Supporting Information

Ligand-to-ligand charge transfer in anthracene-based cyclic trinuclear complexes enhanced photocatalytic deprotection of Weinreb amides

Yun-Zhou Guo,^{†a} Hui-Zhi Wei,^{†a} Xu-Hang Zhong,^a Cui-Zhou Luan,^a Rui Zhou,^b Bingzhe Wang,^a Ji Zheng,^{*a} Shang-Fu Yuan,^{*a} Tao Wu,^a and Dan Li^a

^aCollege of Chemistry and Materials Science, and Guangdong Provincial Key Laboratory of Supramolecular Coordination Chemistry, Jinan University, Guangzhou 510632, China.
^bDepartment of Developmental and Regenerative Biology, Jinan University, Guangzhou, 510632, China.

†These authors contributed equally to this work.

*Corresponding authors: <u>jizheng@jnu.edu.cn</u>; <u>sfyuan@jnu.edu.cn</u>

Table of Contents

1.	Materia	als and physical measurements	3
2.	Support	ing data	5
	Section	1: synthesis and characterization of An-HL and An-Au ₃	5
	Section	2: Characterizations of An-HL and An-Au ₃	8
	Section	3: Optimization of photocatalytic reaction conditions2	5
	1)	General Procedure A model reaction (substrate 1a):2	5
	2)	General Procedure B (For substrates 1b-1d):2	6
	3)	General Procedure C (For substrates 1e-1f):	6
	4)	Substrate Summary	7
	5)	UV-vis Absorption Spectra of the Catalytic System with Different Additions:2	7
	6)	Reaction kinetics experiments:	8
	7)	Free Radical Capture Experiment:	8
	8)	Detection of Formaldehyde:	9
	9)	Stern - Volmer Quenching Studies:	0
3. C	haracter	ization data for products	2
4. N	IMR Spe	ectra:	4
5. R	eference	4	2

1. Materials and physical measurements

materials. Methyl sulfide (Me₂S, \geq 99%, N.N-1.1 Chemicals and liquid), Diisopropylethylamine (DIPEA, distillation grade, ≥99.5%), and 2-bromo-3,3,3-trifluoro-1propene (≥97.0%, GC) were purchased from Aladdin Industrial Corporation. Triethylamine (Et₃N, ≥99.5%, GC) was commercially supplied by Macklin Biochemical Co. Ltd.. 1,8diazabicyclo[5.4.0]undec-7-ene (DBU, 99.0%, liquid) was purchased from Alfa Aesar. 4methylbenzenesulfonhydrazide (≥98%), 9-anthraldehyde (98%), Lithium tetrafluoroborate (LiBF₄, 99%), 4-cyano-N-methoxy-N-methylbenzamide ($C_{10}H_{10}N_2O_2$, 99%), 3-(trifluoromethyl)-1H-pyrazole (C₄H₃F₃N₂, 98%) and 3,5-bis(trifluoromethyl)-1H-pyrazole (>98.0%) were purchased from Bidepharm. Chloroauric acid (HAuCl₄·4H₂O, 99% Au, \geq 47.8%) were purchased from Energy Chemical. All reagents and solvents were commercially available, and used as supplied without further purification.

1.2 Physical measurements: UV-vis absorption spectra were recorded on cary4000 and UV-3600i plus (Shimadzu, Japan). ¹H, ¹³C, and ¹⁹F NMR spectra were carried out on a Bruker AVANCE III HD 400 spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on miniflex600 X-ray Diffractometer (Cu K α , $\lambda = 1.5418$ Å) in a step of 0.02° at 15 kV and 40 mA. Steady-state photoluminescence spectra (PL) and Stern-Volmer quenching experiments were tested on a Fluorolog-3 fluorescence spectrometer (Horiba, USA). X-ray photoelectron spectroscopy (XPS) data were collected on a thermofisher scientific K-Alpha. All binding energies were calibrated using the C (1s) carbon peak (284.8 eV), which was applied as an internal standard. The electrochemical measurements were performed in a conventional threeelectrode cell on a CHI-760E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd, China). Cyclic voltammetry (CV) tests were performed using ferrocene as a calibrator. Glassy carbon electrode acted as the working electrode, a platinum wire electrode served as the counter electrode, and a saturated calomel electrode was used as the reference. Solutions were prepared by dissolving 8 mL of DMSO with 9 mg of An-HL (0.68 mM), 15 mg of An-Au₃ (0.73 mM), or 11 mg of CF3-Au3 (0.82 mM), and supplemented with 170 mg (0.5 mmol) of tetrabutylammonium perchlorate (TBAP) as the electrolyte. The solutions were degassed by purging with N₂ for 20 minutes prior to measurement.

1.3 Catalytic Reaction Chemistry Measurements: Gas chromatography mass spectra (GC-MS) were performed at Agilent 7890B-5977B gas chromatograph mass spectrometer and an ultrainert gas chromatography column (0.25 mm \times 30 m, Film: 0.25 μ m). Acetonitrile was used as the solvent for GC-MS test.

1.4 X-ray Crystallography: Intensity data of **An-Au**₃ was collected at 100 K on an Oxford Diffraction XtalAB system [Rigaku (Cu) dual-wavelength X-ray source, K α , λ =1.5418 Å] equipped with a monochromator and a CCD plate detector (CrysAlisPro CCD, Oxford Diffraction Ltd). Absorption corrections were applied by using the program CrysAlis (multi-

scan). The structures were solved by direct methods using ShelXS in Olex2 1.5, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms.

1.5 fs TAS: To measure transient absorption spectra with time delays of ~ 1 ps to 10 ns, an ultrafast systems EOS sub-nanosecond transient absorption spectrometer was employed. A built-in photonic crystal fiber supercontinuum laser source with a fundamental of 1064 nm at 2 kHz output frequency and pulse width of approximately 1 ns was used to generate the white light.

2. Supporting data

Section 1: synthesis and characterization of An-HL and An-Au₃

2.1. Synthesis of An-HL and An-Au3, CF3-Au3



Scheme S1. The synthesis of An-HL.

Synthesis of An-HL: The synthesis of **An-HL** followed a procedure similar to that described in the literature¹. A mixture of 9-anthracenecarboxaldehyde (450 mg, 2.18 mmol), 4-methylbenzenesulfonhydrazide (487.6 mg, 2.61 mmol), and toluene (20 mL) was placed in a 50 mL round-bottom flask and sonicated for 5 min. The solution was then slowly added with DBU (996 mg, 6.54 mmol) and stirred for 10 min. Subsequently, 2-bromo-3,3,3-trifluoropropene (763.4 mg, 4.36 mmol) was added rapidly, and the mixture was refluxed at 80 °C for 24 h. After cooling, the reaction was quenched with deionized water and extracted with ethyl acetate (EA, 3×15 mL). The combined organic layers were concentrated under reduced pressure to yield a brown oily product. Purification by thin-layer chromatography (TLC eluent: EA/PE = 1:10, V:V) followed by column chromatography (eluent: EA/PE = 1:50, V:V) afforded the target compound. The purified product was dried under vacuum at 30 °C for 12 h to give **An-HL** as a pale- yellow solid (202.5 mg, 45% yield). The ¹H, ¹³C, and ¹⁹F NMR spectra of **An-HL** were displayed in Figs. S1-S3.

Anal. ¹H NMR (400 MHz, DMSO) δ 14.07 (s, 1H, NH_{HPz}), 8.84 (s, 1H, CH_{An}), 8.21 (d, J = 8.5 Hz, 2H, CH_{An}), 7.59 (dd, J = 9.4, 1.2 Hz, 6H, CH_{An}), 7.11 (d, J = 1.8 Hz, 1H, CH_{Pz}). ¹³C NMR (101 MHz, DMSO) δ 142.02, 140.40, 131.14, 131.11, 129.41, 129.05, 127.58, 126.18, 125.56, 123.15, 106.72. ¹⁹F NMR (376 MHz, CDCl₃) δ -61.96.



Scheme S2. The synthesis of An-Au₃.

Synthesis of An-Au3: The synthesis procedure of **An-Au3** is illustrated in Scheme S2. Under standard Schlenk techniques, pre-synthesized (Me₂S)AuCl (94 mg, 0.32 mmol, prepared from chloroauric acid and dimethyl sulfide according to literature method²) and An-HL (100 mg, 0.32 mmol) were dissolved in acetone (10 mL) in a 50 mL Schlenk tube. After three freeze-pump-thaw cycles for oxygen removal, triethylamine (32 mg, 0.32 mmol) was injected under nitrogen atmosphere. The reaction mixture was stirred at room temperature (RT), shielded from light, for 30 min. Then, the mixture was gradually treated with methanol until complete precipitation. Grayish-white precipitates were collected by centrifugation (8500 rpm, 2 min), thoroughly washed with dichloromethane, and vacuum-dried for 12 h to afford **An-Au3** powder (52 mg, 52% yield based on Au). Single crystals suitable for X-ray diffraction analysis were obtained through low-temperature vapor diffusion: 10 mg of the powder dissolved in dichloromethane (2 mL) was allowed to slowly evaporate at -25°C, yielding pale yellow plate-shaped crystals (41% yield based on Au). The ¹H and ¹⁹F NMR spectra of **An-Au3** were present in Fig. S4 and S5, respectively.

Anal. ¹H NMR (400 MHz, DMSO) δ 8.94 (s, 1H), 8.45 (d, J = 9.9 Hz, 2H), 8.30 – 8.24 (m, 2H), 7.89 – 7.83 (m, 4H), 7.68 – 7.58 (m, 6H), 7.38 (d, J = 10.5 Hz, 2H), 7.17 – 6.98 (m, 11H), 6.82 (d, J = 8.8 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ -60.55, -60.64, -62.18.



Scheme S3. The synthesis of CF₃-Au₃.

Synthesis of CF₃-Au₃ {[3,5-(CF₃)₂Pz]Au₃: The synthesis was conducted under ambient conditions following established protocols³. A solution of H[3,5-(CF₃)₂Pz] (0.4

g, 1.95 mmol) in anhydrous THF (15 mL) was treated with 60% excess NaH (0.06 g, 2.48 mmol) and stirred for 5 min to complete deprotonation. Residual NaH was removed by centrifugation. Subsequently, (Me₂S)AuCl (0.5 g, 1.55 mmol) was added to the filtrate under rigorous N₂ protection achieved by three freeze-pump-thaw cycles. After 6 h of photo-protected agitation, the mixture was filtered and the precipitate was washed with THF (3×5 mL). The combined filtrate was concentrated under reduced pressure to afford off-white solids (0.615 g, 60% yield based on Au). Colorless needle-like crystals suitable for single-crystal X-ray analysis were obtained through low-temperature recrystallization from dichloromethane.

Anal. ¹H NMR (C₆D₆): δ 6.50 (s, 6H, NH_{HPZ}). ¹⁹F NMR (C₆D₆): δ –60.8 (s, CF₃).

Section 2: Characterizations of An-HL and An-Au₃

2.2.1. NMR spectra of An-HL and An-Au₃



Fig. S1. ¹H NMR (400 MHz, 298 K, DMSO-d6) of An-HL.



Fig. S2. ¹³C NMR (101 MHz, 298 K, DMSO-d6) of An-HL.



Fig. S3. ¹⁹F NMR (376 MHz, 298 K, DMSO-d6) of An-HL.



Fig. S4. ¹H NMR (400 MHz, 298 K, DMSO-d6) of An-Au3.



Fig. S5. ¹⁹F NMR (376 MHz, 298 K, DMSO-d6) of An-Au₃.

2.2.2. PXRD of An-Au3 and CF3-Au3



Fig. S6. The comparison of experimental and simulated PXRD patterns of a) An-Au3;b) CF3-Au3.



Fig. S7. FI-IR spectra of An-HL and An-Au₃.

2.2.4. TGA of An-Au₃



Fig. S8. TGA profiles of An-Au₃ under N_2 atmosphere. The experimental residual content was measured at 39.4%, which is consistent with the theoretical value of 38.8% and aligns with the molecular formula.

2.2.5. XPS of An-Au₃



Fig. S9. Full XPS spectra of An-Au₃.



Fig. S10. High-resolution Au 4f and N 1s XPS spectra of An-Au3.

2.2.6. Single-crystal structure of An-Au₃



Fig. S11. (a) The photographs of An-Au₃ powder under room light and under 365 nm (b) as well as the An-Au₃ crystals.



Fig. S12. Top view of the An-Au₃ dimer.



Fig. S13. The dimer of An-Au₃ in the crystal and the dash line refers to the distance between the Au₃N₆ planes (9.214 Å).



Fig. S14. The dimer of CF₃-Au₃ in the crystal and the dash line refers to the distance between the Au₃N₆ planes (4.676 Å).

Identification code	An-CF3-Au3
Empirical formula	$C_{111}H_{66}N_{12}F_{18}Cl_6Au_6\\$
Formula weight	3304.26
Temperature/K	100.00(3)
Crystal system	Triclinic
Space group	<i>P</i> -1
$a/{ m \AA}$	14.1872(5)
$b/{ m \AA}$	15.2316(5)
$c/{ m \AA}$	15.6241(5)
$\alpha^{\prime \circ}$	117.120(3)
$eta/^{\circ}$	96.663(3)
$\gamma^{/\circ}$	111.699(3)
Volume/Å ³	2621.60(17)
Ζ	1
$ ho_{calc}{ m g/cm^3}$	2.093
μ/mm^{-1}	17.543
<i>F</i> (000)	1554
Crystal size/mm ³	0.3 imes 0.25 imes 0.04
Radiation	Cu Ka ($\lambda = 1.54184$)
2Θ range for data collection/°	6.76 to 135
Index ranges	$-17 \le h \le 15, -18 \le k \le 16, -15 \le l \le 18$
Reflections collected	19118
Independent reflections	9298 [$R_{int} = 0.0604, R_{sigma} = 0.0659$]
Data/restraints/parameters	9298/426/703
Goodness-of-fit on F^2	1.132
Final <i>R</i> indexes [I>= 2σ (I)]	$R_1 = 0.0849, wR_2 = 0.2299$
Final R indexes [all data]	$R_1 = 0.1024, wR_2 = 0.2368$
Largest diff. peak/hole / e Å ⁻³	4.30/-3.08

Table S1. Crystal system, space group, and unit cell parameters of An-Au₃.

 ${}^{a}R_{1} = \Sigma |F_{o}| - |F_{c}| / \Sigma |F_{o}| \cdot {}^{b}wR_{2} = \{ [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w (F_{o}^{2})^{2}] \}^{1/2}; w = 1 / [\sigma^{2} (F_{o}^{2}) + (aP)^{2} + bP], where P = [max (F_{o}^{2}, 0) + 2F_{c}^{2}] / 3 \text{ for all data.}$

2.2.7. Solution-state UV-vis Absorption Spectra of An-Au3 and CF3-Au3



Fig. S15. UV-vis spectra of a) An-Au₃ (2.5×10^{-4} M) in different solvents and CF₃-Au₃ (2.5×10^{-4} M) in DMSO.

As can be seen in Fig. S15a, **An-Au**₃ is soluble in a wide range of solvents, and its absorption intensity varies with solvent, with maximum absorption observed in DMA and DMSO. In contrast, **CF₃-Au**₃ has no characteristic absorption in the near-UV to visible region.



Fig. S16. Monitoring the stability of **An-Au**₃ (2.5×10^{-4} M) under ambient conditions: a) in DMSO and b) in DMF.

2.2.8. Solution-state Photoluminescence Spectra of An-Au3 and An-HL



Fig. S17. a) Room-temperature emission and excited spectra of **An-Au₃** $(2.5 \times 10^{-4} \text{ M})$ in DMSO (2 ml); b) Room-temperature emission spectra of **An-Au₃** under different excitation wavelengths.



Fig. S18. Room-temperature emission and excited spectra of **An-HL** $(2.5 \times 10^{-4} \text{ M})$ in DMSO (2 ml).

2.2.9. Room-Temperature Photoluminescence Lifetime of An-Au3 and An-HL



Fig. S19. Photoluminescence decay of a) **An-Au**₃ (C = 2.5×10^{-4} M) and b) **An-HL** (C = 2.5×10^{-4} M) obtained via time-correlated single photon counting (Purple and orange), and the line represents a dual-exponential fit of the data.

2.2.10. Solid-state Photoluminescence Spectra of An-Au3 and An-HL



Fig. S20. Comparison of normalized emission and excitation spectrum of a) An-Au₃ and b) An-HL.

2.2.11. Solid-state Photoluminescence Lifetime of An-Au₃ and An-HL



Fig. S21. Photoluminescence decay of a) An-Au₃ and b) An-HL obtained via timecorrelated single photon counting (Purple and orange), and the line represents a dualexponential fit of the data.

complexes	λex (nm)	λ _{em} (nm)	τ (ns)				
An-Au ₃	408	467	6.5ª				
			4.3 ^b				
An-HL	331	532	$ au_1/A_1$ 2.48/0.90	$ au_2/A_2$ 22.71/0.10			

Table S2. Summary of photophysical parameters for the compounds in the solid state

fluorescence decay lifetime: ^a $\lambda_{ex} = 408$ nm. ^b $\lambda_{ex} = 331$ nm.

Table S3. Summary of photophysical parameters for the compounds in DMSO solution

complexes	λex (nm)	λ _{em} (nm)	τ (ns)
An-Au ₃	407	479	5.5 ^a
An-HL	322	430	9.9 ^b

fluorescence decay lifetime: a $\lambda_{ex}=407$ nm. b $\lambda_{ex}=322$ nm.

2.2.12. Cyclic Voltammetry (CV) of An-Au3, An-HL, and CF3-Au3



Fig. S22. CV curves of a) An-HL and b) CF₃-Au₃.



Fig. S23. Normalized emission (E_x : 350 nm) of An-Au₃ and its intercept with the absorption spectrum at 401 nm ($E_{0,0} = 3.10 \text{ eV}$).

Based on the Rehm–Weller formalism⁴, the excited state reduction potential E^*_{red} was determined according to the following equations:

$$\boldsymbol{E}^{*}_{\text{red}} \left(\mathbf{An} - \mathbf{Au}_{3} \right) = \boldsymbol{E}_{\text{red}} \left(\mathbf{An} - \mathbf{Au}_{3} \right) + \boldsymbol{E}_{0,0}$$
(1)
$$\boldsymbol{E}^{*}_{\text{red}} \left(\mathbf{An} - \mathbf{Au}_{3} \right) = 1.15 \text{ V } vs. \text{ SCE}$$

The excited state oxidation potential E^*_{ox} was determined according to the following equations:

$$E^*_{\text{ox}}$$
 (An-Au₃) = E_{ox} (An-Au₃) - $E_{0,0}$
 E^*_{ox} (An-Au₃) = -1.91 V vs. SCE



Fig. S24. fs-TA Spectra of An-HL and An-Au₃.

2.2.14. Computational Details

For ligand An-HL and complexes An-Au₃ and CF₃-Au₃, density functional theory (DFT) and time-dependent density functional theory (TDDFT) computations were conducted utilizing Gaussian 09E program suite⁵, and the solvation model density (SMD)⁶ was adopted for considering the solvent effect of DMSO. The following level of theory was adopted throughout: (1) Functional: the hybrid Perdew, Burke, and Ernzerhof functional (PBE0)^{7,8} in conjunction with D3⁹(BJ)¹⁰ dispersion correlation, (2) Basis sets: the SDD effective core potential (ECP)¹¹ for Au and the 6-311G(d,p) basis set¹² for the other atoms.

Firstly, the geometrical optimization was performed using restricted PBE0 method for obtaining the stable ground-state (S₀) geometries of the molecules of the above three compounds, confirmed by the absent of imaginary frequencies (NIMG = 0). Then, the first 50 singlet-singlet spin-allowed transitions were calculated for these three compounds, and the first 20 singlet-triplet spin-forbidden transitions were calculated for An-HL and An-Au₃. After that, the TDDFT results of the Gaussian software were furtherly treated by using Multiwfn 3.8(dev) program^{13,14} to give the information of electron transitions and the cub files for drawing the electron density differences (EDD) maps. The stable geometries of the first triplet state (T₁) for these three compounds were obtained with NIMG = 0 by unrestricted PBE0. With the wave functions of T₁ states as inputs, Multiwfn program outputs the cub files for drawing the electron spindensity surfaces. Both EDD and spin density maps were drawn with isovalues = 0.0005 a.u. by VMD 1.93 program¹⁵. In the discussions of the TDDFT results of An-HL and An-Au₃ based on the stable S_0 geometries, only the following excited states were selected and shown in Table S5: (1) The singlet excited states (S_n) with the oscillator strength (f) > 0.01 among the first 10 S_n states, (2) T_1 states, (3) the triplet excited states (T_m) with the smallest energy separations with S_1 states (Table S5). Based on the hole-electron analysis embedded in Multiwfn 3.8(dev) program^{13,14}, D, S_r, and S_m indexes were calculated for the selected singlet excited states for quantifying the nature of charge transfer, and the results were listed in Table S6. Among these charge-transfer indexes, a large D index indicates a significant charge-transfer excited state since this index refers to the distances between the mass centers of hole and electron orbitals. In contrast, the small S_r and S_m indexes suggest a significant charge-transfer excited state since both indexes indicate the overlap between the hole and electron orbitals.

Table S4 The single-point energies with zero-point correction (E) of Au₃(3-An-5-CF₃Pz)₃ in C_1 and C_3 symmetries based on the stable S₀ geometries.

$E(C_3)$ (a.u.)	$E(C_1)$ (a.u.)	$E(C_3) - E(C_1)$ (a.u.)	$E(C_3) - E(C_1) (eV)$
-3706.980	-3706.988	0.008	0.2176



Fig. S25. (Up) The vdW isosurfaces (isovalue = 0.001 a.u.) mapped by ESP and (b) the molecular structures of **An-Au3** and **An-HL**.

Based on the stable ground-state (S_0) geometries, the electrostatic potential (ESP) analyses indicate a better charge-transfer (CT) character of **An-Au₃** than **An-HL** (Fig. S24), supported by the lager dipole moment of **An-Au₃** (8.201 Debye) than **An-HL** (6.955 Debye).



Fig. S26. The comparisons of experimental (black curves) and simulated (red curves) of (a) **An-HL**, (b) **An-Au**₃, and (c) **CF**₃-**Au**₃ in DMSO solution.

Compound	S _n /T _m state	E (eV)	λ (nm)	f	EDD maps
	S_1	3.191	388.5	0.151	
	\mathbf{S}_5	4.856	255.3	0.087	
	\mathbf{S}_6	4.970	249.5	1.933	
An-HL	\mathbf{S}_7	5.002	247.9	0.044	
	S_8	5.172	239.7	0.069	
	T_1	1.678	738.8	0.000	
	T ₂	3.248	381.7	0.000	

Table S5. Selected TDDFT results of An-HL, An-Au₃, and CF₃-Au₃.

	S_1	2.914	425.4	0.031	
	S_3	3.190	388.7	0.286	
An-Au ₃	S4	3.208	386.5	0.141	
	T_1	1.653	750.1	0.000	
	T4	3.023	410.2	0.000	
	S_1	4.723	262.5	0.016	
CF3-AU3	S ₁₀	5.618	220.7	0.824	

Table S6. Calculated D, S_r , and S_m indexes of the selected S_n states of An-HL and An-Au₃.

Compound	S _n state	λ (nm)	f	D (Å)	S _r (a.u.)	S _m (a.u.)
An-HL	\mathbf{S}_1	388.5	0.151	0.090	0.888	0.700
	\mathbf{S}_1	425.4	0.031	0.093	0.871	0.679
An-Au ₃	S ₃	388.7	0.286	0.066	0.889	0.700
	S ₄	386.5	0.141	0.062	0.889	0.701

Section3: Optimization of photocatalytic reaction conditions

1) General Procedure A model reaction (substrate 1a):



To a 10 mL rubber-stoppered reaction tube with a magnetic stir bar, **1a** (0.1 mmol), **An-Au₃** (1.5 mg, 1 mol%), and degassed DMSO (2 ml) were added. The system was purged with argon for 15-20 min and sealed. The reaction mixture was stirred under light (410 nm, 12 W LED) for 40 min, with a circulating water cooling system to maintain the temperature (25–30 °C). After the reaction was complete, the reaction was quenched with saturated saline and extracted three times (10 ml/ each) repeatedly with ethyl acetate. The organic phase was collected and the solvent was removed under reduced pressure and the crude residue was purified by column chromatography.





Entry	Modifications of reaction conditions ^a	Yields (%) ^b
1	None	99
2	No Cat.	N. D.
3	DMF, instead of DMSO	99
4	Add DIPEA	99
5	CF ₃ -Au ₃ , instead of An-Au ₃	Trace
6	No Light	N. D.
7	Heat at 45 °C	N. D.
8	410 nm instead of 365 nm	63

^{*a*}Reaction conditions: **1a** (0.1 mmol), **An-Au₃** (1.5 mg, 1 mol%), DMSO (2.0 mL) under Ar atmosphere with purple LEDs (12 W, 365 nm) irradiation for 30 min. ^{*b*}Yields were determined by GC-MS.

2) General Procedure B (For substrates 1b-1d):



To a 10 mL rubber-stoppered reaction tube with a magnetic stir bar, **1b-1d** (0.1 mmol), **An-Au₃** (1.5 mg, 1 mol%), degassed DMSO (2 ml), and 2 eq. of DIPEA (35 μ L) were added. The system was purged with argon for 15-20 min and sealed. The reaction mixture was stirred under light (365 nm, 12 W LED) for 2 hours, with a circulating water-cooling system to maintain the temperature (25–30 °C). After the reaction was complete, the reaction was quenched with saturated saline and extracted three times (10 ml/ each) repeatedly with ethyl acetate. The organic phase was collected, the solvent was removed under reduced pressure and the crude residue was purified by column chromatography.

3) General Procedure C (For substrates 1e-1f):



To a 10 mL rubber-stoppered reaction tube with a magnetic stir bar, **1e-1f** (0.1 mmol), **An-Au**₃ (1.5 mg, 1 mol%), degassed DMSO (2 ml), and 2 eq. of DIPEA (35 μ L) and LiBF₄ (2eq., 0.2 mmol, 18.6 mg) were added. The system was purged with argon for 15-20 min and sealed. The reaction mixture was stirred under light (365 nm, 12 W LED) for 20 hours, with a circulating water-cooling system to maintain the temperature (25– 30 °C). After the reaction was complete, the reaction was quenched with saturated saline and extracted three times (10 ml/ each) repeatedly with ethyl acetate. The organic phase was collected, the solvent was removed under reduced pressure and the crude residue was purified by column chromatography.

4) Substrate Summary



Table S8. Substrate Scope. *Reaction conditions follow General Procedure B. [#]Reaction conditions follow General Procedure C. Product yields were determined by NMR.

5) UV-vis Absorption Spectra of the Catalytic System with Different Additions:



Fig. S27. Absorption spectra of the photocatalytic system of **1a** (0.2 mmol) and **An-Au₃** (1 mol%) with or without DIPEA (2eq., 0.2 mmol), and LiBF₄ (2eq., 0.2 mmol) in CH₃CN (2 ml).

6) Reaction kinetics experiments:



Fig. S28. Reaction kinetics of N-O bond breaking of Weinreb amides catalyzed by An-Au₃.

7) Free Radical Capture Experiment:



Following the general procedure A (1a), procedure B (1b), and procedure C (1f), TEMPO (0.5 mmol, 5 eq.) was added. GC-MS analysis revealed significant inhibition of the reaction, with the yield of 2a decreasing to 29%, and complete suppression of the conversions of 1b and 1f, suggesting that the reaction proceeds via a radical mechanism.

8) Detection of Formaldehyde:



Fig. S29. (a) Target products for N-O bond breaking reactions; (b) ¹H NMR of the reaction mixture of **1a** under general procedure A in d6-DMSO showing the characteristic peak of HCHO at 9.56 ppm.





Fig. S30. Photoluminescence ($\lambda_{ex} = 407 \text{ nm}$) spectra of Ar-saturated DMSO containing 0.25 mM An-Au₃, recorded with increasing concentration of a) 1a (0–30 mM) and b) DIPEA (0–30 mM), and their corresponding Stern-Volmer plots.

Stern–Volmer analyses demonstrated distinct quenching constant (K_{SV}) for DIPEA ($K_{SV} = 0.0286$) and substrate **1a** ($K_{SV} = 0.0159$) toward the excited-state **An-Au**₃ complex. The quenching experiments strongly support the activation of substrate **1a** by **An-Au**₃ at its photoexcited states (i.e. an oxidative quenching mechanism). In addition, DIPEA can function as a sacrificial reagent, donating an electron to the photoexcited **An-Au**₃, thereby facilitating the formation of an **An-Au**₃ radical anion intermediate (i.e. a reductive quenching mechanism). These findings suggest that the **An-Au**₃ catalyst can accommodate the diverse reduction potentials of Weinreb amides through a dual electron transfer mechanism, involving both oxidative and reductive quenching pathways.

3. Characterization data for products



2a: \mathbf{R}_{f} (60% EtOAc in n-pentane) = 0.33. ¹H NMR (400 MHz, DMSO) δ 8.69 (d, J = 6.6 Hz, 1H), 8.00 – 7.94 (m, 4H), 2.80 (d, J = 4.6 Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ 165.67, 138.91, 132.91, 128.38, 118.82, 113.93, 26.82.



2b: \mathbf{R}_{f} (65% EtOAc in n-pentane) = 0.36. ¹H NMR (400 MHz, DMSO) δ 8.66 (d, J = 6.1 Hz, 1H), 8.02 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 2.81 (d, J = 4.5 Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ 165.88, 138.69, 131.60, 131.28, 128.42, 125.81, 125.77, 123.07, 26.78. ¹⁹F NMR (376 MHz, DMSO) δ -61.34.



2c: \mathbf{R}_{f} (50% acetone in Et2O) = 0.30. ¹H NMR (400 MHz, DMSO) δ 8.99 (d, J = 2.5 Hz, 1H), 8.75 – 8.58 (m, 2H), 8.17 (dt, J = 7.9, 2.2 Hz, 1H), 7.48 (ddd, J = 7.7, 4.8, 2.4 Hz, 1H), 2.80 (dd, J = 4.8, 2.5 Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ 165.64, 152.16, 148.72, 135.24, 130.40, 123.88, 26.64.



2d: \mathbf{R}_{f} (50% acetone in DCM) = 0.43. ¹H NMR (400 MHz, DMSO) δ 8.61 (s, 1H), 8.43 (s, 1H), 8.03 – 7.90 (m, 4H), 7.59 (tt, *J* = 7.0, 5.1 Hz, 2H), 2.84 (d, *J* = 4.5 Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ 165.68, 149.26, 148.86, 135.79, 131.56, 129.56, 129.20, 127.85, 127.60, 127.04, 26.76.



2e: \mathbf{R}_{f} (60% EtOAc in n-pentane) = 0.30. ¹H NMR (400 MHz, DMSO) δ 8.51 (s, 1H), 7.77 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 2.77 (d, J = 4.5 Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ 166.14, 134.06, 131.78, 129.65, 128.74, 125.22, 26.73.



2f: \mathbf{R}_{f} (50% EtOAc in n-pentane) = 0.33. ¹H NMR (400 MHz, DMSO) δ 8.45 (s, 1H), 7.92 – 7.86 (m, 2H), 7.32 – 7.26 (m, 2H), 2.78 (d, J = 4.5 Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ 173.33, 166.02, 130.14, 130.05, 128.21, 115.76, 115.54, 26.72.



2g: \mathbf{R}_{f} (70% EtOAc in n-pentane) = 0.32. ¹H NMR (400 MHz, DMSO) δ 8.61 (s, 1H), 8.43 (s, 1H), 8.03 – 7.90 (m, 4H), 7.59 (tt, *J* = 7.0, 5.1 Hz, 2H), 2.84 (d, *J* = 4.5 Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ 167.13, 134.51, 132.64, 132.36, 129.28, 128.32, 128.06, 127.96, 127.73, 127.16, 124.52, 26.83.

4. NMR Spectra:





---61.34



¹³C NMR (101 MHz, DMSO)

165.64	152.16	148.72	135.24	130.40	123.88
		Ι			

1	1	i		
Alfright and the second se			**************************************	¥

							, ,					50				
170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10
f1 (ppm)																

2d: ¹H NMR (400 MHz, DMSO)



¹³C NMR (101 MHz, DMSO)



2e: ¹H NMR (400 MHz, DMSO)









¹³C NMR (101 MHz, DMSO)



f1 (ppm)

5. Reference

- Zhu, C.; Zeng, H.; Liu, C.; Cai, Y.; Fang, X.; Jiang, H. Regioselective Synthesis of 3-Trifluoromethylpyrazole by Coupling of Aldehydes, Sulfonyl Hydrazides, and 2-Bromo-3,3,3-Trifluoropropene. *Org. Lett.* 2020, **22** (3), 809–813.
- (2) Holz, J.; Ayerbe García, M.; Frey, W.; Krupp, F.; Peters, R. Diastereoselective Synthesis, Structure and Reactivity Studies of Ferrocenyloxazoline Gold(I) and Gold(II) Complexes. *Dalton Trans.* 2018, 47 (11), 3880–3905.
- (3) Omary, M. A.; Rawashdeh-Omary, M. A.; Gonser, M. W. A.; Elbjeirami, O.; Grimes, T.; Cundari, T. R.; Diyabalanage, H. V. K.; Gamage, C. S. P.; Dias, H. V. R. Metal Effect on the Supramolecular Structure, Photophysics, and Acid–Base Character of Trinuclear Pyrazolato Coinage Metal Complexes. *Inorg. Chem.* 2005, 44 (23), 8200–8210.
- (4) Farid, S.; Dinnocenzo, J. P.; Merkel, P. B.; Young, R. H.; Shukla, D.; Guirado, G. Reexamination of the Rehm–Weller Data Set Reveals Electron Transfer Quenching That Follows a Sandros–Boltzmann Dependence on Free Energy. *J. Am. Chem. Soc.* 2011, **133** (30), 11580–11587.
- (5) Frisch, M. J.; Trucks, G. W. Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc., Wallingford CT, 2013. Gaussian 09, Revision E.01., 2009.
- (6) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* 2009, 113 (18), 6378–6396.
- (7) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, 77 (18), 3865–3868.
- (8) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. 77, 3865 (1996)]. *Phys. Rev. Lett.* 1997, **78** (7), 1396– 1396.

- (9) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate *Ab Initio* Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* 2010, **132** (15), 154104.
- (10)Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J Comput Chem* 2011, 32 (7), 1456–1465.
- (11)Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. Energy-Adjusted Pseudopotentials for the Actinides. Parameter Sets and Test Calculations for Thorium and Thorium Monoxide. J. Chem. Phys. 1994, 100 (10), 7535–7542.
- (12)Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions. J. Chem. Phys. 1980, 72 (1), 650–654.
- (13)Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. *J Comput Chem* 2012, **33** (5), 580–592.
- (14)Liu, Z.; Lu, T.; Chen, Q. An Sp-Hybridized All-Carboatomic Ring, Cyclo[18]Carbon: Electronic Structure, Electronic Spectrum, and Optical Nonlinearity. Carbon 2020, 165, 461–467.
- (15)Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual Molecular Dynamics. J. Mol. Graph. 1996, 14 (1), 33–38.