

Base-Promoted Aryl-Bromine Bond Cleavage with Cobalt(II) Porphyrins via Halogen Atom Transfer Mechanism

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1. X-ray Craystallographic Data and Structure of Co(tpp)(4-methoxyphenyl) (**3e**)

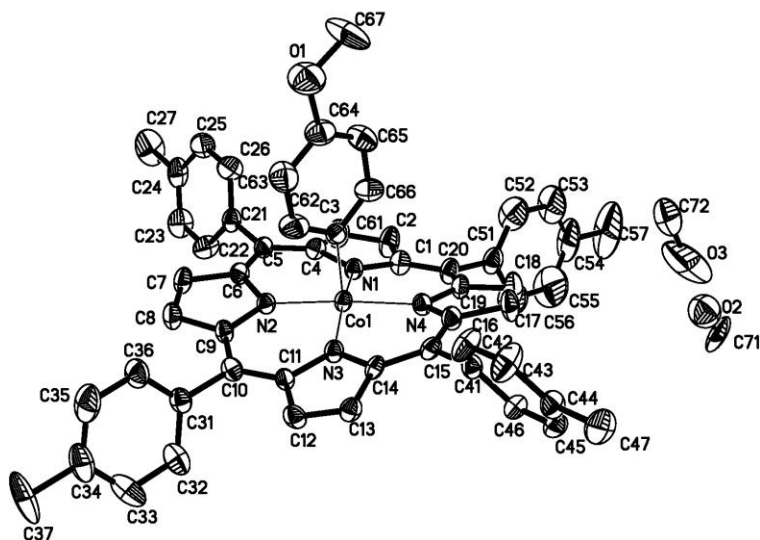


Figure S1. ORTEP presentation of Co(tpp)(4-methoxyphenyl) (**3e**) (30% probability displacement ellipsoids). Hydrogen atoms are omitted for clarity.

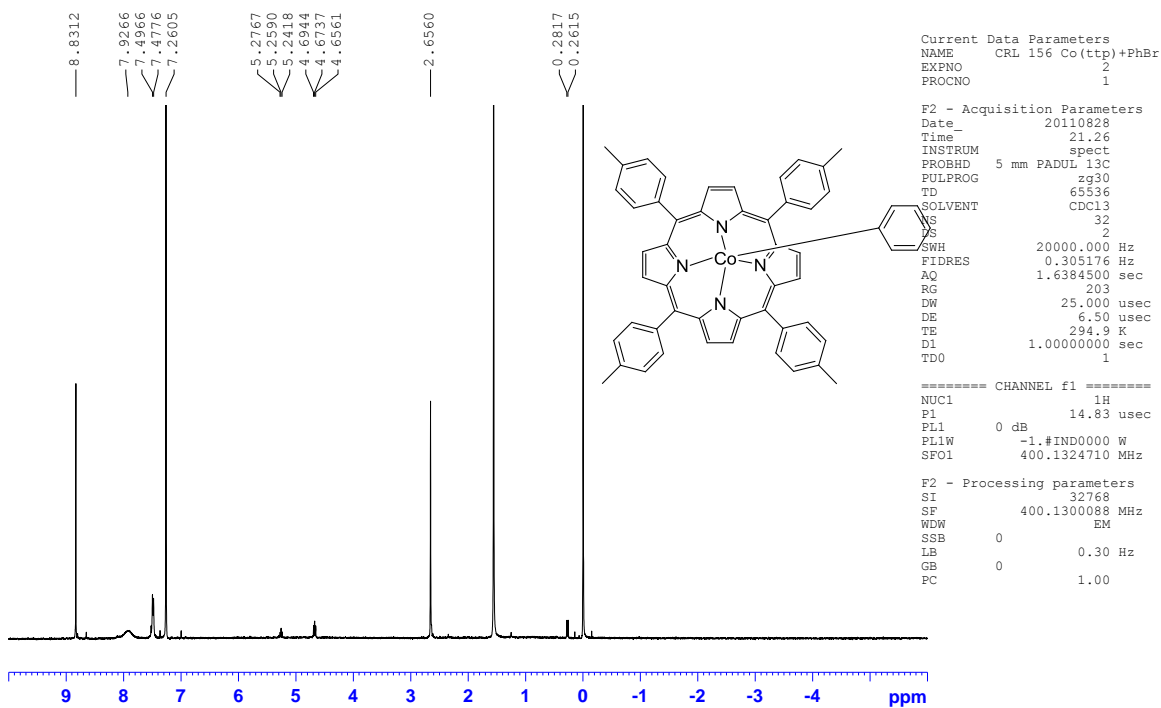
Table S1. Crystal Data and Structure Refinement for Co(ttp)(4-methoxyphenyl) (3e).

| | |
|-----------------------------------|---|
| Compound | Co(ttp)(4-methoxyphenyl) (3e) |
| Empirical formula | C _{55.50} H ₄₅ Co N ₄ O _{1.50} |
| Formula weight | 850.88 |
| Temperature | 296(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, P2(1)/c |
| Unit cell dimensions | a = 21.671(3) Å alpha = 90 deg. b = 14.9796(19) Å beta = 105.867(3) deg. c = 16.421(2) Å gamma = 90 deg. |
| Volume | 5127.6(12) Å ³ |
| Z, Calculated density | 4, 1.102 Mg/m ³ |
| Absorption coefficient | 0.375 mm ⁻¹ |
| F(000) | 1780 |
| Crystal size | 0.40 x 0.30 x 0.20 mm |
| Theta range for data collection | 0.98 to 27.86 deg. |
| Limiting indices | -28<=h<=28, -19<=k<=19, -21<=l<=21 |
| Reflections collected / unique | 44668 / 12177 [R(int) = 0.2426] |
| Completeness to theta = 25.25 | 99.6 % |
| Absorption correction | multi-scan |
| Max. and min. transmission | 0.7076 and 0.5710 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 12177 / 8 / 586 |
| Goodness-of-fit on F ² | 0.991 |
| Final R indices [I>2sigma(I)] | R1 = 0.1181, wR2 = 0.2926 |
| R indices (all data) | R1 = 0.3032, wR2 = 0.3901 |
| Largest diff. peak and hole | 0.963 and -0.586 e.Å ⁻³ |

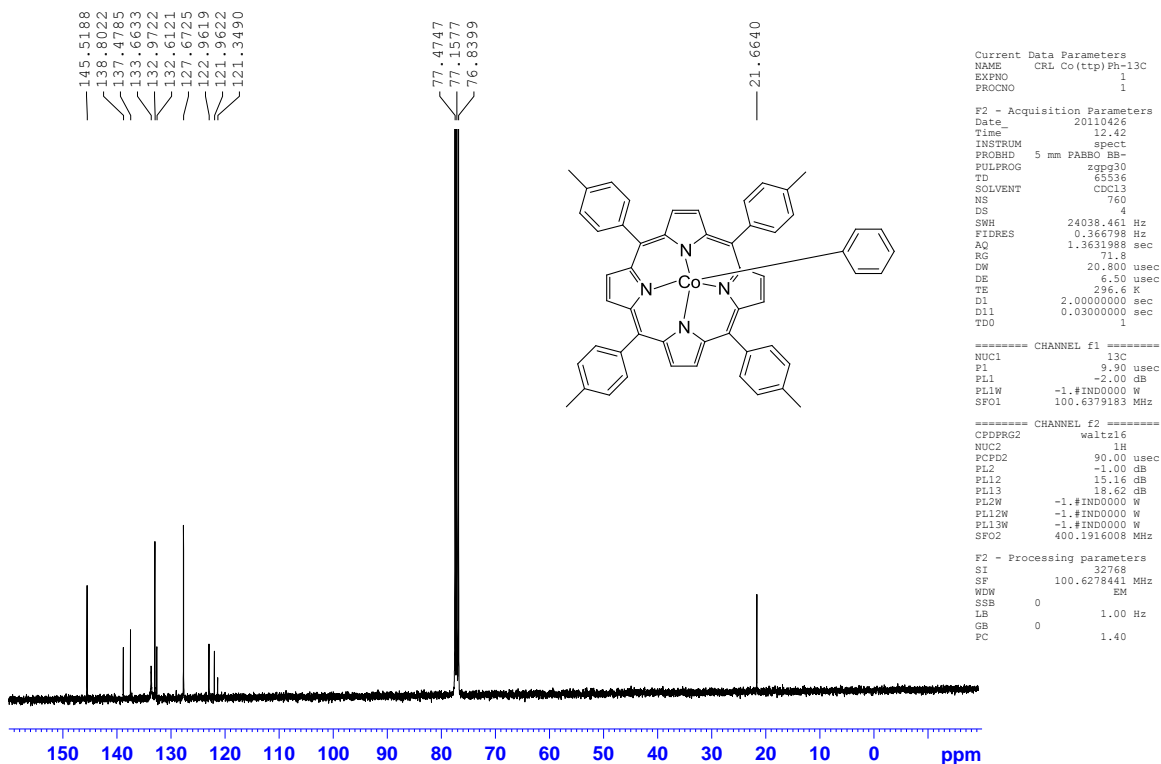
2. NMR Spectra

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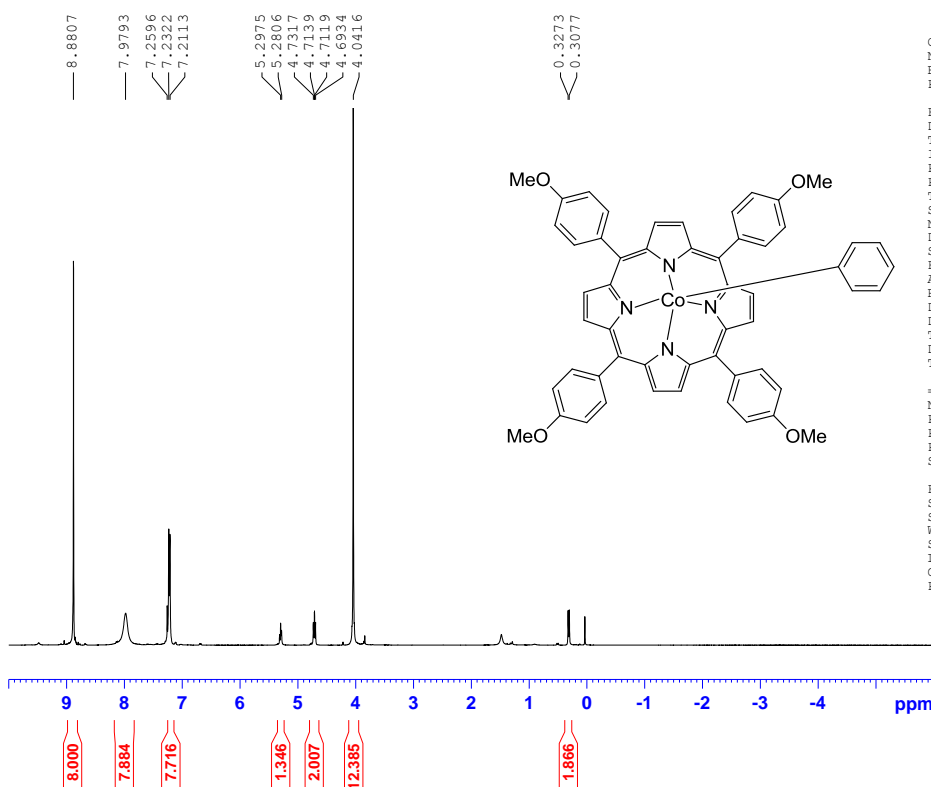
¹H NMR Spectrum of Co^{III}(ttp)Ph (**3a**) (CDCl₃)



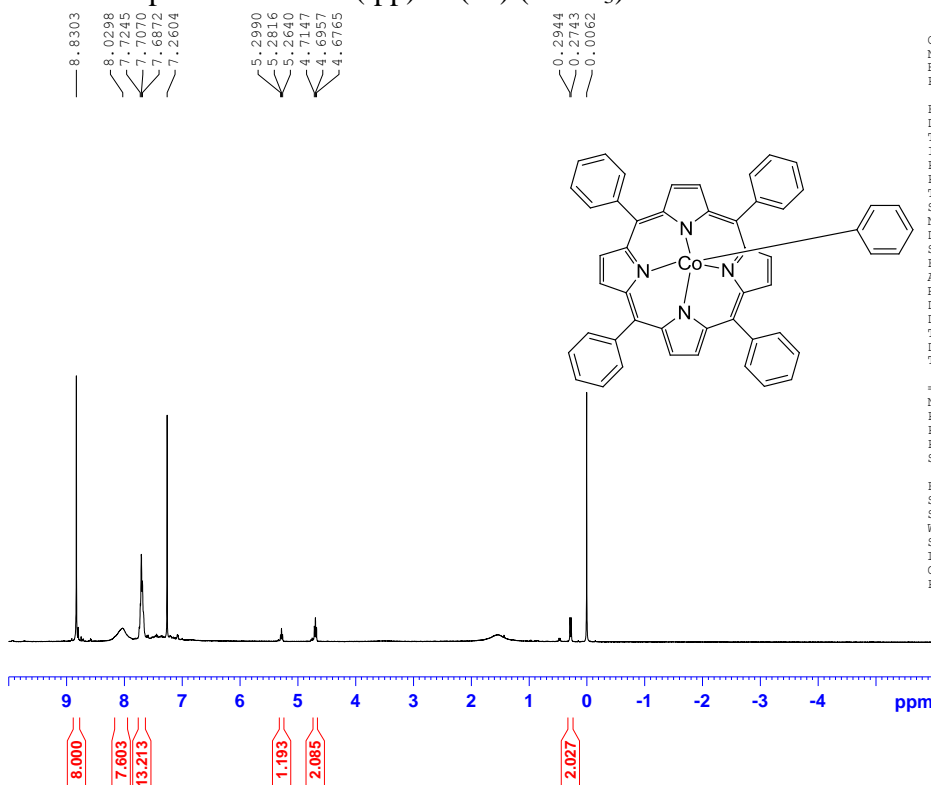
¹³C NMR Spectrum of Co^{III}(ttp)Ph (**3a**) (CDCl₃)



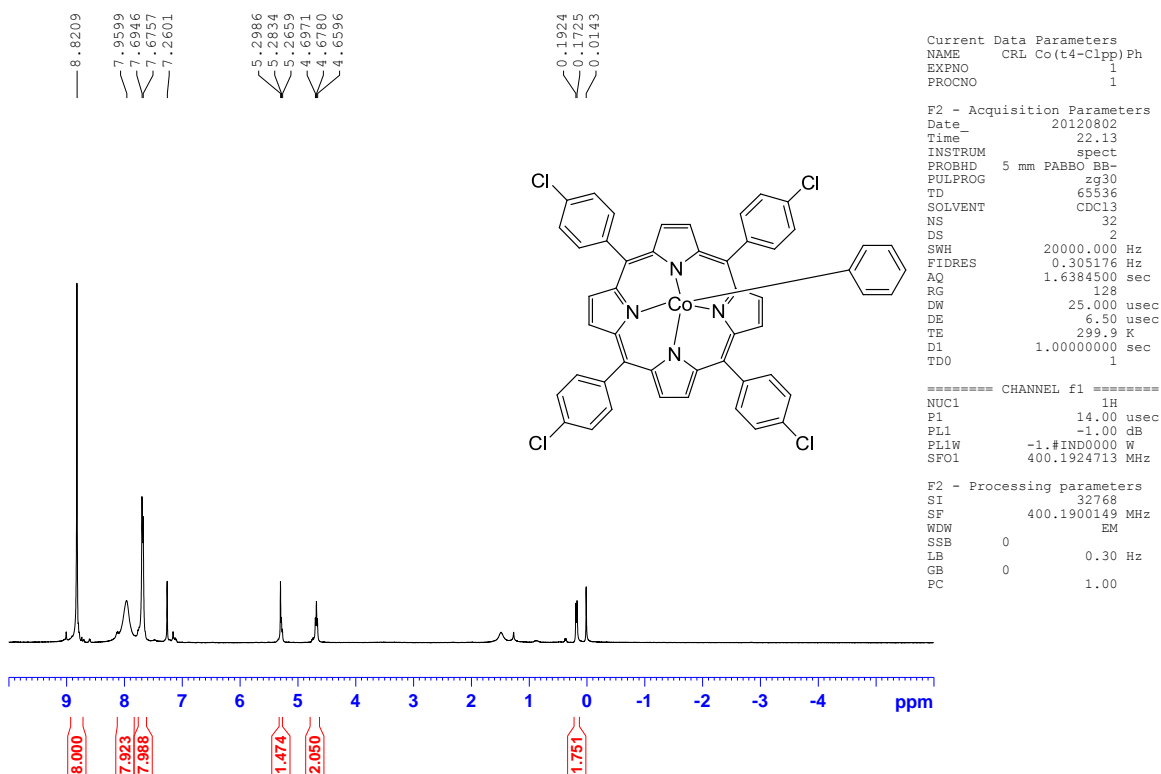
¹H NMR Spectrum of Co^{III}(tap)Ph (**3b**) (CDCl₃)



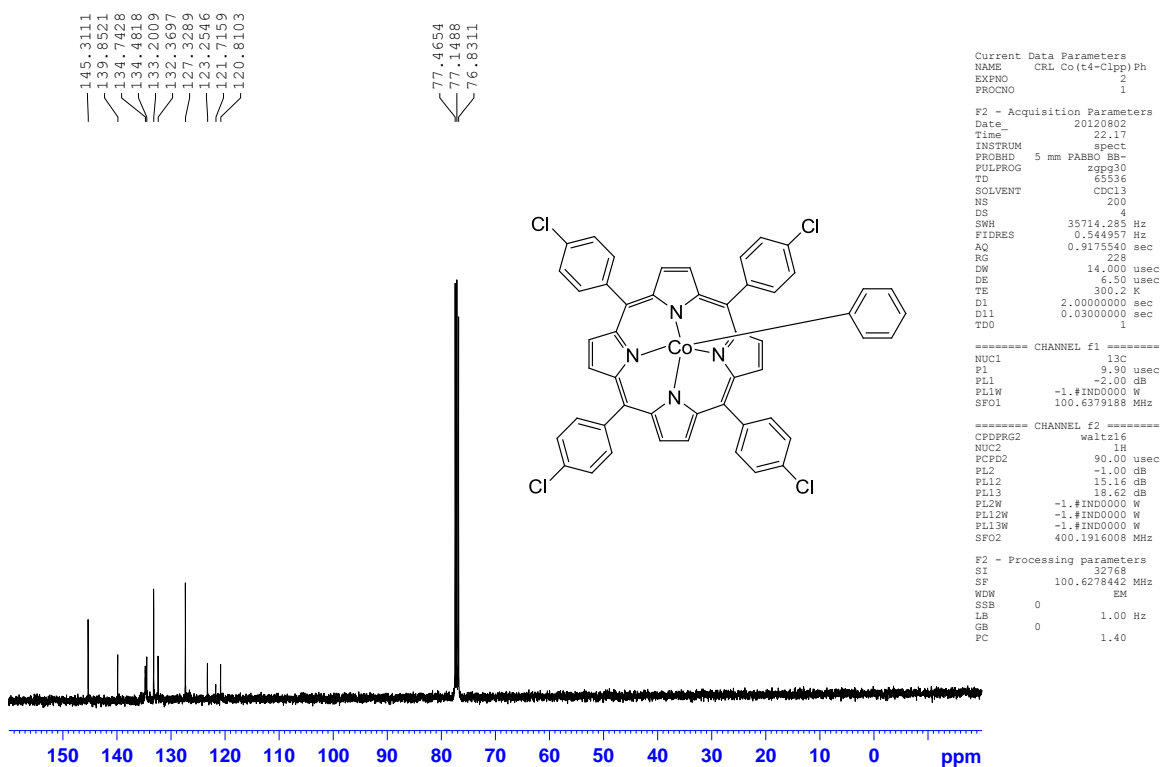
¹H NMR Spectrum of Co^{III}(tpp)Ph (**3c**) (CDCl₃)



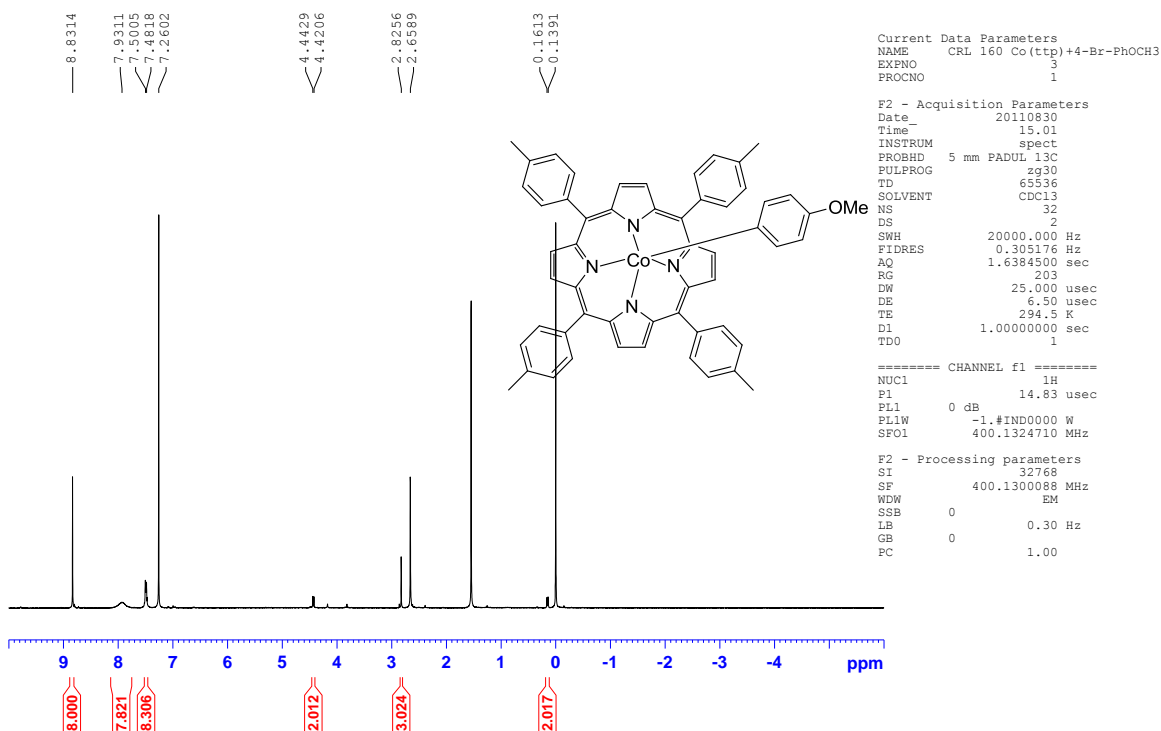
^1H NMR Spectrum of $\text{Co}^{\text{III}}(\text{t}_4\text{-Clpp})\text{Ph}$ (**3d**) (CDCl_3)



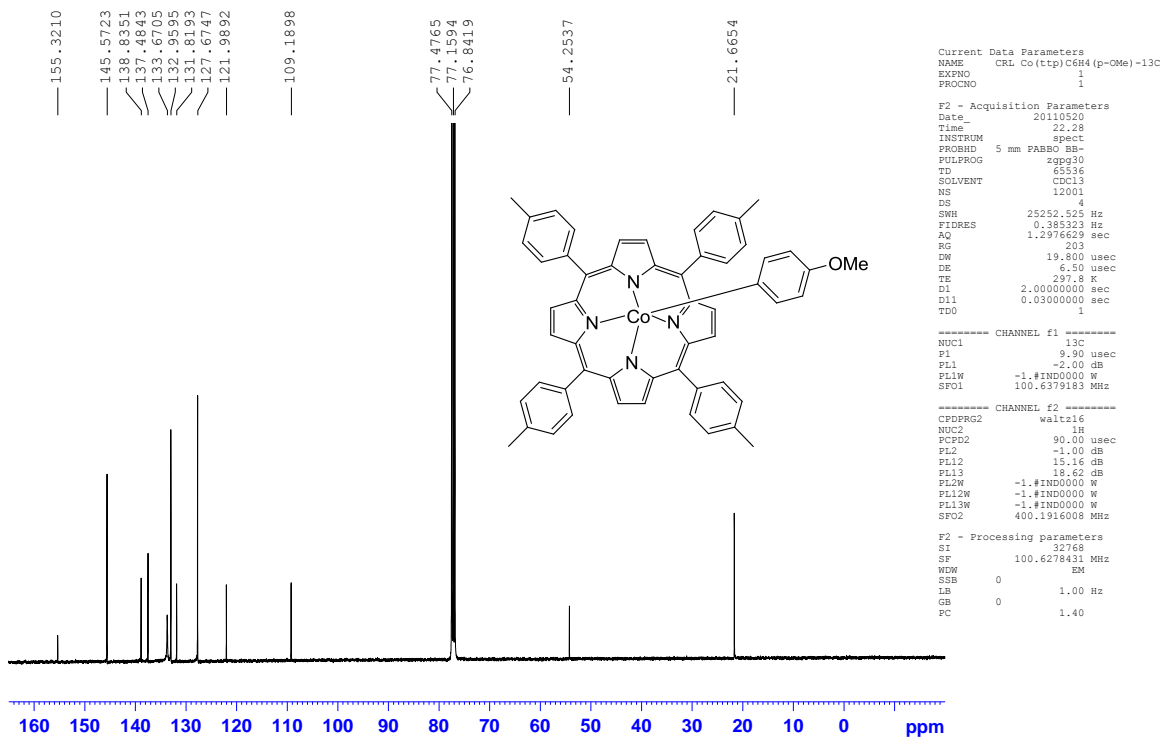
^{13}C NMR Spectrum of $\text{Co}^{\text{III}}(\text{t}_4\text{-Clpp})\text{Ph}$ (**3d**) (CDCl_3)



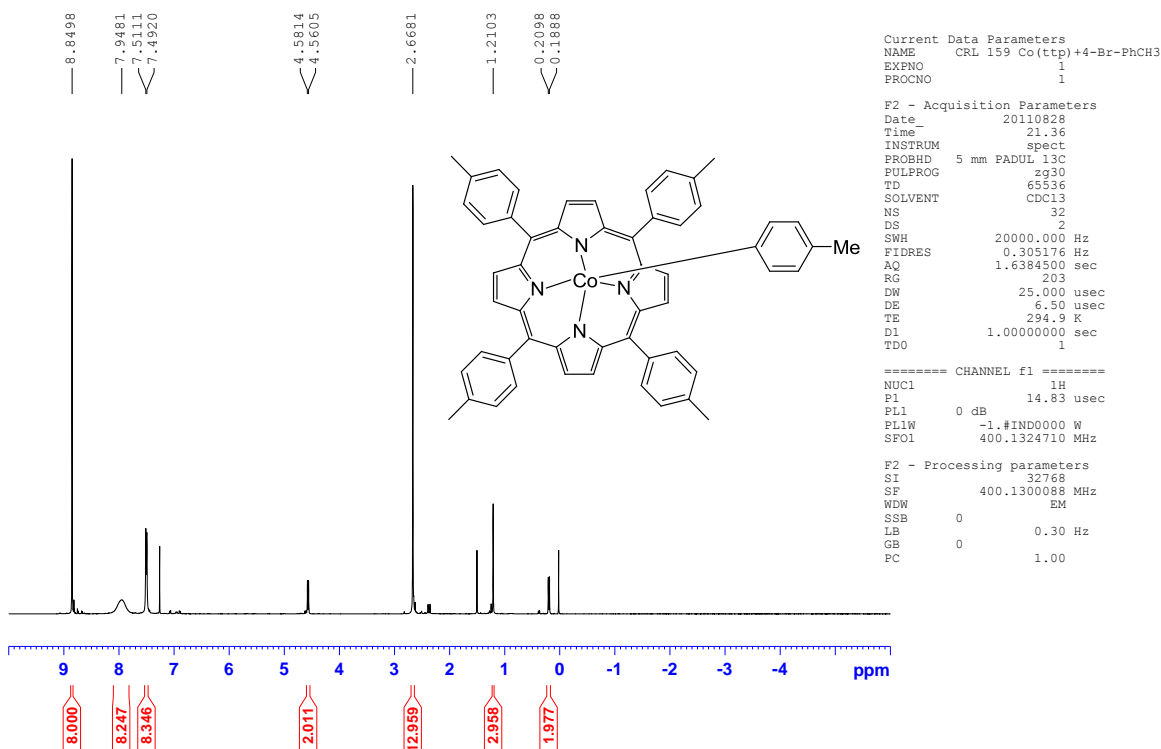
¹H NMR Spectrum of Co^{III}(ttp)C₆H₄(*p*-OMe) (**3e**) (CDCl₃)



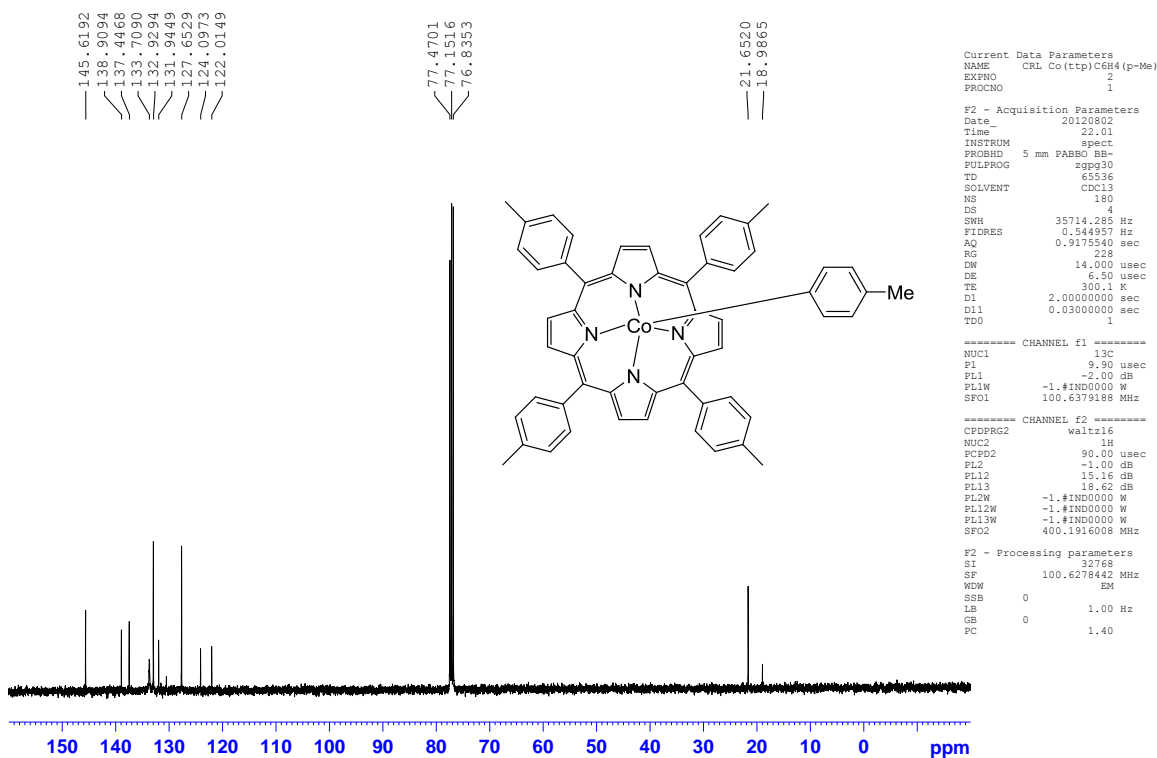
¹³C NMR Spectrum of Co^{III}(ttp)C₆H₄(*p*-OMe) (**3e**) (CDCl₃)



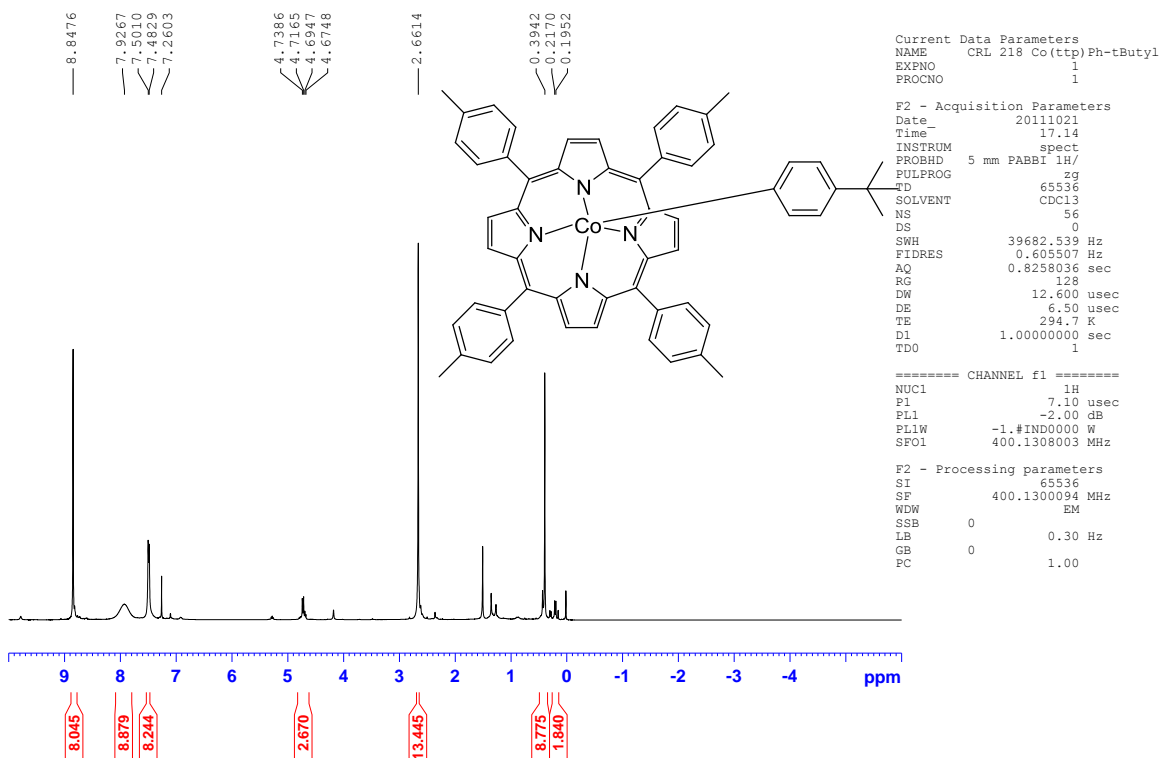
¹H NMR Spectrum of Co^{III}(ttp)C₆H₄(*p*-Me) (**3f**) (CDCl₃)



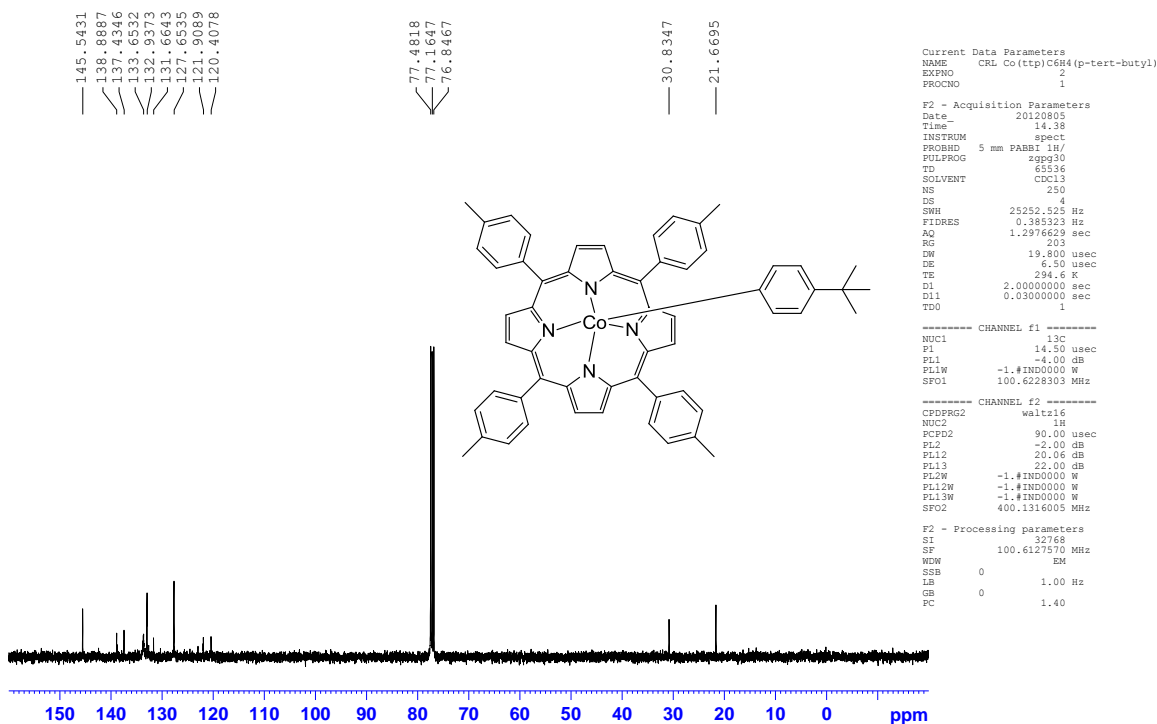
¹³C NMR Spectrum of Co^{III}(tpp)C₆H₄(*p*-Me) (**3f**) (CDCl₃)



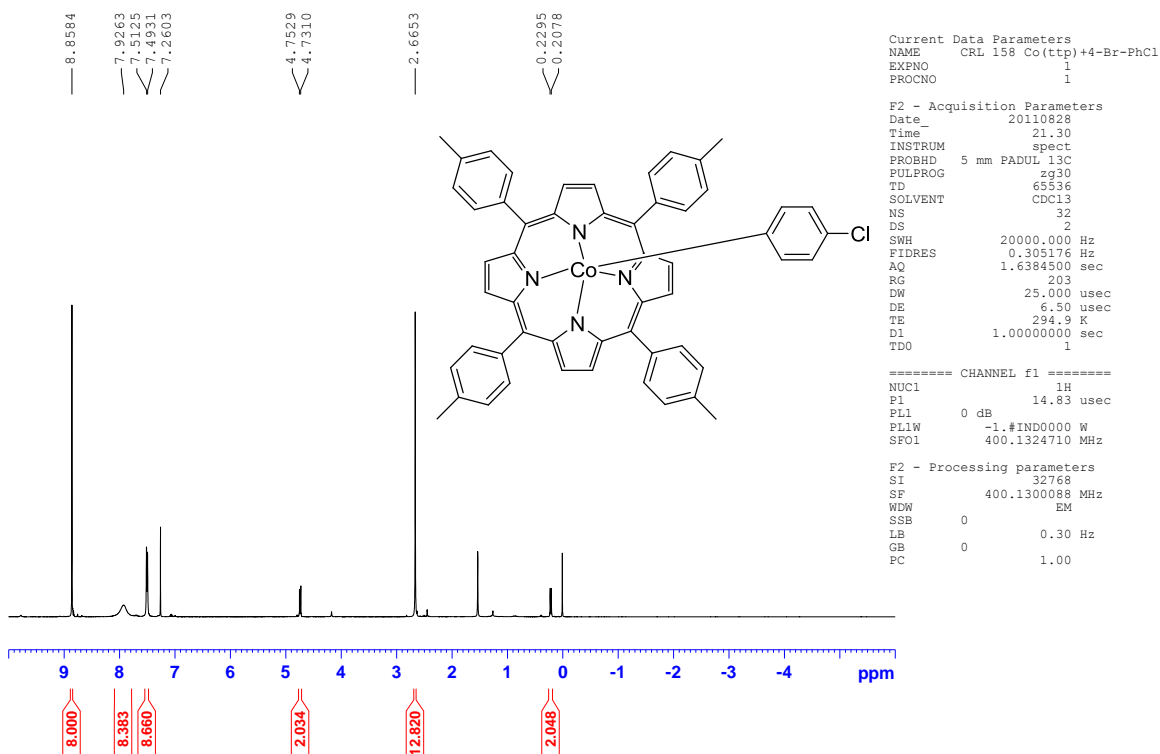
¹H NMR Spectrum of Co^{III}(ttp)C₆H₄(*p*-tert-butyl) (**3g**) (CDCl₃)



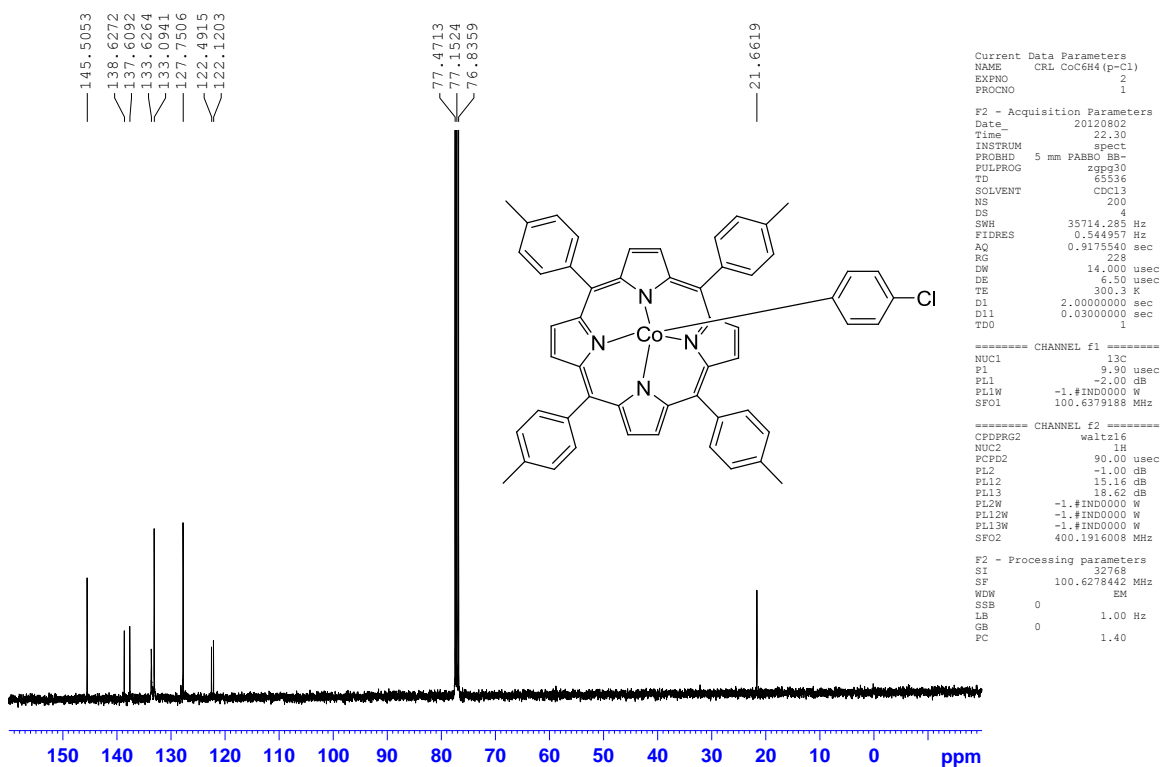
¹³C NMR Spectrum of Co^{III}(tp)C₆H₄(*p*-tert-butyl) (**3g**) (CDCl₃)



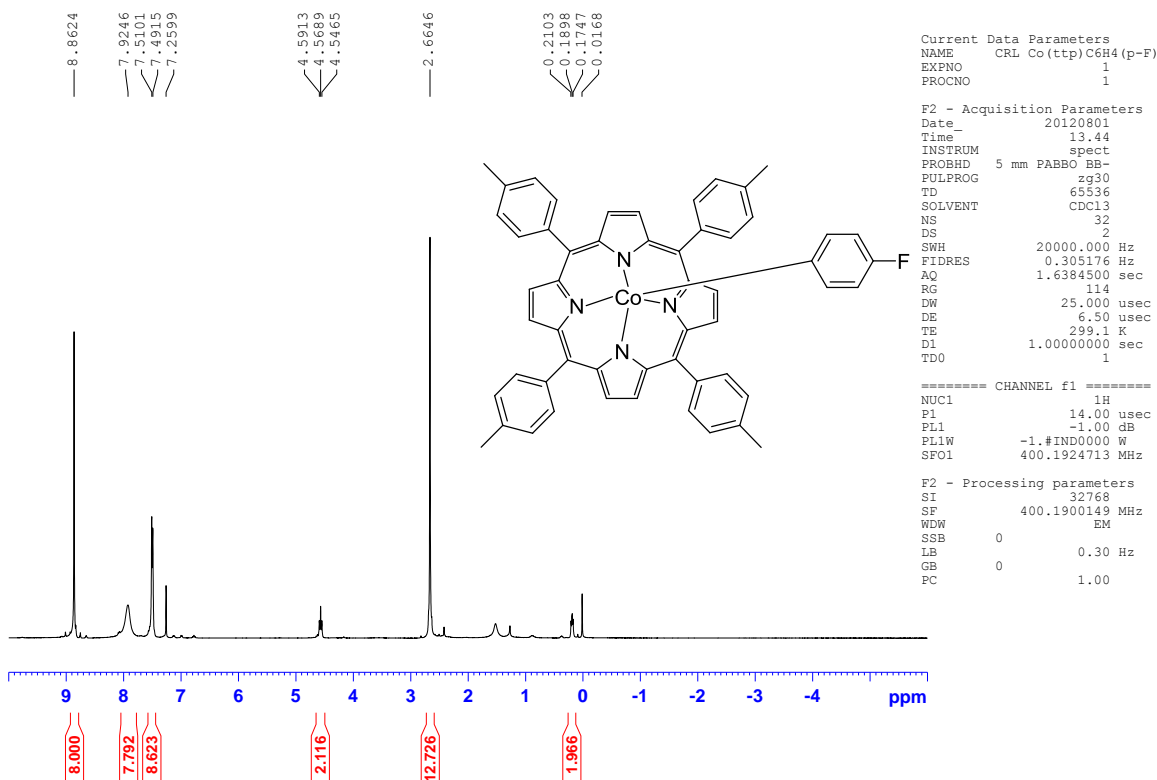
¹H NMR Spectrum of Co^{III}(ttp)C₆H₄(*p*-Cl) (**3h**) (CDCl₃)



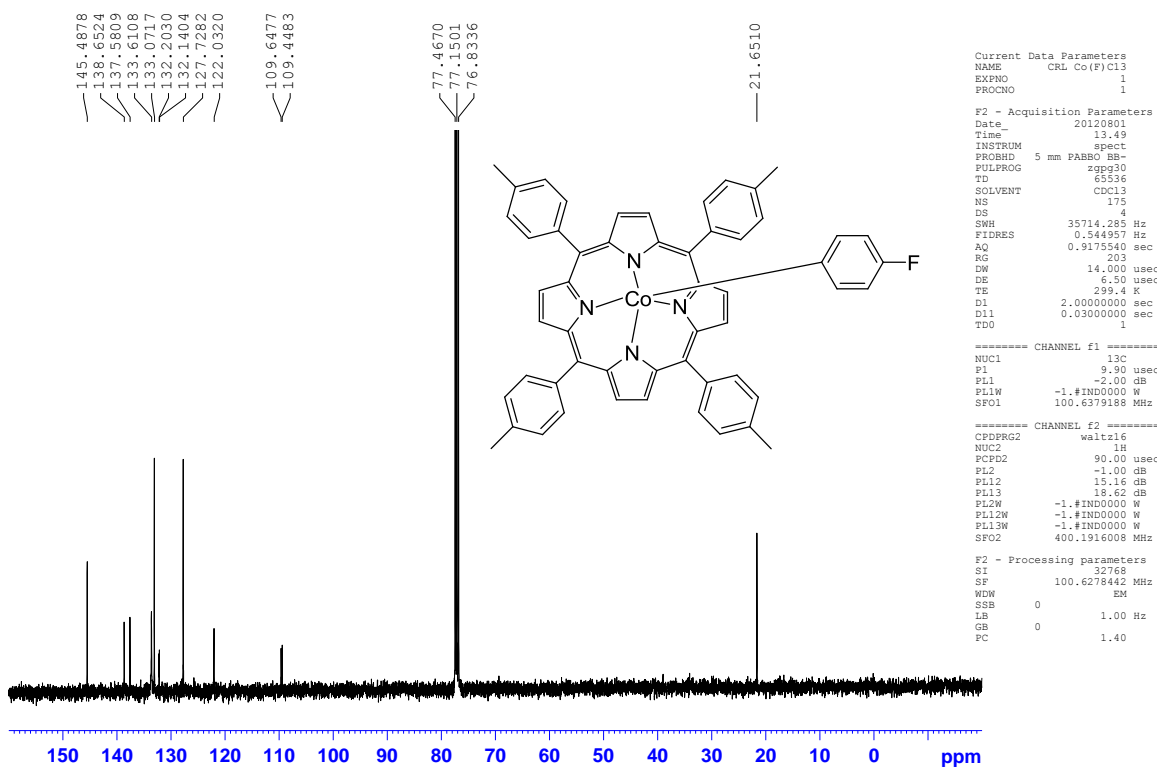
¹³C NMR Spectrum of Co^{III}(tpp)C₆H₄(*p*-Cl) (**3h**) (CDCl₃)



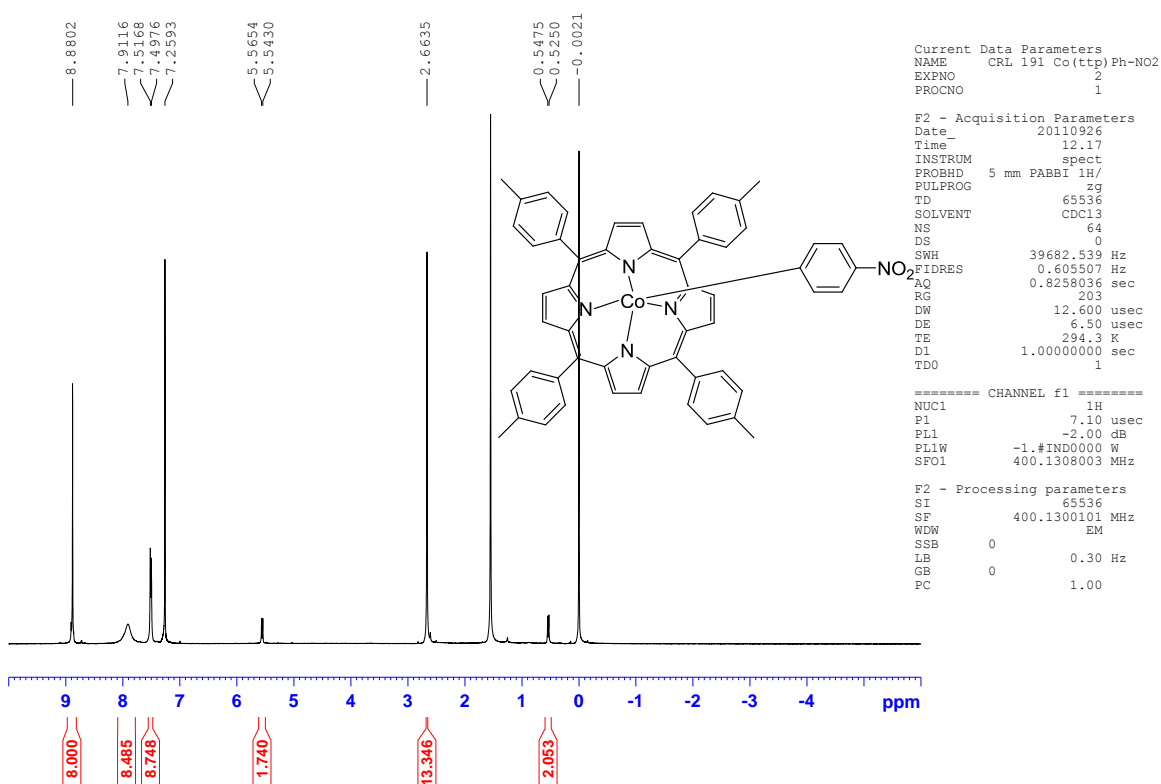
^1H NMR Spectrum of $\text{Co}^{\text{III}}(\text{ttp})\text{C}_6\text{H}_4(p\text{-F})$ (**3i**) (CDCl_3)



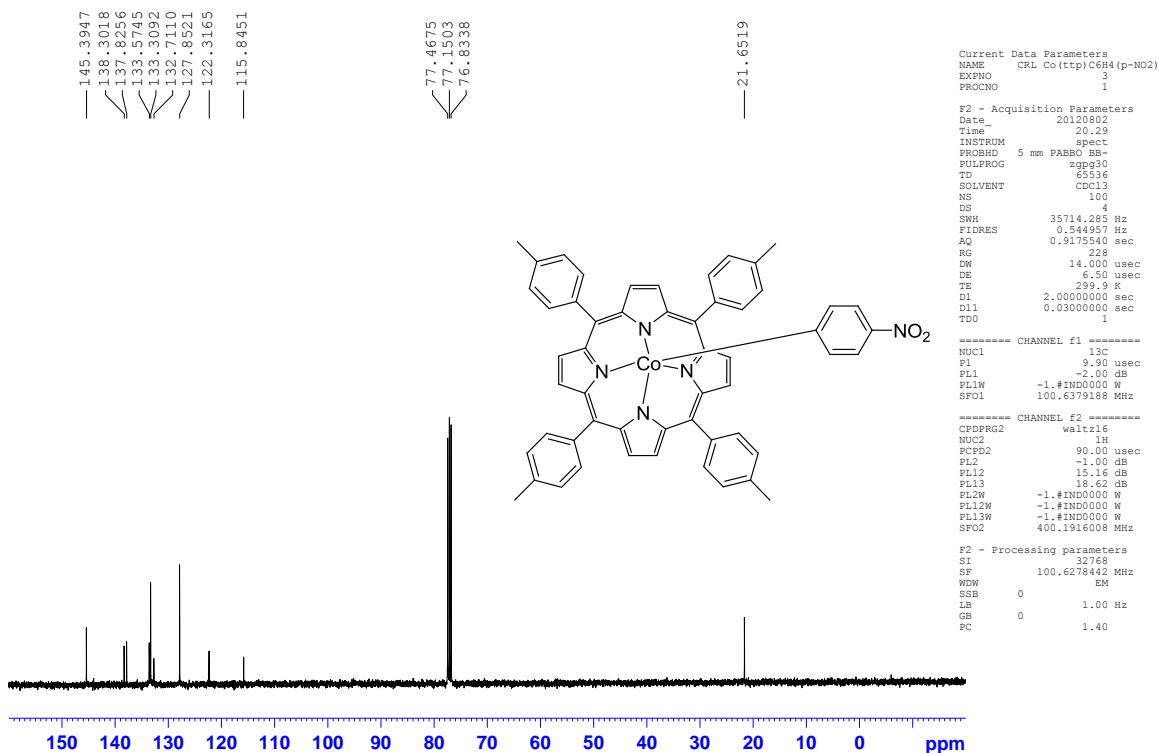
^{13}C NMR Spectrum of $\text{Co}^{\text{III}}(\text{ttp})\text{C}_6\text{H}_4(p\text{-F})$ (**3i**) (CDCl_3)



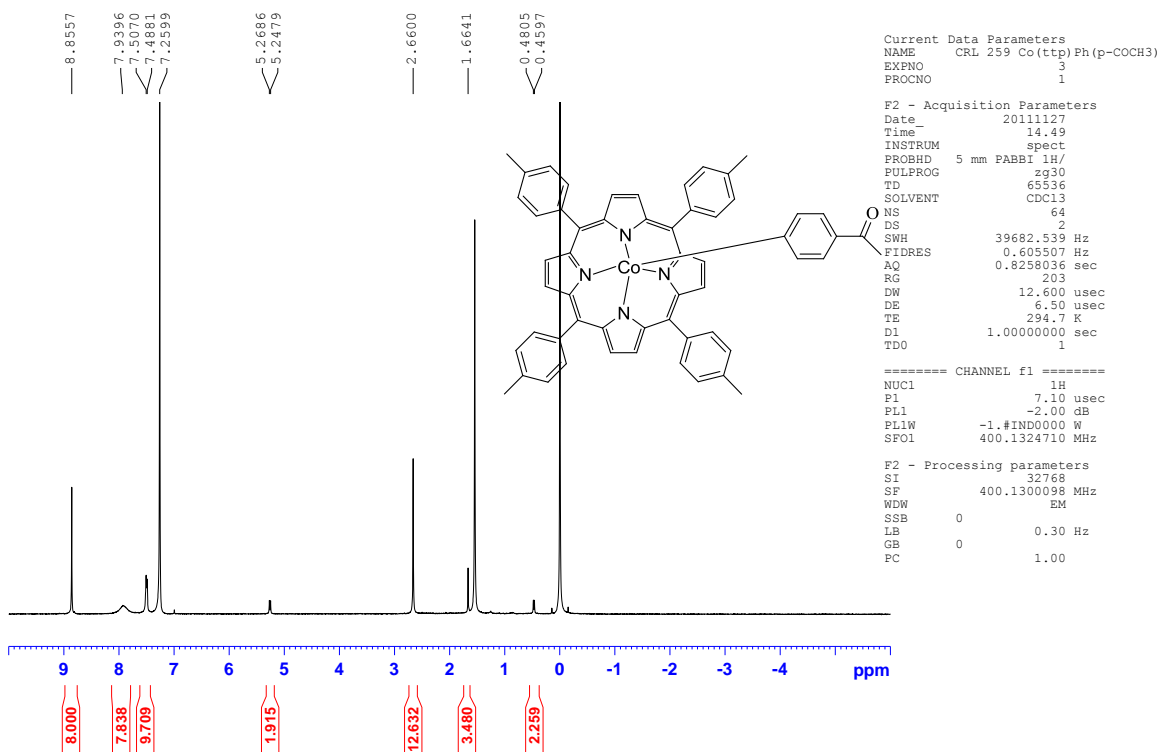
¹H NMR Spectrum of Co^{III}(ttp)C₆H₄(*p*-NO₂) (**3j**) (CDCl₃)



¹³C NMR Spectrum of Co^{III}(ttp)C₆H₄(*p*-NO₂) (**3j**) (CDCl₃)



¹H NMR Spectrum of Co^{III}(ttp)C₆H₄(*p*-C(O)Me) (**3k**) (CDCl₃)



¹³C NMR Spectrum of Co^{III}(ttp)C₆H₄(*p*-C(O)Me) (**3k**) (CDCl₃)

