

Supporting Information for:

Synthesis and reactivity of *N*-heterocyclic carbene gold(I) and gold(III) imidate complexes and their catalytic activity in 1,5-enyne cycloisomerization

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1.0 General Experimental Details

All reactions involving silver salts were carried out in the absence of light. Dichloromethane, acetonitrile and diethyl ether were dried by passing through a column of activated alumina, tetrahydrofuran was distilled from sodium benzophenone ketyl, ethanol was distilled from sodium ethoxide, acetone was distilled from calcium chloride and dimethyl sulfoxide (DMSO) was distilled from calcium hydride. Infra-red spectra were recorded on a Unicam Research Series FT-IR spectrometer. Mass spectrometry was carried out using a Fisons Analytical (VG) Autospec instrument. ¹H, ¹³C and ¹⁹F

NMR spectra were collected on a JEOL ECX400 spectrometer operating at 400, 101 and 376 MHz, respectively, and referenced to residual solvent signals. ^{13}C NMR signals are singlets unless otherwise stated. ^{15}N NMR spectra were collected on a Bruker AMX500 spectrometer operating at 500 MHz. Gas chromatography was carried out on a Varian 430 instrument with a Factor Four Capillary column (VF-1ms, 15 m, 0.25 mm) and a flame ionisation detector. All column chromatography was performed using silica-gel (mesh 220-440) purchased from Fluka Chemicals with the solvent systems specified within the text. TLC analysis was performed using Merck 5554 aluminium backed silica plates, compounds were visualized using UV light (254 nm) and a basic aqueous solution of potassium permanganate. Mps were measured in open capillary tubes using a Stuart SMP3 Digital Melting Point Apparatus and are uncorrected. 1-Phenyl-2-propyn-1-ol, allyltrimethylsilane and AgOTf were purchased from Alfa Aesar. All other chemicals were purchased from Sigma Aldrich Inc. and used without further purification, unless otherwise stated.

2.0 Procedures and Characterization data for Au(I) and Au(III) complexes

2.01 [Au(*N*-succ)(I^tBu)] (11a)

[AuCl(I^tBu)] (**11f**) (121 mg, 294 μmol , 1 equiv.) and silver succinimide (60.3 mg, 294 μmol , 1 equiv.) were dissolved in dichloromethane (10 ml) and stirred at room temperature for 1 hour. The suspension was filtered through CeliteTM and the filtrate reduced to dryness *in vacuo*. The resulting white powder was precipitated from dichloromethane/pentane and washed with diethyl ether to give the title compound as a white powder (122 mg, 256 μmol , 87%). ^1H NMR (400 MHz, CDCl_3) δ 7.08 (s, 2H, imidazole CH), 2.64 (s, 4H, succ CH_2), 1.89 (s, 18H, I^tBu C(CH_3)₃). ^{13}C NMR (400 MHz, CDCl_3) δ 188.8 (succ C=O), 170.8 (carbene Au-C), 116.4 (imidazole CH), 59.1 (I^tBu C(CH_3)₃), 31.8 (I^tBu C(CH_3)₃), 31.6 (succ CH_2). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3684 (w), 3172 (w), 3045 (w), 2972 (m), 2932 (m), 1712 (w), 1645 (s), 1458 (w), 1434 (w), 1408 (w), 1380 (w), 1352 (m), 1285 (m), 1230 (m), 1158 (w). ESI⁺-MS m/z 498.1 (9%, $[\text{MNa}]^+$), 476.2 (100%, $[\text{MH}]^+$), 420.1 (4%, $[\text{M}-\text{I}^t\text{Bu}+2\text{H}]^+$), 405.1 (31%), 349.1 (8%), 293.0 (3%). ESI⁺-HRMS calcd. for $\text{C}_{15}\text{H}_{25}\text{AuN}_3\text{O}_2$ ($[\text{MH}]^+$) 476.1607; found 476.1596. Mp 230 °C (decomp.).

2.02 [Au(*N*-tfs)(I^tBu)] (11b)

[AuCl(I^tBu)] (**11f**) (70.9 mg, 172 μmol , 1 equiv.), silver(I) oxide (24.0 mg, 103 μmol , 0.6 equiv.) and tetrafluorosuccinimide (32.5 mg, 190 μmol , 1.1 equiv.) were mixed in dichloromethane (5 ml) under an atmosphere of N_2 and stirred at room temperature for 2 hours. The suspension was filtered through CeliteTM and the filtrate reduced to dryness *in vacuo*. The resulting white powder was precipitated from

dichloromethane/pentane, washed with diethyl ether and dried *in vacuo* to give the title compound as a white powder (85.6 mg, 157 μmol , 91%). ^1H NMR (400 MHz, CDCl_3) δ 7.15 (s, 2H, imidazole CH), 1.88 (s, 18H, ^tBu C(CH_3)₃). ^{19}F NMR (376 MHz, CDCl_3) δ -127.5 (s, tfs CF_2). ^{13}C NMR (101 MHz, CDCl_3) δ 170.4 (m, tfs C=O),¹ 167.0 (carbene Au-C), 116.9 (imidazole CH), 107.4 (tt, J = 267, 22 Hz, tfs CF_2), 59.2 (^tBu C(CH_3)₃), 31.8 (^tBu C(CH_3)₃). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3471 (w), 3196 (w), 3172 (w), 3061 (w), 2974 (m), 2360 (m), 2341 (m), 1704 (s), 1408 (m), 1400 (m), 1381 (m), 1371 (m), 1305 (s), 1269 (s), 1192 (s), 1150 (s), 1067 (m), 1016 (m). ESI⁺-MS m/z 611.1 (16%, $[\text{MNa}+\text{MeCN}]^+$), 570.1 (100%, $[\text{MNa}]^+$), 548.1 (1%), 445.1 (2%), 418.2 (13%). ESI⁺-HRMS calcd. for $([\text{MNa}]^+)$ $\text{C}_{15}\text{H}_{20}\text{AuF}_4\text{N}_3\text{NaO}_2$ 570.1055; found 570.1047. Mp 166-168 °C.

2.03 [Au(*N*-mal)(^tBu)] (11c)

A protocol similar to that used for **11a** gave the title compound as a white solid {from 120 mg, 291 μmol , of $[\text{AuCl}(\text{I}^t\text{Bu})]$ (**11f**)} (128.7 mg, 272 μmol , 93%). ^1H NMR (400 MHz, CDCl_3) δ 7.09 (s, 2H, imidazole CH), 6.56 (s, 2H, mal CH), 1.88 (s, 18H, ^tBu C(CH_3)₃). ^{13}C NMR (400 MHz, CDCl_3) δ 182.4 (mal C=O), 170.5 (carbene Au-C), 136.0 (mal CH), 116.3 (imidazole CH), 59.0 (^tBu C(CH_3)₃), 31.8 (^tBu C(CH_3)₃). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3171 (w), 3053 (m), 2973 (m), 1662 (s), 1641 (m), 1608 (w), 1567 (w), 1475 (w), 1408 (m), 1380 (m), 1370 (m), 1347 (s), 1304 (w), 1281 (w), 1234 (w), 1213 (m), 1178 (m), 1158 (w). ESI⁺-MS m/z 474.1 (100%, $[\text{MH}]^+$), 418.2 (8%), 181.2 (1%, $[\text{I}^t\text{BuH}]^+$). ESI⁺-HRMS calcd. for $\text{C}_{15}\text{H}_{23}\text{AuN}_3\text{O}_2$ ($[\text{MH}]^+$) 474.1450; found 474.1439. Mp 190 °C (decomp.). Note: 7% of a photo-dimerized product (**17a**) was observed in crude ^1H NMR spectra of this product, for which further characterization was made.

2.04 [Au(*N*-ptm)(^tBu)] (11d)

A protocol similar to that used for **11a** gave the title compound as a white solid {from 121.4 mg, 295 μmol of $[\text{AuCl}(\text{I}^t\text{Bu})]$ (**11f**)} (142 mg, 271 μmol , 92%). ^1H NMR (400 MHz, CDCl_3) δ 7.70 (dd, J = 5.4 Hz and 3.0 Hz, 2H, ptm aromatic CH), 7.55 (dd, J = 5.4 Hz and 3.0 Hz, 2H, ptm aromatic CH), 7.11 (s, 2H, imidazole CH), 1.92 {s, 18H, ^tBu C(CH_3)₃}. ^{13}C NMR (400 MHz, CDCl_3) δ 178.9 (ptm C=O), 170.9 (carbene Au-C), 136.4 (ptm *ortho* aromatic C), 132.1 (ptm *meta* aromatic CH), 121.6 (ptm *para* aromatic CH), 116.4 (imidazole CH), 59.1 { ^tBu C(CH_3)}, 31.8 { ^tBu C(CH_3)₃}. IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3677 (w), 3171 (w), 3058 (w), 2973 (m), 2364 (w), 1736 (m), 1667 (s), 1639 (s), 1606 (m), 1568 (w), 1540 (w), 1464 (m), 1422 (w), 1407 (m), 1374 (s), 1352 (m), 1309 (s), 1214 (m), 1190 (m), 1176 (m), 1158 (w), 1124 (m). ESI⁺-MS m/z 524.2 (100%, $[\text{MH}]^+$), 418.2 (3%), 181.2 (61%, $[\text{I}^t\text{BuH}]^+$). ESI⁺-HRMS calcd. for $\text{C}_{19}\text{H}_{25}\text{AuN}_3\text{O}_2$ ($[\text{MH}]^+$) 524.1607; found 524.1588. Mp 160 °C (decomp.).

2.05 [Au(*N*-obs)(^tBu)] (11e)

[AuCl(^tBu)] (**11f**) (70.9 mg, 172 μ mol, 1 equiv.), silver(I) oxide (24.0 mg, 103 μ mol, 0.6 equiv.), and *o*-benzoic sulfimide (34.7 mg, 190 μ mol, 1.1 equiv.) were mixed in dichloromethane (5 ml) under an inert atmosphere and stirred at room temperature for 2 hours. The suspension was filtered through CeliteTM and the filtrate reduced to dryness *in vacuo*. The resulting white powder was precipitated from dichloromethane/pentane, washed with diethyl ether and dried *in vacuo* to give the title compound as a white powder (85.0 mg, 152 μ mol, 89%). ¹H NMR (400 MHz, CDCl₃) δ 7.94-7.90 (m, 1H, obs aromatic CH), 7.85-7.81 (m, 1H, obs aromatic CH), 7.72-7.64 (m, 2H, obs aromatic CH), 7.12 (s, 2H, imidazole CH), 1.91 (s, 18H, ^tBu C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃) δ 167.5 (carbene Au-C), 166.1 (obs C=O), 141.7 (obs aromatic C), 132.9 (obs aromatic CH), 132.8 (obs aromatic CH), 131.8 (obs aromatic C), 124.1 (obs aromatic CH), 120.3 (obs aromatic CH), 116.7 (imidazole CH), 59.1 {^tBu C(CH₃)₃}, 31.8 {^tBu C(CH₃)₃}. IR (CH₂Cl₂, cm⁻¹) ν_{max} 3364 (m), 3172 (w), 3061 (m), 2973 (m), 1742 (m), 1689 (s) 1559 (w), 1540 (w), 1521 (w), 1459 (m), 1400 (m), 1382 (m), 1371 (m), 1338 (m), 1303 (s), 1266 (s), 1249 (s), 1212 (m), 1173 (s), 1157 (s), 1122 (m), 1057 (w). ESI⁺-MS *m/z* 714.5 (3%), 675.2 (3%), 582.1 (100%, [MNa]⁺), 528.2 (2%), 435.1 (41%, [MNa-obs+Cl]⁺), 394.2 (13%, [M-obs+NH₃]⁺), 360.3 (2%), 274.3 (1%), 172.1 (7%). ESI⁺-HRMS calcd. for C₁₈H₂₄AuN₃NaO₃S ([MNa]⁺) 582.1096; found 582.1083. Mp 150 °C (decomp.).

2.06 [AuBr(^tBu)] (11g)

A protocol reported by de Frémont *et al.* was used.² [AuCl(^tBu)] (**11f**) (105 mg, 255 μ mol, 1 equiv.) and LiBr (186 mg, 2.13 mmol, 8.4 equiv.) were mixed in acetone (4 ml) at room temperature for 24 hours. The resulting solution was reduced to dryness *in vacuo* and redissolved in dichloromethane, dried (MgSO₄) and filtered through a plug of silica-gel. The volume was reduced to <0.5 ml and pentane was added resulting in a white precipitate. This was separated by filtration, washed with cold pentane and dried *in vacuo* to give the title compound as a white powder (99.2 mg, 217 μ mol, 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.09 (s, 2H, imidazole CH), 1.87 (s, 18H, ^tBu CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 172.5 (carbene Au-C), 116.3 (imidazole CH), 59.1 (^tBu quaternary C), 31.8 (^tBu CH₃). ESI⁺-MS *m/z* 479.0 (2%, [MNa]⁺), 405.1 (9%, [M-Br+CO]⁺), 349.1 (21%, [M-Br-^tBu+H+CO]⁺), 293.0 (100%, [M-Br-2^tBu+2H+CO]⁺), 266.0 (3%). ESI⁺-HRMS calcd. for C₁₁H₂₀AuBrN₂Na ([MNa]⁺) 479.0368; found 479.0359.

2.07 $\text{I}^t\text{Pe.HCl}$

A protocol similar to that reported by Jafarpour *et al.* was used.³ *tert*-Pentylamine (5.18 g, 59.4 mmol, 2 equiv.) and glyoxal (3.35 ml, 29.8 mmol, 1 equiv., 40% in water) were dissolved in ethanol (50 ml). Formic acid (4 drops) was added and the solution was stirred at room temperature for 2 days. The resulting yellow solution was reduced *in vacuo* to give a yellow oil and re-dissolved in toluene (60 ml). Paraformaldehyde (0.612 g, 20.4 μmol , 0.7 equiv.) was added and the suspension stirred at 100 °C until a clear solution formed. HCl (5.10 ml, 20.4 μmol , 0.7 equiv., 4 M in dioxane) was added at 40 °C and the solution was then stirred at 70 °C overnight. The resulting white precipitate was separated by filtration and washed with acetone to give the title product as a white powder (2.50 g, 10.2 mmol, 34%). ^1H NMR (400 MHz, CDCl_3) δ 10.45 (t, $J = 2$ Hz, 1H, N_2CH), 7.48 (d, $J = 2$ Hz, 2H, imidazole CH), 2.04 (q, $J = 7.5$ Hz, 4H, $^t\text{Pe CH}_2\text{CH}_3$), 1.75 (s, 12H, $^t\text{Pe C}(\text{CH}_3)_2$), 0.75 (t, $J = 7.5$ Hz, 6H, $^t\text{Pe CH}_2\text{CH}_3$). ^{13}C NMR (101 MHz, CDCl_3) δ 135.3 (N_2CH), 119.7 (imidazole CH), 63.5 (^tPe quaternary C), 35.3 ($^t\text{Pe CH}_2\text{CH}_3$), 27.4 ($\text{C}(\text{CH}_3)_2$), 8.1 ($^t\text{Pe CH}_2\text{CH}_3$). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3657 (w), 3338 (w), 3165 (w), 3041 (w), 2972 (s), 2358 (w), 1534 (w), 1463 (m), 1386 (m), 1274 (m), 1184 (m), 1126 (m). ESI⁺-MS m/z 209.2 (100%, $[\text{MH}]^+$), 139.1 (4%). ESI⁺-HRMS calcd. for $\text{C}_{13}\text{H}_{26}\text{ClN}_2$ ($[\text{MH}]^+$) 209.2012; found 209.2014. Mp 228-230 °C.

2.08 $[\text{AuCl}(\text{I}^t\text{Pe})]$ (**12f**)

A protocol similar to that used for $[\text{AuCl}(\text{I}^t\text{Bu})]$ (**11f**) gave the title compound as a white solid (from 390 mg, 1.60 mmol of $\text{I}^t\text{Pe.HCl}$) (0.642 g, 1.46 mmol, 99%). ^1H NMR (400 MHz, CDCl_3) δ 7.04 (s, 2H, imidazole CH), 2.48 (q, $J = 7.5$ Hz, 4H, $^t\text{Pe CH}_2\text{CH}_3$), 1.79 (s, 12H, $^t\text{Pe CH}_3$), 0.64 (t, $J = 7.5$ Hz, 6H, $^t\text{Pe CH}_2\text{CH}_3$). ^{13}C NMR (400 MHz, CDCl_3) δ 168.1 (carbene Au-C), 117.3 (imidazole C), 61.7 (^tPe quaternary C), 36.3 ($^t\text{Pe CH}_2\text{CH}_3$), 29.3 ($^t\text{Pe CH}_2\text{CH}_3$), 7.8 ($^t\text{Pe C}(\text{CH}_3)_2$). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3680 (w), 3196 (w), 3172 (w), 3046 (m), 2972 (s), 2929 (m), 2880 (m), 2360 (w), 1604 (w), 1567 (w), 1460 (m), 1407 (m), 1393 (s), 1377 (s), 1339 (w), 1309 (m), 1228 (m), 1190 (s), 1152 (w). ESI⁺-MS m/z 463.1 (100%, $[\text{MNa}]^+$), 226.9 (5%). ESI⁺-HRMS calcd. for $\text{C}_{13}\text{H}_{24}\text{AuClN}_2\text{Na}$ ($[\text{MNa}]^+$) 463.1186; found 463.1186. Mp 157-158 °C.

2.09 $[\text{Au}(\text{N-succ})(\text{I}^t\text{Pe})]$ (**12a**)

A protocol similar to that used for **11a** gave the title compound as a white solid {from 120 mg, 269 μmol , of $[\text{AuCl}(\text{I}^t\text{Pe})]$ (**12f**)} (126 mg, 251 μmol , 93%). ^1H NMR (400 MHz, CDCl_3) δ 7.05 (s, 2H, imidazole CH), 2.62 (s, 4H, succ CH_2), 2.48 (q, $J = 7.5$ Hz, 4H, $^t\text{Pe CH}_2$), 1.82 (s, 12H, $^t\text{Pe C}(\text{CH}_3)_2$),

0.66 (t, $J = 7.5$ Hz, 6H, $^1\text{Pe CH}_2\text{CH}_3$). ^{13}C NMR (400 MHz, CDCl_3) δ 188.7 (succ C=O), 170.8 (carbene Au-C), 117.3 (imidazole CH), 61.9 (^1Pe quaternary C), 36.3 ($^1\text{Pe CH}_2\text{CH}_3$), 31.6 (succ CH_2), 29.3 ($^1\text{Pe C}(\text{CH}_3)_2$), 7.9 ($^1\text{Pe CH}_2\text{CH}_3$). IR (solid, cm^{-1}) ν_{max} 2963 (w), 2160 (m), 2028 (m), 1631 (s), 1561 (w), 1460 (w), 1395 (w), 1378 (w), 1353 (s), 1284 (w), 1260 (w), 1227 (s), 1140 (w), 1009 (m), 817 (m), 739 (m), 703 (m), 656 (m), 621 (m). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3670 (w), 3172 (w), 3052 (m), 2970 (m), 2936 (m), 2880 (m), 2360 (w), 1644 (s), 1461 (m), 1435 (w), 1407 (m), 1393 (m), 1379 (m), 1352 (s), 1310 (w), 1285 (m), 1230 (s), 1191 (m). ESI⁺-MS m/z 504.2 (100%, $[\text{MH}]^+$), 433.2 (21%), 363.1 (6%), 292.0 (4%), 209.2 (4%). ESI⁺-HRMS calcd. for $\text{C}_{17}\text{H}_{29}\text{AuN}_3\text{O}_2$ ($[\text{MH}]^+$) 504.1920; found 504.1916. Mp 140-142 °C.

2.10 [Au(N-tfs)(^1Pe)] (12b)

A protocol similar to that used for **11b** gave the title compound as a white solid {from 100 mg, 228 μmol , of $[\text{AuCl}(\text{I}^1\text{Pe})]$ (**12f**)} (122 mg, 212 μmol , 93%). ^1H NMR (400 MHz, CDCl_3) δ 7.11 (s, 2H, imidazole CH), 2.48 (q, $J = 7.5$ Hz, 4H, $^1\text{Pe CH}_2\text{CH}_3$), 1.83 {s, 12H, $^1\text{Pe C}(\text{CH}_3)_2$ }, 0.69 (t, $J = 7.5$ Hz, 6H, $^1\text{Pe CH}_2\text{CH}_3$). ^{19}F NMR (376 MHz, CDCl_3) δ -127.5 (s, CF_2). ^{13}C NMR (101 MHz, CDCl_3) δ 170.4 (m, C=O),¹ 167.5 (carbene Au-C), 117.8 (imidazole CH), 107.4 (tt, $J = 267$ and 22 Hz, tfs CF_2), 62.1 (^1Pe quaternary C), 36.6 ($^1\text{Pe CH}_2\text{CH}_3$), 29.4 ($^1\text{Pe C}(\text{CH}_3)_2$), 7.9 ($^1\text{Pe CH}_2\text{CH}_3$). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3173 (w), 2971 (s), 2930 (m), 2880 (m), 1784 (w), 1704 (s), 1559 (w), 1540 (w), 1461 (m), 1394 (m), 1380 (m), 1305 (s), 1271 (s), 1260 (s), 1193 (s), 1150 (s), 1067 (s), 1016 (s). ESI⁺-MS m/z 598.1 (95%, $[\text{MNa}]^+$), 463.1 (23%), 422.2 (100%), 239.2 (6%). ESI⁺-HRMS calcd. for $\text{C}_{17}\text{H}_{24}\text{AuF}_4\text{N}_3\text{NaO}_2$ ($[\text{MNa}]^+$) 598.1362; found 598.1380. Mp 145-147 °C.

2.11 [Au(N-mal)(^1Pe)] (12c)

A protocol similar to that used for **11a** gave the title compound as a white solid {from 117 mg, 267 μmol , of $[\text{AuCl}(\text{I}^1\text{Pe})]$ (**12f**)} (128 mg, 256 μmol , 96%). ^1H NMR (400 MHz, CDCl_3) δ 7.05 (s, 2H, imidazole CH), 6.54 (s, 2H, mal CH), 2.50 (q, $J = 7.5$ Hz, 4H, $^1\text{Pe CH}_2\text{CH}_3$), 1.82 {s, 12H, $^1\text{Pe C}(\text{CH}_3)_2$ }, 0.67 (t, $J = 7.5$ Hz, 6H, $^1\text{Pe CH}_2\text{CH}_3$). ^{13}C NMR (400 MHz, CDCl_3) δ 182.3 (mal C=O), 170.7 (carbene Au-C), 135.9 (mal CH), 117.3 (imidazole CH), 61.8 (^1Pe quaternary C), 36.3 ($^1\text{Pe CH}_2\text{CH}_3$), 29.3 ($^1\text{Pe C}(\text{CH}_3)_2$), 7.9 ($^1\text{Pe CH}_2\text{CH}_3$). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3680 (w), 3195 (w), 3172 (w), 3062 (w), 2971 (s), 2933 (m), 2880 (w), 1660 (s), 1608 (w), 1567 (w), 1460 (m), 1407 (w), 1393 (m), 1380 (m), 1347 (s), 1310 (w), 1228 (m), 1179 (m). ESI⁺-MS m/z 524.2 (3%, $[\text{MNa}]^+$), 502.2 (100%, $[\text{MH}]^+$), 433.2 (46%), 363.1 (16%), 293.0 (8%), 272.8 (2%). ESI⁺-HRMS calcd. for $\text{C}_{17}\text{H}_{27}\text{AuN}_3\text{O}_2$ ($[\text{MH}]^+$) 502.1763; found 502.1760. Mp 135-137 °C.

Data for photodimer $[\{\text{Au}(\text{N-mal})(\text{I}^t\text{Pe})\}_2]$ (17b): Not isolated $\{[\text{Au}(\text{N-mal})(\text{I}^t\text{Pe})]$ (12c): $[\{\text{Au}(\text{N-mal})(\text{I}^t\text{Pe})\}_2]$ (17) 76:24}. ^1H NMR (400 MHz, CDCl_3) selected peaks δ 7.05 (s, 2H, imidazole CH), 3.33 (s, 2H, imidate CH), 2.50 (q, $J = 7.5$ Hz, 4H, ^tPe CH_2CH_3), 1.82 (s, 12H, ^tPe $\text{C}(\text{CH}_3)_2$), 0.67 (t, $J = 7.5$ Hz, 6H, ^tPe CH_2CH_3). ESI^+ -MS m/z 1025.3 (100%, $[\text{MNa}]^+$), 1003.3 (84%, $[\text{MH}]^+$), 906.3 (99%, $[(\text{ItPe})_2\text{Au}_2(\text{mal})]^+$). ESI^+ -HRMS calcd. for $\text{C}_{34}\text{H}_{52}\text{Au}_2\text{N}_6\text{NaO}_4$ ($[\text{MNa}]^+$) 1025.3273; found 1025.3279.

2.12 $[\text{Au}(\text{N-ptm})(\text{I}^t\text{Pe})]$ (12d)

A protocol similar to that used for **11a** gave the title compound as a white solid {from 127 mg, 288 μmol , of $[\text{AuCl}(\text{I}^t\text{Pe})]$ (12f)} (152 mg, 277 μmol , 96%). ^1H NMR (400 MHz, CDCl_3) δ 7.69 (dd, $J = 5.4$ and 3.0 Hz, 2H, ptm aromatic CH), 7.54 (dd, $J = 5.4$ and 3.0 Hz, 2H, ptm aromatic CH), 7.06 (s, 2H, imidazole CH), 2.56 (q, $J = 7.4$ Hz, 4H, ^tPe CH_2CH_3), 1.85 (s, 12H, ^tPe $\text{C}(\text{CH}_3)_2$), 0.68 (t, $J = 7.4$ Hz, 6H, ^tPe CH_2CH_3). ^{13}C NMR (400 MHz, CDCl_3) δ 178.8 (ptm $\text{C}=\text{O}$), 171.0 (carbene C), 136.4 (ptm *ortho* aromatic C), 132.1 (ptm *meta* aromatic CH), 121.5 (ptm *para* aromatic CH), 117.3 (imidazole CH), 61.9 (^tPe quaternary C), 36.3 (^tPe CH_2CH_3), 29.3 (^tPe $\text{C}(\text{CH}_3)_2$), 7.9 (^tPe CH_2CH_3). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3674 (w), 3172 (w), 3056 (m), 2970 (m), 2933 (w), 2879 (w), 2360 (w), 1736 (w), 1667 (s), 1638 (m), 1606 (m), 1539 (w), 1462 (m), 1393 (m), 1373 (s), 1352 (m), 1309 (s), 1227 (w), 1191 (m), 1176 (m). ESI^+ -MS m/z 552.2 (100%, $[\text{MH}]^+$), 482.1 (6%), 433.2 (5%), 363.1 (2%), 272.8 (5%). ESI^+ -HRMS calcd. for $\text{C}_{21}\text{H}_{29}\text{AuN}_3\text{O}_2$ ($[\text{MH}]^+$) 552.1920; found 552.1927. Mp 140 $^\circ\text{C}$ (decomp.).

2.13 $[\text{Au}(\text{N-obs})(\text{I}^t\text{Pe})]$ (12e)

A protocol similar to that used for **11e** gave the title compound as a white solid {from 90.3 mg, 205 μmol , of $[\text{AuCl}(\text{I}^t\text{Pe})]$ (12f)} (113 mg, 193 μmol , 94%). ^1H NMR (400 MHz, CDCl_3) 7.92-7.88 (m, 1H, obs aromatic CH), 7.83-7.80 (m, 1H, obs aromatic CH), 7.73-7.64 (m, 2H, obs aromatic CH), 7.10 (s, 2H, imidazole CH), 2.52 (q, $J = 7.4$ Hz, 4H, ^tPe CH_2CH_3), 1.85 (s, 12H, CH_3), 0.70 (t, $J = 7.4$ Hz, 6H, ^tPe CH_2CH_3). ^{13}C NMR (101 MHz, CDCl_3) δ 167.9 (carbene Au-C), 166.0 (obs $\text{C}=\text{O}$), 141.8 (obs aromatic C), 132.9 (obs aromatic CH), 132.8 (obs aromatic CH), 131.8 (obs aromatic C), 124.0 (obs aromatic CH), 120.3 (obs aromatic CH), 117.6 (imidazole CH), 62.0 (^tPe quaternary C), 36.4 (^tPe CH_2CH_3), 29.4 (^tPe $\text{C}(\text{CH}_3)_2$), 7.9 (^tPe CH_2CH_3). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3362 (w), 3172 (w), 3061 (m), 2971 (s), 2931 (m), 2880 (w), 1741 (m), 1689 (s), 1596 (m), 1461 (m), 1380 (m), 1303 (s), 1260 (s), 1249 (s), 1173 (s), 1157 (s), 1123 (m), 1057 (m). ESI^+ -MS m/z 678.1 (4%), 610.1 (90%, $[\text{MNa}]^+$), 556.2 (3%), 504.1 (11%), 463.1 (100%, $[\text{MNa-obs+Cl}]^+$), 422.2 (3%), 157.1 (5%). ESI^+ -HRMS calcd. for $\text{C}_{20}\text{H}_{28}\text{AuN}_3\text{NaO}_3\text{S}$ ($[\text{MNa}]^+$) 610.1409; found 610.1408. Mp 150 $^\circ\text{C}$ (decomp.).

2.14 [AuBr(^tPe)] (12g)

A protocol similar to that used for [AuBr(^tBu)] (**11g**) gave the title compound as a white solid {from 83.6 mg, 190 μ mol of [AuCl(^tPe)] (**12f**)} (87.9 mg, 180 μ mol, 95%). ¹H NMR (400 MHz, CDCl₃) δ 7.05 (s, 2H, imidazole CH), 2.48 (q, J = 7.5 Hz, 4H, ^tPe CH₂CH₃), 1.81 {s, 12H, ^tPe C(CH₃)₂}, 0.65 (t, J = 7.5 Hz, 6H, ^tPe CH₂CH₃). ¹³C NMR (400 MHz, CDCl₃) δ 172.3 (carbene Au-C), 117.2 (imidazole CH), 61.8 (^tPe quaternary C), 36.3 (^tPe CH₂CH₃), 29.3 {^tPe C(CH₃)₂}, 7.9 (^tPe CH₂CH₃). IR (CH₂Cl₂, cm⁻¹) ν_{max} 3196 (w), 3172 (w), 3047 (m), 2972 (s), 2930 (m), 2880 (w), 1704 (w), 1566 (w), 1558 (w), 1461 (m), 1406 (w), 1266 (m), 1260 (m), 1229 (m), 1271 (s), 1227 (m), 1191 (s), 1064 (w), 1037 (w), 1005 (w). ESI⁺-MS m/z 507.1 (6%, [MNa]⁺), 433.2 (15%), 413.3 (2%), 363.1 (19%), 293.0 (100%), 266.0 (2%). ESI⁺-HRMS calcd. for C₁₃H₂₄AuBrN₂Na ([MNa]⁺) 507.0681; found. 507.0675. Mp 149-151 °C.

2.15 [Au(*N*-succ)(IMes)] (13a)

A protocol similar to that used for **11a** gave the title compound as a white solid {from 38.2 mg, 71.3 μ mol, of [AuCl(IMes)] (**13f**)} (41.6 mg, 69.4 μ mol, 97%). ¹H NMR (400 MHz, CDCl₃) δ 7.10 (s, 2H, imidazole CH), 7.01 (s, 4H, Mes aromatic CH), 2.40 (s, 4H, succ CH₂), 2.34 (s, 6H, Mes *para* CH₃), 2.16 (s, 12H, Mes *ortho* CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 188.5 (succ C=O), 174.9 (carbene Au-C), 139.4 (Mes aromatic C), 134.7 (Mes aromatic C), 134.6 (Mes aromatic C), 129.4 (Mes aromatic C), 122.3 (imidazole CH), 31.4 (succ CH₂), 21.1 (Mes *para* CH₃), 17.9 (Mes *ortho* CH₃). IR (CH₂Cl₂, cm⁻¹) ν_{max} 3670 (w), 3141 (m), 3052 (m), 2981 (m), 2359 (w), 1648 (s), 1540 (w), 1488 (m), 1435 (w), 1415 (w), 1351 (m), 1285 (m), 1230 (m). ESI⁺-MS m/z 622.2 (15%, [MNa]⁺), 600.2 (100%, [MH]⁺), 528.2 (49%). ESI⁺-HRMS calcd. for C₂₅H₂₉AuN₃O₂ ([MH]⁺) 600.1925; found 600.1924. Mp 170 °C (decomp.).

2.16 [Au(*N*-tfs)(IMes)] (13b)

A protocol similar to that used for **11b** gave the title compound as a white solid {from 101 mg, 188 μ mol, of [AuCl(IMes)] (**13f**)} (109 mg, 163 μ mol, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.17 (s, 2H, imidazole CH), 7.04 (s, 4H, Mes aromatic CH), 2.36 (s, 6H, Mes *para* CH₃), 2.16 (s, 12H, Mes *ortho* CH₃). ¹⁹F NMR (376 MHz, CDCl₃) δ -127.6 (s, tfs CF₂). ¹³C NMR (101 MHz, CDCl₃) δ 171.9 (carbene Au-C), 170.0 (m, tfs C=O), 140.0 (Mes aromatic C), 134.6 (Mes aromatic C), 134.2 (Mes aromatic C), 129.6 (Mes aromatic CH), 122.8 (imidazole CH), 107.1 (tt, J = 267 and 22 Hz, tfs CF₂), 21.1 (Mes *para* CH₃), 17.8 (Mes *ortho* CH₃). IR (CH₂Cl₂, cm⁻¹) ν_{max} 3167 (w), 3141 (w), 3055 (m), 2923 (w), 1784 (w), 1772 (w), 1705 (s), 1670 (w), 1609 (w), 1559 (w), 1540 (w), 1487 (m), 1420 (m), 1381 (w), 1324 (w), 1305 (m), 1235 (w), 1192 (s), 1150 (m), 1067 (m), 1016 (m). ESI⁺-MS m/z 694.1 (100%, [MNa]⁺), 542.2

(55%, [M-tfs+MeCN]⁺), 413.3 (3%), 358.1 (5%), 336.1 (5%). ESI⁺-HRMS calcd. for C₂₅H₂₄AuF₄N₃NaO₂ ([MNa]⁺) 694.1362; found 694.1355. Mp 200 °C (decomp.).

2.17 [Au(*N*-mal)(IMes)] (13c)

A protocol similar to that used for **11a** gave the title compound as a white solid {from 151 mg, 282 μmol, of [AuCl(IMes)] (**13f**)} (157 mg, 263 μmol, 93%). ¹H NMR (400 MHz, CDCl₃) δ 7.10 (s, 2H, imidazole CH), 7.00 (s, 4H, Mes aromatic CH), 6.31 (s, 2H, mal CH), 2.33 (s, 6H, Mes *para* CH₃), 2.16 (s, 12H, Mes *ortho* CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 182.1 (mal C=O), 175.1 (carbene Au-C), 139.5 (Mes aromatic C), 135.7 (mal CH), 134.7 (Mes aromatic C), 134.6 (Mes aromatic C), 129.4 (Mes aromatic C), 122.3 (imidazole CH), 21.1 (Mes *para* CH₃), 18.0 (Mes *ortho* CH₃). IR (CH₂Cl₂, cm⁻¹) *v*_{max} 3677 (w), 3167 (w), 3141 (w), 3063 (w), 2922 (m), 1730 (m), 1662 (s), 1640 (m), 1608 (m), 1488 (m), 1415 (m), 1380 (m), 1345 (s), 1235 (m), 1177 (m). ESI⁺-MS *m/z* 598.2 (11%, [MH]⁺), 528.2 (92%), 305.2 (100%, [IMesH]⁺). ESI⁺-HRMS calcd. for C₂₅H₂₇AuN₃O₂ ([MH]⁺) 598.1763; found 598.1737. Mp 200 °C (decomp.).

2.18 [Au(*N*-ptm)(IMes)] (13d)

A protocol similar to that used for **11a** gave the title compound as a white solid {from 71.1 mg, 132 μmol of [AuCl(IMes)] (**13f**)} (80.3 mg, 124 μmol, 94%). ¹H NMR (400 MHz, CDCl₃) δ 7.54 (dd, *J* = 5.4 and 3.0, 2H, ptm aromatic CH), 7.44 (dd, *J* = 5.4 and 3.0 Hz, 2H, ptm aromatic CH), 7.12 (s, 2H, imidazole CH), 7.02 (s, 4H, Mes aromatic CH), 2.33 (s, 6H, Mes *para* CH₃), 2.20 (s, 12H, Mes *ortho* CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 178.6 (ptm C=O), 175.2 (carbene Au-C), 139.5 (Mes aromatic C), 136.2 (ptm aromatic C), 134.7 (Mes aromatic C), 134.6 (Mes aromatic C), 131.8 (ptm aromatic CH), 129.4 (Mes aromatic CH), 122.3 (imidazole CH), 121.3 (ptm aromatic CH), 21.1 (Mes *para* CH₃), 18.0 (Mes *ortho* CH₃). IR (CH₂Cl₂, cm⁻¹) *v*_{max} 3674 (w), 3458 (w), 3140 (w), 3063 (w), 3045 (m), 2983 (m), 2921 (m), 2324 (w), 1737 (m), 1667 (s), 1639 (m), 1607 (m), 1540 (w), 1488 (m), 1414 (m), 1372 (m), 1351 (m), 1308 (m), 1236 (m), 1176 (m), 1124 (m). ESI⁺-MS *m/z* 648.2 (2%, [MH]⁺), 528.2 (50%), 305.2 (100%, [IMesH]⁺), 267.2 (4%), 136.1 (3%). ESI⁺-HRMS calcd. for C₂₉H₂₉AuN₃O₂ ([MH]⁺) 648.1920; found 648.1908. Mp 150 °C (decomp.).

2.19 [Au(*N*-obs)(IMes)] (13e)

A protocol similar to that used for **11e** gave the title compound as a white solid {from 99.9 mg, 186 μmol, of [AuCl(IMes)] (**13f**)} (115 mg, 168 μmol, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.78-7.76 (m, 1H, obs aromatic CH), 7.72-7.70 (m, 1H, obs aromatic CH), 7.62-7.55 (m, 2H, obs aromatic CH), 7.16 (s,

2H, imidazole *CH*), 7.04 (s, 4H, Mes aromatic *CH*), 2.35 (s, 6H, Mes *para* *CH*₃), 2.19 (s, 12H, Mes *ortho* *CH*₃). ¹³C NMR (101 MHz, CDCl₃) δ 172.9 (carbene Au-C), 165.8 (obs C=O), 141.6 (obs aromatic C), 139.8 (Mes aromatic C), 134.6 (Mes aromatic C), 134.4 (Mes aromatic C), 132.7 (obs aromatic CH), 132.6 (obs aromatic CH), 131.7 (obs aromatic C), 129.5 (Mes aromatic CH), 123.9 (obs aromatic CH), 122.5 (imidazole CH), 120.1 (obs aromatic CH), 21.2 (Mes *para* *CH*₃), 17.9 (Mes *ortho* *CH*₃). IR (CH₂Cl₂, cm⁻¹) *v*_{max} 3167 (w), 3141 (w), 3054 (m), 2982 (w), 2952 (w), 2922 (m), 2861 (w), 1689 (s), 1608 (w), 1599 (w), 1559 (w), 1540 (w), 1487 (m), 1459 (w), 1419 (m), 1380 (m), 1337 (w), 1303 (s), 1248 (m), 1173 (s), 1157 (s), 1123 (w). ESI⁺-MS *m/z* 706.1 (13%, [MNa]⁺), 542.2 (100%, [M-obs+MeCN]⁺), 413.3 (2%), 235.1 (2%). ESI⁺-HRMS calcd. for C₂₈H₂₈AuN₃NaO₃S ([MNa]⁺) 706.1409; found 706.1415. Mp 160 °C (decomp.).

2.20 [AuBr₂(*N*-succ)(I^tBu)] (18a)

[Au(*N*-succ)(I^tBu)] (11a) (28.5 mg, 59.9 μmol, 1 equiv.) was dissolved in dichloromethane (1 ml), bromine (10.5 mg, 65.9 μmol, 1.1 equiv.) was added and the brown solution stirred for 1 hour at room temperature. The solution was reduced *in vacuo* to <0.5 ml and pentane (5 ml) added producing a yellow precipitate. This was separated by filtration, washed (pentane/diethyl ether) and dried *in vacuo* to give the title compound as a yellow powder (32.2 mg, 50.6 μmol, 84%). ¹H NMR (400 MHz, CDCl₃) δ 7.41 (s, 2H, imidazole *CH*), 2.72 (s, 4H, succ *CH*₂), 1.96 {s, 18H, ^tBu C(*CH*₃)₃}. ¹³C NMR (400 MHz, CDCl₃) δ 183.8 (succ C=O), 131.9 (carbene Au-C), 122.1 (imidazole CH), 62.4 (^tBu C(*CH*₃)₃), 32.1 (^tBu C(*CH*₃)₃), 31.4 (succ *CH*₂). IR (CH₂Cl₂, cm⁻¹) *v*_{max} 3168 (w), 3063 (w), 2988 (m), 2360 (w), 1663 (s), 1576.1 (m), 1480 (w), 1415 (w), 1375 (m), 1352 (m), 1284 (w), 1230 (m), 1196 (w), 1182 (m), 1156 (w). ESI⁺-MS *m/z* 636.0 (81%, [MH]⁺), 418.2 (66%), 259.1 (15%, [I^tBuBr]⁺), 181.2 (100%, [I^tBuH]⁺). ESI⁺-HRMS calcd. for C₁₅H₂₃AuBr₂N₃O₂ ([MH]⁺) 633.9949; found 633.9974. Mp 160 °C (decomp.).

2.21 [AuBr₂(*N*-dbs)(I^tBu)] (18b)

[Au(*N*-mal)(I^tBu)] (11c) (30.1 mg, 63.6 μmol, 1 equiv.) was dissolved in dichloromethane (1 ml), bromine (20.4 mg, 128 μmol, 2 equiv.) was added and the yellow solution stirred for 1 hour at room temperature. The solution was reduced *in vacuo* to <0.5 ml and hexane (5 ml) added producing a yellow precipitate. This was separated by filtration, washed (pentane, diethyl ether) and dried *in vacuo* to give the title compound as a yellow powder (37.5 mg, 59.2 μmol, 93%). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (s, 2H, imidazole *CH*), 4.82 (s, 2H, dbs *CH*), 1.99 {s, 18H, ^tBu C(*CH*₃)₃}. ¹³C NMR (400 MHz, CDCl₃) δ 175.7 (dbs C=O), 128.1 (carbene Au-C), 122.4 (imidazole CH), 62.6 (^tBu C(*CH*₃)₃), 46.6 (dbs CH), 32.1 {^tBu C(*CH*₃)₃}. IR (CH₂Cl₂, cm⁻¹) *v*_{max} 3054 (m), 2986 (m), 2360 (m), 2341 (m), 1733 (m), 1690 (s), 1653

(m), 1636 (m), 1559 (m), 1540 (m), 1521 (m), 1507 (m), 1497 (m), 1473 (m), 1457 (m), 1437 (m), 1420 (m), 1376 (m), 1338 (m), 1271 (s), 1230 (m), 1179 (m). ESI⁺-MS *m/z* 815.8 (100%, [MNa]⁺), 733.9 (3%, [MNa-HBr]⁺), 664.9 (4%), 596.9 (4%), 528.9 (4%). ESI⁺-HRMS calcd. for C₁₅H₂₂AuBr₄N₃NaO₂ ([MNa]⁺) 815.7963; found 815.7958. Mp 160 °C (decomp.).

2.22 [AuBr₂(*N*-tfs)(I^tBu)] (18c)

A protocol similar to that used for **18a** gave the title compound as a yellow powder {from 57.0 mg, 104 μmol, of [Au(*N*-tfs)(I^tBu)] (**11b**)} (67.2 mg, 95.0 μmol, 91%). ¹H NMR (400 MHz, CDCl₃) δ 7.51 (s, 2H, imidazole CH), 1.98 {s, 18H, ^tBu C(CH₃)₃}. ¹⁹F NMR (376 MHz, CDCl₃) δ -127.1 (s, tfs CF₂). ¹³C NMR (100 MHz, CDCl₃) δ 167.1 (m, tfs C=O), ¹124.9 (carbene Au-C), 122.8 (imidazole CH), 106.8 (tt, *J* = 269 and 23 Hz, tfs CF₂), 62.8 {^tBu C(CH₃)₃}, 32.0 {^tBu C(CH₃)₃}. IR (CH₂Cl₂, cm⁻¹) *v*_{max} 3491 (w), 3200 (w), 3168 (w), 3056 (w), 2987 (m), 1789 (w), 1718 (s), 1584 (w), 1479 (m), 1418 (m), 1386 (m), 1376 (m), 1322 (m), 1305 (s), 1197 (s), 1156 (s), 1065 (m), 1017 (m). ESI⁺-MS *m/z* 797.9 (3%), 729.9 (100%, [MNa]⁺), 498.9 (2%), 259.1 (6%, [I^tBu+HBr]⁺), 227.0 (3%), 191.1 (1%), 107.2 (2%). ESI⁺-HRMS calcd. for C₁₅H₂₀AuBr₂F₄N₃NaO₂ ([MNa]⁺) 729.9396; found 729.9390. Mp 160 °C (decomp.).

2.23 [AuBr₂(*N*-mal)(I^tBu)] (18d)

[Au(*N*-mal)(I^tBu)] (**11c**) (51.2 mg, 108 μmol, 1 equiv.) was dissolved in dichloromethane (1 ml), bromine (17.3 mg, 108 μmol, 1 equiv.) was added and the brown solution stirred for 1 hour at -78 °C. The solution was reduced under vacuum to <0.5 ml and pentane (5 ml) added producing a yellow precipitate. This was separated by filtration, washed (pentane, diethyl ether) and dried *in vacuo* to give the title compound as a yellow powder (61.3 mg, 96.8 μmol, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (s, 2H, imidazole CH), 6.64 (s, 2H, mal CH), 2.01 {s, 18H, ^tBu C(CH₃)₃}. ¹³C NMR (100 MHz, CDCl₃) δ 177.3 (mal C=O), 136.8 (mal CH), 131.2 (carbene Au-C), 122.2 (imidazole CH), 62.4 {^tBu C(CH₃)₃}, 32.1 {^tBu C(CH₃)₃}. IR (CH₂Cl₂, cm⁻¹) *v*_{max} 3200 (w), 3169 (w), 3055 (m), 2985 (m), 1733 (m), 1676 (s), 1653 (w), 1589 (w), 1540 (w), 1506 (w), 1417 (m), 1376 (m), 1346 (s), 1321 (w), 1271 (s), 1233 (m), 1181 (s), 1155 (m), 1063 (w). ESI⁺-MS *m/z* 656.0 (100%, [MNa]⁺), 498.9 (4%, [MNa-2Br]⁺), 430.9 (4%), 289.2 (10%). ESI⁺-HRMS calcd. for C₁₅H₂₂AuBr₂N₃NaO₂ ([MNa]⁺) 655.9617; found 655.9649. Mp 190 °C (decomp.).

2.24 [AuBr₂(*N*-ptm)(I^tBu)] (18e)

A protocol similar to that used for **11a** gave the title compound as a yellow powder {from 99.1 mg, 189 μmol, of [Au(*N*-ptm)(I^tBu)] (**11d**)} (115 mg, 168 μmol, 89%). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (dd, *J* = 5.4 and 3.0 Hz, 2H, ptm *meta* aromatic CH), 7.57 (dd, *J* = 5.4 and 3.0 Hz, 2H, ptm *para* aromatic CH),

7.45 (s, 2H, imidazole CH), 2.04 {s, 18H, ^tBu C(CH₃)₃}. ¹³C NMR (101 MHz, CDCl₃) δ 174.4 (ptm C=O), 136.4 (ptm aromatic C), 132.2 (ptm aromatic CH), 131.5 (carbene Au-C), 122.1 (imidazole CH), 121.9 (ptm aromatic CH), 62.5 {^tBu C(CH₃)₃}, 32.2 {^tBu C(CH₃)₃}. IR (CH₂Cl₂, cm⁻¹) *v*_{max} 3053 (m), 2987 (m), 2359 (w), 1682 (s), 1646 (m), 1609 (w), 1540 (w), 1465 (m), 1417 (m), 1374 (m), 1352 (m), 1312 (s), 1178 (m), 1157 (w), 1128 (m). ESI⁺-MS *m/z* 684.0 (51%, [MH]⁺), 418.2 (51%), 338.3 (18%), 259.1 (36%, [I^tBuBr]⁺), 181.2 (100%, [ItBuH]⁺). ESI⁺-HRMS calcd. for C₁₉H₂₅AuBr₂N₃O₂ ([MH]⁺) 681.9974; found 681.9988. Mp 210 °C (decomp.).

2.25 [AuBr₂(N-obs)(I^tBu)] (18f)

A protocol similar to that used for **18a** gave the title compound as a yellow powder {from 38.4 mg, 68.7 μmol, of [Au(N-obs)(I^tBu)] (**11e**)} (45.4 mg, 63.1 μmol, 92%). ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.84 (m, 2H, aromatic CH), 7.72-7.66 (m, 2H, aromatic CH), 7.50 (s, 2H, imidazole CH), 2.03 {s, 18H, ^tBu C(CH₃)₃}. ¹³C NMR (100 MHz, CDCl₃) δ 164.0 (obs C=O), 142.3 (obs aromatic C), 133.0 (obs aromatic CH), 131.3 (obs aromatic C), 125.6 (carbene Au-C), 124.1 (obs aromatic CH), 122.7 (imidazole CH), 120.5 (obs aromatic CH), 62.7 {^tBu C(CH₃)₃}, 32.0 {^tBu C(CH₃)₃}. IR (CH₂Cl₂, cm⁻¹) *v*_{max} 3676 (w), 3062 (w), 2986 (m), 2929 (m), 1734 (w), 1694 (s), 1653 (w), 1597 (w), 1559 (w), 1460 (m), 1417 (m), 1376 (m), 1336 (w), 1315 (s), 1287 (m), 1247 (m), 1192 (w), 1176 (s), 1158 (m), 1124 (w), 1014 (w), 979 (m), 971 (m). ESI⁺-MS *m/z* 741.9 (100%, [MNa]⁺), 698.0 (2%), 640.9 (1%), 582.1 (2%), 481.0 (7%), 435.1 (6%), 336.1 (1%), 259.1 (15%), 215.1 (2%), 181.2 (4%), 147.0 (2%). ESI⁺-HRMS calcd. for C₁₈H₂₄AuBr₂N₃NaO₃S ([MNa]⁺) 741.9448; found 741.9442. Mp 150 °C (decomp.).

2.26 [AuBr₃(I^tBu)] (18g)

Prepared by a protocol reported by de Frémont *et al.*² [AuBr(I^tBu)] (**11g**) (40.7 mg, 89.1 μmol, 1 equiv.) was dissolved in dichloromethane (2 ml) and bromine (0.80 ml, 98 μmol, 1.1 equiv.) was added. The orange solution was stirred at room temperature for 1 hour. The volume was reduced *in vacuo* to <0.5 ml and hexane added to give an orange precipitate. This was separated by filtration, washed (hexane) and dried *in vacuo* to give the title compound as an orange powder (53.1 mg, 86.1 μmol, 97%). ¹H NMR (400 MHz, CDCl₃) δ 7.45 (s, 2H, imidazole CH), 1.94 (s, 18H, ^tBu CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 134.8 (carbene Au-C), 122.2 (imidazole CH), 62.4 (^tBu quaternary C), 32.0 (^tBu CH₃). ESI⁺-MS *m/z* 656.8 (61%, [MK]⁺), 640.9 (100%, [MNa]⁺), 633.9 (30%), 582.8 (12%), 526.7 (8%), 481.0 (7%, [MNa-2Br]⁺), 429.4 (16%), 413.3 (58%), 369.3 (36%), 349.1 (24%), 293.0 (70%), 259.1 (77%). ESI⁺-HRMS calcd. for C₁₁H₂₀N₂AuBr₃Na 640.8694 ([MNa]⁺); found 640.8677.

2.27 [AuBr₂(N-succ)(I^tPe)] (19a)

A protocol similar to that used for **18a** gave the title compound as a yellow powder {from 98.8 mg, 196 μmol , of $[\text{Au}(\text{N-succ})(\text{I}^t\text{Pe})]$ (**12a**)} (127 mg, 192 μmol , 98%). ^1H NMR (400 MHz, CDCl_3) δ 7.36 (s, 2H, imidazole CH), 2.74 (s, 4H, succ CH_2), 2.04 (s, 12H, ^tPe C(CH_3)₂), 2.03 (q, $J = 7.5$ Hz, 4H, ^tPe CH_2CH_3), 0.84 (t, $J = 7.5$ Hz, 6H, ^tPe CH_2CH_3). ^{13}C NMR (101 MHz, CDCl_3) δ 183.9 (succ C=O), 132.6 (carbene Au-C), 122.1 (imidazole CH), 65.4 (^tPe quaternary C), 36.8 (^tPe CH_2CH_3), 31.4 (succ CH_2), 29.8 (^tPe C(CH_3)₂), 8.5 (^tPe CH_2CH_3). IR (solid, cm^{-1}) ν_{max} 2967 (w), 1665 (s), 1461 (w), 1414 (w), 1224 (s), 1003 (s), 798 (s), 683 (m). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3686 (w), 3052 (m), 2979 (m), 2940 (w), 2882 (w), 1663 (s), 1540 (w), 1465 (m), 1434 (w), 1414 (w), 1387 (m), 1352 (m), 1284 (m), 1230 (m), 1176 (w). ESI⁺-MS m/z 664.0 (100%, $[\text{MH}]^+$), 593.9 (72%), 523.9 (86%), 472.9 (21%), 433.2 (34%), 414.3 (93%), 391.3 (99%), 289.1 (58%), 217.0 (42%), 149.0 (58%), 127.3 (23%). ESI⁺-HRMS calcd. for $\text{C}_{17}\text{H}_{29}\text{AuBr}_2\text{N}_3\text{O}_2$ ($[\text{MH}]^+$) 662.0287; found 662.0313. Mp 190 °C (decomp.).

2.28 $[\text{AuBr}_2(\text{N-dbs})(\text{I}^t\text{Pe})]$ (**19b**)

A protocol similar to that used for **18b** gave the title compound as a yellow powder {from 31.4 mg, 62.7 μmol , of $[\text{Au}(\text{N-mal})(\text{I}^t\text{Pe})]$ (**12c**)} (36.2 mg, 54.8 μmol , 87%). ^1H NMR (400 MHz, CDCl_3) δ 7.39 (s, 2H, imidazole CH), 4.81 (s, 2H, dbs CH), 2.03 {m, 16H, ^tPe CH_2CH_3 and ^tPe C(CH_3)₂}, 0.85 (t, $J = 7.4$ Hz, 6H, ^tPe CH_2CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ 175.7 (dbs C=O), 128.7 (carbene Au-C), 122.4 (imidazole CH), 65.6 (^tPe quaternary C), 46.6 (dbs C-H), 36.8 (^tPe CH_2CH_3), 29.7 (^tPe C(CH_3)₂), 8.5 (^tPe CH_2CH_3). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3421 (w), 3200 (w), 2976 (w), 2976 (m), 2930 (w), 2360 (m), 2341 (m), 1741 (m), 1690 (s), 1465 (m), 1419 (m), 1387 (m), 1337 (s), 1269 (s), 1227 (m), 1198 (w), 1174 (w). ESI⁺-MS m/z 843.8 (100%, $[\text{MNa}]^+$). ESI⁺-HRMS calcd. for $\text{C}_{17}\text{H}_{26}\text{AuBr}_4\text{N}_3\text{NaO}_2$ ($[\text{MNa}]^+$) 843.8277; found 843.8288. Mp 170 °C (decomp.).

2.29 $[\text{AuBr}_2(\text{N-tfs})(\text{I}^t\text{Pe})]$ (**19c**)

A protocol similar to that used for **18a** gave the title compound as a yellow powder {from 50.5 mg, 87.8 μmol , of $[\text{Au}(\text{N-tfs})(\text{I}^t\text{Pe})]$ (**12b**)} (60.0 mg, 81.6 μmol , 93%). ^1H NMR (400 MHz, CDCl_3) δ 7.43 (s, 2H, imidazole CH), 2.05 {s, 12H, ^tPe C(CH_3)₂}, 2.04 (q, $J = 7.5$ Hz, 4H, ^tPe CH_2CH_3), 0.86 (t, $J = 7.5$ Hz, 6H, ^tPe CH_2CH_3). ^{19}F NMR (376 MHz, CDCl_3) δ -127.1 (s, CF_2). ^{13}C NMR (101 MHz, CDCl_3) δ 167.0 (m, C=O),⁷ 126.0 (carbene Au-C), 122.8 (imidazole CH), 107.0 (tt, $J = 269$ and 23 Hz, CF_2), 65.8 (^tPe quaternary C), 36.8 (^tPe CH_2CH_3), 29.7 (^tPe C(CH_3)₂), 8.5 (^tPe CH_2CH_3). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3490 (w), 3200 (w), 3166 (w), 2979 (m), 2941 (w), 2884 (w), 1819 (w), 1789 (w), 1720 (m), 1716 (s), 1586 (w), 1480 (w), 1465 (w), 1417 (w), 1387 (m), 1322 (m), 1305 (m), 1195 (s), 1156 (m), 1065 (m), 1017 (m).

ESI⁺-MS *m/z* 799.0 (6%, [MNa+MeCN]⁺), 758.0 (100%, [MNa]⁺), 598.1 (3%), 463.1 (4%). ESI⁺-HRMS calcd. for C₁₇H₂₄AuBr₂F₄N₃NaO₂ ([MNa]⁺) 757.9714; found 757.9703. Mp 150 °C (decomp.).

2.30 [AuBr₂(*N*-mal)(I^tPe)] (19d)

A protocol similar to that used for **18d** gave the title compound as a yellow powder {from 30.1 mg, 60.1 μmol, of [Au(*N*-mal)(I^tPe)] (**12c**)} (34.7 mg, 52.5 μmol, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.38 (s, 2H, imidazole *CH*), 6.64 (s, 2H, mal *CH*), 2.07 {s, 12H, ^tPe C(CH₃)₂}, 2.03 (q, *J* = 7.5 Hz, 4H, ^tPe CH₂CH₃), 0.86 (t, *J* = 7.5 Hz, 6H, ^tPe CH₂CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 177.3 (mal C=O), 136.8 (mal *CH*), 132.0 (carbene Au-C), 122.2 (imidazole *CH*), 65.4 (^tPe quaternary C), 36.9 (^tPe CH₂CH₃), 29.8 {^tPe C(CH₃)₂}, 8.6 (^tPe CH₂CH₃). IR (CH₂Cl₂, cm⁻¹) *v*_{max} 3054 (m), 2979 (m), 2940 (w), 2883 (w), 2360 (m), 2342 (m), 1734 (m), 1676 (s), 1437 (m), 1419 (m), 1348 (s), 1269 (s), 1180 (m). ESI⁺-MS *m/z* 684.0 (100%, [MNa]⁺), 649.2 (33%), 619.0 (9%), 524.2 (12%). ESI⁺-HRMS calcd. for C₁₇H₂₆AuBr₂N₃NaO₂ 683.9935; found 683.9901. Mp 160 °C (decomp.).

2.31 [AuBr₂(*N*-ptm)(I^tPe)] (19e)

A protocol similar to that used for **18a** gave the title compound as a yellow powder {98.5 mg, 179 μmol, of [Au(*N*-ptm)(I^tPe)] (**12d**)} (123 mg, 173 μmol, 97%). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (dd, *J* = 5.4 and 3.0 Hz, 2H, ptm aromatic *CH*), 7.56 (dd, *J* = 5.4 and 3.0 Hz, 2H, ptm aromatic *CH*), 7.39 (s, 2H, imidazole *CH*), 2.10 {s, 12H, ^tPe C(CH₃)₂}, 2.05 (q, *J* = 7.4 Hz, 4H, ^tPe CH₂CH₃), 0.86 (t, *J* = 7.4 Hz, 6H, ^tPe CH₂CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 174.3 (ptm C=O), 136.2 (ptm *ortho* aromatic C), 132.4 (carbene Au-C), 132.3 (ptm *meta* aromatic C), 122.3 (ptm *para* aromatic C), 121.8 (imidazole *CH*), 65.3 (^tPe quaternary C), 36.8 (^tPe CH₂CH₃), 29.8 {^tPe C(CH₃)₂}, 8.5 (^tPe CH₂CH₃). IR (CH₂Cl₂, cm⁻¹) *v*_{max} 3199 (w), 3057 (w), 2979 (m), 2940 (w), 2882 (w), 1742 (w), 1682 (s), 1646 (m), 1609 (w), 1540 (w), 1465 (m), 1416 (m), 1373 (m), 1352 (m), 1311 (s), 1284 (m), 1214 (w), 1175 (m), 1128 (m). ESI⁺-MS *m/z* 712.0 (100%, [MH]⁺), 642.0 (41%, [MH-^tPe]⁺), 571.9 (35%, [MH₂-2^tPe]⁺), 472.9 (6%), 391.3 (68%), 363.1 (3%), 289.1 (16%, [I^tPeBr]⁺), 272.7 (18%), 217.0 (14%, [I^tPeBrH-^tPe]⁺), 149.0 (24%), 127.3 (5%). ESI⁺-HRMS calcd. for C₂₁H₂₉AuBr₂N₃O₂ ([MH]⁺) 710.0287; found 710.0309. Mp 220 °C (decomp.).

2.32 [AuBr₂(*N*-obs)(I^tPe)] (19f)

A protocol similar to that used for **18a** gave the title compound as a yellow powder {from 40.6 mg, 69.2 μmol, of [Au(*N*-obs)(I^tPe)] (**12e**)} (48.6 mg, 65.1 μmol, 94%). ¹H NMR (400 MHz, CDCl₃) δ 7.97-7.93 (m, 1H, obs aromatic *CH*), 7.90-7.87 (m, 1H, obs aromatic *CH*), 7.72-7.66 (m, 2H, obs aromatic *CH*), 7.43 (s, 2H, imidazole *CH*), 2.12 {s, 12H, ^tPe C(CH₃)₂}, 2.05 (q, *J* = 7.4 Hz, 4H, ^tPe CH₂CH₃), 0.88 (t, *J* =

7.4 Hz, 6H, $^1\text{Pe CH}_2\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3) δ 164.0 (obs C=O), 142.3 (obs aromatic C), 133.0 (obs aromatic 2CH), 131.3 (obs aromatic C), 126.6 (carbene Au-C), 124.1 (obs aromatic CH), 122.7 (imidazole CH), 120.4 (obs aromatic CH), 65.8 (^1Pe quaternary C), 36.9 ($^1\text{Pe CH}_2\text{CH}_3$), 29.7 {s, $^1\text{Pe C(CH}_3)_2$ }, 8.6 (s, $^1\text{Pe CH}_2\text{CH}_3$). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3675 (w), 3199 (w), 3063 (w), 2979 (m), 2940 (m), 2883 (m), 1694 (s), 1653 (w), 1596 (m), 1506 (w), 1461 (m), 1417 (m), 1388 (m), 1337 (w), 1315 (s), 1287 (s), 1248 (s), 1192 (w), 1176 (s), 1160 (m), 1124 (w), 1059 (w). ESI $^+$ -MS m/z 838.0 (4%), 770.0 (100%, $[\text{MNa}]^+$), 633.0 (12%), 446.2 (11%). ESI $^+$ -HRMS calcd. for $\text{C}_{20}\text{H}_{28}\text{AuBr}_2\text{N}_3\text{NaO}_3\text{S}$ ($[\text{MNa}]^+$) 769.9761; found 769.9764. Mp 180 °C (decomp.).

2.33 $[\text{AuBr}_3(\text{I}^1\text{Pe})]$ (19g)

A protocol similar to that used for **18g** gave the title compound as an orange solid {from 40.7 mg, 89.1 μmol , of $[\text{AuBr}(\text{I}^1\text{Pe})]$ (**12g**)} (53.1 mg, 86.1 μmol , 97%). ^1H NMR (400 MHz, CDCl_3) δ 7.39 (s, 2H, imidazole CH), 2.02 (q, $J = 7.5$ Hz, 4H, $^1\text{Pe CH}_2\text{CH}_3$), 2.01 {s, 12H, $^1\text{Pe C(CH}_3)_2$ }, 0.86 (t, $J = 7.5$ Hz, 6H, $^1\text{Pe CH}_2\text{CH}_3$). ^{13}C NMR (101 MHz, CDCl_3) δ 135.6 (carbene Au-C), 122.2 (imidazole CH), 65.5 (^1Pe quaternary C), 36.7 ($^1\text{Pe CH}_2\text{CH}_3$), 29.6 { $^1\text{Pe C(CH}_3)_2$ }, 8.6 ($^1\text{Pe CH}_2\text{CH}_3$). IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3200 (m), 3165 (m), 3050 (m), 2979 (s), 2941 (m), 2883 (m), 1585 (w), 1465 (m), 1413 (m), 1382 (m), 1281 (w), 1260 (s), 1199 (m), 1175 (s), 1161 (m), 1067 (w), 1033 (w), 1006 (w). ESI $^+$ -MS m/z 666.9 (100%, $[\text{MNa}]^+$), 507.1 (54%), 463.1 (8%), 289 (37%). ESI $^+$ -HRMS calcd. for $\text{C}_{13}\text{H}_{24}\text{AuBr}_3\text{N}_2\text{Na}$ ($[\text{MNa}]^+$) 666.9027; found 666.9066. Mp 170 °C (decomp.).

2.34 $[\text{AuBr}_2(\text{N-succ})(\text{IMes})]$ (20a)

A protocol similar to that used for **18a** gave the title compound as a yellow powder {57.9 mg, 96.7 μmol , of $[\text{Au}(\text{N-succ})(\text{IMes})]$ (**13a**)} (63.3 mg, 83.4 μmol , 86%). ^1H NMR (400 MHz, CDCl_3) δ 7.26 (s, 2H, imidazole CH), 7.06 (s, 4H, Mes aromatic CH), 2.52 (s, 4H, succ CH_2), 2.37 (s, 6H, Mes *para* CH_3), 2.33 (s, 12H, Mes *ortho* CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ 183.1 (succ C=O), 142.2 (carbene Au-C), 140.6 (Mes aromatic C), 135.0 (Mes aromatic C), 133.0 (Mes aromatic C), 129.9 (Mes aromatic CH), 125.5 (imidazole CH), 31.3 (succ CH_2), 21.2 {Mes *para* $\text{C(CH}_3)_2$ }, 19.5 {Mes *ortho* $\text{C(CH}_3)_2$ }. IR (CH_2Cl_2 , cm^{-1}) ν_{max} 3677 (w), 3144 (w), 3055 (m), 2979 (w), 2924 (w), 2363 (w), 1723 (w), 1665 (s), 1608 (w), 1540 (w), 1482 (m), 1434 (m), 1381 (w), 1351 (m), 1281 (m), 1232 (m), 1168 (w). ESI $^+$ -MS m/z 782.0 (10%, $[\text{MNa}]^+$), 760.0 (100%, $[\text{MH}]^+$), 542.2 (5%). ESI $^+$ -HRMS calcd. for $\text{C}_{25}\text{H}_{29}\text{AuBr}_2\text{N}_3\text{O}_2$ ($[\text{MH}]^+$) 758.0287; found 758.0282. Mp 180 °C (decomp.).

2.35 [AuBr₂(*N*-mal)(IMes)] (20b)

A protocol similar to that used for **18d** gave the title compound as a yellow powder {105 mg, 176 μ mol, of [Au(*N*-mal)(IMes)] (**13c**)} (129 mg, 170 μ mol, 96%). ¹H NMR (400 MHz, CDCl₃) δ 7.27 (s, 2H, *CH* imidazole), 7.07 (s, 4H, Mes aromatic *CH*), 6.39 (s, 2H, mal *CH*), 2.33 (m, 18 H, Mes *CH*₃). ¹³C NMR (101 MHz, CDCl₃) δ 176.6 (mal C=O), 141.4 (carbene Au-C), 140.7 (Mes aromatic C), 136.7 (mal *CH*), 135.0 (Mes aromatic C), 133.0 (Mes aromatic C), 129.9 (Mes aromatic *CH*), 125.6 (imidazole *CH*), 21.2 (Mes *para* CCH₃), 19.5 (Mes *ortho* CCH₃). IR (CH₂Cl₂, cm⁻¹) ν_{max} 3686 (w), 3143 (w), 2984 (w), 2352 (w), 1677 (s), 1608 (m), 1540 (w), 1484 (m), 1432 (w), 1380 (w), 1349 (m), 1284 (w), 1229 (m), 1181 (m), 1128 (w). ESI⁺-MS *m/z* 758.0 (1%, [MH]⁺), 620.2 (12%, [MNa-2Br]⁺), 598.2 (88%, [MH-2Br]⁺), 550.2 (4%), 529.2 (64 %), 385.1 (31%, [IMesBr]⁺), 335.2 (2%), 305.2 (100%, [IMesH]⁺), 267.2 (2%). ESI⁺-HRMS calcd. for C₂₅H₂₇AuBr₂N₃O₂ ([MH]⁺) 758.0115; found 758.0185. Mp 190 °C (decomp.).

2.36 [AuBr₂(*N*-ptm)(IMes)] (20c)

A protocol similar to that used for **18a** gave the title compound as a yellow powder {40.3 mg, 62.3 μ mol, of [Au(*N*-ptm)(IMes)] (**13d**)} (48.0 mg, 59.4 μ mol, 95%). ¹H NMR (400 MHz, CDCl₃) δ 7.56 (dd, *J* = 5.4 and 3.0 Hz, 2H, ptm aromatic *CH*), 7.44 (dd, *J* = 5.4 and 3.0 Hz, 2H, ptm aromatic *CH*), 7.29 (s, 2H, imidazole *CH*), 7.09 (s, 4H, Mes aromatic *CH*), 2.38 (s, 6H, Mes *para* CCH₃), 2.34 (s, 12H, Mes *ortho* CCH₃). ¹³C NMR (400 MHz, CDCl₃) δ 173.7 (ptm C=O), 142.2 (carbene Au-C), 140.6 (Mes aromatic C), 136.3 (ptm *ortho* aromatic C), 135.0 (Mes aromatic C), 133.1 (Mes aromatic C), 132.0 (ptm *meta* aromatic *CH*), 129.9 (Mes aromatic *CH*), 125.6 (imidazole *CH*), 121.7 (ptm *para* aromatic *CH*), 21.2 {Mes *para* C(CH₃)}, 19.5 {Mes *ortho* C(CH₃)}. IR (CH₂Cl₂, cm⁻¹) ν_{max} 3686 (w), 3421 (w), 3170 (w), 3143 (w), 2925 (w), 2360 (w), 1777 (w), 1741 (m), 1683 (s), 1646 (m), 1609 (m), 1540 (w), 1484 (m), 1418 (w), 1372 (m), 1351 (m), 1310 (m), 1230 (m), 1172 (m), 1129 (m). ESI⁺-MS *m/z* 808.0 (100%, [MH]⁺), 728.1 (2%, [M-Br]⁺), 648.2 (48%, [MH-2Br]⁺), 622.1 (4%), 542.2 (84%). ESI⁺-HRMS calcd. for C₂₉H₂₉AuBr₂N₃O₂ ([MH]⁺) 808.0268; found 808.0283. Mp 125-127 °C.

2.37 [Au(¹⁵N-succ)(I^tPe)] (¹⁵N-12a)

¹⁵N-Succinimide (15.8 mg, 15.8 μ mol, 1.1 equiv.), silver(I) oxide (20.0 mg, 86.2 μ mol, 0.6 equiv.) and [AuCl(I^tPe)] (**12f**) (63.2 mg, 144 μ mol, 1 equiv.) were mixed in dichloromethane (2 ml) in the absence of light for 18 hours. The suspension was filtered through CeliteTM, reduced to <0.5 ml and pentane added, resulting in a white precipitate. This was washed (cold pentane and diethyl ether) and dried *in vacuo* to give the title compound as a white powder (65.2 mg, 130 μ mol, 90%). ¹H NMR (400 MHz, CDCl₃) δ 7.04 (s, 2H, imidazole *CH*), 2.61 (s, 4H, succ *CH*₂), 2.48 (q, *J* = 7.5 Hz, 4H, ^tPe *CH*₂), 1.81 {s, 12H, ^tPe

C(CH₃)₂}, 0.65 (t, *J* = 7.5 Hz, 6H, ¹Pe CH₂CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 188.7 (d, *J* = 8 Hz, succ C=O), 170.8 (d, *J* = 15 Hz, carbene Au-C), 117.3 (imidazole CH), 61.8 (¹Pe quaternary C), 36.3 (¹Pe CH₂CH₃), 31.6 (d, *J* = 4 Hz, succ CH₂), 29.3 (¹Pe C(CH₃)₂), 7.9 (¹Pe CH₂CH₃). ¹⁵N NMR (50 MHz, CD₂Cl₂) δ 209.4 (s). IR (solid, cm⁻¹) *v*_{max} 2964 (m), 2933 (w), 2533 (w), 2160 (m), 2028 (m), 1978 (m), 1646 (s), 1561 (w), 1459 (w), 1396 (w), 1378 (w), 1333 (s), 1279 (m), 1212 (s), 1152 (w), 1067 (w), 1039 (w), 1006 (w), 972 (w), 919 (w), 816 (m), 759 (m), 759 (w), 732 (m), 701 (m), 653 (m), 620 (m). IR (CH₂Cl₂, cm⁻¹) *v*_{max} 3020 (m), 2971 (m), 2937 (w), 2880 (w), 2005 (w), 2360 (w), 2342 (w), 1646, 1559 (w), 1522 (w), 1461 (w), 1436 (w), 1406 (w), 1393 (w), 1379 (m), 1336 (m), 1310 (w), 1284 (m), 1269 (s), 1217 (s), 1005 (w), 917 (w), 896 (m). ESI⁺-MS *m/z* 527.2 (12%, [MNa]⁺), 505.2 (100%, [MH]⁺), 433.2 (1%), 209.2 (3%, [¹PeH]⁺). ESI⁺-HRMS calcd. for C₁₇H₂₉Au¹⁴N₂¹⁵NO₂ ([MH]⁺) 505.1896; found 505.1891.

2.38 [AuBr₂(¹⁵N-succ)(¹Pe)] (¹⁵N-19a)

[Au(¹⁵N-Succ)(¹Pe)] (72) (41.3 mg, 81.9 μmol, 1 equiv.) was dissolved in dichloromethane (2 ml) and bromine (14.4 mg, 90.0 μmol, 1.1 equiv.) was added dropwise. The yellow solution was stirred at room temperature for 1 hour. The volume was reduced to <0.5 ml *in vacuo* and hexane added resulting in a yellow precipitate. This was separated by filtration, washed (cold hexane and diethyl ether) and dried *in vacuo* to give the title compound as a yellow powder (51.1 mg, 70.0 μmol, 94%). ¹H NMR (400 MHz, CDCl₃) δ 7.36 (s, 2H, imidazole CH), 2.73 (s, 4H, succ CH₂), 2.06 {s, 12H, ¹Pe C(CH₃)₂}, 2.04 (q, *J* = 7.5 Hz, 4H, ¹Pe CH₂CH₃), 0.84 (t, *J* = 7.5 Hz, 6H, ¹Pe CH₂CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 183.9 (d, *J* = 9 Hz, succ C=O), 132.8 (d, *J* = 25 Hz, carbene Au-C), 122.3 (imidazole CH), 65.6 (¹Pe quaternary C), 37.0 (¹Pe CH₂CH₃), 31.5 (d, *J* = 5 Hz, succ CH₂), 29.9 {¹Pe C(CH₃)₂}, 8.7 (¹Pe CH₂CH₃). ¹⁵N NMR (50 MHz, CD₂Cl₂) δ 179.4 (s). IR (solid, cm⁻¹) *v*_{max} 2976 (s), 2165 (m), 2037 (m), 1662 (s), 1461 (m), 1419 (w), 1392 (w), 1331 (s), 1280 (m), 1211 (s), 1164 (m), 1065 (w), 1002 (w), 809 (m). IR (CH₂Cl₂, cm⁻¹) *v*_{max} 2978 (m), 2941 (w), 2881 (w), 1744 (w), 1702 (w), 1662 (s), 1583 (w), 1481 (w), 1464 (w), 1413 (w), 1385 (w), 1337 (m), 1283 (w), 1216 (m), 1176 (w), 1163 (w), 1151 (w), 1066 (w), 1035 (w), 1003 (w). ESI⁺-MS *m/z* 728.0 (2%, [MNa+MeCN]⁺), 687.0 (5%, [MNa]⁺), 665.0 (100%, [MH]⁺), 610.2 (1%), 591.3 (3%), 536.2 (3%), 505.2 (2%, [MH-2Br]⁺), 401.0 (5%), 287.1 (38%, [¹PeBr]⁺), 209.2 (51%, [¹PeH]⁺), 176.4 (3%). ESI⁺-HRMS calcd. for C₁₇H₂₉AuBr₂¹⁴N₂¹⁵NO₂ ([MH]⁺) 665.0242; found 665.0232.

3.0 1,5-Enyne cycloisomerization catalysis

3.1 General procedure for the cycloisomerization of 4-phenyl-1-hexen-5-yne (**24**) – without catalyst preformation

To a solution of 4-phenyl-1-hexen-5-yne (**24**) (50.0 mg, 321 μ mol, 1 equiv.) in CH_2Cl_2 (0.64 mL, 0.50 M), AgOTf (0.8 mg, 3.1 μ mol, 0.01 equiv.) and gold complex (3.2 μ mol, 0.01 equiv.) were added. The solution was stirred at 25 °C for 3 hours and filtered through a plug of silica-gel which was washed with CH_2Cl_2 (2 mL). The solution was reduced *in vacuo* and conversion was determined by ^1H NMR spectroscopy. For characterization purposes the product can be purified by column chromatography on silica-gel using petroleum ether (40-60 °C) as eluent (R_f = 0.76). Fractions containing the product were combined and reduced *in vacuo* to give the title product (**25**) as a white powder.

3.2 General procedure for the cycloisomerization of 4-phenyl-1-hexen-5-yne (**24**) – with catalyst preformation

The test Au complex (3.2 μ mol, 0.01 equiv.) and AgOTf (0.8 mg, 3.2 μ mol, 0.01 equiv.) were mixed in dichloromethane in a screw cap vial (1 min) and the solvent removed *in vacuo*. A solution of 4-phenyl-1-hexen-5-yne (**24**) (50.0 mg, 321 μ mol, 1 equiv.) in 1,2-dichloroethane (1.60 mL, 0.20 M) was added, the vial sealed with a rubber septum and a positive pressure of argon applied *via* an argon balloon. The mixture was stirred at 25 °C in the absence of light. Samples (10 μ L) were taken *via* syringe and added immediately to a solution of tetra-*n*-butylammonium chloride (8 mM, 20 μ L; ‘quench’) in CH_2Cl_2 . Conversion was determined *via* gas chromatography using a 1 μ L sample (and cross-checked by ^1H NMR spectroscopic analysis). The chromatogram was run with an injector temperature of 250 °C and an initial oven temperature of 80 °C (0.5 mins), heated to 160 °C, at a rate of 20 °C.min⁻¹, and maintained at 160 °C (1 minute). The retention times were: 2.58 minutes for 4-phenyl-1-hexen-5-yne (**24**) and 3.89 minutes for 3-phenylbicyclo[3.1.0]hex-2-ene (**25**), and both compounds exhibit the same response factor (confirmed by ^1H NMR spectroscopic analysis).

3.3 4-Phenyl-1-hexen-5-yne (**24**)

1-Phenyl-prop-2-yn-1-ol (2.53 mL, 20.4 mmol, 1 equiv.) and allyltrimethylsilane (9.78 mL, 61.4 mmol, 3 equiv.) were mixed in acetonitrile (40 mL, dry). FeCl_3 (anhydrous, 166 mg, 1.02 mmol, 0.05 equiv.) in acetonitrile (5 mL, dry) was added dropwise. The reaction was stirred (2 hours, r.t.). FeCl_3 (anhydrous, 166 mg, 1.02 mmol, 0.05 equiv.) in dry acetonitrile (5 mL dry) was added dropwise and the reaction stirred (1

hour, r.t.). The solution was reduced *in vacuo* and the product was purified by column chromatography, eluting with 100% petroleum ether (40-60), to give the title compound as a colourless oil (2.70 g, 17.3 mmol, 85%). ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.32 (m, 4H), 7.29-7.24 (m, 1H), 5.87 (ddtd, $J = 17.1$, 10.2, 7.0 and 1.3 Hz, 1H), 5.13-5.06 (m, 2H), 3.72 (td, $J = 7.2$ and 2.4 Hz, 1H), 2.54 (t, $J = 7.2$ Hz, 2H), 2.32 (app. d, $J = 2.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.7, 135.1, 128.5, 127.4, 126.9, 117.1, 85.3, 71.4, 42.4, 37.6. EI^+ -MS m/z 156 (4%, $[\text{M}]^+$), 155 (7%), 141 (8%, $[\text{M}-\text{CH}_3]^+$), 128 (6%, $[\text{M}-\text{C}_2\text{H}_4]^+$), 115 (100%, $[\text{M}-\text{allyl}]^+$), 91 (6%), 89 (8%), 65 (3%), 63 (5%). EI^+ -HRMS calcd. for $\text{C}_{12}\text{H}_{12}$ ($[\text{M}]^+$) 156.0939; found 156.0943.

3.4 3-Phenylbicyclo[3.1.0]hex-2-ene (25)

^1H NMR (400 MHz, CDCl_3) δ 7.45-7.42 (m, 2H), 7.38-7.33 (m, 2H), 7.26 (m, 1H), 6.48 (q, $J = 2$ Hz, 1H), 3.08 (ddd, $J = 17$, 7.5 and 2 Hz, 1H), 2.80 (app. d, $J = 17$ Hz, 1H), 2.01 (m, 1H), 1.79 (m, 1H), 1.00 (td, $J = 7.5$ and 4 Hz, 1H), 0.17 (dd, $J = 7$ and 4 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.7, 136.6, 129.6, 128.2, 126.7, 125.1, 36.3, 23.8, 17.6, 15.4. EI^+ -MS 156 (100%, $[\text{M}]^+$), 141 (56%), 128 (39%), 115 (43%), 102 (7%), 91 (18%), 77 (12%), 63 (5%), 51 (6%). EI^+ -HRMS calcd. for $\text{C}_{12}\text{H}_{12}$ ($[\text{M}]^+$) 156.0939; found 156.0934.

4.0 X-Ray Crystallographic Data

Diffraction data were collected at 110 K on a Bruker Smart Apex diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å) using a SMART CCD camera. Diffractometer control, data collection and initial unit cell determination was performed using “SMART” (v5.625 Bruker-AXS). Frame integration and unit-cell refinement software was carried out with “SAINT+” (v6.22, Bruker AXS). Absorption corrections were applied by SADABS (v2.03, Sheldrick). Structures were solved by direct methods using SHELXS-97 (Sheldrick, 1990) and refined by full-matrix least squares using SHELXL-97 (Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a “riding model” and included in the refinement at calculated positions.

A summary of X-ray data is given below in tabular form, for both series of Au(I) and Au(III) complexes. The data for complex **19c** has been previously reported by our group.⁴

Table S1 Summary of all the X-ray data detailed in the paper.

Compound reference	ijf0802 (20c)	ijf0805m (18a)	ijf0806a (18e)	ijf0807a (11d)	ijf0918m (19a)	vc0801m (13a)	vc0802m (11a)
Chemical formula	C ₂₉ H ₂₈ AuBr ₂ N ₃ O ₂ •C ₆ H ₅ F	C ₁₅ H ₂₄ AuBr ₂ N ₃ O ₂	C ₁₉ H ₂₄ AuBr ₂ N ₃ O ₂	C ₁₉ H ₂₄ AuN ₃ O ₂	2(C ₁₇ H ₂₈ AuBr ₂ N ₃ O ₂)•C ₆ H ₅ F	C ₂₅ H ₂₈ AuN ₃ O ₂	C ₁₅ H ₂₄ AuN ₃ O ₂
Formula Mass	903.43	635.16	683.20	523.38	1422.52	599.47	475.34
Crystal system	Monoclinic	Triclinic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic	Orthorhombic
<i>a</i> /Å	17.6109(3)	9.7911(5)	19.8674(17)	11.8766(6)	11.8901(9)	9.6744(4)	11.3451(8)
<i>b</i> /Å	12.2187(3)	13.9362(7)	13.3922(11)	17.1592(9)	14.8899(11)	20.2249(9)	10.6675(7)
<i>c</i> /Å	16.6542(3)	15.3479(8)	8.3251(7)	9.4378(5)	15.2604(12)	12.7004(6)	27.4051(19)
α /°	90.00	72.3520(10)	90.00	90.00	106.6900(10)	90.00	90.00
β /°	111.8490(10)	74.0220(10)	90.00	90.00	107.2830(10)	109.8040(10)	90.00
γ /°	90.00	86.4790(10)	90.00	90.00	96.2640(10)	90.00	90.00
Unit cell volume/Å ³	3326.26(12)	1918.02(17)	2215.0(3)	1923.36(17)	2414.6(3)	2338.04(18)	3316.7(4)
Temperature /K	120(2)	110(2)	110(2)	110(2)	110(2)	110(2)	110(2)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>Pnma</i>	<i>Pnma</i>	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>Pca</i> 2 ₁
No. of formula units per unit cell, <i>Z</i>	4	4	4	4	2	4	8
No. of reflections measured	44337	22084	20843	14707	27421	26386	33945
No. of independent reflections	7619	10877	2847	2870	13566	6750	8208
<i>R</i> _{int}	0.0509	0.0333	0.0546	0.0309	0.0261	0.0280	0.0349
Final <i>R</i> _{<i>I</i>} values (<i>I</i> > 2σ(<i>I</i>))	0.0285	0.0307	0.0319	0.0200	0.0247	0.0229	0.0213
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.0581	0.0654	0.0845	0.0441	0.0617	0.0525	0.0450
Final <i>R</i> _{<i>I</i>} values (all data)	0.0401	0.0421	0.0352	0.0246	0.0300	0.0271	0.0282
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.0613	0.0688	0.0871	0.0456	0.0639	0.0540	0.0472

5.0 References

- (1) Unresolved due to complicated higher order spin-spin coupling (^{13}C - ^{19}F).
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