Inclusion Complexes of Gold(I)-Dithiocarbamates with β-Cyclodextrin: A Journey from Drug Repurposing towards Drug Discovery

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IR spectra of [Au(N, N-diethyl)dtc]$_2$ (5)

**Figure S1:** Solid state IR-spectra (KBr pellet) of the isolated reaction product from ATM and DSF (1:1); see Scheme 1. The spectrum of the obtained precipitate (orange) is identical to the spectrum of the material obtained by recrystallization from hot DMF (blue) that was identified as gold(I)-dtc complex 5 by X-ray crystallography.
Dose-Response Curves of ATM/DSF and 5

Figure S2: Dose-response curves of the stoichiometric mixture of ATM and DSF (blue) as well as isolated 5 (red) for the treatment of Calu-6 cells (both in the presence of 30-fold excess of 2-hydroxypropyl-β-CD).
Nephelometric Solubility Measurements

Figure S3: Nephelometric solubility data of gold(I)-dtc complexes 29, 32, 33, 34, 38 and 39. A precipitate formed in each well where the concentration of SBE-β-CD was too low in order to solubilize the (fixed) amount of gold(I)-dtc complex. The light scattering intensity is proportional to the amount of precipitation. A visual inspection of the nephelo well-plate was necessary to identify wells with bubble formation – these data points were neglected in the later analysis. Stock solutions (50 mM) of the gold(I)-dtc complexes in DMSO were prepared using a heated sonication bath (56 °C). A 10 mM stock solution of sulfobutylether-β-cyclodextrin (SBE-β-CD, captisol®) in PBS (gibco, DPBS, Dulbecco’s Phosphate Buffered Saline; Life Technologies, Ltd., UK) was diluted in PBS to make 2 mL aliquots of SBE-β-CD in 21 different concentrations ranging from 10 mM to 0 mM (in 0.5 mM increments), of which 100 µL were transferred into the assay wells of a 384 well plate (Corning ® black/clear flat bottom polyesterene, not treated microplate, low flange, without lid, nonsterile; product number 3762). To each well was added 2 µL of the complex stock solution. A manual 16-channel Finnpipette (Thermo Scientific) was used for mixing by pipetting up and down (eight times). Finally, 40 µL of each well were transferred into the 384well Nephelo-plate and measured. Measurements were performed on a Nephelostar Galaxy (BMG Labtech). Raw data (light scatter intensities) were recorded with the corresponding software version 4.30-0; subsequent data processing was done with GraphPad Prism (Version 7.05) using the segmental linear regression model.
NMR Spectra of the Inclusion Complexes

**Figure S4:** NMR spectra of β-CD and the crystalline material obtained by co-crystallization of β-CD and gold(I)-dtc complexes 30, 32, 33 and 39 (top) as well as 36 and 37 (bottom). The
NMR spectra show a distinct 2:1 host–guest ratio. However, a difference of the chemical shifts of β-CD or the gold(I)-dtc complexes compared to the individual compounds was not observed. This is indicative for a dissociation of the inclusion complexes in DMSO that might successfully displace the organic ligands from the cavity of the CD cones.[1]

**Determination of Inclusion Complex Structural Parameters**

![Figure S5: Determination of the structural parameters for the description of the arrangement of the CD cones within the inclusion complexes on the example of [43/(β-CD)$_2$] using Mercury.[2]

For clarity the gold(I)-dtc complex was deleted. For each CD cone a mean plane (purple and yellow, respectively) through all seven glycosidic oxygens (highlighted as red balls) as well as the corresponding centroid (green balls) were defined. The angle between the CD cones is defined as the angle between both formerly defined planes. The sideways shift of the CD cones is calculated using the Pythagorean theorem as depicted above – the mean of both possible values is reported (the difference in both values is a result of the angle between both planes).
Experimental Structure of the Inclusion Complex \([37/(\beta-CD)_2]\)

**Figure S6:** A. Depiction of the experimental structure of \([37/(\beta-CD)_2]\). B. Lateral view. C. Axial view. Hydrogens and water molecules are omitted for clarity and the \(\beta\)-cyclodextrin cones are shown as capped-stick model whereas the gold(I)-dtc complex 37 is shown in ellipsoids (on a 50% probability level). Color code: carbon, grey; oxygen, red; nitrogen, blue; sulfur, yellow; gold, orange.\(^{[2]}\)
| Entry | Compound Name (as appearing in CCDC database) | Stacking of eight-membered chelate ring | Twist angle $\xi$[^*4] | S-Au-S[^*4] | Au-Au [Å][^§] | Database Identifier | Deposition Number | Associated Reference |
|-------|---------------------------------------------|----------------------------------------|----------------------|-------------|---------------|---------------------|------------------|-------------------|
| 1     | catena-(bis($\mu$-Diethylthiocarbamate)-di-gold) | Linear, perpendicular | 27.2, 27.5, 15.8/30.7, 13.9/31.1, 14.5/32.2, 13.6/32.6, 27.0, 27.9 | 176.8, 177.7, 173.3/174.9, 173.4/176.8, 172.4/175.0, 171.7/175.3, 176.7 | 2.79, 2.78, 2.77/2.76, 2.76/2.73, 2.74/2.72, 2.71/2.75, 2.79 | JKEJOY01 | 980959 | Paliwoda et al.[3] |
|       |                                             |                                        |                      |             |               |                     |                  |                   |
| 2     | catena-[bis($\mu$-Diethylthiocarbamato-gold(i)) dichloromethane solvate] | Linear, perpendicular | 26.9, 22.2/31.9/31.0/19.1 | 176.6, 175.1/177.6/176.8/174.4 | 2.79, 2.78/2.77/2.76/2.78 | VOJBUT01 | 980957 | 1996352 | Paliwoda et al.[3]; |
|       |                                             |                                        |                      |             |               |                     |                  |                   |
| 3     | bis($\mu$-di-n-propylthiocarbamato)-di-gold(i) | Linear, coplanar | 37.5, 33.9 | 178.1, 179.7 | 2.81, 2.76 | AUDTHC11 | 203752 | 1103883 | Ho et al.[3]; Hesse et al.[5] |
|       |                                             |                                        |                      |             |               |                     |                  |                   |
| 4     | catena-[bis($\mu$-Diprop-2-en-1-ylcarbamodithioato)-di-gold] | Linear, perpendicular | 27.5 | 176.8 | 2.79 | AHARUY | 830718 | Naeem et al.[6] |
| 5     | bis($\mu$-N,N-Dipentyl-dithiocarbamato-S,S')-di-gold(i) dimethylsulfoxide solvate | Linear, perpendicular | 26.7/33.8 | 176.9/178.8 | 2.78/2.77 | PUCVIS | 1238709 | Mansour et al.[7] |
| 6     | bis($\mu$-N,N-Dipentyl-dithiocarbamato-S,S')-di-gold(i) acetonitrile solvate | Linear, helical | | | | PUCVUE | 1238711 | Mansour et al.[7] |
| 7     | catena[bis($\mu$-N,N-bis(Methoxyethyl)-dithiocarbamato-S,S')-di-gold(i)] | Linear, twisted | 35.0 | 174.0 | 2.79 | PUCZUI | 1238727 | Bishop et al.[8] |
| 8     | catena-[bis($\mu$-1,4,7,10,13-pentaazacyclooctadecane-16-carbodithioato)-di-gold acetonitrile solvate] | Linear, (almost) perpendicular | 3.64 | 170.2 | 2.72 | GOXFQK | 1027267 | 1027268 | Tzeng et al.[9] |
| 9     | catena-[tetakis($\mu$-2,6-dimethylphenyl)(2,6-dimethylphenyl)carbomimidoyl]carbamodithioato)-tetra-gold] | staggered | 15.1/26.5 | 172.6/175.7 | 2.76/2.76 | TUVPAD | 1008664 | Lane et al.[10] |
| 10    | bis($\mu$-(Methyl)[2-(pyridin-2-yl)ethyl]carbamodithioato)-di-gold isophthalic acid | Staggered (co-crystallized with isophthalic acid) | 14.8/15.7 | 171.5/172.0 | 2.75/2.78 | EYURAS | 813945 | Han et al.[11] |
| 11    | bis($\mu$-(Aza-15-crown-5)dithiocarbamato)-di-gold | Isolated (no intermolecular aurophilic bonding) | 0.2 | 171.9 | 2.78 | EBIWAO | 218770 | Tzeng et al.[12] |
| 12    | bis($\mu$-dimethylcarbamodithioato)-di-gold bis(dimethylcarbamodithioato-gold) bis(hexafluorophosphate) | Isolated (co-crystallized with Au(III) complex) | 1.0 | 171.9 | 2.78 | UBALOB | 1063074 | Langaro et al.[13] |
| 13 | hexakis(μ- N-(3,6,9,12-Tetraoxatetradecane-1,14-diyl)dithiocarbamato)-hexa-gold(i) | No eight-membered ring chelate | – | – | VOCRUB | 645163 | Arias et al.[14] |
|---|---|---|---|---|---|---|---|
| [Au(N,N-dibenzyl)dtc]·17 | Isolated | 2.3 | 171.9 | 2.81 | 2068758 | This work |

* \( \tau \) can be calculated by taking the mean of both dihedral angles S(1)-Au(1)-Au(2)-S(2) and S(3)-Au(2)-Au(1)-S(4); see Figure 4.

† reported is the mean value of both angles S(1)-Au(1)-S(4) and S(2)-Au(2)-S(3); see Figure 4.

‡ in deposited structures with two individual gold(I)-dtc complexes found in the asymmetric unit (with different structural parameters) both values are reported.
Table S2: Crystal and structure refinement data of gold(I)-dtc complexes 17 and 23.

| Crystal Data | 17 | 23 |
|--------------|----|----|
| Chemical formula | C₃₀H₂₈Au₂N₂S₄ | C₁₂H₂₂Au₂N₄S₄ |
| MW [g/mol] | 938.72 | 744.51 |
| Temperature [K] | 200(2) | 200(2) |
| Crystal system, space group | monoclinic, \(P_{21}/c\) | monoclinic, \(C_{2/c}\) |
| Unit cell dimensions [Å, °] | \(a = 6.5798(5)\) \(\alpha = 90\) | \(a = 19.7541(13)\) \(\alpha = 90\) |
| | \(b = 13.6628(10)\) \(\beta = 92.2018(10)\) | \(b = 6.0457(4)\) \(\beta = 105.1442(12)\) |
| | \(c = 16.2717(12)\) \(\gamma = 90\) | \(c = 15.7288(10)\) \(\gamma = 90\) |
| Volume [Å³] | 1461.72(19) | 1813.2(2) |
| Density (calculated) [g/cm³] | 2.133 | 2.727 |
| \(Z\) | 2 | 4 |
| Radiation type | Mo K\(_\alpha\), \(\lambda = 0.71073\) Å | 16.624 |
| Absorption coefficient \(\mu\) [mm⁻¹] | 10.334 | 16.624 |
| Crystal shape/color | brick/yellow | needle/yellow |
| Crystal size [mm³] | 0.108 x 0.096 x 0.065 | 0.226 x 0.093 x 0.056 |

Structure Refinement

| Theta range for data collection | 1.9 to 30.9 deg | 2.1 to 26.4 deg |
| Index ranges | -8 ≤ h ≤ 8, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22 | -24 ≤ h ≤ 24, -7 ≤ k ≤ 7, -15 ≤ l ≤ 19 |
| Reflections collected | 18578 | 6051 |
| Independent reflections | 4242 (R(int) = 0.0335) | 1869 (R(int) = 0.0261) |
| Observed reflections | 3076 (I > 2\(\sigma(I)\)) | 1693 (I > 2\(\sigma(I)\)) |
| Absorption correction | Semi-empirical from equivalents |  |
| Max. and min. transmission | 0.56 and 0.46 | 0.49 and 0.31 |
| Refinement method | Full-matrix least-squares on \(F^2\) |  |
| Data/restraints/parameters | 4242 / 0 / 172 | 1869 / 0 / 102 |
| Goodness-of-fit on \(F^2\) | 1.02 | 1.08 |
| Final R indices (I>2\(\sigma(I)\)) | \(R1 = 0.024, wR2 = 0.044\) | \(R1 = 0.018, wR2 = 0.038\) |
| Largest diff. peak and hole [eÅ⁻³] | 0.78 and -0.89 | 0.62 and -1.08 |
Table S3: Crystal and structure refinement data of the inclusion complexes of 33, 37, 39, 43 with β-cyclodextrin.

| Crystal Data | [33(β-CD)2] | [37(β-CD)2] | [39(β-CD)2] | [43(β-CD)2] |
|--------------|-------------|-------------|-------------|-------------|
| Chemical formula | C$_{96}$H$_{164}$Au$_2$N$_2$O$_{88}$S$_4$ | C$_{94}$H$_{98}$Au$_2$N$_2$O$_{83}$S$_4$ | C$_{96}$H$_{164}$Au$_2$N$_2$O$_{96}$S$_4$ | C$_{100.81}$H$_{165.65}$Au$_2$N$_2$O$_{104.06}$S$_4$ |
| MW [g/mol] | 3276.45 | 3105.91 | 3404.46 | 3592.85 |
| Temperature [K] | 200(2) | 200(2) | 200(2) | 200(2) |
| Unit cell dimensions [Å, °] | | | | |
| a | 15.1527(6) | 15.5987(9) | 15.7202(6) | 19.3358(5) |
| b | 15.4306(7) | 24.3169(9) | 18.9348(10) | 24.1261(6) |
| c | 15.7202(6) | 81.827(3) | 76.744(3) | 90.01(11) |
| α | 87.237(3) | 90 | 90.432(2) | 90.01(11) |
| β | 81.827(3) | 110.918(4) | 111.501(2) | 90.01(11) |
| γ | 76.744(3) | 90 | 106.547(2) | 90.01(11) |
| a | 15.5987(9) | 15.5987(9) | 15.7202(6) | 5.1082(4) |
| b | 24.3169(9) | 24.1261(6) | 18.9348(10) | 5.7119(5) |
| c | 19.3358(5) | 90 | 133.24(11) | 111.501(2) |
| α | 90 | 90 | 90 | 90 |
| β | 110.918(4) | 90 | 106.547(2) | 90 |
| γ | 90 | 90 | 90 | 90 |
| β | 90 | 90 | 90 | 90 |
| γ | 90 | 90 | 90 | 90 |
| Volume [Å$^3$] | 3540.9(3) | 6708.8(6) | 28611.4(11) | 3835.3(2) |
| Density (calculated) [g/cm$^3$] | 1.54 | 1.54 | 1.58 | 1.56 |
| Z | 1 | 2 | 8 | 1 |
| Radiation type | Cu K$_{α,\lambda}$ | Cu K$_{α,\lambda}$ | Cu K$_{α,\lambda}$ | Cu K$_{α,\lambda}$ |
| Cu K$_{α,\lambda}$ λ | 1.54178 Å | 1.54178 Å | 1.54178 Å | 1.54178 Å |
| Absorption coefficient μ [mm$^{-1}$] | 5.35 | 5.60 | 5.37 | 5.08 |
| Crystal shape/color | plate/colorless | plate/colorless | brick/colorless | plank/colorless |
| Crystal size [mm$^3$] | 0.068 x 0.063 x 0.024 | 0.060 x 0.055 x 0.015 | 0.060 x 0.055 x 0.015 | 0.060 x 0.055 x 0.015 |
| Structure Refinement | | | | |
| Index ranges | 4.4 to 57.9 deg | 2.5 to 47.2 deg | 2.9 to 57.9 deg | 2.6 to 67.0 deg |
| Reflections collected | 35665 | 26387 | 58456 | 32245 |
| Independent reflections | 9336 (R(int) = 0.0619) | 11004 (R(int) = 0.1641) | 18416 (R(int) = 0.1187) | 14881 (R(int) = 0.0400) |
| Observed reflections | 4749 (I > 2σ(I)) | 4975 (I > 2σ(I)) | 12216 (I > 2σ(I)) | 11676 (I > 2σ(I)) |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max. and min. transmission | 1.94 and 0.56 | 1.68 and 0.46 | 2.06 and 0.48 | 1.69 and 0.61 |
| Reflection method | Full-matrix least-squares on F$^2$ | Full-matrix least-squares on F$^2$ | Full-matrix least-squares on F$^2$ | Full-matrix least-squares on F$^2$ |
| Goodness-of-fit on F$^2$ | 0.91 | 0.94 | 1.07 | 0.98 |
| Final R indices (I>2σ(I)) | R1 = 0.071, wR2 = 0.176 | R1 = 0.092, wR2 = 0.210 | R1 = 0.083, wR2 = 0.190 | R1 = 0.041, wR2 = 0.096 |
| Absolute structure parameter | 0.011(6) | 0.243(12) | 0.162(7) | 0.014(6) |
| Largest diff. peak and hole [eÅ$^{-3}$] | 0.87 and -0.89 | 1.39 and -0.76 | 1.33 and -0.85 | 0.75 and -0.74 |
Syntheses of the Gold(I)-dtc Complexes$^{[15]}$

$\text{[Au}^I(\text{N},\text{N-diethyl} \text{dtc})_2 \text{]}$: A solution of ATM (2.0 g, 5.13 mmol, 1.0 equiv.), dissolved in 80.0 mL of water, and a solution of sodium diethyldithiocarbamate trihydrate (1.39 g, 6.15 mmol, 1.2 equiv.), dissolved in 20.0 mL of water, were combined and vigorously stirred at room temperature over night. The obtained orange powder was filtered and thoroughly washed with water and dried under high vacuum over night (1.55 g, 2.24 mmol, 87%). This material was recrystallized from hot DMF (approximately 500 mL) to afford orange needles as the pure product in a yield of 82% (1.46 g, 2.11 mmol). HRMS-ESI ($m/z$) $[\text{Au}^\text{III} + 2 \text{ dtc}^-]^+$ calcd. for C$_{10}$H$_{20}$Au$_2$N$_2$S$_4$: 493.0175; Found: 493.0170. Anal. calcd for C$_{10}$H$_{20}$Au$_2$N$_2$S$_4$: C, 17.39; H, 2.92; N, 4.06; Found: C, 17.45; H, 3.02; N, 4.22.

$\text{[Au}^I(\text{N-methyl} \text{dtc})_2 \text{]}$: A solution of ATM (352.7 mg, 0.9 mmol, 1.0 equiv.) and a solution of metam (174.4 mg, 1.35 mmol, 1.5 equiv.), dissolved in 10.0 mL of water each, were combined and vigorously stirred at room temperature for 2 h. The obtained slightly greenish powder was thoroughly washed with water, a small amount of ethanol and diethyl ether successively and dried under high vacuum over night. The product was obtained in a yield of 68% (183.6 mg, 0.30 mmol). $^1\text{H NMR}$ (400 MHz, DMSO-$d_6$) $\delta$ 10.71 (q, $J = 5.2$ Hz, 2H), 3.02 (d, $J = 4.7$ Hz, 6H) ppm. $^{13}\text{C NMR}$ (101 MHz, DMSO-$d_6$) $\delta$ 204.4, 35.7 ppm. HRMS-ESI ($m/z$) $[\text{Au}^\text{III} + 2 \text{ dtc}^-]^+$ calcd. for C$_4$H$_8$Au$_2$N$_2$S$_4$: 408.9236; Found: 408.9232. Anal. calcd. for C$_4$H$_8$Au$_2$N$_2$S$_4$: C, 7.92; H, 1.33; N, 4.62; Found C, 8.10; H, 1.49; N, 4.59.

$\text{[Au}^I(\text{N},\text{N-dimethyl} \text{dtc})_2 \text{]}$: Chloro(dimethyl sulfide)gold(I) (325.1 mg, 1.1 mmol, 1.0 equiv.) and dimethyldithiocarbamate (157.5 mg, 1.1 mmol, 1.0 equiv.) were dissolved in 20.0 mL of acetonitrile each. The solutions were combined upon which a yellow solid precipitated. The mixture was stirred at room temperature for 3 h and afterwards filtered through a sintered glass funnel (pore 4). The solid was thoroughly washed with water, a small amount of ethanol and diethy ether successively and dried under high vacuum over night. The product was obtained as a yellow powder in a yield of 35% (121.8 mg, 0.19 mmol). HRMS-ESI ($m/z$) $[\text{Au}^\text{III} + 2 \text{ dtc}^-]^+$ calcd. for C$_8$H$_{12}$Au$_2$N$_2$S$_4$: 436.9549; Found: 436.9561. Anal. calcd. for C$_8$H$_{12}$Au$_2$N$_2$S$_4$: C, 11.36; H, 1.91; N, 4.42; Found C, 11.61; H, 2.00; N, 4.43.
Compound S1

\[
\text{NH} + \text{CS}_2 \xrightarrow{n\text{-BuLi, THF, } -78^\circ\text{C} \text{ - rt, 3h}} \text{Li}^+ \text{S} \xrightarrow{\text{S}} \text{NH}_2 + \text{CS}_2
\]

\(N\)-ethylmethyl amine (0.69 g, 1.0 mL, 11.67 mmol, 1.0 equiv.) was dissolved in 50.0 mL of dry THF and cooled to \(-78^\circ\text{C}\). Then \(n\)-butyllithium (2.5 M in hexane, 4.67 mL, 11.67 mmol, 1.0 equiv.) was added dropwise and the resulting mixture was stirred for 15 minutes whereupon carbon disulfide (0.89 g, 0.7 mL, 11.67 mmol, 1.0 equiv.) was added dropwise. The resulting mixture was stirred at \(-78^\circ\text{C}\) for 15 minutes and afterwards allowed to warm up to room temperature. After a total reaction time of 3 h the solution was concentrated and dried under high vacuum over night. The product was obtained as a reddish solid in quantitative yield and was used in the next step without further purification. \(^1\text{H NMR\ (400 MHz, D}_2\text{O\ ) } \delta 4.09\ (q, J = 7.2 Hz, 2H), 3.45\ (s, 3H), 1.21\ (t, J = 7.2 Hz, 3H) \text{ ppm.}\"

\([\text{AuI(N-ethyl, N-methyl)dtc}]_2; 8\): A solution of ATM (527.0 mg, 1.35 mmol, 1.0 equiv.) and a solution of lithium \(N\)-ethyl, \(N\)-methyl dithiocarbamate \(S1\) (286.6 mg, 2.03 mmol, 1.5 equiv.), dissolved in 10.0 mL of water each, were combined and vigorously stirred at room temperature over night. The obtained orange powder was thoroughly washed with water, a small amount of ethanol and diethyl ether successively and dried under high vacuum over night. The crude product was obtained in a yield of 73% (327.6 mg, 0.99 mmol). This material was further purified by precipitation from hot 1,2-dichloroethane to afford a fluffy, orange colored solid as the pure product. \(\text{HRMS-ESI\ (m/z\ ) } [\text{Au}^{\text{III}} + 2\text{ dtc}]^+\) calcd. for \(\text{C}_{8}\text{H}_{16}\text{Au}_{2}\text{N}_{2}\text{S}_{4}\): 464.9862; Found: 464.9860. \(\text{Anal. Calcd. for }\text{C}_{8}\text{H}_{16}\text{Au}_{2}\text{N}_{2}\text{S}_{4}: \text{C}, 14.51; \text{H}, 2.43; \text{N}, 4.23; \text{Found: C}, 14.59; \text{H}, 2.66; \text{N}, 4.15.\"

\([\text{AuI(N,N-diethyl)dtc}]_2-d_8\ 9\): (i) \(\alpha\)-deuteration of diethylamine:

Diethylamine (0.21 g, 0.30 mL, 2.9 mmol, 1.0 equiv.) and \(\text{RuCl}_2(\text{PPh}_3)_3\) (200.0 mg, 0.21 mmol, 0.07 equiv.) were mixed in 4.0 mL of \(\text{D}_2\text{O}\) and heated under microwave irradiation at 150°C (internal pressure of 8 bar) for 3 h. After cooling to room temperature the suspension was filtered through syringe filter (Milllex \(\text{®-HV\ , 0.45}\ \mu\text{m, Merck-Millipore}). The incorporation of deuterium was determined by \(^1\text{H-NMR\ (in D}_2\text{O\ ) at this stage which was approx. 90%D\ (see Figure S7). An aliquot (2.0 mL\ ) of this solution was used for the next step.}^{16}\)
(ii) *In-situ* dithiocarbamate and subsequent complex formation

Diethylamine-\textit{d}_4 (2.0 mL of D\textsubscript{2}O-solution, \~1.45 mmol, \~1.2 equiv.) was diluted with 15.0 mL of water and potassium hydroxide (81.4 mg, 1.45 mmol, 1.2 equiv.) as well as carbon disulfide (110.4 mg, 0.09 mL, 1.45 mmol, 1.2 equiv.) were added to the mixture which was stirred at rt for 2 h. Then ATM (471.3 mg, 1.21 mmol, 1.0 equiv.) dissolved in 20.0 mL of H\textsubscript{2}O was added to the mixture. An orange-colored precipitate formed immediately. The suspension was stirred at room temperature for 3 h and then filtered through a sintered glass funnel (pore 4). The resulting solid was thoroughly washed with H\textsubscript{2}O (50 mL) and dried under high vacuum. The product was obtained as an orange-colored solid in a yield of 35% (294.6 mg, 0.42 mmol).

HRMS-ESI (\textit{m/z}) \[\text{[Au}^\text{III} + 2\text{dtc-]}^+\] calcd. for C\textsubscript{10}H\textsubscript{12}D\textsubscript{8}AuN\textsubscript{2}S\textsubscript{4}: 501.0677; Found: 501.0677.

*Anal.* calcd. for C\textsubscript{10}H\textsubscript{12}D\textsubscript{8}Au\textsubscript{2}N\textsubscript{2}S\textsubscript{4}: C, 17.19; H, 2.89 *; N, 4.01; Found: C, 17.31; H, 3.18; N, 3.96 (*a device-dependent correction factor \(f = 0.504\) for the measurement of deuterium was applied).

\[\text{[AuI(N,N-diethyl)dtc]}_2\cdot\text{d}_{20}\text{ 10:}\] The complex was synthesized according to the general procedure using diethanolamine-\textit{d}_\textsubscript{10} (0.32 g, 0.40 mL, 3.85 mmol, 1.2 equiv.), potassium hydroxide (0.22 g, 3.85 mmol, 1.2 equiv.), carbon disulfide (0.24 g, 0.19 mL, 3.21 mmol, 1.0 equiv.) in 20.0 mL of water and ATM (1.25 g, 3.21 mmol, 1.0 equiv.) in 60.0 mL of water. A yellow solid was obtained as the pure product in a yield of 30% (678.0 mg, 0.95 mmol). HRMS-ESI (\textit{m/z}) \[\text{[M + Na]}^+\] calcd. for C\textsubscript{10}D\textsubscript{20}Au\textsubscript{2}N\textsubscript{2}S\textsubscript{4}: 733.0988; Found: 733.0993. *Anal.* calcd. for C\textsubscript{10}D\textsubscript{20}Au\textsubscript{2}N\textsubscript{2}S\textsubscript{4}: C, 16.90; H,
2.86; N, 3.94; Found: C, 17.02; H, 3.14; N, 4.04 (a device-dependent correction factor f = 0.504 for the measurement of deuterium was applied).

**Compound S2**

\[
\text{NH} + \text{CS}_2 \rightarrow \text{n-BuLi, THF, -78°C - rt, 3h}
\]

\[\text{N} \overset{\text{S}}{\text{-Li}} \vphantom{+} \]

\[\text{S} \]

\[\text{Li} \]

\[\text{N} \]

\[\text{N} \overset{\text{S}}{\text{-ethyl, N-isopropyl amine (0.72 g, 1.0 mL, 8.26 mmol, 1.0 equiv.) was dissolved in 20.0 mL of dry THF and cooled to –78°C. Then n-butyllithium (2.5 M in hexane, 3.30 mL, 8.26 mmol, 1.0 equiv.) was added dropwise and the resulting mixture was stirred for 15 minutes whereupon carbon disulfide (0.63 g, 0.5 mL, 8.26 mmol, 1.0 equiv.) was added dropwise. The resulting mixture was stirred at –78°C for 15 minutes and afterwards allowed to warm up to room temperature. After a total reaction time of 3 h the solution was concentrated and dried under high vacuum over night. The product was obtained as an off-white solid in quantitative yield and was used for the next step without further purification.} \]

\[\text{H} \text{ NMR (400 MHz, D}_2\text{O) } \delta \text{ (hept, } J = 6.8 \text{ Hz, 1H), 3.90 (q, } J = 7.1 \text{ Hz, 2H), 1.28 (t, } J = 7.0 \text{ Hz, 3H), 1.20 (d, } J = 6.8 \text{ Hz, 6H) ppm.} \]

\[\text{[Au}^{1}(\text{N-ethyl, N-isopropyl})\text{dtc}]_2 \]

**11:** A solution of ATM (230.4 mg, 0.59 mmol, 1.0 equiv.) and a solution of lithium (N-ethyl, N-isopropyl)dithiocarbamate S2 (150.0 mg, 0.89 mmol, 1.5 equiv.), dissolved in 10.0 mL of water each, were combined and vigorously stirred at room temperature for 2 h. The obtained orange to brown powder was filtered and thoroughly washed with water. This material was recrystallized from chloroform/hexane affording dark-orange to brown crystals as the pure product in a yield of 19% (39.8 mg, 0.06 mmol). HRMS-ESI (m/z) [AuIII + 2 dtc]+ calcd. for C12H24AuN2S4: 521.0488; Found: 521.0483. Anal. calcd. for C12H24AuN2S4: C, 20.06; H, 3.37; N, 3.90; Found: C, 19.61; H, 3.44; N, 3.80.

\[\text{[Au}^{1}(\text{N,N-diallyl})\text{dtc}]_2 \]

**12:**[6] The complex was synthesized according to the general procedure using diallyl amine (0.79 g, 1.0 mL, 8.1 mmol; 1.0 equiv.), potassium hydroxide (0.5 g, 8.93 mmol, 1.1 equiv.), carbon disulfide (0.75 g, 0.59 mL, 9.81 mmol, 1.2 equiv.) in 40.0 mL of water and ATM (0.5 g, 1.28 mmol, 1.0 equiv.) in 20.0 mL of water. A dark-yellow solid was obtained as the pure product in a yield of 71% (337.6 mg, 0.46 mmol). \[\text{H} \text{ NMR (400 MHz, CDCl}_3\text{) } \delta \text{ (ddt, } J = 17.2, 10.2, 5.8 \text{ Hz, 4H), 5.31 (dq, } J = 10.2, 1.2 \text{ Hz, 4H), 5.25 (dq, } J = 17.1, 1.4 \text{ Hz, 4H), 4.50 (dt, } J = 5.8, \]

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*S15*
1.4 Hz, 8H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.2, 123.0, 119.6, 58.8 ppm. HRMS-ESI ($m/z$) [Au$^{III} + 2$ dtc]$^+$ calcd. for C$_{13}$H$_{20}$Au$_2$N$_2$S$_4$: 541.0175; Found: 541.0171. Anal. calcd. for C$_{14}$H$_{20}$Au$_2$N$_2$S$_4$: C, 22.77; H, 2.73; N, 3.79; Found: C, 23.25; H, 2.68; N, 4.01.

**Compound S3**

\[
\begin{align*}
\text{NH} + \text{CS}_2 & \xrightarrow{n-\text{BuLi},} \text{THF,} \\
& \text{–78°C - rt, 3h}
\end{align*}
\]

Dipropylamine (1.11 g, 1.5 mL, 10.97 mmol, 1.0 equiv.) was dissolved in 20.0 mL of dry THF and cooled to –78°C. Then n-butyllithium (2.5 M solution in hexane, 4.4 mL, 10.97 mmol, 1.0 equiv.) was added dropwise and the resulting mixture was stirred for 15 minutes whereupon carbon disulfide (0.84 g, 0.66 mL, 10.97 mmol, 1.0 equiv.) was added dropwise. The resulting mixture was stirred at –78°C for 15 minutes and afterwards allowed to warm up to room temperature. After a total reaction time of 3 h the solution was concentrated and dried under high vacuum over night. The product was obtained as an off-white solid in quantitative yield and was used for the next step without further purification. $^1$H NMR (400 MHz, D$_2$O) $\delta$ 3.99 – 3.90 (m, 4H), 1.79 – 1.68 (m, 4H), 0.89 (t, $J = 7.5$ Hz, 6H) ppm.

$[^{[AuI(N,N-di-n-propyl)dtc]_2}]^{13}$: A solution of ATM (478.0 mg, 1.23 mmol, 1.0 equiv.) and a solution of lithium (N,N-di-n-propyl) dithiocarbamate S3 (337.1 mg, 1.84 mmol, 1.5 equiv.), dissolved in 10.0 mL of water each, were combined and vigorously stirred at room temperature over night. The obtained bright yellow powder was thoroughly washed with water, ethanol and diethyl ether successively. The crude product was obtained in a yield of 87% (400.9 mg, 0.54 mmol). Recrystallization from hot 1,2-dichloroethane afforded bright yellow needles as the pure product. HRMS-ESI ($m/z$) [Au$^{III} + 2$ dtc]$^+$ calcd. for C$_{13}$H$_{28}$Au$_2$N$_2$S$_4$: 549.0801; Found: 549.0797. Anal. calcd for C$_{14}$H$_{28}$Au$_2$N$_2$S$_4$: C, 22.52; H, 3.78; N, 3.75; Found: C, 22.31; H, 4.01; N, 3.64.

$[^{[AuI(N,N-di-n-butyl)dtc]_2}]^{14}$: A solution of ATM (407.5 mg, 1.04 mmol, 1.0 equiv.), dissolved in 10.0 mL of water, and a solution of sodium di-n-butyl dithiocarbamate (aqueous solution, 45 wt%; 791.7 mg, 0.73 mL, 1.57 mmol, 1.5 equiv.) were combined and vigorously stirred at room temperature over night. Afterwards, the reaction mixture was extracted with chloroform (2 x 20 mL). The combined organic phases were washed with brine (20 mL), dried over MgSO$_4$ and concentrated. The residue was recrystallized from hot 1,2-dichloroethane to
afford orange needles as the pure product in a yield of 35% (145.6 mg, 0.18 mmol). HRMS-ESI (m/z) [AuIII + 2 dtc]⁺ calcd. for C₁₈H₃₆AuN₂S₄: 605.1427; Found: 605.1422. Anal. calcd. for C₁₈H₃₆Au₂N₂S₄: C, 26.93; H, 4.52; N, 3.49; Found: C, 26.83; H, 4.73; N, 3.30.

**Compound S4**

Diethanolamine (2.81 g, 26.73 mmol, 1.0 equiv.) was dissolved in 50.0 mL of dry DMF. Subsequently tert-butyldimethylsilyl chloride (8.06 g, 53.45 mmol, 2.0 equiv.) and imidazole (3.64 g, 53.45 mmol, 1.0 equiv.) were added. The resulting mixture was stirred at room temperature overnight. The reaction mixture was diluted with 200 mL of ethyl acetate, washed with saturated NaHCO₃ solution (3 x 200 mL) and brine (200 mL), dried with MgSO₄, concentrated and dried under high vacuum overnight. A white to colorless, viscous oil was obtained as the product in a yield of 96% (8.58 g, 25.71 mmol) which was used for the next step without further purification.

**1H NMR (400 MHz, CDCl₃)** δ 3.8 – 3.7 (m, 4H), 2.8 – 2.7 (m, 4H), 0.89 (s, 18H), 0.05 (s, 12H) ppm.

**Compound S5**

Compound S4 (4.84 g, 14.51 mmol, 1.0 equiv.) was dissolved in 50.0 mL of dry THF and cooled to −78°C. Then n-butyllithium (2.5 M solution in hexane, 5.8 mL, 14.51 mmol, 1.0 equiv.) was added dropwise and the resulting mixture was stirred for 15 minutes whereupon carbon disulfide (1.1 g, 0.72 mL, 14.51 mmol, 1.0 equiv.) was added dropwise. The resulting mixture was stirred at −78°C for 15 minutes and afterwards allowed to warm up to room temperature. After a total reaction time of 3 h the solution was concentrated and dried under high vacuum overnight. The product was obtained as an off-white solid in quantitative yield and was used in the next without further purification. **1H NMR (400 MHz, CDCl₃)** δ 4.2 (t, J = 5.8 Hz, 4H), 4.0 (t, J = 5.9 Hz, 4H), 0.88 (s, 18H), 0.05 (s, 12H) ppm.
[Au\(\text{I}(N,N\text{-bis}(\text{2-}(\text{tert-butyl}dime\text{thylsilyl})\text{oxy})\text{ethyl})\text{ dtc})_2\) 15: A solution of ATM (0.5 g, 1.28 mmol, 1.0 equiv) and a solution of compound S5 (798.2 mg, 1.92 mmol, 1.5 equiv.), dissolved in 10.0 mL of water each, were combined and vigorously stirred at room temperature for 2 h. The obtained precipitate was filtered and washed with a small amount of water and dried under high vacuum overnight. A grey powder was obtained as the pure product in a yield of 44% (509.7 mg, 0.42 mmol). 1H NMR (400 MHz, CDCl3) \(\delta 4.17 \text{ (t, } J = 5.5 \text{ Hz, 8H), 4.01 (t, } J = 5.5 \text{ Hz, 8H), 0.90 (s, 36H), 0.08 (s, 24H) ppm.} \) 13C NMR (101 MHz, CDCl3) \(\delta 204.9, 61.3, 60.5, 26.0, 18.3, -5.2 \text{ ppm.} \) HRMS-ESI (m/z) [Au\text{III} + 2 dtc]** calcd. for C34H76AuN2O4Si4: 1013.3430; Found: 1013.3435. Anal. calcd. for C34H76Au2N2O4Si4: C, 33.71; H, 6.32; N, 2.31; Found: C, 33.53; H, 6.39; N, 2.25.

[Au\(\text{I}(\text{N-ethylbenzyl, N-ethyl})\text{ dtc})_2\) 16: The complex was synthesized according to the general procedure using N-ethylbenzylamine (124.4 mg, 0.14 mL, 0.92 mmol, 1.2 equiv.), potassium hydroxide (51.8 mg, 0.92 mmol, 1.2 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A bright yellow solid was obtained as the pure product in a yield of 84% (262.8 mg, 0.32 mmol). 1H NMR (400 MHz, C6D6) \(\delta 7.1 – 7.0 \text{ (m, 10H), 4.7 (s, 4H), 3.4 (q, } J = 7.1 \text{ Hz, 4H), 0.8 (t, } J = 7.1 \text{ Hz, 6H) ppm.} \) HRMS (m/z) [Au\text{III} + 2 dtc]** calcd. for C20H24AuN2S4: 617.0488; Found: 617.0488. Anal. calcd. for C20H24Au2N2S4: C, 29.51; H, 3.22; N, 3.37.

[Au\(\text{I}(\text{N,N-dibenzyl})\text{ dtc})_2\) 17: The complex was synthesized according to the general procedure using ATM (505.1 mg, 1.29 mmol, 1.0 equiv.) dissolved in 10.0 mL of water and sodium dibenzyl dithiocarbamate (573.7 mg, 1.94 mmol, 1.5 equiv.) dissolved in 10.0 mL of methanol. The obtained bright yellow powder was thoroughly washed with water, a small amount of ethanol and diethyl ether successively. Recrystallization from chloroform/hexane afforded brown crystals as the pure product in a yield of 64% (390.5 mg, 0.42 mmol). 1H NMR (400 MHz, CDCl3) \(\delta 7.39 – 7.16 \text{ (m, 20H), 5.07 (s, 8H) ppm.} \) 13C NMR (100 MHz, CDCl3) \(\delta 207.7, 134.6, 129.0, 128.1, 127.8, 58.7 \text{ ppm.} \) Anal. calcd. for C30H28Au2N2S4: C, 38.38; H, 3.01; N, 2.98; Found: C, 38.31; H, 3.28; N, 2.86.
Compound S6

![Chemical structure of Compound S6]

Azetidine (0.85 g, 1.0 mL, 14.89 mmol, 1.0 equiv.) was dissolved in 50.0 mL of dry THF and cooled to –78°C. Then n-butyllithium (2.5 M solution in hexane, 6.0 mL, 14.89 mmol, 1.0 equiv.) was added dropwise and the resulting mixture was stirred for 15 minutes whereupon carbon disulfide (1.13 g, 0.9 mL, 14.89 mmol, 1.0 equiv.) was added dropwise. The resulting mixture was stirred at –78°C for 15 minutes and afterwards allowed to warm up to room temperature. After a total reaction time of 3 h the solution was concentrated and dried under high vacuum over night. The product was obtained as a white solid in quantitative yield and was used for the next step without further purification. $^1$H NMR (400 MHz, D$_2$O) $\delta$ 4.19 – 4.13 (m, 4H), 2.18 – 2.09 (m, 2H) ppm.

[**Au(azetidinyl)dtc]**$_2$ 18: A solution of ATM (646.0 mg, 1.66 mmol, 1.0 equiv.) and a solution of lithium azetidinyl dithiocarbamate S6 (345.7 mg, 2.48 mmol, 1.5 equiv.), dissolved in 10.0 mL of water each, were combined and vigorously stirred at room temperature for 2 h. The obtained bright yellow powder was filtered and thoroughly washed with water, a small amount of ethanol and diethyl ether successively and dried under high vacuum over night. The product was obtained in a yield of 78% (427.9 mg, 0.65 mmol). Anal. calcd. for C$_8$H$_{12}$Au$_2$N$_2$S$_4$: C, 14.59; H, 1.84; N, 4.25; Found: C, 14.68; H, 2.24; N, 4.05.

[**Au(3-pyrrolinyl)dtc]**$_2$ 19: The complex was synthesized according to the general procedure using 3-pyrroline (0.18 g, 0.2 mL, 2.6 mmol, 1.2 equiv.), carbon disulfide (0.2 g, 0.16 mL, 2.6 mmol, 1.2 equiv.), potassium hydroxide (146.1 mg, 2.6 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (845.2 mg, 2.17 mmol, 1.0 equiv.) in 15.0 mL of water. A shiny red solid was obtained as the pure product in a yield of 48% (355.2 mg, 0.517 mmol). Anal. calcd. for C$_{10}$H$_{12}$Au$_2$N$_2$S$_4$: C, 17.60; H, 1.77; N, 4.11; Found: C, 17.75; H, 2.06; N, 3.85.

[**Au(pyrrolidinyl)dtc]**$_2$ 20: A solution of ATM (400.0 mg, 1.03 mmol, 1.0 equiv.) and a solution of ammonium pyrrolidine dithiocarbamate (336.8 mg, 2.05 mmol, 2.0 equiv.), dissolved in 5.0 mL of water each, were combined and vigorously stirred at room temperature over night. The obtained orange powder was centrifuged. The supernatant was taken away and the residue was resuspended in water and again centrifuged (procedure repeated twice). The obtained orange solid was dried under high vacuum over night and afterwards recrystallized form hot DMF to
afford orange-colored needles as the pure product in a yield of 38% (133.8 mg, 0.20 mmol). 
**Anal.** calcd. for C₁₀H₁₆Au₂N₂S₄: C, 17.50; H, 2.35; N, 4.08; Found: C, 17.73; H, 2.53; N, 4.23.

![Image](image1.png)

[**Au**(2-azaspiro[3.3]heptanyl)dtc]₂ 21: The complex was synthesized according to the general procedure using 2-azaspiro[3.3]heptane hydrochloride (122.9 mg, 0.92 mmol, 1.2 equiv.), potassium hydroxide (103.6 mg, 1.84 mmol, 2.4 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A pale yellow solid was obtained as the pure product in a yield of 72% (203.6 mg, 0.28 mmol). **HRMS-ESI** (m/z) [Au⁺³ + 2 dtc⁻]⁺ calcd. for C₄₁H₂₀Au₂N₂S₄: 541.0175; Found: 541.0176. **Anal.** calcd. for C₄₁H₂₀Au₂N₂S₄: C, 22.77; H, 2.73; N, 3.79; Found: C, 23.05; H, 2.86; N, 3.89.

![Image](image2.png)

[**Au**(7-azabicyclo[2.2.1]heptanyl)dtc]₂ 22: The complex was synthesized according to the general procedure using 7-azabicyclo[2.2.1]heptane hydrochloride (123.0 mg, 0.92 mmol, 1.2 equiv.), potassium hydroxide (103.2 mg, 1.84 mmol, 2.4 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A bright red solid was obtained as the pure product in a yield of 42% (124.6 mg, 0.16 mmol). **HRMS-ESI** (m/z) [Au⁺³ + 2 dtc⁻]⁺ calcd. for C₄₁H₂₀Au₂N₂S₄: 541.0175; Found: 541.0173. **Anal.** calcd. for C₄₁H₂₀Au₂N₂S₄ + H₂O: C, 22.23; H, 2.93; N, 3.70; Found: C, 22.17; H, 2.91; N, 3.64.

**Compound S7**

![Image](image3.png)

N-methylpiperidine (1.35 g, 1.5 mL, 13.48 mmol, 1.0 equiv.) was dissolved in 20.0 mL of dry THF and cooled to –78°C. Then n-butyllithium (2.5 M solution in hexane, 5.4 mL, 13.48 mmol, 1.0 equiv.) was added dropwise and the resulting mixture was stirred for 15 minutes whereupon carbon disulfide (1.03 g, 0.81 mL, 13.48 mmol, 1.0 equiv.) was added dropwise. The resulting mixture was stirred at –78°C for 15 minutes and afterwards allowed to warm up to room temperature. After a total reaction time of 3 h the solution was concentrated and dried under high vacuum over night. The product was obtained as an off-white solid in quantitative yield and was used for the next step without further purification. **¹H NMR** (400 MHz, D₂O) δ 4.35 (br. s, 4H), 2.53 (br. s, 4H), 2.29 (s, 3H) ppm.
[AuI(4-methylpiperazinyl)dtc]2 23: A Solution of ATM (502.0 mg, 1.29 mmol, 1.0 equiv.) and a solution of lithium 4-methylpiperazinyl dithiocarbamate S7 (351.7 mg, 1.93 mmol, 1.5 equiv.), dissolved in 10.0 mL of water each, were combined and vigorously stirred at room temperature for 2 h. The obtained bright yellow powder was filtered and thoroughly washed with water, a small amount of ethanol and diethyl ether successively. The crude product was obtained in a yield of 86% (414.8 mg, 0.56 mmol). Recrystallization from hot 1,2-dichloroethane afforded very fine, bright yellow needles as the pure product. HRMS-ESI (m/z) [AuIII + 2 dtc]⁺ calcd. for C₁₂H₂₂AuN₄S₄: 547.0393; Found: 547.0380. Anal. calcd. for C₁₂H₂₂AuN₄S₄: C, 19.36; H, 2.98; N, 7.53; Found: C, 19.42; H, 3.07; N, 7.85.

[AuI(4-methylsulfonylpiperazinyl)dtc]2 24: The complex was synthesized according to the general procedure using 4-methylsulfonylpiperazine (315.3 mg, 1.92 mmol, 1.5 equiv.), potassium hydroxide (118.5 mg, 2.11 mmol, 1.6 equiv.), carbon disulfide (0.15 g, 0.12 mL, 1.92 mmol, 1.5 equiv.) in 20.0 mL of water and ATM (0.5 g, 1.28 mmol, 1.0 equiv.) in 20.0 mL of water. A pale-brown solid was obtained as the pure product in a yield of 69% (385.9 mg, 0.442 mmol). HRMS-ESI (m/z) [AuIII + 2 dtc]⁺ calcd. for C₁₂H₂₂AuN₄O₄S₆: 674.9631; Found: 674.9627. Anal. calcd. for C₁₂H₂₂AuN₄O₄S₆: C, 16.52; H, 2.54; N, 6.42; Found: C, 16.49; H, 2.59; N, 6.51.

[AuI(8-azabicyclo[3.2.1]octanyl)dtc]2 25: The complex was synthesized according to the general procedure using 8-azabicyclo[3.2.1]octane hydrochloride (135.8 mg, 0.92 mmol, 1.2 equiv.), potassium hydroxide (103.6 mg, 1.84 mmol, 2.4 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A pale yellow solid was obtained as the pure product in a yield of 83% (247.0 mg, 0.32 mmol). HRMS-ESI (m/z) [AuIII + 2 dtc]⁺ calcd. for C₁₆H₂₄AuN₂S₄: 569.0488; Found: 569.0486. Anal. calcd. for C₁₆H₂₄AuN₂S₄: C, 25.07; H, 3.16; N, 3.65; Found: C, 25.22; H, 3.12; N, 3.70.

[AuI((3aR, 6aS)-2-methyl octahydro pyrrolo[3,4C] pyrrolidinyl)dtc]2 26: The complex was synthesized according to the general procedure using (3aR, 6aS)-2-methyl octahydropyrrolo[3,4C]pyrrole (116.1 mg, 0.92 mmol, 1.2 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.)
in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A bright yellow solid was obtained as the pure product in a yield of 57% (174.5 mg, 0.22 mmol). HRMS-ESI (m/z) [M]+ calcd. for C\textsubscript{16}H\textsubscript{27}Au\textsubscript{2}N\textsubscript{4}S\textsubscript{4}: 797.0444, Found: 797.0452; (m/z) [Au\textsuperscript{III} + 2 dtc]- calcd. for C\textsubscript{16}H\textsubscript{26}AuN\textsubscript{4}S\textsubscript{4}: 599.0706; Found: 599.0706. Anal. calcd. for C\textsubscript{16}H\textsubscript{26}AuN\textsubscript{4}S\textsubscript{4}: C, 24.12; H, 3.29; N, 7.03; Found: C, 23.80; H, 3.20; N, 7.00.

[Au\textsuperscript{IV}((S)-(+)2-(methoxymethyl)pyrrolidinyl)dtc\textsubscript{2}] 27: The complex was synthesized according to the general procedure using (S)-(+)2-(methoxymethyl)pyrrolidine (106.0 mg, 0.11 mL, 0.92 mmol, 1.2 equiv.), potassium hydroxide (51.8 mg, 0.92 mmol, 1.2 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A bright yellow solid was obtained as the pure product in a yield of 52% (156.0 mg, 0.20 mmol). HRMS-ESI (m/z) [Au\textsuperscript{III} + 2 dtc]- calcd. for C\textsubscript{14}H\textsubscript{24}AuN\textsubscript{2}O\textsubscript{2}S\textsubscript{4}: 577.0391; Found: 577.0393. Anal. calcd. for C\textsubscript{14}H\textsubscript{24}AuN\textsubscript{2}O\textsubscript{2}S\textsubscript{4}: C, 21.71; H, 3.12; N, 3.62; Found: C, 21.60; H, 3.26; N, 3.49.

[Au\textsuperscript{IV}(tert-butyl (L)-prolinyl)dtc\textsubscript{2}] 28: The complex was synthesized according to the general procedure using (L)-proline tert-butyl ester (200.0 mg, 1.17 mmol, 1.2 equiv.), potassium hydroxide (71.8 mg, 1.28 mmol, 1.1 equiv.), carbon disulfide (101.3 mg, 0.08 mL, 1.33 mmol, \~1.4 equiv.) in 5.0 mL of water and ATM (380.0 mg, 0.98 mmol, 1.0 equiv) in 10.0 mL of water. A yellow solid was obtained as the pure product in a yield of 89% (385.7 mg, 0.435 mmol). HRMS-ESI (m/z) [Au\textsuperscript{III} + 2 dtc]- calcd. for C\textsubscript{20}H\textsubscript{32}AuN\textsubscript{2}O\textsubscript{4}S\textsubscript{4}: 689.0910; Found: 689.0907. Anal. calcd. for C\textsubscript{20}H\textsubscript{32}AuN\textsubscript{2}O\textsubscript{4}S\textsubscript{4}: C, 27.09; H, 3.64; N, 3.16; Found: C, 27.17; H, 3.84; N, 3.06.

[Au\textsuperscript{IV}(N-2-hydroxyethyl, N-methyl)dtc\textsubscript{2}] 29: The complex was synthesized according to the general procedure using 2-methylaminoethanol (86.6 mg, 0.09 mL, 1.15 mmol, 1.5 equiv.), potassium hydroxide (76.0 mg, 0.06 mL, 1.0 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A greenish solid was obtained which was recrystallized from hot ethanol to afford small orange-red needles as the pure product in a yield of 73% (196.5 mg, 0.28 mmol). \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) \( \delta \) 5.04 (t, \( J = 5.5 \) Hz, 2H), 4.02 (t, \( J = 5.7 \) Hz, 4H), 3.74 (q, \( J = 5.6 \) Hz, 4H), 3.49 (s, 6H) ppm. \textsuperscript{13}C NMR (100 MHz, DMSO-\textit{d}_6) \( \delta \) 201.4, 61.4, 57.9, 47.0 ppm. HRMS-ESI (m/z)
[Au\textsuperscript{III} + 2 dtc\textsuperscript{-}]\textsuperscript{+} calcd. for C\textsubscript{8}H\textsubscript{16}Au\textsubscript{2}N\textsubscript{2}O\textsubscript{2}S\textsubscript{4}: 496.9760; Found: 496.9757. \textbf{Anal.} calcd. for C\textsubscript{8}H\textsubscript{16}Au\textsubscript{2}N\textsubscript{2}O\textsubscript{2}S\textsubscript{4}: C, 13.84; H, 2.32; N, 4.03; Found: C, 13.76; H, 2.43; N, 3.98.

\[ \text{[Au(I)(N-ethyl, N-2-hydroxyethyl)dtc]_2 30:} \] The complex was synthesized according to the general procedure using 2-ethylaminoethanol (82.0 mg, 0.09 mL, 0.92 mmol, 1.2 equiv.), potassium hydroxide (51.8 mg, 0.92 mmol, 1.2 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A bright red solid was obtained as the pure product in a yield of 44% (123.5 mg, 0.17 mmol).

\textbf{HRMS-ESI (m/z)} \textsuperscript{[Au\textsuperscript{III} + 2 dtc\textsuperscript{-}]\textsuperscript{+} calcd. for C\textsubscript{10}H\textsubscript{20}Au\textsubscript{2}N\textsubscript{2}O\textsubscript{2}S\textsubscript{4}: 525.0073; Found: 525.0080. \textbf{Anal.} calcd. for C\textsubscript{10}H\textsubscript{20}Au\textsubscript{2}N\textsubscript{2}O\textsubscript{2}S\textsubscript{4} + H\textsubscript{2}O: C, 16.22; H, 2.99; N, 3.78; Found: C, 16.15; H, 2.83; N, 3.64.

\[ \text{[Au(I)(N,N-di-2-hydroxyethyl)dtc]_2 31:} \] The complex was synthesized according to the general procedure using diethanolamine (96.7 mg, 0.92 mmol, 1.2 equiv.), potassium hydroxide (51.8 mg, 0.92 mmol, 1.2 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A gold-colored solid was obtained as the pure product in a yield of 34% (98.5 mg, 0.13 mmol).

\textbf{HRMS-ESI (m/z)} \textsuperscript{[Au\textsuperscript{III} + 2 dtc\textsuperscript{-}]\textsuperscript{+} calcd. for C\textsubscript{10}H\textsubscript{20}Au\textsubscript{2}N\textsubscript{2}O\textsubscript{4}S\textsubscript{4}: 556.9971; Found: 556.9977. \textbf{Anal.} calcd. for C\textsubscript{10}H\textsubscript{20}Au\textsubscript{2}N\textsubscript{2}O\textsubscript{4}S\textsubscript{4} + H\textsubscript{2}O: C, 15.92; H, 2.67; N, 3.71; Found: C, 15.62; H, 2.88; N, 3.61.

\[ \text{[Au(I)(N-3-hydroxyethyl, N-methyl)dtc]_2 32:} \] The complex was synthesized according to the general procedure using 3-methylamino-1-propanol (82.0 mg, 0.08 mL, 0.92 mmol, 1.2 equiv.), potassium hydroxide (51.8 mg, 0.92 mmol, 1.2 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A greenish to brown solid was obtained as the pure product in a yield of 76% (210.9 mg, 0.29 mmol).

\textbf{HRMS-ESI (m/z)} \textsuperscript{[Au\textsuperscript{III} + 2 dtc\textsuperscript{-}]\textsuperscript{+} calcd. for C\textsubscript{10}H\textsubscript{20}Au\textsubscript{2}N\textsubscript{2}O\textsubscript{2}S\textsubscript{4}: 525.0073; Found: 525.0070. \textbf{Anal.} calcd. for C\textsubscript{10}H\textsubscript{20}Au\textsubscript{2}N\textsubscript{2}O\textsubscript{2}S\textsubscript{4}: C, 16.62; H, 2.79; N, 3.88; Found: C, 16.38; H, 2.88; N, 3.87.
[Au(I)(N-4-hydroxybutyl, N-methyl)dtc]₂ 33: The complex was synthesized according to the general procedure using 4-(methylamino)-1-butanol (94.9 mg, 0.92 mmol, 1.2 equiv.), potassium hydroxide (51.8 mg, 0.92 mmol, 1.2 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A yellow to orange-colored solid was obtained as the pure product in a yield of 42% (123.7 mg, 0.16 mmol). ¹H NMR (400 MHz, DMSO-d₆) δ 4.48 (t, J = 5.1 Hz, 2H), 3.93 (dd, J = 9.0, 6.2 Hz, 4H), 3.47 – 3.38 (m, 10H), 1.82 – 1.68 (m, 4H), 1.43 (p, J = 6.7 Hz, 4H) ppm. ¹³C NMR (101 MHz, DMSO-d₆) δ 200.9, 60.3, 59.2, 45.3, 29.5, 23.1 ppm. HRMS-ESI (m/z) [Au III + 2 dtc]⁺ calcld. for C₁₂H₂₄AuN₂O₂S₄: 553.0386; Found: 553.0389. Anal. calcld. for C₁₂H₂₄Au₂N₂O₂S₄: C, 19.20; H, 3.22; N, 3.73; Found: C, 19.07; H, 3.37; N, 3.65.

[Au(I)(N-2-(S)-hydroxypropyl, N-methyl)dtc]₂ 34: The complex was synthesized according to the general procedure using (2S)-1-(methylamino)propan-2-ol hydrochloride (115.0 mg, 0.92 mmol, 1.2 equiv.), potassium hydroxide (103.6 mg, 1.84 mmol, 2.4 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A gold-colored solid was obtained as the pure product in a yield of 47% (129.6 mg, 0.18 mmol). ¹H NMR (400 MHz, DMSO-d₆) δ 5.06 (d, J = 5.3 Hz, 2H), 4.25 – 4.05 (m, 4H), 3.62 (dd, J = 13.5, 8.5 Hz, 2H), 3.50 (s, 6H), 1.08 (d, J = 6.3 Hz, 6H) ppm. ¹³C NMR (100 MHz, DMSO-d₆) δ 201.6, 66.1, 64.4, 47.6, 21.2 ppm. HRMS-ESI (m/z) [Au III + 2 dtc]⁺ calcld. for C₁₀H₂₀Au₂N₂O₂S₄: 525.0073; Found: 525.0072. Anal. calcld. for C₁₀H₂₀Au₂N₂O₂S₄: C, 16.62; H, 2.79; N, 3.88; Found: C, 16.35; H, 2.85; N, 3.93.

[Au(I)(3-fluoro-, 3-hydroxymethylazetidinyl)dtc] 2 35: The complex was synthesized according to the general procedure using (3-fluorooazetidin-3-yl)methanol (96.7 mg, 0.92 mmol, 1.2 equiv.), carbon disulfide (70.0 mg, 0.92 mmol, 1.2 equiv.) and potassium hydroxide (51.8 mg, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. This complex did not immediately precipitate from the reaction mixture as for most compounds. Therefore the reaction mixture was allowed to stand at room temperature for 2 days, whereupon a white powder precipitated. The solid was filtered through a sintered glass frit (pore size 4), washed with 10 mL of water and dried under high vacuum. The pure product was obtained as an off-white solid (which upon dissolution in DMSO turns yellow) in a yield of 36% (105.2 mg, 0.139 mmol). ¹H NMR (400 MHz, DMSO-d₆) δ 5.4 (t, J = 6.1 Hz, 2H), 4.5 – 4.3 (m, 8H), 3.7
(dd, J = 19.5, 5.2 Hz, 4H) ppm. $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 200.2 (d, J = 3.2 Hz), 89.4 (d, J = 208.2 Hz), 64.6 (d, J = 28.2 Hz), 61.7 (d, J = 26.6 Hz) ppm. HRMS-ESI (m/z) [M + Na]$^+$ calcd. for C$_{10}$H$_{14}$Au$_2$F$_2$NaO$_2$S$_4$: 776.9130; Found: 776.9136. Anal. calcd. for C$_{10}$H$_{14}$Au$_2$F$_2$NaO$_2$S$_4$: C, 15.92; H, 1.87; N, 3.71; Found: C, 15.80; H, 1.98; N, 3.78.

$^{[Au^I((R)-prolinoyl)dtc]}_2$ 36: The complex was synthesized according to the general procedure using (R)-(−)-prolinol (93.1 mg, 0.92 mmol, 1.2 equiv.), potassium hydroxide (51.8 mg, 0.92 mmol, 1.2 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A yellow to gold-colored solid was obtained as the pure product in a yield of 53% (150.6 mg, 0.20 mmol). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 5.06 (t, J = 5.7 Hz, 2H), 4.53 – 4.46 (m, 2H), 3.81 – 3.73 (m, 4H), 3.74 – 3.52 (m, 4H), 2.22 – 1.94 (m, 8H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 198.2, 68.3, 59.0, 56.6, 27.7, 23.1 ppm. HRMS-ESI (m/z) [Au$^{III}$ + 2 dtc]$^+$ calcd. for C$_{12}$H$_{20}$Au$_2$N$_2$O$_2$S$_4$: 549.0073; Found: 549.0082. Anal. calcd. for C$_{12}$H$_{20}$Au$_2$N$_2$O$_2$S$_4$: C, 19.31; H, 2.70; N, 3.75; Found: C, 19.30; H, 3.00; N, 3.75.

$^{[Au^I((S)-prolinoyl)dtc]}_2$ 37: The complex was synthesized according to the general procedure using (S)-(−)-prolinol (93.1 mg, 0.92 mmol, 1.2 equiv.), potassium hydroxide (51.8 mg, 0.92 mmol, 1.2 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A pale-yellow solid was obtained which was recrystallized from hot ethanol (with a few drops of DMF) to afford red-brownish crystals as the pure product in a yield of 82% (236.8 mg, 0.32 mmol). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 5.11 – 5.01 (m, 2H), 4.54 – 4.44 (m, 2H), 3.81 – 3.74 (m, 4H), 3.74 – 3.52 (m, 4H), 2.24 – 1.93 (m, 8H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 198.2, 68.2, 59.0, 56.6, 27.7, 23.1 ppm. HRMS-ESI (m/z) [Au$^{III}$ + 2 dtc]$^+$ calcd. for C$_{12}$H$_{20}$Au$_2$N$_2$O$_2$S$_4$: 549.0073; Found: 549.0070. Anal. calcd. for C$_{12}$H$_{20}$Au$_2$N$_2$O$_2$S$_4$: C, 19.31; H, 2.70; N, 3.75; Found: C, 19.17; H, 3.00; N, 3.68.

$^{[Au^I(4-((S)-fluoro-(S)-prolinoyl)dtc)]}$ 38: The complex was synthesized according to the general procedure using ((2S, 4S)-4-fluoropyrrolidin-2-yl)methanol hydrochloride (143.2 mg, 0.92 mmol, 1.2 equiv.), potassium hydroxide (103.6 mg, 1.84 mmol, 2.4 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A gold-colored solid was obtained as the pure product in a yield of 64% (192.5 mg, 0.246 mmol).
$^1$H NMR (400 MHz, DMSO-$d_6$) δ 5.4 (dt, $J = 53.9, 4.3$ Hz, 2H), 5.1 (t, $J = 5.8$ Hz, 2H), 4.6 (td, $J = 9.5, 8.2, 4.1$ Hz, 2H), 4.2 (ddd, $J = 35.5, 15.4, 4.6$ Hz, 2H), 4.1 (dt, $J = 9.0, 4.1$ Hz, 2H), 4.0 (dd, $J = 25.5, 15.4$ Hz, 2H), 2.5 – 2.3 (m, 6H) ppm. $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 200.6, 93.1 (d, $J = 174.4$ Hz), 67.4, 62.7 (d, $J = 24.6$ Hz), 59.0 (d, $J = 4.3$ Hz), 33.7 (d, $J = 19.0$ Hz) ppm. HRMS-ESI ($m/z$) [Au$^{III} + 2$ dtc$^{-}$]$^{+}$ calcd. for C$_{12}$H$_{18}$Au$_2$F$_2$N$_2$O$_2$S$_4$: 584.9885; Found: 584.9894. Anal. calcd. for C$_{12}$H$_{18}$Au$_2$F$_2$N$_2$O$_2$S$_4$ + H$_2$O: C, 18.01; H, 2.52; N, 3.50; Found: C, 18.22; H, 2.66; N, 3.63.

$[^{119}$Au$]$(N-2-hydroxy, 2-methylpropyl, N-methyl)dtc$]$

$^{39}$: The complex was synthesized according to the general procedure using 2-methyl-1-(methylamino)propan-2-ol (94.9 mg, 0.92 mmol, 1.2 equiv.), potassium hydroxide (51.8 mg, 0.92 mmol, 1.2 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A gold-colored solid was obtained as the pure product in a yield of 47% (134.5 mg, 0.18 mmol). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 4.84 (s, 2H), 4.03 (s, 4H), 3.53 (s, 6H), 1.18 (s, 12H) ppm. $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 202.8, 71.3, 67.8, 47.2, 27.8 ppm. HRMS-ESI ($m/z$) [Au$^{III} + 2$ dtc$^{-}$]$^{+}$ calcd. for C$_{12}$H$_{24}$AuN$_2$O$_2$S$_4$: 553.0386; Found: 553.0382. Anal. calcd. for C$_{12}$H$_{24}$Au$_2$N$_2$O$_2$S$_4$ + H$_2$O: C, 18.75; H, 3.41; N, 3.65; Found: C, 18.73; H, 3.39; N, 3.61.

$[^{119}$Au$]$(S)-3-hydroxypyrrolidinyl)dtc$]$

$^{40}$: The complex was synthesized according to the general procedure using (S)-(+)3-pyrrolidinol (80.2 mg, 0.92 mmol, 1.2 equiv.), potassium hydroxide (51.8 mg, 0.92 mmol, 1.2 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A bright yellow solid was obtained as the pure product in a yield of 61% (167.6 mg, 0.23 mmol). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 202.8, 71.3, 67.8, 47.2, 27.8 ppm. HRMS-ESI ($m/z$) [Au$^{III} + 2$ dtc$^{-}$]$^{+}$ calcd. for C$_{10}$H$_{16}$Au$_2$N$_2$O$_2$S$_4$: 520.9760; Found: 520.9777. Anal. calcd. for C$_{10}$H$_{16}$Au$_2$N$_2$O$_2$S$_4$ + H$_2$O: C, 16.31; H, 2.46; N, 3.80; Found: C, 16.21; H, 2.46; N, 3.71.

$[^{119}$Au$]$(R)-3-hydroxypyrrolidinyl)dtc$]$

$^{41}$: The complex was synthesized according to the general procedure using (R)-(−)-3-pyrrolidinol (80.2 mg, 0.92 mmol, 1.2 equiv.), potassium hydroxide (51.8 mg, 0.92 mmol, 1.2 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A bright yellow solid was obtained as the pure product in a yield of 65% (179.2 mg, 0.25 mmol). HRMS-ESI ($m/z$) [Au$^{III} + 2$ dtc$^{-}$]$^{+}$ calcd. for C$_{10}$H$_{16}$Au$_2$N$_2$O$_2$S$_4$: 520.9760; Found: 520.9760. Anal. calcd. for C$_{10}$H$_{16}$Au$_2$N$_2$O$_2$S$_4$: C, 16.72; H, 2.24; N, 3.90; Found: C, 16.43; H, 2.40; N, 3.86.
[AuI(4-hydroxypiperidinyl)dtc]_{2} 42: The complex was synthesized according to the general procedure using 4-hydroxypiperidine (101.2 mg, 1.0 mmol, 1.2 equiv.), potassium hydroxide (61.7 mg, 1.1 mmol, 1.2 equiv.), carbon disulfide (63.2 mg, 0.05 mL, 0.83 mmol, 1.0 equiv.) in 5.0 mL of water and ATM (325.1 mg, 0.83 mmol, 1.0 equiv.) in 10.0 mL of water. A bright-yellow powder was obtained as the pure product in a yield of 60% (225.4 mg, 0.30 mmol). HRMS-ESI (m/z) [Au^{III} + 2 dtc]^{+} calcd. for C_{12}H_{20}Au_{2}N_{2}O_{2}S_{4}: 549.0073; Found: 549.0074. Anal. calcd. for C_{12}H_{20}Au_{2}N_{2}O_{2}S_{4}: C, 19.31; H, 2.70; N, 3.75; Found: C, 19.49; H, 2.65; N, 3.94.

[AuI(tropinyl)dtc]_{2} 43: The complex was synthesized according to the general procedure using nortropin hydrochloride (148.7 mg, 0.92 mmol, 1.2 equiv.), potassium hydroxide (103.6 mg, 1.84 mmol, 2.4 equiv.), carbon disulfide (70.0 mg, 0.06 mL, 0.92 mmol, 1.2 equiv.) in 10.0 mL of water and ATM (300.0 mg, 0.77 mmol, 1.0 equiv.) in 15.0 mL of water. A pale yellow solid was obtained as the pure product in a yield of 83% (254.2 mg, 0.32 mmol). HRMS-ESI (m/z) [Au^{III} + 2 dtc]^{+} calcd. for C_{16}H_{24}Au_{2}N_{2}O_{2}S_{4}: 601.0386; Found: 601.0386. Anal. calcd. for C_{16}H_{24}Au_{2}N_{2}O_{2}S_{4}: C, 24.06; H, 3.03; N, 3.51; Found: C, 23.89; H, 3.31; N, 3.42.
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6, 1H, DMSO-d$_6$; 25°C

\[
\text{HN-S-Au-S-NH}
\]

6
6, 13C, DMSO-d6, 25°C
12, 1H, CDCl₃, 25°C
$\text{S32}$

$^{13}C$, CDCl$_3$, 25°C

12

$\text{S32}$
15, 1H, CDCl₃, 25°C
15, 13C, CDCl3, 25°C
17, 1H, CDCl3, 25°C

S36
29, 1H, DMSO-d6, 25°C

29
29, 13C, DMSO-d6, 25°C

![Chemical Structure](image)

![NMR Spectrum](image)
30, 1H, DMSO-d6, 25°C

[Chemical structure image]

S40
30, 13C, DMSO-d6, 25°C

![Chemical Structure]

30
$\text{31, 13C, DMSO-d6, 25}^\circ\text{C}$

![Chemical Structure](image)

$\text{f1 (ppm)}$

![NMR Spectrum](image)
32, 1H, DMSO-d6, 25°C

![Chemical Structure](image)

![NMR Spectrum](image)
32, 13C, DMSO-d6, 25°C
33, 1H, DMSO-d6, 25°C

![Chemical structure diagram](image_url)

![NMR spectrum](image_url)
33, 3°C, DMSO-d6, 25°C

[Chemical structure image]

S47
34, 1H, DMSO-d6, 25°C

![Chemical Structure](image)

![NMR Spectrogram](image)
34, 13C, DMSO-d6, 25°C

\[ \text{HO} \]

\[ \text{N} \]

\[ \text{S} \]

\[ \text{Au} \]

\[ \text{S} \]

\[ \text{N} \]

\[ \text{OH} \]

34
35, 1H, DMSO-d6, 25°C
35, 13C, DMSO-d6, 25°C
36, 1H, DMSO-d6, 25°C
36, 13C, DMSO-d6, 25°C

HO

36

37.67
33.10
27.98
28.38
28.58
28.25
28.13
37, 1H, DMSO-d6, 25°C
37, 13C, DMSO-δ6, 25°C

37
38, 1H, DMSO-d6, 25°C
38, 13C, DMSO-d6, 25°C
39, 1H, DMSO-d6, 25°C
39, 13C, DMSO-d6, 25°C