Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary information for

Stable N-Heterocyclic Carbene (NHC) Cyclometalated (C^C) Gold(III) Complexes as Blue – Blue Green Phosphorescence Emitters

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Table of Contents

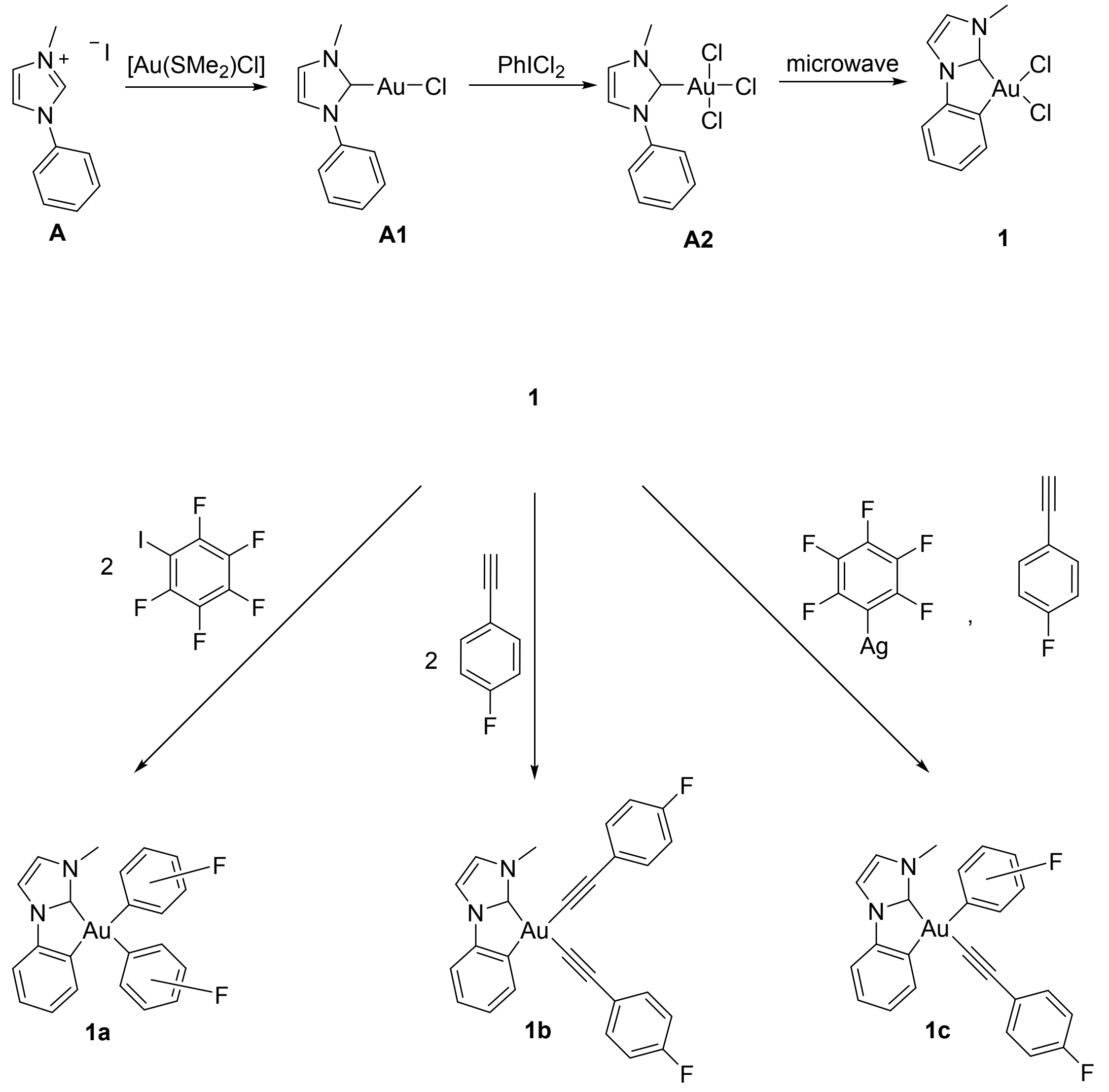
Experimental section

Material and Methods: ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AV-500 (500 MHz), Bruker AV-400 (400 MHz) or Varian Mercury (300 MHz) spectrometer. ^{19}F NMR spectra were recorded on a Varian Mercury (300 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (δ 0.00 ppm) using the residual protio solvent peaks as internal standards (^1H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). ^{19}F NMR was referenced to $CFCl_3$ (δ 0.00 ppm). Coupling constants (J) are quoted in Hertz (Hz) and the following abbreviations are used to describe the signal multiplicities: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublet); td (triplet of doublet); dt (doublet of triplet). Proton and carbon assignments have been made using routine one and two dimensional NMR spectroscopies where appropriate. IR measurements were carried out on a *SpectrumTWO FT-IR Spectrometer* (Perkin–Elmer) equipped with a *Specac Golden Gate^{TM}* with frequencies (v) quoted in wavenumbers (cm^{-1}). Elemental microanalysis was carried out with *Leco CHNS-932 analyser*. TLC analysis was performed on precoated Merck Silica Gel $60F_{254}$ slides and visualised by luminescence quenching either at (short wavelength) 254 nm or (long wavelength) 365 nm. Chromatographic purification of products was performed on a short column (length 15.0 cm: diameter 1.5 cm) using forced flow of eluent. UV-Vis measurements were carried out on a *Perkin-Elmer Lambda 19 UV-Vis spectrophotometer*. Emission spectra were acquired on an *Edinburgh FLS920 spectrophotometer* using 450W Xenon lamp excitation by exciting at the longest-wavelength absorption maxima. All samples for emission spectra were degassed by at least three freeze-pump-thaw cycles in an anaerobic cuvette and were pressurized with N_2 following each cycle. 77 K emission spectra were acquired in frozen 2-methyltetrahydrofuran (2-MeTHF) glass. Phosphorescence lifetimes were measured by time-correlated single photon counting method (TCSPC) performed on an *Edinburgh FLS920 spectrophotometer*, using nF900 lamp source at 40000 Hz frequency with 15 nm excitation and 15 nm emission slit widths. Absolute quantum yields were measured using an integrating sphere from Edinburgh Instruments. YAG:Ce (powder) was used as a calibration reference with ϕ_{em} = 97%. Microwave reactions were carried out in an *Anton Paar Monowave 300*. Thermogravimetric analysis (TGA) was done using a *NETZSCH STA 449C* instrument. Thin films were spin coated on a quartz slide (12 x 12 mm) from a dichloromethane solution consisting of a mixture of poly(methyl methacrylate) (PMMA) and the corresponding Au(III) complex.

Commercially available reagents were purchased from Aldrich, Chemie-Brunschwig and Fluorochem were used as such without further purification. Sodium tetrachloroaurate(III) dihydrate was purchased from Strem chemicals.

General remarks. All the reactions were performed in a Schlenk flask under N_2 atmosphere, except the microwave reactions. This type of reaction was carried out in G30 microwave tubes. The gold(III) dichloro precursors *cis*-[(*pmi*)Au(Cl_2)], *cis*-[(*dbfmi*)Au(Cl_2)], *cis*-[(*flzmi*)Au(Cl_2)] were used without further purification.

1-phenyl-3-methylimidazol-2-ylidene (= pmi) series



Scheme S1. Synthetic pathways for the gold complexes of the *pmi*-series.

3-methyl-1-phenyl-1H-imidazol-3-ium iodide (A). A was synthesized according to literature procedure.

[(*pmi*)Au(Cl)] (A1). A (2.00 g, 6.990 mmol) and Ag_2O (1.62 g, 6.990 mmol) were suspended in dry CH_2Cl_2 (150 mL). The grey/brownish suspension was stirred over night at ambient temperature in the absence of light. [(SMe_2)Au(Cl)] (2.06 g, 6.990 mmol) was dissolved in dry CH_2Cl_2 (50 mL) and cannulated the next day to the silver suspension and stirred for 4 hours at room temperature in the dark. The black suspension was filtered over celite and the solvent was removed under reduced pressure. The orange/brownish residue was washed with hexane (3 x 10 mL) resulting in an orange solid. Yield = 1.47 g, 3.775 mmol, 54%. ^{1}H NMR (500 MHz,

CD_2Cl_2, 300 K): δ 3.94 (s, 3H, N-CH_3), 7.13 (d, $^3J_{H-H}$ = 2 Hz, 1H), 7.24 (d, $^3J_{H-H}$ = 2 Hz, 1H), 7.51-7.56 (m, 2H), 7.64-7.67 (m, 2H); ^{13}C {^1H}NMR (125 MHz, CD_2Cl_2, 300 K): δ 39.2, 122.3, 122.9, 125.5, 129.7, 130.1, 139.7, 171.5; Elemental analysis (%) calcd for: $C_{10}H_{10}AuClN_2$: C, 30.75; H, 2.58; N, 7.17; Found: C, 30.59; H, 2.66; N, 6.99.

[(*pmi*)Au(Cl)$_3$] (A2). A1 (1.00 g, 2.560 mmol) was dissolved in dry CH_2Cl_2 (200 mL) and cooled to 0 °C. Dichloroiodo benzene ($PhICl_2$) (0.84 g, 3.072 mmol) was added to the yellow solution and the reaction mixture was stirred for 20 minutes at 0 °C in the absence of light. Afterwards, the mixture was allowed to warm to room temperature and was stirred for 24 hours resulting in an orange solution. The solvent was removed *in vacuo* to yield in a brownish solid as the crude product. The crude was washed with Et_2O (2 x 100 mL) to afford the title compound as a grey solid. Yield = 1.10 g, 2.380 mmol, 93%. ^1H NMR (500 MHz, CD_2Cl_2, 300 K): δ 4.05 (s, 3H, N-CH_3), 7.35 (d, $^3J_{H-H}$ = 2 Hz, 1H), 7.40 (d, $^3J_{H-H}$ = 2 Hz), 7.62 (s, 5H); ^{13}C {^1H}NMR (125 MHz, CD_2Cl_2, 300 K): δ 38.6, 125.3, 125.6, 126.3, 130.8, 131.2, 137.3, 142.0; Elemental analysis (%) calcd for: $C_{10}H_{10}AuCl_3N_2$: C, 26.02; H, 2.18; N, 6.07; Found: C, 25.80; H, 2.16; N, 5.99.

***cis*-[(*pmi*)Au(Cl)$_2$] (1).** The reaction was performed in the microwave. **A2** (0.100 g, 0.216 mmol) was suspended in H_2O (10 mL) with 10 wt% of PhICl2 (0.010 g). The reaction mixture was heated to 175 °C under continuous stirring for 15 minutes (2 cycles). The brown suspension was filtered and washed with H_2O (100 mL), Et_2O (100 mL) and CH_2Cl_2 (100 mL). Afterwards the grey solid was washed additionally with EtOAc (1'000 mL), the solvent was removed under reduced pressure and the final product was obtained as a white solid. Yield = 0.044 g, 0.104 mmol, 47%. ^1H NMR (400 MHz, DMSO-d_6, 300 K): δ 4.01 (s, 3H, N-CH_3), 7.64-7.72 (m, 4H), 7.98 (d, $^3J_{H-H}$ = 2.0 Hz, 1H), 8.10 (d, $^3J_{H-H}$ = 2.0 Hz, 1H); ^{13}C {^1H}NMR (125 MHz, DMSO-d_6, 300 K): δ 37.5, 114.7, 116.7, 125.5, 126.1, 126.5, 129.4, 130.2, 132.1, 136.7.

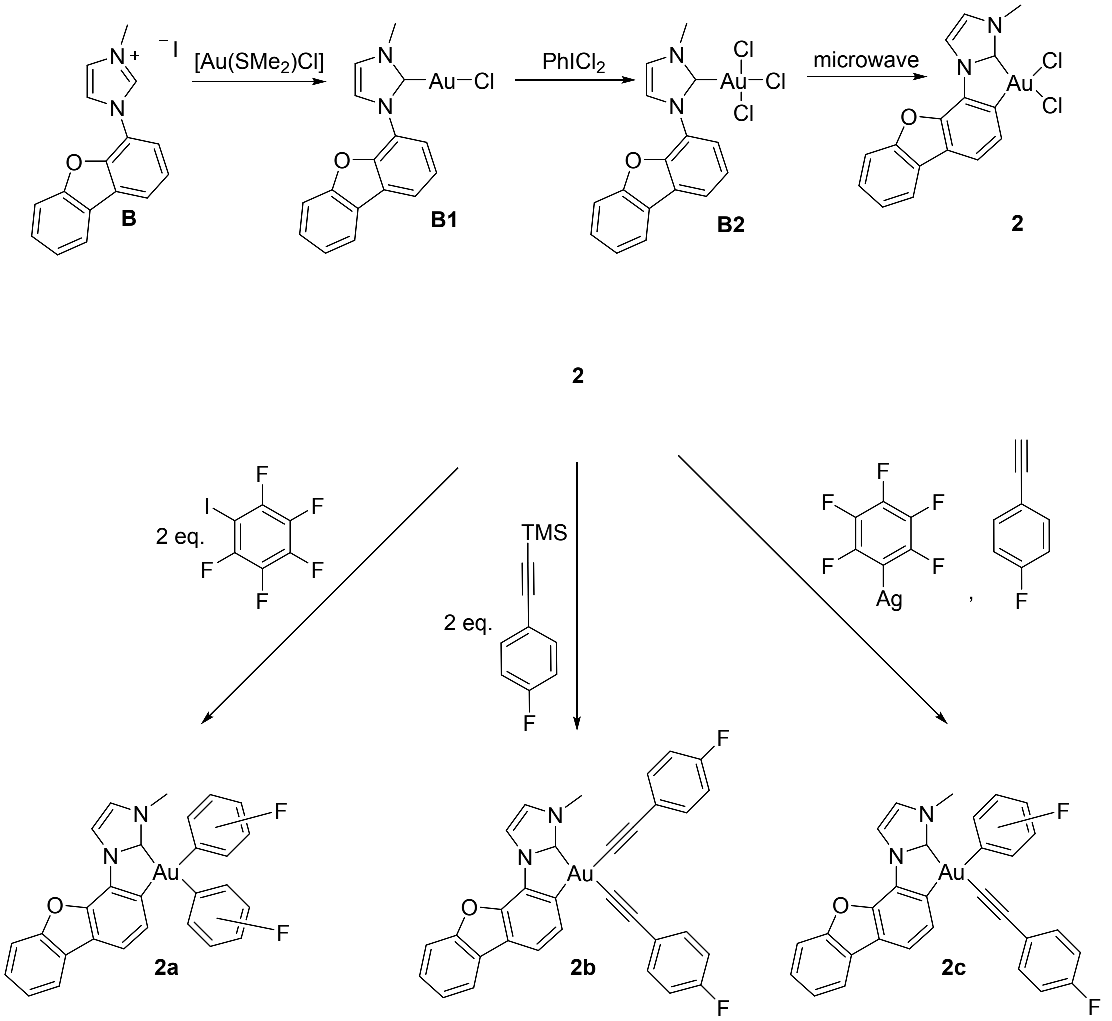
***cis*-[(*pmi*)Au(C_6F_5)$_2$] (1a).** To iodopentafluorobenzene (0.044 g, 0.15 mmol, 0.02 mL) in dry Et_2O (20 mL), 1.6 M *n*-BuLi in hexanes (0.010 g, 0.160 mmol, 0.1 mL) was added slowly via syringe at -78°C. The mixture was stirred for 20 minutes at that temperature and cannulated to another suspension containing 1 (0.030 g, 0.070 mmol) in dry Et_2O (20 mL), precooled to -78°C. The reaction mixture was kept at -78°C for 20 min, was allowed to warm to ambient temperature and stirred for 2 hours. The reaction was quenched with H_2O (50 mL), washed with brine (50 mL) and extracted with EtOAc/CH_2Cl_2 = 1/1 (2 x 50 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo* to give a yellow solid as the crude product. The residue was purified by column chromatography on silica gel (eluent: Hexane/EtOAc = 3/1) to afford the title compound as a white solid. Yield = 0.031 g, 0.040 mmol, 65%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 3.45 (s, 3H, N-CH_3), 6.88 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H), 7.10 (t, $^3J_{H\text{-}H}$ = 7 Hz, 1H), 7.31-7.28 (m, 2H), 7.70 (s, 1H); ^{13}C {^{1}H}NMR (125 MHz, CD_2Cl_2, 300 K): δ 39.2, 76.0, 113.1, 123.4, 128.3, 128.5, 135.8, 142.1, 145.7; ^{19}F NMR (376 MHz, CD_2Cl_2, 300 K): δ -120.80-(-120.89) (m, 2 *o*-F), -121.70-(-121.77) (m, 2 *o*-F), -158.90 (t, *J* = 19.48 Hz, 1 *p*-F), -159.91 (t, *J* = 19.63 Hz, 1 *p*-F), -162.03-(-162.15) (m, 2 *m*-F), -162.97-(-163.09) (m, 2 *m*-F); Elemental analysis (%) calcd for: $C_{22}H_9AuF_{10}N_2$□$^1/_3$ C_6H_{14}: C, 40.20; H, 1.92; N, 3.91; Found: C, 40.21; H, 1.85; N, 3.72.

***cis*-[(*pmi*)Au(C≡$CC_6H_5F)_2$] (1b).** *p*-Fluorophenylacetylene (0.019 g, 0.160 mmol, 18.5 μL) was dissolved in dry CH_2Cl_2 (15 mL). NEt_3 (0.016 g, 0.16 mmol, 22 μL) and CuI (0.031 g 0.160 mmol) were added to the solution and the resulting mixture was stirred for 1.5 hours at ambient temperature. **1** (0.030 g, 0.070 mmol) was added and after stirring for 2.5 hours at room temperature, the reaction was quenched with H_2O (15 mL). The mixture was extracted with CH_2Cl_2 (2 x 50 mL) and washed with brine (50 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to afford a yellowish/white solid as the crude product. The crude was washed additionally with hexane (3 x 5 mL) and further purified by column chromatography on silica gel (eluent: EtOAc/Hexane = 2/1). After slow diffusion crystalisation (CH_2Cl_2/Hexane = 1/1) the title compound was obtained as a white solid. Yield = 0.023 g, 0.038 mmol, 55%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 4.37 (s, 3H, N-CH_3), 6.98-7.04 (m, 4H), 7.09 (s, 1H), 7.25 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H), 7.32 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 1H), 7.44 (t, $^3J_{H\text{-}H}$ = 6.0 Hz, 2H), 7.49 (s, 1H), 7.54 (t, $^3J_{H\text{-}H}$ = 6.0 Hz, 2H), 8.33 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H); ^{13}C {^{1}H}NMR (125 MHz, CD_2Cl_2, 300 K): δ 39.0, 98.4, 102.2, 102.8, 108.4, 112.6, 115.5, 115.6, 116.2, 123.0, 124.2, 127.6, 128.0, 133.4, 133.5, 133.7, 134.0, 137.7, 140.0, 145.9, 161.1, 161.2, 163.0, 163.1, 166.8, 171.2; ^{19}F NMR (376 MHz, CD_2Cl_2, 300 K): δ -115.79 (m, 1 F), -115.89 (m, 1 F); Elemental analysis (%) calcd for: $C_{26}H_{17}AuF_2N_2$□$^1/_6$ CH_2Cl_2: C, 51.82; H, 2.88; N, 4.62; Found: C, 52.06; H, 2.77; N, 4.48; IR (ATR-FTIR): $\tilde{\nu}$(-C≡C-) = 2152 cm^{-1}, 2141 cm^{-1}.

***cis*-[(*pmi*)Au(C_6F_5)($C{\equiv}CC_6H_5F$)] (1c).** *p*-Fluorophenylacetylene (0.030 g, 0.290 mmol, 33 μL) was dissolved in dry CH_2Cl_2 (50 mL). NEt_3 (0.029 g, 0.290 mmol, 40 μL), CuI (0.055 g, 0.290 mmol) were added in this order and the reaction mixture was stirred for 1 hour at room temperature. **1d** (0.150 g, 0.270 mmol) was added to the yellow suspension and the reaction progress was monitored by means of TLC. After completion, the reaction was quenched with H_2O (50 mL), extracted with CH_2Cl_2 (2 x 100 mL) and washed with brine (100 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to give the title compound as a yellow solid. Yield = 0.102 g, 0.159 mmol, 58%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 3.42 (s, 3H, N-CH_3), 6.97 (t, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H), 7.03 (d, $^3J_{H\text{-}H}$ = 1.0 Hz, 1H), 7.28-7.31 (m, 2H), 7.35-7.40 (m, 3H), 7.54 (d, $^3J_{H\text{-}H}$ = 2.0 Hz, 1H), 8.35 (d, $^3J_{H\text{-}H}$ = 7 Hz, 1H); ^{13}C {^{1}H}NMR (125 MHz, CD_2Cl_2, 300 K): δ 38.1, 97.9, 103.2, 112.7, 115.4, 115.6, 116.5, 122.7, 122.7, 124.3, 128.0, 128.3, 133.6, 133.7, 137.4, 142.3, 145.7, 161.2, 163.1, 167.7; ^{19}F NMR (376 MHz, CD_2Cl_2, 300 K): δ -115.66 (s, 1 *p*-F), -121.93-(-122.03) (m, 2 *o*-F), -160.73-(-160.79) (m, 1 *p*-F), -163.50-(-163.63) (m, 2 *m*-F); Elemental analysis (%) calcd for: $C_{24}H_{13}AuF_6N_2$: C, 45.02; H, 2.05; N, 4.37; Found: C, 44.79; H, 2.19; N, 4.31; IR (ATR-FTIR): $\tilde{\nu}$(-C≡C-) = 2033 cm^{-1}.

***cis*-[(*pmi*)Au(C_6F_5)(Cl)] (1d).** AgC_6F_5 (0.145 g, 0.527 mmol) was dissolved in dry CH_2Cl_2 (20 mL) under exclusion of light and cannulated to a suspension of **1** (0.200 g, 0.471 mmol) in dry CH_2Cl_2 (20 mL). The reaction was stirred in the dark 24 hours at ambient temperature. After quenching with H_2O (50 mL) the mixture was extracted with CH_2Cl_2 (2 x 50 mL) and washed with brine (50 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The reddish/brown residue was washed with hexane (5 x 5 mL) and purified by column chromatography on silica gel (eluent: EtOAc) to afford the title compound as a white solid. Yield = 0.197 g, 0.353 mmol, 75%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 3.42 (s, 3H, N-CH_3), 7.10 (d, $^3J_{(H\text{-}H)}$ = 2 Hz, 1H), 7.27 (dd, $^3J_{(H\text{-}H)}$ = 7.5 Hz; $^4J_{(H\text{-}H)}$ = 1.5 Hz, 1H), 7.37-7.34 (m, 2H), 7.57 (d, $^3J_{(H\text{-}H)}$ = 2 Hz, 1H), 8.18 (dd, $^3J_{(H\text{-}H)}$ = 7 Hz; $^4J_{(H\text{-}H)}$ = 1.5 Hz, 1H); ^{13}C {^{1}H}NMR (125 MHz, CD_2Cl_2, 300 K): δ 30.0, 112.5, 116.4, 124.5, 127.7, 128.6, 133.4; ^{19}F NMR (376 MHz, CD_2Cl_2, 300 K): δ -123.04-(-123.23) (m, 2 *o*-F), -159.72-(-159.82) (m, 1 *p*-F), -162.71-(-162.87) (m, 2 *m*-F); Elemental analysis (%) calcd for: $C_{16}H_9AuClF_5N_2$: C, 34.52; H, 1.63; N, 5.03; Found: C, 34.74; H, 1.61; N, 4.91.

1-(dibenzofuranyl)-3-methylimidazol-2-ylidene (= dbfmi) series



Scheme S2. Synthetic pathways for the gold complexes of the *dbfmi*-series.

3-Dibenzofuran-4-yl-1-methyl-3H-imidazole-1-ium-iodide (B). B was synthesized according to literature procedure.

[(*dbfmi*)Au(Cl)] (B1). B (1.50 g, 3.987 mmol) was dissolved in dry CH_2Cl_2 (150 mL) and Ag_2O (0.924 g, 3.987 mmol) was added. The suspension was stirred over night at room temperature in the absence of light. The next day, [(SMe_2)Au(Cl)] (1.17 g, 3.987 mmol) was dissolved in dry CH_2Cl_2 (50 mL), cannulated to the silver suspension and stirred for 4 hours at ambient temperature in the dark. The resulting black suspension was filtered over celite and the solvent was removed under reduced pressure to afford the title compound as an orange solid. Yield = 1.08 g, 2.240 mmol, 57%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 3.99 (s, 3H, N-CH_3), 7.25 (d, $^3J_{H\text{-}H}$ = 2 Hz, 1H), 7.44 (dt, $^3J_{(H\text{-}H)}$ = 7.5 Hz; $^4J_{(H\text{-}H)}$ = 1.0 Hz, 1H), 7.51-7.59 (m, 3H), 7.92 (dd, $^3J_{(H\text{-}H)}$ = 8.0 Hz; $^4J_{(H\text{-}H)}$ = 1.0 Hz, 1H), 8.06 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H), 8.12 (dd,

$^3J_{(H\text{-}H)}$ = 7.5 Hz; $^4J_{(H\text{-}H)}$ = 1.0 Hz, 1H); ^{13}C {^{1}H}NMR (125 MHz, CD_2Cl_2, 300 K): *δ* 39.1, 112.2, 121.6, 122.1, 122.5, 123.2, 123.7, 124.0, 124.1, 124.2, 125.0, 127.0, 128.6, 149.7, 156.7, 172.6; Elemental analysis (%) calcd for: $C_{16}H_{12}AuClN_2O$: C, 39.98; H, 2.52; N, 5.83; Found: C, 39.79; H, 2.58; N, 5.85.

[(*dbfmi*)Au(Cl)$_3$] (B2). $PhICl_2$ (0.69 g, 2.496 mmol) was added to an orange solution of **B1** (1.00 g, 2.080 mmol) in dry CH_2Cl_2 (100 mL) at 0 °C. The reaction mixture was stirred for 20 minutes in the absence of light. Afterwards, the mixture was allowed to warm to room temperature and was stirred for 24 hours in the dark. The solvent of the resulting yellow solution was removed *in vacuo*. The orange solid was slowly precipitated (solvent mixture: CH_2Cl_2/Hexane = 1/1) and the title compound was obtained as a yellow solid. Yield = 0.76 g, 1.373 mmol, 66%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): *δ* 4.12 (s, 3H, N-CH_3), 7.45-7.48 (m, 2H), 7.54-7.62 (m, 3H), 7.67 (d, $^3J_{H\text{-}H}$ = 2.0 Hz, 1H), 7.89 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 1H), 8.08 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H), 8.21 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 1H); ^{13}C {^{1}H}NMR (125 MHz, CD_2Cl_2, 300 K): *δ* 38.8, 102.1, 112.6, 121.9, 123.7, 123.9, 124.3, 124.5, 124.9, 125.6, 126.1, 127.7, 129.2, 157.0; Elemental analysis (%) calcd for: $C_{16}H_{11}AuCl_2N_2O$□CH_2Cl_2: C, 32.08; H, 2.22; N, 4.40; Found: C, 32.03; H, 2.29; N, 4.31.

***cis*-[(*dbfmi*)Au(Cl)$_2$] (2).** The reaction was performed in the microwave. **B2** (0.500 g, 0.906 mmol) was suspended in H_2O (10 mL) with 10 wt% $PhICl_2$ (0.050 g). The reaction mixture was heated to 200 °C under continuous stirring for 10 minutes (2 cycles). The yellow suspension was filtered and washed with H_2O (100 mL), Et_2O (100 mL) and CH_2Cl_2 (100 mL). Afterwards the grey solid was washed additionally with EtOAc (1’000 mL), the solvent was removed under reduced pressure and the title compound was obtained as a white solid. Yield = 0.229 g, 0.444 mmol, 49%. ^{1}H NMR (500 MHz, DMSO-*d*$_6$, 300 K): *δ* 4.33 (s, 3H, N-CH_3), 7.51 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H), 7.67 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H), 7.81 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 1H), 7.96-7.99 (m, 2H), 8.06 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H), 8.20 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H), 8.40 (d, $^3J_{H\text{-}H}$ = 2 Hz, 1H); ^{13}C {^{1}H}NMR (125 MHz, DMSO-*d*$_6$, 300 K): δ 38.2, 112.0, 117.8, 118.6, 121.7, 122.5, 124.0, 125.9, 126.1, 126.4, 128.7, 135.1, 141.6, 152.9, 156.2.

***cis*-[(*dbfmi*)Au(C_6F_5)$_2$] (2a).** Iodopentafluorobenzene (0.071 g, 0.242 mmol) was syringed into Et_2O (50 mL) and cooled to -78 °C. 1.6 M *n*-BuLi in hexanes (0.015 g, 0.244 mmol) was added slowly by syringe to the solution and was stirred for 30 minutes at -78 °C. This mixture was cannulated to another solution containing **2**

(0.050 g, 0.097 mmol) in Et_2O (30 mL) at -78 °C. The reaction mixture was stirred for 10 minutes at -78 °C, before the cooling bath was removed and the mixture was allowed to warm at room temperature. The reaction progress was monitored by means of TLC until completion. After quenching with H_2O (50 mL), the mixture was extracted with CH_2Cl_2 (2 x 100 mL) and washed with brine (50 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The grey residue was purified by column chromatography on silica gel (eluent: Hexane/EtOAc = 3/1) to afford the title compound as a white solid. Yield = 0.031 g, 0.040 mmol, 41%. ^1H NMR (500 MHz, CD_2Cl_2, 300 K): δ 3.50 (s, 3H, N-CH_3), 6.88 (d, $^3J_{H\text{-}H}$ = 8 Hz, 1H), 7.15 (d, $^3J_{H\text{-}H}$ = 2 Hz, 1H), 7.42 (dt, $^3J_{H\text{-}H}$ = 7.5 Hz; $^4J_{(H\text{-}H)}$ = 1 Hz, 1H), 7.54 (dt, $^3J_{H\text{-}H}$ = 7 Hz; $^4J_{(H\text{-}H)}$ = 1 Hz, 1H), 7.67 (d, $^3J_{H\text{-}H}$ = 8 Hz, 1H), 7.71 (d, $^3J_{H\text{-}H}$ = 8 Hz, 1H), 7.99 (dd, $^3J_{H\text{-}H}$ = 7.5 Hz; $^4J_{(H\text{-}H)}$ = 1 Hz, 1H), 8.41 (d, $^3J_{H\text{-}H}$ = 1.5 Hz, 1H); ^{13}C {^1H}NMR (125 MHz, CD_2Cl_2, 300 K): δ 38.4, 112.3, 119.8, 120.3, 121.7, 124.1, 124.4, 126.7, 128.6, 129.7, 143.9, 157.0; ^{19}F NMR (376 MHz, CD_2Cl_2, 300 K): δ -121.85 (m, 2 *o*-F), -122.59 (m, 2 *o*-F), -160.02 (t, *J* = 19.75 Hz, 1 *p*-F), -160.97 (t, *J* = 19.75 Hz, 1 *p*-F), -163.20 (m, 2 *m*-F), -164.06 (m, 2 *m*-F); Elemental analysis (%) calcd for: $C_{28}H_{11}AuF_{10}N_2O$□$^3/_2(C_2H_5)_2O$: C, 45.86; H, 3.06; N, 3.15; Found: C, 45.73; H, 3.01; N, 2.91.

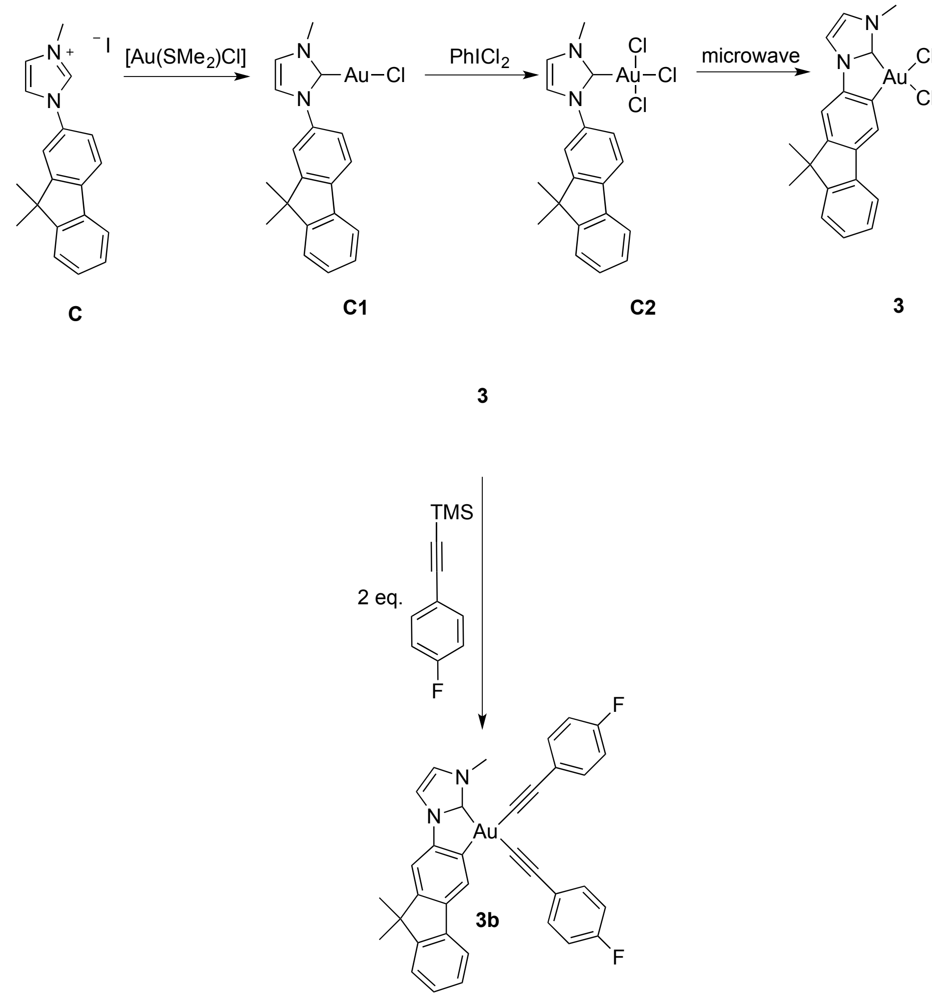
***cis*-[(*dbfmi*)Au(C≡CC$_6$H$_5$F)$_2$] (2b).** (4-fluorophenylethynyl)trimethylsilane (0.164 g, 0.854 mmol) was syringed in DMF (100 mL) under N_2 atmosphere. CsF (0.236 g, 1.152 mmol) and CuI (0.296 g, 1.152 mmol) were added in this order and the reaction mixture was stirred for 20 minutes at ambient temperature resulting in an orange suspension. **2** (0.100 g, 0.194 mmol) was added and the mixture was stirred for 24 hours at room temperature, resulting in a dark orange suspension. The reaction was quenched with H_2O (100 mL), extracted with CH_2Cl_2 (2 x 100 mL) and washed with brine (100 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The orange residue was purified by column chromatography on silica gel (eluent: Hexane/EtOAc = 1.5/1) to afford the title compound as a yellowish/white solid. Yield = 0.101 g, 0.148 mmol, 76%. ^1H NMR (500 MHz, CD_2Cl_2, 300 K): δ 4.41 (s, 3H, N-CH_3), 6.98 (t, $^3J_{(H\text{-}H)}$ = 8.5 Hz, 2H), 7.06 (t, $^3J_{(H\text{-}H)}$ = 8.5 Hz, 2H), 7.13 (d, $^3J_{(H\text{-}H)}$ = 2 Hz, 1H), 7.34 (t, $^3J_{(H\text{-}H)}$ = 7 Hz, 1H), 7.41-7.44 (m, 2H), 7.48 (td, $^3J_{(H\text{-}H)}$ = 7 Hz; $^4J_{(H\text{-}H)}$ = 1Hz, 1H), 7.56-7.59 (m, 3H), 7.71 (d, $^3J_{(H\text{-}H)}$ = 8 Hz, 1H), 7.84 (d, $^3J_{(H\text{-}H)}$ = 7 Hz, 1H), 8.19 (d, $^3J_{(H\text{-}H)}$ = 8 Hz, 1H), 8.21 (d, $^3J_{(H\text{-}H)}$ = 2 Hz, 1H); ^{13}C {^1H}NMR (125 MHz, CD_2Cl_2, 300 K): δ 38.9, 97.8, 101.2, 102.0, 108.1, 111.8, 115.4, 115.5, 118.8, 119.5, 121.2, 122.6, 122.7, 123.7, 123.8, 124.2, 125.8, 128.0, 129.8, 131.0, 133.4, 133.6, 138.8, 143.1, 156.4, 161.8, 162.0, 165.8; ^{19}F NMR (376 MHz, CD_2Cl_2, 300 K): δ - 114.4 (s, *p*-1F), - 114.5 (s, *p*-1F); Elemental analysis (%) calcd for: $C_{32}H_{20}AuF_2N_2O$: C, 56.23; H, 2.95; N, 4.10; Found: C, 56.30; H, 2.89; N, 3.98; IR (ATR-FTIR): $\tilde{\nu}$(-C≡C-) = 2148 cm^{-1}, 2139 cm^{-1}.

***cis*-[(*dbfmi*)Au(C_6F_5)(C≡CC_6H_5F)] (2c).** *p*-Fluorophenylacetylene (0.030 g, 0.250 mmol, 30 μL) was dissolved in dry CH_2Cl_2 (50 mL). NEt_3 (0.025 g, 0.250 mmol, 35 μL), CuI (0.046 g, 0.250 mmol) were added in this order and the reaction mixture was stirred for 1 hour at room temperature. **2d** (0.150 g, 0.230 mmol) was added and the reaction progress was monitored by means of TLC until **2d** disappeared completely. The reaction was quenched with H_2O (50 mL), extracted with CH_2Cl_2 (2 x 100 mL) and washed with brine (100 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to afford the title compound as a yellow solid. Yield = 0.112 g, 0.153 mmol, 66%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 3.45 (s, 3H, N-CH_3), 7.00 (t, $^3J_{(H-H)}$ = 8.5 Hz, 2H), 7.06 (s, 1H), 7.39-7.44 (m, 3H), 7.52 (t, $^3J_{(H-H)}$ = 7 Hz, 1H), 7.63 (d, $^3J_{(H-H)}$ = 8 Hz, 1H), 7.85 (d, $^3J_{(H-H)}$ = 8 Hz, 1H), 8.26-8.27 (m, 2H); ^{13}C {^{1}H}NMR (125 MHz, CD_2Cl_2, 300 K): δ 38.3, 97.6, 103.3, 112.2, 115.6, 115.8, 119.6, 120.1, 121.7, 122.7, 124.1, 124.3, 124.4, 126.4, 128.3, 129.6, 131.2, 133.8, 133.9, 143.5, 156.9, 161.4, 163.3, 167.6; ^{19}F NMR (376 MHz, CD_2Cl_2, 300 K): δ -115.51 (s, 1 *p*-F), -121.81-(-121.93) (m, 2 *o*-F), -160.52 (t, *J* = 25.19 Hz, 1 *p*-F), -163.35-(-163.54) (m, 2 *m*-F); Elemental analysis (%) calcd for: $C_{30}H_{15}AuF_6N_2O$: C, 49.33; H, 2.07; N, 3.84; Found: C, 49.52; H, 2.14; N, 3.71; IR (ATR-FTIR): $\tilde{\nu}$(-C≡C-) = 2040 cm^{-1}.

***cis*-[(*dbfmi*)Au(C_6F_5)(Cl)] (2d).** AgC_6F_5 (0.018 g, 0.065 mmol) was dissolved in dry CH_2Cl_2 (20 mL) under exclusion of light and cannulated to a suspension of **2** (0.030 g, 0.058 mmol) in dry CH_2Cl_2 (20 mL). The mixture was stirred at ambient temperature, in the dark for 24 hours. The reaction was quenched with H_2O (50 mL), extracted with CH_2Cl_2 (2 x 50 mL) and washed with brine (50 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The orange residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2) to afford the title compound as a white solid. Yield = 0.014 g, 0.022 mmol, 75%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 3.48 (s, 3H, N-CH_3), 7.18 (d, $^3J_{(H-H)}$ = 2 Hz, 1H), 7.44 (dt, $^3J_{(H-H)}$ = 8 Hz; $^4J_{(H-H)}$ = 1 Hz, 1H), 7.55 (dt, $^3J_{(H-H)}$ = 7 Hz; $^4J_{(H-H)}$ = 1 Hz, 1H), 7.67 (d, $^3J_{(H-H)}$ = 8.5 Hz, 1H), 7.95 (d, $^3J_{(H-H)}$ = 8 Hz, 1H), 8.04 (d, $^3J_{(H-H)}$ = 7 Hz, 1H), 8.19 (d, $^3J_{(H-H)}$ = 8 Hz, 1H), 8.36 (d, $^3J_{(H-H)}$ = 2 Hz, 1H); ^{13}C {^{1}H}NMR (125 MHz,

CD_2Cl_2, 300 K): δ 38.3, 111.8, 119.0, 119.5, 121.2, 123.5, 123.7, 124.3, 126.4, 126.9, 127.6, 128.1, 142.8, 153.6, 156.6; ^{19}F NMR (376 MHz, CD_2Cl_2, 300 K): δ -123.17-(-123.26) (m, 2 *o*-F), -159.60 (t, *J* = 18.90 Hz, 1 *p*-F), -162.67-(-162.83) (m, 2 *m*-F); Elemental analysis (%) calcd for: $C_{22}H_{11}AuClF_5N_2O$: C, 40.86; H, 1.71; N, 4.33; Found: C, 40.26; H, 1.61; N, 4.27.

1-(9,9-dimethylfluorenyl)-3-methylimidazol-2-ylidene (= flzmi) series



Scheme S3. Synthetic pathways for the gold complexes of the *flzmi*-series.

9,9-dimethylfluorene-2yl-1-methyl-3H-imidazole-1-ium-iodide (C). To a solution of 2-bromo-9,9-dimethylfluorene (5.000 g, 18.304 mmol) in DMF (50 mL) in a Young-Schlenk, imidazole (1.520 g, 22.300 mmol), CuI (0.65 g, 3.391 mmol) and K_2CO_3 (3.400 g, 24.061 mmol) were added in this order. The reaction mixture was stirred at 150 °C for 48 hours. Afterwards, the solution was allowed to cool to room temperature and the brownish suspension was filtered and washed with additional DMF (50 mL). The solvent was removed *in vacuo* resulting in a brownish viscose residue. The residue was dissolved in CH_2Cl_2 (50 mL), washed with a 25% NH_3 solution (20 mL) and with H_2O (20 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure yielding in a brown, viscose solid. The residue was used without further purification for the next step. The residue isolated from the previous reaction was dissolved in THF (50 mL). MeI (7.71 g, 54.361 mmol) was slowly syringed to the brown solution and the reaction mixture was stirred at ambient temperature for 65 hours. The yellow suspension was filtered and the precipitate was washed with THF (150 mL) to obtain the title compound as a yellow solid. Yield: 4.02 g, 9.994 mmol, 54%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 1.58 (s, 6H, $C(CH_3)_2$), 4.25 (s, 3H, N-CH_3), 7.39-7.41 (m, 2H), 7.45 (s, 1H), 7.49-7.51 (m, 1H), 7.64 (s, 1H), 7.67 (d, $^3J_{(H-H)}$ = 8 Hz, 1H), 7.79-7.80 (m, 1H), 7.92 (d, $^3J_{(H-H)}$ = 8.5 Hz, 1H), 8.03 (s, 1H), 10.73 (s, 1H); ^{13}C {^{1}H}NMR (125 MHz, CD_2Cl_2, 300 K): δ 27.1, 37.6, 48.0, 117.6, 121.1, 121.1, 121.2, 121.8, 123.3, 124.3, 127.8, 128.9, 133.8, 136.9, 137.6, 141.8, 154.6, 156.7; Elemental analysis (%) calcd for: $C_{19}H_{19}IN_2$: C, 56.73; H, 4.76; N, 6.96; Found: C, 57.02; H, 4.91; N, 6.72.

[(*flzmi*)Au(Cl)] (C1). [(SMe_2)Au(Cl)] (0.444 g, 2.610 mmol) was added to a solution of **C** (1.00 g, 2.490 mmol) in MeCN (200 mL). The reaction mixture was stirred for 20 minutes at room temperature. NaOAc (3.059 g, 37.288 mmol) was added and the solution was stirred at ambient temperature for 24 hours, resulting in a pink suspension. The reaction was quenched with H_2O (100 mL), extracted with CH_2Cl_2 (2 x 100 mL) and washed with brine (150 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The brown residue was purified by column chromatography on silica gel (eluent: EtOAc/Hexane = 1/1) to afford the title compound as an orange/white solid. Yield = 0.636 g, 1.255 mmol, 50%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 1.54 (s, 6H, $C(CH_3)_2$), 3.96 (s, 3H, N-CH_3), 7.15 (d, $^3J_{(H-H)}$ = 2 Hz, 1H), 7.33 (d, $^3J_{(H-H)}$ = 2 Hz, 1H), 7.39-7.37 (m, 2H), 7.48-7.50 (m, 1H), 7.58 (dd, $^3J_{(H-H)}$ = 8 Hz; $^4J_{(H-H)}$ = 2 Hz, 1H), 7.77-7.79 (m, 1H), 7.83-7.86 (m, 2H); ^{13}C {^{1}H}NMR (125 MHz, CD_2Cl_2, 300 K): δ 27.3, 38.7, 47.8, 119.9, 120.9, 121.1, 121.9, 122.6, 123.2, 123.8, 127.7, 128.5, 138.3, 138.5, 140.6, 154.6, 155.6, 181.7; Elemental analysis (%) calcd for: $C_{19}H_{18}AuClN_2$□$^1/_4$ C_6H_{14}: C, 46.60; H, 4.10; N, 5.30; Found: C, 46.81; H, 4.16; N, 4.96.

[(*flzmi*)Au(Cl)$_3$] (C2). $PhICl_2$ (0.414 g, 1.506 mmol) was added to a solution of **C1** (0.636 g, 1.255 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The mixture was stirred for 20 minutes in the dark. Afterwards, the ice-bath was removed and the mixture was stirred at room temperature for 24 hours, resulting in a red solution. The solvent was removed under reduced pressure and the brownish residue was washed with hexane (2 x 100 mL) to afford the title compound as a bright orange solid. Yield = 0.550 g, 0.952 mmol, 75%. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 1.55 (s, 6H, $C(CH_3)_2$), 4.07 (s, 3H, N-CH_3), 7.35 (s, 1H), 7.42-7.40 (m, 2H), 7.47 (s, 1H), 7.51 (t, $^3J_{(H-H)}$ = 5 Hz, 1H), 7.55 (d, $^3J_{(H-H)}$ = 8 Hz, 1H), 7.74 (s, 1H), 7.82 (t, $^3J_{(H-H)}$ = 5 Hz, 1H), 7.92 (d, $^3J_{(H-H)}$ = 8 Hz, 1H); ^{13}C {^{1}H}NMR (125 MHz, CD_2Cl_2, 300 K): δ 27.2, 38.6, 47.9, 121.3, 121.4, 121.8, 123.5, 125.1, 125.3, 125.5, 128.0, 129.1, 136.0, 138.0, 142.2, 154.7, 156.3; Elemental analysis (%) calcd for: $C_{19}H_{18}AuCl_3N_2$□CH_2Cl_2: C, 36.25; H, 3.04; N, 4.23; Found: C, 36.01; H, 2.78; N, 4.02.

***cis*-[(*flzmi*)Au(Cl)$_2$] (3).** The reaction was performed in the microwave. **C2** (0.200 g, 0.346 mmol) was suspended in H_2O (15 mL), heated to 200 °C and stirred for 15 minutes (2 cycles). The brownish/orange suspension was filtered and the solid washed with H_2O (100 mL) and Et_2O (200 mL) to obtain the title compound as a light brown solid. Yield = 0.118 g, 0.218 mmol, 63%. ^1H NMR (500 MHz, DMSO-*d6*, 300 K): δ 1.49 (s, 6H, $C(CH_3)_2$), 4.25 (s, 3H, N-CH_3), 7.37-7.35 (m, 2H), 7.58 (d, $^3J_{(H\text{-}H)}$ = 6 Hz, 1H), 7.75 (d, $^3J_{(H\text{-}H)}$ = 6 Hz, 1H), 7.82 (d, $^3J_{(H\text{-}H)}$ = 2 Hz, 1H), 7.99 (s, 1H), 8.39-8.37 (m, 2H); ^{13}C {^1H}NMR (125 MHz, DMSO-*d6*, 300 K): *δ* 27.7, 39.3, 47.7, 111.0, 117.6, 121.0, 123.2, 124.0, 127.1, 128.5, 128.8, 137.1, 138.7, 141.7, 153.2, 154.5, 155.5.

***cis*-[(*flzmi*)Au(C≡CC$_6$H$_5$F)$_2$] (3b).** (4-fluorophenylethynyl)trimethylsilane (0.047 g, 0.244 mmol) was dissolved in DMF (50 mL). CsF (0.067 g, 0.443 mmol) and CuI (0.084 g, 0.443 mmol) were added in this order and the reaction mixture was stirred for 20 minutes at room temperature resulting in an orange suspension. **3** (0.030 g, 0.055 mmol) was added and the reaction was stirred for 24 hours at room temperature, resulting in a deep red suspension. The reaction was quenched with H_2O (100 mL), extracted with CH_2Cl_2 (2 x 100 mL) and washed with brine (100 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The brownish residue was purified by column chromatography on silica gel (eluent: Hexane/EtOAc = 1/1) to afford the title compound as an orange/white solid. Yield = 0.016 g, 0.022 mmol, 41%. ^1H NMR (500 MHz, CD_2Cl_2, 300 K): *δ* 1.51 (s, 6H, $C(CH_3)_2$), 4.35 (s, 3H, N-CH_3), 7.00 (t, $^3J_{(H\text{-}H)}$ = 9 Hz, 2H), 7.08- 7.12 (m, 3H), 7.32-7.34 (m, 3H), 7.44-7.49 (m, 3H), 7.59 (d, $^3J_{(H\text{-}H)}$ = 2 Hz, 1H), 7.64-7.69 (m, 3H), 8.69 (s, 1H); ^{13}C {^1H}NMR (125 MHz, CD_2Cl_2, 300 K): *δ* 27.1 (Me), 38.9 (N-CH_3), 47.3, 97.2, 100.9, 102.9, 107.7, 109.0, 115.5, 115.6, 116.2, 120.2, 122.6, 122.7, 122.8, 124.0, 127.5, 129.0, 133.5, 133.8, 138.0, 138.5, 139.1, 144.9, 153.8, 153.9, 162.0, 162.2, 165.7; ^{19}F NMR (376 MHz, CD_2Cl_2, 300 K): *δ* -113.88 (s, *p*-1F), -114.03 (s, *p*-1F); Elemental analysis (%) calcd for: $C_{35}H_{25}AuF_2N_2$: C, 59.33; H, 3.56; N, 3.95; Found: C, 59.67; H, 3.63; N, 3.72; IR (ATR-FTIR): $\tilde{\nu}$(-C≡C-) = 2149 cm^{-1}, 2129 cm^{-1}.

Single Crystal X-ray Diffraction Studies

Crystal structure determinations – Selected single crystals of compounds **1**, **1a**, **1b**, **2a**, **2c**, **C**, **A1**, **A2**, **B1**, **B2** and **C** were studied by X-ray diffraction at 183(1) K on *Rigaku Oxford Diffraction*[1] *SuperNova / Atlas* (**1**, **1a**, **1b**, **2a**, **2c**, **A1**, **B1** and **C2**) and *Xcalibur / Ruby* area-detector diffractometers (**A2**, **B2** and **C**) using a single wavelength Enhance X-ray source with a MoK_α radiation for **1**, **2a**, **C**, **A1**, **A2**, **B1**, **B2** and **C** or a CuK_α radiation for **1a**, **1b** and **2c** from a micro-focus X-ray source and an *Oxford Instruments Cryojet XL* cooler. The selected single crystals were mounted using polybutene oil on a flexible loop fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction and analytical absorption correction[2] were carried out with the program *CrysAlisPro*[3]. Using *Olex2*_ENREF_63,[4] the crystal structures were solved with *ShelXS97*,[5] *SHELXT*[6] or *Superflip*[7] and refined with *SHELXL-2014/7*[8] (except **1** refined with *SHELXL-2013/4*) by full-matrix least-squares minimization on F^2. The results of the X-ray analyses were checked using *PLATON.*[9] For more details about the data collection and final parameters, see Tables S1 – S4 and the CIF files. **Refinement details** – **1**: All non-hydrogen atoms were anisotropically refined. All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H = 0.93 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ for aromatic H atoms, and with C—H = 0.96 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for methyl H atoms. **1a**: Solvent molecules of dichloromethane co-crystallized with the main Au(III) molecules in a ratio 1:1. All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H = 0.93 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ for aromatic H atoms, with C—H = 0.97 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ for methylene H atoms, and with C—H = 0.96 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for methyl H atoms. **1b**: Solvent molecules of hexane co-crystallized with the main Au(III) molecules in a ratio 1:2. The Au(III) molecules lie on mirror planes while the solvent molecules lie on center of inversion. The alkyne ligand *trans* to the carbene moiety and the hexane molecule are disordered over two sets of positions with a fixed site-occupancy factor of 0.5 due to their positions near symmetry elements. Some SHELXL restraints/constraints (DFIX, SADI and SIMU) were used to correct the geometry of some disordered moieties and the anisotropic thermal parameters of the corresponding atoms (see the _shelx_res_file section in the CIF for details). All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H = 0.93 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ for aromatic H atoms, with C—H = 0.97 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ for methylene H atoms, and with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms. **2a**: Solvent molecules of pentane co-crystallized with the main Au(III) molecules in a ratio 1:4. The pentafluorophenyl ligand *trans* to the carbene moiety is disordered over two sets of positions with site-occupancy factors of 0.775(16) and 0.225(16). The pentane molecule is also disordered and the site-occupancy factor was fixed at 0.25 to get reasonable thermal parameters. Many SHELXL restraints/constraints (DFIX, SADI, FLAT, SIMU and EADP) were used to correct the geometry of the disordered parts and the anisotropic thermal parameters of the corresponding atoms (see the _shelx_res_file section in the CIF for details). All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms, with C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) for methylene H atoms, and with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms. **2c**: There are two crystallographically independent Au(III) molecules in the asymmetric unit of **2c** and solvent molecules of dichloromethane co-crystallized with the main Au(III) molecules in a ratio 1:4. The *dbfmi* ligand in one molecule is partially disordered over two sets of positions with site-occupancy factors of 0.52(2) and 0.48(2). The dichloromethane molecule is also disordered and the site-occupancy factor was fixed at 0.25 to get reasonable thermal parameters. Many SHELXL restraints/constraints (DFIX, DANG, SADI, RIGU and EADP) were used to correct the geometry of the disordered parts and the anisotropic thermal parameters of the corresponding atoms (see the _shelx_res_file section in the CIF for details). All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms, with C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) for methylene H atoms, and with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms. **C**: All non-hydrogen atoms were anisotropically refined. All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms, and with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms. **A1**: There are two crystallographically independent Au(I) molecules in the asymmetric unit of **A1**. All non-hydrogen atoms were anisotropically refined. All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms, and with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms. **A2**: All non-hydrogen atoms were anisotropically refined. All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms, and with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms. **B1**: All non-hydrogen atoms were anisotropically refined. All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H = 0.93 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ for aromatic H atoms, and with C—H = 0.96 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for methyl H atoms. **B2**: All non-hydrogen atoms were anisotropically refined. All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H = 0.93 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ for aromatic H atoms, and with C—H = 0.96 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for methyl H atoms. **C2**: All non-hydrogen atoms were anisotropically refined. All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H = 0.93 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ for aromatic H atoms, and with C—H = 0.96 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for methyl H atoms. CCDC 1497778 (**1**), 1497779 (**1a**), 1497780 (**1b**), 1497781 (**A2**), 1497782 (**A1**), 1497783 (**2a**), 1497784 (**2c**), 1497785 (**C**), 1497786 (**B1**), 1497787 (**B2**) and 1497788 (**C2**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre. Copies of data can be obtained free of charge at http://www.ccdc.cam.ac.uk/products/csd/request/.

Table S1. Crystallographic data and refinement parameters for **1**, **1a** and **1b**.

	1	**1a**	**1b**
CCDC number	1497778	1497779	1497780
Empirical formula	$C_{10}H_9AuCl_2N_2$	$C_{22}H_9AuF_{10}N_2$, CH_2Cl_2	$C_{26}H_{17}AuF_2N_2$, 0.5(C_6H_{14})
Formula weight	425.06	773.20	635.47
Temperature/K	183(1)	183(1)	183(1)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Pbca	$P2_1/n$	$P2_1/m$
a/Å	15.0499(2)	7.46130(10)	12.6163(2)
b/Å	7.55959(10)	14.2119(2)	6.87230(10)
c/Å	19.0308(3)	22.5071(4)	15.3236(3)
α/°	90	90	90
β/°	90	90.509(2)	111.884(2)
γ/°	90	90	90
Volume/Å^3	2165.16(5)	2386.56(7)	1232.86(4)
Z	8	4	2
ρ_{calc}mg/mm^3	2.608	2.152	1.712
m/mm^{-1}	14.046	14.545	11.496
F(000)	1568.0	1464.0	618.0
Crystal size/mm^3	0.18 × 0.16 × 0.02	0.21 × 0.13 × 0.01	0.19 × 0.03 × 0.02
Radiation	Mo Kα (λ = 0.71073 Å)	Cu Kα (λ = 1.54184 Å)	CuKα (λ = 1.54184)
2Θ range for data collection	4.28 to 54.97°	7.36 to 148.95°	6.22 to 153.47°
Index ranges	$-19 \leq h \leq 19$, $-9 \leq k \leq 9$, $-24 \leq l \leq 24$	$-9 \leq h \leq 8$, $-17 \leq k \leq 14$, $-28 \leq l \leq 28$	$-15 \leq h \leq 15$, $-8 \leq k \leq 8$, $-18 \leq l \leq 19$
Reflections collected	18519	19315	21225
Independent reflections	2476[R_{int} = 0.0337]	4862[R_{int} = 0.0348]	2807 [R_{int} = 0.0360, R_{sigma} = 0.0153]
Data/restraints/parameters	2476/0/137	4862/0/344	2807/111/225
Goodness-of-fit on F^2	1.091	1.128	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0219, wR_2 = 0.0540	R_1 = 0.0322, wR_2 = 0.0846	R_1 = 0.0243, wR_2 = 0.0641
Final R indexes [all data]	R_1 = 0.0279, wR_2 = 0.0578	R_1 = 0.0330, wR_2 = 0.0853	R_1 = 0.0251, wR_2 = 0.0647
Largest diff. peak/hole / e Å^{-3}	1.77/-0.74	1.56/-0.91	1.85/-0.72

Table S2. Crystallographic data and refinement parameters for **2a**, **2c** and **C**.

	2a	**2c**	**C**
CCDC number	1497783	1497784	1497785
Empirical formula	4($C_{28}H_{11}AuF_{10}N_2O$), C_5H_{12}	4($C_{30}H_{15}AuF_6N_2O$), CH_2Cl_2	$C_{19}H_{19}N_2$, I
Formula weight	6371.12	3006.55	402.26
Temperature/K	183(1)	183(1)	183(1)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	C2/c	$P2_1/n$	Pbca
a/Å	31.2423(17)	14.9429(4)	10.1622(2)
b/Å	13.2690(7)	13.3830(4)	14.9458(4)
c/Å	14.5873(7)	27.7426(13)	22.7760(6)
α/°	90	90	90
β/°	102.587(5)	93.587(3)	90
γ/°	90	90	90
Volume/Å^3	5901.9(5)	5537.1(3)	3459.27(15)
Z	1	2	8
ρ_{calc}mg/mm^3	1.793	1.803	1.545
m/mm^{-1}	5.074	11.036	1.850
F(000)	3044.0	2884.0	1600.0
Crystal size/mm^3	0.2 × 0.15 × 0.05	0.27 × 0.07 × 0.02	0.37 × 0.28 × 0.14
Radiation	Mo Kα (λ = 0.71073 Å)	Cu Kα (λ = 1.54184 Å)	Mo Kα (λ = 0.71073 Å)
2Θ range for data collection	4.21 to 52.74°	6.4 to 136.5°	5.166 to 55.11°
Index ranges	$-38 \leq h \leq 38$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$	$-18 \leq h \leq 17$, $-16 \leq k \leq 16$, $-33 \leq l \leq 33$	$-13 \leq h \leq 13$, $-19 \leq k \leq 19$, $-29 \leq l \leq 29$
Reflections collected	16439	39541	33124
Independent reflections	16439 [R_{sigma} = 0.0456]	10053 [R_{int} = 0.0583, R_{sigma} = 0.0434]	3999 [R_{int} = 0.0388, R_{sigma} = 0.0184]
Data/restraints/parameters	16439/532/475	10053/114/715	3999/0/202
Goodness-of-fit on F^2	1.049	1.047	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0454, wR_2 = 0.1252	R_1 = 0.0732, wR_2 = 0.2042	R_1 = 0.0292, wR_2 = 0.0784
Final R indexes [all data]	R_1 = 0.0800, wR_2 = 0.1379	R_1 = 0.0837, wR_2 = 0.2139	R_1 = 0.0347, wR_2 = 0.0818
Largest diff. peak/hole / e Å^{-3}	1.82/-0.64	3.36/-2.58	1.31/-0.64

Table S3. Crystallographic data and refinement parameters for **A1**, **A2** and **B1.**

	A1	**A2**	**B1**
CCDC number	1497782	1497781	1497786
Empirical formula	$C_{10}H_{10}AuClN_2$	$C_{10}H_{10}AuCl_3N_2$	$C_{16}H_{12}AuClN_2O$
Formula weight	390.62	461.52	480.69
Temperature/K	183(1)	183(1)	183(1)
Crystal system	triclinic	monoclinic	triclinic
Space group	P-1	$P2_1/n$	P-1
a/Å	8.9263(2)	7.9815(2)	7.42395(15)
b/Å	9.1203(2)	19.0268(4)	9.71840(19)
c/Å	13.5093(2)	9.0159(2)	11.1571(2)
α/°	89.5116(17)	90	75.0300(16)
β/°	84.5109(16)	109.315(3)	73.7053(17)
γ/°	77.147(2)	90	69.5966(18)
Volume/Å^3	1067.24(4)	1292.11(6)	712.55(3)
Z	4	4	2
ρ_{calc}mg/mm^3	2.431	2.372	2.240
m/mm^{-1}	13.994	11.979	10.509
F(000)	720.0	856.0	452.0
Crystal size/mm^3	0.25 × 0.22 × 0.04	0.22 × 0.19 × 0.06	0.28 × 0.13 × 0.03
Radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
2Θ range for data collection	4.58 to 56.56°	5.24 to 61.02°	4.54 to 61.01°
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-18 \leq l \leq 18$	$-11 \leq h \leq 11$, $-27 \leq k \leq 27$, $-12 \leq l \leq 12$	$-10 \leq h \leq 10$, $-13 \leq k \leq 13$, $-15 \leq l \leq 15$
Reflections collected	21789	27810	17387
Independent reflections	5281[R_{int} = 0.0327]	3947 [R_{int} = 0.0446, R_{sigma} = 0.0214]	4346 [R_{int} = 0.0235, R_{sigma} = 0.0196]
Data/restraints/parameters	5281/0/255	3947/0/146	4346/0/191
Goodness-of-fit on F^2	1.025	1.139	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0255, wR_2 = 0.0649	R_1 = 0.0208, wR_2 = 0.0483	R_1 = 0.0166, wR_2 = 0.0401
Final R indexes [all data]	R_1 = 0.0294, wR_2 = 0.0674	R_1 = 0.0225, wR_2 = 0.0490	R_1 = 0.0183, wR_2 = 0.0409
Largest diff. peak/hole / e Å^{-3}	1.41/-1.74	0.76/-1.26	0.9/-0.65

Table S4. Crystallographic data and refinement parameters for **B2** and **C2.**

	B2	**C2**
CCDC number	1497787	1497788
Empirical formula	$C_{16}H_{12}AuCl_3N_2O$	$C_{19}H_{18}AuCl_3N_2$
Formula weight	551.59	577.67
Temperature/K	183(1)	183(1)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Pca2_1$
a/Å	12.4966(4)	17.61694(20)
b/Å	10.2798(3)	7.56666(9)
c/Å	13.1496(3)	14.8780(2)
α/°	90	90
β/°	90.296(3)	90
γ/°	90	90
Volume/Å^3	1689.20(8)	1983.26(4)
Z	4	4
ρ_{calc}mg/mm^3	2.169	1.935
m/mm^{-1}	9.187	7.826
F(000)	1040.0	1104.0
Crystal size/mm^3	0.33 × 0.13 × 0.11	0.24 × 0.12 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection	5.03 to 61.01°	4.6 to 52.7°
Index ranges	$-16 \leq h \leq 17$, $-14 \leq k \leq 14$, $-18 \leq l \leq 18$	$-22 \leq h \leq 22$, $-9 \leq k \leq 9$, $-18 \leq l \leq 18$
Reflections collected	25348	18197
Independent reflections	5144 [R_{int} = 0.0413, R_{sigma} = 0.0301]	4044 [R_{int} = 0.0244, R_{sigma} = 0.0192]
Data/restraints/parameters	5144/0/209	4044/1/229
Goodness-of-fit on F^2	1.070	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0239, wR_2 = 0.0555	R_1 = 0.0149, wR_2 = 0.0325
Final R indexes [all data]	R_1 = 0.0302, wR_2 = 0.0585	R_1 = 0.0167, wR_2 = 0.0333
Largest diff. peak/hole / e Å^{-3}	1.18/-1.02	0.42/-0.28
Flack parameter	-	-0.019(3)

Table S5. Selected bond distances (Å) and bond angles (°) for **1**- **1b**, **2a**, **2c**, **C**, **A1**, **A2**, **B1**, **B2** and **C**.

	Au–$C_{(C^\wedge C)carb}$	Au–$C_{(C^\wedge C)phen}$	Au–$C_{C_6F_5}$		Au–$C_{C_8H_4F_5}$		N–$C_{central}$	$C_{(C^\wedge C)carb}$–Au–$C_{(C^\wedge C)phen}$
			trans (C^C)carb.	*trans* (C^C)phen.	*trans* (C^C)carb.	*trans* (C^C)phen.		
1	2.010(5)	2.038(4)	-	-	-	-	1.414(5)	80.08(16)
1a	2.047(4)	2.068(5)	2.065(5)	2.089(4)	-	-	1.428(6)	79.43(17)
1b	2.039(4)	2.037(4)	-	-	2.048(5)	2.073(4)	1.414(6)	79.6(2)
2a	2.051(9)	2.057(8)	2.056(10)	2.117(6)[1] 2.117(9)	-	-	1.426(11)	79.5(4)
2c	2.025(11)[2] 2.056(11)	2.075(12) 2.061(11)	-	2.090(12) 2.067(10)	1.987(10) 1.994(14)	-	1.425(10) 1.410(16)	81.2(5) 80.0(5)
A1	1.980(5)[2] 1.982(5)	-	-	-	-	-	1.446(6) 1.447(6)	-
A2	2.001(3)	-	-	-	-	-	1.442(4)	-
B1	1.980(2)	-	-	-	-	-	1.422(3)	-
B2	1.994(3)	-	-	-	-	-	1.434(4)	-
C2	1.993(4)	-	-	-	-	-	1.439(6)	-
C	-	-	-	-	-	-	1.446(3)	-

[1] two values are given due to the disorder, [2] two values are given due to the two independent molecules in the asymmetric unit.

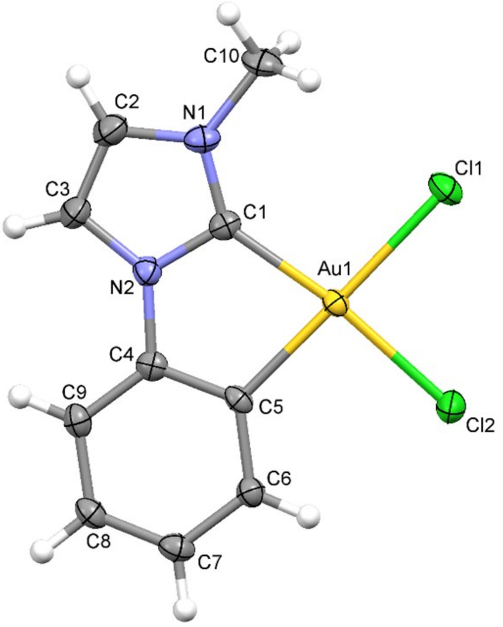


Figure S1. X-ray crystal structure of **1** with thermal ellipsoids shown at 30% probability.

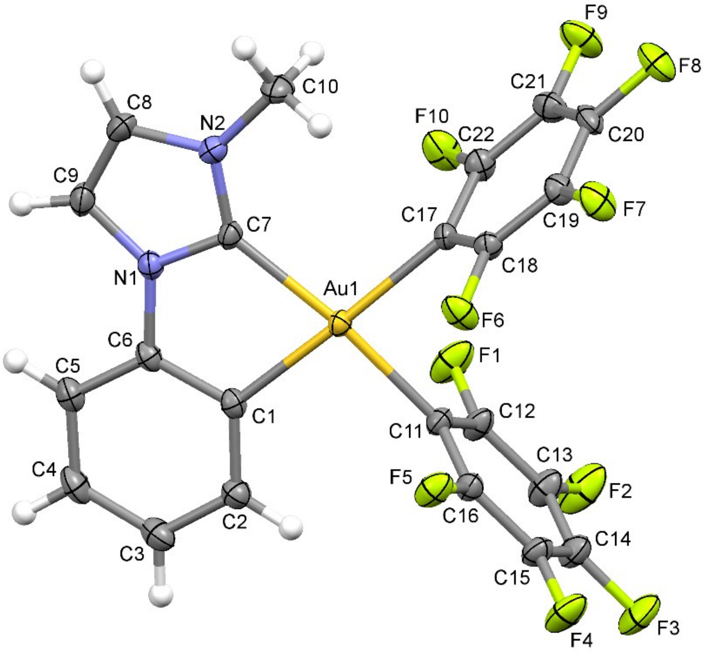


Figure S2. X-ray crystal structure of **1a** with thermal ellipsoids shown at 30% probability (the dichloromethane solvent molecule has been omitted for clarity).

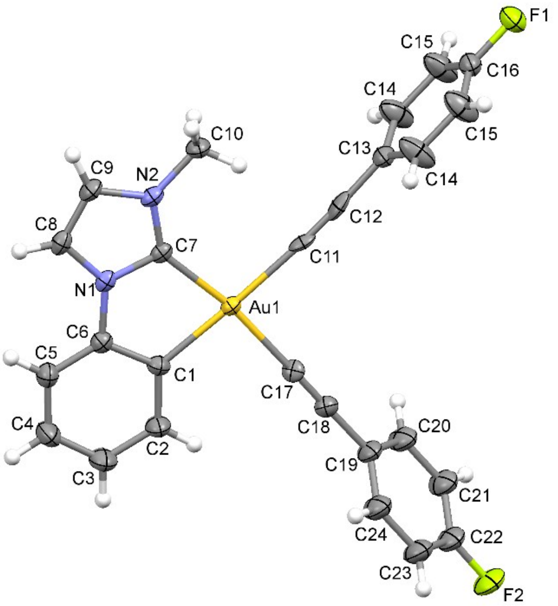


Figure S3. X-ray crystal structure of **1b** with thermal ellipsoids shown at 30% probability (the hexane solvent molecule and the minor component of the disordered alkyne ligand have been omitted for clarity).

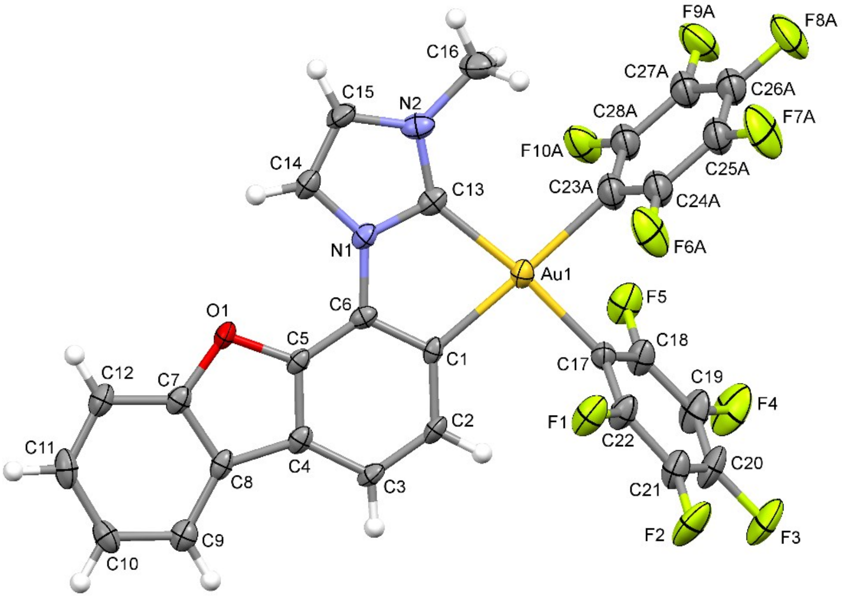


Figure S4. X-ray crystal structure of **2a** with thermal ellipsoids shown at 30% probability (the pentane solvent molecule and the minor component of the disordered pentafluorophenyl have been omitted for clarity).

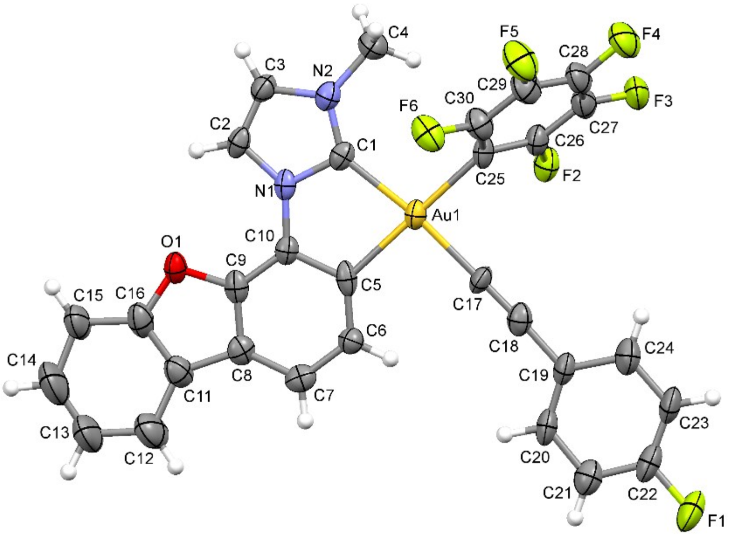


Figure S5. X-ray crystal structure of **2c** with thermal ellipsoids shown at 30% probability (the dichloromethane solvent molecule and the second crystallographically independent Au(III) molecule have been omitted for clarity).

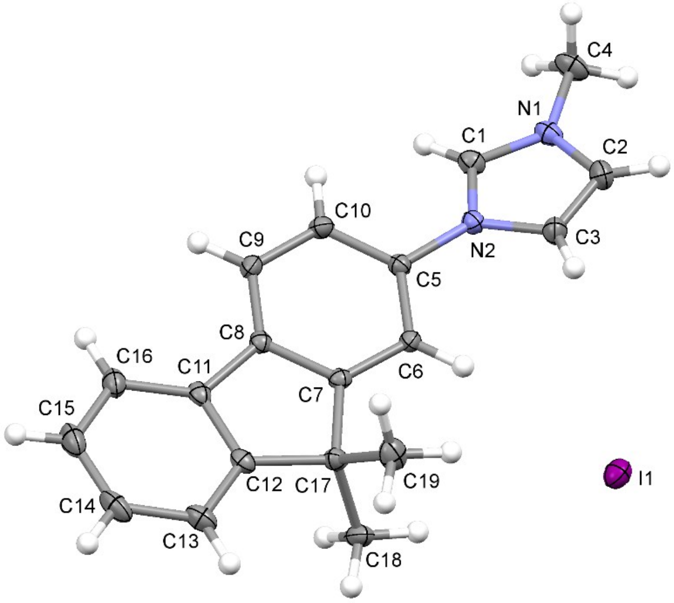


Figure S6. X-ray crystal structure of **C** with thermal ellipsoids shown at 30% probability.

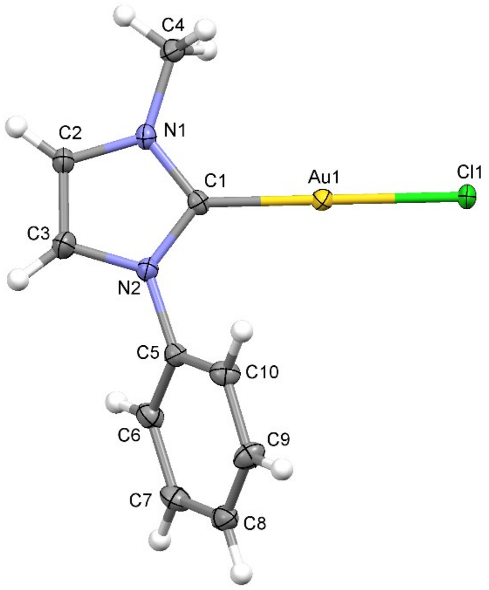


Figure S7. X-ray crystal structure of **A1** with thermal ellipsoids shown at 30% probability (the second crystallographically independent Au(I) molecule has been omitted for clarity).

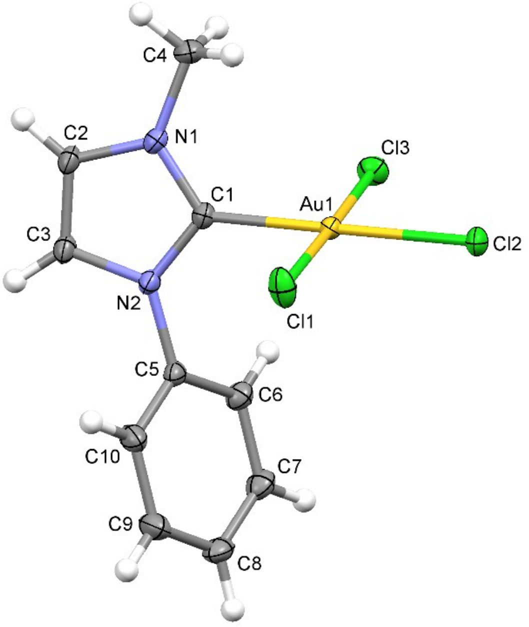


Figure S8. X-ray crystal structure of **A2** with thermal ellipsoids shown at 30% probability.

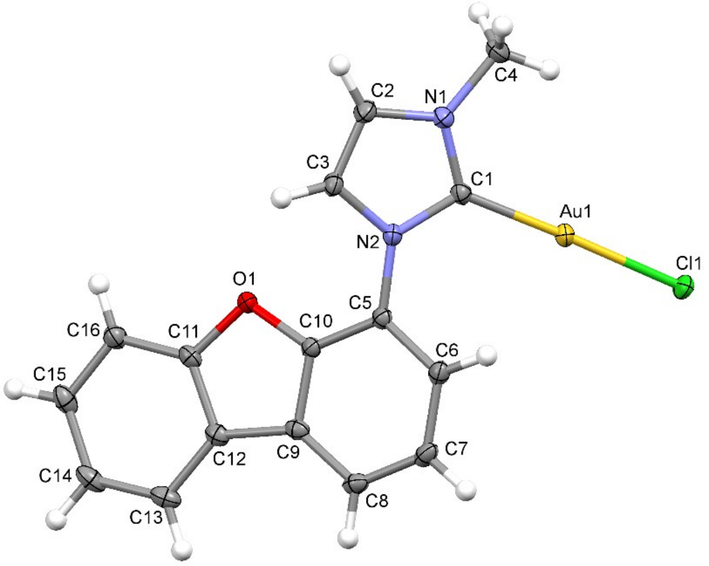


Figure S9. X-ray crystal structure of **B1** with thermal ellipsoids shown at 30% probability.

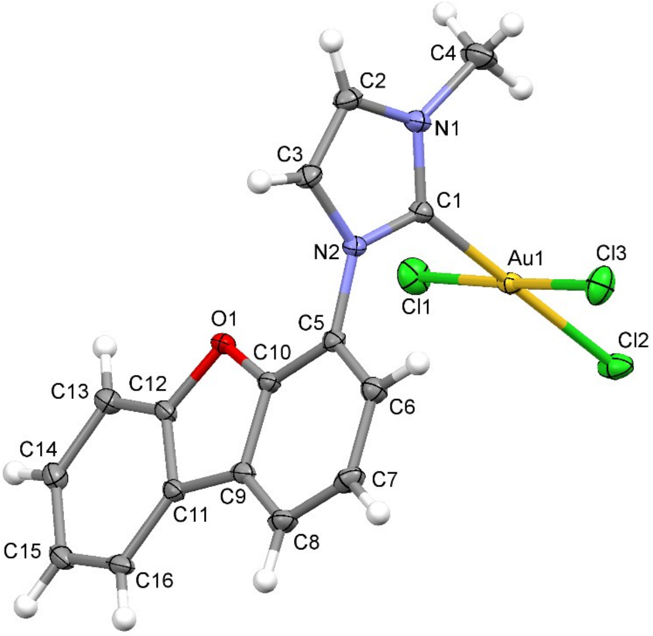


Figure S10. X-ray crystal structure of **B2** with thermal ellipsoids shown at 30% probability.

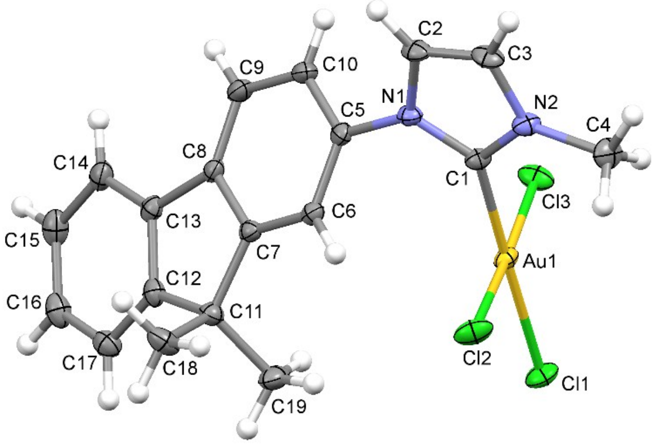


Figure S11. X-ray crystal structure of **C2** with thermal ellipsoids shown at 30% probability.

Photophysical Studies

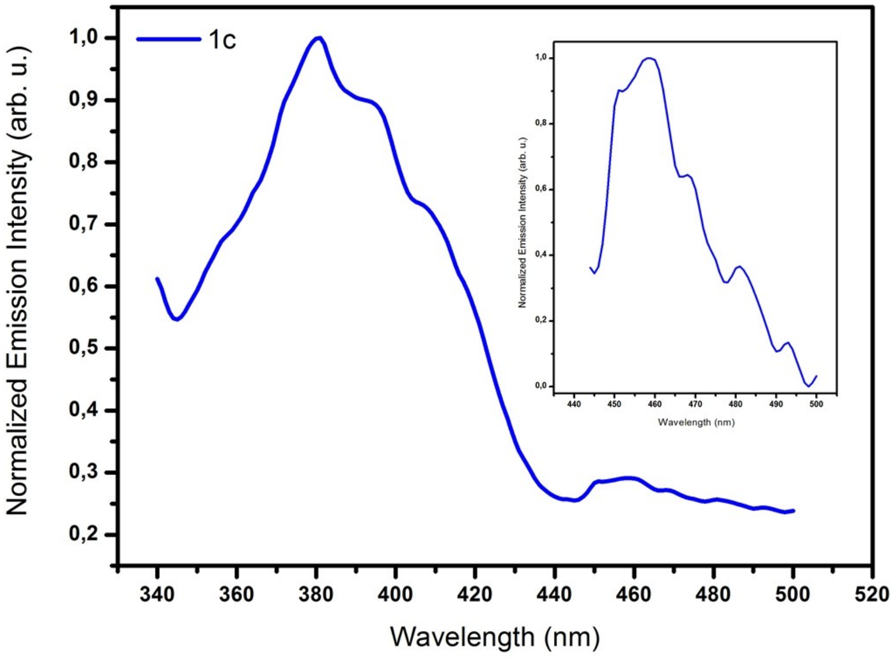


Figure S12. Normalized emission spectra of **1c** in a PMMA matrix (5 wt%). Inset: Enlarged emission spectrum of the phosphorescence emission.

Table S6. Summary of photophysical studies of all luminescent complexes.

Complex	Absorption(a) λ_{max} [nm] (ε_{max} [M^{-1} cm^{-1}])	Emission r.t. solution(a) / 77 K(b) λ_{max} [nm]	τ [μs]	r.t. Φ_P(c) [%]	k_r[s^{-1}] x10^{-3}	k_{nr}[s^{-1}] x10^{-5}	Emission 5wt% PMMA λ_{max} [nm]	Φ_{em}(c) [%]
1a	293 (1720)	409, 433, 460 (77 K)	0.62 (77 K)	-	-	-	414, 433, 450	1.41
1b	295 (17200)	416, 435, 450 (r.t.) 410, 432, 450 (77 K)	0.49 (r.t.) 0.59 (77 K)	<1	-	-	415, 435, 452	5.40
1c	293 (9750)	408, 429, 449 (77 K)	0.52 (77 K)	-	-	-	381, 395, 407 459, 468, 481	1.23(d)
1d	306 (1570)	332, 345, 357 (r.t.)	0.07 (r.t.)	<1	-	-		
2a	311 (12040) 283 (15170) 275 (10930)	450, 481, 514 (r.t.)	4.16 (r.t.)	1.63	3.9	2.4	451, 483, 516	8.13
2b	313 (25370) 284 (24833) 278 (20409)	450, 482, 513 (r.t.)	0.65 (r.t.)	10.42	162.8	13.8	451, 481, 514	12.43
2c	312 (20070) 284 (23303) 276 (18460)	451, 484, 518 (r.t.)	2.94 (r.t.)	1.89	6.4	3.3	451, 483, 516	2.51
2d	312 (11290)	450, 479 (r.t.)	0.74 (r.t.)	<1	-	-		
3b	321 (4804) 296 (8678) 270 (12808)	477, 509, 545 (r.t.)	0.57 (r.t.)	3.93	68.9	16.9	477, 508, 546	16.49

a) Measured in THF. b) Measured in 2-Me-THF. c) Phosphorescence quantum yield doped in PMMA (5wt%). (d) Luminescence quantum yield doped in PMMA (5wt%).

Thermogravimetric analysis

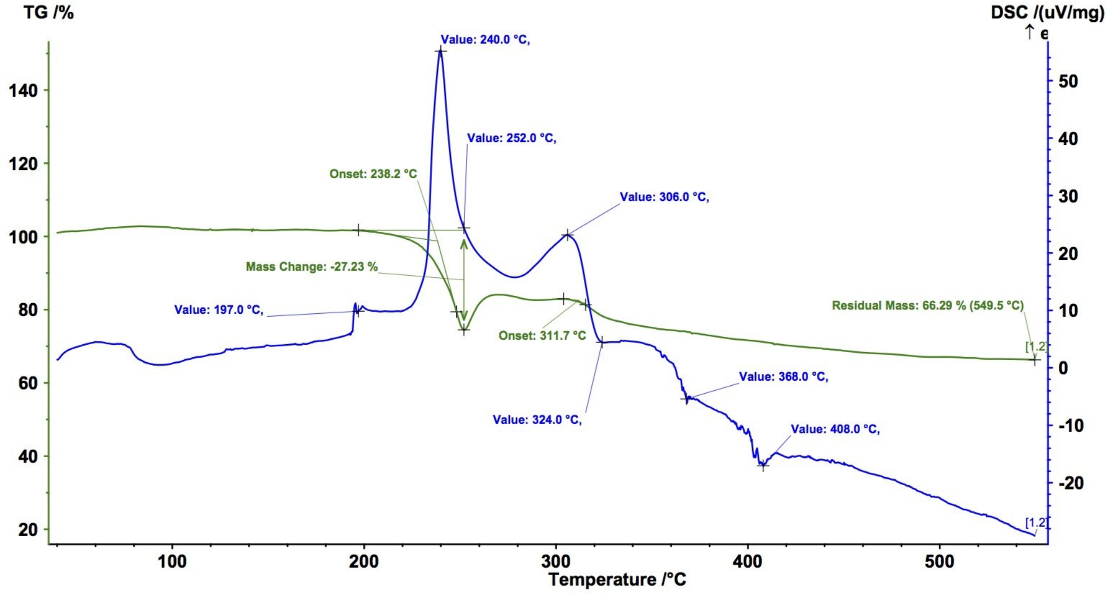


Figure S13. TG analysis and DSC measurement of compound **2b**.

Computational studies

Computational details. The luminescent properties of compounds **1a**, **1b**, **1c** and **2a** were studied by density functional theory (DFT) calculations using the Gaussian 09 program package.[10] The hybrid functional PBE1PBE[11] was associated with the Stuttgart/Dresden effective core potentials (SDD) basis set[12] for the Au center augmented with one *f*-polarization function (α = 1.050) and the standard 6-31+G(d) basis set[13] for the remaining atoms in all calculations. The optimized geometries of the ground states S_0 and lowest triplet states T_1 of the selected compounds were obtained by DFT calculations without symmetry restriction in the gas phase (restricted method for the ground states, unrestricted calculations for the the triplet states). The final geometries were confirmed to be potential energy minima by vibrational frequency calculations at the same level of theory, as no imaginary frequency was found. On the DFT optimized ground-state S_0 geometries, time-dependent DFT (TD-DFT) calculations[14] associated with the conductive polarizable continuum model (CPCM)[15] were used to produce the first twenty lowest singlet–singlet S_0–S_n and the first two singlet–triplet S_0–T_1 vertical excitations in tetrahydrofuran with the corresponding energies, transition coefficients, and oscillator strengths. The molecular orbital and spin density plots reported in the manuscript were generated by *Gaussview*[16] on *Gaussian* output files obtained from the TD-DFT calculations including the solvent effects (CPCM / tetrahydrofuran).

Table S7. Selected singlet (S_1, and S_n with oscillator strength $f > 0.05$) and triplet T_m excited states (m = 1-3) calculated with TD-DFT/CPCM (in tetrahydrofuran): vertical excitation energies (nm), transition coefficients ($c > 0.2$), orbitals involved in the transitions, and oscillator strengths f for compounds **1a**, **1b**, **1c** and **2a**.

	1a	**1b**	**1c**	**2a**
S_0–S_n[a]	n = 1 281.7 (f = 0.017) H→L (c = 0.69)	n = 1 320.0 (f = 0.000) H→L (c = 0.70)	n = 1 309.3 (f = 0.000) H→L (c = 0.69)	n = 1 312.3 (f = 0.137) H→L (c = 0.69)
	n = 8 245.8 (0.062) H-1→L+1 (0.62)	n = 4 263.5 (0.090) H-3→L (0.58) H→L+1 (0.23)	n = 3 268.0 (0.115) H→L+1 (0.68)	n = 2 296.4 (0.328) H-1→L (0.67)
	n = 12 230.6 (0.234) H-6→L (0.67)	n = 5 262.3 (0.532) H→L+1 (0.61)	n = 4 260.2 (0.101) H-4→L (0.50) H-2→L (0.33)	n = 6 258.6 (0.363) H-6→L (0.43) H→L+2 (0.38)
	n = 17 224.1 (0.523) H→L+2 (0.54)	n = 8 254.1 (0.317) H→L+3 (0.46) H→L+2 (0.12)	n = 6 254.5 (0.655) H→L+2 (0.67)	n = 10 249.3 (0.283) H→L+2 (0.45)
		n = 9 251.9 (0.550) H-4→L (0.56) H→L+3 (0.31)	n = 10 244.8 (0.305) H-5→L (0.51) H-1→L+3 (0.30) H-4→L (0.29)	n = 13 242.3 (0.113) H-5→L+1 (0.42)
		n = 10 250.2 (0.230) H-1→L+1 (0.57)	n = 18 226.5 (0.398) H-7→L (0.55) H-1→L+3 (0.28)	n = 19 227.9 (0.110) H→L+3 (0.57)
		n = 12 246.8 (0.301) H-5→L (0.55) H-2→L+2 (0.28) H-3→L (0.23)		
		n = 13 243.9 (0.060) H-1→L+3 (0.55)		
		n = 16 239.6 (0.106) H-1→L+3 (0.46) H-1→L+6 (0.37) H→L+6 (0.30)		
S_0–T_1	387.3 H→L (0.59)	405.8 H→L+1 (0.43) H-7→L+4 (0.25)	404.8 H→L+2 (0.58)	437.9 H→L (0.61)
S_0–T_2	342.0 H-3→L+6 (0.28) H-1→L+5 (0.26) H-3→L+7 (0.24)	402.8 H→L+3 (0.45) H-6→L+5 (0.25)	386.8 H-1→L (0.59)	361.6 H-1→L (0.54)
S_0–T_3	341.5 H-2→L+7 (0.36)	387.4 H-2→L (0.45)	315.5 H→L (0.68)	342.1 H-5→L+4 (0.25) H-4→L+6 (0.24) H-2→L+6 (0.24)

[a] H = HOMO, L = LUMO.

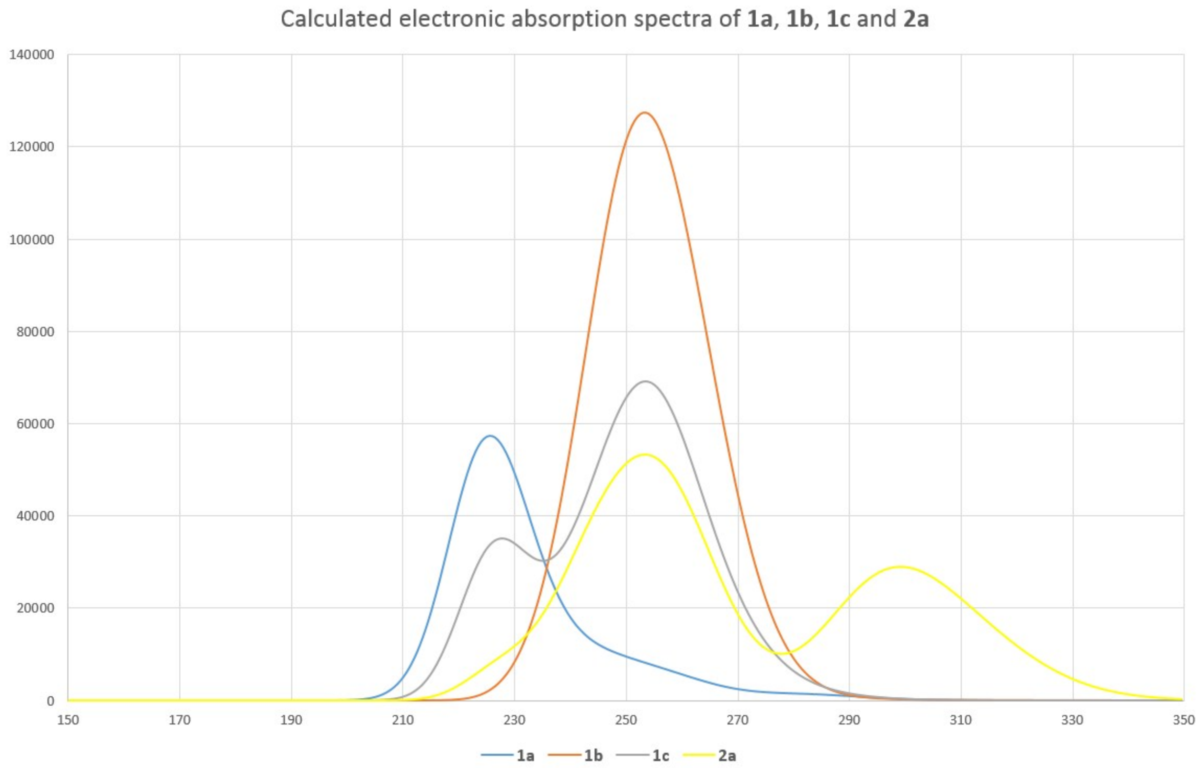
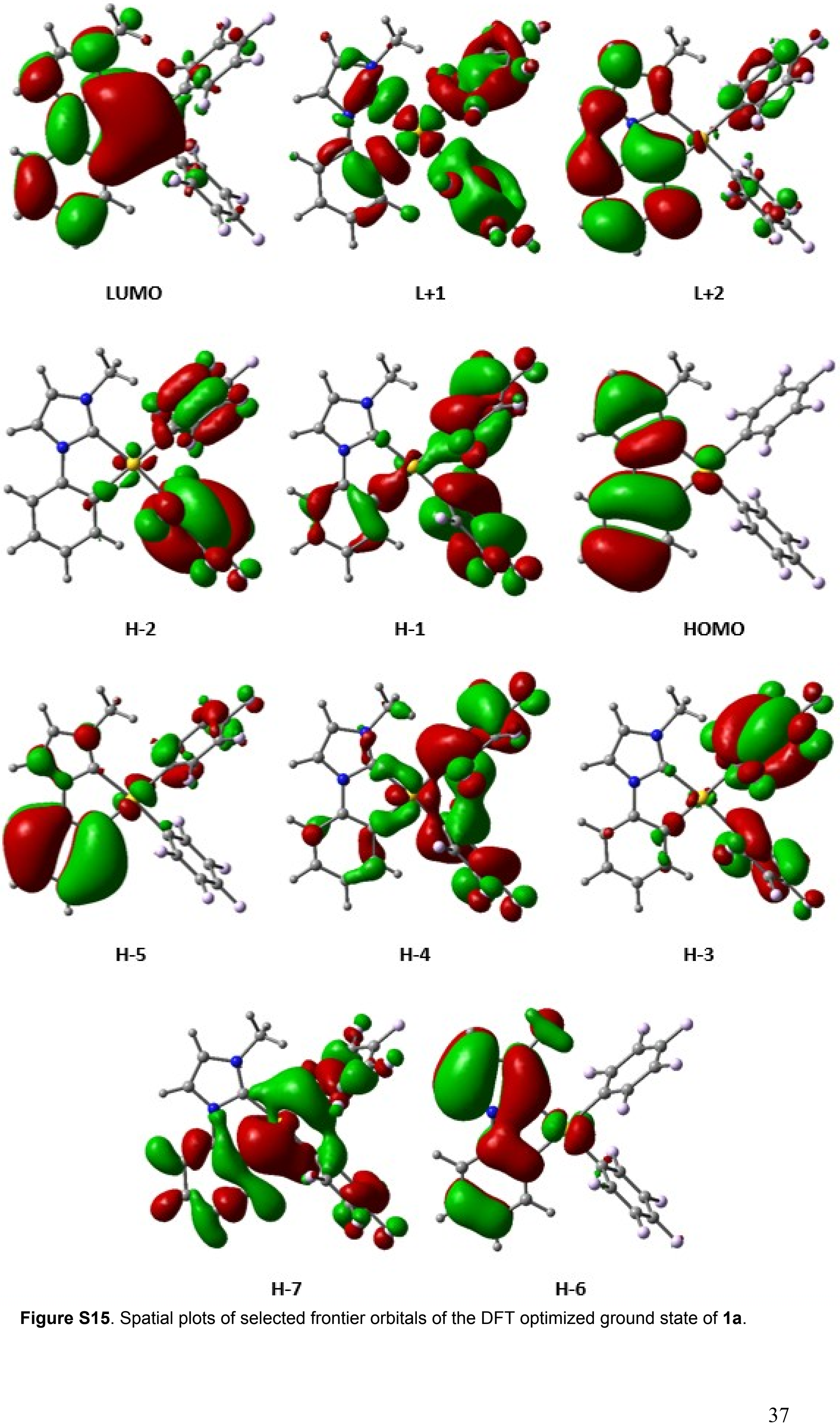


Figure S14. Calculated electronic absorption spectra of **1a**, **1b**, **1c** and **2a** (data from Gaussview[16] with 1500cm^{-1} half-width at half height).



LUMO L+1 L+2

H-2 H-1 HOMO

H-5 H-4 H-3

H-7 H-6

Figure S15. Spatial plots of selected frontier orbitals of the DFT optimized ground state of **1a**.

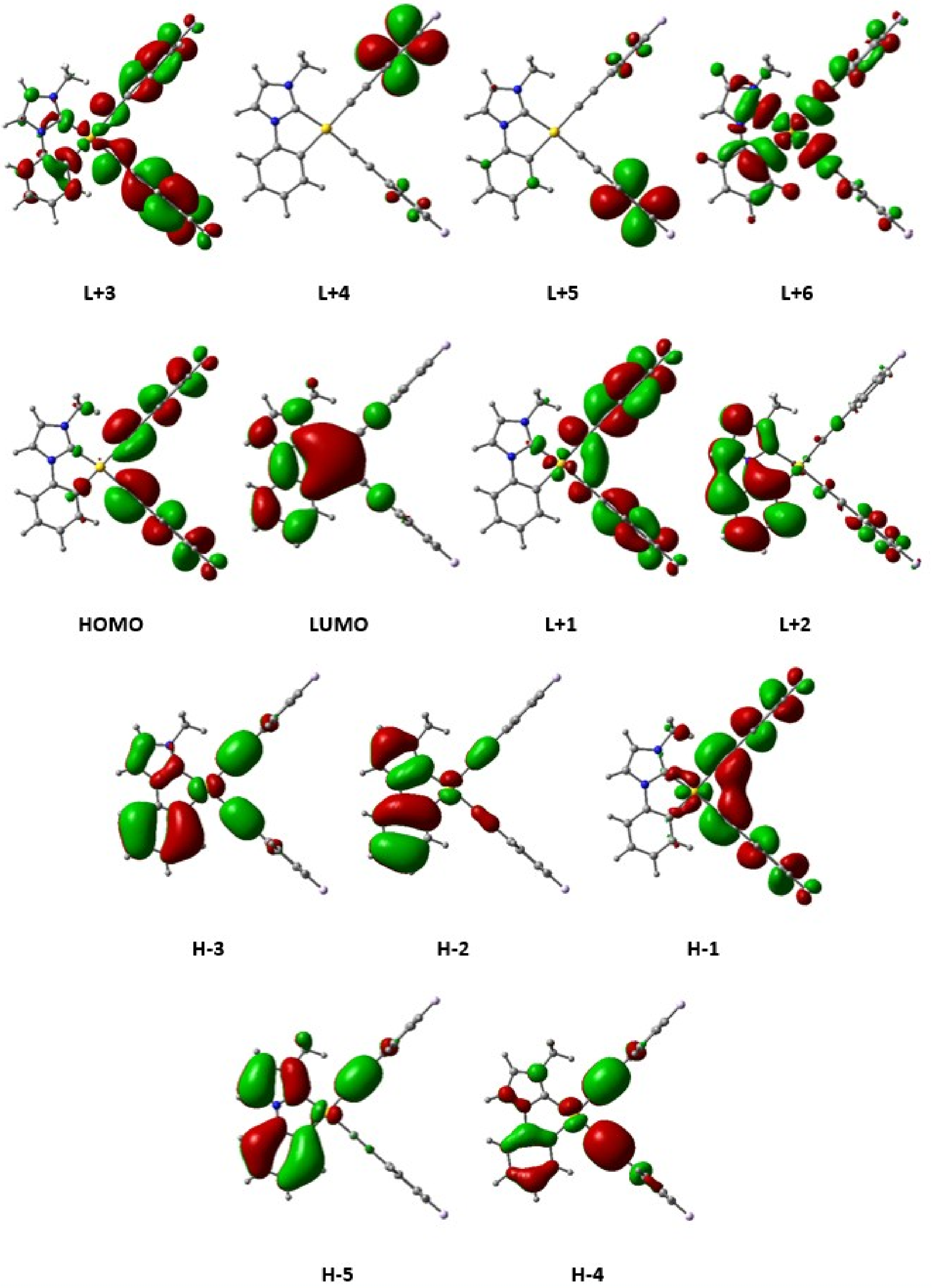


Figure S16. Spatial plots of selected frontier orbitals of the DFT optimized ground state of **1b**.

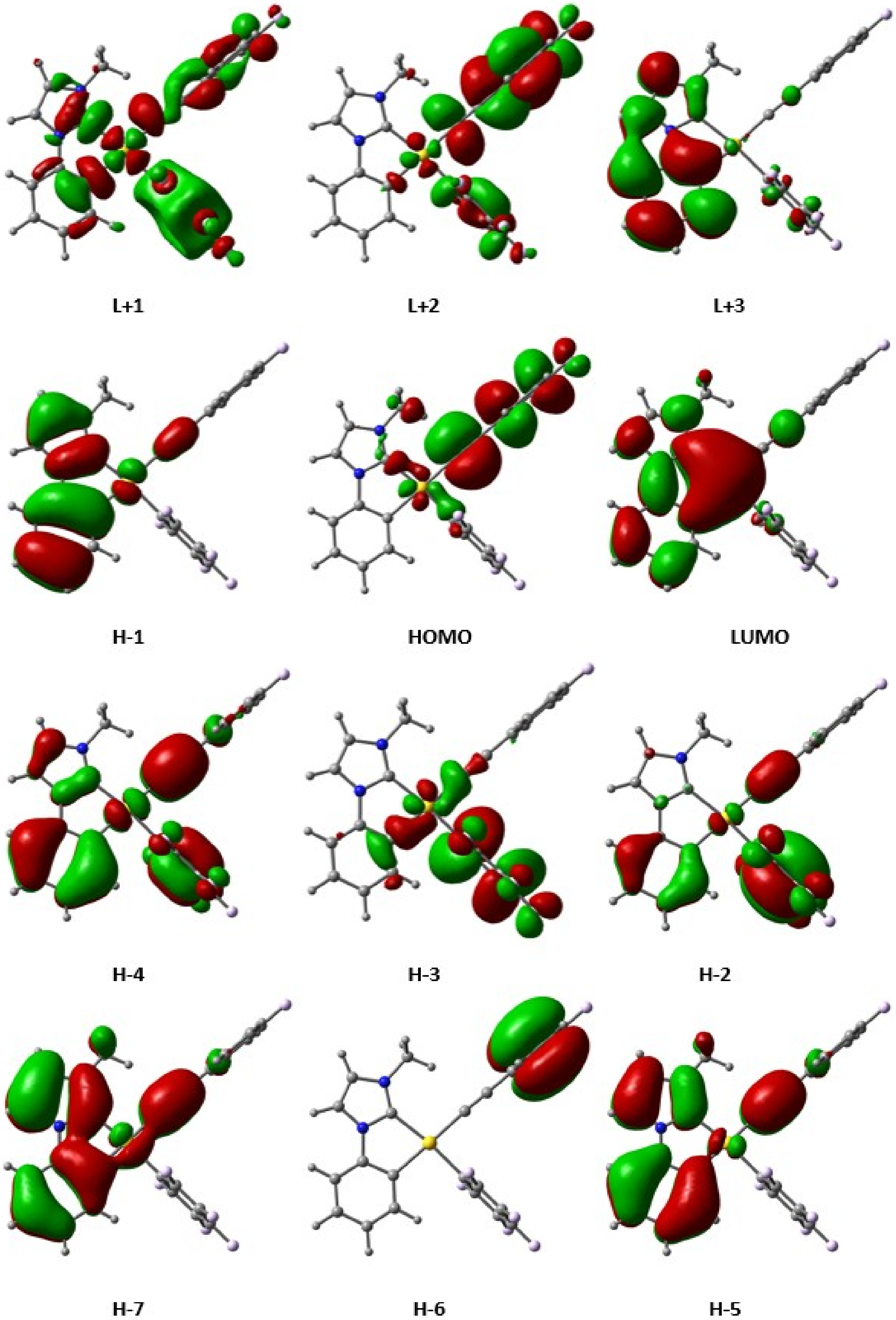
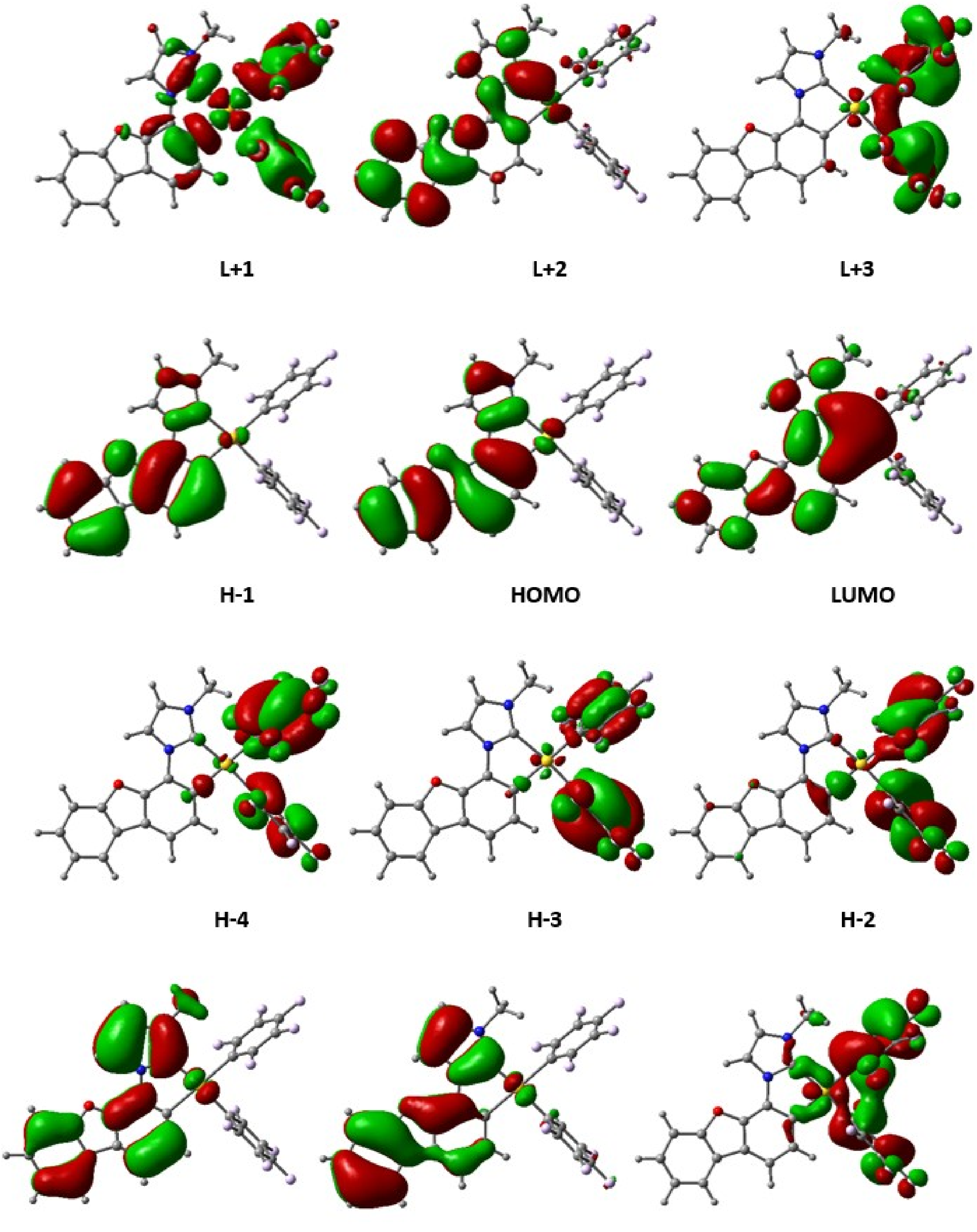


Figure S17. Spatial plots of selected frontier orbitals of the DFT optimized ground state of **1c**.



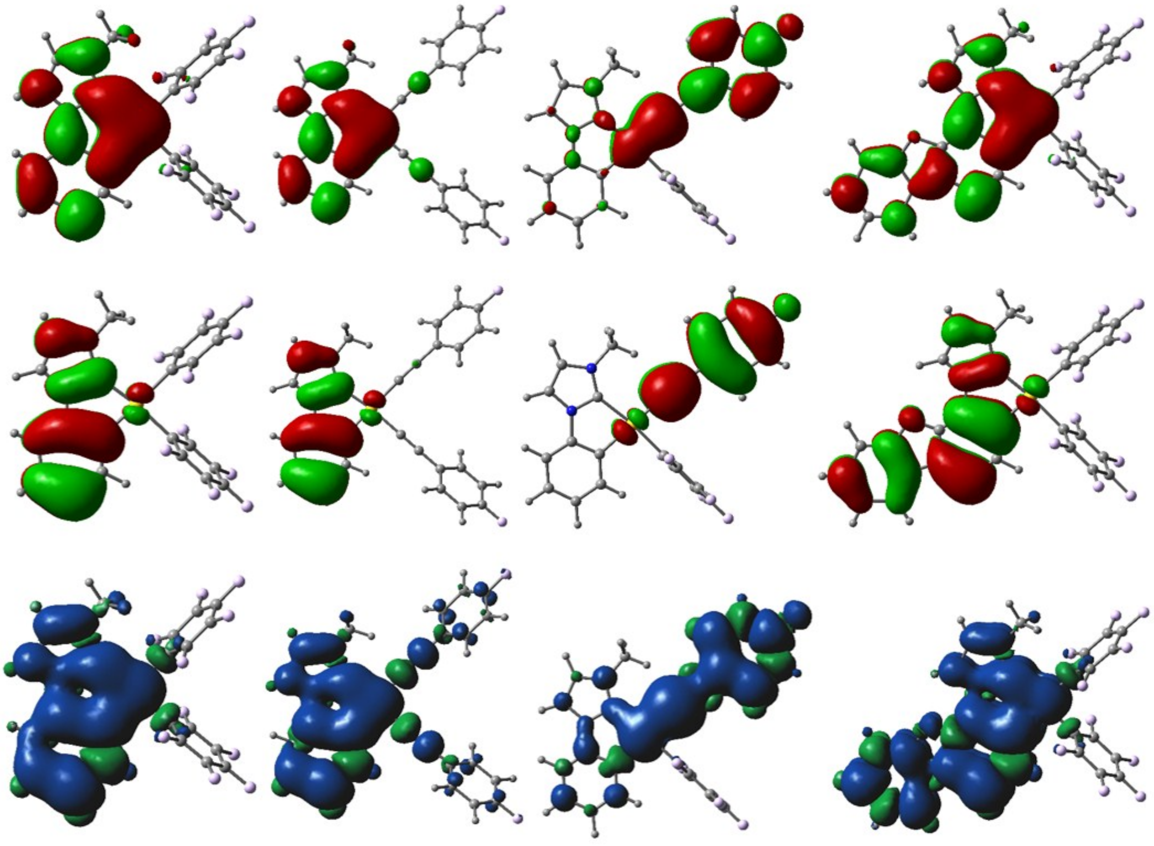
L+1 L+2 L+3

H-1 HOMO LUMO

H-4 H-3 H-2

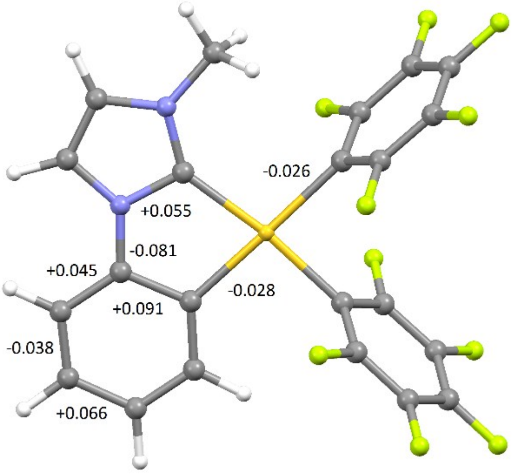
H-7 H-6 H-5

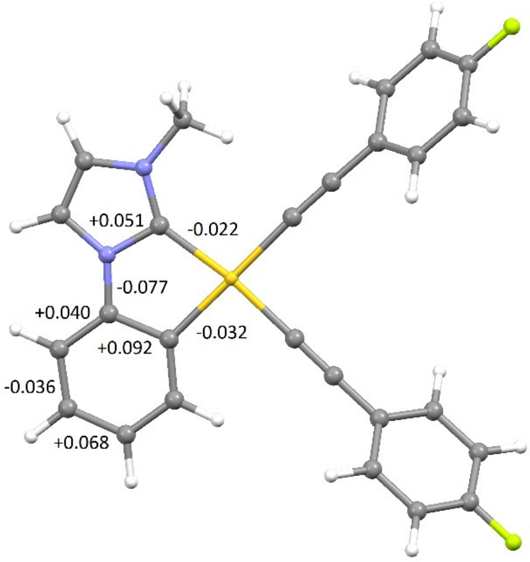
Figure S18. Spatial plots of selected frontier orbitals of the DFT optimized ground state of **2a**.



1a **1b** **1c** **2a**

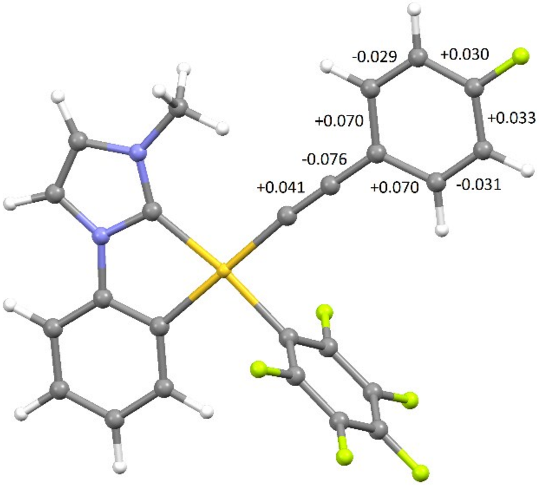
Figure S19. Singly occupied molecular orbitals (top: SOMO, middle: SOMO-1) obtained by restricted open-shell single point calculations on the optimized triplet state geometries and spin density surfaces (bottom) for the optimized triplet states of **1a**, **1b**, **1c** and **2a** (the positive spin densities are shown in blue and the negative ones are in green).


-0.026
+0.055
-0.081
+0.045
-0.028
+0.091
-0.038
+0.066

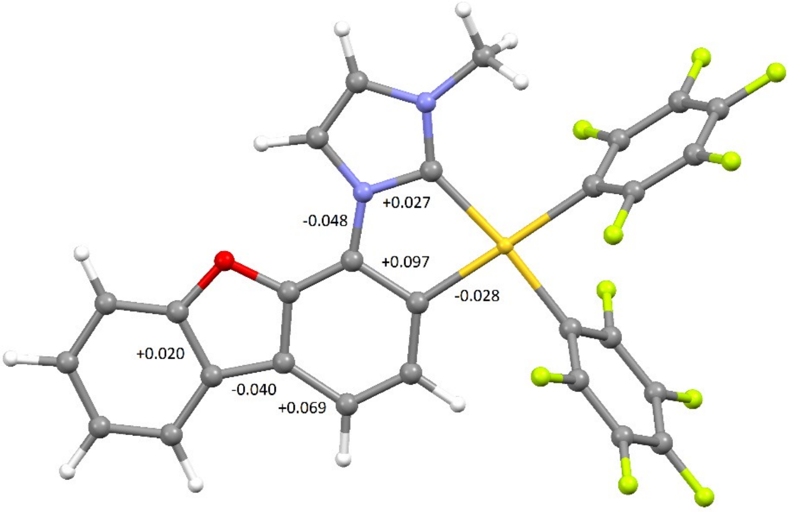

+0.051
-0.022
-0.077
+0.040
-0.032
+0.092
-0.036
+0.068

1a

1b



1c



2a

Figure S20. Main changes in the bond distances (difference larger than 0.02 Å) of the DFT optimized triplet state of **1a**, **1b**, **1c** and **2a** in comparison with the corresponding ground state (values reported on the triplet state geometry)

Cartesian coordinates and energies from the DFT optimized geometry of **1a** (ground state):

Au	-0.68178700	-0.24832700	-0.03118200
C	-2.58861500	0.54117500	0.10709400
C	-2.98159700	1.86995000	0.24689800
H	-2.23118700	2.65443000	0.28245500
C	-4.33335600	2.21610600	0.34311000
H	-4.61468200	3.26072000	0.44864200
C	-5.31748800	1.23307200	0.30539900
C	-4.95788700	-0.10785700	0.17134900
C	-3.60866700	-0.42054400	0.07610700
C	-1.80827500	-1.96521600	-0.14874800
C	-3.83033600	-2.94514600	-0.14954400
H	-4.90607900	-3.01130800	-0.10894500
C	-2.89012600	-3.91549100	-0.29634100
H	-2.99129700	-4.98522900	-0.40216700
C	-0.39583500	-4.00717600	-0.41243700
H	0.32564600	-3.38001500	-0.93435300
H	-0.56307600	-4.92308700	-0.98283600
H	-0.01043600	-4.25613600	0.58000800
C	0.22193400	1.58052500	0.07965100
C	0.84593500	2.02223000	1.23836300
C	1.46890300	3.26231400	1.32839300
C	1.47823000	4.10032500	0.21988400
C	0.86412800	3.69070300	-0.95753100
C	0.24747400	2.44466700	-1.00749900
F	-0.34479100	2.09698600	-2.15974900

```
 F                  0.86878600    4.49648400   -2.02100300
 F                  2.07061500    5.29161300    0.28644400
 F                  2.05425200    3.65572200    2.46096400
 F                  0.86141700    1.24399800    2.33204800
 C                  1.22755200   -1.08374100   -0.10289300
 C                  2.06398200   -0.94629100   -1.20204800
 C                  3.36201400   -1.44714500   -1.23328900
 C                  3.85965700   -2.11256900   -0.11925300
 C                  3.05296800   -2.27290400    1.00156600
 C                  1.76175600   -1.75744800    0.98641500
 F                  1.62736000   -0.31457800   -2.30439100
 F                  4.13206500   -1.29794600   -2.31261800
 F                  5.09859800   -2.60145000   -0.12787400
 F                  3.52349300   -2.92423900    2.06794900
 F                  1.00801500   -1.96625900    2.08316000
 N                 -3.14384900   -1.75846500   -0.06323900
 N                 -1.65735600   -3.29380400   -0.29916200
 H                 -6.36732200    1.50219600    0.38081400
 H                 -5.72436900   -0.87806300    0.14434800

Zero-point correction=                           0.273315 (Hartree/Particle)
Thermal correction to Energy=                    0.304233
Thermal correction to Enthalpy=                  0.305177
Thermal correction to Gibbs Free Energy=         0.208385
Sum of electronic and zero-point Energies=          -2085.081320
Sum of electronic and thermal Energies=             -2085.050402
Sum of electronic and thermal Enthalpies=           -2085.049458
Sum of electronic and thermal Free Energies=        -2085.146249
```

Cartesian coordinates and energies from the DFT optimized geometry of **1b** (ground state):

Au	0.81719500	-0.65051300	-0.00515300
C	2.87028500	-0.46293300	-0.00240100
C	3.63901700	0.69904500	-0.00487700
H	3.13935400	1.66347200	-0.00815400
C	5.03591900	0.63428800	-0.00323800
H	5.61660500	1.55338900	-0.00525400
C	5.68718200	-0.59648900	0.00086000
C	4.94606400	-1.77823100	0.00329600
C	3.56064200	-1.68370000	0.00165700
C	1.37278100	-2.62301400	0.00074400
C	3.00408200	-4.16862600	0.00785200
H	4.01106000	-4.55516100	0.01030000
C	1.80804900	-4.81440500	0.00763200
H	1.57505300	-5.86874700	0.00998200
C	-0.60182300	-4.15232400	0.00359900
H	-1.15880300	-3.21364500	-0.00366700
H	-0.85324400	-4.72432200	0.90096800
H	-0.85151700	-4.73628700	-0.88663000
N	2.71330700	-2.82610400	0.00362100
N	0.82023200	-3.84945100	0.00291100
H	6.77271600	-0.64461700	0.00205900
H	5.45191200	-2.74049600	0.00632700
C	0.53193800	1.30513900	-0.00660700
C	-1.18491100	-0.88494200	-0.00724200
C	0.36955000	2.51481500	-0.00317800
C	-2.40444500	-0.97954000	-0.00382000
C	0.17433200	3.92807200	-0.00120300
C	0.12146500	4.64496400	1.20700500
C	0.03038500	4.63540200	-1.20766300
C	-0.06621100	6.02290300	1.21428500
H	0.22698900	4.10785100	2.14499600
C	-0.15743300	6.01330700	-1.21170600
H	0.06507300	4.09069500	-2.14655000
C	-0.20156400	6.68263700	0.00204400
H	-0.10980100	6.58481300	2.14232600
H	-0.27066300	6.56786600	-2.13827500
C	-3.82649300	-1.09829100	0.00032000
C	-4.54658900	-1.16898300	-1.20550100
C	-4.54076600	-1.14543800	1.21078200
C	-5.93199300	-1.28940700	-1.20676300
H	-4.00651000	-1.12202300	-2.14663700
C	-5.92610500	-1.26581400	1.22105000
H	-3.99609600	-1.08007400	2.14815500
C	-6.59705500	-1.33703500	0.00932800
H	-6.49640100	-1.34191600	-2.13281800
H	-6.48606100	-1.30025600	2.15065000
F	-0.38312300	8.02055000	0.00360400
F	-7.94140000	-1.45494300	0.01373500

```
Zero-point correction=                           0.359732 (Hartree/Particle)
Thermal correction to Energy=                    0.386094
Thermal correction to Enthalpy=                  0.387038
Thermal correction to Gibbs Free Energy=         0.297968
Sum of electronic and zero-point Energies=          -1443.965585
Sum of electronic and thermal Energies=             -1443.939224
Sum of electronic and thermal Enthalpies=           -1443.938280
Sum of electronic and thermal Free Energies=        -1444.027350
```

Cartesian coordinates and energies from the DFT optimized geometry of **1c** (ground state):

Au	-0.74430500	-0.49433900	0.00001600
C	-2.80434200	-0.38676900	-0.00004100
C	-3.62513400	0.73919500	-0.00003300
H	-3.17969100	1.72988100	0.00008300
C	-5.01848000	0.61837900	-0.00018600
H	-5.63605600	1.51293500	-0.00016600
C	-5.61718000	-0.63787100	-0.00037000
C	-4.82584700	-1.78664000	-0.00038500
C	-3.44604200	-1.63501400	-0.00019200
C	-1.22482700	-2.49265100	-0.00002800
C	-2.79546700	-4.09796200	-0.00002100
H	-3.78681700	-4.52299400	-0.00000900
C	-1.57570800	-4.69796300	0.00026000
H	-1.30321900	-5.74282500	0.00048400
C	0.80799000	-3.93948400	0.00035100
H	1.32481300	-2.97815800	0.00041900
H	1.08256800	-4.50600200	-0.89365200
H	1.08245700	-4.50613800	0.89429400
C	-0.50686900	1.53324900	0.00012900
C	-0.41423700	2.25530900	-1.18063000
C	-0.24112400	3.63508400	-1.20110400
C	-0.15410400	4.32807900	0.00021400
C	-0.24063900	3.63494000	1.20148800
C	-0.41374600	2.25516700	1.18094000
F	-0.49364200	1.62517600	-2.36375500
F	-0.15902800	4.29924700	-2.35625000
F	0.01078300	5.65083800	0.00026500
F	-0.15808700	4.29898200	2.35667000
F	-0.49270100	1.62491500	2.36401900
N	-2.55573400	-2.74492900	-0.00013600
N	-0.62552800	-3.69572200	0.00027600
H	-6.69957400	-0.73175300	-0.00051800
H	-5.29041000	-2.76936100	-0.00056500
C	1.26453200	-0.63600200	0.00006500
C	2.48756300	-0.66725900	-0.00000100
C	3.91397700	-0.72032700	-0.00010500
C	4.63213500	-0.74769900	1.20847600
C	4.63196400	-0.74622800	-1.20881600
C	6.02154400	-0.80381000	1.21385100
H	4.08792400	-0.71853300	2.14793500
C	6.02137700	-0.80233800	-1.21445900
H	4.08762400	-0.71594000	-2.14816300
C	6.69140300	-0.83152000	-0.00037000
H	6.58517600	-0.82249000	2.14164700
H	6.58487200	-0.81988900	-2.14236100
F	8.03898700	-0.88700000	-0.00049100

```
Zero-point correction=                           0.316555 (Hartree/Particle)
Thermal correction to Energy=                    0.345632
Thermal correction to Enthalpy=                  0.346576
Thermal correction to Gibbs Free Energy=         0.251931
Sum of electronic and zero-point Energies=          -1764.525994
Sum of electronic and thermal Energies=             -1764.496917
Sum of electronic and thermal Enthalpies=           -1764.495972
Sum of electronic and thermal Free Energies=        -1764.590618
```

Cartesian coordinates and energies from the DFT optimized geometry of **2a** (ground state):

Au	0.32319300	-0.29630600	-0.06337000
C	-0.65335300	-2.10271900	-0.19971000
C	-2.59586200	-3.24334300	-0.25248500
H	-3.66564200	-3.37739600	-0.24196100
C	-1.57483900	-4.13414400	-0.35789200
H	-1.58549400	-5.20945800	-0.45370100
C	0.92137300	-4.02922100	-0.39023000
H	1.60608600	-3.36359100	-0.91416600
H	0.84117300	-4.97193300	-0.93519100
H	1.29821900	-4.21832400	0.61853600
C	1.08236000	1.59668900	0.05734300
C	1.62434500	2.09634200	1.23356700
C	2.15022200	3.38006300	1.33064200
C	2.14274800	4.20420200	0.21175700
C	1.60862300	3.73720100	-0.98311700
C	1.08795100	2.44839900	-1.03999600
F	0.56916300	2.04592200	-2.20954800
F	1.59618800	4.52948900	-2.05663100
F	2.64211600	5.43699900	0.28526000
F	2.65842400	3.82845600	2.47990200
F	1.65195300	1.33384200	2.33782700
C	2.29091100	-0.98065500	-0.07151900
C	3.14058800	-0.80153300	-1.15442700
C	4.47238500	-1.20518900	-1.14627700
C	4.99104300	-1.81106500	-0.00812300
C	4.17200300	-2.00992600	1.09741500
C	2.84691000	-1.59230100	1.04334600
F	2.68452600	-0.22485800	-2.27863300
F	5.25459900	-1.01967400	-2.21107000
F	6.26248700	-2.20668700	0.02091000
F	4.66370800	-2.60480200	2.18685000
F	2.08529600	-1.83635200	2.12681500
N	-2.00504800	-2.00423700	-0.15882100
N	-0.39505700	-3.41569300	-0.32927700
C	-2.56514300	-0.70974200	-0.04784900
C	-1.64445200	0.34580100	0.00980700
C	-3.92291200	-0.44530700	0.00573300
C	-2.13498600	1.65147500	0.12809100
C	-4.40671700	0.86690200	0.11978600
C	-3.50228300	1.92599100	0.18245200
H	-1.43448600	2.47901400	0.18043600
C	-5.84920400	0.73134000	0.14347300
C	-6.10193800	-0.64427200	0.04212000
H	-3.85179000	2.95107600	0.27238200
C	-6.92890100	1.61255700	0.23729800
C	-7.37360400	-1.19102500	0.02869700
C	-8.21757300	1.08759800	0.22592900
H	-6.76760800	2.68420400	0.31682100
C	-8.43640500	-0.29374000	0.12314100
H	-7.53084800	-2.26219400	-0.05124900
H	-9.06985800	1.75750200	0.29769300
H	-9.45385900	-0.67489700	0.11685700
O	-4.93416300	-1.36620500	-0.04156300

```
Zero-point correction=                           0.337747 (Hartree/Particle)
Thermal correction to Energy=                    0.373164
Thermal correction to Enthalpy=                  0.374108
Thermal correction to Gibbs Free Energy=         0.267351
Sum of electronic and zero-point Energies=          -2389.764662
Sum of electronic and thermal Energies=             -2389.729245
Sum of electronic and thermal Enthalpies=           -2389.728301
Sum of electronic and thermal Free Energies=        -2389.835058
```

Cartesian coordinates and energies from the DFT optimized geometry of **1a** (triplet state):

Au	-0.69569600	-0.20977300	-0.00748500
C	-2.53534600	0.66360300	0.12631500
C	-2.88645200	1.99555100	0.27480400
H	-2.10759300	2.75054200	0.33179900
C	-4.22300400	2.39745600	0.35148000
H	-4.47176500	3.44805000	0.46634000
C	-5.30351300	1.42209400	0.27650200
C	-5.03769700	0.09888500	0.13630800
C	-3.66629000	-0.31001400	0.06428200
C	-1.88424500	-1.85213300	-0.12516400
C	-3.98298100	-2.77662100	-0.15376700
H	-5.05959900	-2.82157300	-0.13120200
C	-3.05792200	-3.76211000	-0.27755100
H	-3.20071100	-4.82869900	-0.37764000
C	-0.57078300	-3.96497100	-0.34809900
H	0.09806400	-3.50531800	-1.07815900
H	-0.81105300	-4.98106900	-0.66757700
H	-0.07375200	-3.99719200	0.62553600
C	0.30959000	1.57516900	0.08546100
C	0.98253400	1.98614000	1.22890100
C	1.67515800	3.18997800	1.30290200
C	1.70697700	4.02562900	0.19322700
C	1.04541000	3.64895500	-0.96901800
C	0.36099400	2.43799700	-1.00260100
F	-0.27226000	2.12617900	-2.14413300
F	1.07035000	4.45299700	-2.03442300
F	2.36469500	5.18343400	0.24482600
F	2.30501000	3.55239700	2.42249500
F	0.98022200	1.21330900	2.32628100
C	1.16320300	-1.13803200	-0.09140800
C	1.96953700	-1.07373300	-1.22010200
C	3.23954600	-1.63915500	-1.27761100
C	3.74097100	-2.29731200	-0.16109000
C	2.96512000	-2.38396200	0.98863800
C	1.70027800	-1.80572300	1.00055100
F	1.52962000	-0.45205300	-2.32695600
F	3.97966700	-1.55909800	-2.38558800
F	4.95395500	-2.84790700	-0.19453600
F	3.43861400	-3.02703500	2.05927500
F	0.97976600	-1.94487200	2.12925800
N	-3.26616700	-1.58525200	-0.06071100
N	-1.80179900	-3.20517500	-0.26485600
H	-6.33109500	1.76925600	0.33438100
H	-5.84004500	-0.63120900	0.08056100

```
Zero-point correction=                           0.268572 (Hartree/Particle)
Thermal correction to Energy=                    0.300138
Thermal correction to Enthalpy=                  0.301082
Thermal correction to Gibbs Free Energy=         0.202287
Sum of electronic and zero-point Energies=          -2084.972166
Sum of electronic and thermal Energies=             -2084.940600
Sum of electronic and thermal Enthalpies=           -2084.939656
Sum of electronic and thermal Free Energies=        -2085.038451
```

Cartesian coordinates and energies from the DFT optimized geometry of **1b** (triplet state):

Au	-1.04647500	-0.26152600	0.00529900
C	-2.79597500	0.76675400	0.03937100
C	-3.02063700	2.13647300	0.08950000
H	-2.16407300	2.80458700	0.10958600
C	-4.31196100	2.66027700	0.11723300
H	-4.46680100	3.73425800	0.15873500
C	-5.47894800	1.78222100	0.09313000
C	-5.33642300	0.43194200	0.04582300
C	-4.01159600	-0.10302100	0.02070000
C	-2.36699700	-1.79969500	-0.03820800
C	-4.53411700	-2.54590400	-0.05874200
H	-5.61094700	-2.49723800	-0.05354100
C	-3.69425800	-3.61125800	-0.10189000
H	-3.92220500	-4.66697400	-0.14231200
C	-1.23761900	-4.03060100	-0.14265300
H	-0.33804200	-3.41274200	-0.13979400
H	-1.26478500	-4.63035000	-1.05769300
H	-1.22911800	-4.69215700	0.72931600
N	-3.72040100	-1.41582900	-0.02086700
N	-2.39576400	-3.15923800	-0.08994200
H	-6.47090800	2.22454200	0.11438700
H	-6.20329500	-0.22273200	0.02912700
C	0.05080100	1.38880100	0.02442300
C	0.66887800	-1.30721900	-0.00397500
C	0.72362300	2.40790600	0.02297500
C	1.74755200	-1.88500600	0.00026800
C	1.52538100	3.58755700	0.03231300
C	1.30490400	4.62022300	-0.89621700
C	2.56088300	3.74241200	0.97141300
C	2.08753200	5.76993600	-0.89047600
H	0.51280500	4.50935100	-1.63125100
C	3.34805000	4.88860600	0.98798400
H	2.74270200	2.94874700	1.68997300
C	3.09606200	5.88313800	0.05463900
H	1.92589200	6.57081300	-1.60566900
H	4.14937500	5.01620400	1.70952500
C	3.01553700	-2.53732800	-0.01681400
C	3.28155700	-3.63496400	0.82114600
C	4.03520800	-2.08943300	-0.87662800
C	4.51926100	-4.26912500	0.80266700
H	2.50747900	-3.98297100	1.49932300
C	5.27532500	-2.71706600	-0.90507200
H	3.84208900	-1.23803800	-1.52237400
C	5.49442800	-3.79792800	-0.06358000
H	4.73480900	-5.11446000	1.44914000
H	6.06790600	-2.37780500	-1.56510500
F	3.85802500	6.99790300	0.06568200
F	6.69676200	-4.41047900	-0.08682900

```
Zero-point correction=                           0.354598 (Hartree/Particle)
Thermal correction to Energy=                    0.382831
Thermal correction to Enthalpy=                  0.383775
Thermal correction to Gibbs Free Energy=         0.286437
Sum of electronic and zero-point Energies=          -1443.856140
Sum of electronic and thermal Energies=             -1443.827907
Sum of electronic and thermal Enthalpies=           -1443.826963
Sum of electronic and thermal Free Energies=        -1443.924301
```

Cartesian coordinates and energies from the DFT optimized geometry of **1c** (triplet state):

Au	0.79596300	-0.47967300	-0.00015700
C	2.82000200	-0.13764800	-0.00002600
C	3.50209600	1.07901000	-0.00003000
H	2.94257100	2.00995600	-0.00007500
C	4.89878300	1.12377900	0.00006000
H	5.40550300	2.08544800	0.00006900
C	5.64357300	-0.05321400	0.00012000
C	4.99451900	-1.28711600	0.00011500
C	3.60591700	-1.30247400	0.00004300
C	1.50007300	-2.40667700	-0.00001400
C	3.24780100	-3.82190500	0.00000100
H	4.28164000	-4.12953600	-0.00004000
C	2.10640500	-4.55911600	-0.00011100
H	1.95810900	-5.62873600	-0.00019200
C	-0.34672600	-4.08442300	0.00036800
H	-0.97091900	-3.19047300	-0.00322800
H	-0.55659600	-4.67522000	0.89661400
H	-0.55518600	-4.68168800	-0.89188300
C	0.34425800	1.51548200	-0.00001000
C	0.17446800	2.22397100	1.18106500
C	-0.14696100	3.57718600	1.20151900
C	-0.30886500	4.25688500	0.00028600
C	-0.14704000	3.57742200	-1.20109200
C	0.17437700	2.22419800	-1.18093400
F	0.32083900	1.60864400	2.36479000
F	-0.30162600	4.22856100	2.35652000
F	-0.61736900	5.55373900	0.00042300
F	-0.30177900	4.22902700	-2.35595400
F	0.32069300	1.60911800	-2.36479000
N	2.85352400	-2.50476200	0.00001300
N	1.04559100	-3.67499800	-0.00017600
H	6.72941100	-0.01743600	0.00017100
H	5.57220500	-2.20796800	0.00015500
C	-1.17895500	-0.81648500	-0.00060600
C	-2.43983800	-0.91536600	-0.00039700
C	-3.78884100	-1.00361000	-0.00015500
C	-4.48524800	-2.30495500	0.00081400
C	-4.62968800	0.20920200	-0.00094200
C	-5.84490600	-2.36801200	0.00091200
H	-3.88680500	-3.21058700	0.00147200
C	-5.98630400	0.11727400	-0.00082800
H	-4.13267900	1.17392300	-0.00163200
C	-6.59521300	-1.16540200	0.00007800
H	-6.37341600	-3.31704400	0.00162600
H	-6.61847200	1.00046700	-0.00141400
F	-7.93768500	-1.24316400	0.00017200

```
Zero-point correction=                           0.311917 (Hartree/Particle)
Thermal correction to Energy=                    0.341939
Thermal correction to Enthalpy=                  0.342883
Thermal correction to Gibbs Free Energy=         0.244305
Sum of electronic and zero-point Energies=          -1764.421788
Sum of electronic and thermal Energies=             -1764.391767
Sum of electronic and thermal Enthalpies=           -1764.390823
Sum of electronic and thermal Free Energies=        -1764.489401
```

Cartesian coordinates and energies from the DFT optimized geometry of **2a** (triplet state):

```
 Au                 0.31566500   -0.29579500   -0.05031100
 C                 -0.65674100   -2.08489700   -0.18717600
 C                 -2.60020600   -3.26854100   -0.24882000
 H                 -3.66614700   -3.42811900   -0.24341400
 C                 -1.55850800   -4.13213100   -0.35008700
 H                 -1.55525400   -5.20795800   -0.44684700
 C                  0.93457100   -4.00075400   -0.37631200
 H                  1.56912100   -3.41994400   -1.04672500
 H                  0.83878000   -5.01846700   -0.75987000
 H                  1.38721600   -4.02668700    0.61861900
 C                  1.09360200    1.59586600    0.05770700
 C                  1.65753600    2.09503500    1.22441200
 C                  2.19727600    3.37385300    1.31103000
 C                  2.18172800    4.19599400    0.19092600
 C                  1.62582100    3.73114600   -0.99455200
 C                  1.09259300    2.44689900   -1.04079400
 F                  0.55383200    2.05035100   -2.20372300
 F                  1.60474500    4.52169800   -2.06988900
 F                  2.69343000    5.42469400    0.25459000
 F                  2.72585100    3.82033200    2.45233500
 F                  1.69442600    1.33786700    2.33188400
 C                  2.27876700   -0.98653900   -0.06729000
 C                  3.11522000   -0.82521500   -1.16370000
 C                  4.44651100   -1.23007600   -1.16710600
 C                  4.98012000   -1.81898900   -0.02710500
 C                  4.17569900   -1.99854100    1.09199500
 C                  2.85010900   -1.58038600    1.04976100
 F                  2.64645600   -0.26544600   -2.29132900
 F                  5.21459800   -1.06208300   -2.24561900
 F                  6.25185600   -2.21596400   -0.00906200
 F                  4.68168300   -2.57627600    2.18464000
 F                  2.10652100   -1.80485900    2.14949800
 N                 -2.03670300   -2.00485500   -0.15069500
 N                 -0.38770400   -3.40596700   -0.31705900
 C                 -2.60961200   -0.76890400   -0.04097000
 C                 -1.61961400    0.35402400    0.03360000
 C                 -3.95809000   -0.48026300    0.00638300
 C                 -2.12064500    1.65436200    0.16230200
 C                 -4.43102900    0.82985800    0.12927000
 C                 -3.47804000    1.93749900    0.21267700
 H                 -1.41631100    2.47836200    0.22518600
 C                 -5.83631300    0.73393300    0.14544200
 C                 -6.13450500   -0.65233300    0.02991800
 H                 -3.83772800    2.95636100    0.31176400
 C                 -6.90849900    1.64982600    0.24453300
 C                 -7.41575300   -1.16100400    0.00841500
 C                 -8.19913000    1.15113200    0.22382900
 H                 -6.72114500    2.71582700    0.33379800
 C                 -8.45562400   -0.23073800    0.10792700
 H                 -7.60415400   -2.22615600   -0.08097100
 H                 -9.03875500    1.83672000    0.29833600
 H                 -9.48337900   -0.58177600    0.09559700
 O                 -4.98537100   -1.38601400   -0.05422800
```

```
Zero-point correction=                           0.333109 (Hartree/Particle)
Thermal correction to Energy=                    0.369107
Thermal correction to Enthalpy=                  0.370052
Thermal correction to Gibbs Free Energy=         0.261176
Sum of electronic and zero-point Energies=          -2389.666885
Sum of electronic and thermal Energies=             -2389.630886
Sum of electronic and thermal Enthalpies=           -2389.629942
Sum of electronic and thermal Free Energies=        -2389.738818
```

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