# Supporting Information

***for***

## High-Performance Ketone Sensing in Vapor Phase Enabled by *o*-Carborane-Modified Cyclometalated Alkynyl-Gold(III) Complex-Based Fluorescent Films

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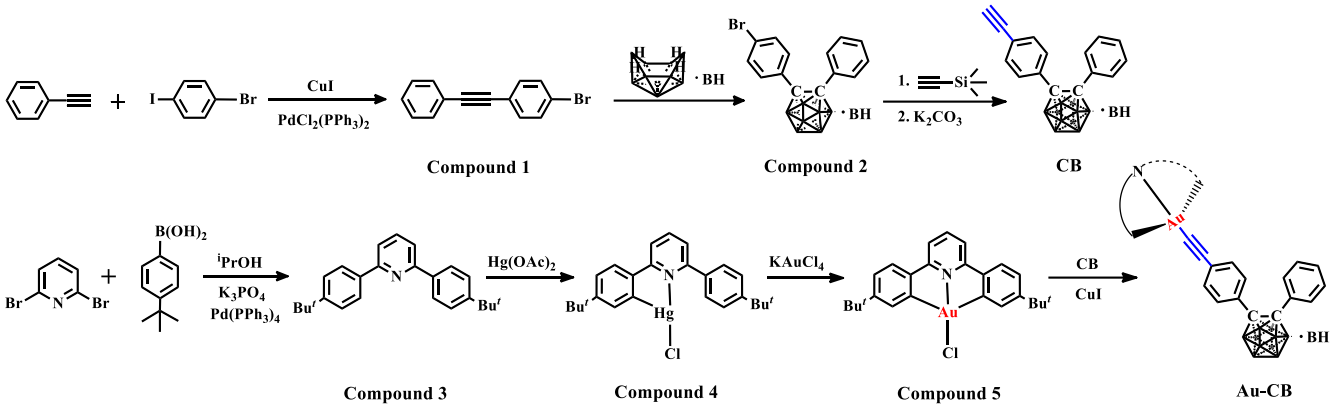
## Contents

# 1. Experimental Details

## 1.1 Synthesis and Characterization of the Related Six Intermediates

The synthetic route for **Au-CB** is shown in **Scheme S1**.




**Scheme S1**. Typical synthesis procedures for the target fluorophore, **Au-CB**

The intermediates **1**, **2** and **CB** are synthesized according to reference 1.[1] And the intermediates **3**, **4** and **5** are synthesized following reference 2.[2]

Compound **1**. Yield: 58%. $^1$H NMR (600 MHz, $CDCl_3$, ppm): $\delta$ 7.52 (m, 2H), 7.48 (m, 2H), 7.39 (m, 2H), 7.35 (m, 3H).

Compound **2**. Yield: 54%. $^1$H NMR (600 MHz, Acetone-$d_6$, ppm): $\delta$ 7.53 (d, $J$ =12.0 Hz, 2H), 7.45 (t, $J$ = 18.0 Hz, 4H), 7.37 (t, $J$ = 18.0 Hz, 1H), 7.28 (t, $J$ = 18.0 Hz, 2H).

Compound **CB**. Yield: 23%. $^1$H NMR (600 MHz, Acetone-$d_6$, ppm): $\delta$ 7.59 (dd, $J$ = 8.2, 2.9 Hz, 4H), 7.34 (t, $J$ = 7.9 Hz, 3H), 7.26 (t, $J$ = 7.8 Hz, 2H), 3.79 (s, 1H).

Compound **3**. Yield: 25%. $^1$H NMR (600 MHz, $CD_2Cl_2$, ppm): $\delta$ 8.08 (d, $J$ = 8.4 Hz, 4H), 7.84 (t, $J$ = 7.8 Hz, 1H), 7.69 (d, $J$ = 7.8 Hz, 2H), 7.54 (d, $J$ = 8.4 Hz, 4H), 5.32 (s, 3H), 1.38 (s, 18H). HRMS (APCI-Orbitrap) *m/z*: $[M+H]^+$ calc. for $C_{25}H_{30}N$ 344.2368, found 344.2373.

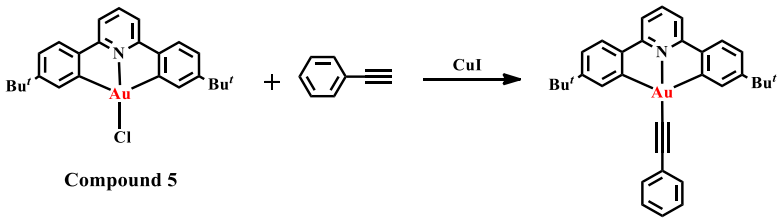
Compound **4**. Yield: 62%. $^1$H NMR (600 MHz, $CD_2Cl_2$, ppm): $\delta$ 7.93 (m, 3H), 7.88 (t, $J$ = 7.8 Hz, 1H), 7.78 (d, $J$ = 7.7 Hz, 1H), 7.74 (d, $J$ = 7.7 Hz, 1H), 7.61 (d, $J$ = 1.9 Hz, 1H), 7.55 (d, $J$ = 8.5 Hz, 2H), 7.48 (dd, $J$ = 8.2, 2.0 Hz, 1H), 1.38 (s, $J$ = 5.2 Hz, 18H). HRMS (APCI-Orbitrap) *m/z*: $[M+H]^+$ calc. for $C_{25}H_{29}HgClN$ 580.1672, found 580.1683.

Compound **5**. Yield: 39%. $^1$H NMR (600 MHz, $CD_2Cl_2$, ppm): $\delta$ 7.92 (d, $J$ = 1.9 Hz, 2H), 7.86 (t, $J$ = 8.0 Hz, 1H), 7.50 (d, $J$ = 8.1 Hz, 2H), 7.43 (d, $J$ = 8.0 Hz, 2H), 7.31 (dd, $J$ = 8.1, 2.0 Hz, 2H), 1.37 (s, 18H). HRMS (APCI-Orbitrap) *m/z*: $[M+H]^+$ calc. for $C_{25}H_{28}AuClN$ 574.1580, found 574.1570.

### 1.2 Synthesis of Au-CB

A mixture of [**Au (ᵗBuC^N^CᵗBu) Cl**] (0.20 g, 0.43 mmol) and **CB** (0.21 g, 0.65 mmol) in the presence of a catalytic amount of CuI (9.0 mg) in triethylamine (2.0 mL) and dichloromethane (35.0 mL) is stirred at room temperature for 3 h. After evaporation to dryness, the solid residue is purified by column chromatography on silica gel using dichloromethane (DCM) as the eluent. Subsequent recrystallization from layering of *n*-hexane onto the concentrated solution gives the product as pale-yellow crystal. Yield: 35%. $^{1}$H NMR (600 MHz, $CD_2Cl_2$, ppm): $\delta$ 8.05 (d, $J$ = 6.0 Hz, 2H), 7.83 (t, $J$ = 12.1 Hz, 1H), 7.53 (dd, $J$ = 12.1 Hz, 6.0 Hz, 4H), 7.44 (m, 4H), 7.35 (d, $J$ = 6.0 Hz, 2H), 7.31 (m, 3H), 7.22 (t, $J$ = 18.2 Hz ,2H), 1.38 (s, 18H); $^{11}$B NMR (192 MHz , $CD_2Cl_2$, ppm): $\delta$ -2.09, -2.99, -10.98, -10.16; $^{13}$C NMR (150 MHz, $CD_2Cl_2$, ppm): $\delta$ 166.78, 164.80, 155.24, 146.53, 142.36, 130.69, 130.34, 128.34, 124.99, 123.92, 116.28, 99.81, 96.56, 85.53, 53.76, 53.58, 53.59, 53.21, 53.03, 35.22, 30.93, 29.68; HRMS (APCI-Orbitrap) *m/z*: $[M+H]^+$ calc. for $C_{41}H_{47}AuB_{10}N$ 860.4339, found 860.4366.

### 1.3 Synthesis of Au-$C_6H_5$




**Scheme S2**. Typical synthesis procedures for the control fluorophore, **Au-$C_6H_5$**.

The compound **Au-$C_6H_5$** was synthesized according to the modification of a reported procedure.[2] Yield: 56%. $^{1}$H NMR (600 MHz, $CD_2Cl_2$, ppm): $\delta$ 8.18 (d, $J$ = 2.0 Hz, 2H), 7.86 (t, $J$ = 8.0 Hz, 1 H), 7.59 (dd, $J$ = 8.2 Hz, 2.0 Hz, 2H), 7.56 (d, $J$ = 8.2 Hz, 2 H), 7.46 (d, $J$ = 8.0 Hz, 2 H), 7.35 (m, 5H), 1.39 (s, 18 H).

## 2. Crystallographic Data

**Table S1**. Crystallographic data of **Au-CB**.

| | |
|---|---|
| CCDC Deposit Number | 2045292 |
| Empirical formula | $C_{41}H_{47}AuB_{10}N$ |
| Formula weight | 860.4339 |
| Temperature/K | 193 K |
| Wavelength | 1.34139 |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | a = 13.2242 (4) Å |
| | b = 13.2802 (4) Å |
| | c = 15.3500 (5) Å |
| | α = 106.647 (1) ° |
| | β = 111.995 (1) ° |
| | γ = 95.364 (1) ° |
| Volume/Å$^3$ | 2332.83 (13) |
| Z | 2 |
| $\rho_{calc}$ g/cm$^3$ | 1.463 |
| μ/mm$^{-1}$ | 5.620 |
| F (000) | 1024.0 |
| Crystal size/mm$^3$ | 0.100 × 0.100 × 0.100 mm$^3$ |
| Radiation | Ca Kα (λ = 1.54178) |
| $\theta$ range for data collection/° | 2.881 to 56.975 ° |
| Index ranges | -16 ≤ h ≤ 16, -16 ≤ k≤ 16, -19 ≤ l ≤ 19 |
| Reflections collected | 32994 |
| Independent reflections | 9494 [R(int) = 0.0647] |
| Data/restraints/parameters | 9494 / 0 / 539 |
| Completeness to theta | 56.975 |
| Max. and min. transmission | 0.599 and 0.570 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Goodness-of-fit on $F^2$ | 1.026 |
| Final R indexes [I≥2σ (I)] | $R_1$ = 0.0434, $wR_2$ = 0.1118 |
| Final R indexes [all data] | $R_1$ = 0.0478, $wR_2$ = 0.1118 |
| Extinction coefficient | 0.00491(19) |
| Largest diff. peak/hole | 1.417 d -1.858 e. Å$^{-3}$ |

## 3. Supplementary Figures and Tables

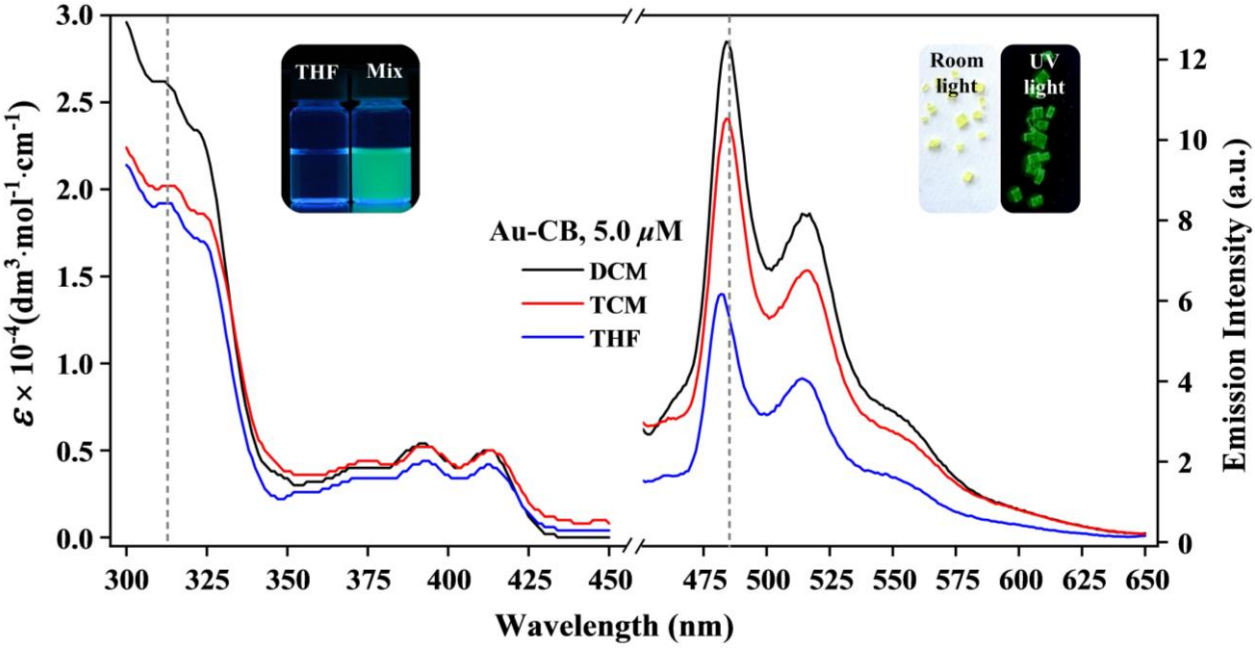



**Figure S1**. UV-vis absorption and fluorescence emission spectra ($\lambda_{ex}$ = 330 nm) of **Au-CB** recorded in $CH_2Cl_2$(DCM), $CHCl_3$ (TCM), and tetrahydrofuran (THF) at a concentration of 5.0 × $10^{-6}$ mol/L. Inset: Fluorescent images of compound **Au-CB** in solution under UV light (365 nm, left: THF; right: THF/$H_2O$ mixture) and solid state under daylight and UV light (365 nm).

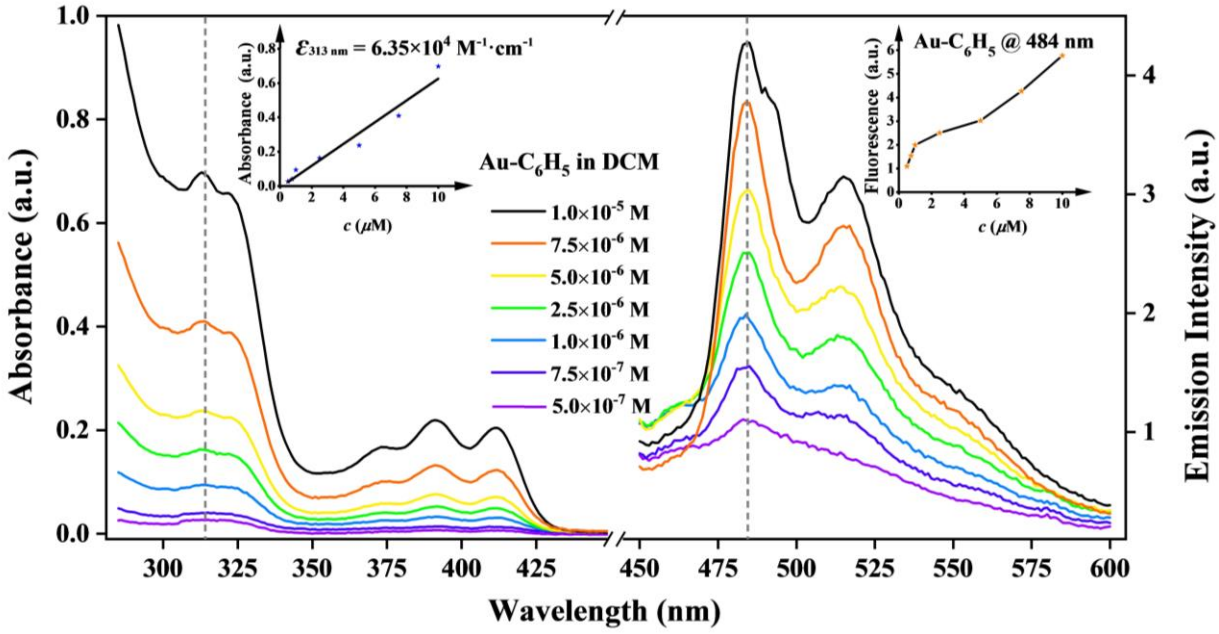



**Figure S2.** UV-vis absorption (left) and fluorescence emission spectra (right, $\lambda_{ex}$ = 330 nm) of **Au-$C_6H_5$** in DCM at different concentrations. Inset: 1) Lambert-Beer plot for the absorption of **Au-$C_6H_5$** in DCM; 2) Plot of fluorescence intensity at 484 nm against the concentration of the control fluorophore **Au-$C_6H_5$**.

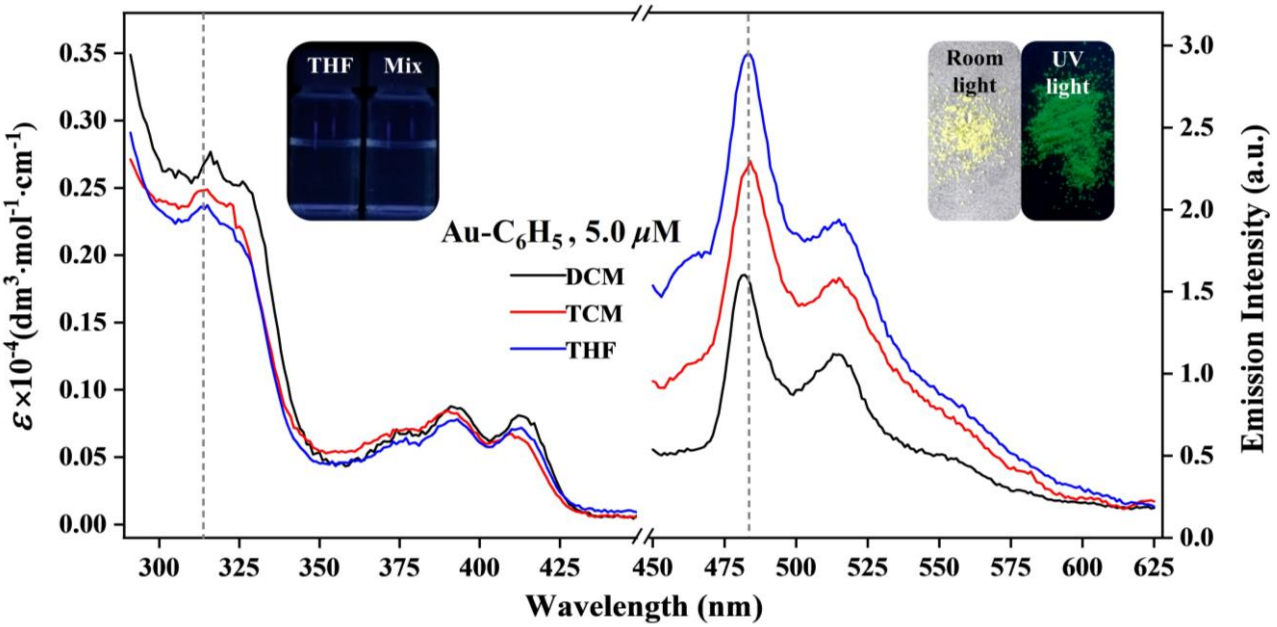



**Figure S3**. UV-vis absorption and fluorescence emission spectra ($\lambda_{ex}$ = 330 nm) of **Au-$C_6H_5$** recorded in DCM, TCM, and THF at a concentration of 5.0 × $10^{-6}$ mol/L. Inset: Fluorescent images of compound in solution under UV light (365 nm, left: THF; right: THF/$H_2O$ mixtures) and solid state under daylight and UV light (365 nm).

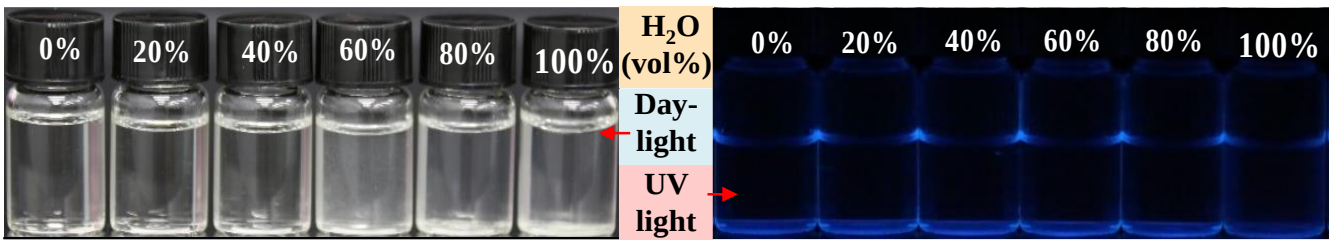



**Figure S4**. Fluorescence images of **Au-$C_6H_5$** in the mixtures of THF/$H_2O$ with different compositions. All the sample concentrations are 5.0 μM.

**Table S2**. Fluorescence lifetime date for **Au-CB** and **Au-$C_6H_5$**.

| | λ（nm） | $\tau_1$ (ns) | $\tau_2$ (ns) | $\chi^2$ |
|---|---|---|---|---|
| **Au-CB** | 302 nm | 7.35 (6.16%) | 105.42 (93.84%) | 1.14 |
| | 343 nm | 6.61 (11.75%) | 99.50 (88.25%) | 1.109 |
| | 405 nm | 6.57 (3.88%) | 113.20 (96.12%) | 1.037 |
| **Au-$C_6H_5$** | 302 nm | 5.56 (15.78%) | 94.69 (94.22%) | 1.032 |
| | 343 nm | 5.22 (8.67%) | 95.62 (91.33%) | 1.043 |
| | 405 nm | 7.42 (3.55%) | 98.15 (96.45%) | 1.055 |

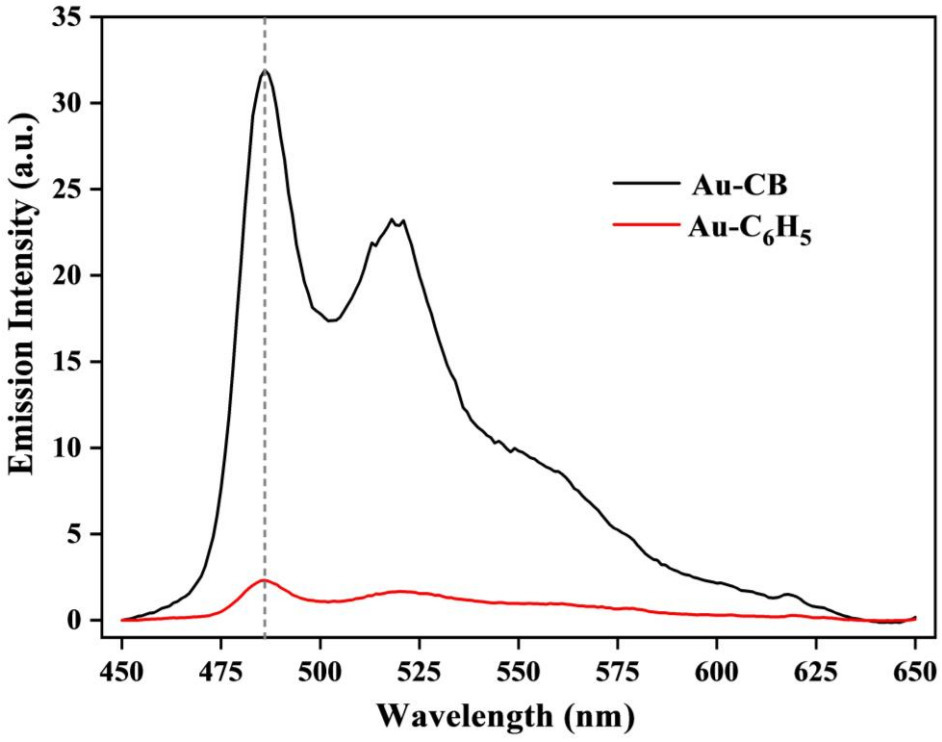



**Figure S5**. Fluorescence emission spectra ($\lambda_{ex}$ = 330 nm) of the fluorescent films based on **Au-CB** (black line) and **Au-$C_6H_5$** (red line).

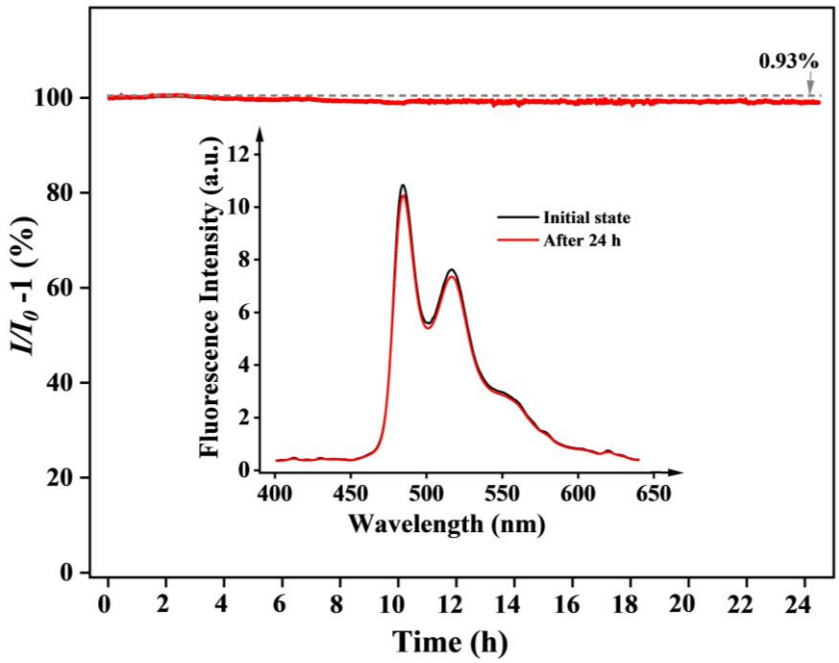



**Figure S6**. Photochemical stability of the **Au-CB**-based fluorescent film monitored using the homemade sensing platform ($\lambda_{ex}$ = 330 nm). Inset: Fluorescence emission spectra of the film monitored before and after the continuous measurement (24 h).

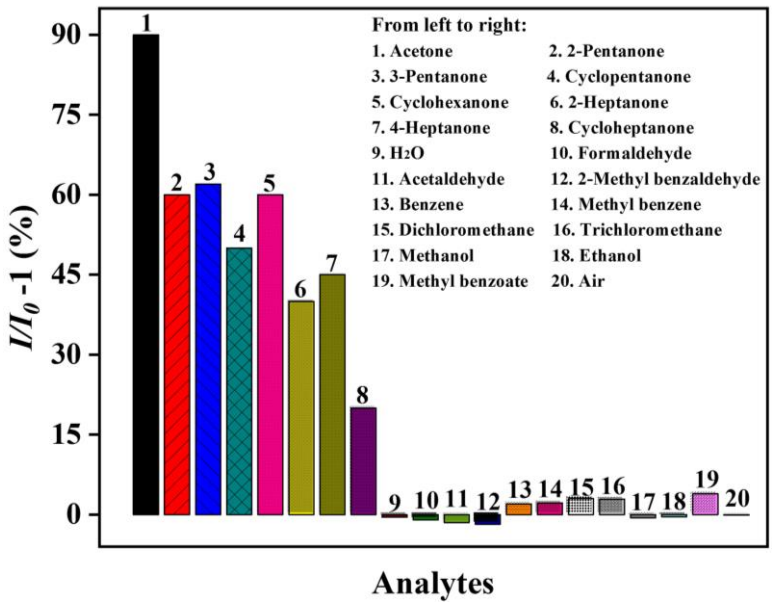



**Figure S7**. Response patterns of the tested analytes and the potential interferences obtained by collecting fluorescence intensity variations of the film device. Notes: the Arabic numbers in the figure stand for different chemicals. Specifically, **1**. Acetone; **2**. 2-Pentanone; **3**. 3-Pentanone; **4**. Cyclopentanone; **5**. Cyclohexanone; **6**. 2-Heptanone; **7**. 4-Heptanone; **8**. Cycloheptanone; **9**. $H_2O$; **10**. Formaldehyde; **11**. Acetaldehyde; **12**. 2-Methyl benzaldehyde; **13**. Benzene; **14**. Methylbenzene; **15**. Dichloromethane; **16**. Trichloromethane; **17**. Methanol; **18**. Ethanol; **19**. Methyl benzoate; **20**. Air.

**Table S3**. Important physical parameters of some tested ketones.

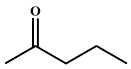
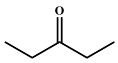
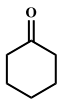
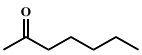
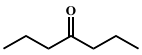
| | Chemical structure | Boiling point (°C) | Vapor pressure (mmHg, 25 °C) |
|---|---|---|---|
| **Acetone** |  | 56.1 | 230.7 |
| **2-Pentanone** |  | 102.2 | 36.5 |
| **3-Pentanone** |  | 102.0 | 37.5 |
| **Cyclopentanone** |  | 130.7 | 12.4 |
| **Cyclohexanone** |  | 155.6 | 2.9 |
| **2-Heptanone** |  | 151.1 | 3.2 |
| **4-Heptanone** |  | 144.0 | 5.2 |
| **Cycloheptanone** |  | 185.2 | 0.9 |

**Table S4**. Response time (RPT) and recovery time (RCT) measurements for acetone and cyclohexanone among the examined ketone vapors.

| Trial | Acetone | | Cyclohexanone | |
|---|---|---|---|---|
| | **RPT/s** | **RCT/s** | **RPT/s** | **RCT/s** |
| **1** | 4.41 | 47.88 | 6.12 | 448.38 |
| **2** | 4.14 | 51.84 | 6.84 | 422.64 |
| **3** | 4.41 | 49.77 | 7.11 | 428.85 |
| **4** | 3.51 | 53.28 | 6.39 | 408.42 |
| **5** | 4.50 | 45.63 | 6.30 | 422.19 |
| **6** | 4.32 | 52.47 | 7.11 | 424.35 |
| **7** | 4.59 | 55.35 | 6.75 | 411.93 |
| **8** | 4.41 | 54.36 | 6.75 | 412.92 |
| **9** | 4.59 | 53.28 | 7.02 | 406.08 |
| **10** | 4.86 | 62.72 | 6.48 | 421.20 |
| **11** | 4.68 | 50.05 | 6.93 | 424.89 |
| **12** | 4.77 | 56.79 | 7.11 | 429.03 |
| **13** | 4.50 | 51.12 | 6.66 | 401.94 |
| **14** | 4.41 | 58.05 | 6.84 | 410.40 |
| **15** | 4.59 | 53.19 | 6.66 | 404.91 |
| **Average** | **4.41** | **53.01** | **6.75** | **419.13** |

Notes: RPT is the abbreviation of response time and RCT is the recovery time, all the time units used are seconds.

## 4. NMR and MS Spectra of the Intermediates and Target Fluorophore

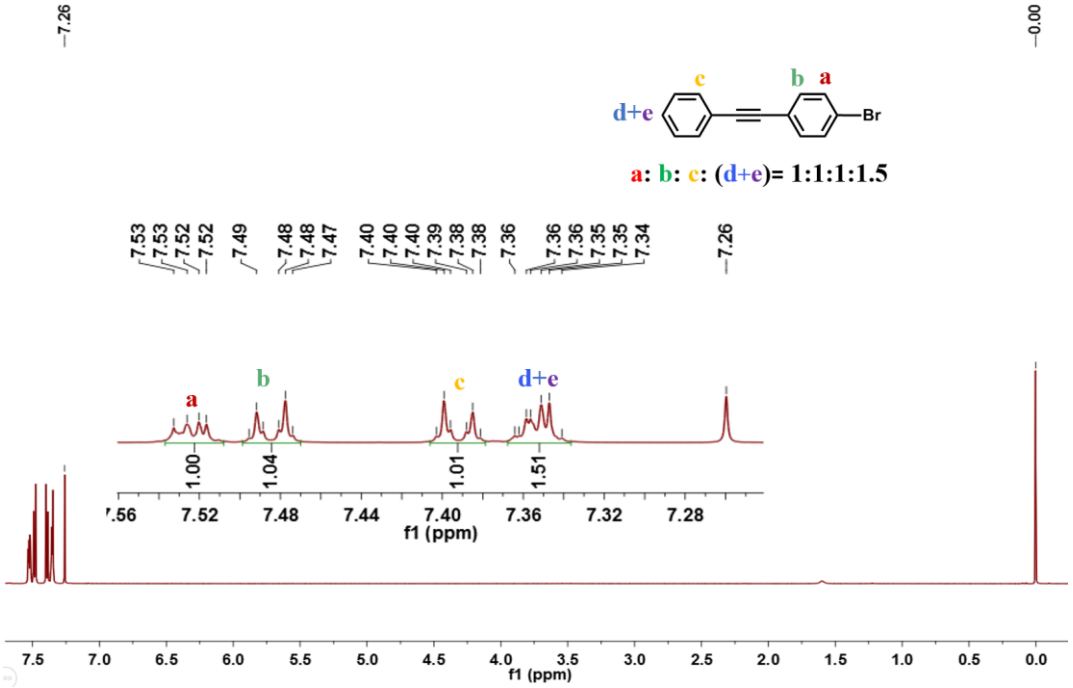



**Figure S8**. $^{1}$H NMR spectrum of compound **1** (600 MHz, $CDCl_3$).

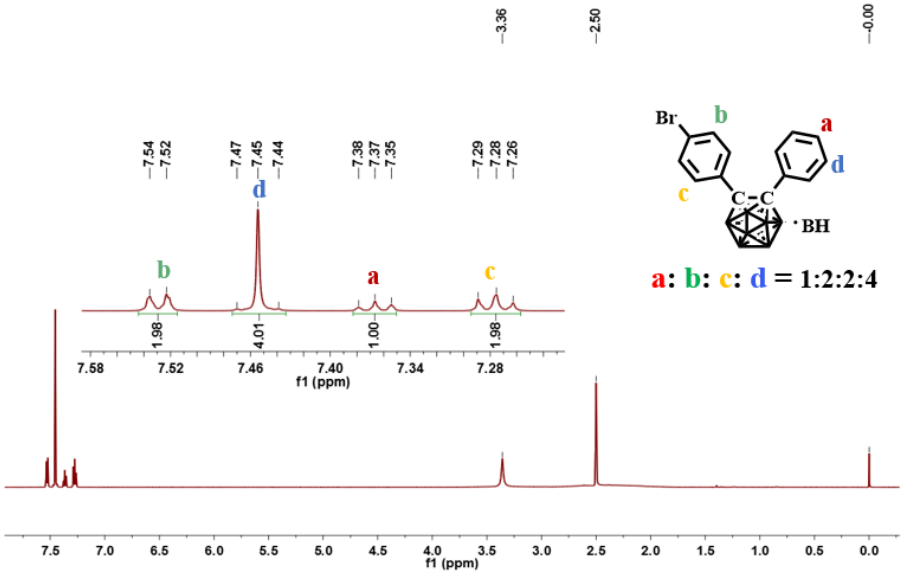



**Figure S9**. $^{1}$H NMR spectrum of compound **2** (600 MHz, Acetone-$d_6$).

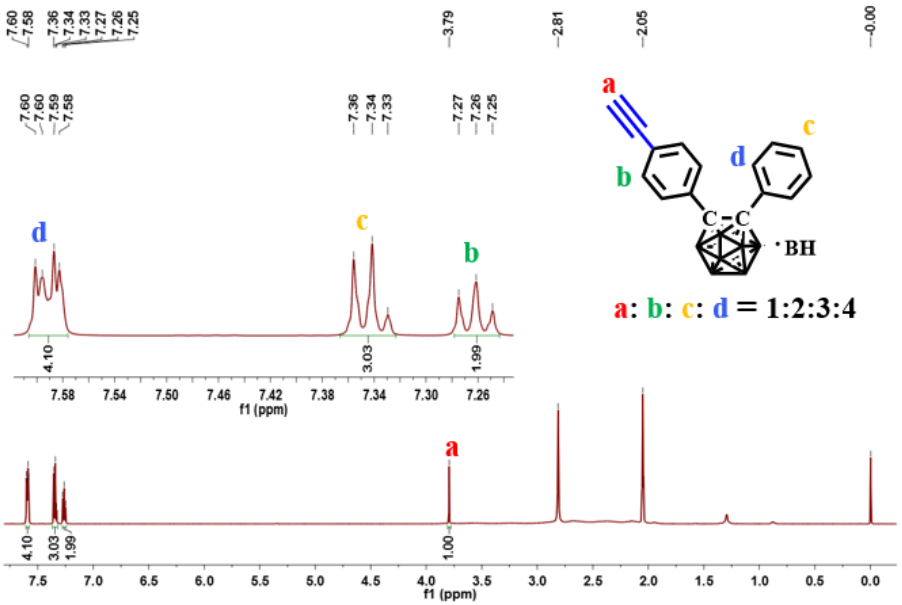



**Figure S10**. $^{1}$H NMR spectrum of compound **CB** (600 MHz, Acetone-$d_6$).

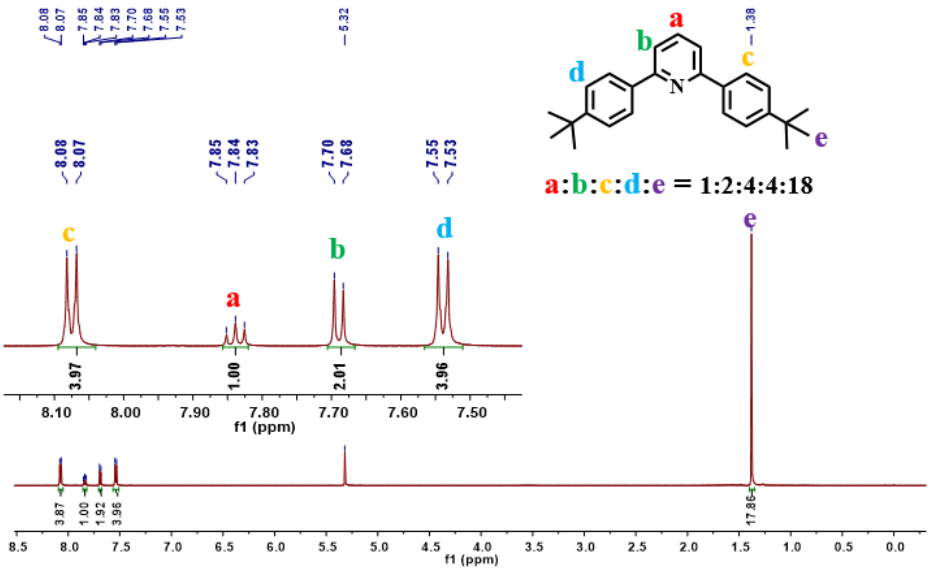



**Figure S11**. $^{1}$H NMR spectrum of compound **3** (600 MHz, $CD_2Cl_2$).

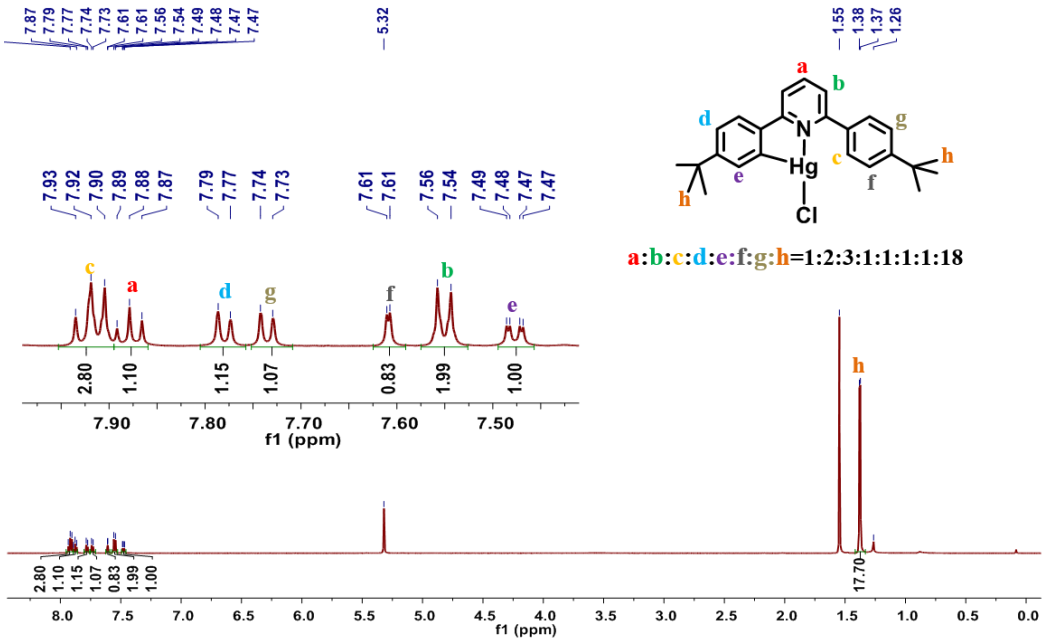



**Figure S12**. $^{1}$H NMR spectrum of compound **4** (600 MHz, $CD_2Cl_2$).

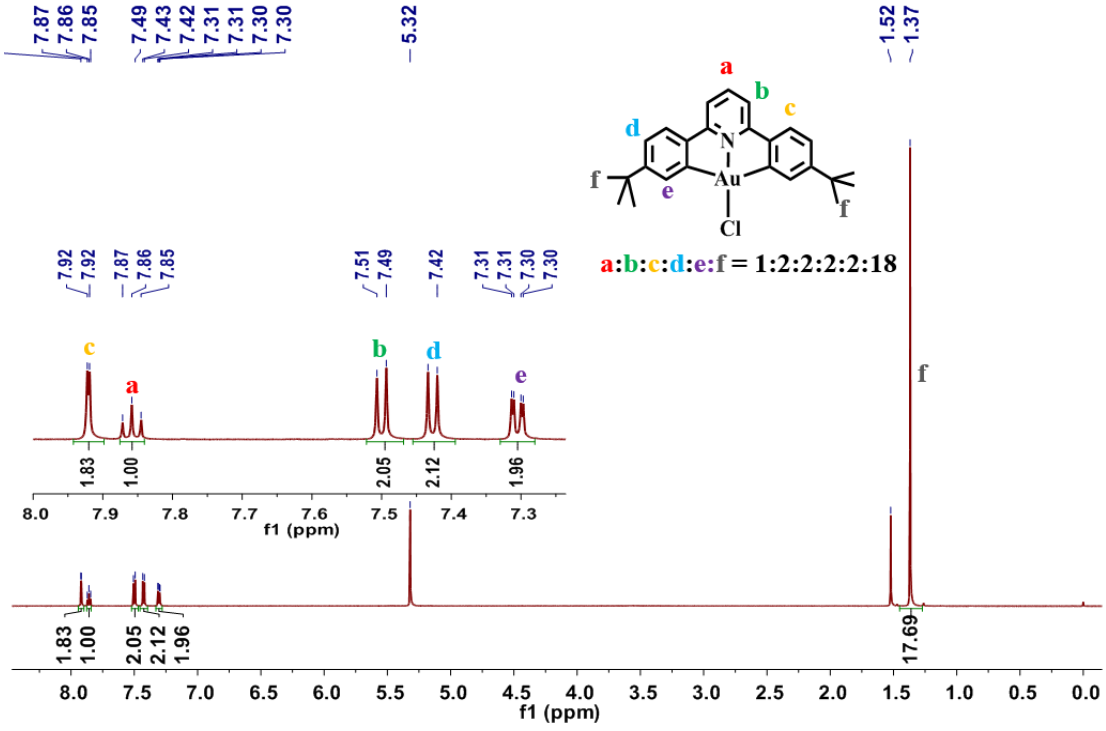



**Figure S13**. $^{1}$H NMR spectrum of compound **5** (600 MHz, $CD_2Cl_2$).

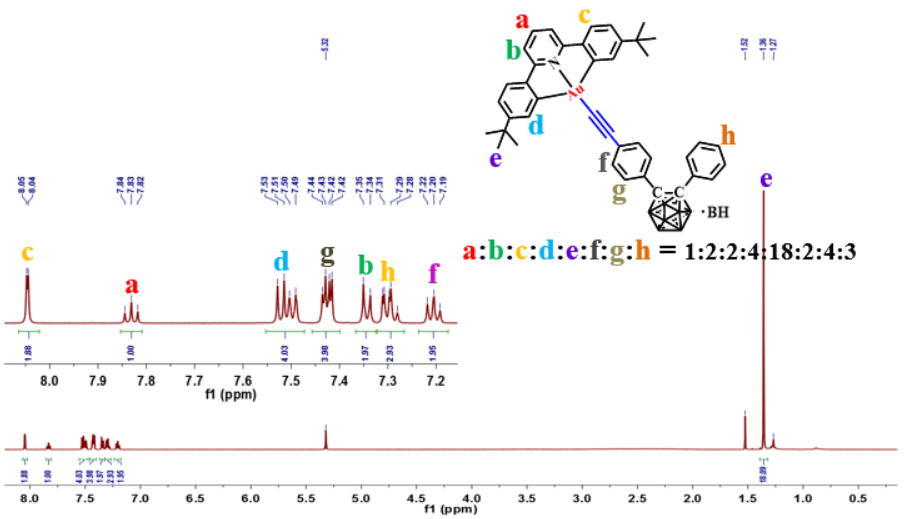



**Figure S14**. $^{1}$H NMR spectrum of compound **Au-CB** (600 MHz, $CD_2Cl_2$).

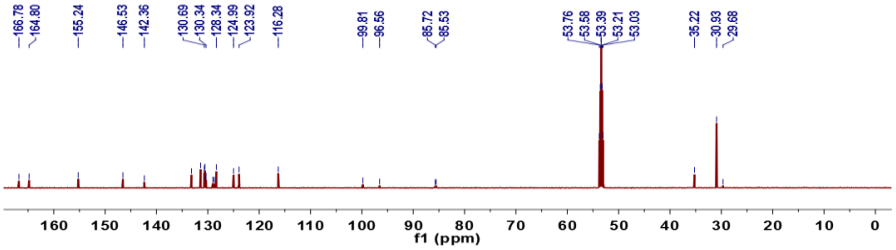



**Figure S15**. $^{13}$C NMR spectrum of compound **Au-CB** (150 MHz, $CD_2Cl_2$).

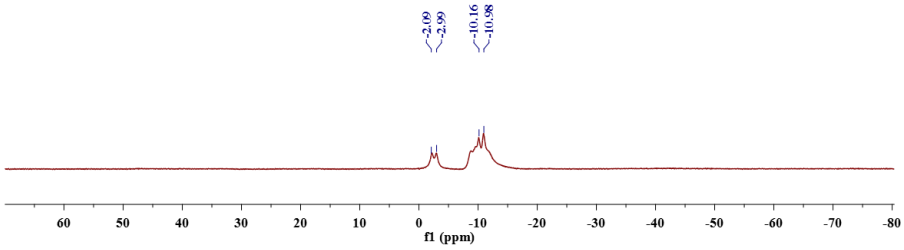



**Figure S16.** $^{11}$B NMR spectrum of compound **Au-CB** (192 MHz, $CD_2Cl_2$).

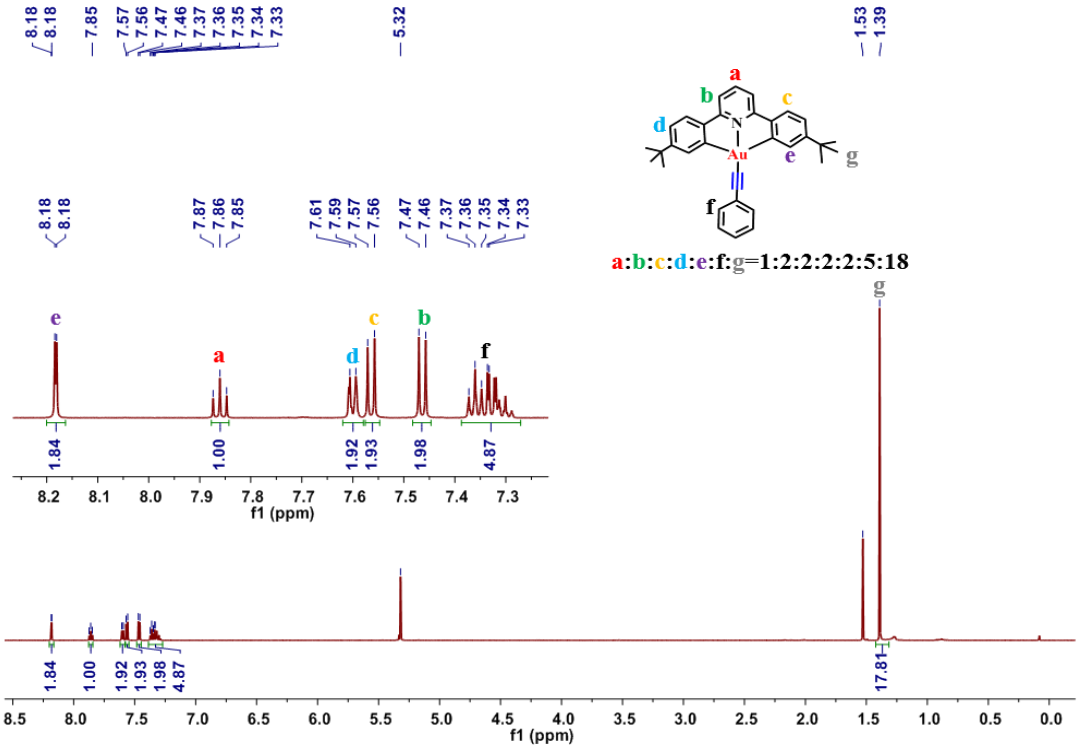



**Figure S17**. $^{1}$H NMR spectrum of compound **Au-C$_6$H$_5$** (600 MHz, $CD_2Cl_2$).

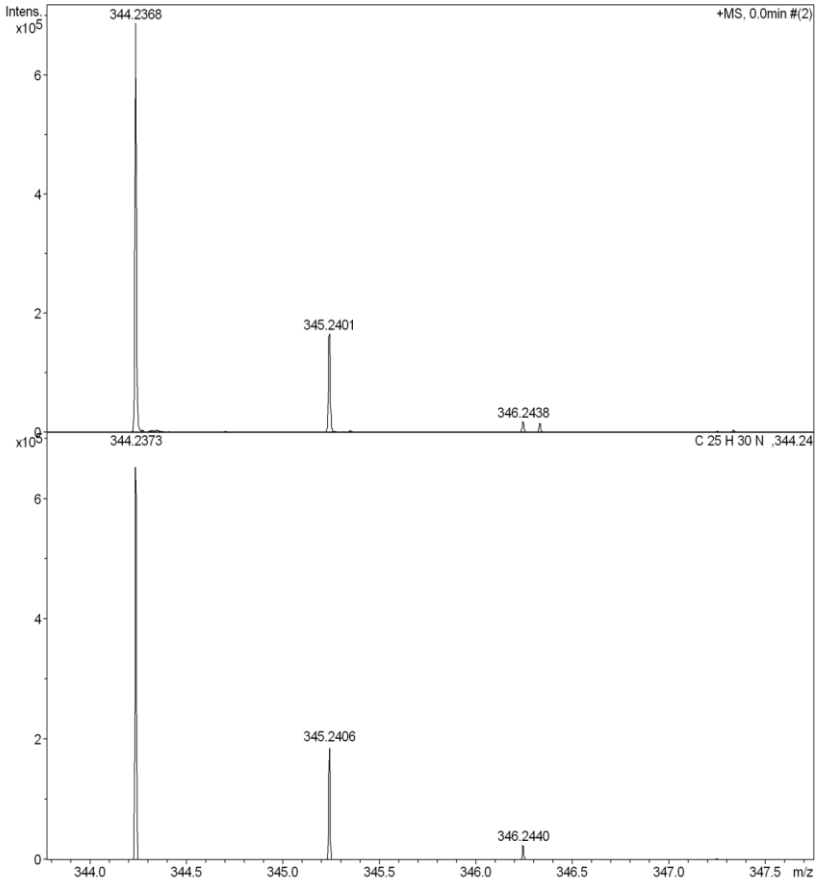



**Figure S18.** HRMS spectrum of compound **3**.

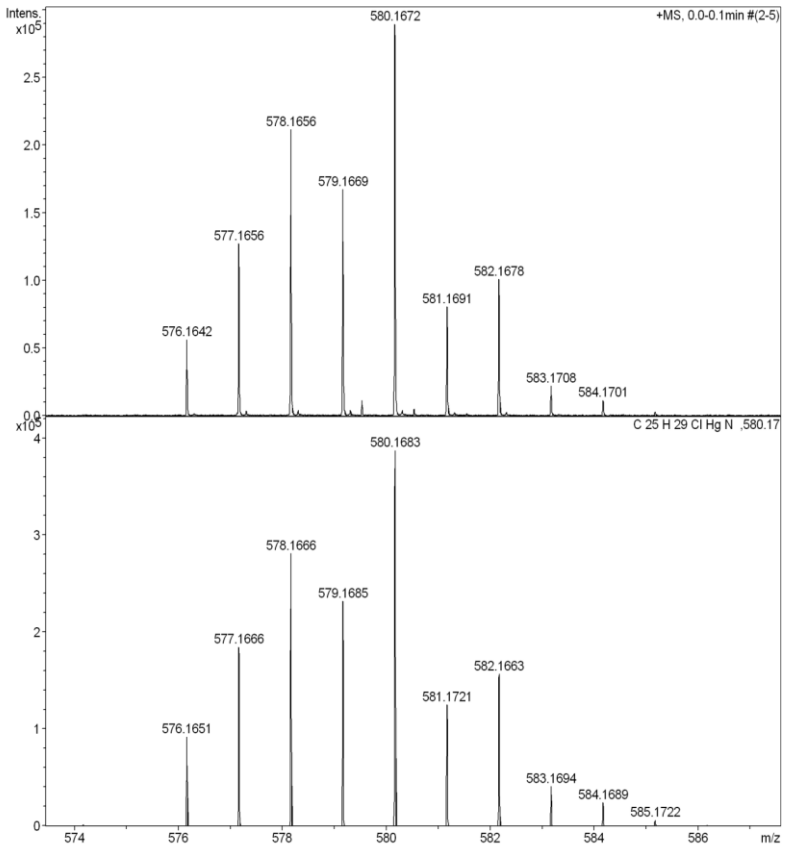



**Figure S19.** HRMS spectrum of compound **4**.

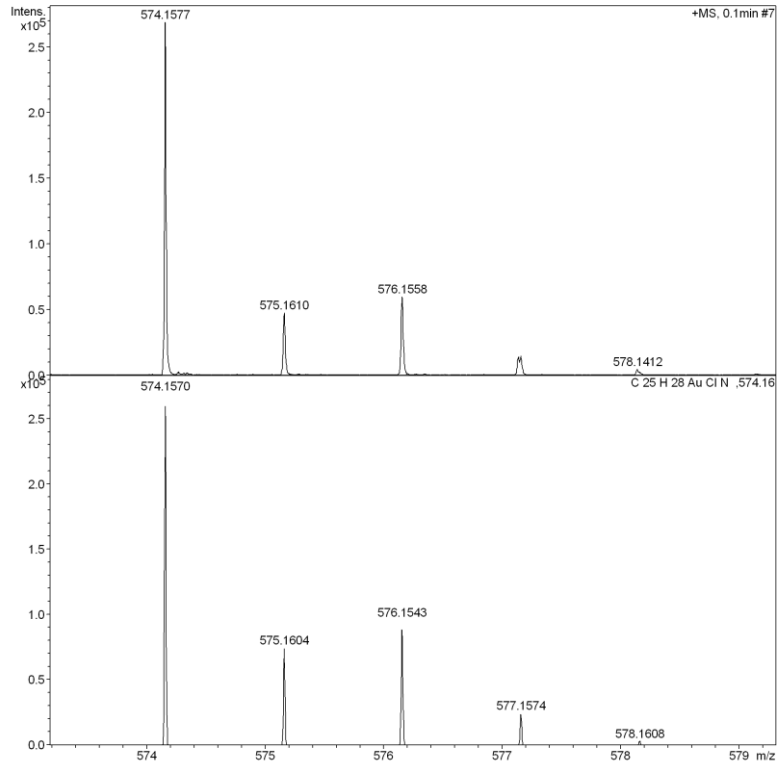



**Figure S20**. HRMS spectrum of compound **5**.

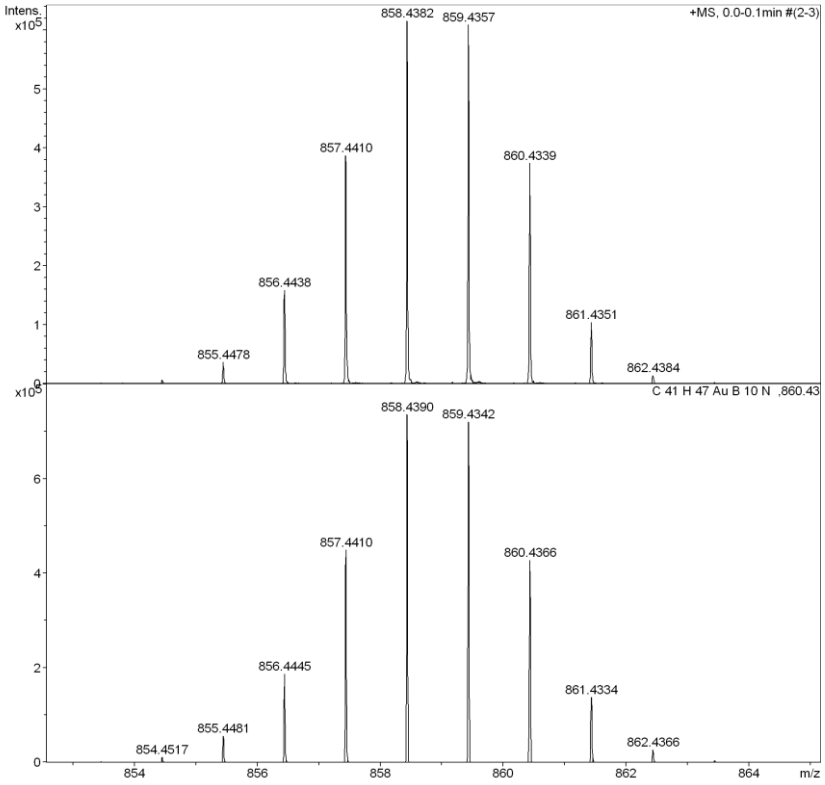



**Figure S21**. HRMS spectrum of compound **Au-CB**.

## References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