Electronic Supplementary Information (ESI) for

# Efficient Synthesis of $Au_{36}(SR)_{24}$ Nanoclusters via Cluster-From-Cluster Approach

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## I. Materials and reagents

All of the reagents and solvents employed were commercially available and used as received. $HAuCl_4 \cdot 4H_2O$, dimethylsulfide and $P(CH_2CH_2COOH)_3 \cdot HCl$ were bought from Shanghai Tuosi Chemicals, TCI and Shanghai Boka Chemicals, respectively. Thiolates were obtained from J&K Chemicals, TCI, Ark Pharm, Inc. and Shanghai Boka Chemicals, respectively. $NaBH_4$ was purchased from Energy Chemicals.

## II. Physical Measurements and instrumentation

UV-Vis spectra were recorded on a Hitachi U-3900 UV-Vis spectrophotometer. MALDI-TOF MS spectra were measured on a Shimadzu AXIMA Performance mass spectrometer.

## III. Synthesis and crystallization details

**$Au_{13}$** was prepared according to our previous procedures.[1]

**$Au_{36}$** nanoclusters were prepared via a similar route to that of **$Au_{25}$** nanoclusters.[1] $Me_2SAuCl$ (0.2 mmol, 59.0 mg) was dissolved in $CH_2Cl_2$ (10 mL) and MeOH (10 mL), which was followed by sequential addition of thiols (0.2 mmol; 4-Me-$C_6H_4$-SH for **1**, 4-MeO-$C_6H_4$-SH for **2**, 4-$^t$Bu-$C_6H_4$-SH for **3**, 4-Cl-$C_6H_4$-SH for **4**, 4-F-$C_6H_4$-SH for **5**, PhSNa for **6**, 3-Me-$C_6H_4$-SH for **7**, 3,4-DiMe-$C_6H_3$-SH for **8**, 3,5-DiMe-$C_6H_3$-SH for **9**, and 2-NAP-SH for **10**) and $Et_3N$ (0.2 mmol, 28.0 μL). Then the suspension was stirred for about 5 min, filtered, and washed with MeOH (5 mL). Mix the $(AuSR)_x$ with **$Au_{13}$** ($7.7 \times 10^{-3}$ mmol, 39.0 mg) in $CH_2Cl_2$ (10 mL) and MeOH (10 mL), and a 1 mL ethanol solution of $NaBH_4$ ($5.3 \times 10^{-2}$ mmol, 2.0 mg) was dropwise added. After it was allowed to stir overnight with exclusive of light, the solution was evaporated to dryness. The solid was washed with water (5 mL × 3) and subsequently a mixture of ether/hexane (1:1, v:v; 5 mL × 3) again. After dried in vacuum overnight at room temperature, **$Au_{36}$** were obtained as dark solids. Crystalizations were performed by layering a ether/hexane (1:1, v:v) mixture onto filtered dichloromethane/toluene/ethanol (3:1:1, v:v:v) solutions of as-synthesized products in tubes at 4ºC. Black block-like crystals of **1**, **2**, **4**, and **7-10** suitable for X-ray diffraction analysis can be obtained after two to three weeks, respectively. Yields: 52.2 mg (62%, based on gold) for **1**, 51.9 mg (60%) for **2**, 33.0 mg (36%) for **3**, 35.6 mg (41%) for **4**, 28.9 mg (34%) for **5**, 43.2 mg (53%) for **6**, 53.0 mg (64%) for **7,** 45.9 mg (53%) for **8**, 48.0 mg (55%) for **9**, and 57.9 mg (64%) for **10**.

## IV. X-ray crystallography

Intensity data were collected on a Rigaku (Agilent) SuperNova Dual system. Cu Kα (λ = 0.1.54184 Å) micro-focus X-ray source was used for compounds **1**, **2**, **4**, and **7-10** at 173 K. Absorption corrections were applied by using the program CrysAlisPro (multi-scan). The structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on $F^2$ using the SHELXTL program. The hydrogen atoms of organic ligands were generated geometrically; hydrogen atoms of some thiolate ligands in **2**, **7**, **8** and **10** were not added, due to disorder. SQUEEZE tool of PLATON was applied in all the structures, due to large solvent voids. One of the 2-thionaphtholate ligand in **10** (containing two independent **$Au_{36}$** molecules) was not identified, due to weak diffraction.

## V. Reference

(1) Z. Lei, J.-J. Li, Z.-A. Nan, Z.-G. Jiang, Q.-M. Wang, *Angew. Chem. Int. Ed.* 2021, **60**, 14415−14419.

## VI. Supporting Figures

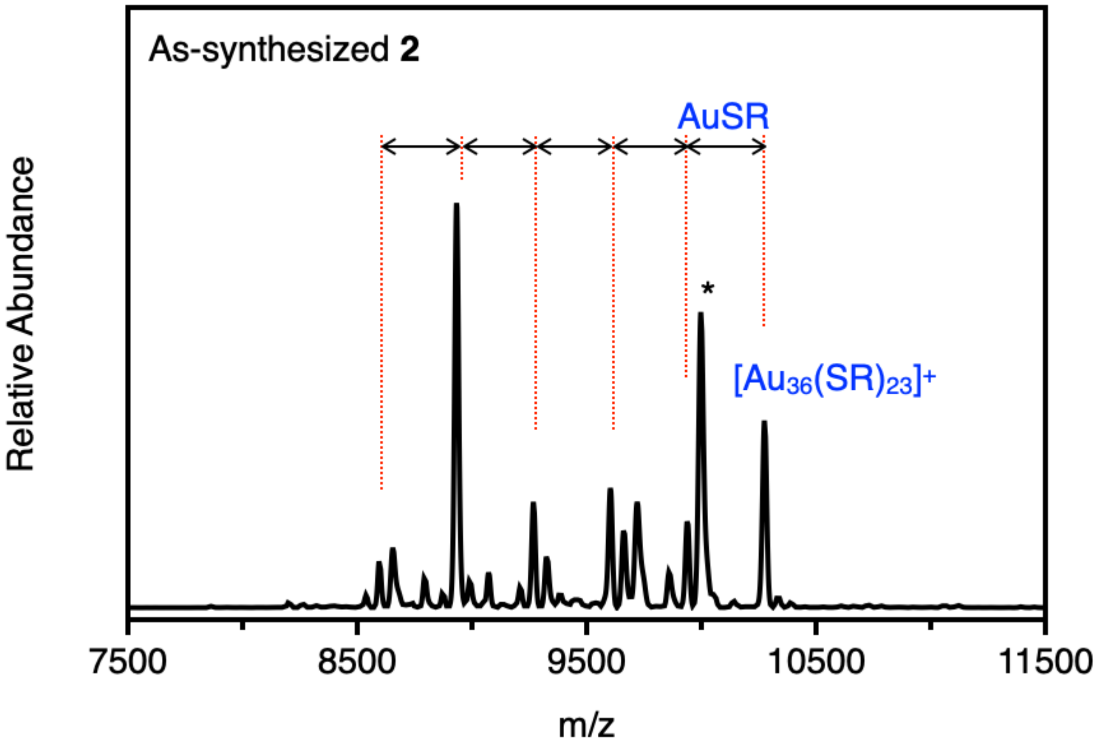

**Figure S1.** MALDI-TOF MS spectrum of as-synthesized $Au_{36}(S\text{-}C_6H_4\text{-}4\text{-}MeO)_{24}$ (**2**). The asterisk indicates fragment $[Au_{36}(SR)_{21}\text{-}2H]^+$.

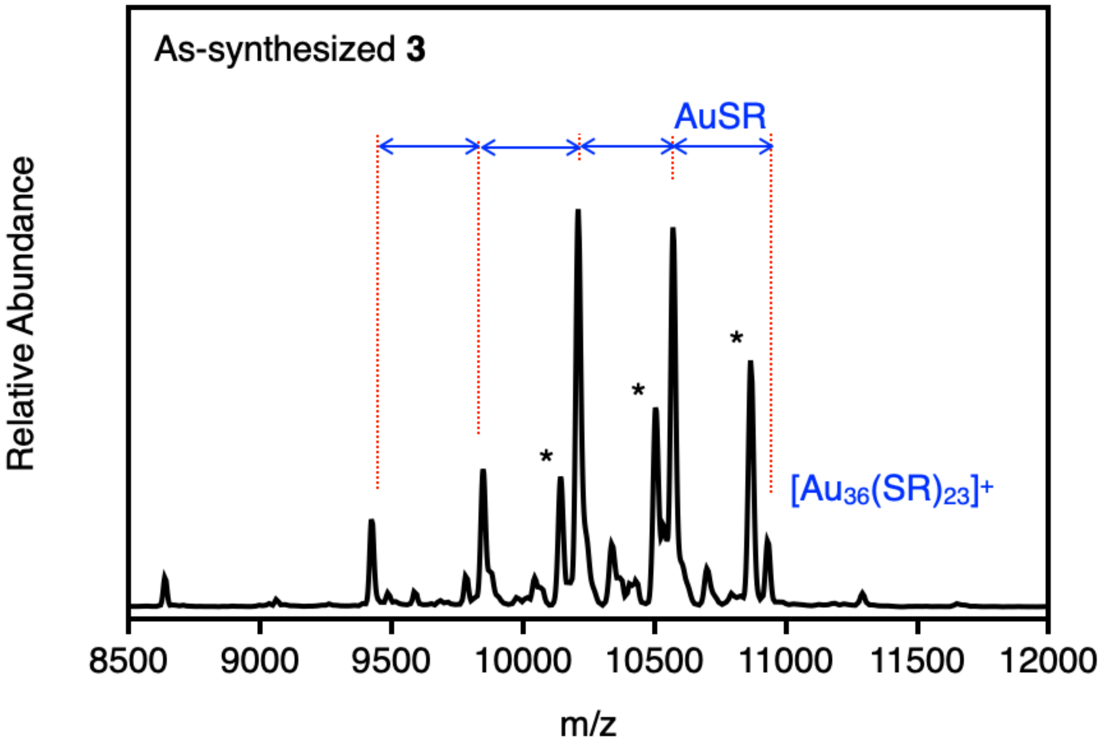

**Figure S2.** MALDI-TOF MS spectrum of as-synthesized $Au_{36}(S\text{-}C_6H_4\text{-}4\text{-}{}^tBu)_{24}$ (**3**). The asterisks indicate fragments $[Au_{35}(SR)_{24}+2H]^+$, $[Au_{34}(SR)_{23}+2H]^+$ and $[Au_{33}(SR)_{22}+2H]^+$.

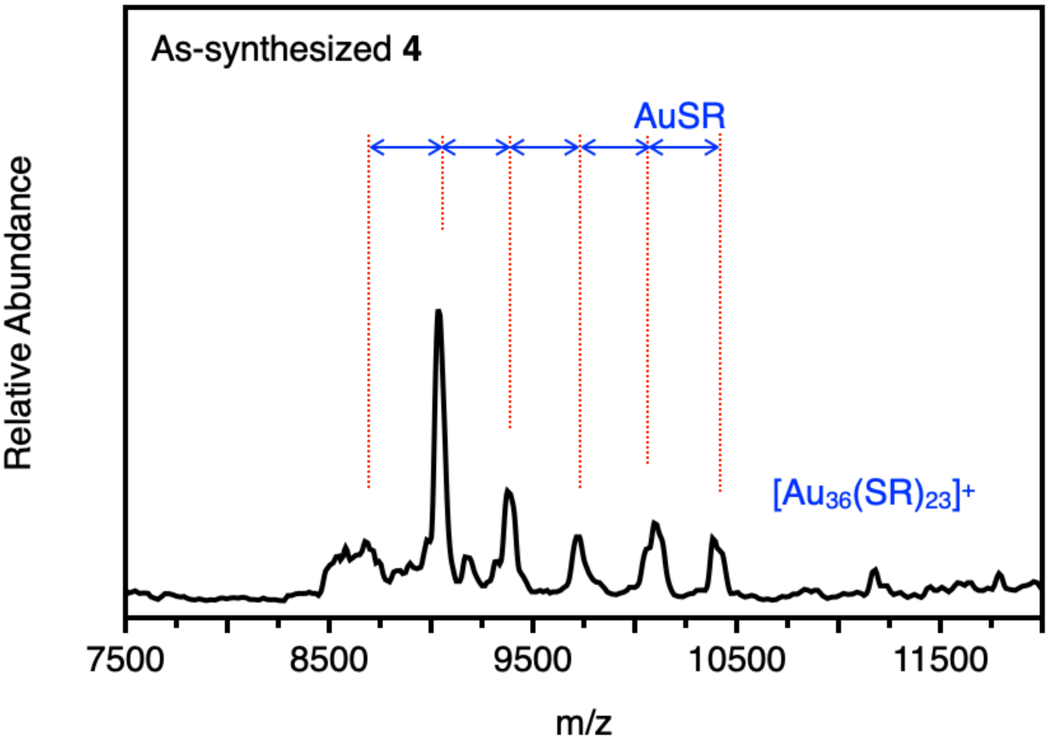

**Figure S3.** MALDI-TOF MS spectrum of as-synthesized $Au_{36}(S\text{-}C_6H_4\text{-}4\text{-}Cl)_{18}$ (**4**).

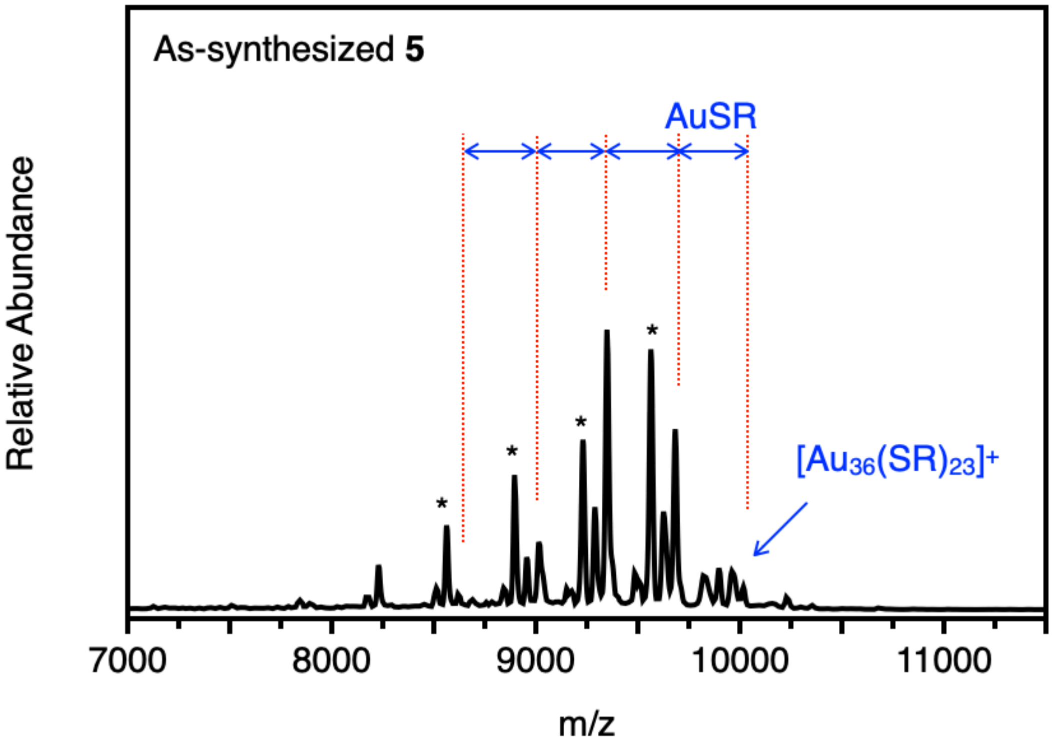

**Figure S4.** MALDI-TOF MS spectrum of as-synthesized $Au_{36}(S\text{-}C_6H_4\text{-}4\text{-}F)_{18}$ (**5**). The asterisks indicate fragments $[Au_{33}(SR)_{24}+4H]^+$, $[Au_{32}(SR)_{23}+4H]^+$, $[Au_{31}(SR)_{22}+4H]^+$ and $[Au_{30}(SR)_{21}+4H]^+$.

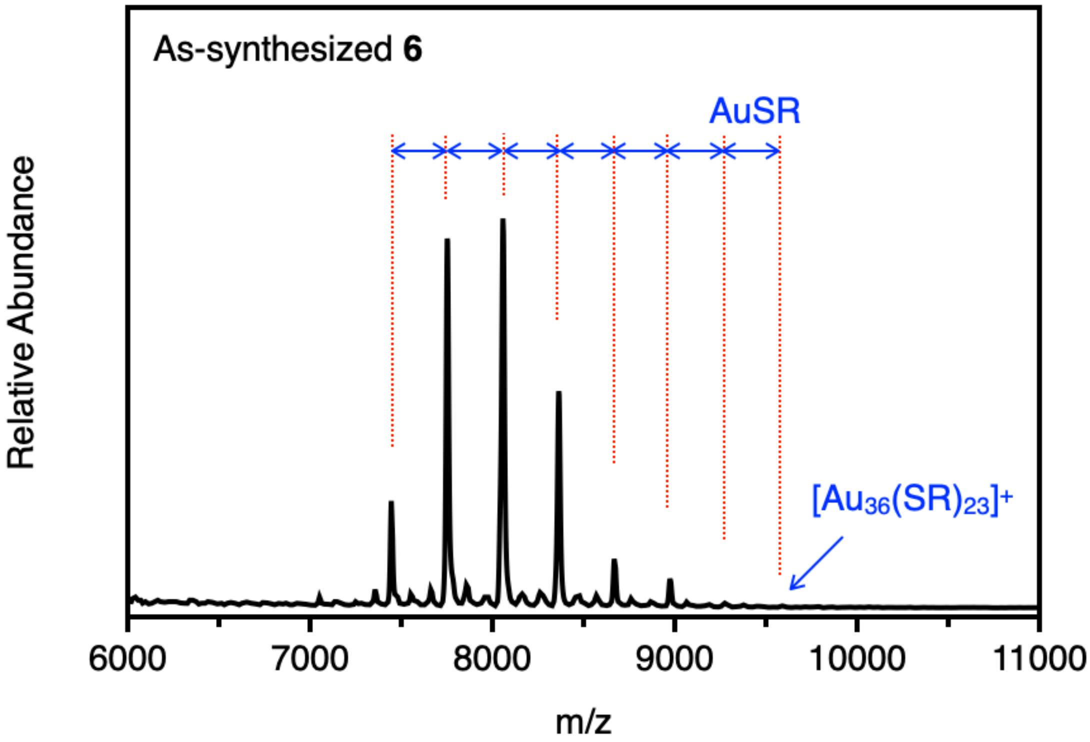

**Figure S5.** MALDI-TOF MS spectrum of as-synthesized $Au_{36}(SPh)_{24}$ (**6**).

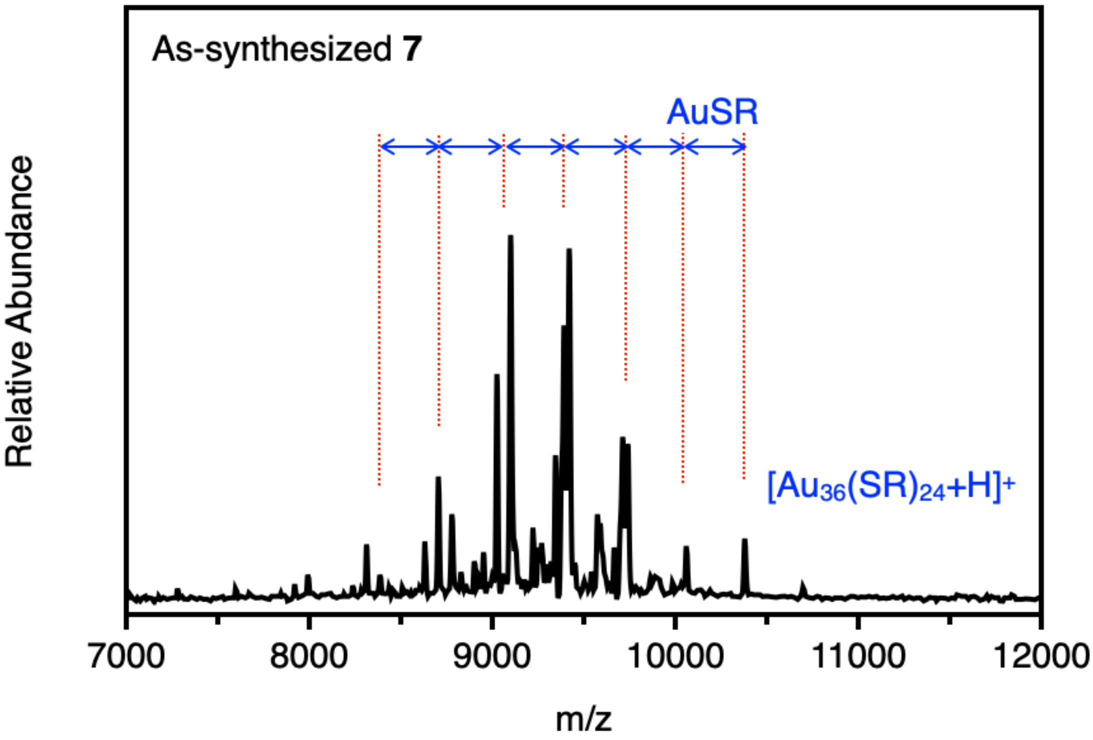

**Figure S6.** MALDI-TOF MS spectrum of as-synthesized $Au_{36}(S\text{-}C_6H_4\text{-}3\text{-}Me)_{24}$ (**7**).

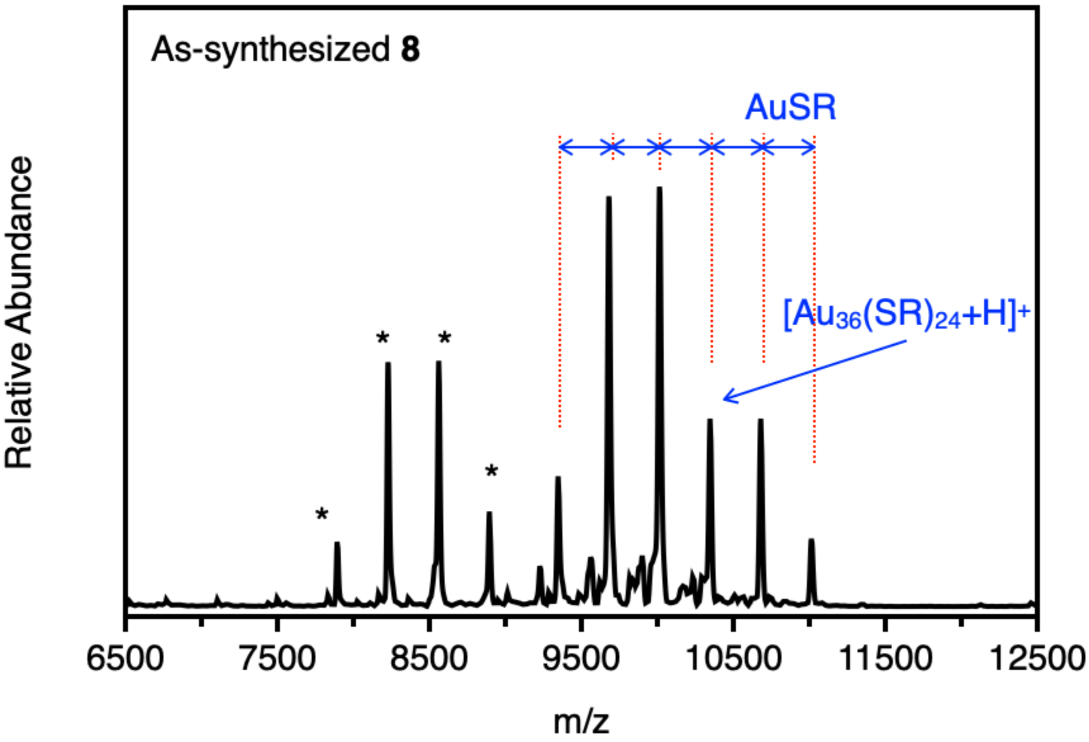

**Figure S7.** MALDI-TOF MS spectrum of as-synthesized $Au_{36}(S\text{-}C_6H_3\text{-}3,4\text{-}DiMe)_{24}$ (**8**). The asterisks indicate fragments $[Au_{30}(SR)_{22}+5H]^+$, $[Au_{29}(SR)_{21}+5H]^+$, $[Au_{28}(SR)_{20}+5H]^+$ and $[Au_{27}(SR)_{19}+5H]^+$.

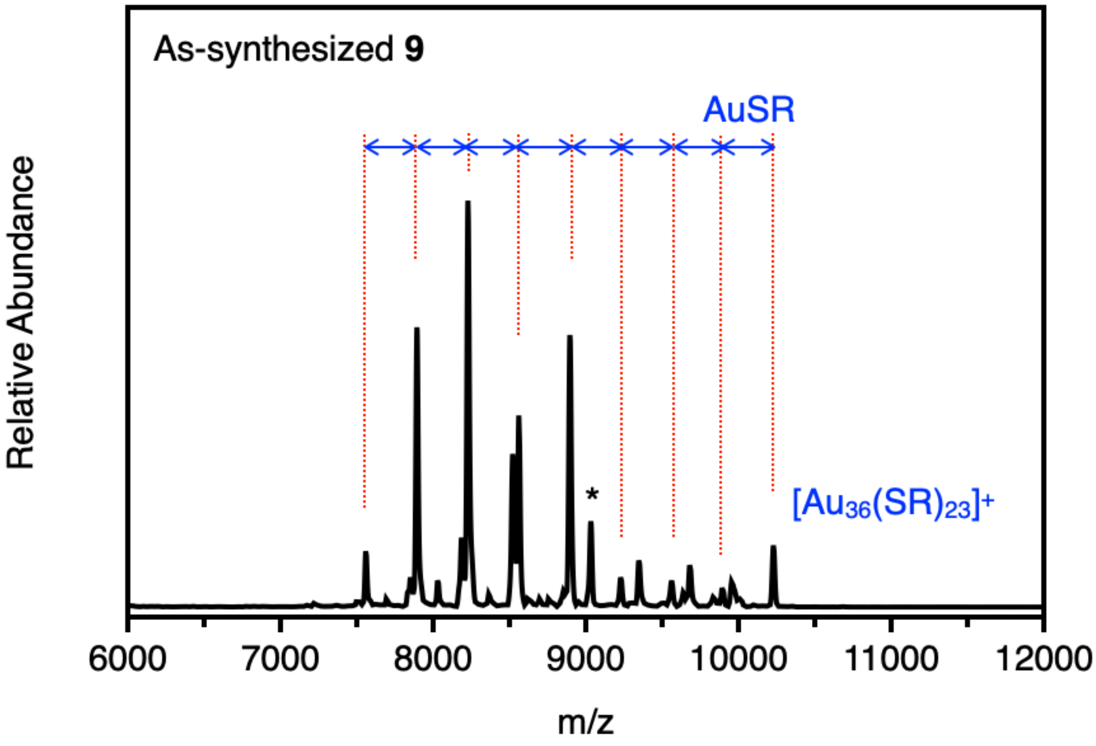

**Figure S8.** MALDI-TOF MS spectrum of as-synthesized $Au_{36}(S\text{-}C_6H_3\text{-}3,5\text{-}DiMe)_{24}$ (**9**). The asterisk indicates fragment $[Au_{33}(SR)_{18}\text{-}2H]^+$.

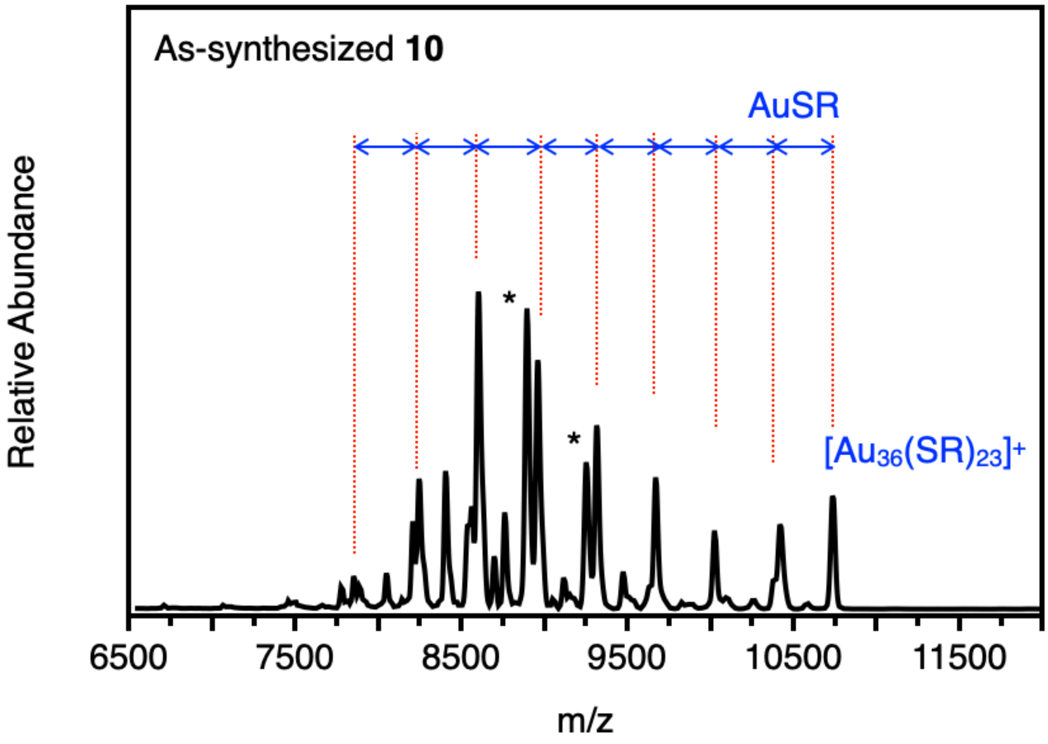

**Figure S9.** MALDI-TOF MS spectrum of as-synthesized $Au_{36}(S\text{-}2\text{-}NAP)_{24}$ (**10**). The asterisks indicate fragments $[Au_{31}(SR)_{20}+2H]^+$ and $[Au_{30}(SR)_{19}+2H]^+$.

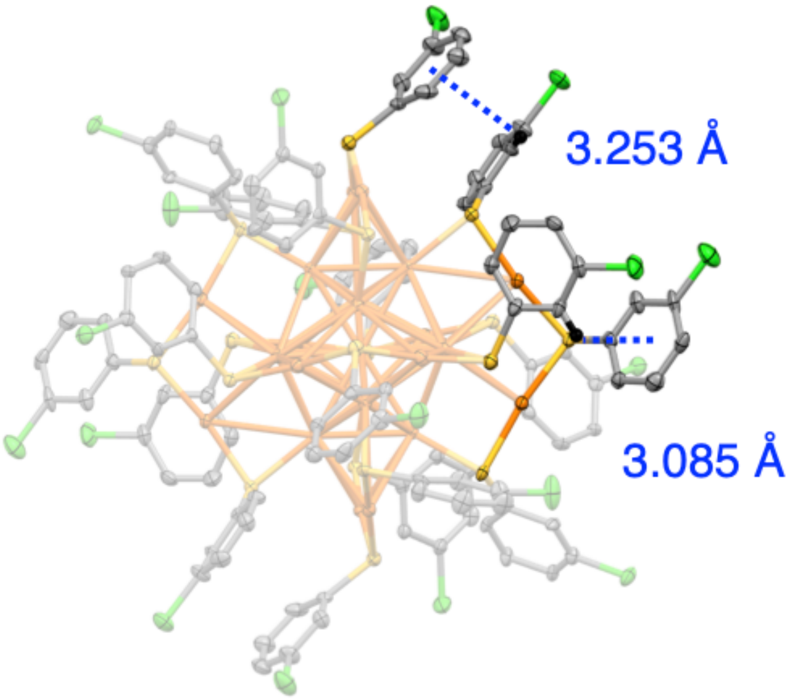

**Figure S10.** H-π interactions between thiolates of different $Au_2(SR)_3$ staple motifs in $[Au_{25}(S\text{-}C_6H_4\text{-}3\text{-}Cl)]^-$.