Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Ligand-Passivated Au/Cu Nanoclusters with Uncoordinated Sites Give Reaction Turnover Numbers up to 4×10^4

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Experimental Details

Reagents: Cuprous oxide (Cu_2O, ≥99.99% trace metals basis, anhydrous), tetrafluoroboric acid solution (HBF_4, 48 wt.% in water), 4-fluorothiophenol (4-F-C_6H_5SH), triethylamine (($(C_2H_5)_3N$, ≥99%) are purchased from Innochem (Beijing, China). Hydrogen tetrachloroaurate ($HAuCl_4 \cdot 4H_2O$, 99.9%), sodium borohydride ($NaBH_4$, 98%), acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2, A.R.), methanol (CH_3OH, A.R.), ethanol (C_2H_5OH, A.R.) and ether ($C_4H_{10}O$, A.R.) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All other reagents except for CH_3CN were used as received without further purification. CH_3CN used in reactions were dried by refluxing over CaH_2 (2g/L) for 1 hour, and fractional distillation, then added dried type 4Å Linde molecular sieves. Water used in all experiments was ultrapure. $AuSMe_2Cl$[1], $[Au_9Cu_2(PPh_3)_8Cl_2]BF_4$[2] and $AuCu_{24}H_{22}(C_{18}H_{11}F_3P)_{12}$[3] were prepared according to literature methods.

Synthesis of $[Cu(CH_3CN)_4]BF_4$. The complex was prepared with slightly modified method reported by Osman et al.: Initially, 2 gm of cuprous oxide and 100 mL of acetonitrile was taken in a round bottom flux. Then the flux was placed in an oil bath and the temperature of the oil bath was maintained at 75°C. After a few minutes of stirring, 15 mL of the tetrafluoro +-boric acid was added to the above solution. The stirring was continued for 10-15 min. During this process, the solution turned to almost transparent. The hot solution was filtered quickly using a filter paper and the filtrate was kept in the fridge (0°C). After 12 h, white crystals of $[Cu(CH_3CN)_4]BF_4$ was collected through filtration and it was washed two times with diethyl ether. Then the complex was transferred to a sample bottle and stored under nitrogen.

Synthesis of $AuSC_6H_4F$. In the absence of light, 63.5 μL 4-fluorothiophenol and then 83 μL NEt_3 were added to 8 mL acetone containing 150 mg $AuSMe_2Cl$. The mixture was stirred for 0.5 h and dried up. Obtained solid was fully washed by water (10 mL), ethanol (10 mL) and ether (10 mL) to give 105.7 mg (90% yield based on Au) of $AuSC_6H_4F$.

Synthesis of $Au_{41}Cu_{33}$: 7.8 mg fresh $[Cu(CH_3CN)_4]BF_4$ (0.025 mmol) was first dissolved in 3 mL mixed solvent of CH_2Cl_2 and MeOH (V(CH_2Cl_2): V(MeOH)=2:1). To the colorless solution were added 2.6 uL of 4-F-C_6H_5SH (0.025 mmol) and 3.5 uL of NEt_3 (0.025 mmol). The solution was stirred for another 20 min before the addition of 8.7 mg $NaBH_4$ (0.23 mmol) in 0.25 mL of MeOH. The solution was further stirred for another 12 h, washed with water (6 mL) for three times to afford copper hydride as pale orangish solution. To above copper hydride solution, 17.8 mg $AuSC_6H_4F$ (0.055 mmol) was added. The polymeric solid dissolved gradually and the solution turned brown after stirring for 5 min. The brown solution was then stirred for 8 h in the absence of light to obtain raw product. After that, the solution was subjected to diffusion of hexane at 4 °C. After two weeks, red block crystals were obtained in the yield of 26.9%.

Characterizations: UV-Vis spectra were collected by Shimadzu UV-2550 Spectrophotometer. Energy-dispersive X-ray spectroscopy was recorded on GeminisEM 500. The data for NMR spectra (^1H NMR, and ^{19}F NMR) were recorded at 293 K on a Bruker Avance NEO 600 MHz and chemical shifts were recorded relative to the solvent resonance. Signal positions were recorded in ppm and the following abbreviations are used singularly or in combination to indicate the multiplicity of signals: *s* singlet, *d* doublet, *t* triplet, *q* quartet, *m* multiplet, Hz Hertz. For ^1H NMR: $CDCl_3$ = δ 7.26 ppm, ^{13}C NMR: $CDCl_3$ = δ 77.16 ppm. Mass spectra were recorded on an Agilent Technologies ESI-TOF-MS.

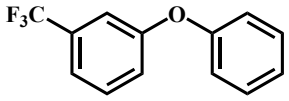
X-ray single-crystal analysis: The diffraction data of the single crystals $[Au_{41}Cu_{33}(RS)_{40}(MeCN)]$ nanocluster was collected on an Agilent Technologies SuperNova system X-ray single-crystal diffractometer using Cu Kα (λ= 1.54184 Å) at 160 K. The data were processed using CrysAlis^{Pro}.[4] The structure was solved and refined using Full-matrix least-squares based on F_2 using ShelXT,[5] ShelXL[6] in Olex2,[7] and Shelxle.[8] Detailed crystal data and structure refinements for the compound are given in Table S1. CCDC 2211306 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT calculation: Density functional theory calculations were carried out using Perdew-Burke-Ernzerhof (PBE) functional[9] as implemented in DMol^3 program[10, 11]. All electron potential and DNP basis set were employed to treat electrons. During optimization, all atoms were allowed to relax until the self-consistent field tolerance was no larger than 10^{-4}, and the orbital cutoff was set as 3.4 Å. The Muliken method[12] was adopted for charge analysis.

General procedure for the C-O coupling (1.2 mmol scale)

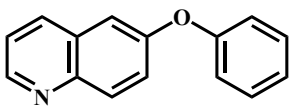
All catalytic reactions were conducted in oven- or flame-dried glassware under an atmosphere of nitrogen unless otherwise noted. In an N_2 glovebox, to phenol coupling partner (1.20 mmol, 1.00 equiv), aryl halide (1.80 mmol, 1.50 equiv), activated 4Å molecular sieves (20.0 mg) and catalyst $Au_{41}Cu_{33}$ (20 mg in activated carbon (XC-72), 2.628 x 10^{-5} mmol, 0.00219 mol%) in a 4.00 mL sealed vial tube were added Cs_2CO_3 (2.4 mmol, 2.0 equiv) and dry CH_3CN (1.2 mL). The resulting mixture was stirred for 24 h at 85^{o}C in the heating module. The reaction mixture was allowed to cool to room temperature, diluted with dichloromethane and filtered through a plug of celite®, the filter cake being further washed with dichloromethane (~ 50 mL). The filtrate was concentrated in vacuo to yield the crude product, that was purified by preparative thin-layer chromatography with developing agent of petroleum ether and ethyl acetate.

1-Phenoxy-3-(trifluoromethyl)benzene (**3a**)



General procedure was used with 1-iodo-3-(trifluoromethyl)benzene (1.8 mmol, 259.5 μL), phenol (1.2 mmol, 94.11 mg). Reaction ran for 24 h at 85 °C. The product was isolated by preparative thin-layer chromatography with petroleum ether, affording **3a** in 67% yield (160.4 mg) as a yellow liquid. R_f = 0.40 (petroleum ether). **NMR Spectroscopy: ^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 4H), 7.26 (s, 1H), 7.19 – 7.14 (m, 2H), 7.06 – 7.02 (m, 2H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.72 (s, 3F). The compound data was in agreement with the literature.[13]

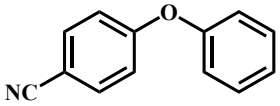
6-Phenoxyquinoline (**3b**)



General procedure was used with 6-iodoquinoline (1.8 mmol, 459.1 mg), phenol (1.2 mmol, 94.11 mg). Reaction ran for 24 h at 85 °C. The product was isolated by preparative thin-layer chromatography with petroleum ether and ethyl acetate (50:1 (v/v)), affording **3b** in 75% yield (166.1 mg) as a yellow solid.

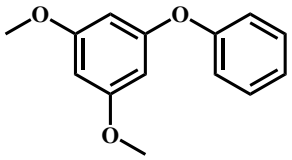
R_f = 0.30 (petroleum ether/ ethyl acetate 20:1 (v/v)). **NMR Spectroscopy: ^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.95 (s, 1H), δ 8.24 (s, 1H), δ 8.07 (s, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.57 – 7.36 (m, 3H), 7.26 – 7.10 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H). The compound data was in agreement with the literature.[14]

4-Phenoxybenzonitrile(**3c**)



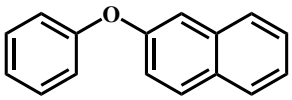
General procedure was used with 4-iodobenzonitrile (1.8 mmol, 412.2 mg), phenol (1.2 mmol, 94.11 mg). Reaction ran for 24 h at 85 °C. The product was isolated by preparative thin-layer chromatography with petroleum ether and ethyl acetate (50:1 (v/v)), affording **3c** in 86% yield (167.9 mg) as a yellow solid.
R_f = 0.30 (petroleum ether/ ethyl acetate 20:1 (v/v)). **NMR Spectroscopy: ^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.44 – 7.39 (m, 2H), 7.26 – 7.21 (m, 1H), 7.09 – 7.05 (m, 2H), 7.03 – 6.98 (m, 2H). The compound data was in agreement with the literature.[15]

1,3-Dimethoxy-5-phenoxybenzene(**3d**)



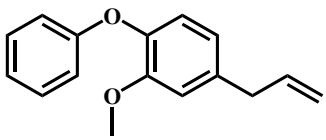
General procedure was used with 1-iodo-3,5-dimethoxybenzene (1.8 mmol, 475.3 mg), phenol (1.2 mmol, 94.11 mg). Reaction ran for 24 h at 85 °C. The product was isolated by preparative thin-layer chromatography with petroleum ether and ethyl acetate (50:1 (v/v)), affording **3d** in 61% yield (174.3 mg) as a colorless solid.
R_f = 0.30 (petroleum ether/ ethyl acetate 20:1 (v/v)). **NMR Spectroscopy: ^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.14 (m, 1H), 7.08 – 7.05 (m, 2H), 6.25 (m, 1H), 6.21 – 6.19 (d, *J* = 2.2 Hz, 2H), 3.77 (s, 6H). The compound data was in agreement with the literature.[16]

2-Phenoxynaphthalene(**3e**)



General procedure was used with iodobenzene (1.8 mmol, 167.8 µL), naphthalen-2-ol (1.2 mmol, 173 mg). Reaction ran for 24 h at 85 °C. The product was isolated by preparative thin-layer chromatography with petroleum ether and ethyl acetate (50:1 (v/v)), affording **3e** in 74% yield (189.7 mg) as a colorless solid.
R_f = 0.30 (petroleum ether/ ethyl acetate 20:1 (v/v)). **NMR Spectroscopy: ^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.75 – 7.71 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.29 (m, 6H), 7.19 – 7.08 (m, 3H). The compound data was in agreement with the literature.[17]

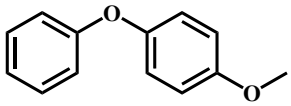
4-Allyl-2-methoxy-1-phenoxybenzene(**3f**)



General procedure was used with iodobenzene (1.8 mmol, 167.8 µL), 4-allyl-2-methoxyphenol (1.2 mmol, 184.7 µL). Reaction ran for 24 h at 85 °C. The product was isolated by preparative thin-layer chromatography with petroleum ether and ethyl acetate (50:1 (v/v)), affording **3f** in 70% yield (201.8 mg) as a yellow liquid.

R_f = 0.30 (petroleum ether/ ethyl acetate 20:1 (v/v)). **NMR Spectroscopy: ^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 2H), 7.05 (m, 1H), 6.98 – 6.93 (m, 3H), 6.85 (s, 1H), 6.79 – 6.76 (d, *J* = 7.7 Hz, 1H), 6.02 (m, 1H), 5.17 – 5.11 (m, 2H), 3.85 (s, 3H), 3.44 – 3.40 (d, *J* =6.7 Hz, 2H). The compound data was in agreement with the literature.[18]

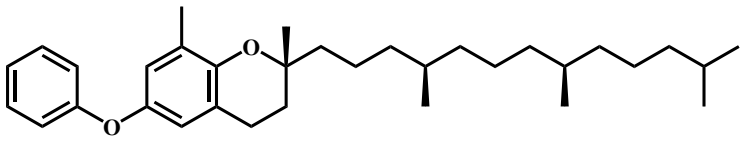
1-Methoxy-4-phenoxybenzene(**3g**)



General procedure was used with iodobenzene (1.8 mmol, 167.8 µL), 4-methoxyphenol (1.2 mmol, 149 mg). Reaction ran for 24 h at 85 °C. The product was isolated by preparative thin-layer chromatography with petroleum ether and ethyl acetate (50:1 (v/v)), affording **3g** in 61% yield (146 mg) as a yellow solid.

R_f = 0.30 (petroleum ether/ ethyl acetate 20:1 (v/v)). **NMR Spectroscopy: ^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.04 (m, 1H), 7.00 – 6.93 (m, 4H), 6.90 – 6.87 (m, 2H), 3.81 (s, 3H). The compound data was in agreement with the literature.[19]

Compound **3h**



General procedure was used with iodobenzene (1.8 mmol, 167.8 µL), D-*delta*-Tocopherol (1.2 mmol, 486.6 µL). Reaction ran for 24 h at 85 °C. The product was isolated by preparative thin-layer chromatography with petroleum ether and ethyl acetate (50:1 (v/v)), affording **3h** in 42% yield (241 mg) as a yellow liquid.

R_f = 0.30 (petroleum ether/ ethyl acetate 20:1 (v/v)). **NMR Spectroscopy: ^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.06 – 7.02 (m, 1H), 6.98 – 6.95 (d, *J* = 7.9 Hz, 2H), 6.71 – 6.67 (d, *J* = 2.1 Hz, 1H), 6.63 – 6.60 (d, *J* = 2.1 Hz, 1H), 2.80 – 2.67 (m, 2H), 2.16 (s, 3H), 1.87 – 1.73 (m, 2H), 1.65 – 1.50 (m, 4H), 1.43 – 1.33 (m, 4H), 1.34 – 1.24 (m, 10H), 1.18 – 1.12 (m, 3H), 1.11 – 1.04 (m, 3H), 0.91 – 0.85 (m, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.0, 148.5, 148.4, 129.6, 127.7, 122.1, 121.5, 120.2, 117.7, 177.6, 76.0, 40.2, 39.5, 37.6, 37.5, 37.4, 32.9, 32.8, 31.3, 28.1, 24.9, 24.6, 24.3, 22.8, 22.7, 22.6, 21.1, 19.9, 19.8, 16.3.

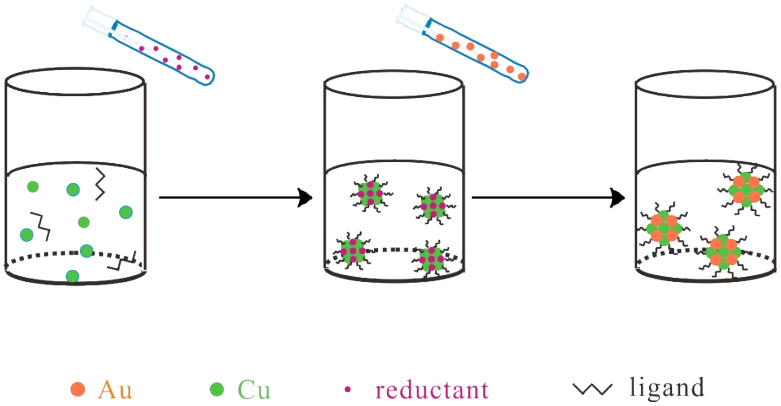


Figure S1. The synthetic strategy of $Au_{41}Cu_{33}$ clusters.

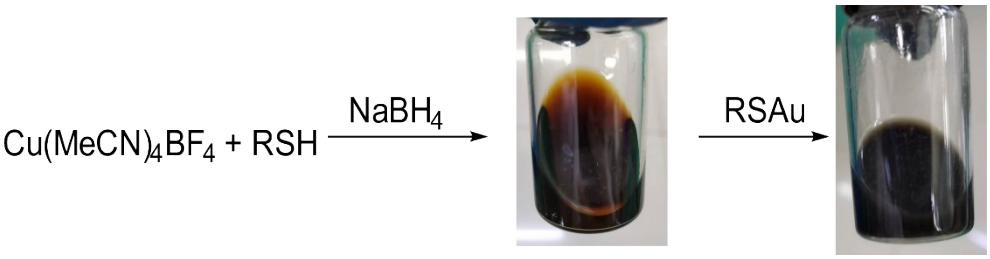


Figure S2. The synthetic procedure of $Au_{41}Cu_{33}$ clusters.

Figure S3. The digital images of $Au_{41}Cu_{33}$ crystals.

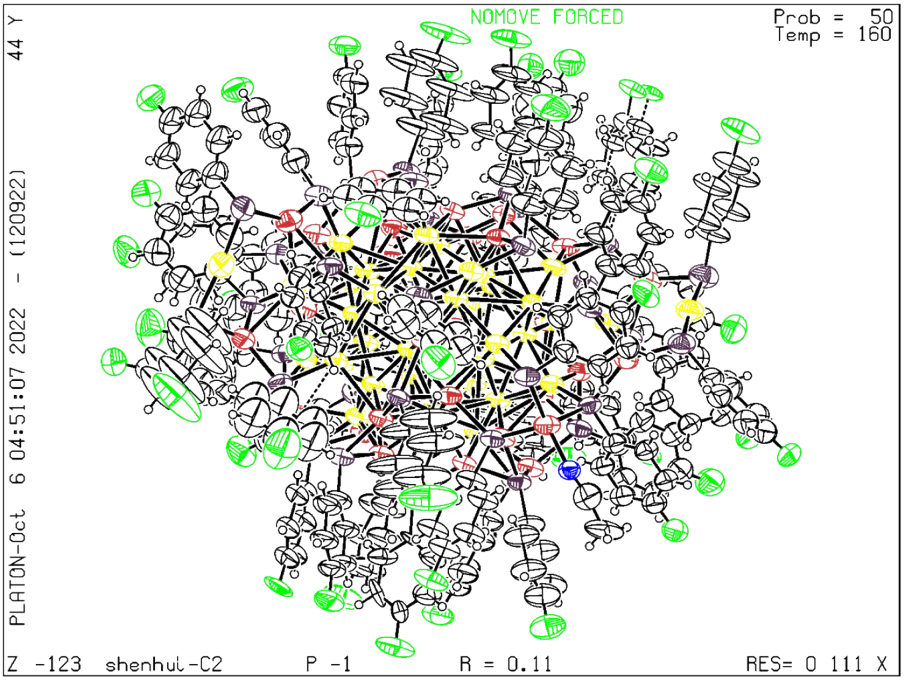


Figure S4. The thermal ellipsoids of the ORTEP diagram of $Au_{41}Cu_{33}$.

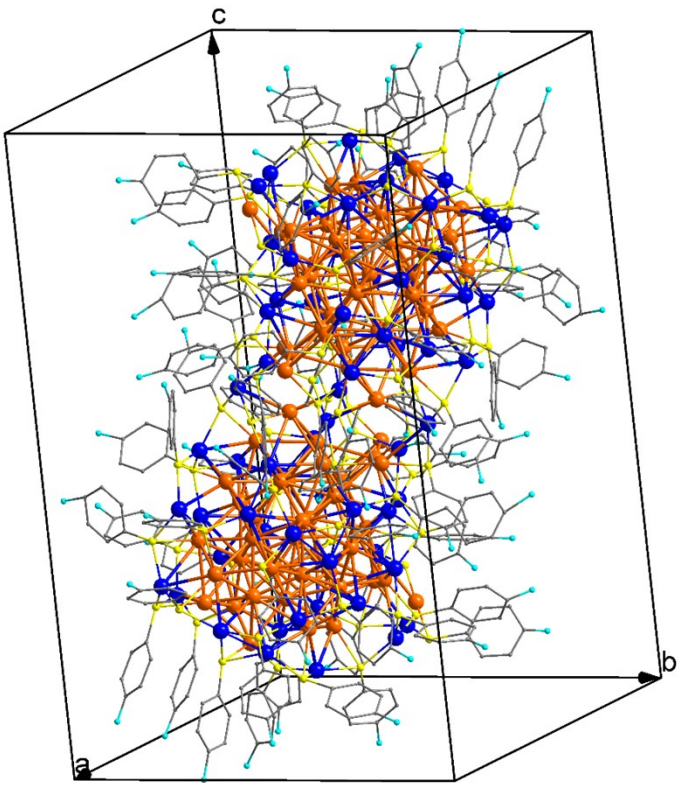


Figure S5. The packing structure of $Au_{41}Cu_{33}(RS)_{40}(MeCN)$ clusters in their single crystals. Color legend: orange spheres, Au; blue spheres, Cu; pink spheres, P; turquoise spheres, Cl; pale green spheres, F; yellow spheres, B; gray spheres, C. All hydrogen atoms are omitted for clarity.

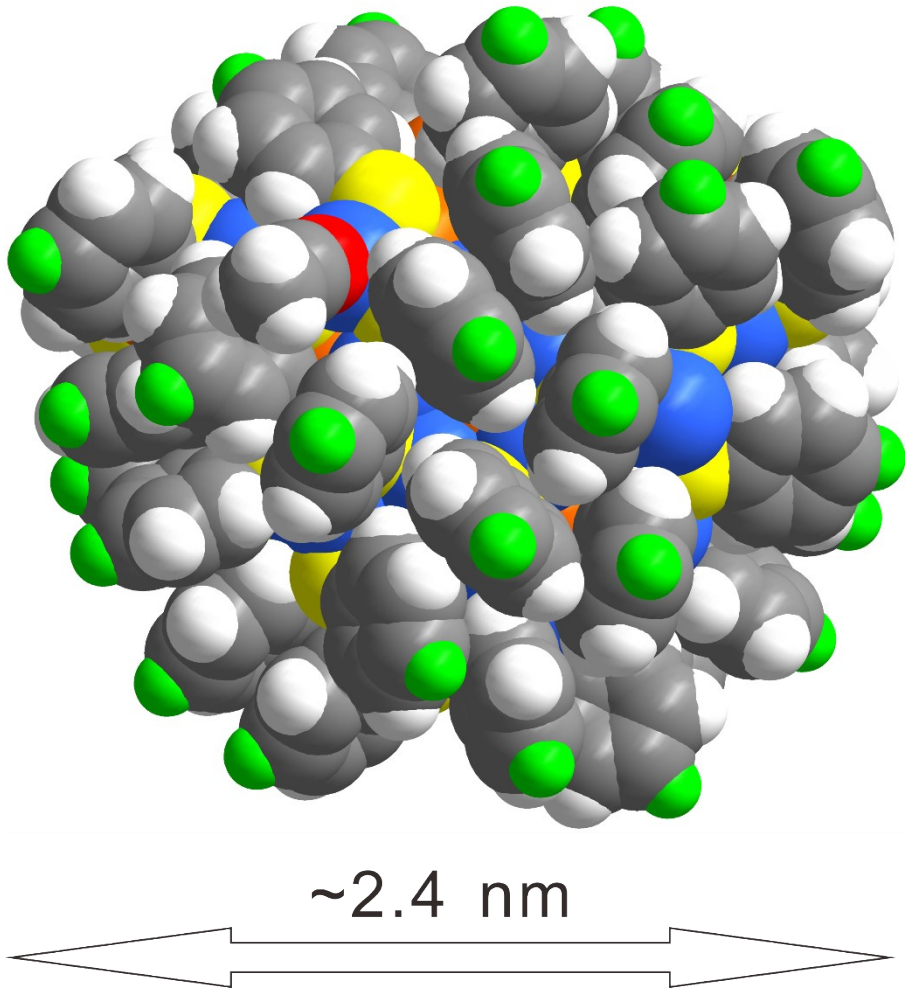


Figure S6. Total structure of $Au_{41}Cu_{33}(RS)_{40}(MeCN)$. Color legend: orange spheres, Au; blue spheres, Cu; pink spheres, P; turquoise, Cl; gray spheres, C. All hydrogen atoms are omitted for clarity.

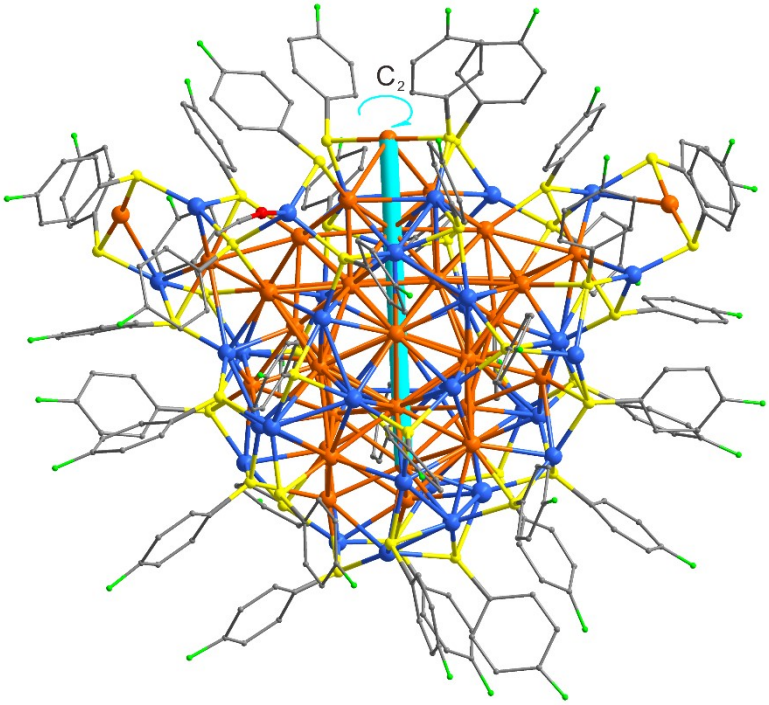


Figure S7. A C_2 axis is present in the structure of $Au_{41}Cu_{33}(RS)_{40}(MeCN)$. Color legend: orange spheres, Au; blue spheres, Cu; pink spheres, P; turquoise, Cl; gray spheres, C. All hydrogen atoms are omitted for clarity.

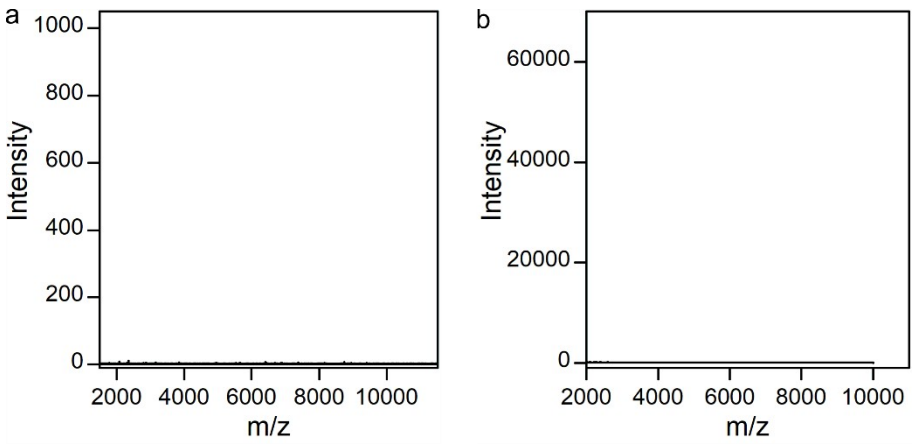
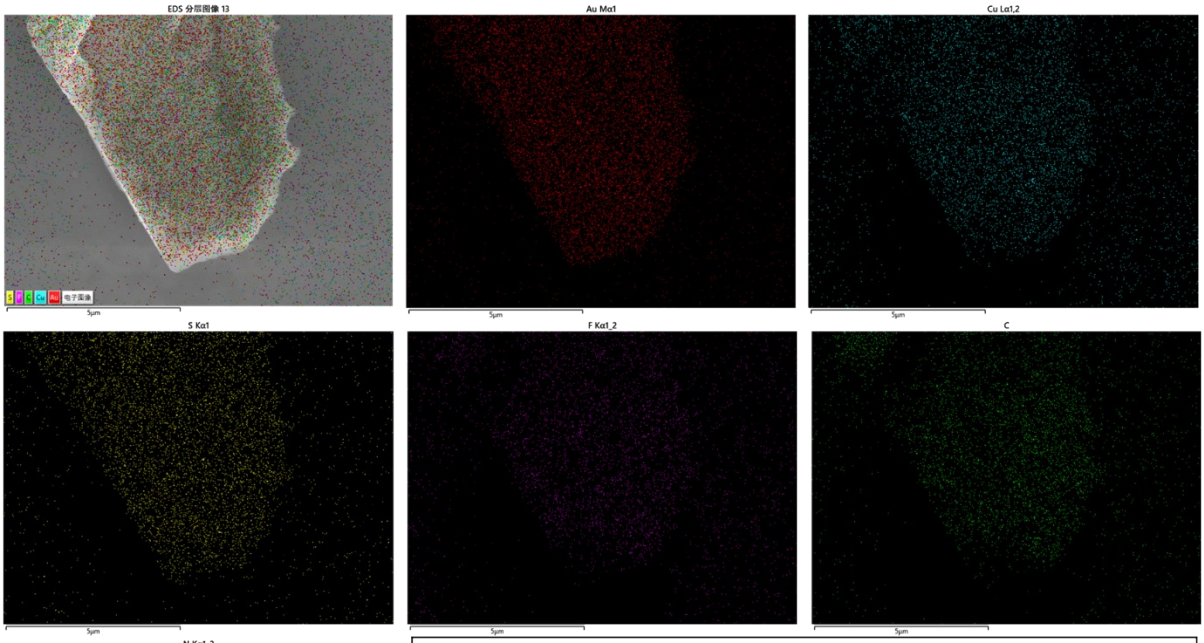


Figure S8. ESI-MS of $Au_{41}Cu_{33}(RS)_{40}(MeCN)$ in the positive (a) and negative mode (b).



Relative element content of sample

Element	Wt% (observed)	Wt% Sigma	Wt% (calculated)
Au	52.49	0.26	53.35
Cu	14.46	0.12	13.85
C	19.29	0.29	19.20
F	5.00	0.08	5.02
S	8.61	0.10	8.47
N	0.15	0.22	0.09
Total	100.00		100.00

Figure S9. Elemental maps and relative element content of samples determined from energy-dispersive X-ray spectra.

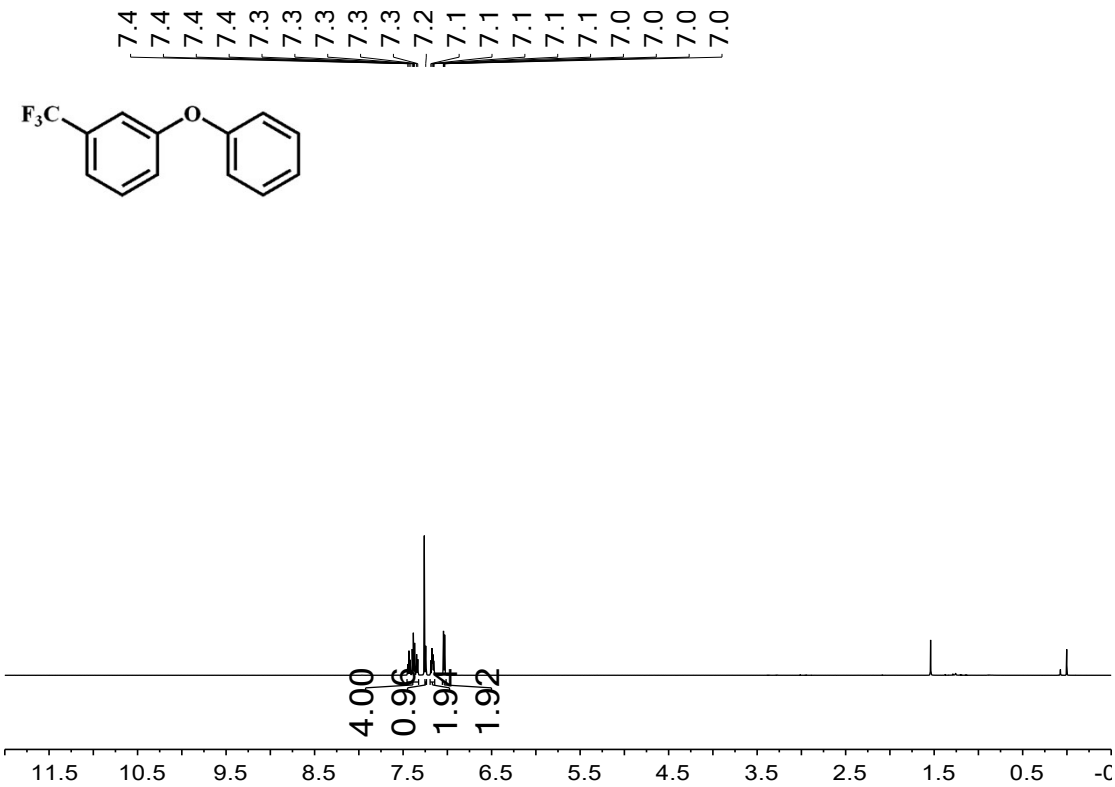


Figure S10. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **3a**.

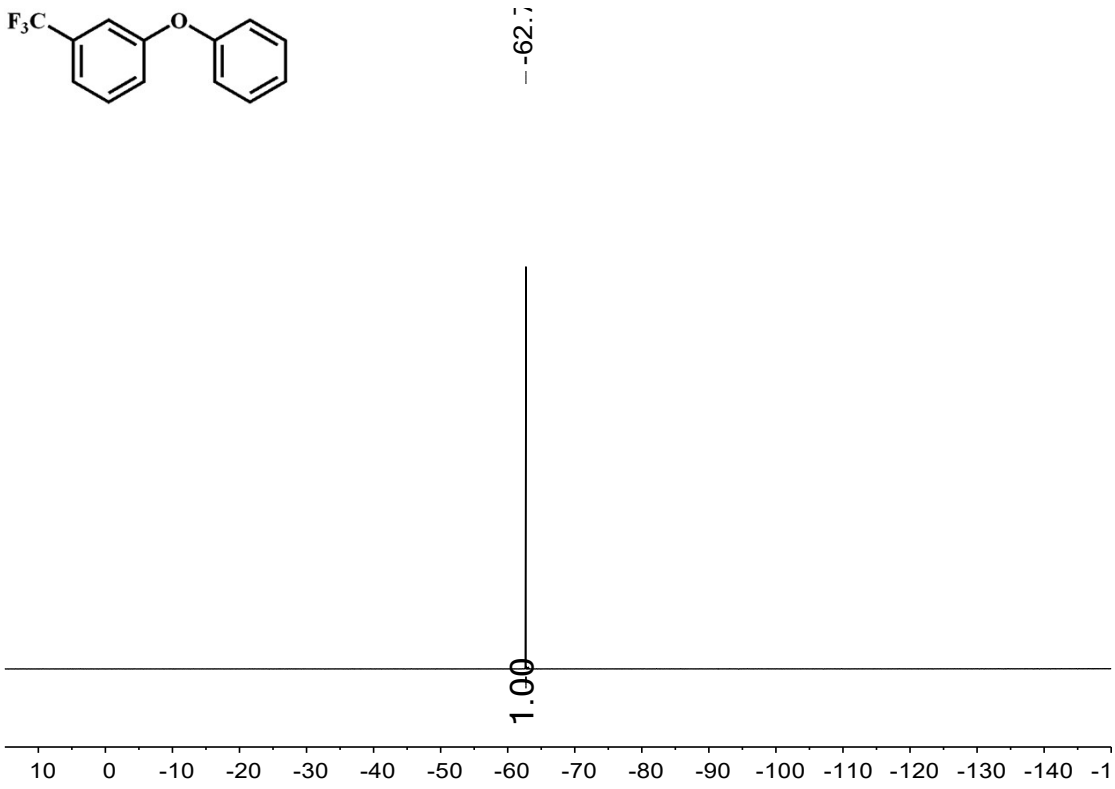


Figure S11. ^{19}F NMR spectrum (565 MHz, $CDCl_3$, 23 ºC) of **3a**.

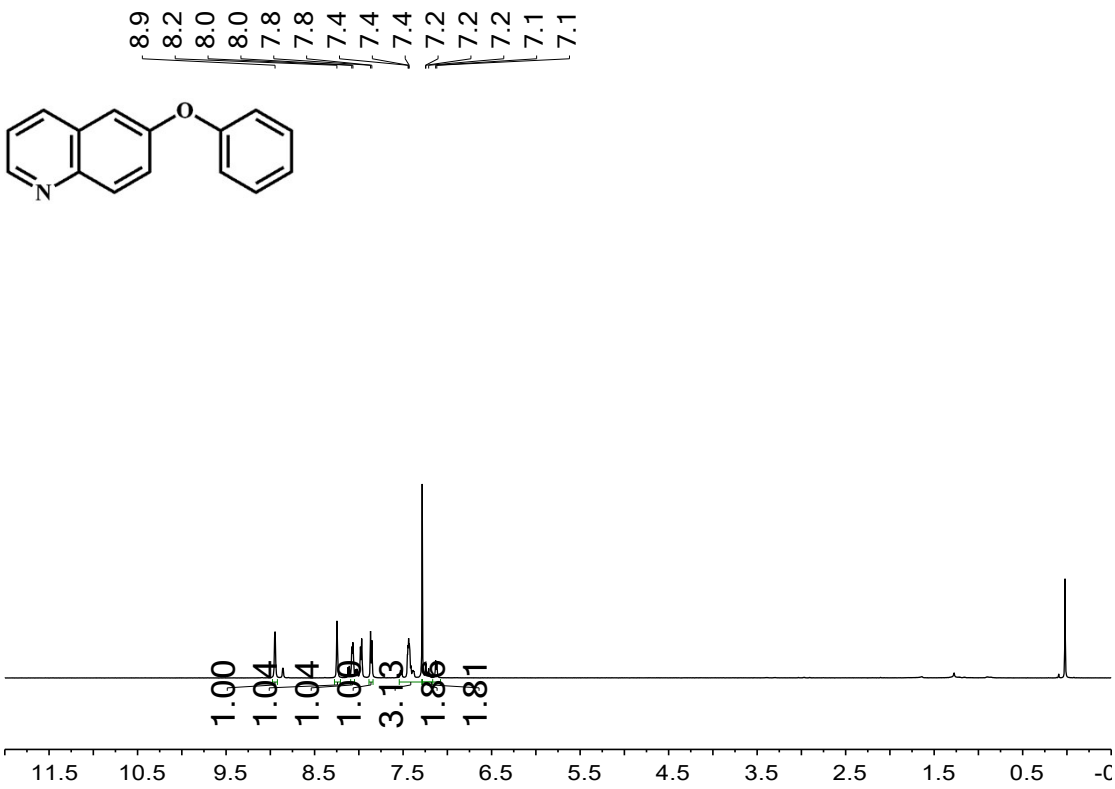


Figure S12. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **3b**.

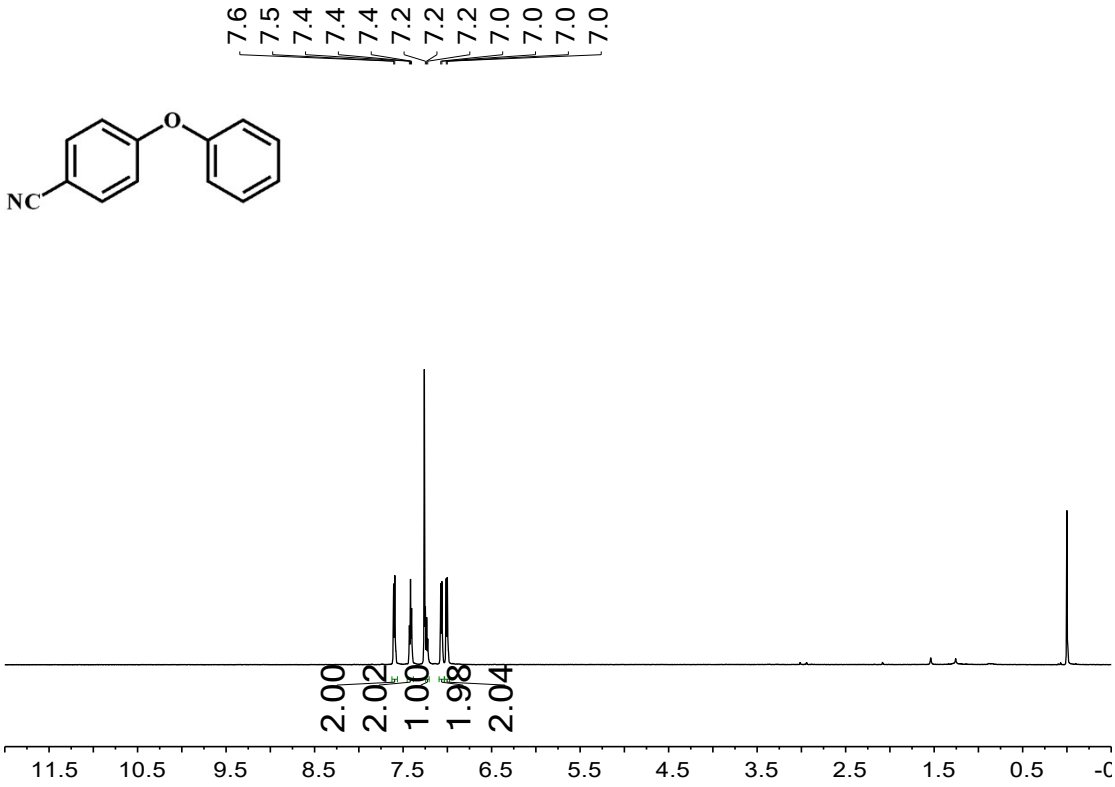


Figure S13. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **3c**.

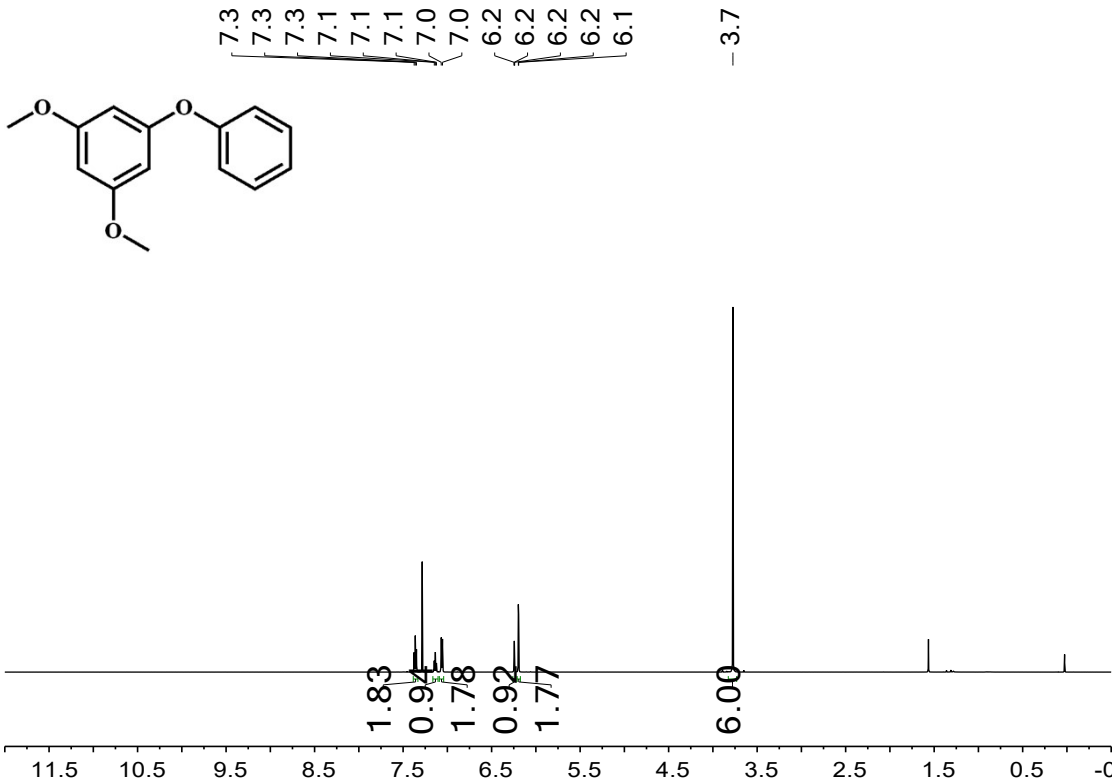


Figure S14. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **3d**.

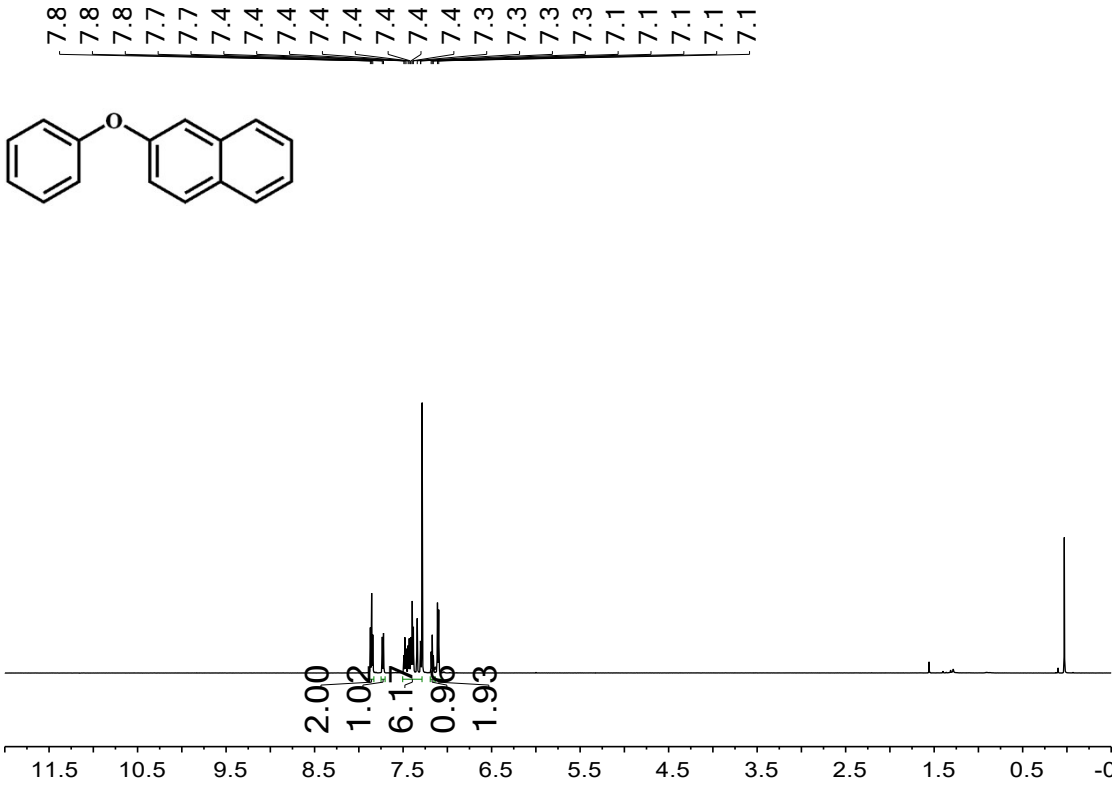


Figure S15. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **3e**.

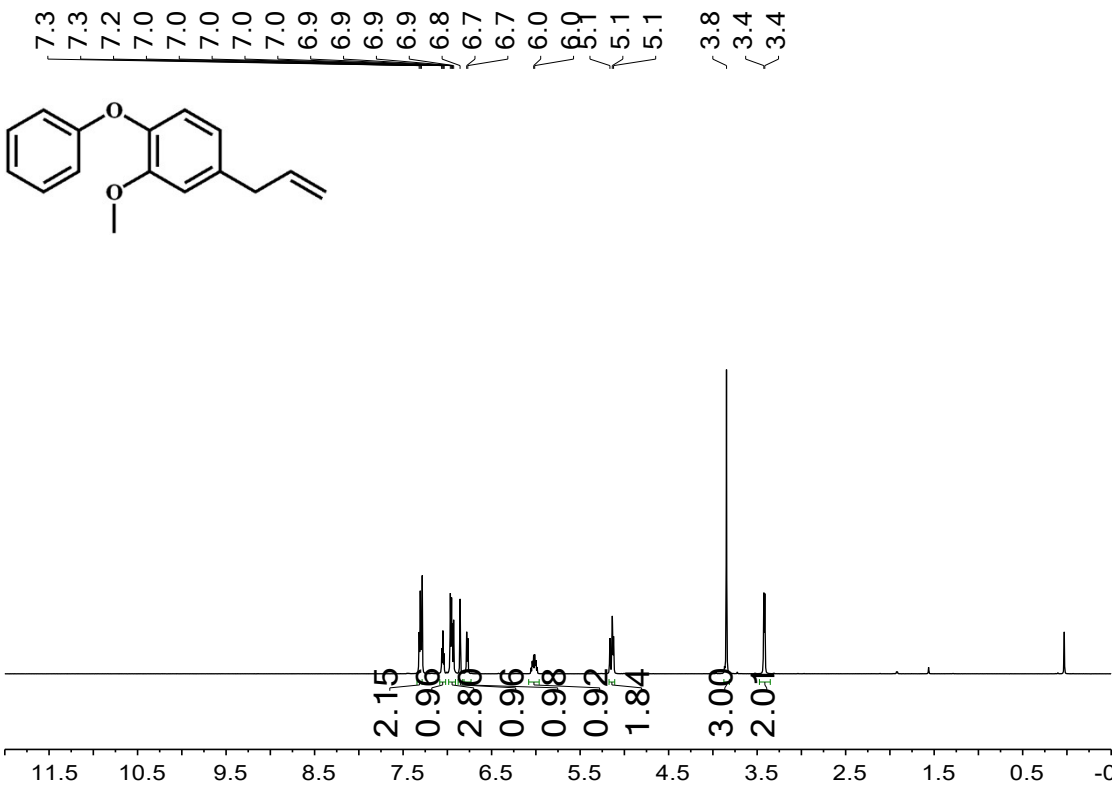


Figure S16. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **3f**.

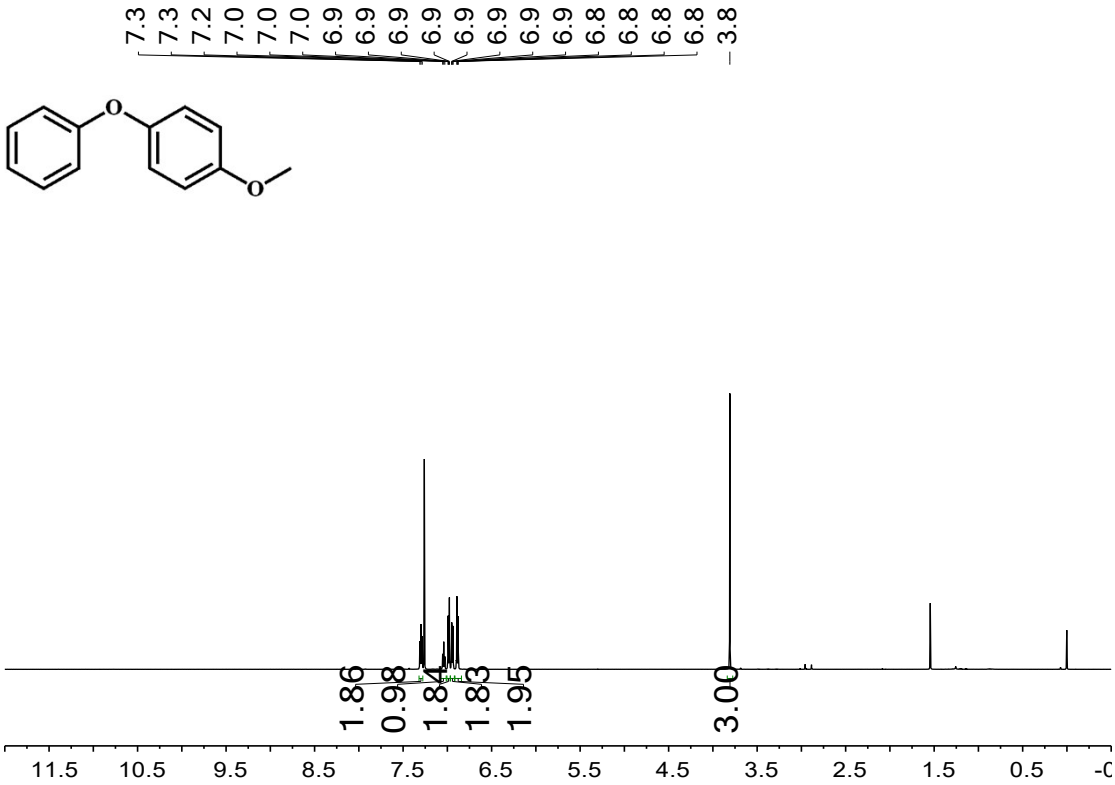


Figure S17. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **3g**.

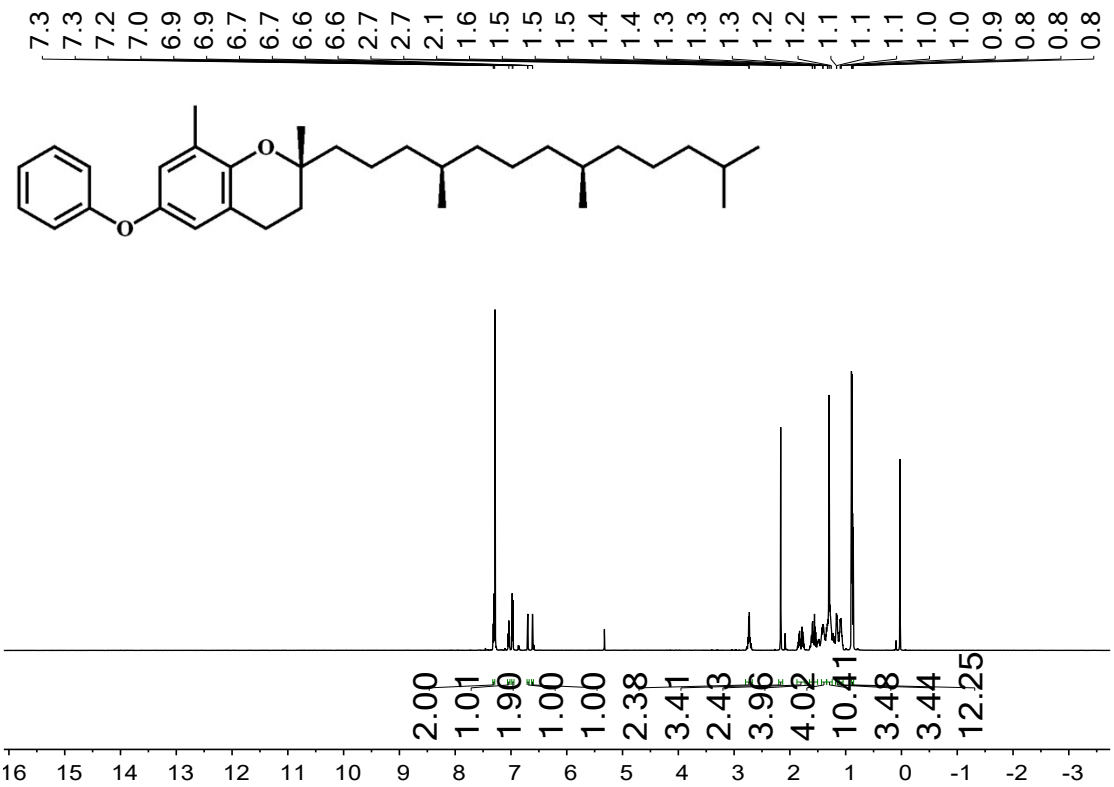


Figure S18. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, 23 ºC) of **3h**.

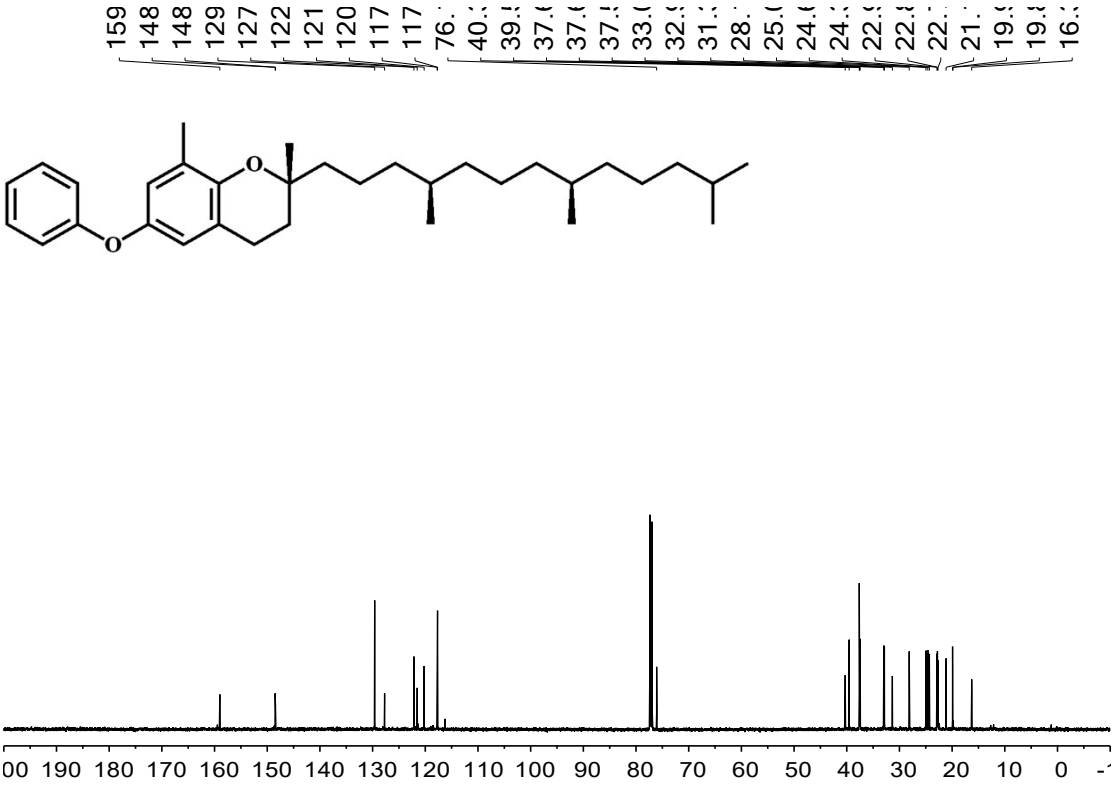


Figure S19. ^{13}C NMR spectrum (151 MHz, $CDCl_3$, 23 ºC) of **3h**.

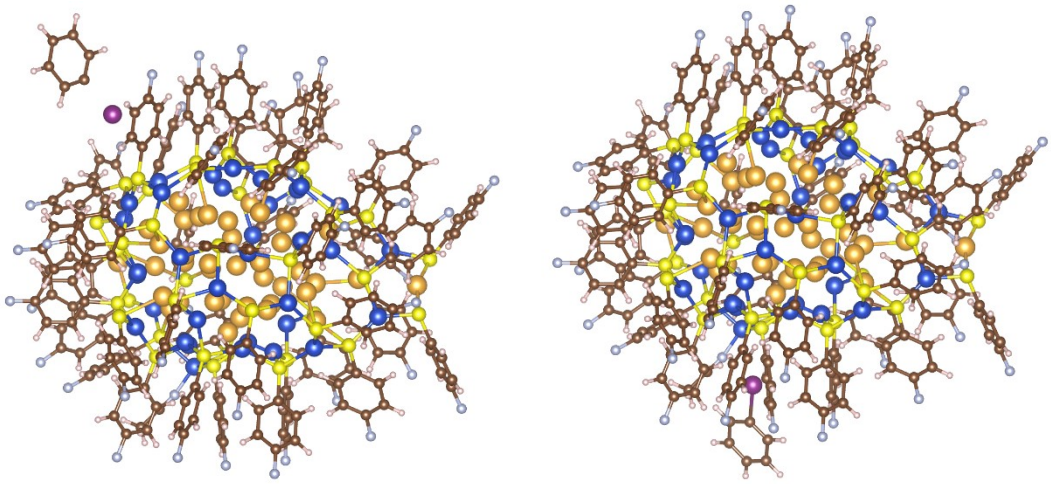


Figure S20. The illustration of C_6H_5-I adsorbed at the uncoordinated cupper site (left) and other Cu sites (right).

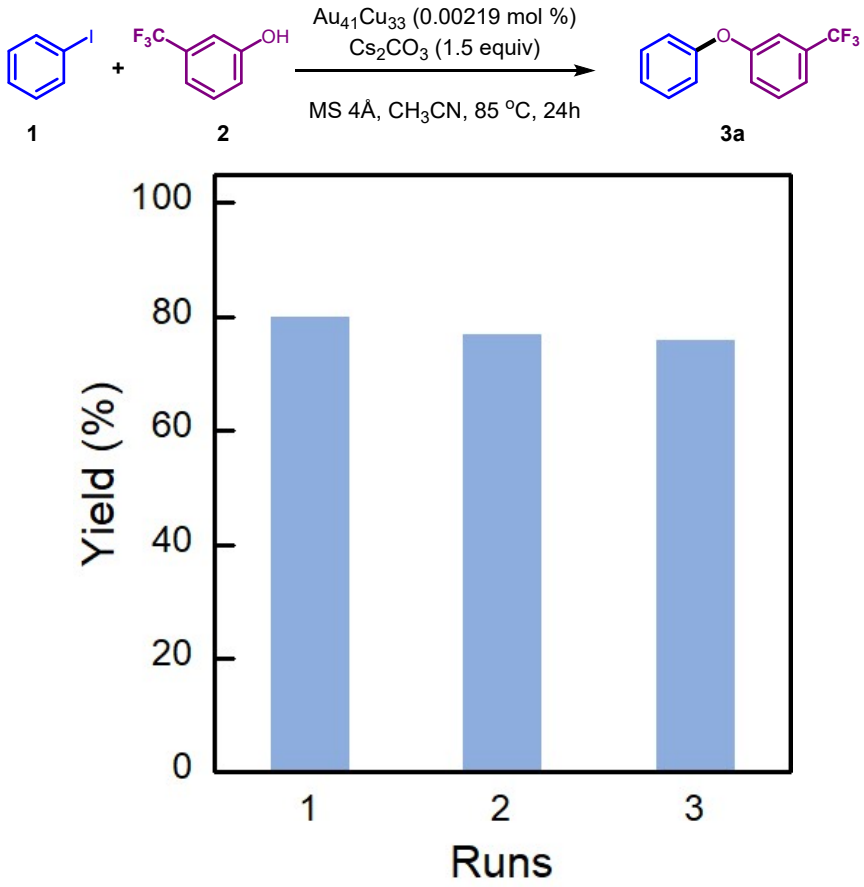


Figure S21. The activity of the recycled $Au_{41}Cu_{33}(RS)_{40}$(MeCN)/XC-72 for C-O bond coupling reaction. Reaction conditions: $Au_{41}Cu_{33}$ (0.00219 mol%), **1** (1.8 mmol, 1.2 equiv), **2** (1.2 mmol, 1 equiv), MS 4Å (20 mg), in CH_3CN (1.2 mL), stirred at 85 °C for 24 h. The yield of **3a** was determined by ^{19}F NMR.

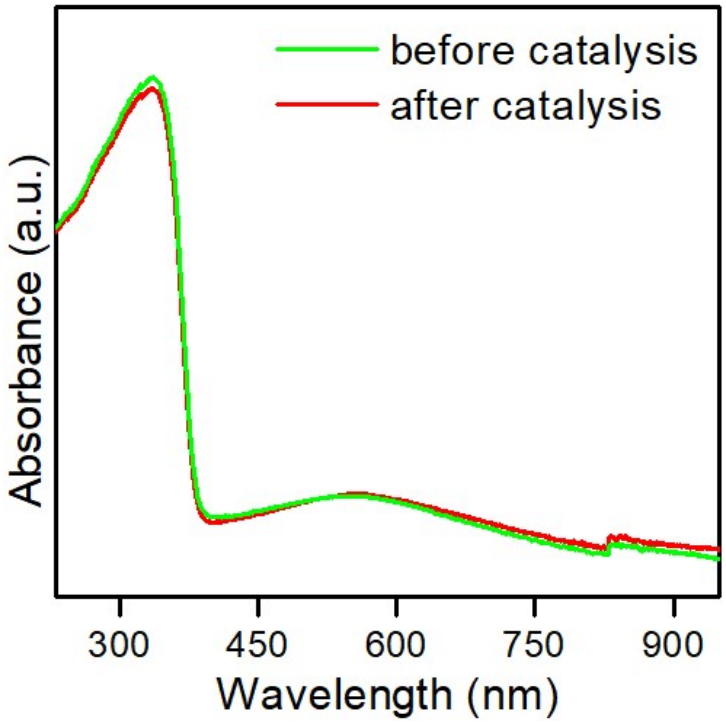


Figure S22. Solid-state UV-Vis spectra of $Au_{41}Cu_{33}(RS)_{40}(MeCN)/TiO_2$ before and after catalysis.

Table S1. Crystal data and structure refinement for $Au_{41}Cu_{33}(RS)_{40}(MeCN)$.

Identification code	$Au_{41}Cu_{33}(RS)_{40}(MeCN)$
Empirical formula	$C_{242}H_{163}Au_{40.39}Cu_{33.61}F_{40}NS_{40}$
Formula weight	15218.18
Temperature/K	160.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	21.5779(10)
b/Å	23.5644(12
c/Å	35.2515(16)
α/°	77.995(4)
β/°	76.716(4)
γ/°	79.904(4)
Volume/Å^3	16909.5(15)
Z	2
ρ_{calc}g/cm^3	2.989
μ/mm^{-1}	36.982
F(000)	13575
Crystal size/mm^3	0.5 × 0.05 × 0.05
Radiation	CuK\a (λ = 1.54184)
2Θ range for data collection/°	3.296 to 61.168
Index ranges	-24 ≤ h ≤ 22, -26 ≤ k ≤ 26, -40 ≤ l ≤ 32
Independent reflections	109178 [R_{int} = 0.1725, R_{sigma} = 0.2093]
Data/restraints/parameters	51944/1958/3209
Goodness-of-fit on F^2	0.937
Final R indexes [I>=2σ (I)]	R_1 = 0.1083, wR_2 = 0.2540
Final R indexes [all data]	R_1 = 0.1908, wR_2 = 0.3389
Largest diff. peak/hole/e Å^{-3}	5.67/-3.36

Table S2. The coordinates and Mulliken charge of each atom in $Au_{41}Cu_{33}$ cluster.

atom	x	y	z	charge
Au	35.99037	19.5891	35.35152	0.051
Au	32.55088	19.4962	38.27537	0.046
Au	32.00708	22.12554	36.451	0.033
Au	34.95527	19.0165	40.03305	0.006
Au	37.33157	21.35476	33.19763	0.109
Au	33.77528	21.71343	40.67554	0.059
Au	34.65256	19.10708	32.7029	0.098
Au	36.96987	21.17554	40.61409	0.013
Au	33.94017	24.26437	35.70395	0.015
Au	30.01558	19.78631	36.73995	0.131
Au	40.60245	22.86057	37.12425	0.118
Au	38.63726	18.58964	34.23988	0.115
Au	35.84081	23.90718	40.63426	0.043
Au	39.71019	20.5289	39.13277	0.107
Au	35.93169	25.01749	37.75887	0.034
Au	32.19443	19.20567	41.21198	0.070
Au	38.90105	23.45396	41.02789	0.103
Au	31.14028	25.12473	36.87095	0.085
Au	33.22541	24.01541	38.67161	0.043
Au	41.30548	20.33648	34.91322	0.207
Au	32.89323	24.50022	41.55995	0.091
Au	37.90329	18.41989	40.97782	0.114
Au	32.02544	23.568	33.56355	0.132
Au	35.30322	20.01348	42.81523	0.135
Au	30.99778	21.61134	39.40167	0.009
Au	35.50909	24.08534	32.92082	0.115
Au	35.27026	21.49468	30.8411	0.159
Au	34.90968	21.51732	37.66833	-0.028
Au	38.62513	20.88713	36.09879	0.046
Au	32.7938	19.45784	35.23361	0.045
Au	36.68238	23.06587	35.53761	0.020
Au	34.29387	21.71828	34.12077	0.001
Au	37.82429	22.8147	38.31914	0.041
Au	34.61781	17.76756	37.27153	0.055
Au	37.17528	19.33796	38.14185	0.025
Au	30.38074	24.37624	39.92303	0.125
Au	39.91454	20.77151	42.29367	0.176
Au	29.12765	22.73179	37.36026	0.160
Au	35.58138	21.71966	27.60777	0.234
Au	42.32122	20.41174	44.56515	0.248
Cu	30.08035	18.48462	39.38084	0.022
Cu	39.34122	23.2372	34.5296	0.012
Cu	34.58372	22.89555	43.13842	-0.025
Cu	29.66663	25.03744	34.39893	0.045
Cu	34.95675	25.96367	42.72546	0.07
Cu	33.66885	26.61659	37.04643	0.006
Cu	39.37032	18.6466	44.44434	0.052

Cu	29.60966	20.2588	41.45715	0.055
Cu	31.60994	26.99114	40.68142	0.073
Cu	28.36951	25.62477	38.26858	0.061
Cu	42.57608	22.3631	42.20369	0.038
Cu	41.50827	24.85243	39.25456	0.059
Cu	28.09453	22.00404	40.02563	0.046
Cu	34.17127	24.13418	29.50312	0.042
Cu	39.51331	18.2538	37.04543	0.020
Cu	36.36331	25.88875	35.09484	0.018
Cu	37.18968	17.20112	36.29992	-0.006
Cu	30.60813	21.13588	34.13897	-0.006
Cu	31.86715	17.22156	36.63285	-0.011
Cu	36.36339	16.67084	39.14232	0.017
Cu	33.34569	16.84205	39.67676	0.004
Cu	38.55045	24.9205	36.59679	0.003
Cu	32.41865	21.0087	32.286	-0.024
Cu	34.6944	26.37594	39.85923	-0.004
Cu	37.05688	22.38144	43.04122	-0.01
Cu	30.15291	18.07491	34.41135	0.024
Cu	34.09719	17.05813	34.68107	0.011
Cu	31.33796	22.22718	42.16467	0.000
Cu	36.64805	19.10831	29.37155	0.068
Cu	36.98709	15.83106	32.24437	0.220
Cu	32.64637	19.4167	44.01	0.046
Cu	33.34904	26.21356	33.07018	0.095
Cu	37.72731	25.78024	39.68437	0.006
Cu	35.82998	16.90048	42.90603	0.104
S	38.45766	16.22633	38.10778	0.170
S	42.03832	20.70109	40.57249	0.066
S	38.56369	25.5553	34.2711	0.164
S	32.75658	22.38417	30.37951	0.122
S	31.2085	16.44789	38.77254	0.207
S	28.68986	26.39214	36.08236	0.134
S	42.7782	24.40602	37.41665	0.110
S	33.01567	27.78634	38.9199	0.164
S	40.69955	22.04884	33.06489	0.097
S	30.41825	18.99353	43.39781	0.132
S	35.03438	15.76647	40.94695	0.161
S	36.2134	24.43825	44.01564	0.183
S	28.06318	18.63689	35.21644	0.095
S	31.00213	26.10742	32.79093	0.126
S	41.43397	24.26285	41.49949	0.113
S	28.92887	22.79489	34.57353	0.095
S	39.61705	26.14519	38.38214	0.146
S	32.83728	27.08735	42.70602	0.115
S	29.34042	26.93862	40.08096	0.105
S	27.02365	23.77897	38.9161	0.127
S	34.42582	17.9474	44.47084	0.154
S	34.59493	25.80101	31.04546	0.122
S	32.71354	21.82419	44.13496	0.140

S	36.53673	27.0727	41.25901	0.163
S	28.02025	19.57228	39.69881	0.163
S	31.82224	16.38262	34.38943	0.187
S	35.72736	17.52877	30.81487	0.053
S	39.15927	16.53074	32.66409	0.070
S	30.70645	19.40003	32.4455	0.172
S	36.12171	15.87646	34.63653	0.126
S	37.89852	20.70154	30.63415	0.071
S	41.77658	18.82178	36.97363	0.075
S	38.25288	20.84815	44.4449	0.102
S	28.99745	22.63875	42.1574	0.169
S	38.22985	17.03092	43.25369	0.097
S	40.95757	18.78343	46.07365	0.095
S	34.46922	27.29889	34.92007	0.170
S	36.90928	19.54619	27.13295	0.100
S	44.29161	21.85476	43.62928	0.097
S	34.2722	23.93867	27.22415	0.091
F	40.67718	25.10506	27.57418	-0.319
F	29.24611	10.72424	38.66805	-0.305
F	38.29017	30.4498	29.96334	-0.312
F	41.19105	19.03966	27.55995	-0.326
F	34.41093	33.65143	38.62654	-0.307
F	26.49901	19.52474	28.12876	-0.313
F	22.50236	22.72924	35.05912	-0.313
F	29.08577	13.11099	43.5513	-0.318
F	47.39604	20.77325	38.81335	-0.323
F	25.41	14.17656	38.3169	-0.320
F	30.15516	32.24999	35.74119	-0.320
F	25.34979	22.47624	46.97475	-0.311
F	44.58574	15.38807	41.90867	-0.317
F	38.11761	28.20098	25.32476	-0.317
F	30.567	19.12346	25.78366	-0.315
F	31.22167	14.64839	27.99702	-0.314
F	33.48364	16.07672	23.56403	-0.317
F	41.05361	24.50281	48.37251	-0.317
F	23.73126	22.38614	31.53403	-0.312
F	37.19602	19.44205	49.61878	-0.320
F	34.10623	9.814181	41.49084	-0.308
F	41.74232	29.12247	45.07177	-0.312
F	37.06906	33.00208	42.3411	-0.312
F	35.05627	10.28652	36.66974	-0.313
F	30.0539	10.74816	33.0426	-0.311
F	25.91687	28.01347	44.93192	-0.313
F	41.87028	30.54928	33.51116	-0.312
F	31.43613	23.71781	49.72288	-0.307
F	34.98361	33.31216	34.62651	-0.304
F	39.89023	10.56419	36.56589	-0.317
F	45.00613	13.9176	35.54571	-0.319
F	35.89337	25.02917	50.02076	-0.312
F	43.8089	13.47736	46.61653	-0.317

F	45.57012	25.18054	31.35476	-0.317
F	45.45901	26.28932	47.55909	-0.317
F	41.21156	11.92386	42.01465	-0.309
F	29.02887	24.8987	27.21211	-0.319
F	24.03132	16.1093	42.63919	-0.314
F	39.84618	32.1336	37.60176	-0.309
F	29.35061	26.73512	47.62413	-0.311
N	36.1961	14.24351	31.46992	-0.196
C	26.79364	18.5276	40.652	-0.259
C	26.05994	19.05286	41.72638	-0.181
H	26.21097	20.08472	42.04608	0.184
C	25.1328	18.24139	42.40142	-0.158
H	24.55165	18.61759	43.24156	0.188
C	24.96714	16.92533	41.96516	0.244
C	25.68153	16.38281	40.89816	-0.174
H	25.50979	15.35319	40.58504	0.210
C	26.61105	17.19959	40.23668	-0.156
H	27.17848	16.80515	39.39443	0.196
C	35.13391	31.35384	38.69554	-0.160
H	36.16728	31.68893	38.63147	0.202
C	34.09439	32.28131	38.7132	0.255
C	32.75352	31.91508	38.81539	-0.159
H	31.98029	32.6793	38.81815	0.188
C	32.43826	30.55088	38.91263	-0.160
H	31.39864	30.23137	38.9769	0.171
C	33.46876	29.60113	38.89617	-0.242
C	34.81049	29.99261	38.79085	-0.163
H	35.60244	29.24636	38.78853	0.174
C	38.4822	12.08946	37.79685	-0.156
H	37.92553	11.24139	38.19393	0.193
C	39.55328	11.88892	36.92486	0.247
C	40.29613	12.93347	36.37665	-0.161
H	41.12629	12.72049	35.70322	0.194
C	39.94837	14.24986	36.72175	-0.179
H	40.51247	15.08596	36.30955	0.208
C	38.87709	14.47774	37.60027	-0.272
C	38.1419	13.40979	38.13729	-0.174
H	37.29886	13.60144	38.80375	0.187
C	39.3761	21.7677	28.47898	-0.171
H	39.39019	20.74844	28.09777	0.213
C	40.04673	22.783	27.77898	-0.170
H	40.59496	22.57248	26.86161	0.195
C	40.01109	24.08015	28.28979	0.242
C	39.34244	24.41512	29.46616	-0.164
H	39.3473	25.44014	29.83322	0.197
C	38.67886	23.39187	30.1589	-0.169
H	38.15355	23.61379	31.08905	0.151
C	38.6894	22.07491	29.66688	-0.263
C	29.14791	28.19334	35.95486	-0.266
C	29.54133	28.74834	34.72584	-0.168

H	29.60975	28.12822	33.83222	0.179
C	29.8697	30.11186	34.64705	-0.158
H	30.18462	30.5653	33.70884	0.189
C	29.7855	30.88392	35.80558	0.241
C	29.37226	30.36294	37.03071	-0.163
H	29.29386	31.00828	37.9046	0.184
C	29.05262	28.99873	37.10022	-0.157
H	28.74414	28.56284	38.04973	0.179
C	43.24905	15.46874	34.97693	-0.166
H	43.07392	14.90797	34.05913	0.188
C	44.2462	15.06569	35.86519	0.251
C	44.52483	15.74161	37.05102	-0.152
H	45.31928	15.39202	37.70736	0.191
C	43.76475	16.8797	37.36519	-0.135
H	43.9585	17.43738	38.2821	0.184
C	42.7474	17.30531	36.4937	-0.264
C	42.48863	16.60229	35.30503	-0.196
H	41.68911	16.92074	34.63456	0.174
C	41.47772	25.75669	42.61333	-0.261
C	42.66577	26.01255	43.31322	-0.163
H	43.52085	25.34338	43.2138	0.202
C	42.76018	27.13995	44.1422	-0.167
H	43.66985	27.35993	44.69785	0.207
C	41.6514	27.98078	44.24785	0.250
C	40.45704	27.74504	43.56673	-0.163
H	39.61388	28.42606	43.67721	0.193
C	40.37072	26.61189	42.74191	-0.196
H	39.44539	26.40938	42.19904	0.178
C	35.30107	18.41934	46.03733	-0.264
C	34.74797	19.41365	46.86127	-0.179
H	33.84032	19.93762	46.55489	0.201
C	35.37001	19.75263	48.07093	-0.161
H	34.95582	20.51547	48.72964	0.197
C	36.54675	19.08874	48.41138	0.237
C	37.12446	18.10789	47.6082	-0.173
H	38.05488	17.63003	47.91153	0.195
C	36.48366	17.76387	46.40886	-0.158
H	36.91074	17.00097	45.75703	0.173
C	43.84837	23.31716	46.0704	-0.152
H	43.06542	22.59638	46.30725	0.171
C	44.14417	24.34861	46.97843	-0.159
H	43.59645	24.4489	47.91462	0.212
C	45.15695	25.24978	46.64907	0.234
C	45.88289	25.17383	45.46166	-0.157
H	46.67294	25.89297	45.25079	0.187
C	45.5791	24.13703	44.56638	-0.143
H	46.14015	24.04224	43.63687	0.170
C	44.55892	23.21395	44.86374	-0.286
C	35.51751	13.44054	30.94264	0.194
C	34.45446	16.33116	28.6009	-0.155

H	35.35318	16.61139	28.05196	0.193
C	33.41657	15.65555	27.93607	-0.180
H	33.48871	15.40848	26.87839	0.205
C	32.26912	15.32933	28.65957	0.228
C	32.10961	15.64614	30.00892	-0.168
H	31.19318	15.38247	30.53398	0.192
C	33.15292	16.32184	30.66208	-0.193
H	33.04517	16.58656	31.71413	0.193
C	34.32238	16.66265	29.95907	-0.266
C	44.42447	24.46546	31.77084	0.249
C	43.72087	23.72306	30.82318	-0.149
H	44.04687	23.70731	29.78505	0.188
C	42.58651	23.0132	31.24477	-0.151
H	42.01051	22.42976	30.52704	0.190
C	42.1899	23.05723	32.59231	-0.278
C	42.90955	23.82349	33.52478	-0.178
H	42.59723	23.86671	34.56903	0.171
C	44.04673	24.5362	33.1111	-0.163
H	44.62118	25.13632	33.81363	0.185
C	34.66667	29.16213	34.8554	-0.289
C	35.89154	29.73954	34.49052	-0.186
H	36.7526	29.11305	34.25404	0.193
C	36.00088	31.13979	34.41331	-0.165
H	36.93445	31.6245	34.12755	0.197
C	34.87688	31.91071	34.71223	0.246
C	33.6569	31.35594	35.09973	-0.166
H	32.81183	31.99725	35.34587	0.219
C	33.55723	29.95803	35.17314	-0.154
H	32.62334	29.4924	35.49026	0.186
C	36.12777	23.4579	46.6912	-0.157
H	36.20934	22.46806	46.24243	0.178
C	36.07496	24.59637	45.87347	-0.256
C	35.95832	25.88042	46.43194	-0.158
H	35.93457	26.76239	45.78917	0.164
C	35.89138	26.03049	47.82615	-0.151
H	35.82337	27.00937	48.29664	0.187
C	35.95218	24.88312	48.61924	0.251
C	36.0692	23.59958	48.08598	-0.167
H	36.12347	22.73581	48.7462	0.198
C	29.34108	19.49101	31.18282	-0.258
C	29.12408	20.66693	30.45032	-0.162
H	29.70433	21.56351	30.66844	0.178
C	28.17275	20.68073	29.41909	-0.163
H	27.99567	21.57311	28.8225	0.197
C	27.4528	19.51456	29.16753	0.248
C	27.63128	18.34018	29.89682	-0.152
H	27.04005	17.45731	29.66074	0.187
C	28.59378	18.33121	30.91779	-0.155
H	28.76728	17.42126	31.49245	0.164
C	31.68877	19.21566	27.91658	-0.168

H	31.7458	18.12942	27.92018	0.210
C	31.08325	19.88848	26.85606	0.240
C	30.97199	21.27654	26.79837	-0.155
H	30.48725	21.75722	25.95064	0.199
C	31.50349	22.02926	27.85722	-0.158
H	31.43609	23.11489	27.83488	0.201
C	32.12527	21.37734	28.93468	-0.272
C	32.2227	19.97601	28.96575	-0.166
H	32.69601	19.47792	29.81215	0.167
C	27.28602	17.27857	36.19873	-0.290
C	25.92302	17.37747	36.54193	-0.147
H	25.35696	18.26497	36.25811	0.170
C	25.2864	16.33789	37.23813	-0.152
H	24.23469	16.39442	37.51414	0.187
C	26.03835	15.21688	37.5871	0.228
C	27.3883	15.08527	37.2654	-0.177
H	27.94238	14.19331	37.55439	0.208
C	28.011	16.13264	36.5684	-0.194
H	29.06791	16.05532	36.30817	0.179
C	34.44371	18.77343	25.89946	-0.163
H	33.99092	19.61977	26.41721	0.180
C	33.65562	17.96853	25.05786	-0.180
H	32.59442	18.17263	24.90909	0.223
C	34.26823	16.8978	24.40749	0.239
C	35.62429	16.59662	24.55059	-0.161
H	36.05822	15.75657	24.01041	0.184
C	36.39869	17.4108	25.39408	-0.151
H	37.46489	17.21256	25.50917	0.174
C	35.81223	18.49446	26.07543	-0.286
C	28.78355	24.66821	29.60287	-0.164
H	27.8662	24.104	29.44255	0.200
C	29.26394	24.92303	30.89651	-0.175
H	28.72094	24.53258	31.75912	0.204
C	30.43756	25.67277	31.07142	-0.260
C	31.13956	26.17056	29.96155	-0.148
H	32.05326	26.74562	30.10428	0.174
C	30.67324	25.91121	28.66365	-0.170
H	31.20667	26.28384	27.79046	0.197
C	29.50287	25.1681	28.51852	0.234
C	30.75228	14.85481	43.44796	-0.163
H	31.52665	14.09243	43.47601	0.193
C	31.07085	16.22096	43.3718	-0.171
H	32.11383	16.54017	43.34969	0.169
C	30.03951	17.17525	43.35756	-0.264
C	28.69329	16.7765	43.40034	-0.149
H	27.90145	17.52236	43.37906	0.188
C	28.36593	15.41429	43.47238	-0.161
H	27.33116	15.07975	43.50402	0.197
C	29.40813	14.48909	43.49709	0.235
C	32.67914	23.70458	46.25234	-0.149

H	33.24725	24.33757	45.57298	0.185
C	32.41069	24.14185	47.55725	-0.154
H	32.75033	25.112	47.91074	0.197
C	31.70324	23.28968	48.40778	0.247
C	31.24722	22.03348	48.01273	-0.157
H	30.69222	21.40904	48.71072	0.190
C	31.52262	21.60254	46.70376	-0.182
H	31.17443	20.62643	46.36258	0.173
C	32.24638	22.43969	45.83426	-0.281
C	34.66118	12.65843	36.84244	-0.173
H	33.97498	12.46501	37.66801	0.205
C	35.31534	11.59838	36.21376	0.245
C	36.21385	11.77207	35.16022	-0.161
H	36.71931	10.91167	34.72231	0.193
C	36.46726	13.07755	34.71206	-0.146
H	37.17284	13.25705	33.90033	0.182
C	35.8079	14.16415	35.31275	-0.255
C	34.92006	13.96019	36.38404	-0.188
H	34.42052	14.80927	36.85707	0.150
C	44.16017	23.26245	37.88021	-0.290
C	44.52644	23.06131	39.22051	-0.154
H	43.95994	23.541	40.02144	0.165
C	45.61276	22.23408	39.53826	-0.168
H	45.9052	22.06782	40.57421	0.187
C	46.30444	21.61736	38.4967	0.241
C	45.96361	21.79276	37.15636	-0.15
H	46.53377	21.2951	36.37258	0.184
C	44.88071	22.62972	36.85076	-0.152
H	44.60382	22.7902	35.80785	0.176
C	41.5723	16.33941	47.2826	-0.149
H	40.86202	16.67289	48.03885	0.180
C	42.22361	15.1069	47.4392	-0.153
H	42.03005	14.46643	48.29831	0.185
C	43.1483	14.71836	46.46659	0.234
C	43.44361	15.50565	45.35562	-0.161
H	44.16479	15.16615	44.61399	0.210
C	42.78286	16.73523	45.21084	-0.165
H	42.99009	17.35529	44.33877	0.174
C	41.84712	17.15897	46.17163	-0.282
C	42.08321	17.86536	40.8024	-0.173
H	41.06565	17.88848	40.41186	0.154
C	42.67147	16.63213	41.12106	-0.161
H	42.12154	15.69744	41.02343	0.210
C	43.9885	16.62895	41.58053	0.230
C	44.74098	17.79156	41.73754	-0.158
H	45.77131	17.74201	42.08544	0.191
C	44.13695	19.02195	41.43321	-0.172
H	44.70135	19.94665	41.54581	0.197
C	42.80793	19.05663	40.97592	-0.253
C	35.73871	27.20804	30.64972	-0.270

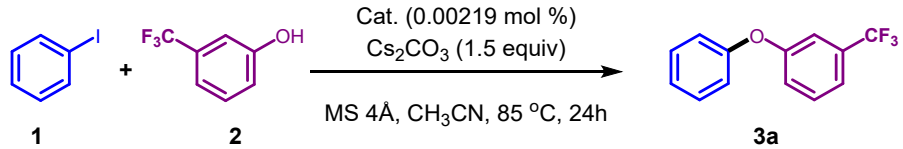
C	36.74356	27.10306	29.67362	-0.179
H	36.85381	26.18517	29.0964	0.208
C	37.59795	28.19416	29.43223	-0.165
H	38.37917	28.14084	28.67744	0.206
C	37.41836	29.35828	30.18057	0.238
C	36.41494	29.4943	31.14058	-0.170
H	36.30337	30.42623	31.69162	0.197
C	35.56803	28.40029	31.37224	-0.168
H	34.77747	28.48522	32.11667	0.183
C	35.49291	25.22457	26.67241	-0.269
C	36.87238	24.96662	26.59074	-0.172
H	37.26331	23.98945	26.87628	0.166
C	37.75861	25.95722	26.13913	-0.171
H	38.83029	25.77376	26.07626	0.211
C	37.23262	27.19551	25.7771	0.245
C	35.8702	27.48431	25.84041	-0.149
H	35.50568	28.46411	25.53912	0.185
C	34.99565	26.48453	26.28926	-0.137
H	33.92497	26.68428	26.34121	0.172
C	28.63063	28.25208	42.44811	-0.127
H	29.50087	28.87071	42.22806	0.161
C	27.83341	28.5453	43.56198	-0.147
H	28.06372	29.38068	44.22095	0.187
C	26.73431	27.72587	43.81764	0.245
C	26.40254	26.63564	43.01509	-0.152
H	25.53904	26.02052	43.26204	0.184
C	27.20469	26.35116	41.89852	-0.172
H	26.95749	25.51143	41.25016	0.178
C	28.30934	27.1667	41.61394	-0.263
C	37.98533	30.97815	41.3963	-0.158
H	38.86473	31.5438	41.09114	0.192
C	36.94645	31.62306	42.0703	0.254
C	35.79012	30.96286	42.484	-0.155
H	34.99373	31.50894	42.98815	0.184
C	35.6753	29.59266	42.21266	-0.175
H	34.77636	29.05086	42.51058	0.179
C	36.71176	28.91905	41.54859	-0.266
C	37.86517	29.60202	41.13228	-0.187
H	38.66768	29.08015	40.60901	0.192
C	39.22931	16.91895	29.86736	-0.141
H	38.42912	16.18026	29.83372	0.160
C	39.76777	17.31014	31.10638	-0.274
C	40.78889	18.27575	31.15173	-0.147
H	41.18286	18.60753	32.11293	0.148
C	41.27773	18.85055	29.96861	-0.153
H	42.05818	19.60741	29.98698	0.186
C	40.72067	18.44079	28.75726	0.233
C	39.70409	17.49256	28.67443	-0.164
H	39.28985	17.21271	27.70896	0.184
C	39.04675	14.88174	41.62443	-0.218

H	38.42342	15.34887	40.86009	0.185
C	39.71973	13.68581	41.32478	-0.184
H	39.62413	13.20951	40.34998	0.211
C	40.5343	13.1255	42.3063	0.248
C	40.70912	13.70264	43.56553	-0.157
H	41.36865	13.23928	44.2974	0.206
C	40.02921	14.89794	43.85675	-0.159
H	40.15851	15.3737	44.82822	0.196
C	39.19153	15.47625	42.89019	-0.253
C	27.30636	22.64791	33.6668	-0.287
C	26.49012	23.78566	33.54348	-0.162
H	26.78811	24.7251	34.01532	0.170
C	25.28402	23.69897	32.82665	-0.153
H	24.62961	24.56116	32.70723	0.187
C	24.9341	22.47136	32.26726	0.248
C	25.71467	21.32267	32.39806	-0.160
H	25.39295	20.38519	31.9484	0.190
C	26.91848	21.4172	33.11768	-0.169
H	27.53625	20.52916	33.25035	0.206
C	34.32872	11.20044	41.36435	0.250
C	35.61056	11.69124	41.60987	-0.156
H	36.40916	11.01153	41.90312	0.193
C	35.82932	13.07374	41.49157	-0.184
H	36.81896	13.48309	41.69629	0.203
C	34.76644	13.91341	41.12039	-0.283
C	33.48513	13.39432	40.87835	-0.187
H	32.66459	14.05741	40.6027	0.203
C	33.2557	12.01374	40.99855	-0.164
H	32.26883	11.58405	40.82998	0.203
C	39.26236	21.58508	46.99095	-0.158
H	38.85124	20.63668	47.3312	0.200
C	39.16508	21.95948	45.64148	-0.279
C	39.70039	23.18403	45.20414	-0.173
H	39.62942	23.47359	44.15595	0.165
C	40.32971	24.04432	46.11496	-0.168
H	40.74557	24.99761	45.79143	0.211
C	40.40999	23.64778	47.44834	0.241
C	39.89972	22.43292	47.90867	-0.152
H	39.98458	22.16338	48.96018	0.194
C	30.64601	26.06198	44.23558	-0.172
H	30.40091	25.45545	43.36199	0.163
C	31.76342	26.91036	44.21953	-0.256
C	32.07438	27.70424	45.33425	-0.150
H	32.93649	28.36882	45.30383	0.163
C	31.26925	27.65034	46.48321	-0.157
H	31.48744	28.25538	47.36195	0.186
C	30.16504	26.79852	46.47452	0.251
C	29.83377	26.00465	45.3789	-0.162
H	28.95716	25.36153	45.41978	0.207
C	32.21259	13.58994	33.99496	-0.196

H	33.2561	13.78978	34.23701	0.205
C	31.27197	14.6324	34.00101	-0.276
C	29.92416	14.37977	33.68552	-0.169
H	29.19686	15.19117	33.69583	0.187
C	29.51025	13.07491	33.36768	-0.154
H	28.47235	12.85534	33.12344	0.195
C	30.46299	12.05838	33.37091	0.242
C	31.80719	12.28033	33.68201	-0.166
H	32.51234	11.45195	33.69206	0.189
C	41.11845	29.36596	33.67388	0.249
C	39.95607	29.20443	32.91935	-0.175
H	39.65198	29.96697	32.20329	0.211
C	39.21787	28.0234	33.09314	-0.173
H	38.30926	27.85799	32.51309	0.195
C	39.64862	27.05797	34.02087	-0.277
C	40.83143	27.23485	34.75348	-0.165
H	41.16136	26.47829	35.46639	0.187
C	41.57842	28.411	34.58272	-0.148
H	42.49438	28.58585	35.14359	0.185
C	29.36118	12.84738	39.80604	-0.162
H	28.78534	12.42475	40.6278	0.214
C	29.68178	12.06401	38.6964	0.246
C	30.41712	12.54671	37.61245	-0.168
H	30.64677	11.89951	36.7665	0.199
C	30.86135	13.87776	37.65297	-0.190
H	31.44061	14.28429	36.82318	0.202
C	30.55028	14.68679	38.75678	-0.288
C	29.8072	14.18047	39.83341	-0.177
H	29.56063	14.81377	40.68508	0.197
C	40.87193	30.10638	38.42092	-0.149
H	41.72059	30.69382	38.7672	0.192
C	39.80364	30.73466	37.77883	0.247
C	38.68684	30.03593	37.31534	-0.183
H	37.86813	30.56531	36.82796	0.213
C	38.63958	28.64723	37.4982	-0.166
H	37.78275	28.07267	37.14258	0.163
C	39.70624	27.99181	38.13278	-0.248
C	40.81807	28.71324	38.59733	-0.165
H	41.64779	28.19958	39.08456	0.170
C	27.87681	22.53812	43.64614	-0.289
C	26.48659	22.62653	43.46682	-0.152
H	26.06508	22.71688	42.46353	0.168
C	25.63518	22.61015	44.58269	-0.160
H	24.55503	22.68658	44.47328	0.187
C	26.204	22.49927	45.85191	0.247
C	27.58139	22.41944	46.05582	-0.156
H	27.98628	22.36256	47.06527	0.193
C	28.42521	22.43479	44.93466	-0.185
H	29.50483	22.37188	45.06857	0.209
C	34.66534	12.43204	30.33616	-0.582

H	34.15634	12.84448	29.45062	0.248
H	33.89443	12.11082	31.05349	0.235
H	35.25965	11.55692	30.03349	0.226
C	25.65429	23.41087	37.70681	-0.261
C	24.77051	24.45774	37.39417	-0.139
H	24.90016	25.43782	37.85335	0.166
C	23.70557	24.23408	36.50908	-0.155
H	23.00117	25.02159	36.24608	0.186
C	23.56662	22.96123	35.9571	0.252
C	24.43359	21.90659	36.24466	-0.154
H	24.30365	20.9424	35.75582	0.197
C	25.4957	22.13808	37.13519	-0.168
H	26.19369	21.33351	37.37732	0.169

Table S3. The comparison of catalytic activity of the different catalysts.



1 2 3a

Entry	Catalysts	TON[a]
1	$Au_{41}Cu_{33}$	30593
2[b]	$Cu(MeCN)_4BF_4$	1167
3[b]	C_6H_4FSAu	0
4[c]	$[Au_9Cu_2(PPh_3)_8Cl_2]BF_4$	18000
5[c]	$AuCu_{24}H_{22}(C_{18}H_{11}F_3P)_{12}$	21788

[a] Reaction conditions: catalysts (0.00219 mol%), **1** (1.8 mmol, 1.2 equiv), **2** (1.2 mmol, 1 equiv), MS 4Å (20 mg), in CH_3CN (1.2 mL), stirred at 85 °C for 24 h. The yield of **3a** was determined by ^{19}F NMR. [b] XC-72 was added to the reaction to keep the same catalysis conditions. [c] The clusters were supported on XC-72 before catalysis.

Table S4. The adsorption results of C_6H_5-I and C_6H_5-OH at uncoordinated copper sites (in normal font) and other Cu sites (in italic).

	Adsorption energy (in eV)	C-I/O-H bond length (in Å)	Charge transfer (in |e|)
C_6H_5-I	1.89	2.74	0.173
	1.67	*2.59*	*0.137*
C_6H_5-OH	0.67	1.37	0.158

	0.18	*1.28*	*0.112*

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