Homogeneous Gold Catalysis Using Complexes Recovered from Waste Electronic Equipment

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1.0. Experimental

1.1. General experimental

All reagents used in this project were purchased from commercial suppliers and used without further purification. THF is used as an abbreviation for tetrahydrofuran throughout. The reactions described were performed under air unless otherwise indicated. All stirrer bars and glassware used to perform catalysis were pre-washed with aqua regia. Crude products purified by column chromatography were passed through silica gel (pore size: 60 Å, 230-400 μm mesh size, 40-63 μm particle size). Thin-layer chromatography plates were visualized by exposure to ultraviolet light. Samples analyzed by mass spectrometry were ionized by electrospray ionization and recorded on a Waters Xevo TQ-MS/Acquity UPLC. $^1$H, $^{19}$F and $^{13}$C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer at room temperature and were referenced to the residual proton signal of the NMR solvent. Chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (J) are given in Hz. IR spectra were recorded on an Agilent Cary 630 FTIR. Unless otherwise stated, provided analytical data are consistent with data found in the literature. HPLC analyses was performed on a PerkinElmer Series 200 HPLC fitted with a Supercosil LC18 (25 cm x 4.6 mm x 5 μm) and a Series 200 EP Diode Array UV-Vis detector measuring at 254 and 238 nm, and the data analyzed in TotalChrom. Design of experiment optimization was conducted in JMP pro 16.

1.2. Synthesis of gold complexes 1a-2b

$^N,N'$-dimethylperhydrodiazepine-2,3-dione

Dimethyloxalate (1.18 g, 10.0 mmol, 1.00 equiv.) was dissolved in toluene (20 mL) with stirring. $^N,N'$-dimethylpropane-1,3-diamine (1.25 mL, 10.0 mL, 1.00 equiv.) was added to the stirring mixture and heated under reflux for 2 h. After cooling, the solvent was removed under reduced pressure to give a white powder crude product. Recrystallisation with hot iPrOH/CH2Cl2 afforded $^N,N'$-dimethylperhydrodiazepine-2,3-dione (1.28 g, 82%) as a white solid. IR (ATR): 2928, 2942, 1645 (C=O), 1608, 1498, 1459, 1442, 1426, 1404, 1263, 1193, 1094, 905, 864, 690 cm$^{-1}$; $^1$H NMR (400 MHz, Chloroform-$_d$) δ 3.44 (t, J = 6.4 Hz, 4H), 3.08 (s, 6H), 2.02 (p, J = 6.3 Hz, 2H) ppm.

Me$_2$dazdt ($^1$-,4-dimethyl-1,4-diazepane-2,3-dithione)

Me$_2$dazdt ($^N,N'$-dimethyl-perhydrodiazepine-2,3-dithione) was prepared using literature conditions and the characterization of the obtained product was consistent with literature data.$^{51}$
N,N’-dimethylperhydrodiazepine-2,3-dione (0.780 g, 5.00 mmol, 1.00 equiv.) and Lawesson’s reagent (3.04 g, 7.50 mmol, 1.50 equiv.) were dissolved in toluene (30 mL) and stirred under reflux for 2 h. After cooling, the solvent was removed in vacuo and the crude residue was purified by silica gel column chromatography (Rf = 0.26 [DCM]) yielding the title compound (706 mg, 75%). IR (ATR): 2922, 2855, 1491, 1435, 1379, 1260, 1185, 1111, 1081, 1025, 973 cm⁻¹. ¹H NMR (Chloroform-d): δ 3.77 (ddd, J = 14.8, 9.6, 7.9 Hz, 2H), 3.58–3.53 (m, 2H), 3.52 (s, 6H), 2.27–2.16 (m, 2H) ppm. HRMS (ESI) m/z [M+H]⁺ calcd. for C₇H₁₃N₂S₂: 189.0521, found: 189.0520.

[AuI₂(Me₂dazdt)]I₃ (1a)

Scheme S1. Gold leaching in solution using Me₂dazdt/I₂.

According to a modified literature procedure,⁵² Me₂dazdt (92 mg, 0.49 mmol), Au powder (96 mg, 0.49 mmol) and I₂ (372 mg, 1.46 mmol) were suspended in THF (70 mL) and stirred at room temperature for 1 h. The product was crystallized from the black solution by vapor phase diffusion with Et₂O. The desired product was isolated as reflective black crystals (437 mg, 88%). Characterization was consistent with literature data. IR (ATR): 3101, 2996, 2948, 2910, 2853, 2778, 2672, 1675, 1646, 1613, 1549, 1451, 1434, 1397, 1353, 1341, 1329, 1295, 1280, 1257, 1181, 1097, 1069, 1034, 1022, 953, 838, 822, 745, 690 cm⁻¹. ¹H NMR (400 MHz, Acetone-d₆): δ 3.79–3.69 (m, 2H), 3.68–3.57 (m, 2H), 3.47 (s, 6H), 2.38–2.29 (m, 2H) ppm.

[AuBr₂(Me₂dazdt)]IBr₂ (2a)

Scheme S2. Gold leaching in solution using Me₂dazdt/IBr.
According to a modified literature procedure, Me$_2$azdt (75 mg, 0.40 mmols), Au powder (80 mg, 0.40 mmols) and IBr (33 mg, 1.60 mmols) were suspended in THF (70 mL) and stirred at room temperature for 2 h. The product was crystallized from the black solution by vapor phase diffusion with Et$_2$O. The desired product was isolated as reflective black crystals (283 mg, 85%). IR (ATR): 2912, 1555, 1451, 1432, 1389, 1266, 1110, 1069, 954, 742, 605 cm$^{-1}$. $^1$H NMR (400 MHz, Acetone-$d_6$): $\delta$ 3.79 (s, 4H), 3.57 (s, 6H), 2.43 (s, 2H) ppm.

[AuI$_2$(Me$_2$azdt)]I$_3$ (1a) and [AuBr$_2$(Me$_2$azdt)]IBr$_2$ (2a) from scrap SIM cards
The complete procedure for metals recovery reported by Deplano et al., was followed in order to demonstrate that 1a and 2a can be obtained from real scrap subscriber identity module (SIM) cards:

Scrap SIM cards (~17 g) were initially ground to a coarse powder. The scrap material was then stirred in refluxing THF (50 mL). After 24 h, the white liquid (indicating the dispersion of the white plastic support) was decanted, and the resulting coarse powder isolated and washed with hot THF (2 x 10 mL). The coarse powder was suspended in a stirred solution of aqueous ammonia (32%, 10 mL) and ammonium sulphate (2.2 g). To the suspension was then added aqueous H$_2$O$_2$ (30 %, 3 mL) dropwise and the solution stirred at room temperature. After 4 h, the deep-blue solution (indicating the oxidation and dissolution of copper metal to form [Cu(NH$_3$)$_4$]SO$_4$) was decanted and the residue washed with distilled H$_2$O (2 x 10 mL). The resulting coarse powder was then suspended in a hot (80 °C) stirred solution of aqueous HCl (2.4 M, 25 mL). After 24 h, the green solution (indicating the oxidation and dissolution of Ni metal to form NiCl$_2$) was decanted and the coarse powder washed with distilled H$_2$O (2 x 10 mL). Finally, the coarse powder was suspended in a stirred solution of Me$_2$azdt (92 mg, 0.53 mmol) and I$_2$ (372 mg, 1.46 mmol) or IBr (404 mg, 1.95 mmol) added in THF (80 mL). After 24, the black liquid was filtered and the filtrate concentrated to ~30 mL. The product was crystallized from the black liquid by vapor diffusion with Et$_2$O (using the vial within a vial method). Both 1a (130 mg) and 2a (105 mg) were isolated as reflective black crystals. Characterization data for these compounds were consistent with those reported in the literature and also with 1a and 2a synthesized from gold metal powder in this study. No difference in catalytic activity was observed between the complexes isolated from scrap SIM cards and the complexes isolated from gold powder.
Scheme S3. Triiodide anion metathesis yielding \([\text{AuI}_2(\text{Me}_{2}\text{dazdt})]\)BF₄ (1b).

\([\text{AuI}_2(\text{Me}_{2}\text{dazdt})]\)I₃ (1a) (150 mg, 0.147 mmol) was dissolved in THF (120 mL). Trimethyloxonium tetrafluoroborate (22 mg, 0.15 mmol) was dissolved in MeNO₂ (4 mL) and the solution transferred to the THF solution in one portion. The reaction mixture was stirred for 1 h, concentrated in vacuo and the crude material recrystallized in MeCN by vapor phase diffusion with CHCl₃, yielding the title compound as reflective black crystals suitable for single crystal XRD (104 mg, 97%). IR (ATR): 1554, 1437, 1399, 1259, 1047, 1029, 948, 822, 746, 605, 519 cm⁻¹. ¹H NMR (400 MHz, Acetonitrile-d₃): δ 3.95 (t, \( J = 6.9 \) Hz, 4H), 3.72 (s, 6H), 2.65 (quin, \( J = 6.9 \) Hz, 2H) ppm. ¹³C\{¹H\} NMR data are not reported due to the poor solubility of 1b in common deuterated solvents including acetonitrile-d₃. Calculated for C₇H₁₂AuBF₄I₂N₂S₂ (Mw = 725.89): C 11.6, H 1.7, N 3.9 %. Found: C 11.7, H 1.6, N 3.5 %.

The purity of the BF₄⁻ salt was confirmed by ¹⁹F NMR analysis of an MeCN-d₃ solution of 1b (10 mg, 0.014 mmol) and fluorobenzene as an internal standard (5.2 µL, 0.055 mmol, 4 equivalents) (Figure S1).
Figure S1. $^{19}$F NMR spectrum of 4:1 equivalents of 1b and fluorobenzene respectively illustrating complete conversion of [AuI$_2$(Me$_2$dazdt)]I$_3$ to [AuI$_2$(Me$_2$dazdt)]BF$_4$.

$[\text{AuBr}_2(\text{Me}_2\text{dazdt})]\text{BF}_4$ (2b)

\[ \begin{array}{c}
\text{[Me}_3\text{O}]\text{BF}_4 \\
\text{THF:MeNO}_2 (v:v [30:1]) \\
\text{r.t., 1 h}
\end{array} \rightarrow \begin{array}{c}
\text{[AuBr}_2(\text{Me}_2\text{dazdt})]\text{BF}_4^+ \\
\text{2b}
\end{array} \]

Scheme S4. Iodine dibromide anion metathesis yielding $[\text{AuBr}_2(\text{Me}_2\text{dazdt})]\text{BF}_4$.

$[\text{AuBr}_2(\text{Me}_2\text{dazdt})]\text{IBr}_2$ (2a) (55 mg, 0.074 mmol) was dissolved in THF (60 mL). Trimethyloxonium tetrafluoroborate (11 mg, 0.074 mmol) was dissolved in MeNO$_2$ (2 mL) and the solution transferred to the THF solution in one portion. The reaction mixture was stirred for 1 h, concentrated in vacuo and the crude material recrystallized in MeCN by vapor phase diffusion with CHCl$_3$, yielding the title compound as reflective black crystals suitable for single crystal XRD (47 mg, 95%) IR (ATR): 1742, 1562, 1437, 1399, 1359, 1262, 1230, 1018, 951, 824, 745, 603, 518, 413 cm$^{-1}$. $^1$H NMR (400 MHz, Acetonitrile-$d_3$) $\delta$ 4.01 (t, $J = 6.9$ Hz, 4H), 3.76 (s, 6H), 2.67 (quin, $J = 6.9$ Hz, 2H) ppm. $^{19}$F NMR: $\delta$ 151.7 (0.20F), 151.7 (0.80F) ppm.
$^{13}$C\textsuperscript{1}H\textsuperscript{1} NMR data are not reported due to the poor solubility of 2b in common deuterated solvents including acetonitrile-$d_3$. Calculated for C\textsubscript{7}H\textsubscript{12}AuBF\textsubscript{4}I\textsubscript{2}N\textsubscript{2}S\textsubscript{2} (Mw = 631.89): C 13.3, H 1.9, N 4.4 %. Found: C 12.8, H 1.7, N 4.0 %.

The purity of the BF\textsubscript{4}\textsuperscript{−} salt was confirmed by $^{19}$F NMR analysis of an MeCN-$d_3$ solution of 2b (4.3 mg, 0.0068 mmol) and fluorobenzene as an internal standard (2.6 μL, 0.027 mmol, 4 equivalents) (Figure S2).

Figure S2. $^{19}$F NMR spectrum of 4:1 equivalents of 2b and fluorobenzene respectively illustrating complete conversion of [AuBr\textsubscript{2}(Me\textsubscript{2}dazdt)]IBr\textsubscript{2} to [AuBr\textsubscript{2}(Me\textsubscript{2}dazdt)]BF\textsubscript{4}.
Scheme S5. Unsuccessful iodine dibromide anion metathesis yielding \([\text{Au}_2\text{Br}_2(\text{Me}_2\text{dazdt})]\).

A suspension of zinc powder (1.3 mg, 0.020 mmol) in a solution of \([\text{AuBr}_2(\text{Me}_2\text{dazdt})]\)IBr\(_2\) (2) (17 mg, 0.020 mmol) in MeCN (20 mL) was stirred at room temperature. After 24 h, the reaction mixture was filtered under gravity and AgOTf (5 mg, 0.02 mmol) was added to the stirred filtrate, resulting in the immediate formation of an off-white precipitate. After 1 h, the suspension was filtered under gravity, the filtrate concentrated in vacuo and the resulting dark-red powder washed with MeOH (2 x 5 mL). The crude material was resuspended in MeCN (~3 mL) and recrystallized by vapor phase diffusion with CHCl\(_3\), yielding \([\text{Au}_2\text{Br}_2(\text{Me}_2\text{dazdt})]\) as reflective red crystals suitable for single crystal XRD (2.6 mg, 35%).

1.3. Synthesis of propargylic amides

\(N\)-(\text{Prop-2-yn-1-yl})benzamide

Scheme S6. Direct amidation of benzoic acid and propargylamine yielding \(N\)-(\text{Prop-2-yn-1-yl})benzamide.

According to the procedure reported by Braddock \textit{et al.},\textsuperscript{S5} a solution of benzoic acid (5.00 mmol, 611 mg), propargylamine (5.00 mmol, 275 mg) and tetramethylorthosilicate (TMOS, 2.22 mL, 15.0 mmol) in toluene (8 mL) was stirred at reflux. After 20 h, the reaction solution was cooled to room temperature, concentrated and the resulting residue dissolved in THF (25 mL). The THF solution was washed with aqueous K\(_2\)CO\(_3\) (75 mL, 0.3 M, 22.5 mmol). Solid NaCl was added continuously until two clear layers formed, the aqueous layer was extracted with THF (2 x 15 mL) and the combined organic layers washed with sat. NH\(_4\)Cl (25 mL). The organic layer was dried over Na\(_2\)SO\(_4\), filtered and concentrated to obtain the desired product (638 mg, 80%) as a white crystalline solid. IR (ATR): 3282, 1637 cm\(^{-1}\). \(^1\)H NMR (400 MHz, Chloroform-\(d\)): \(\delta\) 2.30 (t, \(J = 2.7\) Hz, 1H), 4.28 (dd, \(J = 5.3\) Hz, 2.6 Hz, 2H), 6.33 (s, 1H), 7.45
(m, 2H), 7.53 (tt, \(J = 7.3\) Hz, 6.1 Hz, 2.5 Hz, 1.2 Hz, 1H), 7.80 (m, 2H) ppm. \(^{13}\)C\({}^{1}\)H\(}\) (101 MHz, Chloroform-\(d\)): \(\delta 167.1, 133.7, 131.8, 128.6, 127.0, 79.4, 71.9, 29.8\) ppm.

**N-(3-Phenylprop-2-yn-1-yl)benzamide**

![Scheme S7](image)

**Scheme S7.** Sonogashira cross-coupling yielding N-(3-Phenylprop-2-yn-1-yl)benzamide.

According to the procedure reported by Engle *et al.*,\(^{86}\) a solution of Pd(PPh\(_3\))\(_4\) (2 mol %, 23 mg, 0.02 mmol), CuI (5 mol %, 9.5 mg, 0.05 mmol), N-(prop-2-yn-1-yl)benzamide (1.00 mmol, 159 mg) in anhydrous diethyl ether (3 mL) was stirred at room temperature under an inert atmosphere of N\(_2\). After 10 min, iodobenzene (2.00 mmol, 224 \(\mu\)L) was added, followed by the dropwise addition of diethylamine (3.00 mmol, 310 \(\mu\)L) and the reaction mixture stirred at 35 °C. After 3 h, the reaction mixture was poured into a separating funnel containing brine (20 mL) and extracted with Et\(_2\)O (3 x 25 mL). The combined organic layers were dried over Na\(_2\)SO\(_4\), filtered and concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography (R\(_f\) = 0.23 \([n\)-hexane/EtOAc (4:1)]) yielding the desired amide (177 mg, 75%) as a white solid. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta 7.86 – 7.79\) (m, 2H), 7.58 – 7.50 (m, 1H), 7.50 – 7.42 (m, 4H), 7.33 (m, 3H), 6.36 (s, 1H), 4.51 (d, \(J = 5.1\) Hz, 2H)\(v\) ppm.

**1.4. Catalytic testing of gold recovery products 1a-2b**

**1.4.1. Cyclization of N-propargylic amides**

**5-Methyl-2-phenyloxazole**

![Scheme S8](image)

**Scheme S8.** Cyclisation of N-Propargylbenzamide yielding 5-Methyl-2-phenyloxazole.

N-Propargylbenzamide (32 mg, 0.20 mmol), N-pyridine oxide (2.9 mg, 0.030 mmol) and the respective gold complex (0.01 mmol, 0.05 eq) were dissolved in acetonitrile (1.5 mL). The solution was stirred for the amount of time and at the temperature indicated in the main
manuscript (Table 1). After the indicated time, the reaction solution was concentrated and the yield quantified by $^1$H NMR analysis. Yields were determined by the relative integrals of the amide methylene protons (4.23- 4.25 ppm) and the product vinyl proton (6.85 ppm). A pure sample of the cyclized product was isolated following purification by silica gel column chromatography ($R_f = 0.25 \ [n\text{-hexane/EtOAc (7:1)}]$) yielding the desired oxazole ($^1$H NMR Yield: 96%. Isolated Yield: 28 mg, 89%) as a white solid. $^1$H NMR (400 MHz, Chloroform-d): $\delta$ 8.06 – 7.98 (m, 2H), 7.51 – 7.39 (m, 3H), 6.86 (d, $J = 1.4$ Hz, 1H), 2.42 (d, $J = 1.2$ Hz, 3H) ppm. $^{13}$C($^1$H) NMR (101 MHz, Chloroform-d): $\delta$ 160.7, 148.9, 129.9, 128.7, 127.8, 126.0, 124.2, 11.1 ppm.

(Z)-5-Benzylidene-2-phenyl-4,5-dihydrooxazole and (E)-5-(iodo(phenyl)methylene)-2-phenyl-4,5-dihydrooxazole

Scheme S9. Cyclisation of $N$-(3-phenylprop-2-yn-1-yl)benzamide.

A stirred solution of amide (56 mg, 0.24 mmol), $N$-pyridine oxide (3.4 mg, 0.036 mmol) and [Au] (5 mol%, 0.012 mmol) in MeCN (1.8 mL) was heated to 60 °C for 20 h. The reaction mixture was concentrated in vacuo and the resulting residue purified by silica gel column chromatography [$n$-hexane/EtOAc (7:1)]. Results for each catalyst are presented in the main text (Table 2).

$R_f = 0.18$. HRMS (ESI) $m/z$ [M+H]+ calcd. for C$_{16}$H$_{14}$NO: 236.1075, found: 236.1077. $^1$H NMR (400 MHz, Chloroform-d): $\delta$ 8.10-8.07 (m 1H), 7.66 – 7.61 (m, 2H), 7.58 – 7.51 (m, 3H), 7.43 – 7.39 (m, 3H), 7.28 – 7.21 (m, 1H), 5.68 (t, $J = 2.6$ Hz, 1H), 4.84 (d, $J = 2.6$ Hz, 2H) ppm. $^{13}$C($^1$H) NMR (101 MHz, Chloroform-d): $\delta$ 164.1, 151.8, 135.0, 132.2, 130.7, 128.8, 128.6, 128.3, 127.9, 126.3, 100.8, 59.5 ppm.
R₇ = 0.20. HRMS (ESI) m/z [M+H]+ calcd. for C₁₆H₁₃INO: 362.0042, found: 362.0047. ¹H NMR (400 MHz, Chloroform-d) δ 7.93 (d, J = 7.6 Hz, 2H), 7.68 (d, J = 7.7 Hz, 2H), 7.58 – 7.19 (m, 6H), 4.88 (s, 2H) ppm. ¹³C{¹H} NMR (101 MHz, Chloroform-d): δ 164.2, 152.8, 138.1, 132.3, 129.6, 128.8, 128.3, 128.1, 127.9, 126.7, 70.8, 65.2 ppm.

**Lithiation and hydrolysis of (E)-5-(iodo(phenyl)methylene)-2-phenyl-4,5-dihydrooxazole**

![Scheme S10](image)

**Scheme S10.** Confirmation of 5-exo cyclisation by lithiation and hydrolysis of (E)-5-(iodo(phenyl)methylene)-2-phenyl-4,5-dihydrooxazole.

An Et₂O (1 mL) solution of the vinyl iodide oxazole (30 mg, 0.083 mmol) was cooled to −78 °C. A solution of n-BuLi in Hexanes (2.5 M, 0.087 mmol, 34.9 μL) was added dropwise over 10 minutes. After 1 h, IPA (1 mL) was added dropwise, the mixture was warmed to room temperature and a saturated solution of ammonium chloride (1 mL) was added dropwise to the Et₂O solution. The organic layer was isolated, washed with brine and dried over MgSO₄. The residue was purified by silica-gel chromatography (R₇ = 0.18, [petroleum ether (40-60)/ethyl acetate (7:1)]), yielding the title compound as a white solid (7 mg, 35%). Spectroscopic data obtained were identical to those reported above.

### 1.4.2. Condensation of o-iodoaniline and acetylacetone

**Scheme S11.** Condensation of o-iodoaniline and acetylacetone.
2-Iodoaniline (44 mg, 0.2 mmol) and [Au] (0.005 mmol, 0.025 eq) were dissolved in ethanol (3 mL) and acetylacetone (20 μL, 0.2 mmol) was added to the solution. After 7 h, the reaction mixture was concentrated, the residue dissolved in CDCl₃ and submitted for ¹H NMR analysis. Yields were determined by the relative integrals of the o-iodoaniline starting material (dd 7.65 ppm) and the product (dd 7.91 ppm). Average yields with standard deviations are provided for each catalyst in the main manuscript (Table 3).

**Condensation of o-iodoaniline and acetylacetone – Catalyst recycling**

2-Iodoaniline (44 mg, 0.2 mmol) and [Au] (0.005 mmol, 0.025 eq) were dissolved in ethanol (3 mL) and acetylacetone (20 μL, 0.2 mmol) was added to the solution. After 7 h, the reaction mixture was concentrated and the crude oil triturated with n-hexane (2 x 5 mL). The combined n-hexane fractions were concentrated, yielding a crude mixture of o-iodoanisole and (Z)-4-((2-iodophenyl)amino)pent-3-en-2-one. The black residue containing the gold catalyst material was then reused 8 times with no observed loss in catalytic activity.

### 1.4.3. Addition of nucleophilic arenes to α,β-unsaturated carbonyl compounds

**4-(5-Methylfuran-2-yl)butan-2-one**

![Scheme S12. Addition of 2-methylfuran to methyl vinyl ketone.](image)

A solution of 2-methylfuran (0.089 mL, 82 mg, 1.0 mmol), methyl vinyl ketone (0.083 mL, 70 mg, 1.0 mmol) and [Au] catalyst (0.010 mmol, 1 mol%) in MeCN (4 mL) was stirred at room temperature. After 40 min, the reaction mixture was concentrated and the crude material triturated with n-hexane (2 x 5 mL). The combined n-hexane fractions were concentrated to yield the pure desired product as a colorless oil. ¹H NMR (400 MHz, Chloroform-d) δ 5.90 – 5.80 (m, 2H), 2.90 – 2.81 (m, 2H), 2.78-2.73 (m, 2H), 2.24 (s, 3H), 2.16 (s, 3H) ppm. The black residue containing the gold catalyst material was then reused 5 times with no observed loss in catalytic activity.
4-(5-Methylfuran-2-yl)butan-2-one

Scheme S13. Addition of 2-methylfuran to cyclohex-2-en-1-one.

A solution of 2-methylfuran (0.089 mL, 82 mg, 1.0 mmol), cyclohex-2-en-1-one (0.097 ml, 96 mg, 1.0 mmol) and [Au] catalyst (0.010 mmol, 1 mol%) in MeCN (4 mL) was stirred at room temperature. After 24 h, the reaction mixture was concentrated and the crude material triturated with n-hexane (2 x 5 mL). The combined n-hexane fractions were concentrated to yield the pure desired product as a colorless oil. ¹H NMR (400 MHz, Chloroform-d) δ 5.90 – 5.84 (m, 2H), 3.17–3.09 (m, 1H), 2.69–2.64 (m, 1H), 2.55-2.48 (m, 1H), 2.47 – 2.28 (m, 2H), 2.26 (s, 3H), 2.23 – 2.08 (m, 1H), 2.07-1.99 (m, 1H), 1.92 – 1.70 (m, 2H) ppm. The black residue containing the gold catalyst material was then reused 5 times with no observed loss in catalytic activity.

4,4’-(Azulene-1,3-diyl)bis(butan-2-one)

Scheme S14. Addition of azulene to methyl vinyl ketone.

A stirred solution of azulene (40 mg, 0.3 mmol), methyl vinyl ketone (0.052 ml, 44 mg, 0.62 mmol) and [Au] (0.0031 mmol, 1 mol%) in MeCN (1.7 ml) was heated at 60 ºC. After 3 h, the reaction mixture was concentrated, diluted with CDCl₃ and submitted for ¹H NMR analysis. In all three runs for each gold catalyst, only trace quantities of unreacted azulene were detectable by ¹H NMR analysis of the crude product. ¹H NMR (400 MHz, Chloroform-d) δ 8.20 (d, J = 9.3 Hz, 2H), 7.61 (s, 1H), 7.50 (t, J = 9.8, 1H), 7.01 (t, J = 9.8 Hz, 2H), 3.34-3.30 (m, 4H), 2.90-2.86 (m, 4H), 2.15 (s, 6H) ppm.
**4,4’-(4,6-Dimethoxy-1,3-phenylene)bis(butan-2-one)**

![Chemical structure of 4,4’-(4,6-Dimethoxy-1,3-phenylene)bis(butan-2-one)](image_url)

**Scheme S15.** Addition of 1,3-dimethoxybenzene to methyl vinyl ketone.

A stirred solution of 1,3-dimethoxybenzene (0.131 mL, 138 mg, 1.00 mmol), methyl vinyl ketone (0.332 mL, 278 mg, 4.00 mmol) and [Au] (0.010 mmol, 1 mol%) in MeCN (4 mL) was stirred at 60 °C. After 24 h, the reaction mixture was concentrated, the residue diluted in CDCl3 and the yield determined by 1H NMR analysis, through comparison of the integration of the dialkylated Ar-H singlet at 6.86 ppm, the monoalkylated doublet at 7.02-7.00 ppm and the starting material triplet at 7.21 ppm. Results are shown in Table S1 below:

**Table S1.** Results for the addition of 1,3-dimethoxybenzene to methyl vinyl ketone using 1a, 2a, 1b and 2b.

| Run | Monoalkylated yield (1H NMR) | Dialkylated yield (1H NMR) | Monoalkylated yield (1H NMR) | Dialkylated yield (1H NMR) |
|-----|------------------------------|-----------------------------|------------------------------|-----------------------------|
| 1   | 5                            | 12                          | 93                           | 79                          |
| 2   | 6                            | 14                          | 90                           | 76                          |
| 3   | 4                            | 12                          | 93                           | 78                          |

| Run | Monoalkylated yield (1H NMR) | Dialkylated yield (1H NMR) | Monoalkylated yield (1H NMR) | Dialkylated yield (1H NMR) |
|-----|------------------------------|-----------------------------|------------------------------|-----------------------------|
| 1   | 35                           | 27                          | 33                           | 20                          |
| 2   | 37                           | 22                          | 34                           | 18                          |
| 3   | 33                           | 28                          | 27                           | 27                          |
1.4.4. Oxidative coupling of aryl silanes and arenes

General cross-coupling procedure

Scheme S16. Gold(III) catalysed cross-coupling of arenes and aryl silanes.

Phenyltrimethylsilane (0.50 mmol, 86 µL), o-chloroanisole (0.50 mmol, 64 µL) and 1,4-dinitrobenzene (Internal standard, 0.125 mmol, 21.0 mg) were added to a solution of [AuI₂(Me₂dazdt)]I₃ (0.010 mmol, 10 mg) in CHCl₃ (5 mL) and MeOH (0.1 mL). Iodobenzene diacetate (209 mg, 0.65 mmol) and camphorsulfonic acid (174 mg, 0.75 mmol) were added and the reaction stirred. After 24 h, an aliquot (100 µL) of the reaction mixture was diluted in MeCN (10 mL) and the diluted sample submitted for HPLC analysis. The reaction variables and variable limits modelled in the DoE optimisation are summarized in Table S2.

Table S2. Design of experiments definitive screening design – Variables and variable limits.

| Factor                      | Minimum | Maximum |
|-----------------------------|---------|---------|
| Catalyst loading (mol%)     | 1       | 3       |
| Silver loading (mol%)       | 0       | 6       |
| Temperature (°C)            | 30°     | 60°     |
| Concentration (M)           | 0.1     | 0.25    |
| Arene equivalence           | 1       | 1.5     |

* A lower temperature limit of 30 °C was set to avoid overnight changes in ambient temperature

Models for both cross-coupling and homo-coupling yields were produced using a definitive screening design (Table S3).

DoE procedure.

Stock solutions containing phenyltrimethylsilane and 1,4-dinitrobenzene (internal standard), and o-chloroanisole were used throughout the design of experiments screen. The stock solutions were combined and diluted appropriately in ReactArray reaction vials containing an appropriate quantity of [AuI₂(Me₂dazdt)]I₃ to produce the conditions indicated for each entry in the DoE data table (Table S3). Appropriate quantities of iodobenzene diacetate and camphorsulfonic acid were then added to initiate the reaction, and the reaction stirred at the indicated temperature. DoE model validation and prediction profiles are provided in Figures
S3 and S4 for the cross-coupling product, and Figures S5 and S6 for the homo-coupling product.

Table S3. DoE design and results table.

| Catalyst Loading (mol%) | Concentration (M) | Silver Loading (mol%) | Temperature (°C) | Arene equivalence | Cross-coupling yield (HPLC/%) | Homo-coupling yield (HPLC/%) |
|-------------------------|------------------|----------------------|------------------|------------------|--------------------------------|-------------------------------|
| 2                       | 0.1              | 0                    | 30               | 1                | 10                             | 17                            |
| 2                       | 0.25             | 6                    | 60               | 1.5              | 64                             | 9                             |
| 2                       | 0.175            | 3                    | 45               | 1.25             | 54                             | 16                            |
| 1                       | 0.1              | 6                    | 30               | 1.5              | 60                             | 17                            |
| 3                       | 0.1              | 6                    | 60               | 1.25             | 45                             | 18                            |
| 3                       | 0.25             | 0                    | 60               | 1.5              | 57                             | 12                            |
| 1                       | 0.25             | 6                    | 45               | 1                | 36                             | 22                            |
| 1                       | 0.1              | 0                    | 60               | 1                | 49                             | 16                            |
| 1                       | 0.1              | 0                    | 60               | 1.5              | 66                             | 13                            |
| 1                       | 0.175            | 6                    | 60               | 1.5              | 69                             | 14                            |
| 3                       | 0.1              | 0                    | 45               | 1.5              | 69                             | 12                            |
| 3                       | 0.1              | 3                    | 30               | 1.5              | 39                             | 13                            |
| 1                       | 0.25             | 3                    | 60               | 1                | 44                             | 18                            |
| 1                       | 0.1              | 6                    | 30               | 1                | 29                             | 13                            |
| 3                       | 0.25             | 0                    | 60               | 1                | 47                             | 16                            |
| 1                       | 0.25             | 0                    | 30               | 1.25             | 49                             | 20                            |
| 3                       | 0.175            | 0                    | 30               | 1                | 37                             | 12                            |
| 3                       | 0.1              | 6                    | 60               | 1                | 41                             | 20                            |
| 3                       | 0.25             | 6                    | 30               | 1.5              | 80                             | 7                             |
| 3                       | 0.25             | 6                    | 30               | 1                | 49                             | 11                            |
| 1                       | 0.25             | 0                    | 30               | 1.5              | 74                             | 9                             |

Figure S3. Cross-coupling definitive screening design showing actual vs predicted cross-coupling yield.
Figure S4. Cross-coupling definitive screening design showing prediction profiles illustrating optimum reaction conditions.

Figure S5. Silane homo-coupling definitive screening design showing actual vs predicted cross-coupling yield.

Figure S6. Silane homo-coupling definitive screening design showing prediction profiles illustrating optimum reaction conditions.
Optimized cross-coupling procedure and scope

Phenyll trimethylsilane (0.50 mmol, 0.075 g, 86 µL) and arene (0.75 mmol) were added to a vial containing [Au] (1.0 mol%, 0.005 mmol) in CHCl₃ (2.2 mL, 0.23 M) and MeOH (100 µL). Iodobenzene diacetate (209 mg, 0.649 mmol) and camphorsulfonic acid (174 mg, 0.749 mmol) were added, and the reaction was stirred at room temperature. After 24 h, the reaction mixture was concentrated in vacuo and the crude material purified by column chromatography.

3-Chloro-4-methoxy-1,1'-biphenyl

White solid (1a: 77 mg, 70%; 2a: 82 mg, 75%); Rₓ = 0.26 [n-hexane/toluene (9:1)]; ¹H NMR (400 MHz, Chloroform-d): δ 7.63 (d, J = 2.3 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.51 – 7.39 (m, 3H), 7.39 – 7.30 (m, 1H), 7.01 (d, J = 8.5 Hz, 1H), 3.96 (s, 3H) ppm. ¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 154.5, 139.7, 134.8, 129.0, 127.4, 126.84, 126.4, 122.9, 112.4, 56.4 ppm.

3-Bromo-4-methoxy-1,1'-biphenyl

White solid (1a: 87 mg, 74%; 2a: 94 mg, 80%); Rₓ = 0.26 [n-hexane/toluene (9:1)]; ¹H NMR (400 MHz, Chloroform-d): δ 7.83 (d, J = 2.3 Hz, 1H), 7.59 – 7.49 (m, 3H), 7.49 – 7.40 (m, 2H), 7.40 – 7.31 (m, 1H), 6.98 (d, J = 8.5 Hz, 1H), 3.96 (s, 3H) ppm. ¹³C{¹H} NMR (101 MHz, Chloroform-d) δ 155.3, 139.5, 135.2, 132.0, 128.9, 127.3, 127.1, 126.8, 112.2, 112.1, 56.4 ppm.

3,4-Dimethyl-1,1'-biphenyl

White solid (1a: 56 mg, 61%; 2a: 64 mg, 70%); Rₓ = 0.31 [n-hexane/toluene (100:1)]; ¹H NMR (400 MHz, Chloroform-d) δ 7.64 (m, 2H), 7.52 – 7.33 (m, 5H), 7.27 (d, J = 7.8 Hz, 1H), 2.39
(s, 3H), 237 (s, 3H) ppm. $^{13}$C{$^1$H} NMR (101 MHz, Chloroform-$d$) δ 141.4, 139.0, 137.0, 135.8, 130.2, 128.8, 128.6, 128.6, 127.1, 127.0, 124.6, 20.1, 19.6 ppm.

4-Methyl-1,1'-biphenyl

![4-Methyl-1,1'-biphenyl](image)

White solid (1a: 50 mg, 59%; 2a: 55 mg, 65%); R$_f$ = 0.31 [$n$-hexane/toluene (100:1)]; $^1$H NMR (400 MHz, Chloroform-$d$): δ 7.65 – 7.58 (m, 2H), 7.57 – 7.50 (m, 2H), 7.46 (dd, $J$ = 8.4, 6.9 Hz, 2H), 7.40 – 7.32 (m, 1H), 7.29 (d, $J$ = 7.9 Hz, 2H), 2.43 (s, 3H) ppm. $^{13}$C{$^1$H} NMR (101 MHz, Chloroform-$d$): δ 141.3, 138.5, 137.2, 129.6, 128.9, 127.1, 127.1, 21.2 ppm.

1-Methyl-4-phenylnaphthalene

![1-Methyl-4-phenylnaphthalene](image)

Colorless oil (1a: 57 mg, 52%; 2a: 60 mg, 55%); R$_f$ = 0.61 ([petroleum ether]); $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.26 – 8.18 (m, 1H), 8.12 (t, $J$ = 6.6 Hz, 1H), 7.74 – 7.44 (m, 9H), 2.93 – 2.87 (m, 3H) ppm. $^{13}$C{$^1$H} NMR (101 MHz, Chloroform-$d$): δ 141.2, 138.8, 133.9, 132.9, 131.8, 130.3, 128.3, 127.2, 126.8, 126.7, 126.3, 125.8, 124.5, 19.7 ppm.

2-Bromo-5-phenylthiophene

![2-Bromo-5-phenylthiophene](image)

White solid (1a: 102 mg, 85%; 2a: 108 mg, 90%); R$_f$ = 0.27 [petroleum ether]); $^1$H NMR (400 MHz, Chloroform-$d$): δ 7.58 – 7.50 (m, 2H), 7.45 – 7.36 (m, 2H), 7.36 – 7.28 (m, 1H), 7.11 – 7.03 (m, 2H) ppm. $^{13}$C{$^1$H} NMR (101 MHz, Chloroform-$d$): δ 146.0, 133.8, 131.0, 129.1, 128.0, 125.7, 123.4, 111.5 ppm.
1.5. X-Ray crystallographic information

Figure S7. The X-ray crystal structure of 1b (thermal ellipsoids drawn at 50% probability).

Crystal data for 1b: [C7H12AuI2N2S2](BF4), \( M = 725.88 \), monoclinic, \( P2_1/n \) (no. 14), \( a = 14.2058(2), b = 8.14668(11), c = 15.1256(2) \, \text{Å}, \beta = 105.7976(17)^\circ, V = 1684.37(5) \, \text{Å}^3, Z = 4, D_c = 2.862 \, \text{g cm}^{-3}, \mu(\text{Mo-K\alpha}) = 12.673 \, \text{mm}^{-1}, T = 173 \, \text{K}, \) black blocks, Agilent Xcalibur 3 E diffractometer; 3979 independent measured reflections (\( R_{int} = 0.0416 \)), \( F^2 \) refinement, \(^{S7,S8} R_1(\text{obs}) = 0.0204, wR_2(\text{all}) = 0.0396, 3625 \) independent observed absorption-corrected reflections [\( |F_o| > 4\sigma(|F_o|) \), completeness to \( \theta_{\text{full}}(25.2^\circ) = 99.9\% \)], 196 parameters. CCDC 2156494.

The B10-based tetrafluoroborate anion in the structure of 1b was found to be disordered. Two orientations were identified of \( ca. 87 \) and 13\% occupancy, their geometries were optimized, the thermal parameters of adjacent atoms were restrained to be similar, and only the atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).
Table S4. Table of 1b bond lengths.

| Number | Atom1 | Atom2 | Cyclicity | Length   |
|--------|-------|-------|-----------|----------|
| 1      | Au1   | I1    | acyclic   | 2.6064(3) |
| 2      | Au1   | I2    | acyclic   | 2.6093(4) |
| 3      | Au1   | S1    | cyclic    | 2.3243(9) |
| 4      | Au1   | S2    | cyclic    | 2.3250(9) |
| 5      | S1    | C1    | cyclic    | 1.717(3)  |
| 6      | C1    | C2    | cyclic    | 1.491(5)  |
| 7      | C1    | N7    | cyclic    | 1.297(5)  |
| 8      | C2    | S2    | cyclic    | 1.714(3)  |
| 9      | C2    | N3    | cyclic    | 1.306(4)  |
| 10     | N3    | C4    | cyclic    | 1.483(5)  |
| 11     | N3    | C8    | acyclic   | 1.473(4)  |
| 12     | C4    | H4A   | acyclic   | 0.99      |
| 13     | C4    | H4B   | acyclic   | 0.99      |
| 14     | C4    | C5    | cyclic    | 1.519(7)  |
| 15     | C5    | H5A   | acyclic   | 0.99      |
| 16     | C5    | H5B   | acyclic   | 0.99      |
| 17     | C5    | C6    | cyclic    | 1.519(5)  |
| 18     | C6    | H6A   | acyclic   | 0.989     |
| 19     | C6    | H6B   | acyclic   | 0.99      |
| 20     | C6    | N7    | cyclic    | 1.489(5)  |
| 21     | N7    | C9    | acyclic   | 1.475(4)  |
| 22     | C8    | H8A   | acyclic   | 0.981     |
| 23     | C8    | H8B   | acyclic   | 0.98      |
| 24     | C8    | H8C   | acyclic   | 0.98      |
| 25     | C9    | H9A   | acyclic   | 0.98      |
| 26     | C9    | H9B   | acyclic   | 0.98      |
| 27     | C9    | H9C   | acyclic   | 0.98      |
| 28     | B10   | F11   | acyclic   | 1.379(8)  |
| 29     | B10   | F12   | acyclic   | 1.396(6)  |
| 30     | B10   | F13   | acyclic   | 1.357(8)  |
| 31     | B10   | F14   | acyclic   | 1.370(7)  |
| Number | Atom1 | Atom2 | Atom3 | Angle  | Number | Atom1 | Atom2 | Atom3 | Angle  |
|--------|-------|-------|-------|--------|--------|-------|-------|-------|--------|
| 1      | I1    | Au1   | I2    | 93.60(1) | 29     | H5B   | C5    | C6    | 109.3  |
| 2      | I1    | Au1   | S1    | 177.77(3) | 30     | C5    | C6    | H6A   | 109.4  |
| 3      | I1    | Au1   | S2    | 87.03(3)  | 31     | C5    | C6    | H6B   | 109.4  |
| 4      | I2    | Au1   | S1    | 88.09(3)  | 32     | C5    | C6    | N7    | 111.2(3) |
| 5      | I2    | Au1   | S2    | 179.33(3) | 33     | H6A   | C6    | H6B   | 108.1  |
| 6      | S1    | Au1   | S2    | 91.28(3)  | 34     | H6A   | C6    | N7    | 109.4  |
| 7      | Au1   | S1    | C1    | 97.7(1)   | 35     | H6B   | C6    | N7    | 109.3  |
| 8      | S1    | C1    | C2    | 117.7(3)  | 36     | C1    | N7    | C6    | 120.6(3) |
| 9      | S1    | C1    | N7    | 122.6(3)  | 37     | C1    | N7    | C9    | 120.6(3) |
| 10     | C2    | C1    | N7    | 119.7(3)  | 38     | C6    | N7    | C9    | 118.7(3) |
| 11     | C1    | C2    | S2    | 117.9(3)  | 39     | N3    | C8    | H8A   | 109.4  |
| 12     | C1    | C2    | N3    | 119.6(3)  | 40     | N3    | C8    | H8B   | 109.5  |
| 13     | S2    | C2    | N3    | 122.5(3)  | 41     | N3    | C8    | H8C   | 109.5  |
| 14     | Au1   | S2    | C2    | 99.9(1)   | 42     | H8A   | C8    | H8B   | 109.4  |
| 15     | C2    | N3    | C4    | 121.0(3)  | 43     | H8A   | C8    | H8C   | 109.4  |
| 16     | C2    | N3    | C8    | 121.6(3)  | 44     | H8B   | C8    | H8C   | 109.5  |
| 17     | C4    | N3    | C8    | 117.4(3)  | 45     | N7    | C9    | H9A   | 109.5  |
| 18     | N3    | C4    | H4A   | 109.2     | 46     | N7    | C9    | H9B   | 109.5  |
| 19     | N3    | C4    | H4B   | 109.2     | 47     | N7    | C9    | H9C   | 109.5  |
| 20     | N3    | C4    | C5    | 111.9(3)  | 48     | H9A   | C9    | H9B   | 109.5  |
| 21     | H4A   | C4    | H4B   | 107.9     | 49     | H9A   | C9    | H9C   | 109.5  |
| 22     | H4A   | C4    | C5    | 109.3     | 50     | H9B   | C9    | H9C   | 109.5  |
| 23     | H4B   | C4    | C5    | 109.3     | 51     | F11   | B10   | F12   | 108.5(5) |
| 24     | C4    | C5    | H5A   | 109.3     | 52     | F11   | B10   | F13   | 112.3(5) |
| 25     | C4    | C5    | H5B   | 109.3     | 53     | F11   | B10   | F14   | 109.6(5) |
| 26     | C4    | C5    | C6    | 111.6(3)  | 54     | F12   | B10   | F13   | 107.7(5) |
| 27     | H5A   | C5    | H5B   | 107.9     | 55     | F12   | B10   | F14   | 106.2(5) |
| 28     | H5A   | C5    | C6    | 109.3     | 56     | F13   | B10   | F14   | 112.3(5) |
**Figure S8.** The X-ray crystal structure of 2b (thermal ellipsoids drawn at 50% probability).

*Crystal data for 2b:* \([\text{C}_7\text{H}_{12}\text{AuBr}_2\text{N}_2\text{S}_2](\text{BF}_4)\), \(M = 631.90\), triclinic, \(P-1\) (no. 2), \(a = 7.5558(3)\,\text{Å}\), \(b = 8.0088(3)\,\text{Å}\), \(c = 13.3746(4)\,\text{Å}\), \(\alpha = 99.789(3)^\circ\), \(\beta = 94.425(3)^\circ\), \(\gamma = 109.021(3)^\circ\), \(V = 746.34(5)\,\text{Å}^3\), \(Z = 2\), \(D_c = 2.812\,\text{g cm}^{-3}\), \(\mu(\text{Mo-K}\alpha) = 15.517\,\text{mm}^{-1}\), \(T = 173\,\text{K}\), dark red blocks, Agilent Xcalibur 3 E diffractometer; 3255 independent measured reflections \(R_{\text{int}} = 0.0301\), \(F^2\) refinement, \(^{57,58}R_{\text{I}}(\text{obs}) = 0.0230\), \(wR_{\text{2(all)}} = 0.0522\), 3016 independent observed absorption-corrected reflections \(|F_o| > 4\sigma(|F_o|)\), completeness to \(\theta_{\text{full}}(25.2^\circ) = 100\%\), 175 parameters. CCDC 2156495.
Table S6. Table of 2b bond lengths.

| Number | Atom1 | Atom2 | Cyclicity | Length    |
|--------|-------|-------|-----------|-----------|
| 1      | Au1   | Br1   | acyclic   | 2.4605(5) |
| 2      | Au1   | Br2   | acyclic   | 2.4282(6) |
| 3      | Au1   | S1    | cyclic    | 2.302(1)  |
| 4      | Au1   | S2    | cyclic    | 2.293(1)  |
| 5      | S1    | C1    | cyclic    | 1.707(5)  |
| 6      | C1    | C2    | cyclic    | 1.499(8)  |
| 7      | C1    | N7    | cyclic    | 1.294(6)  |
| 8      | C2    | S2    | cyclic    | 1.715(4)  |
| 9      | C2    | N3    | cyclic    | 1.303(6)  |
| 10     | N3    | C4    | cyclic    | 1.487(6)  |
| 11     | N3    | C8    | acyclic   | 1.467(7)  |
| 12     | C4    | H4A   | acyclic   | 0.99      |
| 13     | C4    | H4B   | acyclic   | 0.99      |
| 14     | C4    | C5    | cyclic    | 1.524(8)  |
| 15     | C5    | H5A   | acyclic   | 0.99      |
| 16     | C5    | H5B   | acyclic   | 0.99      |
| 17     | C5    | C6    | cyclic    | 1.510(7)  |
| 18     | C6    | H6A   | acyclic   | 0.99      |
| 19     | C6    | H6B   | acyclic   | 0.99      |
| 20     | C6    | N7    | cyclic    | 1.487(7)  |
| 21     | N7    | C9    | acyclic   | 1.470(7)  |
| 22     | C8    | H8A   | acyclic   | 0.98      |
| 23     | C8    | H8B   | acyclic   | 0.98      |
| 24     | C8    | H8C   | acyclic   | 0.98      |
| 25     | C9    | H9A   | acyclic   | 0.98      |
| 26     | C9    | H9B   | acyclic   | 0.98      |
| 27     | C9    | H9C   | acyclic   | 0.98      |
| 28     | B10   | F11   | acyclic   | 1.384(8)  |
| 29     | B10   | F12   | acyclic   | 1.377(7)  |
| 30     | B10   | F13   | acyclic   | 1.379(6)  |
| 31     | B10   | F14   | acyclic   | 1.393(8)  |
Table S7. Table of 2b bond angles.

| Number | Atom1 | Atom2 | Atom3 | Angle   | Number | Atom1 | Atom2 | Atom3 | Angle   |
|--------|-------|-------|-------|---------|--------|-------|-------|-------|---------|
| 1      | Br1   | Au1   | Br2   | 94.33(2)| 29     | H5B   | C5    | C6    | 109.6   |
| 2      | Br1   | Au1   | S1    | 179.30(4)| 30     | C5    | C6    | H6A   | 109.1   |
| 3      | Br1   | Au1   | S2    | 87.44(4)| 31     | C5    | C6    | H6B   | 109.1   |
| 4      | Br2   | Au1   | S1    | 86.37(4)| 32     | C5    | C6    | N7    | 112.6(4)|
| 5      | Br2   | Au1   | S2    | 178.22(4)| 33     | H6A   | C6    | H6B   | 107.8   |
| 6      | S1    | Au1   | S2    | 91.86(5)| 34     | H6A   | C6    | N7    | 109.1   |
| 7      | Au1   | S1    | C1    | 99.4(2) | 35     | C6    | N7    | C6    | 120.6(4)|
| 8      | S1    | C1    | C2    | 118.2(4)| 36     | C1    | N7    | C6    | 109.1   |
| 9      | S1    | C1    | N7    | 122.3(4)| 37     | C1    | N7    | C9    | 120.6(4)|
| 10     | C2    | C1    | N7    | 119.5(5)| 38     | C6    | N7    | C9    | 118.5(4)|
| 11     | C1    | C2    | S2    | 117.5(4)| 39     | N3    | C8    | H8A   | 109.5   |
| 12     | C1    | C2    | N3    | 119.7(4)| 40     | N3    | C8    | H8B   | 109.4   |
| 13     | S2    | C2    | N3    | 122.8(4)| 41     | N3    | C8    | H8C   | 109.4   |
| 14     | Au1   | S2    | C2    | 100.3(2)| 42     | H8A   | C8    | H8B   | 109.5   |
| 15     | C2    | N3    | C4    | 121.5(4)| 43     | H8A   | C8    | H8C   | 109.5   |
| 16     | C2    | N3    | C8    | 121.8(5)| 44     | H8B   | C8    | H8C   | 109.5   |
| 17     | C4    | N3    | C8    | 116.8(4)| 45     | N7    | C9    | H9A   | 109.4   |
| 18     | N3    | C4    | H4A   | 109.4   | 46     | N7    | C9    | H9B   | 109.4   |
| 19     | N3    | C4    | H4B   | 109.4   | 47     | N7    | C9    | H9C   | 109.5   |
| 20     | N3    | C4    | C5    | 111.1(4)| 48     | H9A   | C9    | H9B   | 109.5   |
| 21     | H4A   | C4    | H4B   | 108     | 49     | H9A   | C9    | H9C   | 109.5   |
| 22     | H4A   | C4    | C5    | 109.4   | 50     | H9B   | C9    | H9C   | 109.5   |
| 23     | H4B   | C4    | C5    | 109.5   | 51     | F11   | B10   | F12   | 110.1(5)|
| 24     | C4    | C5    | H5A   | 109.6   | 52     | F11   | B10   | F13   | 108.7(5)|
| 25     | C4    | C5    | H5B   | 109.6   | 53     | F11   | B10   | F14   | 109.2(5)|
| 26     | C4    | C5    | C6    | 110.3(4)| 54     | F12   | B10   | F13   | 111.3(5)|
| 27     | H5A   | C5    | H5B   | 108.1   | 55     | F12   | B10   | F14   | 109.2(5)|
| 28     | H5A   | C5    | C6    | 109.6   | 56     | F13   | B10   | F14   | 108.3(5)|
Figure S9. The X-ray crystal structure of [Me₂dazdt(AuBr)₂] (thermal ellipsoids drawn at 50% probability).

Crystal data for [Me₂dazdt(AuBr)₂]: [C₇H₁₂Au₂Br₂N₂S₂], M = 742.06, monoclinic, P2₁/n (no. 14), a = 9.8393(3), b = 10.7280(3), c = 13.4277(3) Å, β = 104.018(3)°, V = 1375.16(6) Å³, Z = 4, Dₑ = 3.584 g cm⁻³, μ(Mo-Kα) = 27.398 mm⁻¹, T = 173 K, red blocks, Agilent Xcalibur 3 E diffractometer; 3214 independent measured reflections (R_{int} = 0.0469), F² refinement, R₁(obs) = 0.0212, wR₂(all) = 0.0434, 2841 independent observed absorption-corrected reflections ([F_o] > 4σ(|F_o|), completeness to θ_{full}(25.2°) = 99.9%), 139 parameters. CCDC 2156496.

Short intermolecular Au…Au contacts (3.103 Å) were observed for [Me₂dazdt(AuBr)₂] with distances comparable to the intramolecular contacts (3.121 Å), resulting in the formation of a chain of molecules along the direction of the b axis (Figure S10).
Table S8. Table of [Me2dazdt(AuBr)2] bond lengths.

| Number | Atom1 | Atom2 | Polymeric | Cyclicity | Length  |
|--------|-------|-------|-----------|-----------|---------|
| 1      | Au1   | Au2   | no        | cyclic    | 3.1209(3) |
| 2      | Au1   | Br1   | no        | acyclic   | 2.3856(6) |
| 3      | Au1   | S1    | no        | cyclic    | 2.273(1)  |
| 4      | Au1   | Au2   | yes       | acyclic   | 3.1032(3) |
| 5      | Au2   | Br2   | no        | acyclic   | 2.3920(6) |
| 6      | Au2   | S2    | no        | cyclic    | 2.275(1)  |
| 7      | Au2   | Au1   | yes       | acyclic   | 3.1032(3) |
| 8      | S1    | C1    | no        | cyclic    | 1.686(5)  |
| 9      | C1    | C2    | no        | cyclic    | 1.500(6)  |
| 10     | C1    | N7    | no        | cyclic    | 1.310(5)  |
| 11     | C2    | S2    | no        | cyclic    | 1.689(5)  |
| 12     | C2    | N3    | no        | cyclic    | 1.315(7)  |
| 13     | N3    | C4    | no        | cyclic    | 1.470(6)  |
| 14     | N3    | C8    | no        | acyclic   | 1.461(7)  |
| 15     | C4    | H4A   | no        | acyclic   | 0.99     |
| 16     | C4    | H4B   | no        | acyclic   | 0.99     |
| 17     | C4    | C5    | no        | cyclic    | 1.515(7)  |
| 18     | C5    | H5A   | no        | acyclic   | 0.99     |
| 19     | C5    | H5B   | no        | acyclic   | 0.99     |
| 20     | C5    | C6    | no        | cyclic    | 1.516(9)  |
| 21     | C6    | H6A   | no        | acyclic   | 0.99     |
| 22     | C6    | H6B   | no        | acyclic   | 0.99     |
| 23     | C6    | N7    | no        | cyclic    | 1.482(7)  |
| 24     | N7    | C9    | no        | acyclic   | 1.465(6)  |
| 25     | C8    | H8A   | no        | acyclic   | 0.98     |
| 26     | C8    | H8B   | no        | acyclic   | 0.979    |
| 27     | C8    | H8C   | no        | acyclic   | 0.98     |
| 28     | C9    | H9A   | no        | acyclic   | 0.98     |
| 29     | C9    | H9B   | no        | acyclic   | 0.98     |
| 30     | C9    | H9C   | no        | acyclic   | 0.98     |
Table S9. Table of [Me\textsubscript{2}dazdt(AuBr)\textsubscript{2}] bond angles.

| Number | Atom1 | Atom2 | Atom3 | Angle  | Number | Atom1 | Atom2 | Atom3 | Angle  |
|--------|-------|-------|-------|--------|--------|-------|-------|-------|--------|
| 1      | Au2   | Au1   | Br1   | 103.93(2) | 29     | H4B   | C4    | C5    | 109.5  |
| 2      | Au2   | Au1   | S1    | 77.90(3)  | 30     | C4    | C5    | H5A   | 109.5  |
| 3      | Au2   | Au1   | Au2   | 131.37(1) | 31     | C4    | C5    | H5B   | 109.5  |
| 4      | Br1   | Au1   | S1    | 176.35(4) | 32     | C4    | C5    | C6    | 110.8(4) |
| 5      | Br1   | Au1   | Au2   | 97.83(2)  | 33     | H5A   | C5    | H5B   | 108.1  |
| 6      | S1    | Au1   | Au2   | 83.08(3)  | 34     | H5A   | C5    | C6    | 109.5  |
| 7      | Au1   | Au2   | Br2   | 106.41(2) | 35     | H5B   | C5    | C6    | 109.5  |
| 8      | Au1   | Au2   | S2    | 74.42(3)  | 36     | C5    | C6    | H6A   | 109.6  |
| 9      | Au1   | Au2   | Au1   | 145.20(1) | 37     | C5    | C6    | H6B   | 109.6  |
| 10     | Br2   | Au2   | S2    | 176.34(4) | 38     | C5    | C6    | N7    | 110.2(4) |
| 11     | Br2   | Au2   | Au1   | 96.68(2)  | 39     | H6A   | C6    | H6B   | 108.1  |
| 12     | S2    | Au2   | Au1   | 84.20(3)  | 40     | H6A   | C6    | N7    | 109.7  |
| 13     | Au1   | S1    | C1    | 107.6(2)  | 41     | H6B   | C6    | N7    | 109.6  |
| 14     | S1    | C1    | C2    | 121.6(3)  | 42     | C1    | N7    | C6    | 119.9(4) |
| 15     | S1    | C1    | N7    | 122.1(4)  | 43     | C1    | N7    | C9    | 122.3(4) |
| 16     | C2    | C1    | N7    | 116.0(4)  | 44     | C6    | N7    | C9    | 117.2(4) |
| 17     | C1    | C2    | S2    | 122.7(4)  | 45     | N3    | C8    | H8A   | 109.4  |
| 18     | C1    | C2    | N3    | 115.6(4)  | 46     | N3    | C8    | H8B   | 109.5  |
| 19     | S2    | C2    | N3    | 121.7(4)  | 47     | N3    | C8    | H8C   | 109.4  |
| 20     | Au2   | S2    | C2    | 106.7(2)  | 48     | H8A   | C8    | H8B   | 109.5  |
| 21     | C2    | N3    | C4    | 120.2(4)  | 49     | H8A   | C8    | H8C   | 109.5  |
| 22     | C2    | N3    | C8    | 120.1(4)  | 50     | H8B   | C8    | H8C   | 109.5  |
| 23     | C4    | N3    | C8    | 118.7(4)  | 51     | N7    | C9    | H9A   | 109.4  |
| 24     | N3    | C4    | H4A   | 109.5     | 52     | N7    | C9    | H9B   | 109.5  |
| 25     | N3    | C4    | H4B   | 109.5     | 53     | N7    | C9    | H9C   | 109.4  |
| 26     | N3    | C4    | C5    | 110.7(4)  | 54     | H9A   | C9    | H9B   | 109.5  |
| 27     | H4A   | C4    | H4B   | 108.1     | 55     | H9A   | C9    | H9C   | 109.5  |
| 28     | H4A   | C4    | C5    | 109.5     | 56     | H9B   | C9    | H9C   | 109.5  |
1.6. Preliminary indicative cost analysis

**Preliminary indicative cost analysis**

The gold recycling process employed in this work\(^4\) can be applied to different kinds of WEEE with costs that will vary depending on the configuration of the industrial plant. However, this report demonstrates the use of the gold complexes produced from this process in catalysis, illustrating the potential of joining up the recovery and catalysis processes using the example of SIM cards as the WEEE feedstock. In order to provide a preliminary indicative cost comparison with the cheapest commercial catalyst used for the same catalytic transformations, a calculation has been performed of the cost to prepare the catalyst \([\text{AuI}_2(\text{Me}_2\text{dazdt})]\)\(_3\) (1a) from used SIM cards based on small-scale reagent pricing by the major suppliers. A more meaningful cost analysis will need and be performed referring to a higher technology readiness level (TRL) plant than the one here.

The preliminary indicative cost below reveals that, depending on whether the cost of SIM cards is included, the same amount of 1a is 29-55\% less than that of commercial \(\text{AuCl}_3\) (the cheapest of the literature catalysts used in the research). It is often estimated that the scale up of a process reduces costs ten-fold so the costs above for the preparation of 1a would be reduced dramatically on scale up. In comparison, the cost of commercial \(\text{AuCl}_3\) is already minimized through the savings of large-scale production. This estimate shows that, even unoptimized, small-scale production of catalyst 1a leads to a significantly lower cost than commercial catalysts derived from environmentally-damaging mining.

![Scheme S17. Synthesis of Me₂dazdt.\(^{S2,S4}\)](attachment)
Table S10. Amounts of reagents and solvents with associated costs for the synthesis of Me$_2$dazdt and the iodine used to make Me$_2$dazdt·2I$_2$ in situ (prices from Merck).

| Chemicals                          | Amount  | Chemicals cost (per unit amount) | Overall cost of Chemicals |
|-----------------------------------|---------|----------------------------------|---------------------------|
| N,N’-dimethyl-1,3-propanediamine  | 15.05 g | € 15.98 per g                    | € 240.50                  |
| Dimethyloxalate                   | 17.45 g | € 0.12 per g                     | € 2.09                    |
| Toluene                           | 400 mL  | € 19.89 per L                    | € 7.96                    |
| Ethanol                           | 50 mL   | € 21.37 per L                    | € 1.07                    |
| Dichloromethane                   | 10 mL   | € 17.60 per L                    | € 1.76                    |
| Isopropanol                       | 50 mL   | € 5.30 per L                     | € 0.27                    |
| Lawesson’s reagent                | 47.45 g | € 1.50 per g                     | € 71.18                   |
| Iodine (to make Me$_2$dazdt·2I$_2$)| 68.57 g | € 0.30 per g                     | € 20.57                   |

Total product 81.29 g € 4.25 ($ 4.25) per g € 345.40

Energy consumption has been considered but not included, as this is difficult to calculate. However, an estimation based on the literature$^{99}$ suggests that values around 2 kWh would be needed (mainly due to 3h refluxing in toluene). The average cost of one kWh over the last 7 years$^{10}$ is € 0.08, rendering the energy cost a negligible € 0.16 ($ 0.16$).

Using the cost of preparing Me$_2$dazdt and its use in situ with iodine (as Me$_2$dazdt·2I$_2$), the cost of synthesizing the catalyst [AuI$_2$(Me$_2$dazdt)]I$_3$ (1a) can be calculated:

Scheme S18. Synthesis of [AuI$_2$(Me$_2$dazdt)]I$_3$ (1a) see Section 1.2 for experimental details.
Table S11. Amounts of reagents and solvents with associated costs for the synthesis of [AuI₂(Me₂dazdt)]I₃ (1a) using prices from Merck apart from for Me₂dazdt·2I₂ (prepared as above) and comparison with the same amount of commercial AuCl₃ catalyst.

| Chemicals                  | Amount in mL/mg | Amount (mmol) | Chemicals cost (per unit) | Overall cost of Chemicals |
|----------------------------|-----------------|---------------|---------------------------|---------------------------|
| Tetrahydrofuran            | 150 mL          |               | € 5.02 per L              | € 0.75                   |
| 32% NH₄OH                  | 10 mL           |               | € 3.60 per L              | € 0.04                   |
| Ammonium sulfate           | 2200 mg         |               | € 0.02 per g              | € 0.05                   |
| 30% H₂O₂                   | 3 mL            |               | € 4.46 per L              | € 0.01                   |
| 37% HCl                    | 4.2 mL          |               | € 3.44 per L              | € 0.02                   |
| Et₂O                       | 25 mL           |               | € 5.70 per L              | € 0.14                   |
| Me₂dazdt·I₂                | 361 mg          |               | **€ 4.25 per g**          | **€ 1.53**               |

| Total of 1a (Mₐ = 1019.81) obtained | 130 mg          | 0.128          | € 19.54 per g             | **€ 2.54 ($2.54)**       |
| AuCl₃ catalyst (Mₐ = 303.33)      | 39 mg           | 0.128          | € 145.83 per g            | **€ 5.69 ($5.69)**       |

The estimations above suggest that the cost of 1a is less than half that of commercial AuCl₃, which is the cheapest of the literature catalysts used in the research. Additional value generated by valorization of [Cu(NH₃)₄](SO₄) and NiCl₂ produced from the SIM cards is not included.

Thirty SIM cards were used to obtain 130 mg of 1a. 1700 used SIM cards are available on ebay for €85 (€0.05 each so 30 would cost €1.50). On scale up, it is anticipated that the cost of used SIM cards would be far lower than €0.05 per card and so this cost would become negligible. Even when including the cost of SIM cars purchased for the purpose of this research, the cost of 1a is 29% less than that of commercial AuCl₃.

It is often estimated that the scale up of a process would reduce the cost ten-fold so the costs above for the preparation of 1a would be reduced dramatically on scale up. In comparison, the cost of commercial AuCl₃ is already minimized through the savings of large-scale production.
1.7. References

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2. NMR Spectra

2.1. $^1$H NMR Spectra

$[\text{AuI}_2(\text{Me}_2\text{dazdt})]\text{BF}_4$ (1b)

![Chemical Structure](image)

Figure S11. $^1$H NMR (400 MHz, Acetonitrile-$d_3$) spectrum of $[\text{AuI}_2(\text{Me}_2\text{dazdt})]\text{BF}_4$ (1b).
[AuBr$_2$(Me$_2$azdt)]BF$_4$ (2b)

Figure S12. $^1$H NMR (400 MHz, Acetonitrile-$d_3$) spectrum of [AuBr$_2$(Me$_2$azdt)]BF$_4$ (2b).
Figure S13. $^1$H NMR (400 MHz, Chloroform-$d$) spectrum of $N$-(prop-2-yn-1-yl)benzamide.
Figure S14. $^1$H NMR (400 MHz, Chloroform-\textit{d}) spectrum of $N$-(3-phenylprop-2-yn-1-yl)benzamide.
5-Methyl-2-phenyloxazole

Figure S15. $^1$H NMR (400 MHz, Chloroform-$d$) spectrum of 5-methyl-2-phenyloxazole.
(Z)-5-Benzylidene-2-phenyl-4,5-dihydrooxazole

Figure S16. $^1$H NMR (400 MHz, Chloroform-d) spectrum of (Z)-5-benzylidene-2-phenyl-4,5-dihydrooxazole
Figure S17. $^1$H NMR (400 MHz, Chloroform-$d$) spectrum of (E)-5-(iodo(phenyl)methylene)-2-phenyl-4,5-dihydrooxazole.
Condensation of o-iodoaniline and acetylacetone

Figure S18. Example $^1$H NMR (400 MHz, Chloroform-$d$) spectrum of a crude o-iodoaniline and acetylacetone condensation reaction mixture illustrating reaction monitoring.
Addition of 1,3-dimethoxybenzene to methyl vinyl ketone.

Figure S19. Example $^1$H NMR (400 MHz, Chloroform-$d$) spectrum of the crude reaction mixture from the addition of 1,3-dimethoxybenzene to methyl vinyl ketone illustrating reaction monitoring.
Figure S20. $^1$H NMR (400 MHz, Chloroform-$d$) spectrum of 4,4’-(azulene-1,3-diyl)bis(butan-2-one)$_2$.
Figure S21. $^1$H NMR (400 MHz, Chloroform-$d$) spectrum of 4-(5-methylfuran-2-yl)butan-2-one.
Figure S22. $^1$H NMR (400 MHz, Chloroform-$d$) spectrum of 3-(5-methylfuran-2-yl)cyclohexan-1-one.
3-Chloro-4-methoxy-1,1'-biphenyl

Figure S23. $^1$H NMR (400 MHz, Chloroform-$d$) spectrum of 3-chloro-4-methoxy-1,1'-biphenyl.
3-Bromo-4-methoxy-1,1'-biphenyl

Figure S24. $^1$H NMR (400 MHz, Chloroform-$d$) spectrum of 3-bromo-4-methoxy-1,1'-biphenyl.
Figure S25. $^1$H NMR (400 MHz, Chloroform-d) spectrum of 3,4-dimethyl-1,1'-biphenyl.
**4-Methyl-1,1'-biphenyl**

**Figure S26.** $^1$H NMR (400 MHz, Chloroform-$d$) spectrum of 4-methyl-1,1'-biphenyl.
1-Methyl-4-phenynaphthalene

Figure S27. $^1$H NMR (400 MHz, Chloroform-$d$) spectrum of 1-methyl-4-phenynaphthalene
2-Bromo-5-phenylthiophene

Figure S28. $^1$H NMR (400 MHz, Chloroform-\textit{d}) spectrum of 2-bromo-5-phenylthiophene.
2.2. $^{13}$C$^1$H NMR Spectra

$N$-(Prop-2-yn-1-yl)benzamide

![N-(Prop-2-yn-1-yl)benzamide structure]

Figure S29. $^{13}$C$^1$H NMR (101 MHz, Chloroform-$d$) spectrum of $N$-(prop-2-yn-1-yl)benzamide.
Figure S30. $^{13}$C\textsuperscript{(1)H} NMR (101 MHz, Chloroform-$d$) spectrum of (Z)-5-benzylidene-2-phenyl-4,5-dihydrooxazole.
3-Chloro-4-methoxy-1,1'-biphenyl

Figure S31. $^{13}$C$\{^1$H$\}$ NMR (101 MHz, Chloroform-$d$) spectrum of 3-chloro-4-methoxy-1,1'-biphenyl.
3-Bromo-4-methoxy-1,1'-biphenyl

Figure S32. $^{13}$C($^1$H) NMR (101 MHz, Chloroform-$d$) spectrum of 3-bromo-4-methoxy-1,1'-biphenyl.
3,4-Dimethyl-1,1'-biphenyl

Figure S33. $^{13}\text{C}^{1\text{H}}$ NMR (101 MHz, Chloroform-$d$) spectrum of 3,4-dimethyl-1,1'-biphenyl.
4-Methyl-1,1′-biphenyl

Figure S34. $^{13}$C{H} NMR (101 MHz, Chloroform-d) spectrum of 4-methyl-1,1′-biphenyl.
1-Methyl-4-phenynaphthalene

Figure S35. $^{13}$C{\textsuperscript{1}H} NMR (101 MHz, Chloroform-$d$) spectrum of 1-methyl-4-phenynaphthalene.
Figure S36. $^{13}$C($^1$H) NMR (101 MHz, Chloroform-$d$) spectrum of 2-bromo-5-phenylthiophene.