^1H COSY spectra of $\text{Re}[\text{TPC-3-CH}(\text{CN})\text{COOH}](\text{O})$ in CDCl_3 at -20°C .

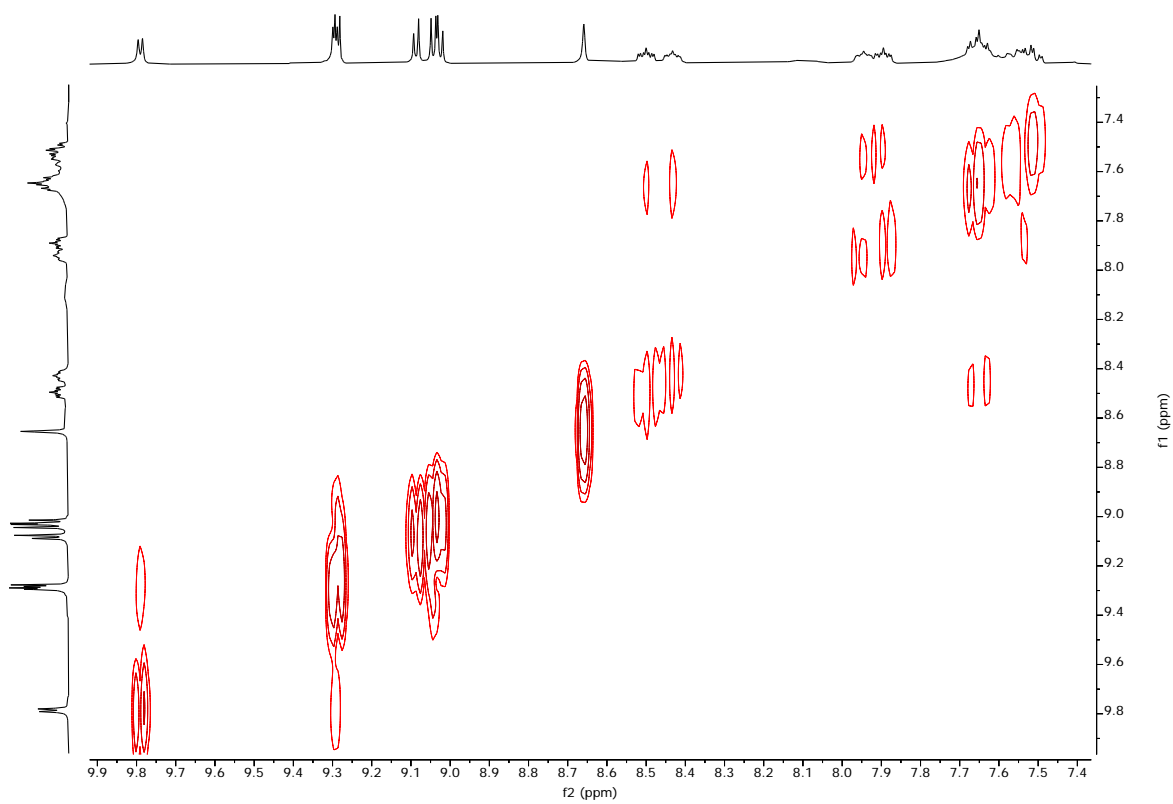
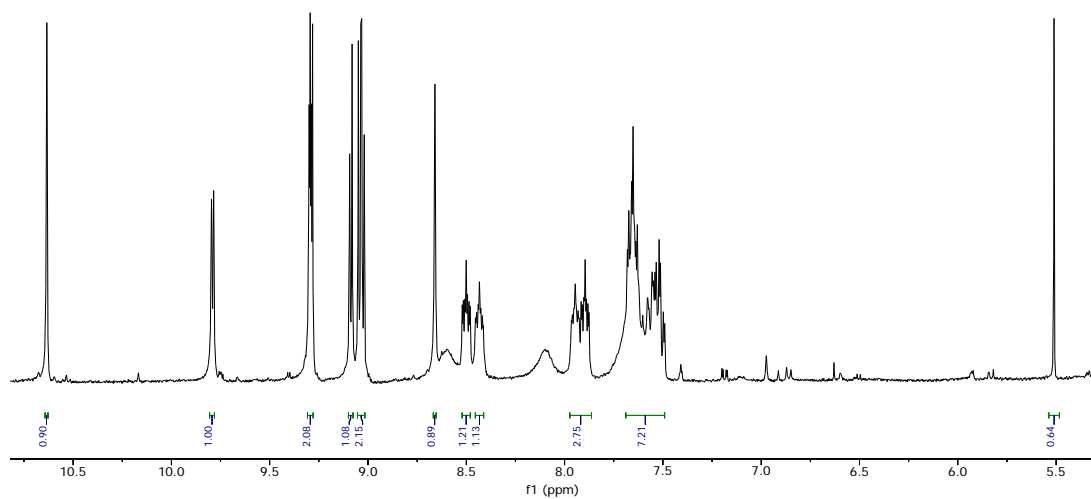


Figure S37. ¹H NMR and ¹H—¹H COSY spectra of Re[TpFPC-3-(CN)COOH](O) in tetrahydrofuran-d₈ at 20°C.

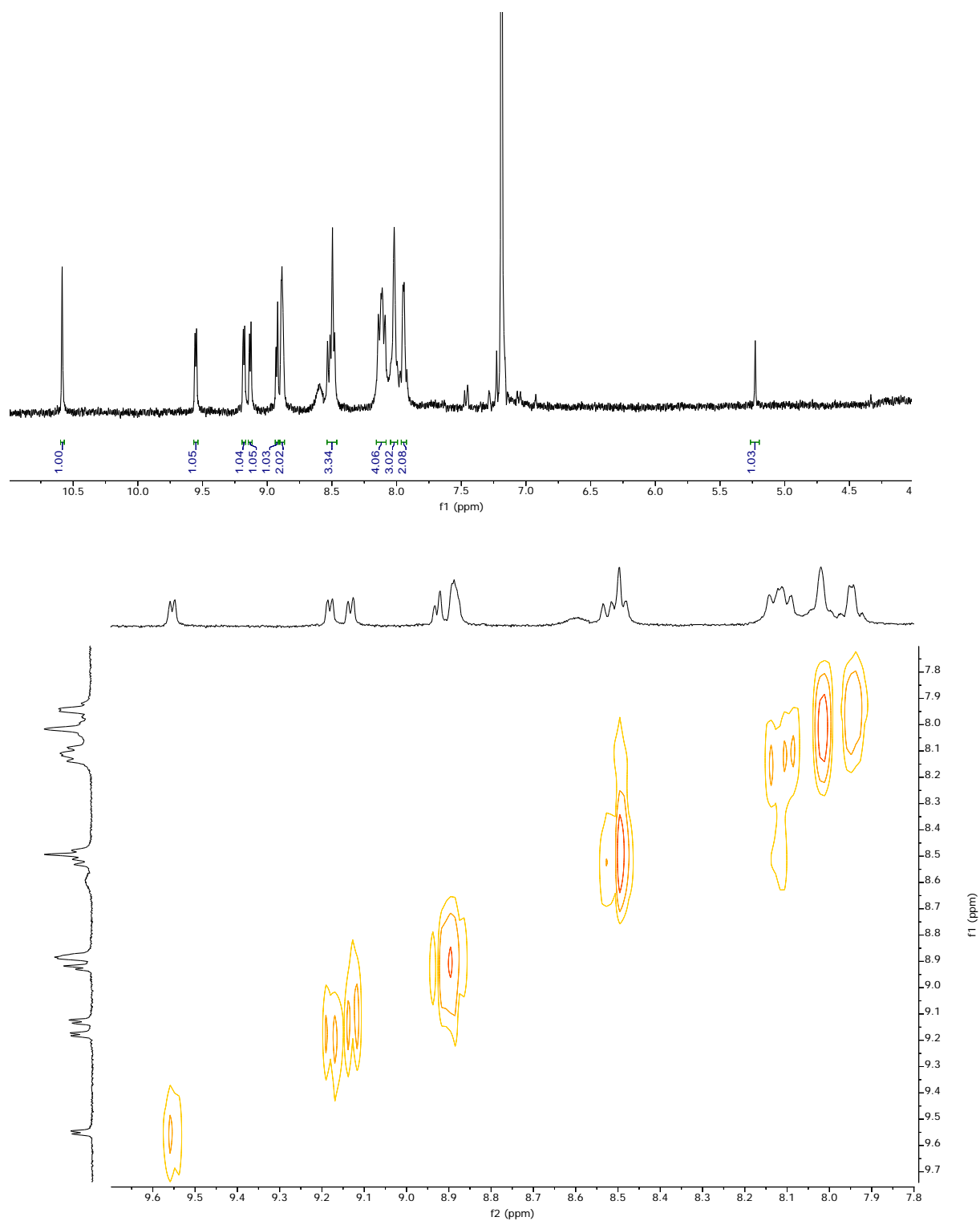


Figure S38. ^1H NMR and ^1H - ^1H COSY spectra of $\text{Re}[\text{TpCF}_3\text{PC-3-(CN)COOH}](\text{O})$ in CDCl_3 at 20°C .

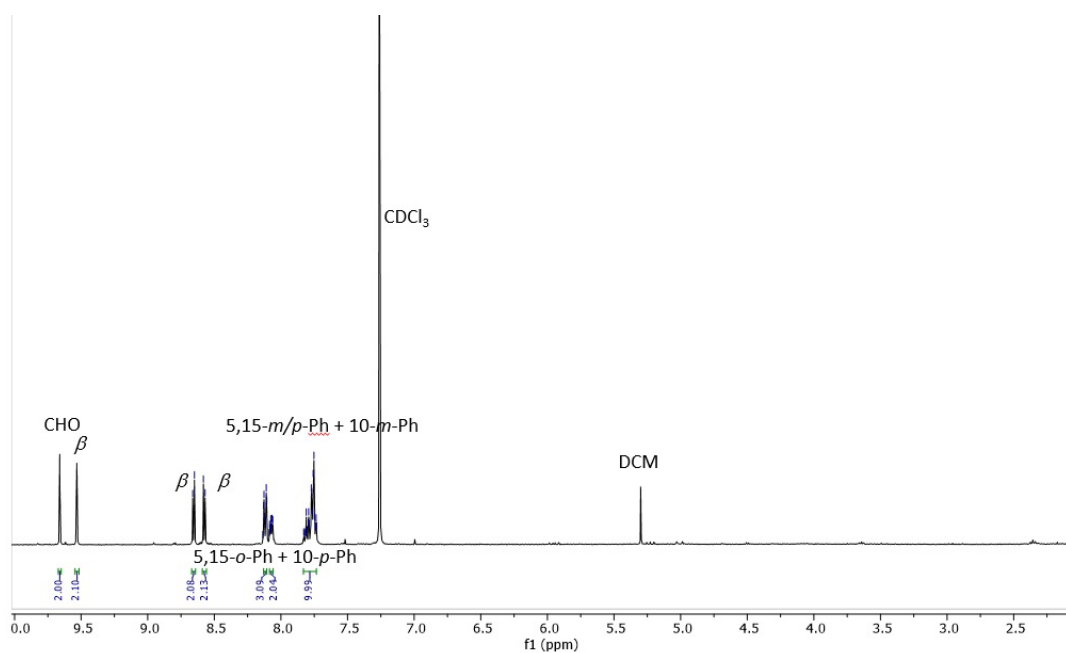


Figure S39. ^1H NMR spectrum of $\text{Au}[\text{TPC-3,17-(CHO)}_2]$ in CDCl_3 at -20°C .

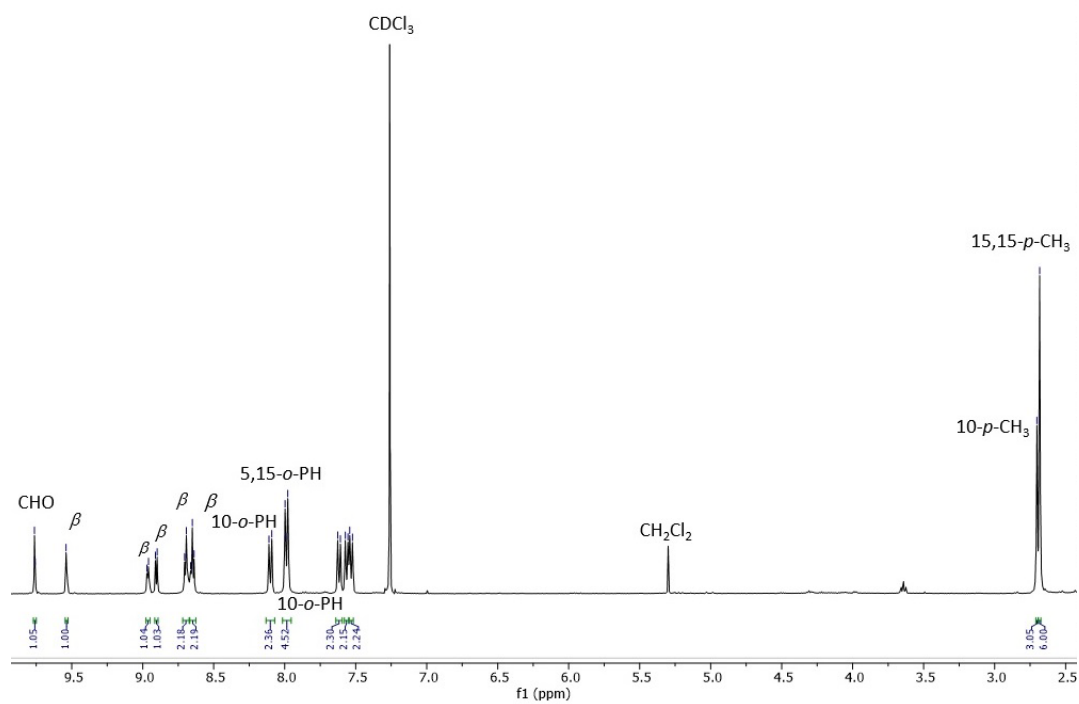


Figure S40. ^1H NMR spectrum of $\text{Au}[\text{TpCH}_3\text{PC-3-CHO}]$ in CDCl_3 at -20°C .

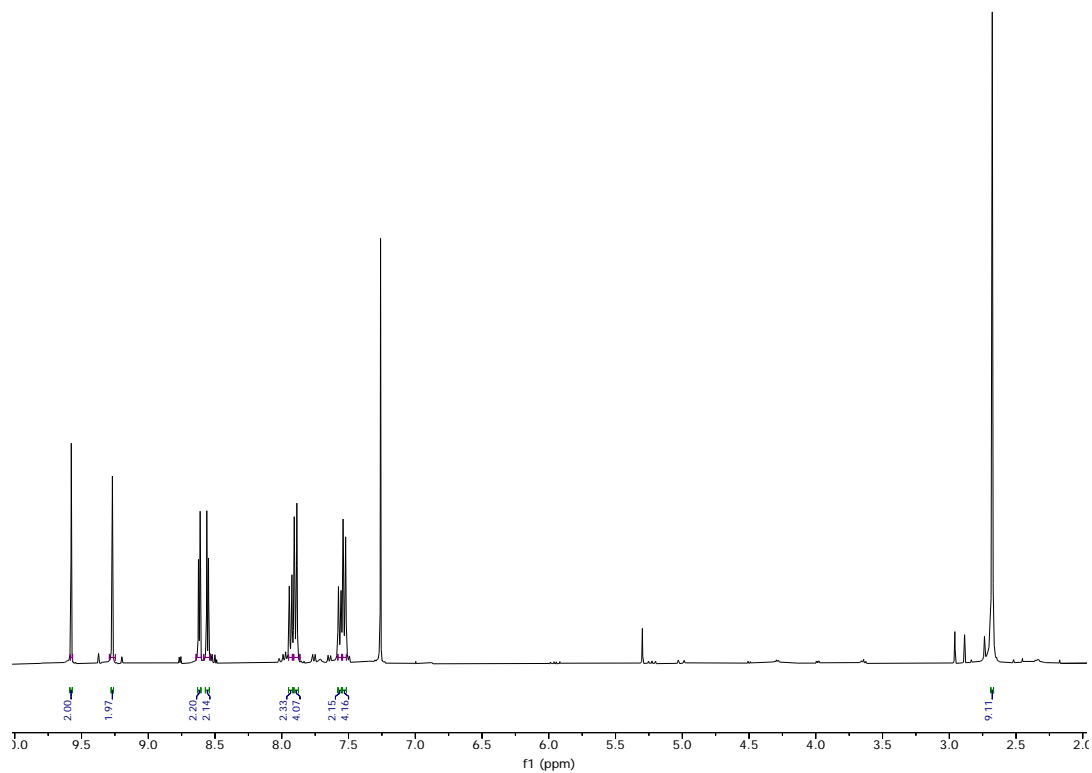


Figure S41. ¹H NMR spectrum of Au[TpCH₃PC-3,17-(CHO)₂] in CDCl₃ at -20°C.

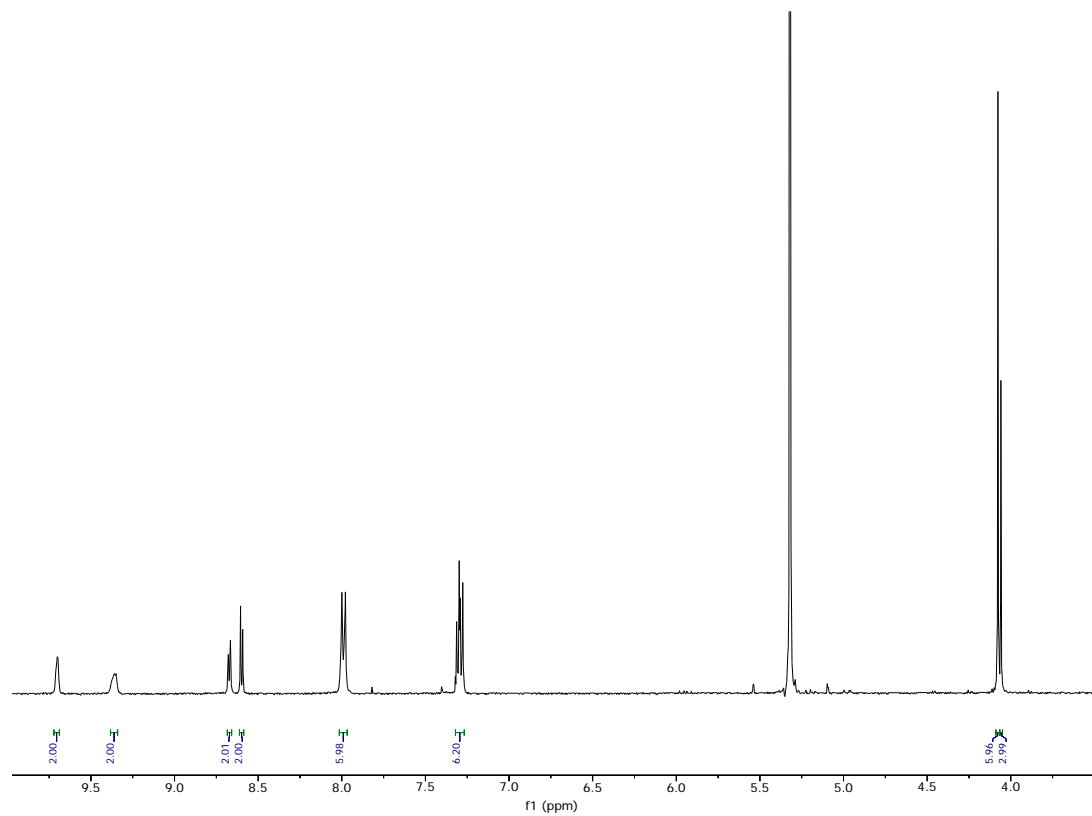


Figure S42. ¹H NMR spectrum of Au[TpOCH₃PC-3,17-(CHO)₂] in CDCl₃ at -20°C.

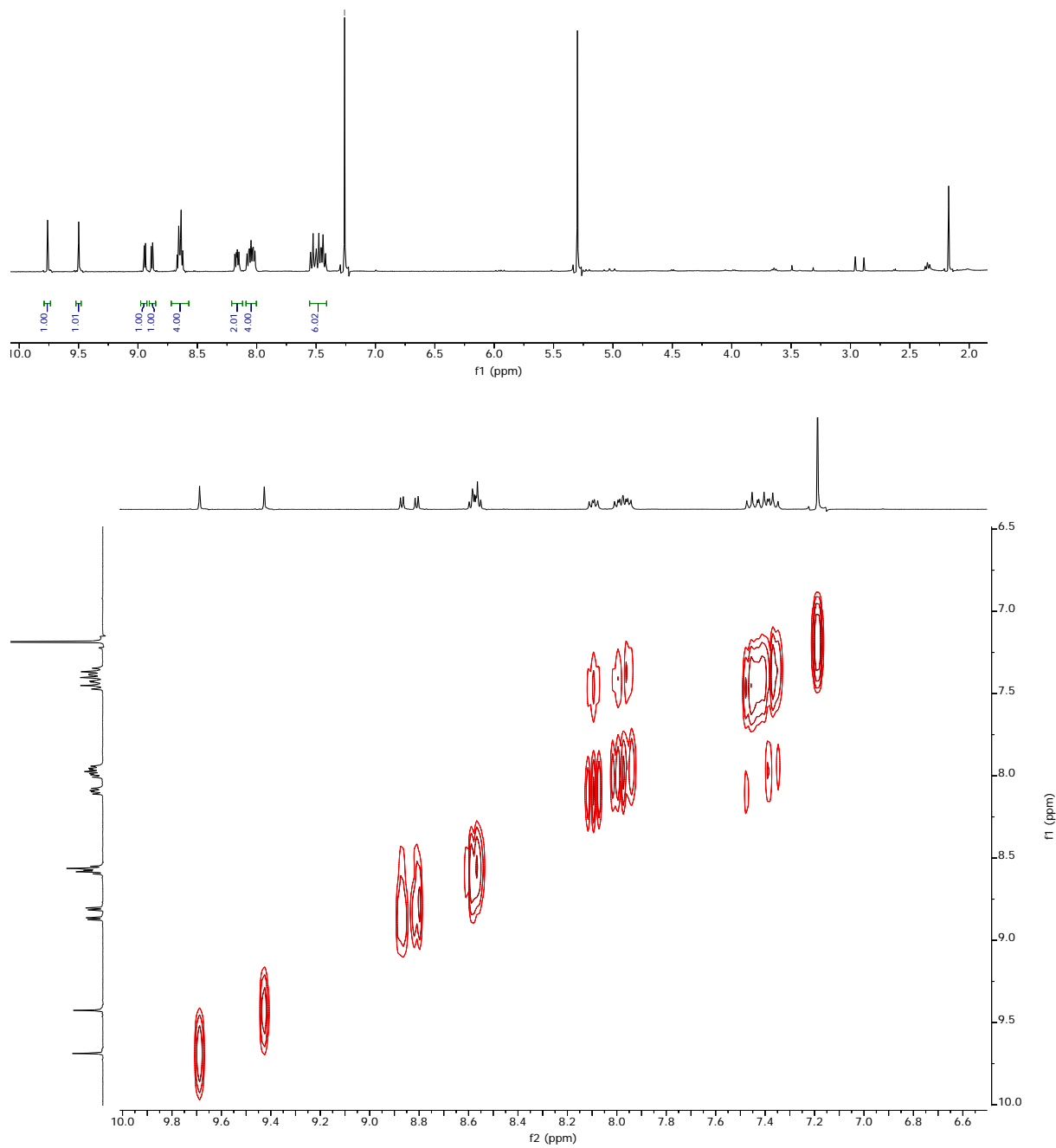


Figure S193. ¹H NMR and ¹H—¹H COSY spectra of Au[TrFPC-3-CHO] in CDCl₃ at 20°C.

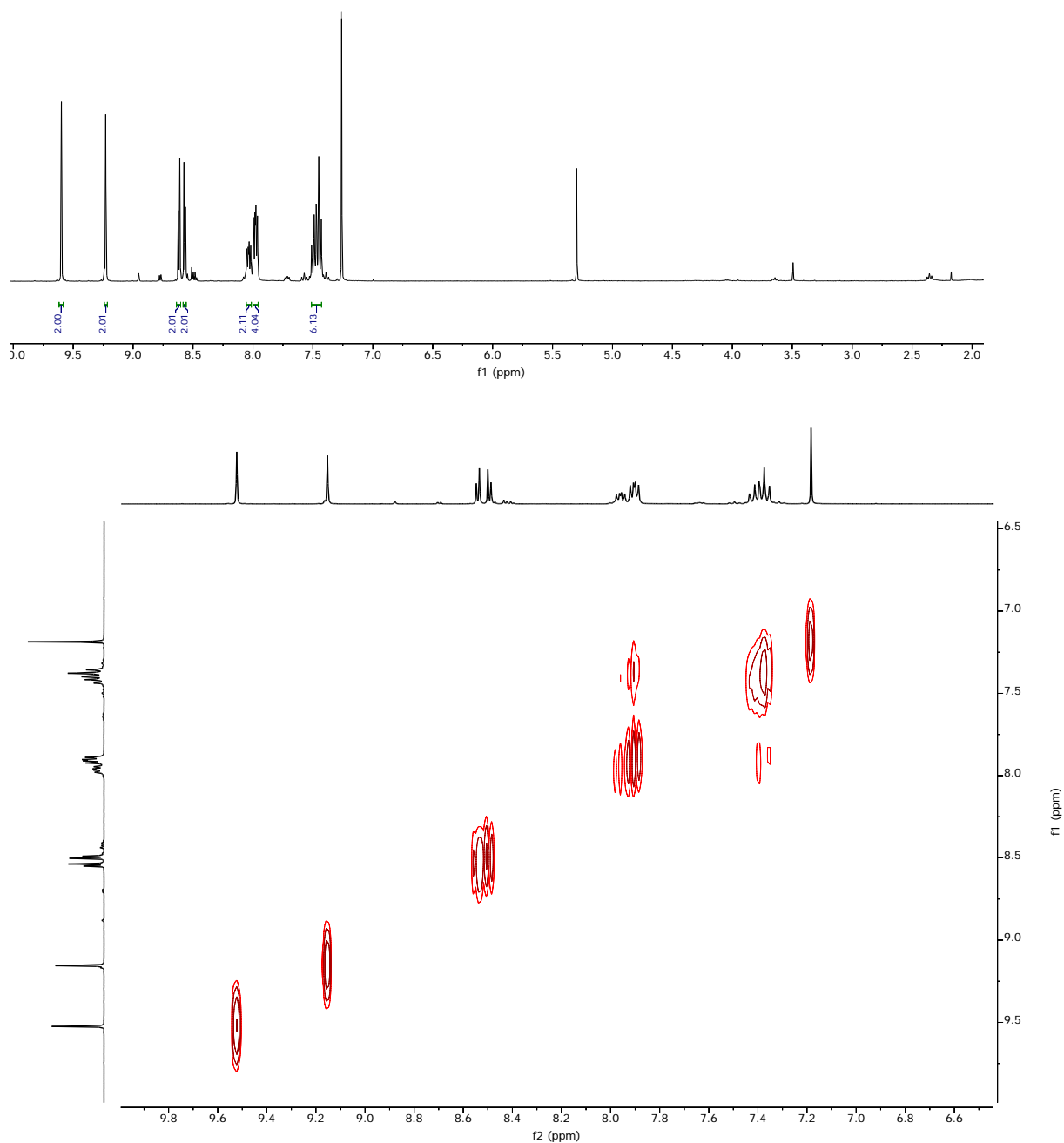


Figure S44. ¹H NMR and ¹H—¹H COSY spectra of Au[TpFPC-3,17-(CHO)₂] in CDCl₃ at 20°C.

D. Partial characterization of minor products

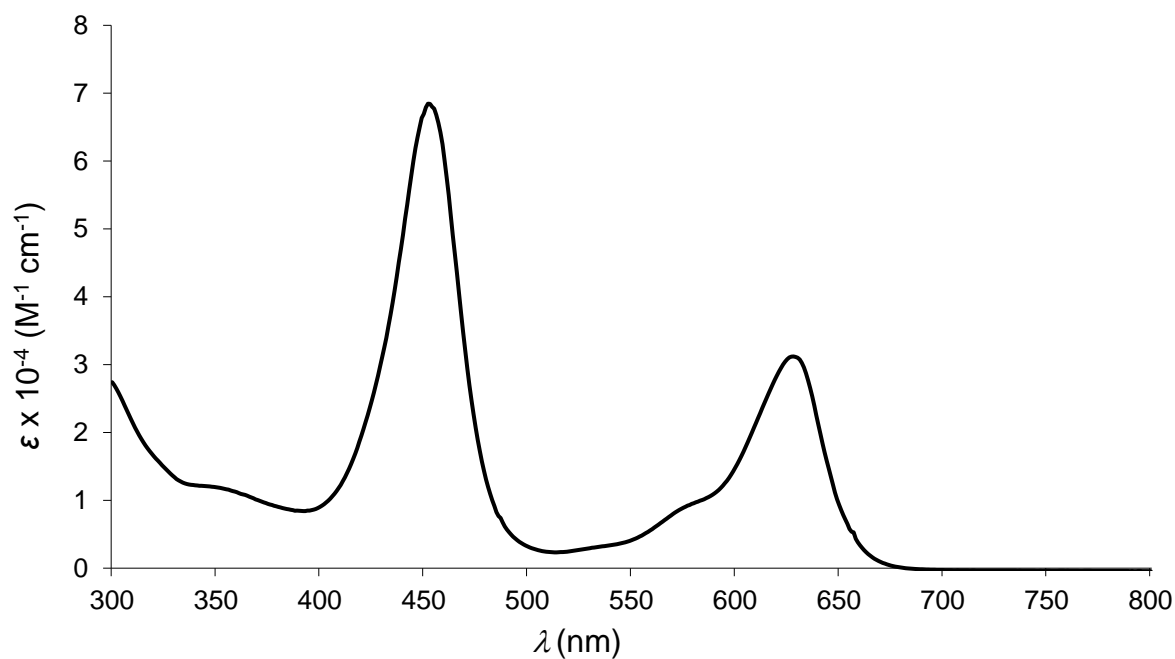


Figure S45. UV-vis spectrum of $\text{Re}[\text{TpCH}_3\text{PC-3,17-(CHO)}_2]$ in dichloromethane.

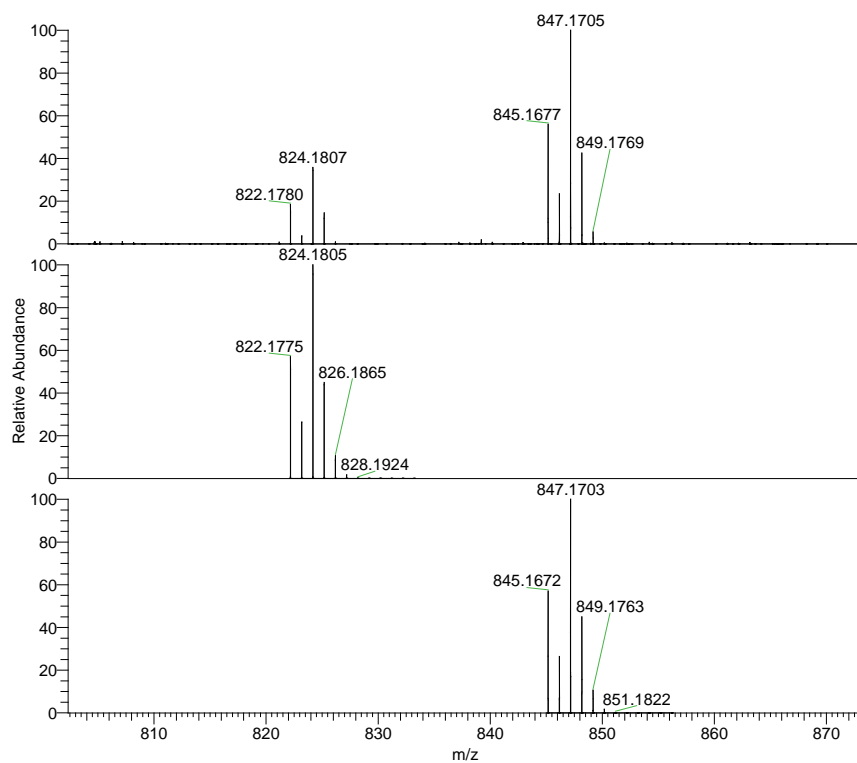


Figure S46. ESI mass spectrum of $\text{Re}[\text{TpCH}_3\text{PC-3,17-(CHO)}_2](\text{O})$.

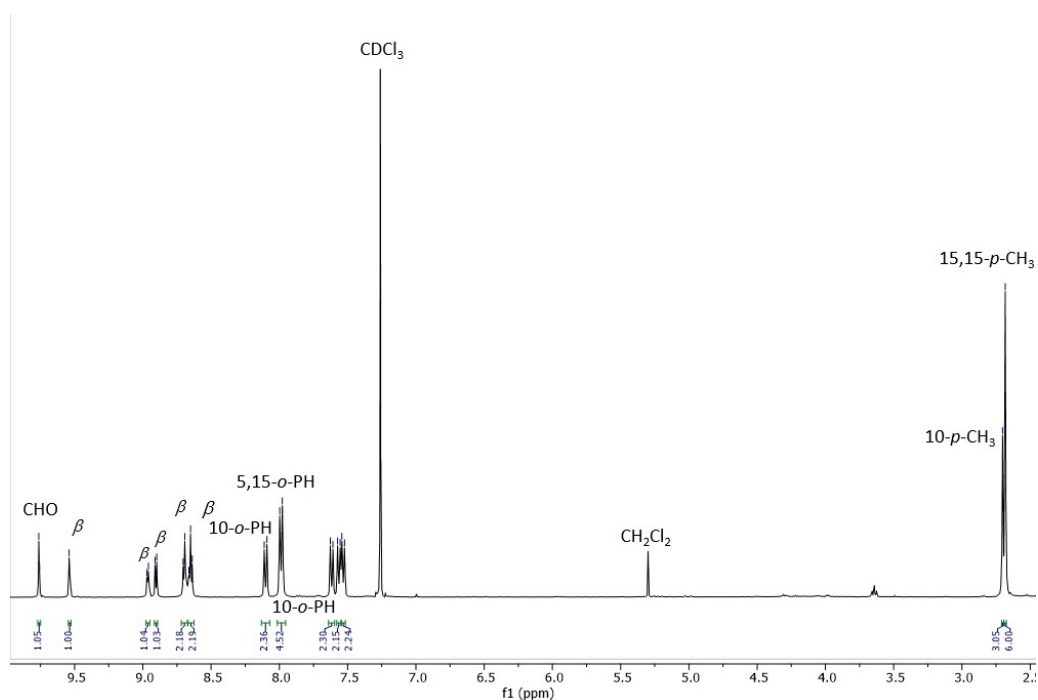


Figure S47. ^1H NMR spectrum of $\text{Au}[\text{TpCH}_3\text{PC-3-CHO}]$ in CDCl_3 at -20°C .

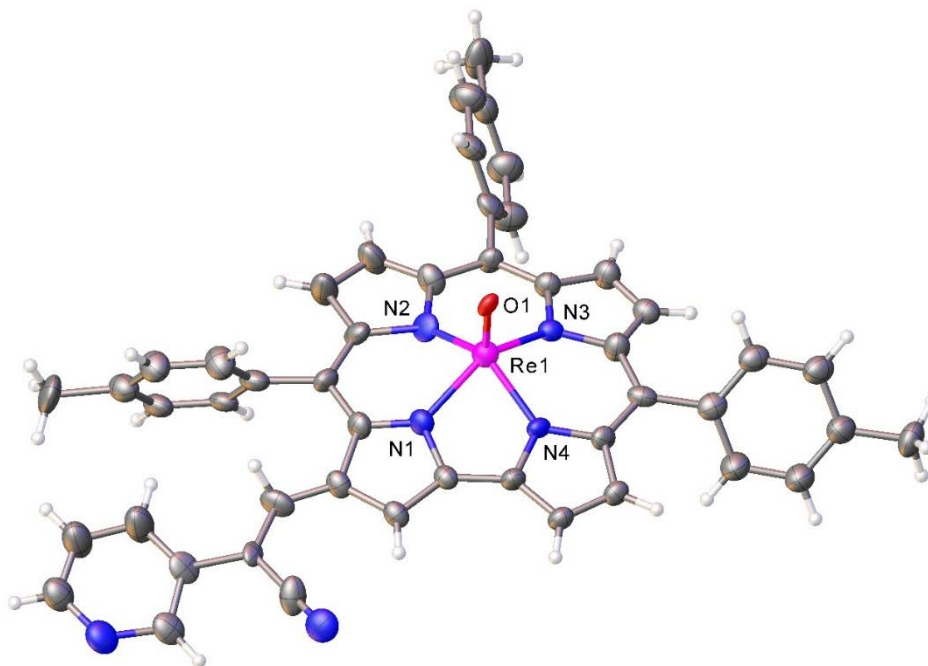


Figure S48. Thermal ellipsoid plot for the Knoevenagel condensate of $\text{Re}[\text{TpCH}_3\text{PC-3-CHO}]$ with pyridin-3-ylacetonitrile. Selected distances (\AA): Re1-N1 2.003(18), Re1-N2 1.87(2), Re1-N3 1.973(18), Re1-N4 1.956(16). Re(1)-N(3) 1.973(18) Re(1)-N(4) 1.956(16). The relatively poor quality of the structure implies that it should be only as proof of connectivity.