

Unexpected Chemoselectivity in the Schiff Condensation of Amines with $\eta^2(\text{C},\text{O})$ - $\eta^1(\text{O})$ -Coordinated Aldehyde

Celedonio M. Álvarez, Raúl García-Rodríguez, José M. Martín-Alvarez and Daniel Miguel*

*IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47005
Valladolid, Spain*

E-mail: dmsj@qi.uva.es

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Experimental Section

Materials and general methods

All operations were performed under an atmosphere of dry nitrogen using Schlenk and vacuum techniques. Dichloromethane and acetonitrile were distilled from CaH_2 . THF and diethylether were distilled from Na/benzophenone. Hexane was distilled from Na. Literature procedures for the preparation of starting materials are quoted in each case. Ligands and other reagents were purchased and used without purification unless otherwise stated. IR spectra in solution were recorded with a Perkin Elmer Spectrum RX I FT-IR instrument,

using cells with CaF₂ windows. All NMR solvents were stored over molecular sieves and degassed prior to use. ¹H NMR experiments were measured on a Bruker AV400 and ARX300 spectrometers. Chemical shift values are given in ppm. ¹H NMR chemical shifts are referenced to TMS, using solvents as an internal reference.

Synthesis of [Cr₂(CO)₆(pyC(H)=O)₂] (**2a**)

To a solution of pyridine-2-carbaldehyde (0.071 g, 0.66 mmol) in THF (40 mL) was added [Cr(CH₃CN)₃(CO)₃] (**1a**)¹ (0.171 g, 0.66 mmol). The mixture was stirred for 20 min. After that, the green solution was concentrated in vacuo, layered with hexane (20 mL) and stored at -20 °C to afford black crystals of **2a**, one of which was used for X-ray analysis. Yield 0.130 g, 81%. Anal. Calcd. for C₁₈H₁₀Cr₂N₂O₈: C 44.46, H 2.07, N 5.76. Found: C 44.65, H 1.98, N 5.51%. IR (THF), ν(CO): 1981 vs, 1920 m, 1865 s cm⁻¹. IR (Nujol), ν(CO): 1973 vs, 1923 vs, 1899 s, 1867 vs, 1849 vs cm⁻¹.

Synthesis of [Mo₂(CO)₆(pyC(H)=O)₂] (**2b**)

A solution of [Mo(CO)₆] (0.200 g, 0.76 mmol) in acetonitrile (20 mL) was refluxed for 3h to form [Mo(CH₃CN)₃(CO)₃] (**1b**). Following the removal of solvent, a solution of pyridine-2-carbaldehyde (0.081 g, 0.76 mmol) in THF (30 mL) was added to the crude pale yellow solid. The mixture immediately turned deep green and it was stirred for 5 min. Addition of hexane and slow solvents evaporation at reduced pressure gave compound **2b** as dark green microcrystals. Yield 0.203 g, 93%. Anal. Calcd. for C₁₈H₁₀Mo₂N₂O₈: C 37.65, H 1.76, N 4.88. Found: C 37.51, H 1.64, N 4.79%. IR (THF), ν(CO): 1987 vs, 1925 m, 1865 s cm⁻¹. IR (Nujol), ν(CO): 1984 vs, 1928 vs, 1904 s, 1963 vs, 1844 vs cm⁻¹. IR (KBr), ν(CO): 1977 vs, 1926 vs, 1904 s, 1860 vs, 1845 vs cm⁻¹. ¹H NMR (300.13 MHz, Acetone-d₆, r.t.) δ = 8.68 [d(5), 1H, pyH⁶], 8.26 [td (8, 2), 1H, pyH⁴], 7.99 [d(8), 1H, pyH³], 7.62 [m, 1H, pyH⁵], 6.73 [s, 1H, pyC(H)=O]. ¹H NMR (300.13 MHz, THF-d₈, r.t.) δ = 8.62 [d(5), 1H, pyH⁶], 8.11 [td (8, 2), 1H, pyH⁴], 7.84 [d(8), 1H, pyH³], 7.46 [m, 1H, pyH⁵], 6.62 [s, 1H, pyC(H)=O].

Synthesis of [W₂(CO)₆(pyC(H)=O)₂] (**2c**)

To a solution of pyridine-2-carbaldehyde (0.041 g, 0.38 mmol) in THF (30 mL) was added [W(CH₃CN)₃(CO)₃] (**1c**) (0.149 g, 0.38 mmol) and the mixture was refluxed for 90 min. After that, the green mixture was concentrated, layered with hexane (20 mL) and after standing at -20 °C for three days, dark green crystals of compound **2c** were obtained. Yield 0.106 g, 74%. Anal. Calcd. for C₁₈H₁₀N₂O₈W₂: C 28.83, H 1.34, N 3.74. Found: C 28.63, H 1.51, N 3.97%. IR (THF), ν(CO): 1985 vs, 1917 m, 1865 s cm⁻¹. IR (Nujol), ν(CO): 1980 vs, 1921 vs, 1894 s, 1959 vs, 1842 vs cm⁻¹. ¹H NMR (300.13 MHz, THF-d₈, r.t.) δ = 8.71 [d (5), 1H, pyH⁶], 8.06 [td (8, 2), 1H, pyH⁴], 7.63 [d(8), 1H, pyH³], 7.35 [m, 1H, pyH⁵], 6.77 [s, 1H, pyC(H)=O].

Reaction of compound [Mo₂(CO)₆(pyC(H)=O)₂] (**2b**) with H₂NⁿBu.

To a freshly prepared solution of [Mo₂(CO)₆(pyC(H)=O)₂] (**2b**) (0.218 g, 0.38 mmol), H₂NⁿBu (0.056 g, 0.76 mmol) was added and stirred at room temperature under CO atmosphere during 15 min. The solvents were evaporated in vacuo, and the residue was washed with hexane (2 x 15mL). The resulting solid residue was dissolved in CH₂Cl₂ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound [Mo(CO)₄(pyC(H)=NⁿBu)] (**4a**) as brown microcrystals. Yield 0.240 g, 85%. Anal. Calcd. for C₁₄H₁₄MoN₂O₄: C 45.42, H 3.81, N 7.57. Found: C 45.21, H 3.70, N 7.33 %. IR (THF), ν(CO): 2012 s, 1902 vs, 1889 sh, 1846 s cm⁻¹. IR (CH₂Cl₂), ν (CO): 2015 s, 1908 vs, 1887 sh, 1837 s cm⁻¹. ¹H NMR (300.13 MHz, Acetone-d₆, r.t.) δ = 9.10 [d(5), 1H, pyH⁶], 8.83 [s, 1H, pyC(H)=N], 8.17 [td(8, 2), 1H, pyH⁴], 8.11 [d(7), 1H, pyH³], 7.67 [m, 1H, pyH⁵], 4.07 [t(7), 2H, NCH₂CH₂CH₂CH₃], 2.05 [q(7), 2H, NCH₂CH₂CH₂CH₃], 1.39 [m, 2H, NCH₂CH₂CH₂CH₃], 0.99 [t(7), 3H, CH₃]. ¹H NMR (300.13 MHz, THF-d₈, r.t.) δ = 9.08 [d(5), 1H, pyH⁶], 8.63 [s, 1H, pyC(H)=N], 8.01 [td(8, 2), 1H, pyH⁴], 7.91 [d(8), 1H, pyH³], 7.52 [m, 1H, pyH⁵], 4.02 [t(7), 2H, NCH₂CH₂CH₂CH₃], 2.02 [m, 2H, NCH₂CH₂CH₂CH₃], 1.38 [m, 2H, NCH₂CH₂CH₂CH₃], 1.00 [t(7), 3H, CH₃].

Reaction of compound [Mo₂(CO)₆(pyC(H)=O)₂] (**2b**) with H₂NCH₂Ph.

To a freshly prepared solution of [Mo₂(CO)₆(pyC(H)=O)₂] (**2b**) (0.218 g, 0.38 mmol), H₂NCH₂Ph (0.083 g, 0.76 mmol) was added and stirred at room temperature under CO atmosphere during 15 min. The solvents were evaporated in vacuo, and the residue was washed with hexane (2 x 15mL). The resulting solid residue was dissolved in CH₂Cl₂ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound [Mo(CO)₄(pyC(H)=NCH₂Ph)] (**4b**) as dark red microcrystals. Yield 0.267 g, 87%. Anal. Calcd. for C₁₇H₁₂MoN₂O₄: C 50.51, H 2.99, N 6.93. Found C 50.69, H 3.09, N 6.71. IR (CH₂Cl₂), ν(CO): 2016 s, 1910 vs, 1886 sh, 1837 s cm⁻¹. IR (THF), ν(CO): 2012 s, 1906 vs, 1888 sh, 1845 s cm⁻¹. ¹H NMR (400.13 MHz, Acetone-d₆, r.t.) δ = 9.08 [d(5), sH, pyH⁶], 9.05 [s, 1H, pyC(H)=N], 8.17 [t(1), 1H, pyH⁴], 8.16 [d(1), 1H, pyH³], 7.66 [m, 1H, pyH⁵], 7.49 [m, 2H, Ph], 7.42-7.32 [m, 3H, Ph], 5.26 [s, 2H, NCH₂].

Reaction of compound [Mo₂(CO)₆(pyC(H)=O)₂] (2b) with H₂N^tBu.

To a freshly prepared solution of [Mo₂(CO)₆(pyC(H)=O)₂] (2b) (0.218 g, 0.38 mmol), H₂N^tBu (0.056 g, 0.76 mmol) was added and stirred at room temperature under CO atmosphere during 24 hours. If this reaction is carried out at refluxing temperature of THF it takes just 8 hours to complete. The solvents were evaporated in vacuo, and the residue was washed with hexane (2 x 15 mL). The resulting solid residue was dissolved in CH₂Cl₂ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound [Mo(CO)₄(pyC(H)=N^tBu)] (4c) as dark red microcrystals. Yield 0.220 g, 78%. Anal. Calcd. for C₁₄H₁₄MoN₂O₄: C 45.42, H 3.81, N 7.57. Found: C 45.57, H 3.66, N 7.66 %. IR (THF), ν(CO): 2013 s, 1902 vs, 1885 sh, 1841 s cm⁻¹. ¹H NMR (300.13 MHz, Acetone-d₆, r.t.) δ = 9.13 [d(5), 1H, pyH⁶], 8.81 [s, 1H, pyC(H)=N], 8.17 [m, 2H, pyH⁴, pyH³], 8.11 [d(7), 1H, pyH³], 7.68 [m, 1H, pyH⁵], 1.62 [s, 9H, C(CH₃)₃].

Synthesis of [Mo(CO)₄(pyC(H)=O)] (3)

Pyridine-2-carbaldehyde (0.064 g, 0.60 mmol) was added to a solution of [Mo(CO)₄(NBD)]² (NBD = norbornadiene) (0.180 g, 0.60 mmol) in THF (20 mL). The color of the solution changed immediately from yellow to deep blue. The solution was stirred for 30 min. Addition of hexane and slow evaporation at reduced pressure gave compound 3 as black solid which was washed with hexane (2 x 10 mL). Yield 0.111 g, 59%. Anal. Calcd. for C₁₀H₅MoNO₅: C 38.12, H 1.60, N 4.44. Found: C 38.37, H 1.49, N 4.34 %. IR (THF), ν(CO): 2018 s, 1909 vs, 1893 sh, 1848 s cm⁻¹. IR (CH₂Cl₂), ν(CO): 2022 s, 1918 vs, 1893 sh, 1843 s cm⁻¹. ¹H NMR (300.13 MHz, Acetone-d₆, r.t.) δ = 10.26 [s, 1H, pyC(H)=O], 9.22 [d(5), 1H, pyH⁶], 8.64 [d(8), 1H, pyH³], 8.39 [td(8, 2), 1H, pyH⁴], 7.97 [m, 1H, pyH⁵]. ¹H NMR (300.13 MHz, THF-d₈, r.t.) δ = 9.99 [s, 1H, pyC(H)=O], 9.19 [d(5), 1H, pyH⁶], 8.40 [d(8), 1H, pyH³], 8.20 [td(8, 2), 1H, pyH⁴], 7.78 [m, 1H, pyH⁵].

Reaction of compound [Mo(CO)₄(pyC(H)=O)] (3) with H₂NⁿBu.

To a solution of H₂NⁿBu (0.017 g, 0.23 mmol) in THF (10 mL) was added [Mo(CO)₄(pyC(H)=O)] (3) (0.073 g, 0.23 mmol). The mixture was stirred at room temperature for 2 hours. The solvents were evaporated in vacuo and the residue was washed with hexane (2 x 15 mL). The resulting solid residue was dissolved in CH₂Cl₂ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound [Mo(CO)₄(pyC(H)=NⁿBu)] (4a) as brown microcrystals. Yield 0.055 g, 65%.

Reaction of compound [Mo(CO)₄(pyC(H)=O)] (3) with H₂NCH₂Ph.

To a solution of H₂NCH₂Ph (0.025 g, 0.23 mmol) in THF (10 mL) was added [Mo(CO)₄(pyC(H)=O)] (3) (0.073 g, 0.23 mmol). The mixture was stirred at room temperature for 2 hours. The solvents were evaporated in vacuo and the residue was washed with hexane (2 x 15 mL). The resulting solid residue was dissolved in CH₂Cl₂ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound [Mo(CO)₄(pyC(H)=NCH₂Ph)] (4b) as red microcrystals. Yield 0.060 g, 64%.

Reaction of compound [Mo(CO)₄(pyC(H)=O)] (3) with H₂N^tBu.

To a solution of H₂N^tBu (0.017 g, 0.23 mmol) in THF (10 mL) was added [Mo(CO)₄(pyC(H)=O)] (3) (0.073 g, 0.23 mmol). The mixture was stirred at room temperature for 2 hours. The solvents were evaporated in vacuo and the residue was washed with hexane (2 x 15 mL). The resulting solid residue was dissolved in CH₂Cl₂ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound [Mo(CO)₄(pyC(H)=N^tBu)] (4c) as dark red microcrystals. Yield 0.047 g, 55%.

Reaction of compound [Mo(CO)₄(pyC(H)=O)] (3) with H₂NPh.

To a solution of H₂NPh (0.021 g, 0.23 mmol) in THF (10 mL) was added [Mo(CO)₄(pyC(H)=O)] (3) (0.073 g, 0.23 mmol). The mixture was stirred at room temperature for 2 hours. The solvents were evaporated in vacuo and the residue was washed with hexane (2 x 15 mL). The resulting solid residue was dissolved in CH₂Cl₂ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compounds [Mo(CO)₄(pyC(H)=NPh)] (4d) as dark purple microcrystals. Yield 0.057 g, 64%. Anal. Calcd. for C₁₆H₁₀MoN₂O₄: C 49.25, H 2.58, N 7.18. Found: C 49.31, H 2.77, N 7.30 %. IR (THF), ν(CO): 2013 s, 1905 vs, 1892 sh, 1850 s cm⁻¹. IR (CH₂Cl₂), ν(CO): 2016 s, 1911 vs, 1889 sh, 1841 s cm⁻¹. ¹H NMR (400.13 MHz, Acetone-d₆, r.t.) δ = 9.19 [d(5), 1H, pyH⁶], 8.98 [s, 1H, pyC(H)=N], 8.29 [d(7), 1H, pyH³], 8.24 [td(8, 1), 1H, pyH⁴], 7.76 [ddd(7, 5, 2), 1H, pyH⁵], 7.65 [m, 2H, Ph], 7.55 [m, 2H, Ph], 7.45 [m, 1H, Ph].

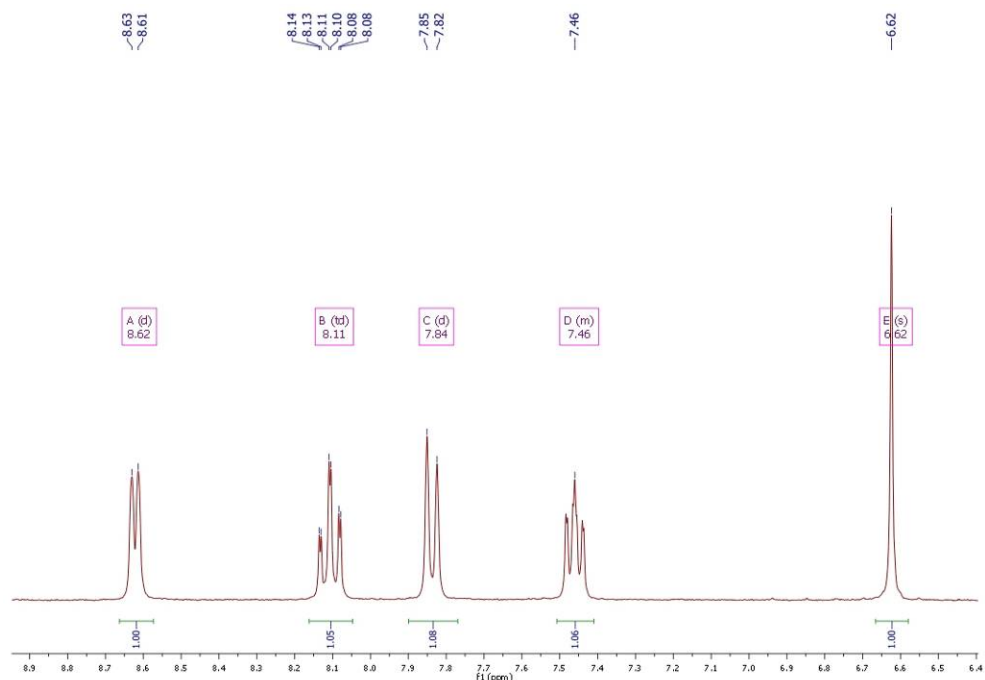


Figure S1: ¹H NMR (300.13 MHz, THF-d₈) spectrum of compound 2b.

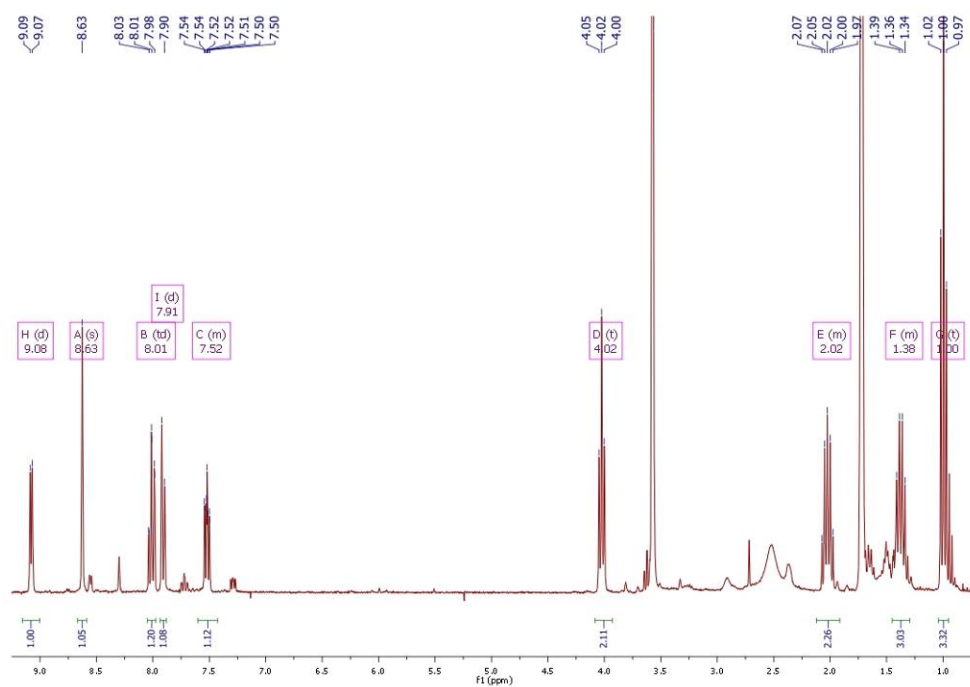


Figure S2: ¹H NMR (300.13 MHz, THF-d₈) spectrum of compound 4a.

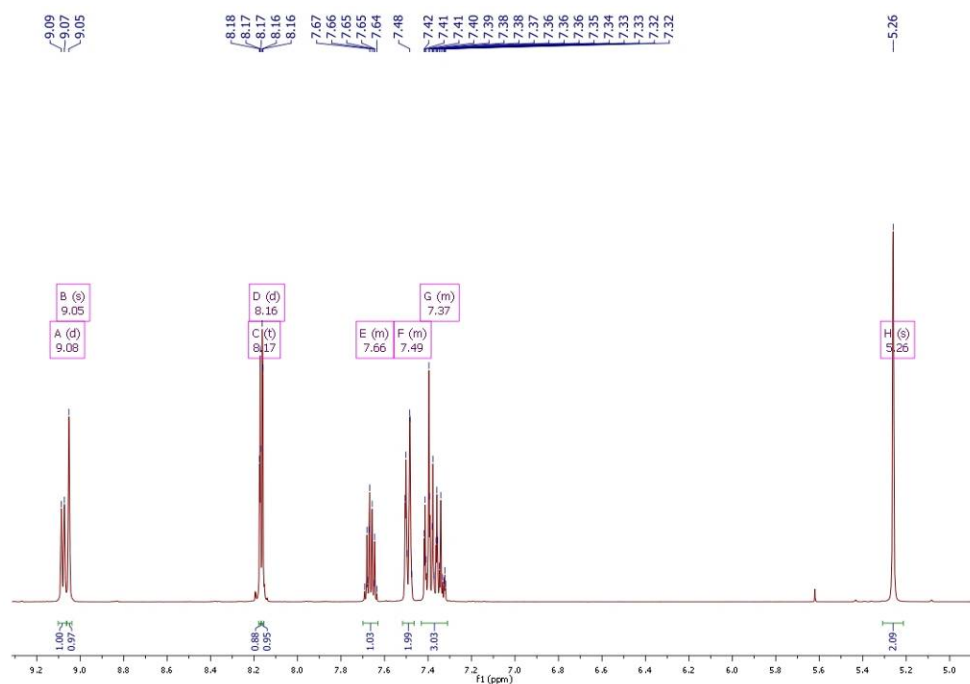


Figure S3: ^1H NMR (400.13 MHz, acetone- d_6) spectrum of compound **4b**.

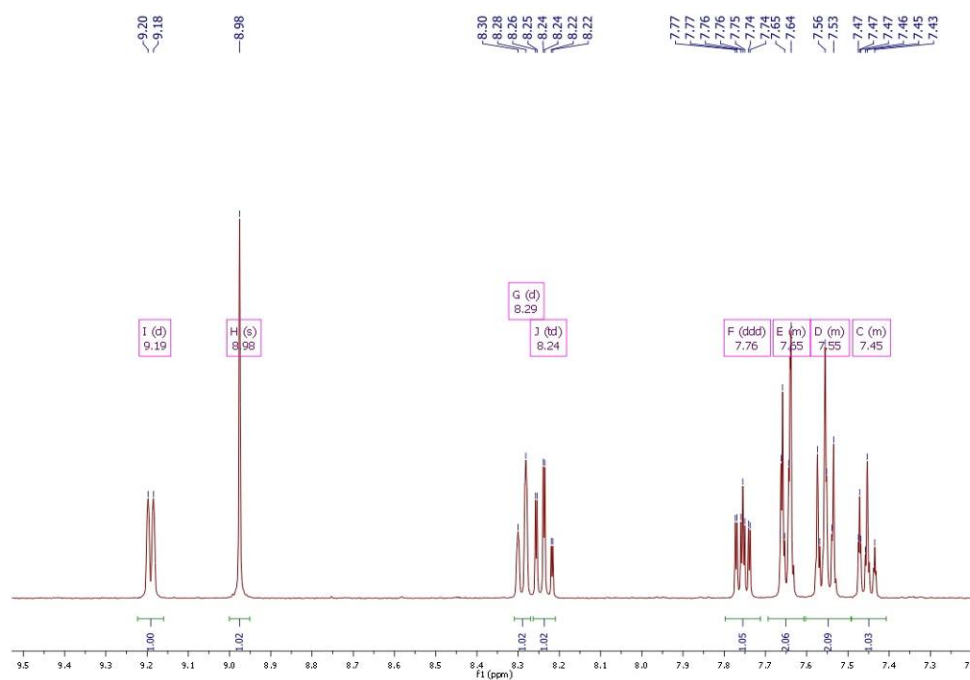


Figure S4: ^1H NMR (400.13 MHz, acetone- d_6) spectrum of compound **4d**.

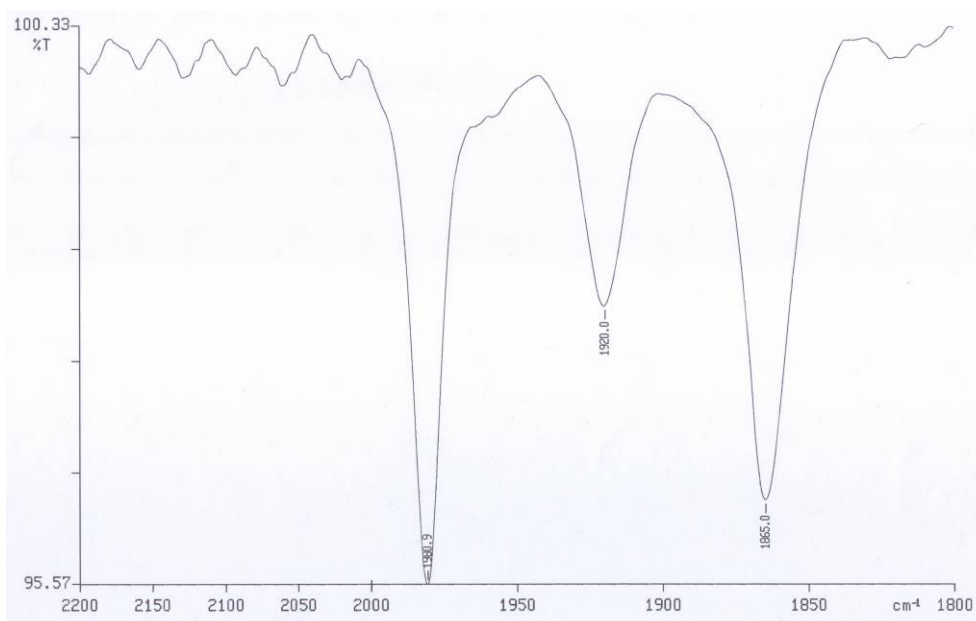


Figure S5: IR spectrum in THF of compound **2a**.

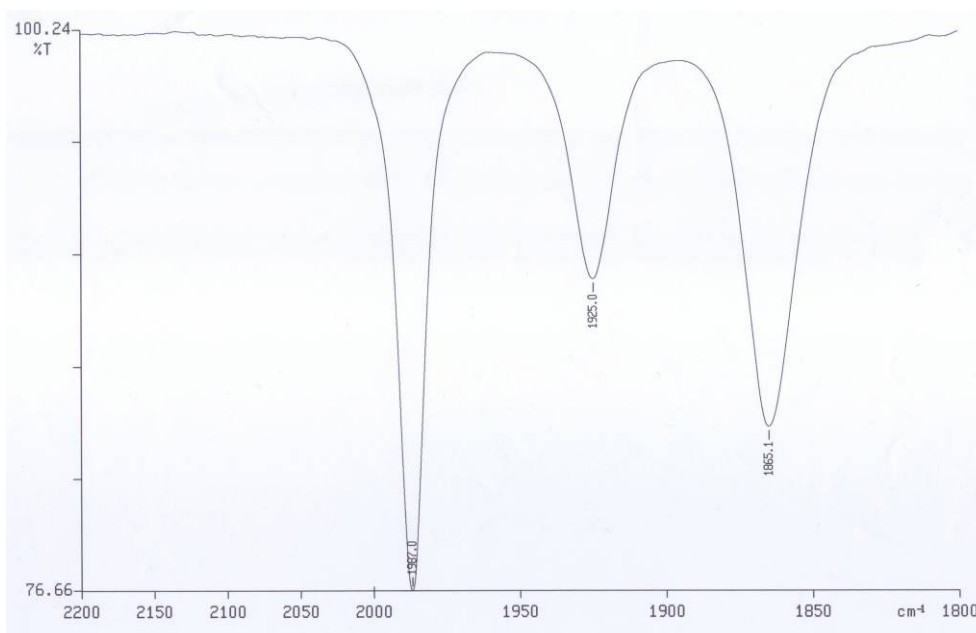


Figure S6: IR spectrum in THF of compound **2b**.

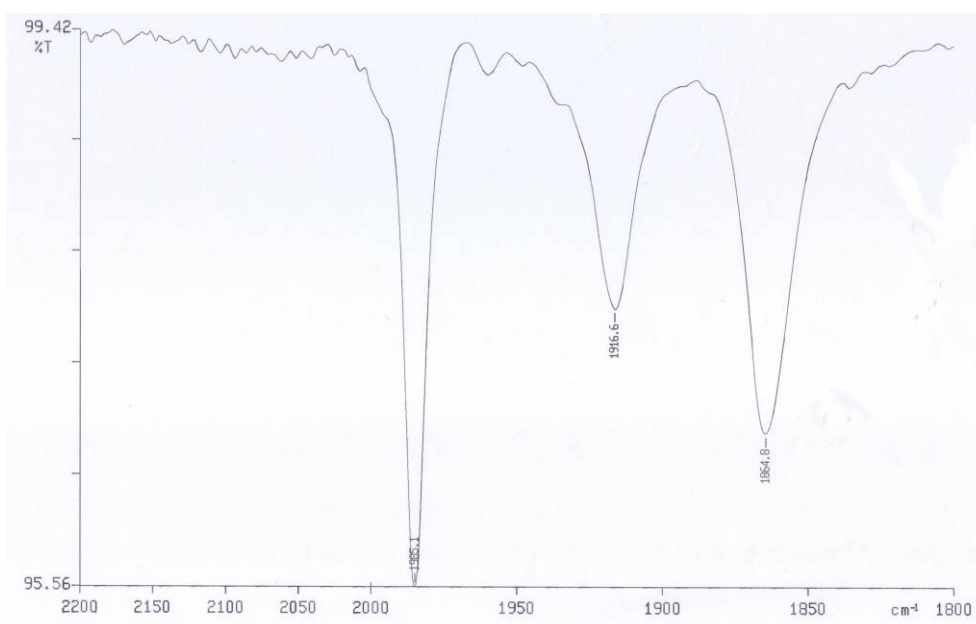


Figure S7: IR spectrum in THF of compound **2c**.

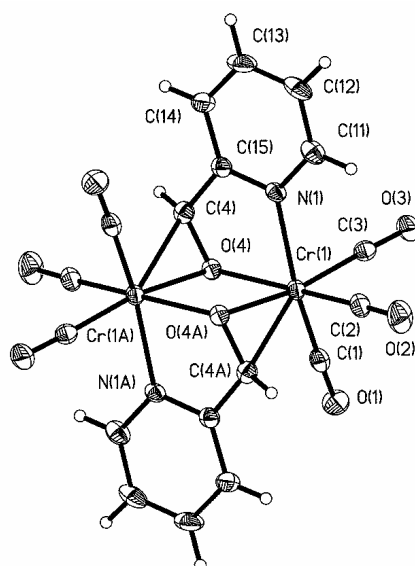


Figure S8: Thermal ellipsoid plots (30 % probability) of the structure of complex **2a**.

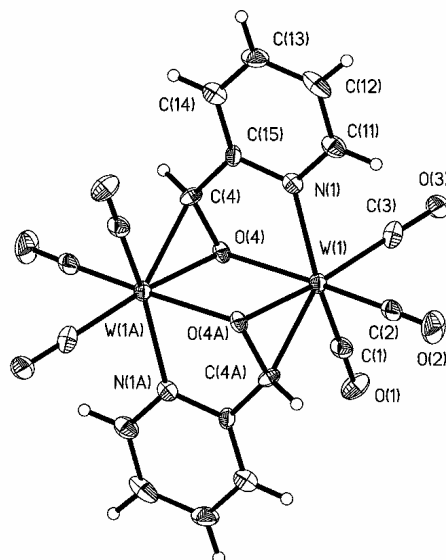


Figure S9: Thermal ellipsoid plots (30 % probability) of the structure of complex **2c**.

¹ D.P. Tate, W.R. Knipple, J.M. Augl, *Inorg. Chem.*, **1962**, *1*, 433-434.

² E. W. Abel, M. A. Bennett, R. Burton, G. Wilkinson, *J. Chem. Soc.*, **1958**, 4559-4563.