Electronic Supplementary Information

for

# NHC-Au-Xanthate Complexes

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## 1. General remarks

NMR spectra were recorded in $CDCl_3$, $CD_2Cl_2$or DMSO-$d_6$ solutions (unless indicated otherwise); chemical shifts are quoted on the δ scale, ppm, with the solvent signal as the internal standard ($CHCl_3$, $^1$H NMR 7.26 ppm; $CDCl_3$, $^{13}C\{^1H\}$ NMR 77.0 ppm, $^1$H NMR DMSO-$d_6$ 2.50 ppm, $^{13}C\{^1H\}$ NMR 39.5 ppm; $CD_3OD$ $^1$H NMR 4.87 ppm; $^{13}C\{^1H\}$ NMR 49.0 ppm; $CD_2Cl_2$$^1$H NMR 5.32 ppm; $^{13}C\{^1H\}$ NMR 54.0 ppm; $D_2O$ $^1$H NMR 4.79 ppm). High resolution mass spectra (HR MS) were taken using EI technique or electrospray ionization (ESI). NHC-Au-Cl complexes were prepared using the mixer mill Retsch MM400 (frequency and time are given below). Column chromatography was performed on Merck silica gel 60, 230-400 mesh. TLC was performed on aluminum sheets, Merck 60F 254. Anhydrous solvents were obtained by distillation over $CaCl_2$ ($CH_2Cl_2$) or Na/benzophenone (THF, 1,4-dioxane, toluene). Air-sensitive reactions were performed in flame-dried glassware under argon atmosphere. Organic extracts were dried over $Na_2SO_4$ or $MgSO_4$ and solvents were evaporated on a rotary evaporator. Reagents were used as they were purchased unless otherwise indicated**.** AuCl•$SMe_2$, AuCl•tht (tht - tetrahydrotiophene),[1] $Bu_4N(acac)$[2] were prepared according to the literature procedure. Xanthate salt **2a** ($X_a$) was received from Sigma Aldrich, and precipitated from a mixture acetone/petroleum ether before use. Xanthate salt **2b**,[3] **2c**,[4] and **2d**[4] were prepared according to literature procedure. To prevent the oxidation of xanthate salts, they were stored in dark glass bottle under atmosphere of argon.

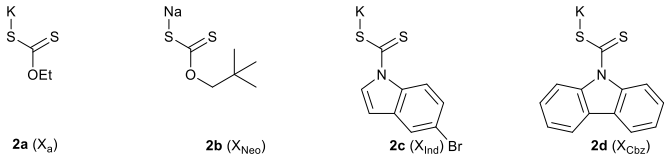



Fig. S1. Xanthate salts used in this studies.

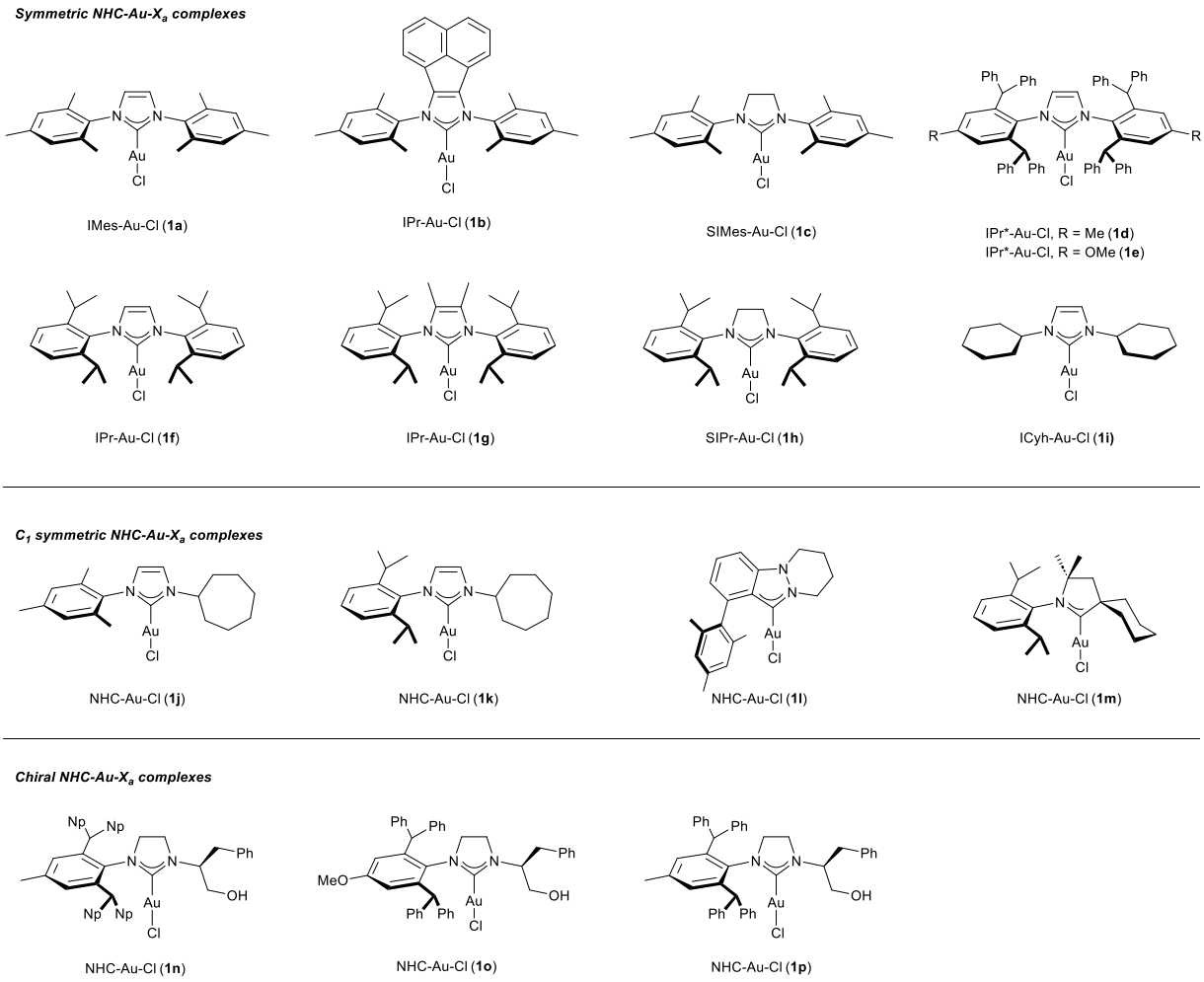



Fig. S2. NHC-Au-Cl complexes used in this studies.

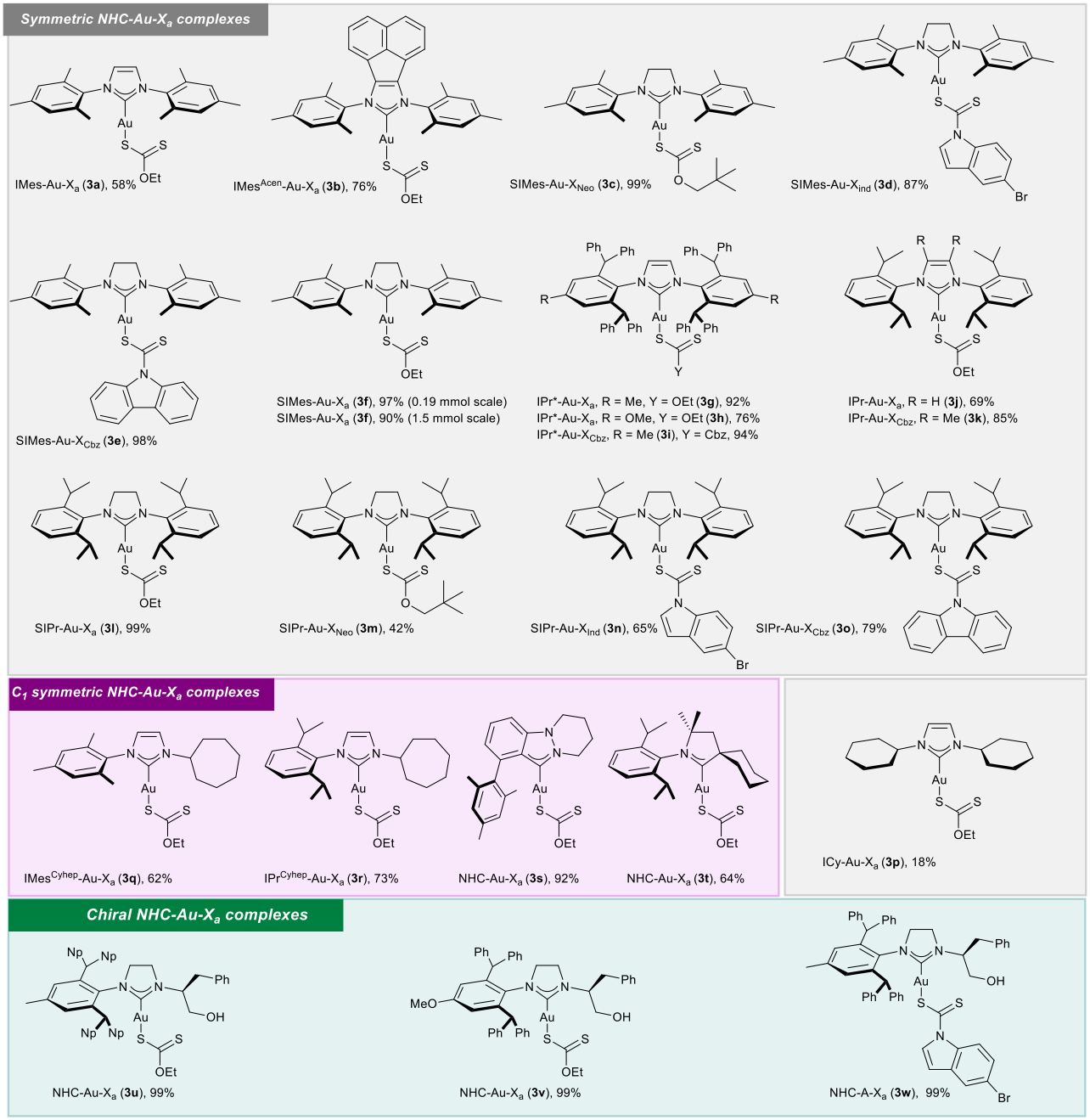



Fig. S3. NHC-Au-xanthate complexes prepared in this study.

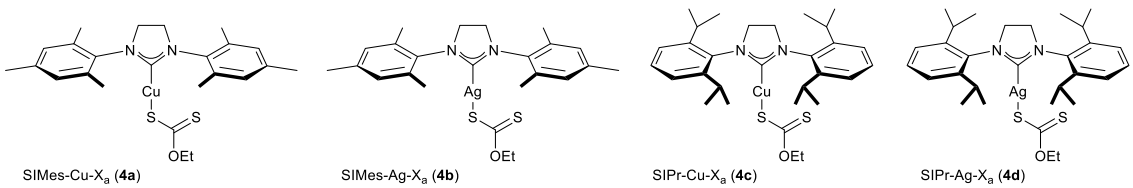



Fig. S4. NHC-Met-xanthate complexes used in this study.

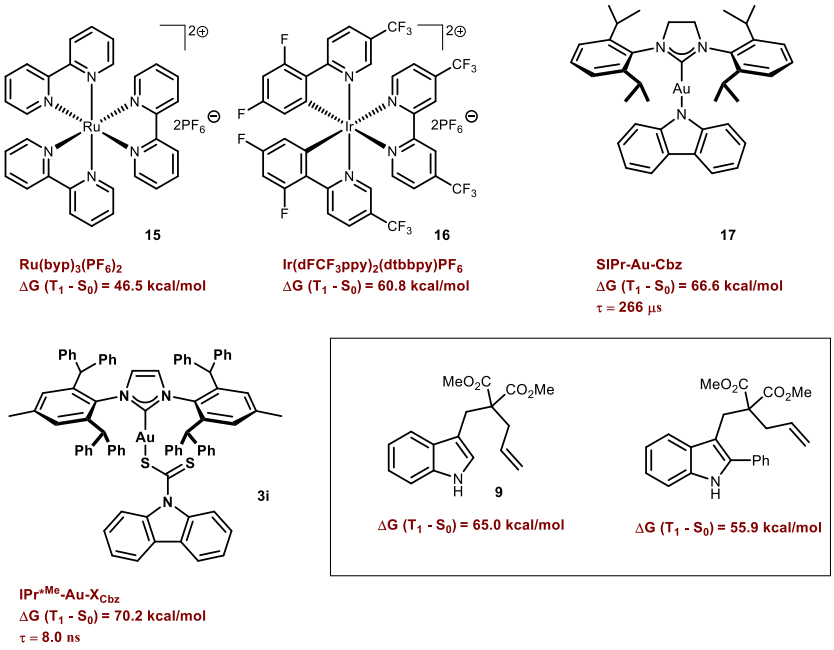
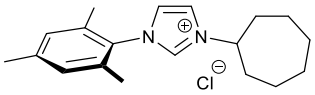


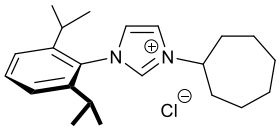

Fig. S5. Metal complexes (Ir, Ru, Au) used in this study to compare the efficiency in cycloadditions of indole **9** and coumarine **7**.

## 2. Synthesis of NHC precursors and xanthate salts



S1a

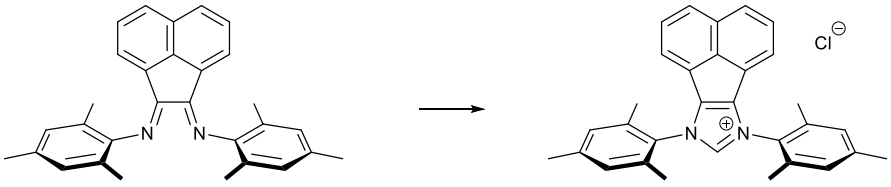
**Salt S1a** was prepared following the literature procedure.[5] To a mixture of 2,4,6-trimetylaniline (1.4 mL, 10.0 mmol) and cycloheptylamine (1.3 mL, 10.0 mmol, 1.0 equiv.), AcOH (2.6 mL) was added, and stirred for 5 min at 40 °|C (mixture A). In a separate 22 mL vial, mixture of 40% aq. formalin (1.15 mL, 10.0 mmol, 1.0 equiv.), glyoxal (740 μL, 10.0 mmol, 1.0 equiv.) and AcOH (2.6 mL) was heated at 40 °C (mixture B). Then mixture B was transferred to mixture A via Pasteur pipette, and stirred for 30 min at 40 °C. Then reaction mixture was cooled to rt, diluted with DCM (50 mL), and washed with water (2 × 50 mL), brine (2 × 50 ml), dried over $Na_2SO_4$, and evaporated. The residue was treated with EtOAc (10 mL), and heated to reflux for 15 min. to give a light yellow precipitate which was filtered, and dried in vacuo (1.19 g, 37%). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.81 – 10.74 (m, 1H), 7.84 – 7.78 (m, 1H), 7.20 – 7.15 (m, 1H), 6.93 (s, 2H), 5.35 – 5.23 (m, 2H), 2.32 – 1.97 (m, 4H) overlapping 2.28 (s, 3H) and 2.02 (br s, 6H), 1.85 – 1.52 (m, 8H). Spectral data are in agreement with those reported.[5]



S1b

**Salt S1b** was prepared in analogy to the reported procedure by Mauduit and co-workers.[6] To a mixture of 2,6-dizopropylaniline (1.9 mL, 10.0 mmol) and cycloheptylamine (1.3 mL, 10.0 mmol, 1.0 equiv.), AcOH (2.6 mL) was added, and stirred for 5 min at 60 °|C, and $MgSO_4$ (2.4 g, 20.0 mmol, 2.0 equiv.) was added (mixture A). In a separate 22 mL vial, mixture of 40% aq. formalin (1.15 mL, 10.0 mmol, 1.0 equiv.), glyoxal (740 μL, 10.0 mmol, 1.0 equiv.) and AcOH (2.6 mL) was heated at 60 °C, and $ZnCl_2$ solution (12.0 mL, 1M in $Et_2O$) was added (mixture B). Then mixture B was transferred to mixture A via Pasteur pipette, and stirred for 30 min at 60 °C. Then reaction mixture was cooled to rt, diluted wit DCM (50 mL), and washed with water (2 × 50 mL), brine (2 × 50 ml), dried over $Na_2SO_4$, and evaporated. The residue was chromatographed on silica (20-30% MTBE/hexanes) to give a brown oil which provided a light-brown foam after being dried under high vacuum (2.64 g). $^1$H NMR confirmed the

structure along with some impurities. The resulting salt was further purified by chromatography on aluminum oxide (acetone-5% EtOH/acetone) to give a light brown solid (1.27 g, 35%). mp 232 – 234 °C (*n*-pentane/DCM); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.88 (t, *J* = 1.8 Hz, 1H), 7.51 – 7.41 (m, 1H), 7.28 – 7.20 (m, 3H), 5.28 – 5.17 (m, 1H), 2.42 – 2.24 (m, 4H), 1.98 – 1.85 (m, 2H), 1.84 – 1.45 (m, 8H), 1.15 (d, *J* = 6.8 Hz, 6H), 1.08 (d, *J* = 6.8 Hz, 6H); $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 145.6, 136.3, 131.4, 130.5, 124.6, 124.4, 121.1, 77.3, 77.0, 76.7, 62.1, 36.0, 28.5, 27.3, 24.4, 24.2, 23.8. HR MS (APCI TOF) calcd for $C_{22}H_{33}N_2$ [M – Cl]$^{+}$: 325.2644; found 325.2646.

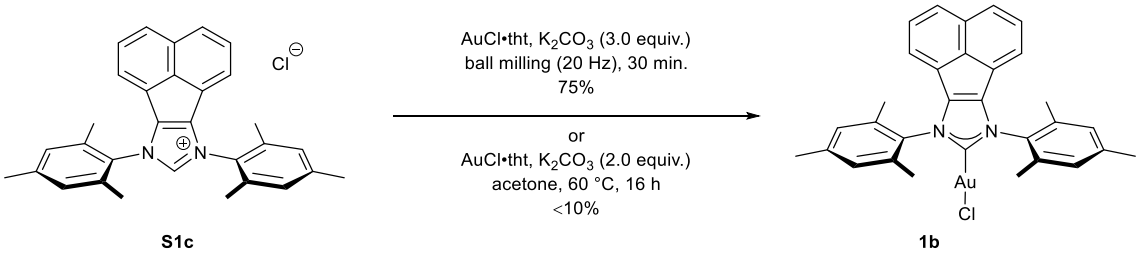



**S2a** **S1c**

**Salt S1c** was obtained via modified literature procedure.[7] Diimine **S2a** [7] was placed in 100 mL thick-wall ampule, and purged with argon. Then $EtOCH_2Cl$ (11.3 mL, 15.0 equiv.) was added, and the resulting mixture was heated at 100 °C (temp. of oil bath) for 16 h (the formation of brown-black solid was observed). Then reaction mixture was cooled to rt, and diluted with $Et_2O$ (20 mL). The resulting solid was filtered (filtrate possess a deep red-violet colour; the reaction mixture should be carefully grinding with s[atula to remove efficiently a colour impurities), washed with $Et_2O$ (2 × 20 mL) to give a dark yellow solid (3.78 g, 98%). $^{1}$H NMR (200 MHz, $CDCl_3$) δ 10.63 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 2H), 7.13 (s, 4H), 2.40 (s, 6H), 2.28 (br s, 12H). Spectral data are in agreement with those reported.[8]

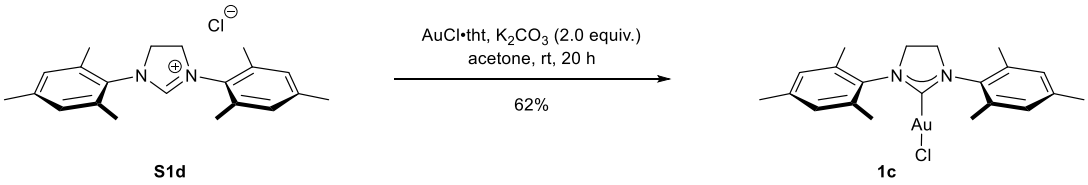
### 3. Synthesis of NHC-Au-Cl complexes

IMes-Au-Cl (**1a**),[9] IPr*Me-Au-Cl (**1d**),[9] IPr$^{*OMe}$-Au-Cl (**1e**),[10] IPr-Au-Cl (**1f**),[9] IPr$^{Me}$-Au-Cl (**1g**),[11] SIPr-Au-Cl (**1h**),[9] NHC-Au-Cl (**1l**),[12] NHC-Au-Cl (**1n**),[13] NHC-Au-Cl (**1o**),[13] and NHC-Au-Cl (**1p**)[13] were prepared according to literature procedure.



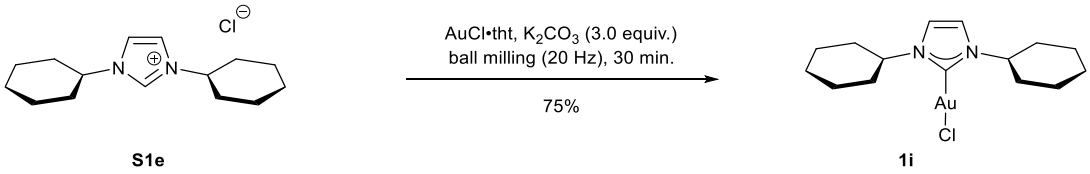

**S1c** **1b**

**Complex 1b** A 10 mL $ZrO_2$ milling jar was charged with slat **S1c** (100 mg, 0.215 mmol), AuCl•tht (68.9 mg, 0.215 mmol, 1.0 equiv, tht – tetrahydrothiophene), and $K_2CO_3$ (89.1 mg, 0.645 mmol, 3.0 equiv.), and the resulting mixture was milled for 30 min. in mixer mill Retsch MM400 at 20 Hz. Then reaction mixture was treated with DCM (20 mL), filtered through celite, and evaporated. The residue was dissolved in minimal volume of DCM, and precipitated with *n*-pentane to give a yellow solid (107.0 mg, 75%). It should be noted that reaction of NHC precursor **S1c** with AuCl•$SMe_2$ in the $K_2CO_3$ in acetone provided product with marginal yield (<10%) after 16 h at 60 °C, and unconsumed NHC precursor **S1c** was only observed. $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.83 (dd, *J* = 8.4, 0.7 Hz, 2H), 7.45 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.19 (q, *J* = 0.8 Hz, 4H), 7.07 (dd, *J* = 7.1, 0.7 Hz, 2H), 2.47 (s, 6H), 2.24 (s, 12H). Spectral data are in agreement with those reported.[14]



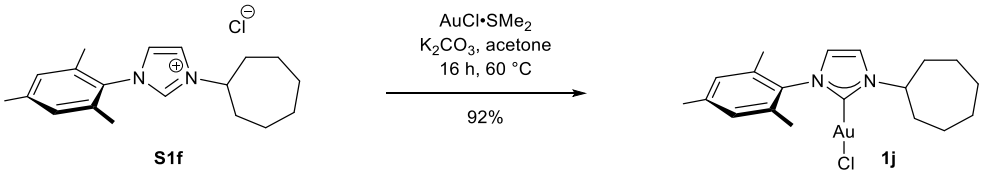

**S1d** **1c**

**Complex 1c** A 50 ml round-bottom flask was charged with NHC precursor **S1d** (200.0 mg, 0.58 mmol) and AuCl•tht (187.0 mg, 0.58 mmol, 1.0 equiv.) and anhydrous DCM (25 mL) was added. After 15 min. anhydrous $K_2CO_3$ (1.21 g, 8.75 mmol, 15.0 equiv.) was added and stirred for 20 h at rt (progress of the reaction was monitored by TLC). After 20 h, the mixture was filtered through pad of Celite, washed with DCM and the solvent was evaporated. The residue was redissolved in minimal volume of DCM (ca. 4 ml) and crashed with *n*-pentane (15 mL). The resulting solid was washed with *n*-pentane (3 ×5 mL), and filtered to give a white solid (195.3 mg, 62%). $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.03 (s, 4H), 4.01 (s, 4H), 2.34 (s, 18H). $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$) δ 195.5, 139.7, 136.3, 135.3, 130.2, 51.3, 21.4, 18.3. Spectral data are in agreement with those reported.[15]



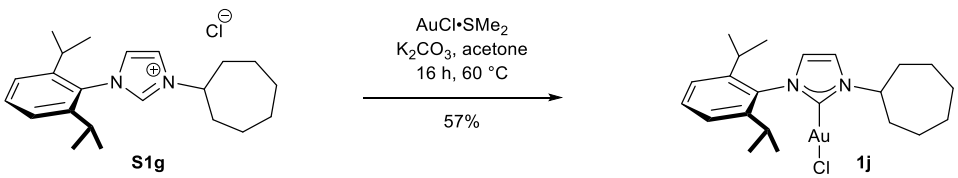

**S1e** **1i**

**Complex 1i** was prepared via modified literature procedure.[16] A 10 mL $ZrO_2$ milling jar was charged with salt **S1e** (100.0 mg, 0.372 mmol), AuCl•$SMe_2$ (109.6 mg, 0.215 mmol, 1.0 equiv.), and $K_2CO_3$ (154.2 mg, 1.12 mmol, 3.0 equiv.). The resulting mixture was milled for 30 min. in RETSCH instrument at 20 Hz. Then reaction mixture was extracted with DCM (20 mL), filtered through pad of Celite, and evaporated. The residue was dissolved in minimal volume of DCM, and precipitated with *n*-pentane to give an off-white solid (130.0 mg, 75%). mp 191 – 194 °C (*n*-pentane/DCM); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.02 (s, 2H), 4.61 – 4.48 (m, 4H), 2.13 – 2.00 (m, 4H), 1.94 – 1.80 (m, 4H), 1.78 – 1.69 (m, 2H), 1.68 – 1.55 (m, 4H), 1.54 – 1.38 (m, 4H), 1.31 – 1.13 (m, 2H); $^{13}$C{$^1$H} NMR (101 MHz, $CD_2Cl_2$) δ 168.9, 117.9, 61.6, 34.5, 26.0, 25.7. Known compound[17] (CAS: 944954-63-6). Lack of spectra for comparison.



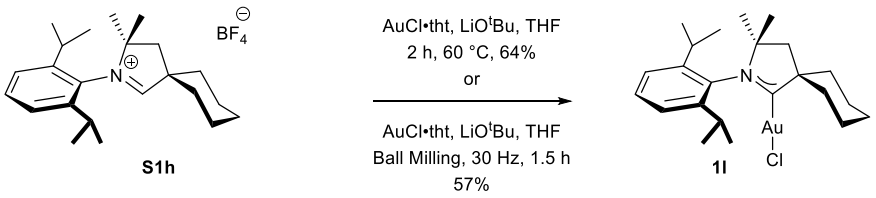

**S1f** **1j**

**Complex 1j** A 10 mL $ZrO_2$ milling jar was charged with NHC precursor **S1f** [5] (100.0 mg, 0.313 mmol), AuCl•$SMe_2$ (92.4 mg, 0.313 mmol) and anhydrous $K_2CO_3$ (130.0 mg, 0.940 mmol). The resulting mixture was milled for 30 min. in RETSCH at 20 Hz. Then reaction mixture was extracted by DCM (20 mL), filtered through a pad of Celite, and evaporated. The residue was treated with *n*-pentane (5 mL), filtered and dried in vacuo to give an off-white solid (147.0 mg, 92%). mp 192 – 194°C (*n*-pentane/DCM); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.25 – 7.21 (m, 1H), 7.02 (br s, 2H), 6.90 (d, *J* = 2.0 Hz, 1H), 4.92 – 4.82 (m, 1H), 2.36 (s, 3H), 2.26 – 2.17 (m, 2H), 2.02 (s, 6H), 1.99 – 1.58 (m, 11H); $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$) δ 171.1, 140.3, 135.8, 135.6, 129.8, 122.8, 118.3, 63.9, 36.8, 28.1, 25.1, 21.5, 18.1. HR MS (APCI TOF) calcd for $C_{19}H_{25}AuClN_2$ [M – H]$^-$: 513.1372; found: 513.1377.




**S1g** **1j**

**Complex 1j** A 4 mL vial was charged with NHC precursor **S1g** (100.0 mg, 0.31 mmol), AuCl•$SMe_2$ (91.9 mg, 0.31 mmol, 1.0 equiv.) and anhydrous $K_2CO_3$ (43.0 mg, 0.31 mmol, 1.0 equiv.) outside the glovebox. Then vial was transfer to glovebox, and anhydrous acetone (2 mL) was added. The resulting reaction mixture was stirred for 16 h at 60 °C, and cooled down to rt. The resulting brown suspension was filtered through syringe filter (washing with DCM), and the solvents were evaporated. The residue was dissolved in minimal volume of DCM (ca. 1 mL), and crashed with *n*-pentane to give an off-white solid. The precipitate was then collected by filtration, washed with *n*-pentane and dried under vacuum (92.7 mg, 57%). mp 187-189°C (*n*-pentane/DCM); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.51 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 2.0 Hz, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 4.93 – 4.82 (m, 1H), 2.37 (h, *J*= 6.9 Hz, 2H), 2.28 – 2.18 (m, 1H), 2.03 – 1.59 (m, 10H), 1.28 (d, *J* = 6.9 Hz, 6H), 1.12 (d, *J* = 6.9 Hz, 6H); $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$) δ 172.2, 146.6, 135.2, 131.0, 124.7, 124.1, 118.0, 63.9, 36.9, 29.0, 28.1, 25.1, 24.7, 24.6. HR MS (APCI TOF) calcd for $C_{22}H_{31}AuClN_2$ $[M - H]^-$ :555.1841 found: 555.1840.



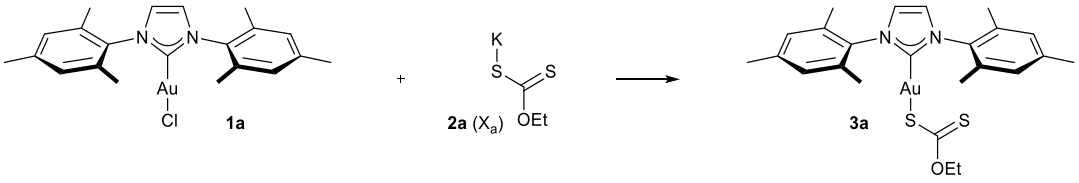

**Complex 1l** was prepared via modified literature procedure.[16] Procedure A: a flame dried Schlenk ampule was charged with NHC precursor **S1h** (100 mg, 0.242 mmol), LiO$^t$Bu (21.3 mg, 0.266 mmol, 1.1 equiv.) and AuCl•tht (93.1 mg, 0.29 mmol, 1.2 equiv.) inside the glovebox and dry THF (10 mL) was added. The reaction mixture was heated at 60 °C for 2 h. The resulting reaction mixture was evaporated under vacuum (during the evaporation the temperature in the heating bath was kept at 25 °C) and purified by column chromatography (DCM ) to give a white solid (86 mg, 64%).

Procedure B: a 10 mL $ZrO_2$ milling jar was charged with NHC precursor **S1h** (80.0 mg, 0.19 mmol), LiO$^t$Bu (17.0 mg, 0.21 mmol, 1.1 equiv.) and AuCl•tht (74.0 mg, 0.23 mmol, , 1.2 equiv.). The resulting mixture was milled at mixer mill Retsch MM400 at 30 Hz for 1.5 h. Then the reaction mixture was extracted by DCM, filtered through a pad of Celite, evaporated, and purified by column chromatography (DCM) to give **1l** as a white solid (61.8 mg, 57%). $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 7.48 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 2H), 2.77 (hept, *J* = 6.7 Hz, 2H), 2.35 – 2.23 (m, 2H), 2.17 (s, 2H), 1.84 – 1.81 (m, 2H), 1.77 – 1.70 (m, 1H), 1.59 – 1.53 (m, 2H), 1.49 – 1.39 (m, 3H), 1.41 – 1.34 (m, 11H), 1.31 (d, *J* = 6.8 Hz, 6H). $^{13}$C{$^1$H}

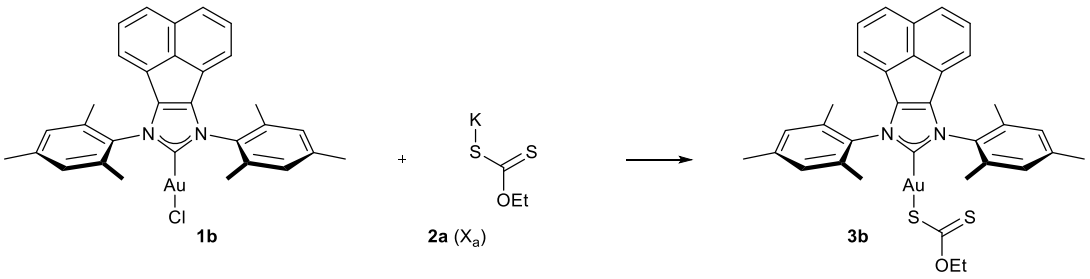
NMR (126 MHz, $CD_2Cl_2$) δ 236.2, 145.7, 134.6, 130.4, 125.5, 80.8, 59.4, 45.8, 41.0, 36.9, 31.1, 29.9, 29.6, 27.3, 25.7, 23.1, 22.2. Spectral data are in agreement with those reported.[15]

## 4. Synthesis of NHC-Au-X (X - xanthate) complexes

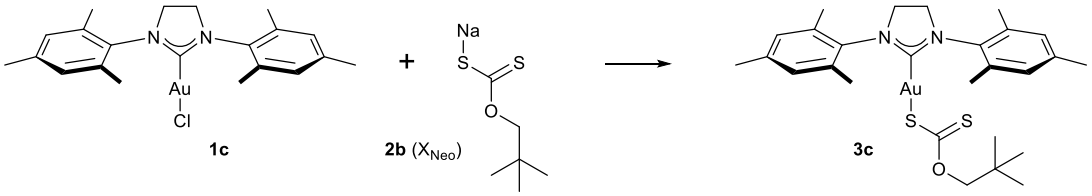
**General procedure 1 (GP1)**: A 4 mL vial was charged with NHC-Au-Cl (**1**) complex and xanthate salt **2** (1.0 equiv.). Then vial was transferred to glovebox, and anhydrous acetone was added (precipitation of a white solid was immediately observed). Then reaction mixture was stirred outside the glovebox for 16 h at rt. The resulting suspension was filtered through syringe filter (or pad of Celite), and evaporated. The residue was usually dissolved in minimal volume of DCM, and crashed with *n*-pentane to give a pure NHC-Au-X (**3**). In some cases, crude NHC-Au-X (**3**) were treated only with $Et_2O$ or *n*-pentane to give a pure product after filtration (in the case where DCM/*n*-pentane solvent system was not proper for the precipitation of the NHC-Au-X complexes, $Et_2O$/*n*-pentane solvent system was used for precipitation or the solid, after evaporation, was layered with *n*-pentane/*n*-heptane and filtered to afford the targeted NHC-Au-X **3** complex).




**Complex 3a** was synthesized according to GP1, using IMes-Au-Cl (**1a**) (100.0 mg, 0.187 mmol), potassium xanthate salt **S1** (29.9 mg, 0.187 mmol, 1.0 equiv) and anhydrous acetone (5 mL). The reaction mixture was stirred for 16 h at rt. The solvent was evaporated, and the residue was redissolved in DCM (3 mL), filtered through syringe filter to remove KCl, and solvent was evaporated. The residue was dissolved in minimal volume of DCM (2 mL), and crashed with *n*-pentane (12 mL) to give a white solid (67.4 mg, 58%). mp 164 – 165 °C (*n*-pentane/DCM); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.19 (s, 2H), 7.10 – 7.05 (m, 4H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 6H), 2.16 (s, 12H), 1.18 (t, *J* = 7.1 Hz, 2H); $^{13}$C{$^1$H} NMR (126 MHz, $CD_2Cl_2$) δ 225.3, 182.6, 140.4, 135.5, 135.4, 129.8, 123.1, 69.6, 21.5, 18.1, 14.3. HR MS (ESI TOF) calcd for $C_{24}H_{29}AuN_2OS_2$ $[M+H]^+$: 623.1465; found: 623.1456. Elem. anal. calcd for $C_{24}H_{29}AuN_2OS_2$: C, 46.30; H, 4.70; N, 4.50. Found: C, 46.25; H, 4.57; N, 4.47.

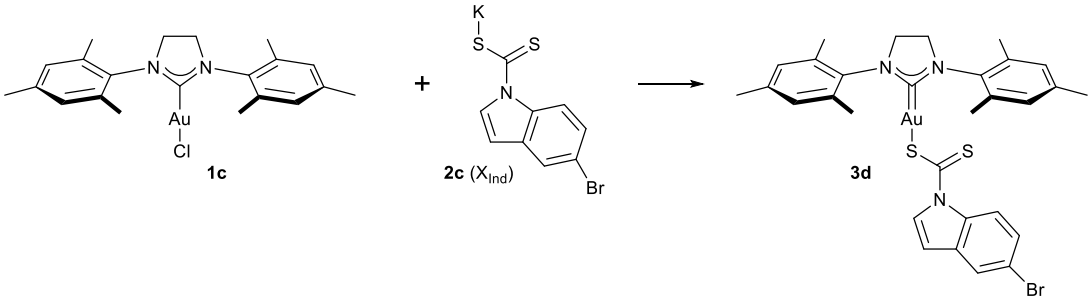



**Complex 3b** was synthesized according to GP1, using NHC-Au-Cl (**1b**) (107.0 mg, 0.162 mmol), potassium xanthate salt **2a** (26.0 mg, 0.162 mmol, 1.0 equiv.) and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt. The reaction mixture was filtered through syringe filter to remove KCl and washed thoroughly with acetone. The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (1.5 mL) and crashed with *n*-pentane (10 mL) to give an off-white solid (91.3 mg, 76%). mp 190 – 192 °C (*n*-pentane/DCM); $^{1}$H NMR (400 MHz, $CD_2Cl_2$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.46 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.18 (s, 4H), 7.07 (d, *J* = 6.9 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 6H), 2.27 (s, 12H), 1.19 (t, *J* = 7.1 Hz, 3H). ); $^{13}$C{$^{1}$H} NMR (50 MHz, $CD_2Cl_2$) δ 225.2, 187.0, 140.6, 138.1, 135.3, 133.9, 130.9, 130.2, 130.1, 129.0, 128.3, 125.8, 121.7, 69.7, 34.7, 22.9, 21.7, 18.3, 14.4. HR MS (ESI TOF) calcd for $C_{34}H_{34}AuN_2OS_2$ $[M+H]^+$: 747.1778; found: 747.1771. Elem. anal. calcd for $C_{34}H_{33}AuN_2OS_2$: C, 54.69; H, 4.45; N, 3.75. Found: C, 54.42; H, 4.48; N, 3.76.

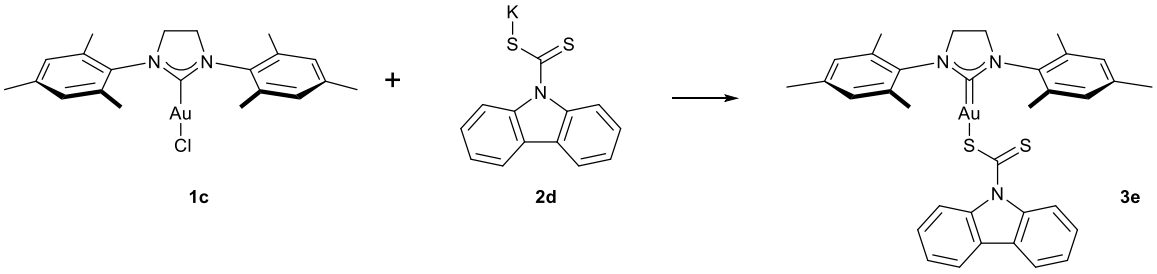



**Complex 3c** was synthesized according to GP1, using SIMes-Au-Cl (**1c**) (50.0 mg, 0.093 mmol), sodium xanthate salt **2b** (17.3 mg, 0.093 mmol, 1.0 equiv.), and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt. Then reaction mixture was filtered through syringe filter to remove NaCl and washed thoroughly with acetone. The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (2 mL) and crashed with *n*-pentane (12 mL) to give an off-white solid (61.0 mg, 99%). mp 203 - 205 °C (*n*-pentane/DCM); $^{1}$H NMR (400 MHz, $CD_2Cl_2$) δ 7.03 – 6.97 (m, 4H), 4.01 (s, 4H), 3.90 (s, 2H), 2.35 (s, 12H), 2.32 (s, 6H), 0.86 (s, 9H); $^{13}$C{$^{1}$H} NMR (101 MHz, $CD_2Cl_2$) δ 225.7, 204.0, 139.5, 136.3, 135.4, 130.2, 83.6, 51.5, 31.8, 27.1, 21.4, 18.4. HR MS (ESI TOF) calcd for $C_{27}H_{38}AuN_2OS_2$:

667.2091; found: 667.2088. Elem. anal. calcd for $C_{27}H_{37}AuN_2OS_2$: C, 48.64; H, 5.59; N, 4.20. Found: C, 48.65; H, 5.50; N, 4.28.

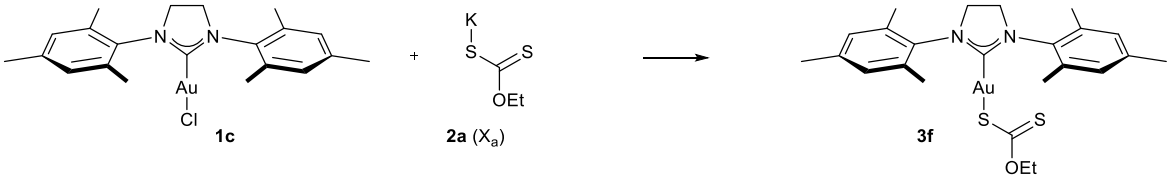



**Complex 3d** was synthesized according to GP1, using SIMes-Au-Cl (**1c**) (50.0 mg, 0.093 mmol), potassium xanthate salt **2c** (28.8 mg, 0.093 mmol, 1.0 equiv.), and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt. The reaction mixture was filtered through syringe filter to remove KCl (string filter was thoroughly washed with acetone). Then solvent was evaporated, and the residue was layered with *n*-pentane and filtered to give an orange solid (64.0 mg, 89%). mp 91 – 94 °C (*n*-pentane/DCM); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 8.77 (d, *J* = 9.0 Hz, 1H), 8.16 (d, *J* = 3.8 Hz, 1H), 7.59 (d, *J* = 2.1 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.10 – 6.93 (m, 4H), 6.38 – 6.37 (m, 1H), 4.04 (s, 4H), 2.39 (s, 12H), 2.33 (s, 6H); $^{13}$C{$^1$H} NMR (50 MHz, $CD_2Cl_2$) δ 213.8, 202.3, 139.4, 136.4, 135.3, 134.5, 131.7, 130.0, 126.9, 123.5, 119.7, 116.1, 105.9, 51.5, 21.5, 18.4. HR MS (ESI TOF) calcd for $C_{30}H_{32}AuN_3OS_2Br$ $[M+H]^+$: 774.0887; found: 774.0872. Elem. anal. calcd for $C_{30}H_{31}AuBrN_3S_2$: C, 46.52; H, 4.03; N, 5.42. Found: C, 46.78; H, 4.16; N, 5.22.

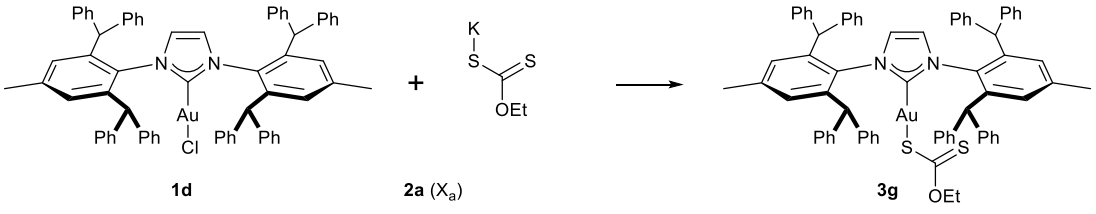



**Complex 3e** was synthesized according to GP1, using SIMes-Au-Cl (**1c**) (50.0 mg, 0.093 mmol), potassium xanthate salt **2d** (26.1 mg, 0.093 mmol, 1.0 equiv.), and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt. Then reaction mixture was filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was layered with *n*-pentane and filtered to give an orange solid (68.0 mg, 98%). mp 158 – 160 °C (*n*-pentane/DCM); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 8.41 – 8.38 (m, 2H), 7.97 – 7.94 (m, 2H), 7.37 – 7.33 (m, 2H), 7.28 – 7.24 (m, 2H), 7.04 –

6.84 (m, 4H), 4.00 (s, 4H), 2.31 (s, 6H), 2.30 (s, 12H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CD_2Cl_2$) δ 217.4, 202.9, 140.7, 139.5, 136.4, 135.3, 130.1, 130.1, 126.3, 125.4, 122.3, 119.7, 116.4, 51.5, 21.5, 18.3. HR MS (ESI TOF) calcd for $C_{34}H_{34}AuN_3S_2$ $[M+H]^+$: 746.1938; found: 746.1924. Elem. anal. calcd for $C_{34}H_{34}AuN_3S_2$: C, 54.76; H, 4.60; N, 5.63. Found: C, 54.68; H, 4.60; N, 5.66.

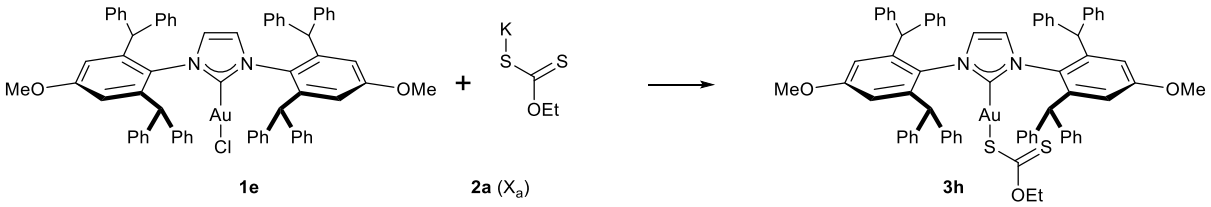



**Complex 3f** was synthesized according to GP1, using SIMes-Au-Cl (**1c**) (100.0 mg, 0.186 mmol), potassium xanthate salt **2a** (29.8 mg, 0.186 mmol, 1.0 equiv.) and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt, and filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (2 mL) and crashed with *n*-pentane (10 mL) to give a white solid (112.5 mg, 97%). The same reaction was conducted on large scale using complex SIMes-Au-Cl (810.0 mg, 1.5 mmol), potassium xanthate salt **2a** (241.0 mg, 1.5 mmol, 1.0 equiv.) and anhydrous acetone (40 mL). The reaction mixture was stirred for 24 h. The reaction mixture was worked up as before to afford complex **3f** as a white solid (810.0 mg, 90%). mp 194 – 197 °C (*n*-pentane/DCM); $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) δ 7.01 (s, 4H), 4.25 (q, $J$ = 7.1 Hz, 2H), 4.01 (s, 4H), 2.36 (s, 12H), 2.32 (s, 6H), 1.14 (t, $J$ = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CD_2Cl_2$) δ 225.2, 203.7, 139.5, 136.4, 135.4, 130.1, 69.5, 51.5, 21.4, 18.4, 14.3; HR MS (ESI TOF) calcd for $C_{24}H_{31}AuN_2OS_2$ $[M+H]^+$: 625.1622; found: 625.1636.

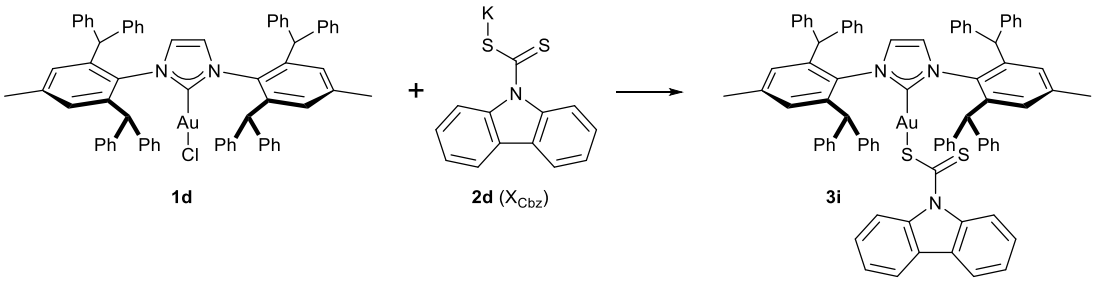



**Complex 3g** was synthesized according to GP1, using IPr*$^{Me}$-Au-Cl (**1d**) (100.0 mg, 0.087 mmol), potassium xanthate salt **2a** (14.0 mg, 0.087 mmol, 1.0 equiv.), and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt. Then reaction mixture was filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (ca. 1 mL)

and crashed with *n*-pentane (12 mL) to give an off-white solid (99.0 mg, 92%). mp 225 – 227 °C (*n*-pentane/DCM); $^{1}$H NMR (400 MHz, $CD_2Cl_2$) δ 7.24 – 7.10 (m, 32H), 6.93 (s, 4H), 6.92 – 6.88 (m, 8H), 5.90 (s, 2H), 5.30 (s, 4H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.24 (s, 6H), 0.89 (t, *J* = 7.1 Hz, 3H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CD_2Cl_2$) δ 225.0, 184.3, 143.3, 143.2, 141.7, 140.8, 134.5, 130.8, 130.3, 129.9, 129.9, 129.0, 129.0, 127.3, 127.2, 124.0, 69.4, 51.8, 22.1, 14.2; HR MS (ESI TOF) calcd for $C_{72}H_{62}AuN_2OS_2$ [M+H]$^{+}$: 1231.3969; found: 1231.3961. Elem. anal. calcd for $C_{72}H_{61}AuN_2OS_2 \bullet H_2O$: C, 69.22; H, 5.08; N, 2.24. Found: C, 69.40; H, 5.00; N, 2.33.

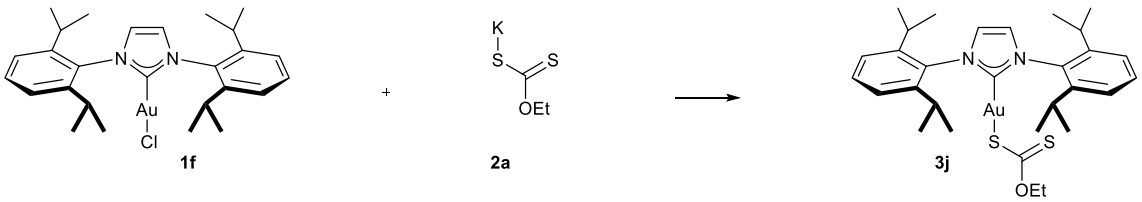



**Complex 3h** was synthesized according to GP1, using IPr*$^{OMe}$-Au-Cl (**1e**) (100.0 mg, 0.085 mmol), potassium xanthate salt **2a** (13.6 mg, 0.085 mmol, 1.0 equiv.), and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt. The reaction mixture was filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (ca. 1 mL) and crashed with *n*-pentane (ca. 10 mL) to give a yellow solid (81.4 mg, 76%). mp > 340 °C (*n*-pentane/DCM); $^{1}$H NMR (400 MHz, $CD_2Cl_2$) δ 7.23 – 7.15 (m, 32H), 6.96 – 6.87 (m, 8H), 6.60 (s, 4H), 5.86 (s, 2H), 5.31 (s, 4H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.59 (s, 6H), 0.92 (t, *J* = 7.1 Hz, 3H); $^{13}$C{$^{1}$H} NMR (50 MHz, $CD_2Cl_2$) δ 224.8, 184.7, 160.6, 143.4, 142.9, 142.9, 130.1, 129.7, 128.9, 128.9, 127.2, 127.2, 124.0, 115.3, 69.4, 55.7, 52.0, 14.2; HR MS (ESI TOF) calcd for $C_{72}H_{62}AuN_2O_3S_2$ [M+H]$^{+}$: 1263.3867; found: 1263.3862. Elem. anal. calcd for $C_{72}H_{61}AuN_2O_3S_2 \bullet H_2O$: C, 67.49; H, 4.96; N, 2.19. Found: C, 69.65; H, 4.85; N, 2.20.

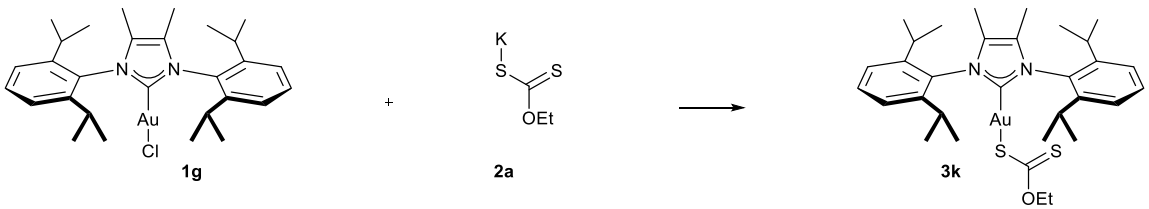



**Complex 3i** was synthesized according to modified GP1, using IPr*$^{Me}$-Au-Cl (**1d**) (72.3 mg, 0.063 mmol), potassium xanthate salt **2d** (21.3 mg, 0.076 mmol, 1.2 equiv.), and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt. Then reaction mixture was

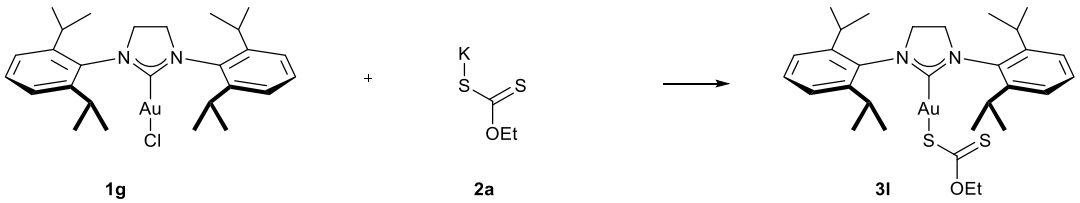
filtered through pad of silica to remove KCl (eluting with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (ca. 1 mL) and crashed with *n*-pentane (12 mL) to give an deep orange solid (79.9 mg, 94%). mp 162 – 164 °C (*n*-pentane/DCM); $^{1}$H NMR (400 MHz, $CD_2Cl_2$) δ 8.65 – 8.61 (m, 2H), 8.07 – 8.03 (m, 2H), 7.53 – 7.48 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.26 (m, 8H), 7.25 – 7.15 (m, 22H), 6.99 (s, 4H), 6.98 – 6.94 (m, 8H), 5.97 (s, 2H), 5.42 (s, 4H), 2.27 (s, 6H); $^{13}$C{$^{1}$H} NMR (100 MHz, $CD_2Cl_2$) δ 216.6, 183.6, 143.6, 143.3, 141.7, 140.9, 140.8, 134.6, 130.8, 130.5, 130.0, 129.0, 129.0, 127.3, 127.2, 126.4, 125.3, 124.1, 122.2, 119.8, 116.2, 52.0, 22.1; HR MS (ESI TOF) calcd for $C_{82}H_{64}AuN_3S_2$ $[M+H]^+$: 1352.4285; found: 1352.4280. Elem. anal. calcd for $C_{82}H_{64}AuN_3S_2$: C, 72.82; H, 4.77; N, 3.11. Found: C, 67.57; H, 4.61; N, 2.90. The discrepancy in the elemental analysis results is likely owing to non-stoichiometric amount of DCM in the solid. Although rigorous drying for prolonged time under high vacuum, DCM could not be removed completely.



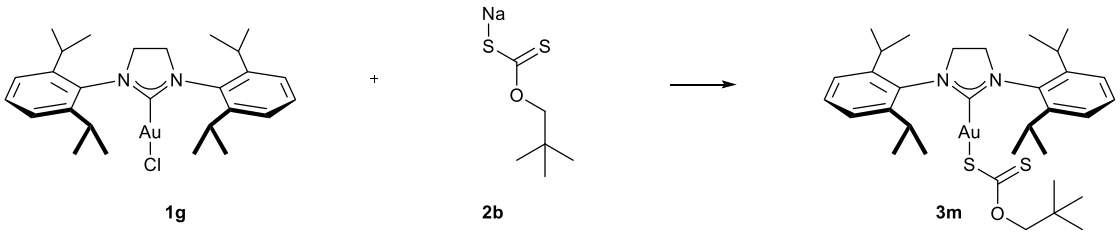

**Complex IPr-Au-X$_a$ (3j)** was synthesized according to GP1, using IPr-Au-Cl (**1f**) (100.0 mg, 0.16 mmol), potassium xanthate salt **2a** (25.8 mg, 0.16 mmol, 1.0 equiv.), and anhydrous acetone (4 mL). The reaction mixture was stirred for 16 h at rt. The solvent was evaporated, and the residue was redissolved in DCM (3 mL), filtered through syringe filter to remove KCl, and solvent was evaporated. The residue was layered with *n*-heptane (8 mL), and stirred for 30 min. at rt. The resulting solid was filtered to give a white solid (53.4 mg, 69%). mp 170 – 172 °C (*n*-heptane); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.41 (m, 2H), 7.33 – 7.26 (m, 4H), 7.18 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.64 – 2.51 (m, 4H), 1.34 (d, *J* = 6.9 Hz, 11H), 1.22 (d, *J* = 6.9 Hz, 10H), 1.08 (t, *J* = 7.1 Hz, 3H); $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) δ $^{13}$C NMR (126 MHz, $CD_2Cl_2$) δ 225.1, 184.5, 146.4, 134.7, 131.1, 124.7, 124.0, 69.3, 29.4, 24.8, 24.3, 14.3. HR MS (ESI TOF) calcd for $C_{30}H_{42}AuN_2OS_2$: 707.2404; found: 707.2394. Elem. anal. calcd for $C_{30}H_{41}AuN_2OS_2$: C, 50.98; H, 5.85; N, 3.96. Found: C, 50.74; H, 5.75; N, 3.94.



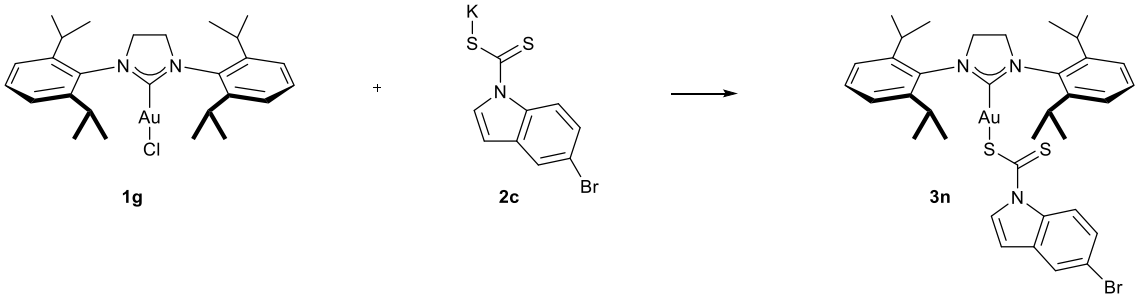
**Complex IPr-Au-X$_a$ (3k)** was synthesized according to GP1, using IPr$^{Me}$-Au-Cl (**1g**) (75.0 mg, 0.116 mmol), potassium xanthate salt **2a** (18.5 mg, 0.116 mmol, 1.0 equiv.), and anhydrous acetone (3 mL). The reaction mixture was stirred for 16 h at rt. The solvent was evaporated, and the residue was passed through pad of celite. Then solvent was evaporated, and the solid residue was treated with $Et_2O$ (2 mL), filtered and dried in vacuo to give product a white solid (72.2 mg, 85%). mp 184 – 186 °C (n-pentane/DCM); $^1$H NMR (400 MHz, $CD_2Cl_3$) δ 7.58 – 7.51 (m, 2H), 7.39 – 7.31 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.57 – 2.43 (m, 4H), 1.96 (s, 6H), 1.35 (d, *J* = 6.9 Hz, 12H), 1.25 (d, *J* = 6.9 Hz, 12H), 1.06 (t, *J* = 7.1 Hz, 3H); $^{13}$C{$^1$H} (100 MHz, $CD_2Cl_2$) δ 225.2, 180.7, 146.7, 133.1, 131.0, 127.1, 124.8, 69.2, 54.5, 54.3, 54.0, 53.7, 53.5, 29.3, 25.4, 23.7, 14.4, 10.0. HR MS (ESI TOF) calcd for $C_{32}H_{46}AuN_2OS_2$: 735.2717; found: 735.2726. Elem. anal. calcd for $C_{32}H_{45}AuN_2OS_2$: C, 52.31; H, 6.17; N, 3.81. Found: C, 52.30; H, 6.16; N, 3.76.




**Complex 3l** was synthesized according to GP1, using SIPr-Au-Cl (**1g**) (100.0 mg, 0.160 mmol), potassium xanthate salt **2a** (25.7 mg, 0.160 mmol, 1.0 equiv.), and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt. The reaction mixture was filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (ca. 1 mL) and crashed with *n*-pentane (10 mL) to give a white solid (115.4 mg, 99%). mp 207 – 210 °C (*n*-pentane/DCM); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.45 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 4H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 4H), 3.17 – 3.07 (m, 4H), 1.43 (d, *J* = 6.8 Hz, 12H), 1.36 (d, *J* = 6.9 Hz, 12H), 1.02 (t, *J* = 7.1 Hz, 3H); $^{13}$C{$^1$H} NMR (50 MHz, $CD_2Cl_2$) δ 224.5, 204.2, 147.3, 134.6, 130.2, 124.9, 69.1, 54.3, 29.5, 25.4, 24.4, 14.3. HR MS (ESI TOF) calcd for $C_{30}H_{44}AuN_2OS_2$ $[M+H]^+$: 709.2561; found: 709.2548. Elem. anal. calcd for $C_{32}H_{43}AuN_2OS_2$: C, 50.84; H, 6.12; N, 3.95. Found: C, 50.65; H, 6.14; N, 3.97.

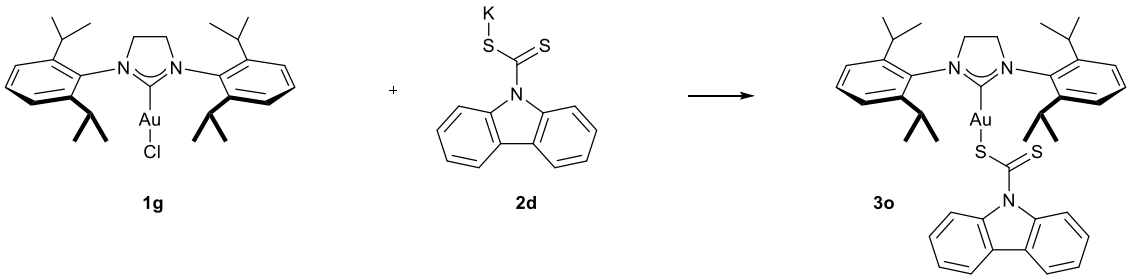



**Complex 3m** was synthesized according to GP1, using SIPr-Au-Cl (**1g**) (100.0 mg, 0.161 mmol), sodium xanthate salt **2b** (29.9 mg, 0.161 mmol, 1.0 equiv.), and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt. Then reaction mixture was filtered through syringe filter to remove NaCl (syringe filter thoroughly washed with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (1 mL) and crashed with *n*-pentane (12 mL) to give an off-white solid (50.0 mg, 42%). mp 199 – 202 °C (*n*-pentane/DCM); $^{1}$H NMR (400 MHz, $CD_2Cl_2$) δ 7.49 – 7.39 (m, 2H), 7.27 (br d, *J* = 7.8 Hz, 4H), 4.06 (s, 4H), 3.83 (s, 2H), 3.15 – 3.08 (m, 4H), 1.43 (d, *J* = 6.8 Hz, 12H), 1.35 (d, *J* = 6.9 Hz, 12H), 0.81 (s, 9H); $^{13}$C{$^{1}$H} NMR (50 MHz, $CD_2Cl_2$) δ 225.6, 204.1, 147.3, 134.8, 130.1, 124.9, 83.4, 54.3, 31.8, 29.5, 26.9, 25.4, 24.5. HR MS (ESI TOF) calcd for $C_{33}H_{49}AuN_2OS_2$ $[M+H]^+$: 751.3030; found: 751.3014. Elem. anal. calcd for $C_{33}H_{49}AuN_2OS_2$: C, 52.79; H, 6.58; N, 3.73. Found: C, 52.72; H, 6.54; N, 3.72.

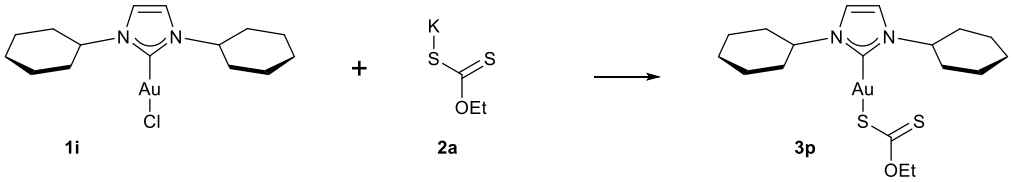



**Complex 3n** was synthesized according to GP1, using SIPr-Au-Cl (**1g**) (100.0 mg, 0.161 mmol), potassium xanthate salt **2c** (49.8 mg, 0.161 mmol, 1.0 equiv.), in anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt. and afterwards filtered through syringe filter to remove KCl and washed thoroughly with acetone. The solvent was evaporated, and the residue was layered with *n*-pentane (12 mL) and filtered to give an orange solid (90.0 mg, 65%). mp 92 – 96 °C (*n*-pentane/DCM); $^{1}$H NMR (400 MHz, $CD_2Cl_2$) δ 8.74 (d, *J* = 9.0 Hz, 1H), 8.14 (d, *J* = 3.8 Hz, 1H), 7.56 (d, *J* = 2.1 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 4H), 7.24 (dd, *J* = 9.0, 2.1 Hz, 1H), 6.34 – 6.33 (m, 1H), 4.10 (s, 4H), 3.18 – 3.11 (m, 4H), 1.46 (d, *J* = 6.8 Hz, 12H), 1.37 (d, *J* = 6.9 Hz, 12H); $^{13}$C{$^{1}$H} NMR (50 MHz, $CD_2Cl_2$) δ 212.9, 203.3, 147.4, 135.9, 134.8, 134.5, 131.7, 130.2, 126.7, 125.0, 123.4, 119.7, 116.0, 105.6, 54.3, 29.6,

25.4, 24.6. HR MS (ESI TOF) calcd for $C_{36}H_{44}AuN_3S_2Br$ $[M+H]^+$: 858.1826; found: 858.1809. Elem. anal. calcd for $C_{41}H_{55}AuBrN_3S_2.0.5(C_5H_{12})$: C, 51.68; H, 5.52; N, 4.70. Found: C, 51.82; H, 5.52; N, 4.55.

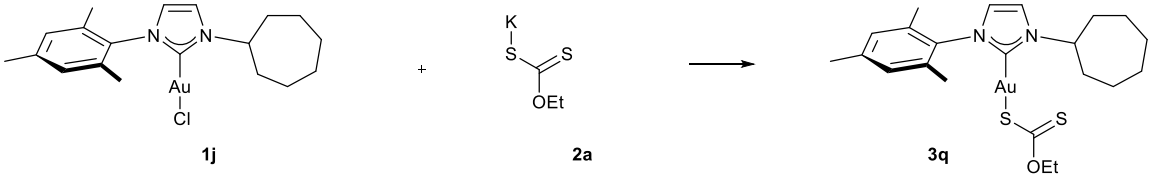



**Complex 3o** was synthesized according to GP1, using SIPr-Au-Cl (**1g**) (100.0 mg, 0.161 mmol), potassium xanthate salt **2d** (45.2 mg, 0.161 mmol, 1.0 equiv.), and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt. The reaction mixture was filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was layered with *n*-heptane (12 mL) and filtered to give an orange solid (105.4 mg, 79%). mp 287 – 290 °C (*n*-heptane); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 8.39 - 8.37 (m, 2H), 7.93 - 7.90 (m, 2H), 7.47 – 7.43 (m, 2H), 7.34 – 7.28 (m, 6H), 7.24 – 7.20 (m, 2H), 4.11 (s, 4H), 3.21 – 3.11 (m, 4H), 1.48 (d, *J* = 6.8 Hz, 12H), 1.37 (d, *J* = 6.9 Hz, 12H); $^{13}$C{$^1$H} NMR (101 MHz, $CD_2Cl_2$) δ 216.6, 203.9, 147.5, 140.7, 134.9, 130.4, 126.3, 125.3, 125.1, 122.2, 119.6, 116.3, 54.3, 29.6, 25.4, 24.6. HR MS (ESI TOF) calcd for $C_{40}H_{47}AuN_3S_2$ $[M+H]^+$: 830.2877; found: 830.2864. Elem. anal. calcd for $C_{40}H_{44}AuN_3S_2.H_2O$: C, 56.66; H, 5.71; N, 4.96. Found: C, 56.79; H, 5.67; N, 4.85.



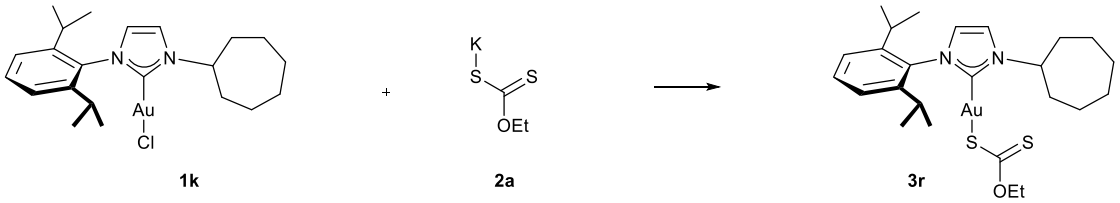

**Complex 3p** was synthesized according to GP1, using ICy-Au-Cl (**1i**) (50.0 mg, 0.108 mmol), potassium xanthate salt **2a** (17.2 mg, 0.108 mmol, 1.0 equiv.), and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt. Then reaction mixture was filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (1 mL) and crashed with *n*-pentane (10 mL) to give an off-white solid (10.5 mg, 18%). mp 159 – 162 °C (*n*-pentane/DCM); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.02 (s, 2H), 4.70 – 4.62 (m, 2H), 4.50 (q, *J* = 7.1 Hz, 2H), 2.18 – 2.05 (m, 4H), 1.93 – 1.83 (m, 4H), 1.79 – 1.71 (m, 2H), 1.69 – 1.58 (m,

4H), 1.55 – 1.43 (m, 4H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.29 – 1.17 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CD_2Cl_2$) δ 226.8, 177.9, 117.8, 70.2, 61.4, 34.7, 26.1, 25.8, 14.6. HR MS (ESI TOF) calcd for $C_{18}H_{30}AuN_2OS_2$ $[M+H]^+$: 551.1465; found: 551.1458. Elem. anal. calcd for $C_{22}H_{31}AuN_2OS_2 \bullet 0.5CH_2Cl_2$: C, 37.47; H, 5.10; N, 4.72. Found: C, 37.43; H, 5.12; N, 4.84.




**1j** **2a** **3q**

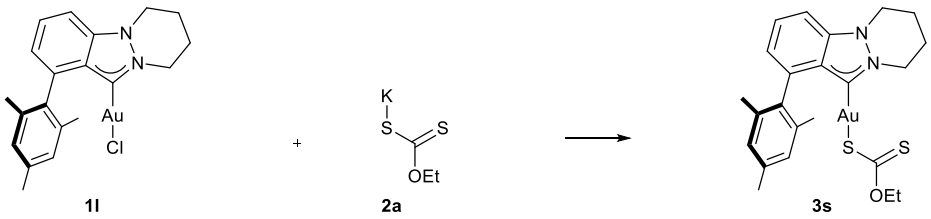
**Complex 3q** was synthesized according to GP1, using NHC-Au-Cl (**1j**) (113.0 mg, 0.219 mmol), potassium xanthate salt **2a** (35.2 mg, 0.219 mmol, 1.0 equiv.), and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt, and then filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (1 mL) and crashed with *n*-pentane (10 mL) to give an off-white solid (82.3 mg, 62%). mp 58 – 61°C (*n*-pentane/DCM); $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) δ 7.25 (br d, *J* = 2.0 Hz, 1H), 7.01 (s, 2H), 6.92 (br d, *J* = 1.9 Hz, 1H), 5.04 – 4.97 (m, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 2.28 – 2.19 (m, 2H), 2.03 (s, 6H), 2.02 – 1.92 (m, 2H), 1.91 – 1.79 (m, 2H), 1.77 – 1.60 (m, 6H), 1.28 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CD_2Cl_2$) δ 226.2, 179.9, 140.1, 135.6, 129.7, 122.9, 118.3, 69.9, 63.7, 36.9, 28.1, 25.2, 21.5, 18.1, 14.5; HR MS (ESI TOF) calcd for $C_{22}H_{32}AuN_2OS_2$ $[M+H]^+$: 601.1622; found: 601.1611. Elem. anal. calcd for $C_{22}H_{31}AuN_2OS_2$: C, 44.00; H, 5.20; N, 4.66. Found: C, 44.28; H, 5.22; N, 4.71.




**1k** **2a** **3r**

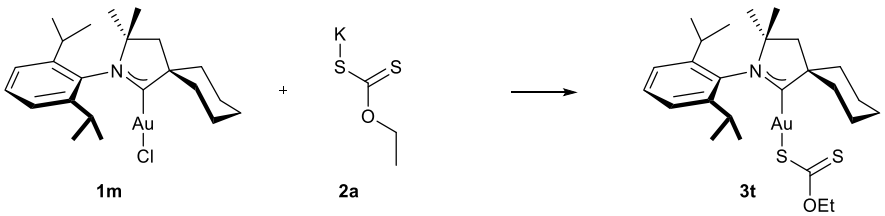
**Complex 3r** was synthesized according to GP1, using NHC-Au-Cl (**1k**) (103.0 mg, 0.198 mmol), potassium xanthate salt **2a** (31.8 mg, 0.198 mmol, 1.0 equiv.), and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt, and then filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (1 mL) and crashed with *n*-pentane (10 mL) to give an off-white solid (93.5 mg, 73%). mp 155 – 157°C (*n*-pentane/DCM); $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) δ 7.52 – 7.45 (m, 1H), 7.31 – 7.23 (m, 3H), 6.97

(d, *J* = 1.9 Hz, 1H), 5.09 – 4.98 (m, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.49 – 2.35 (m, 2H), 2.31 – 2.21 (m, 2H), 2.07 - 1.92 (m, 2H), 1.92 – 1.59 (m, 8H), 1.28 (d, *J* = 6.9 Hz, 6H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.12 (d, *J* = 6.8 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CD_2Cl_2$) δ 226.2, 180.8, 146.6, 135.3, 130.8, 124.6, 124.1, 118.1, 69.8, 63.7, 37.0, 29.0, 28.1, 25.2, 24.6, 24.6, 14.5; HR MS (ESI TOF) calcd for $C_{25}H_{38}AuN_2OS_2$ $[M+H]^+$: 643.2091; found: 643.2101. Elem. anal. calcd for $C_{25}H_{37}AuN_2OS_2$: C, 46.72; H, 5.80; N,4.36. Found: C, 46.74; H, 5.79; N, 4.30.




1l 2a 3s

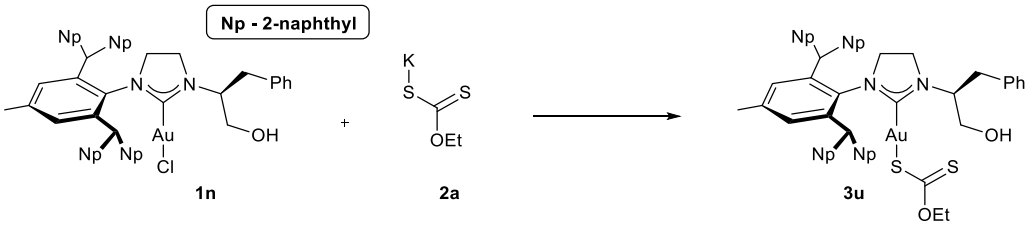
**Complex 3s** was synthesized according to GP1, using gold(I) complex (**1l**) (81.3 mg, 0.159 mmol, NHC precursor was prepared followed by lit. procedure published by Szostak[12]), potassium xanthate salt **2a** (25.5 mg, 0.159 mmol, 1.0 equiv.) and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt, and afterwards filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (1 mL) and crashed with *n*-pentane (6 mL) to give an off-white solid (89.3 mg, 92%). mp 82 – 84°C (*n*-pentane/DCM); $^{1}H$ NMR (500 MHz, $CD_2Cl_2$) δ 7.75 – 7.70 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 7.1 Hz, 1H), 6.94 (s, 2H), 4.80 – 4.70 (m, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.31 – 4.16 (m, 2H), 2.37 – 2.14 (m, 4H) overlapping 2.34 (s, 3H), 1.89 (s, 6H), 1.32 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CD_2Cl_2$) δ 227.2, 180.8, 142.9, 141.9, 138.2, 136.5, 135.7, 132.6, 130.1, 128.6, 124.5, 108.4, 69.8, 48.0, 22.5, 21.6, 21.5, 21.0, 14.6; HR MS (APCI TOF) calcd for $C_{23}H_{38}AuN_2OS_2$ $[M+H]^+$: 609.1309; found: 609.1302. Elem. anal. calcd for $C_{23}H_{27}AuN_2OS_2$: C, 45.39; H, 4.47; N, 4.60. Found: C, 44.34; H, 4.27; N, 4.58.




1m 2a 3t

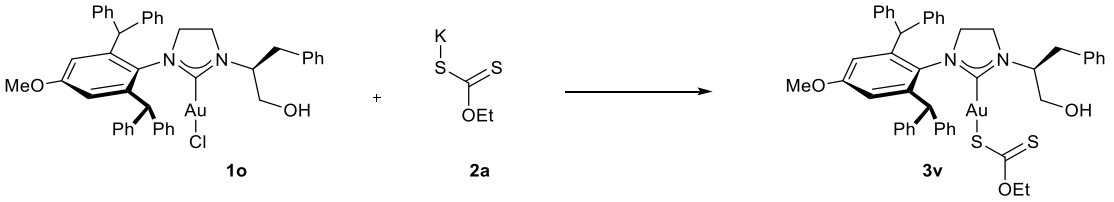
**Complex 3t** was synthesized according to GP1, using CAAC precursor (**1m**) (86.0 mg, 0.154 mmol), potassium xanthate salt **2a** (24.7 mg, 0.154 mmol, 1.0 equiv.) in anhydrous acetone (2

mL). The reaction mixture was stirred for 16 h at rt, and filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM and crashed with *n*-pentane to give a light brown solid (63.7 mg, 64%). mp 157 – 161°C (*n*-pentane/DCM); $^{1}$H NMR (500 MHz, $CD_2Cl_2$) δ 7.44 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.80 (hept, *J* = 6.8 Hz, 2H), 2.4 – 2.35 (m, 3H), 2.18 (s, 2H), 1.85 – 1.83 (m, 3H), 1.75 – 1.74 (m, 1H), 1.58 (d, *J* = 13.0 Hz, 3H), 1.49 – 1.42 (m, 3H), 1.38 – 1.36 (m, 12H), 1.31 (d, *J* = 6.9 Hz, 6H), 1.23 (t, *J* = 7.0 Hz, 4H). $^{13}$C{$^{1}$H} NMR (126 MHz, $CD_2Cl_2$) δ 244.5, 225.5, 145.8, 134.5, 130.3, 125.4, 120.6, 81.2, 71.2, 69.6, 59.8, 46.1, 36.7, 30.0, 29.6, 27.3, 25.8, 23.1, 22.4, 14.5. HR MS (ESI TOF) calcd for $C_{26}H_{41}AuNOS_2$ $[M+H]^+$: 644.2295; found: 644.2291. Elem. anal. calcd for $C_{26}H_{40}AuNOS_2 \bullet CH_2Cl_2$: C, 46.39; H, 6.02; N, 2.04. Found: C, 46.15; H, 5.83; N, 6.21.

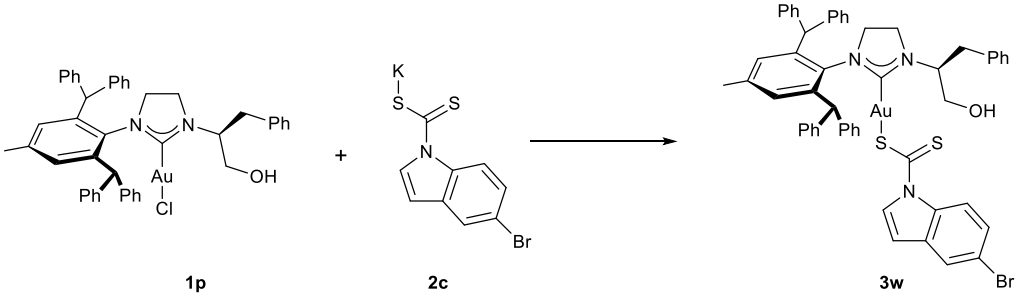



**Complex 3u** was synthesized according to GP1, using NHC-Au-Cl (**1n**) (25.0 mg, 0.024 mmol, Np – 2-Napthyl), potassium xanthate salt **2a** (3.8 mg, 0.024 mmol, 1.0 equiv.) and anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt, and afterwards filtered through syringe filter to remove KCl (syringe filter was washed thoroughly with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (1 mL) and crashed with *n*-pentane (8 mL) to give an off-white solid (27.0 mg, 99%). mp > 220 °C (with decomposition, *n*-pentane/DCM); $[a]_D^{25} = 47.8$ (*c* = 0.67 mg/mL, DCM); $^{1}$H NMR (600 MHz, $CD_2Cl_2$) δ δ 7.85 – 7.65 (m, 13H), 7.60 – 7.53 (m, 2H), 7.49 – 7.35 (m, 12H), 7.32 – 7.25 (m, 2H), 7.08 – 7.04 (m, 1H), 6.86 (d, *J* = 2.1 Hz, 1H), 6.82 (d, *J* = 2.0 Hz, 1H), 6.30 (s, 1H), 5.69 (s, 1H), 5.32 – 5.26 (m, 1H), 4.44 – 4.36 (m, 2H), 4.02 (dd, *J* = 11.9, 4.3 Hz, 1H), 3.90 – 3.82 (m, 1H), 3.21 – 3.03 (m, 3H), 2.88 (dd, *J* = 15.1, 10.9 Hz, 1H), 2.48 – 2.37 (m, 1H), 2.26 – 2.19 (m, 1H), 2.14 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); $^{13}$C{$^{1}$H} NMR (126 MHz, $CD_2Cl_2$) δ 226.5, 203.1, 143.4, 142.6, 141.8, 141.4, 140.5, 140.3, 139.4, 137.3, 135.9, 134.1, 134.0, 133.9 (× 2), 132.9 (× 2), 131.3, 131.1, 129.0 (× 2), 128.9, 128.8, 128.7, 128.5 (× 2), 128.4 (× 2), 128.3 (× 2), 128.1 (× 3), 128.0, 127.6, 126.8 (× 2), 126.5 (× 3), 126.2 (× 2), 70.3, 63.4, 62.4, 52.5, 51.8, 51.1, 45.4, 35.4, 22.0, 14.4. HR MS calcd for $C_{64}H_{56}AuN_2O_2S_2$: 1145.3449; found: 1145.3438.

Elem. anal. calcd for $C_{64}H_{55}AuN_2O_2S_2$: C, 67.12; H, 4.84; N, 2.45. Found: C, 66.96; H, 4.89; N, 2.39.



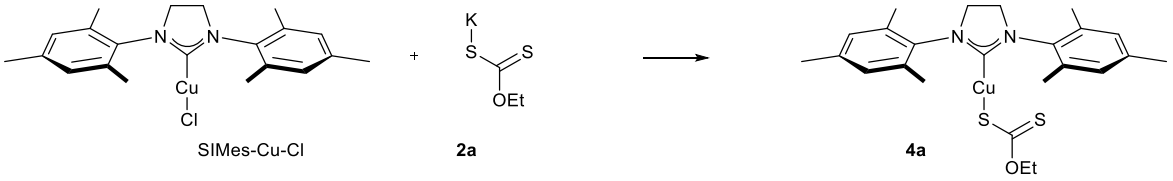

**Complex 3v** was synthesized according to GP1, using NHC-Au-Cl (**1o**) (75.0 mg, 0.086 mmol), potassium xanthate salt **2a** (13.74 mg, 0.086 mmol, 1.0 equiv.), in anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt. and afterwards filtered through syringe filter to remove KCl and washed thoroughly with acetone. The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (ca. 1.5 mL) and crashed with *n*-pentane (12 mL) to give an off-white solid (82.0 mg, 99%). mp 114 – 116 °C (*n*-pentane/DCM); $[a]_D^{25} = 37.6$ ($c$ = 0.86 mg/mL, DCM); $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 7.46 – 7.39 (m, 2H), 7.35 – 7.10 (m, 19H), 7.09 – 7.04 (m, 2H), 6.88 – 6.80 (m, 2H), 6.37 (s, 2H), 5.88 (s, 1H), 5.39 (s, 1H), 5.30 – 5.19 (m, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.98 (dd, *J* = 11.7, 4.2 Hz, 1H), 3.85 (d, *J* = 12.4 Hz, 1H), 3.51 (s, 1H), 3.30 (dd, *J* = 12.3, 9.9 Hz, 1H), 3.26 – 3.16 (m, 1H), 3.07 (dd, *J* = 15.0, 5.2 Hz, 1H), 2.90 (dd, *J* = 15.0, 10.8 Hz, 1H), 2.44 – 2.29 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CD_2Cl_2$) δ 226.6, 203.4, 159.5, 145.3, 144.7, 143.7, 143.6, 142.9, 142.8, 137.3, 131.1, 130.2, 130.1, 129.8, 129.6, 129.4, 129.2, 129.1, 128.9, 128.8, 127.6, 127.3, 127.2, 127.1 (× 2), 115.5, 115.3, 70.3, 63.5, 62.2, 55.5, 52.3, 52.0, 50.9, 45.6, 35.4, 14.4. HR MS calcd for $C_{48}H_{48}AuN_2O_3S_2$ $[M+H]^+$: 961.2772; found: 961.2750. Elem. anal. calcd for $C_{48}H_{47}AuN_2OS_2$: C, 59.99; H, 4.93; N, 2.92. Found: C, 59.92; H, 4.84; N, 2.92.



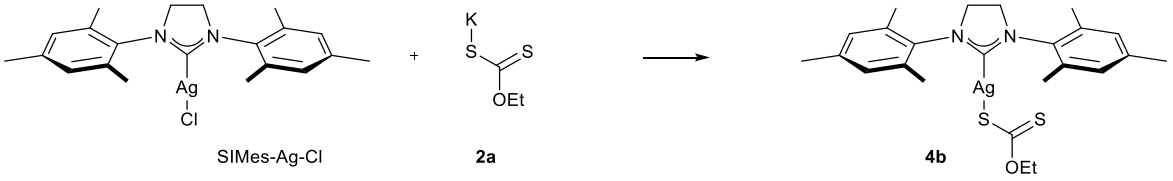

**Complex 3w** was synthesized according to GP1, using NHC-Au-Cl (**1p**) (75.0 mg, 0.087 mmol), potassium xanthate salt **2c** (29.8 mg, 0.096 mmol, 1.1 equiv.), in anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt, filtered through syringe filter (to remove KCl) and the syringe filter washed thoroughly with acetone. Then solvent was evaporated, and the residue was redissolved in minimal volume of DCM and crashed with *n*-pentane to give an

orange solid (95.5 mg, 99%). mp 88 – 90°C (*n*-pentane/DCM); $[\alpha]_D^{25} = 69.7$ (*c* = 0.48 mg/mL, DCM); $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 8.99 (d, *J* = 9.0 Hz, 1H), 8.42 (d, *J* = 3.8 Hz, 1H), 7.68 (d, *J* = 2.1 Hz, 1H), 7.46 (d, *J* = 7.1 Hz, 2H), 7.40 – 7.13 (m, 20H), 7.11 – 7.05 (m, 2H), 6.84 – 6.79 (m, 2H), 6.72 (s, 2H), 6.53 (d, *J* = 3.8 Hz, 1H), 5.90 (s, 1H), 5.40 (s, 1H), 4.07 – 3.99 (m, 1H), 3.91 – 3.80 (m, 1H), 3.42 – 3.32 (m, 1H), 3.32 – 3.22 (m, 1H), 3.10 (dd, *J* = 15.1, 5.2 Hz, 1H), 2.97 – 2.86 (m, 1H), 2.52 – 2.40 (m, 2H), 2.32 (dd, *J* = 8.9, 3.8 Hz, 1H), 2.17 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CD_2Cl_2$) δ 214.7, 202.3, 143.8, 143.7, 143.5, 143.3, 143.1, 142.9, 139.0, 137.3, 136.3, 135.6, 134.9, 132.1, 130.7, 130.6, 130.3, 130.1, 129.8, 129.6, 129.4, 129.2, 129.1, 128.9, 128.8, 127.6, 127.3, 127.1, 127.0 (X 2), 123.8, 120.0, 116.5, 106.5, 63.4, 62.3, 52.1, 51.8, 50.9, 45.4, 35.4, 32.1, 29.7, 22.0. HR MS (APCI TOF) calcd for $C_{54}H_{48}AuN_3OS_2Br$ $[M+H]^+$: 1094.2088; found: 1094.2092. Elem. anal. calcd for $C_{54}H_{47}AuBrN_3OS_2$: C, 59.23; H, 4.33; N, 3.84. Found: C, 59.02; H, 4.51; N, 3.83.

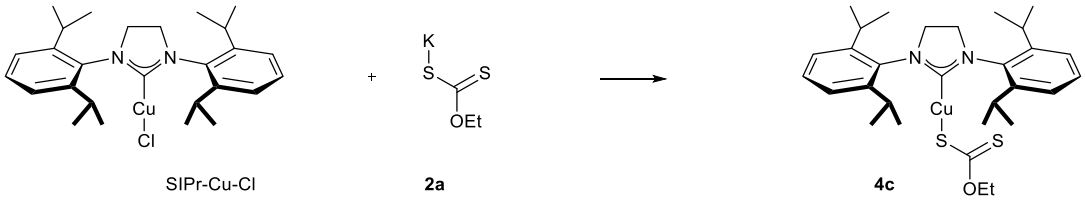
## 5. Synthesis of NHC-Met-X (Met – Ag, Cu; X - xanthate) complexes




**Complex 4a** was synthesized according to GP1, using SIMes-Cu-Cl (prepared followed by lit. procedure[18]) (130.0 mg, 0.320 mmol, 1.0 equiv.), potassium xanthate salt **2a** (51.4 mg, 0.320 mmol, 1.0 equiv.) in anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt, and filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM (1 mL) and crashed with *n*-pentane (8 mL) to give an off-white solid (126.4 mg, 80%). mp 65 – 68°C (*n*-pentane/DCM); $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 7.05 – 6.94 (m, 4H), 4.48 (s, 0.15 × 4H), 4.24 (q, *J* = 7.1 Hz, 1H), 3.95 (s, 0.85 × 4H), 2.38 and 2.35 and 2.33 (s, 18H), 1.25 (t, *J* = 7.1 Hz, 3H); $^{13}$C{$^1$H} NMR (125 MHz, $CD_2Cl_2$) δ 231.4 (m), 207.8, 138.7, 136.6, 136.4, 135.7, 130.6, 129.9, 71.2, 51.4, 21.4, 18.3, 14.4; HR MS (APCI TOF) calcd for $C_{24}H_{32}CuN_2OS_2$ $[M+H]^+$: 491.1252; found: 491.1251. Elem. anal. calcd for $C_{24}H_{31}CuN_2OS_2$: C, 58.69; H, 6.36; N, 5.70. Found: C, 57.82; H, 6.28; N, 5.65.

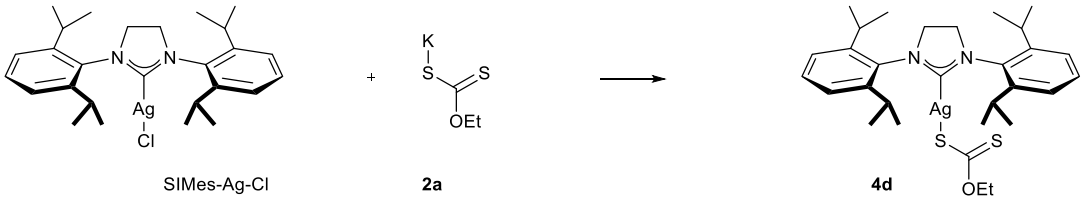



**Complex 4b** was synthesized according to GP1, using SIMes-Ag-Cl (144.2 mg, 0.32 mmol, prepared followed by lit. procedure[19]), potassium xanthate salt **2a** (51.4 mg, 0.32 mmol, 1.0 equiv.) in anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt, and filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the oily residue was treated with $Et_2O$ (1 mL) and *n*-pentane (2 mL), and stirred at rt (ca. 10 min.) till product solidified. The resulting solid was filtered, washed with *n*-pentane (2 × 2 mL) to give an off-white solid (103.9 mg, 61%). *NOTE!!!*: complex **4b** appeared to be unstable, and partial decomposition occurred within 3 days at 4 °C. mp 112 – 116 °C (*n*-pentane/DCM); $^1$H NMR (400 MHz, $CD_2Cl_2$, mixture of rotamers) δ 7.04 (s, 0.08 × 4H), 7.00 (s, 0.65 × 4H), 6.87 (s, 0.27 × 4H), 4.25 (q, *J* = 7.1 Hz, 1H), 4.50 (s, 0.08 × 4H), 4.02 (s, 0.65 × 4H), 3.87 (s, 0.27 × 4H), 2.40 (s, 3H), 2.34 and 2.33 and 2.32 (s, 12H), 1.89 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); $^{13}$C{$^1$H} NMR (101 MHz, $CD_2Cl_2$) δ 231.2, 139.1, 136.5, 136.3, 136.0, 135.6, 135.2, 130.7, 130.0, 130.0, 71.2, 51.7, 21.4, 18.3, 17.7, 14.5 (signals of carbenic atom around 210-215 ppm has missed); HR MS (ESI TOF) calcd for $C_{24}H_{32}AgN_2OS_2$ $[M+H]^+$: 535.1007; found: 535.0993.




**Complex 4c** was synthesized according to GP1, using SIPr-Cu-Cl (157.0 mg, 0.32 mmol, prepared followed by lit. procedure[18]), potassium xanthate salt **2a** (51.4 mg, 0.32 mmol, 1.0 equiv.) in anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt, and filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM/$Et_2O$ (1 mL, 1/1 = v/v) and crashed with *n*-pentane (8 mL) to give an off-white solid (175.0 mg, 95%). mp 157 – 160°C (*n*-pentane/DCM); $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 7.48 – 7.36 (m, 2H), 7.31 – 7.25 (d, *J* = 7.7 Hz, 4H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.04 (s, 4H), 3.24 – 3.14 (m, 4H), 1.36 (d, *J* = 6.9 Hz, 6H), 1.35 (d, *J* = 6.9 Hz, 6H), 1.21 (t, *J* = 7.1 Hz, 3H); $^{13}$C{$^1$H} NMR (125 MHz, $CD_2Cl_2$) δ 31.8, 209.0, 147.7, 136.0, 129.7, 124.8, 71.0, 54.1, 29.4, 25.2, 24.8, 14.3; HR MS

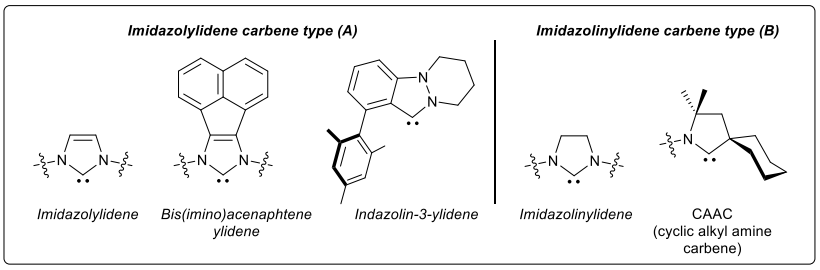
(ESI TOF) calcd for $C_{30}H_{44}CuN_2OS_2$ $[M+H]^+$: 575.2191; found: 575.2197. Elem. anal. calcd for $C_{30}H_{43}CuN_2OS_2 \bullet 0.5H_2O$: C,61.66; H, 7.59; N, 4.79. Found: C, 61.68; H, 7.43; N, 4.75.

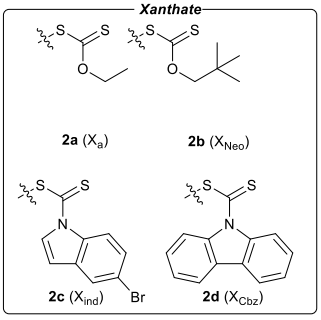



**Complex 4d** was synthesized according to GP1, using SIPr-Ag-Cl (171.2 mg, 0.320 mmol, prepared followed by lit. procedure[19]), potassium xanthate salt **2a** (51.4 mg, 0.320 mmol, 1.0 equiv.) in anhydrous acetone (2 mL). The reaction mixture was stirred for 16 h at rt, and filtered through syringe filter to remove KCl (syringe filter was thoroughly washed with acetone). The solvent was evaporated, and the residue was redissolved in minimal volume of DCM/$Et_2O$ (1 mL, 1/1 = v/v) and crashed with *n*-pentane (6 mL) to give an off-white solid (143.2 mg, 72%). mp 178 – 181 °C (*n*-pentane/DCM); $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 7.46 – 7.40 (m, 2H), 7.31 – 7.25 (m, 4H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.08 (br s, 4H), 3.20 – 3.08 (m, 4H), 1.36 (d, *J* = 6.7 Hz, 6H), 1.35 (d, *J* = 7.0 Hz, 6H), 1.18 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$) δ 231.6, 212.0 (dd, *J* = 234.7, 202.6 Hz), 147.5, 135.7, 130.1, 125.0, 71.3, 54.5, 29.4, 25.5, 24.5, 14.4. HR MS (APCI TOF) calcd for $C_{22}H_{44}AgN_2OS_2$ $[M+H]^+$: 619.1946; found: 619.1945. Elem. anal. calcd for $C_{30}H_{43}AgN_2OS_2$: C, 58.15; H, 6.99; N, 4.52. Found: C, 57.90; H, 6.93; N, 4.43.

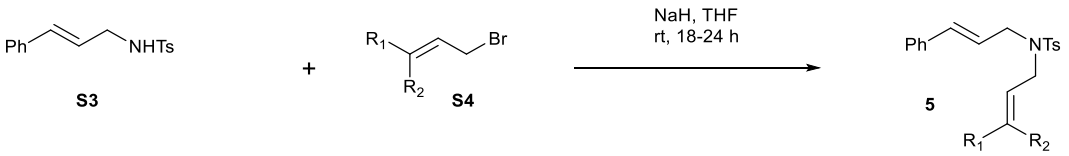
Table S1. Chemical shift of selected signals in $^{13}C$ NMR spectra

| Entry | Complex NHC-Au-X | $^{13}C$ NMR (ppm) C=S | Type of xanthate | $^{13}C$ NMR (ppm) C-Au | Type of NHC skeleton |
|---|---|---|---|---|---|
| **1** | IMes-Au-$X_a$ (**3a**) | 225.3 | $X_a$ | 182.6 | *Imidazolylidene (A)* |
| **2** | $IMes^{Acen}$-Au-$X_a$ (**3b**) | 225.2 | $X_a$ | 187.0 | *Imidazolylidene (A)* |
| **3** | SIMes-Au-$X_{Neo}$ (**3c**) | 225.7 | $X_{Neo}$ | 204.0 | *Imidazolinylidene (B)* |
| **4** | SIMes-Au-$X_{Ind}$ (**3d**) | 213.8 | $X_{Ind}$ | 202.3 | *Imidazolinylidene (B)* |
| **5** | SIMes-Au-$X_{Cbz}$ (**3e**) | 217.4 | $X_{Cbz}$ | 202.9 | *Imidazolinylidene (B)* |
| **6** | SIMes-Au-$X_a$ (**3f**) | 225.2 | $X_a$ | 203.7 | *Imidazolinylidene (B)* |
| **7** | $IPr^{*Me}$-Au-$X_a$ (**3g**) | 225.0 | $X_a$ | 184.3 | *Imidazolylidene (A)* |
| **8** | $IPr^{*OMe}$-Au-$X_a$ (**3h**) | 224.8 | $X_a$ | 184.7 | *Imidazolylidene (A)* |
| **9** | $IPr^{*Me}$-Au-$X_{Cbz}$ (**3i**) | 216.6 | $X_{Cbz}$ | 183.6 | *Imidazolylidene (A)* |
| **10** | IPr-Au-$X_a$ (**3j**) | 225.1 | $X_a$ | 184.5 | *Imidazolylidene (A)* |
| **11** | $IPr^{Me}$-Au-$X_a$ (**3k**) | 225.2 | $X_a$ | 180.7 | *Imidazolylidene (A)* |
| **12** | SIPr-Au-$X_a$ (**3l**) | 225.5 | $X_a$ | 204.2 | *Imidazolinylidene (B)* |
| **13** | SIPr-Au-$X_{Neo}$ (**3m**) | 225.6 | $X_{Neo}$ | 204.1 | *Imidazolinylidene (B)* |
| **14** | SIPr-Au-$X_{Ind}$ (**3n**) | 212.9 | $X_{Ind}$ | 203.3 | *Imidazolinylidene (B)* |
| **15** | SIPr-Au-$X_{Cbz}$ (**3o**) | 216.6 | $X_{Cbz}$ | 203.9 | *Imidazolinylidene (B)* |
| **16** | ICy-Au-$X_a$ (**3p**) | 226.8 | $X_a$ | 177.9 | *Imidazolylidene (A)* |
| **17** | $IMes^{Cyhep}$-Au-$X_a$ (**3q**) | 226.2 | $X_a$ | 179.9 | *Imidazolylidene (A)* |
| **18** | $IPr^{Cyhep}$-Au-$X_a$ (**3r**) | 226.2 | $X_a$ | 180.8 | *Imidazolylidene (A)* |
| **19** | NHC-Au-$X_a$ (**3s**) | 227.2 | $X_a$ | 180.8 | *Imidazolylidene (A)* |
| **20** | NHC-Au-$X_a$ (**3t**) | 225.5 | $X_a$ | 244.5 | *Imidazolinylidene (B)* |
| **21** | NHC-Au-$X_a$ (**3u**) | 226.6 | $X_a$ | 203.1 | *Imidazolinylidene (B)* |
| **22** | NHC-Au-$X_a$ (**3v**) | 226.6 | $X_a$ | 203.4 | *Imidazolinylidene (B)* |
| **23** | NHC-Au-$X_a$ (**3w**) | 214.7 | $X_{Cbz}$ | 202.3 | *Imidazolinylidene (B)* |



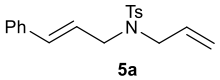




## 6. Synthesis of dienes for gold-catalyzed reactions



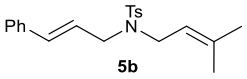

**General procedure 2 (GP2) for synthesis of substituted N-tosylamides.** N-Tosylamides were prepared according to the modified procedure.[20] To a solution of 4-methyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]benzenesulfonamide (**S3**) (4.35 mmol, 1.0 equiv.) in dry THF or dry DMF (40 mL), precooled to 0 °C, NaH (5.22 mmol, 1.2 equiv, 60% suspension in mineral oil) was added portionwise and the mixture was stirred for additional 45 min. Then allyl bromide **S4** (1.2-2.0 equiv.) was added dropwise and the reaction mixture was stirred for additional 18-

24 h at rt (the progress of the reaction was monitored by TLC). The resulting reaction mixture was quenched by slow addition of saturated $NH_4Cl_{aq}$, and the aqueous phases was separated and extracted with $Et_2O$ (2 ×). The combined organic phases were washed with brine (2 ×), dried over $Na_2SO_4$, and evaporated. The crude mixture was purified by flash column chromatography (MTBE/hexanes or EtOAc/hexane) to give the respective N-tosylamides **5**.



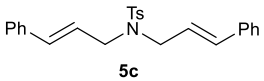

**5a**

**4-Methyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]-*N*-(prop-2-en-1-yl)benzenesulfonamide** (**5a**) was prepared according to GP 2 using 4-methyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]benzenesulfonamide (**S3**)[21] (1.25 g, 4.35 mmol), 60% NaH (208.8 mg, 5.22 mmol), allyl bromide (0.75 mL, 8.70 mmol) and dry THF (15 mL). The residue was chromatographed on silica (10% MTBE/hexanes) to give amide **5a** as a white solid (1.17 g, 82%). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.26 – 7.23 (m, 3H), 6.44 – 6.39 (m, 1H), 5.98 – 5.90 (m, 1H), 5.71 – 5.61 (m, 1H), 5.19 – 5.14 (m, 2H), 3.98 – 3.96 (m, 2H), 3.87 – 3.84 (m, 2H), 2.43 (s, 3H). Spectral data are in agreement with those reported.[22]




**5b**

**4-Methyl-*N*-(3-methylbut-2-en-1-yl)-*N*-[(2E)-3-phenylprop-2-en-1-yl]benzenesulfonamide** (**5b**) was prepared according to GP 2 using 4-methyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]benzenesulfonamide (**S3**)[21] (1.25 g, 4.35 mmol), 60% NaH (208.8 mg, 5.22 mmol), prenyl bromide (0.75 mL, 6.52 mmol) and dry DMF (15 mL). The residue was chromatographed on silica (10% MTBE/hexanes) to give amide **5a** as a white solid (1.35 g, 87%). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.21 (m, 7H), 6.43 – 6.39 (m, 1H), 6.01 – 5.94 (m, 1H), 5.06 – 5.02 (m, 1H), 3.95 – 3.93 (m, 2H), 3.83 (d, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.67 – 1.66 (s, 3H), 1.58 – 1.57 (s, 3H). Spectral data are in agreement with those reported.[23]

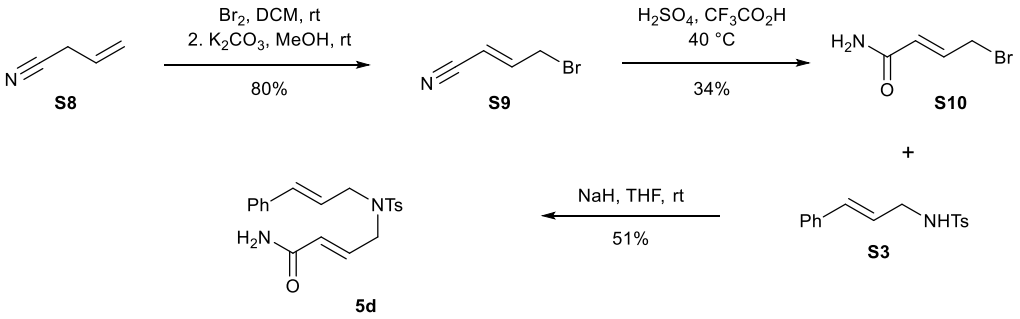



**5c**

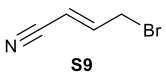
**4-Methyl-*N*,*N*-bis[(2*E*)-3-phenylprop-2-en-1-yl]benzenesulfonamide** (**5c**) To a solution of 4-methyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]benzenesulfonamide (**S3**)[21] (2.17 g, 12.7 mmol, 1.0 equiv.) in dry DMF (40 mL), precooled to 0 °C, NaH (669.7 mg, 27.9 mmol, 2.2 equiv.) was

added portionwise and stirred for additional 30 min. Then cinnamyl bromide (5.0 g, 25.4 mmol, 2.0 equiv.) was added portionwise and stirred at rt for 16 h. Then reaction was quenched addition of sat. solution of $NH_4Cl_{aq}$ (3 mL), and DMF was evaporated. The residue was diluted with water (40 mL), and extracted $Et_2O$ (2 × 20 mL). The combined organic phases were washed with brine, dried over $Na_2SO_4$, and solvent was evaporated. The residue was chromatographed on silica (20% MTBE/hexanes) give amide **5c** as a white crystalline solid (2.17 g, 42%). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 1H), 7.32 – 7.24 (m, 8H), 6.44 (d, *J* = 15.8 Hz, 2H), 6.02 – 5.95 (m, 2H), 4.02 (dd, *J* = 6.6, 1.3 Hz, 4H), 2.44 (s, 3H). The spectral data are in agreement with those reported.[24]

Scheme S3

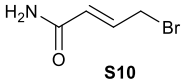



Amide **5d** was following the synthetic route depicted on Scheme S3.



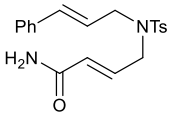
**S9**

**(2*E*)-4-Bromobut-2-enenitrile** (**S9**) was synthesized according to literature procedure.[25] To a solution of allyl cyanide (**S8**) (6.0 mL, 74.5 mmol, 1.0 equiv.) in dry DCM (40 mL), a solution of $Br_2$ (3.8 mL, 74.5 mmol, 1.0 equiv.) in dry DCM (10 mL) was added dropwise at a rate to keep the temperature of the reaction mixture in the range of 15-20 °C, and stirred at rt for 30 min. Then solvent was evaporated, and the residue was redissolved in reagent grade MeOH (50 mL), and argon was bubbled through this solution for 5 min. Then solid $K_2CO_3$ (10.3 g, 74.5 mmol, 1.0 equiv.) was added at once and the reaction mixture was stirred at rt for additional 2 h. The reaction mixture was passed through pad of Celite, solvent was evaporated, the residue was treated with water (50 mL), and was extracted with DCM (3 × 50 mL). The combined organic extracted were over anhydrous $Na_2SO_4$ and evaporated to give a bromide **S9** (8.67 g). $^1$H NMR confirmed the formation of **S9** with some impurities. The crude bromide was used in the next step without further purification.



**S10**

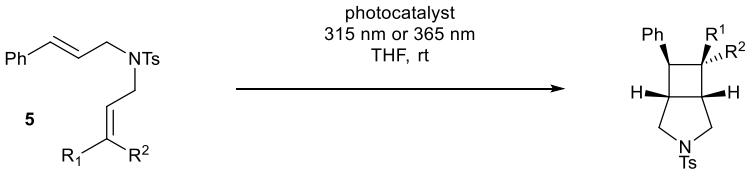
**(2*E*)-4-Bromobut-2-enamide** (**S10**) was synthesized according to the modified literature.[26] Nitrile **S9** (3.0 g, 21.0 mmol) was dissolved in $CF_3CO_2H$ (16.0 mL, 0.21 mol, 10.0 equiv.) and conc. $H_2SO_4$ (3.4 mL, 62.0 mmol, 3.0 equiv.) was added dropwise. Then reaction mixture was stirred at 40 °C for 5 h (the progress of the reaction was monitored by TLC). The reaction mixture was poured into ice cold water, and extracted with EtOAc (3 × 30 mL). The combined organic extracts were washed with brine (2 × 50 mL), dried over anhydrous $Na_2SO_4$, and evaporated. The residue was chromatographed on silica (80-100% EtOAc/hexanes) to give amide **S10** as a white solid (1.13 g, 34%). $^1$H NMR (400 MHz, MeOD) δ 6.97 – 6.89 (m, 1H), 6.27 – 6.23 (m, 1H), 4.18 (dd, *J* = 7.4, 1.2 Hz, 2H). The spectral data are in agreement with those reported.[25]



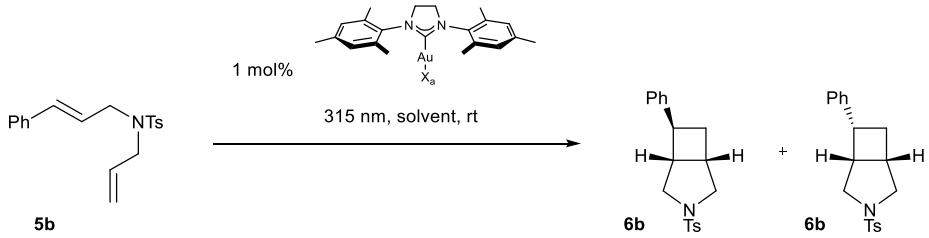
**5d**

**(2*E*)-4-{[(4-Methylphenyl)sulfonyl][(2*E*)-3-phenylprop-2-en-1-yl]amino}but-2-enamide** (**5d**) was synthesized using GP 2 using amide **S3** (140.0 mg, 0.49 mmol, 1.0 equiv.), amide **S10** (79.9 mg, 0.487 mmol, 1.0 equiv.) and 60% NaH (21.4 mg, 0.54 mmol, 1.1 equiv.). The crude reaction mixture was purified by flash column chromatography (80-100% EtOAc/hexanes) to give amide **5d** as a white solid (92.1 mg, 51%). mp 118 - 121°C ($CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.24 (m, 7H), 6.74 – 6.67 (m, 1H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.07 – 6.02 (m, 1H), 5.95 – 5.87 (m, 1H), 5.79 (br s, 2H), 4.01 - 3.98 (m, 4H), 2.45 (s, 3H). $^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$) δ 167.2, 143.9, 140.2, 137.1, 136.0, 134.9, 130.0, 128.8, 128.3, 127.4, 126.6, 125.1, 123.2, 50.1, 47.5, 21.6. HR MS (ESI TOF) calcd for $C_{20}H_{22}N_2O_3SNa$ $[M+Na]^+$: 393.1249; found: 393.1259.

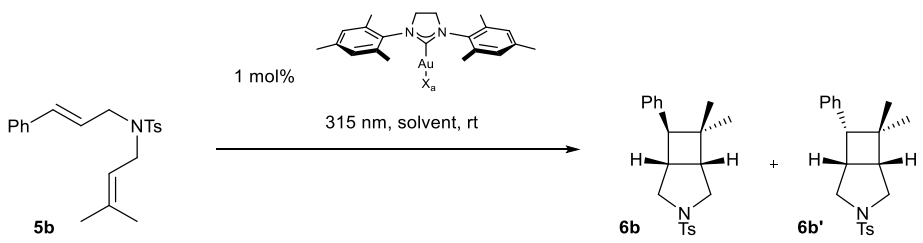
## General Procedure 3 (GP 3) for photocatalytic [2+2] cycloaddition reactions of N – tosyl amides



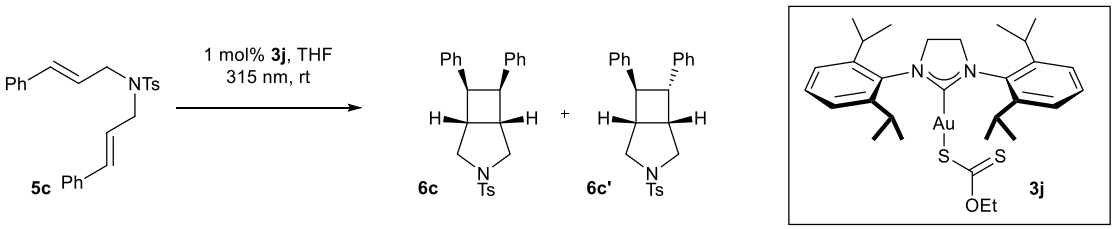
A flame dried Quartz vial, equipped with a magnetic stir bar, was charged with amide **5** and complex **3** (1 mol%). Then, the vial was filled with argon with 5 vacuum – inert gas cycles. Then, the vial taken to the glovebox, degassed THF (6 mL) was added and sealed with a septum. Finally, the vial was purged one final time with the argon gas and kept in a photoreactor (315 nm or 365 nm). Aliquots were taken from the reaction mixture by means of syringe and analyzed by TLC. After completion of the reaction, THF was evaporated and the residue was chromatographed on silica (EtOAc/hexanes) to give a bicyclic product **6**.




**(1*S**,5*R**,6*S**)-3-[(4-Methylphenyl)sulfonyl]-6-phenyl-3-azabicyclo[3.2.0]heptane** (**6a**) and **(1*S**,5*R**,6*R**)-3-[(4-Methylphenyl)sulfonyl]-6-phenyl-3-azabicyclo[3.2.0]heptane** (**6a'**) was synthesized according to GP 3 using amide **5a** (40.0 mg, 122.0 µmol), complex **3f** (0.76 mg, 1.2 µmol, 1 mol%) and THF (3 mL). The reaction mixture was irradiated at 315 nm for 10 h. The residue was chromatographed on silica (15% EtOAc/hexanes) to give amide **6a** as a white solid (29.1 mg, 73%). Amide **6a** was isolated as a mixture of diastereomers in a ratio 89:11 (based on integration of multiplets at 7.73 ppm and 7.63 ppm). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.38 – 7.26 (m, 4H), 7.24 – 7.15 (m, 3H), 3.60 (d, *J* = 9.7 Hz, 1H), 3.54 (d, *J* = 9.7 Hz, 1H), 3.39 (ddd, *J* = 9.8, 7.8, 4.4 Hz, 1H), 2.96 – 2.81 (m, 1H), 2.76 (dd, *J* = 9.7, 6.3 Hz, 1H), 2.67 (dd, *J* = 9.8, 5.2 Hz, 1H), 2.44 (s, 2H), 2.37 – 2.25 (m, 2H). Spectral data are in agreement with those reported.[27] $^1$H NMR (400 MHz, $CDCl_3$, minor isomer, selected signals) δ $^1$H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 0.11 × 2H), 3.46 (d, *J* = 9.5 Hz, 0.11 × 1H), 3.20 (dd, *J* = 10.5, 1.8 Hz, 0.11 × 1H), 3.14 – 3.03 (m, 0.11 × 1H), 2.56 (dd, *J* = 10.5, 8.1 Hz, 0.11 × 1H), 2.42 (s, 0.11 × 3H).

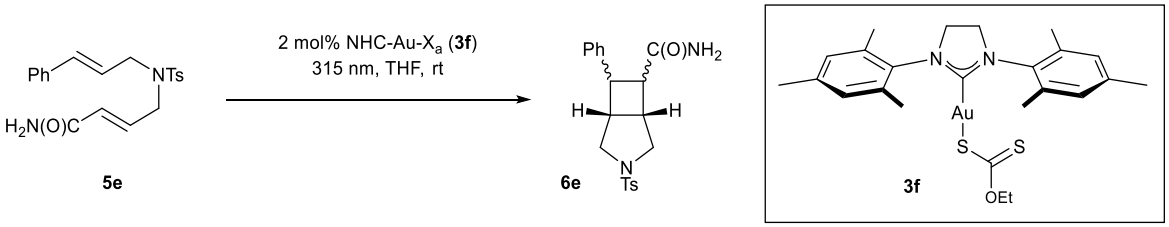


**(1*R**,5*R**,7*R**)-6,6-Dimethyl-3-[(4-methylphenyl)sulfonyl]-7-phenyl-3-azabicyclo[3.2.0]heptane** (**6b**) and **(1*R**,5*R**,7*S**)-6,6-dimethyl-3-[(4-methylphenyl)sulfonyl]-7-phenyl-3-azabicyclo[3.2.0]heptane** (**6b'**) was synthesized according to GP 3 using amide **5b** (40.0 mg, 112 μmol), complex **3f** (0.70 mg, 1.3 μmol, 1 mol%) and THF (3 mL). The reaction mixture was irradiated at 315 nm for 10 h. The residue was chromatographed on silica (15% EtOAc/hexanes) to give amide **6b** as a white solid (32.6 mg, 82%, dr = 91 : 9, based on integral of dd at 3.71 ppm and 3.64 ppm). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (br d, *J* = 8.3 Hz, 2H), 7.38 – 7.15 (m, 5H), 7.08 (d, *J* = 7.6 Hz, 2H), 3.71 (dd, *J* = 10.5, 1.2 Hz, 1H), 3.42 (d, *J* = 9.4 Hz, 1H), 3.25 – 3.11 (m, 2H), 2.64 (ddd, *J* = 11.4, 10.0, 6.5 Hz, 2H), 2.44 (s, 3H), 2.34 – 2.24 (m, 1H), 1.17 (s, 3H), 0.70 (s, 3H). Selected signals of minor diastereomer: 3.64 (dd, *J* = 10.2, 2.4 Hz). Spectral data are in agreement with those reported.[23]




**(1*R**,5*S**,6*R**,7*S**)-3-[(4-Methylphenyl)sulfonyl]-6,7-diphenyl-3-azabicyclo[3.2.0]heptane** (**6c**) **(1*R**,5*S**,6*S**,7*S**)-3-[(4-methylphenyl)sulfonyl]-6,7-diphenyl-3-azabicyclo[3.2.0] heptane** (**6c'**) was synthesized according to GP 3 using amide **5c** (200.0 mg, 0.49 mmol), complex **3f** (3.51 mg, 4.95 μmol, 1 mol%) and THF (10 mL). The reaction mixture was irradiated at 315 nm for 11 h. The residue was chromatographed on silica (15-20% EtOAc/hexanes) to give amide **6c** as a white solid (160.1 mg, 80%). Amide **6e** was isolated as a mixture of diastereomers in a ratio 74:26 (based on integration of signals at 3.68 ppm and 3.61 ppm). The analytical sample recrystallized from $CHCl_3$ to give a mixture of diastereomers >10:1 (mp, $^1$H and $^{13}$C NMR were recorded after crystallization, dr > 10:1). mp 121 - 123°C ($CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.77 (br d, *J* = 8.2 Hz, 2H), 7.44 – 7.25 (m, 2H) overlapping 7.37 (br d, *J* = 8.0 Hz, 2H), 7.09 – 7.03 (m, 4H), 7.02 – 6.96 (m, 2H), 6.90 – 6.84 (m, 4H), 3.90 (d, *J* = 3.9 Hz, 1H), 3.69 (d, *J* = 9.9 Hz, 1H), 3.19 (d, *J* = 5.0 Hz, 2H), 2.87 (ddd, *J* = 10.0, 4.1, 1.9 Hz, 2H), 2.46 (s, 3H). $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) δ 143.9, 140.2, 132.2, 129.8, 128.3, 128.1, 127.9, 125.9, 54.4, 47.3, 40.7, 21.7; HR MS (ESI TOF) calcd for $C_{25}H_{26}NO_2S$ $[M+H]^+$: 404.1684; found: 404.1694.

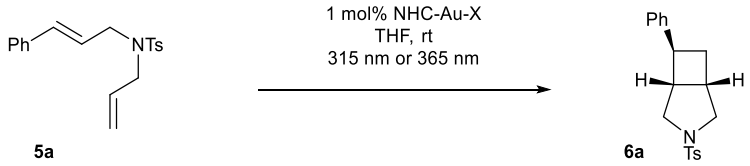
Amide **6** and **6c'** was synthesized according to GP 3 using amide **5c** (40.0 mg, 99.1 μmol), complex **3f** (0.62 mg, 0.99 μmol, 1 mol%) and THF (6 mL). The reaction mixture was irradiated at 315 nm for 10 h. The residue was chromatographed on silica (15-20% EtOAc/hexanes) to give amide **6c** as a white solid (30.7 mg, 77%). Amide **6e** was isolated as a mixture of diastereomers in a ratio 79:21 (based on integration of signals at 3.68 ppm and 3.61 ppm).




**(1*S**,5*S**)-3-[(4-methylphenyl)sulfonyl]-7-phenyl-3-azabicyclo[3.2.0]heptane-6-carboxamide** (**6e**) was synthesized according to GP 3 using amide **5e** (160.0 mg, 0.43 mmol), complex **3f** (8.1 mg, 13.0 μmol, 3 mol%) and THF (6 mL). The reaction mixture was irradiated at 315 nm for 16 h. The residue was chromatographed on silica (80% EtOAc/hexanes) to give amide **6e** as a white solid (88.3 mg, 55%). mp 204 – 207°C (EtOAc); Amide **6e** was isolated as a mixture of diastereomers in a ratio 61:39 (based on integration of multiplets at 3.60 ppm and 3.35 ppm); $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 7.68 (br d, $J$ = 7.9 Hz, 2H), 7.54 – 7.40 (m, 2H), 7.33 – 7.26 (m, 1H), 7.26 – 7.10 (m, 4H), 6.96 and 6.86 and 6.45 (3 × br s, 3H, $NH_2$), 3.60 – 3.55 (m, 0.39 × 1H, minor isomer), 3.52 (dd, $J$ = 10.6, 2.1 Hz, 0.39 × 1H, minor isomer), 3.47 (dd, $J$ = 9.9, 5.5 Hz, 0.61 × 1H, major isomer), 3.41 – 3.33 (m, 1H+0.61 × 1H), 3.22 – 3.12 (m, m, 1H+0.39 × 1H), 3.10 (dd, $J$ = 9.4, 9.4 Hz, m, 0.39 × 1H, minor isomer), 3.06 – 2.94 (m, 1H), 2.89 – 2.84 (m, 0.39 × 1H, minor isomer), 2.75 (dd, $J$ = 10.5, 8.4 Hz, 0.39 × 1H, minor isomer), 2.71 – 2.59 (m, 1H+0.61 × 1H), 2.42 (s, 0.61 × 3H, major isomer), 2.42 (s, 0.61 × 3H, minor isomer); $^{13}$C NMR (126 MHz, DMSO) δ 172.2 (minor diastereomer), 171.8, 143.6, 143.5 (minor diastereomer), 143.4 (minor diastereomer), 140.4, 131.5 (minor diastereomer), 131.3, 129.8, 129.7 (minor diastereomer), 128.3 (minor diastereomer), 127.9, 127.8, 127.6, 126.3 (minor diastereomer), 126.1, 53.9, 53.4, 53.3 (minor diastereomer), 48.8 (minor diastereomer), 46.7, 44.7, 44.5 (minor diastereomer), 42.2 (minor diastereomer), 41.3 (minor diastereomer), 40.9, 36.8 (minor diastereomer), 35.5, 21.98 (major diastereomer), 21.97 (minor diastereomer). HR MS (ESI TOF) calcd for $C_{20}H_{22}N_2O_3SNa$ $[M+Na]^+$: 393.1249; found: 393.1255. The mixture of diastereomer was further partially separated by crystallization from EtOAc to give a mixture in a ratio of dr = 85:15 (based on $^{1}$H NMR, copies of spectra $^{1}$H NMR and $^{13}$C{$^{1}$H} are presented in separate file "Copy of spectra").

## 7. Optimization of photocatalyst for the photochemical [2 + 2] cycloaddition reaction

### General Procedure




A flame dried 10 mL Quartz vial, equipped with a magnetic stirring bar, was charged with amide **5a** (120 mg, 0.366 mmol) and NHC-Au-X (3.66 μmol, 1 mol%). Then, the vial was filled with argon gas with 5 vacuum – inert gas cycles and taken to the glovebox. In side glovebox, degassed THF (6 mL) was added and the vial was sealed with a septum. Finally, the vial was purged one final time with the argon gas (ca. 2 min.) and kept in a photoreactor (315 nm or 365 nm depending upon the catalyst). Aliquots were taken from the reaction mixture every 2 h and analyzed by TLC. After completion of the reaction, THF was evaporated and the yield for the reaction was calculated by $^{1}$H NMR using *p*-methoxy benzyl alcohol as the internal standard.

Table S2. Optimization of the photocatalyst structure.

| Entry | Catalyst | Time (h) | Conditions | Wavelength (nm) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 | SIPr-Au-$X_a$ (**3l**) | 10 | Degassed THF, under Ar | 315 | 66 |
| 2 | SIMes-Au-$X_a$ (**3f**) | 10 | Degassed THF, under Ar | 315 | 76 |
| 3 | SIMes-Au-$X_a$ (**3f**) | 10 | None-degassed THF, air | 315 | 20 |
| 4 | SIMes-Au-$X_a$ (**3f**) | 10 | Degassed THF, under Ar with TEMO | 315 | 5 |
| 5 | SIPr-Au-$X_{Neo}$ (**3m**) | 21 | Degassed THF, under Ar | 315 | 68 |
| 6 | SIMes-Au-$X_{Neo}$ (**3c**) | 21 | Degassed THF, under Ar | 315 | 78 |

| | | | | | |
|---|---|---|---|---|---|
| 7 | SIMes-Au-$X_a$ (**3f**) | 10 | Degassed THF, under Ar | 365 | 33 |
| 8 | SIMes-Au-$X_{Neo}$ (**3c**) | 21 | Degassed THF, under Ar | 365 | 22 |
| 9 | - | 16 | Degassed THF, under Ar | 365 | <10 |
| 10 | SIPr-Au-$X_{Ind}$ (**3n**) | 16 | Degassed THF, under Ar | 365 | 96 |
| 11 | SIMes-Au-$X_{Ind}$ (**3d**) | 16 | Degassed THF, under Ar | 365 | 95 |
| 12 | SIPr-Au-$X_{Cbz}$ (**3o**) | 16 | Degassed THF, under Ar | 365 | 92 |
| 13 | SIMes-Au-$X_{Cbz}$ (**3e**) | 16 | Degassed THF, under Ar | 365 | 95 |
| 14 | SIMes-Au-$X_{Cbz}$ (**3e**) | 16 | None-degassed THF, air | 365 | <5% |
| 15 | SIMes-Au-$X_{Cbz}$ (**3e**) | 16 | Degassed THF, under Ar with TEMO | 365 | <5% |
| 16 | SIMes-Au-$X_{Cbz}$ (**3e**) | 16 | Degassed THF, under Ar with isoprene | 365 | 7% |
| 17 | $IPr^{*Me}$-Au-$X_{Cbz}$ (**3g**) | 16 | Degassed THF, under Ar | 365 | 95 |

[a] yield for the reaction was calculated by $^1$H NMR using *p*-methoxybenzyl alcohol as the internal standard.

Based on the result depicted in Table S2 it was proved that SIMes-Au-X complexes, bearing an alkyl xanthate moiety (**3c**, **3f**) provided bicyclic amide **6a** in higher yield than the respective SIPr-Au-X complexes (**3l**, **3m**) at 315 nm (complexes **3f** and **3c** were provided product with lower yield upon irradiation at 365 nm). Further optimization revealed that complexes bearing indole (**3n**, **3d**) or carbazole subunit (**3o**, **3e**, **3g**) afforded bicyclic product 6a in almost

quantitative yield irrespective of the steric hindrance of NHC ligand as well as its electronic properties.

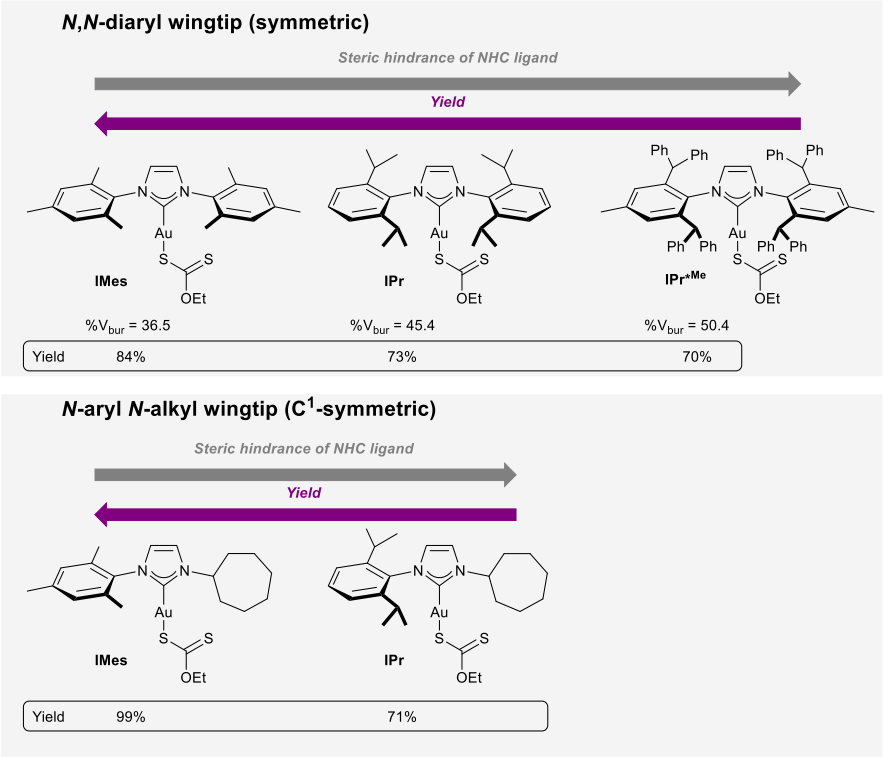



Figure S6. Influence of steric hindrance of NHC-Au-$X_a$ complexes on [2+2]cycloaddition leading to bicyclic amide **6b**.

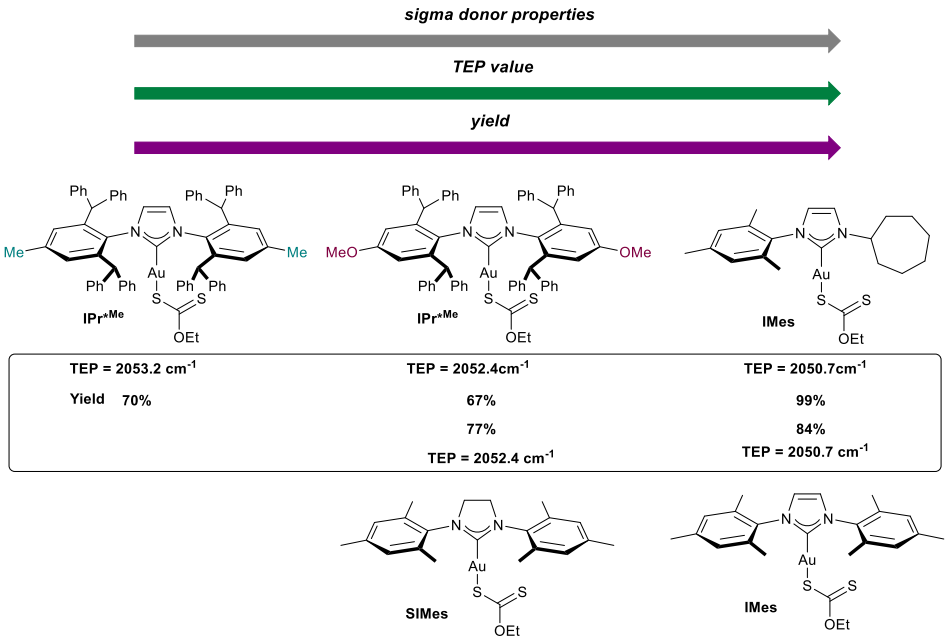
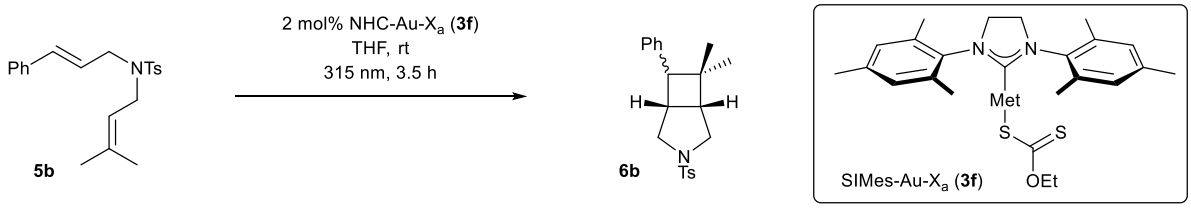



Figure S7. Influence of electronic character of NHC-Au-$X_a$ complexes on [2+2]cycloaddition leading to bicyclic amide **6b**. TEP value are taken from literature data.[28]

**Reactions with solvents of different polarity**



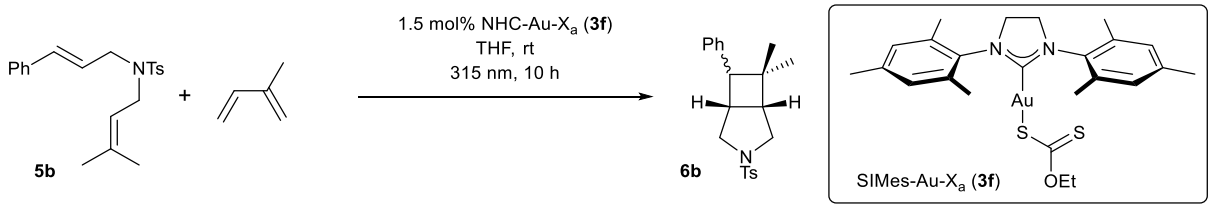

A flame dried 20 mL Quartz vial, equipped with a magnetic stirring bar, was charged with N-tosyl amide **5b** (20.0 mg, 0.056 mmol) and complex SIMes-Au-$X_a$ (**3f**) (0.70 mg, 1.13 μmol, 2 mol%). The vial was filled with argon with 5 vacuum – inert gas cycles. Then, the vial was taken to the glovebox, degassed solvent (6 mL) was added and the vial was sealed with a septum. Finally, the vial was purged one final time with argon gas (2 min.) and kept in a photoreactor (315 nm). After 3.5 h the reaction the irradiation was stopped, solvent was evaporated and the yield for the reaction was calculated by $^1$H NMR using *p* – methoxy benzylalcohol as the internal standard.

Table S3. [2 + 2] cycloaddition reactions at different polarity solvents

| **Entry**[a] | **Solvent** | **Polarity**[b] | **Yield (%)**[c] |
|---|---|---|---|
| 1 | DCM | 3.1 | 53 |
| 2 | *i*-PrOH | 3.9 | 77 |
| 3 | THF | 4.0 | 68 |
| 4 | EtOAc | 4.4 | 70 |
| 5 | 1,4-Dioxane | 4.8 | 64 |

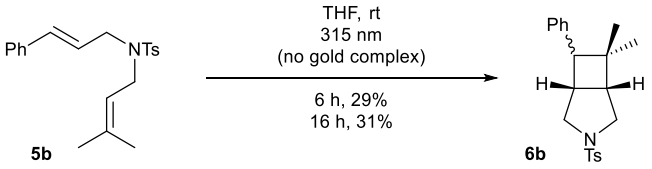
[a] conditions: 2 mol% SIMes-Au-$X_a$ (**3j**), THF, 3.5 h, rt; [b] polarity index according to definition introduced by Snyder, Glajch and Krikland;[29] [c] yield calculated by $^1$H NMR with 1,3,5-trimetoxybenzene as the internal standard (see, experiment procedure above).

**Reaction with triplet quencher**

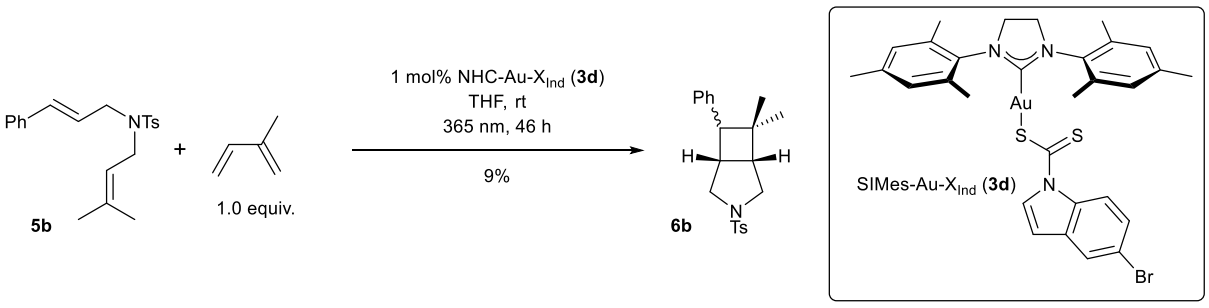



A flame dried 10 mL Quartz vial, equipped with a magnetic stirring bar, was charged with amide **5b** (20.0 mg, 0.56 mmol) and complex **3f** (0.53 mg, 0.84 μmol, 1.5 mol%). The vial was filled with argon with 5 vacuum-inert gas cycles. Then, the vial was taken to the glovebox,

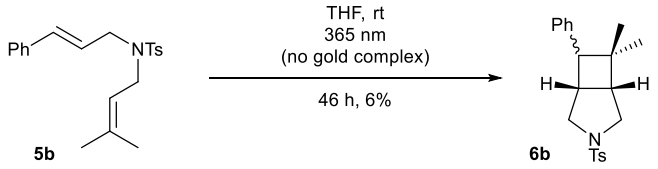
degassed THF (2 mL) was added and the vial was sealed with a septum. Then isoprene (5.6 µL, 0.56 mmol, 1.0 equiv.) was added by means of microsyringe. Then vial was purged one final time with argon gas (ca. 2 min.) and kept in a photoreactor (315 nm). After 10 h, THF was evaporated and the residue was subjected to column chromatography (10-15% EtOAc/hexanes) to give bicyclic amide **6b** (5.2 mg, 26%).




A flame dried 10 mL Quartz vial, equipped with a magnetic stirring bar, was charged with amide **5a** (20.0 mg, 0.56 mmol). The vial was filled with argon with 5 vacuum-inert gas cycles, and was taken to the glovebox. Inside glovebox, a degassed THF (2 mL) was added and the vial was sealed with a septum. Then vial was purged one final time with argon gas (ca. 2 min.) outside glovebox and kept in a photoreactor (315 nm). After 6 h, THF was evaporated and the residue was subjected to column chromatography (10-15% EtOAc/hexanes) to give bicyclic amide **6a** (5.7 mg, 29%, isolated yield). The same reaction was conducted at 315 nm for 16 h, using diene **5a** (33.0 mg, 92.8 µmmol) and THF (3.3 mL) and afforded product **6a** with comparable yield (31%, 10.1 mg, isolated yield).




A flame dried 10 mL Quartz vial, equipped with a magnetic stirring bar, was charged with amide **5b** (45.0 mg, 0.127 mmol) and complex **3d** (0.98 mg, 1.27 µmol, 1 mol%). The vial was filled with argon with 5 vacuum-inert gas cycles. The, the vial was taken to the glovebox, degassed THF (2 mL) was added and the vial was sealed with a septum. Then isoprene (12.7 µL, 0.127 mmol, 1.0 equiv.) was added by means of microsyringe. Then vial was purged one final time with argon gas (ca. 2 min.) and kept in a photoreactor (365 nm). After 46 h, THF was evaporated and the residue was subjected to column chromatography (10-15% EtOAc/hexanes) to give bicyclic amide **6b** (4.1 mg, 9%).




A flame dried 10 mL Quartz vial, equipped with a magnetic stirring bar, was charged with amide **5b** (45.0 mg, 0.127 mmol). The vial was filled with argon with 5 vacuum-inert gas cycles, and was taken to the glovebox. Inside glovebox, a degassed THF (2 mL) was added and the vial was sealed with a septum. Then vial was purged one final time with argon gas (ca. 2 min.) outside glovebox and kept in a photoreactor (365 nm) at rt. After 46 h, THF was evaporated and the residue was subjected to column chromatography (10-15% EtOAc/hexanes) to give bicyclic amide **6b** (2.8 mg, 6%, isolated yield).

**ON/OFF experiment**

A flame dried 20 mL Quartz vial, equipped with a magnetic stirring bar, was charged with amide **5b** (200.0 mg, 0.56 mmol) and complex SIMes-Au-$X_a$ (**3f**) (3.51 mg, 5.6 μmmol, 1 mol%) Then vial was filled with argon with 5 vacuum-inert gas cycles and transferred to the glovebox, and degassed THF (10 mL) was added. Then vial was purged one final time with argon gas (ca. 2 min.) outside the glovebox and kept in a photoreactor (315 nm, equipped with 4 bulbs, 4 × 9W, 315 nm, Philips, the same equipment as for the small scale reaction). After each period, the aliquot (0.5 mL) of reaction mixture was taken under the flow of argon, evaporated, dried under vacuum for 10 min., and stock solution of the internal standard in $CDCl_3$ (0.6 mL of CDCl3 containing 5.745 mg of benzyl trifluoroacetate) was added and analyzed with $^1$H NMR (characteristic signal for benzyl trifluoroacetate: 5.36 ppm, starting amide **5a**: 1.66 ppm and 1.57 ppm, and bicyclic product **6b**: 1.17 ppm and 0.70 ppm). During "On" period the Quartz vial was placed in photoreactor, during "Off" period the lamp was turned off and the tube was covered with aluminum foil without the interruption of stirring.

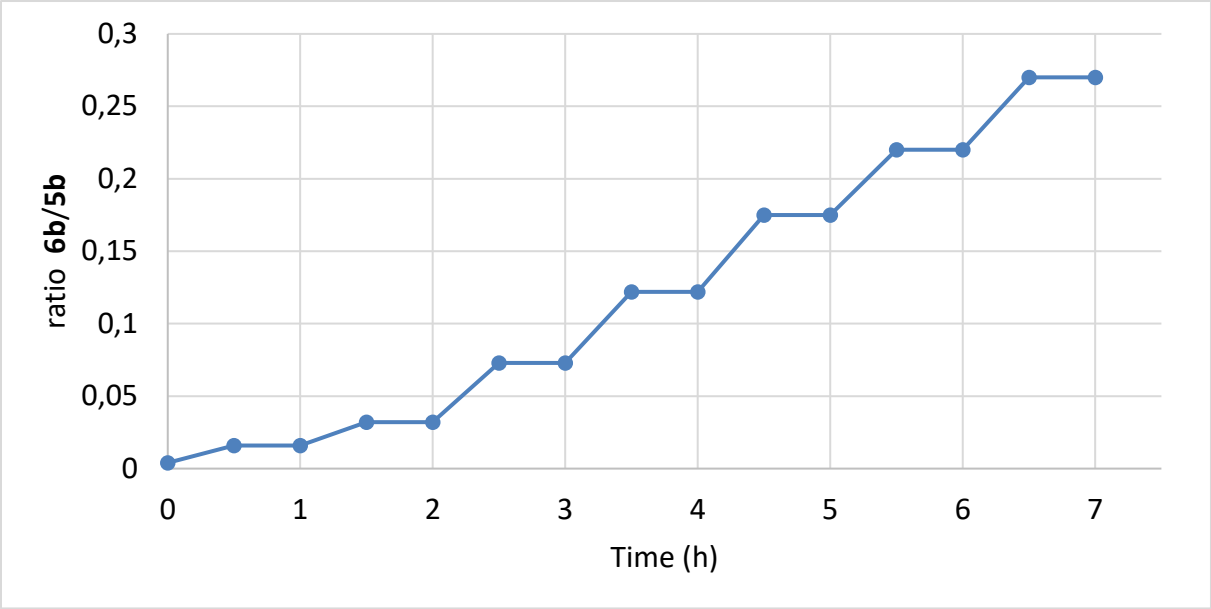



Figure S8. ON/OFF experiment.

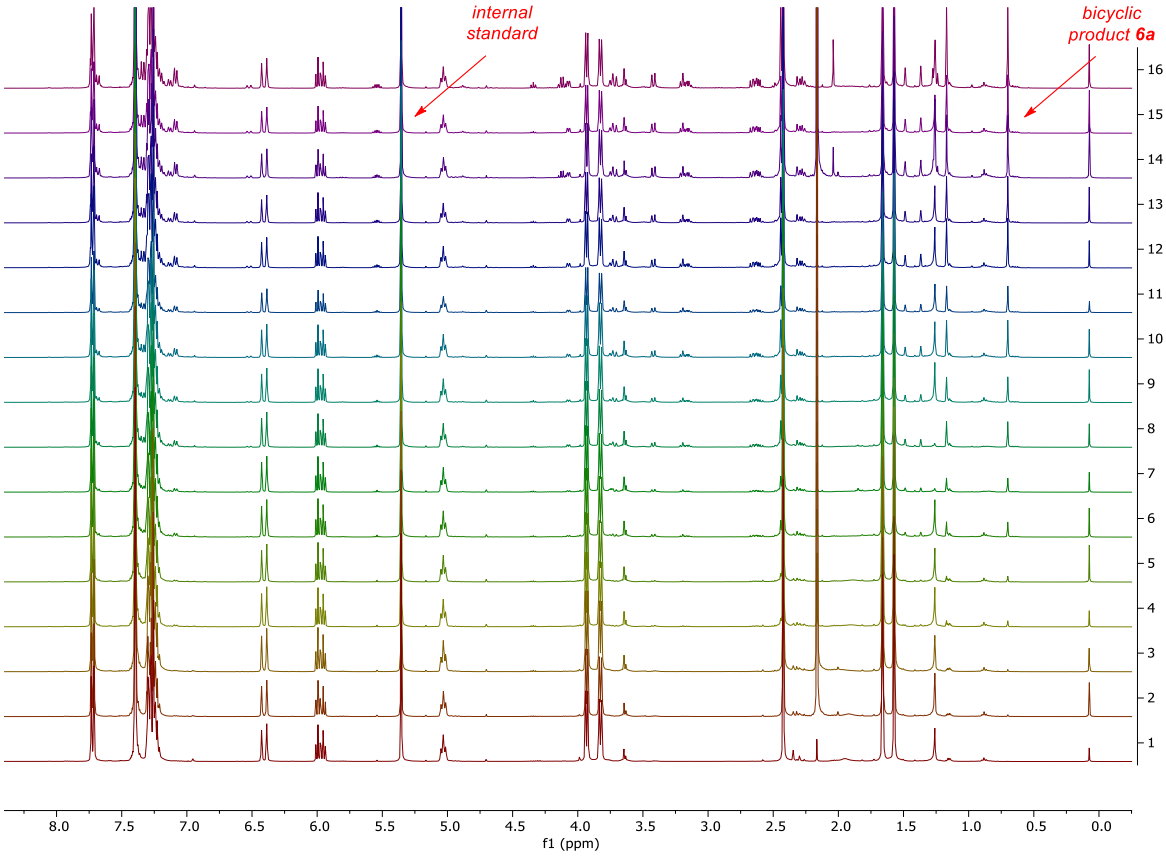
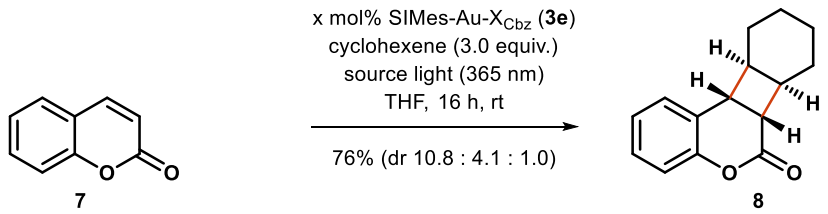



Figure S9. Stack of $^{1}H$ NMR spectra of each aliquots recorded in $CDCl_3$ for the calculation of the ratio **6b**/**5b.**




7 8

Table S4. Influence of reaction conditions on the reactivity of coumarine 7

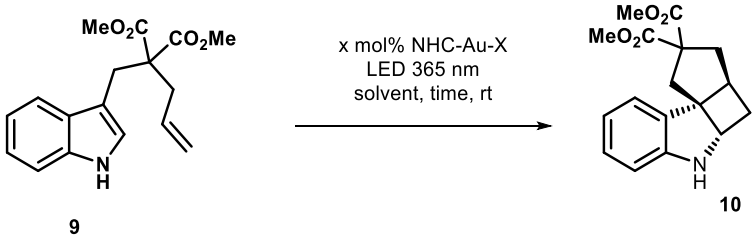
| NHC-Au-X complex | x (mol%) | LED 365 nm | Time (h) | Solvent | Yield (%) |
|---|---|---|---|---|---|
| SIMes-Au-$X_{Cbz}$ (**3e**) | 1 | + | 16 | EtOAc (degassed, under Ar) | 76 (dr 10.8 : 4.1 : 1.0)[a] |
| - | - | + | 16 | EtOAc (degassed, under Ar) | not detected |
| SIMes-Au-$X_{Cbz}$ (**3e**) | 1 | - | 16 | EtOAc (degassed, under Ar) | not detected |
| $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (**16**) | 2 | + | 16 | EtOAc (degassed, under Ar) | 27[b,c] (nd) |
| SIPr-Au-Cbz (**17**) | 0.5 | + | 16 | EtOAc (degassed, under Ar) | 90 (3.6 : 2.0 : 1.0)[c] |

[a] Isolated yield

[b] Yiled calculated by $^1$H NMR with 1,3,5-trimethoxybenzene as internal standard

[c] Nolan et. al.; Ref. 30

**(6a*S***,6b*R***,10a*S***,10b*R***)-6a,6b,7,8,9,10,10a,10b-octahydro-6H-benzo[3,4]cyclobuta[1,2-c]chromen-6-one** (**8**) A 15 ml quartz test tube was charaged with coumarin (58.0 mg, 0.4 mmol) and SIMes-Au-$X_{Cbz}$ (**3e**) complex (1.5 mg, 2.0 µmmol, 0.5 mol%). Then the test tube was flashed with argon/vaccum (3 times) and degassed THF (3 mL) and cyclohexane (97.8 mg, 1.2 mmol, 3.0 equiv.) were added. The resulting mixture was irradiated with 365 nm LED for 16 h (TLC analysis indicated complete consumption of substrate). Then solvent was evaporated, and the residue was chromatographed on silica (12 g column, CombiFlash, 15 mol/min, 5% EtOAc/hexanes) to give colorless oil (69.5 mg, 76%, mixture of 3 diastereomers in a ratio 10.8 : 4.1 : 1.0). The ratio of diastereomers was calculated by analysis of $^1$H NMR and compared to published results by Nolan at al.[30] $^1$H and $^{13}$C NMR of the mixtures of diastereomers can be found in NMR spectra section.




9 10

Table S5. Influence of reaction conditions on the reactivity of indole **9**

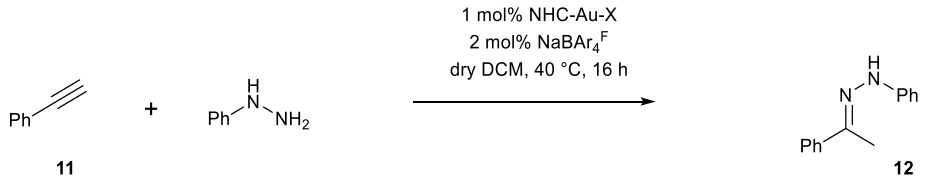
| Entry | NHC-Au-X complex | x (mol%) | Additive) | Solvent | Yield (%) |
|---|---|---|---|---|---|
| 1 | SIMes-Au-$X_{Cbz}$ (**3e**) | 2 | - | THF (degassed, under Ar) | 17[a] |
| 2 | SIPr-Au-$X_{Cbz}$ (**3o**) | 2 | - | THF (degassed, under Ar) | 18[a] |
| 3 | $IPr^{*Me}$-Au-$X_{Cbz}$ (**3i**) | 2 | - | THF (degassed, under Ar) | 39[a] |
| 4 | SIMes-Au-$X_{Cbz}$ (**3e**) | 2 | - | EtOAc (degassed, under Ar) | 14[a] |
| 5 | SIPr-Au-$X_{Cbz}$ (**3o**) | 2 | - | EtOAc (degassed, under Ar) | 38[a] |
| 6 | $IPr^{*Me}$-Au-$X_{Cbz}$ (**3i**) | 2 | - | EtOAc (degassed, under Ar) | 66[b] (72[a]) |
| 7 | $IPr^{*Me}$-Au-$X_{Cbz}$ (**3i**) | 1 | - | EtOAc (degassed, under Ar) | 28[a] |
| 8 | SIPr-Au-$X_{Ind}$ (**3n**) | 2 | - | EtOAc (degassed, under Ar) | 13[a] |
| 9 | SIMes-Au-$X_{Ind}$ (**3d**) | 2 | - | EtOAc (degassed, under Ar) | 8[a] |
| 10 | $IPr^{*Me}$-Au-$X_{Cbz}$ (**3i**) | 2 | - | EtOAc (non-degassed, air) | not detected |
| 11 | $IPr^{*Me}$-Au-$X_{Cbz}$ (**3i**) | 2 | TEMPO | EtOAc (degassed, under Ar) | not detected |
| 12 | $Ru(byp)_3(PF_6)_2$ (**15**) | 2 | - | EtOAc (degassed, under Ar) | not detected |
| 13 | $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (**16**) | 2 | - | EtOAc (degassed, under Ar) | not detected |

[a] Yiled calculated by $^1$H NMR with 1,3,5-trimethoxybenzene as internal standard
[b] isolated yield

**Dimethyl (3a*S***,4a*S***,9b*S***)-3a,4,4a,5-tetrahydro-1*H*-cyclopenta[2,3]cyclobuta[1,2-*b*]indole-2,2(3*H*)-dicarboxylate** (**10**) A 15 mL Quartz tube was charged with NHC-Au-X complex (2 mol%, 1.96 μL) and indole derivative **9** (30.0 mg, 99.6 μL) and transferred to glovebox. Then reagent grade degassed solvent was added, and the reaction mixture was irradiated (one 20 W LED, 365 nm) for 16 h. Then reaction mixture was evaporated, and yield was calculated by $^1$H NMR with 1,3,5-trimethoxybenzene as internal standard. For complex **3i**, product was isolated by chromatography on silica (DCM to 20% EtOAc/hexanes, NOTE: attempts to separate product from substrate on silica using EtOAc/hexanes, MTBE/hexanes or acetone/hexanes have failed; separation of the product and substrate could also be achieved on aluminium oxide 90 active neutral purchased from Merck Milipore, 70-230 mesh, No. 1.01077.100) to give product **10** as light yellow oil (19.8 mg, 66%). 1H NMR (400 MHz, $CDCl_3$): 7.11 – 7.07 (m, 1H), 7.03 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.77 – 6.70 (m, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 4.04 (dd, *J* = 6.9, 4.5 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 2.96 – 2.86 (m, 1H), 2.81 (d, *J* = 14.3 Hz, 1H), 2.63 – 2.56 (m, 1H), 2.53 (d, *J* = 14.7 Hz, 1H), 2.46 (dd, *J* = 14.0, 3.4 Hz, 1H), 2.12 (ddd, *J* = 13.4, 9.0, 4.5 Hz, 1H), 2.03 (ddd, *J* = 13.3, 6.8, 4.5 Hz, 1H). Spectral data are in agreement with those reported.[20] The lack of reactivity of structurally related indoles to

indole 9 (and its analogs) in [2+2] cycloaddition reactions mediated by iridium complex 16 has been reported by Sho-Li You and co-workers.[31]

## 8. General Procedure 4 (GP 4) for catalytic hydrazination of phenyl alkyne




**11** **12**

Table S6. Optimization of the reaction conditions of hydrohydrazination of alkyne **11**.

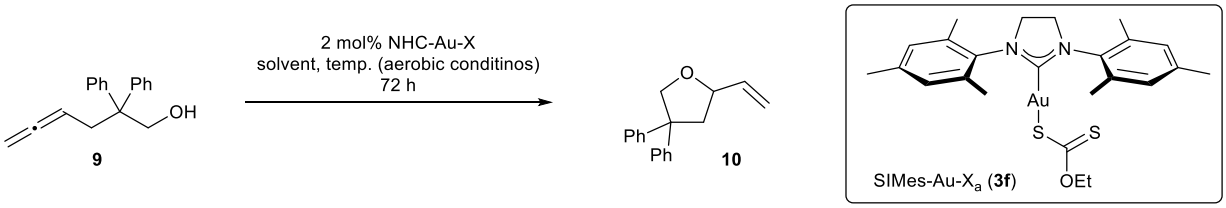
| **Entry** | **NHC-Au-X** (2 mol%) | **Solvent** | **Temperature (°C)** | **Yield (%)[a]** |
|---|---|---|---|---|
| 1 | none | DCM | 40 | - |
| 2 | only $NaBAr_4^F$ | DCM | 40 | - |
| 3 | Imes-Au-Xa (**3a**) | DCM | 40 | 21 |
| 4 | SIMes-Au-$X_a$ (**3f**) | DCM | 40 | 32 |
| 5 | IPr-Au-$X_a$ (**3j**) | DCM | 40 | 78 |
| 6 | **SIPr-Au-$X_{Neo}$** (**3m**) | DCM | 40 | **86** |
| 7 | SIPr-Au-$X_{Ind}$ (**3n**) | DCM | 40 | 37 |
| 8 | SIPr-Au-$X_{Cbz}$ (**3o**) | DCM | 40 | 15 |
| 9 | SIPr-Au-Cl[b] | DCM | 40 | - |

[a] isolated yield; [b] reaction conducted without $NaBAr_4^F$.

**(2*E*)-1-Phenyl-2-(1-phenylethylidene)hydrazine** (**12**) A 4 mL screw cap vial was charged with complex NHC-Au-X (1 mol%) and $NaBAr_4^F$ salt (2 mol%), and dry DCM was added (2 mL). The resulting mixture was stirred for 10 min. at rt and phenyl acetylene (**11**) was added via syringe (20.0 mg, 195 µmol, 1.0 equiv.). After 10 min., freshly distilled phenyl hydrazine (21.17 mg, 195.8 µmol, 1.0 equiv.) was added, and the resulting mixture was heated at 40 °C for 16 h (the progress of the reaction was monitored by TLC). Then solvent was evaporated and the residue was chromatographed Florisil (5% EtOAc/hexanes) to give a light brown oil (*Note*: *hydrazone **12** is highly sensitive and was kept under argon atmosphere all the time and during the manipulation of the crude material e.g., in rotary evaporator, the temp. was kept at 25 °C*). For example, following GP5 hydrazone **12** was isolated in 86% (35.5 mg) after chromatography using complex SIPr-Au-$X_a$ (**3j**) (1.4 mg, 1.96 µmol, 1 mol%), $NaBAr^F$ (3.47 mg, 3.92 µmol, 2 mol%), phenyl acetylene (20.0 mg, 195.8 µmol, 1.0 equiv.), phenyl hydrazine (21.2 mg, 195.8

μmol, 1.0 equiv.) and dry DCM (2 mL) after 16 h at 40 °C. $^1$H NMR (200 MHz, DMSO) δ 9.26 (s, 1H), 7.88 – 7.70 (m, 2H), 7.43 – 7.15 (m, 7H), 6.87 – 6.68 (m, 1H), 2.25 (d, *J* = 0.8 Hz, 3H). Spectral data are in agreement with those reported.[32] *NOTE: attempts to record spectra in $CDCl_3$ have failed; addition of $CDCl_3$ (passed through a pad of alumina before use or stored over 4Å molecular sieves to remove any acidic impurities) caused immediate formation of deep-blue or violet colour.*

## 9. General Procedure 5 (GP 5) for intramolecular hydroalkoxylation of allenes




**2-Ethenyl-4,4-diphenyltetrahydrofuran** (**10**) A 4 mL screw cap vial was charged with allene **9** (20.0 mg, 0.079 mmol, 1.0 equiv.) and NHC-Au-X (**3**) (1.60 μmol, 2 mol%). The solvent was added solvent (1 mL) and the resulting reaction mixture was heated at given temperature (the progress of the reaction was monitored by TLC, eluent 20% EtOAc/hexanes). Upon completion, the solvent was evaporated and the residue was chromatographed on silica (10% EtOAc/hexanes) to give tetrahydrofurane derivative **10** as a colourless oil. For example, following GP4 tetrahydrofurane **10** was isolated in 69% (13.7 mg) after chromatography using complex SIMes-Au-$X_a$ (**3f**) (0.99 mg, 1.60 μmol, 2 mol%) and $CH_3NO_2$ (1 mL) after 72 h at 65 °C. The detail optimization studies are presented in Table S4. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.12 (m, 10H), 5.91 (ddd, *J* = 17.1, 10.3, 6.9 Hz, 1H), 5.25 (d, *J* = 17.1 Hz, 1H), 5.11 (d, *J* = 10.3 Hz, 1H), 4.67 (dd, *J* = 8.7, 1.2 Hz, 1H), 4.44 (dt, *J* = 9.5, 6.4 Hz, 1H), 4.17 (d, *J* = 8.7 Hz, 1H), 2.67 (ddd, *J* = 12.1, 6.0, 1.2 Hz, 1H), 2.45 (dd, *J* = 12.2, 9.6 Hz, 1H). Spectra matched with those reported.[33]

Table S7. Optimization of the reaction conditions of cyclization allene **9**.

| **Entry** | **NHC-Au-X** (2 mol%) | **Solvent** | **Temperature (°C)** | **Yield (%)**[b] |
|---|---|---|---|---|
| 1 | none | DCE | 90 | 0 |
| 2 | SIMes-Au-$X_a$ (**3f**) | DCE | 65 | 0 |
| 3 | SIMes-Au-$X_a$ (**3f**) | DCE | 90 | 56 |
| 4 | SIMes-Au-$X_a$ (**3f**) | toluene | 65 | 0 |

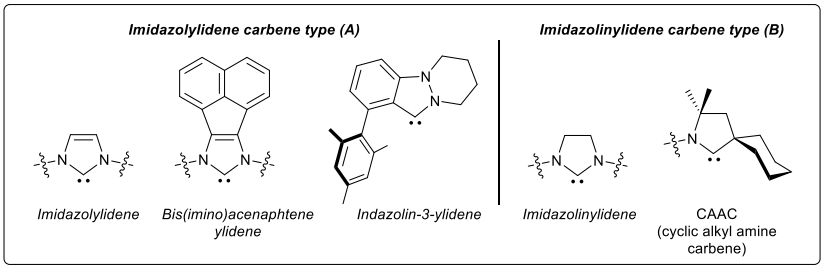
| | | | | |
|---|---|---|---|---|
| 5 | SIMes-Au-$X_a$ (**3f**) | toluene | 90 | 71 |
| 6 | SIMes-Au-$X_a$ (**3f**) | *n*-heptane | 65 | 0 |
| 7 | SIMes-Au-$X_a$ (**3f**) | *n*-heptane | 90 | 0 |
| 8 | none | $CH_3NO_2$ | 65 | 0 |
| 9 | SIMes-Au-$X_a$ (**3f**) | $CH_3NO_2$ | 65 | 69 |
| 10 | IMes-Au-$X_a$ (**3a**) | $CH_3NO_2$ | 65 | 65 |
| 11 | SIMes-Au-$X_a$ (**3c**) | $CH_3NO_2$ | 65 | 69 |
| 12 | IPr-Au-$X_a$ (**3j**) | $CH_3NO_2$ | 65 | 75 |
| 13 | **SIPr-Au-$X_a$** (**3l**) | $CH_3NO_2$ | 65 | **89** |
| 14 | IPr*$^{Me}$-Au-$X_a$ (**3g**) | $CH_3NO_2$ | 65 | 81 |
| 15 | IPr*$^{OMe}$-Au-Xa (**3h**) | $CH_3NO_2$ | 65 | 60 |
| 16 | SIPr-Au-Cl | $CH_3NO_2$ | 65 | 0 |

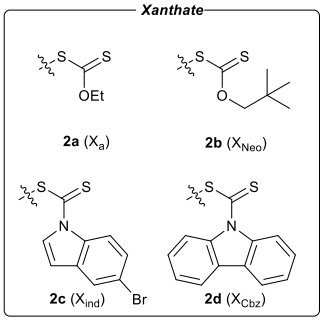
[a] conditions: 2 mol% SIMes-Au-$X_a$ (**3f**), solvent, 72 h, temp; [b] yield calculated by $^1$H NMR with 1,3,5-trimetoxybenzene as the internal standard (see, experiment procedure above).

## 10. Data of UV spectra of NHC-Met-complexes

Table S8. Maxima of absorption of NHC-Met-X complexes (recorded in THF).

| Entry | Complex NHC-Au-X | $\lambda_{max}$ (inTHF) | Xanthate | *Type of NHC skeleton* |
|---|---|---|---|---|
| **1** | IMes-Au-$X_a$ (**3a**) | **314** | **2a** | *Imidazolylidene (A)* |
| **2** | $IMes^{Acen}$-Au-$X_a$ (**3b**) | **320** | **2a** | *Imidazolylidene (A)* |
| **3** | SIMes-Au-$X_{Neo}$ (**3c**) | **312** | **2b** | *Imidazolinylidene (B)* |
| **4** | SIMes-Au-$X_{Ind}$ (**3d**) | **342** | **2c** | *Imidazolinylidene (B)* |
| **5** | SIMes-Au-$X_{Cbz}$ (**3e**) | **356** | **2d** | *Imidazolinylidene (B)* |
| **6** | SIMes-Au-$X_a$ (**3f**) | **314** | **2a** | *Imidazolinylidene (B)* |
| **7** | $IPr^{*Me}$-Au-$X_a$ (**3g**) | **317** | **2a** | *Imidazolylidene (A)* |
| **8** | $IPr^{*OMe}$-Au-$X_a$(**3h**) | **317** | **2a** | *Imidazolylidene (A)* |
| **9** | $IPr^{*Me}$-Au-$X_{Cbz}$ (**3i**) | **359** | **2d** | *Imidazolylidene (A)* |
| **10** | IPr-Au-$X_a$ (**3j**) | **314** | **2a** | *Imidazolylidene (A)* |
| **11** | $IPr^{Me}$-Au-$X_a$ (**3k**) | **314** | **2a** | *Imidazolylidene (A)* |
| **12** | SIPr-Au-$X_a$ (**3l**) | **314** | **2a** | *Imidazolinylidene (B)* |
| **13** | SIPr-Au-$X_{Neo}$ (**3m**) | **315** | **2b** | *Imidazolinylidene (B)* |
| **14** | SIPr-Au-$X_{Ind}$ (**3n**) | **343** | **2c** | *Imidazolinylidene (B)* |
| **15** | SIPr-Au-$X_{Cbz}$ (**3o**) | **355** | **2d** | *Imidazolinylidene (B)* |
| **16** | ICy-Au-$X_a$ (**3p**) | **315** | **2a** | *Imidazolylidene (A)* |
| **17** | $IMes^{Cyhep}$-Au-$X_a$ (**3q**) | **315** | **2a** | *Imidazolylidene (A)* |
| **18** | $IPr^{Cyhep}$-Au-$X_a$ (**3r**) | **315** | **2a** | *Imidazolylidene (A)* |
| **19** | NHC-Au-$X_a$ (**3s**) | **312, 322** | **2a** | *Imidazolylidene (A)* |
| **20** | NHC-Au-$X_a$ (**3t**) | **327** | **2a** | *Imidazolinylidene (B)* |
| **21** | ICy-Au-$X_a$ (**3u**) | **313** | **2a** | *Imidazolinylidene (B)* |
| **22** | NHC-Au-$X_a$ (**3v**) | **314** | **2a** | *Imidazolinylidene (B)* |
| **23** | NHC-Au-$X_a$ (**3w**) | **344** | **2c** | *Imidazolinylidene (B)* |
| **24** | NHC-Cu-$X_a$ (**4a**) | **309** | **2a** | *Imidazolinylidene (B)* |
| **25** | NHC-Ag-$X_a$ (**4b**) | **316** | **2a** | *Imidazolinylidene (B)* |
| **26** | NHC-Cu-$X_a$ (**4c**) | **345** | **2a** | *Imidazolinylidene (B)* |
| **27** | NHC-Ag-$X_a$ (**4d**) | **316** | **2a** | *Imidazolinylidene (B)* |



## 11. Photophysical properties of gold complexes

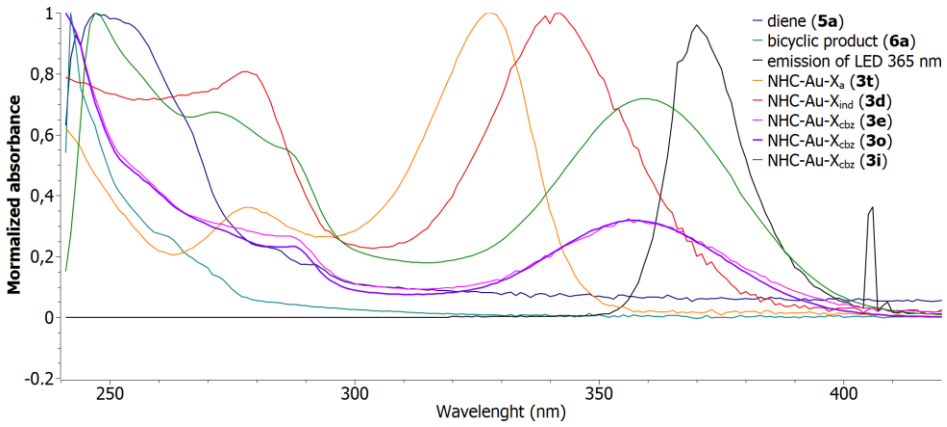



Fig. S11. Normalized spectra of absorption of diene **5a**, bicycle **6a**, complexes **3t**, **3d**, **3e**, **3o**, **3i** and emission of LED 365 nm.

The UV/Vis absorption spectra of investigated complexes are characterized by the presence of broad unstructured band at *ca.* 373 nm, 385 nm or 420 nm for complexes **3f, 3t** and **3d**, respectively (Table S6). These bands are only weakly allowed and according to literature may belong to metal-to-ligand charge transfer states MLCT.[34] At higher energies (in a range of 340 - 390 nm) an intense band assigned to the ligand to ligand transitions are present. Compounds **3f, 3t** and **3d** display very weak luminescence with a broad emission band with a maximum at 340, 370 and 390 nm in air-equilibrated THF at ambient temperature. This broad, unstructured emission may be assigned to phosphorescence from the lowest MLCT state. Unfortunately the short, in a range of several nanoseconds, decay times suggest that the emission is strongly quenched.

The UV/Vis absorption spectra of complexes **3e**, **3i**, and **3o** are similar to each other, with a maximum at 360 nm. The luminescence of these complexes in THF, excited at 300 nm, exhibits a structured band with several peaks at 340, 358, and 376 nm. This luminescence is attributed to the fluorescence of the carbazole ligand. The luminescence of complex **3i** was measured in 2-MTHF at both room temperature and low (77 K) temperature. 2-Methyl tetrahydrofurane (2-MTHF) was chosen as a glassy solvent at low temperature. The spectrum at room temperature, excited at 300 nm, is similar to those measured in THF at room temperature. At low temperature, a new structured band appears at lower energy, with four peaks at 408, 424, 437, and 451 nm. This new band observed at low temperature is assigned to the phosphorescence of the carbazole subunit. The estimated energy of the 0-0

transition (407.5 nm), obtained from the phosphorescence spectrum, corresponds to the energy of the triplet state, which is 70.2 kcal/mol.

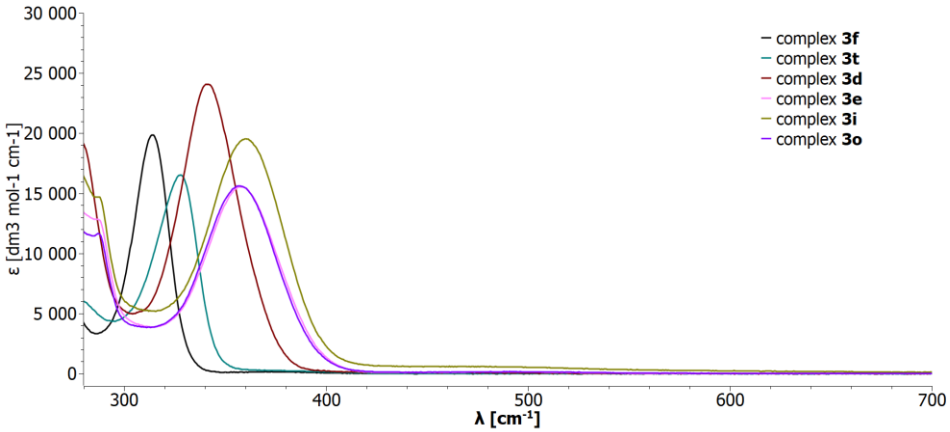



Fig. S12. Normalized spectra of absorption of complexes **3f**, **3t**, **3d**, **3e**, **3o**, **3i**.

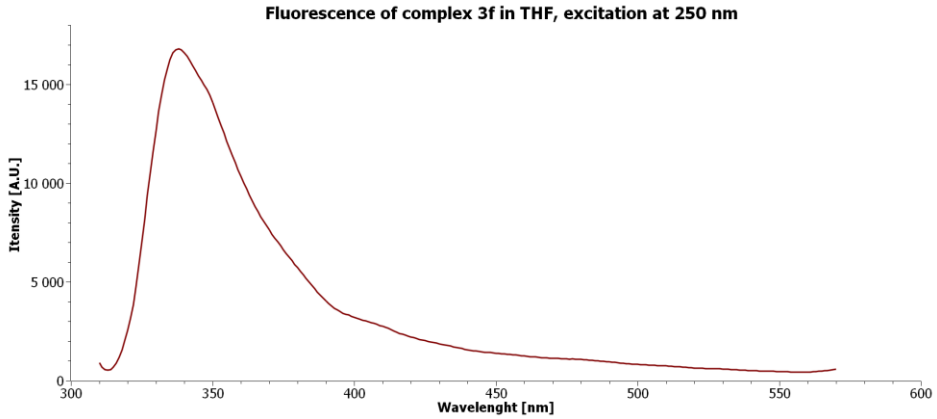



Fig. S13. Fluorescence of complex 3f in THF (excitation at 250 nm).

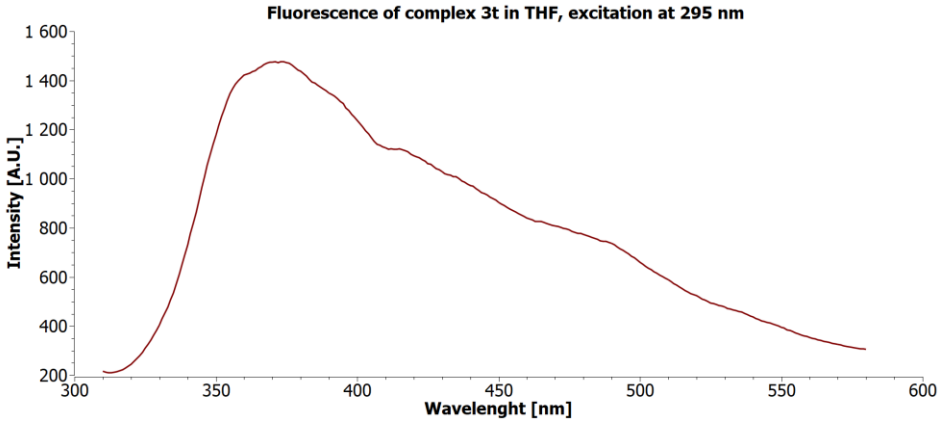



Fig. S14. Fluorescence of complex 3tin THF (excitation at 295 nm).

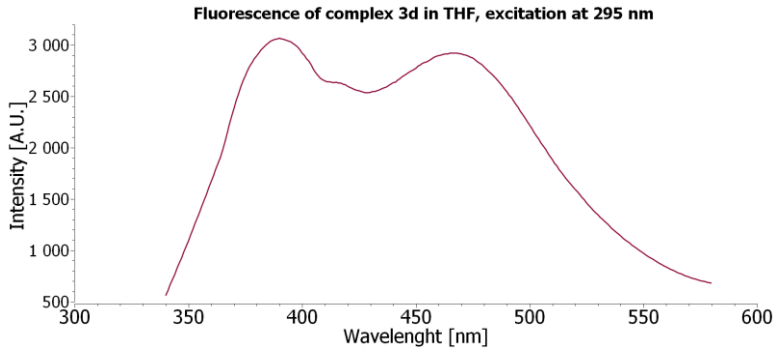



Fig. S15. Fluorescence of complex **3d** in THF (excitation at 295 nm).

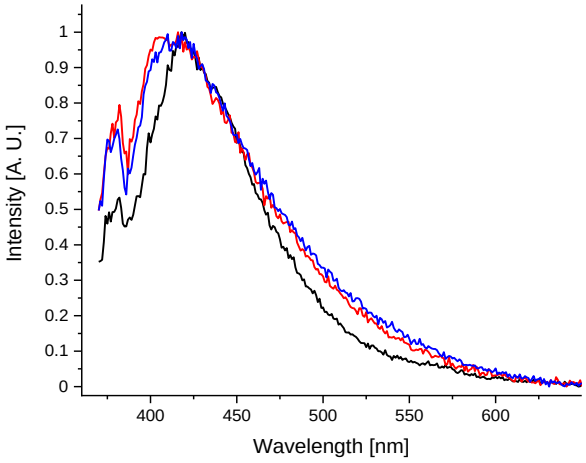



Fig. S16. Luminescence of **3e**, **3o** and **3i** in THF at room temperature excited at 360 nm.

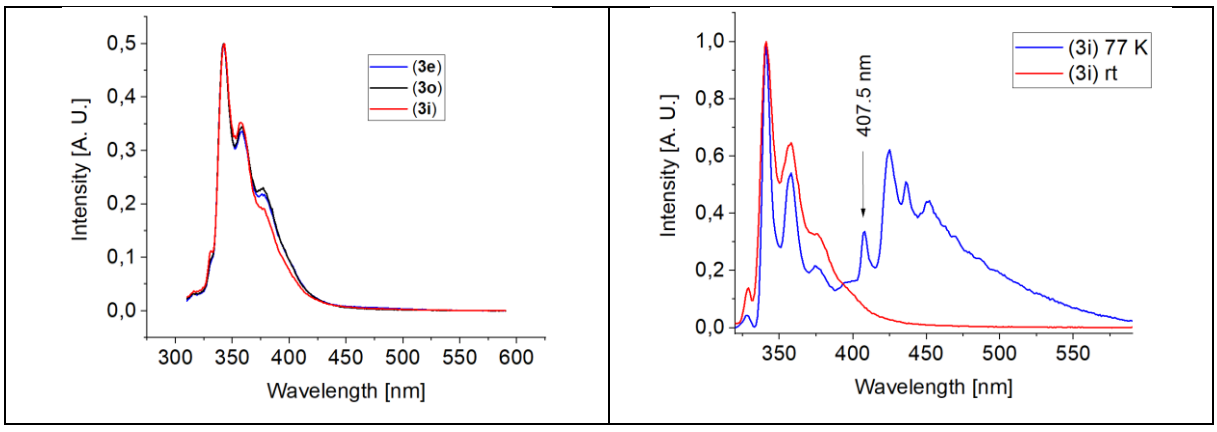



Figure S17. Left: Luminescence of **3e**, **3o** and **3i** in THF at room temperature excited at 300 nm. Right: Luminescence of **3i** in 2-MTHF (2-methyl tetrahydrofuran) at room temperature (red) and 77 K (blue) excited at 300 nm.

Table S9. Photophysical data for complexes **3f**, **3t** and **3d** in air-equilibrated THF and degassed THF (*) at ambient temperature

| Complex | $\lambda_{abs}{}^{1}$,nm ($\varepsilon$ [$\times 10^3$ $M^{-1}$ $cm^{-1}$]) | $\lambda_{abs}{}^{2}$,nm ($\varepsilon$ [$\times 10^3$ $M^{-1}$ $cm^{-1}$]) | $\lambda_{PL}$, nm | $\tau$, ns (amplitude, %)[a] | $\tau$*, ns (amplitude, %)[b] |
|---|---|---|---|---|---|
| **3f** | 373 (0.16) | 314 (19.9) | 340 | 2.0 (21), 7.0 (32) | 5.4 (29), 31 (44) |
| **3t** | 385 (0.24) | 327 (16.5) | 370 | 2.0 (30), 7.0 (44) | 2.5 (25), 10 (37) |
| **3d** | 475 (0.08) | 341 (24.1) | 390 | 1.2 (33), 5.0 (40) | 2 (11), 8 (30) |
| **3e** | 486 (0.12) | 358 (15.5) | 340 | 11.8 | n.d. |
| **3o** | 494 (0.12) | 356 (15.6) | 340 | 9.1 | n.d. |
| **3i** | 490 (0.17) | 360 (19.6) | 340 | 8.0 | n.d. |

[a] air-equilibrated THF; [b] degassed THF

**Unsuccessful Stern-Volmer experiment**

Quenching studies were performed using $5 \cdot 10^{-5}$ M solution of complex **3i** in dry degassed THF and varying concentration of indole **9**. The samples were prepared at once in nitrogen-filled glovebox using degassed THF in screw-cap quartz cuvettes. All samples were excited at $\lambda_{ex}$ = 300 nm, 310 nm, 320 nm and 340 nm and emission was detected at $\lambda_{em}$ = 342 nm and 357 nm, 342 nm and 358 nm, 342 nm and 356 nm, 357 nm and 377 nm, respectively. It was found that each portions of quencher, namely indole **9**, increases the luminescence. A plausible explanation may arise from the short excited state lifetime of the complex **3i** as well as trace absorption of indole **9** in this area (higher concentration of the quencher, namely, indole **9**, increasing overall fluorescence).

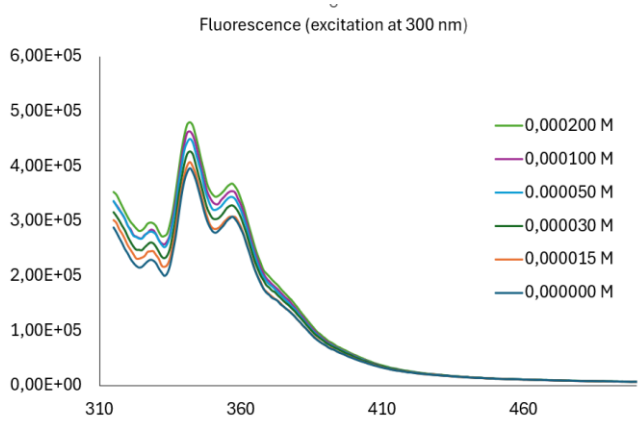



Fig. S18. Quenching studies of complex **3i** with indole **9** (excitation at 300 nm).

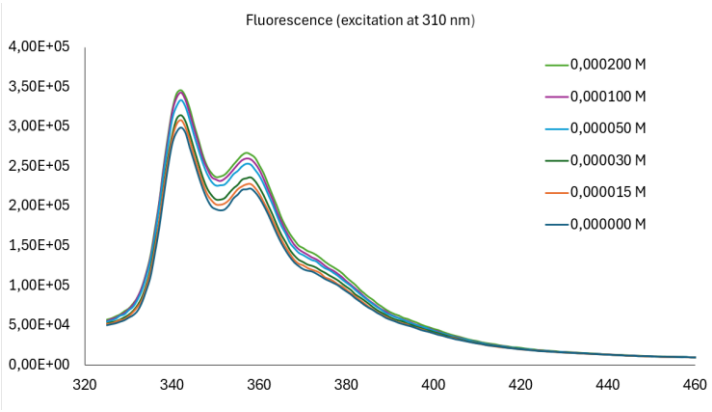



Fig. S19. Quenching studies of complex **3i** with indole **9** (excitation at 320 nm).

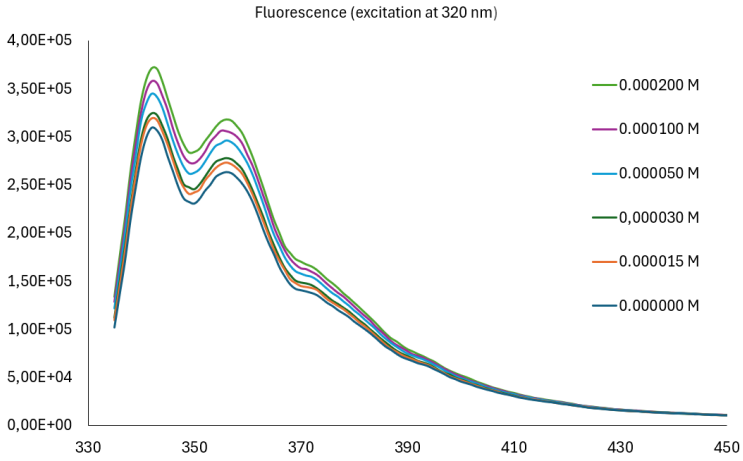



Fig. S20. Quenching studies of complex **3i** with indole **9** (excitation at 320 nm).

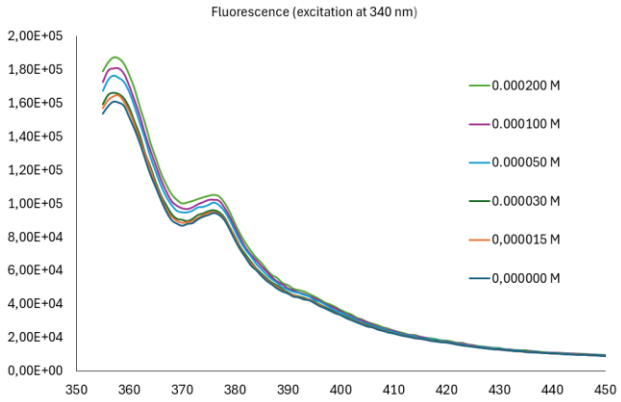



Fig. S21. Quenching studies of complex **3i** with indole **9** (excitation at 340 nm).

## Generation of singlet oxygen experiments

The generation of singlet oxygen was measured for both the reference compound, known from the literature, complex **17**, and complex **3o** (Fig. S22 and Fig. S23). By comparing the amplitudes of singlet oxygen decays measured under the same conditions at room temperature, it is possible to conclude that the intersystem crossing (ISC) in complex **17** is approximately 40 times more efficient than in complex **3o**.

The singlet oxygen decays ($^1O_2$, emission at $\lambda_{max}$ = 1275 nm) were measured using a custom experimental setup based on a BENTHAM DTMc300 double monochromator, equipped with a thermoelectrically cooled photomultiplier (Hamamatsu H10330C-75, 950–1700 nm detection range) and a Yokogawa DL9140 fast oscilloscope. Excitation was provided by an Opotek Radiant 355 laser (210–2500 nm tunable spectral region, 5 ns pulsewidth, 10 Hz repetition rate). The experimental accuracy was estimated to be 10%.

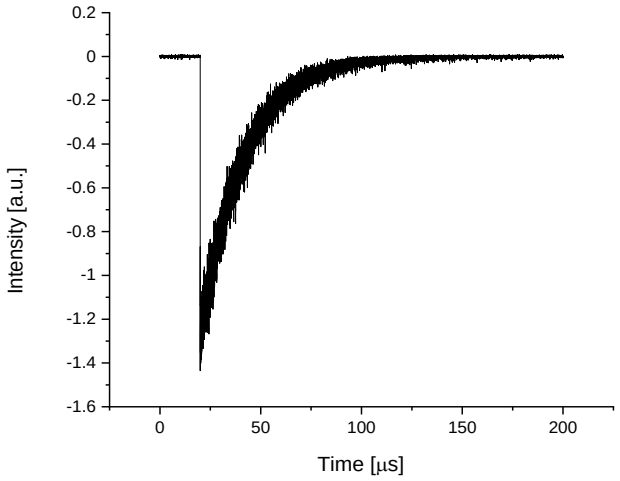



Fig. S22. Decay of singlet oxygen phosphorescence (at 1275 nm) generated by complex **17** in THF with optical density ~ 0.5 at excitation wavelength 340 nm.

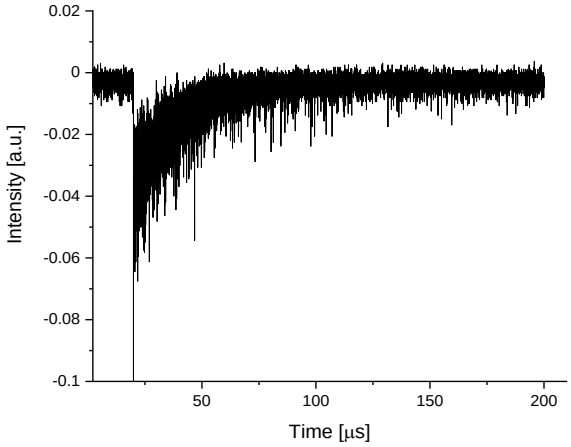



Fig. S23. Decay of singlet oxygen phosphorescence (at 1275 nm) generated by complex **3o** in THF with optical density ~ 0.5 at excitation wavelength 340 nm.

**UV-Vis studies on the possible formation of electron donor-acceptor complex**

To exclude the formation of an electron donor-acceptor (EDA) complex between the NHC-Au-X complexes and the substrate, UV-Vis spectra were recorded for individual solutions of the gold complexes and alkenes (diene **5a**, coumarin **7**, and indole **9**) and directly compared with a mixture containing the NHC-Au-X complex and the alkene. In all cases investigated, the absorption maxima remained unchanged, thereby confirming the absence of EDA complex formation

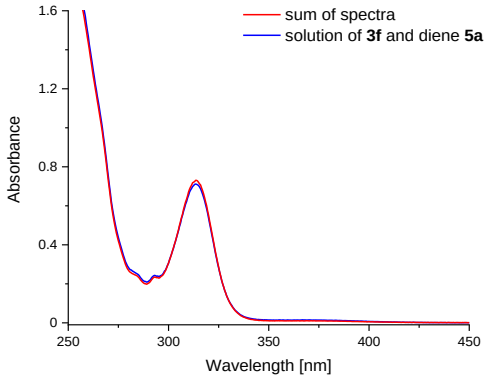



Fig. S24. Comparison of absorption spectra of complex **3f** and diene **5a** in THF (concentration of each component c = $0.83 \cdot 10^{-4}$ M).

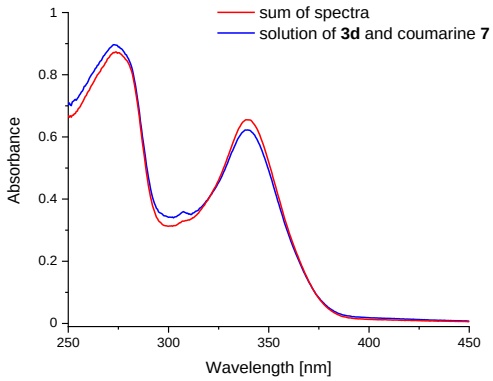



Fig. S25. Comparison of absorption spectra of complex **3d** and coumarine **7** in THF (concentration of each component c = $5.35 \cdot 10^{-5}$ M).

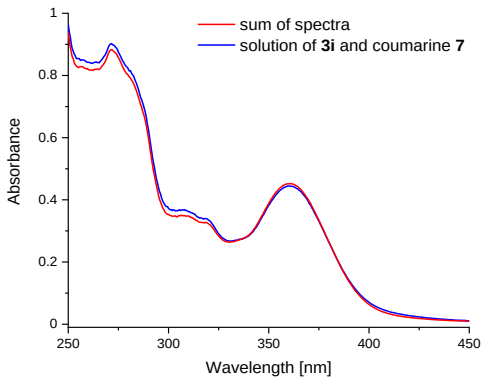



Fig. S26. Comparison of absorption spectra of complex **3i** and coumarine **7** in THF (concentration of each component c = $5.35 \cdot 10^{-5}$ M).

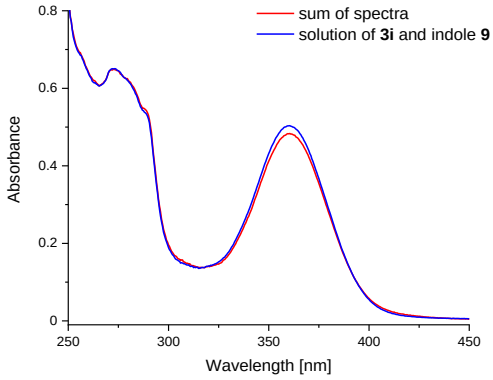



Fig. S27. Comparison of absorption spectra of complex **3i** and indole **9** in THF (concentration of each component c = $5.35 \cdot 10^{-5}$ M).

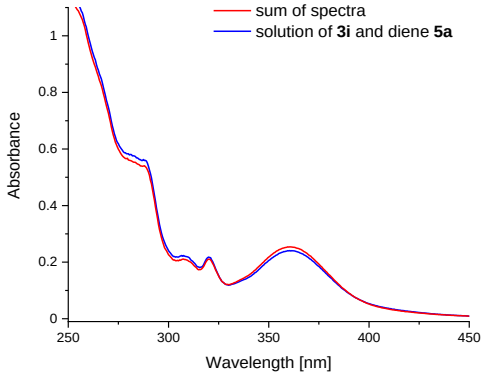



Fig. S28. Comparison of absorption spectra of complex **3i** and diene **5a** in THF (concentration of each component c = $5.35 \cdot 10^{-5}$ M).

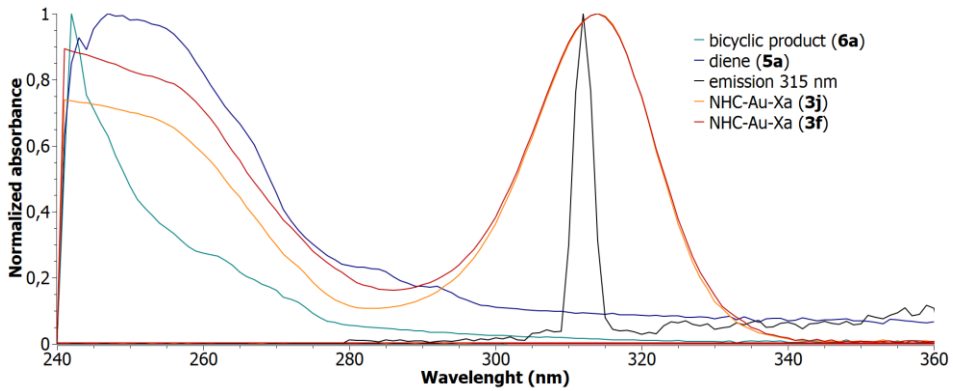



Fig. S29. Normalized spectra of absorption of complexes diene 5a, bibycle 6a, complexes **3j**, **3f** and emission of lamp 315 nm.

## 12. Electrochemical studies

Cyclic voltammetry measurements were conducted on Bio-Loic SAS model SP-200 using tetrabutylammonium hexafluorophosphate as electrolyte (0.1 M in dry degassed MeCN, 77.5 mg/2.0 mL of MeCN). A cylindrical three-electrode cell was equipped with a glassy carbon working electrode, a 25 mm platinum wire as the counter electrode and Ag/AgCl (3.0 M NaCl) electrode as the reference electrode. The scan rate for all experiments was 100 $mV \cdot s^{-1}$.

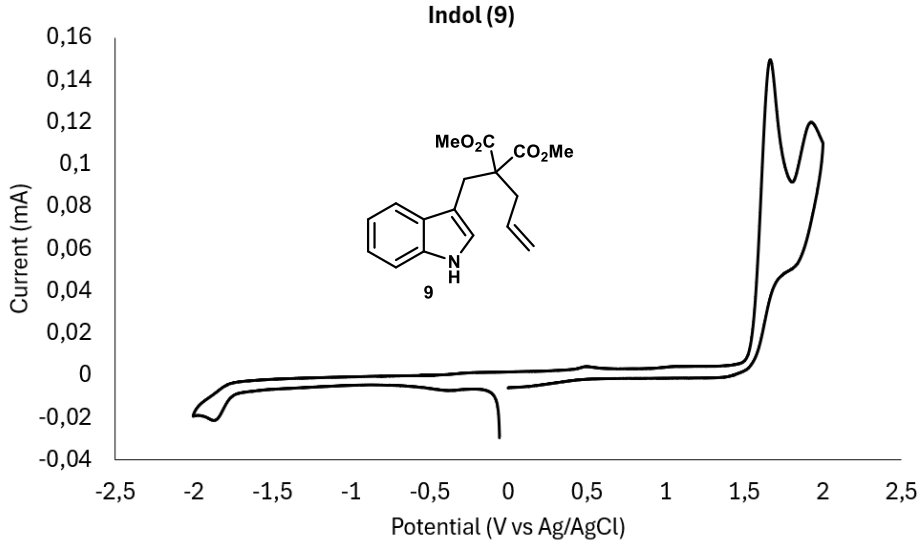



Fig. S30. CV of indole (**9**) in dry degassed MeCN (0.1 M $Bu_4NPF_6$, 100 $mV \cdot s^{-1}$).

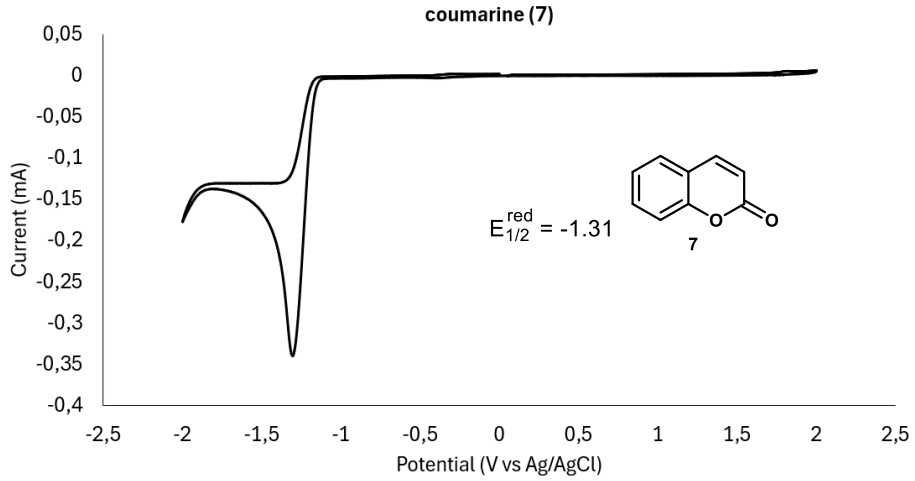



Fig. S31. CV of coumarine (**9**) in dry degassed MeCN (0.1 M $Bu_4NPF_6$, 100 $mV \cdot s^{-1}$).

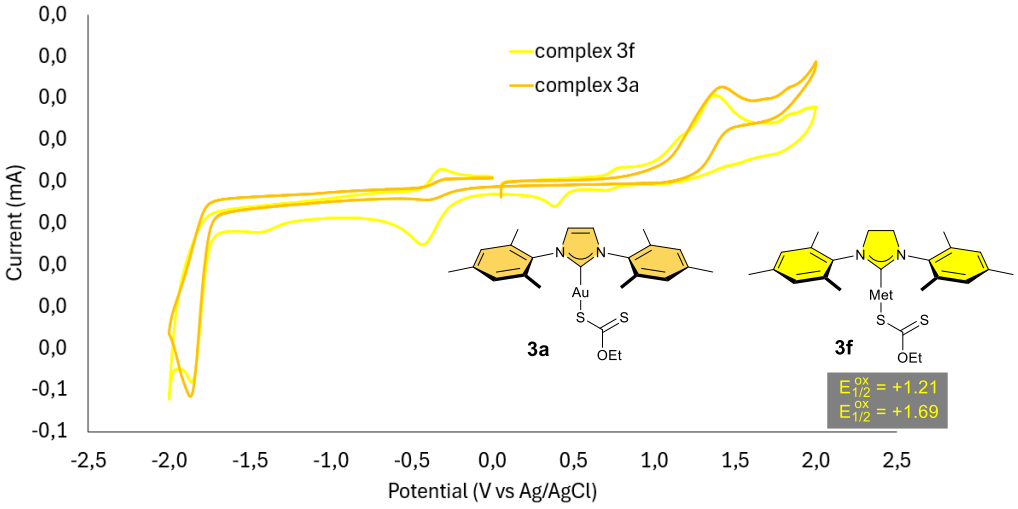



Fig. S32. CV of complexes **3a** and **3f** in dry degassed MeCN (0.1 M $Bu_4NPF_6$, 100 mV·$s^{-1}$).

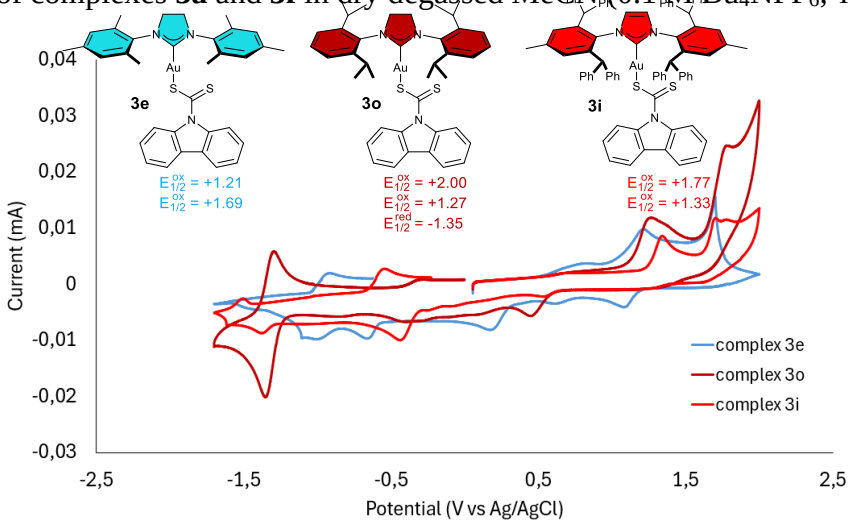



Fig. S33. CV of complexes **3e**, **3o** and **3i** in dry degassed MeCN (0.1 M $Bu_4NPF_6$, 100 mV·$s^{-1}$).

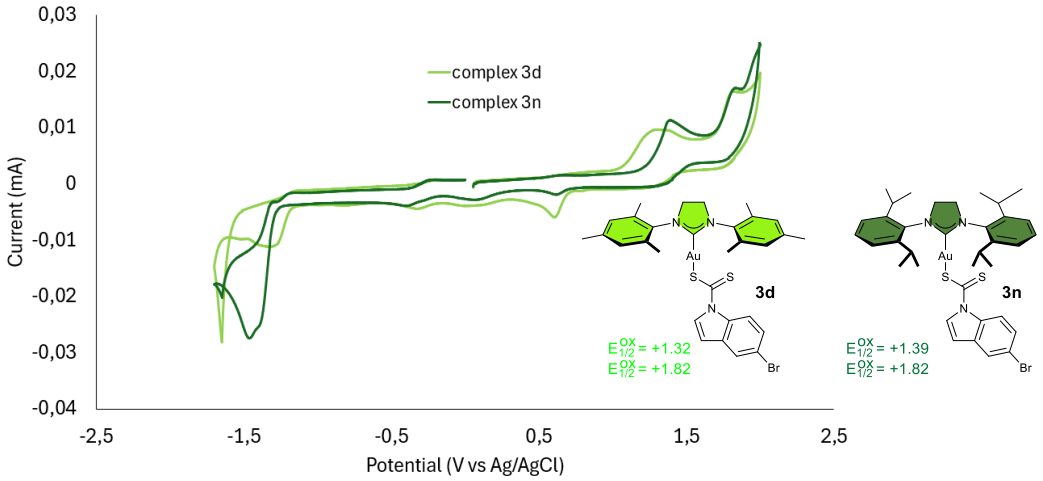



Fig. S34. CV of complexes **3d** and **3n** in dry degassed MeCN (0.1 M $Bu_4NPF_6$, 100 mV·$s^{-1}$).

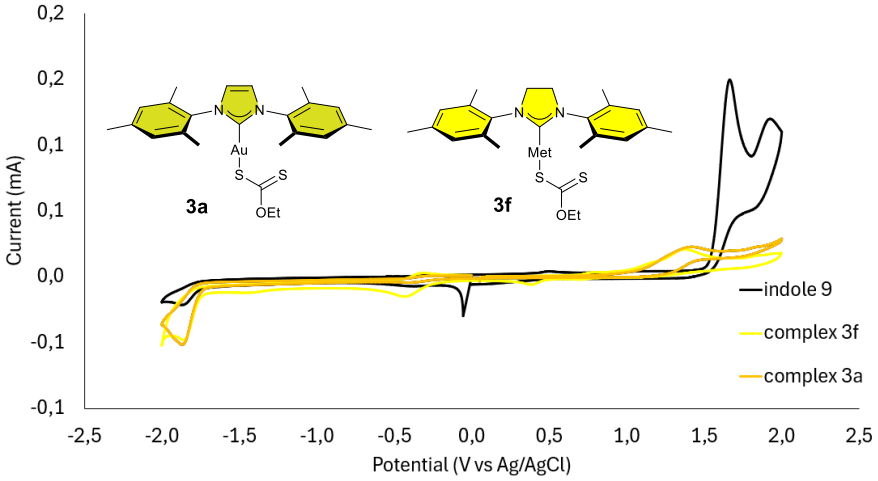



Fig. S35. CV of complexes **3a**, **3f** and indole **9** in dry degassed MeCN (0.1 M $Bu_4NPF_6$, 100 $mV \cdot s^{-1}$).

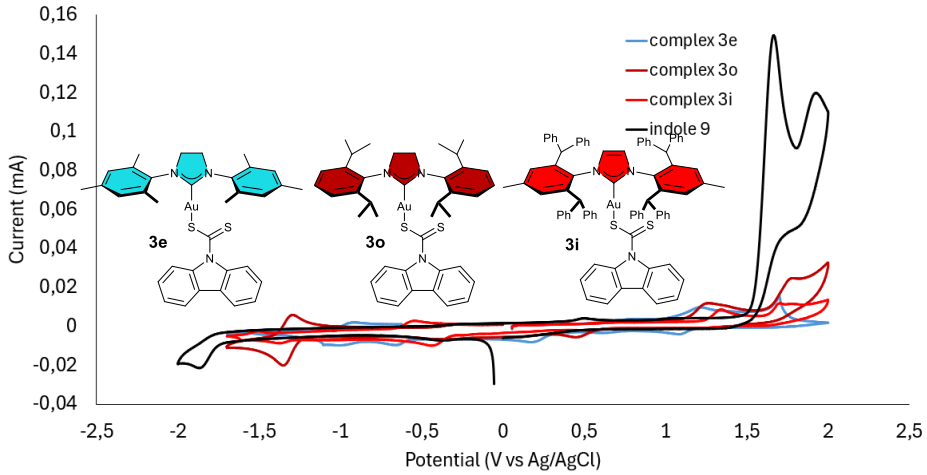



Fig. S36. CV of complexes **3e**, **3o**, **3i** and indole **9** in dry degassed MeCN (0.1 M $Bu_4NPF_6$, 100 $mV \cdot s^{-1}$).

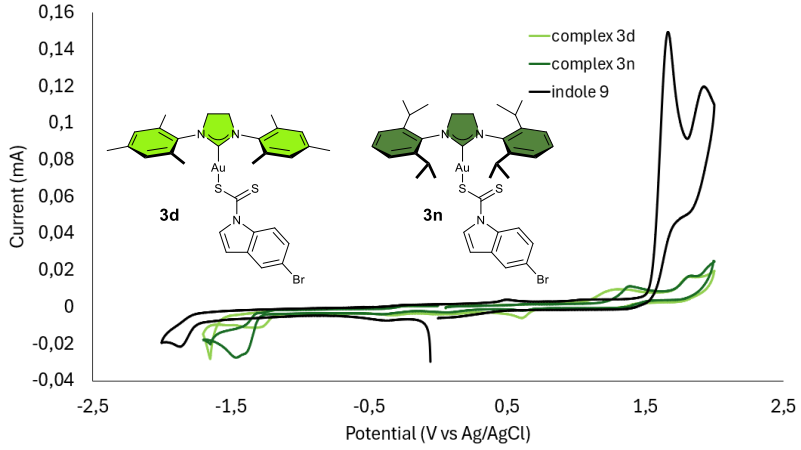



Fig. S37. CV of complexes **3d**, **3n** and indole **9** in dry degassed MeCN (0.1 M $Bu_4NPF_6$, 100 $mV \cdot s^{-1}$).

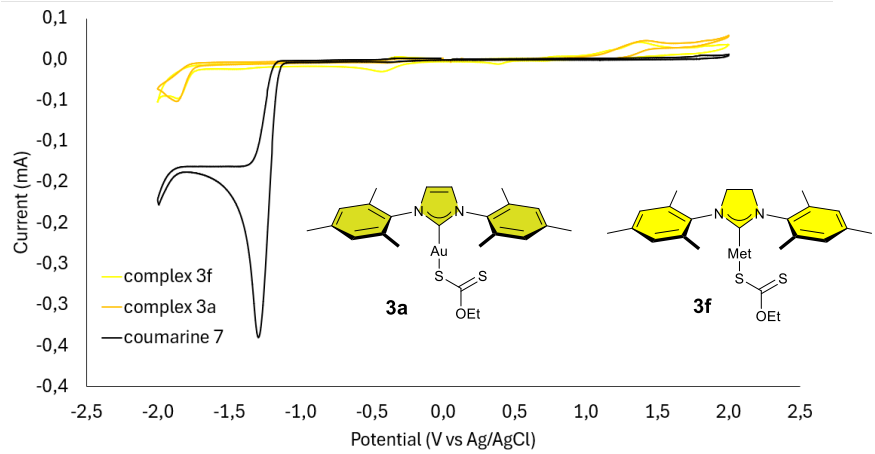



Fig. S38. CV of complexes **3a**, **3f** and coumarine **7** in dry degassed MeCN (0.1 M $Bu_4NPF_6$, 100 $mV \cdot s^{-1}$).

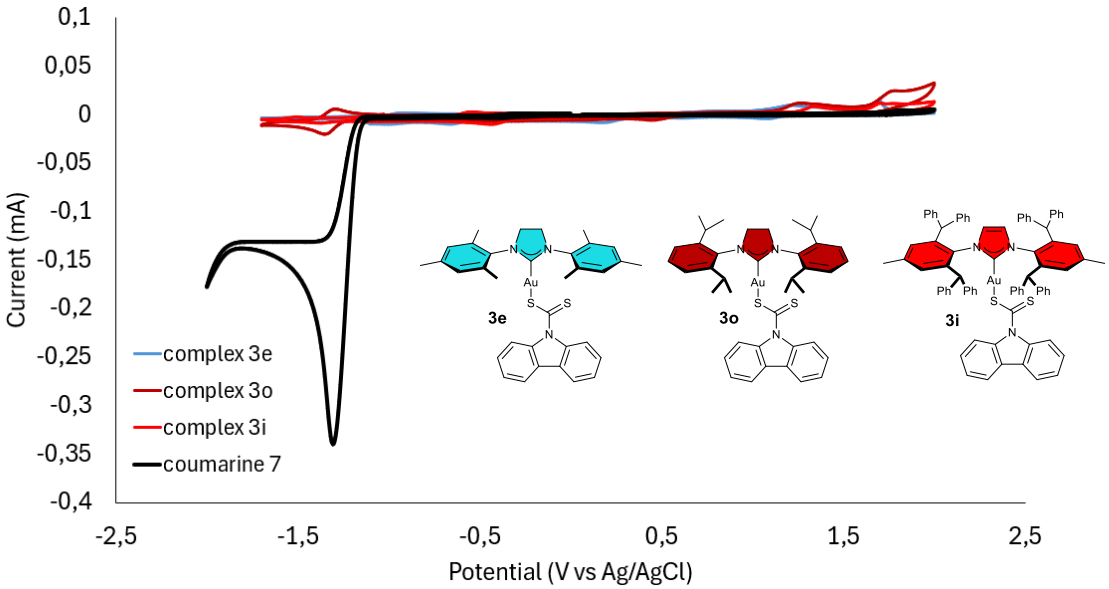



Fig. S39. CV of complexes **3e**, **3o**, **3i** and coumarine **7** in dry degassed MeCN (0.1 M $Bu_4NPF_6$, 100 $mV \cdot s^{-1}$).

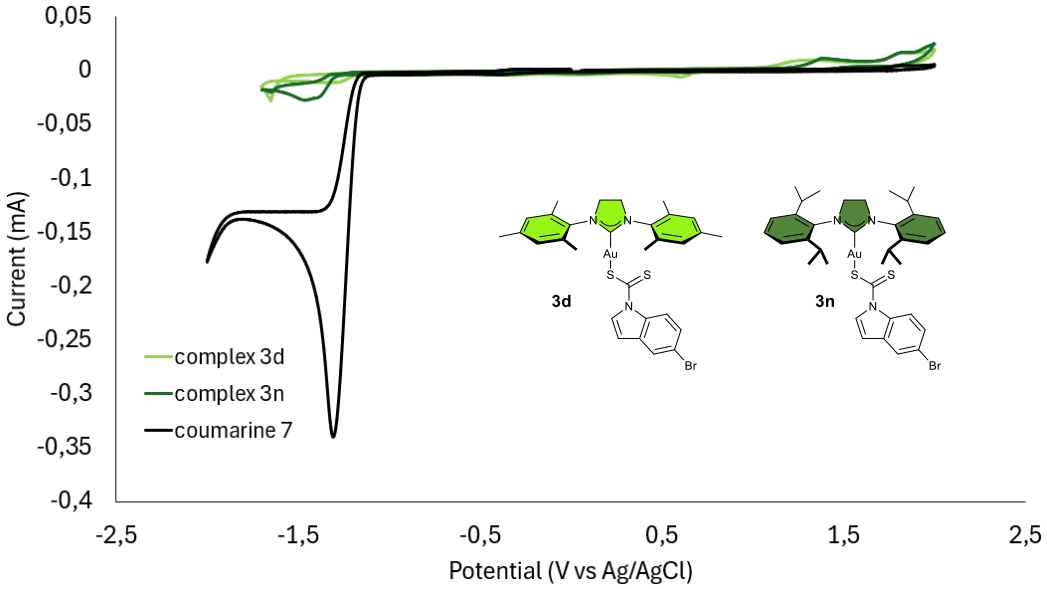
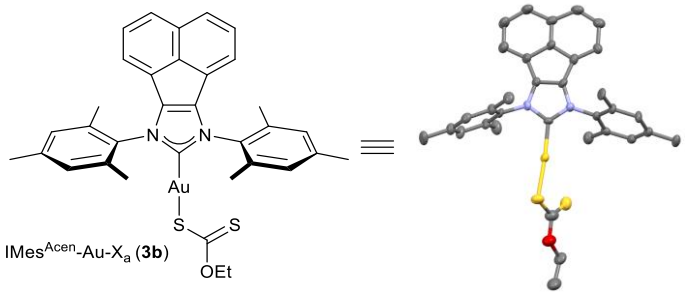



Fig. S40. CV of complexes **3d**, **3n** and coumarine **7** in dry degassed MeCN (0.1 M $Bu_4NPF_6$, 100 $mV \cdot s^{-1}$).

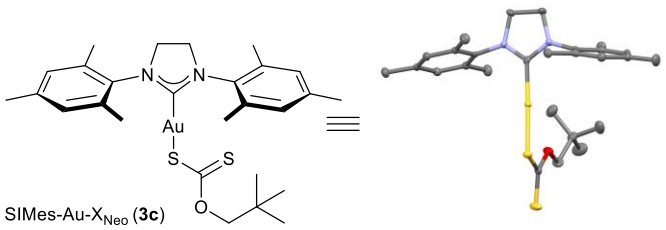
### 13. Single crystal X-ray diffraction

The crystals were embedded in the inert perfluoropolyalkylether (viscosity 1800cSt; ABCR GmbH) and mounted using Hampton Research Cryoloops. The X-ray data were collected on a SuperNova Agilent diffractometer using MoKα (λ = 0.71073 Å) or CuKα (λ = 1.54184 Å) radiation. The crystals were flash cooled to 100.0(1) K in a nitrogen gas stream and kept at this temperature during the experiments. The crystals of the complex **3j** at 250 K were found to be sensitive to the flash freezing, therefore the dataset was collected at 250 K. Then the same crystal was slowly cooled at the nitrogen gas stream at the diffractometer and new dataset was re-collected at 100 K. The data were processed with *CrysAlisPro*.[35] Structures were solved by direct methods and refined using *SHELXL* [36] under *WinGX*.[37]

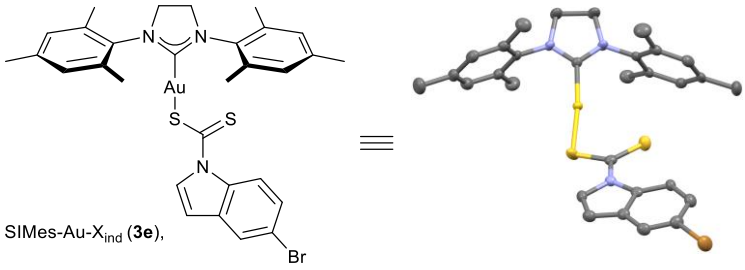



**Crystal data for 3b**: ($C_{34}H_{33}AuN_2OS_2 \cdot CH_2Cl_2$), *Mr* = 831.6, yellow plates, monoclinic, space group *I*2/*a*, *a* = 31.6408(4), *b* = 8.4069(1), *c* = 51.1168(5) Å, *β* = 91.220(1)°, *V* =

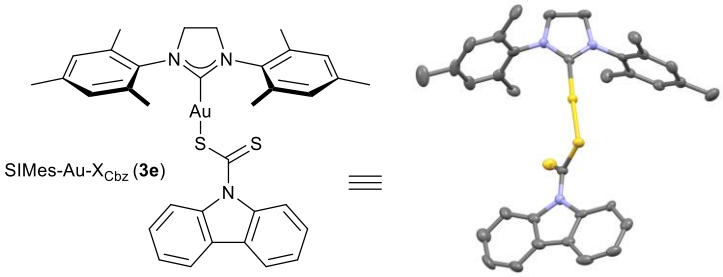
13594.0(3) Å$^3$, $Z$ = 16, $\rho_{calc}$ = 1.62 g cm$^{-3}$, $\mu$(CuK$\alpha$) = 10.96 mm$^{-1}$, $\theta_{max}$ = 68.3°, 165391 reflections measured, 12423 unique, 790 parameters, $R$ = 0.077, $wR$ = 0.189 ($R$ = 0.087, $wR$ = 0.195 for all data), GooF = 1.16. CCDC 2311337.



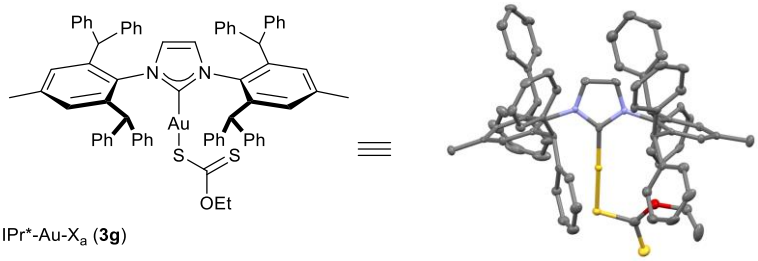

**Crystal data for 3c**: ($C_{27}H_{37}AuN_2OS_2$), $Mr$ = 666.7, colourless prisms, triclinic, space group $P$-1, $a$ = 9.7973(3), $b$ = 10.8525(2), $c$ = 13.7903(3) Å, $\alpha$ = 95.648(2), $\beta$ = 102.280(2), $\gamma$ = 102.271(2)°, $V$ = 1384.05(7) Å$^3$, $Z$ = 2, $\rho_{calc}$ = 1.60 g cm$^{-3}$, $\mu$(MoK$\alpha$) = 5.49 mm$^{-1}$, $\theta_{max}$ = 30.1°, 22044 reflections measured, 7292 unique, 307 parameters, $R$ = 0.026, $wR$ = 0.061 ($R$ = 0.029, $wR$ = 0.063 for all data), GooF = 0.98. CCDC 2311327.




**Crystal data for 3d**: ($C_{30}H_{31}AuBrN_3S_2$), $Mr$ = 774.6, yellow prisms, monoclinic, space group $P2_1/n$, $a$ = 8.74515(7), $b$ = 13.8159(1), $c$ = 23.7678(2) Å, $\beta$ = 96.4039(8)°, $V$ = 2853.77(4) Å$^3$, $Z$ = 4, $\rho_{calc}$ = 1.80 g cm$^{-3}$, $\mu$(MoK$\alpha$) = 6.73 mm$^{-1}$, $\theta_{max}$ = 30.2°, 44942 reflections measured, 7851 unique, 340 parameters, $R$ = 0.031, $wR$ = 0.066 ($R$ = 0.040, $wR$ = 0.069 for all data), GooF = 1.07. CCDC 2311331.

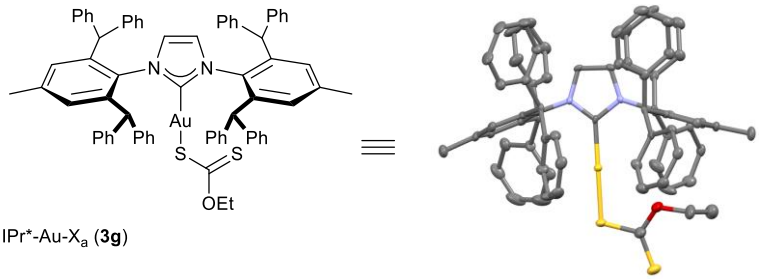


**Crystal data for 3e**: ($C_{34}H_{34}AuN_3S_2$), *Mr* = 745.7, red prisms, monoclinic, space group *Ia*, *a* = 18.8852(4), *b* = 10.4643(2), *c* = 32.3771(6) Å, $\beta$ = 106.267(2)°, *V* = 6142.2(2) Å$^3$, *Z* = 8, $\rho_{calc}$ = 1.61 g cm$^{-3}$, $\mu$(MoK$\alpha$) = 4.95 mm$^{-1}$, $\theta_{max}$ = 28.9°, 39123 reflections measured, 11851 unique, 734 parameters, *R* = 0.037, *wR* = 0.086 (*R* = 0.038, *wR* = 0.087 for all data), GooF = 0.99. CCDC 2311335.



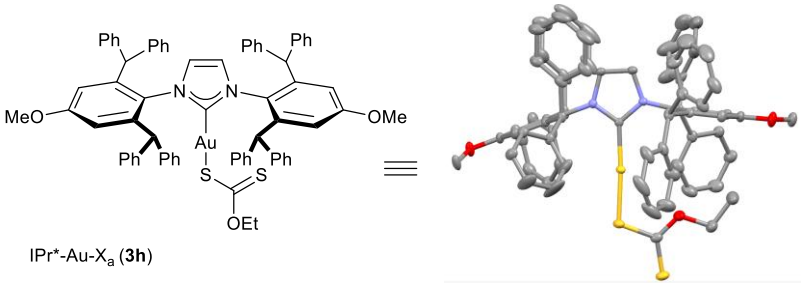
IPr*-Au-X$_a$ (**3g**)

**Crystal data for 3g**: ($C_{72}H_{61}AuN_2OS_2 \cdot CH_2Cl_2$), *Mr* = 1316.2, colourless prisms, orthorhombic, space group *Pbca*, *a* = 18.8330(2), *b* = 24.6372(2), *c* = 25.5224(2) Å, *V* = 11842.2(2) Å$^3$, *Z* = 8, $\rho_{calc}$ = 1.48 g cm$^{-3}$, $\mu$(MoK$\alpha$) = 2.69 mm$^{-1}$, $\theta_{max}$ = 27.5°, 13608 reflections measured, 13608 unique, 731 parameters, *R* = 0.028, *wR* = 0.073 (*R* = 0.066, *wR* = 0.078 for all data), GooF = 0.84. CCDC 2311328.



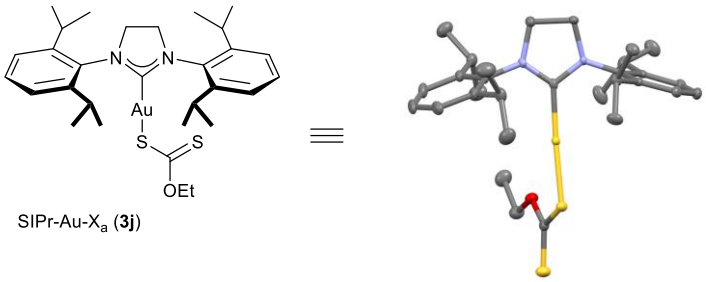
IPr*-Au-X$_a$ (**3g**)

**Crystal data for 3g**: ($C_{72}H_{61}AuN_2OS_2$), *Mr* = 1231.3, colourless prisms, monoclinic, space group $P2_1/c$, *a* = 12.7865(3), *b* = 18.6284(5), *c* = 24.3015(7) Å, $\beta$ = 93.930(2)°, *V* = 5774.8(3) Å$^3$, *Z* = 4, $\rho_{calc}$ = 1.42 g cm$^{-3}$, $\mu$(MoK$\alpha$) = 2.67 mm$^{-1}$, $\theta_{max}$ = 27.5°, 20826 reflections measured, 20826 unique, 704 parameters, *R* = 0.034, *wR* = 0.068 (*R* = 0.060, *wR* = 0.073 for all data), GooF = 0.91. CCDC 2311330.



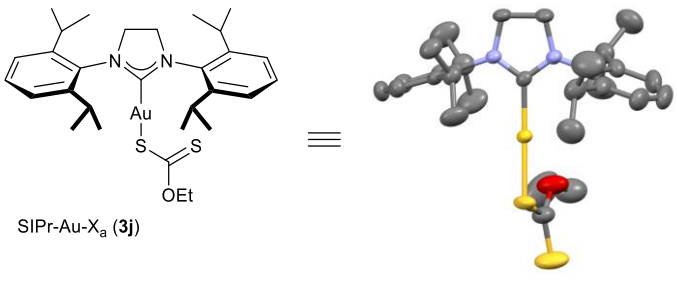

IPr*-Au-$X_a$ (**3h**)

**Crystal data for 3h**: ($C_{72}H_{61}AuN_2O_3S_2 \cdot 3(CH_2Cl_2)$), *Mr* = 1518.1, colourless prisms, monoclinic, space group $P2_1/c$, $a$ = 15.7943(1), $b$ = 18.7129(1), $c$ = 24.2110(2) Å, $\beta$ = 105.269(1)°, $V$ = 6903.14(9) Å$^3$, $Z$ = 4, $\rho_{calc}$ = 1.46 g cm$^{-3}$, $\mu$(MoK$\alpha$) = 2.47 mm$^{-1}$, $\theta_{max}$ = 30.1°, 110109 reflections measured, 18874 unique, 846 parameters, $R$ = 0.033, $wR$ = 0.076 ($R$ = 0.043, $wR$ = 0.082 for all data), GooF = 1.03. CCDC 2311336.




SIPr-Au-$X_a$ (**3j**)

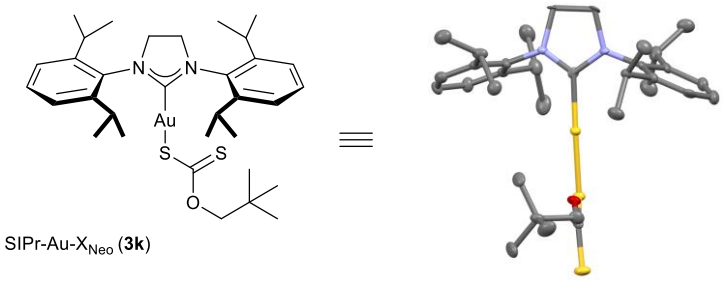
**Crystal data for 3j**: ($C_{30}H_{43}AuN_2OS_2$), *Mr* = 708.6, colourless prisms, triclinic, space group *P-1*, $a$ = 9.8733(3), $b$ = 10.6192(3), $c$ = 15.7019(4) Å, $\alpha$ = 75.269(2), $\beta$ = 87.920(2), $\gamma$ = 74.052(3)°, $V$ = 1529.90(8) Å$^3$, $Z$ = 2, $\rho_{calc}$ = 1.54 g cm$^{-3}$, $\mu$(MoK$\alpha$) = 4.97 mm$^{-1}$, $\theta_{max}$ = 30.3°, 12819 reflections measured, 12819 unique, 326 parameters, $R$ = 0.040, $wR$ = 0.105 ($R$ = 0.046, $wR$ = 0.106 for all data), GooF = 0.98. CCDC 2311326.




SIPr-Au-$X_a$ (**3j**)

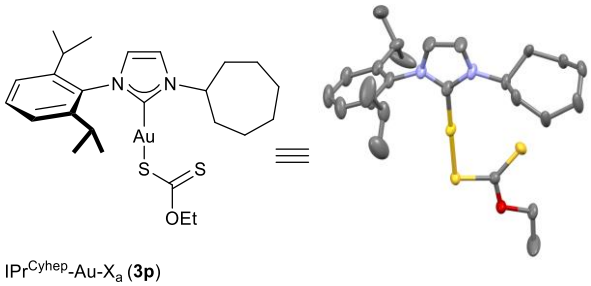
**Crystal data for 3j at 250 K**: ($C_{30}H_{43}AuN_2OS_2$), *Mr* = 708.6, colourless prisms, triclinic, space group *P-1*, $a$ = 9.8420(3), $b$ = 10.6160(2), $c$ = 16.0070(2) Å, $\alpha$ = 95.845(1), $\beta$ = 90.495(2), $\gamma$ = 102.376(2)°, $V$ = 1624.30(6) Å$^3$, $Z$ = 2, $\rho_{calc}$ = 1.45 g cm$^{-3}$, $\mu$(MoK$\alpha$) = 4.68 mm$^{-1}$, $\theta_{max}$ = 30.1°, 26953 reflections measured, 26953 unique, 326

parameters, *R* = 0.046, *wR* = 0.118 (*R* = 0.058, *wR* = 0.123 for all data), GooF = 0.96. CCDC 2311333.



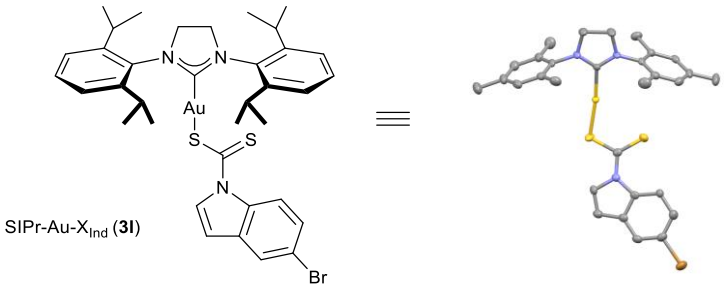

SIPr-Au-$X_{Neo}$ (**3k**)

**Crystal data for 3k**: ($C_{33}H_{49}AuN_2OS_2$), *Mr* = 750.8, colourless prisms, triclinic, space group *P-1*, *a* = 9.776(5), *b* = 10.758(5), *c* = 16.921(5) Å, *α* = 80.495(5), *β* = 84.846(5), *γ* = 77.081(5)°, *V* = 1708.1(13) $Å^3$, *Z* = 2, $\rho_{calc}$ = 1.46 g $cm^{-3}$, *μ*(MoK*α*) = 4.46 $mm^{-1}$, $\theta_{max}$ = 30.2°, 23848 reflections measured, 23848 unique, 353 parameters, *R* = 0.053, *wR* = 0.108 (*R* = 0.071, *wR* = 0.111 for all data), GooF = 0.97. CCDC 2311329.




$IPr^{Cyhep}$-Au-$X_a$ (**3p**)

**Crystal data for**: ($C_{25}H_{37}AuN_2OS_2$), *Mr* = 642.7, yellow prisms, monoclinic, space group $P2_1/n$, *a* = 10.7924(2), *b* = 21.8418(4), *c* = 11.5554(2) Å, *β* = 103.124(2)°, *V* = 2652.76(9) $Å^3$, *Z* = 4, $\rho_{calc}$ = 1.61 g $cm^{-3}$, *μ*(MoK*α*) = 7.72 $mm^{-1}$, $\theta_{max}$ = 30.1°, 42930 reflections measured, 7258 unique, 340 parameters, *R* = 0.037, *wR* = 0.086 (*R* = 0.046, *wR* = 0.095 for all data), GooF = 1.06. CCDC 2311334.



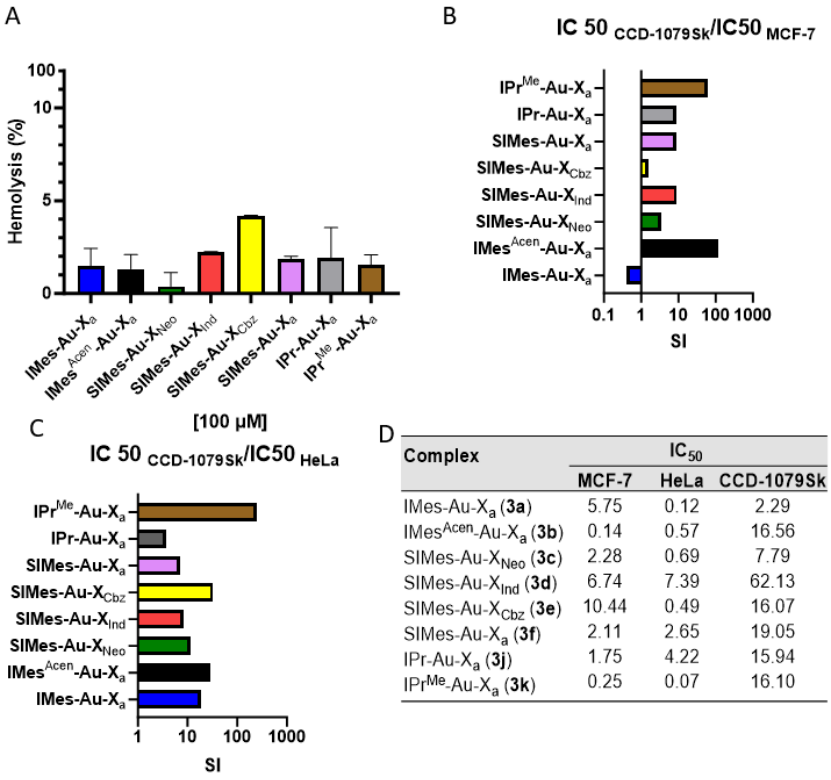
SIPr-Au-X$_{Ind}$ (**3l**)

**Crystal data for 3l**: ($C_{36}H_{43}AuBrN_3S_2$), *Mr* = 858.7, yellow blocks, monoclinic, space group *I*2/*a*, *a* = 24.7221(4), *b* = 14.5417(2), *c* = 24.1478(4) Å, $\beta$ = 113.020(2)°, *V* = 7989.9(2) Å$^3$, *Z* = 8, $\rho_{calc}$ = 1.43 g cm$^{-3}$, $\mu$(MoK$\alpha$) = 4.81 mm$^{-1}$, $\theta_{max}$ = 26.4°, 53485 reflections measured, 8154 unique, 396 parameters, *R* = 0.032, *wR* = 0.078 (*R* = 0.043, *wR* = 0.084 for all data), GooF = 1.03. CCDC 2311332.

## 14. Investigation of biological activity of NHC-Au-X complexes

The antiproliferative activity and viability were assessed via spectrophotometric methods including MTT-assay and Neutral red assay (Fig. S41) against the breast cancer cell line MCF-7 and cervical cancer cells HeLa. Additionally, the cytotoxicity of these complexes was also tested against representative of normal cell line – human fibroblasts cells CCD-1079sk. The results of IC50 have shown that all complexes display significant cytotoxicity toward examined cancer cells. However, more potent activity was noted against cervical cancer HeLa cells than breast cancer MCF-7. Interestingly divergent activity was observed between treated cancer cells. For ex. in the case of MCF-7 cells treated by unsaturated derivatives, 40-fold increased anticancer activity was observed for IMes$^{Acen}$-Au-X$_a$ (**3b**). Considering the series of saturated derivatives (SIMes-Au-X complexes) the activity of the ligand studied against MCF-7 cells was as follow: X$_a$ (**3f**)> X$_{Neo}$ (**3c**)> X$_{Ind}$ (**3d**)> X$_{Cbz}$ (**3e**). The aforementioned tendency was not observed in the case of HeLa cells. However, in the case of both cells lines presence of methyl group in the IPr carbene derivatives markedly increase anticancer efficacy (complexes **3j**, **3k**), 7-fold against MCF-7 cells and 60 – fold in the case of HeLa cells. For comparison tested complexes to known anticancer agent such as cisplatin, their IC50 value for MCF-7 cells and HeLa cells was classified at range 5,1 – 31 and 7,3-37,3 μM respectively, which indicate greater activity of synthesized NHC-gold-xanthate derivatives.[38] It should be emphasize, that exception of IMes-Au-X$_a$ (**3a**), exert low cytotoxic effect towards normal human fibroblasts

cells CCD-1079sk. IC50 value was a generally several times higher than those noted for cancerous cells, which was illustrated as selectivity index in the Fig. S41, part B and C.




D

| Complex | $IC_{50}$ | | |
|---|---|---|---|
| | MCF-7 | HeLa | CCD-1079Sk |
| IMes-Au-$X_a$ (**3a**) | 5.75 | 0.12 | 2.29 |
| IMes$^{Acen}$-Au-$X_a$ (**3b**) | 0.14 | 0.57 | 16.56 |
| SIMes-Au-$X_{Neo}$ (**3c**) | 2.28 | 0.69 | 7.79 |
| SIMes-Au-$X_{Ind}$ (**3d**) | 6.74 | 7.39 | 62.13 |
| SIMes-Au-$X_{Cbz}$ (**3e**) | 10.44 | 0.49 | 16.07 |
| SIMes-Au-$X_a$ (**3f**) | 2.11 | 2.65 | 19.05 |
| IPr-Au-$X_a$ (**3j**) | 1.75 | 4.22 | 15.94 |
| IPr$^{Me}$-Au-$X_a$ (**3k**) | 0.25 | 0.07 | 16.10 |

Fig. S41. Hemocompatibility and selectivity of NHC-Au-X complexes. Panel A show lack of toxicity against human red blod cells. Panel B and C indicated the selectivity indexes (SI) that represents IC50 of normal cells /IC50 for cancer cell lines for MCF-7 and HeLa cells respectively. Panel D - IC50 (µM) values on human cancer cell lines: breast (MCF-7), cervical (HeLa) and normal cell line fibroblasts (CCD 1079 Sk) upon 48 h incubation.

Hemocompatibility of biologically active agents is one of the marked criteria that determine the further successful clinical application. For this purpose, the hemolysis assay was performed to test the hemolytic activity of the NHC-gold complexes by studying their effect on erythrocytes. The above mentioned study measure the ability of the tested agents to disruption of the membranes of the erythrocyte, which in effect causes the release of hemoglobin. The results showed that all gold complexes are compatible on RBCs cells (hemolysis below 5%), if applied on the highest tested concentration 100µM. As shown in Fig. S41, part D, in most cases the IC50 value on cancer cells, is significantly lower than 100 µM, which suggest that the proposed salts exert high anticancer efficacy with low hemolytic activity. To adequately comparing the cytotoxic activity of tested NHC-gold complexes against cancer cell lines ith the activity against normal cells, determination of selectivity index (SI) are required. Based on

obtained results that shown on Fig. S41 panel B and C it could be concluded that tested complexes despite unsaturated IMes-Au-$X_a$ (**3a**) ones, exhibited higher selectivity towards breast and cervical cancer cells than human fibroblasts (SI index >1). In effect, these complexes show high promise as potential chemotherapeutics.

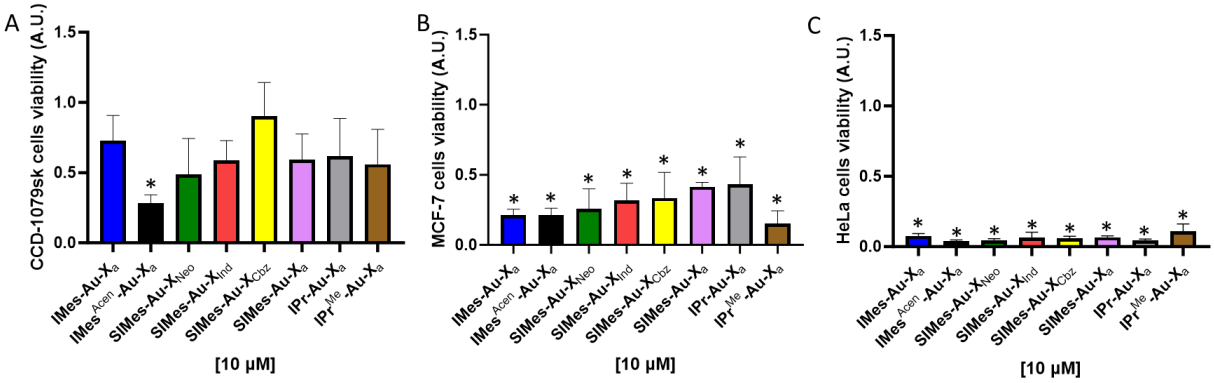



Figure S42. Compatibility and anticancer activity of NHC-gold-xanthate complexes. Panel A show lack of cytotoxicity against representative of normal fibroblast cells. High cytotoxic activity on human cancerous cells MCF-7 and HeLa shown at panel B and C respectively. Statistical significance: vs. control was marked (*) $p \leq 0{,}05$. The data presented constitute average results from three measurements ± SD. Data were normalized to control.

In conclusion, we indicated that new class of NHC-gold-xanthate complexes exert good compatibility with the representatives of host cells and display high cytotoxic effect with low micromolar range towards cancerous cells. Additionally, they do not disrupt RBC plasma membrane and are selective against studied cancer cells, which is the first step to overcome side effect associated with standard non-selective chemotherapy.

***Materials and methods***

*Hemocompatibility studies*

To assess the ability of the tested complexes to release hemoglobin from treated red blood cells, fresh human erythrocytes were obtained from healthy volunteers. the collected cells were suspended in phosphate-buffered saline (PBS) in order to establish a hematocrit of approximately 5%. The tested complexes were prepared at a concentration 0.1 – 100 µM and incubated for one hour at 37 °C. After centrifugation, the relative hemoglobin concentration in the supernatants was spectrophotometrically measured at a wavelength of 540 nm on using Varioscan Lux microplates reader (Termofisher). The 0% hemolysis was obtained from

samples following the addition of 10 µL of PBS, while the 100% hemolysis was obtained from samples in which 10 µL of Triton X-100 was added to disrupt all cell membranes.

*Cells culture*

The compatibility and anticancer activity of NHC-gold-xanthate complexes was determined against skin fibroblast CCD-1079sk, breast cancer cells MCF-7 and cervical cancer cells HeLa obtained from American Type Culture Collection (Manassas, VA, USA). The cells were cultivated in 96-well plates at a density of 5–7 × $10^3$ cells per well until they reached full confluence in Eagle's Minimum Essential Medium -EMEM (ATCC) (for CCD-1079sk, MCF-7 and HeLa), supplemented with 10% fetal bovine serum (FBS) (ATCC), 50 U/mL penicillin, and 50 mg/mL streptomycin (Gibco, Thermo Fisher Scientific, Inc., Waltham, MA, USA) under physiological conditions, at 37°C with 5% $CO_2$.

*Cytotoxicity studies*

In order to assess the cytotoxicity of the tested NHC-gold complexes, MTT based assay has been performed. After 48 h incubation of cancer and normal cells with tested agents at concentration range 0- 100 µM), the MTT assay protocol was followed as published previously.[39] The absorbance was measured at a wavelength of 570 nm on using Varioscan Lux microplates reader (Termofisher). Values were described as a percent of control ±SD. The IC50 values for treated cells were calculated using nonlinear regression in GraphPad Prism 10.1.2 version.

In other set of experiment neutral red cell cytotoxicity assay was used.[40] In brief, after 48 h incubation of cells with tested agents (10 µM), a neutral red solution (10 µL/well) was added and incubated for 2 h. Subsequently, the culturing medium was removed, and the cells were fixed for a period of five minutes. In the next step the fixative solution was discarded, and the acidic solution was added to dissolve the dye. The absorbance was measured at a wavelength of 540 nm on using Varioscan Lux microplates reader (Termofisher). Values were normalized to control ±SD.

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