Supporting Information

Photochemical hydrogen production and cobaloximes: influence of cobalt axial *N*-ligand on the system stability

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H_2 Production

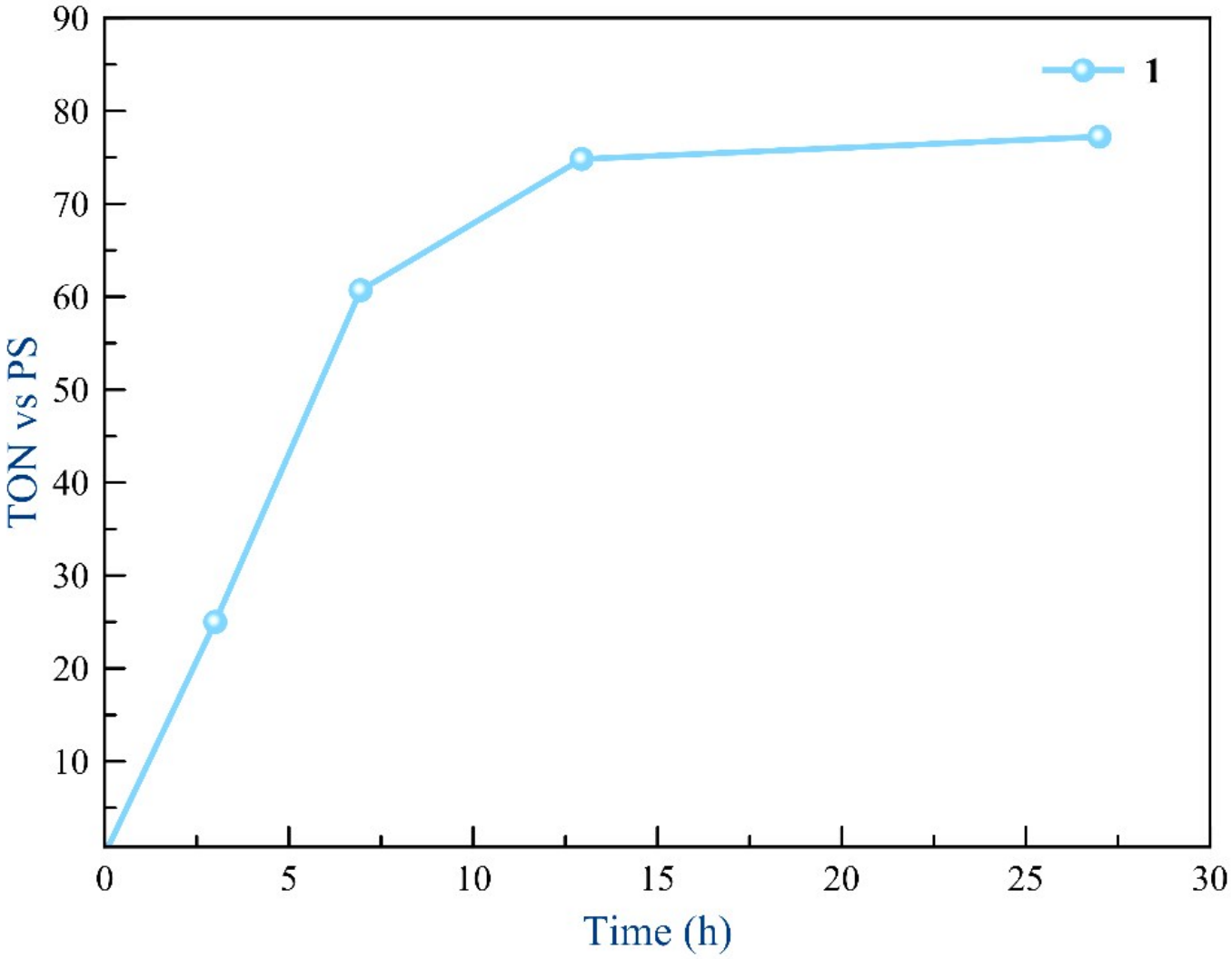

Figure S1. Plot of hydrogen production upon irradiation (λ> 440 nm) of solutions (1:1 acetonitrile/water) containing **PS** (4.0 x 10^{-5}M), **1** (4.9 × 10^{-4}M) and TEOA 5% v/v at pH 7.

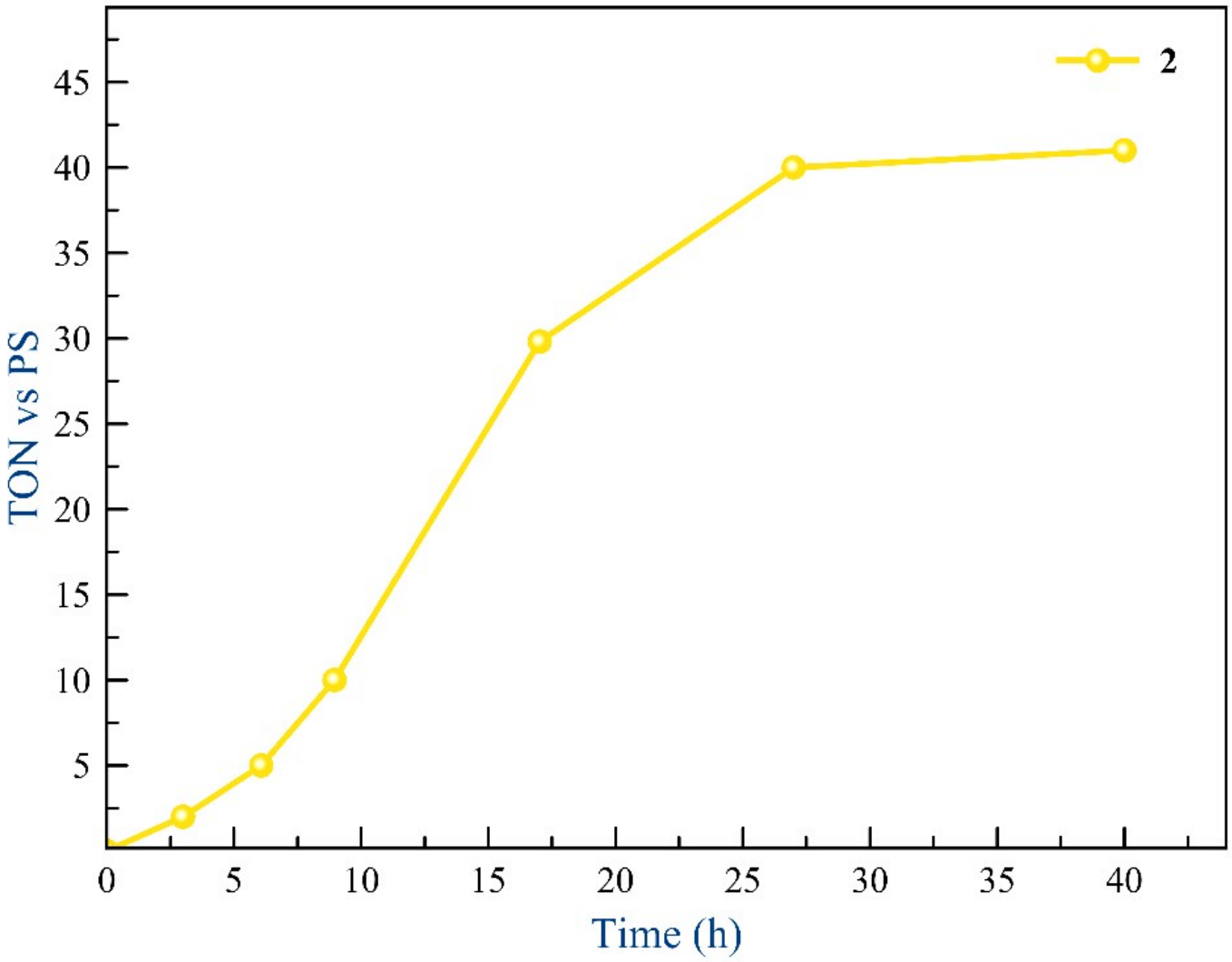

Figure S2. Plot of hydrogen production upon irradiation (λ> 440 nm) of solutions (1:1 acetonitrile/water) containing **PS** (4.0 x 10^{-5}M), **2** (4.9 × 10^{-4}M) and TEOA 5% v/v at pH 7.

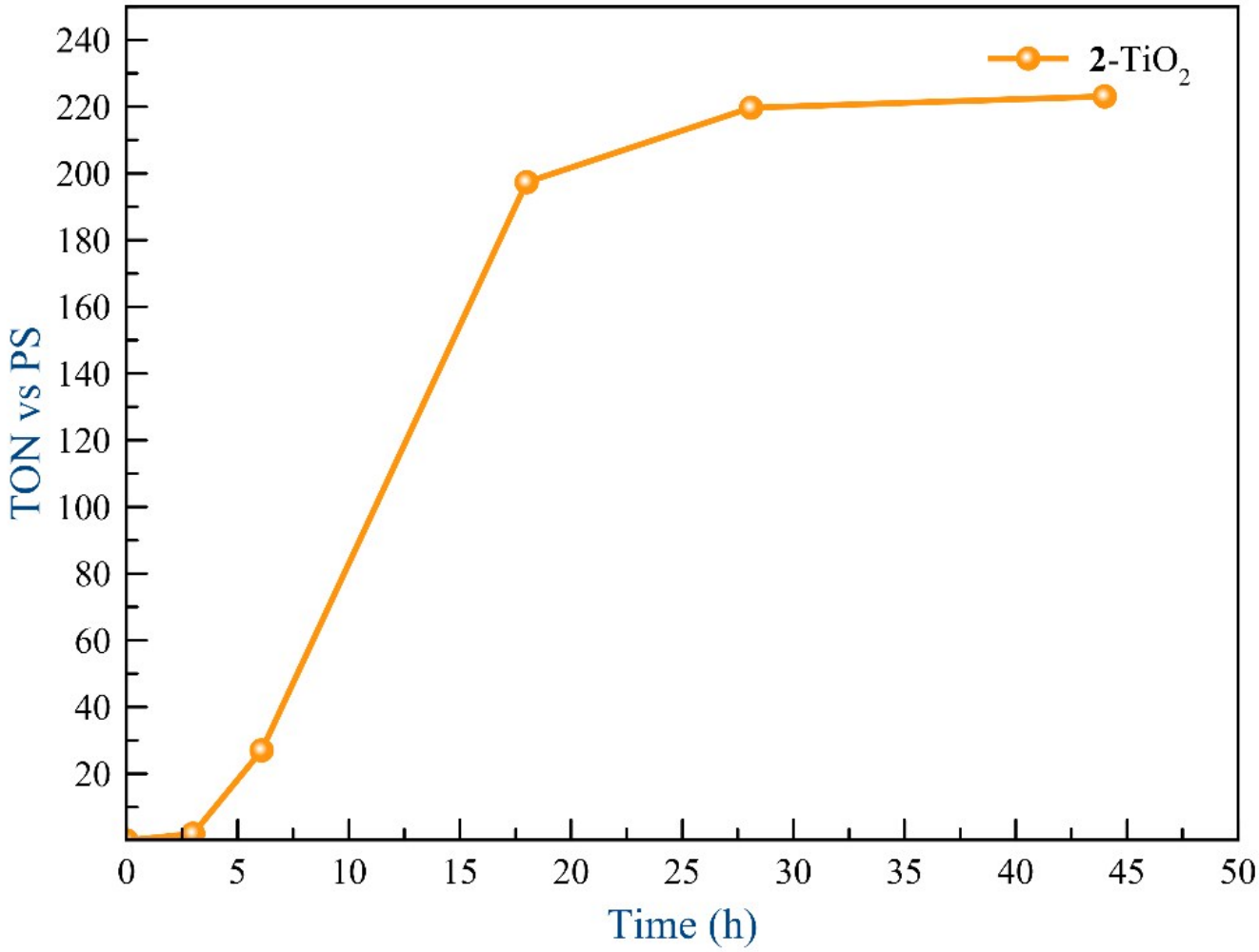

Figure S3. Plot of hydrogen production upon irradiation (λ> 440 nm) of solutions (1:1 acetonitrile/water) containing **PS** (4.0 x 10^{-5}M), **2** (4.9 × 10^{-4}M), TEOA 5% v/v and 10 mgr TiO_2 at pH 7.

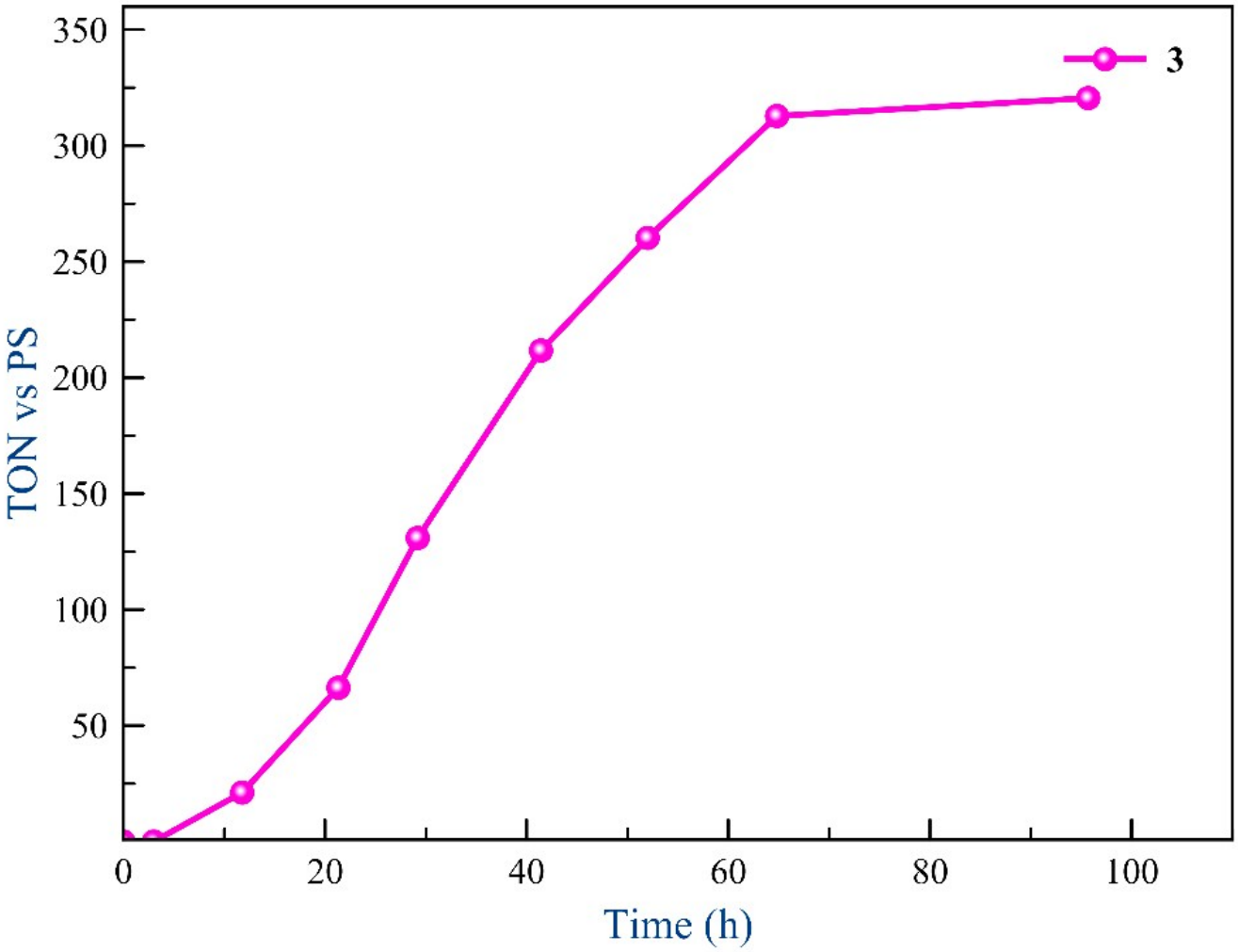

Figure S4. Plot of hydrogen production upon irradiation (λ> 440 nm) of solutions (1:1 acetonitrile/water) containing **PS** (4.0 x 10^{-5}M), **3** (4.9 × 10^{-4}M) and TEOA 5% v/v at pH 7.

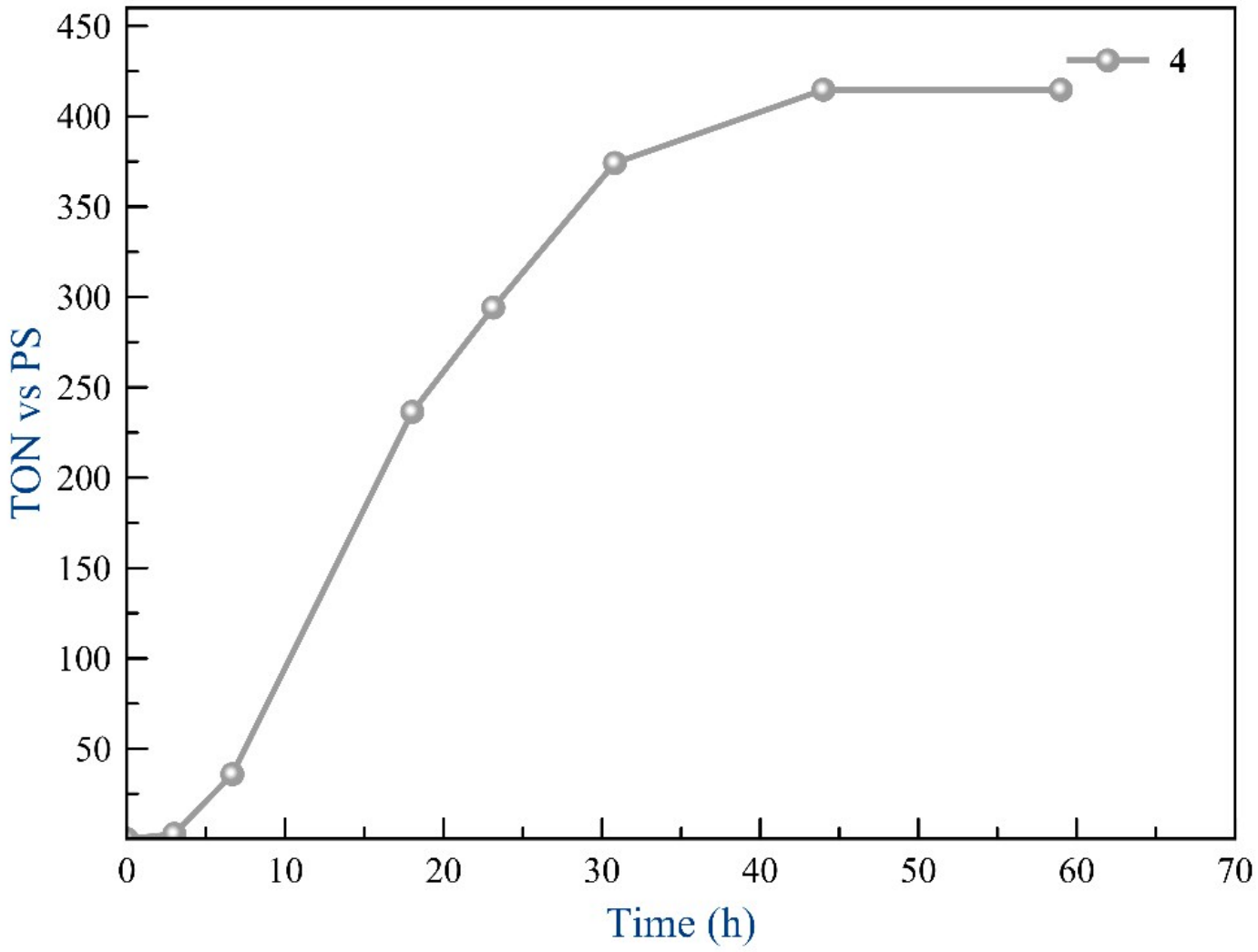

Figure S5. Plot of hydrogen production upon irradiation (λ> 440 nm) of solutions (1:1 acetonitrile/water) containing **PS** (4.0 x 10^{-5}M), **4** (4.9 × 10^{-4}M) and TEOA 5% v/v at pH 7.

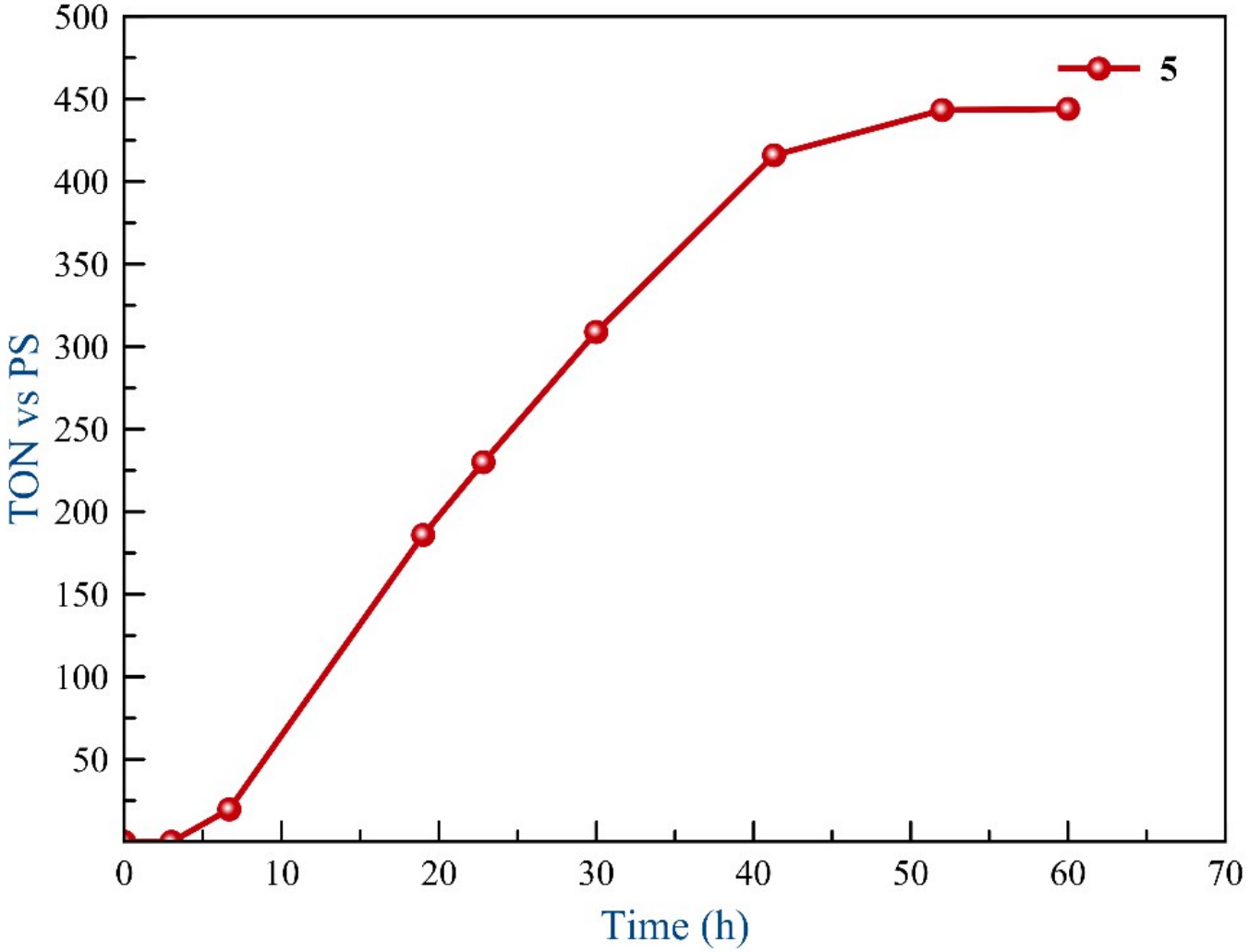

Figure S6. Plot of hydrogen production upon irradiation (λ> 440 nm) of solutions (1:1 acetonitrile/water) containing **PS** (4.0 x 10^{-5}M), **5** (4.9 × 10^{-4}M) and TEOA 5% v/v at pH 7.

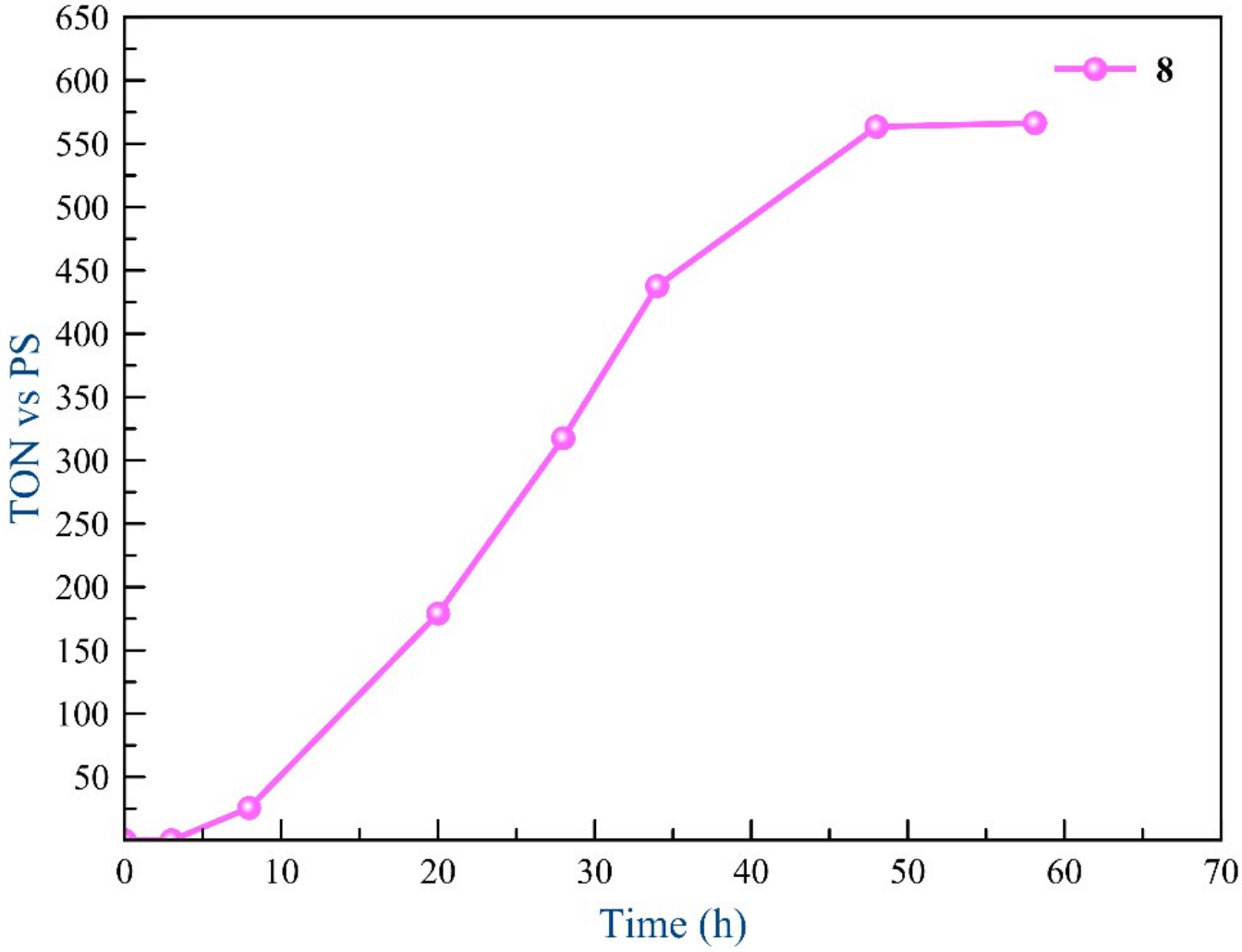

Figure S7. Plot of hydrogen production upon irradiation (λ> 440 nm) of solutions (1:1 acetonitrile/water) containing **PS** (4.0 x 10^{-5}M), **8** (4.9 × 10^{-4}M) and TEOA 5% v/v at pH 7.

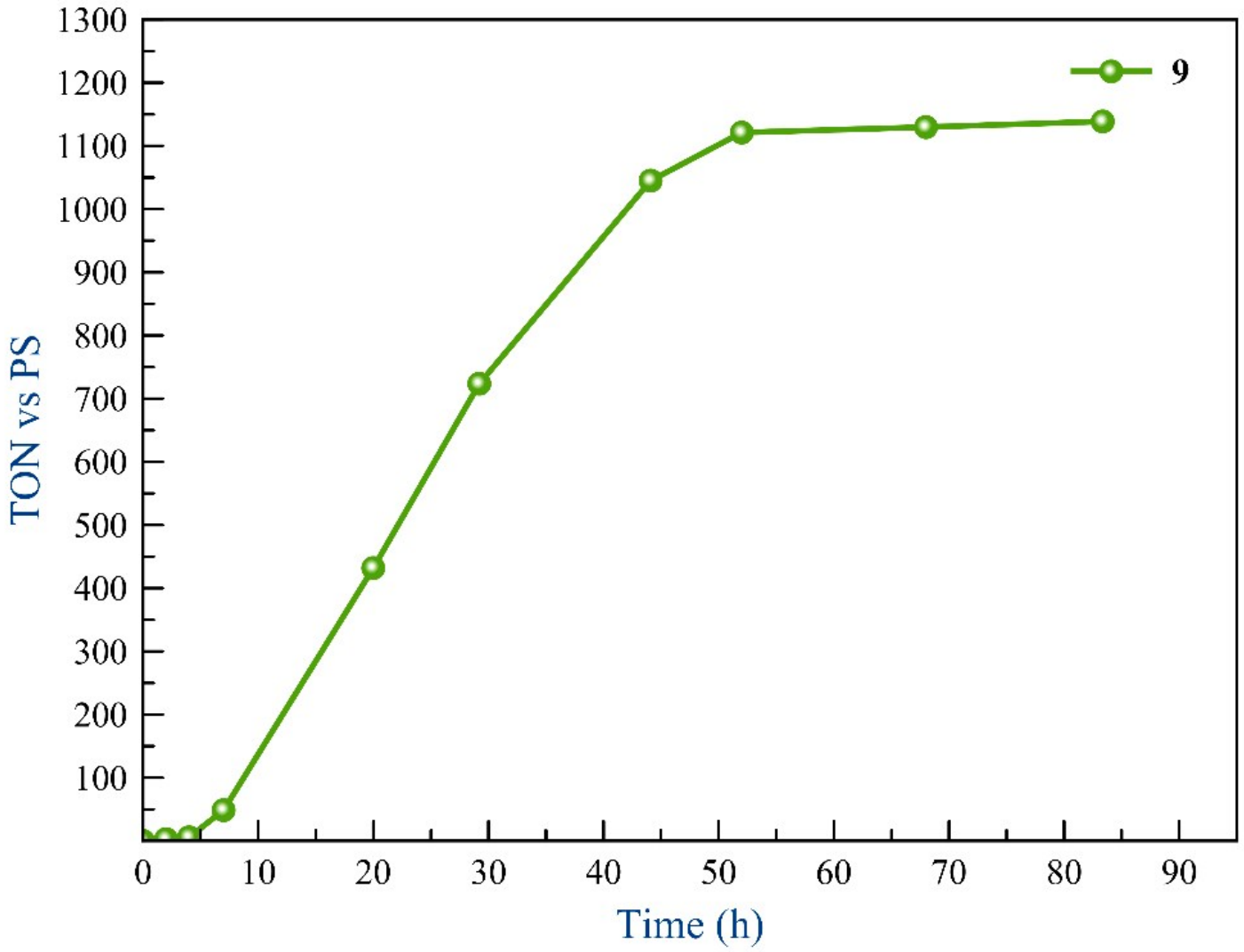

Figure S8. Plot of hydrogen production upon irradiation (λ> 440 nm) of solutions (1:1 acetonitrile/water) containing **PS** (4.0 x 10^{-5}M), **9** (4.9 × 10^{-4}M) and TEOA 5% v/v at pH 7.

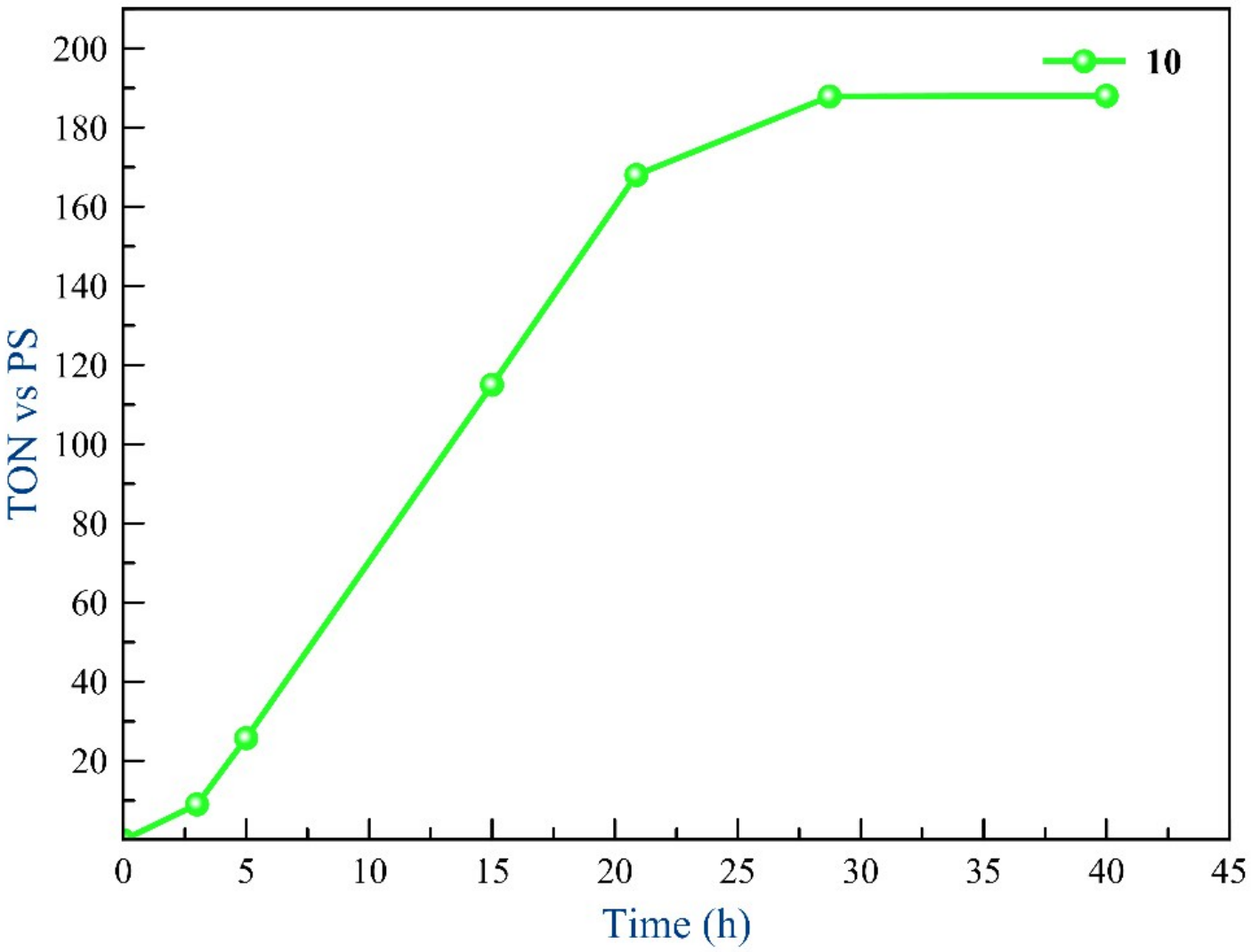

Figure S9. Plot of hydrogen production upon irradiation (λ> 440 nm) of solutions (1:1 acetonitrile/water) containing **PS** (4.0 x 10^{-5}M), **10** (4.9 × 10^{-4}M) and TEOA 5% v/v at pH 7.

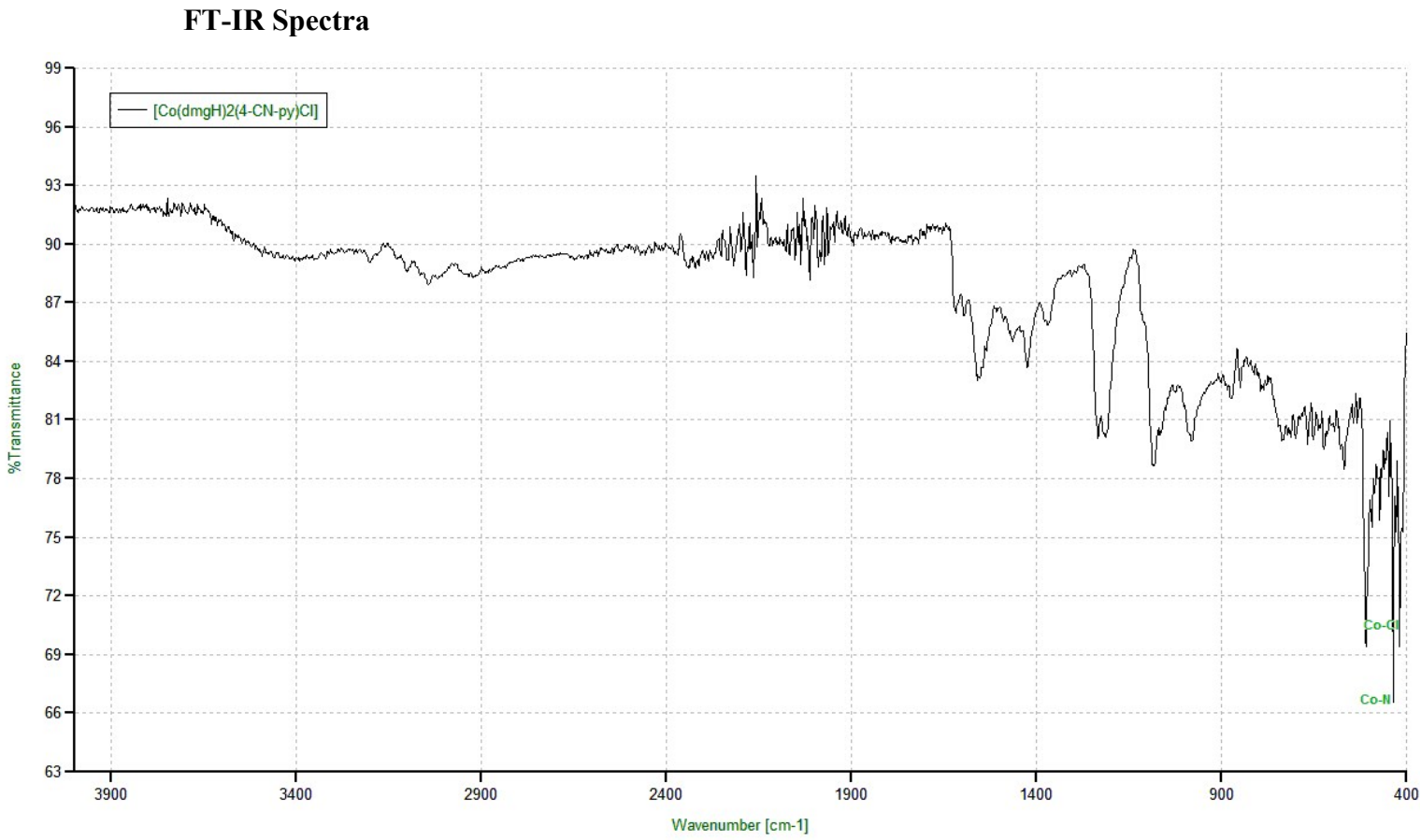

Figure S10. FT-IR spectrum of complex **1**.

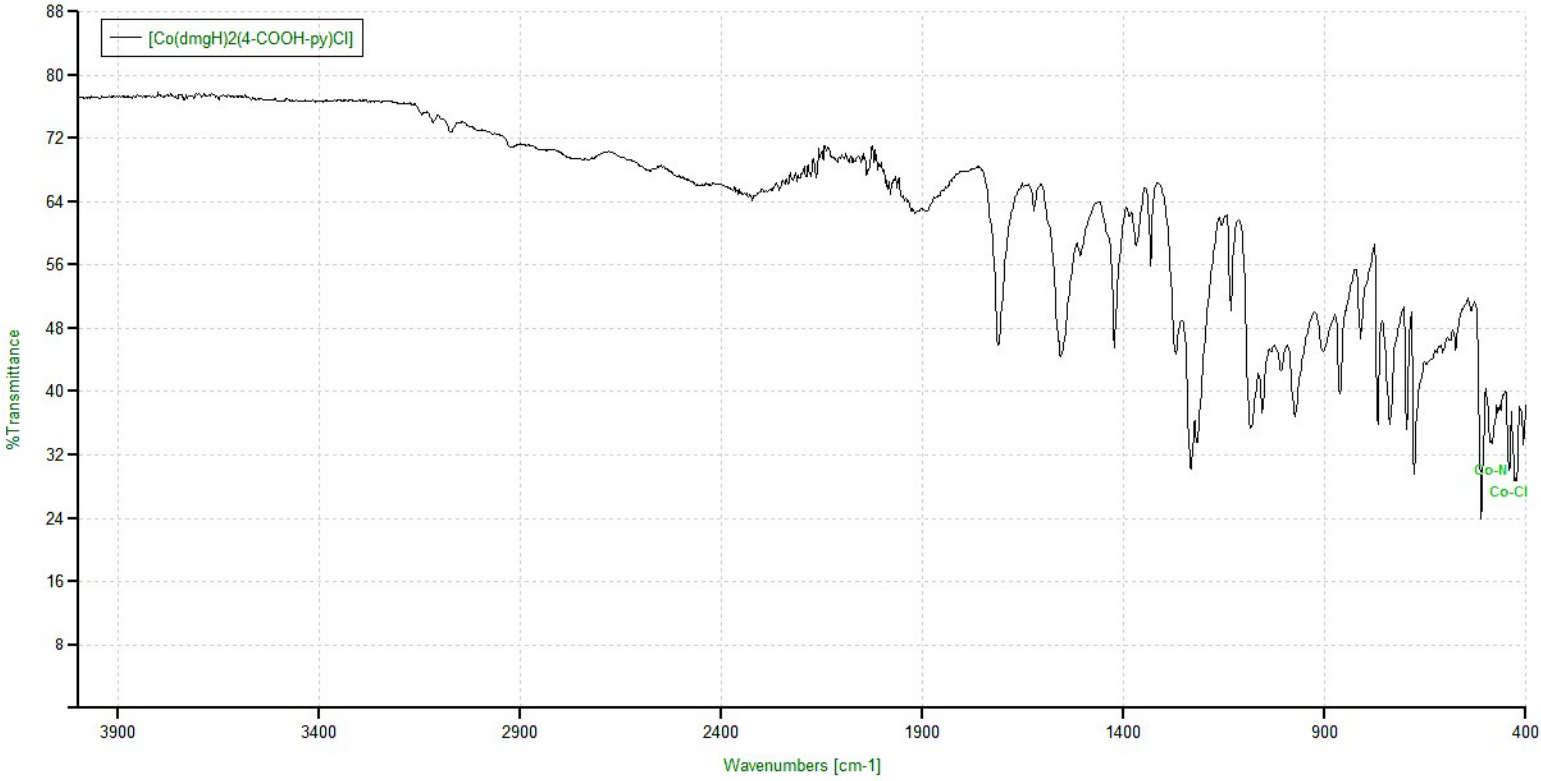

Figure S11. FT-IR spectrum of complex **2**.

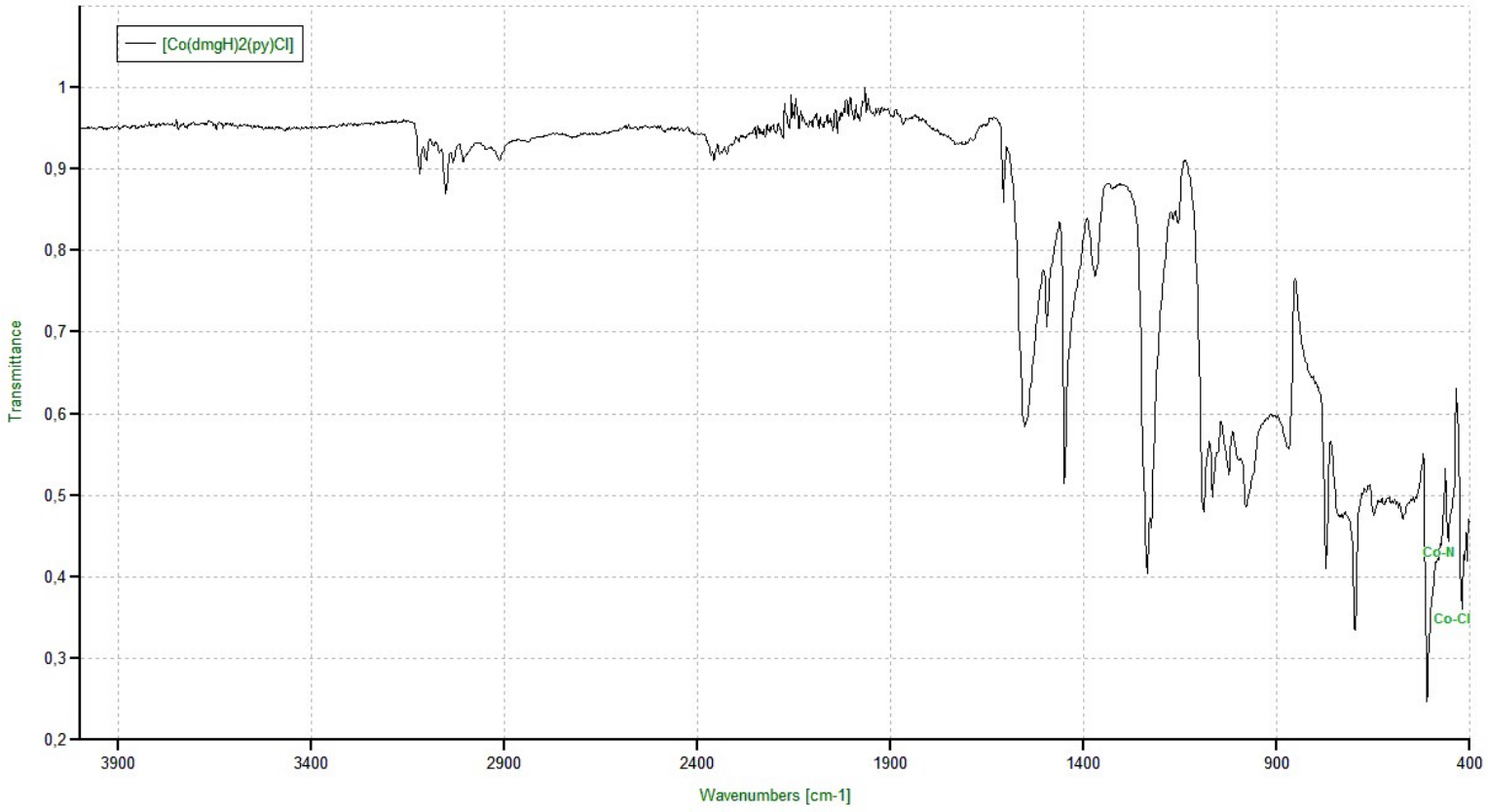

Figure S12. FT-IR spectrum of complex **3**.

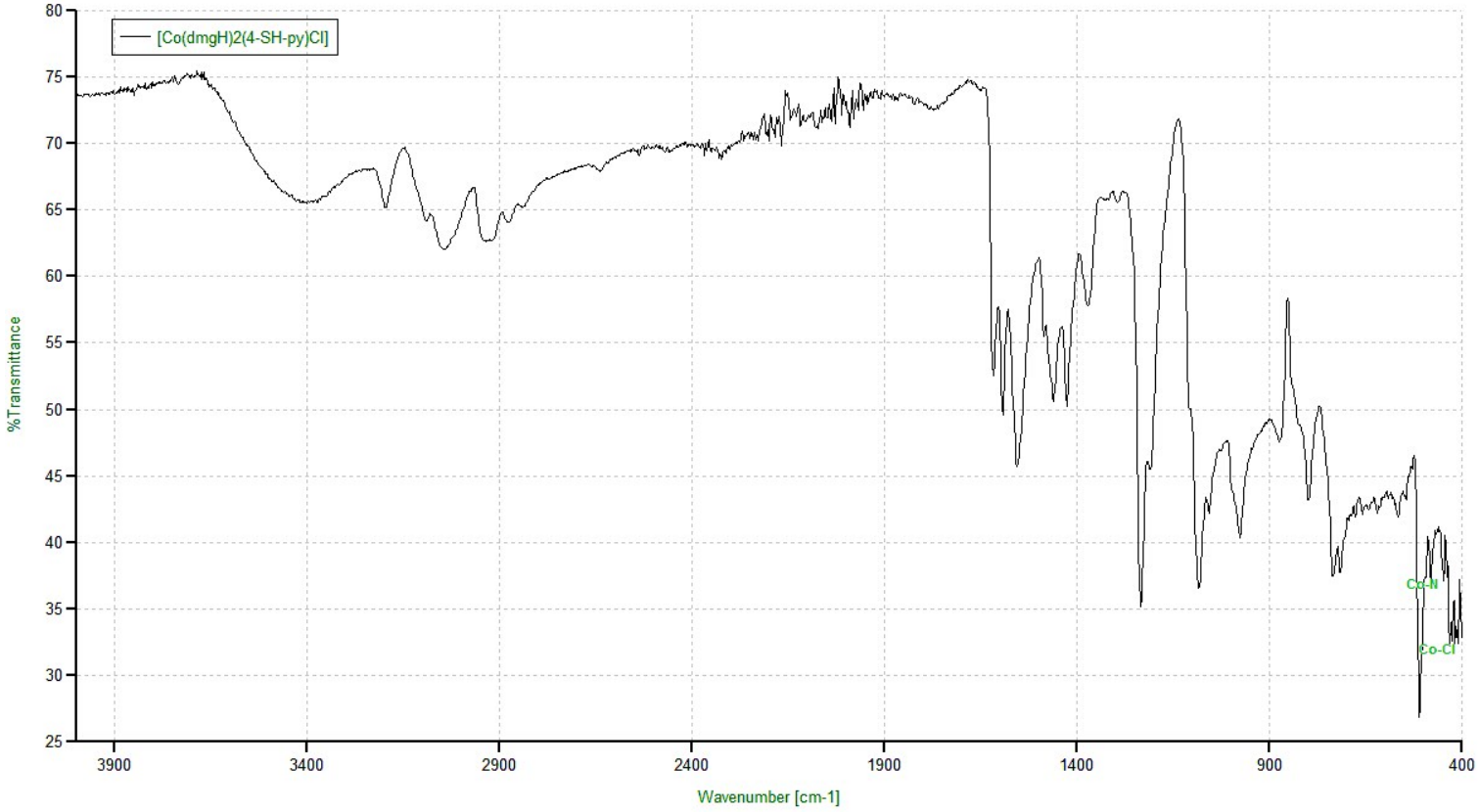

Figure S13. FT-IR spectrum of complex **4**.

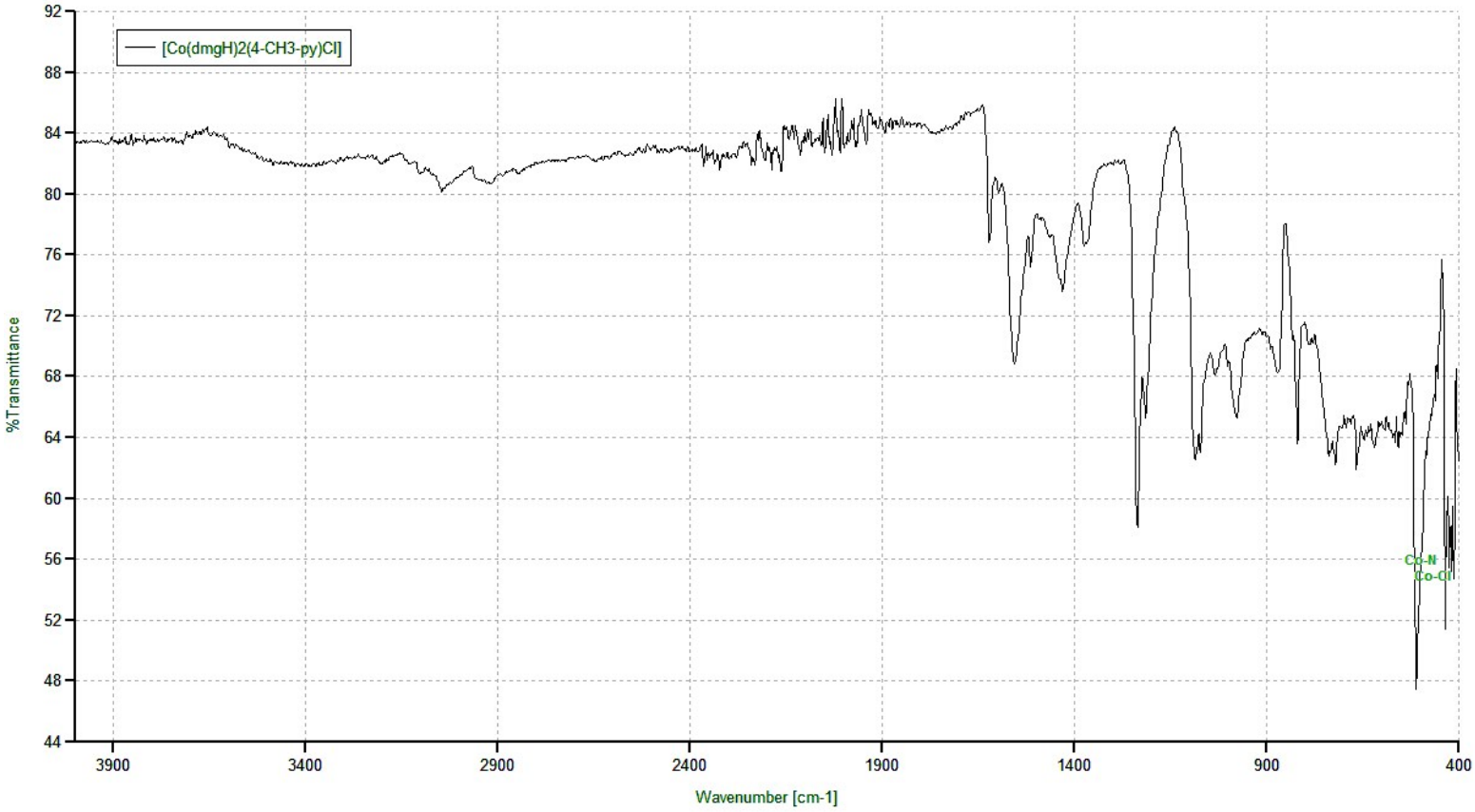

Figure S14. FT-IR spectrum of complex **5**.

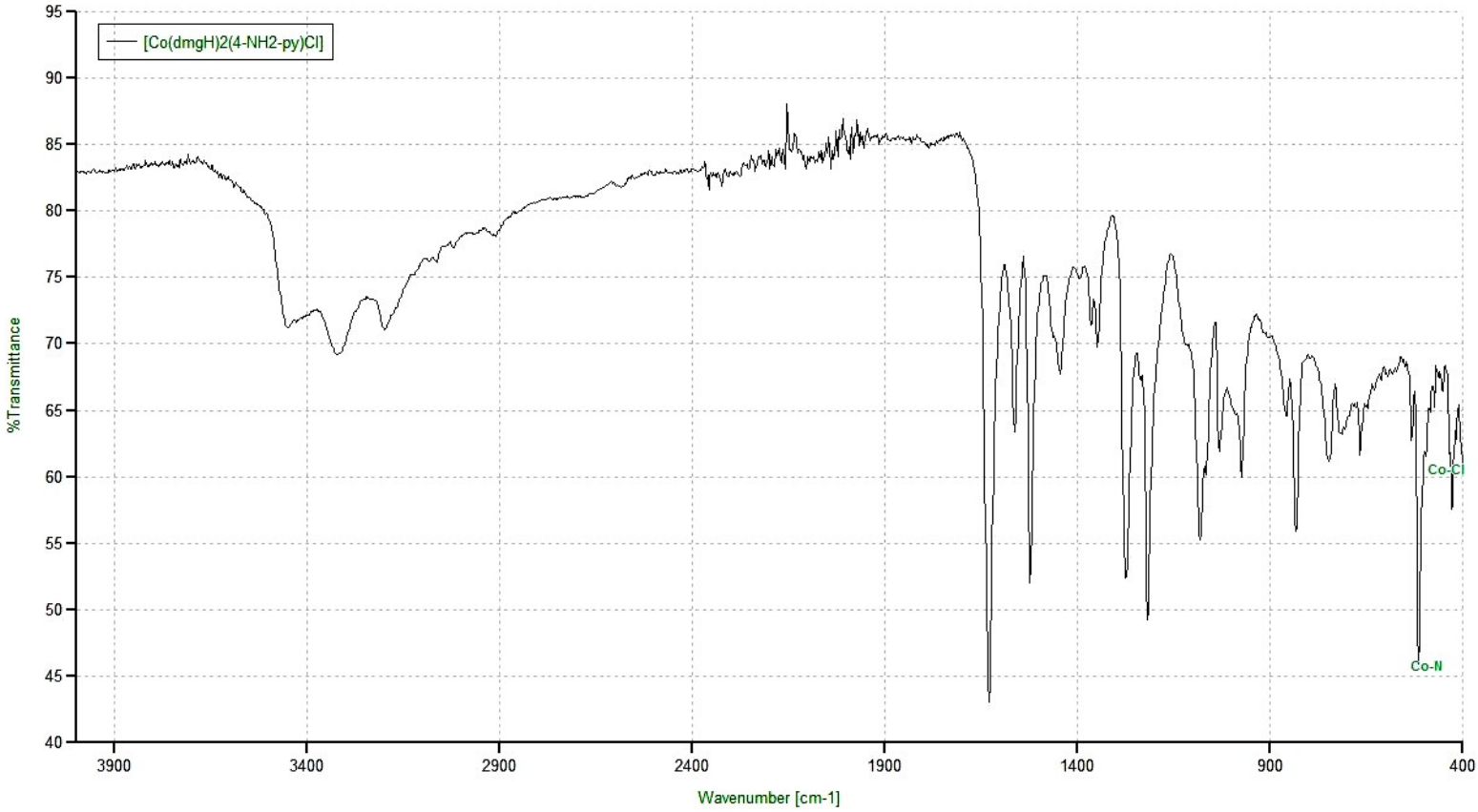

Figure S15. FT-IR spectrum of complex **6**.

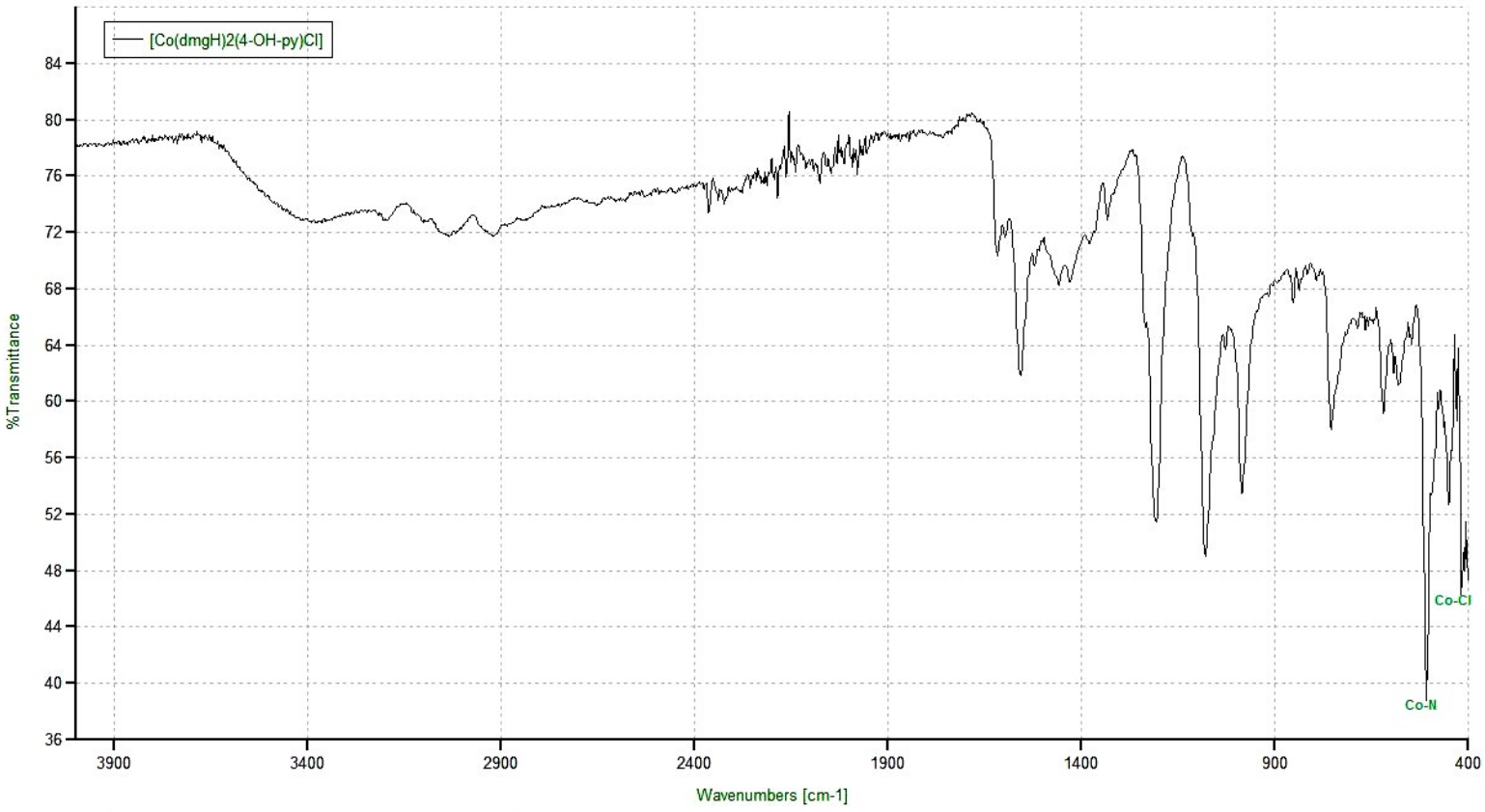

Figure S16. FT-IR spectrum of complex **7**.

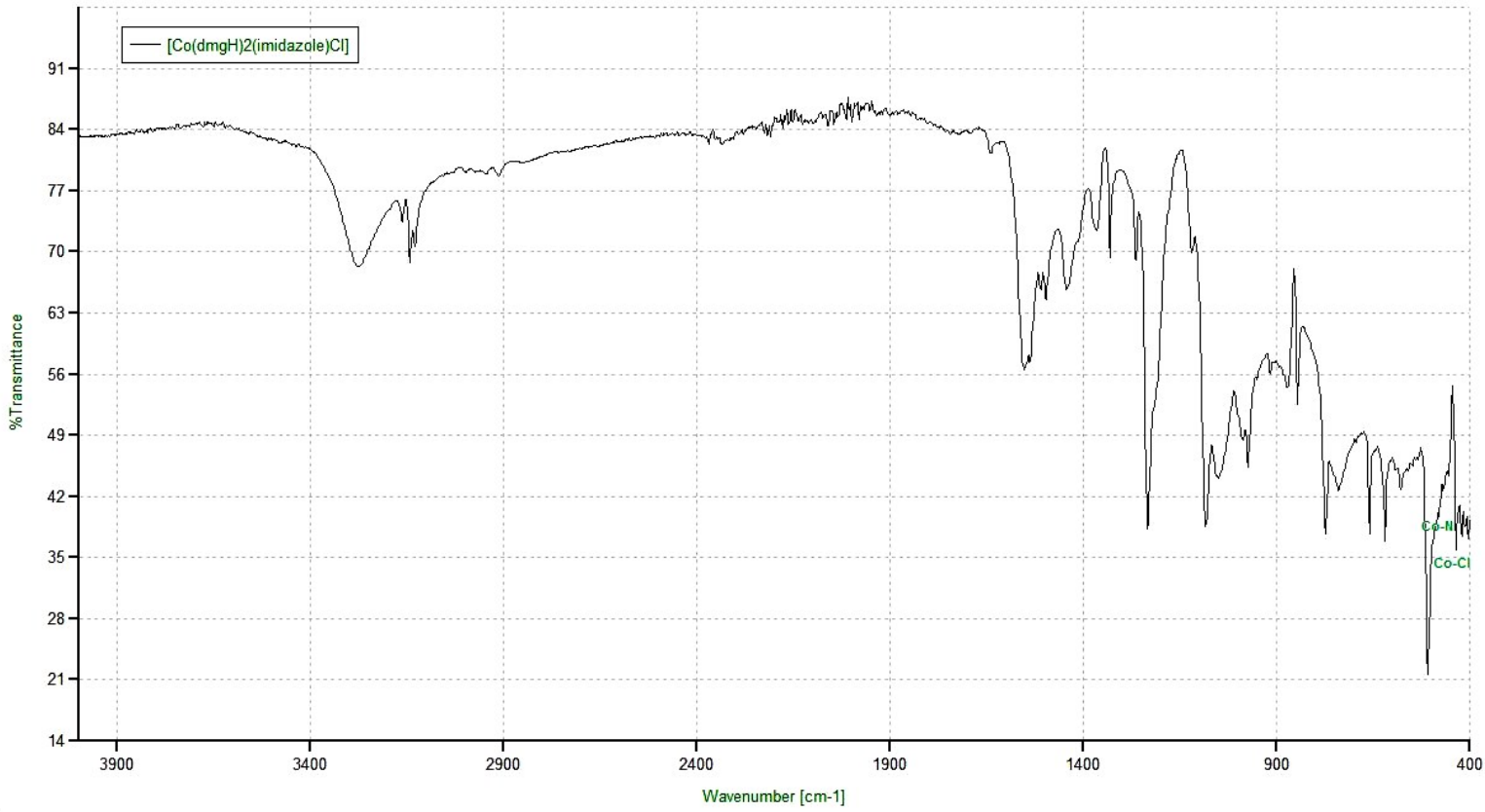

Figure S17. FT-IR spectrum of complex **8**.

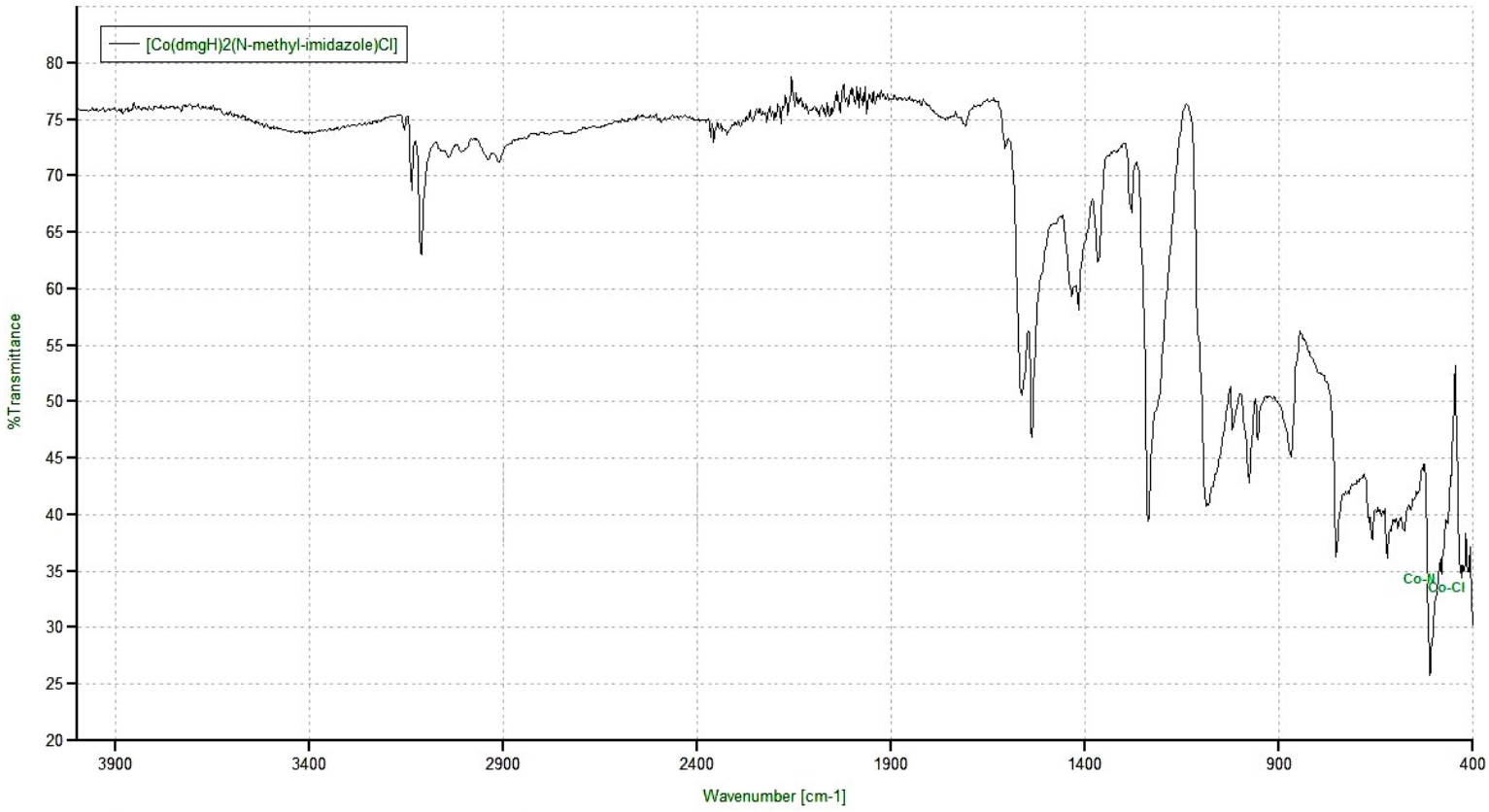

Figure S18. FT-IR spectrum of complex **9**.

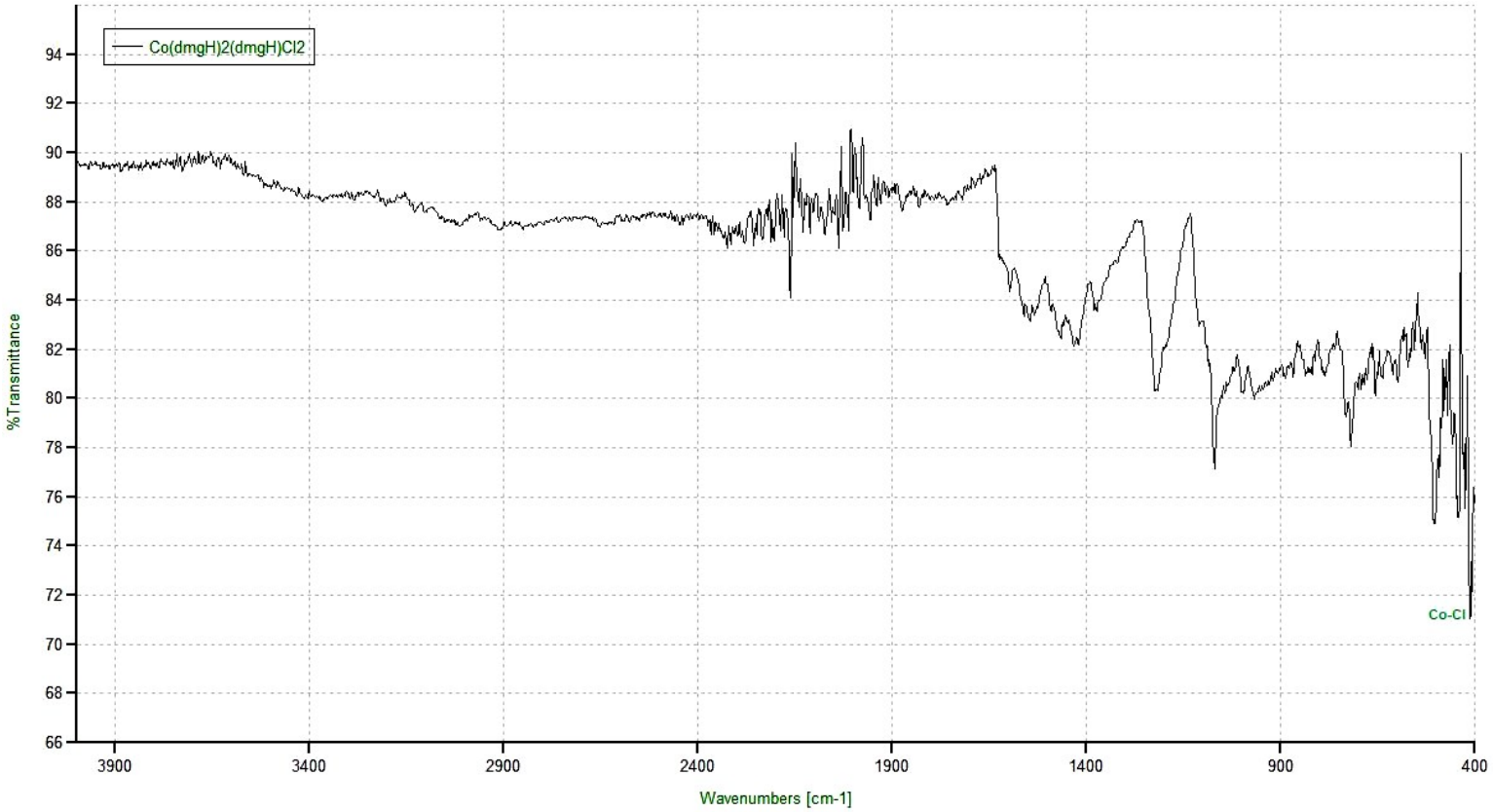

Figure S19. FT-IR spectrum of complex **10**.

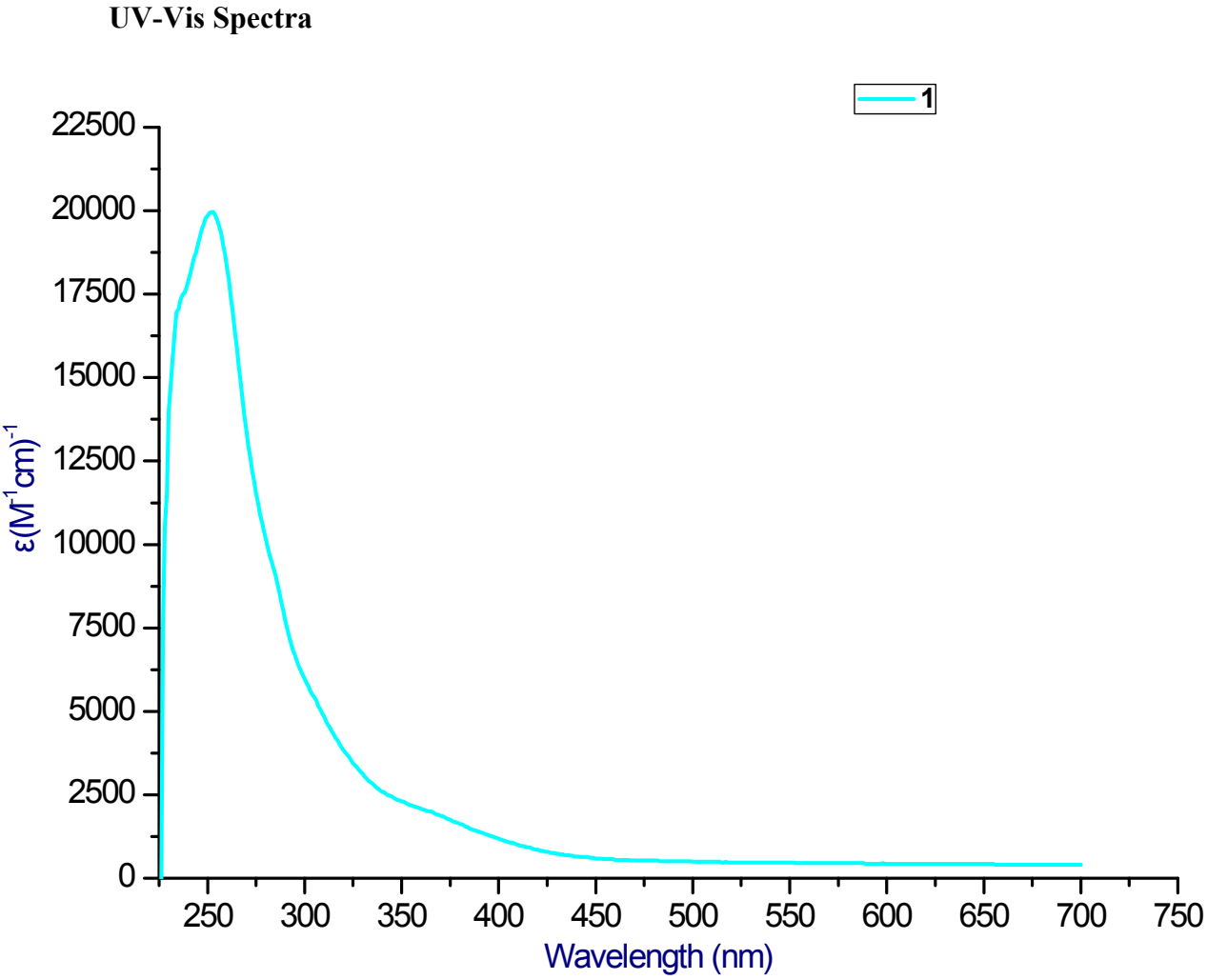

Figure S20. UV-Vis spectrum of complex **1** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.

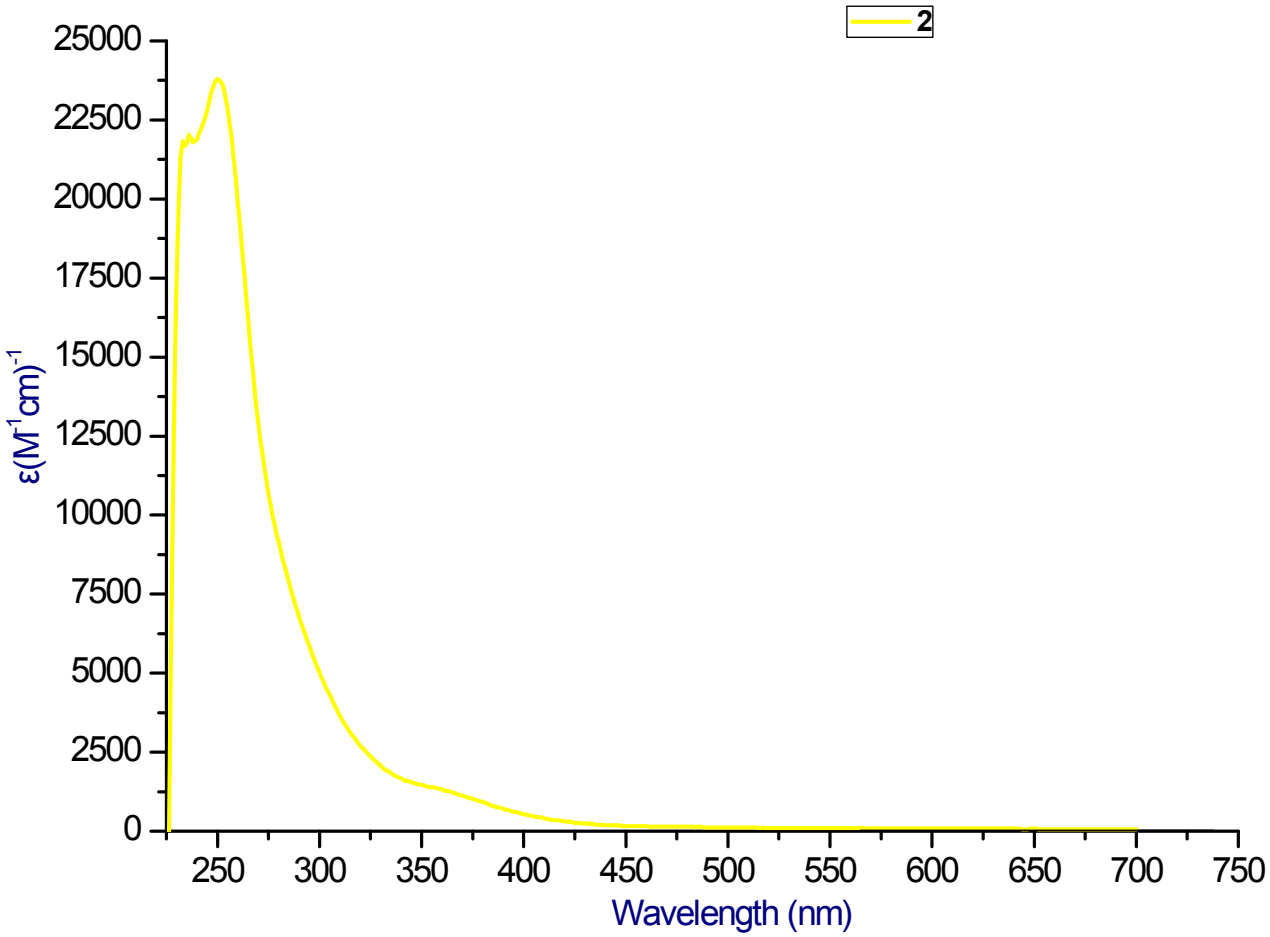

Figure S21. UV-Vis spectrum of complex **2** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.

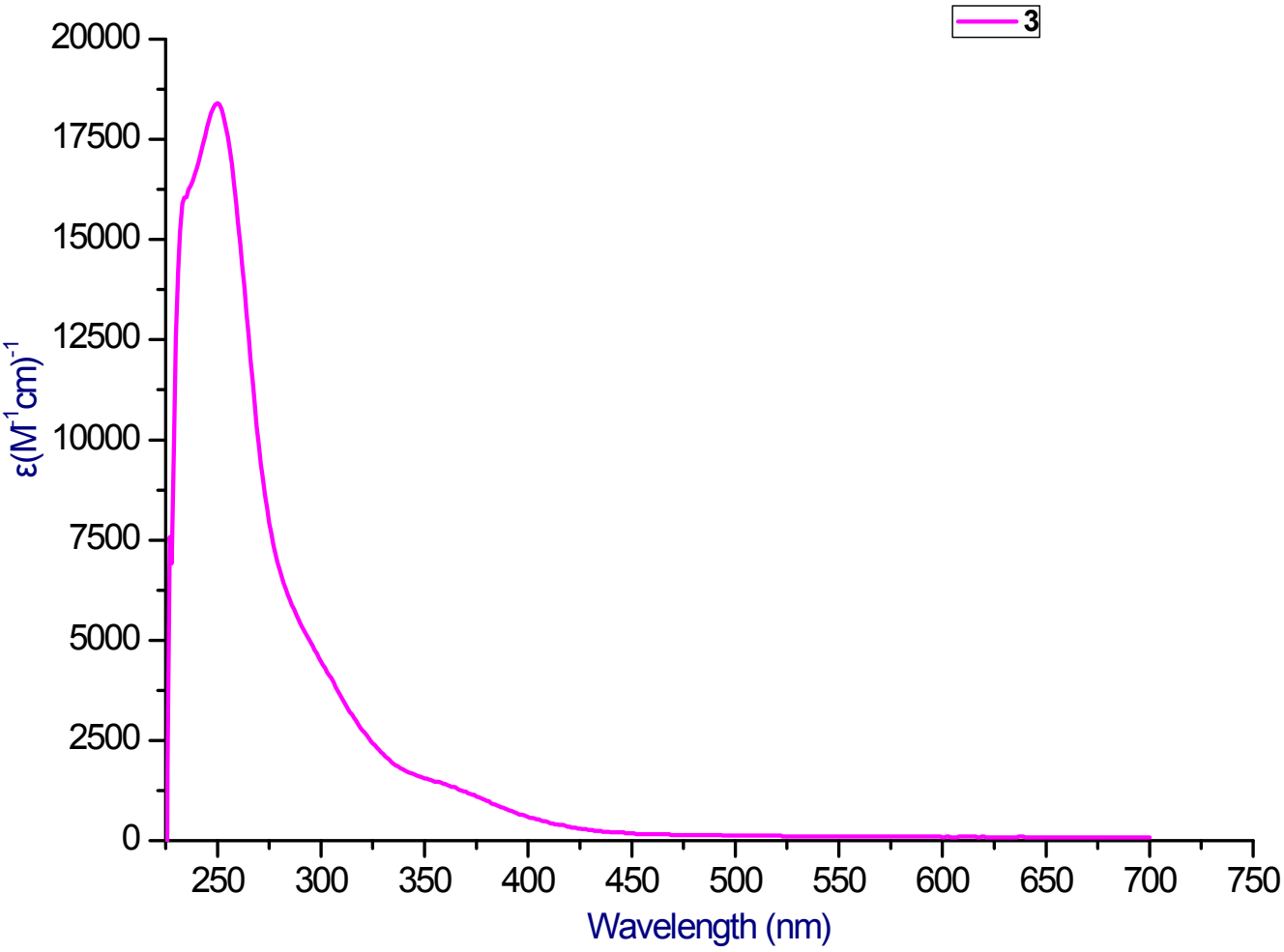

Figure S22. UV-Vis spectrum of complex **3** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.

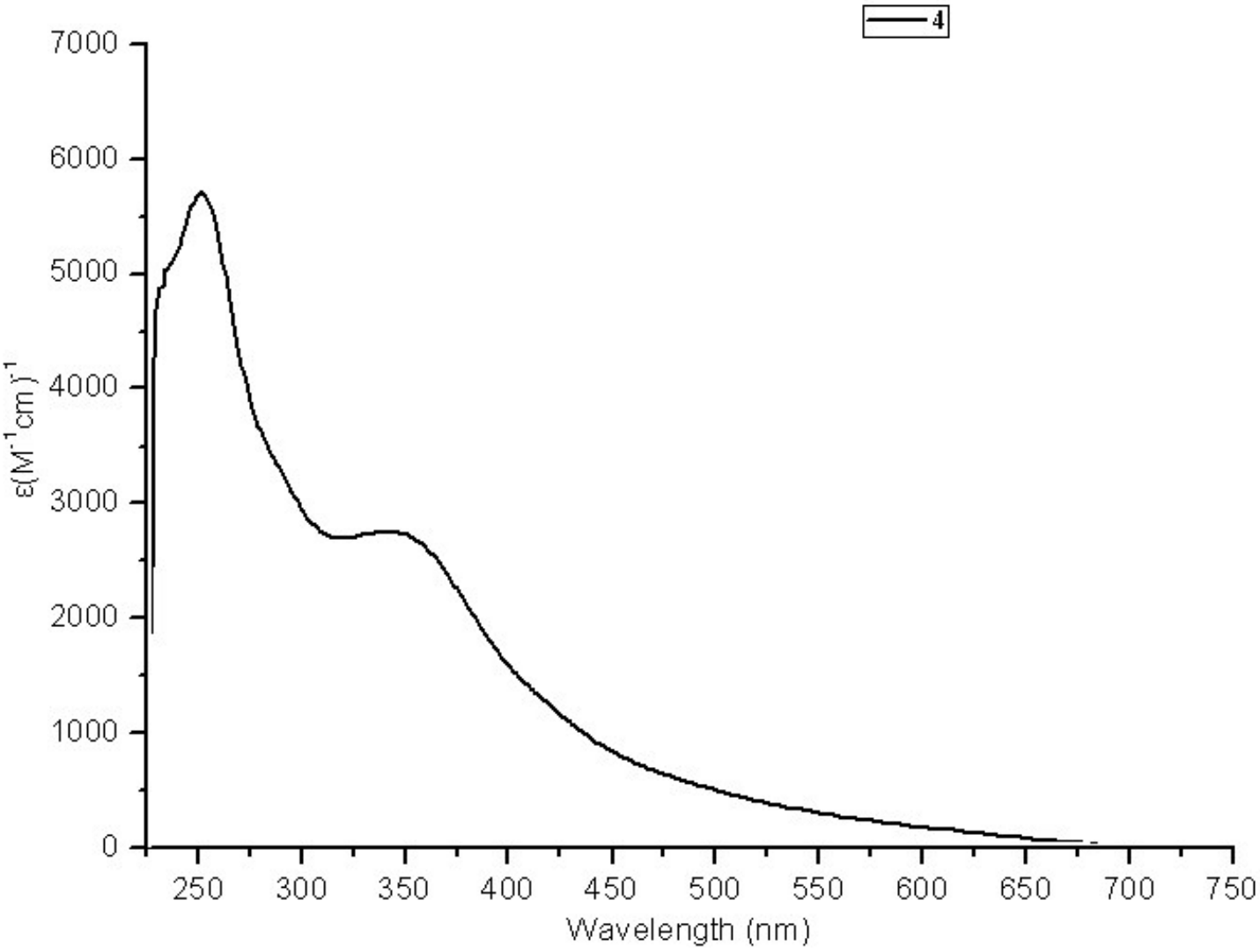

Figure S23. UV-Vis spectrum of complex **4** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.

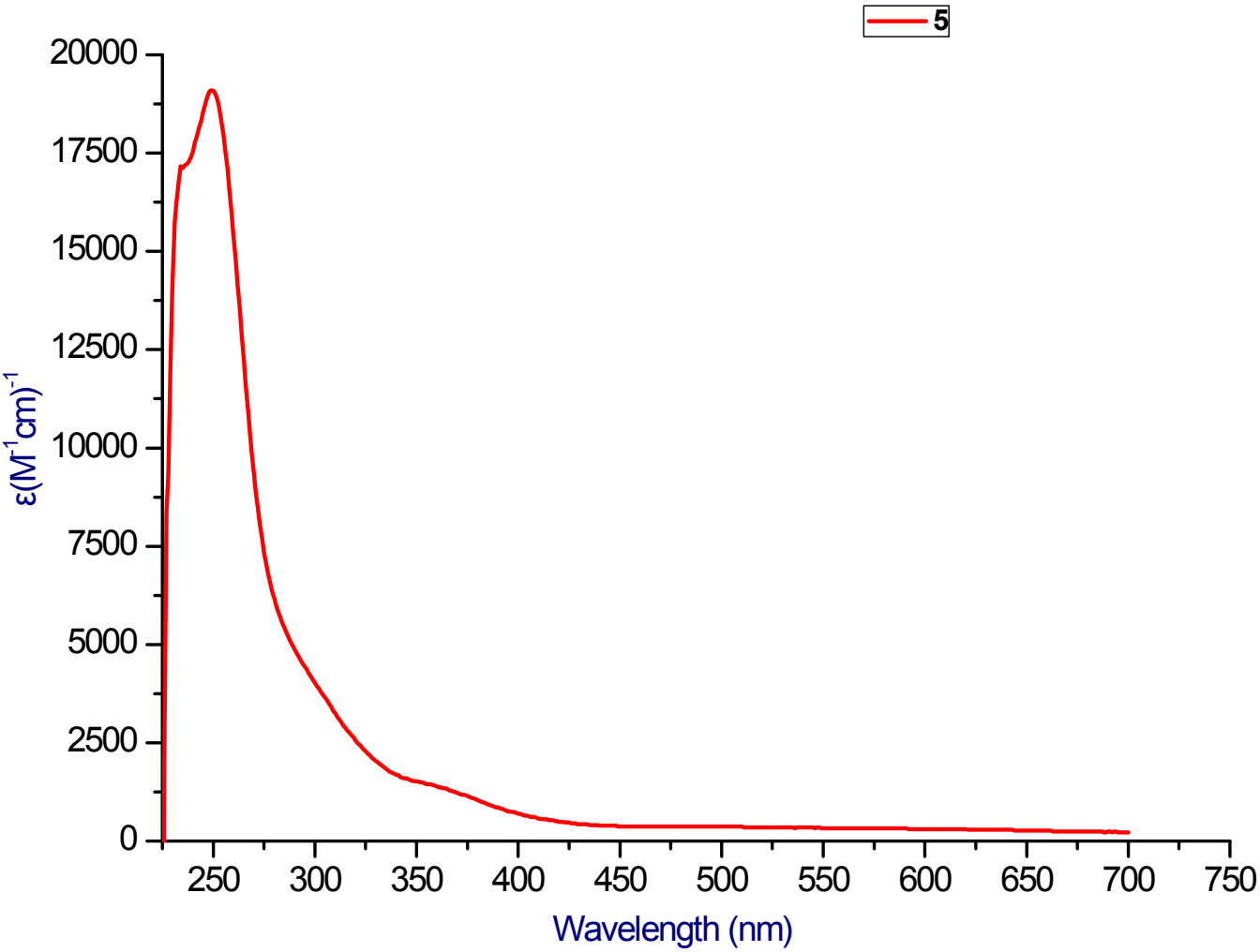

Figure S24. UV-Vis spectrum of complex **5** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.

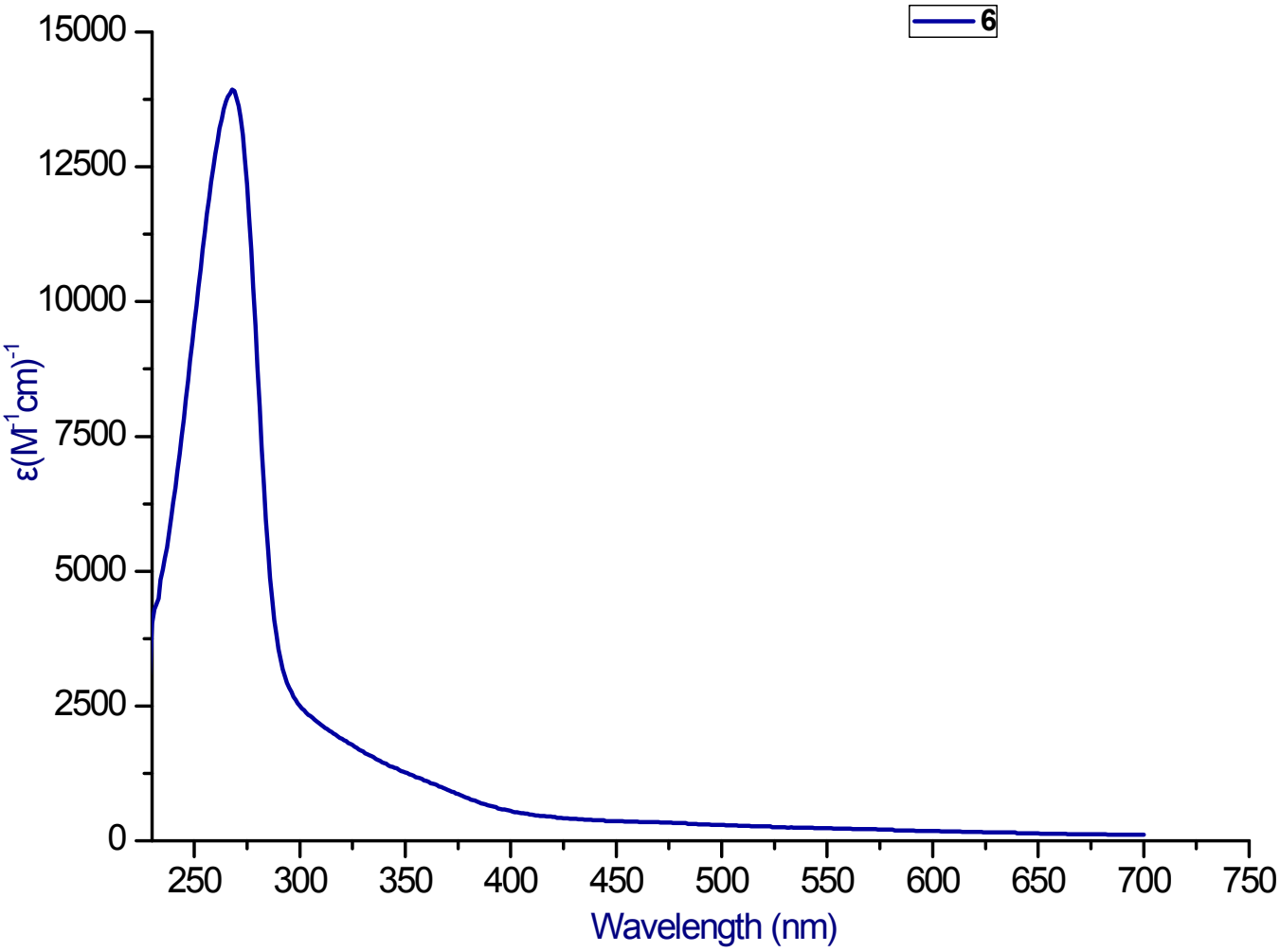

Figure S25. UV-Vis spectrum of complex **6** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.

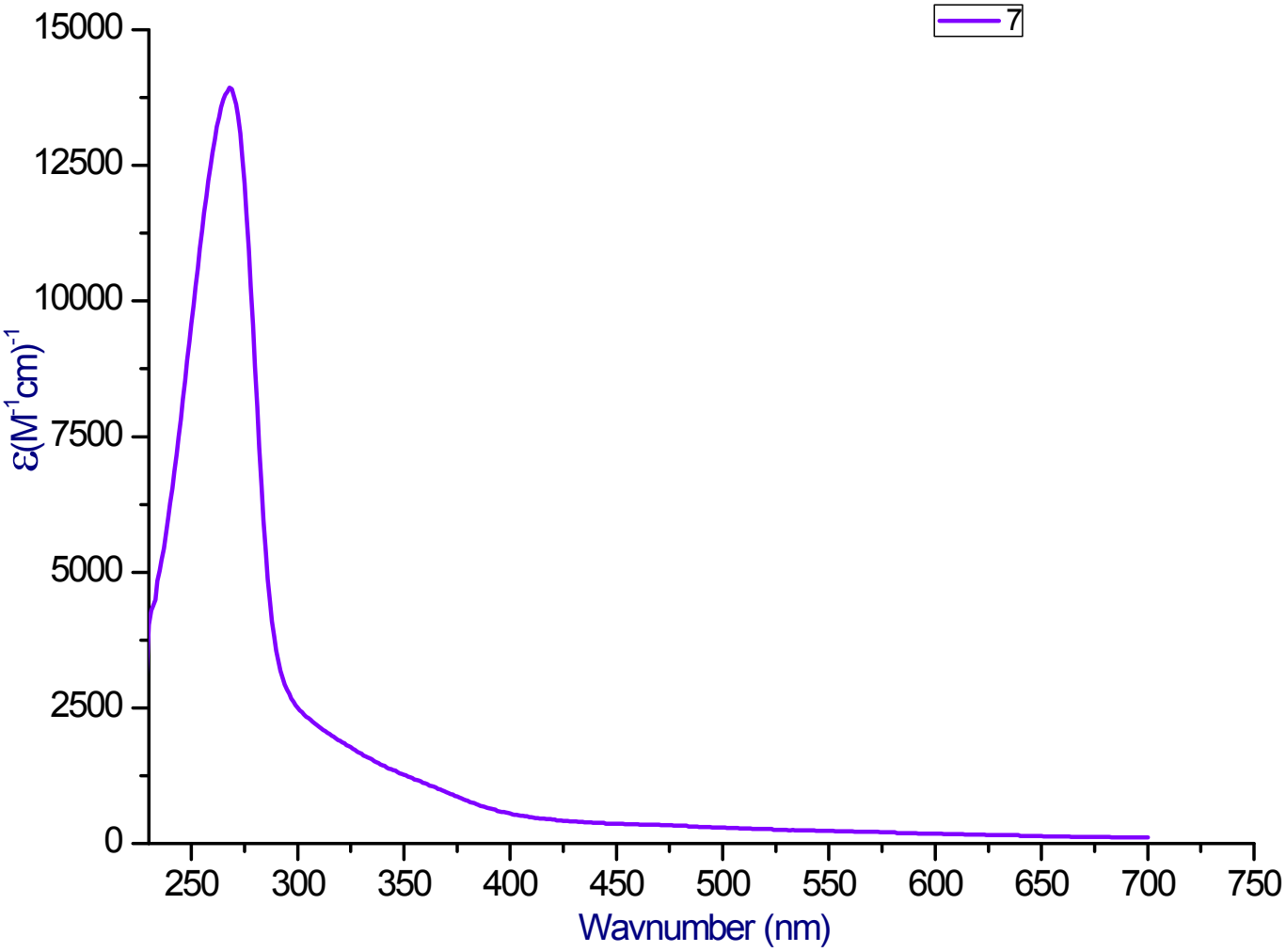

Figure S26. UV-Vis spectrum of complex **7** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.

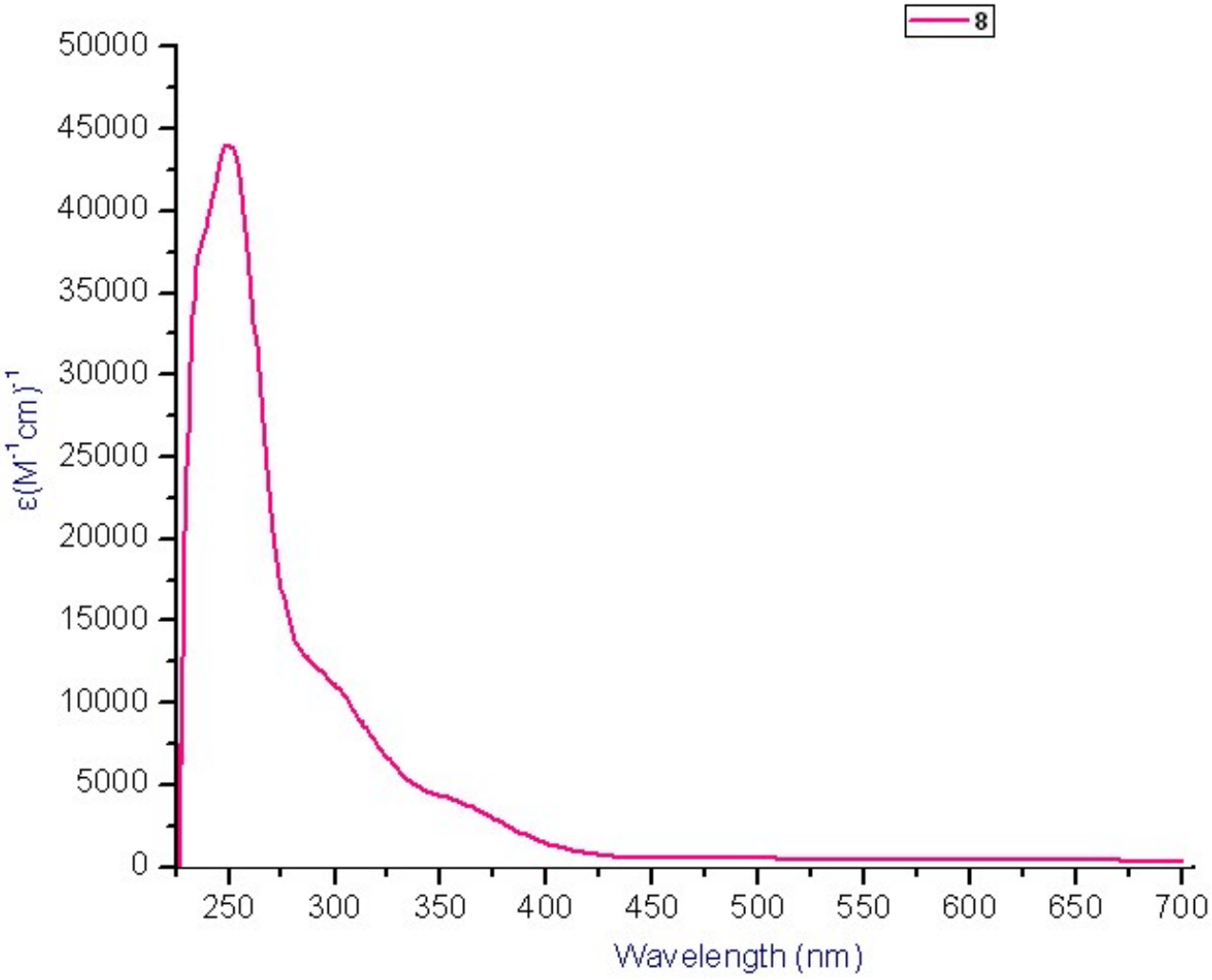

Figure S27. UV-Vis spectrum of complex **8** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.

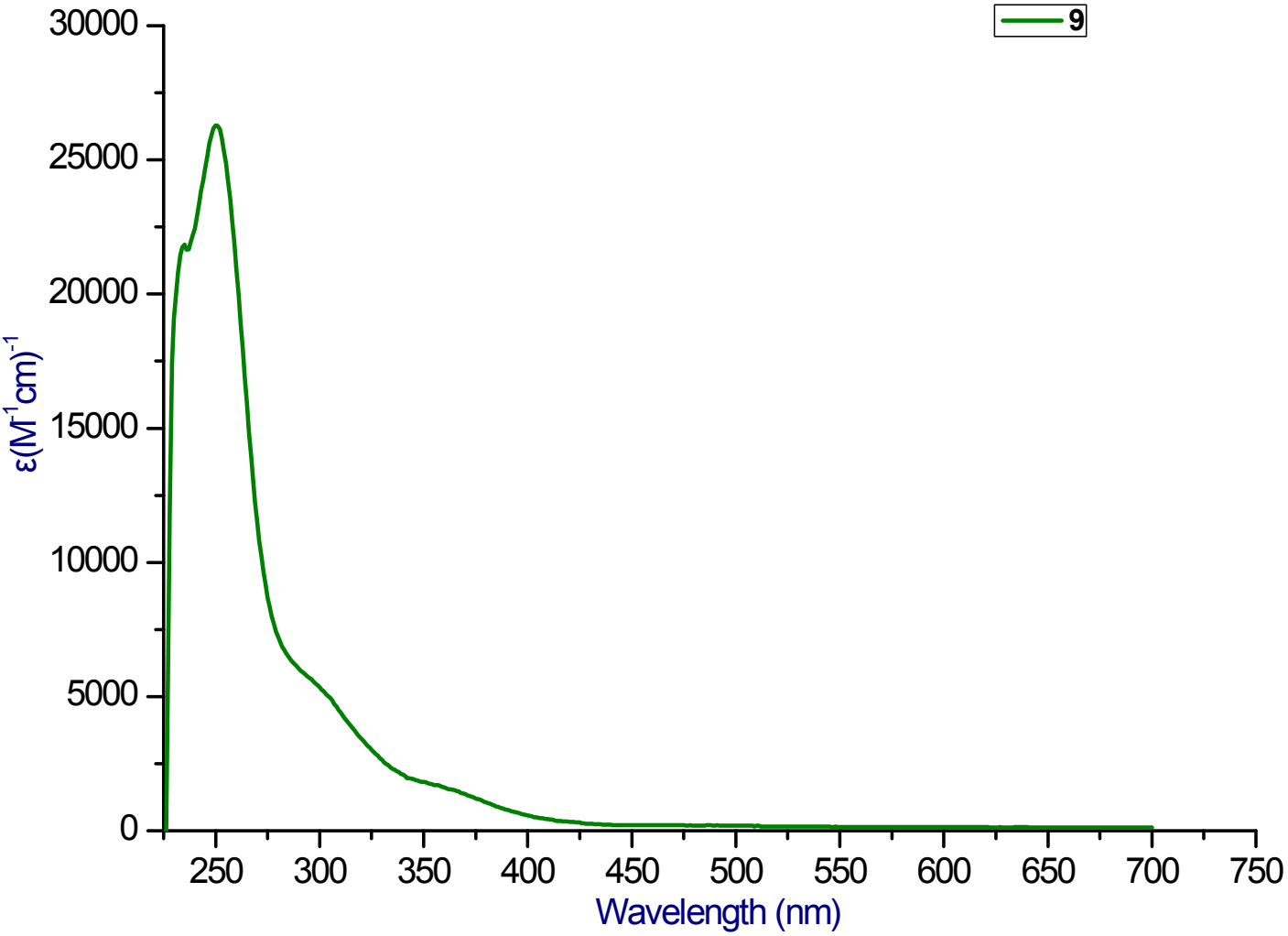

Figure S28. UV-Vis spectrum of complex **9** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.

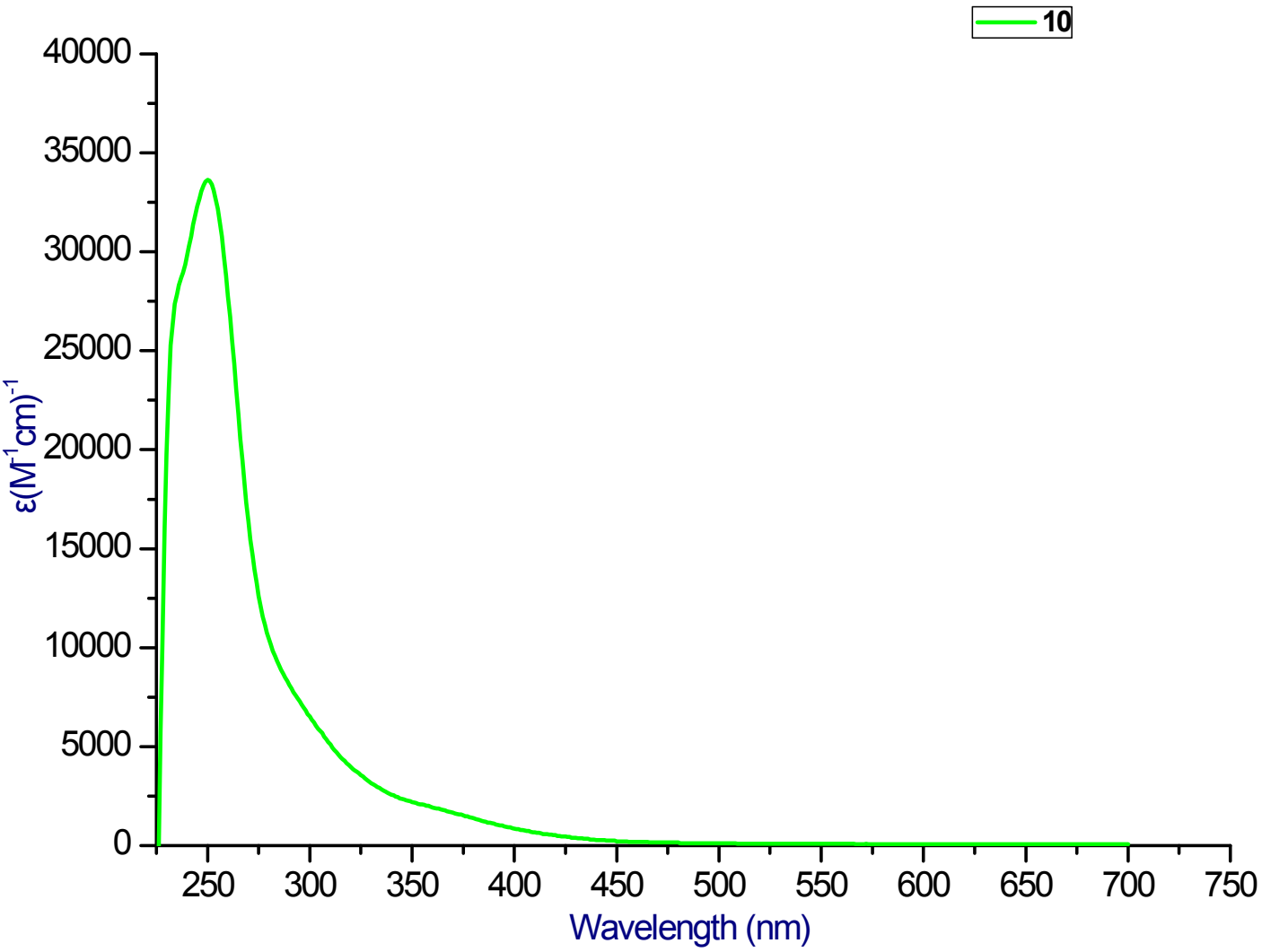

Figure S29. UV-Vis spectrum of complex **10** in solution 1:1 acetonitrile/water containing TEOA 5% v/v at pH 7.

^{1}H &^{13}C NMR Spectra

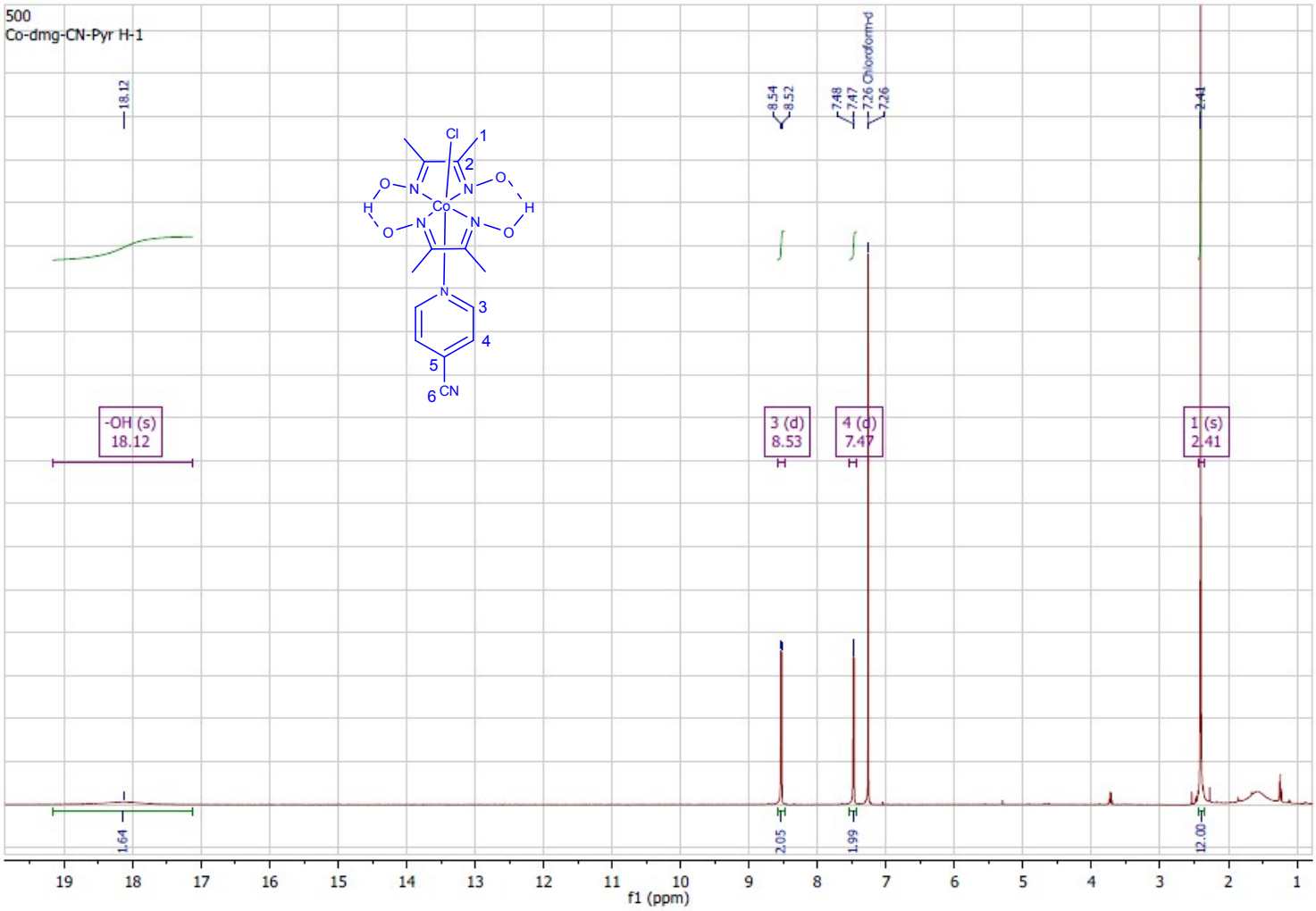

Figure S30. ^{1}H NMR spectrum of complex **1** in $CDCl_3$.

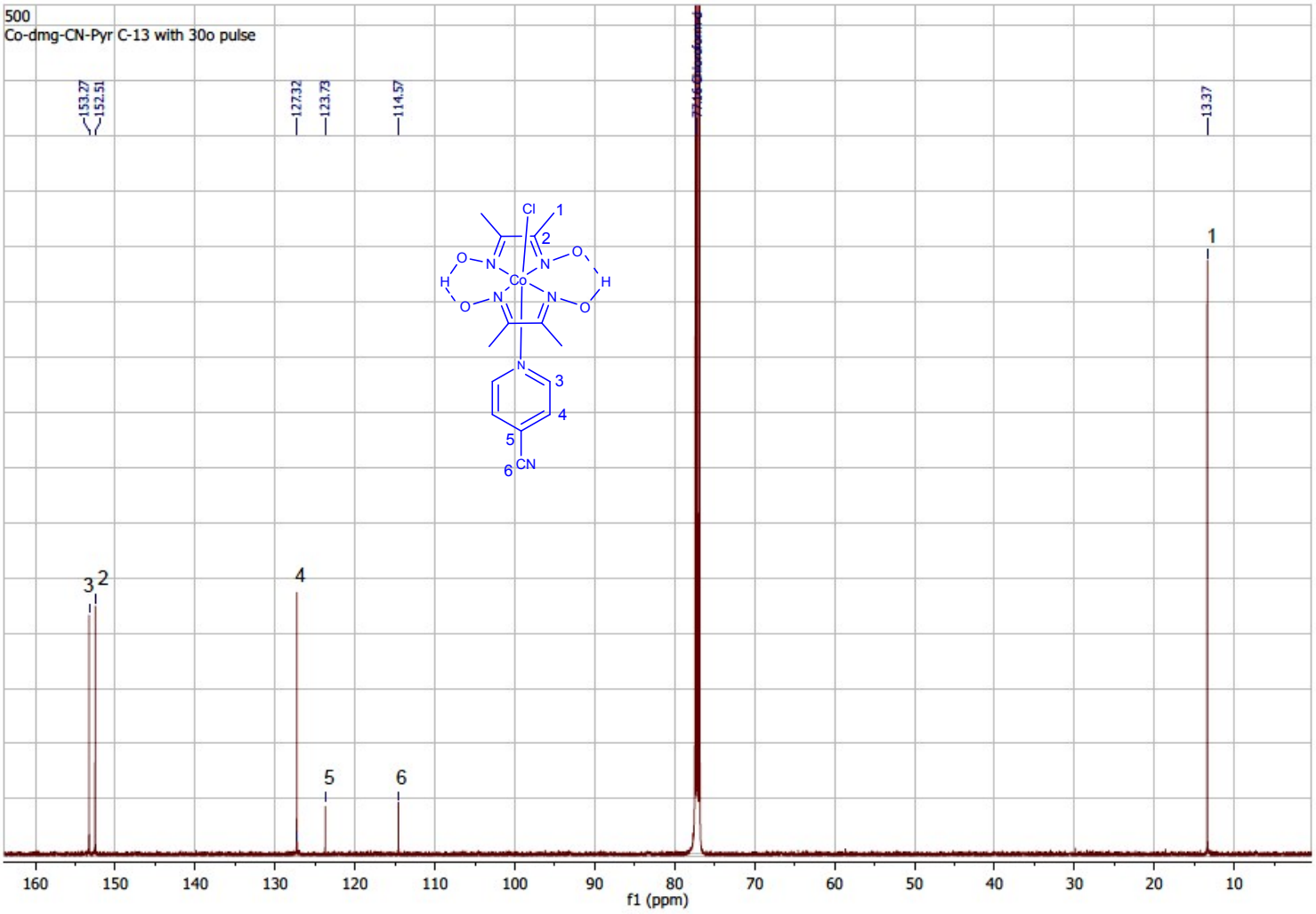

Figure S31. ^{13}C NMR spectrum of complex **1** in $CDCl_3$.

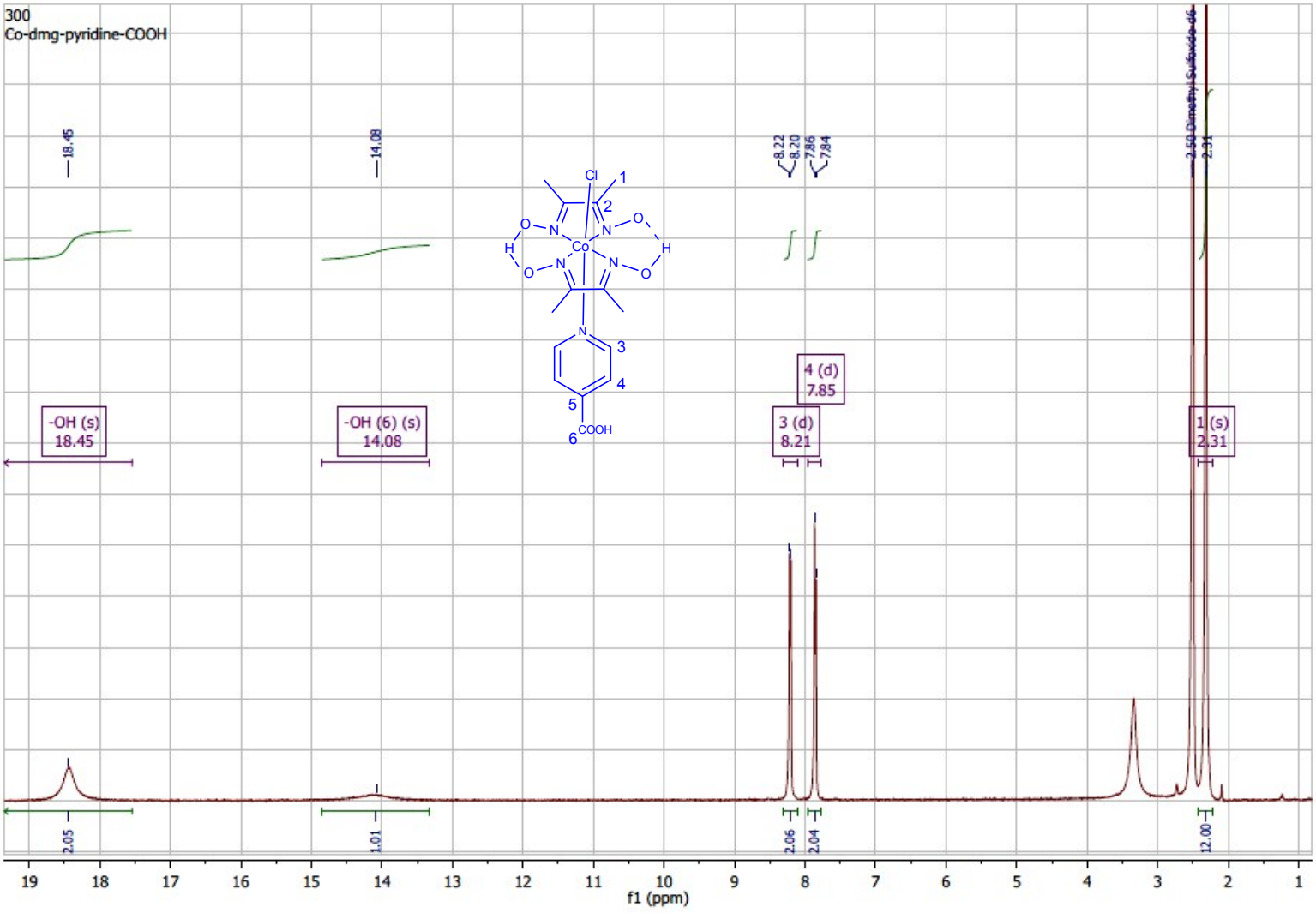

Figure S32. ^{1}H NMR spectrum of complex **2** in DMSO.

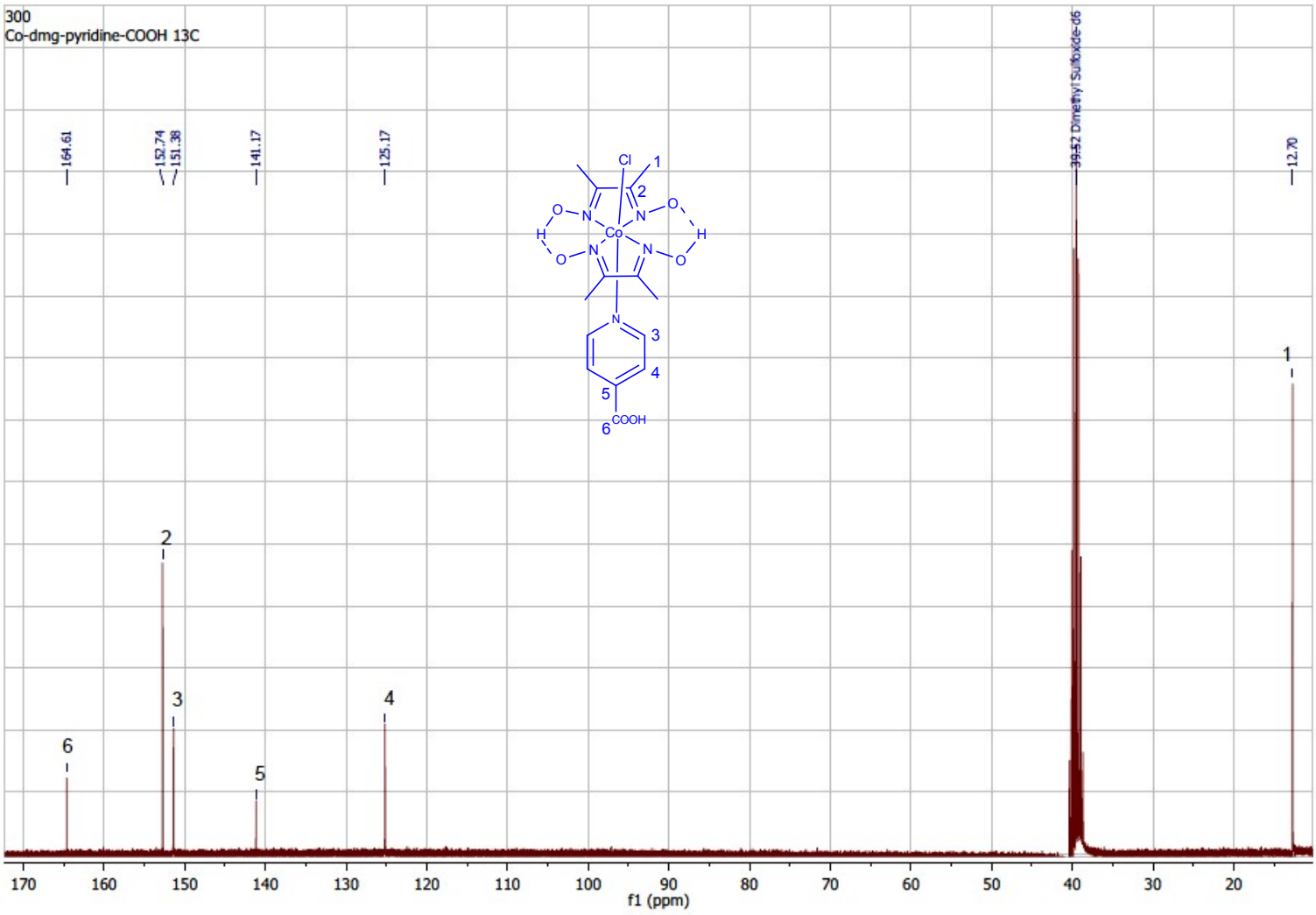

Figure S33. ^{13}C NMR spectrum of complex **2** in DMSO.

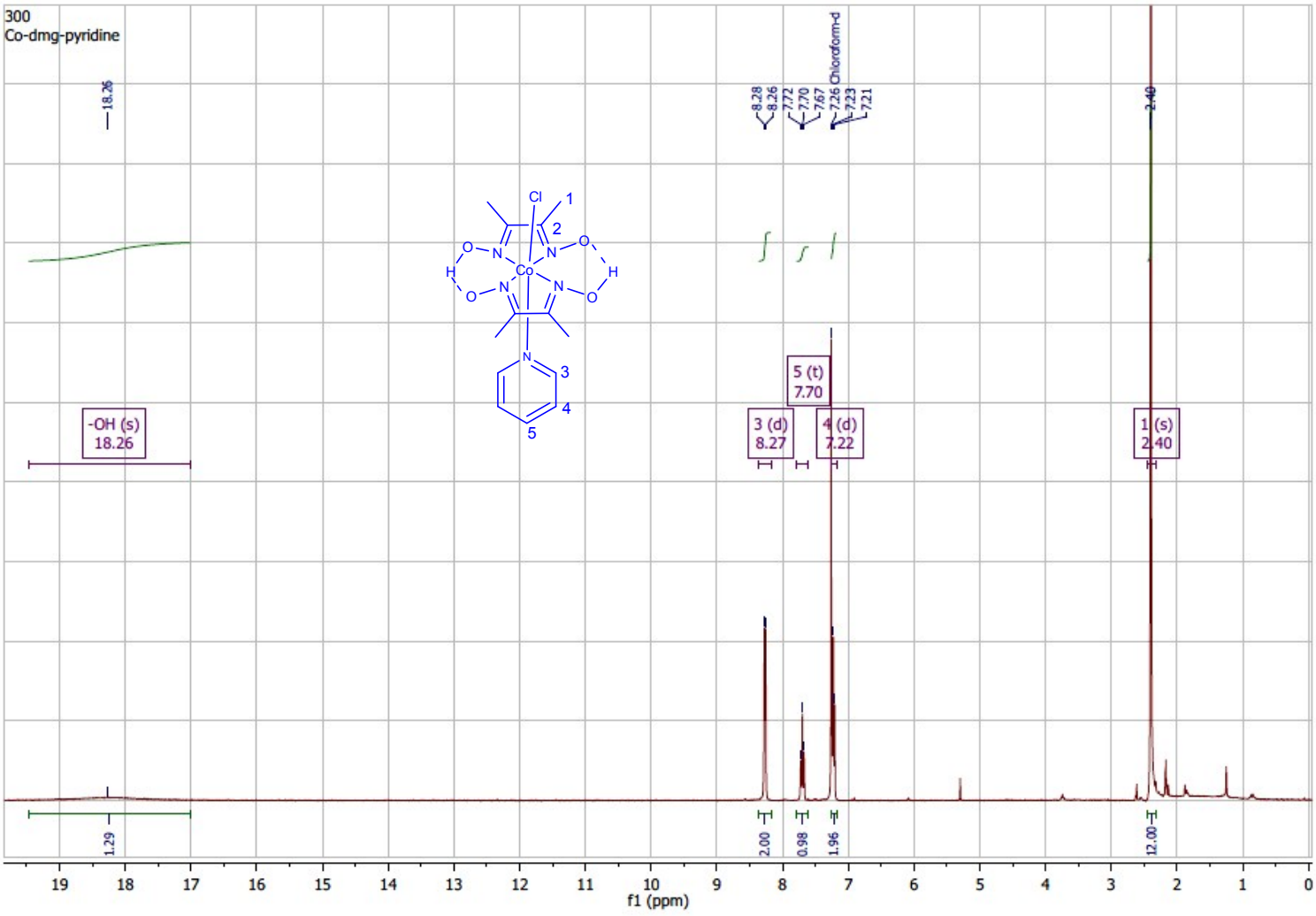

Figure S34. ^{1}H NMR spectrum of complex **3** in $CDCl_3$.

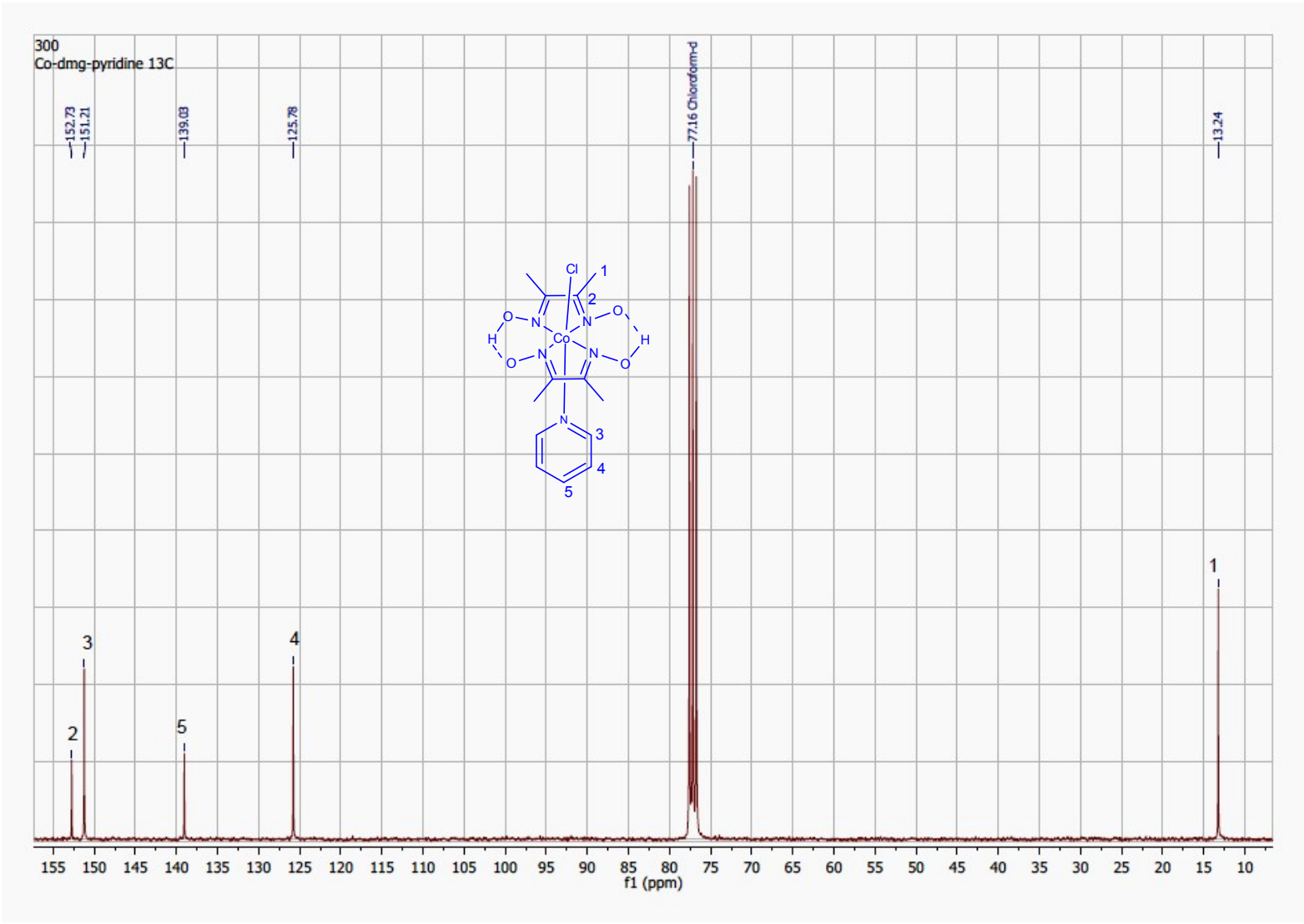

Figure S35. ^{13}C NMR spectrum of complex **3** in $CDCl_3$.

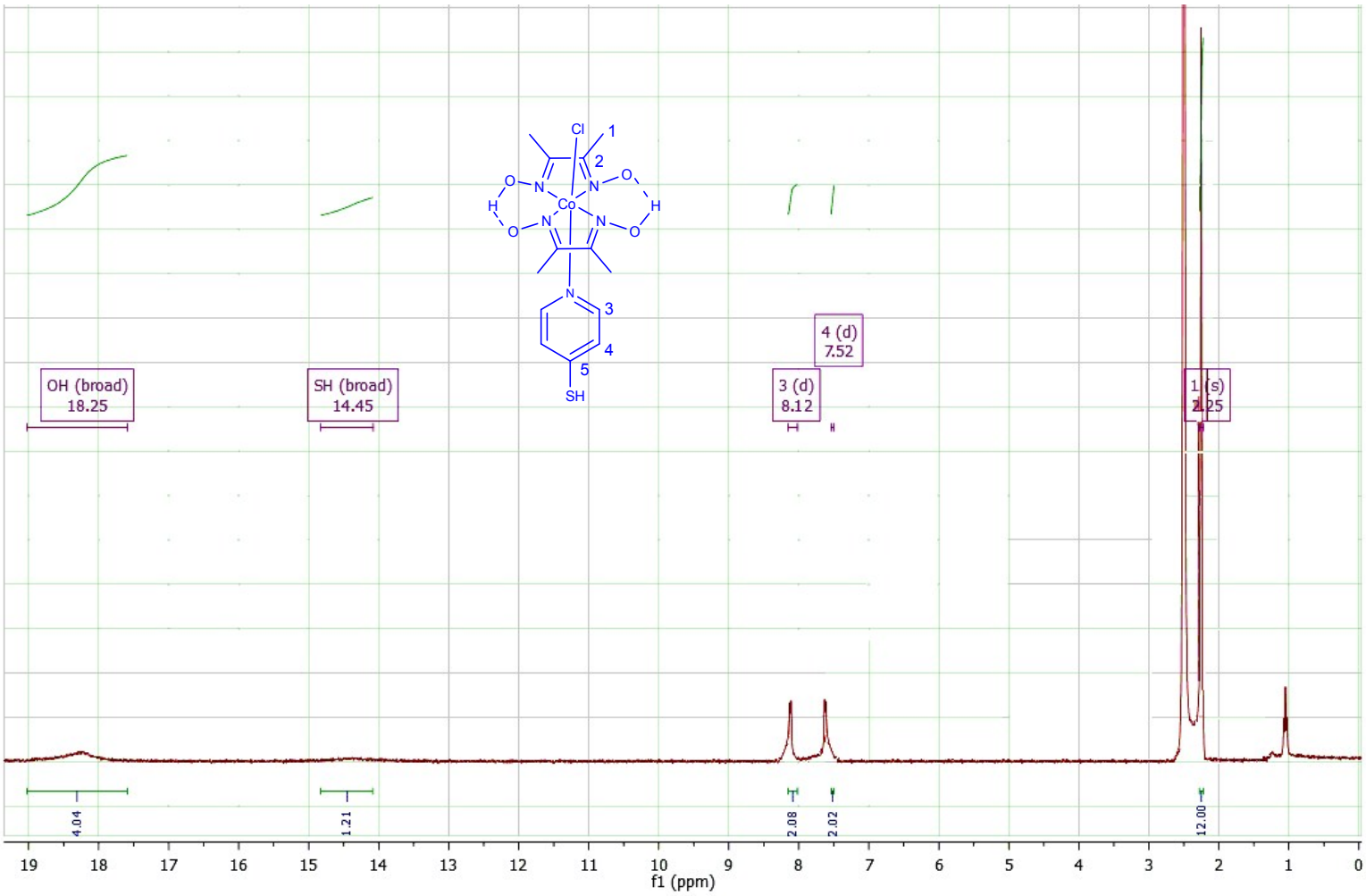

Figure S36. ^{1}H NMR spectrum of complex **4** in DMSO.

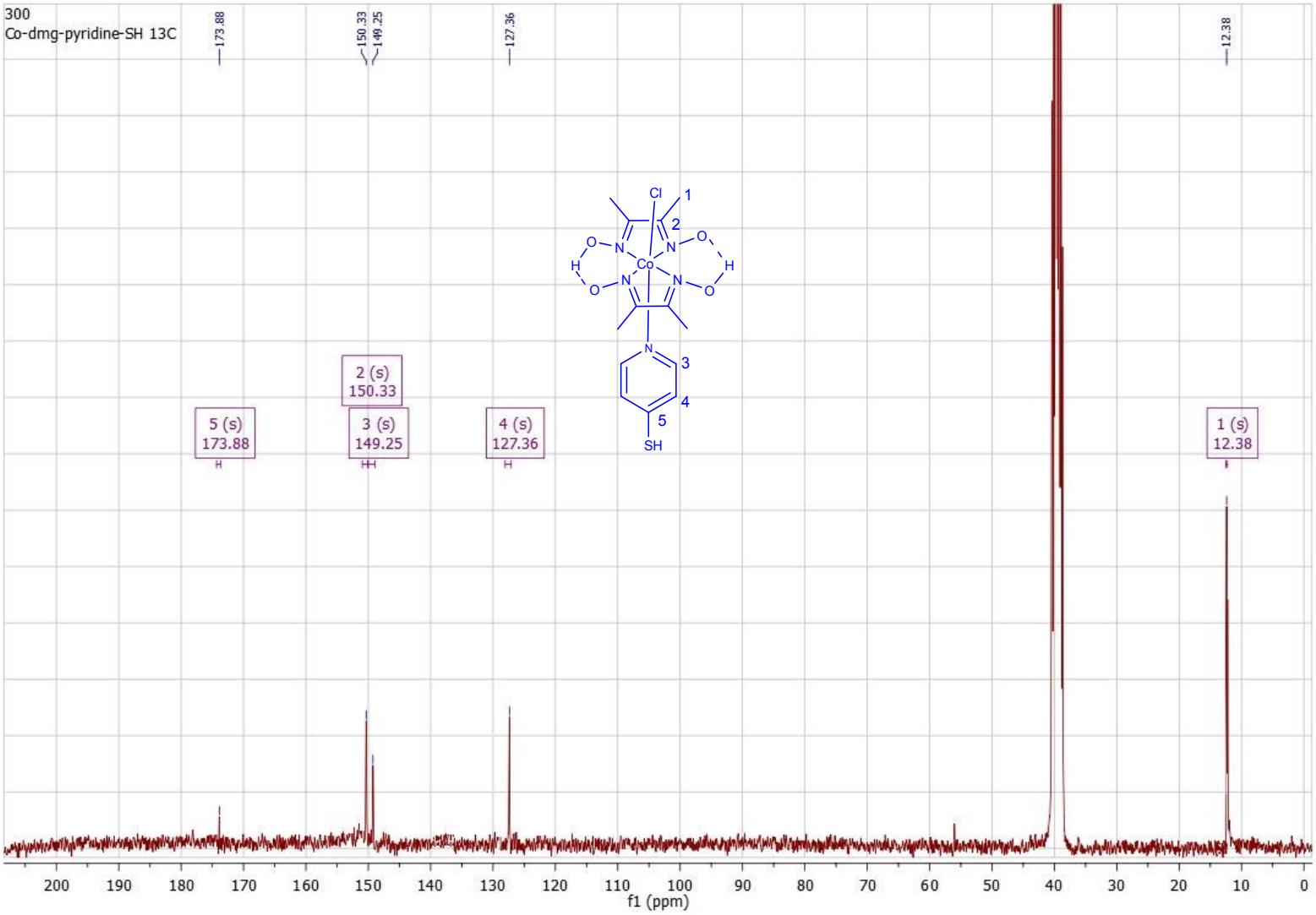

Figure S37. ^{13}C NMR spectrum of complex **4** in DMSO.

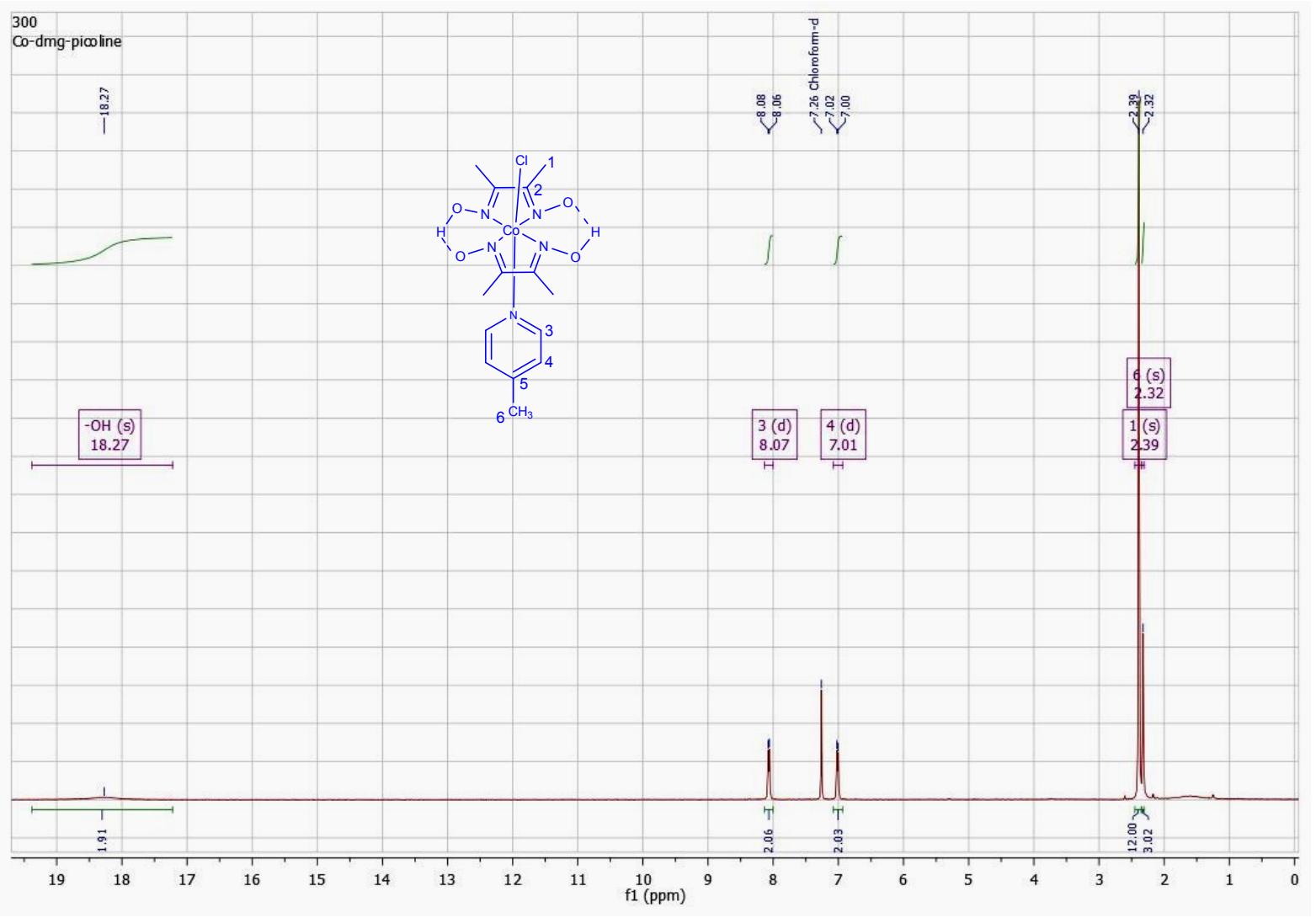

Figure S38. ^{1}H NMR spectrum of complex **5** in $CDCl_3$.

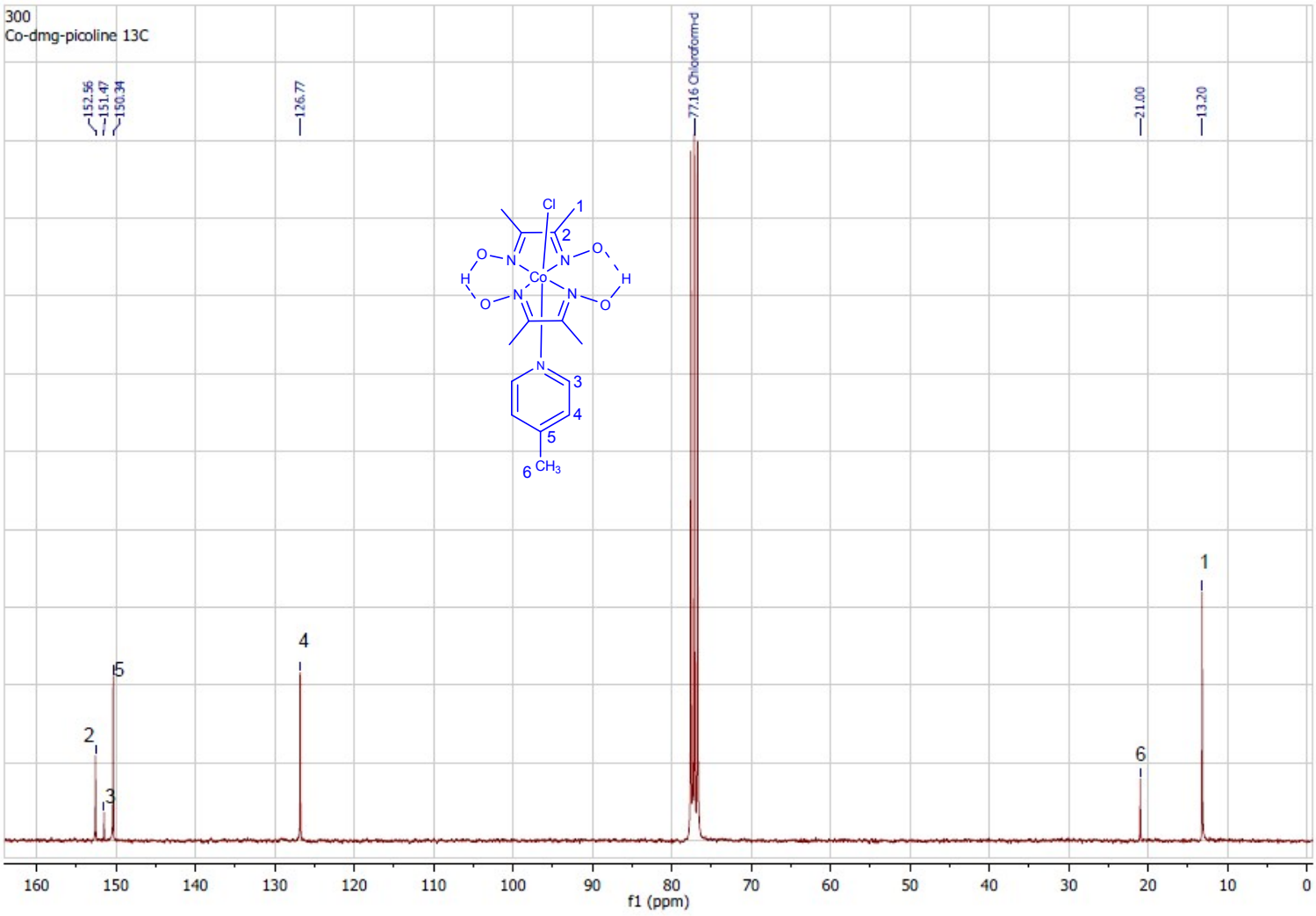

Figure S39. ^{13}C NMR spectrum of complex **5** in $CDCl_3$.

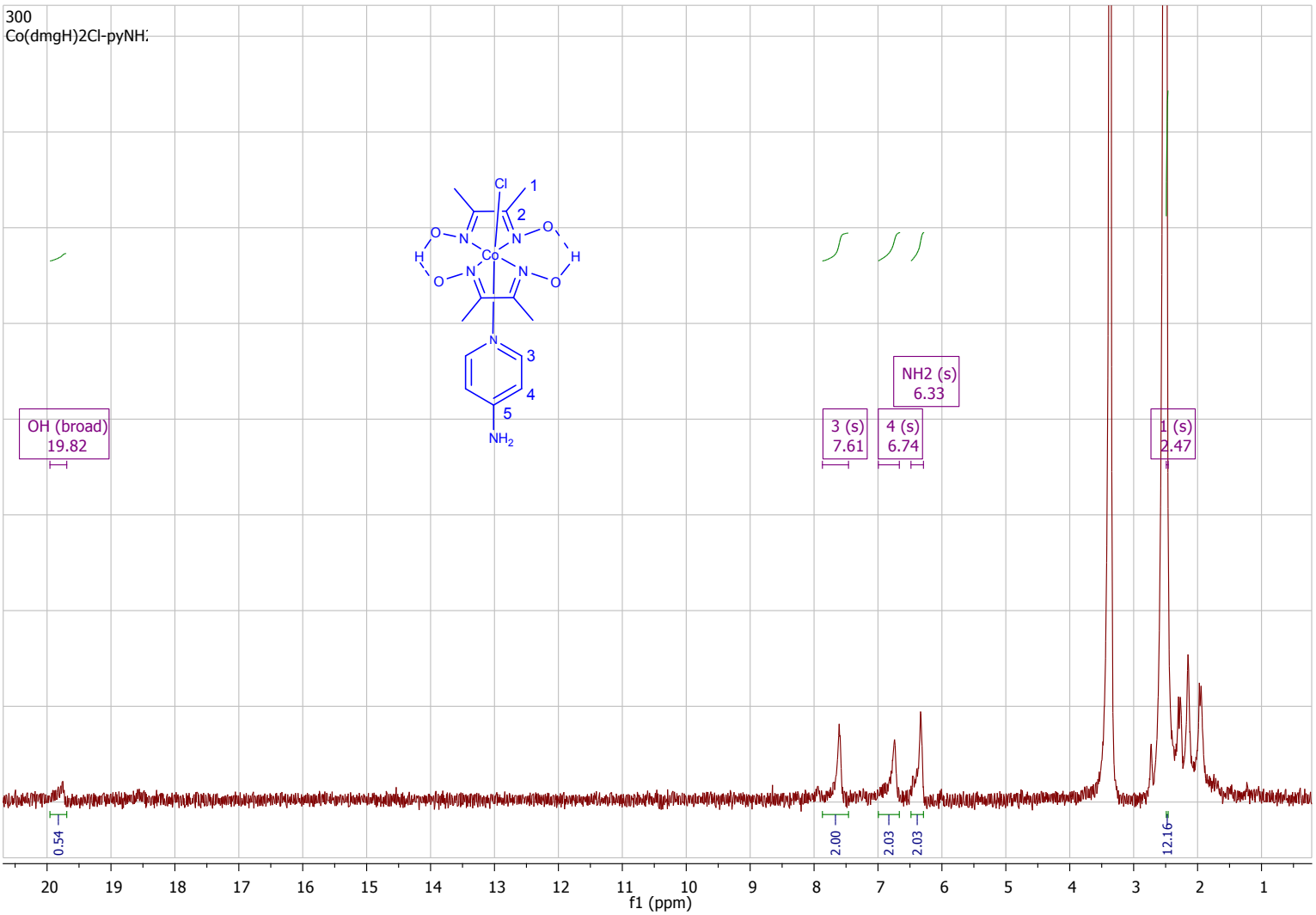

Figure S40. ^{1}H NMR spectrum of complex **6** in DMSO.

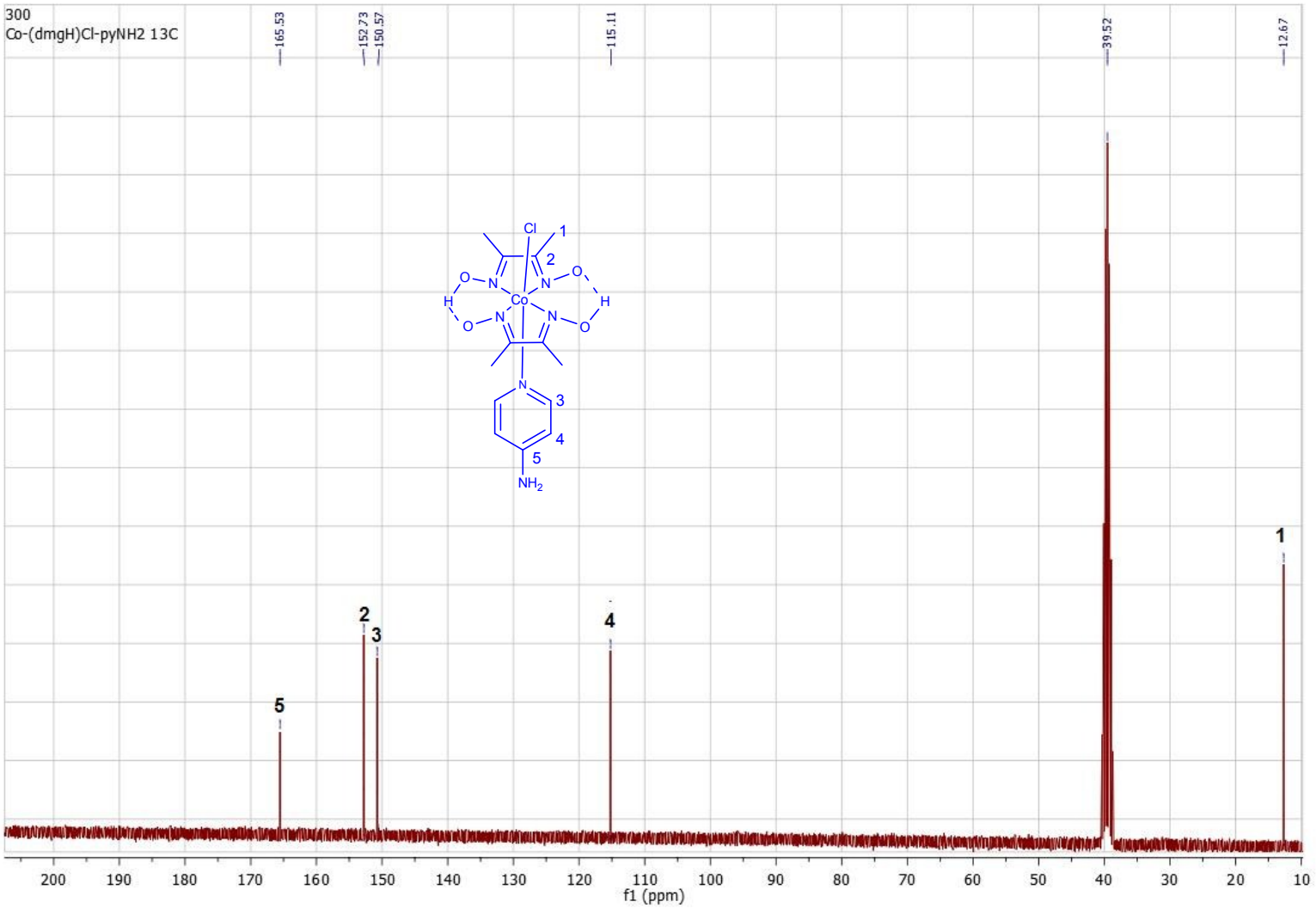

Figure S41. ^{13}C NMR spectrum of complex **6** in DMSO.

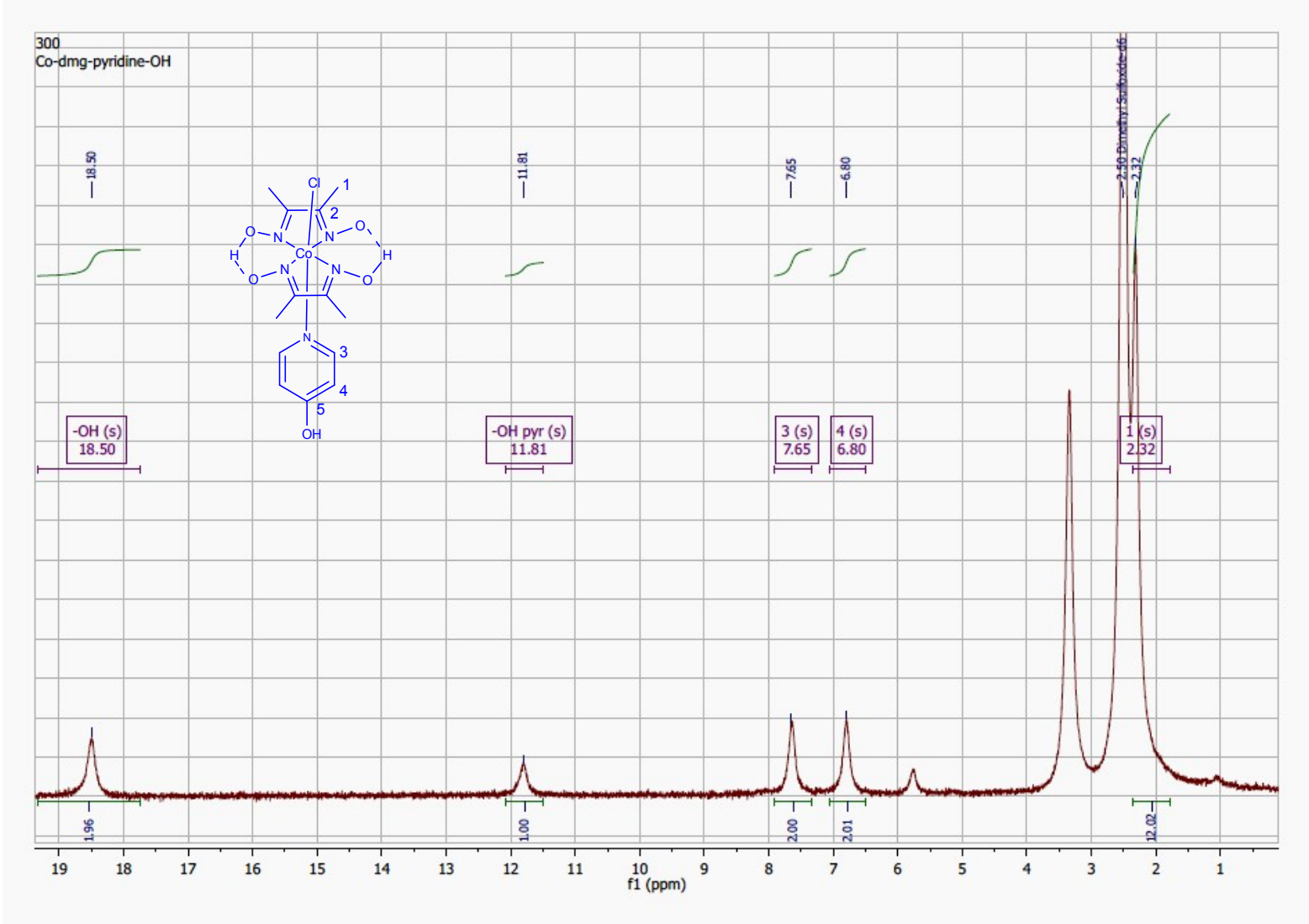

Figure S42. ^{1}H NMR spectrum of complex **7** in DMSO.

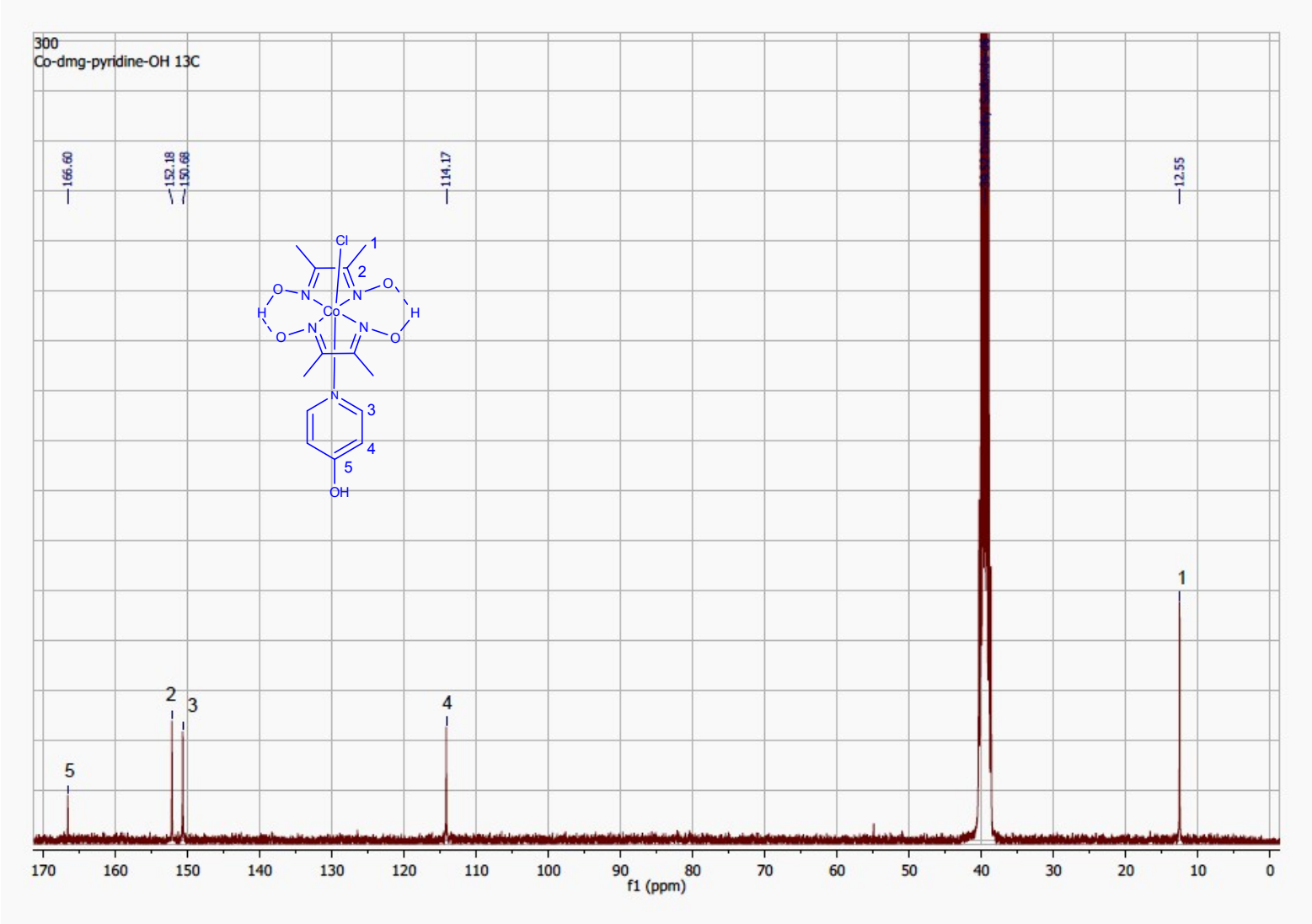

Figure S43. ^{13}C NMR spectrum of complex **7** in DMSO.

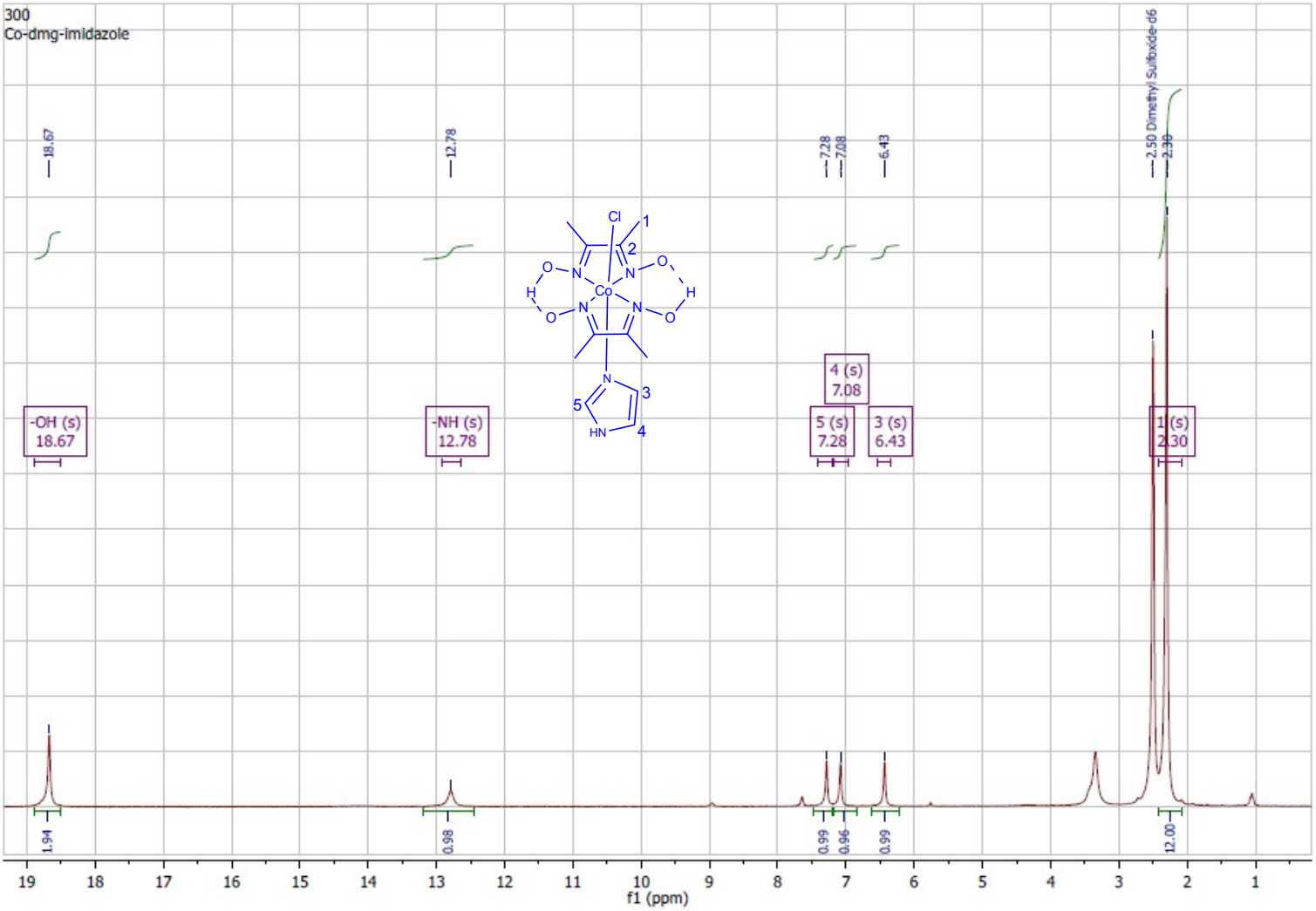

Figure S44. ^{1}H NMR spectrum of complex **8** in DMSO.

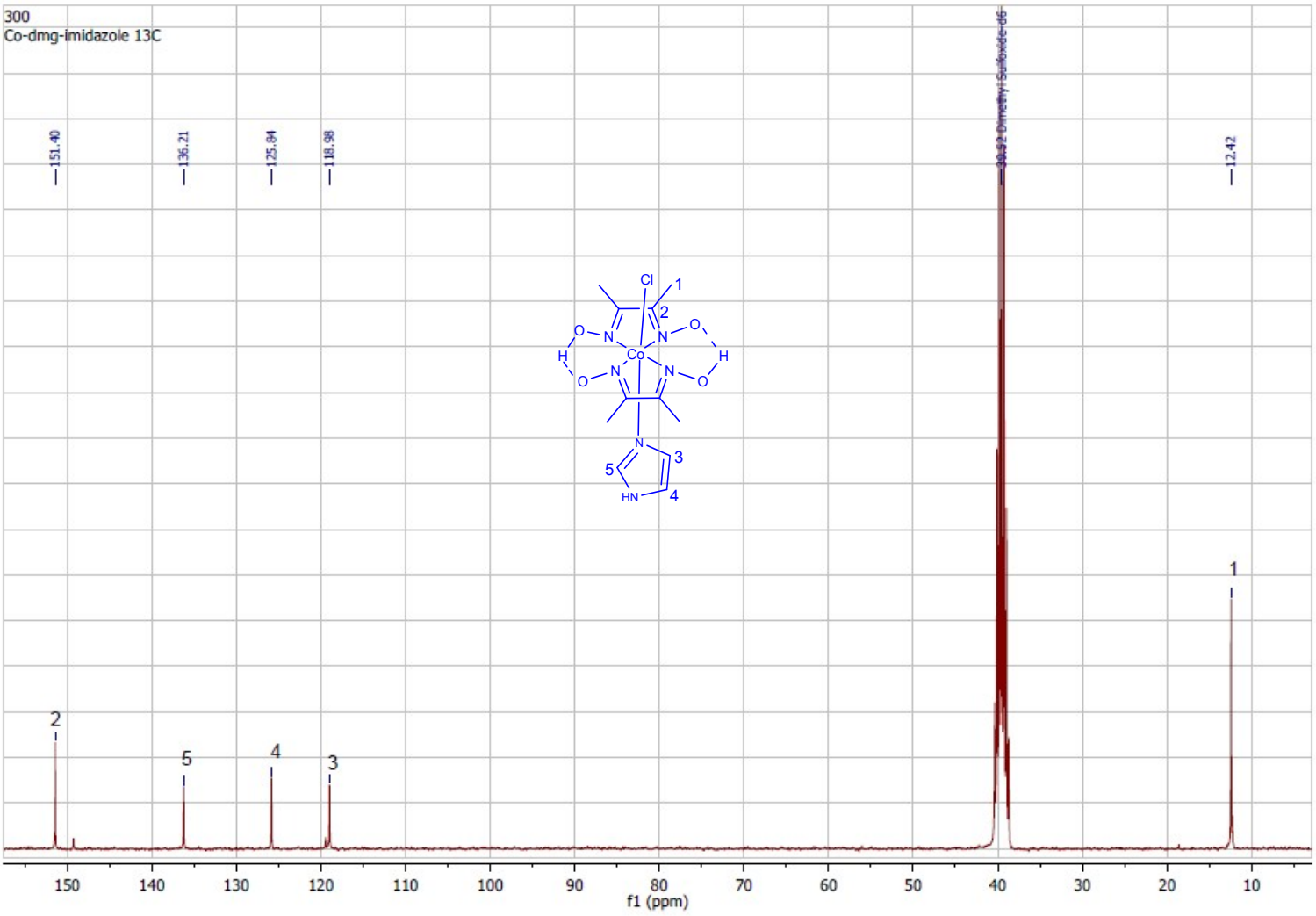

Figure S45. ^{13}C NMR spectrum of complex **8** in DMSO.

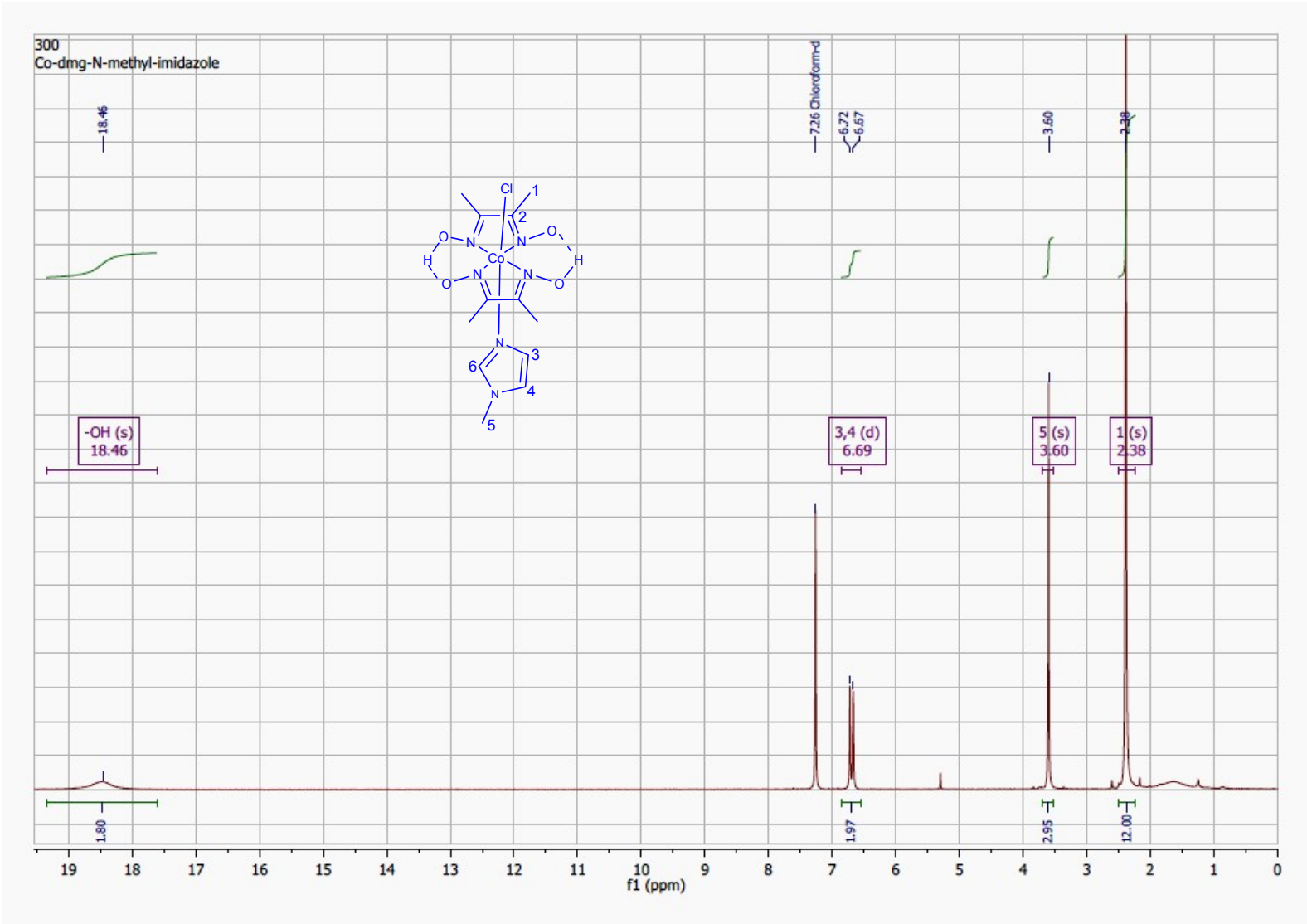

Figure S46. ^{1}H NMR spectrum of complex **9** in $CDCl_3$.

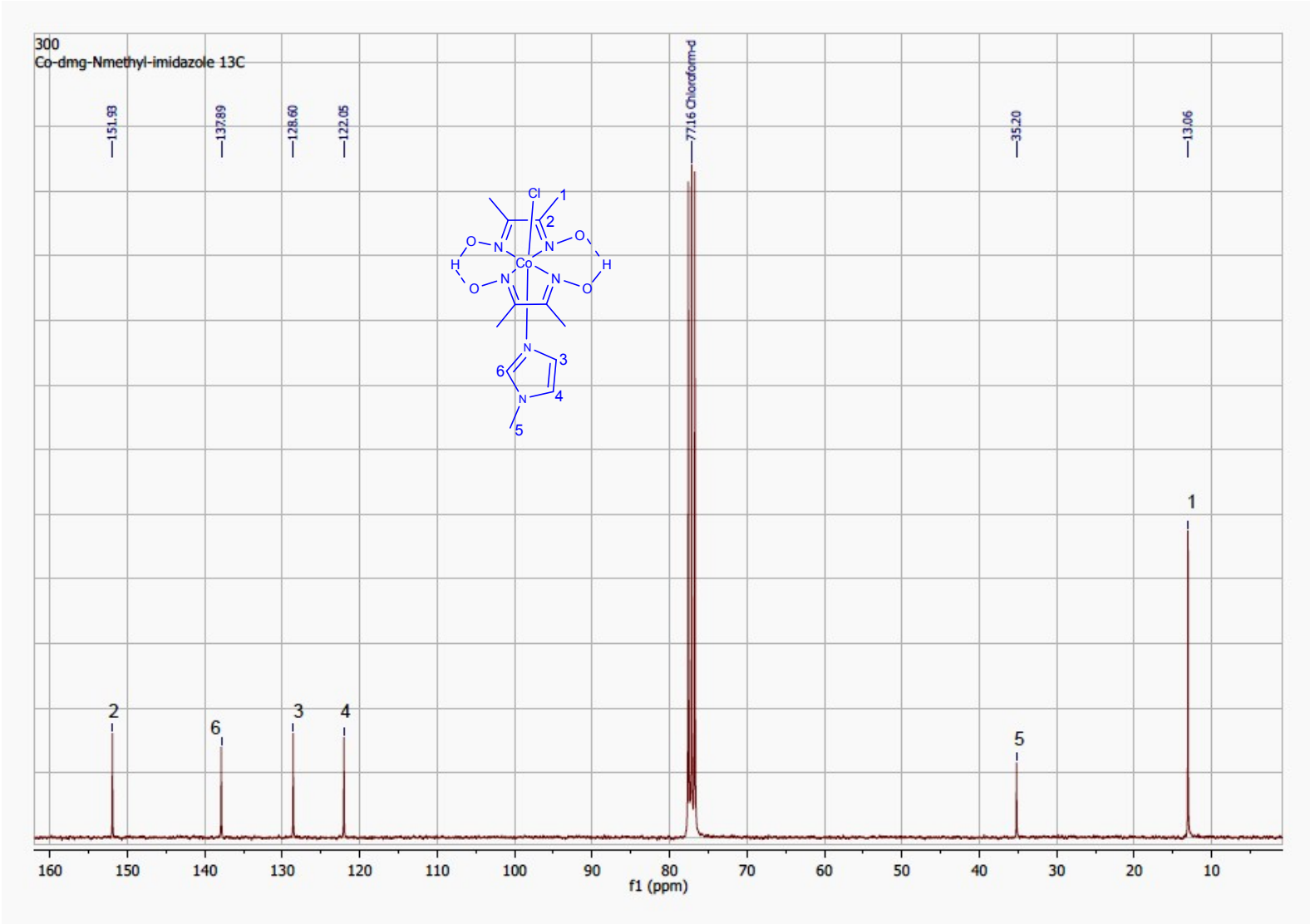

Figure S47. ^{13}C NMR spectrum of complex **9** in $CDCl_3$.

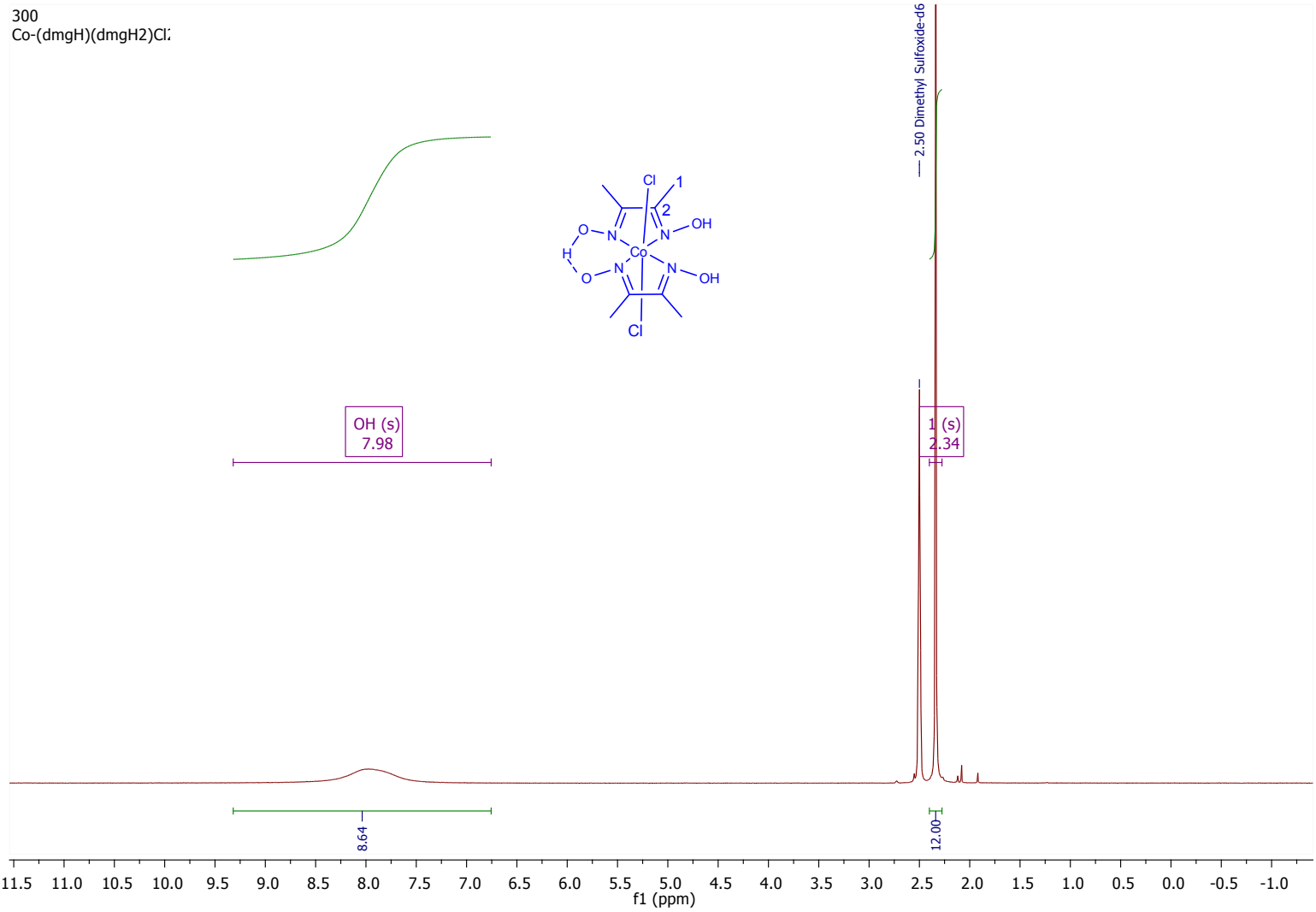

Figure S48. ^{1}H NMR spectrum of complex **10** in DMSO.

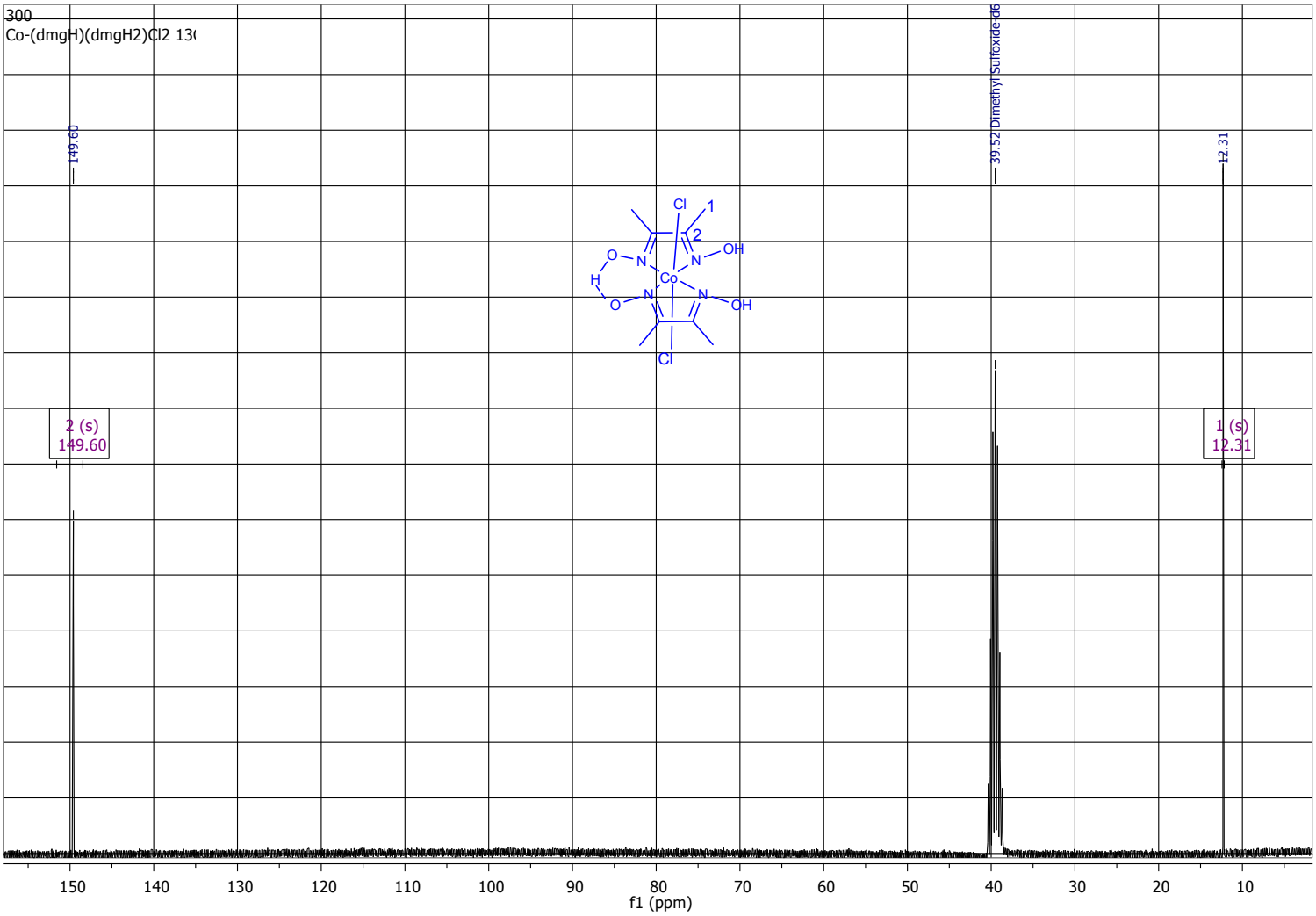

Figure S49. ^{13}C NMR spectrum of complex **10** in DMSO.