Supplementary Information:

Facile Oxidation of NHC-Au(I) to Au(III) Complexes by $CsBr_3$

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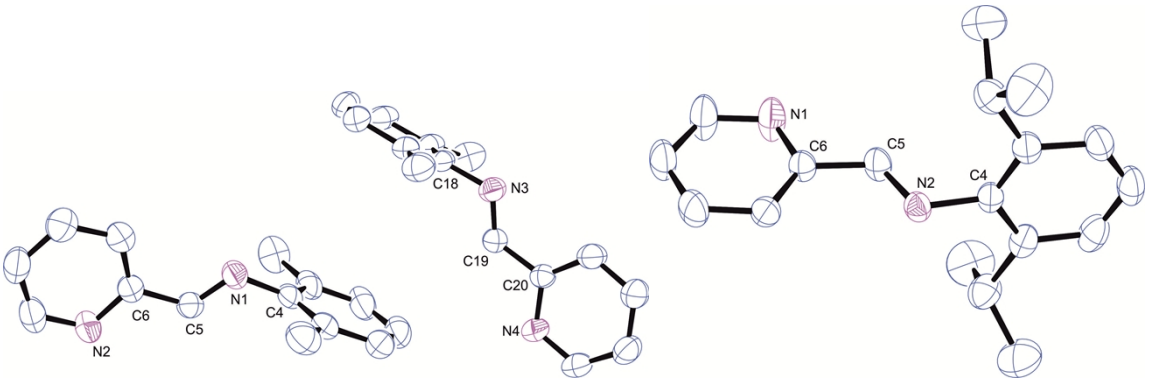

Figure S1. Molecular structures of **1a** (left) and **1b** (right, ellipsoids drawn at the 50% probability level, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°] for **1a**: N2–C6 1.334(3), C5–N1 1.250(3), N1–C5–C6 122.4(2), N4–C20 1.333(3), C19–N3 1.259(2), N3–C19–C20 122.8(2); and for **1b**: N1–C6 1.339(3), C5–N2 1.257(3), N2–C5–C6 123.63(18).

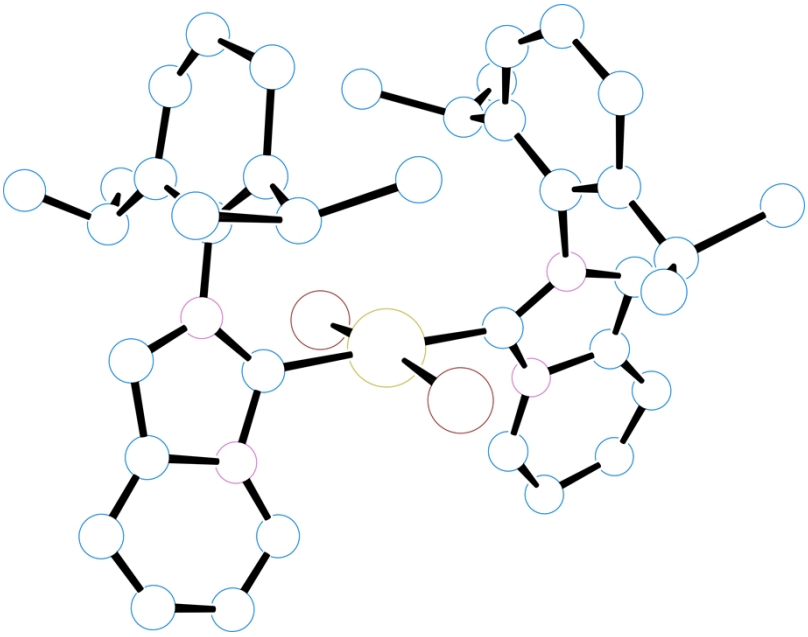

Figure S2. Cation in crystals of **5b** (isotropically refined). Graphic for illustrative reasons and proof of the connectivity of the complex.

Figure S3. Dark red crystals of the neutral gold(III)-complex **5b*** and bright red crystals of the cationic gold complex **5b**.

Photophysical Characterization of 2a, 4a, 4b

Imidazolium-salt **2a**, Au(I) carbene **4a**, Au(III) carbene, **5a**:

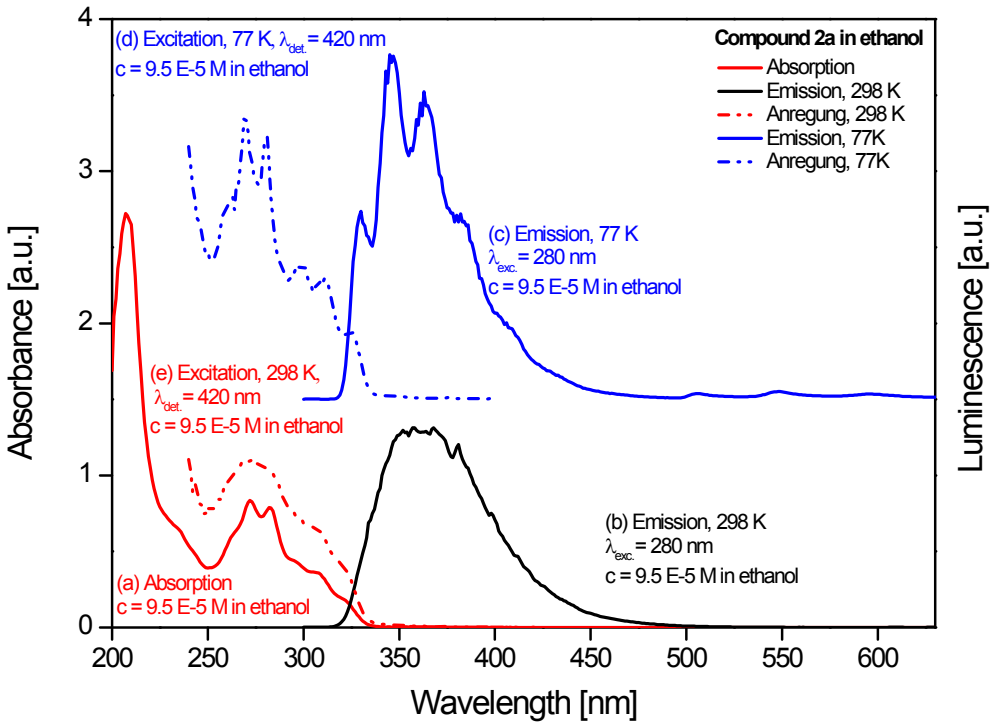

Figure S4. Electronic absorption, excitation and emission spectra of **2a** in ethanolic solution at r.t. and 77 K.

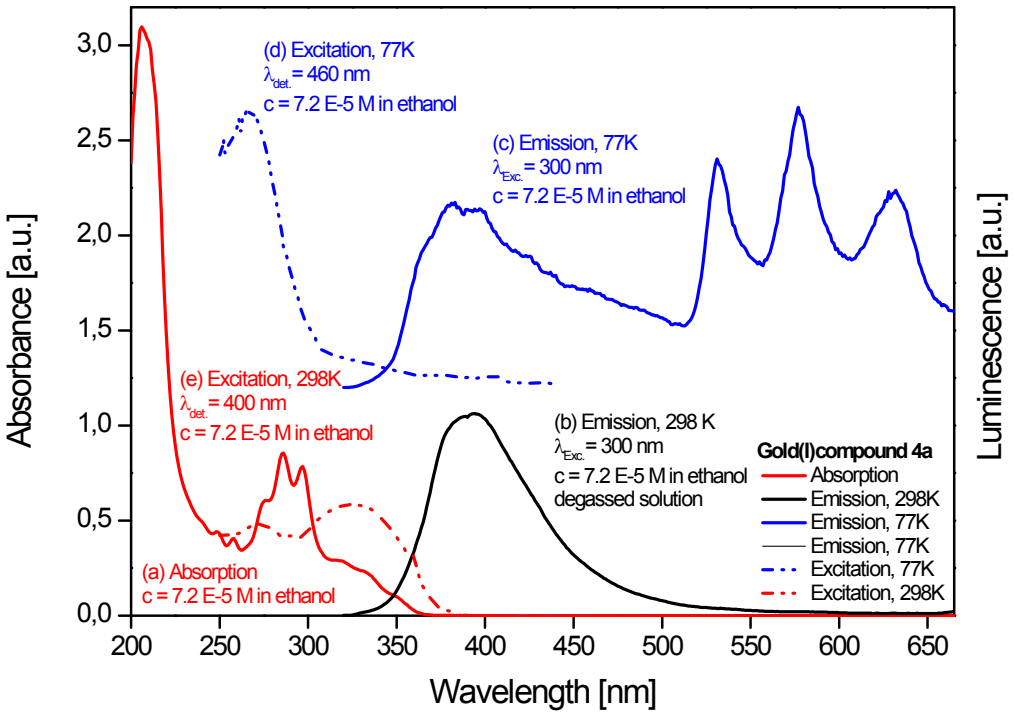

Figure S5: Electronic absorption, excitation and emission spectra of **4a** in ehtanolic solution at r.t. and 77 K.

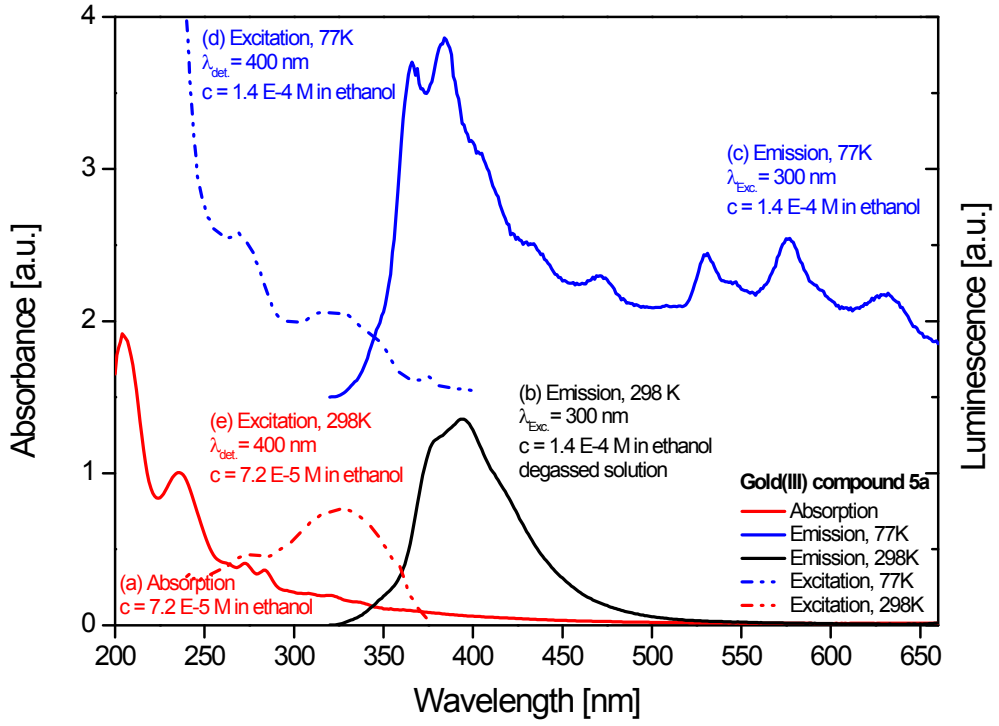

Figure S6: Electronic absorption, excitation and emission spectra of **5a** in ethanolic solution at r.t. and 77 K.

Emission Lifetime Measurements of the Au(I)-Carbene complexes at 77 K

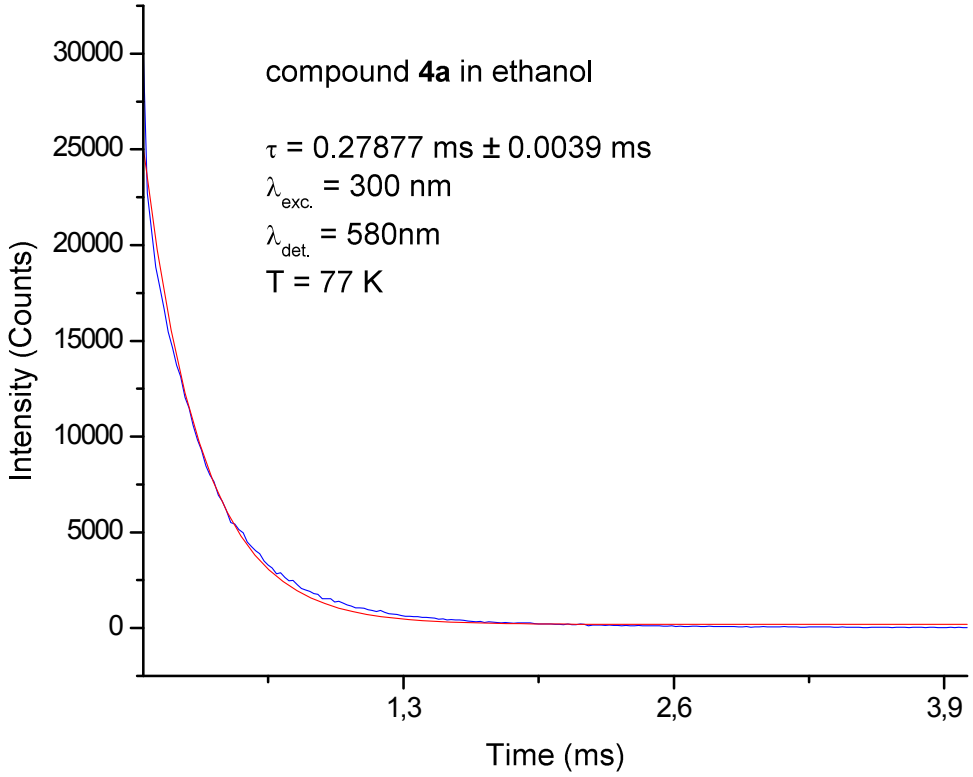

Figure S7. Emission decay of **4a** in ethanol glass (c = 7.2 10^{-5} M, $\lambda_{exc.}$ = 300 nm, $\lambda_{det.}$ = 580 nm) at 77 K.

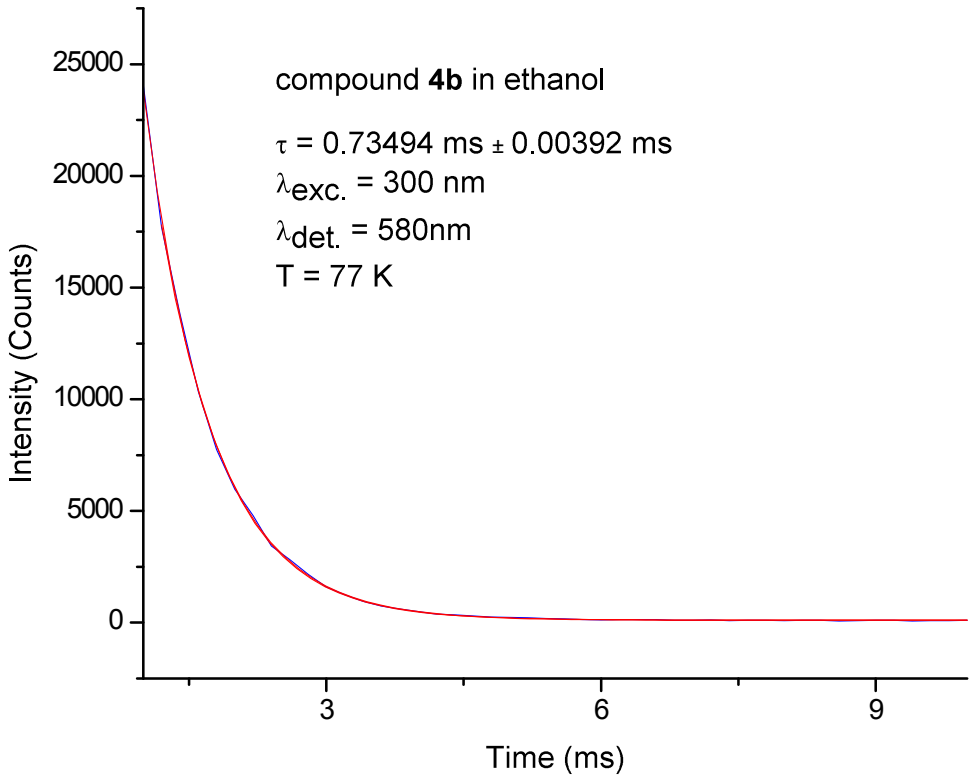

Figure S8. Emission decay of **4b** in ethanol glass (c = 8.5 10^{-5} M, $\lambda_{exc.}$ = 300 nm, $\lambda_{det.}$ = 580 nm) at 77 K.

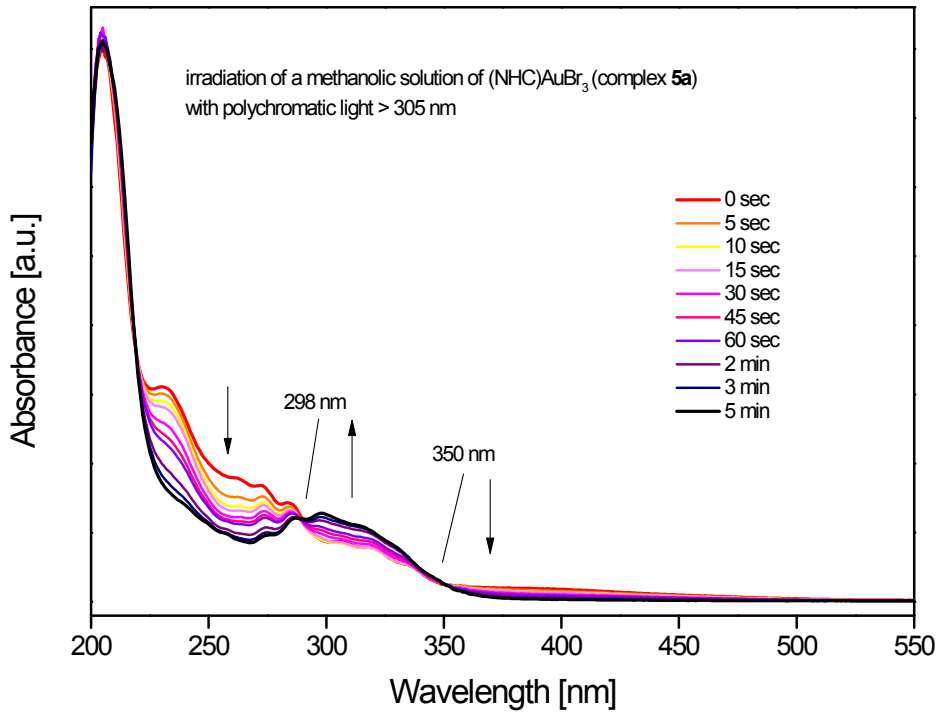

Figure S9. Irradiation of an ethanolic solution of **5a** with polychromatic light (λ > 305 nm).