

Supplementary Materials: In Vitro Antitumor Active Gold(I) Triphenylphosphane Complexes Containing 7-Azaindoles

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1. Results of ESI Mass Spectrometry and FTIR Spectroscopy

1: ESI+ MS (methanol, m/z): 721.2 (calc. 721.2; 100%; $[\text{Au}(\text{PPh}_3)_2]^+$), 577.2 (calc. 577.1; 2%; $\{[\text{Au}(\text{aza})(\text{PPh}_3)] + \text{H}\}^+$), 459.2 (calc. 459.1; 2%; $[\text{Au}(\text{PPh}_3)]^+$), 119.1 (calc. 119.1; 2%; $\{(\text{Haza}) + \text{H}\}^+$). ESI- MS (methanol, m/z): 431.2 (calc. 431.1; 50%; $[\text{Au}(\text{aza})_2]^-$), 117.1 (calc. 117.0; 100%; $(\text{aza})^-$). FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 434m, 462m, 498vs, 542vs, 617m, 639m, 690vs, 711s, 744vs, 774s, 793m, 851w, 895m, 931w, 949m, 987m, 1026m, 1046m, 1071m, 1099vs, 1169s, 1199m, 1265s, 1291s, 1312m, 1334m, 1351s, 1354s, 1404vs, 1433vs, 1463s, 1478m, 1555m, 1585s, 2918m, 2988m, 3007m, 3032m, 3055m, 3088m. FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 241w, 328w, 434m, 462m, 499vs, 543vs, 592w. Raman (cm^{-1}): 329w, 464w, 566w, 617w, 639w, 695w, 712w, 763m, 851w, 877w, 923w, 999vs, 1028m, 1042m, 1072m, 1101m, 1160w, 1185w, 1293w, 1351w, 1407w, 1438w, 1465m, 482m, 1556w, 1585s, 2954w, 3008w, 3056vs, 3108w, 3142w, 3168w.

2: ESI+ MS (methanol, m/z): 721.2 (calc. 721.2; 100%; $[\text{Au}(\text{PPh}_3)_2]^+$), 611.1 (calc. 611.1; 2%; $\{[\text{Au}(3\text{Claza})(\text{PPh}_3)] + \text{H}\}^+$), 459.2 (calc. 459.1; 2%; $[\text{Au}(\text{PPh}_3)]^+$). ESI- MS (methanol, m/z): 499.1 (calc. 499.0; 70%; $[\text{Au}(3\text{Claza})_2]^-$), 151.1 (calc. 151.0; 60%; $(3\text{Claza})^-$). FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 452m, 496vs, 545s, 592m, 669vs, 712s, 747vs, 765vs, 786w, 834m, 850w, 921m, 948w, 972m, 1004s, 1027vs, 1072m, 1102vs, 1150m, 1180s, 1192s, 1204m, 1269s, 1297vs, 1324s, 1350m, 1398vs, 1434vs, 1479vs, 1545m, 1574m, 1590s, 2879m, 2914m, 3033s, 3049s, 3113m. FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 202w, 231w, 248w, 330w, 397w, 431m, 451m, 498vs, 507s, 536vs, 544vs, 591m. Raman (cm^{-1}): 200w, 435w, 542w, 569w, 617w, 694w, 713w, 764m, 923w, 999vs, 1029m, 1103m, 1159w, 1185w, 1270w, 1299w, 1326w, 1345w, 1400w, 1436w, 1480s, 1545w, 1586s, 3954w, 3053vs, 3112w, 3142w, 3171w.

3: ESI+ MS (methanol, m/z): 721.4 (calc. 721.2; 100%; $[\text{Au}(\text{PPh}_3)_2]^+$), 655.2 (calc. 655.0; 5%; $\{[\text{Au}(3\text{Braza})(\text{PPh}_3)] + \text{H}\}^+$), 459.3 (calc. 459.1; 5%; $[\text{Au}(\text{PPh}_3)]^+$), 197.1 (calc. 197.0; 3%; $\{(\text{H3Braza}) + \text{H}\}^+$). ESI- MS (methanol, m/z): 589.2 (calc. 588.9; 100%; $[\text{Au}(3\text{Braza})_2]^-$), 195.2 (calc. 195.0; 20%; $(3\text{Braza})^-$). FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 435w, 450m, 498s, 524m, 542s, 588w, 617w, 688vs, 711m, 747s, 765s, 835m, 866w, 919m, 986s, 1027w, 1071w, 1103vs, 1144m, 1160w, 1181w, 1198m, 1264m, 1293s, 1320m, 1342w, 1392vs, 1433vs, 1468s, 1539w, 1585m, 1670w, 2784w, 2844w, 3029m, 3045m, 3107m, 3169w. FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 354w, 435m, 451m, 497vs, 525s, 543vs, 588m. Raman (cm^{-1}): 282w, 319w, 357w, 398w, 433w, 569w, 619w, 678w, 694w, 714w, 764m, 923w, 1000vs, 1031m, 1104m, 1160w, 1185w, 1260w, 1185w, 1268w, 1297w, 1345w, 1374w, 1396w, 1437w, 1473m, 1542w, 1587s, 2955w, 2993w, 3053vs, 3110w, 3143w, 3172w.

4: ESI+ MS (methanol, m/z): 721.4 (calc. 721.2; 100%; $[\text{Au}(\text{PPh}_3)_2]^+$), 703.3 (calc. 703.0; 10%; $\{[\text{Au}(3\text{Iaza})(\text{PPh}_3)] + \text{H}\}^+$), 459.3 (calc. 459.1; 5%; $[\text{Au}(\text{PPh}_3)]^+$), 245.1 (calc. 245.0; 5%; $\{(\text{H3Iaza}) + \text{H}\}^+$). ESI- MS (methanol, m/z): 683.0 (calc. 682.8; 100%; $[\text{Au}(3\text{Iaza})_2]^-$), 243.1 (calc. 242.9; 80%; $(3\text{Iaza})^-$). FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 448w, 499vs, 516m, 542vs, 587w, 616w, 689vs, 711m, 746s, 766s, 784w, 837w, 917w, 975m, 995m, 1027w, 1102vs, 1158w, 1180m, 1197m, 1215m, 1263m, 1289s, 1315m, 1332w, 1388vs, 1433vs, 1460m, 1479m, 1536w, 1552w, 1583m, 2663w, 3028m, 3047m. FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 243w, 303w, 322w, 397w, 435m, 449m, 497vs, 517s, 542vs, 586m. Raman (cm^{-1}): 280w, 303w, 325w, 520w, 543w, 567w, 617w, 668w, 693w, 712w, 762m, 919w, 999vs, 1032m, 1102m, 1158w, 1183w, 1265w, 1292w, 1318w, 1340w, 1391w, 1462m, 1543w, 1586s, 2988w, 3033m, 3050vs, 3143w, 3170w.

5: ESI+ MS (methanol, m/z): 721.4 (calc. 721.2; 100%; $[\text{Au}(\text{PPh}_3)_2]^+$), 655.2 (calc. 655.0; 10%; $\{[\text{Au}(5\text{Braza})(\text{PPh}_3)] + \text{H}\}^+$), 459.3 (calc. 459.1; 10%; $[\text{Au}(\text{PPh}_3)]^+$), 197.1 (calc. 197.0; 2%; $\{(\text{H5Braza}) + \text{H}\}^+$). ESI- MS (methanol, m/z): 589.2 (calc. 588.9; 100%; $[\text{Au}(5\text{Braza})_2]^-$), 195.2 (calc. 195.0; 70%; $(5\text{Braza})^-$). FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 432w, 471m, 499s, 541vs, 609m, 689vs, 710s, 732s, 745s, 775w, 852w,

871m, 912w, 938m, 996m, 1026m, 1070m, 1100vs, 1165s, 1249m, 1283s, 1335m, 1385s, 1433vs, 1450s, 1478s, 1571 m, 1588m, 1682w, 2683w, 2751w, 2849m, 3054s, 3141m. FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 306w, 434w, 451m, 473m, 499vs, 507s, 541vs, 588m. Raman (cm^{-1}): 309w, 473w, 639w, 777w, 915w, 1000vs, 1030m, 1072m, 1102m, 1183m, 1289w, 1338w, 1469s, 1585s, 3056vs, 3146w, 3212w, 3345w.

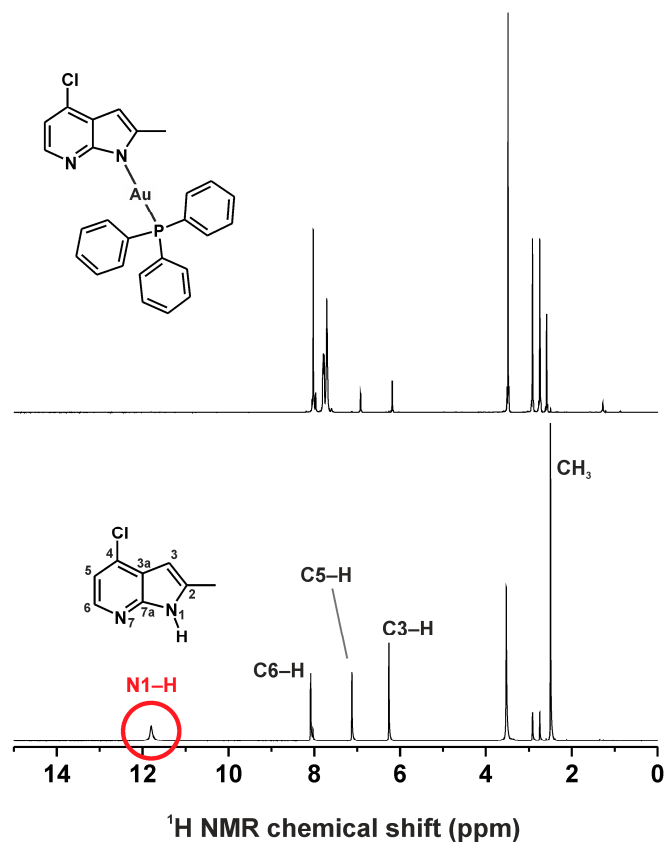
6: ESI+ MS (methanol, m/z): 721.4 (calc. 721.2; 100%; $[\text{Au}(\text{PPh}_3)_2]^+$), 689.1 (calc. 689.0; 5%; $\{[\text{Au}(3\text{Cl}5\text{Braza})(\text{PPh}_3)] + \text{H}\}^+$), 459.3 (calc. 459.1; 10%; $[\text{Au}(\text{PPh}_3)]^+$), 231.1 (calc. 230.9; 2%; $\{(\text{H}3\text{Cl}5\text{Braza}) + \text{H}\}^+$). ESI- MS (methanol, m/z): 657.3 (calc. 656.8; 100%; $[\text{Au}(3\text{Cl}5\text{Braza})_2]^-$), 229.2 (calc. 228.9; 45%; $(3\text{Cl}5\text{Braza})^-$). FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 433m, 456m, 499vs, 541vs, 600m, 615m, 689vs, 710s, 728m, 746s, 781m, 839m, 874m, 927m, 996m, 1010s, 1026w, 1069m, 1099vs, 1147s, 1183s, 1207w, 1249s, 1290s, 1310w, 1330m, 1392vs, 1432vs, 1451s, 1476s, 1532w, 1554w, 1581w, 2682w, 2818w, 2861w, 3051m, 3084w, 3110m, 3143w, 3356w. FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 311w, 431m, 447m, 500vs, 542vs, 589m. Raman (cm^{-1}): 278w, 308w, 342w, 447w, 503w, 546w, 618w, 694w, 712w, 731w, 783w, 851w, 931w, 1000vs, 1029m, 1073w, 1103m, 1159w, 1184w, 1262w, 1295w, 1310w, 1333w, 1395w, 1437w, 1456w, 1475m, 1533w, 1586m, 2987w, 3056vs, 3114w, 3142w, 3168m.

7: ESI+ MS (methanol, m/z): 780.9 (calc. 780.9; 3%; $\{[\text{Au}(3\text{I}5\text{Braza})(\text{PPh}_3)] + \text{H}\}^+$), 721.4 (calc. 721.2; 100%; $[\text{Au}(\text{PPh}_3)_2]^+$), 459.2 (calc. 459.1; 10%; $[\text{Au}(\text{PPh}_3)]^+$), 323.1 (calc. 322.9; 2%; $\{(\text{H}3\text{I}5\text{Braza}) + \text{H}\}^+$). ESI- MS (methanol, m/z): 840.9 (calc. 840.7; 100%; $[\text{Au}(3\text{I}5\text{Braza})_2]^-$), 321.2 (calc. 320.8; 30%; $(3\text{I}5\text{Braza})^-$). FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 444w, 501vs, 523m, 543s, 595m, 690vs, 709s, 747s, 774w, 842m, 876m, 929m, 985s, 1026w, 1071w, 1100vs, 1154m, 1181s, 1250m, 1288s, 1329m, 1381vs, 1433vs, 1453s, 1479m, 1577, 2889w, 3013w, 3050m, 3072w, 3100w. FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 319w, 343w, 436w, 446w, 500vs, 523s, 543vs, 589w, 596m. Raman (cm^{-1}): 279w, 285w, 321w, 346w, 435w, 500w, 600w, 618w, 693w, 712w, 778m, 931w, 1000vs, 1029m, 1071w, 1102m, 1160w, 1183w, 1252w, 1301m, 1332w, 1384w, 1436w, 1458m, 1532w, 1586s, 3019w, 3055vs.

8: ESI+ MS (methanol, m/z): 721.4 (calc. 721.2; 100%; $[\text{Au}(\text{PPh}_3)_2]^+$), 625.2 (calc. 625.1; 10%; $\{[\text{Au}(2\text{Me}4\text{Claza})(\text{PPh}_3)] + \text{H}\}^+$), 459.3 (calc. 459.1; 5%; $[\text{Au}(\text{PPh}_3)]^+$), 167.1 (calc. 167.0; 2%; $\{(\text{H}2\text{Me}4\text{Claza}) + \text{H}\}^+$). ESI- MS (methanol, m/z): 527.6 (calc. 527.0; 100%; $[\text{Au}(2\text{Me}4\text{Claza})_2]^-$), 165.2 (calc. 165.0; 20%; $(2\text{Me}4\text{Claza})^-$). FTIR ($\nu_{\text{ATR}}/\text{cm}^{-1}$): 441w, 501s, 542s, 616w, 647w, 690vs, 713m, 744vs, 781w, 804m, 859m, 959m, 996m, 1024m, 1072w, 1103vs, 1150m, 1180m, 1247s, 1294vs, 1324s, 1372m, 1398vs, 1434vs, 1480m, 1516m, 1539m, 1583s, 1664w, 2690w, 2845w, 2898m, 2935w, 2975m, 3011m, 3056m, 3086w, 3161w, 3278m, 3386s. Raman (cm^{-1}): 269w, 340w, 361w, 403w, 538m, 618w, 647w, 694w, 713w, 758w, 859w, 924w, 960w, 999vs, 1028m, 1071w, 1103m, 1160w, 1183w, 1260w, 1302w, 1330w, 1372w, 1399w, 1439w, 1479w, 1525vs, 1586s, 2849w, 2902w, 2925w, 2955w, 2988w, 3011w, 3052vs, 3109w, 3141w, 3168w.

Table S1. The parameters of selected non-covalent contacts in the crystal structure of the complexes [Au(3I5Braza)(PPh₃)] (7) and [Au(2CH₃4Claza)(PPh₃)]·½H₂O (8').

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)	Symmetry Codes
Complex 7					
C21-H21A...I1 ⁱ	0.95	3.11	3.818(4)	132.3	(i) -x, 1-y, -z
C15-H15A...Br1 ⁱⁱ	0.95	2.95	3.783(4)	147.3	(ii) 1-x, 0.5+y, 0.5-z
C31-H31A...Br1 ⁱⁱⁱ	0.95	2.99	3.738(4)	137.1	(iii) 1-x, 1-y, 1-z
C25-H25A...C11 ^{iv}	0.95	2.77	3.613(5)	148.4	(iv) 1+x, y, z
C33-H33A...N7 ^v	0.95	2.68	3.362(5)	129.1	(v) 2-x, 1-y, 1-z
C34-H34A...N7 ^{iv}	0.95	2.71	3.538(5)	146.2	(iv) 1+x, y, z
C35-H35A...Cg ^{iv}	0.95	2.61	3.396(4)	140.4	(iv) 1+x, y, z
C33...C35 ^v			3.326(6)		(v) 2-x, 1-y, 1-z
Complex 8'					
O1-H1W...N7	0.81(3)	2.17(3)	2.976(3)	170(3)	
C15-H15A...C3A ^{vi}	0.95	2.79	3.602(4)	143.8	(vi) 1.5-x, 1.5-y, 1-z
C21-H21A...C33 ^{vii}	0.95	2.73	3.635(4)	158.5	(vii) x, 1-y, z-0.5
C34-H34A...C22 ^{viii}	0.95	2.90	3.518(4)	124.1	(viii) 1-x, y, 0.5-z
C35-H35A...O1	0.95	2.56	3.496(3)	166.6	

**Figure S1.** ¹H-NMR spectra (DMF-*d*₇) of H₂Me₄Claza (**bottom**) and [Au(2Me₄Claza)(PPh₃)] (8; **top**) proving the deprotonation of the used 7-azaindole derivative; DMF = dimethylformamide.

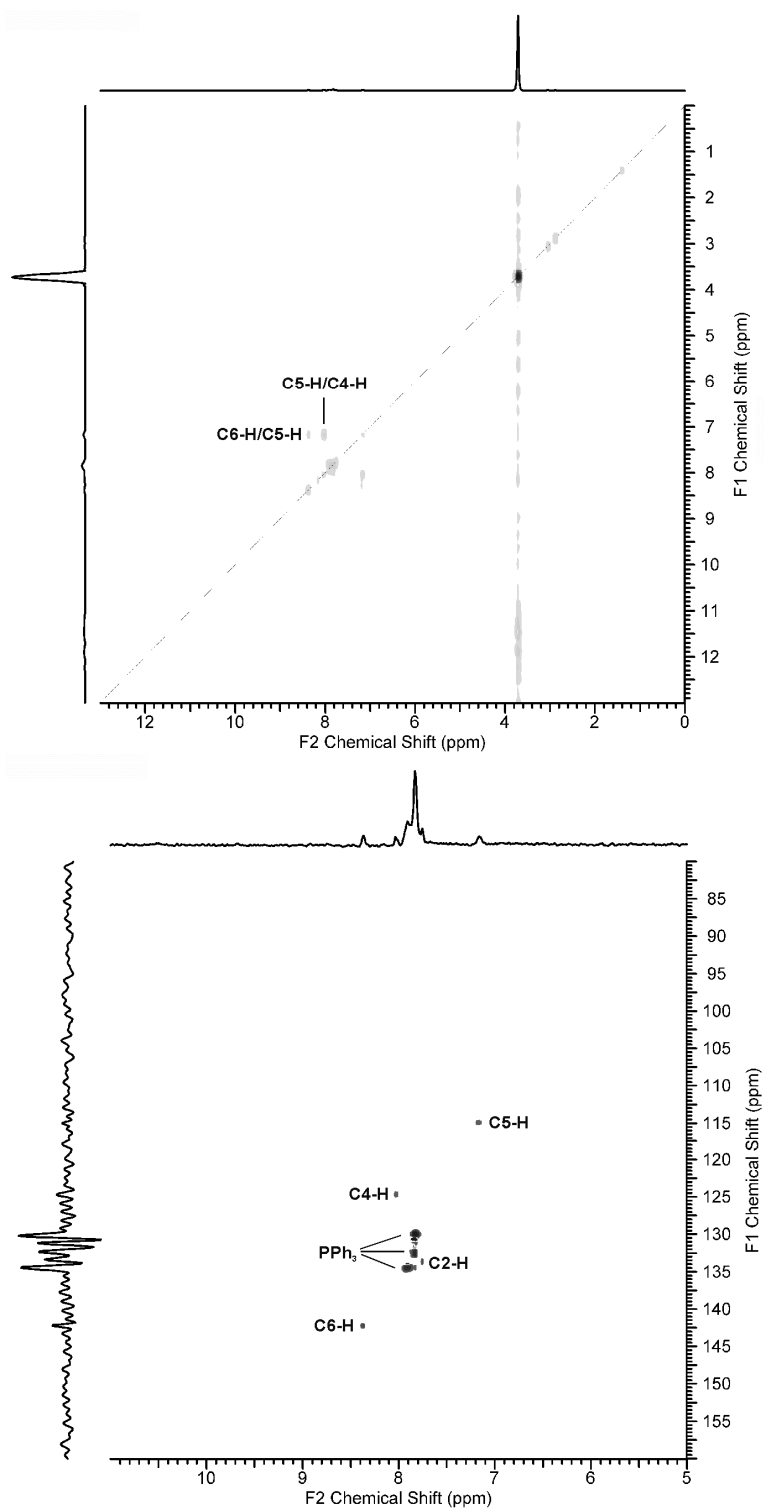


Figure S2. ^1H - ^1H gsCOSY (top) and ^1H - ^{13}C gsHMQC (bottom) spectra of the representative complex $[\text{Au}(\text{3ClBraza})(\text{PPh}_3)]$ (2).

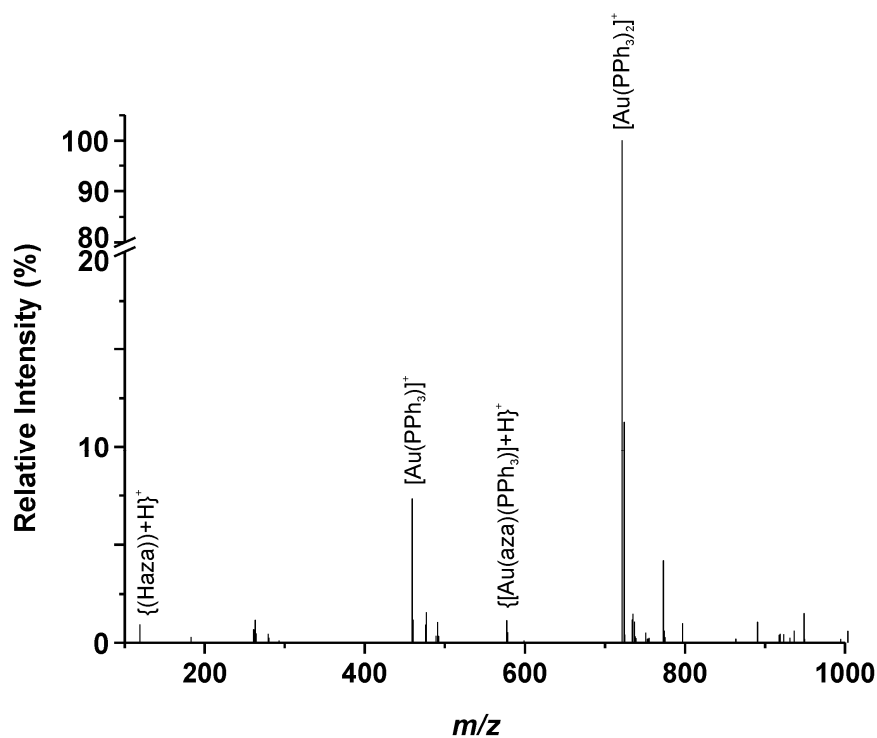


Figure S3. ESI+ mass spectrum of the representative complex $[\text{Au}(\text{aza})(\text{PPh}_3)]$ (1).

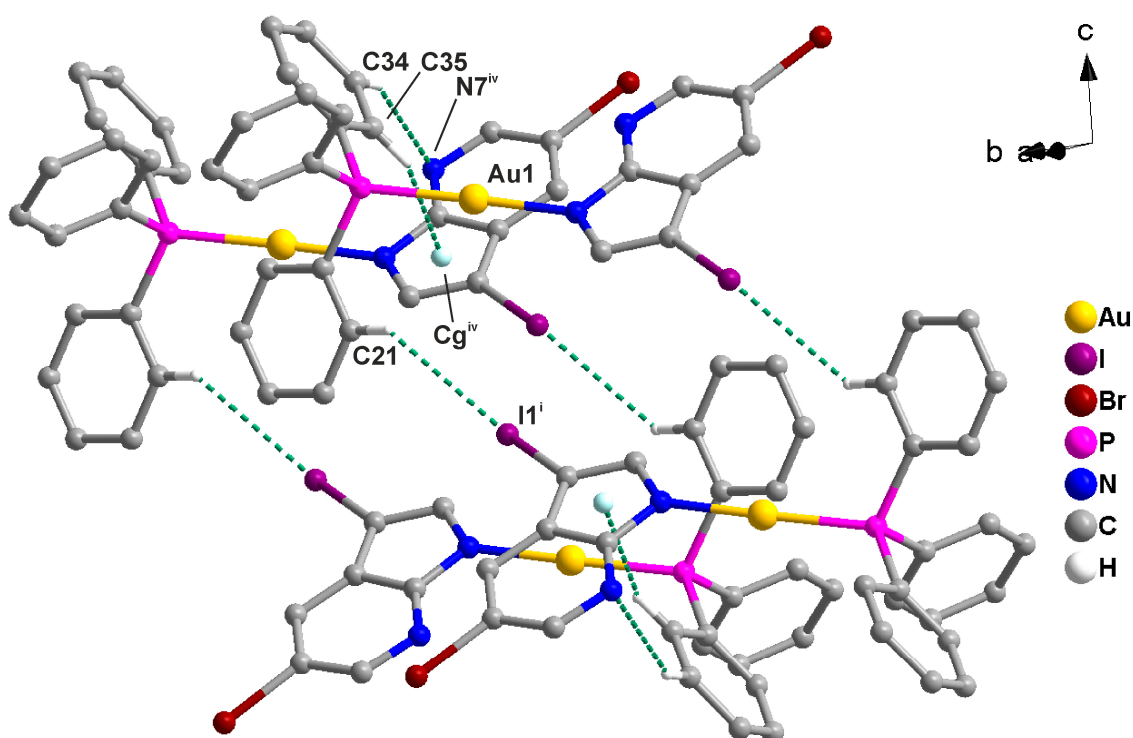


Figure S4. Part of the crystal structure of $[\text{Au}(3\text{I}5\text{Braza})(\text{PPh}_3)]$ (7) with depicted selected C-H $\cdots$ I, C-H $\cdots$ N and C-H $\cdots$ π non-covalent interactions (see Table S1 for parameters) with the hydrogen atoms not involved in the system of non covalent contacts omitted for clarity. Symmetry codes: (i) $-x$, $1-y$, $-z$; (iv) $1+x$, y , z .

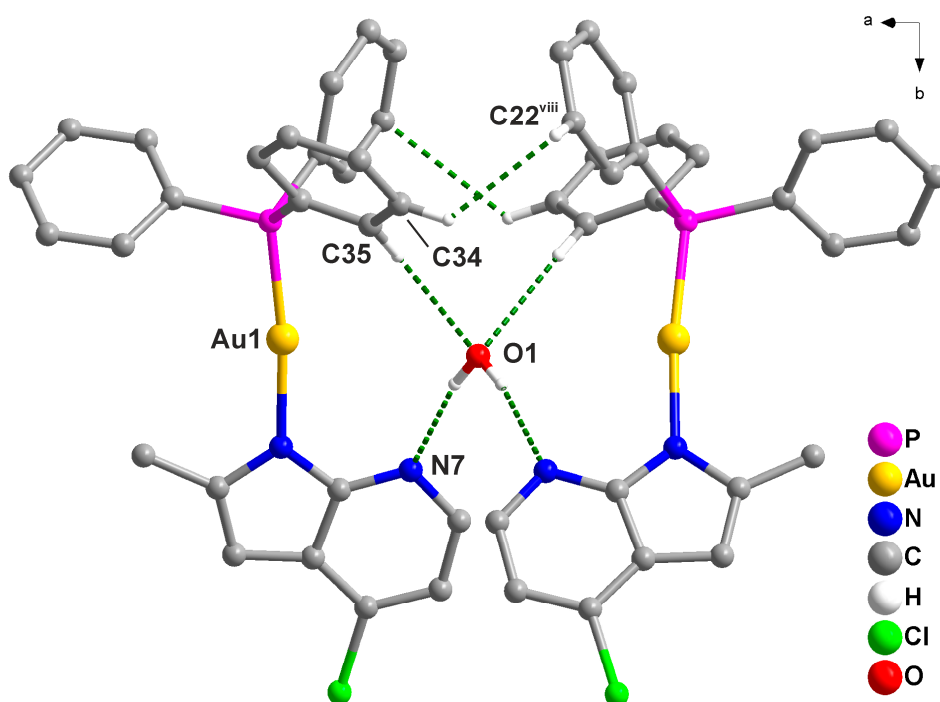


Figure S5. Part of the crystal structure of $[\text{Au}(\text{2CH}_3\text{4Claza})(\text{PPh}_3)] \cdot \frac{1}{2}\text{H}_2\text{O}$ (**8'**) with depicted selected O–H $\cdots$ N, C–H $\cdots$ O and C–H $\cdots$ C non-covalent interactions (see Table S1 for parameters) with the hydrogen atoms not involved in the system of non covalent contacts omitted for clarity. Symmetry codes: viii) $1 - x, y, 0.5 - z$.

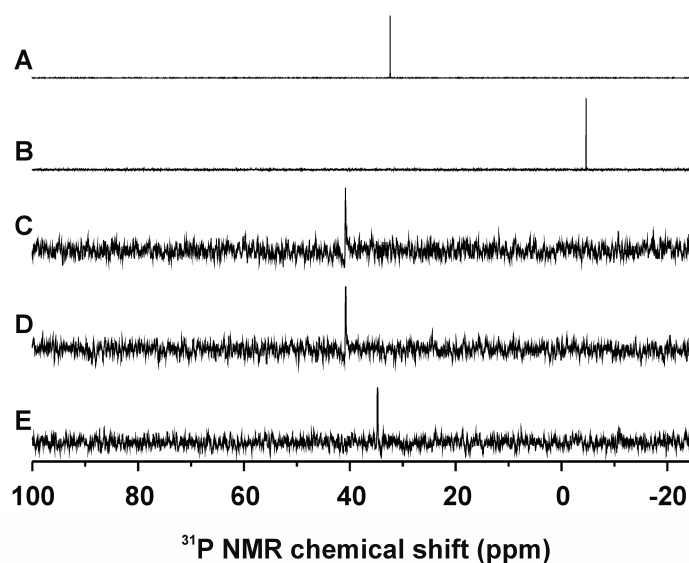


Figure S6. The results of ^{31}P -NMR spectroscopy performed for oxidized triphenylphosphane (O = PPh_3 ; **A**), triphenylphosphane (PPh_3 ; **B**), the mixture of complex **8** and **1** (**C**) or **5** (**D**) mol equiv of reduced glutathione (GSH), and complex **8** (**E**). The samples were dissolved in the 50% $\text{DMF-}d_7$ /50% D_2O mixture.

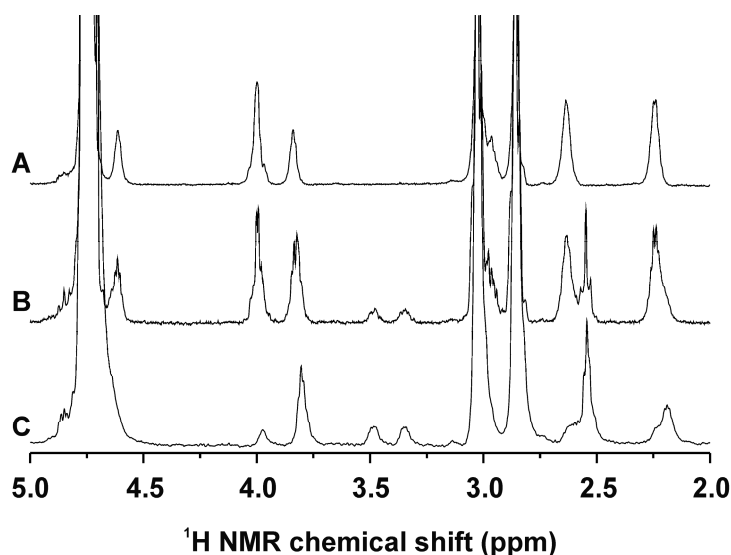


Figure S7. (A) ^1H -NMR spectrum of reduced glutathione (GSH); (B) the ^1H -NMR spectroscopy results of the interaction experiment of complex 8 and 5 mol equiv of GSH; (C) the ^1H -NMR spectroscopy results of the interaction experiment of complex 8 and 1 mol equiv of GSH. The samples were dissolved in the 50% $\text{DMF-}d_7$ /50% D_2O mixture.

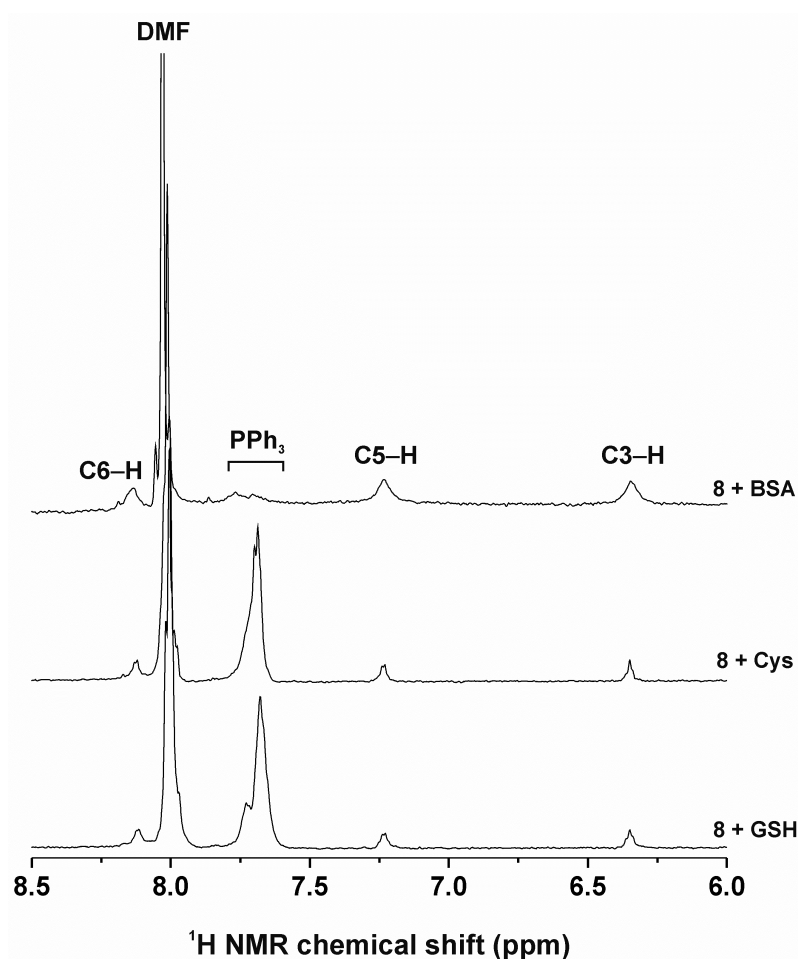


Figure S8. ^1H -NMR spectra of the equimolar mixtures of the representative complex 8 with reduced glutathione (8 + GSH), cysteine (8 + Cys) and bovine serum albumin (8 + BSA). The samples were dissolved in the 50% $\text{DMF-}d_7$ /50% D_2O mixture.