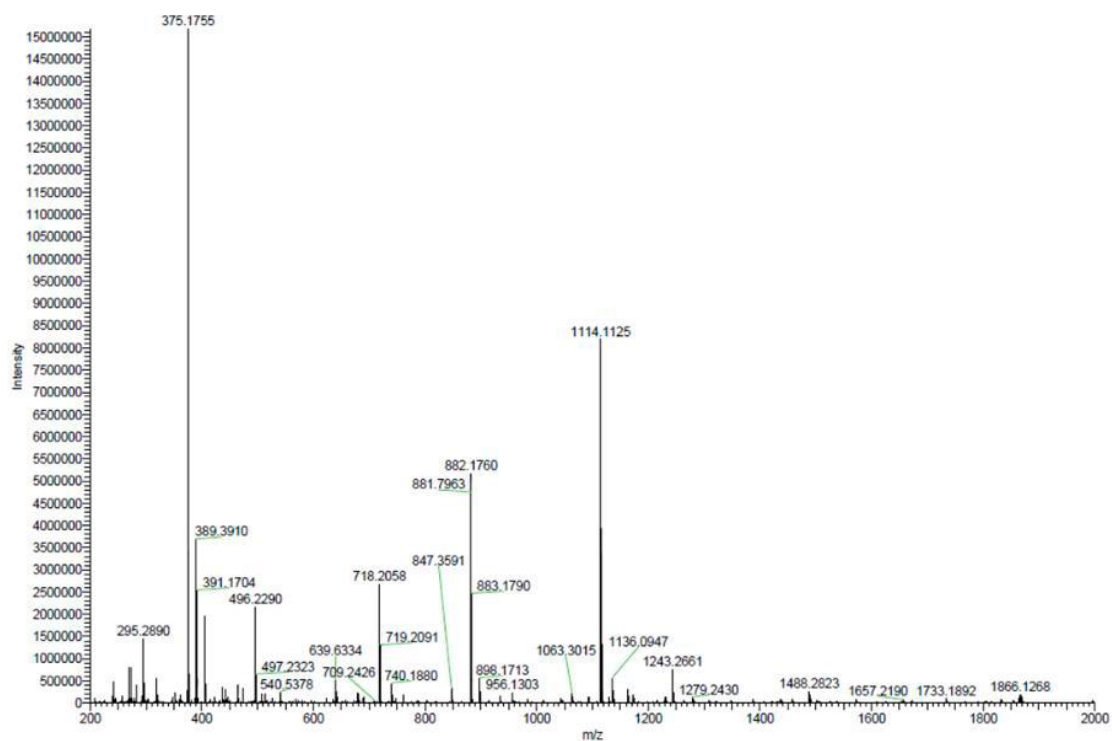


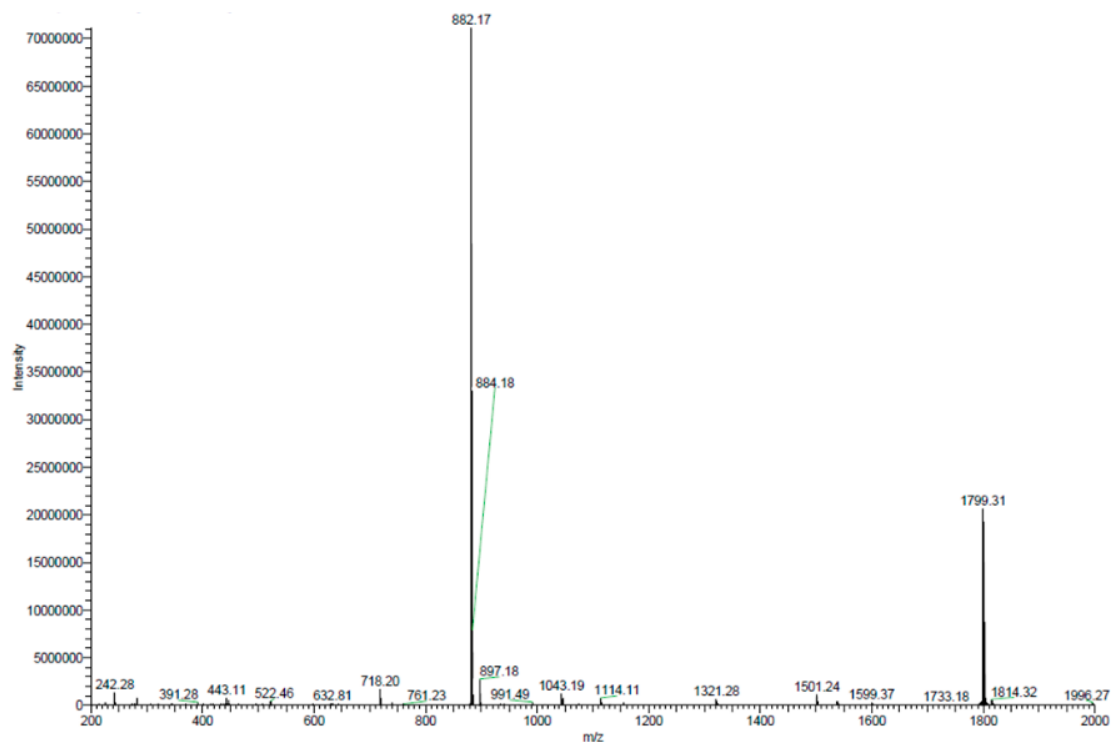
**Structural and theoretical evidence of rare synergic N(amide)H...Au(I)  
and N(amidate)...Au(I) secondary bonding interactions**

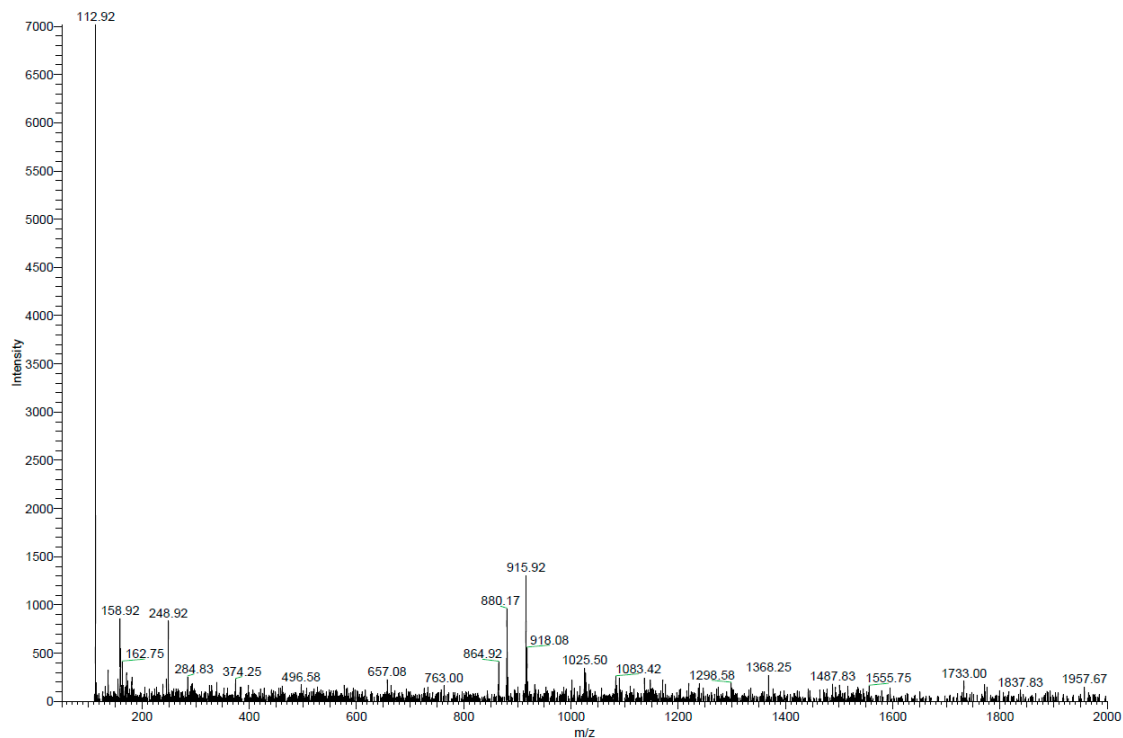
Laura Coconubo-Guio, Sonia Moreno, Giacomo Picci, Miguel Monge, José M. López-de-Luzuriaga, M. Elena Olmos, Claudia Caltagirone, Vito Lippolis

**Electronic Supplementary Information**

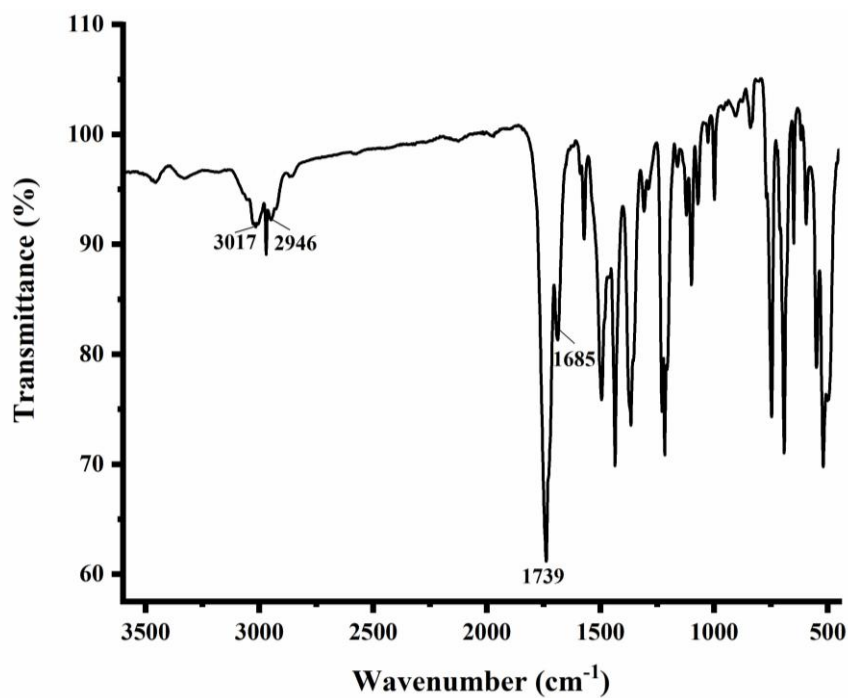


**Figure S1.** ESI positive mass spectrum of  $[(\text{AuCl})_2(\text{L})]$  (**1**):  $m/z = 375.17$   $[\text{C}_{19}\text{H}_{11}\text{N}_3\text{O}_2\text{P}_2]^+$   $[\text{L}-4\text{Ph}_2-2\text{H}]^+$ ,  $1114.1125$   $[\text{C}_{43}\text{H}_{33}\text{Au}_2\text{ClN}_3\text{O}_2\text{P}_2]$   $[\text{M}-\text{Cl}]^+$ ,  $882.1760$   $[\text{C}_{43}\text{H}_{33}\text{AuN}_3\text{O}_2\text{P}_2]$   $[\text{M}-\text{Au}-2\text{Cl}]^+$ .

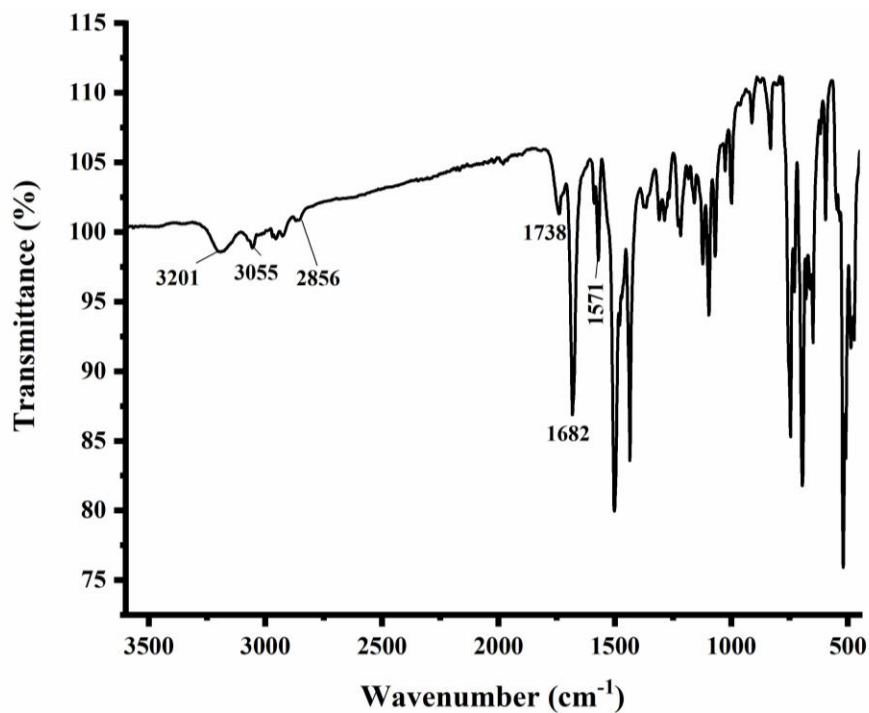




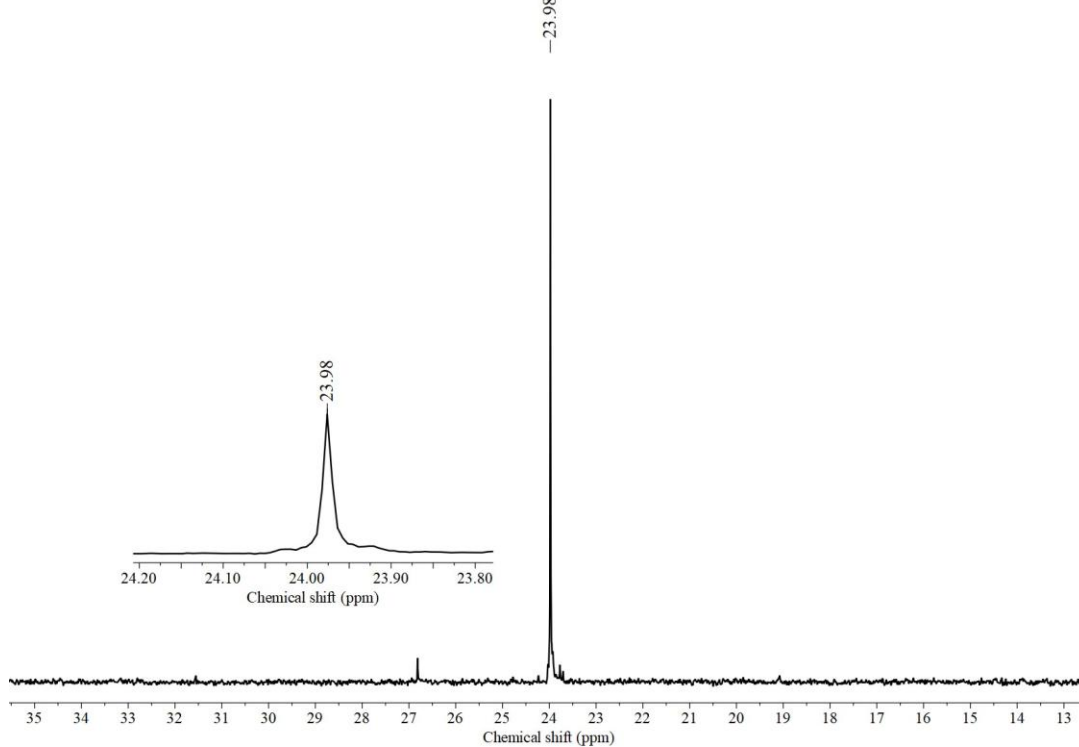
**Figure S2.** ESI mass spectra of  $[\text{AuCl}(\text{L})]$  (**2**): positive mode (top):  $m/z = 882.17$   $[\text{C}_{43}\text{H}_{33}\text{AuN}_3\text{O}_2\text{P}_2]^+ [\text{M}-\text{Cl}]^+$ ; negative mode (bottom):  $m/z = 915.92$   $[\text{C}_{43}\text{H}_{31}\text{AuClN}_3\text{O}_2\text{P}_2]^{2-} [\text{M}-2\text{H}]^{2-}$ .



**Figure S3.** UATR-IR spectrum of  $[(\text{AuCl})_2(\text{L})]$  (**1**):  $\nu$  (N-H) = 3017-2946 (m)  $\text{cm}^{-1}$ ,  $\nu$  (C=O) = 1739 (vs, br)  $\text{cm}^{-1}$ , (C-H<sub>py</sub>) = 1685 (vs, br)  $\text{cm}^{-1}$ .



**Figure S4.** UATR-IR spectrum of [(AuCl)(L)] (**2**):  $\nu$  (N-H) = 3201-286.5 (m) cm<sup>-1</sup>,  $\nu$  (C=O) = 1738 (vs, br) cm<sup>-1</sup>, (C-H<sub>py</sub>) = 1682 (vs, br) cm<sup>-1</sup>.



**Figure S5.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of [(AuCl)<sub>2</sub>(L)] (**1**).

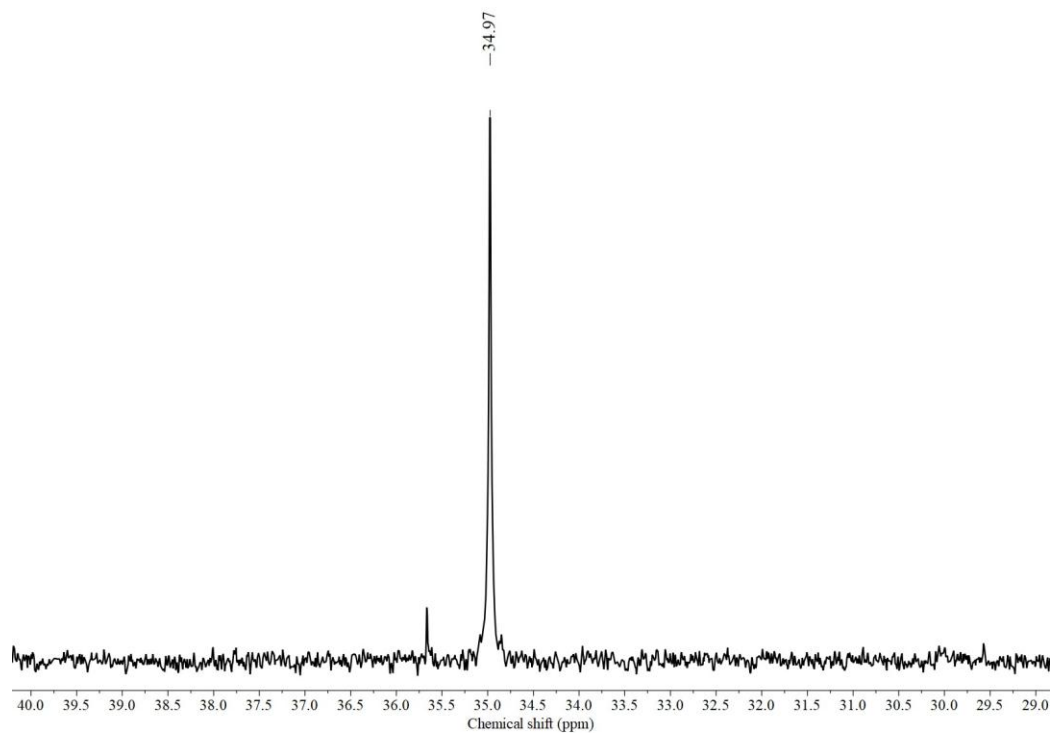


Figure S6.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[(\text{AuCl})(\text{L})]$  (2).

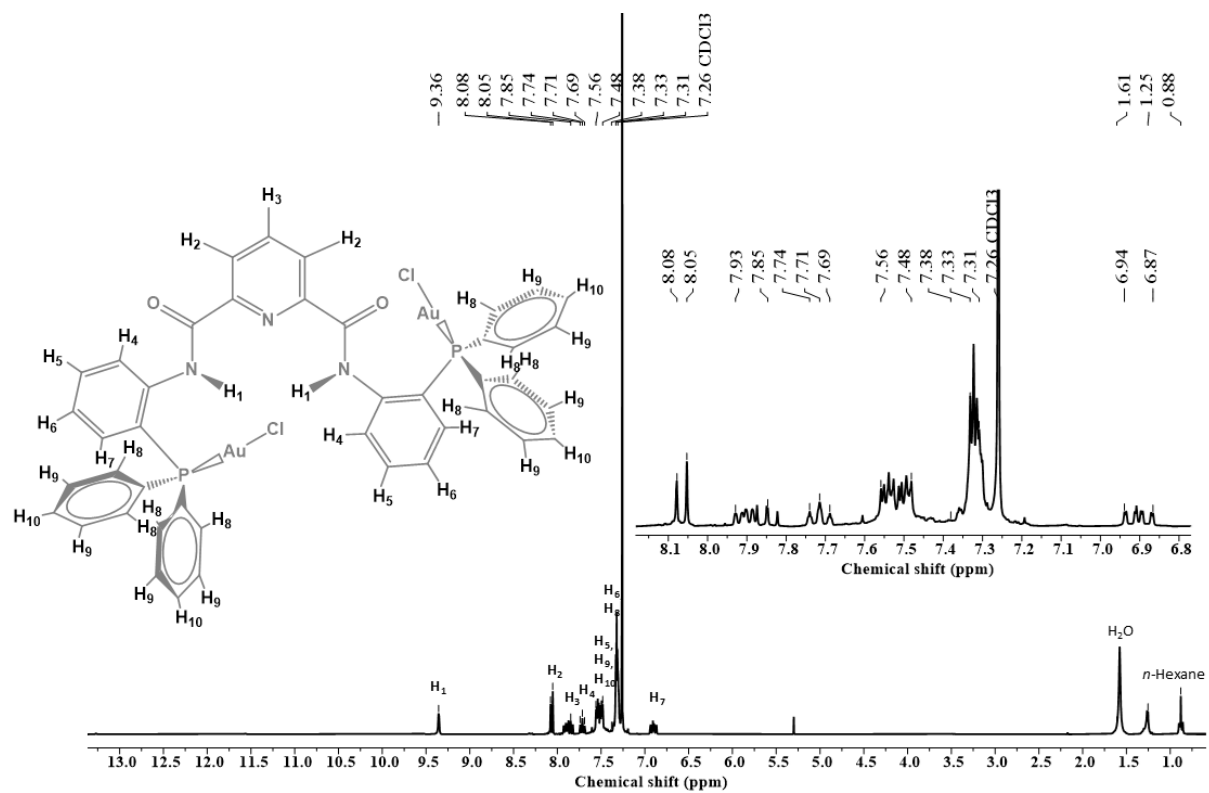


Figure S7.  $^1\text{H}$  NMR spectrum of  $[(\text{AuCl})_2(\text{L})]$  (1).

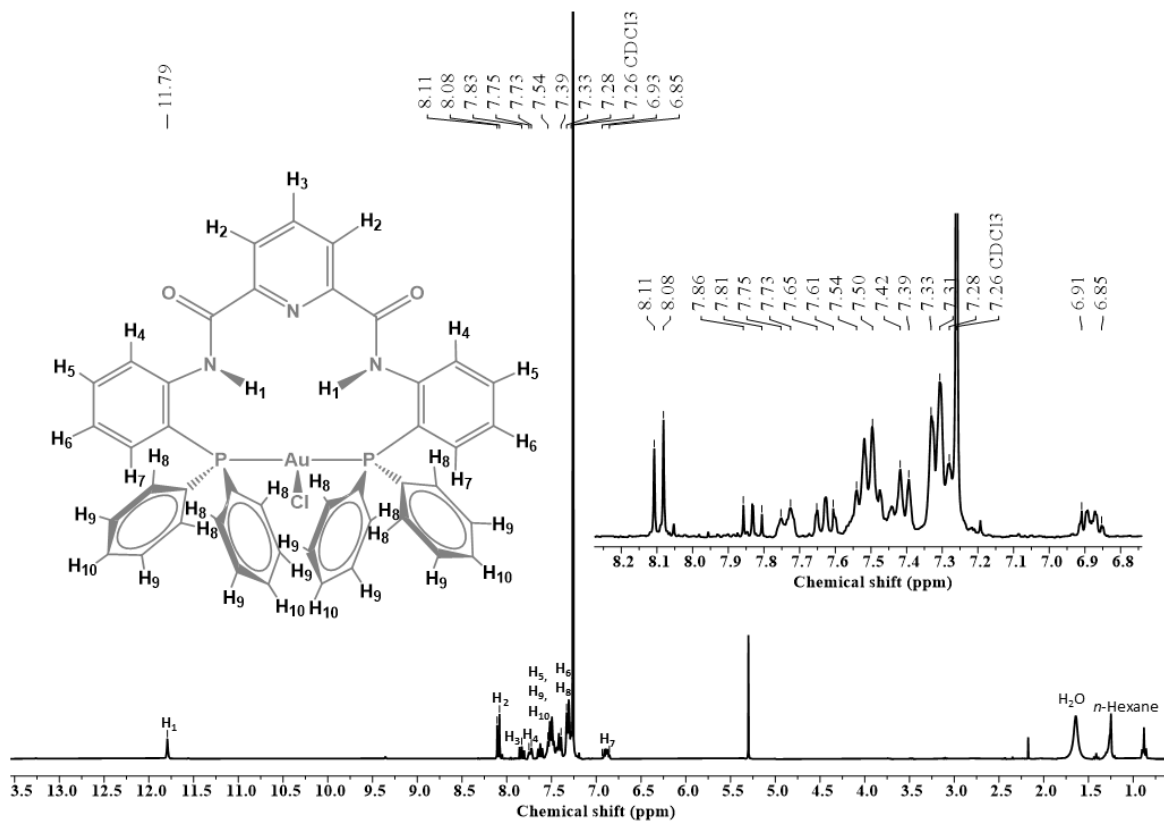


Figure S8.  $^1H$  NMR spectrum of  $[(AuCl)(L)]$  (2).

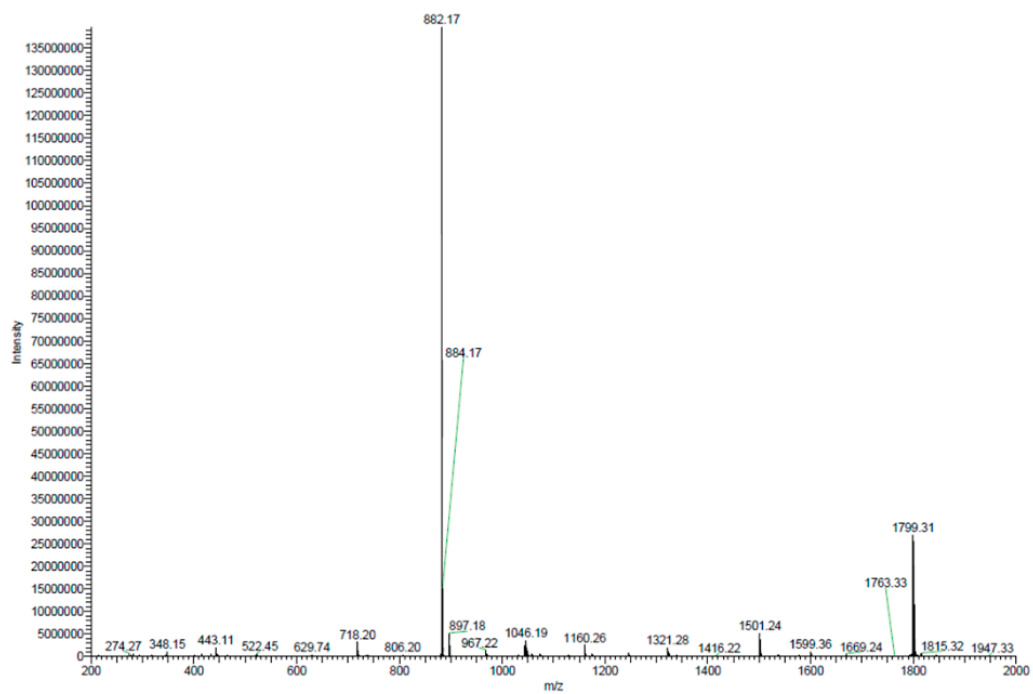
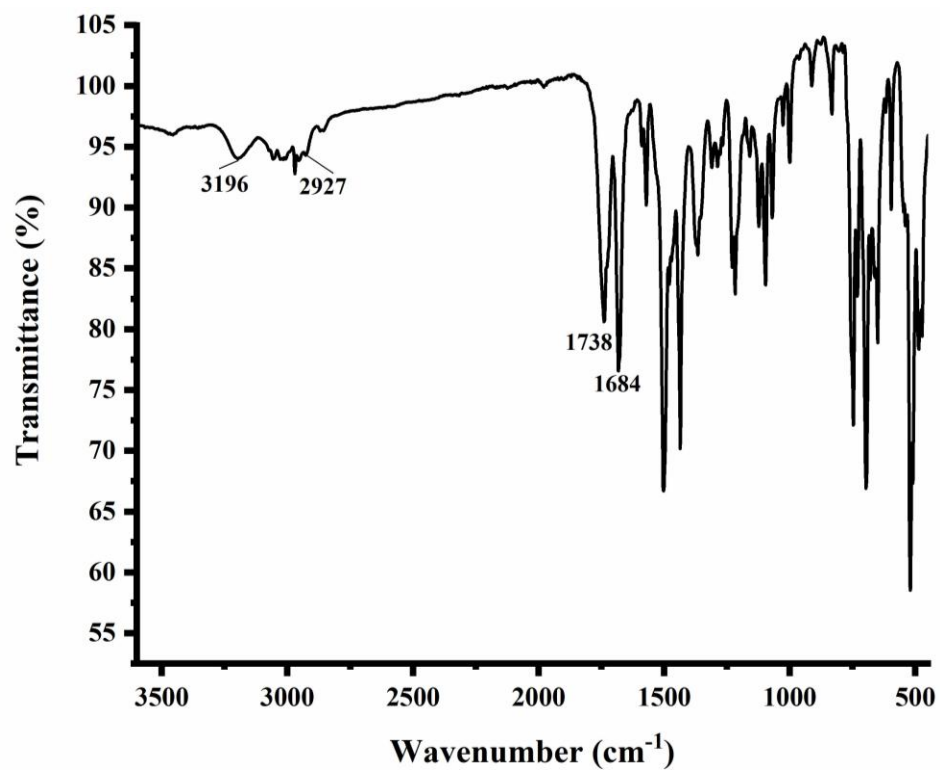
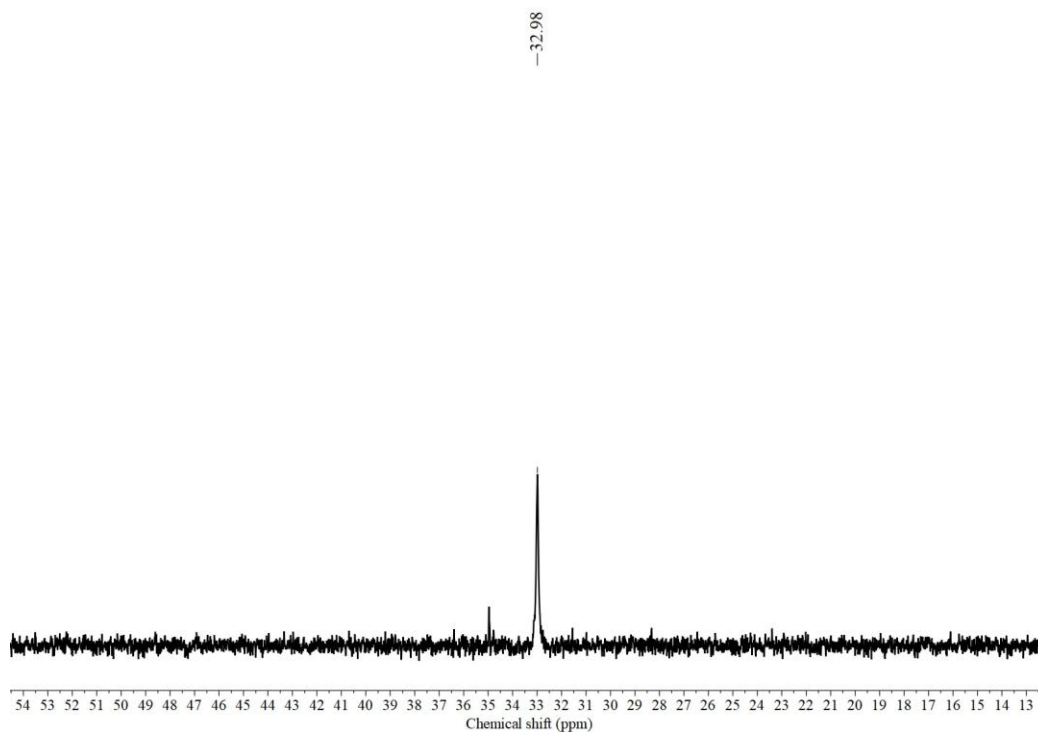


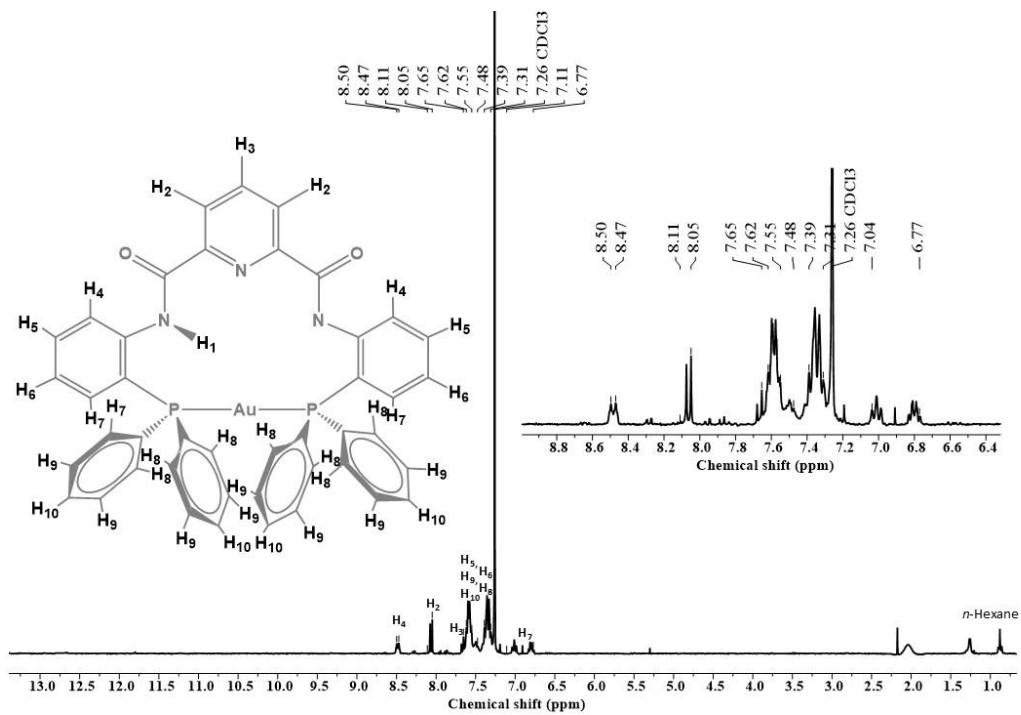
Figure S9. ESI mass spectra of  $[Au(L-H)]$  (3) in positive mode:  $m/z = 882.17$   $[C_{43}H_{33}AuN_3O_2P_2]^+$   $[M]^+$ .



**Figure S10.** UATR-IR spectrum of  $[\text{Au}(\text{L-H})]$  (**3**):  $\nu$  (N-H) = 3196-2927 (m)  $\text{cm}^{-1}$ ,  $\nu$  (C=O) = 1738 (vs, br)  $\text{cm}^{-1}$ , (C-H<sub>py</sub>) = 1684 (vs, br)  $\text{cm}^{-1}$ .



**Figure S11.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Au}(\text{L-H})]$  (**3**).



**Figure S12.**  $^1\text{H}$  NMR spectrum of  $[\text{Au}(\text{L-H})]$  (3).

**Table S1.** Hydrogen bonds for [(L)(AuCl)<sub>2</sub>] (**1**) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...Au(1)	0.69(5)	2.977(48)	3.565(6)	146
C(36)-H(36)...O(1)#1	0.93	2.458(5)	3.388(9)	179.1(5)
C(16)-H(16)...O(2)#2	0.93	2.409(5)	3.278(7)	155.6(4)
C(33)-H(33)...Cl(1)#3	0.93	2.842(2)	3.524(7)	131.1(4)

Symmetry transformations used to generate equivalent atoms:

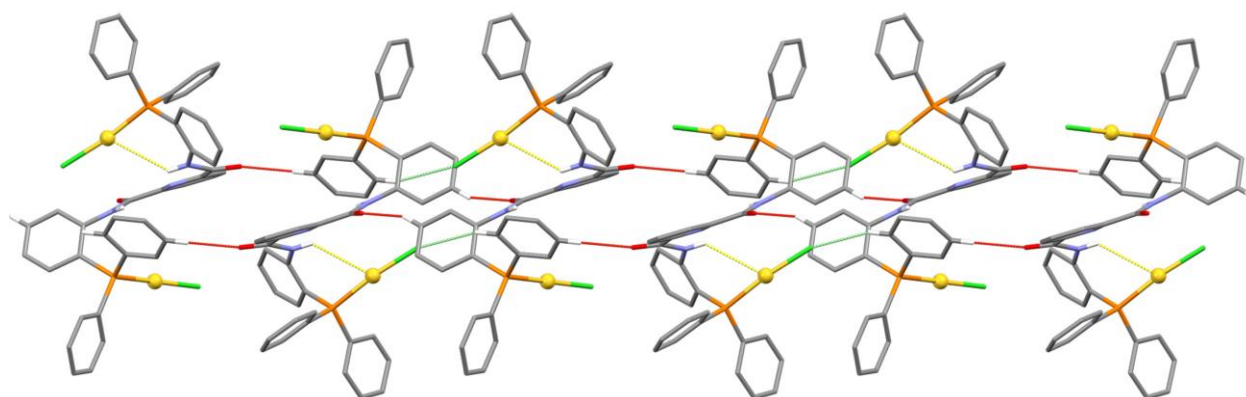
#1 -x+1,-y+1,-z #2 -x+1,-y,-z+1 #3 -x+1,-y+1,-z+1

**Table S2.** Hydrogen bonds for 2·1.5CH<sub>2</sub>Cl<sub>2</sub> [Å] and °.

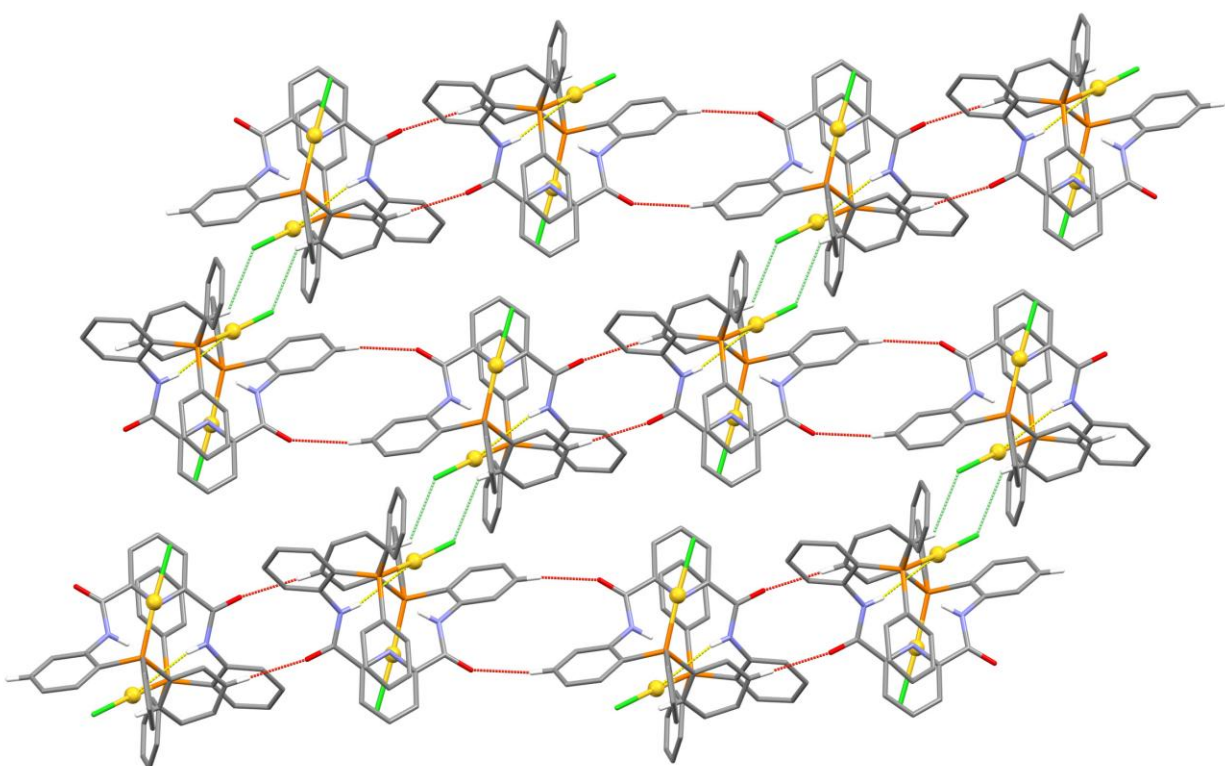
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...Au	0.86	2.8345(1)	3.461(4)	132.1
N(3)-H(3A)...Au	0.86	3.0316(1)	3.620(3)	127.4
N(1)-H(1)...Cl(1)	0.86	2.635(2)	3.359(4)	142.4(4)
N(3)-H(3A)...Cl(1)	0.86	2.586(2)	3.325(4)	144.8(4)
C(34)-H(34)...O(2)#1	0.93	2.699(6)	3.468(12)	140.6(7)
C(5)-H(5)...O(2)#2	0.93	2.605(5)	3.524(6)	169.5(5)
C(23)-H(23)...O(1)#3	0.93	2.569(7)	3.429(14)	154.0(7)
C(18)-H(18)...Cl(1)#4	0.93	2.973(2)	3.646(5)	130.6(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1 #2 -x+1,-y+1,-z+1 #3 -x,-y+1,-z+1 #4 -x+1,y-1/2,-z+1/2

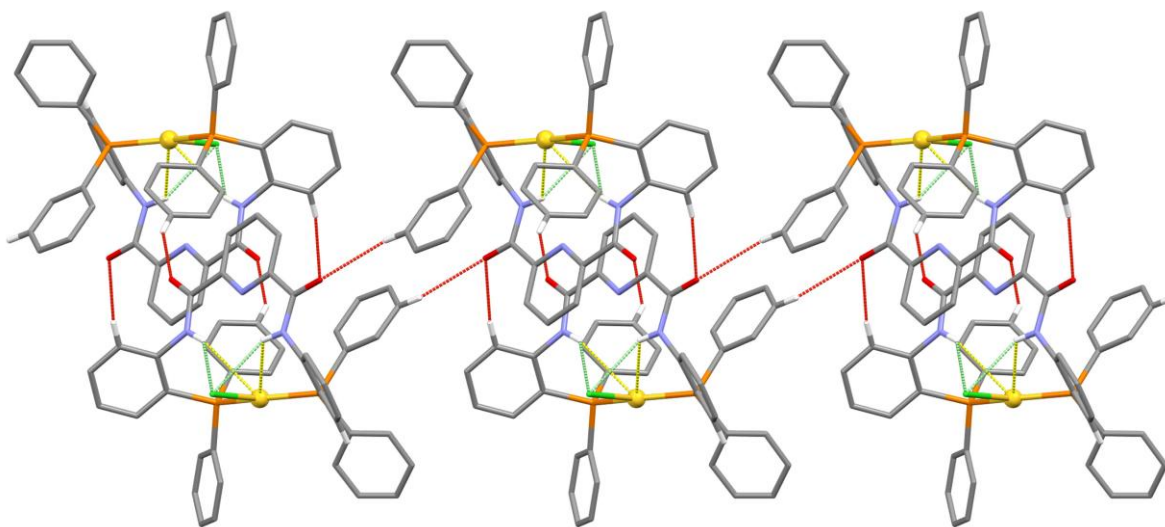


(A)

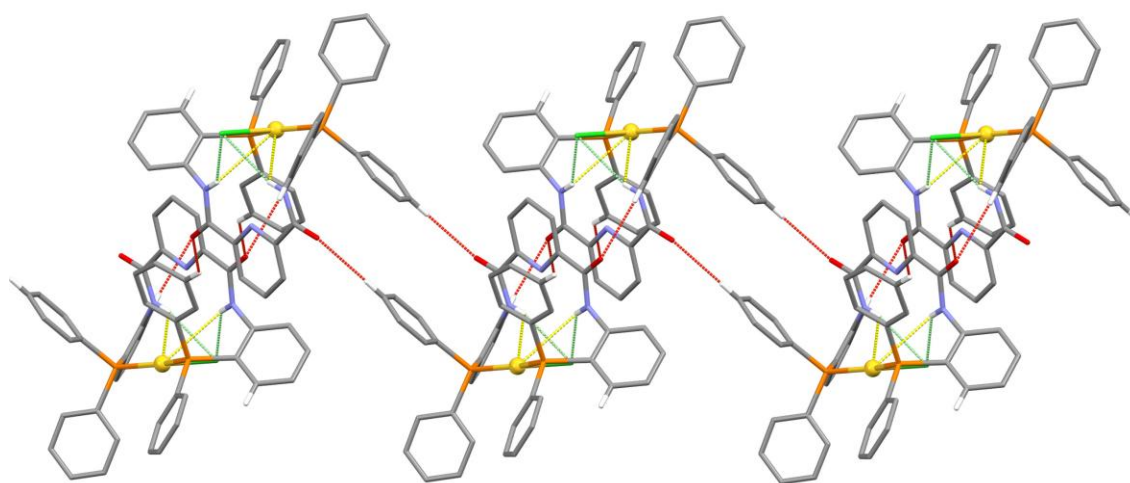


(B)

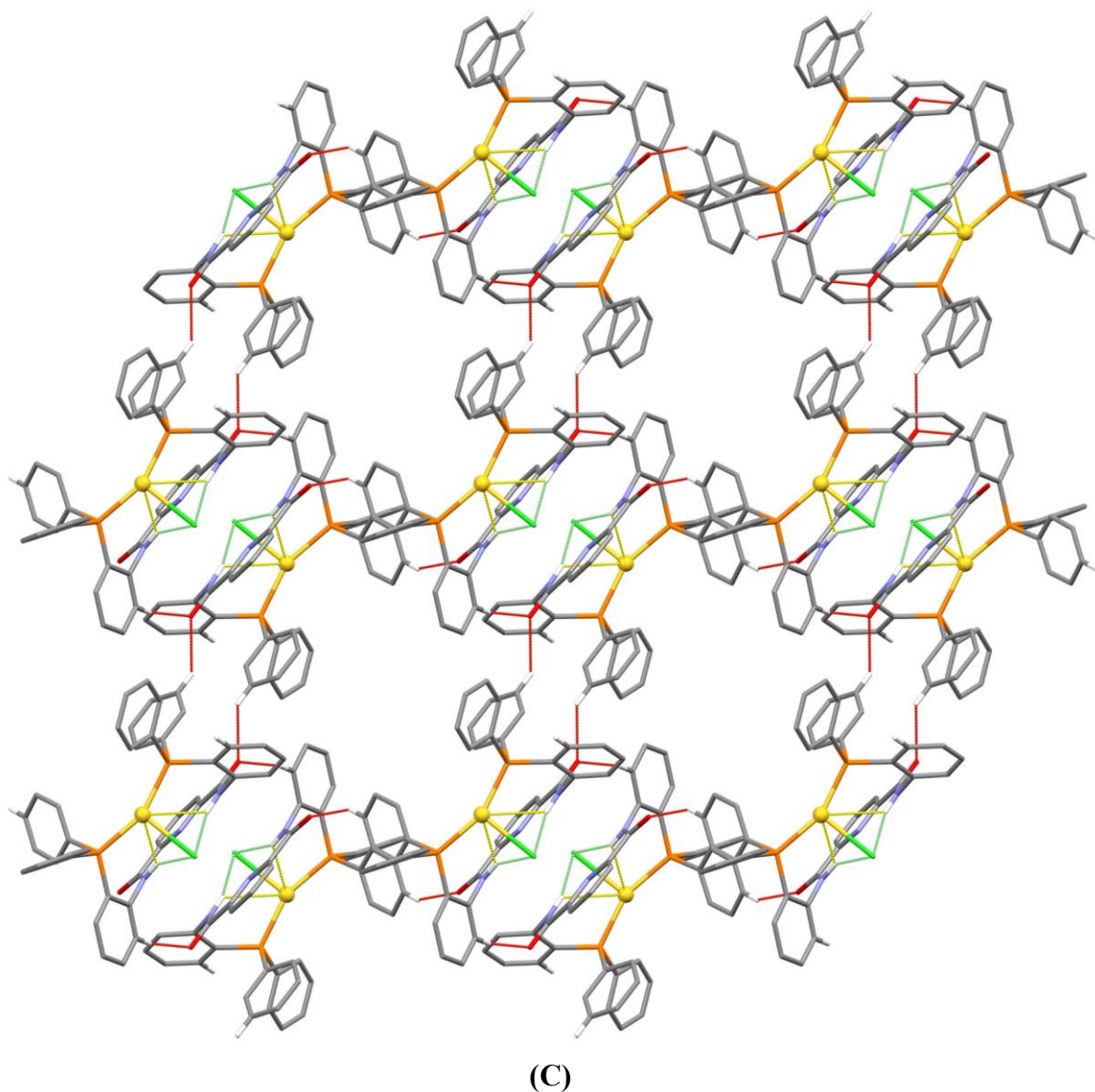
**Figure S13.** Part of the supramolecular structure of **1**: 1D network formed by C-H $\cdots$ O hydrogen bonds viewed from the crystallographic  $y$  axis (A), 2D network formed by C-H $\cdots$ O and C-H $\cdots$ Cl hydrogen bonds viewed from the crystallographic  $x$  axis (B). Hydrogen atoms, except those involved in hydrogen bonds, have been omitted for clarity. Color code: gold (yellow), phosphorus (orange), chlorine (green), nitrogen (purple), oxygen (red), carbon (gray), hydrogen (white), N-H $\cdots$ Au (dashed yellow), C-H $\cdots$ O (dashed red), and C-H $\cdots$ Cl (dashed green) hydrogen bonds.



(A)



(B)



**Figure S14.** Part of the supramolecular of  $2 \cdot 1.5\text{CH}_2\text{Cl}_2$ : 1D network formed by bifurcated C-H...O hydrogen bonds viewed from the crystallographic *a*-axis (A), 2D network formed by C-H...O hydrogen bonds viewed from the crystallographic *b*-axis (B) or *c*-axis (C). Hydrogen atoms (except those involved in hydrogen bonds) have been omitted for clarity. Color code: gold (yellow), phosphorus (orange), chlorine (green), nitrogen (purple), oxygen (red), carbon (gray), hydrogen (white), N-H...Au (dashed yellow), C-H...Cl (dashed green), and C-H...O (dashed red) hydrogen bonds.

**Table S3.** Selected optimized bond lengths (Å) and angles (°) for model systems of compounds **2**, and **3**.

	Au-P	P-Au-P	Au-Cl	N-H...Cl	N-H...N	N-H...Au	N...Au	C-H...Au
<b>2a</b>	2.31-2.32	146.1	2.56	2.30	2.30	2.77-2.85	3.76 (arom)	2.89-3.01
<b>3a</b>	2.31-2.32	175.9	-	-	1.96	2.66	3.51 (arom) 2.99 (amidate)	2.87-3.17

**Table S4.** IBSIW indexes for model systems **2a** and **3a**.

	N-H...Cl	N-H...Au	N(amidate)...Au	C-H...Au
<b>2a</b>	1.98, 1.98	0.90, 0.75	-	0.25, 0.35, 0.54, 0.66
<b>3a</b>	-	1.08	1.27	0.66, 0.36, 0.34, 0.33