

Supporting Information

Synthesis and Photophysical Properties of Multimetallic Gold/Zinc Complexes of (P,N,N,N,P) and (P,N,N)Ligands

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Experimental procedures	2
Measured NMR spectra	6
Measured IR spectra (ATR)	19
Measured and simulated ESI spectra	23
Crystallographic data	25
Measured and calculated UV/Vis spectra	26
Comparison of fluorescence spectra	27
Optimized Structure Geometries in chloroform	29
Potential energy scan for the rotation of the pyrimidine-pyridine bond	31
The effect of rotation and complexation of other ions on the absorption spectra	31
Dipole moments	32
Overview of the first four excitations	32
Orbitals	37
Cooperativity	40
References	41

Experimental procedures

General remarks

All reaction steps were carried out under an argon atmosphere using Schlenk techniques. All reactions involving gold(I) compounds were carried out in the absence of light. 2-Methyl-2-thiopseudothiourea hemisulfate, sodium methoxide, and zinc chloride were purchased from Sigma Aldrich and used without further purification. 2-Diphenylphosphinoethylamine,^[1] 2-(*N,N'*-dimethylamino-1-oxoprop-2-en-1-yl)pyridine,^[2] 2,6-bis[(*N,N'*-dimethylamino)-1-oxoprop-2-en-1-yl]pyridine,^[2] and tetrahydrothiophene gold(I) chloride^[3] were synthesized according to published procedures. All solvents were degassed according to standard techniques before use. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Bruker Spectrospin Avance 400 device, ESI mass spectra were recorded on a Bruker Esquire 6000 equipment. X-ray structures were measured on an Oxford Diffraction Gemini S Ultra device. The structures were resolved and refined with ShelX.^[4]

2-Diphenylphosphinoethylguanidinium sulfate dihydrate (**a**)

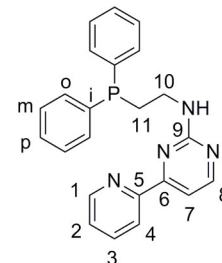
2-Diphenylphosphinoethylamine (24.8 g; 108 mmol) is added to aqueous ammonia (432 mmol of ammonia; 215 mL; 7.5 wt%). Upon stirring, 2-methyl-2-thiopseudothiourea hemisulfate (46.6 g; 167 mmol) is added in one portion and the reaction mixture is heated to 55 °C. The reaction is finished when the evolution of methanethiol ceases. After cooling to room temperature, the supernatant solution is decanted and the residue is washed with water (2×50 mL). The highly viscous yellowish oil is mixed with toluene (100 mL) and stirred at room temperature overnight. After this time, a colourless solid is filtered off and dried *in vacuo*. Yield: 19.8 g (29.2 mmol; 54 %) of a colourless solid. ¹H NMR / ppm (MeOH-*d*₄; 400 MHz): 7.43-7.41 (m; 4H; H_{ortho}), 7.35-7.33 (m; 6H; H_{meta} and H_{para}), 3.25 (q; ³J_{HH} = 7.9 Hz; 2H; NCH₂), 2.57 (s, 1H, NH-CH₂), 2.39 (t; ³J_{HH} = 7.9 Hz; 2H; PCH₂). The amino protons cannot be assigned due to H-D exchange with the solvent. ¹³C NMR / ppm (101 MHz, MeOH-*d*₄): 158.4 (s; C(NH₂)₂), 138.9 (d; ¹J_{CP} = 12.2 Hz; C_{ipso}), 133.8 (d; ²J_{CP} = 19.6 Hz; C_{ortho}), 129.9 (d; ³J_{CP} = 27.0 Hz; C_{meta}), 129.7 (s; C_{para}), 39.9 (d; ²J_{CP} = 25.6 Hz; NCH₂), 28.7 (d; ¹J_{CP} = 13.3 Hz; PCH₂). ³¹P NMR / ppm (MeOH-*d*₄; 162 MHz): -22.0 (s). Elemental analysis / % : calcd. for [C₃₀H₄₂N₆O₆P₂S] C 53.25, H 6.26, N 12.42, S 4.74; found C 53.04, H 5.87, N 11.99, S 4.56. HR-MS / m/z (EI+): calcd. for [**a** - H₂SO₄]⁺ 271.1238; found 271.1241.

2-(2-(2-diphenylphosphinoethylamino)pyrimidin-4-yl)pyridine (**1**)

2-Diphenylphosphinoethylguanidinium sulfate dihydrate (**a**) (2.40 g; 3.80 mmol) is dissolved in ethanol (20 mL). 2-(*N,N'*-dimethylamino-1-oxoprop-2-en-1-yl)pyridine (1.00 g; 6.00 mmol) and sodium methoxide (0.50 g; 9.00 mmol) are added in succession and the resulting yellow suspension is heated to reflux for 24 hours. After cooling to room temperature, the volatiles are evaporated. The residue is extracted three times with dichloromethane (3×20 mL). The combined organic phases are washed with water (3×20 mL) and dried over sodium sulfate. The solvent is evaporated and the crude product is washed with methanol (2×20 mL) and dried *in vacuo*. Yield: 1.10 g (2.80 mmol; 46%) of a colourless solid. ¹H NMR / ppm (400 MHz, CDCl₃): 8.68 (ddd; ³J_{HH} = 4.8 Hz; ⁴J_{HH} = 1.6 Hz, and ⁵J_{HH} = 0.8 Hz; 1H; H1), 8.41 (d; ³J_{HH} = 5.1 Hz; 1H; H8), 8.26 (d; ³J_{HH} = 7.9 Hz; 1H; H4), 7.79 (td; ³J_{HH} = 7.8 Hz and ⁴J_{HH} = 1.8 Hz; 1H; H3), 7.57 (d; ³J_{HH} = 5.1 Hz; 1H; H7), 7.79-7.44 (m; 4H; H_o), 7.38-7.36 (m; 1H; H2); 7.35-7.31 (m; 6H; H_m and H_p), 5.41 (t; ³J_{HH} = 5.8 Hz; 1H; NH), 3.72-3.65 (m; 2H; H11), 2.49-2.46 (m; 2H; H12). ¹³C NMR / ppm (100.6 MHz, CDCl₃): 163.6 (s; C9), 162.3 (s; C8), 159.5 (s; C6), 154.9 (s; C5), 149.4

(s; C1), 138.2 (d; $^1J_{CP} = 12.2$ Hz; C_i), 137.0 (s; C3), 133.0 (d; $^2J_{CP} = 18.8$ Hz; C_o), 128.8 (s; C_p), 128.7 (d; $^3J_{CP} = 6.7$ Hz; C_m), 125.1 (s; C2), 121.6 (s; C4), 107.1 (s; C7), 38.8 (d; $^2J_{CP} = 22.7$ Hz; C10), 28.9 (d; $^1J_{CP} = 13.2$ Hz; C11). ^{31}P NMR / ppm (CDCl₃, 162 MHz): -21.3 (s). Elemental analysis / %: calcd. for [C₂₃H₂₁N₄P] C 71.86, H 5.51, N 14.57; found C 71.81, H 5.44, N 14.57.

For the assignment of the NMR resonances of compound **1** and its corresponding transition metal complexes, the atoms are numbered as shown.



Compound **1Zn**

Zinc dichloride (101 mg; 740 μmol) is dissolved in tetrahydrofuran (10 mL). **1** (284 mL; 740 μmol) is added in one portion and the mixture is stirred at room temperature for 16 hours. The solvent is evaporated. The residue is dissolved in dichloromethane (2 mL). After the addition of diethyl ether (10 mL), the colourless precipitate is filtered and dried in vacuo. Yield: 235 mg (451 μmol , 61 %) of a colourless solid. ^1H NMR / ppm (400 MHz, CDCl₃): 8.82 (d; $^3J_{HH} = 4.8$ Hz; 1H; H1), 8.69 (d; $^3J_{HH} = 4.8$ Hz; 1H; H8), 8.21 (m; 2H; H3 and H4), 7.80 (d; $^3J_{HH} = 4.7$ Hz; 1H; H2), 7.49-7.47 (m; 4H; H_o), 7.35-7.33 (m; 6H; H_m and H_p), 7.29 (d; $^3J_{HH} = 4.7$ Hz; 1H; H7), 6.53 (s; br; 1H; NH), 3.70-3.63 (m; 2H; H10); 2.50-2.46 (m; 2H; H11). ^{13}C NMR / ppm (101 MHz, CDCl₃): 163.6 (s; C9), 160.4 (s; C8), 155.6 (s; C6), 149.5 (s; C1), 148.4 (s; C5), 141.6 (s; C3), 132.9 (d; $^2J_{CP} = 18.8$ Hz; C_o), 131.0 (d; $^1J_{CP} = 9.7$ Hz; C_i), 129.0 (s; C2 and C_p), 128.7 (d; $^3J_{CP} = 6.8$ Hz; C_m), 123.2 (s; C4), 105.9 (s; C7), 39.9 (d; $^2J_{CP} = 26.1$ Hz; C10), 28.2 (d; $^1J_{CP} = 13.6$ Hz; C11). ^{31}P NMR / ppm (162 MHz, CDCl₃): -22.0 (s). Elemental analysis / %: calcd. for [C₂₃H₂₁Cl₂N₄PZn] C 53.05, H 4.06, N 10.76; found C 52.60, H 4.31, N 10.66.

Compound **1Au**

Tetrahydrothiophene gold(I) chloride (130 mg; 400 μmol) is dissolved in dichloromethane (10 mL). **1** (156 mg; 400 μmol) is added in one portion and the mixture is stirred at room temperature for one hour. The colourless solution is concentrated to a volume of about 1 mL. After the addition of diethyl ether (5 mL), a colourless precipitate forms, which is filtered and dried in vacuo. Yield: 222 mg (360 μmol ; 89 %) of a colourless solid. ^1H NMR / ppm (400 MHz, CDCl₃): 8.68 (d; $^3J_{HH} = 4.0$ Hz; 1H; H1), 8.39 (d; $^3J_{HH} = 5.0$ Hz; 1H; H8), 8.32 (d; $^3J_{HH} = 7.4$ Hz; 1H; H4), 7.90 (t; $^3J_{HH} = 7.5$ Hz; 1H; H3), 7.71-7.66 (m; 4H; H_o), 7.61 (d; $^3J_{HH} = 5.0$ Hz; 1H; H7), 7.49-7.41 (m; 6H; H_m and H_p), 7.41-7.39 (m; 1H; H2), 5.48 (t; $^3J_{HH} = 6.0$ Hz; 1H; H10), 3.94-3.86 (m; 2H; H11), 2.97-2.90 (m; 2H; H12). ^{13}C NMR / ppm (101 MHz, CDCl₃): 163.9 (s; C9), 161.7 (s; C8), 159.3 (s; C6), 154.3 (s; C5), 149.2 (s; C1), 137.4 (s; C3), 133.3 (d; $^2J_{CP} = 13.3$ Hz; C_o), 132.1 (d; $^1J_{CP} = 2.4$ Hz; C_i), 129.4 (d; $^3J_{CP} = 11.7$ Hz; C_m), 128.8 (s; C_p), 125.3 (s; C2), 121.8 (s; C4), 107.8 (s; C7), 38.7 (d; $^2J_{CP} = 7.8$ Hz; C13), 28.5 (d; $^1J_{CP} = 35.5$ Hz; C12). ^{31}P NMR / ppm (162 MHz, CDCl₃): 24.4 (s). Elemental analysis / %: calcd. for [C₂₃H₂₁AuClN₄P] C 44.78, H 3.43, N 9.08; found C 44.25, H 3.66, N 8.63.

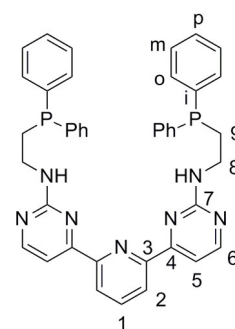
Compound **1AuZn**

Zinc chloride (33.0 mg; 240 μmol) is suspended in dichloromethane (5 mL). **1Au** (150 mg; 240 μmol) is dissolved in dichloromethane and dropwise added to the suspension for 30 minutes. After stirring for 24 hours at room temperature, the solvent is evaporated and the residue is washed with diethyl ether (2 \times 5 ml). Yield: 140 mg (190 μmol , 77 %) of a colourless solid. ^1H NMR / ppm (400 MHz, CDCl_3): 8.76 (m; 1H; H1), 8.68 (s; br; 1H; H8), 8.26 (s; br; 1H; H4), 8.14 (s; br; 1H; H3), 7.73-7.68 (m; 5H; H2 and H_o), 7.53-7.46 (m; 7H; H7, H_m, and H_p), 6.52 (s; 1H; NH), 3.90-3.85 (m; 2H; H10), 2.91 (td; $^2J_{\text{PH}} = 10.8$ Hz and $^3J_{\text{HH}} = 7.8$ Hz; 2H; H11). ^{13}C NMR / ppm (101 MHz, CDCl_3): 163.7 (s; C9), 160.2 (s; C8), 155.9 (s; C6), 149.6 (s; C1), 148.3 (s; C5), 141.7 (s; C3), 133.4 (d; $^2J_{\text{CP}} = 13.5$ Hz; C_o), 132.4 (d; $^1J_{\text{CP}} = 2.6$ Hz; C_i), 129.6 (d; $^3J_{\text{CP}} = 11.8$ Hz; C_m), 128.8 (s; C_p), 128.2 (s; C2), 123.6 (s; C4), 106.8 (s; C5), 38.6 (d; $^2J_{\text{CP}} = 10.8$ Hz; C10), 28.4 (d; $^1J_{\text{CP}} = 36.5$ Hz; C9). ^{31}P NMR / ppm (162 MHz, CDCl_3): 23.5 (s). Elemental analysis / %: calcd. for $[\text{C}_{23}\text{H}_{21}\text{AuCl}_3\text{N}_4\text{PZn}]$ C 36.68, H 2.81, N 7.44; found C 37.24, H 2.81, N 7.37.

2,6-Bis(2-(2-diphenylphosphinoethylamino)pyrimidin-4-yl)pyridine (**2**)

2-Diphenylphosphinoethylguanidinium sulfate dihydrate (**a**) (10.5 g; 15.5 mmol) is dissolved in ethanol (100 mL). 2,6-Bis[(*N,N'*-dimethylamino)-1-oxoprop-2-en-1-yl]-pyridine (2.73 g; 10.0 mmol) and sodium methoxide (1.62 g; 30.0 mmol) are added in succession and the resulting yellow suspension is heated to reflux for 20 hours. Upon heating, a yellow solution forms, followed by the formation of a precipitate. After cooling to -35 $^\circ\text{C}$, the precipitate is filtered and dried. The crude product is added to water (25 ml), stirred for two hours and filtered again. The solid is washed with diethyl ether (2 \times 50 mL) and dried in vacuo. Yield: 4.13 g (5.99 mmol; 60%) of a colourless solid. ^1H NMR / ppm (CDCl_3 , 400 MHz): 8.44 (d; $^3J_{\text{HH}} = 5.1$ Hz; 2H; H6), 8.34 (d; $^3J_{\text{HH}} = 7.8$ Hz; 2H; H2), 7.89 (t; $^3J_{\text{HH}} = 7.8$ Hz; 1H; H1), 7.74 (d; $^3J_{\text{HH}} = 5.1$ Hz; 2H; H5), 7.54-7.42 (m; 8H; H_o), 7.34-7.32 (m; 12H; H_m and H_p), 5.47 (t; $^3J_{\text{HH}} = 5.9$ Hz; 2H; NH), 3.71 (quint; $^3J_{\text{HH}} = 7.3$ Hz; 4H; H8), 2.49 (t; $^3J_{\text{HH}} = 7.6$ Hz; 4H; H9). ^{13}C NMR / ppm (CDCl_3 , 101 MHz): 163.4 (s; C7), 162.3 (s; C4), 159.4 (s; C6), 154.2 (s; C3), 138.2 (d; $^1J_{\text{CP}} = 12.3$ Hz; C_i), 137.9 (s; C1), 132.9 (d; $^2J_{\text{CP}} = 18.7$ Hz; C_o), 128.8 (s; C_p), 128.7 (d; $^3J_{\text{CP}} = 7.0$ Hz; C_m), 122.7 (s; C2), 107.2 (s; C5), 38.9 (d; $^2J_{\text{CP}} = 22.8$ Hz; C8), 28.9 (d; $^1J_{\text{CP}} = 13.1$ Hz; C9). ^{31}P NMR / ppm (CDCl_3 , 162 MHz): -21.2 (s). Elemental analysis / %: calcd. for $[\text{C}_{41}\text{H}_{37}\text{N}_7\text{P}_2]$ C 71.40, H 5.41, N 14.22; found C 70.96, H 5.30, N 14.21. HR-MS / m/z (EI⁺): calcd. for $[\text{C}_{41}\text{H}_{37}\text{N}_7\text{P}_2]^+$ 689.2586; found 689.2580. SI: NMR and IR spectra.

For the assignment of the NMR resonances of compound **2** and its transition metal complexes, the atoms are numbered as shown.



Compound **2Zn**

Zinc dichloride (20.7 mg; 152 μmol) is dissolved in tetrahydrofuran (10 ml). **2** (105 mg; 152 μmol) is added in one portion and the mixture is stirred at room temperature for 16 hours whereby the colourless suspension turns into a yellow solution. The volatiles are evaporated. The residue is mixed with dichloromethane (1.5 mL) and filtered to remove residual zinc chloride. After the addition of diethyl ether (10 mL), a yellow precipitate forms, which is filtered and dried in vacuo. Yield: 108 mg (131 μmol ; 86 %) of a yellow solid. ^1H NMR / ppm (400 MHz, CDCl_3): 8.55 (d; $^3J_{\text{HH}} = 4.8$ Hz; 2H; H6), 8.24 (s; 3H; H1 and H2), 7.53-7.48 (m; 8H H_o), 7.36-7.34 (m; 12H H_m and H_p), 7.22 (d; $^3J_{\text{HH}} = 4.8$ Hz; 2H H5), 3.73-3.68 (m; 4H; H8), 2.60-2.56 (m; 4H; H9). ^{13}C NMR / ppm (101 MHz, CDCl_3): 162.2 (s; C7), 160.9 (s; C6), 154.1 (s; C4), 148.8 (s; C3), 142.9 (s; C1), 133.0 (d; $^2J_{\text{CP}} = 17.9$ Hz; C_o), 131.2 (d; $^1J_{\text{CP}} = 10.2$ Hz; C_i), 129.2 (s; C_p), 128.8 (d; $^3J_{\text{CP}} = 7.1$ Hz; C_m), 124.4 (s; C2), 105.7 (s; C5), 39.5 (d; $^2J_{\text{CP}} = 24.9$ Hz; C8), 27.7 (s; C9). ^{31}P NMR / ppm (162 MHz, CDCl_3): -20.6 (s). Elemental analysis / %: calcd. for $[\text{C}_{41}\text{H}_{37}\text{Cl}_2\text{N}_7\text{P}_2\text{Zn}]$ C 59.62, H 4.51, N 11.87; found C 59.85, H 4.99, N 12.02. SI: NMR, IR, and ESI spectra.

Compound **2Au₂**

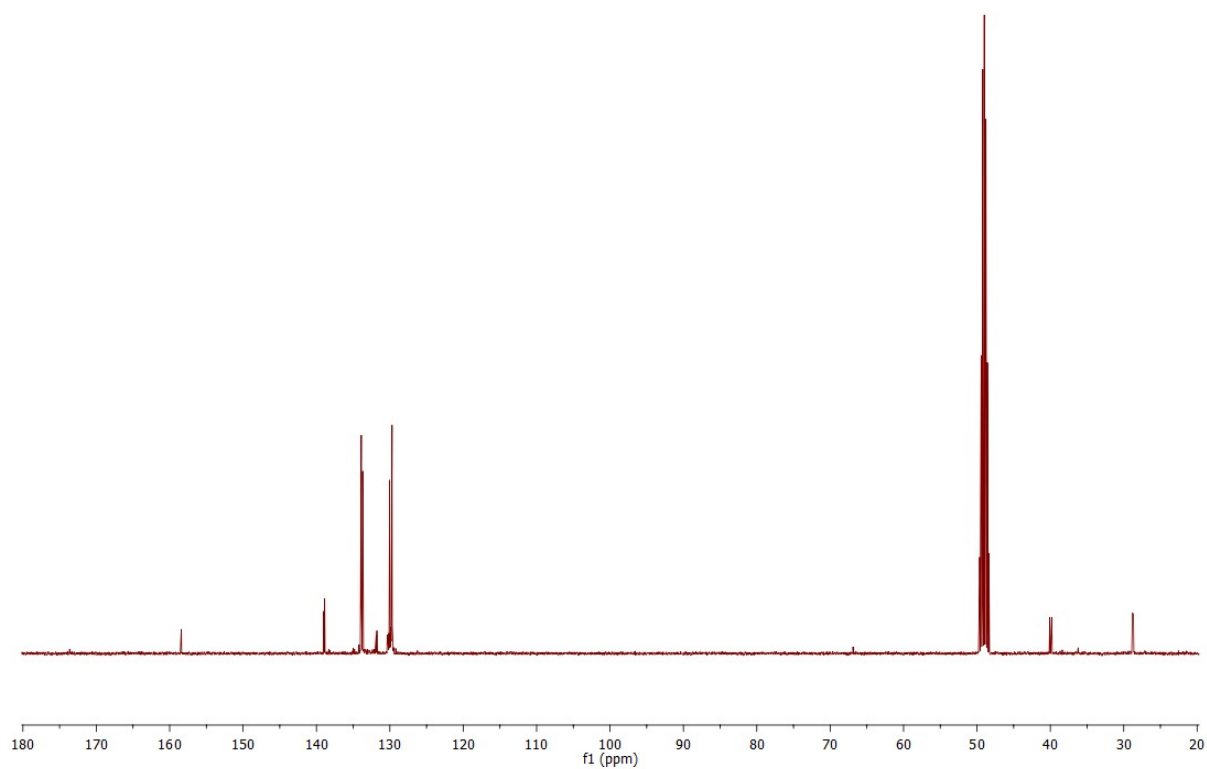
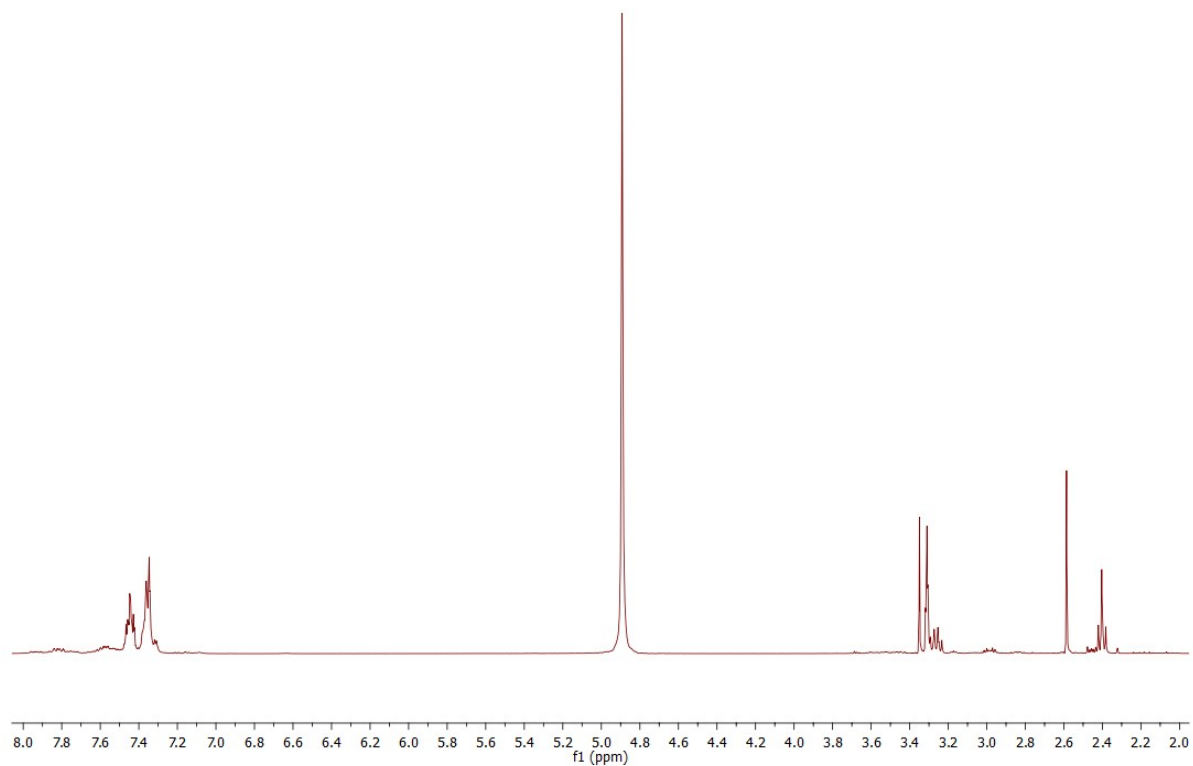
Tetrahydrothiophene gold(I) chloride (138 mg; 430 μmol) is dissolved in dichloromethane (7.5 mL). **2** (141 mg; 205 μmol) is added in one portion and the mixture is stirred at room temperature for 20 minutes. The colourless solution is concentrated to a volume of about 1.5 ml. After the addition of diethyl ether (10 mL), a colourless precipitate forms, which is filtered and dried in vacuo. Yield: 201 mg (174 μmol ; 85 %) of a colourless solid. ^1H NMR / ppm (CDCl_3 , 400 MHz): 8.49-8.39 (m; 4H; H2 and H6), 8.07 (s; br; 1H; H1), 7.77 (d; $^3J_{\text{HH}} = 4.9$ Hz; 2H; H5), 7.71-7.67 (m; 8H; H_o), 7.50-7.44 (m; 12H; H_m and H_p), 5.50 (s; 2H; NH), 3.92 (s; br; 4H; H8), 2.98-2.92 (m; 4H; H9). ^{13}C NMR / ppm (CDCl_3 , 101 MHz): 163.5 (s; C7), 161.8 (s; C6), 153.8 (s; C3 and C4), 133.3 (d; $^2J_{\text{CP}} = 13.3$ Hz; C_o), 132.2 (d; $^1J_{\text{CP}} = 1.7$ Hz; C_i), 129.5 (d; $^3J_{\text{CP}} = 11.8$ Hz; C_m), 128.8 (s; C_p), 123.1 (s; C2), 107.8 (s; C5), 38.6 (d; $^2J_{\text{CP}} = 10.6$ Hz; C8), 28.6 (d; $^1J_{\text{CP}} = 37.3$ Hz; C9). ^{31}P NMR / ppm (CDCl_3 , 162 MHz): 24.23 (s). Elemental analysis / %: calcd. for $[\text{C}_{41}\text{H}_{37}\text{Au}_2\text{Cl}_2\text{N}_7\text{P}_2]$ C 42.65, H 3.23, N 8.49; found C 42.85, H 3.29, N 8.44. SI: NMR, IR and ESI spectra.

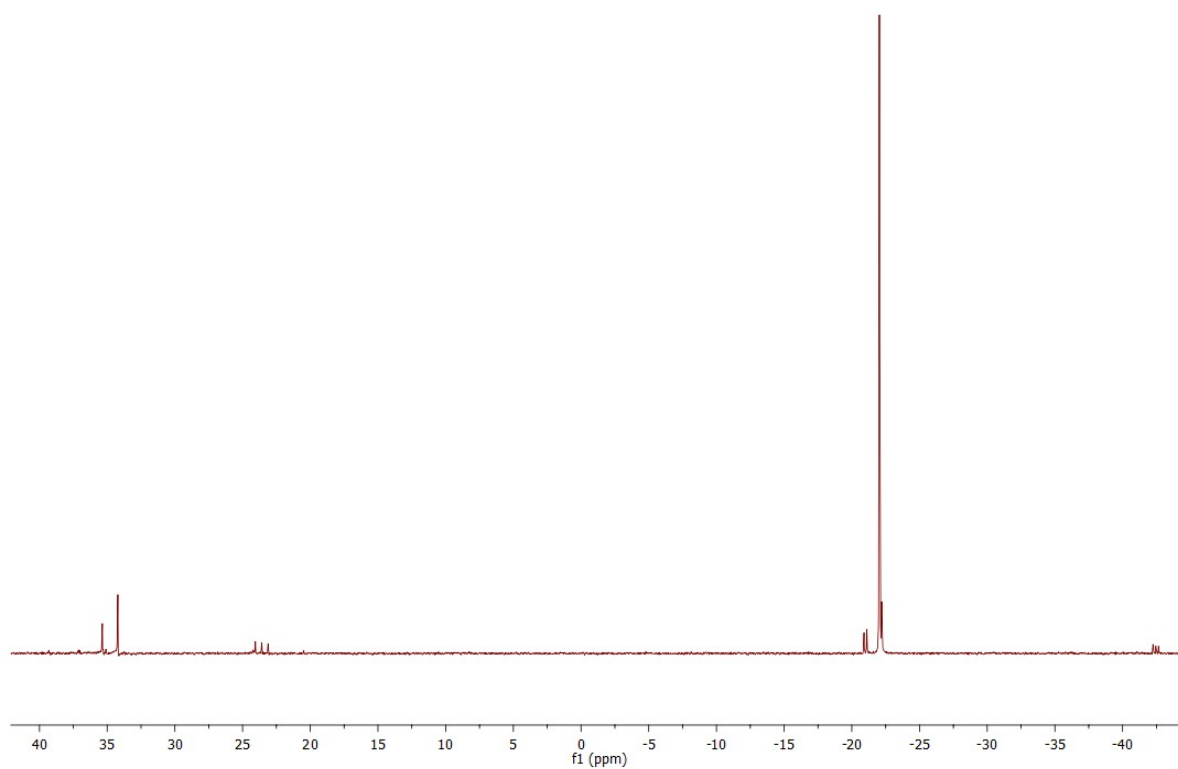
Compound **2Au₂Zn**

Tetrahydrothiophene gold(I) chloride (98.6 mg; 306 μmol) is dissolved in dichloromethane (10 mL). **2Zn** (141 mg; 205 μmol) is added in one portion and the mixture is stirred at room temperature for two hours. The yellowish solution is concentrated to a volume of about 1.5 ml. After the addition of diethyl ether (10 mL), a pale yellow precipitate forms, which is filtered and dried in vacuo. Yield: 145 mg (112 μmol ; 75 %) of a colourless solid. Crystals suitable for X-ray structure analysis were obtained from a concentrated acetonitrile solution. ^1H NMR / ppm (400 MHz, CDCl_3): 8.55 (d; $^3J_{\text{HH}} = 4.9$ Hz; 2H; H6), 8.34 (m; 3H; H1 and H2), 7.75-7.69 (m; 8H; H_o), 7.56-7.47 (m; 14H; NH, H_m , and H_p), 7.35 (d; $^3J_{\text{HH}} = 4.9$ Hz; 2H; H5), 3.91-3.83 (m; 4H; H8), 2.96 (m; 4H; H9). ^{13}C NMR / ppm (101 MHz, CDCl_3): 162.4 (s; C7), 160.8 (s; C6), 154.3 (s; C4), 148.8 (s; C3), 143.0 (s; C1), 133.4 (d; $^2J_{\text{CP}} = 13.6$ Hz; C_o), 132.3 (d; $^1J_{\text{CP}} = 2.4$ Hz; C_i), 129.5 (d; $^3J_{\text{CP}} = 11.9$ Hz; C_m), 129.1 (s; C_p), 128.5 (s; C2), 106.6 (s; C5), 38.5 (d; $^2J_{\text{CP}} = 10.5$ Hz; C8), 28.5 (d; $^1J_{\text{CP}} = 36.5$ Hz; C9). ^{31}P NMR / ppm (162 MHz, CDCl_3): 23.6 (s). Elemental analysis / %: calcd. for $[\text{C}_{41}\text{H}_{37}\text{Au}_2\text{Cl}_4\text{N}_7\text{P}_2\text{Zn}]$ C 38.15, H 2.89, N 7.48; found C 37.76, H 3.05, N 7.48. SI: NMR, IR, and ESI spectra.

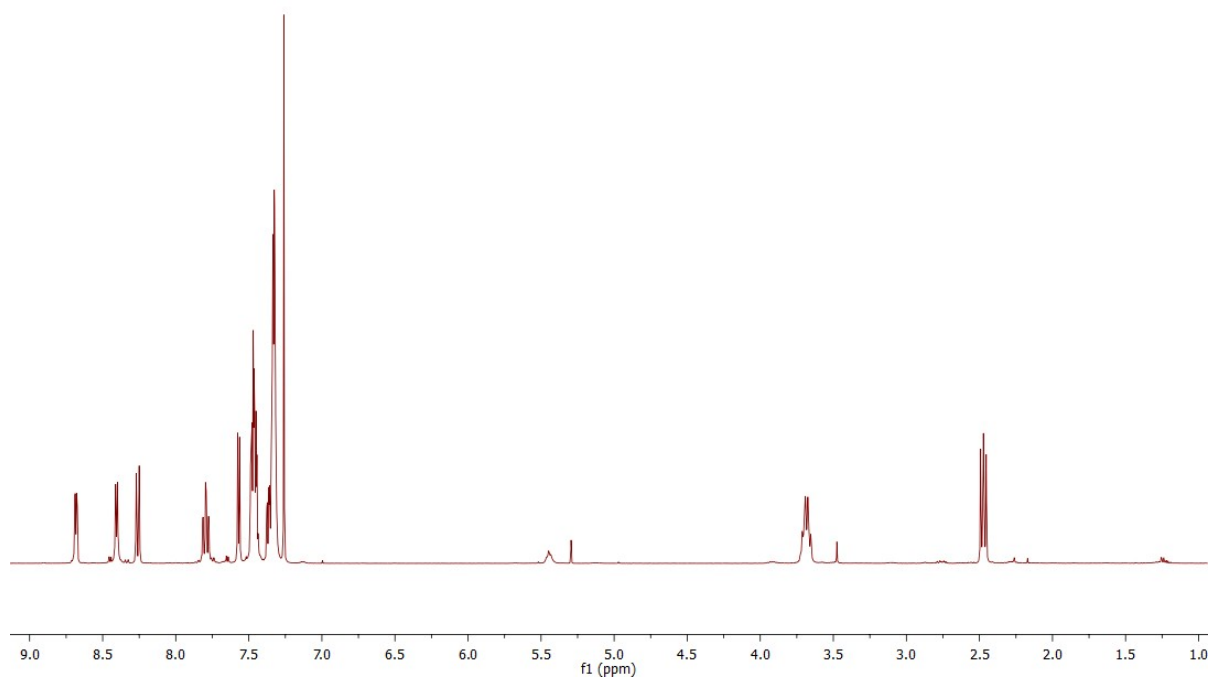
Measured NMR spectra

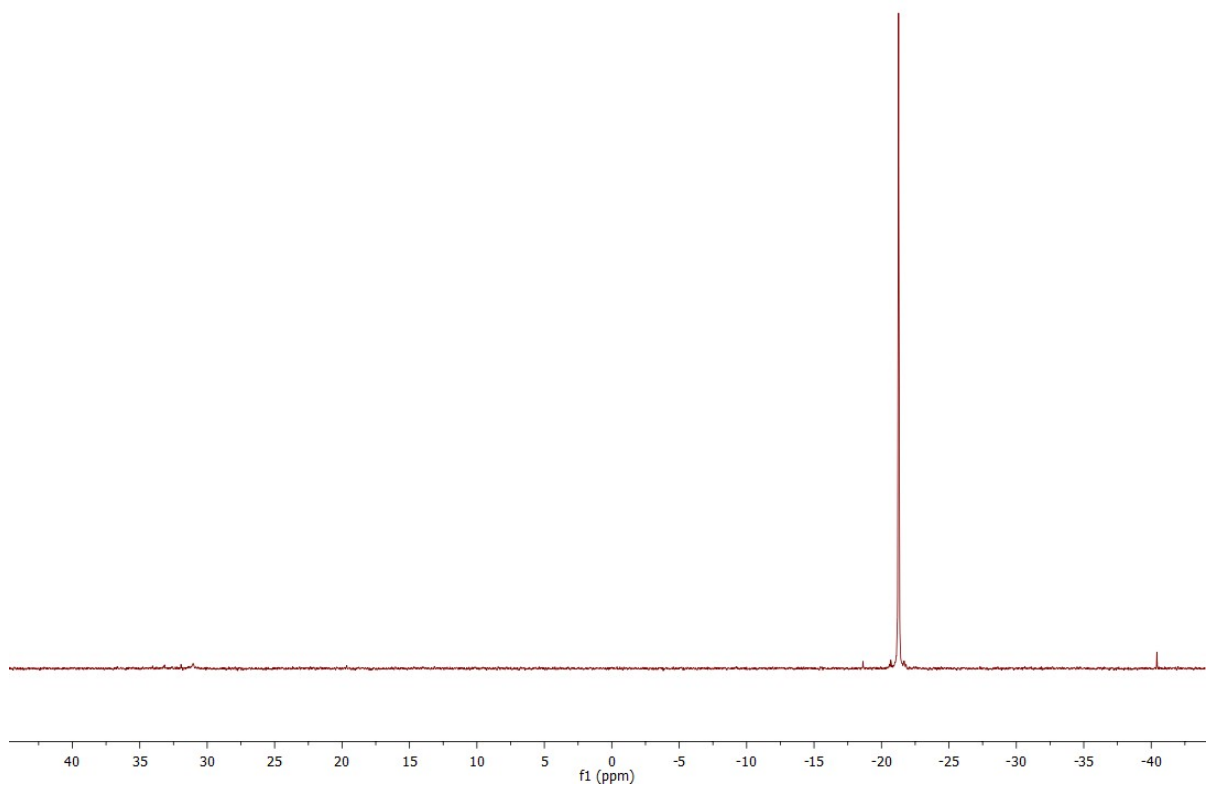
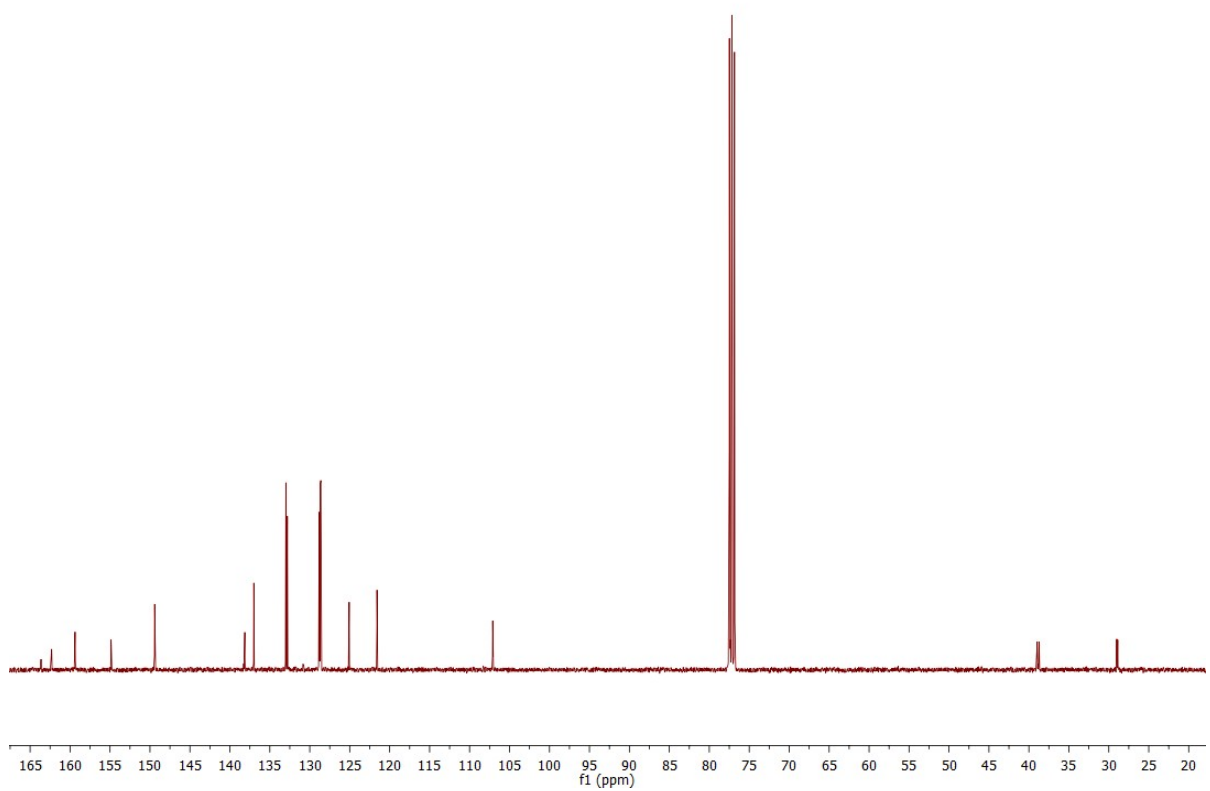
^1H , ^{13}C , and ^{31}P NMR spectrum of **a**



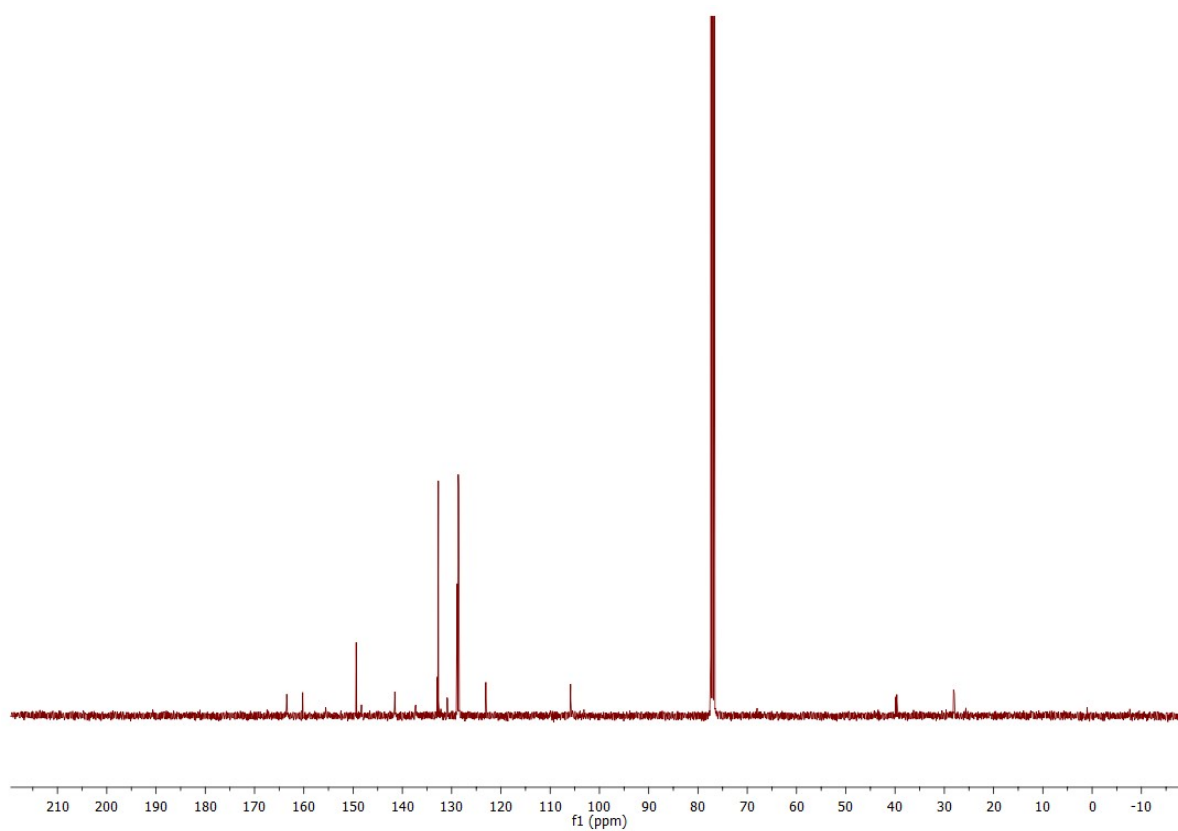
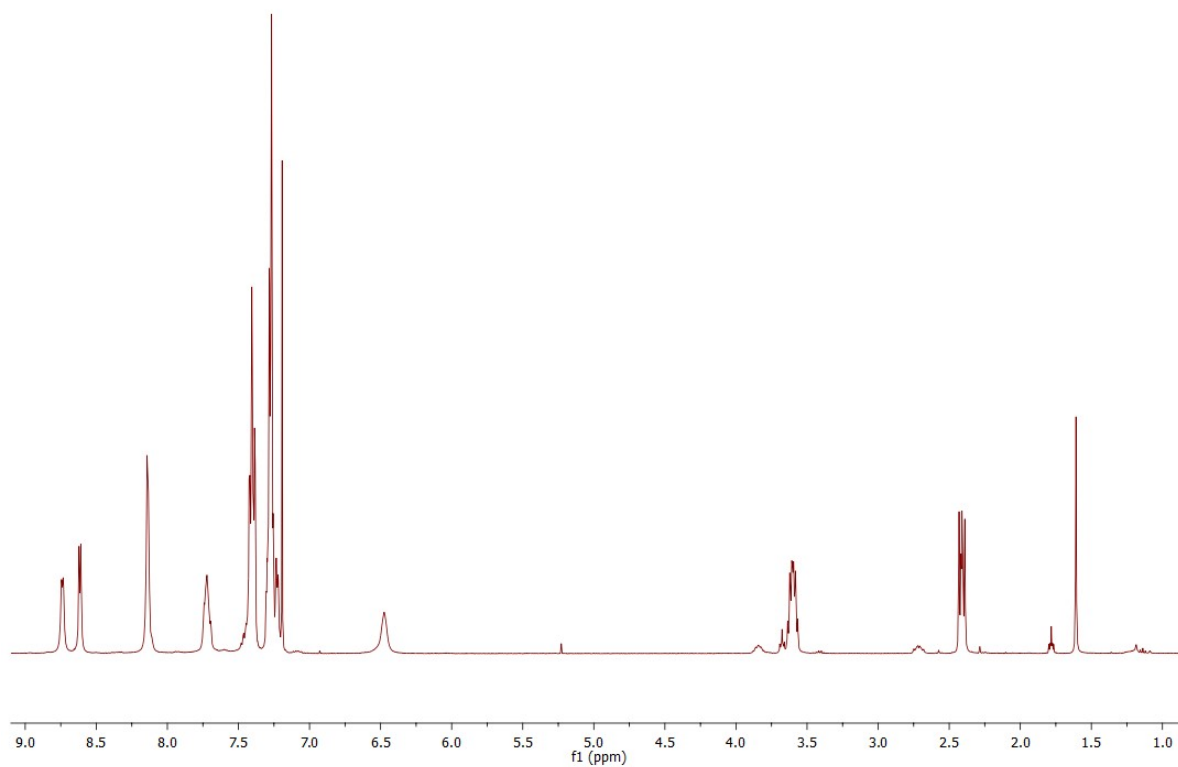


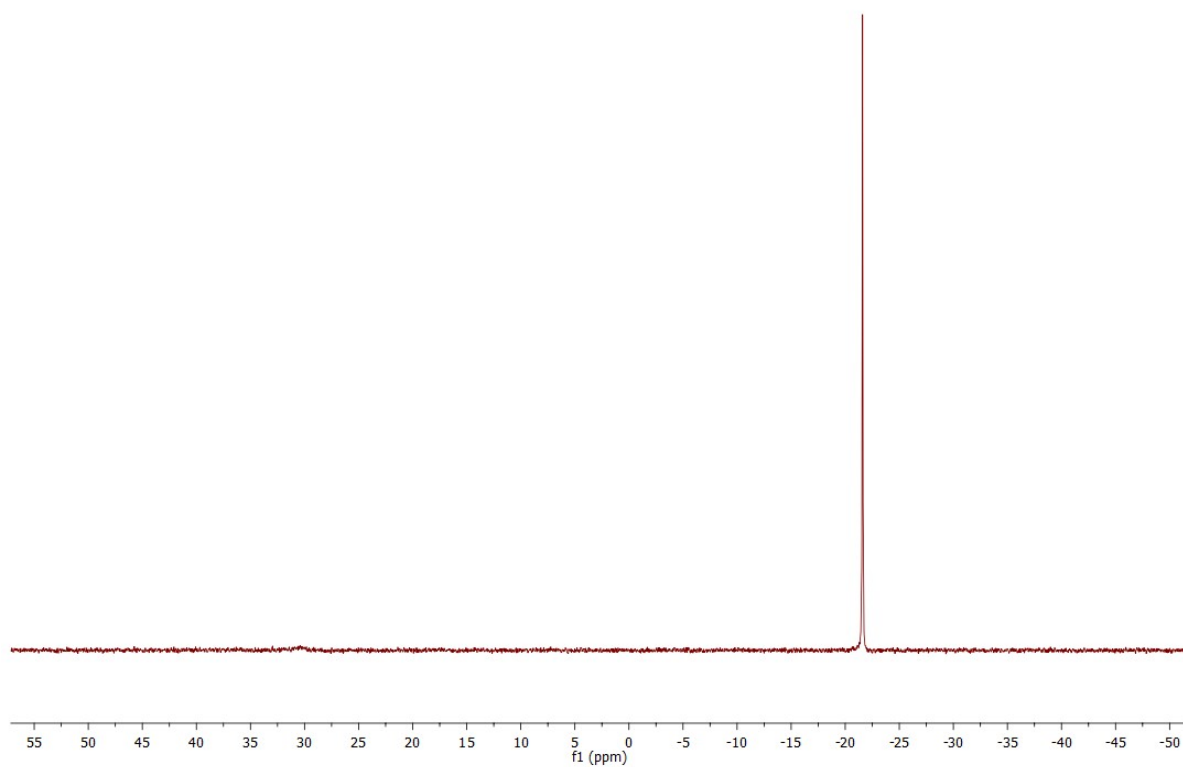
^1H , ^{13}C , and ^{31}P NMR spectrum of **1**



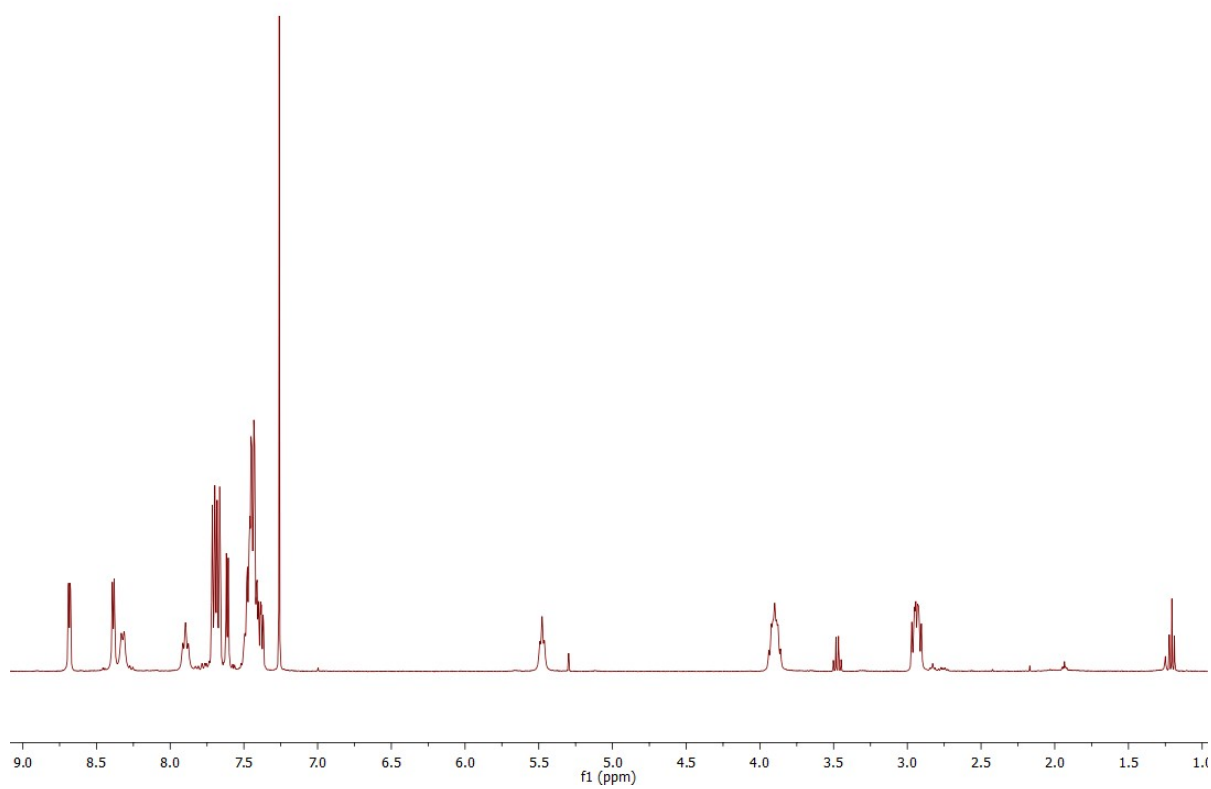


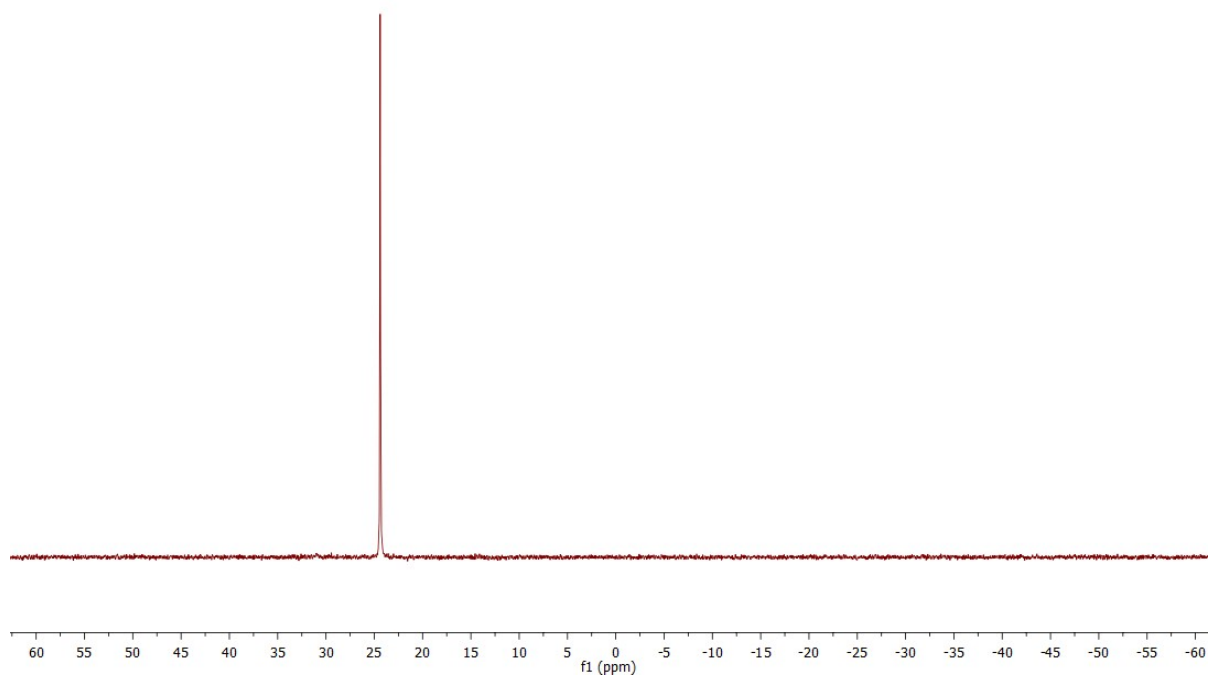
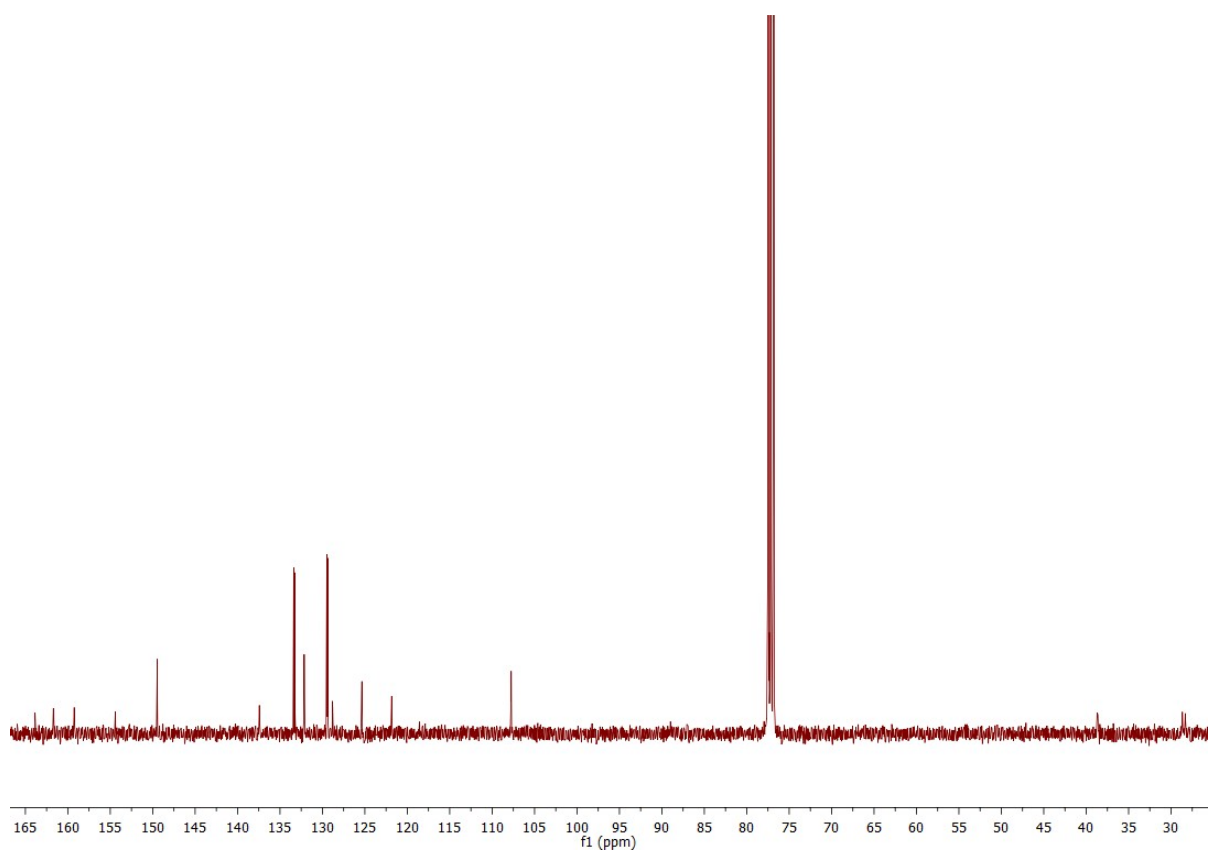
^1H , ^{13}C , and ^{31}P NMR spectrum of **1Zn**



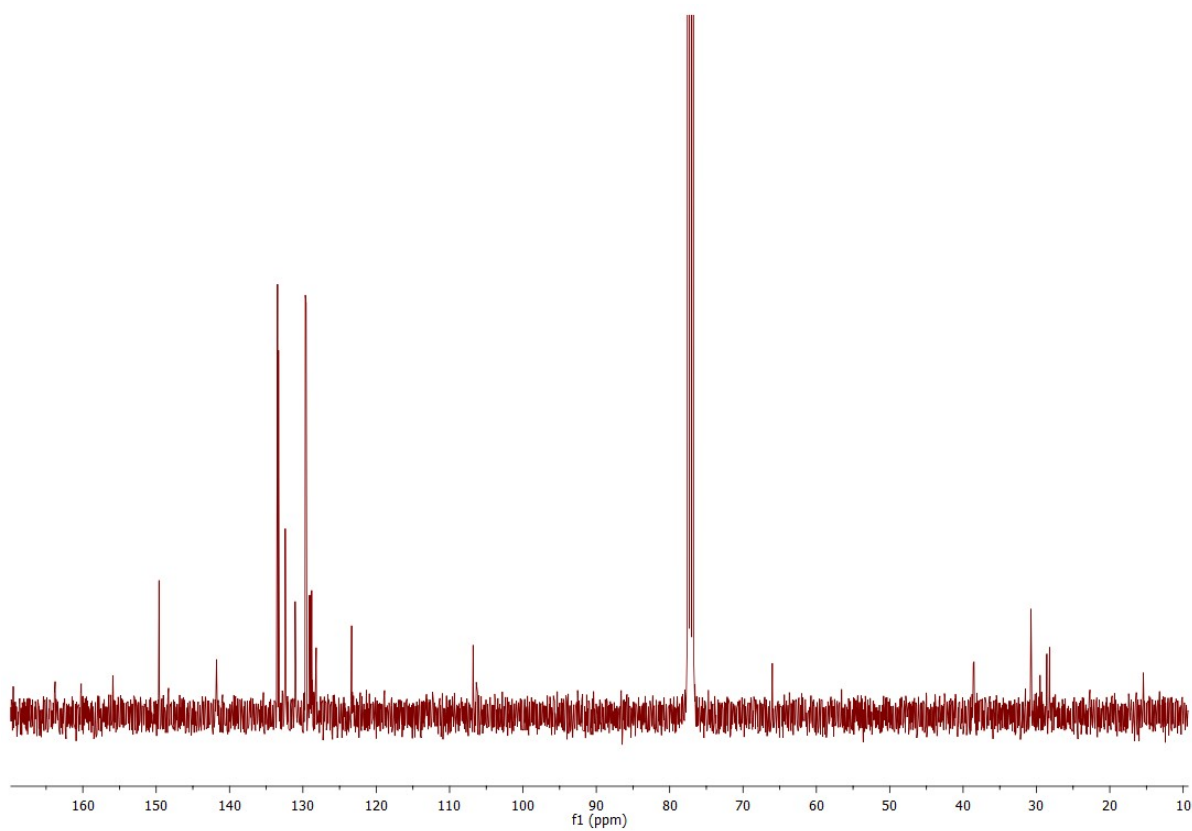
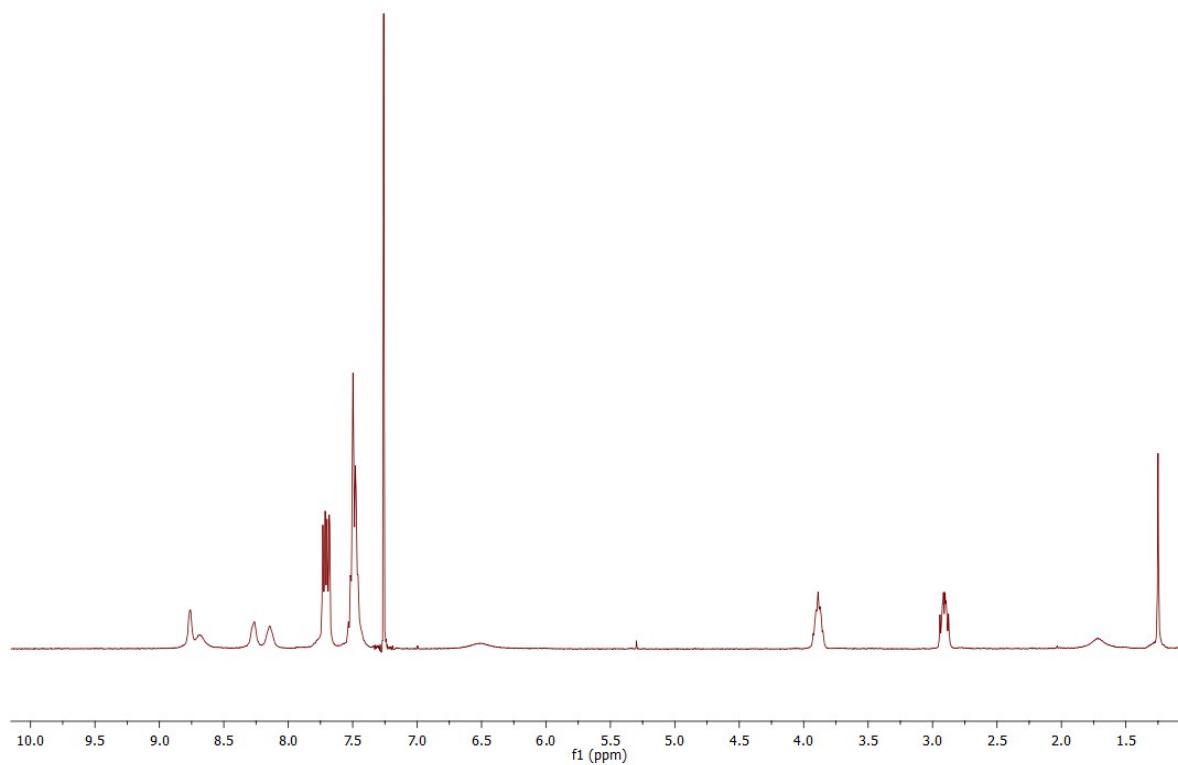


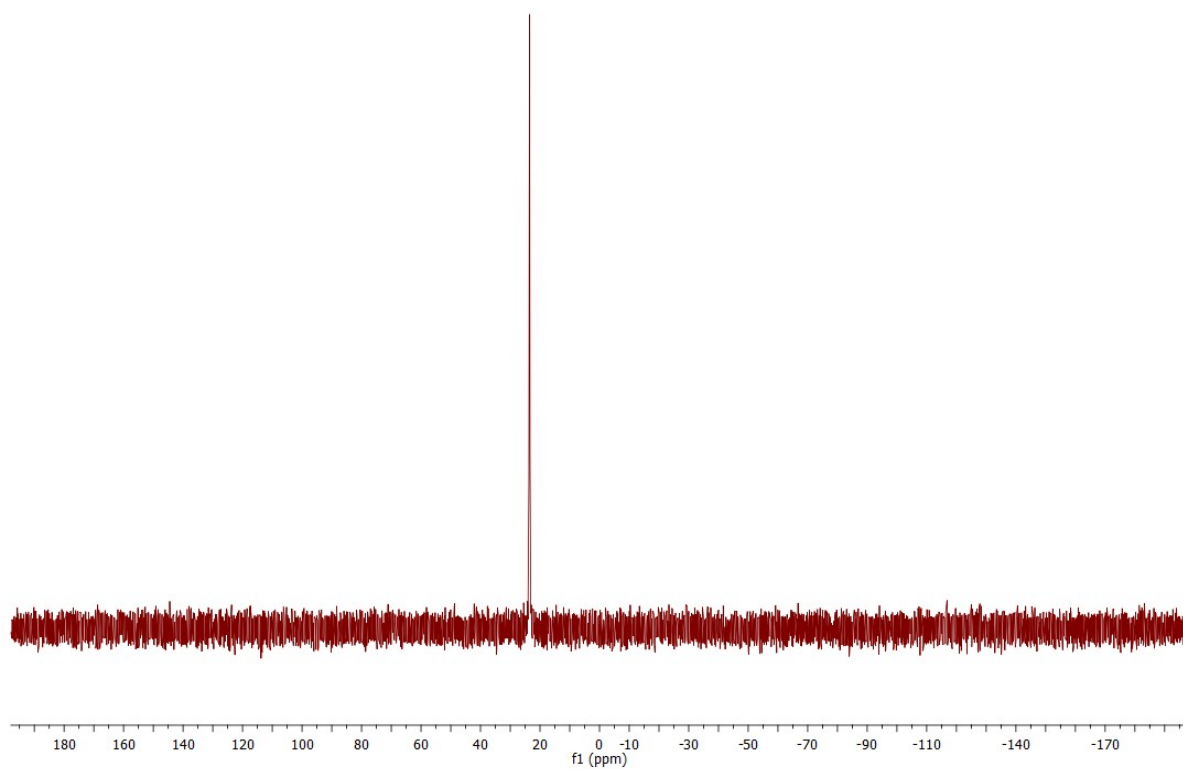
^1H , ^{13}C , and ^{31}P NMR spectrum of **1Au**



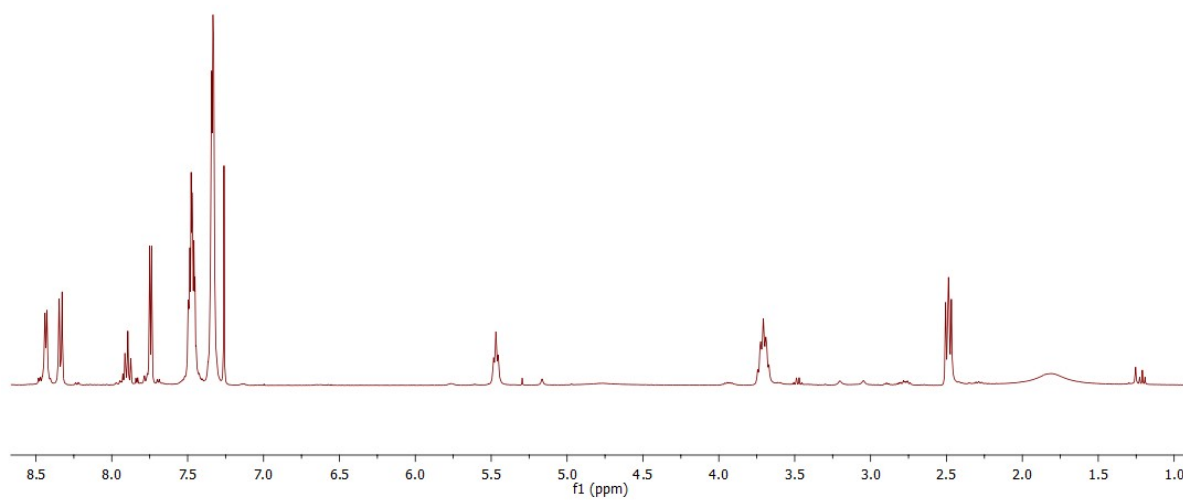


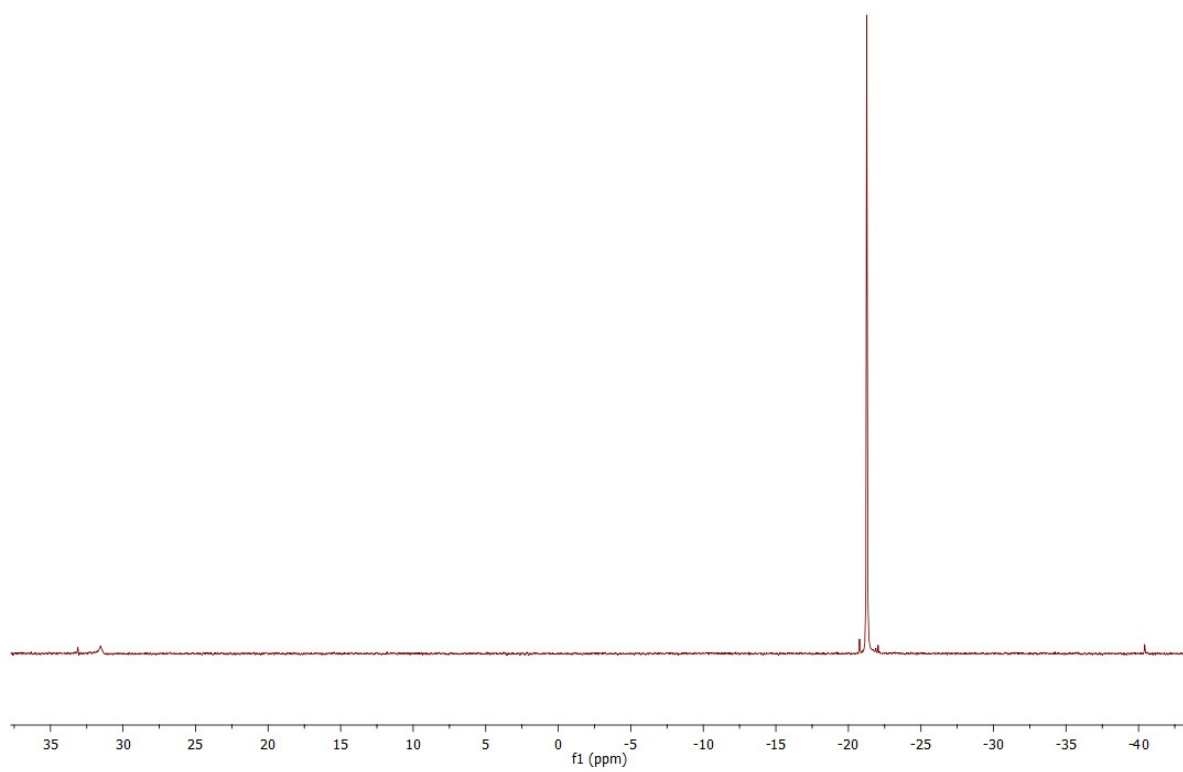
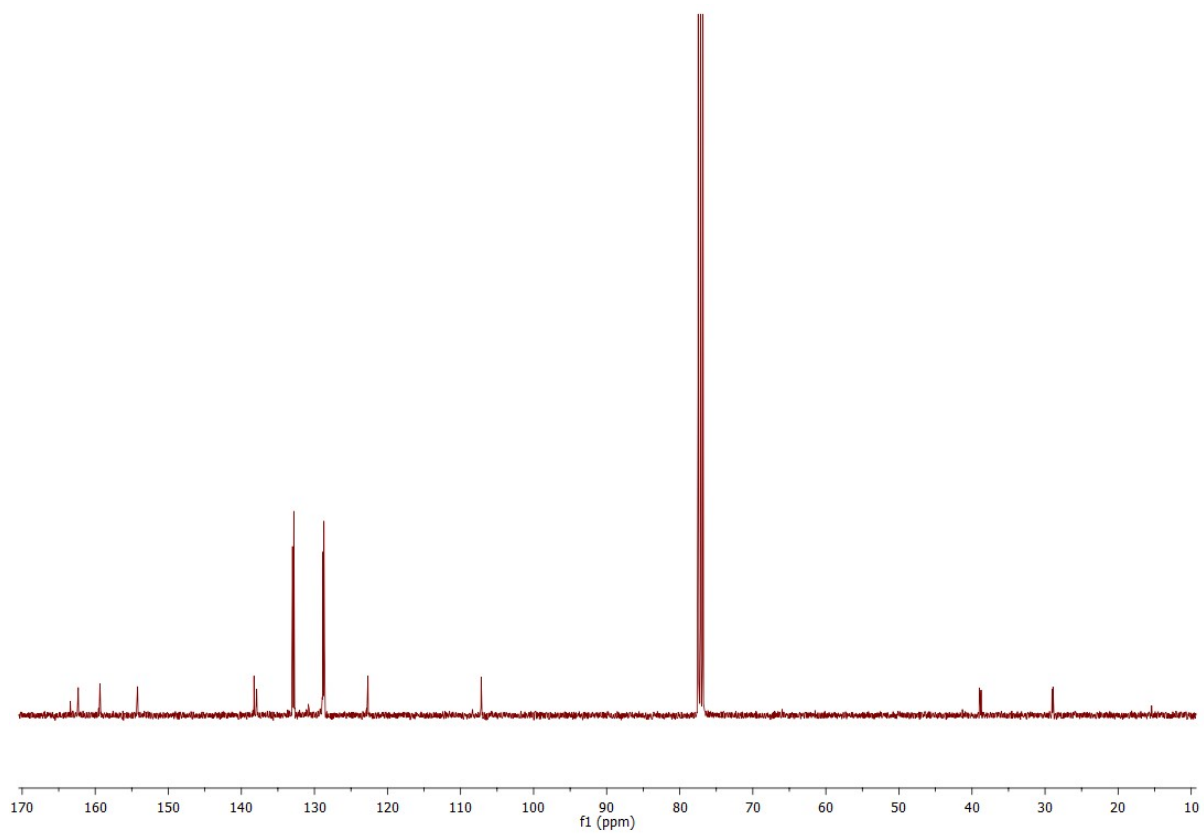
^1H , ^{13}C , and ^{31}P NMR spectrum of **1AuZn**



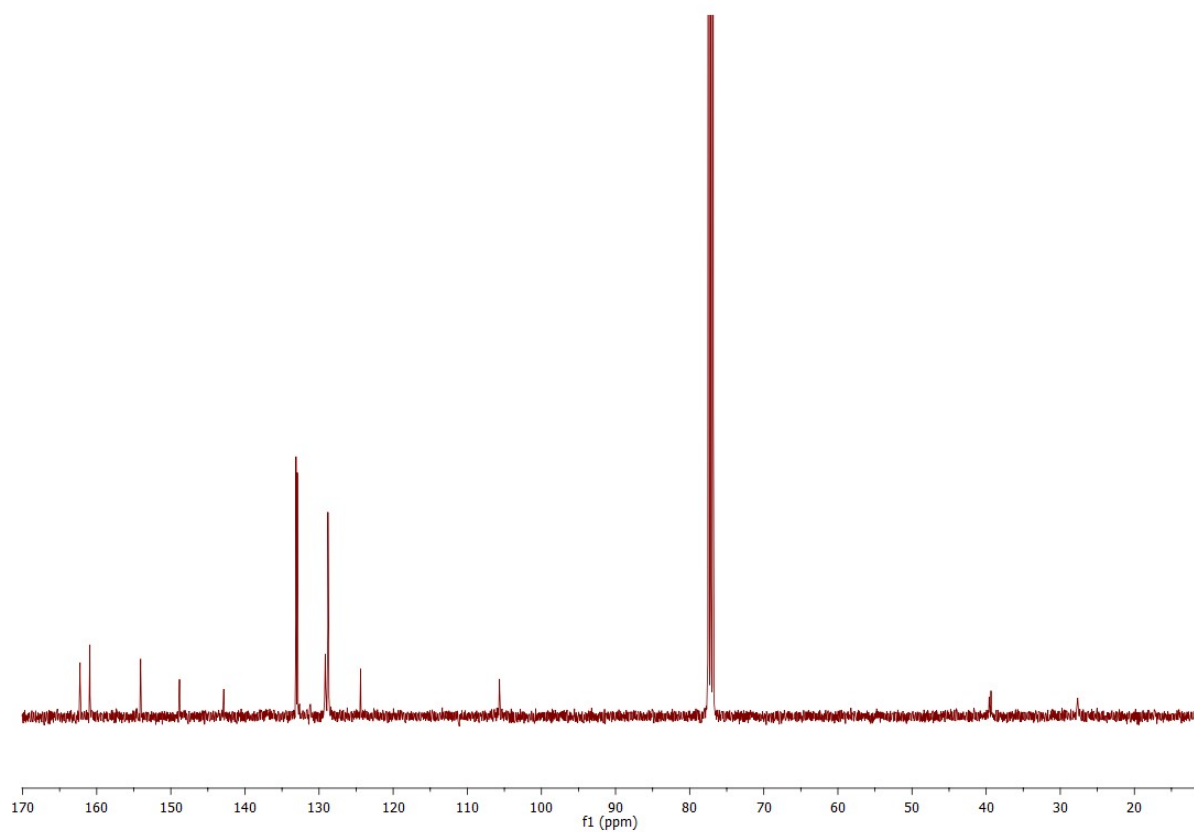
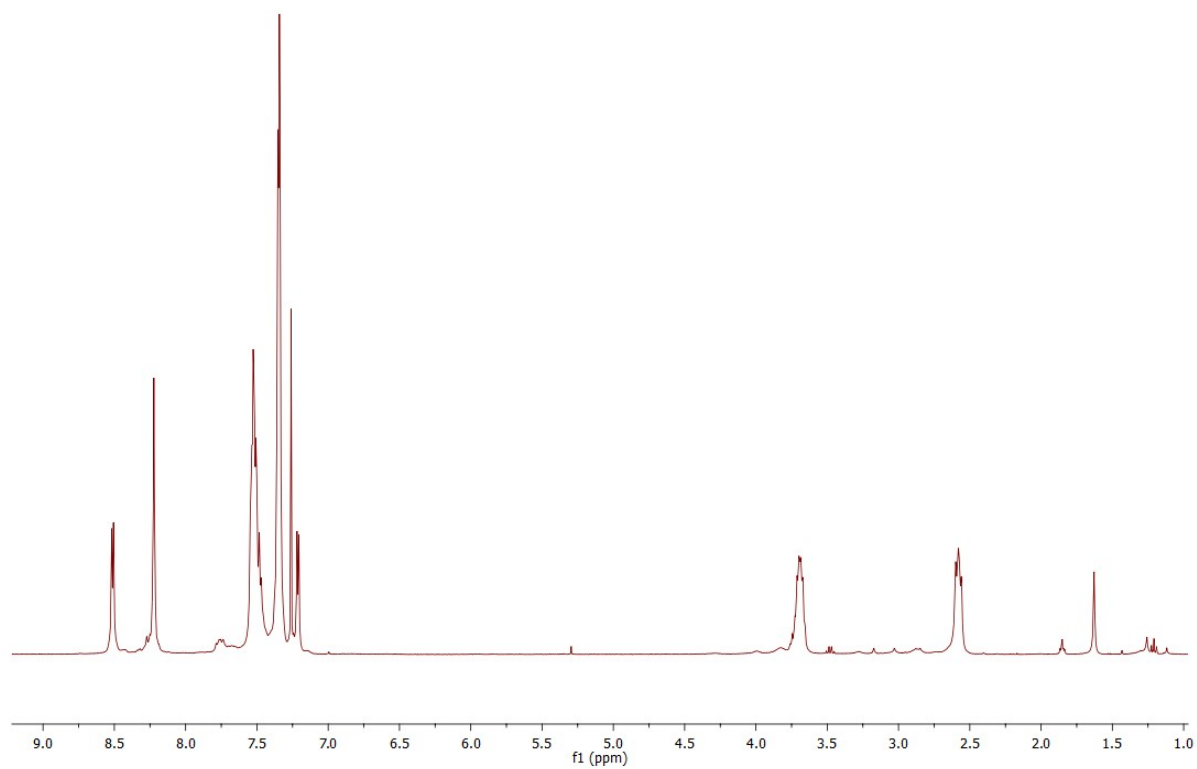


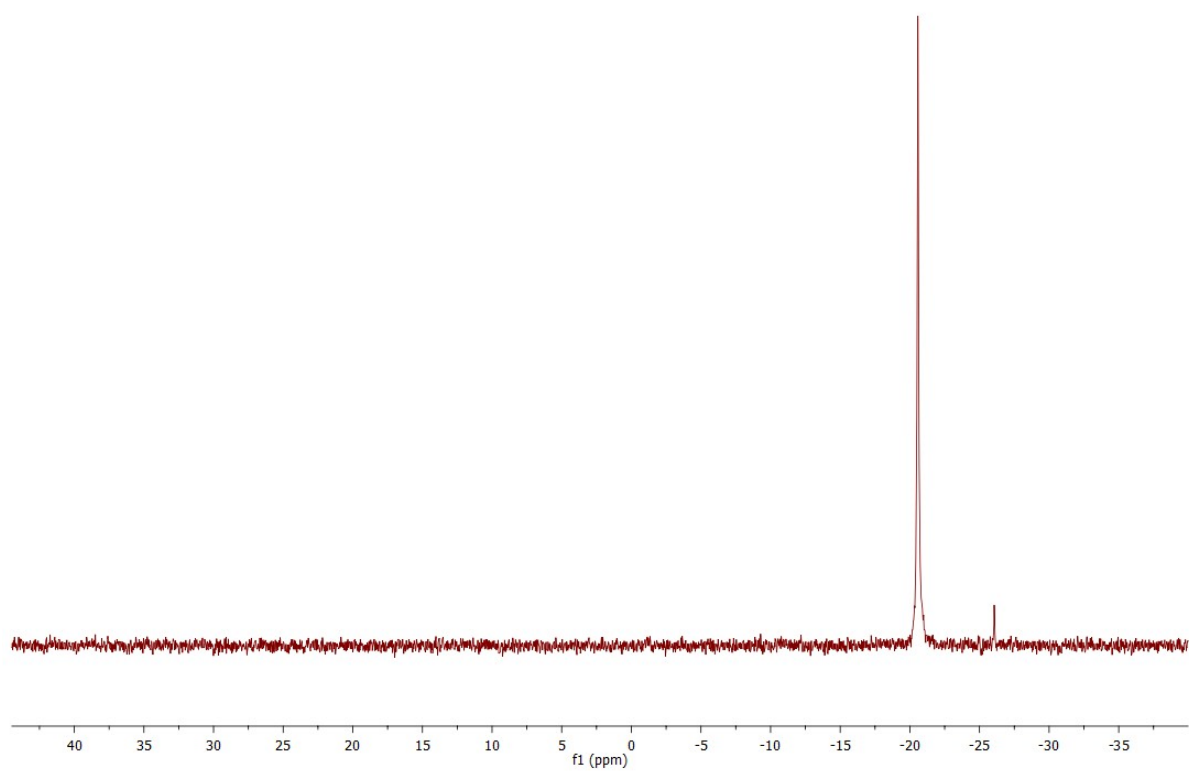
^1H , ^{13}C , and ^{31}P NMR spectrum of **2**



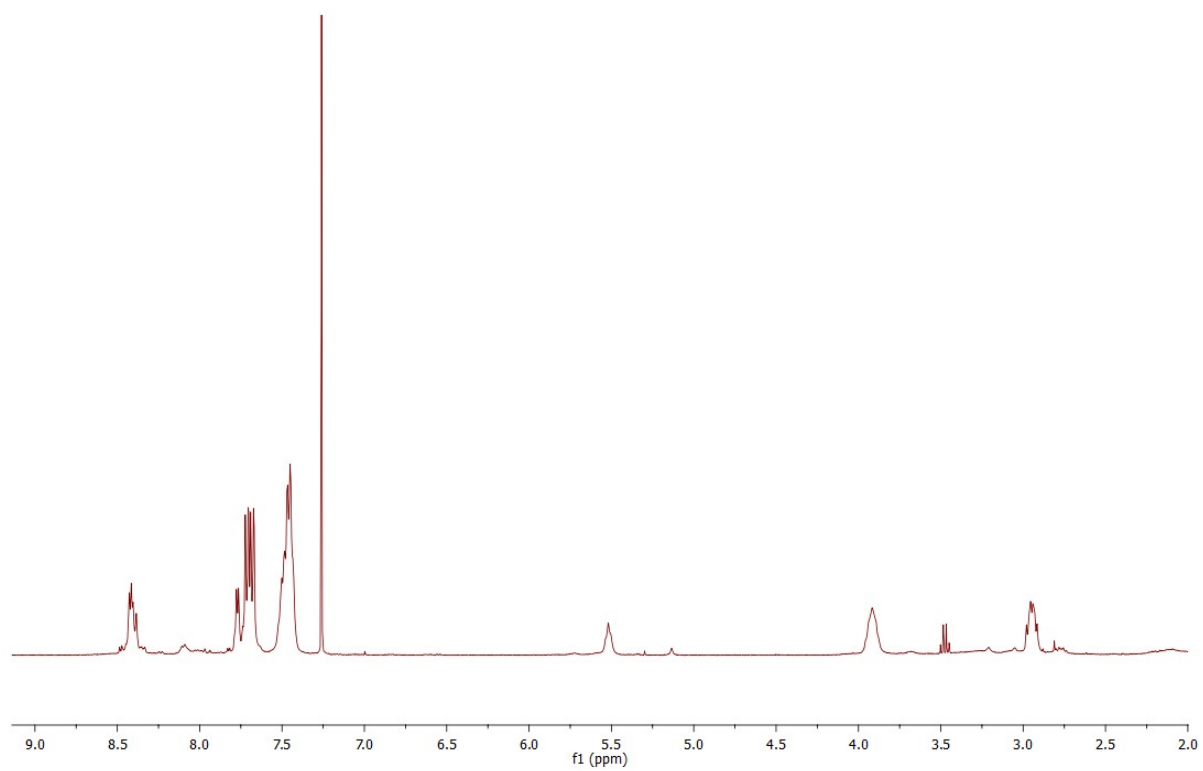


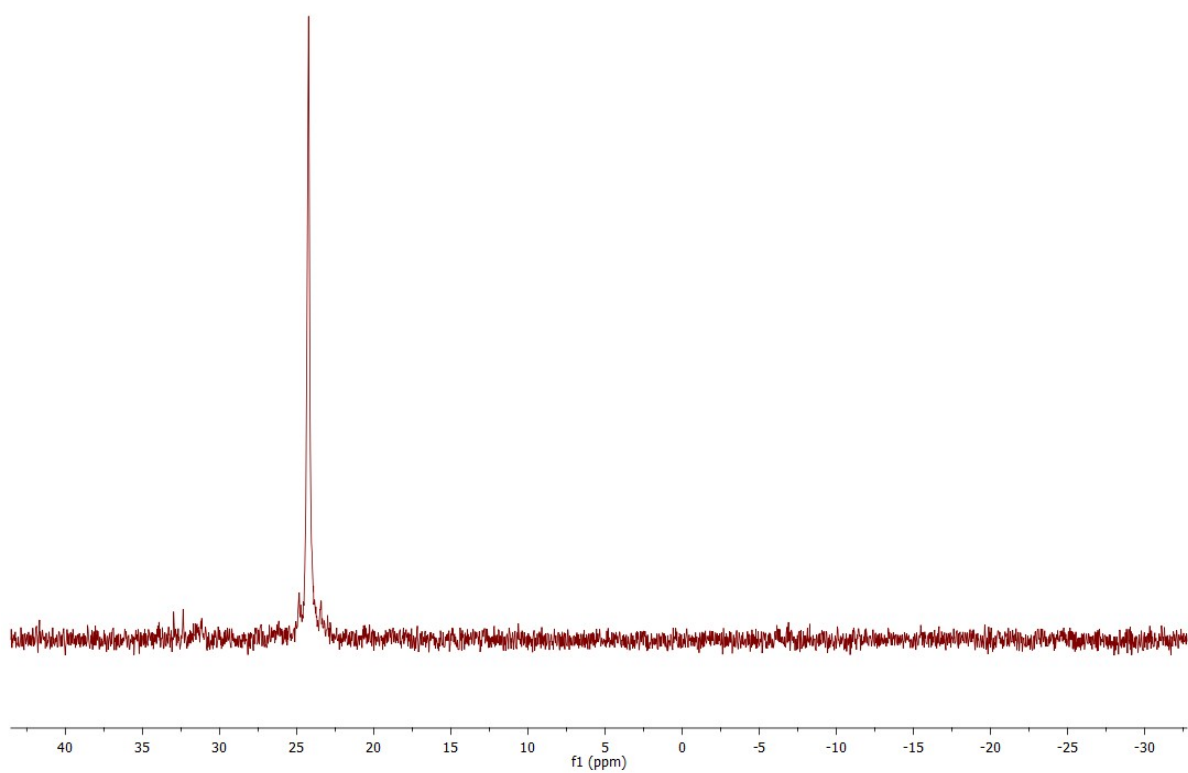
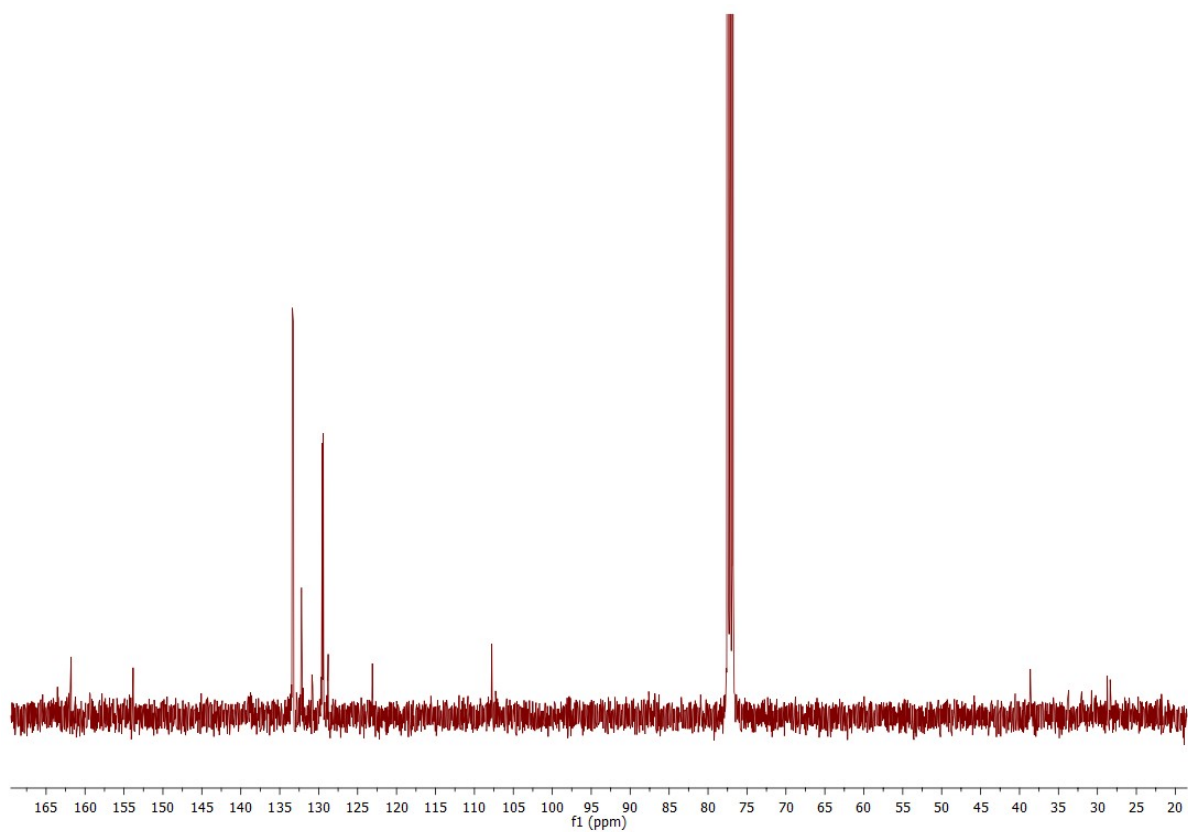
^1H , ^{13}C , and ^{31}P NMR spectrum of **2Zn**



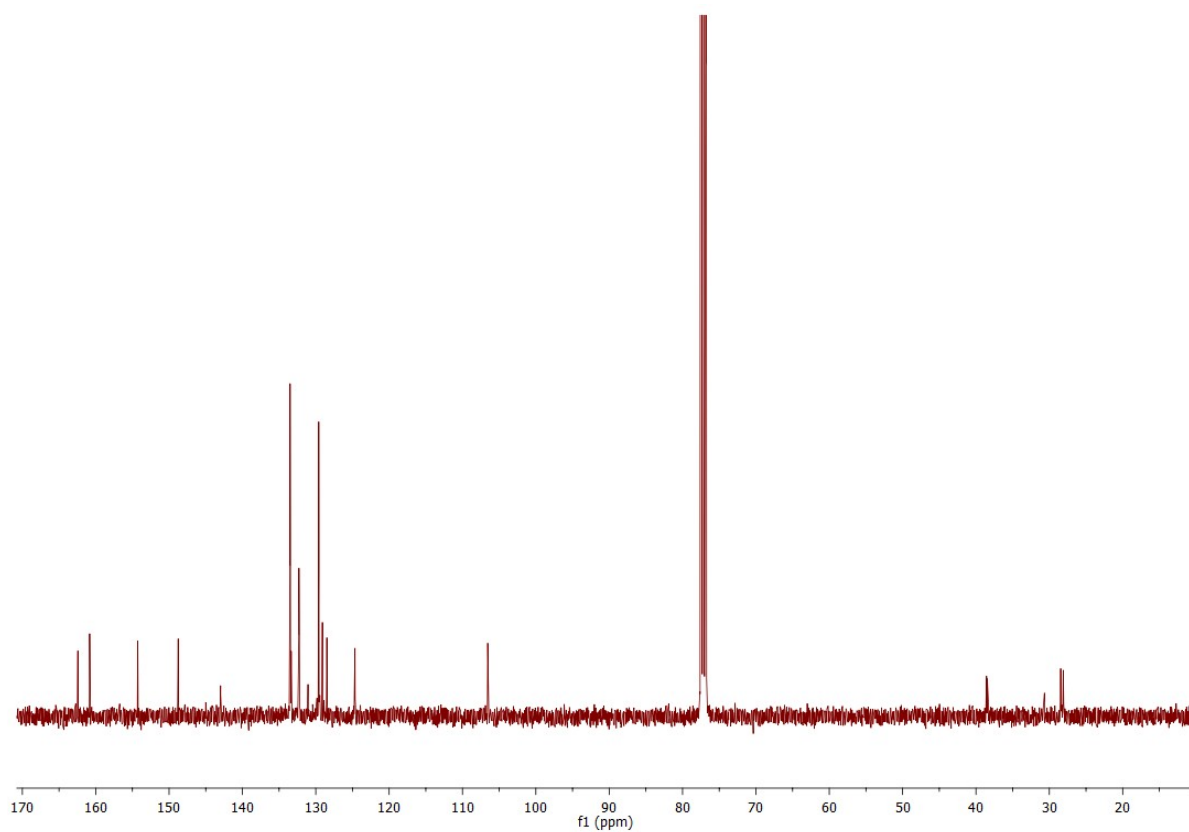
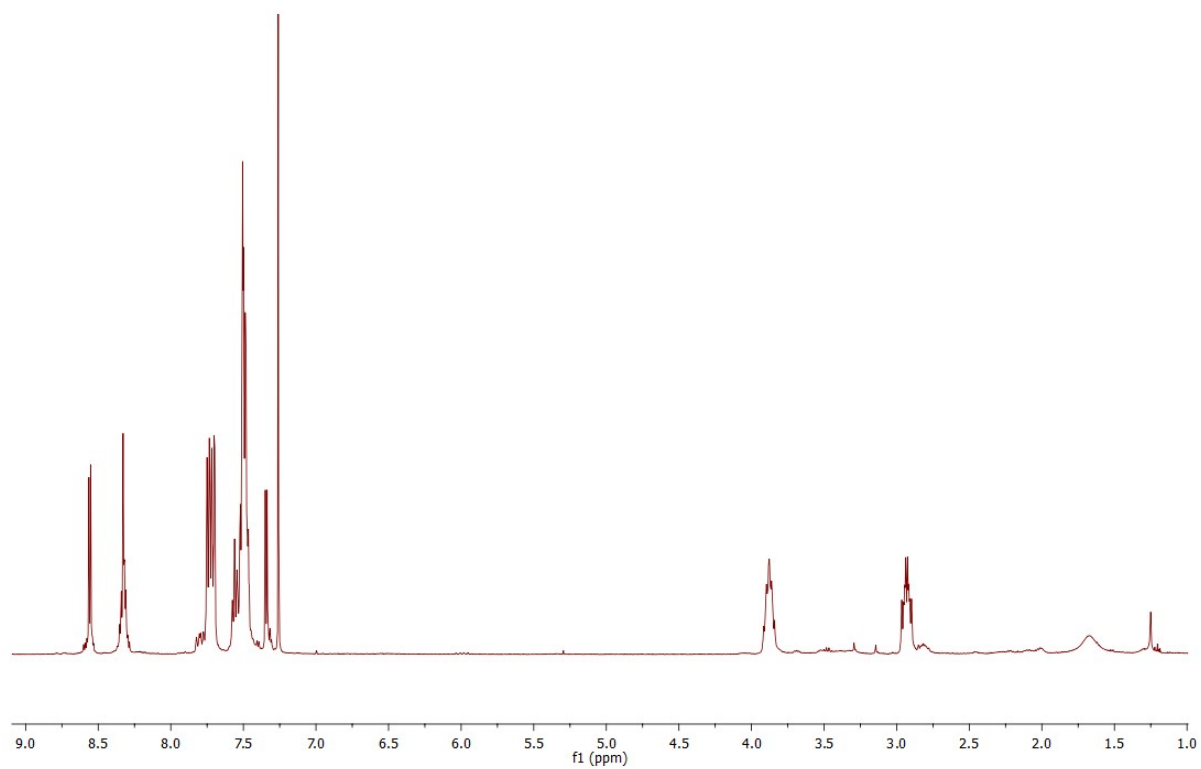


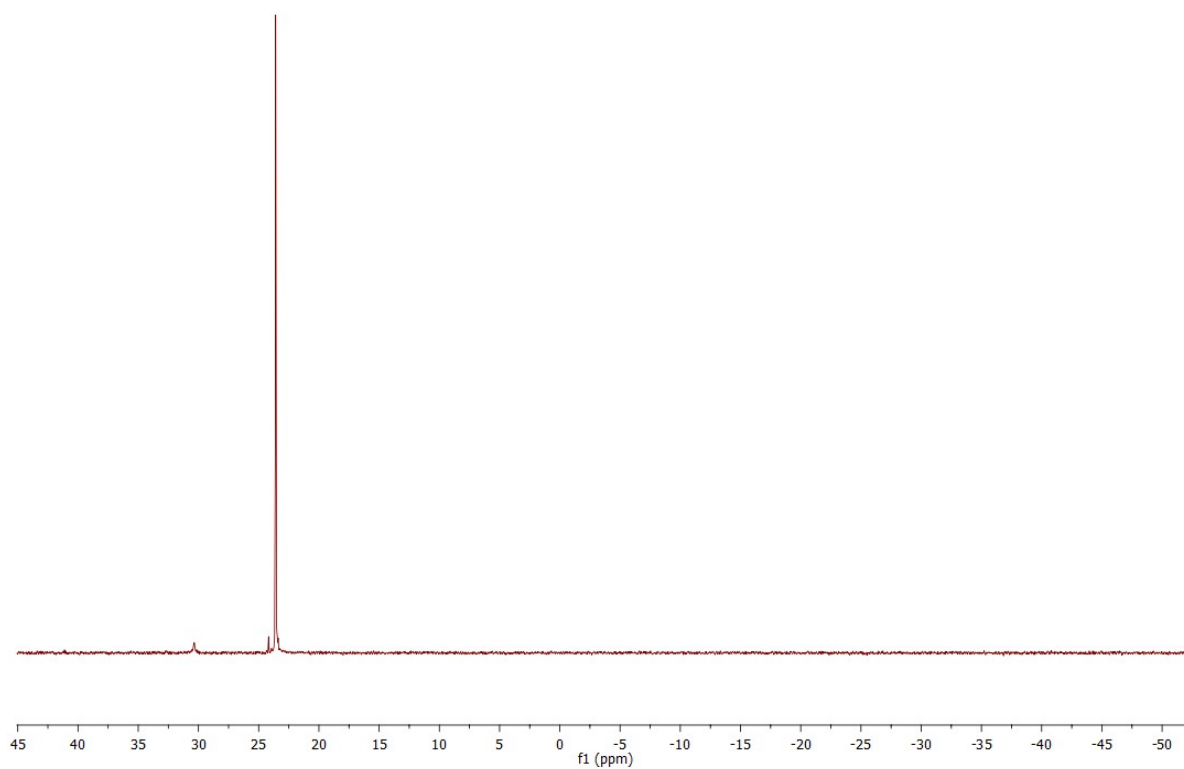
^1H , ^{13}C , and ^{31}P NMR spectrum of **2Au₂**





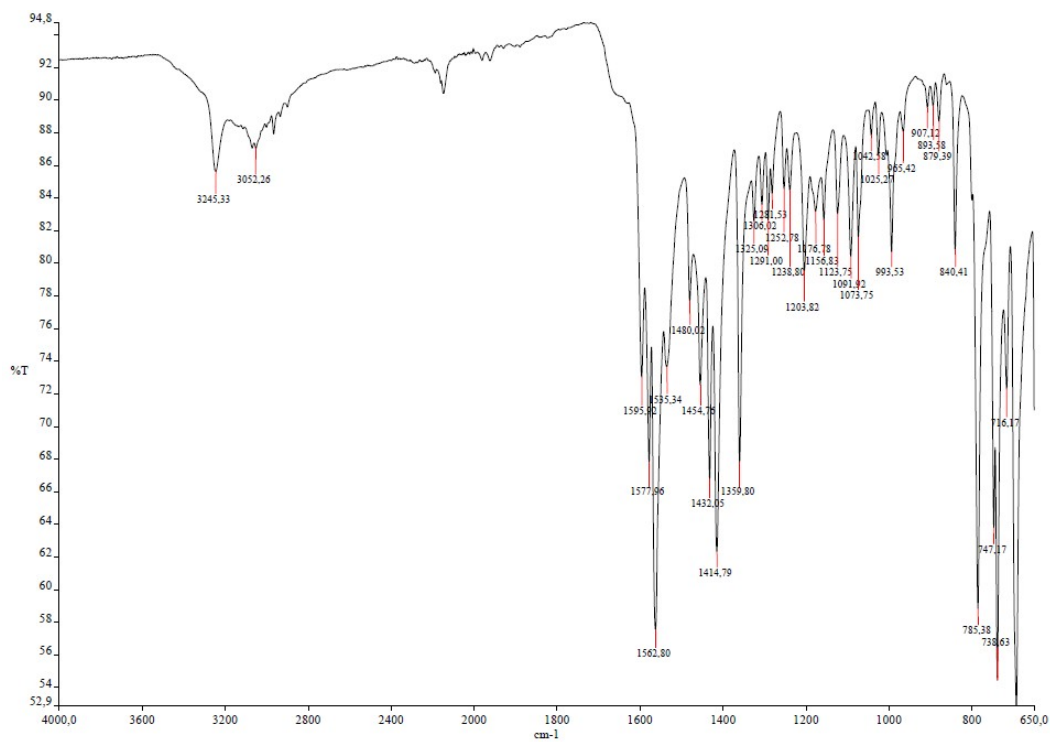
^1H , ^{13}C , and ^{31}P NMR spectrum of **2Au₂Zn**



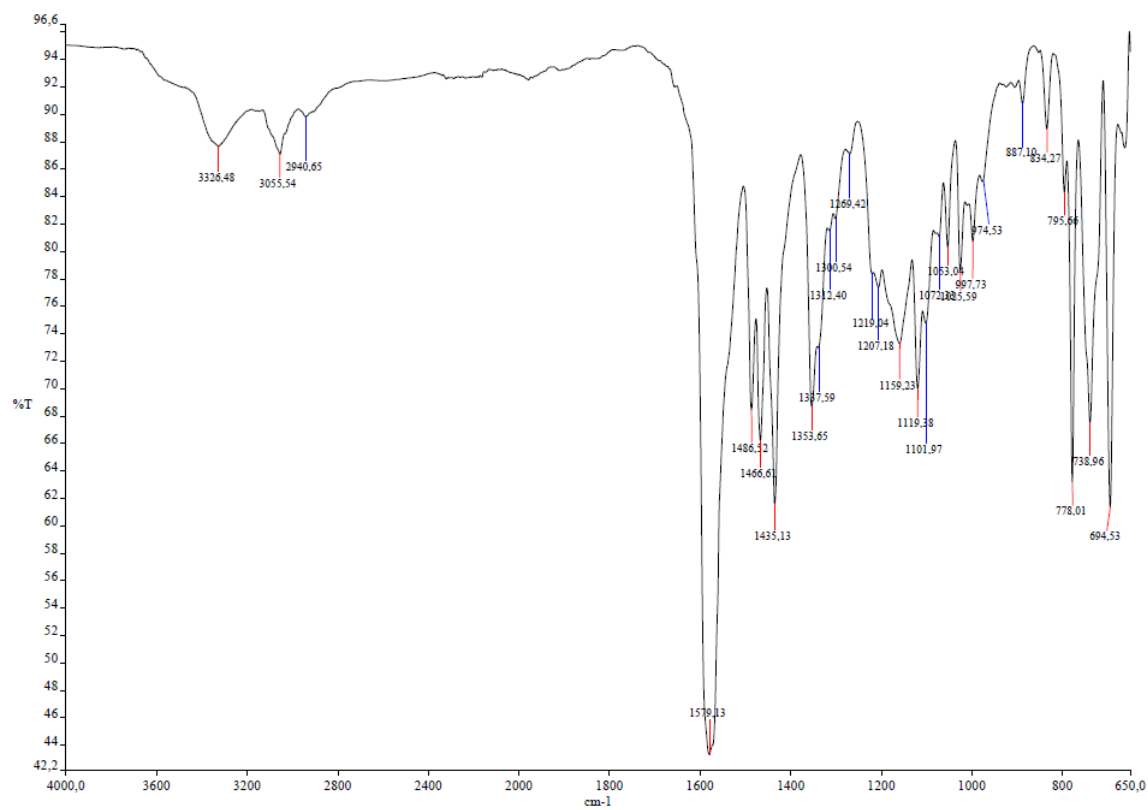


Measured IR spectra (ATR)

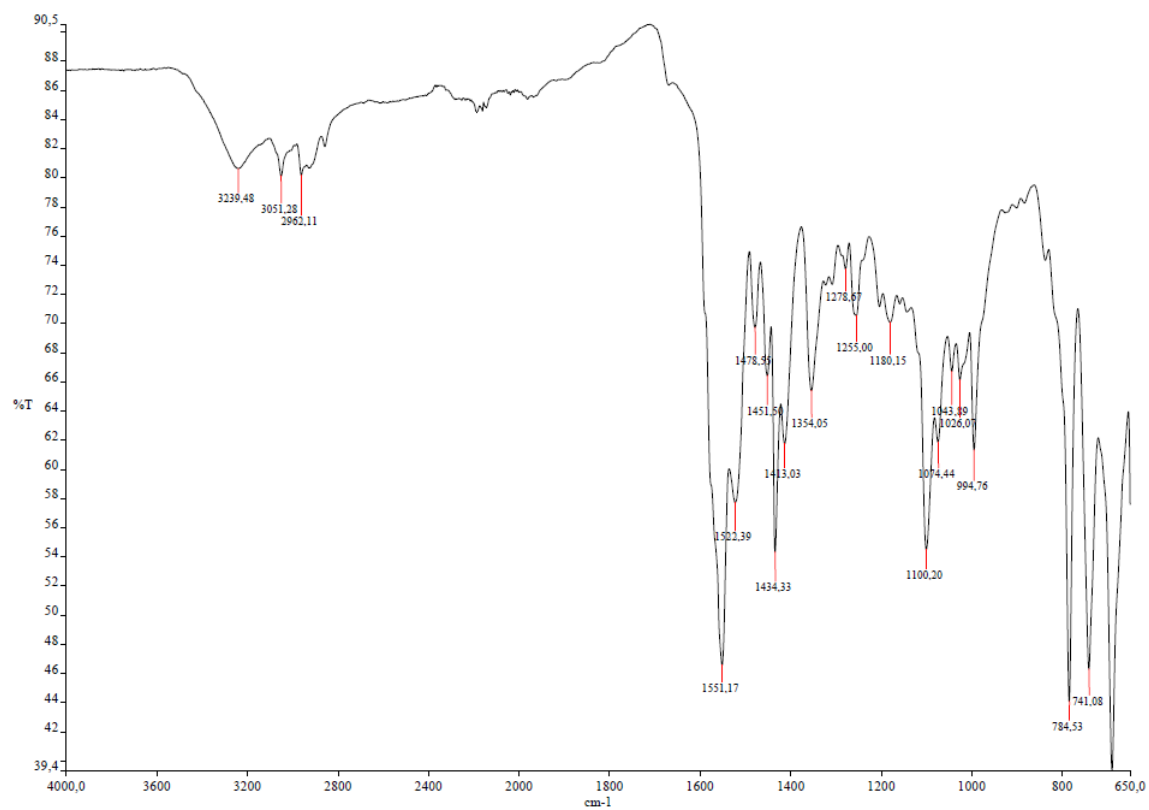
IR spectrum of **1**



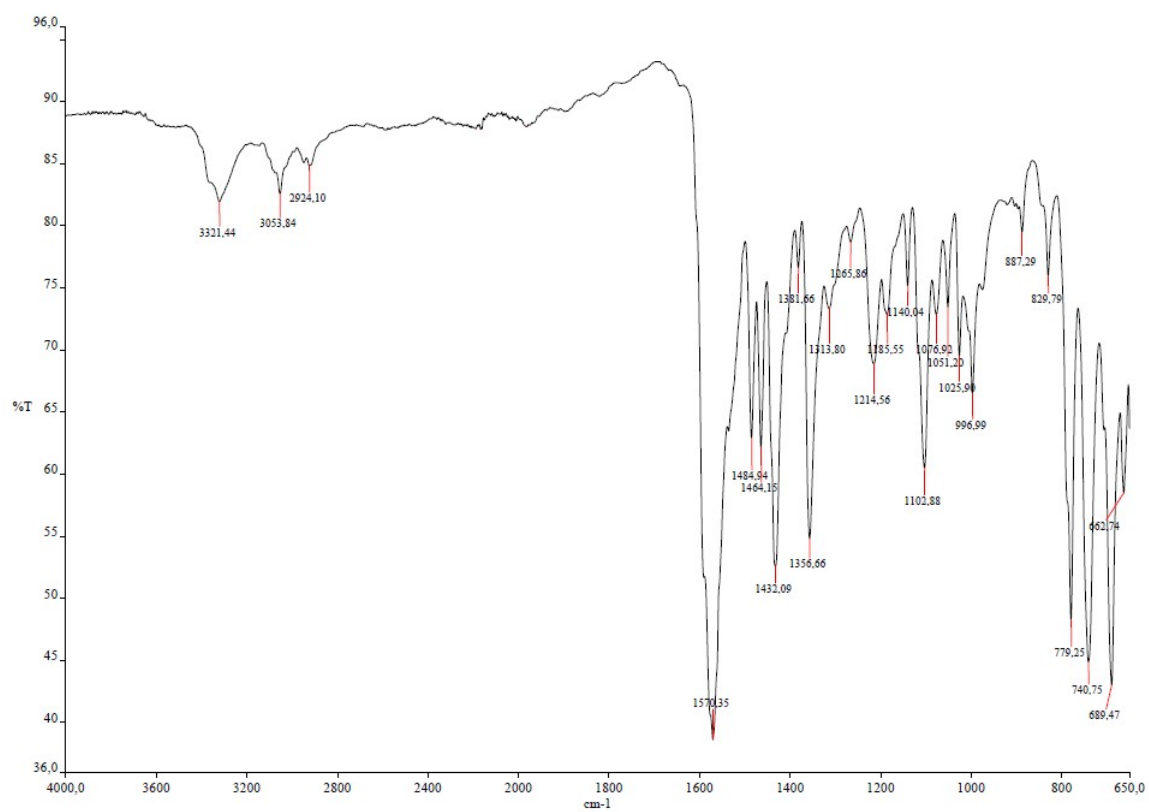
IR spectrum of **1Zn**



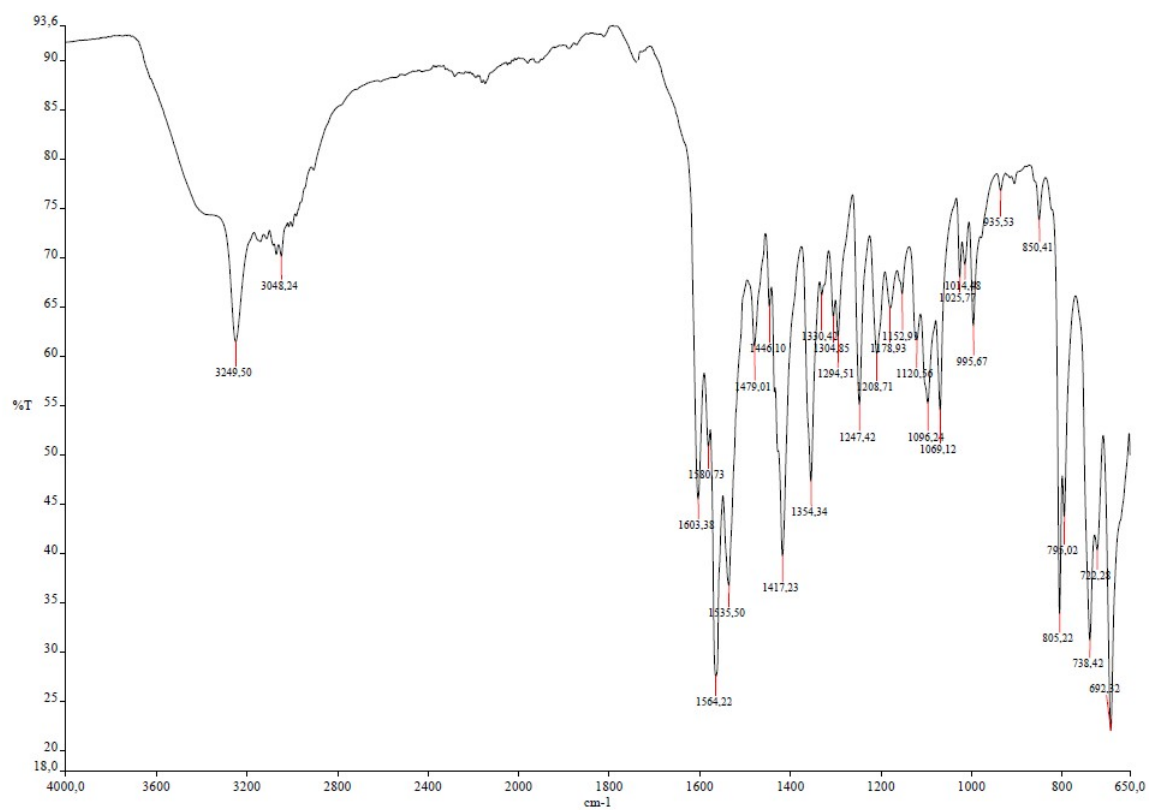
IR spectrum of **1Au**



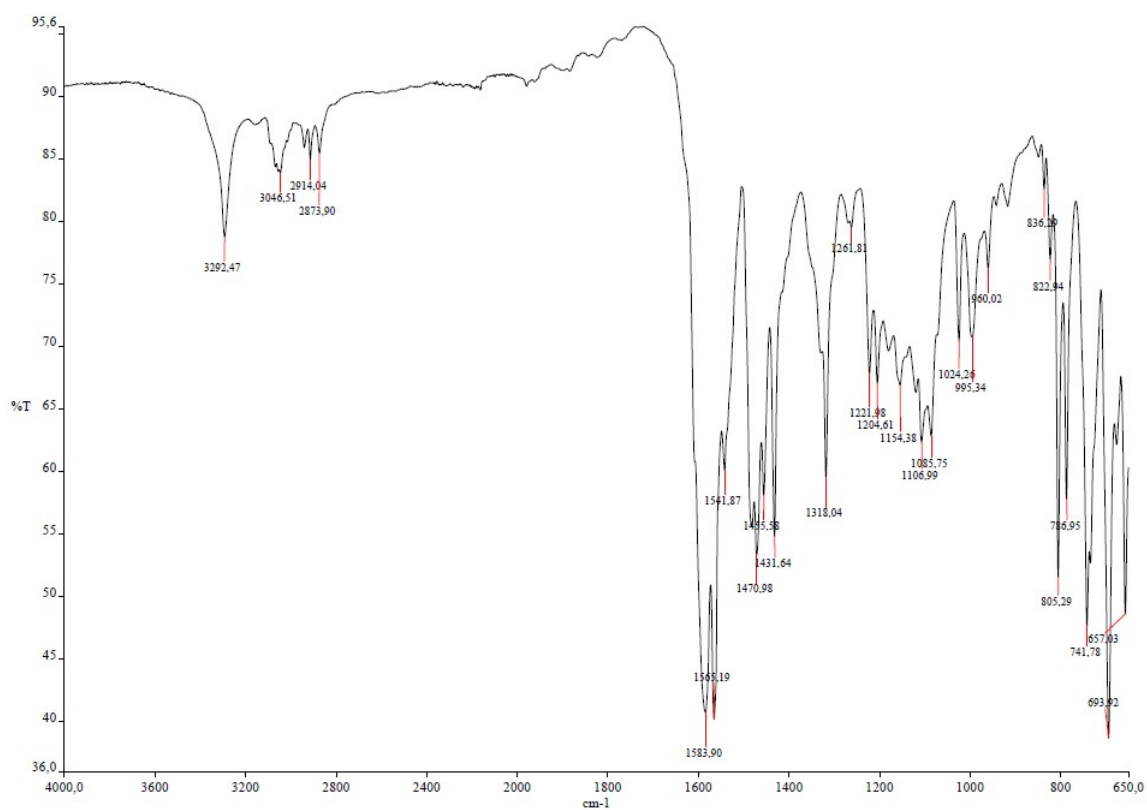
IR spectrum of **1AuZn**



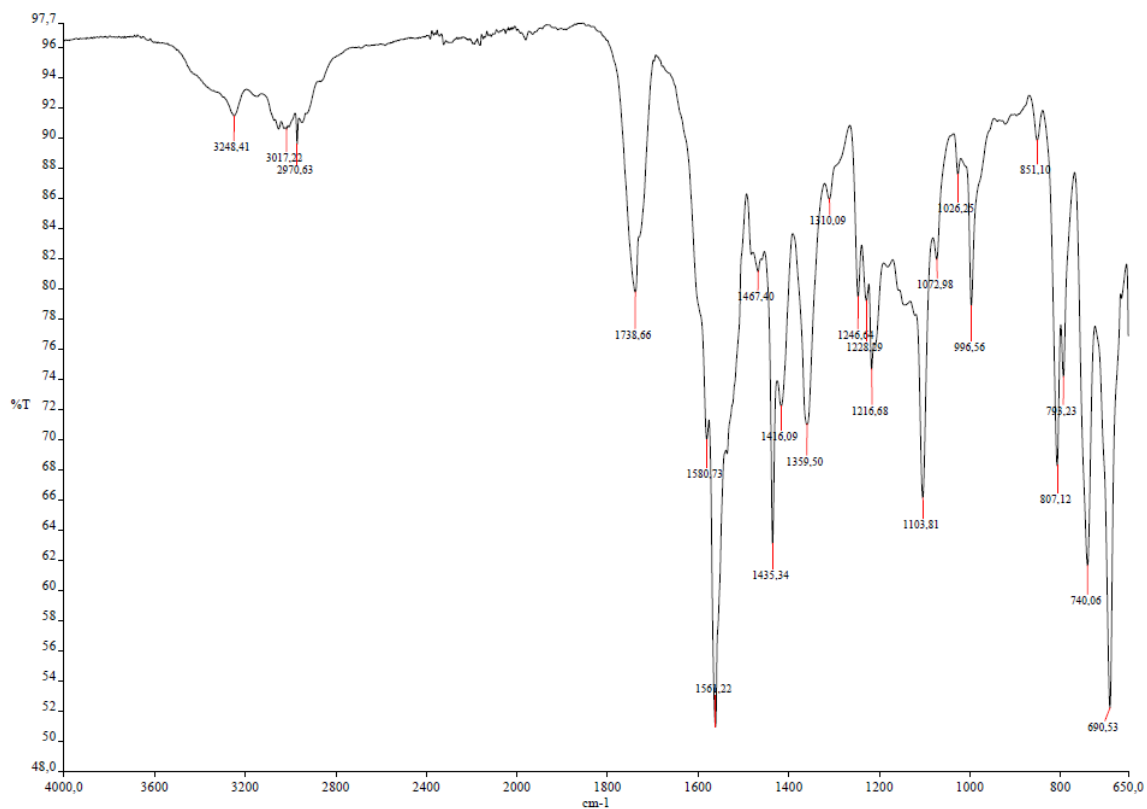
IR spectrum of **2**



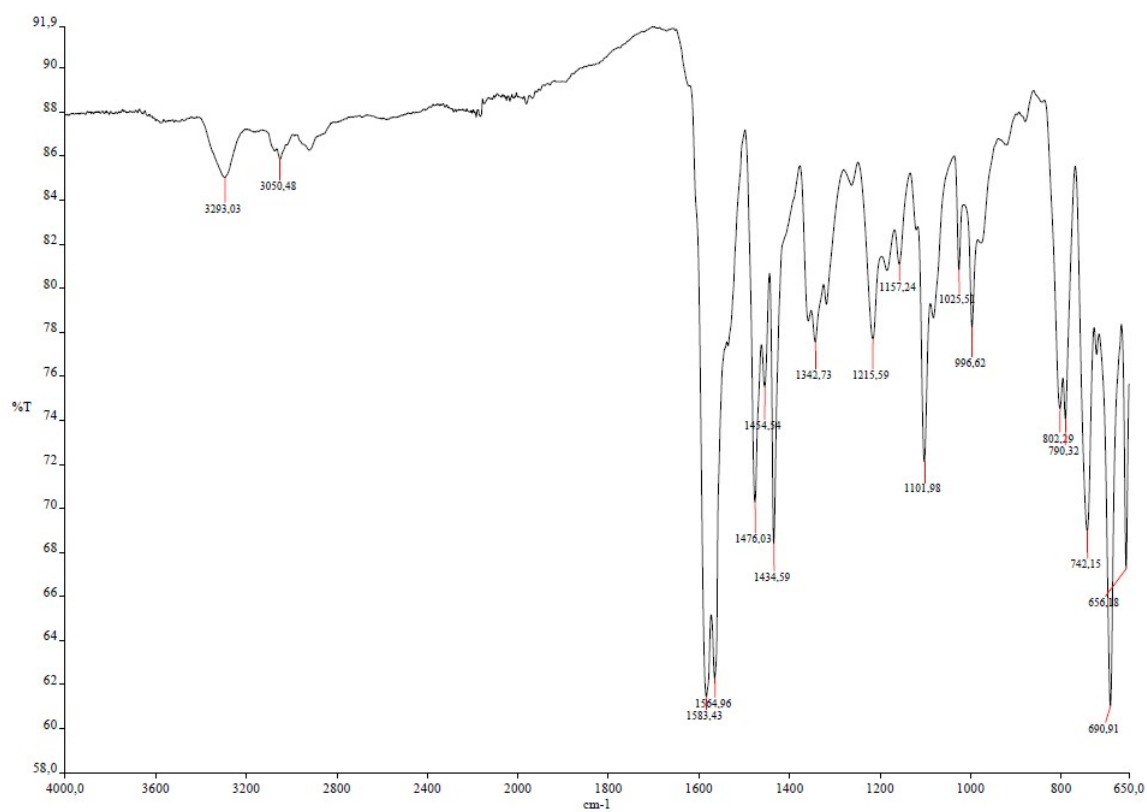
IR spectrum of **2Zn**



IR spectrum of **2Au₂**

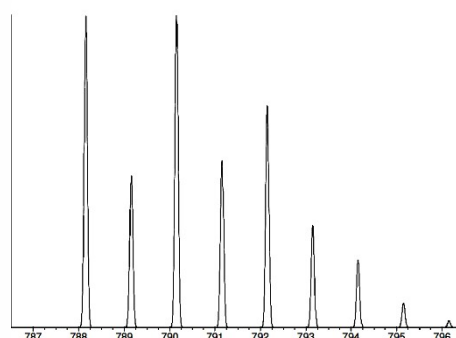
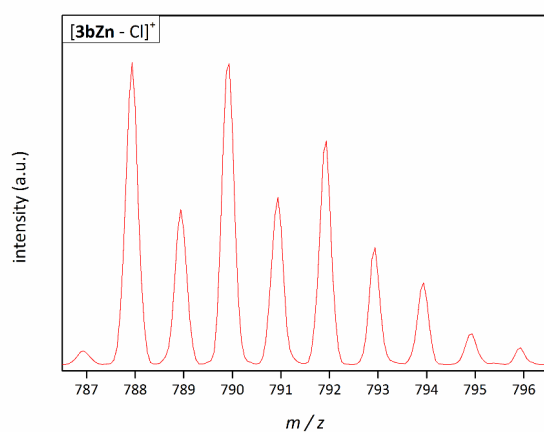


IR spectrum of **2Au₂Zn**

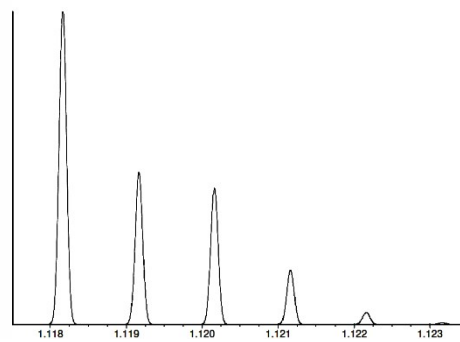
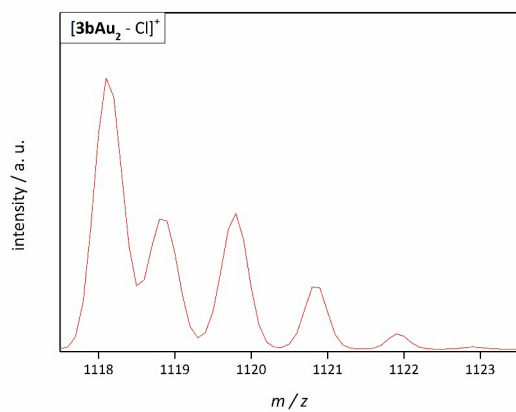


Measured and simulated ESI spectra

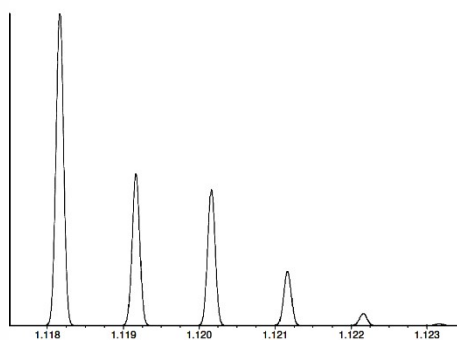
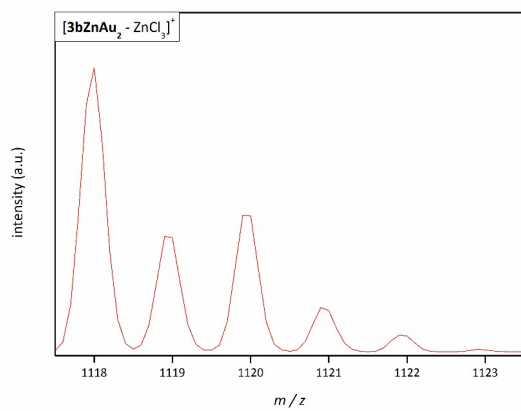
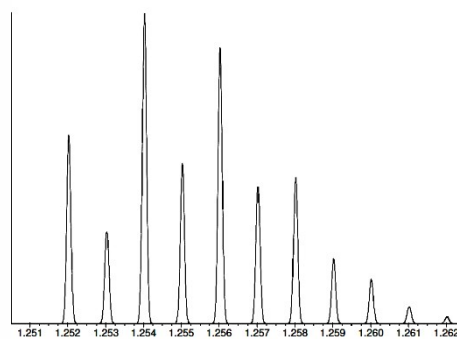
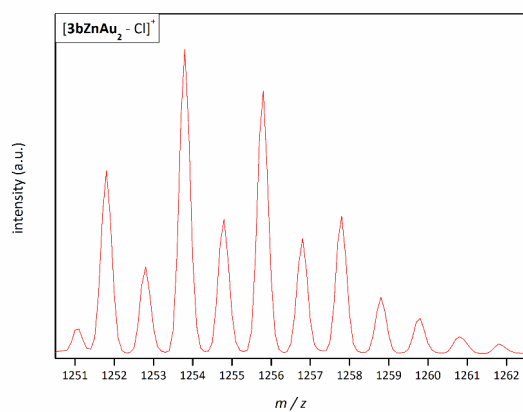
ESI spectra of **2Zn**



ESI spectra of **2Au₂**



ESI spectra of **2Au₂Zn**



Crystallographic data

Table S1. Crystallographic data, data collection and refinement.

	1Au	2Au₂Zn
empirical formula	C ₂₃ H ₂₁ AuClN ₄ P	C ₄₅ H ₄₃ Au ₂ Cl ₄ N ₉ P ₂ Zn
formula weight	616.82	1372.92
crystal size [mm]	0.35x0.08x0.04	0.272x0.114x0.068
<i>T</i> [K]	150(2)	150(2)
<i>l</i> [Å]	0.71073	1.54184
crystal system	Triclinic	Triclinic
space group	P-1	P-1
<i>a</i> [Å]	10.6195(4)	11.5397(3)
<i>b</i> [Å]	12.3785(4)	14.4235(5)
<i>c</i> [Å]	18.7756(5)	15.6048(4)
<i>a</i> [°]	108.768(3)	70.951(3)
<i>b</i> [°]	103.715(3)	79.619(2)
<i>g</i> [°]	92.291(3)	87.626(2)
<i>V</i> [Å ³]	2252.05(13)	2414.47(13)
<i>Z</i>	4	2
<i>r</i> _{calcd.} [g cm ⁻³]	1.819	1.888
<i>m</i> [mm ⁻¹]	6.739	14.781
<i>q</i> -range [°]	2.72-32.50	3.242-62.678
refl. coll.	29506	17276
indep. refl.	14731 [R _{int} = 0.0294]	7676 [R _{int} = 0.0244]
data/restr./param.	14731/2/547	7676/2/576
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0272, 0.0635	0.0331, 0.0839
<i>R</i> indices (all data)	0.0364, 0.0784	0.0354, 0.0856
<i>Goof</i> ^b	1.110	1.066
Δρ _{max/min} (e·Å ⁻³)	1.741/-2.466	3.312/-1.223

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2}$. ^b $Goof = [\sum w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$.

Measured and calculated UV/Vis spectra

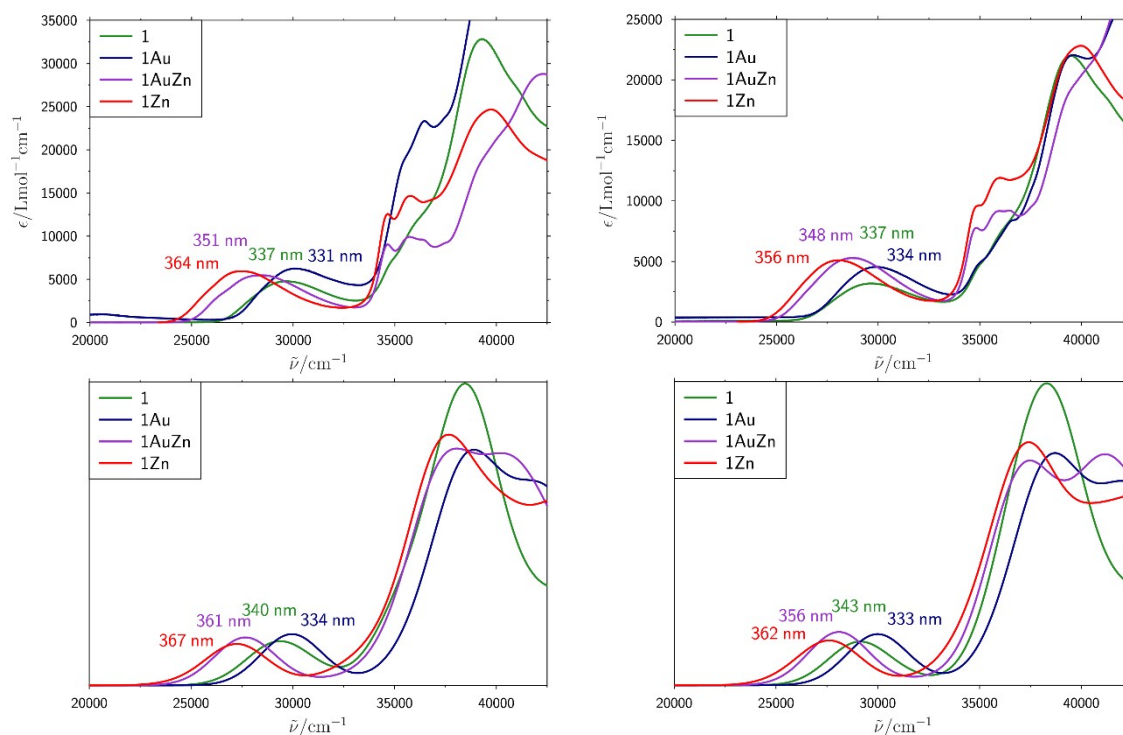


Fig. S1: UV/Vis spectra of compounds **1** (top: measured; bottom: calculated; left: in dichloromethane; right: in acetonitrile).

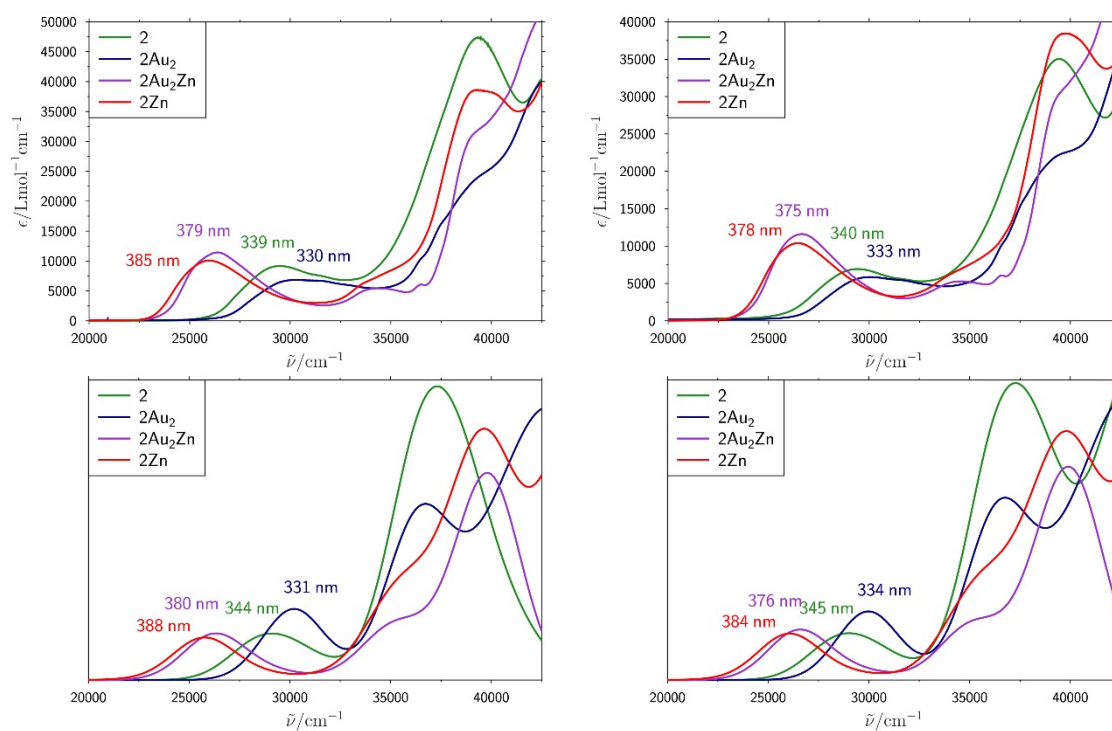


Fig. S2: UV/Vis spectra of compounds **2** (top: measured; bottom: calculated; left: in dichloromethane; right: in acetonitrile).

Table S2. Wavenumber $\tilde{\nu}$ of the maxima of the pre-band in different solvents.

substance	$\tilde{\nu} / \text{cm}^{-1}$ (CH_2Cl_2)	$\tilde{\nu} / \text{cm}^{-1}$ (CHCl_3)	$\tilde{\nu} / \text{cm}^{-1}$ (MeCN)
1	29673 ± 7	29574 ± 15	29679 ± 2
1Au	30182 ± 94	30018 ± 10	29905 ± 2
1AuZn	28456 ± 45	28479 ± 110	28729 ± 5
1Zn	27475 ± 28	27370 ± 40	28087 ± 42
2	29489 ± 2	29399 ± 27	29418 ± 3
2Au₂	30259 ± 29	30291 ± 31	30052 ± 13
2Au₂Zn	26381 ± 4	26194 ± 2	26642 ± 2
2Zn	25967 ± 3	25702 ± 5	26457 ± 2

Comparison of fluorescence spectra

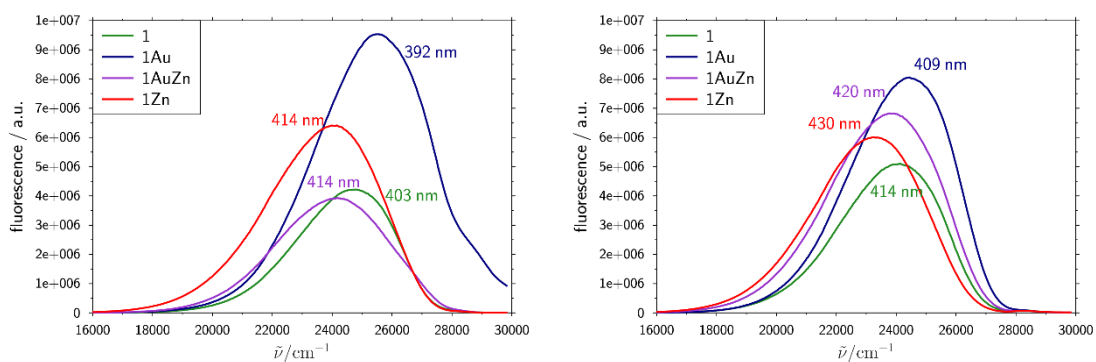


Fig. S3: Fluorescence spectra of compounds **1** (left: in dichloromethane; right: in acetonitrile)

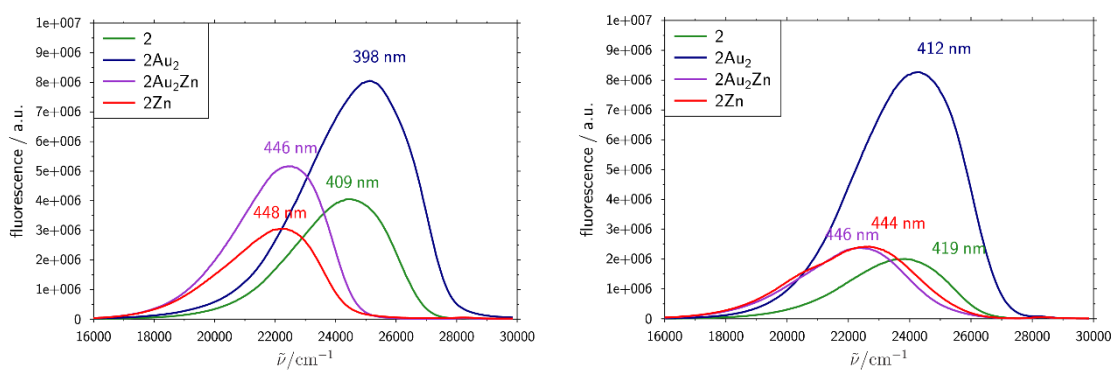


Fig. S4: Fluorescence spectra of compounds **2** (left: in dichloromethane; right: in acetonitrile)

Table S3. Wavenumber $\tilde{\nu}$ of the maxima of the fluorescence band in different solvents.

substance	$\tilde{\nu} / \text{cm}^{-1}$ (CH_2Cl_2)	$\tilde{\nu} / \text{cm}^{-1}$ (CHCl_3)	$\tilde{\nu} / \text{cm}^{-1}$ (MeCN)
1	24814	24570	24155
1Au	25510	25126	24450
1AuZn	24155	24096	23810
1Zn	24155	23202	23256
2	24450	24450	23866
2Au₂	25126	25063	24272
2Au₂Zn	22422	22573	22422
2Zn	22321	22222	22523

Comparison of fluorescence lifetimes

Table S4. Lifetimes in chloroform ($\lambda_{\text{Ex}} = 293 \text{ nm}$), ** ($\lambda_{\text{Ex}} = 313 \text{ nm}$).

substance	τ_1 / ns	a_1	τ_2 / ns	a_2	τ_3 / ns	a_3	χ^2	$\langle \tau \rangle_a / \text{ns}$
1	1.05	0.18	0.244	0.59	3.53	0.23	1.36	1.15
1Au	0.439	0.41	2.10	0.60			1.04	1.43**
1AuZn	0.411	0.17	1.46	0.77	3.18	0.06	1.15	1.37
1Zn	1.45	0.39	3.56	0.61			1.05	2.73
2	0.659	0.29	2.51	0.71			1.07	1.98
2Au₂	0.610	0.54	2.08	0.46			1.21	1.29
2Au₂Zn	0.864	0.68	1.92	0.29	6.22	0.04	1.20	1.37
2Zn	0.616	0.05	2.92	0.75	7.27	0.20	1.25	3.67

Table S5. Lifetimes in dichloromethane ($\lambda_{\text{Ex}} = 293 \text{ nm}$)

substance	τ_1 / ns	a_1	τ_2 / ns	a_2	τ_3 / ns	a_3	χ^2	$\langle \tau \rangle_a / \text{ns}$
1	1.66	0.28	0.198	0.62	3.09	0.10	1.45	0.900
1Au	0.531	0.90	3.25	0.10			1.04	0.807
1AuZn	0.363	0.14	0.948	0.76	5.89	0.10	1.04	1.35
1Zn	1.92	0.49	6.18	0.51			1.09	4.08
2	0.167	0.90	2.35	0.10			1.06	0.381
2Au₂	0.597	0.61	2.07	0.39			1.15	1.18
2Au₂Zn	0.720	0.70	1.84	0.24	5.75	0.06	1.19	1.29
2Zn	0.726	0.06	2.97	0.75	7.34	0.20	1.17	3.71

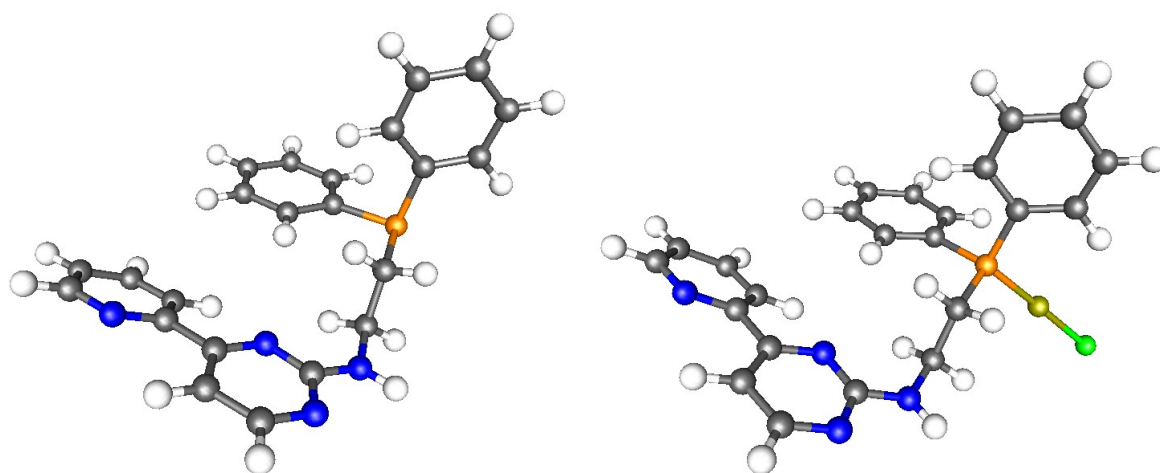
Table S6. Lifetimes in acetonitrile ($\lambda_{Ex} = 293$ nm), * ($\lambda_{Ex} = 273$ nm).

substance	τ_1 / ns	a_1	τ_2 / ns	a_2	τ_3 / ns	a_3	χ^2	$\langle\tau\rangle_a$ / ns
1	2.11	0.15	3.65	0.42	0.274	0.44	1.14	1.95*
1Au	0.395	0.18	1.25	0.75	3.77	0.07	1.15	1.26
1AuZn	0.850	0.74	2.20	0.21	8.93	0.05	1.16	1.52
1Zn	3.28	0.49	0.324	0.15	10.5	0.36	0.89	5.43
2	2.75	0.20	0.210	0.74	5.08	0.06	1.19	1.02
2Au₂	0.462	0.30	1.19	0.64	3.90	0.05	1.06	1.11
2Au₂Zn	0.507	0.75	1.48	0.21	9.85	0.04	1.28	1.06
2Zn	0.987	0.39	3.15	0.51	12.3	0.10	1.78	3.17

Table S7. Luminescence quantum yields estimated from experimental experimental and calculated lifetimes.

substance	Φ (CHCl ₃)	Φ (CH ₂ Cl ₂)	Φ (MeCN)
1	12.31%	9.39%	19.87%
1Au	17.04%	9.32%	12.84%
1AuZn	17.71%	19.06%	21.33%
1Zn	21.70%	36.19%	50.33%
2	30.24%	5.49%	12.98%
2Au₂	44.91%	36.77%	28.73%
2Au₂Zn	21.06%	20.67%	17.15%
2Zn	39.62%	45.48%	39.24%

Optimized structure geometries in chloroform



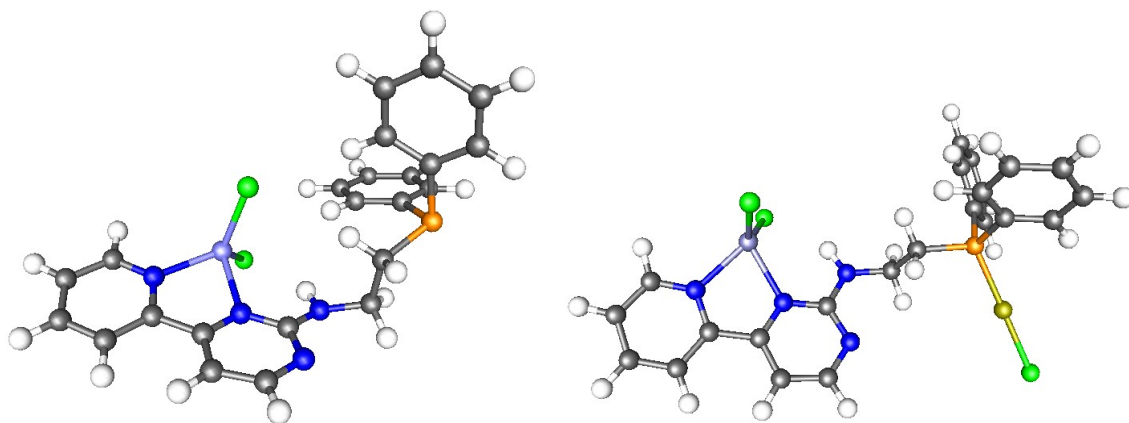


Fig. S5: Geometries of compounds **1**.

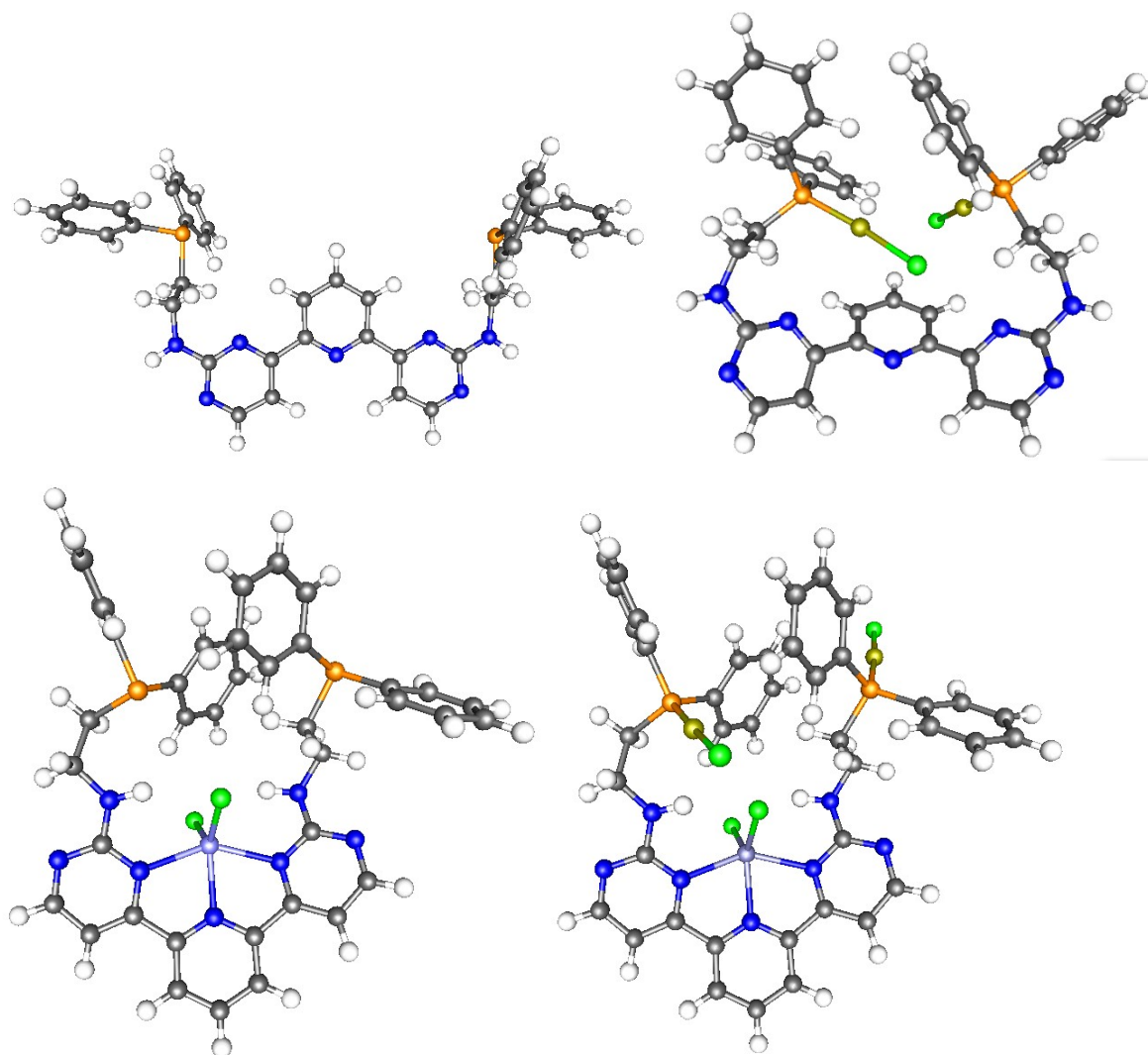


Fig. S6: Geometries of compounds **2**.

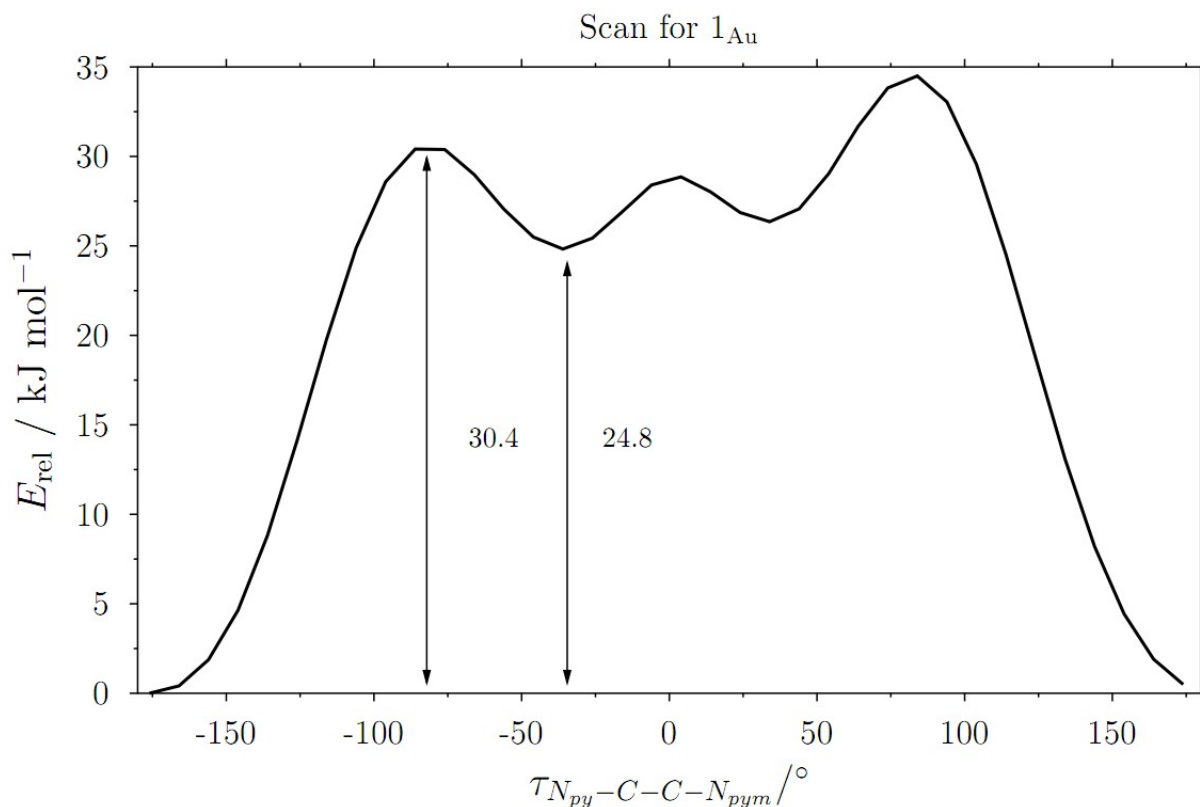


Fig. S7: Potential energy scan for the rotation of the pyrimidine-pyridine bond, calculated for **1Au** at the B3LYP-D3/def2-TZVP level.

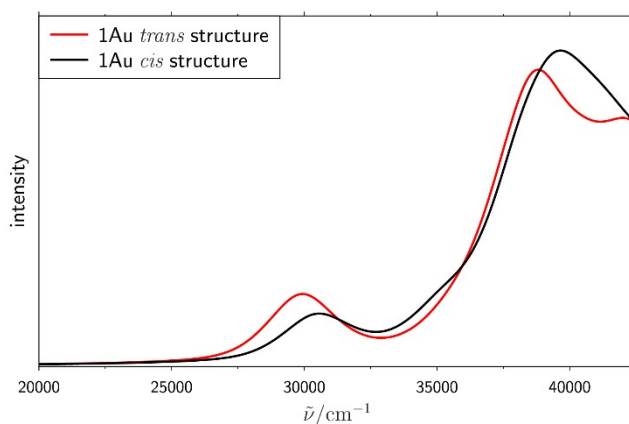


Fig. S8: Comparison of the calculated UV/Vis-spectra of the *trans* and *cis* conformer of **1Au** in CHCl_3 .

Remark: Theoretical investigations are also performed for other metal ions substituting the zinc in complex **1AuZn**. By using magnesium, calcium and cadmium the effect of the ion radius and a possible influence of d-electrons is analyzed. The results are shown in Fig. S9. The spectra for magnesium, calcium and zinc show no significant differences with respect to the first electronic transition. Furthermore, the difference for cadmium is also very small. This leads to the conclusion that the transition is only influenced by the charge of the ion and the resulting coordination.

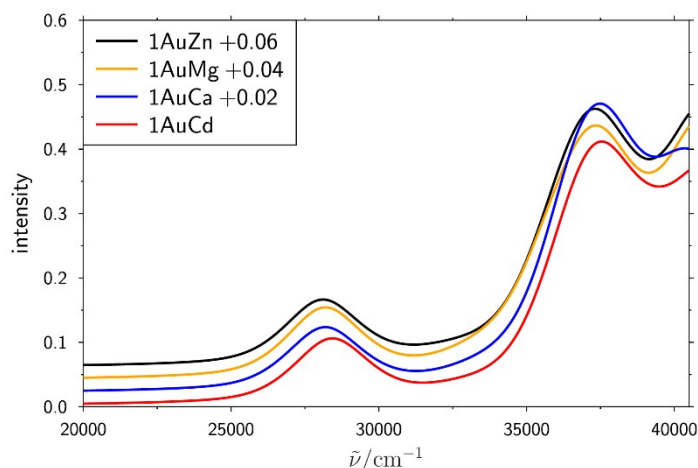


Fig. S9: Comparison of **1Au** with different metal chlorides calculated in acetonitrile.

Dipole moments

Table S8. Comparison of calculated dipole moments in Debye, at the level B3LYP-D3/def2-TZVP.

	1	1Au	1AuZn	1Zn
CHCl ₃	2.82	11.73	9.58	12.80
CH ₂ Cl ₂	3.01	12.20	10.02	13.28
MeCN	3.20	12.67	10.47	13.75
	2	2Au₂	2Au₂Zn	2Zn
CHCl ₃	1.94	7.03	15.54	12.43
CH ₂ Cl ₂	1.94	7.91	16.29	13.32
MeCN	1.93	8.62	17.03	14.26

Data of the first four transitions

Table S9. Overview for **1** in CHCl₃.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	29025	31162	31885	35260
Oszillator strength	7.79E-02	6.83E-03	3.92E-03	3.42E-04
Orbitals & contribution	101 -> 102 95.0%	100 -> 102 87.1%	99 -> 102 86.5%	93 -> 102 91.4 %
transition dipole moment/D	2.40	0.68	0.51	0.15

Table S10. Overview for **1** in CH₂Cl₂.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	29030	31225	31981	35352
Oszillator strength	7.74E-02	6.72E-03	3.91E-03	2.92E-04
Orbitals & contribution	101 -> 102 95.2%	100 -> 102 88.2%	99 -> 102 86.6%	93 -> 102 91.6%
transition dipole moment/D	2.39	0.68	0.51	0.13

Table S11. Overview for **1** in MeCN.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	29037	31284	32073	35438
Oszillator strength	7.68E-02	6.63E-03	3.92E-03	2.42E-04
Orbitals & contribution	101 -> 102 95.3%	100 -> 102 89.2% 99 -> 102 7.5%	99 -> 102 85.0% 100 -> 102 8.0%	93 -> 102 91.7%
transition dipole moment/D	2.38	0.67	0.51	0.12

Table S12. Overview for **1Au** in CHCl₃.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	29694	31987	35216	35418
Oszillator strength	9.13E-02	3.26E-03	8.29E-04	3.18E-02
Orbitals & contribution	119 -> 120 97.5%	118 -> 120 93.2%	111 -> 120 71.3% 112 -> 120 22.8%	119 -> 121 98.4%
transition dipole moment/D	2.57	0.47	0.23	1.38

Table S13. Overview for **1Au** in CH₂Cl₂.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	29706	32088	35317	35554
Oszillator strength	9.06E-02	3.33E-03	7.58E-04	3.31E-02
Orbitals & contribution	119 -> 120 97.5%	118 -> 120 89.7% 117 -> 120 6.5%	111 -> 120 81.6% 113 -> 120 9.5%	119 -> 121 98.3%
transition dipole moment/D	2.56	0.47	0.22	1.40

Table S14. Overview for **1Au** in MeCN.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	29721	32184	35414	35697
Oszillator strength	9.00E-02	3.40E-03	6.81E-04	3.45E-02
Orbitals & contribution	119 -> 120 97.4%	118 -> 120 55.3% 117 -> 120 40.4%	112 -> 120 53.6% 113 -> 120 33.0%	119 -> 121 98.2%
transition dipole moment/D	2.55	0.47	0.20	1.43

Table S15. Overview for **1AuZn** in CHCl₃.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	27729	31523	32817	33460
Oszillator strength	1.10E-01	7.15E-03	5.47E-04	2.40E-03
Orbitals & contribution	151 -> 152 97.6%	145 -> 152 48.1% 143 -> 152 27.5%	150 -> 152 98.8%	143 -> 152 46.9% 145 -> 152 27.2%
transition dipole moment/D	2.91	0.70	0.19	0.40

Table S16. Overview for **1AuZn** in CH₂Cl₂.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	27979	32080	33472	34872
Oszillator strength	1.18E-01	8.81E-03	2.08E-03	5.21E-03
Orbitals & contribution	151 -> 152 97.6%	144 -> 152 68.5%	150 -> 152 98.7%	143 -> 152 74.9%
transition dipole moment/D	3.00	0.77	0.36	0.57

Table S17. Overview for **1AuZn** in MeCN.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	28218	32539	34006	35752
Oszillator strength	1.27E-01	1.04E-02	3.09E-03	4.80E-05
Orbitals & contribution	151 -> 152 97.5%	144 -> 152 74.6%	150 -> 152 98.7%	149 -> 152 99.8%
transition dipole moment/D	3.10	0.83	0.44	0.05

Table S18. Overview for **1Zn** in CHCl₃.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	25262	27426	30294	30859
Oszillator strength	4.68E-03	7.10E-02	7.14E-04	8.18E-04
Orbitals & contribution	133 -> 134 97.6%	132 -> 134 94.8%	131 -> 134 98.2%	130 -> 134 97.0%
transition dipole moment/D	0.63	2.35	0.22	0.24

Table S19. Overview for **1Zn** in CH₂Cl₂.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	26317	27944	31379	32005
Oszillator strength	1.13E-02	7.30E-02	9.83E-04	1.27E-03
Orbitals & contribution	133 -> 134 94.2%	132 -> 134 92.2%	131 -> 134 97.1%	130 -> 134 81.2%
transition dipole moment/D	0.96	2.36	0.26	0.29

Table S20. Overview for **1Zn** in MeCN.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	27242	28538	32391	32679
Oszillator strength	2.89E-02	6.47E-02	2.57E-03	3.76E-03
Orbitals & contribution	133 -> 134 84.8%	132 -> 134 83.4%	131 -> 134 77.8%	127 -> 134 64.3%
transition dipole moment/D	1.50	2.20	0.41	0.50

Table S21. Overview for **2** in CHCl₃.

Excitation Nr.	1		2		3		4	
Energy/cm ⁻¹	28295		28569		29539		29748	
Oszillator strength	5.34E-02		6.50E-02		2.07E-03		1.27E-02	
Orbitals & contribution	181 -> 182	79.2%	180 -> 182	81.4%	180 -> 183	73.7%	181 -> 183	77.0%
transition dipole moment/D	180 -> 183	9.6%	181 -> 183	11.7%	179 -> 183	14.4 %	180 -> 182	12.9%
	2.00		2.21		0.39		0.97	

Table S22. Overview for **2** in CH₂Cl₂.

Excitation Nr.	1		2		3		4	
Energy/cm ⁻¹	28233		28501		29478		29677	
Oszillator strength	5.16E-02		6.46E-02		1.66E-03		1.24E-02	
Orbitals & contribution	181 -> 182	78.6%	180 -> 182	80.8%	180-> 183	73.1%	181 -> 183	76.3%
transition dipole moment/D	180 -> 183	10.0%	181 -> 183	12.1%	179 -> 183	14.6%	180 -> 182	13.4%
	1.97		2.21		0.35		0.96	

Table S23. Overview for **2** in MeCN.

Excitation Nr.	1		2		3		4	
Energy/cm ⁻¹	28178		28445		29420		29615	
Oszillator strength	5.07E-02		6.53E-02		1.36E-03		1.20E-02	
Orbitals & contribution	181 -> 182	78.0%	180 -> 182	80.0%	180 -> 183	72.5%	181 -> 183	75.6%
transition dipole moment/D	180 -> 183	10.3%	181 -> 183	12.5%	179 -> 183	14.7%	180 -> 182	13.9%
	1.95		2.22		0.32		0.95	

Table S24. Overview for **2Au₂** in CHCl₃.

Excitation Nr.	1		2		3		4	
Energy/cm ⁻¹	30055		30482		30927		31593	
Oszillator strength	9.18E-02		1.38E-01		2.77E-02		1.17E-02	
Orbitals & contribution	217 -> 218	49.9%	216 -> 218	52.4%	217 -> 219	75.0%	216 -> 219	62.3%
transition dipole moment/D	216 -> 218	26.7%	217 -> 218	30.0%	216 -> 218	10.0%	215 -> 219	7.6%
	2.55		3.11		1.39		0.90	

Table S25. Overview for **2Au₂** in CH₂Cl₂.

Excitation Nr.	1		2		3		4	
Energy/cm ⁻¹	29881		30225		30852		31306	
Oszillator strength	8.76E-02		1.35E-01		1.96E-02		9.10E-03	
Orbitals & contribution	216 -> 218	70.4%	217 -> 218	70.2%	217 -> 219	74.6%	216 -> 219	72.9%
transition dipole moment/D	217 -> 219	16.5%	216 -> 219	17.1%	216 -> 218	16.4%	217 -> 218	16.3%
	2.49		3.09		1.17		0.80	

Table S26. Overview for **2Au₂** in MeCN.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	29664	29981	30632	31125
Oszillator strength	8.09E-02	1.31E-01	1.77E-02	8.22E-03
Orbitals & contribution	216 -> 218 75.1% 217 -> 219 14.1%	217 -> 218 71.9% 216 -> 219 12.1%	217 -> 219 76.9% 217 -> 218 9.1%	216 -> 219 81.7% 217 -> 218 9.8%
transition dipole moment/D	2.41	3.06	1.12	0.77

Table S27. Overview for **2Au₂Zn** in CHCl₃.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	25940	26734	27878	28285
Oszillator strength	1.34E-01	1.45E-02	7.45E-03	5.56E-03
Orbitals & contribution	249 -> 250 95.2%	248 -> 250 95.4%	249 -> 251 92.3%	247 -> 250 85.4% 245 -> 250 4.8%
transition dipole moment/D	3.31	1.07	0.76	0.64

Table S28. Overview for **2Au₂Zn** in CH₂Cl₂.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	26174	27000	28289	28843
Oszillator strength	1.47E-01	1.10E-02	6.52E-03	5.97E-03
Orbitals & contribution	249 -> 250 95.8%	248 -> 250 95.6%	249 -> 251 93.0%	247 -> 250 79.7% 245 -> 250 6.3%
transition dipole moment/D	3.45	0.93	0.70	0.66

Table S29. Overview for **2Au₂Zn** in MeCN.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	26463	27344	28739	29435
Oszillator strength	1.60E-01	9.35E-03	6.50E-03	1.18E-02
Orbitals & contribution	249 -> 250 96.1%	248 -> 250 95.8%	249 -> 251 93.0%	248 -> 251 93.0%
transition dipole moment/D	3.58	0.85	0.70	0.93

Table S30. Overview for **2Zn** in CHCl₃.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	21735	23506	23990	25332
Oszillator strength	1.71E-03	5.28E-04	2.13E-03	1.18E-01
Orbitals & contribution	213 -> 214 98.9%	213 -> 215 91.0%	212 -> 214 87.8% 213 -> 215 8.3%	211 -> 214 89.0% 212 -> 215 3.8%
transition dipole moment/D	0.41	0.21	0.43	3.14

Table S31. Overview for **2Zn** in CH₂Cl₂.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	22428	24305	24692	25675
Oszillator strength	2.15E-03	3.54E-04	3.71E-03	1.33E-01
Orbitals & contribution	213 -> 214 98.9%	213 -> 215 84.5% 212 -> 214 14.5%	212 -> 214 80.7% 213 -> 215 14.7%	211 -> 214 92.4%
transition dipole moment/D	0.45	0.17	0.56	3.31

Table S32. Overview for **2Zn** in MeCN.

Excitation Nr.	1	2	3	4
Energy/cm ⁻¹	23121	25082	25380	26019
Oszillator strength	2.76E-03	5.39E-04	7.55E-03	1.42E-01
Orbitals & contribution	213 -> 214 98.8%	213 -> 215 65.1% 212 -> 214 32.9%	212 -> 214 60.0% 213 -> 215 33.6%	211 -> 214 91.2%
transition dipole moment/D	0.50	0.21	0.79	3.41

Orbitals

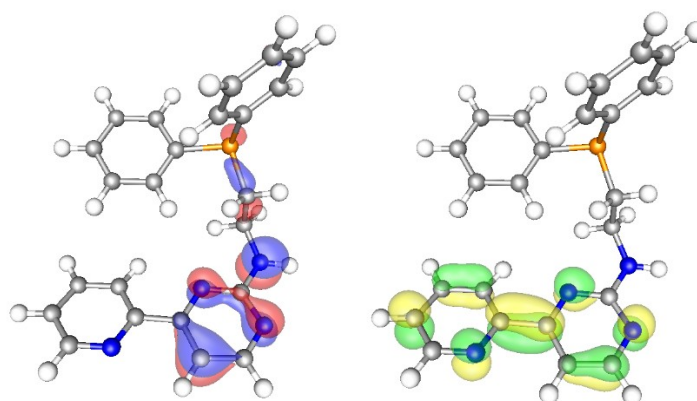


Fig. S10: Orbitals of the transition for **1**, left: HOMO (101); right: LUMO (102).

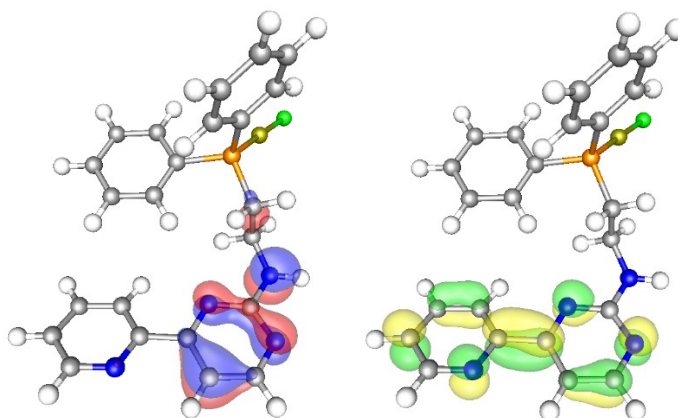


Fig. S11: Orbitals of the transition for **1Au**, left: HOMO (119); right: LUMO (120).

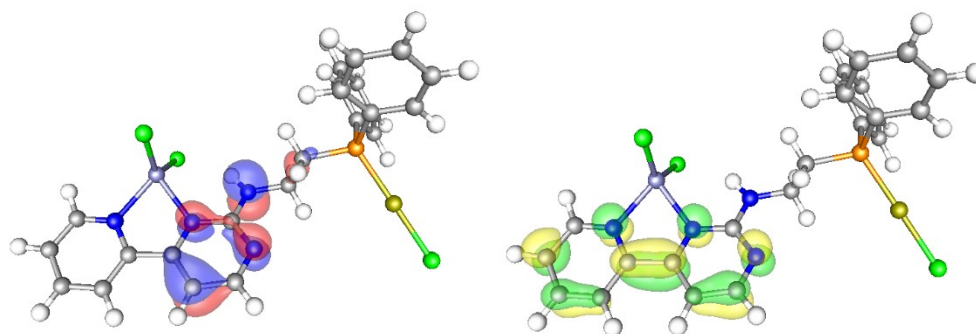


Fig. S12: Orbitals of the transition for **1AuZn**, left: HOMO (151); right: LUMO (152).

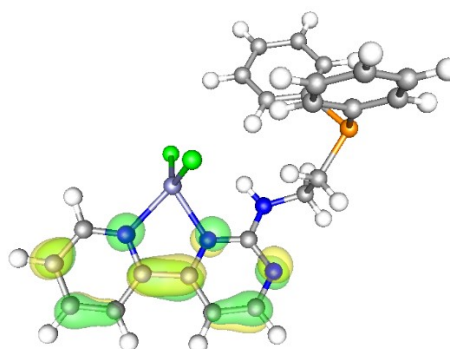


Fig. S13: Orbitals of the transition for **1Zn**, left: HOMO-1 (132); right: LUMO (134).

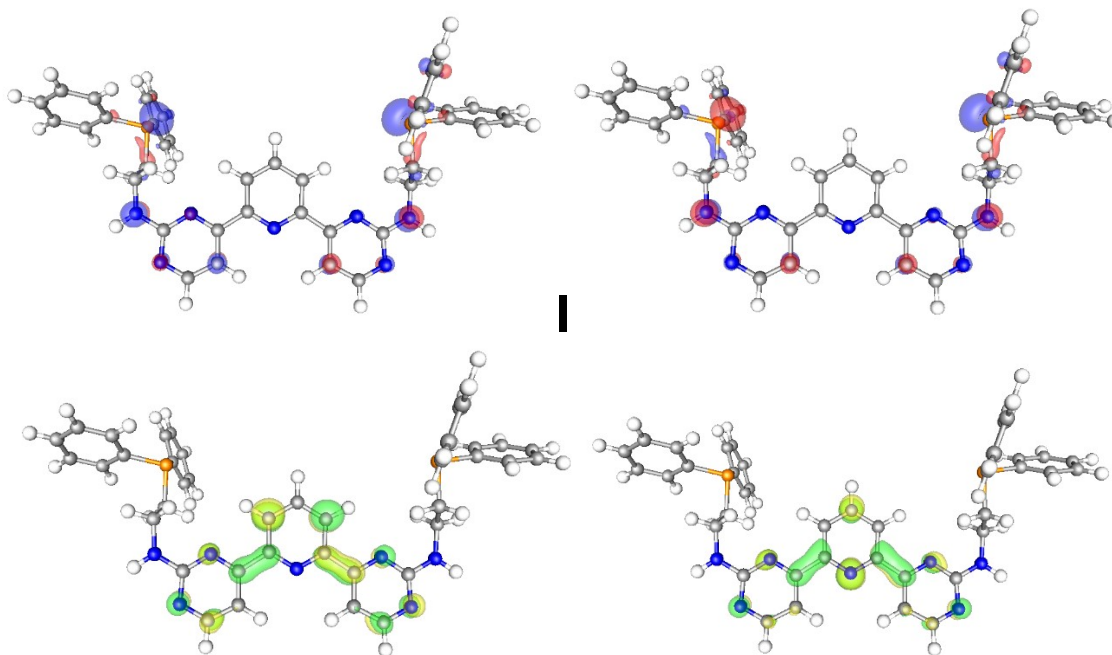


Fig. S14: Orbitals of the transition for **2**, top left: HOMO-1 (180); top right: HOMO (181); bottom left: LUMO (182); bottom right: LUMO+1 (183).

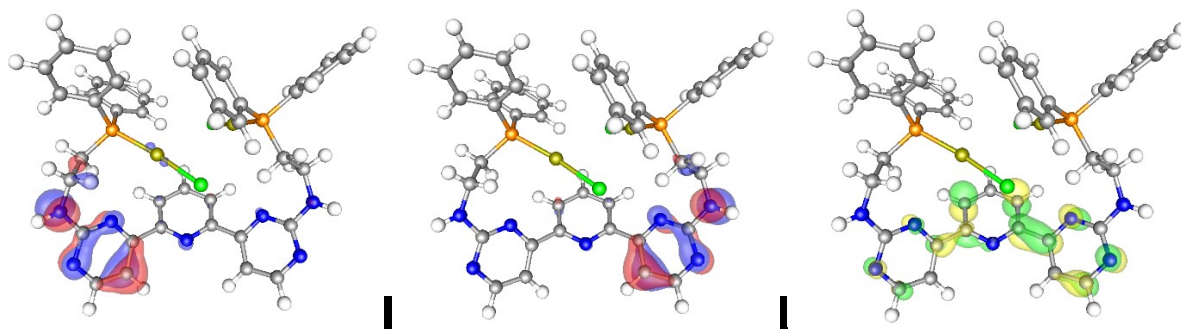


Fig. S15: Orbitals of the transition for **2Au₂**, left: HOMO-1 (216); middle: HOMO (217); right: LUMO (218).

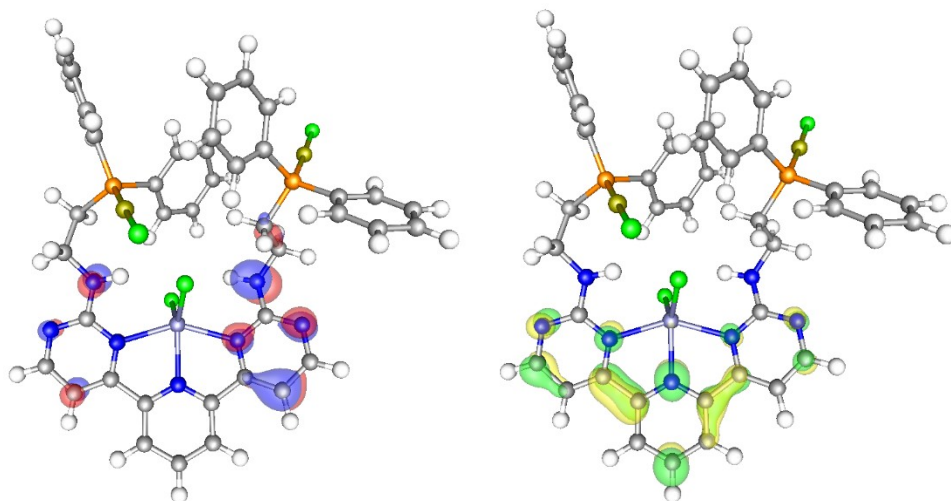


Fig. S16: Orbitals of the transition for **2Au₂Zn**, left: HOMO (249); right: LUMO (250).

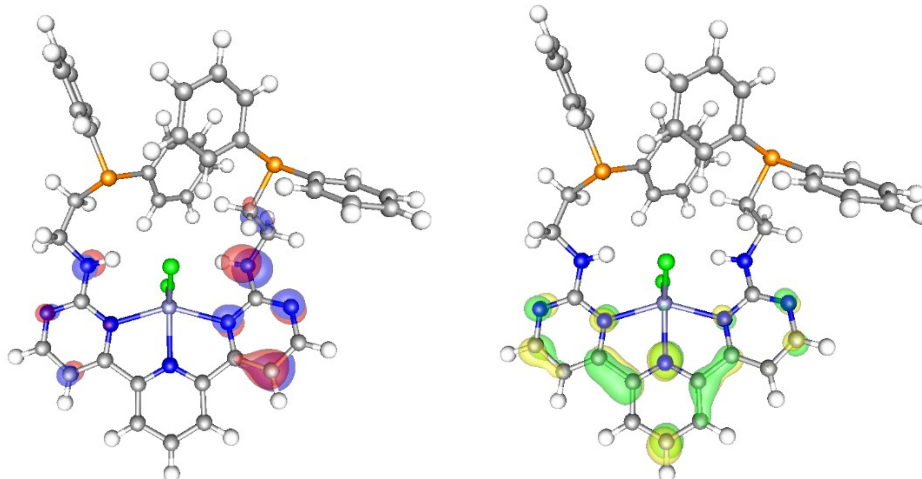


Fig. S17: Orbitals of the transition for **2Zn**, left: HOMO-2 (211); right: LUMO (214).

From Tab. S14-37 it can be seen that for most species the pre-band results from one excitation, characterized as π - π^* transition. For **2** and **2Au**, two transitions nearly equally contribute to the pre-band. The reasons for that can be found in the higher symmetry of **2** (C_2) and separation of the π -systems due to the non-planarity of **2Au**, respectively. The intense excitation representing the pre-band for **1Zn** is $S_0 \rightarrow S_2$. However, the character of the excitation represented by the involved orbitals is analog to **1**, **1Au** and **1AuZn**. The pre-band

of **2Zn** is also not the HOMO – LUMO transition but HOMO-2 – LUMO, representing the excitation from S_0 to S_4 with analog characteristic orbitals like for the other species.

Cooperativity:

The analysis of the cooperativity as shown in Tab. 3 uses the maxima of the Gaussian fits. For a more detailed understanding of the origin, the theoretical values are analyzed with respect to the involved states. For this purpose, the equations (3) and (4) with the energy of the S_0 and S_1 states instead of the absorption maximum are used. As mentioned before, the relevant transitions for **1Zn** and **2Zn** are $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_4$, respectively. Thus, these electronic states are chosen for the calculation of $\tilde{\nu}_{ce}$ in the electronically excited state. The results are summarized in Tab. S32.

Tab. S33: Calculated values of $\tilde{\nu}_{ce}$ in dependence on the electronic state as obtained from (TD)-B3LYP-D3/def2-TZVP calculations. The excitation represents the difference between ground and excited state ($S_1 - S_0$).

Compound/state	$\tilde{\nu}_{ce}/\text{cm}^{-1}$ (CHCl_3)	$\tilde{\nu}_{ce}/\text{cm}^{-1}$ (CH_2Cl_2)	$\tilde{\nu}_{ce}/\text{cm}^{-1}$ (MeCN)
1 / S_0	130.1	36.1	-42.2
1 / S_1	-235.4	-605.3	-1045.8
1 / excitation	-365.6	-641.4	-1003.6
2 / S_0	-1038.8	-996.3	-932.5
2 / S_1	-2190.4	-2145.1	-1974.3
2 / excitation	-1151.6	-1148.8	-1041.7

For compound **1**, it can be observed that $\tilde{\nu}_{ce}$ decreases with the polarity of the solvent, both for the ground state and the excited state. Since the increase of the dipole moments and transition energies also correlate with polarity of the solvent, it can be reasoned that the calculations of these values are consistent. Hence, the values of $\tilde{\nu}_{ce}$ are reliable. In contrast, it can be seen for compound **2** that $\tilde{\nu}_{ce}$ increases with polarity of the solvents. This contrast can be explained by varying behavior of the individual species. The excitation energy of **2** and **2Au₂** decreases with the increasing polarity, while it increases for **2Au₂Zn** and **2Zn**. This might be a result of the rearrangement due to the coordination of the zinc.

Tab. S34: Calculated values of k_{ce} using formula (2) to calculate k and formula (4) and (5) for the cooperative effect.

Compound/state	k_{ce}/ns^{-1} (CHCl_3)	k_{ce}/ns^{-1} (CH_2Cl_2)	k_{ce}/ns^{-1} (MeCN)
1	0.0376	0.0403	0.0476
2	-0.150	-0.130	-0.0935

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