Chloride binding properties of a macrocyclic receptor with an acetylide gold(I) complex: synthesis, characterization and cytotoxicity studies.

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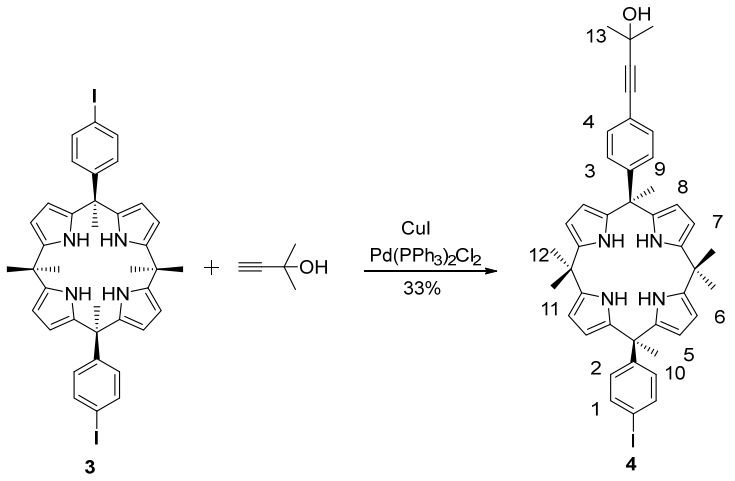
Supporting information

1. Synthesis and characterization data

1.1 Mono-alcohol-mono-iodo calix[4]pyrrole 4



Scheme S 1. *Synthesis of compound* ***4****.*

In a 10 mL Schlenk flask, 10α,20α-bis(4-iodophenyl)calix[4]pyrrole (**3**) (50 mg, 0.062 mmol, 1 equiv.), CuI (0.6 mg, 0.003 mmol, 0.05 equiv.) and $Pd(PPh_3)_2Cl_2$ (2.2 mg, 0.003 mmol, 0.05 equiv.) were dissolved in 5 mL of toluene under Ar atmosphere. Afterwards, triethylamine (0.82 mL, 0.31 mmol, 5 equiv.) and 2-methyl-3-butyn-2-ol (0.03 mL, 0.311 mmol, 5 equiv.) were added. The reaction mixture was stirred for 6 hours at room temperature. Then DCM (5 mL) was added to the reaction mixture and was washed with 0.5 M HCl (10 mL×1) and water (10 mL×2). The collected organic layer was dried with sodium sulfate, filtered and concentrated under vacuum to obtain a brown solid. The product was purified through silica column chromatography using a 9:1 DCM:Hexane mixture as eluent (Rf = 0.25). The product was obtained as a dark orange solid (yield = 33%).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm) H1 (d, 7.54 ppm, 2H, *J*= 8.79 Hz), H4 (d, 7.28 ppm, 2H, *J*= 8.45 Hz), NH (br, 7.20 ppm 4H), H3 (d, 6.90 ppm, 2H, *J*= 8.45 Hz), H2 (d, 6.72 ppm, 2H, *J*= 8.79 Hz), H6; H7 (t, 5.92 ppm, 4H), H5; H8 (m, 5.61 ppm, 4H), H10 (s, 1.87 ppm, 3H), H9 (s, 1.85 ppm,3H), H11 (s, 1.61 ppm, 6H), H13 (s, 1.59 ppm,6H), H12 (s, 1.52 ppm,6H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm) 148.36, 147.97, 138.69 (d, *J*= 14.79 Hz), 136.86, 136.19 (d, *J*= 39.63), 131.12, 129.71, 127.50, 120.89, 106.23, 106.17, 103.44, 103.41, 93.70, 92.09, 82.18, 65.78, 44.79, 44.64, 35.27, 31.66, 30.14, 27.97, 27.81, 27.71. M.p. = 170 ºC. FTIR (ATR): $\bar{\upsilon}_{max}$ (cm^{-1}) = 3419 (s), 2969 (s), 2924 (m), 1573 (m), 1218 (m), 766 (m). HRMS (ESI/ TOF) m/z: $[M-H]^-$ = $[C_{43}H_{44}IN_4O]^-$ Calcd 759.2565; Found 759.2564.

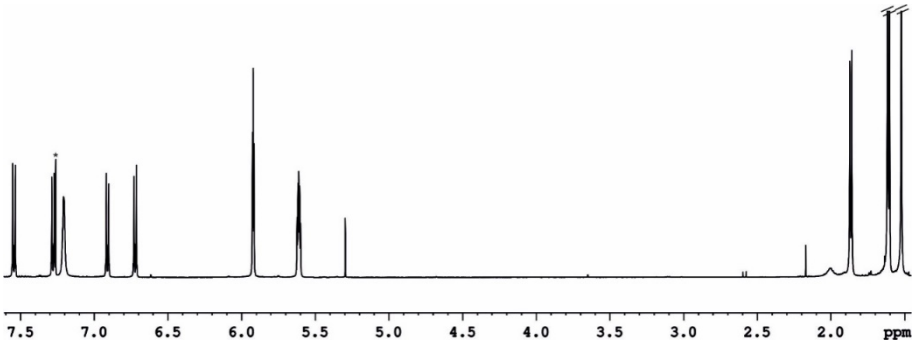


Figure S 1: *^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of* ***4****.*

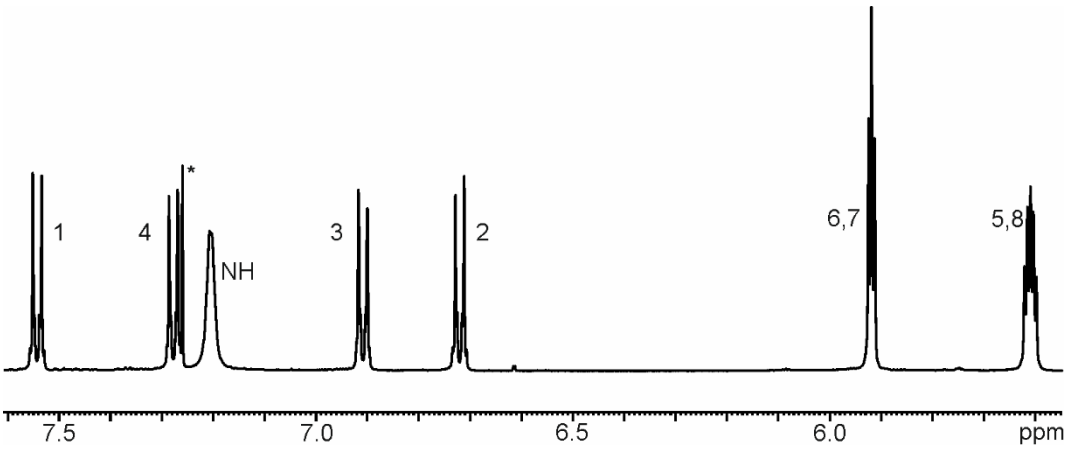


Figure S 2: *Selected downfield region of the ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of* ***4****. See scheme S1 for proton assignment. *Solvent residual peak.*

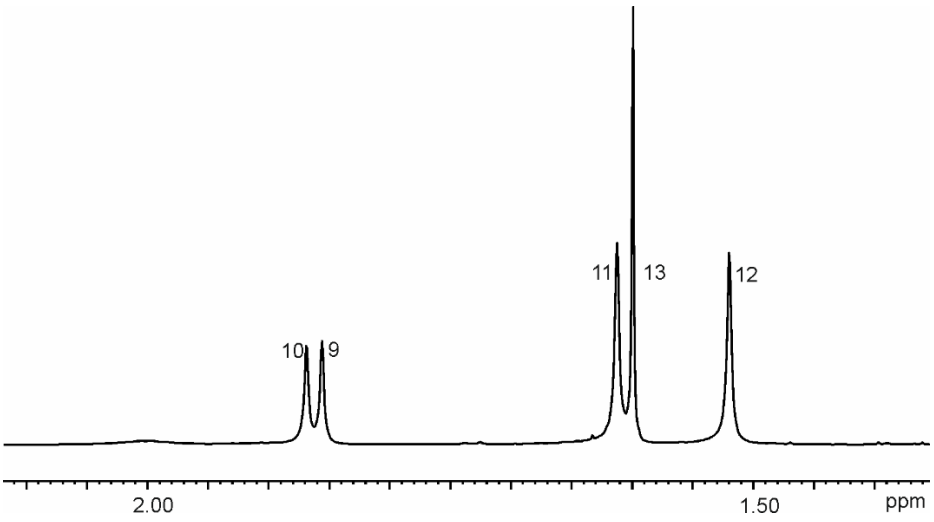


Figure S 3*: Selected upfield region of the ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of* ***4****. See scheme S1 for proton assignment. *Solvent residual peak.*

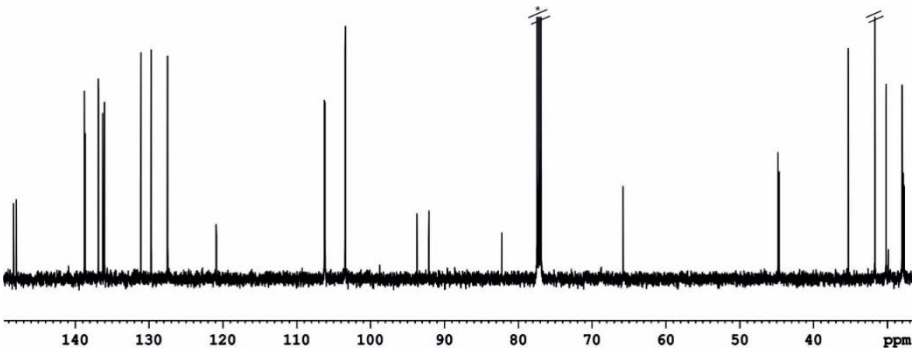


Figure S 4: *^{13}C NMR (125 MHz, $CDCl_3$, 298 K) spectrum of* ***4****.*

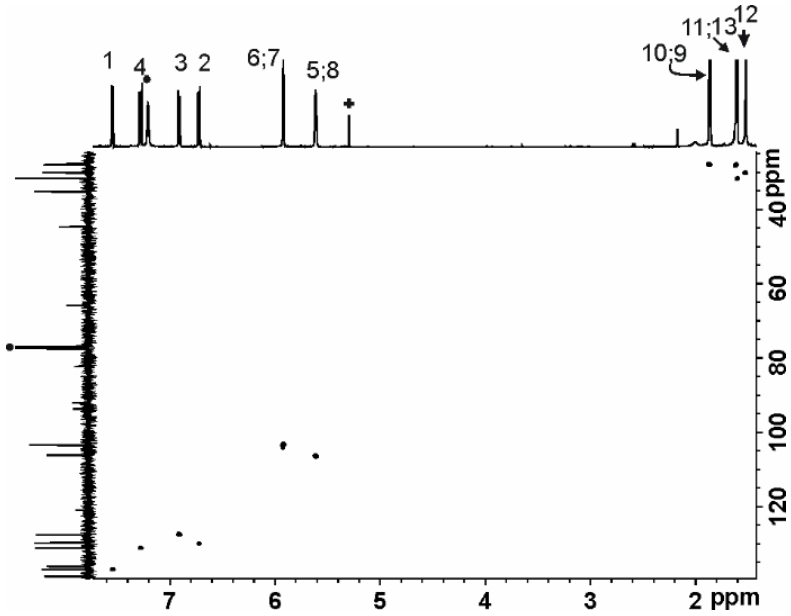


Figure S 5: *2D ^{1}H-^{13}C HSQC NMR ($CDCl_3$, 298 K) spectrum of* ***4.*** *See scheme S1 for proton assignment. *Solvent residual peak.*

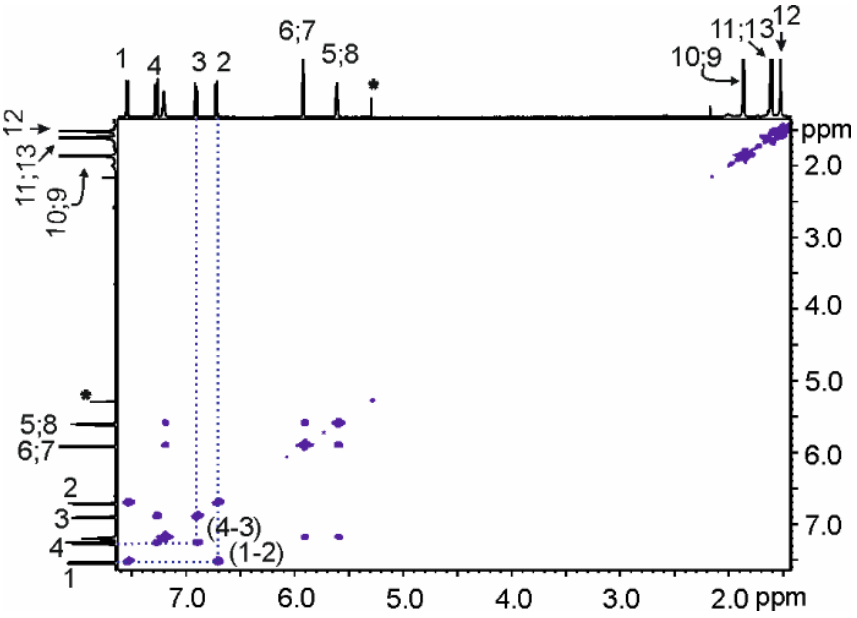
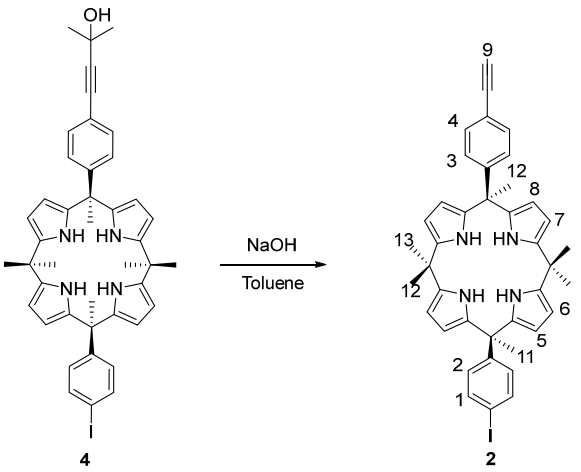


Figure S 6: *2D 1H-1H COSY NMR (500 MHz, $CDCl_3$, 298 K) spectrum of* ***4.*** *See scheme S1 for proton assignment. *Solvent residual peak.*

1.2 *meso*-10α,20α-*p*-ethynylphenyl-*p*-iodophenyl calix[4]pyrrole 2



Scheme S 2. *Synthesis of compound* ***2.***

Compound **4** (52 mg, 0.07 mmol, 1 equiv.) was dissolved in 6.5 mL of dry toluene in a 10 mL round bottom flask. Then, powdered sodium hydroxide (56 mg, 1.2 mmol, 20 equiv.) was added to the solution. The orange mixture was stirred at 90 ºC for 12 h under Ar atmosphere. The reaction mixture was concentrated and washed with DCM (5mL×2). The combined organic phase was washed with 0.5 M HCl (5mL×1) and water (10 mL×2). The collected organic phase was dried with Na_2SO_4, filtered and concentrated under vacuum to give a brown solid as the pure product (34 mg) (70% yield).

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ (ppm) H1 (d, 7.55 ppm, 2H, *J*= 8.48 Hz), H4 (d, 7.35 ppm, 2H, *J*= 8.44 Hz,), NH (br, 7.27 ppm, 4H), H3 (d, 6.92 ppm, 2H, *J*= 8.44 Hz), H2 (d, 6.71 ppm, 2H, *J*= 8.48 Hz), H6; H7 (t, 5.92 ppm, 4H), H5; H8 (q, 5.62 ppm, 4H), H9 (s, 3.08 ppm, 1H), H10 (s, 1.86 ppm, 3H), H11 (s, 1.85 ppm, 3H), H12 (s, 1.62 ppm, 6H), H13 (s, 1.51 ppm, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) δ (ppm) 149.49, 148.48, 139.12 (d, *J*= 6.50 Hz), 137.09, 136.33 (d, *J*= 12 Hz), 131.78, 130.04, 127.89, 120.44, 106.47, 103.65, 92.09, 83.83, 77.17, 45.10, 44.92, 35.40, 30.39, 27.63, 27.54, 27.23. M.P. =273.3 ºC. FTIR (ATR): $\bar{\upsilon}_{max}$ (cm^{-1}) = 3419 (s), 3282 (m), 2967 (m), 2924 (m),1573 (m), 2119 (m), 769 (m). HRMS (ESI/ TOF) m/z: [M -H]$^-$= $[C_{40}H_{38}IN_4]^-$ Calcd 701.2146; Found 701.2153.

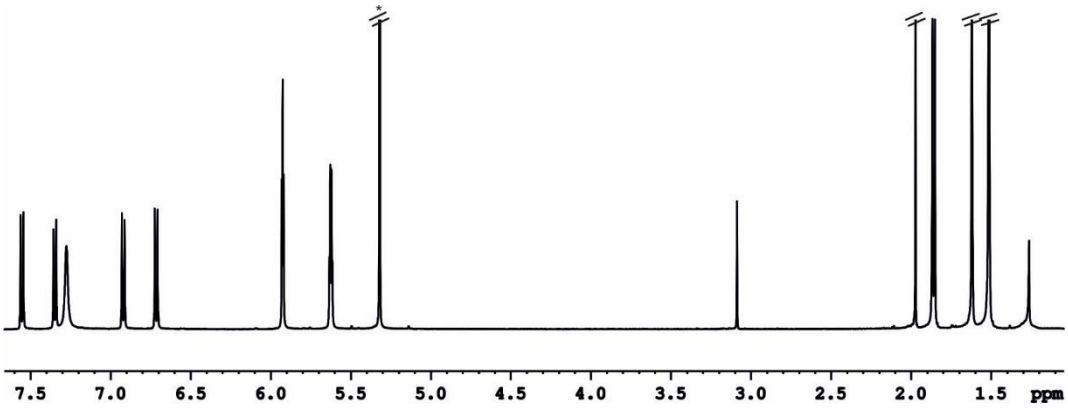


Figure S 7: *^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of* ***2.*** **Solvent residual peak.*

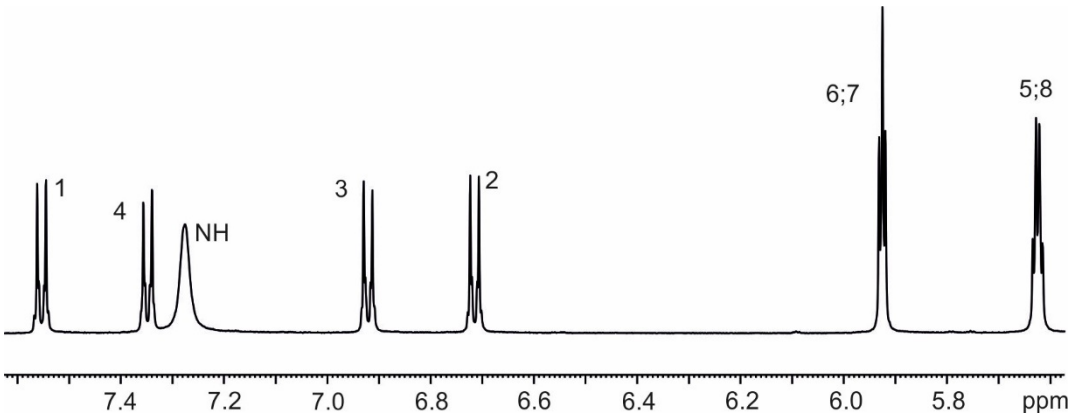


Figure S 8: *Selected downfield region of the ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of* ***2****. See scheme S2 for proton assignment. *Solvent residual peak.*

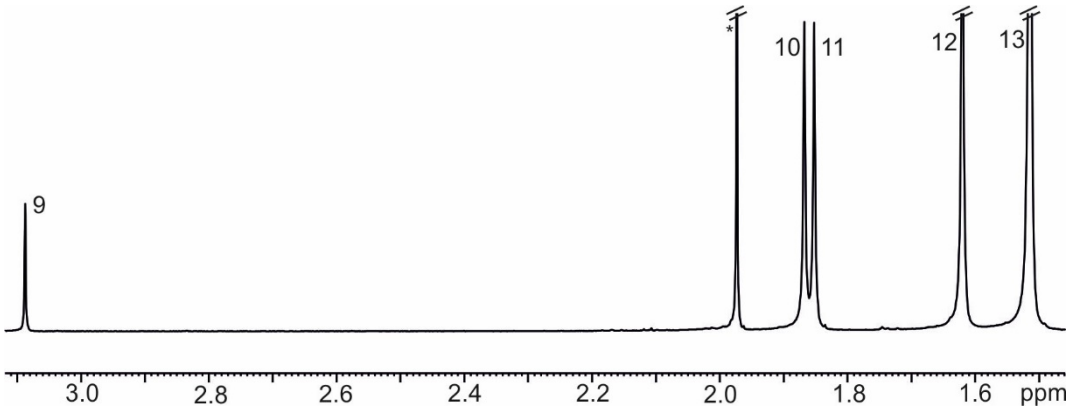


Figure S 9: *Selected upfield region of the ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of* ***2****. See scheme S2 for proton assignment. *Solvent residual peak*

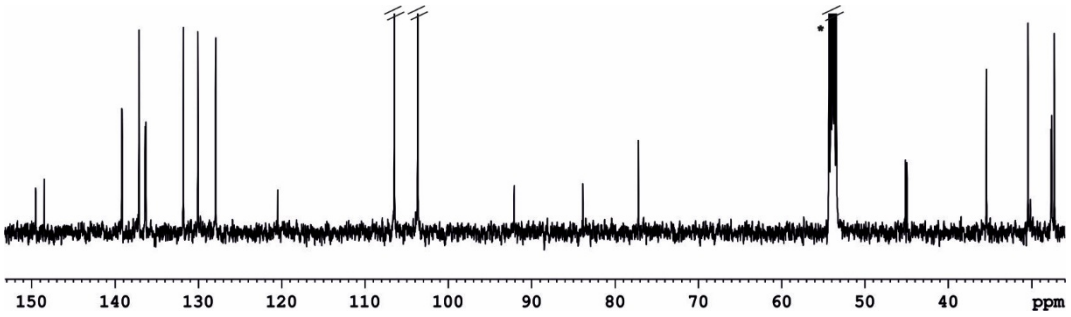


Figure S 10: *^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) spectrum of* ***2****. *Solvent residual peak.*

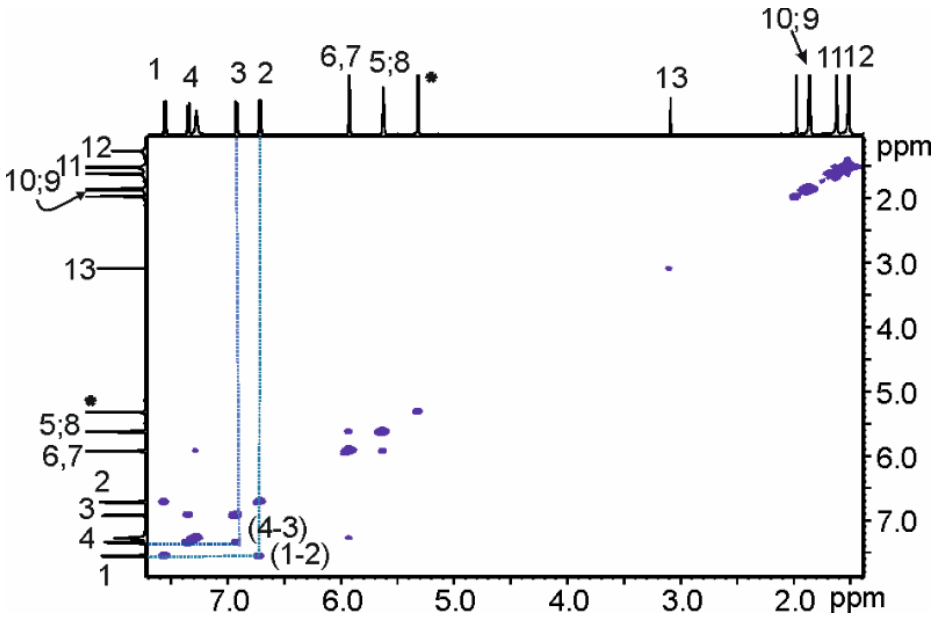


Figure S 11: *2D ^{1}H-^{1}H COSY NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of* ***2****. Some selected COSY cross-peaks are indicated. See scheme S2 for proton assignment. *Solvent residual peak*

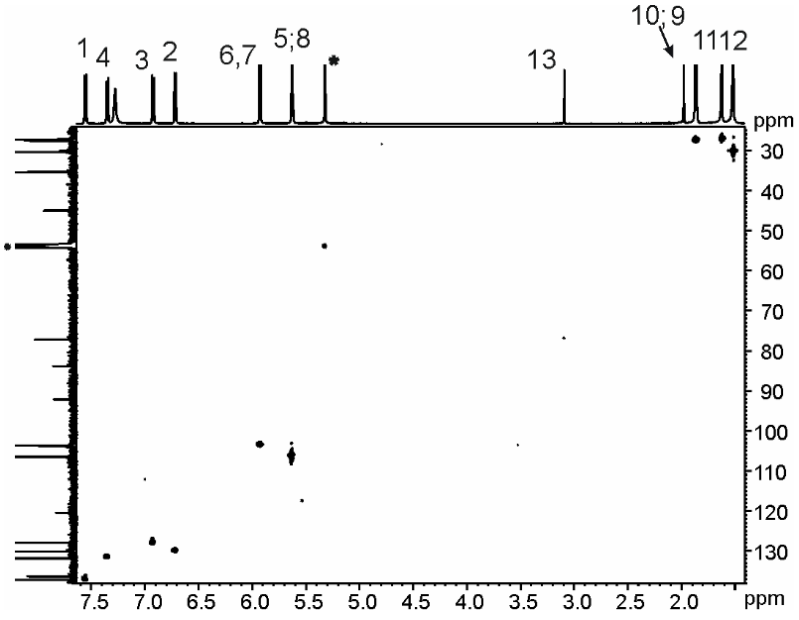


Figure S 12: *2D ^{1}H-^{13}C HSQC NMR (CD_2Cl_2, 298 K) spectrum of* ***2.*** *See scheme S2 for proton assignment. *Solvent residual peak.*

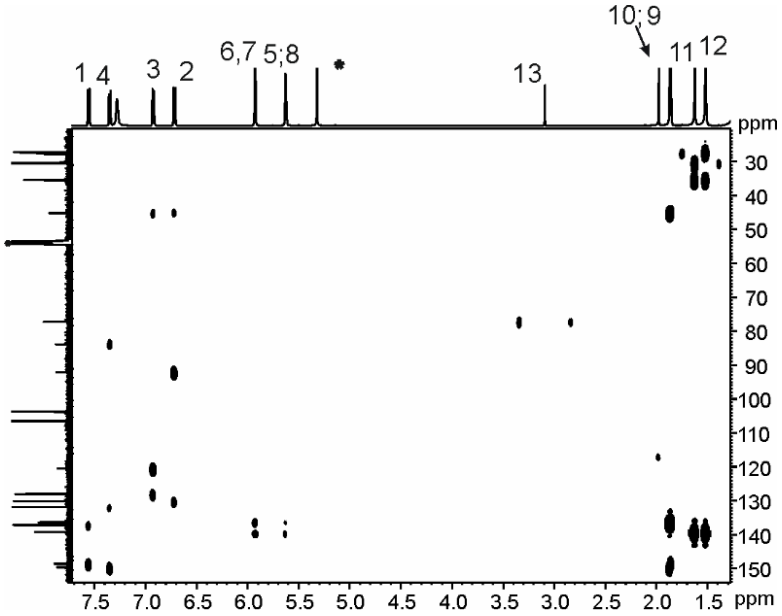
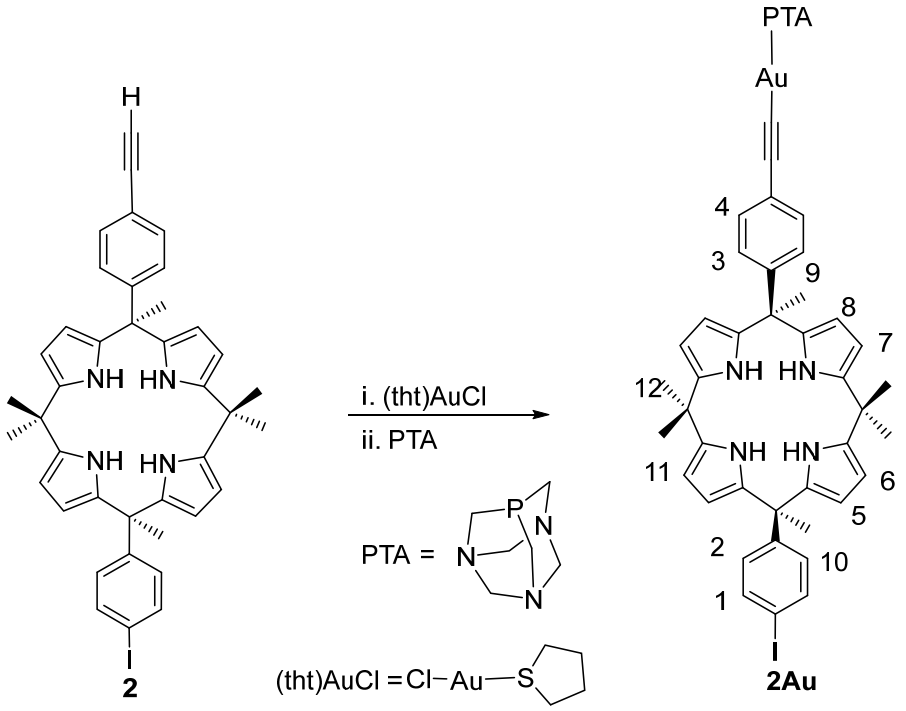


Figure S 13: *2D ^{1}H-^{13}C HMBC NMR (CD_2Cl_2, 298 K) of* ***2****. See scheme S3 for proton assignment. *Solvent residual peak.*

1.3 Gold(I)-phosphine substituted "two-wall" calix[4]pyrrole (2Au)



Scheme S 3. *Synthesis of compound* ***2Au****.*

In a 2 mL solution of **2** (50 mg, 0.071 mmol, 1 equiv.) in DCM, we added (tht)AuCl (25 mg, 0.078 mmol, 1.1 equiv.) dissolved in 1 mL of DCM and triethylamine (TEA) (0.028ml, 0.210 mmol, 3

equiv.). The reaction mixture was stirred under Ar atmosphere for 2 h protected from light. With time it shows the formation of a black precipitate. The suspension was centrifuged and the supernatant was separated from the black solid. The supernatant solution was reduced to ~1 mL under vacuum. Next, we added 2 mL of MeOH to induce the precipitation of the oligomeric gold(I) acetylide **5** as a yellow solid. The yellow solid was washed with a small amount of diethyl ether (10 mL) (35.4 mg of **5**). This solid was used immediately without purification. The oligomeric gold(I) acetylide **5** (35.4 mg, 1 equiv.) was suspended in 5 mL of DCM and we added 6.2 mg of 1,3,5-triaza-7-phosphaadamantane (PTA). The suspension (with black solid) was stirred for 5h under Ar atmosphere and protected from the light. After 5h the suspension was centrifuged and the supernatant was reduced to ~2 ml under vacuum. Finally, the addition of MeOH (7 mL) yields the pure mono-nuclear gold(I) complex **2Au** in 58% yield.

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ (ppm) H^1 (d, 7.55 ppm, 2H, *J*= 8.58 Hz), NH (br, 7.36 ppm, 4H), H^4 (d, 7.19 ppm, 2H, *J*= 8.44 Hz,), H^3 (d, 6.8 ppm, 2H, *J*= 8.44 Hz), H^2 (d, 6.71 ppm, 2H, *J*= 8.85 Hz), H^6; H^7 (m, 5.92 ppm, 4H), H^5; H^8 (q, 5.62 ppm, 4H), PTA region (d, 4.54 ppm, 6H, J= 13.13 Hz, d, 4.46 ppm, 6H, J= 13.13 Hz, s, 4.24 ppm, 10 H), H^9 (s, 1.85 ppm, 3H), H^{10} (s, 1.84 ppm, 3H), H^{11} (s, 1.61 ppm, 6H), H^{12} (s, 1.50 ppm, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) δ (ppm) 148.18, 146.84, 138.84, 138.53, 136.31, 165.84, 131.16, 129.60, 127.19, 105.94, 130.13, 91.65, 73.12, 73.20, 52.37, 44.5, 34.96, 30.17, 27.23, 27.17, 26.73. ^{31}P NMR (161 MHz, CD_2Cl_2, 298 K) δ (ppm) -46.77 ppm. M.p> 240 ºC (decompose). FTIR (ATR): $\bar{\upsilon}_{max}$ (cm^{-1}) 2110 cm^{-1} (C≡C) (w). HRMS (ESI/TOF) m/z: 1056.2649 Calcd for $[C_{46}H_{50}AuIN_7P + H]^+$; Found 1056.2635.

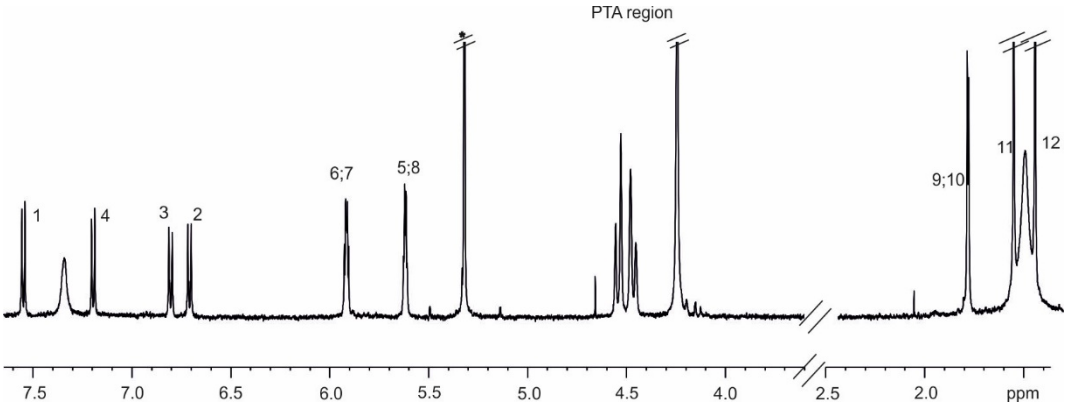


***Figure S 14**: ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of **2Au.** See scheme S3 for proton assignment. *residual solvent peak.*

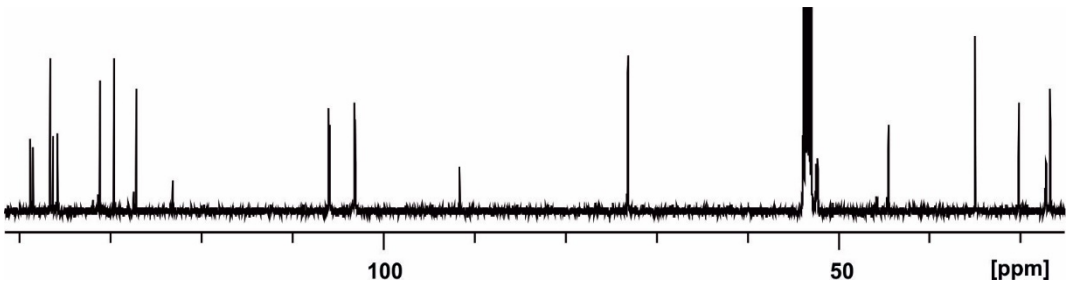


***Figure S 15**: ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K) spectrum of **2Au**.*

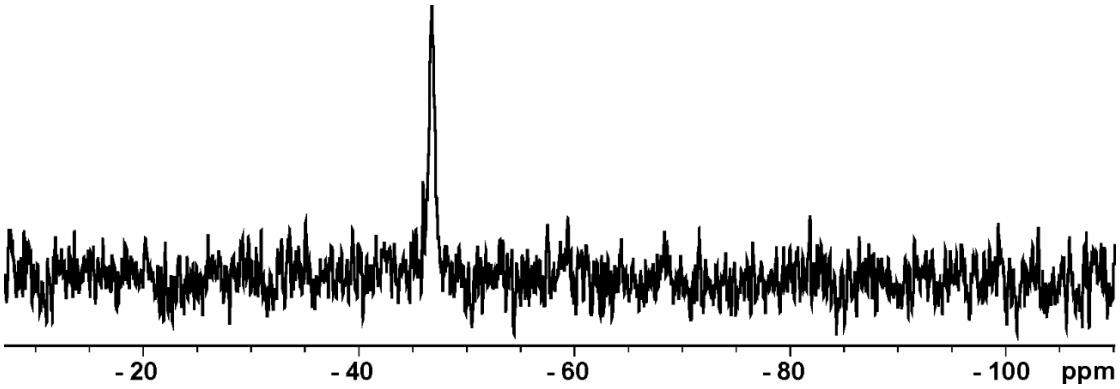


Figure S16: *^{31}P NMR (161 MHz, CD_2Cl_2, 298 K) spectrum of* ***2Au****.*

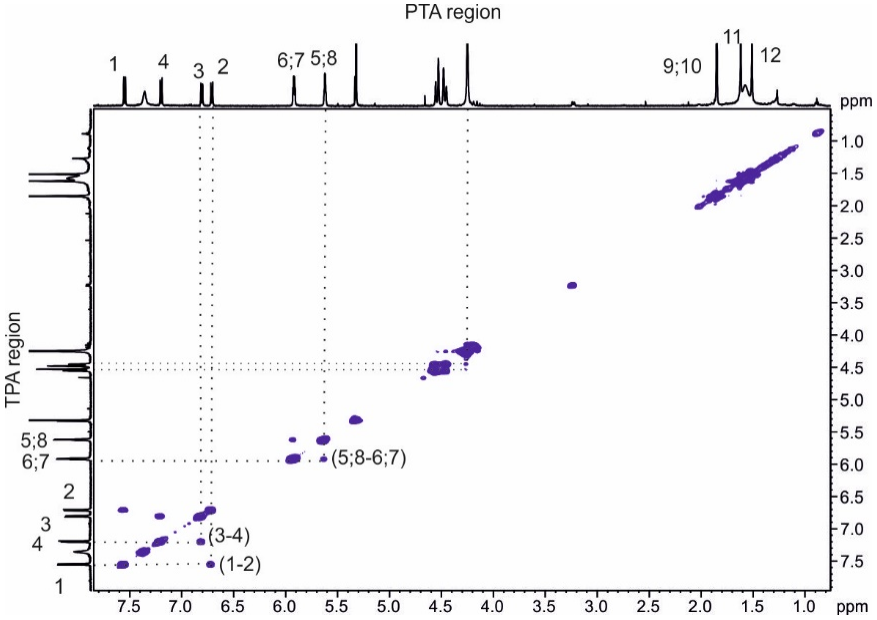


Figure S 17: *2D ^{1}H-^{1}H COSY NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of* ***2Au****. Some selected COSY cross-peaks are indicated. See scheme S3 for proton assignment.*

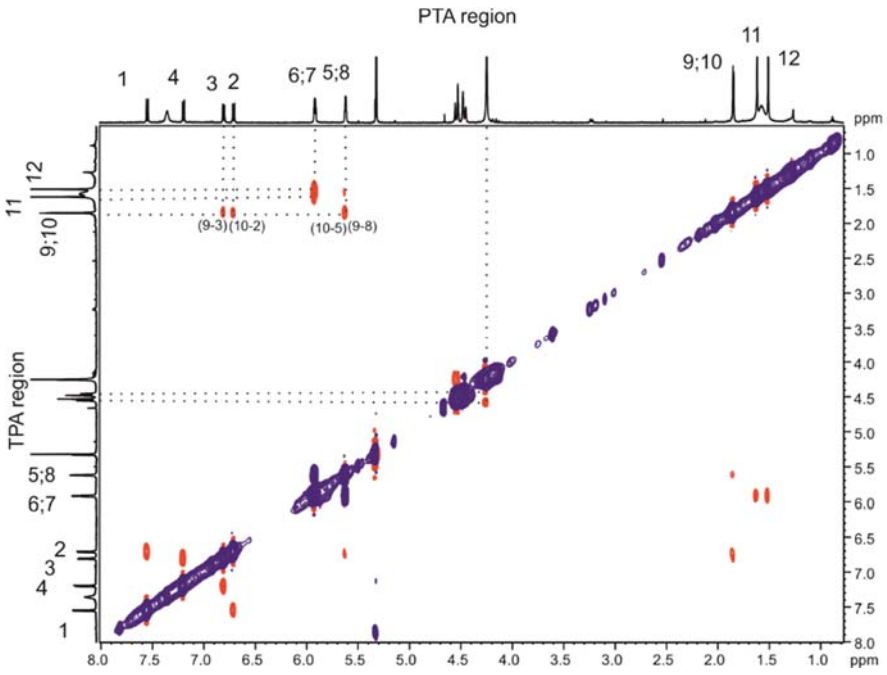
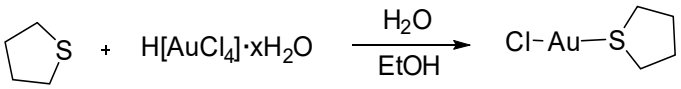


Figure S 18: 2D ^{1}H-^{1}H ROESY NMR (500 MHz, CD_2Cl_2, 298 K, mixing time = 0.3 s) spectrum of **2Au.** Some selected ROESY cross-peaks are indicated. See scheme S3 for proton assignment.

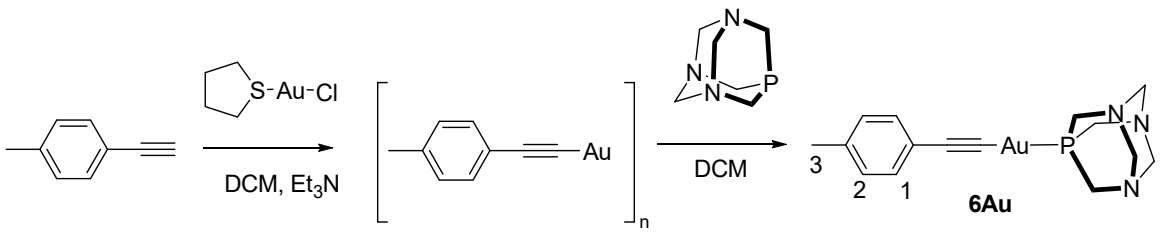
1.4 Preparation of (tht)AuCl



Scheme S 4. Synthesis of **(tht)AuCl**.

To a solution of hydrogen tetracloroaurate (III) (50.9 mg; 0.150 mmol; 1 equiv.) in 0.7 mL of a 5:1 mixture of water:ethanol we added dropwise tetrahydrothiophene (0.022 mL; 0.385 mmol; 2.6 equiv.). We observed the formation of a white precipitate. After the addition, 0.46 mL of ethanol were added and the mixture was stirred to 20 min. The white solid was filtered under vacuum and washed with ethanol. The ^{1}H NMR spectrum was in complete agreement with the one described in the literature[1].

1.5. Preparation of *p*-ethynyl-toluene gold PTA complex 6Au



Scheme S 5. *Synthetic scheme for the preparation of the model p-ethynyl-toluene gold(I) PTA complex* ***6Au****.*

In a 4 mL solution of 4-ethynyl toluene (15 μL, 0.12 mmol, 1 equiv.) in DCM, we added 2 mL of a solution containing (tht)AuCl (38 mg, 0.12 mmol, 1 equiv.) in the same solvent and TEA (47 μL, 0.36 mmol, 3 equiv.). The mixture was stirred for 2 h under Ar atmosphere and protected from the light. Afterwards, the brown suspension was centrifuged to remove a black solid. The supernatant solution was reduced to ~1 ml and 2 mL of MeOH were added to induce the precipitation of a yellowish solid, the oligomeric gold(I) acetylide (21 mg).

The oligomeric gold(I) acetylide was suspended in 4 mL of DCM (21mg) and we added 5.3 mg of PTA (0.067 mmol, 1 equiv.) to the suspension. The suspension was stirred for 5h under Ar atmosphere and protected from the light. After 5h the suspension was centrifuged, and the supernatant was concentrated to a volume of ~2.5 mL. Next, MeOH (7 mL) was added to induce the precipitation of compound **6Au** as a yellow solid. ^{1}H NMR (500 MHz, acetone-d_6, 298 K) δ (ppm) H^1 (d, 7.21 ppm, 2H, *J*= 8.2 Hz), H^2 (d, 7.06 ppm, 2H, *J*= 8.2 Hz), TPA region (d, 4.66 ppm, 3H, J= 12.8 Hz, d, 4.5 ppm, 3H, J= 12.8 Hz, s, 4.42 ppm, 6 H), H^3 (s, 2.29 ppm, 3H). ^{13}C NMR (125 MHz, acetone-d_6, 298 K) δ (ppm) 135.87, 131.49, 128.69, 123.30, 102.43, 72.62 ($J_{C\text{-}N}$= 7.32 Hz), 51.54 ($J_{C\text{-}P}$= 19.43 Hz), 20,41. ^{31}P NMR (161 MHz, acetone-d_6, 298 K) δ (ppm) -46.26 ppm. FTIR (ATR): $\bar{\upsilon}_{max}$ (cm^{-1}) 2111 cm^{-1} (C≡C) (w). HRMS (ESI/TOF) m/z: 470.1075 Calcd for [$C_{15}H_{19}AuN_3P$ + H]$^+$; Found 470.1053.

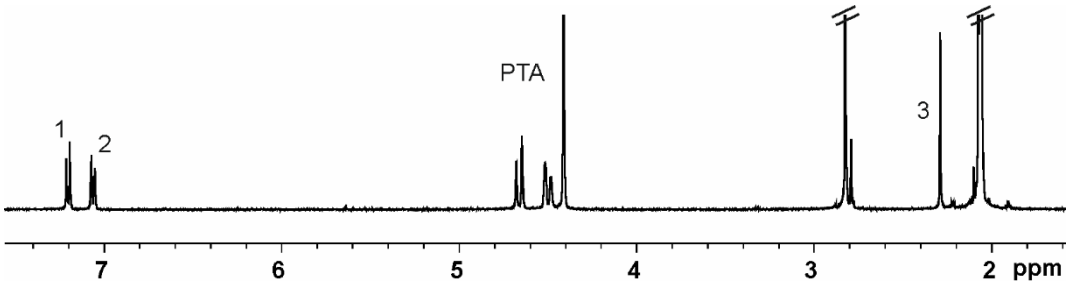


Figure S 19: *^{1}H NMR (500 MHz, acetone-d_6, 298 K) spectrum of* ***6Au.***

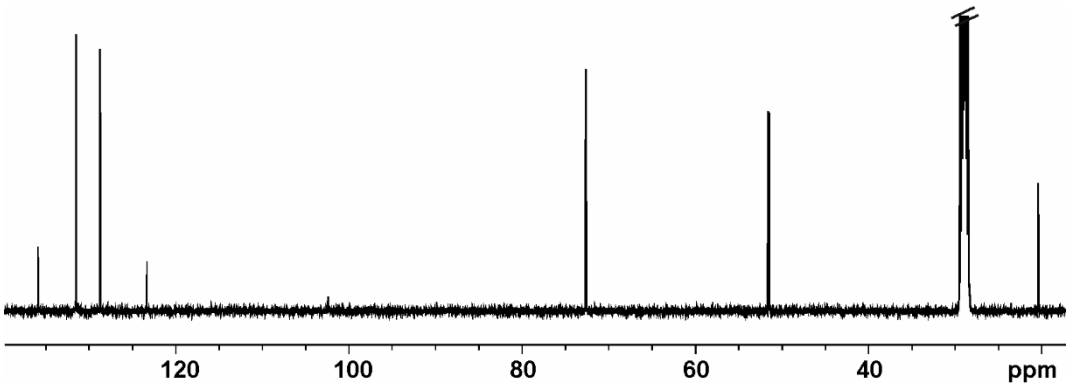


Figure S 20: *^{13}C NMR (125 MHz, acetone-d_6, 298 K) spectrum of* ***6Au****.*

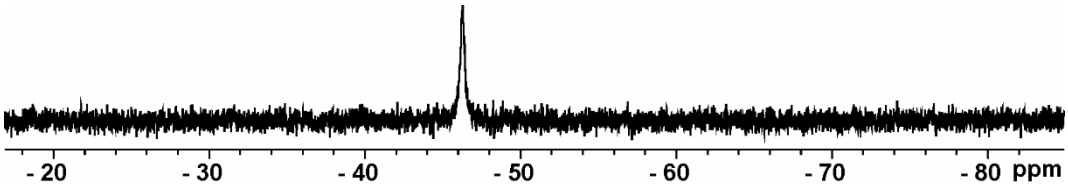
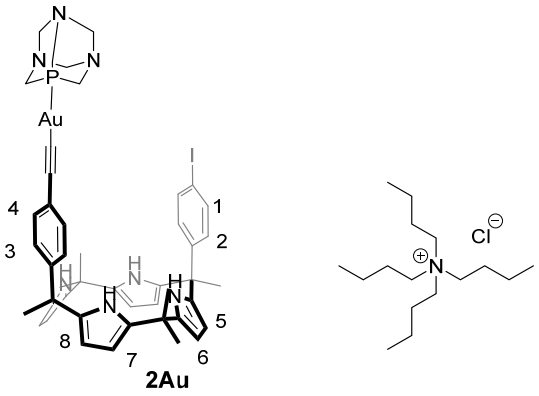


Figure S 21: *^{31}P NMR (161 MHz, acetone-d_6, 298 K) spectrum of* ***6Au****.*

2. ^{1}H NMR binding studies

2.1. ^{1}H NMR titrations in DCM

2Au vs ***TBACl***



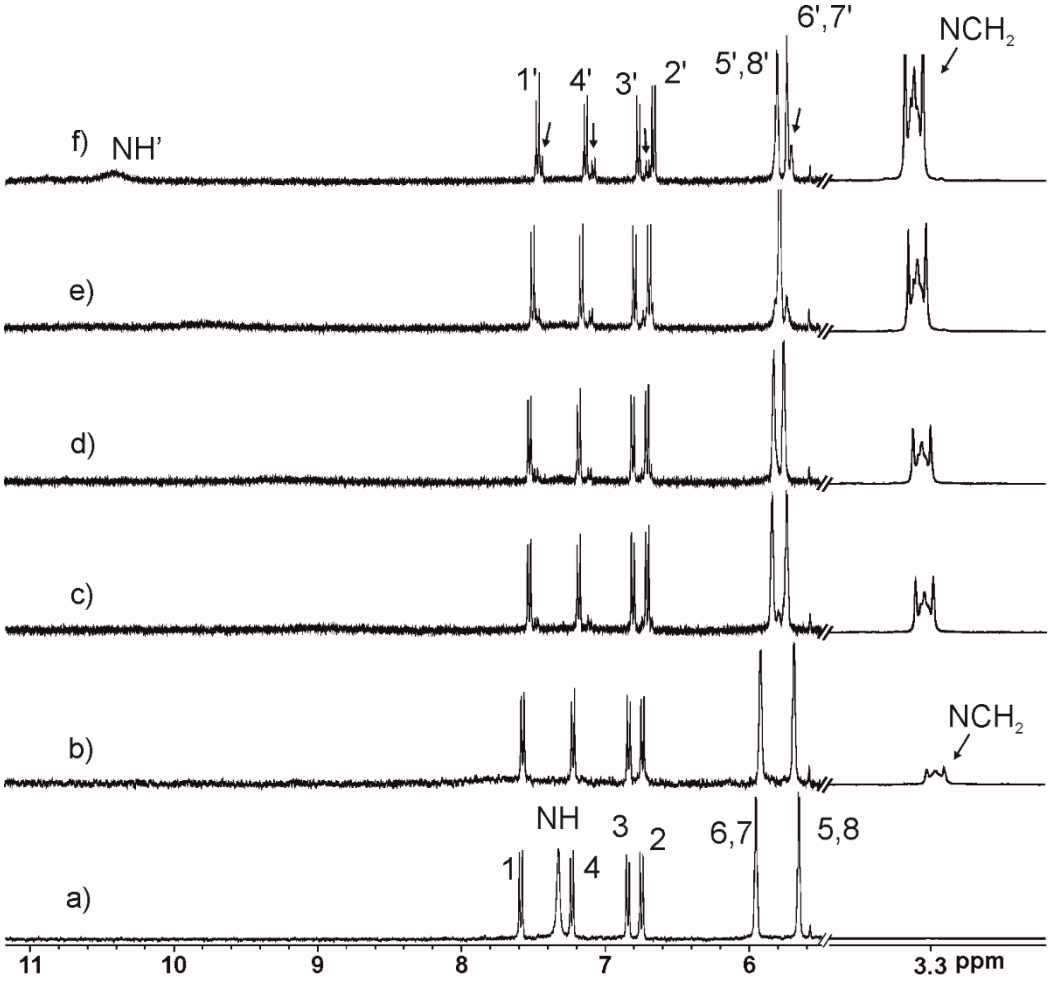


Figure S 22: *Selected regions of the ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) acquired during the titration of the mono-nuclear* ***2Au*** *calix[4]pyrrole receptor ([**2Au**]=1.9 mM) with TBACl: a) 0 b) 1 c) 5.4 d) 10.5 e) 21 and f) 27 equiv. added. See top panel for proton assignment. The scale of the downfield region is increased 16 times with respect to the upfield one in order to show the presence of the second set of aromatic proton signals.*

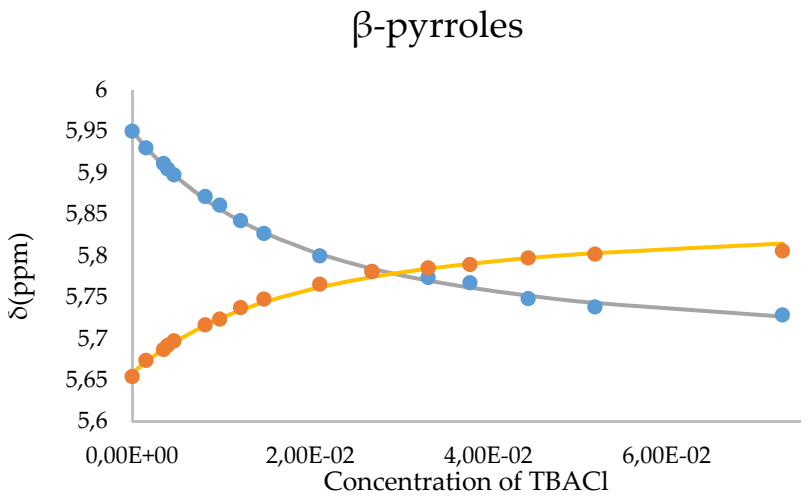


Figure S 23: *Chemical shifts of the β-pyrroles protons of* ***2Au*** *upon incremental amounts of TBACl and fit of the NMR titration data to a theoretical 1:1 binding model.*

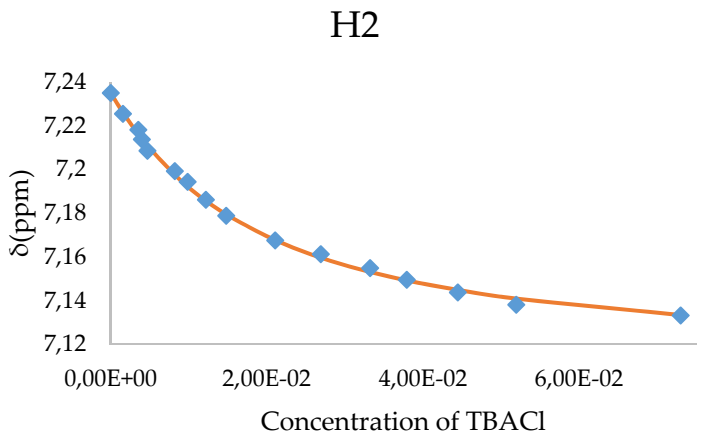


Figure S 24: *Chemical shifts of aromatic protons H2 of* ***2Au*** *upon incremental amounts of TBACl and fit of the NMR titration data to a theoretical 1:1 binding model.*

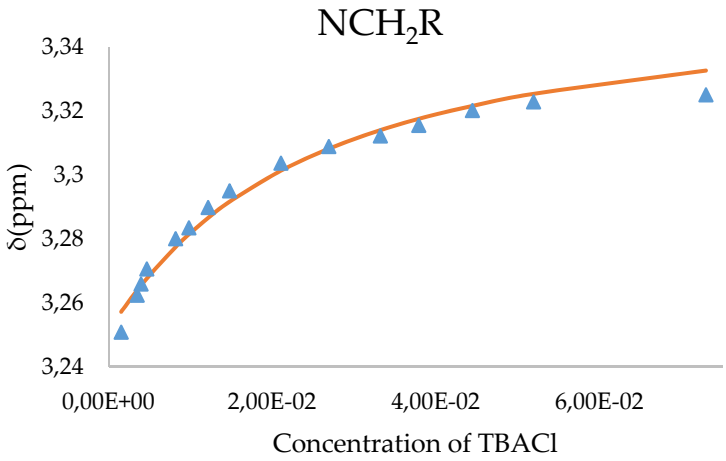


Figure S 25: *Chemical shifts of the CH_2 protons α to the nitrogen of TBA^+ cation upon incremental amounts of TBACl and fit of the NMR titration data to a theoretical 1:1 binding model.*

Table S 1: *Table of induced chemical shifts of the titration of* ***2Au*** *with* ***TBACl****.*

	H1	**H2**	**β-pyrroles H6 and H7**	**β-pyrroles H5 and H8**	**NCH_2**	**NH**
δ_{free}	7.58	7.23	5.96	5.66	2.91	7.42
δ_{bound}	7.44	7.11	5.67	5.85	3.36	10.52
Δδ	-0.14	-0.12	-0.29	+0.19	-0.45	3.1

2 vs **TBA·Cl**

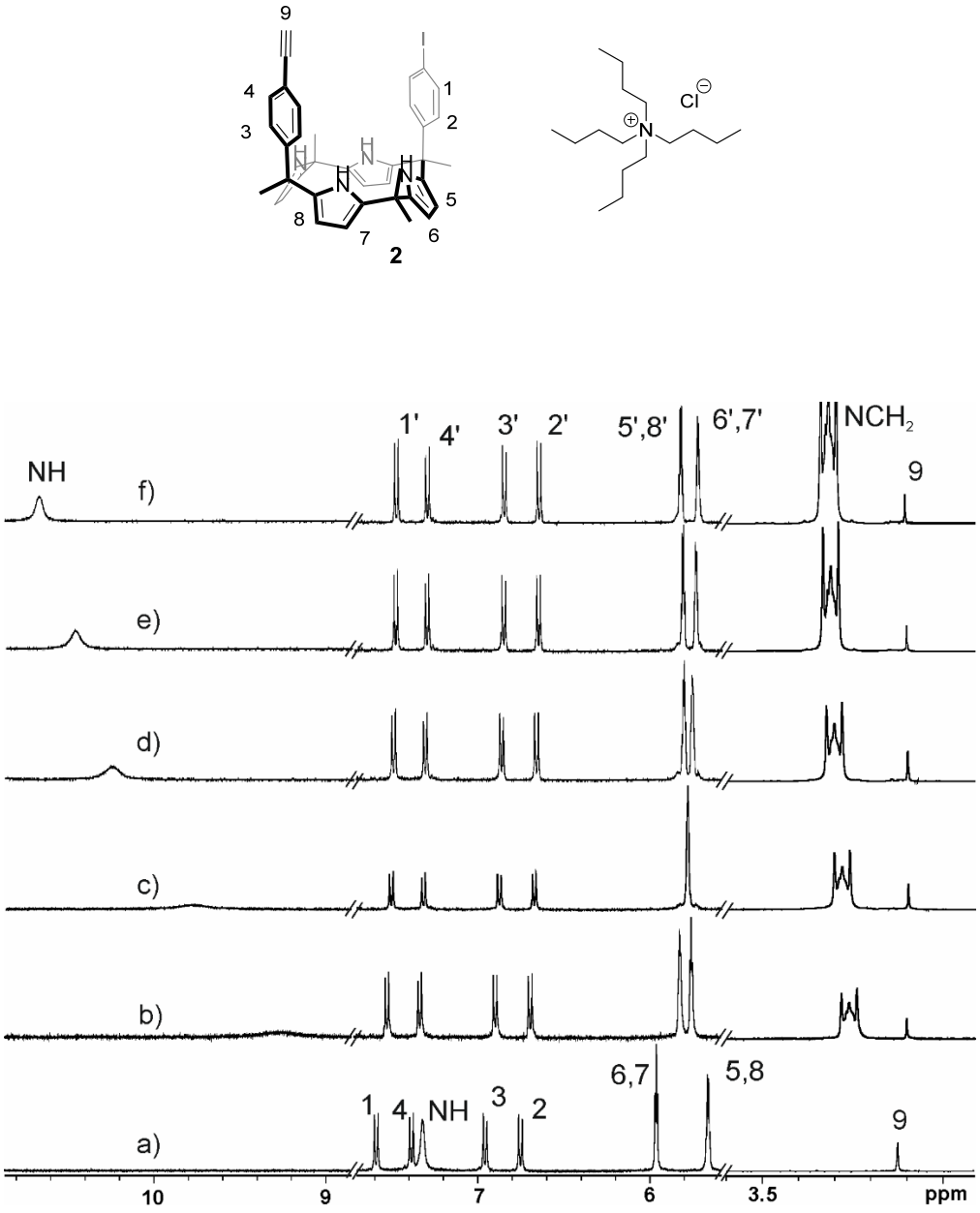


Figure S 26: *Selected regions of the ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of* **2** *(5 mM) (a) with incremental amounts of TBACl b) 2 equiv.; c) 3 equiv.; d) 5 equiv.; e) 7.5 equiv. and f) 11.5 equiv. See top panel for proton assignment.*

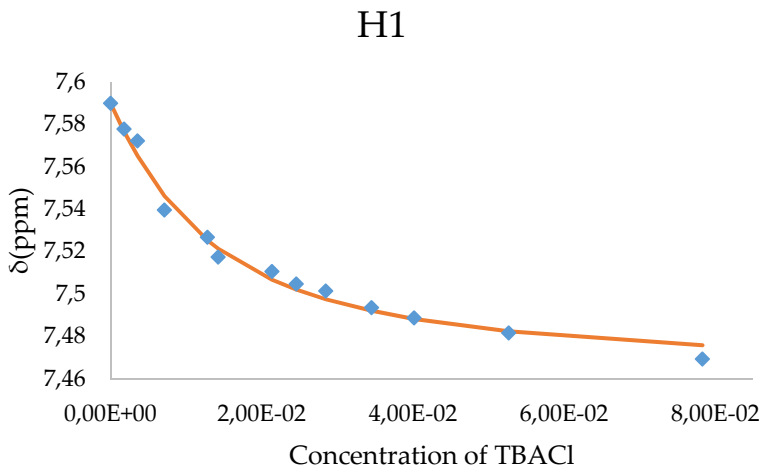


Figure S 27: *Chemical shifts of aromatic protons H1 of* ***2*** *upon incremental amounts of* ***TBACl*** *and fit of the NMR titration data to a theoretical 1:1 binding model.*

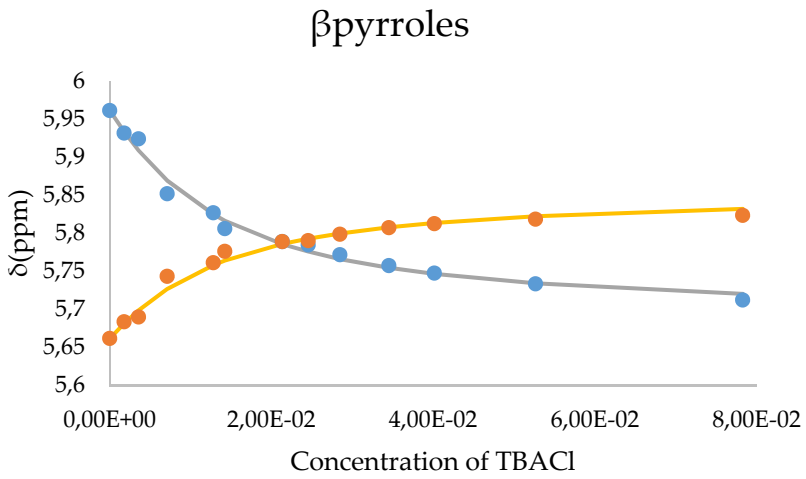


Figure S 28: *Chemical shifts of β- pyrroles protons of* ***2*** *upon incremental amounts of TBACl and fit of the NMR titration data to a theoretical 1:1 binding model.*

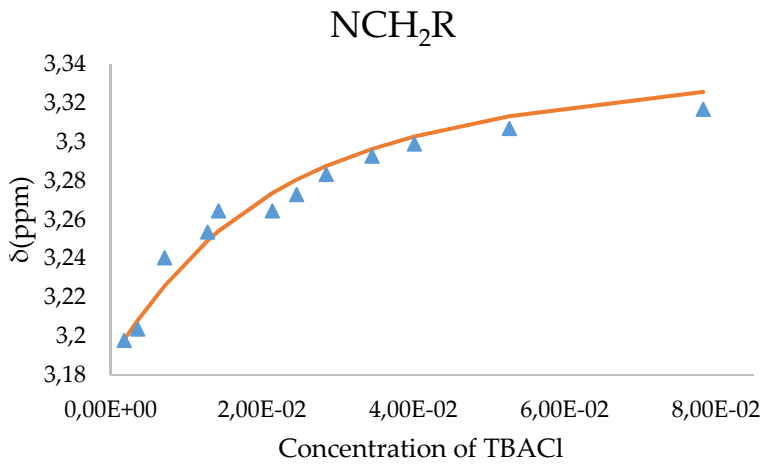


Figure S 29: *Chemical shifts of CH_2 protons α to the nitrogen atom of* ***TBA*** *cation upon incremental amounts of* ***TBACl*** *and fit of the NMR titration data to a theoretical 1:1 binding model.*

Table S 2: *Table of induced chemical shifts of* ***2*** *upon addition of* ***TBACl****.*

	H1	**H4**	**β-pyrroles H6, H7**	**β-pyrroles H5, H8**	**NCH_2**	**NH**
δ_{free}	7.59	7.38	5.96	5.66	2.97	7.33
δ_{bound}	7.46	7.28	5.69	5.85	3.36	10.75
Δδ	-0.13	-0.10	-0.3	+0.19	-0.39	3.42

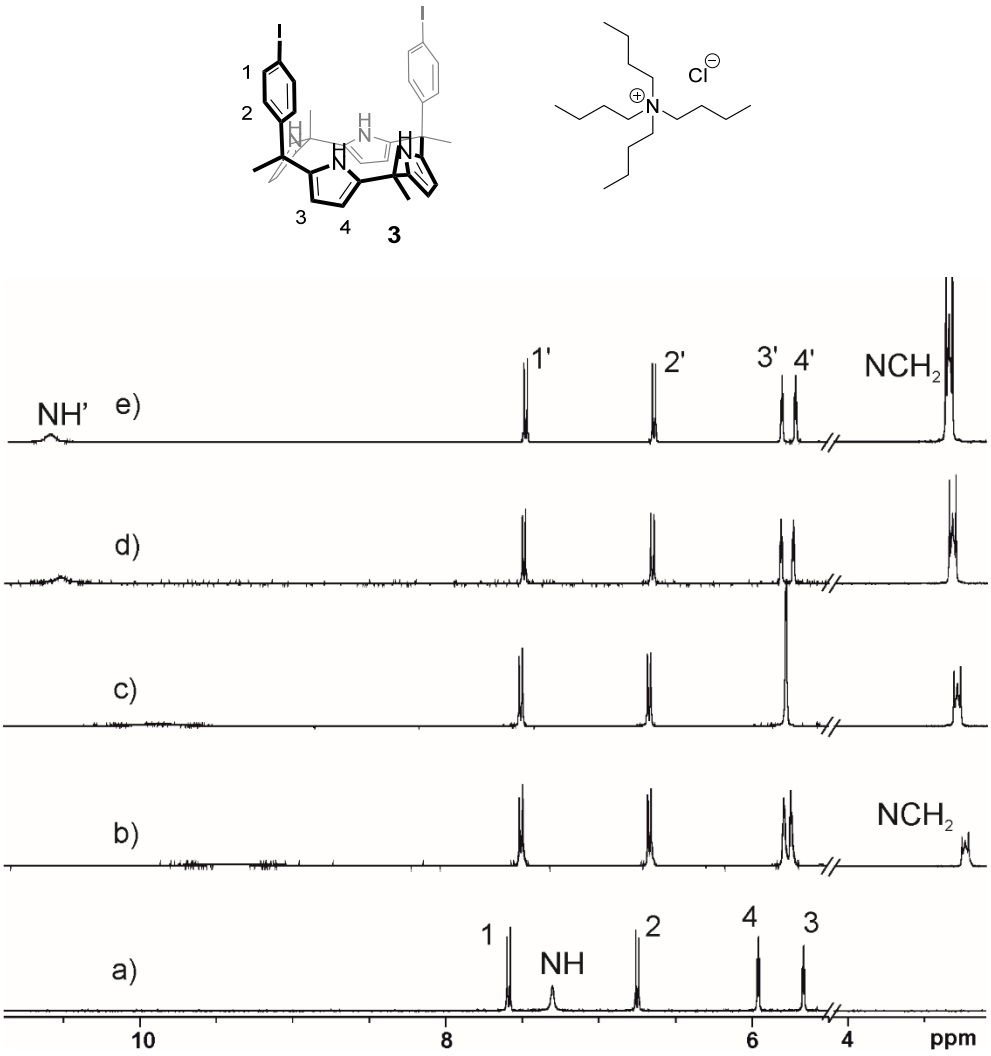


Figure S 30: Selected regions *the ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of* ***3*** *(5 mM) (a) with incremental amounts of* ***TBACl*** *b) 2 equiv.; c) 3 equiv.; d) 5 equiv. and e) 9 equiv. See top panel for proton assignment.*

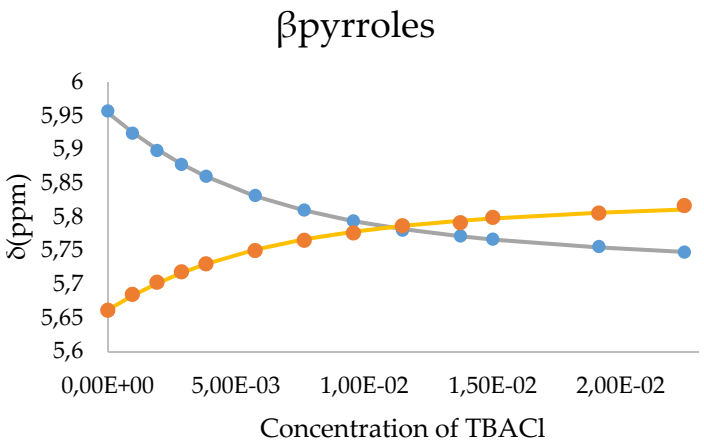


Figure S 31: *Chemical shifts of β- pyrroles protons of* ***3*** *upon incremental amounts of* ***TBACl*** *and fit of the NMR titration data into a theoretical 1:1 binding model.*

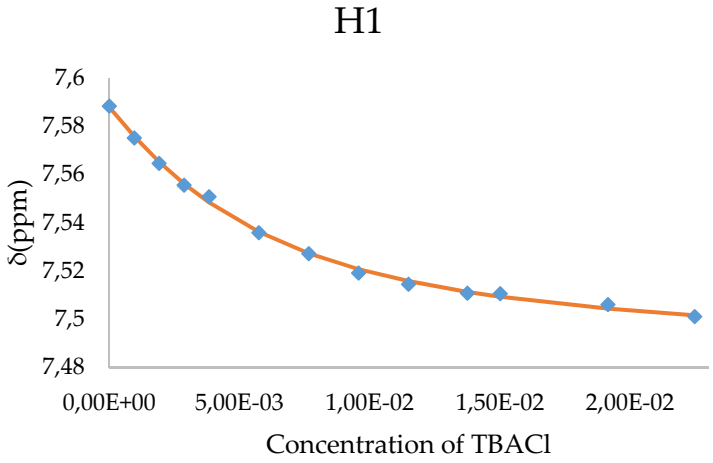


Figure S 32: *Chemical shifts of aromatic protons H1 of* ***3*** *upon incremental amounts of* ***TBACl*** *and fit of the NMR titration data to a theoretical 1:1 binding model.*

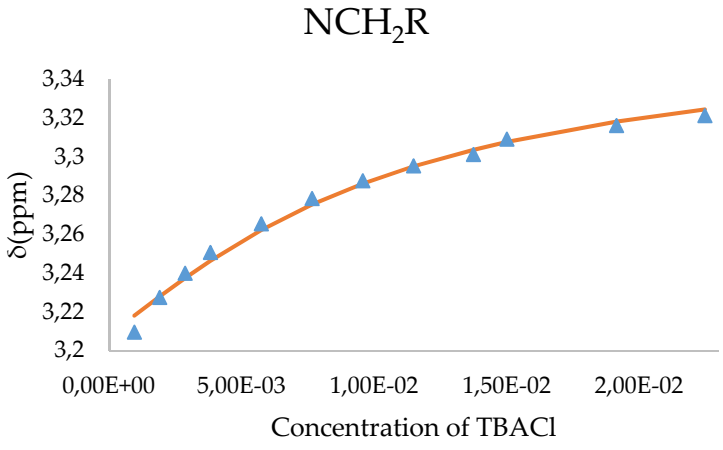


Figure S 33: *Chemical shifts of the CH_2 protons α to the nitrogen atom of* ***TBA*** *cation· upon incremental amount of* ***TBACl*** *and fit of the NMR titration data to a theoretical 1:1 binding model.*

Table S 3: *Table of induced chemical shifts of* ***3*** *upon addition of* ***TBACl****.*

	H1	**H2**	**β-pyrroles H4**	**β-pyrroles H3**	**NCH_2**	**NH**
δ_{free}	7.59	6.75	5.96	5.66	3.20	7.30
δ_{bound}	7.49	6.65	5.73	5.81	3.32	10.60
$\Delta\delta$	-0.1	-0.1	-0.23	+0.15	-0.12	3.3

2.2. ^{1}H NMR titration in Acetone

2 vs TBA·Cl

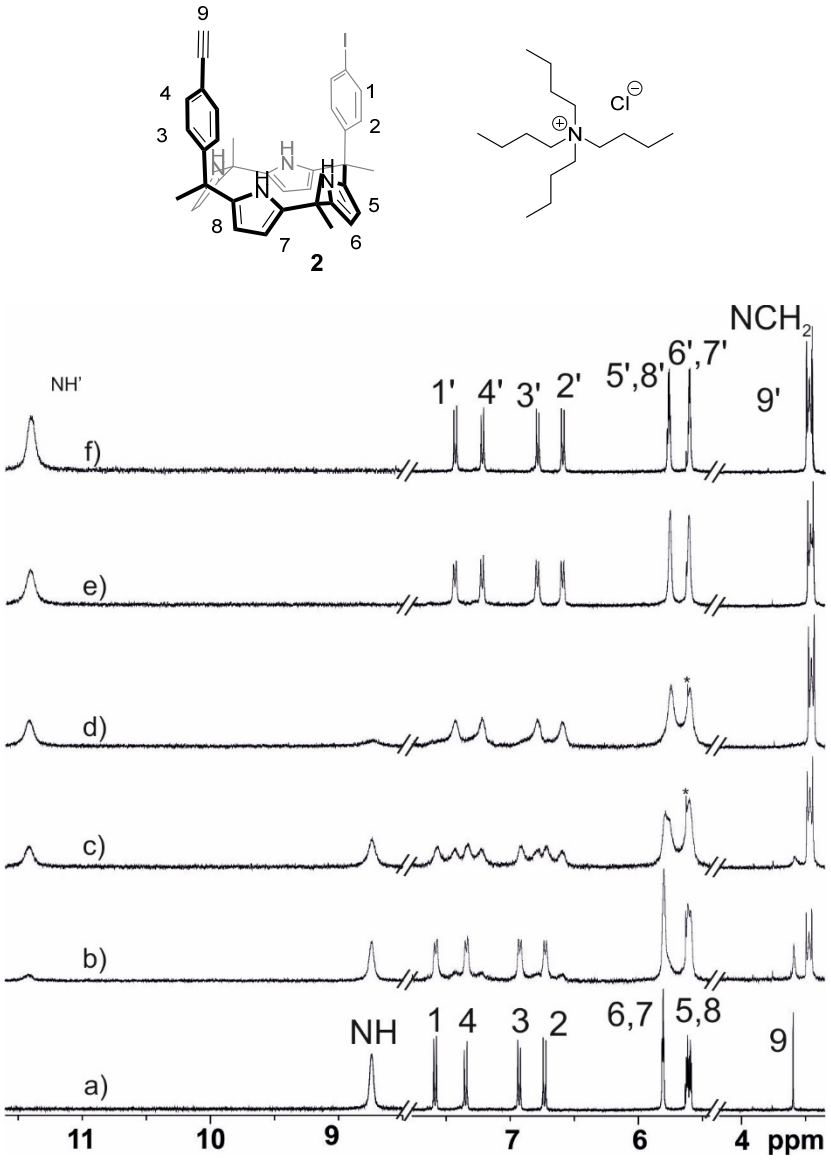


Figure S 34: Selected regions of*the ^{1}H NMR spectra (400 MHz, acetone-d_6, 298 K) of* **2** *(5 mM) (a) with incremental amounts of TBACl b) 0.25 equiv.; c) 0.5 equiv.; d) 0.75 equiv.; e) 1 equiv. and f) 1.2 equiv. See top panel for proton assignment. *Solvent residual peak.*

3 vs **TBA·Cl**

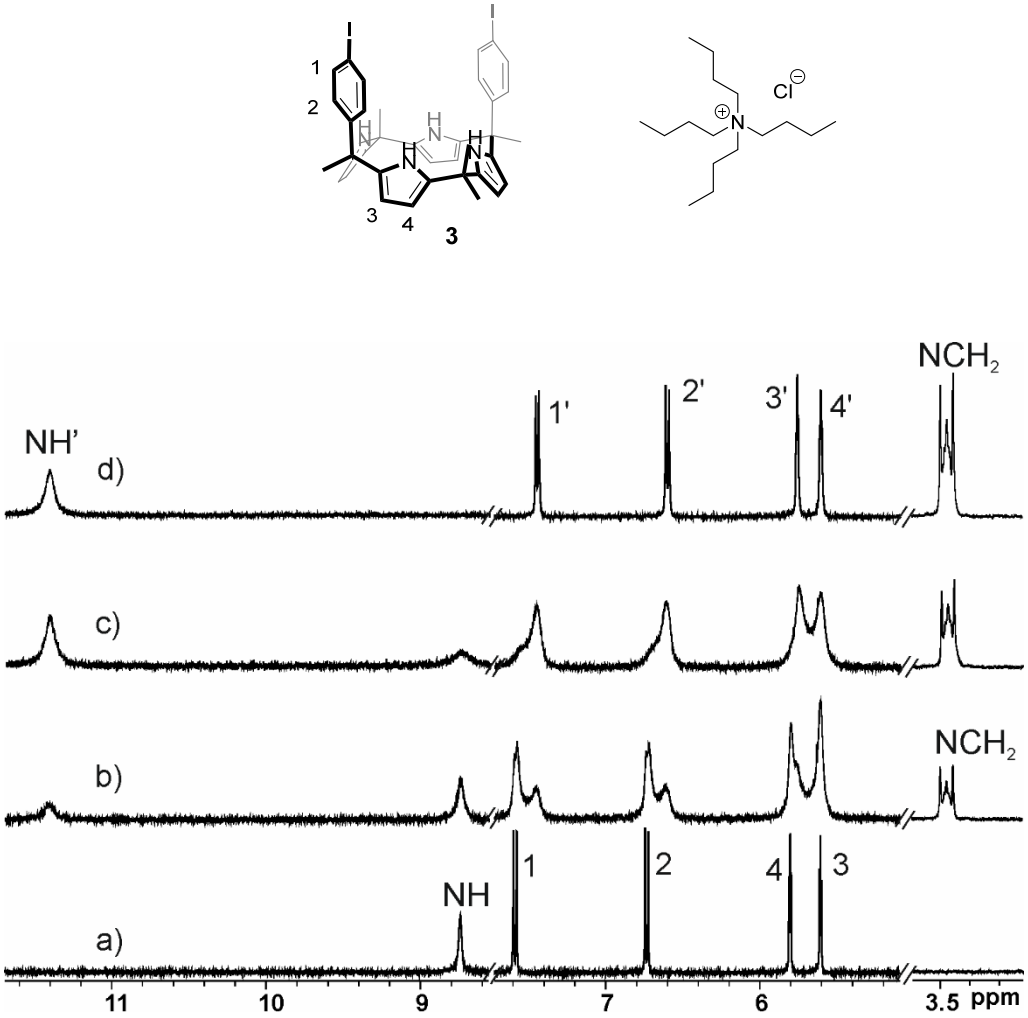


Figure S 35: Selected regions *of the ^{1}H NMR spectra (400 MHz, acetone-d$_6$, 298 K) of **3** (4.3 mM) (a) with incremental amounts of **TBACl** b) 0.25 equiv.; c) 0.5 equiv. and d) 1 equiv. See top panel for proton assignment.*

3. ITC binding studies

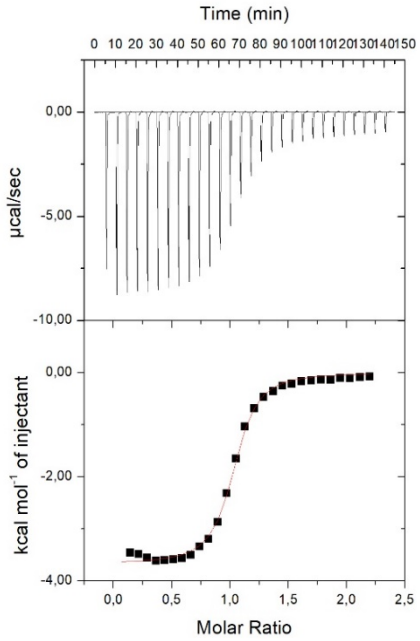


Figure S 36: *(Top) Raw data for the ITC titrations of receptor* ***3*** *with* ***TBACl*** *at 288K in acetone. Bottom) Normalized integration of heat vs* ***TBACl*** */* ***3*** *molar ratio; the fit of the experimental data to the one set of sites binding isotherm (red line) is also shown.* ***[TBACl]*** *= 6.56 mM and* ***[3]*** *= 0.64 mM.*

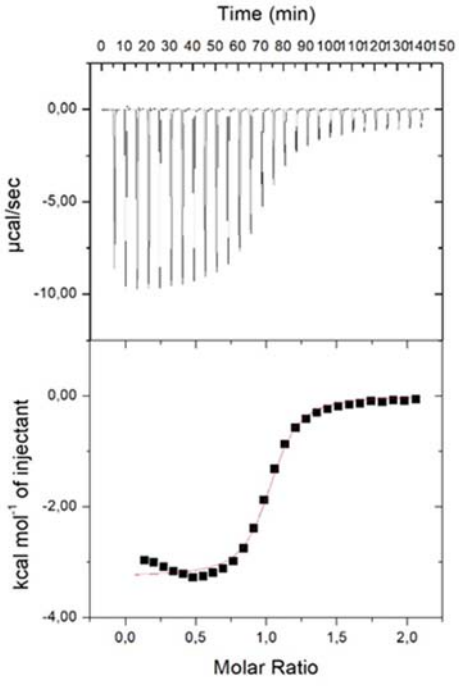


Figure S 37: *(Top) Raw data for the ITC titrations of receptor* ***2*** *with* ***TBACl*** *at 288K in acetone. Bottom) Normalized integration of heat vs* ***TBACl*** */* ***2*** *molar ratio; the fit of the experimental data to the one set of sites binding isotherm (red line) is also shown.* ***[TBACl]*** *= 7.72 mM and* ***[2]*** *= 0.8 mM.*

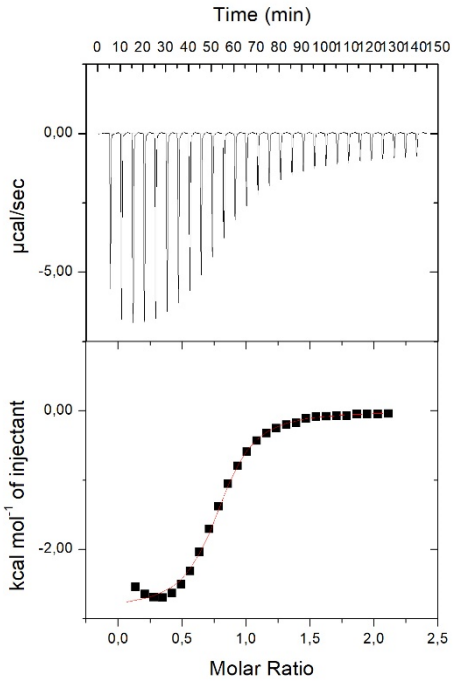


Figure S 38: *(Top) Raw data for the ITC titrations of receptor* ***2Au*** *with* ***TBA·Cl*** *at 288 K in acetone. Bottom) Normalized integration of heat vs* ***TBACl*** */1 molar ratio; the fit of the experimental data to the one set of sites binding isotherm (red line) is also shown.* ***[TBACl]*** *= 6.56 mM and* ***[2Au]*** *= 0.66 mM.*

Table S 4: *Binding constants (K) and the thermodynamic parameters (ΔH, TΔS and ΔG in Kcal·mol^{-1}) obtained from the ITC titration experiments of* ***TBACl*** *and* ***2****,* ***3*** *and* ***2Au*** *at 288 K in acetone.*

Receptor	**2Au**	**2**	**3**
ΔH	-2.83±0.01	-3.29±0.08	-3.70±0.04
TΔS	3.43±0.03	3.25±0.09	3.13±0.04
ΔG	-6.25±0.09	-6.54±0.05	-6.83±0.05
K_a ×10^{-4}	5.54±0.13	9.17±0.628	15.1±0.1

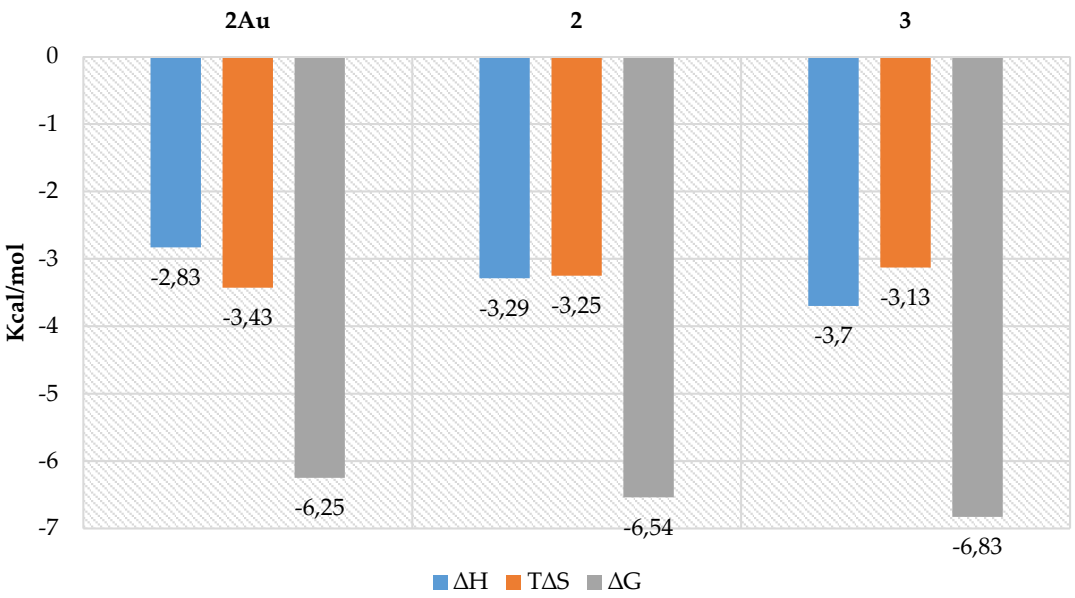
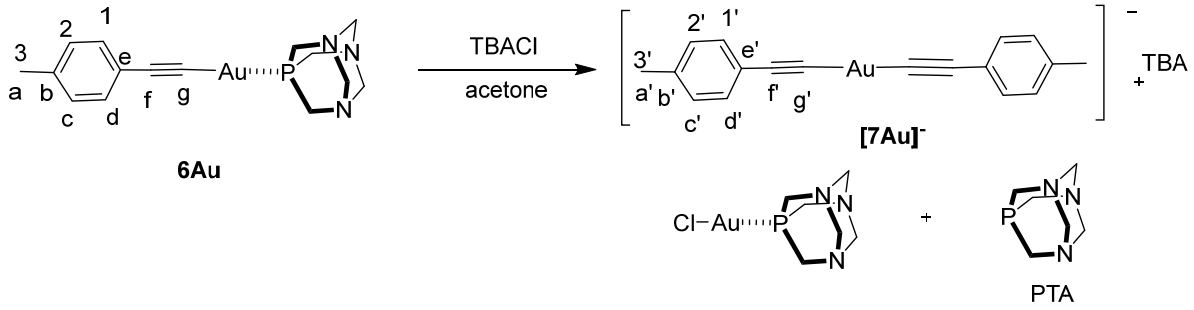


Figure S 39: *Thermodynamic parameters (ΔH, TΔS and ΔG in Kcal·mol^{-1}) of the 1:1 complexes of* ***2Au***, ***2*** *and* ***3*** *with TBACl in acetone*

4. Study of the formation of the anionic-bis(alkynyl)gold(I) complexes [7Au]$^-$ and [8Au]$^-$



Scheme S 6. *Reaction of **6Au** with an excess of TBACl to produce the dimeric anionic species [**7Au**]$^-$*

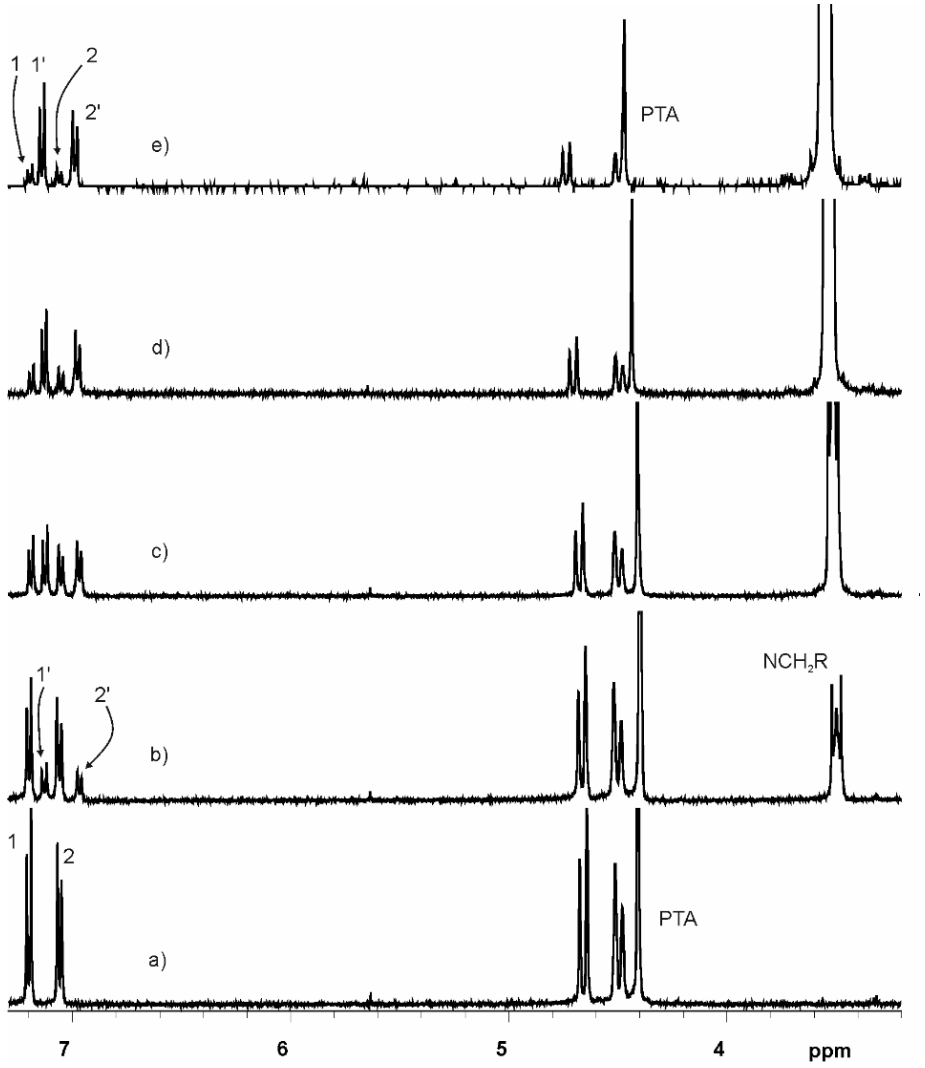


Figure S 40: *Selected region of the ^{1}H NMR spectra (400 MHz, acetone-d_6, 298 K) of the model compound **6Au** (5 mM) (a) with incremental amounts of TBACl b) 0.5 equiv.; c) 1.7 equiv.; d) 5 equiv. and e) 9 equiv. See scheme S6 for proton assignment.*

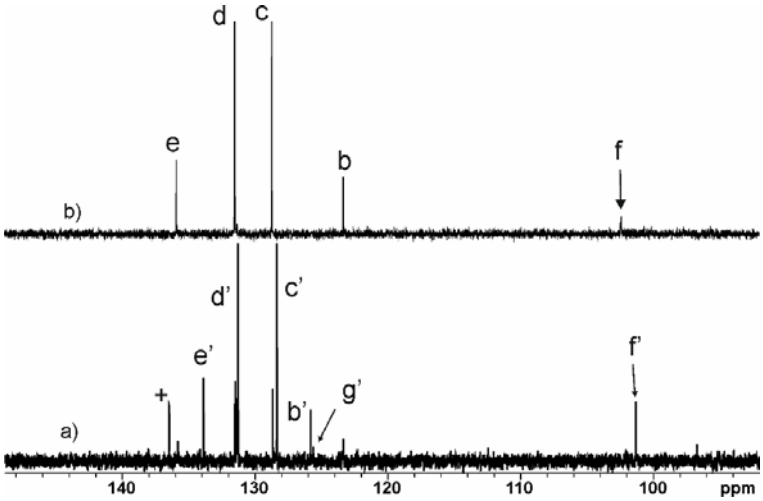


Figure S 41: *Selected region of the ^{13}C NMR (125 MHz, acetone-d_6, 298 K) spectra of the model compound* ***6Au*** *(5 mM) after the addition of 9 equiv. of TBACl (producing the anionic complex* ***[7Au]***$^-$*) and b) the model compound* ***6Au*** *(5 mM). See scheme S6 for proton assignment.*

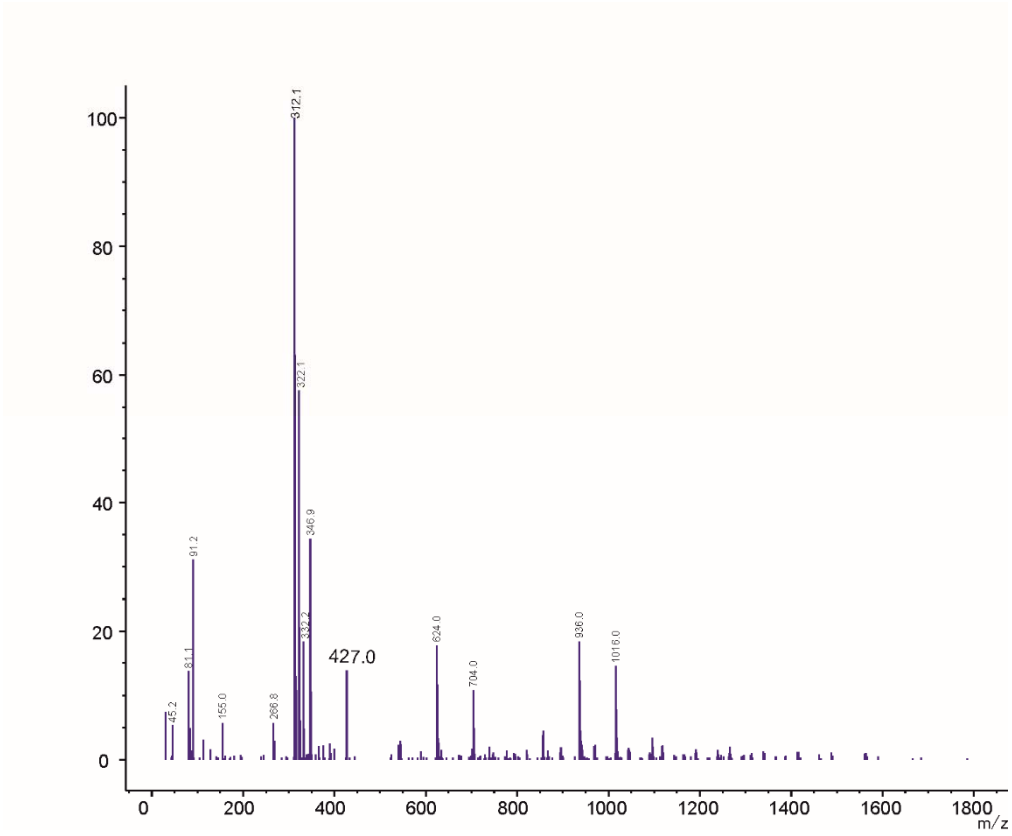


Figure S 42: MS (*ESI/q; negative mode) of* ***[7Au]***$^-$.

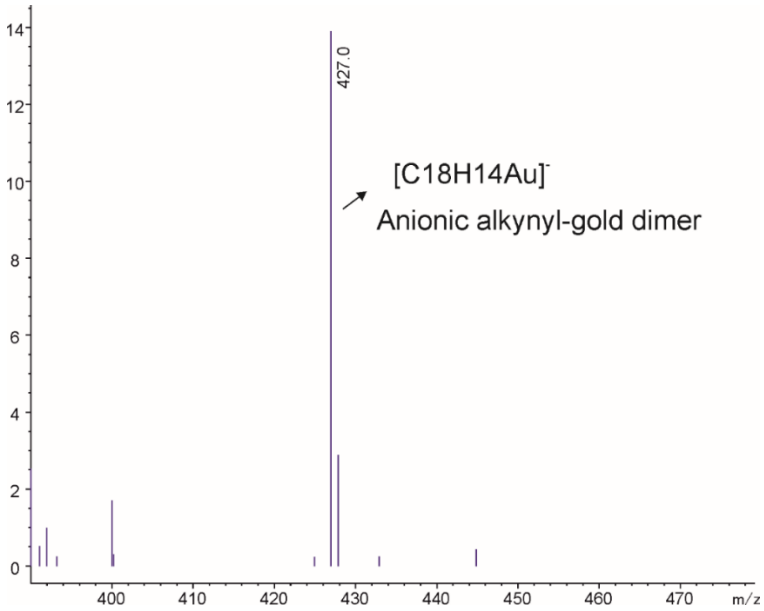


Figure S 43: *Selected region of the MS (ESI/q; negative mode) of* ***[7Au]***$^{-}$*. The peak at m/z = 427.0 corresponds to the molecular ion of the anionic bis(alkynyl)gold(I) complex* ***[7Au]***$^{-}$**.**

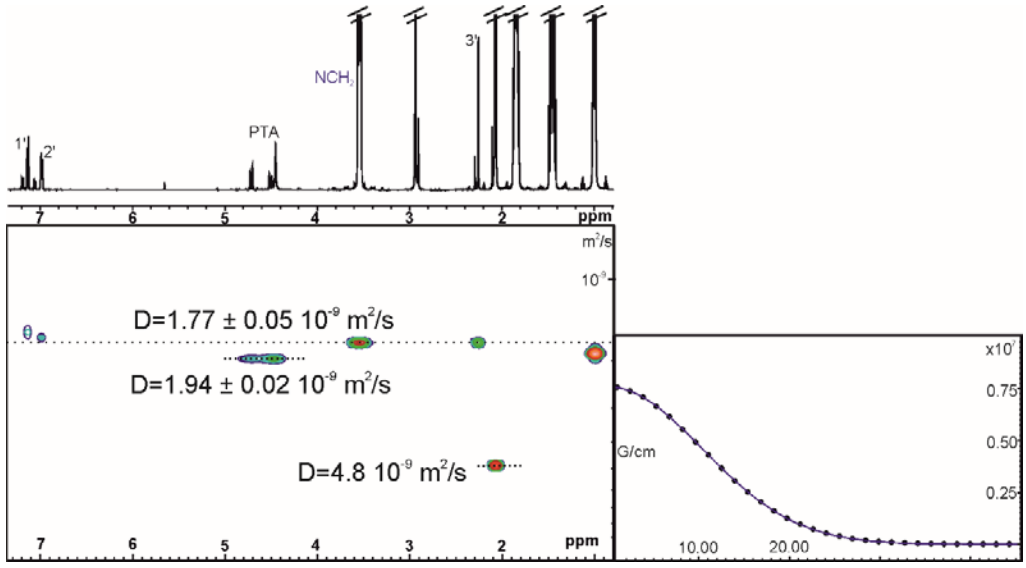
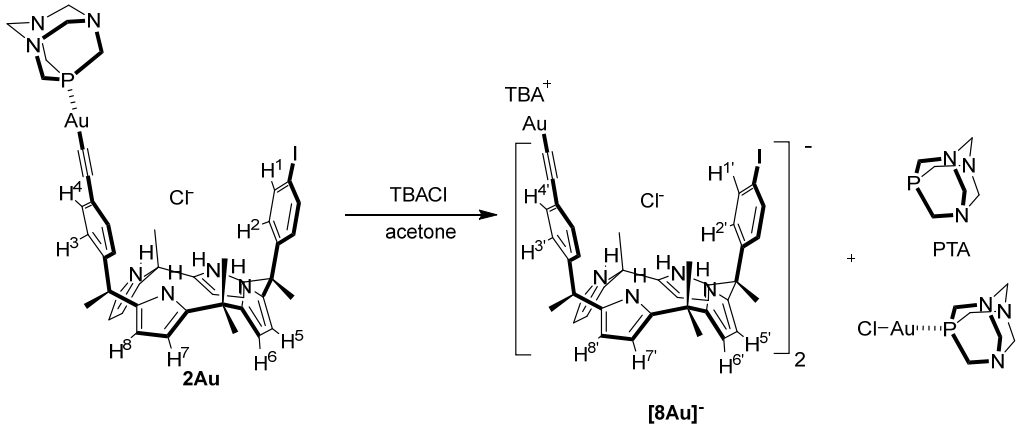


Figure S 44: *Left)* ^{1}*H Pseudo 2D plot of DOSY NMR (500 MHz, acetone-d*$_6$*, 298 K, d20=0.15 s; p30 = 750 ms) of a solution mixture of* ***6Au*** *and* ***[7Au]***$^{-}$*. Right) Fit of the decay of the signal 2' to a mono-exponential function. Primed letters correspond to the protons of the anionic bis(alkynyl)gold(I) complex* ***[7Au]***$^{-}$**.** *See scheme S 6 for proton assignment. Errors are indicated as standard deviations.*



Scheme S 7. *Scheme of the side reaction of the chloride complex of* ***2Au*** *with and excess of TBACl to produce chloride complexes of the anionic dimer* ***[8Au]***$^{-}$.

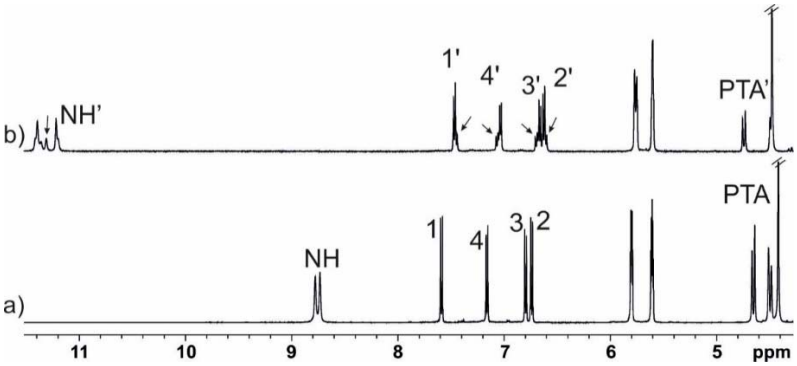


Figure S 45: *Selected region of the* ^{13}*C NMR (500 MHz, acetone-d*$_6$*, 298 K) spectra of the model compound* ***2Au*** *(5 mM) after the addition of 9 equiv. of TBACl (producing the anionic complex* ***[8Au]***$^{-}$*) and b) the model compound* ***2Au*** *(Black arrows indicate the presence of* ***Cl***$^{-}$***●2Au****). Primed letters correspond to the protons of the anionic bis(alkynyl)gold(I) complex* ***[8Au]***$^{-}$***.*** *See scheme S7 for proton assignment.*

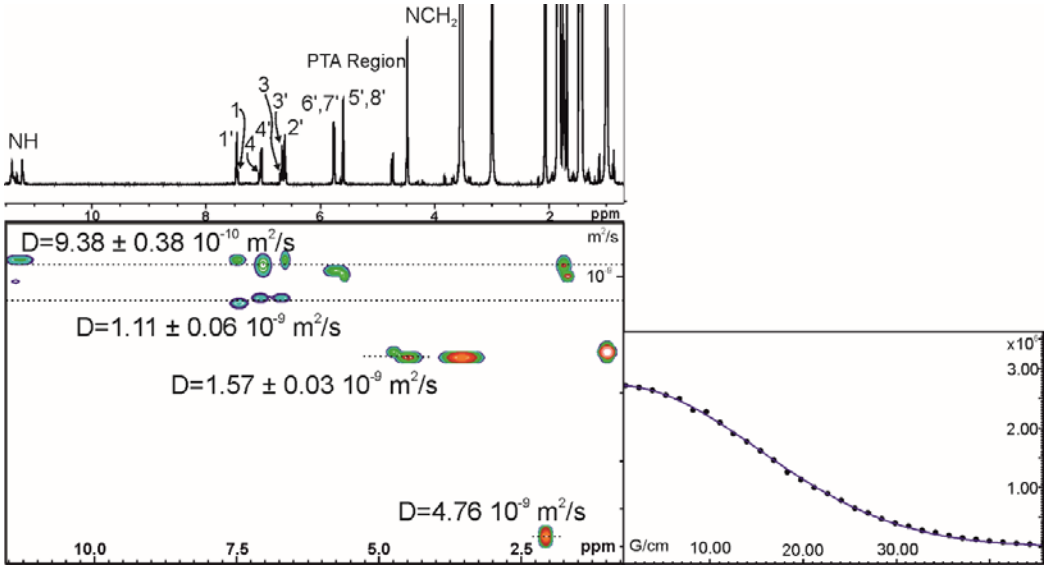


Figure S 46: *Left)* ^{1}*H Pseudo 2D plot of DOSY NMR (500 MHz, acetone-d*$_6$*, 298 K, d20=0.15s; p30 = 750 ms) of a solution of* ***2Au*** *with 9 equiv. of TBACl (producing anionic complex* ***[8Au]***$^{-}$*). Right) Fit of the decay of the signal 4′ to a mono-exponential function. Primed letters correspond to the protons of the anionic bis(alkynyl)gold(I) dimer* ***[8Au]***$^{-}$***.*** *See Scheme S 7 for proton assignment. Errors are indicated as standard deviations.*

5. ^{1}H NMR Pair-wise competitive experiments

In a general pair-wise experiment:

$$A + B + 2G \leftrightarrows AG + BG$$

the following equation was used to calculate the binding constant ratios using the NMR peak integrals:

$$K_{AG} = \frac{[AG]}{[A] * [G]} \; ; \; K_{BG} = \frac{[BG]}{[B] * [G]} \; ;$$

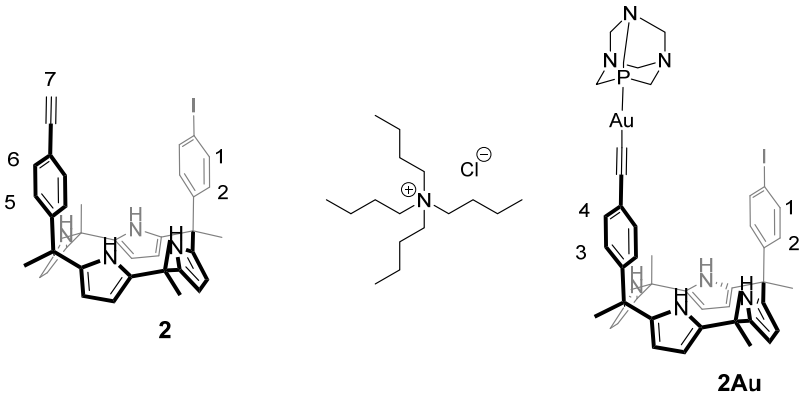
$$\frac{K_{AG}}{K_{BG}} = \frac{[AG] * [B]}{[BG] * [A]} \qquad (1)$$

Equation (1) can be presented as:

$$\frac{K_A}{K_B} = \frac{IntA_{bound} * IntB_{free}}{IntB_{bound} * IntA_{free}} \qquad (2)$$

Where $IntX_{status}$ is the value of the normalized *integral* of proton *X* of the free or bound hosts.

2Au vs 2



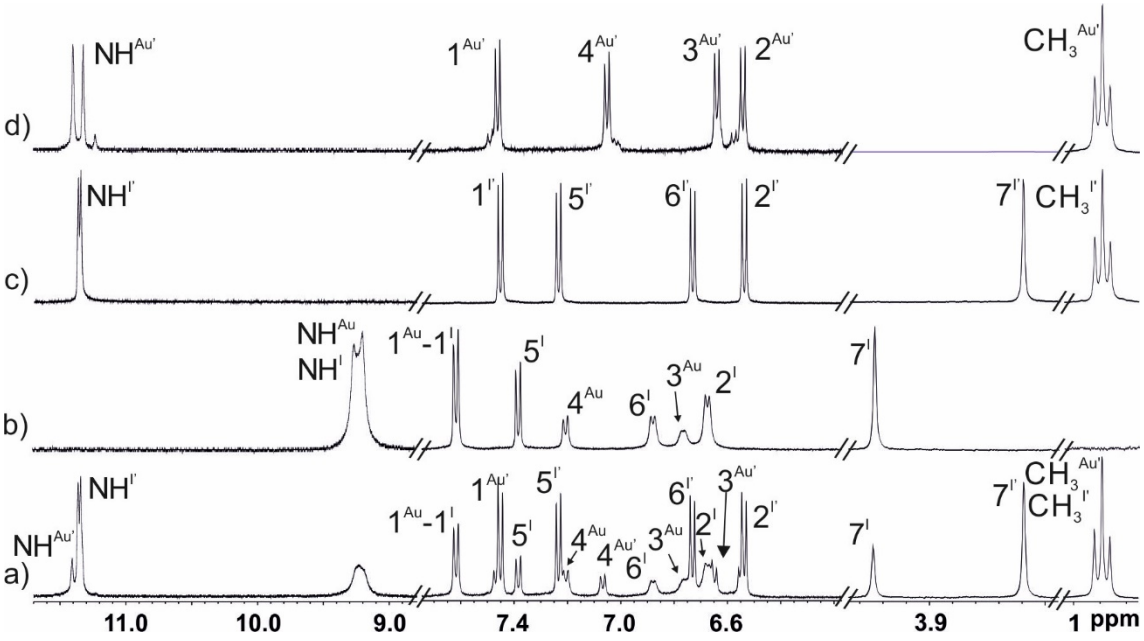


***Figure S 47**: Selected region of the ^{1}H NMR (500 MHz, acetone-d_6, 213 K) spectra of the pair-wise competitive experiment of **2Au, 2** and TBACl: a) mixture of **2Au, 2** and TBACl in a 1:1:1 molar ratio (4.3 mM); b) mixture of **2Au** and **2** in a 1:1 molar ratio (4.6 mM); c) mixture of **2** and TBACl in a 1:1 molar ratio (4.9 mM) (in blue); d) mixture of **2Au** and TBACl in a 1:1 molar ratio (4.7 mM) (in blue). The scales of the regions are different in order to show the presence and/or the absence of the second set of signals. Primed numbers and letters indicate the proton signals of the complexes. See top panel for proton assignment.*

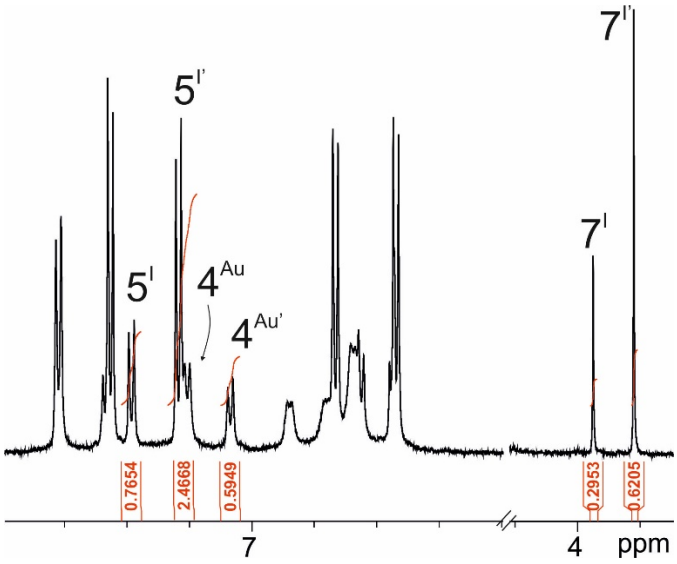


Figure S 48: *Selected regions of the ^{1}H spectrum of the mixture of* ***2Au, 2*** *and TBACl in a 1:1:1 molar ratio (4.3 mM) showed in Figure S47a displaying the values of the integrals used to calculate the binding constants ratio. Primed numbers indicate the proton signals of the complexes. See top panel for the proton assignment.*

2 vs 3

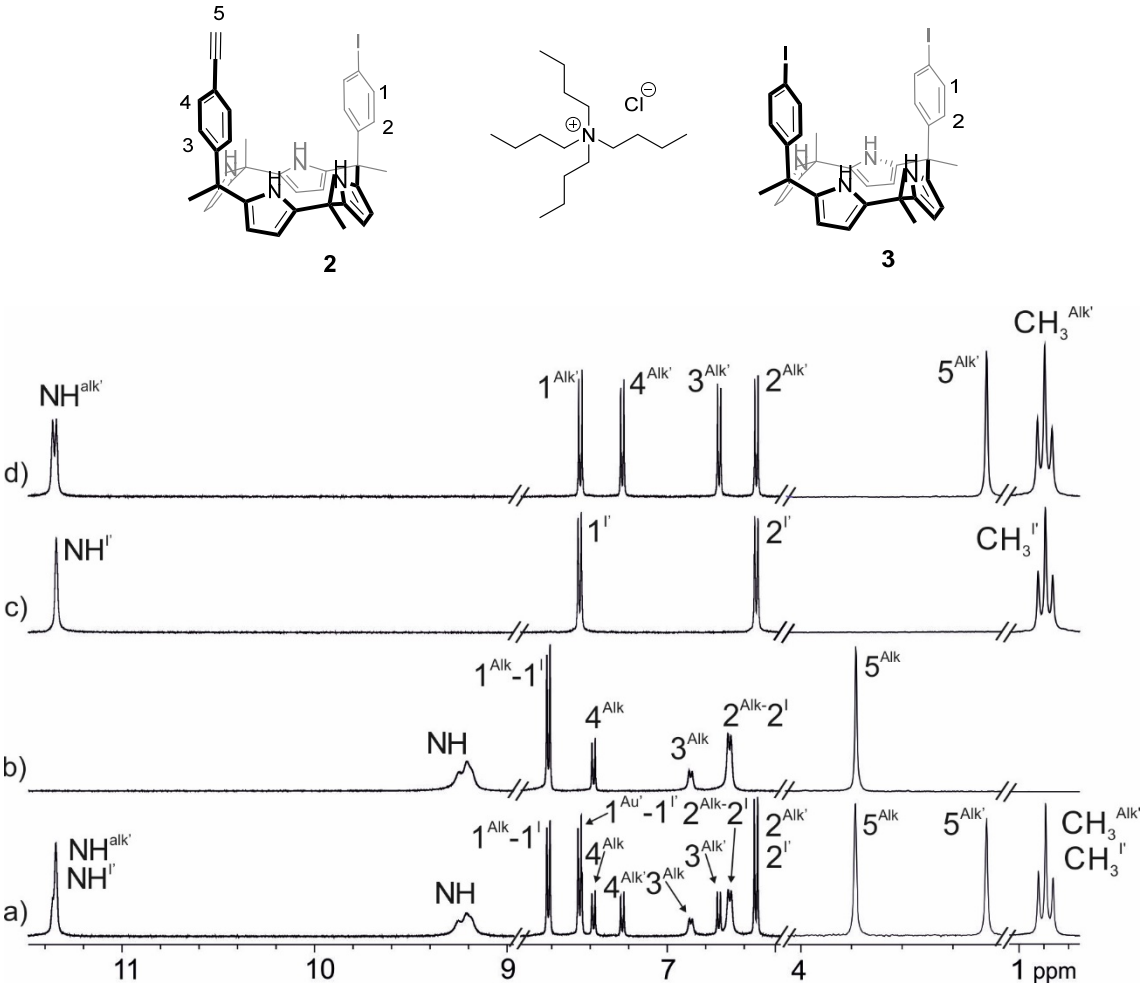


Figure S 49: *Selected region of the ^{1}H NMR (500 MHz, acetone-d_6, 213 K) spectra of the pair-wise competitive experiment of* ***2, 3*** *and TBACl: a) mixture of* ***2, 3*** *and TBACl in a 1:1:1 molar ratio (4.3 mM); b) mixture of* ***3*** *and* ***2*** *in a 1:1 molar ratio (4.6 mM); c) mixture of* ***3*** *and TBACl in a 1:1 molar ratio (4.9 mM) (in blue); d) mixture of* ***2*** *and TBACl in a 1:1 molar ratio (4.7 mM) (in blue). The scales of the regions are different. Primed numbers and letters indicate the proton signals of the complexes. See top panel for proton assignment*

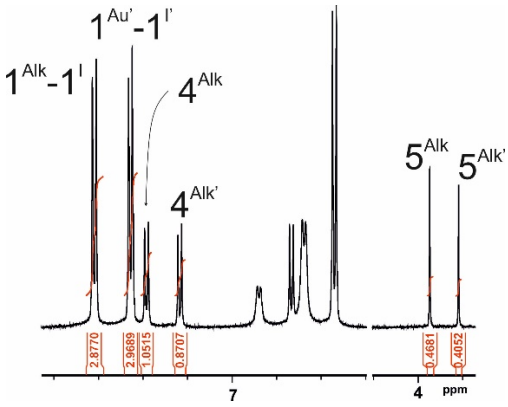


Figure S 50: *Selected regions of the ^{1}H spectrum of the mixture of* ***3, 2*** *and TBACl in a 1:1:1 molar ratio (4.3 mM) showed in Figure S49a displaying the values of the integrals used to calculate the binding constants ratio****.*** *Primed numbers indicate the proton signals of the complexes*

6. References

1 Kemper, B.; Hristova, Y. R.; Tacke, S.; Stegemann, L.; van Bezouwen, L. S.; Stuart, M. C. A.; Klingauf, J.; Strassert, C. A.; Besenius, P., Facile synthesis of a peptidic Au(i)-metalloamphiphile and its self-assembly into luminescent micelles in water. *Chem. Commun.* **2015,** *51* (25), 5253-5256.