Supporting Information

Gold Nanosystem Catalyzed Precise Bromination of Aromatic Feedstock Enabled by Global-Vertexes Stabilization

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1. General information

1.1 Materials and Methods

All reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques unless otherwise noted. Diethyl ether (Et_2O) was freshly distilled from sodium benzophenone ketyl and stored with molecular sieves 3Å prior to use. Tetrahydrofuran (THF) and toluene (Tol) were purchased as dehydrated solvents and used as received.

1-methyl-*o*-carbroane[1], 1-methyl-*m*-carbroane[2], 1,1'-*o*-biscarborane[3], 9,12-diiodo-*o*-carbroane[4], and 9,12-dimethyl-*o*-carborane[5], $AuCl(SMe_2)$[6], PPh_3@AuNPs[6], P(*p*-Tol)$_3$@AuNPs[6], $Au(PPh_3)NO_3$[7], complex-2[8], and $Au_8(PPh_3)_8(NO_3)_2$[9] were prepared according to literature methods.

All other chemicals were purchased from Aladdin (Shanghai, China), Macklin (Shanghai, China), Bide Pharmatech (Shanghai, China) and Sinopharm Chemical Reagent Co. (Beijing, China), and used as received. Column chromatograph was performed on silica gel 300~400 mesh.

1.2 Characterization techniques

1.2.1 HAADF-STEM Images

The high angle annular dark field (HAADF) images and electron energy loss spectroscopy (EELS) spectrum were acquired on an aberration corrected transmission electron microscope (Thermo Scientific Spectra 300) equipped with Gatan Imaging Filter (GIF 1065, Dual EELS mode) under scanning transmission electron microscopy (STEM) mode at 300kV.

1.2.2 Transmission Electron Microscopy (TEM) Images

A Tecnai G2 F20 U-TWIN transmission electron microscope (TEM) was used to observe the characteristics of AuNPs. All TEM imaging was conducted at 200 kV. The particle size distributions of AuNPs were analyzed using Image J. A few drops of the nanoparticle solution were dispensed onto a carbon-coated 300 mesh copper TEM grid. Excess solvent was wicked off with filter paper, and the samples were allowed to dry under ambient conditions.

1.2.3 The X-ray photoelectron spectroscopy (XPS) Characterizations

The X-ray photoelectron spectroscopy (XPS) was measured on Thermo Fisher ESCALAB250Xi. The samples were prepared by sprinkling the AuNPs powder onto the surface of double-sided adhesive carbon tape or pressed into a tablet. The dried samples were put on the sample holder and kept under a high vacuum overnight inside the preparation room. XPS data were collected using monochromatized Al Kα source and the spectra were processed using the Advantage software. The binding energy of all spectra was calibrated using the C(1s) carbon peak (284.8 eV).

1.2.4 Nuclear magnetic resonance (NMR) Characterizations

^{1}H NMR, ^{13}C NMR ,^{31}P and ^{19}F NMR spectra were recorded on a Bruker AVANCE III HD400 spectrometer at 400 MHz, 100 MHz, 162 MHz and 376MHz, respectively. ^{11}B NMR was recorded on a Bruker Ascend TM 400 spectrometer at 128 MHz. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. All NMR data were processed on MestReNova software. The characters used in the NMR report are as follows: s = singlet, d = doublet, t = triplet, and m = multiplet.

1.2.5 Ultraviolet visible (UV/vis) Characterizations

UV-vis spectra were obtained with PerkinElmer 950 UV/VIS/NIR spectrometer using a quartz cuvette of 1mm path length, and reported as wavelength (nm). The spectra were recorded in diluted solutions of samples and the signal of the blank solvent was subtracted.

1.2.6 Infrared (IR) spectra characterizations

IR spectra were recorded from 4000 to 400 cm^{-1} on PerkinElmer Spotlight 200i spectrophotometer using Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) mode, and reported as wavenumber (cm^{-1}). The samples were prepared as KBr pellets.

1.2.7 X-ray single-crystal diffraction Characterizations

The diffraction data of the single crystals of CB-complex-**2** was collected on a Bruker D8 Venture using Cu Kα (λ = 1.54178 Å) at 273 K. The diffraction data of the single crystals of $Au_8(PPh_3)_8(C_6B_{20}H_{26}Au)_2$ were collected on Bruker D8 Venture with Ga Kα radiation (λ = 1.34139 Å). The structures were solved and refined with the Bruker Shelxtl software package using Least Squares minimization. Detailed crystal data and structure refinements for the two compounds were given in **Table S2 and Table S3**.

1.2.8 Electrospray ionization mass spectra (ESI-MS) Characterizations

ESI-MS analyses were recorded using a Thermo Fisher Q-Exactive mass spectrometer. The solutions of Au NPs were prepared by dissolving in ethanol for ESI-MS measurement. Typical parameters used for the measurements were as follows: spray voltage: 2.5 kV; capillary voltage: 30 V; capillary temperature: 180°C; heater temp: 30 ºC.; ion source sheath gas 25; auxiliary gas argon and aux gas 10.

1.2.9. Collision induced dissociation mass spectra (CID-MS) Characterizations

The CID-MS spectra were acquired using a Bruker Solarix mass spectrometer. Solutions of Au NPs were prepared by dissolving in MeCN/HFIP for CID-MS measurement. The precursor ions generated by ESI (flow rate = 2 μL/min) were mass-selected in the front-end quadrupole, and then CID was performed in the quadrupole collision cell using argon as the collision gas. Variable collision energies were obtained by application of the corresponding DC voltage. The other parameters used for the measurements were as follows: capillary voltage 4 kV; end plate offset: -500 V. flow rate: 2 μL/min; dry gas: 1L/min; source temperature: 200 °C.

1.2.10 X-ray absorption fine structure (XAFS) characterizations

X-ray absorption spectra at the Au L_3-edge were collected at beamline BL14W1 of the SSRF with transmission mode. The measurements were performed at 18 K using a cryostat (ARS). The excitation energies (scan range 11719-12719 eV) were selected by a Si (111) double-crystal monochromator.

1.2.11 Other Characterizations

GC-MS analyses were performed on Shimadzu GCMS-QP2020NX or GCMS-QP2010SE. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on Thermo IRIS Series 2. The steady-state photoluminescence (PL) spectroscopy tests were performed using a Hitachi F-7000 fluorescence spectrophotometer.

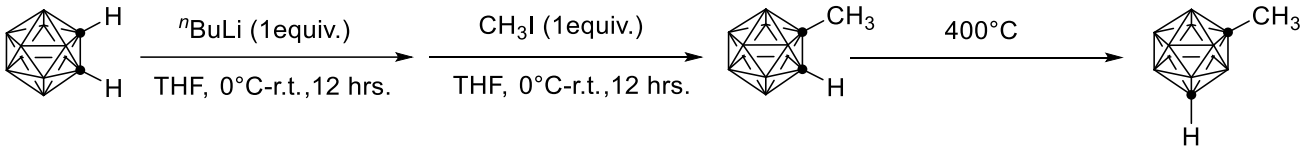
1.3 Stability tests

The thermal stability of Au NPs was performed by tracking UV-vis spectra during heating. Au NP in butanol was placed in an oven-dried 10 mL Schlenk flask equipped with a PTFE stirring bar, then sealed up and heated in oil bath at a specific temperature. After a given time, the samples were allowed to return to room temperature and transferred to cuvettes quickly. The samples were characterized by UV-vis spectroscopy. The thiol stability of Au NPs was examined against 1-dodecanethiol (DDT) and thiophenol (PhSH) using butanol as solvent. The acid/base stability of Au NPs was examined using HCl and NaOH to adjust the *p*H of solution.

2. Synthetic methods

2.1 Synthesis of 1-Methyl-*m*-Carborane

According to the literature procedure,[1] ^{n}BuLi (3 mL, 7.5 mmol, 2.5 M in hexane) was slowly added to a THF solution (40 mL) of *o*-carborane (1.08 g, 7.5 mmol) at 0 ºC, and the mixture was stirred at room temperature for 1 h. CH_3I (0.48 mL, 7.5 mmol) was added dropwise to the above suspension at 0 ºC, and the reaction mixture was stirred at room temperature for 12 h in a closed flask. Then, the reaction was quenched with water (5mL) and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was removed by rotary evaporation. The crude product was purified by chromatography on silica gel using *n*-hexane as eluent to afford 1-methyl-*o*-carborane as white solids (474 mg, 40%). The Ampoule bottle was charged with 1-methyl-*o*-carborane (314 mg, 2.0 mmol). The reactor was sealed under evacuation and heated for 72 h at 400 ºC. After cooling to room temperature, the reactor was opened. GC-MS indicated a conversion of 40%. The crude product was purified by flash column chromatography on silica gel using *n*-hexane as eluent to provide 1-methyl-*m*-carborane as white solids (94 mg, 30%). Characterization data are identical with those reported in the literature.[2]



Scheme S1. Synthesis of 1-Methyl-*m*-Carborane.

2.2 Synthesis of CB@AuNPs

CB@AuNP-1

To 3 mL Et_2O of *o*-carborane (0.1 mmol, 14.4 mg), 0.08 mL ^{n}BuLi (2.5 M in hexanes) was added at 0 ºC. The reaction mixtures were stirred at room temperature for 1 h. $AuCl(SMe_2)$ (0.2 mmol, 58 mg) was then added. After 2 hrs' stirring, AuNPs precipitated out sticking to the flask. The clear solvent was then decanted. The resulting mixtures were centrifuged (12633g, 4mins) and washed with toluene and dichloromethane separately for 3 times to obtain AuNPs.

CB@AuNP-1-SbF_6

To 3 mL CH_3OH of CB@AuNP-**1** (20 mg), $NaSbF_6$ (0.05mmol, 13 mg) was added under vigorous stirring. The reaction mixtures were stirred at room temperature in air for 15 minutes. The resulting mixtures were concentrated to dryness in vacuo, and washed with water for 3 times. The obtained product was dried at 60 ºC in a vacuum oven for 12 h.

CB@AuNP-2

To 3 mL Et_2O: Tol (1:2) of 1,1'-bis(*o*-carborane) (0.1 mmol, 28.6 mg), 0.08 mL ^{n}BuLi (2.5 M in hexanes) was added at 0 ºC. The reaction mixtures were stirred at room temperature for 1 h. $AuCl(SMe_2)$ (0.2 mmol, 58 mg) was then added. After 2 hrs' stirring, AuNPs precipitated out sticking to the flask. The clear solvent was then decanted. The resulting mixtures were centrifuged (12633g, 4mins) and washed with toluene and dichloromethane separately for 3 times to obtain AuNPs.

CB@AuNP-3

To 3 mL Et_2O: Tol (1:2) of 1-methyl-*m*-carborane (0.1 mmol, 15.7 mg), 0.04 mL ^{n}BuLi (2.5 M

in hexanes) was added at 0 ºC. The reaction mixtures were stirred at room temperature for 1 h. AuCl(SMe_2) (0.1 mmol, 29 mg) was then added. After 2 hrs' stirring, the reaction mixtures were centrifuged (12633g, 4mins) and washed with a mixture of hexane and dichloromethane for 5 times to obtain AuNPs.

CB@AuNP-4

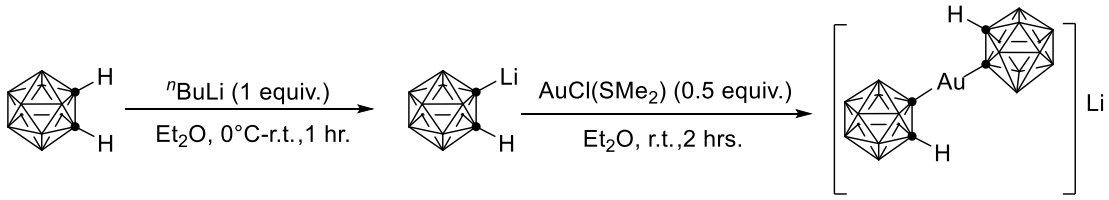
To 3 mL Et_2O:Tol (1:2) of 9,12-diiodo-*o*-carborane (0.1 mmol, 39.6 mg), 0.08 mL ^{n}BuLi (2.5 M in hexanes) was added at 0 ºC. The reaction mixtures were stirred at room temperature for 1 h. AuCl(SMe_2) (0.2 mmol, 58 mg) was then added. After 2 hrs' stirring, AuNPs precipitated out sticking to the flask. The clear solvent was then decanted. The resulting mixtures were centrifuged (12633g, 4mins) and washed with toluene and dichloromethane separately for 3 times to obtain AuNPs.

CB@AuNP-5

To 3 mL Et_2O : Tol (1:2) of 9,12-dimethyl-(*o*-carborane) (0.1 mmol, 17.2 mg), 0.08 mL ^{n}BuLi (2.5 M in hexanes) was added at 0 ºC. The reaction mixtures were stirred at room temperature for 1 h. AuCl(SMe_2) (0.2 mmol, 58 mg) was then added. After 2 hrs' stirring, the resulting mixtures were centrifuged (12633g, 4mins) and washed with toluene and dichloromethane separately for 3 times to obtain Au NPs.

2.3 Synthesis of CB-Complex-1

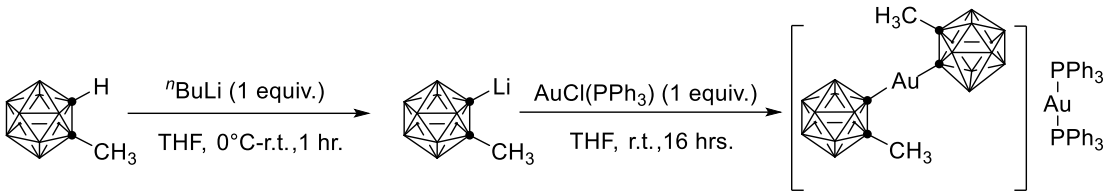
To 3 mL Et_2O of *o*-carborane (0.1 mmol, 14.4 mg), 0.04 mL ^{n}BuLi (2.5 M in hexane) was added at 0 ºC. The mixture was stirred at room temperature for 1 h. AuCl(SMe_2) (0.05 mmol, 14.5mg) was then added. After 2 hrs' stirring, the resulting mixtures were centrifuged (12633g, 4mins). The solids at the bottom of the centrifuge tube were dissolved in CH_2Cl_2 (10 mL). The resulting mixtures were filtered, and the filtrate was collected and concentrated to dryness in vacuo to afford CB-complex-**1** as white floccules.



Scheme S2. Synthesis of CB-Complex-**1**.

2.4 Synthesis of CB-Complex-2

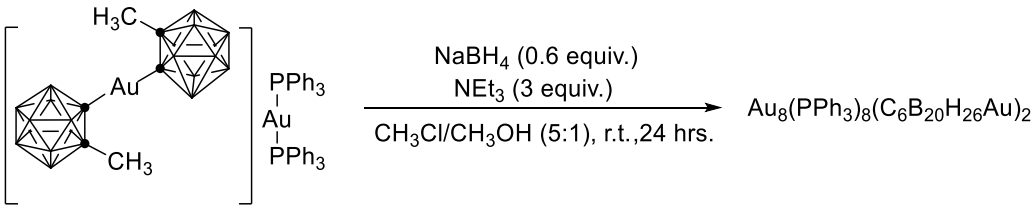
To 10 mL THF of 1-methyl-*o*-carborane (0.4 mmol, 63.2 mg), 0.16 mL ^{n}BuLi (2.5 M in hexane) was added at 0 ºC. The reaction mixtures were stirred at room temperature for 1 h. AuCl(PPh_3) (0.4 mmol, 199mg) was then added. After stirring at room temperature for an additional 16 h, the solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 (10 mL). The solution was filtered to remove lithium chloride and was concentrated in vacuum. The crude product was purified by chromatography on silica gel (hexane / CH_2Cl_2 = 1:1) to afford CB-complex-**2** as white solids (148 mg, 30%).1H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 6H) (CH_3 *H*). 7.60-7.40 (m, 30H) (Ph *H*).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$):δ 134.29 (d, *J*=13.7 Hz), 132.04 (d, *J*=2 Hz), 129.55 (d, *J*=11.3 Hz), 128.96 (s) (Ph *C*), 30.06 (s), δ 27.06 (s) (CH_3 *C*). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.25 (4B), -7.59 (6B), -9.37 (10B). $^{31}P\{^1H\}$-NMR (162 MHz, $CDCl_3$): δ 38.50 (s).



Scheme S3. Synthesis of CB-Complex-**2**.

2.5 Synthesis of $Au_8(PPh_3)_8(C_6B_{20}H_{26}Au)_2$ cluster

The synthetic reaction was taken under ambient conditions at ~25 ºC. CB-complex-**2** (0.025 mmol, 30.8 mg) was dissolved in a mixed solution of chloroform (2.5 mL) and methanol (0.5 mL), and a freshly prepared ethanol solution of $NaBH_4$ (0.56 mg/mL, 1 mL) was dropwise added to the suspension within 1 minutes under stirring. The solution changed from light yellow to clear reddish brown. The mixture was stirred for 5 min, and NEt_3 (10 μL) was then added. After stirring at room temperature for an additional 24 h, the solvent was removed in vacuo. The crude product was purified by chromatography on silica gel (hexane / CH_2Cl_2 = 1:2) to afford $Au_8(PPh_3)_8(C_6B_{20}H_{26}Au)_2$ cluster as brown-red solids. The solids were dissolved in a mixed solution of CH_2Cl_2 (1 mL) and EtOH (1 mL) in a closed vial and placed in the refrigerator at ~-2 °C. Over 3−5 days, crystals of $Au_8(PPh_3)_8(C_6B_{20}H_{26}Au)_2$ cluster formed (3.0 mg, yield 20%, based on Au). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -3.21 (8B), -8.33 (18B), -9.67(14 B). $^{31}P\{^1H\}$-NMR (162 MHz, $CDCl_3$): δ 38.35 (s), 31.75 (s)



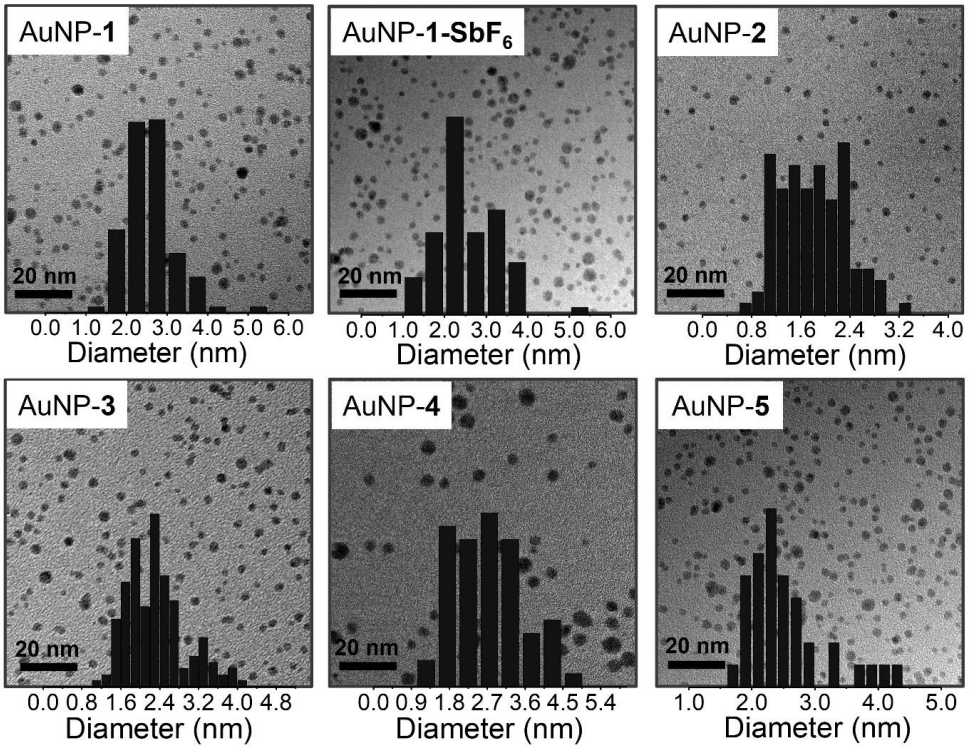
Scheme S4. Synthesis of $Au_8(PPh_3)_8(C_6B_{20}H_{26}Au)_2$ cluster.

3. Characterization of AuNPs

3.1 Transmission Electron Microscopy (TEM)

Table S1. Diameters of AuNPs determined by TEM.

CB@AuNPs	Diameters(nm)
AuNP-**1**	2.52±0.67
AuNP-**1**-SbF_6	2.51±0.75
AuNP-**2**	1.78±0.55
AuNP-**3**	2.31±0.61
AuNP-**4**	2.73±0.84
AuNP-**5**	2.54±0.67



3.2 IR Spectra of Carboranes and Corresponding AuNPs

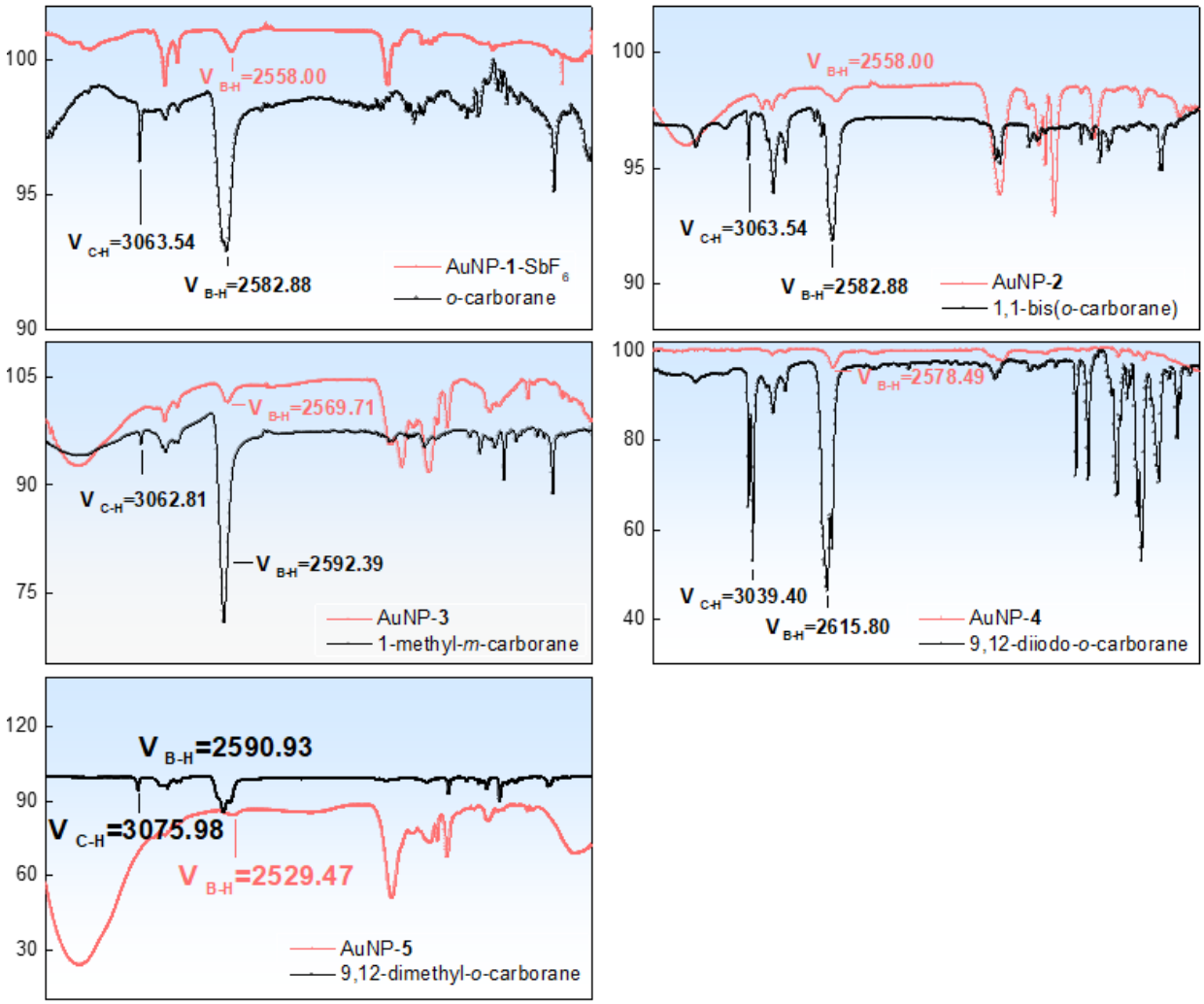
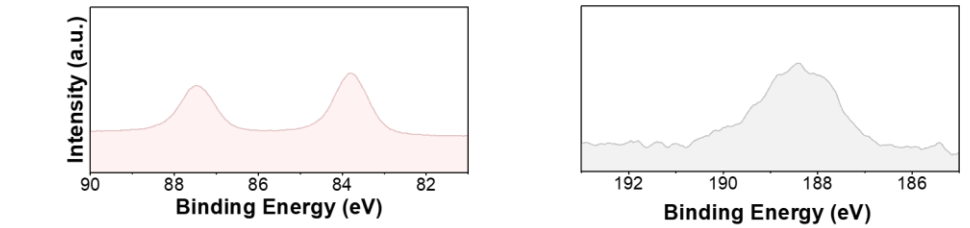
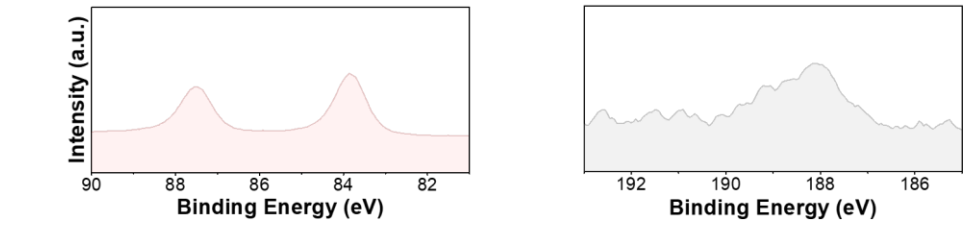


Figure S1. The IR-Spera of CB and the corresponding AuNPs. The shifts of B-Hs are indicative of the electron-donating property of carboranyl ligands. (x axis: wavenumbers range from 3600 to 500 cm^{-1}; y axis: transmittance (%))

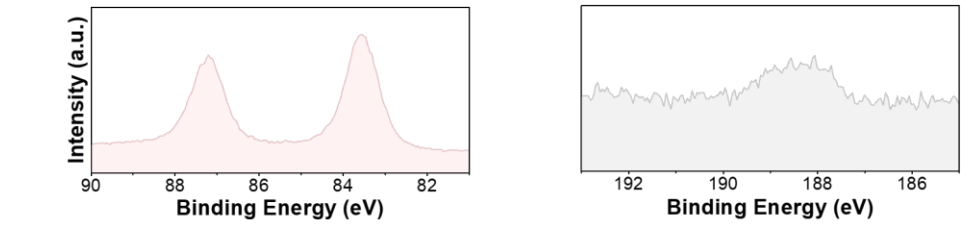
3.3 XPS Spectra of Corresponding AuNPs



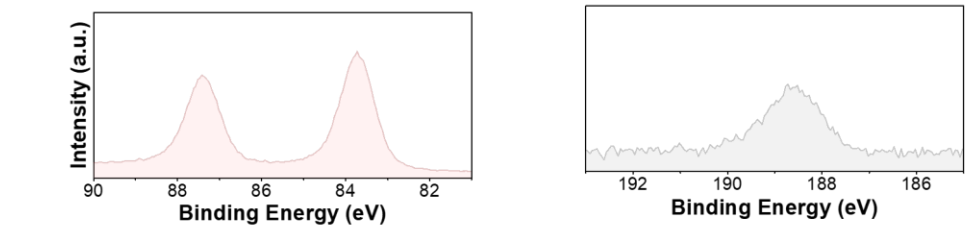
AuNP-**1** [Au(4f):B(1s) = 40.3:59.7]



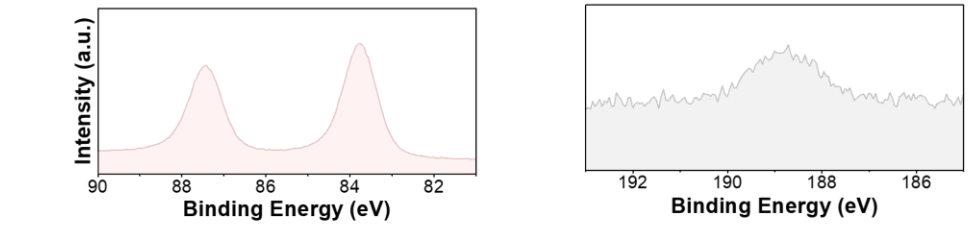
AuNP-**1**-SbF_6 [Au(4f):B(1s) = 53.1:46.9]



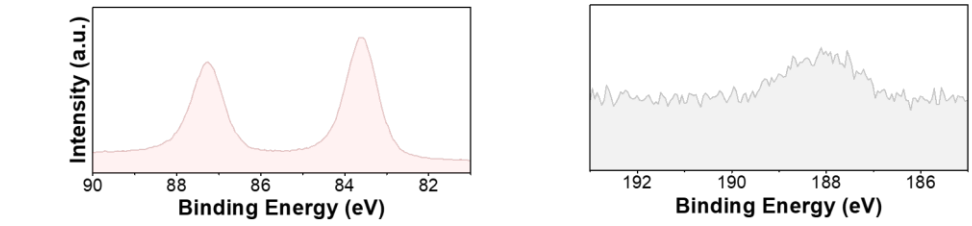
AuNP-**2** [Au(4f):B(1s) = 30.8 : 69.2]



AuNP-**3** [Au(4f):B(1s) = 37.6 : 62.4]



AuNP-**4** [Au(4f):B(1s) = 38.1:71.9]



AuNP-**5** [Au(4f):B(1s) = 49.9:50.1]

Figure S2. Binding energies of B1s and Au4f in CB@AuNPs.

3.4 ESI-MS spectra of AuNPs-2,5

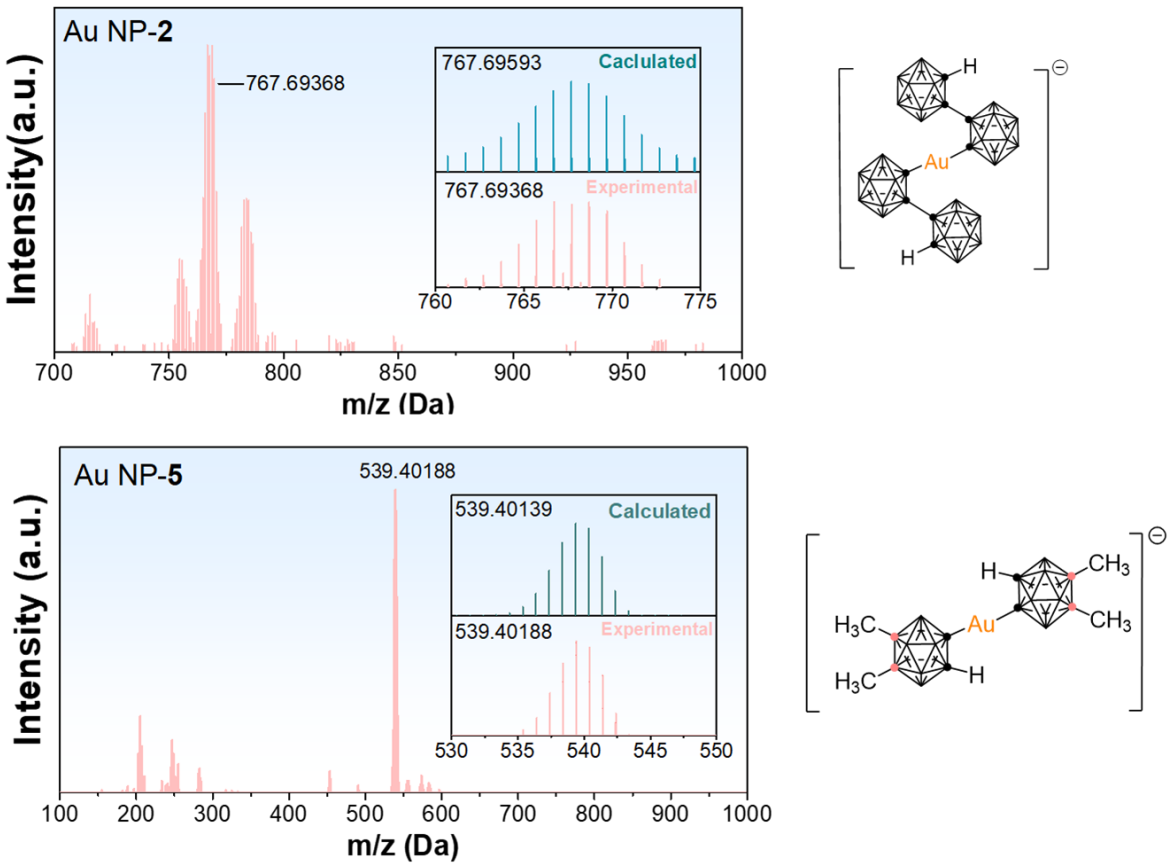


Figure S3. The ESI-MS (anion mode) data of AuNPs-**2**,**5** confirm their Au_{core}-CB_2Au^- structures. The main peaks are assigned as the corresponding CB_2Au^- anions for each AuNPs.

4. Stability studies for CB@AuNP-3 and other Ligands

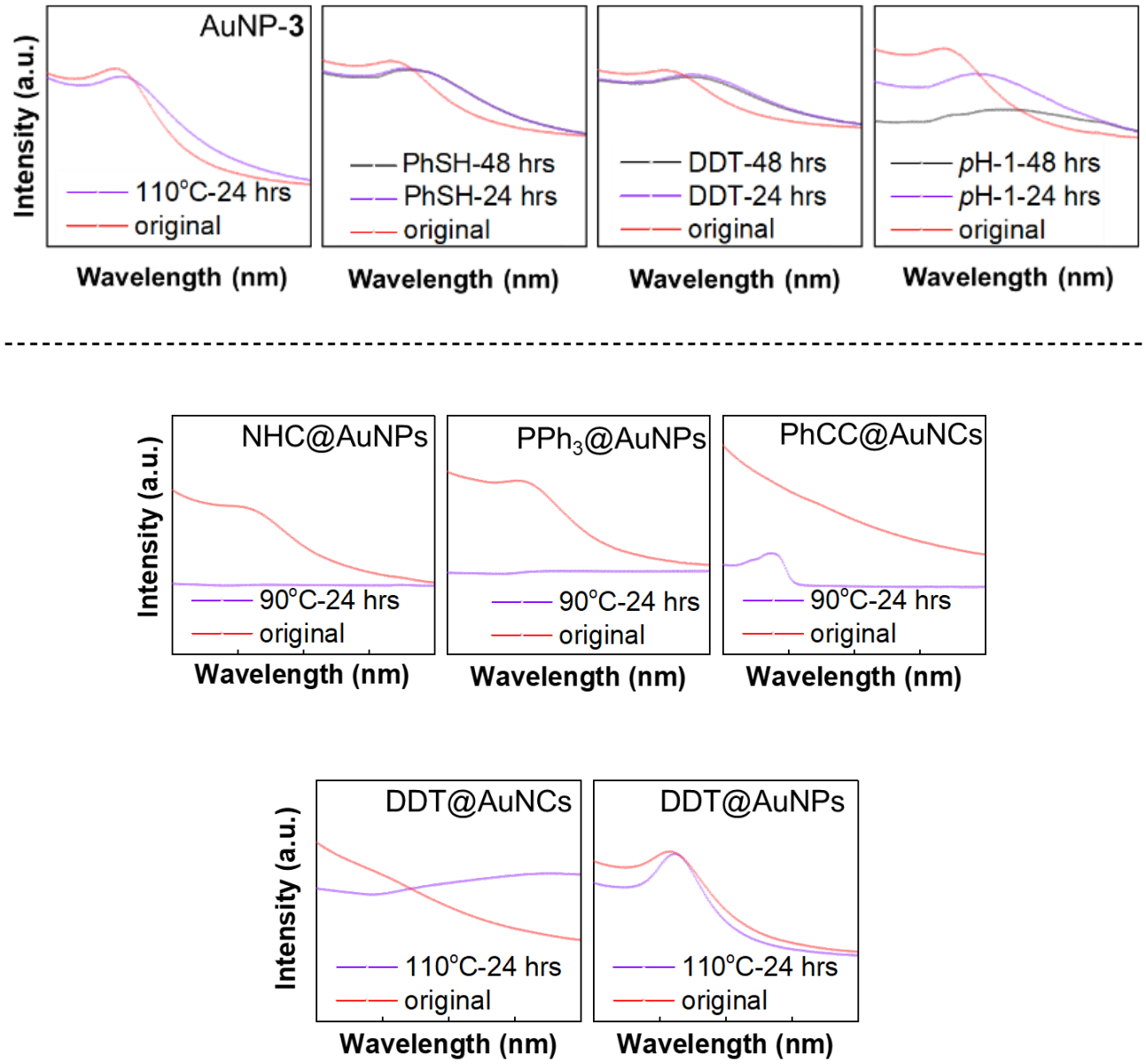
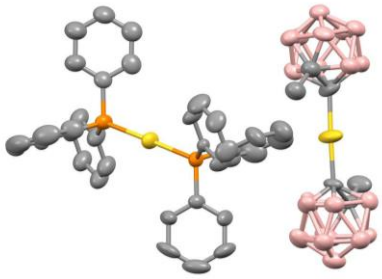


Figure S4. Stability Studies of AuNPs by UV-Vis. AuNPs are stabilized by 1-methyl-*m*-carborane, N,N'-diisopropyl benzannulated N-heterocyclic carbene (NHC), PPh_3, phenylacetylene (PhCC), and DDT. Wavelength scale ranges from 400-800 nm.

5. Characterization of CB-Complex-2 and $Au_8(PPh_3)_8(C_6B_{20}H_{26}Au)_2$

Table S2. Molecular structure of CB-Complex-2



Compd	CB-Complex-**2**
formula	$C_{42}H_{56}Au_2B_{20}P_2$
Cryst size (mm)	0.20x 0.15 x 0.04
fw	1232.94
Cryst syst	Triclinic
Space group	P-1
a, Å	8.9967(3)
b, Å	12.9072(5)
c, Å	12.9834(5)
β, deg	92.025(1)°
V, Å^3	1485.62(10)
Z	1
Dcalcd.Mg/m3	1.378
Radiation(λ), Å	1.54178
2θ range.deg	6.888 to 144.704
μ, mm-1	9.841
F(000)	596.0
No. of obsd reflns	11227
No. of params refind	527
Goodness of fit	1.054
R1	0.0412
wR2	0.1109

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 0 ALERT level A = Most likely a serious problem - resolve or explain
 0 ALERT level B = A potentially serious problem, consider carefully
17 ALERT level C = Check. Ensure it is not caused by an omission or oversight
53 ALERT level G = General information/check it is not something unexpected
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^{1}H NMR

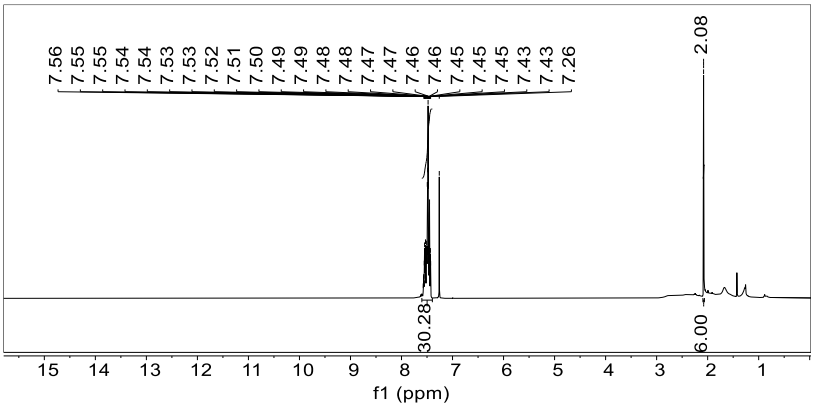


Figure S5. ^{1}H NMR spectrum of CB-Complex-**2** in $CDCl_3$.

^{13}C NMR

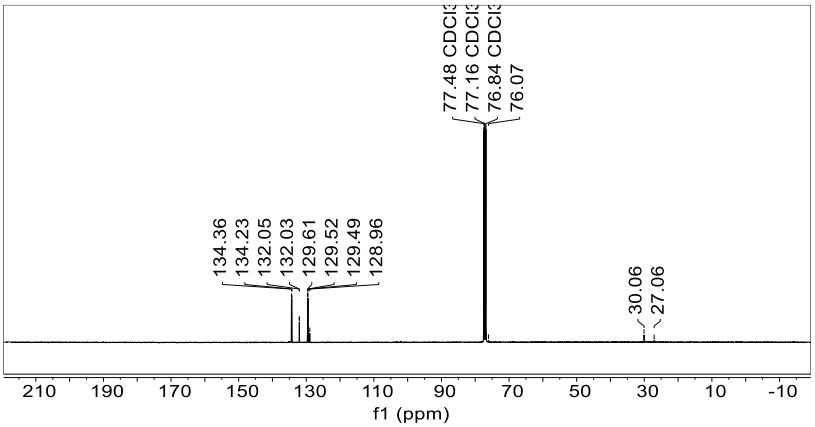


Figure S6. ^{13}C NMR spectrum of CB-Complex-**2** in $CDCl_3$.

^{11}B NMR

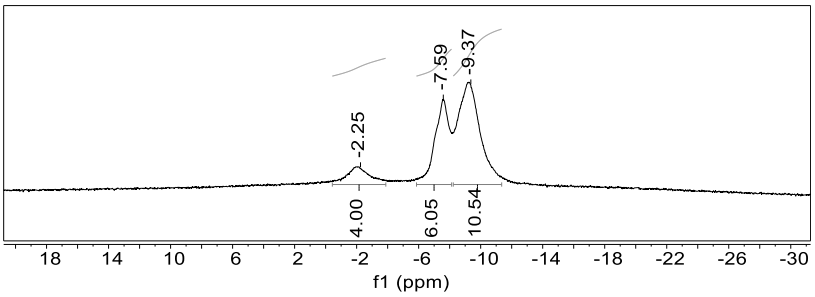


Figure S7. ^{11}B NMR spectrum of CB-Complex-**2** in $CDCl_3$.

^{31}P NMR

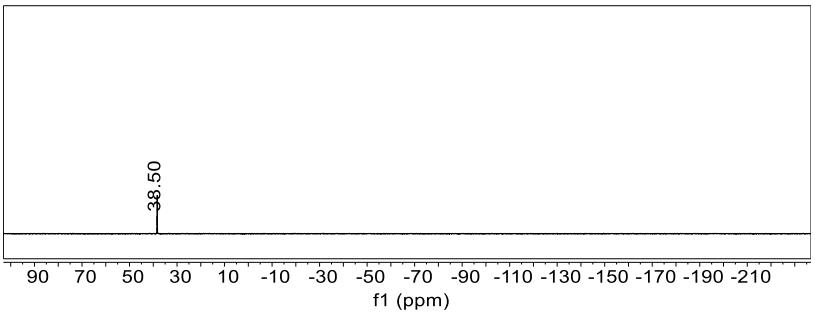
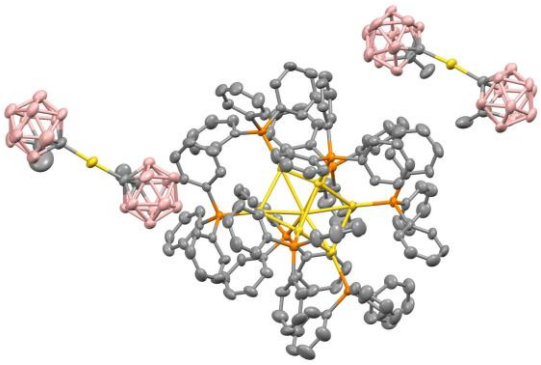


Figure S8. ^{31}P NMR spectrum of CB-Complex-**2** in $CDCl_3$.

Table S3. Molecular structure of $Au_8(PPh_3)_8(C_6B_{20}H_{26}Au)_2$



Compd	$Au_8(PPh_3)_8(C_6B_{20}H_{26}Au)_2$
formula	C_{159} H_{178} Au_{10} B_{40} Cl_6 P_8
Cryst size (mm)	0.07 x 0.07 x 0.05
fw	4951.53
Cryst syst	Triclinic
Space group	P-1
a, Å	16.6274(2)
b, Å	21.1117(3)
c, Å	27.9731(4)
β, deg	73.7920(10)°
V, $Å^3$	8740.5(2)
Z	2
Dcalcd.Mg/m3	1.881
Radiation(λ), Å	0.7508 and 0.5756
2θ range.deg	2.605 to 54.940°
μ, mm-1	11.808
F(000)	4688
No. of obsd reflns	113364
No. of params refind	33052
Goodness of fit	0.960
R1	0.0353
wR2	0.1166

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
 56 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 31 ALERT level G = General information/check it is not something unexpected
```

^{11}B NMR

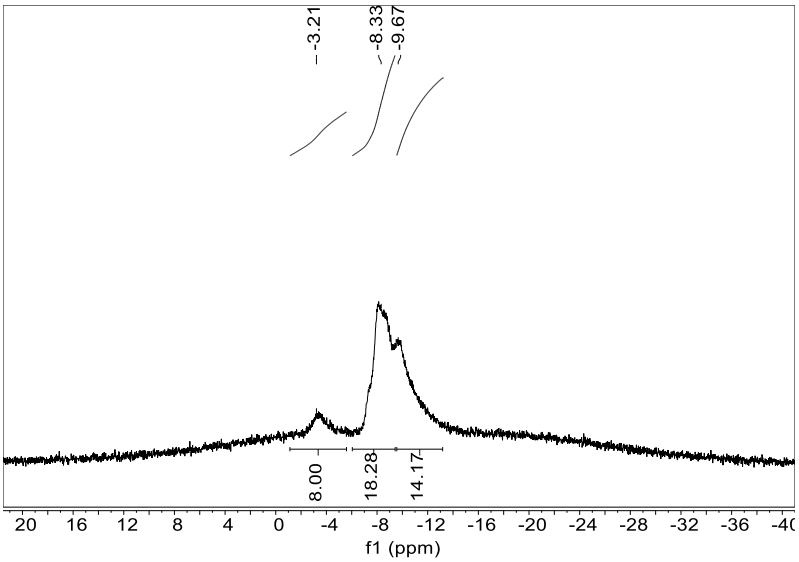


Figure S9. ^{11}B NMR spectrum of $Au_8(PPh_3)_8(C_6B_{20}H_{26}Au)_2$ in $CDCl_3$.

^{31}P NMR

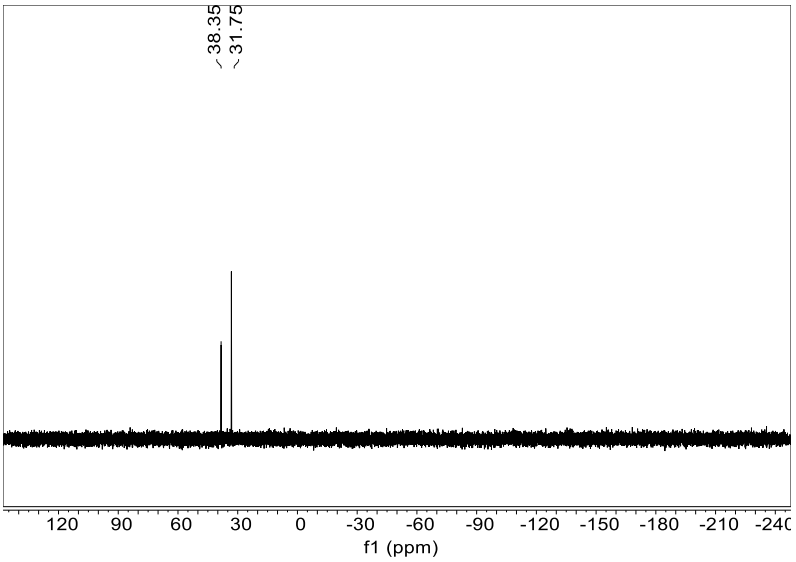


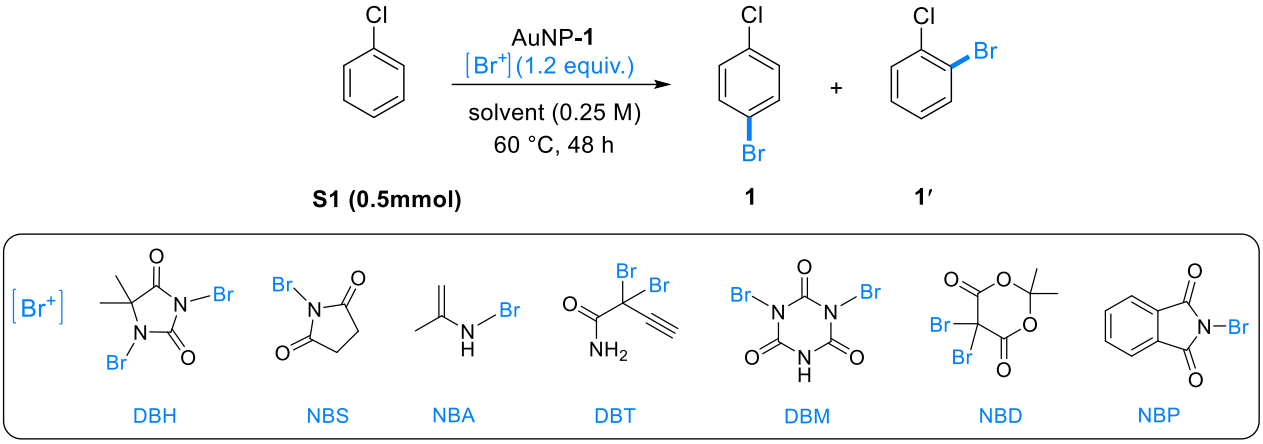
Figure S10. ^{31}P NMR spectrum of $Au_8(PPh_3)_8(C_6B_{20}H_{26}Au)_2$ in $CDCl_3$.

6. Catalytic studies

6.1 Optimization of the catalytic bromination reactions

Chlorobenzene **S1** (0.5 mmol), Au NP-**1** and [Br⁺] (0.6 mmol based on Br) were dissolved in solvent (2 mL) for 48 h at 60 °C under nitrogen. After cooling down to room temperature, the reaction mixture was analyzed by GC-MS with *n*-dodecane as the internal standard to determine the yield of product.

Table S4. Optimization of the Reaction Condition



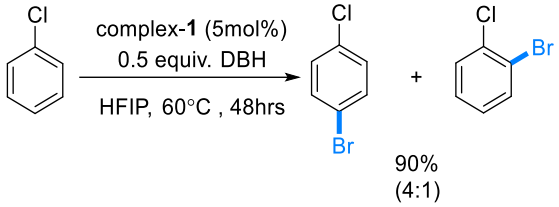
Entry	Catalyst	[Br⁺]	Solvent	T[°C]	**1**[%]	**1'**[%]
1	none	DBH	HFIP	60	trace	0%
2	Au NP-**1**(1mg)	DBH	HFIP	60	28.3	1.7
3	Au NP-**1**(3mg)	DBH	HFIP	60	47.2	2.8
4	Au NP-**1**(5mg)	DBH	HFIP	60	61.4	3.6
5	**Au NP-1(7mg)**	**DBH**	**HFIP**	**60**	**88.2**	**4.8**
6	Au NP-**1**(7mg)	DBH	TFEA	60	28.4	1.7
7	Au NP-**1**(7mg)	DBH	MeCN	60	trace	0
8	Au NP-**1**(7mg)	DBH	EtOH	60	0	0
9	Au NP-**1**(7mg)	DBH	THF	60	0	0
11	Au NP-**1**(7mg)	DBH	DCE	60	trace	0
12	Au NP-**1**(7mg)	DBH	HFIP	r.t.	19.1	1.1
13	Au NP-**1**(7mg)	NBS	HFIP	60	50.0	3.0
14	Au NP-**1**(7mg)	NBA	HFIP	60	30.5	1.8
15	Au NP-**1**(7mg)	DBT	HFIP	60	0	0
16	Au NP-**1**(7mg)	DBM	HFIP	60	0	0
17	Au NP-**1**(7mg)	DBD	HFIP	60	0	0
18	Au NP-**1**(7mg)	NBP	HFIP	60	0	0
19	Au NP-**1**(7mg)	Br_2	HFIP	60	0	0

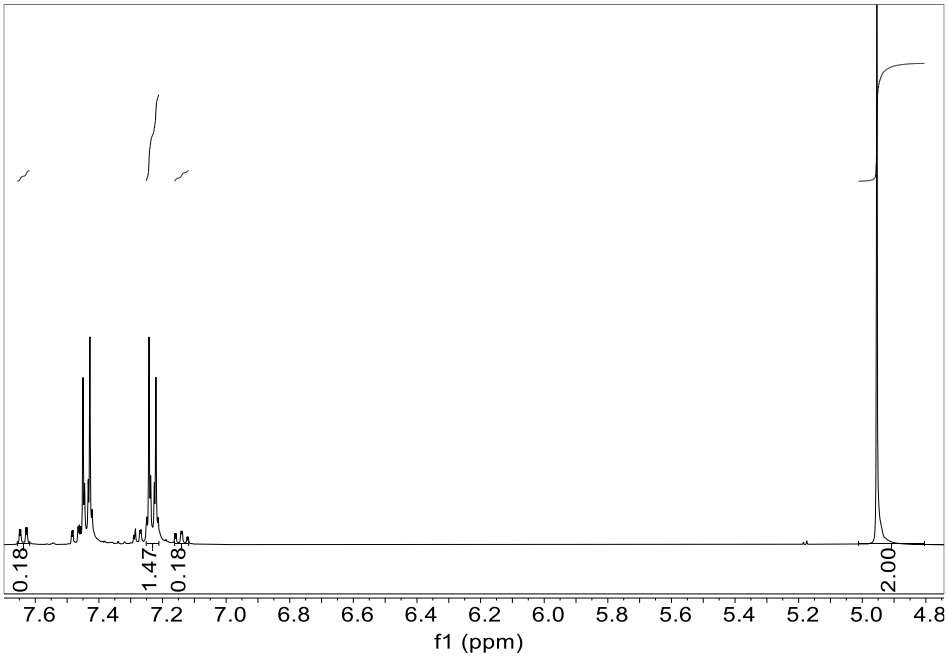
Reactions were carried out with **S1** (0.50 mmol), catalyst and [Br⁺] (0.60 mmol based on Br) in solvent (2.0 mL) for 48 h at 60 °C under nitrogen. Yields were determined by GC-MS analysis using *n*-dodecane as the internal standard. TFEA= 2,2,2-Trifluoroethanol.

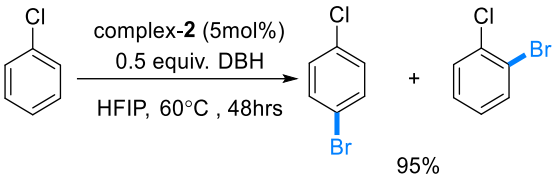
6.2 Procedure for catalyzed bromination of chlorobenzene

Standard Procedure for bromination of chlorobenzene:

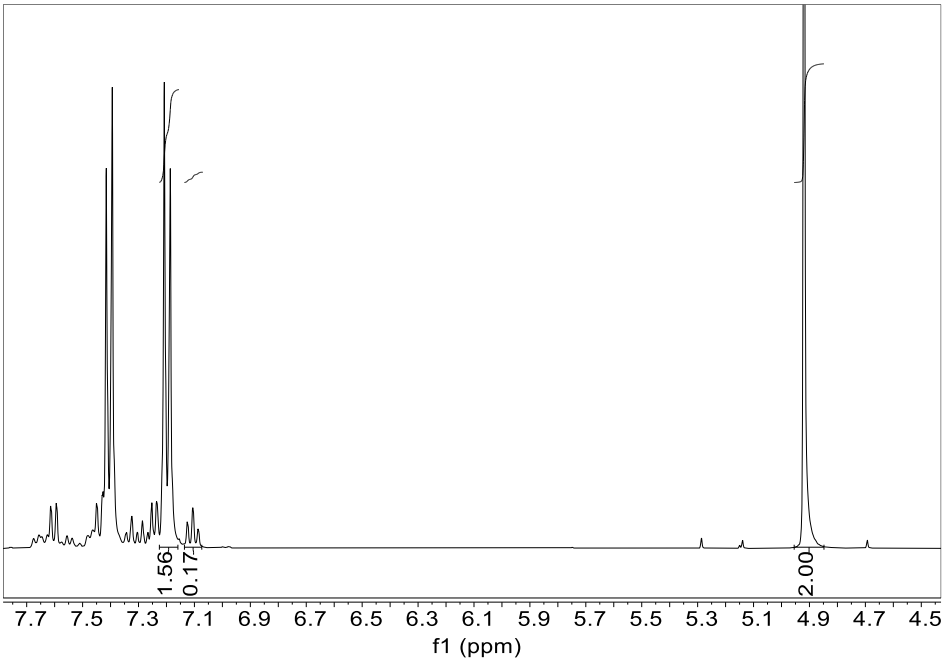
The gold catalyst and DBH (0.25 mmol) were dissolved in HFIP (2mL), then chlorobenzene (0.5 mmol) was added. The mixture was stirred at 60 °C for 48 h under nitrogen. After cooling down to room temperature, the resulting suspension was quenched with saturated $Na_2S_2O_3$ aqueous solution (3 mL) and extracted with ethyl acetate for three times (6 mL×3). The combined organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuum at -20 °C. The residue was analyzed by ^{1}H-NMR to determine the yield and regioselectivity of the product using dibromomethane as the internal standard.






Cl
complex-2 (5mol%)
0.5 equiv. DBH
HFIP, 60°C , 48hrs
Cl
Br
+
Cl
Br

95%
(4.5:1)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0.17
2.00
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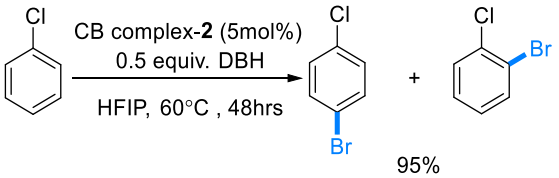
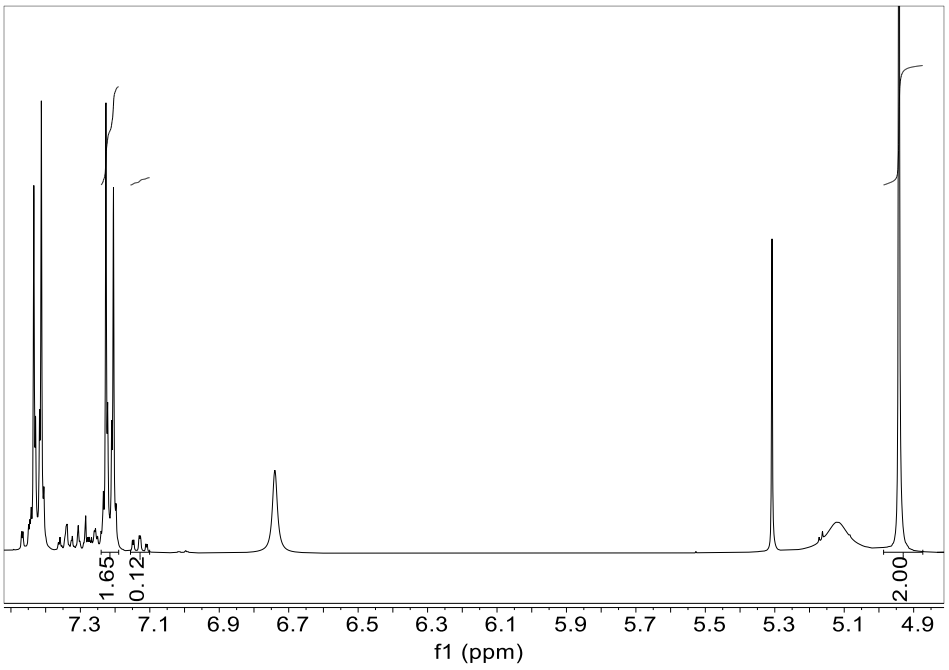
f1 (ppm)


Cl
CB complex-2 (5mol%)
0.5 equiv. DBH
HFIP, 60°C , 48hrs
Cl
Br
+
Cl
Br

95%
(6.5:1)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0.12
2.00
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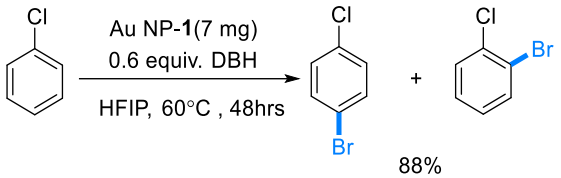
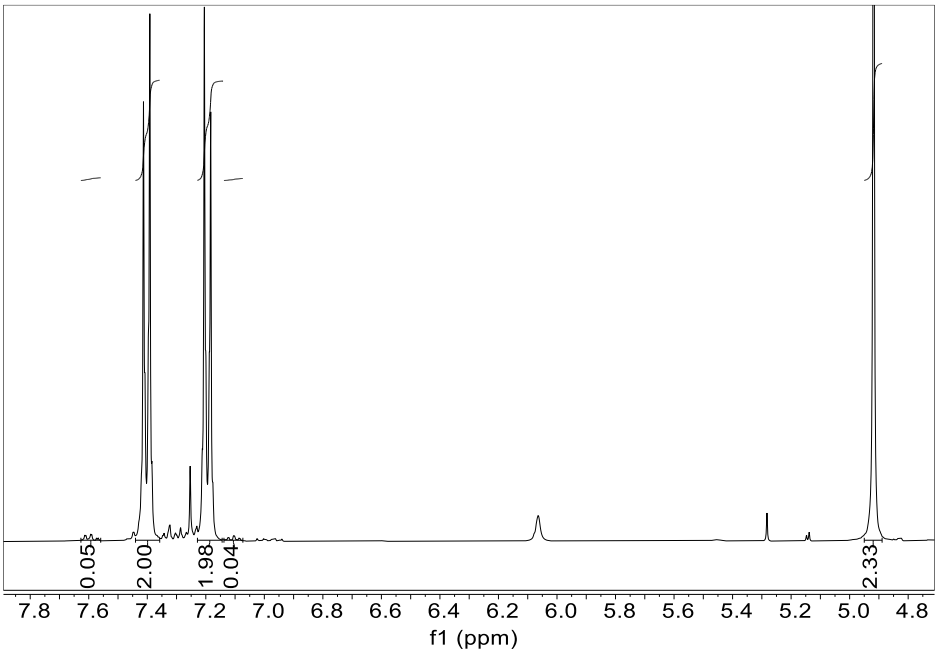
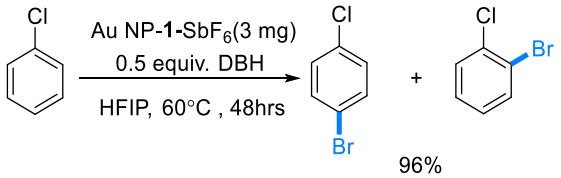
f1 (ppm)

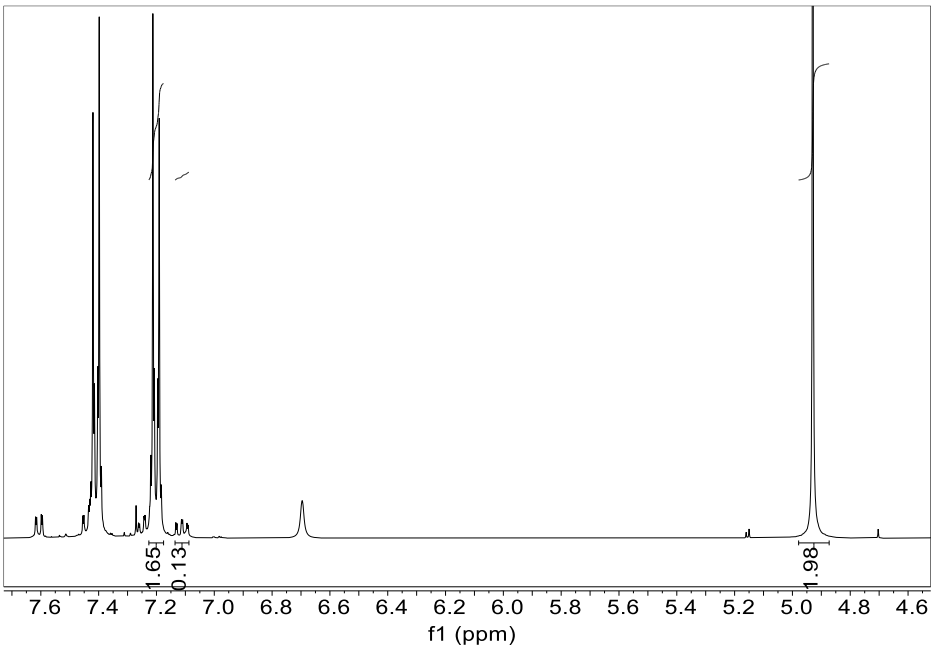

Cl
Au NP-1(7 mg)
0.6 equiv. DBH
HFIP, 60°C , 48hrs
Cl
Br
+
Cl
Br

88%
(20:1)


0.05
2.00
1.98
0.04
2.33
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8
f1 (ppm)


Cl
Au NP-1-SbF6(3 mg)
0.5 equiv. DBH
HFIP, 60°C , 48hrs
Cl
Br
+
Cl
Br

96%
(6.3:1)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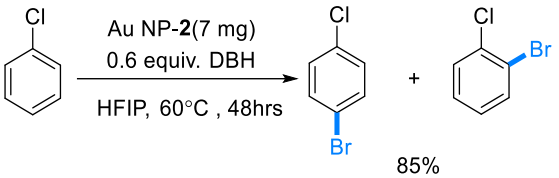
0.13
1.98
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6
f1 (ppm)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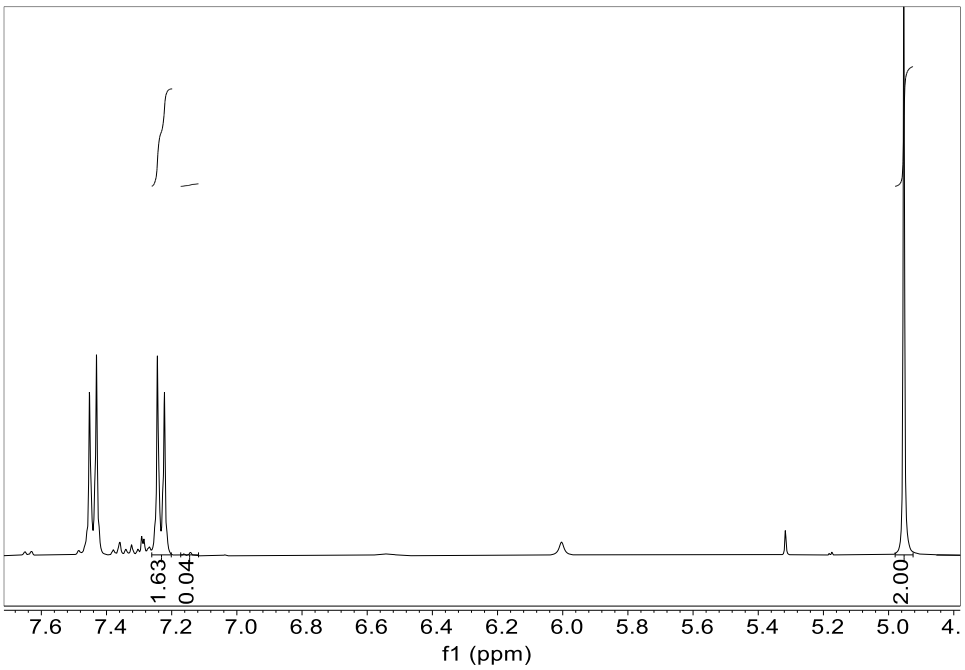
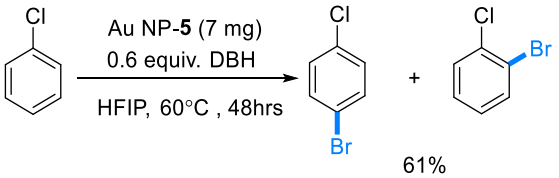
Au NP-2(7 mg)
0.6 equiv. DBH
HFIP, 60°C , 48hrs
Cl
Br
+
Cl
Br

85%
(20:1)


1.63
0.04
2.00
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
f1 (ppm)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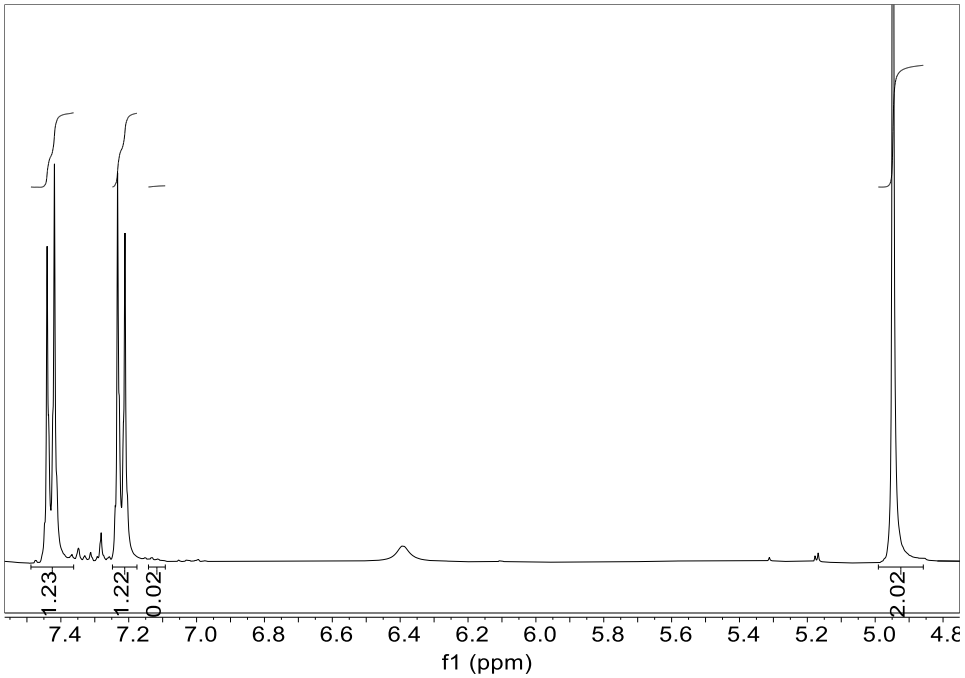
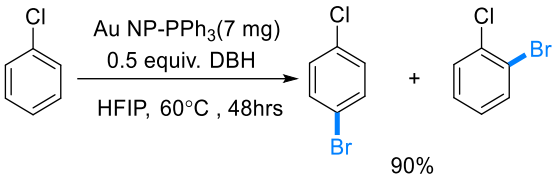
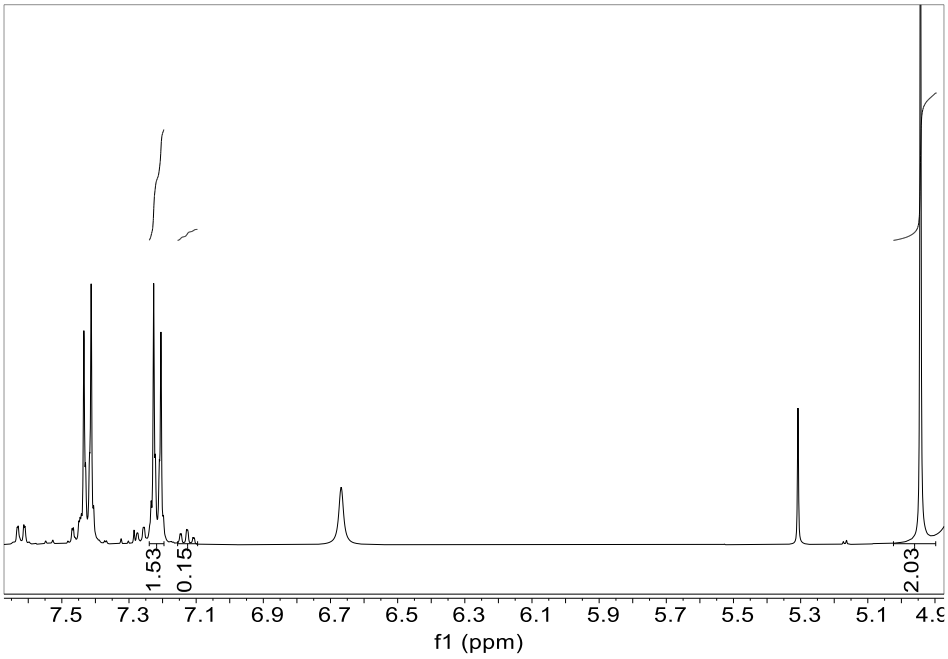
Au NP-5 (7 mg)
0.6 equiv. DBH
HFIP, 60°C , 48hrs
Cl
Br
+
Cl
Br

61%
(>30:1)


1.23
1.22
0.02
2.02
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
f1 (ppm)


Cl
Au NP-PPh3(7 mg)
0.5 equiv. DBH
HFIP, 60°C , 48hrs
Cl
Br
+
Cl
Br

90%
(5:1)


1.53
0.15
2.03
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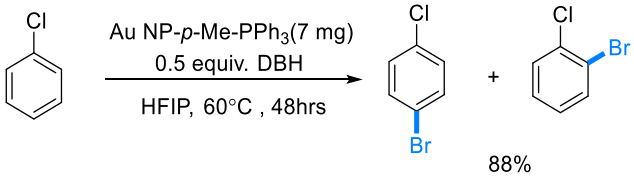
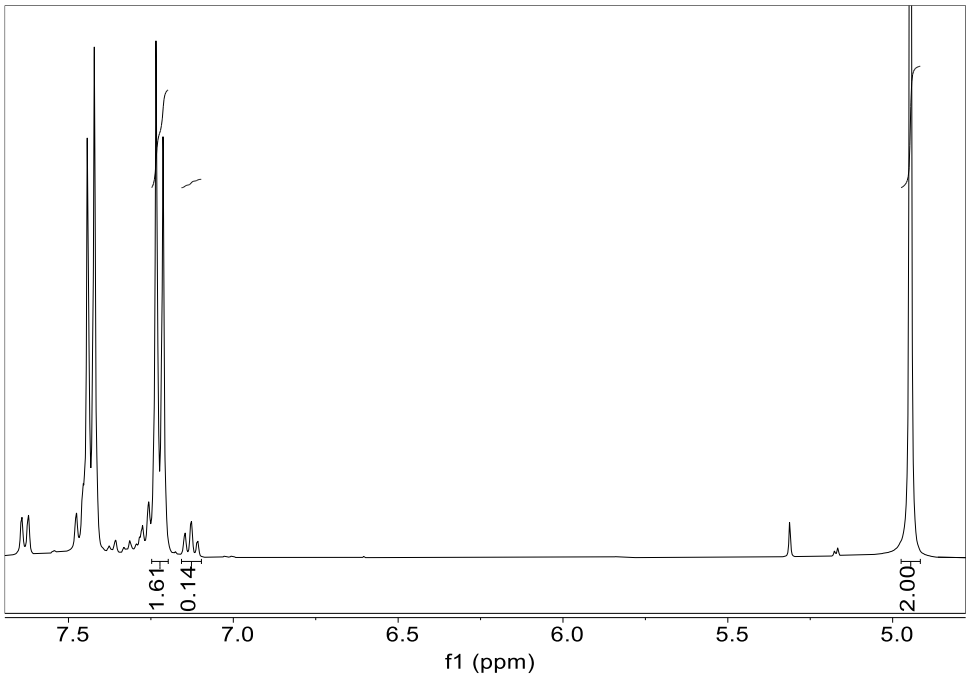
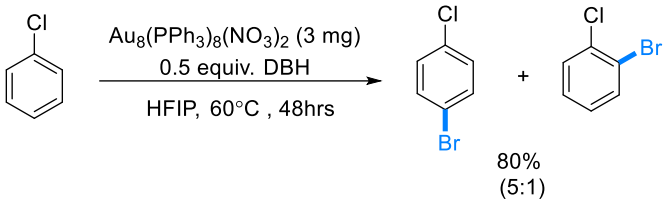
f1 (ppm)

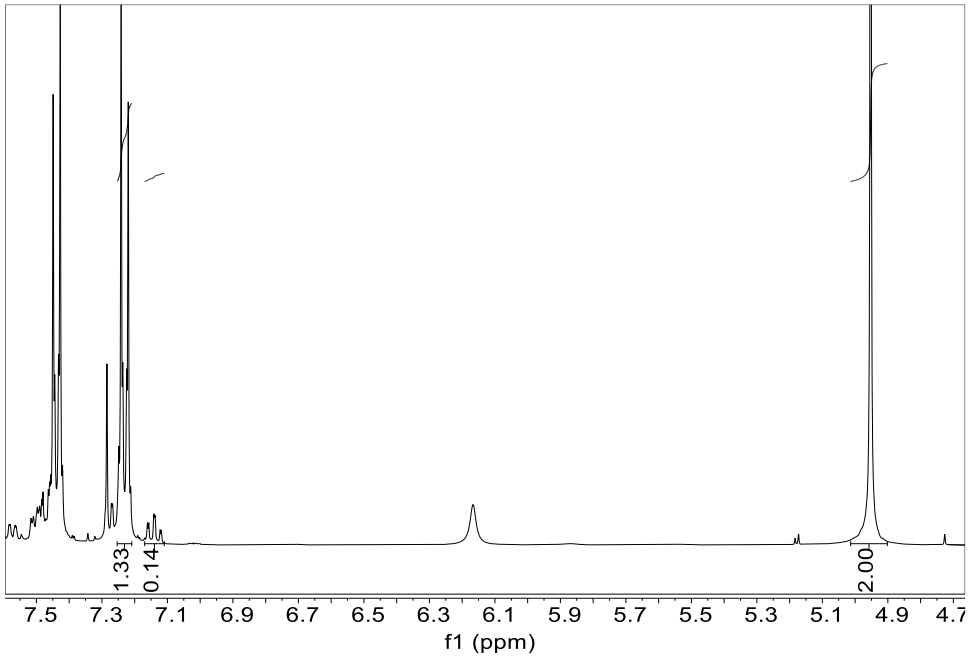

Cl
Au NP-p-Me-PPh3(7 mg)
0.5 equiv. DBH
HFIP, 60°C , 48hrs
Cl
Br
+
Cl
Br

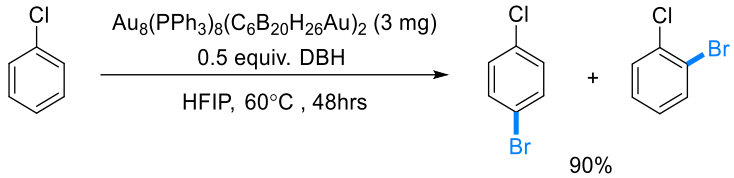
88%
(5.75:1)


1.61
0.14
2.00
7.5 7.0 6.5 6.0 5.5 5.0
f1 (ppm)

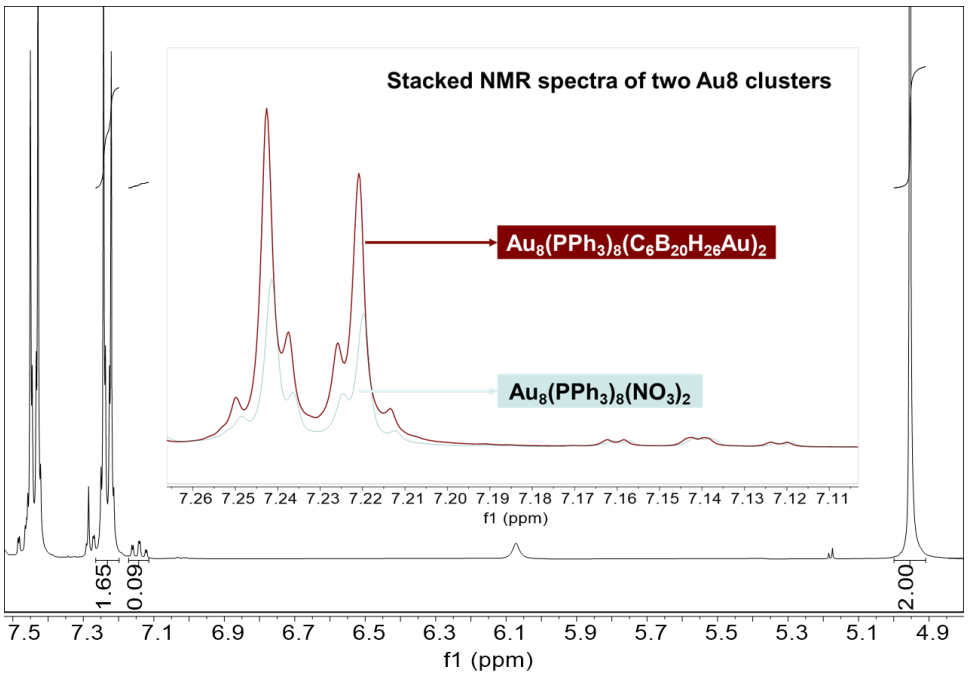

Cl
$Au_8(PPh_3)_8(NO_3)_2$ (3 mg)
0.5 equiv. DBH
HFIP, 60°C , 48hrs
Cl
Br
+
Cl
Br

80%
(5:1)


1.33
0.14
2.00
7.5 7.3 7.1 6.9 6.7 6.5 6.3 6.1 5.9 5.7 5.5 5.3 5.1 4.9 4.7
f1 (ppm)


Cl
$Au_8(PPh_3)_8(C_6B_{20}H_{26}Au)_2$ (3 mg)
0.5 equiv. DBH
HFIP, 60°C , 48hrs
Cl
Br
+
Cl
Br

90%
(9:1)


Stacked NMR spectra of two Au8 clusters
$Au_8(PPh_3)_8(C_6B_{20}H_{26}Au)_2$
$Au_8(PPh_3)_8(NO_3)_2$
7.26 7.25 7.24 7.23 7.22 7.21 7.20 7.19 7.18 7.17 7.16 7.15 7.14 7.13 7.12 7.11
f1 (ppm)
1.65
0.09
2.00
7.5 7.3 7.1 6.9 6.7 6.5 6.3 6.1 5.9 5.7 5.5 5.3 5.1 4.9
f1 (ppm)

6.3 Kinetic isotope effect (KIE) experiment for bromination of chlorobenzene

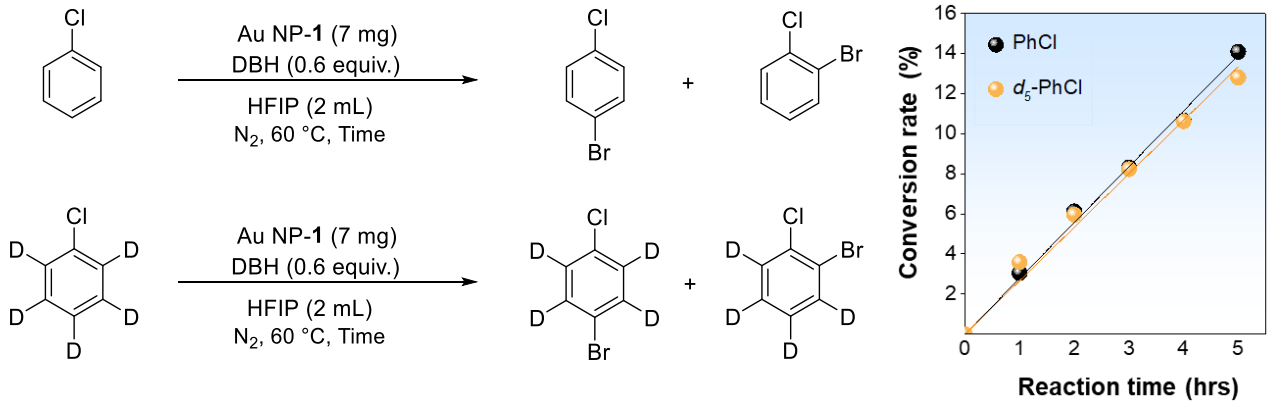


Figure S11. KIE experiments showing that AuNP-**1** catalyzed bromination of chlorobenzene exhibiting typical secondary KIE. PhCl: y=0.0392 x ± 0.000788, R^2=0.99758; d_5-PhCl: y=0.03724 x ± 0.000649, R^2=0.99818.

AuNP-**1** (7 mg) and DBH (0.6 equiv.) were added to an oven-dried 10 mL Schlenk flask equipped with a PTFE stirring bar. Then, chlorobenzene (0.5 mmol)/chlorobenzene-*d*5 (0.5 mmol) and HFIP (2 mL) were added into the Schlenk flask under a nitrogen atmosphere. The reaction mixture was stirred at 60 ºC. At 1 h, 2 h, 3 h, 4 h, and 5 h, the reaction mixture (100 µL) was taken out by micro-syringe into 1 mL EA under a nitrogen atmosphere. The reaction mixture was analyzed by GC-MS with *n*-dodecane as the internal standard to determine the yield of 4-bromochlorobenzene.

6.4. XPS analysis of AuNP-1-SbF_6 before and after catalysis

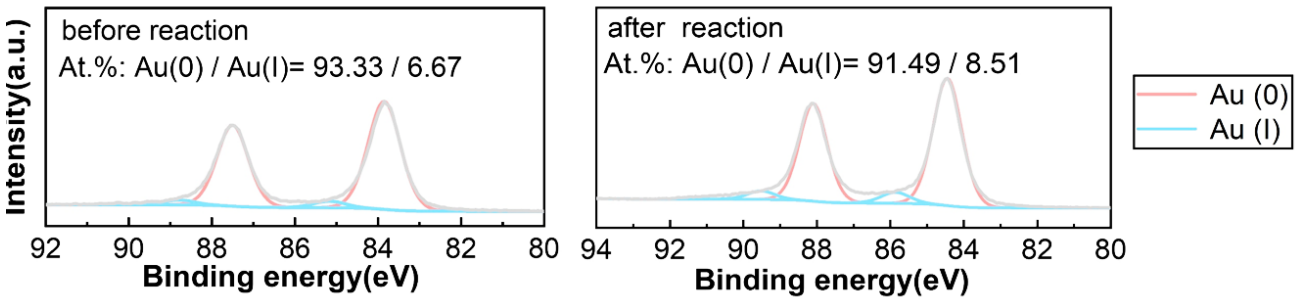


Figure S12. XPS data showing that *ca.* 2% of gold atoms are oxidized after reaction.

7. Computational studies

7.1. Calculation method

All the calculations were carried out with first principles DFT as implemented in VASP code.[10,11] The exchange-correlation function was GGA-PBE. The electron-ion interaction was represented by the projector augmented wave pseudopotential and the kinetics energy cutoff utilized was 450 eV. All the reaction TSs were determined by using the constrained Broyden dimer (CBD) method and the intermediates were obtained by using stochastic surface walking (SSW) global optimization method, as both implemented in LASP code[12]. The Au(111) surface is modeled in four layers. The bottom two layers were fixed at the bulk-truncated position and the top two layers was allowed to be relaxed.

7.2. The reaction pathway of Au-catalyzed bromination of chlorobenzene

DFT calculations were carried out to reveal the reaction pathway of bromination of arenes catalyzed by $Au_8(PPh_3)_8(NO_3)_2$ and AuNP-1. It should be noted that there had been no reaction path way reported in Au-catalyzed bromination of arenes to the best of our knowledge.

Figure S13a shows the $Au_8(PPh_3)_8(NO_3)_2$-catalyzed reaction pathway. During the reaction, the PPh_3 ligand is first desorbed and the DBH is absorbed with its Br atom attracted by the exposed gold atom (1.45 eV). Then Br* was transferred from DBH to gold catalyst (0.73 eV), and the rest of the DBH was protonated by the HFIP with the energy of the system going down to 0.07 eV. Particularly, one more HFIP solvent molecule was explicitly considered here as the solvent effect is apparent in such a protic solvent. Subsequently, the chlorobenzene attacked Br* with its proton left simultaneously in assistant of HFIP anion to yield *p*-product. The energy of the transition state (TS) is 1.20eV. Another possible pathway in which the proton transfer assisted by DBH anion was also calculated, but it requires much higher activation energy compared with the previous pathway (1.53 eV vs 1.20 eV). The difference of the activation energy between two pathway is consistent with the critical role of the protic solvents. The TS in the bromination step to yield *o*-product was also located, whose energy is 0.06 eV higher compared with the TS of *p*-product. It's proposed that repulsion between the bulky ligand PPh_3 and the Cl atom increased the energy of the TS of the *o*-product as the shortest distance between the H atom of the PPh_3 and the Cl atom is 2.95 Å (**Figure S13b**).

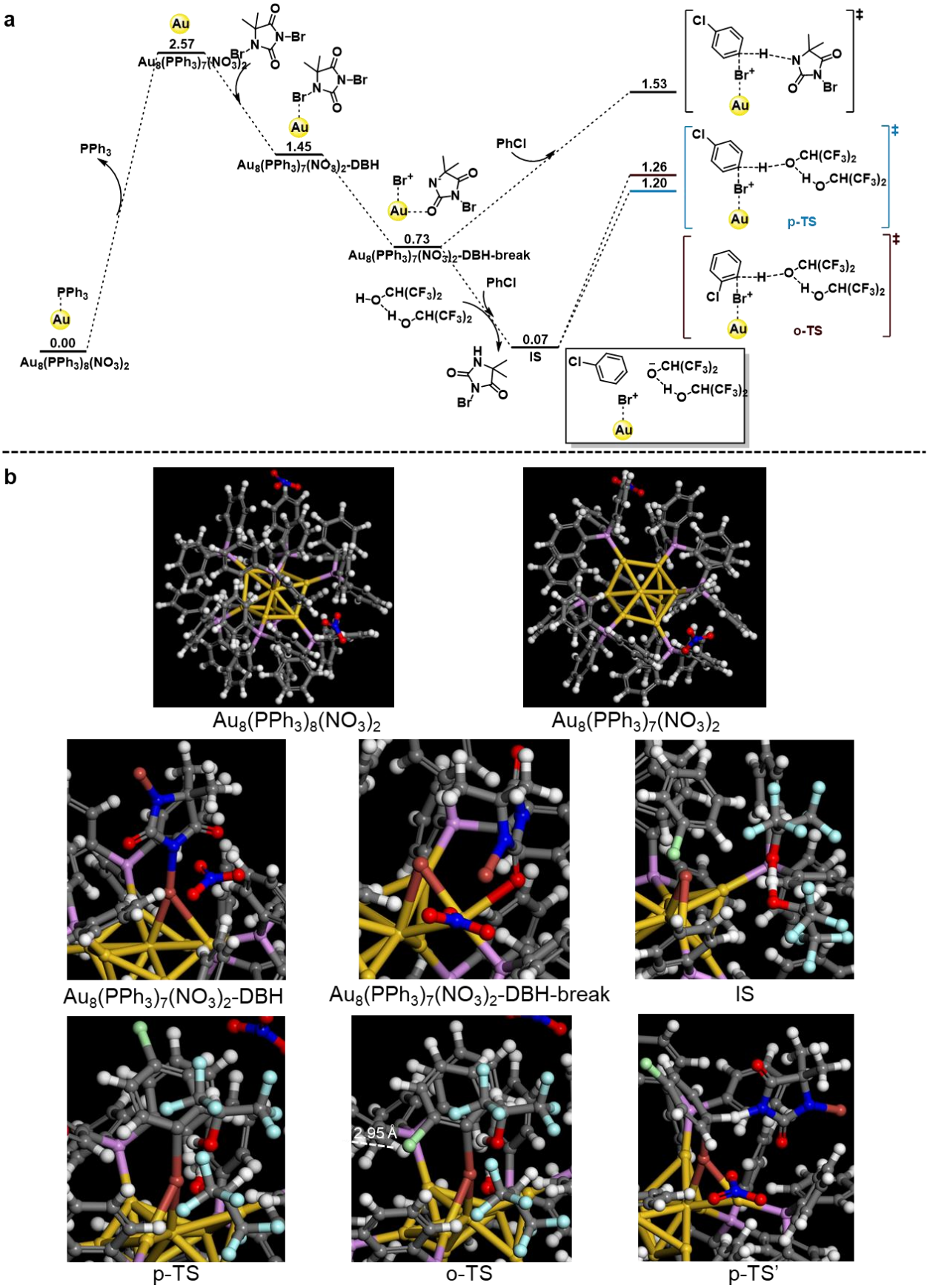


Figure S13. a. The reaction pathway of the $Au_8(PPh_3)_8(NO_3)_2$-catalyzed bromination. **b.** The optimized structure of the intermediate and transition state in the reaction pathway.

We further explored the mechanism of bromination catalyzed by AuNP-1. A simplified model was constructed based on the Au(111) plane, the preferred crystallographic orientation of AuNP-1. **Figure S14a** shows energy profile of the key step, the C-Br bond forming together with the H atom transferred to the HFIP solvent environment. The activation energy for *p*-product and *o*-product is 1.07 eV and 1.31 eV.

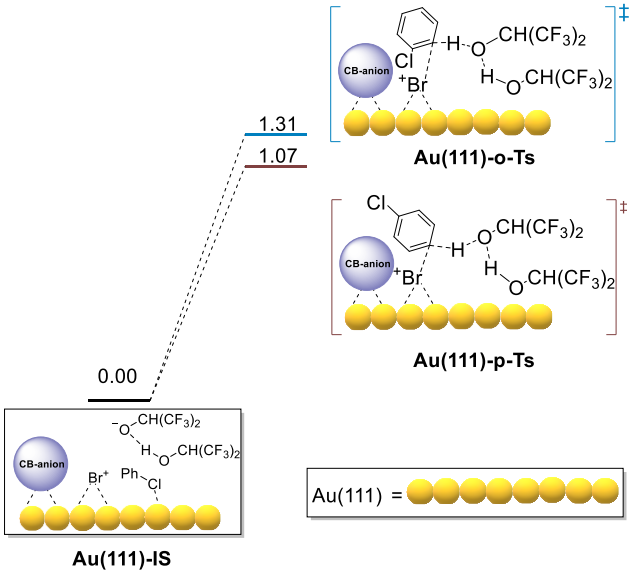
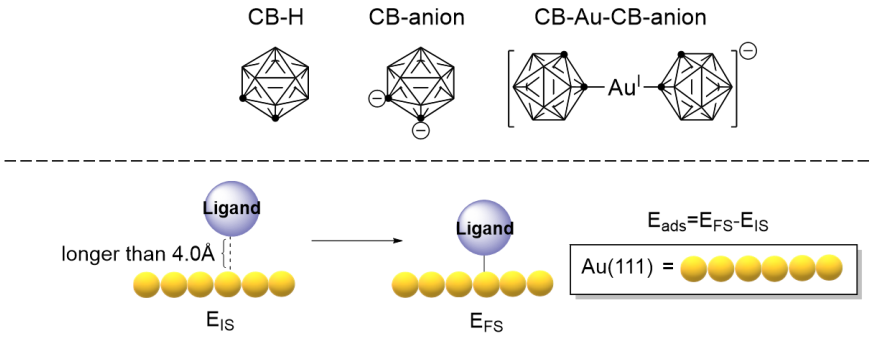


Figure S14. The reaction pathway of the bromination on the Au(111) plane.

7.3. Evaluating the interaction between the ligand/anion and the gold nanoparticle

DFT calculations were carried out to calculated the adsorption energy E_{ads} of different lignds/anions on the Au(111) plane in order to evaluated the strength of interaction between the ligand/anion and the gold nanoparticle (**Figure S15**). The initial structure (IS) with the ligand located 4.0 Å higher above the Au(111) is regarded as the reference.



Ligand	E_{ads} (eV)
PPh_3	-1.84
CB-H	-0.54
CB-anion	-2.90
CB-Au-CB-anion	-2.29
SbF_6^-	-1.24
CO	-0.34

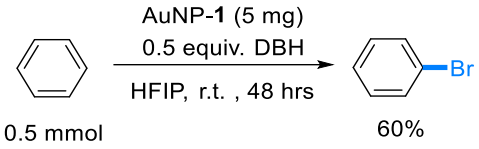
Figure S15. Calculated adsorption energies (E_{ads}) of different ligands/anions.

7.4 Energy of the species in the reaction pathway

Table S5. Energy of the species in the reaction pathway

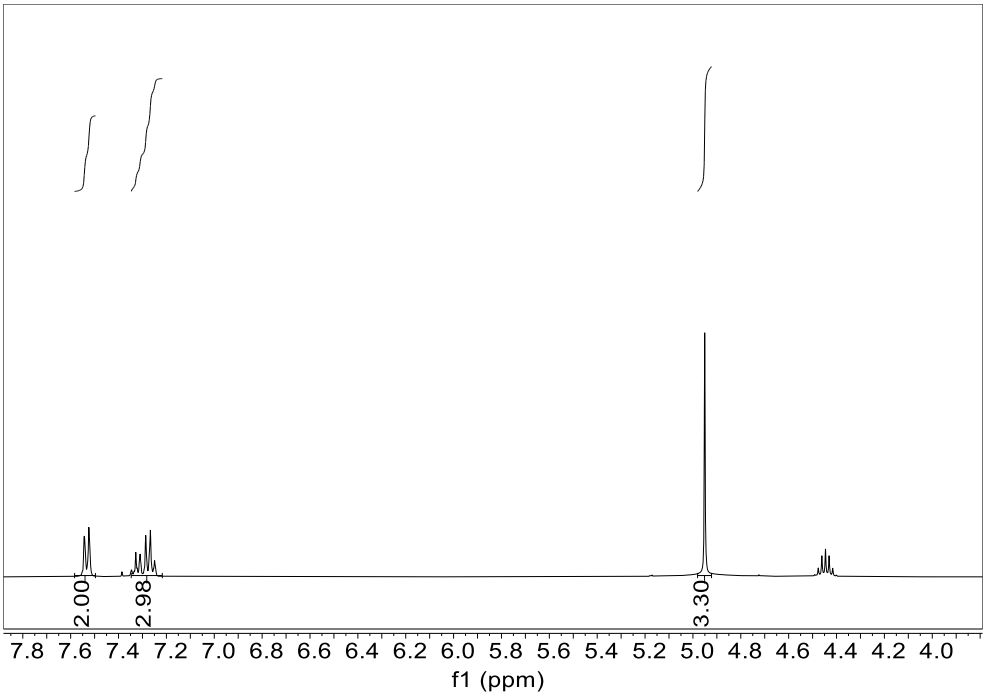
Species	E/eV
PPh_3	-222.299263
PhCl	-74.691100
DBH	-99.630530
HFIP-dimer	-132.774693
DBH-1H	-102.830621
$Au_8(PPh_3)_8(NO_3)_2$	-1863.857218
$Au_8(PPh_3)_7(NO_3)_2$	-1638.987960
$Au_8(PPh_3)_7(NO_3)_2$-DBH	-1739.734465
$Au_8(PPh_3)_7(NO_3)_2$-DBH-break	-1740.677133
IS	-1845.755312
p-TS	-1844.627488
o-TS	-1844.562991
p-TS’	-1813.975501
Au(111)-IS	-845.807695
Au(111)-p-TS	-844.736489
Au(111)-o-TS	-844.495072

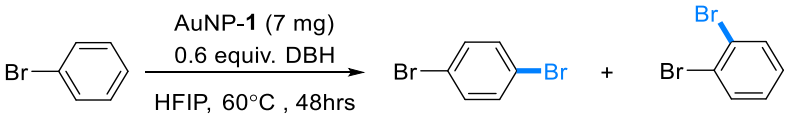
8. Yields determined by ^{1}H NMR



0.5 mmol

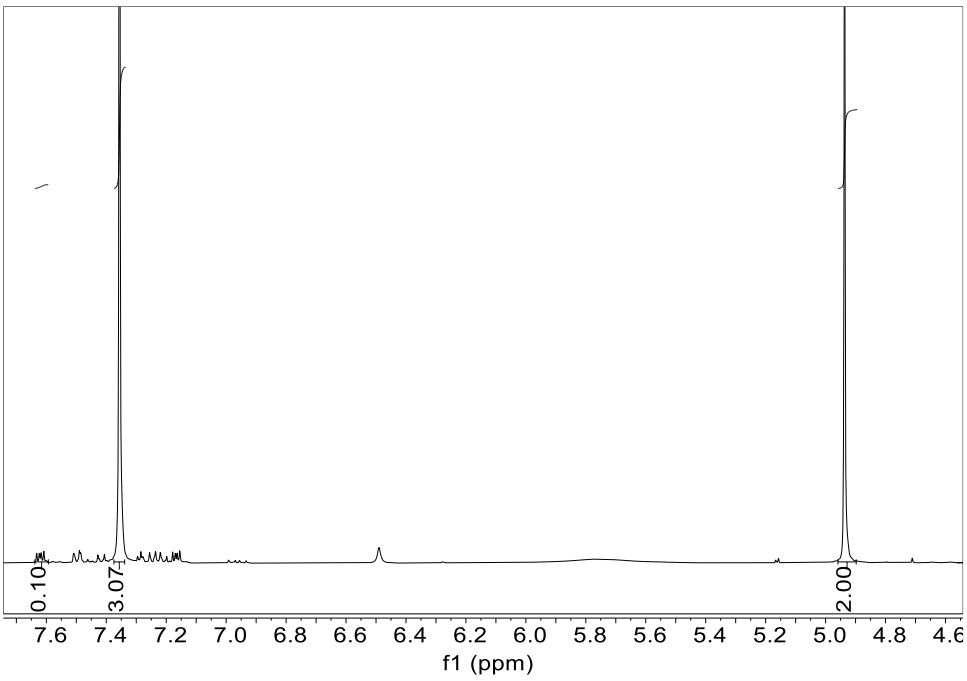
60%

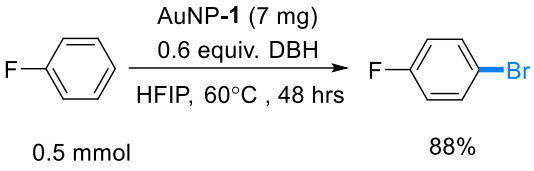




0.5 mmol

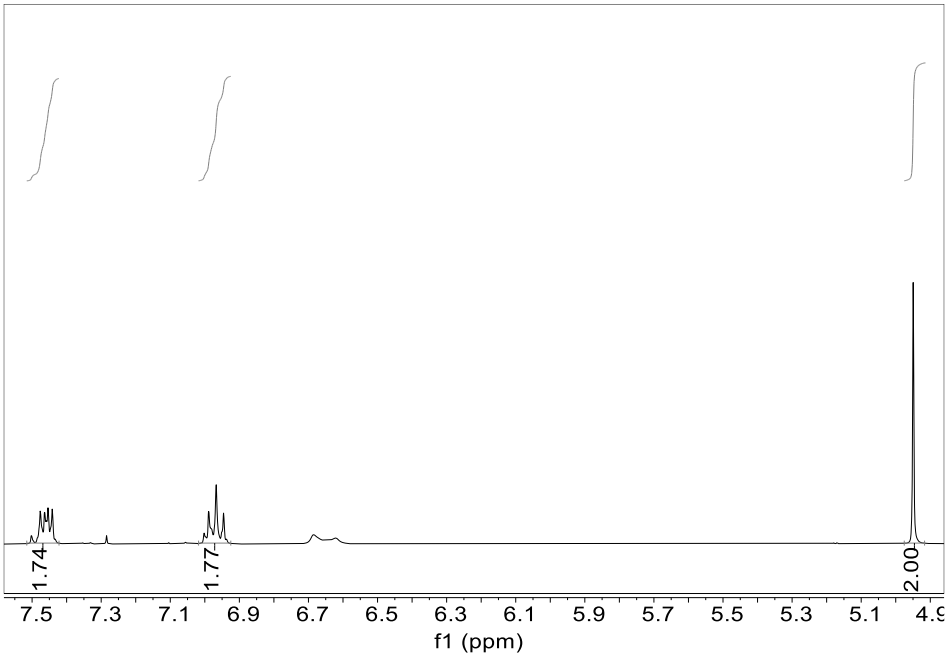
86%
(15:1)

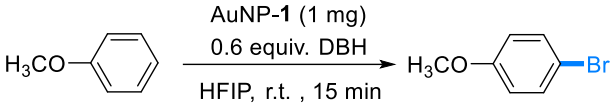




0.5 mmol

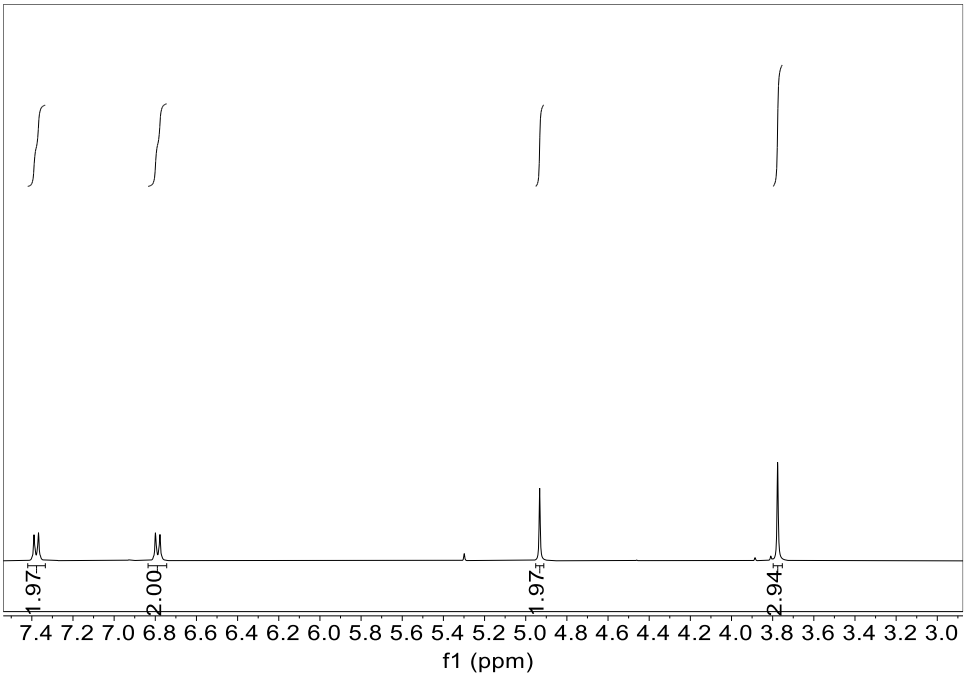
88%

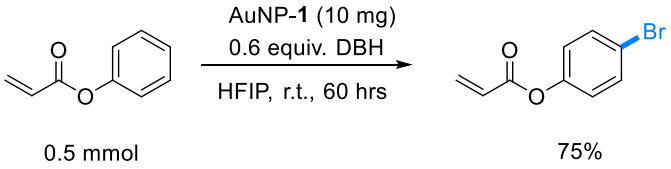




0.5 mmol

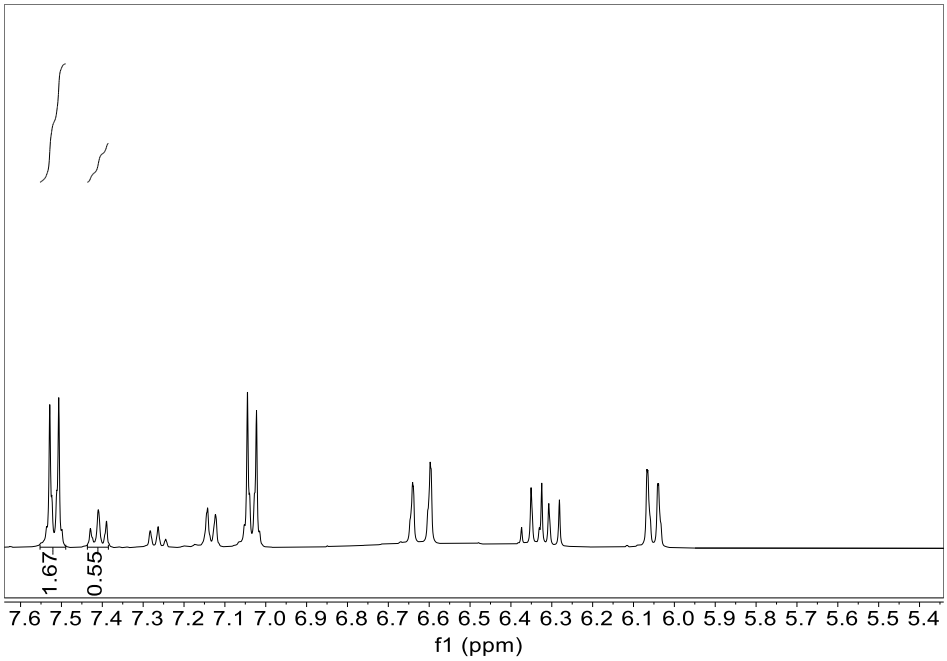
quant.

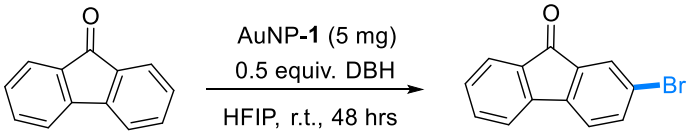




0.5 mmol

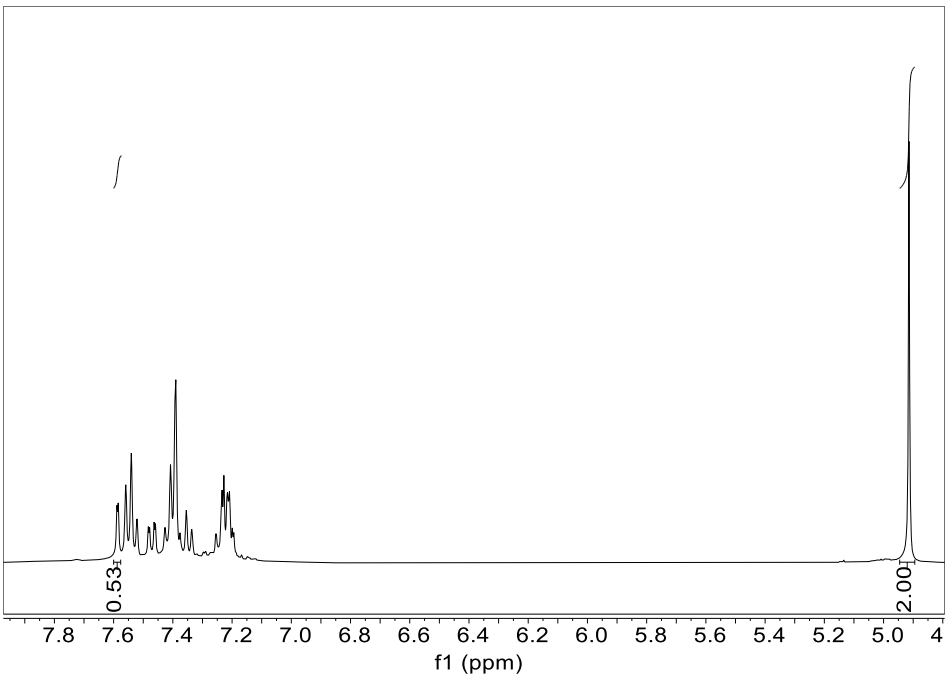
75%

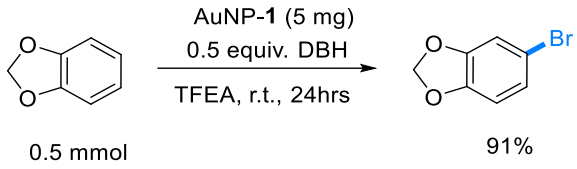




0.5 mmol

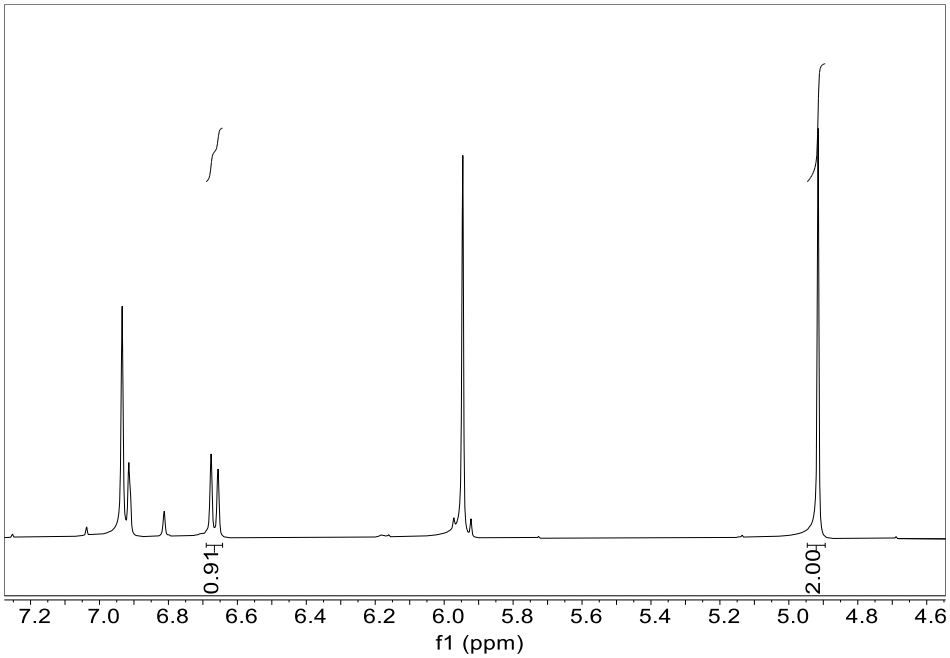
53%

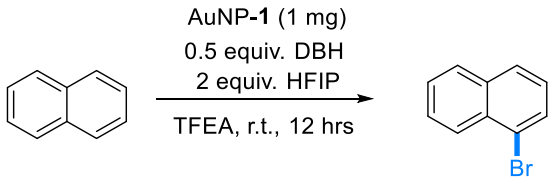




0.5 mmol

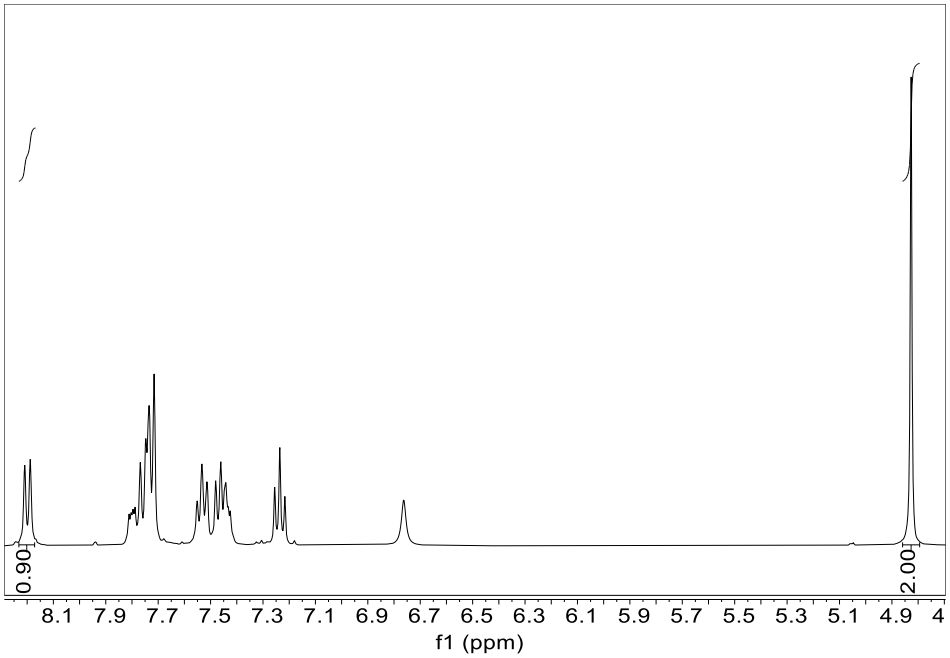
91%

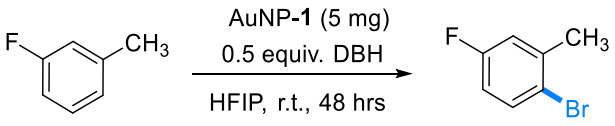




0.5 mmol

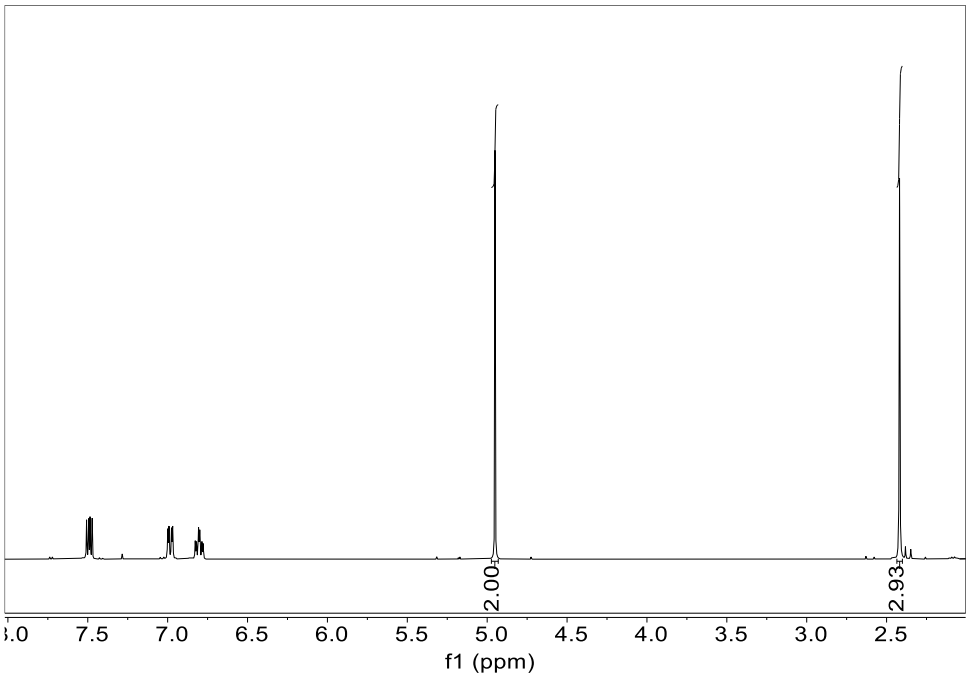
90%

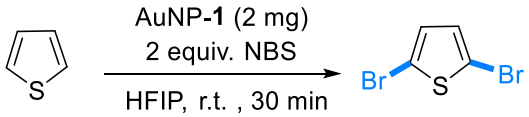




0.5 mmol

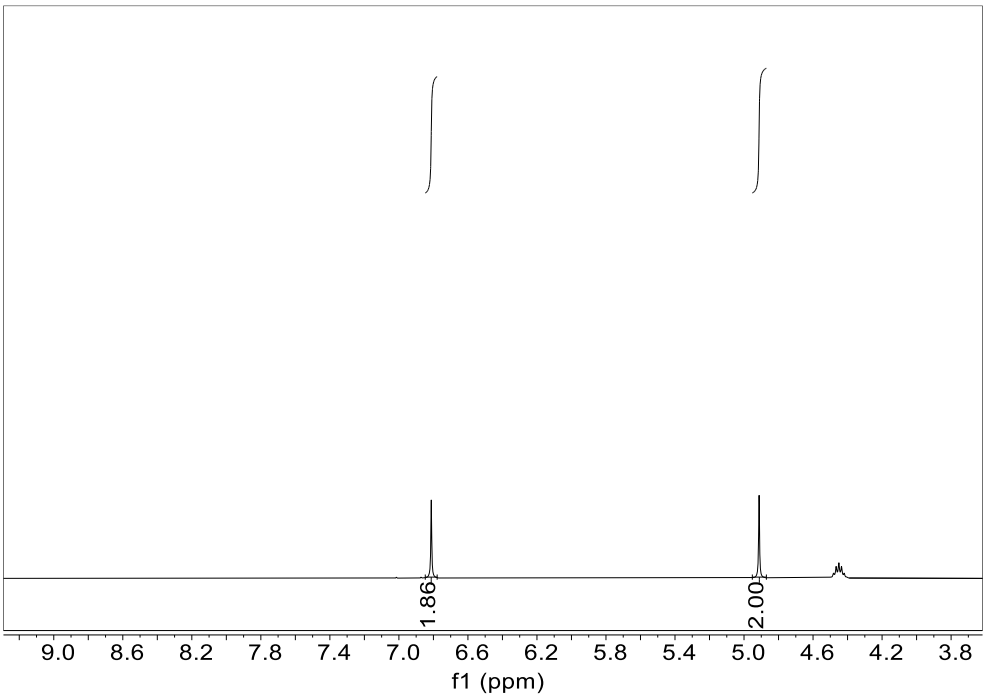
quant.

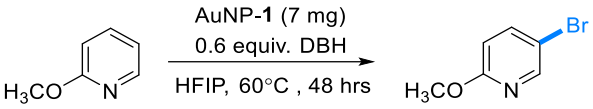




0.5 mmol

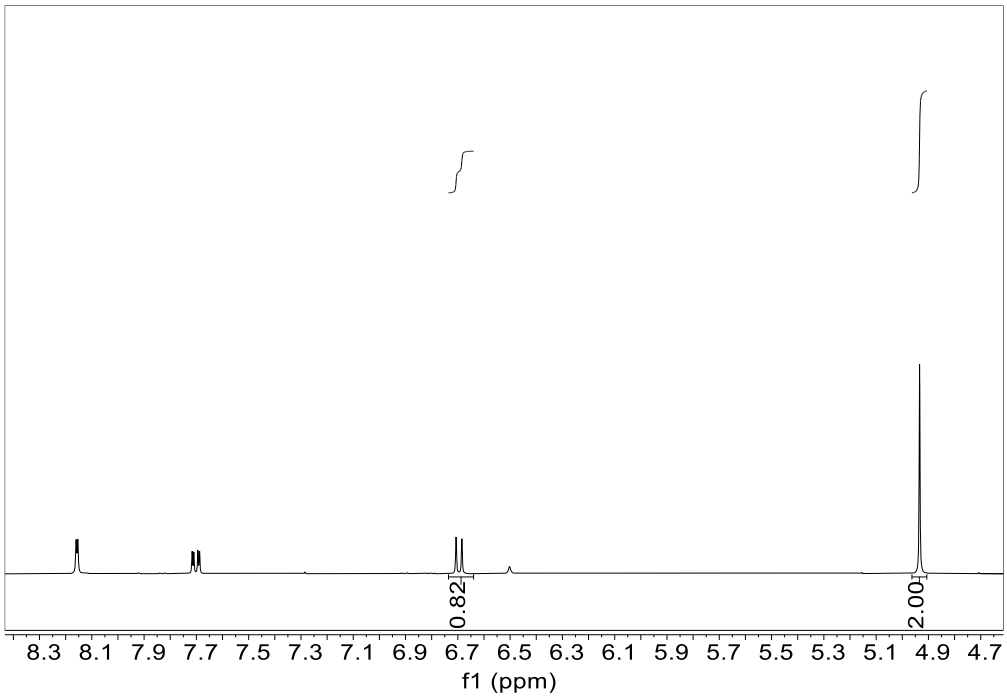
93%

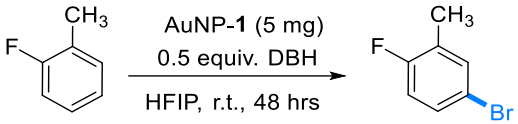




0.5 mmol

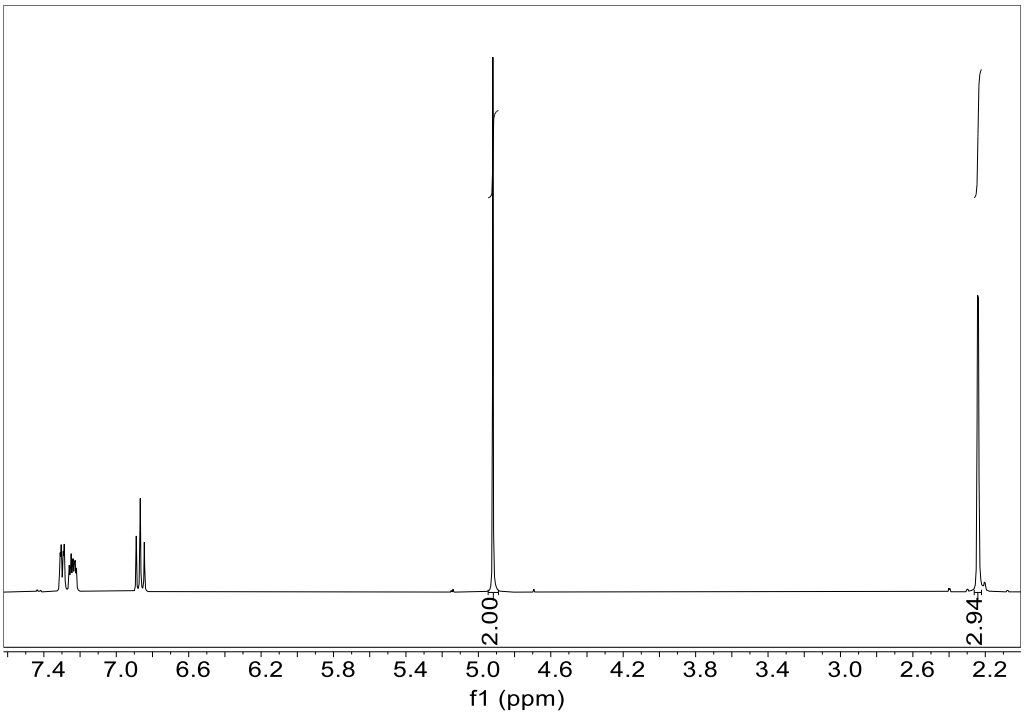
82%





0.5 mmol

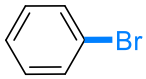
quant.



9. General procedure for Au NP-1-catalyzed bromination

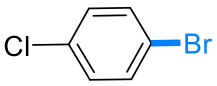
Au NP-**1** and bromination reagents were dissolved in HFIP (2mL) under argon, then substrate (0.5 mmol) was added. The mixture was stirred at specific temperatures for the specified reaction time. After cooling down to room temperature, the resulting suspension was quenched with saturated $Na_2S_2O_3$ aqueous solution (3 mL) and extracted with EA for three times (6 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuum at -20 °C. The residue was analyzed by ^1H NMR to determine the yield of the product using dibromomethane as the internal standard, then the crude product was purified by column chromatography on silica gel using petroleum ether: ethyl acetate as the eluent to afford the brominated products

Bromobenzene (1)



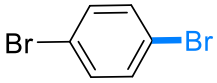
Yield was determined by ^1H NMR using dibromomethane as the internal standard (60%).^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.32-7.21 (m, 3H), Characterization data matched that reported in the literature.[13]

4-Bromochlorobenzene (2)



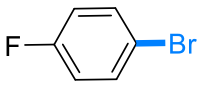
Isolated Yield: 77 mg (80%), white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.38 (m, 2H), 7.24-7.17 (m, 2H). Characterization data matched that reported in the literature.[14]

1,4-Dibromobenzene (3)



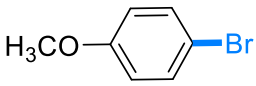
Isolated Yield: 94 mg (80%), white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 4H). Characterization data matched that reported in the literature.[15]

1-Bromo-4-fluorobenzene (4)



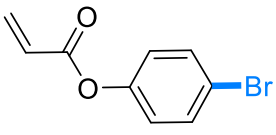
Isolated Yield: 63 mg (72%), colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.8, 4.8 Hz, 2H), 6.99-6.90 (m, 2H). Characterization data matched that reported in the literature.[15]

4-Bromoanisole (5)



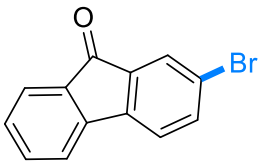
Isolated Yield: 85 mg (90%), colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H). Characterization data matched that reported in the literature.[16]

4-Bromophenyl acrylate (6)



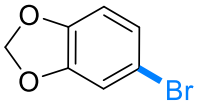
Isolated Yield: 87 mg (77%), colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55-7.47 (m, 2H), 7.08-6.99 (m, 2H), 6.61 (dd, *J* = 1.2, 17.2 Hz, 1H), 6.35-6.26 (m, 1H), 6.03 (dd, *J* = 1.2, 10.4 Hz, 1H). Characterization data matched that reported in the literature.[17]

2-Bromo-9H-fluoren-9-one (7)



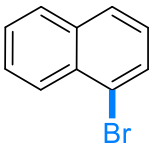
Isolated Yield: 65 mg (50%), yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* =1.6 Hz, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.58 (dd, *J* = 1.6, 8.2 Hz, 1H), 7.50-7.46 (m, 2H), 7.38-7.28 (m, 2H). Characterization data matched that reported in the literature.[17]

5-Bromobenzo[d][1,3]dioxole (8)



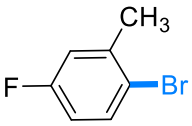
Isolated Yield: 85 mg (85%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99-6.91 (m, 2H), 6.68 (d, *J* = 8.8 Hz, 1H), 5.97 (s, 2H), Characterization data matched that reported in the literature.[18]

1-Bromonaphthalene (9)



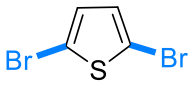
Isolated Yield: 87 mg (84%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.88-7.79 (m, 3H), 7.65-7.53 (m, 2H), 7.34 (t, *J* = 7.6 Hz ,1H). Characterization data matched that reported in the literature.[18]

2-Bromo-5-fluorotoluene (10)



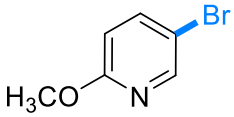
Isolated Yield: 81 mg (85%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.44 (m, 1H), 6.96 (dd, *J* = 2.8, 9.6 Hz, 1H), 6.82-6.75 (m, 1H), 2.39 (s, 3H). Characterization data matched that reported in the literature.[19]

2,5-Dibromothiophene (11)

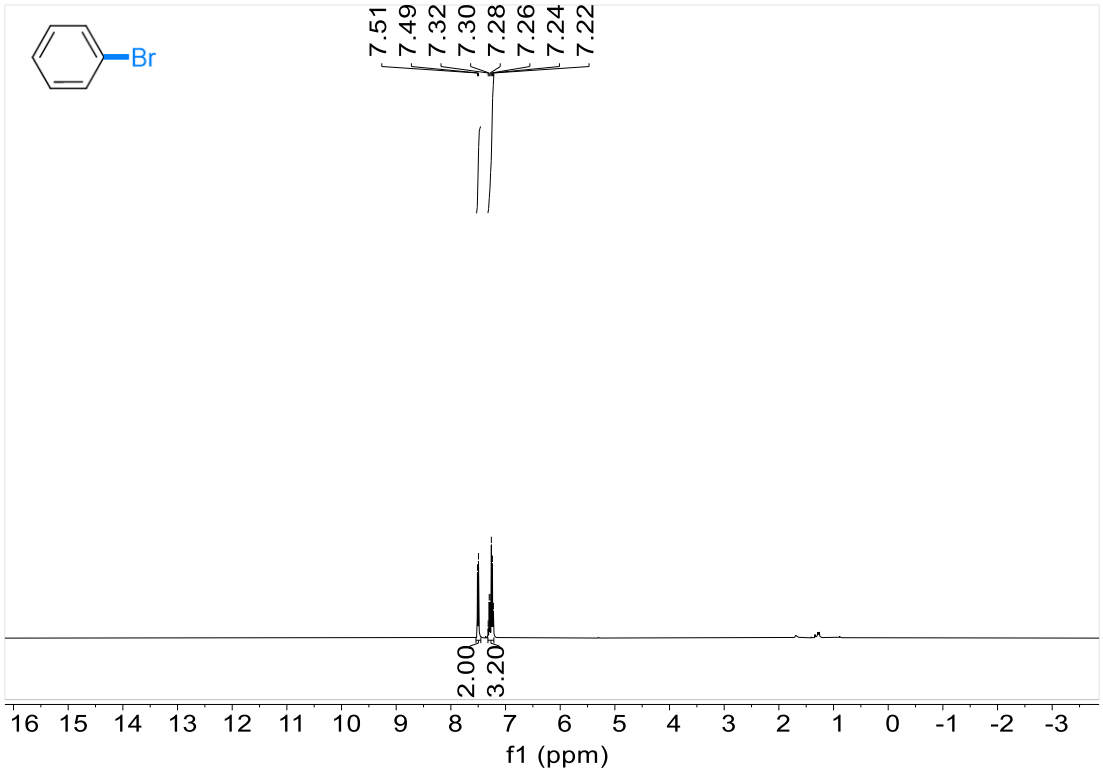


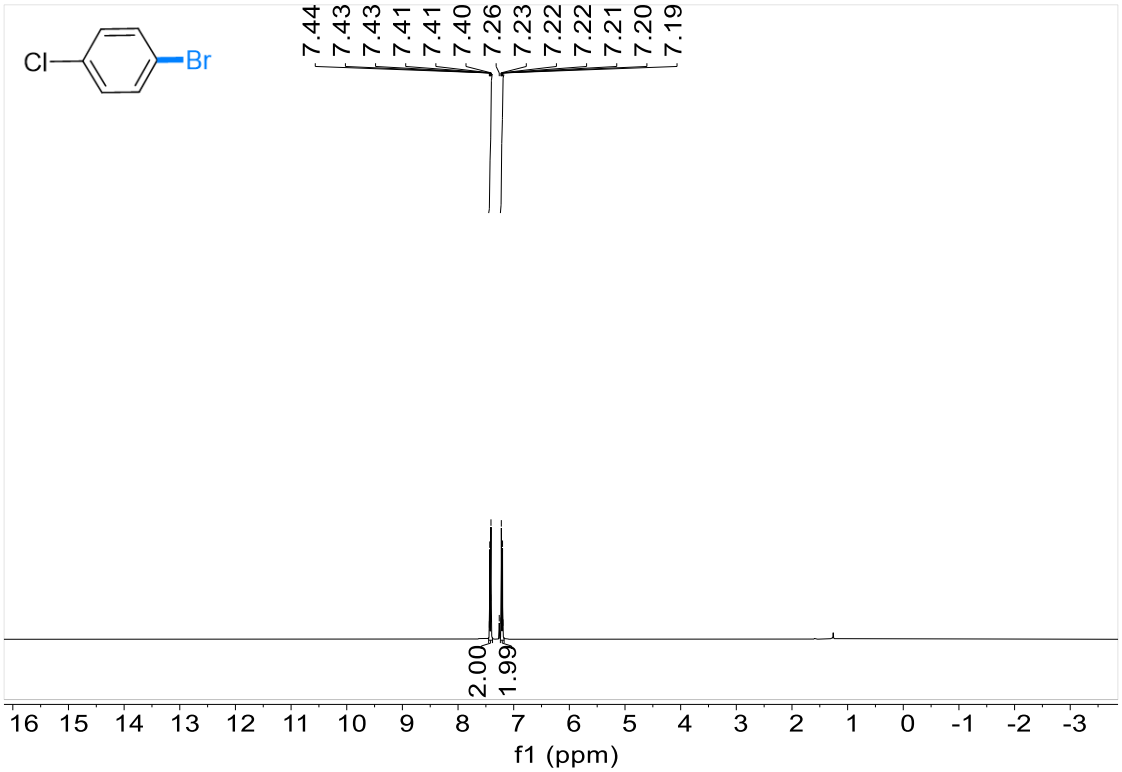
Isolated Yield: 100 mg (83%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 2H). Characterization data matched that reported in the literature.[16]

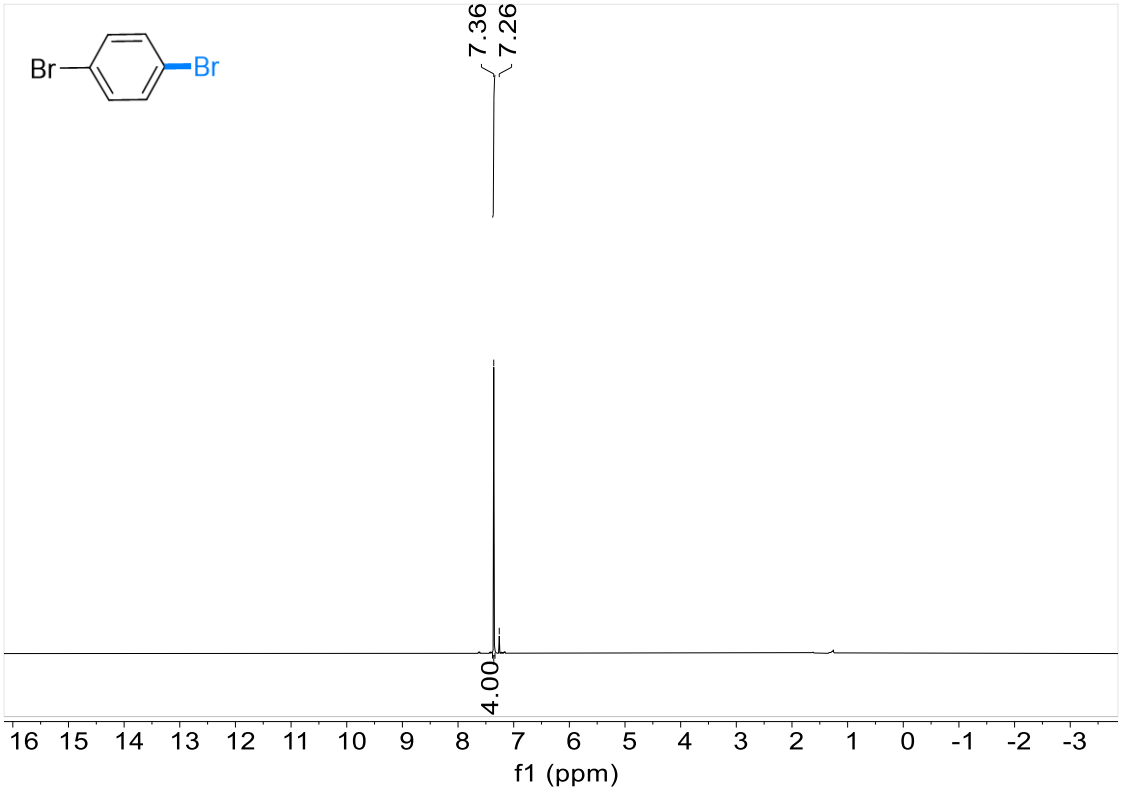
5-Bromo-2-methoxypyridine (12)

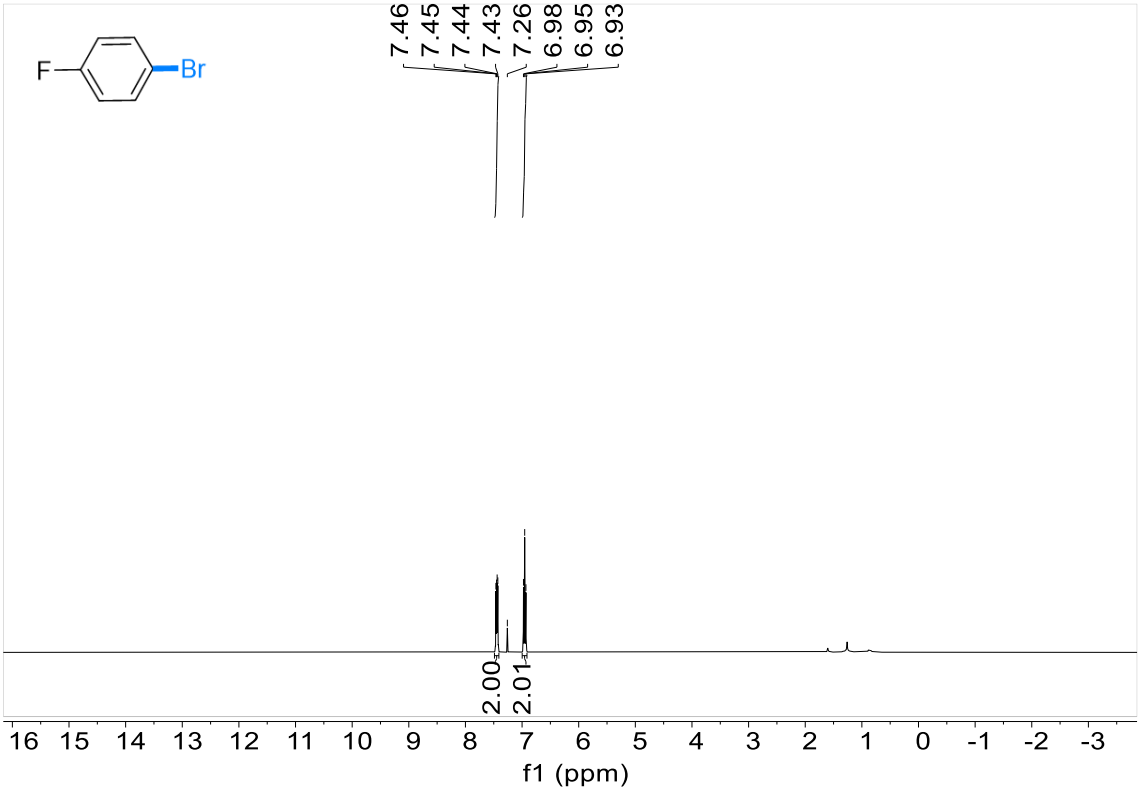


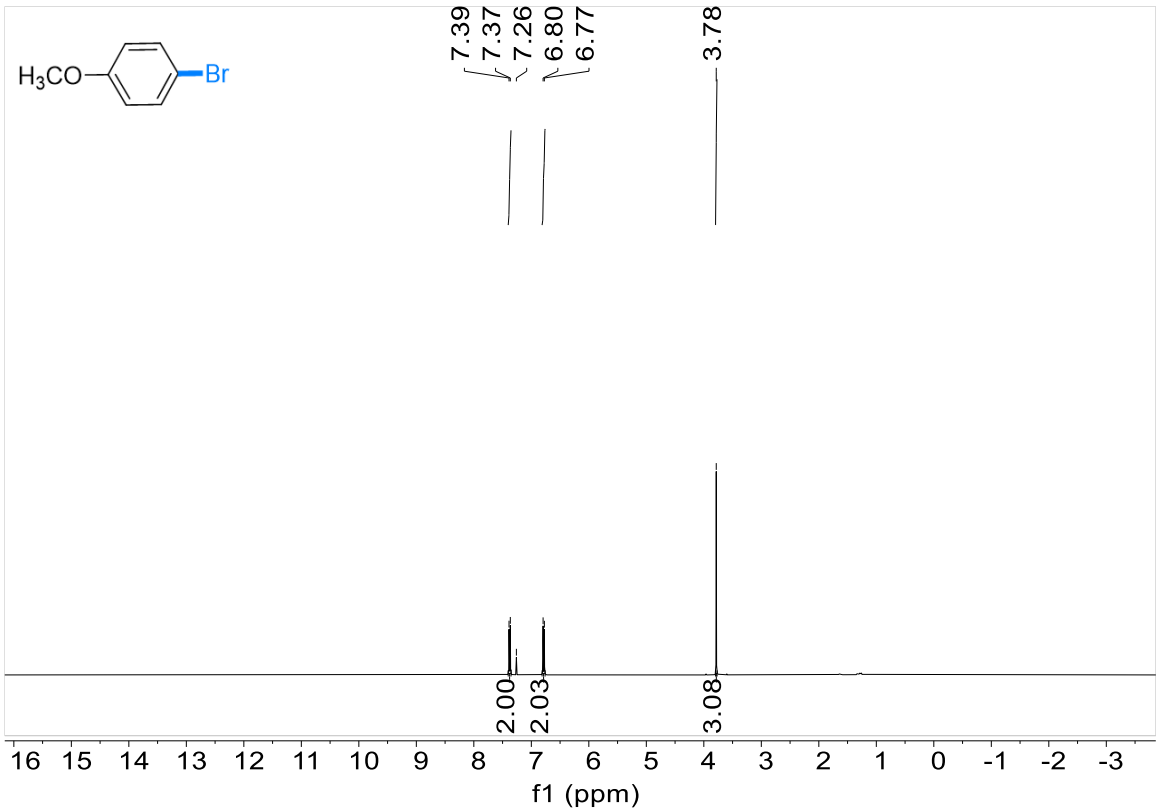
Isolated Yield: 75 mg (80%), pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 2.4 Hz, 1H), 7.63 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.66 (d, *J* = 8.8, 1H), 3.91 (s, 3H). Characterization data matched that reported in the literature.[15]

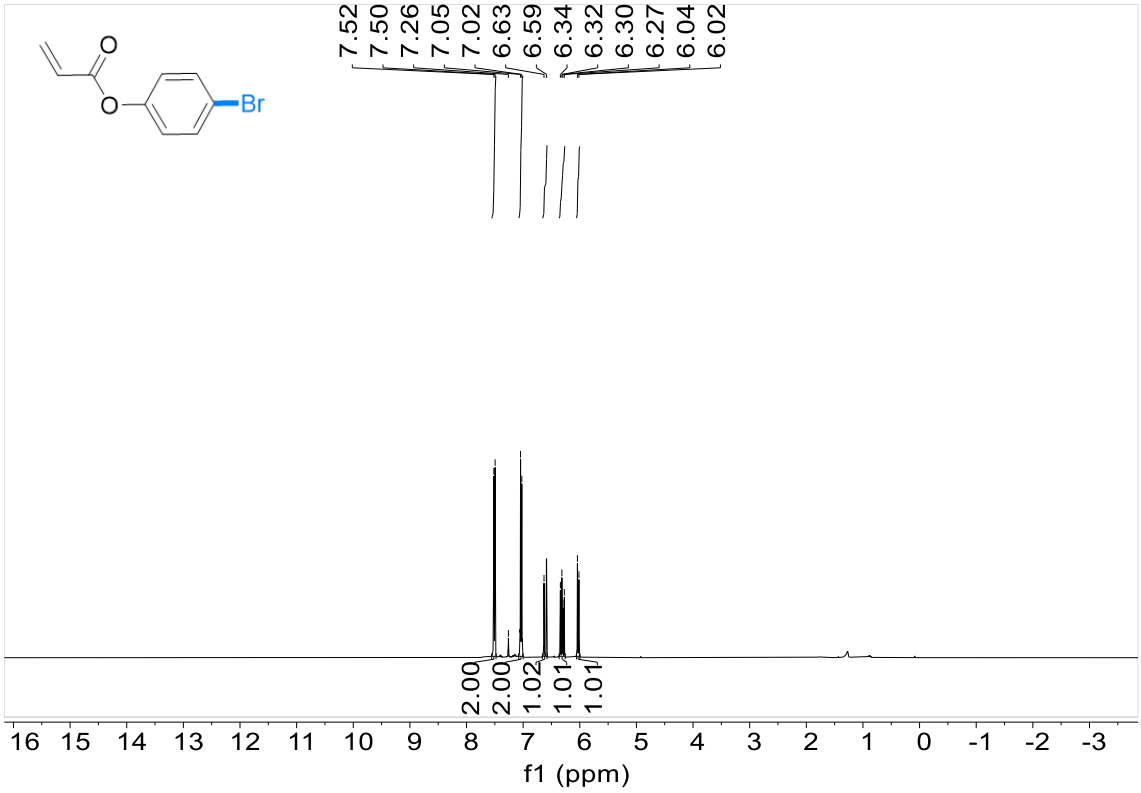

Br
7.51
7.49
7.32
7.30
7.28
7.26
7.24
7.22
2.00
3.20
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

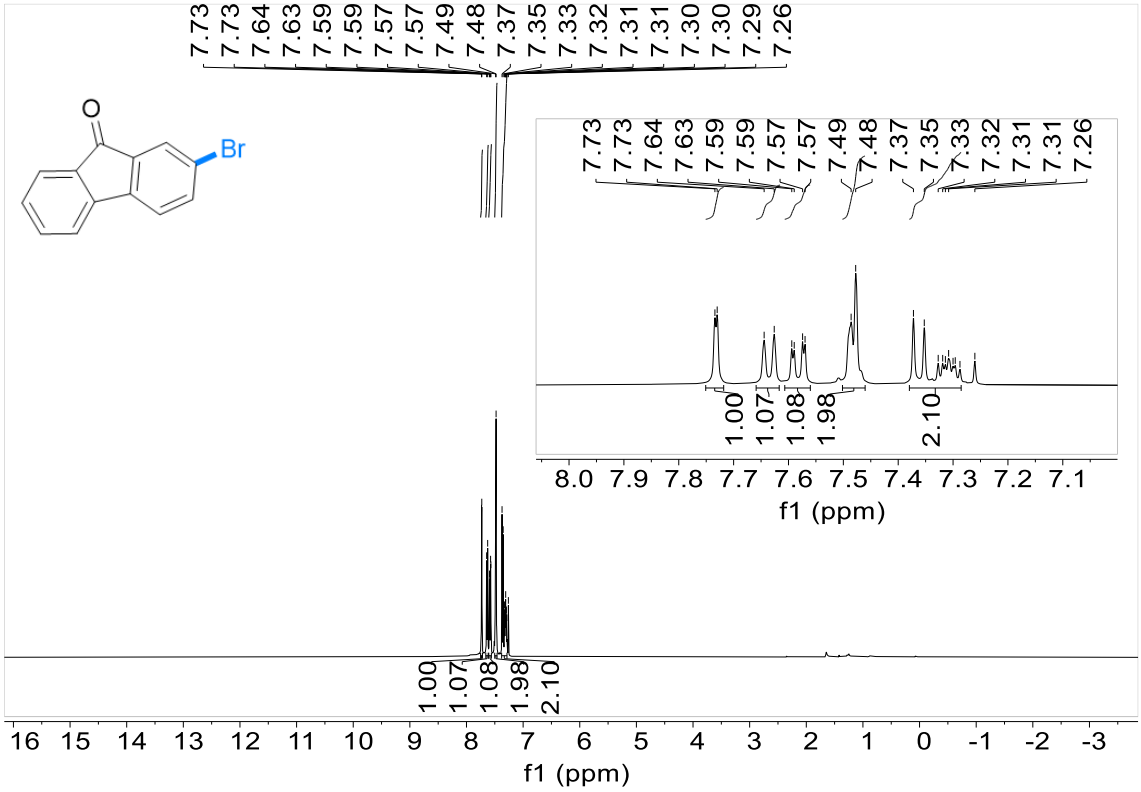

Cl
Br
7.44
7.43
7.43
7.41
7.41
7.40
7.26
7.23
7.22
7.22
7.21
7.20
7.19
2.00
1.99
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

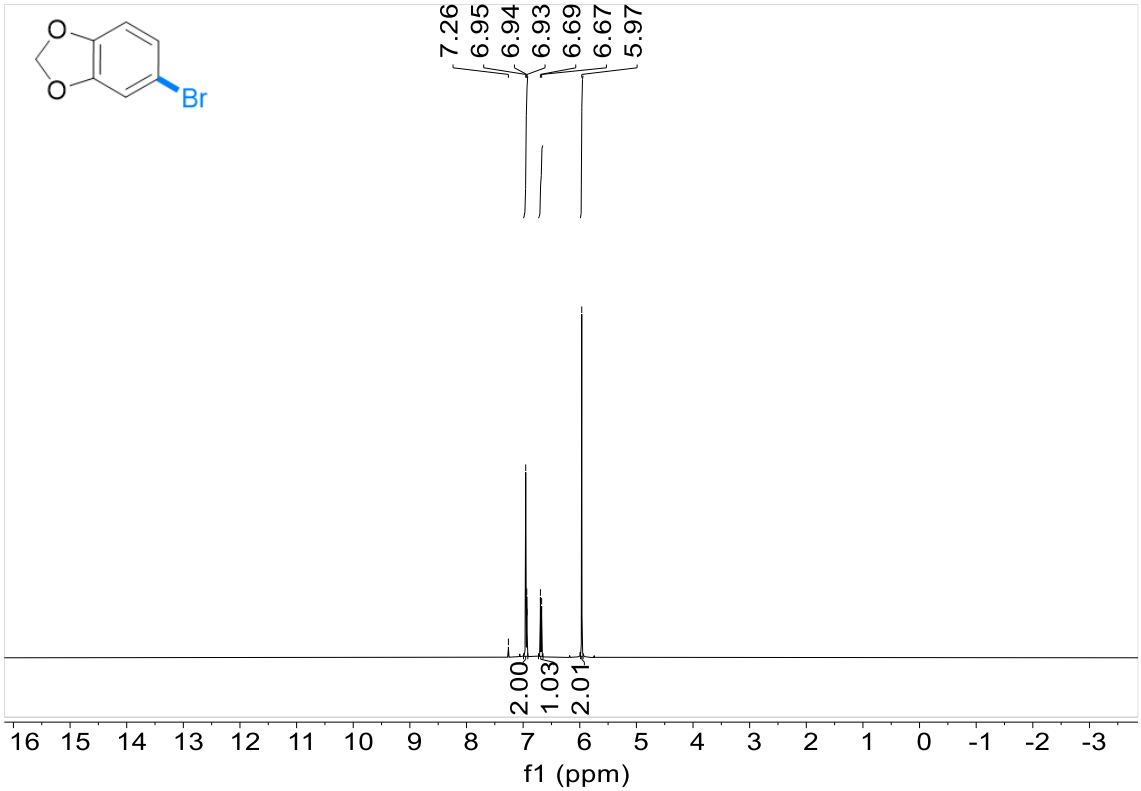

Br
Br
7.36
7.26
4.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

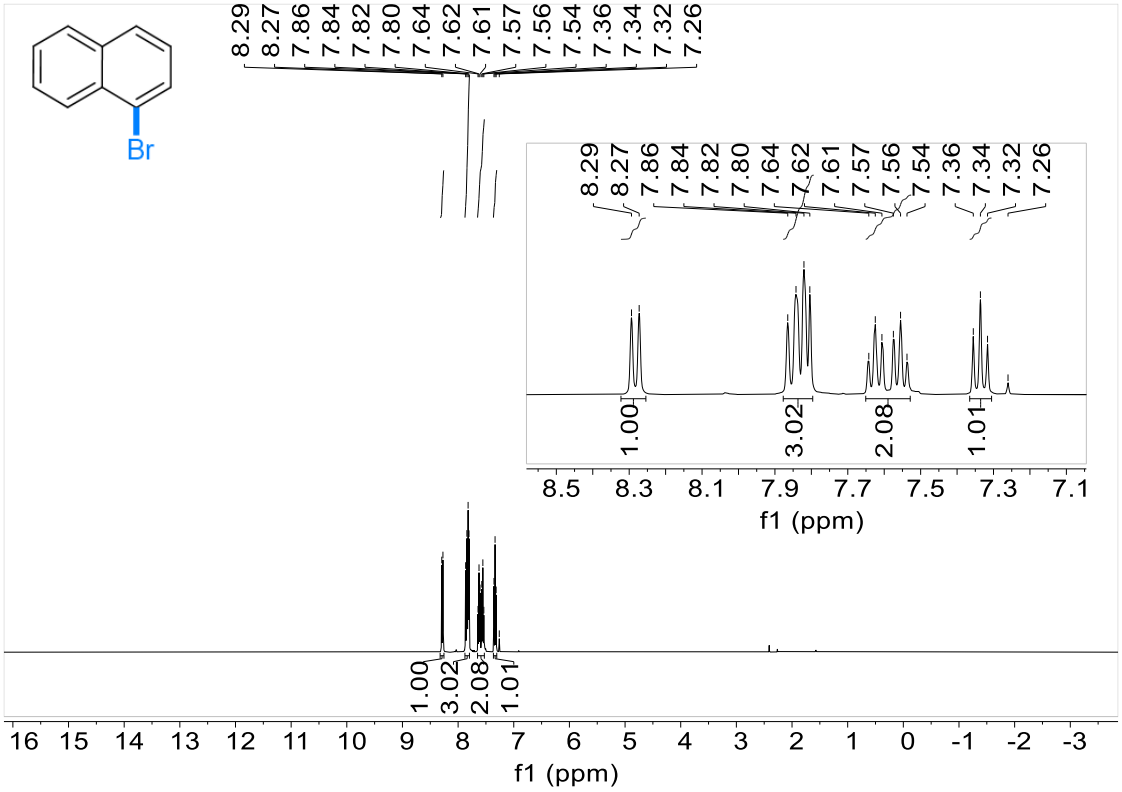

F
Br
7.46
7.45
7.44
7.43
7.26
6.98
6.95
6.93
2.00
2.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

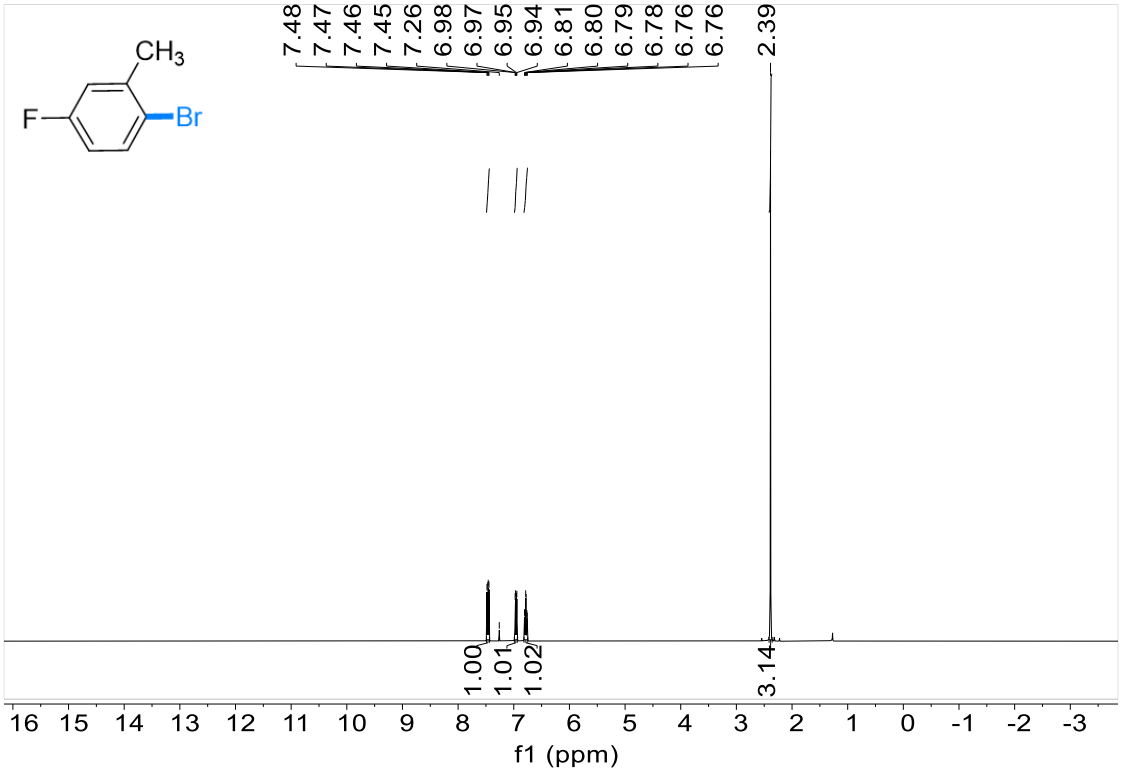

H3CO
Br
7.39
7.37
7.26
6.80
6.77
3.78
2.00
2.03
3.08
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

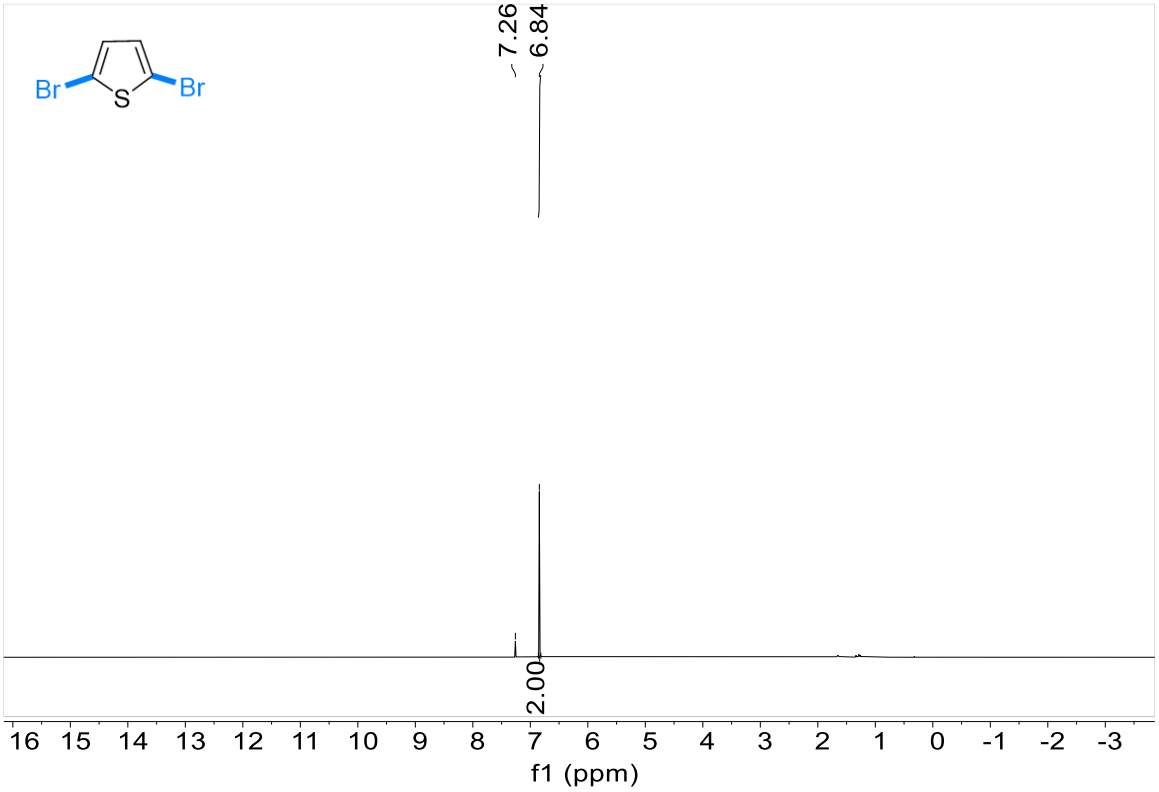

O
O
Br
7.52
7.50
7.26
7.05
7.02
6.63
6.59
6.34
6.32
6.30
6.27
6.04
6.02
2.00
2.00
1.02
1.01
1.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

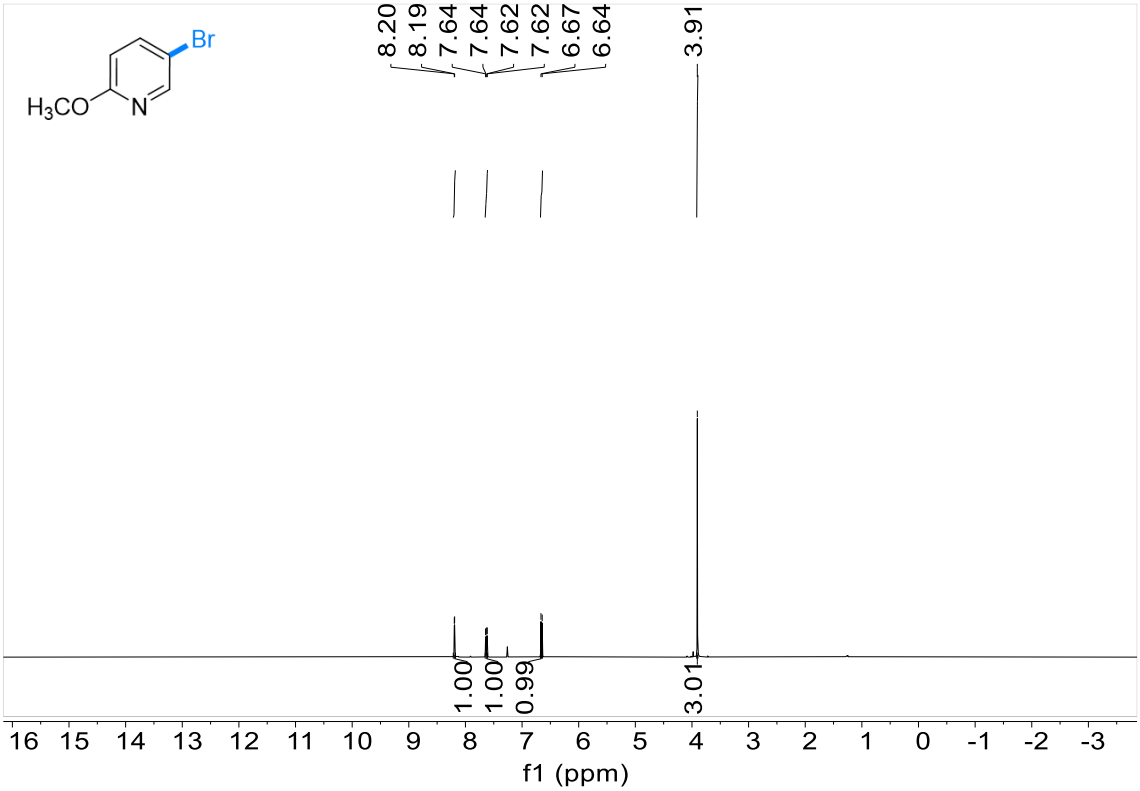

7.73
7.73
7.64
7.63
7.59
7.59
7.57
7.57
7.49
7.48
7.37
7.35
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.26
O
Br
1.00
1.07
1.08
1.98
2.10
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


7.26
6.95
6.94
6.93
6.69
6.67
5.97
O
O
Br
2.00
1.03
2.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Br
8.29
8.27
7.86
7.84
7.82
7.80
7.64
7.62
7.61
7.57
7.56
7.54
7.36
7.34
7.32
7.26
1.00
3.02
2.08
1.01
8.5
8.3
8.1
7.9
7.7
7.5
7.3
7.1
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


CH3
F
Br
7.48
7.47
7.46
7.45
7.26
6.98
6.97
6.95
6.94
6.81
6.80
6.79
6.78
6.76
6.76
2.39
1.00
1.01
1.02
3.14
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


Br
S
Br
7.26
6.84
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Br
H3CO
N
8.20
8.19
7.64
7.64
7.62
7.62
6.67
6.64
3.91
1.00
1.00
0.99
3.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

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